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Chemistry of Heterocyclic Compounds **2020**, *56*(8), 1078–1091

3-Amino(azido)-4,6-aryl(hetaryl)thieno[2,3-*b*]pyridines and benzo(furo,thieno)[*c*]thieno[2,3,4-*i*,*j*]-2,7-naphthyridines on their basis: synthesis, spectral properties, and prediction of biological activity

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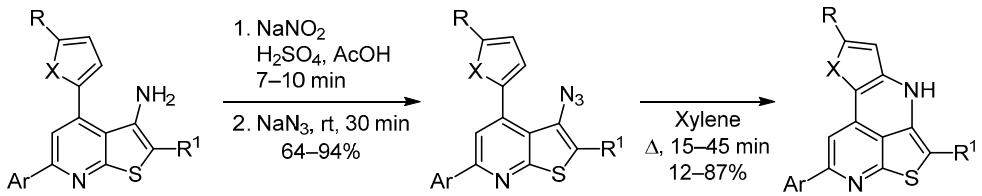


3-Azido-4,6-diarylthienopyridines obtained from the corresponding 3-amino derivatives are convenient precursors in the synthesis of the *peri*-annulated heterocyclic system, benzo(furo,thieno)[*c*]thieno[2,3,4-*i*,*j*]-2,7-naphthyridines. The spectral characteristics of the obtained compounds (IR, UV, NMR (^{1}H, ^{13}C, ^{1}H–^{15}N gHMBC) spectra, luminescence spectra, mass spectra) were studied. Computational prediction of potential biological action has been performed.

Keywords: 3-aminothieno[2,3-*b*]pyridines, 3-azidothieno[2,3-*b*]pyridines, condensed 2,7-naphthyridines, luminescence, thermolysis.

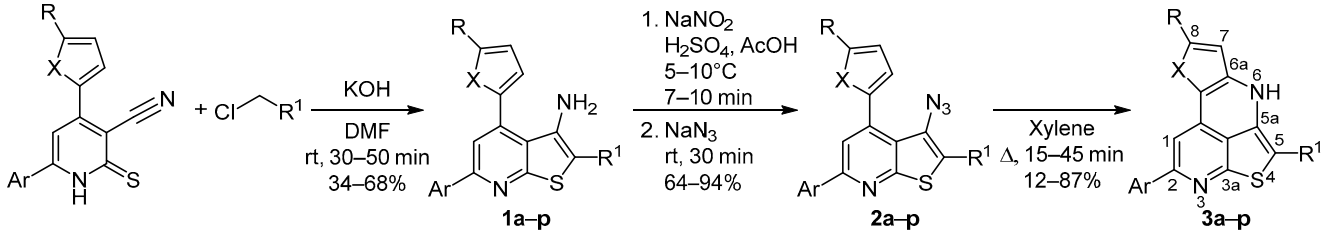
We have shown earlier[1–4] that 3-amino-4,6-dialkylthieno-[2,3-*b*]pyridines can be easily converted to the corresponding azides *via* diazonium salts. Thermal decomposition of 4,6-dialkyl-3-azidothieno[2,3-*b*]pyridines grants access to various condensed systems: isoxazolo[3',4':4,5]thieno[2,3-*b*]-pyridines,[2] 5*H*-pyrido[3',2':4,5]thieno[3,2-*b*]indoles,[3] 7,12-dihydro-6*H*-pyrido[3',2':4,5]thieno[3,2-*b*][1,5]benzodiazepin-6-ones.[4] The azide fragment in thienopyridines is employed as a 1,3-dipole to obtain pyrido[3',2':4,5]thieno[2,3-*e*]-[1,2,3]triazolo[1,5-*a*]pyrimidin-5(4*H*)-ones.[5]

We showed in preliminary reports[6,7] that 4,6-diaryl-3-azidothieno[2,3-*b*]pyridines are convenient precursors in the synthesis of derivatives of benzothieno[2,3,4-*i*,*j*]-2,7-naphthyridine, a novel *peri*-annulated heterocyclic system with a 17π-electronic framework. When working with 3-amino- and 3-azidothienopyridines and conversion products of the latter,[6,7] we noticed that derivatives containing aryl substituents at positions 4 and 6 in the solid state and in solutions exhibit a fairly strong luminescence in sunlight and especially upon irradiation with UV light.

The aim of this work was to obtain a series of new 3-amino(azido)-4,6-diaryl(hetaryl)thieno[2,3-*b*]pyridines and, on their basis, a series of naphthyridine derivatives to study the change in the spectral characteristics of compounds upon the transition from amine → azide → naphthyridine, including luminescent properties, since, as far as we know, fluorescent properties were found only for 6,7-dihydrobenzo-[*f*]thieno[2,3-*c*]isoquinolines,[8] analogs of 3-amino-6-furyl-(thienyl)-4-phenylthienopyridine and 3-amino-6-aryl-4-cyano-thienopyridines.[9a] The luminescent properties of 3-amino-(azido)-4,6-diarylthienopyridines and benzothieno[2,3,4-*i*,*j*]-2,7-naphthyridines have not been described in the literature.

3-Amino-4,6-diaryl(hetaryl)thieno[2,3-*b*]pyridines **1a**–**p**, obtained by us earlier in the reaction of the corresponding

Scheme 1



	Ar	X	R	R^1
a	Ph	CH=CH	H	CO_2Et
b	4-MeC_6H_4	CH=CH	MeO	CO_2Et
c	4-$MeOC_6H_4$	CH=CH	Me	CO_2Et
d	4-BrC_6H_4	CH=CH	MeO	CO_2Et
e	Ph	CH=CH	MeO	CO_2Et
f	4-MeC_6H_4	CH=CH	3,4-$(MeO)_2$	CO_2Et
g	Ph	O	Me	CO_2Et
h	4-MeC_6H_4	S	H	CO_2Et

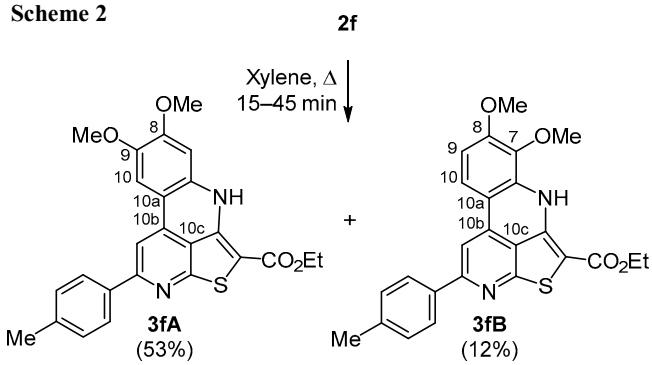
	Ar	X	R	R
i	4-MeC_6H_4	CH=CH	Me	$CO_2C_5H_{11}$
j	Ph	CH=CH	H	CO_2Ph
k	Ph	CH=CH	Me	CO_2Ph
l	Ph	CH=CH	MeO	CO_2(4-MeC_6H_4)
m	Ph	CH=CH	H	CON(Me)Ph
n	Ph	CH=CH	H	$CON(Ph)_2$
o	Ph	CH=CH	H	1-Methylbenzimidazol-2-yl
p	4-BrC_6H_4	CH=CH	Me	1-Methylbenzimidazol-2-yl

4,6-diaryl(hetaryl)-2-thioxo-1,2-dihydropyridine-3-carbonitriles with esters (compounds **1a**,**g**,**i**,**j**,**l**)[6] and amides (compounds **1m**,**n**)[7] of chloroacetic acid in an alkaline medium, were used as the starting materials. 2-Thioxo-1,2-dihydropyridine-3-carbonitriles are easily converted in a basic medium to various thienopyridines.[9b,c] To carry out the study, we have synthesized according to a known procedure[1–4] novel thienopyridinyl-3-amines – 3-amino-2-(1-methyl-1*H*-benzimidazol-2-yl)thieno[2,3-*b*]pyridines **1o**,**p**, the products of alkylation of the corresponding 2-thioxo-1,2-dihydropyridine-3-carbonitriles with 2-chloromethyl-1-methyl-1*H*-benzimidazole. Azides **2a**–**p** were synthesized as a result of successive reactions of diazotization of amines **1a**–**p** by $NaNO_2$ in a mixture of concentrated AcOH and H_2SO_4 at 5–10°C and the reaction of the formed diazonium salt with aqueous NaN_3. Thermal decomposition of azides **2a**–**e**,**g**–**p** was carried out by heating in xylene under reflux for 15–45 min until complete conversion of the starting compound **2** (TLC control, Scheme 1).

Upon thermolysis, dimethoxy derivative **2f** forms two structural isomers **3fA** and **3fB**, isolated as individual substances by flash chromatography using the Isolera Spektra One system (Scheme 2). The higher yield of isomer **3fA** (53%) is apparently explained by steric factors. The attack of the electrophile (nitrene) leading to the formation of isomer **3fB** is hampered by adjacent bulky substituents.

The IR spectra of azides **2a**–**p** contain intense absorption bands of the stretching vibrations of the azido group in the region of 2110–2136 cm^{-1}, and there are no absorption bands of the stretching vibrations of NH bonds characteristic of the IR spectra of amines **1a**–**p** and naphthyridines **3a**–**p**. The IR spectra of amines **1a**–**p** and naphthyridines **3a**–**p** show characteristic absorption bands of stretching vibrations of NH bonds (one or two narrow absorption bands in the 3296–3665 cm^{-1} region). It is noteworthy that the positions of the absorption bands of stretching vibrations of CO bonds in the spectra of compounds **1**–**3 a**–**p** differ significantly. In the spectra of amines **1a**–**p** and naphthyridines **3a**–**p**, absorption bands of

Scheme 2



stretching vibrations of CO bonds of ester and amide groups are in the 1578–1686 and 1613–1676 cm^{-1} range, respectively, which indicates strong conjugation of the peculiar enamine system of bonds NH–C=C–C=O in ring B with the carbonyl group of the substituent. Replacement of the electron-donor amine nitrogen (+*M* >> –*I*) by the azido group (+*M* << –*I*) (according to the authors,[10] the Hammett constants of the azido group and fluorine are practically the same) leads to a shift of the bands of the CO bond to the high-frequency region of up to 1700–1715 cm^{-1}, which indicates a significant change in the distribution of electron density in the N_3–C=C–C=O system of bonds.

In the ^1H NMR spectra of amines **1a**–**p** and naphthyridines **3a**–**p** (Figs. 1, 3), the signals of the protons of the NH groups are in different regions: the two-proton singlet signal of the NH_2 group in the spectra of compounds **1a**–**p** is located in the region of 5.22–6.84 ppm, whereas the narrow singlet signal of the typical secondary diarylamino group in the spectra of naphthyridines **3a**–**p** is in the 8.91–10.76 ppm range.

The change in the electron density distribution in the N–C=C–C=O system of bonds is clearly manifested when comparing the ^{13}C NMR spectra of the synthesized compounds (Figs. 1, 3). Thus, in the spectra of amines **1a**–**p** and naphthyridines **3a**–**p**, the signals of carbon atoms C-2 (C-5 for naphthyridines) and C-3 (C-5a for naphthyridines) are in the ranges of 81.4–112.0 and 136.6–148.7 ppm, respectively. Presumably, the strong +*M*-effect of the

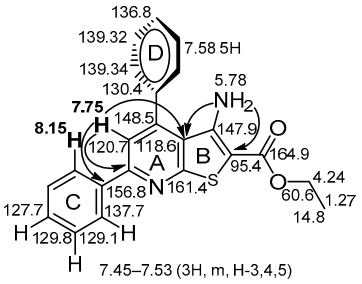


Figure 1. Major correlations and values of chemical shifts (δ, ppm) in ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC spectra of compound **1a**.

amino group in relation to the formally double bond C(2)=C(3) (C(5)=C(5a) for naphthyridines) leads to an increase in the shielding of the C-2 carbon atom (C-5 in compounds **3a**–**p**) and deshielding of the C-3 (C-5a for naphthyridines), which is manifested in the position of the signals of these atoms in the ^{13}C NMR spectra. In the ^{13}C NMR spectra of azides **2a**–**p**, the signals of the corresponding carbon atoms are in the 113.0–121.7 and 126.2–135.5 ppm ranges (Fig. 2), which once again confirms the electron acceptor character of the azido group.

Note also the clearly manifested effect of the π-deficient pyridine ring A on the chemical shifts of the atoms of the aryl rings C and D in the ^{1}H and ^{13}C NMR spectra of the molecules of compounds **1**–**3 a**–**p**, which is clearly seen in the example of 2,6-diphenyl derivatives **1a**, **2a**, and **3a** (Figs. 1–3). The positions of the signals of hydrogen and carbon atoms of the phenyl ring C are clearly determined by the strong electron-withdrawing effect of the π-deficient pyridine ring A on the redistribution of the electron density in the phenyl ring C: the signals of hydrogen atoms form a typical five-spin system AA'MM'X, typical, for example, of nitrobenzene. On the contrary, the signals of all five hydrogen atoms of the phenyl substituent D of amine **1a** and azide **2a** are singlets at 7.58 and 7.46 ppm, respectively, characteristic, for example, of toluene. That is, in this case, the pyridine fragment practically does not have an acceptor effect on the electronic system of the phenyl substituent D. Perhaps this is the result of the steric effect of amino and azido groups, which does not allow the aryl substituent of ring D to be located in the plane of the pyridine ring and leads to the lack of conjugation between the π-electronic systems of rings A and D. As a result of intramolecular closure of ring E and the formation of a

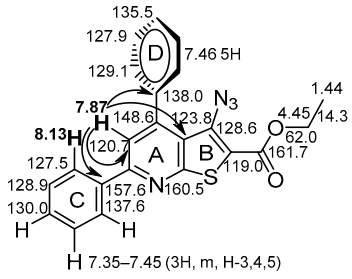


Figure 2. Major correlations and values of chemical shifts (δ, ppm) in ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC spectra of compound **2a**.

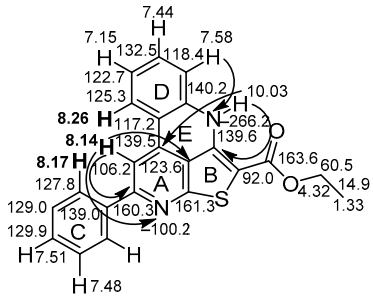


Figure 3. Major correlations and values of chemical shifts (δ, ppm) in ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, and ^{1}H–^{15}N gHMBC spectra of compound **3a** (arrows indicate correlations ^{1}H–^{13}C and ^{1}H–^{15}N).

