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Simple and convenient procedures for the synthesis of novel heterocyclic compounds containing 1-phenyl-3-pyridylpyrazole moiety

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New 1-phenyl-3-pyridin-3-yl-1*H*-thieno[2,3-*c*]pyrazole-5-carboxylic acid ethyl ester has been obtained by the reaction of 5-chloro-1-phenyl-3-pyridin-3-yl-1*H*-pyrazole-4-carbaldehyde with ethyl bromoacetate and sodium sulphide. Alkaline hydrolysis of the ester gave the corresponding acid, while reaction of the same ester with hydrazine hydrate gave the corresponding hydrazide. Reactions of the hydrazide with potassium isocyanate and ammonium isothiocyanate gave the corresponding triazole and thiadiazole, respectively. The treatment of 5-chloro-1-phenyl-3-pyridin-3-yl-1*H*-pyrazole-4-carbaldehyde with hydroxylamine hydrochloride gave 4-cyanopyrazole-5-one. Reaction of the latter with $POCl_3$ afforded 5-chloro-4-cyanopyrazole, which cyclized by hydrazines to give pyrazolo[3,4-*c*]pyrazol-3-yl-amine derivatives. The reaction of 4-nitrosopyrazol-3-ol with *o*-aminophenol and *o*-phenylenediamine afforded the corresponding dipyrazolyl derivative, benzoxiazine and quinoxaline, respectively. The reduction of 4-nitrosopyrazol-3-ol with Zn/AcOH affored 4-(5-hydroxy-1-phenyl-3-pyridin-3-yl-1*H*-pyrazol-4-ylimino)2-phenyl-5-pyridin-3-yl-2,4-dihydropyrazol-3-one, which was also obtained from reaction of 2-phenyl-5-pyridine-3-yl-2*H*-pyrazole-3,4-dione with benzylamine. Finally, the reaction of 4-nitrosopyrazol-3-ol with 5-chloro-1-phenyl-3-pyridin-3-yl-1*H*-pyrazole-4-carbaldehyde gave 3,5-diphenyl-7-pyridin-3-yl-1-pyridin-4-yl-3,5-dihydro-4-oxa-2,3,5,6,8-pentaazocyclopenta [*f*]azulene.

Keywords: pyridyl pyrazolone, thieno[2,3-*c*]pyrazole, 4-nitrosopyrazole, Vilsmeier-Haack reaction.

INTRODUCTION

5-Pyrazolones are very important class of heterocyclic compounds due to their biological and pharmacological activities [1, 2] such as anti-inflammatory [3], herbicidal [4], fungicidal [5], bactericidal [5], plant growth regulation [4], antipyretic properties [6] and protein kinase inhibiting effect [7]. They are also used as key starting materials for the synthesis of commercial arylazopyrazolone dyes [8, 9]. In conjunction with our interest in preparing pyrazolone derivatives, we tried to prepare sulphur heterocyclic moieties fused to pyrazole ring, which might have some interesting bioactive properties. We report herein the results of the reactions of 5-chloro-1-phenyl-3-pyridin-3-yl-1*H*-pyrazole-4-carbaldehyde and 4-nitroso-2-phenyl-5-pyridin-3-yl-2*H*-pyrazol-3-ol with different readily available reagents.

RESULTS AND DISCUSSION

Firstly, the Vilsmeier-Haack reaction of 2-phenyl-5-pyridin-3-yl-2,4-dihydro-pyrazol-3-one (**1**) gave 5-chloro-1-phenyl-3-pyridin-3-yl-1*H*-pyrazole-4-carbaldehyde (**2**) in 55% yield. Treatment of (**2**) with ethyl bromoacetate and sodium sulphide in ethanol produced 1-phenyl-3-pyridin-3-yl-1*H*-thieno [2,3-*c*]pyrazole-5-carboxylic acid ethyl ester (3) in 70% yield.

Alkaline hydrolysis of (**3**) gave 1-phenyl-3-pyridine-3-yl-1*H*-thieno[2,3-*c*]pyrazole-5-carboxylic acid (**4**) in 85% yield. The reaction of (**3**) with hydrazine hydrate afforded 1-phenyl-3-pyridine-3-yl-1*H*-thieno[2,3-*c*]pyrazole-5-carboxylic acid hydrazide (**5**) in 65% yield. When compound (**5**) reacted with potassium cyanate in 50% acetic acid cyclization took place to give 5-(1-phenyl-3-pyridin-3-yl-1*H*-thieno[2,3-*c*]pyrazol-5-yl)-4*H*[1,2,4]-triazol-3-ol (**6**) in 50% yield. Similarly, treatment of (**5**) with ammonium thiocyanate in ethanol in presence of concentrated HCl gave (1-phenyl-3-py-ridin-3-yl-1*H*-thieno[2,3-*c*]pyrazol-5-yl)-[1,3,4]thia-diazol-2-yl-amine (**7**) in 45% yield (Scheme 1). This result is consistent with the one that was reported by Balagh *et al.* [10].

