

## Supplementary Material

# Formation of Naphtodithiophene Isomers by Flash Vacuum Pyrolysis of 1,6-Di(2-thienyl) and 1,6-di(3-thienyl)-1,5-hexadien-3-yne

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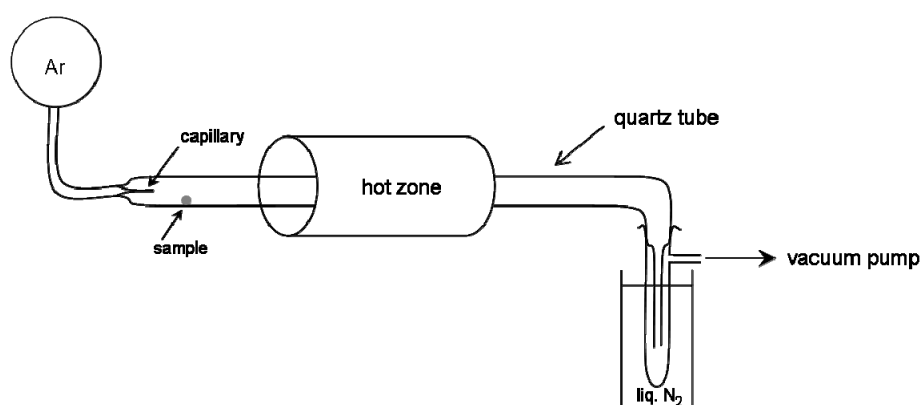
**Plausible Mechanism of Formation of Naphtodithiophene Derivatives from 5b produced by FVP.....S12**

**General.** For FVP apparatus a ceramic electric furnace (Asahi Rika-Seisakusyo, ARF-30K) and a temperature control unit (Asahi Rika-Seisakusyo, AMF-N) were used.  $^1\text{H}$  NMR spectra were recorded on a Varian Mercury 300 spectrometer in  $\text{CDCl}_3$  and with  $\text{Me}_4\text{Si}$  or residual solvent as an internal standard at 30 °C. IR spectra were recorded as KBr disks with a JASCO FTIR-410 spectrometer. Mass spectral analyses were performed on a JEOL JMS-700 spectrometer for EI ionization. Column chromatography was performed with MERCK Aluminiumoxid 60 F254. Preparative GPC separation was undertaken with a JAI LC-908 chromatograph using 600-mm  $\times$  20-mm JAIGEL-1H and 2H GPC columns with  $\text{CHCl}_3$  as an eluent. DFT calculations were performed with Gaussian 03 program package.<sup>[1]</sup> Chemical shifts were calculated by B3LYP/6-31G\*\* method.

**Experimental Procedure of FVP.** The schematic apparatus of FVP is shown in Figure S1. The hot zone consisting of a quartz tube was heated by an electric furnace to temperatures of 850 °C or 1050 °C. Under a slow stream of argon at reduced pressure (about 1 mmHg), a sample **5a** or **5b** (30 mg) was sublimed by heating with a heat-gun. The products passed through the hot zone were collected in a cold trap (liq.  $\text{N}_2$ ). After most of the sample was passed through the hot zone, heating was stopped. After cooling to room temperature, the products were collected by washing the quartz tube and the trap with  $\text{CHCl}_3$ . This procedure was repeated three times to obtain enough amount of products for analysis. The combined crude product was separated by GPC and column chromatography. The relative ratio of the products was estimated on the basis of the  $^1\text{H}$  NMR integration for the characteristic signals.

**FVP of 5a:** GPC separation gave fractions A (compound **1c**, 6 mg) and B (18 mg). Fraction B was subjected to column chromatography to give fraction B1 (compound **2c**, 4 mg) and B2 (mainly compound **1a**, 7 mg). Partial  $^1\text{H}$  NMR spectrum and the spectral data and calculated  $^1\text{H}$  NMR chemical shifts of fraction A (compound **1c**) are shown in Figures S2A and S2B, respectively. Partial  $^1\text{H}$  NMR spectrum and whole  $^1\text{H}$  NMR data and calculated  $^1\text{H}$  NMR chemical shifts of fraction B1 (compound **2c**) are shown in Figures S3A and S3B, respectively. Partial  $^1\text{H}$  NMR spectrum and spectral data and calculated  $^1\text{H}$  NMR chemical shifts of fraction B2 (mainly compound **1a**) are shown in Figures S4A and S4B, respectively.  $^1\text{H}$  NMR spectrum of the crude product and calculated  $^1\text{H}$  NMR chemical shifts of **2a**, **3c**, and **3d** are shown in Figures S5A and S5B, respectively.

