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Heterosynthesis Using Nitriles: Novel Pyrrolo[2,3-*b*]pyridines

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Abstract

2-Amino-4-benzoyl-1-arylpyrrole-3-carbonitriles react with arylidene malonodinitriles, *β*-ketoesters and *β*-diketones to afford pyrrolo[2,3-*b*]pyridine derivatives.

Keywords: N-Arylpyrroles, Cinnamonitriles, Pyrrolo[2,3-*b*]pyridines

1. Introduction

Pyrroles and their fused derivatives represent an important class of heterocyclic compounds due to their diverse biological and pharmaceutical activities [1-4].

In the last two decades we were involved in a program aiming to develop new simple routes for the synthesis of heterocyclic compounds of anticipated biological activity to be evaluated as biodegradable agrochemicals [5-8]. We have reported the synthesis of a variety of pyrrole, N-substituted pyrrole and fused-pyrrole derivatives of biological interest [9-16]. Recently some pyrrolo[2,3-*b*] pyridine derivatives were shown to be effective as inhibitors of tumor necrosis factor alpha [17]. This encouraged us to prepare some new N-substituted pyrrolo-pyridine derivatives for biological evaluation study. The pyrrole derivatives **2a-d** (**Scheme 1**; obtained recently by us) [18] seemed suitable precursors to fulfill this objective through exploring the presence of the enaminonitrile moiety [19] as a site of reaction.

2. Results and Discussion

Pyrrole derivatives **2a-d** (**Scheme 1**; available from enaminone **1** in reaction with aromatic amines) [18] were reacted with the (hetero) arylidenes of malonodinitrile **3a-c** to afford yellow to brown colored products.

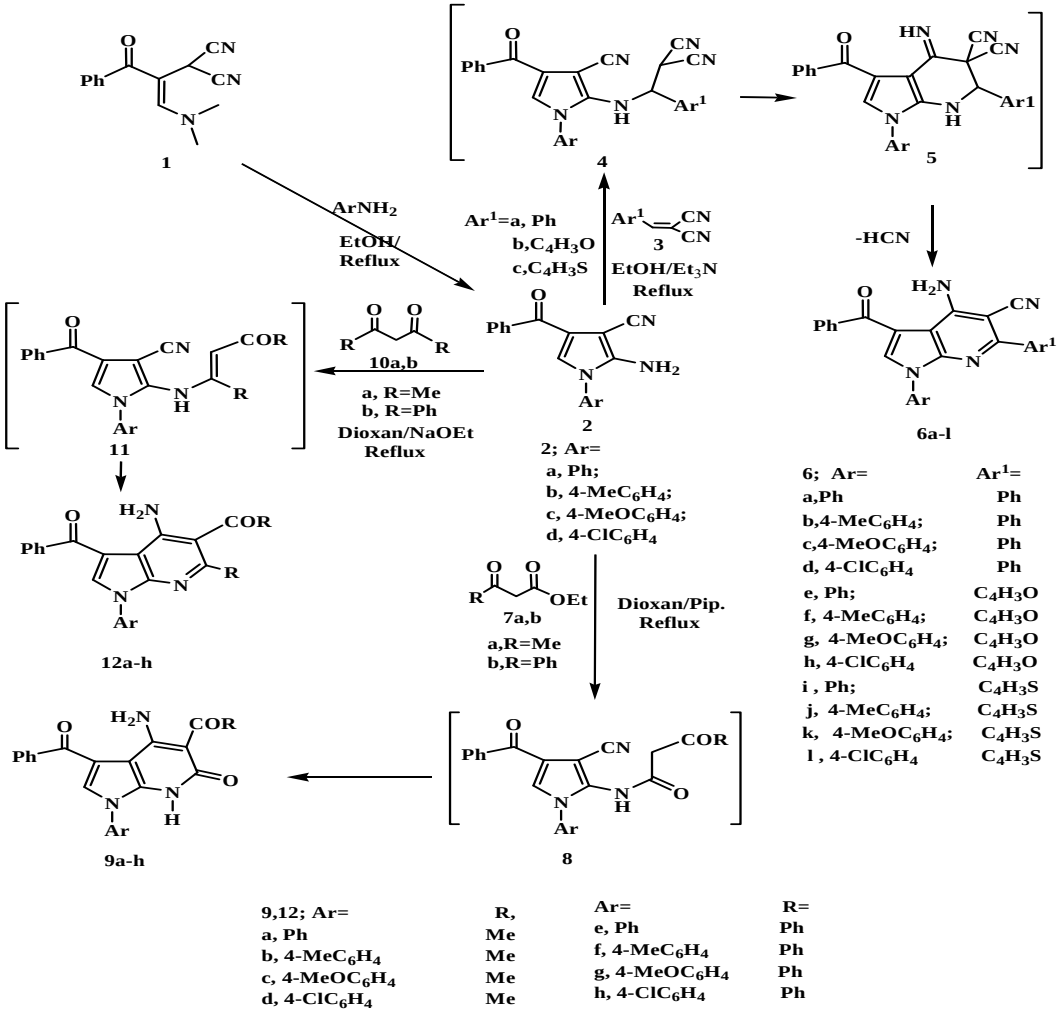
Based on their elemental analyses as well as mass and spectral data structures **6a-l** were assigned to these products. These new compounds are assumed to be formed via nucleophilic addition of the -NH_2 of **2a-d** to the activated double bond in **3** to produce firstly the intermediates **4a-l** which subsequently undergo cyclization via the active methyne protons to yield intermediates **5a-l**, which in role loses HCN to afford the isolable products **6a-l** (**Scheme 1**).

