Electronic Supplementary Information for

Donor/acceptor substituted dithiafulvenes and tetrathiafulvalene vinylogues: electronic absorption, crystallographic, and computational analyses

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1. Experimental

1.1 General

Chemicals were purchased from commercial suppliers and used directly without purification. All reactions were conducted in standard, dry glassware. Evaporation and concentration were carried out with a rotary evaporator. Flash column chromatography was performed with 240-400 mesh silica gel, and thin-layer chromatography (TLC) was carried out with silica gel F254 covered on plastic sheets and visualized by UV light. Melting points (m.p.) were measured using an SRS Opti Melt melting point apparatus and are uncorrected.

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance III 300 MHz multinuclear spectrometer. Chemical shifts (δ) are reported in ppm downfield relative to the signals of the internal reference $SiMe_4$ or residual solvents ($CHCl_3$: δ_H = 7.24 ppm, δ_C = 77.2 ppm; CH_2Cl_2:δ_H = 5.32 ppm, δ_C = 54.0 ppm). Coupling constants (*J*) are given in Hz. Infrared spectra (IR) were recorded on a Bruker Alfa spectrometer. MALDI-TOF MS analysis was performed on Bruker 9.4T Apex-Qe FTICR system. High-resolution (HR) APPI-TOF MS analysis was done on a GCT premier Micromass Technologies instrument.

UV-Vis absorption spectra were measured on a Cary 6000i spectrophotometer. Cyclic voltammetric (CV)) analyses were carried out in a standard three-electrode setup controlled by a BASi Epsilon potentiostat. Experimental conditions were set up as follows. CV analysis: Bu_4NPF_6 (0.1 M) as the supporting electrolyte, glassy carbon as the working electrode, Pt wire as the counter electrode, Ag/AgCl as the reference electrode, scan rate = 100 mV/s.

Single-crystal X-ray diffraction data was collected at 100(2) K on a XtaLAB Synergy-S, Dualflex, HyPix-6000HE diffractometer using Cu *K*α radiation (λ = 1.5406 Å). Crystal was mounted on nylon CryoLoops with Paraton-N. The data collection and reduction were processed within CrysAlisPro (Rigaku OD, 2019). A multi-scan absorption correction was applied to the collected reflections. Using *Olex2*,[1] the structure was solved with the *ShelXT*[2] structure solution program using Intrinsic Phasing and refined with the *ShelXL* refinement package[3] using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically.

[1] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J, Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst*. **2009**, *42*, 339-341.
[2] Sheldrick, G.M. *Acta Cryst*. **2015**, *A71*, 3-8.
[3] Sheldrick, G.M. *Acta Cryst*. **2015**, *C71*, 3-8.

1.2 Synthetic procedures

Synthesis of DTF 3. 4-Nitrobenzaldehyde **(1)** (0.604 g, 3.99 mmol) ,4,5-bis(methylthio)-1,3-dithiole-2-thione **(2)** (1.20 g, 5.29 mmol), and $P(OMe)_3$ (8.0 mL) were added to a 50 mL round-bottomed flask. The flask was placed in an oil bath and heated at 120 °C for 3 h. After that, the reaction mixture was subjected to vacuum distillation at the same temperature to remove unreacted $P(OMe)_3$. The residue was subjected to silica gel column chromatography (hexanes/ CH_2Cl_2, 7: 3) to give pure compound **3** (0.620 g, 1.88 mmol, 46%) as a red crystalline solid. m.p: 136.1–138.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, J = 8.9 Hz, 2H), 7.29 (d, J = 9.1 Hz, 2H), 6.54 (s, 1H), 2.47 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.4, 142.4, 140.0, 128.7, 126.6, 124.2, 111.8, 23.9, 19.1, 18.9; FTIR (neat): υ 3084, 2915, 1586, 1548, 1494, 1479, 1317, 1102, 725, 852,742, 681, cm^{-1}; HRMS (APPI-TOF, positive mode) *m/z* calcd for $C_{12}H_{11}NO_2S_4$ 329.9746, found 329.9766 $[M + H]^+$.

Synthesis of TTFV 4. Compound **3** (0.500 g, 1.59 mmol), iodine (0.920 g, 3.62 mmol) and CH_2CL_2 (10 mL) were added to a 100 mL round-bottom flask. The reaction mixture was stirred under N_2 at room temperature for 5 min. Then 60 mL of the aqueous solution of saturated $Na_2S_2O_3$ was added to the reaction, and the mixture was kept stirring for another 15 min. The mixture was poured into a separatory funnel, and the aqueous layer was separated and extracted with CH_2Cl_2 twice. The organic layers were combined and dried over $MgSO_4$. After filtration and concentration under gentle heating and reduced pressure, the resulting residue was subjected to silica gel column chromatography (hexanes/CH_2Cl_2, 9:1) to give compound **4** (0.410 g, 0.414 mmol, 55%) as a red crystalline solid. m.p: 131.9–132.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, J = 9.1 Hz, 4H), 7.51 (d, J = 9.1 Hz, 4H), 2.48 (s, 6H), 2.40 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.35, 148.18, 144.60, 142.52, 141.17, 132.06, 129.98, 127.13, 126.38, 126.19,124.94, 124.44, 123.13, 120.94, 81.30, 67.53, 19.19, 19.05, 18.93; FTIR (neat): υ 3073, 2919, 2441, 1587, 1505,1464, 1330, 1189, 1106, 1013, 1963, 848, 702 cm^{-1}; HRMS (APPI-TOF, positive mode) *m/z* calcd for $C_{24}H_{21}N_2O_4S_8$ 656.9262, found 656.9264 $[M + H]^+$.

A trace amount of byproduct of **5** was also obtained from the reaction as a yellow crystalline solid, during the recrystallization of **4**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, J = 8.9 Hz, 4H), 7.55 (d, J = 8.2 Hz, 4H), 2.27 (s, 6H), 1.94 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.84, 138.80, 129.21, 124.70, 121.77, 63.45, 29.93, 28.93, 17.43; FTIR (neat): υ 3359, 2920, 2851, 1520, 1345, 1261, 1103, 1016, 881, 857, 801, 697 cm^{-1}.

Synthesis of DTF 7. 4-Methoxybenzaldehyde **(6) (**1.05 g**,** 7.74 mmol), 4,5-bis(methylthio)-1,3-dithiole-2-thione **(2)** (3.50 g, 15.486 mmol), and $P(OMe)_3$ (8.0 mL) were added to a 50 mL round-bottomed flask. The flask was placed in an oil bath and heated at 120 °C for 3 h. After that, the reaction mixture was subjected to vacuum distillation at the same temperature to remove unreacted $P(OMe)_3$. The residue was subjected to silica gel column chromatography (hexanes/ CH_2Cl_2, 7: 3) to give pure compound **7** (2.19 g, 6.96 mmol, 85%) as a white crystalline solid; m.p 60.8–61.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 9.0 Hz,

2H), 6.42 (s, 1H), 3.80 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.78, 129.24, 128.87, 128.15, 126.97, 123.93, 114.95, 113.99, 55.31, 18.91 ppm; FTIR (neat): υ 2962, 2912, 2837, 1556, 1501, 1305, 1283, 1024, 996, 900, 836 cm^{-1} ; HRMS (APPI-TOF, positive) *m/z* calcd for $C_{13}H_{14}OS_4$ 313.9922, found 313.9931 $[M]^{+\bullet}$.

Synthesis of TTFV 8. Compound **7** (0.500 g, 1.59 mmol), iodine (1.02 g, 4.00 mmol), and CH_2Cl_2 (10ml) were added to a 100 mL round-bottom flask. The reaction mixture was stirred under N_2 at room temperature for 5 min. Then 60 mL of the aqueous solution of saturated $Na_2S_2O_3$ was added to the reaction and the mixture was kept stirring for another 15 min. The mixture was poured into a separatory funnel, and the aqueous layer was separated and extracted with CH_2Cl_2 twice. The organic layers were combined and dried over $MgSO_4$. After filtration and concentration under gentle heating and reduced pressure, the resulting residue was subjected to silica gel column chromatography (hexanes/CH_2Cl_2, 9:1) to give compound **8** (0.26 g, 0.414 mmol, 55%) as a pale yellow crystalline solid. m.p 105.7-106.4 °C ;1H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.6, 133.3, 128.1, 127.8, 124.9, 124.5, 113.9, 58.5, 29.2, 23.8, 19.6; FTIR (neat) 2924, 2857, 1728, 1671, 1600, 1252, 1174, 1028, 828 cm$^{-1.}$; HRMS (APPI-TOF, positive mode) *m/z* calcd for $C_{26}H_{27}O_2S_8$ 626.9772, found 626.9810 $[M]^+$.

2. UV-Vis Absorption Data

UV-Vis absorption spectra of compounds **3**, **4**, **5**, **7**, and **8** were measured on a Cary 6000i spectrophotometer at room temperature using dichloromethane as the solvent.