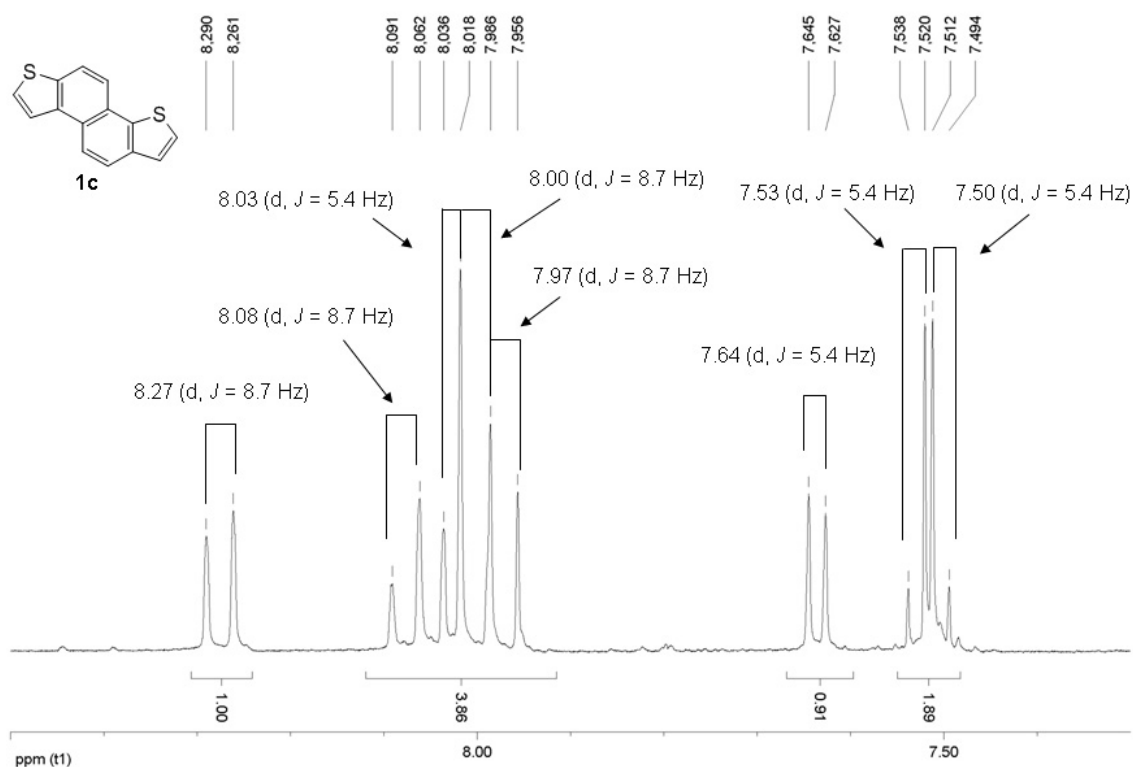
**FVP of 5b:** GPC separation gave fractions C (compound **1c**, 7 mg), D (compound **1a**, 7 mg), and E (13 mg). Partial  $^1\text{H}$  NMR spectrum of fraction C (mainly **1c**) is shown in Figure S6. Partial  $^1\text{H}$  NMR spectrum and the spectral data and calculated  $^1\text{H}$  NMR chemical shifts of fraction D (mainly compound **1b**) are shown in Figures S7A and S7B, respectively. Partial  $^1\text{H}$  NMR spectrum and spectral data and calculated  $^1\text{H}$  NMR chemical shifts of fraction E (mainly compounds **2b** and **2c**) are shown in Figures S8A and S8B, respectively.  $^1\text{H}$  NMR spectrum of the crude product and calculated  $^1\text{H}$  NMR chemical shifts of **3a** and **3d** are shown in Figures S9A and S9B, respectively.



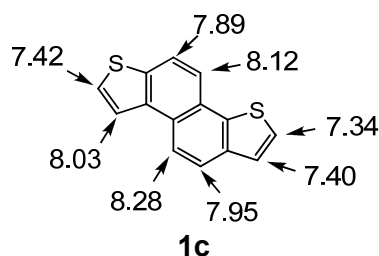
**Figure S1.** Schematic FVP apparatus

#### Reference:

[1] Gaussian 03, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2005.

