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SYNTHESIS AND FUNCTIONALISATION OF PYRIDO[1,2-A]BENZIMIDAZOLE AMINO DERIVATIVES

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Reduced intramolecular heterocyclisation, acylation, S_EAr reaction, pyrido[1,2-a]benzimidazole, N-(2-nitroaryl)pyridinium chloride

Abstract. *We have developed a simple method to produce amino derivatives of pyrido[1,2-a]benzimidazole. Also we proposed the possible ways of their further implementation. In addition, we studied the reaction patterns of the nitration of substituted pyrido[1,2-a]benzimidazoles.*

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Introduction

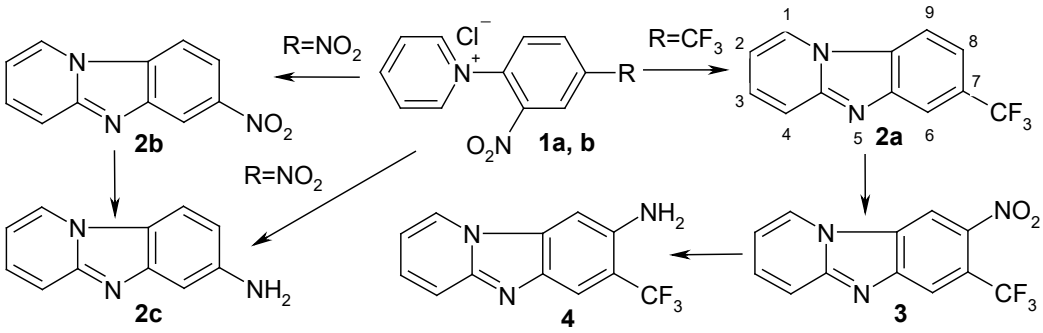
Pyrido[1,2-*a*]benzimidazole (**PBI**) derivatives belong to a privileged class of heterocyclic compounds because of their useful properties. They exhibit various types of biological activity [1-7], have an intense luminescence [8-10] and complexing ability [11]. As a result, these compounds are used in important areas such as the development of new drugs [1-7] and efficient fluorescent dyes [8-10], molecular genetic research [12] and chemosensors [13-15].

The high demand for **PBI** derivatives, especially new ones, raises the problem of having reliable methods for their synthesis. Therefore, this study describes an efficient way of synthesising **PBI** containing an amino group and some of the possible ways of their functional explore.

Main body

We used N-[2-nitro-4-(trifluoromethyl)phenyl]- (**1a**) and N-(2,4-dinitrophenyl)pyridinium chlorides (**1b**) as substrates for the pyrido[1,2-a]benzimidazole cycle formation, which can be easily obtained from pyridine and *ortho*-nitro-halogenarenes [16].

The synthesis of **PBI** amino derivatives was conducted according to the following scheme:



The first step, namely the reductive intramolecular cyclisation reaction, is a well-established process that results from the addition of four electrons by the substrate [17-19]. We conducted the reduction of pyridinium chlorides (**1a, b**) at 40 °C under the condition of *i*-PrOH and 4% HCl for 0.1 h using 2 equivalents of $SnCl_2$ as reducing agent. The reaction products 7-trifluoro- (**2a**) and 7-nitropyrido[1,2-a]benzimidazole (**2b**) were obtained with 98 and 94% yield, respectively.

The structure of the compounds **2a** and **2b** was proved by ^{1}H- and ^{13}C NMR spectroscopy and high-resolution mass spectrometry. Fig. 1 shows the ^{1}H NMR-spectrum of heterocycle **2b.** Four protons of the pyridine ring and three protons of the benzene ring appeared in the spectrum. The H^1 heterocyclic signal released in the faintest part of the spectrum. The most screened of all the protons were H^2, which had the form of a triplet. The proton signals of the benzene ring containing the strong electron acceptor substituent were shifted to the weakly polar spectrum and had values of 8.64 ppm. (H^6), 8.50 ppm. (H^9), 8.20 ppm. (H^8).

