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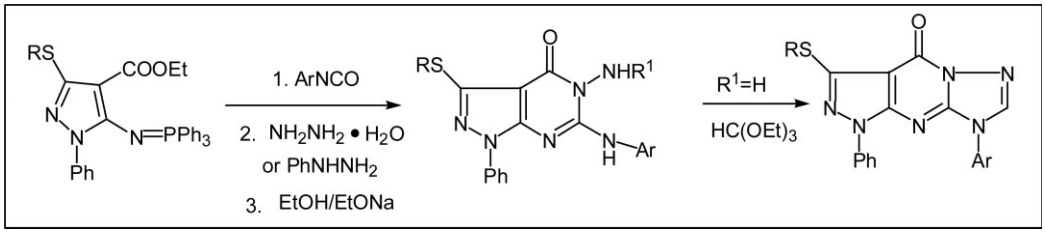

A novel approach to regioselective synthesis of new 5-amino-6-arylamino-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one **5** derivatives *via* a tandem aza-wittig and annulation reaction of iminophosphorance **2**, aromatic isocyanates and hydrazine in 69.6–94.7% isolated yields is reported. The compound **5** reacted with triethyl orthoformate to give compound **6** in good yield (65.8–82.8%). Their structure was clearly confirmed by spectroscopy data (IR, ^{1}H NMR, MS, elemental analysis) and the results of preliminary bioassay indicated that compounds **5** and **6** possess high antifungal activity against *Botrytis cinerea Pers* and *Sclerotinia sclerotiorum*, and compound **5h** showed 100, 96.4, and 90.2% inhibitory rate to *Botrytis cinerea Pers*, *Pyricularia oryzae,* and *Sclerotinia sclerotiorum* at the concentration of 50 mg/L. The antifungal activities of compound **6** were generally higher than those of compound **5**.

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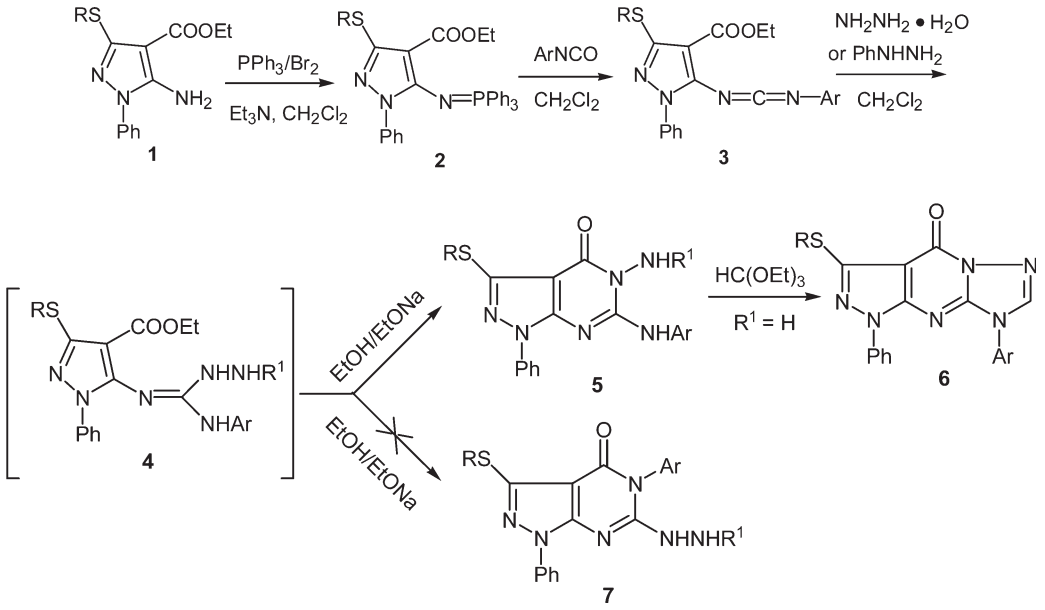
INTRODUCTION

