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SYNTHESIS AND PROPERTIES OF (THIENO[2,3-*b*]PYRIDIN-3-YL)IMINOTRIPHENYL-PHOSPHORANES. MOLECULAR STRUCTURE OF (2-BENZOYL-4-METHOXYMETHYL-6-METHYL-THIENO[2,3-*b*]PYRIDIN-3-YL)IMINO-TRIPHENYLPHOSPHORANE

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Iminophosphoranes containing a thieno[2,3-b]pyridine fragment were obtained through a sequence of reactions: 1) alkylation of 3-cyano-2(1H)-pyridinethiones in alkaline medium by an α-halocarbonyl compound with subsequent Thorpe–Ziegler cyclization of the resultant 2-thioalkylpyridines to give 3-aminothieno[2,3-b]pyridines, 2) diazotization of the amino group and nucleophilic substitution of the diazonium group by an azido group without isolation of the diazonium salts, and 3) reaction of the 3-azidothieno[2,3-b]pyridines with triphenylphosphine.

Keywords: 3-aminothieno[2,3-*b*]pyridines, 3-azidothieno[2,3-*b*]pyridines, 3-cyano-2(1H)-pyridine-thiones, (thieno[2,3-*b*]pyridin-3-yl)-iminotriphenylphosphoranes, molecular structure, synthesis.

Iminophosphoranes, in light of their electronic structure, are promising intermediates for the synthesis of many compounds of different types [1-3]. In the present work, we synthesized thieno[2,3-*b*]-pyridinyliminophosphoranes, for which no data have been available in the literature, and studied the physicochemical properties of these compounds.

Pyridinethione **1**, α-haloacetic acid derivatives **2a-d**, and phenacyl bromide **2e** served as the starting compounds for the preparation of (thieno[2,3-*b*]pyridin-3-yl)iminotriphenylphosphoranes.

The reaction of pyridinethione **1** with α-halocarbonyl compounds **2a-e** were carried out in the presence of two equivalents of KOH to bind the hydrogen halide liberated and provide for the Thorpe–Ziegler isomerization of intermediate S-alkyl derivatives **3a-e** to give 3-aminothieno[2,3-*b*]pyridines **4a-e** (Scheme 1).

3-Aminothieno[2,3-*b*]pyridines **4** are bright-yellow compounds, which are highly soluble in polar solvents (Table 1). Pyridines **4a** and **4e** have already been prepared and some of their properties have been reported in our previous work [4, 5].

The structure of the 3-aminothieno[2,3-*b*]pyridines was confirmed by IR, UV, and ^{1}H NMR spectroscopy (Table 2). The IR spectra of **4a-e** lacked the nitrile group band at 2210 cm^{-1} and thioamide group band at 1215 cm^{-1} characteristic for starting pyridinethione **1** but have stretching bands for the amino group N–H bond at 3465-3400 and 3330-3255 cm^{-1} as well as stretching bands for the conjugated carbonyl group in ester **4a**

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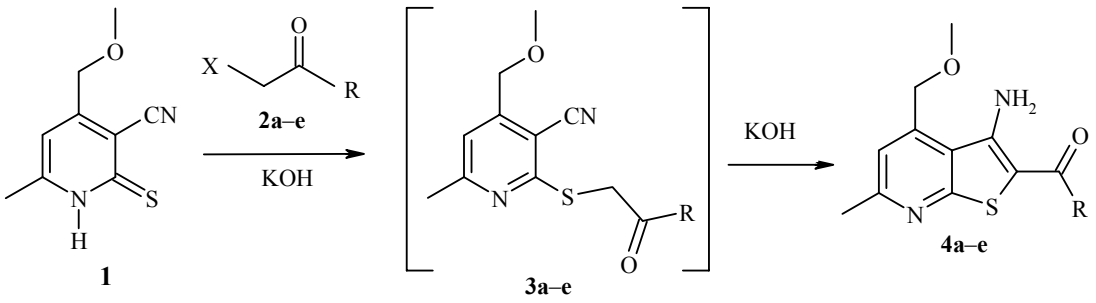
Scheme 1



2-4 a R = OEt, **b** R = $N(CH_2Ph)_2$, **c** R = NPh_2, **d** R = morpholino, **e** R = Ph;
a, e X = Br, **b-d** X = Cl

at 1660 cm^{-1}, amides **4b-d** at 1600-1590 cm^{-1}, and ketone **4e** at 1595 cm^{-1}. The ^1H NMR spectra of **4a-e** have signals for the protons of all the groups; the broad singlet of the amino group is found at 6.13-8.12 ppm.