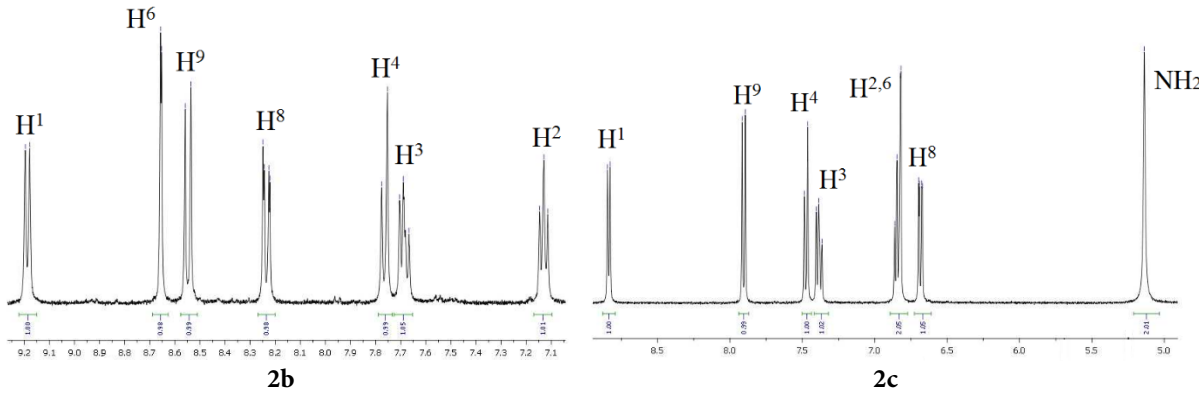


Fig. 1. Fragments of the ^{1}H NMR spectra of 7-nitropyrido[1,2-a]benzimidazole **(2b)** and pyrido[1,2-a]benzimidazole-7-amine **(2c)** (Bruker DRX400, DMSO-*d*6, 303 K)

Nitro compound **2b** was further reduced in an acidic aqueous-alcoholic medium. $SnCl_2$ and $TiCl_3$ were used as reducing agents. A higher yield (95%) of pyrido[1,2-a]benzimidazole-7-amine (**2c**) was obtained using titanium (III) chloride. The total yield of the two-stage **2c** synthesis method was 89%. On the ^{1}H NMR spectrum of this compound seven aromatic and metaromatic proton signals were present, shifted as compared to 7-nitropyrido[1,2-a]benzimidazole to the strongly polar spectrum but with similar multipletting. In addition, a broadened singlet from the amino group bound to the C-7 atom of the heterocycle was released at 5.10 ppm.

We investigate the possibility of efficiently producing **2c** in a single stage. It was difficult to conduct the several chemical processes simultaneously: reductive cyclisation involving the *ortho*-nitro group and the complete reduction of the *para*-nitro group. This could lead to the

formation of by-products such as the complete reduction of the *ortho*-nitro group. It might not be cyclised, but could result in the formation of N-(2,4-diaminophenyl)pyridinium chloride.

We realised that the simultaneous addition of a solution of 5 eq $SnCl_2$ into 4% HCl to an alcoholic solution of **1b** at 40 °C resulted in the formation of a multicomponent mixture of substances. The yield of isolated individually amino compound **2c** was 32%. The yield of **2c** increased to 78%, when we add $SnCl_2$ by two stages: first – 2 eq. to realise the reductive cyclisation; second – after 0.1 h. another 3 eq. to reduce the *para*-nitro aminogroup.

Thus, the one-stage method for the synthesis of the amino derivative **2c** was less efficient than the two-stage one.

In order to obtain the amino derivative **4**, we conducted initially the nitration reaction of 7-trifluoromethylpyrido[1,2-a]benzimidazole (**2a**) (see diagram above). There is a *meta*-orientant trifluoromethyl group in this structure. Therefore, we had to introduce the electrophilic particle at position 9. However, there proceeds the H^8 substitution resction.

