

# Synthesis of Mixed Thiophene/Furan Oligomers by Stille Coupling

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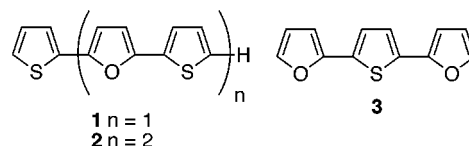
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Received June 16, 1998

A series of mixed thiophene/furan oligomers have been synthesized *via* organometallic Stille coupling. In some cases, beside cross-coupling products, symmetrical coupling products were isolated. Oligomers consisting of up to 11 rings were obtained. Attempts to prepare macrocycles with 10 thiophene and furan units were not successful.

## Introduction

Polymers and copolymers based on pyrrole, furan, and especially thiophene have been under investigation for some years. They possess interesting electrical, optical, and electrochemical properties and are promising materials for field-effect transistors and many other potential applications.<sup>1,2</sup> It has been found that the band gap of polyheterocycles decreases linearly with the amount of quinoid structure the polymer can assume upon doping. Thus, variation of the heteroatom allows control of the electronic and mechanical properties of the polymer.<sup>3,4</sup> Due to controlled chain and conjugation length, and the higher regularity and homogeneity of the chain structure without mislinkages and cross-linkings, oligomers can reach or exceed the properties of polymers. Furthermore, oligomers are used as model compounds to study and predict the properties of the corresponding polymer.<sup>5–7</sup> It is therefore surprising that despite the interest in this field of chemistry, almost no efforts have been undertaken to synthesize higher mixed thiophene/furan oligomers. The integration of furan units should enhance the solubility of the oligomers compared to their thiophene analogues, which is important for potential applications. Until now, not many mixed thiophene/furan oligomers have been made. As far as we are aware, beside 2-(thien-2-yl)furan<sup>8</sup> and a few thiophene/furan oligomers with four and five rings containing one furan unit, only compounds **1–3** are known.<sup>9–12</sup> The difuryl thiophene **3** is the only known compound with furan rings at both ends of the chain. The dithienyl furan **1**, as well as the difuryl thiophene **3**, exhibit high phototoxic activity.<sup>12</sup>



Here we describe a general synthetic route to a series of new mixed thiophene/furan heteropolyaromatic compounds. The coupling of an aldehyde and the Mannich base of an acetyl thiophene/furan has been conveniently used for the synthesis of mixed oligomers with up to five rings.<sup>9,11</sup> Although the buildup of higher oligomers by this method is conceivable, this route was not pursued due to expected low overall yields. We chose instead the versatile Stille coupling<sup>13</sup> which is widely used for the carbon–carbon bond formation between a organic halide and an organostannane.

## Results and Discussion

The required starting materials used in this study are prepared as follows. The trialkylstannyl-substituted compounds were synthesized by lithiation/stannylation of the corresponding heterocycles with *n*-BuLi and trialkylstannyl chloride in excellent yields (>90%) and were used without further purification. The known oligomers SOS **1** and SOSOS **2** were obtained according to literature procedures via Stetter reaction of thiophene-2-aldehyde or thiophene-2,5-dialdehyde and 3-(dimethylamino)-1-thien-2-ylpropanone and cyclization of the resulting di- and tetraketone, respectively, with acetic anhydride.<sup>9,11</sup> Bromination of SOS with 1 equiv of NBS resulted in the formation of a mixture of mono- and dibromo SOS and starting material from which **4** could be isolated in 60% yield. Bromination of SOS **1** with 2 equiv of NBS afforded dibromo SOS **5** in 80% yield. The diiodo compound **6** was prepared by lithiation/iodination of **2** with *n*-BuLi and iodine.

The first target compound was the five-ring heterocycle **10**, which was made by Stille coupling of bis(trimethylstannyl) SOS **7** and 2-iodofuran **8** in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>. An analogous procedure, coupling dibromo SOS **5** with 2-(trimethylstannyl)furan **9a**, afforded **10** in a comparable yield (≈50%). As side reactions, the self-coupling of the tin compound **7**, as well of the bromo compound **5**, took place, which led to the isolation of the

