Electronic Supplementary Information (ESI)

Effects of chalcogen atom substitution on the optoelectronic and charge-transport properties in picene-type π-systems

Tatsuya Oyama,[a,b] Yu Seok Yang,[a] Kyohei Matsuo[a] and Takuma Yasuda*[ab]

[a]INAMORI Frontier Research Center (IFRC), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

[b]Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

*E-mail: yasuda@ifrc.kyushu-u.ac.jp

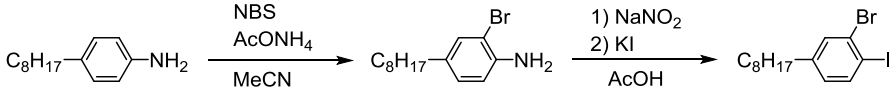
Contents:

1. General Methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer. Chemical shifts of ^{1}H and ^{13}C NMR signals were quoted to tetramethylsilane ($\delta = 0.00$) and $CDCl_3$ ($\delta = 77.0$) as internal standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Daltonics Autoflex III spectrometer using dithranol as the matrix. Elemental analysis was carried out with a Yanaco MT-5 CHN corder. UV–vis absorption spectra were measured with a JASCO V-670Y spectrometer. The HOMO energy levels of materials in thin films were determined using a Riken-Keiki AC-2 ultraviolet photoelectron spectrometer. Cyclic voltammetry (CV) was performed using an ALS CHI 612E electrochemical analyzer and a three-electrode cell equipped with Pt working and counter electrodes and an Ag/Ag^{+} reference electrode. The supporting electrolyte was *n*-Bu_4NClO_4/CH_2Cl_2 (0.1 M). The redox potentials were calibrated with Fc/Fc^{+} couple using ferrocene as a reference. Differential scanning calorimetry (DSC) was performed using a Hitachi High-Tech Science DSC7000X at a heating rate of 10 °C min^{-1} under N_2 atmosphere. The density-functional theory (DFT) computations were performed with the Gaussian 09 program package, using the B3LYP functional with the LanL2DZ basis set.

2. Synthesis and Characterizations

All reagents and solvents were purchased from Sigma-Aldrich, Tokyo Chemical Industry, or Wako Pure Chemical Industries, and were used as received unless otherwise noted. All reactions were performed under N_2 in dry solvents, using standard Schlenk techniques. 2,5-Bis(trimethylstannyl)thiophene (**4a**)[1] and 2,5-bis(trimethylstannyl)-selenophene (**4b**)[1] were prepared according to procedures described in the literature. 2-Bromo-1-iodo-4-octylbanzene was prepared according to Scheme 1, by modifying a reported procedure.[2]



Scheme S1. Synthesis of 2-bromo-1-iodo-4-octylbanzene.

2-Bromo-4-octylaniline: To a stirred solution of 4-octylaniline (49.3 g, 240 mmol) and ammonium acetate (1.85 g, 24 mmol) in acetonitrile (600 mL) was added slowly *N*-bromosuccinimide (NBS, 42.7 g, 240 mmol) at 0 °C. The mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was poured into water, and then extracted with ethyl acetate. The combined organic layers were washed with

water, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 9:1, v/v), and dried under vacuum to afford the desired compound as a brown oil (yield = 66.2 g, 97 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 2.0 Hz, 1H), 6.91 (dd, J = 8.0, 2.0 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 3.97 (br, 2H), 2.46 (t, J = 7.0 Hz, 2H), 1.50-1.66 (m, 2H) , 1.25-1.28 (m, 10H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.69, 134.42, 132.12, 128.36, 115.75, 109.34, 34.70, 31.88, 31.60, 29.46, 29.26, 29.18, 22.67, 14.10. MS (MALDI-TOF): m/z 283.07 $[M]^+$; calcd 283.09.

2-Bromo-1-iodo-4-octylbenzene: To a stirred solution of 2-bromo-4-octylaniline (43.8 g, 154 mmol) in acetic acid (140 mL) was added dropwise a solution of $NaNO_2$ (15.9 g, 231 mmol) in H_2SO_4 (100 mL) at 0 °C. Then, a solution of KI (51.1 g, 308 mmol) in water (200 mL) was slowly added to the mixture, and the reaction mixture was refluxed for 2 h. After cooling to room temperature, the reaction mixture was poured into a large amount of water, and then extracted with ethyl acetate. The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane), and dried under vacuum to afford the desired compound as a color-less oil (yield = 46.6 g, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.1 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H), 6.79 (dd, J = 8.1, 2.0 Hz, 1H), 2.50 (t, J = 7.6 Hz, 2H), 1.54-1.58 (m, 2H), 1.25-1.30 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.96, 139.88, 132.72, 129.43, 128.82, 97.08, 35.09, 31.84, 31.02, 29.36, 29.19, 29.13, 22.64, 14.10. MS (MALDI-TOF): m/z 394.05 $[M]^+$; calcd 393.98.

1,4-Bis(2-bromo-4-octylphenyl)buta-1,3-diyne (5): To a mixture of 2-bromo-1-iodo-4-octylbenzene (7.00 g, 17.7 mmol), 1,4-bis(trimethylsilyl)buta-1,3-diyne (1.81 g, 9.30 mmol), CuI (0.337 g, 1.77 mmol), and $Pd(PPh_3)_4$ (1.02 g, 0.88 mmol) in dry toluene (100 mL) was added dropwise tetrabutylammonium fluoride (26.6 mL, 1 M in THF, 26.6 mmol). The mixture was stirred overnight at 50 °C. The reaction mixture was poured into water, and extracted with chloroform. The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane), and dried under vacuum to give **5** as a yellow solid (yield = 3.56 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 1.6 Hz, 2H), 7.09 (dd, J = 8.0, 1.6 Hz, 2H), 2.58 (t, J = 7.6 Hz, 4H), 1.64-1.56 (m, 4H), 1.36-1.20 (m, 20H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.27, 134.26, 132.47, 127.39, 125.98, 121.24, 81.01, 35.66, 31.84, 30.94, 29.37, 29.19, 22.65, 14.10. MS (MALDI-TOF): m/z 583.80 $[M+H]^+$; calcd

583.16. Anal. calcd (%) for $C_{32}H_{40}Br_2$: C 65.76, H 6.90; found: C 65.87, H 6.98.

2,5-Bis(2-bromo-4-octylphenyl)thiophene (6a): A mixture of 2-bromo-1-iodo-4-octylbenzene (18.0 g, 45.6 mmol), **4a** (7.78 g, 19.0 mmol), and $Pd(PPh_3)_4$ (1.32 g, 1.14 mmol) in dry DMF (150 mL) was stirred for 24 h at 80 °C. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with chloroform. The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane), and dried under vacuum to afford **6a** as a colorless oil (yield = 8.87 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 2.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.27 (s, 2H), 7.14 (dd, J = 8.0, 2.0 Hz, 2H), 2.60 (t, J = 7.8 Hz, 4H), 1.66-1.59 (m, 4H), 1.39-1.22 (m, 20H), 0.89 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.41, 142.18, 133.59, 132.22, 131.53, 127.63, 127.32, 122.28, 35.21, 31.88, 31.16, 29.42, 29.24, 29.23, 22.67, 14.11. MS (MALDI-TOF): *m/z* 615.82 $[M]^+$; calcd 616.14. Anal. calcd (%) for $C_{32}H_{42}Br_2S$: C 62.14, H 6.84; found: C 62.21, H 6.84.

2,5-Bis(2-bromo-4-octylphenyl)selenophene (6b): This compound was synthesized according to the same procedure as described above for the synthesis of **6a**, using 2-bromo-1-iodo-4-octylbenzene (15.2 g, 38.5 mmol), **4b** (7.30 g, 16.0 mmol), and $Pd(PPh_3)_4$ (1.10 g, 0.95 mmol). The product was obtained as a light yellow oil (yield = 6.26 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 1.5 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.41 (s, 2H), 7.14 (dd, J = 7.8, 1.5 Hz, 2H), 2.59 (t, J = 7.8 Hz, 4H), 1.66-1.58 (m, 4H), 1.39-1.22 (m, 20H), 0.89 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.76, 144.30, 134.30, 133.53, 131.31, 129.44, 127.63, 122.08, 35.20, 31.88, 31.15, 29.43, 29.26, 29.24, 22.67, 14.11. MS (MALDI-TOF): *m/z* 663.90 $[M]^+$; calcd 664.08. Anal. calcd (%) for $C_{32}H_{42}Br_2Se$: C 57.76, H 6.36; Found: C 57.91, H 6.43.

