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THREE-COMPONENT SYNTHESIS OF 4-AROYL-2(1),4,5,7-TETRAHYDROPYRAZOLO[3,4-*b*]PYRIDIN-6-ONES AND THEIR PROPERTIES

O. N. Petrova[1], L. L. Zamigajlo[1], I. M. Gella[1,2], V. I. Musatov[1], S. V. Shishkina[1], O. V. Shishkin[1,2], E. V. Vashchenko[1], A. V. Borisov[3], and V. V. Lipson[1,2,4]*

Inspired by the concept of multicomponent reactions, a novel one-pot synthesis involving arylglyoxals, 5-aminopyrazoles, and Meldrum's acid has been developed and employed for the creation of a small library of 4-aroyl-2(1),4,5,7-tetrahydropyrazolo[3,4-b]pyridin-6-ones. The alkylation, acylation, reduction, and oxidation reactions of 4-aroyl-3-methyl-2,4,5,7-tetrahydropyrazolo[3,4-b]pyridin-6-ones have been studied.

Keywords: 5-aminopyrazoles, arylglyoxals, Meldrum's acid, tetrahydropyrazolo[3,4-*b*]pyridines, acylation, alkylation, oxidation, reduction, three-component reaction.

In the last two decades, multicomponent reactions (MCRs) have been recognized as a highly powerful synthetic strategy for the combinatorial synthesis of compound libraries and have received significant attention [1-6]. A central issue in MCRs research is the synthesis of nitrogen heterocycles, since this group of organic compounds holds a special place among pharmaceutically and agrochemically important natural and synthetic products. Pyrazolopyridines among different azoloazines have received more attention as one of the "privileged medicinal scaffolds" which are used for the development of new drug candidates of various applications. Numerous methods for the synthesis of systems incorporating a pyrazolopyridine moiety have been reported with respect to their different structures [7-17].

In the past several years, we and others have developed various MCRs based on the interaction of Meldrum's acid or its derivatives with carbonyl compounds and different nitrogen-containing 1,3-binucleophiles that can provide a facile route to partially hydrogenated fused heterocyclic systems for chemical and biomedical purposes, some natural alkaloids, and their analogs [4-6, 17, 18]. For example, three-component reactions of

*To whom correspondence should be addressed, e-mail: lipson@ukr.net.

[1]State Scientific Institution "Institute for Single Crystals" of National Academy of Sciences of Ukraine, 60 Lenina Ave., Kharkiv 61001, Ukraine; e-mail: olesya.demidchencko@yandex.ru, lalilali@mail.ru.
[2]V. N. Karazin Kharkiv National University, 4 Svobody Sq., Kharkiv 61022, Ukraine; e-mail: info@karazin.ua.
[3]Enamine Ltd., 23 Alexandra Matrosova St., Kyiv 01103, Ukraine; e-mail: enamine@enamine.net.
[4]Antidiabetic Drug Laboratory, SI "V. Ya. Danilevsky Institute for Endocrine Pathology Problems", 10 Artema St., Kharkiv 61002, Ukraine.

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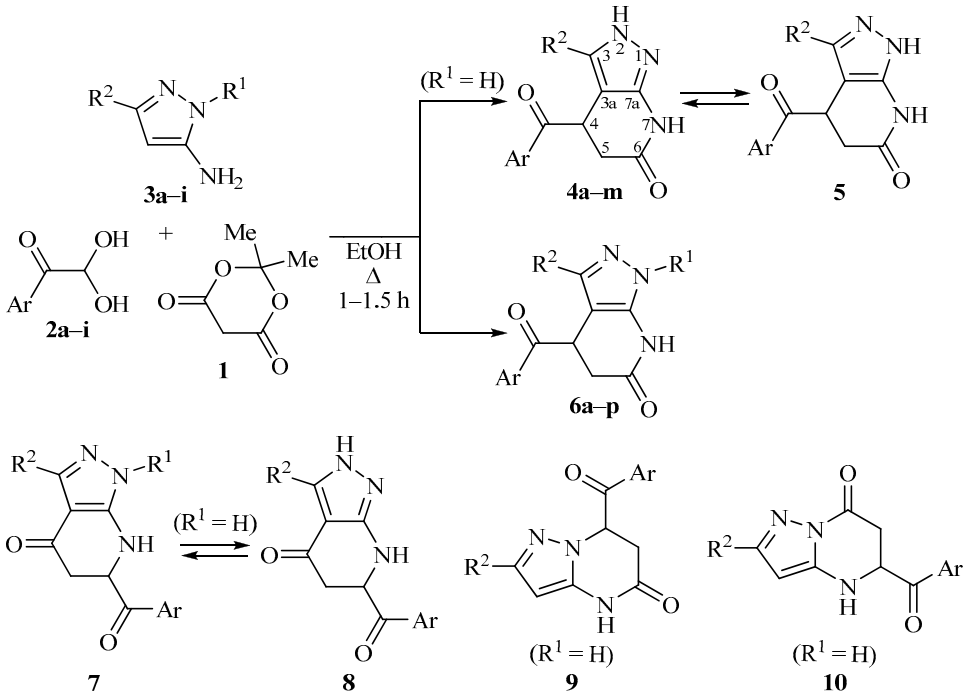
5-aminopyrazoles with aromatic, heterocyclic, or some aliphatic aldehydes and Meldrum's acid were shown to provide facile access to 4-aryl-4,5,6,7-tetrahydropyrazolo[3,4-*b*]pyridin-6-ones [17, 19-22]. Unfortunately, there are only two reaction centers suitable for further chemical modification in their structure [21]. For this reason, the introduction of a new chemically active group, such as the carbonyl moiety, in the tetra-hydro-pyrazolo[3,4-*b*]pyridin-6-one scaffold is a synthetic task of high priority for us. We have selected arylglyoxals as possible building blocks to be used in MCR with 5-aminopyrazoles and Meldrum's acid. They would be able to provide an additional carbonyl group in target heterocycles. These 1,2-dicarbonyl compounds are widely used in the design of different heterocycles [23]. Nevertheless, in the scientific literature there are no publications concerning one-pot synthesis of tetrahydropyrazolo[3,4-*b*]pyridin-6-one derivatives on the base of glyoxals, 5-aminopyrazoles, and Meldrum's acid.

Herein, we would like to report an easy and efficient procedure for synthesis of novel tetra-hydropyrazolo[3,4-*b*]pyridin-6-ones *via* three-component condensation of Meldrum's acid, arylglyoxals, and 5-aminopyrazoles in alcohols and discuss some chemical transformations of the target compounds. The presence of four nonequivalent nucleophilic centers in 3-substituted 5-aminopyrazoles provides various pathways for their reactions with carbonyl 1,3-dielectrophiles, their synthetic precursors, or equivalents and opens up wide possibilities for using these compounds in the synthesis of fused heterocyclic systems.

Earlier, it has been found that reactions of 5-amino-3-arylpyrazoles with methoxymethylene Meldrum's acid derivative, as well as thermolysis of their pyrazolylaminomethylene derivatives, give pyrazolo[1,5-*a*]-pyrimidines rather than pyrazolo[3,4-*b*]pyridines [24]. At the same time, three-component reactions of 5-amino-3-methylpyrazole with aromatic, heterocyclic, or some aliphatic aldehydes and Meldrum's acid yielded pyrazolo[3,4-*b*]pyridinones [20-22].



2 a Ar = Ph, **b** Ar = 4-MeC_6H_4, **c** Ar = 4-MeOC_6H_4, **d** Ar = 4-FC_6H_4, **e** Ar = 4-ClC_6H_4, **f** Ar = 4-BrC_6H_4, **g** Ar = 4-IC_6H_4, **h** Ar = 2-Br-4-FC_6H_3, **i** Ar = 4-PhC_6H_4; **3 a**–**c** R^1 = H, **a** R^2 = Me, **b** R^2 = 4-MeC_6H_4, **c** R^2 = 4-FC_6H_4, **d**–**f** R^1 = Me, **d** R^2 = H, **e** R^2 = Me, **f** R^2 = *t*-Bu, **g**–**i** R^2 = Me, **g** R^1 = cyclopentyl, **h** R^1 = Ph, **i** R^1 = 4-MeOC_6H_4; **4 a**–**i** R^2 = Me, **a** Ar = Ph, **b** Ar = 4-MeC_6H_4, **c** Ar = 4-MeOC_6H_4, **d** Ar = 4-FC_6H_4, **e** Ar = 4-ClC_6H_4, **f** Ar = 4-BrC_6H_4, **g** Ar = 4-IC_6H_4, **h** Ar = 2-Br-4-FC_6H_3, **i** Ar = 4-PhC_6H_4; **4 j** R^2 = 4-MeC_6H_4, Ar = Ph; **k**–**m** R^2 = 4-FC_6H_4, **k** Ar = Ph, **l** Ar = 4-MeOC_6H_4, **m** Ar = 4-FC_6H_4; **6 a**–**e** R^1 = Me, R^2 = H, **a** Ar = Ph, **b** Ar = 4-MeC_6H_4, **c** Ar = 4-MeOC_6H_4, **d** Ar = 4-FC_6H_4, **e** Ar = 4-BrC_6H_4; **f** R^1 = R^2 = Me, Ar = 4-BrC_6H_4; **g**,**h** R^1 = Me, R^2 = *t*-Bu, **g** Ar = 4-FC_6H_4, **h** Ar = 4-BrC_6H_4; **6 i**–**l** R^1 = cyclopentyl, R^2 = Me, **i** Ar = Ph, **j** Ar = 4-MeC_6H_4, **k** Ar = 4-MeOC_6H_4, **l** Ar = 4-FC_6H_4, **m**,**n** R^1 = Ph, R^2 = Me, **m** Ar = 4-MeC_6H_4, **n** Ar = 4-MeOC_6H_4, **o**,**p** R^1 = 4-MeOC_6H_4, R^2 = Me; **o** Ar = 4-MeC_6H_4, **p** Ar = 4-FC_6H_4

We found that a three-component condensation of equimolar amounts of Meldrum's acid (**1**), arylglyoxals **2a-i**, and 1,3-disubstituted 5-aminopyrazoles **3a-i** under refluxing in ethanol leads to 4-aroyl-tetrahydropyrazolo[3,4-*b*]pyridin-6-ones **4a-m**, **6a-p** with high yields. Products of the isomeric structures **5**, **7-10** were not isolated (see the discussion below).

