Synthesis of 4-aminopyrazolo[3,4-*d*]pyrimidine derivatives from 5-acetyl-6-amino-4-methylsulfanyl- or 5-acetyl-6-amino-4-methylsulfonylpyrimidines

A. V. Komkov, V. A. Voronkova, A. S. Shashkov, 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: vador@ioc.ac.ru

Diacetyl ketene *N,S*-acetal was used for the synthesis of 5-acetyl-6-amino-4-methylsulfanylpyrimidines substituted at the exocyclic nitrogen atom, which were further oxidized with *m*-chloroperbenzoic acid to the corresponding methylsulfonylpyrimidines. Reactions of hydrazines with these pyrimidines containing vicinal Ac and MeS (or $MeSO_2$) groups were used for the preparation of new 4-aminopyrazolo[3,4-*d*]pyrimidine derivatives.

Key words: 5-acetyl-6-amino-4-methylsulfanylpyrimidines, oxidation, *m*-chloroperbenzoic acid, 5-acetyl-6-amino-4-methylsulfonylpyrimidines, 4-amino-1*H*-pyrazolo[3,4-*d*]pyrimidines, 4-amino-2-phenyl-2*H*-pyrazolo[3,4-*d*]pyrimidines, hydrazines.

Pyrazolo[3,4-*d*]pyrimidines are of great biological importance since they are purine analogs and antagonists. In the last 10—15 years, 4-amino derivatives of this heterocyclic system are of special interest, which is due to their activity as inhibitors of tyrosine-[1,2] and serine-threonine proteinkinases,[3] as well as of a number of other enzymes,[4—10] thus making them potentially promising antitumor, antiviral, and antibacterial agents.

4-Aminopyrazolo[3,4-*d*]pyrimidines commonly are obtained by annulation of a pyrimidine ring to the corresponding substituted pyrazoles (see, for example, the review[11] and the works[2,5,10,12—16]) or by the action of hydrazines on aminopyrimidines containing vicinal functional groups at positions 4 and 5 (Cl and CHO (see Refs 3, 7, 8, and 17); Cl and CN (see Ref. 18); MeS and CN (see Ref. 19)).

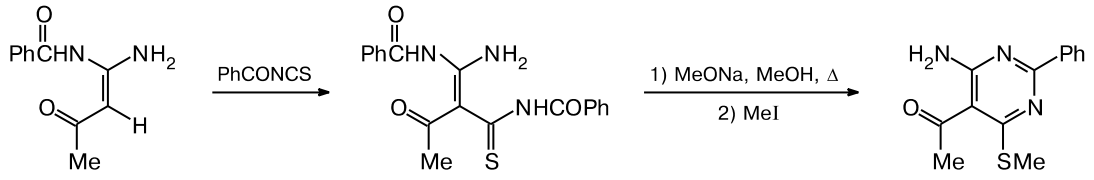
In the present work, we report the use of 5-acetyl-6-amino-4-methylsulfanylpyrimidines and 5-acetyl-6-amino-4-methylsulfonylpyrimidines for the preparation of new 4-aminopyrazolo[3,4-*d*]pyrimidine derivatives.

Earlier,[20] we have shown that *N*-benzoylaminal **1** reacts with benzoyl isothiocyanate as a C-nucleophile to form benzoylthioamide **2**, which is easily converted to 5-acetyl-6-amino-4-methylsulfanyl-2-phenylpyrimidine (**3**) (Scheme 1).

In the present work, we synthesized a number of substituted at the exocyclic nitrogen atom pyrimidines **4a—i** from diacetyl ketene *N,S*-acetal **5** following Scheme 2, which includes formation of ketene aminals **6**, deacetylation of the latter to aminals **7** and preparation of thioamides **8** with their subsequent cyclization to pyrimidinethiones **9** (compounds **9a** and **9h** were synthesized earlier[21]). Readily occurring alkylation of pyrimidinethiones **9a—i** with MeI gives new methylsulfanylpyrimidines **4a—i**.

We found that prolonged reflux in butanol of pyrimidines **4a—d** with a large excess of hydrazine hydrate or methylhydrazine (a 25-fold excess of hydrazine hydrate in the case of pyrimidines **4a—c** and a 50-fold excess in the case of compound **4d** and when methylhydrazine was used) gives rise to the substituted 4-aminopyrazolo[3,4-*d*]-

Scheme 1



1 **2** **3**

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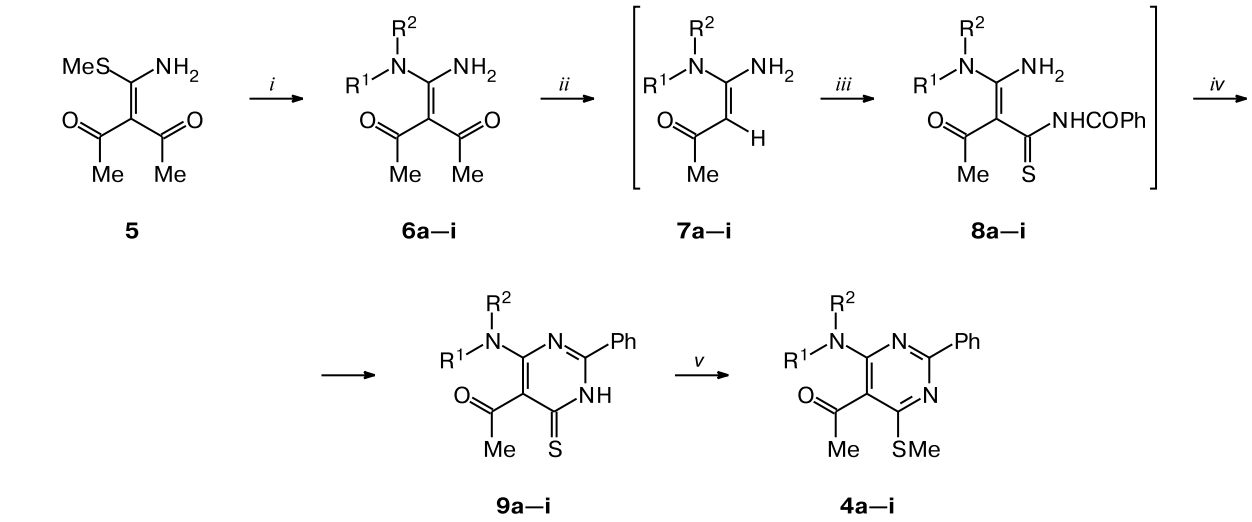
Scheme 2

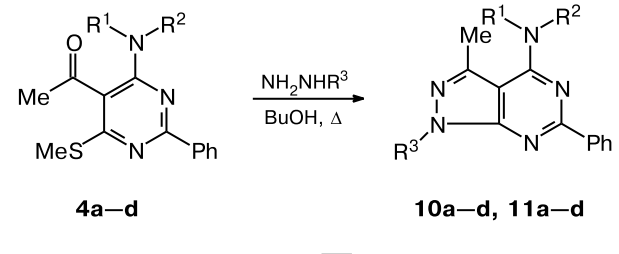


R^1R^2N = O⟨⟩N— (**a**), MeN⟨⟩N— (**b**), 4-$MeOC_6H_4$N⟨⟩N— (**c**), 4-FC_6H_4N⟨⟩N— (**d**),
R^1 = H, R^2 = 3,5-$Me_2C_6H_3$ (**e**), 3-ClC_6H_4 (**f**), 3-$CF_3C_6H_4$ (**g**), $PhCH_2$ (**h**), C_4H_9 (**i**)

Reagents and conditions: *i*. R^1R^2NH, C_6H_6 or *o*-xylene, or THF for **6a**, Δ; *ii*. MeONa, MeOH, 20 °C or Δ; *iii*. PhCONCS, C_6H_6 or toluene, 20 °C; *iv*. 1) MeONa, MeOH, Δ, 2) AcOH, 20 °C; *v*. 1) MeONa, MeOH, 20 °C, 2) MeI, 20 °C.

pyrimidines **10a—d** and **11a—c** with good yields (only compound **11d** was isolated in low yield since a considerable amount of the starting pyrimidine **4d** according to the TLC data was not involved into the reaction, Scheme 3).

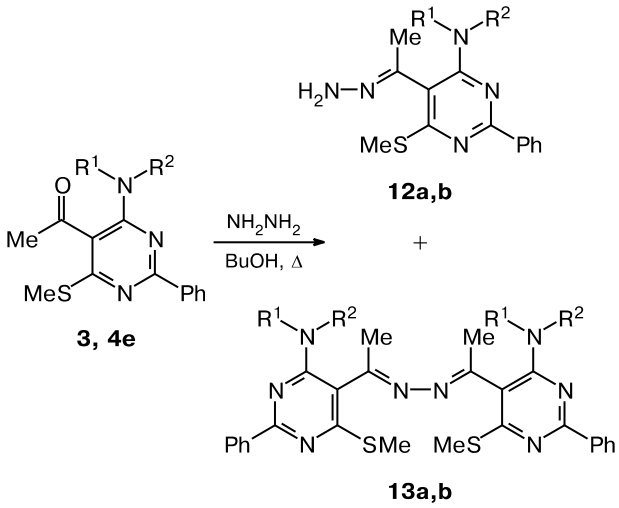
Scheme 3



R^3 = H (**10**), Me (**11**); R^1R^2N = O⟨⟩N— (**a**), MeN⟨⟩N— (**b**),
4-$MeOC_6H_4$N⟨⟩N— (**c**), 4-FC_6H_4N⟨⟩N— (**d**)

However, it turned out that when conditions for the synthesis of compounds **10a—d** and **11a—d** were applied to 4-methylsulfanylpyrimidines **3**, **4e** and hydrazine hydrate, no target pyrazolo[3,4-*d*]pyrimidines were obtained, with the mixtures of hydrazones **12a,b** and azines **13a,b** being formed instead in the molar ratio ~2 : 1 and 8 : 1, respectively (the ^{1}H NMR spectra of which exhibited singlets for the MeS and Me groups of both reaction products at δ ~2.7 and 2.2; Scheme 4).

