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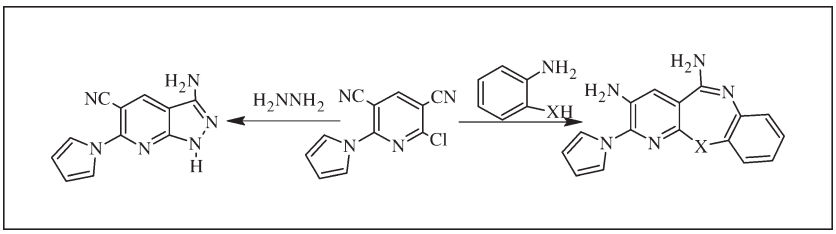

2-Amino-6-chloropyridine-3,5-dicarbonitrile was used as an intermediate for synthesis of new pyrazolopyridine, pyridopyrimidine, benzodiazepine, and benzothiazipine derivatives.

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INTRODUCTION

Pyridine, pyrazole, and pyrimidine derivatives attracted organic chemists very much due to their biological and chemotherapeutic importance. Pyridobenzodiazepine derivatives [1–3], pyrazolopyridine, and related fused heterocycles are of interest as potential bioactive molecules. They are known to exhibit pharmacological activities such as CNS depressant [4,5], neuroleptic [6], and turberculostatic [7]. Pyrazolo[3,4-b] pyridines were reported as antimicrobial agents [8], inhibitors of glycogen synthesis kinase-3(GSK-3) [9], and potent antitumor agents [10]. Compounds containing a fused pyrimidine ring have significant biological activity, particularly in cancer and virus research [11–15].

Therefore, in view of these observations and in conjunction with our previous interest in preparing heterocyclic ring systems [16–21], we wish to report herein the synthesis of some new heterocyclic compounds containing a pyridine moiety fused with pyrazole, pyrimidine, pyrole, thiophene, and benzodiazepine nuclei.

RESULTS AND DISCUSSION

The key 2-amino-6-chloropyridine-3,5-dicarbonitrile **1** was prepared as reported in literature via acidifying the condensation mixture of malononitrile with triethyl orthoformate [22].

A multistep synthesis was required for preparing the pyrazolopyridine derivative **5**. Treatment of compound **1** with 1 mol of 2,5-dimethoxytetrahydrofurane in glacial acetic acid yielded compound **2** which in turn was allowed to react with hydrazine hydrate to give compound **3**. On treating compound **3** with another mole of 2,5-dimethoxytetrahydrofurane gave compound **5**. Otherwise the structure of compound **5** was proved when synthesized via another rout by treating of compound **1** with hydrazine hydrate to yield compound **4** which in turn was treated with 2 mol of 2,5-dimethoxytetrahydrofurane to afford compound **5**.

The chlorine atom attached with compound **2** can be easily substituted with nucleophilic reagents including phenylhydrazine, ethyl mercaptoacetate, ethylglycinate, *o*-aminothiophenol, *o*-phenylenediamine, or ethelenediamine provided the substitution intermediate followed by intramolecular cyclization to yield pyrazolopyridine, thienopyridine, pyrolopyridine, and pyridobenzodiazipine derivatives **6–9**, respectively.

Similar nucleophilic displacement reactions followed by intramolecular cyclization were carried out with thiourea, guanidine, or urea to yield 4-amino-7-(1H-pyrrol-1-yl)-2-thioxo-1,2-dihydropyrido[2,3-d]pyrimidine-6-carbonitrile **10a**, 4-amino-2-oxo-7-(1H-pyrrol-1-yl)-1,2-dihydropyrido [2,3-d] pyrimidine-6-carbonitrile **10b**, and 4-amino-2-imino-7-(1H-pyrrol-1-yl)-1,2-dihydropyrido[2,3-d]pyrimidine-6-carbonitrile **10c**, respectively, (Scheme 1).