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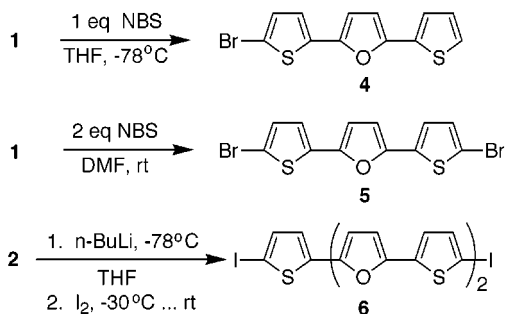
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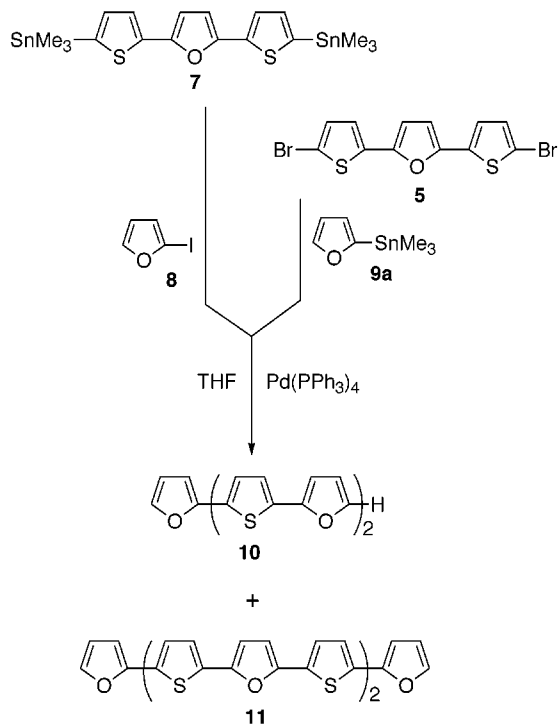
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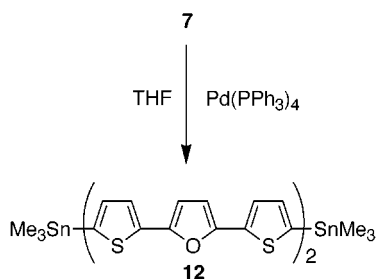
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poorly soluble oligomer **11**. The "dimerization" of the tin compound obviously proceeds faster (24% yield **11**) than the dimerization of the dibromo SOS (10% yield **11**).



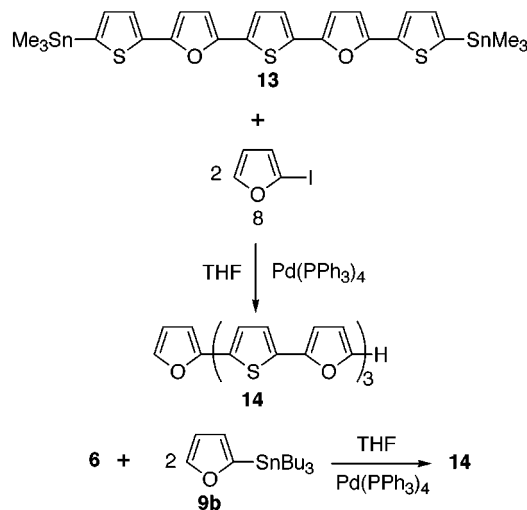
The self-coupling of the bis(trimethylstannyl) SOS also could be achieved by refluxing a solution of **7** with Pd(PPh<sub>3</sub>)<sub>4</sub> in THF. After 5 days, workup gave, besides unreacted **7**, an impure product, which consisted mainly of the dimer **12**. Despite signals of impurities, both <sup>1</sup>H and <sup>13</sup>C NMR indicate clearly the formation of **12**. The observed impurities are probably caused by the presence of monotrimethylstannyl-substituted SOS–SOS or unsubstituted SOS–SOS. The MS shows the easy cleavage of the tin residue: 787 (M<sup>+</sup>, 1%), 625 (M<sup>+</sup> – SnMe<sub>3</sub>, 5%) and 462 (SOS–SOS<sup>+</sup>, basepeak).



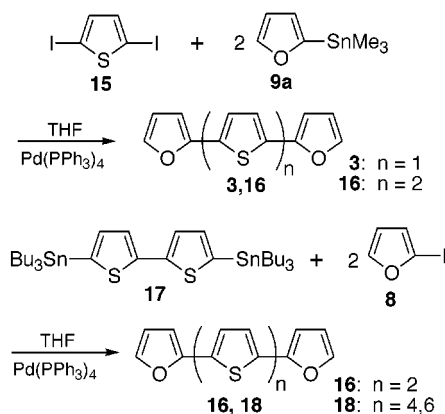
No dimerization was observed by refluxing a solution of **7** in THF without the palladium catalyst. Thus, the

palladium catalyst not only accelerates the cross coupling of the bromo with the tin compound but also the dimerization of the tin compound itself. Other examples of the symmetrical coupling of tin compounds or their destannylation can be found in the literature.<sup>14,15</sup>

The fairly soluble thiophene/furan oligomer **14** with seven rings was obtained by coupling the bis(trimethylstannyl) SOSOS **13** with iodofuran **8**. Coupling of diiodo SOSOS **6** with 2-(tributylstannyl)furan **9b** gave the same heptaheterocycle. However, workup of the crude product mixture resulted in a low yield of an impure product. A higher oligomer, formed via symmetrical coupling of pentaheterocycles **6** and **13**, respectively, could not be found in the reaction product.



