HETEROCYCLES, Vol. 78, No. 8, 2009, pp. 2003 - 2012. © The Japan Institute of Heterocyclic Chemistry
Received, 21st February, 2009, Accepted, 9th April, 2009, Published online, 9th April, 2009.
DOI: 10.3987/COM-09-11686

SYNTHESIS OF FUSED PYRAZOLO[1,5-*a*]PYRIMIDINE DERIVATIVES UNDER MICROWAVE IRRADIATION AND ULTRASOUND, AS ECOFRIENDLY ENERGY SOURCES

Khadijah M. Al-Zaydi*

Chemistry Department, Girls College of Education, King Abdul-Aziz University
Jeddah, P.O. Box 50918 Jeddah 21533, Kingdom of Saudi Arabia
E-mail: alzaydi_kh@yahoo.com

Abstract – 4-(4-Chlorophenylazo)-1*H*-pyrazole-3,5-diamine reacted with ethyl acetoacetate, benzylidenemalononitrile, ethyl propiolate and malononitrile under microwave irradiation to afford pyrazolo[1,5-*a*]pyrimidine derivatives in high yields. The structures of compounds were confirmed by ^{1}H, ^{13}C NMR, MS, elemental analyses and X-ray crystallography.

INTRODUCTION

Pyrazole compounds can provide privileged scaffolds for the generation of target compounds for drug discovery.[1-6] Hence, the synthesis and study of pyrazolo-fused compounds have been of interest due to their wide variety of biological and pharmacological properties.[1,4-6]

The structural diversity and biological importance of pyrimidines have made them attractive targets for the synthesis over many years.[7,8] Pyrazolopyrimidines and related fused heterocycles are of interest as potential bioactive molecules. They are known to exhibit pharmacological activities such as CNS depressant,[9,10] neuroleptic,[11] and tuberculostatic.[12] Furthermore, pyrazolo[1,5-*a*]pyrimidines have recently been prepared as good inhibitors of KDR kinase.[13]

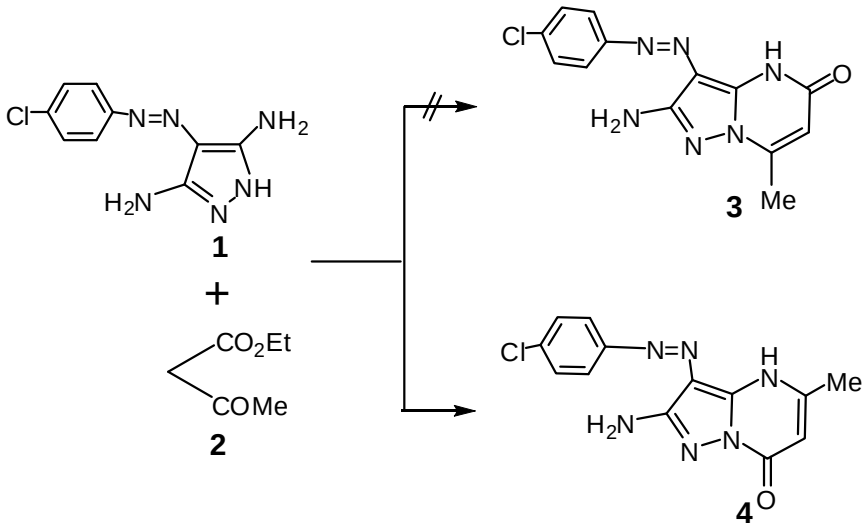
At the dawn of this century, green chemistry has become a major driving force for organic chemists to develop environmentally benign routs to a myriad of materials.[14-16] Generally, application of microwaves and ultrasound in synthesis leads to energy conservation in addition to substantial reductions in reaction times, yield increases, solvent and waste minimization, formation of cleaner products and sometimes, to chemo-, regio- and stereoselectivity changes.[17-19]

It is well known that fused pyrazoles are synthesized, in general, by condensation of aminopyrazoles with

1,3-bifunctional reagents.[20] Although several synthetic approaches for the preparation of fused pyrazoles, especially pyrazolo[1,5-*a*]pyrimidines, in this way have been described in the literature,[21] to our knowledge, their synthesis under microwave and ultrasound irradiation has not been found. Considering the above and continuing our investigations on the application of microwave and ultrasound in organic synthesis,[22-27] We wish to report in this paper an efficient and practical procedure for the synthesis of polyfunctionally substituted pyrazolo[1,5-*a*]pyrimidines *via* reaction of 4-(4-chlorophenylazo)-1*H*-pyrazole-3,5-diamine (**1**) with ethyl acetoacetate, benzylidenemalononitrile, ethyl propiolate and malononitrile under microwave and ultrasound irradiation. The regioorientation of reagents was determined by X-ray crystallography of the products.