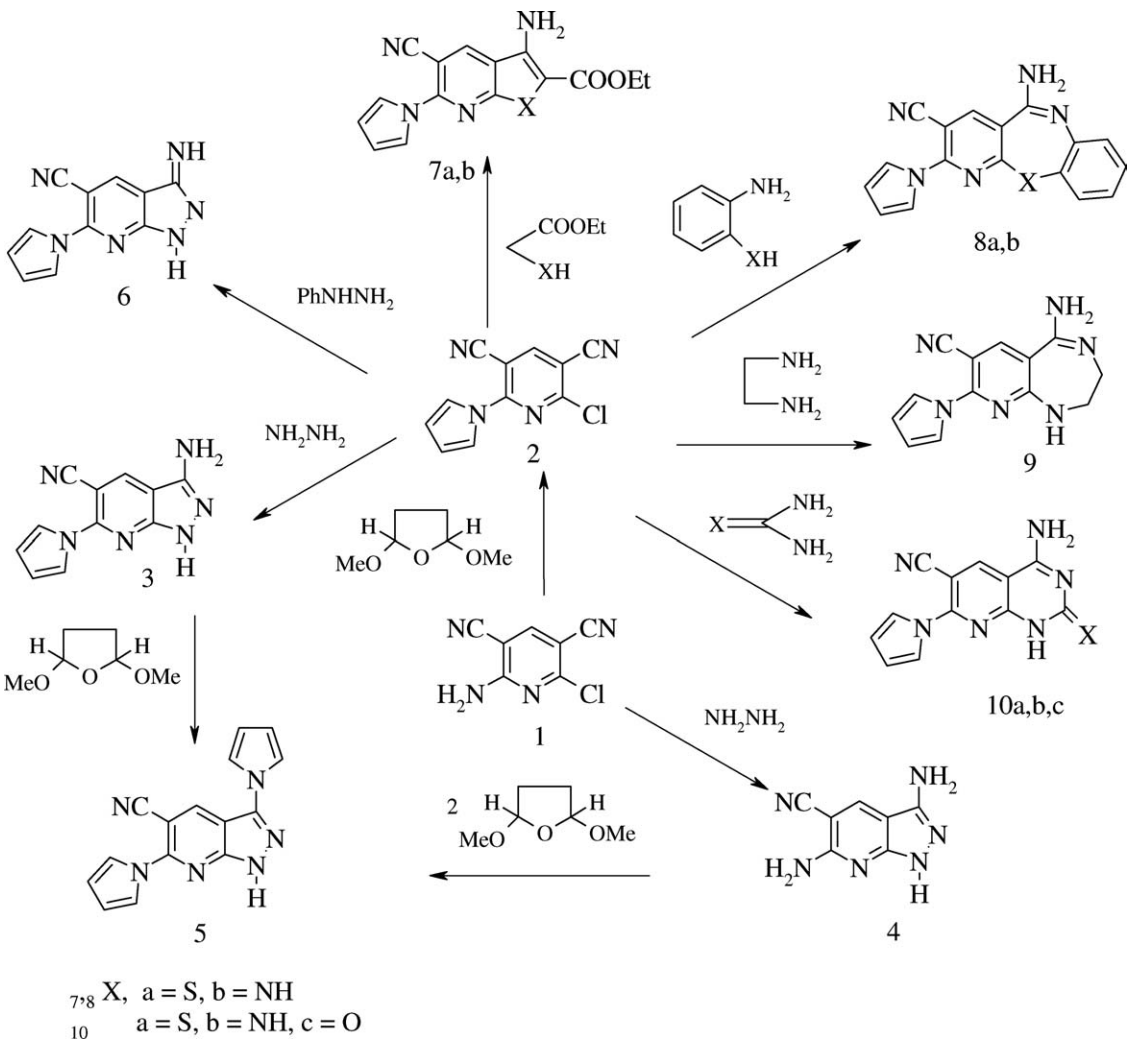
Compound **1** was allowed to react with phenylhydrazine, ethyl mercaptoacetate, ethylglycinate, *o*-aminothiophenol, *o*-phenylenediamine, or ethelenediamine, in ethanol in presence of TEA to give the corresponding pyrrazolo pyridine **11**, thienopyridine **12a**, pyrrolopyridines **12b**, pyridobenzothiazepine **13a**, pyridobenzodiazepine **13b**, or pyridothiazepine **14**, respectively.

The reaction of compound **1** with thiourea, guanidine or urea gave pyridopyrimidine derivatives **15a–c** and with benzoylhydrazide gave compound **16**, (Scheme 2).

