BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Synthesis and properties of tetrathiafulvalenes bearing 6-aryl-1,4-dithiafulvenes

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Synthetic procedures, theoretical chemical and electrochemical details, and copies of NMR spectra

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General comments

Unless otherwise noted, all manipulations were performed under an argon atmosphere and all reagents were purchased from commercial suppliers and used without further purification. Toluene was distilled by standard methods. The products were isolated by silica gel (KANTO KAGAKU Ltd., silica gel 60N 100–210 μm) or alumina gel (Merck Ltd., alumina 90, activated, neutral, activity I, 63–200 μm) column chromatography. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Biospin AVANCE 400 spectrometer equipped with a CryoProbe (400 MHz for ^{1}H, and 100 MHz for ^{13}C) using $CDCl_3$ or C_6D_6/CS_2 as solvents. The chemical shifts were referenced to tetramethylsilane for ^{1}H and ^{13}C NMR or to the solvent resonances for ^{13}C NMR as internal standards ($CDCl_3$: 77.0 ppm, C_6D_6: 128.0 ppm). Mass spectra were recorded on a JEOL JMS-S3000. Melting points were determined with a Yanaco MP-500D. Cyclic voltammetry (CV) was recorded on an ALS/chi 617B electrochemical analyzer. The CV cell consisted of a Pt working electrode, a Pt wire counter electrode, and $Ag/AgNO_3$ as the reference electrode. The measurements were carried out in benzonitrile with 0.1 M *n*-$Bu_4N^+PF_6^-$ as a supporting electrolyte, with a scan rate 50 mV/s at 25 °C. All redox potentials were measured against Ag/Ag^+ and converted to vs Fc/Fc^+.

Preparation of compounds 1–4, 6, 7, 9, 10, 12, 13, and 21

Typical procedure for the synthesis of 1, 2, and 4: $Pd(OAc)_2$ (6.8 mg, 0.0303 mmol), P*t*-$Bu_3 \cdot HBF_4$ (26.3 mg, 0.0906 mmol), and Cs_2CO_3 (196.1 mg, 0.602 mmol) were placed in a 30-mL reaction flask under an argon atmosphere. 1,4-Dioxane (2 mL) was added and the mixture was stirred for 10 min at 50 °C, and then, compound **4a** (182.3 mg, 0.502 mmol), and TTF (20.2 mg, 0.0988 mmol) were added. The mixture was heated at 110 °C for 36 h. The organic compounds were extracted with dichloromethane three times. The combined organic layer was washed with H_2O, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel chromatography with a mixture of dichlorometane/carbon disulfide 2:3 as the eluent to yield **1a** as orange powder (61.3 mg, 46%).

1a: Orange powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42 (s 12H), 2.43 (s 12H), 6.41 (s, 4H), 7.07 (d, *J* = 8.0 Hz, 8H), 7.21 (d, *J* = 8.0 Hz, 8H); ^{13}C NMR (C_6D_6-CS_2, 100 MHz) δ19.2, 19.3, 114.3, 125.1, 127.9, 128.3, 129.1, 129.5, 130.3, 131.3, 134.3, 136.4; Mp 112−113 °C (decomposed); HRMS (MALDI-TOF): m/z calcd for $C_{54}H_{44}S_{20}$: 1331.7857; found: 1331.7732.

1b: Red brown powder; ^{1}H NMR (C_6D_6-CS_2, 400 MHz) δ 1.84 (s 12H), 1.87 (s 12H), 6.18 (s, 4H), 6.95 (d, *J* = 8.0 Hz, 8H), 7.08 (d, *J* = 8.0 Hz, 8H); ^{13}C NMR (C_6D_6-CS_2, 100 MHz) δ 13.0, 13.8, 111.5, 118.4, 120.3, 121.5, 121.9, 126.5, 126.8, 127.0, 129.0, 129.3, 129.4, 136.0, 137.0; Mp 144−145 °C (decomposed); HRMS (MALDI-TOF): m/z calcd for $C_{54}H_{44}S_{12}$: 1076.0091 found: 1076.0004.

2a: Red powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s 6H), 2.43 (s 6H), 6.40 (s, 2H), 7.06 (d, *J* = 8.4 Hz, 4H), 7.10-7.11 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 4H), 7.24-7.25 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.9, 20.0, 108.5, 111.9, 114.7, 122.8, 125.4, 126.8, 127.8, 128.6, 129.4, 130.2, 130.7, 134.6, 137.2, 138.0; Mp 104−105 °C; HRMS (MALDI-TOF): m/z calcd for $C_{34}H_{26}S_{12}$: 817.8683; found: 817.8531.

2b: Red powder; ^{1}H NMR (C_6D_6-CS_2, 400 MHz) δ 1.82 (s 6H), 1.84 (s 6H), 6.18 (s, 2H), 6.92-6.96 (m, 6H), 7.03-708 (m, 6H); ^{13}C NMR (C_6D_6-CS_2, 100 MHz) δ 13.0, 13.8, 107.2, 111.4, 111.7, 121.5, 121.9, 122.0, 125.9, 126.8, 128.6, 129.1, 129.4, 136.2, 137.1, 137.8; Mp 204−205 °C; HRMS (MALDI-TOF): m/z calcd for $C_{34}H_{26}S_8$: 689.9800; found: 689.9817.

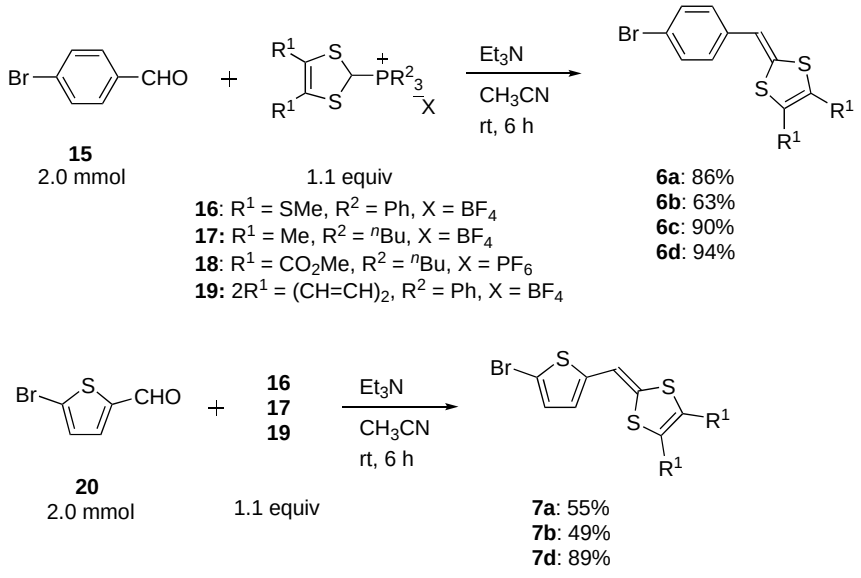
4: Red brown powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.15 (s 12H), 2.21 (s, 12H), 2.27 (s, 12H), 2.31 (s, 12H), 5.79 (s, 4H), 7.10 (d, *J* = 8.0 Hz, 8H), 7.18 (d, *J* = 8.0 Hz, 8H); Mp 157−158 °C (decomposed).

Typical procedure for the synthesis of 3: Compound **10** (15.1 mg, ca. 0.0233 mmol), **11** (43.0 mg, 0.186 mmol), dry toluene (0.9 mL), and $P(OEt)_3$ (0.9 mL) were placed in a 50-mL reaction flask under an argon atmosphere. The mixture was heated at reflux for 12 h. After removal of the solvent and excess $P(OEt)_3$, the residue was purified by silica gel chromatography with dichloromethane as the eluent. The product **3** was obtained by suction filtration with methanol and hexane in 29% yield from TTF (16.7 mg).

3: Brown powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42 (s 12H), 2.44 (s 12H), 6.60 (s, 4H), 6.74 (d, *J* = 4.0 Hz, 4H), 7.02 (d, *J* = 4.0 Hz, 4H); Mp 275–276 ºC. This compound is too insoluble to record a ^{13}C NMR spectrum.

Synthesis of 4 (Scheme 2b): Compound **13** (24.3 mg, 0.017 mmol), **11** (61.2 mg, 0.270 mmol), dry toluene (0.7 mL), and $P(OEt)_3$ (0.7 mL) were placed in a 50-mL reaction flask under an argon atmosphere. The mixture was heated at reflux for 12 h. After removal of the solvent and excess $P(OEt)_3$ in vacuo, the residue was precipitated from dichloromethane/hexane and washed with methanol, hexane, and acetone to give **4** in 44% yield from **1a**.

Compounds 6 and 7 were synthesized as outlined below



Typical procedure for the synthesis of 6 and 7: To a mixture of **15** (370.3 mg, 2.00 mmol) and **16** (1.151 g, 2.11 mmol) in dry acetonitrile (10 mL), triethylamine (2.5 mL) was added at 0 °C under an argon atmosphere, and the mixture was stirred for 6 h at room temperature. After removal of the solvent and excess triethylamine, the residue was purified by suction filtration with cold methanol. The product **6a** was obtained in 86% yield (627.9 mg, 1.73 mmol).

6a: Yellow powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42 (s 3H), 2.44 (s 3H), 6.41 (s 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.9, 19.0, 113.4, 119.3, 124.2, 127.0, 128.2, 131.6, 133.3, 135.1; Mp 91–92 °C; HRMS (MALDI-TOF): m/z calcd for $C_{12}H_{11}BrS_4$: 361.8927; found: 361.8902.

6b: Yellow powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.95 (s 3H), 1.97 (s 3H), 6.34 (s 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.9, 13.6, 110.1, 118.2, 121.1, 121.2, 127.9, 131.4, 135.5 135.9; Mp 91–92 °C; HRMS (MALDI-TOF): m/z calcd for $C_{12}H_{11}BrS_2$: 297.9486; found: 297.9540.

6c: Orange powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.85 (s 3H), 3.87 (s 3H), 6.39 (s 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 53.3, 53.4, 114.2, 120.0, 128.2, 129.0, 131.4, 131.6, 131.7 134.6, 159.6, 160.1; Mp 112–113 °C; HRMS (MALDI-TOF): m/z calcd for $C_{14}H_{11}BrO_4S_2$: 385.9282; found: 385.9268.

6d: White powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.49 (s 1H), 7.10-7.16 (m 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.24-7.28 (m 2H), 7.48 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 106.0, 113.4, 119.6, 121.2, 122.0, 125.9, 126.3, 128.5, 131.7 134.0, 134.8, 135.6; Mp 182–183 °C; HRMS (MALDI-TOF): m/z calcd for $C_{14}H_9BrS_2$: 319.9329; found: 319.9322.

7a: Yellow powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s 3H), 2.45 (s 3H), 6.56 (s 1H), 6.60 (d, *J* = 4.0 Hz, 2H), 6.97 (d, *J* = 4.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.9, 19.1, 107.6, 110.7, 123.7, 125.1, 127.9, 130.1, 131.6 142.0; Mp 41–42 °C (decomposed).

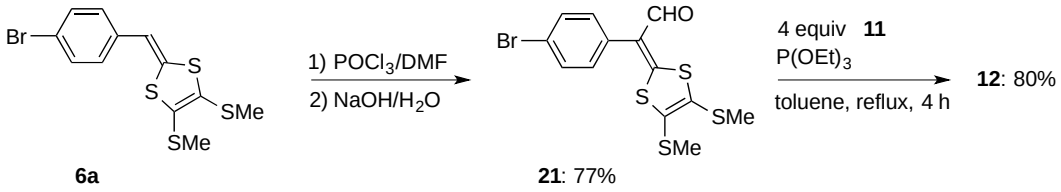
7b: White powder; ^{1}H NMR (C_6D_6, 400 MHz) δ 1.93 (s 3H), 1.97 (s 3H), 6.33 (s 1H), 6.43 (d, *J* = 3.6 Hz, 2H), 6.80 (d, *J* = 3.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.9, 13.6,110.1, 118.2, 121.1, 121.2, 127.9, 131.4, 135.5 135.9; Mp 61–62 °C (decomposed).

7d: White powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.64 (s 1H), 6.68 (d , *J* = 4.0 Hz, 1H), 6.99 (d , *J* = 4.0 Hz, 1H), 7.12-7.17 (m, 2H), 7.23-7.25 (m, 1H) , 7.28-7.32 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 107.4, 110.8, 121.2, 122.0, 124.0, 125.7, 126.2, 130.0, 132.0, 135.2, 136.2, 142.2; Mp 68–69 °C (decomposed).

Synthesis of 9: $Pd(OAc)_2$ (25.5 mg, 0.113 mmol), P*t*-Bu_3·HBF_4 (98.5 mg, 0.340 mmol), and Cs_2CO_3 (737.7 mg, 2.263 mmol) were placed in a 30-mL reaction flask under argon. 1,4-Dioxane (2mL) was added and the mixture was stirred for 10 min at 50 °C. A solution of compound **8** (516.2 mg, 1.947 mmol) in 1,4-dioxane (2 mL) and TTF (38.4 mg, 0.188 mmol) were added. The mixture was heated at 110 °C for 72 h. The obtained solid was washed with dichloromethane and methanol to yield **9** as dark brown oil. Being identified by ^{1}H NMR, this compound was used for the next step without further purification.

Synthesis of 10: To a mixture of **9** (300.8 mg) in DMF (10 mL) and distilled water (10 mL) PTSA·H_2O (244.0 mg, 0.602 mmol) was added at room temperature, and the mixture was stirred for 1 h. The organic compounds were extracted with dichloromethane three times. The combined organic layer was washed with H_2O, sat. $NaHCO_3$ aq., and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The obtained solid was washed with methanol and hexane to yield **10** as black solid. Being identified by ^{1}H NMR, this compound was used for the next step without further purification.

Compound 12 was synthesized as outlined below



Synthesis of 12: Compound **21** (196.1 mg, 0.501 mmol), **11** (456.0 mg, 2.01 mmol), dry toluene (2.4 mL), and $P(OEt)_3$ (2.4 mL) were placed in a 50-mL reaction flask under an argon atmosphere. The mixture was heated at reflux for 4 h. After removal of the solvent and excess $P(OEt)_3$ in vacuo, the residue was precipitated from dichrolomethane/hexane and washed with methanol to give **12** in 80% yield.

