Synthesis of β-Methoxy, Methyl-Capped α-Oligothiophenes

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The first syntheses of structurally defined methoxyoligothiophenes are described. Nine α-coupled oligothiophenes, dimers through hexamers, symmetrically substituted at the "inside" or "outside" β-positions with two or four methoxy groups, and with terminal methyl groups, were prepared. The electron-donor methoxy groups and terminal methyls have been shown to stabilize cationic species formed by oxidation or protonation of these oligomers. The oligomers were built up by the cross coupling of (mono- or oligo-) β-methoxy-α-iodothiophenes and (mono- or oligo-) α-stannylthiophenes catalyzed by Pd(0)/Pd(II) or by the redox homo-coupling of α-thienyllithium compounds with $Fe(acac)_3$. Synthesis by the cross coupling of thienyl Grignard reagents and bromothiophenes with Ni(0) or Suzuki coupling using organoboranes was not successful. An X-ray crystal structure of a dimethoxy quaterthiophene is reported.

Introduction

α-Coupled polythiophenes and their oligomers have unusual properties and have attracted substantial interest.[1] They have been utilized[2] for electrically conducting materials, electrooptical and electronic devices, highly organized molecular assemblies, and even biological research.[3] The polymers have often been produced by oxidative polymerization of thiophene, alkylthiophenes, or small oligothiophenes.[4] Because these polymers can have complex or poorly defined compositions or poor solubility, alternative polymerization techniques, usually involving coupling of organometallic compounds, have been developed.[5] Recently the utility of oligomers with well defined structures has become apparent and a number of these oligomers, which are usually alkylated to enhance solubility, have been reported.[6-11]

There are now several related approaches to the synthesis of these alkyloligothiophenes. One involves diyne or dicarbonyl intermediates which are converted to thiophene rings.[12] A second method involves the oxidative homo-coupling of metalated thiophenes, i.e. reaction of α-thienyllithium with Fe(acac) to produce bithiophene.[13] A third method involves the cross coupling of α-metalated thiophenes with α-halothiophenes catalyzed by nickel or palladium.[7] Related cross coupling reactions utilize α-stannylthiophenes or α-boranylthiophenes. The final products usually have several β-alkyl groups and are sometimes end-capped with alkyl, phenyl, bromo, silyl, or other groups.[14] These methods have been used to produce α-coupled alkyloligothiophenes with as many as eleven,[15] twelve,[16] and sixteen[8c] rings.

Oligothiophenes have been used in their neutral form to prepare electronic and electrooptical devices.[2] They have also been used to model the structure of polythiophene.[6-8,10,11,15] Since polythiophene becomes electrically conducting when it is oxidized, much interest has focused on oligomeric cation radicals and dications that are produced by oxidation. If the terminal α-carbons are capped, it is often possible to stabilize these cationic species sufficiently so that their spectra can be measured. In this way the structure of oxidized polythiophene can be modeled. Indeed, we and others have recently published results from oligomer studies that suggest a rethinking of the structure/conductivity theory for these polymers.[6,8,10,11]

Studies from this laboratory have shown, however, that the cation radicals and dications of terminal-capped, alkyloligothiophenes are often not entirely stable. This prevents a meaningful study of the properties of these

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cations as materials. It is furthermore true that several devices based on oligothiophenes depend on stability of the neutral oligomers. The ready oxidation and further reaction of these compounds is, therefore, a problem of some importance. The present investigation is directed toward the synthesis of oligomers that will form stable cation radicals, dications, and/or monocations (by protonation).

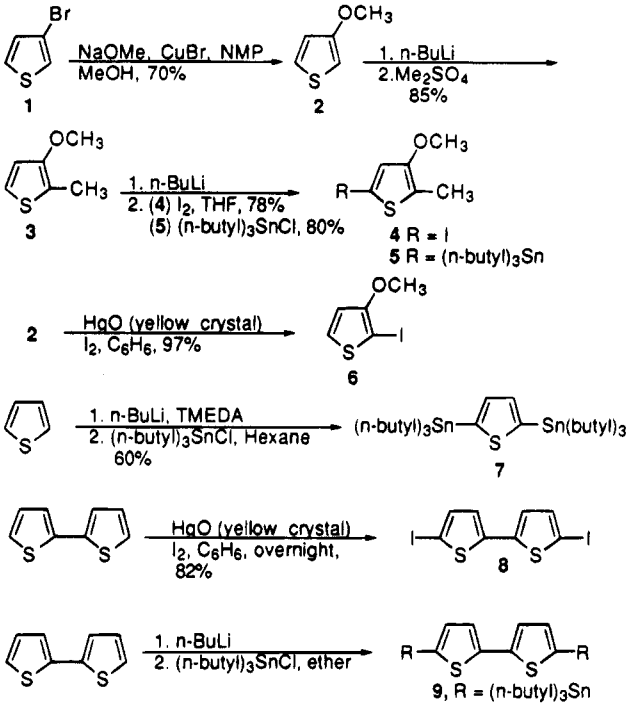
Here we report on the first synthesis of structurally defined methoxy-substituted oligothiophenes. The approach is based on reports that oligomer mixtures from the anodic oxidation of 3-methoxythiophene gave stable cationic species.[17] The utility of the oligomers reported here has already been demonstrated as described in two preliminary communications. Stable oligomer cation radicals were formed in water and provided the first example of oligothiophene π-stacks.[18] The first examples of diamagnetic oligothiophene monocations were formed by protonation of these oligomers.[19]

Results

We define two types of compounds: "Inside methoxy" oligomers are symmetrically substituted with the β-methoxy groups pointing toward the inside of the oligothiophene chain as in 3,3′-dimethoxybithiophene **10**. "Outside methoxy" refers to compounds like the 4,4′-dimethoxybithiophene **19**. After developing useful syntheses of iodo and stannyl substituted monomers **4**–**7** these compounds were taken on to produce a set of inside and outside substituted oligomers. The synthetic routes used to build up oligomers were cross coupling between stannyl thiophenes and iodothiophenes with either Pd(0) or Pd(II) catalysts or the homo-coupling of α-lithiothiophenes with $Fe(acac)_3$.

