

Supporting Information

Studies on the stereochemical behaviors of winding vine-shaped molecular wire of bithiophene dimer with molecular asymmetry

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Experimental

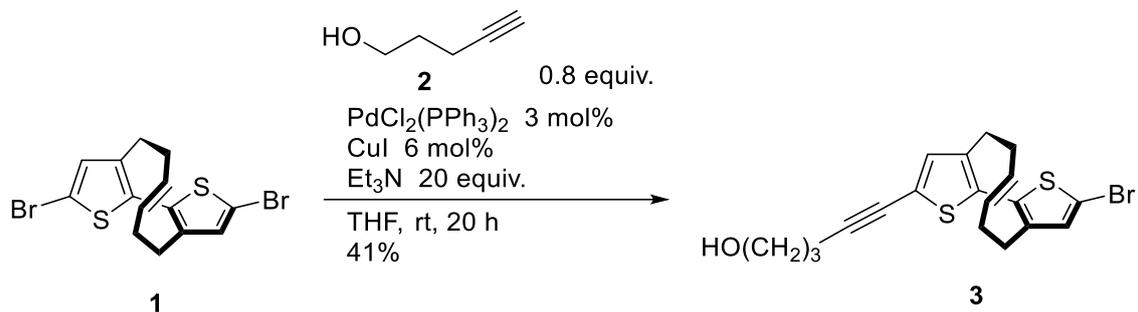
General.

Unless otherwise noted, all the manipulations were carried out under a standard Schlenk technique under a nitrogen or argon atmosphere. Melting points were measured by Yanaco MP-J3 and the temperature was uncorrected. ^1H NMR (400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra were measured on JEOL ECZ400 as a CDCl_3 solution unless noted. The chemical shifts were expressed in ppm with CHCl_3 (7.26 ppm for ^1H) or CDCl_3 (77.16 ppm for ^{13}C) as internal standards. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. XRD analysis was carried out with a Rigaku MiniFlex with the power of 40 kV, 20 mA, and the wavelength of 1.5418 Å ($\text{CuK}\alpha$). The $\theta/2\theta$ method was employed. The incidence angle α of the X-ray beam was 0.20° . Differential scanning calorimetry (DSC) profiles were recorded on a Rigaku DSC8230 with a scan rate of $10^\circ\text{C}/\text{min}$ under dried nitrogen. For thin layer chromatography (TLC) analyses throughout the work, Fujifilm Wako precoated TLC plates (silica gel 70 F₂₅₄) were used. Flash column chromatography was performed on Wakogel® 60N (63–212 μm , Fujifilm Wako Pure Chemical Industries, Ltd.) or high-efficiency irregular silica (25–40 μm , Santai Science Inc.). HPLC analysis was carried out by JASCO LC-2000 Plus with a chiral stationary column (id = 4.6 mm, 25 cm) with the elution rate of 1.0 mL/min using UV and CD detectors at the wavelengths of 254 nm, respectively.

Materials

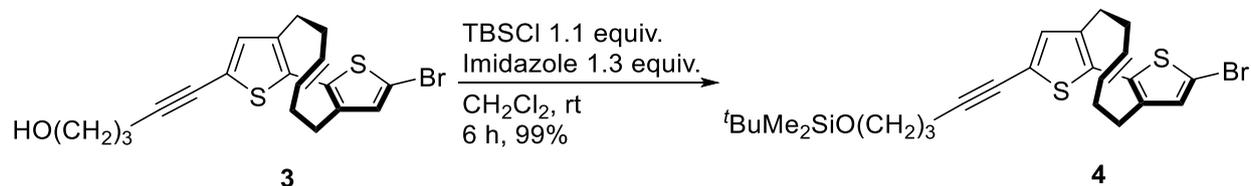
Preparation of 5,5'-dibromo-3,3'-bis(3-buten-1-yl)-2,2'-bithiophene and 4,5,8,9-tetrahydro-2,11-dibromo-(6*E*)-cyclodeca[2,1-*b*:3,4-*b'*]dithiophene (**1**) were carried out in a manner described previously.¹ THF (anhydrous grade) was purchased from Kanto Chemical. Co. Ltd. and passed through alumina and copper column (Nikko Hansen & Co. Ltd.) or distilled from sodium dispersion in a mineral oil/benzophenone ketyl prior to use.² *n*-Butyllithium was purchased from Kanto Chemicals Co. Ltd. as a 1.59 M hexane solution and stored in refrigerator under argon atmosphere. Other chemicals were purchased and used without further purification.

(*E*)-5-(11-Bromo-4,5,8,9-tetrahydrocyclodeca[2,1-*b*:3,4-*b'*]dithiophen-2-yl)pent-4-yn-1-ol (3**):**



To a 100 mL Schlenk tube equipped with a magnetic stirring bar were dissolved bithiophene **1** (1.61 g, 4.0 mmol), 4-pentyn-1-ol (**2**, 296 μL , 3.2 mmol), PdCl₂(PPh₃)₄ (89 mg, 0.12 mmol), CuI (49 mg, 0.24 mmol), triethylamine (11 mL, 80 mmol) in 12 mL of THF under nitrogen atmosphere. After stirring at room temperature for 20 h, the resulting mixture was poured into saturated aqueous ammonium chloride to result in phase separation and the aqueous layer was extracted three times with diethylether. The organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude product. Purification by column chromatography on silica gel (hexane/ethyl acetate = 1:0 to 3:1, gradient) afforded **3** as a light yellow oil (672 mg, 41%). R_f =0.24 (hexane/ ethyl acetate = 3:1); IR (ATR) 3352, 2928, 2858, 1441, 1418, 1201, 1179, 1055, 1009, 969, 848 cm^{-1} ; ¹H NMR: δ 6.90 (s, 1H), 6.83 (s, 1H), 4.46–4.59 (m, 2H), 3.81 (td, J =6.0, 5.2 Hz, 2H), 2.66–2.71 (m, 2H), 2.57 (t, J =6.9 Hz, 2H), 2.37–2.52 (m, 2H), 2.28–2.36 (m, 2H), 1.87 (tt, J = 6.4, 6.4 Hz, 2H) 1.62–1.74 (m, 2H), 1.41 (t, J = 5.2 Hz, 1H); ¹³C{¹H} NMR: δ 142.1, 141.3, 134.0, 132.6, 132.2, 130.9, 129.7, 129.4, 123.5, 111.3, 94.3, 74.2, 61.8, 34.1, 34.0, 31.3x2, 28.4, 16.4; HRMS (ESI+) m/z : calcd for C₁₉H₁₉⁸¹BrNOS₂ (M+Na): 430.9938, Found: 430.9916.

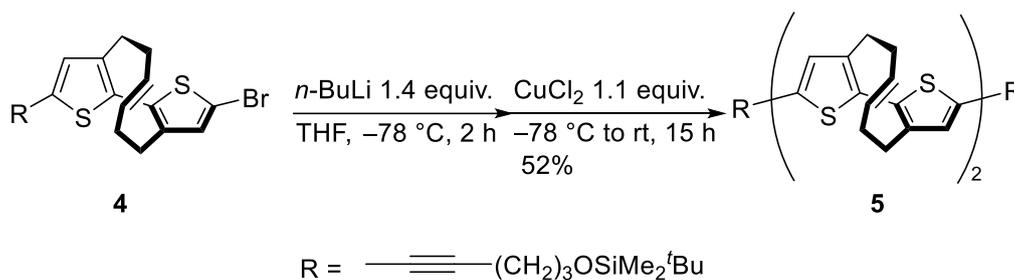
(E)-((5-(11-Bromo-4,5,8,9-tetrahydrocyclodeca[2,1-*b*:3,4-*b'*]dithiophen-2-yl)pent-4-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane (4**):**



To a solution of alkyne **3** (636 mg, 1.5 mmol) and *tert*-butyldimethylchlorosilane (256 mg, 1.7 mmol) in CH₂Cl₂ (4.5 mL) was added imidazole (136 mg, 2.0 mmol). After stirring at room temperature for 6 h, the resulting mixture was poured into water and the aqueous layer was extracted three times with dichloromethane. The combined organic

layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil. Purification by chromatography on silica gel (hexane:diethyl ether = 1:0 to 1:1, gradient) afforded silyl ether **4** as an oil (778 mg, 99%). R_f = 0.83 (hexane:diethyl ether=1:1); IR (ATR) 2928, 2879, 2855, 1470, 1441, 1254, 1105, 1068, 968, 834, 776 cm^{-1} ; ^1H NMR: δ 6.89 (s, 1H), 6.83 (s, 1H), 4.46–4.59 (m, 2H), 3.74 (t, J = 6.0 Hz, 2H), 2.66–2.73 (m, 2H), 2.52 (t, J = 7.2 Hz, 2H), 2.44 (ddd, J =12.8, 12.8, 3.2 Hz, 2H), 2.26–2.36 (m, 2H), 1.79 (tt, J =6.4, 6.4 Hz, 2H), 1.62–1.73 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 142.0, 141.2, 133.7, 132.5, 132.2, 130.7, 129.7, 129.4, 123.8, 111.2, 94.9, 73.8, 61.7, 34.1, 34.0, 31.6, 28.4, 26.1, 18.5, 16.3, -5.2; HRMS (ESI+) m/z : calcd for $\text{C}_{25}\text{H}_{33}^{81}\text{BrOS}_2\text{Si}$ (M+Na): 545.0803, Found: 545.0796.