RESULTS AND DISCUSSION

In this study, We first investigated the condensation of 4-(4-chlorophenylazo)-1*H*-pyrazole-3,5-diamine (**1**) with ethyl acetoacetate, as active methylene bifunctional reagent. Thus, compound **1** was prepared as described in literature.[28] In fact, we found that the reaction of amino-pyrazoles **1** with ethyl acetoacetate (**2**) under 440 W microwave radiation smoothly produced a solid product of molecular formula $C_{13}H_{11}ClN_6O$. Thus, this product could be formulated as pyrazolo[1,5-*a*]pyrimidin-5(4*H*)-one **3** or isomeric pyrazolo[1,5-*a*]-pyrimidin-7(4*H*)-one **4** (Scheme 1). The difficulties encountered to differentiate between the two isomeric structures **3** and **4** were unambiguously solved by X-ray crystallography[29] which established the structure as 4,7-dihydro-pyrazolo[1,5-*a*]pyrimidin-7-one **4** (Figure 1). In order to verify the effect of microwave irradiation, in the absence of microwave, we have performed the reaction of aminopyrazoles **1** with **2** by refluxing in acetic acid for 4h till no starting material (aminopyrazoles **1**) present as examined by TLC.



Scheme 1

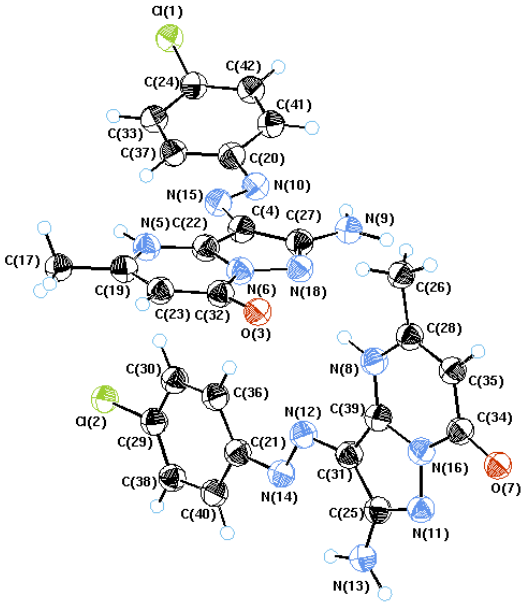
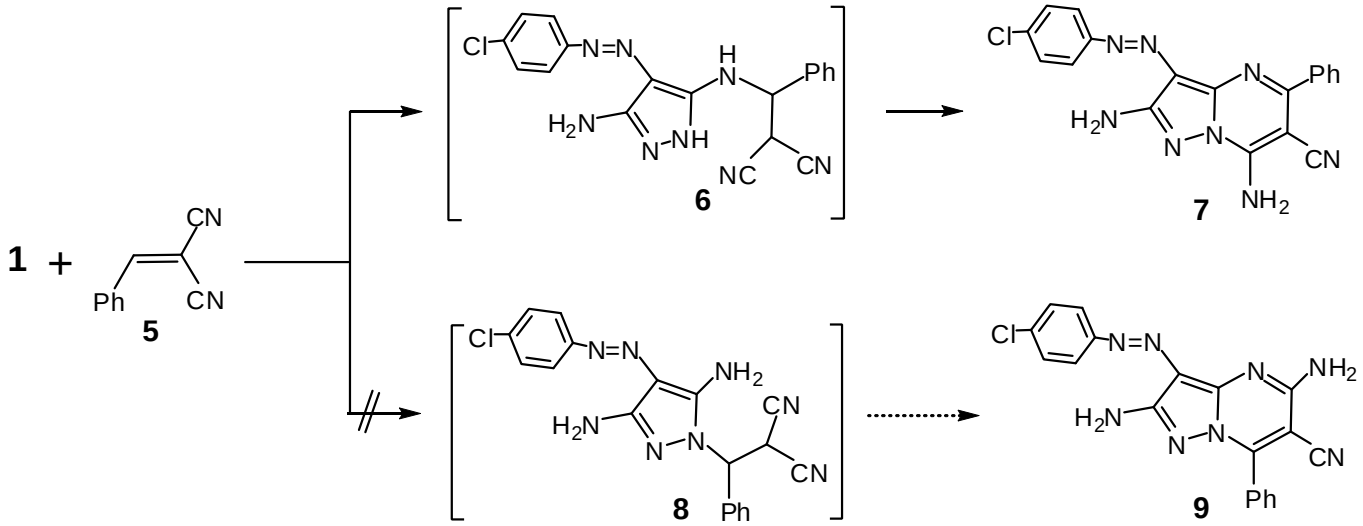