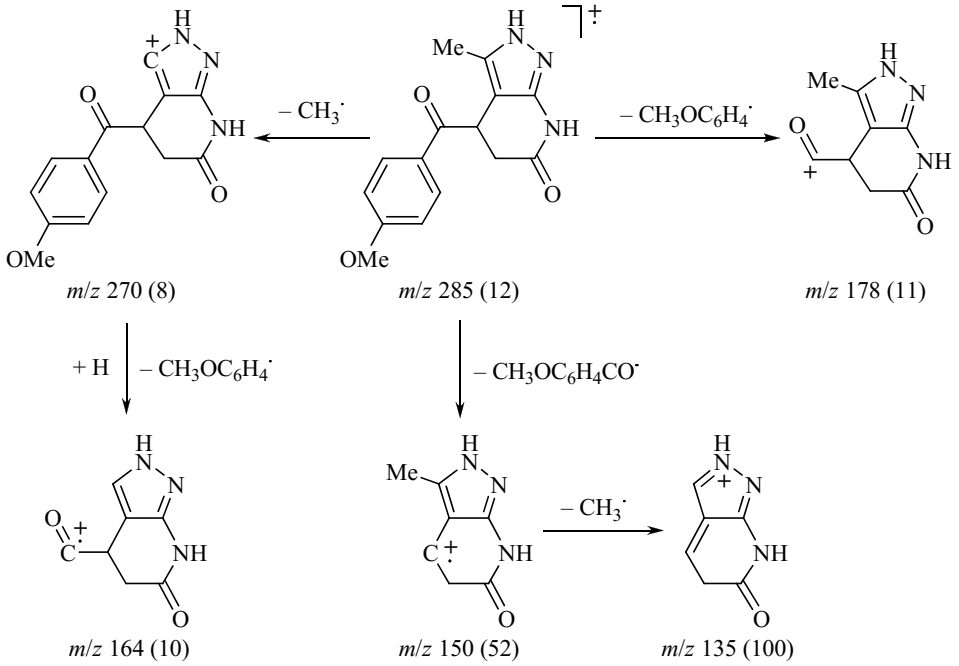


Fig. 1. Basic fragmentation paths for compound **4c** in the EI mass spectrum.

The composition and structure of the obtained compounds **4a-m** were confirmed by the results of elemental analysis and spectral data.

In the IR spectra of compounds **4a**,**b**,**f**, there was a set of typical absorption bands of cyclic amides in the regions 3220-3124 (NH), 1648-1644 (C=O), and a carbonyl group band of the aroyl moiety at 1680-1664 cm^{-1}.

With regard to the mass spectra, upon electron impact (EI) ionization all compounds **4a-m** exhibit similar behavior in their fragmentation, showing a molecular ion peak of low intensity along with a high-intensity peak corresponding to the loss of the aroyl fragment and the base peak corresponding to pyrazolo[3,4-*b*]pyridinone ion (Fig. 1).

However, these data do not permit an assignment to be made for the type of heterocycle fusion (structures **4**, **5**, **8** *vs*. **9**, **10**) or the position of the aroyl group (structures **4**, **5**, **9** *vs*. **8**, **10**).

In the ^1H NMR spectra of compounds **4a-m**, signals of protons of two NH groups, methyl substituent in pyrazole cycle, and aroyl fragment, as well as CH–CH_2 moiety of a partially hydrogenated pyridinone ring were present. The last one formed an ABX proton system. The presence of two broadened singlet signals of NH groups at 11.68-12.39 and 10.03-10.33 ppm and the absence of a signal for a methine proton of the pyrazole ring speaks in favor of assigning the obtained products to a pyrazolopyridine (compounds **4**, **5** or **8**) and not a pyrazolopyrimidine series (compounds **9** or **10**). The choice in favor of 4-aroyl isomer **4** was made on the basis of an NOE experiment carried out for compound **4g** (Fig. 2). Irradiation of the CH_3 group protons at position 3 (1.84 ppm) causes the responses of the NH group proton of the pyrazole ring (11.75 ppm) and a CH proton at position 4 of the bicyclic system (4.90 ppm) which indicates their close spatial disposition.

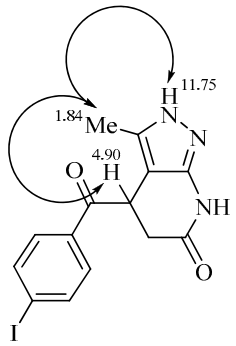


Fig. 2. Interactions in the NOE spectrum of compound **4g**.

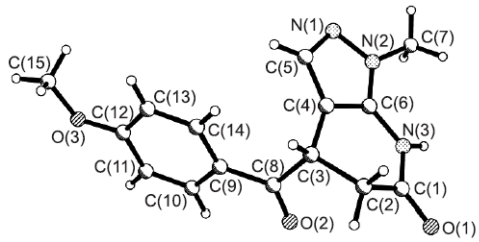
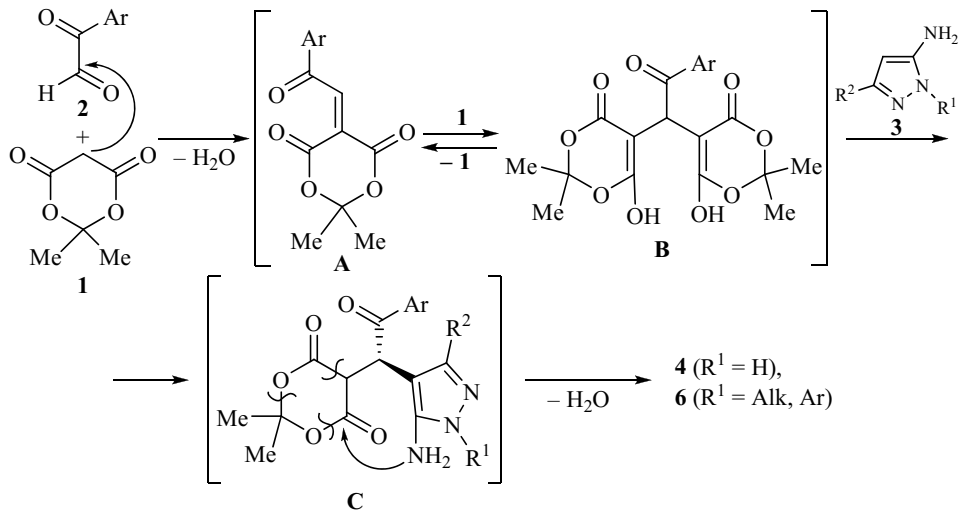


Fig. 3. Molecular structure of compound **6c** according to X-ray diffraction data.

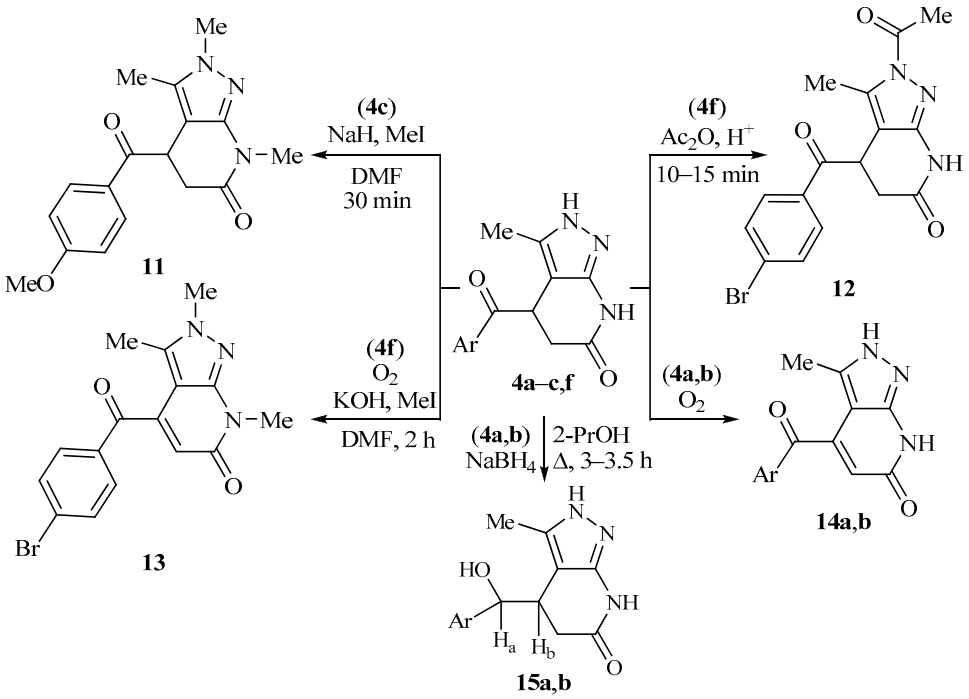
In the case of the *N*-1-substituted aminopyrazole taking part in the discussed three-component condensation, only pyrazolopyridines **6a**-**p** were obtained. The alternative structure **7** (R^1 = Alk, Ar) was not confirmed, since the magnetic coupling between the 6-CH and 7-NH protons of the partially hydrogenated pyridine cycle was not observed in the ^{1}H NMR spectrum. Finally the structure of the pyrazolopyridine **6c** was confirmed on the basis of single crystal X-ray structural analysis (Fig. 3). The tetrahydropyridine ring adopts a twist-boat conformation (the puckering parameters [25] are *S* 0.53, Θ 48.3°, Ψ 23.4°). Deviations of the C(1) and C(2) atoms from the mean plane of the remaining atoms of the ring are -0.26 and -0.64 Å, respectively. The 4 methoxybenzoyl substituent is located in the axial position (the C(8)–C(3)–C(4)–C(6) torsion angle is -94.1(1)°) and it is almost orthogonal to the planar part of the pyrazolopyridine fragment (the C(4)–C(3)–C(8)–O(2) torsion angle is 100.2(2)°). Such location of this substituent is caused, probably, by the steric repulsion between the phenyl ring and the bicyclic fragment, as indicated by the shortened intramolecular contacts H(3)···C(14) 2.71 Å (the sum of the van der Waals radii [26] is 2.87 Å), C(14)···C(4) 3.38 Å, and C(14)···C(5) 3.38 Å (3.42 Å).

