Chemistry of 2-Arylhydrazonopropanals: Novel Synthesis of 1,6-Dihydropyridazines and 5-Heteroaryl Substituted Pyrazolo[1,5-*a*]Pyrimidines and Pyrazolo[3,4-*b*]Pyridines

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Abstract: The reaction of 2-arylhydrazonopropanals **1a–d** with dimethyl acetylenedicarboxylate in anhydrous dichloromethane in the presence of triphenylphosphine afforded 1,6-dihydropyridazines **2a–d**. Compound **1a** reacted with dimethyl acetylenedicarboxylate in refluxing acetic acid yielding the corresponding Michael adduct **4**. Whereas compound **1d** failed to react in acetic acid with diphenylacetylene, its reaction with the same reagent in anhydrous dichloromethane in the presence of triphenylphosphine afforded the Michael adduct **3**. Compounds **2b–d** reacted with hydrazine hydrate affording the corresponding pyridazino[3,4-*d*]pyridazines **6b–d**. 2-Arylhydrazonopropanals **1a**,**b** reacted with 5-methyl-1*H*-pyrazol-3-amine in ethanol yielding the corresponding condensation products **8a**,**b**, which cyclized to the 7-substituted 2-methyl-6-phenylazopyrazolo[1,5-*a*]pyrimidines **9a**,**b** and 4-substituted 3-methyl-5-phenylazopyrazolo[3,4-*b*]pyridines **10a**,**b** on refluxing in acetic acid. 2-Phenylhydrazonopropanal **1a** reacted with *p*-benzoquinone yielding the resorcinol derivative **12**.

Key words: heterocycles, Michael addition, cyclization

The chemistry of 1,2,3-trione-2-arylhydrazones has received considerable interest in the past.[1] However, the chemistry of structurally related 2-arylhydrazono-3-oxopropanals has received very limited interest.[2–4] Some time ago we described an efficient synthesis of 2-arylhydrazonopropanals and reported recently on their potential in heterocyclic synthesis.[2–4] In conjunction with this work we describe here a facile one-pot synthesis of dialkyl 1,6-dihydropyridazine-5,6-dicarboxylates in high yield utilizing the 2-arylhydrazonopropanals **1a–d** as precursors for this ring system. In addition, several new arylazopyrazolo[1,5-*a*]pyrimidines and pyrazolo[3,4-*b*]pyridines have been synthesized utilizing **1a**,**b** as starting materials.

Thus, compounds **1a–d** reacted with dimethyl acetylenedicarboxylate in anhydrous dichloromethane and in the presence of triphenylphosphine to yield the 1,6-dihydropyridazines **2a–d** (Scheme 1). Such products apparently result from the initial addition of triphenylphosphine to the acetylenic ester yielding a 1:1 adduct. This is followed by attack of the hydrazone nitrogen on the formed vinylphosphonium product affording an acyclic adduct that cyclizes via loss of triphenylphosphine oxide. A similar reaction sequence has recently been proposed to account for the formation of dialkyl 1*H*-pyrrolizine-2,3-dicarboxylates from the reaction of pyrrole-2-carbaldehyde with dialkyl acetylenedicarboxylates.[5] Several tautomeric structures seemed possible for the formed dihydropyridazines. For example, the ^{1}H NMR spectrum of **2b** displayed four singlets readily recognizable as arising from the two methoxy (δ = 3.64, 3.83), the NCH (δ = 6.22) and the olefinic CH (δ = 8.06) protons, along with the multiplet in the aromatic region. The ^{13}C NMR spectrum of **2b** revealed three sp^3 carbons which can be assigned to the two methoxy at δ= 52.49, 53.04 and δ = 54.93 for NCH, thus excluding other potential tautomers. The structural assignments made on the basis of the ^{1}H and the ^{13}C NMR spectra of compound **2b** were supported by measurement of its IR spectra that exhibited an ester absorption at ν = 1743, 1716 cm^{-1}. Conjugation with the olefinic bond shifts one of these bands to a lower frequency. However, Michael adduct **3** was obtained from the reaction of **1d** with diphenylacetylene under the same reaction condition, and the adduct **4** was obtained from the reaction of **1a** with dimethyl acetylenedicarboxylate in refluxing acetic acid (Scheme 1). These adducts could not be further cyclized into pyridazinone derivatives. Although synthetic approaches to pyridazines are numerous and well explored,[6–8] to our knowledge none of these approaches would enable an easy access to pyridazine-5,6-dicarboxylate which are interesting starting materials for the rarely described pyridazino[4,5-*c*]ring system.[9]