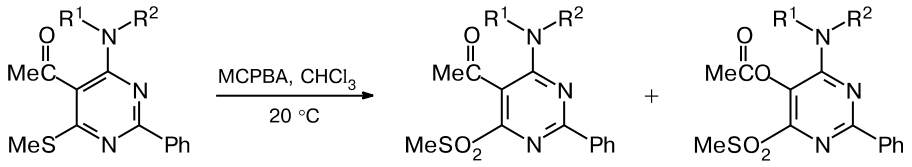
Scheme 4



R^1 = H; R^2 = H (**3**, **12a**, **13a**), 3,5-$Me_2C_6H_3$ (**4e**, **12b**, **13b**)

It could have been suggested that the annulation of the pyrazole ring would occur more readily if the methylsulfanyl group is oxidized to a methylsulfonyl one. In this connection, treatment of sulfanylpyrimidines **3** and **4e—i** with a 2.5-fold excess of 40% MCPBA in chloroform afforded

Scheme 5



3, 4e—i **14a—f** **15a—f**

R^1 = H; R^2 = H (**3**, **14a**, **15a**), 3,5-$Me_2C_6H_3$ (**4e**, **14b**, **15b**), 3-ClC_6H_4 (**4f**, **14c**, **15c**), 3-$CF_3C_6H_4$ (**4g**, **14d**, **15d**), $PhCH_2$ (**4h**, **14e**, **15e**), C_4H_9 (**4i**, **14f**, **15f**)

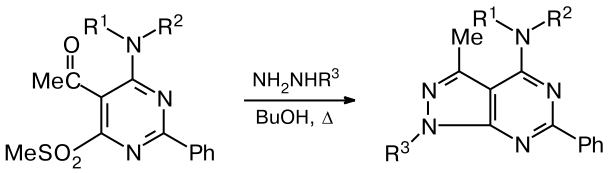
5-acetyl-6-amino-4-methylsulfonylpyrimidines **14a—f** in 24—56% yields (Scheme 5). It was found that the moderate yields of compounds **14a—f** can be accounted for by the formation of side oxidation products, *i.e.*, 5-acetoxy-6-amino-4-methylsulfonylpyrimidines **15a—f** (a type of the Baeyer—Villiger rearrangement). The target compounds **14** should be purified from the side products by column chromatography on silica gel. The ^{1}H NMR spectra showed that before chromatographic purification the content of 5-acetoxypyrimidines **15d**,**e**,**f** in the reaction mixtures was 17, 43, and 60%, respectively. Pyrimidines **15e**,**f** were isolated in the pure form, though, silica gel seems to cause partial decomposition of these compounds.

The structure of methylsulfonylpyrimidines **14a—f** was confirmed by spectroscopic data. Their mass spectra (EI) exhibit strong peaks of molecular ions, whereas in the ^{1}H NMR spectra ($CDCl_3$) the signal for the $MeSO_2$ is observed more downfield (for example, for **14e** at δ 3.39) than the signal for the MeS in the starting methylsulfanylpyrimidines. The presence of the acetyl group is indicated by the signal in the ^{13}C NMR spectrum (for **14e** at δ 201.54). In the ^{13}C NMR spectrum ($CDCl_3$) of acetoxypyrimidine **15e**, the signal for the carbonyl carbon atom was found in much higher field at δ 168.50. In the high resolution mass spectrum (ESI) of compound **15e**, the peak $[M + Na]^+$was observed in the positive range and $[M - H]^-$ in the negative range.

The synthesized 4-methylsulfonylpyrimidines **14a—e** smoothly react with hydrazine hydrate and methylhydrazine upon reflux in butanol to form 4-aminopyrazolo[3,4-*d*]pyrimidines **10e—i** and **11e**,**f**, isolated as colorless crystals in good yields (Scheme 6).

The structure of the synthesized pyrazolopyrimidines was confirmed by spectroscopic methods. Thus, there are strong peaks of molecular ions in the mass spectra (EI) of compounds **10a**,**e—i** and **11a**,**e**,**f**, whereas heterocycles **10b—d** and **11b—d** have very weak molecular ion peaks since electron impact induces successive cleavage of the piperazine ring. Position of the Me group in biheterocycles **11** and of the proton in pyrazolopyrimidines **10** at the atom N(1) was confirmed by 2D NMR spectra. Thus, in the 2D ^{1}H/^{13}C HMBC spectra of compounds **11a**,**e**,**f**, the protons of the NMe group correlate with the carbon atom

Scheme 6



14a—e **10e—i, 11c,f**

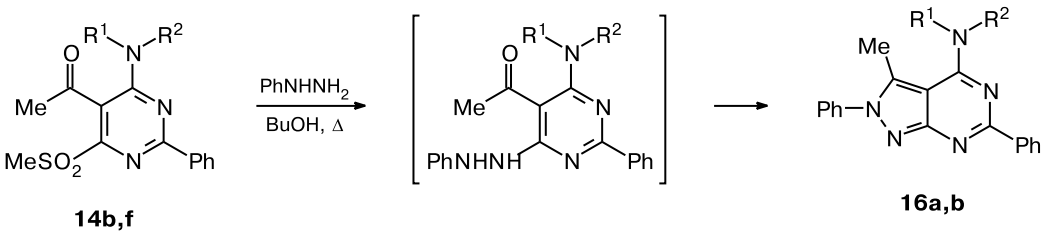
R^3 = H (**10**), Me (**11**); R^1 = R^2 = H (**14a**, **10e**, **11e**), R^1 = H, R^2 = = 3,5-$Me_2C_6H_3$ (**14b**, **10f**, **11f**); R^1 = H, R^2 = 3-ClC_6H_4 (**14c**, **10g**); R^1 = H, R^2 = 3-$CF_3C_6H_4$ (**14d**, **10h**); R^1 = H, R^2 = $PhCH_2$ (**14e**, **10i**)

C(7a), whereas no correlation is observed between the NMe protons and the carbon atom C(3), which, in turn, correlates with the protons of the Me group. In the 2D ^{1}H/^{15}N HMBC spectrum of compound **11f**, the more upfield nitrogen atom N(1) (−200) correlates only with the NMe protons, whereas for the more downfield nitrogen atom N(2) (−72) the correlation is observed with both the NMe protons and the Me protons. In the 2D ^{1}H/^{15}N HMBC spectrum of compound **10i**, a correlation of the protons of the Me group with the nitrogen atom at δ −85 is observed (the chemical shift in the low field indicates that the atom N(2) is attached to a double bond, and, therefore, the proton is attached to the atom N(1)).

Reflux of 4-methylsulfonylpyrimidines **14b**,**f** with excess phenylhydrazine in butanol gives rise to 4-amino-2-phenyl-2*H*-pyrazolo[3,4-*d*]pyrimidines **16a**,**b**, which were isolated only in 29% yield (Scheme 7).

The structure of compounds **16a,b** was confirmed by spectroscopic data. The mass spectrum (EI) of compound **16a** exhibits a strong peak of molecular ion, whereas in the high resolution mass spectrum (ESI) of pyrazolopyrimidine **16b**, the $[M + H]^+$ and $[M + Na]^+$ peaks are observed. The position of the Ph group at the atom N(2) was established based on the ^{1}H NOE spectra, 2D ^{1}H/^{1}H gNOESY and ^{1}H/^{15}N HMBC spectra and confirmed by comparison of the ^{13}C NMR spectra of these compounds with those of 1*H*-pyrazolo[3,4-*d*]pyrimidines **10** and **11**. In the selective 1D spectrum of compound **16b** ($CDCl_3$),

Scheme 7



R^1 = H; R^2 = 3,5-$Me_2C_6H_3$ (**14b**, **16a**), Bu^n = (**14f**, **16b**)

a positive NOE is observed for the *ortho*-protons PhN (2.0%) at δ 7.51 and the proton NH (2.2%) at δ 5.33 when the protons of the Me group at δ 2.68 are irradiated, whereas in the 2D $^1H/^1H$ gNOESY spectrum of compound **16a**, a correlation peak is observed for the methyl protons and the *ortho*-protons of PhN. The 2D $^1H/^{15}N$ HMBC spectra of compounds **16a,b** exhibit correlation peaks for the atom N(2) and the methyl protons, as well as the *ortho*-protons of PhN. In the ^{13}C NMR spectra, the signal for the carbon atom C(3) in 2*H*-pyrazolopyrimidines **16** is found in the higher field as compared to 1*H*-pyrazolopyrimidines **10** and **11**. On the contrary, the signal for the carbon atom C(7a) was found in the lower field (δ 132.45 (C(3)), δ 160.44 (C(7a)) for compound **16a**; δ 140.64 (C(3)), δ 157.26 (C(7a)) for pyrazolopyrimidine **10f**; δ 138.89 (C(3)), δ 155.87 (C(7a)) for heterocycle **11f**).

In conclusion, for the first time we have shown that pyrazolo[3,4-*d*]pyrimidines can be successfully synthesized from pyrimidines with vicinal acetyl and methylsulfonyl groups as the starting compounds.

Experimental

^1H NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz), ^{13}C NMR, ^1H NOE, 2D $^1H/^{13}C$ and $^1H/^{15}N$ HMBC, and $^1H/^1H$ gNOESY spectra were recorded on a Bruker Avance 600 spectrometer (600, 150, and 60.8 MHz for ^1H, ^{13}C, and ^{15}N, respectively). Residual signals of the deuterated solvent (δ 7.27 for $CDCl_3$ and δ 2.50 for DMSO-d_6) were used as a reference in the ^1H NMR spectra. Multiplet signals of the deuterated solvent (δ 39.50 for DMSO-d_6 and δ 77.00 for $CDCl_3$) were the reference in the ^{13}C NMR spectra. ^{15}N chemical shifts were measured using $MeNO_2$ as an external standard (high-field chemical shifts are given as the negative values). IR spectra were recorded on a Specord-M82 spectrometer and mass spectra were recorded on a Kratos MS-30 instrument (EI, 70 eV, the temperature of the injection chamber was 250 °C, direct injection). High resolution mass spectra were recorded on a Bruker micrOTOF II instrument (ESI). Measurements were carried out in the positive and the negative ranges (capillary voltage was 4500 V). The masses were scanned in the range m/z 50 — 3000 Da using an external and an internal calibration (Electrospray Calibrant Solution, Fluka). An acetonitrile solution of a compound was injected by a syringe, the flow rate was 3 μm min^{-1}, nitrogen was a sprayer gas (4 L min^{-1}), the interface temperature was 180 °C. The following reactants were used in the synthesis: anilines, piperazines, and MCPBA from Lancaster and Acros, benzoyl isothiocyanate from Fluka; anhydrous benzene and toluene were obtained by distillation over Na; methanol was fractionally distilled before use. Column chromatography was carried out on Merck Silicagel 60 (0.063—0.200 mm). Diacetyl ketene *N*,*S*-acetal **5** (m.p. 118—119 °C) was obtained according to the known procedure;[22] 5-acetyl-6-morpholino-2-phenylpyrimidine-4(3*H*)-thione (**9a**) (m.p. 209—210 °C) and 5-acetyl-6-amino-4-methylsulfanyl-2-phenylpyrimidine (**3**) (m.p. 152—153 °C) were obtained according to the procedures described earlier.[20,21]

3-[Amino(4-methylpiperazin-1-yl)methylidene]pentane-2,4-dione (6b). A mixture of *N*,*S*-ketene acetal **5** (1.45 g, 8.3 mmol) and *N*-methylpiperazine (1.01 mL, 9.1 mmol) in benzene (18 mL) was refluxed for 1 h, cooled to ~20 °C, a precipitate was filtered off, washed with benzene (5 mL) and light petroleum (10 mL) to obtain ketene aminal **6b** (0.83 g, 44%), m.p. 248—249 °C. Found (%): C, 58.71; H, 8.54; N, 18.40. $C_{11}H_{19}N_3O_2$. Calculated (%): C, 58.64; H, 8.50; N, 18.65. ^1H NMR (DMSO-d_6), δ: 1.98 (s, 6 H, 2 MeCO); 2.20 (s, 3 H, NMe); 2.38 (m, 4 H, 2 CH_2N); 3.49 (m, 4 H, 2 CH_2N); 8.12 (br.s, 1 H, NH); 8.49 (br.s, 1 H, NH).