EXPERIMENTAL

All melting points were determined on a Kofler melting points apparatus and are uncorrected. IR spectra were obtained

Scheme 1



on a Shimadzou FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Varian Gemini at 200 MHz using TMS as an internal reference and DMSO-d_6 as a solvent. Mass spectra were obtained on a Shimadzu GCMS-QP1000 mass spectrometer at 70 ev. Elemental analyses were performed on a Perkin-Elmer CHN-2400C analyzer model.

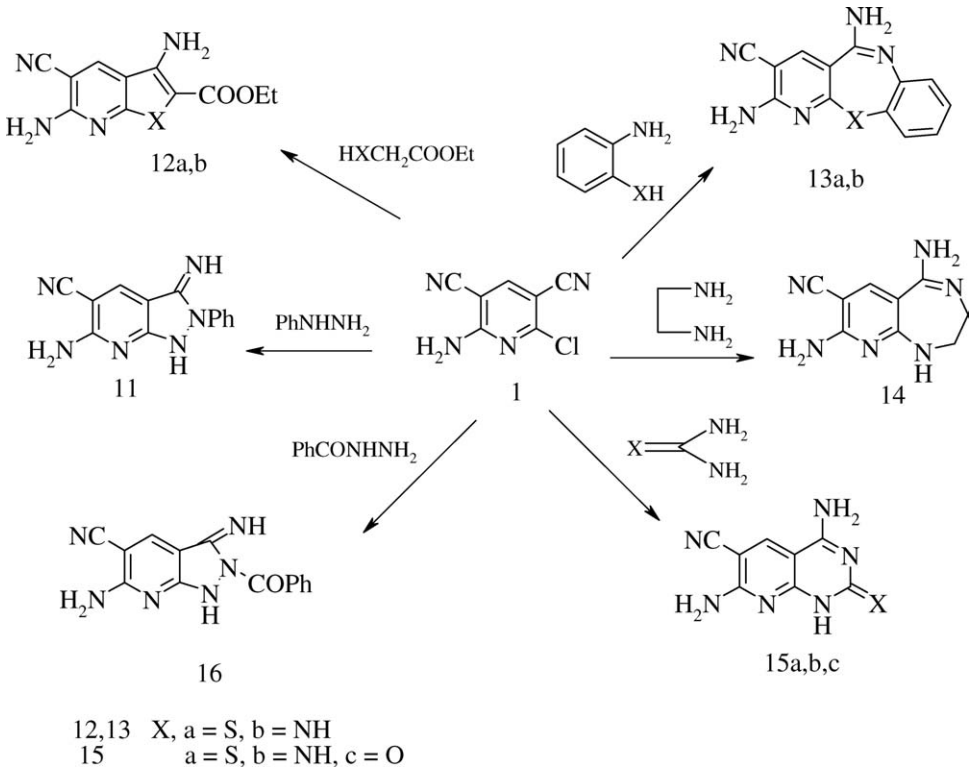
2-Chloro-6-(1H-pyrrol-1-yl)pyridine-3,5-dicarbonitrile (2). A mixture of compound **1** (1.79 g, 0.01 mol), 2,5-dimethoxytetrahydrofuran (1.32 mL, 0.01 mol), and glacial acetic acid (20 mL) was heated under reflux for 1 h. The reaction mixture was left to cool, poured onto ice-water. The precipitated solid was filtered off, washed with water, dried, and crystallized from ethanol, yield 1.95 g (86%), mp 138–140°C, ir: 2199(CN)cm^{-1}; ^{1}H-NMR: δ 8.83 (s, 1H, pyridine), 7.71, 7.61 (d, 2H, pyryl-2,5), 6.50, 6.42 (d,2H, pyryl-3,4). Anal. Calcd. for $C_{11}H_5ClN_4$: C, 57.78; H, 2.20; N, 24.50. Found: C, 57.55; H, 1.95; N, 24.75.

