Functionalized sulfur-containing compounds. 13.* Synthesis of substituted 3-amino-2-(organylsulfinyl)- and -(organylsulfonyl)thieno[2,3-*b*]pyridines

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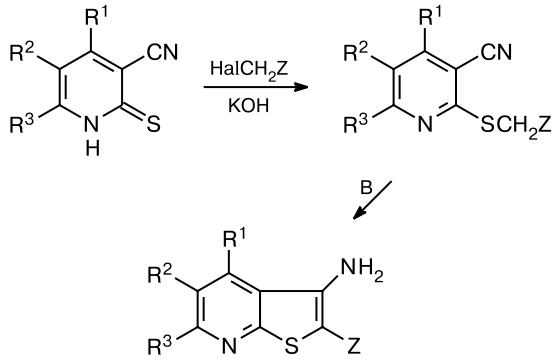
A method for the synthesis of substituted 3-amino-2-(organylsulfinyl)thieno[2,3-*b*]pyridines by the Thorpe—Ziegler intramolecular cyclization of substituted 3-cyano-2-[(organylsulfinyl)methylthio]pyridines was proposed. 3-Amino-2-(organylsulfonyl)thieno[2,3-*b*]pyridines were obtained by reactions of substituted 3-cyanopyridine-2-thiones with chloromethyl organyl sulfones. The reaction intermediates 3-cyano-2-[(organylsulfonyl)methylthio]pyridines were transformed into 3-amino-2-(organylsulfonyl)thieno[2,3-*b*]pyridines.

Key words: intramolecular cyclization, the Thorpe—Ziegler reaction, 3-cyanopyridine-2-thiones, chloromethyl organyl sulfides, chloromethyl organyl sulfones, 3-cyano-2-[(organylsulfinyl)methylthio]pyridines, 3-amino-2-(organylsulfinyl)thieno[2,3-*b*]pyridines, 3-amino-2-(organylsulfonyl)thieno[2,3-*b*]pyridines.

3-Aminothieno[2,3-*b*]pyridine derivatives are of interest as potential drugs.[1—6] They are most commonly synthesized by alkylation of 3-cyanopyridine-2-thiones with α-halogen-containing compounds with an active methylene group such as α-halo carboxylic acids, esters, amides, and nitriles and α-halo ketones followed by the base-catalyzed Thorpe—Ziegler intramolecular cyclization (Scheme 1).[7—14] Alkali metal hydroxides or alkoxides have been usually employed as bases.

Scheme 1



Z = COOH, COOR, CONHR, COR, CN
B is the base

No examples of the synthesis of 3-aminothieno[2,3-*b*]pyridines containing the sulfinyl or sulfonyl group (Z = S(O)R or SO_2R) in position 2 have been documented, although the corresponding alkylated intermediates have sufficiently "acidic" protons and could enter into the Thorpe—Ziegler intramolecular cyclization. For this reason, it was of interest to investigate these reactions.

The target sulfoxides were obtained by alkylation of 3-cyanopyridine-2-thiones **1a—c** with chloromethyl organyl sulfides **2a—c** followed by oxidation of the derived 3-cyano-2-[(organylthio)methylthio]pyridines **3a—h** with H_2O_2 in acetic acid—chloroform (Scheme 2). In this case, only one S atom was oxidized to give 3-cyano-2-[(organylsulfinyl)methylthio]pyridines **4a—h**.

The physical characteristics of sulfides **3a—h** and sulfoxides **4a—h** are given in Table 1. Their spectroscopic characteristics are presented in Table 2.

Intramolecular cyclization of sulfoxides **4a—h** was carried out by adding a solution of KOH in aqueous methanol to a solution of compound **4** in DMF. 3-Amino-2-(organylsulfinyl)thieno[2,3-*b*]pyridines **5a—h** were obtained in good yields (see Table 1). The fact of the cyclization was proven by IR spectroscopy. The spectra of the products showed no absorption bands of the cyano group at 2212—2220 cm^{-1}; instead, absorption bands appeared at 3400—3500 cm^{-1}, which is characteristic of an amino group (Table 3).