Yellow powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.21 (s 3H), 2.32 (s 3H), 2.37 (s 3H), 2.43 (s, 3H), 5.95 (s, 1H) , 7.15 (d , *J* = 8.4 Hz, 2H) 7.52 (d , *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.8, 18.8 (2C), 18.9, 111.7, 122.1, 123.2, 126.0, 126.2, 126.5, 127.0, 131.1, 131.2, 132.3, 132.7, 135.5; Mp 133–134 ºC; HRMS (MALDI-TOF): m/z calcd for $C_{18}H_{17}BrS_8$: 567.8279; found: 567.8280.

Synthesis of 13: To a mixture of **1a** (33.0 mg, 0.025 mmol) in DMF (10 mL) $POCl_3$ (74 μL, 0.79 mmol) was added at 0 °C, and the mixture was warmed to room temperature and stirred for 2 h. Afterwards, 1 M NaOH aq. (1.2 mL) was added at 0 °C and the mixture was warmed to room temperature and stirred for 30 min. The mixture was extracted with dichloromethane. The combined organic layers were washed with H_2O and brine three times, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The product was obtained by suction filtration with dichloromethane and hexane in 44% yield from **1a**. Being identified by ^{1}H NMR, this compound was used for the next step without further purification.

Synthesis of 21: To compound **6a** (1.150 g, 3.16 mmol) in DMF (20 mL) $POCl_3$ (1.2 mL, 12.7 mmol) was added at 0 °C and the mixture was warmed to room temperature and stirred for 2 h. After the reaction, 1 M NaOH aq. (38 mL) was added at 0 °C and the mixture was warmed to room temperature, and stirred for 30 min. The mixture was extracted with dichlorometane. The combined organic layers were washed with H_2O and brine three times,

dried over anhydrous Na_2SO_4, and concentrated in vacuo. The product was obtained by suction filtration with dichlorometane and hexane in 77% yield.

21: Yellow powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s 3H), 2.56 (s 3H), 7.27 (d , *J* = 8.0 Hz, 2H), 7.60 (d , *J* = 8.0 Hz, 2H), 9.31 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.8, 19.2, 121.3, 122.3, 125.8, 130.2, 132.5, 133.6, 135.5, 160.8, 183.2; Mp 158−159 ^{o}C; HRMS (MALDI-TOF): m/z calcd for $C_{13}H_{11}BrOS_4$: 389.8876; found: 389.8856.

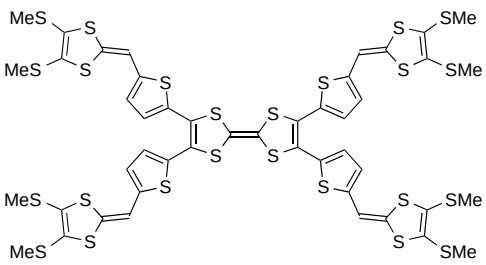
Theoretical calculations

The theoretical calculations of the compounds **1a**, **3a**, and **4**, and their pristine compounds were carried out based on density functional theory (DFT) using the spin-restricted B3LYP/6-31G(d,p) level of theory. The compounds can adopt a number of conformations. The calculations of 14 conformations for the pristine compounds of **1** and **4** and 42 conformations for the pristine compound of **3** were performed and the predominant conformations were determined. The calculations of 14 conformations of **1a** based on the conformations of pristine **1** were also carried out and we confirmed that a lowest-energy conformation was obtained by the same model of pristine **1**. Since the calculations of **3a** and **4** were expected to require high computational costs, several conformations of **3a** and **4**, based on the lower-energy conformation of the pristine compound, were calculated. Frequency calculations were performed to confirm that these structures were indeed local minima. The Gaussian 16 software [1] was used for all calculations.

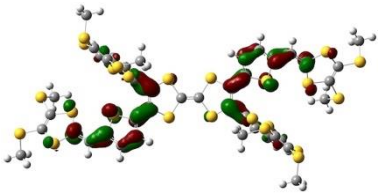
References

[1] Gaussian 16, *Revision C.01*, Gaussian, Inc.: Wallingford CT, 2019.

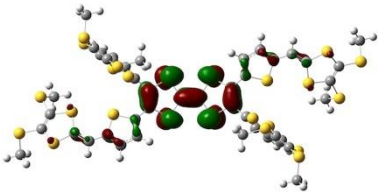
a) **3a**



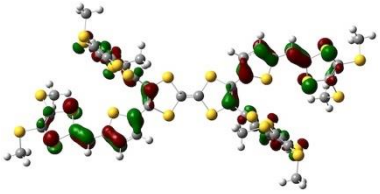
LUMO: –1.75 eV



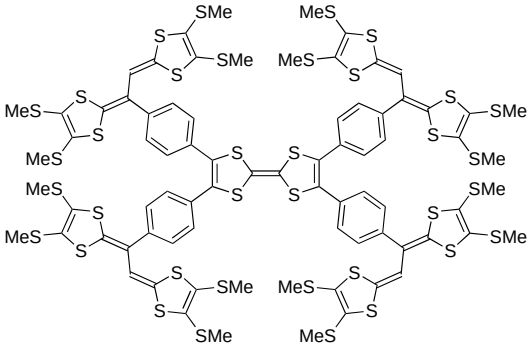
HOMO: –4.49 eV



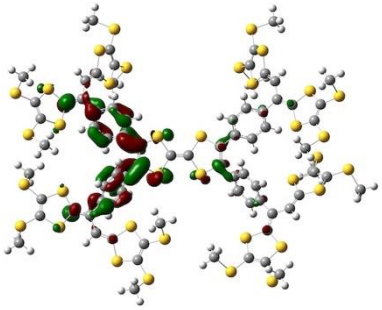
HOMO–1: –4.87 eV



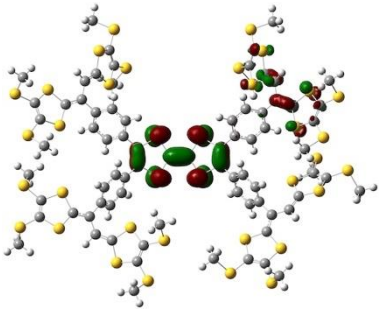
b) **4**



LUMO: –1.72 eV



HOMO: –4.49 eV



HOMO–1: –4.62 eV

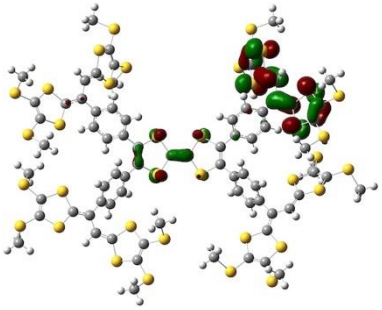
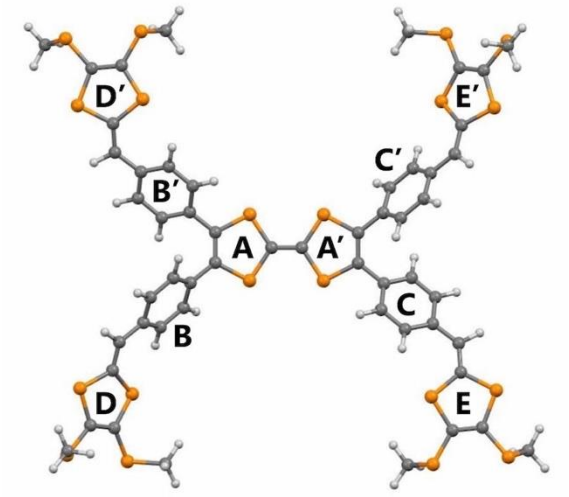
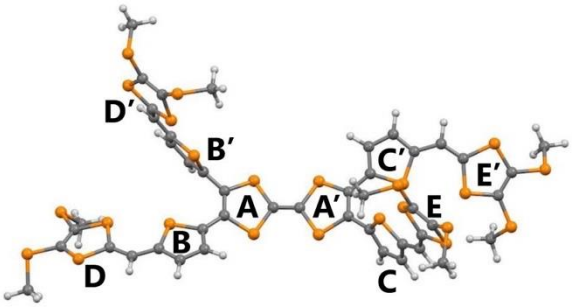


Figure S1: a) Molecular orbitals of **3a** and b) **4**.

Dihedral angles

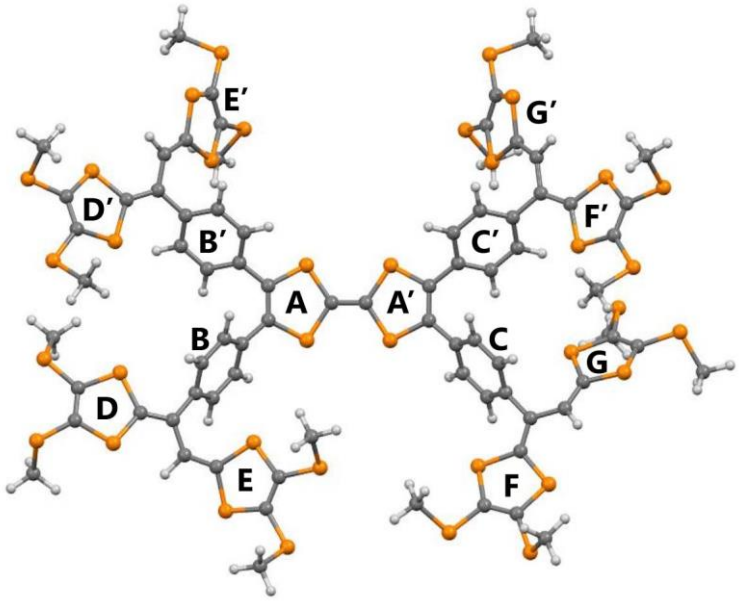
Table S1: Dihedral angles [°] of **1a**, **3a**, and **4**





1a		**3a**	
A–A’	158.0	A–A’	153.0
A–B	49.8	A–B	20.2
A–B’	137.7	A–B’	90.8
A’–C	137.7	A’–C	104.5
A’–C’	49.9	A’–C’	26.6
B–D	28.6	B–D	12.7
B’–D’	28.5	B’–D’	12.4
C–E	28.5	C–E	12.4
C’–E’	28.6	C’–E’	12.6
A–D	153.7	A–D	152.7
A–D’	18.1	A–D’	77.7
A’–E	18.1	A’–E	84.9
A’–E’	153.6	A’–E’	140.8

Table S1: *Continued*



4

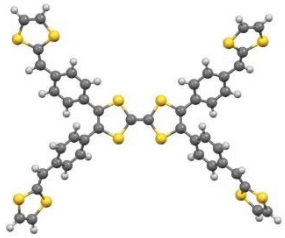
A'–A	153.3		
A–B	49.4	A–B'	138.6
A'–C	49.8	A'–C'	141.2
B–D	112.7	B'–D'	116.9
C–F	110.3	C'–F'	113.0
D–E	32.5	D'–E'	33.8
F–G	29.1	F'–G'	30.8
A–D	18.8	A–D'	21.7
A'–F	23.5	A'–F'	28.5
B–E	95.9	B'–E'	100.6
C–G	95.9	C'–G'	98.6
A–E	144.8	A–E'	134.3
A'–G	130.0	A'–G'	129.5

Optimized geometry

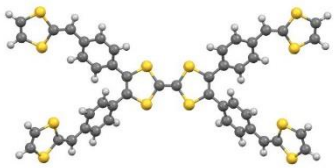
Pristine compound of **1**

Energy data for pristine compound of **1**

	E [hartree]	ZP*E* [hartree]	*E* + ZP*E* [hartree]	Δ*E* [kcal/mol]	Δ(*E* + ZP*E*) [kcal/mol]
model-1	-6547.910164	0.596811	-6547.313353	0.060868	0.062123
model-2	-6547.910070	0.596828	-6547.313242	0.119854	0.131777
model-3	-6547.910116	0.596827	-6547.313289	0.090989	0.102284
model-4	-6547.910095	0.596798	-6547.313297	0.104167	0.097264
model-5	-6547.910174	0.596847	-6547.313327	0.054593	0.078439
model-6	-6547.910179	0.596839	-6547.313340	0.051456	0.070281
model-7	-6547.910154	0.596814	-6547.313340	0.067144	0.070281
model-8	-6547.910216	0.596764	**-6547.313452**	0.028238	**0**
model-9	-6547.910167	0.596848	-6547.313319	0.058986	0.083459
model-10	-6547.910214	0.596840	-6547.313374	0.029493	0.048946
model-11	-6547.910195	0.596802	-6547.313393	0.041416	0.037023
model-12	-6547.910255	0.596840	-6547.313415	0.003765	0.023218
model-13	**-6547.910261**	0.596832	-6547.313429	**0**	0.014433
model-14	-6547.910239	0.596800	-6547.313439	0.013805	0.008158

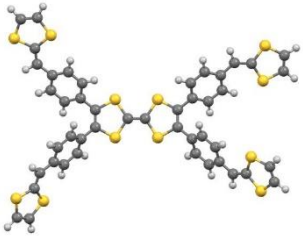


model-1
Δ(*E* + ZP*E*) = 0.062123 kcal/mol

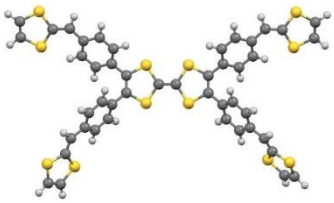


model-2
Δ(*E* + ZP*E*) = 0.131777 kcal/mol

model-3
Δ(*E* + ZP*E*) = 0.102284 kcal/mol

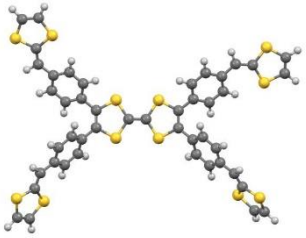


model-4
Δ(*E* + ZP*E*) = 0.097264 kcal/mol

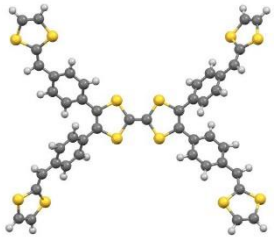


model-5
Δ(*E* + ZP*E*) = 0.078439 kcal/mol

model-6
Δ(*E* + ZP*E*) = 0.070281 kcal/mol

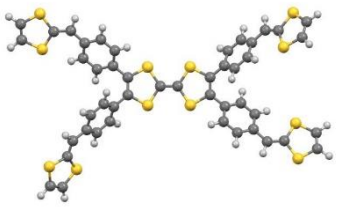


model-7
Δ(*E* + ZP*E*) = 0.070281 kcal/mol

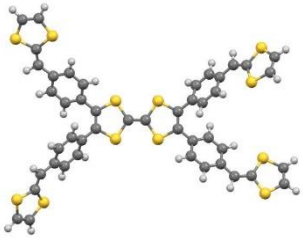


model-8
Δ(*E* + ZP*E*) = 0 kcal/mol

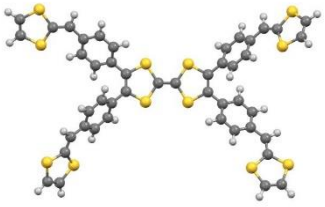
model-9
Δ(*E* + ZP*E*) = 0.083459 kcal/mol