Pyrazolopyrimidines and related fused heterocycles have been the focus of great interest over many years due to the fact that many compounds containing a fused pyrimidinone ring have remarkable biological and chemotherapeutic properties [1]. Pyrazolo[3,4-*d*]-pyrimidines are often employed as mGluR1 antagonists [2], antimicrobial and antifungal or antitumor agents [3], various animal enzyme inhibitors [4], and agrochemicals [5]. Moreover, triazole and its fused heterocycles form part of an extensive investigation of biologically active compounds, such as substituted triazole derivatives [6], triazolo[1,5-*a*]pyrimidine derivatives [7], and their derivatives [8]. In our previous research [5a–d], we reported a reaction of ethyl 3-alkylthio-1-phenyl-5-triphenylphosphoranoimino-1*H*-pyrazole-4-carboxylate (abbreviation iminophosphorane) **2** with isocycanates and alkylamine to give 6-alkylamino-5-aryl-pyrazolo[3,4-*d*]pyrimidin-4-one derivatives, the nitrogen atom of which were from isocycanates. Those compounds showed satisfactory antifungicidal activities. Inspired by the manifold biological activities of pyrazolo[3,4-*d*]pyrimidines and pyrazolotriazolopyrimidine derivatives, we set out to utilize hydrazine to produce new compounds of potential biochemical interest. However, we obtained 5-amino-6-arylamino-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-ones **5** instead of 6-hydrazino-5-aryl-pyrazolo[3,4-*d*]pyrimidin-4-one **7** derivatives. Here, we report a novel facile regioselective synthesis of a new series of 5-amino-6-arylamino-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-ones **5**, having nitrogen atoms from hydrazine, and 2*H*-pyrazolo[3,4-*d*][1,2,4]triazolo[1,5-*a*] pyrimidin-4-one derivatives **6** and their results of preliminary bioassay against *Botrytis cinerea Pers*, *Pyricularia oryzae*, *Gibberella zeae*, and *Sclerotinia sclerotiorum*.

RESULTS AND DISCUSSION

Iminophosphoranes **2** [5a–c] reacted with isocyanates to give the key intermediates carbodiimide **3**. Treatment of **3** with hydrazines at room temperature gave the intermediate guanidines **4** [5a], which, in the presence of NaOEt, reacted to give the crude target compound **5**. After evaporation of part of the solvent, the crude products were collected by filtration. After recrystallization from DMF/petroleum ether or column chromatography on a silica gel, white crystals were obtained in 69.6–94.7% yields (Scheme 1, Table 1). The spectra data

Scheme 1



identified the white crystal as 3-alkylthio-5-amino-6-arylamino-1-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-ones **5** instead of the isomer 3-alkylthio-6-hydrazine-5-aryl-1-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-ones **7**. In this reaction, a variety of substituents can be tolerated in Ar group, such as electron-donating group (*e.g.*, Me), or electron-withdrawing group (*e.g.*, F, Cl). R^1 also could be C_6H_5 or H. In the absence of sodium ethoxide, the compound **5** would be obtained with very low yields if the quantity of hydrazine was equal to iminophosphoranes **2**. In contrast, in the presence of a large excess of hydrazine the reaction took place smoothly and the compound **5** was obtained in satisfactory yields even in the absence of NaOEt. On refluxing Compound **5** with triethyl orthoformate, compound **6** was obtained in 65.8–82.8% yields in the present *p*-TsOH.

The structures of compounds **5** and **6** were deduced from their spectra data (^{1}H NMR, IR, EI-MS, and elementary analysis). ^{1}H NMR spectra of compound **5** showed the signal of NH_2 at δ 5.55–5.74 as singlet and compound **6** showed the signal of triazole at δ 9.23–9.34 as singlet [8b]. A combination of chemical shift and couplings allowed the complete and unambiguous assignment of all signals and demonstrated that the major products correspond to structure. The IR spectra of **5** exhibited N—H, C=O, and C=N absorptions. The EI-MS spectra of **5** and **6** showed the molecular ion peak. All the fragmentation ions were consistent with their structures and could be clearly assigned. In addition, the structures of compound **6** further verified the proposed structure of compound **5**. The results of the elementary analysis are within the acceptable range.

Table 1

Yields of compounds **5** and **6**.