We failed to synthesize similar 3-cyano-2-[(organylsulfonyl)methylthio]pyridines **6** by oxidation of sulfides **3** or sulfoxides **4** because the oxidation also occurred at the S atom bound to the pyridine ring, giving a mixture of

* For Part 12, see Ref. 1.

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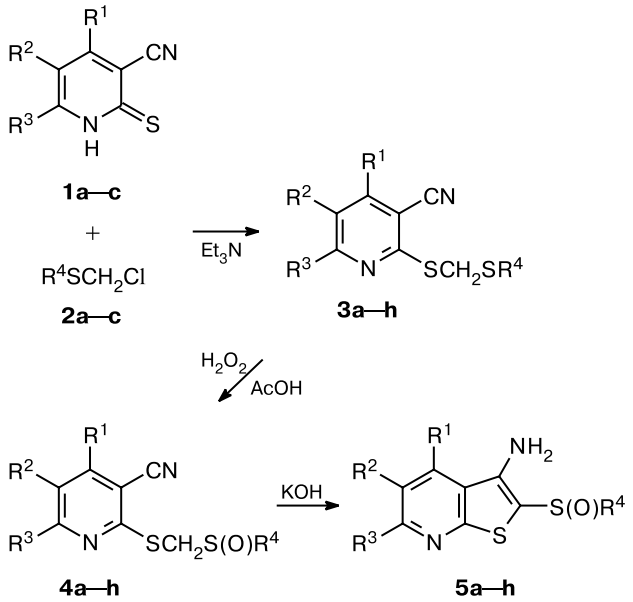
Scheme 2

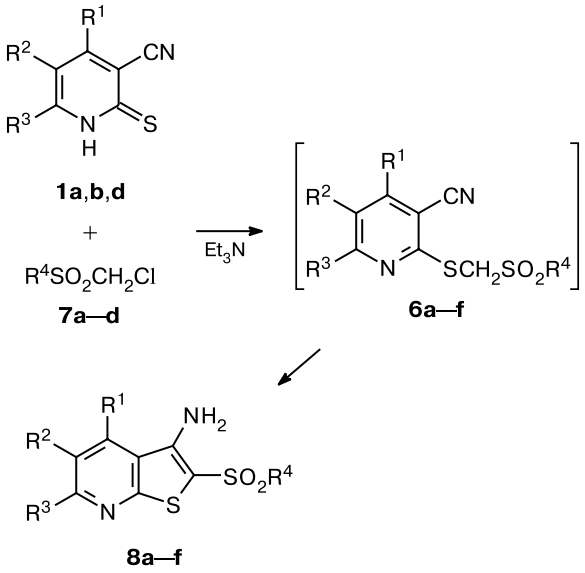


Compound	R^1	R^2	R^3 $R^2—R^3$	Compound	R^4
1a, **3a—c**, **4a—c**, **5a—c**	Me	H	Me	**2a**, **3a**,**d**,**g—5a**,**d**,**g**	C_8H_{17}
1b, **3d—f**, **4d—f**, **5d—f**	H	—$(CH_2)_4$—		**2b**, **3b**,**e**,**h—5b**,**e**,**h**	Ph
1c, **3g**,**h—5g**,**h**	CF_3	H	2-thienyl	**2c**, **3c**,**f—5c**,**f**	CH_2Ph

products. Because of this, we attempted to obtain sulfones **6** by reactions of 3-cyanopyridine-2-thiones **1** with chloromethyl organyl sulfones **7**.

Insofar as sulfones **7** are poorly reactive, their reactions with pyridinethiones **1** were carried out in DMF at 100—110 °C for several hours in the presence of triethylamine. The IR spectra of the products showed no absorption bands characteristic of the cyano group but contained bands characteristic of the amino group (see Table 2). Obviously, intermediate sulfones **6a—f** undergo *in situ* intramolecular cyclization into 3-amino-2-(organylsulfonyl)thieno[2,3-*b*]pyridines **8a—f** (Scheme 3).

