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New substituted dibenzothiophenes have been prepared and characterized. Selective functionalizations utilized substitutions of lithiodibenzothiophenes available from established methodology. New dibenzothiophenes prepared include 2-(bromomethyl)dibenzothiophene (**5**), 2-(thiomethyl)dibenzothiophene (**6**), 2-*S*-phenylthiomethyl dibenzothiophene (**24**), 2-*S*-(2'-dibenzothiophenylmethyl)thiomethyl dibenzothiophene (**25**), 2-*S*-methyl dibenzothiophene (**30**), 2-*S*-(*p*-bromophenyl) dibenzothiophene (**31**), and 2-*S*-benzyl dibenzothiophene (**33**). Dibenzothiophenes prepared from 4-lithiodibenzothiophenes include 4-(bromomethyl) dibenzothiophene (**13**), 4-(thiomethyl) dibenzothiophene (**14**), 4-*S*-(4'-dibenzothiophenylmethyl)thiomethyl dibenzothiophene (**26**), 4-*S*-(*p*-tolyl) dibenzothiophene (**34**), 4-*S*-methyl dibenzothiophene (**35**), 4-*S*-benzyl dibenzothiophene (**37**), and 4-*S*-(*p*-bromophenyl) dibenzothiophene (**36**). Similarly new 2,8-disubstituted dibenzothiophenes prepared include 2,8-*bis*-(thiomethyl) dibenzothiophene (**19**), 2,8-*bis*-(*S*-benzyl) dibenzothiophene (**27**), 2,8-*bis*-(*S*-*p*-tolyl) dibenzothiophene (**28**) and 2,8-*bis*-(*S*-methyl) dibenzothiophene (**29**). The cmr chemical shift data for these dibenzothiophenes are also included.

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Introduction.

Organic bound sulfur in coal has been suggested to include functional groups including benzothiophene, dibenzothiophene, thiosulfides and disulfides [1]. These groups have been differentiated and quantized based on their differences in reactivity. Evidence suggests [2] that coal which is more difficult to desulfurize contains more aromatic sulfur types such as aromatic thiols, thiophenes, benzothiophenes, or dibenzothiophenes. It has been postulated [3] that this relative distribution of sulfur functional groups can be explained in the way that the organic matrix was trapped during the coalification process. The fact that coal desulfurization efficiency ultimately depends on the distribution among organic sulfur types makes it imperative that these organic sulfur types be characterized and quantized in as accurate a method as possible. In order to develop a method to identify sulfur types based on selective catalytic desulfurization, we required a series of model compounds containing different organic sulfur types found in coal. It seemed convenient to append these sulfur functional groups to dibenzothiophene as literature precedent existed for the efficient functionalization of dibenzothiophene at carbons 2, 4, and/or 8.

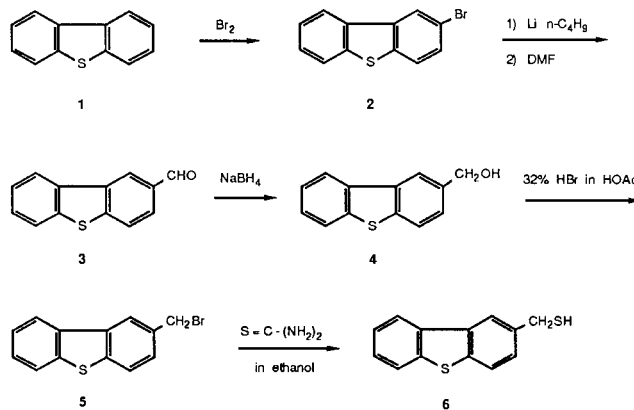
Benzothiophenes and dibenzothiophenes have been studied under coal desulfurization or petroleum processing conditions. The mechanism of desulfurization of dibenzothiophene 5,5-dioxide by pyrolysis under oxidative conditions has been studied [4]. Fundamental synthetic chemistry of dibenzothiophenes carried out by Goodman, Campaigne, Swan, and their co-workers was used in the preparation of sulfur isosteres of biologically active compounds [5]. More recently polycyclic aromatic sulfur het-

erocycles containing thiophenes and dibenzothiophenes have been prepared and used for comparison to related compounds isolated from petroleum and coal liquification residues in a study of their mutagenic, carcinogenic and teratogenic properties [6,7].

Results and Discussion.

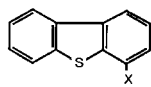
The synthesis of several thiomethyl substituted dibenzothiophenes was carried out, the first of which was 2-(thiomethyl)dibenzothiophene as shown in Scheme I. Bromination of dibenzothiophene (**1**) and conversion of the 2-bromodibenzothiophene (**2**), using the conditions described by Campaigne and Ashby [8], yielded dibenzothiophene-2-carboxaldehyde (**3**), which upon treatment with sodium borohydride gave 2-(hydroxymethyl)dibenzothiophene (**4**). Using the procedure of Boekelheide and co-workers [9], 2-(hydroxymethyl)dibenzothiophene (**4**) was converted to 2-(bromomethyl)dibenzothiophene (**5**), which

Scheme I



was converted to 2-(thiomethyl)dibenzothiophene (**6**) using thiourea in refluxing ethanol.

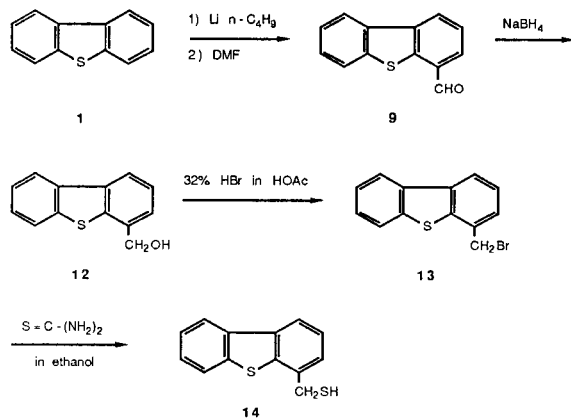
In an early attempt to prepare monoalkyl dibenzothiophenes, Gerdil and Lucken [10] obtained 4,6-dimethyldibenzothiophene along with 4-methyldibenzothiophene in only 15% yield by treatment of dibenzothiophene (**1**) with excess *n*-butyllithium and quenching with dimethylsulfate in refluxing di-*n*-butyl ether [11]. More recently 4-lithiodibenzothiophene has been prepared by treatment of dibenzothiophene (**1**) with one equivalent of *n*-butyllithium at 0°, which was then quenched by reactive electrophiles to give 4-substituted dibenzothiophenes. Using this strategy, Campaigne [11] prepared 4-hydroxydibenzothiophene (**8**). Castle and co-workers prepared dibenzothiophene-4-carboxaldehyde (**9**) using *N,N*-dimethylformamide and 4-ethyldibenzothiophene (**10**) using diethylsulfate [12,13], while Rauchfuss [14] made 4-diphenylphosphinodibenzothiophene (**11**).



