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SYNTHESIS OF 7-AMINOPYRAZOLO[3,4-*c*]PYRIDINE AS A PROBE FOR THE PREPARATION OF COMPOUNDS OF PHARMACOLOGICAL INTEREST

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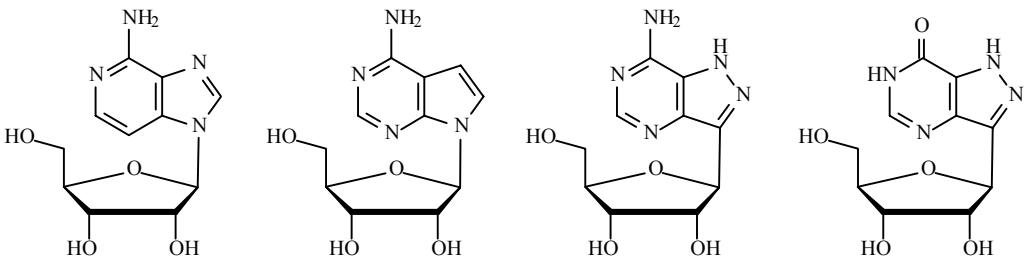
Abstract - A synthetic route towards the preparation of 7-aminopyrazolo[3,4-*c*]pyridine is developed, starting from the readily accessible 2-amino-4-methyl-3-nitropyridine. The unexpected formation of 7-methylimidazolo[4,5-*b*]pyridin-2-one during the reaction sequence is also described.

In view of the interesting biological and pharmacological properties of the deazapurine nucleosides, such as 3-deazaadenosine,[1] 7-deazaadenosine[2] and the formycins[3] (Scheme 1) and in conjunction with our ongoing interest towards the preparation of novel nucleoside analogues,[4] we have recently focused on the synthesis of derivatives of pyrazolo[3,4-*c*]pyridine.[5]

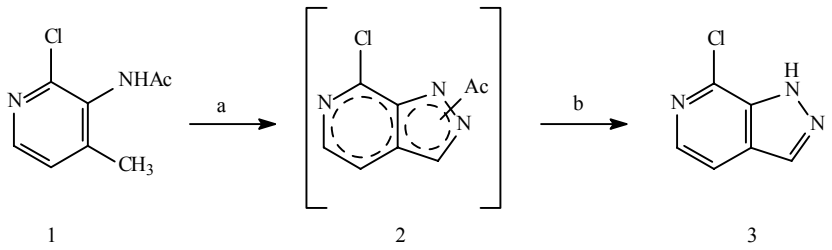
Scheme 1



In this context, we have also decided to develop a synthetic approach for the preparation of 7-aminopyrazolo[3,4-*c*]pyridine. This heterocyclic system can be used as a substrate for the synthesis of derivatives with potential pharmacological interest, since they could be viewed as singly modified (4-deaza analogues) of the formycins.

There are only a few convenient methods for the preparation of pyrazolo[3,4-*c*]pyridines. During our initial attempts towards the synthesis of the target heterocycle, we used 7-chloropyrazolo[3,4-*c*]pyridine, as starting material. The preparation of this compound has already been published in a 39 % yield starting from 3-acetamido-2-methoxy-4-methylpyridine in four steps.[6] Using the methodology that we have previously developed for the preparation of substituted pyrazolo[3,4-*c*]pyridines,[5] we have prepared 7-chloropyrazolo[3,4-*c*]pyridine (**3**) in two steps (Scheme 2) starting from the readily accessible 3-acetamido-2-chloro-4-methylpyridine (**1**)[7] in very good yield (79%). Unfortunately, heating of **3** with liquid ammonia or anhydrous hydrazine in a sealed bomb failed to give the corresponding 7-amino derivative and unchanged starting material was only recovered.