3-{Amino[4-(4-methoxyphenyl)piperazin-1-yl]methylidene}-pentane-2,4-dione (6c) was synthesized similarly to ketene aminal **6b** from *N*,*S*-acetal **5** and *N*-(4-methoxyphenyl)piperazine. The reaction time was 3 h, the yield was 41%, m.p. 231—232 °C. Found (%): C, 64.11; H, 7.27; N, 13.30. $C_{17}H_{23}N_3O_3$. Calculated (%): C, 64.33; H, 7.30; N, 13.24. ^1H NMR (DMSO-d_6), δ: 1.98 (s, 6 H, 2 MeCO); 3.08 (m, 4 H, 2 CH_2N); 3.61 (m, 4 H, 2 CH_2N); 3.68 (s, 3 H, OMe); 6.81 (d, 2 H, C_6H_4, J = 7.5 Hz); 6.92 (d, 2 H, C_6H_4, J = 7.5 Hz); 8.21 (br.s, 1 H, NH); 8.52 (br.s, 1 H, NH).

3-{Amino[4-(4-fluorophenyl)piperazin-1-yl]methylidene}-pentane-2,4-dione (6d) was synthesized similarly to ketene aminal **6b** from *N,S*-acetal **5** and *N*-(4-fluorophenyl)piperazine. The reaction time was 3 h, the yield was 45%, m.p. 235—236 °C. Found (%): C, 62.88; H, 6.77; N, 13.75. $C_{16}H_{20}FN_3O_2$. Calculated (%): C, 62.93; H, 6.60; N, 13.76. ^1H NMR (DMSO-d_6), δ: 1.99 (s, 6 H, 2 MeCO); 3.15 (m, 4 H, 2 CH_2N); 3.62 (m, 4 H, 2 CH_2N); 6.95 (m, 2 H, C_6H_4); 7.04 (m, 2 H, C_6H_4); 8.21 (br.s, 1 H, NH); 8.56 (br.s, 1 H, NH).

Pyrimidine-4(3*H*)-thiones (9b—d). A mixture of the corresponding ketene aminal **6b—d** (3.5 mmol) and MeONa (4.2 mmol) in MeOH (6 mL) was refluxed for 4 h, cooled to ~20 °C, followed by addition of glacial AcOH (0.24 mL, 4.2 mmol). After evaporation of the solvent *in vacuo*, $CHCl_3$ (15 mL) was

added to the residue, AcONa was filtered off, the filtrate was concentrated *in vacuo*, PhCONCS (0.70 mL, 5.2 mmol) in toluene (8 mL) was added to the residue (oil) and the mixture was allowed to stand at 20 °C for 10 h. A precipitate formed was filtered off and washed with light petroleum (20 mL), followed by addition of MeONa (3.5 mmol) in MeOH (9 mL) and reflux for 5 min (until entire dissolution). Then, the mixture was cooled to 20 °C, acidified with AcOH, a precipitate formed was filtered off, washed with MeOH (3 mL) to obtain 5-acetyl-6-(4-methylpiperazin-1-yl)-2-phenylpyrimidine-4(3*H*)-thione (**9b**), 5-acetyl-6-[4-(4-methoxyphenyl)piperazin-1-yl]-2-phenylpyrimidine-4(3*H*)-thione (**9c**), and 5-acetyl-6-[4-(4-fluorophenyl)piperazin-1-yl]-2-phenylpyrimidine-4(3*H*)-thione (**9d**) as yellow crystals. The yields, melting points, and elemental analysis data are given in Table 1, the ^{1}H NMR spectra, in Table 2.

Pyrimidine-4(3*H*)-thiones (9e—i). A mixture of *N*,*S*-ketene acetal **5** (1.0 g, 5.8 mmol) and the corresponding amine (6.3 mmol) in *o*-xylene (10 mL) (in the case of arylamines) or in benzene (10 mL) (in the case of alkylamines) was refluxed for 4 h, the solvent was evaporated *in vacuo*, MeONa (5.8 mmol) in MeOH (8 mL) was added to the residue (oil) and the mixture was allowed to stand at 20 °C for 3—6 h (TLC monitoring). Then, glacial AcOH (0.33 mL, 5.8 mmol) was added, the solvent was evaporated *in vacuo*, benzene (15 mL) was added to the residue, AcONa was filtered off, the filtrate was concentrated *in vacuo*, PhCONCS (1.17 mL, 8.7 mmol) in benzene (10 mL) was added to the residue (oil) and the mixture was allowed to stand at 20 °C for 3 h. Then, light petroleum (20 mL) was added, the solvent was decanted, MeONa (5.8 mmol) in MeOH (6 mL) was added to the oil obtained, heated to boiling point, cooled to 20 °C, and acidified with AcOH. A precipitate formed was filtered off and washed with MeOH (4 mL) to obtain 5-acetyl-6-(3,5-dimethylphenylamino)-2-phenylpyrimidine-4(3*H*)-thione (**9e**), 5-acetyl-6-(3-chlorophenylamino)-2-phenylpyrimidine-4(3*H*)-thione (**9f**), 5-acetyl-2-phenyl-6-(3-trifluoromethylphenylamino)pyrimidine-4(3*H*)-thione (**9g**), 5-acetyl-6-benzylamino-2-phenylpyrimidine-4(3*H*)-thione (**9h**), and 5-acetyl-6-butylamino-2-phenylpyrimidine-4(3*H*)-thione (**9i**) as yellow crystals. The yields, melting points, and elemental analysis data are given in Table 1, the ^{1}H NMR spectra, in Table 2.

4-Methylsulfanylpyrimidines (4a, c—i). Sodium methoxide (5.3 mmol) in MeOH (12 mL) was added to the corresponding pyrimidinethione **9a**,**c—i** (3.5 mmol) and the mixture was stirred for 10 min at 20 °C until complete dissolution, then MeI (0.65 mL, 10.5 mmol) was added and this was allowed to stand at 20 °C for 30 min. A precipitate formed was filtered off to obtain 5-acetyl-4-methylsulfanyl-6-morpholino-2-phenylpyrimidine (**4a**), 5-acetyl-4-methylsulfanyl-6-[4-(4-methoxyphenyl)-piperazin-1-yl]-2-phenylpyrimidine (**4c**), 5-acetyl-6-[4-(4-fluorophenyl)piperazin-1-yl]-4-methylsulfanyl-2-phenylpyrimidine (**4d**), 5-acetyl-4-methylsulfanyl-6-(3,5-dimethylphenylamino)-2-phenylpyrimidine (**4e**), 5-acetyl-6-(3-chlorophenylamino)-4-methylsulfanyl-2-phenylpyrimidine (**4f**), 5-acetyl-4-methylsulfanyl-2-phenyl-6-(3-trifluoromethylphenylamino)-pyrimidine (**4g**), 5-acetyl-6-benzylamino-4-methylsulfanyl-2-phenylpyrimidine (**4h**), and 5-acetyl-6-butylamino-4-methylsulfanyl-2-phenylpyrimidine (**4i**) as colorless or pale yellow crystals. Analytically pure samples were obtained by recrystallization from hexane. The yields, melting points, and elemental analysis data are given in Table 1, the ^{1}H NMR spectra, in Table 2.

5-Acetyl-6-(4-methylpiperazin-1-yl)-4-methylsulfanyl-2-phenylpyrimidine (4b). Sodium methoxide (2.25 mmol) in MeOH (5 mL) was added to pyrimidinethione **9b** (0.50 g, 1.5 mmol) and left to stand at 20 °C for 10 min until complete dissolution, then MeI (0.28 mL, 4.5 mmol) was added and the mixture was allowed to stand at 20 °C for 1 h. Methanol was evaporated *in vacuo*, benzene (15 mL) was added to the residue, NaI was filtered off, benzene was evaporated *in vacuo*, the residue was crystallized with light petroleum (3 mL) to obtained pyrimidine **4b** (0.27 g, 52%) (see Tables 1 and 2).

Pyrazolo[3,4-*d*]pyrimidines (10a—d). A mixture of the corresponding pyrimidine **4a—d** (0.4 mmol) and hydrazine hydrate (0.5 mL, 10 mmol in the case of **4a—c** or 1.0 mL, 20 mmol in the case of **4d**) in BuOH (5 mL) was refluxed for 7—10 h (disappearance of the starting pyrimidines **4** was monitor by TLC). The solvent and excess hydrazine were evaporated *in vacuo*, the residue was washed with diethyl ether (5 mL) to obtain compounds **10a—d** as colorless crystals. Analytically pure samples were isolated by recrystallization from acetonitrile. The yields, melting points, and elemental analysis data are given in Table 3, the ^{1}H NMR spectra, in Table 4.

3-Methyl-4-morpholino-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (10a). MS, m/z (I_{rel} (%)): 295 $[M]^+$ (72), 265 $[M - CH_2O]^+$ (34), 250 $[M - CH_2OCH_3]^+$ (43), 238 $[M - CH_2OCH_2CH]^+$ (93), 209 $[M - (CH_2)_2O(CH_2)_2N]^+$ (58), 66 (100). IR ($CHCl_3$), ν/cm^{-1}: 3456 (NH), 1584, 1552.

3-Methyl-4-(4-methylpiperazin-1-yl)-6-phenyl-1*H*-pyrazolo-[3,4-*d*]pyrimidine (10b). MS, m/z (I_{rel} (%)): 308 $[M]^+$ (8), 252 $[M - MeNCH_2CH]^+$ (19), 238 $[M - MeN(CH)CH_2CH_2]^+$ (100), 209 $[M - MeN(CH_2)_4N]^+$ (31). IR ($CHCl_3$), ν/cm^{-1}: 3456 (NH), 1592 sh, 1580, 1552.

4-[4-(4-Methoxyphenyl)piperazin-1-yl]-3-methyl-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (10c). MS, m/z (I_{rel} (%)): 400 $[M]^+$ (37), 251 $[M - MeOC_6H_4NCH_2CH_2]^+$ (28), 238 $[M - MeOC_6H_4N(CH)CH_2CH_2]^+$ (100), 209 $[M - MeOC_6H_4N(CH_2)_4N]^+$ (33). IR ($CHCl_3$), ν/cm^{-1}: 3460 (NH), 1580, 1552, 1512.