The reaction of 5-chloropyrazole-4-carbaldehyde (**2**) with hydroxylamine hydrochloride in ethanol gave directly 5-oxo-1-phenyl-3-pyridin-3-yl-4,5-dihydro-1*H*-pyrazole-4-carbonitrile (**10**) in 85% yield through the removal of HCl from the nonisolable oxime (**8**). The chlorination of compound (**10**) with $POCl_3$ gave 5-chloro-1-phenyl-3-pyridin-3-yl-1*H*-pyrazole-4-carbonitrile (**11**) in 90% yield. Condensation of compound (**11**) with hydrazine hydrate and phenyl hydrazine afforded the corresponding 6-phenyl-4-pyridin-3-yl-1,6-dihydro-pyrazolo[3,4-*c*] pyrazol-3-yl amine (**12a**) and 1,6-diphenyl-4-pyri-

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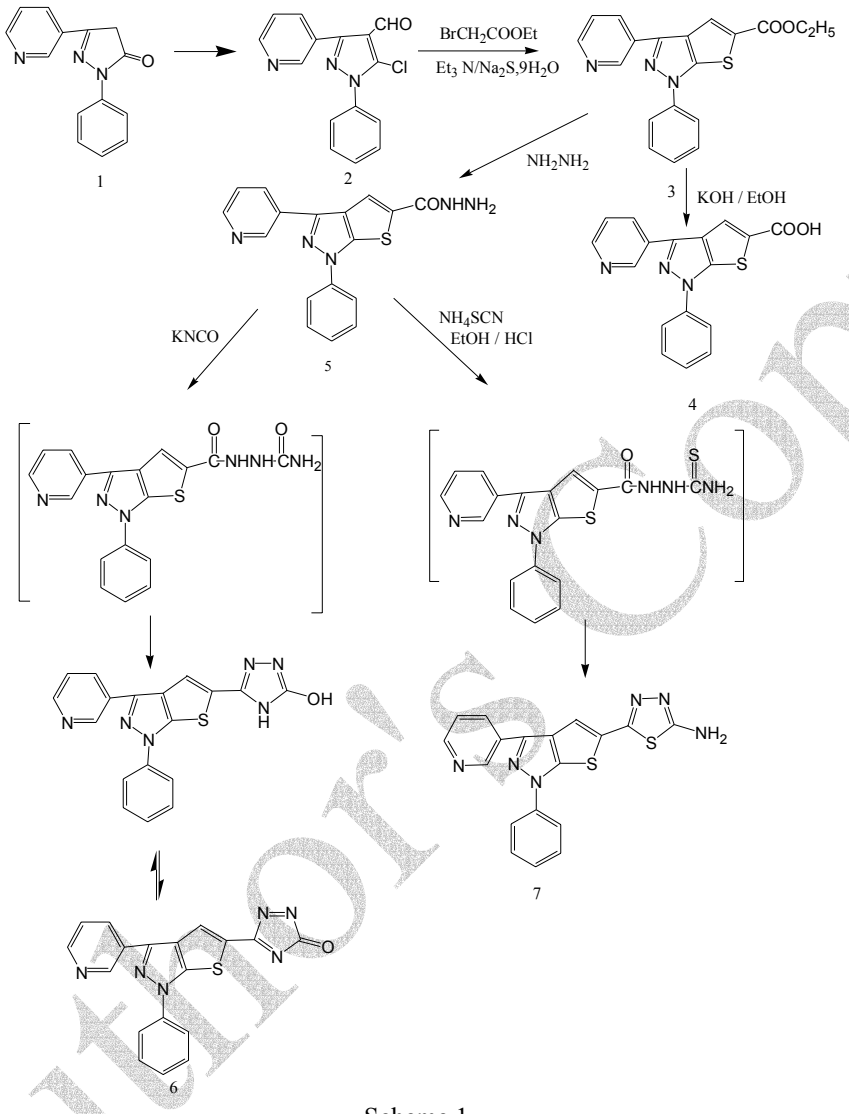
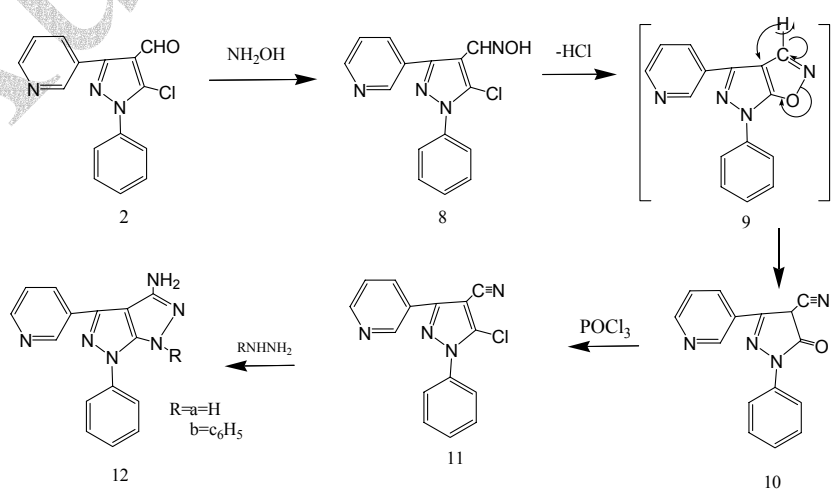
din-3-yl-1,6-dihydro-pyrazolo[3,4-*c*]pyrazol-3-yl amine (**12b**). The mechanism supposed by us for the reaction is outlined in Scheme 2. This mechanism is in accordance with that proposed by El-Sayed *et al*. [11].

