Studies on Alkyl Heterocyclic Aromatic Compounds: New Routes for the Synthesis of Polyazanaphthalenes

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Ethyl 2-Arylhydrazono-3-oxobutanoate, Alkylpyridazines, Alkylpyridines, Cinnoline Derivatives

Several new polyfunctionally substituted polyazanaphthalene derivatives could be synthesized *via* condensing readily obtainable polyfunctional nitriles with substituted alkyl heteroaromatic derivatives and reacting the latter derivatives with electrophilic reagents.

One of the major characteristics of alkyl heteroaromatic compounds is their ability to produce carbanions under mild conditions [1]. Thus they react readily with electrophilic reagents in presence of basic catalysts. Since alkyl aromatic heterocycles are readily obtainable compounds either from natural sources or *via* ring syntheses, thus, this reactivity has been extensively utilized in synthetic heterocyclic chemistry [2]. In the last few years we were involved in programme aimed at developing syntheses of polyfunctionally substituted alkyl heterocycles and exploring their synthetic potentialities [3–5]. In conjunction of this work we report here synthesis of several new alkyl pyridazines and alkyl pyridines and the results of our investigation on the reactivity of their alkyl function toward electrophilic reagents. The work has resulted in developing new approaches for synthesis of polyazanaphthalenes. The synthesized compounds carry latent functional substituents and appear to be interesting for biological evaluation and also for utility in chemical transformations.

A variety of new alkylpyridazines could be synthesized *via* condensing ethyl 2-arylhydrazono-3-oxobutanoate (**1**) with active methylene reagents. Thus **2a–d** were obtained on heating of **1a–d** with ethyl cyanoacetate in the presence of ammonium acetate. The structure of these derivatives was confirmed by their syntheses *via* coupling **3** with aromatic diazonium salts and warming the resulting products in ethanol. Synthesis of **2a,b** has been reported earlier by us utilizing this same synthetic approach [4, 6].

In contrast to its behaviour toward ethyl cyanoacetate **1a,b** condensed with malononitrile to yield the 6-aminopyridazin-3-carboxylates **4a,b.** The formation of **4a,b** is assumed to proceed *via* intermediacy of the ester **5.** This ester is readily hydrolyzed by water eliminated during reaction to yield the aromatic amino compounds **4.** In support of structure **4** compounds **4a,b** could be prepared *via* coupling **6** with aromatic diazonium salts and refluxing the resulting products in aqueous acetic acid for short period.

Compounds **1a,b** also condensed with benzoylacetonitrile to yield product that were formulated as **7a,b**. The formation of **7** is assumed to proceed *via* intermediacy of **8** which is then hydrolyzed into **9.** The latter, consequently, cyclized *via* loss of water to yield **7.** However, possible formation of **10** which is then converted into **7** can not be over looked (*cf.* Chart 1).

Compounds **1a–d** failed to condense with cyclohexanone under a variety of reaction conditions. However, **1b** condensed with 1,1-dimethyl-3,5-diketocyclohexane (**11**) to afford the condensed pyridazine derivative **12** in excellent yield.

Similar to the behaviour of **1a–d,** compound **13** condensed with ethyl cyanoacetate to yield the pyridazine derivative **14.**

A phthalazine synthesis could be achieved *via* reacting **2a,b** and **14** with cinnamonitriles. Thus, **2a,b** and **14** reacted with **15a,b** to yield the phthalazines **16a–f.** Structures of these derivatives were established based on analytical and spectral data. Furthermore compounds **16a–f** could be also obtaines *via* condensing **2a,b** and **14** with aromatic aldehydes and subsequent treatment of the so formed styryl derivatives **17a–f** with malononitrile.

