Acylation of Heteroaromatic Amines: Facile and Efficient Synthesis of a New Class of 1,2,3-Triazolo[4,5-b]pyridine and Pyrazolo[4,3-b]pyridine Derivatives

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Abstract: 1,2,3-Triazolo[4,5-b]pyridines and pyrazolo[4,3-b]pyridines can be readily prepared via cyanoacetylation reactions of 5-amino-1,2,3-triazoles 1a,b and 4-amino-pyrazole 2 followed by subsequent cyclization of the formed cyanoacetamides. Reactions of amines 1a,b with a mixture of p-nitrophenylacetic acid and acetic anhydride under microwave irradiation conditions afforded the corresponding amides 15a,b that underwent cyclization to form 1,2,3-triazolo[4,5-b]pyridines 16a,b upon heating in DMF solutions containing sodium acetate. Reactions of 1a,b with active methylene compounds, including 17a-c, in the presence of zeolites as catalyst also afforded 1,2,3-triazolo[4,5-b]pyridine derivatives 20a-f via the intermediacy of triazole derivatives 19 and not 18.

Keywords: cyanoacetic acid; cyanoacetamides; triazolo[4,5-b]pyridine; pyrazolo[4,3-b]-pyridine; p-nitrophenylacetic acid; zeolite

1. Introduction

Pyrazolo[4,3-b]pyridine and triazolo[4,5-b]pyridine derivatives are of interest for their various applications as vasodilators, hypotensive, hypoglycemic, anti-inflammatory, analgesic, antiasthmatic,
antipyretic agents and as substrates of NAD glycohydrolase [1-3]. Owing to these interesting biological activities and medicinal properties these azolopyridine derivatives have been the targets of investigations by several research groups [4-8]. The present study describes the results of an investigation aimed at the preparation of a new class of 1,2,3-triazolo[4,5-b]pyridine and pyrazolo[4,3-b]pyridine derivatives. Cyanoacetylation of electron rich aromatic compounds and heteroaromatic amines, initially described by Slatt et al. [9] has found extensive utility in efficient routes for the preparation of 3-oxoalkanonitriles [10-15] and cyanoacetamides [16-18]. Cyanoacetylation of o-acyl heteroaromatic amines is expected to give cyanoacetamides in which an active methylene moiety is located in close proximity to a ketone carbonyl function. This enables ready cyclization of the products to form fused pyridines. However, to our knowledge this synthetic approach has not been explored to date. Below, we describe the results of an investigation of the preparation of cyanoacetamides and arylacetamides of 5-amino-1,2,3-triazoles and 4-aminopyrazoles and their utility in the preparation of condensed pyridines.

2. Results and Discussion

Readily obtainable (5-amino-2-phenyl-2H-1,2,3-triazol-4-yl)phenylmethanone (1a) [19], 1-(5-amino-2-phenyl-2H-1,2,3-triazol-4-yl)ethanone (1b) [20] and 4-amino-3-benzoyl-1-phenyl-1H-pyrazole-5-carbonitrile (2) [21] were found to react with a preheated mixture of acetic anhydride and cyanoacetic acid under microwave irradiation conditions to yield the corresponding cyanoacetamides 3 and 4 in excellent yields. These substances undergo cyclization to generate the respective fused pyridones 5 and 6 upon stirring at reflux for 30 min in DMF containing anhydrous sodium acetate (cf. Scheme 1). The structure of 5a was assigned by using X-ray crystallographic analysis (cf. Table 1 and Figure 1).

**Scheme 1.** Reaction of 5-amino-1,2,3-triazoles and 4-aminopyrazole with cyanoacetic acid.
The acylpyrazole 7 underwent ready cyanoacylation to afford the cyanoacetamide 8 in 93% yield. Heating a solution of 8 in DMF containing anhydrous sodium acetate leads to production of a substance whose structure should be either 9 or its isomer 10.

The actual structure of the product was assigned as 10 based on its $^{13}$C-NMR spectroscopic data which showed the absence of an acetyl carbonyl carbon resonance and its replacement by a peak at 186.19 ppm. Moreover, the methyl protons’ resonance at $\delta = 2.12$ ppm displays a HMBC cross peak with the carbon peak at $\delta = 105.72$ ppm that is assigned as C-6. In addition the X-ray crystallographic analysis of this product demonstrated that it has the structure represented by 10 (cf. Scheme 2 and Figure 2).

In a similar manner, bis-acylpyrazole 11 is readily cyanoacylated to afford the corresponding cyanoacetamide 12 in excellent yield. Heating a DMF solution of 12 containing anhydrous sodium acetate afforded a product that may also have the isomeric structures represented by 13 and 14. As before, the actual structure of the product was shown to be 14 based on its $^{13}$C-NMR spectrum, which contained a carbonyl resonance at 202.41 ppm. This chemical shift is expected for an acyl carbonyl at the C-3 position of the pyrazole ring and not at C-5 since in the latter case shielding provided by the N-lone pair should make the resonance appear at a higher field (cf. Scheme 3).
Scheme 2. Synthesis of pyrazolo[4,3-b]pyridine-6-carbonitrile 10.

Figure 2. ORTEP plot of the x-ray crystallographic data determined for 10 containing one DMSO molecule. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 816562 [23].

Scheme 3. Synthesis of pyrazolo[4,3-b]pyridine-6-carbonitrile 14.
We have previously [10] suggested that in the mechanistic pathway for the process described by Slatt [9], the mixed anhydride is formed initially and then it reacts by nucleophilic addition of an amine or electron rich aromatic system at the more electron deficient cyanoacetyl carbonyl. As a consequence of this proposal, we believed that other mixed anhydrides could be used as arylacetamide precursors provided that the reactions occur at the more electron deficient aroyl carbonyl. In fact, heating \( p\)-nitrophenylacetic acid with acetic anhydride, followed by addition of either 1a or 1b and heating the mixture in a microwave oven for 60 s, afforded the corresponding amides 15a and 15b that are readily cyclized to form the respective triazolo[4,5-\( b\)]pyridines derivatives 16a and 16b upon heating in DMF containing anhydrous sodium acetate (cf. Scheme 4).