2,5-Bis(2-bromo-4-octylphenyl)tellurophene (6c): A suspension of tellurium powder (1.83 g, 14.3 mmol) and sodium borohydride (2.17 g, 57.4 mmol) in a mixture of ethanol (296 mL) and water (8 mL) was reflux until the solution turned to purple and to colorless. After the reaction temperature was reduced to 80 °C, a degassed solution of **5** (2.82 g, 4.82 mmol) in ethanol (440 mL) was added, and the reaction mixture was stirred at 80 °C overnight. After cooling to room temperature, the formed black precipitate was removed by filtration through a celite pad. The reaction mixture was poured into water, and then extracted with chloroform. The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane), and dried under vacuum to afford **6c** as an orange oil (yield = 2.85 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 2H),

7.50-7.47 (m, 4H), 7.13 (dd, J = 8.0, 1.6 Hz, 2H), 2.58 (t, J = 7.8 Hz, 4H), 1.67-1.57 (m, 4H), 1.40-1.21 (m, 20H), 0.89 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.11, 143.83, 137.74, 136.35, 133.36, 130.11, 127.73, 122.21, 35.17, 31.88, 31.14, 29.43, 29.26, 29.24, 22.67, 14.11. MS (MALDI-TOF): *m/z* 714.60 $[M]^+$; calcd 714.07. Anal. calcd (%) for $C_{32}H_{42}Br_2Te$: C 53.82, H 5.93; found: C 54.13, H 5.99.

2,5-Bis(2-formyl-4-octylphenyl)thiophene (7a): To a stirred solution of **6a** (3.80 g, 6.14 mmol) in dry THF (150 mL) was added dropwise *n*-butyllithium (2.65 M in hexane, 4.8 mL, 12.9 mmol) at −78 °C. The mixture was allowed to react for 1 h at that temperature. Then, 1-formylpiperidine (1.67 g, 14.8 mmol) was added, and the mixture was stirred overnight at room temperature. The reaction mixture was poured into water, and extracted with chloroform. The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane/chloroform = 4:1, v/v), and dried under vacuum to afford **7a** as a yellow oil (yield = 2.00 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.28 (s, 2H), 7.85 (d, J = 1.5 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.47 (dd, J = 8.0, 2.0 Hz, 2H), 7.07 (s, 2H), 2.71 (t, J = 7.5 Hz, 4H), 1.71-1.62 (m, 4H), 140-1.22 (m, 20H), 0.89 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.03, 143.85, 140.71, 134.85, 134.02, 133.93, 131.22, 129.67, 127.67, 35.54, 31.87, 31.18, 29.42, 29.26, 29.23, 22.67, 14.11. MS (MALDI-TOF): *m/z* 516.99 $[M]^+$; calcd 516.31. Anal. calcd (%) for $C_{34}H_{44}O_2S$: C 79.02, H 8.58; found: C 78.83, H 8.58.

2,5-Bis(2-formyl-4-octylphenyl)selenophene (7b): This compound was synthesized according to the same procedure as described above for the synthesis of **7a**, using **6b** (5.00 g, 7.51 mmol), *n*-butyllithium (2.65 M in hexane, 5.9 mL, 15.7 mmol) and 1-formylpiperidine (2.04 g, 18.0 mmol). The product was obtained as a yellow oil (yield = 1.50 g, 34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.31 (s, 2H), 7.83 (s, J = 1.5 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.45 (dd, J = 8.3, 1.5 Hz, 2H), 7.20 (s, 2H), 2.70 (t, J = 7.8 Hz, 4H), 1.71-1.62 (m, 4H), 1.40-1.22 (m, 20H), 0.89 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.10, 147.11, 143.79, 137.04, 133.94, 133.54, 131.87, 131.49, 127.57, 35.54, 31.87, 31.18, 29.42, 29.26, 29.23, 22.67, 14.11. MS (MALDI-TOF): *m/z* 564.97 $[M]^+$; calcd 564.25. Anal. calcd (%) for $C_{34}H_{44}O_2Se$: C 72.45, H 7.87; found: C 72.18, H 7.91.

2,5-Bis(2-formyl-4-octylphenyl)tellurophene (7c): This compound was synthesized according to the same procedure as described above for the synthesis of **7a**, using **6c** (2.04 g, 2.86 mmol), *n*-butyllithium (2.65 M in hexane, 2.3 mL, 6.1 mmol) and 1-formylpiperidine (0.73 g, 6.44 mmol). The product was obtained as a yellow solid (yield = 0.43 g, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.36 (s, 2H), 7.80 (s, 2H), 7.56 (s, 2H),

7.43-7.41 (m, 4H), 2.69 (t, *J* = 7.8 Hz, 4H), 1.70-1.60 (m, 4H), 1.40-1.22 (m, 20H), 0.89 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.32, 145.74, 143.42, 141.04, 139.37, 133.90, 132.84, 131.76, 127.69, 35.52, 31.88, 31.18, 29.43, 29.26, 29.23, 22.67, 14.11. MS (MALDI-TOF): *m/z* 613.50 $[M]^+$; calcd 614.24. Anal. calcd (%) for $C_{34}H_{44}O_2Te$: C 66.69, H 7.24; found: C 66.71, H 7.29.

2,5-bis(4-octyl-2-oxiranylphenyl)thiophene (8a): To a mixture of **7a** (2.30 g, 4.45 mmol) in dry acetonitrile (120 mL) was added trimethylsulfonium iodide (2.18 g, 10.7 mmol) and KOH (1.37 g, 24.4 mmol). The mixture was stirred for 4 h at 60 °C. After cooling to room temperature, the reaction mixture was added into water, and then extracted with chloroform. The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4. After filtration and evaporation, a crude product of **8a** was obtained as a yellow oil in a quantitative yield. This crude product was used in the next reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 7.5, 3.0 Hz, 2H), 7.19-7.17 (m, 4H), 7.11 (s, 2H), 4.16-4.12 (m, 2H) , 3.20-3.16 (m, 2H), 2.85-2.82 (m, 2H) , 2.62 (t, *J* = 8.0 Hz, 4H), 1.66-1.59 (m, 4H), 1.38-1.22 (m, 20H), 0.89 (t, *J* = 7.0 Hz, 6H). MS (MALDI-TOF): *m/z* 544.23 $[M]^+$; calcd 544.34.

2,5-bis(4-octyl-2-oxiranylphenyl)selenophene (8b): This compound was prepared according to the same procedure as described above for the synthesis of **8a**, using **7b** (1.40 g, 2.48 mmol), trimethylsulfonium iodide (1.20 g, 5.88 mmol), and powdered KOH (0.76 g, 13.5 mmol). The crude product was obtained as a brown oil in a quantitative yield, which was used in the next reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.24 (d, *J* = 2.0 Hz, 2H), 7.17-7.13 (m, 4H), 4.19-4.14 (m, 2H), 3.19-3.15 (m, 2H), 2.85-2.82 (m, 2H), 2.62 (t, *J* = 8.0 Hz, 4H), 1.66-1.58 (m, 4H), 1.38-1.23 (m, 20H), 0.89 (t, *J* = 7.0 Hz, 6H). MS (MALDI-TOF): *m/z* 592.26 $[M]^+$; calcd 592.28.

2,5-bis(4-octyl-2-oxiranylphenyl)tellurophene (8c): This compound was prepared according to the same procedure as described above for the synthesis of **8a**, using **7c** (0.66 g, 1.1 mmol), trimethylsulfonium iodide (0.53 g, 2.6 mmol) and KOH (0.33 g, 5.9 mmol). The crude product was obtained as a brown oil in a quantitative yield, which was used in the next reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.58 (s, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.10-7.14 (m, 4H), 4.18-4.22 (m, 2H) , 3.13-3.17 (m, 2H), 2.82-2.85 (m, 2H), 2.60 (t, *J* = 7.8 Hz, 4H), 1.60-1.70 (m, 4H), 1.20-1.38 (m, 20H), 0.89 (t, *J* = 7.0 Hz, 6H). MS (MALDI-TOF): *m/z* 642.29 $[M]^+$; calcd 642.27.

3,10-Octyl-dinaphto[1,2-*b*:2',1'-*d*]thiophene (1): To a mixture of **8a** (2.40 g, 4.4 mmol) in 1,2-dichloroethane (200 mL) was added anhydrous indium chloride (0.19 g,

0.86 mmol). The mixture was stirred for 24 h at 100 °C. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with chloroform. The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane), and dried under vacuum to afford **1** as a white solid (yield = 1.02 g, 46%). This compound was further purified by temperature-gradient vacuum sublimation before use. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.5 Hz, 2H), 8.15 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 8.5 Hz, 2H), 7.76 (s, 2H), 7.49 (dd, J = 8.3, 2.0 Hz, 2H), 2.83 (t, J = 7.8 Hz, 4H), 1.78-1.71 (m, 4H), 1.44-1.22 (m, 20H), 0.88 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.89, 136.46, 133.29, 132.24, 128.23, 127.57, 127.44, 125.26, 124.11, 119.69, 36.16, 31.91, 31.49, 29.52, 29.38, 29.28, 22.68, 14.11. MS (MALDI-TOF): *m/z* 508.12 $[M]^+$; calcd 508.32. Anal. calcd (%) for $C_{36}H_{44}S$: C 84.98, H 8.72; found: C 85.00, H 8.54.

