Supplementary Information

Conformational control of TTFV π-framework through naphthyl substituents

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Table of Contents

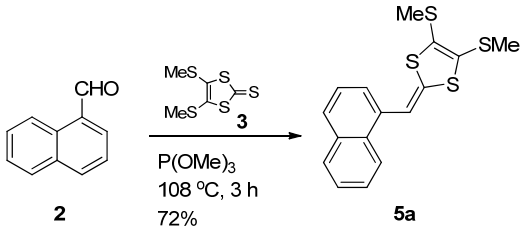
1. Experimental

1.1 General

Chemicals and reagents were purchased from commercial suppliers and used without further purification. Compound **3** was prepared according to literature procedure.[1] All reactions were performed in standard, dry glassware under an inert atmosphere of N_2. Evaporation and concentration was done at H_2O-aspirator pressure. Flash column chromatography were carried out with silica gel 60 (230-400 mesh) from VWR International. Thin-layer chromatography (TLC) was carried out with silica gel 60 F254 covered on plastic sheets and visualized by UV light. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 500 MHz spectrometer or a Tecmag APOLLO 300 MHz spectrometer. Chemical shifts are reported in ppm downfield from the signal of the internal reference $SiMe_4$. Coupling constants (*J*) are given in Hz. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer equipped with a ZnSe ATR module. High-resolution mass spectrometric (HRMS) analyses were performed on a GTC Premier Micromass instrument (MS Technology) using atmospheric pressure chemical ionization (APCI). UV-Vis spectra were measured on a Cary 6000i UV-Vis-NIR spectrophotometer. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) experiments were carried out in a standard three-electrode setup controlled by a BASi epsilon workstation.

1.2 Synthesis

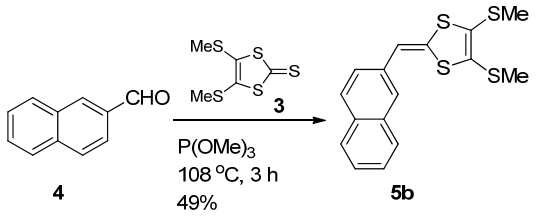
1-Napthyl DTF 5a.



A mixture of 1-napthaldehyde **2** (0.17 mL, 0.19 g, 1.2 mmol) and thione **3** (287 mg, 1.27 mmol) in $P(OMe)_3$ (10 mL) was stirred at 108 °C for 3 h. The unreacted $P(OMe)_3$ was removed by vacuum distillation, and the residue was subjected to column chromatography (CH_2Cl_2/hexanes 1:1) to afford DTF **5a** (303 mg, 0.907 mmol, 72%) as a yellow crystalline solid. m.p.: 91–92 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.0

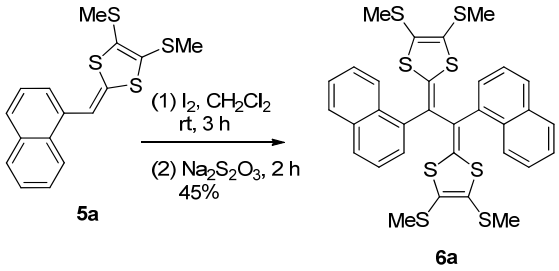
Hz, 1H), 7.74 (m, 1H), 7.54-7.46 (m, 4H), 7.07 (s, 1H), 2.46 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.5, 133.70, 133.66, 130.7, 128.6, 127.4, 126.2, 126.1, 126.0, 125.4, 124.5, 124.2, 123.8, 112.4, 19.0, 18.9; FTIR (neat): 3041, 2992, 2914, 1941, 1559, 1494, 1422, 1310, 1253, 1076, 1012, 965, 878, 826 cm^{-1}; HRMS (APCI, +eV) *m*/*z* calcd for $C_{16}H_{14}S_4$ 333.9973, found 333.9977 $[M]^+$. X-ray.

2-Napthyl DTF 5b.



A mixture of 2-napthaldehyde **4** (0.706 g, 4.52 mmol) and thione **3** (1.007 g, 6.448 mmol) in $P(OMe)_3$ (20 mL) was stirred at 108 °C for 3 h. The unreacted $P(OMe)_3$ was removed by vacuum distillation. The residue was subjected to column chromatography (CH_2Cl_2/hexanes 1:1) to afford DTF **5b** (0.739 g, 2.21 mmol, 49%) as a yellow crystalline solid. m.p.: 58–59 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.62 (s, 1H), 7.49-7.40 (m, 2H), 7.35 (d, *J* = 8.6 Hz, 1H), 6.62 (s, 1H), 2.45 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.9, 133.6, 132.6, 131.7, 128.1, 127.93, 127.91, 127.6, 126.4, 125.9, 125.7, 124.9, 124.2, 114.9, 19.1, 19.0; FTIR (neat): 3053, 2990, 2914, 1941, 1554, 1495, 1421, 1357, 1304, 1013, 959, 894, 857 cm^{-1}; HRMS (APCI, +eV) *m*/*z* calcd for $C_{16}H_{14}S_4$ 333.9973, found 333.9979 $[M]^+$.

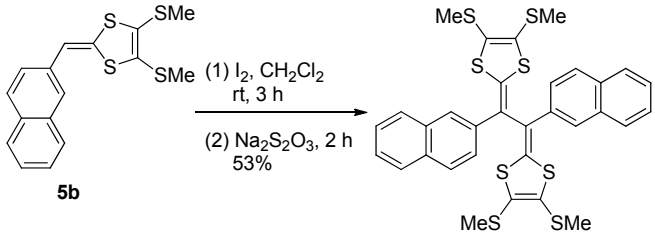
1-Napthyl TTFV 6a.