Compounds **2a–d** obtained appeared to be interesting precursors for the synthesis of condensed pyridazinones. To demonstrate their potential, **2b–d** were reacted with hydrazine hydrate to yield the dihydrazides **5b–d** which cyclized into the pyridazinopyridazines **6b–d** on refluxing in dimethylformamide (Scheme 1).

Compounds **1a**,**b** reacted with 5-methyl-1*H*-pyrazol-3-amine (**7**) in refluxing ethanol to yield the corresponding condensation products **8a**,**b**. These could be smoothly cyclized via loss of water yielding a mixture of the pyrazolo[1,5-*a*]pyrimidines **9** and pyrazolo[3,4-*b*]pyridines **10** (Scheme 2). The ^{1}H NMR spectrum of the mixture displayed six singlets, readily recognizable as arising from two methyls at (δ = 2.43 and 2.60 for 1.5 proton each), a

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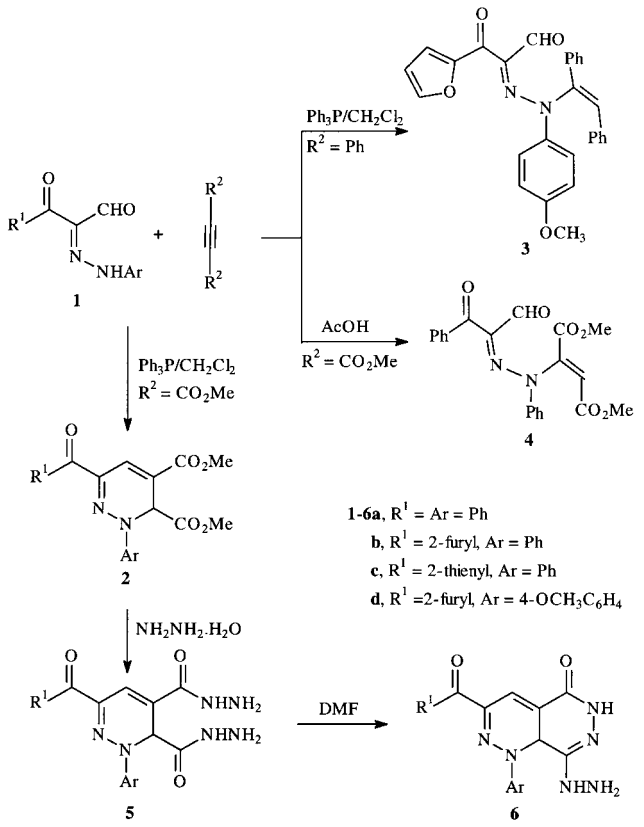
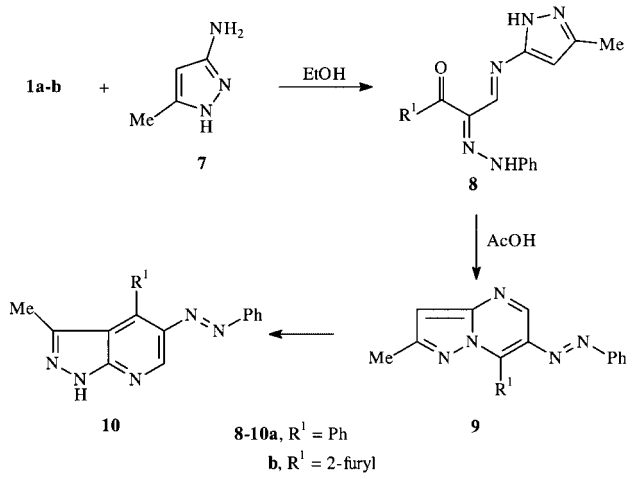
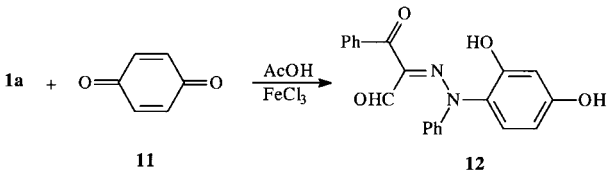


