SYNTHESES OF NEW PYRAZOLO[3,4-*d*]PYRIMIDINE DERIVATIVES STARTING FROM 1,1-DIAMINO-2,2-DICYANOETHYLENE

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Abstract - 3,4-Diamino-6-dimethylamino-1-methylpyrazolo[3,4-*d*]-pyrimidine (**4**) was prepared from the reaction of 6-amino-4-chloro-5-cyano-2-dimethylaminopyrimidine (**3**) with methylhydrazine. It reacted further with different aldehydes giving a variety of new pyrazolo[3,4-*d*]-pyrimidine derivatives.

INTRODUCTION

In continuation of our previous studies of the syntheses of heterocyclic compounds from the starting materials having two cyano groups such as alkyl dicyanoacetates and dicyanoketene ethylene acetal,[1-15] we reported the synthesis of 6-amino-4-chloro-5-cyano-2-dimethylaminopyrimidine (**3**)[16] from dichlormethylenedimethylimmonium chloride (**2**) and 1,1-diamino-2,2-dicyanoethylene (**1**) which is easily obtained from dicyanoketene ethylene acetal and ammonium hydroxide.[17] On account of the presence of 4,5,6-substional substituents (Cl, NH_2, CN), **3** is very possible to be used as intermidiate to synthesize bi- and tricyclic heterocycles.

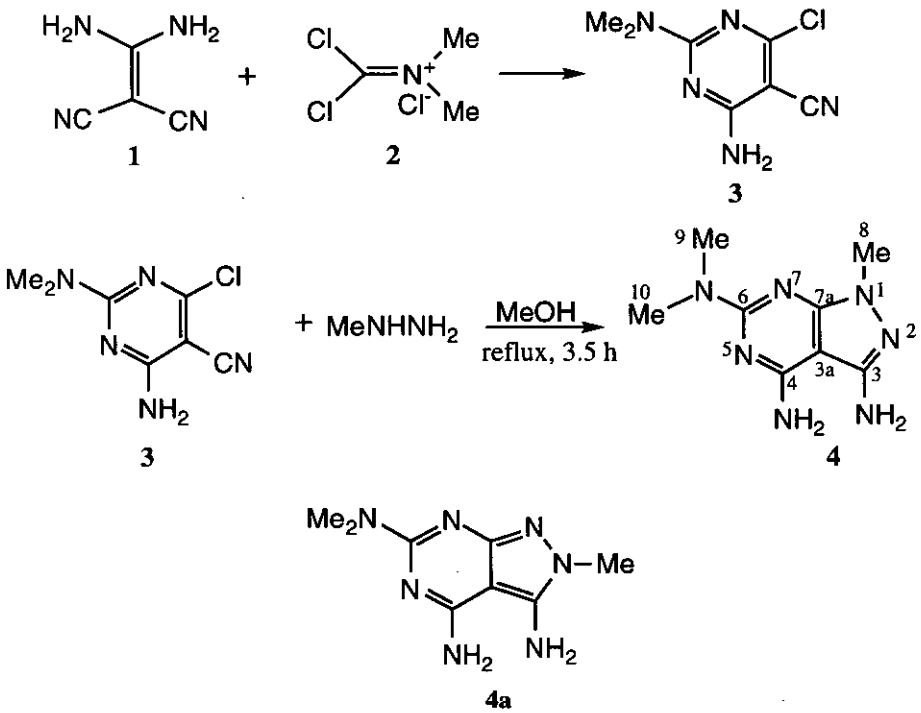
The present paper describes the results of our studies concerning the preparation of 3,4-diamino-6-dimethylamino-1-methylpyrazolo[3,4-*d*]pyrimidine (**4**) from **3** and methylhydrazine as well as the condensation reactions of **4** with different aldehydes.

RESULTS AND DISCUSSION

6-Amino-4-chloro-5-cyano-2-dimethylaminopyrimidine (**3**) reacted with methylhydrazine in methanol under reflux giving 3,4-diamino-6-dimethylamino-1-methylpyrazolo[3,4-*d*]-pyrimidine (**4**) (Scheme 1).The ^{1}H- and ^{13}C-NMR spectra show that the product has only one structure. The ^{1}H-NOE spectrum shows that by radiation of NH_2 at δ=5.38 ppm or δ=6.72 ppm no Overhauser effect was observed at δ=3.48 ppm (NCH_3) (Scheme 2). Therefore, the

product is **4** instead of **4a**. On the other hand, the X-Ray structure of compound (**6a**) (see Figure 1a), the condensation product with 4-chlorobenzaldehyde (**5a**), illustrates clearly that the structure of product must be **4**. The formation of **4** can be assumed to proceed as outlined in Scheme 3.