Figure 1. X-Ray crystal structure of **4**

In order to construct new derivatives of the interesting heterocyclic systems of type **4**, we next have examined the reaction of **1** with benzylidenemalononitrile (**5**) under microwave irradiation. Thus, reacting 1 with 5 under microwave irradiation (440 W, 5 min), gave 1:1 adduct whose structure was assumed to be **7** or **9** (Scheme 2). The structure of pyrazolo[1,5-*a*]pyrimidine derivative **7** was preferred over the possible isomer 9 based on its elemental analysis, spectral data and X-ray crystal structure[29] (Figure 2). Formation of **7** is assumed to proceed *via* the addition of the *exo*-amino group to the *α,β*-unsaturated carbon in **5**. The Michael adduct **6** cyclized spontaneously to yield the dihydropyrazolopyrimidine which aromatized, under these reaction conditions, to give final product **7** (Scheme 2).



Scheme 2

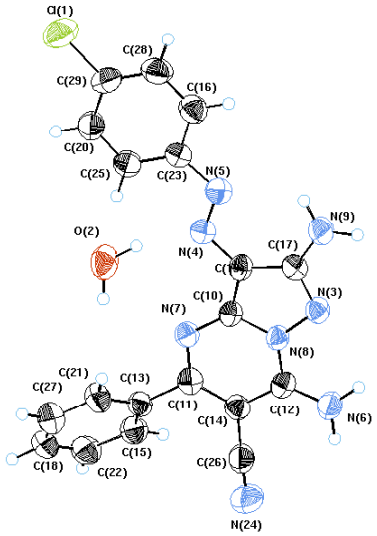
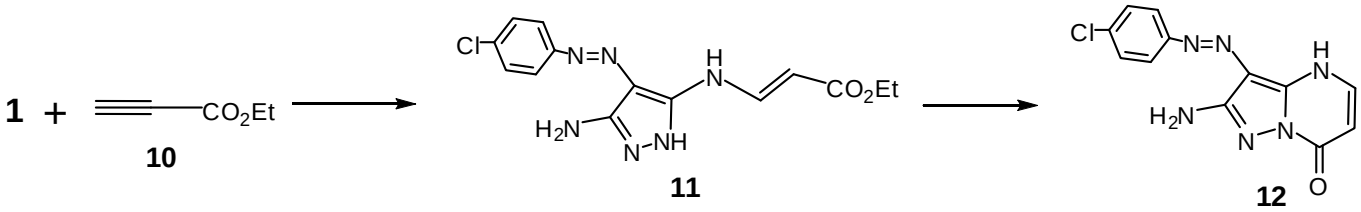