- 1 X = H
 7 X = Li
 8 X = OH
 9 X = CHO
 10 X = CH₂CH₃
 11 X = P(Ph)₂

Our efforts to prepare 4-(thiomethyl)dibenzothiophene utilized this selective lithiation strategy. Dibenzothiophene-4-carboxaldehyde (**9**) was prepared and the aldehyde group was reduced with sodium borohydride to **12**, which was brominated [9] giving 4-(bromomethyl)dibenzothiophene (**13**). Refluxing **13** with thiourea in ethanol [15] afforded 4-(thiomethyl)dibenzothiophene (**14**) as illustrated in Scheme 2.

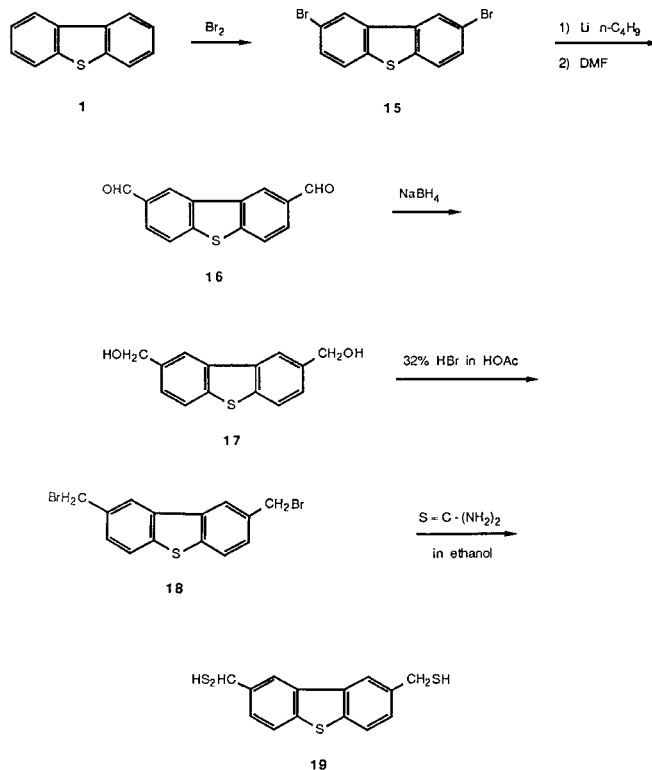
Scheme 2



In addition to the preparation of monosubstituted dibenzothiophenes, several *bis*-substituted dibenzothiophenes were prepared in order to study the relative ease of intramolecular cleavage of different carbon-sulfur bond

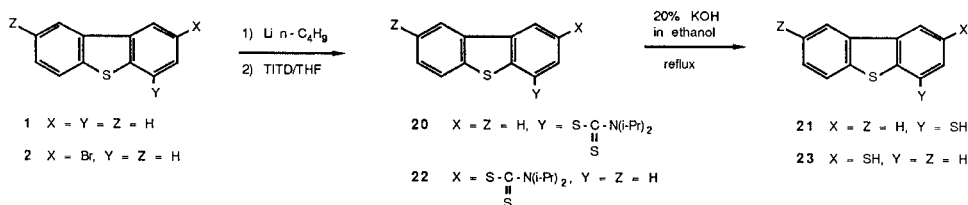
types. Thus 2,8-dibromodibenzothiophene (**15**), available by the procedure of Neumoyer and Amstutz [16] served as the starting material for preparation of 2,8-*bis*-(thiomethyl)dibenzothiophene (**19**) as shown in Scheme 3. The method described by Boekelheide and co-workers [9] was used to convert **15** into 2,8-*bis*-(formyl)dibenzothiophene (**16**) which was reduced with sodium borohydride, affording 2,8-*bis*-(hydroxymethyl)dibenzothiophene (**17**). It was brominated giving 2,8-*bis*-(bromomethyl)dibenzothiophene (**18**) which was refluxed with thiourea in ethanol [15] to give 2,8-*bis*-(thiomethyl)dibenzothiophene (**19**).

Scheme 3



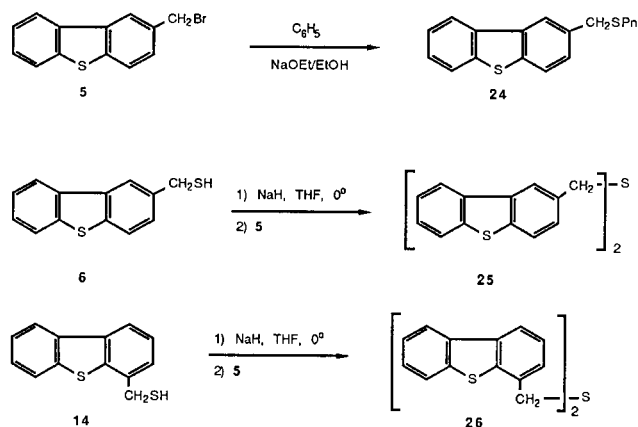
While thiourea in refluxing ethanol [15] proved to be a satisfactory method for the preparation of thiomethyl derivatives **6**, **14** and **19** from their respective bromides, the conversion of aromatic bromides to aromatic thiols *via* their lithio derivatives required an electrophilic thiolating reagent rather than a nucleophilic one. Jen and Cava utilized the electrophilic reactivity of tetraisopropylthiuram disulfide (TITD) [17,18] to prepare various aromatic thiols including 4-dibenzothiophenethiol (**21**) [19]. In our hands, for the preparation of **21** from **7** (using this method), a good yield was obtained using tetrahydrofuran as a solvent. This procedure was also applied to the preparation of 2-dibenzothiophenethiol (**23**) in which the optimum reaction solvent was ether. These results are summarized in Scheme 4.

