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Transformation of 4-Aryl(heteryl)-2,6-diamino-3,5-dicyano-4*H*-thiopyrans into Substituted Acrylonitriles, 1,4-Dihydropyridines, 2,3,4,7-Tetrahydrothiazolo[3,2-*a*]pyridine, and 4,7-Dihydrothieno[2,3-*b*]pyridine

V.D. Dyachenko

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

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Abstract—Cross-recyclization of 4-aryl(heteryl)-2,6-diamino-3,5-dicyano-4*H*-thiopyrans with α-bromoketones or alkyl halides formed substituted 3-aryl-2-(4-R-thiazol-2-yl)acrylonitriles, 2-alkylsulfanyl-1,4-dihydropyridines, 2,3,4,7-tetrahydrothiazolo[3,2-*a*]pyridine, and 4,7-dihydrothieno[2,3-*b*]pyridine.

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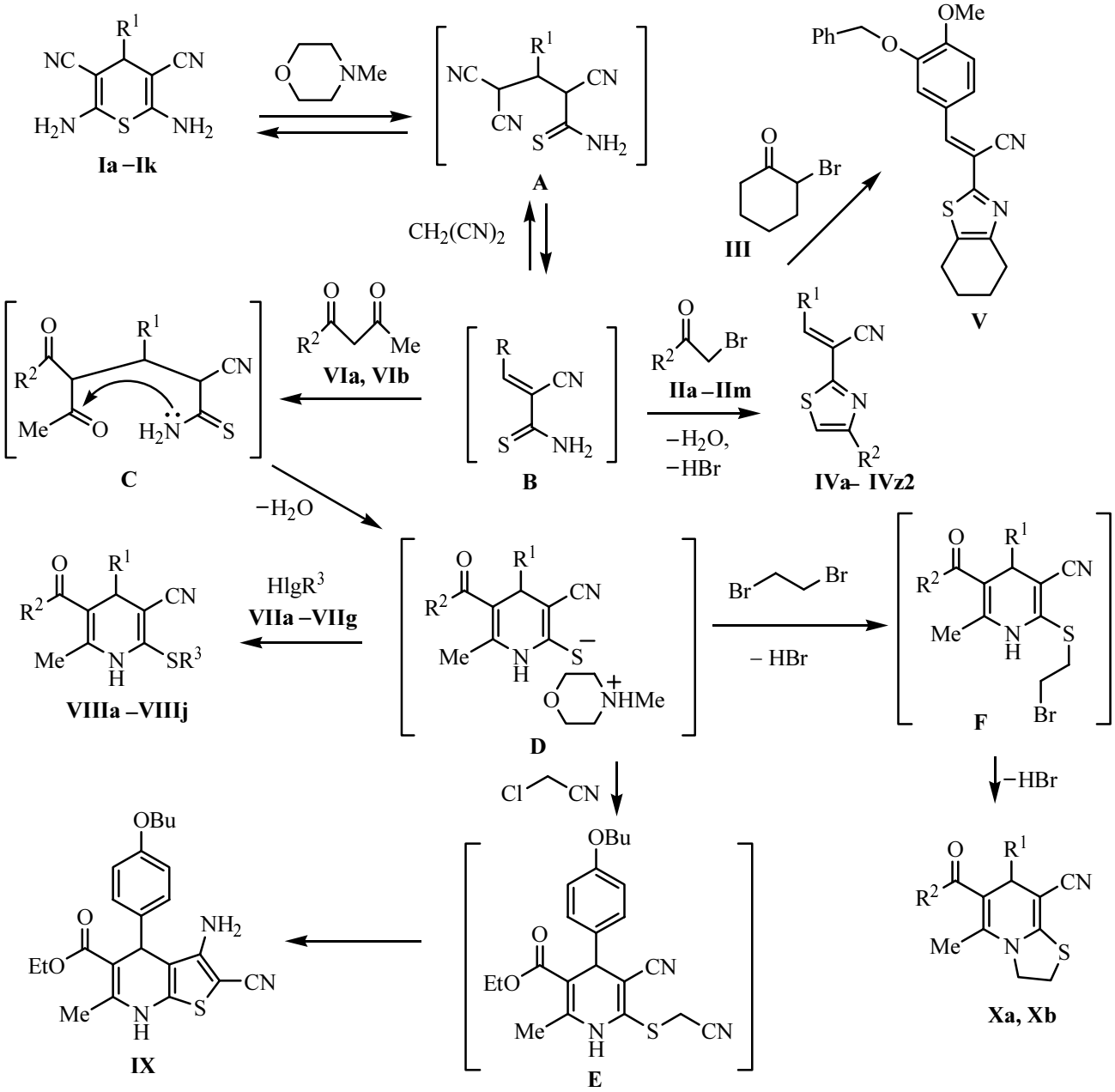
4-Aryl(alkyl,heteryl)-2,6-diamino-3,5-dicyano-4*H*-thiopyrans were formerly prepared by the Michael reaction of aryl(heteryl)methylenemalononitriles with cyanothioacetamide [1] or by three-component condensation of aldehydes, malonodinitrile, and cyanothioacetamide in ethanol in the presence of amines [2]. Initially they were erroneously regarded as heaving not cyclic but linear structure of 2,4,4-tricyano-3-aryl-3-butenoic acid thioamides [3]. Further studies concerned recyclization of the above mentioned substituted 4*H*-thiopyrans in the presence of amines resulting in formation of 6-amino-4-aryl(alkyl, heteryl)-3,5-dicyanopyridine-2(1*H*)-thiones [4], 4-aryl-6-hydroxy-3,5-dicyanopyridine-2(1*H*)-thiones [5], and N-methylmorpholinium 6-amino-4-aryl-3,5-dicyano-1,4-dihydropyridine-2-thiolates [6]. Investigations of transformations occurring with these 4*H*-thiopyrans when acetophenones or dimedone, pyridinium ylides or hydrazine were involved afforded respectively 4-aryl-6-methyl(aryl)-3-cyanopyridine-2(1*H*)-thiones or 2-amino-4-aryl-7,7-dimethyl-5-oxo-3-cyano-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyrans [7], 3-(1-pyridinio)-5-cyano-3,4-*trans*-1,2,3,4-tetrahydropyridine-6-thiolates [8] or 2,6-dihydrazino-4-phenyl-3,5-dicyanopyridine [9].

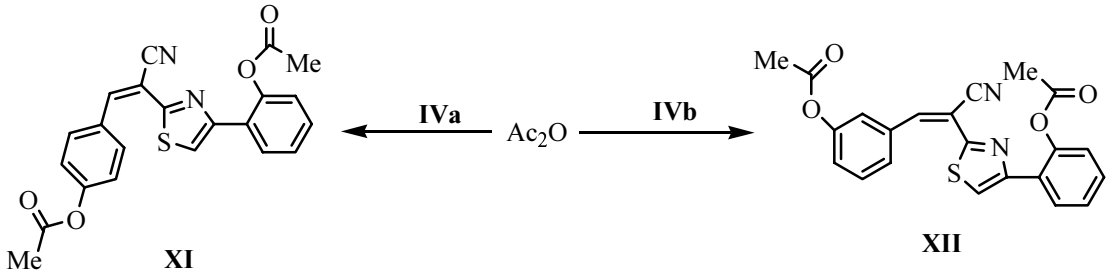
In this study new versions of 2,6-diamino-4-aryl-(heteryl)-3,5-dicyano-4*H*-thiopyran (**I**) recyclization were investigated. It was shown that their boiling in 1-butanol in the presence of an equimolar amount of *N*-methylmorpholine with α-bromocarbonyl compounds **II** or **III** resulted in formation of 3-aryl-2-(4-R-thiazol-2-yl)acrylonitriles (**IV**) and 3-(3-benzyloxy-4-methoxyphenyl)-2-(4,5-tetramethylenethiazol-2-yl)acrylonitrile (**V**) respectively. The reaction path involves apparently the opening of the thiopyran ring into intermediate **A** that further eliminates a malonodinitrile molecule giving aryl(heteryl)methylenecyanothioacetamide **B**. The latter enters into the Hantzsch reaction resulting in substituted acrylonitriles **IV** and **V**, potential biologically active compounds [10].

The introduction into the reaction with substituted 4*H*-thiopyrans **I** of 1,3-dicarbonyl compounds **VI** and alkyl halides **VII** led to derivatives of 2-alkylsulfanyl-1,4-dihydropyridines **VIII**. The formation of the latter in the course of this conversion of 4*H*-thiopyrans **I** may be understood assuming that a Michael reaction occurs involving an exchange of the methylene components [11]: 1,3-Dicarbonyl compound **VI** replaces the malonodinitrile. Thus formed new Michael adduct **C** undergoes a chemoselective heterocyclization into a substituted N-methylmorpholinium 1,4-dihydropyridine-2-thiolate **D** which further suffers regioselective alkylation by compounds **VII** furnishing organic sulfides **VIII**. The use in this reaction as alkylating agents of chloroacetonitrile or 1,2-dibromo-ethane resulted in substituted 1,4-dihydrothieno-[2,3-*b*]pyridine (**IX**) and 2,3,4,7-tetrahydrothiazolo[3,2-*a*]-pyridines (**Xa** and **Xb**) respectively.

