A New Regioselective Synthesis and Bioactivity of 1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one Derivatives

Hong-Qing Wang[1,2], Zhao-Jie Liu [1]*, Li-Min Yang[1], and Ming-Wu Ding[1]

1. Institute of Organic Synthesis, Central China Normal University, Wuhan, 430079, P. R. China
2. College of Chemistry &Chemical Engineer, NanHua University, Hengyang, 421001, P. R. China

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A series of new1*H*-pyrazolo[3,4-*d*]pyrimidin-4(*5H*)-one Derivatives **5** has been designed and regioselectively synthesized *via* a tandem aza-Wittig reaction. The structures of all compounds prepared have been confirmed by ^{1}H NMR, IR, EI-MS spectroscopy and elemental analyses. The results of preliminary bioassay indicate that most compounds **5** possess an inhibition effect against *Botrytis cinereapers* and *Pyricularia oryzae* at the concentration of 50 mg/L.

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Introduction.

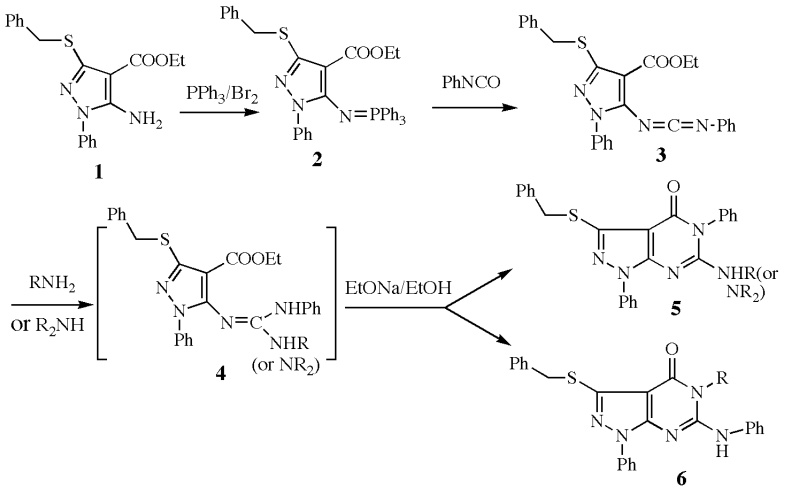
Pyrazolopyrimidinone derivatives play a very important part in the biochemistry of the living cell. Many potential drugs [1-3] and agrochemicals [4,5] have been modeled on it. In previous reports, various synthetic procedures have been devised for the conversion of pyrazole with *o*-aminonitriles or *o*-aminoesters to pyrazolopyrimidinones derivatives which involved, *inter alia*, (a) hydrolysis of aminonitriles followed by reaction with aliphatic ester [6,7], aromatic aldehydes [8], and carboxylic acids [8,9], or (b) treatment of *o*-aminoesters with aryl isothiocycanates and subsequent reaction with hydrazine monohydrate [10,11], or (c) generated pyrazolooxazines or *o*-ethoxymethyleneaminoesters reaction with amines [12]. As a continuation of our search for new biologically active heterocycles [13-15], here we developed a new and facile regioselective annulation process, which proceeded smoothly under mild condition *via* a tandem aza-Wittig and cyclization reaction, to synthesize novel 6-alkylamino-3-benzylthio-1,5-diphenyl-*1H*- pyrazolo[3,4-*d*]pyrimidin-4(*5H*)-ones **5**. The preliminary antifungicidal activities of prepared compounds are also reported.

Results and Discussion.

Synthesis and Structure Characterization of **5**.

