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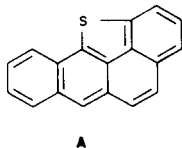
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The synthesis of the potentially mutagenic 1-methyl- (**11**), 3-methyl- (**12**), 4-methyl- (**21**), 5-methyl- (**27**), 7-methyl- (**58**), 8-methyl- (**61**), 9-methyl- (**59**) and 10-methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**60**) is reported.

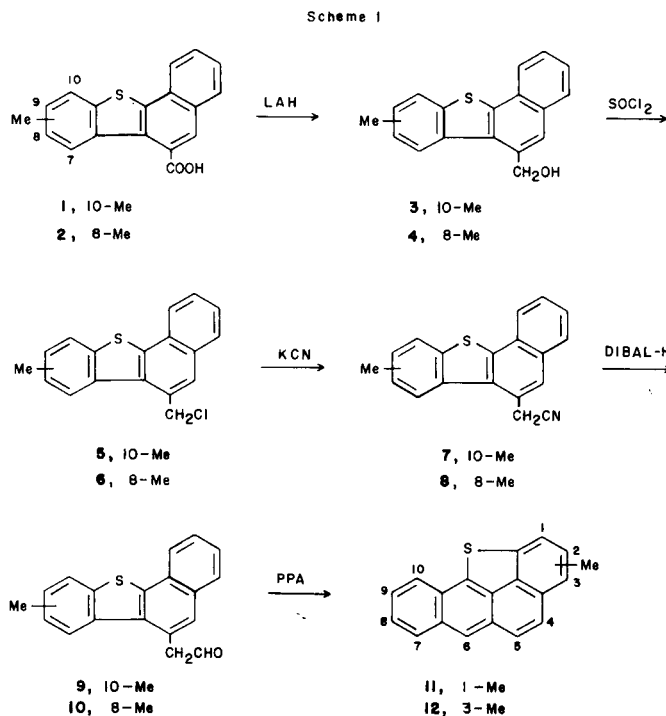
J. Heterocyclic Chem., **20**, 1453 (1983).

The mutagenic activity of benzo[2,3]phenanthro[4,5-*bcd*]thiophene (**A**) [4,5] prompted us to initiate a program to provide the monomethylbenzo[2,3]phenanthro[4,5-*bcd*]thiophenes so that they could be tested for mutagenic activity and also to determine their presence in coal



liquids and related coal-derived products. This is a continuation of our synthetic program to provide standard samples of polycyclic thiophenes and their derivatives [6-23].

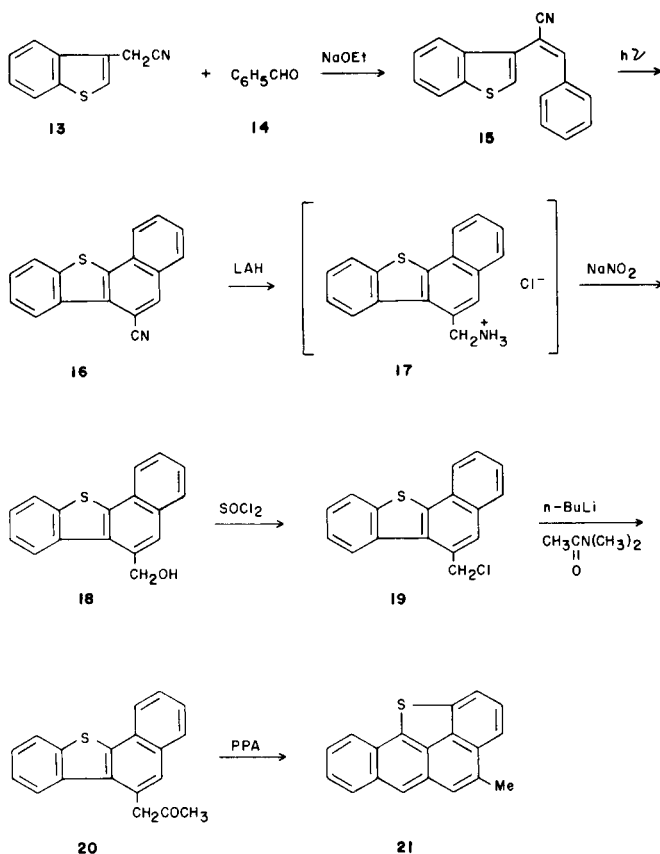
For the synthesis of 1-methyl- (**11**) and 3-methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**12**), 10-methyl- (**1**) [14] and 8-methylbenzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic acid (**2**) [14] served as the starting materials, respectively. Lithium aluminum hydride (LAH) reduction of **1** or **2** gave 6-hydroxymethyl-10-methyl- (**3**) (92% yield) or 6-hydroxymethyl-8-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**4**) (84% yield), respectively. The action of thionyl chloride on **3** or **4** gave 6-chloromethyl-10-methyl- (**5**) (83% yield) or 6-chloromethyl-8-methylbenzo[*b*]naphtho[2,1-*b*]thiophene (**6**) in 79% yield, respectively. Cyanation of **5** or **6** produced 6-cyanomethyl-10-methyl- (**7**) (72% yield) or 6-cyanomethyl-8-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**8**) in 78% yield, respectively. When **7** or **8** was allowed to react with diisobutylaluminum hydride (DIBAL-H), aldehydes **9** (70% yield) or **10** (69% yield) were obtained respectively. Cyclization of **9** or **10** with polyphosphoric acid (PPA) produced 1-methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**11**) (65% yield) or 3-methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**12**) (68% yield), respectively (Scheme I).



