

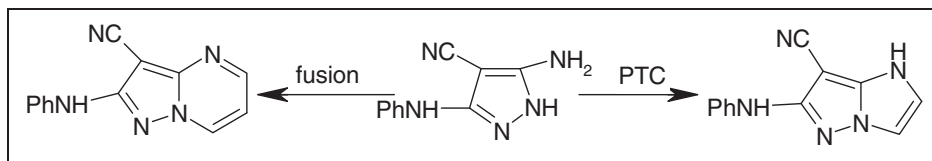
Chemistry Department, Faculty of Science, Sohag University, Sohag, Egypt

\*E-mail: a\_sol2000@yahoo.com; msremaily@yahoo.com

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5-Amino-3-anilino-1H-pyrazole-4-carbonitrile **1** was alkylated with various halo reagents under phase transfer conditions to give the corresponding imidazopyrazole derivatives **2a-c-6**. Pyrazolo[1,5-a] pyrimidine derivatives **11-14** were prepared by treating compound **1** with different dicarbonyl reagents, namely, diethylmalonate, ethyl 3-oxo-3-phenylpropanoate, pentane-2,4-dione or ethyl 3-oxobutanoate.

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## INTRODUCTION

Heterocyclic compounds containing two nitrogen atoms in the molecule (diazoles) represent a very important group of organic molecules because many of them exhibit significant biological activity [1,2], including anti-microbial [3,4] and pharmacological effects [5–7]. The pyrazole derivatives are mainly used as anti-inflammatory, anti-pyretic, and analgesic drugs [8–10].

Pyrazolopyrimidines and related-fused heterocycles are of interest potential bioactive molecules. They are known to exhibit pharmacological activities such as CNS depressant [11], neuroleptic [12], and tuberculostatic [13]. In view of these versatile benefits and in connection with our efforts directed towards the synthesis of heterocyclic ring systems [14–23], we aimed in this study to obtain some new heterocyclic compounds with an expected wide spectrum of potential applications.