3-Amino-6-(1H-pyrrol-1-yl)-1H-pyrazolo[3,4-b]pyridine-5-carbonitrile (3). To a solution of compound **2** (1.15 g, 0.005 mol) in ethanol (25 mL), hydrazine hydrate (0.30 mL, 0.0055 mol) was added. The reaction mixture was refluxed for 1 h. The precipitated product formed on hot was filtered off, dried, and crystallized from ethanol to give 0.80 g (71%), mp 260–262°C, ir: 3417, 3333 (NH_2), 2210 (CN)cm^{-1}; ^{1}H-NMR: δ 8.85 (s, 1H, pyridine), 7.55 (d, 2H, pyryl-2,5), 6.66 (br, 1H, NH), 6.37 (d, 2H, pyryl-3,4), 6.10 (br, 2H, NH_2). Anal. Calcd. for $C_{11}H_8N_6$: C, 58.92; H, 3.60; N, 37.48. Found: C, 58.68; H, 3.36; N, 37.82.

3,6-Diamino-1H-pyrazolo[3,4-b]pyridine-5-carbonitrile (4). To a solution of 2-amino-6-chloropyridine-3,5-dicarbonitrile **1** (1.79 g, 0.01 mol) in ethanol (25 mL), hydrazine hydrate (0.60 mL, 0.011 mol) was added. The mixture was refluxed for 1 h. The precipitated product that formed on hot was filtered off, dried, and crystallized from methanol to yield 1.55 g (89%), mp > 300°C, ir; 3441, 3387, 3310 (NH, NH_2), 3210, 3138 (NH_2), 2207 (CN) cm^{-1}; ^{1}H-NMR: δ 8.23 (s, 1H,pyridine), 7.90 (s, 1H, NH), 6.70 (br, 4H, $2NH_2$). MS: *m/z* (100%): 174 (100%), 119 (23%), 52 (33%). Anal. Calcd. for $C_7H_6N_6$: C, 48.27; H, 3.47; N, 48.25. Found: C, 48.55; H, 3.19; N, 48.67.

3,6-Di-1H-pyrrol-1-yl-1H-pyrazolo[3,4-b]pyridine-5-carbonitrile (5). ***Method A.*** A mixture of compound **3** (0.87 g, 0.0005 mol) and 2,5-dimethoxytetra-hydrofuran (1.32 mL, 0.001 mol) in glacial acetic acid (15 mL) was heated under reflux for 1 h. The reaction mixture was left to cool, poured

Scheme 2



12,13 X, a = S, b = NH
15 a = S, b = NH, c = O

onto ice-cold water. The precipitated solid filtered, washed with water, dried, and crystallized from dioxane to give 1.0 g (73%), mp 330°C (charing), ir: 3425 (NH); 2224 (CN) cm^{-1}. ^{1}H-NMR: δ 8.20 (s, 1H, pyridine), 7.95 (s,1H,NH), 7.65, 7.25 (d, 4H, 2pyryl-2,5), 6.30, 6.23 (d,4H, 2pyryl-3,4). Anal. Calcd. for $C_{15}H_{10}N_6$: C, 65.68; H, 3.67; N, 30.64. Found: C, 65.96; H, 3.32; N, 30.98.

Method B. A mixture of compound **4** (0.56 g, 25 mmol) and 2,5-dimethoxytetra-hydrofuran (0.66 mL, 0.005 mol) in glacial acetic acid (15 mL) was heated under reflux for 1 h and worked up as above.

3-Imino-2-phenyl-6-(1H-pyrrol-1-yl)-2,3-dihydro-1H-pyrazolo[3,4-b] pyridine-5-carbonitrile (6). To a solution of compound **2** (1.15 g, 0.005 mol) in ethanol (25 mL), triethylamine (0.6 mL, 0.0059 mol), and phenylhydrazine (0.54 mL, 0.005 mol) were added. The mixture was refluxed for 4 h, then left to cool and the precipitated product was filtered off, dried, and crystallized from ethanol, yield 1.1 g (73%), mp 250–252°C, ir: 3428 (NH), 2220 (CN) cm^{-1}; ^{1}H-NMR: δ 8.90 (s, 1H, pyridine), 8.15 (d, 2H, CHm), 7.69 (d, 2H, pyryl-2,5), 7.53 (d, 2H, Ho), 7.26 (d, 1H, Hp), 6.55 (m, 2H, 2NH), 6.28 (d, 2H, pyryl-3,4). Anal. Calcd. for $C_{16}H_{12}N_6$: C, 67.99; H, 4.03; N, 27.98. Found: C, 67.65; H, 3.72; N, 28.31.

