Studies with Enamines: Route to Aminoazolopyrimidines and Arylazoazolopyrimidines

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An easy preparation of enaminonitrile derivatives and their transformation into new substituted azolopyrimidines is described. The one-step transformation was carried out under microwave irradiation and by classical heating methods. The use of microwave irradiation led to high conversion and shorter reaction times.

Key words: Azolopyrimidines, Enamines, Azoloazines, Microwave Irradiation

Introduction

The chemistry of azolopyrimidines has in the past received considerable interest [1 – 5] and is still an area of major interest [6, 7]. Recently azoloazines have been shown to be of antimicrobial, antioxidant [8] and agrochemical importance. Moreover they are a promising new class of dyes for D2T2 printing and hair dyes [9, 10].

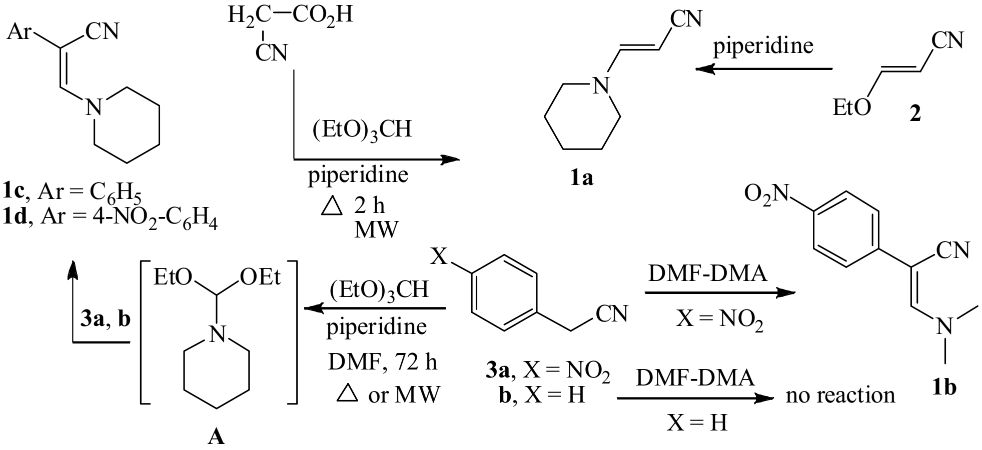
Microwave heating has been employed as a frequent resource for the improvement of classical reactions. The major benefits of performing reactions under microwave conditions are significant rate enhancements and higher product yields as compared to reactions which are run under conventional heating. Key advantages of modern, scientific microwave apparatus are their ability to control reaction conditions precisely by monitoring temperature/pressure and reaction times and ease of isolation of the products after work-up [11, 12].

In conjunction to our interest in the chemistry of enaminonitriles [13 – 16], we report here results of our work aimed at developing efficient environmentally friendly syntheses for several targeted azoloazines utilizing enamines **1a** – **d** as starting materials. In our chemical reactivity studies described here, we principally employed the intermediates **1d** due to their easy preparation and good yields of reactions.