Scheme 1



Scheme 2



Scheme 3

pyrazolyl 4-H proton at (δ = 6.79 for 0.6 proton), pyridyl 2-H and pyrimidyl 4-H at (δ = 8.50 and 9.03 for 0.4 proton each), NH at (δ = 13.55 for 0.4 proton) along with an aromatic multiplet at (δ = 7.51–7.80 for a total of 10 protons). It was thus concluded that the mixture is composed of compounds **9** and **10** in the ratio of 3:2. Triturating the reaction mixture with acetonitrile enabled complete dissolution of one of the two products. The remaining solid was isolated and proved to be pyrazolo[3,4-*b*]pyridines **10**. Samples of pure **9** could not be obtained, as on evaporating the acetonitrile solution, a mixture of **9** and **10** was obtained as **9** rearranged into **10** in most solvents. We believe that **9** is the kinetic product whereas **10** is the thermodynamic product. Rearrangement of some pyrazolo[1,5-*a*]pyrimidines into pyrazolo[3,4-*b*]pyridines has once been observed earlier.[10] It seems that the presence of electron-attracting arylazo function in **9** increases the π-deficiency of the ring moiety and thus facilitates ring-opening process. The obtained arylazo derivatives have an intense orange color and thus seem to be a new class of arylazopyrazolo[3,4-*b*]pyridine dyes (Scheme 2).

Compound **1a** reacted with *p*-benzoquinone **11** in acetic acid in the presence of ferric chloride to yield the resorcinol derivative **12** in good yield (Scheme 3).

In conclusion, the readily obtainable 2-arylhydrazonopropanals are valuable precursors for the synthesis of a variety of, otherwise not readily obtainable, heteroaromatics of potential interest for biological evaluation.

All melting points are uncorrected. IR spectra were recorded as KBr pellets with a Pye Unicam SP 1100 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM-390 400 MHz spectrometer in DMSO-d_6 as solvent and TMS as internal standard; chemical shifts are reported in δ units (ppm). Mass spectra were measured at 70 eV using MS 30 and MS 9 (AEI) spectrometers. Microanalyses were performed on a LECO CHNS-932 apparatus. Microanalytical data were obtained from the Microanalytical Data Unit at Cairo University. Compounds **1a–d** were prepared following published procedure.[2]

1,6-Dihydropyridazines 2a–d; General Procedure

To a magnetically stirred solution of Ph_3P (2.62 g, 10 mmol) and each of 2-arylhydrazonopropanals **1a–d** (10 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of dimethyl acetylenedicarboxylate (1.42 g, 10 mmol) in CH_2Cl_2 (5 mL) at 0 °C over 15 min. The mixture was left at r.t. and stirred for 24 h. The solvent was reduced under vacuum and the solid product was filtered and crystallized from dioxane.

Dimethyl 3-Benzoyl-1,6-dihydro-1-phenylpyridazine-5,6-dicarboxylate (2a)

Yield: 3.47 g (92%); mp 109 °C.