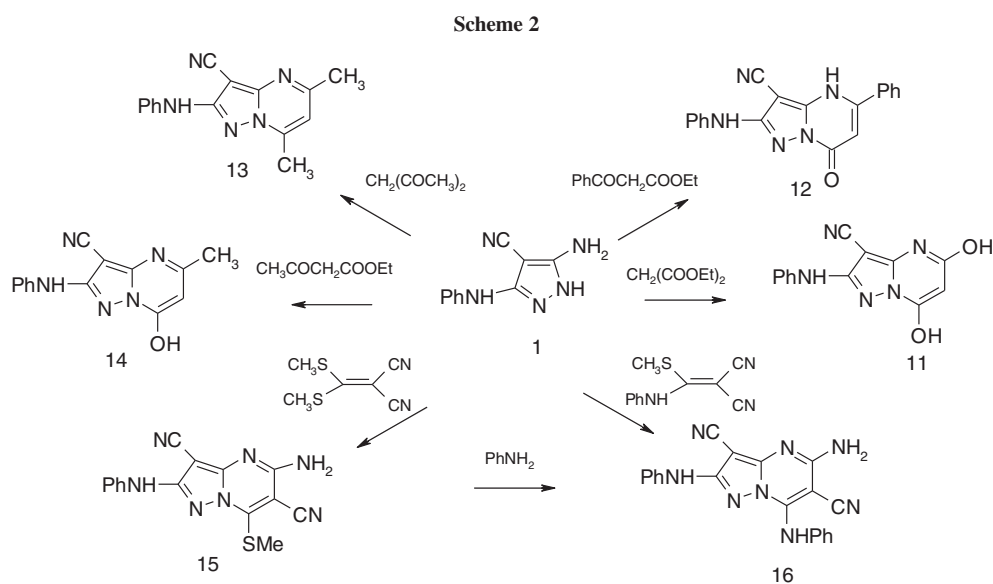
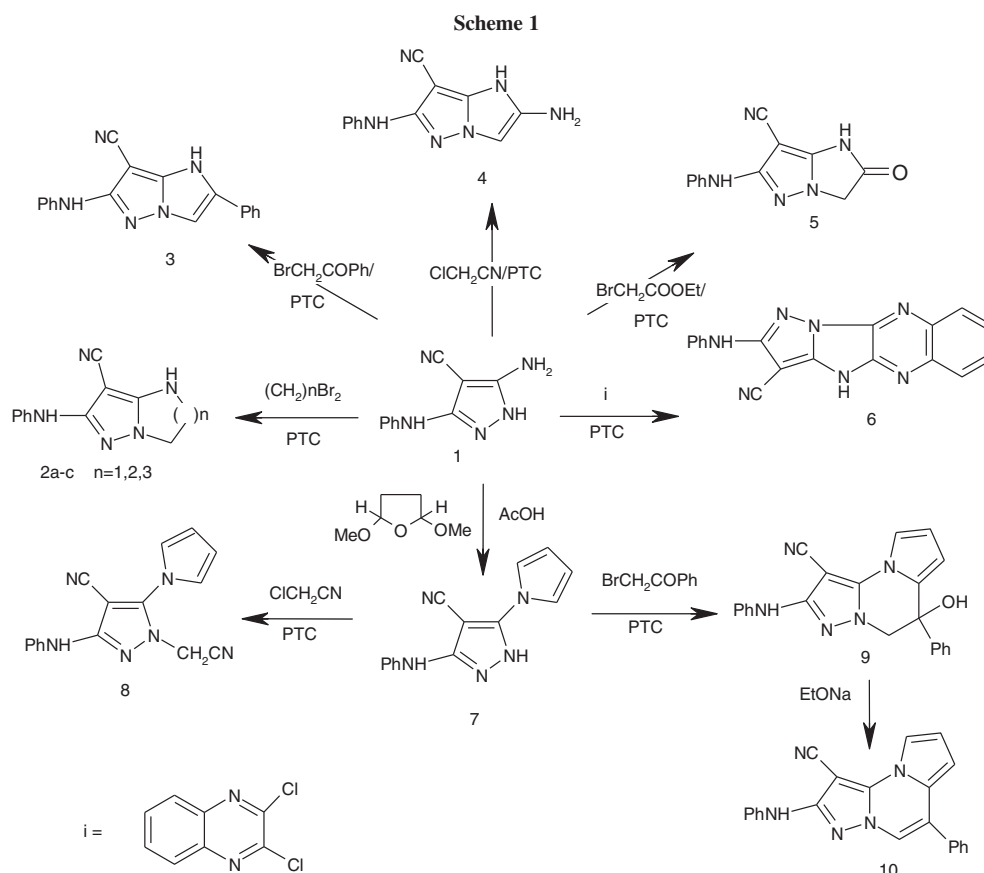
## RESULTS AND DISCUSSION

Under phase transfer conditions using dioxane as the organic phase, potassium carbonate as the solid phase, and tetrabutylammonium bromide as a catalyst, the key precursor 5-Amino-3-anilino-1H-pyrazole-4-carbonitrile **1** [24], containing  $\text{NH}_2$  adjacent to the NH group, was alkylated with various halo reagents, namely, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 2-bromo-1-phenylethanone, chloroacetonitrile, ethyl bromoacetate or 2,3-dichloroquinoxaline followed by intramolecular cyclization to give the corresponding imidazopyrazole derivatives **2a-c-6**, respectively, in good yield. Compound **7** was yielded *via* treatment of compound **1** with 2,5-dimethoxytetrahydrofuran in refluxing glacial acetic acid which in turn reacted under the same previous phase transfer

catalysis conditions with each of chloroacetonitrile and 2-bromo-1-phenylethanone to give compounds **8** and **9**, respectively. Compound **9** was refluxed in ethanol in the presence of sodium ethoxide as a catalyst for 3 h to give product **10** (Scheme 1). The structures of the products **5**, **9**, and **10** were confirmed by the elemental analyses and the spectroscopic data. The IR spectrum of product **5** showed characteristic absorption band at 1680 assignable to CO group. The  $^1\text{H}$  nmr spectrum of product **9** showed a signal at  $\delta$  12.97 and 3.56 assignable to OH and  $\text{CH}_2$  groups, respectively, whereas compound **10** did not show any signals corresponding to OH or  $\text{CH}_2$  while showed a signal at  $\delta$  7.99 assignable to CH of pyrimidine ring.

