

## Synthesis and Characterization of Isomeric $\alpha,\alpha'$ -Bithienyls with $\beta$ -Methylsulfanyl Substituents

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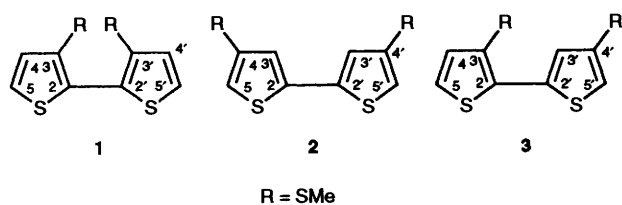
The three isomeric bithienyls, **1**, **2** and **3**, formally related to the dimerization of 3-(methylsulfanyl)-thiophene, have been synthesized by the metal-catalysed coupling between a metallated and a halogenated derivative of thiophene of suitable structure. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are discussed.

Conducting polymers of 3-substituted thiophenes are usually soluble, stable and processable.<sup>1</sup> The precursors of these polymers (monomers, dimers and oligomers) may also be used as model compounds for the structural characterization of the polymers, and the oligomers, in particular, may have independent applications in various fields (e.g. components for molecular electronic;<sup>2-5</sup> optical devices<sup>6</sup>).

Poly(3-alkylthiophenes) and their related oligomers have been extensively investigated<sup>7-20</sup> and a number of heteroatom-functionalized on the side chain of poly(3-alkylthiophenes) are known.<sup>21-23</sup>

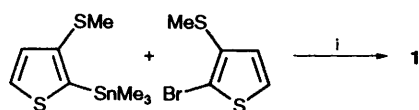
Less attention has been paid to derivatives of 3-(alkylsulfanyl)thiophene, both oligomers and polymers. Polymers of 3-(ethylsulfanyl) and 3,4-bis(ethylsulfanyl)thiophene have been synthesized and characterized.<sup>24,25</sup> An unsatisfactory attempt to polymerize 3'-SR substituted 2,2':5',2''-terthiophenes (R = long alkyl chain) has been reported<sup>26</sup> and, recently, patents claiming the potential pesticide activity of (alkylsulfanyl)-thiophenes have appeared.<sup>27,28</sup>

This paper reports the synthesis and the characterization of 3,3'-bis(methylsulfanyl)-2,2'-bithiophene **1**, 4,4'-bis(methylsulfanyl)-2,2'-bithiophene **2** and 3,4'-bis(methylsulfanyl)-2,2'-bithiophene **3**, dimers which, as found with poly(3-alkylthiophenes),<sup>7,9</sup> may be better starting materials than monomers for the synthesis of stereoregular polymers. Furthermore, thiophene dimers and oligomers may be valuable tools for the assignment of the regiochemistry of the polymer backbone.<sup>9,10</sup>



### Results and Discussion

**Synthesis.**—The bithienyl **1** was obtained (78% yield of isolated product) by coupling 2-bromo-3-(methylsulfanyl)-thiophene with 3-methylsulfanyl-2-(trimethylstannyl)thiophene in refluxing toluene in the presence of  $[\text{PdCl}_2(\text{PPh}_3)_2]$  as catalyst (Scheme 1).

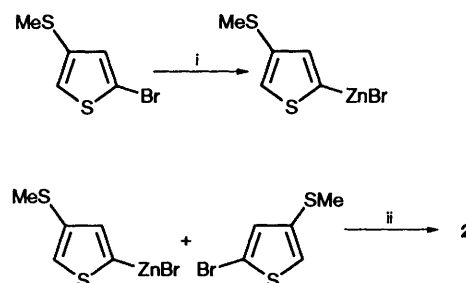


**Scheme 1** Reagents and conditions: i,  $[\text{PdCl}_2(\text{PPh}_3)_2]$  cat., toluene, 20 h reflux (78%)

This catalyst has been successfully used<sup>29-31</sup> for cross-coupling between trialkylstannyl derivatives and halogeno

compounds in boiling THF. In the present case, however, the reaction in boiling THF was very slow, better results being obtained in toluene, probably because of its higher b.p. It should also be mentioned that  $[\text{Pd}(\text{PPh}_3)_4]$  in boiling toluene or xylene is a catalyst currently used<sup>10,32,33</sup> for this type of coupling.