3,10-Octyl-dinaphto[1,2-*b*:2',1'-*d*]selenophene (2): This compound was synthesized according to the same procedure as described above for the synthesis of **1**, using **8b** (1.30 g, 2.2 mmol), anhydrous indium chloride (0.10 g, 0.44 mmol). The product was obtained as a white solid (yield = 0.59 g, 48%). This compound was further purified by temperature-gradient vacuum sublimation before use. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 8.5 Hz, 2H), 7.73 (s, 2H), 7.46 (dd, J = 8.5, 1.5 Hz, 2H), 2.82 (t, J = 7.5 Hz, 4H), 1.78-1.70 (m, 4H), 1.43-1.23 (m, 20H), 0.88 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.05, 138.78, 136.21, 132.28, 129.74, 128.39, 127.46, 125.91, 125.67, 120.95, 36.13, 31.90, 31.45, 29.52, 29.37, 29.28, 22.67, 14.11. MS (MALDI-TOF): *m/z* 556.15 $[M]^+$; calcd 556.26. Anal. calcd (%) for $C_{36}H_{44}Se$: C 77.81, H 7.98; found: C 77.80, H 7.77.

3,10-Octyl-dinaphto[1,2-*b*:2',1'-*d*]tellurophene (3): This compound was synthesized according to the same procedure as described above for the synthesis of **1**, using **8c** (0.60 g, 0.94 mmol), anhydrous indium chloride (0.04 g, 0.19 mmol). The product was obtained as a yellow solid (yield = 0.14 g, 24%). This compound was further purified by temperature-gradient vacuum sublimation before use. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.69 (s, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.42 (dd, J = 8.4, 1.6 Hz, 2H), 2.81 (t, J = 7.6 Hz, 4H), 1.78-1.68 (m, 4H), 1.43-1.22 (m, 20H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.89, 141.33, 134.09, 132.15, 132.02, 129.09, 128.55, 127.41, 126.48, 122.92, 36.08, 31.90, 31.41, 29.52, 29.35, 29.28, 22.67, 14.11. MS (MALDI-TOF): *m/z* 606.28 $[M]^+$; calcd 606.25. Anal. calcd (%) for $C_{36}H_{44}Te$: C 71.55, H 7.34; found: C 71.57, H 7.34.

3. Absorption Spectra in Solution

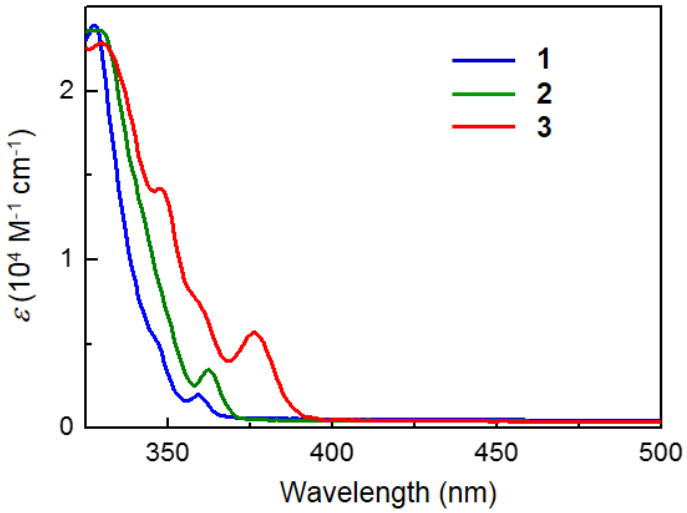


Fig. S1 UV–vis absorption spectra of **1–3** in CH_2Cl_2 solution.

4. Cyclic Voltammetry

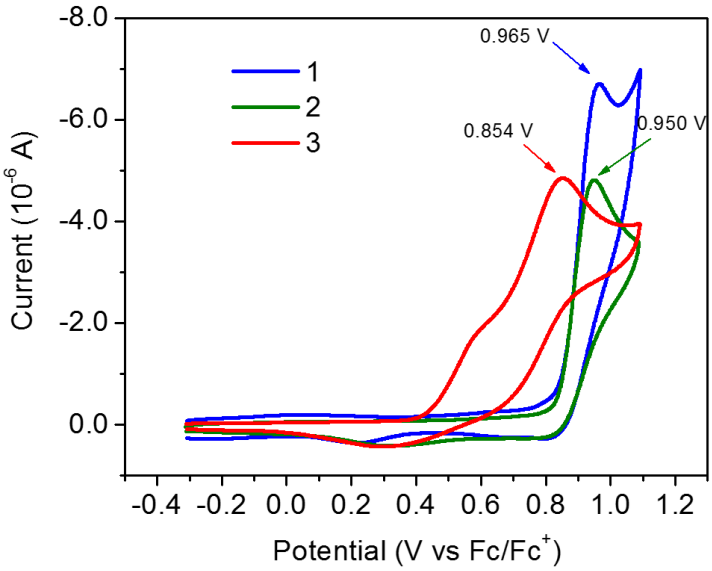


Fig. S2 Cyclic voltammograms of **1–3** in 0.1 M *n*-Bu_4NClO_4/CH_2Cl_2 electrolyte with a scan rate of 50 mV s^{-1}.

5. Differential Scanning Calorimetry

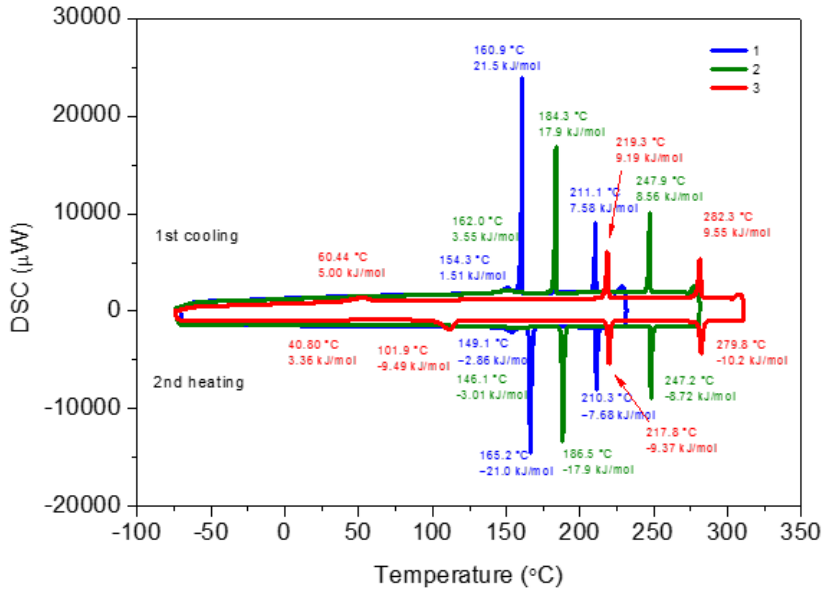


Fig. S3 DSC thermograms of **1–3** at a scanning rate of 10 °C min^{-1} under N_2.

6. Single-Crystal Structure of 3

Single-crystal X-ray measurements were performed using a Rigaku Saturn724 diffractometer with a multi-layer mirror monochromated Mo-Kα radiation. The structure was solved by the direct method (SIR-2008)[3] and refined by the full-matrix least-squares on F^2 for all reflections (SHELXL-97)[4]. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were placed using AFIX instructions. The measurements were carried out 123 K. Total 28319 reflections were collected, among which 6703 reflections were independent (R_{int} = 0.0786). The crystal data are as follows: formula $C_{36}H_{44}Te$, FW = 604.34, crystal size 0.20 × 0.10 × 0.01 mm, monoclinic, $P2_1/c$, (#14), a = 22.506(9), b = 8.456(3), c = 15.962(7) Å, β = 90.729(10)°, V = 3038(2) $Å^3$, Z = 4, D_{calcd} = 1.321 g cm^{-3}; R_1 = 0.1291 ($I > 2\sigma(I)$), wR_2 = 0.3415 (all data), GOF = 1.228. CCDC number: 1527053.

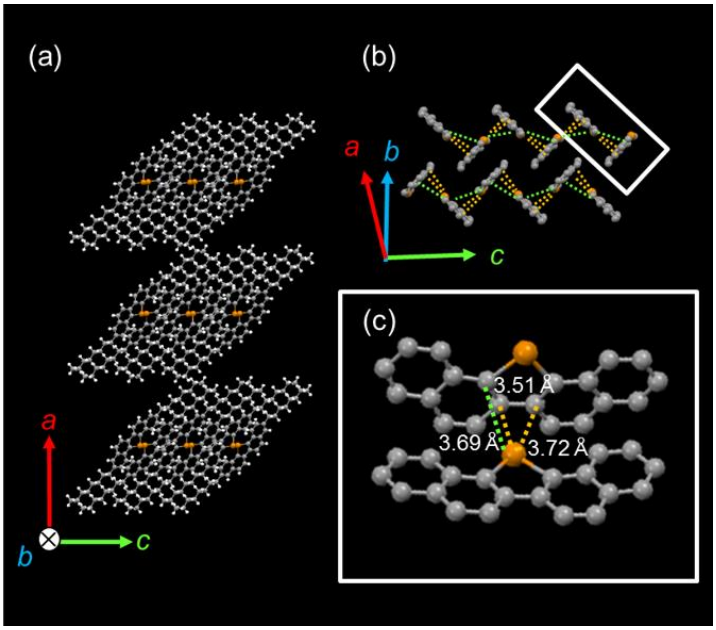


Fig. S4 (a) Molecular packing structure of **3** showing layer-by-layer assembly along the *a*-axis. (b) In-plane molecular arrangement in the *b*–*c* plane. The dashed lines denote the close intramolecular contacts. (c) Magnified view of two neighboring molecules.