Scheme 1

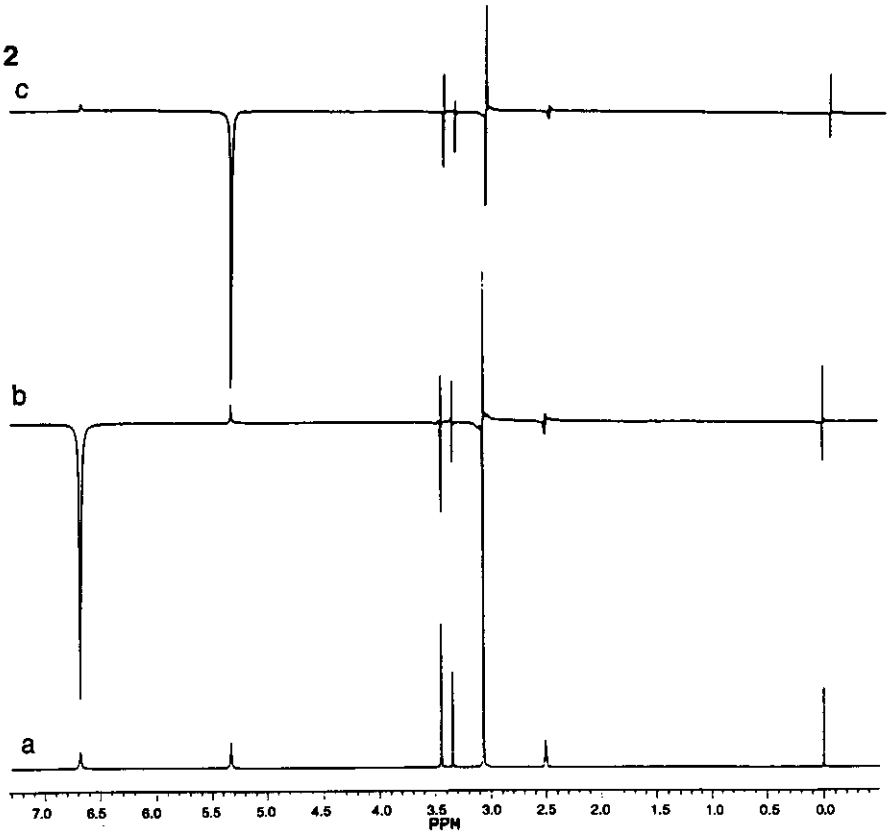


It is necessary to point out that **3** did not react with hydroxylamine, amidine and guanidine, even though upon reflux in the presence of a strong base such as sodium ethoxide.

Unlike 1,8-diaminonaphthalene which reacts with aldehydes giving 2,3-dihydro-1H-perimidine derivatives,[18] only one of the amino groups in **4** reacted with aldehydes (**5a-k**) in ethanol or 2-ethoxyethanol and gave Schiff bases (**6a-k**) instead of *N,N*-acetals (Scheme 4).The X-Ray diffraction study of molecule (**6a**) (Figure 1a) confirms that under our reaction conditions only the amino group at the 3-position can react with aldehyde resulting in the formation of the Schiff base.The dimer structure (see Figure 1b) shows that there are two intra- and intermolecular hydrogen bonds in crystal. The selective INEPT ^{13}C-NMR spectrum of **6a** (Scheme 5) indicates that the signals at δ=149.4(+), 134.3(+) and 130.1(-) ppm due to C-3, C-1′ and C-2′,6′ respectively. Then the signals at δ=137.9(+) and 129.1(-) ppm are naturally due to C-4′ and C-3′,5′.

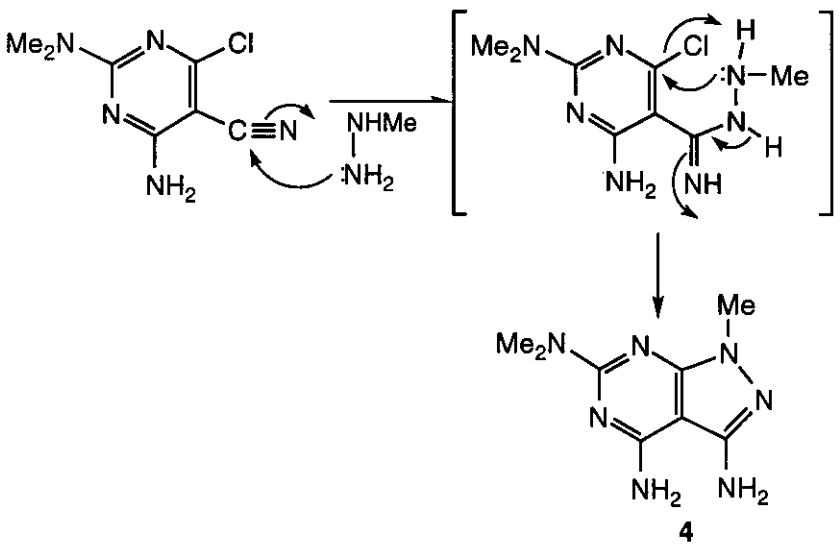
In addition, we stirred **4** with two equivalents (**5b**) in ethanol under reflux for 70 h, besides **6b** no other product was isolated.