General procedure for preparation of thieno and pyrrolopyridine 7a,b and pyridobenzodiazipine derivatives 8a,b, and 9. An equimolar ratio of compound **2** (1.14 g, 0.005 mol), triethyamine (0.6 mL, 0.0059 mol) and ethyl mercaptoacetate, ethylglycinate, *o*-aminothiophenol, *o*-phenelyenediamine, or ethelenediamine (0.005 mol), was heated under reflux in ethanol (20 mL) for 3 h. Concentrated, left to cool, the obtained solid product was filtered off, and crystallized from the proper solvent.

Ethyl 3-amino-5-cyano-6-(1H-pyrrol-1-yl)thieno[2,3-b]pyridine-2-carboxylate 7a. Yield 1.3 g (83%), mp 224–226°C (ethanol); IR: 3410, 3328 (NH_2), 2214 (CN),1720 (CO) cm^{-1}; ^{1}H-NMR: δ 8.23 (s, 1H, pyridine), 7.65 (d, 2H, pyryl-2,5), 7.34 (s, 2H, NH_2), 6.42 (d, 2H, pyryl-3,4), 4.28 (q, 2H, CH_2), 1.31 (t, 3H, CH_3). MS: *m/z* (100%): 312 (100%), 266 (69%), 167 (13%). Anal. Calcd. for $C_{15}H_{12}N_4O_2S$: C, 57.68; H, 3.87; N, 17.94. Found: C, 57.35; H, 3.52; N, 18.32.

Ethyl 3-amino-5-cyano-6-(1H-pyrrol-1-yl)-1H-pyrrolo[2,3-b]pyridine-2-carboxylate 7b. Yield 1.2 g (81%), mp 178–180°C (dioxane); IR: 3405, 3320, 3240 (NH, NH_2), 2212 (CN), 1717 (CO) cm^{-1}; ^{1}H-NMR: δ 8.80–8.60 (m, 2H, pyridine +NH), 7.65, (d, 2H, pyryl-2,5), 6.41 (d, 2H, pyryl-3,4), 4.35–4.00 (m, 4H, CH_2 + NH_2), 1.19 (q, 3H, CH_3). Anal. Calcd. for $C_{15}H_{13}N_5O_2$: C, 61.01; H, 4.44; N, 23.72. Found: C, 60.70; H, 4.09; N, 23.99.

5-Amino-2-(1H-pyrrol-1-yl)pyrido[2,3-b][1,5]benzothiazepine-3-carbonitrile 8a. Yield 1.35 g (85%), mp 195–197°C (ethanol); IR: 3416, 3322 (NH_2), 2215 (CN) cm^{-1}; ^{1}H-NMR: δ 8.73 (s, 1H, pyridine), 7.56 (d, 2H, $H_{7,10}$), 7.41 (d, 2H, pyryl-2,5), 7.20 (d, 2H, $H_{8,9}$), 6.34 (d, 2H, pyryl-3,4), 5.49 (br, 2H, NH_2). Anal. Calcd. for $C_{17}H_{11}N_5S$: C, 64.34; H, 3.49; N, 22.07. Found: C, 64.04; H, 3.15; N, 22.45.

5-Amino-2-(1H-pyrrol-1-yl)-11H-pyrido[2,3-b][1,5]benzodiazepine-3-carbonitrile 8b. Yield 1.15 g (77%), mp 240–242°C (ethanol); IR: 3355, 3299, 3236 (NH, NH_2) cm^{-1}; ^{1}H-NMR: δ 9.50 (br, 1H, NH), 8.66 (s, 1H, pyridine), 7.49 (d, 2H, pyryl-2,5), 7.04 (d, 2H, $H_{7,10}$), 6.82 (d, 1H, H_8), 6.58 (d, 1H, H_9), 6.33 (s, 2H, pyryl-2,5), 5.09 (br, 2H, NH_2). MS: *m/z* (100%): 300 (44%), 134 (100%), 150 (12%). Anal. Calcd. for $C_{17}H_{12}N_6$: C, 67.99; H, 4.03; N, 27.98. Found: C, 67.65; H, 3.72; N, 28.37.

