

Sanaa O. Abdallah, Nadia H. Metwally, Hany F. Anwar and Mohamed H. Elnagdi\*

Department of chemistry, Faculty of Science, Cairo University, Giza-Egypt  
 e-mail: [shelmy@access.com.eg](mailto:shelmy@access.com.eg); Tel.: +202-3448298; fax: +202-3027401  
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2-Formyl-2-arylhydrazoneoethanenitriles **6b-d** were prepared *via* reacting enamionitrile **2b,c** with aromatic diazonium salts. These reacted with phenylhydrazine to yield bis hydrazones that were converted to arylazopyrazoles *via* a novel Vilsmeier-Haack reaction type. Reaction of **6c** with hydroxylamine afforded oxime that could be successfully cyclised into arylazoisoxazole. Reaction of **6c** with hydrazine hydrate to yield arylazoaminopyrazole that proved to be excellent precursors for synthesis functional substituted pyrazolopyrimidines.

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2-Arylhydrazoneketones are readily obtained *via* condensation of arylhydrazines with 1,2-diketone [1,2] or *via* the coupling reaction of active methylene ketones with aromatic diazonium salts [3-5]. 2-Arylhydrazones (**1a**) are prepared *via* coupling enamionones with aromatic diazonium salts, were shown to be excellent precursors to functionally substituted pyridazines [6-8], pyrazoles [9-11], and condensed azoles [12-14].

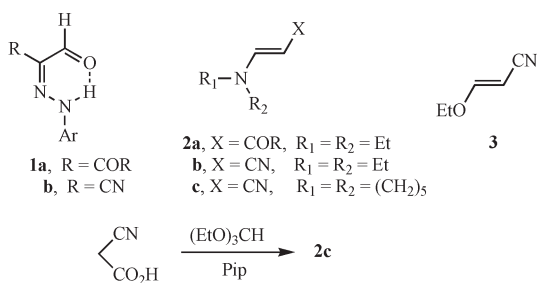


Figure 1

In conjunction to our interest in chemistry of 2-arylhydrazones **2b** [8-14] as precursors to arylazoaminopyrazoles for potential utility in dye industry, we report here on the coupling reaction of the enamionitriles **2b,c** with aromatic diazonium salts and results of our investigation aimed at exploring synthetic potentials of these coupling products. The enamionitrile derivative **2b** needed in this investigation was prepared following literature procedure [15] (Figure 1).

The newly required enamionitrile **2c** was prepared in 73 % *via* reacting cyanoacetic acid with triethylorthoformate and piperidine or in better yield (80 %) *via* reacting 3-ethoxyacrylonitrile (**3**) with piperidine. <sup>1</sup>H-NMR indicate that the reaction product exists solely in the *trans* form as it indicated two olefinic protons at δ 4.0 and 7.1 with *J* = 13.5 Hz typical for *trans* olefinic protons. Appearance the olefinic proton of H-2 at δ 4.0 ppm is a result of shielding by electron donation from lone pair and cyano group anisotropy.

We have found that coupling of **2b** with aromatic diazonium salts affords either only formazanes **7** or mixtures of

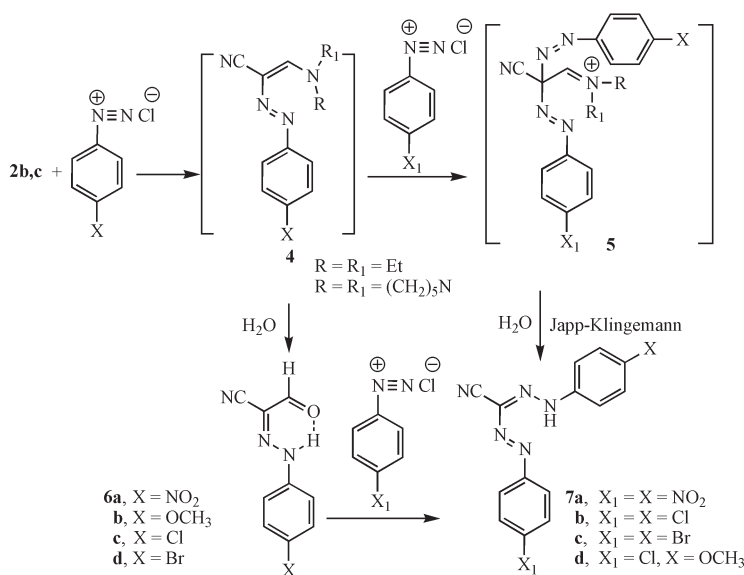


Figure 2

**7** and arylhydrazonals **6**. In all cases yields were poor and products of coupling of aromatic diazonium salts at the enamine nitrogen were traces in every case. Thus coupling of **2b** with *p*-nitrobenzene-diazonium chloride afforded **7a** as the sole isolable product. It is believed that the formed enazo derivative **4** is attacked by a second molecule of diazonium derivative to yield **5** which is hydrolysed into **7** faster than it is hydrolysed to **6**. However, possible initial conversion of **4** into **6a**, which react further to yield **7a**, cannot be ruled out. In order to increase nucleophilicity of C-2 in enamionitrile we prepared the piperidino derivative **2c**. Similar approach has been used to increase the nucleophilicity of the carbon atom in enamionones [16-18].