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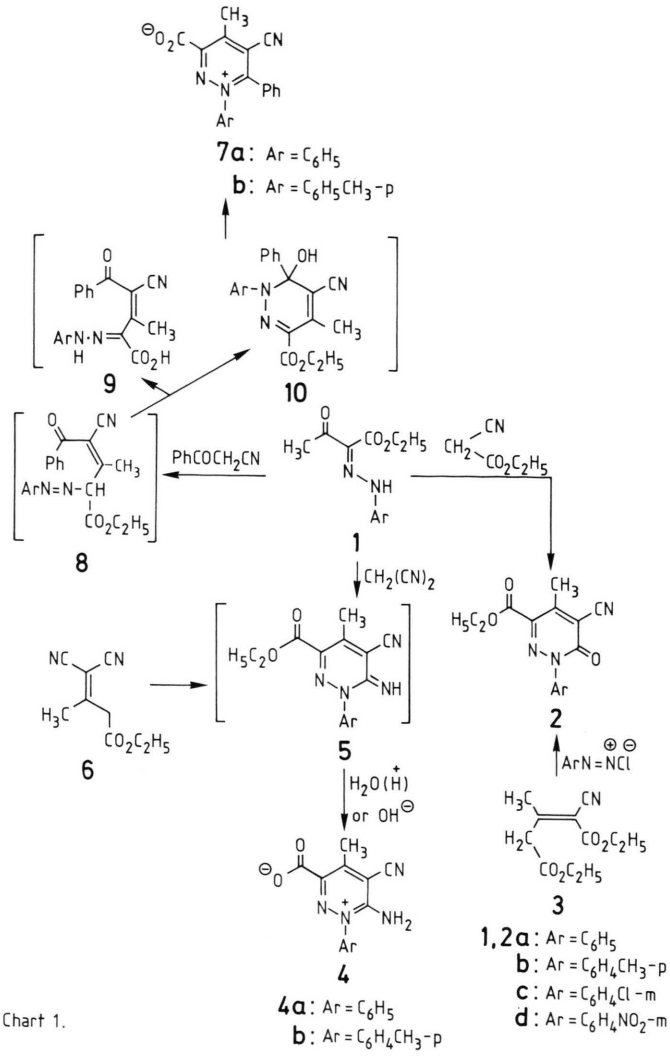
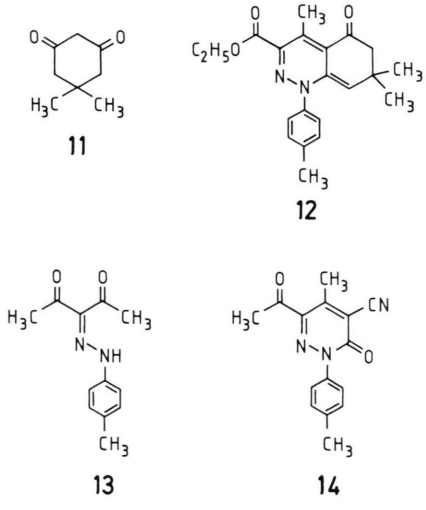


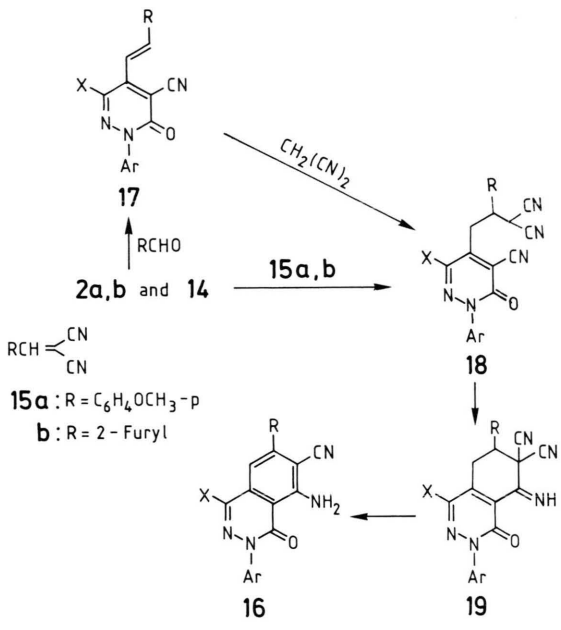
Chart 1.



Formation of **16a–f** *via* reacting **2a,b** and **14** with **15a,b** is assumed to proceed *via* intermediacy of **18** and **19** (*cf.* Chart 2).