Scheme 4



Some of the previously prepared thiomethyldibenzothiophenes and dibenzothiophenethiols were then utilized in the preparation of dibenzothiophene-containing thioethers. For the inclusion of benzylic thioethers, the sodium thiolates of thiophenol [19], 2-thiomethyldibenzothiophene (**6**), and 4-thiomethyldibenzothiophene (**14**) were reacted with bromomethyldibenzothiophenes **5** and **13** to give the benzylic thioethers **24-26** shown in Scheme 5.

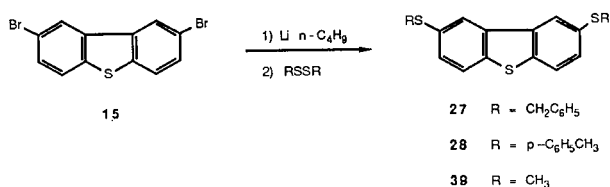
Scheme 5



For preparation of thioethers from these dibenzothiophene thiols, the requisite lithiodibenzothiophenes were quenched with aromatic or benzylic disulfides. Thus treatment of 2,8-dibromodibenzothiophene (**15**) with *n*-butyl lithium in ether at 0° gave 2,8-bis(lithio)dibenzothiophene

which, upon quenching successively with benzyl disulfide, *p*-tolyl disulfide, and methyl disulfide, gave 2,8-bis(*S*-benzyl)dibenzothiophene (**27**), 2,8-bis(*S-p*-tolyl)dibenzothiophene (**28**) and 2,8-bis(*S*-methyl)dibenzothiophene (**29**) as shown in Scheme 6.

Scheme 6



The corresponding 2-substituted dibenzothiophene thioethers were also prepared by lithium exchange of **2** (*n*-butyllithium, ether, 0°) and quenching with the disulfides shown in Scheme 7. In this manner 2-*S*-methyl-dibenzothiophene (**30**), 2-*S*(*p*-bromophenyl)dibenzothiophene (**31**), and 2-*S*-benzyl-dibenzothiophene (**32**) were prepared as shown in Scheme 7. Using 4-lithiodibenzothiophene (**7**)

Scheme 7

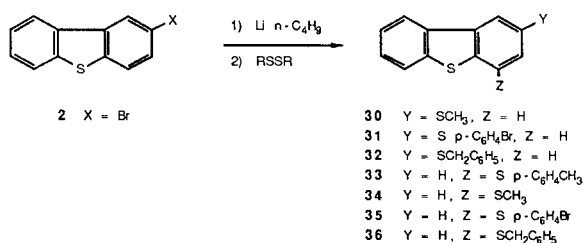


Table I

¹³C Data for 2-Substituted Dibenzothiophenes

#	C _{1a}	C ₁	C ₂	C ₃	C ₄	C _{4a}	C _{5a}	C ₆	C ₇	C ₈	C ₉	C _{9a}
1	135.40	126.57	121.46	122.67	124.22	139.31	137.31	124.22	122.67	121.46	126.57	135.40
3	135.82	127.58	134.04	121.87	125.01	145.98	139.57	123.40	123.17	122.89	126.82	134.79
4	137.29	127.66	120.56	121.57	125.78	139.69	138.61	124.77	123.77	122.57	126.79	135.70
5	137.30	127.60	134.80	121.58	125.85	139.74	138.60	124.35	123.11	122.81	126.75	135.29
6	137.27	129.14	134.45	121.61	125.91	139.77	138.66	125.40	121.93	122.84	126.79	135.32
23	133.21	127.93	124.45	124.17	123.28	139.72	134.02	126.99	122.88	121.61	127.06	132.92
24	135.08	129.40	129.72	123.03	124.96	136.06	135.56	124.02	123.32	123.53	123.83	135.13
30	136.04	126.79	134.27	122.68	122.86	139.78	136.68	122.64	121.43	120.03	124.22	134.04
31	136.68	129.69	130.76	123.71	124.62	139.78	139.43	126.00	122.86	121.75	127.22	136.63
32	136.04	128.81	131.69	127.89	127.31	139.29	137.59	126.88	126.57	121.47	128.56	135.39

Table II

¹³C Data for 4-Substituted Dibenzothiophenes

#	C _{1a}	C ₁	C ₂	C ₃	C ₄	C _{4a}	C _{5a}	C ₆	C ₇	C ₈	C ₉	C _{9a}
1	135.40	126.57	121.46	122.67	124.22	139.31	139.31	124.22	122.67	121.46	126.57	135.40
9	133.44	127.33	124.72	124.29	132.84	141.52	137.22	122.94	122.69	121.42	126.87	133.26
12	135.75	126.72	124.65	124.26	120.21	139.22	137.15	124.67	122.76	121.62	126.60	135.32
13	135.55	127.39	124.93	124.58	131.65	131.21	136.56	124.62	122.78	121.79	127.07	135.48
14	136.16	126.88	124.49	121.77	131.26	138.18	136.21	125.03	122.83	120.48	126.07	135.12
33	136.18	126.90	121.82	122.81	130.86	139.40	137.08	124.41	122.81	120.94	126.63	134.90
34	135.37	126.67	121.89	122.75	135.49	139.37	139.32	124.42	122.83	121.53	126.67	135.40
35	135.71	127.28	121.92	122.86	132.24	139.46	136.32	124.58	122.78	120.41	129.34	135.71
36	136.29	128.88	127.33	127.92	132.49	139.31	137.26	126.92	126.60	121.48	128.57	135.42

[11], several 4-substituted thioethers were synthesized, including 4-*S-p*-tolylidibenzothiophene (**33**), 4-*S*-methylidibenzothiophene (**34**), 4-*S*-(*p*-bromophenyl)dibenzothiophene (**35**), and 4-*S*-benzylidibenzothiophene (**36**) as shown in Scheme 7.

To lend further support to the assigned structures and also because of the fact that the cmr data of dibenzothiophene and its derivatives were not available in the literature, the cmr spectra of each of these 2-substituted and 4-substituted dibenzothiophenes are recorded in Table I and Table II. Because of the numbers of resonances in close proximity, the assignment of very similar carbons of the aromatic rings of dibenzothiophene may be interchangeable. The low solubility of 2,8-*bis*-substituted dibenzothiophenes precluded the determination of their cmr spectra.