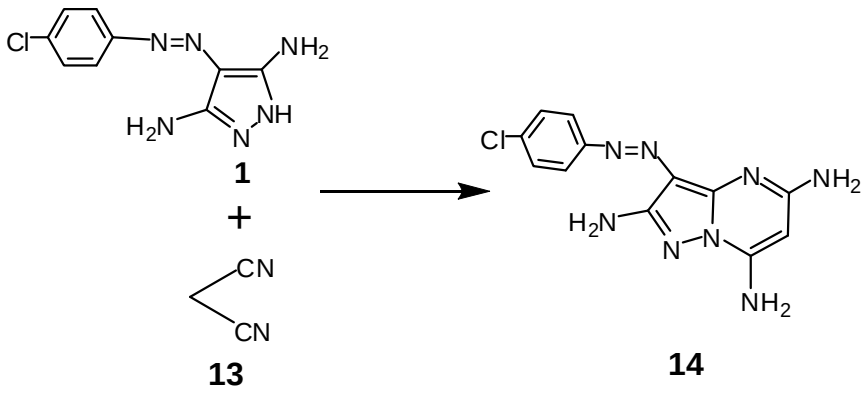
Figure 2. X-Ray crystal structure of **7**

More recently, it has been reported that the pyrazolo[1,5-*a*]pyrimidine derivative of type **12** was obtained upon long reflux of 4-phenylazo-1*H*-pyrazole-3,5-diamine with ethyl propiolate in pyridine.[20] Encouraged by this and due to our interest to synthesize new derivatives of pyrazolo[1,5-*a*]pyrimidines, We next investigated the reaction of **1** with ethyl propiolate (**10**) under microwave irradiation. Similary, when a mixture of **1** and **10** was irradiated in a microwave oven in open vessel with a power of 440 W for 6 min, did not afford the required pyrazolopyrimidines **12** directly, but rather the aminopyrazoles **11** is obtained. The later compound **11** underwent intramolecular condensation, under the same reaction conditions as used for the synthesis of **11**, *via* elimination of one molecule of ethanol, to afford the desired pyrazolo[1,5-*a*]pyrimidines **12** (Scheme 3).



Scheme 3

Also, the reaction of 4-(4-chlorophenylazo)-1*H*-pyrazole-3,5-diamine (**1**) with malononitrile (**13**) was investigated under microwave irradiation it afforded products that were formulated as the pyrazolo[1,5-*a*]pyrimidine derivatives **14** (Scheme 4). The structure of compound **14** was established on the basis of their elemental analysis and spectral data. Thus, the structure **14** is supported by its mass spectrum which shows a molecular ion peak at *m/z* 302. The ^{1}H NMR spectrum of the same compound exhibits two doublet signals at δ 7.22, 7.37 (J = 7 Hz) due to aromatic protons, a three D_2O-exchangeable signals at δ 5.51, 12.10, 13.59 respectively due to NH_2 protons, in addition to singlet signals at δ 6.15 due to pyrimidine proton at C-6 (*Cf. experimental part*).



Scheme 4

The investigated reactions for the preparation of compounds **4**, **7**, **11**, **12** and **14** were compared with the same reactions carried out under the classical conditions of thermal heating (heating the reagents in a solvent). The results are presented in Table 1. The reaction under microwaves or ultrasonic is substantially faster and gives higher yields. The method used can be considered as a "green chemistry" method.

Table 1. Synthesis of pyrazolo[1,5-*a*]pyrimidine derivatives under microwave irradiation (μw), or by conventional heating (Δ)

	Yield (%)			Reaction Time (min.)		
Compound	**Δ**	**μw**	**US**	**Δ**	**μw**	**US**
4	**68**	**89**	**74**	**240**	**5**	**40**
7	**72**	**92**	**88**	**240**	**5**	**40**
11	**60**	**96**	**85**	**120**	**6**	**30**
12	**58**	**95**	**80**	**120**	**2**	**30**
14	**64**	**90**	**86**	**240**	**6**	**30**

CONCLUSION

We have synthesized a class of pyrazolo[1,5-*a*]pyrimidine derivatives under microwave, sonication and classical conditions(heating). In general, improvements in rates and yield of reactions are observed when reactions were carried out under microwave and sonication compared with classical condition. It should be noted, however, that activation occurs at different temperatures with these techniques and, therefore strict comparisons will require a balance between effectiveness and energy costs.