Scheme 2



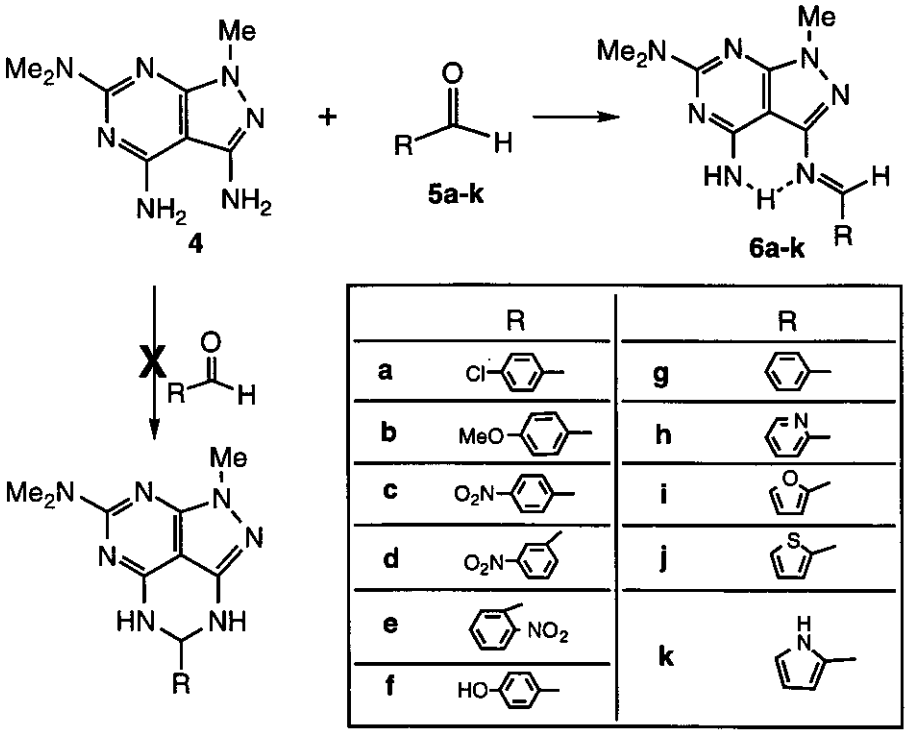
a) 300 MHz ^{1}H-NMR spectrum of **4** in DMSO-d_6.
b) NOE difference spectrum resulting from irradiation of NH_2(6.72 ppm).
c) NOE difference spectrum resulting from irradiation of NH_2(5.38 ppm).

Scheme 3



4

Scheme 4



	R		R
a	Cl-C6H4-	g	C6H5-
b	MeO-C6H4-	h	2-pyridyl
c	O2N-C6H4-	i	2-furyl
d	O2N-C6H4- (2-Me)	j	2-thienyl
e	2-NO2-C6H4-	k	2-pyrrolyl
f	HO-C6H4-		

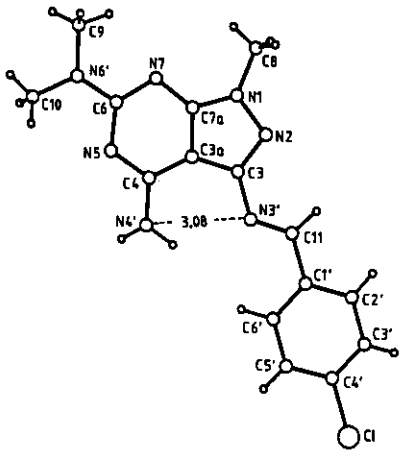


Figure 1a

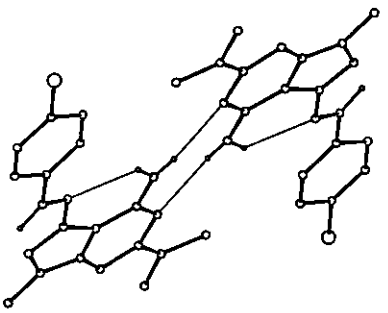
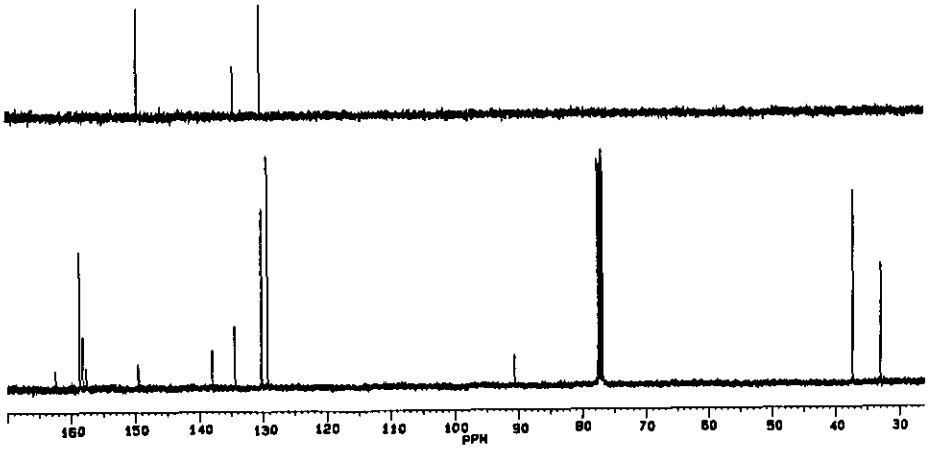