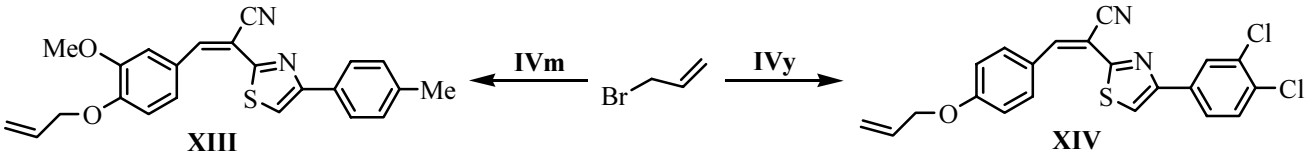


I, R^1=4-$BuOC_6H_4$ (**a**), Ph (**b**), 2-furyl (**c**), 4-FC_6H_4 (**d**), 4-HOC_6H_4 (**e**), 3-$PhCH_2O$-4-$MeOC_6H_3$ (**f**), 3-MeO-4-HOC_6H_3 (**g**), 3-$PhOC_6H_4$ (**h**), 3-HOC_6H_4 (**i**), 3-EtO-4-HOC_6H_3 (j), 3-$MeOC_6H_4$ (**k**); **II**, R^2=2-HOC_6H_4(**a**), 4-MfC_6H_4(**b**), 4-BrC_6H_4(**c**), 4-ClC_6H_4(**d**), 3-coumarinyl(**e**), 4-PhC_6H_4(**f**), Ph(g), 4-$MeOC_6H_4$(**h**), 4-BuC_6H_4(**i**), cyclopropyl(**j**), 4-FC_6H_4(**k**), 3,4-$Cl_2C_6H_3$(**l**), 3,4-Cl_2-coumarin-3-yl(**m**); **IV**, R^1=4-HOC_6H_4, R^2=2-HOC_6H_4(**a**), 3-HOC_6H_4, 2-HOC_6H_4(**b**), 3-MeO-4-HOC_6H_3, 4-MeC_6H_4(**c**), 3-EtO-4-HOC_6H_3, 4-BrC_6H_4(**d**), 3-EtO-4-HOC_6H_3, 4-ClC_6H_4(**e**), 3-EtO-4-HOC_6H_3, 4-MfC_6H_4(**f**), 3-EtO-4-HOC_6H_3, 3-coumarinyl(**g**), 3-EtO-4-HOC_6H_3, 4-PhC_6H_4(**h**), 3-EtO-4-HOC_6H_3, Ph(**i**), 3-EtO-4-HOC_6H_3, 4-$MeOC_6H_4$(**j**), 3-EtO-4-HOC_6H_3, 4-BuC_6H_4(**k**), 3-$MeOC_6H_4$, 4-MeC_6H_4(**l**), 3-MeO-4-HOC_6H_3, 4-MeC_6H_4(**m**), 3-MeO-4-HOC_6H_3, 4-BrC_6H_4(**n**), 3-MeO-4-HOC_6H_3, 4-ClC_6H_4(**o**), 3-MeO-4-HOC_6H_3, 4-$MeOC_6H_4$(**p**), 4-HOC_6H_4, 4-$MeOC_6H_4$(**q**), 3-$PhCH_2O$-4-$MeOC_6H_3$, cyclopropyl(**r**), 3-$PhCH_2O$-4-$MeOC_6H_3$, 4-FC_6H_4(**s**), 3-$PhCH_2O$-4-$MeOC_6H_3$, 3-coumarinyl(**t**), 3-HOC_6H_4, 4-MfC_6H_4(**u**), 3-HOC_6H_4, 3-coumarinyl(**v**), 3-$PhOC_6H_4$, 4-ClC_6H_4(**w**), 4-HOC_6H_4, 4-ClC_6H_4(**x**), 4-HOC_6H_4, 3,4-$Cl_2C_6H_3$(**y**), 4-HOC_6H_4, cyclopropyl (**z**), 4-HOC_6H_4, 6,8-Cl_2-coumarin-3-yl(**z1**), 4-HOC_6H_4, 4-PhC_6H_4(**z2**); **VI**, R^2=Me(**a**), EtO(**b**); **VII**, Hlg=Cl, R^3=4-$BrC_6H_4NHCOCH_2$(**a**), Cl, $PhCH_2$(**b**), Br, 2-$MeC_6H_4CH_2$(**c**), Cl, CH_2CONH_2(**d**), J, Et(**e**), Cl, $CH_2CO_2CH_2Ph$(**f**), Cl, CH(Ph)$CONH_2$(g); **VIII**, R^1=Ph(**a–c, h**), 4-FC_6H_4(**d**), I, 2-furyl(**e–g**), 4-$BuOC_6H_4$(**i, j**); R^2=EtO(**a, e–j**), Me(**b–d**); R^3=4-$BrC_6H_4NHCOCH_2$(**a, i**), $PhCH_2$(**b**), 2-$MeC_6H_4CH_2$ (**c, f**), CH_2CONH_2(**d, j**), Et(**e**), $CH_2CO_2CH_2Ph$(**g**), CH(Ph)$CONH_2$(**h**); **X**, R^1=Ph, R^2 = Me(**a**); R^1 = 2-furyl, R^2 = EtO(**b**).

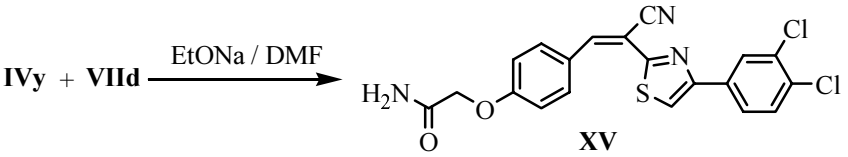
Scheme 1.



Scheme 2.



Scheme 3.



These data can support the formation of salts **D** in the course of the reaction in question involving 4*H*-thiopyrans **I** that are first alkylated into the corresponding thioethers **E** and **F**. Compound **E** further undergoes cyclization by Thorpe–Ziegler [12] into derivative **IX**, and bromides **F** suffer intramolecular alkylation to form thiazoline ring **X**. Note that compound **IX** can be applied to the synthesis of polyheterosystems [13] and to preparation of pharmaceuticals with antitumor [14], cardiovascular [15], and antibacterial action [16].

Physicochemical and spectral characteristics confirm the structure of compounds **IV, V, VIII–X**. For instance, their IR spectra contain characteristic absorption bands of the stretching vibrations of conjugated cyano group at 2187–2200 cm^{-1}. In the ^1H NMR spectra of 1,4-dihydropyridine derivatives **VIII–X** alongside the resonsnces of the substituents appear the proton signals of 1,4-dihydropyridine as singlets at δ 9.51–10.44 (H^1) and 4.32–4.98 ppm (H^4).

At short boiling in acetic anhydride compounds **IVa** and **IVb** were converted into the corresponding acetyl derivatives, esters **XI** and **XII** (Scheme 1). Note that the *o*-hydroxyphenyl group in organic compounds is essential for the antiphlogistic activity of the substances [17] thus increasing the potential practical importance both of compounds **IVa** and **IVb** and their acetyl derivatives.

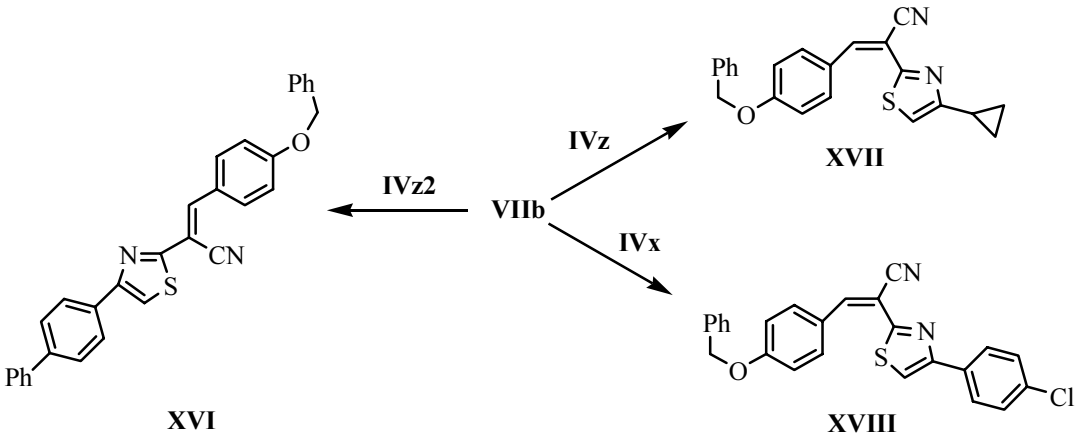
The presence of phenol substituents in acrylonitriles (**IV**) suggests a possibility to use them for preparation of new radioprotectors [18]. This stimulates the study of their chemical properties, first of all alkylation. It was established that in reaction of allyl bromide with acrylonitriles **IVm** and **IVy** in DMF in the presence of EtONa formed the corresponding allyl derivatives **XIII** and **XIV** (Scheme 2).

Under the same conditions 2-chloroacetamide **VIId** reacted with 4-hydroxyphenyl-substituted acrylonitrile **IVy** affording ether **XV** (Scheme 3).

The etherification also occurred readily with benzyl chloride **VIIb** as alkylating agent. For instance, its reaction under similar conditions with compounds **IVx, IVz**, and **IVz2** gave rise to the corresponding ethers **XVI–XVIII** (Scheme 4).