TABLE 1. Physicochemical Properties of 3-Aminothieno[2,3-*b*]pyridines **4a-e**, 3-Azidothieno[2,3-*b*]pyridines **6a-e**, and (Thieno[2,3-*b*]pyridin-3-yl)-iminotriphenylphosphoranes **7a-e**

Compound	Empirical formula	Found, % / Calculated, %			mp, (or dec. p.) °C	UV spectrum, λ_{max}, nm (log ε)	Yield, %
		C	H	N			
4a	$C_{13}H_{16}N_2O_3S$	55.68 / 55.70	5.76 / 5.75	9.95 / 9.99	147.5-148	208 (4.35), 240 (4.05), 288 (4.61), 373 (3.81)	78
4b	$C_{25}H_{25}N_3O_2S$	69.53 / 69.58	5.84 / 5.84	9.70 / 9.74	128-129	207 (4.56), 243 (3.93), 293 (3.27), 367 (3.59)	69
4c	$C_{23}H_{21}N_3O_2S$	68.64 / 68.46	5.24 / 5.25	10.39 / 10.41	187-188	207 (4.62), 298 (4.28), 393 (3.91)	90
4d	$C_{15}H_{19}N_3O_3S$	56.02 / 56.06	5.94 / 5.96	13.05 / 13.07	157-158	207 (4.33), 242 (3.95), 290 (4.27), 366 (3.61)	71
4e	$C_{17}H_{16}N_2O_2S$	65.31 / 65.36	5.13 / 5.16	8.93 / 8.97	137-138	212 (4.44), 283 (4.23), 311 (4.40), 415 (4.05)	92
6a	$C_{13}H_{14}N_4O_3S$	50.97 / 50.93	4.61 / 4.58	18.29 / 18.22	(118-119)	—	82
6b	$C_{25}H_{23}N_5O_2S$	65.63 / 65.59	5.07 / 5.00	15.31 / 15.27	56-58	—	82
6c	$C_{23}H_{19}N_5O_2S$	64.32 / 64.27	4.46 / 4.43	16.31 / 16.30	(177-178)		97
6d	$C_{15}H_{17}N_5O_3S$	51.86 / 51.85	4.93 / 4.91	20.16 / 20.14	(138-139)	—	50
6e	$C_{17}H_{14}N_4O_2S$	60.28 / 60.34	4.17 / 4.20	16.49 / 16.56	115-117		74
7a	$C_{31}H_{29}N_2O_3PS$	68.82 / 68.87	5.38 / 5.41	5.14 / 5.18	235-236	208 (4.83), 246 (4.32), 286 (4.37), 388 (3.99)	69
7b	$C_{43}H_{38}N_3O_2S$	74.66 / 74.65	5.50 / 5.54	6.03 / 6.07	214-215	209 (4.97), 217 (4.42), 340 (3.76)	47
7c	$C_{41}H_{34}N_3O_2PS$	74.16 / 74.19	5.15 / 5.16	6.29 / 6.33	289-290	206 (4.80), 250 (4.77), 394 (3.83)	72
7d	$C_{33}H_{32}N_3O_3PS$	68.13 / 68.14	5.52 / 5.54	7.19 / 7.22	238-239	208 (4.89), 263 (4.39), 340 (3.82)	64
7e	$C_{35}H_{29}N_2O_2PS$	73.38 / 73.41	5.10 / 5.10	4.86 / 4.89	215-216	208 (4.85), 280 (4.23), 322 (4.15), 442 (3.86)	56