(6E,6'E)-11,11'-Bis(5-((*tert*-butyldimethylsilyl)oxy)pent-1-yn-1-yl)-4,4',5,5',8,8',9,9'-octahydro-2,2'-bi(cyclodeca[2,1-*b*:3,4-*b'*]dithiophene) (5**) as a mixture of meso and racemic isomers:**

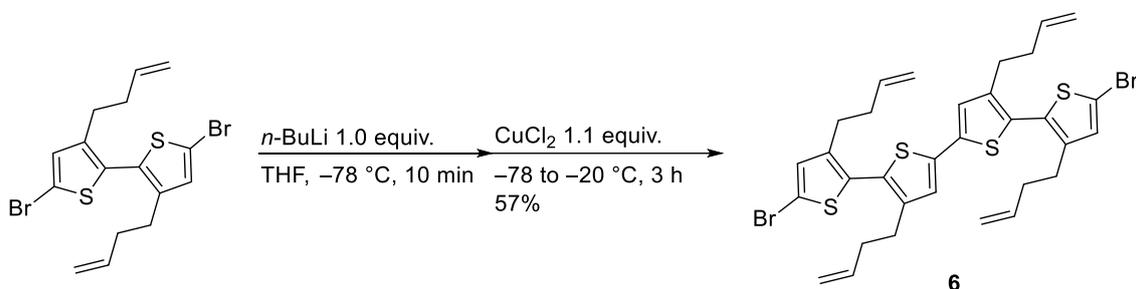


To a 20 mL Schlenk tube equipped with a magnetic stirring bar was added a solution of **4** (600 μL , 0.30 mmol) dissolved in anhydrous THF (0.90 mL) under nitrogen atmosphere. The solution was cooled to -78 $^\circ\text{C}$ and *n*-BuLi (1.59 M in *n*-hexane, 210 μL , 0.45 mmol) was added to the mixture. After stirring was continued at -78 $^\circ\text{C}$ for 2 h, CuCl_2 (45 mg, 0.33 mmol) was added to the solution, which was then allowed to warm to room temperature gradually, and stirring was further continued for 15 h. The resulting mixture was poured into saturated aqueous ammonium chloride and the aqueous layer was extracted three times with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid. Purification by column chromatography on silica gel afforded **5** as a colorless solid (69.4 mg, 52%). M.p. 165.4–166.5 $^\circ\text{C}$ (decomp); IR (ATR) 2926, 2854, 1646, 1465, 1441, 1255, 1105, 969, 834, 776 cm^{-1} ; ^1H NMR: δ 6.933 (s, 2x0.5 H), 6.928 (s, 2x0.5 H), 6.91 (s, 2H), 4.48–4.64 (m, 4H), 3.75 (t, J = 6.0 Hz, 4H), 2.67–2.76 (m, 4H), 2.53 (t, J = 6.8 Hz, 4H), 2.40–2.53 (m, 4H), 2.29–2.37 (m, 4H), 1.81 (tt, J = 6.4, 6.4 Hz, 4H), 1.63–1.77 (m, 4H),

0.91 (s, 18H), 0.08 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 142.2x2, 140.9, 140.8, 136.6x2, 133.8x2, 131.7x2, 129.6x2, 126.1x2, 123.6, 123.5, 94.8x2, 73.9x2, 61.7x2, 34.2, 34.1, 31.7x2, 28.6, 28.4, 26.1x2, 18.5x2, 16.3x2, -5.2x2; HRMS (ESI+) m/z : calcd for $\text{C}_{50}\text{H}_{66}\text{O}_2\text{S}_4\text{Si}_2$ (M+Na): 905.3382, Found: 905.3371. HPLC analysis with a chiral column (DAICEL Chiralpak IF) using hexane/ CH_2Cl_2 = 9:1 as an eluent: t_{R} = 6.03 min (no CD), 8.60 min (CD+), and 9.98 min (CD-).

After **5** was stored in freezer for several months, measurement of HPLC with DAICEL Chiralpak IF under similar conditions: t_{R} = 7.41 min (no CD).

5,5'''-Dibromo-3,3',3''',4''-tetra(but-3-en-1-yl)-2,2':5',2'':5'',2'''-quaterthiophene (6):



To a 20 mL Schlenk tube equipped with a magnetic stirring bar was added dibromobithiophene bearing two 3-buten-1-yl groups at the 3,3'-positions (0.15 mL, 0.50 mmol) dissolved in anhydrous THF (2.5 mL) under nitrogen atmosphere. After the solution was cooled to $-78\text{ }^{\circ}\text{C}$, a hexane solution of *n*-BuLi (1.56 M, 0.33 mL, 0.52 mmol) was added to the mixture and stirring was continued at $-78\text{ }^{\circ}\text{C}$ for 10 min and addition of a suspension of CuCl_2 (75 mg, 0.56 mmol) in THF (4.0 mL) followed. The resulting mixture was allowed to warm to $-20\text{ }^{\circ}\text{C}$ gradually and further stirring was continued for 3 h. The mixture was poured into a saturated aqueous solution of ammonium chloride to result in phase separation and the aqueous layer was extracted three times with diethylether. The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil. Purification by chromatography on silica gel (hexane) afforded **6** as a colorless oil (100 mg, 57%). R_f = 0.41 (hexane); IR (ATR) 3078, 2922, 2852, 1731, 1522, 1451, 1415, 993, 913, 829 cm^{-1} ; ^1H NMR: δ 7.02 (s, 2H), 6.95 (s, 2H), 5.78 (ddt, J = 18.0, 15.0, 6.4 Hz, 4H), 5.08–5.01 (m, 2H), 5.01 (ddd, J = 18.0, 1.5, 1.2 Hz, 2H), 4.97 (dt, J = 15.0, 1.2 Hz, 2H), 2.59 (dt, J = 5.2, 7.2 Hz, 8H), 2.25–2.35 (m, 8H); $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 143.0, 142.6, 137.7, 137.5, 137.3, 131.6, 130.0, 126.9, 125.2, 115.6, 115.5, 112.4, 34.7, 34.6, 28.5, 28.4; HRMS (DART+) m/z : calcd for $\text{C}_{32}\text{H}_{33}^{79}\text{Br}^{81}\text{Br}^{32}\text{S}_4$ (M+H): 704.9811, Found: 704.9800.