Scheme 2



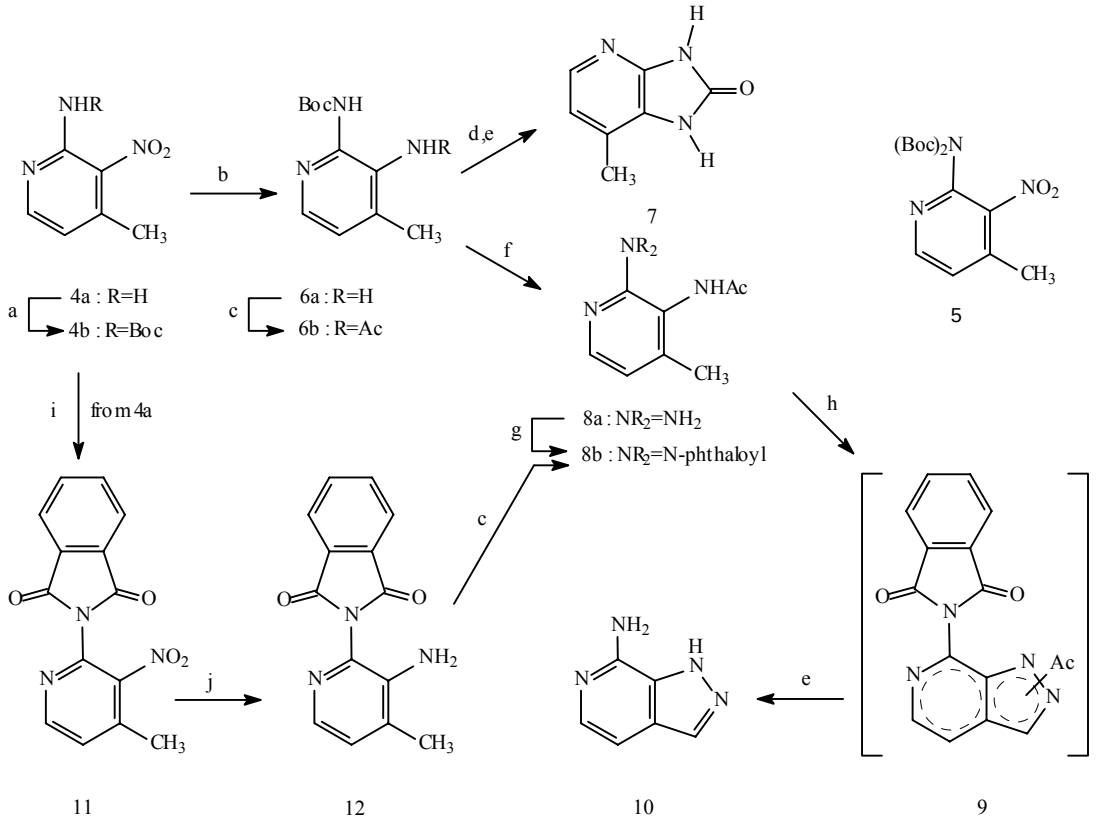
1 2 3

a: AcOK, Ac_2O, isoamyl nitrite, C_6H_6, reflux, b: NH_3/CH_3OH.

Consequently, since the reactivity of the halogen atom towards nucleophilic displacement is reduced compared to 3-deazapurines,[1a] we were obliged to figure out an alternative route for the preparation of the target heterocycle. Thus, we used 2-amino-4-methyl-3-nitropyridine (**4a**) as starting material, which was first converted to the Boc-protected derivative (**4b**) (Scheme 3). The presence of the nitro group renders the amino group less reactive, consequently the anion of **4a** with sodium hydride must be formed prior to the addition of di-*tert*-butyl dicarbonate. The amount of the base is critical, since at least two equivalents should be used in order to obtain a high yield of the desired derivative (**4b**). On the other hand, the use of one equivalent of sodium hydride results in the formation of the di-Boc-protected picoline (**5**), while unreacted starting material is also recovered. The formation of **5** under these conditions is probably due to the increased acidity of the carbamate NH of **4b** versus the 2-NH_2 of **4a**, and so the initial formation of **4b** is followed by its conversion to **5**, as it is obvious from TLC monitoring of the reaction as well. Catalytic hydrogenation of the nitro group of **4b** over Pd/C catalyst provided the aminopicoline (**6a**), which was

