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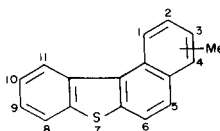
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All isomers of the monomethylbenzo[*b*]naphtho[1,2-*d*]thiophenes were synthesized by photocyclization of 2-styrylbenzo[*b*]thiophenes which were prepared by the Wadsworth-Emmons reaction or the Wittig reaction.

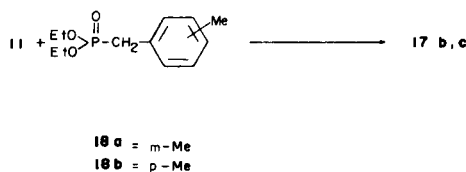
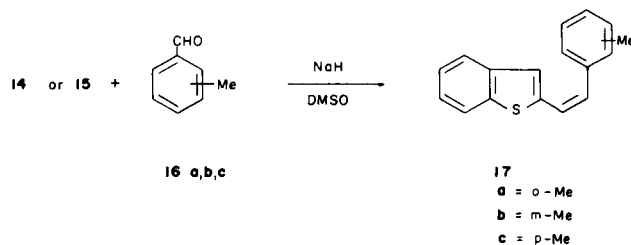
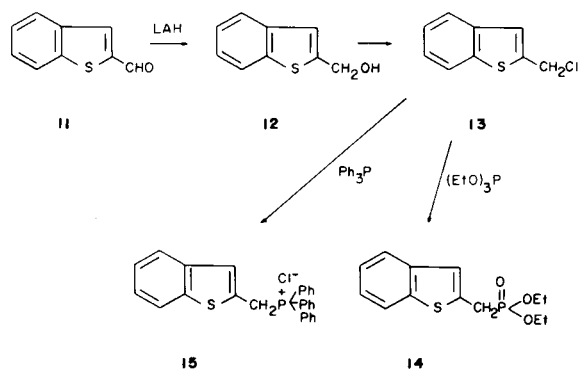
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The synthesis of all of the isomers of the monomethylbenzo[*b*]naphtho[2,1-*d*]thiophenes by the photocyclization of 3-styrylbenzo[*b*]thiophenes have been reported (2). The present paper describes the synthesis of the monomethylbenzo[*b*]naphtho[1,2-*d*]thiophenes following the same general procedure used for the parent benzo[*b*]naphtho[1,2-*d*]thiophene (3).

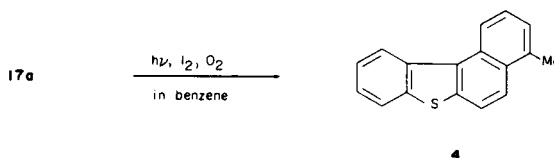


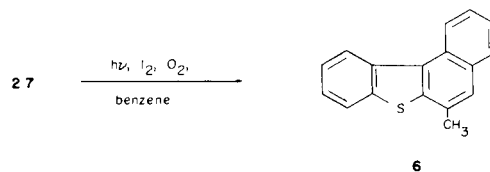
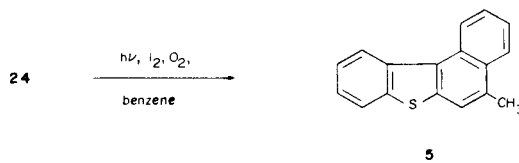
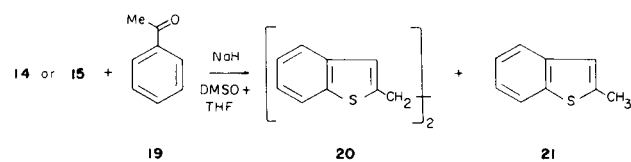
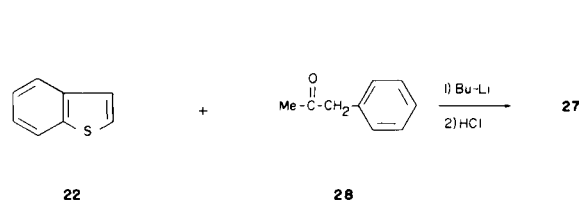
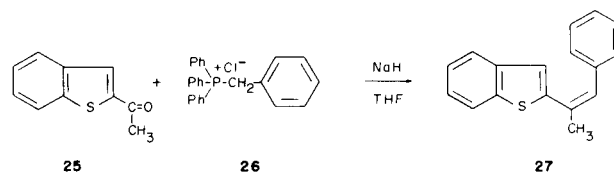
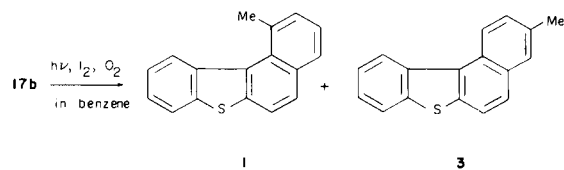
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|----------|------------|
| 1 = 1-Me | 6 = 6-Me |
| 2 = 2-Me | 7 = 8-Me |
| 3 = 3-Me | 8 = 9-Me |
| 4 = 4-Me | 9 = 10-Me |
| 5 = 5-Me | 10 = 11-Me |

Diethyl 2-benzo[*b*]thenylphosphonate (**14**) was prepared from triethyl phosphite and 2-chloromethylbenzo[*b*]thiophene (**13**), which was obtained by the chlorination of 2-hydroxymethylbenzo[*b*]thiophene (**12**). The Wittig reagent, 2-benzo[*b*]thenyltriphenylphosphonium chloride (**15**) was also prepared from **13** and triphenylphosphine in good yield. Compound **14** or **15**, when allowed to react with the requisite *o*-, *m*- or *p*-methylbenzaldehyde in the presence of sodium hydride (**16a,b,c**) in DMSO gave 2-(*o*-methylstyryl)benzo[*b*]thiophene (**17a**, 41% yield), 2-(*m*-methylstyryl)benzo[*b*]thiophene (**17b**, 54% yield) and 2-(*p*-methylstyryl)benzo[*b*]thiophene (**17c**, 47% yield). Furthermore, **17b** and **17c** were also obtained in higher yield (**17b** in 66% and **17c** in 71%) from benzo[*b*]thiophene-2-carboxaldehyde (**11**) upon reaction with diethyl *m*-methylbenzylphosphonate (**18a**) and diethyl *p*-methylbenzylphosphonate (**18b**). Photocyclization of **17a** and **17c** was carried out in dry benzene in the presence of iodine and air to give the corresponding 4-methyl- and 2-methylbenzo[*b*]naphtho[1,2-*d*]thiophene (**4** and **2**) in 42% and 45% yield, respectively. As expected, the photocyclization



of **17b** gave two products, 1-methyl- and 3-methylbenzo[*b*]naphtho[1,2-*d*]thiophene (**1** and **3**) which we were able to separate by a combination of chromatography and frac-

