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Synthesis of end-blocked thienyl oligomers incorporating benzo[*c*]thiophene

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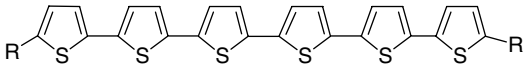
Abstract—A straightforward synthesis of end-capped bithienyl, quaterthienyl and sexithienyl systems incorporating benzo[*c*]thiophene units is presented.

Electronic properties of linear conjugated oligomers have acquired growing importance in many areas of modern chemistry. In particular, thiophene oligomers are frequently used as semiconducting materials in molecular electronic and optical devices.[1] The thiophene oligomers can advantageously replace polythiophene in organic-based electronic devices such as Schotty diodes and field effect transistors.[2]

Among the higher oligomers of thiophene, the hexamer, α-sexithiophene **1a** has been incorporated successfully into electronic and optical data processing devices.[3] α-Sexithiophenes and higher oligomers, however, are practically insoluble in organic solvents and thus are difficult to purify. Moreover, sophisticated high temperature vacuum deposition techniques are needed to incorporate them as thin films in devices. In particular, unsubstituted oligothiophenes suffer from instability as a result of the relatively higher chemical reactivity at the α-carbons of the terminal thiophene ring.[4] On the other hand, β-substitution of thiophene lowers the degree of conjugation and carrier mobility due to the out of plane twisting of the thiophene rings in the β-substituted system.[5] In contrast, substitution at the reactive α-positions of the terminal thiophenes (**1b** and **1c**) results in chemically stable oligomers,[6] Scheme 1. Several workers have reported the electrochemical and chemical synthesis of α,ω-dialkyl sexithiophenes and their utilization in field effect transistors (FETs).[7]



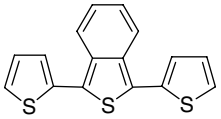
1a R = H
1b R = *n*-C_6H_{13}
1c R = CH_2O-*n*-C_6H_{13}

Scheme 1.

During the last 15 years, the synthesis and characterization of 1,3-dithienylbenzo[*c*]thiophene **2** and several of its derivatives have been reported,[8] Scheme 2.

The above-mentioned reports of oligothiophenes used for field effect transistors (FETs) and other electronic applications encouraged us to initiate our studies on the synthesis of more soluble and easily processable derivatives of oligothiophenes/sexithiophenes incorporating one or two benzo[*c*]thiophene units.

In order to realize this objective, our initial attempts to synthesize one-end-blocked 1,3-dithienylbenzo[*c*]thiophene **4a** starting from the known bromo-benzo[*c*]thiophene **3**[8e] and *n*-hexylmagnesium bromide using $Ni(dppp)Cl_2$ under Kumada conditions were unsuccessful, Scheme 3. Use of other Ni complexes such as $Ni(PPh_3)_2Cl_2$ or $Ni(dppe)Cl_2$ was also ineffective.



2

Scheme 2.

Keywords: Benzo[*c*]thiophene; End-capped thienyl oligomers; Dimerization; Electronic properties.
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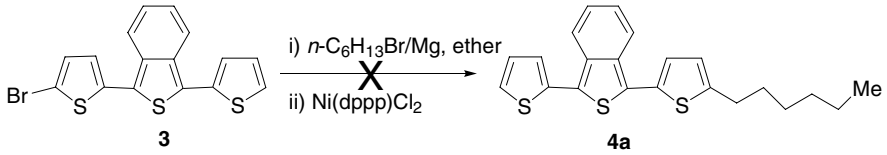
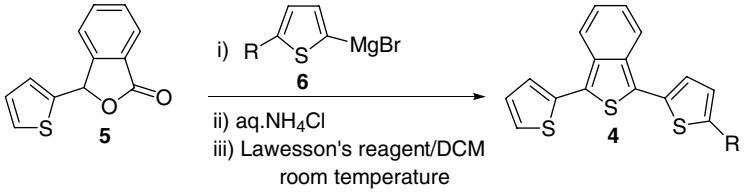


Scheme 3.



