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Synthesis of 2-(1-aryl-1*H*-tetrazol-5-yl)-thieno[2,3-*b*]pyridine derivatives

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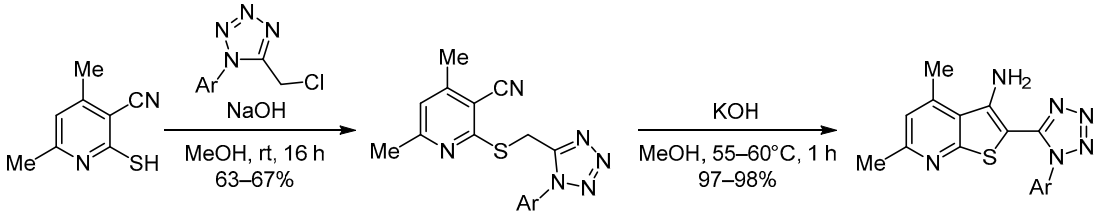


Ar = Ph, 2,4-$Me_2C_6H_3$, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 3-$F_3CC_6H_4$

Alkylation of 4,6-dimethyl-2-sulfanylpyridine-3-carbonitrile with 1-aryl-5-(chloromethyl)-1*H*-tetrazoles yielded 2-{[(1-aryl-1*H*-tetrazol-5-yl)methyl]sulfanyl}-4,6-dimethylpyridine-3-carbonitriles, which easily cyclize by the action of bases to form 2-(1*H*-tetrazol-5-yl)-thieno[2,3-*b*]pyridine derivatives. The use of excess base in the alkylation step leads to direct formation of cyclized products in high yields.

Keywords: 1-aryl-(5-chloromethyl)-1*H*-tetrazole, 2-{[(1*H*-tetrazol-5-yl)methyl]sulfanyl}pyridine, 2-(1*H*-tetrazol-5-yl)thieno[2,3-*b*]-pyridine, alkylation, bioisostere, heterocyclization.

Thieno[2,3-*b*]pyridine derivatives have diverse biological activity and are currently being actively studied.[1] Among them, in particular, compounds with antimicrobial activity,[2] antiviral drugs,[3] anti-inflammatory,[4] antidiabetic,[5] and anti-hypertensive[6] medications were found. In addition, derivatives of 3-aminothieno[2,3-*b*]pyridine-2-carboxylic acids were found to be c-Src tyrosine kinase inhibitors, which are promising antitumor drugs.[7] In this regard, derivatives of 2-(1*H*-tetrazol-5-yl)thieno[2,3-*b*]pyridin-3-amine may be of interest (Fig. 1), since it is known that 5-substituted and 1,5-disubstituted tetrazoles are metabolically stable bioisosteres of carboxylic acids and carboxamides.[8]

Previously, the synthesis of 2-(1*H*-tetrazol-5-yl)thieno-[2,3-*b*]pyridin-3-amine with *N*-unsubstituted tetrazole ring (R^2 = H) was accomplished by the reaction of the corresponding 3-aminothieno[2,3-*b*]pyridine-2-carbonitrile with sodium azide in the presence of NH_4Cl.[9] It was of interest to study the possibility of using other approaches to the synthesis of 2-(1*H*-tetrazol-5-yl)thieno[2,3-*b*]pyridin-3-amine derivatives with 1-substituted tetrazole ring. Since one of the most convenient methods for the synthesis of derivatives of 3-aminothieno[2,3-*b*]pyridine **1** is base-catalyzed cyclization of 2-(methylsulfanyl)pyridine-3-carbo-nitriles **2** containing an active methylene group at the sulfur atom[10] (Scheme 1), it was of interest to explore the possibility of using this method to synthesize 2-(1-aryl-1*H*-tetrazol-5-yl)thieno[2,3-*b*]pyridine-3-amines.

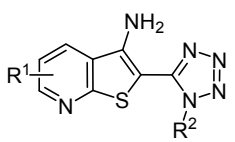
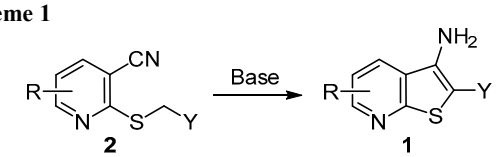


Figure 1. 2-(1*H*-Tetrazol-5-yl)thieno[2,3-*b*]pyridin-3-amines.