To a solution of 1-napthyl DTF **5a** (0.502 g, 1.50 mmol) in CH_2Cl_2 (20 mL) was added I_2 (1.011 g, 3.98 mmol). The mixture was stirred for 3 h at rt. Then aq. $Na_2S_2O_3$ (20 mL, satd.) was

added and the mixture was stirred at rt for another 2 h. The organic layer was separated and dried over $MgSO_4$. Diethyl ether (30 mL) was then added, resulting in the precipitation of 1-napthyl TTFV **6a** which was collected by filtration as a bright orange powder (0.223 g, 0.335 mmol, 45%). m.p.: 251–252 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77-7.67 (m, 4H), 7.62 (d, J = 8.3 Hz, 2H), 7.41-7.33 (m, 4H), 7.12 (broad s, 2H), 2.46 (broad s, 3H), 2.47 (s, 6H), 2.18 (s, 6H); ^{13}C NMR was not obtained due to poor solubility; FTIR (neat): 3045, 2914, 1584, 1506, 1465, 1421, 1309, 1163, 1013, 960, 859 cm^{-1}; HRMS (APCI, +eV) m/z calcd for $C_{32}H_{26}S_8$ 665.9795, found 665.9800 $[M]^+$. X-ray.

2-Napthyl TTFV 6b.



5b **6b**

To a solution of 2-napthyl DTF **5b** (0.508 g, 1.59 mmol) in CH_2Cl_2 (20 mL) was added I_2 (1.037 g, 4.09 mmol). The mixture was stirred for 3 h. Then aq. $Na_2S_2O_3$ (20 mL, satd.) was added and the mixture was stirred for 2 h. The organic layer was separated, dried over $MgSO_4$, and purified by column chromatography (CH_2Cl_2/hexanes 1:1) to afford 2-napthyl TTFV **6b** as a yellow crystalline solid (279 mg, 0.419 mmol, 53%). m.p.: 189–190 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 2H), 7.79 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 8.6 Hz, 4H), 7.55 (d, J = 8.6 Hz, 2H), 7.45-7.38 (m, 4H), 2.43 (s, 6H), 2.39 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.8, 135.0, 133.5, 132.3, 128.33, 128.32, 128.1, 128.0, 127.5, 126.2, 126.0, 125.7, 124.9, 124.8, 19.0, 18.9; FTIR (neat): 2913, 1591, 1532, 1491, 1421, 1308, 1133, 961, 892, 852, 811 cm^{-1}; HRMS (APCI, +eV) m/z calcd for $C_{32}H_{26}S_8$ 665.9795, found 665.9785 $[M]^+$. X-ray.

2. NMR Spectra for New Compounds

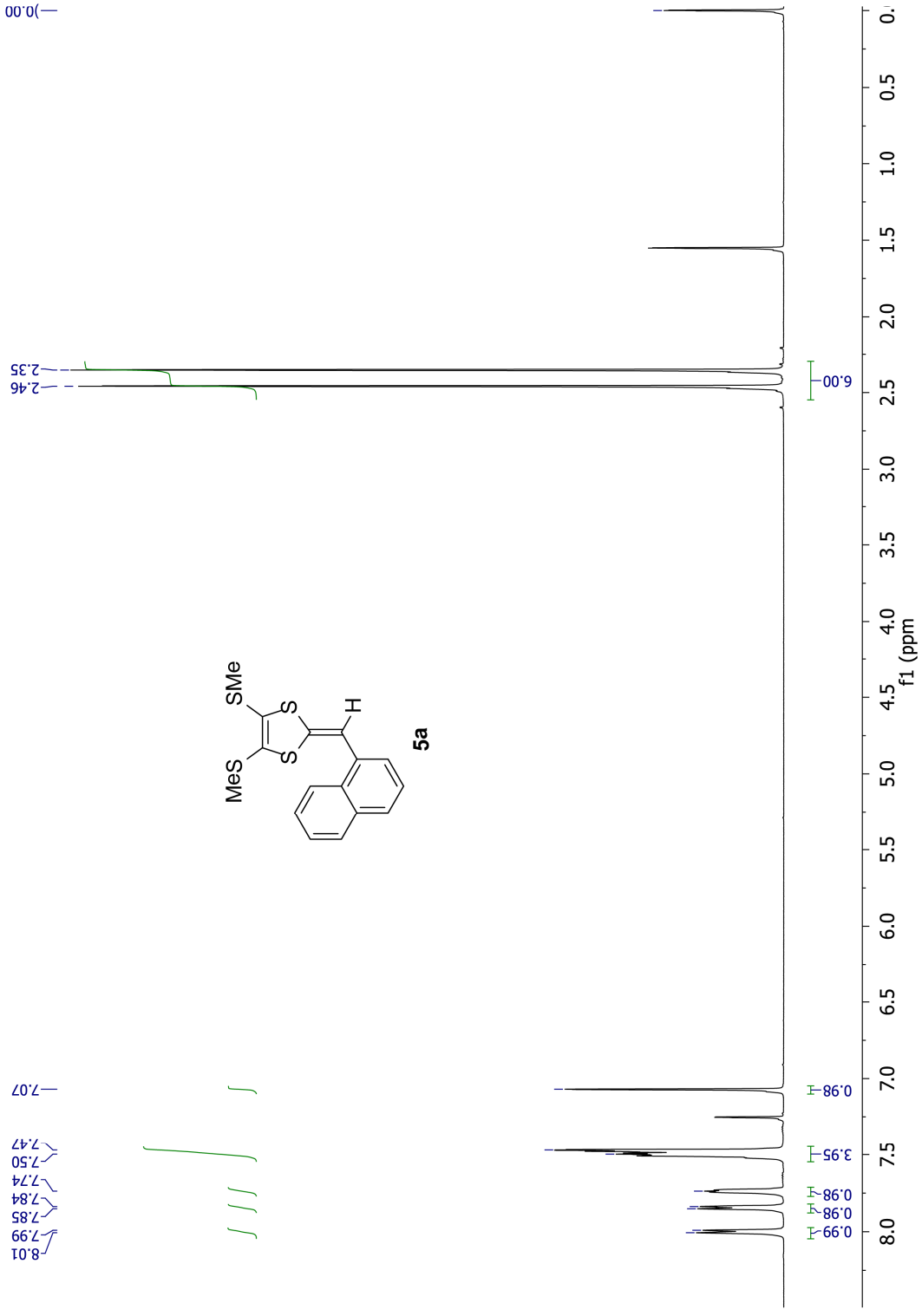


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum for compound **5a**.