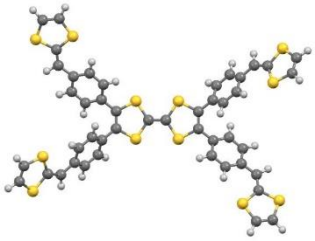
model-10
Δ(*E* + ZP*E*) = 0.048946 kcal/mol



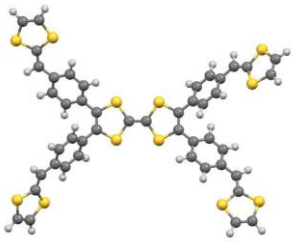
model-11
Δ(*E* + ZP*E*) = 0.037023 kcal/mol



model-12
Δ(*E* + ZP*E*) = 0.023218 kcal/mol



model-13
Δ(*E* + ZP*E*) = 0.014433 kcal/mol

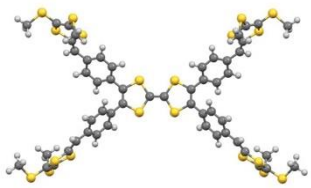


model-14
Δ(*E* + ZP*E*) = 0.008158 kcal/mol

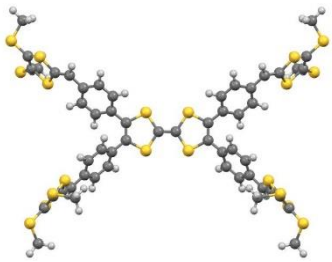
Compound **1a**

Energy data for compound **1a**

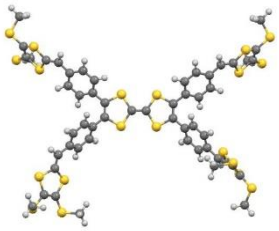
	E [hartree]	ZP*E* [hartree]	*E* + ZP*E* [hartree]	Δ*E* [kcal/mol]	Δ(*E* + ZP*E*) [kcal/mol]
model-1	-10047.929607	0.826758	-10047.102849	0.331325	0.328187
model-2	-10047.929485	0.826703	-10047.102782	0.407881	0.370231
model-3	-10047.929668	0.826734	-10047.102934	0.293047	0.274849
model-4	-10047.929602	0.826712	-10047.102890	0.334463	0.302460
model-5	-10047.929803	0.826737	-10047.103066	0.208333	0.192018
model-6	-10047.929951	0.826762	-10047.103189	0.115462	0.114834
model-7	-10047.929756	0.826761	-10047.102995	0.237826	0.236571
model-8	**-10047.930135**	0.826763	**-10047.103372**	**0**	**0**
model-9	-10047.929555	0.826708	-10047.102847	0.284889	0.288654
model-10	-10047.929718	0.826719	-10047.102999	0.363956	0.329443
model-11	-10047.929870	0.826754	-10047.103116	0.261671	0.234061
model-12	-10047.929867	0.826762	-10047.103105	0.166290	0.160642
model-13	-10047.929881	0.826732	-10047.103149	0.168173	0.167545
model-14	-10047.930047	0.826764	-10047.103283	0.159387	0.139935



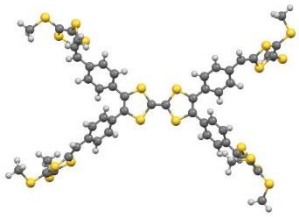
model-1
Δ(*E* + ZP*E*) = 0.328187 kcal/mol



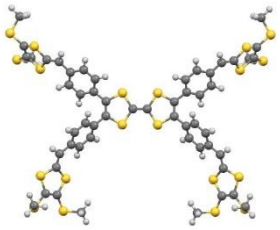
model-2
Δ(*E* + ZP*E*) = 0.370231 kcal/mol



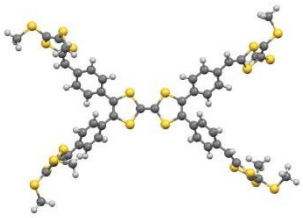
model-3
Δ(*E* + ZP*E*) = 0.274849 kcal/mol



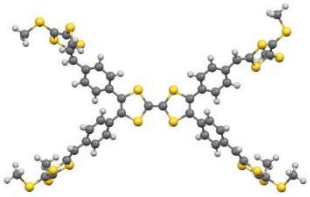
model-4
Δ(*E* + ZP*E*) = 0.302460 kcal/mol



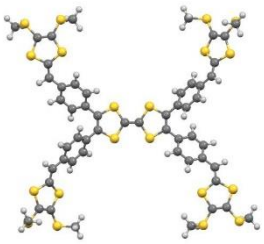
model-5
Δ(*E* + ZP*E*) = 0.192018 kcal/mol



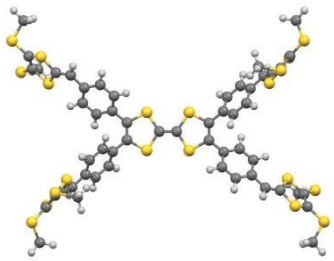
model-6
Δ(*E* + ZP*E*) = 0.114834 kcal/mol



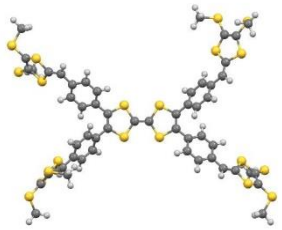
model-7
Δ(*E* + ZP*E*) = 0.236571 kcal/mol



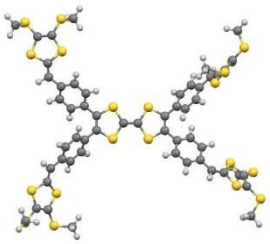
model-8
Δ(*E* + ZP*E*) = 0 kcal/mol



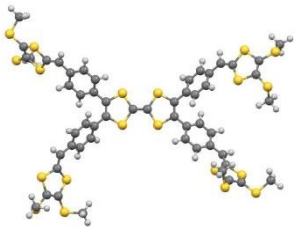
model-9
Δ(*E* + ZP*E*) = 0.288654 kcal/mol



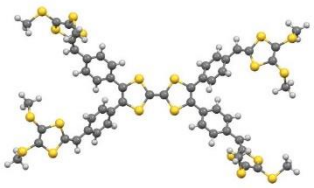
model-10
Δ(*E* + ZP*E*) = 0.329443 kcal/mol



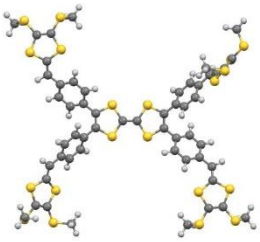
model-11
Δ(*E* + ZP*E*) = 0.234061 kcal/mol



model-12
Δ(*E* + ZP*E*) = 0.160642 kcal/mol



model-13
Δ(*E* + ZP*E*) = 0.167545 kcal/mol

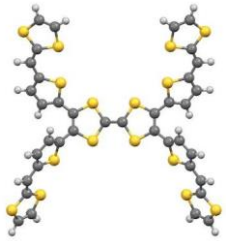


model-14
Δ(*E* + ZP*E*) = 0.139935 kcal/mol

Pristine compound of **3**

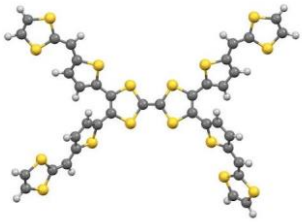
Energy data for pristine compound of **3**

	E [hartree]	ZP*E* [hartree]	*E* + ZP*E* [hartree]	Δ*E* [kcal/mol]	Δ(*E* + ZP*E*) [kcal/mol]
model-1	-7830.927826	0.461865	-7830.465961	0.338372	0.279386
model-2	-7830.925824	0.462149	-7830.463675	1.594665	1.713892
model-3	-7830.926346	0.462078	-7830.464268	1.266634	1.341308
model-4	-7830.926905	0.462016	-7830.464889	0.916333	0.952101
model-5	-7830.926839	0.462012	-7830.464827	0.957724	0.990982
model-6	-7830.926931	0.462019	-7830.464912	0.899736	0.937386
model-7	-7830.927355	0.461943	-7830.465412	0.633741	0.623701
model-8	-7830.928058	0.461865	-7830.466193	0.192645	0.133660
model-9	-7830.925844	0.462154	-7830.463690	1.581952	1.704316
model-10	-7830.926448	0.462092	-7830.464356	1.202936	1.286395
model-11	-7830.926950	0.462009	-7830.464941	0.887926	0.919301
model-12	-7830.926973	0.462011	-7830.464962	0.873493	0.906124
model-13	-7830.927056	0.462028	-7830.465028	0.821410	0.864708
model-14	-7830.927558	0.461945	-7830.465613	0.506400	0.497615
model-15	-7830.928220	0.461918	-7830.466302	0.090989	0.065261
model-16	-7830.926231	0.462186	-7830.464045	1.339105	1.481550
model-17	-7830.926752	0.462110	-7830.464642	1.012173	1.106927
model-18	-7830.927342	0.462051	-7830.465291	0.641942	0.699673
model-19	-7830.927143	0.462064	-7830.465079	0.766817	0.832705
model-20	-7830.927335	0.462075	-7830.465260	0.646335	0.719126
model-21	-7830.927917	0.462011	-7830.465906	0.281124	0.313755
model-22	-7830.928253	0.461962	-7830.466291	0.070281	0.072164
model-23	-7830.926518	0.462218	-7830.464300	1.159010	1.321535
model-24	-7830.926901	0.462154	-7830.464747	0.918674	1.041038
model-25	-7830.927395	0.462081	-7830.465314	0.608684	0.685240
model-26	-7830.927278	0.462105	-7830.465173	0.611822	0.701556
model-27	-7830.927480	0.462114	-7830.465366	0.555346	0.652610
model-28	-7830.927952	0.462044	-7830.465908	0.259161	0.312500
model-29	**-7830.928365**	0.461959	**-7830.466406**	**0**	**0**
model-30	-7830.926614	0.462215	-7830.464399	1.098769	1.259412
model-31	-7830.927204	0.462175	-7830.465029	0.728539	0.864081
model-32	-7830.927504	0.462089	-7830.465415	0.540286	0.621862
model-33	-7830.927586	0.462135	-7830.465451	0.488830	0.599272
model-34	-7830.927771	0.462139	-7830.465632	0.372741	0.485692
model-35	-7830.928066	0.462053	-7830.466013	0.187625	0.246611
model-36	-7830.928134	0.461924	-7830.466210	0.144955	0.122992
model-37	-7830.926193	0.462186	-7830.464007	1.362951	1.505395
model-38	-7830.926755	0.462115	-7830.464640	1.010290	1.108182
model-39	-7830.927247	0.462034	-7830.465213	0.701556	0.748619
model-40	-7830.927147	0.462056	-7830.465091	0.764307	0.825175
model-41	-7830.927325	0.462077	-7830.465248	0.652610	0.726656
model-42	-7830.927828	0.462001	-7830.465827	0.336973	0.363328

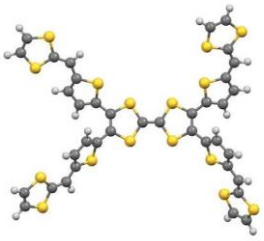


model-1
Δ(*E* + ZP*E*) = 0.279386 kcal/mol

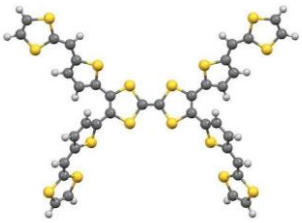
model-2
Δ(*E* + ZP*E*) = 1.713892 kcal/mol



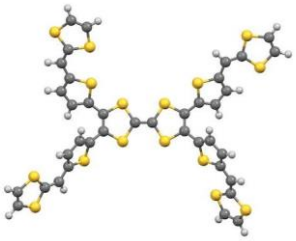
model-3
Δ(*E* + ZP*E*) = 1.341308 kcal/mol



model-4
Δ(*E* + ZP*E*) = 0.952101 kcal/mol

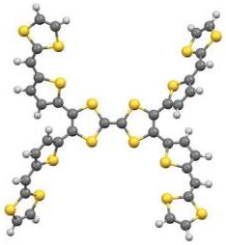


model-5
Δ(*E* + ZP*E*) = 0.990982 kcal/mol

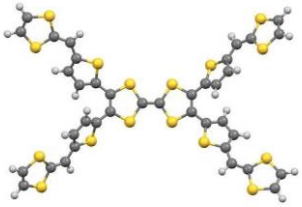


model-6
Δ(*E* + ZP*E*) = 0.937386 kcal/mol

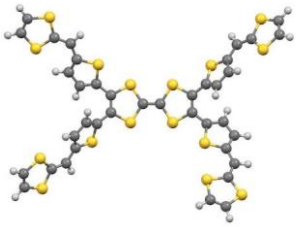
model-7
Δ(*E* + ZP*E*) = 0.623701 kcal/mol



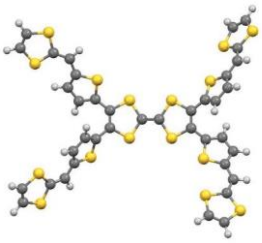
model-8
Δ(*E* + ZP*E*) = 0.133660 kcal/mol