Table S-1 Summary of UV-Vis absorption data

Entry	λ_{max}/nm (ε/mol^{-1} L cm^{-1})
3	449 (1.39×10^3)
4	452 (6.04×10^3), 266 (9.54×10^3)
5	264 (2.33×10^3), 232 (2.89×10^3)
7	341 (3.55×10^4)
8	341 (7.09×10^2), 254 (8.33×10^2)

3. NMR Spectra for New Compounds

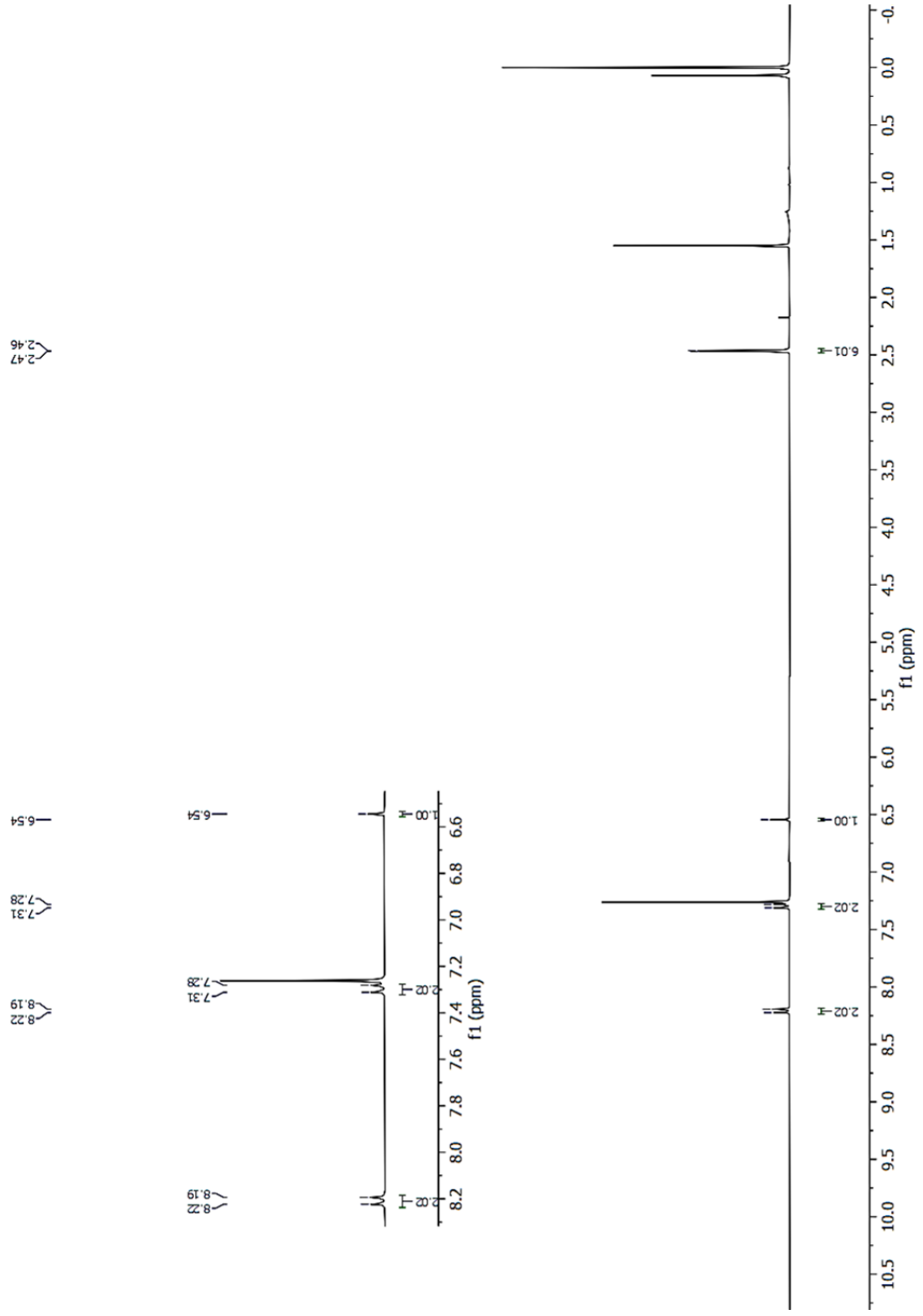

Fig. S-1 ^{1}H NMR (300 MHz, $CDCl_3$) of compound **3**.

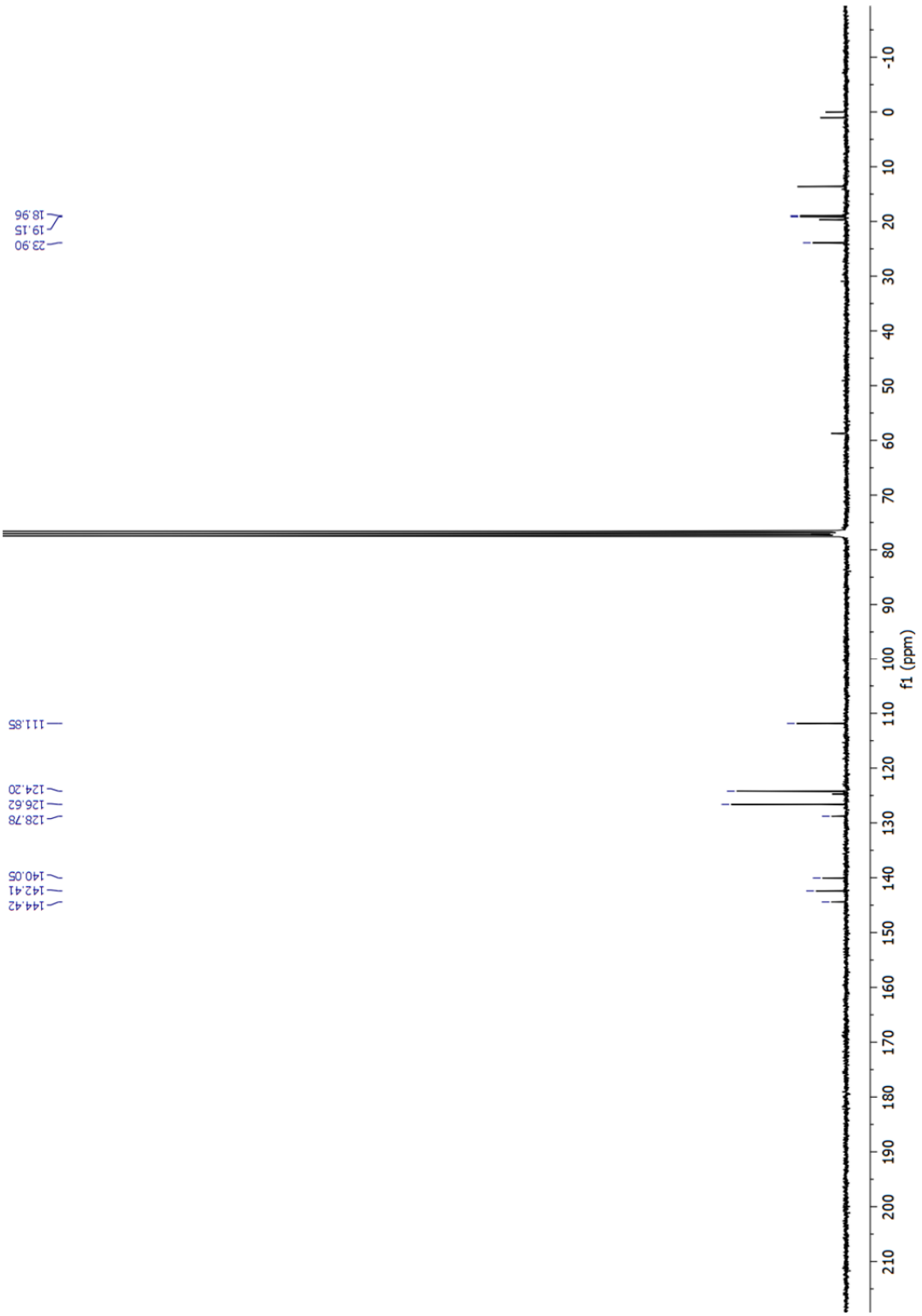

Fig. S-2 ^{13}C NMR (75 MHz, $CDCl_3$) of compound **3**.

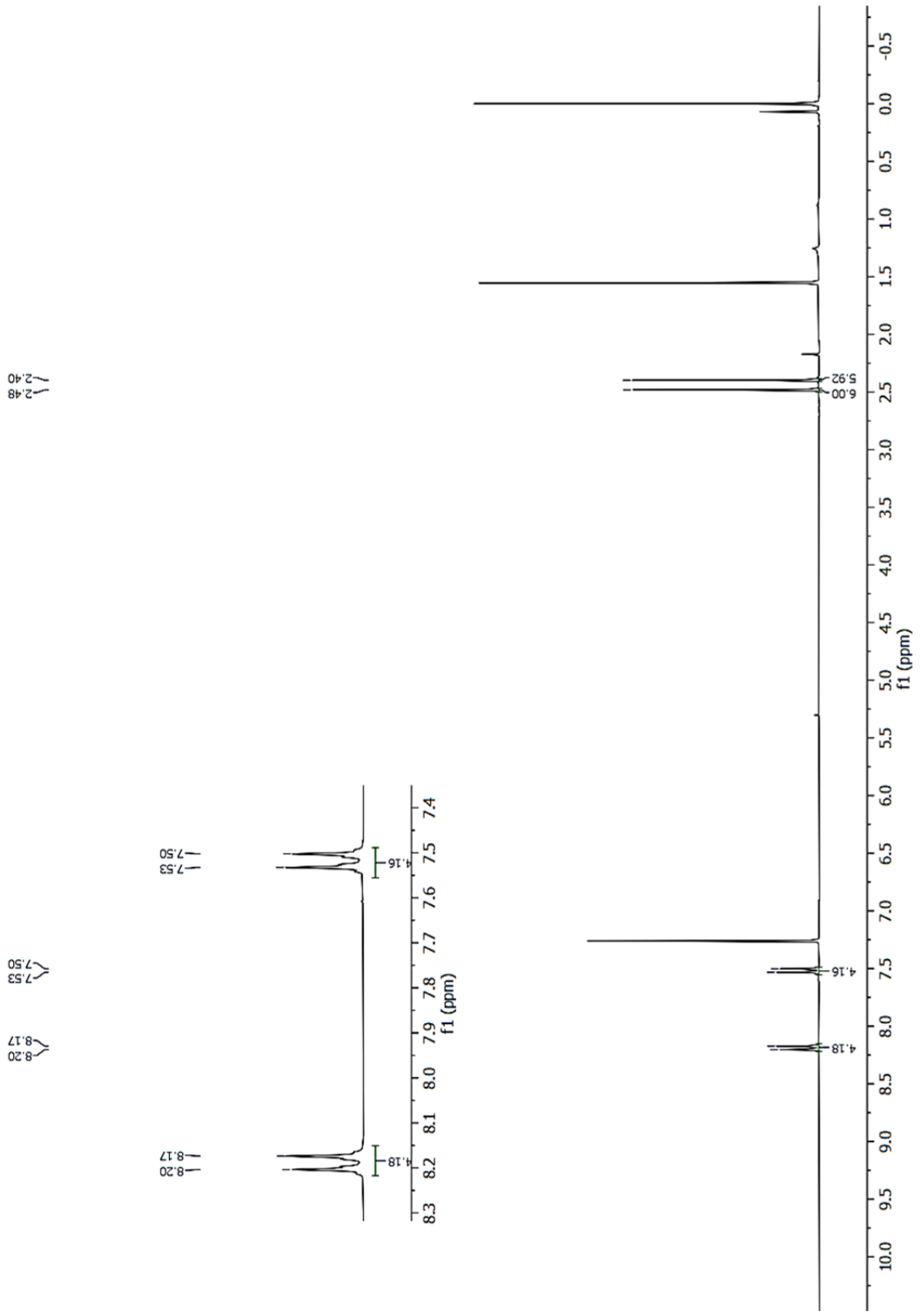

Fig. S-3 ^{1}H NMR (300 MHz, $CDCl_3$) of compound **4**.