Thus, the interaction of 3(5)-aminopyrazoles **3a**-**i** with 2,2-dimethyl-1,3-dioxane-4,6-dione (**1**) and arylglyoxals **2a**-**i** is characterized by high regioselectivity and leads exclusively to the formation of the 4-aroylpyrazolo[3,4-*b*]pyridin-6-one systems **4** or **6**. Such a direction of the process corresponds to the interaction of the β-carbon atom of the possible intermediate **A** (in equilibrium with intermediate **B**), formed initially from Meldrum's acid **1** and glyoxal **2**, with the carbon nucleophilic center in the aminoazole molecule (intermediate **C**), and the carbon atom of the C=O group of 1,3-dioxane-4,6-dione fragment with the exocyclic amino group.



Chemical properties of the synthesized compounds were examined on the pyrazolopyridines **4a**-**c**,**f** and **6n**. We studied the transformations of these compounds upon alkylation, acylation, under oxidation conditions, and in reactions with phenylhydrazine, aniline, and *N*-Boc-substituted piperidine carboxylic acid hydrazide.

Both secondary amino groups in the structure of the synthesized pyrazolopyridine **4c** undergo an electrophilic attack in the alkylation reaction producing the trimethyl derivative **11**. However, in the case of acylation only the amino group at the pyrazole ring takes part in the reaction (product **12**). The alkylation with methyl iodide in DMF/KOH medium in the presence of atmospheric oxygen is accompanied by oxidation of the pyridine ring with the formation of *N*-methyl-substituted heteroaromatic derivative **13**. The position of the substituents in the pyrazole cycle was determined on the basis of the NOE experiment data. An NOE correlation was found between proton signals of the 3-methyl group and *N*-methyl group (for compounds **11**, **13**) or *N*-acyl fragment (for compound **12**) of the pyrazole core. We have found that the oxidation of pyrazolopyridines **4a**,**b** easily occurs both in basic (Py or DMF/KOH) and acidic conditions (AcOH). The proof of heteroaromatization of pyridine cycle is the disappearance of the signals of the ABX system and the presence of the signal of a methine proton in the ^{1}H NMR spectrum of compounds **13** and **14**. Refluxing of the pyrazolopyridines **4a**,**b** with sodium borohydride in isopropyl alcohol yields hydroxy derivatives **15a**,**b**.

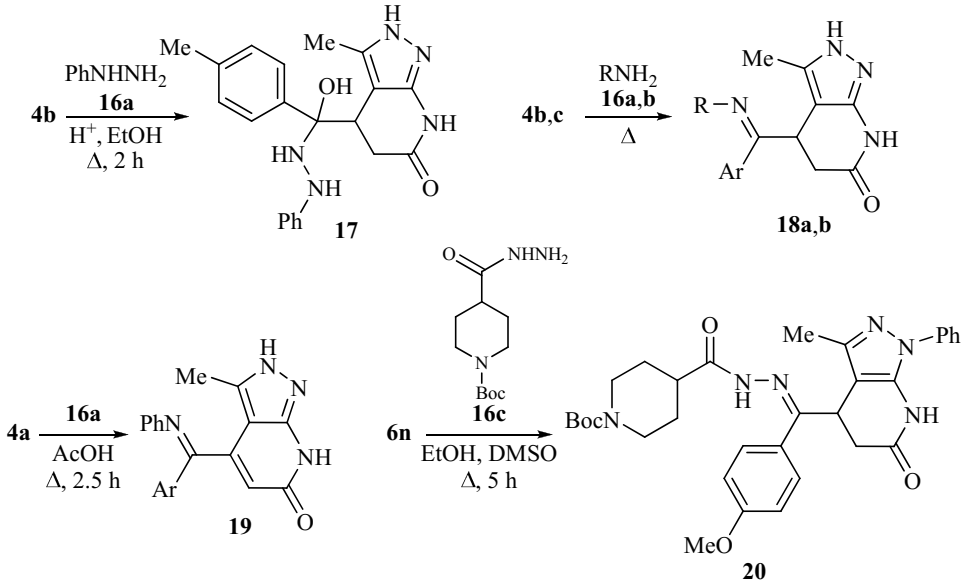


14, **15 a** Ar = Ph, **b** Ar = 4-MeC_6H_4

The ^{1}H NMR spectra of compounds **15a**,**b** correspond to individual diastereomers, but not to isomer mixtures. The diastereoselective formation of hydroxy compounds **15a**,**b** could be explained by the attack of the $NaBH_4$-derived hydride ion on the C=O group carbon atom in pyrazolopyridines **4a**,**b** from the less hindered side, i.e., from the side opposite to the 3-methyl group. The values of the spin-spin coupling constants between protons H_a and H_b in the ^{1}H NMR spectra of the reduction products **15a**,**b** are 4.0 and 4.4 Hz, respectively, which corresponds to the gauche orientation of the indicated hydrogen atoms.

Another series of chemical transformations of the synthesized compounds **4a**-**c**, **6n** investigated in this study involves the carbonyl group of the aroyl fragment. The interaction of compound **4b** with phenylhydrazine (**16a**) in ethanol in the presence of hydrochloric acid allowed us to isolate ketoaminal **17**. It should be expected that attack by phenylhydrazine (**16a**) also takes place in the energetically more favorable conformation of pyrazolopyridine **4b** from the sterically less hindered side. Prolonged refluxing leads to the formation of

hydrazone **18a**. However, the use of acetic acid as a solvent with compound **4a** is accompanied by further heteroaromatization of the pyridine ring (product **19**). The interaction of pyrazolopyridine **4c** with *p*-toluidine (**16b**) leads to the formation of the expected azomethine **18b**. Refluxing of the 1-substituted pyrazolopyridine **6n** with a protected piperidine carboxylic acid hydrazide **16c** in the mixture of EtOH and DMSO likewise yields the corresponding hydrazide **20**.



18 a Ar = 4-MeC_6H_4, **b** Ar = 4-$MeOC_6H_4$; **16**, **18 a** R = NHPh, **b** R = 4-MeC_6H_4

To summarize, the investigation of three-component condensations involving aminopyrazoles, arylglyoxals, and Meldrum's acid has shown that in all cases the reaction takes place regioselectively and leads to the formation of pyrazolo[3,4-*b*]pyridinone systems. In the reactions of pyrazolo[3,4-*b*]pyridinones with electrophilic reagents, the most nucleophilic is the N-2 atom of the pyrazole ring. Heteroaromatization of the pyridine ring of pyrazolo[3,4-*b*]pyridinones takes place under the basic and acidic conditions. The presence of the carbonyl group of the aroyl fragment opens additional opportunities for chemical modification of this molecular platform.

EXPERIMENTAL

IR spectra were recorded in KBr on a Specord M-82 spectrometer. ^{1}H NMR spectra were registered on a Varian Mercury VX-200 instrument (200 MHz), and the ^{13}C NMR spectra were registered on a Bruker AM-400 spectrometer (100 MHz) in DMSO-d_6, using TMS as internal standard. Mass spectra were recorded on a Varian 1220 L mass spectrometer with direct injection of the sample (EI, 70 eV). Elemental analyses were made on a Euro AE-3000 elemental analyzer. Melting points were determined on a Kofler apparatus and were not corrected. Reactions were monitored by TLC (DC-Fertigfolien ALUGRAM Xtra SIL G/UV_{254}) in CH_2Cl_2–2-PrOH, 10:1, or EtOAc–toluene, 1:4, and visualized with UV light or iodine vapor. The starting materials were purchased from commercial suppliers.

4-Aroyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-ones 4a-m and 4-Aroyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-ones 6a-p (General Method). A mixture of 2,2-dimethyl-1,3-dioxane-4,6-dione (**1**) (1 mmol), corresponding arylglyoxal **2** (1 mmol), and aminopyrazole **3** (1 mmol) in 8-10 ml EtOH was refluxed for 1-1.5 h. The product was filtered off and washed with EtOH or MeOH. The products were recrystallized from MeOH (compounds **4a**-**m**) or EtOH (compounds **6a**-**p**) and obtained as white powders.

4-Benzoyl-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4a). Yield 62%, mp 274-276°C. IR spectrum, ν, cm^{-1}: 3220-3160 (NH), 1680 (HNC=O), 1644 (ArC=O), 1592 (C=C), 1524 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.82 (3H, s, 3-CH_3); 2.59 (1H, dd, *J* = 16.2, *J* = 2.8) and 2.70 (1H, dd, *J* = 16.2, *J* = 6.2, 5-CH_2); 4.95 (1H, dd, *J* = 6.0, *J* = 3.0, 4-CH); 7.52 (2H, t, *J* = 7.4, H-3,5 Ph); 7.64 (1H, t, *J* = 7.0, H-4 Ph); 7.99 (2H, d, *J* = 7.4, H-2,6 Ph); 10.10 (1H, br. s, 7-NH); 11.73 (1H, br. s, 2-NH). ^{13}C NMR spectrum, δ, ppm: 10.4 (CH_3); 35.0 (C-4); 36.4 (C-5); 97.1 (C-3a); 129.1 (C-3,5 Ph); 129.2 (C-2,6 Ph); 133.8 (C-4 Ph); 135.5 (C-1 Ph); 136.5 (C-3); 149.8 (C-7a); 169.9 (CONH); 199.8 (COAr). Mass spectrum, *m*/*z* (I_{rel}, %): 255 $[M]^+$ (17), 151 (14), 150 (100), 149 (15), 132 (22), 105 (44), 77 (19). Found, %: C 65.94; H 5.20; N 16.39. $C_{14}H_{13}N_3O_2$. Calculated, %: C 65.87; H 5.13; N 16.46.