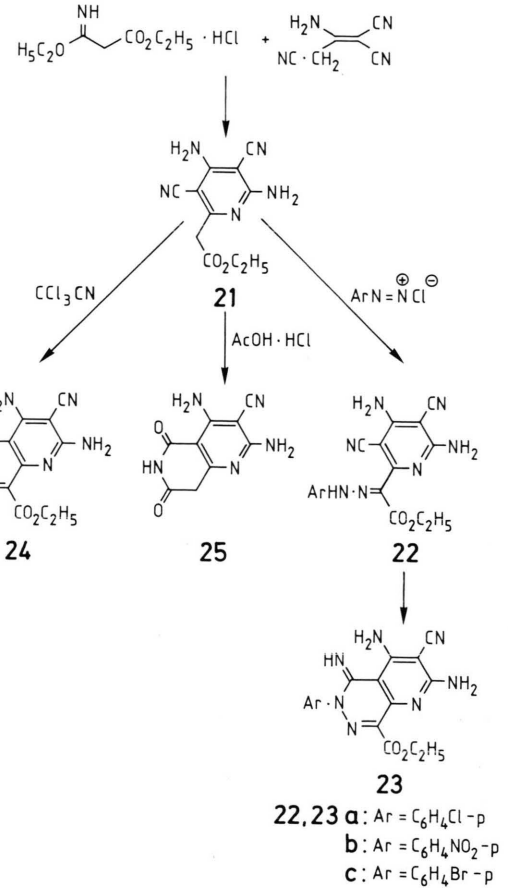
Compounds **2a,b** also reacted with formaldehyde and piperidine to yield the Mannich bases **20a,b.**

Recently we reported synthesis and elucidation of structure of the ethyl pyridine carboxylate (**21**) [3]. Now we have found that compound **21** couples with aromatic diazonium salts to yield the corresponding hydrazones **22a–c** which gave the pyrido[2,3-d]pyridazines **23a–c** on reflux in acetic acid. When compound **21** was treated with trichloroacetonitrile, 1,6-diazanaphthalene derivative (**24**) was obtained.



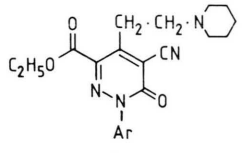
16 - 19 - a: Ar = C_6H_5 ; R = $C_6H_4OCH_3$-p; X = $-CO_2C_2H_5$
b: Ar = C_6H_5 ; R = 2-Furyl; X = $-CO_2C_2H_5$
c: Ar = $C_6H_4CH_3$-p; R = $C_6H_4OCH_3$-p; X = $-CO_2C_2H_5$
d: Ar = $C_6H_4CH_3$-p; R = 2-Furyl; X = $-CO_2C_2H_5$
e: Ar = $C_6H_4CH_3$-p; R = $C_6H_4OCH_3$-p; X = $-COCH_3$
f: Ar = $C_6H_4CH_3$-p; R = 2-Furyl; X = $-COCH_3$

Chart 2.



22,23 a: Ar = C_6H_4Cl-p
b: Ar = $C_6H_4NO_2$-p
c: Ar = C_6H_4Br-p

Chart 3.



20 a: Ar = C_6H_5
b: Ar = $C_6H_5CH_3$-p

Furthermore compound **21** when refluxed in acetic acid-hydrochloric acid mixture afforded **25** (*cf.* Chart 3).

Experimental

All melting points are uncorrected. IR spectra were obtained on a Perkin Elmer SP177 in KBr disc. ^{1}H NMR were measured on a Bruker WP80 CW in DMSO using TMS as internal standard and chemical shifts are expressed as ppm. Analytical data were obtained from the analytical data unit at Cairo University.

Ethyl 1-aryl-5-cyano-1,6-dihydro-4-methyl-6-oxopyridazin-3-carboxylate (**2a–d**)

Method (A):

A mixture of equimolecular amount of **1a–d** (0.5 mol); ethyl cyanoacetate (56.56 g, 0.5 mol) and ammonium acetate (38.52 g, 0.5 mol) was heated in an oil bath at 160 °C for 30 minutes. The resulting product was then triturated with ethanol. The solid product, so formed, was collected by filtration and crystallized from ethanol.

2a: yellow crystals; m.p. 162 °C (literature [5] m.p. 162 °C).

2b: yellow crystals; m.p. 164 °C (literature [5] m.p. 164 °C).

2c: yellow crystals; m.p. 138 °C; yield 80%. IR (KBr, cm^{-1}): $\nu(CH_3$ and $CH_2)$: 3080, 2295; ν(CN): 2215; ν(ester CO): 1725; ν(C=O and C=N): 1690, 1680.

$C_{15}H_{12}ClN_3O_3$ (317.7)

Calcd	C 56.7	H 3.8	N 13.2	Cl 11.2,
Found	C 57.0	H 3.9	N 13.1	Cl 11.1.