Compounds	R	R_1	Ar	Yield of **5** (%)	Yield of **6** (%)
5a, 6a	Me	H	C_6H_5	75.8	71.6
5b, 6b	Me	H	*p*-MeC_6H_4	84.6	73.2
5c, 6c	Me	H	*o*-ClC_6H_4	69.6	82.8
5d, 6d	Me	H	*o*-FC_6H_4	92.5	77.6
5e, 6e	$PhCH_2$	H	C_6H_5	72.3	69.0
5f, 6f	$PhCH_2$	H	*p*-MeC_6H_4	94.7	65.8
5g, 6g	$PhCH_2$	H	*o*-ClC_6H_4	73.8	76.3
5h	Me	H	*p*-ClC_6H_4	77.0	
5i	Me	C_6H_5	*p*-MeC_6H_4	83.0	
5j	Me	C_6H_5	*m*-ClC_6H_4	86.2	
5k	$PhCH_2$	C_6H_5	*p*-MeC_6H_4	74.2	

Isolated yields based on iminophosphoranes **2**.

Table 2

Antifungal activity of compounds **5**, **6**, and thiabendazole (50 mg/L, inhibitory rate %).

Compounds	Relative inhibition (%)			
	Botrytis	*Pyricularia*	*Gibberella*	*Sclerotinia*
5a/6a	13.2/98.6	35.7/80.0	14.3/65.8	80.2/100.0
5b/6b	94.7/82.2	57.1/28.6	40.0/51.4	86.5/96.4
5c/6c	73.3/62.9	0.0/50.0	40.0/23.7	82.1/81.0
5d/6d	93.0/60.0	62.5/5.2	51.2/25.7	97.1/50.0
5e/6e	60.5/73.3	50.0/28.6	28.6/60.0	83.5/92.9
5f/6f	89.5/91.8	85.7/14.3	37.1/48.6	78.5/89.3
5g/6g	42.2/77.8	0.0/28.6	37.1/68.7	60.7/92.9
5h	100.0	96.4	85.7	90.2
5i	26.3	21.4	22.9	81.9
5j	7.9	50.0	5.7	79.3
5k	21.0	28.6	5.7	76.2
Thiabendazole	100	87	100	100

Biological activities. The fungi were obtained from the College of Plant Protect, Central China Agriculture University, China. The antifungal activities of all compounds **5**, **6**, and 2-(4′-thiazoly)-benzimidazole (commercial name: thiabendazole), a commercially available fungicide, were evaluated *in vitro* according to the reported method [9], as shown in Table 2 by contrasting to distilled water. The results showed that all compounds **5** and **6** possessed good inhibition effects against *Sclerotinia sclerotiorum* (inhibition rates 60.7–97.1% and 81.0–100%). Comparing compounds **5** with **6**, it showed that the antifungal activities of compound **6** were generally higher than those of compound **5**. Some of the compounds **5** and **6** exhibited good inhibitory rates against *Botrytis cinerea Pers* and *Pyricularia oryzae*. For example, the inhibitory rates of compounds **6a**, **5b**, **6b**, **5d**, **5f**, and **6f** were 91.8, 94.7, 82.2, 93.0, 89.5, and 91.8% to *Botrytis cinerea Pers* and that of 5**f** was 85.7% to *Pyricularia oryzae* at 50 mg/L. It was also interesting to note that compound **5h** showed high antifungal activities to all of *Botrytis cinerea Pers*, *Pyricularia oryzae*, *Gibberella zeae*, and *Sclerotinia sclerotiorum*.

EXPERIMENTAL

Melting points were determined using a WRS-1B Digital melting point apparatus. MS was measured on a Finnigan Trace Mass 2000 Spectrometer at 70 eV. IR was recorded on an Avatar 360 Spectrometer as KBr pellets with absorption given in cm^{-1}. ^1H NMR spectra were obtained using a Varian Mercury 400 (or 300) Spectrometer with TMS as the internal reference and DMSO-d_6 or $CDCl_3$ as the solvent. Elementary analysis was taken on a Vario EL III elementary analysis instrument. All of the solvents and materials were of reagent grade and purified as required. Ethyl 5-amino-3-alkylthio-1-phenyl-1*H*-pyrazole-4-carboxylate **1** [10], iminophosphoranes **2** [5a–c] were prepared according to literature.