The intermediate products were characterised by spectroscopic methods including IRS, NMR, mass spectra and microanalysis (Tables 1, 2).



Scheme 1.



Scheme 2.

Table 1. Physical data of compounds **2**–**25**.

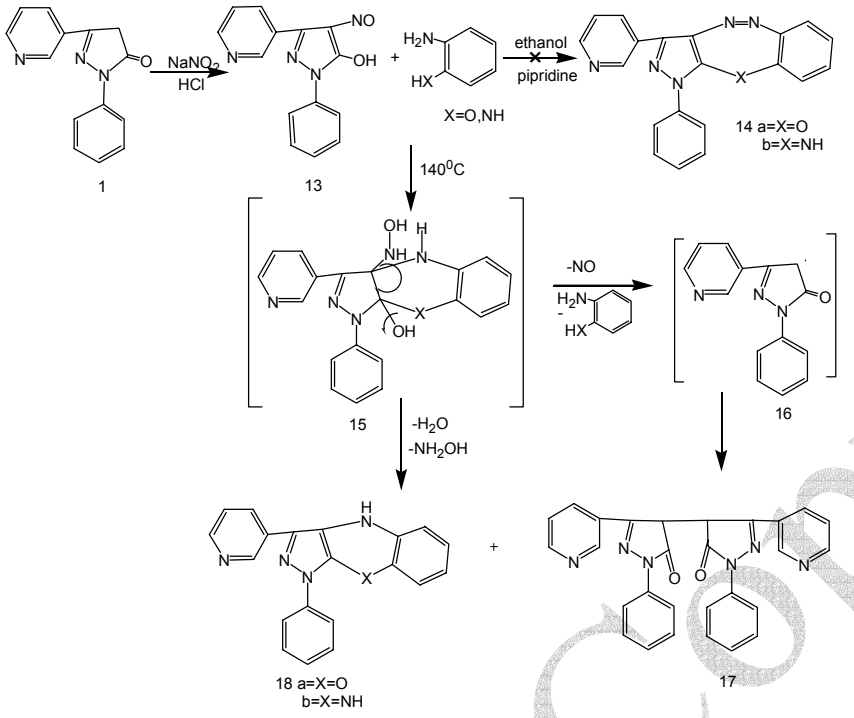
Compound	m.p., °C	Yield %, (colour)	Molecular formula, mass	Analysis, % Calculated/Found				
				C	H	N	Cl	S
2	110–112	55	$C_{15}H_{10}N_3OCl$	63.50	3.55	14.81	12.50	-
		(pale yellow)	283.71	63.23	3.34	14.75	12.32	
3	160–161	70	$C_{19}H_{15}N_3O_2S$	65.31	4.33	12.03	-	9.18
		(white)	349.41	65.20	4-28	11.84		9.00
4	> 300	85	$C_{17}H_{11}N_3O_2S$	63.54	3.45	13.08	-	9.98
		(white)	321.06	63.45	3.35	12.93		9.87
5	258–259	65	$C_{17}H_{13}N_5OS$	60.88	3.91	20.88	-	9.56
		(pale yellow)	335.38	60.52	3.85	20.78		9.40
6	243–245	50	$C_{18}H_{12}N_6OS$	59.99	3.36	23.23	-	8.90
		(pale yellow)	360.39	59.88	3.25	22.98		8.75
7	275–277	45	$C_{18}H_{12}N_6S_2$	57.43	3.21	22.32	-	17.04
		(yellow)	376.46	57.21	3.00	22.10		16.85
10	160–162	85	$C_{15}H_{10}N_4O$	68.69	3.84	21.36	-	-
		(pale yellow)	262.27	68.44	3.64	21.14		
11	150–152	90	$C_{15}H_9N_4Cl$	64.18	3.23	19.96	12.63	-
		(yellow)	280.71	63.98	3.12	19.88	12.22	
12a	210–212	88	$C_{15}H_{12}N_6$	62.21	4.38	30.42	-	-
		(yellow)	276.30	61.88	4.23	30.22		
12b	165–168	30	$C_{21}H_{16}N_6$	71.58	4.58	23.85	-	-
		(dark orange)	352.39	71.20	4.33	23.61		
13	245-248	80	$C_{14}H_{10}N_4O_2$	63.15	3.79	21.04	-	-
		(orange)	266.25	62.89	3.55	20.80		
17	190–192	50	$C_{28}H_{20}N_6O_2$	71.17	4.27	17.79	-	-
		(buff)	472.16	70.86	4.02	17.43		
18a	125–127	60	$C_{20}H_{14}N_4O$	73.61	4.32	17.17	-	-
		(dark brown)	326.35	73.23	4.12	16.94		
18b	184–185	75	$C_{20}H_{15}N_5$	73.83	4.65	21.52	-	-
		(yellow)	325.37	73.44	4.33	21.31		
19	122–124	60	$C_{14}H_9N_3O_2$	66.93	3.61	16.73	-	-
		(yellow)	251.24	66.63	3.33	16.55		
23	270–272	70	$C_{28}H_{19}N_7O_2$	69.27	3.94	20.20	-	-
		(red violet)	485.50	69.02	3.74	19.98		
25	250–252	75	$C_{29}H_{19}N_7O$	72.34	3.98	20.36	-	-
		(brown)	481.51	72.13	3.77	20.11		