7. OFET Characteristics

For all of the OFET devices, heavily doped n-type Si wafers with a thermally grown 300-nm-thick SiO_2 layer were used as substrates. The SiO_2/Si substrates were pretreated with a piranha solution at 90 °C for 1 h, and then copiously cleaned by sonication in deionized water, acetone, and isopropanol in that order. The SiO_2/Si substrates were exposed to a solution of octyltrichlorosilane (OTS) in dry toluene for 10 min with sonication to form a hydrophobic self-assembled monolayer surface. Self-organized crystalline microsheets or microribbons of **1–3** were grown by drop-casting from their solutions in anisole (1–2 g L^{-1}) onto the OTS-treated SiO_2/Si substrates, followed by drying for 12 h in a N_2-filled glove box at room temperature. The devices were completed by evaporating gold (thickness = 50 nm) through a shadow mask to define the source and drain electrodes with a channel length of 50–100 μm. The output and transfer characteristics of the OFETs were measured using an Agilent B1500A semiconductor parameter analyzer under ambient conditions at room temperature. Field-effect mobilities (μ) of the OFETs were determined from the forward transfer curve in the saturation regime using the following equation: $I_D = (W/2L)\mu C_i(V_G - V_{th})^2$, where I_D is the drain current, W and L are the channel width and length, respectively, C_i is the capacitance per

unit area of the gate dielectric (11.1 nF cm^{-2}), V_G and V_{th} are the gate voltage and threshold voltage, respectively. The W and L values were measured using a Keyence VH-5500 digital microscope.

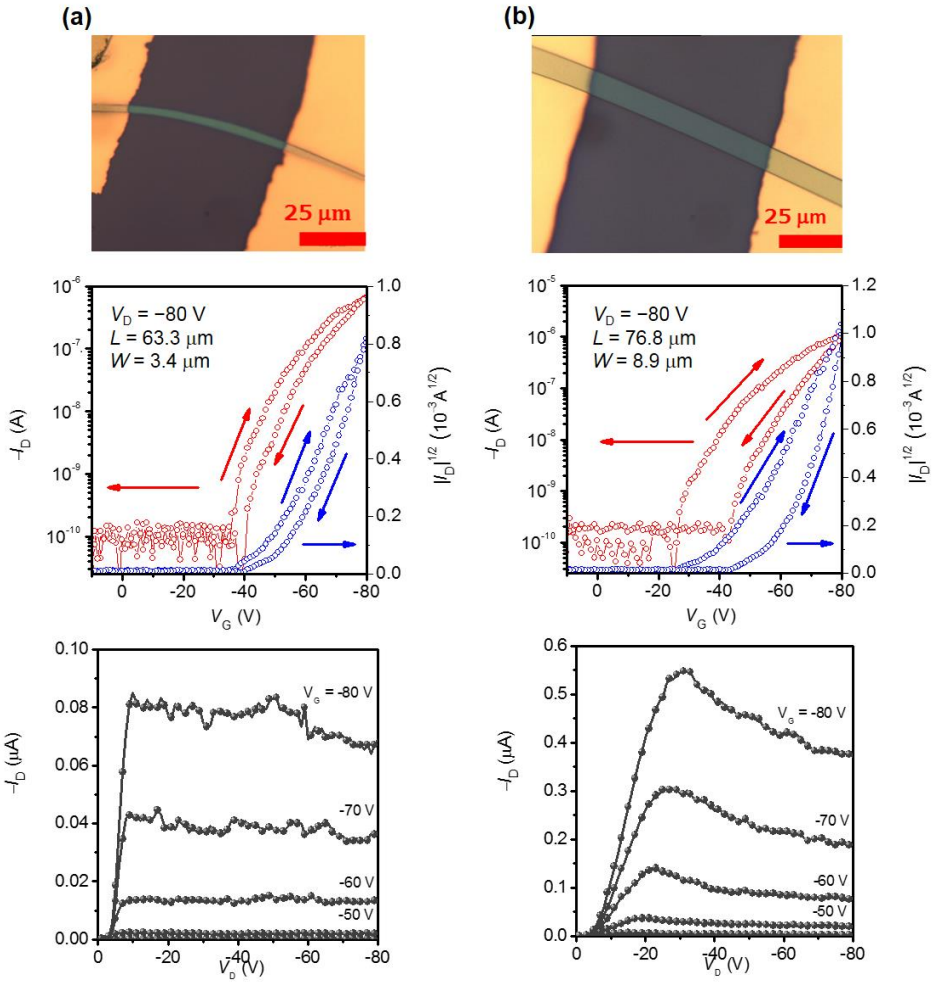
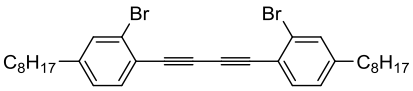
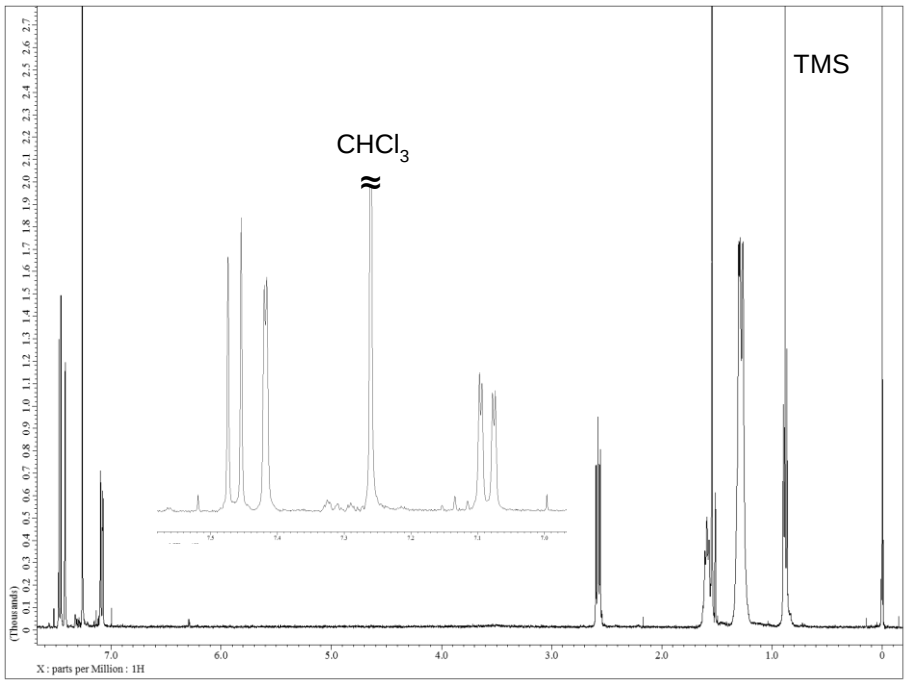


Fig. S5 Optical micrographs (top panels), transfer characteristics (middle panels), and output characteristics of representative OFETs based on microribbons of (a) **2** and (b) **3**.

8. ^{1}H and ^{13}C NMR Spectra





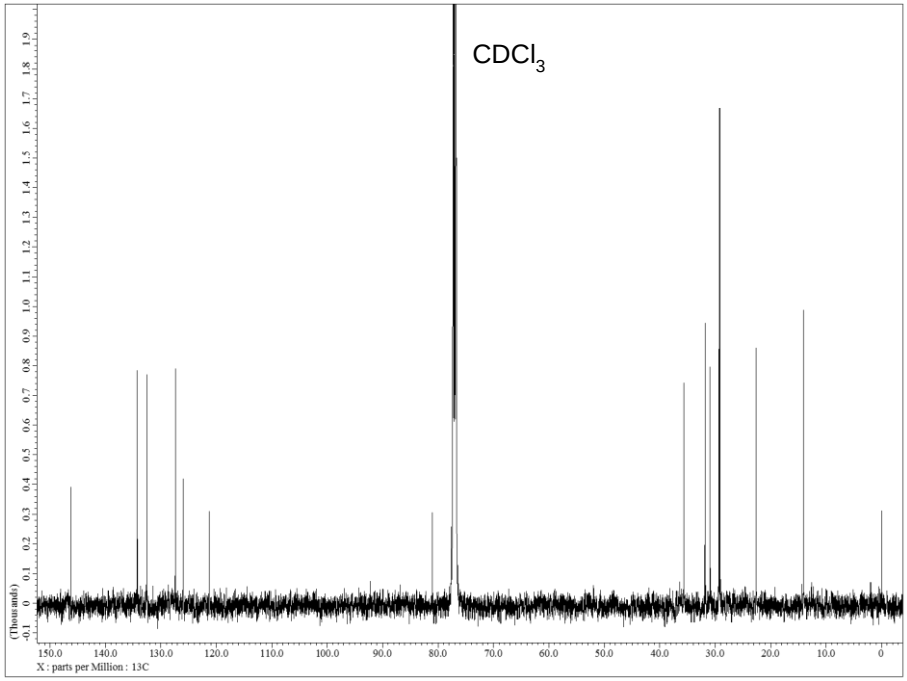


Fig. S6 ^{1}H and ^{13}C NMR spectra of compound **5**.