**Scheme 4.** Reaction of 5-amino-1,2,3-triazoles with \( p\)-nitrophenylacetic acid.

We have explored a possible extension of this methodology, which relies on conversion of the acetamide derivatives of 1,2,3-triazoles to their corresponding 1,2,3-triazolo[4,5-\( b\)]pyridines, by probing the reactivity 1a,b with other active methylene compounds like 17a-c. The results of this study showed that 1a,b underwent condensation with 17a-c in presence of zeolite catalysts, followed by heating to produce the corresponding 1,2,3-triazolo[4,5-\( b\)]pyridine derivatives 20a-f. The structure of 20f was assigned by X-ray crystallographic analysis. Although these products could potentially formed via the intermediacy of either triazole 18 or 19, it is almost certain that 19 is the intermediate as attempts to condense \( N\)-acetyl-1,2,3-triazole derivatives 21 with active methylene compounds failed. Moreover the reaction of 20a with another molecule of 1a afforded 22, which is generated via elimination of ethanol (cf. Figure 3 and Scheme 5).

In contrast, 1b was found to react with ethyl acetoacetate (17b) in absence of zeolite to yield a condensation product that arises by elimination of one molecule of water. X-ray crystallographic analysis of this substance demonstrated that it has the structure represented by 23, a product that is formed via initial addition of the amine to the carbonyl carbon of 17b (Figure 4, Table 2). The fact that 1b reacts with ethyl acetoacetate (17b) to yield either the intermediate 23 or 19f demonstrates the effect of the zeolite, a microporous catalyst that favors formation of slim molecules like 19 rather than bulky ones like 23, so the latter is formed in absence of such a catalyst. Also, 23 separated from the reaction mixture underwent cyclization in refluxing DMF containing anhydrous sodium acetate to form 24 via loss of another molecule of water. (cf. Scheme 6).
**Figure 3.** ORTEP plot of the x-ray crystallographic data determined for 20f. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 815380 [24].

**Scheme 5.** Reaction of 5-amino-1,2,3-triazoles with active methylene compounds.

**Scheme 6.** Reaction of 1b with ethyl acetoacetate to afford 24.
Figure 4. ORTEP plot of the x-ray crystallographic data determined for 23. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 805282 [25].

Table 2. Selected bond lengths and bond angles for 23.

| Bond       | Bond length | Bond       | Bond angle |
|------------|-------------|------------|------------|
| N1-N2      | 1.317       | N1-N2-C8   | 103.8      |
| N1-N3      | 1.359       | N1-N3-C7   | 102.7      |
| N3-C7      | 1.330       | N2-N1-N3   | 116.1      |
| N2-C8      | 1.336       | N3-C7-C8   | 109.0      |
| C8-C9      | 1.462       | N2-C8-C7   | 108.5      |
| N4-C7      | 1.379       | O1-C9-C8   | 119.5      |

Inspection of the crystallographically determined bond angles and lengths of the 1,2,3-triazole rings in both 5a, 20f and 23 indicate that the N3-N1-N2 bond angles deviate significantly from typical sp<sup>3</sup> nitrogen values and are close to those that are associated with sp<sup>2</sup> nitrogens. However, the N2-C8-C7 or N3-C7-C8 bond angles are close to those expected for sp<sup>3</sup> carbons. Similar observations, made earlier in studies of very similar systems by Elnagdi et al., [19] have been taken as evidence for the significant contribution of charge separated resonance forms delocalizing N-1 lone pairs to the ring carbons. Importantly, both 5a, 20f and 23 are planar substances, a fact that adds further support to the conclusion that resonance delocalization of N-1 lone pair occurs in these systems.

3. Experimental

3.1. General

Melting points were recorded on a Griffin melting point apparatus and are reported uncorrected. IR spectra were recorded using KBr disks using a Perkin-Elmer System 2000 FT-IR spectrophotometer. ¹H-NMR (400 MHz) and ¹³C-NMR (100 MHz) spectra were recorded at 25 °C in CDCl₃ or DMSO-d₆ as solvent with TMS as internal standard on a Bruker DPX 400 super-conducting NMR spectrometer.
Chemical shifts are reported in ppm. Mass spectra were measured using a high resolution GC-MS (DFS) thermo spectrometers with El (70 EV). Microanalyses were performed on a LEKO CHNS-932 Elemental Analyzer. Reactions were conducted under microwave irradiation in heavy-walled Pyrex tubes (capacity 10 mL) fitted with PCS caps. Microwave heating was carried out with a single mode cavity Explorer Microwave synthesizer (CEM Corporation, 3100 Smith Farm Road, Matthews, NC, USA). The zeolite (≤ 45 µm) was purchased from Fluka Company with product No. 96096. The crystal structures were determined by a Rigaku R-AXIS RAPID diffractometer using filtered Mo-Kα radiation at Kuwait University. Compounds 1a,b, 2 and 21 were prepared using literature procedures [19-21].

3.2. General Procedure for the Preparation of Cyanoacetamides 3, 4, 8 and 12

A solution of cyanoacetic acid (0.45 g, 5 mmol) in Ac2O (5 mL) was heated in the microwave oven at 85 °C for 10 s then compounds 1, 2, 7 or 11 (5 mmol) were added and the reaction mixture was heated for further 30 s at 100 °C. The reaction mixture was allowed to cool to room temperature and the formed crystalline solid was separated by filtration and washed with cold ethanol and then hot ethanol to afford 3, 4, 8 and 12, respectively, as pure substances.

N-(5-Benzoyl-2-phenyl-2H-1,2,3-triazol-4-yl)-2-cyanoacetamide (3a). Creamy white crystals, yield: 98%, m.p. 210 °C; IR (KBr): ν/cm⁻¹ 3291 (NH), 2257 (CN), 1692, 1634 (2CO); ¹H-NMR (DMSO-d₆): δ = 4.04 (s, 2H, CH₂), 7.50 (t, J = 7.6 Hz, 1H, Ar-H), 7.56–7.64 (m, 4H, Ar-H), 7.73 (t, J = 7.6 Hz, 1H, Ar-H), 8.01 (d, J = 7.6 Hz, 2H, Ar-H), 8.10 (d, J = 7.6 Hz, 2H, Ar-H) and 11.23 ppm (s, 1H, NH); ¹³C-NMR (DMSO-d₆): δ 26.03 (CH₂), 115.35 (CN), 118.76, 126.64, 128.68, 129.91, 129.97, 133.77, 136.04, 137.22, 138.48, 144.19, 161.40 and 185.82 ppm (Ar-C and CO); MS (EI): m/z (%) 331 (M +, 74.35), 332 (M++1, 16.90). Anal. calcd. for C₁₈H₁₃N₅O₂ (331.34): C, 65.25; H, 3.95; N, 21.14. Found: C, 65.28; H, 4.02; N, 21.20.