2d: yellow crystals; m.p. 157 °C; yield 75%. IR (KBr, cm^{-1}): $\nu(CH_3$ and $CH_2)$: 3095, 2295; ν(CN): 2215; ν(ester CO): 1725; ν(C=O and C=N): 1700–1670.

$C_{15}H_{12}N_4O_5$ (328.3)

Calcd	C 54.9	H 3.7	N 17.1,	
Found	C 54.8	H 3.6	N 17.0.	

Method (B):

A solution of **3** (11.26 g, 0.05 mol) in ethanol (100 ml) containing sodium acetate (4.92 g, 0.06 mol) was treated with a solution of the appropriate aryldiazonium salt (prepared from 0.05 mol of the amine; and the appropriate quantities of sodium nitrite and hydrochloric acid and then left at room temperature for 2 h. The solid product, so formed, was collected by filtration, washed with water and left to dry.

A solution of the dry solid product (5 g) in ethanol (30 ml) was refluxed for 15 minutes, left to cool to room temperature. The resulting solid product separated on standing was collected by filtration, crystallized from ethanol and identified (m.p. and mixed m.p.) and also by IR as **2a–d.**

Method (C):

A mixture of **1a–d** (0.5 mol), ethyl cyanoacetate (56.56 g, 0.5 mol), ammonium acetate (4.92 g, 0.06 mol), glacial acetic acid (12 ml) and dry benzene (200 ml) was heated under reflux, using water separator, in an oil bath at 160 °C for 7 h and then left to cool to room temperature. The solid product separated on standing was filtered off, dried, recrystallized from ethanol. Yields were 85, 82, 80 and 80% for **2a–d,** respectively.

Ethyl 1-aryl-5-cyano-1,6-dihydro-4-methyl-6-aminopyridazin-3-carboxylate (**4a,b**)

Method (A):

An equimolecular amount of **1a,b** (0.05 mol); malononitrile (3.3 g, 0.05 mol) and ammonium acetate (3.85 g, 0.05 mol) was heated in an oil bath at 160 °C for seven minutes. The solid product, so formed, was then triturated with ethanol; collected by filtration and recrystallized.

4a: orange crystals (dioxane); m.p. > 270 °C; yield 70%. – IR (KBr, cm^{-1}): $\nu(NH_2)$: 3330, 3250; ν(CN): 2205.

$C_{13}H_{10}N_4O_2$ (254.2)

Calcd	C 61.4	H 4.0	N 22.0,
Found	C 61.6	H 4.1	N 22.3.

4b: red crystals (DMF); m.p. 259 °C; yield 70%. – IR (KBr, cm^{-1}): $\nu(NH_2)$: 3460; ν(CN): 2210. – ^1H NMR (DMSO): δ = 2.3 (ppm) (s, 3H, CH_3); 2.55 (s, 3H, CH_3); 3.52 (s, 2H, NH_2) and 7.25–7.6 (dd, 4H, arom. protons). – MS: m/z = 268 (M^+).

$C_{14}H_{12}N_4O_2$ (268.3)

Calcd	C 62.7	H 4.5	N 20.9,
Found	C 62.7	H 4.7	N 21.2.

Method (B):

A solution of **6** (0.05 mol) in ethanol (100 ml) containing sodium acetate (5 g) was treated with a solution of the appropriate aryldiazonium salt (prepared from 0.05 mol of the amine and the appropriate quantities of sodium nitrite and hydrochloric acid), then left at room temperature for 2 h. The solid product separated on standing was collected by filtration, washed with water and left to dry.

A solution of the dry solid product (5 g) in aqueous acetic acid (30 ml) was refluxed for one hour, left to cool to room temperature, and then triturated with water. The resulting solid product, so formed, on standing was collected by filtration, crystallized from dioxane and identified m.p. and mixed m.p. as **4a, b.**

Reaction of **1a,b** *with benzoylacetonitrile*

A mixture of equimolecular amounts of **1a,b** (0.05 mol); benzoylacetonitrile (7.26 g, 0.05 mol) and anhydrous ammonium acetate (3.85 g, 0.05 mol) was heated in an oil bath at 160 °C for 30 minutes. The resulting product was then triturated with ethanol and the solid product, so formed, was collected by filtration, and recrystallized from dioxane.