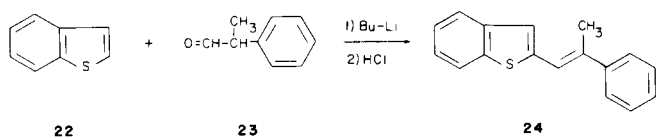
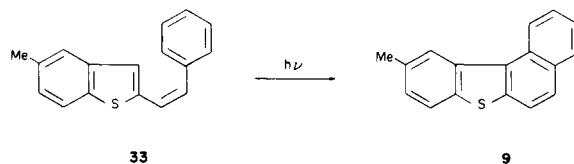
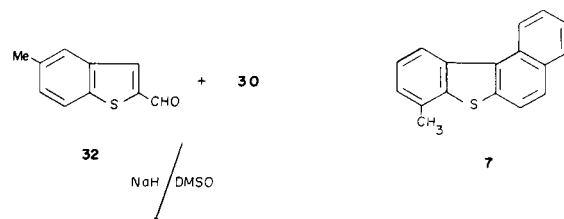
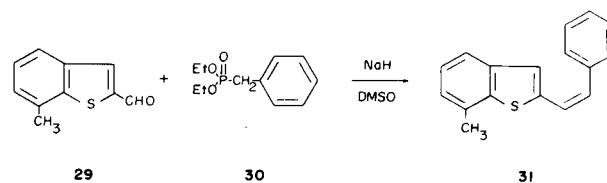




tional crystallization. Evidence for the structures of **1** and **3** was obtained by nmr spectroscopy. In **1** the methyl protons appeared at a lower field (δ 2.78) than the methyl protons of **3** (δ 2.56) due to the deshielding caused by the close proximity of the benzene ring. Furthermore, a doublet centered at δ 7.79 was additional evidence that the methyl group in **3** was indeed at position 3.

For the synthesis of 5-methyl- and 6-methylbenzo[*b*]naphtho[1,2-*d*]thiophenes (**5** and **6**), we required the styrylbenzo[*b*]thiophenes **24** and **27**. The reaction of 2-lithiobenzo[*b*]thiophene with various aldehydes has been reported to give the corresponding alcohols in good yield (4). The reaction of **22** with *n*-butyllithium gave the lithio derivative which reacted with **23** to give the styryl compound **24** in 66% yield. The reaction of **14** or **15** with acetophenone (**19**) failed to give **24**, giving instead two products, namely, 1,2-bis(2-benzo[*b*]thienyl)ethane (**20**) and 2-methylbenzo[*b*]thiophene (**21**). The other styryl compound **27** was obtained in 32% yield by the reaction of **25** and **26** via the Wittig reaction. Compound **27** was also obtained in 62% yield from the lithio derivative of **22** and phenylacetone (**28**). The photocyclization of **24** and **27** in benzene with iodine and oxygen gave 5-methylbenzo[*b*]naphtho[1,2-*d*]thiophene (**5**) in 52% yield and 6-methylbenzo[*b*]naphtho[1,2-*d*]thiophene (**6**) in 69% yield.

8-Methyl- and 10-methylbenzo[*b*]naphtho[1,2-*d*]thiophene (**7** and **9**) were synthesized from 7-methyl- and 5-methylbenzo[*b*]thiophene-2-carboxaldehyde (**29** and **32**) by the Wadsworth-Emmons reaction followed by photocyclization in 40% and 45% yields. Compounds **29** and **32**



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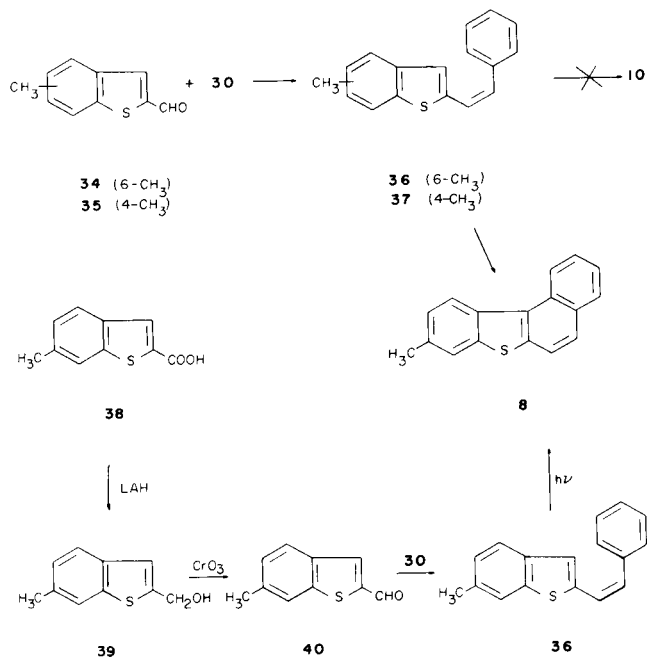
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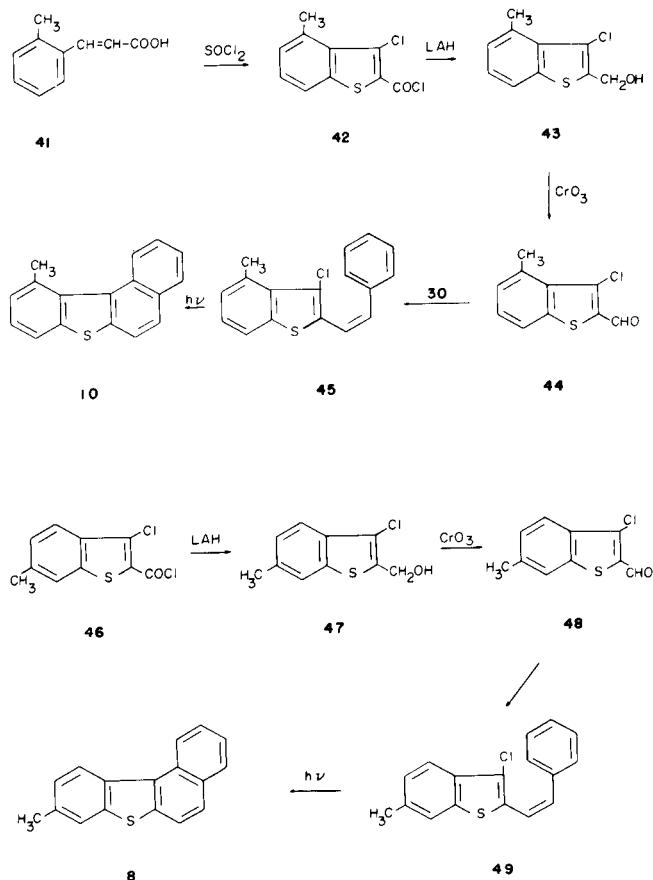
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were readily prepared from *o*- and *p*-methylbenzenethiol *via* the method of Tilak (5). However, in the case of *m*-methylbenzenethiol, this reaction gave a mixture of 4-methyl- and 6-methylbenzo[*b*]thiophene-2-carboxaldehyde (**34** and **35**). When this mixture was allowed to react with **30** in a similar manner, a mixture of two styryl compounds, 4-methyl- and 6-methyl-2-styrylbenzo[*b*]thiophene (**36** and **37**), were obtained which could not be separated either by chromatography or fractional crystallization. The irradiation of the above mixture gave colorless crystals, mp 87° (mp sharp) after chromatography. The structure of this product was established as 9-methylbenzo[*b*]naphtho[1,2-*d*]thiophene (**8**) by an unambiguous synthesis in which **38** (**6**) was converted to 6-methyl-2-styrylbenzo[*b*]thiophene (**36**) which was photocyclized to **8** as colorless needles, mp 87°. The key intermediate for the above synthesis of **8**, 6-methylbenzo[*b*]thiophene-2-carboxaldehyde (**40**), was prepared by the oxidation of 6-methyl-2-hydroxymethylbenzo[*b*]thiophene (**39**) with chromium trioxide-pyridine complex in pyridine at room temperature which was obtained by the reduction of 6-methylbenzo[*b*]thiophene-2-carboxylic acid (**38**). This compound was prepared from *p*-tolualdehyde and rhodanine using the method of Campaigne (6).