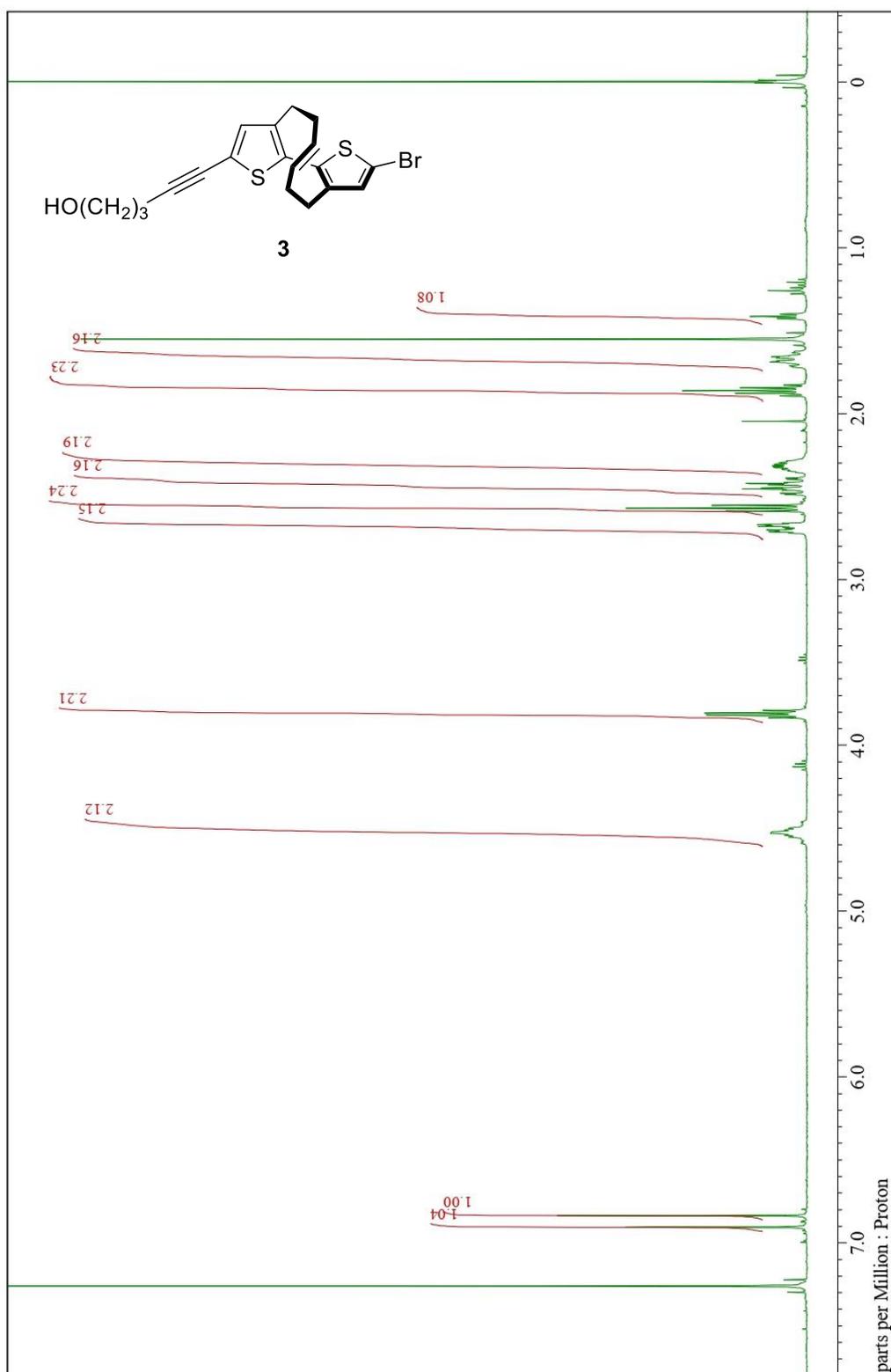


Figure S1. ^1H NMR spectrum of bithiophene **3**

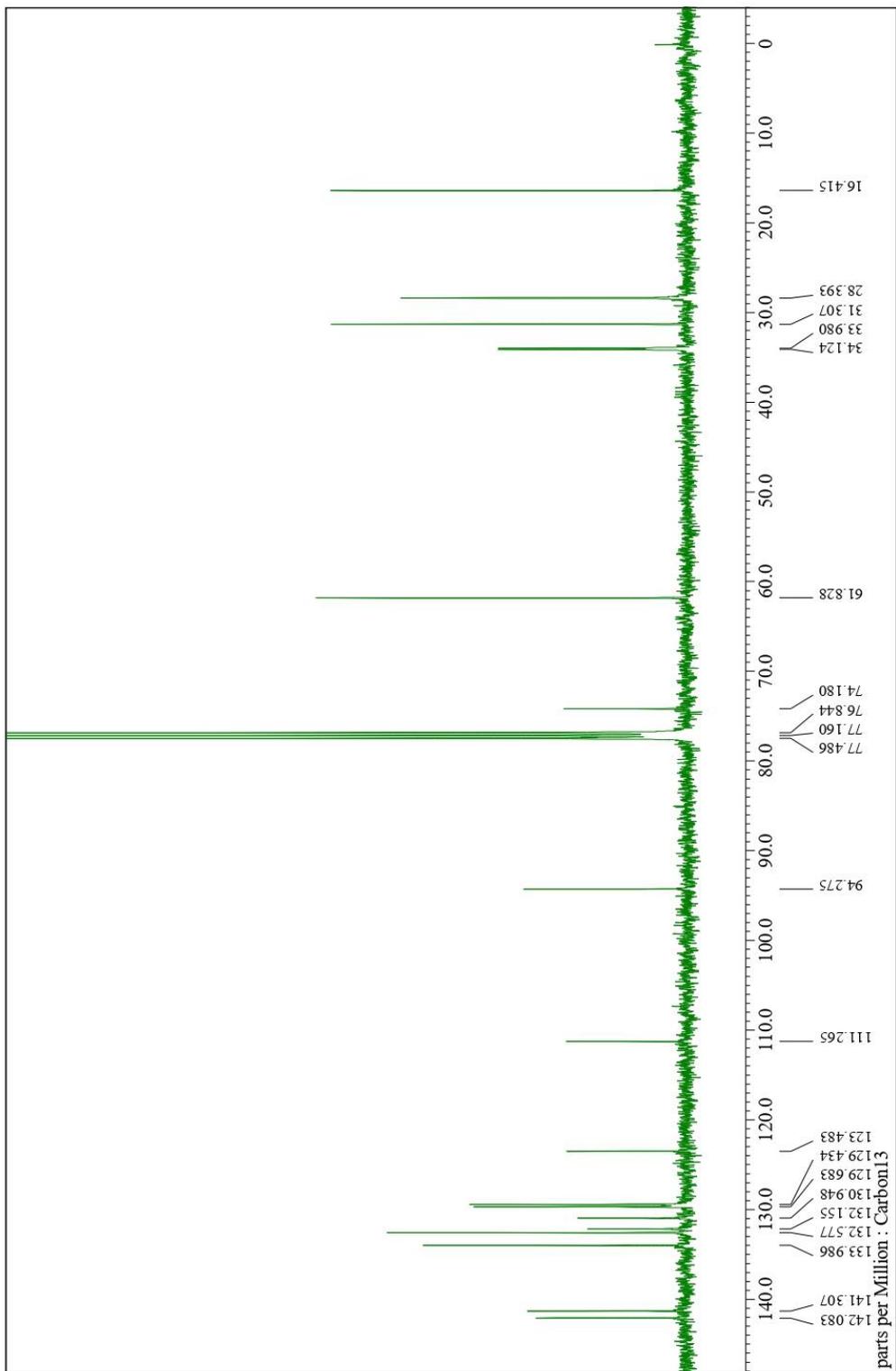


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of bithiophene **3**

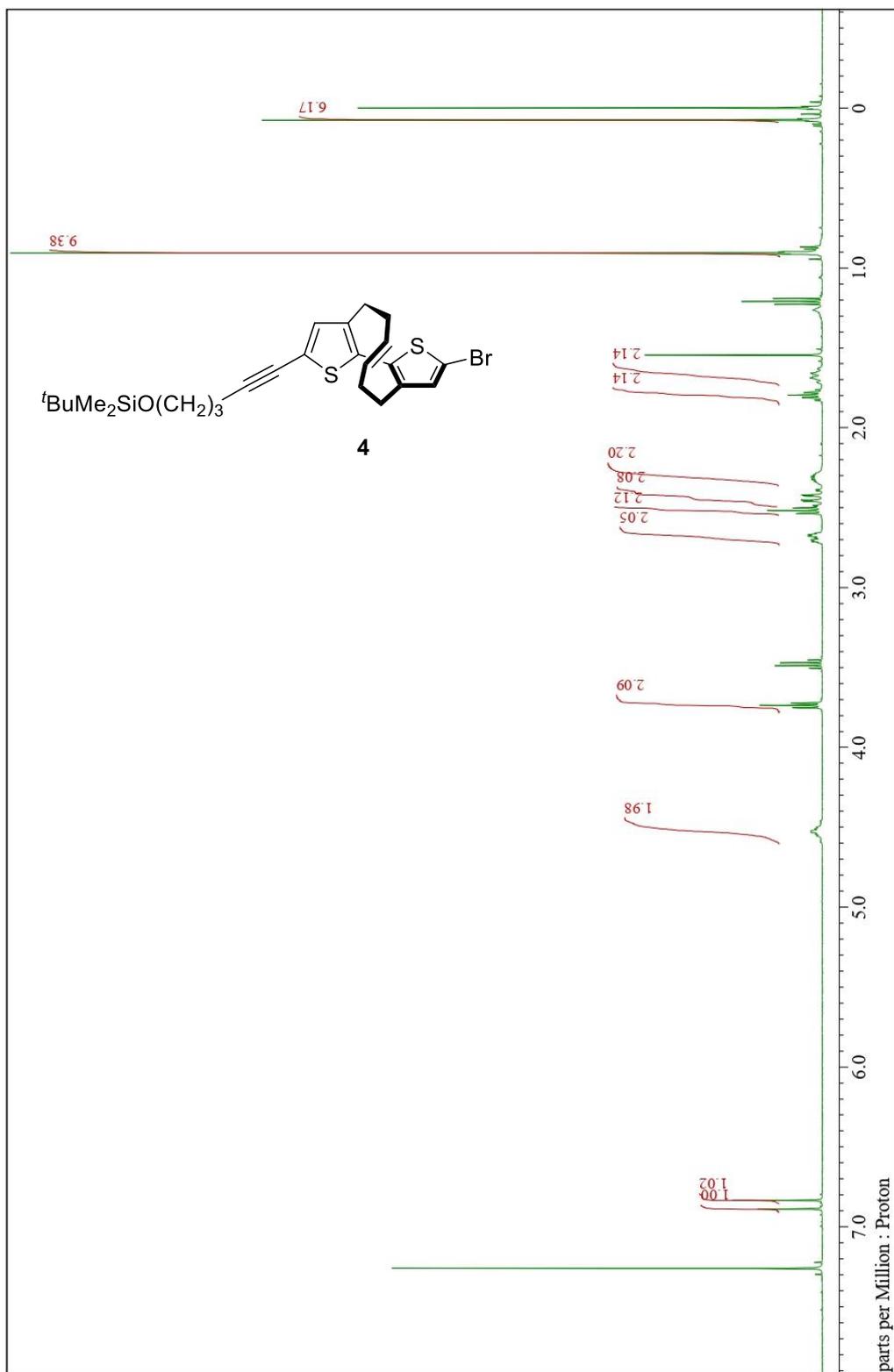