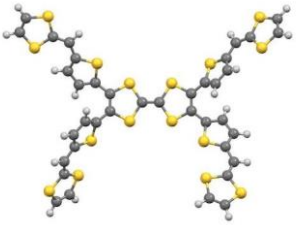
model-9
Δ(*E* + ZP*E*) = 1.704316 kcal/mol



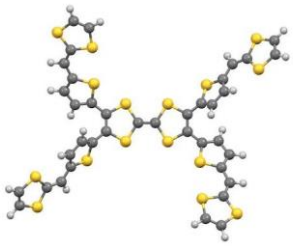
model-10
Δ(*E* + ZP*E*) = 1.286395 kcal/mol



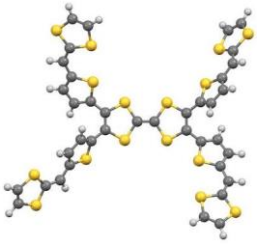
model-11
Δ(*E* + ZP*E*) = 0.919301 kcal/mol



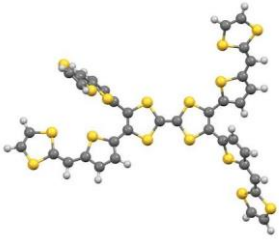
model-12
Δ(*E* + ZP*E*) = 0.906124 kcal/mol



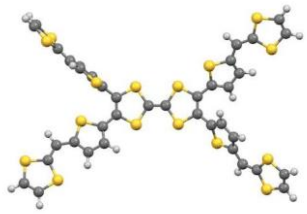
model-13
Δ(*E* + ZP*E*) = 0.864708 kcal/mol



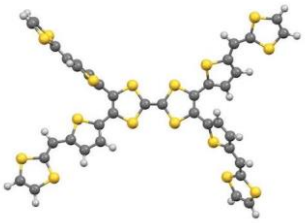
model-14
Δ(*E* + ZP*E*) = 0.497615 kcal/mol



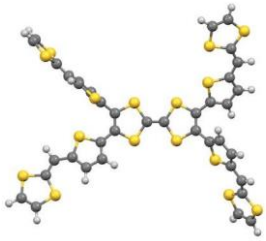
model-15
Δ(*E* + ZP*E*) = 0.065261 kcal/mol



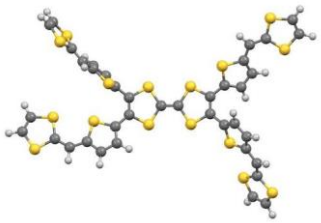
model-16
Δ(*E* + ZP*E*) = 1.481550 kcal/mol



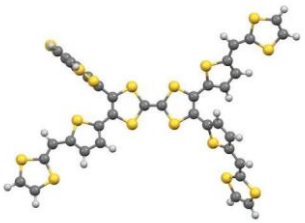
model-17
Δ(*E* + ZP*E*) = 1.106927 kcal/mol



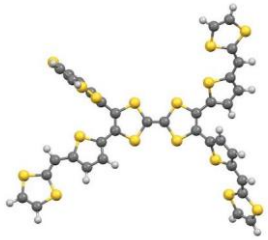
model-18
Δ(*E* + ZP*E*) = 0.699673 kcal/mol



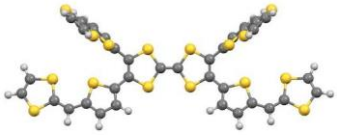
model-19
Δ(*E* + ZP*E*) = 0.832705 kcal/mol



model-20
Δ(*E* + ZP*E*) = 0.719126 kcal/mol

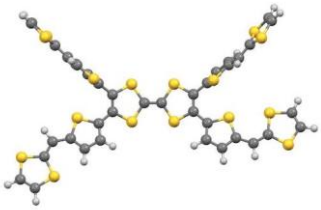


model-21
Δ(*E* + ZP*E*) = 0.313755 kcal/mol

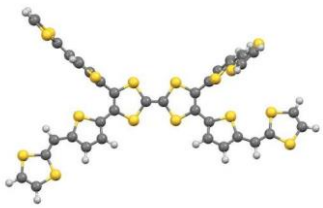


model-22
Δ(*E* + ZP*E*) = 0.072164 kcal/mol

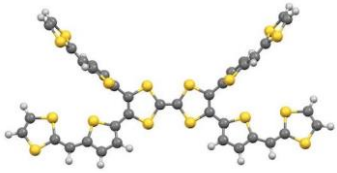
model-23
Δ(*E* + ZP*E*) = 1.321535 kcal/mol



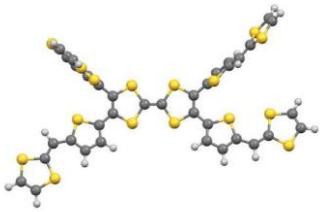
model-24
Δ(*E* + ZP*E*) = 1.041038 kcal/mol



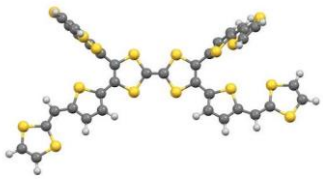
model-25
Δ(*E* + ZP*E*) = 0.685240 kcal/mol



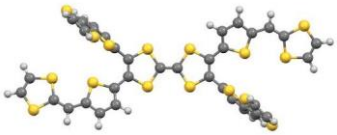
model-26
Δ(*E* + ZP*E*) = 0.701556 kcal/mol



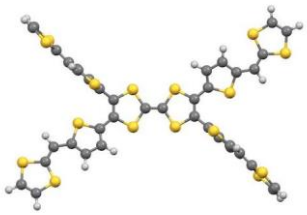
model-27
Δ(*E* + ZP*E*) = 0.652610 kcal/mol



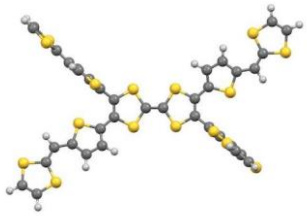
model-28
Δ(*E* + ZP*E*) = 0.312500 kcal/mol



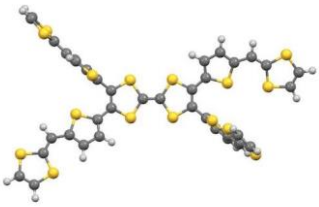
model-29
Δ(*E* + ZP*E*) = 0 kcal/mol



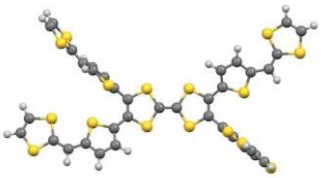
model-30
Δ(*E* + ZP*E*) = 1.259412 kcal/mol



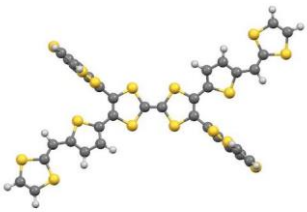
model-31
Δ(*E* + ZP*E*) = 0.864081 kcal/mol



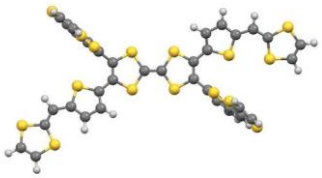
model-32
Δ(*E* + ZP*E*) = 0.621862 kcal/mol



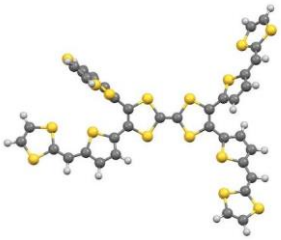
model-33
Δ(*E* + ZP*E*) = 0.599272 kcal/mol



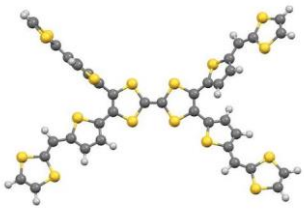
model-34
Δ(*E* + ZP*E*) = 0.485692 kcal/mol



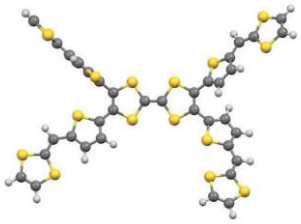
model-35
Δ(*E* + ZP*E*) = 0.246611 kcal/mol



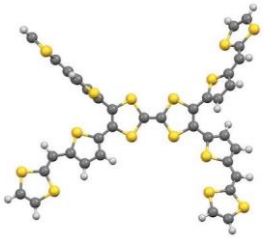
model-36
Δ(*E* + ZP*E*) = 0.122992 kcal/mol



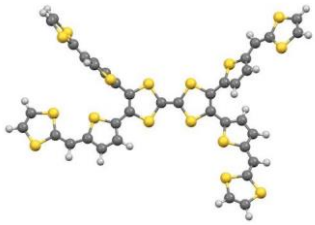
model-37
Δ(*E* + ZP*E*) = 1.505395 kcal/mol



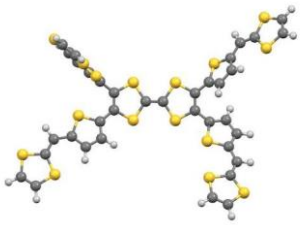
model-38
Δ(*E* + ZP*E*) = 1.108182 kcal/mol



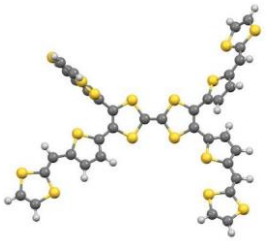
model-39
Δ(*E* + ZP*E*) = 0.748619 kcal/mol



model-40
Δ(*E* + ZP*E*) = 0.825175 kcal/mol



model-41
Δ(*E* + ZP*E*) = 0.726656 kcal/mol

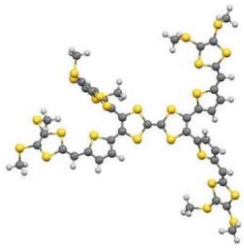


model-42
Δ(*E* + ZP*E*) = 0.008158 kcal/mol

Compound **3a**

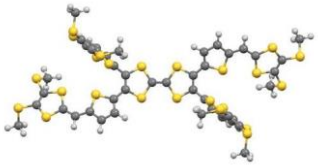
Energy data for compound **3a**

	E [hartree]	ZP*E* [hartree]	*E* + ZP*E* [hartree]	Δ*E* [kcal/mol]	Δ(*E* + ZP*E*) [kcal/mol]
model-15	-11330.947362	0.691799	-11330.255563	0.122992	0.080949
model-22	-11330.947418	0.691850	-11330.255568	0.087851	0.077811
model-29	**-11330.947558**	0.691866	**-11330.255692**	**0**	**0**



model-15
Δ(*E* + ZP*E*) = 0.080949 kcal/mol

model-22
Δ(*E* + ZP*E*) = 0.077811 kcal/mol

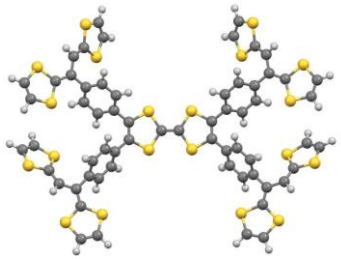


model-29
Δ(*E* + ZP*E*) = 0 kcal/mol

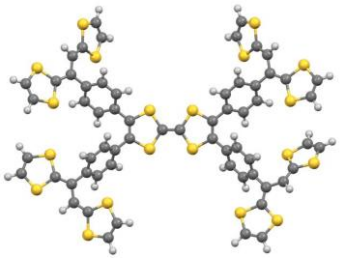
Pristine compound of **4**

Energy data for pristine compound of **4**

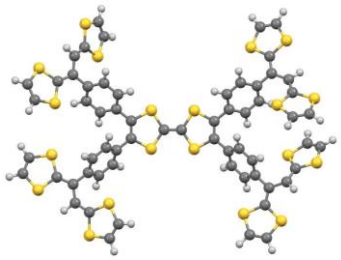
	E [hartree]	ZP*E* [hartree]	*E* + ZP*E* [hartree]	Δ*E* [kcal/mol]	Δ(*E* + ZP*E*) [kcal/mol]
model-1	-10347.811035	0.787141	-10347.023894	0.078439	0.086596
model-2	**-10347.811160**	0.787146	-10347.024014	**0**	0.011295
model-3	-10347.810675	0.787078	-10347.023597	0.304342	0.272967
model-4	-10347.810067	0.787022	-10347.023045	0.685868	0.619352
model-5	-10347.811154	0.787122	**-10347.024032**	0.003765	**0**
model-6	-10347.810643	0.787061	-10347.023582	0.324422	0.282379
model-7	-10347.811128	0.787106	-10347.024022	0.020080	0.006275
model-8	-10347.811079	0.787124	-10347.023955	0.050828	0.048318
model-9	-10347.810858	0.787093	-10347.023765	0.189508	0.167545
model-10	-10347.810333	0.787032	-10347.023301	0.518950	0.458709
model-11	-10347.810658	0.787053	-10347.023605	0.315010	0.267947
model-12	-10347.811041	0.787118	-10347.023923	0.074674	0.068399
model-13	-10347.810513	0.787038	-10347.023475	0.405999	0.349523
model-14	-10347.811096	0.787121	-10347.023975	0.040161	0.035768



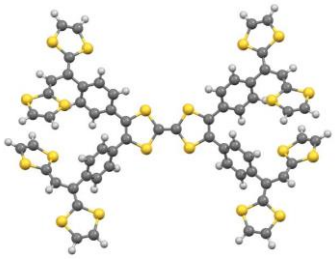
model-1
Δ(*E* + ZP*E*) = 0.086596 kcal/mol



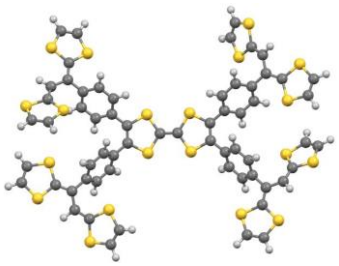
model-2
Δ(*E* + ZP*E*) = 0.011295 kcal/mol



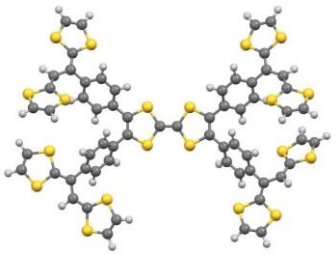
model-3
Δ(*E* + ZP*E*) = 0.272967 kcal/mol