Inside Methoxyoligothiophenes. 3-Methoxythiophene (**2**) was economically prepared from 3-bromothiophene (**1**).[20] Reaction of **2** with *n*-butyllithium followed by dimethyl sulfate gave an 85% yield of compound **3** and only 5% of the 5-substituted isomer (Scheme 1). The major product, which formed via deprotonation at the 2-position, presumably resulted because the lithium positioned at that position could be complexed by the neighboring methoxy group. If this reaction was carried out at lower temperature or using methyl iodide instead of dimethyl sulfate the selectivity and yield decreased substantially. Iodo and tributylstannyl monomers **4** and **5** were prepared by lithiation of **3** followed by treatment with iodine or tri-*n*-butyltin chloride. **4** was not stable and it had to be used within hours of preparation. We note that lithiation of **2** followed by stannylation did not provide good yields of 2-(tri-*n*-butylstannyl)-3-methoxythiophene. The synthesis of monomer **6** was surprisingly easy and effective. 3-Methoxythiophene stirred with HgO and I_2 provided **6** in 97% yield. On the other hand the same procedure failed to provide **4** from **3**. Monomer **7** was a known compound and was prepared accordingly.[21] Compound **8** was prepared following a similar procedure to that for **6**.

Scheme 1



An unmethoxylated bis(tributylstannyl) bithiophene **9**, was prepared from 2 equiv of *n*-butyllithium and 1 equiv of bithiophene followed by treatment with tri-*n*-butyltin chloride. This compound was not very stable, and column chromatography on silica gel converted about half of it to the monostannylbithiophene. Fortunately, the raw product **9** was pure enough for the next step.

The inside oligomers of interest were prepared by coupling together the above reactants. Dimethoxy-dimer **10** was prepared from **2** by the homo-coupling of 2-lithio-3-methoxythiophene with $Fe(acac)_3$ in 79% yield (Scheme 2).[13] Pd(0)/Pd(II) cross coupling between the appropriate organostannyl compounds and thienyl iodides yielded trimer **12**, tetramer **14**, and pentamers **17** and **23** in 40–60% yield. Reaction in a sealed, argon-purged tube, using 0.08 equiv of the catalyst gave the best results. No difference in yield was found between Pd(0) and Pd(II) catalysts, but Pd(II) made product separation easier. When these reactions were carried out under dry nitrogen and reflux conditions the yield usually dropped by 10%. The major side products resulted from homo-coupling of the reactants.

Methylation of compounds **10**, **12**, **14**, **17**, and **23** providing **11**, **13**, **15**, **18**, and **24** was accomplished with *n*-butyllithium followed by methyl sulfate. Yields were typically 85%.

Outside Methoxyoligothiophenes. 4,4′-Dimethoxy-5,5′-dimethylbithiophene **19** was prepared by the $Fe(acac)_3$ oxidation of lithiated **3** (Scheme 3). The outside dimethoxy-trimer **20** and dimethoxy-tetramer **21** were prepared from the appropriate stannyl and iodo compounds using the palladium-catalyzed coupling process in 50 and 48% yields, respectively.

Inside-Outside Tetramethoxyoligothiophenes. The preparation of tetramethoxypentamer **24** started from trimer **12**, which was stannylated giving **22** (Scheme 4). Trimer **22** was then coupled with 2 equiv of monomer **6** to provide pentamer **23**. Methylation gave **24**, with an overall yield for the three steps of 53%. Hexamer **26** was prepared starting by methylation of the inside trimer **12**

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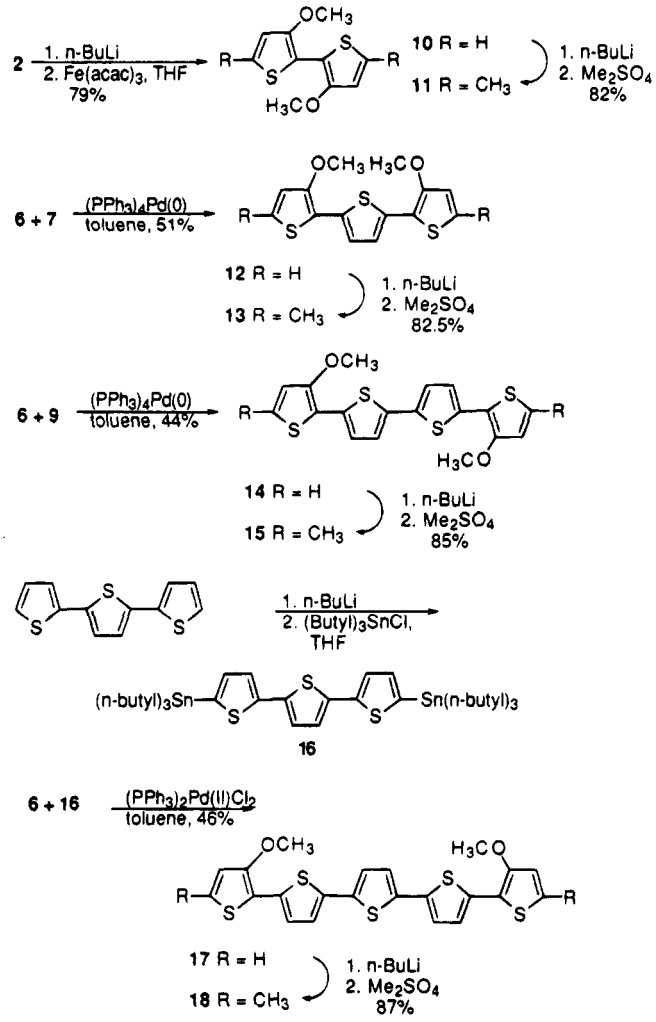
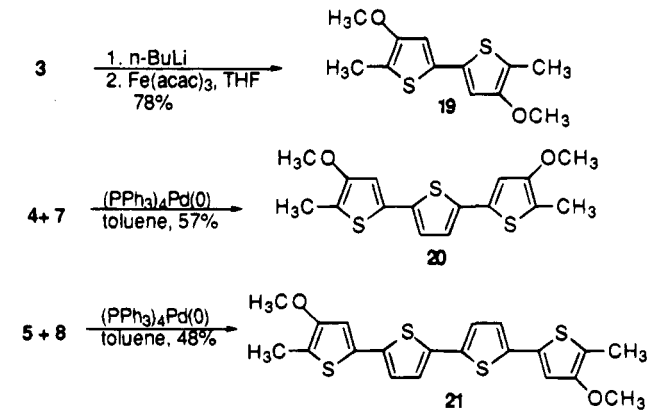
Scheme 2