Recently, Kano, *et al.* (7) reported that the photocyclization of 3-chlorobenzo[*b*]thiophene-2-anilides gave substituted benzo[*b*]thienoquinolines. This approach was applied to the synthesis of 9- and 11-methylbenzo[*b*]naphtho[1,2-*d*]thiophenes **8** and **10**. Substituted cinnamic acids have been shown to react with refluxing thionyl chloride in chlorobenzene to give benzene-substituted 3-chlorobenzo[*b*]thiophene-2-carboxyl chlorides (8,9,10,11,12). Thus,

3-chloro-4-methylbenzo[*b*]thiophene-2-carboxaldehyde (**44**) was prepared by the reduction of 3-chloro-4-methylbenzo[*b*]thiophene-2-carboxyl chloride (**42**) with lithium aluminum hydride, followed by oxidation with chromium trioxide-pyridine complex in good yield. The acid chloride **42** was readily prepared by the reaction of *o*-methylcinnamic acid with thionyl chloride and pyridine in chlorobenzene using the method of Wright, *et al.* (10). Similarly, 3-chloro-6-methyl-2-styrylbenzo[*b*]thiophene (**49**) was easily obtained from **46** as shown in the flow sheet. When **45** was photocyclized, **10** was obtained in 34% yield. Likewise, photocyclization of **49** gave **8** in 35% yield.



EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The ir spectra were obtained on a Beckman Acculab 2 spectrometer and the ¹H nmr spectra were obtained on a JEOL FX90 and on a Varian EM360 spectrometer in the solvents indicated. Mass spectra were obtained on a Hewlett-Packard model 5980 A mass spectrometer. Elemental analysis was performed by MHW Laboratories, Phoenix, Arizona.

Diethyl 2-Benzo[*b*]thenylphosphonate (**14**).

A mixture of 2-chloromethylbenzo[*b*]thiophene (**13**) (13,14) and 10 g (60 mmoles) of triethyl phosphite was heated at 160-170° for 8 hours. The product of the reaction was distilled to give 8 g (56%) of a pale yellow oil,

bp 175-185°/11.5 mm; nmr (deuteriochloroform): δ 1.27 (t, $J = 7$ Hz, $-\text{CH}_2\text{-CH}_3$, 6H), 3.30 and 3.53 (two s, $\text{CH}_2\text{-P}$, 2H), 4.10 (q, O-CH_2 , 4H), 7.10-7.47 (m, *ArH*, 2H), 7.60-7.90 (m, *ArH*, 2H); ms: *m/e* 284 (M^+ , 44), 147 (100), 146 (16.5).

Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{O}_3\text{PS}$: C, 55.03; H, 6.03; P, 10.89; S, 11.28. Found: C, 55.01; H, 6.21; P, 11.10; S, 11.21.

Benzo[*b*]thienyltriphenylphosphonium Chloride (15).

A mixture of 9.1 g (50 mmoles) of 2-chloromethylbenzo[*b*]thiophene (13) (13,14), 13.1 g (50 mmoles) of triphenylphosphine, and 200 ml of absolute ethanol was refluxed for 3 hours. After evaporation of the ethanol, the residue was triturated with ether and the resulting solid was collected by filtration and recrystallized from ethanol to give 21 g (94%) of white crystals, mp 262-268°; ms: *m/e* 408 ($M^+ - \text{HCl}$, 100), 407 (41), 223 (48), 221 (51), 183 (63).

Anal. Calcd. for $\text{C}_{27}\text{H}_{22}\text{ClPS}$: C, 72.88; H, 4.98; P, 6.96; S, 7.21. Found: C, 72.49; H, 5.21; P, 6.87; S, 7.19.

2-(*o*-Methylstyryl)benzo[*b*]thiophene (17a).

Method a.

Sodium hydride (50%, 0.48 g, 10 mmoles) was placed in 50 ml of 1,2-dimethoxyethane and the slurry was cooled to 20° and 1.42 g (5 mmoles) of diethyl 2-benzo[*b*]thienylphosphonate (14) was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 30 minutes. To the yellow solution was added dropwise 0.6 g (5 mmoles) of *o*-tolualdehyde at 25°. The above solution was stirred at room temperature for 2 hours and heated at 50° for 20 minutes. After cooling, a large excess of water was added and the resulting precipitate was extracted with benzene. The benzene layer after drying over sodium sulfate was evaporated at reduced pressure to yield a brown oil which was chromatographed on a silica gel column using hexane as the eluent to give 0.78 g (63%) of colorless crystals, mp 106°.

Method b.

The above reaction was repeated using DMSO as the solvent, giving 17a (41% yield) as colorless leaflets, mp 108°. An analytical sample was recrystallized from ethanol to give colorless leaflets, mp 108°, nmr (deuteriochloroform): δ 2.42 (CH_3 , 3H), 7.14-7.32 (m, *ArH*, 8H), 7.48-7.81 (m, *ArH*, 3H); ms: *m/e* 250 (M^+ , 100), 235 ($M^+ - 15$, 72), 234 ($M^+ - 16$, 66), 214 (21).

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{S}$: C, 81.56; H, 5.64; S, 12.81. Found: C, 81.46; H, 5.79; S, 12.76.