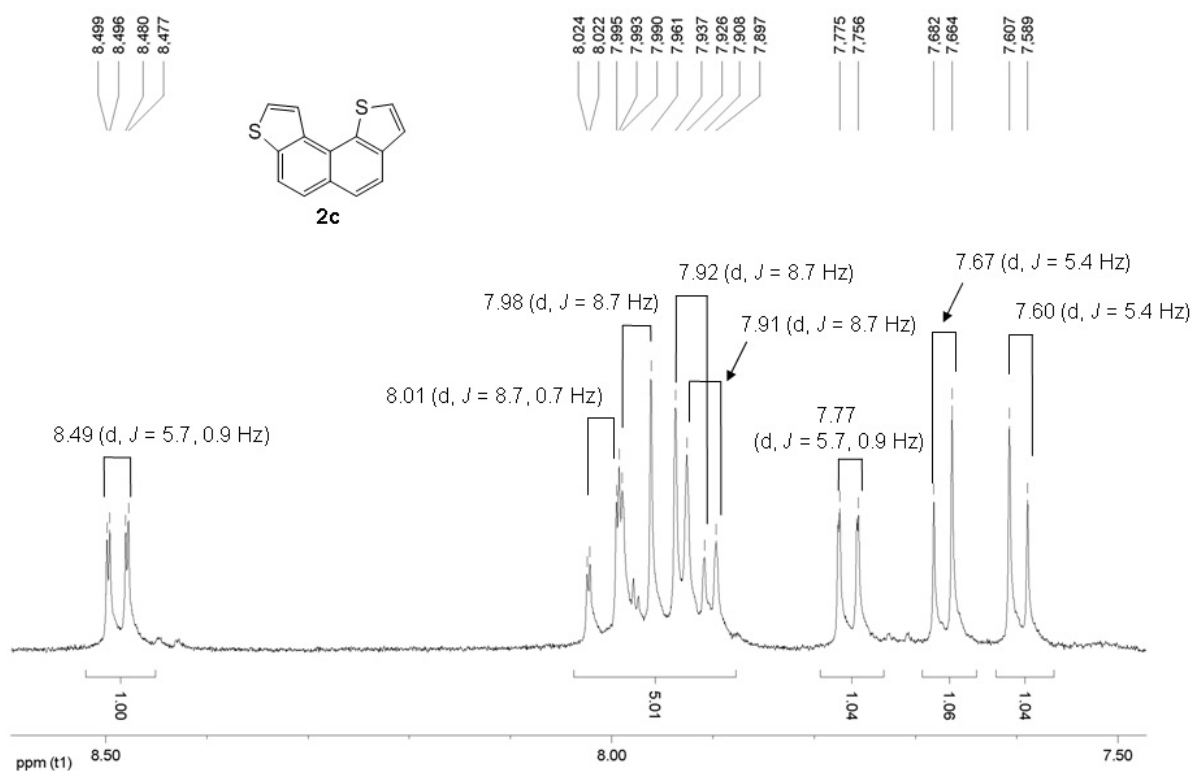


**Figure S2A.** Partial  $^1\text{H}$  NMR spectrum of fraction A (**1c**) in  $\text{CDCl}_3$  at  $30\text{ }^\circ\text{C}$

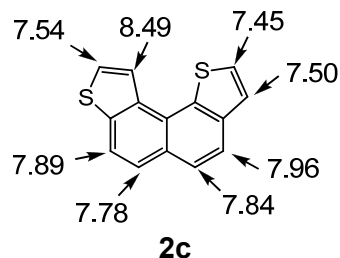


**Figure S2B.** Calculated  $^1\text{H}$  NMR chemical shifts of **1c** by the DFT method

**1c:** m.p.  $139.0\text{--}140.0\text{ }^\circ\text{C}$ ,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $30\text{ }^\circ\text{C}$ )  $\delta$  8.27 (d,  $J = 8.7\text{ Hz}$ , 1H), 8.07 (d,  $J = 8.8\text{ Hz}$ , 1H), 8.03 (d,  $J = 5.4\text{ Hz}$ , 1H), 8.00 (d,  $J = 8.8\text{ Hz}$ , 1H), 7.97 (d,  $J = 8.7\text{ Hz}$ , 1H), 7.64 (d,  $J = 5.4\text{ Hz}$ , 1H), 7.53 (d,  $J = 5.3\text{ Hz}$ , 1H), 7.50 (d,  $J = 5.3\text{ Hz}$ , 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $30\text{ }^\circ\text{C}$ )  $\delta$  138.2, 136.9, 136.8, 136.7, 126.4, 126.3, 126.2, 125.0, 124.8, 122.3, 122.2, 121.2, 120.9, 120.8; IR (KBr) 3098, 2923, 1651, 1556, 1514, 1465, 1415, 1365, 1340, 1293, 1187, 1161, 1101, 1086, 907, 882, 808, 732, 698, 606  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  240 ( $\text{M}^+$ ).