The iminophosphorance **2**, which was prepared from 5-aminopyrazole **1** in the presence of triphenylphosphine and liquid bromine, reacted with phenyl isocyanate to give carbodiimide **3**, which was allowed to react with alkylamines at room temperature to give intermediate guanidines **4**. In the presence of EtONa/EtOH, the cyclization was achieved (see Scheme 1). The pure major products **5** were separated from the reaction mixture by recrystallization or flash chromatography on silica gel. Whenever the primary amine used was small (R = n - Pr) or bulky (R = *t*–Bu), the major products **5** were obtained in moderate to good yields. And **6** was found to exist in minor amount by LC-MS detection, especially in case of **5d**, **5i** and **5k** compounds obtained with low yield, but was not obtained. Its regioselectivity was the same as our previous research [16]. And, in our previous research, it was found that various carbodiimides reacted with nucleophiles followed by cyclization in need of excessive catalytic solid potassium carbonate [13-15]. In this work, the cyclization of guanidines **4** was carried out in the presence of EtONa.

Scheme 1



However, in the absence of any base, the intermediate guanidine **4** did not cyclize completely and was recovered. The results are listed in Table 1.

The structures of 6-alkylamino-3-benzylthio-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-ones (**5**) were deduced from their spectra data. In the ^{1}H NMR spectra of **5**, the corresponding proton of NH displays triplet or doublet multiplicity due to coupling with methene or methyne protons adjacent to the nitrogen atom. Its chemical shift is 4.02 ~ 4.75, *i.e.* more shielded than the one in PhNH (δ>7.0) [17]. For example, the ^{1}H NMR spectral data of **5c** shows the signals of NH at 4.32 as triplet and NCH_2 at 3.35 ~ 3.42 as multiplet, which strongly suggests the existence of $NHCH_2Pr$-*n* group in **5c**. Moreover, when the sample was treated with deuterated water, its NCH_2 showed the signal at 3.39 as triplet with the disappearance of signals of NH absorption. Thus 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 **5**. In addition, the EI-MS spectra of **5** showed the molecular ion peaks (M+, 15% ~ 83%). All the fragmentation ions are consistent with their structures and can be clearly assigned. The IR spectra of **5** exhibited N-H, carbonyl and C=N absorptions.

The formation of major products **5** (Scheme 2) can be rationalized in terms of geometry of the intermediate **4** and stabilization of product **5** and **6** [16]. It is estimated that the configurations of carbodiimide **3** are mainly coplanar due to the resonance effect. When the amines reacted with **3a**, *Z*-**4a** formed since the amines would attack **3a** mainly from the opposite direction of the COOEt group due to the steric hindrance of the COOEt group. When the amines reacted with **3b**, *Z*-**4b** formed since the amines would attack **3b** mainly from the opposite direction of the phenyl group due to the steric hindrance of the pyrazole ring and phenyl group. Actually, *Z*-**4b** must convert to *Z*-**4a** in order to undergo cyclization, and *Z*-**4a** may convert to *E*-**4c** through C—N single bond rotation. *Z*-**4a** is suitable for the arylamine group to cyclize and *E*-**4c** is suitable for the alkylamine group to cyclize. However, the initially formed *Z*-**4a** more easily undergoes cyclization to give **5** than to divert to **4c** to give **6**. Compounds **5** are more stable than compounds **6** because of the conjugative effect and there is steric hindrance between alkyl group and ester group. And comparison of the yields between **5a** and **5b**, **5c** and **5e**, **5h** and **5i** and **5j**, **5k** and **5l** gave the same result. That is to say, the bulkier the R group, the larger the steric hindrance between the alkyl group and ester group and the more difficult for *Z*-**4a** to divert to *E*-**4c**, and the higher of yields.

In conclusion, we have developed a facile and efficient regioselective method for the preparation of 6-alkylamino-3-benzylthio-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one **5** *via* a tandem aza-Wittig annulation process.