2-(*m*-Methylstyryl)benzo[*b*]thiophene (17b).

This compound was synthesized from 14, 15, or 11 by the following three methods. Methods a and b are similar to the method used for the preparation of 17a. Method c is described below. The yields by methods a, b and c were 56%, 54% and 66%, respectively.

Method c.

Sodium hydride (50%, 2.88 g, 60 mmoles) was placed in 200 ml of dry dimethyl sulfoxide. The slurry was cooled to 20° and 9.68 g (40 mmoles) of diethyl *p*-methylbenzylphosphonate (18b) was added dropwise with stirring. To the above yellow solution, 6.48 g (40 mmoles) of benzo[*b*]thiophene-2-carboxaldehyde (11) was added dropwise at room temperature and stirred for five more hours. A large excess of water was added and the resulting precipitate was collected by filtration and recrystallized from hexane to give 6.7 g (66%) of pale yellow crystals, mp 140°. An analytical sample was recrystallized from methanol to give colorless crystals, mp 143°; nmr (deuteriochloroform): δ 2.36 (s, CH_3 , 3H), 7.05 (s, 3-H, 1H), 7.10-7.46 (m, *ArH*, 8H), 7.60-7.90 (m, *ArH*, 2H); ms: *m/e* 250 (M^+ , 100), 235 (82), 234 (87), 249 (36).

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{S}$: C, 81.56; H, 5.64; S, 12.81. Found: C, 81.34; H, 5.52; S, 12.97.

2-(*p*-Methylstyryl)benzo[*b*]thiophene (17c).

This compound was also synthesized from 14, 15 or 11 by the following three methods. Methods a, b and c are similar to the method used for

the preparation of 17a and b. The yields by method a (from 14), b (from 15) and c (from 11) were 44%, 47% and 71%, respectively. An analytical sample was recrystallized from methanol to give pale yellow crystals, mp 151°; nmr (deuteriochloroform): δ 2.33 (s, CH_3 , 3H), 7.05-7.45 (m, *ArH*, 8H), 7.62-7.86 (m, *ArH*, 3H); ms: *m/e* 250 (M^+ , 100), 235 (80), 234 (88), 249 (35).

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{S}$: C, 81.56; H, 5.64; S, 12.81. Found: C, 81.43; H, 5.49; S, 13.01.

4-Methylbenzo[*b*]naphtho[1,2-*d*]thiophene (4).

A solution of 0.5 g (2 mmoles) of 17a and 0.05 g of iodine in 360 ml of dry benzene was irradiated for 4 hours with a 450 Watt Hanovia medium pressure mercury lamp. During the course of the reaction, a slow stream of air was passed through the solution. The solvent was evaporated *in vacuo* and the residue was purified by chromatography on silica gel using hexane as an eluent giving 0.21 g (42%) of colorless crystals. An analytical sample was recrystallized from methanol to give colorless needles, mp 95°; nmr (deuteriochloroform): δ 2.77 (s, 4- CH_3 , 3H), 7.34-7.68 (m, 2-H, 3-H, 9-H, 10-H, 4H, *ArH*), 7.88 (d, $J = 3$ Hz, 5- or 6-H, 1H), 7.92 (dd, $J = 1, 8$ Hz, 8-H, 1H, *ArH*), 8.06 (d, $J = 3$ Hz, 5- or 6-H, 1H), 8.76-8.91 (m, H-1, H-8, H-11, 3H, *ArH*); ms: *m/e* 248 (M^+ , 100), 249 (20), 247 (35), 245 (21).

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{S}$: C, 82.22; H, 4.87; S, 12.91. Found: C, 82.19; H, 5.03; S, 13.05.

1-Methylbenzo[*b*]naphtho[1,2-*d*]thiophene (1) and 3-Methylbenzo[*b*]naphtho[1,2-*d*]thiophene (3).

A solution of 0.5 g (2 mmoles) of 17b and 0.05 g of iodine in 360 ml of dry benzene was irradiated in a manner similar to that used for the synthesis of 4. After evaporation of the solvent, the residue was chromatographed on a silica gel column using hexane as the eluent giving 0.27 g of colorless crystals. The nmr (deuteriochloroform) of this product exhibited two methyl signals at 2.76 ppm and 2.50 ppm (1:1) due to the methyl protons on the 1 and 3 positions of benzo[*b*]naphtho[1,2-*d*]thiophene. These products were recrystallized twice from methanol to give 0.11 g (22%) of colorless needles of 3 mp 97°; nmr (deuteriochloroform): δ 2.78 (s, 1- CH_3 , 3H), 7.31-7.64 (m, 2-H, 3-H, 9-H, 10-H, 4H, *ArH*), 7.77 (s, 5-H, 6-H, 2H, *ArH*), 7.77-8.19 (m, 4-H, 8-H, 11-H, 3H, *ArH*); ms: *m/e* 248 (M^+ , 100), 247 (45), 245 (30).

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{S}$: C, 82.22; H, 4.87; S, 12.91. Found: C, 81.80; H, 4.98; S, 13.03.

The above mother liquor was evaporated and the residue was again chromatographed on a neutral alumina column using petroleum ether as the eluent giving 0.05 g (10%) of colorless leaflets of 1, mp 101-102°. An analytical sample was recrystallized from hexane to give colorless leaflets, mp 101-102°; nmr (deuteriochloroform): δ 2.56 (s, 3- CH_3 , 3H), 7.43-7.69 (m, 2H, 9-H, 10-H, 3H, *ArH*), 7.79 (s, 4-H, 5-H, 6-H, 3H, *ArH*), 7.99 (near dd, $J = 8$ Hz, 8-H, 1H), 9.88 (bd, 1-H, 11-H, 2H, *ArH*); ms: *m/e* 248 (M^+ , 100), 247 (40), 245 (26).

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{S}$: C, 82.22; H, 4.87; S, 12.91. Found: C, 81.86; H, 4.95; S, 12.69.

2-Methyl[*b*]naphtho[1,2-*d*]thiophene (2).

This compound was synthesized by photolysis of a mixture of 17c, (1.0 g), iodine (0.06 g) and 360 ml of benzene in the same manner as described for 4. Compound 2 was obtained as colorless needles in 45% yield, mp 92°; nmr (deuteriochloroform): δ 2.64 (s, $-\text{CH}_3$, 3H), 7.34 (near dd, $J = 1$ and 8 Hz, 3-H, 1H, *ArH*), 7.36-7.58 (m, 9-H, 10-H, 2H, *ArH*), 7.77 (s, 5-H, 6-H, 2H, *ArH*), 7.67-7.93 (m, 4-H, 8-H, 2H, *ArH*), 8.73 (near d, 1-H, 1H, *ArH*), 7.79 (dd, $J = 1, 8$ Hz, 11-H, *ArH*); ms: *m/e* 248 (M^+ , 100), 247 (30), 245 (23).