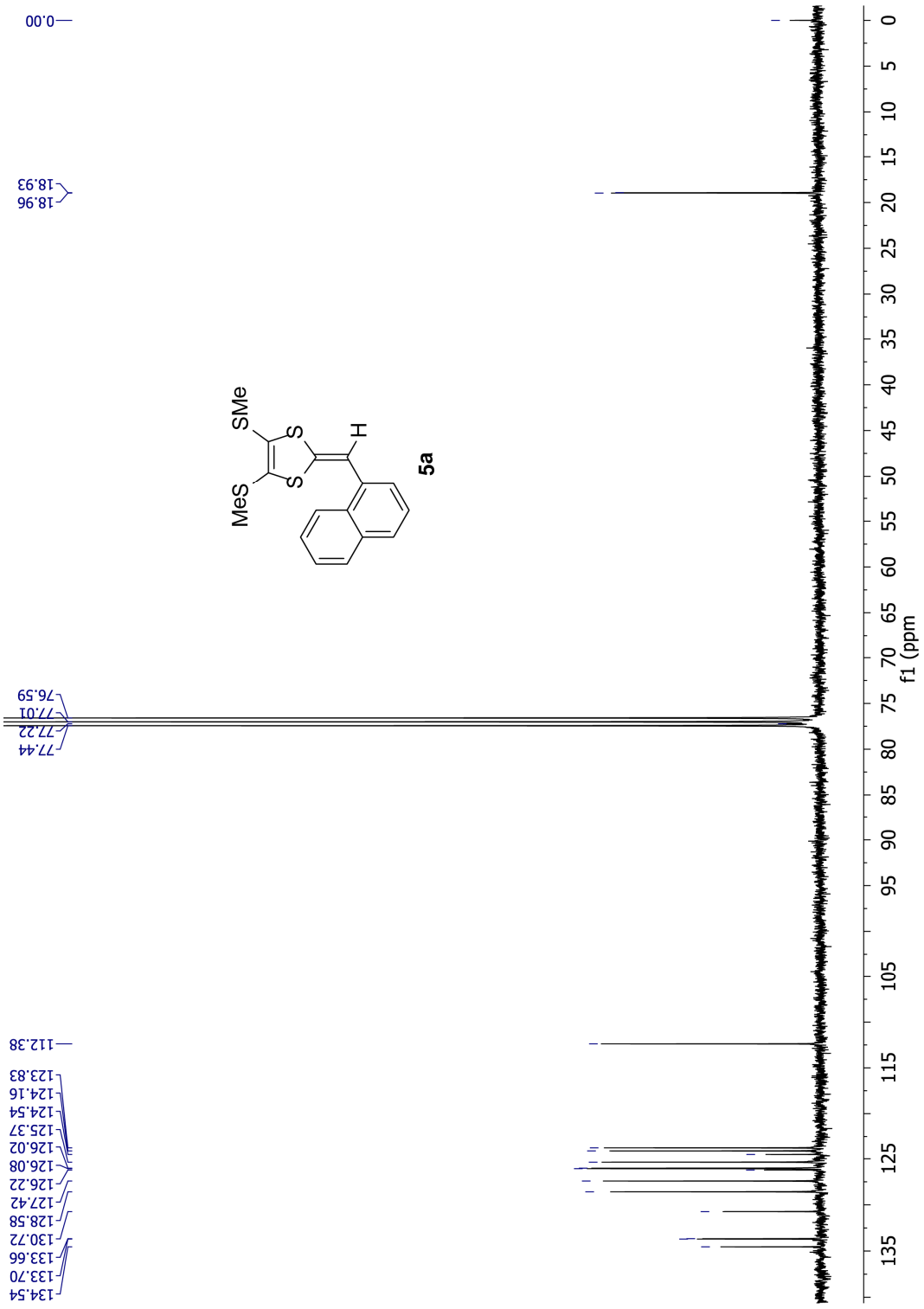


Figure S2. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for compound **5a**.

