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An efficient synthesis of dinaphthothiophene derivatives

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ABSTRACT

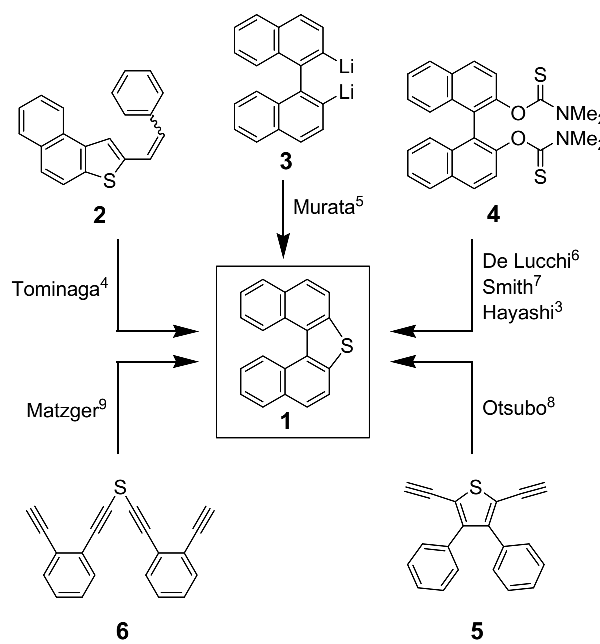
A short and efficient synthesis of dinaphthothiophene and its derivatives was achieved by employing oxidative photocyclization of the corresponding dinaphthyl sulfides as a key step.

1. Introduction

Dinaphthothiophene **1** can be classified as a sulfur-containing heteroaromatic system with a unique structure. Despite its helical structure, the molecule does not exhibit optical activity due to rapid racemization at ambient temperature.[1,2] The molecule has received much attention recently due to its potential as a precursor for the synthesis of axially chiral binaphthyl derivatives, which are effective chiral building blocks in asymmetric reactions.[2,3]

A number of dinaphthothiophene syntheses have been reported in the literature as outlined in Scheme 1. For example, in chronological order, Tominaga and co-workers reported the synthesis of dinaphthothiophene derivatives via the photocyclization of **2**.[4] Later Murata et al. reported that the reaction between the lithiated binaphthyl **3** and sulfur provided dinaphthothiophene **1** in 19% yield.[5] De Lucchi et al.[6] and Smith et al.[7] reported the application of the Newman–Kwart thermal rearrangement of the dimethylthiocarbamate of binaphthol **4** to provide the desired product **1**. This approach was later improved by Hayashi and co-workers and the yield was increased to 68%.[3] In 1999, Otsubo and co-workers[8] reported an approach via the flash vacuum pyrolysis of diethynyl thiophene **5**. Finally, Matzger and co-workers[9] employed a cascade Bergman cyclization of **6** to furnish dinaphthothiophene **1** in trace amount.

Our research focuses on the development of new methodology towards helical conjugated structures.[10] Interestingly, it was reported, by Zeller and Petersen,[11] that the oxidative photocyclization of diphenyl sulfide could lead to dibenzothiophene. It was envisioned that such an approach could be applied for the direct synthesis of dinaphthothiophene **1**. Retrosynthetic disconnection at the C1–C1′ bond of dinaphthothiophene suggested that the precursor for photochemical reaction could be dinaphthyl sulfide **7** which could be derived straightforwardly from the acid-mediated nucleophilic aromatic substitution between 2-naphthol **8** and 2-naphthalenethiol **9** (Scheme 2).[12]



Scheme 1. Reported syntheses of dinaphthothiophene **1**.

2. Result and discussion

The reaction of 2-naphthol **8** and 2-naphthalenethiol **9** was thus carried out in the presence of *p*-TsOH in refluxing toluene for 2 h to provide the desired dinaphthyl sulfide **7** in 97% yield. The sulfide **7** was then subjected to oxidative photocyclization in the presence of I_2 and propylene oxide (PO), Scheme 3.[11,13] Conditions for the oxidative photo-cyclization process and yields are summarized in Table 1.

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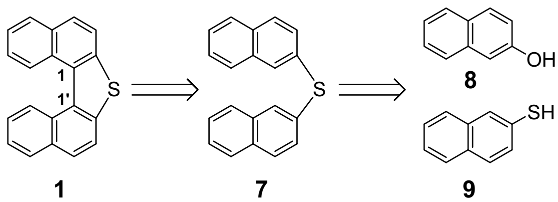
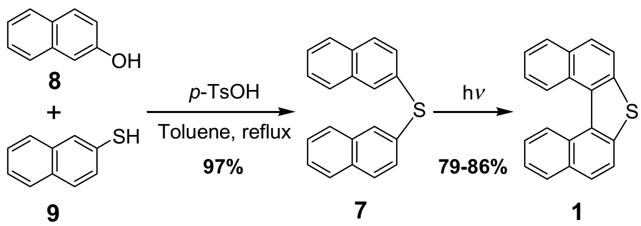


Scheme 2. Retrosynthetic analysis of dinaphthothiophene **1**.