N-(5-Acetyl-2-phenyl-2H-1,2,3-triazol-4-yl)-2-cyanoacetamide (3b). Buff crystals, yield: 95%, m.p. 205 °C; IR (KBr): ν/cm⁻¹ 3302 (NH), 2262 (CN), 1685, 1638 (2CO); ¹H-NMR (DMSO-d₆): δ 2.62 (s, 3H, CH₃), 4.11 (s, 2H, CH₂), 7.51 (t, J = 8.0 Hz, 1H, Ar-H), 7.62 (t, J = 8.0 Hz, 2H, Ar-H), 8.03 (d, J = 8.0 Hz, 2H, Ar-H) and 10.67 ppm (s, 1H, NH); ¹³C-NMR (DMSO-d₆): δ 26.28 (CH₂), 27.71 (CH₃), 115.51 (CN), 118.79, 128.65, 129.90, 137.79, 138.46, 143.32, 161.66 and 191.69 ppm (Ar-C and CO); MS (EI): m/z (%) 269 (M⁺, 100), 270 (M⁺+1, 25.6). Anal. calcd. for C₁₃H₁₁N₅O₂ (269.26): C, 57.99; H, 4.12; N, 26.14. Found: C, 58.04; H, 4.06; N, 25.93.

N-(3-Benzoyl-5-cyano-1-phenyl-1H-pyrazol-4-yl)-2-cyanoacetamide (4). Creamy white crystals, yield: 93%, m.p. 234 °C; IR (KBr): ν/cm⁻¹ 3259 (NH), 2227, 2263 (2CN), 1712, 1631 (2CO); ¹H-NMR (DMSO-d₆, 25 °C): δ = 4.13 (s, 2H, CH₂), 7.57–7.72 (m, 6H, Ar-H), 7.83 (d, J = 7.6 Hz, 2H, Ar-H), 8.14 (d, J = 7.6 Hz, 2H, Ar-H) and 10.83 ppm (s, 1H, NH); ¹³C-NMR (DMSO-d₆): δ 25.84 (CH₂), 109.64, 110.24, 115.41, 124.20, 128.60, 128.75, 129.76, 130.08, 130.20, 133.74, 135.94, 137.70, 141.38, 161.56 and 186.71 ppm (2CN, Ar-C and CO); MS (EI): m/z (%) 355 (M⁺, 73.20), 356 (M⁺+1, 20.35). Anal. calcd. for C₂₀H₁₃N₅O₂ (355.36): C, 67.60; H, 3.69; N, 19.71. Found: C, 67.57; H, 3.75; N, 19.74.
N-(5-Acetyl-3-benzoyl-1-phenyl-1H-pyrazol-4-yl)-2-cyanoacetamide (8). Orange crystals, yield: 93%, m.p. above 300 °C; IR (KBr): υ/cm⁻¹ 3297 (NH), 22114 (CN), 1687 (br), 1636 (3CO); ¹H-NMR (DMSO-d₆): δ = 2.40 (s, 3H, CH₃), 4.02 (s, 2H, CH₂), 7.53–7.60 (m, 7H, Ar-H), 7.69 (t, J = 7.2 Hz, 1H, Ar-H), 8.10 (d, J = 7.6 Hz, 2H, Ar-H) and 10.45 ppm (s, 1H, NH); ¹³C-NMR (DMSO-d₆): δ 25.72 (CH₂), 29.87 (CH₃), 115.54 (CN), 122.13, 124.88, 129.13, 129.17, 130.14, 133.42, 135.78, 136.26, 139.65, 142.76, 162.14, 187.20 and 189.62 ppm (Ar-C and CO); MS (EI): m/z (%) 372 (M⁺, 30.20), 373 (M⁺⁺, 8.57). Anal. calcd. for C₂₁H₁₆N₄O₃ (372.39): C, 67.73; H, 4.33; N, 15.05. Found: C, 67.69; H, 4.31; N, 15.10.

2-Cyano-N-(3,5-diacetyl-1-phenyl-1H-pyrazol-4-yl)acetamide (12). Creamy white crystals, yield: 89%, m.p. 230 °C; IR (KBr): υ/cm⁻¹ 3284 (NH), 2260 (CN), 1685 (br), 1637 (3CO); ¹H-NMR (DMSO-d₆): δ = 2.33 (s, 3H, CH₃), 2.57 (s, 3H, CH₃), 4.03 (s, 2H, CH₂), 7.49–7.57 (m, 5H, Ar-H) and 10.34 ppm (s, 1H, NH); ¹³C-NMR (DMSO-d₆): δ 26.16 (CH₂), 27.72 (CH₃), 30.22 (CH₃), 116.01 (CN), 125.95, 127.94, 129.63, 129.68, 137.18, 140.05, 143.17, 162.64, 190.18 and 193.80 ppm (Ar-C and CO); MS (EI): m/z (%) 310 (M⁺, 55.1), 311 (M⁺⁺, 10.75). Anal. calcd. for C₁₆H₁₄N₄O₃ (310.31): C, 61.93; H, 4.55; N, 18.05. Found: C, 61.88; H, 4.57; N, 17.98.

3.3. General Procedure for the Cyclization of Cyanoacetamides to Azolo Pyridines 5, 6, 10 and 14

Independent solutions of cyanoacetamides 3, 4, 8 and 12 (5 mmol), in DMF (10 mL) containing anhydrous sodium acetate (1 g) were stirred at reflux for 1 h. Then, the reaction mixture was cooled to room temperature and poured into ice cold water. The formed crude products were collected by filtration, washed with water and recrystallized from the appropriate solvent to afford the corresponding azolo pyridine derivatives 5, 6, 10 and 14, respectively.