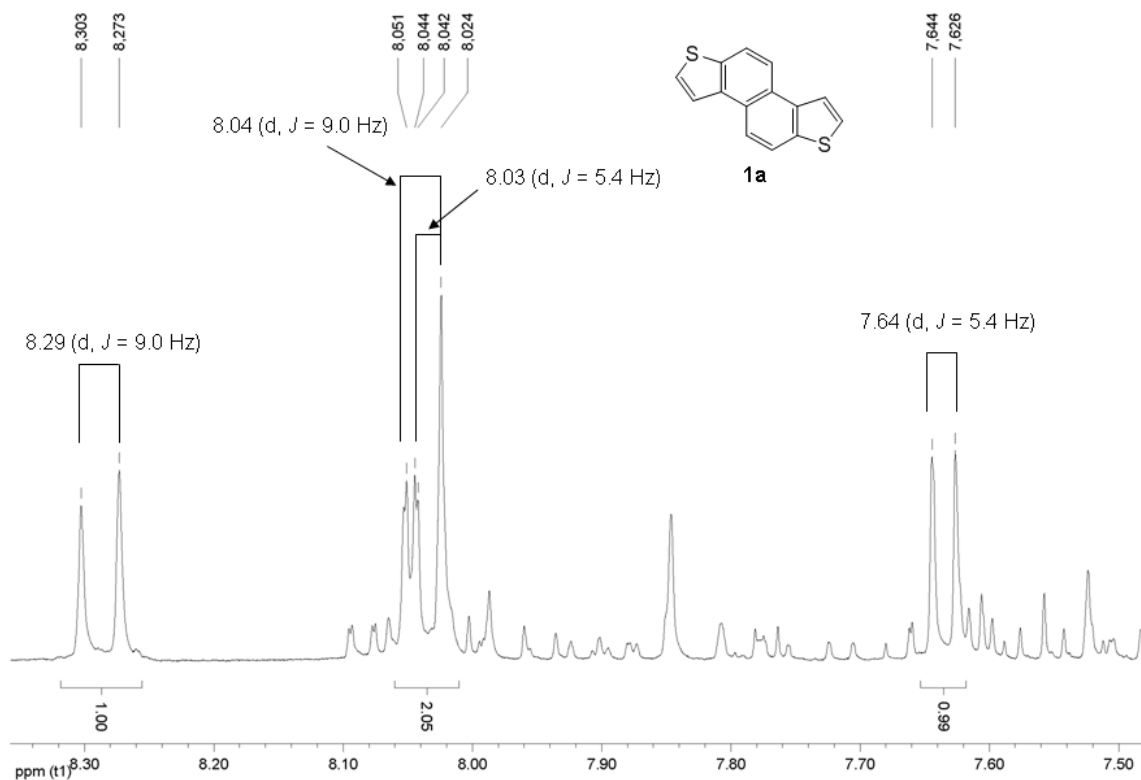


**Figure S3A.** Partial  $^1\text{H}$  NMR spectrum of fraction B1 (**2c**) in  $\text{CDCl}_3$  at  $30\text{ }^\circ\text{C}$

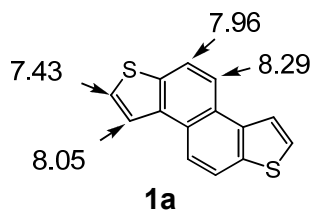


**Figure S3B.** Calculated  $^1\text{H}$  NMR chemical shifts of **2c** by the DFT method

**2c:** m.p.  $101.5\text{--}102.5\text{ }^\circ\text{C}$ ,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $30\text{ }^\circ\text{C}$ )  $\delta$  8.49 (dd,  $J = 5.7, 0.9\text{ Hz}$ , 1H), 8.01 (dd,  $J = 8.7, 0.7\text{ Hz}$ , 1H), 7.98 (d,  $J = 8.7\text{ Hz}$ , 1H), 7.92 (d,  $J = 8.7\text{ Hz}$ , 1H), 7.91 (d,  $J = 8.7\text{ Hz}$ , 1H), 7.77 (d,  $J = 5.7, 0.9\text{ Hz}$ , 1H), 7.67 (d,  $J = 5.4\text{ Hz}$ , 1H), 7.60 (d,  $J = 5.4\text{ Hz}$ , 1H), MS (EI)  $m/z$  240 ( $\text{M}^+$ ).

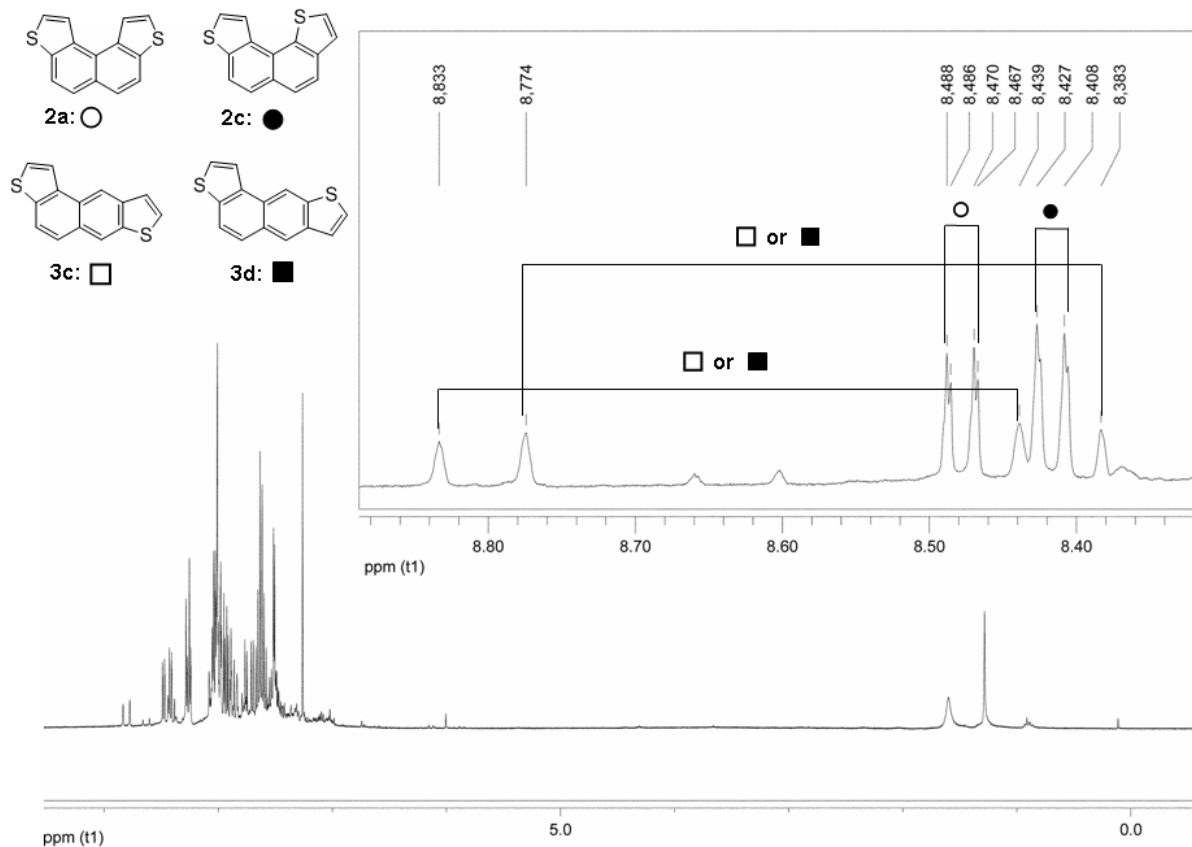


**Figure S4A.** Partial  $^1\text{H}$  NMR spectrum of fraction B2 (mainly **1a**) in  $\text{CDCl}_3$  at  $30\text{ }^\circ\text{C}$