4-Methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene has been synthesized in six steps from 3-cyanomethylbenzo[*b*]thiophene (**13**) [24] and benzaldehyde [14]. When **13** and **14** were allowed to condense in the presence of sodium ethoxide as the base, 2-(3-benzo[*b*]thienyl)-3-phenylpropenenitrile (**15**) was obtained in 92% yield. Photocyclization of **15** gave 6-cyanobenzo[*b*]naphtho[2,1-*d*]thiophene (**16**) in 90% yield. Reduction of **16** with LAH followed by treatment with hydrochloric acid gave the crystalline amine hydrochloride **17** in 90% yield (purified). Diazotization of **17** gave 6-hydroxymethylbenzo[*b*]naphtho[2,1-*d*]thiophene (**18**) in 68% yield. When **18** was allowed to react with thionyl chloride, 6-chloromethylbenzo[*b*]naphtho[2,1-*d*]thiophene (**19**) was obtained in 91% yield. Lithiation of

19 followed by treatment of the lithio derivative with *N,N*-dimethylacetamide produced the ketone **20** in 70% yield as a pale yellow oil which was cyclized (PPA) directly into 4-methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**21**) in 67% yield (Scheme II).

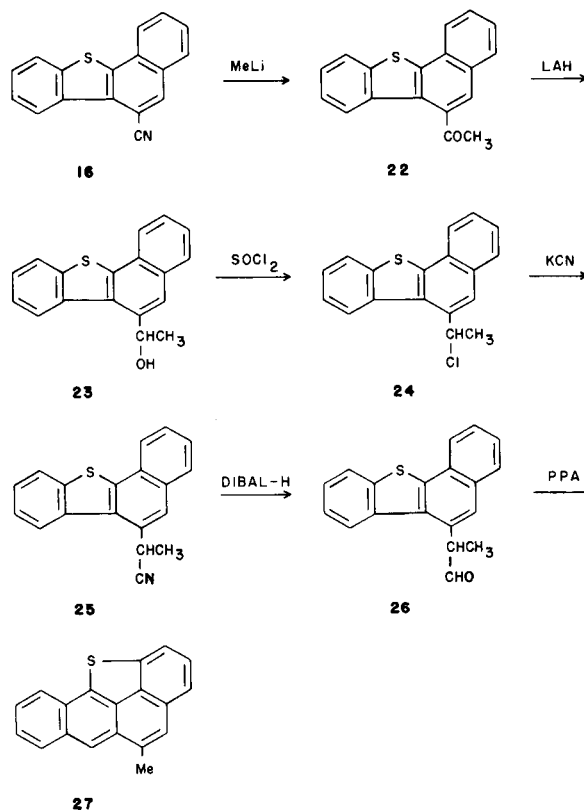
Scheme II



5-Methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**27**) was synthesized in six steps from 6-cyanobenzo[*b*]naphtho[2,1-*d*]thiophene (**16**) which was prepared as described above (Scheme II). When **16** was allowed to react with methyl lithium, 6-acetylbenzo[*b*]naphtho[2,1-*d*]thiophene (**22**) was obtained in 72% yield. Reduction (LAH) of **22** gave the alcohol **23** in 85% yield. Treatment of **23** with thionyl chloride gave the chloro compound **24** in 82% yield. Cyanation of **24** produced 2-(6-benzo[*b*]naphtho[2,1-*d*]thienyl)propanitrile (**25**) in 70% yield. The reaction of **25** with DIBAL-H gave the aldehyde **26** in 62% yield which was directly cyclized (PPA) into 6-methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene in 62% yield (Scheme III).

The synthesis of the 7-, 8-, 9- and 10-methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophenes was accomplished in seven steps from 3-cyanomethylbenzo[*b*]thiophene (**13**) and the three isomeric *o*-, *p*- and *m*-methylbenzaldehydes **28**, **29** and **30**. When **13** was allowed to react with **28**, **29** or **30** the product in each instance was 2-(3-benzo[*b*]thienyl)-3-(*o*-

Scheme III

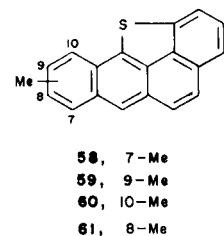
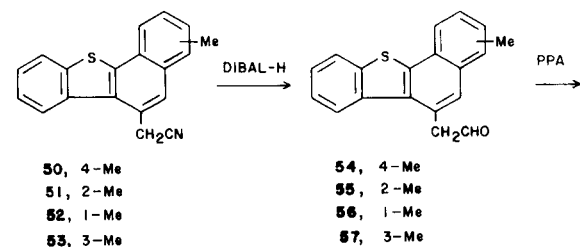
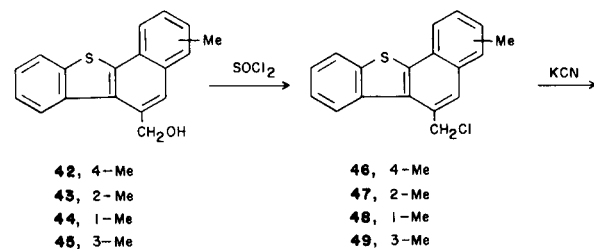
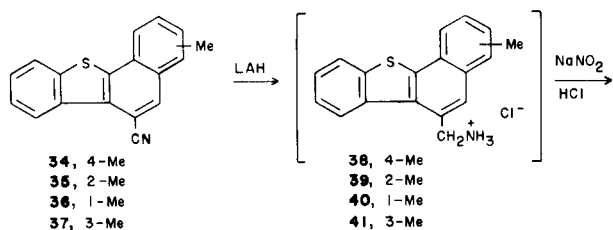
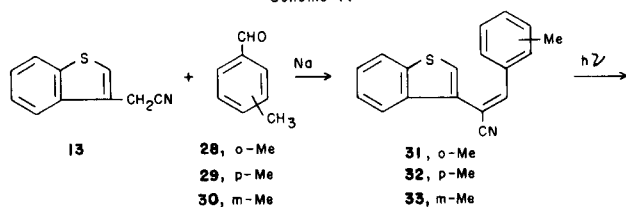