Next, compounds **2a-d** were treated with β-ketoesters **7a** and **7b** to yield pyrrolo-[2,3-*b*]-pyridine derivatives **9a-h** via, most likely, the intermediates **8a-h** which were formed by trans amidation followed by an intramolecular addition of the active methylene to the cyano group. Elemental analyses and spectral data were in complete agreement with the proposed structures **9a-h**.

Compounds **2a-d** also react with *β*-diketones **10a** and **10b** to give highly colored products. It is assumed that this third type of cyclocondensation reaction occurred via the intermediates **11a-h** which then undergo addition of the active methylene to the CN group to yield the pyrrolo [2,3-*b*]pyridine derivatives **12a-h**. Elemental analyses and spectral data were fully consistent with the proposed structures **12a-h**.

3. Experimental

Melting points were measured on an Electrothermal (9100) apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Perkin Elmer 1430 spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were carried out on a Varian Gemini 300 MHz spectrometer in DMSO-d_6 using TMS as internal standard and chemical shifts are expressed in δ ppm values. Assignments were made by correlation of the off-resonance decoupled ^{13}C-NMR spectra and determination of the ^{1}H-chemical shifts. Mass spectra were recorded on a Shimadzu GCMS-GB 1000 PX (70 ev). Elemental analyses were carried out at the Micro-analytical Center at Cairo University.



Scheme 1. The derivation of pyrrole.

Preparation of pyrrolo[2,3-*b*]pyridines 6a-l:

To a solution of each of the pyrrole derivatives **2a-d** (0.01 mol) in ethanol (20 mL) 0.01 mol of each of (hetero) benzylidenemonitriles **3a, 3b** or **3c** was added followed by few drops of triethylamine as catalyst. The reaction mixture was refluxed for 2 h and then left to cool overnight. The precipitated solids were collected by filtration and recrystallized from ethanol/DMF to give the title compounds **6a-l**.