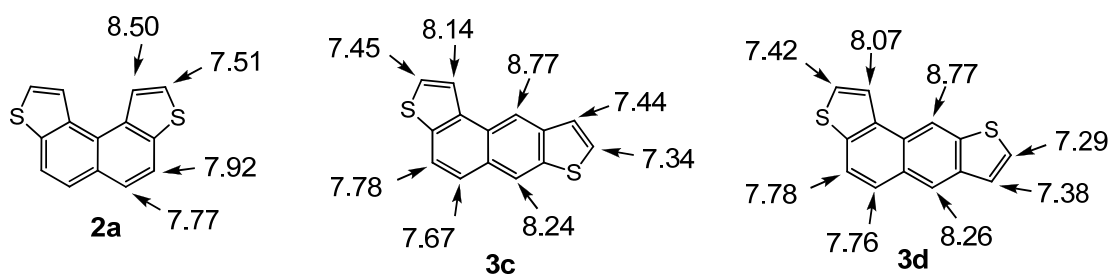


**Figure S4B.** Calculated  $^1\text{H}$  NMR chemical shifts of **1a** by the DFT method

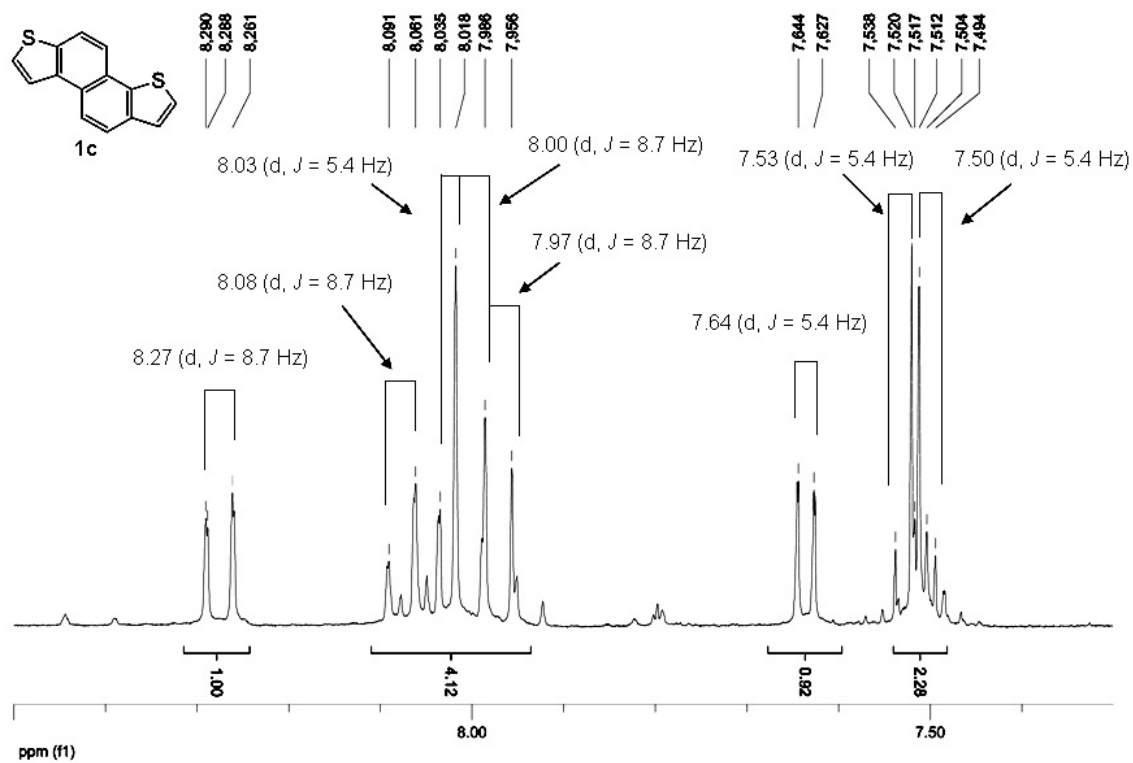
**1a:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $30\text{ }^\circ\text{C}$ )  $\delta$  8.29 (d,  $J = 9.0\text{ Hz}$ , 2H), 8.04 (d,  $J = 9.0\text{ Hz}$ , 2H), 8.03 (d,  $J = 5.4\text{ Hz}$ , 2H), 7.64 (d,  $J = 5.4\text{ Hz}$ , 1H); MS (EI)  $m/z$  240 ( $\text{M}^+$ ).