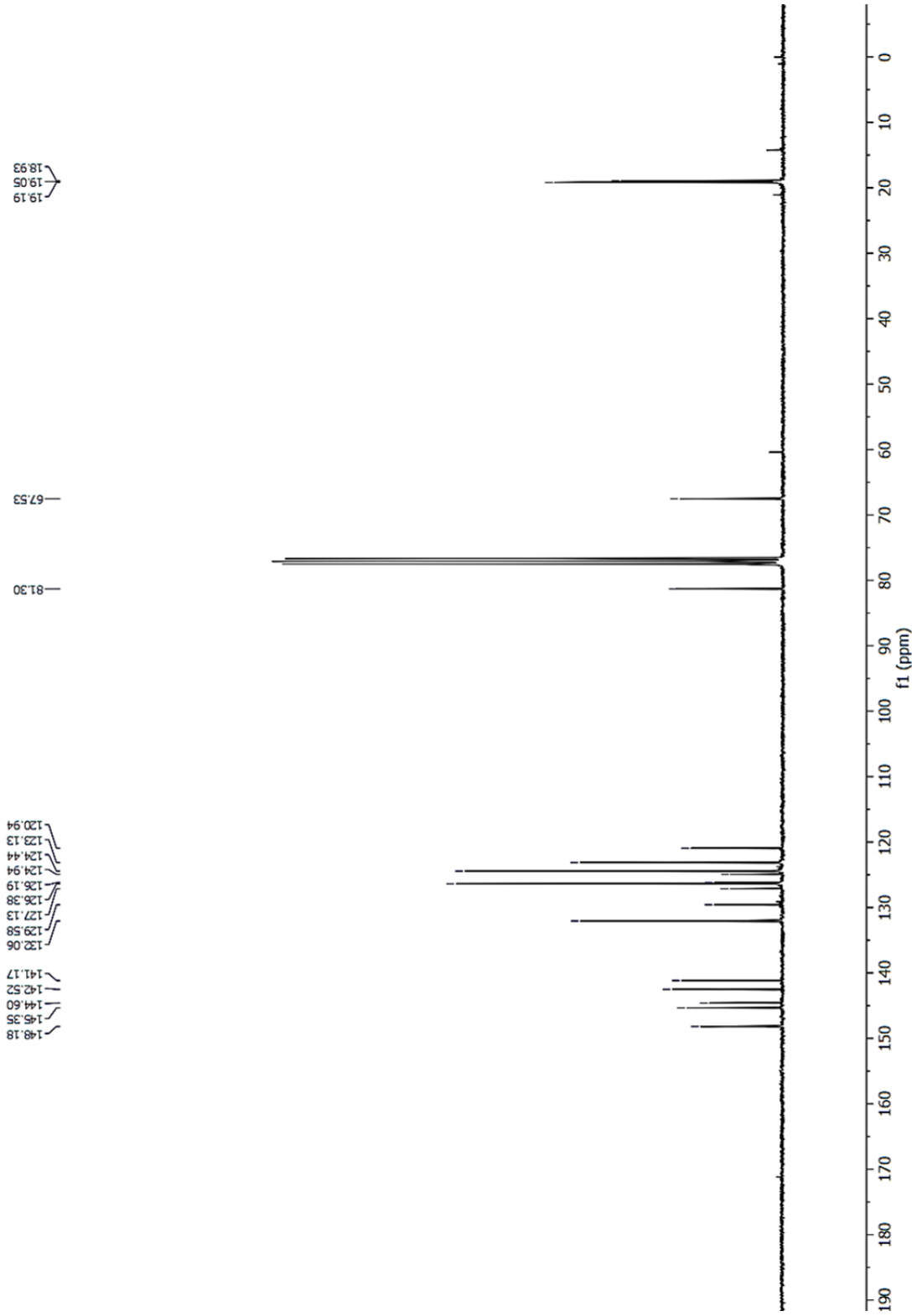

Fig. S-4 ^{13}C NMR (75 MHz, $CDCl_3$) of compound **4**.

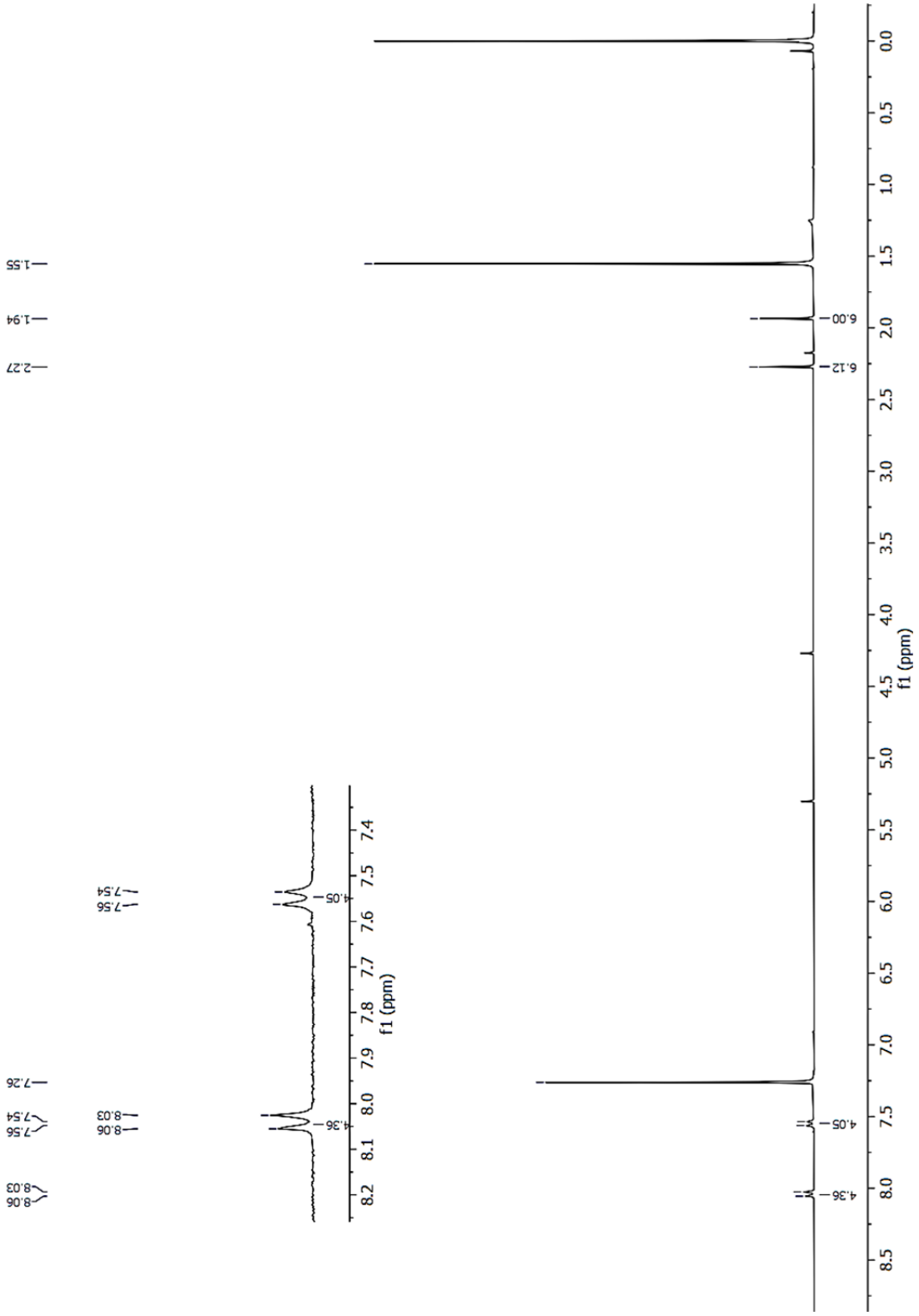

Fig. S-5 ^{1}H NMR (300 MHz, $CDCl_3$) of compound **5**.