converted to the corresponding acetamide (**6b**). Treatment of **6b** with isoamyl nitrite in the presence of potassium acetate and acetic anhydride in refluxing benzene followed by treatment of the resulting derivative with methanolic ammonia did not provide the expected Boc-protected 7-aminopyrazolo[3,4-*c*]pyridine, as it was obvious from the ^{1}H-NMR spectrum of the product. In this spectrum, the signal of the Boc group was not present, but we observed a singlet at 2.24 ppm ascribable to a methyl group together with two doublets at 6.78 and 7.73 ppm (J= 5.37 Hz) corresponding to neighboring aromatic protons and two broad singlets corresponding to acidic protons (D_2O exchangeable). This compound furnished crystals from ethanol suitable for an X-Ray analysis study, which provided the unambiguous assignment of its structure as the imidazolopyridinone (**7**) (Figure 1).

Scheme 3

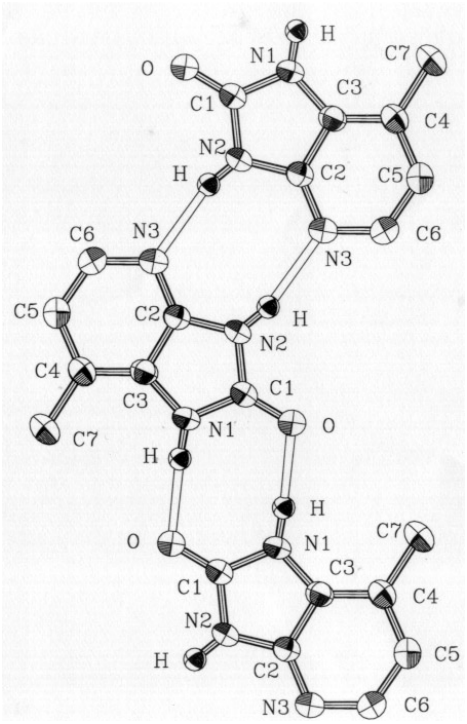


a: 1) NaH (2.5 eq.), THF, rt, 2) Boc_2O, THF, b: H_2, 10% Pd/C, EtOH, 50 psi, c: Ac_2O, toluene, rt, d: AcOK, Ac_2O, C_6H_6, reflux, e: NH_3/CH_3OH, f: CF_3CO_2H, CH_2Cl_2, rt, g: phthalic anhydride, toluene, 50 ^oC, h: AcOK, Ac_2O, isoamyl nitrite, C_6H_6, reflux, i: AcOH, phthalic anhydride, reflux, j: AcOH, Fe, acetone, H_2O, reflux.

The crystallographic analysis reveals that there exist two hydrogen bonds [N2-H---N3 = 163 $(2)^0$, N1-H---O = 176 $(2)^0$], which through centers of symmetry generate chains of H-bonded molecules. There is also an extensive overlap between the chains and the distance between overlapped molecules is 3.4 Å. This

derivative was probably obtained by the intermolecular nucleophilic attack of the acetamide nitrogen of **6b** on the carbamate carbonyl followed by ring closure and elimination of *tert*-butanol. Cyclizations in related systems have also been reported previously, but their formation required the presence of strong bases or extreme reaction conditions.[8] According to the abovementioned mechanism, prior nitrosation of **6b** is not required. So we have repeated the ring-closure reaction in the absence of isoamyl nitrite, and we have isolated compound (**7**), after treatment with methanolic ammonia. Consequently, we removed the Boc-protective group of **6b** by treatment with trifluoracetic acid, and the resulting aminopicoline (**8a**) was converted to the corresponding phthaloyl derivative (**8b**). Treatment of **8b** with isoamyl nitrite in the presence of potassium acetate and acetic anhydride in refluxing benzene provided a mixture of the regioisomers (**9**), which were not isolated, but were treated with methanolic ammonia to result in 7-aminopyrazolo[3,4-*c*]pyridine (**10**).