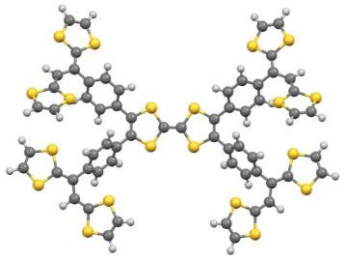
model-4
Δ(*E* + ZP*E*) = 0.619352 kcal/mol



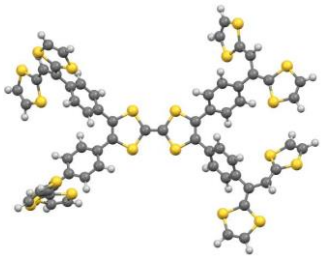
model-5
Δ(*E* + ZP*E*) = 0 kcal/mol



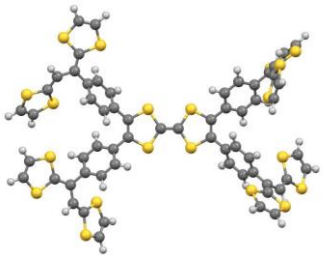
model-6
Δ(*E* + ZP*E*) = 0.282379 kcal/mol



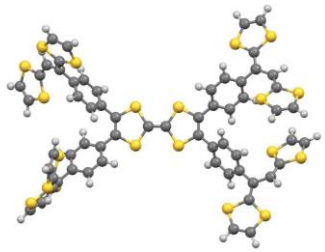
model-7
Δ(*E* + ZP*E*) = 0.006275 kcal/mol



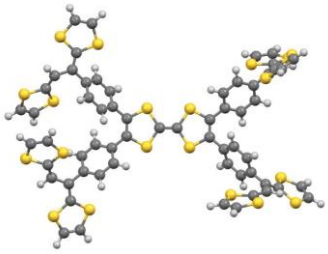
model-8
Δ(*E* + ZP*E*) = 0.048318 kcal/mol



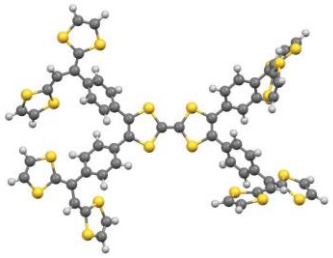
model-9
Δ(*E* + ZP*E*) = 0.167545 kcal/mol



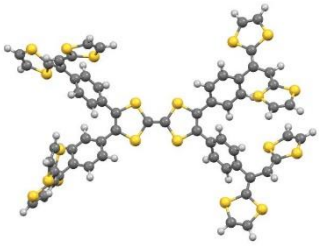
model-10
Δ(*E* + ZP*E*) = 0.458709 kcal/mol



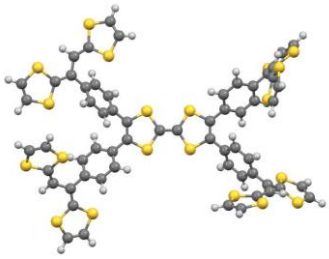
model-11
Δ(*E* + ZP*E*) = 0.267947 kcal/mol



model-12
Δ(*E* + ZP*E*) = 0.068399 kcal/mol



model-13
Δ(*E* + ZP*E*) = 0.349523 kcal/mol

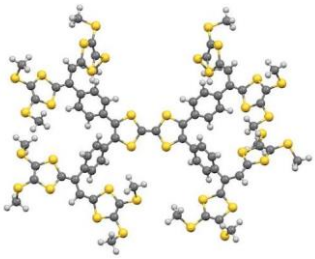


model-14
Δ(*E* + ZP*E*) = 0.035768 kcal/mol

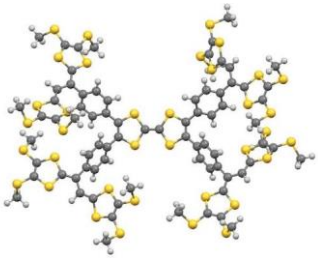
Compound of **4**

Energy data for compound **4**

	E [hartree]	ZP*E* [hartree]	*E* + ZP*E* [hartree]	Δ*E* [kcal/mol]	Δ(*E* + ZP*E*) [kcal/mo l]
model-2	**-17347.853473**	1.247282	**-17346.606191**	**0**	**0**
model-5	-17347.853193	1.247262	-17346.605931	0.175703	0.163152



model-2
Δ(*E* + ZP*E*) = 0 kcal/mol



model-5
Δ(*E* + ZP*E*) = 0.163152 kcal/mol

Cyclic voltammograms

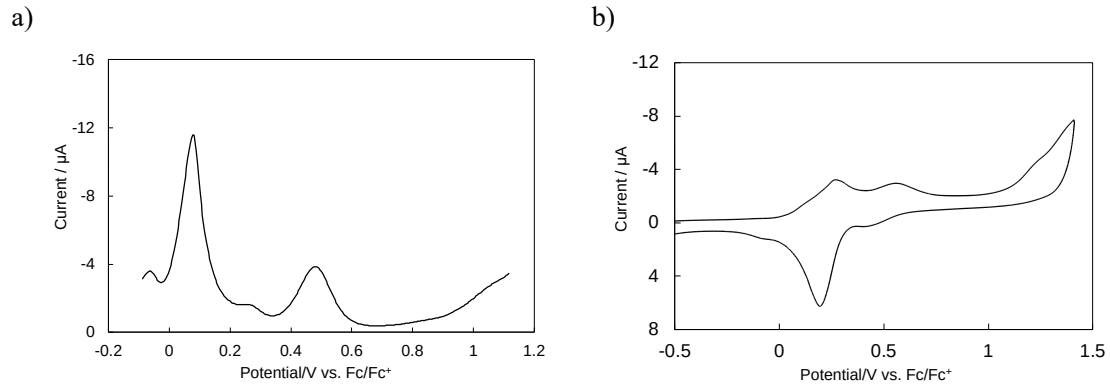
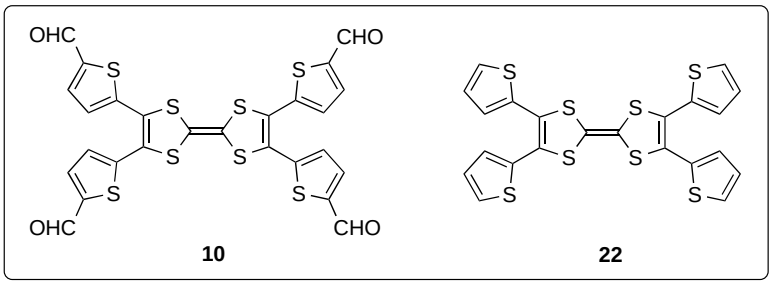


Figure S2: a) Differential pulse voltammetry of **2a** and b) cyclic voltammogram of **3a** in $PhCN/CS_2$ 1:1 (v/v, 0.3 mM) solution in the designated solvent containing 0.1 M *n*-Bu_4NPF_6.

Table S2: Redox potentials of compounds **2a** and **3a**, and related compounds[a].

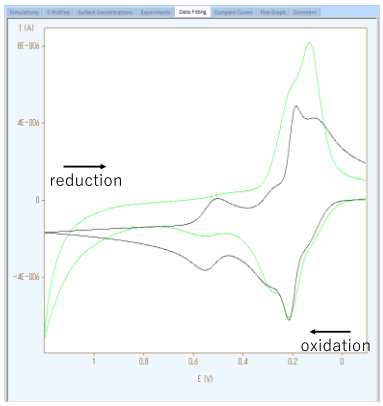
	E_1/V	E_2/V	E_3/V	E_4/V	E_5/V	E_6/V
2a[b]	–0.05	+0.08		+0.48		
3a	+0.14		+0.25			+0.52
10[c]	+0.25	+0.60				
22[c]	+0.00	+0.47				

[a]In $PhCN/CS_2$ 1:1(v/v) containing 0.1 M *n*-Bu_4NPF_6; all potentials were measured against Ag/Ag^+ as the reference electrode and converted to vs Fc/Fc^+. [b]Differential pulse voltammetry. [c]In PhCN containing 0.1 M *n*-Bu_4NPF_6, all potentials were measured against Ag/Ag^+ as the reference electrode and converted to vs Fc/Fc^+.



Results of the digital simulations of 1a and 4

a) **1a**



b) **4**

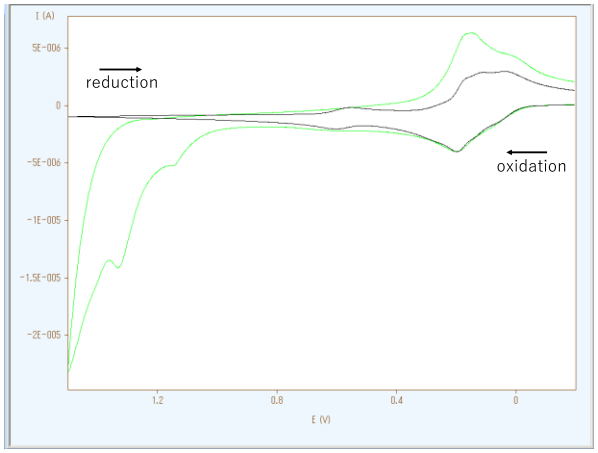


Figure S3: The results of the digital simulations of a) **1a** and b) **4**. Black line: digital simulated wave. Green line: observed wave.

Table S3: The following charge-transfer reaction and redox potentials were used for the digital simulations of **1a** and **4**.

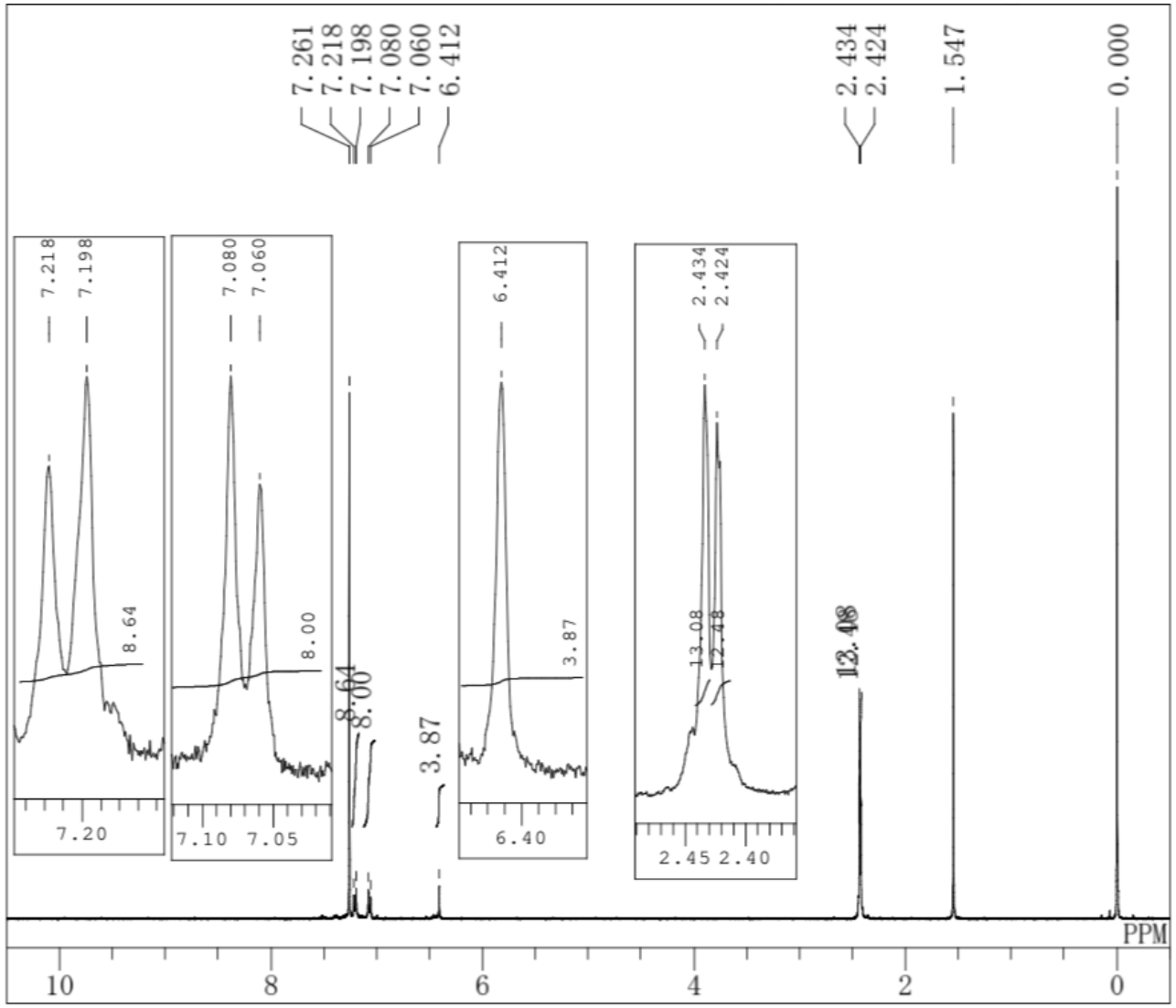
a) **1a**

charge-transfer reaction	redox potentials (V)
A + e = B	0.502
B + e = C1	0.285
C + 2e = D1	0.2
D1 + e = D2	0.15
D2 + e = D3	0.1

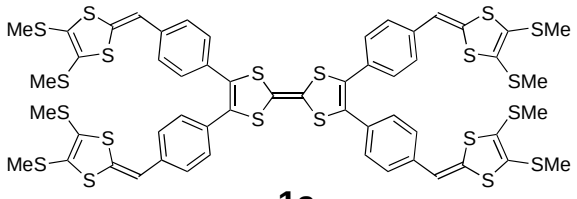
b) **4**

charge-transfer reaction	redox potentials (V)
A + e = B	0.582
B + e = C1	0.26
C1 + e = C2	0.19
C2 + e = C3	0.184
C3 + e = C4	0.18
C4 + e = D	0.133
D + e = E1	0.129
E1 + e = E2	0.088
E2 + e = E3	0.05
E3 + e = F	0.02