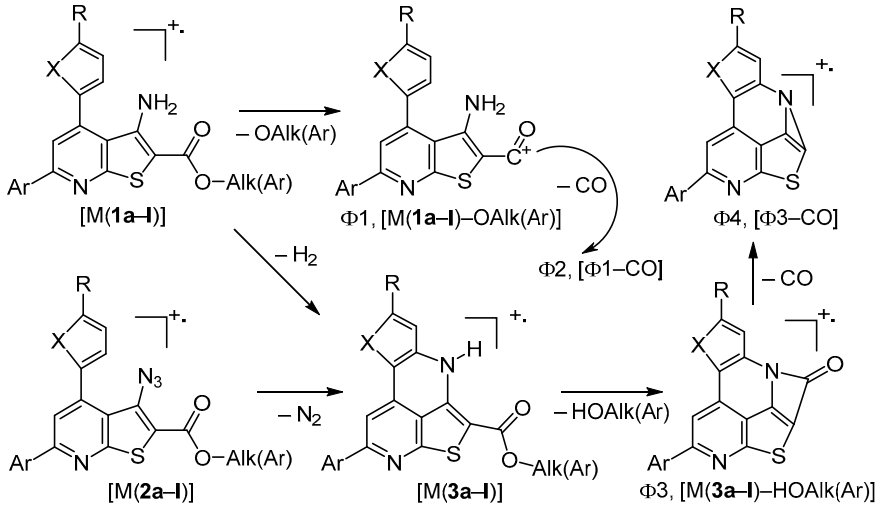
planar benzonaphthyridine system, in the ^{1}H NMR spectra of naphthyridines **3**, typical signals of spin systems ABCD (compounds **3a**,**j**,**m**–**o**) and AMX (compounds **3b**–**e**,**i**,**k**,**l**,**p**) appear, which are characteristic of 1,2-di- and 1,2,4-trisubstituted benzene derivatives. ^{1}H NMR spectra make it easy to distinguish the structural isomers **3fA** and **3fB**: in the spectrum of 8,9-dimethoxy derivative **3fA**, two single-proton singlet signals of the atoms H-7 (6.31 ppm) and H-10 (7.02 ppm) are observed, while the spectrum of isomer **3fB** contains a coupled pair of one-proton doublets, signals of hydrogen atoms H-9 (6.54 ppm) and H-10 (7.37 ppm) with a coupling constant of 8.9 Hz.

In the ^{1}H–^{15}N gHMBC correlation spectra of naphthyridines **3a**,**f**, two cross peaks corresponding to the spin-spin interaction between atoms H-7/N-6 and H-1/N-3 are observed, which, on the one hand, proves the structure of the obtained compounds, and, on the other, allows the determination of the chemical shifts of nitrogen atoms: the amine nitrogen atom N-6 resonates in the region of –266.2÷–268.6 ppm, while the pyridine nitrogen atom is in the –93.5÷–100.6 ppm range. Moreover, in some cases, it is possible to observe the spin-spin interaction of the hydrogen atom H-6 with nitrogen atom N-6 and determine the value of the CSCC $^{1}J_{HN}$ equal to 92–97 Hz. In the ^{1}H–^{15}N gHMBC spectrum of isomer **3fA**, two cross peaks at 6.34/–268.6 and 7.34/–100.6 ppm are observed, corresponding to the spin interaction between atoms H-7/N-6 and H-1/N-3. In the same spectrum of isomer **3fB**, only one cross peak at 7.40/–93.5 ppm is present, which corresponds to the spin-spin interaction of atoms H-1/N-3, additionally confirming the structures of the obtained compounds **3fA** and **3fB**. The ^{1}H–^{15}N gHMBC spectrum of monomethoxy derivative **3e** (DMSO-d_6, 100°C), like the spectrum of compound **3fA**, exhibits two cross peaks at 7.11/–204.5 and 7.89/–113.2 ppm, corresponding to the spin–spin interaction between atoms H-7/N-6 and H-1/N-3.

As a result of intramolecular cyclization, a single singlet signal of the hydrogen atom H-7 of the furan ring is observed in the ^{1}H NMR spectrum of the furan derivative **3g**, whereas in the spectrum of bisthiophene derivative **3h**, a pair of doublets with a SSCC of 5.3 Hz, typical of 2,3-disubstituted thiophenes, is recorded.

The formation of the naphthyridine fragment leads to intramolecular contacts of hydrogen atoms H-1 and H-10,

Scheme 3



which distorts the sphericity of their electron shells and, as a consequence, displaces their signals into anomalously strong fields in the ^{1}H NMR spectra (Fig. 3). It is possible that the position of the H-10 proton signal is also influenced by the electron-withdrawing action of the pyridine ring A, since in the benzonaphthyridine system conjugation undoubtedly exists between the aryl and pyridine aromatic systems.

In the spectra of furo- and thienonaphthyridines **3g** and **3h**, in which the H(1)···H(10) contacts characteristic of benzonaphthyridines are absent, the signals of atoms H-1 are located upfield (at 7.15 and 7.36 ppm, respectively).

Thus, according to the IR and NMR spectra, the transition from amines **1a**–**p** to azides **2a**–**p** leads to the loss of conjugation in the N–C=C–C=O bond system. On the contrary, during the transition azide → naphthyridine an electronic system similar to the system in starting amines **1a**–**p** in molecules **3a**–**p** is restored, which, as shown below, is also manifested in the electronic absorption and luminescence spectra.

In electron ionization mass spectra of compounds **1a**–**n** (Scheme 3), peaks of molecular ions are always present, the further fragmentation of which is associated with the characteristic processes of destruction of ester and amide groups. In addition, a series of peaks starting from [M–H_2], characteristic of the fragmentation of the corresponding naphthyridines are observed, that is, the cyclization in the gas phase of the amine radical cation → naphthyridine radical cation with the release of a hydrogen molecule probably occurs. On the contrary, in the mass spectra of azides **2a**–**p**, the molecular ion peak is either absent or has an extremely low intensity. The [M–N_2] peaks have the maximum intensity, fragmentation of which is identical to the fragmentation of the corresponding naphthyridines **3**. That is, in this case, the nitrene radical cation arising in the gas phase may cyclize into the corresponding naphthyridine radical cation. Benzimidazolyl derivatives **1o**,**p** and **3o**,**p** are characterized by resistance to electron impact: their mass spectra contain peaks of molecular ions of maximum intensity and several low-intensity peaks of intermediate fragmentation products.

The presence in the molecules of compounds **1**–**3 a**–**p** of several aromatic fragments differently conjugated to each other leads to the appearance of rather complex electronic absorption spectra, which have 3 or 4 maxima in the UV region and a "shoulder" in the visible region of the spectrum, which ultimately determines the color of the molecules. Typical UV absorption and emission spectra of amine **1a**, azide **2a**, and naphthyridine **3a** are shown in Figure 4. For amines **1**, four absorption lines in the ranges of 250, 300, 350, and 400 nm are the most prominent. The spectra of naphthyridines **3** keep this general pattern, although most of the absorption bands undergo a bathochromic shift, which is obviously associated with the expansion of conjugation in the planar aromatic system.

The relative intensity of the absorption bands also changes, although the absorption band in the region of 320–350 nm, which corresponds to the absorption of the heterocyclic conjugated system, is the most intense.[11] In the spectra of azides, two broad high-intensity lines are most visible, with the rest either having low intensity or overlapping with more intense ones. There is also a noticeable shift of the absorption bands to longer wavelengths due to the replacement of the amino group by the highly electronegative azide group. This effect is comparable to the effect of the expansion of the conjugated aromatic system observed in naphthyridines, and is possibly due to a decrease in the energy level of HOMO. An analysis of the absorption spectra shows that the most optimal band for the excitation of luminescence is an intense band in the range of 300–350 nm, which was taken into account when recording the luminescence spectra (Table 1).

The luminescence spectra of all studied compounds are broad bands (100–150 nm). The maximum emission is observed in the 449.5–558.5 nm range, and the same tendency as in the case of absorption spectra can be observed: a bathochromic shift on going from amine to azide and then to naphthyridine. For triad **1–3 m**, the same order is observed, but for amine **1m** the value of the luminescence maximum is much lower (449.5 nm), and for naphthyridine **3m** it is much higher (541 nm). For triad

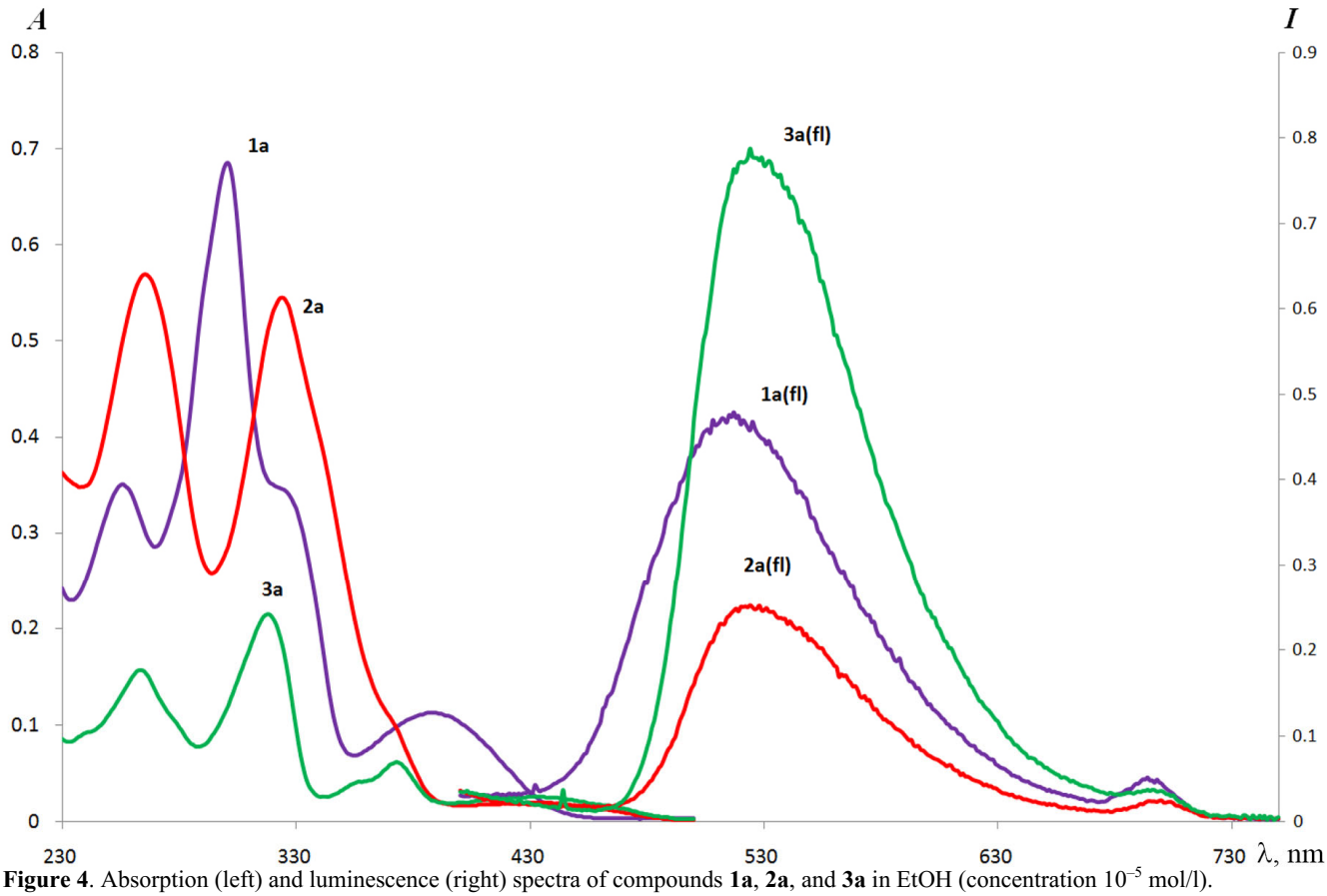


Figure 4. Absorption (left) and luminescence (right) spectra of compounds **1a**, **2a**, and **3a** in EtOH (concentration 10^{-5} mol/l).

1–**3 i**, the pattern of luminescence of amine **1i** and naphthyridine **3i** is similar to the luminescence of the series of compounds **1**, **3 a**,**b**, although azide **2i** has an anomalous luminescence spectrum with a very low intensity and a maximum at 558.5 nm. Based on the obtained luminescence spectra, the luminescence quantum yield φ of the studied compounds was calculated (Table 1). The highest values of the quantum yield are for amine **1i** (61.271%) and azide **2m** (63.698%). The Stokes shift Δλ is defined as the difference between the values of the maxima of intense bands in the luminescence and absorption spectra. As can be seen in Table 1, large values of Δλ (143.5–235.5 nm) are characteristic of all three series of compounds studied by us and coincide with the data presented in the work[9] in which the Stokes shift for 3-amino-6-arylthienopyridine derivatives was given as 131–157 nm.

Table 1. Spectral characteristics of compounds **1**, **2**, **3 a**,**b**,**i**,**m** (EtOH, *c* 1×10^{-5} – 1×10^{-6} mol/l)

Compound	Electronic absorption spectra								Luminescence spectra		
	λ_1, nm	log ε_1	λ_2, nm	log ε_2	λ_3, nm	log ε_3	λ_4, nm	log ε_4	λ_{max}, nm	Δλ, nm	φ*, %
1a	256	4.55	301	4.84	389	4.05	326	4.53	517	216	27.920
2a	266	4.76	323	4.74	371	4.02	433	3.30	525	202	1.549
3a	263	4.19	318	4.33	373	3.79	434	3.41	525	207	25.917
1b	257	4.91	303	4.99	387	4.51	329	4.73	506.5	203.5	13.660
2b	275	4.77	323	4.70	369	4.26			508	185	7.005
3b	278	4.81	333	4.93	373	4.45	429	4.07	517	184	13.710
1i	263	4.24	302	4.55	387	3.83	329	4.26	507.5	205.5	61.271
2i	276	4.74	323	4.69					558.5	235.5	3.229
3i	272	4.78	321	4.88	372	4.37	432	4.00	520	199	8.968
1m	253	4.53	306	4.72	396	4.08	337	4.36	449.5	143.5	6.036
2m	265	4.73	324	4.51	373	4.00			525	201	63.698
3m	265	4.62	325	4.731	379	4.27	437	3.81	541	216	5.153

* Quantum yield φ was calculated using a published method.[10]

At present, a preliminary assessment of the profiles of biological activity at the early stages of research is widely used for the targeted synthesis of new heterocyclic systems with the desired biological activity, which makes it possible to formulate criteria for the selection of the most promising basic structures. Methods based on the structure of the target macromolecule and/or on the structures of ligands are currently widely used to predict the biological activity of chemical compounds.[12]

In this work, the predicted spectrum of targeted biological activity for novel compounds **3a**–**p** was calculated using the original Microcosm BioS system by the method of maximum similarity with standards.[13,14] Among benzothienopyridines **3a**–**p**, compounds were identified with a maximum index of the expected activity level equal to 5. Thus, naphthyridine **3h** is a promising for binding with corticotropin-releasing factor binding protein (CRF-BP), compound **3j** – with type 1 cannabinoid receptors (CB1), compound **3p** – with eukaryotic translation initiation factor 2 alpha-kinase 3, compound **3d** – with myeloid leukemia cells Mcl-1; compounds **3a**,**c**,**d**,**e**,**h**,**j**,**l** – with beta-lactamase, compound **3n** – with the induced differentiation protein of myeloid leukemia cells Mcl-1, compound **3o** – with the VEGFR-2 receptor, compounds **3b**,**c** – with ATP-binding cassette transporter (ABCG2), compounds **3h**,**j**,**m** – with the Epstein–Barr virus gene (BZLF2), compounds **3i**,**j**,**l**,**m**,**n** – with mitogen-activated protein kinase kinase kinase 8. The high level of expected activity for corticotropin-releasing factor binding protein (CRF-BP) found for compound **3h** makes it very interesting for further investigation. Corticotropin-releasing factor (CRF) and peptides of the CRF family are major regulators of the stress response due to their dual roles as hormones and neuromodulators acting in response to stress.[15] Therefore, the data obtained using the Microcosm BioS system suggests that compound **3h** is of interest as a very promising stress response regulator that can be used to reduce the consequences of post-traumatic stress disorder and various neurodegenerative diseases. A similar application is predicted for compound **3j**, which shows high potential activity against the target protein of type 1 cannabinoid receptors (CB1).