tolyl)propenenitrile (**31**) (93% yield), 2-(3-benzo[*b*]thienyl)-3-(*p*-tolyl)propenenitrile (**32**) (90% yield) and 2-(3-benzo[*b*]thienyl)-3-(*m*-tolyl)propenenitrile (**33**) (94% yield), respectively. Photocyclization of **31** or **32** gave 6-cyano-4-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**34**) (71% yield) or 6-cyano-2-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**35**) (74% yield), respectively. Photocyclization of **33** gave a mixture of 6-cyano-1-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**36**) and 6-cyano-3-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**37**). Compounds **36** and **37** were not separated, however the ratio was 2:5 for **36** and **37**, respectively, as estimated from the methyl peak in the nmr spectrum. The combined yield was 68%. Reduction (LAH) of **34** or **35** gave the crystalline amine hydrochlorides **38** (88% yield) or **39** (82% yield), respectively which were immediately diazotized to give 6-hydroxymethyl-4-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**42**) (69% yield) or 6-hydroxymethyl-2-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**43**) (67% yield), respectively. The mixture of **36** and **37** was reduced (LAH) followed by treatment with hydrochloric acid to give a mixture of the crystalline amine hydrochlorides **40** and **41** (87% combined yield) immediately followed by diazotization of the mixture which gave a combined yield of 74% of 6-hydroxymethyl-1-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**44**) and 6-hydroxymethyl-3-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**45**). Treatment of **42** or **43** with thionyl chloride

gave 6-chloromethyl-4-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**46**) (82% yield) or 6-chloromethyl-2-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**47**) (76% yield), respectively. When the mixture of **44** and **45** (ratio 2:5) was allowed to react with thionyl chloride, a mixture of 6-chloromethyl-1-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**48**) and 6-chloromethyl-3-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**49**) was obtained in a combined yield of 81%. Cyanation of **46** or **47** gave 6-cyanomethyl-4-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**50**) (69% yield) or 6-cyanomethyl-2-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**51**) (80% yield),

respectively. The mixture of **48** and **49** was cyanated to give a combined yield of 78% of 6-cyanomethyl-1-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**52**) and 6-cyanomethyl-3-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**53**). When **50**, **51** or the mixture of **52** and **53** were allowed to react with DIBAL-H, the individual aldehydes **54** (65% yield) and **55** (62% yield) as well as the mixture of aldehydes **56** and **57** (60% combined yield) were obtained in the respective instances. Cyclization (PPA) of either **54** or **55** gave 7-methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**58**) (60% yield) or 9-methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**59**) (65% yield), respectively. When the mixture of aldehydes **56** and **57** was allowed to cyclize (PPA), a chromatographically separable mixture of **60** and **61** was obtained. 10-Methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**60**) (21% yield) was obtained upon basic alumina chromatography using hexane as the eluent. Further elution of the basic alumina with hexane-benzene (1:1) gave 8-methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**61**) in 48% yield (Scheme IV).

Scheme IV



EXPERIMENTAL

Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. The ¹H-nmr spectra were obtained on a Varian EM 360A spectrometer. Mass spectra were obtained on a Hewlett Packard model 5980A spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

6-Hydroxymethyl-10-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**3**).

A solution of **1** (2.0 g, 6.8 mmoles) [14] in 100 ml of dry tetrahydrofuran was added dropwise to a suspension of lithium aluminum hydride (0.6 g, 15.8 mmoles) in 50 ml of dry tetrahydrofuran. After refluxing at room temperature for 3 hours, the reaction mixture was carefully quenched by cautiously adding 30 ml of water and enough 20% aqueous hydrochloric acid to dissolve the inorganic salts. The reaction mixture was poured into ice-water and the precipitate was collected by filtration. The product was recrystallized from methanol to give 1.75 g (92%) of tan needles, mp 193-194°; ir (potassium bromide): 3410 cm⁻¹ (OH); nmr (deuteriochloroform): δ 2.85 (s, CH₃, 3H), 5.25 (s, CH₂OH, 2H), 7.18-8.00 (m, H-1, H-2, H-3, H-4, H-7, H-8, H-9, 7H, ArH), 7.73 (s, H-5, 1H, ArH); ms: m/e 279 (M⁺+1, 20), 278 (M⁺, 100), 261 (19), 249 (44), 234 (80).

Anal. Calcd. for C₁₈H₁₄OS: C, 77.67; H, 5.07; S, 11.52. Found: C, 77.47; H, 4.99; S, 11.49.

6-Hydroxymethyl-8-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**4**).

This compound was prepared from compound **2** [14] in a similar manner to the preparation of compound **3** and colorless crystals (84%) were obtained, mp 144-145°; ir (potassium bromide): 3400 cm⁻¹ (OH); nmr (deuteriochloroform): δ 2.48 (s, CH₃, 3H), 5.23 (s, CH₂OH, 2H), 7.17-7.97 (m, H-1, H-2, H-3, H-4, H-7, H-9, 6H, ArH), 7.68 (s, H-5, 1H, ArH), 8.08 (s, H-10, 1H, ArH); ms: m/e 278 (M⁺, 100), 249 (29), 245 (22), 234 (42).

Anal. Calcd. for C₁₈H₁₄OS: C, 77.67; H, 5.07; S, 11.52. Found: C, 77.79; H, 5.35; S, 11.28.

6-Chloromethyl-10-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**5**).

A mixture of **3** (0.85 g, 3.1 mmoles), thionyl chloride (1.5 ml) and dry benzene was refluxed for two hours. After removal of benzene and excess thionyl chloride, the residue was recrystallized from hexane to give 0.75 g of colorless crystals (83%), mp 176-177°; nmr (deuteriochloroform): δ 2.84 (s, CH₃, 3H), 5.26 (s, CH₂Cl, 2H), 7.16-7.98 (m, H-1, H-2, H-3, H-4, H-7, H-8, H-9, 7H, ArH), 7.74 (s, H-5, 1H, ArH); ms: m/e 298 (M⁺+2, 22),

297 ($M^+ + 1$, 12), 296 (M^+ , 100), 262 (21), 261 (100), 259 (10), 258 (11), 245 (14).

Anal. Calcd. for $C_{18}H_{13}ClS$: C, 72.84; H, 4.41; S, 10.80. Found: C, 72.79; H, 4.34; S, 10.70.

6-Chloromethyl-8-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (6).