Entry	R	Yield
4a	*n*-hexyl	60%
4b	2-ethylhexyl	55%
4c	*n*-butyl	50%

Scheme 4.

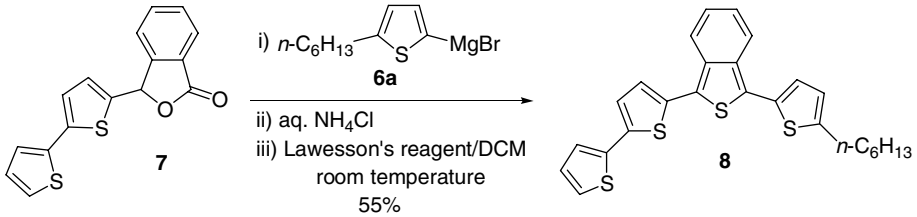
However, one-end-blocked terthienyl analogues **4a**–**c** were prepared smoothly via conventional ring opening of lactone **5** using freshly prepared 5-alkyl thienylmagnesium bromides **6**[9] in dry THF, followed by thionation and intramolecular cyclization, Scheme 4.

Similarly, one-end-blocked quaterthienyl system **8** was prepared from the known lactone **7**[8e] via lactone ring opening with 5-*n*-hexylthienylmagnesium bromide **6a**[9] followed by thionation and intramolecular cyclization using Lawesson's reagent, Scheme 5.

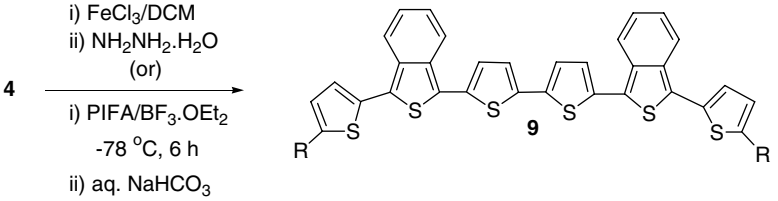
Having prepared one-end-blocked benzo[*c*]thiophenes **4** and **8**, the next task was to dimerize them in a controlled manner to afford the respective products in reasonable yields. In general, the controlled oligomerization/dimerization of several thienyl monomers is reported via oxidation of the corresponding thienyl α-carbanion using $CuCl_2$.[10] A regioselective oligomerization of 3-(alkylsulfanyl)thiophenes using $FeCl_3$ has been reported.[11] Mustafa and Shepherd reported a simple dimerization of β-trimethylsilyl substituted terthiophenes using ceric ammonium nitrate[12] (CAN). Recently Kita and co-workers reported a simple synthesis of 2,2′-bithiophene derivatives involving oxidative coupling of the corresponding alkylthiophenes using a combination of phenyliodide bis(trifluoroacetate) and $BF_3{\cdot}OEt_2$.[13] A mild $FeCl_3$ mediated oligomerization of β-substituted 1,3-dithienylbenzo[*c*]thiophenes led to the isolation of annelated sexithiophene and nonathiophene analogues.[8e]

In order to identify suitable conditions to dimerize benzo[*c*]thiophenes, various conditions were explored. Dimerization of **4a** using CAN in acetonitrile led to the isolation of **9a** in low yield (~10%). Similarly, dimerization using the lithio derivative of **4a** (generated using *n*-BuLi) and $CuCl_2$ was also found to proceed in low yield. The expected dimerization of one-end-blocked terthienyl system **4** was carried out smoothly using two different sets of conditions, Scheme 6. The conditions employed for the dimerization of benzo[*c*]thiophenes **4** and the results obtained are outlined in Table 1.