The bithienyl **2** was isolated in equally good yield (77%) by coupling 2-bromo-4-(methylsulfanyl)thiophene with 4-methylsulfanyl-2-thienylzinc bromide obtained from 2-bromo-4-(methylsulfanyl)thiophene by direct metallation with a highly reactive form of zinc ( $\text{Zn}^*$ , from zinc dichloride by reduction with lithium naphthalenide).<sup>34</sup> This coupling occurred in THF at room temperature (RT) in the presence of a nickel(II) complex as catalyst (Scheme 2), and can be considered an extension of a known methodology<sup>35</sup> for the synthesis of biaryls.

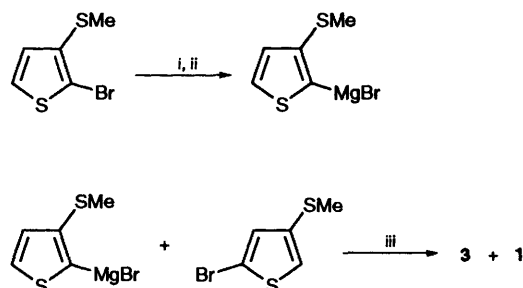


**Scheme 2** Reagents and conditions: i,  $\text{Zn}^*$ , THF, 2 h, RT; ii,  $[\text{Ni}(\text{dppp})\text{Cl}_2]$  cat., THF, 15 h, RT (77%)

The synthesis of **2**, via an organomagnesium instead of an organozinc derivative, has been recently described in two patents (66%).<sup>27,28</sup>

Metal-catalysed cross-coupling between an organometallic and a halogenoorganic compound having a different or an isomeric organic structure, as required for the synthesis of the dimer **3**, is usually accompanied<sup>36</sup> by variable amounts of homocoupling by-products (due, for example, to an exchange of functionalities between the reagents, a process which could also be catalysed by the coupling catalyst through the reversibility of some steps of the catalytic cycle). Several methods were tried for the selective production of the dimer **3**, but none of them was completely satisfactory: the method used for the synthesis of **1** [coupling 3-methylsulfanyl-2-(trimethylstannyl)thiophene with 2-bromo-4-(methylsulfanyl)thiophene] yielded (84%) a liquid mixture of the three possible dimers (**3**, 74%; **2**, 16%; **1**, 10%; by  $^1\text{H}$  NMR analysis). The dimer **3** could not be isolated in a pure state from this mixture, since the dimers **3** and **2** had identical chromatographic behaviour whether in normal or reversed-phase. The method used for the synthesis of **2** [coupling 3-methylsulfanyl-2-thienylzinc bromide with 2-bromo-4-(methyl-

sulfanyl)thiophene] yielded (46%) an inseparable mixture of the dimers **3** (60%) and **2** (40%); a third method,<sup>37,38</sup> namely, the nickel-catalysed coupling of the Grignard reagent obtained from 2-bromo-3-(methylsulfanyl)thiophene (through lithiation followed by cation exchange with MgBr<sub>2</sub>) with 2-bromo-4-(methylsulfanyl)thiophene, afforded a crude product containing the dimer **3** and minor amounts of the dimer **1**, from which it was possible to isolate pure **3** by column chromatography (Scheme 3).



**Scheme 3** Reagents and conditions: i, BuLi, hexane-Et<sub>2</sub>O, -78 °C; ii, MgBr<sub>2</sub>·Et<sub>2</sub>O, -30 to 0 °C; iii, [Ni(dppp)Cl<sub>2</sub>] cat., Et<sub>2</sub>O, 20 h reflux (45%); **3**: **1** (90:10)