Scheme 3

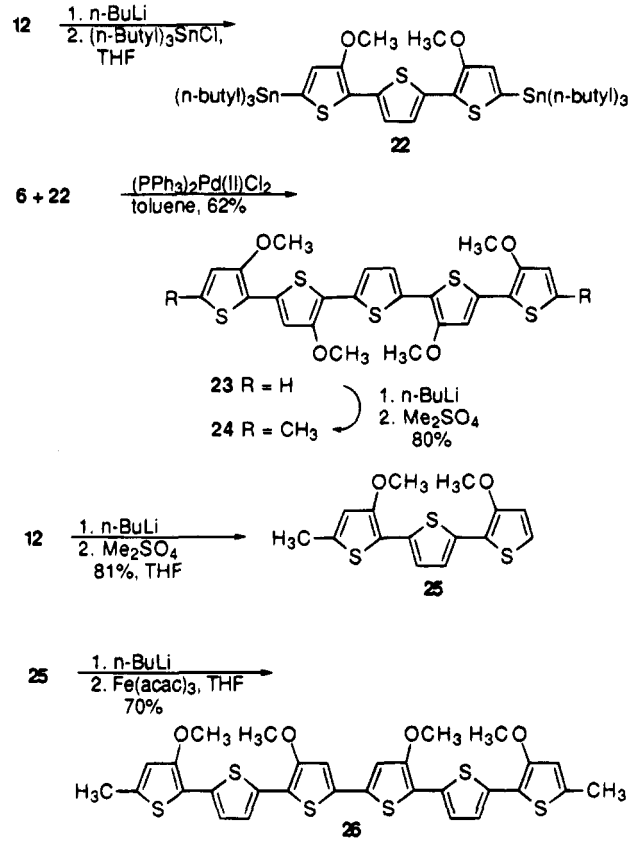


producing a monomethyl **25** contaminated with dimethyl **13**. This mixture was reacted with $Fe(acac)_3$ to give **26**, which was easily separated from the unreacted **13**.

Discussion

The nine target compounds were prepared in reasonable yields and satisfactory purity using the approach described. Several of the intermediates proved to be unstable and required some care in handling. The stannylated compounds **16** and **22**, like **9**, could not be purified chromatographically because of destannylation and were used directly. Longer oligothiophenes without

Scheme 4



end caps, i.e., **17**, **23**, were very acid sensitive. For example, workup with undried CH_2Cl_2 or $CHCl_3$ generated black precipitates. Previous results from this laboratory showed that oligothiophenes could be photooxidized with acid (TFA) present in solution.[6b] The oligomers we prepared can be even more sensitive due to the electron-donating methoxy groups and in fact we recently reported the formation of stable cations by protonation of compounds **20** and **21**.[19]

The most widely used method to make alkyloligothiophenes and poly(alkylthiophenes) is the catalyzed cross coupling of thienyl Grignard reagents and thienyl halides. Unfortunately, 2-bromo-3-methoxythiophene could not be transformed to its Grignard reagent, and the Grignard reagent formed from bromothiophene did not couple with 3-methoxy-2-bromothiophene using Ni(II) as catalyst. Coupling reactions between organozinc compounds, which were formed by reacting the thienyllithium with $ZnCl_2$, and thienyl bromides with Pd(0) as catalyst, were also performed. The yields turned out to be comparable with those from organostannyl coupling reactions. Cross coupling under Suzuki conditions, which was attempted using 2-thienylboronic acid, was unsuccessful. Several homo-coupling reactions had also been tried.[12] And as a result, homo-coupling of organolithium by reacting with $Fe(acac)_3$ was proven to be very effective.

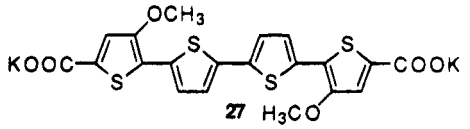
The utility of this method has been demonstrated by the synthesis of the water soluble quatrathiophene **27** from **14**.[18] The carboxylate-terminated inside-dimethoxy quaterthiophene **27** was oxidized in water to produce a stable cation radical. This stability allowed us to demonstrate spectroscopically that it aggregated into π-stacks. Lyophilization produced an electrically conducting salt with $\sigma = 2 \times 10^{-3}$ S cm^{-1}. Partial oxidation followed by lyophilization led to a mixed valence salt with $\sigma = 2 \times 10^{-2}$ S cm^{-1}. The stability of the cation radical was quite

Table 1. Vis Data for Methyl Capped Oligothiohenes[a]

cmpd	λ_{max} (nm) dimer	trimer	tetramer	pentamer
no methoxy[b]	306	364	397	422
inside dimethoxy[c]	325	384	414	438
outside dimethoxy[d]	330	389	419	

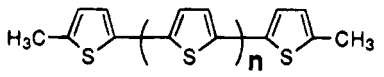
[a] $CHCl_3$ solutions. [b] Compounds **28**, n = 0–3, ref 11a. [c] Compounds **11**, **13**, **15**, **18**. [d] Compounds **19**, **20**, **21**.

good in the solid and even in the nucleophilic solvent water. Thus, the main goal of this project was fulfilled.



