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Synthesis of 1,3-disubstituted benzo[*c*]thiophene analogs containing benzo[*b*]thiophene/benzo[*b*]pyrrole

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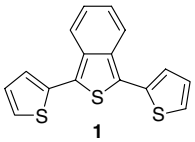
Abstract—The synthesis of 1,3-disubstituted benzo[*c*]thiophene analogs incorporating benzo[*b*]thiophene/benzo[*b*]pyrrole units is described.

The realization of durable thin layer electro-optical devices employing organic semiconductors has resulted in the design and development of different types of organic materials for application in organic light-emitting diodes (OLEDs),[1] organic solar cells (OSC)[2] and organic field-effect transistors (OFETs).[3] In recent years, there has been considerable interest in the synthesis of new low band-gap oligomers in view of their potentially superior conductivity and nonlinear optical properties. In particular, thiophene oligomers are the most frequently used semi-conducting materials in molecular electronic and optical devices.[4] The synthesis and investigation of well-defined model oligomers has recently become useful in gaining insight into the structural and electronic peculiarities of the corresponding polymers. In particular, the extent of conjugation does not lead to major differences between thienyl oligomers and polymers, since electronic properties are saturated after a particular chain length.



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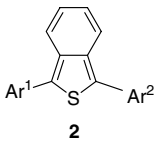

2

The synthesis and characterization of 1,3-dithienylbenzo-[*c*]thiophene **1** has been reported independently by four different groups.[5] During the last fifteen years, a plethora of 1,3-disubstituted benzo[*c*]thiophene analogs have been reported.[6–8] Since benzo[*c*]thiophenes containing other heterocycles are yet to be explored, our focus is centred on the synthesis of such types of reasonably stable derivatives as potential electro-optical materials.

In continuation of our studies on the synthesis of 1,3-diarylbenzo[*c*]thiophenes,[9] we report here our preliminary work on the synthesis of benzo[*c*]thiophene analogs incorporating heterocycles such as benzo[*b*]thiophene/benzo[*b*]pyrrole.

Conventional Friedel–Crafts phthaloylation of benzo[*b*]heterocycles **4a–c**[10] in the presence of anhydrous $AlCl_3$ in DCM led to the isolation of keto-acids **5a–c**. Reduction of the ketone-carbonyl function of **5a–c** using $NaBH_4$ in THF–MeOH at reflux followed by acid catalyzed cyclization afforded the corresponding lactones **6a–c**[11] in moderate yields (Scheme 1).

Ring-opening of lactones **6a–c** using freshly prepared aryl/hetero-aryl Grignards,[12] followed by workup using aq NH_4Cl solution, led to the corresponding keto-alcohols. A DCM solution of the keto-alcohol on thionation using 0.5 equiv of Lawesson's reagent followed by cyclization and subsequent column chromatographic purification afforded benzo[*c*]thiophene analogs **7a–o**[13] in 40–60% yields (Scheme 2).

Details such as the nature of the lactones, Grignards and the respective products obtained along with their yields are presented in Table 1.

Keywords: Benzo[*c*]thiophene; Lactones; Grignard; Thionation; Benzo[*b*]thiophene; Benzo[*b*]pyrrole.
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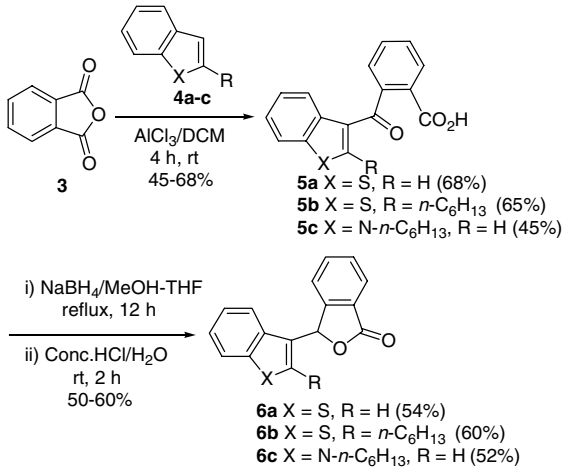
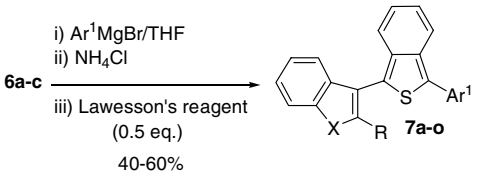


Scheme 1.