The difuryl thiophene **3**, which is required for the preparation of **21**, was made by the coupling of 2,5-diiodothiophene **15** with (trimethylstannyl)furan **9a**. As a byproduct, the quarterheterocycle **16** was obtained in 10% yield, formed through symmetrical coupling of **15**. The compound **16** is also accessible via coupling of the tin compound **17** with 2-iodofuran **8**. In this case, self-coupling of **17** occurs, and the oligomer mixture **18** could be isolated in low yield (≈5%).

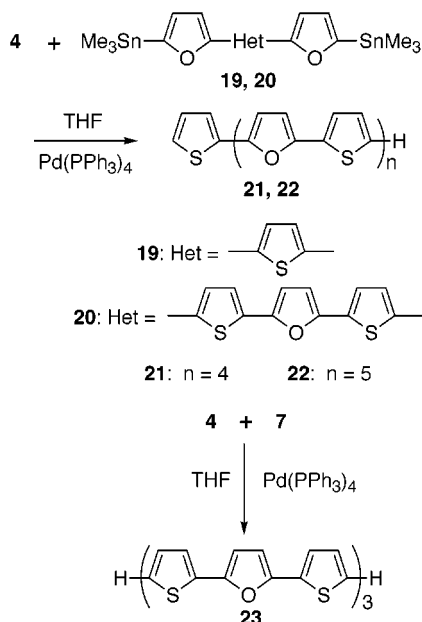


Lithiation of **3** and reaction with trimethylstannyl chloride gave **19**, which coupled with monobromo SOS **4** to furnish the nine-ring oligomer **21**. Despite its length,

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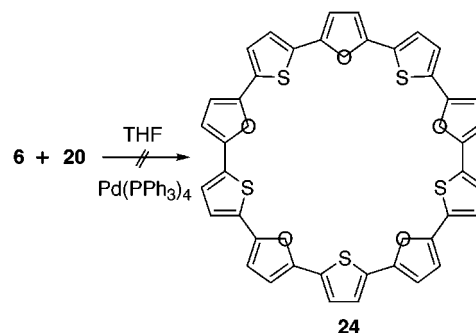
**21** is moderately soluble in halogenated solvents such as methylene chloride. On the other hand, the nine-ring **23**, prepared by coupling of monobromo SOS **4** and bis(trimethylstannyl) SOS **7**, is a highly insoluble solid. Oligomer **23** is even more insoluble than the poorly soluble oligomer **22** consisting of 11 rings. Compound **22** was made by coupling bis(trimethylstannyl) OSOSO with monobromo SOS **4** and is the longest mixed thiophene/furan oligomer known.



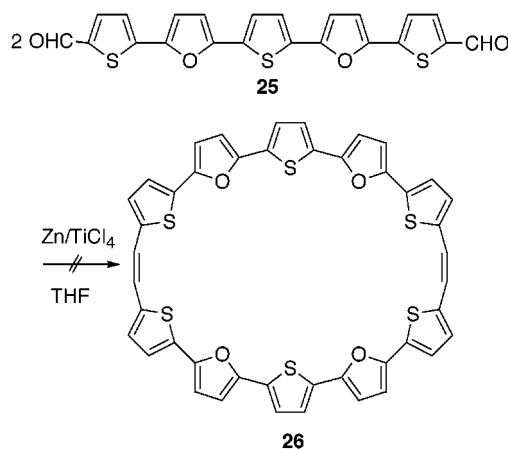
The solubility of the prepared oligomers not only depends on the length of the chain, but on the number of furan rings, and most on all of the thiophene/furan ratio. For example, compound **23** with a thiophene/furan ratio 2:1 is insoluble in methylene chloride. Oligomer **21**, consisting of nine rings as well, but with a ratio 1.25:1, is comparatively well soluble. The direct linkage of two thiophene units also seems to decrease the solubility. This explains the low solubility of **11** (8 rings, OSOS-SOSO, ratio 1:1).

Using the Stille protocol, it seemed possible to develop access to the interesting macrocycle **24** by coupling of diiodo SOSOS **6** with bis(trimethylstannyl) OSOSO **20**. Two experiments, which were carried out in a dilute solution (THF and DMF), led to a complex mixture of more and less soluble components, from which no macrocycle could be isolated. However, the mass spectra of the insoluble product showed (magnification of the mol peak region by 500) signals at 741 and 742 (expected  $M^+$  for **24** = 740), which could point to the formation of the macrocycle in minor amount. However, these peaks could also be mass fragments of a dimer of **6** and **20** or of a higher oligomer.

The earlier success of our group in the use of the McMurry coupling of a dialdehyde of a mixed five ring thiophene/pyrrole oligomer to form a macrocycle<sup>16</sup> suggested the possibility of carrying out a similar synthesis using the SOSOS dialdehyde **25**. Dialdehyde **25** was easily obtained from **2** in over 80% yield by Vilsmeier formylation as well as by lithiation followed by addition of DMF and hydrolysis. The reaction of the dialdehyde



**25** with  $\text{Zn/TiCl}_4$  did not lead to the isolation of the macrocycle **26**, but a highly insoluble black solid was obtained. The MS of this product shows no expected mol peak of the macrocycle **26** ( $M^+$  = 808).



