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We describe the synthesis of thieno[2,3-*c*]dibenzothiophene (**6**), thieno[3,2-*c*]dibenzothiophene (**10**), thieno[3,2-*a*]dibenzothiophene (**14**), thieno[2,3-*a*]dibenzothiophene (**16**), benzo[1,2-*b*:4,3-*b'*]bisbenzo[*b*]thiophene (**18**), benzo[1,2-*b*:3,4-*b'*]bisbenzo[*b*]thiophene (**20**), benzo[2,1-*b*:3,4-*b'*]bisbenzo[*b*]thiophene (**22**), benzo[1,2-*b*:3,4-*g'*]bisbenzo[*b*]thiophene (**27**), benzo[1,2-*b*:4,3-*e'*]bisbenzo[*b*]thiophene (**29**), benzo[2,1-*b*:3,4-*g'*]bisbenzo[*b*]thiophene (**36**), benzo[2,1-*b*:4,3-*e'*]bisbenzo[*b*]thiophene (**38**), benzo[1,2-*b*:4,3-*g'*]bisbenzo[*b*]thiophene (**41**), benzo[1,2-*b*:4,5-*g'*]bisbenzo[*b*]thiophene (**42**), benzo[1,2-*b*:3,4-*e'*]bisbenzo[*b*]thiophene (**44**) and benzo[1,2-*b*:5,4-*e'*]bisbenzo[*b*]thiophene (**45**).

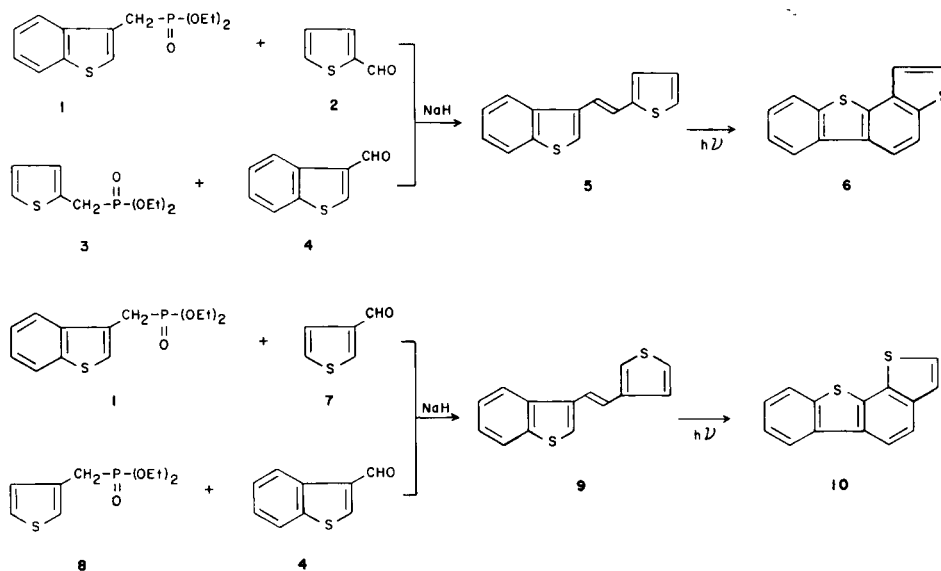
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In our earlier work [2-19] we have prepared a number of unsubstituted polycyclic thiophenes and methyl or ethyl derivatives some of which have been shown to occur in coal liquids, coal-derived products and shale oils [20-22]. In each of the polycyclic thiophenes previously reported, only one thiophene ring was present in the polycyclic system.

In order to search for polycyclic thiophenes which may occur in coal liquids, coal-derived products or shale oils, we have undertaken the synthesis of polycyclic thiophenes containing two thiophene rings. An examination of the literature revealed that all of the isomeric unsubstituted benzodithiophenes have been synthesized [23-26]. We followed their procedures in order to provide authentic specimens of those compounds.

A search of the literature failed to reveal reports on the synthesis of any angular [*b*]fused thienodibenzothiophenes. We now report the synthesis of all four isomeric angular [*b*]fused thienodibenzothiophenes. 1-(3-Benzo[*b*]thienyl)-2-(2-thienyl)ethene (**5**) has been prepared from thiophene-2-carboxaldehyde (**2**) and diethyl 3-benzo[*b*]thienylphosphonate (**1**) [3] in 80% yield and also from benzo[*b*]thiophene-3-carboxaldehyde (**4**) and diethyl 2-thienylphosphonate (**3**) [2] in 84% yield. Photocyclization of the yellow prisms **5** gave thieno[2,3-*c*]dibenzothiophene (**6**) in 80% yield. 1-(3-Benzo[*b*]thienyl)-2-(3-thienyl)ethene (**9**) was obtained by the condensation of 3-thiophenecarboxaldehyde (**7**) and diethyl 3-benzo[*b*]thienylphosphonate (**1**) [3] in 81% yield and also from the condensation of benzo[*b*]thiophene-3-carboxaldehyde (**4**) with diethyl

Scheme 1



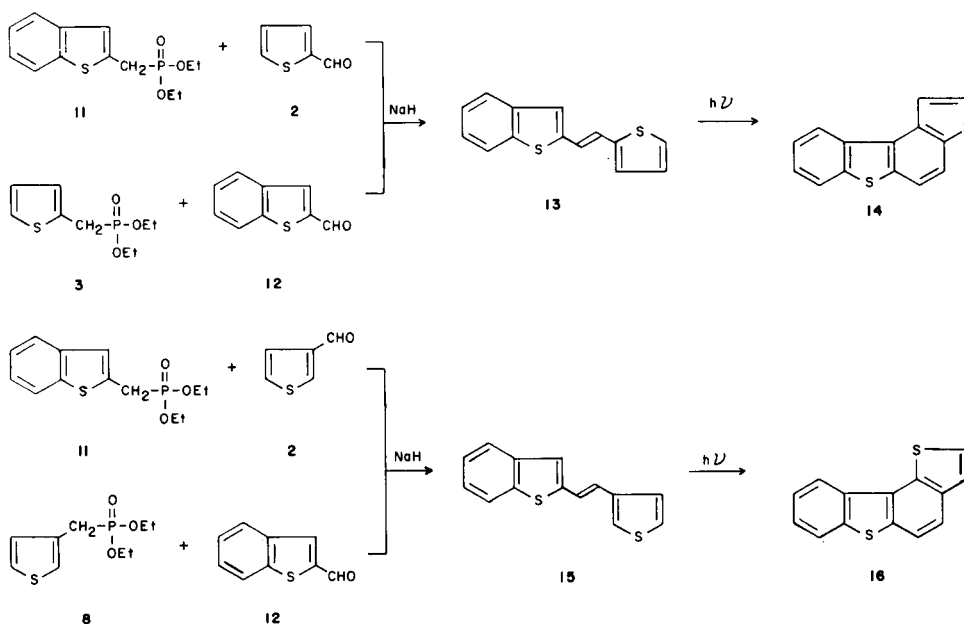
3-thienylphosphonate (**8**) [2] in 81% yield. Photocyclization of **9** gave thieno[3,2-*c*]dibenzothiophene (**10**) in 21% yield as colorless crystals (Scheme I).