EXPERIMENTAL

All melting points were measured on a Gallenkamp electrothermal melting point apparatus and are uncorrected. The IR spectra were recorded on a Nicolet Magna 520FT IR spectrophotometer (KBr pellets). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-400 and Bruker-DPX-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometers with DMSO as solvent and TMS as an internal standard. Chemical shifts are expressed in δ values (ppm). MS were measured on a Shimadzu GCMS-QP 1000 EX mass spectrometer at 70 eV. X-Ray crystallography was carried out on a Kappa CCD Enraf Nonius FR 590 diffractometer at National Research Center, Dokki, Cairo, Egypt. Microwave irradiation was carried out using the commercial microwave oven (SGO 1000 w) with a thermocouple to monitor the temperature inside the vessel. It was found that ≈ 105-110 °C. Ultrasound, microprcess controlled-2004, high intensity ultrasonic processor with temperature controller (750 W). The ultrasonic frequency of the cleaning bath used equal 25 KHz. The reaction temperature stabilized at 35-40 °C by addition or removal of water in ultrasonic bath to keep the required temperature. Elemental analyses were recorded on Perkin Elmer 2400 CHN Elemental analyzer flowchart. All reagents were of commercial quality or were purified before use and the organic solvents were of analytical grade or purified by standard procedures.

General procedure for the synthesis of pyrazolo[1,5-*a*]pyrimidines 4, 7 , 12 and 14.

Method (A): To a suspension of compound **1** (0.01 mol) in AcOH (30 mL), ethyl acetoacetate (**2**), benzylidenemalononitrile **(5)** or malononitrile **(13)** (0.01 mol) was added. The reaction mixture was heated under reflux for 4 h. After concentration and cooling to rt, a small amount of EtOH (2 mL) was added. Then, the resulting solid product was collected by filtration, dried and recrystallized from DMF to give compounds **4**, **7** or **14**, respectively. In the case of compound **12**, a solution of compound **11** (0.01 mol) in AcOH was refluxed for 2 h and then worked up as described above to give **12**.

Method (B): To a mixture of compound **1** (0.01 mol), ethyl acetoacetate **(2)**, benzylidenemalononitrile **(5)** or malononitrile **(13)** (0.01 mol) in a pyrex conical flask, a few drops of AcOH was added. Then, it was irradiated at 440 W in the microwave oven for the appropriate time in 1 min intervals (Table 1) until completion of the reaction (monitored by TLC). The reaction mixture left to cool to rt. After addition of EtOH (10 mL), the resulting solid product so formed was collected by filtration and recrystallized from EtOH to give compounds **4**, **7** or **14,** respectively. In the case of compound **12**, compound **11** (0.01 mol) was irradiated for 2 min, under the same reaction conditions, and then worked up as described above to give **12**.

Method (C): To a mixture of compound **1** (0.01 mol), ethyl acetoacetate (**2**), benzylidenemalononitrile (**5**) or malononitrile **(13)** (0.01 mol) in a pyrex conical flask, 30 mL of AcOH was added. Then, it was heated under ultrasound irradiation at 40 ºC for the appropriate time (Table 1) until completion of the reaction (monitored by TLC). The reaction mixture left to cool to rt. The resulting solid product so formed was collected by filtration and recrystallized from EtOH to give compounds **4, 7 or 14**,

respectively. In the case of compound **12**, compound **11** (0.01 mol) was irradiated with ultrasonic for 30 min, under the same reaction conditions, and then worked up as described above to give **12**.

Synthesis of ethyl 3-(3-amino-4-((4-chlorophenyl)diazenyl)-1*H*-pyrazol-5-ylamino) acrylate (11):

Method (A): To a suspension of compound **1** (0.01 mol) in dioxane (30 mL), ethyl propiolate **(10)** (0.01 mol) was added. The reaction mixture was refluxed for 2 h and then left to cool to rt. The solid product so formed was filtered off and recrystallized from EtOH.

Method (B): To a mixture of compound **1** (0.01 mol) and ethyl propiolate **(10)** (0.01 mol) in a pyrex conical flask, a few drops of dioxane was added. The reaction mixture was placed in the microwave oven and irradiated at 440 W for 6 min. Then, it was left to cool to rt The solid product so formed was filtered off and recrystallized from EtOH.