The structure of compounds obtained **XIII–XVIII** was proved by the data of physicochemical and spectral analysis. The absorption band of the stretching vibrations of the OH group lacked in their IR spectra. In the ^1H NMR spectra of compounds **XIII–XVIII** instead of the peaks of the OH group appear the proton signal of the corresponding alkyl substituents in the characteristic regions of chemical shifts. Mass spectrum of the substituted acrylonitrile **XIII** contained the peak of the molecular ion whose numerical value corresponded to

Scheme 4.



the "nitrogen rule" [19], and also a peak of ion $[M - C_3H_5]^+$.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer IKS-40 from mulls in mineral oil. ^{1}H NMR spectra were registered on spectrometers Bruker WP-100SY (100 MHz) (compounds **Ig, IVg, IVe, IVh–IVk, IVn–IVq**, **IVt, IVw–IVz, IVz2, VIIIa–VIIIj, IX, Xa, XVI, XVIII**), Gemini-200 (199.975 MHz) (compounds **IVa, IVb**, **IVf, IVr, IVs, IVu, XIV, XV, XVII**), Bruker AC 200 (200.13 MHz) (compound **IVg**), Bruker AM-300 (300.13 MHz) (compounds **Ih** and **IVv**), Varian Mercury-400 (400.397 MHz) (compounds **If, Ii–Ik, IVc**, **IVm, Xb, XI, XII**), and Bruker DR×500 (500.13 MHz) (compounds **IVl, IVz1, V, XIII**) in DMSO-d_6 using TMS as internal reference. Mass spectra were measured on a Kratos MS-890 instrument (70 eV) with a direct admission of a simple into the ion source. The melting points were estimated on a Koeffler heating block. The reaction progress was monitored and the homogeneity of compounds obtained was checked by TLC on Silufol UV-254 plates, eluent acetone–hexane, 3:5, spots visualized in iodine vapor and under UV irradiation.

4-Aryl(heteryl)-2,6-diamino-4*H*-thiopyran-3,5-dicarbonitriles Ia–Ij were prepared by procedure [20]. Compound **Ia** was characterized in [21], **Ib** and **Id**, in [20], **Ic**, in [22], **Ie**, in [23].

2,6-Diamino-4-(3-benzyloxy-4-methoxyphenyl)-4*H*-thiopyran-3,5-dicarbonitrile (If). Yield 3.44 g (88%), mp 173–174°C (from EtOH). IR spectrum, cm^{-1}: 3356, 3302, 3200 (NH_2), 2192 sh (C≡N), 1650 [δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 3.77 s (3H, Me), 4.13 (1H, C^{4}H), 5.01 s (2H, CH_2), 6.12 br.s (4H, 2NH_2), 6.78 d (1H_{arom}, *J* 7.41 Hz), 6.82 d (1H_{arom}, *J* 7.41 Hz), 6,92 s (1H_{arom}), 7.24 m (1H, Ph), 7.42 t (2H, Ph, *J* 6.91 Hz), 7.46 d (2H, Ph, *J* 7.02 Hz). Found, %: C 64.42; H 4.52; N 14.20. $C_{21}H_{18}N_4O_2S$. Calculated, %: C 64.60; H 4.65; N 14.35.

2,6-Diamino-4-(4-hydroxy-3-methoxyphenyl)-4*H*-thiopyran-3,5-dicarbonitrile (Ig). Yield 2.13 g (71%), mp 140–142°C (from EtOH). IR spectrum, cm^{-1}: 3590 (OH), 3440, 3302, 3195 (NH_2), 2176 sh (C≡N), 1640 [δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 3.73 s (3H, Me), 4.16 s (1H, C^{4}H), 6.48–6.95 m (7H, C_6H_3 and 2NH_2), 8,92 br.s (1H, OH). Found, %: C 55.80; H 3.89; N 18.58. $C_{14}H_{12}N_4O_2S$. Calculated, %: C 55.99; H 4.03; N 18.65.

2,6-Diamino-4-(3-phenoxy)-4*H*-thiopyran-3,5-dicarbonitrile (Ih). Yield 2.77 g (80%), mp 196–198°C (from EtOH). IR spectrum, cm^{-1}: 3455, 3333, 3202 (NH_2), 2185 sh (C≡N), 1648 [δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 4.32 s (1H, C^{4}H), 6.99 br.s (4H, 2NH_2), 7.07 s (1H_{arom}), 7.12–7.58 m (8H_{arom}). Found, %: C 65.71; H 3.90; N 16.14. $C_{19}H_{14}N_4OS$. Calculated, %: C 65.88; H 4.07; N 16.17.

2,6-Diamino-4-(3-hydroxyphenyl)-4*H*-thiopyran-3,5-dicarbonitrile (Ii). Yield 1.84 g (68%), mp 187–189°C (from EtOH). IR spectrum, cm^{-1}: 3590 (OH), 3436, 3312, 3198 (NH_2), 2191 sh (C≡N), 1637 [δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 4.13 s (1H, C^{4}H), 6.64 br.s (4H, 2NH_2), 6.22 m (3H_{arom}), 7.04 t (1H_{arom}, *J* 7.14 Hz), 9.14 br.s (1H, OH). Found, %: C 57.60; H 3.58; N 20.66. $C_{13}H_{10}N_4OS$. Calculated, %: C 57.76; H 3.73; N 20.73.

2,6-Diamino-4-(4-hydroxy-3-ethoxyphenyl)-4*H*-thiopyran-3,5-dicarbonitrile (Ij). Yield 2.20 g (70%), mp 156–158°C (from EtOH). IR spectrum, cm^{-1}: 3597 (OH), 3440, 3300, 3212 (NH_2), 2188 sh (C≡N), 1642

[δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 1.32 t (3H, Me, *J* 6.17 Hz), 3.99 q (2H, CH_2), 4.14 s (1H, C^{4}H), 6.61 d (1H_{arom}, *J* 6.99 Hz), 6.74 d (1H_{arom}, *J* 6.99 Hz), 6.78 s (1H_{arom}), 6.87 br.s (4H, 2NH_2), 8.90 br.s (1H, OH). Found, %: C 57.12; H 4.28; N 17.70. $C_{15}H_{14}N_4O_2S$. Calculated, %: C 57.31; H 4.49; N 17.82.

2,6-Diamino-4-(3-methoxyphenyl)-4*H*-thiopyran-3,5-dicarbonitrile (Ik). Yield 1.99 g (70%), mp 173–175°C (from EtOH). IR spectrum, cm^{-1}: 3410, 3311, 3199 (NH_2), 2187 sh (C≡N), 1639 [δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 3.74 s (3H, Me), 4.24 s (1H, C^{4}H), 6.76 s (1H), 6.82 t (2H_{arom}, *J* 7.02 Hz), 6.97 br.s (4H, 2NH_2), 7.55 t (1H_{arom}, *J* 7.00 Hz). Found, %: C 58.97; H 4.10; N 19.62. $C_{14}H_{12}N_4OS$. Calculated, %: C 59.14; H 4.25; N 19.70.

3-Aryl-2-(4-*R*-thiazol-2-yl)acrylonitriles IVa–IVz2. A mixture of 10 mmol of thiopyran **I**, 10 mmol of α-bromoketone **II**, and 1.1 ml (10 mmol) of *N*-methylmorpholine in 20 ml of 1-butanol was boliled at reflux for 3 h and then left standing for 48 h. The separated precipitate was filtered off, washed with 1-butanol and heptane, and recrystallized from 1-butanol. Compounds **IVx**, **IVy**, and **IVz2** were identical in melting points, chromatographic characteristics, and IR spectra to those previously obtained by Hantzsch method [23]. Yield of these compounds was: **IVx**, 62%; **IVy**, 71%; **IVz2**, 65%.

3-(4-Hydroxyphenyl)-2-[4-(2-hydroxyphenyl)-thiazol-2-yl]acrylonitrile (IVa). Yield 2.24 g (70%), mp 215–218°C. IR spectrum, cm^{-1}: 3590 (OH), 2215 (C≡N). ^{1}H NMR spectrum, δ, ppm: 6.89 m (4H_{arom}), 7.12 m (1H_{arom}), 7.94 d and 8.13 d (2H each, C_6H_4, *J* 8.60 Hz), 8.08 s (1H, C^{3}H=), 10.28 br.s and 10.46 br.s (1H each, 2OH). Mass spectrum, *m/z* (I_{rel}, %): 322(4)[*M*+2]$^+$, 321(22)[*M*+1]$^+$, 320(100) [*M*]$^+$, 303(14), 294(28), 287(6), 121(37), 89(8), 77(11). Found,%: C 67.29; H 3.55; N 8.61. $C_{18}H_{12}N_2O_2S$. Calculated,%: C 67.48; H 3.78; N 8.74.

3-(3-Hydroxyphenyl)-2-[4-(2-hydroxyphenyl)-thiazol-2-yl]acrylonitrile (IVb). Yield 2.11g (66%), mp 194–195°C. IR spectrum, cm^{-1}: 3587 (OH), 2222 (C≡N). ^{1}H NMR spectrum, δ, ppm: 6.84–6.96 m (3H_{arom}), 7.15 t (1H_{arom}, *J* 7.74 Hz), 7.26–7.40 m (2H, H_{arom}), 7.48 s (1H, H$^5_{thiazole}$), 8.09 m (2H_{arom}), 8.20 s (1H, C^{3}H=), 9.68 br.s and 10.40 br.s (1H each, 2OH). Mass spectrum of compound, *m/z* (I_{rel}, %): [*M*]$^+$ lacking, 322(2)[*M*+2]$^+$, 321(13)[*M*+1]$^+$, 319(25)[*M*–1]$^+$, 318(88)[*M*–2]$^+$, 317(100)[*M*–3]$^+$, 303(9), 292(28), 159(12), 150(44), 140(15), 121(47), 105(19), 89(10), 78(26), 63(9), 51(12), 39(10). Found,%: C 67.33; H 3.61; N 8.64. $C_{18}H_{12}N_2O_2S$. Calculated,%: C 67.48; H 3.78; N 8.74.