Compound **1** was fused at  $200^\circ\text{C}$  with different dicarbonyl reagents namely diethylmalonate, ethyl 3-oxo-3-phenylpropanoate, pentane-2,4-dione or ethyl 3-oxobutanoate to obtain pyrazolo[1,5-a]pyrimidine derivatives **11-14**, respectively. On refluxing compound **1** with ketenedithioacetal ([bis(methylthio)methylene] malononitrile) in absolute ethanol, in presences of TEA as a catalyst until evolution of methyl mercaptane was ceased, compound **15** was separated which in turn fused with aniline to give compound **16**. Also, compound **16** was yielded from the reaction of compound **1** with ketene aminothioacetal ([anilino (methylthio) methylene] malononitrile under the same previous reaction conditions, (Scheme 2). The assignments of the structures of products **11** and **12** were based on their correct elemental analyses and spectroscopic data. The IR spectrum of product **11** showed two characteristic absorption bands at 3344 and  $3205\text{ cm}^{-1}$ , assignable to OH and NH groups, respectively, whereas product **12** showed two characteristic absorption bands at 3442 and 3333 assignable to 2NH groups and clear band at 1652 assignable to CO group.

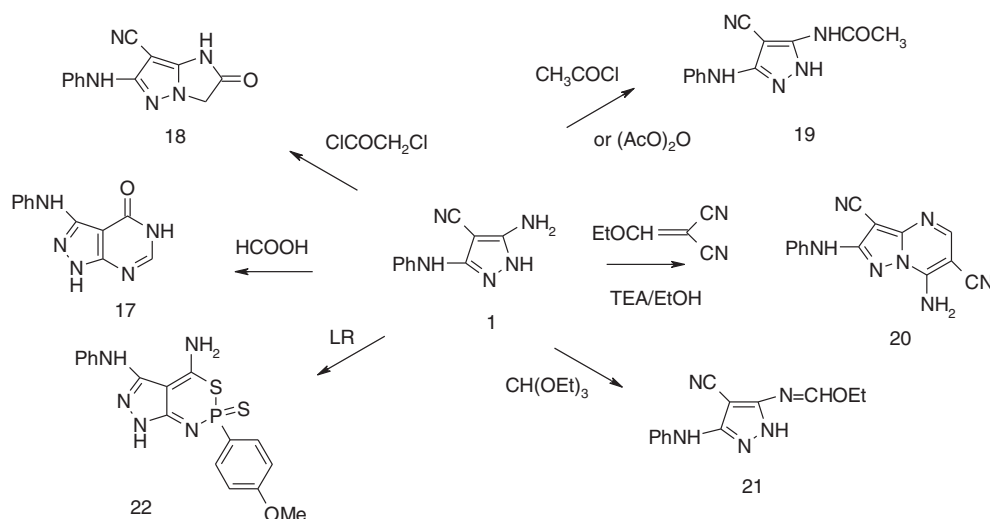
Also, compound **1** was refluxed in excess formic acid to give 3-anilino-1H-pyrazolo[3,4-d]pyrimidin-4-ol **17**. The



acetylation of compound **1** with chloroacetyl chloride in pyridine gave 6-anilino-2-hydroxy-1H-imidazo[1,2-b]pyrazole-7-carbonitrile **18** and when treated with acetyl chloride or acetic anhydride gave the acetylated compound **19**. Also, ethoxymethylenemalononitrile, triorthoformate,

and Lawesson's reagent were allowed to react with compound **1** to give compounds **20–22**, respectively (Scheme 3). The structures of the products **17** and **18** were confirmed by the correct elemental analyses and spectroscopic data. The IR spectra of products **17** and **18** showed

Scheme 3



characteristic absorption bands corresponding to NH groups and two absorption bands at 1675, 1698 assignable to CO groups in each compound, respectively.

When compound **21** was subjected to react with hydrazine or phenylhydrazine, the starting compound **1** was separated and did not give the cyclic compound as we expected. This was interpreted by calculating the minimized energy structure by (MM2 and AM1) of compound **21**, which revealed that the imidoformate lies out of plan with the cyano group in Figure 1, so underwent hydrolysis.

## EXPERIMENTAL

All melting points were determined on a Kofler melting point apparatus and are uncorrected. IR spectra were obtained on a Nicolet 710 FT-IR spectrometer.  $^1\text{H}$  nmr spectra were recorded on a Varian Gemini at 200 MHz using Trimethyl selenium as an internal reference and DMSO- $d_6$  as a solvent. Elemental analyses were performed on a Perkin-Elmer CHN-2400 C analyzer model.