As anticipated compounds **2c** coupled smoothly with *p*-methoxy, *p*-chloro, and *p*-bromobenzene diazonium chloride to yield arylhydrazonals **6b-d** in 60-73% yields. These further coupled with aromatic diazonium salts yielding **7b-d** (Figure 2).

Although **6** can adopt several tautomeric structures spectral data indicated that these products exist solely in the hydrazone form. Thus <sup>1</sup>H NMR revealed formyl signal at δ 9.47 ppm. The appearance of NH signal at δ 12.6 ppm indicates its involvement in hydrogen bonding with formyl function.

Compounds **6c,d** further coupled with aromatic diazonium salts yielding **7b,c** (Figure 2). These products were found identical with those obtained earlier *via* coupling cyanoacetic acid with excess of aromatic diazonium salts. The mixed formazane **7d** was obtained on coupling **6b** with *p*-chloro benzene diazonium chloride or by coupling **6c** with *p*-anizidine diazonium chloride.

Compound **6c** reacted with phenylhydrazine to yield the phenylhydrazone **8** in excellent yield (Figure 3). The <sup>1</sup>H

NMR of reaction product **8** revealed that it exists as a mixture of two or more tautomeric structure. Thus **8** is believed to exist as an equilibrium mixture of **8** and **8A**.

Under a variety of conditions this phenylhydrazone **8** failed to cyclise into aminopyrazole derivative. Recently Brehme *et al* [16-19] has reported that aldehyde hydrazones are readily formylated on heating with phosphorus trichloride POCl<sub>3</sub> and dimethylformamide (DMF) (Vilsmeier-Haack reagent). However they noted that in their hands hydrazine with an electron donating substitute should be used. In contrast to this compound **8** was readily formylated yielding a product that may be formulated as **9** or isomeric **10**. Structure **9** was readily ruled out based on IR spectrum that revealed absence of signal for cyano function. Structure **10** was established based on spectral data which revealed presence of amide carbonyl at δ 151.12 ppm. (<sup>13</sup>C NMR) and 1692.4 cm<sup>-1</sup> (IR). Also <sup>1</sup>H NMR further support proposed structure as it showed a broad signal at δ 10.7 ppm for NH<sub>2</sub>, singlet at δ 8.15 ppm for pyrazole-H, two doublets at δ 7.47 and 7.76 ppm for aryl four protons and multiplet at δ 7.58 for five protons of phenyl moiety (Figure 3).

Compound **6c** also reacted with hydroxylamine hydrochloride to yield the oxime **11** in good yield. This cyclises readily into acetylaminoisoxazole **12** on reflux in acetic anhydride (Figure 4). These structures were established based on elemental analysis and spectral data. Thus IR spectrum of compound **11** showed two absorption band for NH and OH at 3348, 3498 cm<sup>-1</sup> and 2217 cm<sup>-1</sup> for CN group. The <sup>1</sup>H NMR showed broad band at δ 11.7 ppm for OH and other broad band at δ 7.8 ppm for NH and one proton signal for oxime CH carbon at δ 7.44 ppm. In addition, aryl protons appeared as two multiplets at δ 7.3 and 7.8 ppm. <sup>1</sup>H NMR of **12** was also concordant with proposed structure.

Compound **6c** reacted with chloroacetone to yield the pyrazolecarbonitrile **13**, formed most likely *via* alkylation of **6c** and subsequent cyclization (Figure 4). This is an extension of recently reported synthesis of arylpyrazoles from arylhydrazonals and haloketones [10].

Compound **6c** reacted with hippuric acid in refluxing Ac<sub>2</sub>O to yield **16**, formed most likely *via* condensation with oxazolone **14**, which is produced from hippuric acid under reaction condition, to yield **15**. The latter rearranges into **16** under these reaction conditions. This is an extension of Elnagdi's reported pyridazine synthesis [7] (Figure 5).

It has been reported earlier that 2-arylhyaazonopropanals cyclise into cinnolines on treatment with concentrated sulphuric acid *via* initial enolization followed by 6π electrocyclicization [9]. Treatment of **6c** with concentrated sulphuric acid has afforded the cinnolines **17** formed *via* initial similar cyclization and hydrolysis of the cyano function into amide by water eliminated in the cyclization step (Figure 5).