Scheme 2.

The reaction proceeded smoothly with a variety of aryl/hetero-aryl Grignards[12] to afford benzo[*c*]thiophenes **7a**–**o**[13] in moderate yields. The ring opening of lactone **6a** using thienyl-2-magnesium bromide followed by thionation afforded benzo[*c*]thiophene **7a** in 54% yield as an orange solid (entry 1). Reaction of lactone **6a** with hexyl-substituted-2-thienylmagnesium bromides led to the corresponding benzo[*c*]thiophenes **7b** and **7c** as thick

Table 1. Synthesis of benzo[*c*]thiophene analogs containing benzo[*b*]thiophene/benzo[*b*]pyrrole

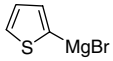
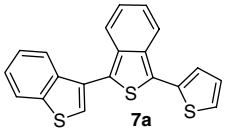
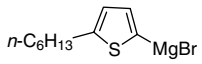
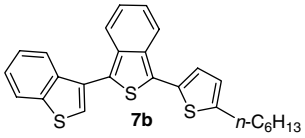
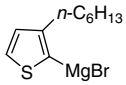
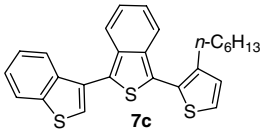
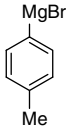
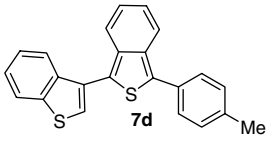
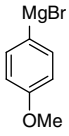
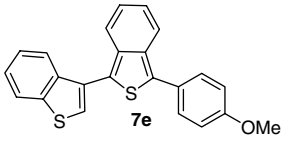
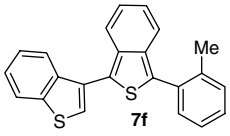
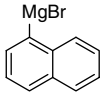
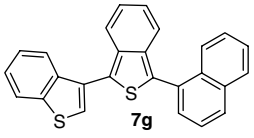
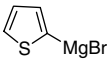
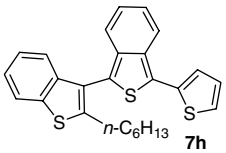
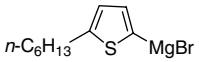
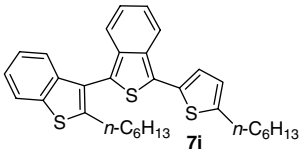
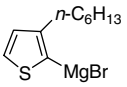
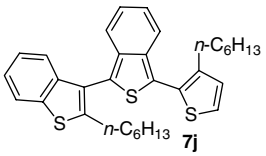
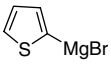
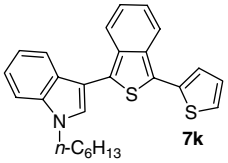
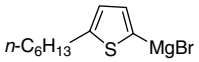
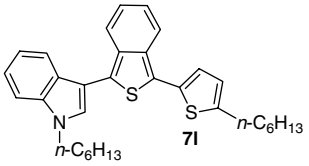
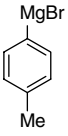
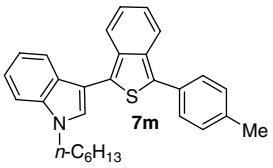
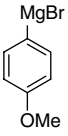
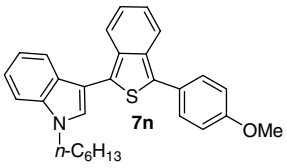
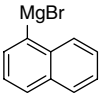
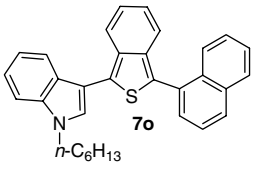
Entry	Lactone	ArMgBr[12]	Product[13]	Yield[a] (%) mp
1	**6a**		 **7a**	54 (118 °C)
2	**6a**		 **7b**	56 (thick liquid)
3	**6a**		 **7c**	60 (thick liquid)
4	**6a**		 **7d**	48 (thick liquid)
5	**6a**		 **7e**	55 (105 °C)
6	**6a**		 **7f**	50 (62 °C)
7	**6a**		 **7g**	40 (78 °C)

Table 1 (*continued*)