Figure 1. X-Ray crystal structure of **7**



Since our initial goal was to discover an efficient procedure for the preparation of the abovementioned heterocycle, we have finally altered the synthetic approach and have prepared the target compound in a reasonable overall yield starting from the commercially available picoline (**4a**), which was converted to the phthaloyl derivative (**11**). Due to the presence of the deactivating 3-nitro group, this derivative was prepared by treatment with phthalic anhydride in the presence of acetic acid.[9] The nitro group was then reduced with iron and acetic acid in aqueous acetone,[10] and the resulting 3-aminopicoline (**12**) was acetylated to give the corresponding acetamide (**8b**). This acetamide was ring closed according to the already mentioned procedure[5] to provide compound (**10**) in a 49 % overall yield.

In conclusion, we have developed and optimized a facile procedure for the preparation of 7-aminopyrazolo[3,4-*c*]pyridine. In addition, we have clarified the structure of 7-methylimidazolo[4,5-*b*]pyridin-2-one, which was unexpectedly formed during the reaction sequence.

EXPERIMENTAL

All chemicals were purchased from Aldrich Chemical Co. Melting points were determined on a Büchi apparatus and are uncorrected. ^{1}H-NMR spectra and 2-D spectra were recorded on a Bruker Avance 400

instrument at 400 MHz, whereas ^{13}C-NMR spectra were recorded on a Bruker AC 200 spectrometer at 50 MHz in deuterated solvents and were referenced to TMS (δ scale). The signals of ^{1}H and ^{13}C spectra were unambiguously assigned by using 2D NMR techniques: ^{1}H-^{1}H COSY, HMBC and HMQC. Flash chromatography was performed on Merck silica gel 60 (0.040-0.063 mm). Analytical TLC was carried out on precoated (0.25 mm) Merck silica gel F-254 plates. Elemental analyses were performed at the Microanalytical Sections of the National Hellenic Research Foundation on a Perkin-Elmer PE 240C elemental analyzer (Norwalk, CT).

7-Chloropyrazolo[3,4-*c*]pyridine (3)

Potassium acetate (130 mg, 1.32 mmol) and acetic anhydride (0.25 mL, 2.64 mmol) were added to a solution of 3-acetamido-2-chloro-4-methylpyridine (**1**) (162 mg, 0.88 mmol)[7] in dry benzene (40 mL) under Ar. The reaction mixture was heated at 80 ^{o}C, isoamyl nitrite (0.12 mL, 0.88 mmol) was added and the resulting mixture was refluxed for 8 h. The insoluble material was then filtered off, the solvent was vacuum-evaporated and the residue was purified by column chromatography (silica gel) with cyclohexane/ethyl acetate (60/40, v/v) as the eluent, to give **3** (106 mg, 79 %), mp 163 ^{o}C (toluene), (lit.,[6] 161-163 ^{o}C); (^{1}H-NMR spectral data are identical to those reported in the literature[6]); ^{13}C-NMR ($CDCl_3$) δ: 114.6 (C-4), 128.8 (C-3a), 134.6 (C-7a), 135.1 (C-7), 135.3 (C-3), 138.8 (C-5).