In addition, compounds **3a**,**c**,**d**,**e**,**h**,**j**,**l** are likely to have high inhibitory activity toward beta-lactamase, the enzyme responsible for the formation of resistance to beta-lactam antibiotics (penicillins, cephalosporins). Attention is drawn to the activity predicted for compounds **3i**,**j**,**l**,**m**,**n** with a high index against the target protein of mitogen-activated protein kinase kinase kinase 8, which is a component of signaling pathways that are responsible for immune inflammatory processes. The obtained results indicate that benzonaphthyridines are very promising for molecular docking and additional assessment by biological tests *in vitro* and *in vivo*.

In conclusion, it should be noted that, according to the spectral data, the obtained pericyclic system of benzo(furo,thieno)naphthyridine containing 18π-electrons and 17π-electron system is an electronic analog of 2-amino-4-aryl(hetaryl)thieno[2,3-*b*]pyridine. It was shown by the ^{1}H–^{15}N gHMBC method that the nitrogen atom N-6 of benzo(furo,thieno)naphthyridine molecules is a common nitrogen atom of the secondary diarylamino group and, by its electronic action, has the same effect on the thienopyridine system as the amino group in position 3 of aminothienopyridines. It was experimentally established that 2-amino(azido)-4,6-diarylthienopyridines and benzonaphthyridines are luminophores with high Stokes shift values (143.5–235.5 nm). It has been shown by the method of computer prediction that the search for substances with high biological activity among benzonaphthyridines is promising.

Experimental

IR spectra were registered on a PerkinElmer Spectrum Two FT-IR spectrometer with the ATR attachment. ^{1}H, ^{13}C, ^{15}N NMR and correlation spectra were acquired on an Agilent 400-MR spectrometer (400, 101, and 41 MHz, respectively) in DMSO-d_6 or $CDCl_3$ at room temperature (unless indicated otherwise). The full assignment of signals in the spectra was done using COSY, ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, and ^{1}H–^{15}N gHMBC correlation techniques. Chemical shifts of signals are given relative to TMS (hydrogen and carbon atoms) or relative to nitromethane (nitrogen atoms). Mass spectra were recorded on a Kratos MS-30 apparatus, EI ionization (70 eV). Elemental analysis was performed on a Flash EA 1112 CHN-analyzer. Melting points were determined on a Stuart SMP 30 apparatus and are uncorrected. Absorption spectra in the UV and visible regions were recorded on a U-3900 spectrophotometer (Hitachi), luminescence and excitation spectra were acquired on a Fluorat-02-Panorama fluorimeter (Lumex) in EtOH in quartz cells with a thickness of the absorbing layer of 1 cm at a sample concentration of 10^{-5} mol/l. The determination of luminescence quantum yield was carried out according to a published procedure[10] using a solution of quinine bisulfate in 0.5 M H_2SO_4 as a standard. Sorbfil (Sorbpolimer) plates were used for TLC, visualization in iodine or bromine vapor. An Isolera Spektra One flash chromatographic system was used for preparative separation of the mixture of structural isomers **3fA** and **3fB** (eluent hexane–EtOAc, gradient of EtOAc from 40 to 55%, Biotage Snap Cartridge KP-Sil 50g).

Compounds **1a**,**g**,**j**,[6] **1m**,**n**,[7] **2a**,**g**,**j**,[6] **2m**,**n**,[7] **3a**,**g**,**j**,[6] and **3m**,**n**[7] have been described by us earlier.

Synthesis of 3-amino-4,6-diaryl(hetaryl)thieno[2,3-*b*]-pyridines 1a–p (General method[1–4]). The alkylating agent (2 mmol) was added to a mixture of 2-thioxo-1,2-dihydropyridine-3-carbonitrile (2 mmol), 10% aqueous KOH (11.2 ml, 2 mmol), and DMF (20 ml). The reaction mixture was stirred at room temperature for 30–40 min until a precipitate formed, which was separated by filtration, washed with cold EtOH (7 ml), and air-dried. Then the precipitate was dissolved in DMF (10 ml), one more portion of KOH solution (1 mmol) was added, and the reaction mixture was stirred on a magnetic stirrer for 30–50 min until the formation of a precipitate. The crystals were separated by filtration and washed with cold EtOH (7 ml).

Ethyl 3-amino-4,6-diphenylthieno[2,3-*b*]pyridine-2-carboxylate (1a). Yield 441 mg (59%), yellow crystals, mp 154–155°C (EtOH). IR spectrum, ν, cm^{-1}: 1674 (C=O), 3355–3493 (NH_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.27 (3H, t, *J* = 7.2, $C\underline{H}_3CH_2O$); 4.24 (2H, q, *J* = 7.2, $CH_3C\underline{H}_2O$); 5.78 (2H, br. s, NH_2); 7.45–7.53 (3H, m, H-3,4,5 6-Ph); 7.58 (5H, s, H 4-Ph); 7.75 (1H, s, H-5); 8.15 (2H, d, *J* = 8.3, H-2,6 6-Ph). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.8 ($\underline{C}H_3CH_2O$); 60.6 ($CH_3\underline{C}H_2O$); 95.4 (C-2), 118.6 (C-3a); 120.7 (C-5); 127.7 (C-3,5 6-Ph); 129.1 (C-2,6 6-Ph); 139.3 (C-2,3,5,6 4-Ph); 129.8 (C-4 6-Ph); 130.4 (C-1 4-Ph); 136.8 (C-4 4-Ph); 137.7 (C-1 6-Ph); 147.9 (C-3); 148.5 (C-4); 156.8 (C-6); 161.4 (C-7a); 164.9 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 375 $[M+H]^+$ (26), 374 $[M]^+$ (100), 345 (14), 327 (22), 326 (44), 301 (17), 300 (10), 299 (16), 298 (53), 59 (10), 58 (11), 43 (41), 42 (26). Found, %: C 70.64; H 4.76; N 7.50. $C_{22}H_{18}N_2O_2S$. Calculated, %: C 70.57; H 4.85; N, 7.48.

Ethyl 3-amino-4-(4-methoxyphenyl)-6-(4-methylphenyl)thieno[2,3-*b*]pyridine-2-carboxylate (1b). Yield 535 mg (64%), yellow powder, mp 162–163°C (EtOAc). IR spectrum, ν, cm^{-1}: 1667 (C=O), 3358–3481 (NH_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.31 (3H, t, *J* = 7.3, $C\underline{H}_3CH_2O$); 2.40 (3H, s, CH_3); 3.87 (3H, s, OCH_3); 4.28 (2H, q, *J* = 7.3, $CH_3C\underline{H}_2O$); 5.86 (2H, s, NH_2); 7.10 (2H, d, *J* = 8.1, H-3,5 $C_6H_4OCH_3$); 7.31 (2H, d, *J* = 8.1, H-2,6 $C_6H_4OCH_3$); 7.50 (2H, d, *J* = 8.8, H-3,5 $C_6H_4CH_3$); 7.71 (1H, s, H-5); 8.10 (2H, d, *J* = 8.8, H-2,6 $C_6H_4CH_3$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.5; 20.8; 55.2; 59.8; 90.5; 101.2; 104.3; 109.9; 110.1; 122.0; 126.0; 127.0 (2C); 129.0 (2C); 135.7; 138.7; 139.0; 139.2; 141.3; 158.1; 160.3; 162.2; 163.0. Mass spectrum, *m*/*z* (I_{rel}, %): 419 $[M+H]^+$ (26), 418 $[M]^+$ (100), 416 (11), 373 (15), 372 (17), 371 (72), 345 (10), 344 (11), 343 (12), 301 (12), 44 (13). Found, %: C 68.84; H 5.27; N 6.61. $C_{24}H_{22}N_2O_3S$. Calculated, %: C 68.88; H 5.30; N 6.69.

Ethyl 3-amino-4-(4-methylphenyl)-6-(4-methoxyphenyl)thieno[2,3-*b*]pyridine-2-carboxylate (1c). Yield 376 mg (45%), yellow powder, mp 164–166°C (EtOAc). IR spectrum, ν, cm^{-1}: 1667 (C=O), 3342–3480 (NH_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.28 (3H, t, *J* = 7.3, $C\underline{H}_3CH_2O$); 2.48 (3H, s, CH_3); 3.80 (3H, s, OCH_3); 4.28 (2H, q, *J* = 7.3, $CH_3C\underline{H}_2O$); 5.22 (2H, s, NH_2); 7.03 (2H, d, *J* = 8.0, H-3,5 $C_6H_4OCH_3$); 7.35 (2H, d, *J* = 8.3, H-3,5 $C_6H_4CH_3$); 7.55 (2H, d, *J* = 8.3, H-2,6 $C_6H_4CH_3$); 7.62 (1H, s, H-5); 8.12 (2H, d, *J* = 8.0, H-2,6 $C_6H_4OCH_3$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 13.9; 20.4; 52.7; 59.1; 93.9; 112.6; 112.9 (2C); 122.3; 125.3 (2C); 127.4 (2C); 127.8 (2C); 136.3; 138.7; 139.8; 139.9; 143.1 159.2 (2C); 161.3; 162.9. Mass spectrum, *m*/*z* (I_{rel}, %): 419 $[M+H]^+$ (16), 418 $[M]^+$ (100), 373 (11), 372 (15), 371 (28), 343 (15), 44 (17), 41 (10). Found, %: C 69.00; H 5.38; N 6.81. $C_{24}H_{22}N_2O_3S$. Calculated, %: C 68.88; H 5.30; N 6.69.

Ethyl 3-amino-6-(4-bromophenyl)-4-(4-methoxyphenyl)thieno[2,3-*b*]pyridine-2-carboxylate (1d). Yield 386 mg (40%), yellow powder, mp 176–177°C (EtOAc). IR spectrum, ν, cm^{-1}: 1670 (C=O), 3350–3488 (NH_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.30 (3H, t, *J* = 7.3, $C\underline{H}_3CH_2O$); 3.84 (3H, s, CH_3O); 4.28 (2H, q, *J* = 7.3, $CH_3C\underline{H}_2O$); 5.80 (2H, s, NH_2); 7.10 (2H, d, *J* = 8.8, H-3,5 $C_6H_4OCH_3$); 7.50 (2H, d, *J* = 8.8, H-2,6 $C_6H_4OCH_3$); 7.70 (2H, d, *J* = 8.1, H-3,5 C_6H_4Br); 8.00 (1H, s, H-5); 8.10 (2H, d, *J* = 8.1, H-2,6 C_6H_4Br). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.3 ($\underline{C}H_3CH_2O$); 54.2 (OCH_3); 60.7 ($O\underline{C}H_2O$); 96.7 (C-2); 117.9 (C-5); 114.0 (C-3,5 $C_6H_4OCH_3$); 122.2 (C-3a); 127.8 (C-2,6 $C_6H_4OCH_3$); 128.8 (C-2,6 C_6H_4Br); 129.4 (C-1 $C_6H_4OCH_3$); 131.2 (C-3,5 C_6H_4Br); 132.2 (C-4 C_6H_4Br); 138.2 (C-1 C_6H_4Br); 147.3 (C-4); 148.0 (C-3); 154.1 (C-6); 160.1 (C-4 $C_6H_4OCH_3$); 162.3 (C-7a); 163.6 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 485 $[M]^+$(19), 484 $[M]^+$ (99), 483 $[M]^+$ (22), 482 $[M]^+$ (100), 439 (27), 437 (27), 237 (22), 161 (26), 133 (10), 91 (12), 90 (11), 45 (21), 44 (43), 43 (23). Found, %: C 58.15; H 3.96; N 5.80. $C_{23}H_{19}BrN_2O_3S$. Calculated, %: C 58.22; H 3.88; N 5.87.

Ethyl 3-amino-4-(4-methoxyphenyl)-6-phenylthieno-[2,3-*b*]pyridine-2-carboxylate (1e). Yield 364 mg (45%), yellow powder, mp 164–166°C (EtOH). IR spectrum, ν, cm^{-1}: 1675 (C=O), 3338–3450 (NH_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.38 (3H, t, *J* = 7.2, $C\underline{H}_3CH_2O$); 3.81 (3H, s, OCH_3); 4.32 (2H, q, *J* = 7.2, $CH_3C\underline{H}_2O$); 5.75 (2H, s, NH_2); 7.05 (2H, d, *J* = 8.4, H-3,5 $C_6H_4OCH_3$); 7.41 (2H, d, *J* = 8.4, H-2,6 $C_6H_4OCH_3$); 7.43 (1H, t, *J* = 7.5, H-4 Ph); 7.45 (2H, d, *J* = 7.5, H-3,5 Ph); 7.45 (1H, s, H-5); 8.08 (2H, d, *J* = 7.5, H-2,6 Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.5 ($C\underline{H}_3CH_2O$); 55.4 (OCH_3); 60.4 ($CH_3C\underline{H}_2O$); 97.1 (C-2); 114.4 (C-3,5 $C_6H_4OCH_3$); 118.4 (C-5); 120.8 (C-3a); 127.4 (C-2,6 Ph); 128.8 (C-2,6 $C_6H_4OCH_3$); 129.1 (C-1 $C_6H_4OCH_3$); 129.6 (C-4 Ph); 129.9 (C-3,5 Ph); 138.4 (C-1 Ph); 147.5 (C-4); 147.7 (C-3); 157.1 (C-6); 160.3 (C-4 $C_6H_4OCH_3$); 162.2 (C-7a); 165.6 (C=O). Found, %: C 68.38; H 4.87; N 6.85. $C_{23}H_{20}N_2O_3S$. Calculated, %: C 68.30; H 4.98; N 6.93.