EXPERIMENTAL

The spectra were recorded for solutions in deuteriochloroform using a Nicolet-200 spectrometer. The pmr spectra are reported referenced to internal TMS at 200 MHz. The cmr spectra were recorded at 50.3 MHz, referenced to deuteriochloroform (77.00). Multiplicities from off resonance decoupling experiments are in agreement with the assignments. Mass spectra were obtained using a Kratos MS-80 medium resolution mass spectrometer in either low resolution electron impact (EI) or chemical ionization (CI, methane), mode or in the high resolution mode with peak matching to perfluorokerosene. The ir spectra were recorded on a Nicolet FTIR spectrometer. Tlc and column chromatography were performed on silica gel GF₂₅₄(230-400 mesh, Merck). Analytical hplc was performed using a 30 cm Waters 5μ Microporasil column. All solvents were distilled shortly before use from an appropriate drying agent. Ether and tetrahydrofuran were distilled from sodium metal in the presence of benzophenone ketyl.

2-(Hydroxymethyl)dibenzothiophene (**4**).

To a cold solution of dibenzothiophene-2-carboxaldehyde (**3**) (1 g, 47 mmoles) in 50 ml of absolute ethanol was added excess sodium borohydride (1 g) with stirring. The reaction mixture was slowly and carefully heated to reflux and the temperature was maintained at 78° for 1 hour. After cooling the reaction mixture to room temperature, the solu-

tion was neutralized with 10% sulfuric acid. The white precipitate was dissolved in dichloromethane and separated. After washing with water, drying and concentrating, white needles of 2-(hydroxymethyl)dibenzothiophene (**4**) were obtained (0.98 g, 98%); mp 105°; pmr (deuteriochloroform): δ 1.82 (s, 1H, OH), 4.82 (s, 2H, CH₂O), 7.44-7.50 (m, 3H, 3-H, 7-H, 8-H), 7.81-7.88 (m, 2H, 4-H, 6-H), 8.13-8.17 (m, 2H, 1-H, 9-H); ms: HREI (C₁₃H₁₀SO) Calcd: 214.0453. Found: 214.0450; m/e (%) 214 (28), 197 (100), 185 (15), 184 (2); cmr (deuteriochloroform): δ 137.29 (C-1a), 127.66 (C-1), 120.56 (C-2), 121.57 (C-3), 125.78 (C-4), 139.69 (C-4a), 138.61 (C-5a), 124.77 (C-6), 123.77 (C-6), 122.57 (C-8), 126.79 (C-9), 135.70 (C-9a), and 65.31 (C-10).

2-(Bromomethyl)dibenzothiophene (**5**).

A mixture of 2-(hydroxymethyl)dibenzothiophene (**4**) (2.9 g, 13.55 mmoles) in 34 ml of glacial acetic acid was warmed to 45°. A 32% solution of hydrogen bromide in 17 ml of acetic acid was added in one portion and the resulting mixture refluxed for 2 hours, stirred at 25-27° overnight (16 hours), and then cooled to 0°. The resulting precipitate was collected by filtration, dissolved in chloroform, washed with water, dried, and concentrated to give **5** (2.6 g, 69%), mp 113-115°; pmr (deuteriochloroform): δ 4.68 (s, 2H, -CH₂Br), 7.43-7.48 (m, 3H, 3-H, 7-H, 8-H), 7.77-7.85 (m, 2H, 4-H, 6-H), 8.08-8.13 (m, 2H, 1-H, 9-H); ms: HREI (C₁₃H₉SBr) Calcd: 275.9608. Found: 275.9633; m/e (%) 278 (8), 276 (7.5), 197 (92); cmr (deuteriochloroform): δ 137.30 (C-1a), 127.60 (C-1), 134.80 (C-2), 121.58 (C-3), 125.85 (C-4), 139.74 (C-4a), 138.60 (C-5a), 124.35 (C-6), 123.11 (C-7), 122.81 (C-8), 126.75 (C-9), 135.29 (C-9a), and 32.08 (C-10).

2-(Thiomethyl)dibenzothiophene (**6**).

In a 100 ml three necked flask were placed thiourea (0.19 g, 2.5 mmoles), 25 ml of water and 80 ml of absolute ethanol. The solid was dissolved by warming with stirring. The 2-(bromomethyl)dibenzothiophene (1.38 g, 5 mmoles) was added to the reaction mixture and the resulting solution refluxed for 2.5 hours, then cooled to room temperature. Aqueous sodium hydroxide (10%, 125 ml) was added and the reaction mixture refluxed 6 hours. The mixture was cooled, neutralized with 10% sulfuric acid and extracted with dichloromethane (3 x 50 ml). The combined extracts were dried, filtered, and concentrated to afford 2-(thiomethyl)dibenzothiophene (**6**) (0.92 g, 80%), mp 67°; pmr (deuteriochloroform): δ 1.80 (s, 1H, SH), 4.75 (s, 2H, CH₂S), 7.40-7.46 (m, 3H, 3-H, 7-H, 8-H) 7.75-7.81 (m, 2H, 4-H, 6-H), 8.10-8.16 (m, 2H, 1-H, 9-H); ms: HREI (C₁₃H₁₀S₂) Calcd: 230.0224. Found: 230.1150; m/e (%) 230 (35), 197 (100), 184 (10); cmr (deuteriochloroform): δ 137.27 (C-1a), 129.14 (C-1), 134.45 (C-2), 121.61 (C-3), 125.91 (C-4), 139.77 (C-4a), 138.66 (C-5a), 125.40 (C-6), 121.93 (C-7), 122.84 (C-8), 126.79 (C-9), 135.32 (C-9a), and 28.25 (C-10).

Anal. Calcd. for C₁₃H₁₀S₂ (230.0224): C, 67.81; H, 4.38. Found: C, 68.23; H, 4.39.

4-(Hydroxymethyl)dibenzothiophene (**12**).

To a 0° solution of dibenzothiophene-4-carboxaldehyde (**7**) (1 g, 4.7 mmoles) in 50 ml of absolute ethanol, excess sodium borohydride (1 g) was added slowly. The resulting solution was slowly heated to reflux for 1 hour. After workup described for the synthesis of **4**, **12** was isolated (0.95 g, 95%), mp 129-130°; pmr (deuteriochloroform): δ 1.56 (s, 1H, O-H), 5.02 (s, 2H, CH₂O), 7.43-7.52 (m, 3H, 2-H, 7-H, 8-H), 7.85-7.89 (m, 2H, 3-H, 6-H), 8.13-8.20 (m, 2H, 1-H, 9-H); ms: HREI (C₁₃H₁₀SO) Calcd: 214.0453. Found: 214.0453, m/e (%) 214 (15), 212 (18), 197 (10), 184 (100); cmr (deuteriochloroform): δ 135.75 (C-1a), 126.72 (C-1), 124.65 (C-2), 124.26 (C-3), 120.21 (C-4), 139.22 (C-4a), 137.15 (C-5a), 124.67 (C-6), 122.76 (C-7), 121.62 (C-8), 126.60 (C-9), 135.32 (C-9a), and 63.32 (C-10).

