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Synthesis of 5-alkyl-4-amino-2-(trifluoromethyl)pyridines and their transformation into trifluoromethylated 1*H*-pyrazolo[4,3-*c*]pyridines

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Abstract—5-Alkyl-4-amino-2-(trifluoromethyl)pyridines were prepared in good yields starting from the corresponding pyridinols either using condensation with tosyl isocyanate or by alkylation with 2-chloroacetamide and subsequent Smiles type rearrangement. The cyclisation of diazonium salts, generated from 5-alkyl-4-amino-2-(trifluoromethyl)pyridines, afforded trifluoromethylated 1*H*-pyrazolo[4,3-*c*]pyridines.

1. Introduction

4-Aminopyridine (fampridine) is one of the most useful heterocyclic amines, which has important applications both in organic synthesis and in medicinal chemistry. Recently, 2-trifluoromethylated fampridine has been prepared by nitration and subsequent reduction of 2-(trifluoromethyl)pyridine *N*-oxide,[1] and used for the synthesis of biologically active compounds.[1,2] Related 4-amino-2-(trifluoromethyl)pyridines, bearing an alkyl substituent at the 3 (or 5)-position of the heteroaromatic ring, are suitable precursors of fused nitrogen-containing heterocycles,[3–5] but only fragmentary data concerning the preparation and properties of such amines are available in the literature.[5]

We have previously reported that 4-amino-5-aryl-2-(trifluoromethyl)pyridines are accessible from the corresponding 4*H*-pyran-4-ones and were successfully converted to trifluoromethylated benzo[*c*][1,6]naphthyridines.[6,7] The present work was undertaken to extend these investigations in order to prepare 5-alkyl-4-amino-2-(trifluoromethyl)-pyridines **5** which were then employed for the synthesis of pyrazolo[4,3-*c*]pyridines **7**. Such heteroaromatic compounds, along with their [3,4-*c*]fused analogues, are structurally related to some biologically active purine type heterocycles like, for example, the nucleoside antibiotics *formicins*,[8,9] the antihyperuricemic drug *allopurinol*,[10] and also possess interesting pharmacological properties as antihypertensive[11] and antidepressive agents.[12]

2. Results and discussion

To accomplish the conversion of 5-alkyl-2-(trifluoromethyl)-4*H*-pyran-4-ones **1a–c**[6] into 4-aminopyridines **5a–c**, compounds **1a–c** were treated initially with aqueous ammonia in boiling MeOH or *i*-PrOH; the expected 4-pyridinols **2a–c** were obtained in 83–94% yield. Following our procedure[7] for the preparation of 5-arylated congeners of **5a–c**, pyridinols **2a–c** were condensed with tosyl isocyanate in toluene at reflux and the resulting tosylamidopyridine intermediates **3a–c** were hydrolysed with hot 90% H_2SO_4 to the desired 4-aminopyridines **5a–c** in 86–88% yield (Scheme 1, method A).

Although this route to alkylated 4-aminopyridines **5a–c** is quite efficient, our intention was to elaborate a more general approach excluding harsh acidic conditions at the work-up stage and potentially allowing the preparation of analogues of **5a–c** with acid sensitive functional groups. Toward this end, a simplified two-step procedure, proposed earlier[13] for the preparation of 2-aminopyridines from 2(1*H*)-pyridinones via a rearrangement of the intermediate 2-(2-pyridyloxy)acetamides under basic conditions, was employed for the synthesis of 4-aminopyridines **5a–c**. To our knowledge, such transformation of 4-pyridinols to 4-aminopyridines has not been reported previously.[14]

Keywords: 4*H*-pyran-4-ones; 4-aminopyridines; 1*H*-pyrazolo[4,3-*c*]pyridines; Smiles rearrangement.