Ethyl 3-amino-4-(3,4-dimethoxyphenyl)-6-(4-methylphenyl)thieno[2,3-*b*]pyridine-2-carboxylate (1f). Yield 331 mg (38%), yellow powder, mp 164–166°C (EtOAc). IR spectrum, ν, cm^{-1}: 1667 (C=O), 3342–3480 (NH_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.30 (3H, t, *J* = 7.2, $C\underline{H}_3CH_2O$); 2.37 (3H, s, $C\underline{H}_3C_6H_4$); 3.84 (3H, s, 4-OCH_3); 3.87 (3H, s, 3-OCH_3); 4.29 (2H, q, *J* = 7.2, $CH_3C\underline{H}_2O$); 5.85 (2H, s, NH_2); 7.07 (1H, d, *J* = 7.9, H-5 $C_6H_3(OCH_3)_2$); 7.15 (1H, d, *J* = 2.5, H-2 $C_6H_3(OCH_3)_2$); 7.16 (1H, dd, *J* = 7.9, *J* = 2.5, H-6 $C_6H_3(OCH_3)_2$); 7.31 (2H, d, *J* = 7.3, H-3,5 4-$CH_3C_6H_4$); 7.66 (1H, s, H-5); 8.06 (2H, d, *J* = 7.3, H-2,6 4-$CH_3C_6H_4$). ^{13}C NMR spectrum (DMSO-d_6, 100°C), δ, ppm: 15.0 ($\underline{C}H_3CH_2$); 21.1 (4-$\underline{C}H_3C_6H_4$); 56.6 (4-OCH_3); 56.7 (3-OCH_3); 60.5 ($CH_3\underline{C}H_2$); 113.5 (C-5 $C_6H_3(OCH_3)_2$); 113.6 (C-2 $C_6H_3(OCH_3)_2$); 113.9 (C-6 $C_6H_3(OCH_3)_2$); 118.5 (C-5); 120.9 (C-3a); 121.8 (C-1 $C_6H_3(OCH_3)_2$); 127.6 (C-2,6 4-$CH_3C_6H_4$); 129.9 (C-3,5 4-$CH_3C_6H_4$); 135.5 (C-1 4-$CH_3C_6H_4$); 140.0 (C-4 4-$CH_3C_6H_4$); 149.9 (C-4); 150.6 (C-4 $C_6H_3(OCH_3)_2$); 150.9 (C-3 $C_6H_3(OCH_3)_2$); 157.2 (C-6); 161.7 (C-7a); 169.9 (C=O). Found, %: C 69.69; H 5.72; N 6.11. $C_{25}H_{24}N_2O_4S$. Calculated, %: C 66.94; H 5.39; N 6.25.

Ethyl 3-amino-4-(5-methylfuran-2-yl)-6-phenylthieno-[2,3-*b*]pyridine-2-carboxylate (1g). Yield 461 mg (61%), yellow powder, mp 140–141°C (EtOAc). IR spectrum,

ν, cm^{-1}: 1666 (C=O), 3344–3454 (NH_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.30 (3H, t, *J* = 7.1, $C\underline{H}_3CH_2O$); 2.44 (3H, s, CH_3); 4.25 (2H, q, *J* = 7.1, $CH_3C\underline{H}_2O$); 6.43 (1H, d, *J* = 3.6, H-4 furan); 6.84 (2H, s, NH_2); 7.24 (1H, d, *J* = 3.6, H-3 furan); 7.45–7.55 (3H, m, H-3,4,5 Ph); 7.97 (1H, s, H-5); 8.18 (2H, d, *J* = 8.1, H-2,6 Ph). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.0 ($\underline{C}H_3CH_2O$); 14.9 (CH_3 furan); 60.7 ($CH_3\underline{C}H_2O$); 94.9 (C-2); 109.7 (C-4 furan); 115.6 (C-3 furan); 115.9 (C-5); 118.7 (C-3a); 127.6 (C-2,6 6-Ph); 129.3 (C-3,5 6-Ph); 130.5 (C-4 6-Ph); 137.6 (C-1 6-Ph); 148.2 (C-4); 148.7 (C-3); 155.6 (C-2 furan); 156.9 (C-6); 159.9 (C-5 furan); 162.5 (C-7a); 165.0 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 379 (31) $[M+H]^+$, 378 (100) $[M]^+$, 350 (15), 332 (19), 331 (48), 306 (11), 262 (15), 261 (13), 189 (4), 152 (4), 53 (17), 44 (13), 43 (37). Found, %: C 66.80; H 4.85; N 7.51. $C_{21}H_{18}N_2O_3S$. Calculated, %: C 66.65; H 4.79; N 7.40.

Ethyl 3-amino-6-(4-methylphenyl)-4-(thiophen-2-yl)-thieno[2,3-*b*]pyridine-2-carboxylate (1h). Yield 268 mg (34%), bright-yellow powder, mp 154–155°C (EtOAc). IR spectrum, ν, cm^{-1}: 1664 (C=O), 3349–3482 (NH_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.29 (3H, t, *J* = 7.2, $C\underline{H}_3CH_2O$); 2.56 (3H, s, CH_3); 4.27 (2H, q, *J* = 7.1, $CH_3C\underline{H}_2O$); 6.08 (2H, s, NH_2); 7.29 (2H, d, *J* = 8.3, H-3,5 $C_6H_4CH_3$); 7.30 (1H, dd, *J* = 5.6, *J* = 4.3, H-4 thiophene); 7.43 (1H, d, *J* = 4.3, H-3 thiophene); 7.79 (1H, s, H-5); 7.89 (1H, d, *J* = 5.6, H-5 thiophene); 8.07 (2H, d, *J* = 8.3, H-2,6 $C_6H_4CH_3$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.9 ($\underline{C}H_3CH_2O$); 21.4 (CH_3Ph); 60.7 ($CH_3\underline{C}H_2O$); 95.5 (C-2); 119.4 (C-5); 120.6 (C-3a); 127.6 (C-2,6 Ph); 128.5 (C-4 thiophene); 129.7 (C-3 thiophene); 129.9 (C-5 thiophene); 130.0 (C-3,5 Ph); 134.7 (C-4); 136.7 (C-1 Ph); 140.4 (C-4 Ph); 141.0 (C-2 thiophene); 147.9 (C-2); 156.7 (C-6); 161.7 (C-7a); 164.8 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 396 $[M+2]^+$ (11), 395 $[M+H]^+$ (34), 394 $[M]^+$ (100), 349 (31), 321 (17), 29 (15). Found, %: C 63.98; H 4.67; N 7.14. $C_{21}H_{18}N_2O_2S_2$. Calculated, %: C 63.93; H 4.60; N 7.10.

Pentyl 3-amino-4,6-bis(4-methylphenyl)thieno[2,3-*b*]-pyridine-2-carboxylate (1i). Yield 561 mg (63%), yellow crystals, mp 106–107°C (EtOAc). IR spectrum, ν, cm^{-1}: 1666 (C=O), 3347–3483 (NH_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.83 (3H, t, *J* = 6.6, $C\underline{H}_3CH_2CH_2CH_2CH_2O$); 1.16–1.36 (2H, m, $CH_3C\underline{H}_2CH_2CH_2CH_2O$); 1.71–1.75 (2H, m, $CH_3CH_2C\underline{H}_2CH_2CH_2O$); 2.37 (3H, s, 4-$C_6H_4C\underline{H}_3$); 2.42 (3H, s, 6-$C_6H_4C\underline{H}_3$); 4.02–4.06 (2H, m, $CH_3CH_2CH_2C\underline{H}_2CH_2O$); 4.22 (2H, t, *J* = 7.2, $CH_3CH_2CH_2CH_2C\underline{H}_2O$); 5.80 (2H, br. s, NH_2); 7.30–7.34 (4H, m, 4-$C_6\underline{H}_4CH_3$); 7.70 (2H, d, *J* = 8.4, H-3,5 6-$C_6H_4CH_3$); 7.82 (1H, s, H-5); 8.0 (2H, d, *J* = 8.4, H-2,6 6-$C_6\underline{H}_4CH_3$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 16.2 ($\underline{C}H_3CH_2CH_2CH_2CH_2O$); 21.3 (6-$CH_3$); 21.7 (4-$CH_3$); 24.2 ($CH_3\underline{C}H_2CH_2CH_2CH_2O$); 27.1 ($CH_3CH_2\underline{C}H_2CH_2CH_2O$); 28.4 ($CH_3CH_2CH_2\underline{C}H_2CH_2O$); 67.5 ($CH_3CH_2CH_2CH_2\underline{C}H_2O$); 98.1 (C-2); 118.5 (C-5); 122.0 (C-3a); 127.1 (C-2,6 4-$C_6H_4CH_3$); 127.2 (C-3,5 6-$C_6H_4CH_3$); 129.5 (C-3,5 4-$C_6H_4CH_3$); 129.6 (C-1 4-$C_6H_4CH_3$); 130.2 (C-2,6 6-$C_6H_4CH_3$); 136.1 (C-4 6-$C_6H_4CH_3$); 137.7 (C-1 6-$C_6H_4CH_3$); 138.2 (C-4 4-$C_6H_4CH_3$); 145.3 (C-4); 147.7 (C-3); 154.2 (C-6); 161.3 (C-7a); 163.6 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 445 $[M+H]^+$ (20), 444 $[M]^+$ (100), 368 (16), 356 (10), 355 (13), 329 (69), 236 (62), 235 (17), 222 (13), 221 (29), 119 (16), 117 (25), 115 (13), 91 (36), 65 (32), 43 (22), 42 (15), 40 (13). Found, %: C 72.98; H 6.37; N 6.27. $C_{27}H_{28}N_2O_2S$. Calculated, %: C 72.94; H 6.35; N 6.30.

Phenyl 3-amino-4,6-diphenylthieno[2,3-*b*]pyridine-2-carboxylate (1j). Yield 491 mg (58%), yellow crystals, mp 178–179°C (EtOAc). IR spectrum, ν, cm^{-1}: 1686 (C=O), 3356–3493 (NH_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 5.95 (2H, br. s, NH_2); 7.21 (2H, d, *J* = 8.4, H-2,6 COOPh); 7.27 (1H, t, *J* = 8.3, H-4 COOPh); 7.43 (2H, dd, *J* = 8.4, *J* = 8.3, H-3,5 COOPh); 7.48 (2H, t, *J* = 8.0, H-3,5 6-Ph); 7.50 (1H, t, *J* = 8.0, H-4 6-Ph); 7.60 (5H, s, H 4-Ph); 7.79 (1H, s, H-5); 8.21 (2H, d, *J* = 8.0, H-2,6 6-Ph). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 93.7; 118.8; 120.4; 122.5 (2C); 126.3; 127.8 (2C); 129.0 (2C); 129.4 (2C); 129.5 (2C); 129.8; 129.9 (2C); 130.6; 136.6; 137.6; 148.8; 149.7; 150.6; 157.4; 161.8; 163.2. Mass spectrum, *m*/*z* (I_{rel}, %): 423 $[M+H]^+$ (16), 422 $[M]^+$ (90), 331 (12), 330 (24), 329 (100), 301 (18), 300 (35), 299 (11), 241 (5), 227 (4), 224 (4). Found, %: C 73.98; H 4.38; N 6.54. $C_{26}H_{18}N_2O_2S$. Calculated, %: C 73.91; H 4.29; N 6.63.

Phenyl 3-amino-4-(4-methylphenyl)-6-phenylthieno-[2,3-*b*]pyridine-2-carboxylate (1k). Yield 218 mg (25%), yellow crystals, mp 102–103°C (EtOAc). IR spectrum, ν, cm^{-1}: 1686 (C=O), 3352–3452 (NH_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.39 (3H, s, 4-$C_6H_4C\underline{H}_3$); 6.00 (2H, br. s, NH_2); 7.20 (2H, d, *J* = 8.1, H-2,6 COOPh); 7.26 (1H, t, *J* = 8.0, H-4 COOPh); 7.38 (2H, t, H-3,5 COOPh); 7.50–7.65 (7H, m, H Ar); 7.71 (1H, s, H-5); 8.17 (2H, d, *J* = 8.5, H-2,6 6-Ph). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 21.4; 93.6; 118.8; 120.5; 122.5 (2C); 126.8; 127.7 (2C); 128.9 (2C); 129.3 (2C); 129.9 (2C); 130.0 (2C); 130.5; 133.7; 137.7; 139.4; 141.8; 149.8; 150.6; 157.3; 162.0; 163.2. Mass spectrum, *m*/*z* (I_{rel}, %): 437 $[M+H]^+$ (13), 436 $[M]^+$ (39), 344 (25), 343 (100), 300 (18). Found, %: C 74.22; H 4.67; N 6.47. $C_{27}H_{20}N_2O_2S$. Calculated, %: C 74.29; H 4.62; N 6.42.

4-Methylphenyl 3-amino-4-(4-methoxyphenyl)-6-phenyl-thieno[2,3-*b*]pyridine-2-carboxylate (1l). Yield 634 mg (68%), yellow crystals, mp 161–162°C (EtOAc). IR spectrum, ν, cm^{-1}: 1681 (C=O), 3354–3487 (NH_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.29 (3H, s, CH_3); 3.83 (3H, s, OCH_3); 6.03 (2H, br. s, NH_2); 7.07 (2H, d, *J* = 7.8, H-2,6 $C_6H_4CH_3$); 7.13 (2H, d, *J* = 8.1, H-3,5 4-$C_6H_4OCH_3$); 7.20 (2H, d, *J* = 7.8, H-3,5 $C_6H_4CH_3$); 7.48 (2H, t, *J* = 8.0, H-3,5 6-Ph); 7.49 (1H, t, *J* = 8.0, H-5 6-Ph); 7.52 (2H, d, *J* = 8.1, H-2,6 4-$C_6H_4OCH_3$); 7.73 (1H, s, 5-H); 8.20 (2H, d, *J* = 8.0, H-2,6 6-Ph). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 20.9; 55.8; 93.6; 114.9 (2C); 119.0; 120.6; 122.2 (2C); 127.7 (2C); 128.6; 129.3 (2C); 130.2 (2C); 130.5; 130.6 (2C); 135.4; 137.7; 148.4; 148.7; 149.8; 156.3; 160.5; 161.9; 163.4. Mass spectrum, *m*/*z* (I_{rel}, %): 467 $[M+H]^+$ (10), 466

$[M]^+$ (31), 360 (23), 359 (100), 287 (10). Found, %: C 72.12; H 4.77; N 5.94. $C_{28}H_{22}N_2O_3S$. Calculated, %: C 72.08; H 4.75; N 6.00.

3-Amino-*N*-methyl-*N*,4,6-triphenylthieno[2,3-*b*]pyridine-2-carboxamide (1m).[7] Yield 479 mg (55%), bright-yellow crystals, mp 217–218°C (EtOH). IR spectrum, ν, cm^{-1}: 1578 (C=O), 3334–3465 (NH_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.25 (3H, s, NCH_3); 6.08 (2H, br. s, NH_2); 7.37 (2H, d, *J* = 8.1, H-2,6 NPh); 7.46–7.55 (11H, m, H Ph); 7.63 (1H, s, H-5); 8.06 (2H, d, *J* = 8.3, H-2,6 6-Ph). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 39.1; 98.1; 118.4; 120.0; 127.5 (2C); 128.7; 129.1 (2C); 129.2 (4C); 129.3 (2C); 129.6; 130.1 (2C); 130.2; 137.1; 137.8; 143.8; 147.7; 148.0; 156.0; 161.4; 166.1. Mass spectrum, *m*/*z* (I_{rel}, %): 436 $[M+H]^+$ (10), 435 $[M]^+$ (32), 330 (23), 329 (100), 301 (16), 300 (34), 218 (12), 107 (29), 106 (12), 77 (29), 32 (52). Found, %: C 74.42; H 4.79; N 9.67. $C_{27}H_{21}N_3OS$. Calculated, %: C 74.46; H 4.86; N 9.65.