Scheme 1

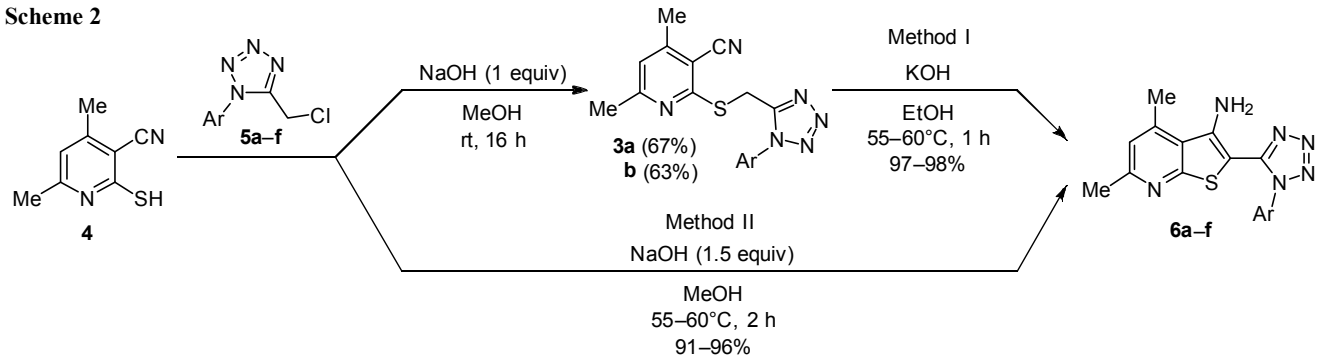


2 **1**

Y = 4-$O_2NC_6H_4$, CN, C(O)Ar, $C(O)NH_2$, CO_2Alk, $CH{=}CHCO_2Et$

In the present work, it was shown that 2-{[(1-aryl-1*H*-tetrazol-5-yl)methyl]sulfanyl}-4,6-dimethylpyridine-3-carbo-nitriles **3a**,**b**, accessible by alkylation of 4,6-dimethyl-2-sulfanylpyridine-3-carbonitrile (**4**) with 1-aryl-5-(chloro-methyl)-1*H*-tetrazoles **5a**,**b**, readily cyclizes into derivatives of thieno[2,3-*b*]pyridine **6a**,**b** by the action of a strong base: when a solution of KOH in EtOH is added to solutions of sulfides **3a**,**b** in hot EtOH, crystalline precipitates of cyclization products **6a**,**b** immediately form.

Scheme 2



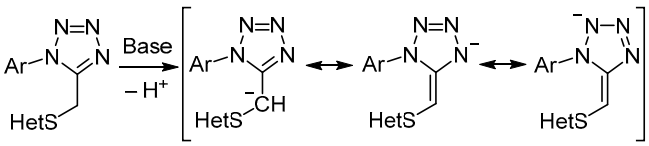
a Ar = Ph, **b** Ar = 2,4-$Me_2C_6H_3$, **c** Ar = 4-FC_6H_4, **d** Ar = 4-ClC_6H_4, **e** Ar = 4-BrC_6H_4, **f** Ar = 3-$F_3CC_6H_4$

If an excess of base is used at the alkylation stage, thieno[2,3-*b*]pyridines **6a**–**f** can be obtained in high yields, by passing the isolation of sulfides **3a**–**f** (Scheme 2). Compounds **3a**–**f** are often difficult to isolate with high purity due to the formation of mixtures of cyclized and uncyclized products even when using an equimolar amount of base.