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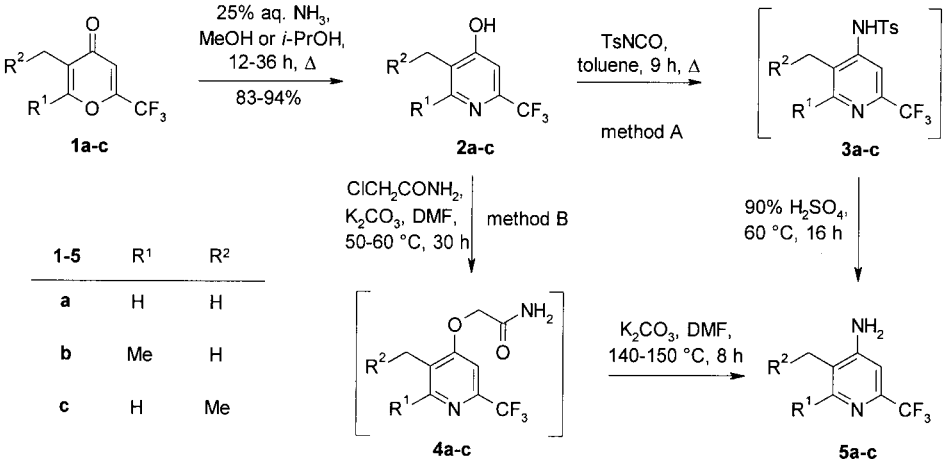


Scheme 1.

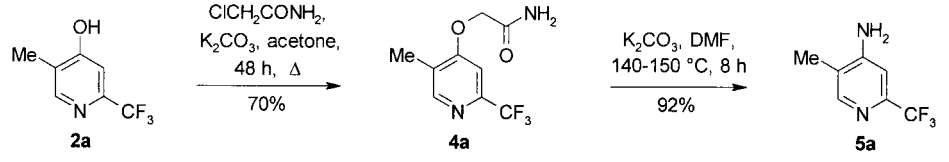
Thus, the reaction of pyridinols **2a–c** with 2-chloroacetamide in the presence of potassium carbonate in DMF at 50–60°C followed by heating at 140–150°C with an additional portion of potassium carbonate directly produced the target 4-aminopyridines **5a–c** in a one-pot procedure in 86–89% yield (Scheme 1, method B). This transformation of compounds **2a–c** apparently proceeds through the formation of 2-(4-pyridyloxy)acetamides **4a–c**, which underwent a Smiles type rearrangement upon heating with base.[15] In the case of pyridinol **2a**, intermediate acetamide **4a** was isolated, when the alkylation of compound **2a** was performed in boiling acetone and smoothly converted into aminopyridine **5a** under the action of potassium carbonate in DMF at reflux (Scheme 2).

The 4-aminopyridines **5a–c** prepared were readily converted into the corresponding pyrazolo[4,3-*c*]pyridines **7a–c** via a simple and practical procedure as follows (Scheme 3). 5-Alkyl-4-aminopyridines **5a–c** were diazotized in a conventional manner by the action of sodium nitrite in 50% sulphuric acid. Treatment of the diazonium salts **6a–c** thus formed with aqueous sodium acetate solution gave the desired trifluoromethylated pyrazolo[4,3-*c*]pyridines **7a–c** as high-melting crystalline materials which can be purified by sublimation in vacuo. Spectral analysis of crude **7a** also revealed the presence of the diazo-coupling product of compound **7a** with diazonium salt **6a**. In order to minimise this side reaction, the generated **6a–c** were slowly added to a large excess of cold, vigorously stirred aqueous sodium acetate. In this way, pyrazolopyridines **7a–c** were obtained in 40–77% yield.