4-[4-(4-Fluorophenyl)piperazin-1-yl]-3-methyl-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (10d). MS, m/z (I_{rel} (%)): 388 $[M]^+$ (6), 251 $[M - FC_6H_4NCH_2CH_2]^+$ (55), 238 $[M - FC_6H_4N(CH)CH_2CH_2]^+$ (100), 210 $[M - FC_6H_4N(CH_2)_3CHN]^+$ (52), 209 $[M - FC_6H_4N(CH_2)_4N]^+$ (47). IR ($CHCl_3$), ν/cm^{-1}: 3460 (NH), 1580, 1552, 1512.

1-Methylpyrazolo[3,4-*d*]pyrimidines (11a—d). A mixture of the corresponding pyrimidine **4a—d** (0.75 mmol) and methylhydrazine (2.0 mL, 37.5 mmol) in BuOH (5 mL) was refluxed for 14 h. In the synthesis of compounds **11a**,**b**,**d**, the solvent and excess hydrazine were evaporated *in vacuo*, the residue was subjected to column chromatography on SiO_2 (eluent: chloroform, then chloroform—MeOH 50 : 0.2, 50 : 0.5, 50 : 1). The solvent from the corresponding fractions was evaporated *in vacuo*, the residue was washed with light petroleum (2 mL) to obtain compounds **11a**,**b**,**d** as colorless crystals. In the preparation of compound **11c**, the reaction mixture was cooled to 20 °C, a precipitate formed was filtered off, washed with light petroleum (5 mL) to obtain pyrazolopyrimidine **11c**. Analytically pure samples of compounds **11a—d** were obtained by recrystallization from acetonitrile. The yields, melting points, and elemental analysis data are given in Table 3, the ^{1}H NMR spectra, in Table 4.

1,3-Dimethyl-4-morpholino-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (11a). MS, m/z (I_{rel} (%)): 309 $[M]^+$ (100), 279 $[M - CH_2O]^+$ (30), 265 $[M - CH_2OCH_2]^+$ (43), 252 $[M - CH_2OCH_2CH]^+$

Table 1. Yields, melting points. and elemental analysis data for pyrimidinethiones **9b—i**, methylsulfanylpyrimidines **4a—i**, and methylsulfonylpyrimidines **14a—f**

Compound	Yield (%)	M.p./°C	Found / Calculated (%)				Molecular formula
			C	H	N	S	
4a	84	105—106	61.87	5.73	12.92	9.81	$C_{17}H_{19}N_3O_2S$
			61.98	5.81	12.76	9.73	
4b	52	101—102	62.88	6.31	16.02	9.40	$C_{18}H_{22}N_4OS$
			63.13	6.48	16.36	9.36	
4c	77	133—134	66.54	6.04	12.60	7.28	$C_{24}H_{26}N_4O_2S$
			66.33	6.03	12.89	7.38	
4d	85	140—141	65.09	5.42	13.32	—	$C_{23}H_{23}FN_4OS$
			65.38	5.49	13.26		
4e	85	118—119	69.08	5.90	11.37	8.63	$C_{21}H_{21}N_3OS$
			69.39	5.82	11.56	8.82	
4f	88	113—114	61.56	4.40	11.25	—	$C_{19}H_{16}ClN_3OS$
			61.70	4.36	11.36		
4g	94	114—115	59.25	3.88	10.17	—	$C_{20}H_{16}F_3N_3OS$
			59.54	4.00	10.42		
4h	93	137—138	68.56	5.39	11.95	9.05	$C_{20}H_{19}N_3OS$
			68.74	5.48	12.03	9.18	
4i	91	80—81	64.57	6.58	13.21	10.02	$C_{17}H_{21}N_3OS$
			64.73	6.71	13.32	10.16	
9b	49*	227—228	62.13	6.04	16.93	9.88	$C_{17}H_{20}N_4OS$
			62.17	6.14	17.06	9.76	
9c	64*	219—220	65.41	5.66	13.39	7.44	$C_{23}H_{24}N_4O_2S$
			65.69	5.75	13.32	7.63	
9d	42*	226—228	64.56	5.18	13.79	—	$C_{22}H_{21}FN_4OS$
			64.68	5.18	13.72		
9e	23**	229—230	68.67	5.68	12.08	9.08	$C_{20}H_{19}N_3OS$
			68.74	5.48	12.03	9.18	
9f	27**	180—181	60.58	4.05	11.65	—	$C_{18}H_{14}ClN_3OS$
			60.75	3.97	11.81		
9g	22**	188—189	58.43	3.47	10.54	—	$C_{19}H_{14}F_3N_3OS$
			58.60	3.67	10.79		
9h	48**	205—206 (Ref. 21: 205—206)	—	—	—	—	—
9i	31**	156—157	63.80	6.29	13.87	10.56	$C_{16}H_{19}N_3OS$
			63.76	6.35	13.94	10.64	
14a	54	189—190	53.97	4.43	14.25	10.92	$C_{13}H_{13}N_3O_3S$
			53.59	4.50	14.42	11.01	
14b	40	232—233	63.82	5.31	10.65	7.95	$C_{21}H_{21}N_3O_3S$
			63.78	5.35	10.63	8.11	
14c	56	206—207	56.84	4.15	10.31	—	$C_{19}H_{16}ClN_3O_3S$
			56.78	4.01	10.46		
14d	54	188—189	54.87	3.89	9.43	—	$C_{20}H_{16}F_3N_3O_3S$
			55.17	3.70	9.65		
14e	44	189—190	63.22	5.03	10.74	8.33	$C_{20}H_{19}N_3O_3S$
			62.97	5.02	11.02	8.41	
14f	24	122—123	58.84	6.06	11.90	9.15	$C_{17}H_{21}N_3O_3S$
			58.77	6.09	12.10	9.23	

* Yields are calculated based on ketene aminals **6b—d**.
** Yields are calculated based on *N*,*S*-ketene acetal **5**.

(86), 224 $[M - CH_2OCH_2CHNCH_2]^+$ (52). IR ($CHCl_3$), ν/cm^{-1}: 1568, 1552. ^{13}C NMR ($CDCl_3$), δ: 17.16 (Me); 33.41 (NMe); 48.87 (2 CH_2N); 66.71 (2 CH_2O); 100.38 (C(3a)); 128.20 (*m*-C_{Ph}); 128.34 (*o*-C_{Ph}); 130.21 (*p*-C_{Ph}); 138.25 (*ipso*-C_{Ph}); 139.10 (C(3)); 156.95 (C(7a)); 160.18 (C(6)), 160.22 (C(4)). The signals were assigned based on the 2D $^1H/^{13}C$ HMBC spectrum.

Table 2. The ^{1}H NMR spectra of pyrimidinethiones **9b—i**, methylsulfanylpyrimidines **4a—i**, and methylsulfonylpyrimidines **14a—f** in $CDCl_3$

