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SYNTHESIS AND STUDY OF FLUORESCENT PROPERTIES OF BENZOTHIAZOLYLTHIENO-THIOPHENE DERIVATIVES*

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A number of benzothiazolylthienothiophenes have been synthesized. Spectral studies have revealed that all these compounds have fluorescent properties that depend on their structure. Dependence of absorption and fluorescence bands positions on the nature of substituents have been established. Increase of the electron-withdrawing nature of substituents led to bathochromic shift of the absorption and fluorescence bands as well as to decrease of the fluorescence intensity.

Keywords: benzothiazolylthienothiophenes, Schiff bases, stilbenes, absorption spectra, fluorescence properties.

The idea of creating photochromic recording media with nondestructive fluorescent reading of optical information [1, 2] has recently been implemented by the development of photochromic recording media for three-dimensional optical memory [3]. In particular, this concept can be realized by synthesis of hybrid photochromic compounds containing a photochromic fluorescent fragment [4-9]. Earlier we have proposed to use the strongly luminescenting benzothiazolylthieno[3,2-*b*]thiophene derivatives as such a fragment. Thus, the reaction of 5-(1,3-benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thiophene-2-carbaldehyde (**1**) with aniline derivatives of fulgimides led to photochromes containing fulgimide and fluorescing benzothiazolylthienothiophene fragments. The absorption and fluorescence spectral properties of these compounds were studied [10]. In the present work, thiophene **1** obtained from (3-pentylthieno[3,2-*b*]thiophen-2-yl)-1,3-benzothiazole (**2**) [10] was used as a starting material to prepare hydrazones **3a,b**, azomethine derivatives **3c-e**, as well as stilbenes **4a-d**. The spectral parameters of these compounds were studied.

Schiff bases **3a-e** were synthesized in 60-70% yield according to Scheme 1.

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*To our dear colleague, Prof. M. G. Voronkov on the occasion of his 90th birthday.

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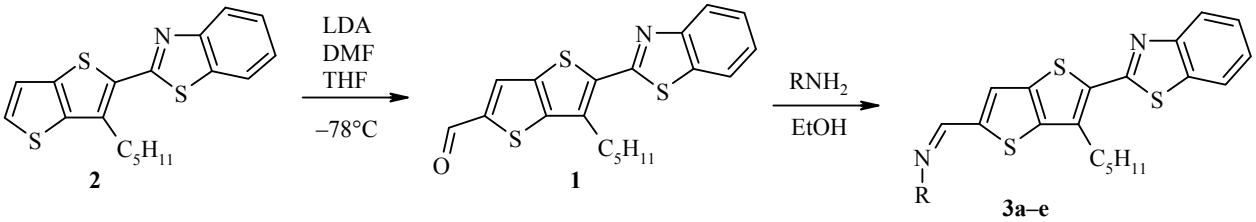
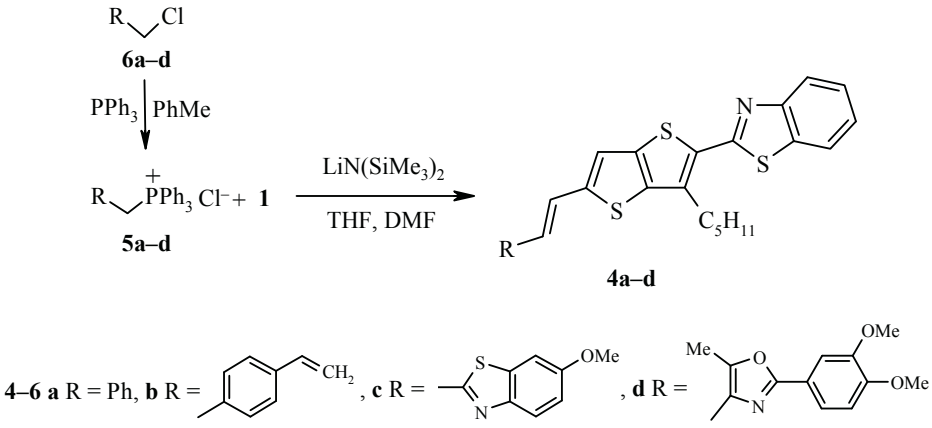
Stilbenes **4a-d** were obtained by the Wittig reaction of aldehyde **1** with phosphonium chlorides **5a-d**, which, in turn, were prepared by the reaction of triphenylphosphine with chlorides **6a-d*** in toluene (Scheme 2).