5-Oxo-2,7-diphenyl-4,5-dihydro-2H-[1,2,3]triazolo[4,5-b]pyridine-6-carbonitrile (5a). Recrystallized from a EtOH/dioxane (1:1) mixture as yellow crystals, yield: 87%, m.p. above 300 °C; IR (KBr): υ/cm⁻¹ 3437 (NH), 2230 (CN), 1651 (CO); ¹H-NMR (DMSO-d₆): δ 7.47 (t, J = 7.6 Hz, 1H, Ar-H), 7.56 (t, J = 8.0 Hz, 2H, Ar-H), 7.65–7.67 (m, 3H, Ar-H), 7.89 (d, J = 7.6 Hz, 2H, Ar-H), 7.97 (d, J = 8.0 Hz, 2H, Ar-H) and 13.30 ppm (s, 1H, NH); ¹³C-NMR (DMSO-d₆): δ 105.22, 115.73 (CN), 119.10, 128.81, 129.21, 129.95, 130.3, 131.14, 131.51, 138.62, 148.07, 151.23 and 160.14 ppm (Ar-C and CO); MS (EI): m/z (%) 313 (M⁺, 100), 314 (M⁺⁺, 10.75). Anal. calcd. for C₁₈H₁₁N₅O (313.32): C, 69.03; H, 3.54; N, 22.35. Found: C, C, 69.03; H, 3.48; N, 22.39.

3.3.1. Crystallographic Analysis for 5a

The crystals were mounted on a glass fiber. All measurements were performed on a Rigaku R-AXIS RAPID diffractometer using filtered Mo-Kα radiation. The data were collected at a temperature of 20 ± 1 °C to a maximum 20 value of 55.0° using the ω scanning technique. The structure was solved by charge flipping method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.
3.3.2. Crystal Data

C$_{18}$H$_{11}$N$_5$O, M = 313.32, triclinic, a = 6.861(4)Å, b = 11.229(6)Å, c = 12.987(7)Å, V = 869.3(8)Å$^3$, α = 110.560(9)°, β = 103.584(9)°, γ = 100.858(9)°, space group: P-1, Z = 2, D$_{calc}$ = 1.365 g cm$^{-3}$, No. of reflection measured 3956, 2$θ$$_{max}$ = 55.0°, R1 = 0.12. Figure 1 illustrates the structure as determined. Full data can be obtained on request from the CCDC [22].

7-Methyl-5-oxo-2-phenyl-4,5-dihydro-2H-[1,2,3]triazolo[4,5-b]pyridine-6-carbonitrile (5b). Recrystallized from an EtOH/dioxane (2:1) mixture as yellow crystals, yield: 83%, m.p. above 300 °C; IR (KBr): ν/cm$^{-1}$ 3410 (NH), 2228 (CN), 1658 (CO); $^1$H-NMR (DMSO-d$_6$): δ = 2.64 (s, 3H, CH$_3$), 7.48 (t, J = 8.0 Hz, 1H, Ar-H), 7.58 (t, J = 8.0 Hz, 2H, Ar-H), 8.00 (d, J = 8.0 Hz, 2H, Ar-H), and 13.04 ppm (s, 1H, NH); $^{13}$C-NMR (DMSO-d$_6$): δ = 16.94 (CH$_3$), 107.37, 115.30 (CN), 119.39, 129.57, 130.41, 131.96, 139.07, 147.66, 152.55 and 160.07 ppm (Ar-C and CO); MS (EI): m/z (%) 251 (M$^+$, 100), 252 (M$^+$+1, 30.58). Anal. calcd. for C$_{13}$H$_9$N$_5$O (251.25): C, 62.15; H, 3.61; N, 27.87. Found: C, 62.19; H, 3.55; N, 27.91.

5-Oxo-2,7-diphenyl-4,5-dihydro-2H-pyrazolo[4,3-b]pyridine-3,6-dicarbonitrile (6). Recrystallized from a EtOH/dioxane (1:1) mixture as beige crystals, yield: 80%, m.p. above 300 °C; IR (KBr): ν/cm$^{-1}$ 3375 (NH), 2227 (br, 2CN), 1656 (CO); $^1$H-NMR (DMSO-d$_6$): δ = 7.64–7.66 (m, 6H, Ar-H), 7.79 (d, J = 7.6 Hz, 2H, Ar-H), 7.85 (d, J = 7.2 Hz, 2H, Ar-H) and 13.30 ppm (s, 1H, NH); $^{13}$C-NMR (DMSO-d$_6$): δ = 100.37, 105.99, 109.67, 115.83, 124.37, 129.02, 129.91, 130.18, 130.77, 131.22, 131.71, 133.12, 135.46, 138.11, 152.78 and 159.81 ppm (2CN, Ar-C and CO); MS (EI): m/z (%) 337 (M$^+$, 100), 338 (M$^+$+1, 25.0). Anal. calcd. for C$_{20}$H$_{11}$N$_5$O (337.34): C, 71.21; H, 3.29; N, 20.76. Found: 71.19; H, 3.36; N, 20.83.

3-Benzoyl-7-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazolo[4,3-b]pyridine-6-carbonitrile (10). Recrystallized from DMSO as brown crystals, yield: 77%, m.p. 238–240 °C; IR (KBr): ν/cm$^{-1}$ 3381 (NH), 2223 (CN), 1681, 1658 (2CO); $^1$H-NMR (DMSO-d$_6$): δ = 2.12 (s, 3H, CH$_3$), 7.56–7.81 (m, 8H, Ar-H), 8.22 (d, J = 7.2 Hz, 2H, Ar-H) and 12.02 ppm (s, 1H, NH); $^{13}$C-NMR (DMSO-d$_6$): δ = 18.23 (CH$_3$), 105.72, 115.34 (CN), 126.28, 127.04, 127.57, 128.59, 129.15, 129.45, 129.60, 130.07, 130.63, 133.52, 136.00, 138.95, 159.17 and 186.19 ppm (Ar-C and CO); MS (EI): m/z (%) 354 (M$^+$, 100), 355 (M$^+$+1, 27.1). Anal. calcd. for C$_{21}$H$_{14}$N$_4$O$_2$ (354.37): C, 71.18; H, 3.95; N, 15.81. Found: 71.24; H, 4.02; N, 15.77.