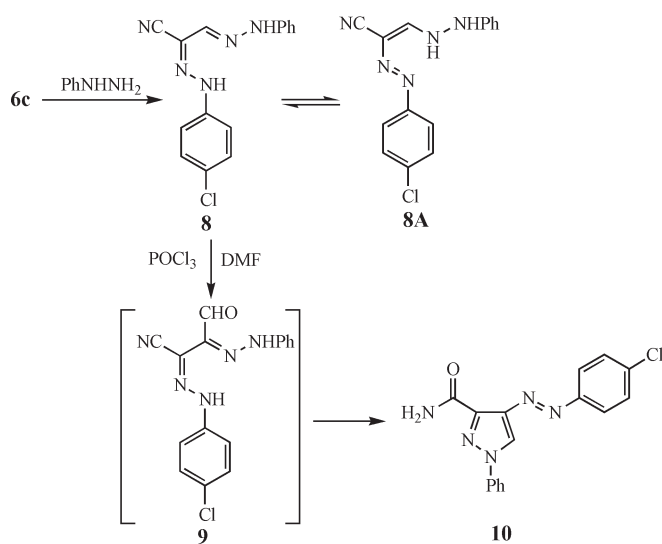


Figure 3

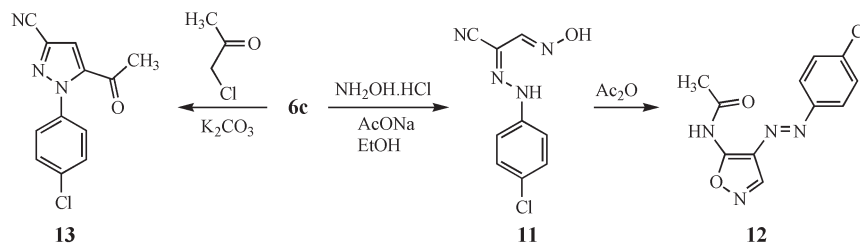


Figure 4

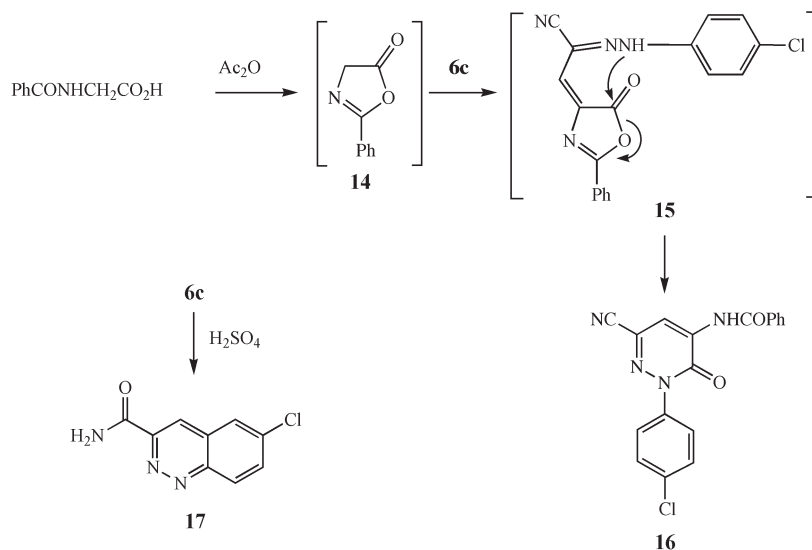


Figure 5

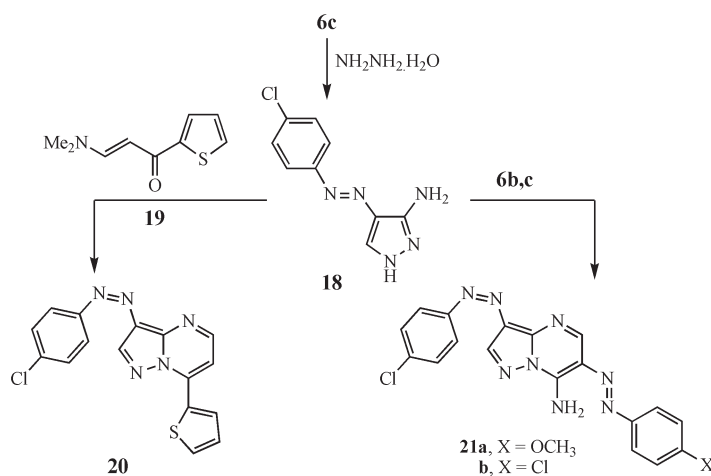


Figure 6

Similar to the behavior of 2-arylhydrazonepropanals toward hydrazines, compound **6c** reacted with hydrazine hydrate to yield 4-arylazo-5-amino-pyrazole **18**. The pyrazole **18** proved to be an excellent precursor to aryla-

zopyrazolo[1,5-*a*]pyrimidines and arylazopyrazolo[5,1-*c*]-1,2,4-triazines. Thus reacting **18** with the enaminone **19**, has afforded **20**. On the other hand, reacting **18** with **6b,c** has afforded **21a,b**. This is similar to the reported

reactivity of enamines toward aminopyrazoles [20,21] (Figure 6).

## EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded as KBr disks using a FTIR unit Bruker-vector 22 spectrophotometer. The  $^1\text{H-NMR}$  and  $^{13}\text{C}$  NMR spectra with  $d_6\text{-DMSO}$  and  $\text{CDCl}_3$  as solvent and TMS as internal standard chemical shifts are reported in  $\delta$  units (ppm). Mass spectra were measured on a Shimadzu GMMS-QP-1000 EX mass spectrometer at 70 eV. Microanalyses were performed at the microanalytical Center, Cairo University.