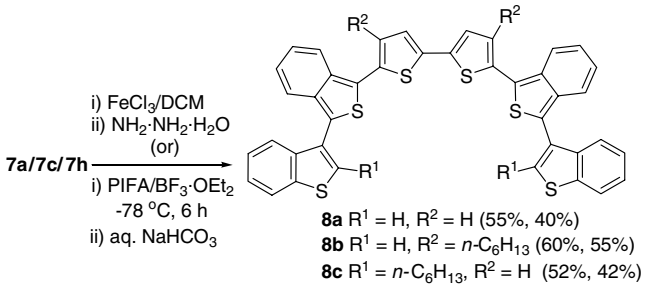
Entry	Lactone	ArMgBr[12]	Product[13]	Yield[a] (%) mp
8	**6b**		 **7h**	45 (thick liquid)
9	**6b**		 **7i**	50 (thick liquid)
10	**6b**		 **7j**	56 (thick liquid)
11	**6c**		 **7k**	45 (thick liquid)
12	**6c**		 **7l**	48 (thick liquid)
13	**6c**		 **7m**	42 (thick liquid)
14	**6c**		 **7n**	45 (thick liquid)
15	**6c**		 **7o**	40 (thick liquid)

[a] Isolated yield after column chromatography.

yellow liquids (entries 2 and 3). Lactone**6a** underwent similar reactions with aryl Grignards to afford products **7d**–**g** (entries 4–7).

Ring opening of the 2-hexyl-substituted benzo[*b*]thiophenyl lactone **6b** with thienyl-2-magnesium bromides followed by thionation led to the isolation of benzo[*c*]thiophenes **7h**–**j** as thick yellow liquids (entries 8–10). Reaction of 1-hexylindolyl lactone **6c** with aryl/heteroaryl Grignards followed by thionation afforded the corresponding benzo[*c*]thiophenes **7k**–**o** as thick yellow liquids (entries 11–15).

The benzo[*c*]thiophenes **7a/7c/7h** were smoothly dimerized using either anhydrous $FeCl_3$ in DCM at room temperature or PIFA–$BF_3{\cdot}OEt_2$ at −78 °C to yield the respective dimers **8a**–**c**[14] as dark solids in moderate yields, Scheme 3.



Scheme 3.

It should be noted that with **7a** and **7c**, the dimerization proceeded selectively at the thiophene-2-position rather than the 2-position of benzo[*b*]thiophene.

Finally, Vilsmeier–Haack formylation of **7a** using DMF–$POCl_3$ in dry DCM at 60 °C followed by column chromatographic purification led to mono-aldehyde **9**[15] in 70% yield as a red solid. Condensation of aldehyde **9** with malononitrile using piperidine/thiophene-2-acetonitrile and ^{t}BuOK as a base afforded cyano-vinylenes **10a** and **10b**[16] in 55% and 60% yields, respectively (Scheme 4). Wittig reaction of aldehyde **9** with 4-*N*,*N*-dibutylaminobenzylphosphonium iodide using THF-MeOH/*n*-BuLi afforded the corresponding *Z*-vinylene **11**[17] in 48% yield as a thick red liquid.

In summary, the synthesis of a variety of benzo[*c*]thiophene analogs possessing heterocycles such as benzo[*b*]thiophene/benzo[*b*]pyrrole has been achieved in reasonable yields. The free benzo[*c*]thiophenes were smoothly dimerized using either anhydrous $FeCl_3$ or PIFA–BF_3·OEt_2. The Vilsmeier–Haack formylation of 1-benzo[*b*]thienyl-3-thienyl-benzo[*c*]thiophene followed by condensation led to the synthesis of conjugated vinylenes. Further work on photophysical/electrochemical properties of these benzo[*c*]thiophene analogs is in progress.

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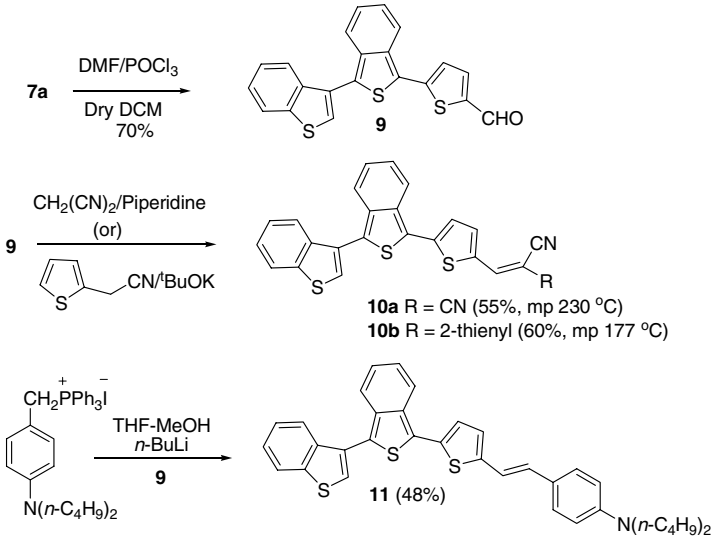

Scheme 4.

