REACTIONS WITH HETEROCYCLIC AMIDINES: NEW ROUTES FOR THE SYNTHESIS OF NOVEL AZOLO[1,5-a]PYRIMIDINE, BENZO[4,5]IMIDAZO[1,2-a]PYRIMIDINE, SOME PYRIDINE, PYRAN AND PYRAZOLE DERIVATIVES CONTAINING THE ANTIPYRINE MOIETY

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† This paper is dedicated to the soul of Prof. Zaghloul E. Kandeel

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Abstract
Some novel pyrazolo[1,5-a]pyrimidines 5a,e, 1,2,4-triazolo[1,5-a]pyrimidine 10 and benzo[4,5]imidazo[1,2-a]pyrimidine 15 could be synthesized by reacting 3-dimethylamino-2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazole-4-carbonyl)-acrylonitrile (2) with 5-amino-3,4-substituted-1H-pyrazoles 3a-e, 3-amino-1,2,4-triazole 9 and 2-aminobenzimidazole 12 respectively. The reaction of 2 with 2-benzimidazolylacetonitrile (17) afforded the benzo[4,5]imidazo[1,2-a]pyridine 18. On the other hand, the reaction of 2 with hydrazine, phenylhydrazine, malononitrile dimer and ethyl cyanoacetate dimer produced the pyrazoles 22, 23, the pyridine 26 and the pyrone 28, respectively.

Introduction
1-Phenyl-2,3-dimethyl-3-pyrazoline-5-one (antipyrine or phenazone) has attracted a great deal of interest due to its wide applications in the field of pharmaceuticals. In continuation of our interest in the development of new and simple methods for the synthesis of polyfunctionally substituted heterocycles with anticipated biological activity that could be used as biodegradable agrochemicals, we report here on the reactivity of phenazonylacetonitrile (1) towards some nitrogen containing compounds. The work has resulted in the formation of a variety of heterocyclic compounds incorporating an antipyrine moiety. Also, the biological activity reported for pyrazolo[1,5-a]pyrimidines have stimulated chemists to develop the chemistry of this class of compounds. Enaminones have recently been reported as useful precursors for the synthesis of pyrazolo[1,5-a]pyrimidines. Therefore in continuation of our previous interest in the synthesis of a variety of heterocyclic systems from the readily obtainable inexpensive starting materials for biological screening program in our laboratory, we report here on the behavior of the hitherto unreported 3-dimethylamino-
2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazole-4-carbonyl)acrylonitrile (2) towards some nitrogen nucleophiles.

Results and discussion

It seemed much better to prepare compound 2 by heating an equimolar amounts of phenazonylacetonitrile (1) and N,N-dimethylformamide dimethyl acetal (DMFDMA) in dry xylene under gentle reflux for a short time rather than following a recently reported procedure by Kappe et al.19 The structure of compound 2 was elucidated on the basis of its elemental analysis and spectral data (Scheme 1).

Compound 2 reacted with some substituted 5-amino-1H-pyrazole derivatives 3a-e in ethanol in the presence of piperidine as a catalyst to afford the substituted pyrazolo[1,5-a]pyrimidine derivatives 5a-e. Structure of the latter products was confirmed on the basis of their correct elemental and spectral data (cf. experimental). The formation of compounds 5a-e assumed to take place via an initial Michael addition of the exocyclic amino group in compound 3 to the activated double bond in 2 to give the acyclic non-isolable intermediate 4 (route A), which undergo cyclization and aromatization via loss of both dimethylamine and water molecules producing the final isolable products 5a-e. Although the endocyclic imino group in compounds 3a-e is the most nucleophilic center,20-22 nevertheless, it is the most sterically hindered site23 therefore, the reaction is assumed to take place via route A rather than route B as shown in Scheme 1. Structure 5 was further confirmed via an independent synthesis of compound 5a by reacting equimolar amounts of 8a with 1 in ethanol under reflux to provide a product identical in all aspects (m.p., TLC, and spectra) with those of the proposed structure 5.