IR (KBr): 1743, 1715 (ester CO), 1618 cm^{-1} (CO).

MS (EI): *m/z* (%) = 378 (M^+).

^{1}H NMR (DMSO-d_6): δ = 3.65 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 6.24 (s, 1 H, NCH), 7.51–7.68 (m, 5 H, arom-H), 7. 74–7.81 (m, 5 H, arom-H), 8.11 (s, 1 H, 4-H).

Anal. Calcd for $C_{21}H_{18}N_2O_5$ (378.4): C, 66.66; H, 4.80; N, 7.40. Found: C, 66.50; H, 4.93; N, 7.52.

Dimethyl 1,6-Dihydro-3-(2-furoyl)-1-phenylpyridazine-5,6-dicarboxylate (2b)
Yield: 3.30 g (90%); mp 135 °C.

IR (KBr): 1743, 1716 (ester CO), 1620 cm^{-1} (CO).

MS (EI): *m/z* (%) = 368 (M^+).

^1H NMR (DMSO-d_6): δ = 3.65 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 6.25 (s, 1 H, NCH), 6.77–6.78 (m, 1 H, furyl-H), 7.29–7.33 (m, 1 H, furyl-H), 7.49–7.65 (m, 6 H, 5 arom-H, 1 furyl-H), 8.11 (s, 1 H, 4-H).

^{13}C NMR (DMSO-d_6): δ = 174.06 (CO), 168.05 (ester CO), 164.13 (ester CO), 149.76 (C-3), 148.16, 144.15, 139.50, 129.45, 125.56, 121.76, 120.82, 118.27, 117.60, 112.55, 54.93 (NCH), 53.04, 52.49 (OCH_3).

Anal. Calcd for $C_{19}H_{16}N_2O_6$ (368.3): C, 61.95; H, 4.38; N, 7.61. Found: C, 61.91; H, 4.39; N, 7.80.

Dimethyl 1,6-Dihydro-1-phenyl-3-(2-thienoyl)pyridazine-5,6-dicarboxylate (2c)
Yield: 3.64 g (95%); mp 110 °C.

IR (KBr): 1745, 1715 (ester CO), 1610 cm^{-1} (CO).

MS (EI): *m/z* (%) = 384 (M^+).

^1H NMR (DMSO-d_6): δ = 3.65 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 6.24 (s, 1 H, NCH), 7.24–7.32 (m, 2 H, thienyl-H), 7.47–8.02 (m, 6 H, 5 arom-H, 1 H thienyl-H), 8.11 (s, 1 H, 4-H).

^{13}C NMR (DMSO-d_6): δ = 178.29 (CO), 168.00 (ester CO), 164.12 (ester CO), 144.06 (C-3), 139.66, 138.82, 136.12, 135.03,129.42, 127.87, 125.60, 120.93, 118.45, 117.83, 55.04 (NCH), 53.06 and 52.51 (OCH_3).

Anal. Calcd for $C_{19}H_{16}N_2O_5S$ (384.3): C, 59.37; H, 4.20; N, 7.29; S, 8.32. Found: C, 59.47; H, 4.38; N, 7.31; S, 8.16.

Dimethyl 1,6-Dihydro-3-(2-furoyl)-1-(4-methoxyphenyl)pyridazine-5,6-dicarboxylate (2d)
Yield: 3.74 g (94%); mp 138 °C.

IR (KBr): 1744, 1715 (ester CO), 1615 cm^{-1} (CO).

MS (EI): *m/z* (%) = 398 (M^+).

^1H NMR (DMSO-d_6): δ = 3.32 (s, 3 H, OCH_3), 3.80 (s, 3 H, CO_2CH_3), 3.82 (s, 3 H, CO_2CH_3), 6.20 (s, 1 H, NCH), 6.75–6.76 (m, 1 H, furyl-H), 7.05–7.07 (m, 2 H, furyl-H), 7.54–7.75 (m, 4 H, arom-H), 8.09 (s, 1 H, 4-H).