3.3.3. Crystallographic Analysis for 10

The crystals were mounted on a glass fiber. All measurements were performed on a Rigaku R-AXIS RAPID diffractometer using filtered Mo-Kα radiation. The data were collected at a temperature of 20 ± 1 °C to a maximum 20 value of 55.0° using the ω scanning technique. The structure was solved by charge flipping method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.
3.3.4. Crystal Data

\[ \text{C}_{21}\text{H}_{14}\text{N}_{4}\text{O}_{2}^+ \text{ one DMSO molecule, M} = 354.37, \text{ monoclinic, } a = 11.518(2) \text{ Å}, b = 9.386(2) \text{ Å}, c = 19.655(3) \text{ Å}, V = 2123.5(5) \text{ Å}^3, \alpha = \gamma = 90.00^\circ, \beta = 92.069(7)^\circ, \text{ space group: P2}_1/n, Z = 4, D_{\text{calc}} = 1.353 \text{ g cm}^{-3}, \text{ No. of reflection measured 4731, } 2\theta_{\text{max}} = 55.0^\circ, \text{ } R1 = 0.1088. \text{ Figure 2 illustrates the structure as determined. Full data can be obtained on request from the CCDC [23].} \]

3-Acetyl-7-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazolo[4,3-b]pyridine-6-carbonitrile (14). Recrystallized from DMF as buff crystals, yield: 80%, m.p. above 300 °C; IR (KBr): \( \nu / \text{cm}^{-1} \) 3183 (NH), 2221 (CN), 1673, 1639 (2CO); \( ^1\text{H-NMR (DMSO-d}_6\): \( \delta \) 2.15 (s, 3H, CH\(_3\)), 2.60 (s, 3H, CH\(_3\)), 7.49–7.71 (m, 5H, Ar-H) and 11.91 ppm (s, 1H, NH); \( ^{13}\text{C-NMR (TFA-d): } \delta 19.82 \text{ (CH}_3\)), 27.25 \text{ (CH}_3\)), 107.63, 116.18 \text{ (CN), 125.08, 129.39, 131.18, 131.62, 132.45, 134.48, 138.03, 140.46, 154.60 and 202.41 ppm (Ar-C and CO); MS (EI): m/z (%) 292 (M\(^+\), 100), 293 (M\(^++1\), 20.45). Anal. calcd. for \( \text{C}_{16}\text{H}_{12}\text{N}_{4}\text{O}_{2} \) (292.30): C, 65.75; H, 4.14; N, 19.17. Found: C, 65.81; H, 4.17; N, 19.19.

3.4. General Procedure for the Preparation of 15

Independent solutions of \( p \)-nitrophenylacetic acid (0.9 g, 5 mmol) in \( \text{Ac}_2\text{O} \) (5 mL) were heated in a microwave oven at 100 °C for 20 s. To these mixtures, 1a,b (5 mmol) were added and the mixtures were heated for further 60 s at the same temperature. The reaction mixtures were cooled to room temperature the crystalline solid formed were separated by filtration and washed by cold ethanol and then hot ethanol to afford 15a,b, respectively, as pure substances.

N-(5-Benzoyl-2-phenyl-2H-1,2,3-triazol-4-yl)-2-(4-nitrophenyl)acetamide (15a). White crystals, yield: 90%, m.p. 196 °C; IR (KBr): \( \nu / \text{cm}^{-1} \) 3294 (NH), 1690, 1632 (2CO); \( ^1\text{H-NMR (CDCl}_3\): \( \delta \) 4.02 (s, 2H, CH\(_2\)), 7.43 (t, \( J = 7.6 \text{ Hz, 1H, Ar-H} \)), 7.50–7.62 (m, 6H, Ar-H), 7.68 (t, \( J = 7.6 \text{ Hz, 1H, Ar-H} \)), 8.15 (d, \( J = 8.0 \text{ Hz, 2H, Ar-H} \)), 8.27 (d, \( J = 7.6 \text{ Hz, 2H, Ar-H} \)), 8.43 (d, \( J = 8.0 \text{ Hz, 2H, Ar-H} \)) and 10.02 ppm (s, 1H, NH); \( ^{13}\text{C-NMR (CDCl}_3\): } \delta 43.90 \text{ (CH}_2\)), 119.47, 124.05, 128.59, 128.76, 129.65, 130.41, 130.54, 132.99, 133.95, 135.98, 138.99, 141.04, 147.40, 148.35, 166.42 and 195.23 ppm (Ar-C and CO); MS (EI): m/z (%) 427 (M\(^+\), 56.75), 428 (M\(^++1\), 15.55). Anal. calcd. for \( \text{C}_{23}\text{H}_{17}\text{N}_{5}\text{O}_{4} \) (427.42): C, 64.63; H, 4.01; N, 16.39. Found: C, 64.59; H, 3.94; N, 16.43.

N-(5-Acetyl-2-phenyl-2H-1,2,3-triazol-4-yl)-2-(4-nitrophenyl)acetamide (15b). Beige crystals, yield: 87%, m.p. 207 °C; IR (KBr): \( \nu / \text{cm}^{-1} \) 3358 (NH), 1686, 1641(2CO); \( ^1\text{H-NMR (CDCl}_3\): \( \delta \) 2.69 (s, 3H, CH\(_3\)), 3.99 (s, 2H, CH\(_2\)), 7.43 (t, \( J = 7.6 \text{ Hz, 1H, Ar-H} \)), 7.51 (t, \( J = 7.6 \text{ Hz, 2H, Ar-H} \)), 7.60 (d, \( J = 8.0 \text{ Hz, 2H, Ar-H} \)), 8.12 (d, \( J = 7.6 \text{ Hz, 2H, Ar-H} \)), 8.26 (d, \( J = 8.0 \text{ Hz, 2H, Ar-H} \)) and 9.51 ppm (s, 1H, NH); \( ^{13}\text{C-NMR (CDCl}_3\): } \delta 27.02 \text{ (CH}_3\)), 43.81 (CH\(_2\)), 119.38, 124.06, 128.74, 129.42, 130.56, 133.67, 138.99, 140.97, 146.14, 147.43, 166.43 and 195.23 ppm (Ar-C and CO); MS (EI): m/z (%) 365 (M\(^+\), 27.35), 366 (M\(^++1\), 6.91). Anal. calcd. for \( \text{C}_{18}\text{H}_{15}\text{N}_{5}\text{O}_{4} \) (365.35): C, 59.18; H, 4.14; N, 19.17. Found: C, 59.24; H, 4.07; N, 19.14.
3.5. General Procedure for the Preparation of 16

Independent solutions of amides 15a, b (5 mmol) in DMF (10 mL) containing anhydrous sodium acetate (1 g) were stirred at reflux for 1 h. Then, the reaction mixtures were cooled to rt and poured onto ice cold water. The crude products were collected by filtration, washed with water and recrystallized from the appropriate solvent to afford the corresponding azolo pyridine derivatives 16a, b respectively.