We conducted the S_EAr reaction in concentrated sulphuric acid using potassium nitrate as nitrating agent at 30 °C. The yield of isolated 8-nitro-7-trifluoromethylpyrido[1,2-a]benzimidazole **(3)** in 1.5 h was 96%. The ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and X-ray structure analysis proved the product 3 structure. Its ^1H NMR spectrum contains (Fig. 2) the signals of 6 (het)aromatic protons. In the faintest part of the spectrum an H^9 signal *ortho*-positioned with respect to the nitro group emerged, shifting to a singlet form. The second aromatic proton also had the form of a singlet and was less shielded than the heteroaromatic protons $H^{2,3,4}$.

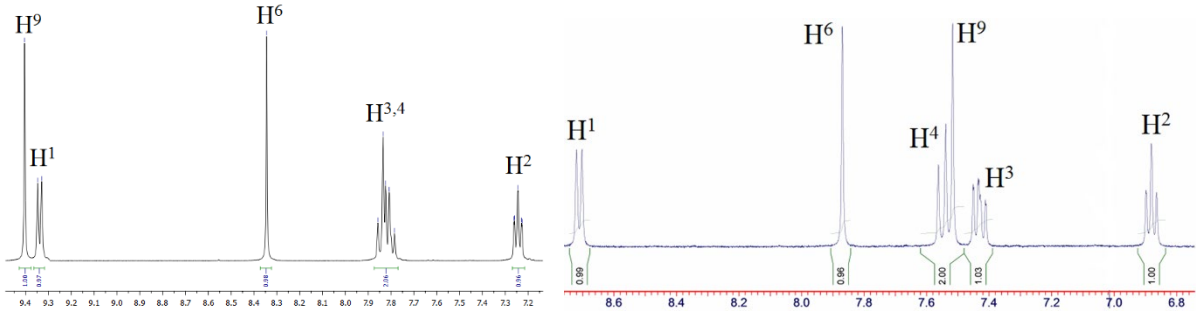
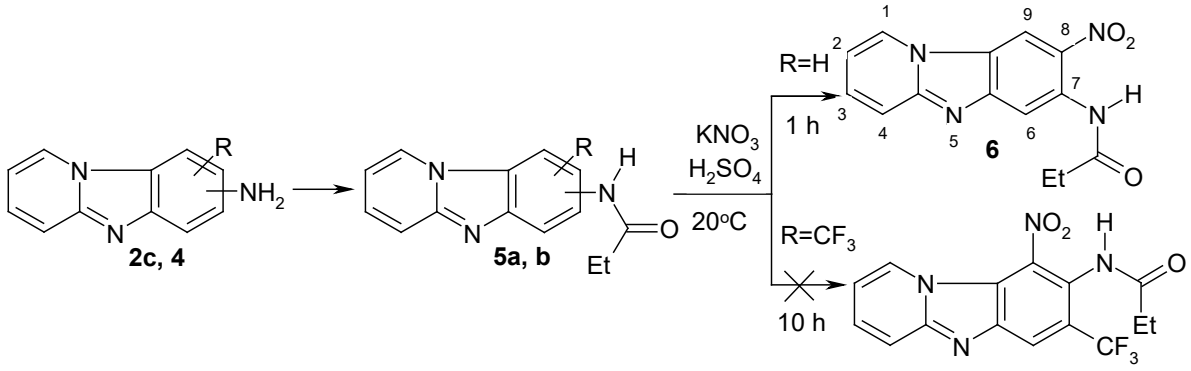


Fig. 2. Fragments of the ^1H NMR spectra of 7-trifluoromethyl-8-nitropyrido[1,2-a]benzimidazole **(3)** and 7-trifluoromethylpyrido[1,2-a]benzimidazole-8-amine **(4)** (Bruker DRX400, DMSO-*d*6, 303 K)