***tert*-Butyl-*N*-(4-methyl-3-nitropyridin-2-yl) carbamate (4b)**

To a solution of 2-amino-4-methyl-3-nitropyridine (**4a**) (5 g, 32.68 mmol) in dry THF (180 mL) sodium hydride (3.27 g, 82 mmol, 60% suspension in paraffin oil) was added under argon at 0 ^{o}C and the resulting mixture was stirred at rt for 90 min. It was then cooled at 0 ^{o}C, a solution of di-*tert*-butyl dicarbonate (7.5 mL, 32.68 mmol) in dry THF (20 mL) was added dropwise and the mixture was stirred at rt for an additional 18 h. The solvent was vacuum-evaporated, a solution of HCl (0.5 N, 60 mL) was added to the residue and the product was extracted with ethyl acetate. The organic extracts were dried (Na_2SO_4) and concentrated to dryness to give pure **4b** (8 g, 97%), mp 154-155 ^{o}C (Et_2O/*n*-pentane); ^{1}H-NMR ($CDCl_3$) δ: 1.52 (s, 9H, $(CH_3)_3C$), 2.50 (s, 3H, CH_3), 7.08 (d, 1H, H-5, $J_{5,6}$=5.13 Hz), 8.43 (d, 1H, H-6, $J_{6,5}$=5.13 Hz), 9.55 (br s, 1H, -NHBoc, D_2O exchangeable); ^{13}C-NMR ($CDCl_3$) δ: 19.4 (4-$\underline{C}H_3$), 28.1 [$(\underline{C}H_3)_3C$], 82.3 [$(CH_3)_3\underline{C}$], 122.2 (C-5), 143.9 (C-4), 144.5 (C-3), 147.2 (C-2), 149.9 (C-6), 151.4 (C=O). *Anal*. Calcd for $C_{11}H_{15}N_3O_4$: C, 52.17; H, 5.97; N, 16.59. Found: C, 51.93; H, 5.79; N, 16.27.

2-Bis(*tert*-butoxycarbonyl)amino-4-methyl-3-nitropyridine (5)

This compound was prepared by an analogous procedure to **4b** with the use of one equivalent of sodium hydride and one equivalent of di-*tert*-butyl dicarbonate. Yield: 43 %, mp 93 ^{o}C (Et_2O/*n*-pentane); ^{1}H-

NMR ($CDCl_3$) δ: 1.44 (s, 18H, 2 x $(CH_3)_3C$), 2.46 (s, 3H, CH_3), 7.29 (d, 1H, H-5, $J_{5,6}$=5.12 Hz), 8.50 (d, 1H, H-6, $J_{6,5}$=5.12 Hz); ^{13}C-NMR ($CDCl_3$) δ: 17.8 (4-$\underline{C}H_3$), 27.7 [2 x $(\underline{C}H_3)_3C$], 84.1 [2 x $(CH_3)_3\underline{C}$], 126.5 (C-5), 142.2 (C-4), 144.0 (C-3), 149.6 (C-2), 149.8 (C-6), 150.2 (2 x C=O). *Anal*. Calcd for $C_{16}H_{23}N_3O_6$: C, 54.38; H, 6.56; N, 11.89. Found: C, 54.47; H, 6.45; N, 11.67.

***tert*-Butyl-*N*-(3-amino-4-methylpyridin-2-yl) carbamate (6a)**

A solution of **4b** (8 g, 31.6 mmol) in dry ethanol (150 mL) was hydrogenated in the presence of 10% Pd/C (500 mg) under a pressure of 45 psi at rt for 3 h. The solution was filtered through a celite pad to remove the catalyst and the filtrate was evaporated to dryness to give pure **6a** (7 g, 99%), mp >250 ^{o}C (EtOH); ^{1}H-NMR ($CDCl_3$) δ: 1.49 [s, 9H, $(CH_3)_3C$], 2.20 (s, 3H, CH_3), 4.24 (br s, 2H, -NH_2, D_2O exchangeable), 6.88 (d, 1H, H-5, $J_{5,6}$=4.76 Hz), 7.74 (d, 1H, H-6, $J_{6,5}$=4.76 Hz), 8.37 (br s, 1H, -NHBoc, D_2O exchangeable); ^{13}C-NMR ($CDCl_3$) δ: 17.4 (4-$\underline{C}H_3$), 28.4 [$(\underline{C}H_3)_3C$], 81.0 [$(CH_3)_3\underline{C}$], 123.2 (C-5), 133.6 (C-3), 135.0 (C-4), 137.2 (C-6) 138.6 (C-2), 154.3 (C=O). *Anal*. Calcd for $C_{11}H_{17}N_3O_2$: C, 59.17; H, 7.67; N, 18.82. Found: C, 59.03; H, 7.71; N, 18.63.