Anal. Calcd for $C_{20}H_{18}N_2O_7$ (398.4): C, 60.30; H, 4.55; N, 7.03. Found: C, 60.37; H, 4.55; N, 7.20.

3-(2-Furyl)-2-(*N*-diphenylethyleno-4-methoxyphenylhydrazono)-3-oxopropanal (3)
To a magnetically stirred solution of Ph_3P (2,62 g, 10 mmol) and 2-phenylhydrazonopropanal **1a** (2.52 g, 10 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of diphenylacetylene (1.78 g, 10 mmol) in CH_2Cl_2 (5 mL) at 0 °C over 15 min. The mixture was left at r.t. and stirred for 24 h. The solvent was reduced under vacuum and the solid product was filtered and crystallized from dioxane.

Yield: 4.05 g (90%); mp 103 °C.

IR (KBr): 1639, 1619 cm^{-1} (CO).

MS (EI): *m/z* (%) = 450 (M^+).

^1H NMR (DMSO-d_6): δ = 3.77 (s, 3 H, OCH_3), 6.73–6.74 (m, 1 H, furyl-H), 7.01–7.04 (m, 2 H, furyl-H), 7.23–7.25 (m, 5 H, arom-H), 7.36–7.46 (m, 5 H, arom-H), 7.47–7.48 (m, 2 H, arom-H), 7.52–7.55 (m, 2 H, arom-H), 5.31 (s, 1 H, vinyl-H), 9.91 (s, 1 H, CHO).

^{13}C NMR (DMSO-d_6): δ = 187.09 (CHO), 176.55 (CO), 158.02 (C-2), 149.96, 147.51, 136.82, 136.67, 136.67, 134.77, 133.33, 133.07, 131.26, 131.30, 128.87, 128.70, 128.61, 128.50, 121.04, 118.55, 115.07, 112.35, 55.48 (OCH_3).

Anal. Calcd for $C_{28}H_{22}N_2O_4$ (450.5): C, 74.65; H, 4.92; N, 6.22. Found: C, 74.70; H, 4.85; N, 6.20.

Dimethyl {1,3-Dioxo-1-phenyl-2-[2′-(1′-phenylhydrazono)propan-1-yl]}fumarate (4)
A solution of **1a** (2.52 g, 10 mmol) and dimethyl acetylenedicarboxylate (1.42 g, 10 mmol) in AcOH (20 mL) were refluxed for 3 h. After cooling, the precipitate was filtered and recrystallized from AcOH.

Yield: 3.19 g (82%); mp 138 °C.

IR (KBr): 1718 (ester CO), 1621 cm^{-1} (CO).

MS (EI): *m/z* (%) = 394 (M^+).

^1H NMR (DMSO-d_6): δ = 3.80 (s, 3 H, CO_2CH_3), 3.82 (s, 3 H, CO_2CH_3), 7.17–7.96 (m, 10 H, arom-H), 5.82 (s, 1 H, vinyl-H), 10.03 (s, 1 H, CHO).

Anal. Calcd for $C_{21}H_{18}N_2O_6$ (394.4): C, 63.95; H, 4.60; N, 7.10. Found: C, 63.88; H, 4.75; N, 7.20.

Dihydrazides 5b–d; General Procedure
A mixture of each of the compounds **2b–d** (10 mmol) in EtOH (30 mL) was treated with hydrazine hydrate (10 mL). The mixture was heated under reflux for 1 h and allowed to cool to r.t. The solid product was filtered and crystallized from dioxane.

1,6-Dihydro-3-(2-furoyl)-1-phenylpyridazine-5,6-dicarboxydihydrazide (5b)
Yield: 3.31 g (90%); mp 235 °C.

IR (KBr): 3301, 3178 (NH, NH_2), 1674, 1620 cm^{-1} (CO).

MS (EI): *m/z* (%) = 368 (M^+).

