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A New Version of Multicomponent Synthesis of 4,6-Diaryl-2-sulfanylidene-1,2-dihydropyridine-3-carbonitrile Derivatives

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Abstract—Multicomponent condensation of aromatic aldehydes with acetophenones, cyanothioacetamide, and alkylating agents has been shown to provide synthetic routes to various pyridine and thienopyridine derivatives. The structure of some of the synthesized heterocycles has been confirmed by X-ray analysis.

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In recent time, syntheses of heterocyclic compounds by multicomponent condensations have become more and more popular. Accessibility of initial reactants, simplicity of experimental procedures, high yields of the target compounds, and increasing demands of environmental safety make this approach quite attractive for the synthesis of complex molecules [1–3]. By using multicomponent reactions, we previously synthesized functionalized pyridines [4], 4-spiro-fused 1,4-dihydropyridines [5], 1,4-dihydro-1,6-naphthyridines [6], pyrido[2,3-*d*]pyrimidines [7], 5,6,7,8-tetrahydroquinolines [8], and 5,6,7,8-tetrahydroisoquinolines [9].

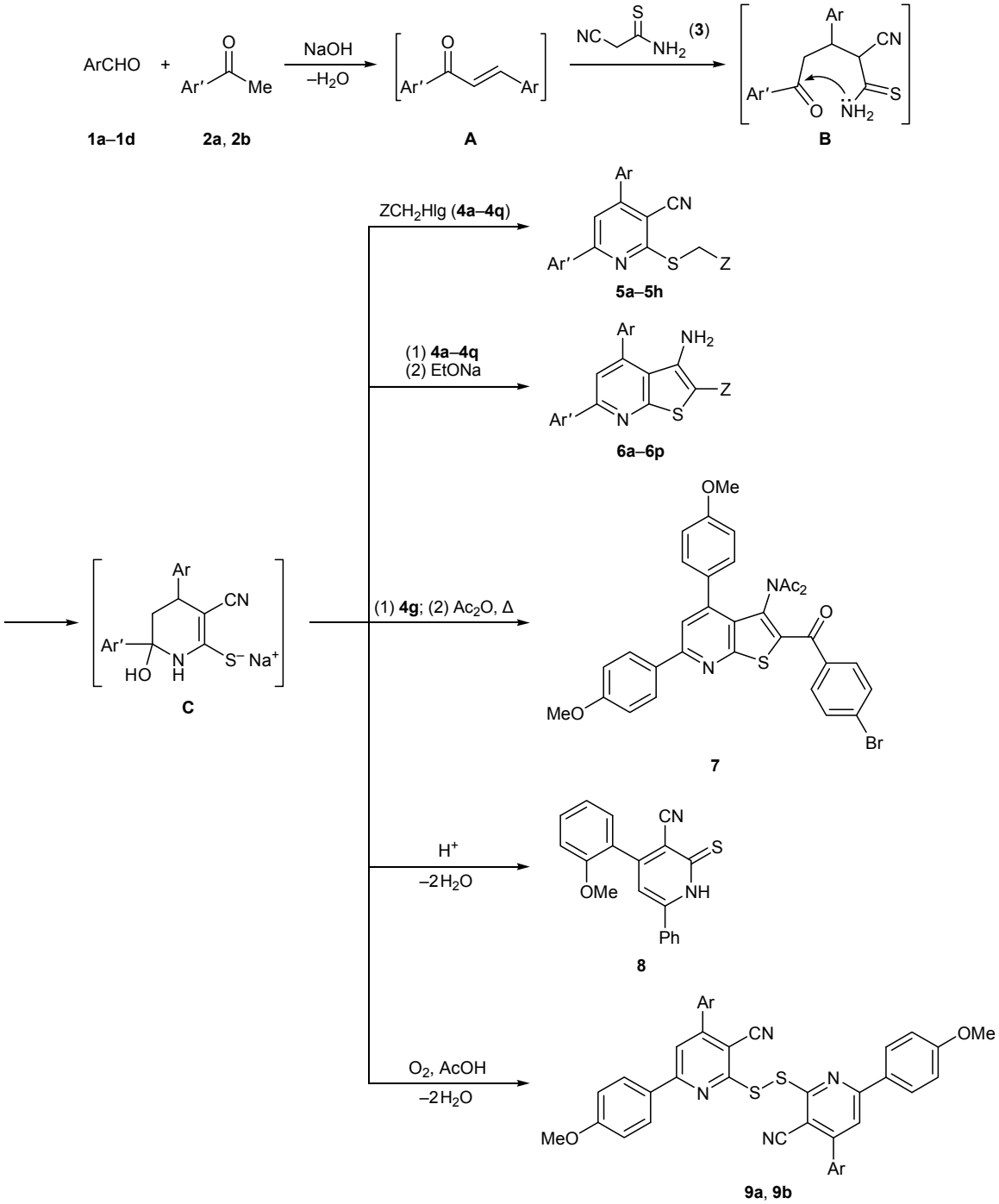
In continuation of our studies of multicomponent reactions [10–12], herein we report the multicomponent condensation of aromatic aldehydes **1a**–**1d** with acetophenones **2a** and **2b**, cyanothioacetamide (**3**), and alkylating agents **4a**–**4q**. By varying the reaction conditions and alkylating agent, we succeeded in obtaining 2-(alkylsulfanyl)-4,6-diarylpyridine-3-carbonitriles **5a**–**5h**, 3-amino-4,6-diarylthieno[2,3-*b*]pyridines **6a**–**6p** and **7**, 4-(2-methoxyphenyl)-6-phenyl-2-sulfanylidene-1,2-dihydropyridine-3-carbonitrile (**8**), and 2,2′-(disulfanediyl)bis(4,6-diarylpyridine-3-carbonitriles) **9a** and **9b** (Scheme 1). The reactions were carried out at 0°C in ethanol in the presence of alkali.

The mechanism of formation of pyridine-3-carbonitrile derivatives **5** includes initial condensation of aldehyde **1** with acetophenone **2** to give chalcone **A** which reacts with cyanothioacetamide (**3**) to form Michael adduct **B**. Intramolecular cyclization of the latter leads to substituted sodium 1,4,5,6-tetrahydropyridine-2-thiolate **C**, and its alkylation with halogen derivative **4** yields sulfide **5**. Compounds **5** can be used as intermediate products in the synthesis of antihypertensive [13–15] and antidiabetic agents [16].

Addition of sodium ethoxide to the reaction mixture catalyzed intramolecular cyclization of sulfides **5** *in situ* to produce 3-amino-4,6-diarylthieno[2,3-*b*]pyridine derivatives **6a**–**6p**. Compounds of this series can be used for the treatment of inflammatory [17] and oncological diseases [18–20]. Functionalized pyridine and thienopyridine derivatives like **5** and **6** attract interest as intermediate products for the synthesis of more complex heterocyclic systems [21–23].

Substituted thieno[2,3-*b*]pyridine **7** was synthesized by multicomponent condensation of 4-methoxybenzaldehyde (**1d**) with 4-methoxyacetophenone (**2b**), cyanothioacetamide (**3**), 4-bromobenzoyl bromide (**4g**), and acetic anhydride under analogous conditions. Obviously, in the final reaction stage the amino group in intermediate thienopyridine **6** underwent double

Scheme 1.