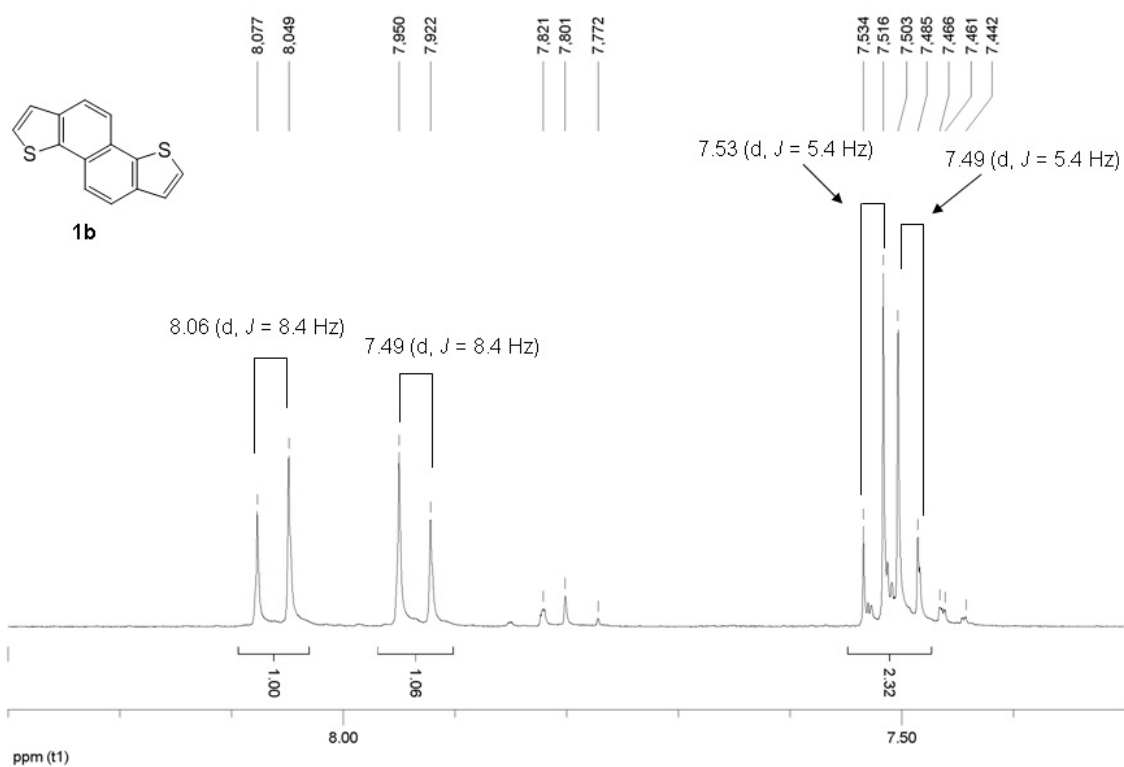
**Figure S5A.**  $^1\text{H}$  NMR spectrum of crude product of FVP of **5a** at  $850\text{ }^\circ\text{C}$  in  $\text{CDCl}_3$  at  $30\text{ }^\circ\text{C}$ . Inset: Expansion of the low field region. Open circle  $\circ$ , closed circle  $\bullet$ , open square  $\square$ , and closed square  $\blacksquare$  indicate the signals assigned to **2a**, **2c**, **3c**, and **3d**, respectively.



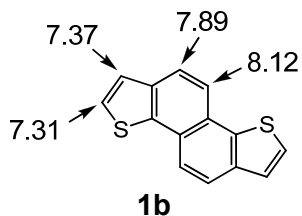
**Figure S5B.** Calculated  $^1\text{H}$  NMR chemical shifts of **2a**, **3c**, and **3d** by the DFT methods.



**Figure S6.** Partial  $^1\text{H}$  NMR spectrum of fraction C (mainly **1c**) in  $\text{CDCl}_3$  at  $30\text{ }^\circ\text{C}$