Figure S3. ^1H NMR spectrum of bithiophene **4**

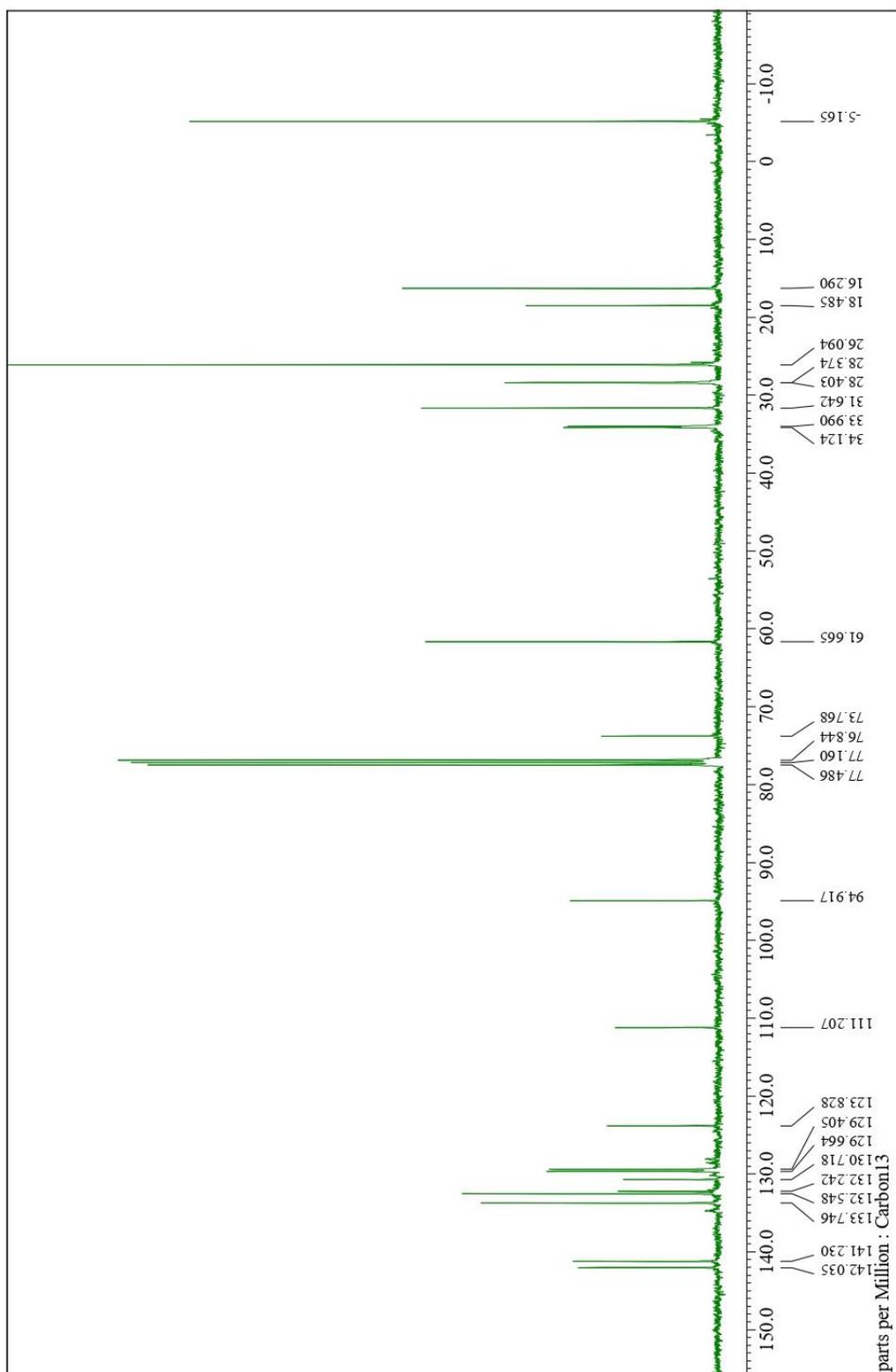


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of bithiophene 4

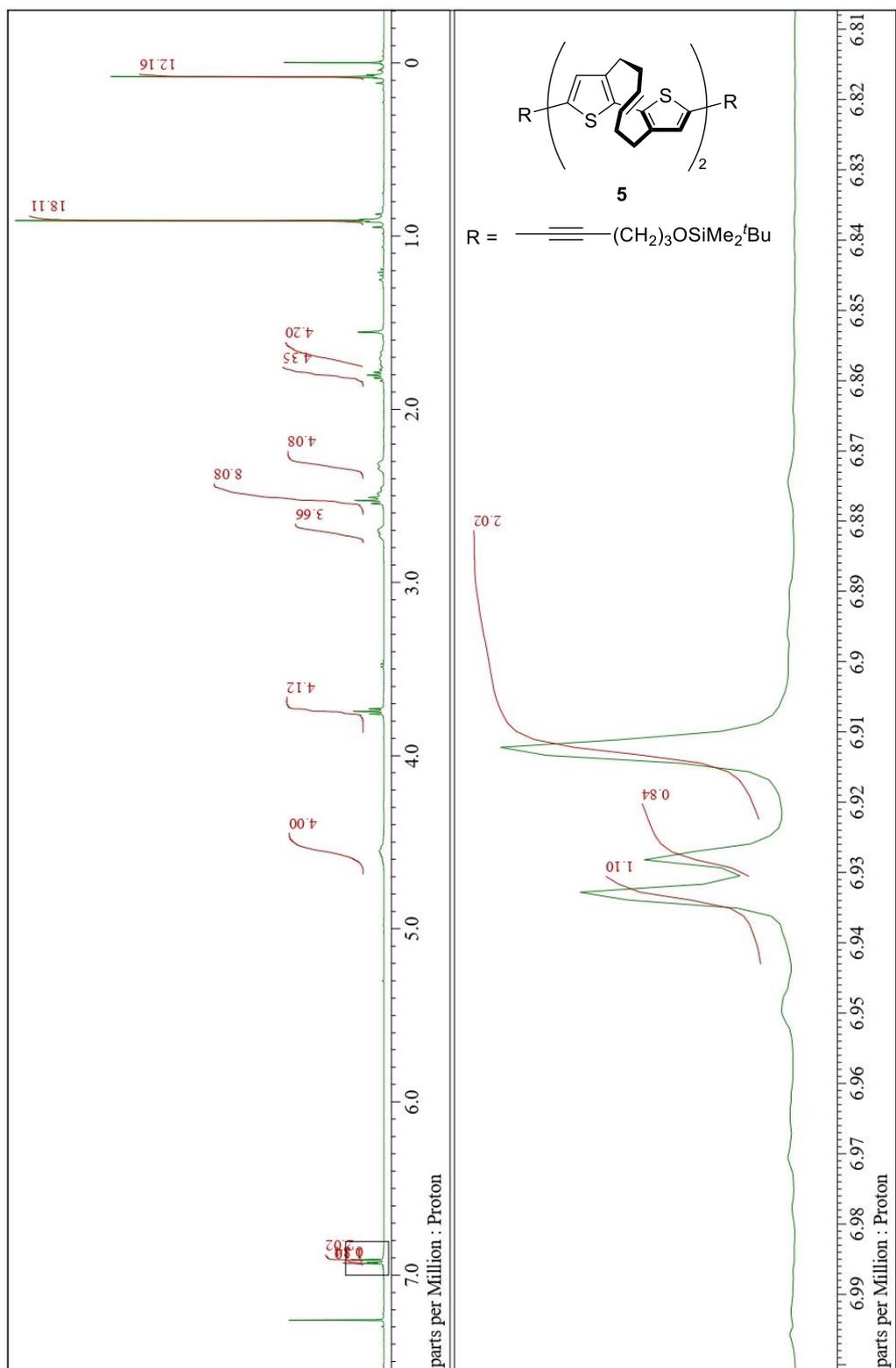


Figure S5. 1H NMR spectrum of bithiophene dimer **5**

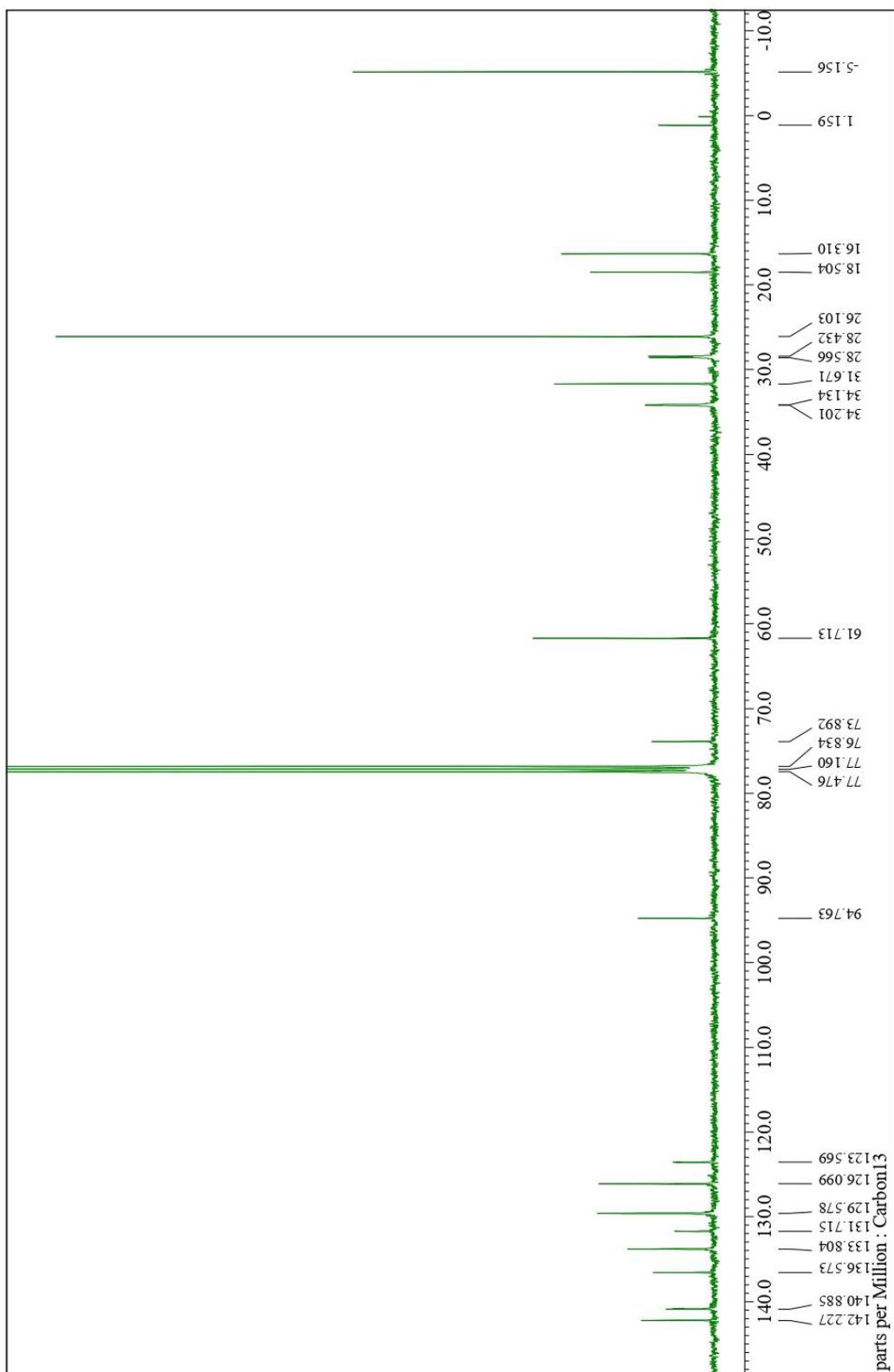