TABLE 2. Spectral Data of Products

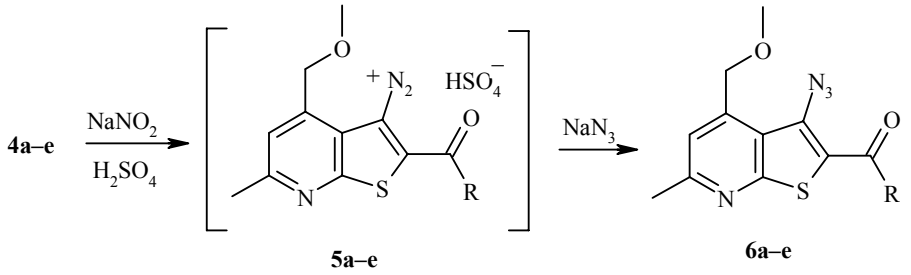
Compound	IR spectrum, ν, cm^{-1}			^1H NMR spectrum, δ, ppm (*J*, Hz)				
	C=O	NH_2 (N_3)	C–O–C	CH_3 (3H, s)	O–CH_3 (3H, s)	O–CH_2 (2H, s)	H_{Py} (1H, s)	other signals
1	2	3	4	5	6	7	8	9
4a	1660	3420, 3330	1275*, 1190*, 1120	2.56	3.41	4.82	7.20	1.32 (3H, t , *J* = 7.2, $CH_2\underline{CH_3}$); 4.30 (2H, q, *J* = 7.2, $\underline{CH_2}CH_3$); 6.92 (2H, br. s, NH_2)
4b	1595	3400, 3305	1145, 1100, 1070	2.80	3.43	4.81	7.08	4.71 (4H, s, N–CH_2); 7.25-7.35 (10H, m, $2C_6H_5$); 6.62 (2H, br. s, NH_2)
4c	1600	3410, 3310	1110, 1070	2.50	3.40	4.80	7.14	7.20-7.44 (10H, m, $2C_6H_5$); 7.25 (2H, br. s, NH_2)
4d	1590	3420, 3310	1120, 1090, 1065	2.58	3.41	4.79	7.10	3.65–3.70 (8H, m, morpholino); 6.13 (2H, br. s, NH_2)
4e	1595	3465, 3255	1095	2.66	3.45	4.80	7.0	7.27–7.89 (5H, m, C_6H_5); 8.12 (2H, br. s, NH_2)
6a	1720	(2130)	1280*, 1190*, 1130, 1100, 1050	2.55	3.41	4.88		1.38 (3H, t , *J* = 7.2, $CH_2\underline{CH_3}$); 4.27 (2H, q, *J* = 7.2, $\underline{CH_2}CH_3$)
6b	1620	(2115)	1120, 1085	2.59	3.52	4.93		4.67 (4H, s, N–CH_2); 7.20-7.36 (11H, m, $H_{Py,}C_6H_5$)
6c	1635	(2120)	1120, 1090	2.54	3.46	4.92		7.22-7.45 (11H, m, H_{Py}, C_6H_5)

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9
6d	1625	(2115)	1120, 1070	2.64	3.51	4.94	7.33	3.66-3.70 (8H, m, OCH_2, NCH_2)
6e	1625	(2110)	1110	2.50	3.38	4.76	7.26	7.07-7.62 (5H, m, C_6H_5)
7a	1680	—	1255*, 1170*, 1120, 1080	2.50	3.08	4.86	7.18	0.79 (3H, t , *J* = 7.2, $OCH_2\underline{CH_3}$); 3.55 (2H, q, *J* = 7,2, $O\underline{CH_2}CH_3$); 7.48-7.62 (15H, m, C_6H_5)
7b	1620	—	1100, 1080	2.50	3.10	4.87		4.08 (4H, s, $N–CH_2$); 7.00-7.67 (26H, m, H_{Py}, C_6H_5)
7c	1640	—	1120, 1070	2.47	3.21	5.04		6.67-7.69 (26H, m, H_{Py} , C_6H_5)
7d	1605	—	1115, 1085	2.55	3.20	4.99	7.15	3.05 (4H, s, $N–CH_2$); 3.42 (4H, s, $O–CH_2$); 7.44-7.64 (15H, m, C_6H_5)
7e	1600	—	1120, 1080	2.53	3.15	4.96		6.87-7.85 (21H, m, H_{Py}, C_6H_5)

* Bands for ester C–O–C.