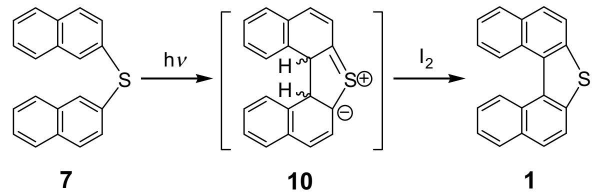
Scheme 3. Synthesis of dinaphthothiophene **1**.

Table 1
Conditions and yields of the oxidative photocyclization reaction of dinaphthyl sulfide **7**[a]

Entry	Time (min)	I_2 (equiv)	PO (equiv to I_2)	Yield % (conversion %)[b]
1	10	1.0	10.0	79 (48)
2	20	1.0	10.0	83 (78)
3	30	1.0	10.0	85 (87)
4	40	1.0	10.0	84 (89)
5	60	1.0	10.0	86 (88)
6	30	0.8	10.0	82 (86)
7	30	1.2	10.0	85 (91)
8	30	1.5	10.0	84 (92)
9	30	1.2	0.0	81 (80)
10	30	1.2	5.0	85 (90)

[a] The reaction was conducted in a 1 L Hanovia 450 W medium pressure Hg lamp photochemical reactor. All experiments were performed on 1 mmol scale at a concentration of 1 mM.
[b] The % conversion refers to the percentage of reacted starting material; the % yield refers to the percentage of the product from the reacted starting material.

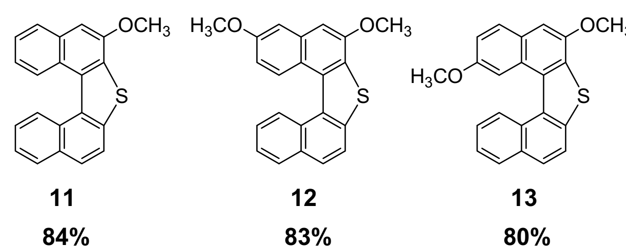
It was found that a stoichiometric amount of I_2 was required for the reaction. On 1 mmol scale, the appropriate reaction time was 30 min. A shorter reaction time led to a decreased percent conversion whilst prolonged irradiation did not increase the yield and % conversion, but did result in the formation of a brownish stain on the surface of the quartz tube and reactor. Addition of propylene oxide did not significantly improve the percent yield and conversion, but it did influence the purity of the crude product.

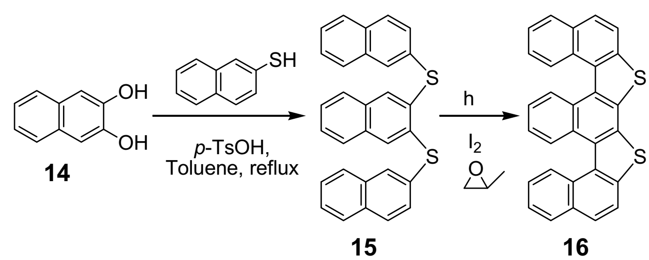


Scheme 4. Mechanism of the oxidative photocyclization.

The mechanism of the reaction is proposed to be similar to that reported by Zeller and Petersen[11] (Scheme 4). Electrocyclic ring closure of dinaphthyl sulfide **7** provided the cyclic intermediate **10** which, upon reaction with I_2, yielded the dinaphthothiophene **1**. Propylene oxide served as a HI-quencher.[13] The decreased extent of aromatic energy in naphthalene is believed to facilitate the photo-electrocyclic process and this provides a rationalization for the better yield and higher conversion when compared to the reaction of diphenyl sulfide.

This oxidative photocyclization was a very efficient and convenient procedure for the construction of other dinaphthothiophene derivatives. For example, compounds **11**, **12** and **13** could be prepared by photocyclization of their corresponding dinaphthyl sulfides in 84%, 83% and 80% yields, respectively.





Scheme 5. Two-step synthesis of **16**.

