

# New Synthetic Method for Functionally Substituted Morpholinium 1,4-Dihydropyridine-2-thiolates and Their Derivatives

V. D. Dyachenko

Taras Shevchenko National Pedagogical University, Lugansk, 91011 Ukraine  
e-mail: dvd\_lug@online.lg.ua

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**Abstract**—By condensation of aromatic aldehydes with cyanothioacetamide and enamines of 1,3-dicarbonyl compounds functionally substituted morpholinium 1,4-dihydropyridine-2-thiolates were obtained applied to the synthesis of 2-alkylsulfanyl-1,4-dihydropyridines, 1,4-dihydrothieno[2,3-*b*]-pyridines, and 2,3,4,7-tetrahydrothiazolo[3,2-*a*]pyridine.

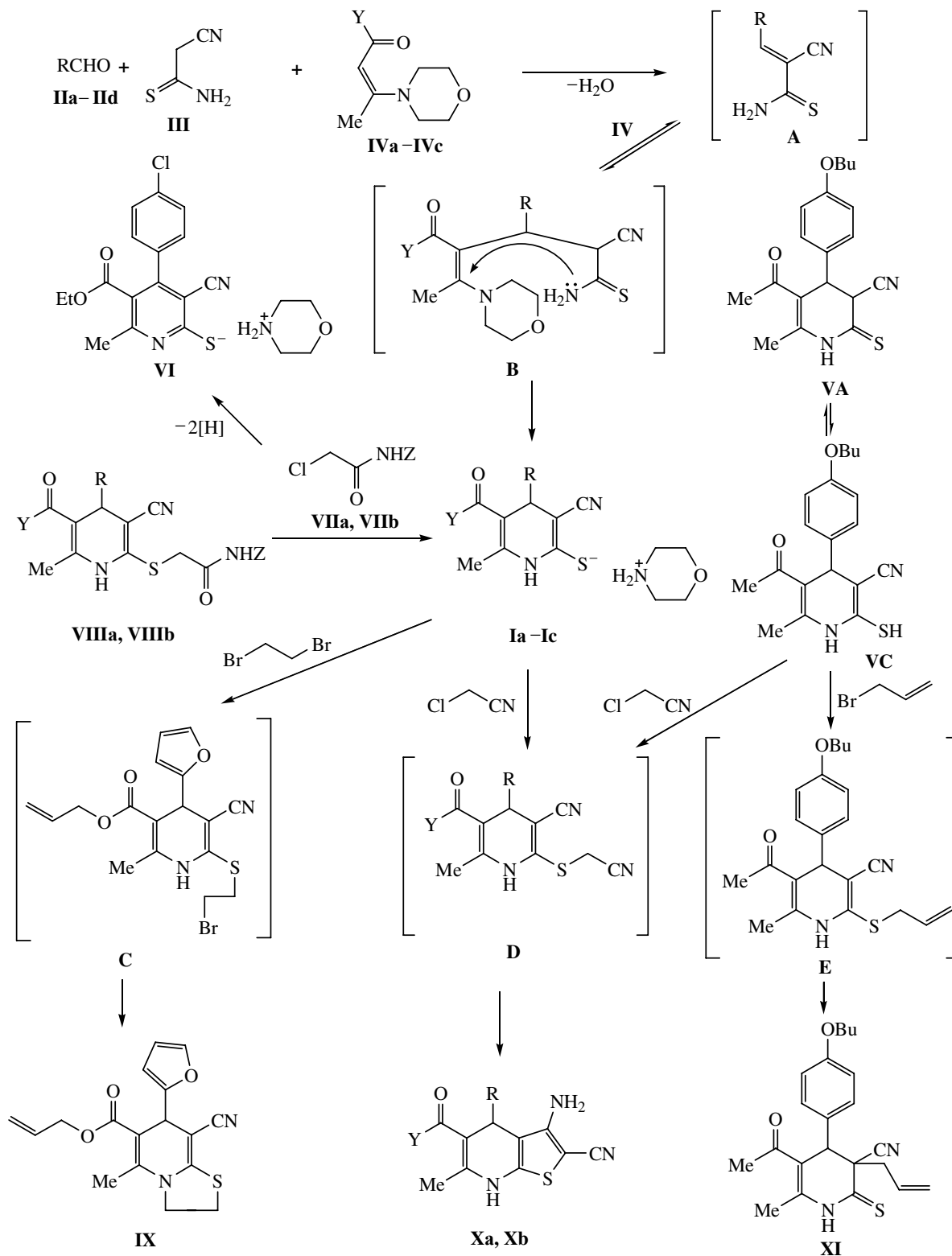
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Interest in functionalized ammonium 1,4-dihydropyridine-2-thiolates is due to opportunities of preparing therefrom biologically active compounds with antioxidant [1], hepatoprotector [2], and cardiovascular [3] qualities. The following methods of synthesis for this class compounds were developed: three-component condensation of aldehydes, cyanothioacetamide, and 1,3-dicarbonyl compounds [4], reaction of aryl(heteryl)methylenecyanothioacetamide with 1,3-dicarbonyl compounds [5], and reaction of substituted ethyl acrylates with cyanothioacetamide [6].