Scheme 1



3 a R = NHPh, **b** R = NHC(O)($C_6H_4NO_2$-*p*), **c** R = Bu, **d** R = $(CH_2)_2NEt_2$, **e** R = $(CH_2)_3NHEt$

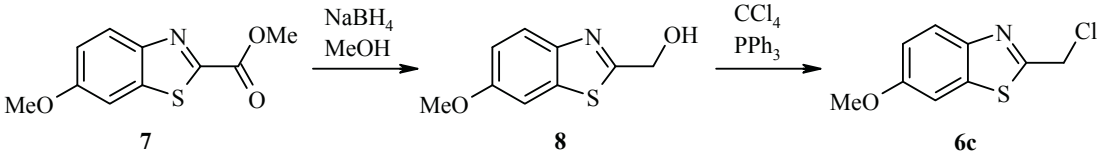
Scheme 2



4–6 a R = Ph, **b** R = , **c** R = , **d** R =

2-(Chloromethyl)-6-methoxy-1,3-benzothiazole (**6c**) was synthesized by the reduction of methyl ester **7** [11] using sodium borohydride in methanol with subsequent chlorination of the resultant (6-methoxy-1,3-benzothiazol-2-yl)methanol (**8**) (Scheme 3).

Scheme 3



The reaction of aldehyde **1** with phosphonium chlorides **5a-d** in THF in the presence of $LiN(SiMe_3)_2$ with the intermediate generation of phosphoric ylides led to (*E*)-isomers of stilbenes **4a-d** in 63-68% yield. The *trans* geometry of the double bond in products **4a-d** was assigned by the ^1H NMR spectra where coupling constants were in the range of 14.3-16.0 Hz, which is a characteristic value for the *trans* orientation.

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The results of the study of the absorption spectra of these compounds along with their fluorescence properties are given in Table 1 and Figs. 1-3. All these compounds appeared to be fluorescent. We note that benzothiazole **2** obtained in our previous work [10] displays coinciding absorption and fluorescence excitation bands with maximum at 353 nm as well as a fluorescence band with maximum at 413 nm, which is shifted toward longer wavelengths by 60 nm relative to the absorption band (Fig. 1, Table 1).

Introduction of the electron-withdrawing carbonyl group into benzothiazole **2** lead to the bathochromic shift of the absorption and fluorescence bands by 25 nm for the thienothienylbenzothiazole aldehyde **1** (Table 1).

Schiff bases **3a-e** give a hypsochromic shift of both the absorption and the fluorescence bands. This shift also depends on the nature of the substituents. Table 1 shows that the bathochromic spectral shift for compounds **3a** and **3c-e** increases in the order **3e < 3d < 3c < 3a.**

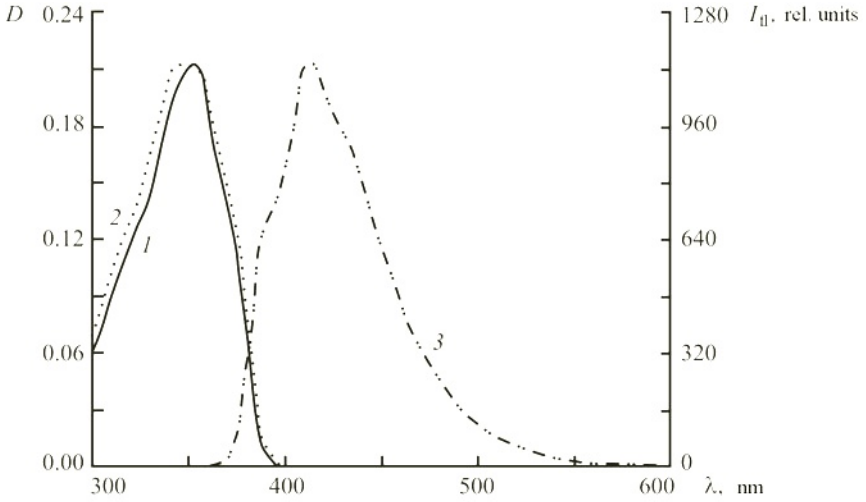

Fig. 1. Absorption (*1*), fluorescence excitation (*2*), and fluorescence spectra (*3*) for benzothiazole **2** in toluene.