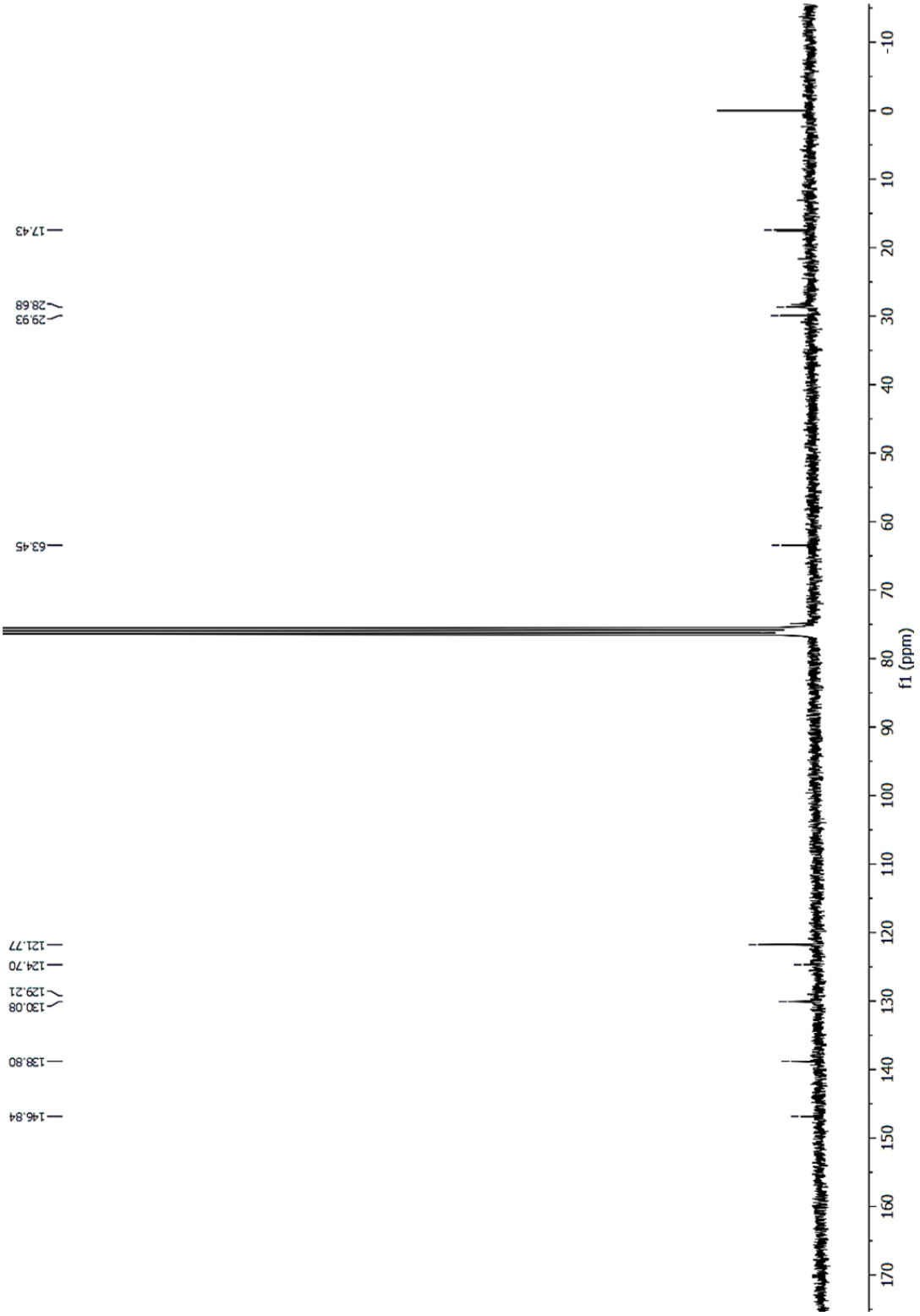

Fig. S-6 ^{13}C NMR (300 MHz, $CDCl_3$) of compound **5**.

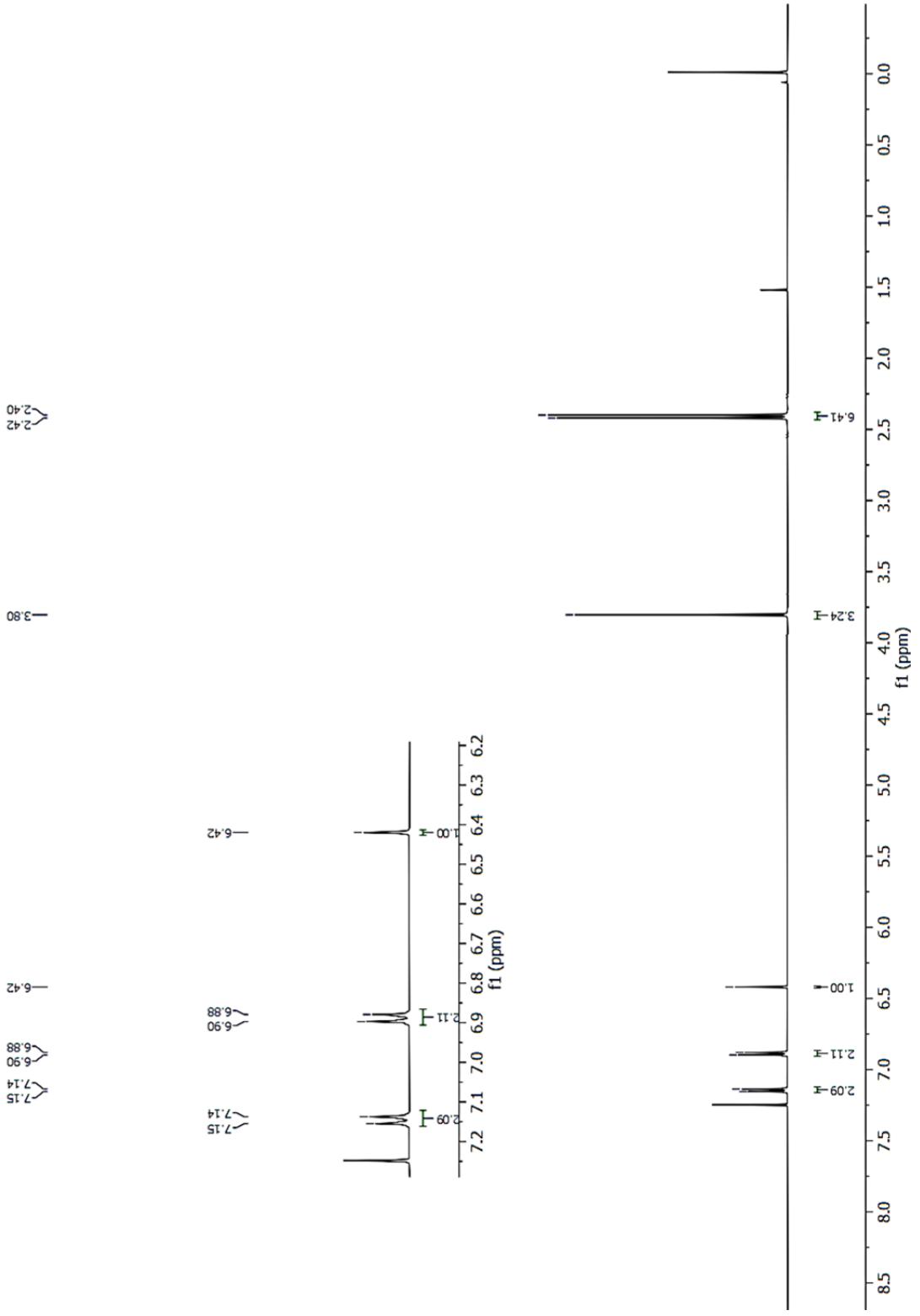

Fig. S-7 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **7**.

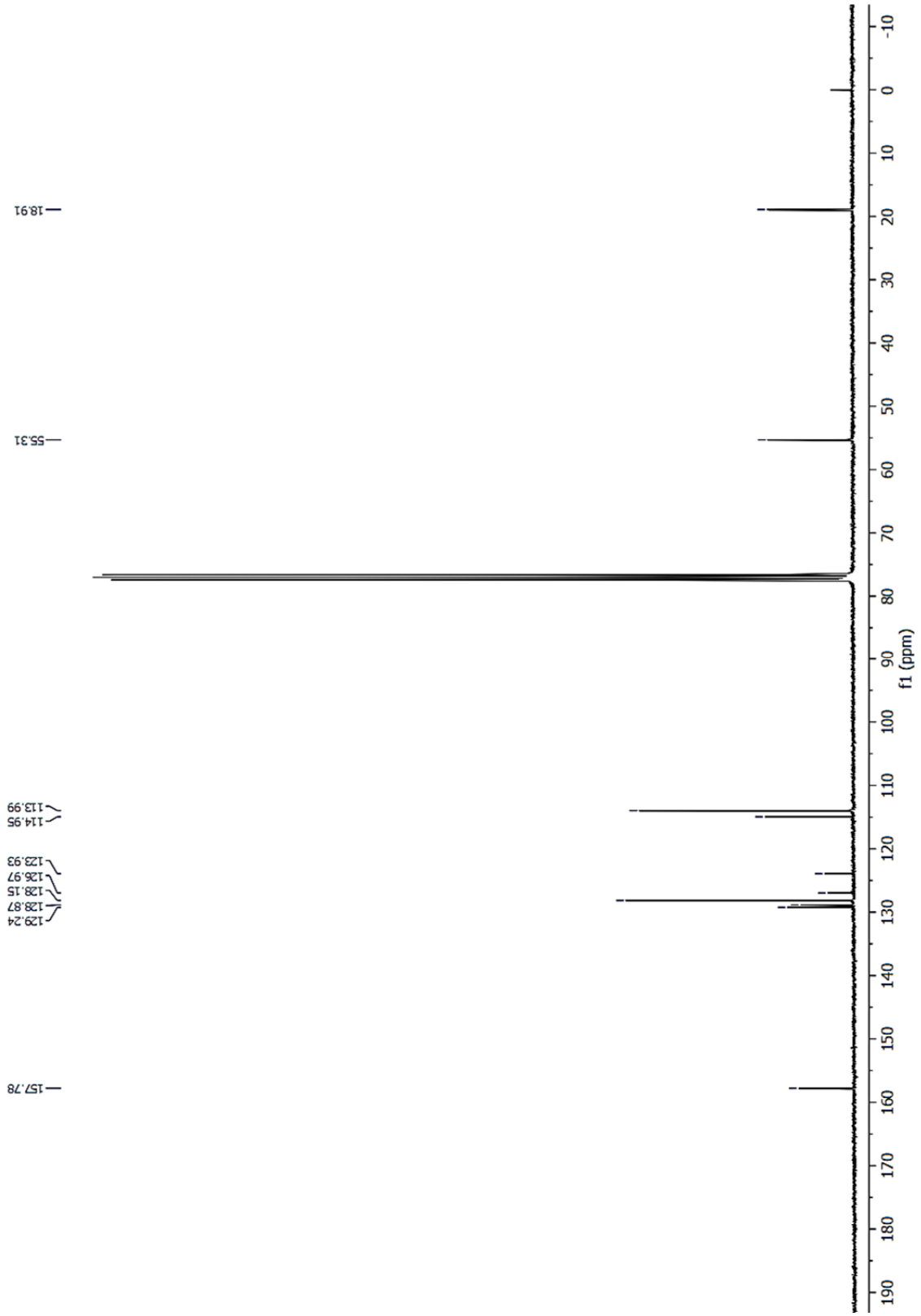

Fig. S-8 ^{13}C NMR (500 MHz, $CDCl_3$) of compound **7**.