4-Amino-3-benzoyl-1,6-diphenyl-1*H*-pyrrolo[2,3-*b*] pyridine-5-carbonitrile 6a: Yellow crystalline solid; yield 75% (3.1 g); mp 212˚C - 213˚C. υ_{max} = 3350, 3230 (NH_2), 2210 (CN), 1653 (CO) cm^{-1}; MS: *m/z* = 414 (M^+). δ_H = 5.56 (s, 2H D_2O exch., NH_2), 6.85 (s, 1H, pyrrole 2-H), 7.25 - 8.05 (m, 15H, Ar-H); δ_C = 87.7 (s), 104.4 (s), 106.3 (s), 120.3 (d), 125.4 (d), 127.2 (d), 127.2 (d), 117.3 (s), 127.3 (d), 128.7 (d), 129.0 (d), 129.4 (d), 129.6 (d), 132.9 (d), 133.3 (s), 139.7 (s), 140.5 (s), 154.5 (s), 155.3 (s), 158.7 (s), 187.5 (s). *Anal*. Calcd for $C_{27}H_{18}N_4O$ (414.46): C, 78.24; H, 4.38; N, 13.52. Found: C, 78.30; H, 4.41; N, 13.42.

4-Amino-3-benzoyl-6-phenyl-1-*p*-tolyl-1*H*-pyrrolo[2, 3-*b*]pyridine-5-carbonitrile 6b: Yellow crystalline solid; yield 68% (2.91 g); mp 224˚C - 225˚C. υ_{max} = 3352, 3235 (NH_2), 2212 (CN), 1655 (CO) cm^{-1}; δ_H = 2.32 (s, 3H, CH_3), 5.55 (s, 2H D_2O exch., NH_2), 6.83 (s, 1H, pyrrole 2-H), 7.26 - 8.00 (m, 14H, Ar-H). *Anal*. Calcd for $C_{28}H_{20}N_4O$ (428.48): C, 78.49; H, 4.70; N, 13.08. Found: C, 78.55; H, 4.52; N, 13.22.

4-Amino-3-benzoyl-1-(4-methoxyphenyl)-6-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile 6c: Yellow crystalline solid; yield 68% (3.0 g); mp 229˚C - 230˚C. υ_{max} = 3355, 3238 (NH_2), 2215 (CN), 1668 (CO) cm^{-1}; MS: *m/z* = 444 (M^+). δ_H = 3.76 (s, 3H, CH_3), 5.57 (s, 2H D_2O exch., NH_2), 6.84 - 8.02 (m, 15H, Ar-H). *Anal*. Calcd for $C_{28}H_{20}N_4O_2$ (444.48): C, 75.66; H, 4.54; N, 12.60. Found: C, 75.70; H, 4.58; N, 12.48.

4-Amino-3-benzoyl-1-(4-chlorophenyl)-6-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile 6d: Yellowish green crystalline solid; yield 78% (3.5 g); mp 235˚C - 237˚C. υ_{max} = 3353, 3235 (NH_2), 2213 (CN), 1663 (CO) cm^{-1}; δ_H = 5.54 (s, 2H D_2O exch., NH_2), 6.88 (s, 1H, pyrrole 2-H), 7.25 - 8.05 (m, 14H, Ar-H). *Anal*. Calcd for $C_{27}H_{17}ClN_4O$ (448.90): C, 72.24; H, 3.82; N, 12.48. Found: C, 72.30; H, 3.85; N, 12.55.

4-Amino-3-benzoyl-6-(furan-2-yl)-1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile 6e: Yellowish brown powder; yield 65% (2.63 g); mp 169˚C - 170˚C. υ_{max} = 3328, 3230 (NH_2), 2213 (CN), 1658 (CO) cm^{-1}; MS: *m/z* = 404 (M^+). δ_H = 5.57 (s, 2H D_2O exch., NH_2), 6.35 - 7.85 (m, 14H, Ar-H). *Anal*. Calcd for $C_{25}H_{16}N_4O_2$ (404.42): C, 74.25; H, 3.99; N, 13.85. Found: C, 74.32; H, 3.95; N, 13.65.