Compound	δ (*J*/Hz)
4a	2.48 (s, 3 H, MeCO); 2.63 (s, 3 H, SMe); 3.64 (m, 4 H, 2 CH_2N); 3.81 (m, 4 H, 2 CH_2O); 7.50 (m, 3 H, Ph); 8.47 (m, 2 H, Ph)
4b	2.32 (s, 3 H, NMe); 2.46 (s, 3 H, MeCO); 2.51 (m, 4 H, 2 CH_2N); 2.64 (s, 3 H, SMe); 3.71 (m, 4 H, 2 CH_2N); 7.49 (m, 3 H, Ph); 8.47 (m, 2 H, Ph)
4c	2.52 (s, 3 H, MeCO); 2.68 (s, 3 H, SMe); 3.18 (m, 4 H, 2 CH_2N); 3.78 (s, 3 H, OMe); 3.85 (m, 4 H, 2 CH_2N); 6.88 (m, 4 H, C_6H_4); 7.50 (m, 3 H, Ph); 8.49 (m, 2 H, Ph)
4d	2.50 (s, 3 H, MeCO); 2.65 (s, 3 H, SMe); 3.21 (m, 4 H, 2 CH_2N); 3.82 (m, 4 H, 2 CH_2N); 6.91 (m, 2 H, C_6H_4); 6.98 (m, 2 H, C_6H_4); 7.49 (m, 3 H, Ph); 8.48 (m, 2 H, Ph)
4e*	2.32 (s, 6 H, 2 Me); 2.72 and 2.80 (both s, 6 H, COMe and SMe); 6.81 (s, 1 H, *p*-$H_{C_6H_3}$); 7.45 (m, 5 H, *m*-H_{Ph}, *p*-H_{Ph} and *o*-$H_{C_6H_3}$); 8.48 (m, 2 H, *o*-H_{Ph}); 11.35 (br.s, 1 H, NH)
4f	2.78 and 2.87 (both s, 6 H, COMe and SMe); 7.12 (d, 1 H, *p*-$H_{C_6H_4}$, *J* = 7.8); 7.32 (t, 1 H, *m*-$H_{C_6H_4}$, *J* = 7.8); 7.51 (m, 4 H, *m*-H_{Ph}, *p*-H_{Ph} and *o*-$H_{C_6H_4}$); 8.02 (s, 1 H, *o*-$H_{C_6H_4}$); 8.48 (m, 2 H, *o*-H_{Ph}); 11.53 (br.s, 1 H, NH)
4g	2.79 and 2.88 (both s, 6 H, COMe and SMe); 7.41 (d, 1 H, *p*-$H_{C_6H_4}$, *J* = 7.8); 7.49 (m, 4 H, *m*-H_{Ph}, *p*-H_{Ph} and *m*-$H_{C_6H_4}$); 7.72 (d, 1 H, *o*-$H_{C_6H_4}$, *J* = 7.8); 8.40 (s, 1 H, *o*-$H_{C_6H_4}$); 8.46 (m, 2 H, *o*-H_{Ph}); 11.63 (br.s, 1 H, NH)
4h	2.73 and 2.80 (both s, 6 H, COMe and SMe); 4.90 (d, 2 H, CH_2, *J* = 5.0); 7.25—7.54 (m, 8 H, 3 H_{Ph} and 5 $H_{\underline{Ph}CH_2}$); 8.48 (m, 2 H, Ph); 9.88 (br.t, 1 H, NH)
4i	0.97 (t, 3 H, $\underline{Me}CH_2$, *J* = 7.2); 1.45 (m, 2 H, CH_2); 1.68 (m, 2 H, CH_2); 2.72 and 2.78 (both s, 6 H, COMe and SMe); 3.69 (m, 2 H, CH_2N); 7.49 (m, 3 H, Ph); 8.49 (m, 2 H, Ph); 9.51 (br.t, 1 H, NH)
9b	2.31 (s, 3 H, NMe); 2.51 (m, 4 H, 2 CH_2N); 2.82 (s, 3 H, MeCO); 3.70 (m, 4 H, 2 CH_2N); 7.58 (m, 3 H, Ph); 7.97 (m, 2 H, Ph); 10.02 (br.s, 1 H, NH)
9c	2.85 (s, 3 H, MeCO); 3.18 (m, 4 H, 2 CH_2N); 3.80 (s, 3 H, OMe); 3.85 (m, 4 H, 2 CH_2N); 6.88 (m, 4 H, C_6H_4); 7.58 (m, 3 H, Ph); 7.98 (m, 2 H, Ph); 10.25 (br.s, 1 H, NH)
9d	2.85 (s, 3 H, MeCO); 3.21 (m, 4 H, 2 CH_2N); 3.82 (m, 4 H, 2 CH_2N); 6.85 (m, 2 H, C_6H_4); 6.94 (m, 2 H, C_6H_4); 7.60 (m, 3 H, Ph); 7.98 (m, 2 H, Ph); 10.32 (br.s, 1 H, NH)
9e	2.32 (s, 6 H, 2 Me); 3.32 (s, 3 H, COMe); 6.87 (s, 1 H, *p*-$H_{C_6H_3}$); 7.21 (s, 2 H, *o*-$H_{C_6H_3}$); 7.56 (t, 2 H, *m*-H_{Ph}, *J* = 7.8); 7.65 (t, 1 H, *p*-H_{Ph}, *J* = 7.8); 7.91 (m, 2 H, *o*-H_{Ph}); 10.28 (br.s, 1 H, NH); 12.43 (br.s, 1 H, $\underline{NH}C_6H_3$)
9f	3.04 (s, 3 H, COMe); 7.21 (d, 1 H, *p*-$H_{C_6H_4}$, *J* = 7.8); 7.31 (t, 1 H, *m*-$H_{C_6H_4}$, *J* = 7.8); 7.40 (d, 1 H, *o*-$H_{C_6H_4}$, *J* = 7.8); 7.59 (t, 2 H, *m*-H_{Ph}, *J* = 7.8); 7.66 (t, 1 H, *p*-H_{Ph}, *J* = 7.8); 7.81 (s, 1 H, *o*-$H_{C_6H_4}$); 7.99 (d, 2 H, *o*-H_{Ph}, *J* = 7.8); 10.31 (br.s, 1 H, NH); 12.64 (br.s, 1 H, $\underline{NH}C_6H_4$)
9g	3.04 (s, 3 H, COMe); 7.41—7.74 (m, 6 H, *m*-H_{Ph}, *p*-H_{Ph}, *o*-$H_{C_6H_4}$, *m*-$H_{C_6H_4}$, *p*-$H_{C_6H_4}$); 7.99 (d, 2 H, *o*-H_{Ph}, *J* = 7.8); 8.20 (s, 1 H, *o*-$H_{C_6H_4}$); 10.38 (br.s, 1 H, NH); 12.75 (br.s, 1 H, $\underline{NH}C_6H_4$)
9h	3.00 (s, 3 H, COMe); 4.91 (d, 2 H, CH_2, *J* = 5.0); 7.32 (m, 5 H, $\underline{Ph}CH_2$); 7.56 (t, 2 H, *m*-H_{Ph}, *J* = 7.8); 7.63 (t, 1 H, *p*-H_{Ph}, *J* = 7.8); 7.99 (d, 2 H, *o*-H_{Ph}, *J* = 7.8); 10.22 (br.s, 1 H, NH); 11.10 (br.t, 1 H, $\underline{NH}CH_2$)
9i	0.96 (t, 3 H, $\underline{Me}CH_2$, *J* = 7.2); 1.42 (m, 2 H, CH_2); 1.69 (m, 2 H, CH_2); 2.98 (s, 3 H, COMe); 3.68 (m, 2 H, CH_2N); 7.56 (t, 2 H, *m*-H_{Ph}, *J* = 7.8); 7.62 (t, 1 H, *p*-H_{Ph}, *J* = 7.8); 8.01 (d, 2 H, *o*-H_{Ph}, *J* = 7.8); 10.11 (br.s, 1 H, NH); 10.78 (br.t, 1 H, $\underline{NH}CH_2$)
14a	2.79 (s, 3 H, MeCO); 3.40 (s, 3 H, SO_2Me); 6.62 (br.s, 2 H, NH_2); 7.50 (m, 3 H, Ph); 8.35 (d, 2 H, Ph, *J* = 7.8)
14b	2.38 (s, 6 H, 2 Me); 2.84 (s, 3 H, MeCO); 3.41 (s, 3 H, SO_2Me); 6.87 (s, 1 H, *p*-$H_{C_6H_3}$); 7.31 (s, 2 H, *o*-$H_{C_6H_3}$); 7.51 (m, 3 H, Ph); 8.38 (d, 2 H, Ph, *J* = 7.8); 8.91 (br.s, 1 H, NH)
14c	2.88 (s, 3 H, MeCO); 3.42 (s, 3 H, SO_2Me); 7.19 (d, 1 H, *p*-$H_{C_6H_4}$, *J* = 7.8); 7.36 (t, 1 H, *m*-$H_{C_6H_4}$, *J* = 7.8); 7.45 (d, 1 H, *o*-$H_{C_6H_4}$, *J* = 7.8); 7.53 (m, 3 H, *m*-H_{Ph}, *p*-H_{Ph}); 7.91 (s, 1 H, *o*-$H_{C_6H_4}$); 8.48 (d, 2 H, *o*-H_{Ph}, *J* = 7.8); 9.12 (br.s, 1 H, NH)
14d	2.91 (s, 3 H, MeCO); 3.45 (s, 3 H, SO_2Me); 7.43—7.62 (m, 5 H, *p*-$H_{C_6H_4}$, *m*-$H_{C_6H_4}$, *m*-H_{Ph}, *p*-H_{Ph}); 7.66 (d, 1 H, *o*-$H_{C_6H_4}$, *J* = 7.8); 8.31 (s, 1 H, *o*-$H_{C_6H_4}$); 8.39 (d, 2 H, *o*-H_{Ph}, *J* = 7.8); 9.30 (br.s, 1 H, NH)
14e**	2.79 (s, 3 H, MeCO); 3.39 (s, 3 H, SO_2Me); 4.86 (d, 2 H, CH_2, *J* = 6.0); 7.32 (m, 1 H, *p*-H_{PhCH_2}); 7.38 (m, 4 H, *o*-H_{PhCH_2}, *m*-H_{PhCH_2}); 7.43 (br.t, 1 H, NH); 7.50 (t, 2 H, *m*-H_{Ph}, *J* = 7.8); 7.55 (t, 1 H, *p*-H_{Ph}, *J* = 7.8); 8.40 (d, 2 H, *o*-H_{Ph}, *J* = 7.8)
14f	0.98 (t, 3 H, $\underline{Me}CH_2$, *J* = 7.2); 1.44 (m, 2 H, CH_2); 1.69 (m, 2 H, CH_2); 2.78 (s, 3 H, COMe); 3.39 (s, 3 H, SO_2Me); 3.67 (m, 2 H, CH_2N); 7.10 (br.t, 1 H, NH); 7.51 (m, 3 H, Ph); 8.40 (d, 2 H, Ph, *J* = 7.8)

* Here and in the ^{1}H NMR spectra reported below, positions of the protons in disubstituted and trisubstituted benzene rings are given with respect to the carbon atom bonded the nitrogen atom.

** The spectrum was recorded on a spectrometer with the operational frequency of 600 MHz.

Table 3. Yields, melting points, and elemental analysis data for pyrazolopyrimidines **10a—i**, **11a—f**

Compound	Yield (%)	M.p. /°C	Found / Calculated (%)			Molecular formula
			C	H	N	
10a	62	240—241	65.17 65.07	5.89 5.80	24.04 23.71	$C_{16}H_{17}N_5O$
10b	81	230—231	65.85 66.21	6.31 6.54	26.96 27.25	$C_{17}H_{20}N_6$
10c	72	218—219	69.01 68.98	6.27 6.04	21.00 20.99	$C_{23}H_{24}N_6O$
10d	61	218—219	67.79 68.02	5.41 5.45	21.71 21.64	$C_{22}H_{21}FN_6$
10e	62	317—320	63.71 63.99	4.89 4.92	30.79 31.09	$C_{12}H_{11}N_5$
10f	80	272—273	72.70 72.92	5.85 5.81	20.91 21.26	$C_{20}H_{19}N_5$
10g	74	301—303	64.11 64.38	4.10 4.20	20.73 20.86	$C_{18}H_{14}ClN_5$
10h	80	264—265	61.54 61.79	3.77 3.82	18.59 18.96	$C_{18}H_{14}F_3N_5$
10i	76	215—216	72.09 72.36	5.28 5.43	22.05 22.21	$C_{19}H_{17}N_5$
11a	57	131—132	65.64 66.00	6.01 6.19	22.38 22.64	$C_{17}H_{19}N_5O$
11b	48	159—160	67.00 67.06	7.10 6.87	25.84 26.07	$C_{18}H_{22}N_6$
11c	64	184—185	69.43 69.54	6.27 6.32	20.08 20.28	$C_{24}H_{26}N_6O$
11d	26	198—199	68.45 68.64	5.54 5.76	20.74 20.88	$C_{23}H_{23}FN_6$
11e	55	170—171	65.02 65.25	5.25 5.48	28.98 29.27	$C_{13}H_{13}N_5$
11f	65	195—196	73.12 73.44	6.23 6.16	20.34 20.39	$C_{21}H_{21}N_5$

1,3-Dimethyl-4-(4-methylpiperazin-1-yl)-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (11b). MS, m/z (I_{rel} (%)): 322 $[M]^+$ (1), 252 $[M - MeN(CH)CH_2CH_2]^+$ (100), 240 $[M - MeN(CH_2C)CH_2CH]^+$ (44), 223 $[M - MeN(CH_2)_4N]^+$ (59). IR ($CHCl_3$), ν/cm^{-1}: 1564, 1548.

4-[4-(4-Methoxyphenyl)piperazin-1-yl]-1,3-dimethyl-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (11c). IR ($CHCl_3$), ν/cm^{-1}: 1580, 1552, 1512.

4-[4-(4-Fluorophenyl)piperazin-1-yl]-1,3-dimethyl-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (11d). MS, m/z (I_{rel} (%)): 402 $[M]^+$ (3), 265 $[M - FC_6H_4NCH_2CH_2]^+$ (32), 252 $[M - FC_6H_4N(CH)CH_2CH_2]^+$ (100), 238 $[M - FC_6H_4N(CHCH_2)CH_2CH_2]^+$ (35), 223 $[M - FC_6H_4N(CH_2)_4N]^+$ (57). IR ($CHCl_3$), ν/cm^{-1}: 1552, 1512.