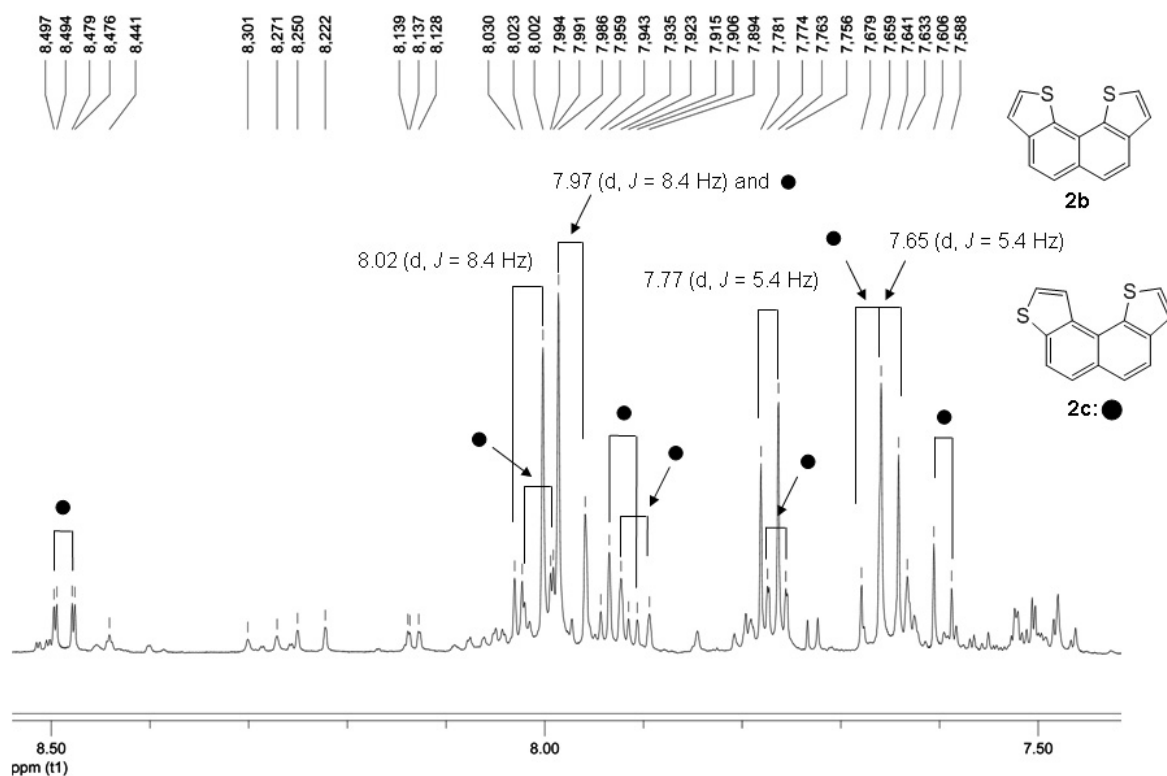


**Figure S7A.** Partial  $^1\text{H}$  NMR spectrum of fraction D (mainly **1b**) in  $\text{CDCl}_3$  at  $30\text{ }^\circ\text{C}$

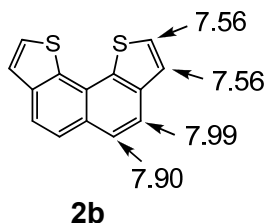


**Figure S7B.** Calculated  $^1\text{H}$  NMR chemical shifts of **1b** by the DFT method

**1b:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $30\text{ }^\circ\text{C}$ )  $\delta$  8.06 (d,  $J = 8.4\text{ Hz}$ , 1H), 7.94 (d,  $J = 8.4\text{ Hz}$ , 1H), 7.53 (d,  $J = 5.1\text{ Hz}$ , 1H), 7.49 (d,  $J = 5.1\text{ Hz}$ , 1H). MS (EI)  $m/z$  240 ( $\text{M}^+$ ).