3-Methyl-4-(4-methylbenzoyl)-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4b). Yield 61%, mp 274-276°C. IR spectrum, ν, cm^{-1}: 3164-3136 (NH), 1664 (HNC=O), 1648 (ArC=O), 1604 (C=C), 1524 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.84 (3H, s, 3-CH_3); 2.37 (3H, s, $CH_3C_6H_4$); 2.55 (1H, dd, *J* = 15.8, *J* = 3.4) and 2.68 (1H, dd, *J* = 15.8, *J* = 6.4, 5-CH_2); 4.92 (1H, dd, *J* = 6.2, *J* = 3.4, 4-CH); 7.32 (2H, d, *J* = 7.8, H-3,5 Ar); 7.90 (2H, d, *J* = 7.6, H-2,6 Ar); 10.10 (1H, br. s, 7-NH); 11.72 (1H, br. s, 2-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 269 $[M]^+$ (12), 150 (67), 149 (10), 119 (100), 91 (32). Found, %: C 67.01; H 5.69; N 15.69. $C_{15}H_{15}N_3O_2$. Calculated, %: C 66.90; H 5.61; N 15.60.

4-(4-Methoxybenzoyl)-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4c). Yield 64%, mp 202-204°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.88 (3H, s, 3-CH_3); 2.57 (1H, dd, *J* = 16.2, *J* = 3.8) and 2.69 (1H, dd, *J* = 16.2, *J* = 6.2, 5-CH_2); 3.84 (3H, s, OCH_3); 4.91 (1H, dd, *J* = 6.0, *J* = 3.8, 4-CH); 7.05 (2H, d, *J* = 8.8, H-3,5 Ar); 8.01 (2H, d, *J* = 8.6, H-2,6 Ar); 10.03 (1H, br. s, 7-NH); 11.68 (1H, br. s, 2-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 285 $[M]^+$ (12), 178 (11), 164 (10), 150 (52), 135 (100), 107 (19). Found, %: C 63.04; H 5.22; N 14.65. $C_{15}H_{15}N_3O_3$. Calculated, %: C 63.15; H 5.30; N 14.73.

4-(4-Fluorobenzoyl)-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4d). Yield 44%, mp 316-318°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.84 (3H, s, 3-CH_3); 2.59 (1H, dd, *J* = 17.8, *J* = 1.8) and 2.63 (1H, dd, *J* = 17.8, *J* = 6.6, 5-CH_2); 4.96 (1H, dd, *J* = 6.4, *J* = 1.8, 4-CH); 7.36 (2H, d, *J* = 8.0, H-3,5 Ar); 8.01 (2H, d, *J* = 8.2, H-2,6 Ar); 10.11 (1H, br. s, 7-NH); 11.75 (1H, br. s, 2-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 273 $[M]^+$ (14), 240 (10), 178 (14), 150 (49), 123 (100). Found, %: C 61.64; H 4.50; N 15.29. $C_{14}H_{12}FN_3O_2$. Calculated, %: C 61.53; H 4.43; N 15.38.

4-(4-Chlorobenzoyl)-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4e). Yield 73%, mp 340-342°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.84 (3H, s, CH_3); 2.59 (1H, dd, *J* = 16.2, *J* = 2.8) and 2.68 (1H, dd, *J* = 16.2, *J* = 6.2, 5-CH_2); 4.94 (1H, dd, *J* = 6.2, *J* = 2.8, 4-CH); 7.60 (2H, d, *J* = 8.0, H-3,5 Ar); 8.02 (2H, d, *J* = 8.2, H-2,6 Ar); 10.12 (1H, br. s, 7-NH); 11.77 (1H, br. s, 2-NH). ^{13}C NMR spectrum, δ, ppm: 10.4 (3-CH_3); 34.8 (C-4); 36.4 (C-5); 96.9 (C-3a); 129.4 (C-3,5 Ar); 131.1 (C-2,6 Ar); 135.2 (C-1 Ar); 135.5 (C-3); 138.8 (C–Cl); 149.8 C-7a); 169.7 (CONH); 198.7 (COAr). Mass spectrum, *m*/*z* (I_{rel}, %): 291 [M (^{37}Cl)]$^+$ (3), 289 [M (^{35}Cl)]$^+$ (8), 150 (100), 141 (24), 139 (78), 132 (78), 111 (27), 107 (10). Found, %: C 57.96; H 4.09; N 14.42. $C_{14}H_{12}ClN_3O_2$. Calculated, %: C 58.04; H 4.17; N 14.50.

4-(4-Bromobenzoyl)-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4f). Yield 72%, mp 342-344°C. IR spectrum, ν, cm^{-1}: 3164–3124 (NH), 1672 (HNC=O), 1648 (ArC=O), 1524 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.84 (3H, s, CH_3); 2.59 (1H, dd, *J* = 16.2, *J* = 2.8) and 2.68 (1H, dd, *J* = 16.2, *J* = 6.6, 5-CH_2); 4.93 (1H, dd, *J* = 6.4, *J* = 2.8, 4-CH); 7.72 (2H, d, *J* = 8.2, H-3,5 Ar); 7.96 (2H, d, *J* = 8.2, H-2,6 Ar); 10.11 (1H, br. s, 7-NH); 11.78 (1H, br. s, 2-NH). Found, %: C 50.42; H 3.53; N 12.65. $C_{14}H_{12}BrN_3O_2$. Calculated, %: C 50.32; H 3.62; N 12.57.

4-(4-Iodobenzoyl)-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4g). Yield 68%, mp 328-330°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.84 (3H, s, CH_3); 2.59 (1H, dd, *J* = 16.2, *J* = 2.4) and 2.67 (1H, dd, *J* = 16.2, *J* = 6.2, 5-CH_2); 4.90 (1H, dd, *J* = 6.0, *J* = 2.6, 4-CH); 7.75 (2H, d, *J* = 7.8, H-3,5 Ar); 7.91 (2H, d, *J* = 8.0, H-2,6 Ar); 10.10 (1H, br. s, 7-NH); 11.75 (1H, br. s, 2-NH). ^{13}C NMR spectrum, δ, ppm: 10.4 (3-CH_3); 34.9 (C-4); 36.3 (C-5); 96.9 (C-3a); 102.4 (C–I); 130.8 (C-2,6 Ar); 135.5 (C-1 Ar); 135.8 (C-3); 138.2

(C-3,5 Ar); 149.8 (C-7a); 169.7 (CONH); 199.3 (COAr). Mass spectrum, *m*/*z* (I_{rel}, %): 381 $[M]^+$ (12), 164 (16), 132 (100), 127 (21), 95 (40). Found, %: C 44.20; H 3.28; N 10.91. $C_{14}H_{12}IN_3O_2$. Calculated, %: C 44.11; H 3.17; N 11.02.

4-(2-Bromo-4-fluorobenzoyl)-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4h). Yield 58%, mp 171-173°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.48 (3H, s, CH_3); 2.54 (1H, dd, *J* = 15.8, *J* = 2.8) and 2.61 (1H, dd, *J* = 15.8, *J* = 5.4, 5-CH_2); 4.52 (1H, dd, *J* = 5.4, *J* = 2.8, 4-CH); 7.40 (1H, dd, *J* = 8.4, *J* = 2.0, H-5 Ar); 7.62-7.70 (2H, m, H-3,6 Ar); 10.14 (1H, br. s, 7-NH); 11.78 (1H, br. s, 2-NH). ^{13}C NMR spectrum, δ, ppm: 9.2 (3-CH_3); 33.4 (C-4); 41.0 (C-5); 94.8 (C-3a); 115.2 (C-5 Ar); 115.4 (C-3 Ar); 121.1 (C–Br); 131.0 (C-6, Ar); 136.1 (C-1 Ar); 137.5 (C-3); 149.8 (C-7a); 163.8 (C–F); 169.4 (CONH); 199.8 (COAr). Found, %: C 47.86; H 3.23; N 12.03. $C_{14}H_{11}BrFN_3O_2$. Calculated, %: C 47.75; H 3.15; N 11.93.

4-[(1,1'-Biphenyl)-4-carbonyl]-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4i). Yield 49%, mp 290-292°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.89 (3H, s, CH_3); 2.62 (1H, dd, *J* = 16.8, *J* = 2.8) and 2.70 (1H, dd, *J* = 17.0, *J* = 6.0, 5-CH_2); 4.99 (1H, dd, *J* = 6.0, *J* = 2.8, 4-CH); 7.41-7.51 (3H, m, H-3,4,5 Ph); 7.73-7.85 (4H, m, H-2,6 Ph, H-3,5 Ar); 8.09 (2H, d, *J* = 7.8, H-2,6 Ar); 10.10 (1H, br. s, 7-NH); 11.73 (1H, br. s, 2-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 332 $[M+H]^+$ (22), 331 $[M]^+$ (100), 316 (21), 254 (11), 181 (53), 178 (15), 153 (17), 150 (43), 136 (12). Found, %: C 72.56; H 5.09; N 12.57. $C_{20}H_{17}N_3O_2$. Calculated, %: C 72.49; H 5.17; N 12.68.

4-Benzoyl-3-(*p*-tolyl)-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4j). Yield 70%, mp 282-284°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.27 (3H, s, CH_3); 2.56 (1H, dd, *J* = 16.0, *J* = 2.4) and 3.03 (1H, dd, *J* = 16.2, *J* = 7.0, 5-CH_2); 5.22 (1H, dd, *J* = 7.0, *J* = 2.6, 4-CH); 7.12-7.38 (6H, m, H-2,3,5,6 Ar, H-3,5 Ph); 7.55 (1H, t, *J* = 7.5, H-4 Ph); 7.83 (2H, d, *J* = 7.4, H-2,6 Ph); 10.33 (1H, br. s, 7-NH); 12.39 (1H, br. s, 2-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 331 $[M]^+$ (10), 254 (14), 240 (19), 226 (100), 163 (10), 135 (12). Found, %: C 72.54; H 5.24; N 12.59. $C_{20}H_{17}N_3O_2$. Calculated, %: C 72.49; H 5.17; N 12.68.

4-Benzoyl-3-(4-fluorophenyl)-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4k). Yield 49%, mp 315-317°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.58 (1H, dd, *J* = 15.4, *J* = 2.4) and 2.91 (1H, dd, *J* = 16.2, *J* = 7.2, 5-CH_2); 5.16 (1H, dd, *J* = 7.2, *J* = 2.4, 4-CH); 7.10 (2H, t, *J* = 7.5, H-3,5 Ar); 7.30-7.54 (5H, m, H-3,4,5 Ph, H-2,6 Ar); 7.80 (2H, d, *J* = 7.8, H-2,6 Ph); 10.16 (1H, br. s, 7-NH); 12.30 (1H, br. s, 2-NH). Found, %: C 67.96; H 4.28; N 12.62. $C_{19}H_{14}FN_3O_2$. Calculated, %: C 68.05; H 4.21; N 12.53.