Scheme 3



Compound	R^1	R^2	R^3 $R^2—R^3$	Compound	R^4
1d, **8f**	Ph	H	4-(MeO)C_6H_4	**7a**, **8a**,**f**	Bu
8a—c	Me	H	Me	**7b**, **8b**	C_8H_{17}
8d,**e**	H	—$(CH_2)_4$—		**7c**, **8c**,**d**	Ph
				7d, **8e**	CH_2Ph

The reaction of pyridinethione **1a** with chloromethyl octyl sulfoxide **9** under analogous conditions gave a mixture of sulfoxides **4a** and **5a** (Scheme 4).

The latter result suggests that the sufficiently high acidity of the methylene group in both sulfones **6** and sulfoxides **4** allows intramolecular cyclization in the presence of such a base as triethylamine.

Table 1. Physical characteristics of compounds **3—5** and **8**

Compound	Molecular formula	Found / Calculated (%)				M.p./°C	Yield (%)
		C	H	S	N		
3a	$C_{17}H_{26}N_2S_2$	63.19 63.31	8.22 8.13	20.02 19.88	8.60 8.69	Oil	85
3b	$C_{15}H_{14}N_2S_2$	63.04 62.90	4.87 4.93	22.23 22.39	9.69 9.78	62—64	87
3c	$C_{16}H_{16}N_2S_2$	63.81 63.97	5.32 5.37	21.43 21.34	9.38 9.32	Oil	84
3d	$C_{19}H_{28}N_2S_2$	65.32 65.47	8.14 8.10	18.54 18.40	7.98 8.04	32—34	84

(*to be continued*)

Table 1 (*continued*)

Compound	Molecular formula	Found / Calculated (%)				M.p./°C	Yield (%)
		C	H	S	N		
3e	$C_{17}H_{16}N_2S_2$	65.20 / 65.35	5.11 / 5.16	20.66 / 20.52	9.03 / 8.97	86—87	83
3f	$C_{18}H_{18}N_2S_2$	66.41 / 66.22	5.63 / 5.56	19.50 / 19.64	8.50 / 8.58	Oil	86
3g	$C_{20}H_{23}F_3N_2S_3$	54.26 / 54.03	5.25 / 5.21	21.70 / 21.63	6.20 / 6.30	77—78	83
3h	$C_{18}H_{11}F_3N_2S_3$	52.73 / 52.93	2.65 / 2.71	23.70 / 23.55	6.95 / 6.86	123—125	85
4a	$C_{17}H_{26}N_2OS_2$	60.50 / 60.32	7.80 / 7.74	18.76 / 18.94	8.25 / 8.28	Oil	93
4b	$C_{15}H_{14}N_2OS_2$	59.37 / 59.58	4.62 / 4.67	21.34 / 21.20	9.22 / 9.26	162—164	90