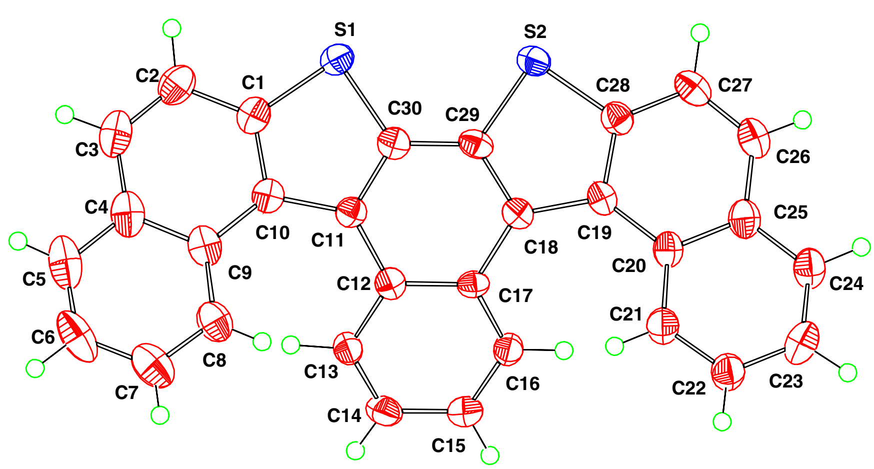


Figure 1. ORTEP diagram of compound **16**.

Compounds with complicated skeletons, such as **16**, could also be accessed via this oxidative photocyclization method. Indeed, treatment of 2,3-naphthalenediol **14** with 2-naphthalenethiol **9** in refluxing toluene in the presence of *p*-TsOH yielded **15** (87%), which upon oxidative photocyclization by the aforementioned procedure provided **16** in 83% yield (Scheme 5).

X-ray analysis of compound **16**[14] (Fig. 1) revealed an interesting structural feature where the product adopted a conformation that possessed a plane of symmetry, rather than a C_2-axis. A detailed investigation of this molecule as a new type of organic material is currently in progress.

In conclusion, an alternative synthesis of dinaphthothiophene has been described. The method is highly efficient and can be applied to the synthesis of a variety of dinaphthothiophene derivatives.

3. General procedures[15]

3.1. Synthesis of dinaphthyl sulfide 7

A solution of 2-naphthol **8** (1.24 g, 8.60 mmol) and 2-naphthalenethiol **9** (2.07 g, 12.90 mmol) in the presence of *p*-TsOH (1.64 g, 8.60 mmol) was refluxed in toluene for 2 h. The reaction was cooled down and then quenched with saturated $NaHCO_3$ solution. The mixture was then extracted with CH_2Cl_2 (3 times), and the combined organic extracts were washed with H_2O, dried over Na_2SO_4 and then evaporated to dryness. The crude product was purified by column chromatography (SiO_2, hexane as eluent) to yield dinaphthyl sulfide **7** (2.39 g, 97% yield).

3.2. Oxidative photocyclization of diaryl sulfide: synthesis of dinaphthothiophene 1

A solution of dinaphthyl sulfide **7** (300 mg, 1.05 mmol) and I_2 (320 mg, 1.26 mmol) in cyclohexane (1000 mL) was charged into a 1 L Hanovia photochemical reactor equipped with a 450 W medium pressure Hg lamp. The solution was purged with argon for 20 min. Then, propylene oxide (366 mg, 0.44 mL, 6.30 mmol) was added and the solution was irradiated for 30 min. Upon completion, the solution was evaporated to dryness and the crude product was subjected to column chromatography (SiO_2, hexane as eluent) to yield dinaphthothiophene **1** (228 mg, 85% yield, 90% conversion).

Acknowledgements

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Supplementary data

Supplementary data (^{1}H and ^{13}C NMR spectra of compounds **1**, **7**, **11**, **12**, **13**, **15** and **16**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.05.045.