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of bithiophene dimer 5

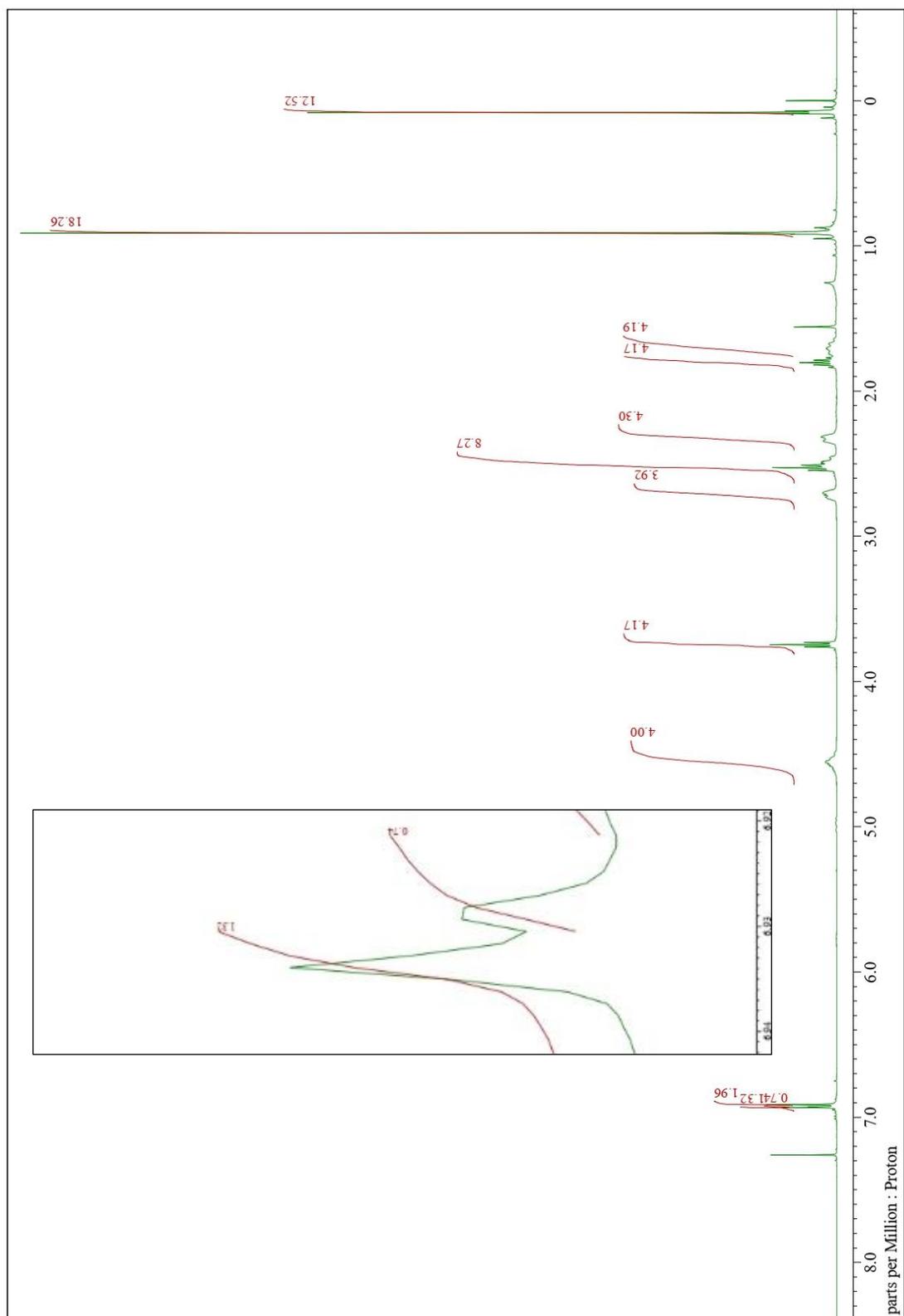


Figure S7. ^1H NMR spectrum of meso-enriched bithiophene dimer **5a**

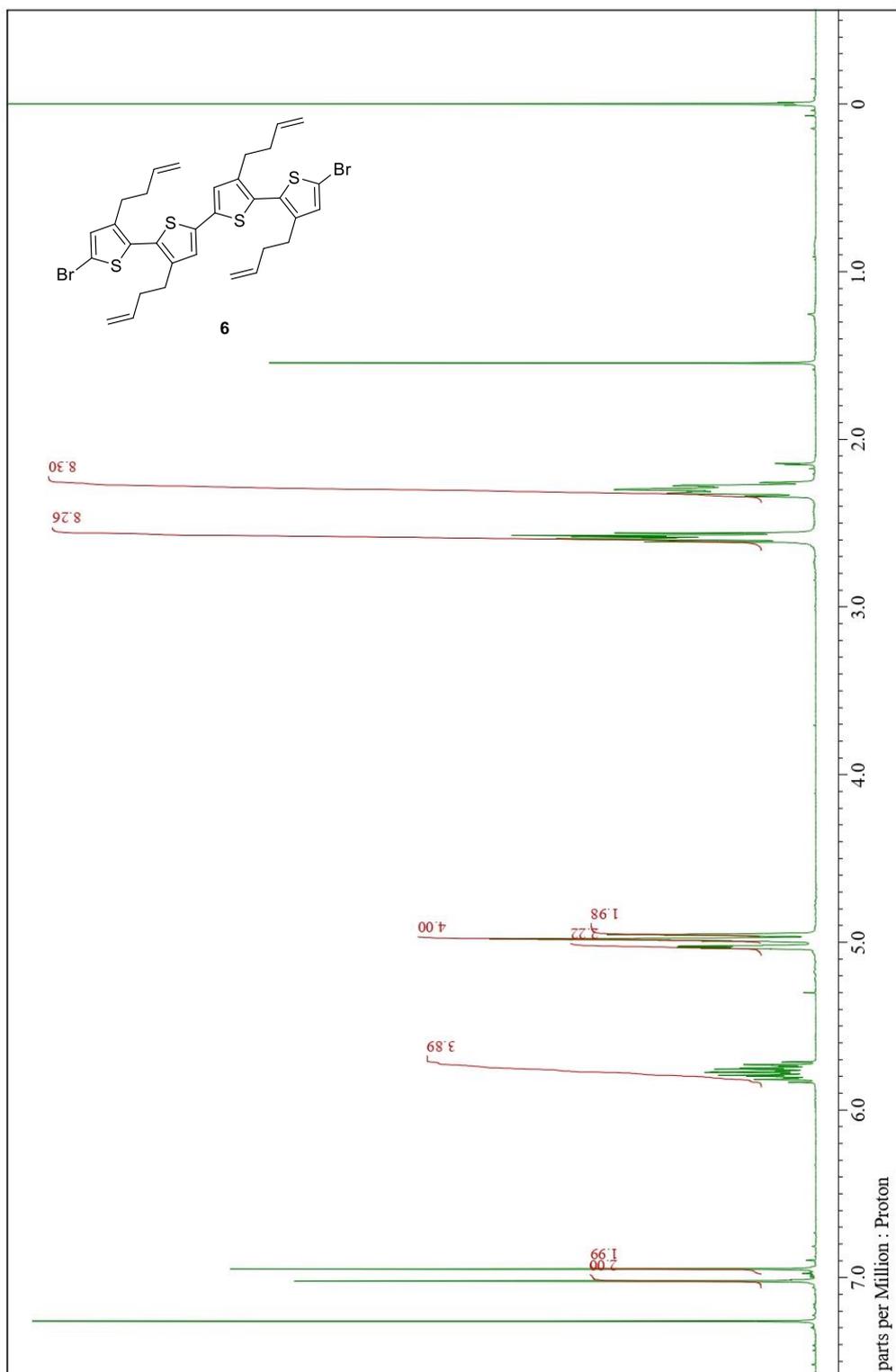


Figure S8. ¹H NMR spectrum of quaterthiophene **6**