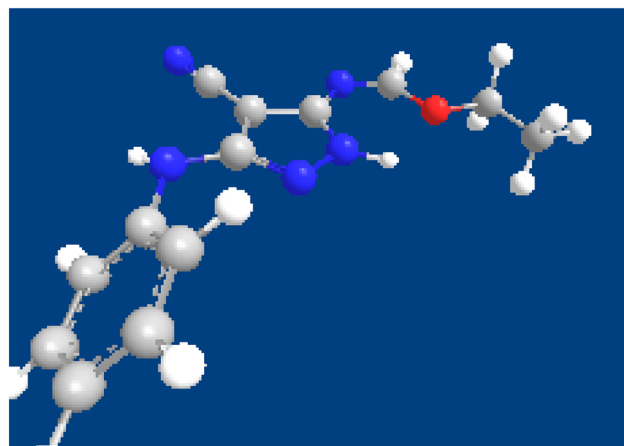
**General procedure for preparation of imidazopyrazole derivatives 2a-c-6, 8, and 9.** An equimolar mixture of compound **1** (1.99 g, 0.01 mol) and the halo reagents, namely, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromo butane, 2-bromo-1-phenylethanone, chloroacetonitrile, ethyl bromoacetate, 2,3-dichloroquinoxaline or chloroacetonitrile in dioxane (50 mL) was treated with anhydrous potassium carbonate (9 g) and a catalytic amount of tetrabutylammonium bromide (6% mol/mol of substrate). The reaction mixture was stirred 2 h at 60–70 °C, left to cool, filtered off, and the filtrate was evaporated *in vacuo*, and the resulting solid was recrystallized from ethanol.

**6-Anilino-2,3-dihydro-1H-imidazo[1,2-b]pyrazole-7-carbonitrile (2a).** Yield: 1.95 g, 87%, pale brown, mp 164–166 °C; IR: 3342 (2NH), 2208 (CN)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  8.40 (br, 1H,

NH phenyl), 7.60–6.75(m, 5H, phenyl), 6.47 (s, 1H, NH imidazolidine), 4.37–4.12(m, 4H, 2CH<sub>2</sub>); *Anal.* calcd. for C<sub>12</sub>H<sub>11</sub>N<sub>5</sub> (225.25): C, 63.99; H, 4.92; N, 31.09. Found: C, 63.79; H, 4.62; N, 31.12.

**2-Anilino-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (2b).** Yield: 2.2 g, 92%, buff, mp 149–150 °C; IR: 3335, 3208 (2NH), 2206 (CN)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  8.40 (br, 1H, NH phenyl), 7.45–6.76(m, 5H, phenyl), 6.52 (s, 1H, NH hydro-pyrimidine), 3.86 (br, 4H, 2CH<sub>2</sub>), 2.03 (br, 2H, CH<sub>2</sub>); *Anal.* calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>5</sub> (239.28): C, 65.25; H, 5.48; N, 29.27. Found: C, 65.05; H, 5.28; N, 29.57

**2-Anilino-5,6,7,8-tetrahydro-4H-pyrazolo[1,5-a][1,3]diazepine-3-carbonitrile (2c).** Yield: 2.1 g, 83%, buff, mp 138–140 °C; IR: 3343 (2NH), 2206 (CN)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  8.40 (br, 1H,



**Figure 1.** Minimized energy structure by (MM2 and AM1) of compound **21**. The optimization was carried out using semi-empirical calculation with MM2 and AM1 force fields. The optimization was carried out for 50,000 steps. Calculations were performed using ChemOffice software developed by Cambridge Soft. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

NH phenyl), 7.47–6.75(m, 5H, phenyl), 6.60 (s, 1H, NH diazepane), 3.90–3.80(m, 4H, 2CH<sub>2</sub>), 1.86–1.67 (m, 4H, 2CH<sub>2</sub>); *Anal.* calcd. for C<sub>14</sub>H<sub>15</sub>N<sub>5</sub> (253.30): C, 66.38; H, 5.97; N, 27.65. Found: C, 66.55; H, 5.75; N, 27.95.