***tert*-Butyl-*N*-(3-acetamido-4-methylpyridin-2-yl) carbamate (6b)**

To a solution of **6a** (7 g, 31.4 mmol) in dry toluene (120 mL) acetic anhydride (6 mL, 65 mmol) was added and the resulting solution was stirred at rt for 1 h. The solvent was vacuum-evaporated and the residue was purified by column chromatography (silica gel) with cyclohexane/ethyl acetate (60/40, v/v) as the eluent to give pure **6b** (8.15 g, 98 %), mp 148 ^{o}C (Et_2O/*n*-pentane); ^{1}H-NMR ($CDCl_3$) δ: 1.53 (s, 9H, $(CH_3)_3C$), 2.13 (s, 3H, CH_3), 2.29 (s, 3H, $COCH_3$), 7.04 (d, 1H, H-5, $J_{5,6}$=4.73 Hz), 7.65 (br s, 1H, -NHBoc, D_2O exchangeable), 8.15 (d, 1H, H-6, $J_{6,5}$=4.73 Hz), 8.72 (br s, 1H, -NHAc, D_2O exchangeable); ^{13}C-NMR ($CDCl_3$) δ: 18.7 (4-$\underline{C}H_3$), 23.5 ($\underline{C}H_3$-CO), 28.3 [$(\underline{C}H_3)_3C$], 81.9 [$(CH_3)_3\underline{C}$], 123.1 (C-5), 124.9 (C-3), 145.5 (C-6), 146.6 (C-4), 148.5 (C-2), 154.8 (t-BuO$\underline{C}$O), 168.3 (NH$\underline{C}$OCH_3). *Anal*. Calcd for $C_{13}H_{19}N_3O_3$: C, 58.85; H, 7.22; N, 15.84. Found: C, 59.06; H, 7.17; N, 15.59.

7-Methylimidazolo[4,5-*b*]pyridin-2-one (7)

Potassium acetate (56 mg, 0.57 mmol) and acetic anhydride (0.11mL, 1.14 mmol) were added under argon to a solution of **6b** (100 mg, 0.38 mmol) in dry benzene (30 mL) and the reaction mixture was refluxed for 6 h. The precipitate was filtered off, the filtrate was concentrated to dryness and the residue was treated with methanolic ammonia at 0^{o}C for 15 min. The solvent was then vacuum-evaporated and the solid residue was purified by flash chromatography on silica gel (dichloromethane/methanol: 90/10, v/v, as eluent) to afford **7** (47 mg, 83%), mp >250 ^{o}C (EtOH/H_2O); ^{1}H-NMR (DMSO-d_6) δ: 2.24 (s, 3H, CH_3), 6.78 (d, 1H, H-6, $J_{6,5}$=5.37 Hz), 7.73 (d, 1H, H-5, $J_{5,6}$=5.37 Hz), 10.92 (br s, 1H, NH, D_2O

exchangeable), 11.20 (br s, 1H, NH, D_2O exchangeable); ^{13}C-NMR (DMSO-d_6) δ: 15.7 (CH_3), 118.5 (C-6), 122.9 (C-7a), 125.6 (C-7), 139.8 (C-5), 144.4 (C-3a), 154.7 (C-2). *Anal*. Calcd for $C_7H_7N_3O$: C, 56.37; H, 4.73; N, 28.17. Found: C, 56.02; H, 4.69; N, 28.27.