In extension of our studies on the chemistry of partially hydrogenated pyridine-2-chalcogenones [7] we developed a new synthetic procedure for morpholinium 4-aryl(heteryl)-6-methyl-3-cyano-1,4-dihydropyridine-2-thiolates **Ia–Ic** involving a three-component condensation of aromatic aldehydes **IIa–IIc**, cyanothioacetamide (**III**), and enamines of 1,3-dicarbonyl compounds **IVa–IVc** in ethanol at 20°C in the presence of morpholine. The reaction pathway is likely to start with the formation of aryl(heteryl)methylenecyanothioacetamides **A** resulting from condensation of aldehydes **IIa–IIc** with cyanothioacetamide (**III**) by Knoevenagel reaction. Then follows the alkylation of alkenes **A** with enamines of 1,3-dicarbonyl compounds **IVa–IVc** by Stork reaction type [8]. Adducts **B** thus formed undergo an intramolecular transamination that finishes in heterocyclization into substituted morpholinium 4-aryl(heteryl)-6-methyl-3-cyano-1,4-dihydropyridine-2-thiolates **Ia–Ic**.

The structure of salts **Ia–Ic** was confirmed by spectral findings. In the IR spectra characteristic absorption bands were observed of the stretching vibrations of a conjugated cyano group and a carbonyl group at 2180–2194 and 1684–1695 cm<sup>-1</sup> respectively. <sup>1</sup>H NMR spectra of compounds **Ia–Ic** alongside the characteristic signals of the substituents and of the morpholinium cation contained proton signals from the 1,4-dihydropyridine ring as singlets at δ 4.21–4.42 (C<sup>4</sup>H) and 8.01–8.31 (N<sup>1</sup>H) ppm in agreement with the data of [7, 9].

Involving in this condensation 4-butoxybenzaldehyde (**IIc**) resulted in the formation of 5-acetyl-4-(4-butoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyridine-3-carbonitrile (**V**) existing in DMSO solution as a mixture of nearly equal amounts of thionethiol prototropic tautomers **VA** and **VB** as showed <sup>1</sup>H NMR spectra. The direction of the chemical transformation of salts **Ia–Ic** and thione **V** also confirms their structure. In particular, the boiling in ethanol of compound **Ia** results in the aromatization of the 1,4-dihydropyridine ring, apparently by air oxygen, and in the formation of morpholinium 6-methyl-4-(4-chlorophenyl)-3-cyano-5-ethoxycarbonylpyridine-2-thiolate (**VI**). Alkylation of salts **Ib** and **Ic** in DMF with compounds **VIIa** and **VIIb** gives the corresponding thioethers **VIIIa** and **VIIIb**. At the same time the alkylation of salt **Ic** with 1,2-dibromoethane did not stop at the formation of the corresponding thioether **C**, but an intramolecular alkylation of a nitrogen from the dihydropyridine ring with the bromoethyl moiety occurred providing allyl-5-methyl-