6-(4-Nitrophenyl)-2,7-diphenyl-2,4-dihydro[1,2,3]triazolo[4,5-b]pyridin-5-one (16a). Recrystallized from an EtOH/dioxane (1:1) mixture as yellow crystals, yield: 82%, m.p. 302 °C; IR (KBr): ν/cm⁻¹ 3435 (NH), 1645 (CO); ¹H-NMR (DMSO-d₆): δ 7.32–7.35 (m, 5H, Ar-H), 7.44 (d, J = 8.0 Hz, 3H, Ar-H), 7.56 (t, J = 7.6 Hz, 2H, Ar-H), 8.00 (d, J = 8.0 Hz, 2H, Ar-H), 8.10 (d, J = 8.0 Hz, 2H, Ar-H) and 12.90 ppm (s, 1H, NH); ¹³C-NMR (DMSO-d₆): δ 118.62, 122.51, 128.18, 128.25, 128.89, 129.82, 129.86, 130.66, 132.29, 132.64, 133.14, 139.02, 140.68, 142.80, 146.36, 146.65 and 161.83 ppm (Ar-C and CO); MS (EI): m/z (%) 409 (M⁺, 100), 410 (M⁺+1, 30.72). Anal. calcd. for C₂₃H₁₅N₅O₃ (409.41): C, 67.48; H, 3.69; N, 17.11. Found: C, 67.51; H, 3.70; N, 17.08.

7-Methyl-6-(4-Nitrophenyl)-2-phenyl-2,4-dihydro[1,2,3]triazolo[4,5-b]-pyridin-5-one (16b). Recrystallized from an EtOH/dioxane (2:1) mixture as buff crystals, yield: 85%, m.p. 298 °C; IR (KBr): ν/cm⁻¹ 3285 (NH), 1643 (CO); ¹H-NMR (DMSO-d₆): δ 2.30 (s, 3H, CH₃), 7.46 (t, J = 7.6 Hz, 1H, Ar-H), 7.58–7.63 (m, 4H, Ar-H), 8.05 (d, J = 8.0 Hz, 2H, Ar-H), 8.30 (d, J = 8.0 Hz, 2H, Ar-H), and 12.67 ppm (s, 1H, NH); ¹³C-NMR (DMSO-d₆): δ 15.16 (CH₃), 118.48, 122.99, 128.13, 129.84, 131.14, 131.86, 133.08, 138.08, 139.10, 142.38, 145.94, 146.81 and 161.63 ppm (Ar-C and CO); MS (EI): m/z (%) 347 (M⁺, 100), 348 (M⁺+1, 21.87). Anal. calcd. for C₁₈H₁₃N₅O₃ (347.34): C, 62.25; H, 3.77; N, 20.16. Found: C, 62.19; H, 3.81; N, 20.12.

3.6. General Procedure for the Preparation of 20a-f

Independent mixtures of 5-amino-1,2,3-triazoles 1a, b (10 mmol), active methylene compounds 17a-c (15 mmol) and zeolite (10% by weight) were heated at 150 °C for 1 h. Dioxane was added to the reaction mixtures followed by filtration to remove the zeolite. The crystals formed upon cooling the filtrates were collected by filtration and washed with methanol.

Ethyl-5-oxo-2,7-diphenyl-4,5-dihydro-2H-[1,2,3]triazolo[4,5-b]pyridine-6-carboxylate (20a). Pale orange crystals, yield: 76%, m.p. 205 °C; IR (KBr): ν/cm⁻¹ 3391(NH), 1733, 1650 (2CO); ¹H-NMR (DMSO-d₆): δ 1.30 (t, J = 7.2 Hz, 3H, CH₂CH₂), 4.13 (q, J = 7.2 Hz, 2H, CH₂CH₂), 7.46 (t, J = 7.6 Hz, 1H, Ar-H), 7.56–7.60 (m, 5H, Ar-H), 7.65–7.67 (m, 2H, Ar-H), 8.00 (d, J = 7.6 Hz, 2H, Ar-H), and 13.00 ppm (s, 1H, NH); ¹³C-NMR (DMSO-d₆): δ 13.65 (CH₂CH₂), 61.17 (CH₂CH₂), 118.81, 128.54, 128.57, 128.67, 129.86, 129.87, 130.10, 130.85, 132.11, 138.97, 140.27, 146.93, 160.14 and 165.01 ppm (Ar-C and CO); MS (EI): m/z (%) 347 (M⁺, 100), 348 (M⁺+1, 21.87). Anal. Calcd. for C₂₀H₁₆N₄O₃ (360.38): C, 66.66; H, 4.48; N, 15.55. Found: C, 66.72; H, 4.40; N, 15.49.

6-Benzoyl-2,7-diphenyl-2,4-dihydro[1,2,3]triazolo[4,5-b]-pyridin-5-one (20b). Canary yellow crystals, yield: 80%, m.p. above 300 °C; IR (KBr): ν/cm⁻¹ 3423 (NH), 1672, 1644 (2CO); ¹H-NMR (DMSO-
6-Acetyl-2,7-diphenyl-2,4-dihydro[1,2,3]triazolo[4,5-b]pyridin-5-one \( \text{(20c)} \). Pale yellow crystals, yield: 79%, m.p. 249 °C; IR (KBr): /v/cm\(^{-1} \) 3299 (NH), 1709, 1646 (2CO); \(^1\)H-NMR (DMSO-\(d_6\)): \( \delta \) 2.33 (s, 3H, CH\(_3\)), 7.47 (t, \( J = 7.6 \) Hz, 1H, Ar-H), 7.53–7.60 (m, 7H, Ar-H), 7.99 (d, \( J = 8.0 \) Hz, 2H, Ar-H) and 12.96 ppm (s, 1H, NH); \(^1\)C-NMR (DMSO-\(d_6\)): \( \delta \) 14.04 (CH\(_3\)CH\(_2\)), 61.28 (CH\(_3\)CH\(_2\)), 118.52, 127.22, 128.33, 129.61, 129.76, 131.86, 138.90, 146.12, 159.82 and 165.08 ppm (Ar-C and CO); MS (EI): \( m/z \) (%) 330 (M\(^+\), 100), 331 (M\(^{+1}\), 19.84). Anal. calcd. for C\(_{19}\)H\(_{14}\)N\(_4\)O\(_2\) (330.35): C, 69.08; H, 4.27; N, 16.96. Found: C, 68.98; H, 4.35; N, 16.88.