27

Worthy of comment from the spectroscopic data we have collected on the neutral oligomers described above are the vis spectra. The trends we have observed are illustrated in Table 1 and compared with unmethoxylated oligothiophenes **28**.[11a] (1) As expected[6-11] longer oligo-



28, n = 0, 1, 2, 3

mers absorb at longer wavelength. (2) Adding two inside methoxy groups to an oligomer increases the λ_{max} by about 17 nm. Two outside methoxy groups increase the λ_{max} by about 22 nm. (3) Two terminal methyls increase λ_{max} by about 4 nm. It is thus clear that these substituents do not perturb the HOMO–LUMO gap of oligothiophenes very much and we infer that they do not perturb the electronic structure very much. This supports the claim that such methoxy oligomers can be models for segments of unmethoxylated polythiophenes.

X-ray crystallography has been used to deduce the details of molecular structure for tetramer **14**.[22] The structure in Figure 1 shows that there are two slightly different sites in the crystal. Molecules in both sites have their thiophene rings arranged in a nearly coplanar array with a s-trans configuration between the rings.[23] In this way the methoxy groups are aligned with the sulfur groups on the adjacent rings, avoiding the repulsive interaction between methoxy and hydrogen that would result if the s-cis geometry was adopted. It can be seen that "type a" molecules lie in a slipped stack with essentially no overlap between the π-systems of the molecules along the stack. Only the methoxy of one molecule is close to the π-system of the next molecule in the stack. The spacing between molecules in this stack is greater than 3.8 Å. "Type b" molecules are found in separate stacks, which are orthogonal to the type a stacks. The type b stack has less planar molecules, but better intermolecular overlap between the π–systems of the molecules in the stack. Because of the slipped stack structure only two rings of one molecule interact with two rings of its nearest neighbor. The closest spacings of ring carbon atoms between these nearest neighbors are 3.5 Å.

(22) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Center. The coordinates can be obtained from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CBZ.IEZ, UK.

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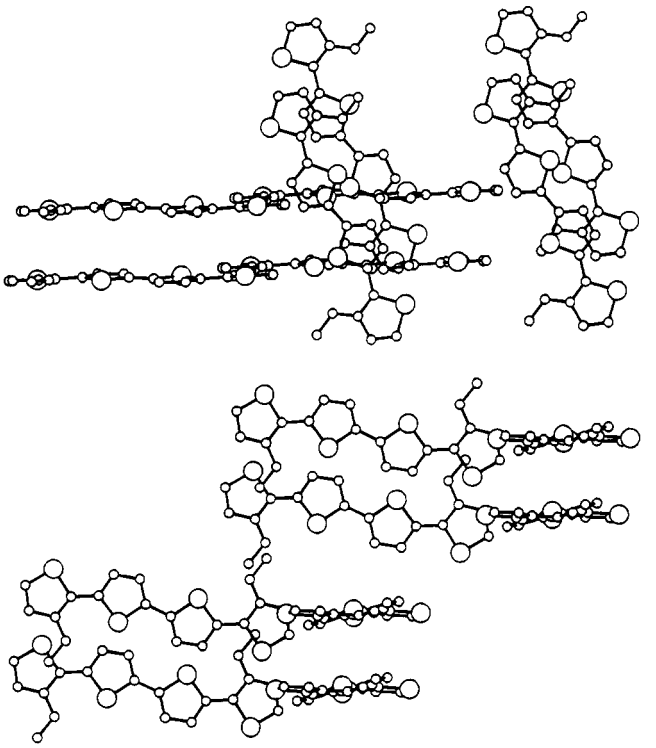

Figure 1. Two perspectives of the X-ray crystallographic results for compound **14**. The lower left hand molecule in both pictures is a "type a" molecule (see text). The two pictures are related by a 90° rotation.

Experimental Section

General Procedures. All operations except where indicated were carried out under a dry nitrogen or argon atmosphere. Proton NMR spectra were recorded at 200, 300, or 500 MHz with TMS as an internal standard. Melting points were determined without calibration. IR spectra were run in $CHCl_3$ solution or as a KBr pellet. Thiophene, 3-bromothiophene, 2,2′-bithiophene, 2,2′:5′,2″-terthiophene, and *n*-butyllithium (2.5 M in hexane) were purchased from Aldrich Chemical Co. Bulk grade THF, toluene, and methylene chloride were distilled before use. The purity of all compounds was checked by GC and TLC.

3-Methoxy-2-methylthiophene (3). n-Butyllithium (3.52 mL, 8.8 mmol) was added dropwise to a solution of 3-methoxythiophene (1 g, 9 mmol) in 50 mL dry ethyl ether at 0 °C. The reaction mixture was allowed to stir at reflux for 0.5 h before being cooled back to rt. To that solution, dimethyl sulfate (0.83 mL, 8.8 mmol) was added dropwise. Then the reaction was stirred at 35 °C for another 0.5 h. Cooling in an ice bath, a saturated NH_4OH solution was added. After stirring at rt for 1 h the aqueous layer was extracted twice with ether. The combined organic layer was washed with brine and dried with Na_2SO_4. Solvent was removed by rotary evaporation, and the product was purified by vacuum distillation to give **3** (0.95 g, 85%) as a colorless liquid. UV-vis (ether) λ_{max} 257 nm (ϵ 6.1 × 10^3); IR (neat) 2926, 1073 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.97 (d, J = 5.5 Hz, 1H), 6.81 (d, J = 5.5 Hz, 1H) , 3.82 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 154.3, 134.2, 120.0, 117.2, 59.2, 10.7; HRMS calcd for C_6H_8OS 128.0296, found 128.0298.