7a: brown crystals; m.p. 210 °C; yield 60%. – IR (KBr, cm^{-1}): ν(CN): 2200; ν(CO): 1740.

$C_{19}H_{13}N_3O_2$ (315.3)

Calcd	C 72.4	H 4.2	N 13.3,
Found	C 72.2	H 4.2	N 13.3.

7b: brown crystals; m.p. 197 °C; yield 60%. – IR (KBr, cm^{-1}): ν(CN): 2210, ν(CO): 1730.

$C_{20}H_{15}N_3O_2$ (329.3)

Calcd	C 72.9	H 4.6	N 12.8,
Found	C 72.8	H 4.6	N 12.6.

Ethyl 5-oxo-1,5,6,7-tetrahydro-1-p-tolyl-4,7,7-trimethylcinnoline-3-carboxylate (**12**)

A mixture of equimolecular amounts of **1b** (12.46 g; 0.05 mol); dimedone (7 g, 0.05 mol) and ammonium acetate (3.85 g, 0.05 mol) was heated in an oil bath at 170 °C for 30 minutes. The resulting product was then triturated with ethanol and the solid product, so formed, was collected by filtration and recrystallized from dioxane as red crystals; m.p. 217 °C; yield 80%. – IR (KBr, cm^{-1}): ν(CO): 1670–1650.

$C_{21}H_{24}N_2O_3$ (352.4)
Calcd C 71.6 H 6.9 N 8.0,
Found C 71.5 H 6.8 N 7.9.

3-Acetyl-1,6-dihydro-4-methyl-6-oxo-1-p-tolylpyridazine-5-carbonitrile (**14**)

Compound **14** was synthesized following method A and C utilized for synthesis of **2a–d.** The reaction product was recrystallized from dioxane as orange crystals; m.p. 163 °C; yield 75%. – IR (KBr, cm^{-1}): $\nu(CH_3)$: 2990; ν(CN): 2230; ν(acetyl and ring CO): 1690–1680.

$C_{15}H_{13}N_3O_2$ (267.3)
Calcd C 67.4 H 4.9 N 15.7,
Found C 67.3 H 4.8 N 15.5.

Ethyl 8-amino-2-aryl-7-cyano-1,2-dihydro-6-substituted-1-oxo-phthalazine-4-carboxylate (**16a–f**)

Method (A):

A solution of **2a,b, 14** (0.01 mol) and piperidine (1 ml) in dioxane (30 ml) was added to the appropriate cinnamonitrile derivative **15a,b** (0.01 mol). The reaction mixture was refluxed for 1 h, then left to cool to room temperature. The solid product separated on standing was collected by filtration and recrystallized from dioxane.

16a: yellow crystals; m.p. 244 °C; yield 70%. – IR (KBr; cm^{-1}): $\nu(NH_2)$: 3460, 3410; $\nu(CH_3$ and $CH_2)$: 2295–2280; ν(CN): 2210; ν(ester CC): 1725; ν(CO): 1670.

$C_{25}H_{20}N_4O_4$ (440.4)
Calcd C 68.2 H 4.6 N 12.7,
Found C 68.3 H 4.7 N 12.6.

16b: yellow crystals; m.p. 248 °C; yield 70%. – IR (KBr, cm^{-1}): $\nu(NH_2)$: 3420; ν(CN): 2220; ν(ester CO): 1730; ν(CO): 1660.

$C_{22}H_{16}N_4O_4$ (440.4)
Calcd C 66.0 H 4.0 N 14.0,
Found C 66.3 H 4.0 N 14.1.

16c: yellow crystals; m.p. 265 °C; yield 75%. – IR (KBr, cm^{-1}): $\nu(NH_2)$: 3440, 3320; $\nu(CH_3$ and $CH_2)$: 2990–2920; ν(CN): 2210; ν(ester CO): 1725; ν(C=O and C=N): 1640–1610.

$C_{26}H_{22}N_4O_4$ (454.5)
Calcd C 68.7 H 4.9 N 12.3,
Found C 68.5 H 4.7 N 12.2.

16d: yellow crystals; m.p. 263 °C; yield 72%. – IR (KBr, cm^{-1}); $\nu(NH_2)$: 3460, 3320; ν(CN): 2210; ν(ester CO): 1730; ν(ring CO): 1680. – MS: m/z = 414 (M^+).