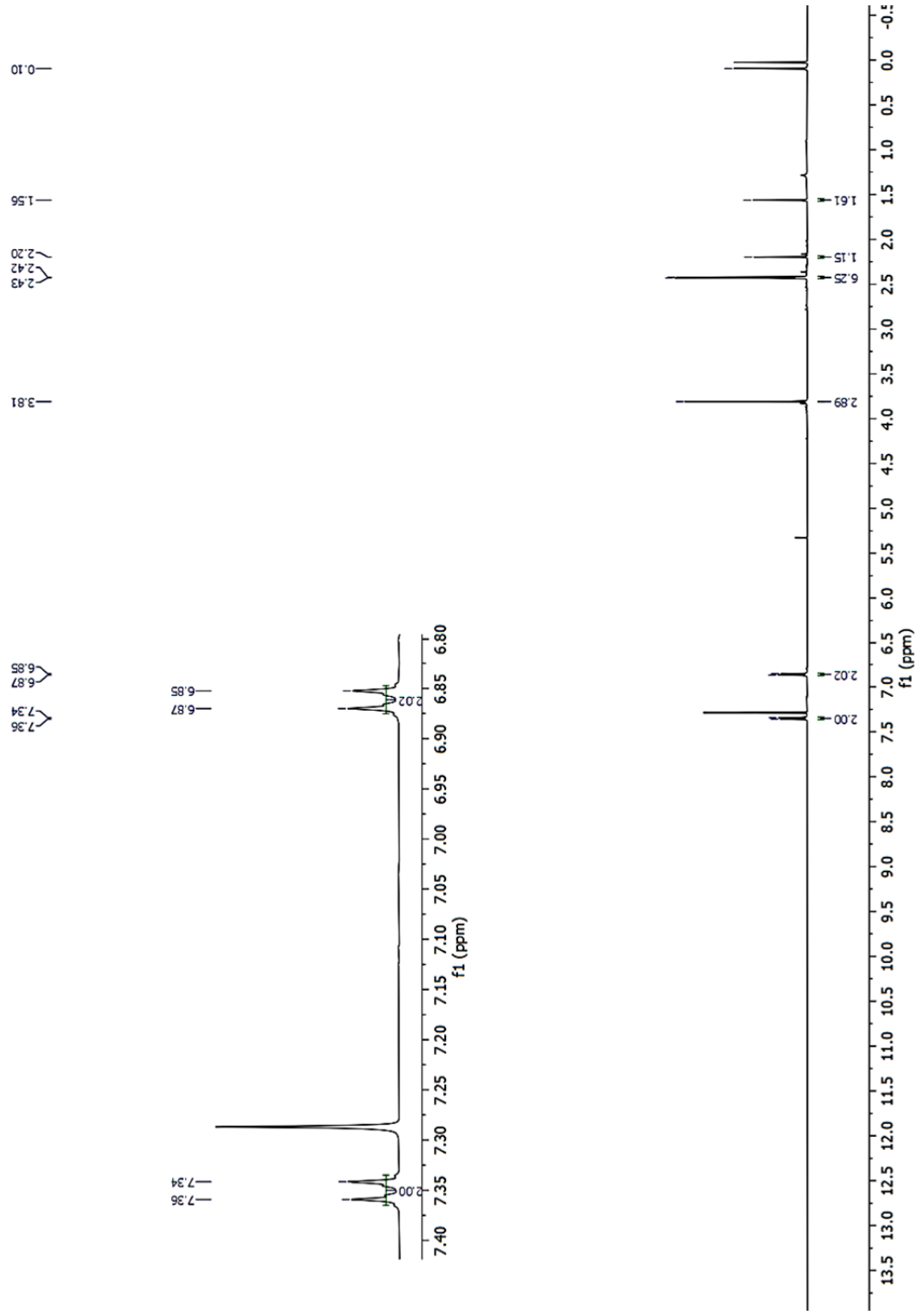

Fig. S-9 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**.

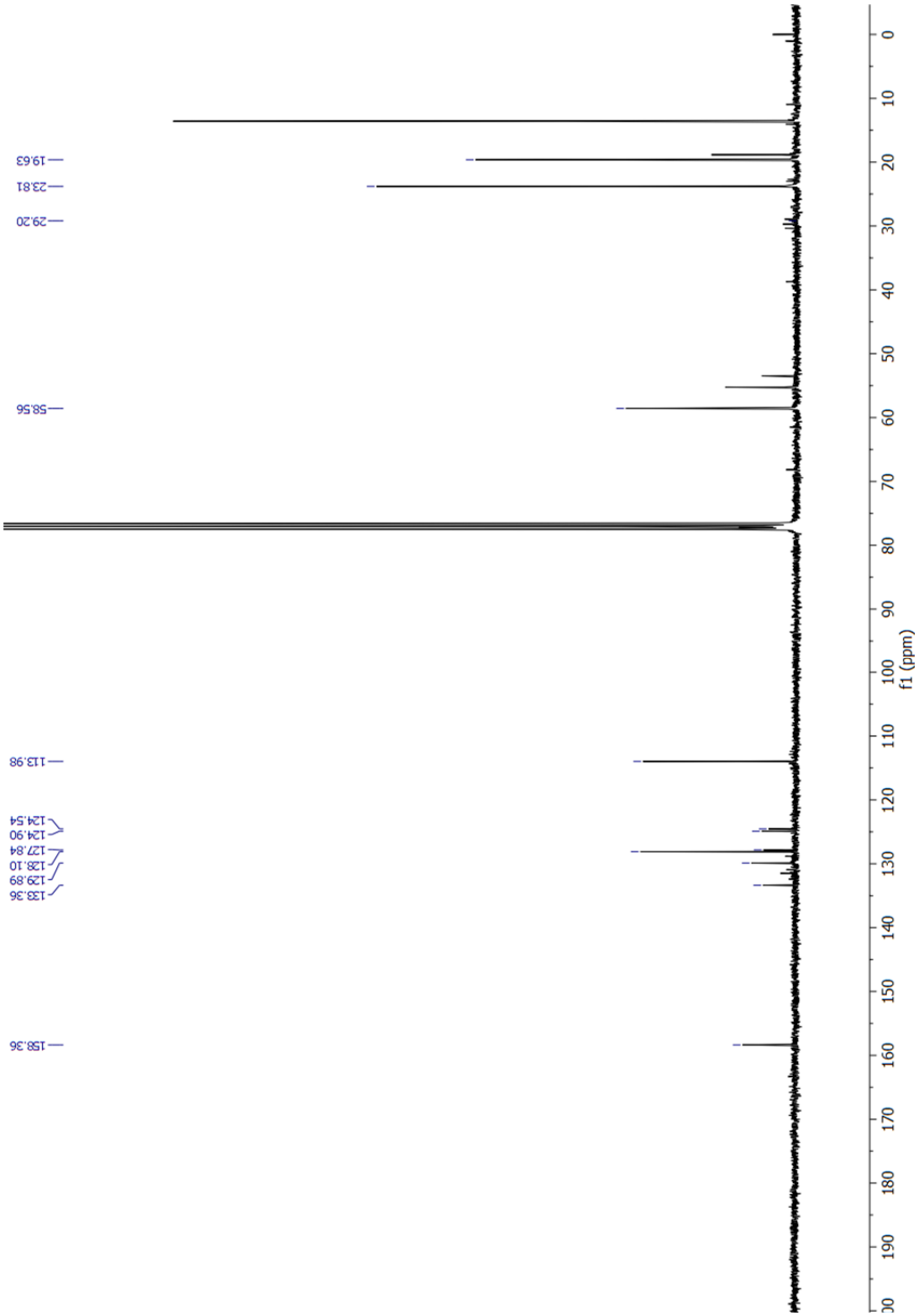

Fig. S-10 ^{13}C NMR (75 MHz, CDCl3) of compound **8**.

4. Crystallographic Data for Compounds 3, 4, 5, 7, and 8

Table S-2 Crystal data and structure refinement for 3

Empirical formula	$C_{12}H_{11}NO_2S_4$
Formula weight	329.46
Temperature/K	99.99(10)
Crystal system	triclinic
Space group	*P*-1
a/Å	7.3968(3)
b/Å	8.3340(2)
c/Å	11.6041(3)
α/°	82.169(2)
β/°	89.492(2)
γ/°	73.337(2)
Volume/Å^3	678.56(4)
Z	2
ρ_{calc}g/cm^3	1.612
μ/mm^{-1}	6.410
F(000)	340.0
Crystal size/mm^3	0.11 × 0.09 × 0.05
Radiation	Cu *K*α (λ = 1.54184)
2θ range for data collection/°	7.694 to 154.428
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 9$, $-14 \le l \le 14$
Reflections collected	17088
Independent reflections	2845 [R_{int} = 0.0460, R_{sigma} = 0.0258]
Data/restraints/parameters	2845/0/174
Goodness-of-fit on F^2	1.161
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0323, wR_2 = 0.0913
Final *R* indexes [all data]	R_1 = 0.0334, wR_2 = 0.0923
Largest diff. peak/hole / e Å^{-3}	0.32/-0.44

Table S-3 Crystal data and structure refinement for 4

Empirical formula	$C_{24}H_{20}N_2O_4S_8$
Formula weight	656.90
Temperature/K	100(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	10.0328(4)
b/Å	11.4799(6)
c/Å	12.7909(4)
α/°	81.281(3)
β/°	88.789(3)
γ/°	72.880(4)
Volume/Å^3	1391.22(10)
Z	2
ρ_{calc}mg/mm^3	1.568
μ/mm^{-1}	6.252
F(000)	676.0
Crystal size/mm^3	0.392 × 0.193 × 0.04
2*θ* range for data collection	6.994 to 154.606°
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-15 \le l \le 12$
Reflections collected	32133
Independent reflections	5776[*R*(int) = 0.0530]
Data/restraints/parameters	5776/0/347
Goodness-of-fit on F^2	1.083
Final *R* indexes [$I>=2\sigma$ (I)]	R_1 = 0.0462, wR_2 = 0.1212
Final *R* indexes [all data]	R_1 = 0.0538, wR_2 = 0.1255
Largest diff. peak/hole / e Å^{-3}	0.49/-0.39

Table S-4 Crystal data and structure refinement for 5

Empirical formula	$C_{24.75}H_{23.5}Cl_{1.5}N_2O_4S_9$
Formula weight	754.67
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.54193(13)
b/Å	14.0748(3)
c/Å	27.4895(5)
β/°	97.1341(16)
Volume/Å^3	3279.36(10)
Z	4
ρ_{calc}g/cm^3	1.529
μ/mm^{-1}	7.061
F(000)	1550.0
Crystal size/mm^3	0.235 × 0.075 × 0.038
Radiation	Cu $K\alpha$ (λ = 1.54184)
2θ range for data collection/°	6.48 to 154.882
Index ranges	$-10 \le h \le 10$, $-16 \le k \le 17$, $-34 \le l \le 34$
Reflections collected	41395
Independent reflections	6877 [R_{int} = 0.0576, R_{sigma} = 0.0380]
Data/restraints/parameters	6877/0/413
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0672, wR_2 = 0.1818
Final R indexes [all data]	R_1 = 0.0758, wR_2 = 0.1892
Largest diff. peak/hole / e Å^{-3}	1.20/-0.78