Reaction of 5-acetyl-6-amino-4-methylsulfanyl-2-phenylpyrimidine (3) with hydrazine hydrate. A mixture of pyrimidine **3** (0.10 g, 0.4 mmol) and hydrazine hydrate (0.5 mL, 10 mmol) in butanol (5 mL) was refluxed for 6 h, the solvent and excess hydrazine was evaporated *in vacuo*, benzene (5 mL) was added to the residue to the residue, which was dissolved by heating, then the mixture was cooled to 20 °C, light petroleum (5 mL) was added, a precipitate formed was filtered off to obtain a white substance (0.074 g) (two close spots on a TLC plate with the R_f values of 0.18 and 0.24 in the system chloroform—EtOH 20 : 1). According to the ^{1}H NMR spectrum, this is a mixture of two compounds **12a** and **13a** in molar ratio ~2 : 1. ^{1}H NMR of compound **12a** ($CDCl_3$), δ: 2.19 (s, 3 H, Me); 2.70 (s, 3 H, SMe); 4.88 (br.s, 2 H, NH_2); 5.28 (br.s, 2 H, NH_2); 7.48 (m, 3 H, Ph); 8.42 (m, 2 H, Ph). ^{1}H NMR of compound **13a** ($CDCl_3$), δ: 2.17 (s, 6 H, 2 Me); 2.70 (s, 6 H, 2 SMe); 5.50 (br.s, 4 H, 2 NH_2); 7.48 (m, 6 H, 2 Ph); 8.42 (m, 4 H, 2 Ph).

Reaction of 5-acetyl-4-(3,5-dimethylphenylamino)-4-methylsulfanyl-2-phenylpyrimidine (4e) with hydrazine hydrate. A mixture of pyrimidine **4e** (0.082 g, 0.23 mmol) and hydrazine hydrate (0.27 mL, 5.6 mmol) in butanol (5 mL) was refluxed for 4 h, the solvent and excess hydrazine were evaporated *in vacuo*, the residue was washed with light petroleum to obtain a mixture of compounds **12b** and **13b** (0.061 g) in the ratio ~8 : 1. ^{1}H NMR of compound **12b** ($CDCl_3$), δ: 2.19 (s, 3 H, Me); 2.35 (s, 6 H, 2 Me); 2.72 (s, 3H, SMe); 5.60 (br.s, 2 H, NH_2); 6.75 (s, 1 H, *p*-$H_{C_6H_3}$); 7.36 (s, 2 H, *o*-$H_{C_6H_3}$); 7.48 (m, 3 H, Ph); 8.38 (br.s, 1 H, NH); 8.49 (m, 2 H, Ph). ^{1}H NMR of compound **13b** ($CDCl_3$), δ: 2.21 (s, 6 H, 2 Me); 2.35 (s, 12 H, 4 Me); 2.72 (s, 6 H, 2 SMe); 6.75 (s, 2 H, 2 C_6H_3); 7.36 (s, 4 H, 2 C_6H_3); 7.48 (m, 6 H, 2 Ph); 8.49 (m, 4 H, 2 Ph).

4-Methylsulfonylpyrimidines (14a—d). A mixture of the corresponding 4-methylsulfanylpyrimidine **3**,**4e—g** (0.5 mmol) and 40% MCPBA (0.54 g, 1.25 mmol) in chloroform (14 mL) was stirred for 30 min at ~20 °C, chloroform was evaporated *in vacuo* at ~20 °C, benzene (12 mL) was added to the residue, a precipitate of *m*-chlorobenzoic acid was filtered off, the filtrate was shaken with saturated aqueous K_2CO_3, the organic layer was separated and, without concentration, was subjected to column chromatography on SiO_2 (eluent benzene). The solvent was evaporated *in vacuo*, the residue was washed with light petroleum (5 mL) to obtain pyrimidines **14a—d** as colorless crystals. The yields, melting points, and elemental analysis data are given in Table 1, the ^{1}H NMR spectra, in Table 2.

5-Acetyl-6-amino-4-methylsulfonyl-2-phenylpyrimidine (14a). MS, m/z (I_{rel} (%)): 291 $[M]^+$ (70), 276 $[M - Me]^+$ (94), 228 $[M - SOMe]^+$ (24), 214 $[M - Ph]^+$ (60), 104 $[PhC{=}NH]^+$ (100), 76 (78), 67 (91). IR ($CHCl_3$), ν/cm^{-1}: 3512 and 3400 (NH_2), 1680 (CO), 1604, 1552, 1508.

5-Acetyl-6-(3,5-dimethylphenylamino)-4-methylsulfonyl-2-phenylpyrimidine (14b). MS, m/z (I_{rel} (%)): 395 $[M]^+$ (100), 316 $[M - SO_2Me]^+$ (63). IR ($CHCl_3$), ν/cm^{-1}: 3370 (NH), 1676 (CO), 1616, 1572, 1548.

5-Acetyl-6-(3-chlorophenylamino)-4-methylsulfonyl-2-phenylpyrimidine (14c). MS, m/z (I_{rel} (%)): 401 $[M]^+$ (15), 322 $[M - SO_2Me]^+$ (12), 276 $[M - ClC_6H_4N]^+$ (15), 219 $[M - SO_2Me - PhCN]^+$ (33), 177 $[M - SO_2Me - PhCN - CH_2CO]^+$ (100). IR (KBr), ν/cm^{-1}: 3356 (NH), 1676 (CO), 1592, 1564, 1536.

5-Acetyl-4-methylsulfonyl-2-phenyl-6-(3-trifluoromethylphenylamino)pyrimidine (14d). MS, m/z (I_{rel} (%)): 435 $[M]^+$ (100), 356 $[M - SO_2Me]^+$ (19), 355 $[M - SO_2Me - H]^+$ (22), 253 $[M - SO_2Me - PhCN]^+$ (13), 211 $[M - SO_2Me - PhCN - CH_2CO]^+$ (25). IR (KBr), ν/cm^{-1}: 3280 (NH), 1684 (CO), 1604, 1588, 1552.

5-Acetyl-6-benzylamino-4-methylsulfonyl-2-phenylpyrimidine (14e) and 5-acetoxy-6-benzylamino-4-methylsulfonyl-2-phenylpyrimidine (15e). Oxidation of pyrimidine **4h** and work-up of the reaction mixture were carried out similarly to those in the prepa-

Table 4. The ^{1}H NMR spectra of pyrazolopyrimidines **10a—i**, **11a—f**

Compound	Solvent	δ, *J*/Hz
10a	$CDCl_3$	2.66 (s, 3 H, Me); 3.92 (s, 8 H, 2 CH_2N and 2 CH_2O); 7.50 (m, 3 H, Ph); 8.49 (m, 2 H, Ph); 11.65 (br.s, 1 H, NH)
10b	$CDCl_3$	2.42 (s, 3 H, NMe); 2.65 (m, 4 H, 2 CH_2N); 2.66 (s, 3 H, Me); 3.98 (m, 4 H, 2 CH_2N); 7.51 (m, 3 H, Ph); 8.50 (m, 2 H, Ph); 11.50 (br.s, 1 H, NH)
10c	$CDCl_3$	2.71 (s, 3 H, Me); 3.30 (m, 4 H, 2 CH_2N); 3.82 (s, 3 H, OMe); 4.10 (m, 4 H, 2 CH_2N); 6.88 (d, 2 H, C_6H_4, J = 7.8); 6.97 (d, 2 H, C_6H_4, J = 7.8); 7.51 (m, 3 H, Ph); 8.51 (m, 2 H, Ph); 11.68 (br.s, 1 H, NH)
10d	$CDCl_3$	2.71 (s, 3 H, Me); 3.32 (m, 4 H, 2 CH_2N); 4.03 (m, 4 H, 2 CH_2N); 6.99 (m, 4 H, C_6H_4); 7.52 (m, 3 H, Ph); 8.52 (m, 2 H, Ph); 11.89 (br.s, 1 H, NH)
10e	DMSO-d_6	2.53 (s, 3 H, Me); 7.18 (br.s, 2 H, NH_2); 7.49 (m, 3 H, Ph); 8.37 (m, 2 H, Ph); 12.95 (br.s, 1 H, NH)
10f*	DMSO-d_6	2.34 (s, 6 H, 2 Me); 2.69 (s, 3 H, Me); 6.80 (s, 1 H, *p*-$H_{C_6H_3}$); 7.48 (m, 3 H, *m*-H_{Ph}, *p*-H_{Ph}); 7.52 (s, 2 H, *o*-$H_{C_6H_3}$); 8.35 (m, 2 H, *o*-H_{Ph}); 8.50 (br.s, 1 H, $\underline{NH}C_6H_3$); 13.23 (br.s, 1 H, NH)
10g	DMSO-d_6	2.72 (s, 3 H, Me); 7.19 (d, 1 H, *p*-$H_{C_6H_4}$, J = 7.8); 7.48 (m, 4 H, *m*-H_{Ph}, *p*-H_{Ph}, *m*-$H_{C_6H_4}$); 7.82 (d, 1 H, *o*-$H_{C_6H_4}$, J = 7.8); 8.10 (s, 1 H, *o*-$H_{C_6H_4}$); 8.36 (m, 2 H, *o*-H_{Ph}); 8.80 (br.s, 1 H, $\underline{NH}C_6H_4$); 13.31 (br.s, 1 H, NH)
10h	DMSO-d_6	2.74 (s, 3 H, Me); 7.45 (m, 4 H, *m*-H_{Ph}, *p*-H_{Ph}, *p*-$H_{C_6H_4}$); 7.68 (t, 1 H, *m*-$H_{C_6H_4}$, J = 7.8); 8.08 (d, 1 H, *o*-$H_{C_6H_4}$, J = 7.8); 8.34 (m, 2 H, *o*-H_{Ph}); 8.48 (s, 1 H, *o*-$H_{C_6H_4}$); 8.95 (br.s, 1 H, NH); 13.37 (br.s, 1 H, NH)
10i	DMSO-d_6	2.61 (s, 3 H, Me); 4.87 (d, 2 H, CH_2, J = 5.4); 7.21 (t, 1 H, *p*-H_{PhCH_2}, J = 7.2); 7.31 (t, 2 H, *m*-H_{PhCH_2}, J = 7.2); 7.43 (m, 3 H, *m*-H_{Ph}, *p*-H_{Ph}); 7.46 (d, 2 H, *o*-H_{PhCH_2}, J = 7.2); 7.80 (br.t, 1 H, $\underline{NH}CH_2$); 8.33 (m, 2 H, *o*-H_{Ph}); 13.05 (br.s, 1 H, NH)
11a*	$CDCl_3$	2.61 (s, 3 H, Me); 3.87 (m, 4 H, 2 CH_2N); 3.88 (m, 4 H, 2 CH_2O); 4.03 (s, 3 H, NMe); 7.46 (m, 3 H, Ph); 8.51 (m, 2 H, Ph)
11b	$CDCl_3$	2.41 (s, 3 H, NMe); 2.63 (s, 3 H, Me); 2.68 (m, 4 H, 2 CH_2N); 3.93 (m, 4 H, 2 CH_2N); 4.03 (s, 3 H, NMe); 7.48 (m, 3 H, Ph); 8.51 (m, 2 H, Ph)
11c	$CDCl_3$	2.68 (s, 3 H, Me); 3.29 (m, 4 H, 2 CH_2N); 3.79 (s, 3 H, OMe); 4.04 (m, 7 H, 2 CH_2N and NMe); 6.88 and 6.96 (both d, 2 H each, C_6H_4, J = 7.5); 7.49 (m, 3 H, Ph); 8.55 (m, 2 H, Ph)
11d	$CDCl_3$	2.68 (s, 3 H, Me); 3.31 (m, 4 H, 2 CH_2N); 4.02 (m, 4 H, 2 CH_2N); 4.04 (s, 3 H, NMe); 6.98 (m, 4 H, C_6H_4); 7.49 (m, 3 H, Ph); 8.52 (m, 2 H, Ph)
11e	$CDCl_3$	2.61 (s, 3 H, Me); 4.01 (s, 3 H, NMe); 5.62 (br.s, 2 H, NH_2); 7.47 (m, 3 H, Ph); 8.44 (m, 2 H, Ph)
11f*	$CDCl_3$	2.41 (s, 6 H, 2 Me); 2.71 (s, 3 H, Me); 4.04 (s, 3 H, NMe); 6.83 (s, 1 H, *p*-$H_{C_6H_3}$); 6.90 (br.s, 1 H, NH); 7.50 (m, 5 H, *m*-H_{Ph}, *p*-H_{Ph}, *o*-$H_{C_6H_3}$); 8.55 (m, 2 H, *o*-H_{Ph})