1-(2-Benzo[*b*]thienyl)-2-(2-thienyl)ethene (**13**) was prepared *via* the Wadsworth-Emmons reaction of **2** and **11** [12] in 83% yield and also from **3** [2] and **12** in 86% yield. Photocyclization of the yellow prisms **13** gave thieno[3,2-*a*]dibenzothiophene (**14**) in 88% yield. 1-(2-Benzo[*b*]thienyl)-2-(3-thienyl)ethene (**15**) was synthesized from **2** and **11** [12] in 81% yield under Wadsworth-Emmons conditions and also from **8** [12] and **12** in 83% yield under the same reaction conditions. Photocyclization of **15** gave thieno[2,3-*a*]dibenzothiophene (**16**) as colorless crystals in 83% yield (Scheme II).

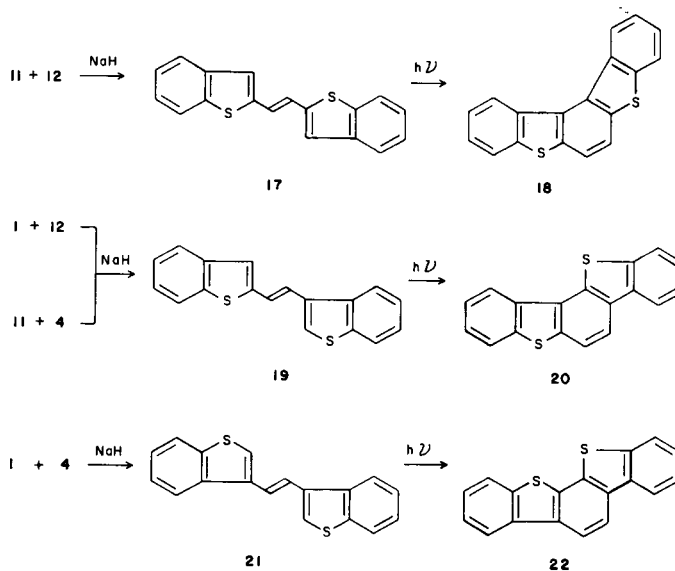
In order to provide samples of angular pentacyclic thiophenes containing two thiophene rings, 11 angular benzo-bisbenzo[*b*]thiophenes were selected for synthesis. Three of the benzobisbenzo[*b*]thiophenes have been previously reported *via* a different synthetic route. The remaining eight benzobisbenzo[*b*]thiophenes are novel ring systems.

1,2-Bis(2,2'-benzo[*b*]thienyl)ethene (**17**) was prepared from **12** and **11** [12] under Wadsworth-Emmons conditions in 81% yield as yellow prisms. Photocyclization of **17** gave benzo[1,2-*b*:4,3-*b'*]bisbenzo[*b*]thiophene (**18**) in 85% yield. Compound **18** has been reported by Rao and Tilak [23] and by Groen *et al* [27]. Our method requires fewer steps with higher yields than those previously reported. 1,2-Bis(2,3'-benzo[*b*]thienyl)ethene (**19**) has been prepared *via* the

Scheme II

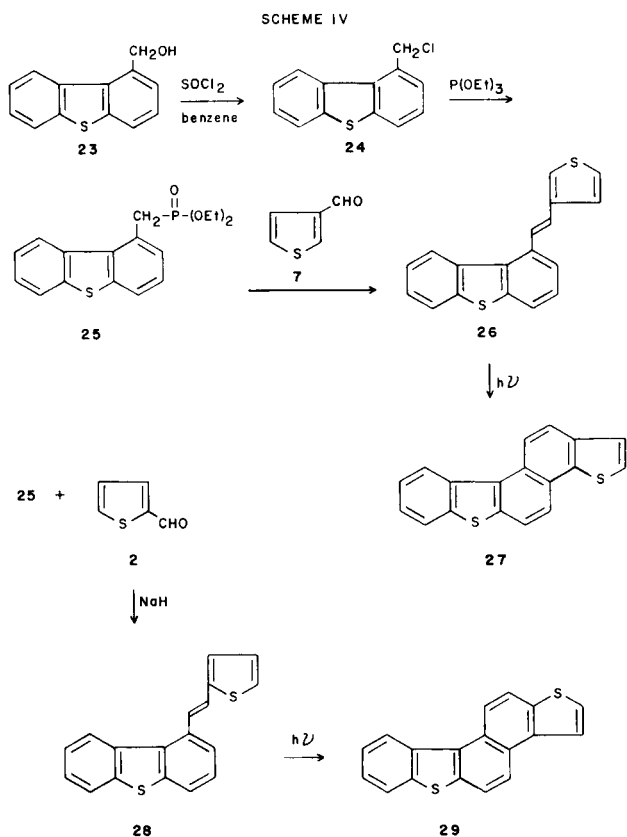


Scheme III



Wadsworth-Emmons reaction of **12** and **1** [3] (80% yield) and also from **11** [12] and **4** (Wadsworth-Emmons conditions) in 84% yield. Photocyclization of **19** gave benzo[1,2-*b*:3,4-*b'*]bisbenzo[*b*]thiophene (**20**) in 71% yield. Compound **20** has been previously prepared by Davies and Porter [28] and by Zander [29]. Our application of the Wadsworth-Emmons reaction followed by photocyclization provided much higher overall yields and fewer steps than the previously reported methods. 1,2-Bis(3,3'-benzo[*b*]thienyl)ethene (**21**) was prepared by the condensation of **1** [3] and **4** in 83% yield. Photocyclization of **21** gave benzo[2,1-*b*:3,4-*b'*]bisbenzo[*b*]thiophene (**22**) in 28% yield. Compound **22** has previously been prepared by Rao and Tilak [23] and by Zander [29]. Likewise our approach to **22** is a much shorter sequence of reactions in higher overall yield (Scheme III).

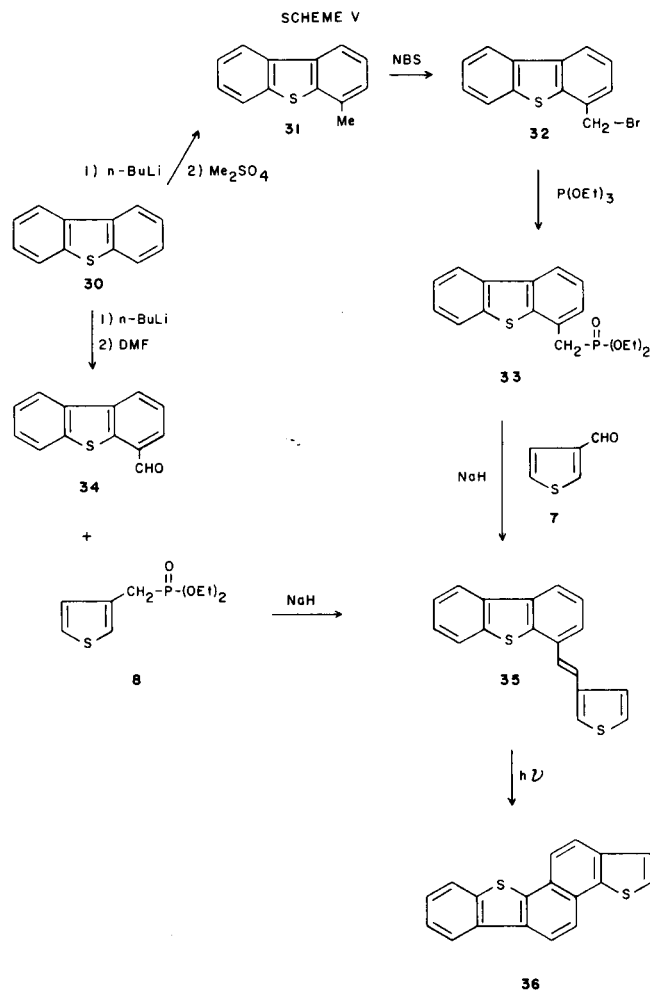
Benzo[1,2-*b*:3,4-*g'*]bisbenzo[*b*]thiophene (**27**) was prepared in four steps from 1-hydroxymethyldibenzothiophene (**23**) [30]. When the alcohol **23** was allowed to react with thionyl chloride, 1-chloromethyldibenzothiophene (**24**) [18,30] was obtained in 77% yield. Diethyl 1-dibenzothienylphosphonate (**25**) was obtained as a pale yellow oil in 81% yield from compound **24** and triethyl phosphite. Condensation of the phosphonate **25** with thiophene-3-carboxaldehyde (**7**) under Wadsworth-Emmons conditions (sodium hydride and dimethoxyethane) gave 1-(1-dibenzo-