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{S}$: C, 82.22; H, 4.87; S, 12.91. Found: C, 82.02; H, 5.03; S, 12.82.

Reaction of 14 with Acetophenone.

Sodium hydride (50%, 0.48 g, 10 mmoles) was placed in 50 ml of dry dimethyl sulfoxide. The slurry was cooled to 20° and 1.42 g (5 mmoles) of

diethyl 2-benzo[*b*]thienylphosphonate (**14**) was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 30 minutes. To the solution, maintained below 25°, was added dropwise 0.6 g (5 mmoles) of acetophenone. The solution was stirred at room temperature for 10 hours. After cooling, a large excess of water was added and the mixture was extracted with benzene. The benzene layer was dried over sodium sulfate and evaporated at reduced pressure to yield a brown oil which was chromatographed on a silica gel column using cyclohexane as the eluent giving 0.12 g (8% yield) of pale yellow crystals. An analytical sample was recrystallized from hexane to give pale yellow leaflets of **20**, mp 217°; nmr (deuteriochloroform): δ 3.34 (s, CH₃, 4H), 7.04 (bs, 3-H, 2H, ArH), 7.17-7.42 (m, 5-H, 6-H, 4H, ArH), 7.57-7.82 (m, 4-H, 7-H, 4H, ArH); ms: m/e 295 (M⁺ + 1, 18), 294 (84), 148 (13), 147 (100).

Anal. Calcd. for C₂₀H₁₄S₂: C, 75.43; H, 4.43; S, 20.13. Found: C, 75.09; H, 4.82; S, 20.52.

Reaction of **15** with Acetophenone.

Sodium hydride (50%, 0.96 g, 20 mmoles) was placed in a mixture of 50 ml of dry tetrahydrofuran and 50 ml of dry dimethyl sulfoxide. The slurry was cooled to 0° and 4.44 g (10 mmoles) of 2-benzo[*b*]thienyltriphenylphosphonium chloride (**15**) was added dropwise with stirring under a nitrogen atmosphere. After the addition, the solution was stirred at the same temperature for 20 minutes. To the above solution, maintained below 0°, was added dropwise 1.2 g (10 mmoles) of acetophenone. The solution was stirred at 0° for 14 hours. A large excess of water was added to the reaction mixture and the mixture was extracted with benzene. The benzene layer was dried over sodium sulfate and evaporated at reduced pressure to yield a brown oil which was chromatographed on a silica gel column using hexane as the eluent giving 0.75 g (51%) of 2-methylbenzo[*b*]thiophene (**21**), mp 52°; [lit (15) 51-52°] ms: m/e 148 (M⁺, 61), 147 (100); nmr (deuteriochloroform): δ 2.57 (s, CH₃, 3H), 6.94 (s, 3-H, 1H, ArH), 7.14-7.38 (m, 5-H, 6-H, 2H, ArH), 7.54-7.81 (m, 4-H, 7-H, 2H, ArH).

Further elution of the silica gel column with cyclohexane gave 0.20 g of the byproduct **20**.

2-(β -Methylstyryl)benzo[*b*]thiophene (**24**).

Benzo[*b*]thiophene (**22**) (10 g, 76 mmoles) dissolved in 100 ml of dry ether was cooled to -70° while protected from air by dry nitrogen. *n*-Butyllithium (54 ml of 1.6 M solution) was added dropwise. After the addition, the mixture was stirred for one hour between -20 and -10° and then for 2 hours at room temperature. The mixture was then cooled to -70° and 2-phenylpropionaldehyde (15 g, 110 mmoles) in 50 ml of dry ether was added dropwise. After the addition, the solution was allowed to warm to 25° and stirred for an additional 4 hours. The ether solution was poured into 500 ml of 10% hydrochloric acid and the mixture was extracted with 2 × 200 ml portions of chloroform. The chloroform layer was dried over sodium sulfate and the chloroform was removed to give a pale yellow oil; nmr (deuteriochloroform): δ 1.36 (d, J = 7 Hz, CH₃, 3H), 2.20 (bs, OH, 1H), 3.16 (m, β -H, 1H), 5.01 (d, J = 6 Hz, α -H, 1H), 6.93 (s, 3-H, 1H, ArH), 7.20-7.85 (m, ArH, 9H).

A mixture of the above crude alcohol and 200 ml of concentrated hydrochloric acid solution was refluxed for 1.5 hours and then the reaction mixture was extracted with benzene. The benzene layer was dried over sodium sulfate and the benzene evaporated *in vacuo* to give a brown oil. This crude product was purified by chromatography on a silica gel column using hexane as the eluent giving 8.25 g (71%) of colorless crystals, mp 118°. An analytical sample was recrystallized from methanol to give colorless needles, mp 123°; nmr (deuteriochloroform): δ 2.15 and 2.43 (two s, β -CH₃, 3H), 6.62 (s, α -H, 1H), 6.90 (s, 3-H, 1H, ArH), 7.00-7.90 (m, ArH, 9H); ms: m/e 250 (M⁺, 100), 235 (92), 234 (59), 147 (32).

Anal. Calcd. for C₁₇H₁₄S: C, 81.56; H, 5.64; S, 12.81. Found: C, 81.59; H, 5.53; S, 12.79.

5-Methylbenzo[*b*]naphtho[1,2-*d*]thiophene (**5**).

This compound was synthesized from 0.5 g (2 mmoles) of 2-(β -methylstyryl)benzo[*b*]thiophene (**24**) and 0.05 g of iodine in a manner similar to that used for the preparation of **4** and was obtained as colorless needles

in 52% yield. An analytical sample was recrystallized from methanol to give colorless needles, mp 128°; nmr (deuteriochloroform): δ 2.75 (s, CH₃, 3H), 7.37-7.71 (m, 2-H, 3-H, 9-H, 10-H, 4H, ArH), 7.71 (s, 6-H, 1H, ArH), 7.79-8.21 (m, 4-H, 8-H, 2H, ArH), 8.77 (near dd, J = 1, 8 Hz, 1- or 11-H, 1H, ArH), 9.00 (near dd, J = 1, 8 Hz, 1- or 11-H, 1H, ArH); ms: m/e 248 (M⁺, 100).

Anal. Calcd. for C₁₇H₁₂S: C, 82.22; H, 4.87; S, 12.91. Found: C, 82.20; H, 4.99; S, 12.71.

2-(α -Methylstyryl)benzo[*b*]thiophene (**27**).

Method a.