* The spectra were recorded on a spectrometer with the operational frequency of 600 MHz.

ration of pyrimidines **14a—d**. Isolation was performed by column chromatography on SiO_2 (eluent benzene, then a 4 : 1 mixture of benzene and chloroform, then chloroform). The first fractions contained pyrimidine **14e** (yield 44%), whereas the following fractions contained pyrimidine **15e** (yield 11%). Pyrimidine **14e** (m.p., elemental analysis data, and ^{1}H NMR spectrum see Tables 1 and 2), MS, *m*/*z* (*I*$_{rel}$ (%)): 381 $[M]^+$ (74), 303 $[M - CH_2SO_2]^+$ (35), 302 $[M - SO_2Me]^+$ (30), 225 $[M - SO_2Me - Ph]^+$ (24), 91 $[PhCH_2]^+$ (100). IR (KBr), ν/cm^{-1}: 3334 (NH), 1681 (CO), 1588, 1570, 1496. ^{13}C NMR ($CDCl_3$), δ: 33.98 ($\underline{Me}CO$); 40.58 ($MeSO_2$); 45.50 (CH_2); 110.11 (C(5)); 127.63 (*o*-C_{PhCH_2}); 127.68 (*p*-C_{PhCH_2}); 128.51 (*m*-C_{Ph}); 128.71 (*o*-C_{Ph}); 128.80 (*m*-C_{PhCH_2}); 131.93 (*p*-C_{Ph}); 135.84 (*ipso*-C_{Ph}); 137.61 (*ipso*-C_{PhCH_2}); 159.94 (C(6)); 162.89 (C(4)); 163.84 (C(2)); 201.54 (CO). The signals were assigned based on the 2D ^{1}H/^{13}C HSQC and HMBC spectra. ^{15}N NMR ($CDCl_3$), δ:* −278 (NH), (correlations with the protons NH and CH_2), −133 (N(1)), (correlation with the proton NH). Pyrimidine **15e**, m.p. 172—173 °C. Found (%): C, 60.08; H, 4.78; N, 10.18; S, 7.94. $C_{20}H_{19}N_3O_4S$. Calculated (%): C, 60.44; H, 4.82; N, 10.57; S, 8.07. HRMS (MCBP): found: *m*/*z* 420.0989 $[M + Na]^+$; 396.1022 $[M - H]^-$; $C_{20}H_{19}N_3O_4S$; calculated: $[M + Na]^+$ = 420.0988; $[M - H]^-$ = = 396.1024. IR (KBr), ν/cm^{-1}: 3347 (NH), 1779 (CO_2), 1595, 1577, 1498. ^{1}H NMR ($CDCl_3$), δ: 2.40 (s, 3 H, Me); 3.33 (s, 3 H, $MeSO_2$); 4.87 (d, 2 H, CH_2, J = 4.8 Hz); 5.64 (br.s, 1 H, NH); 7.32 (m, 1 H, *p*-H_{PhCH_2}); 7.37 (m, 4 H, *o*-H_{PhCH_2}, *m*-H_{PhCH_2}); 7.48 (m, 3 H, *m*-H_{Ph}, *p*-H_{Ph}); 8.23 (d, 2 H, *o*-H_{Ph}, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.85 ($\underline{Me}CO_2$); 39.86 ($MeSO_2$); 45.15 (CH_2); 126.34 (C(5)); 127.68 (*o*-C_{PhCH_2}); 127.82 (*p*-C_{PhCH_2}); 128.39 (*m*-C_{Ph}); 128.41 (*o*-C_{Ph}); 128.88 (*m*-C_{PhCH_2}); 131.09 (*p*-C_{Ph}); 136.25 (*ipso*-C_{Ph}); 137.67 (*ipso*-C_{PhCH_2}); 152.75 (C(4)); 157.47 (C(6)); 161.01 (C(2)); 168.50 (CO_2). The signals were assigned based on the 2D ^{1}H/^{13}C HSQC and HMBC spectra. ^{15}N NMR ($CDCl_3$), δ:* −287 (NH), (correlations with the protons NH and CH_2), −130 (N(1)), (correlation with the proton NH).

5-Acetyl-6-butylamino-4-methylsulfonyl-2-phenylpyrimidine (14f) and 5-acetoxy-6-butylamino-4-methylsulfonyl-2-phenyl-

* Chemical shifts were measured based on the analysis of the 2D ^{1}H/^{15}N HMBC spectrum.

pyrimidine (15f) were synthesized similarly to compounds **14e** and **15e** from pyrimidine **4i**. Pyrimidine **14f** (24%) and pyrimidine **15f** (11%) was obtained, m.p. 148—149 °C. Found (%): C, 56.35; H, 6.01; N, 11.81; S, 8.68. $C_{17}H_{21}N_3O_4S$. Calculated (%): C, 56.18; H, 5.82; N, 11.56; S, 8.82. MS, *m/z* (I_{rel} (%)): 363 $[M]^+$ (6), 321 $[M - CH_2CO]^+$ (100), 304 $[M - MeCO_2]^+$ (21), 292 $[M - C_4H_9N]^+$ (65), 278 $[M - CH_2CO - C_3H_7]^+$ (49), 265 $[M - BuNHCN]^+$ (30), 241 $[M - MeSO_2 - MeCO]^+$ (50), 104 $[PhC{=}NH]^+$ (49). IR spectrum of **14f** (KBr), ν/cm^{-1}: 3345 (NH), 1684 (CO), 1590, 1575, 1480 (see also Tables 1 and 2). IR spectrum of **15f** (KBr), ν/cm^{-1}: 3378 (NH), 1785 (CO_2), 1599, 1582, 1511. ^{1}H NMR ($CDCl_3$), δ: 0.98 (t, 3 H, $\underline{Me}CH_2$, *J* = 7.2 Hz); 1.44 (m, 2 H, CH_2); 1.69 (m, 2 H, CH_2); 2.42 (s, 3 H, $MeCO_2$); 3.32 (s, 3 H, $MeSO_2$); 3.67 (m, 2 H, NCH_2); 5.30 (br.t, 1 H, NH); 7.51 (m, 3 H, Ph); 8.37 (d, 2 H, Ph, *J* = 7.5 Hz).

Pyrazolo[3,4-*d*]pyrimidines (10e—i). A mixture of the corresponding 4-methylsulfonylpyrimidine **14a**—**e** (0.5 mmol) and hydrazine hydrate (0.5 mL, 10 mmol) in BuOH (10 mL) was refluxed for 2 h, cooled to 20 °C. A formed precipitate of pyrazolopyrimidine **10g** was filtered off. in other cases butanol and excess hydrazine were evaporated *in vacuo*, the residue was recrystallized from acetonitrile to obtain compounds **10e**,**f**,**l** as colorless crystals. Pyrazolopyrimidine **10h** was obtained after dilution of acetonitrile with water. For elemental analysis, pyrazolopyrimidine **10e** additionally was recrystallized from methanol. The yields, melting points, and elemental analysis data are given in Table 3, the ^{1}H NMR spectra, in Table 4.

4-Amino-3-methyl-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (10e). MS, *m/z* (I_{rel} (%)): 225 $[M]^+$ (100), 122 $[M - PhCN]^+$ (26), 104 $[PhC{=}NH]^+$ (60), 76 (85). IR (KBr), ν/cm^{-1}: 3424 (NH), 3312 (NH), 3184, 1636, 1592, 1568, 1472.

4-(3,5-Dimethylphenylamino)-3-methyl-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (10f). MS, *m/z* (I_{rel} (%)): 329 $[M]^+$ (100), 328 $[M - H]^+$ (92), 314 $[M - Me]^+$ (11), 209 $[M - Me_2C_6H_3NH]^+$ (24). IR (KBr), ν/cm^{-1}: 3428 (NH), 3132, 2924, 2852, 1624, 1600, 1588, 1568, 1500. ^{13}C NMR (DMSO-d_6), δ: 14.64 (Me); 21.06 (2 Me); 98.33 (C(3a)); 120.06 (*o*-$C_{C_6H_3}$); 124.95 (*p*-$C_{C_6H_3}$); 127.81 (*m*-C_{Ph}); 128.34 (*o*-C_{Ph}); 130.21 (*p*-C_{Ph}); 137.25 (*m*-$C_{C_6H_3}$); 138.19 (*ipso*-$C_{C_6H_3}$); 138.88 (*ipso*-C_{Ph}); 140.64 (C(3)); 154.86 (C(4)); 157.26 (C(7a)); 160.16 (C(6)). The signals were assigned based on the 2D ^{1}H/^{13}C HMBC spectrum.

4-(3-Chlorophenylamino)-3-methyl-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (10g). MS, *m/z* (I_{rel} (%)): 335 $[M]^+$ (76), 334 $[M - H]^+$ (22), 209 $[M - ClC_6H_4NH]^+$ (24), 104 $[PhC{=}NH]^+$ (73), 77 $[Ph]^+$ (100). IR (KBr), ν/cm^{-1}: 3444 (NH), 3132, 3036, 2944, 2836, 1616, 1592, 1568, 1504.