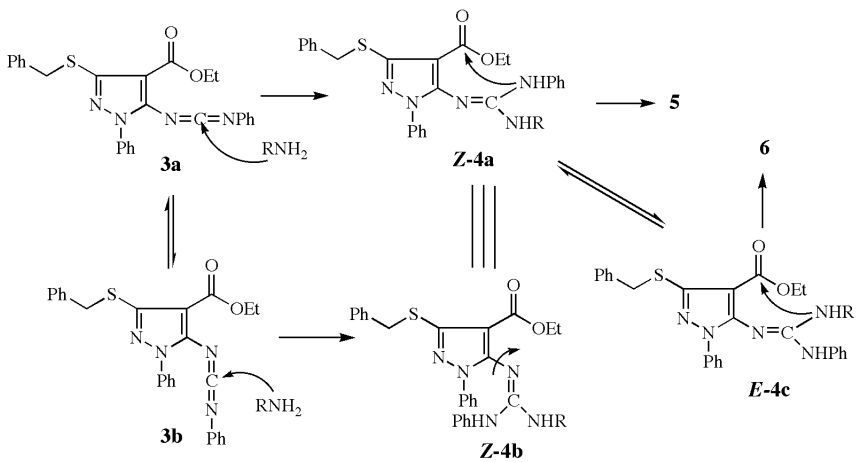
Table 1

Physical Constants of 6-Alkylamino-3-benzylthio-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-ones

Compounds	R	Appearance	mp (°C)	Yield (%) [a]
5a	*n*-Pr	White crystals	149.7~150.5	85.8
5b	*iso*-Pr	White crystals	169.1~171.7	92.8
5c	*n*-Bu	White crystals	112.0~113.0	65.7
5d	*iso*-Bu	White crystals	163.0~163.2	53.3
5e	*t*-Bu	White crystals	212.0~213.0	93.5
5f	$R_2 = Et_2$	White crystals	119.0~120.0	78.5
5g	*n*-Amyl	White crystals	182.0~182.3	73.8
5h	*o*-$CH_3C_6H_4CH_2$	White crystals	168.0~169.0	80.1
5i	*p*-$CH_3C_6H_4CH_2$	White crystals	157.0~158.0	65.8
5j	*o*-$FC_6H_4CH_2$	White crystals	198.0~198.2	66.9
5k	*p*-$FC_6H_4CH_2$	White crystals	148.0~151.0	40.2
5l	*o*-$ClC_6H_4CH_2$	White crystals	197.0~198.0	76.7

[a] isolate based on iminophosphorane **2**.

Scheme 2



Biological Activities.

Compounds **5** were tested for *in vitro* antifungicidal activity against four plant diseases according to a previously reported method [20]. The fungi were obtained from the College of Plant Protect, Central China Agriculture University, China, all of which were chemically pure active ingredients. The tested compounds were dissolved in acetone and added to a sterile agarized Czapek-Dox medium at 45 °C. In preliminary screenings compounds were used in a concentration of 50 mg/L. The control sample contained only one equivalent of acetone. The media were poured onto 8-cm Petri dishes (10 mL for each dish) and were inoculated with 5-mm PDA discs of overgrown mycelium. After the tested dishes being incubated at 25 °C in the dark for 48 hours, the diameters of the mycelium were measured. The percentage inhibition of fungal growth was determined by comparison between the development of fungi colonies on media containing compounds and on the control. Three replicates of each test were carried out. The biological data are presented in Table 2. The results showed that compounds **5** possessed an inhibition effect against *Botrytis cinereapers* and *Pyricularia oryzae*, but weak against *Gibberella zeae* and *Cercopora beticola*. For example, the inhibitory rate of compound **5a** was 80.6% to *Pyricularia oryzae* and that of **5b**, **5f**, **5h**, **5i** and **5k** were 87.9%, 81.8%, 84.9%, 84.8% and 84.9% to *Botrytis cinereapers* at 50mg/L.