**6-Anilino-2-phenyl-1H-imidazo[1,2-b]pyrazole-7-carbonitrile (3).** Yield: 2.4 g, 80%, yellow, mp 268–270 °C; IR: 3335 (2NH), 2212 (CN) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 9.62 (br, 1H, NH imidazole), 8.32 (br, 1H, NH phenyl), 8.13–7.10(m, 11H, 2phenyl, CH imidazole); *Anal.* calcd. for C<sub>18</sub>H<sub>13</sub>N<sub>5</sub> (299.33): C, 72.23; H, 4.92; N, 23.40. Found: C, 72.45; H, 4.62; N, 23.75.

**2-Amino-6-anilino-1H-imidazo[1,2-b]pyrazole-7-carbonitrile (4).** Yield: 1.25 g, 53%, brown, mp 225–227 °C; IR: 3435, 3351, 3240 (NH, NH<sub>2</sub>), 2209 (CN) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 8.73(br, 1H, NH, imidazol), 8.40 (br, 1H, NH phenyl), 7.45–6.80 (m, 5H, phenyl), 5.30 (br, 2H, NH<sub>2</sub>), 4.66 (s, 1H, CH, imidazol); *Anal.* calcd. for C<sub>12</sub>H<sub>10</sub>N<sub>6</sub> (238.25): C, 60.50; H, 4.23; N, 35.27. Found: C, 60.30; H, 4.00; N, 35.57.

**6-Anilino-2-oxo-2,3-dihydro-1H-imidazo[1,2-b]pyrazole-7-carbonitrile (5).** Yield: 1.3 g, 55%, buff, mp 160–162 °C; IR: 3341 (2NH), 2218 (CN), 1680 (CO) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 8.73(br, 1H, NH, imidazol), 8.40 (br, 1H, NH phenyl), 7.45–6.80 (m, 5H, phenyl), 4.80(s, 2H, CH<sub>2</sub>); *Anal.* calcd. for C<sub>12</sub>H<sub>9</sub>N<sub>5</sub>O (239.23): C, 60.25; H, 3.79; N, 29.27. Found: C, 60.50; H, 3.55; N, 29.60.

**2-Anilino-4H-pyrazolo[1',5':1,2]imidazo[4,5-b]quinoxaline-3-carbonitrile (6).** Yield: 2.8 g, 86%, yellow, mp 360 °C; IR: 3414, 3337 (2NH), 2213 (CN) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 9.40 (br, 2H, NH), 8.00–7.00 (m, 9H, 2 phenyl); *Anal.* calcd. for C<sub>18</sub>H<sub>11</sub>N<sub>7</sub> (325.33): C, 66.45; H, 3.41; N, 30.14. Found: C, 66.70; H, 3.11; N, 30.44.

**3-Anilino-5-(1H-pyrrol-1-yl)-1H-pyrazole-4-carbonitrile (7).** An equimolar ratio of compound **1** (0.005 mol, 1 g) and 2,5-dimethoxytetrahydro furan (0.4 ml) in 10 ml of glacial acetic acid was heated under reflux for 1 h, left to cool, and then poured onto ice cold water. The precipitated solid was filtered off, washed well with water, dried, and crystallized from ethanol. Yield: 2.3 g, (92%), pale brown, mp 290 °C; IR: 3207 (NH), 2217 (CN) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 13.10 (br, 1H, NH pyrazole), 9.30 (br, 1H, NH phenyl), 7.33–6.98(br, 7H, phenyl+pyrrole), 6.30 (s, 2H, pyrrole); *Anal.* calcd. for C<sub>14</sub>H<sub>11</sub>N<sub>5</sub> (249.27): C, 67.46; H, 4.45; N, 28.10. Found: C, 67.46; H, 4.15; N, 28.40.

**3-Anilino-1-(cyanomethyl)-5-(1H-pyrrol-1-yl)-1H-pyrazole-4-carbonitrile (8).** Yield: 2.6 g, 70%, pale brown, mp 178–180 °C; IR: 3420 (OH), 3220 (NH), 2221 (CN) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 13.10 (br, 1H, OH), 9.30 (br, 1H, NH phenyl), 7.80–7.00 (br, 13H, 2 phenyl + pyrrole), 6.30 (s, 2H, CH<sub>2</sub>); *Anal.* calcd. for C<sub>22</sub>H<sub>17</sub>N<sub>5</sub>O (367.40): C, 71.92; H, 4.66; N, 19.06. Found: C, 71.72; H, 4.41; N, 19.37.