The diazotization of 3-aminothieno[2,3-*b*]pyridines **4a-e** was carried out in acetic acid in the presence of conc. sulfuric acid. Diazonium salts **5a-e** obtained in solution were used for nucleophilic substitution by means of sodium azide immediately after eliminating excess nitrous acid.

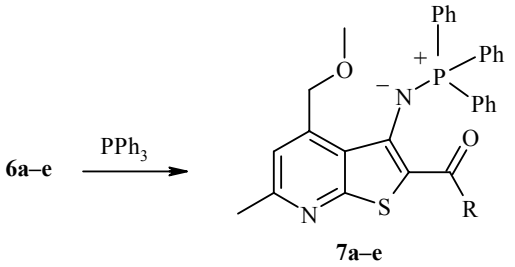


5, 6 a R = OEt, **b** R = $N(CH_2Ph)_2$, **c** R = NPh_2, **d** R = $N(CH_2CH_2)_2O$, **e** R = Ph

The resultant 3-azidothieno[2,3-*b*]pyridines **6a-e** are colorless or light-yellow compounds, which decompose upon storage (Table 1).

The IR spectral data provide the most helpful information for establishing the structure of 3-azidothieno[2,3-*b*]pyridines **6** (Table 2). The substitution of the amino groups at $C_{(3)}$ in thieno[2,3-*b*]pyridines **4** by azido groups leads to the disappearance of the two N–H stretching bands and a shift in the carbonyl group band toward higher frequencies: by 60 cm^{-1} for ester **6a**, by 25-65 cm^{-1} for amides **6b-d**, and by 30 cm^{-1} for ketone **6e**. The characteristic band for the azido group appears at 2130-2110 cm^{-1}. The ^1H NMR spectra of azides **6** lack the amino group proton signals found in the spectra of starting thieno[2,3-*b*]pyridines **4** (Table 2).

The reaction of 3-azidothieno[2,3-*b*]pyridines **6** with triphenylphosphine was carried out in benzene. This reaction proceeds with the liberation of nitrogen. The cessation of nitrogen liberation indicates the end of this reaction.



7 a R = OEt, **b** R = $N(CH_2Ph)_2$, **c** R = NPh_2, **d** R = $N(CH_2CH_2)_2O$, **e** R = Ph

The resultant iminophosphoranes **7a,c,e** are yellow, while **7b** and **7d** are colorless. These products form crystals with high melting points (Table 1). The presence of the heteroaromatic substituent at the nitrogen atom in triphenylphosphoranes **7** provides for their resistance to the action of water. Phosphoranes **7** are insoluble in alkanes and diethyl ether but have moderate solubility in ethanol and good solubility in DMF and DMSO.

In comparison to the IR spectra of the corresponding azides, the spectra of iminophosphoranes **7** (Table 2) lack the azido group band and show stronger C–H_{ar} stretching bands. The structure of iminosphosphoranes **7** was confirmed by their ^1H NMR spectra.

An X-ray diffraction structural analysis was carried out for iminophosphorane **7e** which has a benzoyl substituent at $C_{(2)}$ of the thiophene system (Fig. 1, Tables 3 and 4).

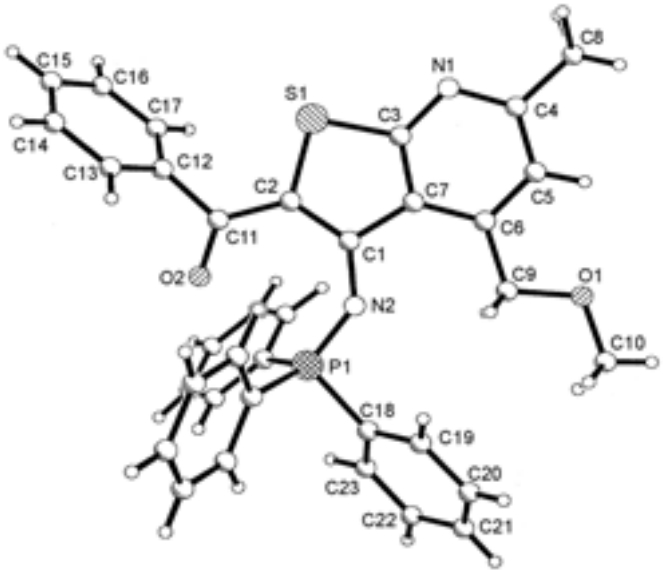


Fig. 1. Projection of the structure of **7e**.