TABLE 1. Spectral Properties of Benzothiazolylthienothiophenes **1, 2, 3a-e** and Stilbenes **4a-d** in Toluene*

Compound	λ_{abs}^{max}, nm	$\varepsilon_{max}\,10^{-4}$, $l\cdot mol^{-1}\cdot cm^{-1}$	λ_{exc}^{max}, nm	λ_{fl}^{max}, nm	$\lambda_{fl}^{max} - \lambda_{exc}^{max}$, nm	I_{fl}, rel. units
1	378	5.0	377	438	60	145
2	353	4.2	353	413	60	1140
3a	377	5.2	375	436	61	130
3b	398	2.4	420	506	109	0.12
3c	376	8.4	376	436	60	405
3d	374	5.6	362	425	51	225
3e	362	3.6	360	420	58	1230
4a	415	9.0	415	457	71	2660
4b	403	3.4	403	474	71	1840
4c	430	6.6	430	505	75	1615
4d	410	6.2	408	482	72	990

*λ_{abs}^{max}, λ_{exc}^{max}, and λ_{fl}^{max} are the maxima of the long-wavelength absorption band, fluorescence excitation band and fluorescence band, respectively, ε_{max} is the molar extinction coefficient at the absorption band maximum, I_{fl} is the fluorescence intensity at the fluorescence band maximum.

Diamine **3e** has the shortest-wavelength absorption (362 nm) and fluorescence bands (420 nm) (Fig. 2) as well as the strongest fluorescence in comparison with other compounds described (Table 1). The Stokes shift ($\lambda_{fl}^{max} - \lambda_{exc}^{max}$) for this compound is 61 nm. The fluorescence intensity for the diamine **3e** is much higher than for derivatives **3a, 3c,** and **3d**. Introduction of the strong electron-withdrawing 4-nitrophenylhydrazone fragment into **3b**, as in the case of compound **1**, leads to a bathochromic shift of the absorption bands (from 377 to 398 nm) and a rather significant shift of λ_{fl}^{max} from 436 to 506 nm (Table 1). In this case, the fluorescence intensity also drops sharply, while the Stokes shift increases to 109 nm.

Dependence of the fluorescence band shift on the electron-withdrawing capacity of substituents is also found for stilbenes **4a-d**. Table 1 shows that the maxima of fluorescence bands are shifted toward longer wavelengths with increasing electron-withdrawing capacity of substituents (**4a < 4b < 4d < 4c**). The Stokes shift for all these compounds is about 70 nm. No clear tendencies are found in the behavior of the absorption bands although a trend for the bathochromic spectral shift is noted. As in the case of compounds examined above, the fluorescence intensity decreases with increasing electron-donor capacity of the substituents. A typical change in the spectral parameters in the case of the spectrum of compound **4d** is shown in Fig. 3.

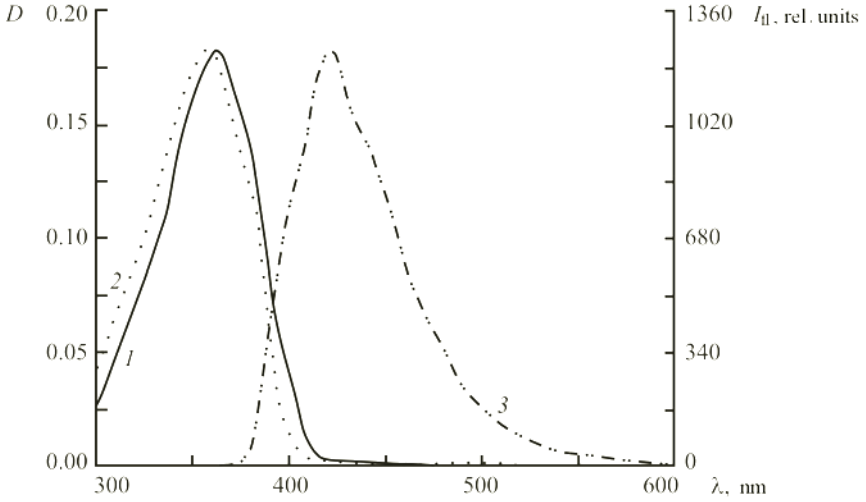

Fig. 2. Spectra for the absorption (*1*), fluorescence excitation (*2*), and fluorescence (*3*) of compound **3c** in toluene.