thienyl)-2-(3-thienyl)ethene (**26**) as pale yellow prisms in 85% yield. Photocyclization of **26** gave benzo[1,2-*b*:3,4-*g*]bisbenzo[*b*]thiophene (**27**) in 45% yield.

Diethyl 1-dibenzothienylphosphonate (**25**) upon treatment with sodium hydride followed by the addition of thiophene-2-carboxaldehyde (**2**) gave 1-(1-dibenzothienyl)-2-(2-thienyl)ethene (**28**) as pale yellow flakes in 82% yield. Compound **28** was irradiated under a 450 watt medium pressure Hanovia mercury lamp for four hours in the presence of air and iodine to give benzo[1,2-*b*:4,3-*e*]bisbenzo[*b*]thiophene (**29**) as colorless flakes in 78% yield (Scheme IV).

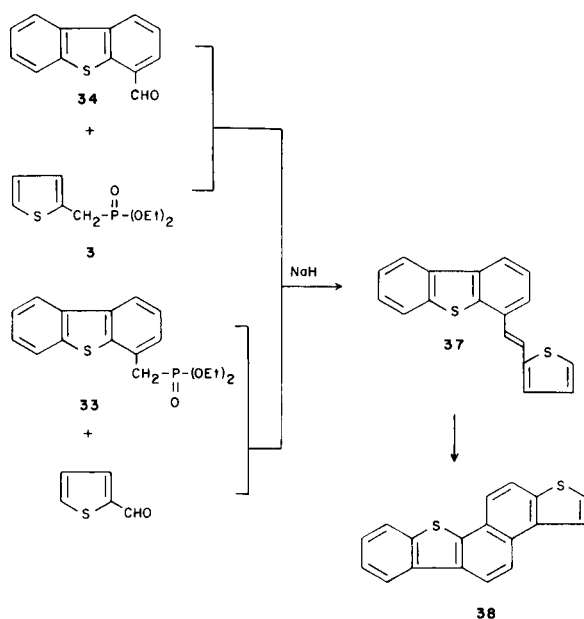
When dibenzothiophene (**30**) was lithiated with *n*-butyllithium followed by treatment with dimethylsulfate, 4-methyldibenzothiophene (**31**) [31] was produced in 52% yield which was brominated *via* the Wohl-Ziegler reaction (NBS) according to the Gourier and Canonne method [31] to give 4-bromomethyldibenzothiophene (**32**) [31] (65% yield). Reaction of the bromo compound **32** with triethyl phosphite gave diethyl 4-dibenzothienylphosphonate (**33**) as a colorless oil in 79% yield. Condensation of compound **33** with thiophene-3-carboxaldehyde (**7**) gave 1-(4-dibenzo-



thienyl)-2-(3-thienyl)ethene (**35**) in 62% yield. The colorless prisms **25** were also obtained in better yields (76%) from the reaction of dibenzothiophene-4-carboxaldehyde (**34**) [32] with diethyl 3-thienylphosphonate (**8**) [12] under Wadsworth-Emmons conditions. Photocyclization of **35** gave benzo[2,1-*b*:3,4-*g*]bisbenzo[*b*]thiophene (**36**) in 62% yield (Scheme V).

1-(4-Dibenzothiienyl)-2-(2-thienyl)ethene (**37**) has been prepared from diethyl 2-thienylphosphonate (**3**) [2] and dibenzothiophene-4-carboxaldehyde (**34**) [32] in 79% yield and also from diethyl dibenzothiienylphosphonate (**33**) and thiophene-2-carboxaldehyde (**2**) in 71% yield. Photocyclization of **37** gave benzo[2,1-*b*:4,3-*e*]bisbenzo[*b*]thiophene (**38**) as colorless crystals in 75% yield (Scheme VI).

SCHEME VI

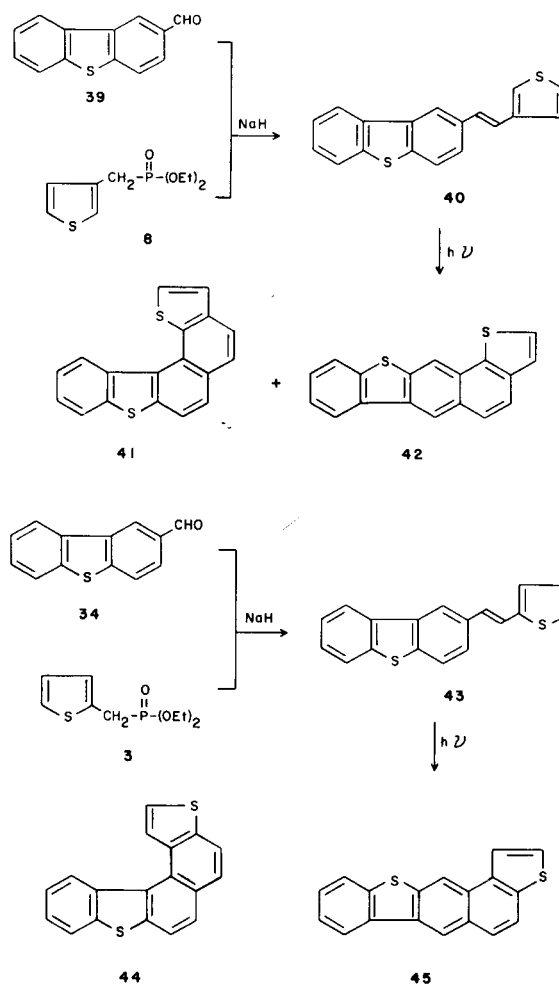


1-(2-Dibenzothiienyl)-2-(3-thienyl)ethene (**40**) was prepared from dibenzothiophene-2-carboxaldehyde (**39**) [34] and diethyl 3-thienylphosphonate (**8**) [12] under Wadsworth-Emmons conditions in 68% yield. Photocyclization of **40** gave a crystalline mixture of benzo[1,2-*b*:4,3-*g*]bisbenzo[*b*]thiophene (**41**) and benzo[1,2-*b*:4,5-*g*]bisbenzo[*b*]bisbenzo[*b*]thiophene (**42**). Separation of the mixture **41** and **42** was achieved by column chromatography on a neutral alumina column using hexane as the eluent. Compound **41** eluted first in pure form. By this procedure the second fraction consisted of a mixture of **41** and **42** which was separated by a second column chromatography (basic alumina) using pentane as the eluent. Compound **41** again eluted first in pure form and the combined yields of **41** from the two column chromatography was 47%. Compound **42** eluted last in pure form from the basic alumina column in 19% yield. The structures of compounds **41** and **42** were discriminated principally on the basis of the differences

observed in the nmr spectra. The nmr of compound **42** has two singlets, one at  $\delta$  8.19 ppm due to the H-6 proton and the second peak at  $\delta$  9.13 ppm due to the H-12 proton. The melting point and solubilities were consistent with the proposed structures. Benzo[1,2-*b*:4,5-*g*]bisbenzo[*b*]thiophene (**42**) is more linear than benzo[1,2-*b*:4,3-*g*]bisbenzo[*b*]thiophene (**41**); therefore, **42** should have a higher melting point (mp 298-299°) and be more insoluble than **41** (mp 137-138°). As expected, compound **42**, being more insoluble, eluted last when chromatographed on either neutral or basic alumina.