3-(4-Hydroxy-3-methoxyphenyl)-2-[4-(4-tolyl)-thiazol-2-yl]acrylonitrile (IVc). Yield 2.58 d (74%), mp 155–156°C. IR spectrum, cm^{-1}: 3600 (OH), 2220 (C≡N). ^{1}H NMR spectrum, δ, ppm: 2.38 s (3H, Me), 3.90 c (3H, MεO), 6.90 d (1H_{arom}, *J* 8.42 Hz), 7.20 d and 7.86 d (2H each, C_6H_4, *J* 8.10 Hz), 7.46 d (1H_{arom}, *J* 8.46 Hz), 7.70 s (1H_{arom}), 7.83 s (1H, H$^5_{thiazole}$), 8.12 s (1H, C^{3}H=), 9.84 br.s (1H, OH). Found,%: C 68.81; H 4.49; N 7.85. $C_{20}H_{16}N_2O_2S$. Calculated,%: C 68.95; H 4.63; N 8.04.

2-[4-(4-Bromophenyl)thiazol-2-yl]-3-(4-hydroxy-3-ethoxyphenyl)acrylonitrile (IVd). Yield 3.46 g (81%), mp 196–197°C. IR spectrum, cm^{-1}: 3588 (OH), 2224 (C≡N). ^{1}H NMR spectrum, δ, ppm: 1.34 t (3H, Mε, *J* 6.19 Hz), 4.09 q (2H, CH_2), 6.97 d (1H_{arom}, *J* 7.12 Hz), 7.67 m (4H_{arom}), 7.97 d (2H_{arom}, *J* 7.02 Hz), 8.18 s (1H, H$^5_{thiazole}$), 8.25 s (1H, C^{3}H=), 10.14 br.s (1H, OH). Found,%: C 56.09; H 3.42; N 6.39. $C_{20}H_{15}BrN_2O_2S$. Calculated,%: C 56.22; H 3.54; N 6.56.

3-(4-Hydroxy-3-ethoxyphenyl)-2-[4-(4-chlorophenyl)thiazol-2-yl]acrylonitrile (IVe). Yield 2.87 g (75%), mp 180–181°C. IR spectrum, cm^{-1}: 3590, 3223 (OH). ^{1}H NMR spectrum, δ, ppm: 1.38 t (3H, Me, *J* 6.47 Hz), 4.10 q (2H, CH_2), 6.97 d (1H_{arom}, *J* 7.13 Hz), 7.49 d and 8.02 d (2H each, C_6H_4, *J* 6.99 Hz), 7.69 m (2H_{arom}), 8.18 s (1H, H$^5_{thiazole}$), 8.23 s (1H, C^{3}H=), 10.11 br.s (1H, OH). Found,%: C 62.58; H 3.71; N 7.17. $C_{20}H_{15}ClN_2O_2S$. Calculated,%: C 62.74; H 3.95; N 7.32.

3-(4-Hydroxy-3-ethoxyphenyl)-2-[4-(4-tolyl)-thiazol-2-yl]acrylonitrile (IVf). Yield 2.50 g (69%), mp 159–160°C. IR spectrum, cm^{-1}: 3595 (OH), 2219 (C≡N). ^{1}H NMR spectrum, δ, ppm: 1.47 t (3H, $CH_2C\underline{H}_3$, *J* 6.68 Hz), 2.39 s (3H, Me), 4.13 q (2H, CH_2), 6.92 d (1H_{arom}, *J* 8.48 Hz), 7.22 d (2H_{arom}, *J* 8.00 Hz), 7.46 d (1H_{arom}, *J* 8.36 Hz), 7.69 s (1H_{arom}), 7.80 s (1H, H$^5_{thiazole}$), 7.87 d (2H_{arom}, *J* 8.00 Hz), 8.11 s (1H, C^{3}H=), 9.78 br.s (1H, OH). Found,%: C 69.42; H 4.88; N 7.60. $C_{21}H_{18}N_2O_2S$. Calculated,%: C 69.59; H 5.00; N 7.73.

3-(4-Hydroxy-3-ethoxyphenyl)-2-[4-(3-coumarinyl)thiazol-2-yl]acrylonitrile (IVg). Yield 3.62 g (87%), mp 186–188°C. IR spectrum, cm^{-1}: 3590 (OH), 2222 (C≡N), 1718 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.48 t (3H, Mε, *J* 6.33 Hz), 4.14 q (2H, CH_2), 6.93 d (1H_{arom}, *J* 7.01 Hz), 7.32–7.68 m (4H_{arom}), 7.70 s (1H_{arom}), 7.85 d (1H_{arom}, *J* 6.84 Hz), 8.19 s (1H, H$^5_{thiazole}$), 8.42 s (1H, C^{3}H=), 8.86 s (1H, H$^4_{coumarin}$), 9.91 br.s (1H, OH). Found,%: C 66.18; H 3.69; N 6.59. $C_{23}H_{16}N_2O_4S$. Calculated,%: C 66.34; H 3.87; N 6.73.

2-[4-(4-Biphenyl)-thiazol-2-yl]3-(4-hydroxy-3-ethoxyphenyl)acrylonitrile (IVh). Yield 2.89 g (68%),

mp 199–201°C. IR spectrum, cm^{-1}: 3584 (OH), 2226 (C≡N). ^{1}H NMR spectrum, δ, ppm: 1.40 t (3H, Me, *J* 6.44 Hz), 4.11q (2H, CH_2), 6.48 d (1H$_{arom}$, *J* 8.11 Hz), 7.35–7.59 m (5H$_{arom}$), 7.64–7.83 m (4H$_{arom}$), 8.05 d (2H$_{arom}$, *J* 7.19 Hz), 8.11 c (1H, H^5$_{thiazole}$), 8.23 s (1H, C^{3}H=), 10.16 br.s (1H, OH). Found,%: C 73.70; H 4.61; N 6.52. $C_{26}H_{20}N_2O_2S$. Calculated,%: C 73.56; H 4.75; N 6.60.

3-(4-Hydroxy-3-ethoxyphenyl)-2-(4-phenylthiazol-2-yl)acrylonitrile (IVi). Yield 2.26 g (65%), mp 140–142°C. IR spectrum, cm^{-1}: 3587 (OH), 2220 (C≡N). ^{1}H NMR spectrum, δ, ppm: 1.40 t (3H, Me, *J* 7.14 Hz), 4.11 q (2H, CH_2), 6.98 d (1H$_{arom}$, *J* 7.16 Hz), 7.42–7.65 m (4H$_{arom}$), 7.79 s (1H$_{arom}$), 7.91–8.15 m (3H$_{arom}$), 8.20 s (1H, C^{3}H=), 10.14 br.s (1H, OH). Found,%: C 68.81; H 4.48; N 7.87. $C_{20}H_{16}N_2O_2S$. Calculated,%: C 68.95; H 4.63; N 8.04.

3-(4-Hydroxy-3-ethoxyphenyl)-2-[4-(4-methoxyphenyl)thiazol-2-yl]acrylonitrile (IVj). Yield 2.35 g (62%), mp 165–166°C. IR spectrum, cm^{-1}: 3595 (OH), 2217 (C≡N). ^{1}H NMR spectrum, δ, ppm: 1.39 t (3H, Me, *J* 6.98 Hz), 3.81 s (3H, MeO), 4.10 q (2H, CH_2), 6.90 d (1H$_{arom}$, *J* 7.07 Hz), 7.09 d (2H$_{arom}$, *J* 7.00 Hz), 7.58 d (1H$_{arom}$, *J* 7.06 Hz), 7.71 c (1H$_{arom}$), 8.02 d (2H$_{arom}$, *J* 7.00 Hz), 8.11 c (1H, H^5$_{thiazole}$), 8.18 s (1H, C^{3}H=), 10.12 br.s (1H, OH). Found,%: C 66.39; H 4.60; N 7.28. $C_{21}H_{18}N_2O_3S$. Calculated,%: C 66.65; H 4.79; N 7.40.

2-[4-(4-Butylphenyl)thiazol-2-yl]3-(4-hydroxy-3-ethoxyphenyl)acrylonitrile (IVk). Yield 2.59 g (64%), mp 116–117°C. IR spectrum, cm^{-1}: 3600 (OH), 2228 (C≡N). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, Me, *J* 6.01 Hz), 1.39 t (3H, C$\underline{H}_3$CH$_2$O, *J* 6.18 Hz), 1.48–1.70 m (4H, 2CH$_2$), 2.61 t (2H, CH$_2$, *J* 6.32 Hz), 4.10 q (2H, CH$_3$C$\underline{H}_2$O), 6.97 d (1H$_{arom}$, *J* 8.01 Hz), 7.27 d and 7.91 d (2H each, C_6H_4, *J* 8.12 Hz), 7.58 d (1H$_{arom}$, *J* 8.00 Hz), 7.73 s (1H$_{arom}$), 8.09 s (1H, H^5$_{thiazole}$), 8.14 s (1H, C^{3}H=), 10.13 (1H, OH). Found,%: C 71.04; H 6.10; N 7.14. $C_{24}H_{24}N_2O_2S$. Calculated,%: C 71.26; H 5.98; N 6.93.