### Preparation of $\beta$ -Cyanoenamine (**2b**).

A mixture of cyanoacetic acid (42.5 g, 0.5 mol), triethylorthoformat (0.5 mol) and diethylamine (0.5 mol) is heated under reflux during 2 h. The mixture is evaporated and the crude residue is diluted with dichloromethane (300 mL), washed with 1 molar sodium carbonate solution (100 mL) and water (100 mL). After drying with anhydrous sodium sulphate, the solution is evaporated [15] to give **2b**, sufficiently pure for further reactions.

### 3-Piperidin-1-yl-acrylonitrile (**2c**).

#### Method A.

A mixture of cyanoacetic acid (42.5 g, 0.5 mol), triethylorthoformat (0.5 mol) and piperidine (0.5 mol) is heated under reflux during 2 h. The mixture is evaporated and the crude residue is diluted with dichloromethane (300 mL), washed with 1 molar sodium carbonate solution (100 mL) and water (100 mL). After drying with anhydrous sodium sulphate, the solution is evaporated. This compound was obtained as yellow crystals in yield 73%; mp. 43-45 °C; IR (KBr):  $\nu = 2214\text{ cm}^{-1}$  (CN);  $^1\text{H NMR}$  ( $d_6\text{-DMSO}$ ):  $\delta = 1.4\text{-}1.5$  (m, 6H), 3.1 (t,  $J = 4.2$  Hz, 4H), 4.0 (d, 1H,  $J = 13.5$  Hz, olefinic H), 7.1 (d, 1H,  $J = 13.5$  Hz, olefinic H); MS (70 eV):  $m/z = 136$  ( $\text{M}^+$ , 100%), (137, 100%).

*Anal.* Calcd. for  $\text{C}_8\text{H}_{12}\text{N}_2$ : C, 70.55; H, 8.88; N, 20.57. Found C, 70.26; H, 8.91; N, 20.12.

#### Method B.

A mixture of 3-ethoxyacrylonitrile (10 mmol) and piperidine (15 ml) was refluxed 24 hours then left to cool. The resulting product was washed with petroleum ether (40-60) and 80 % solid product so formed was collected by filtration and recrystallized from petroleum ether.

### Preparation of 2-(4-Substituted-phenylhydrazono)-3-oxo-propionitrile **6b-d**.

#### General Procedure.

A cold solution of aryldiazonium salts (10 mmol) was prepared by adding a solution of sodium nitrite (1.5 g into 10 mL  $\text{H}_2\text{O}$ ) to cold solution of arylamine hydrochloride (10 mmol of arylamine in 5 mL concentrated HCl) with stirring. The resulting solution of the aryldiazonium salts were then added to a cold solution of enamionitrile either **2b** or preferably **2c** (10 mmol), in ethanol (50 mL) containing sodium acetate (3 g). The mixture was stirred at r.t. for 1 h and the solid product, so formed, was collected by filtration and crystallized from ethanol.

### 2-(4-Methoxyphenylhydrazono)-3-oxo-propionitrile (**6b**).

Compound **6b** was obtained as orange crystals, mp. 157-159 °C; yield 73%; IR (KBr):  $\nu_{\text{max}} = 3447$  (NH), 2836 (CH aliphatic), 2207 (CN), 1662  $\text{cm}^{-1}$  (CO);  $^1\text{H NMR}$  ( $d_6\text{-DMSO}$ ):  $\delta = 3.77$  (s, 3H,  $\text{OCH}_3$ ), 6.99 (d,  $J = 9$  Hz, 2H, Ar-H), 7.49 (d,  $J = 9$  Hz, 2H, Ar-H), 9.49 (s, 1H, CHO), 12.60 (s, 1H, NH); MS (70 eV):  $m/z = 203$  ( $\text{M}^+$ , 80%), (122, 100%).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_2$ : C, 59.11; H, 4.46; N, 20.68. Found C, 59.20; H, 4.51; N, 20.73.

### 2-(4-Chlorophenylhydrazono)-3-oxo-propionitrile (**6c**).

Compound **6c** was obtained as orange red crystals. mp. 164-166 °C; yield 64%; IR (KBr):  $\nu_{\text{max}} = 3560\text{-}3447$  (NH), 3867 (CH aldehyde), 2214 (CN), 1660  $\text{cm}^{-1}$  (CO);  $^1\text{H NMR}$  ( $d_6\text{-DMSO}$ ):  $\delta = 7.64\text{-}7.57$  (m, 4H, Ar-H), 9.20 (s, 1H, CHO), 11.61 (s, 1H, NH); MS (70 eV):  $m/z = 207$  ( $\text{M}^+$ , 62%), (107, 100%).

*Anal.* Calcd. for  $\text{C}_9\text{H}_6\text{ClN}_3\text{O}$ : C, 52.17; H, 2.91; N, 20.24. Found C, 52.09; H, 2.64; N, 20.16.

### 2-(4-Bromophenylhydrazono)-3-oxo-propionitrile (**6d**).

Compound **6d** was obtained as red crystals, mp. 190-191 °C; yield 60%; IR (KBr):  $\nu_{\text{max}} = 3552\text{-}3452$  (NH), 2214 (CN), 1672  $\text{cm}^{-1}$  (CO);  $^1\text{H NMR}$  ( $d_6\text{-DMSO}$ ):  $\delta = 7.52\text{-}7.64$  (m, 4H, Ar-H), 9.49 (s, 1H, CHO), 12.4 (s, 1H, NH)- MS (70 eV):  $m/z = 251$  ( $\text{M}^+$ , 45%), ( $\text{M}^++2$ , 47%), (157, 100%).