Figure 1b

Table 1 Bond Distances (in Å) of **6a**

N1--N2 1.358(3)	N4--N4′ 1.342(4)	C1′--C6′ 1.386(4)
N1--C7a 1.354(4)	N5--C6 1.374(4)	C2′--C3′ 1.372(4)
N1--C8 1.453(4)	C6--N7 1.345(4)	C3′--C4′ 1.364(4)
N2--C3 1.331(4)	C6--N6′ 1.353(4)	C4′--C5′ 1.370(5)
C3--C3a 1.405(4)	N7--C7a 1.345(4)	C4′--Cl4 1.735(3)
C3--N3′ 1.403(4)	N3′--C11 1.271(4)	C5′--C6′ 1.369(5)
C3a--C4 1.405(4)	N6′--C9 1.450(4)	
C3a--C7a 1.383(4)	C11--C1′ 1.461(4)	
C4--N5 1.327(4)	C1′--C2′ 1.389(4)	



Scheme 5 ^{13}C-NMR INEPT of **6a** resulting from irradiation of **H-11**(9.07 ppm).

EXPERIMENTAL

Melting points were determined on a Reichert hot microscope and are uncorrected. IR spectra were measured with a Perkin-Elmer spectrophotometer 283 using potassium bromide and are given as cm^{-1}. ^{1}H- and ^{13}C-NMR spectra were recorded on either a Bruker WM-250 (^{1}H-NMR: 250.13 MHz, ^{13}C-NMR: 62.89 MHz) or a Varian XL 300 (^{1}H-NMR: 299.95 MHz, ^{13}C-NMR: 75.43 MHz) spectrometer in DMSO-d_6 or $CDCl_3$. The chemical shifts are reported in parts per million (ppm) downfield from internal tetramethylsilane. Electron impact MS spetra were obtained on a Varian MAT 311A instrument. Element analyses were performed on a Heraeus Vario EL CHNS apparatus.

3,4-Diamino-6-dimethylamino-1-methylpyrazolo[3,4-*d*]pyrimidine (4)
A solution of **3** (198 mg, 10 mmol) and 5mL of methylhydrazine in 150 mL of methamol was refluxed for 3.5 h. After removing of the solvent under reduced pressure, about 100 mL of water was added. The resulting precipitate was washed with water and dried. Recrystallisation from methanol gave 1.84 g of white crystals (88.9%). mp 221-223 °C. IR (KBr): 3418, 3135 (NH); 1646, 1602, 1545 (C=N, C=C); 970, 918, 790, 748 (arom.). ^{1}H-NMR (300 MHz, DMSO-d_6): δ=3.08 (s, 6H, N(C**H**$_3$)$_2$); 3.48 (s, 3H, NC**H**$_3$); 5.38 (s, 2H, C3-N**H**$_2$); 6.72 (s, 2H, C4-N**H**$_2$). ^{13}C-NMR (62.89 MHz, DMSO-d_6): δ=31.85 (-, **C**-8); 36.76 (-, **C**-9, **C**-10); 84.30 (+, **C**-3a); 147.2 (+, **C**-3); 156.6 (+, **C**-7a); 157.6 (+, **C**-4); 161.6 (+, **C**-6). MS m/z (%): [M+1]$^+$: 208 (11); M$^+$: 207 (100); 192 (37); 178 (22); 147 (11); 104 (6); 44 (9). HRMS: Calcd for $C_8H_{13}N_7$: 207.1233. Found: 207.1234. *Anal.* Calcd for $C_8H_{13}N_7$: C, 46.37; H, 6.32; N, 47.31. Found: C, 46.54; H, 6.70; N, 46.77.

General procedure for preparation of 6a-b and 6d-j:
A solution of 1 mmol of **4** and 1 mmol of the corresponding aldehyde in 20 mL of ethanol was refluxed for 8-45 h. Then it was cooled to 0 °C overnight, the crystals were filtered and washed with petroleum ether and dried, then receystallized from ethyl acetate.