3-(3-Methoxyphenyl)-2-[4-(4-tolyl)thiazol-2-yl]-acrylonitrile (IVl). Yield 2.39 g (72%), mp 87–88°C. IR spectrum, cm^{-1}: 2196 (C≡N). ^{1}H NMR spectrum, δ, ppm: 2.38 s (3H, Me), 3.85 s (3H, MeO), 7.18 d (1H$_{arom}$, *J* 7.07 Hz), 7.31 d and 7.94 d (2H each, C_6H_4, *J* 6.94 Hz), 7.50 t (1H$_{arom}$, *J* 7.00 Hz), 7.66 m (2H$_{arom}$), 8.22 s (1H, H^5$_{thiazole}$), 8.33 s (1H, C^{3}H=). Found,%: C 72.09; H 4.67; N 8.25. $C_{20}H_{16}N_2OS$. Calculated,%: C 72.26; H 4.85; N 8.43.

3-(4-Hydroxy-3-methoxyphenyl)-2-[4-(4-tolyl)-thiazol-2-yl]acrylonitrile (IVm). Yield 2.66 g (80%), mp 153–154°C. IR spectrum, cm^{-1}: 3594 (OH), 2218 (C≡N). ^{1}H NMR spectrum, δ, ppm: 2.33 s (3H, Me), 3.86 s (3H, MeO), 6.98 d (1H$_{arom}$, *J* 7.06 Hz), 7.29 d and 7.91 d (2H each, C_6H_4, *J* 7.12 Hz), 7.62 d (1H$_{arom}$, *J* 6.99 Hz), 7.73 s (1H$_{arom}$), 8.15 s (1H$_{arom}$), 8.22 s (1H, C^{3}H=), 10.22 br.s (1H, OH). Found,%: C 69.11; H 4.47; N 7.86. $C_{20}H_{16}N_2O_2S$. Calculated,%: C 68.95; H 4.63; N 8.04.

2-[4-(4-Bromophenyl)thiazol-2-yl]-3-(4-hydroxy-3-methoxyphenyl)acrylonitrile (IVn). Yield 3.10 g (75%), mp 179–180°C. IR spectrum, cm^{-1}: 3593 (OH), 2222 (C≡N). ^{1}H NMR spectrum, δ, ppm: 3.86 s (3H, Mε), 6.96 d (1H$_{arom}$, *J* 7.19 Hz), 7.52–7.81 m (4H$_{arom}$), 7.98 d (2H$_{arom}$, *J* 8.21 Hz), 8.20 s (1H, H^5$_{thiazole}$), 8.29 s (1H, C^{3}H=), 10.24 br.s (1H, OH). Found,%: C 55.09; H 2.98; N 6.58. $C_{19}H_{13}BrN_2O_2S$. Calculated,%: C 55.22; H 3.17; N 6.78.

3-(4-Hydroxy-3-methoxyphenyl)-2-[4-(4-chlorophenyl)thiazol-2-yl]acrylonitrile (IVo). Yield 2.25 g (61%), mp 87–88°C. IR spectrum, cm^{-1}: 3602 (OH), 2220 (Ca"N). ^{1}H NMR spectrum, δ, ppm: 3.86 s (3H, Me), 6.95 d (1H$_{arom}$, *J* 7.14 Hz), 7.57 d and 8.03 d (2H each, C_6H_4, *J* 8.13 Hz), 7.65 m (2H$_{arom}$), 8.19 s (1H, H^5$_{thiazole}$), 8.22 s (1H, C^{3}H=), 10.24 br.s (1H, OH). Found,%: C 61.69; H 3.42; N 7.47. $C_{19}H_{13}ClN_2O_2S$. Calculated,%: C 61.87; H 3.55; N 7.60.

3-(4-Hydroxy-3-methoxyphenyl)-2-[4-(4-methoxyphenyl)thiazol-2-yl]acrylonitrile (IVp). Yield 2.44 g (67%), mp 146–148°C. IR spectrum, cm^{-1}: 3588 (OH), 2224 (C≡N). ^{1}H NMR spectrum, δ, ppm: 3.81 s and 3.86 s (3H each, 2Me), 6.90 d (1H$_{arom}$, *J* 7.04 Hz), 7.00 d and 7.95 d (2H each, C_6H_4, *J* 8.13 Hz), 7.60 d (1H$_{arom}$, *J* 7.03 Hz), 7.77 s (1H$_{arom}$), 8.02 s (1H, H^5$_{thiazole}$), 8.19 s (1H, C^{3}H=), 10.19 br.s (1H, OH). Found,%: C 66.14; H 4.25; N 7.48. $C_{20}H_{16}N_2O_3S$. Calculated,%: C 65.92; H 4.43; N 7.69.

3-(4-Hydroxyphenyl)-2-[4-(4-methoxyphenyl)-thiazol-2-yl]acrylonitrile (IVq). Yield 2.47 g (74%), mp 257–259°C (sublimation at 200°C). IR spectrum, cm^{-1}: 3596 (OH), 2225 (C≡N). ^{1}H NMR spectrum, δ, ppm: 3.89 s (3H, Me), 6.95 d and 7.97 d (2H each, 4-MeOC_6H_4, *J* 8.12 Hz), 7.17 d and 8.04 d (2H each, 4-HOC_6H_4, *J* 8.93 Hz), 8.15 s (1H, H^5$_{thiazole}$), 8.29 s (1H, C^{3}H=), 10.53 br.s (1H, OH). Found,%: C 68.07; H 4.12; N 8.17. $C_{19}H_{14}N_2O_2S$. Calculated,%: C 68.25; H 4.22; N 8.38.

3-(3-Benxyloxy-4-methoxyphenyl)-2-(4-cyclopropylthiazol-2-yl)acrylonitrile (IVr). Yield 3.15 g (81%), mp 128–129°C. IR spectrum, cm^{-1}: 2226 (C≡N). ^{1}H NMR spectrum, δ, ppm: 0.95 d (4H, 2CH$_2$, *J* 6.68

Hz), 2.04 t (1H, $CH_{cyclopropane}$), 3.92 s (3H, Me), 5.13 s (2H, CH_2O), 7.05 d ($2H_{arom}$, *J* 8.46 Hz), 7.12 c ($1H_{arom}$), 7.21–7.58 m ($5H_{arom}$), 7.75 s (1H, $H^5_{thiazole}$), 7.98 s (1H, C^3H=). Found,%: C 70.95; H 4.98; N 7.06. $C_{23}H_{20}N_2O_2S$. Calculated,%: C 71.11; H 5.19; N 7.21.

3-(3-Benzyloxy-4-methoxyphenyl)-2-[4-(4-fluorophenyl)thiazol-2-yl]acrylonitrile (IVs). Yield 3.10 g (70%), mp 157–159°C. IR spectrum, cm^{-1}: 2224 (C≡N). ^1H NMR spectrum, δ, ppm: 3.90 s (3H, Me), 5.13 s (2H, CH_2), 7.10 d ($1H_{arom}$, *J* 8.46 Hz), 7.16 d ($2H_{arom}$, *J* 8.89 Hz), 7.31–7.49 m ($4H_{arom}$), 7.66 d ($1H_{arom}$, *J* 8.56 Hz), 7.79 s ($1H_{arom}$), 8.02 m ($3H_{arom}$), 8.08 s (1H, $H^5_{thiazole}$), 8.17 s (1H, C^3H=). Found,%: C 70.40; H 4.16; N 6.15. $C_{26}H_{19}FN_2O_2S$. Calculated,%: C 70.57; H 4.33; N 6.33.

3-(3-Benzyloxy-4-methoxyphenyl)-2-[4-(3-coumarinyl)thiazol-2-yl]acrylonitrile (IVt). Yield 3.05 g (62%), mp 225–227°C. IR spectrum, cm^{-1}: 2220 (C≡N), 1714 (C=O). ^1H NMR spectrum, δ, ppm: 3.90 s (3H, Me), 5.16 s (2H, CH_2), 7.21 d ($1H_{arom}$, *J* 8.35 Hz), 7.33–7.72 m ($10H_{arom}$), 7.81 t ($1H_{arom}$, *J* 7.06 Hz), 8.20 s (1H, $H^5_{thiazole}$), 8.44 s (1H, C^3H=), 8.78 s (1H, $H^4_{coumarin}$). Found,%: C 70.63; H 3.92; N 5.47. $C_{29}H_{20}N_2O_4S$. Calculated,%: C 70.72; H 4.09; N 5.69.

3-(3-Hydroxyphenyl)-2-[4-(4-tolyl)thiazol-2-yl]acrylonitrile (IVu). Yield 2.45 g (77%), mp 171–172°C. IR spectrum, cm^{-1}: 3590 (OH), 2223 (C≡N). ^1H NMR spectrum, δ, ppm: 2.40 s (3H, Me), 6.93 d ($1H_{arom}$, *J* 7.72 Hz), 7.21 d ($2H_{arom}$, *J* 8.10 Hz), 7.30 m ($3H_{arom}$), 7.47 s (1H, $H^5_{thiazole}$), 7.86 d ($2H_{arom}$, *J* 8.10 Hz), 7.92 s (1H, C^3H=), 9.16 br.s (1H, OH). Found,%: C 71.59; H 4.22; N 8.65. $C_{19}H_{14}N_2OS$. Calculated,%: C 71.68; H 4.43; N 8.80.