*Anal.* Calcd. for  $\text{C}_9\text{H}_6\text{BrN}_3\text{O}$ : C, 43.88; H, 2.40; N, 16.67. Found C, 43.21; H, 2.21; N, 16.62.

### (4-Substituted phenylhydrazono)-(4'-substitutedphenylazo)acetonitrile **7a-c**.

#### General Procedure.

A cold solution of aryldiazonium salt (20 mmol, prepared as described above) added to a cold solution of enamionitrile **2b,c** (10 mmol) in ethanol (70 mL) containing sodium acetate (7 g). The mixture was stirred at r.t. for 1 h and the solid product, was collected by filtration and crystallized from ethanol.

### (4-Nitrophenylhydrazono)-(4'-nitrophenylazo)acetonitrile (**7a**).

Compound **7a** was obtained as dark red crystals, mp. 218-219 °C; yield 85%; IR (KBr):  $\nu_{\text{max}} = 3205$  (NH), 2198 (CN), 1509  $\text{cm}^{-1}$  (C=N);  $^1\text{H NMR}$  ( $d_6\text{-DMSO}$ ):  $\delta = 7.33\text{-}7.59$  (m, 8H, Ar-H), 12.52 (s, 1H, NH); MS (70 eV):  $m/z = 339$  ( $\text{M}^+$ , 7.7%), (122, 100%).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_9\text{N}_7\text{O}_4$ : C, 49.56; H, 2.67; N, 28.90. Found C, 49.11; H, 2.57; N, 28.77.

### (4-Chlorophenylhydrazono)-(4'-chlorophenylazo)acetonitrile (**7b**).

Compound **7b** was obtained as orange crystals, mp. 240-242 °C; yield 80%; IR (KBr):  $\nu_{\text{max}} = 3427$  (NH), 2219 (CN), 1534  $\text{cm}^{-1}$  (C=N);  $^1\text{H NMR}$  ( $d_6\text{-DMSO}$ ):  $\delta = 7.52\text{-}7.66$  (m, 8H, Ar-H), 12.24 (s, 1H, NH); MS (70 eV):  $m/z = 317$  ( $\text{M}^+$ , 7.7%), (111, 100%).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_9\text{Cl}_2\text{N}_5$ : C, 52.85; H, 2.85; N, 22.01. Found C, 51.87; H, 2.90; N, 22.10.

### (4-Bromophenylhydrazono)-(4'-bromophenylazo)acetonitrile (**7c**).

Compound **7c** was obtained as red crystals, mp. 258-259 °C; yield 87%; IR (KBr):  $\nu_{\text{max}} = 3232$  (NH), 2218 (CN), 1529  $\text{cm}^{-1}$  (C=N);  $^1\text{H NMR}$  ( $d_6\text{-DMSO}$ ):  $\delta = 7.42\text{-}7.65$  (m, 8H, Ar-H), 11.61 (s, 1H, NH). MS (70 eV):  $m/z = 405$  ( $\text{M}^+$ , 5.6%), ( $\text{M}^++2$ , 11.8), ( $\text{M}^++4$ , 5.8%), (155, 100%).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_9\text{Br}_2\text{N}_5$ : C, 41.31; H, 2.23; N, 17.20. Found C, 41.12; H, 2.12; N, 16.98.

(4-Chlorophenylhydrazono)-(4'-methoxyphenylazo)acetonitrile (**7d**).

A cold solution of *p*-methoxybenzene diazonium salt (10 mmol) (prepared as described above) added to a cold solution of **6c** (10 mmol) in EtOH and DMF containing sodium acetate (3.5 g) the mixture was stirred at r.t. for 1 h and the solid product, so formed, was collected by filtration and crystallized from ethanol. This compound was obtained as dark orange crystals; mp. 215-216 °C; yield 86%; IR (KBr):  $\nu_{\max}$  = 3234 (NH), 2222  $\text{cm}^{-1}$  (CN);  $^1\text{H NMR}$  ( $d_6$ -DMSO):  $\delta$  = 3.91 (s, 3H, CH<sub>3</sub>), 7.12 (d,  $J=9$ , 2H, Ar-H), 7.40 (d,  $J=7.8$  Hz, 2H, Ar-H), 7.61 (d,  $J=7.8$  Hz, 2H, Ar-H), 7.82 (br, 1H, NH), 8.07 (d,  $J=9$  Hz, 2H, Ar-H)- MS (70 eV):  $m/z$  = 313 (M<sup>+</sup>, 15.1%), (135, 39.6%), (107, 100%).

*Anal.* Calcd. for C<sub>15</sub>H<sub>12</sub>ClN<sub>5</sub>O C, 57.42; H, 3.86; N, 22.32. Found C, 57.38; H, 3.80; N, 22.13.

2-[(4-Chlorophenyl)-hydrazono]-3-(phenylhydrazono)-propionitrile (**8**).