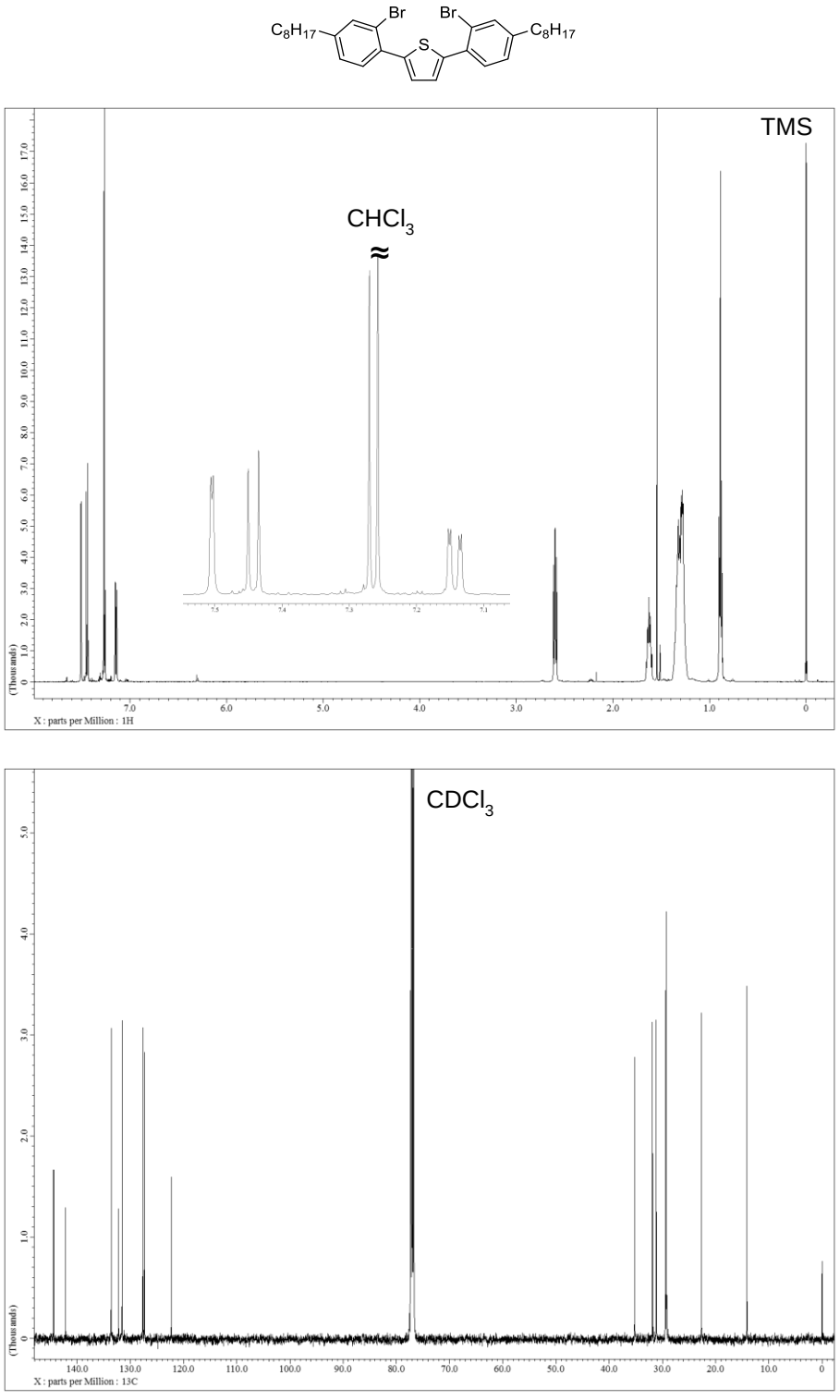
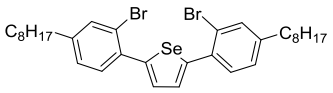
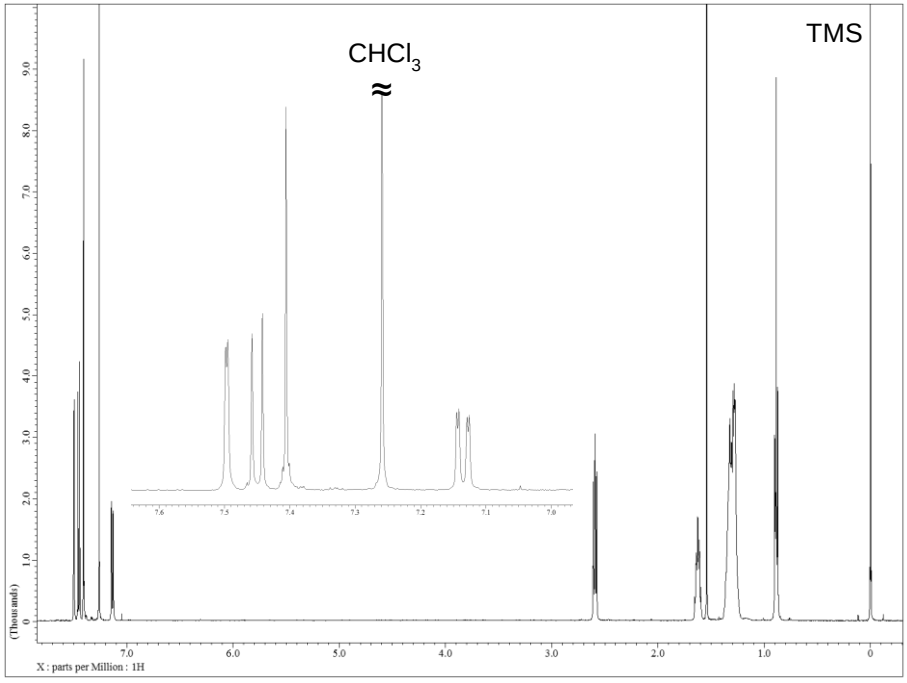


Fig. S7 ^{1}H and ^{13}C NMR spectra of compound **6a**.





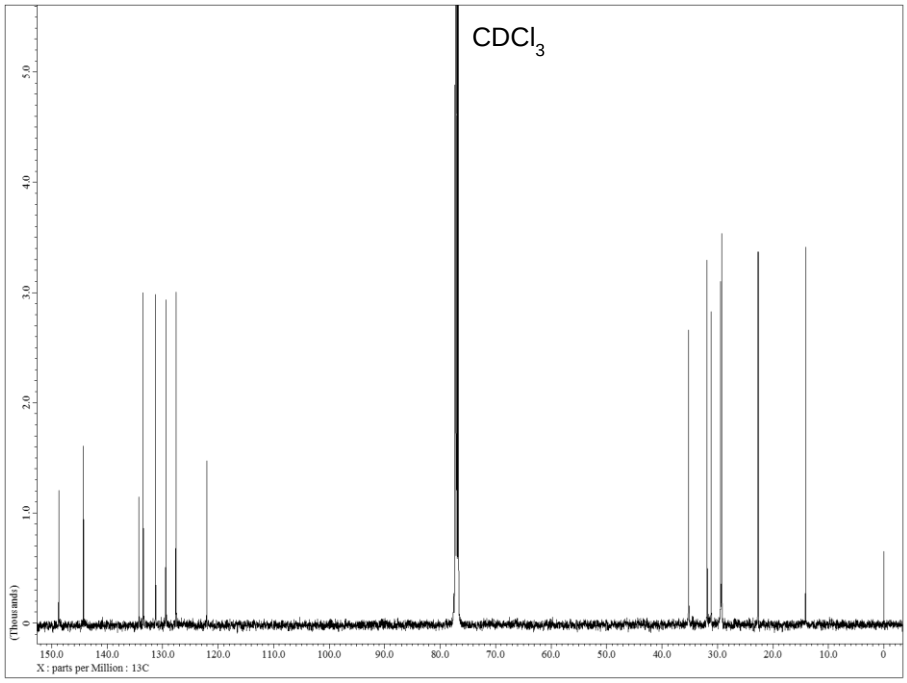


Fig. S8 ^{1}H and ^{13}C NMR spectra of compound **6b**.