3-(3-Hydroxyphenyl)-2-[4-(3-coumarinyl)thiazol-2-yl]acrylonitrile (IVv). Yield 2.57 g (69%), mp 243–244°C. IR spectrum, cm^{-1}: 3597 (OH), 2218 (C≡N), 1704 (C=O). ^1H NMR spectrum, δ, ppm: 7.01 d ($1H_{arom}$, *J* 7.80 Hz), 7.37–7.50 m ($6H_{arom}$), 7.68 t ($1H_{arom}$, *J* 6.90 Hz), 7.95 d ($1H_{arom}$, *J* 6.90 Hz), 8.33 s (1H, C^3H=), 8.55 s (1H, $H^4_{coumarin}$), 8.88 br.s (1H, OH). Found,%: C 67.60; H 3.04; N 7.41. $C_{21}H_{12}N_2O_3S$. Calculated,%: C 67.73; H 3.25; N 7.52.

3-(3-Phenoxyphenyl)-2-[4-(4-chlorophenyl)-thiazol-2-yl]acrylonitrile (IVw). Yield 2.99 g (72%), mp 154–155°C. IR spectrum, cm^{-1}: 2225 (C≡N). ^1H NMR spectrum, δ, ppm: 7.13–7.14 m ($7H_{arom}$), 7.56 d and 8.03 d (2H each, 4-ClC_6H_4, *J* 8.56 Hz), 7.80 m ($3H_{arom}$), 8.32 s (1H, C^3H=). Found,%: C 69.31; H 3.49; N 6.65. $C_{24}H_{15}ClN_2OS$. Calculated,%: C 69.48; H 3.64; N 6.75.

3-(4-Hydroxyphenyl)-2-(4-cyclopropylthiazol-2-yl)acrylonitrile (IVz). Yield 2.09 g (78%), mp 159–161°C. IR spectrum, cm^{-1}: 3600 (OH), 2221 (C≡N). ^1H NMR spectrum, δ, ppm: 0.90 m (4H, $2CH_2$), 2.12 m (1H, $CH_{cyclopropane}$), 6.93 d and 7.93 d (2H each, C_6H_4, *J* 8.53 Hz), 7.36 s (1H, $H^5_{thiazole}$), 8.04 s (1H, C^3H=), 10.50 br.s (1H, OH). Found,%: C 66.97; H 4.38; N 10.26. $C_{15}H_{12}N_2OS$. Calculated,%: C 67.14; H 4.51; N 10.44.

3-(4-Hydroxyphenyl)-2-[4-(6,8-dichlorocoumarin-3-yl)thiazol-2-yl]acrylonitrile (IVz1). Yield 3.62 g (82%), mp 350°C (decomp.) (sublimation at 260°C). IR spectrum, cm^{-1}: 3585 (OH), 2222 (C≡N), 1714 (C=O). ^1H NMR spectrum, δ, ppm: 6.95 d and 7.95 d (2H each, C_6H_4, *J* 8.49 Hz), 7.86 s ($1H_{arom}$), 8.04 s ($1H_{arom}$), 8.21 s (1H, $H^5_{thiazole}$), 8.50 s (1H, C^3H=), 8.85 s (1H, $H^4_{coumarin}$), 10.42 br.s (1H, OH). Found,%: C 56.97; H 2.01; N 6.12. $C_{21}H_{10}Cl_2N_2O_3S$. Calculated,%: C 57.16; H 2.28; N 6.35.

3-(3-Benzyloxy-4-methoxyphenyl)-2-(4,5,6,7-tetrahydrobenzo[*d*]thiazol-2-yl)acrylonitrile (V) was prepared similarly to compounds **IV** using as initial reagents thiopyran **If** and α-bromocyclohexanone (**III**). Yield 2.58 g (64%), mp 131–133°C. Fluorescence was observed at UV irradiation. IR spectrum, cm^{-1}: 2219 (C≡N). ^1H NMR spectrum, δ, ppm: 1.85 m (4H, $2CH_2$), 2.75 t (2H, CH_2, *J* 7.14 Hz), 2.89 t (2H, CH_2, *J* 7.10 Hz), 3.89 s (3H, Me), 5.12 s (2H, CH_2O), 7.13 d ($1H_{arom}$, *J* 6.95 Hz), 7.32–7.49 m ($5H_{arom}$), 7.68 d ($1H_{arom}$, *J* 7.02 Hz), 7.75 s ($1H_{arom}$), 7.97 s (1H, C^3H=). Found,%: C 71.52; H 5.38; N 7.15. $C_{24}H_{22}N_2O_2S$. Calculated,%: C 71.62; H 5.51; N 6.96.

Substituted 1,4-dihydropyridine-3-carbonitriles VIIIa–VIIIj. A mixture of 10 mmol of an appropriate thiopyran **I**, CH-acid **VI**, and 1.1 ml (10 mmol) of *N*-methylmorpholine in 15ml of 1-butanol was boliled at reflux for 3 h. On cooling to the reaction mixture was added at stirring 10 mmol of an appropriate alkyl halide **VII**, and the mixture was left standing for 24 h and then it was diluted with an equal volume of water. The separated precipitate was filtered off, washed with water, ethanol, and hexane.

Ethyl 6-(4-bromophenylcarbamoylmethylsulfanyl)-2-methyl-4-phenyl-5-cyano-1,4-dihydropyridine-3-carboxylate (VIIIa). Yield 3.48 g (68%), mp 200–202°C (from 1-BuOH). IR spectrum, cm^{-1}: 3310 (NH), 2195 (C≡N), 1718 (C=O). ^1H NMR spectrum, δ, ppm: 1.80 t (3H, $C\underline{H}_3CH_2$, *J* 6.17 Hz), 2.3 s (3H, Me), 3.93 s (2H, SCH_2), 3.96 q (2H, OCH_2, *J* 6.17 Hz), 4.54 s (1H, H^4), 7.23 m (4H, C_6H_4), 7.53 s (5H, Ph), 9.77 br.s

(1H, H^1), 10.47 br.s (1H, NHCO). Found, %: C 56.12; H 4.18; N 8.01. $C_{24}H_{22}BrN_3O_3S$. Calculated, %: C 56.26; H 4.33; N 8.20.

5-Acetyl-2-benzylsulfanyl-6-methyl-4-phenyl-1,4-dihydropyridine-3-carbonitrile (VIIIb). Yield 2.24 g (62%), mp 101–103°C (from MeOH). IR spectrum, cm^{-1}: 3300 (NH), 2188 (C≡N), 1728 (C=O). ^1H NMR spectrum, δ, ppm: 2.01 s (3H, MeCO), 2.34 s (3H, Me), 4.23 s (2H, CH_2), 4.55 s (1H, H^4), 6.72–7.31 m (10H, 2Ph), 9.51 br.s (1H, NH). Found, %: C 73.19; H 5.41; N 7.60. $C_{22}H_{20}N_2OS$. Calculated, %: C 73.30; H 5.59; N 7.77.

5-Acetyl-6-methyl-2-(2-tolylmethylsulfanyl)-4-phenyl-1,4-dihydropyridine-3-carbonitrile (VIIIc). Yield 2.58 g (69%), mp 125–127°C (from 1-BuOH). IR spectrum, cm^{-1}: 3314 (NH), 2189 (C≡N), 1722 (C=O). ^1H NMR spectrum, δ, ppm: 2.02 s (3H, MeCO), 2.34 s (6H, 2Me), 4.24 s (2H, CH_2), 4.54 s (1H, H^4), 6.92–7.54 m ($9H_{arom}$), 9.55 br.s (1H, NH). Found, %: C 73.60; H 6.12; N 7.22. $C_{23}H_{22}N_2OS$. Calculated, %: C 73.77; H 5.92; N 7.48.

6-Acetyl-6-methyl-2-carbamoylmethylsulfanyl-4-(4-fluorophenyl)-1,4-dihydropyridine-3-carbonitrile (VIIId). Yield 2.59 g (75%), mp 180–182°C (from 1-BuOH). IR spectrum, cm^{-1}: 3333 (NH), 2198 (C≡N), 1723 (C=O). ^1H NMR spectrum, δ, ppm: 2.07 s (3H, MeCO), 2.31 s (3H, Me), 3.55 d and 3.81 d (1H each, SCH_2, ^2J 14.22 Hz), 4.68 s (1H, H^4), 7.01–7.34 m (4H, C_6H_4), 7.57 br.s and 7.95 br.s (1H each, NH_2), 10.40 br.s (1H, NH). Found, %: C 58.95; H 4.51; N 11.99. $C_{17}H_{16}FN_3O_2S$. Calculated, %: C 59.12; H 4.67; N 12.17.

Ethyl 2-methyl-4-(2-furyl)-5-cyano-6-ethylsulfanyl-1,4-dihydropyridine-3-carboxylate (VIIIe). Yield 2.45 g (77%), mp 103–104°C (from *i*-PrOH). IR spectrum, cm^{-1}: 3328 (NH), 2200 (C≡N), 1725 (C=O). ^1H NMR spectrum, δ, ppm: 1.09 t (3H, Me, *J* 6.22 Hz), 1.15 t (3H, Me, *J*6.18 Hz), 2.30 s (3H, C^6Me), 2.99 q (2H, SCH_2, *J* 6.24 Hz), 4.02 q (2H, OCH_2, *J* 6.19 Hz), 4.68 s (1H, H^4), 6.04 d (1H, H^3_{furan}, *J* 2.95 Hz), 6.35 d.d (1H, H^4 of furan, *J* 3.59, *J* 2.38 Hz), 7.53 d (1H, H^5_{furan}, *J* 1.20 Hz), 9.63 br.s (1H, NH). Found, %: C 60.19; H 5.58; N 8.66. $C_{16}H_{18}N_2O_3S$. Calculated, %: C 60.36; H 5.70; N 8.80.