R. M. *J. Org. Chem.* **1998**, *63*, 3105–3112; (b) Strassler, C.; Davis, N. E.; Kool, E. T. *Helv. Chim. Acta* **1999**, *82*, 2160–2171; (c) Tan, S.; Bhowmik, A. K.; Thakur, M.; Lakshmikantham, M. V.; Cava, M. P. *J. Chem. Phys.* **2000**, *112*, 383–385.

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10. 2-Hexyl-benzo[*b*]thiophene **4b** was prepared from **4a** via lithiation using *n*-BuLi/THF at −78 °C followed by quenching with hexyl bromide. *N*-*n*-Hexylbenzo[*b*]pyrrole **4c** was prepared via 1-hexylation of indole under PTC conditions.
11. *A representative procedure for the preparation of lactone* **6a**: A suspension of anhydrous aluminium chloride (1.8 g, 1.35 mmol) and phthalic anhydride (1 g, 0.67 mmol) in dry CH_2Cl_2 (50 mL) was stirred for 0.5 h at room temperature. A solution of benzo[*b*]thiophene (0.99 g, 0.74 mmol) in CH_2Cl_2 (10 mL) was slowly added (10 minutes). The resulting red coloured reaction mixture was stirred for 4 h at room temperature, then poured into ice water containing HCl (25 mL in 100 mL of water). The organic layer was separated and dried (Na_2SO_4). Removal of the solvent in vacuo afforded **5a** (1.29 g, 68%). Keto-acid **5a** (1.2 g, 4.25 mmol) was dissolved in THF–MeOH (50 mL 2:5 v/v), and $NaBH_4$ (1.57 g, 42.55 mmol) was added slowly at 0 °C. The reaction mixture was refluxed for 12 h and poured into crushed ice. It was then acidified with conc. HCl and stirred for 2 h at room temperature. The precipitated lactone **6a** was filtered and dried (0.61 g, 54%). Compound **6a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.80 (s, 1H), 7.35 (s, 1H), 7.38–7.41 (m, 2H), 7.50 (d, $J = 7.5$ Hz, 1H), 7.63 (d, $J = 7.5$ Hz, 1H), 7.68–7.74 (m, 2H), 7.88 (t, $J = 4.5$ Hz, 1H), 8.03 (d, $J = 7.5$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.72, 122.00, 123.06 (2C), 124.74, 125.09, 125.94, 126.30, 126.72, 129.73, 131.04, 134.35, 137.16, 140.84, 148.11, 170.18.
12. The required aryl/hetero-aryl Grignard reagents were prepared from the corresponding bromo compounds by refluxing with magnesium in dry THF under an N_2 atmosphere.
13. *A representative procedure for* **7a**: Freshly prepared thienyl magnesium bromide [from 2-bromo thiophene (0.36 g, 2.25 mmol) and Mg (0.06 g, 2.65 mmol)] was added to a solution of phthalide **6a** (0.5 g, 1.87 mmol) at 0 °C. After the addition was completed, the reaction mixture was stirred at room temperature for 4 h, then poured over ice-cooled NH_4Cl solution and extracted with CH_2Cl_2 (100 mL) and dried (Na_2SO_4). The filtered solution was then treated with Lawesson's reagent (0.37 g, 0.93 mmol) and stirred at room temperature for 3 h. The solvent was removed and the residue was gently heated on a steam bath with ethanol (10 mL). The ethanol was removed and the crude product was purified by column chromatography (alumina, hexane) to afford benzo[*c*]thiophene **7a** as an orange solid (0.35 g, 54%).
Compound **7a**: mp 118 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04–7.10 (m, 2H), 7.18–7.21 (m, 1H), 7.35 (d, $J = 4.8$ Hz, 1H), 7.45–7.50 (t, $J = 7.8$ Hz, 1H), 7.53–7.58 (m, 2H), 7.71 (d, $J = 4.2$ Hz, 1H), 7.76–7.80 (m, 2H), 7.95 (d, $J = 7.8$ Hz, 1H), 8.60 (d, $J = 7.8$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 119.79, 119.88, 120.91, 122.00, 122.30, 122.77, 122.86, 123.86, 124.33, 124.98, 125.03, 125.33, 125.39, 127.11, 127.95, 133.85, 136.79, 139.79, 140.20, 140.85. Anal. Calcd for $C_{20}H_{12}S_3$: C, 68.93; H, 3.47; S, 27.60. Found: C, 68.79; H, 3.57; S, 27.64.