3-(4-Fluorophenyl)-4-(4-methoxybenzoyl)-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4l). Yield 43%, mp 302-304°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.55 (1H, d, *J* = 16.5) and 2.89 (1H, dd, *J* = 16.8, *J* = 6.8, 5-CH_2); 3.83 (3H, s, OCH_3); 5.00 (1H, d, *J* = 6.8, 4-CH); 6.84 (2H, d, *J* = 8.4, H-3,5 ArCO); 7.11 (2H, dd, *J* = 8.0, *J* = 2.2, H-3,5 Ar); 7.42 (2H, t, *J* = 8.2, H-2,6 Ar); 7.82 (2H, d, *J* = 8.4, H-2,6 ArCO); 10.16 (1H, br. s, 7-NH); 12.31 (1H, br. s, 2-NH). Found, %: C 65.82; H 4.48; N 11.44. $C_{20}H_{16}FN_3O_3$. Calculated, %: C 65.75; H 4.41; N 11.50.

4-(4-Fluorobenzoyl)-3-(4-fluorophenyl)-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (4m). Yield 41%, mp 305-307°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.56 (1H, d, *J* = 16.5) and 2.89 (1H, dd, *J* = 16.2, *J* = 6.2, 5-CH_2); 5.16 (1H, d, *J* = 6.2, 4-CH); 7.03-7.14 (4H, m, H-3,5 Ar, H-3,5 ArCO); 7.42 (2H, dd, *J* = 8.4, *J* = 5.0, H-2,6 Ar); 7.88 (2H, dd, *J* = 8.0, *J* = 5.6, H-2,6 ArCO); 10.19 (1H, br. s, 7-NH); 12.32 (1H, br. s, 2-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 353 $[M]^+$ (12), 231 (20), 230 (100), 123 (36), 95 (34), 76 (15). Found, %: C 64.62; H 3.63; N 12.00. $C_{19}H_{13}F_2N_3O_2$. Calculated, %: C 64.59; H 3.71; N 11.89.

4-Benzoyl-1-methyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6a). Yield 51%, mp 175-177°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.55 (1H, dd, *J* = 16.2, *J* = 4.2) and 2.70 (1H, dd, *J* = 16.2, *J* = 6.2, 5-CH_2); 3.60 (3H, s, NCH_3); 4.92 (1H, dd, *J* = 6.2, *J* = 4.2, 4-CH); 6.93 (1H, s, 3-CH); 7.91-7.81 (3H, m, H-3,4,5 Ph); 8.06 (2H, d, *J* = 7.6, H-2,6 Ph); 10.60 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 255 $[M]^+$ (7), 150 (100), 105 (22), 77 (19). Found, %: C 65.76; H 5.01; N 16.62. $C_{14}H_{13}N_3O_2$. Calculated, %: C 65.87; H 5.13; N 16.46.

1-Methyl-4-(4-methylbenzoyl)-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6b). Yield 54%, mp 197-199°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.43 (3H, s, CH_3); 2.62 (1H, dd, *J* = 16.0, *J* = 4.0) and 2.71 (1H, dd, *J* = 16.2, *J* = 6.4, 5-CH_2); 3.60 (3H, s, NCH_3); 4.86 (1H, dd, *J* = 6.2, *J* = 3.8, 4-CH); 6.88 (1H, s, 3-CH); 7.33 (2H, d, *J* = 8.0, H-3,5 Ar); 7.94 (2H, d, *J* = 7.8, H-2,6 Ar); 10.56 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 269 $[M]^+$ (10), 213 (14), 150 (100), 119 (20). Found, %: C 67.01; H 5.50; N 15.56. $C_{15}H_{15}N_3O_2$. Calculated, %: C 66.90; H 5.61; N 15.60.

4-(4-Methoxybenzoyl)-1-methyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6c). Yield 56%, mp 170-172°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.64 (1H, dd, *J* = 16.2, *J* = 4.4) and 2.70 (1H, dd, *J* = 16.2, *J* = 6.0, 5-CH_2); 3.61 (3H, s, NCH_3); 3.88 (3H, s, OCH_3); 4.84 (1H, dd, *J* = 6.0, *J* = 4.4, 4-CH); 6.90 (1H, s, 3-CH); 7.02 (2H, d, *J* = 8.6, H-3,5 Ar); 8.01 (2H, d, *J* = 8.6, H-2,6 Ar); 10.55 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 285 $[M]^+$ (8), 239 (10), 178 (11), 150 (100), 135 (27). Found, %: C 63.06; H 5.41; N 14.68. $C_{15}H_{15}N_3O_3$. Calculated, %: C 63.15; H 5.30; N 14.73.

4-(4-Fluorobenzoyl)-1-methyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6d). Yield 77%, mp 177-179°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.65 (1H, dd, *J* = 16.4, *J* = 3.6) and 2.71 (1H, dd, *J* = 16.2, *J* = 6.0, 5-CH_2); 3.60 (3H, s, NCH_3); 4.90 (1H, dd, *J* = 6.0, *J* = 3.4, 4-CH); 6.92 (1H, s, 3-CH); 7.29 (2H, d, *J* = 8.4, H-3,5 Ar); 8.14 (2H, dd, *J* = 8.0, *J* = 7.6, H-2,6 Ar); 10.59 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 273 $[M]^+$ (8), 151 (10), 150 (100), 123 (18), 106 (5), 105 (22). Found, %: C 61.61; H 4.37; N 15.47. $C_{14}H_{12}FN_3O_2$. Calculated, %: C 61.53; H 4.43; N 15.38.

4-(4-Bromobenzoyl)-1-methyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6e). Yield 71%, mp 217-219°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.64 (1H, dd, *J* = 15.6, *J* = 4.8) and 2.70 (1H, dd, *J* = 15.8, *J* = 6.2, 5-CH_2); 3.60 (3H, s, NCH_3); 4.89 (1H, dd, *J* = 6.2, *J* = 4.4, 4-CH); 6.93 (1H, s, 3-CH); 7.70 (2H, d, *J* = 8.6, H-3,5 Ar); 8.00 (2H, d, *J* = 8.6, H-2,6 Ar); 10.60 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 335 $[M\ (^{81}Br)]^+$ (4), 333 $[M\ (^{79}Br)]^+$ (5), 320 (11), 318 (12), 279 (9), 277 (10), 239 (14), 185 (27), 183 (29), 178 (10), 150 (100), 124 (12). Found, %: C 50.41; H 3.57; N 12.49. $C_{14}H_{12}BrN_3O_2$. Calculated, %: C 50.32; H 3.62; N 12.57.

4-(4-Bromobenzoyl)-1,3-dimethyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6f). Yield 65%, mp 252-254°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.73 (3H, s, 3-CH_3); 2.56 (1H, dd, *J* = 15.6, *J* = 2.2) and 2.74 (1H, dd, *J* = 16.2, *J* = 6.6, 5-CH_2); 3.50 (3H, s, NCH_3); 4.89 (1H, dd, *J* = 6.6, *J* = 2.2, 4-CH); 7.74 (2H, d, *J* = 8.4, H-3,5 Ar); 7.93 (2H, d, *J* = 8.6, H-2,6 Ar); 10.54 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 349 (5) $[M\ (^{81}Br)]^+$, 347 (6) $[M\ (^{79}Br)]^+$, 253 (11), 185 (11), 183 (12), 164 (100), 150 (38). Found, %: C 51.83; H 3.97; N 11.98. $C_{15}H_{14}BrN_3O_2$. Calculated, %: C 51.74; H 4.05; N 12.07.

3-(*tert*-Butyl)-4-(4-fluorobenzoyl)-1-methyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6g). Yield 63%, mp 267-269°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.08 (9H, s, $C(CH_3)_3$); 2.38 (1H, d, *J* = 16.0) and 2.98 (1H, dd, *J* = 16.0, *J* = 6.4, 5-CH_2); 3.63 (3H, s, NCH_3); 5.06 (1H, d, *J* = 6.2, 4-CH); 7.28 (2H, t, *J* = 7.0, H-3,5 Ar); 8.16 (2H, dd, *J* = 7.2, *J* = 6.8, H-2,6 Ar); 10.57 (1H, br. s, 7-NH). ^{13}C NMR spectrum, δ, ppm: 30.3 ($C(\underline{C}H_3)_3$); 32.9 ($\underline{C}(CH_3)_3$); 35.1 (NCH_3); 36.3 (C-4); 37.4 (C-5); 96.1 (C-3a); 116.6 (C-3(5) Ar); 116.8 (C-5(3) Ar); 131.8 (C-2(6) Ar); 132.1 (C-6(2) Ar); 141.6 (C-1 Ar); 154.4 (C-3); 164.9 (C-7a); 166.9 (C–F); 168.9 (CONH); 199.1 ($\underline{C}$OAr). Mass spectrum, *m*/*z* (I_{rel}, %): 329 $[M]^+$ (15), 234 (11), 206 (100), 123 (56), 95 (12). Found, %: C 65.72; H 6.02; N 12.85. $C_{18}H_{20}FN_3O_2$. Calculated, %: C 65.64; H 6.12; N 12.76.

4-(4-Bromobenzoyl)-3-(*tert*-butyl)-1-methyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6h). Yield 68%, mp 303-305°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.28 (9H, s, $C(CH_3)_3$); 2.55 (1H, d, *J* = 16.0) and 3.08 (1H, dd, *J* = 16.0, *J* = 6.8, 5-CH_2); 3.84 (3H, s, NCH_3); 5.28 (1H, d, *J* = 6.8, 4-CH); 7.74 (2H, d, *J* = 7.6, H-3,5 Ar); 8.07 (2H, d, *J* = 7.6, H-2,6 Ar); 11.11 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 391 $[M\ (^{81}Br)]^+$ (4), 389 $[M\ (^{79}Br)]^+$ (5), 207 (32), 206 (100), 150 (63). Found, %: C 55.32; H 5.09; N 10.85. $C_{18}H_{20}BrN_3O_2$. Calculated, %: C 55.40; H 5.17; N 10.77.