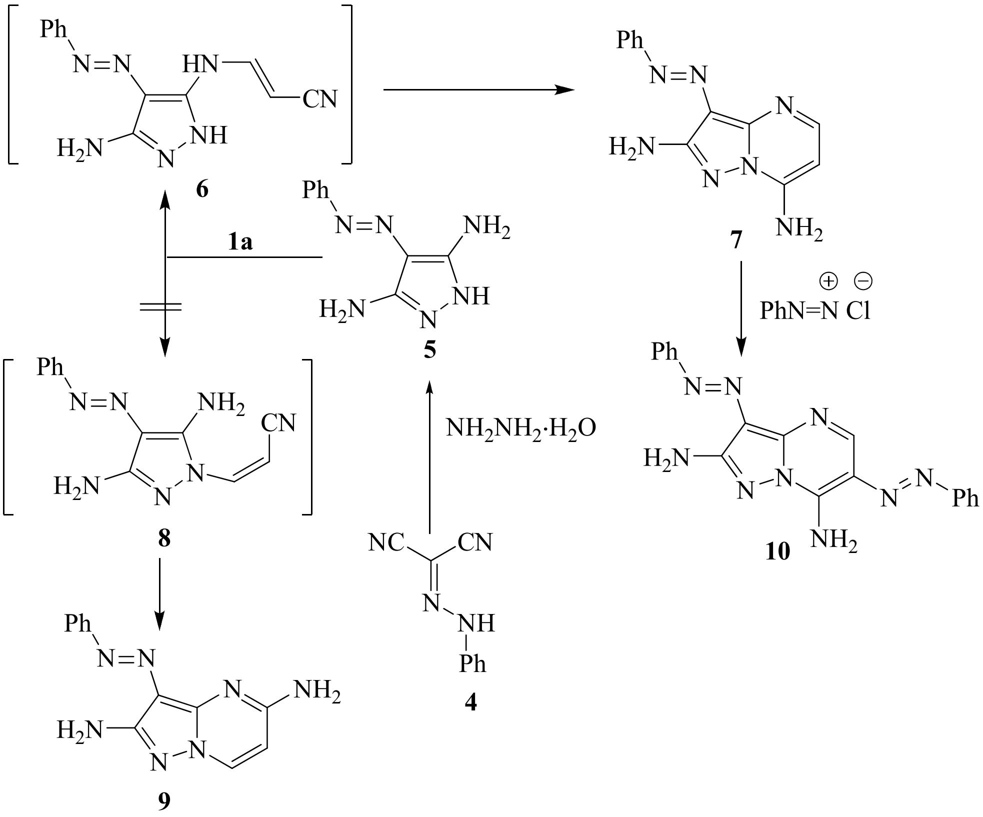
Result and Discussions

The enamine **1a** could be prepared either *via* heating cyanoacetic acid, piperidine and triethyl orthoformate in a microwave oven or, as has been described recently [6, 7], *via* heating a mixture of triethyl orthoformate, piperidine and cyanoacetic acid under reflux for two hours. A synthesis of **1a** *via* heating 3-ethoxyacrylonitrile (**2**) and piperidine in a microwave oven for five minutes was also achieved. This reaction required 12 hours reflux for completion [7] (Scheme 1).

The enaminonitrile **1b** could be easily obtained *via* reacting *p*-nitrobenzylcyanide (**3a**) and dimethylformamide dimethylacetal (DMF-DMA) in refluxing dioxane. Trials to condense benzyl cyanide (**3b**) with DMF-DMA failed. Compounds **1c**, **d** could be readily obtained by refluxing a mixture of **3a**, **b**, triethyl orthoformate and piperidine in DMF solution for 72 h to produce **1c** or 24 h to isolate **1d**. We believe that the *in situ*-generated amidoacetal 1-(diethoxymethyl) piperidine (A) is initially formed, and then this reacts with **3a**, **b** to yield the enaminonitriles **1c**, **d** [13]. This condensation could be effected by microwave heating, and the products were found identical in all details (melting point and TLC analysis, NMR) to the compounds obtained by the other method.



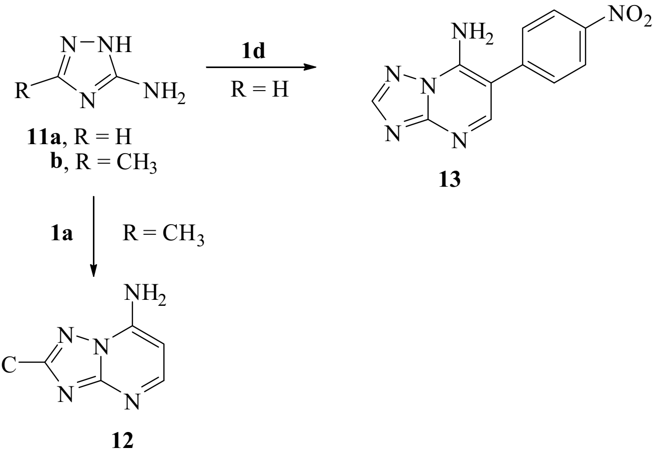
Scheme 1. DMF-DMA: dimethylformamide dimethylacetal.