^1H NMR (DMSO-d_6): δ = 5.98 (s, 1 H, NCH), 6.75–6.79 (m, 1 H, furyl-H), 7.22–8.01 (m, 11 H, 2 H furyl-H, 5 H arom-H, 4 H 2 NH_2), 8.10 (s, 1 H, H-4), 9.14 (br s, 1 H, NH), 10.04 (br s, 1 H, NH).

Anal. Calcd for $C_{17}H_{16}N_6O_4$ (368.4): C, 55.43; H, 4.38; N, 22.82. Found: C, 55.40; H, 4.43; N, 22.94.

1,6-Dihydro-1-phenyl-3-(2-thienoyl)pyridazine-5,6-dicarboxydihydrazide (5c)
Yield: 3.64 g (95%); mp 220 °C.

IR (KBr): 3309, 3178 (NH, NH_2), 1674, 1604 cm^{-1} (CO).

MS (EI): *m/z* (%) = 384 (M^+).

^1H NMR (DMSO-d_6): δ = 5.97 (s, 1 H, NCH), 7.15–7.44 (m, 2 H, thienyl-H), 7.48–7.99 (m, 8 H, 1 H thienyl-H, 5 H arom-H, 2 H NH_2), 8.06–8.07 (m, 2 H, NH_2), 8.13 (s, 1 H, H-4), 9.14 (br s, 1 H, NH), 10.05 (br s, 1 H, NH).

Anal. Calcd for $C_{17}H_{16}N_6O_3S$ (384.4): C, 53.12; H, 4.20; N, 21.87; S, 8.32. Found: C, 53.32; H, 4.18; N, 21.80; S, 8.12.

1,6-Dihydro-3-(2-furoyl)-1-(4-methoxyphenyl)pyridazine-5,6-dicarboxydihydrazide (5d)
Yield: 3.58 g (90%); mp 240 °C.

IR (KBr): 3304, 3178 (NH, NH_2), 1674, 1618 cm^{-1} (CO).

MS (EI): *m/z* (%) = 398 (M^+).

^1H NMR (DMSO-d_6): δ = 3.80 (s, 3 H, OCH_3), 5.95 (s, 1 H, N-CH), 6.73–6.79 (m, 1 H, furyl-H), 7.02–7.07 (m, 2 H, furyl-H), 7.53–7.98 (m, 8 H, 4 H arom-H, 4 H 2 NH_2), 8.10 (s, 1 H, H-4), 9.14 (br s, 1 H, NH), 10.05 (br s, 1 H, NH).

Anal. Calcd for $C_{18}H_{18}N_6O_5$ (398.4): C, 54.27; H, 4.55; N, 21.10. Found: C, 54.40; H, 4.56; N, 21.00.

Pyridazinopyridazines 6b–d; General Procedure
Each of the hydrazide **5b**–**d** (10 mmol) in DMF (10 mL) was refluxed for 1 h, then poured onto ice-water . The solid product was filtered and crystallized from DMF.

3-(2-Furoyl)-8-hydrazino-1-phenyl-1,5,6,8a-tetrahydropyridazino[3,4-*d*]pyridazin-5-one (6b)
Yield: 3.15 g (90%); mp 212 °C.

IR (KBr): 3410, 3330, 2935 (NH, NH_2), 1680, 1620 cm^{-1} (CO).

MS (EI): *m/z* (%) = 350 (M^+).

^1H NMR (DMSO-d_6): δ = 5.93 (s, 1 H, NCH), 6.75–6.79 (m, 1 H, furyl-H), 7.28–8.06 (m, 9 H, 2 H furyl-H, 5 H arom-H, 2 H NH_2), 8.10 (s, 1 H, 4-H), 9.18 (br s, 1 H, NH), 10.00 (br s, 1 H, NH).

Anal. Calcd for $C_{17}H_{14}N_6O_3$ (350.3): C, 58.28; H, 4.03; N, 23.99. Found: C, 58.10; H, 4.09; N, 24.12.