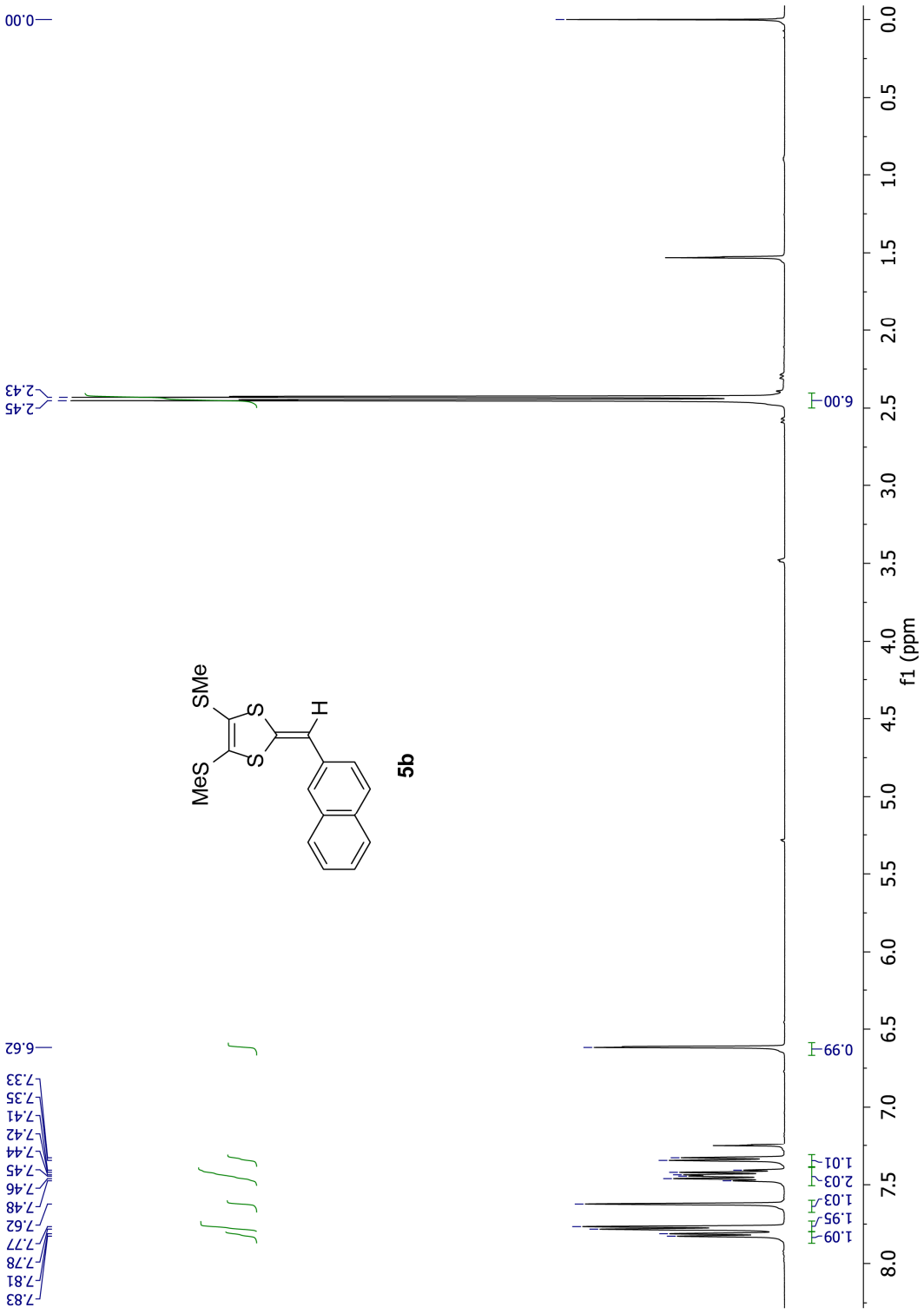


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum for compound **5b**.

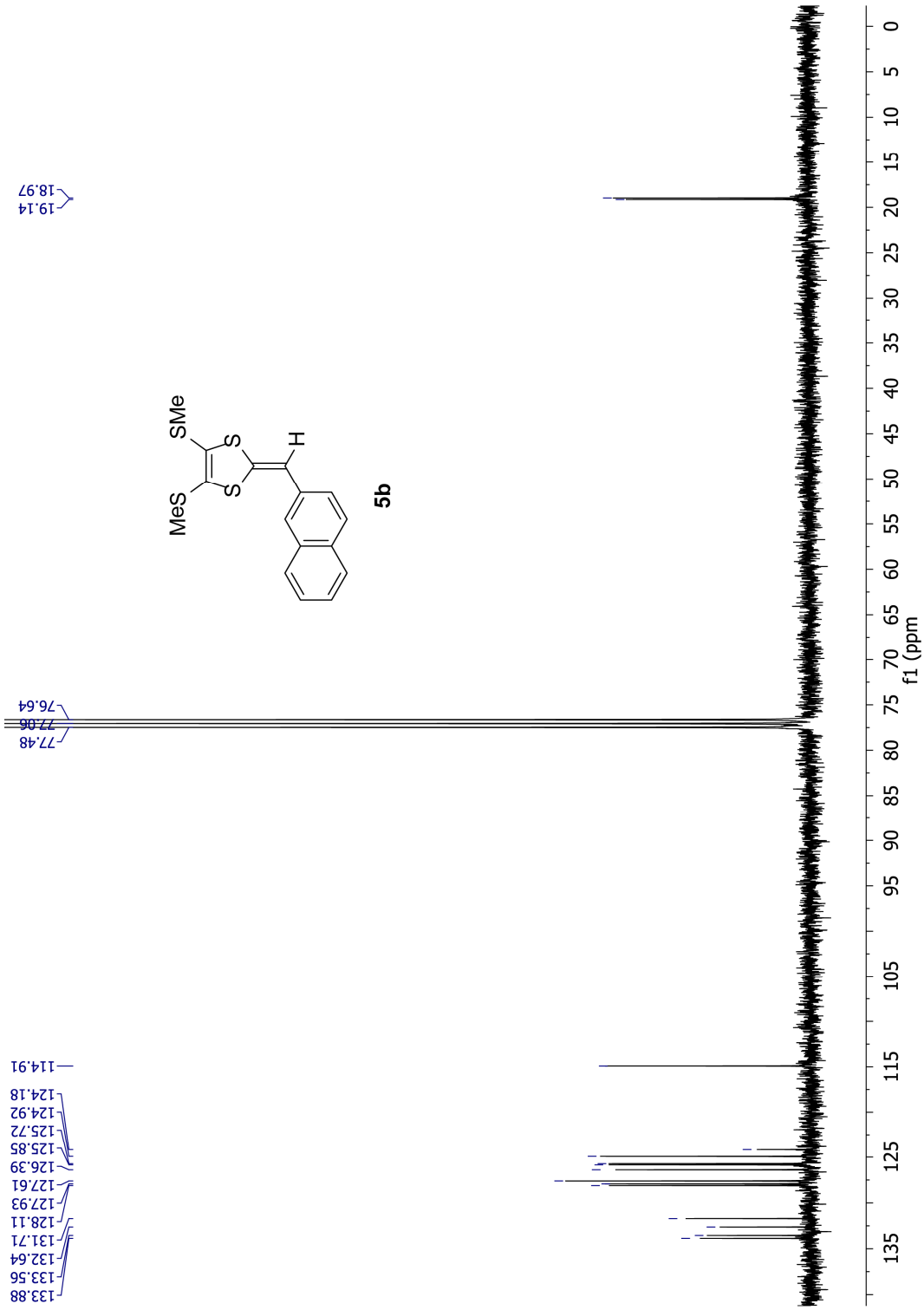


Figure S4. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for compound **5b**.