4-Amino-3-benzoyl-6-(furan-2-yl)-1-*p*-tolyl-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile 6f: Brownish powder; yield 63% (2.63 g); mp 173˚C - 175˚C. υ_{max} = 3330, 3232 (NH_2), 2213 (CN), 1660 (CO) cm^{-1}; δ_H = 2.33 (s, 3H, CH_3), 5.62 (s, 2H D_2O exch., NH_2), 6.32 - 7.82 (m, 13H, Ar-H). *Anal*. Calcd for $C_{26}H_{18}N_4O_2$ (418.45): C, 74.63; H, 4.34; N, 13.34. Found: C, 74.52; H, 4.45; N, 13.55.

4-Amino-3-benzoyl-1-(4-methoxyphenyl)-6-(furan-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile 6g: Brown powder; yield 67% (2.91 g); mp 178˚C - 179˚C. υ_{max} = 3335, 3228 (NH_2), 2211 (CN), 1663 (CO) cm^{-1}; MS: *m/z* = 434 (M^+). δ_H = 3.83 (s, 3H, CH_3), 5.63 (s, 2H D_2O exch., NH_2), 6.35 - 7.85 (m, 13H, Ar-H). *Anal*. Calcd for $C_{26}H_{18}N_4O_3$ (434.45): C, 71.88; H, 4.18; N, 12.90. Found: C, 71.92; H, 4.25; N, 13.05.

4-Amino-3-benzoyl-1-(4-chlorophenyl)-6-(furan-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile 6h: Greenish brown powder; yield 69% (3.0 g); mp 192˚C - 193˚C. υ_{max} = 3342, 3235 (NH_2), 2217 (CN), 1668 (CO) cm^{-1}; δ_H = 5.65 (s, 2H D_2O exch., NH_2), 6.37 - 7.88 (m, 13H, Ar-H). *Anal*. Calcd for $C_{25}H_{15}ClN_4O_2$ (438.87): C 68.42; H 3.45; Cl 8.08; N 12.77. Found: C 68.45; H 3.52; Cl 8.18; N 12.85.

4-Amino-3-benzoyl-1-phenyl-6-(thiophen-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile 6i: Yellowish crystalline solid; yield 72% (3.0 g); mp 174˚C - 175˚C. υ_{max} = 3329, 3232 (NH_2), 2218 (CN), 1654 (CO) cm^{-1}; δ_H = 5.55 (s, 2H D_2O exch., NH_2), 6.95 - 7.84 (m, 14H, Ar-H). *Anal*. Calcd for $C_{25}H_{16}N_4OS$ (420.49): C, 71.41; H, 3.84; N, 13.32. Found: C 71.48; H 3.92; N 13.45.

4-Amino-3-benzoyl-6-(thiophen-2-yl)-1-*p*-tolyl-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile 6j: Brownish fine crystals; yield 68% (2.95 g); mp 181˚C - 182˚C. υ_{max} = 3333, 3235 (NH_2), 2220 (CN), 1667 (CO) cm^{-1}; MS: *m/z* = 434 (M^+). δ_H = 2.34 (s, 3H, CH_3), 5.63 (s, 2H D_2O exch., NH_2), 6.92 - 7.82 (m, 13H, Ar-H). *Anal*. Calcd for $C_{26}H_{18}N_4OS$ (434.51): C, 71.87; H, 4.18; N, 12.89; S, 7.38. Found: C, 71.95; H, 4.25; N, 12.62; S, 7.52.

4-Amino-3-benzoyl-1-(4-methoxyphenyl)-6-(thiophen-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile 6k: Brown fine crystals; yield 66% (2.97 g); mp 205˚C - 206˚C. υ_{max} = 3340, 3238 (NH_2), 2215 (CN), 1670 (CO) cm^{-1}; MS: *m/z* = 450 (M^+). δ_H = 3.78 (s, 3H, CH_3), 5.62 (s, 2H D_2O exch., NH_2), 6.85 - 7.84 (m, 13H, Ar-H). *Anal*. Calcd for $C_{26}H_{18}N_4O_2S$ (450.51): C, 69.32; H, 4.03; N, 12.44; S, 7.12. Found: C, 69.38; H, 4.13; N, 12.55; S, 7.25.