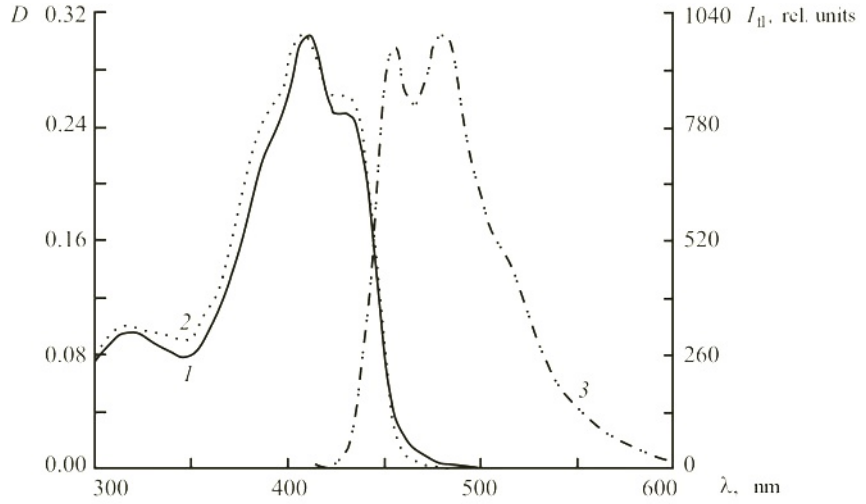

Fig. 3. Spectra for the absorption (*1*), fluorescence excitation (*2*), and fluorescence (*3*) of compound **4d** in toluene.

We should note that stilbenes **4a-d** stand out among the other products due to their high fluorescence intensity, which is independent on the substituents nature (Table 1). A characteristic feature of these compounds is the fine structure in the absorption and, especially, the fluorescence spectra (Fig. 3).

Thus, we have prepared a series of new benzothiazolylthienothiophenes possessing fluorescent properties. The spectral studies have shown that the fluorescent properties of these products depend on the substituent at the second position of the thieno[3,2-*b*]thiophene fragment. The best fluorescence properties were found for the stilbene derivatives. Dependence was found between the position of the absorption and fluorescence bands and the nature of the substituents. A bathochromic shift of the absorption and fluorescence bands was noted with increase of the electron-withdrawing nature of the substituents, which led us to assume the feasibility of controlling the spectral characteristics of benzothiazolylthienothiophenes by means of the fine chemical modification of these compounds.

EXPERIMENTAL

The spectrophotometric measurements (photostationary spectra) of the studied compounds were recorded on a Varian Carey 50 Bio spectrophotometer in toluene solution. The spectrofluorimetric measurements were carried out on a Varian Carey Eclipse spectrofluorimeter under identical experimental conditions (spectrofluorimeter slit width, sample position, and concentration). The spectrofluorimetric measurements were recorded using cells with 10 mm path length. A solution with concentration $5 \cdot 10^{-6}$ mol/l was taken as the working concentration for taking the absorption, excitation, and emission spectra. The concentration for compound **4b** was $1 \cdot 10^{-5}$ mol/l.

The ^{1}H NMR spectra were recorded on a Bruker AC-300 spectrometer at 300 MHz with the residual solvent protons as internal standard (DMSO-d_6, δ 2.51 ppm; $CDCl_3$, δ 7.27 ppm). The electron impact mass spectra were taken on a Kratos spectrometer with direct sample inlet into the radiation source with ionization energy 70 eV and control voltage 1.75 kV. The melting points were determined on a Boethius heating block and were not corrected.

Commercial substances **6a** and **6b** were obtained from Acros. Commercially available reagents from Acros and Sigma-Aldrich were used in this work.

5-(1,3-Benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thiophene-2-carbaldehyde Phenylhydrazone (3a). Phenylhydrazine hydrochloride (0.047 g, 0.323 mmol) was added to a solution of compound **1** (0.100 g, 0.269 mmol) in ethanol (15 ml). The reaction mixture was stirred for 4 h at 60°C. The dark-brown precipitate formed was filtered off, washed with petroleum ether, and dried in vacuum to give compound **3a.** Yield 65%; mp 155-157°C (ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.87 (3H, t, *J* = 6.9, CH_3); 1.40 (4H, m, CH_2CH_2); 1.77 (2H, m, CH_2); 3.17 (2H, t, *J* = 7.6, CH_2); 6.80 (1H, t, *J* = 7.3, H Ar); 7.05-7.30 (4H, m, H Ar); 7.40-7.60 (2H, m, H Ar); 7.55 (1H, s, H-3); 8.00 (2H, m, H Ar); 8.15 (1H, s, N=CH); 8.20 (1H, s, NH). Mass spectrum, *m/z* (I_{rel}, %): 462 (19), 461 $[M]^+$ (55), 418 $[M\text{-}C_3H_7]^+$ (3), 93 (100). Found, %: C 64.68; H 5.44; N 9.45, S 20.43. $C_{25}H_{23}N_3S_3$. Calculated, %: C 65.04; H 5.02; N 9.10; S 20.84.