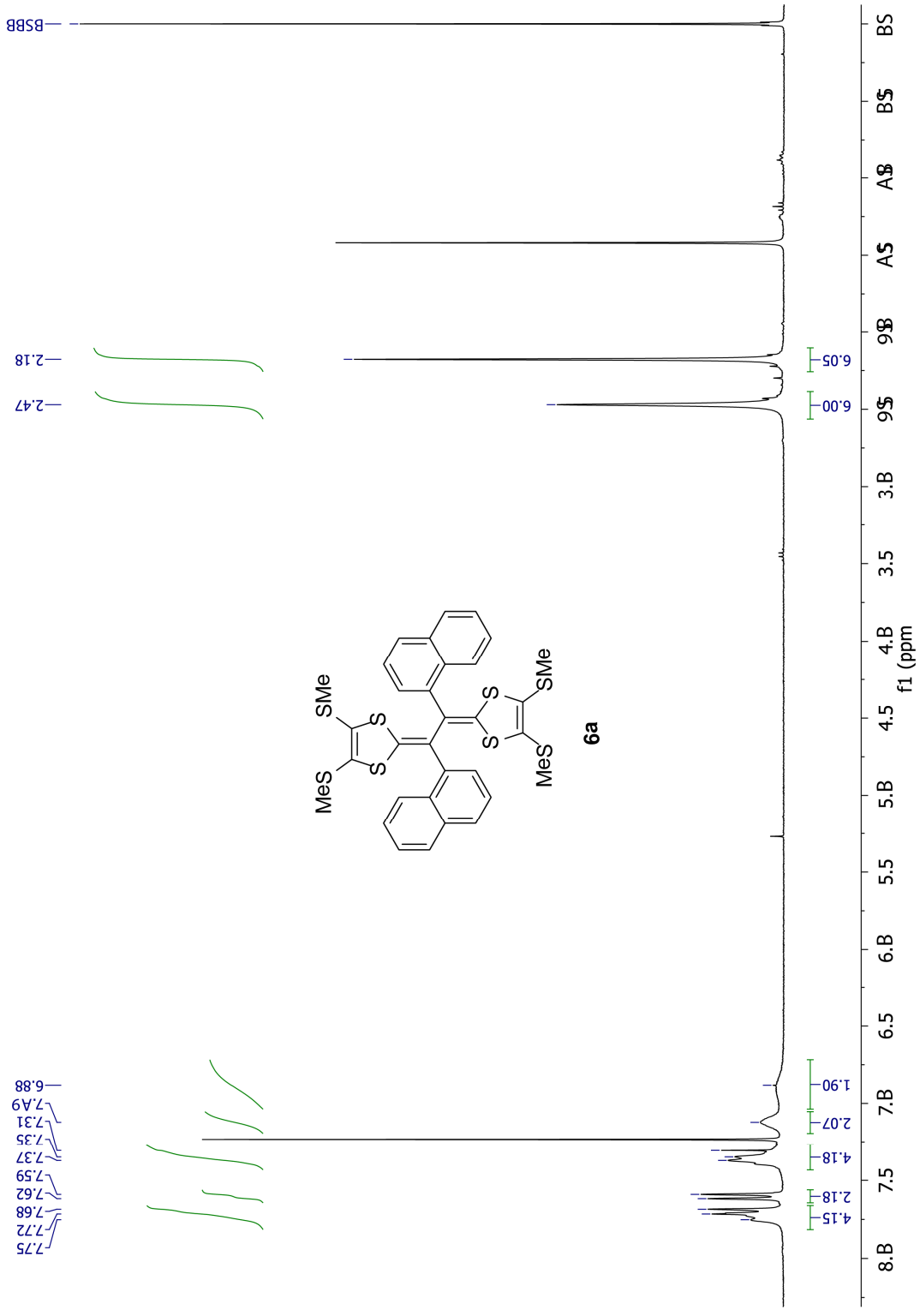


Figure S5. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for compound **6a**.