$C_{23}H_{18}N_4O_4$ (414.4)
Calcd C 66.7 H 4.4 N 13.5,
Found C 66.9 H 4.3 N 13.3.

16e: yellow crystals; m.p. 219 °C; yield 70%. – IR (KBr, cm^{-1}): $\nu(NH_2)$: 3460, 3310; $\nu(CH_3$ and $CH_2)$: 2990–2940; ν(CN): 2210; ν(acetyl CO): 1710; ν(ring CO): 1665.

$C_{25}H_{20}N_4O_3$ (424.4)
Calcd C 70.7 H 4.8 N 13.2,
Found C 70.9 H 4.7 N 13.1.

16f: greenish yellow crystals; m.p. >275 °C; yield 70%. – IR (KBr, cm^{-1}): $\nu(NH_2)$: 3420, 3320; ν(CN): 2220; ν(acetyl CO): 1700; ν(ring CO): 1660.

$C_{22}H_{16}N_4O_3$ (384.4)
Calcd C 68.7 H 4.2 N 14.6,
Found C 68.9 H 4.1 N 14.2.

Method (B):

(i) Reaction of **2a,b** *and* **14** *with aldehydes*

To a solution of **2a,b** or **14** (0.01 mol) in dioxane (50 ml) catalyzed with piperidine (1 ml) the appropriate aldehyde (0.01 mol) was added. The reaction mixture was refluxed for 3 h, then left to cool to room temperature. The solid product, so formed, on standing was collected by filtration and crystallized from dioxane-ethanol mixture.

Ethyl 1-aryl-5-cyano-1,6-dihydro-4-styryl-6-oxo-pyridazin-3-carboxylate (**17a–d**)

17a: orange crystals; m.p. 193 °C; yield 70%. – IR (KBr, cm^{-1}): $\nu(CH_3$ and $CH_2)$: 2990–2920; ν(CN): 2220; ν(ester CO): 1725; ν(ring CO): 1670.

$C_{23}H_{19}N_3O_4$ (401.4)
Calcd C 68.8 H 4.8 N 10.5,
Found C 68.6 H 4.5 N 10.3.

17b: orange crystals; m.p. 204 °C; yield 80%. – IR (KBr, cm^{-1}): $\nu(CH_3$ and $CH_2)$: 2995–2985; ν(CN): 2220; ν(ester CO): 1725; ν(ring CO): 1670.

$C_{20}H_{15}N_3O_4$ (361.3)
Calcd C 66.5 H 4.2 N 11.6,
Found C 66.5 H 4.2 N 11.5.

17c: orange crystals; m.p. 191 °C; yield 75%. – IR (KBr, cm^{-1}): $\nu(CH_3$ and $CH_2)$: 2990, 2960; ν(CN): 2220; ν(ester CO): 1725; ν(ring CO): 1670. – ^1H NMR (DMSO): δ = 1.25 ppm (t, 3H, CH_3); 2.39 (s, 3H, CH_3); 3.85 (s, 3H, OCH_3); 4.3 (q, 2H, CH_2); 7.1 (d, 1H, styryl H); 7.3–7.50 (m, 8H, aromatic H) and 7.7 (d, 1H, styryl H).

$C_{24}H_{21}N_3O_4$ (415.4)
Calcd C 69.4 H 5.1 N 10.1,
Found C 69.3 H 5.1 N 10.0.

17d: orange crystals; m.p. 222 °C; yield 70%. – IR (KBr, cm^{-1}): $\nu(CH_3$ and $CH_2)$: 2995–2985; ν(CN): 2220; ν(ester CO): 1725; ν(ring CO): 1670. – MS: m/z = 375 (M^+).

$C_{21}H_{17}N_3O_4$ (375.4)
Calcd C 67.2 H 4.6 N 11.2,
Found C 67.0 H 4.6 N 11.1.

3-Acetyl-1,6-dihydro-6-oxo-4-styryl-1-p-tolyl-pyridazin-5-carbonitrile (**17e, f**)

17e: brown crystals; m.p. 227 °C; yield 70%. – IR (KBr, cm^{-1}): $\nu(CH_3$ and $CH_2)$: 2960–2900; ν(CN): 2220; ν(acetyl CO): 1740; ν(ring CO): 1680–1660.