A mixture of **6c** (0.01 mol) and phenylhydrazine (0.01 mol) in ethanol (20 mL) was refluxed for 45 min. then poured into H<sub>2</sub>O. The solid, so formed was collected by filtration and crystallized from ethanol to give orange crystals; m.p. 203-205 °C; yield 87%; IR (KBr):  $\nu_{\max}$  = 3424, 3277 (NH), 3033 (CH aliphatic), 2219  $\text{cm}^{-1}$  (CN);  $^1\text{H NMR}$  ( $d_6$ -DMSO):  $\delta$  = 7.0-7.91 (m, 9H, Ar-H), 10.70 (s, 1H, CH), 11.11 (br, 1H, NH), 12.0 (s, 1H, NH); MS (70 eV):  $m/z$  = 297 (M<sup>+</sup>, 98.4%), (236, 32.3%), (77, 100%).

*Anal.* Calcd. for C<sub>15</sub>H<sub>12</sub>ClN<sub>5</sub>: C, 60.51; H, 4.06; N, 23.52. Found C, 60.15; H, 3.89; N, 23.12.

1-(4-Chlorophenyl)-4-phenylazo-1H-pyrazol-3-carboxylic Acid Amide (**10**).

A mixture of **6c** (1.5 mmol) in dry DMF (1 ml) was added the Vilsmeier-Haack reagent (0.9 g, 3 mmol) [1 mol= 300 g, from POCl<sub>3</sub> (150 g, 1 mol) and DMF (150 g, 2 mol)] and the mixture was kept at 70 °C for 1 h. After cooling the mixture was poured onto ice. To the clear solution was added carefully dilute aqueous NaOH solution under cooling until a pH value of 8-9 was reached. The precipitate was separated and recrystallized from ethanol to give yellow crystals; m.p. 198-200 °C; yield 60%; IR (KBr):  $\nu_{\max}$  = 3116, 3070 (NH<sub>2</sub>), 1692  $\text{cm}^{-1}$  (CO);  $^1\text{H NMR}$  ( $d_6$ -DMSO):  $\delta$  = 7.47 (d,  $J=8.0$  Hz, 2H, aryl-H), 7.58 (m, 5H, phenyl), 7.76 (d,  $J=8.0$  Hz, 2H, aryl-H), 8.15 (s, 1H, pyrazole-H), 10.71 (br, 1H, NH<sub>2</sub>);  $^{13}\text{C NMR}$  ( $d_6$ -DMSO):  $\delta$  = 123.5, 123.6, 123.9, 128.4, 129.3, 129.5, 129.7, 130.2, 135.0, 137.8, 151.1, 151.2; - MS (70 eV):  $m/z$  = 325 (M<sup>+</sup>, 25.8%), (M+2, 6.7%), (297, 79.2%).

*Anal.* Calcd. for C<sub>16</sub>H<sub>12</sub>ClN<sub>5</sub>O: C, 58.99; H, 3.71; N, 21.50. Found C, 58.87; H, 3.43; N, 21.21.

2-[(4-Chlorophenyl)-hydrazono]-3-hydroxyiminopropionitrile (**11**).

A mixture of **6c** (0.01 mol), hydroxylamine hydrochloride (0.01 mol), and sodium acetate (0.01 mol) in ethanol (20 ml) was refluxed for 15 min. then poured into H<sub>2</sub>O. The solid, so formed was collected by filtration and crystallized from ethanol to give orange crystals; m.p. 262-263 °C; yield 82%; IR (KBr):  $\nu_{\max}$  = 3498, 3348 (OH and NH), 2989 (CH aliphatic), 2212  $\text{cm}^{-1}$  (CN);  $^1\text{H NMR}$  ( $d_6$ -DMSO):  $\delta$  = 7.37 (m, 2H, aryl-H), 7.40 (s, 1H, CH), 7.65 (m, 2H, aryl-H), 7.80 (br, 1H, NH), 11.73 (br, 1H, OH)- MS (70 eV):  $m/z$  = 222 (M<sup>+</sup>, 100%), (M+2, 44.5%).

*Anal.* Calcd. for C<sub>9</sub>H<sub>7</sub>ClN<sub>4</sub>O: C, 48.55; H, 3.17; N, 25.17. Found C, 48.24; H, 3.11; N, 25.07.

N-[4-(4-Chlorophenylazo)-isoxazol-5-yl]-acetamide (**12**).

A mixture **11** (0.01 mol) and acetic anhydride (20 ml) was refluxed for 2 h. then poured into H<sub>2</sub>O. The solid that formed was collected by filtration and crystallized from ethanol to give dark red crystals, m.p. 185-187 °C; yield 62%; IR (KBr):  $\nu_{\max}$  = 3335 (NH), 3090 (CH aliphatic), 1683  $\text{cm}^{-1}$  (CO);  $^1\text{H NMR}$  ( $d_6$ -DMSO):  $\delta$  = 2.24 (s, 3H, CH<sub>3</sub>), 3.17 (br, 1H, NH), 7.40 (s, 1H, isoxazole-H), 7.66-7.72 (m, 4H, Ar-H); MS (70 eV):  $m/z$  = 264 (M<sup>+</sup>, 7.8%), (248, 7.8%), (194, 90%).