Sodium hydride (50%, 1.44 g, 33 mmoles) was placed in 200 ml of dry tetrahydrofuran. The slurry was cooled to 20° and 7.76 g (20 mmoles) of benzyltriphenylphosphonium chloride (**26**) was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 30 minutes. To the orange solution, maintained below 25°, was added dropwise 3.52 g (20 mmoles) of 2-acetylbenzo[*b*]thiophene (**25**). The solution was stirred at room temperature for 30 minutes and refluxed for 2 hours. After cooling, a large excess of water was added, followed by acidification with 10% hydrochloric acid. The mixture was extracted with 500 ml of benzene. The benzene layer was dried with sodium sulfate and evaporated to give an oily product. The crude product was chromatographed on a silica gel column using hexane as the eluent to give 1.6 g (32%) of **27** as colorless crystals. An analytical sample was recrystallized from methanol to give colorless leaflets, mp 134°.

Method b.

The reaction of 6.4 g (50 mmoles) of benzo[*b*]thiophene (**22**) and 6.7 g (50 mmoles) of phenylacetone (**28**) in a manner similar to that used for the preparation of **24** gave **27** as colorless crystals in 62% yield, mp 135°; nmr (deuteriochloroform): δ 2.34 (s, CH₃, 3H), 7.08 (s, 3-H, 1H, ArH), 7.26-7.56 (bs, phenyl protons, 5-H, 6-H, and ethenyl proton, 8H), 7.61-7.82 (m, 4-H, 7-H, 2H, ArH); ms: m/e 250 (M⁺, 100), 249 (27), 235 (90), 234 (83).

Anal. Calcd. for C₁₇H₁₄S: C, 81.56; H, 5.64; S, 12.81. Found: C, 81.33; H, 5.48; S, 12.56.

6-Methylbenzo[*b*]naphtho[1,2-*d*]thiophene (**6**).

This compound was synthesized by photolysis of 0.8 g (3.2 mmoles) of 2-(α -methylstyryl)benzo[*b*]thiophene (**27**) and 0.05 g of iodine in a manner similar to that used for the preparation of **4** and was obtained as colorless needles in 69% yield. An analytical sample was recrystallized from methanol to give colorless needles, mp 105°; nmr (deuteriochloroform): δ 2.60 (s, CH₃, 3H), 7.32-7.60 (m, 2-H, 3-H, 9-H, 10-H, 4H, ArH), 7.63 (s, 5-H, 1H, ArH), 7.68-7.99 (m, 4-H, 8-H, 2H, ArH), 8.67-8.96 (m, 1-H, 11-H, 2H, ArH); ms: m/e 248 (100), 247 (36), 256 (13).

Anal. Calcd. for C₁₇H₁₂S: C, 82.22; H, 4.87; S, 12.91. Found: C, 82.07; H, 4.97; S, 12.80.

7-Methyl-2-styrylbenzo[*b*]thiophene (**31**).

This compound was synthesized from 1.7 g (10 moles) of **29**, 2.3 g (10 moles) of diethyl benzylphosphonate and 0.5 g (10 moles) of sodium hydride in a manner similar to that used for the preparation of **17a,b,c** and was obtained as tan crystals in 80% yield. An analytical sample was recrystallized from hexane to give colorless leaflets, mp 94°; nmr (deuteriochloroform): δ 2.52 (s, CH₃, 3H), 7.06 (s, 3-H, 1H, ArH), 7.13-7.60 (m, ethenyl and aromatic protons, 10H); ms: m/e 250 (M⁺, 100), 249 (56), 235 (47), 234 (69).

Anal. Calcd. for C₁₇H₁₄S: C, 81.56; H, 5.64; S, 12.81. Found: C, 81.49; H, 5.74; S, 12.71.

8-Methylbenzo[*b*]naphtho[1,2-*d*]thiophene (**7**).

This compound was synthesized from 0.5 g (2 mmoles) of **31** in a manner similar to the preparation of **4** and was obtained as colorless crystals in 40% yield. An analytical sample was recrystallized from methanol to give colorless leaflets, mp 100-102°; nmr (deuteriochloroform): δ 2.61 (s, CH₃, 3H), 7.28-7.67 (m, 2-H, 3-H, 9-H, 10-H, 4H, ArH), 7.83 (s, 5-H, 6-H, 2H, ArH), 7.94 (dd, J = 1, 8 Hz, 4-H, 1H, ArH), 8.65 (d, J = 8 Hz, 11-H,

1H, ArH), 8.92 (dd, $J = 1, 8$ Hz, 1-H, 1H, ArH); ms: m/e 248 (M^+ , 100), 247 (36), 245 (19).

Anal. Calcd. for $C_{17}H_{12}S$: C, 82.22; H, 4.87; S, 12.91. Found: C, 82.40; H, 4.86; S, 12.87.

5-Methyl-2-styrylbenzo[*b*]thiophene (33).

This compound was synthesized from 1.7 g (10 mmoles) of **32**, 2.2 g of **30**, 0.5 g of sodium hydride in a manner similar to that used in the preparation of **31** and was obtained as colorless leaflets in 81% yield, mp 187-188°. An analytical sample was recrystallized from hexane to give colorless leaflets, mp 188°; nmr (deuteriochloroform): δ 2.47 (s, CH_3 , 3H), 7.08 (s, 3-H, 1H, ArH), 7.18-7.57 (m, aromatic and ethenyl protons, 8H), 7.69 (d, $J = 8$ Hz, 7-H, 1H, ArH); ms: m/e 250 (M^+ , 100), 249 (17), 247 (32), 245 (18).

Anal. Calcd. for $C_{17}H_{14}S$: C, 81.50; H, 5.64; S, 12.81. Found: C, 81.30; H, 5.51; S, 12.97.

10-Methylbenzo[*b*]naphtho[1,2-*d*]thiophene (9).

This compound was synthesized from 1 g of **33** (4 mmoles) in a manner similar to that used in the preparation of **7** and was obtained as colorless crystals in 45% yield. An analytical sample was recrystallized from methanol to give colorless needles, mp 117-118°; nmr (deuteriochloroform): δ 2.62 (s, CH_3 , 3H), 7.29 (d, $J = 8$ Hz, 9-H, 1H, ArH), 7.44-7.94 (m, 2-H, 3-H, 4-H, 3H, ArH), 7.84 (s, 5-H, 6-H, 2H, ArH), 7.98 (d, $J = 8$ Hz, 8-H, 1H, ArH), 8.64 (s, 11-H, 1H, ArH), 9.00 (dd, $J = 1, 8$ Hz, 1-H, 1H, ArH); ms: m/e 248 (M^+ , 100), 247 (35), 245 (19).

Anal. Calcd. for $C_{17}H_{12}S$: C, 82.22; H, 4.87; S, 12.91. Found: C, 82.40; H, 5.07; S, 13.09.

4-Methyl- and 6-Methyl-2-styrylbenzo[*b*]thiophene (36, 37).