4-Amino-3-benzoyl-1-(4-chlorophenyl)-6-(thiophen-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile 6l: Pale greenish brown powder; yield 73% (3.3 g); mp 209˚C - 210˚C. υ_{max} = 3344, 3238 (NH_2), 2221 (CN), 1672 (CO) cm^{-1}; δ_H = 5.66 (s, 2H D_2O exch., NH_2), 6.95 - 7.79 (m, 13H, Ar-H). *Anal*. Calcd for $C_{25}H_{15}ClN_4OS$ (454.93): C, 66.00; H, 3.32; Cl, 7.79; N, 12.32; S, 7.05. Found: C, 66.10; H, 3.38; Cl, 8.00; N, 12.45; S, 7.23.

Preparation of pyrrolo[2,3-*b*]pyridines 9a-h:

To a solution of each of the pyrrole derivatives **2a-d** (0.01 mol) in dioxane (20 mL) 0.01 mol of *β*-ketoesters **7a** or **7b** was added followed by few drops of piperidine catalyst. The reaction mixture was refluxed for 2 h then left to cool overnight. The precipitated solids were collected by filtration and recrystallized from dioxane to afford the title compounds **9a-h**.

5-Acetyl-4-amino-3-benzoyl-1-phenyl-1,7-dihydropyrrolo[2,3-*b*]pyridine-6-one 9a: Yellow crystals; yield 75% (2.78 g); mp 207˚C - 208˚C. υ_{max} = 3420 - 2235 (br. NH & NH_2), 1645, 1653 & 1678 (3CO) cm^{-1}; MS: *m/z* = 371 (M^+). δ_H = 2.35 (s, 3H, CH_3), 5.56 (s, 2H D_2O exch., NH_2), 6.93 (s, 1H, pyrrole 2-H), 7.28 - 7.85 (m, 10H, Ar-H), 8.22 (s, 1H, NH); δ_C = 22.4 (q), 111.2 (s), 112.3 (s), 112.4 (s), 119.9 (s), 120.2 (d), 120.6 (s), 125.4 (d), 128.6 (d), 129.2 (d), 129.5 (d), 132.4 (d), 133.3 (s), 140.5 (s), 163.7 (s), 167.4 (s), 186.7 (s), 196.5 (s). *Anal*. Calcd for $C_{22}H_{17}N_3O_3$ (371.39): C, 71.15; H, 4.61; N, 11.31. Found: C, 71.20; H, 4.68; N, 11.50.

5-Acetyl-4-amino-3-benzoyl-1-(*p*-tolyl)-1,7-dihydropyrrolo[2,3-*b*]pyridine-6-one 9b: Yellow crystals; yield 73% (2.8 g); mp 210˚C - 212˚C. υ_{max} = 3425 - 2232 (br. NH & NH_2), 1646, 1650 & 1673 (3CO) cm^{-1}; MS: *m/z* = 385 (M^+). δ_H = 2.33 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 5.55 (s, 2H D_2O exch., NH_2), 6.91 (s, 1H, pyrrole 2-H), 7.15 - 7.84 (m, 9H, Ar-H), 8.14 (s, 1H, NH); *Anal*. Calcd for $C_{23}H_{19}N_3O_3$ (385.42): C 71.67; H 4.97; N 10.90. Found: C 71.62; H 5.05; N 10.58.

5-Acetyl-4-amino-3-benzoyl-1-(4-methoxyphenyl)-1,7-dihydropyrrolo[2,3-*b*]pyridine-6-one 9c: Yellow crystals; yield 74% (2.96 g); mp 199˚C - 201˚C. υ_{max} = 3428 - 2233 (br. NH & NH_2), 1644, 1652 & 1674 (3CO) cm^{-1}; δ_H = 2.32 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 5.57 (s, 2H

D_2O exch., NH_2), 6.84 - 7.82 (m, 10H, Ar-H), 8.58 (s, 1H, NH); *Anal*. Calcd for $C_{23}H_{19}N_3O_4$ (401.41): C, 68.82; H 4.77; N 10.47. Found: C 68.60; H 5.00; N 10.65.