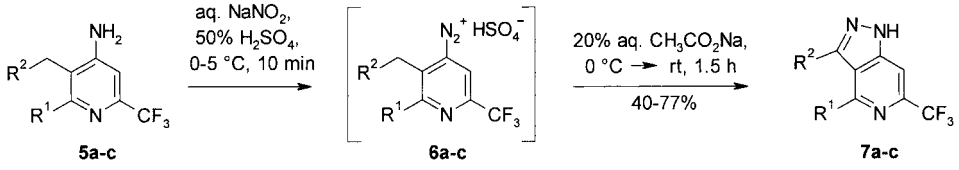
It should be noted that a series of pyrazolo[3,4-*c*]pyridines has been prepared previously by nitrosation of 3-acetamido-4-methylpyridines, and subsequent rearrangement and cyclisation of the *N*-nitroso compounds produced.[4,5,9] Under similar conditions, *N*-acylated 4-amino-3-methylpyridines were found to give the corresponding pyrazolo[4,3-*c*]pyridines in poor yield.[5]

All new compounds were characterised by spectral and microanalytical data. Mass spectra of compounds **7a–c** showed the molecular ion as the base peak. As expected, in the ^{1}H NMR spectra of compounds **7a–c**, signals assigned to the pyridine protons are significantly shifted downfield ($\Delta\delta$=0.78–1.19 ppm) compared to the pyridine precursors **2a–c**, **5a–c**.[4]

In conclusion, practical routes to 5-alkyl-4-amino-2-(trifluoromethyl)pyridines **5** starting from the corresponding



Scheme 2.



5-7: **a** $R^1 = R^2 = H$; **b** $R^1 = Me$, $R^2 = H$; **c** $R^1 = H$, $R^2 = Me$

Scheme 3.

4*H*-pyran-4-ones were developed. Diazotisation of 5-alkylated 4-aminopyridines, followed by sodium acetate treatment of the obtained diazonium salts, offers a convenient procedure for the synthesis of trifluoromethylated pyrazolo[4,3-*c*]pyridines.

3. Experimental

3.1. General

IR spectra were measured on a Specord 75 IR (CCl_4 or $CHCl_3$ solution) or a UR 20 (KBr) spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer at 200 and 50.3 MHz, respectively, with Me_4Si as the internal standard. Mass spectra were obtained on a Shimadzu QP-5000 GC/MS spectrometer. Melting points are uncorrected. All chemicals were reagent grade; solvents were dried and distilled prior to use. 5-Methyl-2-(trifluoromethyl)-4*H*-pyran-4-one (**1a**) and 5,6-dimethyl-2-(trifluoromethyl)-4*H*-pyran-4-one (**1b**) were prepared as previously reported.[6]

3.1.1. 5-Ethyl-2-(trifluoromethyl)-4*H*-pyran-4-one (1c). This compound was prepared from 2-acetyl-2-ethyloxirane[16] in 36% overall yield according to the previously described two-step procedure.[6] **1c**: bp 68–69°C/10 mmHg; n_D^{20}=1.4393; IR (CCl_4) 1675, 1640, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (t, *J*=7.5 Hz, 3H), 2.45 (q, *J*=7.5 Hz, 2H), 6.71 (s, 1H), 7.74 (s, 1H). EIMS (70 eV) *m/z* (rel. int.) 192 (M^+, 77), 191 (100), 177 (4), 164 (9), 145 (9), 139 (17), 123 (3), 95 (44), 75 (9), 69 (47), 54 (8), 53 (88), 52 (11), 51 (18), 50 (9), 41 (16), 40 (6), 39 (90), 38 (11). Anal. Calcd for $C_8H_7F_3O_2$: C, 50.01; H, 3.67. Found: C, 50.19; H, 3.83.

3.1.2. Conversion of pyranones 1a–c into pyridinols 2a–c. To a solution of starting pyranones **1a–c** (10 mmol) in 5 mL of MeOH (compounds **1a** and **1c**) or *i*-PrOH (compound **1b**), 25% aqueous ammonia (1.9 mL, 25 mmol) was added. The resulting solution was heated at reflux for 12–36 h. After evaporation of the solvent under reduced pressure, the solid residue was recrystallised to afford compounds **2a–c** as white crystals.