4c	$C_{16}H_{16}N_2OS_2$	60.55 / 60.73	5.02 / 5.10	20.22 / 20.26	8.76 / 8.85	124—126	88
4d	$C_{19}H_{28}N_2OS_2$	62.44 / 62.60	7.70 / 7.74	17.75 / 17.59	7.61 / 7.68	76—78	90
4e	$C_{17}H_{16}N_2OS_2$	62.25 / 62.17	4.96 / 4.91	19.46 / 19.52	8.60 / 8.53	184—186	92
4f	$C_{18}H_{18}N_2OS_2$	63.04 / 63.13	5.34 / 5.30	18.86 / 18.72	8.12 / 8.18	172—174	90
4g	$C_{20}H_{23}F_3N_2OS_3$	52.36 / 52.15	5.10 / 5.03	20.68 / 20.88	6.03 / 6.08	123—125	90
4h	$C_{18}H_{11}F_3N_2OS_3$	50.81 / 50.93	2.56 / 2.61	22.62 / 22.66	6.67 / 6.60	172—174	93
5a	$C_{17}H_{26}N_2OS_2$	60.18 / 60.32	7.68 / 7.74	18.88 / 18.94	8.37 / 8.28	66—68	80
5b	$C_{15}H_{14}N_2OS_2$	59.70 / 59.58	4.64 / 4.67	21.13 / 21.20	9.30 / 9.26	130—133	82
5c	$C_{16}H_{16}N_2OS_2$	60.88 / 60.73	5.16 / 5.10	20.11 / 20.26	8.93 / 8.85	137—139	80
5d	$C_{19}H_{28}N_2OS_2$	62.84 / 62.60	7.81 / 7.74	17.38 / 17.59	7.63 / 7.68	103—106	78
5e	$C_{17}H_{16}N_2OS_2$	62.39 / 62.17	5.00 / 4.91	19.56 / 19.52	8.45 / 8.53	164—166	82
5f	$C_{18}H_{18}N_2OS_2$	63.05 / 63.13	5.32 / 5.30	18.86 / 18.72	8.22 / 8.18	172—174	83
5g	$C_{20}H_{23}F_3N_2OS_3$	52.31 / 52.15	5.07 / 5.03	20.92 / 20.88	6.01 / 6.08	86—88	74
5h	$C_{18}H_{11}F_3N_2OS_3$	51.07 / 50.93	2.65 / 2.61	22.74 / 22.66	6.53 / 6.60	171—173	78
8a	$C_{13}H_{18}N_2O_2S_2$	52.45 / 52.32	6.12 / 6.08	21.33 / 21.49	9.48 / 9.39	105—107	72
8b	$C_{17}H_{26}N_2O_2S_2$	57.41 / 57.59	7.35 / 7.39	18.01 / 18.09	8.02 / 7.90	113—114	74
8c	$C_{15}H_{14}N_2O_2S_2$	56.74 / 56.58	4.48 / 4.43	20.21 / 20.14	8.63 / 8.80	197—199	68
8d	$C_{17}H_{16}N_2O_2S_2$	59.44 / 59.28	4.62 / 4.68	18.48 / 18.62	8.18 / 8.13	198—200	70
8e	$C_{18}H_{18}N_2O_2S_2$	60.18 / 60.31	5.00 / 5.06	18.04 / 17.89	7.90 / 7.81	201—203	72
8f	$C_{24}H_{24}N_2O_3S_2$	63.47 / 63.69	5.38 / 5.34	14.28 / 14.17	6.24 / 6.19	124—126	65