4-Benzoyl-1-cyclopentyl-3-methyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6i). Yield 59%, mp 221-223°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.60-1.67 (2H, m) and 1.82-1.91 (2H, m, $2CH_2$);

1.95 (3H, s, 3-CH_3); 1.99-2.08 (4H, m, 2CH_2); 2.82-2.94 (2H, m, 5-CH_2); 4.40-4.53 (1H, m, *J* = 7.0, $(CH_2)_2C\underline{H}$); 4.77 (1H, dd, *J* = 6.0, *J* = 4.0, 4-CH); 7.50 (2H, t, *J* = 7.2, H-3,5 Ph); 7.61 (1H, t, *J* = 7.2, H-4 Ph); 7.99 (2H, d, *J* = 7.4, H-2,6 Ph); 10.34 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 323 $[M]^+$ (13), 219 (17), 218 (100), 150 (28), 105 (14), 77 (13). Found, %: C 70.47; H 6.48; N 13.05. $C_{19}H_{21}N_3O_2$. Calculated, %: C 70.57; H 6.55; N 12.99.

1-Cyclopentyl-3-methyl-4-(4-methylbenzoyl)-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6j). Yield 76%, mp 176-178°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.54-1.59 (2H, m, CH_2); 1.80-1.89 (9H, m, 3-CH_3, 3CH_2); 2.10 (3H, s, $C\underline{H}_3C_6H_4$); 2.60 (1H, dd, *J* = 16.4, *J* = 2.4) and 2.70 (1H, dd, *J* = 15.8, *J* = 6.2, 5-CH_2); 4.52-4.63 (1H, m, $(CH_2)_2C\underline{H}$); 4.86 (1H, dd, *J* = 6.2, *J* = 2.4, 4-CH); 7.28 (2H, d, *J* = 8.6, H-3,5 Ar); 8.09-8.13 (2H, d, *J* = 8.6, H-2,6 Ar); 10.39 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 338 $[M+H]^+$ (20), 337 $[M]^+$ (100), 322 (11), 218 (16), 149 (12), 119 (17), 91 (10). Found, %: C 71.27; H 6.95; N 12.53. $C_{20}H_{23}N_3O_2$. Calculated, %: C 71.19; H 6.87; N 12.45.

1-Cyclopentyl-4-(4-methoxybenzoyl)-3-methyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6k). Yield 58%, mp 215-217°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.53-1.59 (2H, m, CH_2); 1.83-1.90 (9H, m, 3-CH_3, 3CH_2); 2.60 (1H, dd, *J* = 15.6, *J* = 2.6) and 2.69 (1H, dd, *J* = 15.8, *J* = 6.6, 5-CH_2); 3.87 (3H, s, OCH_3); 4.53−4.64 (1H, m, $(CH_2)_2C\underline{H}$); 4.82 (1H, dd, *J* = 6.6, *J* = 2.6, 4-CH); 7.02 (2H, d, *J* = 8.6, H-3,5 Ar); 8.01 (2H, d, *J* = 8.6, H-2,6 Ar); 10.35 (1H, br. s, 7-NH). ^{13}C NMR spectrum, δ, ppm: 13.4 (3-CH_3); 24.6 (2CH_2); 31.9 (CH_2); 32.4 (CH_2); 35.3 (C-4); 35.9 (C-5); 56.1 (OCH_3); 57.1 ($(CH_2)_2\underline{C}H$); 96.2 (C-3a); 114.5 (C-3,5 Ar); 128.8 (C-1 Ar); 131.5 (H-2,6 Ar); 140.1 (C-4 Ar); 143.0 (C-3); 163.9 (C-7a); 170.3 (CONH); 198.5 (<u>C</u>OAr). Mass spectrum, *m*/*z* (I_{rel}, %): 354 $[M+H]^+$ (21), 353 $[M]^+$ (100), 338 (12), 322 (19), 284 (14), 270 (12), 218 (22), 149 (11), 135 (31). Found, %: C 68.05; H 6.65; N 12.00. $C_{20}H_{23}N_3O_3$. Calculated, %: C 67.97; H 6.56; N 11.89.

1-Cyclopentyl-4-(4-fluorobenzoyl)-3-methyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6l). Yield 39%, mp 229-231°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.53-1.58 (2H, m, CH_2); 1.80-1.89 (9H, m, 3-CH_3, 3CH_2); 2.58 (1H, dd, *J* = 16.0, *J* = 2.4) and 2.70 (1H, dd, *J* = 16.4, *J* = 6.8, 5-CH_2); 4.51-4.62 (1H, m, $(CH_2)_2C\underline{H}$); 4.85 (1H, dd, *J* = 6.8, *J* = 2.4, 4-CH); 7.28 (2H, t, *J* = 8.8, H-3,5 Ar); 8.11 (2H, dd, *J* = 8.8, *J* = 5.2, H-2,6 Ar); 10.39 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 341 $[M]^+$ (11), 272 (10), 218 (100), 136 (12). Found, %: C 66.95; H 6.01; N 12.40. $C_{19}H_{20}FN_3O_2$. Calculated, %: C 66.85; H 5.91; N 12.31.

3-Methyl-4-(4-methylbenzoyl)-1-phenyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6m). Yield 64%, mp 187-189°C. IR spectrum, ν, cm^{-1}: 3320-3252 (NH), 1640 (C=O), 1572 (C=C), 1508 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.86 (3H, s, 3-CH_3); 2.05 (3H, s, $C\underline{H}_3C_6H_4$), 2.65 (1H, d, *J* = 15.6) and 2.88 (1H, dd, *J* = 15.4, *J* = 6.2, 5-CH_2); 5.05 (1H, d, *J* = 6.0, 4-CH); 7.32-7.68 (7H, m, H Ph, H-3,5 Ar); 8.06 (2H, d, *J* = 7.0, H-2,6 Ar); 10.40 (1H, br. s, 7-NH). ^{13}C NMR spectrum, δ, ppm: 13.0 (3-CH_3); 31.2 ($\underline{C}H_3C_6H_4$); 35.1 (C-4); 36.6 (C-5); 98.8 (C-3a); 123.4 (C-2,6 Ph); 127.4 (C-4 Ph); 129.3 (C-2,6 Ar); 129.3 (C-3,5 Ar); 129.7 (C-3,5 Ph); 134.1 (C-1 Ar); 136.3 (C-1 Ar); 138.3 (C-4 Ar); 140.4 (C-3); 145.7 (C-7a); 170.3 (CONH); 199.2 (<u>C</u>OAr). Mass spectrum, *m*/*z* (I_{rel}, %): 345 $[M]^+$ (17), 330 (10), 268 (13), 226 (100), 119 (43). Found, %: C 72.95; H 5.64; N 12.25. $C_{21}H_{19}N_3O_2$. Calculated, %: C 73.03; H 5.54; N 12.17.

4-(4-Methoxybenzoyl)-3-methyl-1-phenyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6n). Yield 82%, mp 192-194°C. IR spectrum, ν, cm^{-1}: 3324-3252 (NH), 1640 (C=O), 1580 (C=C), 1508 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.06 (3H, s, 3-CH_3); 2.68 (1H, d, *J* = 15.8) and 2.82-3.01 (1H, dd, *J* = 16.0, *J* = 6.0, 5-CH_2); 3.78 (3H, s, OCH_3); 5.29 (1H, d, *J* = 6.0, 4-CH); 6.95 (2H, d, *J* = 8.4, H-3,5 Ar); 7.72-7.43 (5H, m, H Ph); 7.79 (2H, d, *J* = 8.4, H-2,6 Ar); 10.35 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 361 $[M]^+$ (18), 284 (11), 226 (100), 135 (38). Found, %: C 69.86; H 5.21; N 11.71. $C_{21}H_{19}N_3O_3$. Calculated, %: C 69.79; H 5.30; N 11.63.

1-(4-Methoxyphenyl)-3-methyl-4-(4-methylbenzoyl)-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6o). Yield 61%, mp 187-189°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.91 (3H, s, 3-CH_3); 2.44 (3H, s, $C\underline{H}_3C_6H_4$); 2.65 (1H, dd, *J* = 16.2, *J* = 3.2) and 2.79 (1H, dd, *J* = 16.4, *J* = 6.4, 5-CH_2); 3.82 (3H, s, OCH_3); 4.90 (1H, dd, *J* = 6.2, *J* = 3.0, 4-CH); 6.96 (2H, d, *J* = 9.0, H-3,5 Ar); 7.30-7.36 (4H, m, H-2,6 Ar, H-3,5 ArCO); 7.97 (2H, d, *J* = 7.8, H-2,6 ArCO); 10.14 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 376 $[M+H]^+$ (44), 375

$[M]^+$ (19), 360 (10), 346 (18), 315 (13), 268 (10), 256 (100), 239 (15), 177 (10), 107 (11). Found, %: C 70.45; H 5.57; N 11.10. $C_{22}H_{21}N_3O_3$. Calculated, %: C 70.38; H 5.64; N 11.19.

4-(4-Fluorobenzoyl)-1-(4-methoxyphenyl)-3-methyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (6p). Yield 54%, mp 170-172°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.90 (3H, s, 3-CH_3); 2.65 (1H, dd, *J* = 15.4, *J* = 1.8) and 2.78 (1H, dd, *J* = 15.8, *J* = 6.8, 5-CH_2); 3.82 (3H, s, OCH_3); 4.98 (1H, dd, *J* = 6.6, *J* = 2.4, 4-CH); 6.96 (2H, d, *J* = 8.6, H-3,5 Ar); 7.28-7.36 (4H, m, H-2,6 Ar, H-3,5 ArCO); 8.16 (2H, dd, *J* = 8.6, *J* = 5.4, H-2,6 ArCO); 10.17 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 379 $[M]^+$ (17), 257 (24), 256 (100), 123 (23), 95 (27). Found, %: C 66.57; H 4.69; N 11.01. $C_{21}H_{18}FN_3O_2$. Calculated, %: C 66.48; H 4.78; N 11.08.