Table S-5 Crystal data and structure refinement for 7

Empirical formula	$C_{13}H_{14}OS_4$
Formula weight	314.48
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.4907(2)
b/Å	5.32821(5)
c/Å	13.26611(11)
β/°	100.5862(9)
Volume/Å^3	1423.73(2)
Z	4
ρ_{calc}g/cm^3	1.467
μ/mm^{-1}	6.002
F(000)	656.0
Crystal size/mm^3	0.16 × 0.1 × 0.08
Radiation	Cu $K\alpha$ (λ = 1.54184)
2θ range for data collection/°	4.386 to 154.596
Index ranges	$-25 \leq h \leq 25$, $-6 \leq k \leq 6$, $-16 \leq l \leq 15$
Reflections collected	33850
Independent reflections	3010 [R_{int} = 0.0639, R_{sigma} = 0.0279]
Data/restraints/parameters	3010/0/166
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0336, wR_2 = 0.0881
Final R indexes [all data]	R_1 = 0.0368, wR_2 = 0.0906
Largest diff. peak/hole / e Å^{-3}	0.36/-0.38

Table S-6 Crystal data and structure refinement for 8

Empirical formula	$C_{26}H_{26}O_2S_8$
Formula weight	626.95
Temperature/K	100(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	10.11380(10)
b/Å	13.0705(2)
c/Å	21.6545(2)
α/°	98.3050(10)
β/°	93.3530(10)
γ/°	94.9550(10)
Volume/Å^3	2814.63(6)
Z	4
ρ_{calc}g/cm^3	1.480
μ/mm^{-1}	6.071
F(000)	1304.0
Crystal size/mm^3	0.116 × 0.067 × 0.05
Radiation	Cu *K*α (λ = 1.54184)
2θ range for data collection/°	4.134 to 155.316
Index ranges	$-12 \le h \le 12$, $-16 \le k \le 16$, $-27 \le l \le 24$
Reflections collected	22234
Independent reflections	22234 [R_{sigma} = 0.0251]
Data/restraints/parameters	22234/0/662
Goodness-of-fit on F^2	1.038
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0651, wR_2 = 0.1859
Final *R* indexes [all data]	R_1 = 0.0785, wR_2 = 0.1957
Largest diff. peak/hole / e Å^{-3}	0.81/-0.71

5. DFT Computational Results

5.1 Computational methods

Density functional theory (DFT) computational studies were performed using the *Gaussian 16* software package.[4] Molecular geometries of monomers and dimers of donor/acceptor-substituted DTF and TTFV derivatives **3**, **4**, **7**, and **8** were optimized in the gas phase at the M06-2X/Def2SVP level of theory. The optimized geometries were subjected to frequency calculations at the same level to validate they are energy minima (zero imaginary frequency) as well as to obtain thermodynamic energies. Time-dependent density functional theory (TD-DFT) calculations of **3**, **4**, **7**, and **8** were performed on their optimized geometries at the CAM-B3LYP/6-311+G(2d,p) level of theory. *GaussSum* software package[5] was used to generate simulated UV-Vis absorption spectrums. Molecular structures and frontier molecular orbitals were visualized by *VMD* software package.[6] Molecular electrostatic potential maps were generated using GaussView 5[7] and the maximum and minimum electrostatic potentials on the molecular density surface were calculated by the *Multiwfn* software.[8]

5.2 TD-DFT results for compounds 3, 4, 7, and 8

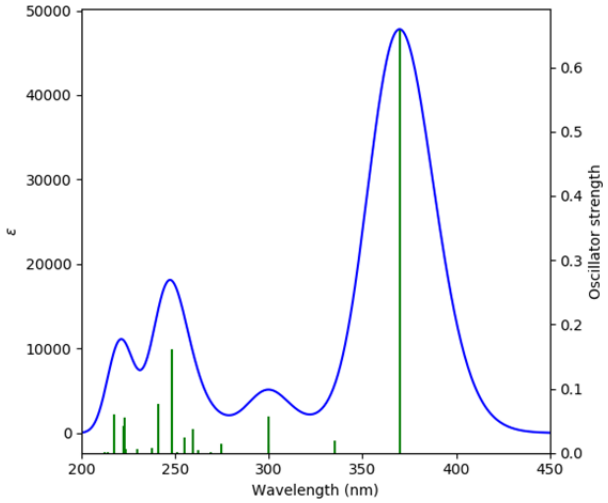

Fig. S-11 Simulated UV-Vis spectrum of compound **3**.

[4] Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

[5] Tenderholt, A.; Langner, K.; O'Boyle, N. *J. Comp. Chem*. **2008**, *29*, 839-845.

[6] Humphrey, W.; Dalke, A.; Schulten, K. *J. Molec. Graphics*, **1996**, *14*, 33-38.

[7] Dennington, R.; Keith, T.; Millam. J. *GaussView*, Version 5, Semichem Inc, Shawnee Mission KS, 2009

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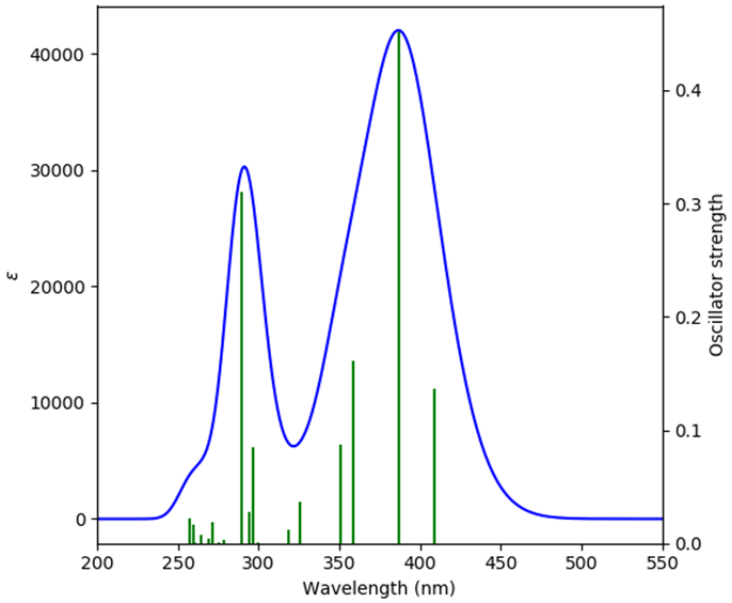

Fig. S-12 Simulated UV-Vis spectrum of compound **4**.

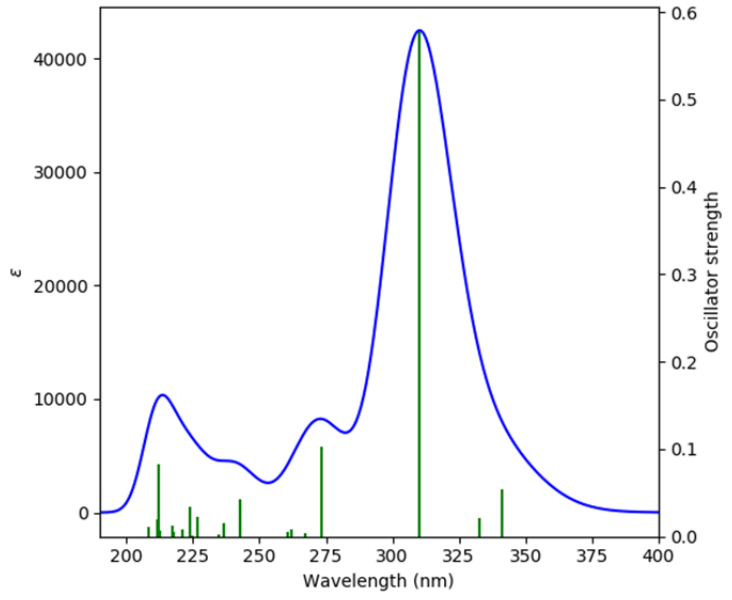

Fig. S-13 Simulated UV-Vis spectrum of compound **7**.

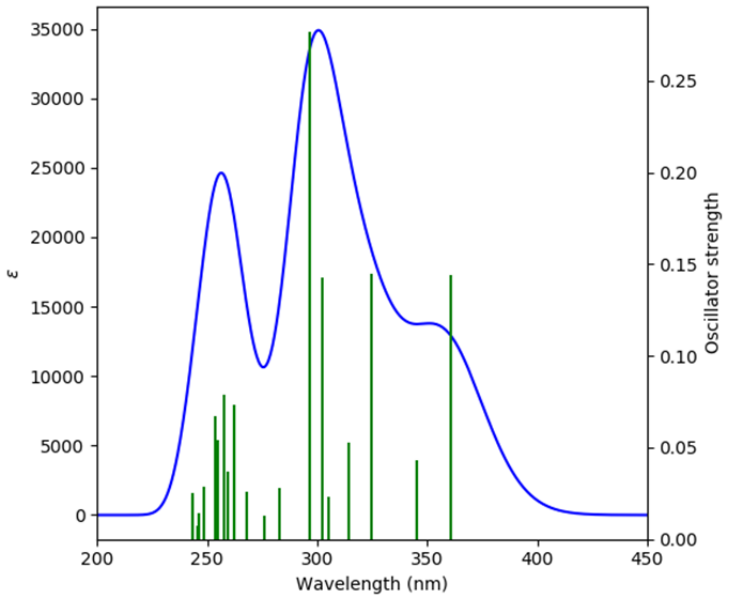

Fig. S-14 Simulated UV-Vis spectrum of compound **8**.