Table 2. Spectroscopic characteristics of compounds **3**—**5** and **8**

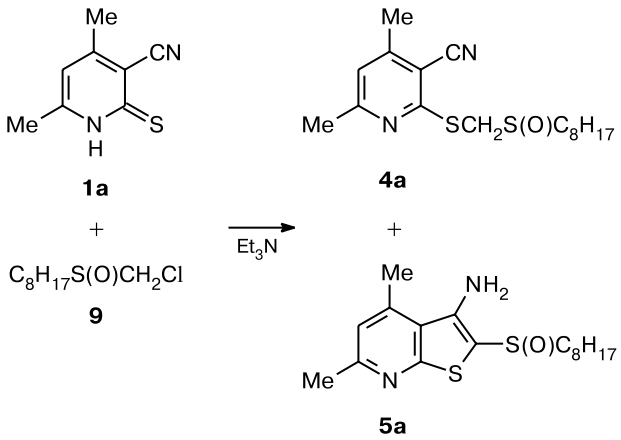
Compound	IR (KBr), ν/cm^{-1}	^1H NMR δ (J/Hz)
3a	2216 (CN)	0.87 (t, 3 H, Me, J = 7.0); 1.31 (m, 8 H, 4 CH_2); 1.42, 1.71 (both m, 2 H each, CH_2); 2.45, 2.53 (both s, 3 H each, Me); 2.62 (m, 2 H, CH_2S); 4.45 (s, 2 H, CH_2S); 6.82 (s, 1 H, H(5) pyridine)
3b	2212 (CN)	2.45, 2.53 (both s, 3 H each, Me); 4.76 (s, 2 H, CH_2S); 6.82 (s, 1 H, H(5) pyridine); 7.35 (m, 3 H, Ph); 7.50 (m, 2 H, Ph)
3c	2216 (CN)	2.45, 2.55 (both s, 3 H each, Me); 3.72 (m, 2 H, CH_2Ph); 4.47 (s, 2 H, CH_2S); 6.82 (s, 1 H, H(5) pyridine); 7.25 (m, 5 H, Ph)
3d	2222 (CN)	0.87 (t, 3 H, Me, J = 7.0); 1.31 (m, 8 H, 4 CH_2); 1.42 (m, 2 H, CH_2); 1.78 (m, 6 H, CH_2); 2.56 (m, 2 H, CH_2S); 2.70 (t, 3 H, Me, J = 7.5); 2.85 (t, 3 H, Me, J = 7.5); 4.45 (s, 2 H, CH_2S); 7.80 (s, 1 H, H(4) pyridine)
3e	2222 (CN)	1.78 (m, 4 H, 2 CH_2); 2.68, 2.85 (both t, 3 H each, Me, J = 7.5); 4.80 (s, 2 H, CH_2S); 7.30 (m, 3 H, Ph); 7.45 (m, 2 H, Ph); 7.80 (s, 1 H, H(4) pyridine)
3f	2224 (CN)	1.80 (m, 4 H, 2CH_2); 2.71, 2.85 (both t, 3 H each, Me, J = 7.5); 3.73 (m, 2 H, CH_2Ph); 4.47 (s, 2 H, CH_2S); 7.25 (m, 5 H, Ph); 7.82 (s, 1 H, H(4) pyridine)
3g	2228 (CN)	0.87 (t, 3 H, Me, J = 7.0); 1.31 (m, 8 H, 4 CH_2); 1.42, 1.71 (both m, 2 H each, CH_2); 2.58 (m, 2 H, CH_2S); 4.50 (s, 2 H, CH_2S); 7.20 (t, 1 H, H(4) thiophene, J = 5.5); 7.50 (d, 1 H, H(3) thiophene, J = 5.5); 7.65 (d, 1 H, H(5) thiophene, J = 5.5); 7.84 (s, 1 H, H(5) pyridine)
3h	2228 (CN)	4.86 (s, 2 H, CH_2S); 7.20 (t, 1 H, H(4) thiophene, J = 5.5); 7.30 (m, 3 H, Ph); 7.50 (m, 3 H, Ph, H(3) thiophene, J = 5.5); 7.68 (d, 1 H, H(5) thiophene, J = 5.5); 7.87 (s, 1 H, H(5) pyridine)
4a	2216 (CN); 1030 (SO)	0.87 (t, 3 H, Me, J = 7.0); 1.31 (m, 8 H, 4 CH_2); 1.42, 1.72 (both m, 2 H each, CH_2); 2.45, 2.55 (both s, 3 H each, Me); 2.92 (m, 2 H, CH_2SO); 4.38, 4.64 (both d, 1 H each, CH_2SO, J = 13); 6.82 (s, 1 H, H(5) pyridine)
4b	2220 (CN); 1036 (SO)	2.40, 2.50 (both s, 3 H each, Me); 4.77, 4.90 (both d, 1 H each, CH_2SO, J = 15); 7.08 (s, 1 H, H(5) pyridine); 7.50 (m, 3 H, Ph); 7.68 (m, 2 H, Ph)