4-Amino-6-dimethylamino-3-(*p*-chlorphenyl)azomethino-1-methylpyrazolo[3,4-*d*]pyrimidine (6a) (71.3%). mp 215-216 °C. IR (KBr): 3424, 3322 (NH); 1653, 1616, 1591, 1559 (C=C, C=N); 970, 820, 786 (arom.). ^{1}H-NMR (300 MHz, $CDCl_3$): δ=3.21 (s, 6H, N(C**H**$_3$)$_2$); 3.84 (s, 3H, NC**H**$_3$); 5.64 (s, 2H, N**H**$_2$); 7.44 (d, J=8.4 Hz, 2H, **H**-3′, 5′); 7.86 (d, J=8.7 Hz, 2H, **H**-2′, 6′); 9.07 (s, 1H, **H**-11). ^{13}C-NMR (90.56 MHz, $CDCl_3$): δ=32.92 (-, **C**-8); 37.24 (-, **C**-9, **C**-10); 90.5 (+, **C**-3a); 129.1 (-, **C**-3′, **C**-5′); 130.1 (-, **C**-2′, **C**-6′); 134.3 (+, **C**-1′); 137.9 (+, **C**-4′); 149.4 (+, **C**-3); 157.5 (+, **C**-7a); 158.0 (+, **C**-4); 158.6 (-, **C**-11); 162.3 (+, **C**-6). MS m/z(%): [M+2]$^+$: 331 (37); [M+1]$^+$: 330 (25); M$^+$: 329 (100); 314 (37); 300 (27); 191 (7); 173 (11); 71 (16); 44 (17). HRMS: Calcd for $C_{15}H_{16}N_7Cl$: 329.1155. Found: 329.1154. *Anal.* Calcd for $C_{15}H_{16}N_7Cl$: C, 54.63; H, 4.89; N, 29.73. Found: C, 54.63; H, 5.16; N, 29.00.

4-Amino-6-dimethylamino-3-(*p*-methoxyphenyl)azomethino-1-methylpyrazolo-[3,4-*d*]pyrimidine (6b) (69.2%). mp 198-200 °C. IR (KBr): 3428, 3320 (NH); 1647, 1611, 1598, 1569, 1534 (C=C, C=N); 1027 (C-O); 833, 794 (arom.). ^{1}H-NMR (300 MHz, $CDCl_3$): δ=3.21 (s, 6H, N(C**H**$_3$)$_2$); 3.83 (s, 3H, NC**H**$_3$); 3.87 (s, 3H, OC**H**$_3$); 5.72 (s, 2H, N**H**$_2$); 6.98 (d, J=8.7 Hz, 2H, **H**-3′,5′); 7.88 (d, J=9.0 Hz, 2H, **H**-2′,6′); 9.04 (s, 1H, **H**-11). ^{13}C-NMR (90.56 MHz, $CDCl_3$): δ=32.85 (-, **C**-8); 37.28 (-, **C**-9, **C**-10); 55.45 (-, O**C**H$_3$); 70.59 (+, **C**-4′); 90.3 (+, **C**-3a); 114.3 (-, **C**-3′, **C**-5′); 128.9 (+, **C**-1′); 130.9 (-, **C**-2′, **C**-6′); 150.2 (+, **C**-3); 157.3 (+, **C**-7a); 158.1 (+, **C**-4); 159.6 (-, **C**-11); 162.7 (+,C-6). MS m/z(%): [M+1]$^+$: 326 (20); M$^+$: 325 (100); 310 (22); 296 (15); 191 (6); 71 (8); 44 (8). HRMS: Calcd for $C_{16}H_{19}N_7O$: 325.1649. Found: 325.1647. *Anal.* Calcd for $C_{16}H_{19}N_7O$: C, 59.06; H, 5.98; N, 30.13. Found: C, 58.67;

H, 6.16; N, 29.34.

4-Amino-6-dimethylamino-1-methyl-3-(3′-nitrophenyl)azomethinopyrazolo[3,4-*d*]pyrimidine (6d) (88.2%). mp 277-279 °C. IR (KBr): 3423, 3308 (NH); 1653, 1611, 1546 (C=C,C=N); 1350 (NO_2); 794 (arom.). ^{1}H-NMR (250.13 MHz, DMSO-d_6): δ=3.15 (s, 6H, N(C**H**$_3$)$_2$); 3.75 (s, 3H, NC**H**$_3$); 7.82 (t, J=8.0 Hz, 1H, H-5′); 8.38 (d, J=8.2 Hz, 1H, **H**-6′); 8.60 (d, J=8.0 Hz, 1H, H-4′); 8.87 (s, 1H, **H**-2′); 9.24 (s, 1H, **H**-11). ^{13}C-NMR (62.89 MHz, DMSO-d_6): δ=32.69 (-, **C**-8); 36.74 (-, **C**-9,**C**-10); 89.3 (+, **C**-3a); 123.4 (-, **C**-4′); 125.9 (-, C-2′); 130.2 (-,**C**-5′); 135.0 (-, **C**-6′); 137.1 (+, **C**-1′); 148.2 (+, **C**-3); 148.3 (+, **C**-7a); 157.7 (+, **C**-4); 158.0 (-, **C**-11); 161.8 (+, **C**-6). MS m/z(%): $[M+1]^+$: 341 (17); M^+: 340 (100); 325 (26); 311 (24); 280 (9); 191 (3); 175 (7); 106 (5); 71 (11); 44 (14). HRMS: Calcd for $C_{15}H_{16}N_8O_2$: 340.1395. Found: 340.1394. *Anal.* Calcd for $C_{15}H_{16}N_8O_2$: C, 52.94; H, 4.74; N, 32.92. Found: C, 52.98; H, 5.01; N, 32.10.