Next we conducted the reduction of 8-nitro-7-trifluoromethylpyrido[1,2-a]benzimidazole **(3)**. Initially the reduction reaction proceeds with tin(II) chloride. However, we obtained a mixture of substances containing a chlorinated product. The reduction process proceeds through the formation of an adduct, hydroxylamine, and $SnCl_2$ slowly reduces it to an amine. A side process, the chlorination of hydroxylamine with further rearrangement of the chlorine atom into the benzene ring, is therefore possible [20]. Therefore, we used titanium (III) chloride. The reduction of the alcohol solution of nitro derivative **3** proceeds at 60 °C for 0.1 h. The yield of 7-trifluoromethylpyrido[1,2-a]benzimidazole-8-amine **(4)** was 94%. On the ^1H NMR spectrum, the signal of the amino group protons came out in the field of 5.48 ppm and had the form of a wide singlet. Compared to the spectrum of nitro compound **3**, there was a strong shift of the H^9 proton signal to the stronger region of the spectrum (see Fig. 2). There was also a significant shift of the absorption band of another aromatic proton H^6 from 8.31 ppm to 7.88 ppm.

We use acylation and nitration reactions to functionalise amino compounds **2c** and **4**:



Heterocyclic amine **2c** reacted with propionic anhydride much easier than amino compound **4**. The yield of the reaction N-(pyrido[1,2-a]benzimidazole-7-yl)propionamide **(5a)** at room temperature only in 1 hour was 96%. We conduct the acylation process at 100 °C for 2 hours to obtain N-(7-trifluoromethylpyrido[1,2-a]benzimidazol-8-yl)propionamide **(5b)**; its yield was 79%.

The ^{1}H NMR spectrum of propionamide **5b** is shown on Fig. 3. The amino group proton signal was absent. A NH-group proton signal was detected in the weak-field region of the spectrum at 9.65 ppm and aliphatic proton peaks were clearly visible in the strong-field region of the spectrum at 2.3 and 1.1 ppm.

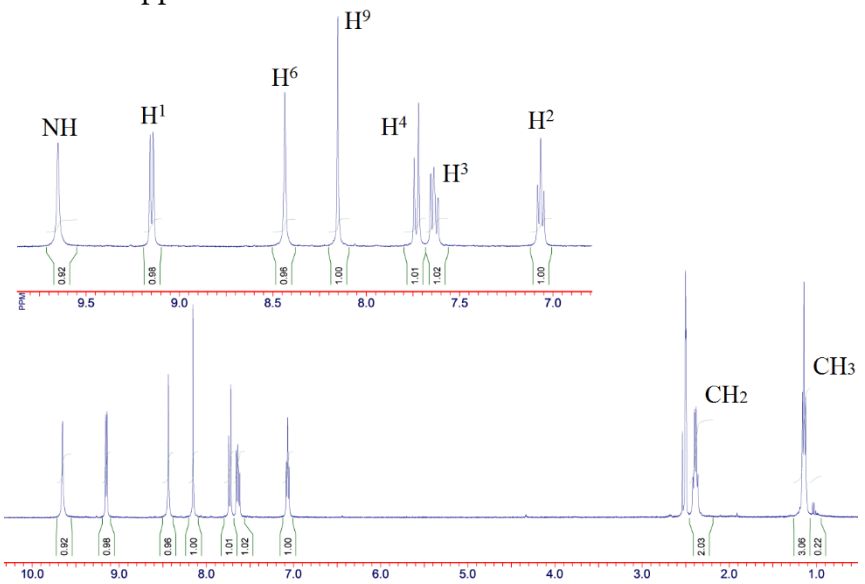


Fig. 3. ^{1}H NMR spectrum of N-(7-trifluoromethylpyrido[1,2-a]benzimidazol-8-yl)propionamide **(5b)** (Bruker DRX400, DMSO-d_6, 303 K)

The acylated amino derivatives of pyrido[1,2-a]benzimidazole **5a,b** were further functionalized by electrophilic aromatic substitution.

We conducted the nitration reaction **5a** for 1 h at 20 °C, using KNO_3/H_2SO_4 as the nitrating mixture. The implementation of the nitro group of the two possible *ortho*-positions to the acylated amino group was realised in the 8th. The yield of N-(8-nitropyrido[1,2-a]benzimidazole-7-yl)propionamide **(6)** was 92%.