General procedure for the preparation of 3-alkylthio-5-amino-6-arylamino-1-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-ones (5). To a solution of iminophosphorane **2** (2 mmol) in dry methylene dichloride (20 mL) aryl isocyanate (2 mmol) was added under nitrogen atmosphere at room temperature. After the reaction mixture was stirred for 1.5 h, 0.118 g (2.0 mmol, 85%) of hydrazine hydrate or 0.227 g (2.0 mmol) phenylhydrazine was added, and the resulting mixture was stirred for an additional 30 min. Then the solvent was removed under reduced pressure, and 25 mL anhydrous ethanol and 1.5 mL of sodium ethoxide (3 mol/L) in ethanol were added to the mixture. After 3 h of stirring at room temperature, the solution was concentrated under reduced pressure and successively cooled. The crude product was collected by filtration. After recrystallization from DMF/petroleum ether or column chromatography on silica gel, white crystal was obtained.

5-Amino-3-methylthio-1-phenyl-6-phenylamino-1H-pyrazolo[3,4-d]pyrimidin-4(5H)-one (5a). White crystals, mp 236.2–238.1°C; IR (KBr) ν (cm^{-1}): 3336, 3267, 1692, 1596, 1554, 909, 770, 743, 688; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.60 (s, 3H, SCH_3), 5.57 (br s, 2H, NH_2), 7.11 (t, 1H, $J = 7.2$ Hz, Ph), 7.25 (t, 1H, $J = 7.2$ Hz, Ph), 7.36 (t, 2H, $J = 7.6$ Hz, Ph), 7.46 (d, 2H, $J = 7.6$ Hz, Ph), 7.73 (d, 2H, $J = 7.5$ Hz, Ph), 8.03 (d, 2H, $J = 7.8$ Hz, Ph), 9.67 (s, 1H, *NH*Ph); EI-MS (70 eV, *m/z*, rel. int.) 365 (M + 1, 49), 364 (M^+, 81); *Anal.* Calcd. for $C_{18}H_{16}N_6OS$: C, 59.32; H, 4.43; N, 23.06; Found: C, 59.1; H, 4.37; N, 22.96.

5-Amino-3-methylthio-1-phenyl-6-tolylamino-1H-pyrazolo[3,4-d]pyrimidin-4(5H)-one (5b). White crystals, mp 235.3–238.6°C; IR (KBr) ν (cm^{-1}): 3333, 3261, 1691, 1597, 1555, 751, 690; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.30 (s, 3H, *p*-$CH_3C_6H_4$), 2.60 (s, 3H, SCH_3), 5.55 (s, 2H, NH_2), 6.85–7.68 (m, 7H, Ar), 8.03 (d, 2H, $J = 7.5$ Hz, Ar), 9.57 (s, 1H, NH); EI-MS (70 eV, *m/z*, rel. int.) 379 (M + 1, 31), 378 (M^+,100); *Anal.* Calcd. for $C_{19}H_{18}N_6OS$: C, 60.30; H, 4.79; N, 22.21; Found: C, 59.99; H, 4.61; N, 22.45.

5-Amino-3-methylthio-1-phenyl-6-(o-chlorophenylamino)-1H-pyrazolo[3,4-d]pyrimidin-4(5H)-one (5c). White crystals, mp 248.1–248.8°C; IR (KBr) ν (cm^{-1}): 3328, 3189, 1688,

1598, 1582, 1562, 1543, 1398, 752, 682; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.61 (s, 3H, SCH_3), 5.74 (s, 2H, NH_2), 7.20 (t, 1H, J = 7.6 Hz, Ar), 7.30 (t, 1H, J = 7.6 Hz, Ar), 7.43–7.50 (m, 3H, Ar), 7.58 (d, 1H, J = 8.0 Hz, Ar), 8.00 (d, 2H, J = 7.6 Hz, Ar), 8.30 (d, 1H, J = 8.0 Hz, Ar), 9.85 (br s, 1H, NH); EI-MS (70 eV, *m*/*z*, rel. int.) 399 (M + 1, 41), 398 (M^+, 66); *Anal*. Calcd. for $C_{18}H_{15}ClN_6OS$: C, 54.20; H, 3.79; N, 21.07; Found: C, 54.32; H, 3.76; N, 21.22.