This compound was prepared from **4** in a manner similar to the preparation of compound **5** and colorless crystals (79%) were obtained, mp 183-184°; nmr (deuteriochloroform): δ 2.47 (s, CH_3 , 3H), 5.25 (s, CH_2Cl , 2H), 7.14-7.93 (m, H-1, H-2, H-3, H-4, H-7, H-9, 6H, *ArH*), 7.67 (s, H-5, 1H, *ArH*), 8.00 (s, H-10, 1H, *ArH*); ms: *m/e* 298 ($M^+ + 2$, 28), 296 (M^+ , 72), 262 (21), 261 (100).

Anal. Calcd. for $C_{18}H_{13}ClS$: C, 72.84; H, 4.41; S, 10.80. Found: C, 72.60; H, 4.52; S, 10.69.

6-Cyanomethyl-10-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (7).

A mixture of **5** (0.89 g, 3 mmoles), sodium cyanide (2.0 g, 41 mmoles), water (1 ml) and DMSO (20 ml) was stirred at 40° for 6 hours. The reaction mixture was poured into 200 ml of ice-water and extracted with benzene. The benzene layer was dried over anhydrous sodium sulfate and evaporated giving a brown solid. The residue was chromatographed on a neutral alumina column using hexane as the eluent affording compound **5** (15%) and using cyclohexane as the eluent gave compound **7** in 72% yield. This compound was recrystallized from methanol to give colorless needles, mp 182-183°; ir (potassium bromide): 2210 cm^{-1} ($C \equiv N$); nmr (deuteriochloroform): δ 2.82 (s, CH_3 , 3H), 4.38 (s, CH_2CN , 2H), 7.19-8.02 (m, 8H, *ArH*); ms: *m/e* 288 ($M^+ + 1$, 23), 287 (M^+ , 100), 286 (32), 245 (7).

Anal. Calcd. for $C_{19}H_{13}NS$: C, 79.41; H, 4.56; S, 11.16; N, 4.87. Found: C, 79.60; H, 4.51; S, 11.01; N, 4.88.

6-Cyanomethyl-8-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (8).

This compound was prepared from compound **6** in a manner similar to the preparation of compound **7** and colorless needles (78%) were obtained, mp 206-207°; ir (potassium bromide): 2200 cm^{-1} ($C \equiv N$); nmr (deuteriochloroform): δ 2.56 (s, CH_3 , 3H), 4.38 (s, CH_2CN , 2H), 7.21-8.23 (m, 8H, *ArH*); ms: *m/e* 289 ($M^+ + 2$, 7), 288 ($M^+ + 1$, 22), 287 (M^+ , 100), 286 (32), 258 (11).

Anal. Calcd. for $C_{19}H_{13}NS$: C, 79.41; H, 4.56; S, 11.16. Found: C, 79.14; H, 4.64; S, 11.31.

1-Methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (11).

Diisobutylaluminum hydride (25% solution in toluene, 1.5 mmoles) was added *via* a syringe to a solution of **7** (0.4 g, 1.4 mmoles) in dry benzene (15 ml) under a nitrogen atmosphere. The mixture was stirred at room temperature for 2.5 hours. Aqueous 10% hydrochloric acid was added and then the reaction mixture was stirred for 1.5 hours. The organic layer was separated and the aqueous layer was extracted twice with 40 ml of chloroform. The organic layer and extracts were combined, washed with water, dried over anhydrous sodium sulfate and evaporated *in vacuo* affording an oil (70%). The aldehyde **9** was used in the next reaction without further purification.

A mixture of the crude aldehyde **9** and 10 g of polyphosphoric acid was heated at 100-120° for 2 hours with continuous stirring. After cooling the reaction mixture was poured into 200 ml of ice-water and extracted twice with benzene. The combined extracts were washed with water, dried over sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on a silica gel column using hexane as the eluent giving yellow needles (65%), mp 164-166°. An analytical sample was recrystallized from hexane to give pale yellow needles, mp 172°; nmr (deuteriochloroform): δ 2.54 (s, CH_3 , 3H), 7.11-8.39 (m, 9H, *ArH*); ms: *m/e* 273 ($M^+ + 1$, 21), 272 (M^+ , 100), 271 (54), 269 (11).

Anal. Calcd. for $C_{19}H_{12}S$: C, 83.79; H, 4.44; S, 11.77. Found: C, 83.78; H, 4.65; S, 11.55.

3-Methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (12).

Compound **10** was prepared from compound **8** in a similar manner to the preparation of compound **9**. The crude aldehyde was obtained as an

oil in 69% yield and used without further purification.

Compound **12** was prepared from the crude aldehyde **10** in a manner similar to the preparation of compound **11** and yellow crystals (68%) were obtained. An analytical sample was prepared by column chromatography (silica gel) using hexane as the eluent and pale yellow needles were obtained, mp 154-155°; nmr (deuteriochloroform): δ 2.78 (s, CH_3 , 3H), 7.18-8.48 (m, 9H, *ArH*); ms: *m/e* 274 ($M^+ + 2$, 6), 273 ($M^+ + 1$, 23), 272 (M^+ , 100), 269 (11).

Anal. Calcd. for $C_{19}H_{12}S$: C, 83.79; H, 4.44; S, 11.77. Found: C, 84.01; H, 4.60; S, 11.56.

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

Compound **14** (29.4 g, 0.28 mole) was added slowly to a solution of compound **13** [24] (43 g, 0.25 mole), absolute ethanol (200 ml) and sodium ethoxide (prepared from sodium metal (5.8 g, 0.25 g-atom) and absolute ethanol (150 ml)). The reaction mixture was refluxed with stirring for 3 hours. After cooling, the product was poured into 10% cold aqueous hydrochloric acid, extracted twice with 150 ml of chloroform, dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on a silica gel column using cyclohexane:benzene (1:1) as the eluent affording pale yellow needles (92%), mp 105-106°; nmr (deuteriochloroform): δ 7.09-8.11 (m, *CH* and 11H of *ArH*); ms: *m/e* 263 ($M^+ + 2$, 6), 262 ($M^+ + 1$, 21), 261 (M^+ , 100), 260 (99), 259 (38), 234 (46).

Anal. Calcd. for $C_{17}H_{11}NS$: C, 78.13; H, 4.24; N, 5.36. Found: C, 77.95; H, 4.42; N, 5.16.

6-Cyanobenzo[*b*]naphtho[2,1-*d*]thiophene (16).