These compounds were synthesized from a mixture of **34** and **35** in a manner similar to that used in the preparation of **33** and were obtained as colorless crystals in 72% yield; nmr (deuteriochloroform): δ 7.0-7.8 (m, ArH, olefin, 11H), 2.5-2.6 (two s, CH_3 , in 1:3 ratio, 3H).

Photoreaction of a Mixture of 36 and 37.

A mixture of **36** and **37** was irradiated in a manner similar to that used for the preparation of **7**. Only one product was obtained as colorless crystals, mp 87°. This compound was 9-methylbenzo[*b*]naphtho[1,2-*d*]thiophene (**8**), a fact which was confirmed by the unambiguous conversion of **38** to **8**.

6-Methyl-2-styrylbenzo[*b*]thiophene (36).

A solution of 1.92 g (10 mmoles) of the carboxylic acid **38** in 50 ml of dry ether was added dropwise to a suspension of 1 g (26 mmoles) of lithium aluminum hydride in 50 ml of dry ether. After refluxing for 3 hours, the reaction mixture was carefully quenched by cautiously adding 10 ml of water and enough 10% hydrochloric acid to dissolve the inorganic salts. The ether phase was separated and the aqueous phase extracted with ether. The combined ether extracts were dried over sodium sulfate. Evaporation of the ether *in vacuo* yielded the alcohol **39** as a tan oil which was not characterized but used directly in the next step.

A solution of the alcohol **39** in 10 ml of dry pyridine was added slowly to a suspension of chromium trioxide-pyridine complex made from 1.5 g of chromium trioxide and 20 ml of dry pyridine. After stirring for 2 hours at room temperature, the reaction mixture was filtered and the residue was washed with chloroform. The filtrate was washed with 10% hydrochloric acid and 10% sodium carbonate solution successively. After drying over sodium sulfate, the chloroform was evaporated *in vacuo* to leave 1.1 g (13% from **38**) of the crude aldehyde **40** as a brown oil.

6-Methyl-2-styrylbenzo[*b*]thiophene (36).

This compound was synthesized from 1 g of the crude aldehyde **40** and 1.3 g of diethyl benzylphosphonate (**30**) in a manner similar to that described for the preparation of **17**; **36** was obtained in 60% yield. An analytical sample was recrystallized from hexane to give pale yellow needles, mp 188-189°; nmr (deuteriochloroform): δ 2.45 (s, CH_3 , 3H), 7.01 (s, 3-H, 1H), 7.18-7.59 (m, aromatic and ethenyl protons, 10H); ms: m/e

250 (M^+ , 100), 249 (50), 235 (30), 234 (44).

Anal. Calcd. for $C_{17}H_{14}S$: C, 81.56; H, 5.64; S, 12.81. Found: C, 81.34; H, 5.64; S, 12.88.

9-Methylbenzo[*b*]naphtho[1,2-*d*]thiophene (8).

Method a.

This compound was synthesized from 1 g of pure **36** in a manner similar to that used for the preparation of **4**. There was obtained 0.45 g (45% yield) of **8**, mp 87° *via* this method.

Method b.

Compound **8** was also prepared from **46** in a manner similar to that used for the preparation of **10** from **42** and was obtained in 35% yield. An analytical sample was recrystallized from methanol to give colorless needles, mp 87°; nmr (deuteriochloroform): δ 2.50 (s, 9- CH_3 , 3H), 7.30 (dd, $J = 1, 8$ Hz, 10-H, 1H, ArH), 7.69 (bs, 8-H, 1H, ArH), 7.78 (s, 5-H, 6-H, 2H, ArH), 7.93 (dd, $J = 1, 8$ Hz, 4-H, 1H, ArH), 8.63 (d, $J = 8$ Hz, 11-H, 1H, ArH), 8.89 (dd, $J = 1, 8$ Hz, 1-H, 1H, ArH); ms: m/e 248 (M^+ , 100), 247 (35), 249 (21), 245 (17).

Anal. Calcd. for $C_{17}H_{14}S$: C, 82.22; H, 4.87; S, 12.91. Found: C, 82.17; H, 5.02; S, 12.88.

3-Chloro-4-methyl-2-benzo[*b*]thiophene-2-carbonyl Chloride (42).

A mixture of 8.1 g (50 mmoles) of 2-methylcinnamic acid (**41**), 0.4 ml (0.5 mmole) of pyridine, 18.2 ml (250 mmoles) of thionyl chloride and 50 ml of chlorobenzene was heated at reflux temperature for 4 days and filtered to remove insoluble material. The filtrate was concentrated and the residue was triturated with 25 ml of hexane and filtered to give 6.2 g (51%) of yellow needles. The product was generally analytically pure after one recrystallization from hexane, mp 112°; nmr (deuteriochloroform): δ 2.90 (s, 4- CH_3 , 3H), 7.24 (m, 6-H, 1H, ArH), 7.47 (d, $J = 6$ Hz, 7-H, 1H, ArH), 7.67 (bd, $J = 7$ Hz, 5-H, 1H, ArH); ir (potassium bromide): 1750 (C=O); ms: m/e 246 ($M^+ + 2$, 13), 244 (M^+ , 19), 211 (33), 209 (100), 204 (44).

Anal. Calcd. for $C_{10}H_6ClOS$: C, 49.00; H, 2.47; S, 13.08. Found: C, 49.20; H, 2.08; S, 12.94.

3-Chloro-2-hydroxymethyl-4-methylbenzo[*b*]thiophene (43).

To a stirred solution of 1.89 g (50 mmoles) of lithium aluminum hydride in 300 ml of dry ether was slowly dropped 7.3 g (30 mmoles) of **42**. When the addition was completed the reaction mixture was allowed to reflux for 3 hours. After cooling, the reaction mixture was quenched cautiously by adding water and enough 6*N* hydrochloric acid to dissolve the inorganic salts. The ether phase was separated and the aqueous layer was extracted with 2 \times 150 ml portions of benzene. The combined benzene and ether solution was dried over sodium sulfate. Evaporation of the solvent *in vacuo* yielded pale brown crystals which were recrystallized from hexane to give 48 g (75%), mp 92°; nmr (deuteriochloroform): δ 2.13 (bs, OH, 1H), 2.82 (s, CH_3 , 3H), 4.90 (bs, $-CH_2-O$, 2H); 7.06 (m, 6-H, 1H, ArH), 7.25 (d, $J = 6$ Hz, 7-H, 1H, ArH), 7.58 (dd, $J = 2, 7$ Hz, 5-H, 1H, ArH); ir (potassium bromide): 3260 (OH, broad); ms: m/e 214 ($M^+ + 2$, 40), 212 (M^+ , 100), 177 (56).