Table S-7 Summary of TD-DFT calculated electronic transitions of **3**

λ (nm)	*f*	Major MO Contributions
369.8	0.658	HOMO→LUMO (89%)
335.4	0.019	HOMO→L+1 (25%), HOMO→L+2 (41%), HOMO→L+3 (13%), HOMO→L+5 (10%)
299.7	0.057	H-6→LUMO (14%), HOMO→L+1 (54%), HOMO→L+2 (10%)
299.6	0.012	H-6→LUMO (62%), HOMO→L+1 (12%)
274.5	0.014	H-3→LUMO (27%), HOMO→L+3 (32%), HOMO→L+5 (21%)
268.8	0.000	H-7→LUMO (74%)
262.1	0.004	HOMO→L+4 (41%), HOMO→L+5 (10%)
259.2	0.036	H-1→LUMO (12%), HOMO→L+2 (14%), HOMO→L+3 (21%), HOMO→L+4 (16%)
254.7	0.024	HOMO→L+4 (10%), HOMO→L+6 (56%)
251.0	0.000	H-2→L+1 (73%), H-2→L+3 (16%)
247.9	0.161	H-3→LUMO (11%), H-1→LUMO (49%)
241.1	0.076	H-3→LUMO (38%), HOMO→L+5 (34%)
237.4	0.007	HOMO→L+7 (20%), HOMO→L+9 (14%), HOMO→L+11 (17%)
229.7	0.006	H-1→L+1 (40%), H-1→L+2 (11%), HOMO→L+7 (18%)
223.3	0.007	H-2→LUMO (51%)
222.8	0.055	H-2→LUMO (26%), HOMO→L+9 (11%)
222.5	0.041	H-2→LUMO (11%), H-1→L+1 (18%), H-1→L+2 (18%), H-1→L+3 (15%), HOMO→L+8 (11%)
217.0	0.059	HOMO→L+8 (43%)
213.7	0.001	H-1→L+2 (17%), HOMO→L+7 (15%), HOMO→L+10 (19%)
212.5	0.001	HOMO→L+10 (28%), HOMO→L+11 (12%), HOMO→L+13 (12%)

Table S-8 Summary of TD-DFT calculated electronic transitions of **4**.

λ (nm)	*f*	Major MO Contributions
409.0	0.136	HOMO→LUMO (74%), HOMO→L+1 (10%)
387.0	0.452	HOMO→LUMO (10%), HOMO→L+1 (74%)
358.3	0.161	H-1→LUMO (69%)
350.8	0.087	H-1→L+1 (64%), H-1→L+2 (14%)
325.4	0.037	H-1→LUMO (13%), HOMO→L+2 (29%), HOMO→L+3 (10%)
318.8	0.012	H-1→L+1 (18%), HOMO→L+3 (28%)
299.8	0.001	H-12→L+1 (65%)
299.7	0.000	H-13→LUMO (65%)
296.3	0.085	H-1→L+4 (23%), HOMO→L+4 (52%)
294.4	0.028	HOMO→L+5 (20%), HOMO→L+6 (23%)
289.7	0.309	H-1→L+3 (10%), HOMO→L+2 (29%), HOMO→L+5 (23%)
278.5	0.002	H-7→LUMO (10%), HOMO→L+6 (16%), HOMO→L+10 (18%)
275.2	0.001	H-6→L+1 (15%), HOMO→L+7 (29%)
271.3	0.019	H-1→L+2 (46%)
269.3	0.000	H-16→LUMO (52%), H-14→L+1 (15%)
269.2	0.004	H-16→LUMO (13%), H-14→L+1 (51%)
264.4	0.008	H-1→L+9 (12%), HOMO→L+7 (11%), HOMO→L+8 (24%)
260.3	0.001	H-7→LUMO (10%), H-1→L+3 (18%)
259.8	0.016	HOMO→L+9 (19%)
256.9	0.022	H-7→LUMO (11%), H-6→L+1 (17%), HOMO→L+7 (18%), HOMO→L+8 (14%)

Table S-9 Summary of TD-DFT calculated electronic transitions of **7**.

λ (nm)	*f*	Major MO Contributions
341.3	0.053	HOMO→LUMO (77%)
332.8	0.021	HOMO→LUMO (12%), HOMO→L+2 (55%)
309.9	0.577	HOMO→L+1 (89%)
273.3	0.103	HOMO→L+2 (12%), HOMO→L+5 (55%)
267.3	0.003	H-2→LUMO (60%), H-1→LUMO (26%)
262.1	0.008	H-3→LUMO (47%), HOMO→L+3 (17%)
260.6	0.004	H-3→LUMO (33%), HOMO→L+3 (30%), HOMO→L+6 (12%)
242.8	0.042	HOMO→L+4 (30%), HOMO→L+14 (15%)
236.7	0.015	HOMO→L+4 (24%), HOMO→L+7 (17%), HOMO→L+10 (13%)
234.7	0.003	HOMO→L+3 (15%), HOMO→L+4 (12%), HOMO→L+6 (28%), HOMO→L+8 (10%)
226.8	0.023	H-1→L+1 (15%), HOMO→L+9 (23%)
224.8	0.001	H-1→L+1 (11%), HOMO→L+7 (21%)
223.8	0.034	H-1→L+1 (40%)
221.09	0.008	HOMO→L+8 (35%), HOMO→L+9 (13%)
217.5	0.006	HOMO→L+12 (13%), HOMO→L+13 (25%)
217.2	0.0124	H-4→L+1 (13%), H-1→L+2 (13%)
212.5	0.007	H-1→LUMO (10%), HOMO→L+10 (19%)
212.2	0.083	H-1→LUMO (29%)
211.6	0.019	H-2→L+2 (19%), H-1→L+2 (26%)
208.5	0.011	H-2→L+4 (10%)

Table S-10 Summary of TD-DFT calculated electronic transitions of **8**.

λ (nm)	*f*	Major MO Contributions
360.5	0.143	HOMO→LUMO (88%)
345.1	0.043	HOMO→L+1 (33%), HOMO→L+3 (15%), HOMO→L+5 (12%)
324.5	0.145	HOMO→L+1 (25%), HOMO→L+2 (20%), HOMO→L+3 (13%)
314.2	0.052	H-1→L+1 (11%), HOMO→L+1 (13%), HOMO→L+2 (27%), HOMO→L+5 (12%)
304.9	0.023	H-1→LUMO (61%), HOMO→L+2 (12%)
302.5	0.142	H-1→L+3 (20%), HOMO→L+3 (22%), HOMO→L+5 (14%), HOMO→L+6 (10%)
296.6	0.277	H-1→L+2 (11%), HOMO→L+2 (17%), HOMO→L+6 (17%)
282.8	0.028	H-1→L+1 (26%), H-1→L+2 (16%)
275.9	0.013	H-1→L+4 (10%), HOMO→L+4 (51%)
267.8	0.026	H-2→LUMO (2%), H-2→L+6 (2%), H-1→L+4 (3%), HOMO→L+4 (2%), HOMO→L+5 (9%), HOMO→L+7 (6%), HOMO→L+8 (9%), HOMO→L+9 (6%), HOMO→L+10 (2%), HOMO→L+11 (9%), HOMO→L+12 (3%), HOMO→L+13 (4%), HOMO→L+14 (2%)
262.2	0.073	H-1→L+2 (15%), HOMO→L+6 (11%)
259.2	0.037	HOMO→L+11 (10%)
257.6	0.078	H-1→L+1 (13%), H-1→L+2 (24%)
254.7	0.053	H-4→L+3 (36%)
253.6	0.067	H-1→L+3 (28%)
248.7	0.028	H-5→L+1 (24%), H-5→L+2 (21%)
246.4	0.014	H-1→L+5 (15%)
245.8	0.007	H-1→L+6 (12%)
243.4	0.025	H-2→LUMO (13%)
243.1	0.023	H-2→LUMO (18%)

5.3 Calculations of interaction energies for the π-dimer of DTF 3

Interaction energy (ΔEint) for each of the π-dimer of DTF **3** is calculated as follows:

$$\Delta E_{\text{int}} = E(\text{dimer}) - 2 \times E(\text{monomer})$$

where E(dimer) is the total electronic energy of the dimeric assembly with zero-point energy (ZPE) correction taken into account, and E(monomer) is the total electronic energy of the individual molecule of **3** (optimized in the gas phase) with ZPE correction.

5.4 Cartesian coordinates of optimized molecular geometries

DTF **3**: (E = -2260.405392 Hartree, dipole moment = 7.873671 Debye)

S	1.98373200	-1.74144400	-0.14712200
S	0.75977500	0.92841600	-0.34256200
S	4.82324400	-0.60945800	-0.09615100
S	3.43113300	2.35734300	-0.30860300
O	-6.92053600	-0.28307700	0.50176400

O	-6.29743100	1.61292000	-0.28195300
N	-6.08292100	0.48332200	0.08857300
C	0.48380300	-0.79919800	-0.17633000
C	3.08234900	-0.37251100	-0.17301700
C	2.52365700	0.85255300	-0.26420900
C	4.93746400	-2.38692700	0.24065500
H	4.53002200	-2.97864900	-0.58911700
H	4.44131800	-2.65000700	1.18314900
H	6.01124000	-2.59265400	0.32879700
C	3.52825900	2.68924800	1.48023400
H	2.52145700	2.77805800	1.90594000
H	4.06009900	3.64243500	1.59255000
H	4.09101000	1.89076000	1.97930500
C	-0.70211200	-1.44357200	-0.05771800
H	-0.64167800	-2.52477300	0.09370000
C	-2.05425700	-0.89796700	-0.05952700
C	-2.39213500	0.39704700	-0.50160000
H	-1.63863300	1.05788600	-0.92614700
C	-3.70514300	0.84973100	-0.45398100
H	-3.97900700	1.84626900	-0.79655700
C	-4.69313200	0.00295000	0.03331500
C	-4.40807100	-1.29132300	0.45988500
H	-5.21518500	-1.92419000	0.82499500
C	-3.09523000	-1.73052200	0.40533300
H	-2.85530700	-2.74190400	0.73765000

π-dimer of **3**: (*E* = -4520.848524 Hartree, dipole moment = 0 Debye)

S	1.54168000	-2.58874700	1.07552700
S	2.26108700	0.14827300	1.84976100
S	1.86170900	-3.65957300	3.90988500
S	2.88429600	-0.62197000	4.71119100
O	1.32991600	4.33693300	-4.75682600
O	1.82938800	5.38621500	-2.95605300
N	1.58973900	4.37383400	-3.57802900
C	1.72517000	-0.90905200	0.55775600
C	1.97909500	-2.34219300	2.75502800
C	2.32912700	-1.08686000	3.11255300
C	1.47749100	-5.07268800	2.84131400
H	2.33250900	-5.33761300	2.20675000
H	0.58223600	-4.89656400	2.23020300
H	1.26023000	-5.89668700	3.53278700
C	1.42660500	0.27787700	5.32670600
H	1.19675900	1.13376000	4.67887000
H	1.69306900	0.64567100	6.32561700
H	0.56069300	-0.39030300	5.40592100
C	1.45333400	-0.57925900	-0.73027600
H	1.10184600	-1.39950900	-1.36258300