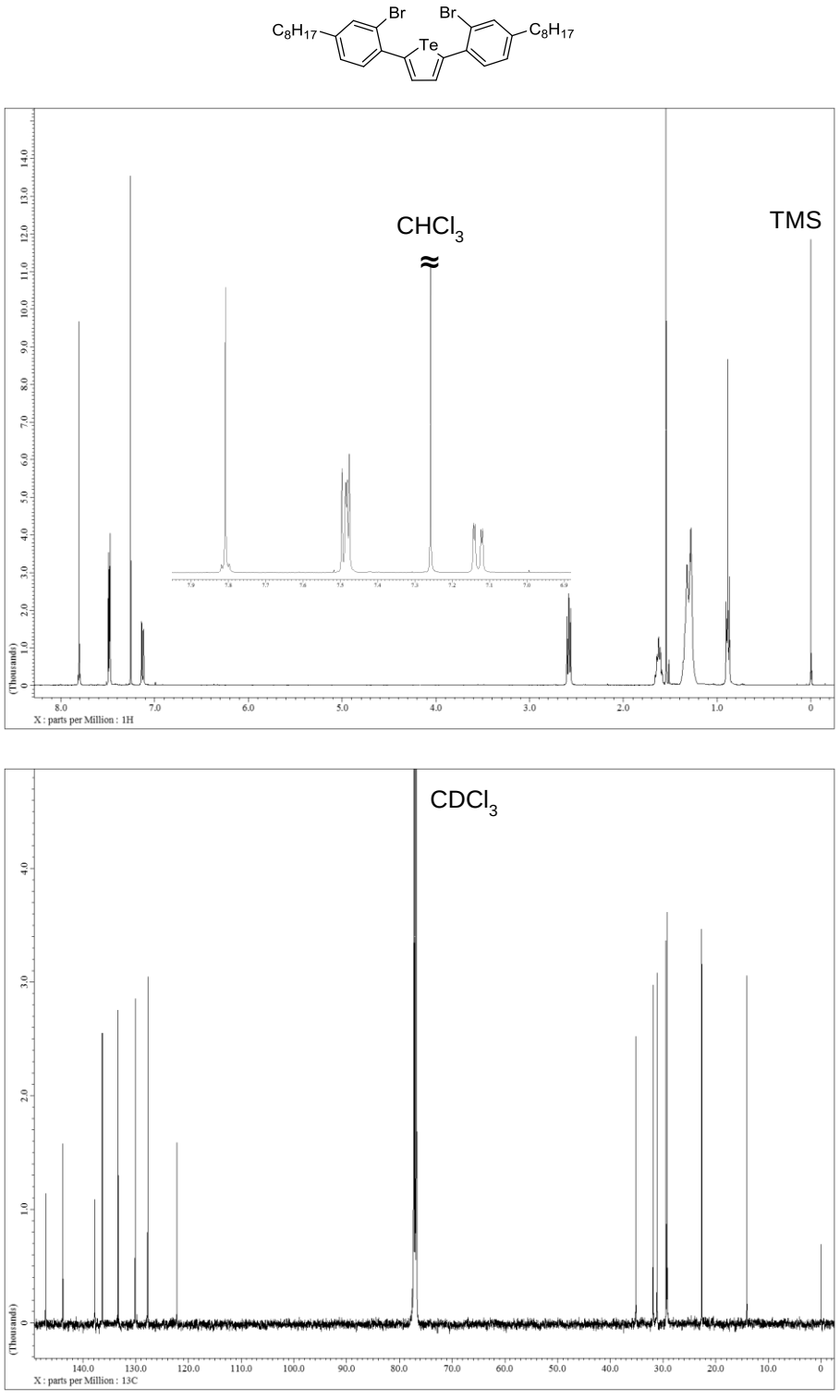


Fig. S9 ^{1}H and ^{13}C NMR spectra of compound **6c**.

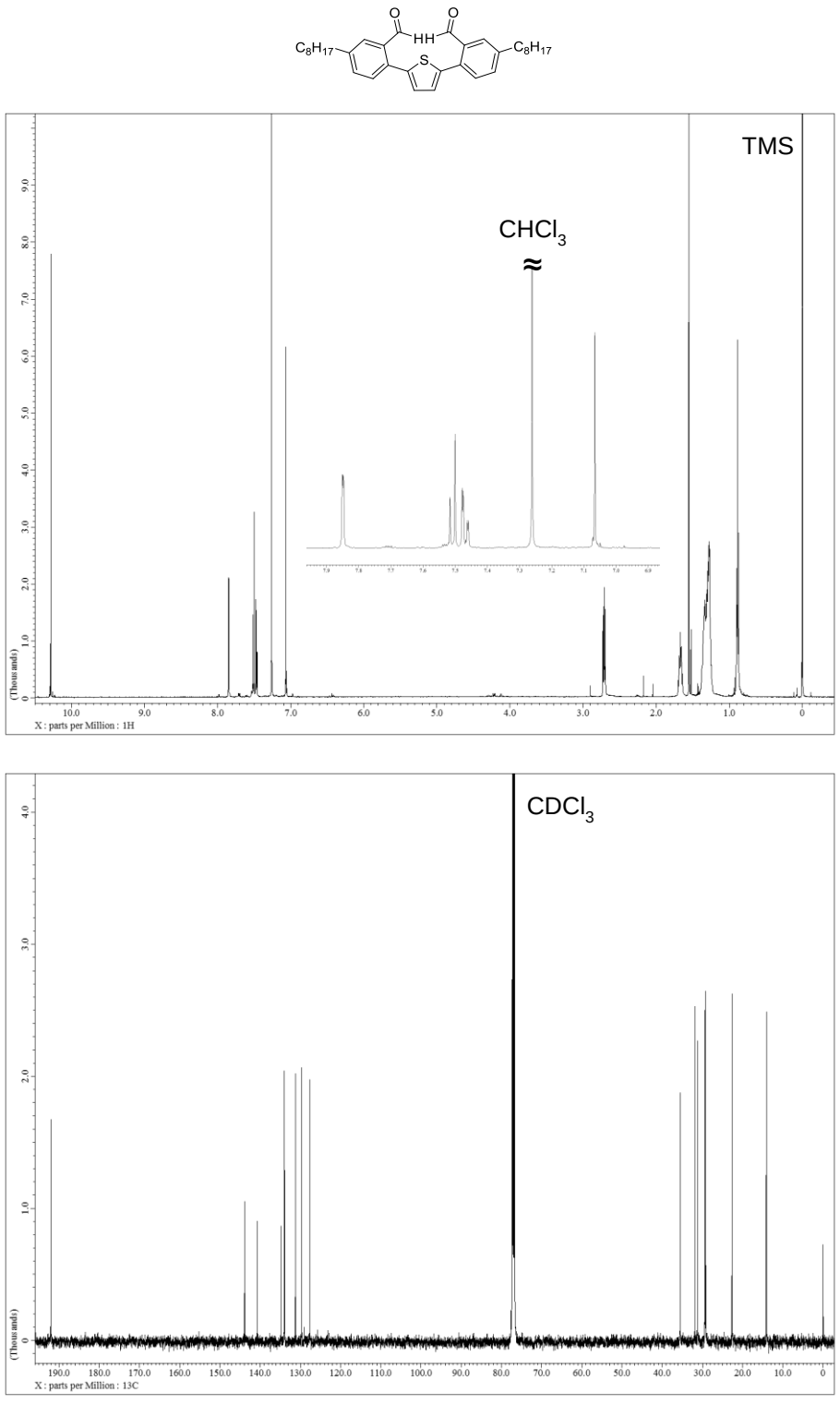
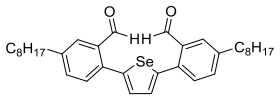
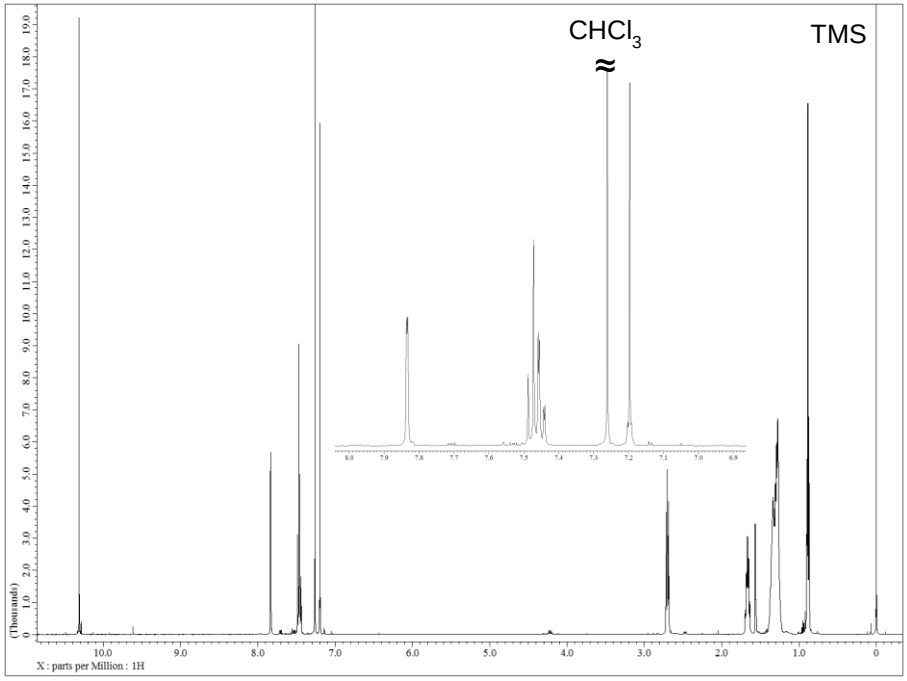


Fig. S10 ^{1}H and ^{13}C NMR spectra of compound **7a**.