5-Iodo-3-methoxy-2-methylthiophene (4). *n*-Butyllithium (1.6 mL, 4.0 mmol) was added dropwise to a solution of 3-methoxy-2-methylthiophene (500 mg, 3.9 mmol) in 30 mL of dry ether at 0 °C. The reaction mixture was allowed to reflux for 0.5 h before being cooled to rt, followed by the dropwise addition of iodine (1.02 g, 4.0 mmol) in THF (10 mL). After standing overnight, water was added, the water phase was extracted with ether, and the combined organic layer was washed with saturated $Na_2S_2O_3$ and dried over Na_2SO_4. The

solvent was removed by rotary evaporation, and the residue was purified by MPLC (100% hexane) to provide 721 mg (78%) of product **4** as a bright yellowish liquid. UV-vis (ether) λ_{max} 271 nm (ϵ 6.8 × 10^3); IR (neat) 2923, 1567 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.91 (s, 1H), 3.77 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 154.3, 127.0, 122.8, 66.3, 59.5, 10.9; HRMS calcd for C_6H_7OSI 253.9262, found 253.9270.

5-(Tri-*n*-butylstannyl)-3-methoxy-2-methylthiophene (5). To a two-necked round bottom flask which was charged with compound **3** (500 mg, 3.9 mmol) in 25 mL of dry ether at 0 °C was added dropwise *n*-butyllithium (1.6 mL, 4.0 mmol). After refluxing for 0.5 h, the reaction mixture was cooled to rt and tributyltin chloride (1.08 mL, 4.0 mmol) was introduced. This reaction mixture was allowed to stir at rt overnight before water was added. The aqueous layer was extracted twice with ether, and the combined organic phase was dried over $MgSO_4$. Solvent was removed by rotary evaporation, and the residue was purified by MPLC (100% hexane) to provide 1.30 g (80%) of the title product as a yellow liquid: UV-vis (ether) λ_{max} 268 nm (ϵ 6.4 × 10^3); IR (neat) 2948, 1560, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.80 (s, 1 H), 3.80 (s, 3H), 1.57 (pent, 6H), 1.38 (sext, 6H), 1.15 (t, J = 8.1 Hz, 6H), 0.98 (t, J = 7.3 Hz, 9H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 156.0, 131.0, 124.9, 122.1, 59.1, 29.4, 27.7, 13.8, 11.0, 9.1.

2-Iodo-3-methoxythiophene (6). To a solution of 3-methoxythiophene (684 mg, 6.0 mmol) in benzene (10 mL) at 0 °C was added (in small portions) mercuric oxide (1.32 g, 6.1 mmol, yellow crystal) and iodine (1.57 g, 6.2 mmol). The mixture was stirred at rt for 0.5 h, and the precipitate was filtered out and washed with ether. The filtrate and washings were combined and washed with aqueous $Na_2S_2O_3$ and dried over Na_2SO_4. Solvent was removed by rotary evaporation, and the residue was purified by MPLC (100% hexane) to provide 1.40 g (97%) of **6** as a light-yellow liquid: UV-vis (CH_2Cl_2) λ_{max} 265 nm (ϵ 6.7 × 10^3); IR (neat) 2916, 1542 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.42 (d, J = 5.7 Hz, 1H), 6.68 (d, J = 5.7 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 130.0, 115.8, 59.3, 53.6; HRMS calcd for C_5H_5SOI 239.9106, found 239.9108; bp 131 °C/15 mmHg.

5,5′-Diiodo-2,2′-bithiophene (8). To a solution of bithiophene (1.46 g, 8.8 mmol) in benzene (10 mL) was added alternately, in small portions at 0 °C, mercuric oxide (3.84 g, 17.9 mmol, yellow crystal) and iodine (4.52 g, 17.8 mmol). The reaction mixture was then allowed to warm to rt and stirred overnight. An additional portion of iodine (0.51 g, 2.01 mmol) was added at rt, and the mixture was stirred at rt overnight once more. The reaction mixture was dissolved in chloroform and washed with saturated KI and $Na_2S_2O_3$ aqueous solution. The organic layer was then dried over Na_2SO_4. Solvent was removed by rotary evaporation, and the residue was recrystallized from a mixed-solvent of 5% chloroform/95% ethanol to provide 3.02 g (82%) of **8** as off-white flakes; UV-vis (CH_2Cl_2) λ_{max} 325nm (ϵ 1.4 × 10^4); IR (KBr) 1409 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.13 (d, J = 3.8 Hz, 2H), 6.77 (d, J = 3.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 137.7, 125.6, 72.6; HRMS calcd for $C_8H_4S_2I_2$ 417.7844, found 417.7837; mp 165–166 °C.

5,5′-Bis(tri-*n*-butyltin)-2,2′-bithiophene (9). To a two-necked round bottom flask charged with dry ether (30 mL) and bithiophene (1.8 g, 10.8 mmol) at 0 °C was added *n*-butyllithium (8.68 mL, 21.7 mmol) dropwise. The reaction mixture was allowed to reflux for 1 h at 45 °C before being cooled back to rt. Then tri-*n*-butyltin chloride (5.88 mL, 21.7 mmol) was introduced slowly, and the resulting solution was refluxed at 45 °C for 1.5 h and then reacted at rt overnight. The reaction was quenched with water, the aqueous phase was extracted with ether three times, and the combined organic phase was washed with saturated $CuSO_4$ solution and dried with Na_2SO_4. The solvent was removed by rotary evaporation and the remaining 7.07 g (88%) product was spectroscopically pure as a yellow liquid: UV-vis (CH_2Cl_2) λ_{max} 317 nm (ϵ 1.5 × 10^4); ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 3.3 Hz, 2H), 7.06 (d, J = 3.3 Hz, 2H), 1.57 (pent, 12H), 1.37 (sext, 12H), 1.16 (t, J = 8.1 Hz, 12H), 0.98 (t, J = 7.3 Hz, 18H); ^{13}C NMR (75 MHz,$CDCl_3$) δ 143.1, 136.1, 136.0, 124.7, 29.0, 27.3, 13.7, 10.9.