1-(2-Dibenzothiienyl)-2-(2-thienyl)ethene (**43**) was prepared by the condensation of dibenzothiophene-2-carboxaldehyde (**39**) [34] and diethyl 2-thienylphosphonate (**3**) [2] in 88% yield. Photocyclization of **43** gave a mixture of benzo[1,2-*b*:3,4-*e*]bisbenzo[*b*]thiophene (**44**) and benzo[1,2-*b*:5,4-*e*]bisbenzo[*b*]thiophene (**45**). Separation of the mixture **44** and **45** was achieved by column chromatography on a neutral alumina column using hexane as the eluent. Compound **44** eluted first in pure form. By this procedure the second fraction consisted with a mixture of

SCHEME VII



**44** and **45** which was separated by a second column chromatography (basic alumina) using pentane as the eluent. Compound **44** again eluted first in pure form and the combined yields of **44** from the two column chromatography was 65%. Compound **45** eluted last in pure form from the basic alumina column in 20% yield (Scheme VII). A substantial difference in the yields of **41:42** (47%:19%) with respect to **44:45** (68%:20%) was observed. This is consistent with what one should expect. The 3-position in thiophene is much more reactive than the 2-position in photocyclization reactions [2,4,24]. The structural assignments of compounds **44** and **45** were based principally upon the nmr spectra. Compound **45** shows two singlets in the nmr, one at  $\delta$  7.91 ppm due to the H-6 proton and the other at  $\delta$  8.91 ppm due to the H-12 proton. Their melting points and solubility were consistent with our structural assignment. The more angular one (compound **44**) had a melting point of 128-129° and it eluted first in both basic and neutral alumina column chromatography. Compound **45** had a melting point of 281-282°.

Some of these angular polycyclic aromatic thiophenes are being screened against TA-98 and TA-100 in the Ames test (S9 liver homogenate activation) and these results will be published elsewhere.

## EXPERIMENTAL

Melting points were determined in open capillary tubes on a Thomas-Hoover capillary melting point apparatus. These melting points are uncorrected. The proton magnetic resonance spectra (<sup>1</sup>H-nmr) of all compounds were obtained on a Varian EM-360-A spectrometer in the solvents indicated. Chemical shifts are reported in ppm from TMS as an internal standard and are given in  $\delta$  units. Mass spectra were obtained on a Hewlett-Packard model 5980-A mass spectrometer. The spectra were run using electron impact ionization. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

### 1-(3-Benzo[*b*]thienyl)-2-(2-thienyl)ethene (**5**).

#### Method A.

Sodium hydride (50%, 1.4 g, 58 mmoles) was placed in 100 ml of dry 1,2-dimethoxyethane. Sodium hydride was used after washing twice with 40 ml of hexane. The slurry was cooled to 20° and compound **1** (7.1 g, 25 mmoles) [3] 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°, 2-thiophenecarboxaldehyde (**2**) (2.8 g, 25 mmoles) was added dropwise. The solution was stirred at room temperature for 3.5 hours. A large excess of water was added and the resulting precipitate was collected by filtration. This product was recrystallized from methanol to give 4.8 g (80%) of pale yellow prisms, mp 89-90°.

#### Method B.

Compound **5** was prepared from compound **3** (3.5 g, 15 mmoles) [2] and compound **4** (2.42 g, 15 mmoles) in a manner similar to the preparation of compound **5** (Method A) and 3.04 g (84%) of pale yellow prisms were obtained, mp 89-90°; nmr (deuteriochloroform):  $\delta$  6.95-7.51 (m, 2  $\times$  ethylene-H, H-3, H-4, H-5 of thiophene, H-5', H-6' of benzo[*b*]thiophene, 8H), 7.68-8.01 (m, H-4', H-7' of benzo[*b*]thiophene, 2H, ArH); ms: m/e 242 (M<sup>+</sup>, 100), 241 (96).

Anal. Calcd. for C<sub>14</sub>H<sub>10</sub>S<sub>2</sub>: C, 69.38; H, 4.16; S, 26.46. Found: C, 69.42; H, 4.34; S, 26.21.

### Thieno[2,3-*c*]dibenzothiophene (**6**).

A solution of compound **5** (1.0 g, 4 mmoles) and 0.1 g of iodine in 360 ml of benzene was irradiated for 3.5 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 chromatographed on a silica gel column using hexane:benzene (1:1) as the eluent giving 0.82 g (80%) of colorless crystals, mp 216-217°; nmr (deuteriochloroform):  $\delta$  7.20-7.84 (m, H-1, H-2, H-4, H-5, H-8, H-9, 6H, ArH), 7.93 (d, J = 4 Hz, H-7, 1H, ArH), 8.01-8.22 (m, H-10, 1H, ArH); ms: m/e 242 (M<sup>+</sup> + 2, 11), 241 (M<sup>+</sup> + 1, 17), 240 (M<sup>+</sup>, 100).

Anal. Calcd. for C<sub>14</sub>H<sub>8</sub>S<sub>2</sub>: C, 69.96; H, 3.36; S, 26.68. Found: C, 69.83; H, 3.42; S, 26.72.

### 1-(3-Benzo[*b*]thienyl)-2-(3-thienyl)ethene (**9**).

#### Method A.

Compound **9** was prepared from compound **1** (7.1 g, 25 mmoles) [3] and compound **7** (2.8 g, 25 mmoles) in a manner similar to the preparation of compound **5** and 4.9 g (81%) of yellow prisms was obtained, mp 85-86°.

#### Method B.

Compound **9** was prepared from compound **8** (3.5 g, 15 mmoles) [2] and compound **4** (2.42 g, 15 mmoles) in a manner similar to the preparation of compound **5** and 2.93 g (81%) of yellow prisms was obtained, mp 85-86°; (deuteriochloroform):  $\delta$  7.01-7.42 (m, 2  $\times$  ethylene-H, H-2, H-4, H-5 of thiophene, H-5', H-6' of benzo[*b*]thiophene, 8H), 7.62-7.98 (m, H-4', H-7' of benzo[*b*]thiophene, 2H, ArH); ms: m/e 242 (M<sup>+</sup>, 88), 241 (100), 240 (37).

Anal. Calcd. for C<sub>14</sub>H<sub>10</sub>S<sub>2</sub>: C, 69.38; H, 4.16; S, 26.46. Found: C, 69.40; H, 4.24; S, 26.13.