3.1.3. 5-Methyl-2-(trifluoromethyl)-4-pyridinol (2a). 94%. Mp 143–144°C (toluene); IR ($CHCl_3$) 3555, 1637 (weak), 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.29 (s, 3H), 7.22 (s, 1H), 8.18 (s, 1H), 11.86 (brs, 1H). ^{13}C NMR (DMSO-d_6) δ 12.73 (CH_3), 107.15 (s, *C*H=CCF$_3$), 121.91 (q, *J*=274 Hz, CF_3), 123.98 (*C*CH_3), 146.10 (q, *J*=33 Hz, *C*CF_3), 151.40 (*C*H=CCH_3), 163.33 (C–OH). EIMS (70 eV) *m/z* (rel. int.) 177 (M^+, 100), 176 (13), 159 (9), 158 (14), 157 (19), 148 (10), 128 (7), 108 (18), 102 (17), 101 (9), 81 (16), 80 (11), 79 (11), 75 (12), 69 (10), 68 (15), 63 (10), 55 (12), 53 (32), 52 (14), 51 (12), 39 (10). Anal. Calcd for $C_7H_6F_3NO$: C, 47.47; H, 3.41. Found: C, 47.61; H, 3.58.

3.1.4. 5,6-Dimethyl-2-(trifluoromethyl)-4-pyridinol (2b). 94%. Mp 137–138°C (cyclohexane–benzene, 1:1); IR ($CHCl_3$) 3570, 3400, 1645 (weak), 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (s, 3H), 2.49 (s, 3H), 6.99 (s, 1H), 8.07 (brs, 1H). ^{13}C NMR (DMSO-d_6) δ 10.66 (CH_3), 22.40 (CH_3), 105.62 (q, *J*=2.5 Hz, *C*H=CCF$_3$), 121.53 (*C*CH_3), 121.97 (q, *J*=274 Hz, CF_3), 144.23 (q, *J*=33 Hz, *C*CF_3), 158.83 (*C*CH_3), 162.68 (C–OH). EIMS (70 eV) *m/z* (rel. int.) 191 (M^+, 100), 176 (5), 172 (12), 171 (17), 163 (7), 162 (26), 148 (6), 142 (9), 128 (10), 102 (24), 94 (10), 91 (7), 81 (21), 75 (11), 69 (11), 67 (12), 55 (17), 53 (23), 51 (19), 42 (34), 39 (20). Anal. Calcd for $C_8H_8F_3NO$: C, 50.27; H, 4.22. Found: C, 50.38; H, 4.39.

3.1.5. 5-Ethyl-2-(trifluoromethyl)-4-pyridinol (2c). 83%. Mp 128–129°C (cyclohexane–toluene, 1:1); IR ($CHCl_3$) 3565, 3400, 1640 (weak), 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (t, *J*=7.5 Hz, 3H), 2.72 (q, *J*=7.5 Hz, 2H), 7.18 (s, 1H), 8.12 (s, 1H), 11.01 (brs, 1H). EIMS (70 eV) *m/z* (rel. int.) 191 (M^+, 49), 190 (12), 177 (8), 176 (100), 172 (7), 128 (6), 126 (15), 101 (4), 78 (5), 69 (6), 68 (3), 55 (4), 53 (13), 52 (8), 51 (11), 50 (4), 39 (13). Anal. Calcd for $C_8H_8F_3NO$: C, 50.27; H, 4.22. Found: C, 50.35; H, 4.41.

3.1.6. Preparation of 4-aminopyridines 5a–c. *Method A*. Tosyl isocyanate (2.7 mL, 17.5 mmol) was added in one portion to a suspension of 4-pyridinols **2a–c** (10 mmol) in 20 mL of dry toluene. The reaction mixture was then heated at reflux for 9 h. The solution was cooled to 0°C, and 90% sulphuric acid (3.0 mL) was added. The two-phase mixture was stirred at 60°C for 16 h. After cooling to 0°C, crushed ice (10 g) was added followed by 46% aqueous sodium hydroxide (8.7 mL). The precipitated sodium sulphate was then filtered off and washed thoroughly with CH_2Cl_2. The filtrate was extracted with CH_2Cl_2 (10 mL×5). The combined organic phases were stirred at reflux with 50 mL of 15% HCl for 30 min. The organic layer was separated and washed with 10 mL of 15% HCl. The combined aqueous acid phases were treated with 46% aqueous sodium hydroxide until alkaline, extracted with CH_2Cl_2 (10 mL×5), the extract being washed with brine and dried over Na_2SO_4. After evaporation of the solvent, the residue was recrystallised to obtain 4-aminopyridines **5a**,**b** or diluted with ether and filtered through a short pad of silica gel to provide, after concentration, 4-aminopyridine **5c**.