5-Amino-3-methylthio-1-phenyl-6-(o-fluorophenylamino)-1H-pyrazolo[3,4-d]pyrimidin-4(5H)-one (5d). White crystal, mp 238–239°C; IR (KBr) ν (cm^{-1}): 3352, 3314, 3266, 1721, 1621, 1600, 1542 (Ar), 1455, 922, 768; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.61(s, 3H, SCH_3), 5.65 (s, 2H, NH_2), 7.25–7.46 (m, 6H, Ar), 7.98 (d, 3H, J = 8.4 Hz, Ar), 9.61(s, 1H, *o*-FC_6H_4*NH*); EI-MS (70 eV, *m*/*z*, rel. int.): 384 (M + 2, 13), 383 (M + 1, 49), 382 (M^+, 89); *Anal*. Calcd. for $C_{18}H_{15}FN_6OS$: C, 56.53; H, 3.95; N, 21.98; Found: C, 56.39; H, 3.92; N, 22.03.

5-Amino-3-benzylthio-1-phenyl-6-phenylamino-1H-pyrazolo[3,4-d]pyrimidin-4(5H)-one (5e). White crystals, mp 226.0–227.8°C, IR (KBr) ν (cm^{-1}): 3319, 1684, 1596, 1554, 927, 759, 689,501; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.47 (s, 2H, CH_2Ph), 5.58 (s, 2H, NH_2), 7.12 (t, 1H, J = 7.2 Hz, Ph), 7.20–7.50 (m, 10H, Ph), 7.73 (d, 2H, J = 8.1 Hz), 8.04 (d, 2H, J = 8.4 Hz), 9.69 (s, 1H, Ph*NH*); EI-MS (70 eV, *m*/*z*, rel. int.): 442 (M + 2, 2), 441 (M^+, 7); *Anal*. Calcd. for $C_{24}H_{20}N_6OS$: C, 65.44; H, 4.58; N, 19.08; Found: C, 65.52; H, 4.43; N, 19.07.

5-Amino-3-benzylthio-1-phenyl-6-(p-tolylamino)-1H-pyrazolo[3,4-d]pyrimidin-4(5H)-one (5f). White crystals, mp 250.0–250.6°C; IR (KBr) ν (cm^{-1}): 3314, 3255, 1689, 1596, 1556, 770, 692; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.29 (s, 3H, CH_3), 4.46 (s, 2H, $PhCH_2$), 5.56 (s, 2H, NH_2), 6.83–6.91 (m, 1H, Ar), 7.16 (d, 2H, J = 7.5 Hz, Ar) 7.14–7.49 (m, 7H, Ar), 7.59 (d, 2H, J = 7.8 Hz, Ar), 8.04 (d, 2H, J = 8.1 Hz, Ar), 9.54 (br s, 1H, NH); EI-MS (70 eV, *m*/*z*, rel. int.) 454 (M^+, 26); *Anal*. Calcd. for $C_{25}H_{22}N_6OS$: C, 66.06; H, 4.88; N, 18.49; Found: C, 66.25; H, 4.89; N, 18.36.

5-Amino-3-benzylthio-1-phenyl-6-(o-chlorophenylamino)-1H-pyrazolo[3,4-d]pyrimidin-4(5H)-one (5g). White crystals, mp 219.6–220.3°C; IR (KBr) ν (cm^{-1}): 3333, 3257, 3192, 1677, 1598, 1585, 1545, 1215, 754, 687; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 4.48 (s, 2H, PhCH_2), 5.74 (br s, 2H, NH_2), 7.22–7.52 (m, 10H, Ar), 7.59 (d, 1H, J = 7.6 Hz, Ar), 7.99 (d, 2H, J = 7.6 Hz, Ar), 8.30 (d, 1H, J = 8.0 Hz, Ar), 9.83 (br s, 1H, NH); EI-MS (70 eV, *m*/*z*, rel. int.) 474 (M^+, 13); *Anal*. Calcd. for $C_{24}H_{19}ClN_6OS$: C, 60.69; H, 4.03; N, 17.69; Found: C, 60.58; H, 4.09; N, 17.82.