X-Ray crystal data of 7

Compound (**7**) crystallizes from ethanol. $C_7H_7N_3O$, *M*= 149.157. *α*=7.110(3), *b*= 7.516 (3), *c*= 13.112 (6), *β*= 98.10 (1)^o, V= 693.8 (4) Å ^{3}, space group $P2_1/n$, Z=4, T= 298 K. Reflections measured/independent 1385/1222. *D*c= 1.428 mg.m^{-3}, $\mu(M_0K\alpha)$= 1.02 cm^{-1}, F(000)= 312, crystal size= 005 x 0.25 x 0.5 mm. Crystal Logic diffractometer. *R*1 0.044, *w*R2 0.114, 142 parameters.

***N*-(2-Amino-4-methylpyridin-3-yl)acetamide (8a)**

Trifluoroacetic acid (0.07 mL, 0.9 mmol) was added at 0^{o}C to a solution of **6b** (200 mg, 0.75 mmol) in dry dichloromethane and the mixture was stirred at rt for 12 h. The solvent was vacuum-evaporated and the residue was treated with a saturated $NaHCO_3$ solution and ethyl acetate. The organic layer was dried (Na_2SO_4) and concentrated to dryness. The residue was purified by flash chromatography (silica gel) with dichloromethane/methanol (90/10, v/v) as the eluent to give **8a** (0.12 mg, 97%) as an oil. ^{1}H-NMR ($CDCl_3$) δ: 2.19 (s, 3H, CH_3), 2.24 (s, 3H, $COCH_3$), 4.32 (br s, 2H, -NH_2, D_2O exchangeable), 6.58 (d, 1H, H-5, $J_{5,6}$=5.10 Hz), 6.82 (br s, 1H, -NHAc, D_2O exchangeable), 7.88 (d, 1H, H-6, $J_{6,5}$=5.10 Hz); ^{13}C-NMR ($CDCl_3$) δ: 18.0 (CH_3), 23.5 ($\underline{C}H_3CO$), 117.2 (C-5), 119.6 (C-3), 145.3 (C-4), 146.6 (C-6), 155.5 (C-2), 169.4 (C=O). *Anal*. Calcd for $C_8H_{11}N_3O$: C, 58.17; H, 6.71; N, 25.44. Found: C, 58.30; H, 6.62; N, 25.19.

***N*-(4-Methyl-2-phthalimidopyridin-3-yl)acetamide (8b)**

A mixture of the aminopyridine (**8a)** (220 mg, 1.33 mmol) and phthalic anhydride (197 mg, 1.33 mmol) in dry toluene (60 mL) was heated at 50 ^{o}C under argon for 12 h. The precipitate was filtered off, the filtrate was vacuum-evaporated and the solid residue was recrystallized to give pure **8b** as a white solid (350 mg, 89%), mp >250 ^{o}C (EtOH); ^{1}H-NMR (DMSO-d_6) δ: 1.84 (s, 3H, CH_3), 2.27 (s, 3H, $COCH_3$), 7.48 (d, 1H, H-5, $J_{5,6}$=4.76 Hz), 7.91 (m, 2H, H-4', H-5'), 7.98 (m, 2H, H-3', H-6'), 8.38 (d, 1H, H-6, $J_{6,5}$=4.76 Hz), 9.67 (br s, 1H, -NHAc, D_2O exchangeable); ^{13}C-NMR (DMSO-d_6) δ: 18.1 (4-$\underline{C}H_3$), 22.5 ($\underline{C}H_3CO$), 123.6 (C-3', C-6'), 126.5 (C-5), 130.2 (C-2a', C-6a'), 131.5 (C-3), 134.9 (C-4', C-5'), 142.7 (C-2), 146.0 (C-6), 147.1 (C-4), 166.0 [C=O(Phth)], 167.8 ($\underline{C}OCH_3$). *Anal*. Calcd for $C_{16}H_{13}N_3O_3$: C, 65.08; H, 4.44; N, 14.23. Found: C, 64.82; H, 4.51; N, 13.96.