5-Amino-8-(1H-pyrrol-1-yl)-2,3-dihydro-1H-pyrido[2,3-e][1,4]diazepine-7-carbonitrile 9. Yield 0.9 g (71%), mp 233–235°C (ethanol); ir: 3428, 3343, 3264 (NH, NH_2), 2215 (CN) cm^{-1}; ^{1}H-NMR: δ 8.62 (s, 1H, pyridine), 7.79 (d, 2H, pyryl-2,5), 6.41 (d, 2H, pyryl-3,4), 6.34 (s, 2H, NH_2), 3.75, 3.03 (tr, 4H, $2CH_2$). Anal. Calcd. for $C_{13}H_{12}N_6$: C, 61.89; H, 4.79; N, 33.31. Found: C, 61.60; H, 4.46; N, 33.69.

General procedure for preparation of pyrido[2,3-d]pyrimidine derivatives 10a–c. A mixture of compound **2** (1.14 g, 0.005 mol), sodium carbonate (0.5 g, 0.005 mol) and thiourea, urea, or guanidine were refluxed in ethanol for 6 h concentrated, left to cool, and then poured onto ice/cold water. The obtained solid was collected and crystallized from the proper solvent.

4-Amino-7-(1H-pyrrol-1-yl)-2-thioxo-1,2-dihydropyrido[2,3-d]pyrimidine-6-carbonitrile 10a. Yield 1.25 g (79%), mp 233–235°C (dioxane); ir: 3428, 3343, 3264 (NH, NH_2), 2215 (CN) cm^{-1}; ^{1}H-NMR: δ 9.30 (br, 1H, NH), 8.70 (s, 1H, pyridine), 7.66 (d, 2H, pyryl-2,5), 6.25 (d, 2H, pyryl-3,4), 5.95 (s, 2H, NH_2). Anal. Calcd. for $C_{12}H_8N_6S$: C, 53.72; H, 3.01; N, 31.32. Found: C, 53.99; H, 2.78; N, 31.66.

4-Amino-2-oxo-7-(1H-pyrrol-1-yl)-1,2-dihydropyrido[2,3-d]pyrimidine-6-carbonitrile 10b. Yield 0.86 g (68%), mp 170–172°C (methanol); ir: 3410, 3335, 3245 (2NH, NH_2), 2228 (CN) cm^{-1}; ^{1}H-NMR: δ 9.65, 8.76 (br, 2H, 2NH), 8.45 (s, 1H, pyridine), 7.58 (d, 2H, pyryl-2,5), 6.30 (d, 2H, pyryl-3,4), 4.90 (s, 2H, NH_2). Anal. Calcd. for $C_{12}H_8N_6O$: C, 57.14; H, 3.20; N, 33.32. Found: C, 57.43; H, 2.90; N, 33.70.

4-Amino-2-imino-7-(1H-pyrrol-1-yl)-1,2-dihydropyrido[2,3-d]pyrimidine-6-carbonitrile 10c. Yield 0.83 g (66%), mp 233–235°C (ethanol); ir: 3418, 3333, 3254 (NH, NH_2), 2215 (CN), 1678 (CO) cm^{-1}; ^{1}H-NMR: δ 9.15 (br, 1H, NH), 8.57 (s, 1H, pyridine), 7.56 (d, 2H, pyryl-2,5), 6.15 (d, 2H, pyryl-3,4), 5.85 (s, 2H, NH_2). Anal. Calcd. for $C_{12}H_9N_7$: C, 57.37; H, 3.61; N, 39.02. Found: C, 57.07; H, 3.30; N, 39.39.

6-Amino-3-imino-2-phenyl-2,3-dihydro-1H-pyrazolo[3,4-b]pyridine-5-carbonitrile 11. A solution of compound **1** (0.90 g, 0.005 mol) in ethanol (25 mL) was treated with phenylhydrazine (0.54 mL, 0.005 mol). The reaction mixture was refluxed for 3 h, then left to cool. The precipitated product was filtered off, dried, and crystallized from ethanol, yield 0.81 g (65%), mp 320°C (ethanol); ir: 3428, 3368, 3182 (2NH, NH_2), 2223 (CN) cm^{-1}; ^{1}H-NMR: δ 8.54 (s, 1H, pyridine), 7.62–7.46 (m, 5H, phenyl), 7.44, 7.34 (s, 2H, 2NH), 7.24 (br, 2H, NH_2). Anal. Calcd. for $C_{13}H_{10}N_6$: C, 62.39; H, 4.03; N, 33.58. Found: C, 62.70; H, 3.78; N, 33.95.