**NMR Spectroscopic Structural Assignment.**—<sup>1</sup>H and <sup>13</sup>C NMR chemical shifts for the derivatives **1–3** [and of 3-(methylsulfanyl)thiophene **4** for comparison] are reported in Table 1.\* The <sup>1</sup>H spectrum of derivative **1** shows the characteristic pattern of a 2,3-disubstituted thiophene ring: two doublets at 7.05 and at 7.36 ppm are present in the aromatic region with a coupling constant of 5.3 Hz. The unambiguous assignment of the two proton signals together with the directly-bonded carbon signals was achieved through the <sup>1</sup>J(H,C) value, which is higher for 5-H, C-5 (~190 Hz) and lower for 4-H, C-4 (~170 Hz) in thiophenes.<sup>39</sup> These coupling constants were measured from an inverse detected <sup>1</sup>H, <sup>13</sup>C undecoupled chemical-shift correlation spectrum obtained through the heteronuclear multiple-quantum coherence (HMQC) technique.<sup>40</sup> The aromatic region of the <sup>1</sup>H spectrum of derivative **2** presents two doublets with a coupling constant of 1.5 Hz, characteristic of a 2,4-disubstituted thiophene ring.

In derivative **3** the two types of thiophene rings are clearly recognized from the proton-proton coupling constant values (5.3 and 1.5 Hz for the 2,3- and the 2,4-disubstituted ring, respectively). The assignment of <sup>1</sup>H and of <sup>13</sup>C signals of protonated carbons of **2** and **3** was achieved through the HMQC technique as described above. Quaternary carbons were assigned through inverse detected <sup>1</sup>H, <sup>13</sup>C heteronuclear multiple-bond correlation experiments (HMBC)<sup>41</sup> based on the evolution of <sup>n</sup>J(H,C) coupling constants. The results confirmed the α,α'-regiochemistry of the three dimers. The presence of a long-range coupling constant between SMe protons and the thiophene carbon bearing the methylsulfanyl substituent enables the assignment of each SMe substituent to the corresponding ring to be made unambiguously in derivative **3**. This long-range coupling constant was measured in 3-(methylsulfanyl)thiophene **4** (<sup>3</sup>J 4.3 Hz) and this value was employed to set the evolution delay in HMBC experiments. Cross-peaks between SMe protons and the thiophene carbon bearing the methylsulfanyl substituent were found in all HMBC spectra of derivatives **1–3**.

\* The chemical shifts in Table 1 are arranged in such a manner that analogy between directly comparable positions in the various thienyl structures becomes immediately apparent.

**Table 1** <sup>1</sup>H and <sup>13</sup>C chemical shifts<sup>a</sup> (ppm) of derivatives **1–3** and of 3-(methylsulfanyl)thiophene **4**<sup>b</sup>

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
2-H				6.95
4-H	7.05		7.00	6.97
5-H	7.36		7.17	7.30
3-SMe	2.38		2.43	2.45
3'-H		7.02	7.20	
5'-H		6.82	6.92	
4'-SMe		2.45	2.46	
C-2	130.17		132.82	119.47
C-3	133.65		130.16	134.17
C-4	129.24		130.41	128.06
C-5	126.28		123.88	126.22
3-SMe	18.59		18.68	17.69
C-2'		137.52	136.28	
C-3'		124.70	126.69	
C-4'		135.04	134.31	
C-5'		118.55	119.75	
4'-SMe		17.51	17.57	

<sup>a</sup> δ Values are referred to internal Me<sub>4</sub>Si. <sup>b</sup> δ Values of aromatic carbons are in accordance with H. Lumbroso, J. Curé, C. Mahatsekake and C. G. Andrieu, *J. Mol. Struct.*, 1990, **216**, 315.

Inspection of Table 1 shows that chemical shifts are regiochemically dependent, in particular the 3'-H, SMe carbon and protons and 2,2' quaternary carbon chemical shifts. In fact, the 3'-H in the head-to-tail dimer **3** is the more deshielded β-proton. The second thiophene ring slightly shields the proton signal of a SMe group which is adjacent to the α,α'-connection (3-SMe in **1** and **3**) and deshields the corresponding carbon of about 1 ppm. The more shielded 2,2' quaternary carbons are found in the head-to-head dimer **1** and the more deshielded ones in the tail-to-tail dimer **2**. An intermediate situation is present in **3**. These parameters can be useful for the regiochemical characterization of higher oligomers and polymers.

## Experimental

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 400.13 and 100.61 MHz, respectively, on 0.1 mol dm<sup>-3</sup> solutions in CDCl<sub>3</sub>. Chemical shifts, in ppm, refer to internal Me<sub>4</sub>Si. Coupling constants are given in Hz. UV spectra were collected on a Varian CARY 3 spectrometer.