3-Amino-*N*,*N*,4,6-tetraphenylthieno[2,3-*b*]pyridine-2-carboxamide (1n).[7] Yield 477 mg (48%), yellow crystals, mp 257–258°C (EtOH). IR spectrum, ν, cm^{-1}: 1584 (C=O), 3296–3470 (NH_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 6.13 (2H, s, NH_2); 7.25–7.34 (6H, m, H Ph); 7.35–7.48 (7H, m, H Ph); 7.50–7.60 (5H, m, H Ph); 7.65 (1H, s, H-5); 8.09 (2H, d, *J* = 8.1, H-2,6 6-Ph). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 118.4; 120.1; 127.3 (2C); 127.6 (2C); 128.7 (4C); 129.0 (2C); 129.2 (2C); 129.3 (2C); 129.6; 129.7 (4C); 130.1; 137.3; 138.2; 143.7; 143.8 (2C); 148.0; 149.3; 156.7; 161.9; 166.9. Mass spectrum, *m*/*z* (I_{rel}, %): 497 $[M]^+$ (8), 330 (25), 329 (100), 301 (12), 300 (27), 169 (21), 168 (10), 167 (19), 77 (19), 43 (31), 32 (100), 29 (14). Found, %: C 77.18; H 4.72; N 8.49. $C_{32}H_{23}N_3OS$. Calculated, %: C 77.24; H 4.66; N 8.44.

2-(1-Methyl-1*H*-benzimidazol-2-yl)-4,6-diphenylthieno-[2,3-*b*]pyridin-3-amine (1o). Yield 553 mg (64%), yellow crystals, mp 257–259°C (EtOAc). IR spectrum, ν, cm^{-1}: 3249–3476 (NH_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 4.08 (3H, s, NCH_3); 6.25 (2H, br. s, NH_2); 7.12–7.31 (2H, m, H Ar); 7.42–7.53 (3H, m, H Ar); 7.53–7.58 (2H, m, H Ar); 7.60 (5H, s, H 4-Ph); 7.81 (1H, s, H-5); 8.23 (2H, d, *J* = 7.1, H-2,6 6-Ph). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 32.1; 95.6; 110.4; 118.2; 118.8; 121.1; 122.6; 122.7; 127.2 (2C); 127.5 (2C); 129.3 (2C); 129.4 (2C); 129.6; 130.1; 135.8; 137.3; 138.0; 142.4 (2C); 149.8; 154.8; 157.4; 160.5. Mass spectrum, *m*/*z* (I_{rel}, %): 433 $[M+H]^+$ (30), 432 $[M]^+$ (100), 431 (41), 416 (23), 216 (18), 208 (11), 43 (17), 32 (79). Found, %: C 74.92; H 4.71; N 12.91. $C_{27}H_{20}N_4S$. Calculated, %: C 74.97; H 4.66; N 12.95.

6-(4-Bromophenyl)-2-(1-methyl-1*H*-benzimidazol-2-yl)-4-(4-methylphenyl)thieno[2,3-*b*]pyridin-3-amine (1p). Yield 576 mg (55%), yellow crystals, mp 257–258°C (DMSO). IR spectrum, ν, cm^{-1}: 3303–3390 (NH_2). ^1H NMR spectrum (DMSO-d_6, 80°C), δ, ppm (*J*, Hz): 2.39 (3H, s, CH_3); 4.21 (3H, s, NCH_3); 6.16 (2H, br. s, NH_2); 7.16–7.28 (2H, m, H-5,6 benzimidazole); 7.31 (2H, d, *J* = 8.1, H-3,5 $C_6H_4CH_3$); 7.48 (1H, d, *J* = 7.2, H-7); 7.51 (2H, d, *J* = 8.1, H-2,6 $C_6H_4CH_3$); 7.71 (1H, d, *J* = 7.2, H-4); 7.74 (2H, d, *J* = 8.3, H-2,6 C_6H_4Br); 8.17 (2H, d, *J* = 8.3, H-3,5 C_6H_4Br); 8.21 (1H, s, H-5). ^{13}C NMR spectrum (DMSO-d_6, 80°C), δ, ppm: 21.4; 33.4; 97.6; 109.2; 117.7; 118.7; 122.1; 122.5; 122.7; 126.3 (2C); 127.3 (2C); 129.3 (2C); 129.6; 129.8 (2C); 131.6; 134.3; 137.6; 137.9; 139.2; 142.1; 151.9; 156.0; 158.1; 161.0. Mass spectrum, *m*/*z* (I_{rel}, %): 527 $[M]^+$(17), 526 $[M]^+$ (97), 525 $[M]^+$ (15), 395 (60), 393 (65), 81 (22), 79 (25). Found, %: C 64.06; H 3.97; N 10.54. $C_{28}H_{21}BrN_4S$. Calculated, %: C 64.00; H 4.03; N 10.66.

Synthesis of azides 2a–**p** (General method). Azides **2a**–**p** were obtained following a published method[6,7] consisting of successive diazotation of amines **1a**–**p** with $NaNO_2$ in a mixture of concentrated AcOH and H_2SO_4 at 5–10°C and reacting of the formed diazonium salt with aqueous NaN_3. The obtained compounds **2a**–**p** were used in the next steps, generally without additional purification. In the case of some compounds, the formation of azides was proven only by IR spectroscopy.

Ethyl 3-azido-4,6-diphenylthieno[2,3-*b*]pyridine-2-carboxylate (2a). Yield 600 mg (75%), bright-yellow powder, mp 165–166°C (decomp., EtOAc). IR spectrum, ν, cm^{-1}: 1703 (C=O), 2125 (N_3). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.44 (3H, t, *J* = 7.1, $C\underline{H}_3CH_2O$); 4.45 (2H, q, *J* = 7.1, $CH_3C\underline{H}_2O$); 7.35–7.45 (3H, m, H-3,4,5 6-Ph); 7.46 (5H, s, H 4-Ph); 7.87 (1H, s, H-5); 8.13 (2H, d, *J* = 7.0, H-2,6 6-Ph). ^{13}C NMR spectrum, δ, ppm: 14.3 ($\underline{C}H_3CH_2O$); 62.0 ($CH_3\underline{C}H_2O$); 119.0 (C-2); 123.8 (C-3a); 127.5 (C-2,6 6-Ph); 127.9 (C-3,5 4-Ph); 128.6 (C-3); 128.9 (C-3,5 6-Ph); 129.1 (C-2,6 4-Ph); 130.0 (C-4 6-Ph); 135.5 (C-4 4-Ph); 137.6 (C-1 6-Ph); 138.0 (C-1 4-Ph); 148.6 (C-4); 157.6 (C-6); 160.5 (C-7a); 161.7 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 400 $[M]^+$ (2), 372 $[M–N_2]^+$ (100), 326 $[M–N_2–EtOH]^+$ (78), 298 $[M–N_2–EtOH–CO]^+$ (67). Found, %: C 65.87; H 3.95; N 14.12. $C_{22}H_{16}N_4O_2S$. Calculated, %: C 65.98; H 4.03; N 13.99.

Ethyl 3-azido-4-(4-methoxyphenyl)-6-(4-methylphenyl)-thieno[2,3-*b*]pyridine-2-carboxylate (2b). Yield 568 mg (64%), light-yellow crystals, mp 117–120°C (decomp.). IR spectrum, ν, cm^{-1}: 1707 (C=O), 2124 (N_3). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.34 (3H, t, *J* = 7.2, $C\underline{H}_3CH_2O$); 2.37 (3H, s, $C_6H_4C\underline{H}_3$); 3.85 (3H, s, OCH_3); 4.39 (2H, q, *J* = 7.2, $CH_3C\underline{H}_2O$); 7.08 (2H, d, *J* = 8.3, H-3,5 $C_6H_4OCH_3$); 7.36 (2H, d, *J* = 8.3, H-2,6 $C_6H_4OCH_3$); 7.64 (2H, d, *J* = 8.0, H-3,5 $C_6H_4CH_3$); 7.82 (1H, s, H-5); 8.15 (2H, d, *J* = 8.0, H-2,6 $C_6H_4CH_3$). Mass spectrum, *m*/*z* (I_{rel}, %): 444 $[M]^+$ (4), 416 (100), 370 (92), 91 (43), 43 (49). Found, %: C 64.77; H 4.44; N 12.72. $C_{24}H_{20}N_4O_3S$. Calculated, %: C 64.85; H 4.54; N 12.60.

Ethyl 3-azido-6-(4-methoxyphenyl)-4-(4-methylphenyl)-thieno[2,3-*b*]pyridine-2-carboxylate (2c). Yield 737 mg (83%), light-yellow crystals. IR spectrum, ν, cm^{-1}: 1704 (C=O), 2125 (N_3).

Ethyl 3-azido-6-(4-bromophenyl)-4-(4-methoxyphenyl)-thieno[2,3-*b*]pyridine-2-carboxylate (2d). Yield 896 mg (88%), light-yellow crystals, mp 176–178°C (decomp.). IR spectrum, ν, cm^{-1}: 1690 (C=O), 2136 (N_3). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.11 (3H, t, *J* = 7.2, $OCH_2C\underline{H}_3$); 3.84 (3H, s, OCH_3); 4.25 (2H, q, *J* = 7.2,

$OC\underline{H}_2CH_3$); 7.05 (2H, d, J = 8.5, H-3,5 $C_6H_4OCH_3$); 7.50 (2H, d, J = 8.5, H-2,6 $C_6H_4OCH_3$); 7.61 (1H, s, H-5); 7.75 (2H, d, J = 8.1, H-3,5 C_6H_4Br); 8.15 (2H, d, J = 8.1, H-2,6 C_6H_4Br). Found, %: C 54.34; H 3.27; N 11.11. $C_{23}H_{17}BrN_4O_3S$. Calculated, %: C 54.23; H 3.36; N 11.00.

Ethyl 3-azido-4-(4-methoxyphenyl)-6-phenylthieno-[2,3-*b*]pyridine-2-carboxylate (2e). Yield 679 mg (79%), yellow crystals, mp 117–120°C (decomp.). IR spectrum, ν, cm^{-1}: 1712 (C=O), 2117 (N_3). ^1H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 1.43 (3H, t, J = 7.2, $C\underline{H}_3CH_2O$); 3.90 (3H, s, OCH_3); 4.13 (2H, q, J = 7.2, $CH_3C\underline{H}_2O$); 7.03 (2H, d, J = 8.2, H-3,5 $C_6H_4OCH_3$); 7.41 (2H, d, J = 8.2, H-2,6 $C_6H_4OCH_3$); 7.44–7.54 (3H, m, H-3,4,5 Ph); 7.45 (1H, s, H-5); 8.10 (2H, d, J = 7.6, H-2,6 Ph). $C_{23}H_{18}N_4O_3S$. Found, %: C 64.20; H 4.21; N 13.00. Calculated, %: C 64.17; H 4.21; N 13.01.

Ethyl 3-azido-4-(3,4-dimethoxyphenyl)-6-(4-methyl-phenyl)thieno[2,3-*b*]pyridine-2-carboxylate (2f). Yield 589 mg (64%), light-yellow crystals, mp 117–120°C (decomp.). IR spectrum, ν, cm^{-1}: 1707 (C=O), 2124 (N_3). ^1H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 1.43 (3H, t, J = 7.6, $C\underline{H}_3CH_2$); 2.42 (3H, s, $C\underline{H}_3C_6H_4$); 3.95 (3H, s, 4-OCH_3); 3.98 (3H, s, 3-OCH_3); 4.25 (2H, q, J = 7.3, $CH_3C\underline{H}_2$); 6.98 (1H, d, J = 7.9, H-5 $C_6H_3(OCH_3)_2$); 7.02 (1H, d, J = 7.9, H-6 $C_6H_3(OCH_3)_2$); 7.04 (1H, s, H-2 $C_6H_3(OCH_3)_2$); 7.29 (2H, d, J = 8.3, H-3,5 $CH_3C_6H_4$); 7.63 (1H, s, H-5); 8.00 (2H, d, J = 8.3, H-2,6 $CH_3C_6H_4$). ^{13}C NMR spectrum, δ, ppm: 14.3 ($\underline{C}H_3CH_2$); 24.4 ($C\underline{H}_3C_6H_4$); 55.1 (4-OCH_3); 55.7 (3-OCH_3); 61.9 ($CH_3\underline{C}H_2$); 110.5 (C-5 $C_6H_3(OCH_3)_2$); 112.7 (C-2 $C_6H_3(OCH_3)_2$); 118.5 (C-6 $C_6H_3(OCH_3)_2$); 119.5 (C-5); 121.7 (C-2); 123.5 (C-3a); 127.3 (C-2,6 $CH_3C_6H_4$); 129.7 (C-3,5 $CH_3C_6H_4$); 130.2 (C-1 $C_6H_3(OCH_3)_2$); 135.2 (C-1 $CH_3C_6H_4$); 135.5 (C-3); 140.2 (C-4 $CH_3C_6H_4$); 148.2 (C-4 $C_6H_3(OCH_3)_2$); 148.3 (C-4); 149.4 (C-3 $C_6H_3(OCH_3)_2$); 157.5 (C-6); 160.6 (C-7a); 161.7 (C=O). Found, %: C 63.36; H 4.77; N 11.73. $C_{25}H_{22}N_4O_4S$. Calculated, %: C 63.28; H 4.67; N 11.81.

Ethyl 3-azido-4-(5-methylfuran-2-yl)-6-phenylthieno-[2,3-*b*]pyridine-2-carboxylate (2g). Yield 638 mg (79%), dark-red powder. IR spectrum, ν, cm^{-1}: 1696 (C=O), 2119 (N_3).

Ethyl 3-azido-6-(4-methylphenyl)-4-(thiophen-2-yl)-thieno[2,3-*b*]pyridine-2-carboxylate (2h). Yield 664 mg (79%), orange crystals, mp 166–167°C (decomp.). IR spectrum, ν, cm^{-1}: 1707 (C=O), 2130 (N_3). ^1H NMR spectrum (DMSO-d_6), δ, ppm (J, Hz): 1.47 (3H, t, J = 7.2, $C\underline{H}_3CH_2O$); 2.53 (3H, s, CH_3); 4.56 (2H, q, J = 7.2, $CH_3C\underline{H}_2O$); 7.35 (1H, dd, J = 4.9, J = 3.5, H-4 thiophene); 7.48 (2H, d, J = 8.1, H-3,5 $C_6H_4CH_3$); 7.66 (1H, d, J = 3.5, H-3 thiophene); 7.80 (2H, d, J = 8.1, H-2,6 $C_6H_4CH_3$); 7.85 (1H, d, J = 4.9, H-5 thiophene); 8.06 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 13.0 ($\underline{C}H_3CH_2O$); 21.0 (CH_3); 64.1 ($CH_3\underline{C}H_2O$); 113.0 (C-2); 118.7 (C-3a); 122.3 (C-5); 126.2 (C-3); 126.7 (C-1 $C_6H_4CH_3$); 127.7 (C-2,6 $C_6H_4CH_3$); 128.8 (C-4 thiophene); 131.1 (C-3,5 $C_6H_4CH_3$); 132.9 (C-5 thiophene); 134.2 (C-2 thiophene); 134.6 (C-3 thiophene); 146.0 (C-4 $C_6H_4CH_3$); 150.9 (C-4); 153.0 (C-6); 160.0 (C-7a); 161.1 (C=O). Found, %: C 59.94; H 3.78; N 13.27. $C_{21}H_{16}N_4O_2S_2$. Calculated, %: C 59.98; H 3.84; N 13.32.