4-(4-Methoxybenzoyl)-2,3,7-trimethyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (11). Sodium hydride (0.05 g, 2.1 mmol) was added to a stirred solution of compound **4c** (0.285 g, 1.0 mmol) in DMF (2 ml). After the hydrogen evolution had subsided, methyl iodide (0.13 ml, 2.1 mmol) was added dropwise to the reaction mixture, and the stirring was continued for 30 min. Then distilled water (20 ml) was added to the reaction mixture, and the white precipitate was filtered off, washed on the filter with water, and crystallized from EtOH. Yield 37%, white powder, mp 225-227°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.28 (3H, s, 3-CH_3); 2.55 (1H, dd, *J* = 16.2, *J* = 4.0) and 2.63 (1H, dd, *J* = 16.2, *J* = 6.2, 5-CH_2); 3.48 (3H, s, 7-CH_3); 3.72 (3H, s, 2-CH_3); 3.79 (3H, s, OCH_3); 5.56 (1H, dd, *J* = 6.0, *J* = 4.0, 4-CH); 6.98 (2H, d, *J* = 8.0, H-3,5 Ar); 7.90 (2H, d, *J* = 8.2, H-2,6 Ar). Found, %: C 65.27; H 6.01; N 13.48. $C_{17}H_{19}N_3O_3$. Calculated, %: C 65.16; H 6.11; N 13.41.

2-Acetyl-4-(4-bromobenzoyl)-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (12). Sulfuric acid (1-2 drops) was added to a stirred solution of compound **4f** (0.334 g, 1 mmol) in acetic anhydride (5 ml), and reaction mixture was stirred for 10-15 min at room temperature. Distilled water (50 ml) was added, and the white precipitate was filtered off, washed on the filter with warm water, and crystallized from MeOH. Yield 53%, white powder, mp 274-276°C. IR spectrum, ν, cm^{-1}: 3296-3250 (NH), 1712 (MeC=O), 1676 (C=O), 1604 (C=C), 1532 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.22 (3H, s, 3-CH_3); 2.44 (3H, s, CH_3CO); 2.56 (1H, d, *J* = 16.6) and 2.79 (1H, dd, *J* = 16.6, *J* = 6.8, 5-CH_2); 5.11 (1H, d, *J* = 5.2, 4-CH); 7.75 (2H, d, *J* = 8.4, H-3,5 Ar); 7.96 (2H, d, *J* = 8.4, H-2,6 Ar); 10.17 (1H, br. s, 7-NH). Found, %: C 50.99; H 3.68; N 11.25. $C_{16}H_{14}BrN_3O_3$. Calculated, %: C 51.08; H 3.75; N 11.17.

4-(4-Bromobenzoyl)-2,3,7-trimethyl-2,7-dihydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (13). A mixture of compound **4f** (0.334 g, 1.0 mmol), powdered KOH (0.12 g, 2.1 mmol), and methyl iodide (0.13 ml, 2.1 mmol) was dissolved in DMF (2 ml) and stirred for 2 h. Then distilled water (20 ml) and a few drops of dilute hydrochloric acid (to the pH ~7) were added to this solution. The pale-yellow precipitate was filtered off, washed on the filter with water, and crystallized from ethanol. Yield 48%, pale-yellow powder, mp 229-231°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.06 (3H, s, 3-CH_3); 3.44 (3H, s, 7-NCH_3); 3.79 (3H, s, 2-CH_3); 6.18 (1H, s, 5-CH); 7.74–7.84 (4H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 10.5 (3-CH_3); 28.6 (7-CH_3); 37.2 (2-CH_3); 86.2 (C-3a); 101.3 (C–Br); 132.2 (C-2,6 Ar); 132.8 (C-3,5 Ar); 134.7 (C-5); 135.0 (C-1 Ar); 137.0 (C-4 Ar); 142.4 (C-3); 149.7 (C-4); 161.6 (C-7a); 170.1 (CONH); 193.3 (COAr). Mass spectrum, *m*/*z* (I_{rel}, %): 362 $[M+H\ (^{81}Br)]^+$ (40), 360 $[M+H\ (^{79}Br)]^+$ (42), 361 $[M\ (^{81}Br)]^+$ (99), 359 $[M\ (^{79}Br)]^+$ (100), 344 (17), 342 (18), 333 (50), 331 (52), 332 (81), 330 (83), 304 (11), 302 (12), 185 (50), 183 (52), 157 (39), 155 (40). Found, %: C 53.26; H 4.01; N 11.58. $C_{16}H_{14}BrN_3O_2$. Calculated, %: C 53.35; H 3.92; N 11.67.

4-Benzoyl-3-methyl-2,7-dihydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (14a). A. A solution of compound **4a** (0.255 g, 1 mmol) in pyridine (5 ml) was refluxed for 8 h. The solution was cooled, and the yellow precipitate was filtered off and washed on the filter with MeOH. Yield 60%, yellow powder, mp 265-267°C.

B. A solution of compound **4a** (0.255 g, 1 mmol) in acetic acid (5 ml) was refluxed for 5 h. The solution was cooled, and the yellow precipitate was filtered and washed on the filter with MeOH. Yield 63%, yellow powder, mp 264-266°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.97 (3H, s, 3-CH_3); 6.06 (1H, s, 5-CH); 7.56 (2H, d, *J* = 7.4, H-3,5 Ph); 7.72 (1H, t, *J* = 7.0, H-4 Ph); 7.87 (2H, d, *J* = 7.4, H-2,6 Ph), 11.92 (1H, br. s, 7-NH); 12.96 (1H, br. s, 2-NH). ^{13}C NMR spectrum, δ, ppm: 11.3 (3-CH_3); 84.49 (C-3a); 129.4 (C-2,6 Ph);

130.3 (C-3,5 Ph); 135.0 (C-1 Ph); 136.8 (C-5); 144.3 (C-4 Ph); 147.8 (C-3); 149.2 (C-4); 150.3 (C-7a); 163.1 (CONH); 194.5 (COAr). Mass spectrum, *m*/*z* (I_{rel}, %): 254 $[M+H]^+$ (21), 253 $[M]^+$ (100), 252 $[M-H]^+$ (10), 225 (68), 224 (55), 105 (83), 77 (52). Found, %: C 66.49; H 4.29; N 16.51. $C_{14}H_{11}N_3O_2$. Calculated, %: C 66.40; H 4.38; N 16.59.

3-Methyl-4-(4-methylbenzoyl)-2,7-dihydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (14b). Powdered of KOH (0.057 g, 1 mmol) was added to a solution of compound **4b** (0.269 g, 1 mmol) in DMF (2 ml), and the reaction mixture was stirred for 3 h. Then distilled water (20 ml) and a few drops of dilute hydrochloric acid (to pH ~7) were added to this solution. The yellow precipitate was filtered, washed on the filter with water, and crystallized from EtOH. Yield 63%, yellow powder, mp 273-275°C. IR spectrum, ν, cm^{-1}: 3364-3312 (NH), 1652 (C=O), 1604 (C=C), 1556 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.98 (3H, s, 3-CH_3); 2.37 (3H, s, CH_3C$_6$H$_4$); 6.03 (1H, s, 5-CH); 7.37 (2H, d, *J* = 8.2, H-3,5 Ar); 7.69 (2H, d, *J* = 8.0, H-2,6 Ar); 11.89 (1H, br. s, 7-NH); 12.97 (1H, br. s, 2-NH). ^{13}C NMR spectrum, δ, ppm: 13.1 (3-CH_3); 21.8 (CH_3C$_6$H$_4$); 79.6 (C-3a); 130.2 (C-2,6 Ar); 130.4 (C-3,5 Ar); 133.3 (C-1 Ar); 134.7 (C-5); 144.5 (C-4 Ar); 145.8 (C-3,4); 150.4 (C-7a); 163.2 (CONH); 193.9 (COAr). Found, %: C 67.31; H 5.00; N 15.64. $C_{15}H_{13}N_3O_2$. Calculated, %: C 67.40; H 4.90; N 15.72.

4-[Hydroxy(aryl)methyl]-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-ones 15a,b (General Method). $NaBH_4$ (0.04 g, 1 mmol) was added to a solution of compound **4a** or **4b** (1 mmol) in 2-PrOH (18-20 ml), and the obtained mixture was refluxed for 3-3.5 h. After cooling, the white precipitate that formed was filtered off, washed on the filter with warm *i*-PrOH, and crystallized from ethanol.

4-[Hydroxy(phenyl)methyl]-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (15a). Yield 92%, mp 278-280°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.45 (3H, s, 3-CH_3); 2.27 (1H, d, *J* = 16.0) and 2.56 (1H, dd, *J* = 15.8, *J* = 7.6, 5-CH_2); 2.91-2.97 (1H, m, 4-CH); 4.53 (1H, d, *J* = 4.0, CHOH); 5.26 (1H, br. s, OH); 7.10-7.25 (5H, m, Ph); 9.87 (1H, br. s, 7-NH); 11.50 (1H, br. s, 2-NH). Found, %: C 65.43; H 5.92; N 16.23. $C_{14}H_{15}N_3O_2$. Calculated, %: C 65.35; H 5.88; N 16.33.

4-[Hydroxy(*p*-tolyl)methyl]-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (15b). Yield 83%, mp 313-315°C. IR spectrum, ν, cm^{-1}: 3300–3260 (NH, OH, H-bond), 1648 (C=O), 1616 (C=C), 1524 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.55 (3H, s, 3-CH_3); 2.23 (1H, d, *J* = 15.4) and 2.57 (dd, 1H, *J* = 15.4, *J* = 8.0, 5-CH_2); 2.25 (3H, s, CH_3C$_6$H$_4$); 2.88-2.94 (1H, m, 4-CH); 4.46 (1H, t, *J* = 4.4, CHOH); 5.20 (1H, d, *J* = 4.2, OH); 6.99 (2H, d, *J* = 8.0, H-3,5 Ar); 7.06 (2H, d, *J* = 8.0, H-2,6 Ar); 9.88 (1H, br. s, 7-NH); 11.51 (1H, br. s, 2-NH). Found, %: C 66.51; H 6.41; N 15.40. $C_{15}H_{17}N_3O_2$. Calculated, %: C 66.40; H 6.32; N 15.49.