1, Ar = 2-$MeOC_6H_4$ (**a**), Ph (**b**), 4-$O_2NC_6H_4$ (**c**), 4-$MeOC_6H_4$ (**d**); **2**, Ar′ = Ph (**a**), 4-$MeOC_6H_4$ (**b**); **4**, Hlg = Cl, Z = $PhCH_2OC(O)$ (**a**), $H_2NC(O)$ (**b**), Ph (**c**); Hlg = Br, Z = CH_2=CH (**d**); Hlg = Cl, Z = 2-MeC_6H_4NHCO (**e**), 4-BrC_6H_4NHCO (**f**); Hlg = Br, Z = 4-BrC_6H_4CO (**g**), 4-MeC_6H_4CO (**h**); 3,4-$Cl_2C_6H_3CO$ (**i**); Hlg = Cl, Z = naphthalen-1-ylcarbamoyl (**j**), EtOC(O) (**k**), PhNHCO (**l**); Hlg = Br, Z = PhCO (**m**); Hlg = Cl, Z = $Me(CH_2)_7OC(O)$ (**n**), $Me(CH_2)_8OC(O)$ (**o**), 4-AcC_6H_4NHCO (**p**), 1,3-thiazol-2-ylcarbamoyl (**q**); **5**, Ar = Ar′ = 4-$MeOC_6H_4$, Z = $PhCH_2OC(O)$ (**a**), H_2NCO (**b**); Ar = 4-$O_2NC_6H_4$, Ar′ = Ph, Z = H_2NCO (**c**); Ar′ = Z = Ph (**d**); Ar′ = Ph, Z = CH_2=CH (**e**); Ar = Ar′ = Ph, Z = CH_2=CH (**f**); Ar = 2-$MeOC_6H_4$, Ar′ = Ph, Z = CH_2=CH (**g**), 2-MeC_6H_4NHCO (**h**); **6**, Ar = Ar′ = 4-$MeOC_6H_4$, Z = 4-BrC_6H_4NHCO (**a**); Ar = 4-$O_2NC_6H_4$, Ar′ = Ph, Z = H_2NCO (**b**); Ar = 2-$MeOC_6H_4$, Ar′ = Ph, Z = 4-BrC_6H_4CO (**c**), 4-MeC_6H_4CO (**d**), 3,4-$Cl_2C_6H_3CO$ (**e**), naphthalen-1-ylcarbamoyl (**f**), EtOC(O) (**g**), PhNHCO (**h**), $PhCH_2OC(O)$ (**i**), H_2NCO (**j**); Ar = Ar′ = Ph, Z = PhCO (**k**), $PhCH_2OC(O)$ (**l**), $Me(CH_2)_7OC(O)$ (**m**), $Me(CH_2)_8OC(O)$ (**n**), 4-AcC_6H_4NHCO (**o**); Ar = 4-$MeOC_6H_4$, Ar′ = Ph, Z = 1,3-thiazol-2-ylcarbamoyl (**p**); **9**, Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**).

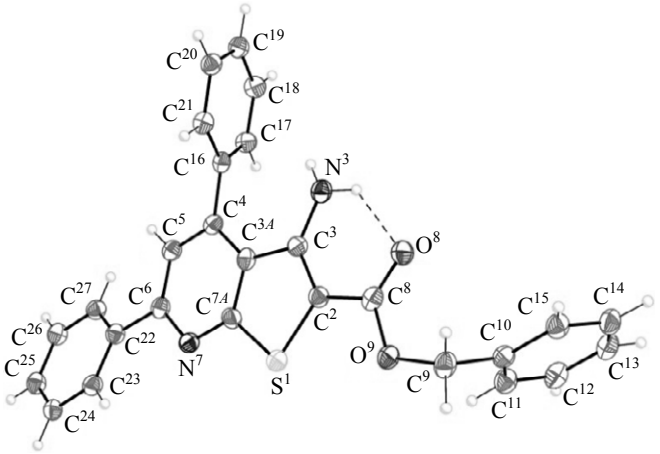


Fig. 1. Molecular structure of benzyl 3-amino-4,6-diphenylthieno[2,3-*b*]pyridine-2-carboxylate (**6l**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

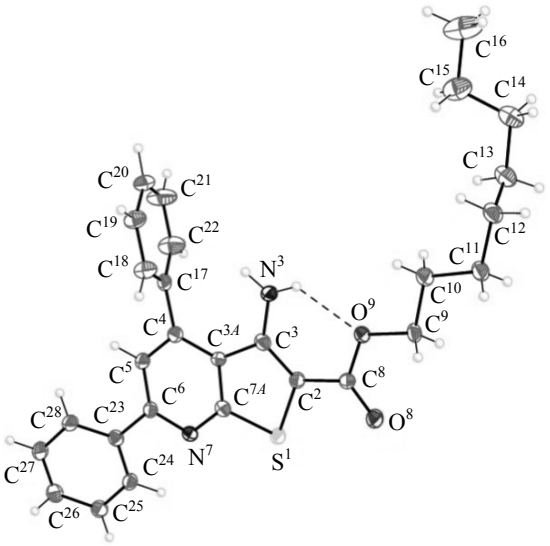


Fig. 2. Molecular structure of octyl 3-amino-4,6-diphenylthieno[2,3-*b*]pyridine-2-carboxylate (**6m**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

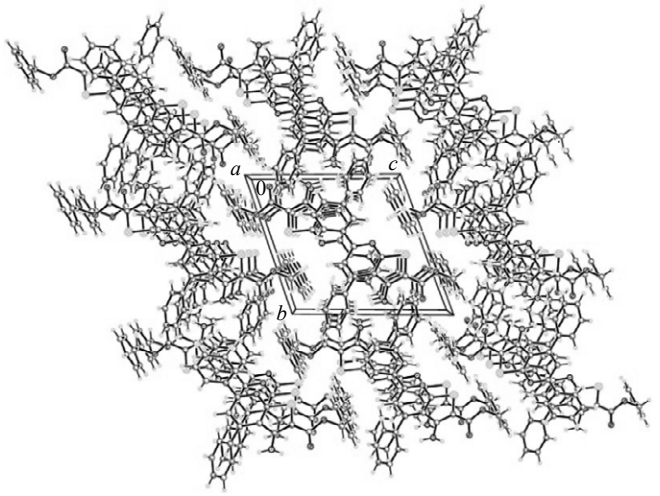


Fig. 3. Crystal packing of benzyl 3-amino-4,6-diphenylthieno[2,3-*b*]pyridine-2-carboxylate (**6l**).

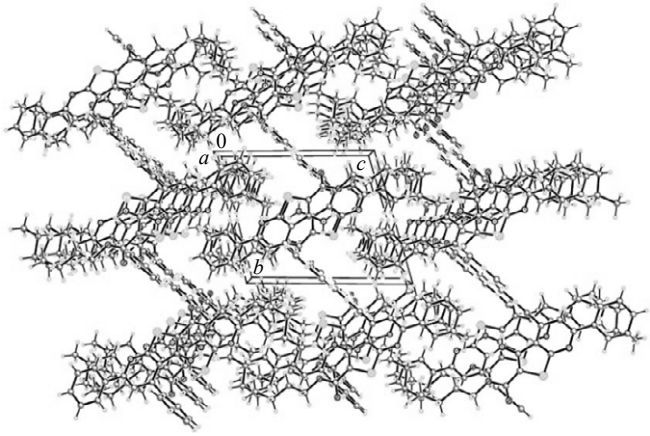


Fig. 4. Crystal packing of octyl 3-amino-4,6-diphenylthieno-[2,3-*b*]pyridine-2-carboxylate (**6m**).

acetylation. We previously described analogous acylation of 2-amino-7-hydroxy-4-(4-hydroxyphenyl)quinoline-3-carbonitrile [24].

The structure of compounds **5** and **6** was confirmed by spectral data (see Experimental). The IR spectra of **5** characteristically showed an absorption band at 2216–2223 cm^{-1} due to stretching vibrations of the conjugated cyano group. No CN stretching band was observed in the IR spectra of thienopyridines **6**; instead, NH stretching and bending vibration bands were present at 3275–3398 and 1634–1645 cm^{-1}, respectively.

In the ^1H NMR spectra of **5** and **6**, the 5-H proton of the pyridine ring resonated as a singlet at δ 7.25–8.00 ppm. The ^1H NMR spectra of **5** also contained a singlet in the region δ 4.02–4.72 ppm, which is typical of SCH_2 group [25–28]. Unlike compounds **5**, the ^1H NMR spectra of **6** lacked SCH_2 signal, but a broadened singlet appeared at δ 5.39–6.90 ppm due to protons of the amino group. The ^{13}C NMR spectra of **5a**–**5h** and **6a**–**6p** were consistent with the assigned structures (see Experimental).

The structure of thienopyridines **6l** and **6m** was unambiguously determined by X-ray analysis (Figs. 1, 2).