Pentyl 3-azido-4,6-bis(4-methylphenyl)thieno[2,3-*b*]-pyridine-2-carboxylate (2i). Yield 884 mg (94%), yellow crystals, mp 108–110°C (decomp.). IR spectrum, ν, cm^{-1}: 1711 (C=O), 2125 (N_3). ^1H NMR spectrum (DMSO-d_6), δ, ppm (J, Hz): 0.78 (3H, t, J = 7.0, $C\underline{H}_3CH_2CH_2CH_2CH_2O$); 1.00–1.20 (4H, m, $CH_3C\underline{H}_2C\underline{H}_2CH_2CH_2O$); 1.50–1.70 (2H, m, $CH_3CH_2CH_2C\underline{H}_2CH_2O$); 2.35 (3H, s, 4-$C_6H_4C\underline{H}_3$); 2.51 (3H, s, 6-$C_6H_4C\underline{H}_3$); 4.11 (2H, t, J = 7.2, OCH_2); 7.22 (2H, d, J = 8.0, H-3,5 4-$C_6H_4CH_3$); 7.34 (2H, d, J = 8.0, H-2,6 4-$C_6H_4CH_3$); 7.68 (2H, d, J = 7.8, H-3,5 6-$C_6H_4CH_3$); 7.72 (1H, s, H-5); 7.98 (2H, J = 7.8, H-2,6 6-$C_6H_4CH_3$). Found, %: C 69.04; H 5.48; N 11.79. $C_{27}H_{26}N_4O_2S$. Calculated, %: C 68.91; H 5.57; N 11.91.

Phenyl 3-azido-4,6-diphenylthieno[2,3-*b*]pyridine-2-carboxylate (2j). Yield 753 mg (84%), orange crystals, mp 184–185°C (decomp.). IR spectrum, ν, cm^{-1}: 1709 (C=O), 2122 (N_3). ^1H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 7.22 (2H, d, J = 8.3, H-2,6 OPh); 7.41–7.67 (11H, m, H Ar); 7.72 (1H, s, H-5); 8.16 (2H, J = 8.1, H-2,6 6-Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 119.9; 121.1; 121.7 (2C); 123.8; 126.4; 127.6 (2C); 128.0 (2C); 128.4; 129.0 (2C); 129.1; 129.2 (2C); 129.6 (2C); 130.2; 137.6; 137.9; 148.9; 150.2; 158.0; 160.1; 161.0. Found, %: C 69.53; H 3.59; N 12.60. $C_{26}H_{16}N_4O_2S$. Calculated, %: C 69.62; H 3.60; N 12.49.

Phenyl 3-azido-4-(4-methylphenyl)-6-phenylthieno-[2,3-*b*]pyridine-2-carboxylate (2k). Yield 785 mg (85%), light-yellow crystals, mp 124–125°C (decomp.). IR spectrum, ν, cm^{-1}: 1715 (C=O), 2123 (N_3). ^1H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 2.26 (3H, s, CH_3); 7.09 (2H, d, J = 8.1, H-2,6 OPh); 7.22–7.60 (10H, m, H Ar); 7.70 (1H, s, H-5); 8.13 (2H, d, J = 7.9, H-2,6 6-Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 21.6; 121.0; 121.6 (2C); 126.3; 127.5 (2C); 127.9; 128.7 (2C); 129.0 (2C); 129.1 (2C); 130.1; 131.1; 131.9; 134.5; 136.0; 138.8; 140.2; 149.1; 159.2; 160.1; 163.3. Found, %: C 70.23; H 3.71; N 12.20. $C_{27}H_{18}N_4O_2S$. Calculated, %: C 70.11; H 3.82; N 12.11.

4-Methylphenyl 3-azido-4-(4-methoxyphenyl)-6-phenyl-thieno[2,3-*b*]pyridine-2-carboxylate (2l). Yield 836 mg (85%), light-yellow crystals. IR spectrum, ν, cm^{-1}: 1715 (C=O), 2125 (N_3).

3-Azido-*N*-methyl-*N*,4,6-triphenylthieno[2,3-*b*]pyridine-2-carboxamide (2m).[7] Yield 848 mg (92%), light-yellow crystals. IR spectrum, ν, cm^{-1}: 1636 (C=O), 2110 (N_3). ^1H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 3.53 (3H, s, NCH_3); 7.20–7.28 (3H, m, H Ph); 7.29–7.38 (4H, m, H Ph); 7.40–7.49 (6H, m, H Ph); 7.59 (1H, s, H-5); 8.04 (2H, dd, J = 8.3, J = 1.6, H-2,6 6-Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 38.1; 119.4; 122.2; 123.3; 126.9 (2C); 127.3 (2C); 127.7; 127.9 (2C); 128.6; 128.8 (2C); 129.2 (2C); 129.5 (2C); 129.6; 130.1; 137.4; 138.1; 143.1; 147.3; 156.1; 160.5; 162.6. Found, %: C 70.37; H 4.07; N 15.27. $C_{27}H_{19}N_5OS$. Calculated, %: C 70.26; H 4.15; N 15.17.

3-Azido-*N*,*N*,4,6-tetraphenylthieno[2,3-*b*]pyridine-2-carboxamide (2n).[7] Yield 931 mg (89%), light-yellow crystals. IR spectrum, ν, cm^{-1}: 1635 (C=O), 2116 (N_3). ^1H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 7.20–7.64 (18H, m, H Ph); 7.70 (1H, s, H-5); 7.99 (2H, d, J = 7.1, H-2,6 6-Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 117.4; 122.1;

124.3; 127.5 (2C); 128.6 (2C); 128.7 (4C); 128.9 (2C); 129.0 (2C); 129.1; 129.4 (2C); 129.6 (4C); 130.2; 132.2; 138.8; 139.5; 142.6 (2C); 149.5; 158.3; 160.7; 162.8. Found, %: C 70.23; H 3.71; N 12.20. $C_{32}H_{21}N_5OS$. Calculated, %: C 73.40; H 4.04; N 13.38.

3-Azido-2-(1-methyl-1*H*-benzimidazol-2-yl)-4,6-diphenylthieno[2,3-*b*]pyridine (2o). Yield 797 mg (87%), yellow powder. IR spectrum, ν, cm^{-1}: 2110 (N_3).

3-Azido-6-(4-bromophenyl)-2-(1-methyl-1*H*-benzimidazol-2-yl)thieno[2,3-*b*]pyridine (2p). Yield 970 mg (88%), yellow powder. IR spectrum, ν, cm^{-1}: 2115 (N_3).

Synthesis of naphthyridines 3a–p by thermolysis of 3-azidothieno[2,3-*b*]pyridines 2a–p (General method). A suspension of azide **2a**–**p** (3 mmol) in xylene (15 ml) was heated under reflux until complete disappearance of the starting azide (15–45 min, TLC control). The reaction mixture was then evaporated to 1/3 of the starting volume and left to crystallize. The formed crystals were filtered off and washed with cold EtOH.

Ethyl 2-phenyl-6*H*-benzo[*c*]thieno[2,3,4-*i,j*]-2,7-naphthyridine-5-carboxylate (3a). Yield 637 mg (57%), yellow crystals, mp 202–203°C (EtOAc). IR spectrum, ν, cm^{-1}: 1645 (C=O), 3317 (NH). ^{1}H NMR spectrum (DMSO-d_6, 90°C), δ, ppm (*J*, Hz): 1.33 (3H, t, *J* = 7.3, C<u>H</u>$_3$CH$_2$O); 4.32 (2H, q, *J* = 7.3, CH$_3$C<u>H</u>$_2$O); 7.15 (1H, t, *J* = 7.9, H-9); 7.44 (1H, d, *J* = 7.9, H-8); 7.48 (2H, t, *J* = 7.3, H-3,5 Ph); 7.51 (1H, t, *J* = 7.3, H-4 Ph); 7.58 (1H, t, *J* = 7.9, H-7); 8.14 (1H, s, H-1); 8.17 (2H, d, *J* = 7.3, H-2,6 Ph); 8.26 (1H, d, *J* = 7.9, H-10); 10.03 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6, 90°C), δ, ppm: 14.9 (<u>C</u>H$_3$CH$_2$O); 60.5 (CH$_3$<u>C</u>H$_2$O); 92.0 (C-5); 106.2 (C-1); 117.2 (C-10a); 118.4 (C-7); 122.7 (C-9); 123.6 (C-10c); 125.3 (C-10); 127.8 (C-2,6 Ph); 129.0 (C-3,5 Ph); 129.9 (C-4 Ph); 132.5 (C-8); 139.0 (C-1 Ph); 139.5 (C-5a,10b); 140.2 (C-6a); 160.3 (C-2); 161.3 (C-3a); 163.6 (C=O). ^{15}N NMR spectrum (DMSO-d_6, 90°C), δ, ppm: –100.2 (N-3); –266.2 (N-6). Mass spectrum, *m*/*z* (I_{rel}, %): 373 $[M+H]^+$ (8), 372 $[M]^+$ (30), 371 (15), 327 (10), 326 (32), 300 (36), 299 (31), 298 (100), 297 (20), 254 (10), 252 (10), 239 (17), 226 (10), 148 (10), 43 (36). Found, %: C 71.08; H 4.39; N 7.44. $C_{22}H_{16}N_2O_2S$: Calculated, %: C 70.95; H 4.33; N 7.52.

Ethyl 8-methoxy-2-(4-methylphenyl)-6*H*-benzo[*c*]-thieno[2,3,4-*i,j*]-2,7-naphthyridine-5-carboxylate (3b). Yield 986 mg (79%), yellow crystals, mp 141°C (EtOH). IR spectrum, ν, cm^{-1}: 1661 (C=O), 3384 (NH). ^{1}H NMR spectrum (DMSO-d_6, 80°C), δ, ppm (*J*, Hz): 1.32 (3H, t, *J* = 7.2, C<u>H</u>$_3$CH$_2$O); 2.36 (3H, s, CH$_3$); 3.77 (3H, s, OCH$_3$); 4.27 (2H, q, *J* = 7.2, CH$_3$C<u>H</u>$_2$O); 6.65 (1H, d, *J* = 8.0, H-9); 7.20 (1H, s, H-7); 7.22 (2H, d, *J* = 7.9, H-3,5 $C_6H_4CH_3$); 7.91 (1H, s, H-1); 8.04 (2H, d, *J* = 7.9, H-2,6 $C_6H_4CH_3$); 8.06 (1H, d, *J* = 8.0, H-10); 10.04 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6, 80 °C), δ, ppm: 14.5; 20.8; 55.2; 59.8; 90.5; 101.2; 104.3; 109.9; 110.1; 122.0; 126.0; 127.0 (2C); 129.0 (2C); 135.7; 138.7; 139.0; 139.2; 141.3; 158.1; 160.3; 162.2; 163.0. Mass spectrum, *m*/*z* (I_{rel}, %): 417 $[M+H]^+$ (19), 416 $[M]^+$ (100), 370 (97), 343 (21), 327 (24), 91 (42), 43 (49). Found, %: C 69.24; H 4.24; N 6.81. $C_{24}H_{20}N_2O_3S$. Calculated, %: C 69.21; H 4.84; N 6.73.

Ethyl 2-(4-methoxyphenyl)-8-methyl-6*H*-benzo[*c*]-thieno[2,3,4-*i,j*]-2,7-naphthyridine-5-carboxylate (3c). Yield 1.1 g (87%), yellow crystals, mp 168°C (EtOH). IR spectrum, ν, cm^{-1}: 1676 (C=O), 3415 (NH). ^{1}H NMR spectrum (DMSO-d_6, 80 °C), δ, ppm (*J*, Hz): 1.35 (3H, t, *J* = 7.03, C<u>H</u>$_3$CH$_2$O); 2.37 (3H, s, 8-CH$_3$); 3.85 (3H, s, OCH$_3$); 4.34 (2H, q, *J* = 7.0, CH$_3$C<u>H</u>$_2$O); 7.00 (1H, d, *J* = 8.4, H-9); 7.05 (2H, d, *J* = 8.6, H-3,5 $C_6H_4OCH_3$); 7.45 (1H, s, H-7); 8.06 (1H, s, H-1); 8.17 (2H, d, *J* = 8.6, H-2,6 $C_6H_4OCH_3$); 8.18 (1H, d, *J* = 8.4, H-10); 9.91 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6, 80 °C), δ, ppm: 15.0 (<u>C</u>H$_3$CH$_2$O); 21.7 (8-CH$_3$); 55.9 (OCH$_3$); 60.5 (CH$_3$<u>C</u>H$_2$O); 89.5 (C-5); 105.1 (C-1); 114.7 (C-3,5 $C_6H_4OCH_3$); 115.5 (C-10c); 118.4 (C-7); 122.9 (C-10a); 124.0 (C-9); 125.2 (C-10); 129.2 (C-2,6 $C_6H_4OCH_3$); 131.7 (C-1 $C_6H_4OCH_3$); 139.5 (C-5a); 139.7 (C-6a); 140.2 (C-10b); 142.9 (C-8); 160.1 (C-2); 161.3 (C-3a); 161.4 (C-4 $C_6H_4OCH_3$); 163.7 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 418 $[M+2]^+$ (11), 417 $[M+H]^+$ (27), 416 $[M]^+$ (68), 371 (100), 370 (28), 344 (38), 343 (20), 342 (36), 132 (16), 91 (22), 64 (30), 60 (34), 57 (37), 45 (46), 43 (73). Found, %: C 69.57; H 4.74; N 6.61. $C_{24}H_{20}N_2O_3S$. Calculated, %: 69.21; H 4.84; N 6.73.

Ethyl 2-(4-bromophenyl)-8-methoxy-6*H*-benzo[*c*]-thieno[2,3,4-*i,j*]-2,7-naphthyridine-5-carboxylate (3d). Yield 1.07 g (74%), yellow crystals, mp 173°C (EtOH). IR spectrum, ν, cm^{-1}: 1665 (C=O), 3443 (NH). ^{1}H NMR spectrum (DMSO-d_6, 80°C), δ, ppm (*J*, Hz): 1.35 (3H, t, *J* = 7.3, C<u>H</u>$_3$CH$_2$O); 3.81 (3H, s, O<u>C</u>H$_3$); 4.29 (2H, q, *J* = 7.3, CH$_3$C<u>H</u>$_2$O); 6.23 (1H, d, *J* = 8.1, H-6); 7.37 (1H, s, H-7); 7.64 (2H, d, *J* = 8.0, H-3,5 C_6H_4Br); 8.15 (2H, d, *J* = 8.0, H-2,6 C_6H_4Br); 8.17 (1H, s, H-1); 8.25 (1H, d, *J* = 8.1, H-10); 10.35 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6, 80°C), δ, ppm: 13.0 (<u>C</u>H$_3$CH$_2$O); 54.6 (OCH$_3$); 56.5 (CH$_3$<u>C</u>H$_2$O); 91.0 (C-5); 104.0 (C-7); 106.2 (C-9); 122.7 (C-1); 125.6 (C-10a); 127.7 (C-2,6 C_6H_4Br); 128.3 (C-10a); 130.3 (C-10b); 130.5 (C-3,5 C_6H_4Br); 132.7 (C-4 C_6H_4Br); 132.8 (C-10); 137.7 (C-5a); 139.4 (C-1 C_6H_4Br); 141.7 (C-6a); 158.2 (C-2); 160.5 (C-8); 160.6 (C-3a); 163.1 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 483 $[M]^+$ (16), 482 $[M]^+$ (98), 481 $[M]^+$ (15), 480 (100) $[M]^+$, 437 (46), 434 (45), 410 (20), 408 (19), 43 (28). Found, %: C 57.22; H 3.41; N 5.97. $C_{23}H_{17}BrN_2O_3S$. Calculated,%: C 57.39; H 3.56; N 5.82.