The structure of the synthesized compounds **6a**–**f** and **3a**,**b** was confirmed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis data. The cyclization products **6a**–**f**, in contrast to sulfides **3a**,**b**, have a significantly higher melting point, lower solubility in organic solvents, and the ability to fluoresce under UV light. In the ^{1}H NMR spectra of compounds **3a**,**b**, the characteristic singlet of SCH_2 protons is observed at 4.83 and 4.87 ppm, respectively, while in the ^{1}H NMR spectra of products **6a**–**f** a broadened singlet signal of NH_2 protons in the range of 6.89–7.00 ppm can be observed. Comparison of mass spectra of isomeric compounds **3b** and **6b** reveals a significantly higher intensity of the peak of the molecular ion for the cyclized product **6b**.

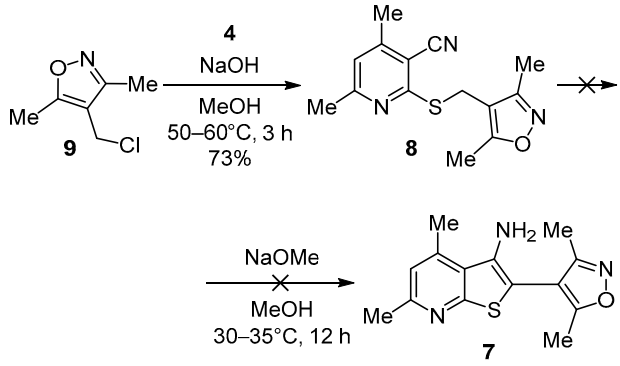
The mechanism of heterocyclization of sulfides **2** involves the generation of an α-carbanion followed by its attack on the carbon atom of the nitrile group.[11] In this connection, the ease of intramolecular cyclization of compounds **3a**–**f** can be explained by the resonance stabilization of the intermediate carbanion (Scheme 3).

Scheme 3



In this regard, it is interesting to note that an attempt to extend this approach to the synthesis of the derivative of 2-(1,2-oxazol-4-yl)thieno[2,3-*b*]pyridine **7** by cyclization of sulfide **8** obtained from 4-(chloromethyl)-3,5-dimethyl-1,2-oxazole (**9**) was unsuccessful: stirring a solution of compound **8** in MeOH in the presence of NaOMe at 30–35°C for 12 h did not show any signs of reaction (Scheme 4). The stability of sulfide **8** to the action of the base can be explained by the impossibility of resonance stabilization of the corresponding carbanion.

Scheme 4



To conclude, an accessible method for the synthesis of 2-(1-aryl-1*H*-tetrazol-5-yl)thieno[2,3-*b*]pyridine derivatives, which may be of interest as potential carcinolytic drugs, has been proposed. The ease of intramolecular cyclization of 2-{[(1-aryl-1*H*-tetrazol-5-yl)-methyl]sulfanyl}-4,6-dimethylpyridine-3-carbonitriles by the action of bases to the corresponding thieno[2,3-*b*]pyridines has been demonstrated and explained. Due to the presence of a primary amino group, the obtained thieno[2,3-*b*]pyridine derivatives can be further functionalized in the search for new biologically active compounds.

Experimental

^{1}H NMR spectra were acquired on Varian VNMRS 400 (400 MHz, compounds **6a**,**c**–**e**) and Bruker DRX 500 (500 MHz, compounds **5a**–**f**, **3a**,**b**, **6b**,**f**, **8**) spectrometers in DMSO-d_6, with TMS as internal standard. ^{13}C NMR spectra were acquired on a Varian VNMRS 400 spectrometer (101 MHz) in $CDCl_3$ (compound **8**) or in DMSO-d_6 with 5% CCl_4 (compounds **3a**,**b** and **6a**–**f**). Mass spectra were recorded on a Finnigan MAT INCOS 50 mass spectrometer (EI ionization, 70 eV). Elemental analysis was performed on a Vario MICRO cube CHNS-analyzer. Melting points were determined on a "Khimlaborpribor" PTP-M apparatus.