The nitrosation of 2-phenyl-5-pyridin-3-yl-2,4-dihydro-pyrazol-3-one (**1**) gave 4-nitroso-2-phenyl-5-pyridin-3-yl-2*H*-pyrazol-3-ol (**13**) in 80% yield (Scheme 3). When compound (**13**) was heated with 2-aminophenol and 2-phenylenediamine at 140°C with ammonium acetate afforded the dimer (**17**), pyrazolo[3,4-*b*]benzoxazine (**18a**) and pyrazolo [3,4-*b*]quinoxaline (**18b**). This result could be explained by the nucleophilic attack of both amino groups of 2-phenylenediamine or hydroxyl and amino groups of *o*-aminophenol on the C_4 and C_5 of nitroso compound (**13**) to give intermediate (**15**) followed by simultaneous elimination of both water and hydroxylamino molecules yielding the pyrazolo[3,4-b]benzoxiazine (**18a**) and pyrazolo[3,4-b] quinoxaline (**18b**) (Scheme 3). However, dipyrazolyl compound (**17**) could be formed from pyrazole radical (**16**), which would be obtained from the intermediate (**15**) *via* elimination of an amine molecule and nitric oxide (Scheme 3). Analogous results were previously reported by El-Rady [12].

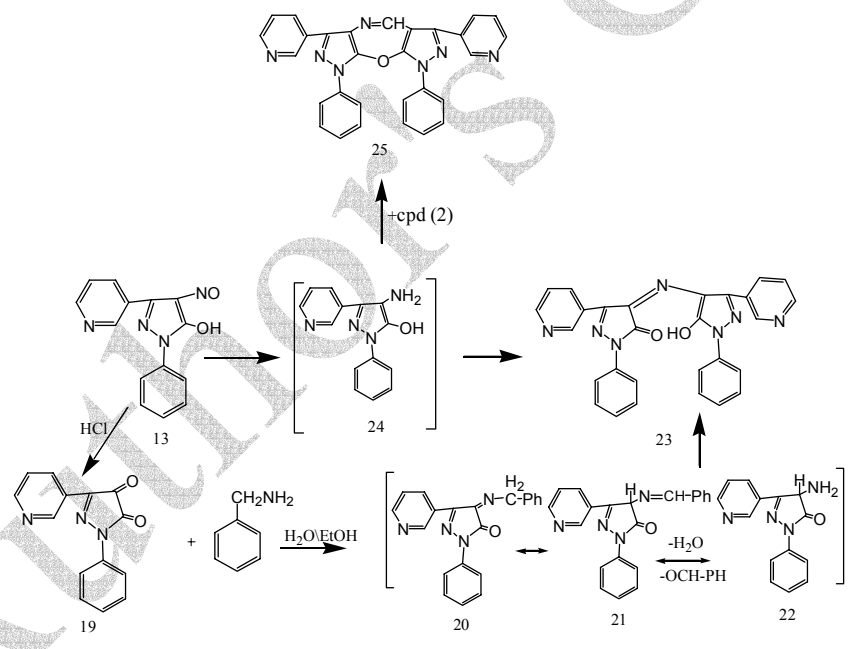
The acidic hydrolysis of 4-nitrosopyrazole (**13**) with concentrated HCl at 0°C gave the expected dione (**19**) in 60% yield (Scheme 4). Compound (**23**) could be obtained by two routes: (a) by the reaction of compound (**19**) with benzylamine in alcoholic medium, which produced the imine intermediates (**20**) and (**21**) followed by air oxidation of amino compound (**22**) to afford (**23**). The route (b) involved the air oxidation of intermediate (**24**). Finally, compound (**25**) was obtained in 75% yield by the reaction of (**2**) with the amino intermediate (**24**), which could be obtained by reduction of nitroso compound (**13**).

EXPERIMENTAL

All melting points were measured on a Gallen-Kamp melting point apparatus and are uncorrected. The IR spectra were measured on Perkin-Elmer-1430 spectrophotometer using KBr tablets technique. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements at Chemistry Department, University of Wales Swansea, UK.



Scheme 3.



Scheme 4.

Low-resolution mass spectra were recorded on a VG 12.253 spectrometer, electron impact (EI) at 70 eV. Microanalyses were performed by the Microanalysis Laboratory at Cairo University. Progress of reaction was monitored by thin-layer chromatography (TLC) using benzene/acetone (3:1) mixture as an eluent.

5-Chloro-1-phenyl-3-pyridin-3-yl-1H-pyrazole-4-carbaldehyde (**2**). The pyrazolone (**1**) [13] (1.3 g, 0.0057 mol) was added to a cold Vilsmeier reagent prepared by the addition of POCl3 (2.75 ml, 0.0285 mol) to DMF (5 ml, 0.068 mol) at 0°C, and the reaction mixture was heated for 8 h at 80°C. The reaction mixture was poured onto ice-cold water (10 ml) and basified with K_2CO_3 solution to reach pH = 9. The pale yellow solid phase thus separated was filtered and recrystallized from benzene.

1-Phenyl-3-pyridin-3-yl-1H-thieno[2,3-c]pyrazole-5-carboxylic acid ethyl ester (**3**). A solution of (**2**) (22.98 g, 0.081 mol) in ethanol (50 ml) was added to a solution of sodium sulphide nonahydrate (19.41 g 0.081 mol) in ethanol (500 ml) at 40°C. The reaction mixture was refluxed for 2 h, and then ethyl bromoacetate (9.0 ml, 0.0081mol) was added in a

dropwise manner. The reaction temperature was kept constant at 50°C and triethylamine (11 ml) was added and the reaction mixture was allowed to stay overnight at room temperature. The precipitate, which was formed, was then filtered and recrystallized from ethanol.

1-Phenyl-3-pyridin-3-yl-1H-thieno[2,3-c]pyrazole-5-carboxylic acid (**4**). A solution of (**3**) (3.5 g, 0.01 mol) in a mixture of ethanol (62.5 ml) and water (15 ml) was treated with aqueous 85% potassium hydroxide (0.95 g, 0.017 mol). The reaction mixture was refluxed for 2 h. The reaction mixture was left to cool down and water was added to dissolve the salt obtained. Concentrated hydrochloride acid was added in a dropwise manner until the solution became acidic. The formed solid phase was filtered, washed with water and recrystallized from water/ethanol solvent.

1-Phenyl-3-pyridin-3-yl-1H-thieno[2,3-c]pyrazole-5-carboxylic acid hydrazide (**5**). A mixture of (**3**) (3.5 g, 0.01 mol), 98% hydrazine hydrate (7.5 g, 0.15 mol) and ethanol (100 ml) was heated under reflux on a steam bath for 2 h. A colourless solid was formed, filtered and recrystallized from ethanol.