Similarly, compound 2 reacted with 3-amino-1,2,4-triazole (9) to yield the triazolopyrimidine 10 in good yield (Scheme 2). The structure of compound 10 was assigned by means of its spectral properties. Furthermore, the structure of compound 10 was confirmed by an independent synthesis of the same compound via reacting an equimolar amount of compound 11 with 1 in ethanol containing catalytic amount of piperidine under reflux to afford a product identical in all aspects to compound 10.
In contrast to its behavior towards compounds 5 and 10, compound 2 reacted with 2-aminobenzimidazole 12 under the same experimental conditions to afford the benzo[4,5]imidazo[1,2-a]pyrimidine derivative 15 (Scheme 2). The structure of compound 15 was established on the basis of elemental analysis and spectral data of the isolated reaction product. Formation of 15 is assumed to proceed via an initial Michael addition of the imino function in compound 12 to the activated double bond in 2 to form the non-isolable acyclic intermediate 13 (route B) that undergoes cyclization and
aromatization affording 15. The discrepancy in the behavior of compounds 5, 10 and 15 can be explained on the basis of steric factors. Thus if the final product proceeds according to route A, the formation of compound 16 would be difficult due to steric interaction of the antipyrinyl moiety and the benzene ring of benzimidazole nucleus.

In a similar manner, compound 2 was subjected to react with 2-benzimidazolylacetonitrile (17), under the same experimental conditions and afforded a yellow crystalline product, which was identified as 18 on the basis of its elemental analysis and spectral data (Scheme 2).

Also, compound 2 underwent cyclocondensation on treatment with hydrazine hydrate or its derivatives 19 to afford the non-readily available pyrazole 22. Structure of
was established on the basis of elemental analysis and spectral data of the isolated reaction product. On the other hand, compound 2 reacted with phenylhydrazine (19b) under the same experimental conditions and afforded the pyrazolone derivative 23. Formation of compounds 22 and 23 is assumed to proceed via addition of the amino function in hydrazine hydrate (19a) or phenylhydrazine (19b) to the activated double bond in 2 to form the non-isolable acyclic hydrazine derivatives 20 and 21 that underwent cyclization via either loss of one water molecule and dimethylamine providing 22 or addition of the NH-group to the cyano function yielding 23, respectively (Scheme 3).

\[
\begin{align*}
\text{NH}_2\text{NHR.H}_2\text{O} & \quad \text{An} \quad \text{O} \quad \text{CN} \\
\text{RHNHN} & \quad \text{NMe}_2 \\
\text{20} & \quad -\text{H}_2\text{O} \\
\text{22} & \quad -\text{HNMe}_2 \\
\text{An} & \quad \text{O} \quad \text{CN} \\
\text{Me}_2\text{N} & \quad \text{NHNHR} & \quad \text{HNMe}_2 \\
\text{21} & \quad \text{Ph} \\
\end{align*}
\]

Scheme 3

In addition, compound 2 was allowed to react with malononitrile dimer (24) to give the pyridine derivative 26. Compound 26 was assigned as a reaction product in accordance with elemental analysis and spectral data (cf. experimental). Following the same manner, compound 2 reacted with ethyl cyanoacetate dimer (27) to afford the pyrone derivative 28. Formation of the compound 28 is thought to proceed via initial
addition of the active methylene group in 27 to the activated double bond in 2 followed by elimination of ethanol and dimethylamine molecules producing the final isolable product 28 (Scheme 4).

\[ \text{27} \xrightarrow{\text{addition}} \text{28} \]

**Scheme 4**

**Experimental**

All melting points are uncorrected. IR spectra were recorded in KBr disks using a Shimadzu IR-740 spectrophotometer. \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker Ac-80 spectrometer with \([^{2}\text{H}_6]\) DMSO as solvent and TMS as internal standard; chemical shifts are reported in δ units (ppm). Mass spectra were measured on Gs/MS INCOS XL Finnigan MAT. Microanalysis was performed on LECOCHNS-932.
3-Dimethylamino-2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1\textit{H}-pyrazole-4-carbonyl)acrylonitrile (2).