Compound **7b**: thick yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, $J = 7.05$ Hz, 3H), 1.30–1.44 (m, 6H), 1.73 (m, 2H), 2.86 (t, $J = 7.65$ Hz, 2H), 6.81 (d, $J = 3.6$ Hz, 1H), 7.02 (t, $J = 6.4$ Hz, 1H), 7.11 (t, $J = 6.15$ Hz, 1H), 7.18 (d, $J = 3.6$ Hz, 1H), 7.38–7.42 (m, 2H), 7.54 (d, $J = 9.0$ Hz, 1H), 7.59 (s, 1H), 7.91–8.00 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.10, 22.61, 28.86, 30.29, 31.63 (2C), 121.56, 121.72, 122.91, 123.37, 124.06, 124.40, 124.60, 124.88 (2C), 125.25, 125.37, 126.12, 127.93, 129.11, 133.18, 134.48, 137, 138.32, 140.30, 146.59. Anal. Calcd for $C_{26}H_{24}S_3$: C, 72.18; H, 5.59; S, 22.23. Found: C, 72.28; H, 5.52; S, 22.20.
Compound **7h**: thick yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.71 (t, $J = 7.5$ Hz, 3H), 1.08–1.31 (m, 6H), 1.60–1.69 (m, 2H), 2.89 (t, $J = 7.8$ Hz, 2H), 6.78–6.83 (m, 1H), 6.87–6.93 (m, 1H), 6.99–7.09 (m, 2H), 7.15–7.32 (m, 3H), 7.36 (d, $J = 3.0$ Hz, 1H), 7.60–7.72 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.11, 22.61, 29.00, 29.88, 31.62, 31.90, 119.78, 120.20, 120.46, 121.93, 122.19, 122.27, 122.54, 122.95, 123.55, 123.84, 124.17, 124.56, 124.58, 125.17, 125.42, 127.89, 134.02, 138.18, 139.25, 146.91. Anal. Calcd for $C_{26}H_{24}S_3$: C, 72.18; H, 5.59; S, 22.23. Found: C, 72.30; H, 5.45; S, 22.25.
Compound **7l**: thick yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82–0.92 (m, 6H), 1.29–1.42 (m, 12H), 1.68–1.78 (m, 2H), 1.84–1.93 (m, 2H), 2.84 (t, $J = 7.65$ Hz, 2H), 4.16 (t, $J = 7.2$ Hz, 2H), 6.79 (d, $J = 3.6$ Hz, 1H), 6.97–7.02 (m, 1H), 7.07–7.12 (m, 1H), 7.14 (d, $J = 3.3$ Hz, 1H), 7.16–7.19 (m, 1H), 7.21–7.31 (m, 1H), 7.38–7.41 (m, 2H), 7.70 (d, $J = 8.7$ Hz, 1H), 7.91 (d, $J = 7.8$ Hz, 1H), 7.94 (d, $J = 9$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.04, 14.13, 22.58, 22.63, 26.75, 28.89, 30.20, 30.30, 31.45, 31.64 (2C), 46.68, 108.55, 109.79, 120.13, 120.44, 121.47, 122.16, 122.41, 123.14, 124.32, 124.50, 124.74, 125.18, 127.14, 127.19 (2C), 133.92, 134.67, 135.44, 136.53, 145.73. Anal. Calcd for $C_{32}H_{37}NS_2$: C, 76.90; H, 7.46; N, 2.80, S, 12.83. Found: C, 76.78; H, 7.62; N, 2.63, S, 12.96.
14. Compound **8a**: mp 130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.05–7.10 (m, 2H), 7.17–7.28 (m, 4H), 7.32–7.33 (m, 2H), 7.39–7.44 (m, 4H), 7.59 (d, $J = 8.7$ Hz, 2H), 7.64 (s, 2H), 7.94–7.98 (m, 4H), 8.07 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.43, 121.76, 121.94, 122.95, 123.29, 123.52, 124.26, 124.36, 124.69, 124.98, 125.39, 125.97, 126.43, 126.81, 134.80, 135.03, 136.72, 137.17, 138.20, 140.33. Anal. Calcd for $C_{40}H_{22}S_6$: C, 69.13; H, 3.19; S, 27.68. Found: C, 69.00; H, 3.10; S, 27.90.
Compound **8b**: mp 180 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (t, $J = 6.5$ Hz, 6H), 1.17–1.24 (m, 12H), 1.54–1.65 (m, 4H), 2.69 (t, $J = 7.54$ Hz, 4H), 7.05–7.20 (m, 7H), 7.34–7.41 (m, 4H), 7.57–7.62 (m, 3H), 7.74–7.77 (m, 3H), 7.90–7.98 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.12, 22.61, 29.13, 29.40, 30.86, 31.63, 121.57, 121.67, 122.97, 123.38, 124.06, 124.43, 124.67, 124.87, 124.96, 126.00, 126.29, 127.34, 127.88, 129.08, 136.34, 137.23, 137.29, 138.30, 140.37, 143.14. Anal. Calcd for $C_{52}H_{46}S_6$: C, 72.34; H, 5.37; S, 22.29. Found: C, 72.50; H, 5.30; S, 22.20.
15. Compound **9**: mp 148 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10–7.15 (m, 1H), 7.28–7.31 (m, 1H), 7.42–7.48 (m, 3H), 7.62 (d, $J = 9.0$ Hz, 1H), 7.68 (s, 1H), 7.78 (d, $J = 3.9$ Hz, 1H), 7.91–7.98 (m, 2H), 8.11 (d, $J = 9.0$ Hz, 1H), 9.92 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.14, 122.26, 123.01, 123.10, 124.55, 124.84, 125.14, 125.19, 126.41, 127.16, 128.31, 130.03, 135.89, 137.08 (2C), 137.45, 137.97, 140.35, 141.83, 146.13, 182.33. Anal. Calcd for $C_{21}H_{12}OS_3$: C, 66.99; H, 3.21; S, 25.55. Found: C, 66.86; H, 3.41; S, 25.71.