**I**, R = 4-ClC<sub>6</sub>H<sub>4</sub>, Y = EtO (a), R = 4-HOC<sub>6</sub>H<sub>4</sub>, Y = Me (b), R = 2-furyl, Y = CH<sub>2</sub>=CHCH<sub>2</sub>O (c); **II**, R = 4-ClC<sub>6</sub>H<sub>4</sub> (a), 4-HOC<sub>6</sub>H<sub>4</sub> (b), 2-furyl (c), 4-BuOC<sub>6</sub>H<sub>4</sub> (d); **IV**, Y = EtO (a), Me (b), CH<sub>2</sub>=CHCH<sub>2</sub>O (c); **VII**, Z = H (a), 2-thiazolyl (b); **VIII**, R = 4-HOC<sub>6</sub>H<sub>4</sub>, Y = Me, Z = H (a), R = 2-furyl, Y = CH<sub>2</sub>=CHCH<sub>2</sub>O, Z = 2-thiazolyl (b); **X**, R = 2-furyl, Y = CH<sub>2</sub>=CHCH<sub>2</sub>O (a), R = 4-BuOC<sub>6</sub>H<sub>4</sub>, Y = Me (b).

7-(2-furyl)-8-cyano-2,3,4,7-tetrahydrothiazolo[3,2-*a*]pyridine-6-carboxylate (**IX**). A reaction of salt **Ic** and thione **V** with  $\alpha$ -chloroacetonitrile in DMF led to the formation of substituted 4,7-dihydrothieno[2,3-*b*]pyridines **Xa** and **Xb** resulting from the intramolecular dimerization of **D** by Thorpe–Ziegler reaction [10]. Alkylation of mercaptan **V** with allyl bromide in DMF did not finish at the formation of the corresponding thioether **E** due to the ready trans-formation of the latter under the reaction conditions into 3-allyl-5-acetyl-4-(4-butoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyridine-3-carbonitrile (**XI**) originating from the regioselective [3,3]-sigmatropic rearrangement characteristic of the substituted 2-allylsulfanyl-1,4-dihydropyridine systems [11].

The spectral characteristics of compounds **V**, **VI**, **VIIIa**, **VIIIb**, and **IX–XI** confirm their structure. The special feature of the  $^1\text{H}$  NMR spectra of thioethers **VIIIa** and **VIIIb** consists in the nonequivalence of the protons in the  $\text{SCH}_2$  group giving rise to appearance of the signals as two doublets with a coupling constant  $^2J$ . This fact may be understood assuming the lack of free rotation of the alkylsulfanyl moiety around the ordinary bonds originating likely from the existence of an intramolecular hydrogen bond between the  $\text{H}^I$  atom of the dihydropyridine ring and the oxygen of the amide fragment. The presence of such a bond in the molecules of the 1,4-dihydropyridine systems can increase their stability against aromatization [12].

## EXPERIMENTAL

IR spectra were recorded on a spectrophotometer IKS-40 from mulls in mineral oil.  $^1\text{H}$  NMR spectra were registered on spectrometers Bruker WP-100SY (100 MHz) (compounds **Ib**, **Ic**, **VIIIa**, **Xb**) Gemini-200 (199.975 MHz) (compound **Ia**), Bruker AM-300 (300.13 MHz) (compound **VI**), Varian Mercury-400 (400.397 MHz) (compounds **VIIIb**, **XI**), and Bruker DRX 500 (500.13 MHz) (compounds **IX**, **Xa**) from solutions in  $\text{DMSO}-d_6$  with TMS as an internal reference. Mass spectrum of compound **VIIIb** was measured on Chromas GC/MS-Hewlett-Packard 5890/5972 instrument, column HP-5MS (70 eV) in  $\text{CH}_2\text{Cl}_2$  solution. Melting points were determined on a Koeffler heating block. The reactions progress was monitored and the purity of compounds obtained was checked by TLC on Silufol UV-254 plates, eluent acetone–hexane, 3:5, development in iodine vapor or under UV irradiation.