### UV-Visible Spectra

The UV-vis spectra of the mixed oligomers show nonstructured absorption bands between 240 and 470 nm and a bathochromic shift of  $\lambda_{\text{max}}$  with increasing chain length (Table 1). Thus, the triheterocycles **1** and **3** absorb at approximately 365 nm. Compared to **1**, the long wavelength band of the 11-ring oligomer **22** shows a red shift of 100 nm. As expected, the bathochromic shift caused by the introduction of a new thiophene or furan unit decreases with increasing chain length. Whereas an extension of the chain from three (**1** and **3**) to five rings (**2** and **10**) results in a bathochromic shift of  $\lambda_{\text{max}}$  of about 50 nm, this amount drops to 34 nm between **2** or **10** and the heptaheterocycle **14**, and only 13 nm between **14** and the nine-ring **23**. An extension of the chain above nine rings causes only a minor red shift. Up to nine rings, the size dependence of the absorption band follows roughly the law  $\lambda \sim n^{1/2}$  ( $n$  = number of double bonds). Longer chains probably cause twists and distortions in the polyene structure and affect  $\lambda_{\text{max}}$ .<sup>17</sup> As is typical for polyenes, an increasing absorption intensity with increasing length of the conjugated system was found (**1**  $\epsilon$  = 4.07, **22**  $\epsilon$  = 4.79). Furthermore, at a given chain length, no significant influence of the furan/thiophene ratio on  $\lambda_{\text{max}}$  can be observed. For example, both the pentaheterocycles **2** and **10** absorb at almost the same wavelength as  $\alpha$ -quinquethiophene<sup>6</sup> ( $\lambda_{\text{max}}$  = 416 nm,  $\text{CHCl}_3$ ).

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**Table 1.** UV-Visible Spectra Data (in CH<sub>2</sub>Cl<sub>2</sub>)

entry	compound	$\lambda$ [nm] (log $\epsilon$ )
1	<b>1</b> SOS	241 (3.91), 328 (4.22), 366 (4.07)
2	<b>3</b> OSO	242 (3.95), 333 (4.29), 362 (4.16)
3	<b>16</b> OSSO	243 (4.12), 393 (4.47)
4	<b>2</b> SOSOS	241 (4.08), 332 (4.13), 413 (4.57)
5	<b>10</b> OSOSO	334 (4.16), 413 (4.56)
6	<b>14</b> O-SOSOS-O	246 (4.13), 379 (4.4), 447 (4.62)
7	<b>11</b> O-SOS-SOS-O	339 (4.20), 396 (4.41), 456 (4.53)
8	<b>23</b> SOS-SOS-SOS	460
9	<b>21</b> SOS-OSO-SOS	413 (4.60), 458 (4.65)
10	<b>22</b> SOS-OSOSO-SOS	251 (4.39), 431 (4.78), 465 (4.79)

### Cyclic Voltammetry

Electrochemical experiments with the oligomers were performed using a PAR Model 263 instrument in a single-compartment cell with a platinum disk working electrode, a platinum wire counter electrode, and standard calomel (SCE) as reference electrode. For each study, a 0.1 M solution of tetrabutylammonium hexafluorophosphate in 1,2-dichloroethane was employed with a oligomer concentration of 0.1–1 mM.

The earlier described pentaheterocycle **2** exhibits a reversible CV with two redox waves ( $E_{1/2} = 0.79, 1.09$  mV) and is a remarkably stable compared to quinque-thiophene, which undergoes dimerization.<sup>18</sup> No satisfactory CV could be obtained from the pentamer **10**. During the first scan, a small anodic peak at 0.75 mV was observed, which points to the formation of the radical cation. After repeated cycles, this peak disappeared, perhaps due to dimerization of **10**, and a black deposit was observed on the working electrode. However, the formation of a new electroactive species with a new anodic peak could not be detected. Increase of the scan rate from 20 to 200 mV/s resulted in no improvement of the CV. The square wave voltammogram of **10** shows, after the initial scan (scan rate 120 mV/s), a broad peak at 1.18 mV. After 10 scans, a small new peak at 0.45 mV can be found, whereby the peak at 1.18 mV disappears. The peak at 0.45 mV could be caused by a dimer of **10**.

The analysis of the other oligomers by CV and SWV also gave poor and contradictory results. In the most cases a black deposit was found on the working electrode. Apparently, the higher thiophene/furan oligomers are easily oxidized and undergo after the first oxidation step to the cation radical a dimerization or polymerization.