4-(Bromomethyl)dibenzothiophene (**13**).

A mixture of 4-(hydroxymethyl)dibenzothiophene (**12**) (3 g, 14 mmoles) in 34 ml of glacial acetic acid was warmed and to it, hydrobromic acid (20 ml) in acetic acid was added. After refluxing for 2 hours, followed by overnight stirring at room temperature, workup as described for **5** yielded **13** (2.58 g, 67%), mp 110°; pmr (deuteriochloroform): δ 4.78 (s, 2H, CH₂, Br), 7.42-7.51 (m, 3H, 2-H, 7-H, 8-H), 7.88-7.92 (m, 2H, 3-H, 6-H), 8.10-8.18 (m, 2H, 1-H, 9-H); ms: HREI (C₁₃H₉SBr) Calcd: 275.9608. Found: 275.9642, m/e (%) 278 (19), 276 (9.8), 212 (3), 197 (100), cmr (deuteriochloroform): δ 135.55 (C-1a), 127.39 (C-1), 124.93 (C-2), 124.58 (C-3), 131.65 (C-4), 131.21 (C-4a), 136.56 (C-5a), 124.62 (C-6), 122.78 (C-7), 121.79 (C-8), 127.07 (C-9), 135.48 (C-9a), and 32.06 (C-10).

4-(Thiomethyl)dibenzothiophene (**14**).

Using the procedure for **6**, 4-(bromomethyl)dibenzothiophene (**13**) (1.38 g, 5 mmoles) was converted to **14** (0.915 g, 8%), mp 69-70°; pmr (deuteriochloroform): δ 1.78 (s, 1H, SH), 4.76 (s, 2H, CH₂S), 7.77-7.80 (m, 2H, 3-H, 6-H), 8.14-8.18 (m, 2H, 1-H, 9-H); ms: HREI (C₁₃H₁₀S₂) Calcd: 230.0223. Found: 230.0207; m/e (%) 230 (30), 212 (7), 197 (100), 184 (10); cmr (deuteriochloroform): δ 136.16 (C-1a), 126.88 (C-1), 124.49 (C-2), 121.77 (C-3), 131.26 (C-4), 138.18 (C-4a), 136.21 (C-5a), 125.03 (C-6), 122.83 (C-7), 120.48 (C-8), 126.07 (C-9), 135.12 (C-9a), and 28.24 (C-1).

Anal. Calcd. for C₁₃H₁₀S₂ (230.0224): C, 67.81; H, 4.38. Found: C, 67.00; H, 4.05.

2,8-Bis(thiomethyl)dibenzothiophene (**19**).

A solution of 2,8-bis(bromomethyl)dibenzothiophene (**18**) (0.184 g, 0.5 mmole) and thiourea (0.152 g, 0.2 mmole) in 95% ethanol (10 ml) was refluxed for 2.5 hours. After neutralization (10% sulfuric acid) **19** was obtained (0.72 g, 87%), mp > 300°; pmr (deuteriochloroform): δ 1.86-1.89 (broad, 2H, SH), 4.87 (s, 4H, CH₂S), 7.43-7.48 (d, J = 9 Hz, 2H, 3-H, 7-H), 7.81-7.85 (d, J = 8 Hz, 2H, 4-H, 6-H), 8.16 (s, 2H, 1-H, 9-H); ms: HREI (C₁₄H₁₂S₃) Calcd: 276.0109. Found: 276.0087; m/e (%) 275 (4), 244 (3), 202 (4), 181 (7), 135 (15), 119 (109), 105 (40), 91 (100).

Anal. Calcd. for C₁₄H₁₂S₃ (276.0109): C, 60.86; H, 4.34. Found: C, 61.01; H, 4.26.

4-Dibenzothiophenethiol (**21**).

To a solution of dibenzothiophene (1.0 g, 5.4 mmoles) in THF (2 ml) at 0°, *n*-butyllithium, (0.7 ml, 1.6 M in *n*-hexane) was added dropwise. The resulting deep orange solution was allowed to warm to 25° and stirring continued for 5 hours. Tetraisopropylthiuram disulfide (TITD) (0.176 g, 5.4 mmoles) was added slowly, during which the orange color faded and a yellow color developed. This yellow reaction mixture was allowed to stir at 25° for 16 hours, then quenched with water and neutralized with 10% hydrochloric acid and extracted with dichloromethane (3 x 15 ml). The combined extracts were dried, filtered, and concentrated affording the intermediate dithiocarbamate **20** (1.078 g, 61%), mp 145-146°. Crude **20** was then refluxed in potassium hydroxide ethanol (20%, 10 ml) for 6 hours, cooled to 25°, and neutralized with 18% hydrochloric acid. The aqueous solution was extracted with dichloromethane (3 x 15 ml). The combined extracts were dried, filtered, and concentrated to afford 4-dibenzothiophenethiol (**21**) (1.0 g, 86%), mp 86°; pmr (deuteriochloroform): δ 8.11-8.17 (m, 2H, 1-H, 9-H), 7.85-7.9 (m, 2H, 3-H, 6-H), 7.45-7.53

(m, 3H, 2-H, 7-H, 8-H), 3.39 (broad, 1H, S-H); ms: HREI (C₁₂H₈S₂) Calcd: 216.0067. Found: 216.0070; m/e (%) 216 (100), 209 (29), 184 (100), 171 (26), 105 (22); ir (potassium chloride): 2500 cm⁻¹ (S-H).

Anal. Calcd. for C₁₂H₈S₂ (216.0067): C, 66.66; H, 3.70. Found: C, 67.06; H, 4.01.

2-Dibenzothiophenethiol (**23**).