**Morpholinium 6-methyl-4-(4-chlorophenyl)-3-cyano-5-ethoxycarbonyl-1,4-dihydropyridine-2-**

**thiolate (Ia).** To a mixture of 1.4 g (10 mmol) of 4-chlorobenzaldehyde (**IIa**) and 1.0 g (10 mmol) of cyanothioacetamide (**III**) in 15 ml of ethanol was added at 20°C 2 drops of morpholine, and the mixture was stirred for 10 min. Therewith the initial compounds dissolved, and alkene **A** formed. Then 1.99 g (10 mmol) of ethyl acetoacetate enamine (**IVa**) was added, and the reaction mixture was stirred for 1 h and left standing for 24 h. Then the precipitate formed was filtered off, washed with ethanol and hexane. Yield 2.70 g (64%), yellow powder, mp 147–149°C. IR spectrum,  $\text{cm}^{-1}$ : 2194 ( $\text{C}\equiv\text{N}$ ), 1692 ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.10 t (3H,  $\text{MeCH}_2$ ,  $J$  7.04 Hz), 2.55 s (3H, Me), 3.07 t (4H,  $\text{CH}_2\text{NCH}_2$ ,  $J$  4.78 Hz), 3.75 t (4H,  $\text{CH}_2\text{OCH}_2$ ), 3.93 q (2H,  $\text{CH}_2$ ), 4.32 s (1H,  $\text{C}^4\text{H}$ ), 7.10 d and 7.16 d (2H each,  $\text{C}_6\text{H}_4$ ,  $J$  8.42 Hz), 8.01 br.s (1H, NH). Found, %: C 56.80; H 5.61; N 9.79.  $\text{C}_{20}\text{H}_{24}\text{ClN}_3\text{O}_3\text{S}$ . Calculated, %: C 56.93; H 5.73; N 9.96.

**Morpholinium 5-acetyl-4-(4-hydroxyphenyl)-6-methyl-3-cyano-1,4-dihydropyridine-2-thiolate (Ib)** was obtained similarly from 4-hydroxybenzaldehyde (**IIb**) and acetylacetone enamine (**IVb**). Yield 2.65 g (71%), colorless powder, mp 144–146°C. IR spectrum,  $\text{cm}^{-1}$ : 3595 (OH), 2188 ( $\text{C}\equiv\text{N}$ ), 1684 ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.92 C (3H, MeCO), 2.23 C (3H, Me), 3.06 t (4H,  $\text{CH}_2\text{NCH}_2$ ,  $J$  4.73 Hz), 3.74 t (4H,  $\text{CH}_2\text{OCH}_2$ ), 4.21 s (1H,  $\text{C}^4\text{H}$ ), 6.63 d and 6.90 d (2H each,  $\text{C}_6\text{H}_4$ ,  $J$  8.53 Hz), 8.18 br.s (1H, NH), 10.11 br.s (1H, OH). Found, %: C 60.89; H 6.02; N 11.04.  $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_3\text{S}$ . Calculated, %: C 61.10; H 6.21; N 11.25.

**Morpholinium 5-allyloxycarbonyl-6-methyl-4-(2-furyl)-3-cyano-1,4-dihydropyridine-2-thiolate (Ic)** was obtained similarly to salt **Ia** from furfural and enamine **IVc**. Yield 3.46 g (89%), red powder, mp 178–180°C (sublim. at 150°C). IR spectrum,  $\text{cm}^{-1}$ : 2180 ( $\text{C}\equiv\text{N}$ ), 1695 ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 2.20 C (3H, Me), 3.08 t (4H,  $\text{CH}_2\text{NCH}_2$ ,  $J$  4.69 Hz), 3.74 t (4H,  $\text{CH}_2\text{OCH}_2$ ), 4.42 s (1H,  $\text{C}^4\text{H}$ ), 4.48 d (2H,  $\text{CH}_2\text{O}$ ,  $J$  6.41 Hz), 5.03 d (1H,  $\text{CH}_2=$ ,  $J_{\text{trans}}$  9.44 Hz), 5.17 d (1H,  $\text{CH}_2=$ ,  $J_{\text{cis}}$  9.45 Hz), 5.78 d (1H,  $\text{C}^3\text{H}$  of furan,  $J$  2.99 Hz), 5.81 m (1H, =CH), 6.23 d.d (1H,  $\text{C}^4\text{H}$  of furan,  $J$  2.38 Hz), 7.40 d (1H,  $\text{C}^5\text{H}$  of furan,  $J$  1.20 Hz), 8.31 br.s (1H, NH). Found, %: C 58.40; H 7.78; N 10.66.  $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_4\text{S}$ . Calculated, %: C 58.59; H 7.95; N 10.79.