A mixture of phenazonylacetonitrile 1 (0.01 mol), xylene (10 ml) and \( N,N \)-dimethylformamide dimethylacetal (0.01 mol) was heated under reflux for 2 hours, cooled and the solid product that deposited was filtered off and recrystallized from EtOH to give 2 as yellow crystals, yield 85%, m.p. 205-207 °C. IR (cm\(^{-1}\)): 2202 (CN), 1700 (CO), 1639 (CO-antipyrinyl). \(^1\)H NMR \( \delta_H \): 3.15 (s, 3H, CH\(_3\)), 3.20 (s, 3H, CH\(_3\)), 3.25 (s, 3H, CH\(_3\)), 3.36 (3H, CH\(_3\)), 7.22-7.42 (m, 5H, Ph), 7.9 (s, 1H, ylidenic H). \(^1\)^3C NMR \( \delta_C \): 187.0 (CO), 160.0 (CO-amide), 176.0, 174.0, 112.7, 91.5 (vinyllic-carbons), 142.0, 129.0, 118.9, 117.2, 112.0, 112.0 (aromatic-carbons), 40.7, 40.7, 35.3, 17.3 (aliphatic-carbons). Anal.Calcd. for C\(_{17}\)H\(_{18}\)N\(_4\)O\(_2\) (310.34). C, 65.79; H, 5.85; N, 18.05. Found: C, 65.60; H, 5.67; N, 18.23. MS: 310 m\(^+\)/z.

The preparation of compounds 5a-e.

Method (A):

A solution of 2 (0.01 mol) in abs. ethanol (30ml) was mixed with the appropriate pyrazole derivative 3a-e (0.01 mol) and a few drops of piperidine. The reaction mixture was heated under reflux for 3 hours, and the solvent was evaporated \textit{in vacuo}. The remaining product was collected by filtration and recrystallized to give 5a-e.

Method (B):

A solution of compound 8a (0.01 mol) in abs. ethanol (30ml) was treated with the the enamine 1 (0.01 mol). The reaction mixture was heated under reflux for 3 hours, and the solvent was evaporated \textit{in vacuo}. The remaining product was collected by filtration and recrystallized to give 5a.

7-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1\textit{H}-pyrazol-4-yl)-2-phenyl pyrazolo[1,5-\textit{a}]pyrimidine-6-carbonitrile (5a). Compound 5a was obtained as yellow crystals from ethanol, yield 80%, m.p. 265-267 °C. IR (cm\(^{-1}\)): 2229 (CN), 1656 (CO-antipyrinyl). \(^1\)H NMR \( \delta_H \): 2.38 (s, 3H, CH\(_3\)), 3.38 (s, 3H, CH\(_3\)), 7.05 (s, 1H, CH), 7.39-7.94 (m, 10H, 2Ph), 8.49 (s, 1H, CH). \(^1\)^3C NMR \( \delta_C \): 160.7 (CO-amide), 165.9, 161.8, 105.3 (pyrimidine-carbons), 150.4, 134.4, 103.7 (pyrazole-carbons), 154.5, 107.9 (vinyle-carbons), 118.7 (nitrile-carbon), 142.0, 136.0, 129.0, 129.0, 129.0, 128.5,
7-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-2-methyl pyrazolo[1,5-a]pyrimidine-6-carbonitrile (5b). Compound 5b was obtained as yellow crystals from ethanol, yield 70%, m.p. 225-227 °C. IR (cm\(^{-1}\)): 2229 (CN), 1656 (CO-antipyrinyl). \(^1\)H NMR \(\delta_H\): 2.36 (s, 3H, CH\(_3\)), 2.51 (s, 3H, CH\(_3\)), 3.33 (s, 3H, CH\(_3\)), 7.43-7.60 (m, 5H, Ph), 8.73 (s, 1H, CH). \(^{13}\)C NMR \(\delta_C\): 161.0 (CO-amide), 166.0, 161.9, 105.5 (pyrimidine-carbons), 144.4, 135.8, 105.3 (pyrazole-carbons), 154.5, 108.0 (vinyle-carbons), 118.2 (nitrile-carbon), 142.2, 129.0, 118.9, 112.0, 112.0 (aromatic-carbons), 35.5, 17.2, 13.9 (aliphatic-carbons). Anal. Calcd. for C\(_{24}\)H\(_{18}\)N\(_6\)O (406.15) C, 70.92; H, 4.46; N, 20.68. Found: C, 70.60; H, 4.67; N, 20.23. MS: 406 m\(^+\)/z.