All the reactions involving use or formation of organometallic compounds were performed in Ar atmosphere in flame-dried apparatus. The diethyl ether and THF solvents were distilled from sodium diphenyl ketyl prior to use.

3-(Methylsulfanyl)thiophene **4**,<sup>42,43</sup> 2-bromo-3-(methylsulfanyl)thiophene<sup>44</sup> and 2,5-dibromo-3-(methylsulfanyl)thiophene<sup>44</sup> were prepared according to methods described in the literature.

**2-Bromo-4-(methylsulfanyl)thiophene.**—It has been reported<sup>44</sup> that 2-bromo-3-(methylsulfanyl)thiophene, by lithiation with lithium diisopropylamide (LDA) in the presence of catalytic amounts of 2,5-dibromo-3-(methylsulfanyl)thiophene (formed *in situ* or externally added), completely isomerizes into 2-bromo-4-(methylsulfanyl)thiophene after acidic quenching. However, the following procedure, patterned after this report, yielded a mixture containing ca. 80% of isomerized product, which was then obtained in a pure form by chromatographic techniques, since fractional distillation was inefficient in removing the by-products. Butyllithium in hexane (1.6 mol dm<sup>-3</sup>; 21 cm<sup>3</sup>, 33.6 mmol) and then a solution of diisopropylamine (freshly distilled from KOH, 3.6 g, 35.6 mmol) in THF (20 cm<sup>3</sup>) were stirred into THF (30 cm<sup>3</sup>), which had previously been cooled to -70 °C and was maintained at a temperature of

< -60 °C. To this LDA solution was slowly added (45 min) a THF solution (50 cm<sup>3</sup>) of 2-bromo-3-(methylsulfanyl)thiophene (5 g, 23.9 mmol) and then rapidly a THF solution (4 cm<sup>3</sup>) of 2,5-dibromo-3-(methylsulfanyl)thiophene (1 g, 3.5 mmol) at -70 °C. After being stirred at -70 °C for 1 h, the reaction was quenched by addition of 0.1 mol dm<sup>-3</sup> HCl to the mixture. The organic phase was separated and the aqueous phase extracted with ether. The combined organic phases were washed with water, dried (MgSO<sub>4</sub>), and evaporated and the residue was fractionally distilled at reduced pressure to afford an oil (4.5 g, 89%), b.p. 92 °C/2.5 mmHg, containing the desired product (80%, by <sup>1</sup>H NMR analysis), 2-bromo-3-(methylsulfanyl)thiophene (main impurity) and 2,5-dibromo-3-(methylsulfanyl)thiophene (traces). Purification was achieved by flash chromatography<sup>45</sup> on silica gel (230–400 mesh), with light petroleum (b.p. 40–70 °C) as eluent, followed by distillation: b.p. 89 °C/2.5 mmHg; *n*<sub>D</sub><sup>25</sup> 1.6395; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 2.41 (3 H, s, SMe), 6.84 (1 H, d, *J*<sub>3,5</sub> 1.7, 5-H) and 6.92 (1 H, d, *J*<sub>3,5</sub> 1.7, 3-H).

**3-Methylsulfanyl-2-(trimethylstannyl)thiophene.**—Butyllithium in hexane (1.6 mol dm<sup>-3</sup>; 25 cm<sup>3</sup>, 40 mmol) was stirred drop by drop into a diethyl ether solution (100 cm<sup>3</sup>) of 2-bromo-3-(methylsulfanyl)thiophene (8.37 g, 40 mmol) which had previously been cooled to -78 °C and was maintained at a temperature < -70 °C. After the mixture had been stirred for 15 min at -78 °C a diethyl ether solution (34 cm<sup>3</sup>) of trimethyltin chloride (8.37 g, 42 mmol) was added dropwise (15 min) at a temperature < -70 °C. After being stirred at -70 °C for 30 min, the reaction mixture was allowed to reach room temperature, at which point it was poured onto crushed ice and diluted with water. The organic phase was separated and the aqueous phase extracted with ether. The combined organic phases were washed with saturated brine, dried (MgSO<sub>4</sub>), and evaporated. The residue upon fractional distillation afforded a stable colourless oil (10.88 g, 93%), b.p. 72–74 °C/0.1 mmHg; *n*<sub>D</sub><sup>25</sup> 1.5825; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 0.41 [9 H, s with <sup>117</sup>Sn and <sup>119</sup>Sn satellites, <sup>2</sup>*J*(<sup>119</sup>Sn, Me) 58.3; <sup>2</sup>*J*(<sup>117</sup>Sn, Me) 55.6, SnMe<sub>3</sub>], 2.40 (3 H, s, SMe), 7.24 (1 H, d, *J*<sub>4,5</sub> 5.0, 4-H) and 7.58 (1 H, d, *J*<sub>4,5</sub> 5.0, 5-H).