8-Hydrazino-1-phenyl-1,5,6,8a-tetrahydro-3-(2-thienoyl)pyridazino[3,4-*d*]pyridazin-5-one (6c)
Yield: 3.47 g (95%); mp 221 °C.

IR (KBr): 3420, 3330, 2918 (NH, NH_2), 1679, 1614 cm^{-1} (CO).

MS (EI): *m/z* (%) = 366 (M^+).

^1H NMR (DMSO-d_6): δ = 5.97 (s, 1 H, NCH), 7.15–7.44 (m, 2 H, thienyl-H), 7.32–8.08 (m, 10 H, 1 H thienyl-H, 5 H arom-H, 2 H NH_2), 8.10 (s, 1 H, 4-H), 9.16 (br s, 1 H, NH), 10.11 (br s, 1 H, NH).

Anal. Calcd for $C_{17}H_{14}N_6O_2S$ (366.3): C, 55.73; H, 3.85; N, 22.94; S, 8.73. Found: C, 55.84; H, 4.08; N, 23.81; S, 8.62.

3-(2-Furoyl)-8-hydrazino-1-(4-methoxyphenyl)-1,5,6,8a-tetrahydropyridazino[3,4-*d*]pyridazin-5-one (6d)
Yield: 3.34 g (88%); mp 215 °C.

IR (KBr): 3420, 3332, 2939 (NH, NH_2), 1681, 1620 cm^{-1} (CO).

MS (EI): *m/z* (%) = 380 (M^+).

^1H NMR (DMSO-d_6): δ = 3.80 (s, 3 H, OCH_3), 5.92 (s, 1 H, N-CH), 6.76–6.77 (m, 1 H, furyl-H), 7.04–7.07 (m, 2 H, furyl-H), 7.42–7.74 (m, 4 H, 2 H arom-H, 2 H NH_2), 7.57–7.59 (m, 2 H, arom-H), 8.08 (s, 1 H, 4-H), 9.10 (br s, 1 H, NH), 10.00 (br s, 1 H, NH).

Anal. Calcd for $C_{18}H_{16}N_6O_4$ (380.4): C, 56.84; H, 4.24; N, 22.10. Found: C, 56.92; H, 4.12; N, 22.00.

Condensation Products 8a,b; General Procedure
Each of the compounds **1a**,**b** (10 mmol) in EtOH (30 mL) was treated with 5-methyl-1*H*-pyrazol-3-amine (0.97 g, 10 mmol). The mixture was heated under reflux for 1 h and allowed to cool to r.t. The solid product was filtered and crystallized from dioxane.

(1-Phenyl-2-phenylhydrazonopropane)-3-(3′-methyl-1′*H*-pyrazol-5′-yl)imine-1-one (8a)

Yield: 2.81 g (85%); mp 196 °C.

IR (KBr): 3170 (NH), 1643 cm^{-1} (CO).

MS (EI): *m/z* (%) = 331 (M^+).

^1H NMR (DMSO-d_6): δ = 2.28 (s, 3 H, CH_3), 6.38 (s, 1 H, pyrazolyl-H), 7.17–7.62 (m, 8 H, arom-H), 7.87–7.90 (m, 2 H, arom-H), 9.03 (s, 1 H, amidine-H), 12.69 (br s, 1 H, NH), 15.40 (br s, 1 H, NH).

Anal. Calcd for $C_{19}H_{17}N_5O$ (331.4): C, 68.86; H, 5.17; N, 21.14. Found: C, 68.92; H, 5.14; N, 20.98.

1-(2-Furyl)-2-phenylhydrazonopropane)-3-(3′-methyl-1′*H*-pyrazol-5′-yl)imine-1-one (8b)
Yield: 2.79 g (87%); mp 202 °C.

IR (KBr): 3150 (NH), 1620 cm^{-1} (CO).