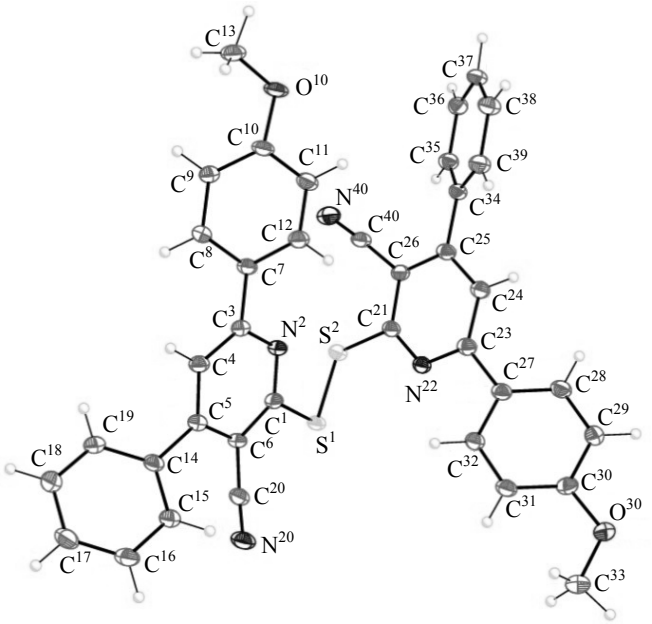


Fig. 5. Molecular structure of 2,2′-(disulfanediyl)bis-[6-(4-methoxyphenyl)-4-phenylpyridine-3-carbonitrile] (**9a**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

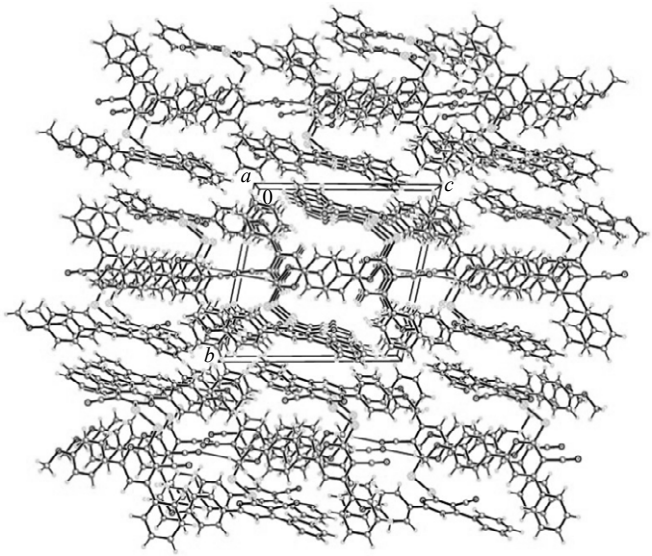


Fig. 6. Crystal packing of 2,2′-(disulfanediyl)bis[6-(4-methoxyphenyl)-4-phenylpyridine-3-carbonitrile] (**9a**).

The central 3-aminothieno[2,3-*b*]pyridine-2-carboxylate fragment in molecules **6l** and **6m** is planar: the average deviation of atoms from the mean-square plane is 0.040 (**6l**) or 0.020 Å (**6m**); the planar conformation of this fragment is stabilized by intramolecular hydrogen bonds N^3–$H^{3A}\cdots O^9$ [$N\cdots O$ 2.836(5), $H\cdots O$ 2.14(5) Å, ∠NHO 133(4)° (**6l**); $N\cdots O$ 2.783(2), $H\cdots O$ 2.17(2) Å, ∠NHO 129.9(18)° (**6m**)] and N^3–$H^{3B}\cdots\pi(C^{17}C^{16}C^{21})$ [$N^3\cdots C^{16}$ 3.106(5), $H^{3B}\cdots C^{16}$ 2.45(5) Å, $\angle N^3H^{3B}C^{16}$ 127(4)°] (**6l**) or N^3–$H^{3B}\cdots\pi(C^{18}C^{17}C^{22})$ [$N^3\cdots C^{17}$ 3.071(3), $H^{3B}\cdots C^{17}$ 2.45(2) Å, $\angle N^3H^{3B}C^{17}$ 130(2)°] (**6m**). The benzene rings are turned with respect to the central fragments through angles of 75.97(10), 21.63(13)° (**6l**) and 80.38(6), 12.99(9)° (**6m**). The octyl substituent in molecule **6m** adopts a *t*–*g*$^-$–*t*–*g*$^-$–*t* conformation ("*t*" stands for *trans*, and "*g*," for *gauche*).

Molecules **6l** and **6m** in crystal are packed in stacks along the *a* crystallographic axis (Figs. 3, 4). The distance between their molecules in a stack corresponds to van der Waals interactions.

Acidification of the reaction mixture led to the formation of 4,6-diaryl-2-sulfanylidene-1,2-dihydropyridine-3-carbonitrile **8** which was synthesized previously by three-component condensation of 2-methoxybenzaldehyde with cyanothioacetamide and 4,4,4-trifluoro-1-phenylbutane-1,3-dione [29]. Intermediate **C** is readily oxidized with atmospheric oxygen in the presence of acetic acid to give disulfides **9a** and **9b**. The structure of **9a** was confirmed by X-ray analysis (Fig. 5).

Disulfide **9a** molecule in crystal has a *gauche* conformation [torsion angle $C^1S^1S^2C^{21}$ 79.11(17)°], which is energetically more favorable due to orbital (generalized anomeric) effect. The pyridine rings are almost orthogonal to each other: the dihedral angle between their planes is 82.89(7)°. The benzene rings are turned with respect to the pyridine ring linked thereto by 21.76(9), 47.21(6)° and 35.51(7), 37.76(6)°. The methoxy groups are almost coplanar to the corresponding phenyl substituents (the deviations of the non-hydrogen atoms of the MeO groups from the mean-square planes are 0.047 and 0.037 Å). Molecules **9a** in crystal are stacked at van der Waals distances from each other along the *a* crystallographic axis (Fig. 6).

EXPERIMENTAL

The X-ray diffraction data for compounds **6l**, **6m**, and **9a** were obtained on a *Belok* synchrotron station with a Rayonix SX165 two-coordinate CCD detector at the "Kurchatov Institute" National Research Center (λ 0.96990 Å, ω-scanning with a step of 1.0°). The data were processed using iMOSFLM program implemented in CCP4 package [30]. A correction for absorption was applied by SCALA program [31]. The principal crystallographic and structure refinement

Table 1. X-Ray diffraction data for compounds **6l**, **6m**, and **9a**

Parameter	**6l**	**6m**	**9a**
Formula	$C_{27}H_{20}N_2O_2S$	$C_{28}H_{30}N_2O_2S$	$C_{38}H_{26}N_4O_2S_2$
Molecular weight	436.51	458.60	634.75
Temperature, K	100(2)	100(2)	100(2)
Single crystal dimensions, mm	0.10×0.20×0.30	0.07×0.15×0.30	0.15×0.20×0.30
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
Unit cell parameters:			
a, Å	8.6690(11)	10.400(2)	8.2601(17)
b, Å	11.8751(13)	10.620(2)	14.024(3)
c, Å	12.1222(14)	12.070(2)	14.100(3)
α, deg	68.60(3)	72.74(3)	100.11(3)
β, deg	81.42(3)	80.96(3)	97.76(3)
γ, deg	71.28(3)	70.48(3)	101.36(3)
V, Å^3	1099.7(4)	1197.4(5)	1552.0(6)
Z	2	2	2
d_{calc}, g/cm^3	1.318	1.272	1.358
F(000)	456	488	660
μ, mm^{-1}	0.395	0.368	0.492
$2\theta_{max}$, deg	76.84	76.84	76.82
Total number of reflections	10138	10758	20196
Number of independent reflections (R_{int})	3785 (0.037)	4096 (0.066)	5293 (0.044)
Number of reflections with $I > 2\sigma(I)$	2898	3334	4785
Number of variables	296	306	418
R_1, wR_2 [reflections with $I > 2\sigma(I)$]	0.079, 0.187	0.048, 0.128	0.045, 0.115
R_1, wR_2 (all independent reflections)	0.108, 0.222	0.066, 0.139	0.052, 0.123
Goodness of fit with respect to F^2	1.017	1.083	1.073
Extinction coefficient	0.108(9)	0.012(1)	0.0062(6)
T_{min}, T_{max}	0.880, 0.950	0.885, 0.968	0.860, 0.920

parameters are given in Table 1. The structures were solved by the direct method and were refined against F^2 by the full-matrix least-squares method in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of the amino groups of **6l** and **6m** were localized by the difference Fourier syntheses, and their positions were refined according to the riding model with fixed isotropic thermal displacement parameters [$U_{iso}(H) = 1.2U_{eq}(N)$]. The positions of the other hydrogen atoms in all compounds were calculated geometrically and were refined with fixed positional (riding model) and isotropic thermal parameters [$U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 groups, $U_{iso}(H) = 1.2U_{eq}(C)$ for other hydrogens]. All calculations were performed using SHELXTL software package [32]. The tabulated coordinates of atoms, bond lengths, bond and torsion angles, and anisotropic thermal displacement parameters for compounds **6l**, **6m**, and **9a** were deposited to the Cambridge Crystallographic Data Centre [CCDC entry nos. 1844206 (**6l**), 1844207 (**6m**), 1844208 (**9a**)].