5-Amino-3-methylthio-1-phenyl-6-(p-chlorophenylamino)-1H-pyrazolo[3,4-d]pyrimidin-4(5H)-one (5h). White crystals, mp 245.2–247.5°C; IR (KBr) ν (cm^{-1}): 3380, 3311, 3125, 1718, 1601, 1562, 1543, 925, 768; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.60 (s, 3H, SCH_3), 5.57 (s, 2H, NH_2), 7.28 (t, 1H, J = 7.2 Hz, Ar), 7.40 (d, 2H, J = 8.7 Hz, Ar), 7.49 (t, 2H, J = 7.9 Hz, Ar), 7.78 (d, 2H, J = 8.7 Hz, Ar), 8.00 (d, 2H, J = 7.8 Hz, Ar), 9.81 (s, 1H, NH); EI-MS (70 eV, *m*/*z*, rel. int.) 399 (M + 1, 41), 398 (M^+, 78); *Anal*. Calcd. for $C_{18}H_{15}ClN_6OS$: C, 54.20; H, 3.79; N, 21.07; Found: C, 54.07; H, 3.71; N, 21.30.

3-Methylthio-1-phenyl-5-phenylamino-6-(p-tolylamino)-1H-pyrazolo[3,4-d]pyrimidin-4(5H)-one (5i). White crystals, mp 222.4–222.8°C; IR (KBr) ν (cm^{-1}): 3369, 3252, 1690, 1598, 1546, 949, 761, 689; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H, $C_6H_4CH_3$), 2.58 (s, 3H, SCH_3), 6.86 (d, 2H, J = 7.5 Hz, Ar), 6.91 (t, 1H, J = 7.2 Hz, Ar), 7.06 (br s, 1H, Ph*NH*N), 7.13 (d, 2H, J = 8.1 Hz, Ar), 7.24–7.27 (m, 3H, Ar), 7.41 (t, 2H, J = 8.0 Hz, Ar), 7.50 (d, 2H, J = 8.1 Hz, Ar), 8.06 (d, 2H, J = 8.1 Hz, Ar), 8.35 (s, 1H, NH); EI-MS (70 eV, *m*/*z*, rel. int.) 455 (M + 1, 46), 454 (M^+, 81); *Anal*. Calcd. for $C_{25}H_{22}N_6OS$: C, 66.06; H, 4.88; N, 18.49; Found: C, 65.80; H, 4.85; N, 18.57.

3-Methylthio-1-phenyl-5-phenylamino-6-(m-chlorophenylamino)-1H-pyrazolo[3,4-d]pyrimidin-4(5H)-one (5j). White crystals, mp 208.5–210.5°C; IR (KBr) ν (cm^{-1}): 3342, 3261, 1695, 1599, 1545, 951, 759, 683; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.54 (s, 3H, SCH_3), 6.84 (d, 2H, J = 7.5 Hz, Ar), 7.01 (t, 2H, J = 7.2 Hz), 7.08–7.29 (m, 5H, Ar and Ph*NH*N), 7.45 (t, 2H, J = 7.8 Hz, Ar), 8.01 (d, 2H, J = 7.8 Hz, Ar), 8.14 (s, 1H, *m*-ClC_6H_4), 8.51 (s, 1H, Ar*NH*); EI-MS (70 eV, *m*/*z*, rel. int.) 475 (M + 1, 35), 474 (M^+, 69); *Anal*. Calcd. for $C_{24}H_{19}ClN_6OS$: C, 60.69; H, 4.03; N, 17.69; Found: C, 60.39; H, 4.00; N, 17.72.

3-Benzylthio-1-phenyl-5-phenylamino-6-(p-tolylamino)-1H-pyrazolo[3,4-d]pyrimidin-4(5H)-one (5k). White crystals, mp 198.6–198.8°C; IR (KBr) ν (cm^{-1}): 3317, 3271, 1701, 1592, 1547, 772, 688; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H, $C_6H_4CH_3$), 4.42 (s, 2H, PhCH_2), 6.86 (d, 2H, J = 7.5 Hz, Ar), 7.01 (t, 2H, J = 6.9 Hz, Ar), 7.12–7.28 (m, 8H, Ar and Ph*NH*N), 7.39–7.43 (m, 4H, Ar), 7.48 (t, 2H, J = 6.4 Hz, Ar), 8.07 (d, 2H, J = 7.8 Hz, Ar), 8.33 (s, 1H, NH); EI-MS (70 eV, *m*/*z*, rel. int.) 531 (M + 1, 26), 530 (M^+, 50); *Anal*. Calcd. for $C_{31}H_{26}N_6OS$: C, 70.17; H, 4.94; N, 15.84; Found: C, 69.89; H, 5.00; N, 15.63.