When nitrating **5b** it was assumed that the attack of the electrophilic particle would also take place at the *ortho*-position to the acylated amino group. However, the S_EAr reaction product could not be obtained. Increasing the process time to 10 h did not help the reaction.

According to the study, we can conclude:

- the electronic nature of the substituent at the 7th position of the heterocycle does not affect the orientation of the S_EAr reaction;

- the 9th position of the pyrido[1,2-a]benzimidazoles is strongly deactivated. Even with a consistent orientation of the substituents and the presence of a strong electron-donor group in the *ortho*-position, no electrophilic substitution product can be obtained;

- we found the efficient methods for the synthesis and functionalization of pyrido[1,2-a]benzimidazole amino derivatives. These compounds can be used to develop new drugs based on them.

Experimental part

We determined the melting points by apparatus PolyTherm A at a heating rate of 3 °C/min and did not correct the conditions. We recorded NMR spectra for DMSO-d6 solutions on a Bruker DRX-400. The remaining solvent proton signals in ^{1}H NMR (δ 2.50 ppm) were the reference for the chemical shift counts. The recording of the mass spectra conducted by a FINNIGAN MAT INCOS 50, the electron flux energy was 70 eV.

We added 0.0075 mol of tin(II) chloride dissolved in 10 ml of 4% hydrochloric acid to a solution of 0.0036 mol of N-(2-nitro-4-R-phenyl)pyridinium chloride **(1a,b)** in 10 ml isopropyl alcohol and 3 ml water. The reaction was conducted at 40 °C for 0.1 h. At the end of the synthesis we cooled down and alkalised the reaction mixture to pH = 7-8 with an aqueous ammonia solution. Then we extracted the resulting precipitate with chloroform. After distillation of the chloroform we obtained substances **2a,b**.

7-trifluoromethylpyrido[1,2-a]benzimidazole (2a)

Yield is 98%. Melting point is 233–235 °C. ^{1}H NMR spectrum (DMSO-d_6) δ, ppm: 7.09 t (1H, H^2, J = 6.7 Hz), 7.66 t (1H, H^3, J = 8.0 Hz), 7.68 d (1H, H^9, J = 8.0 Hz), 7.75 d (1H, H^4, J = 9.0 Hz), 8.16 d (1H, H^6, J = 1.5 Hz), 8.53 dd (1H, H^8, J = 2 Hz, J = 8 Hz), 9.15 d (1H, H^1, J = 6.8 Hz). Spectrum ^{13}C NMR ^{1}H (DMSO-d_6) δ, ppm: 111.33; 111.82; 117.31; 117.99; 125.57; 126.32; 128.20; 128.63; 130.23; 131.17; 142.75; 149.29. Found: *m/z* 237.0637 $[M+H]^+$. $C_{12}H_8F_3N_2^+$. Calculated: M 237.0634.

7-nitropyrido[1,2-a]benzimidazole (2b)

Yield is 94%. Melting point is 280–284 °C. Spectrum ^{1}H NMR (DMSO-d_6) δ, ppm: 7.11 (t, 1H, H^2, J = 7 Hz); 7.67 (t, 1H, H^3, J = 7.5 Hz); 7.78 (d, 1H, H^4, J = 9.0 Hz); 8.20 (dd, 1H, H^8, J = 8.5 Hz, J = 2.0 Hz); 8.50 (d, 1H, H^9, J = 8.5 Hz); 8.64 (d, 1H, H^6, J = 1.5 Hz); 9.13 (d, 1H, H^1, J = 7.0 Hz). Spectrum ^{13}C NMR (DMSO-d_6) δ, ppm: 112.4, 113.4, 115.5, 115.8, 118.1, 128.1, 132.4, 133.3, 144.2, 146.6, 151.5. Found: *m/z* 214.0611 $[M+H]^+$. $C_{11}H_8N_3O_2$. Calculated: *m/z* 214.0617.