Method B. 2-Chloroacetamide (0.94 g, 10 mmol), potassium carbonate (3.45 g, 25 mmol) and sodium iodide (0.04 g, 0.25 mmol) were added to a solution of 4-pyridinols **2a–c** (10 mmol) in 25 mL of dry DMF. The stirred reaction mixture was heated at 50–60°C for 30 h. Then, a fresh portion of potassium carbonate (3.45 g, 25 mmol) was added and the mixture was heated at 140–150°C for 8 h. The bulk of the DMF was evaporated under reduced pressure, the residue diluted with 10 mL of water and extracted with ether (10 mL×5). The combined organic extracts were washed with brine and dried over Na_2SO_4. Evaporation of the solvent afforded pure 4-aminopyridines **5a–c**, identical in all aspects with samples obtained according to method A.

3.1.7. 4-Amino-5-methyl-2-(trifluoromethyl)pyridine (5a). 87% method A; 89% method B, white crystals. Mp 109–110°C (cyclohexane–toluene, 1:1); IR (CCl_4) 3500, 3405, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.17 (s, 3H), 4.47 (brs, 2H), 6.89 (s, 1H), 8.19 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 13.67 (CH_3), 105.67 (q, *J*=2.5 Hz, *C*H=CCF$_3$), 119.30 (*C*CH_3), 122.10 (q, *J*=274 Hz, CF_3), 146.95 (q, *J*=33 Hz, *C*CF_3), 150.18 (*C*H=CCH_3), 152.60 (C–NH_2). EIMS (70 eV) *m/z* (rel. int.) 176 (M^+, 100), 175 (22), 157 (11), 156 (25), 148 (5), 129 (5), 107 (12), 101 (4), 81 (5), 80 (54), 78 (5), 75 (5), 69

(6), 66 (5), 63 (8), 54 (10), 53 (15), 52 (17), 41 (8), 40 (6), 39 (19). Anal. Calcd for $C_7H_7F_3N_2$: C, 47.73; H, 4.01. Found: C, 47.87; H, 4.18.

3.1.8. 4-Amino-5,6-dimethyl-2-(trifluoromethyl)pyridine (5b). 88% method A; 86% method B, white crystals. Mp 94–95°C (cyclohexane–benzene, 1:1); IR (CCl_4) 3505, 3410, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10 (s, 3H), 2.51 (s, 3H), 4.30 (brs, 2H), 6.78 (s, 1H). EIMS (70 eV) *m/z* (rel. int.) 190 (M^+, 100), 189 (14), 175 (4), 171 (11), 170 (42), 162 (5), 149 (4), 129 (6), 102 (7), 95 (5), 81 (6), 80 (62), 78 (6), 77 (6), 69 (7), 67 (7), 66 (7), 54 (11), 52 (16), 51 (12), 42 (17), 41 (11), 39 (12). Anal. Calcd for $C_8H_9F_3N_2$: C, 50.53; H, 4.77. Found: C, 50.69; H, 4.93.

3.1.9. 4-Amino-5-ethyl-2-(trifluoromethyl)pyridine (5c). 86% method A; 87% method B, pale yellow oil; IR (CCl_4) 3515, 3425, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (t, J=7.5 Hz, 3H), 2.54 (q, J=7.5 Hz, 2H), 4.57 (brs, 2H), 6.89 (s, 1H), 8.18 (s, 1H). EIMS (70 eV) *m/z* (rel. int.) 190 (M^+, 48), 176 (8), 175 (100), 171 (4), 169 (3), 148 (1), 128 (2), 125 (5), 94 (2), 78 (2), 75 (2), 69 (3), 63 (1), 54 (2), 52 (5), 51 (3), 42 (1), 41 (2), 39 (5). Anal. Calcd for $C_8H_9F_3N_2$: C, 50.53; H, 4.77. Found: C, 50.70; H, 4.95.