General Procedure for the preparation of 3-alkylthio-8-aryl-phenyl-1,8-dihydropyrazolo[3,4-*d*][1,2,4]triazolo[1,5-*a*] pyrimidin-4-one (6). To a suspension of the appropriate 5-amino-3-alkylthio-6-arylamino-1-phenyl-1*H*- pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one **5** (1.5 mmol) in 25 mL of triethyl orthoformate *p*-toluenesulfonic acid (*p*-TsOH) (0.4 g, 2.25 mmol) was added. The reaction mixture was refluxed for 15 h under stirring. After cooling to room temperature, a yellowish substance precipitated. The crude product was collected by filtration and washed with water. After recrystallization from dimethylformamide, the products were obtained as colorless crystal.

3-Methylthio-1,8-diphenyl-1,8-2H-pyrazolo[3,4-d][1,2,4]triazolo[1,5-a]pyrimidin-4-one (6a). White crystals, mp 253–255°C, IR (KBr) ν (cm^{-1}): 3144, 3081, 2925, 1718, 1605, 1578, 1560, 1527, 1388, 1265, 1165, 902, 768; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.65 (s, 3H, SCH_3), 7.31 (t, 1H, J = 6.8 Hz, Ph), 7.49–7.57 (m, 3H, Ph), 7.67 (t, 2H, J = 8.2 Hz, Ph), 7.93 (d, 2H, J = 8.0 Hz, Ph), 8.08 (d, 2H, J = 8.4 Hz, Ph), 9.34 (s, 1H, triazole-H); EI-MS (70 eV, *m*/*z*, rel. int.) 375 (M + 1, 13), 374 (M^+, 36); *Anal*. Calcd. for $C_{19}H_{14}N_6OS$: C, 60.95; H, 3.77; N, 22.45; Found: C, 61.02; H, 3.75; N, 22.53.

3-Methylthio-1-phenyl-8-(p-methylphenyl)-1,8-2H-pyrazolo[3,4-d][1,2,4]triazolo[1,5-a]pyrimidin-4-one (6b). White crystals, mp 253–256°C, IR(KBr) ν (cm^{-1}): 3133, 3076, 2919, 1721, 1596, 1574, 1398, 1169, 900, 767, 673; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.41 (s, 3H, *p*-CH_3Ph), 2.67 (s, 3H, SCH_3), 7.31 (t, 1H, J = 7.6 Hz, Ar), 7.45–7.53 (m, 4H, Ar), 7.80 (d, 2H, J = 8.0 Hz, Ar), 8.07 (d, 2H, J = 8.0 Hz, Ar), 9.29 (s, 1H,

triazole-H); EI-MS (70 eV, *m*/*z*, rel. int.) 389 (M + 1, 22), 388 (M^+, 62); *Anal*. Calcd. for $C_{20}H_{16}N_6OS$: C, 61.84; H, 4.15; N, 21.63; Found: C, 61.90; H, 4.13; N, 21.65.

3-Methylthio-1-phenyl-8-(o-chlorophenyl)-1,8-dihydropyrazolo[3,4-d][1,2,4]triazolo[1,5-a]pyrimidin-4-one (6c). White crystals, mp 216–218°C, IR (KBr) ν (cm^{-1}): 3139, 3069, 1722, 1609, 1585, 1525, 1398, 1229, 1124, 902, 766, 687; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.64 (s, 3H, SCH_3), 7.27 (t, 1H, J = 7.6 Hz, Ar), 7.44 (t, 2H, J = 7.8 Hz, Ar), 7.66–7.70 (m, 2H, Ar), 7.83–7.90 (m, 2H, Ar), 7.94 (d, 2H, J = 8.0 Hz, Ph), 9.23 (s, 1H, triazole-H); EI-MS (70 eV, *m*/*z*, rel. int.): 409 (M + 1, 32), 408 (M^+, 57); *Anal*. Calcd. for $C_{19}H_{13}ClN_6OS$: C, 55.81; H, 3.20; N, 20.55; Found: C, 55.85; H, 3.22; N, 20.51.