### Thieno[3,2-*c*]dibenzothiophene (**10**).

This compound was prepared from compound **9** (1.0 g, 4 mmoles) in a manner similar to the preparation of compound **6** and 0.21 g (21%) of colorless crystals was obtained, mp 56°; nmr (deuteriochloroform):  $\delta$  7.29-7.80 (m, H-2, H-3, H-4, H-5, H-7, H-8, 6H, ArH), 8.00 (d, J = 4 Hz, H-6, 1H, ArH), 8.12-8.30 (m, H-9, 1H, ArH); ms: m/e 242 (M<sup>+</sup> + 2, 3), 241 (M<sup>+</sup> + 1, 9), 240 (M<sup>+</sup>, 100).

Anal. Calcd. for C<sub>14</sub>H<sub>8</sub>S<sub>2</sub>: C, 69.96; H, 3.36; S, 26.68. Found: C, 70.03; H, 3.43; S, 26.40.

### 1-(2-Benzo[*b*]thienyl)-2-(2-thienyl)ethene (**13**).

#### Method A.

This compound was prepared from compound **11** (7.1 g, 25 mmoles) [12] and compound **2** (2.8 g, 25 mmoles) in a manner similar to the preparation of compound **5** and yellow prisms were obtained (83%), mp 176-177°.

#### Method B.

This compound was prepared from compound **3** (3.5 g, 15 mmoles) [2] and compound **12** (2.42 g, 15 mmoles) in a manner similar to the preparation of compound **5** and yellow prisms were obtained (86%), mp 176-177°; (deuteriochloroform):  $\delta$  6.98-7.39 (m, 2  $\times$  ethylene-H, H-3, H-4, H-5 of thiophene, H-5', H-6' of benzo[*b*]thiophene, 8H), 7.53-7.88 (m, H-4', H-7' of benzo[*b*]thiophene, 2H, ArH); ms: m/e 242 (M<sup>+</sup>, 100).

Anal. Calcd. for C<sub>14</sub>H<sub>10</sub>S<sub>2</sub>: C, 69.38; H, 4.16; S, 26.46. Found: C, 69.28; H, 4.16; S, 26.53.

### Thieno[3,2-*a*]dibenzothiophene (**14**).

Compound **14** was prepared from compound **13** (1.2 g, 5 mmoles) in a manner similar to compound **6** and colorless crystals were obtained (88%), mp 148-149°; nmr (deuteriochloroform):  $\delta$  7.36-8.09 (m, H-1, H-2, H-4, H-5, H-8, H-9, 6H, ArH), 8.20 (d, J = 4 Hz, H-7, 1H, ArH), 8.36-8.79 (m, H-10, 1H, ArH); ms: m/e 242 (M<sup>+</sup> + 2, 10), 241 (M<sup>+</sup> + 1, 17), 240 (M<sup>+</sup>, 100).

Anal. Calcd. for C<sub>14</sub>H<sub>8</sub>S<sub>2</sub>: C, 69.96; H, 3.36; S, 26.68. Found: C, 69.99; H, 3.41; S, 26.71.

1-(2-Benzo[*b*]thienyl)-2-(3-thienyl)ethene (15).

## Method A.

Compound **15** was prepared from compound **11** (7.1 g, 25 mmoles) [12] and compound **2** (2.8 g, 25 mmoles) in a manner similar to the preparation of compound **5** and yellow prisms were obtained (81%), mp 208°.

## Method B.

Compound **15** was prepared from compound **8** (3.5 g, 15 mmoles) [2] and compound **12** (2.52 g, 15 mmoles) in a manner similar to the preparation of compound **5** and yellow prisms were obtained (83%), mp 208°; nmr (deuteriochloroform):  $\delta$  7.00-7.41 (m, 2  $\times$  ethylene-*H*, H-2, H-4, H-5 of thiophene, H-5', H-6' of benzo[*b*]thiophene, 8H), 7.50-7.86 (m, H-4', H-7' of benzo[*b*]thiophene, 2H, Ar*H*); ms: *m/e* 242 ( $M^+$ , 100), 241 (99), 277 (38).

*Anal.* Calcd. for  $C_{18}H_{10}S_2$ : C, 69.38; H, 4.16; S, 26.46. Found: C, 69.19; H, 4.07; S, 26.80.

Thieno[2,3-*a*]dibenzothiophene (16).

This compound was prepared from compound **15** (1.2 g, 5 mmoles) in a manner similar to compound **6** and colorless crystals were obtained (83%), mp 104-105°; nmr (deuteriochloroform):  $\delta$  7.30-7.61 (m, H-2, H-3, H-8, H-9, 4H, Ar*H*), 7.73-8.01 (m, H-7, 1H, Ar*H*), 7.76 (s, H-4, H-5, 2H, Ar*H*), 8.24-8.65 (m, H-10, 1H, Ar*H*); ms: *m/e* 240 ( $M^+$ , 100).

*Anal.* Calcd. for  $C_{14}H_8S_2$ : C, 69.96; H, 3.36; S, 26.68. Found: C, 70.05; H, 3.49; S, 26.80.

1,2-Bis(2,2'-benzo[*b*]thienyl)ethene (17).

Compound **17** was prepared from compound **11** (1.75 g, 6.2 mmoles) [12] and compound **12** (1.0 g, 6.2 mmoles) in a manner similar to the preparation of compound **5** and yellow prisms were obtained (81%), mp 289-290°; nmr (deuteriochloroform):  $\delta$  7.15-7.48 (m, 2  $\times$  ethylene-*H*, H-3, H-3', H-5, H-5', H-6, H-6', 8H), 7.50-8.09 (m, H-4, H-4', H-7, H-7', 4H, Ar*H*); ms: *m/e* 294 ( $M^+$  + 2, 10), 293 ( $M^+$  + 1, 26), 292 (100), 291 (77), 290 (42).

*Anal.* Calcd. for  $C_{18}H_{12}S_2$ : C, 73.93; H, 4.14; S, 21.93. Found: C, 73.58; H, 4.50; S, 22.05.

Benzo[1,2-*b*:4,3-*b'*]bisbenzo[*b*]thiophene (18).

This compound was prepared from compound **17** (1.1 g, 3.8 mmoles) in a manner similar to the preparation of compound **6** and colorless crystals were obtained (85%), mp 184-185° (lit mp 181-183° [23], 183-185° [26]); nmr (deuteriochloroform):  $\delta$  7.11-8.02 (m, H-2, H-3, H-4, H-6, H-7, H-9, H-10, H-11, 8H, Ar*H*), 8.70-9.17 (m, H-1, H-12, 2H, Ar*H*); ms: *m/e* 292 ( $M^+$  + 2, 10), 291 ( $M^+$  + 1, 21), 290 ( $M^+$ , 100), 289 (24), 288 (43).

*Anal.* Calcd. for  $C_{18}H_{10}S_2$ : C, 74.45; H, 3.47; S, 22.08. Found: C, 74.36; H, 3.53; S, 22.18.

1,2-Bis(2,3'-benzo[*b*]thienyl)ethene (19).

## Method A.

Compound **19** was prepared from compound **1** (1.75 g, 6.2 mmoles) [3] and compound **12** (1.0 g, 6.2 mmoles) in a manner similar to the preparation of compound **5** and yellow prisms were obtained (80%), mp 157-158°.