$C_{23}H_{19}N_3O_3$ (385.4)
Calcd C 71.7 H 5.0 N 11.0,
Found C 71.5 H 5.1 N 11.0.

17f: brown crystals; m.p. 216 °C; yield 73%. – IR (KBr, cm^{-1}): ν(CN): 2220; ν(acetyl CO): 1710; ν(ring CO): 1675.

$C_{20}H_{15}N_3O_3$ (345.3)
Calcd C 69.6 H 4.4 N 12.2,
Found C 69.7 H 4.2 N 12.1.

(ii) Reaction of (**17a–f**) *with malononitrile*

A solution of malononitrile (0.66 g, 0.01 mol) in dioxane (10 ml) was added to a solution of each **17a–f** (0.01 mol) in dioxane (30 ml) and sodium metal (0.23 g, 0.01 mol). The reaction mixtures were refluxed for 4 h, then evaporated *in vacuo*. The remaining products were triturated with water and filtered off. The filtrates were acidified and left for 2 h. The solid products separated on standing were collected by filtration and recrystallized from dioxane. Yields were 70, 70, 75, 74, 70 and 70% as **16a–f,** respectively.

Mannich reaction with **2a, b**

A solution of **2a, b** (0.02 mol) in methanol (30 ml) was treated with piperidine (1.70 g, 0.02 mol), and formalin (0.60 g, 0.02 mol). The reaction mixture was refluxed for 3 h then left to cool to room temperature. The solid product, so formed, on standing was collected by filtration and recrystallized from dioxane.

20a: brown crystals; m.p. 214 °C; yield 80%. – IR (KBr, cm^{-1}): $\nu(CH_2)$: 2940; ν(CN): 2210; ν(ester CO): 1730; ν(C=O and C=N): 1675–1640.

$C_{21}H_{24}N_4O_3$ (380.4)
Calcd C 66.3 H 6.3 N 14.7,
Found C 65.9 H 6.1 N 14.5.

20b: brown crystals; m.p. 196 °C; yield 75%. – IR (KBr, cm^{-1}): ν(CH, CH_2 and CH_3): 3020, 2980–2890; ν(CN): 2215; ν(ester CO): 1725; ν(C=O, C=N): 1690–1650.

$C_{22}H_{26}N_4O_3$ (394.5)
Calcd C 67.0 H 6.5 N 14.2,
Found C 66.7 H 6.4 N 14.0.

Ethyl 4,6-diamino-3,5-dicyanopyridin-2-ylacetate (**21**)

A mixture of equimolecular amounts of diethyl malonic monoimidate hydrochloride (0.5 mol), 2-amino-1,1,3-tricyanoprop-1-ene (0.5 mol) and triethylamine (0.5 mol) in chloroform (200 ml) was refluxed for 2 h, then left to cool to room temperature. The solid product, so formed, was washed several times with water and collected by filtration. Recrystallization from ethanol afforded colourless crystals; m.p. 235 °C; literature [3] m.p. 235 °C.

Ethyl 2-(4,6-diamino-3,5-dicyanopyridin-2-yl)-2-arylhydrazonoglyoxalate (**22a–c**)

A solution of **21** (12.26 g, 0.05 mol) in DMF-ethanol mixture containing sodium acetate (5 g) was treated with a solution of the appropriate aryldiazonium salt (prepared from 0.05 mol of the amine and the appropriate quantities of sodium nitrite and hydrochloric acid), then left at room temperature for 2 h. The solid product separated on standing was collected by filtration and crystallized from dioxane.

22a: orange crystals; m.p. >280 °C; yield 80%. – IR (KBr, cm^{-1}): $\nu(NH_2$ and NH): 3450, 3380–3320, 3220–3050; $\nu(CH_3$ and $CH_2)$: 3000–2940; ν(CN): 2210; ν(ester CO): 1725; ν(C=N): 1615.

$C_{17}H_{14}ClN_7O_2$ (383.8)
Calcd C 53.2 H 3.7 N 25.5 Cl 9.2,
Found C 53.1 H 3.7 N 25.4 Cl 9.1.

22b: brown crystals; m.p. 224 °C; yield 75%. – IR (KBr, cm^{-1}): $\nu(NH_2$ and NH): 3360–3320, 3220; ν(CN): 2210; ν(ester CO): 1725; ν(C=N): 1610.