5-(1-Phenyl-3-pyridin-3-yl-1H-thieno[2,3-c]pyrazol-5-yl)-4H-[1,2,4]-3-ol (**6**). A solution of potassium cyanate (1.7 g, 0.022 mol) in (10 ml) water was added dropwise to a cold (0°C) solution of (**5**) (6.7 g, 0.02 mol) a mixture of acetic acid (40 ml) and water (40 ml). The reaction mixture was left for one hour at 0°C upon stirring and then heated under reflux for 4 h. A pale yellow solid was formed after 3 h. The formed solid phase was filtered, washed with water, dried and recrystallized from ethanol.

5-(1-Phenyl-3-pyridin-3-yl-1H-thieno[2,3-c]pyrazol-5-yl)-4H-[1,3,4]thiodiazol-2-ylamine (**7**). A mixture of (**5**) (3.35 g, 0.01 mol), ammonium thiocyanate (2.3 g, 0.03 mol) and concentrated HCl (9 M, 4 ml) in ethanol (200 ml) was heated under reflux for 15 h. The solvent was removed by distillation and water (500 ml) was added. The formed solid phase was dried and recrystallized from ethanol.

5-Oxo-1-phenyl-3-pyridin-3-yl-4,5-dihydro-1H-pyrazole-4-carbonitrile (**10**). Hydroxylamine hydrochloride (2.0 g, 0.29 mol) in water (5 ml) was treated with NaOH solution (4 M) to reach pH = 8. A solution of (2) (2.83 g, 0.01 mol) in ethanol (40 ml) was added and the reaction mixture was heated under reflux for 2 h. The mixture was left to cool down, poured into ice-cold water (100 ml) and acidified with 20% aqueous HCl (4 M). The formed solid phase was filtered, washed with water, dried and recrystallized from ethanol.

5-Chloro-1-phenyl-3-pyridin-3-yl-4,5-dihydro-1H-pyrazole-4-carbonitrile (**11**). Compound (**10**) (2.6 g, 0.01 mol) was heated under reflux with $POCl_3$ (15 ml) for 1 h. The reaction mixture was left to cool down, poured into ice-cold water. The formed solid phase was filtered and recrystallized from ethanol.

Table 2. Spectroscopic data of compounds **2**–**25**.

Comp	IR spectra (ν_{max} in cm^{-1})	^1H NMR (δ in ppm), ^{13}C NMR (δ in ppm), Mass spectra
2	1680 (C=O), 1580 (C=N)	δ 7.3–9.3 (m, 9H, Ar–H), δ 10.0 (s, 1H,CHO), M.S: 283 (100%).
3	1605 (C=N), 1599 (C=O)	δ 1.35 (t, 3H, CH_3CH_2O), δ 4.35 (q, 2H, CH_3CH_2O), δ 7.4–9.3 (m, 9H, Ar–H), δ 7.5 (s, 1H, H_4), M.S: 349 (75%).