### Experimental Section

**General.** All melting points are uncorrected. NMR spectra were obtained on a Bruker AM360 (360 MHz/90 MHz). All NMR spectra are reported in ppm. UV-vis spectra were recorded on a Perkin-Elmer (Lambda 4B). Column chromatography was carried out on silica gel. The palladium(0) catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> was prepared freshly according to literature.<sup>19</sup> Due to the ease of decomposition, all tin compounds but the solid **7** were used immediately after preparation. The purity was checked by <sup>1</sup>H NMR.

**Monobromo SOS 4.** To a stirred solution of the triheterocycle **1** (930 mg, 4.01 mmol) in 50 mL of THF was added NBS (710 mg, 3.99 mmol) portionwise during 2 h at –60 to –70 °C. The solution was stirred for 3 h at room temperature. Water was added, and the mixture was extracted two times with CH<sub>2</sub>Cl<sub>2</sub>. Column chromatography (hexanes) afforded dibromo

SOS **5** (180 mg, 22%), monobromo SOS **4** (610 mg, 49%, and 170 mg containing about 20% **1**), and starting material **1** (170 mg, 18%). **4**: mp 59–60 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.30 (dd, 1 H,  $J = 0.9, 3.4$  Hz), 7.25 (dd, 1 H,  $J = 0.9, 5.0$  Hz), 7.05 (2d, 1 H,  $J = 3.6, 5.0$  Hz), 7.03 (d, 1 H,  $J = 4$  Hz), 7.00 (d, 1 H,  $J = 3.8$  Hz), 6.53 (d, 1 H,  $J = 3.4$  Hz); 6.50 (d, 1 H,  $J = 3.6$  Hz); <sup>13</sup>C NMR  $\delta$  148.9, 147.4, 134.9, 133.2, 130.6, 127.7, 124.5, 122.9, 122.6, 111.2, 107.5, 107.1. Anal. Calcd for C<sub>12</sub>H<sub>7</sub>OS<sub>2</sub>Br (M = 311.22): C, 46.30; H, 2.25; S, 20.58. Found: C, 46.10; H, 2.12; S, 20.47.

**Dibromo SOS 5.** In the absence of light, a solution of NBS (1.61 g, 9.04 mmol) in 30 mL of DMF was added dropwise to a solution of **1** (930 mg) in 40 mL of DMF at room temperature. After stirring overnight, water was added, and the mixture extracted with saturated aq NaCl solution. The organic extract was washed with water and dried. Evaporation of the solvent and recrystallization of the residue from EtOH gave **5** as yellow needles (1.4 g, 83%): mp 116–118 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.02 (d, 2 H,  $J = 3.9$  Hz), 6.99 (d, 2 H,  $J = 3.9$  Hz), 6.48 (s, 2 H); <sup>13</sup>C NMR  $\delta$  147.7, 134.6, 130.6, 122.8, 111.5, 107.4. Anal. Calcd for C<sub>12</sub>H<sub>6</sub>OS<sub>2</sub>Br<sub>2</sub> (M = 390.12); C, 36.92; H, 1.54; S, 16.41. Found: C, 36.90; H, 1.44; S, 16.60.

**Diiodo SOSOS 6.** A stirred solution (mechanical stirrer) of the pentaheterocycle **2** (2 g, 5.26 mmol) in dry THF (100 mL) was cooled at –70 °C, and a 2.5 M solution of n-BuLi in hexanes (4.8 mL, 12 mmol) was added dropwise under N<sub>2</sub>. The mixture was allowed to come at room temperature and stirred for 30 min. After cooling at –30 °C, a solution of iodine (3.05 g, 12 mmol) in 40 mL of THF was added dropwise. The cooling bath was removed and the mixture stirred for 90 min. The reaction mixture was poured in a aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic solution was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the residue extracted with EtOAc. Evaporation of EtOAc and recrystallization of the residue from cyclohexane afforded **6** as orange brown solid (1.61 g, 48%). A analytical pure sample was obtained by flash chromatography (hexanes/benzene 5:1): mp 172–173 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.21 (s, 2 H), 7.19 (d, 2 H,  $J = 3.7$  Hz), 6.97 (d, 2 H,  $J = 3.8$  Hz), 6.55 (d, 2 H,  $J = 3.5$  Hz), 6.52 (d, 2 H,  $J = 3.5$  Hz); <sup>13</sup>C NMR  $\delta$  148.5, 147.6, 139.1, 137.6, 131.9, 124.4, 123.5, 107.9, 107.6, 72.2; MS 632 (M<sup>+</sup>, 6%). Anal. Calcd for C<sub>20</sub>H<sub>10</sub>O<sub>2</sub>S<sub>3</sub>I<sub>2</sub> (M = 632.31); C, 37.97; H, 1.58; S, 15.49. Found: C, 38.55; H, 1.74; S, 15.50.