2-Bromodibenzothiophene (2.63 g, 10 mmoles), was suspended in ether (25 ml) and cooled to 0°. *n*-Butyllithium (1.6 M in hexane, 6.6 ml) was added and stirring continued 10 minutes; TITD (3.52 g, 10 mmoles) was added slowly, and the resulting mixture warmed to 25° followed stirring for 66 hours. As described for compound **20**, workup afforded the crude **23** which was hydrolyzed with 20% potassium hydroxide in ethanol to afford **23** (3.0 g, 85%); mp 81-83°; pmr (deuteriochloroform): δ 4.08 (s, 1, -SH), 7.43-7.47 (m, 3H, 3-H, 7-H, 8-H), 7.77-7.81 (m, 2H, 4-H, 6-H), 8.03-8.09 (9-H), 8.21-8.29 (1-H); ms: HREI (C₁₂H₈S₂) Calcd: 216.0067. Found: 216.0042; m/e (%) 216 (16), 205 (100), 184 (86), 161 (34), 145 (30), 105 (57); cmr (deuteriochloroform): δ 133.21 (C-1a), 127.93 (C-1), 124.45 (C-2), 124.17 (C-3), 123.28 (C-4), 139.72 (C-4a), 134.02 (C-5a), 126.99 (C-6), 122.88 (C-7), 121.61 (C-8), 127.06 (C-9), and 132.92 (C-9a).

Anal. Calcd. for C₁₂H₈S₂ (216.0067): C, 66.66; H, 3.70. Found: C, 66.46; H, 3.99.

2-S-Phenylthiomethyl-dibenzothiophene (**24**).

A solution of thiophenol (0.275 g, 2.5 mmoles) in 10% sodium ethoxide in ethanol (2 ml) was added, with stirring, to a refluxing solution of 2-bromomethyl-dibenzothiophene (0.692 g, 2.5 mmoles) in ethanol (4 ml). The resulting solution was refluxed 2 hours, filtered, the filtrate cooled and the resulting white solid was recrystallized from hot ethanol affording 2-S-phenylthiomethyl-dibenzothiophene (**24**), (0.765 g, 83%), mp > 300°; pmr (deuteriochloroform): δ 4.26 (s, 2H, CH₂S), 7.28 (s, 5H, phenyl), 7.72-7.79 (m, 3H, 3-H, 7-H, 8-H), 7.90-7.93 (m, 2H, 4-H, 6-H), 8.14-8.18 (m, 2H, 1-H, 9-H); ms: HREI m/e (%) 306 (10), 218 (40), 197 (100); cmr (deuteriochloroform): δ 135.08 (C-1a), 129.40 (C-1), 129.72 (C-2), 123.03 (C-3), 124.96 (C-4), 136.06 (C-4a), 135.56 (C-5a), 124.02 (C-6), 123.32 (C-7), 123.53 (C-8), 123.83 (C-9), 135.13 (C-9a), 65.90 (C-10), 150.37 (C-1'), 149.83 (C-2'), 149.30 (C-3'), 150.19 (C-4').

Anal. Calcd. for C₁₉H₁₄S₂ (306.0536): C, 74.50; H, 4.57. Found: C, 73.66; H, 4.49.

2-S-(2'-Dibenzothiophenylmethyl)thiomethyl-dibenzothiophene (**25**).

A solution of 2-(thiomethyl)dibenzothiophene (**6**) (0.39 g, 1.7 mmoles) in THF (20 ml) was stirred with sodium hydride (0.48 g, 2.0 mmoles) for 15 minutes at 0°. 2-(Bromomethyl)dibenzothiophene (**5**) (0.457 g, 1.7 mmoles) was added slowly and the mixture refluxed for 4 hours, then cooled and neutralized with 5% hydrochloric acid. The crude product was filtered and purified affording **25** (0.527 g, 73%); pmr (deuteriochloroform): δ 3.80 (s, 4H, CH₂), 7.38-7.42 (m, 4H, H-4, H-6, H-4', H-6'), 7.45-7.50 (m, 2H, 7-H, H-7'), 7.65-7.69 (m, 2H, 3-H, 3'-H), 7.75-7.80 (m, 2H, 8-H, 8'-H), 8.79-8.18 (m, 4H, 1-H, 9-H, 1'-H, 9'-H); ms: HREI (C₂₆H₁₈S₃) Calcd: 426.0510. Found: 426.055, m/e (%) 426 (10), 339 (5), 306 (8), 212 (100).

Anal. Calcd. for C₂₆H₁₈S₃ (426.0510): C, 73.23; H, 4.25. Found: C, 73.58; H, 4.65.

4-S-(4'-dibenzothiophenylmethyl)thiomethyl-dibenzothiophene (**26**).

Using the procedure described for **25**, 4-(thiomethyl)dibenzothiophene (**14**) (0.12 g, 0.5 mmole), sodium hydride (0.14 g, 0.6 mmole) in THF (10 ml) and 4-(bromomethyl)dibenzothiophene (**13**) (0.14 g, 0.5 mmole) were reacted to afford **26** (0.150 g, 71%), mp 168-170°; pmr (deuteriochloroform): δ 7.38-7.50 (m, 8H, 2-H, 8-H, 2'-H, 8'-H, 3-H, 7-H, 3'-H, 7'-H), 7.82-7.87 (m, 2H, 6-H, 6'-H), 8.06-8.18 (m, 4H, 1-H, 9-H, 1'-H, 9'-H); ms: HREI (C₂₆H₁₈S₃) Calcd: 426.0510. Found: 426.0505; m/e (%) 426 (8), 393 (6), 284 (6), 256 (15), 205 (55) and 197 (88).

Anal. Calcd. for C₂₆H₁₈S₃ (426.0510): C, 73.23; H, 4.25. Found: C, 73.58; H, 4.65.

General Procedure for the Preparation of Compounds 27-29.

A suspension of 2,8-dibromodibenzothiophene (**15**) (1 g, 2.9 mmoles) in ethyl ether (25 ml) was cooled to 0°. *n*-Butyllithium (1.6 *M* in *n*-hexane, 3.75 ml) was added, followed by dropwise addition of a solution of appropriate disulfide (5.8 mmoles) in ethyl ether (5 ml). The reaction was refluxed for 2.5 hours, (except for compound **29** which was refluxed for 24 hours), stirred at 25° for 18 hours, quenched with water (10 ml), neutralized with 10% hydrochloric acid and extracted with dichloromethane (3 x 15 ml). The combined extracts were dried, filtered and concentrated to afford each product.

2,8-Bis-(*S*-benzyl)dibenzothiophene (**27**).

This compound was obtained (0.642 g, 52%), mp 159-160°; pmr (deuteriochloroform): δ 3.72 (s, 4H, CH₂), 7.27-7.31 (s, 10H, phenyl), 7.67-7.72 (d, 2H, J = 8 Hz, 3-H, 7-H), 7.95-7.99 (d, 2H, J = 9 Hz, 4-H, 6-H), 8.61-8.62 (s, 2H, 1-H, 9-H); ms: HREI (C₂₆H₂₀S₃) Calcd: 428.0725. Found: 428.0743, m/e (%) 428 (100), 386 (73), 341 (40), 306 (62), 262 (40), 214 (78).