General procedure for preparation of compounds 12a,b. An equimolar ratio of compound **1** (0.90 g, 0.005 mol) and ethyl mercaptoacetate (0.60 mL, 0.005 mol) in ethanol (20 mL) was treated with triethylamine (0.6 mL, 0.0059 mol). The reaction mixture was refluxed for 4 h, then left to cool. The precipitated solid was filtered off and crystallized from the proper solvent.

Ethyl 3,6-diamino-5-cyanothieno[2,3-b]pyridine-2-carboxylate 12a. Yield 0.9 g (69%), mp 280–282°C (dioxane); ir: 3415, 3328, 3224 ($2NH_2$), 2210 (CN), 1728 (CO) cm^{-1}; ^{1}H-NMR: δ 8.63 (s, 1H, pyridine), 7.40, 7.14 (s, 4H, $2NH_2$), 4.25–4.18 (q, 2H, CH_2 ester), 1.28–1.23 (t, 3H, CH_3 ester). MS: *m/z* (100%): 262 (100%), 216 (92%), 144 (18%). Anal. Calcd. for $C_{11}H_{10}N_4O_2S$: C, 50.37; H, 3.84; N, 21.36. Found: C, 50.65; H, 3.55; N, 21.73.

Ethyl 3,6-diamino-5-cyano-1H-pyrrolo[2,3-b]pyridine-2-carboxylate 12b. Yield 0.86 g (70%), mp 178–180°C (ethanol); ir: 3416, 3380, 3334, 3231 (NH, $2NH_2$), 2212 (CN), 1725 (CO) cm^{-1}; ^{1}H-NMR: δ 8.10 (s, 1H, pyridine), 7.74 (br, 1H, NH), 7.37 (s, 2H, NH_2), 4.20–4.00 (m, 4H, NH_2 + CH_2 ester), 1.28–1.23 (t, 3H, CH_3 ester). MS: *m/z* (100%): 245 (17%), 172 (100%). Anal. Calcd. for $C_{11}H_{11}N_5O_2$: C, 53.87; H, 4.52; N, 28.56. Found: C, 53.59; H, 4.22; N, 28.90.

General procedure for preparation of compounds 13a,b and 14. A solution of compound **1** (0.90 g, 0.005 mol) and ortho aminothiophenol, benzene-1,2-diamine, or ethylenediamine (0.005 mol) in ethanol (20 mL) was treated with triethylamine (0.6 mL, 0.0059 mol). The reaction mixture was refluxed for 1 h and 3 h, respectively, then left to cool. The precipitated solid was filtered off and crystallized from the proper solvent.

2,5-Diaminopyrido[2,3-b][1,5]benzothiazepine-3-carbonitrile 13a. Yield 0.92 g (69%), mp 270–272°C (methanol); ir: 3422, 3327, 3224 ($2NH_2$), 2216 (CN) cm^{-1}; ^{1}H-NMR: δ 9.25 (s, 1H, pyridine), 7.64–7.20 (m, 8H, arom., $2NH_2$). Anal. Calcd. for $C_{13}H_9N_5S$: C, 58.41; H, 3.39; N, 26.20. Found: C, 58.10; H, 3.08; N, 26.55.

2,5-Diamino-11H-pyrido[2,3-b][1,5]benzodiazepine-3-carbonitrile 13b. Yield 0.79 g (63%), mp 198–200°C (ethanol); ir: 3420, 3341, 3296, 3226 (NH, $2NH_2$), 2217 (CN) cm^{-1}; ^{1}H-NMR: δ 8.44 (br, 1H, NH), 8.12 (s, 1H, pyridine), 7.25 (br, 2H, NH_2), 7.12 (d, 1H, H7), 6.97 (d, 1H, H10), 6.78 (d, 1H, H8), 6.58 (d, 1H, H9), 4.92 (br, 2H, NH_2). MS: *m/z* (100%): 250 (45%), 178 (100%), 143 (67%), 89 (47%). Anal. Calcd. for $C_{13}H_{10}N_6$: C, 62.39; H, 4.03; N, 33.58. Found: C, 62.11; H, 3.75; N, 33.94.