Ethyl 8-methoxy-2-phenyl-6*H*-benzo[*c*]thieno[2,3,4-*i,j*]-2,7-naphthyridine-5-carboxylate (3e). Yield 1.05 g (87%), yellow crystals, mp 191–193°C (EtOH). IR spectrum, ν, cm^{-1}: 1676 (C=O), 3415 (NH). ^{1}H NMR spectrum (DMSO-d_6, 100 °C), δ, ppm (*J*, Hz): 1.34 (3H, t, *J* = 6.9, C<u>H</u>$_3$CH$_2$O); 3.83 (3H, s, OCH$_3$); 4.34 (2H, q, *J* = 6.9, CH$_3$C<u>H</u>$_2$O); 6.71 (1H, dd, *J* = 8.6, *J* = 2.2, H-9); 7.18 (1H, d, *J* = 2.2, H-7); 7.46 (1H, dd, *J* = 7.4, *J* = 2.5, H-4 Ph); 7.48 (2H, dd, *J* = 7.9, *J* = 7.4, H-3,5 Ph); 7.96 (1H, s, H-1); 8.08 (1H, d, *J* = 8.6, H-10); 8.13 (2H, d, *J* = 7.9, H-2,6 Ph); 9.91 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6, 100°C), δ, ppm: 14.9 (<u>C</u>H$_3$CH$_2$O); 56.0 (OCH$_3$); 60.4 (CH$_3$<u>C</u>H$_2$O); 91.9 (C-5); 102.1 (C-7); 105.3 (C-1); 110.6 (C-10a); 110.9 (C-9); 122.9 (C-10c); 126.3 (C-10); 127.7 (H-2,6 Ph); 128.9 (C-3,5 Ph); 129.8 (C-4 Ph); 139.3 (C-1 Ph); 139.5 (C-10b); 139.7 (C-5a); 142.0 (C-6a);

160.2 (C-2); 161.2 (C-3a); 163.2 (C-8); 163.6 (C=O). ^{15}N NMR spectrum (DMSO-d_6, 100°C), δ, ppm: –113.2 (N-3); –204.5 (N-6). Found, *m/z*: 403.1116 $[M+H]^+$. $C_{23}H_{19}N_2O_3S$. Calculated, *m/z*: 403.1111. Found, %: C 68.73; H 4.44; N 6.05. $C_{23}H_{18}N_2O_3S$. Calculated, %: C 68.64; H 4.51; N 6.96.

Ethyl 8,9-dimethoxy-2-(4-methylphenyl)-6*H*-benzo[*c*]-thieno[2,3,4-*i*,*j*]-2,7-naphthyridine-5-carboxylate (3fA). Preparative separation of isomers **3fA** and **3fB** was performed by the flash chromatography described above. Yield 687 mg (53%), yellow powder, mp 191–193°C (EtOH). IR spectrum, ν, cm^{-1}: 1676 (C=O), 3415 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.36 (3H, t, *J* = 7.3, C$\underline{H}_3$CH$_2$O); 2.41 (3H, s, C$_6$H$_4$C$\underline{H}_3$); 3.81 (3H, s, 8-CH$_3$O); 3.97 (3H, s, 9-CH$_3$O); 4.28 (2H, q, *J* = 7.3, CH$_3$C$\underline{H}_2$O); 6.31 (1H, s, H-7); 7.02 (1H, s, H-10); 7.25 (2H, d, *J* = 8.1, H-3,5 C$_6$H$_4$CH$_3$); 7.30 (1H, s, H-1); 7.89 (2H, d, *J* = 8.1, H-2,6 C$_6$H$_4$CH$_3$); 8.91 (1H, s, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.5 (C$\underline{H}_3$CH$_2$O); 21.3 (C$_6$H$_4$C$\underline{H}_3$); 55.9 (8-CH$_3$O); 56.3 (9-CH$_3$O); 60.3 (CH$_3$C$\underline{H}_2$O); 92.6 (C-5); 99.2 (C-7); 103.9 (C-1); 105.1 (C-10); 109.2 (C-10a); 122.2 (C-10c); 127.3 (C-2,6 C$_6$H$_4$CH$_3$); 129.4 (C-3,5 C$_6$H$_4$CH$_3$); 134.3 (C-10b); 136.6 (C-1 C$_6$H$_4$CH$_3$); 138.4 (C-6a); 139.4 (C-4 C$_6$H$_4$CH$_3$); 140.3 (C-5a); 145.2 (C-9); 152.8 (C-8); 160.2 (C-2); 160.5 (C-3a); 165.2 (C=O). ^{15}N NMR spectrum ($CDCl_3$), δ, ppm: –100.6 (N-3); –268.6 (N-6). Found, %: C 67.34; H 5.11; N 6.19. $C_{25}H_{22}N_2O_4S$. Calculated, %: C 67.25; H 4.97; N 6.27.

Ethyl 7,8-dimethoxy-2-(4-methylphenyl)-6*H*-benzo[*c*]-thieno[2,3,4-*i*,*j*]-2,7-naphthyridine-5-carboxylate (3fB). Yield 156 mg (12%), yellow needles, mp 191–193°C (EtOH). IR spectrum, ν, cm^{-1}: 1676 (C=O), 3415 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.41 (3H, t, *J* = 7.1, C$\underline{H}_3$CH$_2$O); 2.42 (3H, s, C$_6$H$_4$C$\underline{H}_3$); 3.91 (3H, s, 8-CH$_3$O); 3.98 (3H, c 7-CH$_3$O); 4.35 (2H, q, *J* = 7.1, CH$_3$C$\underline{H}_2$O); 6.54 (1H, d, *J* = 8.9, H-9); 7.23 (2H, d, *J* = 8.2, H-3,5 C$_6$H$_4$CH$_3$); 7.37 (1H, d, *J* = 8.9, H-10); 7.42 (1H, s, H-1); 7.87 (2H, d, *J* = 8.2, H-2,6 C$_6$H$_4$CH$_3$); 9.37 (1H, s, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.5 (C$\underline{H}_3$CH$_2$O); 21.3 (C$_6$H$_4$C$\underline{H}_3$); 55.9 (8-CH$_3$O); 60.4 (CH$_3$C$\underline{H}_2$O); 60.6 (7-CH$_3$O); 92.7 (C-5); 104.6 (C-1); 106.3 (C-9); 111.5 (C-10a); 119.4 (C-10); 122.4 (C-10c); 127.3 (C-2,6 C$_6$H$_4$CH$_3$); 129.4 (C-3,5 C$_6$H$_4$CH$_3$); 133.7 (C-10b); 135.1 (C-7); 136.5 (C-1 C$_6$H$_4$CH$_3$); 136.6 (C-5a); 138.5 (C-6a); 139.4 (C-4 C$_6$H$_4$CH$_3$); 154.1 (C-8); 160.4 (C-2); 161.8 (C-3a); 164.7 (C=O). ^{15}N NMR spectrum ($CDCl_3$, 25 °C), δ, ppm: –93.5 (N-3). Found, %: C 67.18; H 5.07; N 6.34. $C_{25}H_{22}N_2O_4S$. Calculated, %: C 67.25; H 4.97; N 6.27.

Ethyl 8-methyl-2-phenyl-6*H*-furo[3,2-*c*]thieno[2,3,4-*i*,*j*]-2,7-naphthyridine-5-carboxylate (3g). Yield 711 mg (63%), yellow crystals, mp 231–232°C (EtOH). IR spectrum, ν, cm^{-1}: 1633 (C=O), 3308 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.27 (3H, t, *J* = 7.2, OCH$_2$C$\underline{H}_3$); 2.30 (3H, s, 8-CH$_3$); 4.21 (2H, q, *J* = 7.2, OC$\underline{H}_2$CH$_3$); 6.37 (1H, s, H-7); 7.15 (1H, s, H-1); 7.40–7.44 (3H, m, H-3,4,5 Ph); 8.02 (2H, d, *J* = 8.3, H-2,6 Ph); 10.75 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.5 (8-CH$_3$); 15.0 (OCH$_2$C$\underline{H}_3$); 60.0 (OC$\underline{H}_2$CH$_3$); 89.3 (C-5); 99.2 (C-1); 101.3 (C-7); 123.1 (C-9c); 127.4 (C-2,6 Ph); 128.9 (C-3,5 Ph); 129.2 (C-4 Ph); 131.7 (C-9a); 132.4 (C-6a); 136.7 (C-9b); 138.9 (C-1 Ph); 140.8 (C-5a); 158.5 (C-8); 159.8 (C-2); 160.7 (C-3a); 163.3 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 377 $[M+H]^+$ (15), 376 $[M]^+$ (71), 332 (14), 331 (15), 330 (100), 304 (15), 303 (53), 302 (81), 301 (11), 261 (7), 259 (7), 258 (10), 242 (5), 216 (6), 165 (19), 164 (19), 152 (13), 151 (34), 140 (7), 106 (21), 105 (24), 102 (10), 92 (20), 91 (59), 77 (13), 76 (39), 51 (16), 44 (13), 43 (33). Found, %: C 67.05; H 4.36; N 7.39. $C_{21}H_{16}N_2O_3S$. Calculated, %: C 67.00; H 4.28; N 7.44.

Ethyl 2-(4-methylphenyl)-6*H*-dithieno[2,3,4-*i*,*j*:3',2'-*c*]-2,7-naphthyridine-5-carboxylate (3h). Yield 423 mg (36%), bright-yellow crystals, mp 232–234°C (EtOH). IR spectrum, ν, cm^{-1}: 1644 (C=O), 3316 (NH). ^{1}H NMR spectrum (DMSO-d_6, 100°C), δ, ppm (*J*, Hz): 1.33 (3H, t, *J* = 7.4, C$\underline{H}_3$CH$_2$O); 2.35 (3H, s, CH$_3$); 4.31 (2H, q, *J* = 7.4, CH$_3$C$\underline{H}_2$O); 7.24 (2H, d, *J* = 7.8, H-3,5 C$_6$H$_4$CH$_3$); 7.33 (1H, d, *J* = 5.3, H-7); 7.36 (1H, s, H-1); 7.80 (1H, d, *J* = 5.3, H-8); 7.95 (2H, d, *J* = 7.8, H-2,6 C$_6$H$_4$CH$_3$); 10.75 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6, 100°C), δ, ppm: 14.8 (C$\underline{H}_3$CH$_2$O); 21.1 (CH$_3$); 60.3 (CH$_3$C$\underline{H}_2$O); 91.0 (C-5); 103.5 (C-1); 113.6 (C-6a); 119.4 (C-7); 123.0 (C-9c); 127.5 (C-2,6 C$_6$H$_4$CH$_3$); 129.6 (C-3,5 C$_6$H$_4$CH$_3$); 131.5 (C-8); 136.3 (C-9b); 137.8 (C-5a); 139.7 (C-1 C$_6$H$_4$CH$_3$); 140.8 (C-4 C$_6$H$_4$CH$_3$); 144.6 (C-9a); 160.5 (C-2); 161.1 (C-3a); 163.5 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 394 $[M+2]^+$ (13), 393 $[M+H]^+$ (26), 392 $[M]^+$ (100), 347 (18), 346 (72), 320 (13), 319 (33), 318 (58), 303 (17), 274 (12), 29 (43), 27 (14). Found, %: C 64.23; H 4.17; N 7.08. $C_{21}H_{16}N_2O_2S_2$. Calculated, %: C 64.26; H 4.11; N 7.14.

Pentyl 8-methyl-2-(4-methylphenyl)-6*H*-benzo[*c*]-thieno[2,3,4-*i*,*j*]-2,7-naphthyridine-5-carboxylate (3i). Yield 782 mg (59%), yellow powder, mp 164–165°C (EtOAc). IR spectrum, ν, cm^{-1}: 1676 (C=O), 3415 (NH). ^{1}H NMR spectrum (DMSO-d_6, 80°C), δ, ppm (*J*, Hz): 0.91 (3H, t, C$\underline{H}_3$CH$_2$CH$_2$CH$_2$CH$_2$O); 1.32–1.38 (4H, m, CH$_3$C$\underline{H}_2$C$\underline{H}_2$CH$_2$CH$_2$O); 1.71–1.77 (2H, m, CH$_3$CH$_2$CH$_2$C$\underline{H}_2$CH$_2$O); 2.28 (3H, s, 8-CH$_3$); 2.36 (3H, s, C$_6$H$_4$C$\underline{H}_3$); 4.22 (2H, t, *J* = 7.2, CH$_3$CH$_2$CH$_2$CH$_2$C$\underline{H}_2$O); 6.86 (1H, d, *J* = 8.1, H-9); 7.24 (1H, s, H-7); 7.25 (2H, d, *J* = 7.9, H-3,5 C$_6$H$_4$CH$_3$); 7.90 (1H, s, H-1); 7.96 (1H, d, *J* = 8.1, H-10); 8.01 (2H, d, *J* = 7.9, H-2,6 C$_6$H$_4$CH$_3$); 9.66 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6, 80°C), δ, ppm: 14.4 (C$\underline{H}_3$CH$_2$CH$_2$CH$_2$CH$_2$O); 21.3 (8-CH$_3$); 21.7 (C$_6$H$_4$C$\underline{H}_3$); 22.3 (CH$_3$C$\underline{H}_2$CH$_2$CH$_2$CH$_2$O); 28.1 (CH$_3$CH$_2$C$\underline{H}_2$CH$_2$CH$_2$O); 28.6 (CH$_3$CH$_2$CH$_2$C$\underline{H}_2$CH$_2$O); 64.2 (CH$_3$CH$_2$CH$_2$CH$_2$C$\underline{H}_2$O); 91.6 (C-5); 105.1 (C-1); 114.8 (C-8); 118.0 (C-7); 123.0 (C-10c); 123.8 (C-9); 124.8 (C-10); 127.5 (2C, C-2,4 C$_6$H$_4$CH$_3$); 129.5 (C-3,5 C$_6$H$_4$CH$_3$); 136.1 (C-10a); 139.1 (C-5a); 139.5 (C-1 C$_6$H$_4$CH$_3$); 139.6 (C-4 C$_6$H$_4$CH$_3$); 139.8 (C-6a); 142.3 (C-10b); 160.1 (C-2); 161.2 (C-3a); 163.6 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 444 $[M+2]^+$ (19), 443 $[M+H]^+$ (34), 442 $[M]^+$ (100), 355 (15), 354 (44), 328 (14), 327 (24), 326 (25), 28 (10). Found, %: C 73.33; H 5.88; N 6.38. $C_{27}H_{26}N_2O_2S$. Calculated, %: C 73.27; H 5.92; N 6.33.