Ethyl-7-methyl-5-oxo-2-phenyl-4,5-dihydro-2H-[1,2,3]triazolo[4,5-b]pyridine-6-carboxylate \( \text{(20d)} \). Yellow crystals, yield: 82%, m.p. 219 °C; IR (KBr): /v/cm\(^{-1} \) 3263 (NH), 1735, 1659 (2CO); \(^1\)H-NMR (DMSO-\(d_6\)): \( \delta \) 1.31 (t, \( J = 7.2 \) Hz, 3H, CH\(_3\)CH\(_2\)), 4.33 (q, \( J = 7.2 \) Hz, 2H, CH\(_3\)CH\(_2\)), 7.47 (t, \( J = 8.0 \) Hz, 1H, Ar-H), 7.60 (t, \( J = 8.0 \) Hz, 2H, Ar-H), 8.04 (d, \( J = 8.0 \) Hz, 2H, Ar-H) and 12.75 ppm (s, 1H, NH); \(^1\)C-NMR (DMSO-\(d_6\)): \( \delta \) 14.31 (CH\(_3\)), 14.04 (CH\(_3\)CH\(_2\)), 61.28 (CH\(_3\)CH\(_2\)), 118.52, 127.22, 128.33, 129.61, 131.86, 138.90, 146.12, 159.82 and 165.08 ppm (Ar-C and CO); MS (EI): \( m/z \) (%) 298 (M\(^+\), 61.90), 299 (M\(^{+1}\), 12.75). Anal. calcd. for C\(_{15}\)H\(_{14}\)N\(_4\)O\(_3\) (298.30): C, 60.40; H, 4.73; N, 18.78. Found: C, 60.33; H, 4.84; N, 18.76.

6-Benzoyl-7-methyl-2-phenyl-2,4-dihydro[1,2,3]triazolo[4,5-b]pyridin-5-one \( \text{(20e)} \). Creamy white crystals, yield: 79%, m.p. 298 °C; IR (KBr): /v/cm\(^{-1} \) 3429 (NH), 1668, 1641 (2CO); \(^1\)H-NMR (DMSO-\(d_6\)): \( \delta \) 2.30 (s, 3H, CH\(_3\)), 7.47 (t, \( J = 7.6 \) Hz, 1H, Ar-H), 7.55 (t, \( J = 8.0 \) Hz, 2H, Ar-H), 7.61 (t, \( J = 7.6 \) Hz, 2H, Ar-H), 7.69 (t, \( J = 7.6 \) Hz, 1H, Ar-H), 7.92 (d, \( J = 7.6 \) Hz, 2H, Ar-H), 8.06 (d, \( J = 8.0 \) Hz, 2H, Ar-H) and 12.75 ppm (s, 1H, NH); \(^1\)C-NMR (DMSO-\(d_6\)): \( \delta \) 14.18 (CH\(_3\)), 138.95, 138.83, 139.08, 146.45, 161.04 and 194.41 ppm (Ar-C and CO); MS (EI): \( m/z \) (%) 330 (M\(^+\), 100), 331 (M\(^{+1}\), 22.88). Anal. calcd. for C\(_{19}\)H\(_{14}\)N\(_4\)O\(_3\) (330.35): C, 69.08; H, 4.27; N, 16.96. Found: C, 69.15; H, 4.21; N, 17.02.

6-Acetyl-7-methyl-2-phenyl-2,4-dihydro[1,2,3]triazolo[4,5-b]pyridin-5-one \( \text{(20f)} \). Yellow crystals, yield: 86%, m.p. 242 °C; IR (KBr): /v/cm\(^{-1} \) 3435 (NH), 1694, 1648 (2CO); \(^1\)H-NMR (DMSO-\(d_6\)): \( \delta \) 2.36 (s, 3H, CH\(_3\)), 2.47 (s, 3H, CH\(_3\)), 7.44 (t, \( J = 8.0 \) Hz, 1H, Ar-H), 7.57 (t, \( J = 8.0 \) Hz, 2H, Ar-H), 8.00 (d, \( J = 8.0 \) Hz, 2H, Ar-H) and 12.71 ppm (s, 1H, NH); \(^1\)C-NMR (DMSO-\(d_6\)): \( \delta \) 13.98 (CH\(_3\)), 30.98 (CH\(_3\)), 118.57, 128.34, 129.79, 132.46, 133.31, 138.53, 138.95, 146.09, 160.99 and 201.93 ppm (Ar-C and CO); MS (EI): \( m/z \) (%) 268 (M\(^+\), 76.45), 269 (M\(^{+1}\), 13.89). Anal. calcd. for C\(_{14}\)H\(_{12}\)N\(_4\)O\(_2\) (268.28): C, 62.68; H, 4.51; N, 20.88. Found: C, 62.74; H, 4.47; N, 20.94.
3.6.1. Crystallographic Analysis for 20f

The crystals were mounted on a glass fiber. All measurements were performed on a Rigaku R-AXIS RAPID diffractometer using filtered Mo-Kα radiation. The data were collected at a temperature of 20 ± 1 °C to a maximum 2θ value of 55.0° using the ω scanning technique. The structure was solved by charge flipping method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

3.6.2. Crystal Data

C14H12N4O2, M = 268.28, triclinic, a = 4.003(4)Å, b = 13.07(2)Å, c = 13.49(2)Å, V = 643(1)Å³, α = 113.65(1)°, β = 91.13(2)°, γ = 94.89(2)°, space group: P-1, Z= 2, Dcalc = 1.385 g cm⁻³, No. of reflection measured 2935, 2θmax= 55.0°, R1= 0.053. Figure 3 illustrates the structure as determined. Full data can be obtained on request from the CCDC [24].