A solution of **15** (2.0 g, 7.7 mmoles), 0.05 g of iodine and 500 ml of dry benzene was irradiated for 8 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 a neutral alumina using benzene as the eluent giving colorless crystals (90%), mp 225-226°; nmr (deuteriochloroform): δ 7.25-8.06 (m, H-1, H-2, H-3, H-4, H-8, H-9, H-10, 7H, *ArH*), 8.16 (s, H-5, 1H, *ArH*), 8.72-9.07 (m, H-7, 1H, *ArH*); ms: *m/e* 261 ($M^+ + 2$, 6), 260 ($M^+ + 1$, 20), 259 (M^+ , 100), 214 (6).

Anal. Calcd. for $C_{17}H_9NS$: C, 78.74; H, 3.50; N, 5.40. Found: C, 78.60; H, 3.69; N, 5.26.

6-Hydroxymethylbenzo[*b*]naphtho[2,1-*d*]thiophene (18).

Lithium aluminum hydride (7.0 g, 0.18 mole) was slowly added *via* a spatula to a solution of compound **16** (10 g, 36.6 mmoles) in 200 ml of dry ether. The reaction mixture was stirred at room temperature for 5 hours and then cautiously quenched by adding 40 ml of ice-water. The reaction mixture was poured into 200 ml of cold 20% aqueous hydrochloric acid solution affording white crystals. The crystals were collected by filtration and recrystallized from methanol giving colorless crystals (90%). Compound **17**, which was not very stable, was dissolved in 200 ml of chloroform and a mixture of 300 ml of 10% hydrochloric acid and 1 g of aliquat 336 was slowly added. The reaction mixture was cooled to 0° with continuous stirring and sodium nitrite (10 g) in 50 ml of water was added over a period of 30 minutes. After stirring for five hours, the organic layer was separated, dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was recrystallized from hexane:benzene (1:1) to give the alcohol **18** (68%), mp 162-163°; nmr (deuteriochloroform): δ 2.43 (bs, CH_2OH , 1H), 5.03 (s, CH_2 , 2H), 7.23-8.32 (m, 9H, *ArH*); ms: *m/e* 279 ($M^+ + 1$, 6), 278 (M^+ , 21), 277 (100), 276 (45), 234 (38).

Anal. Calcd. for $C_{18}H_{14}OS$: C, 77.67; H, 5.07; S, 11.51. Found: C, 77.63; H, 5.07; S, 11.47.

6-Chloromethylbenzo[*b*]naphtho[2,1-*d*]thiophene (19).

This compound was prepared from compound **18** (7.0 g, 26.5 mmoles), thionyl chloride (10 ml) and dry benzene (100 ml) in a manner similar to the preparation of compound **5** and pale yellow crystals (81%) were obtained, mp 144-145°; nmr (deuteriochloroform): δ 5.21 (s, CH_2 , 2H), 7.28-8.52 (m, 9H, *ArH*); ms: *m/e* 284 ($M^+ + 2$, 21), 282 (M^+ , 57), 247 (100), 215 (20).

Anal. Calcd. for C₁₇H₁₁ClS: C, 72.20; H, 3.92; S, 11.34. Found: C, 72.05; H, 4.11; S, 11.59.

4-Methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (21).

n-Butyllithium (4.5 ml of 1.6 *M* solution in hexane) was added *via* a syringe over a period of 10 minutes to a dry mixture of **19** (1.2 g, 4.3 mmoles) and 50 ml of dry ether under nitrogen at -78°. The mixture was allowed to warm to -5° and then it was cooled to -78°, after which *N,N*-dimethylacetamide (0.41 g, 4.7 mmoles) was added slowly *via* a syringe. The mixture was allowed to warm slowly and was then stirred for six hours at room temperature. It was then poured into ice-water, the layers separated and extracted twice with 50 ml of ether. The organic layer was dried over magnesium sulfate and evaporated giving a pale yellow oil (70%); *ir* (neat): 1735 cm⁻¹ (C=O). The crude ketone was mixed with 15 g of PPA and heated to 100° for 90 minutes with continuous stirring. After cooling, the reaction mixture was poured into ice-water, extracted twice with 30 ml of benzene, dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on a silica gel column using hexane as the eluent giving pale yellow needles (67%), mp 157-158°; nmr (deuteriochloroform): δ 2.70 (s, CH₃, 3H), 7.18-8.37 (m, 9H, *ArH*); ms: *m/e* 273 (M⁺+1, 20), 272 (M⁺, 100), 271 (48), 269 (11).

Anal. Calcd. for C₁₉H₁₂S: C, 83.79; H, 4.44; S, 11.77. Found: C, 83.82; H, 4.43; S, 11.68.

6-Acetylbenzo[*b*]naphtho[2,1-*d*]thiophene (22).

Methylolithium (45 ml of 1.5 *M* in hexane) was added to a solution of **16** (14 g, 54.1 mmoles) and dry ether (250 ml) at 0° under nitrogen. After the addition, the mixture was allowed to stir at room temperature for five hours. The reaction mixture was poured into 10% hydrochloric acid solution, the organic layer was separated and the aqueous layer extracted twice with 100 ml of ether. The organic layer and extracts were combined, dried over anhydrous magnesium sulfate and evaporated *in vacuo*. The residue was chromatographed on a silica gel column using benzene as the eluent giving colorless crystals (72%), mp 96-98°. An analytical sample was prepared by recrystallization from hexane giving colorless crystals, mp 102-103°; nmr (deuteriochloroform): δ 2.58 (s, CH₃, 3H), 7.19-8.80 (m, 9H, *ArH*); ms: *m/e* 276 (M⁺, 100), 261 (96), 233 (83), 232 (31).

Anal. Calcd. for C₁₈H₁₂OS: C, 78.23; H, 4.38; O, 5.79. Found: C, 78.46; H, 4.56; O, 5.65.

6-(1-Hydroxyethyl)benzo[*b*]naphtho[2,1-*d*]thiophene (23).