Ethyl 2-methyl-6-(2-tolylmethylsulfanyl)-4-(2-furyl)-5-cyano-1,4-dihydropyridine-3-carboxylate (VIIIf). Yield 2.25 g (57%), mp 101–102°C (from EtOH). IR spectrum, cm^{-1}: 3322 (NH), 2194 (C≡N), 1728 (C=O). ^1H NMR spectrum, δ, ppm: 1.08 t (3H, $C\underline{H}_3CH_2$, *J*6.20 Hz), 2.30 s (3H, Me), 2.34 s (3H, Me), 3.98 s (2H, SCH_2), 4.05 q (2H, CH_2O, *J* 6.18 Hz), 4.52 s (1H, H^4), 6.12 d (1H, H^3_{furan}, *J* 2.90 Hz), 6.31 d.d (1H, H^4_{furan}, *J* 3.31, 2.40 Hz), 6.84–7.42 m (5H, H^5_{furan} and C_6H_4), 9.60 br.s (1H, NH). Found, %: C 67.15; H 5.40; N 6.88. $C_{22}H_{22}N_2O_3S$. Calculated, %: C 66.98; H 5.62; N 7.10.

Ethyl 6-benzyloxycarbinylmethylsulfanyl-2-methyl-4-(2-furyl)-5-cyano-1,4-dihydropyridine-3-carboxylate (VIIIg). Yield 3.07 g (70%), mp 84–86°C (from MeOH). IR spectrum, cm^{-1}: 3312 (NH), 2188 (C≡N), 1724 (C=O). ^1H NMR spectrum, δ, ppm: 1.17 t (3H, $C\underline{H}_3CH_2$, *J*6.16 Hz), 2.22 s (3H, Me), 3.91–4.25 m (4H, SCH_2 and $OC\underline{H}_2CH_3$), 4.59 s (1H, H^4), 5.12 s (2H, CH_2), 6.01 d (1H, H^3_{furan}, *J* 2.92 Hz), 6.32 d.d (1H, H^4_{furan}, *J* 3.72, 2.44 Hz), 7.33 s (5H, Ph), 7.51 d (1H, H^5_{furan}, *J* 1.18 Hz), 9.59 br.s (1H, NH). Found, %: C 62.81; H 4.95; N 6.17. $C_{23}H_{22}N_2O_5S$. Calculated, %: C 63.00; H 5.06; N 6.39.

Ethyl 2-methyl-6-[(1-carbamoyl-1-phenyl)-methylsulfanyl]-4-phenyl-5-cyano-1,4-dihydropyridine-3-carboxylate (VIIIh). Yield 2.51 g (58%), mp 179–181°C (from BuOH). IR spectrum, cm^{-1}: 3338 (NH), 2190 (C≡N), 1726 (C=O), 1677 (CONH). ^1H NMR spectrum, δ, ppm: 1.03 t (3H, Me, *J* 6.18 Hz), 2.28 s (3H, Me), 3.91 q (2H, CH_2, *J* 6.18 Hz), 4.32 s (1H, H^4), 5.35 s (1H, SCH), 6.96 m ($2H_{arom}$), 7.19–7.38 m ($8H_{arom}$), 7.50 br.s and 7.76 br.s (1H each, NH_2), 9.77 br.s (1H, NH). Found, %: C 66.38; H 5.22; N 9.50. $C_{24}H_{23}N_3O_3S$. Calculated, %: C 66.49; H 5.35; N 9.69.

Ethyl 6-(4-bromophenylcarbamoylmethylsulfanyl)-4-(4-butoxyphenyl)-2-methyl-5-cyano-1,4-dihydropyridine-3-carboxylate (VIIIi). Yield 4.50 g (77%), mp 194–196°C (from EtOH). IR spectrum, cm^{-1}: 3300 (NH), 2188 (C≡N), 1719 (C=O), 1667 (CONH). ^1H NMR spectrum, δ, ppm: 0.92 t (3H, Me, *J* 6.14 Hz), 1.09 t (3H, Me, *J* 6.21 Hz), 1.22–1.78 m (4H, $2CH_2$), 2.30 s (3H, Me), 3.78–4.10 m (6H, CH_2S and $2CH_2O$), 4.44 s (1H, H^4), 6.77 d and 7.04 d (2H each, C_6H_4, *J* 8.83 Hz), 7.53 s (4H, $4\text{-}BrC_6H_4$), 9.70 br.s (1H, NH), 10.44 br.s (1H, NHCO). Found, %: C 57.38; H 4.96; N 6.99. $C_{28}H_{30}BrN_3O_4S$. Calculated, %: C 57.54; H 5.17; N 7.19.

Ethyl 4-(4-butoxyphenyl)-6-carbamoylmethylsulfanyl-2-methyl-5-cyano-1,4-dihydropyridine-3-carboxylate (VIIIj). Yield 2.58 g (60%), mp 148–150°C (from EtOH). IR spectrum, cm^{-1}: 3298 (NH), 2187 (C≡N), 1717 (C=O), 1672 (CONH). ^1H NMR spectrum, δ, ppm: 0.90 t (3H, Me, *J* 6.15 Hz), 1.08 t (3H, Me, *J* 6.17 Hz), 1.22–1.80 m (4H, $2CH_2$), 2.27 s (3H, Me),

3.52 d and 3.94 d (1H each, SCH_2, ^2J 16.22), 3.95–4.11 m (4H, $2CH_2O$), 4.43 s (1H, H^4), 6.83 d and 7.06 d (2H each, C_6H_4, J 8.47 Hz), 7.59 br.s and 7.90 br.s (1H each, NH_2), 10.32 br.s (1H, NH). Found, %: C 61.40; H 6.22; N 9.59. $C_{22}H_{27}N_3O_4S$. Calculated, %: C 61.52; H 6.34; N 9.78.

Ethyl 3-amino-4-(4-butoxyphenyl)-6-methyl-2-cyano-1,4-dihydrothieno[2,3-*b*]pyridine-5-carboxylate (IX) was obtained in the same way as compounds **VIII** from thiopyran **Ia**, ethyl acetoacetate (**VIb**), and chloroacetonitrile. Yield 2.72 g (66%), mp 185–187°C (from EtOH). IR spectrum, cm^{-1}: 3410, 3312, 3195 (NH, NH_2), 2200 (C≡N), 1719 (C=O), 1644 [δ(NH_2)]. ^1H NMR spectrum, δ, ppm: 0.91 t (3H, Me, J 6.16 Hz), 1.15 t (3H, Me, J 6.17 Hz), 1.22–1.82 m (4H, $2CH_2$), 2.27 s (3H, Me), 3.79–4.12 m (4H, $2CH_2O$), 4.98 s (1H, H^4), 6.07 br.s (2H, NH_2), 6.75 d and 7.16 d (2H each, C_6H_4, J 8.88 Hz), 9.83 br.s (1H, NH). Found, %: C 64.00; H 5.94; N 10.15. $C_{22}H_{25}N_3O_3S$. Calculated, %: C 64.21; H 6.12; N 10.21.

6-Acetyl-5-methyl-7-phenyl-2,3,4,7-tetrahydrothiazolo[3,2-*a*]pyridine-8-carbonitrile (Xa) was obtained in the same way as compounds **VIII** from thiopyran **Ib**, acetylacetone (**VIa**), and 1,2-dibromoethane. Yield 2.13 g (72%), mp 182–184°C (from MeCN). IR spectrum, cm^{-1}: 2192 (C≡N), 1720 (C=O). ^1H NMR spectrum, δ, ppm: 2.03 s (3H, MeCO), 2.37 s (3H, Me), 3.36 m (2H, SCH_2), 4.17 m (2H, NCH_2), 4.72 s (1H, H^4), 7.15–7.43 m (5H, Ph). Found, %: C 68.69; H 5.25; N 9.24. $C_{17}H_{16}N_2OS$. Calculated, %: C 68.89; H 5.44; N 9.45.

Ethyl 5-methyl-7-(2-furyl)-8-cyano-2,3,4,7-tetrahydrothiazolo[3,2-*a*]pyridine-6-carboxylate (Xb) was obtained in the same way as compounds **VIII** from thiopyran **Ic**, ethyl acetoacetate (**VIb**), and 1,2-dibromoethane. Yield 1.93 g (61%), mp 110–112°C (from *i*-PrOH). IR spectrum, cm^{-1}: 2190 (C≡N), 1719 (C=O). ^1H NMR spectrum, δ, ppm: 1.19 t (3H, Me, J 6.14 Hz), 2.48 s (3H, Me), 3.39 t (2H, SCH_2, J 6.22 Hz), 4.05–4.23 m (4H, NCH_2 and OCH_2), 4.72 s (1H, H^4), 6.01 d (1H, H^3_{furan}, J 2.95 Hz), 6.28 d.d (1H, H^4_{furan}, J 3.42 J 2.38 Hz), 7.37 d (1H, H^5_{furan}, J 1.18 Hz). Found, %: C 60.61; H 4.95; N 8.70. $C_{16}H_{16}N_2O_3S$. Calculated, %: C 60.74; H 5.10; N 8.85.