The dimerization of hexylated terthiophene **4a** using anhydrous $FeCl_3$ at room temperature for 12 h followed

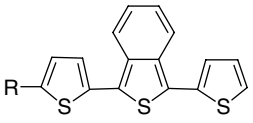
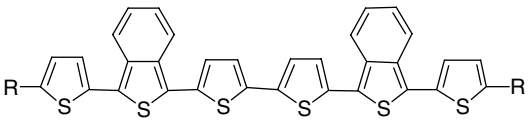
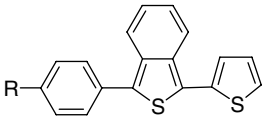
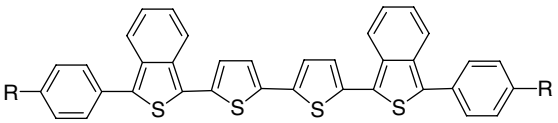
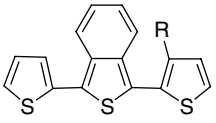
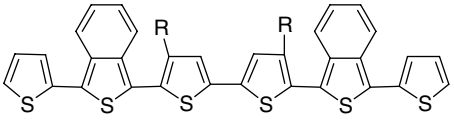
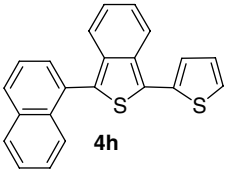
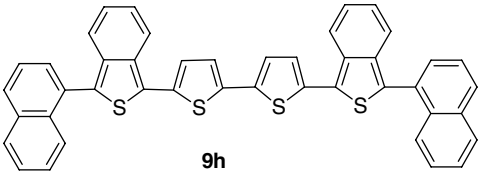
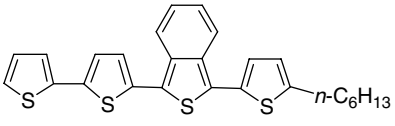


Scheme 5.



Scheme 6.

Table 1. Dimerization of benzo[*c*]thiophenes

Entry	Benzo[*c*]thiophene[14]	Dimer[15]	Yield (%)/mp
1	 **4a** R = *n*-hexyl **4b** R = 2-ethylhexyl **4c** R = *n*-butyl	 **9a** R = *n*-hexyl **9b** R = 2-ethylhexyl **9c** R = *n*-butyl	55,[a] 60[b] (liquid) 60,[a] 65[b] (liquid) 50,[a] 54[b] (liquid)
2	 **4d** R = O-*n*-C_6H_{13} **4e** R = OMe **4f** R = Me	 **9d** R = O-*n*-C_6H_{13} **9e** R = OMe **9f** R = Me	65,[a] 35[b] (220 °C) 60,[a] 40[b] (160 °C) 25,[a] 35[b] (163 °C)
3	 **4g** R = *n*-hexyl	 **9g** R = *n*-hexyl	50,[a] 65[b] (liquid)
4	 **4h**	 **9h**	27,[a] 22[b] (liquid)
5	 **8**	No reaction	

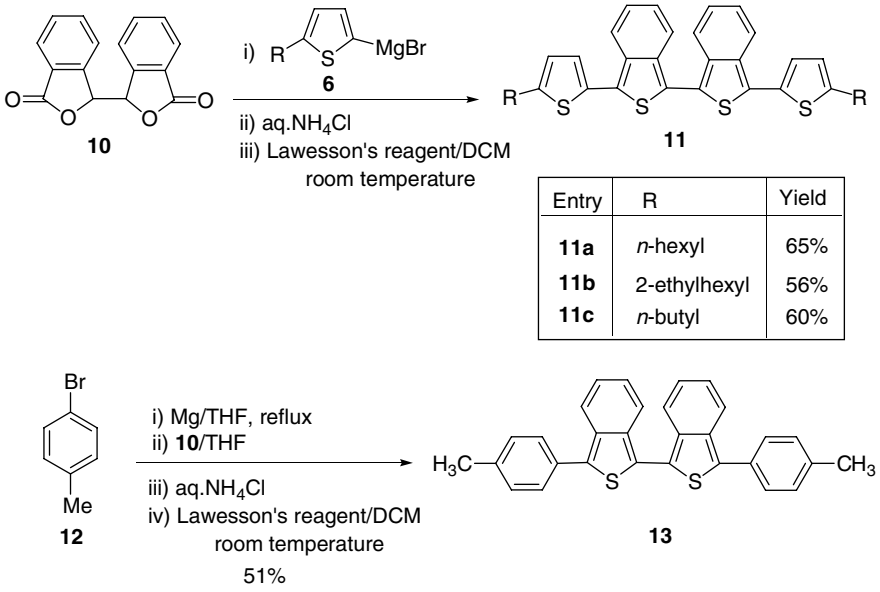
[a] Isolated yield using $FeCl_3$–DCM.
[b] Isolated yield using PIFA–BF_3·OEt_2.