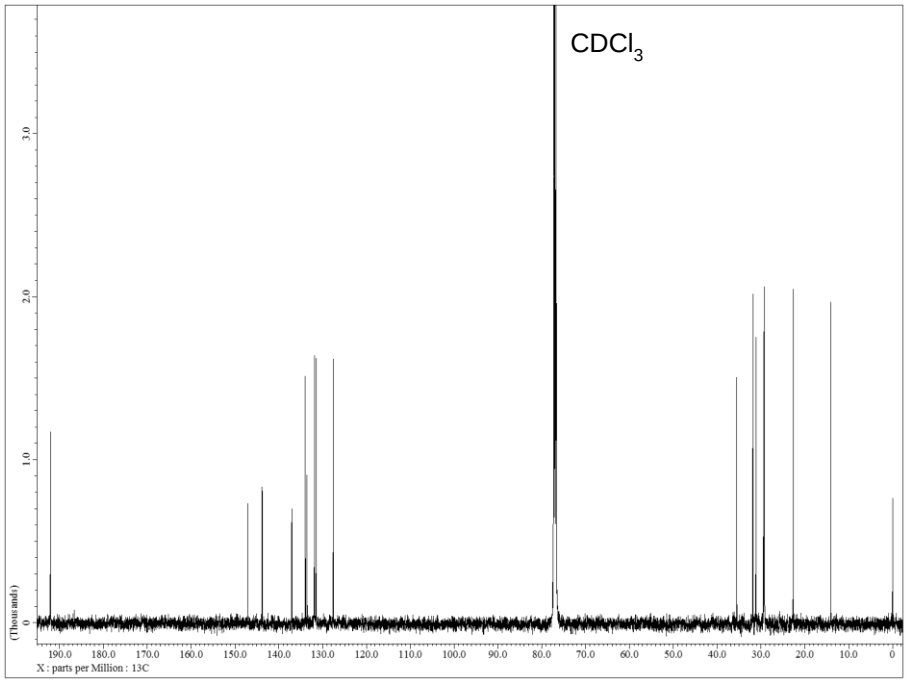
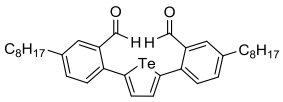
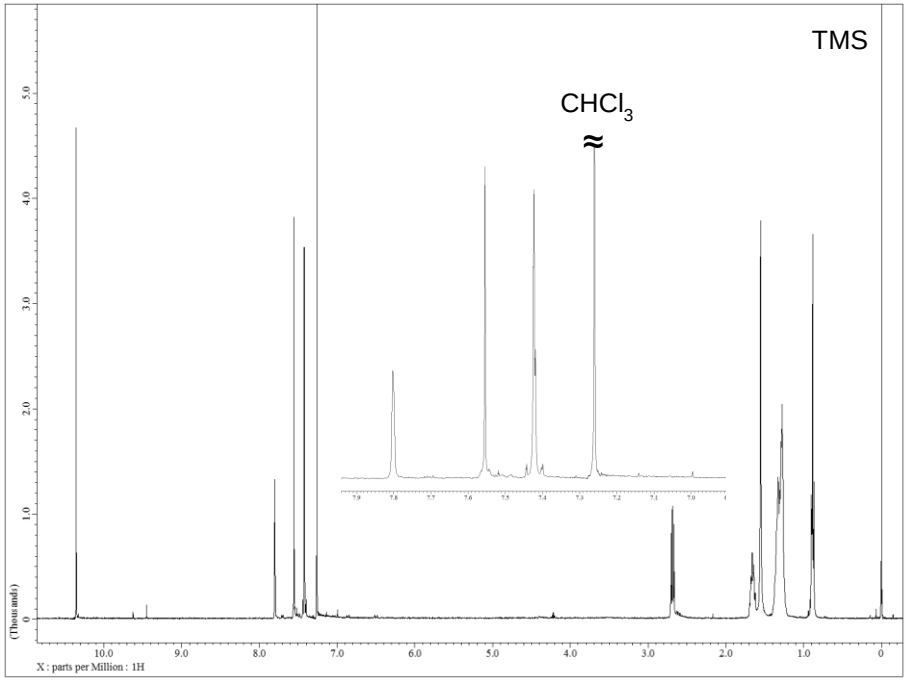


Fig. S11 ^{1}H and ^{13}C NMR spectra of compound **7b**.





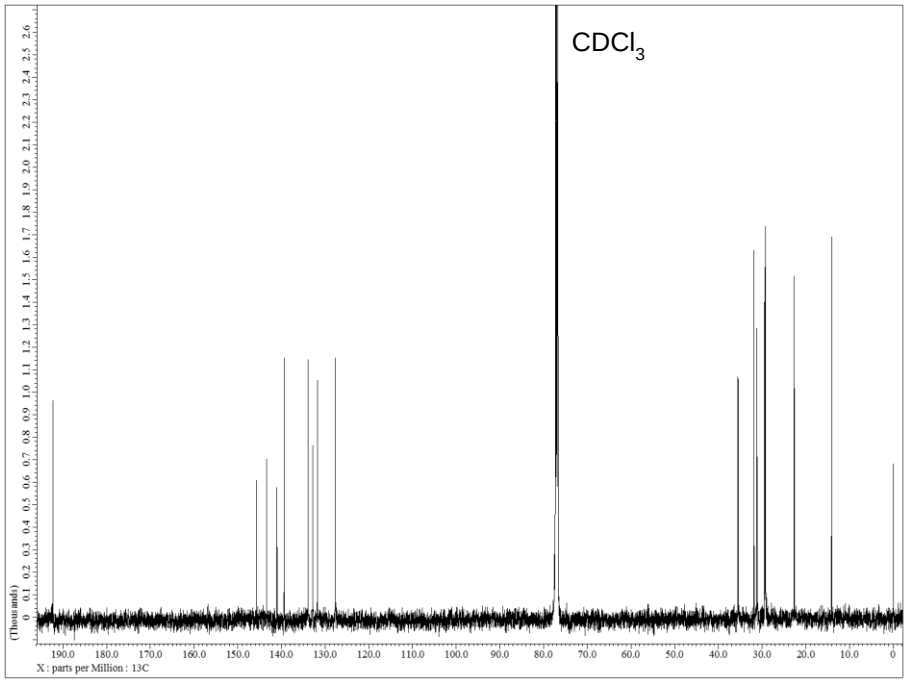


Fig. S12 ^{1}H and ^{13}C NMR spectra of compound **7c**.

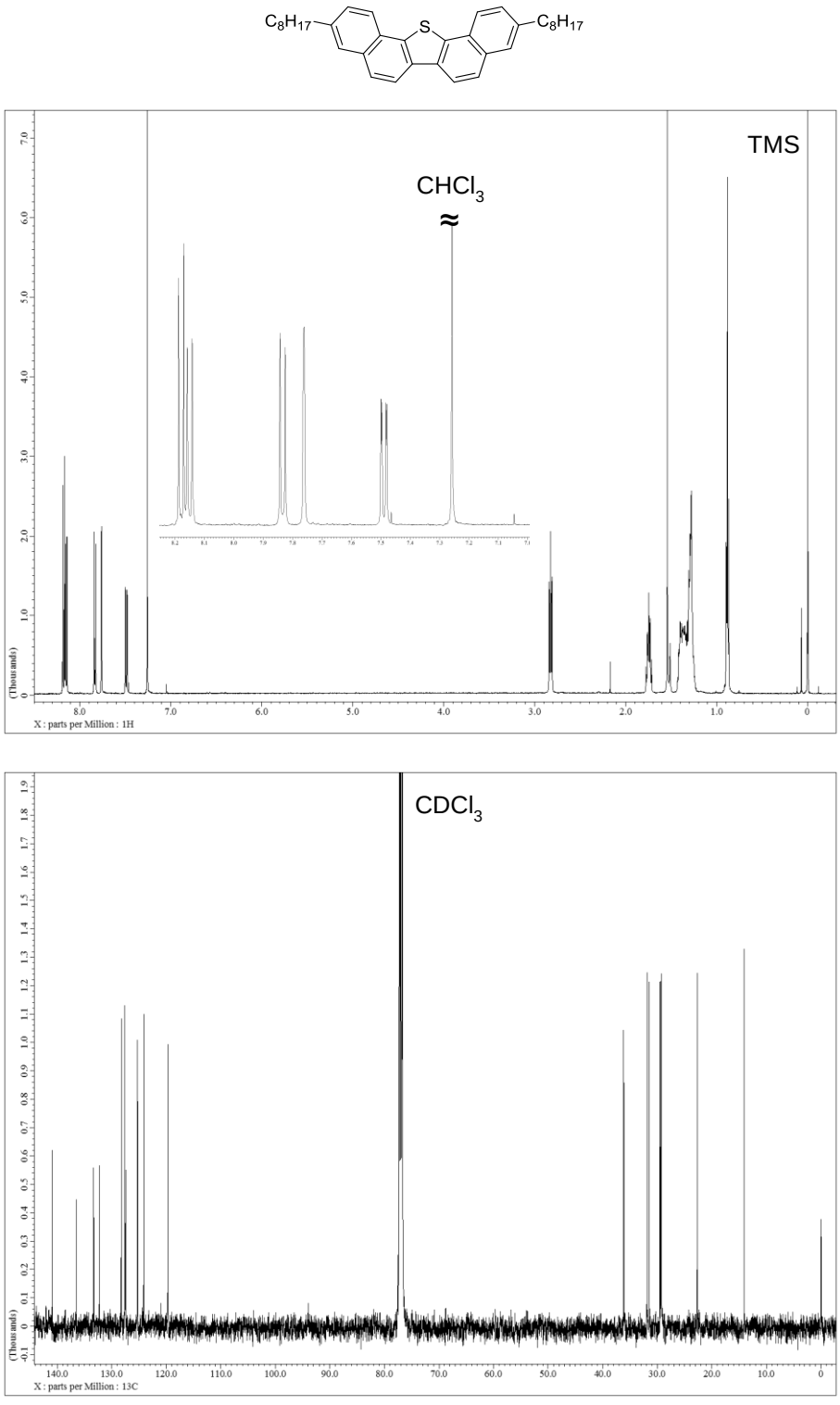


Fig. S13 ^{1}H and ^{13}C NMR spectra of compound **1**.