Methodology for the synthesis of 8-nitro-7-trifluoromethylpyrido[1,2-a]benzimidazole (3)

We slowly dropped 0.0055 mol KNO_3 in 15 ml H_2SO_4 into the solution of 0.005 mol **2a** in 30 ml H_2SO_4 at 25 °C and stirred the resulting solution for 1.5 hours at 30 °C. Than we poured

the obtained solution into ice, neutralized with NH_4OH to pH = 7-8, filtered off the residue, washed it several times with water, and dried it.

Yield is 96%. Melting point is 225-228 °C. Spectrum ^{1}H NMR (DMSO-d_6) δ, ppm: 7.23 (td, 1H, H^2, *J* = 6.6, *J* = 1.4 Hz); 7.80 dd (1H, H^3, *J* = 9.2, *J* =6.5, *J* =1.2 Hz); 7.83 dt (1H, H^4, *J* = 9.2, *J* =1.2 Hz); 8.31 c (1H, H^6, *J* = 7.2); 9.32 dt (1H, H^1, *J* = 6.8, *J* =1.1 Hz); 9.38 c (1H, H^9, *J* = 8.45). Spectrum ^{13}C NMR (DMSO-d_6) δ, ppm: 152.1 (C^{4a}), 145.3 (C^{5a}), 139.5 (C^8), 133.6 (C^3), 129.2 (C^{9a}), 128.4 (C^1), 122.8 (kv, CF_3, *J* 272.5 Hz), 119.4 (kv, C^7, *J* 33.0 Hz), 118.7 (kv, C^6, *J* 6.0 Hz), 117.4 (C^4), 112.8 (C^2), 112.7 (C^9). Found: *m/z* 282.0485 $[M+H]^+$. $C_{12}H_7F_3N_3O_2$ Calculated: *m/z* 282.0492.

Methodology for the synthesis of compounds 2c and 4

We added 24 mL (0.028 mol) of a 15% solution of titanium (III) chloride at 10% hydrochloric acid to a solution of 0.0035 mol **2b** or **3** at 125 ml isopropyl alcohol. Then we stirred the mixture for 0.1 h at 60 °C. After that we cooled the reaction mixture, adjusted the medium to pH=7-8 with a 25% aqueous ammonia solution. We extracted the precipitate with several portions of hot chloroform and distilled off the solvent.

pyrido[1,2-a]benzimidazole-7-amine (2c)

Yield is 95%. Melting point is 178–182 °C. Spectrum ^{1}H NMR (DMSO-d_6) δ, ppm: 5.10 c (2H, NH_2, *J* = 6.7 Hz); 6.87-6.91 m (1H, H^2, *J* = 7.4 Hz); 7.44 m (1H, H^3, *J* = 6.72 Hz); 6.7 d (1H, H^8, *J* = 6.8 Hz); 7.52 s (1H, H^9, *J* = 9.15 Hz); 7.56 d (1H, H^4, *J* = 9.3 Hz); 7.88 s (1H, H^6, *J* = 8.51 Hz); 8.72 d (1H, H^1, *J* = 6.9 Hz). Spectrum ^{13}C NMR (DMSO-d_6) δ, ppm: 100.9, 110.1, 111.6, 112.4, 116.5, 121.7, 126.8, 129.1, 146.5, 148.1, 148.3. Found: *m/z* 184.0868 $[M+H]^+$. $C_{11}H_{10}N_3$ Calculated: *m/z* 184.0875.

7-trifluoromethylpyrido[1,2-a]benzimidazole-8-amine (4)

Yield is 98%. Melting point 233–235 °C. Spectrum ^{1}H NMR (DMSO-d_6) δ, ppm: 5.40 s (2H, NH_2, *J* = 6.8 Hz); 6.87-6.91 m (1H, H^2, *J* = 7.4 Hz); 7.44 m (1H, H^3, *J* = 6.72 Hz); 7.52 s (1H, H^9, *J* = 9.15 Hz); 7.56 d (1H, H^4, *J* = 9.3 Hz); 7.88 s (1H, H^6, *J* = 8.51 Hz); 8.72 d (1H, H^1, *J* = 6.9 Hz). Spectrum ^{13}C NMR (DMSO-d_6) δ, ppm: 97.0, 110.2, 112.8 kv (*J* 6.0 Hz), 117.0 kv (*J* 33.0 Hz), 124.1 kv (CF_3, *J* 272 Hz), 126.2, 126.7, 129.5, 132.1, 135.3, 140.9, 147.8 Found: *m/z* 252.0743 $[M+H]^+$. $C_{12}H_9F_3N_3$ Calculated: *m/z* 252.0749.