4-[Hydroxy(2-phenylhydrazinyl)(*p*-tolyl)methyl]-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]-pyridin-6-one (17). A mixture of compound **4b** (0.269 g, 1 mmol) and phenylhydrazine (**16a**) (0.098 ml, 1 mmol) in EtOH (8-10 ml) with a catalytic amount of HCl (3-4 drops) was refluxed for 2 h. After cooling, a pale-yellow precipitate formed. The precipitate was filtered off and washed twice on the filter with EtOH. Yield 42%, pale- yellow powder, mp 260-262°C. IR spectrum, ν, cm^{-1}: 3220–3140 (NH), 1660 (C=O), 1600 (C=C), 1500 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.41 (3H, s, 3-CH_3); 2.37 (3H, s, CH_3C$_6$H$_4$); 2.65 (1H, dd, *J* = 15.0, *J* = 7.0) and 2.87 (1H, d, *J* = 15.0, 5-CH_2); 3.81 (1H, br. s, OH); 4.00 (1H, d, *J* = 6.8, 4-CH); 6.67 (1H, t, *J* = 7.0, H-4 Ph); 7.04-7.13 (7H, m, H-2,3,5,6 Ph, H-3,5 Ar, NHPh); 7.30 (2H, d, *J* = 7.4, H-2,6 Ar); 8.36 (1H, d, *J* = 9.4, NHC(OH)); 10.06 (1H, br. s, 7-NH); 11.56 (1H, br. s, 2-NH). ^{1}H NMR spectrum (DMSO-d_6+D_2O), δ, ppm (*J*, Hz): 1.39 (3H, s, 3-CH_3); 2.31 (3H, s, CH_3C$_6$H$_4$); 2.60 (1H, dd, *J* = 16.0, *J* = 6.4) and 2.84 (1H, d, *J* = 16.2, 5-CH_2); 3.97 (1H, d, *J* = 6.0, 4-CH); 6.63 (1H, t, *J* = 6.8, H-4 Ph); 6.95-7.09 (6H, m, H-2,3,5,6 Ph, H-3,5 Ar); 7.25 (2H, d, *J* = 7.4, H-2,6 Ar). ^{13}C NMR spectrum, δ, ppm: 9.0 (3-CH_3); 21.5 (CH_3C$_6$H$_4$); 36.4 (C-5); 36.8 (C-4); 79.6 (C-3a); 99.8 (C–OH); 113.1 (C-2,6 Ph); 118.9 (C-4 Ph); 129.0 (C-2,6 Ar); 130.2 (C-3,5 Ar); 131.2 (C-3,5 Ph); 135.1 (C-1 Ar); 138.5 (C-4 Ar); 146.8 (C-3); 149.1 (C-1 Ph); 159.8 (C-7a); 170.6 (CONH). Mass spectrum, *m*/*z* (I_{rel}, %): 376 $[M–H]^+$ (11), 359 (21), 150 (100), 149 (58), 132 (16), 121 (14), 93 (51), 92 (92), 91 (15), 65 (47). Found, %: C 66.76; H 6.19; N 18.62. $C_{21}H_{23}N_5O_2$. Calculated, %: C 66.83; H 6.14; N 18.55.

3-Methyl-4-[(2-phenylhydrazono)(*p*-tolyl)methyl]-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (18a). A mixture of compound **4b** (0.269 g, 1 mmol) and phenylhydrazine (**16a**) (0.098 ml, 1 mmol) in EtOH (8-10 ml) with a catalytic amount of HCl (3-4 drops) was refluxed for 4 h. The solution was cooled, and the yellow precipitate was filtered off and washed twice on the filter with EtOH. Yield 64%, mp 340-342°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.36 (3H, s, 3-CH_3); 2.34 (3H, s, C$\underline{H}_3C_6H_4$); 2.62 (1H, dd, *J* = 15.0, *J* = 7.0) and 2.85 (1H, d, *J* = 15.4, 5-CH_2); 3.98 (1H, d, *J* = 6.8, 4-CH); 6.72 (1H, t, *J* = 7.2, H-4 Ph); 6.98-7.10 (6H, m, H-2,3,5,6 Ph, H-3,5 Ar); 7.27 (2H, d, *J* = 8.0, H-2,6 Ar); 8.34 (1H, br. s, N$\underline{H}$–N=); 10.04 (1H, br. s, 7-NH); 11.55 (1H, br. s, 2-NH). Found, %: C 70.09; H 5.96; N 19.56. $C_{21}H_{21}N_5O$. Calculated, %: C 70.17; H 5.89; N 19.48.

4-[(4-Methoxyphenyl)(*p*-tolylimino)methyl]-3-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (18b). A mixture of compound **4c** (0.285 g, 1 mmol) and *p*-toluidine (**16b**) (0.107 g, 1 mmol) in xylene (7-8 ml) was refluxed for 8 h. The solution was cooled, and the beige precipitate was filtered off, washed twice on the filter with xylene, and crystallized from MeOH. Yield 64%, mp 334-336°C. IR spectrum, ν, cm^{-1}: 3228-3180 (NH), 1664 (C=O), 1584 (C=C), 1504 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.22 (3H, s, 3-CH_3); 2.29 (3H, s, C$\underline{H}_3C_6H_4$); 2.53 (1H, d, *J* = 16.4) and 2.96 (1H, dd, *J* = 16.4, *J* = 7.2, 5-CH_2); 3.86 (3H, s, OCH_3); 5.18 (1H, d, *J* = 7.0, 4-CH); 7.13 (2H, d, *J* = 8.0, H-3,5 ArN); 7.22 (2H, d, *J* = 8.0, H-2,6 ArN); 7.45 (2H, d, *J* = 8.4, H-3,5 Ar); 7.68 (2H, d, *J* = 8.4, H-2,6 Ar); 10.36 (1H, br. s, 7-NH); 12.39 (1H, br. s, 2-NH). Found, %: C 70.65; H 6.01; N 15.04. $C_{22}H_{22}N_4O_2$. Calculated, %: C 70.57; H 5.92; N 14.96.

3-Methyl-4-[phenyl(2-phenylhydrazono)methyl]-2,7-dihydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (19). A solution of compound **4a** (0.255 g, 1 mmol) and phenylhydrazine (**16a**) (0.098 ml, 1 mmol) in acetic acid (10 ml) was refluxed for 2.5 h. After cooling, the pale-yellow precipitate was filtered off, washed on the filter with warm water, and crystallized from EtOH. Yield 80%, mp 314-316°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.87 (3H, s, 3-CH_3); 5.92 (1H, s, 5-CH); 6.75 (1H, t, *J* = 7.8, H-4 PhN); 7.14-7.34 (7H, m, H-3,4,5 Ph, H-2,3,5,6 PhN); 7.56 (2H, d, *J* = 7.4, H-2,6 Ph); 9.26 (1H, br. s, N$\underline{H}$–N=); 11.80 (1H, br. s, 7-NH); 12.70 (1H, br. s, 2-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 343 $[M]^+$ (100), 343 $[M-H]^+$ (55), 251 (11), 167 (11), 148 (14), 105 (33), 92 (12), 77 (52). Found, %: C 70.03; H 5.07; N 20.33. $C_{20}H_{17}N_5O$. Calculated, %: C 69.96; H 4.99; N 20.40.

***tert*-Butyl 4-({2-[(4-Methoxyphenyl)(3-methyl-6-oxo-1-phenyl-4,5,6,7-tetrahydro-1*H*-pyrazolo[3,4-*b*]-pyridin-4-yl)methylidene]hydrazino}carbonyl)piperidine-1-carboxylate (20)**. A solution of compound **6n** (0.361 g, 1 mmol) and 1-*tert*-butylpiperidine-4-carbohydrazide (**16c**) (0.200 g, 1 mmol) in a mixture EtOH–DMSO, 2:1 (~6 ml) was refluxed for 5 h. After cooling, the pale-yellow precipitate was filtered off and washed on the filter with EtOH. Yield 68%, mp 93-95°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.37 (9H, s, C(C$\underline{H}_3$)$_3$); 1.91 (3H, s, 3-CH_3); 2.35-2.43 (2H, m, CH_2); 2.51-2.92 (6H, m, 5-CH_2, 2CH_2); 3.73-3.80 (2H, m, CH_2); 3.85 (3H, s, OCH_3); 3.88-4.04 (1H, m, CHC=O); 5.01 (1H, d, *J* = 4.0, 4-CH); 7.02–7.10 (3H, m, H-3,5 Ar, NH–N=); 7.34 (1H, t, *J* = 7.6, H-4 Ph); 7.40-7.45 (4H, m, H-2,3,5,6 Ph); 8.07 (2H, d, *J* = 8.6, H-2,6 Ar); 10.38 (1H, br. s, 7-NH). Mass spectrum, *m*/*z* (I_{rel}, %): 485 $[M-Boc]^+$ (2), 227 (21), 226 (100), 135 (22), 77 (10). Found, %: C 65.60; H 6.47; N 14.24. $C_{32}H_{38}N_6O_5$. Calculated, %: C 65.51; H 6.53; N 14.32.

X-ray Diffraction Study of Compound 6c. The colorless crystals (crystallized from EtOH) of compound **6c** ($C_{15}H_{15}N_3O_3$) are monoclinic. At 293 K: *a* 13.7791(7), *b* 10.9180(6), *c* 9.1462(6) Å; β 92.870(5)°; *V* 1374.2(1) Å^3; M_r 285.30; *Z* 4; space group $P2_1/c$; d_{calc} 1.379 g/cm^3; μ(MoKα) 0.098 mm^{-1}, *F*(000) 600. Intensities of 13261 reflections (4000 independent, R_{int} 0.029) were measured on an Xcalibur-3 diffractometer (graphite monochromator, CCD detector, ω-scanning, $2\theta_{max}$ 60°). The structure was solved by the direct method using the SHELXTL package [27]. The positions of hydrogen atoms were found from electron density difference maps and refined by "rider" model with $U_{iso} = nU_{eq}$ (*n* = 1.5 for methyl group and *n* = 1.2 for other hydrogen atoms) for the carrier atom. The hydrogen atom of the NH group was refined in isotropic approximation. Full-matrix least-squares refinement against F^2 in anisotropic approximation for non-hydrogen atoms using 3934 reflections converged to wR_2 0.140 (R_1 0.049 for 2534 reflections with $F > 4\sigma(F)$, *S* 1.003). The final atomic coordinates and crystallographic data for molecule **6c** have been deposited at the Cambridge Crystallographic Data Center (deposit CCDC 981626).

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