*Anal.* Calcd. for C<sub>11</sub>H<sub>9</sub>ClN<sub>4</sub>O<sub>2</sub>: C, 49.92; H, 3.43; N, 21.17. Found C, 50.20; H, 3.31; N, 21.09.

5-Acetyl-1-(4-chloro-phenyl)-1H-pyrazole-3-carbonitrile (**13**).

A mixture of **6c** (0.01 mol), chloroacetone (0.01 mol) and K<sub>2</sub>CO<sub>3</sub> (0.02 mol) in dioxane (20 mL) was refluxed for 2 h. The solvent was then evaporated under reduced pressure and the residue poured on water and neutralized by HCl. The product was collected by filtration and crystallized from ethanol to give brown crystals; m.p. 180-181 °C; yield 60%; IR (KBr):  $\nu_{\max}$  = 3139 (CH aliphatic), 2243 (CN), 1697  $\text{cm}^{-1}$  (C=O);  $^1\text{H NMR}$  ( $d_6$ -DMSO):  $\delta$  = 2.54 (s, 3H, CH<sub>3</sub>), 7.52-7.60 (m, 4H, Ar-H), 8.07 (s, 1H, CH);  $^{13}\text{C NMR}$  ( $d_6$ -DMSO):  $\delta$  = ten signals at 20, 107, 116, 120, 126, 129.6, 131, 135, 136 and 190; MS (70 eV):  $m/z$  = 245 (M<sup>+</sup>, 88%), (230, 100%).

*Anal.* Calcd. for C<sub>12</sub>H<sub>8</sub>N<sub>3</sub>OCl: C, 58.67; H, 3.28; N, 17.10. Found C, 58.56; H, 3.24; N, 17.11.

N-[2-(4-Chlorophenyl)-6-cyano-3-oxo-2,3-dihydro-pyridazin-4-yl]-benzamide (**16**).

A mixture of **6c** (0.01 mol), hippuric acid (0.01 mol) and acetic anhydride (15 ml) refluxed for 2 h. then poured into H<sub>2</sub>O, the solid so formed was collected by filtration and crystallized from ethanol to give brown crystals m.p. 220-222 °C; yield 71%; IR (KBr):  $\nu_{\max}$  = 3375 (NH), 2244 (CN), 1709  $\text{cm}^{-1}$  (CO);  $^1\text{H NMR}$  ( $d_6$ -DMSO):  $\delta$  = 7.55-7.68 (m, 7H, 5H phenyl-H, and 2H Ar-H), 7.97 (d,  $J=7.2$  Hz, 2H, Ar-H), 8.42 (s, 1H, pyridazinyl-H), 10.05 (s, 1H, NH)- MS (70 eV):  $m/z$  = 350 (M<sup>+</sup>, 8%), (M+2, 3.2%), (105, 100%).

*Anal.* Calcd. for C<sub>18</sub>H<sub>11</sub>ClN<sub>4</sub>O<sub>2</sub>: C, 61.64; H, 3.16; N, 16.97. Found C, 61.25; H, 3.12; N, 15.89.

6-Chloro-cinnoline-3-carboxylic Acid Amide (**17**).

Compound **6c** (0.01 mol) was heated with conc. H<sub>2</sub>SO<sub>4</sub> (3-5 mL) at 198-200 °C for 5 min and kept overnight and then poured into H<sub>2</sub>O. The solid product, so formed, was collected by filtration and crystallized from ethanol. This compound was obtained as orange crystals, yield 45%; m.p. 285 °C; IR (KBr):  $\nu_{\max}$  = 3426, 3278 (NH<sub>2</sub>), 1681  $\text{cm}^{-1}$  (CO);  $^1\text{H NMR}$  ( $d_6$ -DMSO):  $\delta$  = 7.21 (br, 2H, NH<sub>2</sub>), 7.67-8.07 (m, 4H, Ar-H, and cinnoline-H);  $^{13}\text{C NMR}$  nine signals at 120, 124, 125.2, 128.5, 129.1, 133.7, 147.4, 162.6 and 185; MS (70 eV):  $m/z$  = 207 (M<sup>+</sup>, 100%), (164, 77.1%).

*Anal.* Calcd. for C<sub>9</sub>H<sub>6</sub>ClN<sub>3</sub>O: C, 52.07; H, 2.91; N, 20.24. Found C, 52.10; H, 2.74; N, 20.14.

4-(4-Chlorophenylazo)-1H-pyrazol-3-ylamine. (**18**).

A mixture of **6c** (0.01 mol) and hydrazine hydrate (0.01 mol) in ethanol (25 mL) was refluxed for 2 h then poured into H<sub>2</sub>O.

The solid, so formed was collected by filtration and crystallized from ethanol to give orange crystals; m.p. 215-216 °C; yield 70%; IR (KBr):  $\nu_{\max}$  = 3414 (NH), 3278- 3310 (NH<sub>2</sub>)- <sup>1</sup>H NMR (d<sub>6</sub>-DMSO):  $\delta$  = 5.79 (br, 2H, NH<sub>2</sub>), 6.76-7.24 (m, 5H, Ar-H and pyrazol-H), 11.0 (br, 1H, NH); <sup>13</sup>C NMR (d<sub>6</sub>-DMSO):  $\delta$  = seven signals at 121.05, 121.06, 127.59, 127.6, 131.81, 150.37 and 150.38; MS (70 eV):  $m/z$  = 221 (M<sup>+</sup>, 45.4%), (110, 100%).