3-Methyl-6-phenyl-4-(3-trifluoromethylphenylamino)-1*H*-pyrazolo[3,4-*d*]pyrimidine (10h). MS, *m/z* (I_{rel} (%)): 369 $[M]^+$ (100), 368 $[M - H]^+$ (59), 209 $[M - CF_3C_6H_4NH]^+$ (17), 145 $[CF_3C_6H_4]^+$ (10), 104 $[PhC{=}NH]^+$ (28). IR (KBr), ν/cm^{-1}: 3444 (NH), 3132, 1620, 1592, 1572, 1332(CF_3).

4-Benzylamino-3-methyl-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (10i). MS, *m/z* (I_{rel} (%)): 315 $[M]^+$ (88), 210 $[M - PhCH_2N]^+$ (21), 106 $[PhCH_2NH]^+$ (100). IR (KBr), ν/cm^{-1}: 3452 (NH), 3131, 3032, 2910, 1595, 1576, 1502. ^{13}C NMR (DMSO-d_6), δ: 14.65 (Me); 43.49 (CH_2); 97.60 (C(3a)); 126.55 (*p*-C_{PhCH_2}); 127.22 (*o*-C_{PhCH_2}); 127.82 (*o*-C_{Ph}); 128.14 (*m*-C_{PhCH_2}); 128.17 (*m*-C_{Ph}); 129.93 (*p*-C_{Ph}); 138.45 (*ipso*-C_{Ph}); 140.31 (*ipso*-C_{PhCH_2} and C(3)); 156.61 (C(4)); 157.00 (C(7a)); 160.33 (C(6)). The signals were assigned based on the 2D ^{1}H/^{13}C HMBC spectrum. ^{15}N NMR (DMSO-d_6), δ:* −287 (NH), (correlations on the protons NH and CH_2), −164 (N(5)), (correlation on the proton NH), −85 (N(2)), (correlations on the protons of the Me group).

1-Methylpyrazolo[3,4-*d*]pyrimidines (11e,f). A mixture of the corresponding 4-methylsulfonylpyrimidine **14a**,**b** (0.5 mmol) and methylhydrazine (0.27 mL, 5 mmol) in BuOH (10 mL) was refluxed for 2 h, butanol and excess methylhydrazine were evaporated *in vacuo*, the residue was subjected to column chromatography on SiO_2 (eluent chloroform). the solvent was evaporated *in vacuo*, the residue was crystallized with light petroleum (5 mL) to obtain compounds **11e,f** as colorless crystals. Analytically pure samples were obtained by recrystallization from a 1 : 1 mixture of benzene—hexane. The yields, melting points, and elemental analysis data are given in Table 3, the ^{1}H NMR spectra, in Table 4.

4-Amino-1,3-dimethyl-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (11e). MS, *m/z* (I_{rel} (%)): 239 $[M]^+$ (100), 136 $[M - PhCN]^+$ (37), 104 $[PhC{=}NH]^+$ (37). IR (KBr), ν/cm^{-1}: 3496 and 3304 (NH_2), 3104, 1648, 1592, 1568, 1520. ^{13}C NMR ($CDCl_3$), δ: 14.61 (Me); 33.30 (NMe); 98.39 (C(3a)); 128.28 (*m*-C_{Ph}); 128.42 (*o*-C_{Ph}); 130.25 (*p*-C_{Ph}); 138.12 (*ipso*-C_{Ph}); 139.98 (C(3)); 155.90 (C(7a)); 157.98 (C(4)); 162.25 (C(6)). The signals were assigned based on the 2D ^{1}H/^{13}C HMBC spectrum.

1,3-Dimethyl-4-(3,5-dimethylphenylamino)-6-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (11f). MS, *m/z* (I_{rel} (%)): 343 $[M]^+$ (100), 328 $[M - Me]^+$ (6). IR (KBr), ν/cm^{-1}: 3448 (NH), 3020, 2916, 1620, 1596, 1584, 1564, 1508. ^{13}C NMR ($CDCl_3$), δ: 14.93 (Me); 21.46 (2 Me); 33.32 (NMe); 99.02 (C(3a)); 118.81 (*o*-$C_{C_6H_3}$); 125.65 (*p*-$C_{C_6H_3}$); 128.27 (*m*-C_{Ph}); 128.57 (*o*-C_{Ph}); 130.30 (*p*-C_{Ph}); 138.35 (*ipso*-C_{Ph}); 138.47 (*ipso*-$C_{C_6H_3}$); 138.64 (*m*-$C_{C_6H_3}$); 138.89 (C(3)); 155.05 (C(4)); 155.87 (C(7a)); 161.92 (C(6)). The signals were assigned based on the 2D ^{1}H/^{13}C HMBC spectrum. ^{15}N NMR ($CDCl_3$), δ:* −267 (NH, correlations with the protons NH and *o*-C_6H_3), −200 (N(1), correlation with the protons of the NMe group), −153 (N(5), correlation with the proton NH), −72 (N(2), correlations with the protons of the NMe and Me groups).

4-(3,5-Dimethylphenylamino)-3-methyl-2,6-diphenyl-2*H*-pyrazolo[3,4-*d*]pyrimidine (16a). A mixture of 4-methylsulfonylpyrimidine **14b** (40 mg, 0.1 mmol) and phenylhydrazine (0.1 mL, 1 mmol) in BuOH (4 mL) was refluxed for 2 h, butanol was evaporated *in vacuo*, the residue (oil) was dissolved in benzene (4 mL) and diluted with light petroleum (16 mL). A precipitate formed was filtered off and recrystallized from benzene to obtain a colorless compound **16a** (12 mg, 29%), m.p. 228—229 °C. Found (%): C, 76.62; H, 5.58; N, 16.95. $C_{26}H_{23}N_5$. Calculated (%): C, 77.01; H, 5.72; N, 17.27. MS, *m/z* (I_{rel} (%)): 405 $[M]^+$ (100), 227 (7), 219 (8), 148 (18), 101 (57), 57 (78). IR (KBr), ν/cm^{-1}: 3444 (NH), 3012, 2916, 1620, 1596, 1552, 1528, 1504. ^{1}H NMR ($CDCl_3$), δ: 2.41 (s, 6 H, 2 Me); 2.82 (s, 3 H, Me); 6.85 (s, 1 H, *p*-$H_{C_6H_3}$); 6.95 (br.s, 1 H, NH); 7.42—7.55 (m, 5 H, *o*-$H_{C_6H_3}$, *m*-H_{Ph}, *p*-H_{Ph}); 7.55—7.62 (m, 5 H, *o*-H_{PhN}, *m*-H_{PhN}, *p*-H_{PhN}); 8.62 (m, 2 H, *o*-H_{Ph}). ^{13}C NMR ($CDCl_3$), δ: 13.69 (Me); 21.42 (2 Me); 101.17 (C(3a)); 119.34 (*o*-$C_{C_6H_3}$); 125.95 (*o*-C_{PhN}); 126.15 (*p*-$C_{C_6H_3}$); 128.22 (*m*-C_{PhN}); 128.79 (*o*-C_{Ph}); 129.15 (*p*-C_{PhN}); 129.27 (*m*-C_{Ph}); 130.42 (*p*-C_{Ph}); 132.45 (C(3)); 138.00 (*ipso*-C_{PhN}); 138.20 (*ipso*-C_{Ph}); 138.61

* Chemical shifts were measured based on the analysis of the 2D ^{1}H/^{15}N HMBC spectrum.

(*ipso*-$C_{C_6H_3}$); 138.71 (*m*-$C_{C_6H_3}$); 156.27 (C(4)); 160.44 (C(7a)); 161.80 (C(6)). The signals were assigned based on the 2D $^1H/^{13}C$ HMBC spectrum. ^{15}N NMR ($CDCl_3$), δ:* −263 (NH, correlations with the protons *o*-C_6H_3), −150 (N(2), correlations with the protons of the Me group and the *ortho*-protons of the NPh group).

4-Butylamino-3-methyl-2,6-diphenyl-2*H*-pyrazolo[3,4-*d*]-pyrimidine (16b). A mixture of 4-methylsulfonylpyrimidine **14f** (77 mg, 0.22 mmol) and phenylhydrazine (0.22 mL, 2.2 mmol) in BuOH (5 mL) was refluxed for 3 h, butanol was evaporated *in vacuo*, benzene (3 mL) and light petroleum (12 mL) were added to the residue, the solution was decanted, an oil obtained was dissolved in boiling benzene ((2 mL), cooled to 20 °C, a precipitate formed by scraping was filtered off and subjected to column chromatography on SiO_2 (eluent chloroform). The solvent was evaporated *in vacuo*, the residue was crystallized with light petroleum (2 mL) to obtain a colorless compounds **16b** (23 mg, 29%), m.p. 150—151 °C. Found (%): C, 73.51; H, 6.23; N, 19.53. $C_{22}H_{23}N_5$. Calculated (%): C, 73.92; H, 6.49; N, 19.59. HRMS: found: *m/z* 358.2026 $[M + H]^+$; 380.1843 $[M + Na]^+$; $C_{22}H_{23}N_5$; calculated: $[M + H]^+ = 358.2026$; $[M + Na]^+ = 380.1846$. IR (KBr), ν/cm^{-1}: 3456 (NH), 3060, 2956, 2931, 2872, 2859, 1617, 1596, 1560, 1504. ^1H NMR ($CDCl_3$), δ: 1.00 (t, 3 H, $\underline{Me}CH_2$, $J = 7.2$ Hz); 1.48 (m, 2 H, CH_2); 1.70 (m, 2 H, CH_2); 2.68 (s, 3 H, Me); 3.74 (m, 2 H, CH_2N); 5.33 (br.s, 1 H, NH); 7.42—7.52 (m, 8 H, *o*-H_{PhN}, *m*-H_{PhN}, *p*-H_{PhN}, *m*-H_{Ph}, *p*-H_{Ph}); 8.62 (d, 2 H, *o*-H_{Ph}, $J = 6.6$ Hz). ^{13}C NMR ($CDCl_3$), δ: 13.50 ($\underline{Me}CH_2$); 13.86 (Me); 20.24 (CH_2); 31.55 (CH_2); 40.75 (NCH_2); 100.99 (C(3a)); 125.81 (*o*-C_{PhN}); 128.00 (*m*-C_{PhN}); 128.59 (*o*-C_{Ph}); 128.72 (*p*-C_{PhN}); 129.08 (*m*-C_{Ph}); 129.96 (*p*-C_{Ph}); 132.08 (C(3)); 138.78 (*ipso*-C_{PhN}); 138.91 (*ipso*-C_{Ph}); 158.67 (C(4)); 160.63 (C(7a)); 162.25 (C(6)). The signals were assigned based on the 2D $^1H/^{13}C$ HMBC spectrum. ^{15}N NMR ($CDCl_3$), δ:* −280 (NH, correlations with the protons NH, NCH_2. and $NCH_2\underline{CH_2}$), −154 (N(2), correlations with the protons of the Me and *ortho*-protons of the NPh group).

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