4,6-Dimethyl-2-sulfanylpyridine-3-carbonitrile (**4**)[12] and 4-(chloromethyl)-3,5-dimethyl-1,2-oxazole (**9**)[13] were synthesized following published methods. 1-Aryl-5-(chloromethyl)-1*H*-tetrazoles **5a**–**f** were obtained by a modified method of Harvill et al.[14]

Synthesis of 1-aryl-5-(chloromethyl)-1*H*-tetrazoles 5a–f (General method). Finely ground PCl_5 (35.0 g, 0.17 mol) was added to a suspension of chloroacetic acid arylamide (0.15 mol) in PhH (150 ml). The reaction mixture was stirred protected from atmospheric moisture until evolution of HCl ceased, gradually increasing the temperature to 50–60°C. The mixture was then cooled to 5–10°C, and a solution of HN_3 (0.25–0.30 mol) in PhH (150 ml) was added in small portions with stirring.[15] The reaction mixture was slowly heated to boiling with stirring, maintaining a moderate evolution of HCl, then heated under reflux for 1 h, cooled, and poured into a mixture of water and ice (250–300 ml). After the ice melted, the formed two-phase mixture was heated under reflux for 30 min with vigorous stirring to decompose $POCl_3$. After the reaction mixture was cooled to room temperature, the organic layer was separated and washed with H_2O (2×100 ml). The solvent was evaporated under reduced pressure, and the residue was crystallized from CCl_4. Compound **5b** was obtained as an oil, which was used in the next step without additional purification.

5-(Chloromethyl)-1-phenyl-1*H*-tetrazole (5a). Yield 27.8 g (95%), colorless compact crystals, mp 75–76°C (mp 76–77°C[14]). ^{1}H NMR spectrum, δ, ppm: 5.00 (2H, s, CH_2); 7.63–7.71 (5H, m, H Ph).

5-(Chloromethyl)-1-(2,4-dimethylphenyl)-1*H*-tetrazole (5b). Yield 29.4 g (88%), yellow oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.04 (3H, s, CH_3); 2.33 (3H, s, CH_3); 5.14 (2H, s, CH_2); 7.15 (1H, d, *J* = 8.3, H-5); 7.19 (1H, s, H-3); 7.48 (1H, d, *J* = 8.3, H-6).

5-(Chloromethyl)-1-(4-fluorophenyl)-1*H*-tetrazole (5c). Yield 25.5 g (80%), colorless needles, mp 68–70°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.12 (2H, s, CH_2); 7.55 (2H, t, *J* = 8.5, H-3,5); 7.81 (2H, dd, *J* = 8.5, *J* = 4.3, H-2,6).

5-(Chloromethyl)-1-(4-chlorophenyl)-1*H*-tetrazole (5d). Yield 27.8 g, 81%), colorless crystals, mp 70–71°C (mp 71–73°C[16]). ^{1}H NMR spectrum, δ, ppm: 5.15 (2H, s, CH_2); 7.78 (4H, s, H Ar).

1-(4-Bromophenyl)-5-(chloromethyl)-1*H*-tetrazole (5e). Yield 33.6 g (82%), gray compact crystals, mp 72–74°C (mp 73–75°C[16]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.15 (2H, s, CH_2); 7.71 (2H, d, *J* = 9.0, H-2,6); 7.91 (2H, d, *J* = 9.0, H-3,5).

5-(Chloromethyl)-1-[3-(trifluoromethyl)phenyl]-1*H*-tetrazole (5f). Yield 33.9 g (86%), colorless needles, mp 82–84°C. ^{1}H NMR spectrum, δ, ppm: 5.19 (2H, s, CH_2); 7.95 (1H, t, *J* = 8.6, H-5); 8.09 (2H, d, *J* = 8.6, H-4,6); 8.21 (1H, s, H-2).

Synthesis of 2-{[(1-aryl-1*H*-tetrazol-5-yl)methyl]-sulfanyl}pyridine-3-carbonitriles 3a,b (General method). A solution of 1-aryl-5-(chloromethyl)-1*H*-tetrazole **5a**,**b** (10 mmol) in MeOH (10 ml) was added with stirring to a solution of NaOH (0.40 g, 10 mmol) and compound **4** (1.64 g, 10 mmol) in MeOH (15 ml). The reaction mixture was stirred for 2 h at room temperature, then kept at room temperature without stirring for 14 h. The formed precipitate was filtered off, washed subsequently with MeOH (10 ml) and H_2O (20 ml), and air-dried. Then, the product was heated under reflux for 1–2 min with PhH (40 ml). The insoluble byproduct was filtered off, the filtrate was diluted with an equal volume of hexane. After cooling, the formed crystals were filtered off, washed with PhH–hexane, 1:1 mixture (16 ml), and air-dried. The product was recrystallized from EtOH.