Lithium aluminum hydride (10 g) was added *via* a spatula to a solution of compound **22** (8 g, 29 mmoles) and dry ether (200 ml). After the addition the reaction mixture was stirred at room temperature for four hours and cautiously quenched by adding 40 ml of ice-water. The mixture was then poured into ice-water and enough 20% aqueous hydrochloric acid solution was added to dissolve the inorganic salts. The organic layer was separated and the aqueous layer extracted twice with ether. The organic layer and extracts were combined, dried over anhydrous magnesium sulfate and evaporated. The residue was chromatographed on a silica gel column using benzene as the eluent giving a pale yellow oil (85%); nmr (deuteriochloroform): δ 1.42 (d, J = 8 Hz, CH₃, 3H), 3.94 (bs, OH, 1H), 5.48 (q, J = 6 Hz, CH-CH₃, 1H), 7.10-8.11 (m, 9H, *ArH*); ms: *m/e* 280 (M⁺+2, 5), 279 (M⁺+1, 15), 278 (M⁺, 74), 263 (21), 235 (100), 234 (63).

Anal. Calcd. for C₁₈H₁₄OS: C, 77.67; H, 5.07; S, 11.51. Found: C, 77.50; H, 5.12; S, 11.43.

6-(1-Chloroethyl)benzo[*b*]naphtho[2,1-*d*]thiophene (24).

This compound was prepared from **23** (4.0 g, 14.4 mmoles) and thionyl chloride (7.5 ml) in a manner similar to the preparation of compound **5** and colorless crystals (82%) were obtained, mp 207-208°; ms: *m/e* 298 (M⁺+2, 12), 297 (M⁺+1, 6), 296 (M⁺, 30), 261 (M⁺-35, 100), 260 (83), 259 (83), 258 (61).

Anal. Calcd. for C₁₈H₁₃ClS: C, 72.84; H, 4.41; S, 10.80. Found: C, 72.63; H, 4.58; S, 10.63.

2-(6-Benzo[*b*]naphtho[2,1-*d*]thienyl)propanenitrile (25).

This compound was prepared from **24** (3.0 g, 10 mmoles) and potas-

sium cyanide (8.5 g) in a manner similar to the preparation of compound **7** and a brown oil (70%) was obtained. An analytical sample was purified by column chromatography (neutral alumina) using benzene as the eluent affording a pale yellow oil; nmr (deuteriochloroform): δ 1.63 (d, J = 8 Hz, CH₃, 3H), 4.60 (q, J = 8 Hz, CH, 1H), 7.11-8.12 (m, 9H, *ArH*); ms: *m/e* 289 (M⁺+2, 7), 288 (M⁺+1, 23), 287 (M⁺, 100), 272 (38).

Anal. Calcd. for C₁₉H₁₃NS: C, 79.41; H, 4.56; S, 11.16. Found: C, 79.28; H, 4.70; S, 11.09.

6-Methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (27).

Compound **26** was prepared from **25** in a similar manner to the preparation of compound **9** and 72% of a tan oil was obtained. The crude aldehyde **26** was cyclized with PPA in a similar manner to the preparation of compound **11** and pale yellow crystals (62%) were obtained, mp 130-131°. An analytical sample was chromatographed on neutral alumina using cyclohexane:benzene as the eluent giving pale yellow needles, mp 136-137°; nmr (deuteriochloroform): δ 2.68 (s, CH₃, 3H), 7.11-8.40 (m, 9H, *ArH*); ms: *m/e* 272 (M⁺, 100), 271 (46), 259 (31), 258 (26).

Anal. Calcd. for C₁₉H₁₂S: C, 83.79; H, 4.44; S, 11.77. Found: C, 83.83; H, 4.38; S, 11.81.

2-(3-Benzo[*b*]thienyl)-3-(*o*-tolyl)propenenitrile (31).

This compound was prepared from **13** (26.5 g, 0.15 mole) [24] and **28** (18.8 g, 0.16 mole) in a manner similar to the preparation of compound **15** and yellow crystals (93%) were obtained, mp 145-146°; nmr (deuteriochloroform): δ 2.33 (s, CH₃, 3H), 7.15-8.21 (m, CH and *ArH*, 9H); ms: *m/e* 277 (M⁺+2, 4), 276 (M⁺+1, 13), 275 (M⁺, 57), 274 (21), 260 (100), 259 (34).

Anal. Calcd. for C₁₈H₁₁NS: C, 79.09; H, 4.06; S, 5.12. Found: C, 79.19; H, 4.21; S, 5.14.

2-(3-Benzo[*b*]thienyl)-3-(*p*-tolyl)propenenitrile (32).

This compound was prepared from compound **13** and **29** in a similar manner to the preparation of **15** and pale yellow crystals (90%) were obtained, mp 154-155°; nmr (deuteriochloroform): δ 2.32 (s, CH₃, 3H), 7.18-8.10 (m, CH and *ArH*, 9H); ms: *m/e* 277 (M⁺+2, 5), 276 (M⁺+1, 15), 275 (M⁺, 67), 274 (27), 260 (100), 259 (54).

Anal. Calcd. for C₁₈H₁₃NS: C, 78.51; H, 4.76; N, 5.09. Found: C, 78.71; H, 5.00; N, 4.81.

2-(3-Benzo[*b*]thienyl)-3-(*m*-tolyl)propenenitrile (33).

This compound was prepared from compound **13** [24] and **30** in a similar manner to the preparation of **15** and a yellow oil was obtained in 94% yield; nmr (deuteriochloroform): δ 2.39 (s, CH₃, 3H), 7.16-8.20 (m, CH and *ArH*, 9H); ms: *m/e* 277 (M⁺+2, 4), 276 (M⁺+1, 13), 275 (M⁺, 60), 274 (21), 260 (100), 259 (46), 248 (21).

Anal. Calcd. for C₁₈H₁₃NS: C, 78.51; H, 4.76; N, 5.09. Found: C, 78.38; H, 4.98; N, 4.93.

6-Cyano-4-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (34).