**2-Anilino-6-hydroxy-6-phenyl-5,6-dihydropyrazolo[1,5-a]pyrrolo[1,2-c] pyrimidine-1-carbonitrile (9).** Yield: 2.15 g, 75%, buff, mp 303–305 °C; IR: 3214 (NH), 2217 (CN) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 8.40 (br, 1H, NH phenyl), 7.30–6.80 (m, 5H, arom.), 6.10 (br, 2H, CH<sub>2</sub>); *Anal.* calcd. for C<sub>16</sub>H<sub>12</sub>N<sub>6</sub>

(288.31): C, 66.66; H, 4.20; N, 29.15. Found: C, 66.38; H, 3.90; N, 29.45

**General procedure for preparation of pyrazolopyrimidine derivatives (11–14).** A mixture of compound **1** (0.005 mol, 1 g) and 10 ml of diethylmalonate, ethyl benzoylacetate, acetylacetone, or ethylacetoacetate was heated at 200 °C for 1 h. The solid products were filtered off and washed with ethanol.

**2-Anilino-5,7-dihydroxypyrazolo[1,5-a]pyrimidine-3-carbonitrile (11).** Yield: 2.2 g, 82%, reddish brown, mp 320–322 °C; IR: 3344 (OH), 3205 (NH), 2217 (CN) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 9.16 (br, 2H, OH), 8.90 (br, 1H, NH phenyl), 7.95–6.90 (m, 5H, arom.), 4.12 (s, 1H, CH pyrimidine); *Anal.* calcd. for C<sub>13</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub> (267.24): C, 58.43; H, 3.39; N, 26.21. Found: C, 58.68; H, 3.70; N, 26.51.

**2-Anilino-7-oxo-5-phenyl-4,7-dihydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (12).** Yield: 2.85 g, 87%, pale yellow, mp 358–360 °C; IR: 3442, 3333 (2NH), 2220 (CN), 1652 (CO) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 9.24 (s, 1H, NH phenyl), 7.97–6.88 (br, 11H, 2 phenyl+NH), 6.40 (s, 1H, CH pyrimidine); *Anal.* calcd. for C<sub>19</sub>H<sub>13</sub>N<sub>5</sub>O (327.34): C, 69.71; H, 4.00; N, 21.39. Found: C, 69.41; H, 3.70; N, 21.07.

**2-Anilino-5,7-dimethylpyrazolo[1,5-a]pyrimidine-3-carbonitrile (13).** Yield: 2.25 g, 86%, pale brown, mp 280–282 °C; IR: 3318 (NH), 2209 (CN) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 9.38 (s, 1H, NHphenyl), 7.74 (d, 2H, Ho), 7.29 (t, 2H, Hm), 6.93 (d, 1H, Hp), 6.88 (d, 4H, 7-aryl), 7.43 (s, 1H, CH pyrimidine), 2.60–2.46 (m, 6H, 2CH<sub>3</sub>); *Anal.* calcd. for C<sub>15</sub>H<sub>13</sub>N<sub>5</sub> (263.30): C, 68.72; H, 4.65; N, 26.30. Found: C, 68.80; H, 4.50; N, 26.23.

**2-Anilino-7-hydroxy-5-methylpyrazolo[1,5-a]pyrimidine-3-carbonitrile (14).** Yield: 2.10 g, 79%, pale brown, mp 360 °C; IR: 3329 (OH), 3160 (NH), 2223 (CN) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 13.00 (OH), 9.15 (s, 1H, NH phenyl), 7.74 (d, 2H, Ho), 7.28 (t, 2H, Hm), 6.92 (d, 1H, Hp), 5.78 (s, 1H, CH pyrimidine), 2.29 (s, 3H, CH<sub>3</sub>); *Anal.* calcd. for C<sub>14</sub>H<sub>11</sub>N<sub>5</sub>O (265.27): C, 63.39; H, 4.18; N, 26.40. Found: C, 63.55; H, 3.90; N, 26.70.