3.7. N-(5-Benzoyl-2-phenyl-2H-1,2,3-triazol-4-yl)-5-oxo-2,7-diphenyl-4,5-dihydro-2H-[1,2,3]-triazolo[4,5-b]pyridine-6-carboxamide (22)

A mixture of 5-amino-1,2,3-triazole 1a (0.66 g, 2.5 mmol), pyrazolo[4,3-b]pyridine 20a (0.9 g, 2.5 mmol) and zeolite (10% by weight) in dioxane (10 mL) was stirred at reflux for 2 h, filtered to remove the zeolite, and cooled to room temperature. The solid which formed was collected by filtration, washed with ethanol, and recrystallized from dioxane giving beige crystals, yield: 68%, m.p. 271 °C; IR (KBr): ν/cm⁻¹ 3404, 3314 (2NH), 1711, 1663, 1635 (3CO); ¹H-NMR (DMSO-d₆): δ = 7.49–7.73 (m, 14H, Ar-H), 8.01–8.12 (m, 6H, Ar-H), 11.48 (s, 1H, NH) and 12.93 ppm (s, 1H, NH); ¹³C-NMR (DMSO-d₆): δ 118.83, 128.52, 128.60, 128.70, 129.04, 129.75, 129.90, 130.87, 131.39, 132.26, 133.67, 136.35, 136.46, 138.61, 139.01, 140.66, 144.50, 147.02, 161.14, 162.51, and 185.99 ppm (Ar-C and CO); MS (EI): m/z (%) 578 (M⁺, 46.25), 579 (M⁺+1, 17.30). Anal. calcd. for C₃₃H₂₂N₈O₃ (578.60): C, 68.51; H, 3.83; N, 19.37. Found: C, 68.44; H, 3.87; N, 19.42.

3.8. (E)-Ethyl-3-(5-acetyl-2-phenyl-2H-1,2,3-triazol-4-ylamino)but-2-enoate (23)

A mixture of 5-amino-1,2,3-triazole 1b (2.02 g, 10 mmol) and ethyl acetoacetate (1.95 g, 15 mmol) was fused at 140 °C for 20 min. The mixture was poured into water and cooled to room temperature. The crude solid which formed was collected by filtration, washed with cold ethanol, and recrystallized from ethanol to give creamy white crystals, yield: 71%, m.p. 158 °C; IR (KBr): ν/cm⁻¹ 3435 (NH), 1672, 1620 (2CO); ¹H-NMR (CDCl₃): δ 1.30 (t, J = 7.2 Hz, 3H, CH₃CH₂), 2.50 (s, 3H, CH₃), 2.68 (s, 3H, CH₃CO), 4.27 (q, J = 7.2 Hz, 2H, CH₂CH₂), 4.93 (s, 1H, olefinic CH), 7.38(t, J = 8.0 Hz, 1H, Ar-H), 7.49 (t, J = 8.0 Hz, 2H, Ar-H), 8.05 (d, J = 8.0 Hz, 2H, Ar-H) and 11.95 ppm (s, 1H, NH); ¹³C-NMR (CDCl₃): δ 14.55 (CH₃CH₂), 22.75 (CH₃), 26.84 (CH₃), 59.40 (CH₃CH₂), 92.61, 118.76, 128.05, 129.35, 133.81, 139.16, 149.00, 154.87, 168.94 and 193.51 ppm (Ar-C, olefinic C and CO); MS (EI): m/z (%) 314 (M⁺, 100), 315 (M⁺+1, 22.85). Anal. Calcd. for C₁₆H₁₈N₄O₃ (314.35): C, 61.14; H, 5.77; N, 17.82. Found: C, 61.17; H, 5.75; N, 17.86.
3.8.1. Crystallographic Analysis for 23

The crystals were mounted on a glass fiber. All measurements were performed on a Rigaku R-AXIS RAPID diffractometer using filtered Mo-Kα radiation. The data were collected at a temperature of 20 ± 1 °C to a maximum 2θ value of 55.0° using the ω scanning technique. The structure was solved by charge flipping method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

3.8.2. Crystal Data

C₁₆H₁₈N₄O₃, M = 314.35, monoclinic, a = 4.949(2)Å, b = 14.130(4)Å, c = 23.315(7)Å, V = 1629.14(9)Å³, α = γ = 90.00°, β = 92.190(2)°, space group: P2₁/n, Z = 4, Dcalc = 1.282 g cm⁻³, No. of reflection measured 3733, 2θmax = 55.0°, R1 = 0.0807. Figure 4 illustrates the structure as determined. Full data can be obtained on request from the CCDC [25].

3.9. Ethyl-5,7-dimethyl-2-phenyl-2H-[1,2,3]triazolo[4,5-b]pyridine-6-carboxylate (24)

A solution of 23 (1.57 g, 5 mmol) in DMF (10 mL) containing anhydrous sodium acetate (1 g) was stirred at reflux for 1 h. The mixture was cooled to room temperature and poured into ice cold water. The formed solid was collected by filtration, washed with water and recrystallized from EtOH/H₂O (2:1) to give pale brown crystals, yield: 71%, m.p. 78 °C; IR (KBr): υ/cm⁻¹ 1719 (CO); ¹H-NMR (DMSO-d₆): δ 1.46 (t, J = 7.2 Hz, 3H, CH₃CH₂), 2.74 (s, 3H, CH₃), 2.75 (s, 3H, CH₃), 4.50 (q, J = 7.2 Hz, 2H, CH₃CH₂), 7.49 (t, J = 8.0 Hz, 1H, Ar-H), 7.57 (t, J = 8.0 Hz, 2H, Ar-H) and 8.40 ppm (d, J = 8.0 Hz, 2H, Ar-H); ¹³C-NMR (DMSO-d₆): δ 14.27 (CH₃), 14.71(CH₃), 24.42 (CH₂), 61.89 (CH₂), 120.59, 128.72, 129.50, 129.55, 136.67, 137.78, 140.14, 154.96, 158.88 and 168.10 ppm (Ar-C and CO); MS (EI): m/z (%) 296 (M⁺, 100), 297 (M⁺+1, 29.8). Anal. calcd. for C₁₆H₁₆N₄O₂ (296.33): C, 64.85; H, 5.44; N, 18.91. Found: C, 64.78; H, 5.51; N, 18.94.

4. Conclusions

A simple and efficient approach to the preparation of condensed pyridines, utilizing o-acyl heteroarmatic amines as precursors, has been developed. By using the new approach, difficulties with the classical synthesis of these substances from active methylene compounds and o-aminonitriles are overcome.

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22. Crystallographic data for 5a (ref. CCDC 804721) can be obtained on request from the director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EW, UK.

23. Crystallographic data for 10 (ref. CCDC 816562) can be obtained on request from the director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EW, UK.

24. Crystallographic data for 20f (ref. CCDC 815380) can be obtained on request from the director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EW, UK.

25. Crystallographic data for 23 (ref. CCDC 805282) can be obtained on request from the director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EW, UK.

\textit{Sample Availability:} Samples of the compounds 3, 5, 15, 16 and 20 a-f are available from the authors.

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