Method (C): To a mixture of compound **1** (0.01 mol), and ethyl propiolate **(10)** (0.01 mol) in a pyrex conical flask, 20 mL of dioxane was added. Then, it was heated under ultrasound irradiation at 35-40 ºC for the 30 min (Table 1) until completion of the reaction (monitored by TLC). The reaction mixture left to cool to rt. The resulting solid product so formed was collected by filtration and recrystallized from EtOH.

2-Amino-3-(4-chlorophenylazo)-5-methyl-pyrazolo[1,5-*a*]pyrimidin-7(4*H*)-one (4). Yellow crystals; mp 284-286 °C (lit.,[30] 285-287 °C); IR (KBr) υ 3445, 3350, 3230 (NH, NH_2), and 1640 (CO), 1605 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.23 (s, 3H, CH_3), 5.57 (br, 2H, NH_2, D_2O exchangeable), 7.18 (d, *J*= 7 Hz, 2H, Ar-H), 7.27 (d, *J*= 7 Hz, 2H, Ar-H), 7.67 (s, 1H, CH at C_6), 12.10 (s, 1H, NH, D_2O exchangeable); ^{13}C NMR (DMSO-d_6) δ 162.80, 156.77, 150.89, 143.55, 133.11, 130.19, 126.23, 123.32, 105.7, 95.44, 24.11 ppm; MS *m/z* (%) 302 (M^+); Anal. Calcd for $C_{13}H_{11}Cl\,N_6O$ (302.72): C, 51.58; H, 3.66; N, 27.76. Found: C, 51.45; H, 3.86; N, 27.57.

2,7-Diamino-3-(4-chlorophenylazo)-5-phenylpyrazolo[1,5-*a*]pyrimidin-6-carbonitrile (7).

Orange crystals from dioxane; mp 200 ºC; IR (KBr) υ 3440, 3332 (NH_2), 3417,3300 (NH_2) and 2220 (CN), 1612 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.47 (br, 2H, NH_2, D_2O exchangeable), 7.11-7.36 (m, 9H, Ar-H), 8.14 (br, 1H, NH_2 D_2O exchangeable) ppm; ^{13}C NMR (DMSO-d_6) δ 169.88, 161.08, 158.78, 150.71, 146.50, 142.11, 138.19, 129.46, 129.23, 126.23, 123.32, 112.61,118.34, 96.55, 70.93 ppm; MS *m/z* (%) 388 (M^+); Anal. Calcd for $C_{19}H_{13}ClN_8$ (388.10); C 58.69, H 3.37, N 28.82; Found C 58.55, H 3.35, N 28.92.

(2*E*)-Ethyl 3-(3-amino-4-((4-chlorophenyl)diazenyl)-1*H*-pyrazol-5-ylamino)acrylate (11).

Orange crystals; mp 279-281 °C (lit.,[30] 280-282 °C); IR (KBr) υ 3430, 3329, 3315, 3200 (NH, NH_2) and 1742 (CO ester) cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.41 (t, 3H, *J* = 7 Hz, CH_3), 3.78 (q, 2H, *J* = 7 Hz, CH_2), 5.52 (br s, 2H, NH_2), 7.17 (d, *J*= 8 Hz, 2H, Ar-H), 7.33 (d, *J*= 8 Hz, 2H, Ar-H), 7.56 (d, *J*= 16 Hz, 1H,

=CHNH), 7.76 (d, *J*= 16 Hz, 1H, CH), 9.84 (s, H, NH), 11.10 (s, 1H, pyrazole NH). ^{13}C NMR (DMSO-d_6) δ 167.05, 153.20, 150.87, 149.81, 133.11, 130.19, 126.23, 123.32, 102.40, 79.87, 53.11, 17.25; MS *m/z* (%) 334 (M^+); Anal. Calcd for $C_{14}H_{15}ClN_6O_2$ (334.09): C, 50.23; H, 4.52; N, 25.10; Found: C, 50.56; H, 4.39; N, 24.90.

2-Amino-3-(4-chlorophenylazo)pyrazolo[1,5-*a*]pyrimidin-7(4*H*)-one (12).