**5-Amino-2-anilino-7-(methylthio)pyrazolo[1,5-a]pyrimidine-3,6-dicarbonitrile (15).** An equimolar ratio of compound **1** (0.005 mol, 1 g) and [bis(methylthio)methylene] malononitrile (0.005 mol, 0.85 g) in absolute ethanol (20 mL) and few drops of TEA as a catalyst was refluxed. The solid product started to form after 15–20 min, whereas refluxing was continued until the evolution of methyl mercaptan was ceased. The reaction mixture was filtered on hot, and the precipitate was crystallized from ethanol. Yield: 2.6 g, 81%, yellow, mp 313–315 °C; IR: 3454, 3332, 3157 (NH, NH<sub>2</sub>), 2208 (CN), cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 9.52 (s, 1H, NH phenyl), 7.80–7.05 (br, 7H, phenyl, NH<sub>2</sub>), 3.03 (s, 3H, CH<sub>3</sub>); *Anal.* calcd. for C<sub>15</sub>H<sub>11</sub>N<sub>7</sub>S (321.36): C, 56.06; H, 3.45; N, 30.51. Found: C, 56.36; H, 3.15; N, 30.81.

**5-Amino-2, 7 -dianilinopyrazolo[1,5-a]pyrimidine-3,6-dicarbonitrile (16).** An equimolar ratio of compound **1** (0.005 mol, 1 g) and [anilino(methylthio) methylene] malononitrile (0.005 mol, 1.1 g) in absolute ethanol (20 mL) and few drops of TEA as a catalyst was refluxed



for 3 h. The reaction mixture was left to cool; the obtained solid was filtered and crystallized from ethanol. Yield: 2.7 g, 74%, buff, mp 318–320 °C; IR: 3465, 3371, 3297, 3143 (2NH, NH<sub>2</sub>), 2205 (CN), cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 10.11 (s, 1H, NH phenyl-5), 9.20 (s, 1H, NH phenyl-3), 7.85 (d, 2H, Ho), 7.27 (t, 2H, Hm), 6.90 (d, 1H, Hp), 7.44 (s, 2H, NH<sub>2</sub>); *Anal.* calcd. for C<sub>20</sub>H<sub>14</sub>N<sub>8</sub> (366.38): C, 65.56; H, 3.85; N, 30.58. Found: C, 65.21; H, 3.55; N, 30.88.

**3-Anilino-1,5-dihydro-4H-pyrazolo[3,4-d]pyrimidin-4-one (17).** Compound **1** (0.005 mol, 1 g) and excess of formic acid (10 mL) was heated under reflux for 10 h. The mixture was left to cool and poured onto ice cold water. The obtained solid product was filtered, washed with water, and crystallized from ethanol. Yield: 1.8 g, 79%, brown, mp 358–360 °C; IR: 3414, 3203, (2NH), 1675 (CO), cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 12.85 (s, 1H, NH pyrimidine), 12.03 (s, 1H, NH pyrazole), 7.99 (s, 1H, CH pyrimidine), 7.86 (s, 1H, NH phenyl), 7.67 (d, 2H, Ho), 7.23 (t, 2H, Hm), 6.87 (t, 1H, Hp); *Anal.* calcd. for C<sub>11</sub>H<sub>9</sub>N<sub>5</sub>O (227.22): C, 58.14; H, 3.99; N, 30.82. Found: C, 58.44; H, 3.65; N, 30.52.

**6-Anilino-2-oxo-2,3-dihydro-1H-imidazo[1,2-b]pyrazole-7-carbonitrile (18).** To a solution of compound **1** (0.005 mol, 1 g) in pyridine (15 mL), chloroacetyl chloride (0.005 mol, 0.4 ml) was added dropwise with stirring at room temperature for 30 min and then refluxed for 6 h. The precipitated solid was filtered and crystallized from ethanol. Yield: 1.50 g, 63%, dark brown, mp 360 °C; IR: 3419 (NH), 2220 (CN), 1698 (CO) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 9.67 (s, 1H, NH imidazolidine), 8.35 (br, 1H, NH phenyl), 7.65–6.80 (m, 5H, phenyl), 3.67 (s, 2H, CH<sub>2</sub> imidazolidine); *Anal.* calcd. for C<sub>12</sub>H<sub>9</sub>N<sub>5</sub>O (239.23): C, 60.25; H, 3.79; N, 29.27. Found: C, 60.55; H, 3.49; N, 29.57.