Table 2

Fungicidal Activity of Compounds **5**: (50 mg/L, inhibitory rate %)

	5a	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**	**5h**	**5i**	**5j**	**5k**	**5l**
Pyricularia oryzae	80.6	60.0	42.9	42.9	34.3	42.9	40.0	54.3	54.3	37.1	54.3	45.7
Botrytis cinereapers	12.1	87.9	78.9	60.6	63.6	81.8	48.5	84.9	84.8	72.7	84.9	69.7
Gibberella zeae	21.6	59.7	40.5	40.5	32.4	48.6	32.4	54.1	59.5	32.4	51.4	43.2
Cercopora beticola	15.6	65.6	46.9	40.6	21.9	53.1	31.2	65.6	56.2	37.5	46.9	56.2

EXPERIMENTAL

Melting points were determined with a WRS-1B Digital melting point apparatus and are uncorrected. EI-MS spectra were measured on a Finnigan Trace Mass Spectrometer, and LC-MS spectra were measured on API 2000. IR spectra were recorded on a Shimadzu IR-408 infrared Spectrometer. ^{1}H NMR spectra were taken on a Varian XL-300 Spectrometer. Elementary Analysis were recorded on a Vario EL III elementary analysis instrument. All of the solvents and materials were reagent grade and purified as required.

5-Aminopyrazole **1** was prepared according to the literature procedures [18] in yield 85.6%, mp 85.7~86.5 °C. Iminophosphorane **2** was prepared according to the reported procedures [19] in yield 80.2%, mp 162.0~163.2 °C. MS (70eV) (relative intensity %): m/z 615 (M+2, 6), 614 (M+1, 18), 613 (M+, 44), 580 (41), 536 (36), 262 (100), 183 (99), 108 (54), 77 (22).

General Procedure for the Preparation of 6-Alkylamino-3-benzylthio-1,5-diphenyl-1*H*- pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-ones (**5**).

To a solution of iminophosphorane **2** (1.84 g, 3 mmol) in dry methylene dichloride (20 mL) was added phenyl isocyanate (0.36 g, 3 mmol) under nitrogen at room temperature. After the reaction mixture was stirred for 1.5 hours, alkylamine was added to the reaction solution and stirred for an addition 30 min. Then the solvent was removed under reduced pressure and 25 mL of anhydrous ethanol and 1.5 ml of sodium ethoxide in ethanol (3 *M*) were added to the mixture. After stirring for 3~5 hours, concentrating under reduce pressure, and cooling, the mixture was filtered, furnishing a white solid which was either recrystallized from dichloromethane/petroleum ether or purified on silica gel to give pure 6-alkylamino-3-benzylthio-1,5-diphenyl-1*H*- pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one **5**.

3-Benzylthio-1,5-diphenyl-6-propylamino-1*H*-pyrazolo[3,4-*d*]-pyrimidin-4(5*H*)-one (**5a**).

This compound was prepared according to the general procedure above to give **5a**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.86 (t, 3H, J = 7.2Hz, *CH_3*), 1.52 ~ 1.57 (m, 2H, *CH_2*CH_3), 3.34 (q, 2H, J = 6.1Hz, N*CH_2*), 4.35 (m, 1H, *NH*), 4.47 (s, 2H, S*CH_2*Ph), 7.18 ~ 7.58 (m, 13H, *Ph*), 8.16 (d, 2H, J = 8.1Hz, *Ph*); IR (KBr): ν 3412, 1695, 1596, 1555, 1455, 1385, 1035 cm^{-1}; MS (70eV) (relative intensity %): m/z 469 (M+2, 13), 468 (M+1, 34), 467 (M+, 53), 435 (100), 246 (27), 169 (22), 161(33), 119(70), 91(61), 77(55)

Anal. Calcd. for $C_{27}H_{25}N_5OS$: C, 69.35; H, 5.39; N, 14.98. Found: C, 69.46; H, 5.32; N, 15.05.

3-Benzylthio-6-isopropylamino-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]-pyrimidin-4(5*H*)one (**5b**).