C	1.53911500	0.71058100	-1.39849300
C	2.00893800	1.90341800	-0.80732000
H	2.37856400	1.92116600	0.21461600
C	2.02905800	3.09683200	-1.51718500
H	2.38276700	4.02156000	-1.06374800
C	1.59145200	3.10832600	-2.83694800
C	1.14853300	1.95010200	-3.47089900
H	0.81986600	2.01096000	-4.50792100
C	1.11784200	0.77008400	-2.74689800
H	0.75500900	-0.14226900	-3.22405600
S	-1.54168000	2.58874700	-1.07552700
S	-2.26108700	-0.14827300	-1.84976100
S	-1.86170900	3.65957300	-3.90988500
S	-2.88429600	0.62197000	-4.71119100
O	-1.32991600	-4.33693300	4.75682600
O	-1.82938800	-5.38621500	2.95605300
N	-1.58973900	-4.37383400	3.57802900
C	-1.72517000	0.90905200	-0.55775600
C	-1.97909500	2.34219300	-2.75502800
C	-2.32912700	1.08686000	-3.11255300
C	-1.47749100	5.07268800	-2.84131400
H	-2.33250900	5.33761300	-2.20675000
H	-0.58223600	4.89656400	-2.23020300
H	-1.26023000	5.89668700	-3.53278700
C	-1.42660500	-0.27787700	-5.32670600
H	-1.19675900	-1.13376000	-4.67887000
H	-1.69306900	-0.64567100	-6.32561700
H	-0.56069300	0.39030300	-5.40592100
C	-1.45333400	0.57925900	0.73027600
H	-1.10184600	1.39950900	1.36258300
C	-1.53911500	-0.71058100	1.39849300
C	-2.00893800	-1.90341800	0.80732000
H	-2.37856400	-1.92116600	-0.21461600
C	-2.02905800	-3.09683200	1.51718500
H	-2.38276700	-4.02156000	1.06374800
C	-1.59145200	-3.10832600	2.83694800
C	-1.14853300	-1.95010200	3.47089900
H	-0.81986600	-2.01096000	4.50792100
C	-1.11784200	-0.77008400	2.74689800
H	-0.75500900	0.14226900	3.22405600

TTFV **4**: (*E* = -4519.638715 Hartree, dipole moment = 4.939739 Debye)

S	2.26924400	-0.30724500	-1.37851700
S	2.37209400	2.52279100	-0.57043500
S	5.16634800	2.92931200	-1.66350200
S	5.07594400	-0.22758900	-2.58193300

S	-2.18999600	0.34169400	-1.52684600
S	-2.31615300	-2.39516400	-0.44777800
S	-5.11315700	-2.87894700	-1.57922800
S	-4.95378800	0.19701700	-2.75150100
O	-2.78336200	5.86266000	2.49660400
O	-3.48900100	4.33368100	3.82388400
O	3.24689700	-3.90658300	4.32154100
O	2.67530800	-5.50717400	3.01413900
N	-2.83346600	4.72066000	2.88601000
N	2.67687000	-4.34766900	3.35280900
C	0.26862900	0.79030200	0.08786500
C	-0.51720700	1.82829400	0.78726000
C	-0.53891400	3.17289100	0.37386500
H	0.00104200	3.48044500	-0.52155600
C	-1.28999300	4.12231000	1.05657600
H	-1.32214800	5.16385400	0.74094100
C	-2.03332800	3.71987300	2.15935500
C	-2.05934300	2.39619900	2.58744700
H	-2.66419600	2.12570800	3.45134900
C	-1.30725400	1.45868600	1.89441900
H	-1.32782200	0.41489300	2.21239400
C	-0.24517600	-0.61395800	0.12616700
C	0.49653100	-1.60042200	0.93830600
C	1.20106100	-1.16105400	2.07674700
H	1.18911300	-0.10092500	2.33600500
C	1.90772000	-2.05126300	2.87298100
H	2.44549600	-1.72707700	3.76244800
C	1.92439200	-3.39624500	2.51694200
C	1.26835500	-3.86709500	1.38586500
H	1.33429800	-4.92370300	1.13128100
C	0.56172900	-2.96478000	0.60007700
H	0.09146400	-3.32364000	-0.31584600
C	1.45873500	1.02032500	-0.53710600
C	3.74350500	0.56945600	-1.75626800
C	3.79359200	1.86626300	-1.38616600
C	6.11097000	2.58135500	-0.14486400
H	7.00642700	3.21439100	-0.18233000
H	6.40597000	1.52502100	-0.12139400
H	5.51681400	2.83798600	0.74046900
C	4.52963200	-1.95640900	-2.57646700
H	3.61924900	-2.09058100	-3.17461400
H	4.37847500	-2.32665700	-1.55469500
H	5.34825100	-2.51579400	-3.04551400
C	-1.40778400	-0.87988300	-0.53485200
C	-3.66474000	-0.57295500	-1.83361800
C	-3.72572300	-1.82555600	-1.33609000
C	-4.77164700	-4.21551000	-0.40227000

H	-4.68281800	-3.83515100	0.62290800
H	-3.87388100	-4.78072700	-0.68347200
H	-5.64179500	-4.88032100	-0.46587000
C	-5.84020900	0.99395300	-1.37381900
H	-5.16718900	1.66760300	-0.82936600
H	-6.25149900	0.23100000	-0.70165700
H	-6.65758800	1.57350200	-1.82084000

DTF **7**: (*E* = -2170.523492 Hartree, dipole moment = 1.871593 Debye)

C	-2.76982500	-0.54255700	-0.17128500
C	-2.21705000	0.65701900	0.10086800
S	-0.46118800	0.77603300	0.00414400
S	-1.67451800	-1.84639100	-0.60475400
C	-0.17199000	-0.93856700	-0.34322400
C	1.02756900	-1.55392800	-0.38922500
H	1.00171800	-2.63744600	-0.54011800
C	2.36416300	-0.97795900	-0.22220100
C	4.99138600	-0.00055900	0.17031500
C	2.67737200	0.37176000	-0.42786700
C	3.41863600	-1.83342700	0.15991200
C	4.70309200	-1.36116500	0.35734700
C	3.96975200	0.86298600	-0.23291500
H	1.91866800	1.06701900	-0.78767900
H	3.21090100	-2.89491100	0.31098800
H	5.51512200	-2.02287500	0.65962200
H	4.16481200	1.91949900	-0.41044500
S	-3.08863600	2.12859300	0.54104900
S	-4.49872900	-0.91110300	-0.15546900
C	-4.76650600	-0.95143900	1.64345000
H	-4.12102800	-1.71033400	2.10139100
H	-5.81898300	-1.22358100	1.79265900
H	-4.57291000	0.04024500	2.07006000
C	-3.83714700	2.53087300	-1.06731100
H	-3.05388900	2.65818100	-1.82394600
H	-4.37178700	3.47895700	-0.92784800
H	-4.54281900	1.74382100	-1.35889700
O	6.26951900	0.37798900	0.39004800
C	6.60325000	1.72814900	0.21079600
H	6.43272500	2.05232900	-0.82942000
H	7.66907400	1.82355800	0.44529300
H	6.02516200	2.38040000	0.88647500

TTFV **8**: (*E* = -4339.876518 Hartree, dipole moment = 4.987881 Debye)

S	1.48666300	-0.33862900	1.18759900

S	0.48951700	-3.00851800	0.38936400
S	4.24450600	-1.38015900	1.88644500
S	3.16774800	-4.34967800	1.01917400
S	1.02955300	0.72189300	-2.00281800
S	0.10641500	3.27832100	-0.91863400
S	3.83580200	1.66866200	-2.54918900
S	2.73599900	4.69004900	-1.42908800
O	-5.25166900	-3.50505300	-2.37094500
O	-4.98015900	3.26306900	3.01906600
C	-0.91121800	-0.67083000	-0.11917400
C	0.17931600	-1.25907500	0.43098800
C	2.61574100	-1.68960300	1.29433100
C	2.16244900	-2.90688400	0.93068600
C	4.00793700	-1.81781700	3.63922400
H	4.97166100	-1.65361600	4.13761900
H	3.72296200	-2.87407900	3.72498100
H	3.24439600	-1.17309300	4.09070200
C	2.00587500	-5.64291600	0.50707000
H	2.58295800	-6.57520600	0.53646700
H	1.64826900	-5.47380600	-0.51642600
H	1.15982100	-5.72161300	1.20120300
C	-2.04885700	-1.41884300	-0.70242900
C	-2.57520600	-2.58376900	-0.11727800
H	-2.16148000	-2.95319800	0.82330600
C	-3.63985000	-3.25917800	-0.69403400
H	-4.05694600	-4.15871800	-0.24072300
C	-4.22214000	-2.78384700	-1.87677100
C	-3.72806600	-1.61204700	-2.46142300
H	-4.16597600	-1.21099700	-3.37412600
C	-2.65946900	-0.94276400	-1.86865100
H	-2.28163100	-0.02778900	-2.33073200
C	-5.87254100	-3.06039000	-3.54760100
H	-5.16390300	-3.02993600	-4.39187700
H	-6.31536900	-2.05897600	-3.41739700
H	-6.66892700	-3.77772000	-3.77401300
C	-0.98974700	0.82229400	-0.14756400
C	-0.10779100	1.51752200	-0.90696600
C	2.21989300	2.02543400	-1.95467200
C	1.79250600	3.21073900	-1.46884100
C	4.30071300	0.36563700	-1.36172200
H	4.30339200	0.76417200	-0.33879700
H	5.31490000	0.05024700	-1.63761400
H	3.61690800	-0.49139900	-1.42638800
C	2.63175600	5.10163900	0.34006500
H	3.19719900	6.03348800	0.46550900
H	3.09024300	4.30914400	0.94388800
H	1.59214300	5.26115900	0.65067000

C	-2.04210100	1.45823700	0.67418300
C	-2.72754300	2.61503200	0.26331900
H	-2.52117700	3.05012100	-0.71669400
C	-3.69877200	3.19637300	1.06367400
H	-4.23850600	4.08895300	0.74672800
C	-4.02424300	2.63135600	2.30390400
C	-3.36965800	1.46591200	2.72040900
H	-3.60845200	0.99740400	3.67390700
C	-2.39826200	0.89137600	1.90397300
H	-1.89223500	-0.01817200	2.23522300
C	-5.34770500	2.72639300	4.26149000
H	-6.12543900	3.38097800	4.66984100
H	-4.49444100	2.70140500	4.95960800
H	-5.75310200	1.70617900	4.15740300