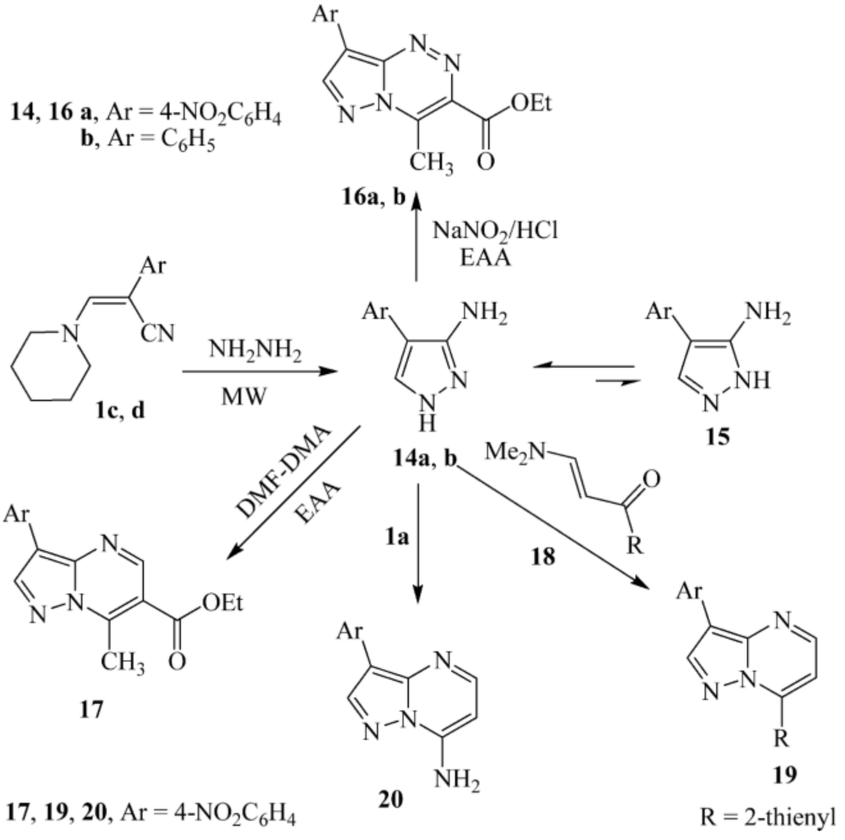
Scheme 2.

The yellow 4-(phenylazo)pyrazole-3,5-diamine (**5**) was prepared by heating 2-(phenylazo)mesoxalonitrile (**4**) and hydrazine hydrate in dioxane in a microwave oven or by conventional heating [17].

Compound **5** condensed with **1a** *via* piperidine elimination upon reflux in pyridine solution or upon heating in a microwave oven to yield products that may be formulated as **6**–**9** (Scheme 2). Thus ini-



Scheme 3.



Scheme 4. EAA: ethyl acetoacetate.

tial condensation with the exocyclic amino function would afford **6** which can then cyclizes into **7**. Alternately, **8** may be initially formed which then cyclizes into **9**. Acyclic structures **6** and **8** were readily ruled out based on the absence of a CN band in the IR spectrum and the presence of two amino functions according to the ^{1}H NMR spectrum.

Structure **7** is preferred over **9** based on the appearance of an NH_2 singlet at $\delta = 8.0$ ppm. Isomeric **9** should show this function at higher field [18, 19]. Compound **7** could be coupled with benzenediazonium chloride to yield **10** (*cf.* Scheme 2).

Similarly, aminotriazoles **11b** reacted with **1a** to yield **12**. Compound **12** could not be coupled further with aromatic diazonium salts (Scheme 3). It is of value to report that reaction of **11a** with the enamine **1d** yields **13**. Structure **13** was established based on the ^{1}H NMR spectrum which revealed the triazolopyrimidine CH signal at almost the same chemical shift as for **11a**, and an amino signal that appeared at $\delta = 8.2$ ppm. Compound **1c** failed to condense with **11a** or **11b**.

Enamine **1d** was readily converted into aminopyrazole **14a** on reflux with hydrazine hydrate in DMF solution or on heating in a microwave oven, also in DMF. However, **1c** did not react under similar conditions. On the other hand, under microwave irradiation and in the presence of acetic acid the aminopyrazole **14b** was formed (Scheme 4) [20].