4c	2216 (CN); 1052 (SO)	2.45, 2.55 (both s, 3 H each, Me); 4.07 (d, 1 H, CH_2SO, J = 13); 4.28 (m, 2 H, CH_2Ph); 4.70 (d, 1 H, CH_2SO, J = 13); 6.82 (s, 1 H, H(5) pyridine); 7.30 (m, 5 H, Ph)
4d	2222 (CN), 1032 (SO)	0.87 (t, 3 H, Me, J = 7.0); 1.31 (m, 8 H, 4 CH_2); 1.42 (m, 2 H, CH_2); 1.78 (m, 6 H, CH_2); 2.70, 2.85 (both t, 2 H each, CH_2, J = 7.5); 2.92 (m, 2 H, CH_2SO); 4.40, 4.64 (both d, 1 H each, CH_2SO, J = 14); 7.82 (s, 1 H, H(4) pyridine)
4e	2224 (CN), 1036 (SO)	1.82 (m, 4 H, 2 CH_2); 2.85, 2.95 (both t, 2 H each, CH_2, J = 7.5); 4.75, 4.90 (both d, 1 H each, CH_2SO, J = 15); 7.45 (m, 3 H, Ph); 7.65 (m, 2 H, Ph) 7.72 (s, 1 H, H(4) pyridine)
4f	2220 (CN), 1042 (SO)	1.85 (m, 4 H, 2 CH_2); 2.88, 2.98 (both t, 2 H each, CH_2, J = 7.5); 4.03 (d, 1 H, CH_2SO, J = 13); 4.30 (m, 2 H, CH_2Ph); 4.70 (d, 1 H, CH_2SO, J = 13); 7.30 (m, 5 H, Ph); 7.70 (s, 1 H, H(4) pyridine)
4g	2230 (CN); 1036 (SO)	0.87 (t, 3 H, Me, J = 7.0); 1.31 (m, 8 H, 4 CH_2); 1.42 (m, 2 H, CH_2); 1.71 (m, 2 H, CH_2); 2.92 (m, 2 H, CH_2SO); 4.43, 4.58 (both d, 1 H each, CH_2SO, J = 13); 7.20 (t, 1 H, H(4) thiophene, J = 5.5); 7.50 (d, 1 H, H(3) thiophene, J = 5.5), 7.68 (d, 1 H, H(5) thiophene, J = 5.5); 7.84 (s, 1 H, H(5) pyridine)
4h	2228 (CN); 1044 (SO)	4.75, 4.92 (both d, 1 H each, CH_2SO, J = 15); 7.23 (t, 1 H, H(4) thiophene, J = 5.5); 7.50 (d, 1 H, H(3) thiophene, J = 5.5); 7.70 (d, 1 H, H(5) thiophene, J = 5.5); 7.84 (s, 1 H, H(5) pyridine)
5a	3384, 3326, 3228 (NH_2); 1016 (S=O)	0.87 (t, 3 H, Me, J = 7.0); 1.31 (m, 8 H, 4 CH_2); 1.42, 1.71 (both m, 2 H each, CH_2); 2.55, 2.70 (both s, 3 H each, Me); 3.15 (m, 2 H, CH_2SO); 5.10 (s, 2 H, NH_2); 6.85 (s, 1 H, H(5) pyridine)
5b	3424, 3388, 3212 (NH_2); 1016 (S=O)	2.53, 2.70 (both s, 3 H each, Me); 5.23 (s, 2 H, NH_2); 6.77 (s, 1 H); 7.45 (m, 3 H, Ph); 7.70 (m, 2 H, Ph)
5c	3390, 3328, 3220 (NH_2); 1012 (S=O)	2.50, 2.67 (both s, 3 H each, Me); 4.32 (m, 2 H, CH_2Ph); 5.20 (s, 2 H, NH_2); 6.90 (s, 1 H, H(5) pyridine); 7.30 (m, 5 H, Ph)