**Bis(trimethylstannyl) SOS 7.** A 2.5 M solution of n-BuLi in hexanes (4 mL, 10 mmol) was added dropwise to a stirred solution of the triheterocycle **1** (1 g, 4.31 mmol) in 50 mL of dry THF containing TMEDA (1.44 mL, 9.6 mmol) at –60 °C under N<sub>2</sub>. The mixture was allowed to come at room temperature and stirred for 30 min. To the white suspension was added dropwise a solution of trimethyltin chloride (2 g, 10 mmol) in 20 mL of dry THF at –60 °C. The reaction mixture was raised to room temperature and stirred for 2 h. The mixture was poured into aqueous NH<sub>4</sub>Cl solution and extracted two times with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed three times with water and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent gave **7** as a gray solid (2.3 g, 95%); mp 87–88 °C (EtOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.41 (d, 2 H,  $J = 3.3$  Hz), 7.12 (d, 2 H,  $J = 3.4$  Hz), 6.52 (s, 2 H), 0.41 (t, 18 H,  $J = 29$  Hz); <sup>13</sup>C NMR  $\delta$  148.6, 139.0, 137.0, 135.7, 123.7, 107.0, –8.2; UV-vis (1,2-DCE)  $\lambda_{\text{max}}$  384 nm, 335 nm; MS 558 (M<sup>+</sup>, 100%). Anal. Calcd for C<sub>18</sub>H<sub>24</sub>OS<sub>2</sub>Sn<sub>2</sub> (M = 557.94): C, 38.7; H, 4.3; S, 11.5. Found: C, 38.7; H, 4.3; S, 11.6.

**Bis(trimethylstannyl) OSO 19.** Compound **19** was prepared as described for **7** using **3** (148 mg, 0.687 mmol), TMEDA (0.23 mL, 1.53 mmol), 2.5 M n-BuLi in hexanes (0.68 mL, 1.7 mmol), and trimethylstannyl chloride (330 mg, 1.65 mmol) to give a brown oil (340 mg, 91%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.16 (s, 2H); 6.61 (d, 2H,  $J = 3.1$  Hz); 6.52 (d, 2H,  $J = 3.2$  Hz); 0.37 (t, 18H,  $J = 28$  Hz).

**Bis(trimethylstannyl) SOSOS 13.** Compound **13** was prepared as described for **7** using **2** (500 mg, 1.32 mmol), TMEDA (0.44 mL, 2.9 mmol), 2.5 M n-BuLi in hexanes (1.3 mL, 3.25 mmol), and trimethylstannyl chloride (630 mg, 3.16 mmol) to give a brown oil (930 mg, 100%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.43 (d, 2H,  $J = 3.3$  Hz); 7.23 (s, 2H); 7.13 (d, 2H,  $J = 3.4$

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H<sub>z</sub>); 6.56 (d, 2H, *J* = 3.4 Hz); 6.54 (d, 2H, *J* = 3.4 Hz); 0.41 (t, 18 H, *J* = 28 Hz).

**Bis(trimethylstannyl) OSOSO 20.** Compound **20** was prepared as described for **7** using **10** (250 mg, 0.687 mmol), TMEDA (0.23 mL, 1.53 mmol), 2.5 M *n*-BuLi in hexanes (0.68 mL, 1.7 mmol), and trimethylstannyl chloride (330 mg, 1.65 mmol) to give a brown oil (430 mg, 91%): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.23 (d, 2 H, *J* = 4.0 Hz), 7.18 (d, 2 H, *J* = 3.9 Hz), 6.63 (d, 2 H, *J* = 3.3 Hz), 6.56 (s, 2 H), 6.55 (d, 2 H, *J* = 3.2 Hz), 0.27 (t, 18 H, *J* = 29 Hz).

**Bis(tributylstannyl) Bithiophene 17.** Compound **17** was prepared as described for **7** using 2,2'-bithiophene (1 g, 6 mmol), 2.5 M *n*-BuLi in hexanes (5.4 mL, 13.5 mmol), and tributylstannyl chloride (4.39 g, 13.5 mmol) to give a brown oil (4.46 g, 100%): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.32 (d, 2H, *J* = 3.1 Hz); 7.08 (d, 2H, *J* = 3.2 Hz); 1.61 (m, 12H); 1.38 (m, 12H); 1.15 (t, 12H, *J* = 8 Hz); 0.94 (t, 18H, *J* = 7.3 Hz).

**OSOSO 10 and O-SOS-SOS-O 11. Method A:** The tin compound **7** (2.3 g, 4.12 mmol) and 2-iodofuran **8** (1.9 g, 9.79 mmol) were dissolved in dry THF (30 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.3 g, 0.26 mmol) was added. The mixture was refluxed for 2 d under N<sub>2</sub>. After cooling, the precipitate of **11** was filtered off, washed with THF and ether, and dried (red brown solid, 300 mg, 24%). The filtrate was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed several times with water, and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent followed by flash chromatography eluting with hexanes:benzene (5:1), yielded **10** as a yellow solid (750 mg, 50%). **Method B:** A solution 2-(trimethylstannyl)furan **9a** (1.27 g, 5.5 mmol), dibromo SOS **5**, and Pd(PPh<sub>3</sub>)<sub>4</sub> (350 mg, 0.3 mmol) in dry THF (50 mL) was refluxed for 2 d. The precipitate of **11** was filtered off and washed with THF and ether (80 mg, 10%). The filtrate was evaporated to dryness, and a small amount MeOH was added. The undissolved solid was separated and subjected to flash chromatography (hexanes:benzene 5:1) to yield **10** (500 mg, 54%).