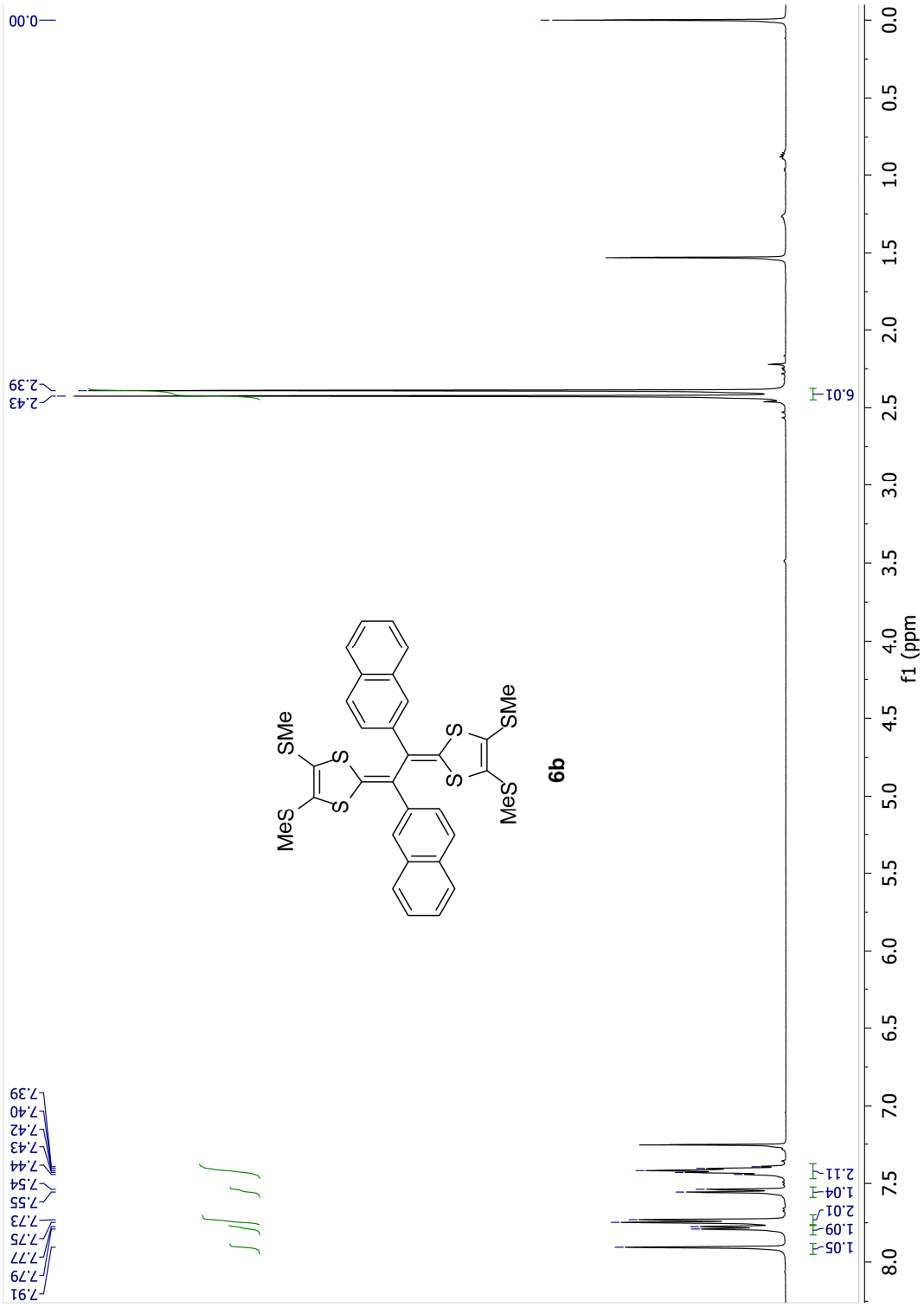


Figure S6. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for compound **6b**.

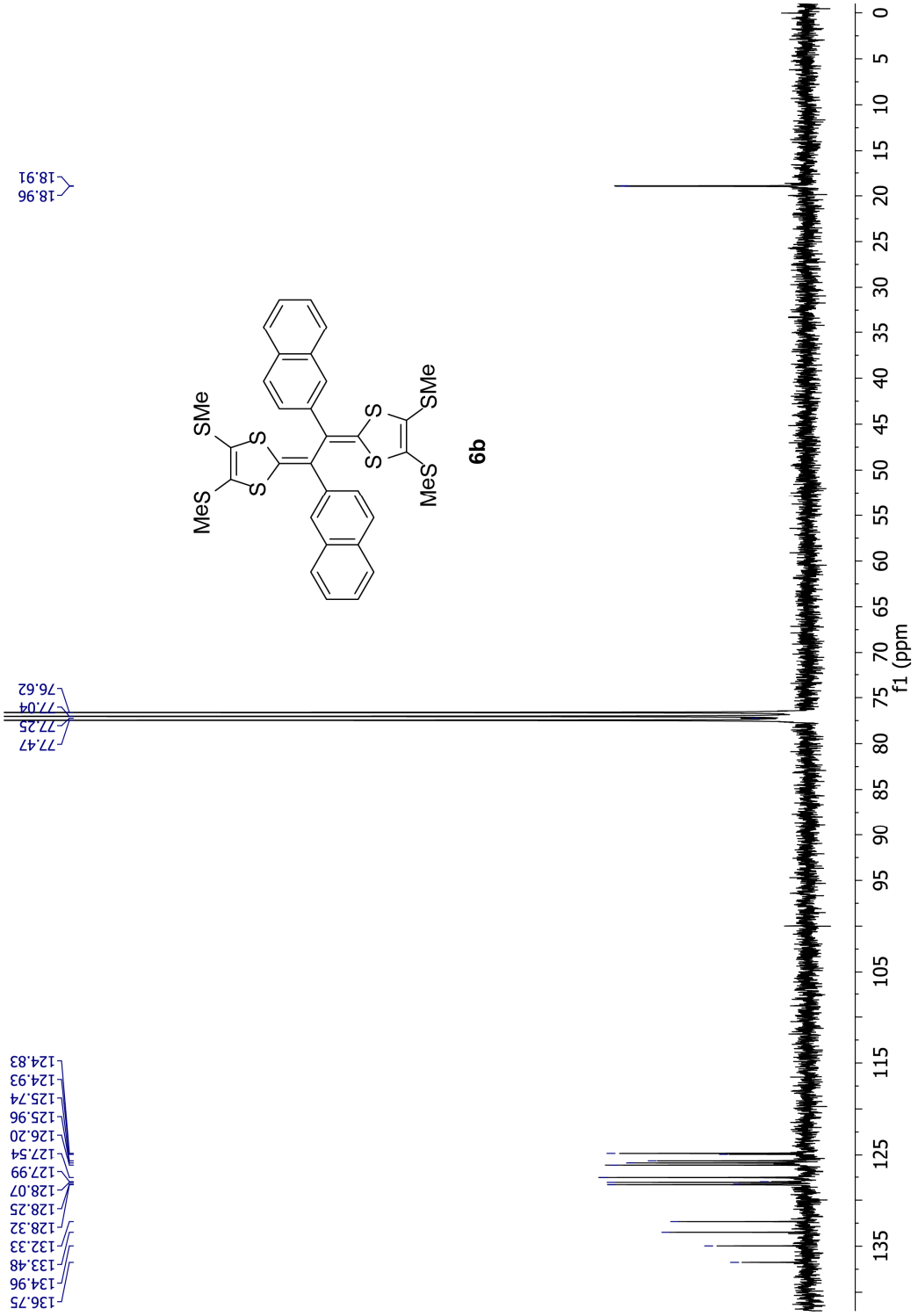
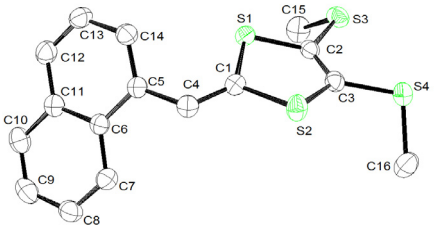


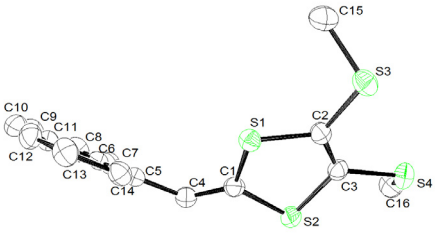
Figure S7. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for compound **6b**.