This compound was prepared according to the general procedure above to give **5b**: ^{1}H NMR ($CDCl_3$, 300 MHz) : δ 1.16 (d, 6H, J = 6.6Hz, *Me_2*), 4.08 (d, 1H, J = 6.6Hz, *NH*), 4.16 ~ 4.22 (m, 1H, Me_2*CH*), 4.47 (s, 2H, Ph*CH_2*), 7.20 ~ 7.57 (m, 13H, *Ph*), 8.15 (d, 2H, J = 8.1Hz, *Ph*); IR (KBr): ν 3429, 1696, 596, 1541, 1385, 1033 cm^{-1}; MS (70eV) (relative intensity %): m/z 469 (M+2, 17), 468 (M+1, 50), 467 (M+, 83), 435 (59), 434 (100), 246 (33), 119 (84), 91 (97), 77 (84).

Anal. Calcd. for $C_{27}H_{25}N_5OS$: C, 69.35; H, 5.39; N, 14.98. Found: C, 69.59; H, 5.45; N, 14.72.

6-Butylamino-3-benzylthio-1,5-diphenyl-1*H*- pyrazolo[3,4-*d*]-pyrimidin-4(5*H*)-one (**5c**).

This compound was prepared according to the general procedure above to give **5c**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.91 (t, 3H, J = 7.2Hz, N$(CH_2)_3$*Me*), 1.24 ~ 1.32 (m, 2H, NCH_2CH_2*CH_2*Me),

1.48 ~ 1.53 (m, 2H, NCH_2CH_2Et), 3.35 ~ 3.42 (2H, m, NCH_2Pr-*n*, J = 6.6Hz (after the D_2O exchange)), 4.32 (t, 1H, J = 5.6Hz, *NH*), 4.47 (s, 2H, SCH_2Ph), 7.19 ~ 7.59 (m, 13H, *Ph*), 8.16 (d, 2H, J = 7.5Hz, *Ph*); IR (KBr): ν 3429, 1700, 1595, 1554, 1454, 1385, 1029 cm^{-1}; MS (70eV) (relative intensity %): m/z 483 (M+2, 11), 482 (M+1, 35), 481 (M+, 72), 448 (96), 246 (20), 169 (20), 119 (79), 91 (100), 77 (88).

Anal. Calcd: for $C_{28}H_{27}N_5OS$: C, 69.83; H, 5.65; N, 14.54. Found: C, 70.02; H, 5.56; N, 14.62.

3-Benzylthio-6-isobutylamino-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]-pyrimidin-4(5*H*)-one (**5d**).

This compound was prepared according to the general procedure above to give **5d**: ^1H NMR ($CDCl_3$, 300 MHz): δ 0.85 (d, 6H, J = 6.6Hz, Me_2CH), 1.86 ~ 1.93 (m, 1H, Me_2CHCH_2N), 3.20 (t, 2H, J = 6.2Hz, $CHCH_2N$), 4.40 (m, 1H, *NH*), 4.48 (s, 2H, $PhCH_2$), 7.19 ~ 7.60 (m,13H, *Ph*), 8.15 (d, 2H, J = 8.1Hz, *Ph*); IR (KBr): ν 3441, 1704, 1598, 1548, 1454, 1386, 1034; MS (70eV) (relative intensity %): m/z 483(M+2,4), 482 (M+1, 12), 481(M+, 34), 448 (88), 246 (12), 169 (12), 119 (51), 91 (100), 77 (62), 57 (22).

Anal. Calcd. for $C_{28}H_{27}N_5OS$: C, 69.83; H, 5.65; N 14.54. Found: C, 69.87; H, 5.69; N, 14.66.

6-*tert*-Butylamino-3-benzylthio-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]-pyrimidin-4(5*H*)-one (**5e**).