**10.** mp 152–154 °C (cyclohexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.42 (d, 2 H, *J* = 1.4 Hz), 7.22 (d, 2 H, *J* = 3.9 Hz), 7.19 (d, 2 H, *J* = 3.7 Hz), 6.56 (s, 2 H), 6.53 (d, 2 H, *J* = 3.3 Hz), 6.46 (2d, 2 H, *J* = 3.6, 1.8 Hz); <sup>13</sup>C NMR δ 149.1, 148.3, 141.8, 132.4, 131.7, 123.2, 123.1, 111.8, 107.5, 105.3; UV-vis (1,2-DCE) λ<sub>max</sub> 413 nm; MS 364 (M<sup>+</sup>, 100%). Anal. Calcd for C<sub>20</sub>H<sub>12</sub>O<sub>3</sub>S<sub>2</sub> (M = 364.45): C, 65.9; H, 3.3; S, 17.6. Found: C, 66.1; H, 3.3; S, 17.7.

**11.** mp 265–270 °C (dec); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 70 °C) δ 7.68 (d, 2H, *J* = 1.4 Hz), 7.39 (2d, 4H, *J* = 3.9 Hz), 7.36 (d, 2H, *J* = 3.8 Hz), 7.34 (d, 2H, *J* = 3.8 Hz), 6.90 (d, 2H, *J* = 3.6 Hz), 6.89 (d, 2H, *J* = 3.6 Hz), 6.78 (d, 2H, *J* = 3.3 Hz), 6.59 (2d, 2H, *J* = 1.9, 3.2 Hz); HRMS (EI) calcd for C<sub>32</sub>H<sub>18</sub>O<sub>4</sub>S<sub>4</sub> 594.0088, found 594.0082.

**O-SOSOS-O 14. Method A.** A solution of bis(trimethylstannyl) SOSOS **13** (900 mg, 1.275 mmol), 2-iodofuran **8** (550 mg, 2.835 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (150 mg, 0.13 mmol) in THF (50 mL) was refluxed under N<sub>2</sub> for 2.5 d. The solvent was removed, and methanol was added to the residue. The solid was separated and washed with MeOH. Washing with a small amount acetone gave **14** as a brown solid (230 mg, 35%). Evaporation of the acetone and column chromatography of the residue (CH<sub>2</sub>Cl<sub>2</sub>:hexanes 1:3) provided another 190 mg (29%)

**14. Method B.** A solution of diiodo SOSOS **6** (930 mg, 1.5 mmol), (tributylstannyl)furan **9b** (1.35 g, 3.78 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (150 mg, 0.13 mmol) in THF (70 mL) was refluxed under N<sub>2</sub> for 2 d. The solvent was evaporated and the residue washed with MeOH. Column chromatography of the resulting solid (EtOAc:hexanes 1:3) gave 350 mg (≈45%) of impure **14**: mp 170–175 °C (dec); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 7.74 (d, 2H, *J* = 1.2 Hz); 7.46 (s, 2H); 7.44 (d, 2H, *J* = 3.9 Hz); 7.37 (d, 2H, *J* = 3.9 Hz); 6.99 (d, 2H, *J* = 3.4 Hz), 6.97 (d, 2H, 3.5 Hz), 6.85 (d, 2H, *J* = 3.3 Hz); 6.61 (2d, 2H, *J* = 1.9, 3.3 Hz); <sup>13</sup>C NMR δ

148.2, 147.8, 147.7, 143.0, 131.8, 130.9, 130.6, 124.4, 124.3, 123.9, 112.5, 108.9, 108.8, 106.3; HRMS (EI) calcd for C<sub>28</sub>H<sub>16</sub>O<sub>4</sub>S<sub>3</sub> 512.0211, found 512.0211.

**OSO 3.** A solution of 2,5-diiodothiophene **15** (2.68 g, 7.98 mmol), 2-(trimethylstannyl)furan (3.74 g, 16.2 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (930 mg, 0.8 mmol) in THF (70 mL) was refluxed under N<sub>2</sub> for 3 d. The solvent was evaporated and the residue column chromatographed (hexanes) to give **3** as colorless crystals (700 mg, 40%) and **16** (100 mg, 8%).