7-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-3-bromo-2-phenyl pyrazolo[1,5-a]pyrimidine-6-carbonitrile (5c). Compound 5c was obtained as yellow crystals from aq. ethanol, yield 63%, m.p. 185-187 °C. IR (cm\(^{-1}\)): 2220 (CN), 1640 (CO-antipyrinyl). \(^1\)H NMR \(\delta_H\): 2.39 (s, 3H, CH\(_3\)), 3.39 (s, 3H, CH\(_3\)), 7.04-7.85 (m, 10H, 2 Ph), 8.48 (s, 1H, CH). \(^{13}\)C NMR \(\delta_C\): 160.9 (CO-amide), 165.7, 161.6, 105.1 (pyrimidine-carbons), 150.7, 134.7, 90.9 (pyrazole-carbons), 154.4, 107.7 (vinyle-carbons), 118.0 (nitrile-carbon), 142.3, 136.0, 129.1, 129.1, 129.1, 128.7, 127.2, 118.8, 112.2, 112.2 (aromatic-carbons), 35.6, 17.6 (aliphatic-carbons). Anal. Calcd. for C\(_{24}\)H\(_{17}\)BrN\(_6\)O (484.34) C, 59.39; H, 3.53; N, 17.32. Found: C, 59.60; H, 3.67; N, 17.23. MS: 484 m\(^+\)/z.

7-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-3-bromo-2-methyl pyrazolo[1,5-a]pyrimidine-6-carbonitrile (5d). Compound 5d was obtained as yellow crystals from ethanol, yield 70%, m.p. 194-196 °C. IR (cm\(^{-1}\)): 2224 (CN), 1645 (CO-antipyrinyl). \(^1\)H NMR \(\delta_H\): 2.39 (s, 3H, CH\(_3\)), 2.57 (s, 3H, CH\(_3\)), 3.39 (s, 3H, CH\(_3\)), 7.04-7.85 (m, 5H, Ph), 8.48 (s, 1H, CH). \(^{13}\)C NMR \(\delta_C\): 160.7 (CO-amide), 165.7, 161.6, 105.1 (pyrimidine-carbons), 144.7, 135.1, 92.5 (pyrazole-carbons), 154.4, 107.7 (vinyle-carbons), 118.0 (nitrile-carbon), 142.2, 129.0, 118.9, 112.0, 112.0 (aromatic-carbons). Anal. Calcd. for C\(_{24}\)H\(_{18}\)N\(_6\)O (406.15) C, 70.92; H, 4.46; N, 20.68. Found: C, 70.60; H, 4.67; N, 20.23. MS: 406 m\(^+\)/z.
2-Amino-7-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-3-(4-methoxyphenylazo)-pyrazolo[1,5-a]pyrimidine-6-carbonitrile (5e). Compound 5e was obtained as reddish brown crystals from aq. ethanol, yield 75%, m.p. 245-247 °C. IR (cm\(^{-1}\)): 3411-3263 (NH\(_2\)), 2219 (CN), 1656 (CO-antipyrinyl), 1616 (N=N). \(^1\)H NMR \(\delta_H\): 2.35 (s, 3H, CH\(_3\)), 3.32 (s, 3H, CH\(_3\)), 3.80 (s, 3H, OCH\(_3\)), 7.29-7.41 (m, 10H, 2 Ph), 8.55 (s, 1H, CH). \(^13\)C NMR \(\delta_C\): 160.9 (CO-amide), 165.7, 161.6, 105.1 (pyrimidine-carbons), 154.1, 132.7, 91.9 (pyrazole-carbons), 154.5, 107.9 (vinyle-carbons), 118.3 (nitrile-carbon), 159.0, 142.3, 143.2, 129.0, 129.0, 123.3, 123.3, 118.9, 114.6, 114.6, 112.2, 112.2 (aromatic-carbons), 56.2, 35.5, 17.4 (aliphatic-carbons). Anal. Calcd. for C\(_{19}\)H\(_{15}\)BrN\(_6\)O (423.27) C, 53.91; H, 3.57; N, 19.86. Found: C, 53.80; H, 3.67; N, 19.90. MS: 423 m\(^+\)/z.

Reaction of 2 with 3-amino-1,2,4-triazole, 2-aminobenzimidazole, benzimidazole-2-acetonitrile, hydrazine hydrate and phenylhydrazine: Formation of compounds 10, 15, 18, 22 and 23.

A solution of 2 (0.01 mol) and 0.01 mol of compounds 9, 12, 17, hydrazine and/or hydrazine hydrate in absolute ethanol (30 ml) containing catalytic amount of piperidine was heated under reflux for 8 hours. The reaction mixture was cooled and the solid product formed, was collected by filtration and recrystallized to give 10, 15, 16, 22 and 23, respectively.