Compounds **14a**, **b** reacted with sodium nitrite to afford a diazonium salt that coupled with ethyl acetoacetate to yield **16a**, **b**, while the reaction of **14a** with DMF-DMA followed by ethyl acetoacetate (EAA) yielded **17**. Reaction of **14a** with enamine **18** [21] and enaminonitrile **1a** afforded pyrazolopyrimidine **19** and **20**, respectively, (Scheme 4). The structures of these compounds were established based on their elemental analysis and spectral data (*cf.* Experimental Section).

Conclusion

In conclusion, *in situ* generation of less volatile amide acetals from piperidine diethylacetal enables to apply drastic reaction conditions in the condensation of amide acetals with active methylene compounds, so that less reactive compounds can be applied for condensation reactions. This method implies the use of less expensive chemicals. The conversion of the methylene compounds to enamines enhances the reactivity toward electrophiles. Shorter reaction times and higher yields were obtained by microwave irradiation.

Experimental Section

All melting points are uncorrected. IR spectra were recorded in KBr with a Bruker Vector 22 spectrophotometer. The ^{1}H NMR (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were recorded on a Varian Mercury 300 MHz spectrometer in [D$_6$]DMSO as solvent and with TMS as internal standard; chemical shifts are reported in δ units (ppm). Mass spectra were measured at 70 eV using a Shimadzu GCMS-QP-1000 EX mass spectrometer. Microanalyses were performed on a Leco CHN-932 instrument by the Microanalysis Unit of Cairo University. Microwave experiments were conducted in a CEM MARS oven. Compounds **1a** and **5** were provided by Prof. Elnagdi, while compounds **14b** and **18** were prepared as previously reported by us [20, 21].

*3-Dimethylamino-2-(4-nitrophenyl)acrylonitrile (**1b**)*

A mixture of **3a** (0.01 mol, 1.62 g) and DMF-DMA (0.012 mol) in dioxane (15 mL) was refluxed for three h and then cooled and poured onto water. The green solid product formed was collected by filtration and crystallized from ethanol to give **1b**. Yield 70 %; m. p. 178 – 180 °C. – IR (KBr): $\nu = 2222$ (CN), 1610 (C=C) cm^{-1}. – ^{1}H NMR (300 MHz,): $\delta = 3.27$ (s, 3 H, CH_3), 3.33 (s, 3 H, CH_3), 7.50 (d, 2 H, $J = 9$ Hz, Ar-H), 7.80 (s, 1 H, olefinic-H), 8.12 (d, 2 H, $J = 9$ Hz, Ar-H). – ^{13}C NMR (75.4 MHz,): $\delta = 43.64$ (2 *C*H$_3$), 97.27 (*C*=CH), 122.54 (CN), 123.36, 132.40, 144.45, 145.75, 150.50 (C=*C*H). – MS (EI, 70 eV): m/z (%) = 217 (100) [M]$^+$. – $C_{11}H_{11}N_3O_2$ (217.22): calcd. C 60.82, H 5.10, N 19.34; found C 60.85, H 5.03, N 19.30.

*General procedure for the preparation of compounds **1c**, **d***

Method A. To a mixture of 4-nitrobenzyl cyanide **3a** or benzyl cyanide **3b** (0.3 mol), triethyl orthoformate (0.32 mol), and piperidine (0.3 mol) DMF (40 mL) was added, and the solution was refluxed for 72 h. The reaction mixture was then cooled and poured onto water. The solid product formed was collected by filtration and crystallized from ethanol (**1c** 70 %; **1d** 65 %).

Method B. Under microwave irradiation. Into a round bottom flask of 250 mL equipped with a condenser, 4-nitrobenzyl cyanide **3a** or benzyl cyanide **3b** (0.3 mol), triethyl orthoformate (0.32 mol), piperidine (0.3 mol) and DMF (40 mL) were added, and the mixture was heated at reflux during 20 min (for **1c**) and 10 min (for **1d**) under microwave irradiation (at a constant power of 400 W). After cooling to r. t., the reaction mixture was poured onto water to give a solid, which was identical in all respects with that obtained from the above reactions (TLC, m. p., NMR), (**1c** 85 %; **1d** 77 %).