3.1.10. 2-[5-Methyl-2-(trifluoromethyl)-4-pyridyloxy]-acetamide (4a). 2-Chloroacetamide (0.94 g, 10 mmol), potassium carbonate (3.45 g, 25 mmol) and sodium iodide (0.04 g, 0.25 mmol) were added to a solution of 4-pyridinol **2a** (1.77 g, 10 mmol) in 35 mL of dry acetone. The stirred reaction mixture was heated at reflux for 48 h and cooled to room temperature. The salts were filtered off and washed thoroughly with acetone. The filtrate and washings were combined and evaporated under reduced pressure. The residue was recrystallised to give 1.64 g (70%) of compound **4a** as colourless crystals. Mp 175–177°C (*i*-PrOH–toluene, 3:2); IR ($CHCl_3$) 3520, 3400, 1700, 1575 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.27 (s, 3H), 4.77 (s, 2H), 7.30 (s, 1H), 7.51 (brs, 1H), 7.57 (brs, 1H), 8.44 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 12.96 (CH_3), 66.82 (CH_2), 104.25 (q, J=2.5 Hz, *C*H=CCF$_3$), 121.78 (q, J=274 Hz, CF_3), 125.76 (*C*CH$_3$), 146.45 (q, J=33 Hz, *C*CF$_3$), 151.00 (*C*H=CCH$_3$), 163.22 (C–O), 169.00 (C=O). EIMS (70 eV) *m/z* (rel. int.) 234 (M^+, 31), 215 (7), 191 (19), 190 (16), 176 (23), 161 (8), 160 (23), 141 (15), 140 (6), 113 (8), 110 (5), 83 (10), 75 (5), 69 (6), 65 (6), 63 (16), 59 (100), 58 (30), 53 (6), 51 (6), 44 (70), 42 (12), 39 (24). Anal. Calcd for $C_9H_9F_3N_2O_2$: C, 46.16; H, 3.87. Found: C, 46.28; H, 3.98.

3.1.11. Transformation of compound 4a to 4-amino-pyridine 5a. Compound **4a** (1.50 g, 6.4 mmol) was dissolved in 25 mL of dry DMF, then potassium carbonate (3.45 g, 25 mmol) was added and the mixture was refluxed for 8 h. The bulk of the DMF was evaporated under reduced pressure, the residue diluted with 5 mL of water and extracted with ether (10 mL×5). The combined organic extracts were washed with brine and dried over Na_2SO_4. Evaporation of the solvent afforded 1.04 g (92%) of 4-aminopyridine **5a** as white crystals.

3.1.12. General procedure for the synthesis of 1*H*-pyrazolo[4,3-*c*]pyridines 7a–c. A solution of $NaNO_2$ (0.38 g, 5.5 mmol) in 0.7 mL of water was added dropwise over a period of 10 min to an ice cooled solution of 4-aminopyridines **5a–c** (5 mmol) in 4.2 mL of 50% H_2SO_4. During the addition of the $NaNO_2$ solution, the reaction mixture was vigorously stirred and the temperature was maintained at 0–5°C. The resulting clear solution was added dropwise over a period of 30 min to vigorously stirred 20% aqueous sodium acetate (80 mL), cooled to 0–5°C. After the addition, the reaction mixture was allowed to warm at room temperature and stirred for 1 h. The resulting yellow–orange suspension was extracted with ethyl acetate. The combined organic extracts were washed with $NaHCO_3$, brine, and dried over Na_2SO_4. Evaporation of the solvent gave an orange solid which on sublimation in vacuo (180–200°C, 10 mmHg) afforded pyrazolopyridines **7a–c** as pale yellow crystals. Recrystallisation gave analytical samples of **7a–c** as white crystals.