4-Amino-6-dimethylamino-1-methyl-3-(*o*-nitrophenyl)azomethinopyrazolo[3,4-*d*]pyrimidine (6e) (85.3%). mp 220-221 °C. IR (KBr): 3450, 3326, 3198 (NH); 1653, 1621, 1577, 1549 (C=N,C=C); 1351 (NO_2); 790 (arom.). ^{1}H-NMR (250.13 MHz, DMSO-d_6): δ=3.14 (s, 6H, N(C**H**$_3$)$_2$); 3.75 (s, 3H, NC**H**$_3$); 7.82 (m, 2H, **H**-4′,5′); 8.06 (d, J=7.8 Hz, 1H, **H**-6′); 8.47 (d, J=7.6 Hz, 1H, **H**-3′); 9.33 (s, 1H, **H**-11). ^{13}C-NMR (62.89 MHz, DMSO-d_6): δ=32.75 (-, **C**-8); 36.77 (-, **C**-9, **C**-10); 89.8 (+, **C**-3a); 124.1 (-, **C**-5′); 128.8 (+, **C**-1′); 130.5 (-, **C**-4′); 131.2 (-, **C**-6′); 133.2 (-, **C**-3′); 147.9 (+, **C**-2′); 149.3 (+, **C**-3); 155.1 (-, **C**-11); 157.0 (+, **C**-7a); 157.6 (+, **C**-4); 161.8 (+, **C**-6). MS m/z(%): $[M+1]^+$: 341 (17); 340 (100); 325 (3); 294 (14); 251 (15); 105 (13); 71 (20); 44 (14). HRMS: Calcd for $C_{15}H_{16}N_8O_2$: 340.1395. Found: 340.1394. *Anal.* Calcd for $C_{15}H_{16}N_8O_2$: C, 52.94; H, 4.74; N, 31.92. Found: C, 52.84; H, 5.07; N, 31.99.

4-Amino-6-dimethylamino-3-(*p*-hydroxyphenyl)azomethino-1-methylpyrazolo-[3,4-*d*]pyrimidine (6f) (74.0). mp 251-254 °C. IR (KBr): 3454, 3332 (NH); 1635, 1612, 1596, 1569, 1545 (C=C,C=N); 1152 (C-O); 974, 870, 795, 745 (arom.). ^{1}H-NMR (300 MHz, DMSO-d_6): δ=3.14 (s, 6H, N(C**H**$_3$)$_2$); 3.71 (s, 3H, NC**H**$_3$); 6.90 (d, J=8.7 Hz, 2H, **H**-3′,5′); 7.94 (d, J=8.7 Hz, 2H, **H**-2′,6′); 8.96 (s, 1H, **H**-11); 10.25 (s, 1H, O**H**). ^{13}C-NMR (75.43 MHz, DMSO-d_6): δ=32.47 (-, **C**-8); 36.69 (-, **C**-9, **C**-10); 89.1 (+, **C**-3a); 115.4 (-, **C**-3′, **C**-5′); 126.7 (+, **C**-1′); 131.1 (-, **C**-2′, **C**-6′); 149.0 (+, **C**-4′); 156.4 (+, **C**-3); 157.6 (+, **C**-7a); 159.1 (-, **C**-11); 160.9 (+, **C**-4); 161.5(+, **C**-6). MS m/z(%): $[M+1]^+$: 312 (17); M^+: 311 (100); 296 (27); 282 (22); 191 (6); 107 (6); 44 (9). HRMS: Calcd for $C_{15}H_{17}N_7O$: 311.1495. Found: 311.1495. *Anal.* Calcd for $C_{15}H_{17}N_7O$: C, 57.87; H, 5.50; N, 31.49. Found: C, 58.19; H, 5.81; N, 31.51.