3. X-ray Crystallographic Data

(a)



(b)



(c)

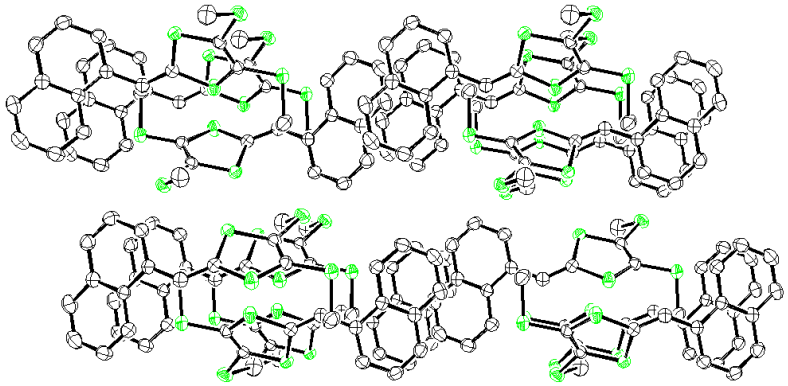


Figure S8. ORTEP plots of **5a** at 50% ellipsoid probability. (A) Front view; (B) side view, and (C) crystal packing diagram. Selected bond distances (Å): C(1)-C(4) 1.348(3), C(4)-C(5) 1.466(3), C(5)-C(6) 1.434(2), C(1)-S(1) 1.760(2), C(1)-S(2) 1.764(2), S(1)-C(2) 1.766(2), S(2)-C(3) 1.761(2), C(2)-C(3) 1.347(3). Selected bond angles (°): S(1)-C(1)-S(2) 112.2(1), S(1)-C(1)-C(4) 126,1(2), C(1)-C(4)-C(5) 125.4(2), C(1)-S(1)-C(2) 95.1(1). Selected torsion angles (°):C(1)-S(1)-C(2)-C(3) -12.2(1), S(1)-C(1)-C(4)-C(5) -4.9(3), C(3)-S(2)-C(1)-S(1) -19.1(1), C(1)-C(4)-C(5)-C(6) 140.0(2).

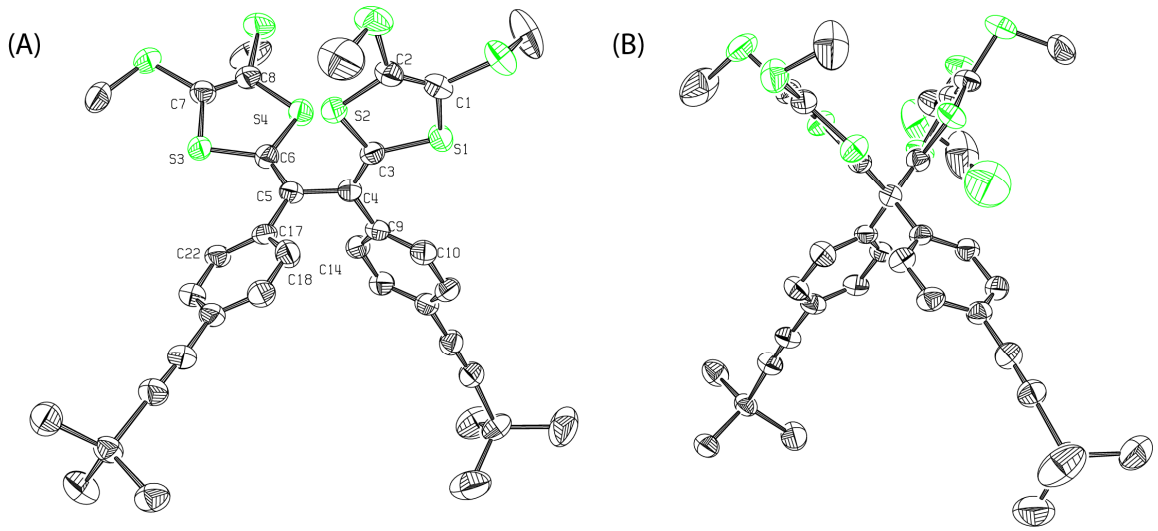


Figure S9. ORTEP plots of diphenyl-substituted TTFV **7** at 50% ellipsoid probability. (A) Front view; (B) side view. Selected bond distances (Å): S(1)-C(1)1.754(5),S(1)-C(3) 1.762(6), S(2)-C(2) 1.764(7), S(2)-C(3) 1.754(4), C(1)-C(2) 1.329(9), C(3)-C(4) 1.341(7), C(4)-C(5) 1.495(8), C(4)-C(9) 1.484(6). Selected bond angles (°):S(1)-C(1)-S(5) 117.2(3), C(3)-C(4)-C(5) 117.2(4), C(3)-C(4)-C(9) 125.6(5). Selected torsion angles (°):S(1)-C(3)-C(4)-C(9) 9.5(6), C(3)-C(4)-C(5)-C(6) 75.3(5), C(3)-C(4)-C(9)-C(10) 36.2(6).

DTF 5a: $C_{16}H_{14}S_4$, M = 334.53, monoclinic, a = 13.299(6) Å, b = 7.856(3) Å, c = 15.682(7) Å, β = 106.279(6)°, V = 1572.7(12) Å^3, T = 163(2) K, space group $P2_1/c$, Z = 4, μ(MoKα) = 0.590 mm^{-1}, 19238 reflections measured, 3574 independent reflections (R_{int} = 0.0357). R_1 = 0.0411 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.1092 (all data). GoF on F^2 =1.099. CCDC XXXXX. Single crystals were obtained by slow evaporation of a solution of **DTF 5a** in $CDCl_3$ at 4 °C.

TTFV 6a: $C_{32}H_{26}S_8$, M = 667.04, triclinic, a = 10.433(8) Å, b = 12.641(8) Å, c = 12.954(8) Å, α = 66.52(3)°, β = 73.94(2)°, γ = 83.87(3)°, V = 1505.8(18) Å^3, T = 163(2) K, space group $P\bar{1}$, Z = 2, μ(MoKα) = 0.616 mm^{-1}, 11348 reflections measured, 5514 independent reflections (R_{int} = 0.0460). R_1 = 0.0987 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.3004 (all data). GoF on F^2 =1.089. CCDC 88258. Single crystals were obtained by slow crystallization from a CS_2 solution of **TTFV 6a** at 4 °C.