4,6-Dimethyl-2-{[(1-phenyl-1*H*-tetrazol-5-yl)methyl]-sulfanyl}pyridine-3-carbonitrile (3a). Yield 2.16 g (67%), beige crystals, mp 144–146°C. ^{1}H NMR spectrum, δ, ppm: 2.31 (3H, s, CH_3); 2.42 (3H, s, CH_3); 4.83 (2H, s, CH_2); 6.97 (1H, s, H-5); 7.57–7.70 (5H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 19.6; 21.8; 24.1; 103.9; 114.5; 120.9; 125.0; 129.8; 130.4; 133.3; 152.6; 153.1; 158.1; 161.2. Found, %: C 59.69; H 4.46; N 26.01; S 9.99. $C_{16}H_{14}N_6S$. Calculated, %: C 59.61; H 4.38; N 26.07; S 9.94.

2-({[1-(2,4-Dimethylphenyl)-1*H*-tetrazol-5-yl]methyl}-sulfanyl)-4,6-dimethylpyridine-3-carbonitrile (3b). Yield 2.20 g (63%), beige powder, mp 140–142°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.92 (3H, s, CH_3); 2.29 (3H, s, CH_3); 2.33 (3H, s, CH_3); 2.38 (3H, s, CH_3); 4.87 (2H, s, CH_2); 7.10 (1H, s, H-5); 7.10 (1H, d, *J* = 7.9, H-5'); 7.17 (1H, s, H-3'); 7.34 (1H, d, *J* = 7.9, H-6'). ^{13}C NMR spectrum, δ, ppm: 16.8; 19.5; 20.6; 20.7; 24.0; 104.1; 114.5; 121.0; 126.7; 127.4; 129.4; 131.5; 134.4; 140.9; 152.6; 154.0; 157.3; 161.2. Mass spectrum, *m*/*z* (I_{rel}, %): 350 $[M]^+$ (9), 307 $[M–N_2–CH_3]^+$ (11), 289 (17), 262 (10), 177 (100), 164 (25), 159 (56). Found, %: C 61.80; H 5.20; N 23.88; S 9.12. $C_{18}H_{18}N_6S$. Calculated, %: C 61.69; H 5.18; N 23.98; S 9.15.

Synthesis of 2-(1-aryl-1*H*-tetrazol-5-yl)thieno[2,3-*b*]-pyridin-3-amines 6a–f (General procedure). Method I. Sulfide **3a**,**b** (1.6 mmol) was dissolved with heating in 95% EtOH (15 ml). 5% KOH in EtOH (2–3 ml) was added with stirring. The reaction mixture was stirred at 55–60°C for 1 h. After cooling to room temperature, the precipitate was filtered off, washed with EtOH (5 ml) and H_2O (10 ml), and dried at 100°C. An analytically pure sample was prepared by recrystallizing from a large volume of EtOH.

Method II. A solution of 1-aryl-5-(chloromethyl)-1*H*-tetrazole **5a–f** (10 mmol) in MeOH (10 ml) was added with stirring to a solution of NaOH (0.60 g, 15 mmol) and compound **4** (1.64 g, 10 mmol) in MeOH (15 ml). The reaction mixture was stirred at room temperature for 2 h, then at 55–60°C for 2 h. After cooling to room temperature, the precipitate was filtered off, washed with MeOH (10 ml) and H_2O (20 ml), and dried at 100°C. An analytically pure sample was prepared by recrystallizing from a large volume of EtOH.