MS (EI): *m/z* (%) = 321 (M^+).

^1H NMR (DMSO-d_6): δ = 2.28 (s, 3 H, CH_3), 6.38 (s, 1 H, pyrazolyl-H), 6.80–6.81 (m, 1 H, furyl-H), 7.23–7.26 (m, 2 H, furyl-H), 7.50–7.62 (m, 3 H, arom-H), 7.92–8.09 (m, 2 H, arom-H), 8.95 (s, 1 H, amidine-H), 12.69 (br s, 1 H, NH), 15.42 (br s, 1 H, NH).

Anal. Calcd $C_{17}H_{15}N_5O_2$ (321.3): C, 63.54; H, 4.70; N, 21.80. Found: C, 63.71; H, 4.66; N, 21.98.

Pyrazolo[3,4-*b*]pyridines 10a,b; General Procedure
Each of the compounds **8a**,**b** (10 mmol) in AcOH (10 mL) was refluxed for 1h and then allowed to cool to r.t. The solid product obtained was filtered and triturated with MeCN. The filtrate was concentrated under vacuum and the residue was crystallized from dioxane to afford compound **10** in pure form.

3-Methyl-4-phenyl-5-phenylazo-1*H*-pyrazolo[3,4-*b*]pyridine (10a)
Yield: 1.12 g (36%); mp 180 °C.

IR (KBr): 3180 cm^{-1} (NH).

MS (EI): *m/z* (%) = 313 (M^+).

^1H NMR (DMSO-d_6): δ = 2.43 (s, 3 H, CH_3), 7.51–7.77 (m, 10 H, arom-H), 8.50 (s, 1 H, pyridyl-H), 13.55 (s, 1 H, NH).

Anal. Calcd for $C_{19}H_{15}N_5$ (313.4): C, 72.82; H, 4.83; N, 22.35. Found: C, 72.86; H, 4.67; N, 22.10.

4-(2-Furyl)-3-methyl-5-phenylazo-1*H*-pyrazolo[3,4-*b*]pyridine (10b)
Yield: 0.96 g (32%); mp 277 °C.

IR (KBr): 3170 cm^{-1} (NH).

MS (EI): *m/z* (%) = 303 (M^+).

^1H NMR (DMSO-d_6): δ = 2.51 (s, 3 H, CH_3), 6.73–6.75 (m, 1 H, furyl-H), 7.15–7.16 (m, 1 H, furyl-H), 7.61–7.66 (m, 3 H, 2 H arom-H, 1 H furyl-H), 7.75–7.98 (m, 3 H, arom-H), 8.43 (s, 1 H, pyridyl-H).

Anal. Calcd for $C_{17}H_{13}N_5O$ (303.3): C, 67.31; H, 4.32; N, 23.09. Found: C, 67.29; H, 4.21; N, 22.90.

3-Oxo-2-[*N*-(2,5-dihydroxyphenyl)-*N*-phenylhydrazono]-3-phenylpropanal (12)
Compound **1a** (2.52 g, 10 mmol) in AcOH (30 mL) was treated with *p*-benzoquinone (1.08 g, 10 mmol). The mixture was heated under reflux for 3 h and allowed to cool to r.t. The solid product was filtered and crystallized from dioxane.

Yield: 2.88 g (80%); mp 230 °C.

IR (KBr): 3330 br (OH), 1635, 1621 cm^{-1} (CO).

MS (EI): *m/z* (%) = 360 (M^+).

^1H NMR (DMSO-d_6): δ = 7.17–7.89 (m, 13 H, arom-H), 10.01 (s, 1 H, CHO), 13.26 (br s, 1 H, OH), 14.25 (br s, 1 H, OH).

Anal. Calcd for $C_{21}H_{16}N_2O_4$ (360.4): C, 69.99; H, 4.48; N, 7.77. Found: C, 69.92; H, 4.44; N, 7.83.

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