4	3050 (OH), 1581(C=N)	δ 7.4–9.3 (m, 9H, Ar–H), δ 7.5 (s, 1H, H_4), δ 11 (s, 1H, OH), M.S : 321 (100%).
5	1660 (C=O), 1620 (NH_2), 1605 (C=N), 1570 (C–N–H amide)	δ 4.6 (s, 2H, exch., NH_2,), δ 7.4–9.2 (m, 9H, Ar–H), δ 7.5 (s, 1H, H_4), δ 9.9 (s, exch., 1H, NH), 107 (C_{2c}), 124.64 (C_{3c}), 138.10 (C_4), 142.29 (C_3), 143.09 (C_5), 118.02, 126.8, 130.44, 138.86 (C_{phenyl}), 128.86, 133.51, 134.20, 147.35, 150.17 ($C_{pyridyl}$), 161.86 (C=O), M.S: 335 (35%).
6	3450 (OH), 3100 (NH), 1650 (C=N)	δ 6.2 (s, exch., 1H, OH), δ 7.4–9.3 (m, 9H, Ar–H), δ 7.5 (s, 1H, H_4), δ 10.4 (s, exch., 1H, NH); M.S: 360 (80%).
7	3390 (NH_2), 1605 (C=N)	δ 6 (s, exch., 2H, NH_2), δ 7.4–9.3 (m, 9H, Ar–H), δ 7.5 (s, 1H, H_4), M.S: 376 (65%)
10	2220 (C≡N), 1660 (C=O), 1610 (C=N)	δ 3.4 (s, 1H, H_4), δ 7.4–9.2 (m, 9H, Ar–H), M.S: 263 (100%).
11	2230 (C≡N), 1612 (C=N)	δ 7.4–9.2 (m, 9H, Ar–H); M.S : 280 (90%).
12a	3450 (NH_2), 3100 (NH), 1605 (C=N)	δ 4.2 (s, exch., 2H, NH_2), δ 7.4–9.2 (m, 9H, Ar–H), δ 13.3 (s, exch., 1H, NH); M.S: 276 (80%).
12b	3300 (NH_2), 1612 (C=N)	δ 4 (s, exch., 2H, NH_2), δ 7.4–9.2 (m, 14H, Ar–H), M.S: 352 (75%).
13	3380 (OH), 1604 (NO)	δ 4.8 (s, 1H, OH), δ 7.3–9.1 (m, 9H, Ar–H), 118.51 (C_4), 128.68 (C_3), 139.37 (C_5), 118.87, 123.86, 129.05, 135.05 (C_{phenyl}), 124.28, 135.78, 146.89, 149.13, 149.91 ($C_{pyridyl}$); M.S: 266 (100%).
17	1700 (C=O), 1612 (C=N)	δ 3.1 (s, 2H, H_4, $H_{4'}$), δ 7.2–9.3 (m, 18H, Ar–H); M.S: 472 (34%).
18a	3150 (NH), 1615 (C=N), 1320 (C-O)	δ 6 (s, exch., 1H, NH), δ 7.0–9.3 (m, 13H, Ar–H; M.S: 326 (56%).
18b	3150 (NH), 1620 (C=N)	δ 6.2 (s, exch., 2H, NH), δ 7.3–9.1 (m, 13H, Ar–H; M.S: 325 (34%)
19	1670(C=O), 1625(C=N)	δ 7.3–9.1 (m, 9H, Ar–H), 153.65 (C_5), 187.73 (C_4), 160 (C_3), 120.42, 124.16, 128.73, 138.31 (C_{phenyl}), 123.70, 126.3, 136.25, 150.30, 152.1 ($C_{pyridyl}$); M.S: 251 (100%).
23	3030 (OH), 1760 (=N), 1690 (C=N)	δ 5.4 (s, 1H, OH), δ 7.3–9.3 (m, 18H, Ar–H); M.S : 485 (98%).
25	1670(C=N), 1612 (CH=N), 1312 (C–O)	δ 7.3-9.2(m, 18H, Ar–H), δ 9.7 (s, 1H, CH=N); M.S : 481 (100%).