16. Compound **10b**: mp 178 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07–7.18 (m, 2H), 7.26 (d, $J = 6.6$ Hz, 2H), 7.34 (s, 1H), 7.41–7.50 (m, 4H), 7.58–7.65 (m, 3H), 7.91–7.98 (m, 2H), 8.09 (d, $J = 8.4$ Hz, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ 102.03, 117.22, 121.39, 122.11, 122.96, 123.21, 124.48, 124.78, 125.06, 125.24, 125.83, 125.93, 126.08, 126.75, 126.82, 128.25, 128.58 (2C), 131.64, 133.46, 135.37, 136.61, 137.37, 138.04, 139.08, 140.34, 140.99. Anal. Calcd for $C_{27}H_{15}NS_4$: C, 67.33; H, 3.14; N, 2.91, S, 26.63. Found: C, 67.23; H, 3.24; N, 3.12, S, 26.39.
17. Compound **11**: thick red liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, $J = 7.35$ Hz, 6H), 1.32–1.42 (m, 4H), 1.53–1.63 (m, 4H), 3.28 (t, $J = 7.5$ Hz, 4H), 6.46 (d, $J = 8.4$ Hz, 2H), 6.89 (d, $J = 15.9$ Hz, 1H), 6.98–7.07 (m, 3H), 7.15 (t, $J = 8.7$ Hz, 1H), 7.25 (d, $J = 5.1$ Hz, 1H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.40–7.54 (m, 2H), 7.56 (d, $J = 8.7$ Hz, 1H), 7.61 (s, 1H), 7.92–7.97 (m, 2H), 8.07 (d, $J = 9.0$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.02, 20.37, 29.52, 50.80, 111.71, 116.66, 121.68, 121.83, 122.91, 123.37, 124.01, 124.18, 124.63, 124.92, 125.39, 125.69 (2C), 126.21, 127.73 (2C), 127.97, 129.06, 129.12, 133.10, 134.52, 137.17, 138.28, 140.31, 144.26, 147.95. Anal. Calcd for $C_{36}H_{35}NS_3$: C, 74.82; H, 6.10; N, 2.42, S, 16.65. Found: C, 74.62; H, 6.28; N, 2.22, S, 16.84.