4-Amino-6-dimethylamino-1-methyl-3-phenylazomethinopyrazolo[3,4-*d*]-pyrimidine (6g) (60.3%). mp 179-181 °C. IR (KBr): 3418, 3320 (NH); 1647, 1610, 1575, 1559, 1540 (C=C,C=N). ^{1}H-NMR (300 MHz, DMSO-d_6): δ=3.14 (s, 6H, N(C**H**$_3$)$_2$); 3.73 (s, 3H,

NCH_3); 7.55 (m, 3H, **H**-3′,4′,5′); 8.10 (d, J=5.4 Hz, 2H, H-2′,6′); 9.10 (s, 1H, **H**-11). ^{13}C-NMR (90.56 MHz, DMSO-d_6): δ=32.62 (-, **C**-8); 36.75 (-, **C**-9, **C**-10); 89.5 (+, **C**-3a); 128.3 (-, **C**-3′, **C**-5′); 128.7 (-, **C**-2′, **C**-6′); 131.8 (-, **C**-4′); 135.5 (+, **C**-1′); 148.7 (+, **C**-3); 156.8 (+, **C**-7a); 157.7 (+, **C**-4); 157.8 (-, **C**-11); 161.7 (+, **C**-6). MS m/z(%): $[M+1]^+$: 296 (24); M^+: 295 (100); 280 (36); 266 (29); 251 (13); 191 (5); 148 (10); 91 (7); 71 (11); 44 (10). *Anal.* Calcd for $C_{15}H_{17}N_7$: C, 61.00; H, 5.80; N, 33.20. Found: C, 61.18; H, 6.10; N, 33.05.

4-Amino-6-dimethylamino-1-methyl-3-(2′-pyridyl)azomethinopyrazolo[3,4-*d*]-pyrimidine (6h) (54.1%). mp 183 °C. IR (KBr): 3416, 3297 (NH); 1653, 1598, 1540 (C=C,C=N). ^{1}H-NMR (300 MHz, DMSO-d_6): δ=3.15 (s, 6H, $N(CH_3)_2$); 3.75 (s, 3H, NCH_3); 7.53 (m, 1H, **H**-4′); 7.96 (m, 1H, **H**-5′); 8.52 (d, J=7.8 Hz, 1H, **H**-3′); 8.72 (m, 1H, **H**-6′); 9.03 (s, 1H, **H**-11). ^{13}C-NMR (90.56 MHz, DMSO-d_6): δ=32.79 (-, **C**-8); 36.79 (-, **C**-9, **C**-10); 89.8 (+, **C**-3a); 122.1 (-, **C**-4′); 125.8 (-, **C**-5′); 136.9 (-, **C**-3′); 148.0 (+, **C**-2′); 149.7 (-, **C**-6′); 153.7 (+, **C**-3); 157.0 (+, **C**-7a); 157.7 (+, **C**-4); 159.8 (-, **C**-11); 161.8 (+, **C**-6). MS m/z(%): $[M+1]^+$: 297 (18); M^+: 297 (100); 281 (19); 191 (10); 148 (9); 127 (10); 105 (6); 71 (7); 44 (8). *HRMS: Calcd for $C_{14}H_{16}N_8$: 296.1497. Found 296.1496.*

4-Amino-6-dimethylamino-3-(2′-furyl)azomethino-1-methylpyrazolo[3,4-*d*]-pyrimidine (6i) (75.8%). mp 183 °C. IR (KBr): 3435, 3318 (NH); 1646, 1616, 1599, 1576 (C=C,C=N). ^{1}H-NMR (250.13 MHz, DMSO-d_6): δ=3.13 (s, 6H, $N(CH_3)_2$); 3.72 (s, 3H, NCH_3); 6.74 (q, J=1.8 Hz, 1H, **H**-4′); 7.38 (d, J=3.5 Hz, 1H, **H**-3′); 8.00 (d, J=1.3 Hz, 1H, **H**-5′); 8.87 (s, 1H, **H**-11). ^{13}C-NMR (62.89 MHz, DMSO-d_6): δ=32.64 (-, **C**-8); 36.80 (-, **C**-9, **C**-10); 89.6 (+, **C**-3a); 112.8 (-, **C**-4′); 118.5 (-, **C**-3′, **C**-5′); 147.1 (-, **C**-11); 148.7 (+, **C**-2′); 151.7 (+, **C**-3); 156.9 (+, **C**-7a); 157.9 (+, **C**-4); 161.9 (+, **C**-6). MS m/z(%): $[M+1]^+$: 286 (17); M^+: 285 (100); 270 (30); 256 (22); 142 (10); 191 (3); 148 (6); 71 (8); 44 (7). HRMS: Calcd for $C_{13}H_{15}N_7O$: 285.1337. Found: 285.1336. *Anal.* Calcd for $C_{13}H_{15}N_7O$: C, 54.73; H, 5.30; N, 34.37. Found: C, 54.97; H, 5.70; N, 33.63.