*2-Phenyl-3-(piperidin-1-yl)acrylonitrile (**1c**)*

Yield: 85 %; m. p. 116 – 117 °C. – IR (KBr): $\nu = 2190$ (CN), 1616 (C=C) cm^{-1}. – ^{1}H NMR (300 MHz,): $\delta = 1.60$

(s, 6 H, 3 CH_2), 3.63 (s, 4 H, 2 CH_2), 7.16 (s, 1 H, olefinic-H), 7.26 – 7.45 (m, 5 H, Ar-H). – ^{13}C NMR (75.4 MHz,): $\delta = 24.36$, 26.41, 51.96, 75.41 (*C*=CH), 121.59 (CN), 124.48, 125.51, 129.14, 137.27, 149.29 (C=*C*H). – MS (EI, 70 eV): m/z (%) = 212 (42) $[M]^+$. – $C_{14}H_{16}N_2$ (212.29): calcd. C 79.21, H 7.60, N 13.20; found C 79.29, H 7.67, N 13.17.

*2-(4-Nitrophenyl)-3-(piperidin-1-yl)acrylonitrile (**1d**)*

Yield: 77 %; m. p. 130 – 132 °C. – IR (KBr): $\nu = 2206$, (CN), 1618 (C=C), 1595, 1330 (NO_2) cm^{-1}. – ^1H NMR (300 MHz,): $\delta = 1.75$ (m, 6 H, 3 CH_2); 3.70 (m, 4 H, 2 CH_2); 7.10 (s, 1 H, olefinic-H); 7.45 (d, 2 H, $J = 10$ Hz, Ar-H), 8.08 (d, 2 H, $J = 10$ Hz, Ar-H). – MS (EI, 70 eV): m/z (%) = 257 (42) $[M]^+$. – $C_{14}H_{15}N_3O_2$ (257.29): calcd. C 65.35, H 5.88, N 16.33; found C 65.15, H 5.70, N 16.44.

*3-(2-Phenyldiazenyl)pyrazolo[1,5-a]pyrimidine-2,7-diamine (**7**)*

Method A. A mixture of **5** (0.01 mol, 2.02 g) and enaminonitrile **1a** (0.01 mol, 1.36 g) in pyridine (25 mL) was refluxed for 3 h. The reaction mixture was then acidified with concentrated hydrochloric acid, refluxed for 10 min and then poured onto water. The solid formed was collected by filtration and crystallized from ethanol (yield 65 %).

Method B. A mixture of **5** (0.01 mol, 2.02 g) and **1a** (0.01 mol, 1.36 g) in DMF (10 mL) was heated in a microwave oven for 5 min and then left to cool. The solid formed was collected and identified as **7** (m. p, mixed m. p. and TLC). Yield 80%; m. p. 185 – 187 °C. – IR (KBr): $\nu = 3340$ (NH_2), cm^{-1}. – ^1H NMR (300 MHz): $\delta = 6.65$ (d, 1 H, $J = 8$ Hz, 6-H), 7.20 – 7.35 (m, 5 H, Ar-H), 8.0 (s, 2 H, NH_2), 8.10 (d, 1 H, $J = 8$ Hz, H-5), 11.81 (s, 2 H, NH_2). – MS (EI, 70 eV): m/z (%) = 253 (56) $[M]^+$. – $C_{12}H_{11}N_7$ (253.26): calcd. C 56.91; H 4.38; N 38.71; found C 56.80, H 4.42, N 38.77.