## Method B.

This compound was prepared from compound **11** (1.75 g, 6.2 mmoles) [12] and compound **4** (1.0 g, 6.2 mmoles) in a manner similar to the preparation of compound **5** and yellow prisms were obtained (84%), mp 157-158°; nmr (deuteriochloroform):  $\delta$  7.17-7.58 (m, 2  $\times$  ethylene-*H*, H-2, H-3', H-5, H-5', H-6, H-6', 8H), 7.60-8.12 (m, H-4, H-4', H-7, H-7', 4H, Ar*H*); ms: *m/e* 294 ( $M^+$  + 2, 10), 293 ( $M^+$  + 1, 26), 292 ( $M^+$ , 100), 291 (90), 290 (53), 258 (34).

*Anal.* Calcd. for  $C_{18}H_{12}S_2$ : C, 73.93; H, 4.14; S, 21.93. Found: C, 73.75; H, 4.26; S, 22.00.

Benzo[1,2-*b*:3,4-*b'*]bisbenzo[*b*]thiophene (20).

Compound **20** was prepared from compound **19** (1.1 g, 3.8 mmoles) in a

manner similar to the preparation of compound **6** and colorless crystals were obtained (71%), mp 166° (lit mp 165.5-166° [28], 164-165° [29]); nmr (deuteriochloroform):  $\delta$  7.13-7.67 (m, H-2, H-3, H-5, H-6, H-9, H-10, 6H, Ar*H*), 7.82-8.22 (m, H-1, H-4, H-8, H-11, 4H, Ar*H*); ms: *m/e* 292 ( $M^+$  + 2, 11), 291 ( $M^+$  + 1, 20), 290 ( $M^+$ , 100).

*Anal.* Calcd. for  $C_{18}H_{10}S_2$ : C, 74.45; H, 3.47; S, 22.08. Found: C, 74.64; H, 3.66; S, 21.89.

1,2-Bis(3,3'-benzo[*b*]thienyl)ethene (21).

This compound was prepared from compound **1** (1.75 g, 6.2 mmoles) [3] and compound **4** (1.0 g, 6.2 mmoles) in a manner similar to the preparation of compound **5** and orange crystals were obtained (83%); nmr (deuteriochloroform):  $\delta$  7.11-7.55 (m, 2  $\times$  ethylene-*H*, H-2, H-2', H-5, H-5', H-6, H-6', 8H), 7.58-8.08 (m, H-4, H-4', H-7, H-7', 4H, Ar*H*); ms: *m/e* 294 ( $M^+$  + 2, 10), 293 ( $M^+$  + 1, 27), 292 ( $M^+$ , 100).

*Anal.* Calcd. for  $C_{18}H_{12}S_2$ : C, 73.93; H, 4.14; S, 21.93. Found: C, 73.85; H, 4.23; S, 21.75.

Benzo[2,1-*b*:3,4-*b'*]bisbenzo[*b*]thiophene (22).

This compound was prepared from compound **21** in a manner similar to the preparation of compound **6** and pale yellow crystals were obtained (28%), colorless crystals, mp 265-266° (lit mp 264-265° [29], 270° [23]); nmr (deuteriochloroform):  $\delta$  7.03-7.79 (m, H-2, H-3, H-5, H-6, H-8, H-9, 6H, Ar*H*), 7.91 (dd, *J* = 1, 6 Hz, H-1, H-10, 2H, Ar*H*), 8.02 (d, *J* = 2 Hz, H-4, H-7, 2H, Ar*H*); ms: *m/e* 291 ( $M^+$  + 1, 20), 290 ( $M^+$ , 100).

*Anal.* Calcd. for  $C_{18}H_{10}S_2$ : C, 74.45; H, 3.47; S, 22.08. Found: C, 74.53; H, 3.57; S, 21.98.

## Diethyl 1-Dibenzothienylphosphonate (25).

A mixture of 1-chloromethylthiophene (**24**) (10 g, 0.036 mole) [18,30] and triethylphosphite (6 g, 0.036 mole) was heated to 150° for eight hours giving, upon distillation, a pale yellow liquid (79% yield); nmr (deuteriochloroform):  $\delta$  0.98 (t, *J* = 6 Hz, -O-CH<sub>2</sub>CH<sub>3</sub>, 6H), 3.61 (d, *J* = 8 Hz, CH<sub>2</sub>-P, 2H, 3.87 (near quintet, *J* = 2 Hz, -O-CH<sub>2</sub>-CH<sub>3</sub>, 4H), 7.03-7.50 (m, H-2, H-3, H-7, H-8, 4H, Ar*H*), 7.52-7.86 (m, H-4, H-6, 2H, Ar*H*), 8.18-8.49 (dd, *J* = 2, 8 Hz, H-9, 1H, Ar*H*).

*Anal.* Calcd. for  $C_{17}H_{19}O_3PS$ : C, 61.07; H, 5.73; S, 9.59. Found: C, 61.00; H, 5.85; S, 9.35.

## 1-(1-Dibenzothieryl)-2-(3-thienyl)ethene (26).

Sodium hydride (50% dispersion in mineral oil, 0.9 g, 0.04 mole) was placed in dry 1,2-dimethoxyethane (75 ml). Sodium hydride was used after washing twice with hexane (30 ml). The slurry was cooled to 20° and diethyl 1-dibenzothienylphosphonate (**25**) (3.3 g, 0.01 mole) was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 20 minutes. To the yellow solution maintained below 20°, thiophene-3-carboxaldehyde (**7**) (1.1 g, 0.01 mole) was added dropwise. The solution was stirred at room temperature for five hours. The reaction mixture was slowly poured into a large excess of ice-water and the resulting precipitate was collected by filtration. The product was recrystallized from methanol affording pale yellow prisms in 85% yield, mp 109-110°; nmr (deuteriochloroform):  $\delta$  7.18 (d, *J* = 2 Hz, H-5 of thiophene, 1H, Ar*H*), 7.38-7.54 (m, 2  $\times$  ethylene-*H*, H-2, H-3, H-7, H-8 of dibenzothiophene, H-2', H-4' of thiophene, 8H), 7.61-7.97 (m, H-4, H-6 of dibenzothiophene, 2H, Ar*H*), 8.12-8.40 (m, H-9 of dibenzothiophene, 1H, Ar*H*); ms: *m/e* 292 ( $M^+$ , 100).

*Anal.* Calcd. for  $C_{18}H_{12}S_2$ : C, 73.93; H, 4.14; S, 21.93. Found: C, 73.81; H, 4.25; S, 22.07.

Benzo[1,2-*b*:3,4-*g'*]bisbenzo[*b*]thiophene (27).

A solution of compound **26** (1.0 g, 0.0034 mole) and iodine (0.10 g) in benzene (550 ml) was irradiated for four 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 chromatographed on a neutral alumina column using hexane:benzene (2:1) as the eluent giving colorless crystals (45% yield), mp 161-162°; nmr (deuteriochloroform):  $\delta$  7.19-7.59 (m, H-1, H-2, H-8, H-9, 4H, Ar*H*), 7.74-8.12 (m, H-5, H-7, H-12, H-10 or H-11, 4H,

ArH), 8.58-9.02 (m, H-4, H-10 or H-11, 2H, ArH); ms: m/e 291 ( $M^+ + 1$ , 21), 290 ( $M^+$ , 100).