**5-Acetyl-4-(4-butoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyridine-3-carbonitrile (V)** was obtained similarly from 4-butoxybenzaldehyde and enamine **IVb**. Yield 2.33 g (68%), yellow powder, mp 172–174°C (EtOH). IR spectrum,  $\text{cm}^{-1}$ : 2248 ( $\text{C}\equiv\text{N}$ ),

1684 (C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.92 t (3H, MeCH<sub>2</sub>, *J* 6.11 Hz), 1.14–1.79 m (4H, 2CH<sub>2</sub>), 2.03 s (3H, MeCO), 2.33 s (3H, Me), 3.93 t (2H, OCH<sub>2</sub>, *J* 5.99 Hz), 4.31 d (0.5H, C<sup>3</sup>H, *J* 4.13 Hz), 4.46 s and 4.95 d (1H, C<sup>4</sup>H), 6.86 d and 7.07 d (2H each, C<sub>6</sub>H<sub>4</sub>, *J* 8.51 Hz), 11.99 br.s and 12.19 br.s (1H, NH). Found, %: C 66.49; H.32; N 8.14. C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S. Calculated, %: C 66.64; H.48; N 8.18.

**Morpholinium 6-methyl-4-(4-chlorophenyl)-3-cyano-5-ethoxycarbonylpyridine-2-thiolate (VI).** A suspension of 4.22 g (10 mmol) of salt **Ia** in 15 ml of ethanol was boiled for 2 h, on cooling the precipitate was filtered off and washed with acetone. Yield 3.44 g (82%), yellow crystals, mp 210–212°C (sublim. at 150°C). IR spectrum, cm<sup>-1</sup>: 2212 (C≡N), 1726 (C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.80 t (3H, MeCH<sub>2</sub>, *J* 6.90 Hz), 2.35 s (3H, Me), 3.11 t (4H, CH<sub>2</sub>NCH<sub>2</sub>, *J* 4.80 Hz), 3.76 t (4H, CH<sub>2</sub>OCH<sub>2</sub>), 3.86 q (2H, MeCH<sub>2</sub>), 7.27 d and 7.53 d (2H each, C<sub>6</sub>H<sub>4</sub>, *J* 8.70 Hz). Found, %: C 57.02; H.12; N 9.85. C<sub>20</sub>H<sub>22</sub>ClN<sub>3</sub>O<sub>3</sub>S. Calculated, %: C 57.21; H.28; N 10.00.

**5-Acetyl-4-(4-hydroxyphenyl)-2-carbamoyl-ethylsulfanyl-1,4-dihydropyridine-3-carbonitrile (VIIIa).** To a suspension of 3.73 g (10 mmol) of salt **Ib** in 15 ml of DMF was added 0.94 g (10 mmol) of  $\alpha$ -chloroacetamide, the mixture was stirred for 3 h and diluted with an equal volume of water. After 24 h the precipitate was filtered off and washed with water, ethanol, and hexane. Yield 2.44 g (71%), yellow powder, mp 189–191°C (PrOH). IR spectrum, cm<sup>-1</sup>: 3300 (NH), 2192 (C≡N), 1690 (C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.03 s (3H, MeCO), 2.28 s (3H, Me), 3.55 d and 3.81 d (1H, SCH<sub>2</sub>, <sup>2</sup>*J* 14.13 Hz), 4.51 s (1H, C<sup>4</sup>H), 6.70 d and 6.99 d (2H each, C<sub>6</sub>H<sub>4</sub>, *J* 7.99 Hz), 7.50 br.s and 7.88 br.s (1H each, NH<sub>2</sub>), 9.30 br.C (1H, NH), 10.25 br.s (1H, OH). Found, %: C 59.33; H.78; N 12.07. C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>S. Calculated, %: C.46; H.99; N 12.24.