The IR spectra were recorded in mineral oil on an IKS-40 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Varian VXR-400 spectrometer at 399.97 and 100 MHz, respectively, using DMSO-d_6 as solvent and tetramethylsilane as internal standard. The high-resolution mass spectra were obtained on a Thermo Fischer Scientific Orbitrap Elite instrument;

samples were dissolved in 1 mL of DMSO, diluted by a factor of 100 with 1% formic acid in acetonitrile, and introduced at a flow rate of 40 μL/min into electrospray ionization source using a syringe pump, the source gas flow being turned off (needle voltage 3.5 kV, capillary temperature 275°C; positive and negative ion detection in the orbital trap, resolution 480 000); the mass scale was calibrated against [2DMSO + H^+] (internal, *m*/*z* 157.03515) for positive ions and dodecyl sulfate anion (*m*/*z* 265.14789) for negative ions. The other mass spectra (electron impact, 70 eV) were recorded on an Agilent 1100 Series LC/MSD instrument; samples were introduced in acetic acid. The elemental analyses were obtained with a Perkin Elmer CHN analyzer. The melting points were measured on a Kofler hot stage. The progress of reactions was monitored, and the purity of the isolated compounds was checked, by TLC on Silufol UV-254 plates using acetone–hexane (3 : 5) as eluent; spots were visualized by treatment with iodine vapor and under UV light.

Compounds 5a–5h (*general procedure***).** A mixture of 0.4 g (10 mmol) of sodium hydroxide, 5 mL of water, and 5 mL of 95% ethanol was cooled to 0°C, 10 mmol of acetophenone **2** and 10 mmol of aromatic aldehyde **1** were added, and the mixture was stirred for 1 h at that temperature. A solution of 1 g (10 mmol) of cyanothioacetamide (**3**) in 20 mL of ethanol was added, and the mixture was left to stand for 2 h at 0°C. Halogen derivative **4**, 10 mmol, was then added with stirring, and the mixture was stirred for 30 min at room temperature and diluted with an equal volume of water. The precipitate was filtered off and washed with water, ethanol, and hexane.

Benzyl 2-[3-cyano-4,6-bis(4-methoxyphenyl)-pyridin-2-ylsulfanyl]acetate (5a). Yield 3.7 g (74%), yellow powder, mp 182–184°C (from 1,4-dioxane). IR spectrum, ν, cm^{-1}: 2220 (C≡N), 1715 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.76 s (3H, MeO), 3.85 s (3H, MeO), 4.34 s (2H, SCH_2), 5.15 s (2H, OCH_2), 6.92 d (2H, H_{arom}, *J* = 8.8 Hz), 7.13 d (2H, H_{arom}, *J* = 8.7 Hz), 7.31 br.s (5H, Ph), 7.72 d (2H, H_{arom}, *J* = 8.7 Hz), 7.81 s (1H, 5-H), 8.16 d (2H, H_{arom}, *J* = 8.8 Hz). Mass spectrum: *m*/*z* 497 (I_{rel} 100%) [*M* + H]$^+$. Found, %: C 70.08; H 4.82; N 5.55. $C_{29}H_{24}N_2O_4S$. Calculated, %: C 70.14; H 4.87; N 5.64. *M* 496.583.

2-[3-Cyano-4,6-bis(4-methoxyphenyl)pyridin-2-ylsulfanyl]acetamide (5b). Yield 3.4 g (83%), colorless powder, mp 253–255°C (from 1,4-dioxane). IR spectrum, ν, cm^{-1}: 3318, 3295, 3204 (NH_2), 2218 (C≡N), 1649 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.81 s (3H, MeO), 3.82 s (3H, MeO), 4.02 s (2H, SCH_2), 7.01 d (2H, H_{arom}, *J* = 9.0 Hz), 7.10 d (2H, H, H_{arom}, *J* = 8.9 Hz), 7.21 br.s and 7.65 br.s (1H each, NH_2), 7.68 d (2H, H_{arom}, *J* = 8.9 Hz), 7.77 s (1H, 5-H), 8.25 d (2H, H_{arom}, *J* = 9.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 34.33, 55.82, 55.85, 101.64, 114.64 (2C), 114.75, 115.32, 116.60, 116.63, 128.30, 129.53, 129.94 (2C), 130.66 (2C), 153.97, 158.04, 161.21, 161.88, 162.58, 169.36. Found: *m*/*z* 406.1220 [*M* + H]$^+$. $C_{22}H_{19}N_3O_3S$. Calculated: *M* + H 406.1147.

2-[3-Cyano-4-(4-nitrophenyl)-6-phenylpyridin-2-ylsulfanyl]acetamide (5c). Yield 3.1 g (79%), colorless powder, mp 238–240°C (from AcOH). IR spectrum, ν, cm^{-1}: 3325, 3300, 3282 (NH_2), 2216 (C≡N), 1675 (NO_2), 1648 (C=O). ^{1}H NMR spectrum, δ, ppm: 4.10 s (2H, SCH_2), 7.26 br.s (1H, NH_2), 7.54 br.s (3H, H_{arom}), 7.72 br.s (1H, NH_2), 7.98 s (1H, 5-H), 8.02 d (2H, H_{arom}, *J* = 8.4 Hz), 8.30 d (2H, Ph, *J* = 7.8 Hz), 8.41 d (2H, H_{arom}, *J* = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 34.18, 103.6, 115.35, 116.20, 123.90 (2C), 127.92 (2C), 128.97 (2C), 130.43 (2C), 131.05, 136.44, 141.92, 148.39, 152.09, 158.34, 162.55, 168.82. Found: *m*/*z* 389.0712 [*M* – H]$^+$. $C_{20}H_{14}N_4O_3S$. Calculated: *M* – H 389.0787.

2-(Benzylsulfanyl)-4-(4-nitrophenyl)-6-phenylpyridine-3-carbonitrile (5d). Yield 2.9 g (69%), yellow powder, mp 211–213°C (from BuOH). IR spectrum, ν, cm^{-1}: 2221 (C≡N), 1670 (NO_2). ^{1}H NMR spectrum, δ, ppm: 4.72 s (2H, SCH_2), 7.24 t (1H, H_{arom}, *J* = 7.3 Hz), 7.30 t (2H, H_{arom}, *J* = 7.1 Hz), 7.47 d (2H, H_{arom}, *J* = 7.3 Hz), 7.52–7.59 m (3H, H_{arom}), 7.95 s (1H, 5-H), 7.99 d (2H, H_{arom}, *J* = 8.6 Hz), 8.21–8.29 m (2H, H_{arom}), 8.37 d (2H, H_{arom}, *J* = 8.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 34.47, 103.40, 115.51, 116.87, 124.16 (2C), 127.71, 128.10 (2C), 128.92 (2C), 129.24 (2C), 129.41 (2C), 130.79 (2C), 131.38, 136.99, 137.67, 142.39, 148.93, 152.72, 158.81, 162.86. Mass spectrum: *m*/*z* 424 (I_{rel} 100%) [*M* + H]$^+$. Found, %: C 70.80; H 3.96; N 9.81. $C_{25}H_{17}N_3O_2S$. Calculated, %: C 70.91; H 4.05; N 9.92. *M* 423.49.