5-Acetyl-4-amino-3-benzoyl-1-(4-chlorophenyl)-1,7-dihydropyrrolo[2,3-*b*]pyridine-6-one 9d: Greenish yellow crystalline solid; yield 77% (3.12 g); mp 215˚C - 216˚C. υ_{max} = 3430 - 2235 (br. NH & NH_2), 1640, 1654 & 1673 (3CO) cm^{-1}; δ_H = 2.34 (s, 3H, CH_3), 5.58 (s, 2H D_2O exch., NH_2), 6.95 (s, 1H, pyrrole 2-H), 7.18 - 7.80 (m, 9H, Ar-H), 8.65 (s, 1H, NH); *Anal*. Calcd for $C_{22}H_{16}ClN_3O_3$ (405.83): C 65.11; H 3.97; Cl 8.74; N 10.35. Found: C 65.20; H 4.07; Cl 8.65; N 10.25.

4-Amino-3,5-dibenzoyl-1-phenyl-1,7-dihydropyrrolo[2,3-*b*]pyridine-6-one 9e: Dark yellow crystals; yield 75% (3.25 g); mp 237˚C - 238˚C. υ_{max} = 3460 - 3235 (br. NH & NH_2), 1642, 1653 & 1655 (3CO) cm^{-1}; MS: *m/z* = 433 (M^+). δ_H = 6.95 (s, 1H, pyrrole 2-H), 7.25 - 7.84 (m, 15H, Ar-H), 8.15 (s, 2H D_2O exch., NH_2), 10.4 (s, 1H D_2O exch., NH); *Anal*. Calcd for $C_{27}H_{19}N_3O_3$ (433.46: C, 74.81; H, 4.42; N, 9.69. Found: C, 74.70; H, 4.45; N, 9.55.

4-Amino-3,5-dibenzoyl-1-(*p*-tolyl)-1,7-dihydropyrrolo[2,3-*b*]pyridine-6-one 9f: Brownish yellow powder; yield 65% (2.90 g); mp 220˚C - 222˚C. υ_{max} = 3455 - 3228 (br. NH & NH_2), 1647, 1655 & 1658 (3CO) cm^{-1}; MS: *m/z* = 447 (M^+). δ_H = 2.36 (s, 3H, CH_3), 6.94 (s, 1H, pyrrole 2-H), 7.12 - 7.84 (m, 14H, Ar-H), 8.18 (s, 2H D_2O exch., NH_2), 10.6 (s, 1H D_2O exch., NH); *Anal*. Calcd for $C_{28}H_{21}N_3O_3$ (447.48): C, 75.15; H, 4.73; N, 9.39. Found: C, 74.90; H, 4.50; N, 9.52.

4-Amino-3,5-dibenzoyl-1-(4-methoxyphenyl)-1,7-dihydropyrrolo[2,3-*b*]pyridine-6-one 9g: Brownish yellow powder; yield 64% (2.96 g); mp 210˚C - 212˚C. υ_{max} = 3455 - 3228 (br. NH & NH_2), 1644, 1655 & 1658 (3CO) cm^{-1}; δ_H = 2.36 (s, 3H, CH_3), 6.94 (s, 1H, pyrrole 2-H), 7.12 - 7.84 (m, 14H, Ar-H), 8.18 (s, 2H D_2O exch., NH_2), 10.6 (s, 1H D_2O exch., NH); *Anal*. Calcd for $C_{28}H_{21}N_3O_4$ (463.48): C, 72.56; H, 4.57; N, 9.07. Found: C, 72.72; H, 4.52; N, 9.22.