4,6-Dimethyl-2-(1-phenyl-1*H*-tetrazol-5-yl)thieno-[2,3-*b*]pyridin-3-amine (6a). Yield 0.51 g (98%) (method I), 2.92 g (91%) (method II), beige powder, mp 251–252°C (decomp.) (method I), 249–251°C (decomp.) (method II). ^{1}H NMR spectrum, δ, ppm: 2.42 (3H, s, CH_3); 2.75 (3H, s, CH_3); 6.95 (2H, br. s, NH_2); 7.03 (1H, s, H-5); 7.65–7.82 (5H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 19.8; 23.7; 86.2; 121.4; 121.9; 128.1; 129.6; 131.7; 133.1; 144.3; 146.1; 151.3; 158.4; 159.9. Found, %: C 59.55; H 4.37; N 26.11; S 9.93. $C_{16}H_{14}N_6S$. Calculated, %: C 59.61; H 4.38; N 26.07; S 9.94.

4,6-Dimethyl-2-[1-(2,4-dimethylphenyl)-1*H*-tetrazol-5-yl]thieno[2,3-*b*]pyridin-3-amine (6b). Yield 0.54 g (97%) (method I), 3.22 g (92%) (method II), light-beige powder, mp 249–251°C (decomp.) (method I), 247–250°C (decomp.) (method II). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.88 (3H, s, CH_3); 2.44 (3H, s, CH_3); 2.48 (3H, s, CH_3); 2.77 (3H, s, CH_3); 7.00 (2H, br. s, NH_2); 7.07 (1H, s, H-5); 7.33 (1H, d, *J* = 7.9, H-5'); 7.40 (1H, s, H-3'); 7.48 (1H, d, *J* = 7.9, H-6'). ^{13}C NMR spectrum, δ, ppm: 16.6; 19.8; 21.0; 23.7; 85.9; 121.5; 121.9; 127.9; 128.6; 129.6; 131.7; 136.0; 142.1; 144.4; 146.1; 151.5; 158.4; 160.1. Mass spectrum, *m*/*z* (I_{rel}, %): 350 $[M]^+$ (48), 322 $[M–N_2]^+$ (14), 217 (28), 203 (41), 178 (31), 164 (60), 145 (84), 131 (100). Found, %: C 61.77; H 5.24; N 23.89; S 9.14. $C_{18}H_{18}N_6S$. Calculated, %: C 61.69; H 5.18; N 23.98; S 9.15.

2-[1-(4-Fluorophenyl)-1*H*-tetrazol-5-yl]-4,6-dimethylthieno[2,3-*b*]pyridin-3-amine (6c). Yield 3.09 g (91%) (method II), beige powder, mp 237–239°C (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.43 (3H, s, CH_3); 2.76 (3H, s, CH_3); 6.95 (2H, br. s, NH_2); 7.05 (1H, s, H-5); 7.55 (2H, t, *J* = 8.3, H-3',5'); 7.82 (2H, dd, *J* = 8.3, *J* = 4.3, H-2',6'). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 19.8; 23.7; 86.1; 116.7 (d, $^2J_{CF}$ = 24.3); 121.4; 122.0; 129.4; 130.8 (d, $^3J_{CF}$ = 8.7); 144.3; 146.1; 151.5; 158.4; 159.9; 163.7 (d, $^1J_{CF}$ = 249.7). Found, %: C 56.55; H 3.83; N 24.60; S 9.35. $C_{16}H_{13}FN_6S$. Calculated, %: C 56.46; H 3.85; N 24.69; S 9.42.

2-[1-(4-Chlorophenyl)-1*H*-tetrazol-5-yl]-4,6-dimethylthieno[2,3-*b*]pyridin-3-amine (6d). Yield 3.36 g (94%) (method II), light-beige powder, mp 238–239°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 2.43 (3H, s, CH_3); 2.75 (3H, s, CH_3); 6.94 (2H, br. s, NH_2); 7.04 (1H, s, H-5); 7.78 (4H, s, H Ar). ^{13}C NMR spectrum, δ, ppm: 19.9; 23.7; 86.0; 121.4; 122.1; 129.8; 130.2; 132.1; 136.6; 144.5; 146.2; 151.4; 158.6; 159.9. Found, %: C 53.77; H 3.51; N 23.39; S 9.03. $C_{16}H_{13}ClN_6S$. Calculated, %: C 53.86; H 3.67; N 23.55; S 8.98.