Phenyl 2-phenyl-6*H*-benzo[*c*]thieno[2,3,4-*i*,*j*]-2,7-naphthyridine-5-carboxylate (3j). Yield 758 mg (60%), yellow crystals, mp 214–216°C (EtOAc). IR spectrum, ν, cm^{-1}: 1665 (C=O), 3375 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 7.17 (1H, t, *J* = 7.1, H-9); 7.23–7.38 (3H, m, H Ar); 7.40–7.58 (6H, m, H Ar); 7.73 (1H, d, *J* = 8.3, H-7); 8.24 (2H, d, *J* = 6.7, H-2,6 2-Ph); 8.29 (1H, s, H-1); 8.57 (1H, d, *J* = 7.9, H-10); 10.63 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 106.4 (C-1); 112.0 (C-5); 117.2 (C-10a); 118.7 (C-7); 122.7 (C-2,6 OPh); 123.0 (C-9); 123.4 (C-10c); 125.5 (C-10); 126.2 (C-4 OPh); 127.9 (C-2,6 Ph); 129.2 (C-3,5 Ph); 129.8 (C-3,5 OPh); 130.3 (C-4 Ph); 132.7 (C-8); 138.7 (C-1 Ph); 139.7 (C-5a); 140.1 (C-6a); 140.9 (C-10b); 150.9 (C-1 OPh); 160.4 (C-2); 161.5 (C-3a); 161.7 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 421 $[M+H]^+$ (13), 420 $[M]^+$ (48), 217 (100), 328 (25), 327 (100), 301 (11), 299 (53), 298 (16), 265 (10), 255 (10), 229 (10), 228 (13), 218 (10), 140 (13), 107 (14), 94 (57), 80 (15), 58 (19), 52 (10), 43 (33), 42 (14), 40 (17). Found, %: C 72.34; H 3.79; N 6.59. $C_{26}H_{16}N_2O_2S$. Calculated, %: C 72.27; H 3.84; N 6.66.

Phenyl 8-methyl-2-phenyl-6*H*-benzo[*c*]thieno[2,3,4-*i*,*j*]-2,7-naphthyridine-5-carboxylate (3k). Yield 885 mg (68%), yellow crystals, mp 308–310°C (EtOAc). IR spectrum, ν, cm^{-1}: 1661 (C=O), 3371 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.24 (3H, s, CH_3); 6.92 (1H, d, *J* = 8.3, H-9); 7.26 (2H, d, *J* = 8.9, H-2,6 OPh); 7.29 (1H, t, *J* = 8.0, H-4 OPh); 7.37 (2H, dd, *J* = 8.9, *J* = 8.0, H-3,5 OPh); 7.40 (1H, s, H-7); 7.48 (2H, dd, *J* = 8.5, *J* = 8.0, H-3,5 2-Ph); 7.53 (1H, t, *J* = 8.0, H-4 2-Ph); 8.08 (1H, s, H-1); 8.10 (1H, d, *J* = 8.3, H-10); 8.18 (2H, d, *J* = 8.5, H-2,6 2-Ph); 10.33 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 21.8 (CH_3); 90.2 (C-5); 105.9 (C-1); 114.8 (C-10a); 118.5 (C-7); 120.5 (C-2,6 OPh); 123.1 (C-10c); 124.2 (C-9); 125.1 (C-10); 126.1 (C-4 O-Ph); 127.8 (C-2,6 2-Ph); 129.1 (C-3,5 2-Ph); 129.8 (C-3,5 OPh); 130.2 (C-4 2-Ph); 138.8 (C-1 2-Ph); 139.5 (C-5a); 139.9 (C-6a); 140.9 (C-10b); 142.8 (C-8); 150.9 (C-1 OPh); 160.1 (C-2); 161.4 (C-3a); 161.7 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 435 $[M+H]^+$ (18), 434 $[M]^+$ (57), 341 (100), 340 (45), 319 (28), 56 (34). Found, %: C 74.68; H 4.24; N 6.49. $C_{27}H_{18}N_2O_2S$. Calculated, %: C 74.63; H 4.18; N 6.45.

4-Methylphenyl 8-methoxy-2-phenyl-6*H*-benzo[*c*]-thieno-[2,3,4-*i*,*j*]-2,7-naphthyridine-5-carboxylate (3l). Yield 933 mg (67%), yellow crystals, mp 310–312°C (EtOAc). IR spectrum, ν, cm^{-1}: 1661 (C=O), 3371 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.31 (3H, s, CH_3); 3.76 (3H, s, OCH_3); 6.77 (1H, d, *J* = 8.0, H-9); 7.16 (2H, d, *J* = 8.3, H-2,6 $C_6H_4CH_3$); 7.23 (2H, d, *J* = 8.3, H-3,5 $C_6H_4CH_3$); 7.35 (1H, s, H-7); 7.48 (2H, t, *J* = 8.1, H-3,5 2-Ph); 7.51 (1H, t, *J* = 8.1, H-4 2-Ph); 8.12 (1H, s, H-1); 8.20 (1H, d, *J* = 8.0, H-10); 8.22 (2H, d, *J* = 8.1, H-2,6 2-Ph); 10.43 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 20.9 (CH_3); 55.8 (OCH_3); 92.0 (C-5); 102.0 (C-7); 105.5 (C-1); 110.6 (C-10a); 111.3 (C-9); 122.3 (C-2,6 $C_6H_4CH_3$); 122.7 (C-10c); 126.8 (C-10); 127.8 (C-2,6 2-Ph); 129.1 (C-3,5 2-Ph); 130.1 (C-3,5 $C_6H_4CH_3$); 135.2 (C-4 $C_6H_4CH_3$); 138.7 (C-1 2-Ph); 139.3 (C-4 2-Ph); 139.7 (C-10b); 140.9 (C-5a); 141.9 (C-6a); 148.7 (C-1 $C_6H_4CH_3$); 160.2 (C-2); 161.4 (C-3a); 161.8 (C=O); 162.8 (C-8). Mass spectrum, *m*/*z* (I_{rel}, %): 465 $[M+H]^+$ (21), 464 $[M]^+$ (97), 358 (12), 357 (100), 329 (44), 43 (66). Found, %: C 72.54; H 4.17; N 5.91. $C_{28}H_{20}N_2O_3S$. Calculated, %: C 72.39; H 4.34; N 6.02.

***N*-Methyl-*N*,2-diphenyl-6*H*-benzo[*c*]thieno[2,3,4-*i*,*j*]-2,7-naphthyridine-5-carboxamide (3m)**.[7] Yield 922 mg (71%), bright-yellow crystals, mp 283–285°C (DMSO). IR spectrum, ν, cm^{-1}: 1624 (C=O), 3296 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.44 (3H, s, NCH_3); 7.05 (1H, d, *J* = 8.0, H-7); 7.06 (1H, t, *J* = 8.0, H-9); 7.35–7.53 (9H, m, H Ph, H-8); 7.66 (1H, s, H-1); 7.90 (1H, d, *J* = 8.0, H-10); 7.96 (2H, d, *J* = 8.3, H-2,6 2-Ph); 10.48 (1H, s, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 38.5 (NCH_3); 94.0 (C-5); 105.3 (C-1); 117.1 (C-7); 117.4 (C-10a); 121.1 (C-9); 122.4 (C-10); 124.2 (C-10c); 127.4 (C-2,6 2-Ph); 128.7; (C-2,6 NPh); 129.0 (C-4 NPh); 129.3 (C-4 2-Ph); 129.4 (C-3,5 2-Ph); 130.0 (C-3,5 NPh); 132.0 (C-8); 138.8 (C-10b); 139.7 (C-1 2-Ph); 139.8 (C-6a); 141.1 (C-5a); 142.8 (C-1 NPh); 160.4 (C-2); 162.4 (C-3a); 166.1 (C=O). ^{15}N NMR spectrum ($CDCl_3$), δ, ppm: –266.2 (N-6); –263.5 (CON); –102.7 (N-3). Mass spectrum, *m*/*z* (I_{rel}, %): 434 $[M+H]^+$ (11), 433 $[M]^+$ (72), 327 (100), 326 (40), 300 (16), 299 (44), 298 (14), 227 (107), 108 (21), 107 (47), 106 (76), 43 (13). Found, %: C 74.75; H 4.47; N 9.63. $C_{27}H_{19}N_3OS$. Calculated, %: C 74.80; H 4.42; N 9.69.

***N*,*N*,2-Triphenyl-6*H*-benzo[*c*]thieno[2,3,4-*i*,*j*]-2,7-naphthyridine-5-carboxamide (3n)**.[7] Yield 743 mg (50%), orange crystals, mp 235–237°C (DMSO). IR spectrum, ν, cm^{-1}: 1623 (C=O), 3308 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.91 (1H, d, *J* = 7.6, H-7); 7.03 (1H, t, *J* = 7.6, H-9); 7.32 (1H, t, *J* = 7.6, H-8); 7.36–7.51 (13H, m, H Ph); 7.62 (1H, s, H-1); 7.82 (1H, d, *J* = 7.6, H-10); 7.98 (2H, d, *J* = 7.4, H-2,6 2-Ph); 10.46 (1H, s, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 94.5 (C-5); 105.3 (C-1); 117.1 (C-7); 117.4 (C-10a); 121.9 (C-9); 122.1 (C-10c); 124.1 (C-10); 127.4 (C-2,6 2-Ph); 127.5 (2C-4 NPh); 128.6 (C-3,5 2-Ph); 128.7 (2C-2,6 NPh); 129.4 (C-4 6-Ph); 129.5 (2C-3,5 NPh); 132.0 (C-8); 138.7 (C-10b); 139.4 (C-1 6-Ph); 139.5 (C-6a); 142.4 (C-5a); 142.5 (2C-1 NPh); 160.5 (C-2); 162.8 (C-3a); 166.4 (C=O). ^{15}N NMR spectrum ($CDCl_3$), δ, ppm: –263.7 (N-6); –240.5 (CON); –102.9 (N-3). Mass spectrum, *m*/*z* (I_{rel}, %): 495 $[M]^+$ (15), 327 (19), 170 (29), 169 (100), 168 (60), 167 (32), 66 (29), 65 (19), 51 (13), 44 (14). Found, %: C 77.48; H 4.22; N 8.55. $C_{32}H_{21}N_3OS$. Calculated, %: C 77.55; H 4.27; N 8.48.

5-(1-Methyl-1*H*-benzimidazol-2-yl)-2-phenyl-6*H*-benzo-[*c*]thieno[2,3,4-*i*,*j*]-2,7-naphthyridine (3o). Yield 645 mg (50%), orange crystals, mp 310–312°C (DMSO). IR spectrum, ν, cm^{-1}: 1620 (C=O), 3657 (NH). ^{1}H NMR spectrum (DMSO-d_6, 120 °C), δ, ppm (*J*, Hz): 4.04 (3H, s, NCH_3); 7.12 (1H, dd, *J* = 8.0, *J* = 7.8, H-9); 7.26 (1H, dd, *J* = 8.1, *J* = 7.6, H-5 benzimidazole); 7.34 (1H, d, *J* = 7.7, H-7); 7.42 (2H, t, *J* = 7.3, H-3,5 2-Ph), 7.50 (1H, dd, *J* = 7.8, *J* = 7.7, H-8); 7.52 (1H, d, *J* = 8.3, H-7 benzimidazole); 7.54 (1H, dd, *J* = 8.3, *J* = 7.6, H-6 benzimidazole); 7.57 (1H, t, *J* = 7.3, H-4 2-Ph); 7.70 (1H, d, *J* = 8.1, H-4 benzimidazole); 8.14 (1H, s, H-1); 8.22 (2H,

d, *J* = 7.3, H-2,6 2-Ph); 8.25 (1H, d, *J* = 8.0, H-10); 10.76 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6, 120°C), δ, ppm: 31.3 (NCH_3); 106.6 (C-1); 106.7 (C-5); 110.1 (C-7 benzimidazole); 117.5 (C-10c); 118.4 (C-4 benzimidazole); 121.7 (C-9); 122.1 (C-6 benzimidazole); 122.3 (C-7); 122.5 (C-5 benzimidazole); 125.6 (C-10); 127.5 (C-2,6 2-Ph); 129.1 (C-3,5 2-Ph); 132.8 (C-10a); 136.2 (C-7a benzimidazole); 139.3 (C-10b); 140.2 (C-8); 140.7 (C-3a benzimidazole); 141.3 (C-1 2-Ph); 141.4 (C-5a); 141.6 (C-6a); 143.6 (C-4 2-Ph); 149.9 (C-2 benzimidazole); 159.3 (C-3a); 159.7 (C-2). Mass spectrum, *m*/*z* (I_{rel}, %): 432 $[M+2]^+$ (14), 431 $[M+1]^+$ (45), 430 $[M]^+$ (100), 415 (32), 215 (12). Found, %: C 75.37; H 4.26; N 12.94. $C_{27}H_{18}N_4S$. Calculated, %: C 75.32; H 4.21; N 13.01.

2-(4-Bromophenyl)-8-methyl-5-(1-methyl-1*H*-benzimidazol-2-yl)-6*H*-benzo[*c*]thieno[2,3,4-*i*,*j*]-2,7-naphthyridine (3p). Yield 989 mg (63%), bright-orange crystals, mp 338–340°C (DMSO). IR spectrum, ν, cm^{-1}: 1613 (C=O), 3665 (NH). ^{1}H NMR spectrum ($CDCl_3$–CF_3CO_2H), δ, ppm (*J*, Hz): 2.53 (3H, s, 8-CH_3); 4.18 (3H, s, NCH_3); 7.13 (1H, s, H-7); 7.32 (1H, d, *J* = 8.4, H-9); 7.73 (2H, d, *J* = 7.8, H-3,5 C_6H_4Br); 7.78–7.81 (4H, m, H benzimidazole); 7.92 (2H, d, *J* = 7.8, H-2,6 C_6H_4Br); 8.04 (1H, s, H-1); 8.15 (1H, d, *J* = 8.4, H-10); 10.06 (1H, s, NH). ^{13}C NMR spectrum ($CDCl_3$–CF_3CO_2H), δ, ppm: 21.2 (8-CH_3); 32.2 (NCH_3); 81.4 (C-5); 111.9 (C-7 benzimidazole); 112.3 (C-10a); 113.8 (C-4 benzimidazole); 117.7 (C-7); 125.7 (C-10); 126.0 (C-10c); 126.8 (C-9); 127.1 (C-2,6 C_6H_4Br); 127.9 (C-5 benzimidazole); 128.5 (C-6 benzimidazole); 130.2 (C-3,5 C_6H_4Br); 130.3 (C-7a benzimidazole); 130.8 (C-1 C_6H_4Br); 132.6 (C-3a benzimidazole); 133.5 (C-4 C_6H_4Br); 136.8 (C-5a); 141.3 (C-6a); 141.5 (C-2 benzimidazole); 146.9 (C-10b); 150.5 (C-8); 151.7 (C-3a); 156.0 (C-2). Mass spectrum, *m*/*z* (I_{rel}, %): 445 (31), 444 (100), 222 (29), 77 (11). Found, %: C 64.18; H 3.82; N 10.64. $C_{28}H_{19}BrN_4S$. Calculated, %: C 64.25; H 3.66; N 10.70.

Supplementary information file containing the data of the calculation of the predicted spectrum of the targeted biological activity of the synthesized compounds, is available at the journal website at http://link.springer.com/journal/10593.

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