^{1}H NMR of **1a**

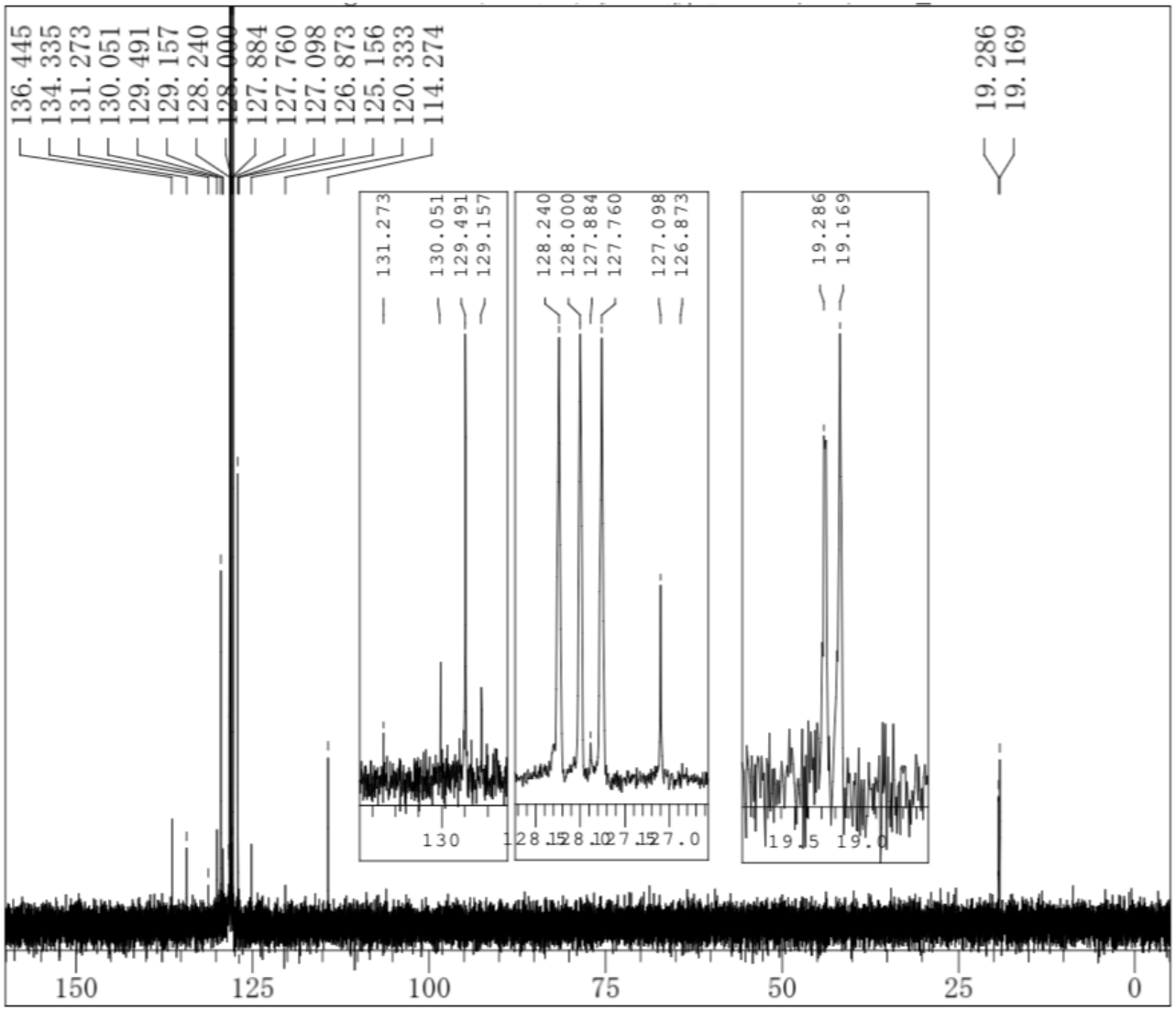



```
DFILE   1a_4-PhSMeDT-TTF H.a
COMNT   TTF-Bz-SMe
DATIM   /prog/mod/proc1d /op
OBNUC   1H
EXMOD   zg30
OBFRQ         400.13 MHz
OBSET           2.47 KHz
OBFIN           0.97 Hz
POINT          32768
FREQU        8278.15 Hz
SCANS            16
ACQTM         0.0000 sec
PD            0.0000 sec
PW1            10.00 usec
IRNUC
CTEMP           22.5 c
SLVNT   CDC13
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN           362
```

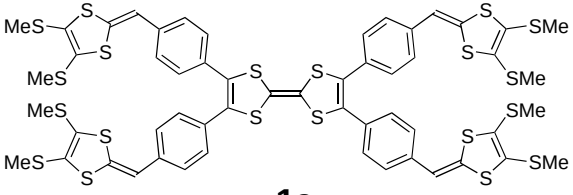


1a

^{13}C NMR of **1a**

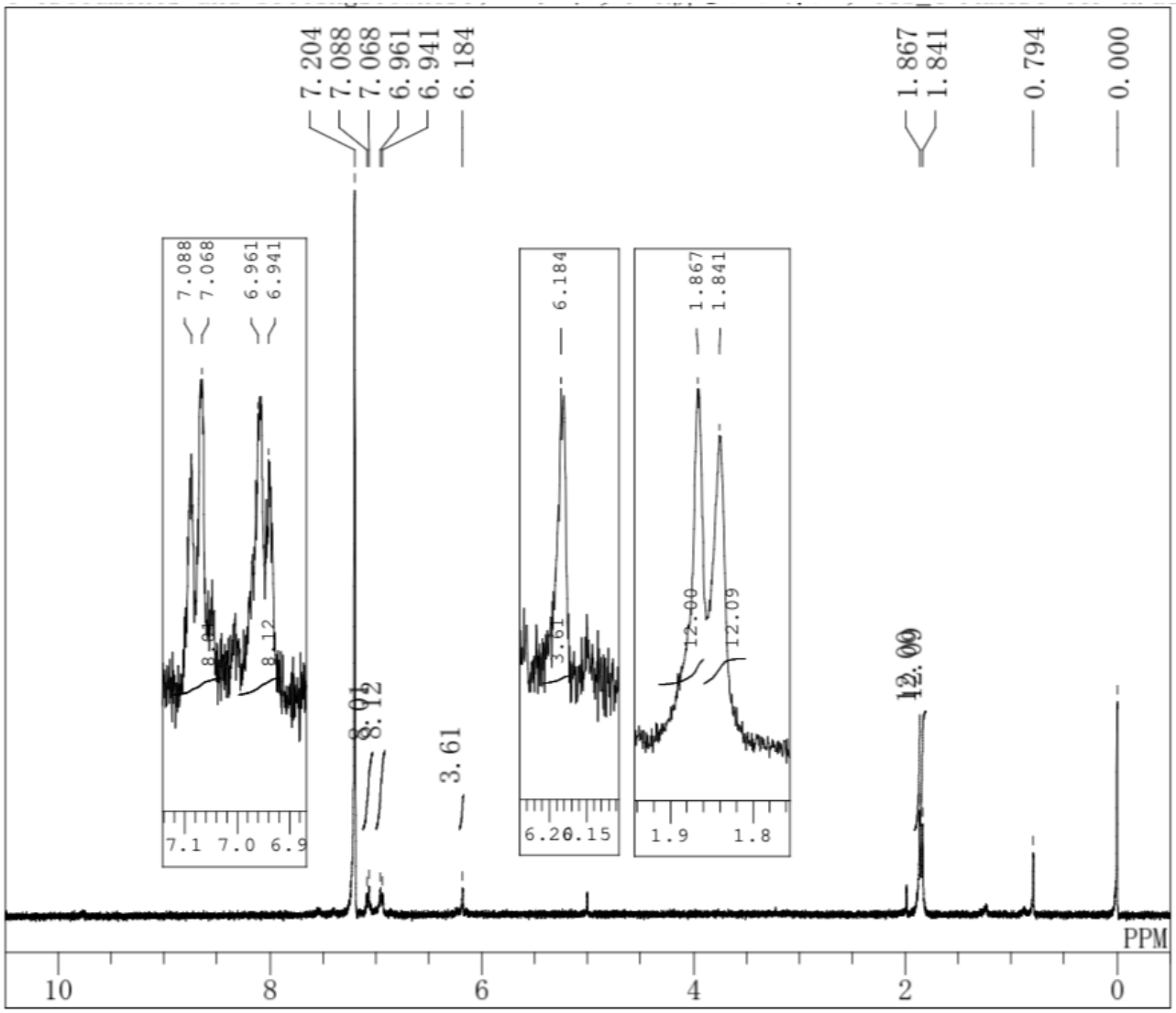



```
DFILE   1a_4-PhSMeDT-TTF C 1
COMNT   4-PhSMeDT-TTF C
DATIM   /prog/mod/proc1d /op
OBNUC   13C
EXMOD   zgpg30
OBFRQ         100.62 MHz
OBSET           2.82 KHz
OBFIN           9.80 Hz
POINT          32768
FREQU       23980.81 Hz
SCANS           1024
ACQTM         0.0000 sec
PD            0.0000 sec
PW1             10.00 usec
IRNUC
CTEMP            24.0 c
SLVNT   C6D6
EXREF         128.00 ppm
BF              0.00 Hz
RGAIN          20642
```

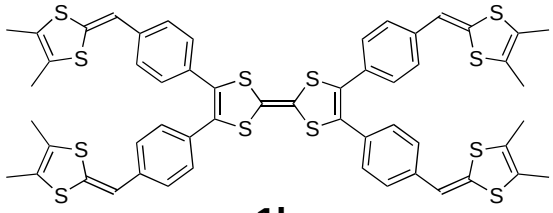


1a

^{1}H NMR of **1b**

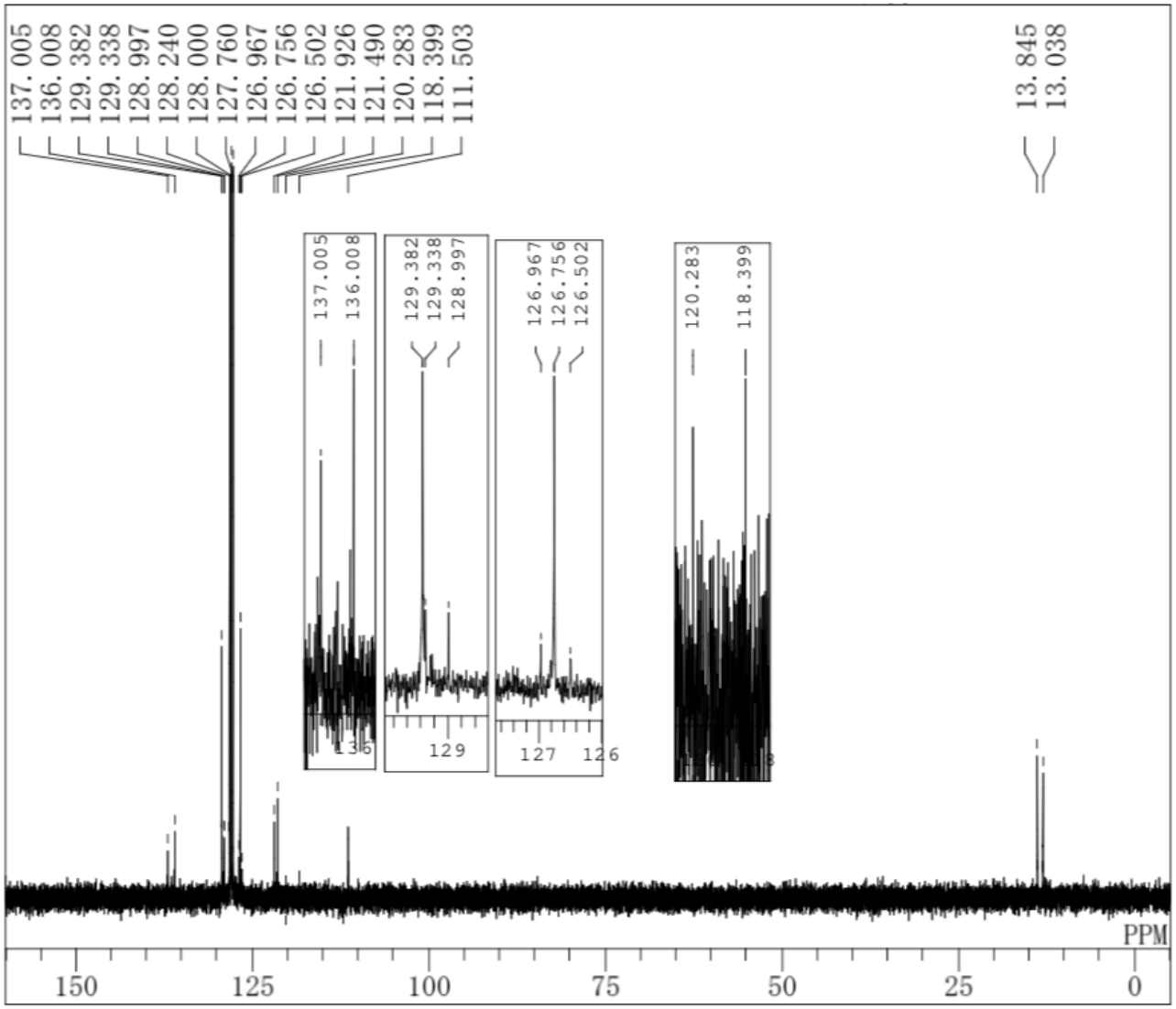



```
DFILE   1b_4-PhMeDT-TTF H.al
COMNT   Me
DATIM   /prog/mod/proc1d /op
OBNUC   1H
EXMOD   zg30
OBFRQ         400.13 MHz
OBSET           2.47 KHz
OBFIN           0.97 Hz
POINT          32768
FREQU        8278.15 Hz
SCANS            16
ACQTM         0.0000 sec
PD            0.0000 sec
PW1            10.00 usec
IRNUC
CTEMP           22.4 c
SLVNT   C6D6
EXREF          0.00 ppm
BF             0.00 Hz
RGAIN           456
```