7-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-1,2,4-triazolo[1,5-a]pyrimidine-6-carbonitrile (10). Compound 10 was obtained as yellow crystals from ethanol/DMF, yield 60%, m.p. 247-249 °C. IR (cm\(^{-1}\)): 2245 (CN), 1664 (CO-antipyrinyl). \(^1\)H NMR \(\delta_H\): 2.56 (s, 3H, CH\(_3\)), 3.26 (s, 3H, CH\(_3\)), 7.20-7.40 (m, 5H, Ph), 8.45 (s, 1H, CH). \(^13\)C NMR \(\delta_C\): 165.9, 161.8, 105.3 (pyrimidine-carbons), 160.7 (CO-amide), 147.9, 147.9 (triazole-carbons), 154.5, 107.9 (vinyle-carbons), 142.2, 129.0, 129, 119.0, 112.0, 112.0 (aromatic-carbons), 35.6, 17.5 (aliphatic-carbons). Anal. Calcd. for C\(_{17}\)H\(_{13}\)N\(_7\)O (331.33) C, 61.62; H, 3.95; N, 29.59. Found: C, 61.60; H, 3.67; N, 29.40. MS: 331 m\(^+\)/z.
1-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)benzo[4,5]imidazo[1,2-a]pyrimidine-3-carbonitrile (15). Compound 15 was obtained as yellow crystals from ethanol, yield 80%, m.p. 223-225°C. IR (cm⁻¹): 2205 (CN), 1641 (CO-antipyrinyl). ¹H NMR δH: 2.56 (s, 3H, CH₃), 3.26 (s, 3H, CH₃), 7.20-7.40 (m, 9H, Ph + benzoimidazolyl H), 8.45 (s, 1H, CH). ¹³C NMR δC: 166.7, 161.0, 105.3 (pyrimidine-carbons), 160.8 (CO-amide), 154.5, 107.9 (vinyl-carbons), 141.5, 137.9, 137.9, 122.9, 122.9, 115.4, 115.4 (benzimazole-carbons), 142.5, 129.1, 129, 119.5, 112.2, 112.0 (aromatic-carbons) 118.2 (nitrile-carbon), 35.4, 17.2 (aliphatic-carbons). Anal. Calcd. for C₂₂H₁₆N₆O (380.39) C, 69.46; H, 4.24; N, 22.09. Found: C, 69.60; H, 4.37; N, 22.00. MS: 380 m⁺/z.

1-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)benzo[4,5]imidazo[1,2-a]pyridin-2,4-dicarbonitrile (18). Compound 18 was obtained as yellow crystals from ethanol, yield 72%, m.p. 273-275 °C. IR (cm⁻¹): 2231 (CN), 1670 (CO-antipyrinyl). ¹H NMR δH: 2.42 (s, 3H, CH₃), 3.36 (s, 3H, CH₃), 7.51-8.01 (m, 9H, arom-H). ¹³C NMR δC: 163.5, 145.5, 109.3, 108.1 (pyridine-carbons), 160.6 (CO-amide), 154.2, 111.9 (vinyl-carbons), 141.8, 137.3, 137.3, 123.9, 123.9, 115.6, 115.6 (benzimazole-carbons), 143.5, 129.5, 129.5, 119.4, 112.6, 112.6 (aromatic-carbons) 118.5, 118.5 (nitrile-carbons), 35.6, 17.5 (aliphatic-carbons). Anal. Calcd. for C₂₄H₁₆N₆O (404.42) C, 71.28; H, 3.99; N, 20.78. Found: C, 71.34; H, 3.67; N, 20.70. MS: 404 m⁺/z.