(*to be continued*)

Table 2 (*continued*)

Compound	IR (KBr), ν/cm^{-1}	^{1}H NMR δ (*J*/Hz)
5d	3420, 3396, 3308, 3212 (NH_2); 1016 (S=O)	0.87 (t, 3 H, Me, *J* = 7.0); 1.31 (m, 8 H, 4CH_2); 1.42, 1.71 (both m, 2 H each, CH_2); 1.87 (m, 4 H, 2 CH_2); 2.85, 2.98 (both t, 2 H each, CH_2, *J* = 7.5); 3.15 (m, 2 H, CH_2SO); 4.57 (s, 2 H, NH_2); 7.50 (s, 1 H, H(4) pyridine)
5e	3380, 3328, 3224 (NH_2); 1016 (S=O)	1.87 (m, 4 H, 2 CH_2); 2.86, 2.95 (both t, 2 H each, CH_2, *J* = 7.5); 5.00 (s, 2 H, NH_2); 7.50 (m, 4 H, Ph, H(4) pyridine); 7.93 (m, 2 H, Ph)
5f	3464, 3296 (NH_2); 1008 (S=O)	1.90 (m, 4 H, 2 CH_2); 2.90, 2.98 (both t, 2 H each, CH_2, *J* = 7.5); 4.37 (s, 2 H, CH_2Ph); 4.57 (s, 2 H, NH_2); 7.22 (m, 5 H, Ph); 7.45 (s, 1 H, H(4) pyridine)
5g	3504, 3320 (NH_2); 1024 (S=O)	0.87 (t, 3 H, Me, *J* = 7.0); 1.31 (m, 8 H, 4 CH_2); 1.42, 1.71 (both m, 2 H each, CH_2); 3.20 (m, 2 H, CH_2SO); 5.25 (s, 2 H, NH_2); 7.20 (t, 1 H, H(4) thiophene, *J* = 5.5); 7.50 (d, 1 H, H(3) thiophene, *J* = 5.5); 7.74 (d, 1 H, H(5) thiophene, *J* = 5.5); 7.90 (s, 1 H, H(5) pyridine)
5h	3496, 3304 (NH_2); 1020 (S=O)	5.40 (s, 2 H, NH_2); 7.20 (t, 1 H, H(4) thiophene, *J* = 5.5); 7.50 (m, 4 H, Ph, H(3) thiophene); 7.70 (m, 2 H, Ph); 7.74 (d, 1 H, H(5) thiophene, *J* = 5.5); 7.86 (s, 1 H, H(5) pyridine)
8a	3492, 3380 (NH_2); 1276, 1144 (SO_2)	0.93 (t, 3 H, Me, *J* = 7.0); 1.42, 1.85 (both m, 2 H each, CH_2); 2.55, 2.70 (both s, 3 H each, Me); 3.22 (m, 2 H, CH_2SO_2); 5.15 (s, 2 H, NH_2); 6.87 (s, 1 H, H(5) pyridine)
8b	3494, 3380 (NH_2); 1276, 1140 (SO_2)	0.87 (t, 3 H, Me, *J* = 7.0); 1.30 (m, 8 H, 4 CH_2); 1.42, 1.70 (both m, 2 H each, CH_2); 2.55, 2.70 (both s, 3 H each, Me); 3.20 (m, 2 H, CH_2SO_2); 5.07 (s, 2 H, NH_2); 6.87 (s, 1 H, H(5) pyridine)
8c	3500, 3384 (NH_2); 1300, 1148 (SO_2)	2.55, 2.70 (both s, 3 H each, Me); 5.40 (s, 2 H, NH_2); 6.85 (s, 1 H, H(5) pyridine); 7.50 (m, 3 H, Ph); 8.00 (m, 2 H, Ph)
8d	3448, 3284 (NH_2); 1304, 1140 (SO_2)	1.85 (m, 4 H, 2 CH_2); 2.88, 2.95 (both t, 2 H each, CH_2, *J* = 7.5); 5.60 (s, 2 H, NH_2); 7.50 (s, 1 H, H(4) pyridine); 7.55 (m, 3 H, Ph); 7.93 (m, 2 H, Ph)
8e	3448, 3304 (NH_2); 1300, 1140 (SO_2)	1.90 (m, 4 H, 2CH_2); 2.88, 2.98 (both t, 2 H each, CH_2, *J* = 7.5); 4.40 (s, 2 H, CH_2Ph); 4.92 (s, 2 H, NH_2); 7.25 (m, 5 H, Ph); 7.48 (s, 1 H, H(4) pyridine)
8f	3476, 3372 (NH_2); 1300, 1116 (SO_2)	0.92 (t, 3 H, Me, *J* = 7.0); 1.41, 1.85 (both m, 2 H each, CH_2); 3.85 (s, 3 H, MeO); 5.10 (s, 2 H, NH_2); 7.10 (d, 2 H, *J* = 5.5); 7.60 (m, 5 H, Ph); 7.80 (s, 1 H, H(5) pyridine); 7.90 (d, 2 H, *J* = 5.5)

Scheme 4



Experimental

IR spectra were recorded on a Perkin-Elmer-577 instrument (chloroform or Nujol). ^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250 MHz) in DMSO-d_6.