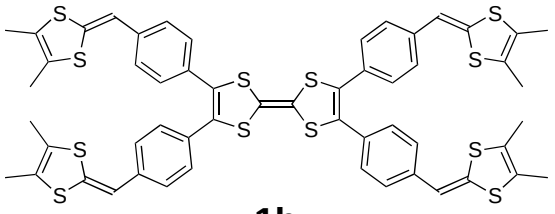


1b

^{13}C NMR of **1b**

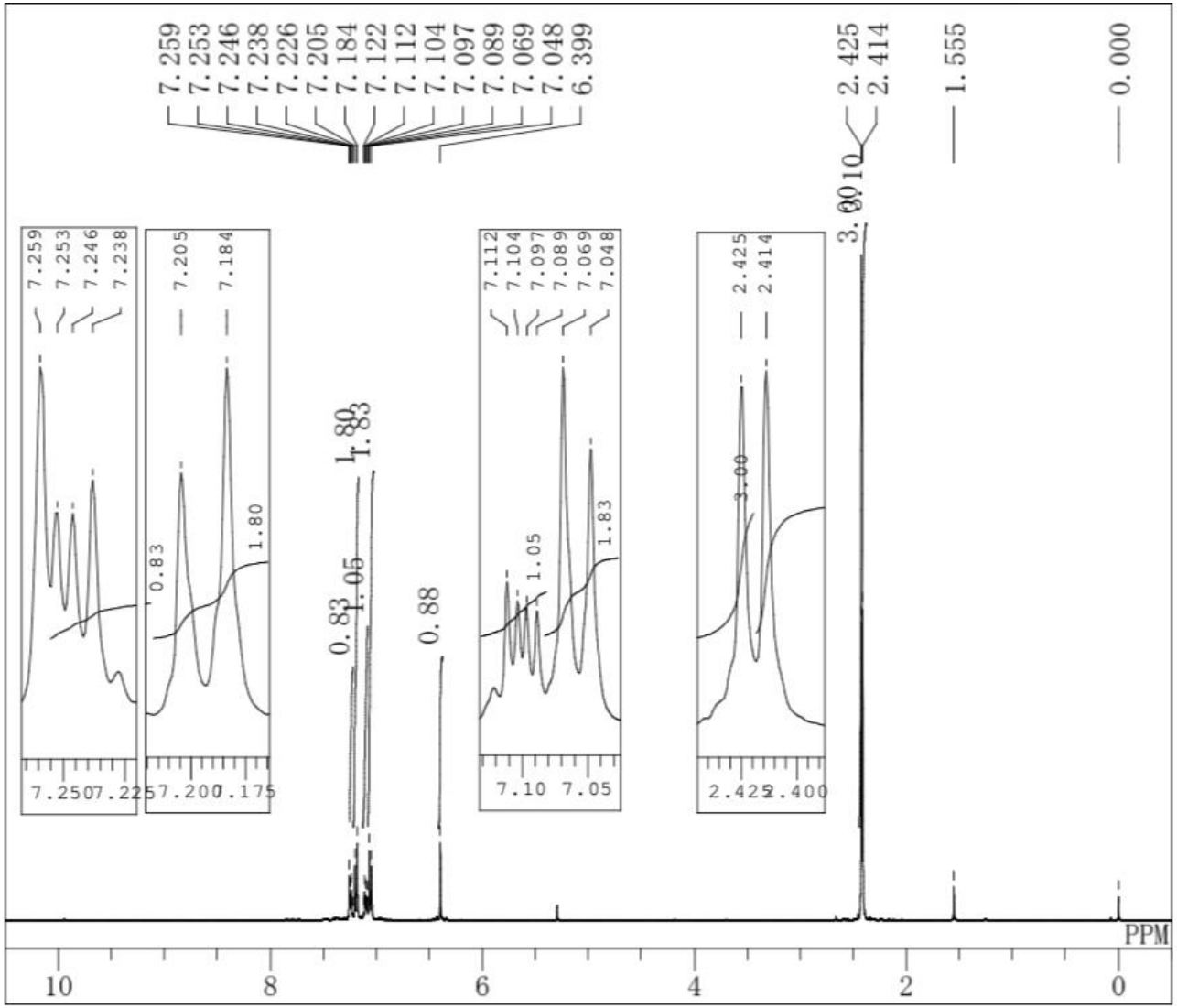


DFILE fid
COMNT 4-PhMeDT-TTF C
DATIM /prog/mod/proc1d /op
OBNUC 13C
EXMOD zgpg30
OBFRQ 100.62 MHz
OBSET 2.82 KHz
OBFIN 9.80 Hz
POINT 32768
FREQU 23980.81 Hz
SCANS 1024
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 23.9 c
SLVNT C6D6
EXREF 128.00 ppm
BF 0.00 Hz
RGAIN 20642

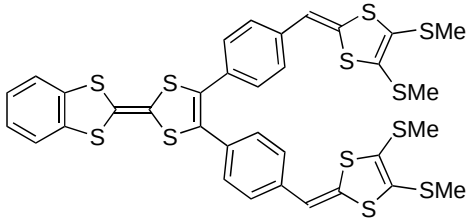


1b

^{1}H NMR of **2a**

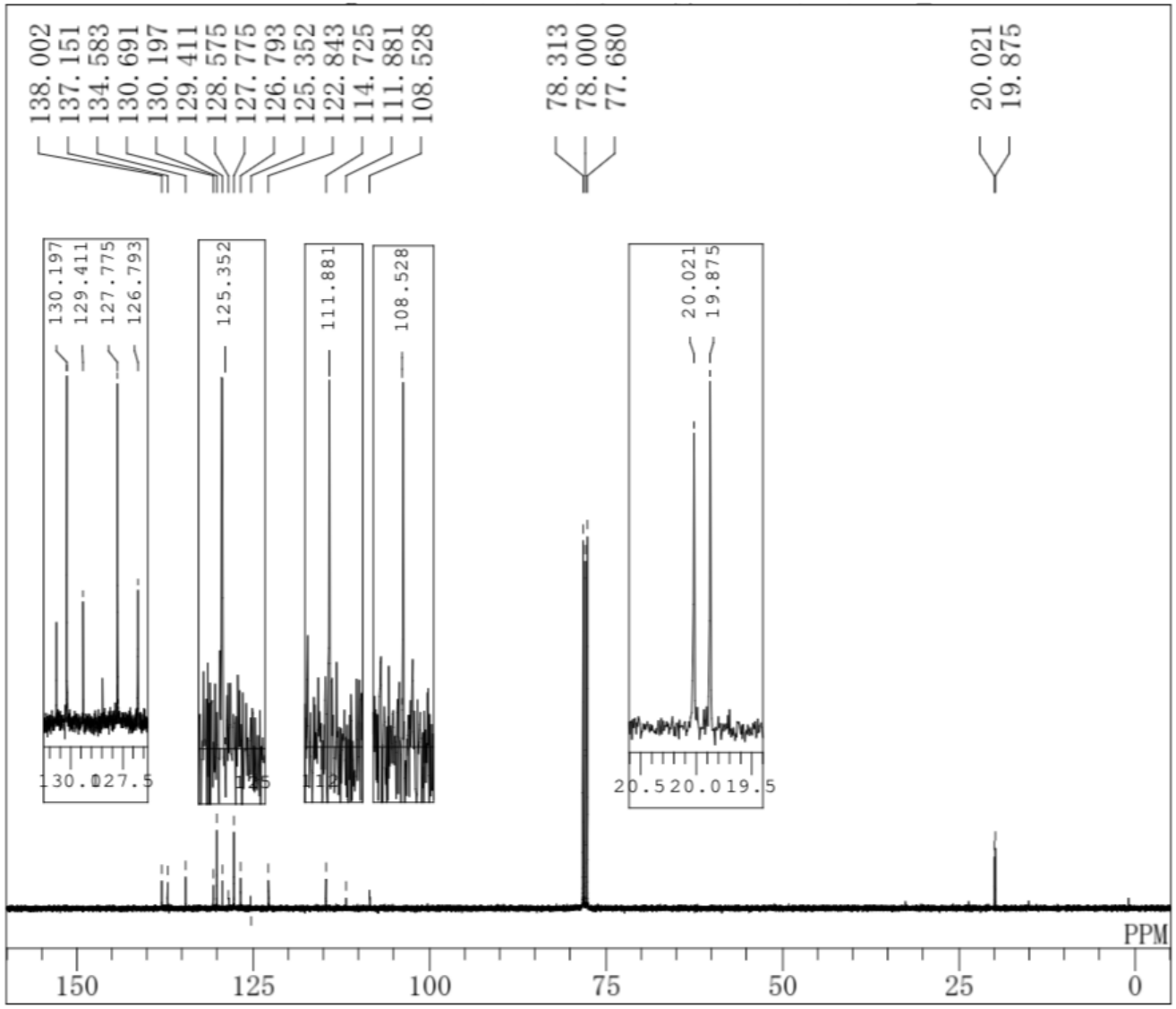


DFILE	21_4-PhSMeDT-BzTTF H
COMNT	4-PhSMeDT-BzTTF
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.4 c
SLVNT	CDC13
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	181

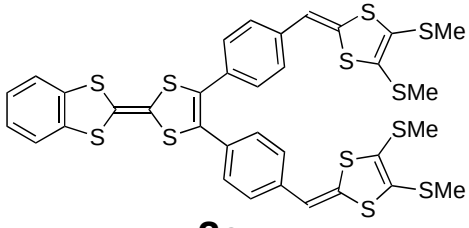


2a

^{13}C NMR of **2a**

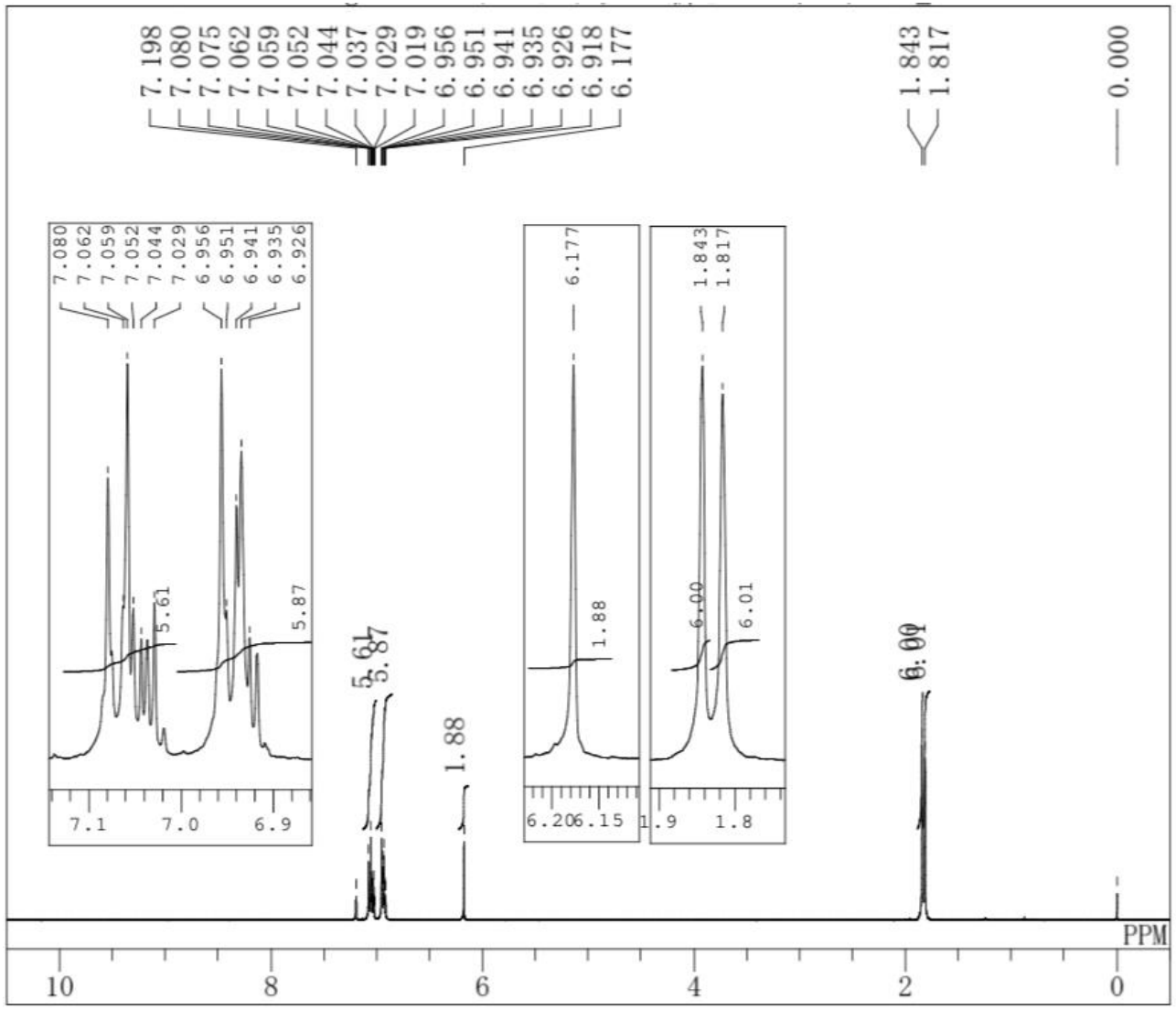


DFILE 2a_4-PhSMeDT-BzTTF C.
COMNT 4-PhSMeDT-BzTTF
DATIM /prog/mod/proc1d /op
OBNUC 13C
EXMOD zgpg30
OBFRQ 100.62 MHz
OBSET 2.82 KHz
OBFIN 9.80 Hz
POINT 32768
FREQU 23980.81 Hz
SCANS 912
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 23.9 c
SLVNT CDC13
EXREF 78.00 ppm
BF 0.12 Hz
RGAIN 23170