Anal. Calcd. for  $C_{18}H_{10}S_2$ : C, 74.45; H, 3.47; S, 22.08. Found: C, 74.53; H, 3.35; S, 21.98.

#### 1-(1-Dibenzothiényl)-2-(2-thienyl)ethene (28).

This compound was prepared from diethyl 1-dibenzothiénylphosphonate (25) (3.3 g, 0.01 mole) and thiophene-2-carboxaldehyde (2) (1.1 g, 0.01 mole) in a manner similar to the preparation of compound 26 and pale yellow flakes were obtained in 82% yield, mp 101-102°; nmr (deuteriochloroform):  $\delta$  6.91-7.48 (m, H-3', H-4', H-5' of thiophene, 2  $\times$  ethylene-H, H-2, H-3, H-7, H-8 of dibenzothiophene, 9H), 7.52-7.87 (m, H-4, H-6 of dibenzothiophene, 2H, ArH), 8.03-8.37 (m, H-9 of dibenzothiophene, 1H, ArH); ms: m/e 294 ( $M^+ + 2$ , 11), 293 ( $M^+ + 1$ , 24), 292 ( $M^+$ , 100).

Anal. Calcd. for  $C_{18}H_{12}S_2$ : C, 73.93; H, 4.14; S, 21.93. Found: C, 73.96; H, 4.18; S, 21.82.

#### Benzo[1,2-b:4,3-e']bisbenzo[b]thiophene (29).

Compound 29 was prepared from 1-(dibenzothiényl)-2-(2-thienyl)ethene (28) (1.0 g, 0.0034 mole) and iodine (0.1 g) in a manner similar to the preparation of compound 27. An analytical sample was chromatographed on a neutral alumina column using hexane:benzene (2:1) as the eluent affording colorless flakes in 78% yield, mp 172-173°; nmr (deuteriochloroform):  $\delta$  7.16 (d, J = 2 Hz, H-2, 1H, ArH), 7.33-7.68 (m, H-3, H-8, H-9, 3H, ArH), 7.74-8.27 (m, H-4, H-7, H-12, 3H, ArH), 8.32 (d, J = 8 Hz, H-5, 1H, ArH), 8.67-9.03 (m, H-10, H-11, 2H, ArH); ms: m/e 290 ( $M^+$ , 100).

Anal. Calcd. for  $C_{18}H_{10}S_2$ : C, 74.45; H, 3.47; S, 22.08. Found: C, 74.32; H, 3.30; S, 21.82.

#### Diethyl 4-Dibenzothiénylphosphonate (33).

A mixture of 4-bromomethylthiophene (32) (10 g, 0.036 mole) [31] and triethyl phosphite (6 g, 0.036 mole) was heated to 160° for 10 hours giving, upon distillation colorless oil (79% yield); nmr (deuteriochloroform):  $\delta$  1.01 (t, J = 6 Hz, -O-CH<sub>2</sub>-CH<sub>3</sub>, 6H), 3.58 (d, J = 8 Hz, CH<sub>2</sub>-P, 2H), 3.68 (d, J = 2 Hz, -O-CH<sub>2</sub>-CH<sub>3</sub>, 4H), 7.00-7.47 (m, H-2, H-3, H-7, H-8, 4H, ArH), 7.53-7.74 (m, H-6, 1H, ArH), 7.90-8.35 (m, H-1, H-9, 2H, ArH).

Anal. Calcd. for  $C_{17}H_{15}O_3PS$ : C, 61.07; H, 5.73; S, 9.59. Found: C, 60.89; H, 5.62; S, 9.38.

#### 1-(4-Dibenzothiényl)-2-(3-thienyl)ethene (35).

##### Method A.

Compound 35 was synthesized from diethyl 4-dibenzothiénylphosphonate (33) (3.3 g, 0.01 mole) and thiophene-3-carboxaldehyde (7) (1.1 g, 0.01 mole) in a manner similar to the preparation of 1-(1-dibenzothiényl)-2-(3-thienyl)ethene (26) and colorless prisms were obtained in 62% yield, mp 119-120°.

##### Method B.

This compound was prepared via the condensation of dibenzothiophene-4-carboxaldehyde (34) (20 g, 0.01 mole) [32] and diethyl 3-thienylphosphonate (8) (2.3 g, 0.01 mole) [12] in a manner similar to the preparation of compound 26 and colorless prisms were obtained in 76% yield; mp 119-120°; nmr (deuteriochloroform):  $\delta$  7.11-7.60 (m, H-2', H-4', H-5' of thiophene, 2  $\times$  ethylene-H, H-2, H-3, H-7, H-8 of dibenzothiophene, 9H), 7.52-7.88 (m, H-6 of dibenzothiophene, 1H, ArH), 7.91-8.28 (m, H-1, H-9 of dibenzothiophene, 2H, ArH); ms: m/e 292 ( $M^+$ , 100).

Anal. Calcd. for  $C_{18}H_{12}S_2$ : C, 73.93; H, 4.14; S, 21.93. Found: C, 74.11; H, 4.08; S, 21.85.

#### Benzo[2,1-b:3,4-g']bisbenzo[b]thiophene (36).

Compound 36 was prepared from 35 (1.0 g, 0.0034 mole) and iodine (0.10 g) in a manner similar to the preparation of compound 27. Purification was done by column chromatography on a neutral alumina column using hexane:benzene (2:1) as the eluent affording colorless crystals (62% yield), mp 229°; nmr (deuteriochloroform):  $\delta$  7.17-7.80 (m, H-1, H-2,

H-5, H-6, H-7, H-8, H-12, 7H, ArH), 7.82-8.40 (m, H-4, H-9, H-11, 3H, ArH); ms: m/e 290 ( $M^+$ , 100).

Anal. Calcd. for  $C_{18}H_{10}S_2$ : C, 74.45; H, 3.47; S, 22.08. Found: C, 74.38; H, 3.53; S, 22.38.

#### 1-(4-Dibenzothiényl)-2-(2-thienyl)ethene (37).

##### Method A.

Compound 37 was prepared from dibenzothiophene-4-carboxaldehyde (34) (3.0 g, 0.013 mole) [32] and diethyl 2-thienylphosphonate (3) (2.5 g, 0.012 mole) [2] in a manner similar to the preparation of compound 26 and pale yellow flakes were obtained in 79% yield, mp 139-140°.

##### Method B.

This compound was prepared via the Wadsworth-Emmons method from diethyl 4-dibenzothiénylphosphonate (33) (3.3 g, 0.01 mole) and thiophene-2-carboxaldehyde (2) (1.1 g, 0.01 mole) in a manner similar to the preparation of compound 26 and pale yellow flakes (71% yield) were obtained, mp 139-140°; nmr (deuteriochloroform):  $\delta$  6.89-7.64 (m, H-3', H-4', H-5' of thiophene, 2  $\times$  ethylene-H, H-2, H-3, H-7, H-8 of dibenzothiophene, 9H), 8.70-9.21 (m, H-1, H-6, H-9 of dibenzothiophene, 3H, ArH); ms: m/e 293 ( $M^+ + 1$ , 10), 292 ( $M^+$ , 100).

Anal. Calcd. for  $C_{18}H_{12}S_2$ : C, 73.93; H, 4.14; S, 21.93. Found: C, 74.03; H, 4.09; S, 21.83.