***N*'-{[5-(1,3-Benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thiophen-2-yl]methylidene}-4-trobenzohydrazide (3b).** 4-Nitrobenzohydrazide (0.058 g, 0.323 mmol) was added to a solution of compound **1** (0.100 g, 0.269 mmol) in ethanol (15 ml). The reaction mixture was stirred for 3.0-3.5 h at 60°C. The yellow precipitate formed was filtered off, washed with petroleum ether, and dried in vacuum to give compound **3b. Y**ield 70%; mp 162-163°C (ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.90 (3H, t, *J* = 6.6, CH_3); 1.40 (4H, m, CH_2CH_2); 1.80 (2H, m, CH_2); 3.17 (2H, t, *J* = 7.3, CH_2); 7.40-7.60 (2H, m, H Ar); 7.87 (1H, s, H-3); 7.90-8.10 (2H, m, H Ar); 8.15 (2H, d, *J* = 7.7, H Ar); 8.35 (2H, d, *J* = 7.7, H Ar); 8.70 (1H, s, N=CH); 12.20 (1H, s, NH). Mass spectrum, *m/z* (I_{rel}, %): 534 $[M]^+$ (35), 418 $[M\text{-}C_3H_7]^+$ (5), 120 (100). Found, %: C 58.73; H 4.56; N 10.10; S 17.51. $C_{26}H_{22}N_4O_3S_3$. Calculated, %: C 58.41; H 4.15; N 10.48; S 17.99.

***N*-{[5-(1,3-Benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thiophen-2-yl]methylidene}butane-1-amine (3c).** Butyl-amine (0.060 ml, 0.646 mmol) was added to a solution of compound **1** (0.100 g, 0.269 mmol) in ethanol(15 ml). The reaction mixture was stirred for 6 h at 60°C. The precipitate formed was filtered off, washed with petroleum ether, and dried in vacuum to give compound **3c**. Yield 60%; mp 145-147°C (ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.85-0.95 (6H, m, $2CH_3$); 1.27-1.50 (6H, m, $3CH_2$); 1.60 (2H, m, CH_2); 1.75 (2H, m, CH_2); 3.15 (2H, t, *J* = 7.8, CH_2); 3.55 (2H, t, *J* = 6.8, CH_2); 7.40-7.60 (2H, m, H Ar); 7.80 (1H, s, H-3); 8.05 (1H, d, *J* = 8.0, H Ar); 8.15 (1H, d, *J* = 7.9, H Ar); 8.50 (1H, s, N=CH). Mass spectrum, *m/z* (I_{rel}, %): 427 (17), 426 $[M]^+$ (100). Found, %: C 64.32; H 6.39; N 6.39; S 22.90. $C_{23}H_{26}N_2S_3$. Calculated, %: C 64.75; H 6.14; N 6.57; S 22.55.

***N*-{[5-(1,3-Benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thiophen-2-yl]methylidene}-*N*',*N*'-diethylethane-1,2-diamine (3d).** *N*,*N*-Diethylethylidenediamine (0.045 ml, 0.323 mmol) was added to a solution of compound **1** (0.100 g, 0.269 mmol) in ethanol (15 ml). The reaction mixture was stirred for 4.0-4.5 h at 60°C. The yellow precipitate was filtered off, washed with petroleum ether, and dried in vacuum to give compound **3d.** Yield 70%; mp 150-152°C (ethanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.95 (3H, t, *J* = 7.0, CH_3); 1.00-1.11 (6H, m, $2CH_3$); 1.45 (4H, m, CH_2CH_2); 1.85 (2H, m, CH_2); 2.68 (4H, m, CH_2CH_2); 2.85 (2H, t, *J* = 6.9, CH_2); 3.20 (2H, t, *J* = 7.9, CH_2); 3.75 (2H, t, *J* = 6.9, CH_2); 7.35-7.50 (3H, m, H Ar, H-3); 7.90 (1H, d, *J* = 8.0, H Ar); 8.05 (1H, d, *J* = 8.1, H Ar); 8.45 (1H, s, N=CH). Mass spectrum, *m/z* (I_{rel}, %): 469 $[M]^+$ (7), 87 (100). Found, %: C 63.86; H 6.88; N 8.72; S 20.64. $C_{25}H_{31}N_3S_3$. Calculated, %: C 63.92; H 6.65; N 8.95; S 20.48.