by quenching with hydrazine hydrate afforded the corresponding dimer **9a** in 55% yield. Under similar conditions, dimerization of one-end-blocked benzo[*c*]thiophenes **4b** and **4c** afforded **9b** and **9c** in 60% and 50% yields, respectively (Table 1, entry 1).

It should be noted that during the above-mentioned dimerization using anhydrous $FeCl_3$, a small amount (~5%) of the starting materials **4a**–**c** was recovered even on extended reaction (more than 24 h for entry 1). Dimerization of **4a**–**c** using PIFA–BF_3·OEt_2 at −78 °C in dry THF gave the respective products **9a**–**c** in somewhat better yields. Additionally, under the PIFA–BF_3·OEt_2 conditions, the monomeric benzo[*c*]thiophenes **4a**–**c** were fully consumed. The arylated bithienyl systems **4d**–**f** were converted into the respective dimers **9d**–**f** using anhydrous $FeCl_3$ as well as PIFA–BF_3·OEt_2 (Table 1, entry 2). The β-substituted benzo[*c*]thiophene **4g** was converted into the known product **9g** in higher yield using PIFA–BF_3·OEt_2 compared to anhydrous $FeCl_3$ (Table 1, entry 3). The naphthylated benzo[*c*]thiophene **4h** afforded the corresponding dimer **9h** in poor yields (Table 1, entry 4). In the case of one-end-blocked benzo[*c*]thiophene **8**, the dimerization was found to be unsuccessful using both sets of conditions.

Finally, the end-capped benzo[*c*]thiophene based tetrathienyl systems **11a**–**c** were prepared via the lactone ring opening of commercially available diphthalide **10** using excess 5-substituted-2-thienylmagnesium bromide[9] in dry THF, Scheme 7. Work-up followed by thionation led to expected products **11a**–**c**[16] in 65%, 56% and 60% yields, respectively. Using identical conditions, ring opening of **10** with freshly prepared *p*-tolylmagnesium bromide led to the formation of *p*-tolyl-capped benzo[*c*]thiophene **13**[16] in 51% yield.

The UV–vis spectra of the benzo[*c*]thiophenes exhibited strong absorption between 438 and 510 nm, the exact values are presented in Table 2. The introduction of alkyl α-substituents (*n*-hexyl, 2-ethylhexyl, *n*-butyl) into **2** (433 nm)[8e] increased the absorption (Table 2, **4a**–**c**). A similar effect was observed for **8** compared to the parent benzo[*c*]thiophene (458 nm).[8e] The long-wavelength



Entry	R	Yield
11a	*n*-hexyl	65%
11b	2-ethylhexyl	56%
11c	*n*-butyl	60%

Scheme 7.

Table 2. UV–vis spectral data of benzo[*c*]thiophenes

	Benzo[*c*]thiophenes															
	4a	**4b**	**4c**	**8**	**9a**	**9b**	**9c**	**9d**	**9e**	**9f**	**9g**	**9h**	**11a**	**11b**	**11c**	**13**
λ_{max} (nm) (DCM)	440	442	438	468	504	510	508	495	480	490	484	476	468	472	494	449

Table 3. Fluorescence spectral data of benzo[*c*]thiophenes

	Benzo[*c*]thiophenes							
	4a	**4c**	**8**	**9a**	**9e**	**9d**	**11a**	**13**
$\lambda_{excitation}$ (nm) ($CHCl_3$)	440	438	468	504	480	495	468	449
$\lambda_{emission}$ (nm) ($CHCl_3$)	561	543	584	600	582	602	531	600

absorption bands for dimers **9a**–**c** were shifted by 64 nm, 68 nm and 70 nm from the respective monomers **4a**–**c**.