3,3′-Dimethoxy-2,2′-bithiophene (10). At 0 °C, *n*-butyllithium (4.1 mL, 10.1 mmol) was added dropwise to a solution of 3-methoxythiophene (1.19 g, 10.1 mmol) in THF (20 mL). Then the reaction mixture was stirred at 0 °C for 2 h before being transferred via cannula to a solution of $Fe(acac)_3$ (3.56 g, 10.1 mmol) in THF (70 mL). After refluxing for 2 h at 80 °C, the reaction was allowed to cool to rt. The red precipitate was filtered and washed with ether, and the combined organic layer was treated with saturated NH_4Cl solution and dried over Na_2SO_4. After the solvent was removed by rotary evaporation the crude product was flash chromatographed (100% hexane) and yielded 928 mg (79%) of **10** as yellow crystals: UV-vis (CH_2Cl_2) λ_{max} 320 nm (ϵ 1.6 × 10^4); IR (KBr) 2934, 1525 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, J = 5.6 Hz, 2H), 6.86 (d, J = 5.6 Hz, 2H), 3.92 (s, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 152.9, 121.9, 115.7, 113.5, 58.8; HRMS calcd for $C_{10}H_{10}O_2S_2$ 226.0122, found 226.0126; mp 112–113 °C.

3,3′-Dimethoxy-5,5′-dimethyl-2,2′-bithiophene (11). At −78 °C *n*-butyllithium (0.36 mL, 0.90 mmol) was added dropwise to a solution of compound **10** (100 mg, 0.44 mmol) in 15 mL of THF. The reaction mixture was warmed with stirring to 0 °C for 0.5 h and then recooled back to −78 °C, followed by the addition of Me_2SO_4 (113 mg, 0.9 mmol). The mixture was stirred for 3 h at −78 °C, warmed to rt for 1 h, and poured into water. The aqueous layer was extracted with ether, and the combined organic extracts were washed with brine and dried with Na_2SO_4. Solvent was removed by rotary evaporation, and the residue was purified by flash chromatography to yield 92 mg (82%) of the title compound as yellow crystals: UV-vis (CH_2Cl_2) λ_{max} 325 nm (ϵ 1.7 × 10^4); IR (KBr) 2935, 1558 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.55 (q, J = 1.54 Hz, 2H), 3.87 (s, 6H), 2.42 (d, J = 1.54 Hz, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 151.0,135.2, 114.2, 111.1, 58.5, 15.4; HRMS calcd for $C_{12}H_{14}O_2S_2$ 255.0519, found 255.0516; mp 124–125 °C.

3,3″-Dimethoxy-2,2′:5′2″-terthiophene (12). A flask was charged with compound **6** (1 g, 4 mmol), **7** (1.35 g, 2.04 mmol), 200 mg of tetrakis(triphenylphosphine)palladium(0), and toluene (15 mL). The reaction mixture was first purged with argon for 20 min and then heated to 100–110 °C overnight before being poured into saturated NH_4Cl solution. The aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over Na_2SO_4. Solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (1% of ethyl acetate in hexane) to provide 320 mg (51%) **12** as yellow crystals: UV-vis (CH_2Cl_2) λ_{max} 379 nm (ϵ 2.3 × 10^4); IR (KBr) 2934, 1560 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.14 (s, 2H), 7.04 (d, J = 5.5 Hz, 2H), 6.86 (d, J = 5.5 Hz, 2H), 3.96 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 133.4, 123.0, 121.3, 117.0, 115.7, 58.9; HRMS calcd for $C_{14}H_{12}S_3O_2$ 307.9999, found 307.9993; mp 69–70 °C.

3,3″-Dimethoxy-5,5″-dimethyl-2,2′:5′2″-terthiophene (13). Using the general procedure described above for the synthesis of **11**, compound **13** (82.5%) was obtained as yellow crystals from **12**. **13** was purified by flash chromatography (5% ethyl acetate in hexane): UV-vis (CH_3CN) λ_{max} 384 nm (ϵ 2.6 × 10^4); IR (KBr) 2910, 1564 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.00 (s, 2H), 6.56 (q, J = 1.54 Hz, 2H), 3.96 (s, 6H), 2.42 (d, J = 1.54 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0, 135.6, 133.0, 122.2, 115.6, 113.3, 58.7, 16.1; HRMS calcd for $C_{16}H_{16}S_3O_2$ 336.0312, found 336.0307; mp 80–81 °C.

3,3‴-Dimethoxy-2,2′:5′,2″:5″,2‴-quaterthiophene (14). Using the general procedure describe above for the synthesis of **12**, compound **13** was prepared from **5**, **9**, and Pd(0) reagent. Flash chromatography using 100% hexane, 3% ethyl acetate in hexane, followed by 8% ethyl acetate in hexane gave orange crystals (44%): UV-vis (CH_2Cl_2) λ_{max} 411 nm (ϵ 3.2 × 10^4); IR (KBr) 2926, 1553 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.1 (d, J = 5.5 Hz, 2H), 7.06 (d, J = 3.5 Hz, 4H), 7.05 (d, J = 3.5 Hz, 2H), 6.86 (d, J = 5.5 Hz, 2H), 3.97 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 135.6, 133.8, 123.4, 123.1, 121.6, 116.9, 115.4, 59.0; HRMS calcd for $C_{18}H_{14}O_2S_4$ 389.9878, found 389.9884; mp 127–128 °C.

3,3‴-Dimethoxy-5,5‴-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene (15). Using the general procedure described above

for the synthesis of **11**, compound **15** was obtained from **14**. **15** was purified by flash chromatography (5% ethyl acetate in hexane) giving orange crystals (85%): UV-vis λ_{max} (CH_2Cl_2) 414 nm (ϵ 3.5 × 10^4); IR (KBr) 2958, 1567 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.01 (d, J = 3.6 Hz, 2H), 7.06 (d, J = 3.6 Hz, 2H), 6.57 (q, J = 1.5 Hz, 2H), 3.92 (s, 6H), 2.43 (d, J = 1.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 136.2, 135.1, 134.0, 122.8, 122.6, 115.5, 113.0, 58.9, 16.1; HRMS calcd for $C_{20}H_{18}O_2S_4$ 418.0189, found 418.0205; mp 173–174 °C.