**3:** mp 63–65 °C (lit. 67–69 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.41 (d, 2H, *J* = 1.8 Hz); 7.17 (s, 2H); 6.51 (d, 2H, *J* = 3.3 Hz); 6.45 (2d, 2H, *J* = 3.3, 1.8 Hz); <sup>13</sup>C NMR δ 149.2, 141.8, 132.3, 123.0, 111.8, 105.2.

**OSSO 16.** A solution of bis(tributylstannyl) SS **17** (1.8 g, 2.42 mmol), 2-iodofuran **8** (1 g, 5.15 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (250 mg, 0.22 mmol) in THF (50 mL) was refluxed under N<sub>2</sub> for 3 d. The orange brown precipitate of **18** was filtered off and washed with THF and MeOH (30 mg). The filtrate was evaporated and the residue column chromatographed (benzene:hexanes 1:4) to yield crude **16**. Recrystallization from EtOH gave pure **16** as yellow crystals (300 mg, 42%).

**16.** mp 166–167 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.41 (d, 2H, *J* = 1.6 Hz); 7.15 (d, 2H, *J* = 3.9 Hz); 7.10 (d, 2H, *J* = 3.9 Hz); 6.51 (d, 2H, *J* = 3.4 Hz); 6.45 (2d, 2H, *J* = 1.7, 3.4 Hz); <sup>13</sup>C NMR δ 149.0, 141.8, 135.8, 132.5, 124.1, 123.2, 111.8, 105.4; MS 298 (M<sup>+</sup>, 100%). Anal. Calcd for C<sub>16</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub>: C, 64.43; H, 3.36; S, 21.48. Found: C, 64.33; H, 3.36; S, 21.58.

**18.** MS 462 (OSSSSO, M<sup>+</sup>, 100%); 626 (OSSSSSSO, M<sup>+</sup>, 40%).

**SOS-OSO-SOS 21.** A solution of bis(trimethylstannyl) OSO **19** (700 mg, 1.29 mmol), monobromo SOS **4** (840 mg, 2.7 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (250 mg, 0.2 mmol) in THF (60 mL) was refluxed under N<sub>2</sub> for 2.5 d. A small amount of a precipitate was filtered off. THF was evaporated, and the residue was treated with EtOH. The resulting precipitate was washed several times with EtOH and acetone to furnish **21** as an orange solid (500 mg, 57%): mp 178–182 °C (dec); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) 7.53 (dd, 2H, *J* = 0.7, 4.9 Hz), 7.35–7.45 (m, 8H), 7.13 (2d, 2H, *J* = 3.9, 4.9 Hz), 6.92 (s, 4H), 6.89 (d, 2H, *J* = 3.6 Hz), 6.82 (d, 2H, *J* = 3.3 Hz); <sup>13</sup>C NMR δ 148.3; 147.8, 147.7, 147.4, 134.8, 132.1, 131.0, 130.8, 130.7, 128.3, 125.6, 124.4, 124.2, 123.5, 108.9, 108.9, 108.7, 108.1; MS 676 (M<sup>+</sup>, 60%). Anal. Calcd for C<sub>36</sub>H<sub>20</sub>O<sub>4</sub>S<sub>5</sub> (M = 676.88): C, 63.91; H, 2.96; S, 23.67. Found: C, 63.82; H, 2.88; S, 23.54.

**SOS-SOS-SOS 23.** A solution of monobromo SOS **4** (240 mg, 0.772 mmol), bis(trimethylstannyl) SOS **7** (215 mg, 0.386 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (90 mg, 0.08 mmol) in THF (50 mL) was refluxed under N<sub>2</sub> for 2 d. The red-brown precipitate of **23** was separated and washed with MeOH and CH<sub>2</sub>Cl<sub>2</sub> (190 mg, 71%): mp 307–309 °C; HRMS (EI) calcd for C<sub>36</sub>H<sub>20</sub>O<sub>3</sub>S<sub>6</sub> 691.9737, found 691.9729.

**SOS-OSOSO-SOS 22.** A solution of bis(trimethylstannyl) OSOSO **20** (430 mg, 0.623 mmol), monobromo SOS **4** (390 mg, 1.25 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (150 mg, 0.13 mmol) in THF (50 mL) was refluxed under N<sub>2</sub> for 2 d. A small amount of a precipitate was filtered off. The solvent was evaporated and the residue washed with MeOH, followed by CH<sub>2</sub>Cl<sub>2</sub> to give **22** as a brown solid (210 mg, 41%): mp 220–225 °C (dec); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 70 °C) δ 7.52 (d, 2H, *J* = 5.0 Hz); 7.3–7.5 (m, 10H), 7.13 (t, 2H, *J* = 4.3 Hz), 6.92 (s, 6H), 6.87 (broad d, 2H), 6.81 (broad d, 2H); HRMS (EI) calcd for C<sub>44</sub>H<sub>24</sub>O<sub>5</sub>S<sub>6</sub> 823.9948, found 823.9957.

**Acknowledgment.** This work was supported by a grant from the National Science Foundation (CHE-9612350).

JO981159L