**Allyl 6-methyl-2-(thiazol-2-ylcarbamoylmethylsulfanyl)-4-(2-furyl)-3-cyano-1,4-dihydropyridine-5-carboxylate (VIIIb)** was obtained in the same way as thioether VIIIa from salt **Ic** and compound **VIIIb**. Yield 3.49 g (79%), colorless powder, mp 209–210°C (1-BuOH). IR spectrum, cm<sup>-1</sup>: 3312 (NH), 2198 (C≡N), 1693 (C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.38 s (3H, Me), 3.84 d and 3.96 d (iO 1H, SCH<sub>2</sub>, <sup>2</sup>*J* 13.98 Hz), 4.52 m (2H, CH<sub>2</sub>O), 4.71 s (1H, C<sup>4</sup>H), 5.10 d (1H, CH<sub>2</sub>=, *J*<sub>cis</sub> 9.49 Hz), 5.18 d (1H, CH<sub>2</sub>=, *J*<sub>trans</sub> 17.33 Hz), 5.84 m (1H, =CH), 6.00 d (1H, C<sup>3</sup>H of furan, *J* 2.88 Hz), 6.21 d.d (1H, C<sup>4</sup>H of furan, *J* 2.41 Hz), 7.05 d (1H, C<sup>5</sup>H of thiazole, *J* 3.01 Hz), 7.32 d

(1H, C<sup>5</sup>H of furan, *J* 1.21 Hz), 7.44 d (1H, C<sup>4</sup>H of thiazole), 9.72 br.s (1H, NH), 12.43 br.s (1H, CONH). Mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 443 (100)[*M* + 1]<sup>+</sup>, 440 (39)[*M* – 2]<sup>+</sup>, 375 (28), 343 (15), 275 (22), 101 (14). Found, %: C 54.10; H.95; N 12.48. C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>. Calculated, %: C.28; H.10; N 12.66. *M* 442.51.

**Allyl 5-methyl-7-(2-furyl)-8-cyano-2,3,4,7-tetrahydrothiazolo[3,2-*a*]pyridine-6-carboxylate (IX)** was obtained similarly from salt **Ic** and 1,2-dibromoethane. Yield 2.75 g (84%), dark red crystals, mp 105°C (MeOH). IR spectrum, cm<sup>-1</sup>: 2200 (C≡N), 1688 (C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.45 s (3H, Me), 3.41 m (2H, NCH<sub>2</sub>), 4.19 m (2H, SCH<sub>2</sub>), 4.54 m (2H, OCH<sub>2</sub>), 4.76 s (1H, C<sup>7</sup>H), 5.15 d (1H, CH<sub>2</sub>=, *J*<sub>cis</sub> 9.31 Hz), 5.24 d (1H, CH<sub>2</sub>=, *J*<sub>trans</sub> 17.48 Hz), 5.86 m (1H, =CH), 6.06 d (1H, C<sup>3</sup>H of furan, *J* 2.81 Hz), 6.37 d.d (1H, C<sup>4</sup>H of furan, *J* 2.35 Hz), 7.51 d (1H, C<sup>5</sup>H of furan, *J* 1.18 Hz). Found, %: C 61.98; H.78; N.42. C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>S. Calculated, %: C.18; H.91; N 8.53. *M* 328.39.