***N*-{[5-(1,3-Benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thiophen-2-yl]methylidene}-*N*'-ethylpropane-1,3-diamine (3e).** *N*-Ethyl-1,3-propanediamine (0.033 g, 0.323 mmol) was added to a solution of compound **1** (0.100 g, 0.269 mmol) in ethanol (15 ml). The reaction mixture was stirred for 5 h at 60°C. The yellow precipitate was filtered off, washed with petroleum ether, and dried in vacuum to give compound **3e.** Yield 70%; mp 153-154°C (ethanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.90 (3H, t, *J* = 7.0, CH_3); 1.15 (3H, t, *J* = 5.9, CH_3); 1.50 (4H, m, $2CH_2$); 1.85-1.90 (4H, m, $2CH_2$); 2.68 (2H, m, CH_2); 3.10 (2H, t, *J* = 7.0, CH_2); 3.25 (2H, t, *J* = 7.6, CH_2); 3.85 (2H, t, *J* = 7.7, CH_2); 7.30-7.40 (3H, m, H Ar, H-3); 8.05 (1H, d, *J* = 8.0, H Ar); 8.15 (1H, d, *J* = 8.0, H Ar); 8.55 (1H, s, N=CH). Mass spectrum, *m/z* (I_{rel}, %): 456 (9), 455 $[M]^+$ (43), 82 (100). Found, %: C 63.44; H 6.02; N 9.04; S 21.50. $C_{24}H_{29}N_3S_3$. Calculated, %: C 63.26; H 6.41; N 9.22; S 21.11.

(6-Methoxy-1,3-benzothiazol-2-yl)methanol (8). $NaBH_4$ (0.42 g, 11.052 mmol) was added in portions with stirring to a solution of ester **7** (1.10 g, 4.933 mmol) in methanol (30 ml). After 2 h stirring at room temperature, the solvent was evaporated in vacuum. The reaction mixture was then brought to pH 7 by adding 2% hydrochloric acid. The precipitate formed was filtered off, washed with water, and dried in vacuum to give compound **8.** Yield 83%; mp 160-162°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.85 (3H, s, OCH_3); 4.85 (2H, s, CH_2); 6.25 (1H, s, OH); 7.10 (1H, d, *J* = 8.0, H Ar); 7.65 (1H, s, H Ar); 7.80 (1H, d, *J* = 8.1, H Ar). Mass spectrum, *m/z* (I_{rel}, %): 195 $[M]^+$ (47), 166 $[M\text{-}CH_2OH]^+$ (100). Found, %: C 55.59; H 4.21; N 7.42; S 16.03. $C_9H_9NO_2S$. Calculated, %: C 55.37; H 4.65; N 7.17; S 16.42.

2-Chloromethyl-6-methoxy-1,3-benzothiazole (6c). Triphenylphosphine (1.6 g, 6.1 mmol) was added to a solution of compound **8** (0.8 g, 4.1 mmol) in CCl_4 (15 ml). The reaction mixture was heated at reflux for 2 h. After cooling, the solvent was evaporated in vacuum. The residue was separated by thin-layer chromatography using 1:1 ethyl acetate–hexane to give compound **6c.** Yield 45%; mp 145-147°C (ethanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.90 (3H, s, CH_3); 4.90 (2H, s, CH_2); 7.10 (1H, d, *J* = 8.1, H Ar); 7.35 (1H, s, H Ar); 7.95 (1H, d, *J* = 7.9, H Ar). Mass spectrum, *m/z* (I_{rel}, %): 214 $[M]^+$ (54). Found, %: C 50.88; H 3.98; Cl 16.23; N 6.87; S 14.72. C_9H_8ClNOS. Calculated, %: C 50.59; H 3.77; Cl 16.59; N 6.55; S 15.01.