#### Benzo[2,1-b:4,3-e']bisbenzo[b]thiophene (38).

Photocyclization of compound 37 (1.0 g, 0.0034 mole) and iodine (0.1 g) in a manner similar to the preparation of benzo[1,2-b:3,4-g']bisbenzo[b]thiophene (27) gave colorless crystals 20 in 75% yield, mp 290-291°; nmr (deuteriochloroform):  $\delta$  7.14-7.50 (m, H-2, H-3, H-7, H-8, 4H, ArH), 7.51-8.34 (m, H-4, H-5, H-6, H-9, H-11, H-12, 6H, ArH); ms: m/e 291 ( $M^+ + 1$ , 20), 290 ( $M^+$ , 100).

Anal. Calcd. for  $C_{18}H_{10}S_2$ : C, 74.45; H, 3.47; S, 22.08. Found: C, 74.43; H, 3.39; S, 22.05.

#### 1-(2-Dibenzothiényl)-2-(3-thienyl)ethene (40).

Compound 40 was prepared from the condensation of diethyl 3-thienylphosphonate (8) (3.0 g, 0.013 mole) [12] and dibenzothiophene-2-carboxaldehyde (39) (2.8 g, 0.013 mole) [34] in a manner similar to the preparation of compound 26 and pale yellow crystals were obtained (68%), mp 181-182°; nmr (deuteriochloroform):  $\delta$  6.98-7.99 (m, H-3, H-4, H-6, H-7, H-8, H-9 of dibenzothiophene, H-2', H-4', H-5' of thiophene, 2  $\times$  ethylene-H, 11H), 8.21 (s, H-1 of dibenzothiophene, 1H, ArH); ms: m/e 294 ( $M^+ + 2$ , 12), 293 ( $M^+ + 1$ , 26), 292 ( $M^+$ , 100), 291 (46).

Anal. Calcd. for  $C_{18}H_{12}S_2$ : C, 73.93; H, 4.14; S, 21.93. Found: C, 74.06; H, 4.01; S, 22.30.

Benzo[1,2-b:4,3-g']bisbenzo[b]thiophene (41) and Benzo[1,2-b:4,5-g']bisbenzo[b]thiophene (42).

Compounds 41 and 42 were obtained from compound 40 (1.2 g, 0.005 mole) in a manner similar to the preparation of compound 27. The residue was chromatographed on a neutral alumina column. Compound 41 eluted first using hexane as the eluent. The second fraction consisted of a mixture of compounds 41 and 42. A second column chromatography (basic alumina) was used to separate the second fraction. Compound 41 again eluted first in pure form from pentane followed by elution of pure 42 also using pentane as the eluent. The total yield of compound 41 from the two column chromatography was 47% and for compound 42 the total yield was 19%.

##### Compound 41.

Compound 41 eluted first and was obtained as colorless needles (47%), mp 137-138°; nmr (deuteriochloroform):  $\delta$  7.21-7.58 (m, H-2, H-3, H-10, H-11, 4H, ArH), 7.62-8.10 (m, H-4, H-5, H-6, H-7, H-9, 5H, ArH), 8.48-8.73 (m, H-12, 1H, ArH); ms: m/e 290 ( $M^+$ , 100).

Anal. Calcd. for  $C_{18}H_{10}S_2$ : C, 74.45; H, 3.47; S, 22.08. Found: C, 74.48; H, 3.58; S, 22.21.

## Compound 42.

Compound 42 eluted last and was obtained as silver flakes in 19% yield, mp 298-299°; nmr (deuteriochloroform):  $\delta$  7.00-8.04 m, H-2, H-3, H-4, H-5, H-7, H-8, H-9, 7H, ArH), 8.19 (s, H-6, 1H, ArH), 8.17-8.32 (m, H-10, 1H, ArH), 9.13 (s, H-12, 1H, ArH); ms: m/e 290 (M<sup>+</sup>, 100).

Anal. Calcd. for C<sub>18</sub>H<sub>10</sub>S<sub>2</sub>: C, 74.45; H, 3.47; S, 22.08. Found: C, 74.31; H, 3.45; S, 21.87.

## 1-(2-Dibenzothiényl)-2-(2-thienyl)ethene (43).

Compound 43 was prepared from diethyl 2-thienylphosphonate (3) (3.0 g, 0.013 mole) [2] and dibenzothiophene-2-carboxaldehyde (39) (2.5 g, 0.012 mole) [34] in a manner similar to the preparation of compound 26 and colorless crystals were obtained (88%), mp 193-194°; nmr (deuteriochloroform):  $\delta$  7.00-8.01 (m, H-3, H-4, H-6, H-7, H-8, H-9 of dibenzothiophene, H-3', H-4', H-5' of thiophene, 2 × ethenyl-H, 11H), 8.18 (s, H-1 of dibenzothiophene, 1H, ArH); ms: m/e 294 (M<sup>+</sup>+2, 11), 293 (M<sup>+</sup>+1, 24), 292 (M<sup>+</sup>, 100), 291 (41), 290 (27).

Anal. Calcd. for C<sub>18</sub>H<sub>12</sub>S<sub>2</sub>: C, 73.93; H, 4.14; S, 21.93. Found: C, 73.88; H, 4.10; S, 21.87.

## Benzo[1,2-b:3,4-e']bisbenzo[b]thiophene (44) and Benzo[1,2-b:5,4-e']bisbenzo[b]thiophene (45).

Compounds 44 and 45 were obtained from compound 43 (1.5 g, 0.005 mole) in a manner similar to the preparation of compound 27 and colorless crystals were obtained. Compound 44 eluted first in pure form from a neutral alumina column using hexane as the eluent. The second fraction consisted of a mixture of compounds 44 and 45 which were separated via a second column chromatography (basic alumina) using pentane as the eluent. The first fraction consisted of pure 44 followed by pure 45 as the second fraction. The overall yield of 44 from the two column chromatography was 65% and for 45 the total yield was 20%.

## Compound 44.

Compound 44 eluted first and it was obtained as colorless needles in 65% yield (0.96 g), mp 128-129°; nmr (deuteriochloroform):  $\delta$  7.13-7.59 (m, H-2, H-10, H-11, 3H, ArH), 7.63-8.07 (m, H-4, H-5, H-6, H-7, H-9, 5H, ArH), 8.35 (d, J = 6 Hz, H-1, 1H, ArH), 8.51-8.91 (m, H-12, 1H, ArH); ms: m/e 290 (M<sup>+</sup>, 100).

Anal. Calcd. for C<sub>18</sub>H<sub>10</sub>S<sub>2</sub>: C, 74.45; H, 3.47; S, 22.08. Found: C, 74.57; H, 3.34; S, 22.10.

## Compound 45.

This compound eluted last and it was obtained as silver flakes in 20% yield (0.3 g), mp 281-282°; nmr (deuteriochloroform):  $\delta$  7.13-7.70 (m, H-2, H-4, H-5, H-8, H-9, 5H, ArH), 7.75-8.26 (m, H-7, H-10, 2H, ArH), 7.91 (s, H-6, 1H, ArH), 8.82 (d, J = 6 Hz, H-1, 1H, ArH), 8.91 (s, H-12, 1H, ArH); ms: m/e 290 (M<sup>+</sup>, 100).

Anal. Calcd. for C<sub>18</sub>H<sub>10</sub>S<sub>2</sub>: C, 74.45; H, 3.47; S, 22.08. Found: C, 74.39; H, 3.57; S, 21.93.

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