Compounds **1a** (see Ref. 7), **1b** (see Ref. 14), **1c** (see Ref. 15), and **1d** (see Ref. 10) were prepared according to known procedures.

Chloromethyl organyl sulfides **2a**—**c** and chloromethyl organyl sulfones **7a**—**d** were prepared as described earlier.[16]

3-Cyano-2-[(organylthio)methylthio]pyridines 3a—h (general procedure). Triethylamine (15 mmol) was added to a solution of 3-cyanopyridine-2-thione **1** (10 mmol) and chloromethyl organyl sulfide **2** (10 mmol) in dry acetonitrile (15 mL). The reaction mixture was refluxed for 20 min, cooled, and diluted with ether (40 mL). The precipitate that formed was filtered off, the filtrate was concentrated under reduced pressure, and the residue was chromatographed on silica gel with hexane—ben-

zene (8 : 1) as an eluent. The eluate was concentrated and the residue was crystallized from acetone—methanol.

3-Cyano-2-[(organylsulfinyl)methylthio]pyridines 4a—h (general procedure). Acetic acid (10 mL) and 30% H_2O_2 (0.6 mL, 6 mmol) were added to a solution of sulfide **3** (5 mmol) in chloroform (10 mL). The reaction mixture was kept at 30—35 °C for 30 min and neutralized in a separatory funnel with a solution of Na_2CO_3. Organic material from the aqueous layer was extracted with chloroform. The combined extract was dried over $MgSO_4$, the solvent was removed *in vacuo*, and the residue was crystallized from ether.

3-Amino-2-(organylsulfinyl)thieno[2,3-*b*]pyridines 5a—h (general procedure). A solution of KOH (3 mmol) in a mixture of water (2 mL) and methanol (10 mL) was added to a solution of sulfoxide **4** (5 mmol) in DMF (10—20 mL). The reaction mixture was kept at 35—40 °C for 30 min and cooled. If a precipitate formed, it was filtered off and washed with methanol; if no precipitate formed, the reaction mixture was poured into a separatory funnel with water (100 mL) and the product was extracted with chloroform. The combined extract was dried over $MgSO_4$, the solvent was removed *in vacuo*, and the residue was crystallized from ether.

3-Amino-2-(organylsulfonyl)thieno[2,3-*b*]pyridines 8a—f (general procedure). A solution of 3-cyanopyridine-2-thione **1** (5 mmol), chloromethyl organyl sulfone **7** (5 mmol), and triethylamine (8 mmol) in DMF (5 mL) was kept at 100—110 °C for 7 h, cooled, and worked up as described for compounds **5**. Sulfones **8a—f** were purified by crystallization from methanol or ethanol.

Chloromethyl octyl sulfoxide (9). A solution of monoperoxyphthalic acid (3.65 g, 20 mmol) in ether (50 mL) was added at −15 to −10 °C to a stirred solution of chloromethyl octyl sulfide (3.9 g, 20 mmol) in anhydrous ether (100 mL). The reaction mixture was stirred at this temperature for 30 min, allowed to warm to 0 °C, and treated with a solution of Na_2CO_3. The organic phase was dried over $MgSO_4$ and concentrated. The residue was crystallized from ether—hexane. The yield of compound **9** was 3.6 g, m.p. 43 °C. Found (%): C, 51.44; H, 9.15; S, 15.10; Cl, 16.70. $C_9H_{19}ClO_5$. Calculated (%): C, 51.29; H, 9.09; S, 15.21; Cl, 16.82.

Reaction of 3-cyano-4,6-dimethylpyridine-2-thione (1a) with chloromethyl octyl sulfoxide (9). A solution of compound **1a** (0.82 g, 5 mmol), sulfoxide **9** (1.05 g, 5 mmol), and triethylamine (8 mmol) in DMF (7 mL) was kept at 100—110 °C for 7 h and worked up as described for compounds **5**. The residue was chromatographed on silica gel with chloroform—acetone (10 : 1) as an eluent to give sulfoxide **4a** (1 g) and thienopyridine **5a** (0.55 g).

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