6-Phenyl-4-pyridine-3-yl-1,6-dihydro-pyrazolo [3,4-c]pyrazol-3-ylamine (**12a**) and *1,6-diphenyl-4-pyridin-3-yl-1,6-dihydro-pyrazolo[3,4-c]pyrazol-3-yl amine* (**12b**). Compound (**11**) (2.8 g, 0.01 mol) was heated with hydrazine derivatives (0.51 mol) for 6 h in ethanol (30 ml). The reaction mixture was left to cool down and poured into water. The formed solid phase was filtered and recrystallized from ethanol.

4-Nitroso-2-phenyl-5-pyridin-3-yl-2H-pyrazol-3-ol (13). A solution of 2-phenyl-5-pyridin-3-yl-2,4-dihydro-pyrazol-3-one (**1**) (2.37 m, 0.01 mol) in acetic acid (40 ml) was added in a dropwise manner to a solution of sodium nitrite (0.075 g, 0.01 mol) in water (2 ml). The mixture was left for 15 min upon stirring. An orange solid phase was formed, filtered and washed with petroleum ether.

2,2′-Dipenyl-5,5′-di-pyridin-3-yl-2,4,2′,4′-tetra-hydro-[4,4′]bipyrazolyl-3,3′-dione (**17**). A mixture of (**13**) (0.8 g, 0.003 mol), ammonium acetate (1 g, 0.013 mol), *o*-aminophenol and/or *o*-phenylene-diamine (0.003 mol) and ammonium acetate (1 g, 0.013 mol) was heated at 140°C for 30 min then diluted with methanol. A buff crystal was precipitated, washed with hot methanol and filtered.

1-Phenyl-3-pyridin-4-yl-4-hydro-1H-pyrazolo [3,4-b]benzoxiazine (**18a**) and *1-phenyl-3-pyridin-4-yl-4,9-dihydro-1H-pyrazolo[3,4-b]quinoxaline* (**18b**). A mixture of (**13**) (0.8 g, 0.003 mol), ammonium acetate (1 g, 0.013 mol), *o*-aminophenol and/or *o*-phenylenediamine (0.003 mol) and ammonium acetate (1 g, 0.013 mol) was heated at 140°C for 30 min, diluted with methanol, the formed precipitate was filtered. The filtrate was concentrated and the coloured precipitate was filtered off and recrystallized from ethanol.