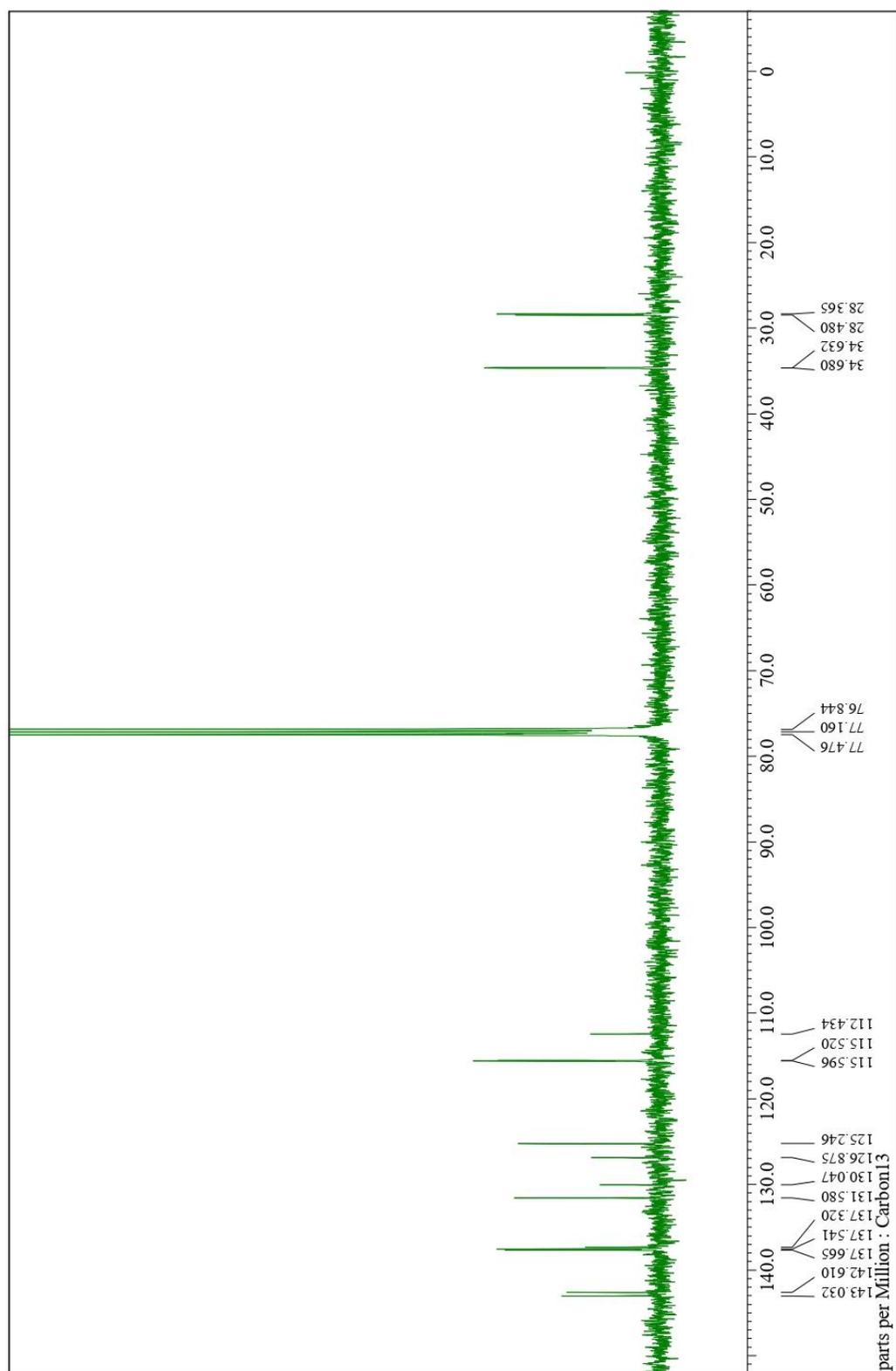


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of quaterthiophene **6**

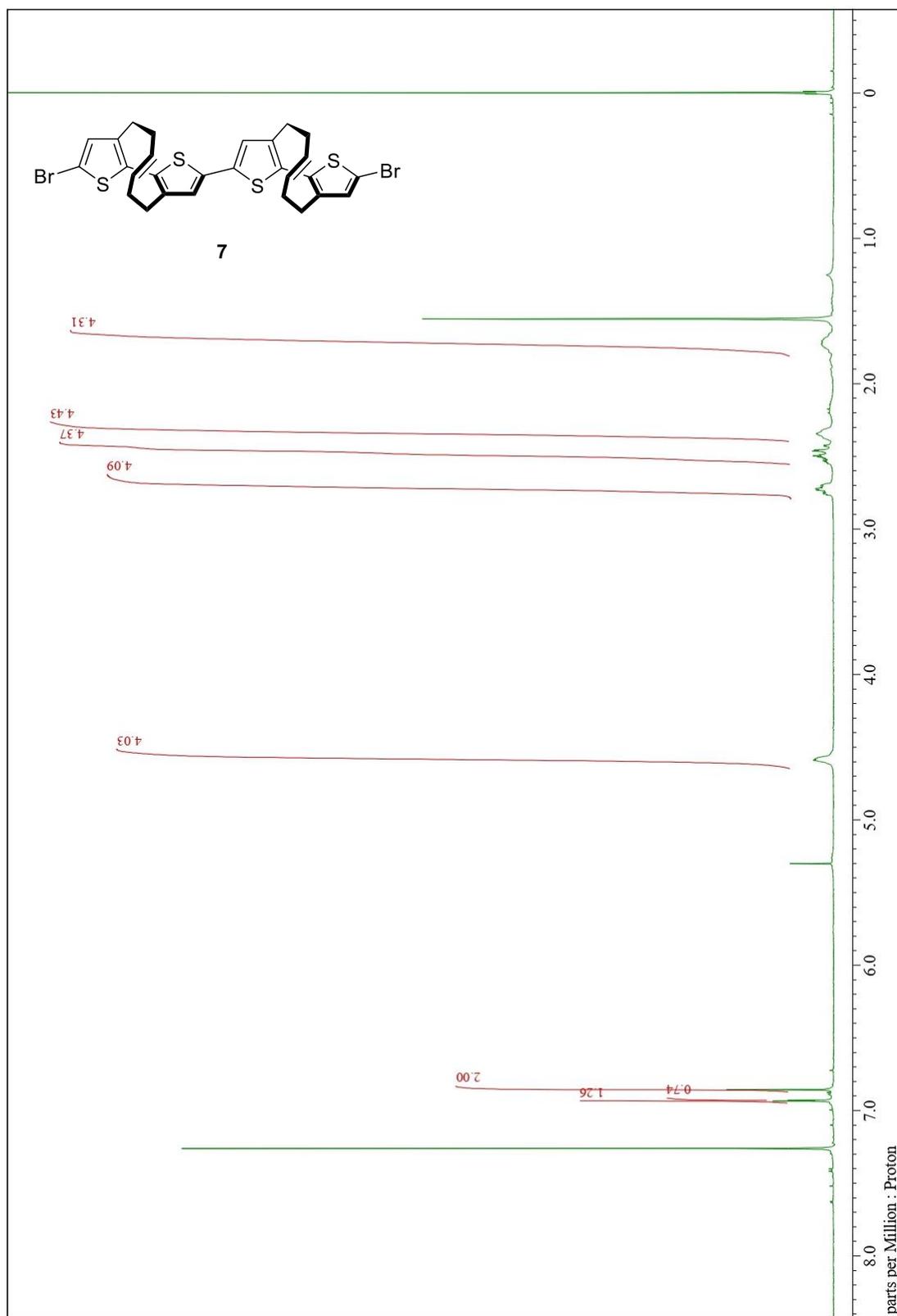


Figure S10. ¹H NMR spectrum of bithiophene dimer **7a**

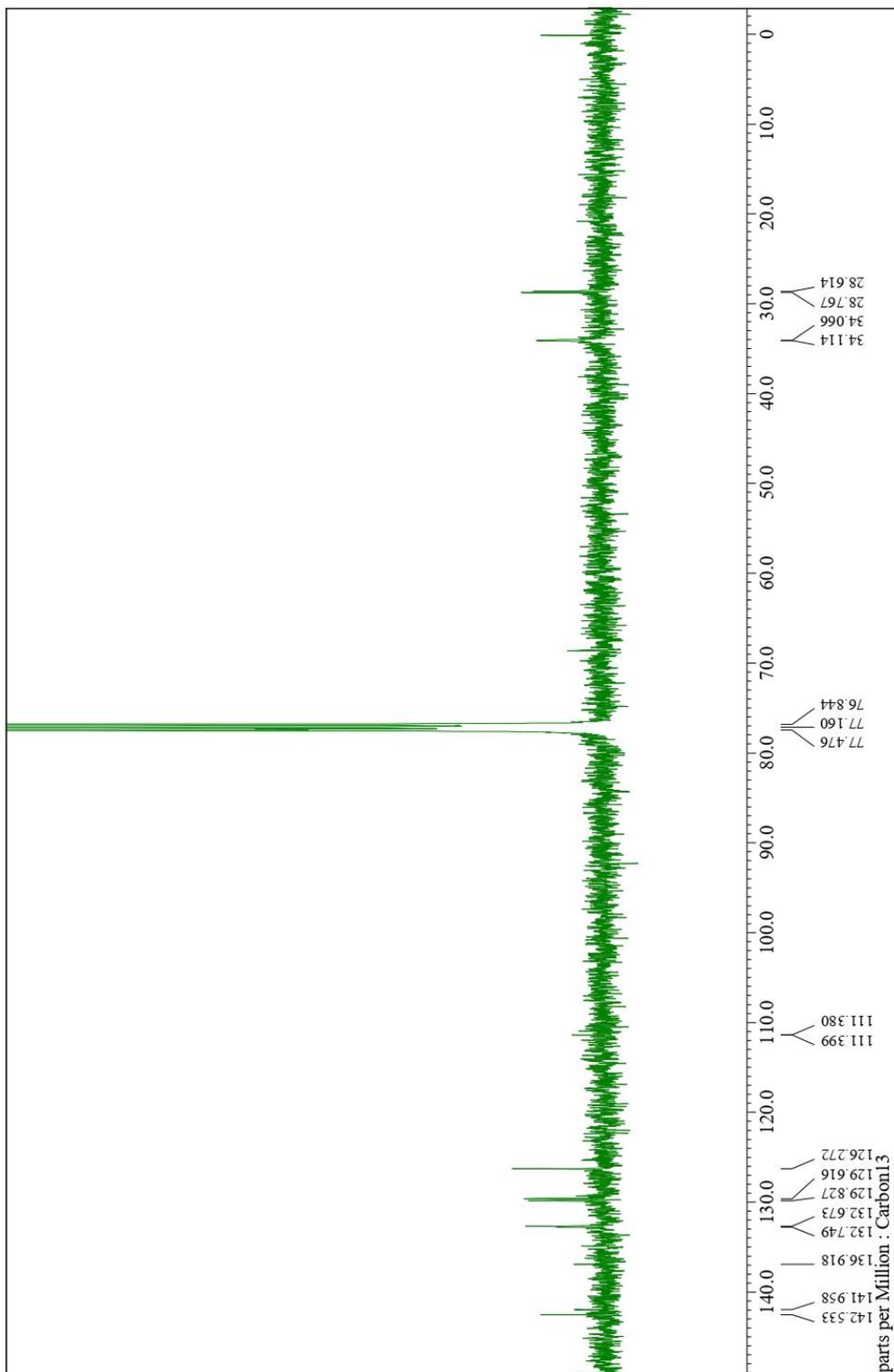