This compound was prepared from **31** (1.0 g, 3.6 mmoles) in a manner similar to the preparation of compound **16** and colorless crystals (71%) were obtained, mp 202-203°; nmr (deuteriochloroform): δ 2.73 (s, CH₃, 3H), 7.11-8.04 (m, H-1, H-2, H-3, H-8, H-9, H-10, 6H, *ArH*), 8.32 (s, H-5, 1H, *ArH*), 8.65-9.03 (m, H-7, 1H, *ArH*); ms: *m/e* 275 (M⁺+2, 7), 274 (M⁺+1, 22), 273 (M⁺, 100), 272 (33), 259 (11).

Anal. Calcd. for C₁₈H₁₁NS: C, 79.09; H, 4.06; N, 5.12. Found: C, 78.81; H, 4.09; N, 5.01.

6-Cyano-2-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (35).

This compound was prepared from compound **32** in a manner similar to the preparation of compound **16** and colorless crystals (74%) were obtained, mp 210-211°; nmr (deuteriochloroform): δ 2.56 (s, CH₃, 3H), 7.17 (s, H-1, 1H, *ArH*), 7.34-7.76 (m, H-3, H-4, H-8, H-9, H-10, 5H, *ArH*), 8.15 (s, H-5, 1H, *ArH*), 8.78-9.10 (m, H-7, 1H, *ArH*); ms: *m/e* 276 (M⁺+2, 6), 274 (M⁺+1, 21), 273 (M⁺, 100), 272 (31), 246 (7).

Anal. Calcd. for C₁₈H₁₁NS: C, 79.09; H, 4.06; N, 5.12. Found: C, 79.19; H, 4.21; N, 5.14.

6-Cyano-1-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**36**) and 6-Cyano-3-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**37**).

The mixture **36** and **37** was obtained from compound **33** in a manner similar to the preparation of compound **16**. Purification was accomplished on a neutral alumina column using hexane as the eluent and colorless crystals (68%) were obtained. The mp of the mixture was 138-142°; nmr (deuteriochloroform): δ 2.49 (s, CH₃ of **37**, 3H), 3.01 (s, CH₃ of **36**, 3H). From the nmr peak ratio we could determine the ratio of **36** and **37** which was 2:5, respectively.

Anal. Calcd. of the mixture, C₁₈H₁₁NS: C, 79.09; H, 4.06; N, 5.12. Found: C, 78.86; H, 4.32; N, 5.15.

6-Hydroxymethyl-4-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**42**).

Compound **38** was prepared from **34** in a manner similar to the preparation of **17** and unstable colorless crystals (88%) were obtained. Compound **42** was prepared from **38** in a similar manner to the preparation of **18** and colorless crystals (69%) were obtained, mp 149-150°; nmr (deuteriochloroform): δ 2.71 (s, CH₃, 3H), 5.19 (s, CH₂OH, 2H), 7.20-8.52 (m, 9H, ArH); ms: m/e 279 (M⁺ + 1, 6), 278 (M⁺, 23), 277 (100), 261 (45), 260 (52), 248 (43).

Anal. Calcd. for C₁₈H₁₄OS: C, 77.67; H, 5.07; S, 11.51. Found: C, 77.39; H, 5.21; S, 11.31.

6-Hydroxymethyl-2-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**43**).

Compound **39** was prepared from **35** in a manner similar to the preparation of compound **17** and unstable colorless crystals (82%) were obtained, mp 154-155°. Compound **43** was prepared from **39** in a manner similar to the preparation of compound **18** and colorless crystals (67%) were obtained, mp 185-186°; nmr (deuteriochloroform): δ 2.53 (s, CH₃, 3H), 5.17 (s, CH₂OH, 2H), 7.12-8.03 (m, H-3, H-4, H-8, H-9, H-10, 5H, ArH), 7.63 (s, H-1, 1H, ArH), 7.78 (s, H-5, 1H, ArH), 8.20-8.53 (m, H-7, 1H, ArH); ms: m/e 279 (M⁺ + 1, 6), 278 (M⁺, 21), 277 (100), 276 (45), 261 (43), 234 (38).

Anal. Calcd. for C₁₈H₁₄OS: C, 77.67; H, 5.07; S, 11.51. Found: C, 77.63; H, 5.07; S, 11.47.

6-Hydroxymethyl-1-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**44**) and 6-Hydroxymethyl-3-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**45**).

Compounds **40** and **41** were obtained from the mixture of **36** and **37** in a similar manner to the preparation of compound **17**. The combined yield was 87%. The unstable mixture was not separated at this stage. Compounds **44** and **45** were obtained from the mixture of **40** and **41** and colorless crystals were obtained (74%). The mp of the mixture was 160-165°; nmr (deuteriochloroform): δ 2.51 (s, CH₃ of **45**, 3H), 3.02 (s, CH₃ of **44**, 3H). From the nmr peak ratio we could determine the ratio of **44** and **45** which was 2:5, respectively.

Anal. Calcd. of the mixture **44** and **45**, C₁₈H₁₄OS: C, 77.67; H, 5.07; O, 5.75. Found: C, 77.78; H, 4.66; O, 5.69.

6-Chloromethyl-4-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**46**).

Compound **46** was obtained from **42** in a manner similar to the preparation of compound **5** and pale yellow crystals (82%) were obtained, mp 177-178°; nmr (deuteriochloroform): δ 2.78 (s, CH₃, 3H), 5.18 (s, CH₂Cl, 2H), 7.19-8.61 (m, H-1, H-2, H-3, H-8, H-9, H-10, 6H, ArH), 7.80 (s, H-5, 1H, ArH), 8.19-8.43 (m, H-7, 1H, ArH); ms: m/e 297 (M⁺, 12), 262 (22), 261 (100).

Anal. Calcd. for C₁₈H₁₃ClS: C, 72.84; H, 4.41; S, 10.80. Found: C, 72.68; H, 4.63; S, 11.01.

6-Chloromethyl-2-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**47**).

This compound was prepared from **43** in a manner similar to the preparation of compound **5** and pale yellow crystals (76%) were obtained, mp 185-186°; nmr (deuteriochloroform): δ 2.54 (s, CH₃, 3H), 5.26 (s, CH₂Cl, 2H), 7.13-8.01 (m, H-2, H-3, H-8, H-9, H-10, 5H, ArH), 7.63 (s, H-1, 1H, ArH), 7.78 (s, H-5, 1H, ArH), 8.25-8.45 (m, H-7, 1H, ArH); ms: m/e 297 (M⁺, 20), 296 (55), 262 (21), 261 (100).