4-Amino-3,5-dibenzoyl-1-(4-chlorophenyl)-1,7-dihydropyrrolo[2,3-*b*]pyridine-6-one 9h: Greenish yellow powder; yield 66% (3.1 g); mp 227˚C - 229˚C. υ_{max} = 3455 - 3228 (br. NH & NH_2), 1646, 1654 & 1660 (3CO) cm^{-1}; δ_H = 2.34 (s, 3H, CH_3), 6.94 (s, 1H, pyrrole 2-H), 7.16 - 7.83 (m, 14H, Ar-H), 8.18 (s, 2H D_2O exch., NH_2), 10.65 (s, 1H D_2O exch., NH); *Anal*. Calcd for $C_{27}H_{18}ClN_3O_3$ (467.90): C 69.31; H 3.88; Cl 7.58; N 8.98. Found: C 69.35; H 3.95; Cl 7.74; N 9.08.

Synthesis of pyrrolo[2,3-*b*]pyridines 12a-h:

To a solution of each of the pyrrole derivatives **2a-d** (0.01 mol) in dioxane (20 mL) 0.01 mol of each of *β*-diketones **10a** or **10b** was added followed by a catalytic amount of sodium ethoxide. The reaction mixture was refluxed for 3 h and then left to cool to room temperature. The reaction mixture was then poured on ice cold water and neutralized with few drops of conc. HCl (pH 7). The precipitated solids were collected by filtration and recrystallized from ethanol/DMF to afford the title compounds **12a-h**.

5-Acetyl-4-amino-3-benzoyl-6-methyl-1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine 12a: Yellow flakes; yield 72% (2.66 g); mp 230˚C - 231˚C. υ_{max} = 3355 & 3228 (NH_2), 1655 & 1662 (2CO) cm^{-1}; MS: *m/z* = 369 (M^+). δ_H = 2.44 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 6.92 (s, 1H, pyrrole 2-H), 7.25 - 7.85 (m, 10H, Ar-H), 8.22 (s, 2H D_2O exch., NH_2); δ_C = 14.3(q), 22.6 (q), 102.7(s), 107.2 (s), 111.2(s), 120.3(d), 125.3(d), 128.3(d), 128.7(d), 129.2(d), 129.6(d), 132.5(d), 133.4(s), 140.5(s), 147.2(s), 148.7(s), 153.8(s), 185.3(s), 195.5(s). *Anal*. Calcd for $C_{23}H_{19}N_3O_2$ (369.42): C, 74.78; H, 5.18; N, 11.37. Found: C, 74.85; H, 5.22; N, 11.50.

5-Acetyl-4-amino-3-benzoyl-6-methyl-1-(*p*-tolyl)-1*H*-pyrrolo[2,3-*b*]pyridine 12b: Dark yellow powder; yield 68% (2.6 g); mp 237˚C - 239˚C. υ_{max} = 3358 & 3232 (NH_2), 1656 & 1665 (2CO) cm^{-1}; δ_H = 2.37 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 6.88 (s, 1H, pyrrole 2-H), 7.05 - 7.82 (m, 9H, Ar-H), 8.25 (s, 2H D_2O exch., NH_2); *Anal*. Calcd for $C_{24}H_{21}N_3O_2$ (383.44): C, 75.18; H, 5.52; N, 10.96. Found: C, 75.35; H, 5.28; N, 10.75.

5-Acetyl-4-amino-3-benzoyl-1-(4-methoxyphenyl)-6-methyl-1*H*-pyrrolo[2,3-*b*]pyridine 12c: Brownish yellow powder; yield 66% (2.63 g); mp 245˚C - 246˚C. υ_{max} = 3354 & 3222 (NH_2), 1653 & 1660 (2CO) cm^{-1}; MS: *m/z* = 399 (M^+). δ_H = 2.45 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 3.77 (s, 3H, CH_3), 6.79 - 7.84 (m, 10H, Ar-H), 8.35 (s, 2H D_2O exch., NH_2); *Anal*. Calcd for $C_{24}H_{21}N_3O_3$ (399.44): C, 72.16; H, 5.30; N, 10.52. Found: C, 72.32; H, 5.25; N, 10.70.