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of bithiophene dimer **7**

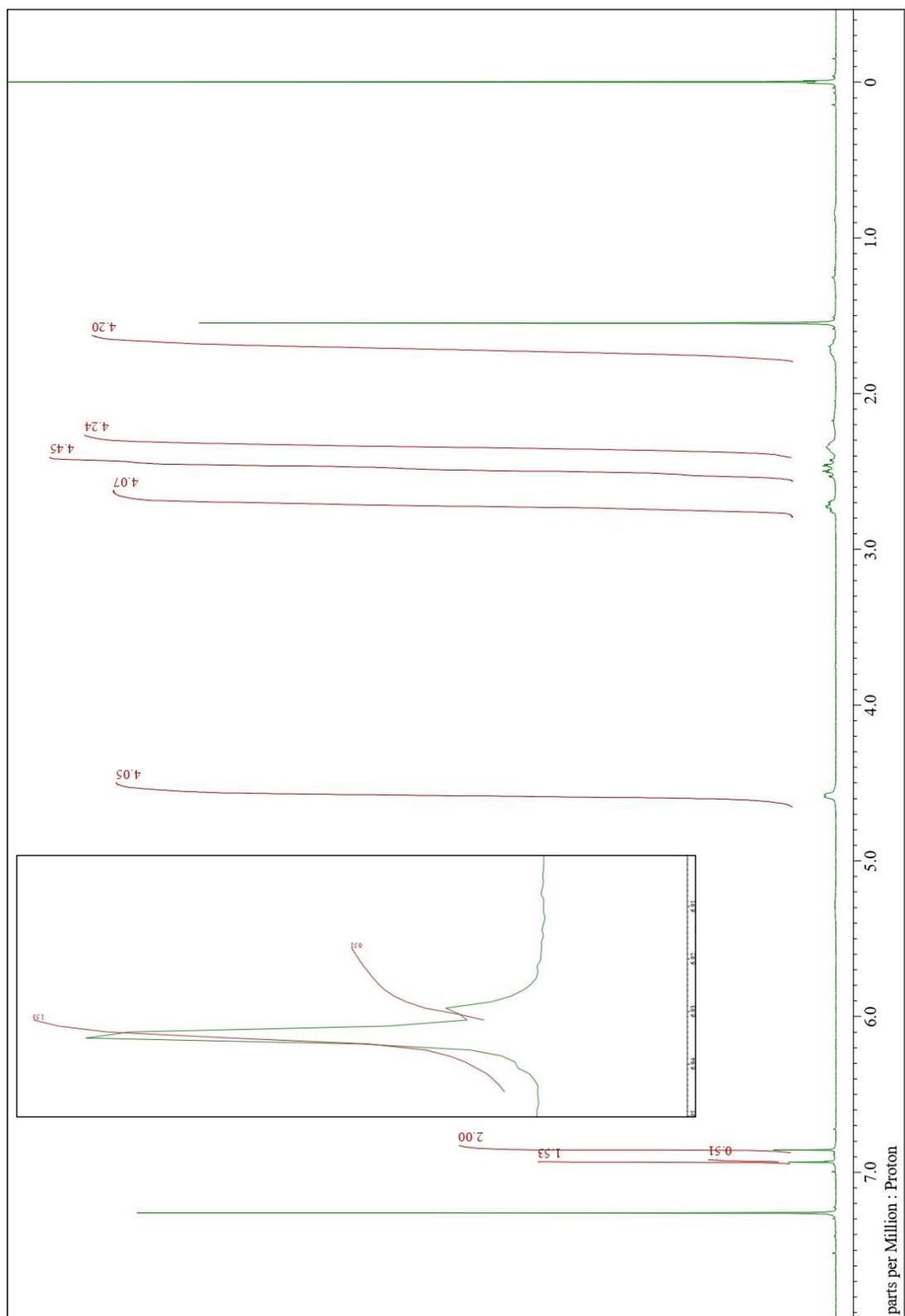


Figure S12. ^1H NMR spectrum of meso-enriched bithiophene dimer **7a**

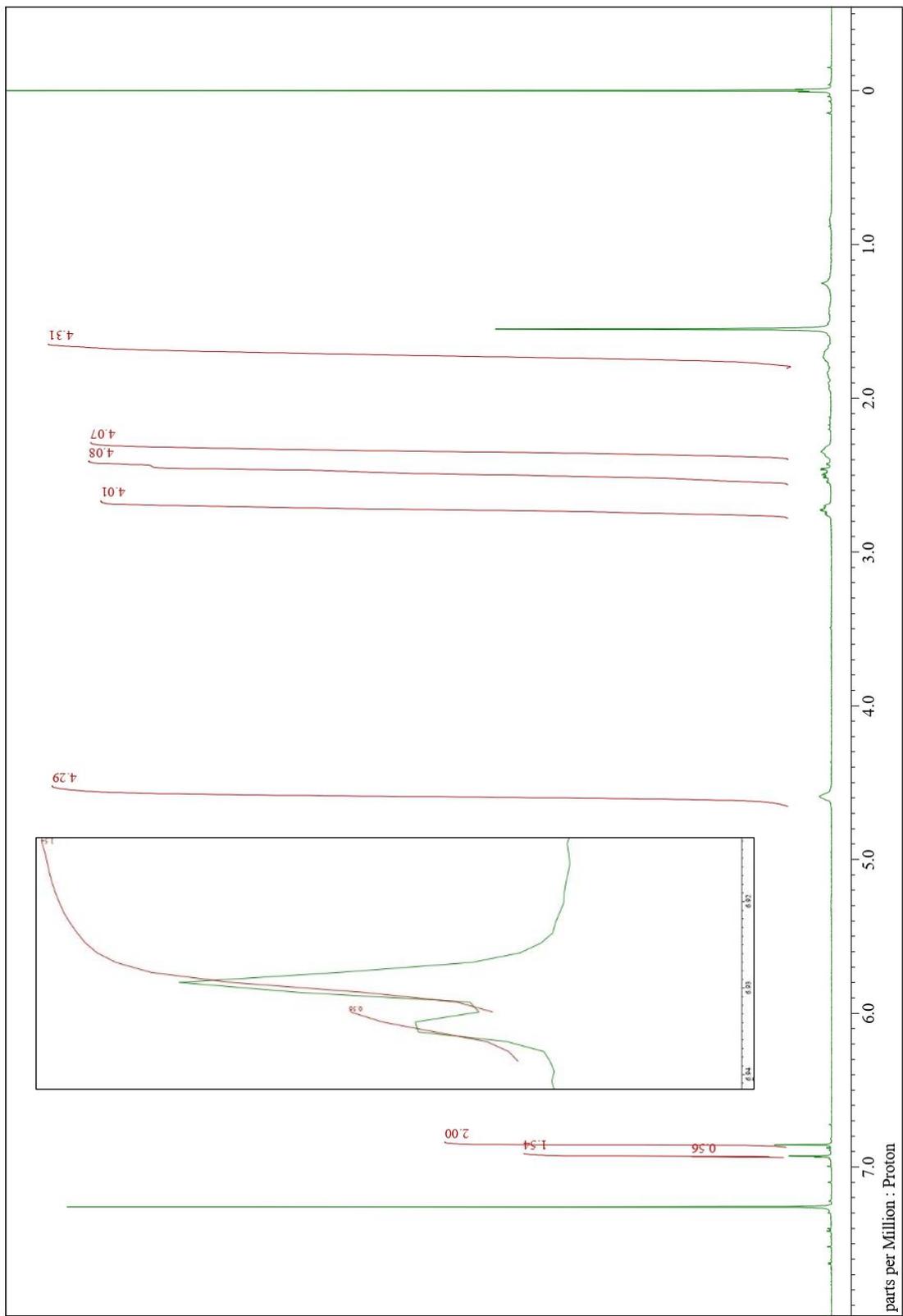
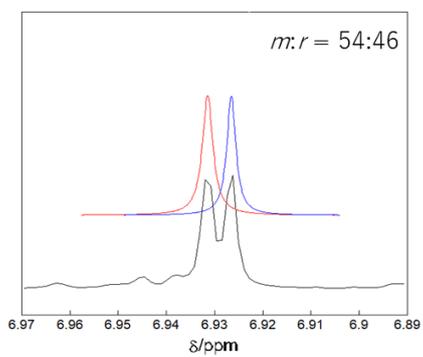