Anal. Calcd. for C₁₈H₁₃ClS: C, 72.84; H, 4.41; S, 10.80. Found: C, 72.84; H, 4.67; S, 10.59.

6-Chloromethyl-1-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**48**) and 6-Chloromethyl-3-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**49**).

The mixture **48** and **49** was obtained from compounds **44** and **45** in a manner similar to the preparation of compound **5** and yellow crystals (81%) were obtained. The mp of the mixture was 178-183°; nmr (deuteriochloroform): δ 2.56 (s, CH₃ of **49**, 3H), 3.18 (s, CH₃ of **48**, 3H). From the nmr peak ratio we could determine the ratio of **48** and **49** which was 2:5, respectively.

Anal. Calcd. of the mixture **48** and **49**, C₁₈H₁₃ClS: C, 72.84; H, 4.41; S, 10.80. Found: C, 72.68; H, 4.53; S, 10.57.

6-Cyanomethyl-4-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**50**).

This compound was prepared from compound **46** in a manner similar to the preparation of compound **7** and pale yellow crystals (69%) were obtained, mp 188-189°; nmr (deuteriochloroform): δ 2.62 (s, CH₃, 3H), 4.21 (s, CH₂CN, 2H), 7.28-8.20 (m, H-1, H-2, H-3, H-8, H-9, H-10, 6H, ArH), 7.88 (s, H-5, 1H, ArH), 8.38-8.52 (m, H-7, 1H, ArH); ms: m/e 288 (M⁺ + 1, 23), 287 (M⁺, 100), 286 (27), 247 (10).

Anal. Calcd. for C₁₉H₁₃NS: C, 79.41; H, 4.56; N, 4.87. Found: C, 79.28; H, 4.68; N, 4.73.

6-Cyanomethyl-2-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**51**).

This compound was prepared from compound **47** in a manner similar to the preparation of compound **7** and pale yellow crystals (80%) were obtained, mp 179-180°; nmr (deuteriochloroform): δ 2.49 (s, CH₃, 3H), 4.02 (s, CH₂CN, 2H), 7.17-7.99 (m, H-3, H-4, H-8, H-9, H-10, 5H, ArH), 7.56 (s, H-1, 1H, ArH), 7.70 (s, H-5, 1H, ArH), 8.13-8.42 (m, H-7, 1H, ArH); ms: m/e 287 (M⁺, 100), 286 (31), 245 (7).

Anal. Calcd. for C₁₉H₁₃NS: C, 79.41; H, 4.56; N, 4.87. Found: C, 79.39; H, 4.58; N, 4.72.

6-Cyanomethyl-1-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**52**) and 6-Cyanomethyl-3-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**53**).

Compounds **52** and **53** were obtained from the mixture **48** and **49** and yellow crystals (78%) were obtained. The mp of the mixture was 149-155°. The mixture was not separated at this stage.

Anal. Calcd. for compounds **52** and **53**, C₁₉H₁₃NS: C, 79.41; H, 4.56; N, 4.87. Found: C, 79.53; H, 4.81; N, 4.62.

7-Methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**58**).

Compound **54** was obtained from compound **50** in a manner similar to the preparation of compound **9** and a tan oil (65%) was obtained. Compound **58** was prepared from the crude aldehyde **54** in a manner similar to the preparation of compound **11** and pale yellow needles were obtained (60%), mp 167-168°; nmr (deuteriochloroform): δ 2.88 (s, CH₃, 3H), 7.07-8.35 (m, 9H, ArH); ms: m/e 273 (M⁺ + 1, 20), 272 (M⁺, 100), 271 (36), 248 (31).

Anal. Calcd. for C₁₉H₁₂S: C, 83.79; H, 4.44; S, 11.77. Found: C, 83.69; H, 4.52; S, 11.79.

9-Methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**59**).

Compound **55** was prepared from compound **51** in a manner similar to the preparation of compound **9** and a tan oil (62%) was obtained. Compound **59** was prepared from crude **55** in a manner similar to the preparation of compound **11** and pale yellow needles (65%) were obtained; mp 174-175°; nmr (deuteriochloroform): δ 2.54 (s, CH₃, 3H), 7.13-8.30 (m, 9H, ArH); ms: m/e 272 (M⁺, 100), 271 (30), 269 (11).

Anal. Calcd. for C₁₉H₁₂S: C, 83.79; H, 4.44; S, 11.77. Found: C, 83.59; H, 4.38; S, 11.77.

10-Methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**60**) and 8-Methylbenzo[2,3]phenanthro[4,5-*bcd*]thiophene (**61**).

Compounds **56** and **57** were obtained from the mixture **52** and **53** in a manner similar to the preparation of compound **9** and a tan oil (60%) was obtained. Compounds **60** and **61** were obtained from the mixture of crude aldehydes **56** and **57** in a manner similar to the preparation of compound **11** and a pale yellow oil was obtained. The mixture was separated by column chromatography (basic alumina) using hexane and ben-

zene as the eluent. Compound **60** eluted first (hexane) and it was obtained as pale yellow needles (21%), mp 165-166°; nmr (deuteriochloroform): δ 2.85 (s, CH₃, 3H), 7.12-8.30 (m, 9H, ArH); ms: m/e 272 (M⁺, 100). Compound **61** eluted last (hexane:benzene (1:1)) and it was obtained as pale yellow needles (48%), mp 174-175°; nmr (deuteriochloroform): δ 2.30 (s, CH₃, 3H), 7.15-8.30 (m, 9H, ArH); ms: m/e 272 (M⁺, 100).

Anal. Calcd. for **60**, C₁₉H₁₂S: C, 83.79; H, 4.44; S, 11.77. Found: C, 83.78; H, 4.30; S, 11.58.

Anal. Calcd. for **61**, C₁₉H₁₂S: C, 83.79; H, 4.44; S, 11.77. Found: C, 83.95; H, 4.56; S, 11.82.

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