7-Aminopyrazolo[3,4-*c*]pyridine (10)

This compound was prepared by an analogous procedure to **3** and the product was purified by flash chromatography (silica gel) with dichloromethane/methanol (90/10, v/v) as the eluent to afford **10** (82%), mp 165-167 ^{o}C (MeOH); ^{1}H-NMR (DMSO-d_6) δ: 6.38 (br s, 2H, NH_2, D_2O exchangeable), 6.85 (d, 1H, H-4, $J_{4,5}$=5.85 Hz), 7.48 (d, 1H, H-5, $J_{5,4}$=5.85 Hz), 7.97 (s, 1H, H-3), 13.2 (br s, 1H, NH, D_2O exchangeable); ^{13}C-NMR (DMSO-d_6) δ: 103.7 (C-4), 125.9 (C-3a), 127.5 (C-7a), 132.5 (C-3), 137.1 (C-5), 146,4 (C-7). *Anal*. Calcd for $C_6H_6N_4$: C, 53.73; H, 4.50; N, 41.77. Found: C, 53.91; H, 4.57; N, 41.52.

***N*-(4-Methyl-3-nitropyridin-2-yl)phthalimide (11)**

A mixture of **4a** (1.3 g, 8.5 mmol) and phthalic anhydride (1.25 g, 8.5 mmol) in acetic acid (4 mL) was heated at reflux for 24 h. Dichloromethane (50 mL) was then added and the solution was washed with water and a saturated Na_2CO_3 solution. The organic phase was dried (Na_2SO_4) and concentrated to dryness to provide **11** as a white solid (1.88 g, 78 %), mp 228 ^{o}C (MeOH); ^{1}H-NMR ($CDCl_3$) δ: 2.56 (s, 3H, CH_3), 7.46 (d, 1H, H-5, $J_{5,6}$=4.88 Hz), 7.83 (m, 2H, H-4', H-5'), 7.98 (m, 2H, H-3', H-6'), 8.68 (d, 1H, H-6, $J_{6,5}$=4.88 Hz); ^{13}C-NMR ($CDCl_3$) δ: 18.6 (4-$\underline{C}H_3$), 124.4 (C-3', C-6'), 127.4 (C-5), 131.7 (C-2a', C-6a'), 134.9 (C-4', C-5'), 139.2 (C-2), 142.3 (C-4), 143.7 (C-3), 150.7 (C-6), 165.7 (C=O). *Anal*. Calcd for $C_{14}H_9N_3O_4$: C, 59.37; H, 3.20; N, 14.84. Found: C, 59.08; H, 3.12; N, 15.12.

***N*-(3-Amino-4-methylpyridin-2-yl)phthalimide (12)**

The protected pyridine (**11**) (300 mg, 1.06 mmol) was dissolved in hot acetone (30 mL) and acetic acid (3 mL) and water (3 mL) were added. The resulting solution was refluxed and finely powdered iron (712 mg, 12.7 mmol) was added in portions. The reaction was stirred and refluxed for an additional 90 min. The solids were then filtered through a celite pad and washed with acetone, and acetone was vacuum-evaporated. A saturated solution of sodium bicarbonate was added to the residue, and the precipitate was filtered, washed with water and air-dried to give pure **12** as a white solid (268 mg, 78%), mp 214 ^{o}C (EtOH); ^{1}H-NMR ($CDCl_3$) δ: 2.28 (s, 3H, CH_3), 3.79 (br s, 2H, -NH_2, D_2O exchangeable), 7.08 (d, 1H, H-5, $J_{5,6}$=4.39 Hz), 7.78 (m, 2H, H-4', H-5'), 7.98 (m, 3H, H-6, H-3', H-6'); ^{13}C-NMR ($CDCl_3$) δ: 17.3 (4-$\underline{C}H_3$), 124.0 (C-3', C-6'), 126.6 (C-5), 132.0 (C-3), 132.2 (C-2a', C-6a'), 134.0 (C-4), 134.6 (C-4', C-5'), 138.5 (C-2), 139.1 (C-6), 167.2 (C=O). *Anal*. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59. Found: C, 66.61; H, 4.53; N, 16.32.

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