5,8-Diamino-2,3-dihydro-1H-pyrido[2,3-e][1,4]diazepine-7-carbonitrile 14. Yield 0.74 g (73%), mp 213–215°C (methanol); ir: 3342, 3215, 3150 (NH, $2NH_2$), 2209 (CN) cm^{-1}; ^{1}H-NMR: δ 8.03 (s, 1H, pyridine), 7.41, 7.27 (br, 4H, $2NH_2$), 3.56 (t, 2H, H_8), 3.44 (t, 2H, H_7). Anal. Calcd. for $C_9H_{10}N_6$: C,53.46; H, 4.98; N, 41.56. Found: C, 53.18; H, 4.70; N, 41.90.

General procedure for preparation of compounds 15a–c. A solution of compound **1** (0.90 g, 0.005 mol) and thiourea, guanidine, or urea (0.005 mol) in DMF (20 mL) was refluxed for 3 h then left to cool. The precipitated solid was filtered off and crystallized from the proper solvent.

4,7-Diamino-2-thioxo-1,2-dihydropyrido[2,3-d]pyrimidine-6-carbonitrile 15a. Yield 0.85 g (78%), mp > 300°C (DMF); ir: 3440, 3361, 3315 (NH, $2NH_2$), 2060 (CN) cm^{-1}; ^{1}H-NMR: δ 9.35 (br, 1H, NH), 8.34 (s, 1H, pyridine), 8.06, 7.56 (br, 4H, $2NH_2$). Anal. Calcd. for $C_8H_6N_6S$: C,44.03; H, 2.77; N, 38.51. Found: C, 43.74; H, 2.47; N, 38.89.

4,7-Diamino-2-imino-1,2-dihydropyrido[2,3-d]pyrimidine-6-carbonitrile 15b. Yield 0.76 g (76%), mp 201–203°C (ethanol); ir: 3423, 3332, 3232 (2NH, $2NH_2$), 2221 (CN) cm^{-1}; ^{1}H-NMR: δ 8.78 (br, 1H, NH), 8.32 (s, 1H, pyridine), 7.87, 4.41 (br, 4H, $4NH_2$). Anal. Calcd. for $C_8H_7N_7$: C,47.76; H, 3.51; N, 48.73. Found: C, 47.46; H, 3.22; N, 49.08.

4,7-Diamino-2-oxo-1,2-dihydropyrido[2,3-d]pyrimidine-6-carbonitrile 15c. Yield 0.73 g (72%), mp 213–215°C (ethanol); ir: 3407, 3352, 3238 (NH, $2NH_2$), 2212 (CN), 1662 (CO) cm^{-1}; ^{1}H-NMR: δ 8.05 (s, 1H, pyridine), 7.40–7.00 (br, $2NH_2$). Anal. Calcd. for $C_8H_6N_6O$: C,47.53; H, 2.99; N, 41.57. Found: C, 47.26; H, 2.62; N, 41.94.

6-Amino-2-benzoyl-3-imino-2,3-dihydro-1H-pyrazolo[3,4-b]pyridine-5-carbonitrile 16. An equimolar ratio of compound **1** (0.90 g, 0.005 mol) and benzoylhydrazide (0.68 g, 0.005 mol) in ethanol (20 mL) was treated with triethylamine (0.6 mL, 0.0059 mol). The reaction mixture was refluxed for 3 h, then left to cool. The precipitated solid was filtered off and crystallized from ethanol. Yield 0.96 g (69%), mp 250–252°C, ir: 3434, 3337, 3237 (2NH, NH_2), 2216 (CN) cm^{-1}, ^{1}H-NMR: δ 10.57, 9.45 (br, 2H, 2NH), 8.15 (s, 1H, pyridine), 7.93 (br, 2H, NH_2), 7.60–7.10 (m, 5H, arom). Anal. Calcd. for $C_{14}H_{10}N_6O$: C,60.43; H, 3.62; N, 30.20. Found: C, 60.13; H, 3.33; N, 30.57.

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