**Allyl 3-amino-6-methyl-4-(2-furyl)-2-cyano-4,7-dihydrothieno[2,3-*b*]pyridine-5-carboxylate (Xa)** was obtained similarly from salt **Ic** and  $\alpha$ -chloroacetonitrile. Yield 2.35 g (69%), yellow powder, mp 204–207°C (1-BuOH), fluorescent under UV irradiation. IR spectrum, cm<sup>-1</sup>: 3295–3442 (NH<sub>2</sub>), 2194 (C≡N), 1688 (C=O), 1647 [ $\delta$ (NH<sub>2</sub>)]. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.29 s (3H, Me), 4.51 m (2H, OCH<sub>2</sub>), 5.11 d (1H, CH<sub>2</sub>=, *J*<sub>cis</sub> 9.37 Hz), 5.20 d.d (1H, C<sup>4</sup>H), 5.25 d (1H, CH<sub>2</sub>=, *J*<sub>trans</sub> 17.42 Hz), 5.79 m (1H, =CH), 6.03 br.s (2H, NH<sub>2</sub>), 6.09 d (1H, C<sup>3</sup>H of furan, *J* 2.81 Hz), 6.22 d.d (1H, C<sup>4</sup>H of furan, *J* 2.38 Hz), 7.34 d (1H, C<sup>5</sup>H of furan, *J* 1.24 Hz), 9.86 br.s (1H, NH). Found, %: C 59.70; H.35; N.18. C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>S. Calculated, %: C.81; H.43; N 12.31.

**3-Amino-5-acetyl-4-(4-butoxyphenyl)-6-methyl-4,7-dihydrothieno[2,3-*b*]pyridine-2-carbonitrile (Xb).** To a stirred solution of 3.42 g (10 mmol) of pyridinethiol **V** in 15 ml of DMF was added in succession 5.6 ml (10 mmol) of 10% water solution of KOH and 0.63 ml (10 mmol) of  $\alpha$ -chloroacetonitrile, the mixture was stirred for 3 h, diluted with equal volume of water, and left standing for 24 h. The precipitate was filtered off, washed with water, ethanol, and hexane. Yield 2.74 g (72%), yellow crystals, mp 205–207°C (AcOH–EtOH, 1:1). IR spectrum, cm<sup>-1</sup>: 3285–3449 (NH<sub>2</sub>), 2204 (C≡N), 1687 (C=O), 1649 [ $\delta$ (NH<sub>2</sub>)]. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.89 t (3H, MeCH<sub>2</sub>, *J* 7.12 Hz), 1.15–1.87 m (4H, 2CH<sub>2</sub>), 2.08 s (3H, MeCO), 2.28 s (3H, Me), 3.86 t (2H, OCH<sub>2</sub>, *J* 7.08 Hz), 5.07 s (1H, C<sup>4</sup>H), 6.28 br.s (2H, NH<sub>2</sub>), 6.77 d and 7.22 d (2H each, C<sub>6</sub>H<sub>4</sub>, *J* 8.55 Hz), 9.88 br.s (1H,

NH). Found, %: C 65.91; H.89; N.84.  $C_{21}H_{23}N_3O_2S$ . Calculated, %: C.12; H.08; N 11.01.

**3-Allyl-5-acetyl-4-(4-butoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyridine-3-carbonitrile (XI)** was obtained similarly from allyl bromide. Yield 2.60 g (68%), yellow powder, mp 151–153°C (EtOH). IR spectrum,  $cm^{-1}$ : 2255 ( $C\equiv N$ ), 1679 ( $C=O$ ).  $^1H$  NMR spectrum,  $\delta$ , ppm: 0.98 t (3H,  $\underline{Me}CH_2$ ,  $J$  7.09 Hz), 1.48 m (2H,  $CH_2$ ), 1.73 m (2H,  $CH_2$ ), 2.00 s (3H, MeCO), 2.36 s (3H, Me), 2.61 m (2H,  $\underline{CH_2}CH=$ ), 3.91 m (3H,  $C^4H$  and  $SCH_2$ ), 5.19 d (1H,  $CH_2=$ ,  $J_{trans}$  17.45 Hz), 5.36 d (1H,  $CH_2=$ ,  $J_{cis}$  9.16 Hz), 5.97 m (1H, =CH), 6.79 d and 7.08 d (2H each,  $C_6H_4$ ,  $J$  8.49 Hz), 11.94 br.C (1H, NH). Found, %: C 68.92; H.74; N.19.  $C_{22}H_{26}N_2O_2S$ . Calculated, %: C.08; H.85; N 7.32.

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