*3,6-Di(2-phenyldiazenyl)pyrazolo[1,5-a]pyrimidine-2,7-diamine (**10**)*

A cold solution of benzenediazonium chloride (0.01 mol) was prepared by adding a solution of sodium nitrite (0.01 mol in 2 mL of H_2O) to a cold solution of the aniline in concentrated hydrochloric acid with stirring. The resulting solution of the benzenediazonium chloride was added to a cold solution of **7** in ethanol (50 mL) containing sodium acetate (5 g). The reaction mixture was stirred at room temperature for 30 min. The solid product formed was collected by filtration, washed with water and crystallized from ethanol. Yield 81 %; m. p. 162 – 163 °C. – IR (KBr): $\nu = 3360$ (NH_2) cm^{-1}. – ^1H NMR (300 MHz): $\delta = 7.35$ (s, 1 H, 5-H), 7.51 (t, 6 H, $J = 9$ Hz, Ar-H), 7.61 (s, 2 H, NH_2), 7.83 (d, 4 H, $J = 9$ Hz, Ar-H), 12.60 (s, 2 H, NH_2). – MS (EI, 70 eV): m/z (%) = 357 (44) $[M]^+$. – $C_{18}H_{15}N_9$ (357.37): calcd. C 60.50, H 4.23, N 35.27; found C 60.60, H, 4.30, N 35.30.

*2-Methyl-[1,2,4]triazolo[1,5-a]pyrimidin-7-amine (**12**)*

Method A. A mixture of **11b** (0.01 mol, 0.98 g) and enaminonitrile **1a** (0.01 mol, 1.36 g) in pyridine (25 mL) was refluxed for 3 h. The reaction mixture was left to cool to room temperature, and the solid formed was collected by filtration and crystallized from ethanol to afford **12** (yield 60 %).

Method B. A mixture of aminotriazole **11b** (0.01 mol, 0.98 g) and enaminonitrile **1a** (0.01 mol, 1.36 g) was heated in a microwave oven for 5 min. The resulting product was triturated with ethanol, and the formed solid was collected by filtration, crystallized from ethanol and identified as **12** (m. p. mixed m. p. and TLC). Yield 86 %; m. p. 222 – 224 °C. – IR (KBr): $\nu = 3340$ (NH_2) cm^{-1}. – ^1H NMR (300 MHz): $\delta = 2.25$ (s, 3 H, CH_3), 6.55 (d, 1 H, $J = 7$ Hz, 6-H), 7.90 (s, 2 H, N H_2), 8.15 (d, 1 H, $J = 7$ Hz, H-5). – ^{13}C NMR (75.4 MHz): $\delta = 14.8$ (CH_3), 95.90 (C-6), 145.7 (C-7), 150.3 (C-5), 153.2 (C-3a), 155.7 (C-2). – MS (EI, 70 eV): m/z (%) = 149 (44) $[M]^+$. – $C_6H_7N_5$ (149.15): calcd. C 48.32; H 4.73; N 46.95; found C 48.30, H 4.80, N 46.80.

*6-(4-Nitrophenyl)-[1,2,4]triazolo[1,5-a]pyrimidin-7-amine (**13**)*

Method A. A mixture of **11a** (0.01 mol, 0.84 g) and enaminonitrile **1d** (0.01 mol, 2.57 g) in pyridine (25 mL) was refluxed for 3 h. The reaction mixture was left to cool to room temperature, and the solid so formed was collected by filtration and crystallized from ethanol to afford **13** (yield 67 %).

Method B. A mixture of aminotriazole **11a** (0.01 mol, 0.84 g) and enaminonitrile **1d** (0.01 mol, 2.57 g) was heated in a microwave oven for 6 min. The same work up procedure as mentioned above was used. Yield; 88 %; m. p. 185 – 187 °C. – IR (KBr): $\nu = 3340$ (NH_2), 1578, 1366 (NO_2) cm^{-1}. – ^1H NMR (300 MHz): $\delta = 6.60$ (s, 2 H, NH_2), 7.45 (d, 2 H, $J = 10$ Hz, Ar-H), 7.75 (d, 2 H, $J = 10$ Hz, Ar-H), 7.89 (s, 1 H, 2-H), 8.68 (s, 1 H, 5-H). – MS (EI, 70 eV): m/z (%) = 256 (74) $[M]^+$. – $C_{11}H_8N_6O_2$ (256.22): calcd. C 51.56, H 3.15, N 32.80; found C 51.60, H, 3.00, N 32.95.