5-Acetyl-4-amino-3-benzoyl-1-(4-chlorophenyl)-6-methyl-1*H*-pyrrolo[2,3-*b*]pyridine 12d: Lemon yellow powder; yield 70% (2.82 g); mp 257˚C - 259˚C. υ_{max} = 3355 & 3226 (NH_2), 1648 & 1656 (2CO) cm^{-1}; δ_H = 2.48 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 6.93 (s, 1H, pyrrole 2-H), 7.15 - 7.84 (m, 9H, Ar-H), 8.24 (s, 2H D_2O exch., NH_2); *Anal*. Calcd for $C_{23}H_{18}ClN_3O_2$ (403.86): C, 68.40; H, 4.49; Cl, 8.78; N, 10.40. Found: C, 68.48; H, 4.55; Cl, 8.85; N, 10.50.

4-Amino-3,5-dibenzoyl-1,6-diphenyl-1*H*-pyrrolo[2,3-*b*]pyridine 12e: Reddish yellow powder; yield 76% (3.75 g); mp 272˚C - 273˚C. υ_{max} = 3345 & 3186 (NH_2), 1642 & 1650 (2CO) cm^{-1}; MS: *m/z* = 493 (M^+). δ_H = 6.92 (s, 1H, pyrrole 2-H), 7.18 - 7.85 (m, 20H, Ar-H), 8.44 (s, 2H D_2O exch., NH_2); *Anal*. Calcd for $C_{33}H_{23}N_3O_2$ (493.55): C, 80.31; H, 4.70; N, 8.51. Found: C, 80.35; H, 4.78; N, 8.65.

4-Amino-3,5-dibenzoyl-6-phenyl-1-*p*-tolyl-1*H*-pyrrolo[2,3-*b*]pyridine 12f: Red powder; yield 72% (3.65 g); mp 279˚C - 280˚C. υ_{max} = 3346 & 3192 (NH_2), 1640 & 1652 (2CO) cm^{-1}; δ_H = 2.30 (s, 3H, CH_3), 6.95 (s, 1H, pyrrole 2-H), 7.15 - 7.82 (m, 19H, Ar-H), 8.39 (s, 2H D_2O exch., NH_2); *Anal*. Cal- cd for $C_{34}H_{25}N_3O_2$ (507.58): C, 80.45; H, 4.96; N, 8.28. Found: C, 80.36; H, 4.80; N, 8.60.

4-Amino-3,5-dibenzoyl-1-(4-methoxyphenyl)-6-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine 12g: Red powder; yield 72% (3.76 g); mp 290˚C - 292˚C. υ_{max} = 3348 & 3222 (NH_2), 1641 & 1655 (2CO) cm^{-1}; δ_H = 3.80 (s, 3H, CH_3), 6.78 - 7.83 (m, 20H, Ar-H), 8.22 (s, 2H D_2O exch., NH_2); *Anal*. Calcd for $C_{34}H_{25}N_3O_3$ (523.58): C, 77.99; H, 4.81; N, 8.03. Found: C, 80.76; H, 4.80; N, 8.20.

4-Amino-3,5-dibenzoyl-1-(4-chlorophenyl)-6-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine 12h: Crimson red powder; yield 73% (3.85 g); mp 305˚C - 307˚C. υ_{max} = 3354 & 3229 (NH_2), 1652 & 1658 (2CO) cm^{-1}; δ_H = 6.91 (s, 1H, pyrrole 2-H), 7.18 - 7.83 (m, 19H, Ar-H), 8.36 (s, 2H D_2O exch., NH_2); *Anal*. Calcd for $C_{33}H_{22}ClN_3O_2$ (528.00): C, 75.07; H, 4.20; Cl, 6.71; N, 7.96. Found: C, 75.00; H, 4.25; Cl, 6.78; N, 7.75.

4. Conclusions

A rapid and concise synthesis of three new series of highly functionalized pyrrolo[2,3-*b*]pyridines was described as occurring with satisfactory to good yields. They were offset by the simplicity of our strategy together with the structural profits gained. The envisaged biological activity of compounds is in progress.

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