**3,3'-Bis(methylsulfanyl)-2,2'-bithiophene 1.**—2-Bromo-3-(methylsulfanyl)thiophene (2.59 g, 12.4 mmol) and 3-methylsulfanyl-2-(trimethylstannyl)thiophene (3.64 g, 12.4 mmol) were refluxed in dry toluene (40 cm<sup>3</sup>) under an Ar atmosphere in the presence of [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.44 g, 0.62 mmol). After 20 h under reflux the reagents were practically undetectable on TLC (SiO<sub>2</sub>, light petroleum–diethyl ether 20:5) and the solution, initially yellow, was now red. The reaction mixture was cooled, washed with water, dried (MgSO<sub>4</sub>), and evaporated and the residue distilled in a short-path apparatus at reduced pressure. An initial low-boiling fraction (mainly Me<sub>3</sub>SnBr) was followed by an oily product, which readily solidified (2.5 g, 78%), b.p. 133 °C/0.1 mmHg, m.p. 50–55 °C. Crystallization from cyclohexane (12 cm<sup>3</sup>) yielded white crystals (2.0 g), m.p. 53–55 °C (Found: C, 46.4; H, 3.9; S, 49.1. C<sub>10</sub>H<sub>10</sub>S<sub>4</sub> requires C, 46.5; H, 3.9; S, 49.6%); λ<sub>max</sub>(CHCl<sub>3</sub>)/nm 279 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 1520) and 325sh (850); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 2.38 (3 H, s, SMe), 7.05 (1 H, d, *J*<sub>4,5</sub> 5.3, 4-H) and 7.36 (1 H, d, *J*<sub>4,5</sub> 5.3, 5-H).

**4,4'-Bis(methylsulfanyl)-2,2'-bithiophene 2.**—Finely cut lithium (0.14 g, 20 mmol) was added under a stream of Ar to a solution of naphthalene (2.86 g, 21 mmol) in THF (10 cm<sup>3</sup>) and the suspension was stirred for 2 h at room temperature (the metal was slowly consumed to afford a dark-green solution of lithium naphthalenide). In a second reaction vessel, dry<sup>46</sup> ZnCl<sub>2</sub> (1.36 g, 10 mmol) under a stream of Ar was fused for a few minutes and then after being allowed to cool was dissolved

in THF (10 cm<sup>3</sup>). The solution obtained was added dropwise *via* a cannula to the lithium naphthalenide solution (a precipitate of activated Zn is formed). After the mixture had been stirred for 15 min at room temperature, a solution of 2-bromo-4-(methylsulfanyl)thiophene (1.046 g, 5 mmol) in THF (4 cm<sup>3</sup>) was introduced with a syringe (slightly exothermic reaction) and the suspension was stirred for 2 h at 25–30 °C to complete the formation of the organozinc bromide. The solution was left for 3 h to allow the excess of Zn to settle. The supernatant solution was then carefully transferred *via* a cannula to a third reaction vessel containing a solution of 2-bromo-4-(methylsulfanyl)thiophene (1.046 g, 5 mmol) and [Ni(dppp)Cl<sub>2</sub>] (0.136 g, 0.25 mmol) in THF (10 cm<sup>3</sup>). After being stirred overnight at room temperature the reaction mixture was poured into saturated aqueous NH<sub>4</sub>Cl and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extract was dried (MgSO<sub>4</sub>) and evaporated and the residue was distilled *in vacuo* in a short-path apparatus. Initially the naphthalene sublimed and this was followed by an oily compound, which readily solidified\* (0.99 g, 77%); b.p. 151–154 °C/0.1 mmHg; m.p. 101–103 °C. Slow crystallization of this from isopropyl ether (15 cm<sup>3</sup>) afforded white crystals (0.59 g), m.p. 102–103 °C, one of which was selected for X-ray diffraction analysis<sup>47</sup> (Found: C, 46.7; H, 3.9; S, 50.2. C<sub>10</sub>H<sub>10</sub>S<sub>4</sub> requires C, 46.5; H, 3.9; S, 49.6%); λ<sub>max</sub>(CHCl<sub>3</sub>)/nm 265 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 2790) and 327 (1480); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 2.45 (3 H, s, SMe), 6.82 (1 H, d, *J*<sub>3,5</sub> 1.5, 5-H) and 7.02 (1 H, d, *J*<sub>3,5</sub> 1.5, 3-H).