5,5″-Bis(tri-*n*-butylstannyl)-2,2′:5′,2″-terthiophene (16). At −78 °C *n*-butyllithium (3.3 mL, 8.3 mmol) was added dropwise to a solution of 2,2′:5′2″-terthiophene (1.02 g, 4.1 mmol) in 15 mL of THF. The reaction mixture was allowed to stir at 0 °C for 0.5 h and then recooled to −78 °C. Tri-*n*-butyltin chloride (2.25 mL, 8.3 mmol) was introduced, and the reaction was allowed to warm to rt and continued to react at that temperature for 1 h before water was added. The aqueous phase was extracted three time with ethyl ether, and the combined organic layer was washed with saturated $CuSO_4$ and dried over $MgSO_4$. Solvent was removed, and the residue was pure enough for the next step of the reaction: UV-vis (THF) λ_{max} 366 nm (ϵ 2.1 × 10^4); ^1H NMR (500 MHz, $CDCl_3$) δ 7.321 (d, J = 3.5 Hz, 2H), 7.107 (s, 2H), 7.106 (d, J = 3.5 Hz, 2H), 1.57 (pent, 12H), 1.36 (sext, 12H), 1.16 (t, J = 8.1 Hz, 12H), 0.95 (t, J = 7.3 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 136.7, 136.2, 127.8, 124.7, 124.0, 29.0, 27.3, 13.7, 11.0.

3,3‴″-Dimethoxy-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (17). An oven-dried tube was charged with compound **16** (2.3 g, 2.8 mmol), compound **6** (1.36 g, 5.7 mmol), 180 mg of bis(triphenylphosphine)palladium(II) chloride, and toluene (10 mL). The reaction mixture was first bubbled with argon for 20 min and then sealed. The tube was heated to 100–110 °C and stirred for 48 h before being cooled and poured into saturated NH_4Cl solution. The aqueous layer was extracted with dry ethyl acetate, and the organic extracts were washed with brine and dried over with Na_2SO_4. Solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (20% ethyl acetate in hexane) to provide 608 mg (46%) of the title product as red crystals: UV-vis (THF) λ_{max} 431 nm (ϵ 4.0 × 10^4); IR (KBr) 2930 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.148 (d, J = 5.5 Hz, 2H), 7.139 (d, J = 4.0 Hz, 2H), 7.112 (s, 2H), 7.109 (d, J = 4.0 Hz, 2H), 6.930 (d; J = 5.5 Hz, 2H), 3.999 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 136.3, 135.2, 134.7, 124.2, 123.8, 123.5, 122.3, 117.3, 115.1, 59.2; HRMS calcd for $C_{22}H_{16}S_5O_2$ 471.9754, found 471.9747; mp 139–140 °C.

3,3⁗″-Dimethoxy-5,5⁗″-dimethyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (18). Using the general procedure described above for the synthesis of **11**, compound **18** was obtained giving dark red crystals (87%) from **17**. **18** was purified by flash column (20% ethyl acetate in hexane): UV-vis (CH_2Cl_2) λ_{max} 438 nm (ϵ 4.2 × 10^4); IR (KBr) 2956, 1573, 786 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.077 (s, 2H), 7.067 (d, J = 4 Hz, 2H), 7.014 (d, J = 4 Hz, 2H), 6.640 (q, J = 1.5 Hz, 2H), 3.950 (s, 6H), 2.460 (d, J = 1.5 Hz, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.2, 137.1, 136.3, 135.0, 134.5, 123.9, 123.7, 122.6, 115.8, 112.6, 59.1, 16.2; HRMS calcd for $C_{24}H_{20}O_2S_5$ 500.0067, found 500.0024; mp 164–165 °C.

4,4′-Dimethoxy-5,5′-dimethyl-2,2′-bithiophene (19). Using the general procedure described above for the synthesis of **10**, **19** was obtained from **3**. Purification by flash chromatography gave light yellow crystals (78%): UV-vis ($CHCl_3$) λ_{max} 329 nm (ϵ 1.7 × 10^4); IR (KBr) 2930, 1556, 1453, 1338, 1131 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.79 (s, 2H), 3.82 (s, 6H), 2.26 (s, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.0,131.4, 112.3, 112.0, 58.6, 10.2; HRMS calcd for $C_{12}H_{14}O_2S_2$ 255.0519, found 255.0514; mp 83–84 °C.

4,4″-Dimethoxy-5,5″-dimethyl-2,2′:5′,2″-terthiophene (20). Using the general procedure describe above for the synthesis of **17**, compound **20** was obtained as yellow crystals from **4** and **7**. **20** was purified by flash chromatography (2% ethyl acetate in hexane) giving 57% yield: UV-vis (CH_2Cl_2) λ_{max} 389 nm (ϵ 2.7 × 10^4); IR (KBr) 2910, 1567 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.95 (s, 2H), 6.86 (s, 2H), 3.84 (s, 6H), 2.28 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 136.6, 131.1, 123.4, 116.1, 113.6, 59.3, 10.7; HRMS calcd for $C_{16}H_{16}S_3O_2$ 336.0312, found 336.0309; mp 103–104 °C.

4,4‴″-Dimethoxy-5,5⁗″-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene (21). Using the general procedure describe above for the synthesis of **17**, compound **21** was obtained from **5** and **9**. **21** was purified by flash chromatography (5% ethyl acetate in hexane) giving orange crystals (48%): UV-vis (CH_3CN) λ_{max} 419 nm (ϵ 3.5 × 10^4); IR (KBr) 2960, 1569 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.02 (d, J = 3.8 Hz, 2H), 6.97 (d, J = 3.8 Hz, 2H), 6.87 (s, 2H), 3.84 (s, 6H), 2.27 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 136.9, 135.4, 130.8, 124.1, 123.2, 116.1, 113.3, 59.1, 10.7; HRMS calcd for $C_{20}H_{18}S_4O_2$ 418.0190, found 418.0173; mp 182–183 °C.