TTFV 6b: $C_{32}H_{26}S_8$, M = 667.04, monoclinic, a = 20.472(8) Å, b = 9.432(3) Å, c = 15.900(6) Å, β = 93.519(5)°, V = 3064.4(19) Å^3, T = 163(2) K, space group $C2/c$, Z = 4, μ(MoKα) = 0.606

mm^{-1}, 20685 reflections measured, 3517 independent reflections (R_{int} = 0.0361). R_1 = 0.0568 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.1647 (all data). GoF on F^2 =1.182. CCDC 88259. Single crystals were obtained by slow diffusion of MeOH into a CH_2Cl_2 solution of **TTFV 6b** at 4 °C.

Crystal data for diphenyl TTFV **7**: $C_{34}H_{38}S_8Si_2 \bullet CH_2Cl_2$, M = 844.26, triclinic, a = 8.853(7) Å, b = 15.935(13) Å, c = 17.189(14) Å, α = 113.950(4)°, β = 100.455(8)°, γ = 100.051(9)°, V = 2095(3) $Å^3$, T = 193(2) K, space group $P\bar{1}$, Z = 2, μ(MoKα) = 0.635 mm^{-1}, 17256 reflections measured, 8552 independent reflections (R_{int} = 0.0446). The final R_1 and $wR(F^2)$ values were 0.0834 ($I > 2\sigma(I)$) and 0.2453 (all data), respectively. The goodness of fit on F^2 was 1.075. CCDC 845793. Compound **7** was prepared according to the method we previously reported,[2] and its single crystals were obtained by slow diffusion of MeOH into a CH_2Cl_2 solution of **7** at 4 °C.

4. Theoretical Modeling Studies

The molecular structures and frontier molecular orbital properties of naphthyl-TTFV derivatives **6a** and **6b** were investigated by density functional theory (DFT) calculations. To reduce computational cost, the SMe groups of **6a** and **6b** were replaced with H atoms. Structure optimization and MO calculations were done at the B3LYP/6-31G* level using Spartan'10 (Wavefunction, Inc.).

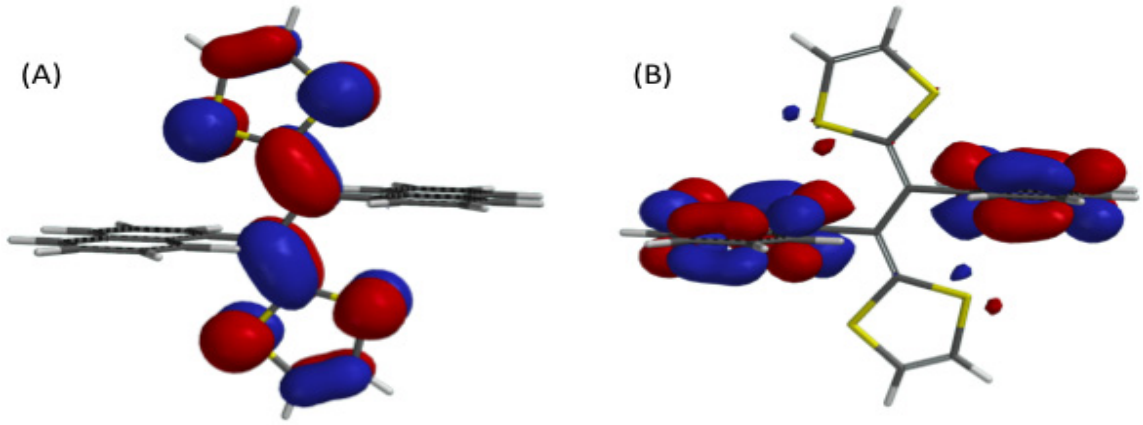


Figure S10. (A) Plot of HOMO (E = -4.17 eV) of **6a**. (B) Plot of LUMO (E = -1.17 eV) of **6a**.

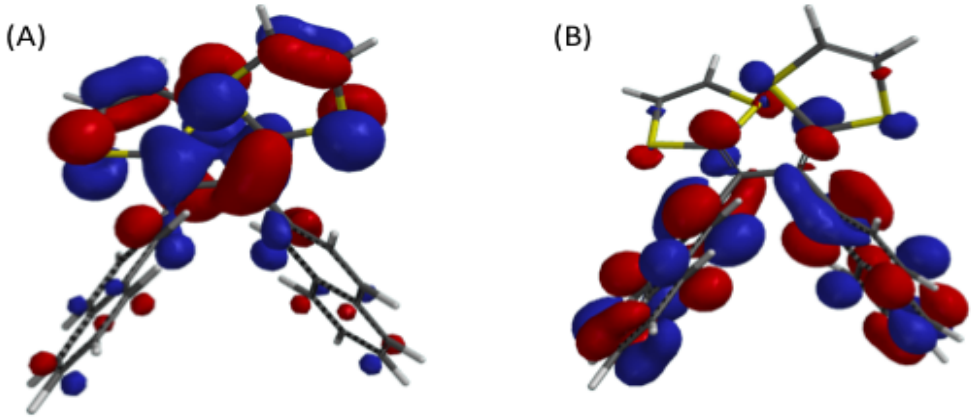


Figure S11. (A) Plot of HOMO (E = -4.68 eV) of **6b**. (B) Plot of LUMO (E = -1.15 eV) of **6b**.

References:

1. (a) G. Steimecke, H. J. Sieler, R. Kirmse and E. Hoyer, *Phosphor. Sulf.* 1979, **7**, 49; (b) M. R. Bryce and A. J. Moore, *Synthesis* 1991, 26.

2. (a) G. Chen, I. Mahmud, L. Dawe and Y. Zhao, *Org. Lett*. 2010, **12**, 704. (b) G. Chen, I. Mahmud, L. N. Dawe, D. Lee, Y. Zhao, *J. Org. Chem.* 2011, **76**, 2701.