Anal. Calcd. for C₂₆H₂₀S₃ (428.0743): C, 72.88, H, 4.67. Found: C, 72.41; H, 4.72.

2,8-Bis-(*S*-*p*-tolyl)dibenzothiophene (**28**).

This compound was obtained (0.601 g, 49%), mp 155-157°; pmr (deuteriochloroform): δ 2.28 (s, 6H, CH₃), 7.34-7.38 (d, 8H, J = 9 Hz, phenyl), 7.79-7.83 (d, 2H, J = 9 Hz, 3-H, 7-H), 8.09-8.13 (d, 2H, J = 9 Hz, 4-H, 6-H), 8.60 (s, 2H, 1-H, 9-H); ms: HREI (C₂₆H₂₀S₃) Calcd: 428.0729. Found: 428.0714, m/e (%) 428 (100), 398 (70).

Anal. Calcd. for C₂₆H₂₀S₃ (428.0729): C, 72.88; H, 4.67. Found: C, 72.64; H, 4.79.

2,8-Bis-(*S*-methyl)dibenzothiophene (**29**).

This compound was obtained (0.620 g, 78%), mp 145-146°; pmr (deuteriochloroform): δ 2.56 (s, 6H, CH₃), 7.46-7.51 (d, 2H, J = 10 Hz, 3-H, 7-H), 7.65-7.69 (d, 2H, J = 8 Hz, 4-H, 6-H), 8.15-8.16 (s, 2H, 1-H, 9-H); ms: HREI (C₁₄H₁₂S₃) Calcd: 276.0100. Found: 276.0076, m/e (%) 276 (13), 275 (5), 251 (7), 182 (100); cmr (deuteriochloroform): δ 134.99 (C-1a, C-9a), 122.95 (C-1, C-9), 130.15 (C-2, C-8), 119.76 (C-3, C-7), 124.41 (C-4, C-6), 136.51 (C-4a, C-5a), 17.00 (CH₃).

Anal. Calcd. for C₁₄H₁₂S₃ (276.0100): C, 60.86; H, 4.34. Found: C, 60.40; H, 4.34.

General Procedure for the Preparation of Compounds 30 to 32.

A suspension of 2-bromodibenzothiophene (**2**) in ether was cooled to 0° and *n*-butyllithium (1.6 *M* solution in *n*-hexane, 1 equivalent) was added. To the resulting mixture, a solution of the appropriate disulfide (1 equivalent) in ether (5 ml) was added dropwise. The reaction mixture was refluxed 1.5 hours and then stirred at 25° for 16 hours. The mixture was then neutralized with 10% hydrochloric acid and extracted with dichloromethane (3 x 15 ml). The combined extracts were dried, filtered, and concentrated affording the desired compound.

2-*S*-Methyldibenzothiophene (**30**).

From compound **2** (1.4 g, 5 mmoles) in ether (25 ml), **30** was obtained as a white solid (0.97 g, 84%), mp 67-73°; pmr (deuteriochloroform): δ 2.57 (s, 3H, CH₃), 7.39-7.45 (m, 3H, 3-H, 7-H, 8-H), 7.70-7.84 (m, 2H, 4-H, 6-H), 8.02-8.08 (s, 1H, 1-H), 8.10-8.11 (m, 1H, 9-H); ms: HREI (C₁₃H₁₀S₂) Calcd: 230.0223. Found: 230.0200, m/e (%) 230 (100), 215 (62), 197 (5), 184 (13); cmr (deuteriochloroform): δ 136.04 (C-1a), 126.79 (C-1), 134.27 (C-2), 122.68 (C-3), 122.86 (C-4), 139.78 (C-4a), 136.68 (C-5a), 122.64 (C-6), 121.43 (C-7), 120.03 (C-8), 124.22 (C-9), 134.04 (C-9a), and 16.87 (CH₃).

Anal. Calcd. for C₁₃H₁₀S₂ (230.0223): C, 67.81; H, 4.38. Found: C, 67.71; H, 4.41.

2-*S*-(*p*-Bromophenyl)dibenzothiophene (**31**).

From **2** (0.262 g, 0.7 mmole) in ether (3 ml), **31** was obtained as a white solid (0.225 g, 87%), mp 83-85°; pmr (deuteriochloroform): δ 7.0-7.2 (d, J = 13 Hz, 4H, C₆H₄), 7.4-7.7 (m, 4H, 3-H, 4-H, 6-H, 7-H), 8.1-8.15 (m, 2H, 1-H, 9-H); ms: HREI (C₁₈H₁₁BrS₂) Calcd: 369.9486. Found: 369.9497; m/e

(%) 372 (98), 370 (100), 340 (10), 290 (38), and 258 (15); cmr (deuteriochloroform): δ 136.68 (C-1a), 129.69 (C-1), 130.76 (C-2), 123.71 (C-3), 124.62 (C-4), 139.78 (C-4a), 139.43 (C-5a), 126.00 (C-6), 122.86 (C-7), 121.75 (C-8), 127.22 (C-9), 136.63 (C-9a), 131.02 (C-1'), 131.76 (C-2'), 132.12 (C-3'), and 130.22 (C-4').

Anal. Calcd. for C₁₈H₁₁BrS₂ (369.9486): C, 58.38; H, 2.97. Found: C, 58.11; H, 3.11.

2-*S*-Benzylidibenzothiophene (**32**).

From compound **2** (1.4 g, 10 mmoles) in ether (50 ml), **32** was obtained as a white solid (1.1 g, 72%), mp 56-58°; pmr (deuteriochloroform): δ 3.65 (s, 2H, CH₂), 7.2-7.25 (s, 5H, C₆H₅), 7.6-7.8 (m, 5H, 3-H, 4-H, 6-H, 7-H, 8-H), 8.0-8.1 (m, 2H, 1-H, 9-H); ms: HREI (C₁₅H₁₄S₂) Calcd: 306.0537. Found: 306.0530; m/e (%) 306 (5), 184 (100), 152 (10), 139 (15), 91 (22); cmr (deuteriochloroform): δ 136.04 (C-1a), 128.81 (C-1), 131.69 (C-2), 127.89 (C-3), 127.31 (C-4), 139.29 (C-4a), 137.59 (C-5a), 126.88 (C-6), 126.57 (C-7), 121.47 (C-8), 128.56 (C-9), 135.39 (C-9a).