Phosphonium chlorides 5a-d (General Method). Triphenylphosphine (8.0 mmol) was added to a solution of benzyl chloride (**6a**), 4-vinylbenzyl chloride (**6b**), 2-chloromethyl-6-methoxy-1,3-benzothiazole (**6c**), or 4-chloromethyl-2-(3,4-dimethoxyphenyl)-5-methyl-1,3-oxazole (**6d**) in toluene. The reaction mixture was heated at reflux for 12 h in an argon atmosphere. The precipitate formed was filtered off, washed with petroleum ether, and dried in vacuum.

Benzyl(triphenyl)phosphonium Chloride (5a). Yield 75%; mp 118-120°C (ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 5.15-5.25 (2H, s, CH_2); 7.00 (2H, m, H Ar); 7.20-7.35 (3H, m, H Ar); 7.60-7.80 (9H, m, H Ar); 7.85-8.00 (6H, m, H Ar). Mass spectrum, *m/z* (I_{rel}, %): 352 $[M\text{-}Cl\text{-}H]^+$ (45), 351$[M\text{-}Cl\text{-}2H]^+$ (51), 183 (100). Found, %: C 77.50; H 5.36; Cl 9.35; P 7.79. $C_{25}H_{22}ClP$. Calculated, %: C 77.22; H 5.70; Cl 9.12; P 7.97.

4-Vinylbenzyl(triphenyl)phosphonium Chloride (5b). Yield 69%; mp 135-137°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.15 (1H, d, *J* = 7.7) and 5.70 (1H, d, *J* = 7.5, $=CH_2$); 5.40 (2H, s, CH_2); 6.50-6.65 (1H, m, =CH–); 7.00-7.20 (4H, m, H Ar); 7.50-7.85 (15H, m, H Ar). Mass spectrum, *m/z* (I_{rel}, %): 277 (1), 276 $[M\text{-}Cl\text{-}CH_2{=}CHC_6H_4]$ (9), 183 (100). Found, %: C 78.52; H 5.44; Cl 8.06; P 7.98. $C_{27}H_{24}ClP$. Calculated, %: C 78.16; H 5.83; Cl 8.54; P 7.47.

[(6-Methoxy-1,3-benzothiazol-2-yl)methyl]triphenylphosphonium Chloride (5c). Yield 73%; mp 130-132°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.80 (3H, s, OCH_3); 6.00 (2H, s, CH_2); 7.05 (1H, d, *J* = 7.5, H Ar); 7.60-7.95 (17H, m, H Ar). Mass spectrum, *m/z* (I_{rel}, %): 440 $[M\text{-}Cl]^+$ (9). Found, %: C 68.41; H 5.04; Cl 7.13; N 2.68; P 6.83; S 6.45. $C_{27}H_{23}ClNOPS$. Calculated, %: C 68.13; H 4.87; Cl 7.45; N 2.94; P 6.51; S 6.74.

{[2-(3,4-Dimethoxyphenyl)-5-methyl-1,3-oxazol-2-yl]methyl}triphenylphosphonium Chloride (5d). Yield 69%; mp 135-137°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.05 (3H, s, CH_3); 3.80 (6H, s, $2OCH_3$); 5.15 (2H, s, CH_2); 7.05 (1H, d, *J* = 7.7, H Ar); 7.12 (1H, s, H Ar); 7.30 (1H, d, *J* = 7.5, H Ar); 7.70-7.95 (15H, m, H Ar). Mass spectrum, *m/z* (I_{rel}, %): 494 $[M\text{-}Cl]^+$ (6), 493 $[M\text{-}H\text{-}Cl]^+$ (19), 262 (100). Found, %: C 70.58; H 5.23; Cl 6.37; N 2.96; P 5.49. $C_{31}H_{29}ClNO_3P$. Calculated, %: C 70.25; H 5.52; Cl 6.69; N 2.64; P 5.84.

3-Alkyl-5-arylvinyl-2-(1,3-benzothiazol-2-yl)thieno[3,2-*b*]thiophenes 4a-d (General Method). A solution of $LiN(SiMe_3)_2$ (5.30 ml, 1.0 mol/l) in THF was added to a suspension of compound **5a-d** (4.8 mmol) in dry THF (40 ml) and stirred for 30 min. Then, a solution of compound **1** (1.79 g, 4.8 mmol) in THF (40 ml) and DMF (2 ml) was added. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then poured into water and extracted with methylene chloride. The extract was washed with water, and dried over magnesium sulfate, and evaporated. The residue was subjected to chromatography on silica gel using 4:1 hexane–ethyl acetate as the eluent.