4-Amino-6-dimethylamino-1-methyl-3-(2′-thienyl)azomethinopyrazolo[3,4-*d*]-pyrimidine (6j) (77.1%). mp 239-241 °C. IR (KBr): 3427, 3320, 3189 (NH); 1467, 1608, 1593, 1575, 1541 (C=C,C=N). ^{1}H-NMR (300 MHz, DMSO-d_6): δ=3.13 (s, 6H, $N(CH_3)_2$); 3.72 (s, 3H, NCH_3); 7.23 (t, J=3.6 Hz, 1H, **H**-4′); 7.85 (d, J=3.6 Hz, 1H, **H**-3′); 7.88 (d, J=4.8 Hz, 1H, **H**-5′); 9.21 (s, 1H, **H**-11). ^{13}C-NMR (62.89 MHz, DMSO-d_6): δ=32.61 (-, **C**-8); 36.74 (-, **C**-9, **C**-10); 89.3 (+, **C**-3a); 128.5 (-, **C**-5′); 132.0 (-, **C**-3′); 134.8 (-, **C**-4′); 141.9 (+, **C**-2′); 148.4 (+, **C**-3); 153.1 (-, **C**-11); 156.7 (+, **C**-7a); 157.8 (+, **C**-4); 161.8 (+, **C**-6). MS m/z(%): $[M+1]^+$: *302 (18), M^+: 301 (100); 286 (27); 272 (23); 191 (5); 173 (12); 97 (10); 71 (9); 44 (8). Anal.* Calcd for $C_{13}H_{15}N_7S$: C, 51.81; H, 5.02; N, 32.53; S, 10.64. Found: C, 51.98; H, 5.10; N, 32.41; S,10.90.

4-Amino-6-dimethylamino-1-methyl-3-(*p*-nitrophenyl)azomethinopyrazolo[3,4-*d*]pyrimidine (6c)

A solution of 207 mg (1 mmol) of **4** and 150 mg (1 mmol) of **5c** in 20 mL of ethanol was refluxed for 8 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica column (70-230 mesh) using ethyl acetate/petroleum ether(1:1) as eluent to give 97 mg of **6c** (28.5%). mp 274-276 °C. IR (KBr): 3429, 3320 (NH); 1653, 1612, 1591, 1539 (C=C,C=N); 1340 (NO_2). ^{1}H-NMR (250.13 MHz, DMSO-d_6): δ=3.14 (s, 6H, N(CH_3)$_2$); 3.75 (s, 3H, NCH_3); 6.8 (2H, NH_2); 8.35 (m, 4H, $H_{arom.}$); 9.23 (s, 1H, **H**-11). ^{13}C-NMR (90.56 MHz, DMSO-d_6): δ=32.73 (-, **C**-8); 36.73 (-, **C**-9, **C**-10); 89.8 (+, **C**-3a); 123.7 (-, **C**-3´, **C**-5´); 130.2 (-, **C**-2´, **C**-6´); 141.1 (+, **C**-1´); 148.0 (+, **C**-4); 148.9 (+, **C**-3); 157.0 (+, **C**-7a); 157.5 (-, **C**-11); 157.6 (+, **C**-4); 161.7 (+, **C**-6). MS m/z(%): $[M+1]^+$: 341 (19); M^+: 340 (100); 325 (28); 311 (25); 250 (12); 191 (4); 148 (8); 106 (6); 71 (13); 44 (18). HRMS: Calcd for $C_{15}H_{16}N_8O_2$: 340.1395. Found: 340.1394. *Anal.* Calcd for $C_{15}H_{16}N_8O_2$: C, 52.94; H, 4.74; N, 32.92. Found: C, 53.25; H, 4.98; N, 32.53.

4-Amino-6-dimethylamino-1-methyl-3-(2´-pyrolyl)azomethinopyrazolo[3,4-*d*]-pyrimidine (6k)

A solution of 207 mg (1 mmol) of **4** and 105 mg (1 mmol) of **5k** in 20 mL of 2-ethoxyethanol was refluxed for 47 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica column (70-230 mesh) using ethyl acetate/petroleum ether(1:1) as eluent to give 100 mg of **6k** (35.2%). mp 120 °C. IR (KBr): 3349, 3337 (NH); 1617, 1594, 1544 (C=C,C=N). ^{1}H-NMR (250.13 MHz, $CDCl_3$): δ=3.12 (s, 6H, N(CH_3)$_2$); 3.88 (s, 3H, NCH_3); 6.23 (q, J=2.5 Hz, 1H, **H**-5´); 6.52 (s, 2H, NH_2); 6.73 (q, J=1.3 Hz, 1H, **H**-4´); 6.84 (d, J=1.1 Hz, 1H, **H**-3´); 8.83 (s, 1H, **H**-11); 10.70 (s, 1H, **H**-1´). ^{13}C-NMR (90.56 MHz, $CDCl_3$): δ=33.01 (-, **C**-8); 37.41 (-, **C**-9,**C**-10); 89.4 (+, **C**-3a); 110.9 (-, **C**-5´); 119.2 (-, **C**-4´); 124.8 (-, **C**-3´); 130.6 (+, **C**-2´); 149.5 (+, **C**-3); 149.9 (-, **C**-11); 157.9 (+, **C**-7a); 158.5 (+, **C**-4); 161.9 (+, **C**-6). MS m/z(%): $[M+1]^+$: 285 (17); M^+: 284 (100); 269 (18); 255 (11); 192 (6); 80 (13); 68 (20); 44 (8). HRMS: Calcd for $C_{13}H_{16}N_8$: 284.1497. Found 284.1496.

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