The steric strain in the O(2)–C(11)–C(2)–C(1)–N(2)–P(1) fragment leads to significant distortions of the bond angles at these atoms. Thus, the C(24)–P(1)–C(30), N(2)–P(1)–C(24), and N(1)–P(1)–C(30) bond angles are expanded to 113.59, 115.74, and 114.34°, respectively, probably due to the repulsion of the

TABLE 3. Bond Lengths (*d*) in **7e** Obtained in an X-Ray Diffraction Structural Analysis

Bond	*d*, Å	Bond	*d*, Å
S(1)–C(3)	1.723(3)	C(12)–C(13)	1.378(4)
S(1)–C(2)	1.763(3)	C(13) –C(14)	1.373(4)
P(1)–N(2)	1.575(2)	C(14)–C(15)	1.365(5)
P(1)–C(24)	1.799(3)	C(15)–C(16)	1.357(5)
P(1)–C(30)	1.814(3)	C(16)–C(17)	1.386(5)
P(1)–C(18)	1.817(3)	C(18)–C(23)	1.379(4)
O(1)–C(9)	1.404(4)	C(18)–C(19)	1.379(4)
O(1)–C(10)	1.416(4)	C(19)–C(20)	1.377(5)
O(2)–C(11)	1.231(3)	C(20)–C(21)	1.366(6)
N(1)–C(4)	1.330(4)	C(21)–C(22)	1.368(6)
N(1)–C(3)	1.346(3)	C(22)–C(23)	1.384(5)
N(2)–C(1)	1.354(3)	C(24)–C(29)	1.382(4)
C(1)–C(2)	1.403(4)	C(24)–C(25)	1.391(4)
C(1)–C(7)	1.458(4)	C(25)–(26)	1.375(5)
C(2)–C(11)	1.432(4)	C(26)–C(27)	1.359(6)
C(3)–C(7)	1.397(4)	C(27)–C(28)	1.370(6)
C(4)–C(5)	1.394(4)	C(28)–C(29)	1.388(5)
C(4)–C(8)	1.502(4)	C(30)–C(35)	1.386(4)
C(5)–C(6)	1.374(4)	C(30)–C(31)	1.389(4)
C(6)–C(7)	1.405(4)	C(31)–C(32)	1.381(5)
C(6)–C(9)	1.495(4)	C(32)–C(33)	1.359(6)
C(11)–C(12)	1.498(4)	C(33)–C(34)	1.364(6)
C(12)–C(17)	1.376(4)	C(34)–C(35)	1.388(5)

TABLE 4. Bond Angles (θ) in **7e** Obtained in an X-Ray Diffraction Structural Analysis