**3,4'-Bis(methylsulfanyl)-2,2'-bithiophene 3.**—Butyllithium in hexane (1.3 mol dm<sup>-3</sup>; 4.6 cm<sup>3</sup>, 6 mmol) was stirred dropwise into a solution of 2-bromo-3-(methylsulfanyl)thiophene (1.25 g, 6 mmol) in diethyl ether (10 cm<sup>3</sup>) at -78 °C. The temperature of the reaction mixture was raised to -30 °C when a mixture of MgBr<sub>2</sub> and diethyl ether, freshly prepared as described below, was added with vigorous stirring at a temperature of between -30 and -20 °C during addition; the mixture was stirred then for a further 30 min at 0 °C. The MgBr<sub>2</sub> and diethyl ether mixture was prepared<sup>48</sup> by dropwise addition of 1,2-dibromoethane (1.34 g, 7.2 mmol) to Mg turnings (0.35 g, 14.4 mmol) in diethyl ether (5 cm<sup>3</sup>) at reflux temperature during addition. After a further 30 min, the oily underlayer of MgBr<sub>2</sub>·Et<sub>2</sub>O and the supernatant layer of diethyl ether were then transferred *via* a cannula to the solution of the lithium derivative, the excess of Mg being discarded. The ether solution of Grignard reagent obtained at this point was slowly added (30 min) *via* a cannula to a solution of 2-bromo-4-(methylsulfanyl)thiophene (1.05 g, 5 mmol) and [Ni(dppp)Cl<sub>2</sub>] (0.068 g, 0.125 mmol) in diethyl ether (3 cm<sup>3</sup>) with cooling in an ice-bath. After 20 h under reflux, the reaction mixture was hydrolysed by addition to aqueous HCl (2 mol dm<sup>-3</sup>; 20 cm<sup>3</sup>) and diethyl ether in a separatory funnel. The aqueous layer was separated and extracted with ether and the combined ether solutions were washed with aqueous NaHCO<sub>3</sub> and water, dried (MgSO<sub>4</sub>) and evaporated. The residue was short-path distilled to yield an oily product (0.58 g, 45%), b.p. 145–152 °C/0.1 mmHg, as a mixture of isomers **3** (90%) and **1** (10%). Purification of isomer **3** was achieved by column chromatography (SiO<sub>2</sub>, light petroleum) followed by distillation to provide an oily product (0.36 g), b.p. 148–151 °C/0.1 mmHg; λ<sub>max</sub>(CHCl<sub>3</sub>)/nm 265 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 1620) and 331 (1460); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 2.43 (3 H, s, 3-SMe), 2.46 (3 H, s, 4'-SMe), 6.92 (1 H, d, *J*<sub>3,5</sub> 1.5, 5'-H), 7.00 (1 H, d, *J*<sub>4,5</sub> 5.3, 4-H), 7.17 (1 H, d, *J*<sub>4,5</sub> 5.3, 5-H) and 7.20 (1 H, d, *J*<sub>3,5</sub> 1.5, 3'-H).

\* Since, in diethyl ether, compound **2** is almost insoluble while naphthalene is readily soluble, an alternative isolation method, avoiding the distillation process, is to triturate the residue in diethyl ether and then decant or filter the suspension.

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