Qualitative fluorescence spectral data for some of the benzo[*c*]thiophenes are presented in Table 3. Monomeric benzo[*c*]thiophenes **4a**, **4c** and **8**, emit light at 563 nm, 543 nm and 584 nm, respectively. Bis-benzannelated tetra-thiophene **11a**, and bis-benzannelated symmetrical bi-thiophene **13**, emit light at 531 nm and 600 nm, respectively. Dimeric benzo[*c*]thiophene analogs **9a**, **9d**, and **9e** emit light in the 582–602 region.

In summary, one-end-blocked benzannelated terthienyl and quaterthienyl systems are prepared in reasonable yields. Dimerization of the one-end-blocked terthienyl system led to the formation of benzo[*c*]thiophene incorporated sexithiophenes in reasonable yields using anhydrous $FeCl_3$ or PIFA–$BF_3{\cdot}OEt_2$. Except for benzo[*c*]thiophenes possessing alkoxy units, the dimerization yield was good when PIFA–$BF_3{\cdot}OEt_2$ was used. Apart from benzo[*c*]thiophene **13**, all the other benzo[*c*]thiophenes were found to be soluble in common organic solvents. The highly soluble nature of these end-blocked benzo[*c*]thiophenes may allow them to find use in LED and field effect transistor (FET) applications.

Acknowledgements

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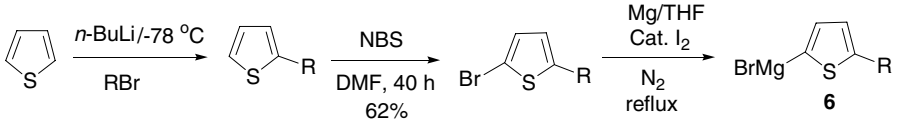
9. The required 5-substituted thienylmagnesium bromides **6** were prepared as mentioned below:



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14. For the preparation of **4d**–**h**: see Ref. 8h.
Representative procedure for the preparation of **4a**–**c** *and* **8**: A solution of 2-bromo-5-(2-ethylhexyl)thiophene (2.28 g, 8.32 mmol) in dry THF (20 mL) was added dropwise (~15 min) to a refluxing mixture of magnesium turnings (0.239 g, 9.98 mmol) containing a catalytic amount of iodine (20 mg) in dry THF (100 mL) under N_2. The reaction mixture was refluxed for 2 h to ensure the completion of Grignard formation. The Grignard reagent was slowly added via an addition funnel to a solution of 3-(2-thienyl)phthalide **5** (1.7 g, 8.32 mmol) in dry THF (30 mL) at room temperature. The reaction mixture was stirred for 6 h at room temperature and then poured over ice-cold ammonium chloride solution. The crude product was extracted into DCM (75 mL) and dried (Na_2SO_4). Then it was treated with Lawesson's reagent (1.67 g, 4.14 mmol) at room temperature for 6 h. The solvent was removed, and the residue was gently heated (fume hood) on a steam bath with ethanol (20 mL). Purification of the crude product by column chromatography (neutral alumina; eluent:hexane) afforded **4b** as a thick yellow liquid (1.86 g, 55%).
Spectral data: For **4b**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.99–0.98 (m, 7H), 1.40–1.57 (m, 8H), 2.81 (d, $J = 6.80$ Hz, 2H), 6.63 (d, $J = 3.2$ Hz, 1H), 6.89–6.91 (m, 1H), 6.96 (d, $J = 3.6$ Hz, 1H), 7.03 (t, $J = 3.7$ Hz, 1H), 7.22–7.29 (m, 2H), 7.45–7.47 (m, 2H), 8.06 (m, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 10.78, 14.09, 22.97, 25.54, 28.77, 32.22, 33.78, 34.63, 121.41, 121.68, 122.85, 125.13, 125.55, 126.48, 126.80, 127.77, 129.27, 133.19, 134.78, 135.21, 135.77, 144.27, 145.10, 146.12. MS *m/z* (%): 410 (22, M^+), 311 (73), 215 (54), 114 (08). $C_{24}H_{26}S_3$: C, 70.19; H, 6.38; S, 23.43. Found: C, 70.10; H, 6.31; S, 23.59.
For **8**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.92 (t, $J = 6.87$ Hz, 3H), 1.27–1.36 (m, 4H), 1.43 (t, $J = 7.20$ Hz, 2H), 1.71–1.77 (m, 2H), 2.85 (t, $J = 7.65$ Hz, 2H), 6.81 (d, $J = 3.8$ Hz, 1H), 7.03–7.05 (m, 1H), 7.11–7.16 (m, 3H), 7.18–7.21 (m, 1H), 7.22–7.25 (m, 3H), 7.94–7.97 (m, 2H). ^{13}C NMR ($CDCl_3$, 125.6 MHz): δ 14.23, 22.72, 28.96, 30.37, 31.70, 123.76, 124.60, 124.65, 125.01, 125.47, 125.82, 128.05, 146.86. $C_{26}H_{24}S_4$: C, 67.20; H, 5.21; S, 27.60. Found: C, 67.08; H, 5.25; S, 27.62.
15. *Representative procedure for* **9a**–**h**:
Dimerization using $FeCl_3$: A solution of **4b** (0.2 g, 0.48 mmol) in CH_2Cl_2 (30 mL) was treated with $FeCl_3$ (0.07 g, 0.48 mmol) under a nitrogen atmosphere at room temperature for 12 h. The reaction mixture was then treated with a dilute solution of $NH_2NH_2{\cdot}H_2O$ (3 × 5 mL). The organic layer was separated and dried (Na_2SO_4). Removal of the solvent followed by column chromatographic purification (silica gel; EtOAc–hexane; 1:1) gave dimer **9b** as a dark brown liquid (0.23 g, 60%).
Dimerization using $PIFA–BF_3{\cdot}OEt_2$: $BF_3{\cdot}Et_2O$ (0.074 g, 0.532 mmol) and PIFA (0.226 g, 0.532 mmol) were added sequentially to a stirred solution of **4a** (0.2 g, 0.590 mmol) in CH_2Cl_2 (20 mL) at −78 °C under a nitrogen atmosphere. The reaction mixture was stirred at the same temperature for 6 h. Aqueous work-up with saturated $NaHCO_3$ (10 mL) at 0 °C followed by column chromatographic purification (silica gel; EtOAc–hexane; 1:1) gave dimer **9a** as a red sticky liquid (0.23 g, 60%).
Spectral data: For **9b**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.91–1.21 (m, 12H), 1.41–1.72 (m, 18H), 2.85 (d, $J = 5.88$ Hz, 4H), 6.83–6.91 (m, 2H), 7.16–7.23 (m, 4H), 7.37–7.40 (m, 6H), 7.83–8.06 (m, 4H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 10.68, 14.09, 22.96, 25.39, 28.73, 32.34, 34.16, 41.29, 121.53, 121.77, 123.23, 124.48, 125.58, 125.93, 126.33, 126.54, 128.94, 130.47, 135.65, 136.18, 139.08, 141.75, 145.18, 146.79. GC MS: (818 M^+), $C_{48}H_{50}S_6$: C, 70.37; H, 6.15; S, 23.48. Found: C, 70.24; H, 6.21; S, 23.55.
For **9d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, $J = 6.84$ Hz, 6H), 1.34–1.47 (m, 8H), 1.51–1.55 (m, 4H), 1.81 (quin, $J = 7.3$ Hz, 4H), 4.01 (t, $J = 6.6$ Hz, 4H), 7.04 (d, $J = 8.8$ Hz, 4H), 7.11–7.21 (m, 4H), 7.24 (d, $J = 3.88$ Hz, 2H), 7.27 (d, $J = 3.92$ Hz, 2H), 7.59 (d, $J = 8.76$ Hz, 4H), 7.77 (d, $J = 8.8$ Hz, 2H), 8.02 (d,

$J = 8.8$Hz, 2H). MS (MALDI-TOF) calcd 782.2. Found: 782.6. $C_{48}H_{46}S_4O_2$: C, 73.62; H, 5.92; S, 16.38. Found: C, 73.56; H, 6.10; S, 16.45.