4-(4-Nitrophenyl)-6-phenyl-2-(prop-2-en-1-ylsulfanyl)pyridine-3-carbonitrile (5e). Yield 2.5 g (68%), yellow powder, mp 189–191°C (from PrOH). IR spectrum, ν, cm^{-1}: 2223 (C≡N), 1672 (NO_2). ^{1}H NMR spectrum, δ, ppm: 4.09 d (2H, SCH_2, *J* = 6.8 Hz), 5.13 d (1H, =CH_2, J_{cis} = 8.4 Hz), 5.36 d (1H, =CH_2, J_{trans} = 17.0 Hz), 5.96–6.06 m (1H, CH=), 7.49–7.58 m (3H, Ph), 8.00 s (1H, 5-H), 8.02 d (2H, C_6H_4, *J* = 8.8 Hz), 8.22–8.29 m (2H, Ph), 8.39 d (2H, C_6H_4,

J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 32.97, 103.59, 115.71, 116.71, 118.92, 124.25 (2C), 128.03 (2C), 129.50 (2C), 130.86 (2C), 134.48, 133.75, 136.87, 142.34, 148.77, 152.67, 158.58, 162.56. Mass spectrum: m/z 374 (I_{rel} 100%) $[M + H]^+$. Found, %: C 67.42; H 3.96; N 11.15. $C_{21}H_{15}N_3O_2S$. Calculated, %: C 67.54; H 4.05; N 11.25. M 373.43.

4,6-Diphenyl-2-(prop-2-en-1-ylsulfanyl)pyridine-3-carbonitrile (5f). Yield 2.1 g (65%), light yellow needles, mp 91–93°C (from AcOH). IR spectrum: ν 2219 cm^{-1} (C≡N). ^{1}H NMR spectrum, δ, ppm: 4.10 d (2H, SCH_2, J = 6.8 Hz), 5.15 d (1H, =CH_2, J_{cis} = 10.0 Hz), 5.39 d (1H, =CH_2, J_{trans} = 17.0 Hz), 5.81–6.16 m (1H, CH=), 7.52–7.60 m (6H, H_{arom}), 7.69–7.72 m (2H, H_{arom}), 7.93 s (1H, 5-H), 8.23–8.28 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 32.95, 103.52, 116.10, 116.65, 118.81, 127.95 (2C), 129.12 (2C), 129.28 (2C), 129.43 (2C), 130.54, 131.25, 133.83, 136.11, 137.07, 154.74, 158.35, 162.49. Mass spectrum: m/z 329 (I_{rel} 100%) $[M + H]^+$. Found, %: C 76.71; H 4.88; N 8.40. $C_{21}H_{16}N_2S$. Calculated, %: C 76.80; H 4.91; N 8.53. M 328.43.

4-(2-Methoxyphenyl)-6-phenyl-2-(prop-2-en-1-ylsulfanyl)pyridine-3-carbonitrile (5g). Yield 2.5 g (69%), colorless lustrous crystals, mp 89–91°C (from MeOH). IR spectrum: ν 2216 cm^{-1} (C≡N). ^{1}H NMR spectrum, δ, ppm: 3.78 s (3H, MeO), 4.07 d (2H, SCH_2, J = 6.8 Hz), 5.14 d (1H, =CH_2, J_{cis} = 8.3 Hz), 5.36 d (1H, =CH_2, J_{trans} = 17.0 Hz), 5.79–6.11 m (1H, CH=), 7.09 t (1H, H_{arom}, J = 7.6 Hz), 7.21 d (1H, H_{arom}, J = 7.8 Hz), 7.40 d (1H, H_{arom}, J = 7.6 Hz), 7.45–7.53 m (4H, H_{arom}), 7.82 s (1H, 5-H), 8.19–8.22 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 32.85, 55.98, 105.69, 112.27, 115.81, 117.70, 118.81, 121.22, 125.08, 127.85 (2C), 129.46 (2C), 130.84, 131.18, 132.01, 133.91, 137.13, 152.71, 156.36, 158.33, 161.34. Found: m/z 359.1214 $[M + H]^+$. $C_{22}H_{18}N_2OS$. Calculated: M + H 359.1140.

2-[3-Cyano-4-(2-methoxyphenyl)-6-phenylpyridin-2-ylsulfanyl]-*N*-(4-methylphenyl)acetamide (5h). Yield 3.7 g (79%), colorless lustrous crystals, mp 198–200°C (from 1,4-dioxane). IR spectrum, ν, cm^{-1}: 3310 (NH), 2218 (C≡N), 1675 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.13 s (3H, Me), 3.81 s (3H, MeO), 4.40 s (2H, SCH_2), 7.01–7.15 m (3H, H_{arom}), 7.17 d (1H, H_{arom}, J = 7.3 Hz), 7.23 d (1H, H_{arom}, J = 8.4 Hz), 7.37 d (1H, H_{arom}, J = 7.6 Hz), 7.39–7.44 m (3H, H_{arom}), 7.47 d (1H, H_{arom}, J = 7.2 Hz), 7.54 t (1H, H_{arom}, J = 8.3 Hz), 7.84 s (1H, 5-H), 8.26 d (2H, H_{arom}, J = 7.3 Hz), 9.71 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 18.24, 34.94, 56.00, 112.32 (2C), 115.90, 117.83 (2C), 121.29 (2C), 125.04, 125.66, 126.38, 128.12 (2C), 129.30 (2C), 130.78, 130.87, 131.20, 132.09, 136.66, 137.07, 152.67, 156.43, 158.58, 161.55, 166.31. Found: m/z 466.1582 $[M + H]^+$. $C_{28}H_{23}N_3O_2S$. Calculated: M + H 466.1511.

2-Substituted 3-amino-4,6-diarylthieno[2,3-*b*]-pyridines 6a–6p were synthesized as described above for compounds **5**, but instead of dilution of the reaction mixture with water a solution of 0.1 g (5 mmol) of metallic sodium in 15 mL of ethanol was added. The mixture was then stirred for 2 h at room temperature and diluted with an equal volume of water, and the precipitate was filtered off and washed with water, ethanol, and hexane.

3-Amino-*N*-(4-bromophenyl)-4,6-bis(4-methoxyphenyl)thieno[2,3-*b*]pyridine-2-carboxamide (6a). Yield 4.3 g (77%), bright yellow powder fluorescing under UV irradiation, mp 120–122°C (from AcOH). IR spectrum, ν, cm^{-1}: 3345, 3312, 3275 (NH, NH_2), 1664 (CONH), 1642 (δNH_2). ^{1}H NMR spectrum, δ, ppm: 3.87 s (3H, MeO), 3.91 s (3H, MeO), 6.04 br.s (2H, NH_2), 6.70 d (2H, H_{arom}, J = 8.5 Hz), 7.06 d (2H, H_{arom}, J = 8.6 Hz), 7.25 s (1H, 5-H), 7.31–7.49 m (6H, H_{arom}), 8.07 d (2H, H_{arom}, J = 8.8 Hz), 8.10 s (1H, NH). Mass spectrum: m/z 561 (I_{rel} 100%) $[M + H]^+$. Found, %: C 59.87; H 3.82; N 7.38. $C_{28}H_{22}BrN_3O_3S$. Calculated, %: C 60.00; H 3.96; N 7.50. M 560.468.

3-Amino-4-(4-nitrophenyl)-6-phenylthieno-[2,3-*b*]pyridine-2-carboxamide (6b). Yield 3.3 g (84%), yellow powder, mp 307–309°C (from 1,4-dioxane), sublimes at 240°C. IR spectrum, ν, cm^{-1}: 3340, 3300, 3281, 3250 (NH_2), 1666 (C=O), 1642 (δNH_2). ^{1}H NMR spectrum, δ, ppm: 5.95 br.s (2H, NH_2), 7.31 br.s (2H, $CONH_2$), 7.42–7.54 m (3H, H_{arom}), 7.83 s (1H, 5-H), 7.86 d (2H, H_{arom}, J = 8.7 Hz), 8.22 d (2H, H_{arom}, J = 8.0 Hz), 8.39 d (2H, H_{arom}, J = 8.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 99.86, 118.52, 121.24, 124.07 (2C), 127.62 (2C), 129.39 (2C), 130.39, 131.06 (2C), 137.81, 143.57, 145.79, 145.95, 148.30, 156.02, 160.23, 167.36. Mass spectrum: m/z 391 (I_{rel} 100%) $[M + H]^+$. Found, %: C 61.40; H 3.55; N 14.21. $C_{20}H_{14}N_4O_3S$. Calculated, %: C 61.53; H 3.61; N 14.35. M 390.423.