Angle	θ, deg	Angle	θ, deg
C(3)–S(1)–C(2)	91.16(13)	C(17)–C(12)–C(13)	118.6(3)
N(2)–P(1)–C(24)	115.74(13)	C(17)–C(12)–C(11)	124.0(3)
N(2)–P(1)–C(30)	114.34(13)	C(13)–C(12)–C(11)	117.3(3)
C(24)–P(1)–C(30)	113.59(13)	C(14)–C(13)–C(12)	120.8(3)
N(2)–P(1)–C(18)	104.81(13)	C(15)–C(14)–C(13)	120.0(4)
C(24)–P(1)–C(18)	104.56(13)	C(16)–C(15)–C(14)	120.1(3)
C(30)–P(1)–C(18)	101.74(13)	C(15)–C(16)–C(17)	120.3(3)
C(9)–O(1)–C(10)	111.8(3)	C(12)–C(17)–C(16)	120.1(3)
C(4)–N(1)–C(3)	115.2(3)	C(23)–C(18)–C(19)	118.7(3)
C(1)–N(2)–P(1)	137.5(2)	C(23)–C(18)–P(1)	123.4(3)
N(2)–C(1)–C(2)	130.9(2)	C(19)–C(18)–P(1)	117.9(2)
N(2)–C(1)–C(7)	118.3(2)	C(20)–C(19)–C(18)	120.9(4)
C(2)–C(1)–C(7)	110.8(2)	C(21)–C(20)–C(19)	119.9(4)
C(1)–C(2)–C(11)	127.5(2)	C(20)–C(21)–C(22)	120.1(4)
C(1)–C(2)–S(1)	112.5(2)	C(21)–C(22)–C(23)	120.1(4)
C(11)–C(2)–S(1)	119.3(2)	C(18)–C(23)–C(22)	120.3(4)
N(1)–C(3)–C(7)	126.5(3)	C(29)–C(24)–C(25)	118.5(3)
N(1)–C(3)–S(1)	120.4(2)	C(29)–C(24)–P(1)	124.4(2)
C(7)–C(3)–S(1)	113.1(2)	C(25)–C(24)–P(1)	117.0(2)
N(1)–C(4)–C(5)	122.7(3)	C(26)–C(25)–C(24)	120.9(4)
N(1)–C(4)–C(8)	117.2(3)	C(27)–C(26)–C(25)	120.1(4)
C(5)–C(4)–C(8)	120.2(3)	C(26)–C(27)–C(28)	120.2(4)
C(6)–C(5)–C(4)	121.9(3)	C(27)–C(28)–C(29)	120.5(4)
C(5)–C(6)–C(7)	116.8(3)	C(24)–C(29)–C(28)	119.8(4)
C(5)–C(6)–C(9)	120.7(3)	C(35)–C(30)–C(31)	119.2(3)
C(7)–C(6)–C(9)	122.5(2)	C(35)–C(30)–P(1)	119.5(2)
C(3)–C(7)–C(6)	116.9(2)	C(31)–C(30)–P(1)	121.1(2)
C(3)–C(7)–C(1)	112.5(2)	C(32)–C(31)–C(30)	119.8(3)
C(6)–C(7)–C(1)	130.6(2)	C(33)–C(32)–C(31)	120.7(4)
O(1)–C(9)–C(6)	110.5(2)	C(32)–C(33)–C(34)	120.1(4)
O(2)–C(11)–C(2)	122.4(3)	C(33)–C(34)–C(35)	120.6(4)
O(2)–C(11)–C(12)	117.8(3)	C(30)–C(35)–C(34)	119.6(3)
C(2)–C(11)–C(12)	119.7(2)		

C(24)···C(29) and C(30)···C(35) benzene rings and C(1)–O(1) carbonyl group. This repulsion would also account for the expansion of the bond angle at N(2) (by 17.5°) relative to the standard value for sp^2-hybridized nitrogen.

The phosphorus atom is found in an sp^3-hybridized state: the mean value of the bond angles at the phosphorus atom is 109.12°.

The phenyl ring of the benzoyl substituent is extruded from the plane of the heterocyclic system by 65.2° as the result of repulsion of the sulfur atom and hydrogen atom at C(17).

The S(1)–C(3) bond (1.723 Å) is shortened relative to the S(1)–C(2) bond (1.763 Å) due to displacement of an electron pair of this sulfur atom toward the pyridine ring with π-electron deficiency.

EXPERIMENTAL

The UV spectra were taken in ethanol on Specord UV-vis and Specord M-40 spectrometers at 200-700 nm in quartz cells; the path length was 10 mm. The IR spectra were taken on Specord-71 and UR-20 spectrometers at 3600-650 cm^{-1} using NaCl and KBr plates. The crystalline compounds were taken in vaseline mull. The ^1H NMR spectra were taken on a Bruker WM-250 spectrometer at 250 MHz in DMSO-d_6 with TMS as the internal standard.