*4-(4-Nitrophenyl)-1H-pyrazol-3-amine (**14a**)*

Method A. A mixture of **1d** (0.01 mol, 2.57 g) and hydrazine hydrate (0.01 mol) in DMF (15 mL) was refluxed for 3 h. The reaction mixture was left to cool to room temperature, and the solid formed was collected by filtration and crystallized from ethanol yield (yield 60 %).

Method B. A mixture of enaminonitrile **1d** (0.01 mol, 2.57 g) and hydrazine hydrate (0.01 mol) in DMF (10 mL) was heated in a microwave oven for 5 min and the product worked up as mentioned above. Yield 85 %; m. p. 184 – 186 °C. – IR (KBr): $\nu = 3340$ (NH_2), 3280 (NH), 1565, 1360 (NO_2) cm^{-1}. – ^1H NMR (300 MHz): $\delta = 7.69$ (d, 2 H, $J = 9$ Hz, Ar-H), 7.82 (s, 2 H, NH_2), 8.15 (s, 1 H, NH), 8.22 (d, 2 H, $J = 9$ Hz, Ar-H), 8.32 (s, 1 H, pyrazole-H). – MS (EI, 70 eV): m/z (%) = 204 (55) $[M]^+$. – $C_9H_8N_4O_2$ (204.19): calcd. C 52.94, H 3.95, N 27.44; found C 52.90, H 4.05, N 27.40.

*Ethyl 4-methyl-8-substituted pyrazolo[5,1-c][1,2,4]-triazine-3-carboxylates (**16a**, **b**)*

A cold solution of pyrazolediazonium chloride (0.01 mol) was prepared by adding a solution of sodium nitrite (0.01 mol in 2 mL of H_2O) to a cold solution of the aminopyrazole **14a** in concentrated hydrochloric acid with stirring. The resulting solution of the pyrazolediazonium chloride was added to a cold solution of ethyl acetoacetate in ethanol (50 mL) containing sodium acetate (5 g). The reaction mixture was stirred at room temperature for 30 min. The solid product formed was collected by filtration, washed with water and crystallized from ethanol to afford **16a**, **b**.

*Ethyl 4-methyl-8-(4-nitrophenyl)pyrazolo[5,1-c]-[1,2,4]triazine-3-carboxylate (**16a**)*

Yield 68 %; m. p. 223 – 225 °C. – IR (KBr): $\nu = 1705$ (CO) 1560, 1367 (NO_2) cm^{-1}. – ^1H NMR (300 MHz): $\delta = 1.18$ (t, 3 H, $J = 7.5$ Hz, CH_3), 2.32 (s, 3 H, CH_3), 4.20 (q, 2 H, $J = 7.5$ Hz, CH_2), 7.20 (d, 2 H, $J = 10$ Hz, Ar-H), 8.18 (d, 2 H, $J = 10$ Hz, Ar-H), 8.32 (s, 1 H, H-7). – MS (EI, 70 eV): m/z (%) = 327 (90) $[M]^+$. – $C_{15}H_{13}N_5O_4$ (327.29): calcd. C 55.05, H 4.00, N 21.40; found C 54.95, H 4.10, N 21.20.

*Ethyl 4-methyl-8-phenyl pyrazolo[5,1-c][1,2,4]triazine-3-carboxylate (**16b**)*

Yield 78 %; m. p. 202 – 203 °C. – IR (KBr): $\nu = 1690$ (CO) cm^{-1}. – ^1H NMR (300 MHz): $\delta = 1.15$ (t, 3 H, $J = 7.5$ Hz, CH_3), 2.30 (s, 3 H, CH_3), 4.10 (q, 2 H, $J = 7.5$ Hz, CH_2), 7.20 – 7.45 (m, 5 H, Ar-H), 8.25 (s, 1 H, H-7). – MS (EI, 70 eV): m/z (%) = 282 (98) $[M]^+$. – $C_{15}H_{14}N_4O_2$ (282.30): calcd. C 63.82, H 5.00, N 19.85; found C 63.70, H 4.90, N 19.90.