$C_{17}H_{14}N_8O_4$ (394.4)
Calcd C 51.8 H 3.6 N 28.4,
Found C 51.7 H 3.5 N 28.2.

22c: brown crystals; m.p. >280 °C; yield 75%. – IR (KBr, cm^{-1}): $\nu(NH_2$ and NH): 3400–3360,

3310–3260, 3225–3180; ν(CH_3 and CH_2): 3000–2960; ν(CN): 2220; ν(ester CO): 1710; ν(C=N): 1640.

$C_{17}H_{14}BrN_7O_2$ (428.3)

Calcd	C 47.7	H 3.3	N 22.9	Br 18.7,
Found	C 48.0	H 3.3	N 22.7	Br 18.5.

Ethyl 6,8-diamino-7-cyano-1,2-dihydro-2-aryl-1-iminopyrido[2,3-d]pyridazin-3-carboxylate (**23a–c**)

A solution of **22a–c** (0.01 mol) in acetic acid (30 ml) was refluxed for 2 h, then left to cool to room temperature and triturated with water. The solid product, so formed, was collected by filtration and recrystallized from DMF/H_2O.

23a: brownish crystals; m.p. 234 °C; yield 60%. – IR (KBr, cm^{-1}): ν(NH_2 and chelated NH): 3400–3310, 3220, 3160; ν(CH, CH_2 and CH_3): 3010–2990; ν(CN): 2210; ν(ester CO): 1725.

$C_{17}H_{14}ClN_7O_2$ (383.8)

Calcd	C 53.2	H 3.7	N 25.5	Cl 9.2,
Found	C 53.1	H 3.7	N 25.3	Cl 9.0.

23b: buff crystals; m.p. >280 °C; yield 60%. – IR (KBr, cm^{-1}): ν(NH_2 and chelated NH): 3460, 3400–3280; ν(CN): 2220; ν(ester CO): 1725.

$C_{17}H_{14}N_8O_4$ (394.4)

Calcd	C 51.8	H 3.6	N 28.4,	
Found	C 51.6	H 3.6	N 28.2.	

23c: brown crystals; m.p. >280 °C; yield 63%. – IR (KBr, cm^{-1}): ν(NH_2 and chelated NH): 3490–3100; ν(CN): 2220; ν(ester CO): 1720.

$C_{17}H_{14}BrN_7O_2$ (428.3)

Calcd	C 47.7	H 3.3	N 22.9	Br 18.7,
Found	C 47.7	H 3.4	N 22.8	Br 18.5.

Ethyl 2,4,5-triamino-3-cyano-7-trichloromethyl-1,6-diazanaphthalen-8-carboxylate (**24**)

A solution of **21** (4.91 g, 0.02 mol) in dioxane (20 ml) treated with trichloroacetonitrile (2.88 g, 0.02 mol), then a few drops of triethylamine was added. The resulting solution was then refluxed for 3 h, left to cool to room temperature and triturated with water. The solid product, so formed, was collected by filtration and recrystallized from dioxane as grey crystals; m.p. 210 °C; yield 75%. – IR (KBr, cm^{-1}): ν(NH_2): 3320, 3230; ν(CN): 2220; ν(CO): 1725; (other vibrations and deformations): 1660–1640.

$C_{13}H_{11}Cl_3N_6O_2$ (389.6)

Calcd	C 40.1	H 2.9	N 21.6	Cl 27.3,
Found	C 40.2	H 3.1	N 21.5	Cl 27.1.

2,4-Diamino-5,7-dioxo-5,6,7,8-tetrahydro-1,6-diazanaphthalen-3-carbonitrile (**25**)

Compound **21** (2.45 g, 0.01 mol) was refluxed in a solution of acetic (30 ml) hydrochloric (3 ml) acids mixture for 2 h. The reaction product was poured onto water. The solid product, so formed, was collected by filtration and recrystallized from dioxane as greenish yellow crystals; m.p. >270 °C; yield 65%. – IR (KBr, cm^{-1}): ν(chelated NH and OH): 3450–2700, ν(CN): 2220; ν(CO groups and NH_2 deformations): 1700–1630.

$C_9H_7N_5O_2$ (217.2)

Calcd	C 49.8	H 3.3	N 32.3,	
Found	C 49.7	H 3.3	N 32.2.	

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