Methodology for the synthesis of compounds 5a,b

We added 0.003 mol of propionic anhydride to a solution of 0.0025 mol **2c** or **4** in 5 mL of DMFA. We stirred the reaction mixture at 20 °C for 1 h for synthesis **5a** and 2 h at 100 °C for synthesis **5b**. We cooled the solution to room temperature and then added 50 ml of water while stirring. We filtered out the precipitate under vacuum and dried it.

N-(pyrido[1,2-a]benzimidazole-7-yl)propionamide (5a)

Yield is 96%. Melting point is 189–193 °C. Spectrum ^{1}H NMR (DMSO-d_6) δ, ppm: 1.12 t (3H, CH_3, *J* = 7.7 Hz); 2.36 kv (2H, CH_2, *J* = 7.5 Hz); 7.06 t (1H, H^2, *J*= 6.7 Hz); 7.62 t (1H, H^3, *J* = 9.0 Hz); 6.7 d (1H, H^8, *J* = 6.8 Hz); 7.73 d (1H, H^4, *J* = 9.3 Hz); 8.15 s (1H, H^9, *J* = 8.3 Hz); 8.43 s (1H, H^6, *J* = 6.8 Hz); 9.14 d (1H, H^1, *J* = 6.9 Hz); 9.34 s (1H, NH, *J* = 8.3 Hz).

N-(7-trifluoromethylpyrido[1,2-a]benzimidazol-8-yl)propionamide (5b)

Yield is 79%. Melting point is 241–245 °C. Spectrum ^{1}H NMR (DMSO-d_6) δ, ppm: 1.14 t (3H, CH_3, *J* = 7.5 Hz); 2.39 kv (2H, CH_2, *J* = 7.6 Hz); 7.06 t (1H, H^2, *J* = 6.7 Hz); 7.62 t (1H, H^3,

J = 9.0 Hz); 7.73 d (1H, H^4, *J* = 9.3 Hz); 8.15 s (1H, H^9, *J* = 8.3 Hz); 8.43 s (1H, H^6, *J* = 6.8 Hz); 9.14 d (1H, H^1, *J* = 6.9 Hz); 9.64 s (1H, NH, *J* = 8.4 Hz).

Methodology for the synthesis of N-(8-nitropyrido[1,2-a]benzimidazol-7-yl)propionamide (6)

We slowly added a nitrating mixture of 0.0022 mol **KNO_3** in 7 ml H_2SO_4 to a solution of 0.002 mol 5a in 10 ml of concentrated sulphuric acid and stirred for 1 h at 20 °C. We poured the resulting solution into ice, then treated with an aqueous ammonia solution to pH = 7-8. We filtered out the resulting precipitate under vacuum, washed thoroughly with water, and dried.

Yield is 92%. Melting point is 207-211 °C. Spectrum ^{1}H NMR (DMSO-d_6) δ, ppm: 1.12 t (3H, CH_3, *J* = 7.7 Hz); 2.36 kv (2H, CH_2, *J* = 7.5 Hz); 7.06 t (1H, H(2), *J*= 6.7 Hz); 7.62 t (1H, H(3), *J* = 9.0 Hz); 7.73 d (1H, H(4), *J* = 9.3 Hz); 8.15 s (1H, H(9), *J* = 8.3 Hz); 8.43 s (1H, H(6), *J* = 6.8 Hz); 9.14 d (1H, H(1), *J* = 6.9 Hz); 9.34 s (1H, NH, *J* = 8.3 Hz).

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