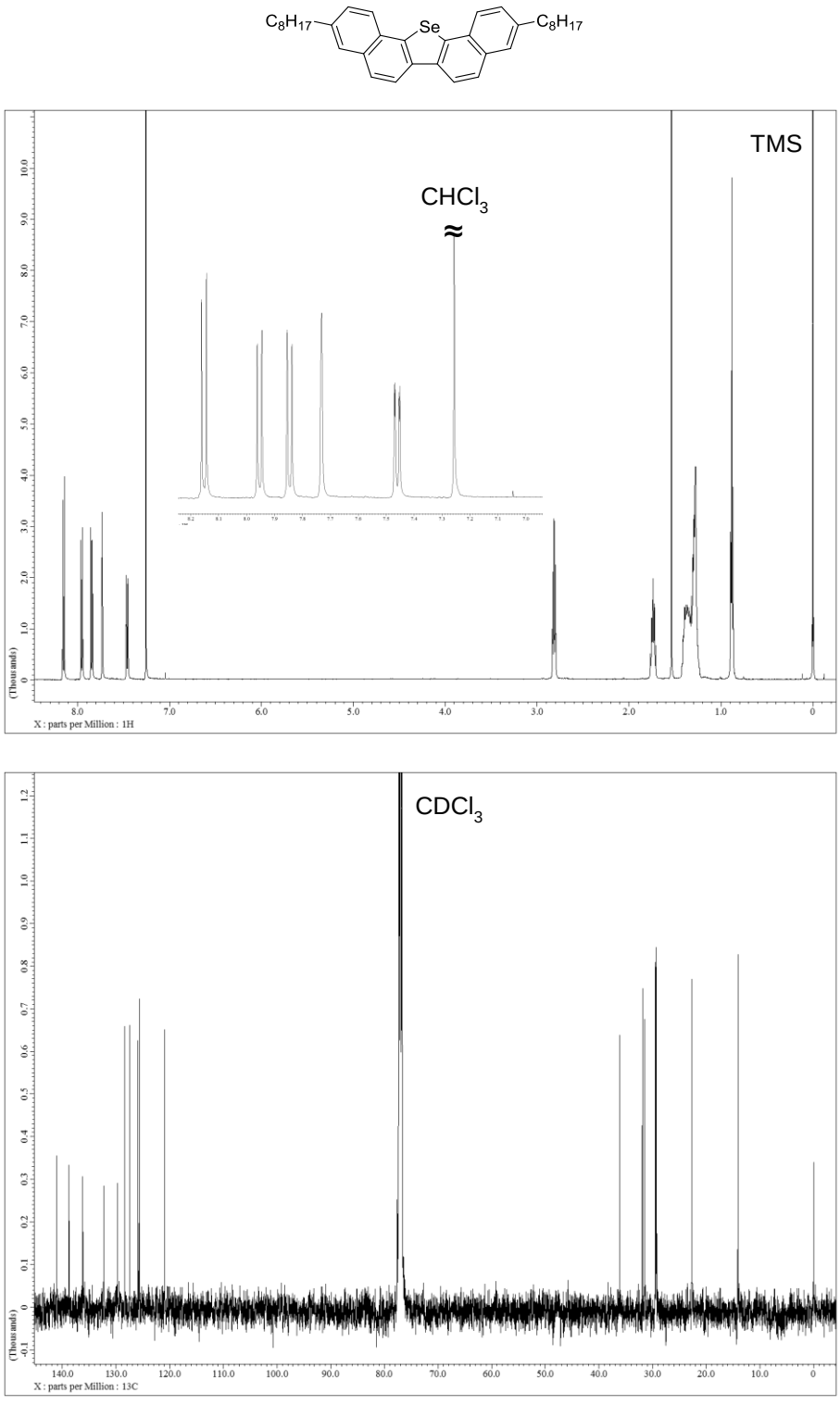


Fig. S14 ^{1}H and ^{13}C NMR spectra of compound **2**.

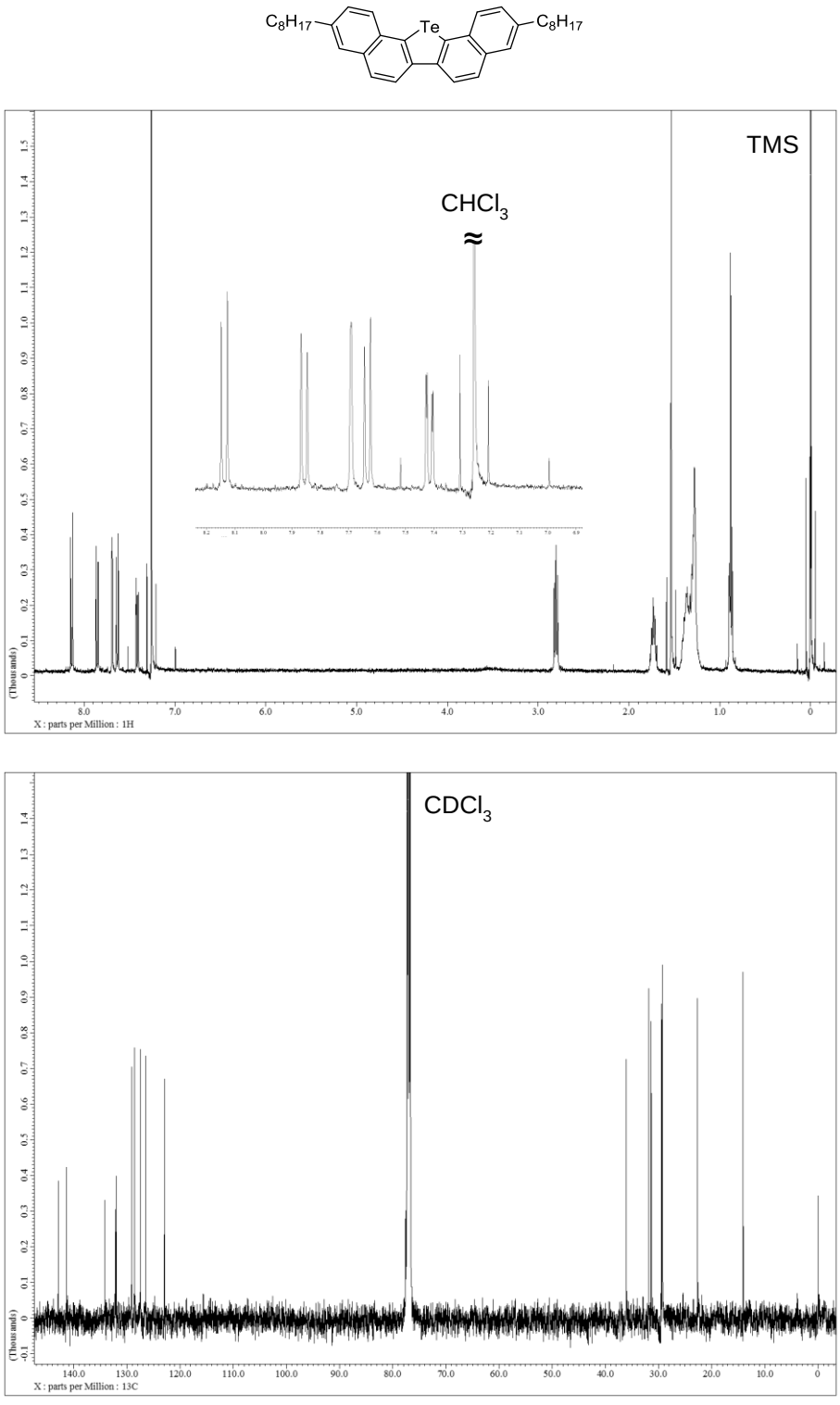


Fig. S15 ^{1}H and ^{13}C NMR spectra of compound **3**.

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