3,3″-Dimethoxy-5,5″-bis(tri-*n*-butylstannyl)-2,2′:5′2″-terthiophene (22). Using the general procedure describe above for the synthesis of **16**, compound **22** was obtained as a bright yellow oil from **12**. **20** was spectroscopically pure and was used for the next step: UV-vis ($CHCl_3$) λ_{max} 392 nm (ϵ 2.7 × 10^4); ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (s, 2H), 6.86 (s, 2H), 3.96 (s, 6H), 1.53 (pent, 12H), 1.33 (sext, 12H), 1.17 (t, J = 8.1 Hz, 12H), 0.95 (t, J = 7.3 Hz, 18H); ^{13}C NMR (75 MHz, CDCl3) δ 154.7, 133.4, 133.6, 124.4, 122.6, 121.4, 58.8, 28.9, 27.3, 13.7, 10.8.

3,4′,3‴,3⁗″-Tetramethoxy-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗″,2⁗″-quinquethiophene (23). Using the general procedure describe above for the synthesis of **17**, **23** was obtained from **6** and **22**. **23** was purified by flash chromatography (15% ethyl acetate in hexane) giving red crystals (62%): UV-vis ($CDCl_3$) λ_{max} 449 nm (ϵ 4.3 × 10^4); IR (KBr) 2933, 1564, 1536 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.10 (s, 2H), 7.03 (d, J = 5.6 Hz, 2H), 6.94 (s, 2H), 6.83 (d, J = 5.6 Hz. 2H), 3.95 (s, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.9, 153.2, 133.4, 130.6, 122.6, 122.5, 116.8, 114.0, 112.6, 112.6, 58.9, 58.8; HRMS calcd for $C_{24}H_{20}O_4S_5$ 531.9965, found 531.9959; mp 150–151 °C.

3,4′,3‴,3⁗″-Tetramethoxy-5,5⁗″-dimethyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (24). Using the general procedure describe above for the synthesis of **11**, compound **24** was obtained as dark red crystals from **13**. **24** was purified by flash column (20% ethyl acetate in hexane) giving an 80% yield: UV-vis (CH_2Cl_2) λ_{max} 455 nm (ϵ 4.3 × 10^4); IR (KBr) 2940, 1570, 1634, 1098, 1077, 780 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.10 (s, 2H), 6.97 (s, 2H), 6.60 (q, J = 1.5 Hz, 2H), 3.97 (s, 6H), 3.93 (s, 6H), 2.44 (d, J = 1.5 Hz, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.2, 152.9, 134.5, 132.5, 131.5, 122.8, 121.5, 116.0, 113.0, 112.9, 59.1, 59.0, 16.1; HRMS calcd for $C_{26}H_{24}O_4S_5$ 560.0278, found 560.0280; mp 171–172 °C.

3,3″-Dimethoxy-5-methyl-2,2′:5′2″-terthiophene (25). To a solution of compound **12** (160 mg, 0.52 mmol) in THF at −78 °C was added dropwise *n*-butyllithium (0.22 mL, 0.55 mmol). The reaction mixture was allowed to warm to rt for 0.5 h before recooled back to −78 °C, and dimethyl sulfate (69 mg, 0.55 mmol) was added. The reaction mixture was then warmed up to rt again and kept stirring for 1 h before being poured into saturated NH_4OH solution. The aqueous layer was extracted with ether, and the combined organic layer was dried over Na_2SO_4. After solvent was removed, the residue was purified by MPLC (5% of ethyl acetate in hexane) to yield 135 mg (81%) of **25** as yellow crystals: UV-vis (CH_2Cl_2) λ_{max} 379 nm (ϵ 2.5 × 10^4); ^1H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, J = 3.8 Hz, 1H), 7.08 (d, J = 5.4 Hz, 1H), 7.04 (d, J = 3.8 Hz, 1H), 6.90 (d, J = 5.5 Hz, 1H), 6.62 (q, J = 0.9 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 2.44 (d, J = 0.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 152.8, 136.5, 134.0, 132.9, 123.1, 122.2, 121.6, 117.4, 116.0, 115.7, 112.9, 59.2, 59.1, 16.2; HRFABMS calcd for $C_{15}H_{14}O_2S_3$ 322.0156, found 322.0160.

3,3″,4‴,3⁗″-Tetramethoxy-5,5⁗″-dimethyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗″,2⁗″-sexithiophene (26). At 0 °C, *n*-butyllithium (0.14 mL, 0.35 mmol) was added dropwise into a solution of compound **25** (110 mg, 0.34 mmol) in 10 mL of THF. Then the reaction mixture was stirred at 0 °C for 1 h before transfer via cannula to a solution of $Fe(acac)_3$ (124 mg, 0.35 mmol) in 25 mL of THF. After refluxing 24 , the reaction was allowed to cool to rt. The red precipitate was filtered out and washed with methylene chloride, the combined organic layer was treated with saturated NH_4Cl solution and dried over Na_2SO_4. After solvent was removed, the title product was recrystallized

from 10% methylene chloride in methanol and yielded 77 mg (70%) of **26** as dark red crystals: UV-vis (CH_2Cl_2) λ_{max} 486 nm (ϵ 4.9 × 10^4); IR (KBr) 2936, 1640 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 7.43 (s, 2H), 7.13 (d, J = 3.7 Hz, 2H), 7.04 (d, J = 3.7 Hz, 2H), 6.89 (q, J = 1.4 Hz, 2H), 4.01 (s, 6H), 3.92 (s, 6H), 2.43 (d, J = 1.4 Hz, 6H); HRFABMS calcd for $C_{30}H_{26}O_4S_6$ 642.0155, found 642.0161; mp 234–236 °C.

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Supporting Information Available: ^1H or ^{13}C spectra of the compounds reported are provided (23 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead for ordering information.

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