2-[1-(4-Bromophenyl)-1*H*-tetrazol-5-yl]-4,6-dimethylthieno[2,3-*b*]pyridin-3-amine (6e). Yield 3.85 g (96%) (method II), pink-beige powder, mp 253–255°C (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.47 (3H, s, CH_3); 2.79 (3H, s, CH_3); 6.89 (2H, br. s, NH_2); 6.97 (1H, s, H-5); 7.60 (2H, d, *J* = 7.9, H-2',6'); 7.85 (2H, d, *J* = 7.9, H-3',5'). ^{13}C NMR spectrum, δ, ppm: 19.9; 23.7; 85.9; 121.4; 122.0; 125.2; 130.2; 132.4; 132.7; 144.4; 146.2; 151.3; 158.5; 159.9. Found, %: C 47.99; H 3.41; N 20.88; S 8.05. $C_{16}H_{13}BrN_6S$. Calculated, %: C 47.89; H 3.27; N 20.94; S 7.99.

4,6-Dimethyl-2-{1-[3-(trifluoromethyl)phenyl]-1*H*-tetrazol-5-yl}thieno[2,3-*b*]pyridin-3-amine (6f). Yield 3.67 g (94%) (method II), light-beige powder, mp 254–256°C (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.44 (3H, s, CH_3); 2.78 (3H, s, CH_3); 7.00 (2H, br. s, NH_2); 7.08 (1H, s, H-5); 7.95 (1H, t, *J* = 7.9, H-5'); 8.10 (1H, d, *J* = 7.9, H-4'); 8.18 (1H, d, *J* = 7.9, H-6'); 8.33 (1H, s, H-2'). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 19.8; 23.6; 85.7; 121.4; 122.0; 123.3 (q, $^1J_{CF}$ = 272.3); 125.4 (q, $^3J_{CF}$ = 4.3); 128.3 (q, $^3J_{CF}$ = 4.3); 130.3 (q, $^2J_{CF}$ = 32.9); 131.0; 132.3; 133.9; 144.4; 146.3; 151.4; 158.5; 159.7. Mass spectrum, *m*/*z* (I_{rel}, %): 390 $[M]^+$ (68), 362 $[M–N_2]^+$ (66), 341 (10), 231 (55), 203 (34), 190 (54), 172 (28), 164 (89), 145 (100). Found, %: C 52.12; H 3.30; N 21.35; S 8.22. $C_{17}H_{13}F_3N_6S$. Calculated, %: C 52.30; H 3.36; N 21.53; S 8.21.

4,6-Dimethyl-2-{[(3,5-dimethyl-1,2-oxazol-4-yl)methyl]sulfanyl}pyridine-3-carbonitrile (8). A solution of 4-(chloromethyl)-3,5-dimethyl-1,2-oxazole (**9**) (1.46 g, 10 mmol) in MeOH (6 ml) was added to a solution of NaOH (0.44 g, 11 mmol) and compound **4** (1.64 g, 10 mmol) in MeOH (15 ml). The reaction mixture was stirred at 50–60°C for 3 h. H_2O (7 ml) was then added, and the mixture was kept at 5–10°C for 12 h. The formed precipitate was filtered off, washed with MeOH–H_2O, 3:1 mixture (10 ml), and recrystallized from the same mixture. Yield 1.98 g (73%), colorless crystals, mp 90–92°C. ^{1}H NMR spectrum, δ, ppm: 2.23 (3H, s, CH_3); 2.39 (3H, s, CH_3); 2.42 (3H, s, CH_3); 2.53 (3H, s, CH_3); 4.33 (2H, s, CH_2); 7.14 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 10.4; 11.5; 20.2; 22.3; 24.8; 105.2; 109.9; 115.0; 120.5; 152.2; 159.7; 161.0; 161.4; 166.7. Mass spectrum, *m*/*z* (I_{rel}, %): 273 $[M]^+$ (16), 164 (78), 142 (13), 110 (44), 68 (100). Found, %: C 61.58; H 5.61; N 15.26; S 11.69. $C_{14}H_{15}N_3OS$. Calculated, %: C 61.52; H 5.53; N 15.37; S 11.73.

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