Anal. Calcd. for C₁₅H₁₄S₂ (306.0537): C, 74.50; H, 4.57. Found: C, 74.76; H, 4.76.

General Procedure for the Preparation of Compounds 33 to 36.

To a solution of dibenzothiophene (**1**) in THF at 0° was added *n*-butyllithium (1.6 *M* in *n*-hexane, 1 equivalent). The resulting anion was stirred at 0° for 5 hours, then a solution of the appropriate disulfide (1 equivalent) in ether was added dropwise. The reaction mixture was refluxed for 1.5 hours, (except in the preparation of compound **36**, where it was refluxed for 12 hours), then stirred at 25° for 16 hours, quenched with water (15 ml), neutralized with 10% hydrochloric acid, and extracted with dichloromethane (3 x 15 ml). The combined extracts were dried, filtered, and concentrated to afford products **33** to **36**.

4-(*p*-Tolyl)dibenzothiophene (**33**).

From compound **1**, (1.84 g, 10 mmoles) in THF (25 ml), **33** was obtained as a white solid (0.78 g, 50%), mp 89-91°; pmr (deuteriochloroform): δ 2.30 (s, 3H, CH₃), 7.33 (m, 2H, 2-H, 2'-H), 7.38 (m, 2H, 1-H, 1'-H), 7.42-7.48 (m, 4H, 2-H, 3-H, 7-H, 8-H), 7.85-7.88 (m, 1H, 6-H), 8.14-8.18 (m, 2H, 1-H, 9-H); ms: HREI (C₁₅H₁₄S₂) Calcd: 306.0536. Found: 306.0542; m/e (%) 290 (100), 274 (33), 258 (28), 214 (13), 184 (53); cmr (deuteriochloroform): δ 136.18 (C-1a), 126.90 (C-1), 121.82 (C-2), 122.81 (C-3), 130.86 (C-4), 139.00 (C-4a), 137.08 (C-5a), 124.41 (C-6), 122.81 (C-7), 120.94 (C-8), 126.63 (C-9), 134.90 (C-9a), 149.80 (C-1'), 130.46 (C-2'), 129.93 (C-3'), 144.90 (C-4'), 21.09 (CH₃).

Anal. Calcd. for C₁₅H₁₄S₂ (306.0536): C, 74.50; H, 4.57. Found: C, 74.56, H, 4.67.

4-*S*-Methyldibenzothiophene (**34**).

From compound **1**, (1.84 g, 10 mmoles) in THF (25 ml), **34** was obtained as a white solid (1.52 g, 66%), mp 68-70°; pmr (deuteriochloroform): δ 2.64 (s, 3H, CH₃), 7.44-7.49 (m, 4H, 2-H, 3-H, 7-H, 8-H), 7.83-7.86 (m, 1H, 6-H), 8.13-8.18 (m, 2H, 1-H, 9-H); ms: HREI (C₁₃H₁₀S₂) Calcd: 230.0223. Found: 229.9971; m/e (%) 230 (100), 215 (55), 197 (6), 139 (8); cmr (deuteriochloroform): δ 135.37 (C-1a), 126.67 (C-1), 121.89 (C-2), 122.75 (C-3), 135.49 (C-4), 139.37 (C-4a), 139.32 (C-5a), 124.42 (C-6), 122.83 (C-7), 121.53 (C-8), 126.67 (C-9), 135.40 (C-4a), 16.72 (CH₃).

Anal. Calcd. for C₁₃H₁₀S₂ (230.0223): C, 67.8; H, 4.38. Found: C, 67.87; H, 4.39.

4-*S*-(*p*-Bromophenyl)dibenzothiophene (**35**).

From compound **1**, (0.184 g, 1 mmole) in THF (3 ml), **35** was obtained as white solid (0.235 g, 81%), mp 73-75°; pmr (deuteriochloroform): δ 7.08-7.26 (m, 4H, C₆H₄), 7.53-7.58 (m, 4H, 2-H, 3-H, 7-H, 8-H), 7.83-7.88 (m, 1H, 6-H), 8.14-8.18 (m, 2H, 1-H, 9-H); ms: HREI (C₁₈H₁₁BrS₂) Calcd: 369.9486. Found: 369.9490; m/e (%) 372 (83), 290 (50), 258 (17), 215 (12), 184 (42), 145 (33), and 108 (6); cmr (deuteriochloroform): δ 135.71 (C-1a), 127.28 (C-1), 121.92 (C-2), 122.86 (C-3), 132.24 (C-4), 139.46 (C-4a), 136.32 (C-5a), 124.58 (C-6), 122.78 (C-7), 120.41 (C-8), 129.34 (C-9), 135.71 (C-9a), 128.71 (C-1'), 130.48 (C-2'), 134.52 (C-4').

Anal. Calcd. for $C_{18}H_{11}BrS_2$ (369.9486): C, 58.38; H, 2.97. Found: C, 58.56; H, 2.73.

4-S-Benzyldibenzothiophene (36).

From compound **1** (1.84 g, 10 mmoles) in THF (25 ml) **36** was obtained as a white solid (1.7 g, 56%), mp 90-91°; pmr (deuteriochloroform): δ 3.7 (s, 2H, CH_2), 7.3 (s, 5H, C_6H_5), 7.3-7.5 (m, 4H, 2-H, 3-H, 7-H, 8-H), 7.7-7.8 (m, 1H, 6-H), 8.1 (m, 2H, 1-H, 9-H); ms: HREI ($C_{18}H_{14}S_2$) Calcd: 306.0537. Found: 306.0551; m/e (%) 306 (6), 197 (100) and 183 (18); cmr (deuteriochloroform): δ 136.29 (C-1a), 128.88 (C-1), 127.33 (C-2), 127.92 (C-3), 132.49 (C-4), 139.31 (C-4a), 137.26 (C-5a), 126.92 (C-6), 126.60 (C-7), 121.48 (C-8), 128.57 (C-9), 135.42 (C-9a), 129.32 (C-1'), 124.24 (C-2'), 122.70 (C-3'), 128.39 (C-4') and 43.15 (CH_2).

Anal. Calcd. for $C_{18}H_{14}S_2$ (306.0537): C, 74.50; H, 4.57. Found: C, 74.45; H, 4.81.

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