**N-(3-anilino-4-cyano-1H-pyrazol-5-yl)acetamide (19).** Compound **1** (0.005 mol, 1 g) in DMF (15 mL) and acetyl chloride (0.005 mol, 0.4 ml) or acetic anhydride (10 mL) was stirred at room temperature for 30 min. The reaction mixture was refluxed for 3 h and then allowed to cool. The precipitated solid was filtered and crystallized from ethanol. Yield: 1.70 g, 71%, pale orange, mp 240 °C; IR: 3401, 3221 (2NH), 2219 (CN), 1667 (CO) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 12.90 (s, 1H, NH acetyl), 10.77 (s, 1H, NH pyrazole), 8.45 (br, 1H, NH phenyl), 7.60–6.75 (m, 5H, phenyl), 2.00 (s, 3H, CH<sub>3</sub>); *Anal.* calcd. for C<sub>12</sub>H<sub>11</sub>N<sub>5</sub>O (241.25): C, 59.74; H, 4.60; N, 29.03. Found: C, 59.44; H, 4.30; N, 29.35.

**7-Amino-2-anilinopyrazolo[1,5-a]pyrimidine-3,6-dicarbonitrile (20).** An equimolar ratio of compound **1** (0.005 mol, 1 g) and (ethoxymethylene) malononitrile (0.005 mol, 0.3 g) in absolute ethanol (30 ml) and three drops of TEA was heated under reflux for 6 h. The reaction mixture was concentrated and left to cool. The solid product was separated by filtration and crystallized from ethanol. Yield: 2.0 g, 73%, brown, mp 180 °C; IR: 3409, 3326, 3207 (NH, NH<sub>2</sub>), 2200 (CN) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 9.34 (s, 1H, NH phenyl), 8.42 (s, 1H, CH pyrimidine), 7.89–6.96 (m, 7H,

phenyl, NH<sub>2</sub>); *Anal.* calcd. for C<sub>14</sub>H<sub>9</sub>N<sub>7</sub> (275.27): C, 61.09; H, 3.30; N, 35.62. Found: C, 61.32; H, 3.05; N, 35.92.

**Ethyl (3-amino-4-cyano-1H-pyrazol-5-yl)imidofornate (21).** A mixture of compound **1** (0.005 mol, 1 g), triethyl orthoformate (3 mL) and acetic anhydride (10 mL) was heated under reflux for 4 h. The reaction mixture was concentrated and poured onto ice cold water. The solid product was filtered and recrystallized from ethanol. Yield: 1.7 g, 67%, brown, mp 140 °C; IR: 3390, 3331 (2NH), 2219 (CN) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 8.34 (s, 1H, NH phenyl), 7.42–6.40 (m, 5H, phenyl), 5.20 (s, 1H, CH), 3.33 (q, 2H, CH<sub>2</sub>), 1.80 (t, 3H, CH<sub>3</sub>); *Anal.* calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>5</sub>O (255.28): C, 61.17; H, 5.13; N, 27.43. Found: C, 61.39; H, 4.90; N, 27.70.

**2-(4-Methoxyphenyl)-N5-phenyl-2,7-dihydropyrazolo[3,4-d][1,3,2]thiaza-phosphinine-4,5-diamine 2-sulfide (22).** A mixture of compound **1** (0.005 mol, 1 g) and 2,4-bis (4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-dithione (Lawesson's reagent) (0.005 mol, 2.1 g) in dry p-xylene (20 ml) was heated under reflux for 6 h. The solvent was removed under reduced pressure, and the obtained residue was triturated with cold methanol (20 ml). The precipitate was filtered off and crystallized from dioxane. Yield: 2.95 g, 74%, reddish brown, mp 298–300 °C; IR: 3423, 3330 (NH<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 10.00 (s, 1H, NH phenyl), 7.67–6.26 (m, 11H, 2 phenyl, NH<sub>2</sub>), 3.78 (s, 3H, CH<sub>3</sub>); *Anal.* calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>5</sub>S<sub>2</sub>OP (401.45): C, 50.86; H, 4.02; N, 17.45; S, 15.97. Found: C, 50.61; H, 3.80; N, 17.65; S, 15.62.

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