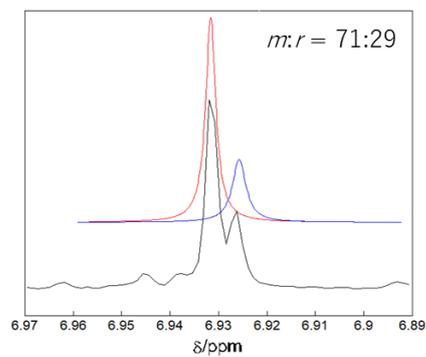
Figure S13. ^1H NMR spectrum of racemate-enriched bithiophene dimer **7b**

(a)

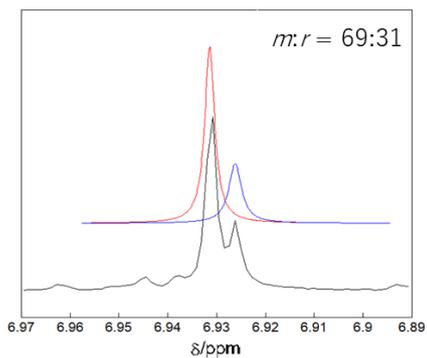
bithiophene **7** as prepared



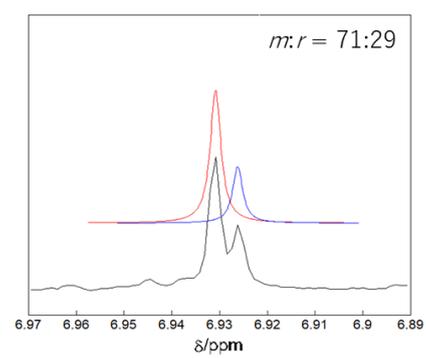
after 22 days kept as a solid state at $-20\text{ }^{\circ}\text{C}$



after 16 days kept as a solid state at $-20\text{ }^{\circ}\text{C}$

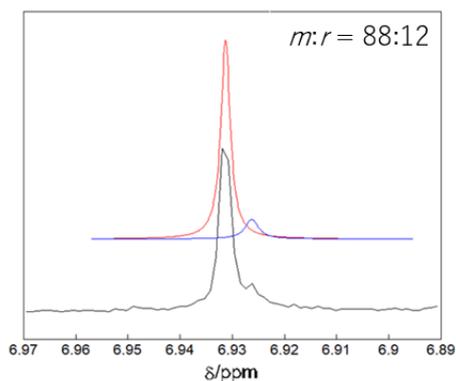


meso-enriched **7** after heating the solid at $80\text{ }^{\circ}\text{C}$ for 3 days

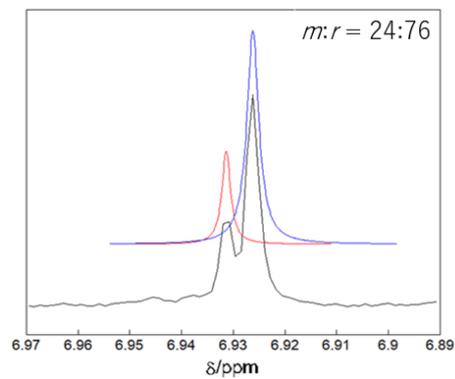


(b)

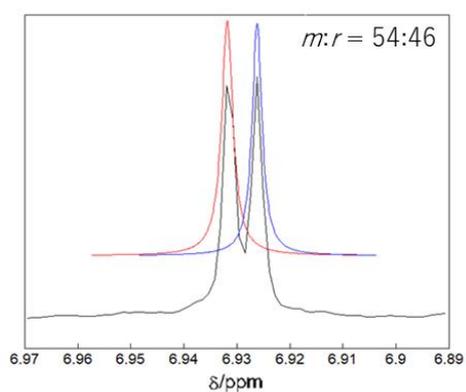
Meso-enriched **7** by recrystallization



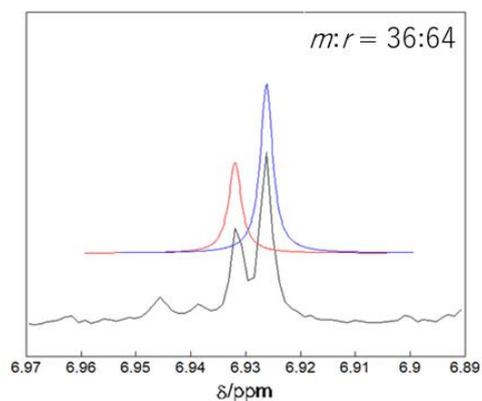
Racemate-enriched **7** (filtrate after recrystallization) as obtained



Meso-enriched **7** after heating the solution at 50 °C for 30 min



Racemate-enriched **7** after 7 days kept in the solid state at -20 °C



Racemate-enriched **7** after 54 days kept in the solid state at -20 °C

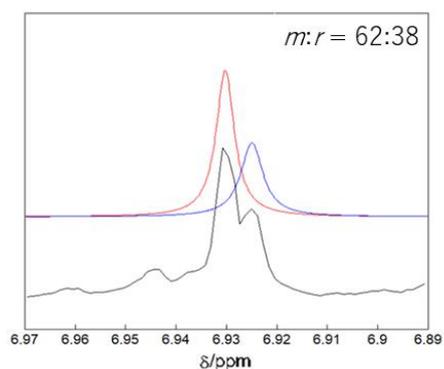
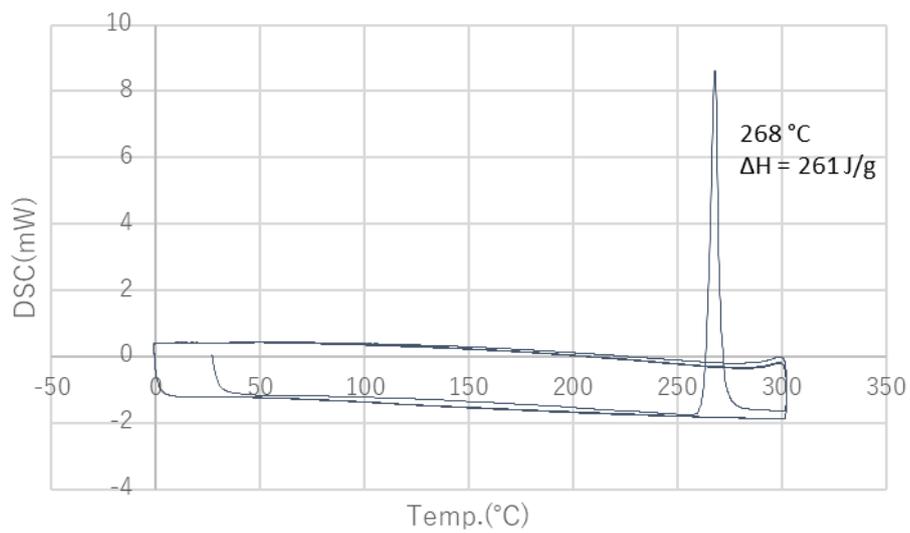


Figure S14. ^1H NMR spectra of bithiophene **7** shown in Figure 2 for the determination of the diastereomeric ratios with curve fitting

(a)



(b)

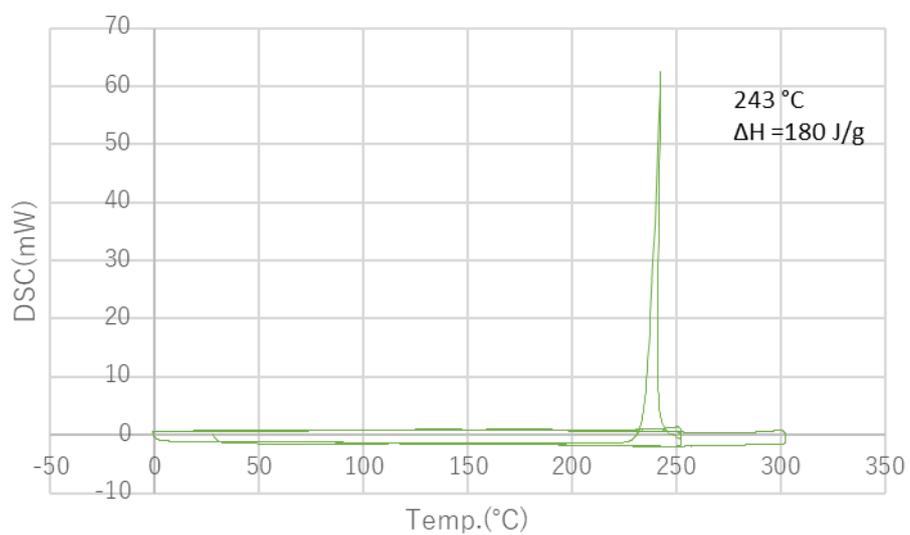


Figure S15. DSC profile of bithiophene wire **7** (a) meso-enriched (ca. 8:2) and (b) ca. 1:1 mixture of meso and racemic isomers

References

- 1 S. Ashida, N. Tanaka, Y. Ito, M. Matsuoka, T. Hashimoto, K. Okano, Y. Miyazaki, T. Kobayashi, T. Yaita and A. Mori, *J. Org. Chem.*, 2018, **83**, 14797–14801.
- 2 R. Inoue, M. Yamaguchi, Y. Murakami, K. Okano and A. Mori, *ACS Omega*, 2018, **3**, 12703–12706.
- 3 R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2006, **45**, 3760–3765.