This compound was prepared according to the general procedure above to give **5e**: ^1H NMR ($CDCl_3$, 300 MHz): δ 1.36 (s, 9H, *t-Bu*), 4.20 (s, 1H, *NH*), 4.47 (s, 2H, $PhCH_2$), 7.21 ~ 7.56 (m, 13H, *Ph*), 8.09 (d, 2H, J = 7.5Hz, *Ph*); IR (KBr): ν 3414, 1705, 1598, 1454, 1388, 1034; MS (70eV) (relative intensity %): m/z 483 (M+2, 3), 482 (M+1, 8), 481 (M+, 23), 448 (53), 392 (16), 119 (47), 91 (100), 77 (59).

Anal. Calcd. for $C_{28}H_{27}N_5OS$: C, 69.83; H, 5.65; N, 14.54. Found: C, 69.82; H, 5.76; N, 14.70.

3-Benzylthio-6-diethylamino-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]-pyrimidin-4(5*H*)-one (**5f**).

This compound was prepared according to the general procedure above to give **5f**: ^1H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, 6H, J = 6.9Hz, CH_2CH_3), 3.15 (q, 4H, J = 6.9Hz, CH_2CH_3), 4.46 (s, 2H, $PhCH_2$), 7.18 ~ 7.47 (m,13H, *Ph*), 8.13 (d, 2H, J = 7.8Hz, *Ph*); IR (KBr): ν 1699, 1601, 1555, 1454, 1392, 1033; MS (70eV) (relative intensity %): m/z 483 (M+2, 5), 482 (M+1, 17), 481 (M+, 49), 448 (90), 345 (10), 119 (37), 91 (100), 77 (66).

Anal. Calcd. for $C_{28}H_{27}N_5OS$: C, 69.83; H, 5.65; N, 15.54. Found: C, 69.86; H, 5.71; N, 14.60.

3-Benzylthio-6-pentylamino-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]-pyrimidin-4(5*H*)-one (**5g**).

This compound was prepared according to the general procedure above to give **5g**: ^1H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, 3H, J = 6.9Hz, $N(CH_2)_4CH_3$), 1.22 ~ 1.31 (m, 4H, $NCH_2CH_2CH_2CH_2CH_3$), 1.52 ~ 1.54 (m, 2H, $NCH_2CH_2CH_2CH_2$), 3.34 ~ 3.40 (m, 2H, NCH_2CH_2), 4.33 (s, 1H, *NH*), 4.47 (s, 2H, $PhCH_2$), 7.17 ~ 7.58 (m, 13H, *Ph*), 8.16 (d, 2H, J = 8.1Hz, *Ph*); IR (KBr): ν 3430, 1702, 1595, 1565, 1497, 1385, 1035; MS (70eV) (relative intensity %): m/z 497 (M+2, 7), 496 (M+1, 21), 495 (M+, 54), 463 (45), 462 (87), 119 (54), 91 (100), 77 (64).

Anal. Calcd. for $C_{29}H_{29}N_5OS$: C, 70.28; H, 5.90; N, 14.13. Found: C, 70.15; H, 5.92; N, 14.26.

3-Benzylthio-6-(2-methylbenzylamino)-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (**5h**).

This compound was prepared according to the general procedure above to give **5h**: ^1H NMR ($CDCl_3$, 300 MHz): δ 2.25 (s, 3H, $PhCH_3$-*o*), 4.46 (s, 2H, $PhCH_2S$), 4.55 (s, 1H, *NH*), 4.56 (s, 2H, CH_2N), 7.12 ~ 7.58 (m, 17H, *Ar*), 8.01 (d, 2H, J = 8.4Hz, *Ar*); IR (KBr): ν 3421, 1709, 1600, 1554, 1386, 1032; MS (70eV) (relative intensity %): m/z 530 (M+1, 6), 529 (M+, 15), 496 (32), 181 (12), 105 (100), 91 (56), 77 (31).

Anal. Calcd. for $C_{32}H_{27}N_5OS$: C, 72.56; H, 5.14; N, 13.22. Found: C, 72.71; H, 5.11; N, 13.39.

3-Benzylthio-6-(4-methylbenzylamino)-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (**5i**).