2-*Phenyl-5-pyridin-3-yl-2H-pyrazole-3,4-dione* (**19**). To a stirred solution of (**13**) (2.66 g, 0.01 mol) in ether (100 ml), 10% H_2SO_4 (100 ml) was added dropwise at 0°C. The mixture was stirred for 30 min at room temperature. The organic layer was separated and ammonium sulphate (5 g) was added, the aqueous layer was extracted with ethyl acetate (100 ml). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The formed solid phase was collected, washed with cold ethanol and recrystallized from ethanol.

4-(5-Hydroxy-1-phenyl-3-pyridin-3-yl-1H-pyrazol-4-ylimino)-2-phenyl-5-pyridin-3-yl-2,4-dihydro-pyrazol-3-one (**23**). *Method (a)*: A mixture of (**19**) (2.5 g, 0.01 mol) and benzyl amine (1.072 g, 0.01 mol) in a mixture of water (20 ml) and ethanol (10 ml) was heated under reflux for 30 min. The mixture was concentrated and the precipitate obtained on cooling was isolated under vacuum and recrystallized from ethanol. *Method (b)*: To a cold (0°C) solution of (**13**) (1.3 g, 0.005 mol) in acetic acid (10 ml) Zn powder (2.0 g, 0.03 mol) was added upon stirring for 1 h. The Zn powder was removed by filtration. The filtrate was concentrated. A red violet solid substance formed was filtered, washed with cold ethanol and recrystallized from ethanol.

3,5-Diphenyl-7-pyridin-3-yl-1-pyridin-4-yl-3,5-dihydro-4-oxa-2,3,5,6,8-pentaazacyloazacyclopen-ta[f]azulene (**25**). To a cold (0°C) solution of (**13**) (1.3 g, 0.005 mol) in acetic acid (10 ml) Zn powder was added (2 g, 0.03 mol) upon stirring. The Zn powder was filtered off and the filtrate was transferred to a flask containing (**2**) (1.8 g, 0.005 mol) in acetic acid (10 ml). The reaction mixture was refluxed for 4 h and left to cool down and the formed solid phase was filtered, washed with water and recrystallized from acetic acid.

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ПРОСТИ И ПОДХОДЯЩИ ПРОЦЕДУРИ ЗА СИНТЕЗАТА НА НОВИ ХЕТЕРОЦИКЛИЧНИ СЪЕДИНЕНИЯ СЪДЪРЖАЩИ 1-ФЕНИЛ-3-ПИРИДИЛАЗОЛОВА ЧАСТ

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(Резюме)

Получен е нов етилов естер на 1-фенил-3-пиридин-3-ил-1*H*-тиено[2,3-*c*]пиразол-5-карбоксилова киселина чрез реакция на 5-хлор-1-фенил-3-пиридин-3-ил-1*H*-пиразол-4-карбалдехид с етилбромацетат и натриев сулфид. При алкалната хидролиза на естера се получава съответната киселина, докато при реакцията на същия естер с хидразинхидрат се получава съответния хидразид. При реакциите на хидразида с калиев изоцианат и амониев изотиоцианат се получават съответния триазол и тиодиазол. При взаимодействието на 5-хлор-1-фенил-3-пиридин-3-ил-1*H*-пиразол-4-карбалдехид с хидроксиламин хидрохлорид се получава 4-цианопиразол-5-он. Реацията на последния с $POCl_3$ дава 5-хлор-4-цианопиразол, който циклизира с хидразини до пиразоло[3,4-c]пиразол-3-иламинови производни. Реакцията на 4-нитрозопиразол-3-ол с *o*-аминофенол и *o*-фенилендиамин дава съответното дипиразолилово производно, бензоксиазин и хиноксалин. Редукцията на 4-нитрозопиразол-3-ол с Zn/AcOH дава 4-(5-хидрокси-1-фенил-3-пиридин-3-ил-1*H*-пиразол-4-илимино)2-фенил-5-пиридин-3-ил-2,4-дихидропиразол-3-он, който бе получен също при реакция на 2-фенил-5-пиридин-3-ил-2*H*-пиразол-3,4-дион с бензиламин. Накрая, реакцията на 4-нитрозопиразол-3-ол с 5-хлор-1-фенил-3-пиридин-3-ил-1*H*-пиразол-4-карбалдехид дава 3,5-дифенил-7-пиридин-3-ил-1-пиридин-4-ил-3,5-дихидро-4-окса-2,3,5,5,8-пентаазоцикло-пента[*f*]азулен.