3-(4-Acetoxyphenyl)-2-[4-(2-acetoxyphenyl)-thiazol-2-yl]acrylonitrile (XI). A dispersion of 4.05 g (10 mmol) of compound **IVa** in 15 ml of Ac_2O was boiled at reflux for 40 min. On cooling the reaction mixture the precipitate was filtered off and recrystallized from glacial AcOH. Yield 3.16 g (78%), mp 144–145°C. Fluorescence was observed at UV irradiation. IR spectrum, cm^{-1}: 2184 (C≡N), 1747 (C=O). ^1H NMR spectrum, δ, ppm: 2.34 s and 2.38 s (3H each, 2Me), 7.15 d ($1H_{arom}$, J 7.14 Hz), 7.28 d ($2H_{arom}$, J 7.33 Hz), 7.35–7.47 m ($2H_{arom}$), 7.89 s (1H, $H^5_{thiazole}$), 8.11 m ($3H_{arom}$), 8.25 c (1H, C^3H=). Found,%: C 65.18; H 4.15; N 7.12. $C_{22}H_{16}N_2O_4S$. Calculated,%: C 65.34; H 3.99; N 6.93.

3-(3-Acetoxyphenyl)-2-[4-(2-acetoxyphenyl)-thiazol-2-yl]acrylonitrile (XII) was prepared analogously to compound **XI** using compound **IVb** instead of nitrile **IVa**. Yield 3.74 g (85%), mp 156–157°C. IR spectrum, cm^{-1}: 2182 (C≡N), 1744 (C=O). ^1H NMR spectrum, δ, ppm: 2.16 s and 2.18 s (3H each, 2Me), 7.11 d ($2H_{arom}$, J 7.04 Hz), 7.16–7.23 m ($2H_{arom}$), 7.33 t ($1H_{arom}$, J 6.98 Hz), 7.37 s ($1H_{arom}$), 7.96 d ($1H_{arom}$, J 7.00 Hz), 8.02 d ($1H_{arom}$, J 7.12 Hz), 8.09 c (1H, $H^5_{thiazole}$), 8.17 s (1H, C^3H=). Found,%: C 65.22; H 3.94; N 6.80. $C_{22}H_{16}N_2O_4S$. Calculated,%: C 65.34; H 3.99; N 6.93.

3-(4-Allyloxy-3-methoxyphenyl)-2-[4-(4-tolyl)-thiazol-2-yl]acrylonitrile (XIII). To a stirred solution of 3.48 g (10 mmol) of nitrile **IVm** in 15ml of DMF at 20°C was added a solution of 0.23 g (10 mmol) of Na in 15 ml of anhydrous ethanol and then 0.85 ml (10 mmol) of allylbromide. The reaction mixture was stirred for 4 h, then diluted with an equal volume of water, and it was left standing for 24 h. The arising precipitate was filtered off, washed with water, ethanol, and hexane. Yield 2.56 g (66%), mp 94–95°C (from 1-BuOH). IR spectrum, cm^{-1}: 2185 (C≡N). ^1H NMR spectrum, δ, ppm: 2.39 s (3H, Me), 3.90 s (3H, MeO), 4.63 d (2H, CH_2O, J 4.76 Hz), 5.27 d and 5.44 d (1H each, CH_2=, $^3J_{cis}$ 10.10 and $^3J_{trans}$ 16.76 Hz), 6.05 m (1H, C^2H_{allyl}), 7.01 d (1H, H_{arom}, J 3.44 Hz), 7.20 d ($2H_{arom}$, J 7.36 Hz), 7.54 d ($1H_{arom}$, J 8.48 Hz), 7.72 s ($1H_{arom}$), 7.87 m ($3H_{arom}$), 8.17 s (1H, C^3H=). Mass spectrum, m/z (I_{rel}, %): 390(3)[M+2]$^+$, 389(15)[M+1]$^+$, 388(53)[M]$^+$, 387(2)[M–1]$^+$, 347(100)[M–C_3H_5]$^+$, 319(18), 303(12), 288 (10), 275 (21), 147(18), 115(13), 103(8), 91(10)[PhCH_2]$^+$, 77(8)[Ph]$^+$, 41(17)[C_3H_5]$^+$. Found,%: C 70.98; H 5.00; N 7.12. $C_{23}H_{20}N_2O_2S$. Calculated,%: C 71.11; H 5.19; N 7.21.

3-(4-Allyloxyphenyl)-2-[4-(3,4-dichlorophenyl)thiazol-2-yl]acrylonitrile (XIV) was prepared in the same way as compound **XIII** using nitrile **IVy** instead of compound **IVm**. Yield 3.06 g (74%), mp 141–142°C. IR spectrum, cm^{-1}: 2190 (C≡N). ^1H NMR spectrum, δ, ppm: 4.66 d (2H, SCH_2, J 5.24 Hz), 5.30 d and 5.44 d (1H each, CH_2=, $^3J_{cis}$ 10.52, $^3J_{trans}$ 17.26 Hz),

5.96–6.16 m (1H, =CH), 7.12 d ($2H_{arom}$, *J* 8.88 Hz), 7.66 d ($1H_{arom}$, *J* 8.42 Hz), 8.04 s ($1H_{arom}$), 8.21 m ($2H_{arom}$), 8.22 m ($2H_{arom}$), 8.35 s (1H, C^3H=). Found,%: C 60.88; H 3.22; N 6.67. $C_{21}H_{14}Cl_2N_2OS$. Calculated,%: C 61.03; H 3.41; N 6.78.

3-(4-Carbamoylmethoxy)-2-[4-(3,4-dichlorophenyl)thiazol-2-yl]acrylonitrile (XV) was prepared in the same way as compound **XIII** using nitrile **IVy** and amide **VIId**. Yield 3.49 g (81%), mp 213–214°C. IR spectrum, cm^{-1}: 2187 (C≡N), 1682 (C=O). ^1H NMR spectrum, δ, ppm: 4.53 s (2H, CH_2), 7.14 d and 8.05 d (2H each, C_6H_4, *J* 8.56 Hz), 7.36 br.s (2H, NH_2), 7.60 d ($1H_{arom}$, *J* 8.58 Hz), 7.98 c ($1H_{arom}$), 8.25 m ($3H_{arom}$ and C^3H=). Found,%: C 55.70; H 2.89; N 9.64. $C_{20}H_{13}Cl_2N_3O_2S$. Calculated,%: C 55.83; H 3.05; N 9.77.

3-(4-Benzyloxyphenyl)-2-[4-(4-biphenyl)thiazol-2-yl]acrylonitrile (XVI) was prepared in the same way as compound **XIII** using chloride **VIIb** and nitrile **IVz2**. Yield 3.72 g (79%), mp 158–159°C. IR spectrum, cm^{-1}: 2185 (C≡N). ^1H NMR spectrum, δ, ppm: 5.24 s (2H, CH_2), 7.24 d ($2H_{arom}$, *J* 8.15 Hz), 7.32–7.63 m ($8H_{arom}$), 7.69–7.75 m ($4H_{arom}$), 7.78 s (1H, $H^5_{thiazole}$), 8.05 d ($2H_{arom}$, *J* 8.19 Hz), 8.14 d ($2H_{arom}$, *J* 7.99 Hz), 8.27 s (1H, C^3H=). Found,%: C 78.95; H 4.60; N 6.13. $C_{31}H_{22}N_2OS$. Calculated,%: C 79.12; H 4.71; N 5.95.

3-(4-Benzyloxyphenyl)-2-[4-cyclopropylthiazol-2-yl]acrylonitrile (XVII) was prepared in the same way as compound **XIII** using chloride **VIIb** and nitrile **IVz**. Yield 3.19 g (89%), mp 113–115°C. IR spectrum, cm^{-1}: 2189 (C≡N). ^1H NMR spectrum, δ, ppm: 0.95 m (4H, $2CH_2$), 2.08 m (1H, $H^1_{cyclopropane}$), 5.19 s (2H, CH_2O), 7.12 d and 7.95 d (2H each, C_6H_4, *J* 8.94 Hz), 7.17 s (1H, $H^5_{thiazole}$), 7.31–7.46 m (5H, Ph), 8.02 s (1H, C^3H=). Found,%: C 73.59; H 4.88; N 8.01. $C_{22}H_{18}N_2OS$. Calculated,%: C 73.72; H 5.06; N 7.82.

3-(4-Benzyloxyphenyl)-2-[4-(4-chlorophenyl)-thiazol-2-yl]acrylonitrile (XVIII) was prepared in the same way as compound **XIII** using chloride **VIIb** and nitrile **IVx**. Yield 3.26 g (76%), mp 221–223°C. IR spectrum, cm^{-1}: 2193 (C≡N). ^1H NMR spectrum, δ, ppm: 4.28 s (2H, CH_2), 6.94 d ($2H_{arom}$, *J* 8.11 Hz), 7.51 d ($2H_{arom}$, *J* 8.72 Hz), 7.67 d ($2H_{arom}$, *J* 7.69 Hz), 7.85–8.11 m ($7H_{arom}$), 8.19 s (1H, $H^5_{thiazol}$), 8.22 s (1H, C^3H=). Found,%: C 69.84; H 3.91; N 6.39. $C_{25}H_{17}ClN_2OS$. Calculated,%: C 70.00; H 4.00; N 6.53.

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