[3-Amino-4-(2-methoxyphenyl)-6-phenylthieno-[2,3-*b*]pyridin-2-yl](4-bromophenyl)methanone (6c). Yield 3.8 g (73%), yellow powder, mp 129–131°C (from BuOH). IR spectrum, ν, cm^{-1}: 3338, 3304, 2291 (NH_2), 1697 (C=O), 1635 (δNH_2). ^{1}H NMR spectrum, δ, ppm: 3.75 s (3H, Me), 6.84 br.s

(2H, NH_2), 7.20 t (1H, H_{arom}, J = 7.5 Hz), 7.28 d (1H, H_{arom}, J = 8.3 Hz), 7.42 d (1H, H_{arom}, J = 7.5 Hz), 7.46–7.53 m (3H, H_{arom}), 7.60 t (1H, H_{arom}, J = 6.8 Hz), 7.63–7.71 m (4H, H_{arom}), 7.79 s (1H, 5-H), 8.20 d (2H, H_{arom}, J = 6.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 56.31, 113.11, 118.89 (2C), 121.16 (2C), 124.32, 127.30, 127.75, 128.64, 129.44 (2C), 129.79 (2C), 129.96 (2C), 130.30, 130.59, 131.00, 131.97, 132.04, 144.68, 149.30, 154.63, 157.44, 162.33, 188.23. Found: m/z 515.0422 $[M + H]^+$. $C_{27}H_{19}BrN_2O_2S$. Calculated: M + H 515.0351.

[3-Amino-4-(2-methoxyphenyl)-6-phenylthieno-[2,3-*b*]pyridin-2-yl](4-methylphenyl)methanone (6d). Yield 3.1 g (68%), bright yellow powder, mp 203–205°C (from AcOH). IR spectrum, ν, cm^{-1}: 3352, 3303, 3276 (NH_2), 1694 (C=O), 1644 (δNH_2). ^{1}H NMR spectrum, δ, ppm: 2.39 s (3H, Me), 3.75 s (3H, MeO), 6.79 br.s (2H, NH_2), 7.13–7.52 m (8H, H_{arom}), 7.54–7.76 m (4H, H_{arom}), 8.14–8.22 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 22.14, 53.84, 113.14 (2C), 118.74 (2C), 119.13 (2C), 119.47, 121.11, 123.15, 125.96, 127.17, 127.81 (2C), 128.98, 129.05, 129.53, 129.80, 130.15, 130.46, 131.08, 131.66, 132.14, 145.57, 148.49, 154.72, 186.15. Found: m/z 451.1474 $[M + H]^+$. $C_{28}H_{22}N_2O_2S$. Calculated: M + H 451.1402.

[3-Amino-4-(2-methoxyphenyl)-6-phenylthieno-[2,3-*b*]pyridin-2-yl](3,4-dichlorophenyl)methanone (6e). Yield 4 g (80%), bright yellow powder, mp 128–130°C (from AcOH). IR spectrum, ν, cm^{-1}: 3341, 3300, 3288 (NH_2), 1711 (C=O), 1635 (δNH_2). ^{1}H NMR spectrum, δ, ppm: 3.77 s (3H, Me), 6.88 br.s (2H, NH_2), 7.21 t (1H, H_{arom}, J = 7.4 Hz), 7.30 d (1H, H_{arom}, J = 8.4 Hz), 7.43 d (1H, H_{arom}, J = 7.3 Hz), 7.48–7.54 m (3H, H_{arom}), 7.62 t (1H, H_{arom}, J = 7.9 Hz), 7.77–7.84 m (3H, H_{arom}), 7.98 s (1H, 5-H), 8.22 d (2H, H_{arom}, J = 5.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 56.24, 103.30, 112.55, 119.34, 121.38, 121.66, 124.82, 127.77, 128.02 (2C), 129.44, 129.89 (2C), 130.47 (2C), 130.76, 131.38, 131.96, 132.01, 134.39, 137.52, 146.53, 151.59, 156.23, 158.29, 162.39, 186.26. Mass spectrum: m/z 506 (I_{rel} 100%) $[M + H]^+$. Found, %: C 64.01; H 3.42; N 5.44. $C_{27}H_{18}Cl_2N_2O_2S$. Calculated, %: C 64.16; H 3.59; N 5.54. M 505.426.

3-Amino-4-(2-methoxyphenyl)-*N*-(naphthalen-1-yl)-6-phenylthieno[2,3-*b*]pyridine-2-carboxamide (6f). Yield 4 g (79%), yellow powder, mp 199–201°C (from AcOH). IR spectrum, ν, cm^{-1}: 3354, 3300, 3286 (NH_2, NH), 1666 (C=O), 1640 (δNH_2). ^{1}H NMR spectrum, δ, ppm: 3.73 s (3H, Me), 5.93 br.s (2H, NH_2), 7.08 d (1H, H_{arom}, J = 8.1 Hz), 7.11–7.18 m (1H, H_{arom}), 7.25 s (1H, 5-H), 7.33 d (1H, H_{arom}, J = 7.4 Hz), 7.35–7.56 m (7H, H_{arom}), 7.59 s (1H, NH), 7.73 d (1H, H_{arom}, J = 7.7 Hz), 7.81–7.89 m (3H, H_{arom}), 7.97 d (1H, H_{arom}, J = 7.4 Hz), 8.13 d (1H, H_{arom}, J = 6.0 Hz). Mass spectrum: m/z 502 (I_{rel} 100%) $[M + H]^+$. Found, %: C 74.12; H 4.55; N 8.21. $C_{31}H_{23}N_3O_2S$. Calculated, %: C 74.23; H 4.62; N 8.38. M 501.606.

Ethyl 3-amino-4-(2-methoxyphenyl)-6-phenylthieno[2,3-*b*]pyridine-2-carboxylate (6g). Yield 2.7 g (68%), light yellow needles, mp 183–185°C (from BuOH). IR spectrum, ν, cm^{-1}: 3333, 3307, 2281 (NH_2), 1704 (C=O), 1645 (δNH_2). ^{1}H NMR spectrum, δ, ppm: 1.28 t (3H, **Me**CH_2, J = 6.8 Hz), 3.72 s (3H, MeO), 4.25 q (2H, OCH_2, J = 6.8 Hz), 5.71 br.s (2H, NH_2), 7.16 t (1H, H_{arom}, J = 7.2 Hz), 7.24 d (1H, H_{arom}, J = 8.1 Hz), 7.38 d (1H, H_{arom}, J = 6.4 Hz), 7.41–7.52 m (3H, H_{arom}), 7.58 t (1H, H_{arom}, J = 7.2 Hz), 7.73 s (1H, 5-H), 8.18 d (2H, H_{arom}, J = 5.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 15.02, 56.34, 60.64, 112.35, 118.98 (2C), 121.43 (2C), 124.72, 127.64 (2C), 129.39 (2C), 130.44, 130.55, 131.70, 137.52, 145.59, 147.72, 156.56, 156.96, 160.68, 165.31. Found: m/z 405.1272 $[M + H]^+$. $C_{23}H_{20}N_2O_3S$. Calculated: M + H 405.1195.

3-Amino-4-(2-methoxyphenyl)-*N*,6-diphenylthieno[2,3-*b*]pyridine-2-carboxamide (6h). Yield 3.7 g (82%), bright yellow powder, mp 206–208°C (from 1,4-dioxane). IR spectrum, ν, cm^{-1}: 3338, 3302, 3290 (NH, NH_2), 1669 (C=O), 1634 (δNH_2). ^{1}H NMR spectrum, δ, ppm: 3.73 s (3H, Me), 5.92 br.s (2H, NH_2), 7.07 t (1H, H_{arom}, J = 7.3 Hz), 7.17 t (1H, H_{arom}, J = 7.4 Hz), 7.24 d (1H, H_{arom}, J = 8.4 Hz), 7.31 t (2H, H_{arom}, J = 8.1 Hz), 7.40 d (1H, H_{arom}, J = 7.4 Hz), 7.46–7.59 m (4H, H_{arom}), 7.66 d (2H, H_{arom}, J = 8.2 Hz), 7.74 s (1H, 5-H), 8.21 d (2H, H_{arom}, J = 8.1 Hz), 9.52 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 56.14, 98.01, 112.29, 119.06 (2C), 121.35, 121.77 (2C), 122.58, 124.04, 125.41, 127.58 (2C), 128.88 (2C), 129.39 (2C), 130.31, 130.57, 131.58, 137.91, 139.25, 144.96, 147.42, 156.50, 159.99, 164.26. Found: m/z 452.1428 $[M + H]^+$. $C_{27}H_{21}N_3O_2S$. Calculated: M + H 452.1354.