*Anal.* Calcd. for C<sub>9</sub>H<sub>8</sub>ClN<sub>5</sub>: C, 48.77; H, 3.64; N, 31.60. Found C, 48.83; H, 3.51; N, 31.7.

3-(4-Chlorophenylazo)-7-thiophen-2-yl-pyrazolo[1,5-*a*]pyrimidine (**20**).

A mixture of enaminone **19** (0.01 mol) and **18** (0.01 mol) was refluxed in pyridine (20 mL) for 3 h. The reaction mixture was then poured into water and acidified with conc. HCl then boiled for 5 min. The solid so formed was collected by filtration and crystallized from ethanol to give red crystals, mp. 190-192 °C; yield 67%; IR (KBr):  $\nu_{\max}$  = 1535 cm<sup>-1</sup> (C=N)- <sup>1</sup>H NMR (d<sub>6</sub>-DMSO):  $\delta$  = 7.32 (m, 1H, thiophenyl H-3), 7.42 (d,  $J$  = 5.6 Hz, 1H, pyrimidine H-6), 7.47 (s, 1H, pyrazole-H), 7.81 (d,  $J$  = 5.6 Hz, 2H, Ar-H), 7.90 (d,  $J$  = 5.6 Hz, 2H, Ar-H), 8.44 (d,  $J$  = 5.6 Hz, 1H, pyrimidine H-5), 8.75 (m, 2H, thiophenyl H-4 and H-5); <sup>13</sup>C NMR (d<sub>6</sub>-DMSO):  $\delta$  = fourteen signals at 105.6, 123.61, 123.62, 127.88, 129.0, 129.1, 130.0, 132.4, 133.5, 135.2, 135.7, 151.2, 151.5 and 159.0; MS (70 eV):  $m/z$  = 339 (M<sup>+</sup>, 43.7%), (228, 100%), (121, 68%).

*Anal.* Calcd. for C<sub>16</sub>H<sub>10</sub>ClN<sub>5</sub>S: C, 56.55; H, 2.97; N, 20.61; S, 9.43. Found C, 56.59; H, 3.0; N, 20.62; S, 9.35.

3-(4-Chlorophenylazo)-6-(4'-substituedphenylazo)pyrazolo[1,5-*a*]pyrimidin-7-ylamine **21a,b**.

General Procedure.

A mixture of **18** (0.01 mol) and **6b,c** (0.01 mol) was refluxed in solution of pyridine (15 mL) for 3 h. The reaction mixture was then poured into water then conc. HCl was added and the reaction mixture was boiled for 5 min. The solid so formed was collected by filtration and crystallized.

3-(4-Chlorophenylazo)-6-(4-methoxyphenylazo)pyrazolo[1,5-*a*]pyrimidin-7-ylamine (**21a**).

Compound **21a** was obtained as dark red crystals from DMF yield 77%; 303-305 °C; IR (KBr):  $\nu_{\max}$  = 3275 (NH<sub>2</sub>), 3064 (CH aliphatic), 1581cm<sup>-1</sup> (C=N); <sup>1</sup>H NMR (d<sub>6</sub>-DMSO):  $\delta$  = 3.59 (s, 3H, OCH<sub>3</sub>), 6.7 (br, 2H, NH<sub>2</sub>), 7.10-7.62 (m, 8H, Ar-H), 8.28 (s, 1H, pyrazolo H-2), 8.76 (s, 1H, pyrimidinyl H); MS (70 eV):  $m/z$  = 406 (M<sup>+</sup>, 100%), (267, 54.2%).

*Anal.* Calcd. for C<sub>19</sub>H<sub>15</sub>ClN<sub>8</sub>O: C, 56.09; H, 3.72; N, 27.54. Found C, 56.02; H, 3.45; N, 27.28.

3,6-Bis-(4-chlorophenylazo)pyrazolo[1,5-*a*]pyrimidin-7-ylamine (**21b**).

Compound **21b** was obtained as dark red crystals from ethanol; yield 74%; m.p. >300 °C; IR (KBr):  $\nu_{\max}$  = 3426 (NH<sub>2</sub>), 1586 cm<sup>-1</sup> (C=N); <sup>1</sup>H NMR (d<sub>6</sub>-DMSO):  $\delta$  = 5.83 (br, 2H, NH<sub>2</sub>), 6.6-7.2 (m, 9H, Ar-H, pyrazolo H), 8.61 (s, 1H, pyrimidinyl H); MS (70 eV):  $m/z$  = 410 (M<sup>+</sup>, 37.4%), (299, 39.5%), (271, 42.7%), (111, 100%).

*Anal.* Calcd. for C<sub>18</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>8</sub>: C, 52.57; H, 2.94; N, 27.25. Found C, 52.47; H, 2.99; N, 27.28.

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