*Ethyl 7-methyl-3-(4-nitrophenyl)pyrazolo[1,5-a]pyrimidine-6-carboxylate (**17**)*

A mixture of **14a** (0.01 mol, 2.04 g), DMF-DMA (0.01 mol) and ethyl acetoaceate (0.01 mol) in pyridine (25 mL) was refluxed for 3 h. The reaction mixture was left to cool to room temperature, and the solid formed was collected by filtration and crystallized from ethanol. Yield 69 %; m. p. 218 – 220 °C. – IR (KBr): $\nu = 1708$ (CO), 1570, 1355 (NO_2) cm^{-1}. – ^1H NMR (300 MHz): $\delta = 1.12$ (t, 3 H, $J = 7.5$ Hz, CH_3), 2.32 (s, 3 H, CH_3), 4.18 (q, 2 H, $J = 7.5$ Hz, CH_2), 7.45 (d, 2 H, $J = 9$ Hz, Ar-H), 7.92 (d, 2 H, $J = 9$ Hz, Ar-H), 8.22 (s, 1 H, 2-H), 8.52 (s, 1 H, 5-H). – MS (EI, 70 eV): m/z (%) = 326 (64) $[M]^+$. – $C_{16}H_{14}N_4O_4$ (326.32): calcd. C 58.89, H 4.32, N 17.17; found C 58.80, H 4.35, N 17.25.

*3-(4-Nitrophenyl)-7-thiophen-2-yl-pyrazolo[1,5-a]pyrimidine (**19**)*

A mixture of **14a** (0.01 mol, 2.04 g) and enaminone **18** (0.01 mol, 1.81 g) in pyridine (25 mL) was refluxed for 3 h. The reaction mixture was left to cool to room temperature, and the solid formed was collected by filtration and crystallized from ethanol to afford **19**. Yield 62 %; m. p. 250 – 251 °C. – IR (KBr): $\nu = 2985$ (CH Ar), 1565, 1370 (NO_2), cm^{-1}. – ^1H NMR (300 MHz): $\delta = 7.0 – 7.31$ (m, 3 H, thiophene-H), 7.45 (d, 2 H, $J = 9$ Hz, Ar-H), 7.55 (d, 1 H, $J = 7$ Hz, 6-H), 8.23 (d, 2 H, $J = 9$ Hz, Ar-H), 8.66 (s, 1 H, 2-H), 8.80 (d, 1 H, $J = 7$ Hz, 5-H). – MS (EI, 70 eV): m/z (%) = 322 (74) $[M]^+$. – $C_{16}H_{10}N_4O_2S$ (322.24): calcd. C 59.62, H 3.13, N 17.38, S 9.95; found C 59.50, H 3.20, N 17.35, S 10.0.

*3-(4-Nitrophenyl)-pyrazolo[1,5-a]pyrimidin-7-ylamine (**20**)*

A mixture of **14a** (0.01 mol, 2.04 g) and enaminonitrile **1a** (0.01 mol, 1.36 g) in pyridine (25 mL) was refluxed for 3 h. The reaction mixture was left to cool to room temperature, and the solid formed was collected by filtration and crystallized from ethanol to afford **20**. Yield 77 %; m. p. 160 – 162 °C. – IR (KBr): $\nu = 3350$ (NH_2) 1560, 1365 (NO_2) cm^{-1}. – ^1H NMR (300 MHz): $\delta = 6.59$ (d, 1 H, $J = 7$ Hz, 6-H), 7.15 (s, 2 H, NH_2), 7.55 (d, 2 H, $J = 10$ Hz, Ar-H), 8.16 (d, 2 H, $J = 10$ Hz, Ar-H), 8.33 (d, 1 H, $J = 7$ Hz, 5-H), 8.49 (s, 1 H, 2-H). – ^{13}C NMR (75.4 MHz): $\delta = 95.9$ (C-6), 102.2 (C-3), 122.36 (C-3′,5′),132.30 (C-2′,6′), 134.10 (C-3a), 135.20 (C-1′), 137.8 (C-2), 146.10 (C-4′), 148.7 (C-7), 155.5 (C-5). – MS (EI, 70 eV): m/z (%) = 255 (80) $[M]^+$. – $C_{12}H_9N_5O_2$ (255.23): calcd. C 56.47, H 3.55, N 27.44; found C 56.40, H 3.50, N, 27.55.

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