3-Methylthio-1-phenyl-8-(o-fluorophenyl)-1,8-dihydropyrazolo[3,4-d][1,2,4]triazolo[1,5-a]pyrimidin-4-one (6d). White crystal, mp 224–225°C; IR (KBr) ν (cm^{-1}): 3146, 1712, 1607, 1585, 1525, 1509, 1398, 1234, 904, 769, 752; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.65 (s, 3H, SCH_3), 7.29 (t, 1H, J = 7.4 Hz, Ar), 7.44–7.69 (m, 5H, Ar), 7.92 (t, 1H, J = 7.6 Hz, Ar), 8.00 (d, 2H, J = 8.0 Hz, Ar), 9.23 (s, 1H, triazole-H); EI-MS (70 eV, *m*/*z*, rel. int.): 393 (M + 1, 31), 392 (M^+, 63); *Anal*. Calcd. for $C_{19}H_{13}FN_6OS$: C, 58.15; H, 3.34; N, 21.42; Found: C, 58.13; H, 3.32; N, 21.48.

3-Benzylthio-1,8-diphenyl-1,8-dihydropyrazolo[3,4-d][1,2,4]triazolo[1,5-a]pyrimidin-4-one (6e). White crystals, mp 224–226°C; IR (KBr) ν (cm^{-1}): 3118, 3064, 1718, 1608, 1580, 1528, 1389, 1163, 757, 685; ^1H NMR (DMSO-d_6, 400 MHz) δ 4.51 (s, 2H, PhCH_2), 7.26 (t, 1H, J = 7.2 Hz, Ph), 7.34 (t, 3H, J = 7.4 Hz, Ph), 7.50–7.67 (m, 7H, Ph), 7.92 (d, 2H, J = 7.6 Hz, Ph), 8.08 (d, 2H, J = 7.6 Hz, Ph), 9.34 (s, 1H, triazole-H); EI-MS (70 eV, *m*/*z*, rel. int.) 450 (M^+, 8); *Anal*. Calcd. for $C_{25}H_{18}N_6OS$: C, 66.65; H, 4.03; N, 18.65; Found: C, 66.70; H, 4.02; N, 18.70.

3-Benzylthio-8-(p-tolyl)-1-phenyl-1,8-dihydropyrazolo[3,4-d][1,2,4]triazolo[1,5-a]pyrimidin-4-one (6f). White crystals, mp 257–259°C; IR (KBr) ν (cm^{-1}): 3137, 2923, 1718, 1601, 1580, 1527, 1390, 1165, 978, 769, 702; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.41 (s, 3H, *p*-CH_3Ph), 4.52 (s, 2H, PhCH_2), 7.32–7.53 (m, 10H, Ar), 7.79 (d, 2H, J = 8.0 Hz, Ar), 8.08 (d, 2H, J = 8.0 Hz, Ar), 9.29 (s, 1H, triazole-H); EI-MS (70 eV, *m*/*z*, rel. int.): 464 (M^+, 6); *Anal*. Calcd. for $C_{26}H_{20}N_6OS$: C, 67.22; H, 4.34; N, 18.09; Found: C, 67.26; H, 4.37; N, 18.12.

3-Benzylthio-8-(o-chlorophenyl)-1-phenyl-1,8-dihydropyrazolo[3,4-d][1,2,4]triazolo[1,5-a]pyrimidin-4-one (6g). White crystals, mp 221–223°C; IR (KBr) ν (cm^{-1}): 3144, 1718, 1704, 1605, 1561, 1399, 1122, 1065, 905, 770, 687; ^1H NMR (DMSO-d_6, 400 MHz) δ 4.52 (s, 2H, PhCH_2), 7.26–7.89 (m, 12H, Ar), 7.94 (d, 2H, J = 8.4 Hz, Ar), 9.23 (s, 1H, triazole-H); EI-MS (70 eV, *m*/*z*, rel. int.): 393 (M + 1, 9), 392 (M^+, 6); *Anal*. Calcd. for $C_{15}H_{17}ClN_6OS$: C, 61.92; H, 3.53; N, 17.33; Found: C, 62.00; H, 3.58; N, 17.32.

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