For **9e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 6H), 7.05 (d, $J = 8.8$ Hz, 4H), 7.22–7.27 (m, 6H), 7.29 (d, $J = 3.92$ Hz, 2H), 7.59 (d, $J = 8.8$ Hz, 4H), 7.75 (d, $J = 8.8$Hz, 2H), 8.01 (d, $J = 8.8$ Hz, 2H). MS (MALDI-TOF) $C_{38}H_{26}O_2S_4$: calcd 642.0. Found: 642.4. $C_{38}H_{26}S_4O_2$: C, 70.99; H, 4.08; S, 19.95. Found: C, 70.85; H, 4.19; S, 20.05.

For **9h**: ^{1}H NMR (400 MHz, $CDCl_3$): 6.79–6.81 (m, 4H), 6.96–7.18 (m, 4H), 7.27–7.37 (m, 4H), 7.22 (d, $J =$ 4.41 Hz, 2H), 7.42 (d, $J = 7.84$ Hz, 2H), 7.46 (d, $J = 0.96$ Hz, 2H), 7.48 (d, $J = 1.44$ Hz, 2H) 7.75 (d, $J =$ 8.28 Hz, 2H), 7.79 (d, $J = 8.28$ Hz, 2H), 7.86 (d, $J = 8.81$ Hz, 2H), MS (MALDI-TOF) $C_{44}H_{26}S_4$: calcd 682.0. Found: 681.83. $C_{44}H_{26}S_4$: C, 77.38; H, 3.84; S, 18.78. Found: C, 77.51; H, 3.80; S, 18.69.

16. *Representative procedure for* **11a–c** *and* **13**: 2-Bromo-5-butylthiophene (4.93 g, 22.5 mmol) was added slowly to a refluxing mixture of magnesium turnings (0.65 g, 27.13 mmol) and iodine (20 mg) in dry THF and then refluxed for 6 h to ensure completion of Grignard formation. The cooled Grignard reagent was added slowly via an addition funnel to a solution of diphthalide **10** (2 g, 7.51 mmol) in dry THF (50 mL) at 0 °C. The reaction mixture was stirred for 6 h at room temperature and then poured over ice-cold ammonium chloride solution. The intermediate was extracted into CH_2Cl_2 (2×50 mL) and dried (Na_2SO_4). The dried extract was treated with Lawesson's reagent (3.05 g, 7.51 mmol) and then stirred at room temperature for 6 h. Work-up and column chromatographic purification (neutral alumina, hexane) furnished **11c** as a black solid (2.44 g, 60%); mp 80 °C. *Spectral data*: For **11c**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.02 (t, $J = 3.85$ Hz, 6H), 1.44–1.50 (m, 4H), 1.71–1.77 (m, 4H), 2.85 (t, $J = 7.27$ Hz, 4H), 6.82 (d, $J = 3.05$ Hz, 2H), 6.91–7.21 (m, 6H), 7.85 (d, $J = 9.2$ Hz, 2H), 8.01 (d, $J = 9.2$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.6 MHz): δ 13.99, 22.38, 30.07, 33.86, 121.74, 122.02, 123.82, 124.79, 125.06, 125.43, 133.11, 134.84, 136.92, 146.78. $C_{32}H_{30}S_4$: C, 70.80; H, 5.57; S, 23.63. Found: C, 70.64; H, 5.53; S, 23.83.

For **13**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.43 (s, 6H), 7.09–7.11 (m, 4H), 7.30 (d, $J = 7.08$ Hz, 4H), 7.60 (d, $J = 8.0$ Hz, 4H), 7.83–7.86 (m, 4H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 21.26, 121.21, 121.85, 124.35, 129.11, 129.79, 131.14, 134.87, 135.75, 136.89, 137.62. MS m/z (%): 446 (22, M^+), 298 (64), 208 (72), 165 (54). $C_{30}H_{22}S_2$: C 80.68; H, 4.96; S, 14.36. Found: C, 80.79; H, 4.91; S, 14.30.