This compound was prepared according to the general procedure above to give **5i**: ^1H NMR ($CDCl_3$, 300 MHz): δ 2.31 (s, 3H, $PhCH_3$-*p*), 4.46 (s, 2H, $PhCH_2S$), 4.52 (d, 2H, J = 4.5Hz, CH_2N), 4.70 (d, 1H, J = 5.1Hz, *NH*), 7.21 ~ 7.57 (m, 17H, *Ar*), 8.04 (d, 2H, J = 7.5Hz, *Ar*); IR (KBr): ν 3359, 1686, 1598, 1541, 1361, 1035; MS (70eV) (relative intensity %): m/z 530 (M+1,6), 529 (M+, 14), 496 (31), 181 (20), 105 (100), 91 (59), 77 (33).

Anal. Calcd. for $C_{32}H_{27}N_5OS$: C, 72.56; H, 5.14; N, 13.22. Found: C, 72.47; H, 5.20 ; N, 13.36.

3-Benzylthio-6-(2-fluorobenzylamino)-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (**5j**).

This compound was prepared according to the general procedure above to give **5j**: ^1H NMR ($CDCl_3$, 300 MHz): δ 4.45 (s, 2H, $PhCH_2S$), 4.59 (t, 2H, J = 5.4Hz, CH_2N), 4.84 (t, 1H, J = 5.1 Hz, *NH*), 6.99 ~7.60 (m, 17H, *Ar*), 8.02 (d, 2H, J = 7.5Hz, *Ar*); IR (KBr): ν 3364, 1694, 1590, 1360, 1032; MS (70eV) (relative intensity %): m/z 535 (M+2, 3), 534 (M+1, 8), 533 (M+, 24), 500 (53), 392 (16), 109 (64), 91 (100), 77 (19).

Anal. Calcd. for $C_{31}H_{24}FN_5OS$: C, 69.77; H, 4.53; N, 13.12. Found: C, 69.65; H, 4.60; N, 13.25.

3-Benzylthio-6-(4-fluorobenzylamino)-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (**5k**).

This compound was prepared according to the general procedure above to give **5k**: ^1H NMR ($CDCl_3$, 300 Hz): δ 4.51 (s, 2H, $PhCH_2S$), 5.37 (s, 2H, CH_2N), 6.49 (s, 1H, *NH*), 6.94 ~7.49 (m, 17H, *Ar*), 8.03 (d, 2H, J=8.1Hz, *Ar*); IR(KBr): ν 3303, 1675, 1594, 1555, 1386; MS (70eV) (relative intensity %): m/z 535 (M+2, 3), 534 (M+1, 9), 533 (M+, 26), 500 (54), 109 (66), 91 (100), 77 (20).

Anal. Calcd. for $C_{31}H_{24}FN_5OS$: C, 69.77; H, 4.53; N 13.12. Found: C, 69.86; H, 4.49; N, 13.22.

3-Benzylthio-6-(2-chlorobenzylamino)-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (**5l**).

This compound was prepared according to the general procedure above to give **5l**: ^1H NMR ($CDCl_3$, 300 MHz): δ 4.45 (s, 2H, $PhCH_2S$), 4.60 (t, 2H, J = 5.7Hz, CH_2N), 4.99 (t, 1H, J = 5.4Hz, *NH*), 7.13 ~ 7.60 (m, 17H, *Ar*), 8.01 (d, 2H, J = 7.8Hz, *Ar*); IR (KBr): ν 3356, 1695, 1598, 1538, 1358, 1023; MS (70eV) (relative intensity %): m/z 551 (M+1, 13), 549 (M+, 31), 516 (67), 127 (32), 125 (100), 91 (97), 77 (42).

Anal. Calcd. for $C_{31}H_{24}ClN_5OS$: C, 67.69; H, 4.40; N, 12.73. Found: C, 67.48; H, 4.42; N, 12.91.

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