Benzyl 3-amino-4-(2-methoxyphenyl)-6-phenylthieno[2,3-*b*]pyridine-2-carboxylate (6i). Yield 3.9 g (84%), bright yellow powder, mp 156–158°C (from BuOH). IR spectrum, ν, cm^{-1}: 3338, 3305, 2907 (NH_2), 1713 (C=O), 1636 (δNH_2). ^{1}H NMR spectrum, δ, ppm: 3.78 s (3H, Me), 5.30 s (2H, CH_2), 5.78 br.s (2H, NH_2), 7.17 t (1H, H_{arom}, J = 7.4 Hz), 7.24 d (1H, H_{arom}, J = 8.4 Hz), 7.26–7.50 m (8H, H_{arom}), 7.59 t (2H, H_{arom},

J = 7.5 Hz), 7.75 s (1H, 5-H), 8.18 d (2H, H_{arom}, J = 5.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 56.15, 65.81, 112.36, 119.03, 121.44, 122.11, 125.06, 127.66 (2C), 128.27 (2C), 129.40, 130.48 (2C), 130.55 (2C), 131.73 (2C), 135.12, 136.03, 137.06, 137.72, 145.49, 148.77, 156.42, 157.60, 161.08, 164.51. Found: m/z 467.1422 $[M + H]^+$. $C_{28}H_{22}N_2O_3S$. Calculated: M + H 467.1351.

3-Amino-4-(2-methoxyphenyl)-6-phenylthieno-[2,3-*b*]pyridine-2-carboxamide (6j). Yield 2.9 g (77%), bright yellow powder fluorescing under UV irradiation, mp 208–210°C (from EtOAc). IR spectrum, ν, cm^{-1}: 3388, 3012, 2285 (NH_2), 1666 (C=O), 1639 (δNH_2). ^1H NMR spectrum, δ, ppm: 3.76 s (3H, Me), 5.39 br.s (2H, NH_2), 5.86 br.s (2H, $CONH_2$), 7.06 d (1H, H_{arom}, J = 8.2 Hz), 7.12 t (1H, H_{arom}, J = 7.0 Hz), 7.30 d (1H, H_{arom}, J = 7.4 Hz), 7.39–7.50 m (4H, H_{arom}), 7.55 s (1H, 5-H), 8.09 d (2H, H_{arom}, J = 6.6 Hz). Mass spectrum: m/z 376 (I_{rel} 100%) $[M + H]^+$. Found, %: C 76.01; H 4.44; N 11.00. $C_{21}H_{17}N_3O_2S$. Calculated, %: C 67.18; H 4.56; N 11.19. M 375.448.

(3-Amino-4,6-diphenyltieno[2,3-*b*]pyridin-2-yl)-(phenyl)methanone (6k). Yield 3.2 g (79%), bright yellow powder fluorescing under UV irradiation, mp 156–158°C (AcOH). IR spectrum, ν, cm^{-1}: 3333, 3015, 2284 (NH_2), 1697 (C=O), 1641 (δNH_2). ^1H NMR spectrum, δ, ppm: 6.90 br.s (2H, NH_2), 7.34–7.58 m (6H, H_{arom}), 7.61 s (5H, Ph), 7.75 d (2H, H_{arom}, J = 6.6 Hz), 7.81 s (1H, 5-H), 8.20 d (2H, H_{arom}, J = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 103.90, 116.63, 118.90, 120.26, 127.76 (4C), 128.96 (4C), 129.38 (2C), 129.54, 129.95, 130.68, 131.68, 136.60, 137.56, 141.17, 149.40, 150.56, 157.76, 162.60, 189.45. Found: m/z 407.1214 $[M + H]^+$. $C_{26}H_{18}N_2OS$. Calculated: M + H 407.1140.

Benzyl 3-amino-4,6-diphenylthieno[2,3-*b*]pyridine-2-carboxylate (6l). Yield 3.5 g (81%), light yellow powder fluorescing under UV irradiation, mp 176–178°C (from BuOH). IR spectrum, ν, cm^{-1}: 3342, 3307, 3288 (NH_2), 1713 (C=O), 1644 (δNH_2). ^1H NMR spectrum, δ, ppm: 5.29 s (2H, CH_2), 5.85 br.s (2H, NH_2), 7.31 d (1H, H_{arom}, J = 6.7 Hz), 7.36–7.44 m (3H, H_{arom}), 7.46–7.53 m (4H, H_{arom}), 7.58 s (5H, Ph), 7.78 s (1H, 5-H), 8.20 d (2H, H_{arom}, J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 65.81, 118.74, 120.66, 127.70 (2C), 128.23 (4C), 128.48 (2C), 128.96 (4C), 129.06, 129.37, 129.81, 130.50, 136.67, 136.85, 137.66, 148.42, 148.60, 156.98, 161.45, 164.48. Found: m/z 437.1322 $[M + H]^+$. $C_{27}H_{20}N_2O_2S$. Calculated: M + H 437.1245.

Octyl 3-amino-4,6-diphenylthieno[2,3-*b*]pyridine-2-carboxylate (6m). Yield 3.2 g (70%), yellow cubic crystals fluorescing under UV irradiation, mp 106–108°C (from AcOH). IR spectrum, ν, cm^{-1}: 3330, 3295, 3287 (NH_2), 1712 (C=O), 1645 (δNH_2). ^1H NMR spectrum, δ, ppm: 0.81 t (3H, Me, J = 6.6 Hz), 1.17–1.34 m (10H, CH_2), 1.54–1.60 m (2H, CH_2), 4.17 t (2H, OCH_2, J = 6.6 Hz), 5.77 br.s (2H, NH_2), 7.38–7.51 m (3H, H_{arom}), 7.57 s (5H, Ph), 7.76 s (1H, 5-H), 8.18 d (2H, H_{arom}, J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.38, 22.50, 25.83, 28.69, 29.02, 29.04, 31.62, 64.50, 95.32, 118.65, 120.71, 127.66, 129.05 (2C), 129.33 (2C), 129.75 (4C), 130.43, 136.72, 137.69, 147.92, 148.48, 156.80, 161.37, 164.75. Found: m/z 459.2105 $[M + H]^+$. $C_{28}H_{30}N_2O_2S$. Calculated: M + H 459.2028.

Nonyl 3-amino-4,6-diphenylthieno[2,3-*b*]pyridine-2-carboxylate (6n). Yield 2.9 g (67%), bright yellow powder fluorescing under UV irradiation, mp 67–68°C (from EtOH). IR spectrum, ν, cm^{-1}: 3337, 3302, 3000 (NH_2), 1712 (C=O), 1636 (δNH_2). ^1H NMR spectrum, δ, ppm: 0.82 t (3H, Me, J = 6.7 Hz), 1.14–1.38 m (12H, CH_2), 1.63 t (2H, CH_2, J = 6.9 Hz), 4.18 t (2H, OCH_2, J = 6.3 Hz), 5.79 br.s (2H, NH_2), 7.49 d (3H, H_{arom}, J = 7.2 Hz), 7.60 s (5H, Ph), 7.77 s (1H, 5-H), 8.20 d (2H, H_{arom}, J = 7.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.36, 22.56, 25.88, 28.74, 29.10, 29.37, 31.73, 33.40, 64.54, 95.61, 108.92, 118.62, 120.76 (2C), 127.68 (2C), 129.07 (2C), 129.32 (2C), 129.35, 129.77, 136.83, 137.81, 147.94, 148.46, 156.84, 161.50, 164.82. Mass spectrum: m/z 473 (I_{rel} 100%) $[M + H]^+$. Found, %: C 73.60; H 6.71; N 5.85. $C_{29}H_{32}N_2O_2S$. Calculated, %: C 73.70; H 6.82; N 5.93. M 472.65.