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14. Crystallographic data for compound **16** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 680516. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/data_request/cif).
15. *Compound characterization*: *Dinaphthyl sulfide* **7**: ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 7.48–7.55 (m, 6H, Ar–H); 7.76–7.78 (m, 6H, Ar–H); 7.94 (br s, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 133.8, 133.1, 132.3, 129.8, 128.9, 128.7, 127.7, 127.4, 126.6, 126.2. MS (EI [70 eV], *m*/*z* (%)): 286 (100) [M$^+$]; 252 (34) [{M−H_2S}$^+$]. CHN: Required for $C_{20}H_{14}S$: C, 83.88; H, 4.93. Found: C, 83.72; H, 4.53. Melting point 157–160 °C.
Dinaphthothiophene **1**: ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 7.60 (m, 4H, Ar–H); 7.95 (d, *J* = 8.6 Hz, 2H, Ar–H); 7.99 (d, *J* = 8.6 Hz, 2H, Ar–H); 8.06 (m, 2H, Ar–H); 8.90 (m, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 138.5, 132.1, 131.4, 129.9, 128.6, 127.4, 126.1, 125.2, 124.8, 120.8. MS (EI [70 eV], *m*/*z* (%)): 284 (72) [M$^+$]. CHN: Required for $C_{20}H_{12}S$: C, 84.47; H, 4.25. Found: C, 84.92; H, 4.18. Melting point 213–216 °C.
6-Methoxy-dinaphthothiophene **11**: ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 4.20 (s, 3H, OCH_3); 7.26 (s, 1H, Ar–H); 7.47 (m, 1H, Ar–H); 7.54–7.62 (m, 3H, Ar–H); 7.93–8.07 (m, 4H, Ar–H); 8.85–8.94 (m, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 152.5, 139.0, 134.1, 133.4, 132.2, 131.7, 131.6, 130.0, 128.6, 127.6, 127.4, 126.2, 126.0, 125.9, 125.5, 125.2, 124.8, 122.5, 121.1, 103.5, 55.9. MS (EI [70 eV], *m*/*z* (%)): 314 (100) [M$^+$]; 282 (60) [{M–CH_3OH}$^+$]. CHN: Required for $C_{21}H_{14}OS$: C, 80.22; H, 4.49. Found: C, 80.57; H, 4.41. Melting point 190–192 °C.
3,6-Dimethoxy-dinaphthothiophene **12**: ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 4.02 (s, 3H, OCH_3); 4.17 (s, 3H, OCH_3); 7.12 (dd, *J* = 2.69, 9.21 Hz, 1H, Ar–H); 7.18 (s, 1H, Ar–H); 7.33 (d, *J* = 2.65, 1H, Ar–H); 7.56–7.62 (m, 2H, Ar–H); 7.93 (d, *J* = 8.65 Hz, 1H, Ar–H); 7.98 (d, *J* = 8.64 Hz, 1H, Ar–H); 8.04 (m, 1H, Ar–H); 8.77 (d, *J* = 9.21 Hz, 1H, Ar–H); 8.89 (m, 1H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 157.4, 153.1, 139.0, 135.7, 133.5, 132.1, 131.5, 130.3, 129.2, 128.6, 127.5, 127.3, 126.0, 125.1, 124.8, 121.1, 120.9, 113.4, 107.2, 103.1, 55.9, 55.4. MS (EI [70 eV], *m*/*z* (%)): 344 (100) [M$^+$]; 312 (20) [{M–H_3OH}$^+$]. CHN: Required for $C_{22}H_{16}O_2S$: C,76.72; H,4.68. Found: C, 76.97; H, 4.65. Melting point 213–216 °C.
2,6-Dimethoxy-dinaphthothiophene **13**: ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 3.89 (s, 3H, OCH_3); 4.17 (s, 3H, OCH_3); 7.23–7.26 (m, 2H, Ar–H); 7.58–7.62 (m, 2H, Ar–H); 7.87 (d, *J* = 8.88 Hz, 1H, Ar–H); 7.94–8.08 (m, 3H, Ar–H); 8.18 (d, *J* = 2.27 Hz, 1H, Ar–H); 8.92 (m, 1H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 155.4, 151.0, 138.9, 132.5, 132.2, 132.0, 131.6, 129.7, 129.0, 128.7 (2C), 127.2, 126.7, 126.6, 125.2, 124.3, 121.1, 117.3, 106.6, 103.6, 55.9, 55.4. MS (EI [70 eV], *m*/*z* (%)): 344 (100) [M$^+$]. CHN: Required for $C_{22}H_{16}O_2S$: C, 76.72; H, 4.68. Found: C, 76.38; H, 4.57. Melting point 184–186 °C.
2,3-Dinaphthyl disulfide **15**: ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 7.43 (m, 2H, Ar–H); 7.48–7.55 (m, 6H, Ar–H); 7.64 (m, 2H, Ar–H); 7.74–7.80 (m, 4H, Ar–H); 7.83–7.88 (m, 4H, Ar–H); 7.93 (br s, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 135.3, 134.0, 132.8, 132.5, 132.2, 130.9, 130.6, 129.0, 128.9, 127.8, 127.5, 127.1, 126.5, 126.3. MS (EI [70 eV], *m*/*z* (%)): 444 (75) [M$^+$]; 284 (100) [{M–$C_{10}H_8S$}$^+$]. CHN: Required for $C_{30}H_{20}S_2$: C, 81.04; H, 4.53. Found: C, 80.46; H, 4.52. Melting point 122–125 °C.
Compound **16**: ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 7.57 (m, 2H, Ar–H); 7.65 (m, 4H, Ar–H); 7.98 (d, *J* = 8.68 Hz, 2H, Ar–H); 8.03 (d, *J* = 8.63 Hz, 2H, Ar–H); 8.09 (m, 2H, Ar–H); 8.98 (m, 2H, Ar–H); 9.05 (m, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 137.9, 133.3, 132.3, 131.7, 131.6, 129.7, 129.3, 128.8, 127.5, 126.4, 126.1, 125.5, 125.3, 124.7, 120.9. MS (EI [70 eV], *m*/*z* (%)): 440 (100) [M$^+$]. CHN: Required for $C_{30}H_{16}S_2$: C, 81.78; H, 3.66. Found: C, 81.91; H, 3.55. Melting point 316–318 °C.