N,N-Diphenyl-3-amino-4-methoxymethyl-6-methylthieno[2,3-*b*]pyridine-2-carboxamide (4c). 10% aq. KOH (5.6 ml, 10 mmol) was added to a suspension of 3-cyano-2(1H)-pyridinethione **1** (1.94 g, 10 mmol) in DMF (20 ml). Then, N,N-diphenylchloracetamine (**2c**) (2.46 g, 10 mmol) was added with stirring. The mixture was maintained for 10-15 min at room temperature. Then, an additional 10% aq. KOH (5.6 ml, 10 mmol) was added and the reaction mixture was stirred for 6 h at 80-85°C. After cooling of the reaction mixture, the precipitate formed was separated, washed consecutively with water and 1:1 ethanol–water, and dried in the air. The filtrate was diluted with a two-fold volume of water and the flocculent precipitate was separated, washed with water, and dried. The product was recrystallized from ethanol–DMF. The total yield was 3.63 g (90%).

Products 4b,d,e were similarly obtained.

N,N-Diphenyl-3-azido-4-methoxymethyl-6-methylthieno[2,3-*b*]pyridine-2-carboxamide (6c). Compound **4c** (2.02 g, 5 mmol) was dissolved in glacial acetic acid (12 ml) and conc. sulfuric acid (0.6 ml) was added. The reaction mixture was cooled in an ice bath to 5-9°C and then, a solution of $NaNO_2$ (0.48 g, 7 mmol) in water (2 ml) was added slowly in small portions. The mixture was stirred for 20 min and then, the excess nitrous acid was neutralized by adding urea (monitored by iodine–starch paper). A solution of NaN_3 (0.46 g, 7 mmol) in water (2 ml) was added dropwise over 10 min. The mixture was stirred for 1 h and then slowly poured into water containing finely ground ice. The precipitate of azide **6c** was separated, washed on the filter with cold water until the wash water was neutral, and dried over conc. sulfuric acid in the absence of light to give 2.08 g (97%) of **6c**.

3-Azidothieno[2,3-*b*]pyridines 6a,b,d were similarly obtained.

(2-Benzoyl-4-methoxymethyl-6-methylthieno[2,3-*b*]pyridin-3-yl)iminotriphenylphosphorane (7e). Triphenylphosphine (2.62 g, 10 mmol) was added to a solution of 3-azidothieno[2,3-*b*]pyridine **6e** (3.38 g, 10 mmol) in benzene (100 ml). The reaction mixture was stirred until gas bubbles were no longer observed and left overnight. The precipitate formed was filtered off, washed with benzene, and dried in the air. The filtrate was evaporated in vacuum and the residue was triturated with diethyl ether. The crystals formed were filtered off, washed with benzene, and dried in the air. The product was recrystallized from ethanol–DMF. The total yield of **7e** was 3.2 g (56%). Yellow monoclinic crystals of **7e** were obtained by crystallization from ethanol. The unit cell parameters are as follows: a = 9.869(2), b = 16.644(3), c = 17.853(4) Å, β = 92.58(3)°, V = 2929.6(10) $Å^3$, space group $P2(1)/n$, Z = 4. The unit cell parameters and intensities of 2293 independent reflections were measured on a CAD-4 automatic diffractometer using Mo$K\alpha$ radiation, β-filter, and θ/2θ-scanning to $2\theta_{max}$ = 44.6°. The structure was deciphered by the direct method using the SHELXTL program package [6] and refined anisotropically for the nonhydrogen atoms and isotropically for the hydrogen atoms to R_1 = 0.0268 and R_w = 0.0709.

Products 7a,c were similarly obtained.

(N-Morpholyl-2-carbamoyl-4-methoxymethyl-6-methylthieno[2,3-*b*]pyridin-3-yl)iminotriphenyl-phosphorane (7d). Triphenylphosphine (2.62 g, 10 mmol) was added to a solution of 3-azidothieno[2,3-*b*]-pyridine **6d** (3.47 g, 10 mmol) in benzene (100 ml). The reaction mixture was stirred until there was no further liberation of gas and left overnight. The mixture was then evaporated in vacuum by 4/5 and hexane (10 ml) was added. The crystals formed were filtered off, washed with hexane, and dried in the air. The product was recrystallized from ethanol–DMF. The total yield of **7d** was 3.66 g (63%).

Product **7b** was similarly obtained.

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