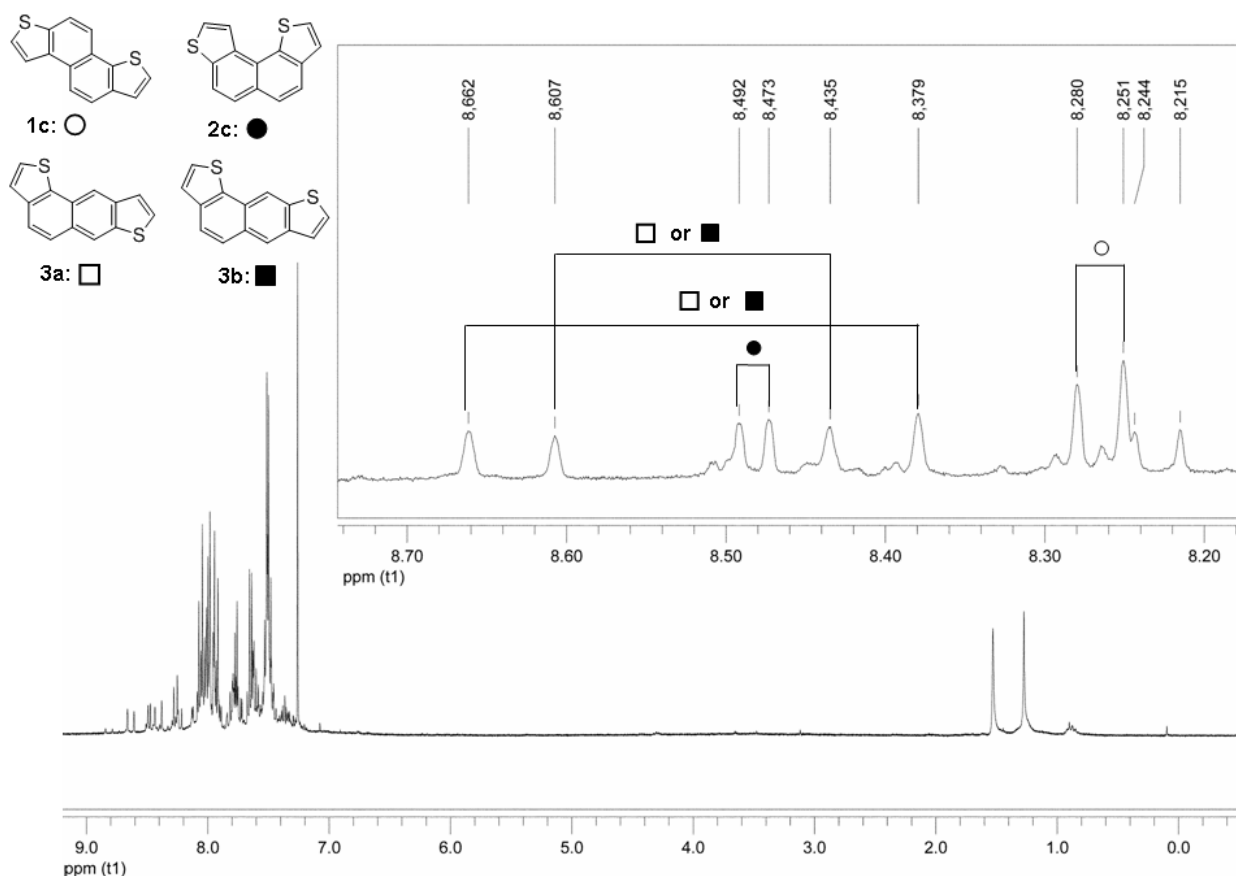


**Figure S8A.** Partial  $^1\text{H}$  NMR spectrum of fraction E (mainly **2b** and **2c**) in  $\text{CDCl}_3$  at  $30\text{ }^\circ\text{C}$ . Closed circles ● show the signals assigned to **2c**.

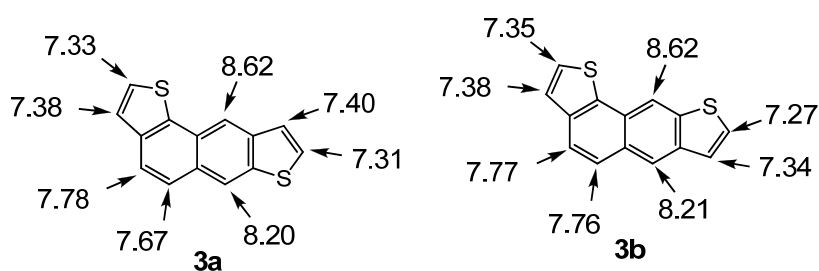


**Figure S8B.** Calculated  $^1\text{H}$  NMR chemical shifts of **2b** by the DFT method

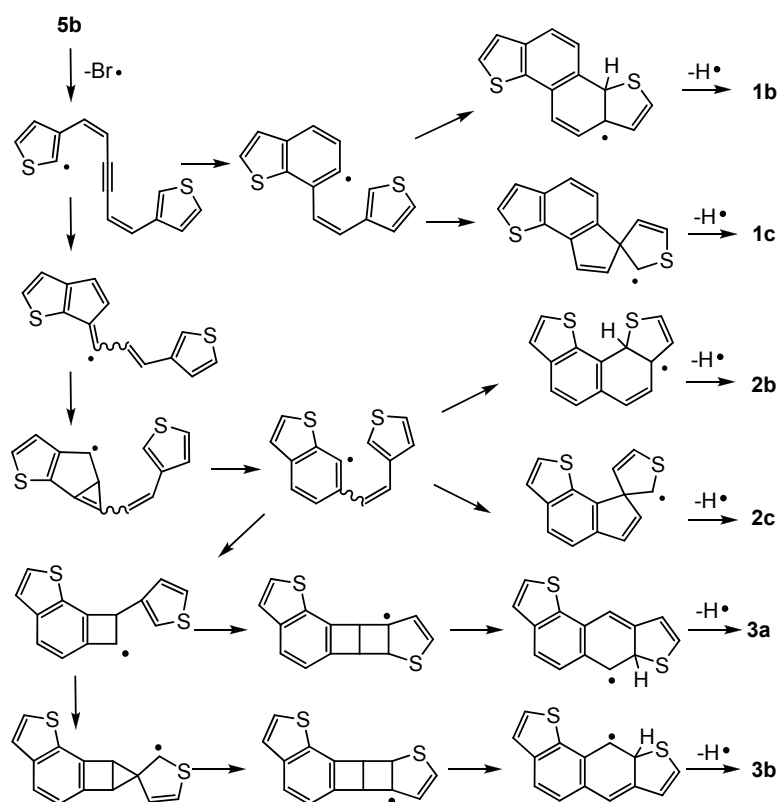
**2b:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $30\text{ }^\circ\text{C}$ )  $\delta$  8.02 (d,  $J = 8.1\text{ Hz}$ , 1H), 7.97 (d,  $J = 8.1\text{ Hz}$ , 1H), 7.77 (d,  $J = 5.4\text{ Hz}$ , 1H), 7.65 (d,  $J = 5.4\text{ Hz}$ , 1H).



**Figure S9A.**  $^1\text{H}$  NMR spectrum of the crude product of FVP of **5b** at 850 °C in  $\text{CDCl}_3$  at 30 °C. Inset: Expansion of the low field region. Open circle  $\circ$ , closed circle  $\bullet$ , open square  $\square$ , and closed square  $\blacksquare$  indicate the signals assigned to **1c**, **2c**, **3a**, and **3b**, respectively.



**Figure S9B.** Calculated  $^1\text{H}$  NMR chemical shifts of **3a** and **3b** by the DFT methods.



**Scheme S1.** A plausible mechanism for the formation of naphthodithiophene derivatives from **5b** by FVP