3.1.13. 6-(Trifluoromethyl)-1*H*-pyrazolo[4,3-*c*]pyridine (7a). 64%. Mp 238–239°C (*i*-PrOH–toluene, 1:1); IR (KBr) 3300–2700, 1630, 1505 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.07 (s, 1H), 8.51 (s, 1H), 9.28 (s, 1H), 14.02 (brs, 1H). ^{13}C NMR (DMSO-d_6) δ 103.72 (q, J=3 Hz, *C*H=CCF$_3$), 121.68 (C_{quat}), 122.63 (q, J=273 Hz, CF_3), 134.42 (CH=N–NH), 141.11 (q, J=33 Hz, *C*CF$_3$), 142.17 (C–NH), 145.95 (CH=N). EIMS (70 eV) *m/z* (rel. int.) 187 (M^+, 100), 168 (12), 137 (11), 118 (33), 94 (3), 91 (12), 81 (6), 75 (4), 69 (10), 66 (6), 64 (25), 63 (13), 62 (10), 52 (17), 51 (4), 40 (7), 39 (7). Anal. Calcd for $C_7H_4F_3N_3$: C, 44.93; H, 2.15. Found: C, 45.08; H, 2.26.

3.1.14. 4-Methyl-6-(trifluoromethyl)-1*H*-pyrazolo[4,3-*c*]-pyridine (7b). 77%. Mp 181–183°C (toluene); IR (KBr) 3300–2600, 1620, 1605, 1510 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.83 (s, 3H), 7.86 (s, 1H), 8.52 (s, 1H), 13.91 (brs, 1H). ^{13}C NMR (DMSO-d_6) δ 21.98 (CH_3), 101.50 (*C*H=CCF$_3$), 121.00 (C_{quat}), 122.62 (q, J=273 Hz, CF_3), 134.27 (CH=N–NH), 140.81 (q, J=33 Hz, *C*CF$_3$), 142.08 (C–NH), 155.12 (CH$_3$–*C*=N). EIMS (70 eV) *m/z* (rel. int.) 201 (M^+, 100), 182 (10), 181 (18), 180 (5), 173 (2), 162 (14), 161 (8), 154 (28), 135 (3), 131 (5), 127 (11), 105 (10), 91 (5), 81 (7), 78 (7), 77 (7), 75 (5), 69 (10), 66 (7), 62 (6), 52 (12), 51 (12), 50 (7), 39 (10). Anal. Calcd for $C_8H_6F_3N_3$: C, 47.77; H, 3.01. Found: C, 47.89; H, 3.19.

3.1.15. 3-Methyl-6-(trifluoromethyl)-1*H*-pyrazolo[4,3-*c*]-pyridine (7c). 40%. Mp 274–276°C (ethyl acetate); IR (KBr) 3300–2600, 1630, 1495 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.64 (s, 3H), 7.96 (s, 1H), 9.22 (s, 1H), 13.58 (br s, 1H). ^{13}C NMR (DMSO-d_6) δ 11.76 (CH_3), 103.24 (q, J=3 Hz, *C*H=CCF$_3$), 120.85 (C_{quat}), 122.62 (q, J=273 Hz, CF_3), 141.16 (q, J=33 Hz, *C*CF$_3$), 142.91 (CH$_3$–*C*=N–NH and C–NH), 145.20 (CH=N). EIMS (70 eV) *m/z* (rel. int.) 201 (M^+, 100), 200 (79), 182 (9), 174 (4), 173 (11), 154 (3), 150 (3), 147 (2), 132 (4), 91 (4), 78 (4), 77 (4), 75 (7), 69 (8), 66 (4), 64 (9), 52 (9), 51 (8), 50 (6), 42 (8), 39 (4). Anal. Calcd for $C_8H_6F_3N_3$: C, 47.77; H, 3.01. Found: C, 47.92; H, 3.17.

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