Yellow crystals; mp 240-241 ºC; IR (KBr) *υ* 3430, 3332, 3170 (NH, NH_2) and 1640 (CO) cm^{-1}, ^{1}H NMR (DMSO-d_6) δ 5.59 (br s, 2H, NH_2, D_2O exchangeable), 6.56 (d, *J*= 7 Hz, 1H, H-6), 7.16 (d, *J*= 7 Hz, 2H, Ar-H), 7.23 (d, *J*= 7 Hz, 2H, Ar-H), 7.98 (d, *J*= 7 Hz, 1H, H-5), 9.10 (s, 1H, NH, D_2O exchangeable). ^{13}C NMR (DMSO-d_6) δ 160.2, 156.8, 150.9, 143.6, 133.1, 130.2, 126.2, 123.3, 112.6, 81.7; MS *m/z* (%) 288 (M^+); Anal. Calcd for $C_{12}H_9ClN_6O$ (288.69): C, 49.92; H, 3.14; N, 29.11. Found: C, 49.85; H, 3.21; N, 29.37.

2,5,7-Triamino-3-(4-chlorophenylazo)pyrazolo[1,5-*a*]pyrimidine (14).

Yellow crystals; mp 284-286 °C; IR (KBr) *υ* 3410, 3350, 3320 3220, 3159, 3110 ($3NH_2$), and 1607 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 5.51 (br, 2H, NH_2, D_2O exchangeable), 6.15 (s, 1H, CH at C_6), 7.22 (d, *J*= 7 Hz, 2H, Ar-H), 7.37 (d, *J*= 7 Hz, 2H, Ar-H), 12.10, 13.59 (2s, 2H, $2NH_2$, D_2O exchangeable); ^{13}C NMR (DMSO-d_6) δ 167.54, 155.12, 150.98, 136.11, 134.23, 130.22, 126.77, 123.32, 97.52, 90.12 ppm; MS *m/z* (%) 302 (M^+); Anal. Calcd for $C_{12}H_{11}ClN_8$ (302.08): C, 47.61; H, 3.66; N, 37.02. Found: C, 47.80; H, 3.57; N, 36.92.

X-RAY CRYSTALLOGRAPHY:

The crystal structure were solved and refind using maxus (nonius,Deflt and MacScience, Japan). Mo-Kα radiation (λ = 0.71073 Å) and a graphit monochromator were used for data collection.

Compound **4** was recrystalized as yellow crystal from dry EtOH. Chemical formula $C_{13}H_{11}ClN_6O$, Mr=302.725, monoclinic, crystallize in space group C2/c, a = 22.1453(8), b = 21.7359(11), c = 15.5716(8) Å, T= 298 ^{0}K, V= 5694.9 (5) Å^3, Z= 8, D_x = 0.706Mg m^{-3}, θ range 1.018-18.00^o, absorption coefficient μ = 0.14 mm^{-1}.The unique reflections measured 7605, of which 2134 independent reflections and 1367 observed reflections with threshold expression I>3σ(I), Refinement parameters are R_{int}=0.061, R(all)= 0.093, wR(ref)= 0.139, wR(all)=0.143, S(ref) = 4.850, S(all)= 4.470, D/s_{max}= 0.008, Dr_{max}= 0.38 eÅ^3, Dr_{min} = -0.33 eÅ^3. The chemical formula and ring labeling system is shown in Figure 1.

Compound **7** was recrystalized as orange crystal from dry EtOH. Chemical formula $C_{19}H_{13}ClN_8$, Mr=388.10, monoclinic, crystallize in space group C2/c, a = 28.7991(9), b = 8.4375(3), c = 16.0136(7) Å, T= 298 ^{0}K, V= 3868.2 (2) Å^3, Z= 8, D_x = 1.401Mg m^{-3}, θ range 2.910-21.036^o, absorption coefficient μ =

0.23 mm^{-1}.The unique reflections measured 3988, of which 2205 independent reflections and 1631 observed reflections with threshold expression I>3σ(I), Refinement parameters are R_{int}=0.042, R(all)= 0.059, wR(ref)= 0.080, wR(all)=0.083, S(ref) = 2.436, S(all)= 2.341, D/s_{max}= 0.014, Dr_{max}= 0.30 $eÅ^3$, Dr_{min} = -0.45 $eÅ^3$. The chemical formula and ring labeling system is shown in Figure 2.

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