1′,5′-Dimethyl-3′-oxo-2′-phenyl-2′,3′-dihydro-2H,1′H-[3,4′]bipyrazolyl-4-carbonitrile (22). Compound 22 was obtained as yellow crystals from ethanol, yield 90%, m.p. 275-278 °C. IR (cm⁻¹): 3300 (NH), 2189 (CN), 1652 (CO-antipyrinyl). ¹H NMR δH: 2.41(s, 3H, CH₃), 3.14 (s, 3H, CH₃), 7.28 (s, 1H, CH), 7.29-7.45 (m, 5H, Ph), 9.12 (s, 1H, NH). ¹³C NMR δC: 133.3, 133.3, 104.7 (pyrazole-carbons), 160.8 (CO-amide), 154.5, 118.0 (vinyl-carbons), 142.5, 129.2, 129.2, 119.3, 112.1, 112.1 (aromatic-carbons), 118.0 (nitrile-carbon), 35.4, 17.3 (aliphatic-carbons). Anal. Calcd. for C₁₅H₁₃N₃O (279.29) C, 64.51; H, 4.69; N, 25.08. Found: C, 64.60; H, 4.63; N, 25.18. MS: 279 m⁺/z.
4-(5-Amino-1-phenyl)-1H-pyrazole-4-carbonyl)-1,5-dimethyl-2-phenyl-1,2-dihydropyrazole-3-one (23). Compound 23 was obtained as yellow crystals from ethanol, yield 80%, m.p. 282-284 °C. IR (cm⁻¹): 3340-3256 (NH₂), 2200 (CN), 1650 (CO-antipyrinyl). ¹H NMR δ_H: 2.31(s, 3H, CH₃), 3.24 (s, 3H, CH₃), 5.63 (s, 2H, NH₂), 6.32 (s, 1H, CH), 6.66-7.45 (m, 10H, 2Ph). ¹³C NMR δ_C: 147.0, 139.0, 94.0 (pyrazole-carbons), 187.1 (CO), 160.8 (CO-amide), 166.5, 105.4 (vinyl-carbons), 142.5, 142.5, 139.7, 129.2, 129.2, 129.0, 129.0, 126.0, 118.3, 118.3, 112.0, 112.0 (aromatic-carbons), 35.5, 17.3 (aliphatic-carbons). Anal. Calcd. for C₂₁H₁₉N₅O₂ (373.40) C, 67.55; H, 5.13; N, 18.76. Found: C, 67.60; H, 5.23; N, 18.20. MS: 373 m⁺/z.

Reaction of 2 with malononitrile dimer and ethyl cyanoacetate dimer:

Formation of compounds 26 / and 28.

A solution of compound 2 (0.01 mol) and (0.01 mol) of malononitrile dimer or ethyl cyanoacetate dimer in dry pyridine (30 ml) was heated under reflux for 8 hours. The solvent was evaporated in vacuo and the product that deposited after cooling was collected by filtration and identified as 26 and 28 respectively.

2-Dicyanomethylene-6-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (26). Compound 26 was obtained as brown crystals from aq. ethanol, yield 60%, m.p. 220-222 °C. IR (cm⁻¹): 3300 (NH), 2192-2164 (CN), 1630 (CO-antipyrinyl). ¹H NMR δ_H: 2.52 (s, 3H, CH₃), 3.30 (s, 3H, CH₃), 7.19-7.46 (m, 6H, Ph and NH), 7.70 (s, 1H,CH). ¹³C NMR δ_C: 175.7, 154.2, 152.5, 144.1, 112.8, 109.0, 82.8, 52.1 (vinyl-carbons), 160.7 (CO-amide), 142.5, 129.2, 129.2, 119.3, 112.1, 112.1 (aromatic-carbons), 117.5, 117.5, 117.5, 117.5 (nitrile-carbons), 35.5, 17.3 (aliphatic-carbons). Anal. Calcd. for C₂₁H₁₃N₇O (379.36) C, 66.48; H, 3.45; N, 25.84. Found: C, 66.60; H, 3.22; N, 25.26. MS: 379 m⁺/z.

3-Amino-3-cyano-2-[5-cyano-6-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-2-oxo-2H-pyran-3-yl]acrylicacidethylester (28). Compound 28 was obtained as yellow crystals from ethanol, yield 75%, m.p. 192-194 °C. IR (cm⁻¹): 3300-3228 (NH₂), 2208 (CN), 1630 (CO-antipyrinyl). ¹H NMR δ_H: 1.3 (t, 3H, CH₃), 2.52 (s, 3H, CH₃), 3.00 (s, 2H, NH₂), 3.30 (s, 3H, CH₃), 4.19 (q, 2H, CH₂), 6.71-7.25 (m, 6H, Ph and CH-4). ¹³C NMR ([¹H₆] DMSO) δ_C: 162.5, 152.5, 139.7, 134.5, 128.4, 127.2, 109.3.

Povzetek
Sintetizirali smo nove derive pirazolo[1,5-a]pirimidina, 1,2,4-triazolo[1,5-a]pirimidina in benzo[4,5]imidazo[1,2-a]pirimidina iz ustrezno substituiranih pirazolov, triazolov oziroma iz 2-aminobenzimidazola.

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