2-{3-Pentyl-5-[(*E*)-2-phenylvinyl]thieno[3,2-*b*]thiophen-2-yl)-1,3-benzothiazole (4a). Yield 63%; mp 145-147°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.98 (3H, t, *J* = 6.9, CH_3); 1.50 (4H, m, CH_2CH_2); 1.89 (2H, m, CH_2); 3.21 (2H, t, *J* = 7.8, CH_2); 7.00 (1H, d, *J* = 16.0, CH vinyl); 7.20-7.70 (9H, m, CH vinyl, H-6, H Ar); 7.90 (1H, d, *J* = 7.8, H Ar); 8.18 (1H, d, *J* = 8.1, H Ar). Mass spectrum, *m/z* (I_{rel}, %): 446 (12), 445 $[M]^+$ (50), 402 $[M\text{-}CH_2CH_2CH_3]^+$ (72), 41 (100). Found, %: C 70.42; H 5.53; N 2.88; S 21.17. $C_{26}H_{23}NS_3$. Calculated, %: C 70.07; H 5.20; N 3.14; S 21.59.

2-{5-[(*E*)-2-(4-Vinylphenyl)vinyl]-6-pentylthieno[3,2-*b*]thiophen-2-yl}-1,3-benzothiazole (4b). Yield 65%; mp 158-160°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.98 (3H, t, *J* = 7.0, CH_3); 1.50 (4H, m, CH_2CH_2); 1.89 (2H, m, CH_2); 3.20 (2H, t, *J* = 7.9, CH_2); 5.20 (1H, d, *J* = 8.0) and 5.70 (1H, d, *J* = 7.7, $=CH_2$); 6.60-6.70 (1H, m, =CH–); 7.09 (1H, d, *J* = 16.0, H vinyl); 7.20-7.60 (8H, m, CH vinyl, H-6, H Ar); 7.90 (1H, d, *J* = 8.2, H Ar); 8.18 (1H, d, *J* = 8.4, H Ar). Mass spectrum, *m/z* (I_{rel}, %): 472 $[M]^+$ (9), 54 (100). Found, %: C 71.46; H 5.17; N 2.72; S 20.65. $C_{28}H_{25}NS_3$. Calculated, %: C71.30; H 5.34; N 2.97; S 20.39.

2-{(*E*)-2-[5-(1,3-Benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thiophen-2-yl]vinyl}-6-methoxy-1,3-benzothiazole (4c). **Y**ield 68%; mp 158-160°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.95 (3H, t, *J* = 7.0, CH_3); 1.50 (4H, m, $2CH_2$); 1.90 (2H, m, CH_2); 3.20 (2H, t, *J* = 8.0, CH_2); 3.90 (3H, s, OCH_3); 7.05 (1H, d, *J* = 14.3, CH vinyl); 7.20-7.70 (7H, m, CH vinyl), H-6, H Ar); 7.90 (1H, d, *J* = 8.2, H Ar); 8.10 (1H, d, *J* = 8.2, H Ar). Mass spectrum, *m/z* (I_{rel}, %): 532 $[M]^+$ (7). Found, %: C 63.51; H 4.33; N 5.56; S 23.87. $C_{28}H_{24}N_2OS_4$. Calculated, %: C 63.12; H 4.54; N 5.26; S 24.08.

2-(5-{(*E*)-[4-(3,4-Dimethoxyphenyl)-5-methyl-1,3-oxazol-4-yl]vinyl}-3-pentylthieno[3,2-*b*]thiophen-2-yl]-1,3-benzothiazole (4d). Yield 68%; mp 158-160°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.98 (3H, t, *J* = 7.0, CH_3); 1.50 (4H, m, CH_2CH_2); 1.85 (2H, m, CH_2); 2.50 (3H, s, CH_3); 3.20 (2H, t, *J* = 7.9, CH_2); 3.95 (3H, s, OCH_3); 4.05 (3H, s, OCH_3); 6.85 (1H, d, *J* = 14.3, CH vinyl); 6.95 (1H, s, H Ar); 7.20-7.70 (6H, m, CH vinyl, H-6, H Ar); 7.90 (1H, d, *J* = 8.2, H Ar); 8.10 (1H, d, *J* = 8.4, H Ar). Mass spectrum, *m/z* (I_{rel}, %): 586 $[M]^+$ (16). Found, %: C 65.43; H 5.22; N 4.58; S 16.57. $C_{32}H_{30}N_2O_3S_3$. Calculated, %: C 65.50; H 5.15; N 4.77; S 16.39.

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