***N*-(4-Acetylphenyl)-3-amino-4,6-diphenylthieno-[2,3-*b*]pyridine-2-carboxamide (6o).** Yield 3.3 g (72%), yellow powder, mp 210–212°C (from BuOH). IR spectrum, ν, cm^{-1}: 3398, 3330, 3284 (NH, NH_2), 1707 (MeC=O), 1669 (CONH), 1635 (δNH_2). ^1H NMR spectrum, δ, ppm: 2.51 s (3H, Me), 6.44 br.s (2H, NH_2), 7.41–7.54 m (3H, H_{arom}), 7.60 s (5H, Ph), 7.78 s (1H, 5-H), 7.82 d (2H, C_6H_4, J = 8.8 Hz), 7.89 d (2H, C_6H_4, J = 8.8 Hz), 8.21 d (2H, H_{arom}, J = 7.7 Hz), 12.41 br.s (1H, CONH). ^{13}C NMR spectrum, δ_C, ppm: 26.85, 118.75, 120.67 (2C), 127.64 (4C), 129.15 (4C), 129.29 (4C), 129.36 (4C), 129.53, 137.03, 137.91, 148.04, 156.28, 160.57, 164.86, 196.90. Found: m/z 464.1425 $[M + H]^+$. $C_{28}H_{21}N_3O_2S$. Calculated: M + H 464.1354.

3-Amino-4-(2-methoxyphenyl)-6-phenyl-*N*-(1,3-thiazol-2-yl)thieno[2,3-*b*]pyridine-2-carboxamide (6p). Yield 3.2 g (70%), yellow powder,

mp 165–167°C (from AcOH). IR spectrum, ν, cm^{-1}: 3339, 3325, 3300 (NH, NH_2), 1662 (C=O), 1635 (δNH_2). ^1H NMR spectrum, δ, ppm: 3.87 s (3H, Me), 6.16 br.s (2H, NH_2), 7.02 d (1H, 5′-H, J = 3.5 Hz), 7.15 d (2H, H_{arom}, J = 8.4 Hz), 7.44 d (1H, 4′-H, J = 3.5 Hz), 7.46–7.66 m (5H, H_{arom}), 7.72 s (1H, 5-H), 8.22 d (2H, H_{arom}, J = 8.7 Hz), 12.63 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 55.82, 105.14, 112.03, 114.18, 114.70 (2C), 117.32, 118.67, 123.19, 127.59 (2C), 129.14, 129.34 (2C), 130.19, 130.64 (2C), 138.12, 147.89, 152.06, 157.14, 158.93, 160.38, 161.36. Mass spectrum: m/z 459 (I_{rel} 100%) $[M + H]^+$. Found, %: C 62.73; H 3.81; N 12.08. $C_{24}H_{18}N_4O_2S$. Calculated, %: C 62.86; H 3.96; N 12.22. M 458.564.

***N*-Acetyl-*N*-[2-(4-bromobenzoyl)-4,6-bis(4-methoxyphenyl)thieno[2,3-*b*]pyridin-3-yl]acetamide (7)** was synthesized as described above for compounds **6** from aldehyde **1d**, acetophenone **2b**, cyanothioacetamide (**3**), and 4-bromobenzoyl bromide (**4d**). The precipitate was separated and heated in acetic anhydride for 5 min under reflux. After 24 h, the precipitate was filtered off and washed with diethyl ether. Yield 4.7 g (75%), bright yellow powder fluorescing under UV irradiation, mp 170–172°C (from AcOH). IR spectrum, ν, cm^{-1}: 1692, 1665 (C=O). ^1H NMR spectrum, δ, ppm: 3.33 s (6H, MeCO), 3.82 s (3H, MeO), 3.88 s (3H, MeO), 7.04 d (2H, H_{arom}, J = 8.6 Hz), 7.17 d (2H, H_{arom}, J = 8.5 Hz), 7.55 d (2H, H_{arom}, J = 8.4 Hz), 7.68–7.77 m (5H, 5-H, H_{arom}), 8.18 d (2H, H_{arom}, J = 8.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 55.78 (2C), 55.84 (2C), 103.14, 114.75, 115.03 (2C), 118.36, 119.63, 125.24, 128.68, 129.33 (2C), 129.91 (4C), 130.03, 130.43, 131.98 (4C), 140.26, 149.16, 151.39, 157.66, 160.59, 161.56, 162.88, 187.85. Mass spectrum: m/z 630 (I_{rel} 100%) $[M + H]^+$. Found, %: C 60.92; H 3.88; N 4.35. $C_{32}H_{25}BrN_2O_5S$. Calculated, %: C 61.05; H 4.00; N 4.45. M 629.53.

4-(2-Methoxyphenyl)-6-phenyl-2-sulfanylidene-1,2-dihydropyridine-3-carbonitrile (8). The procedure was the same as described above for compounds **5** before the addition of alkyl halide **4**. Instead, the mixture was diluted with 10% aqueous HCl to pH 5 and was left to stand for 24 h. The precipitate was filtered off and washed with water, ethanol, and hexane. Yield 2.2 g (68%), yellow powder, mp 141–143°C (from BuOH); published data [29]: mp 138–140°C. ^{13}C NMR spectrum, δ_C, ppm: 56.12, 112.40, 114.54, 115.73, 116.93, 121.14, 125.76, 127.76, 129.22 (2C), 129.35 (2C), 131.66, 131.92, 132.30, 152.49, 155.01, 156.49, 179.32. Mass spectrum: m/z 319 (I_{rel} 100%) $[M + H]^+$. $C_{19}H_{14}N_2OS$. Calculated: M 318.396.

2,2′-(Disulfanediyl)bis[6-(4-methoxyphenyl)-4-phenylpyridine-3-carbonitrile] (9a) was synthesized as described above for compound **8** before the dilution with aqueous HCl. Instead, the mixture was diluted with 10 mL of glacial acetic acid and was left to stand for 48 h at 20°C. The mixture was then diluted with an equal volume of water, and the precipitate was filtered off. Yield 2.1 g (66%), colorless fine plates, mp 171–173°C (from EtOH). IR spectrum: ν 2219 cm^{-1} (C≡N). ^1H NMR spectrum, δ, ppm: 3.73 s (6H, Me), 6.86 d (4H, H_{arom}, J = 7.0 Hz), 7.56–7.62 m (6H, H_{arom}), 7.73–7.79 m (4H, H_{arom}), 7.98 s (2H, 5-H), 8.03 d (4H, H_{arom}, J = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 55.79 (2C), 102.97 (2C), 114.67 (4C), 116.09 (2C), 117.79 (2C), 128.90 (2C), 129.21 (4C), 129.38 (4C), 129.66 (4C), 130.75 (2C), 135.79 (2C), 154.84 (2C), 158.53 (2C), 159.33 (2C), 162.10 (2C). Found: m/z 635.1570 $[M + H]^+$. $C_{38}H_{26}N_4O_2S_2$. Calculated: M + H 635.1497.

2,2′-(Disulfanediyl)bis[4,6-bis(4-methoxyphenyl)-pyridine-3-carbonitrile] (9b) was synthesized in a similar way from 4-methoxybenzaldehyde **1a**. Yield 2.1 g (60%), yellow wool-like material, mp 123–125°C (from PrOH). IR spectrum: ν 2220 cm^{-1} (C≡N). ^1H NMR spectrum, δ, ppm: 3.73 s (6H, Me), 3.83 s (6H, Me), 6.85 d (2H, H_{arom}, J = 8.7 Hz), 6.94 t (2H, H_{arom}, J = 8.9 Hz), 7.01 d (2H, H_{arom}, J = 8.5 Hz), 7.14 d (1H, H_{arom}, J = 8.6 Hz), 7.32 d (1H, H_{arom}, J = 8.3 Hz), 7.44 d (2H, H_{arom}, J = 8.6 Hz), 7.74 d (2H, H_{arom}, J = 8.3 Hz), 7.93 s (2H, 5-H), 8.01 d (2H, H_{arom}, J = 8.7 Hz), 8.13 d (1H, H_{arom}, J = 8.7 Hz), 8.24 d (1H, H_{arom}, J = 8.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 55.69, 55.79, 55.88, 55.91, 102.53 (2C), 109.98 (4C), 114.45, 114.51, 114.64 (4C), 116.37, 117.42, 127.74, 127.84 (2C), 129.02, 129.46 (2C), 129.60 (4C), 130.64 (2C), 130.86 (4C), 154.45, 158.34, 159.41, 161.24, 161.44, 162.03. Found: m/z 695.1778 $[M + H]^+$. $C_{40}H_{30}N_4O_4S_2$. Calculated: M + H 695.1708.

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