Anal. Calcd. for $C_{11}H_8ClOS$: C, 56.47; H, 4.27; S, 15.07. Found: C, 56.19; H, 4.55; S, 14.89.

3-Chloro-4-methyl-2-benzo[*b*]thiophene-2-carboxaldehyde (44).

A solution of 4 g (18.8 mmoles) of **43** in 20 ml of dry pyridine was added to a suspension of chromium trioxide-pyridine complex made from 5 g (50 mmoles) of chromium trioxide and 30 ml of dry pyridine. After stirring for 2 hours at room temperature, the reaction mixture was filtered and washed with chloroform. The filtrate was washed successively with 10% hydrochloric acid and saturated sodium carbonate solution and then dried over sodium sulfate. Evaporation of the chloroform yielded pale brown crystals which were recrystallized from hexane to give 3.1 g (78%); mp 87°; nmr (deuteriochloroform): δ 2.90 (s, 4- CH_3 , 3H), 7.22 (m, 6-H, 1H, ArH), 7.41 (d, $J = 6$ Hz, 7-H, 1H, ArH), 7.63 (dd, $J = 2, 7$ Hz, 5-H, ArH), 10.29 (s, CHO , 1H); ir (potassium bromide): 1650 (C=O); ms: m/e 212 ($M^+ + 2$, 15), 211 ($M^+ + 1$, 19), 210 (M^+ , 45), 204 (100).

Anal. Calcd. for $C_{16}H_{17}ClOS$: C, 57.01; H, 3.35; S, 15.22. Found: C, 57.22; H, 3.53; S, 15.02.

3-Chloro-4-methyl-2-styrylbenzo[*b*]thiophene (45).

Sodium hydride (50%, 0.6 g, 12.5 mmoles) was placed in 50 ml of dry dimethyl sulfoxide. The slurry was cooled to 20° and 1.24 g (5 mmoles) of diethyl benzylphosphonate (30) was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 20 minutes. To the pale yellow solution, maintained below 25°, was added dropwise 1.05 g (5 moles) of 44. The solution was stirred at room temperature for 4 hours. The reaction mixture was poured into a large excess of water to decompose the excess sodium hydride and the resulting precipitate was collected by filtration. The crude product was purified by chromatography on a silica gel column using hexane as the eluent giving 0.67 g (48%) of product as yellow needles, mp 110°; nmr (deuteriochloroform): δ 2.84 (s, CH_3 , 3H), 7.04-7.62 (m, aromatic and ethenyl protons, 10H); ms: m/e 286 ($M^+ + 2$, 38), 284 (M^+ , 100), 249 (27), 234 (75).

Anal. Calcd. for $C_{17}H_{11}ClS$: C, 71.69; H, 4.60; S, 11.26. Found: C, 71.86; H, 4.88; S, 11.02.

11-Methylbenzo[*b*]naphthothiothiophene (10).

A stirred solution of 0.4 (1.4 mmoles) of 45 and 0.1 ml of triethylamine in 360 ml of benzene was irradiated for 6 hours with a 450 Watt Hanovia medium pressure mercury lamp under stirring. The benzene was evaporated *in vacuo* and the residue was purified by chromatography on a silica gel column using hexane as the eluent giving 0.15 g (34%) of white leaflets, mp 136°. An analytical sample was recrystallized from methanol to give white leaflets, mp 136°; nmr (deuteriochloroform): δ 2.84 (s, CH_3 , 3H), 7.11-8.06 (m, 2-H, 3-H, 4-H, 8-H, 9-H, 5H, *ArH*), 7.85 (s, 5-H, 6-H, 2H, *ArH*), 8.18 (dd, $J = 1, 8$ Hz, 1-H, 1H, *ArH*); ms: m/e 248 (M^+ , 100), 247 (66), 245 (39).

Anal. Calcd. for $C_{17}H_{12}S$: C, 82.22; H, 4.87; S, 12.91. Found: C, 82.00; H, 5.00; S, 12.66.

3-Chloro-2-hydroxymethyl-6-methylbenzo[*b*]thiophene (47).

This compound was synthesized from 46 in a manner similar to that used for the preparation of 43 and was obtained in 75% yield. An analytical sample was recrystallized from hexane to give colorless needles, mp 99°; nmr (deuteriochloroform): δ 2.45 (s, CH_3 , 3H), 4.85 (s, $2-CH_2-O$, 2H), 7.12 (dd, $J = 1, 8$ Hz, 5-H, 1H, *ArH*), 7.56 (s, 7-H, 1H, *ArH*), 7.63 (d, $J = 8$ Hz, 4-H, 1H, *ArH*); ir (potassium bromide): 3200 (OH broad); ms: m/e 214 ($M^+ + 2$, 38), 212 (M^+ , 100), 195 (47), 177 (56).

Anal. Calcd. for $C_{16}H_9ClOS$: C, 56.47; H, 4.27; S, 15.07. Found: C, 56.22; H, 4.17; S, 14.88.

3-Chloro-6-methylbenzo[*b*]thiophene-2-carboxaldehyde (48).

This compound was synthesized from 47 in a manner similar to the preparation of 44 and was obtained in 70% yield. An analytical sample was recrystallized from hexane to give pale yellow needles, mp 109°; nmr (deuteriochloroform): δ 2.49 (s, CH_3 , 1H), 7.27 (d, $J = 8$ Hz, 5-H, 1H,

ArH), 7.59 (s, 7-H, 1H, *ArH*), 7.85 (d, $J = 8$ Hz, 4-H, 1H, *ArH*), 10.31 (s, $-CH=O$, 1H); ir (potassium bromide): 1650 (C=O); ms: m/e 212 ($M^+ + 2$, 15), 211 ($M^+ + 1$, 19), 210 ($M^+ + 1$, 45), 209 (M^+ , 45), 204 (100), 181 ($M^+ - 29$, 26).

Anal. Calcd. for $C_{16}H_7ClOS$: C, 57.01; H, 3.35; S, 15.22. Found: C, 57.29; H, 3.42; S, 15.03.

3-Chloro-6-methyl-2-styrylbenzo[*b*]thiophene (49).

This compound was synthesized from 48 in a manner similar to that used for the preparation of 45 and was obtained in 50% yield. An analytical sample was recrystallized from hexane to give pale yellow needles, mp 126°; nmr (deuteriochloroform): δ 2.44 (s, CH_3 , 3H), 7.04-7.68 (m, vinyl, phenyl and thiophene ring protons, 10H); ms: m/e 286 ($M^+ + 2$, 41), 285 ($M^+ + 1$, 23), 284 (M^+ , 100), 249 (43), 248 (29), 234 (90).

Anal. Calcd. for $C_{17}H_{11}ClS$: C, 71.69; H, 4.60; S, 11.60. Found: C, 71.46; H, 4.70; S, 10.97.

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