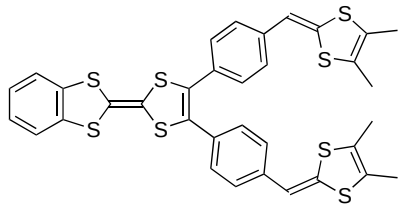


2a

^{1}H NMR of **2b**

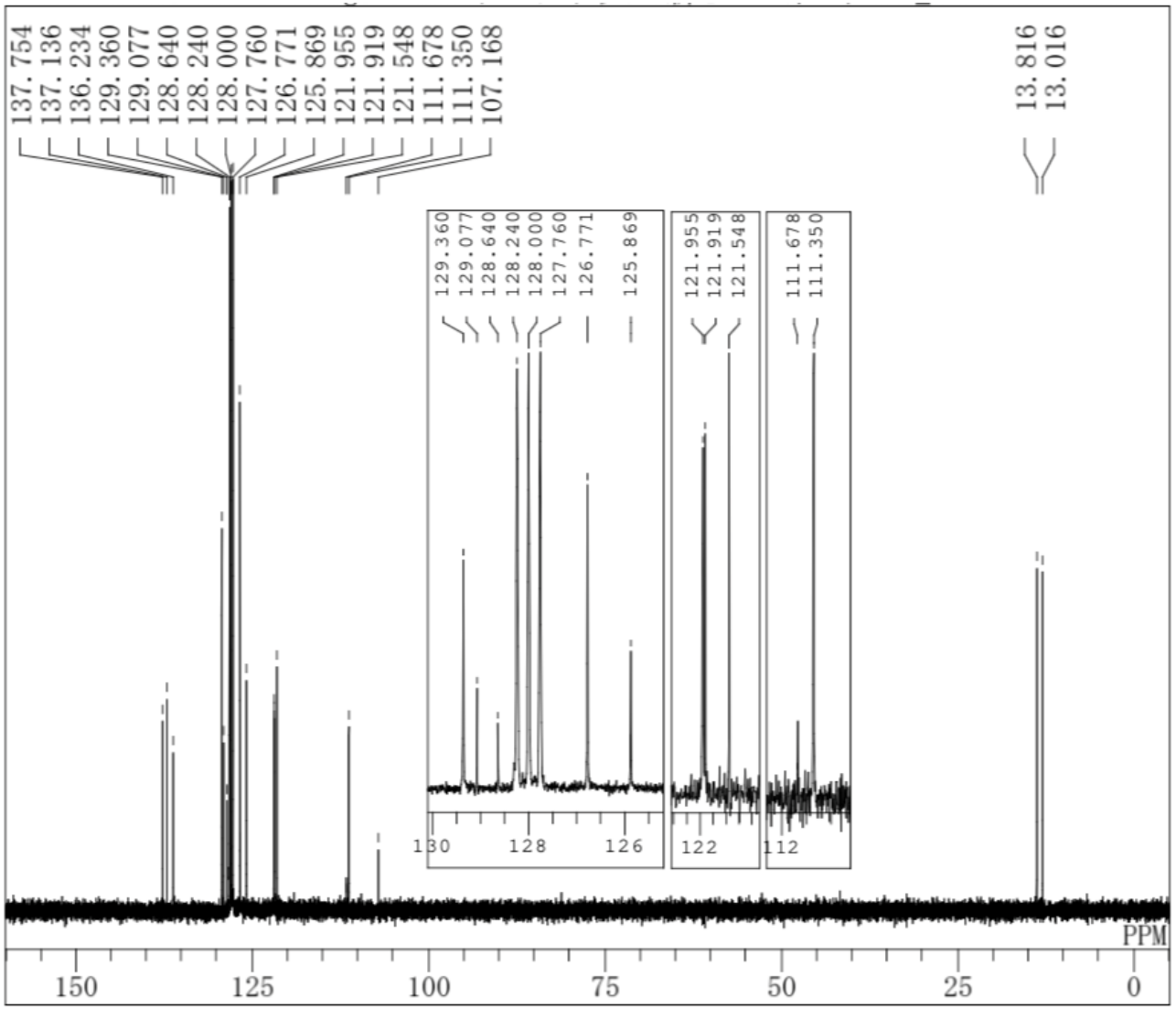



```
DFILE   2b_4-PhMeDT-BzTTF H
COMNT   4-PhMeDT-BzTTF H
DATIM   /prog/mod/proc1d /op
OBNUC   1H
EXMOD   zg30
OBFRQ          400.13 MHz
OBSET            2.47 KHz
OBFIN            0.97 Hz
POINT           32768
FREQU         8278.15 Hz
SCANS              16
ACQTM          0.0000 sec
PD             0.0000 sec
PW1              10.00 usec
IRNUC
CTEMP             23.2 c
SLVNT   C6D6
EXREF             0.00 ppm
BF                0.00 Hz
RGAIN              228
```

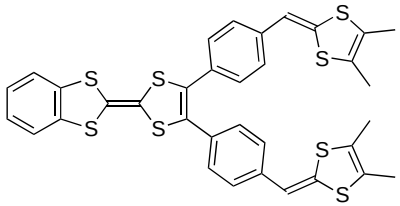


2b

^{13}C NMR of **2b**

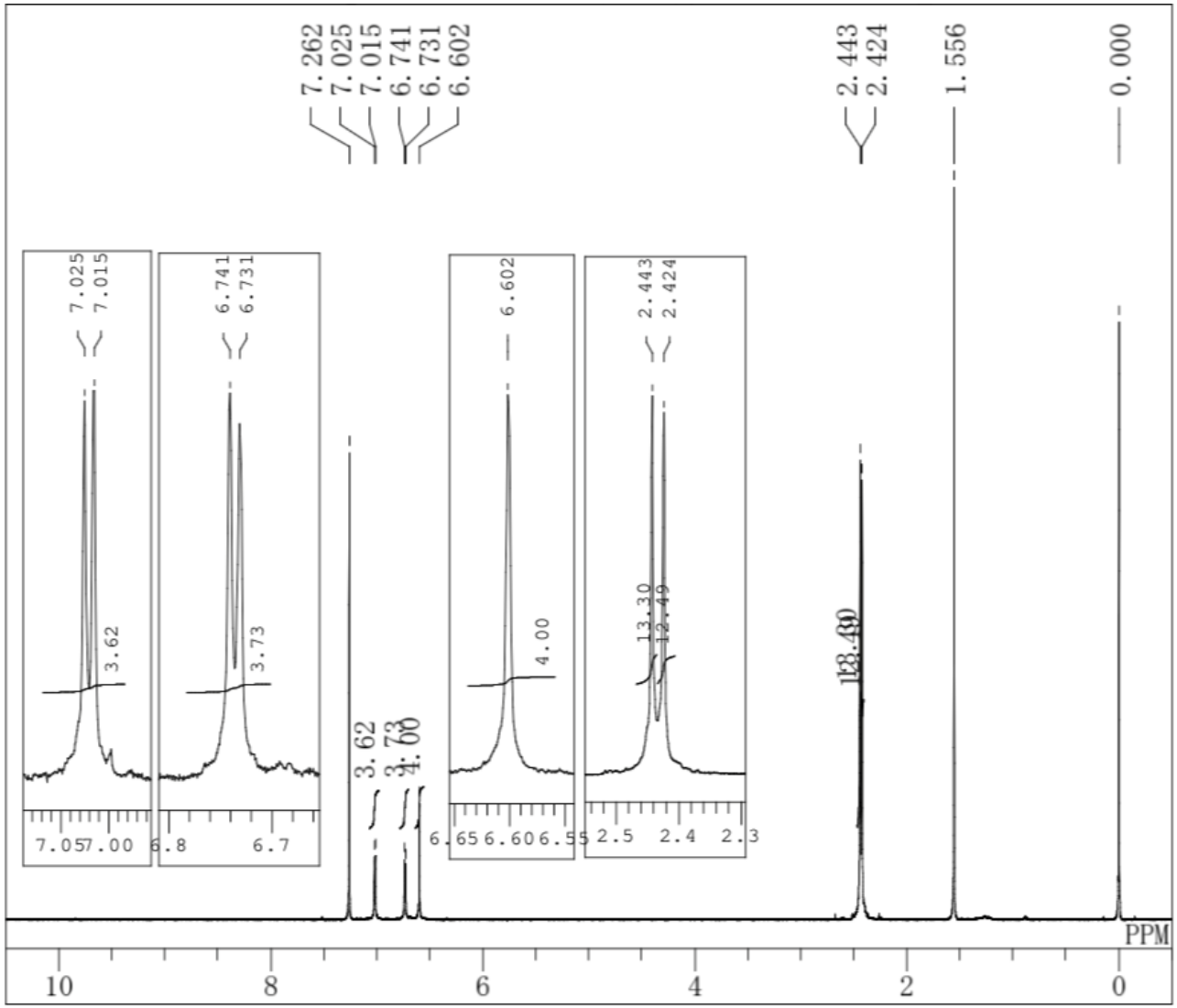


DFILE	2b_4-PhMeDT-BzTTF C.
COMNT	4-PhMeDT-BzTTF C
DATIM	/prog/mod/proc1d /op
OBNUC	13C
EXMOD	zgpg30
OBFRQ	100.62 MHz
OBSET	2.82 KHz
OBFIN	9.80 Hz
POINT	32768
FREQU	23980.81 Hz
SCANS	1024
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	23.5 c
SLVNT	C6D6
EXREF	128.00 ppm
BF	0.00 Hz
RGAIN	20642

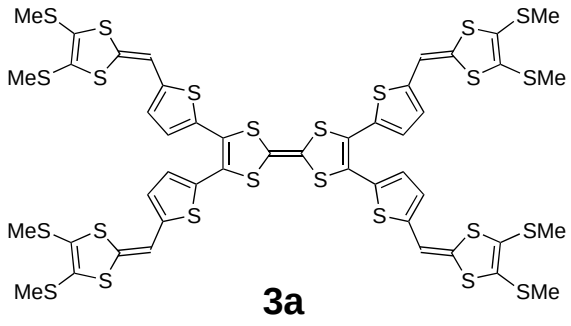


2b

^{1}H NMR of **3a**

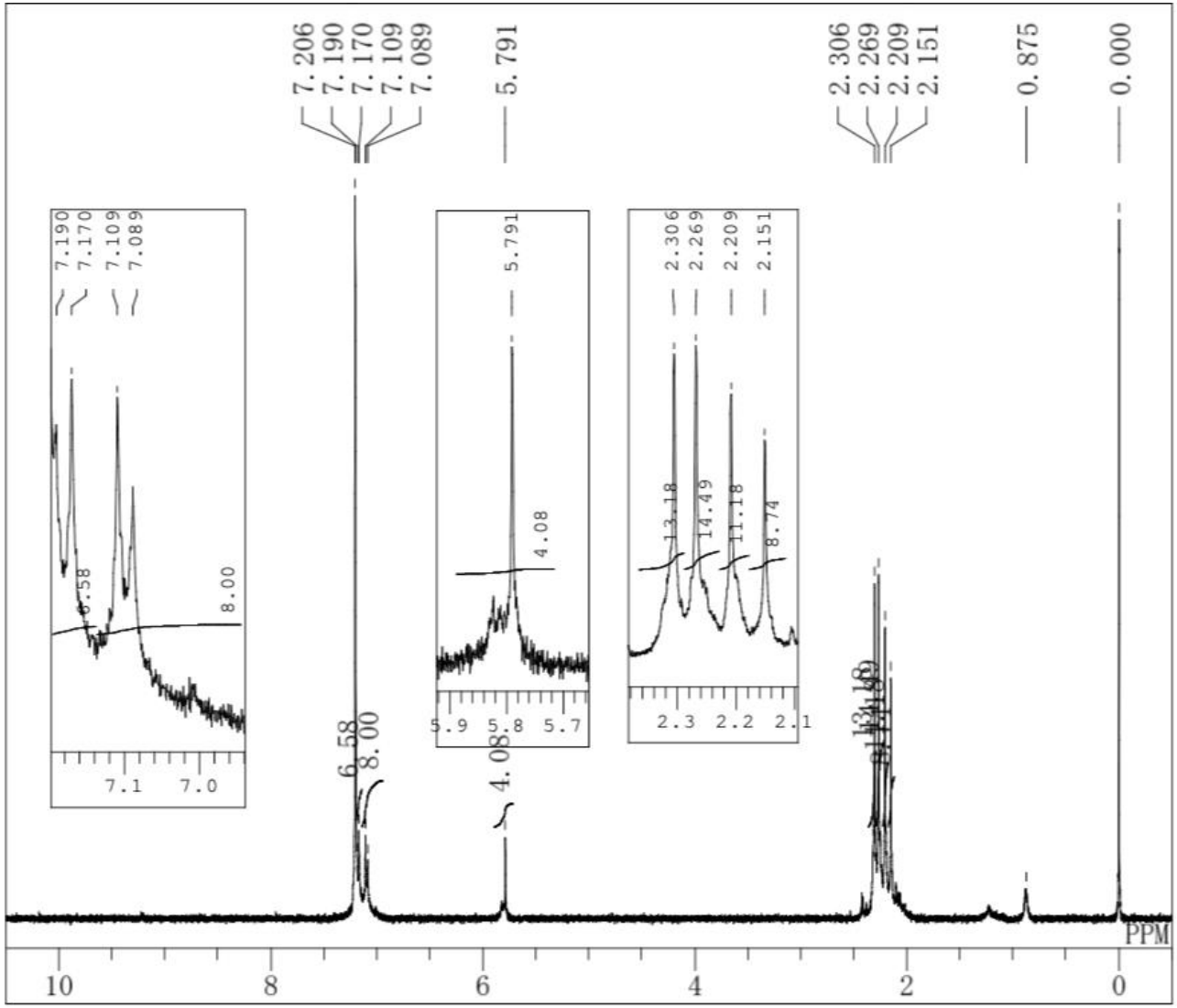



```
DFILE   12_2-ThioSMeDT-TTF.a
COMNT   Thio-SMe-fr2
DATIM   /prog/mod/proc1d /op
OBNUC   1H
EXMOD   zg30
OBFRQ          400.13 MHz
OBSET            2.47 KHz
OBFIN            0.97 Hz
POINT           32768
FREQU         8278.15 Hz
SCANS              16
ACQTM          0.0000 sec
PD             0.0000 sec
PW1              10.00 usec
IRNUC
CTEMP             22.4 c
SLVNT   CDC13
EXREF             0.00 ppm
BF                0.12 Hz
RGAIN              362
```

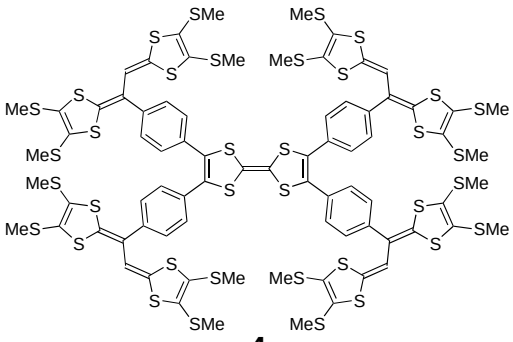


3a

^{1}H NMR of **4**

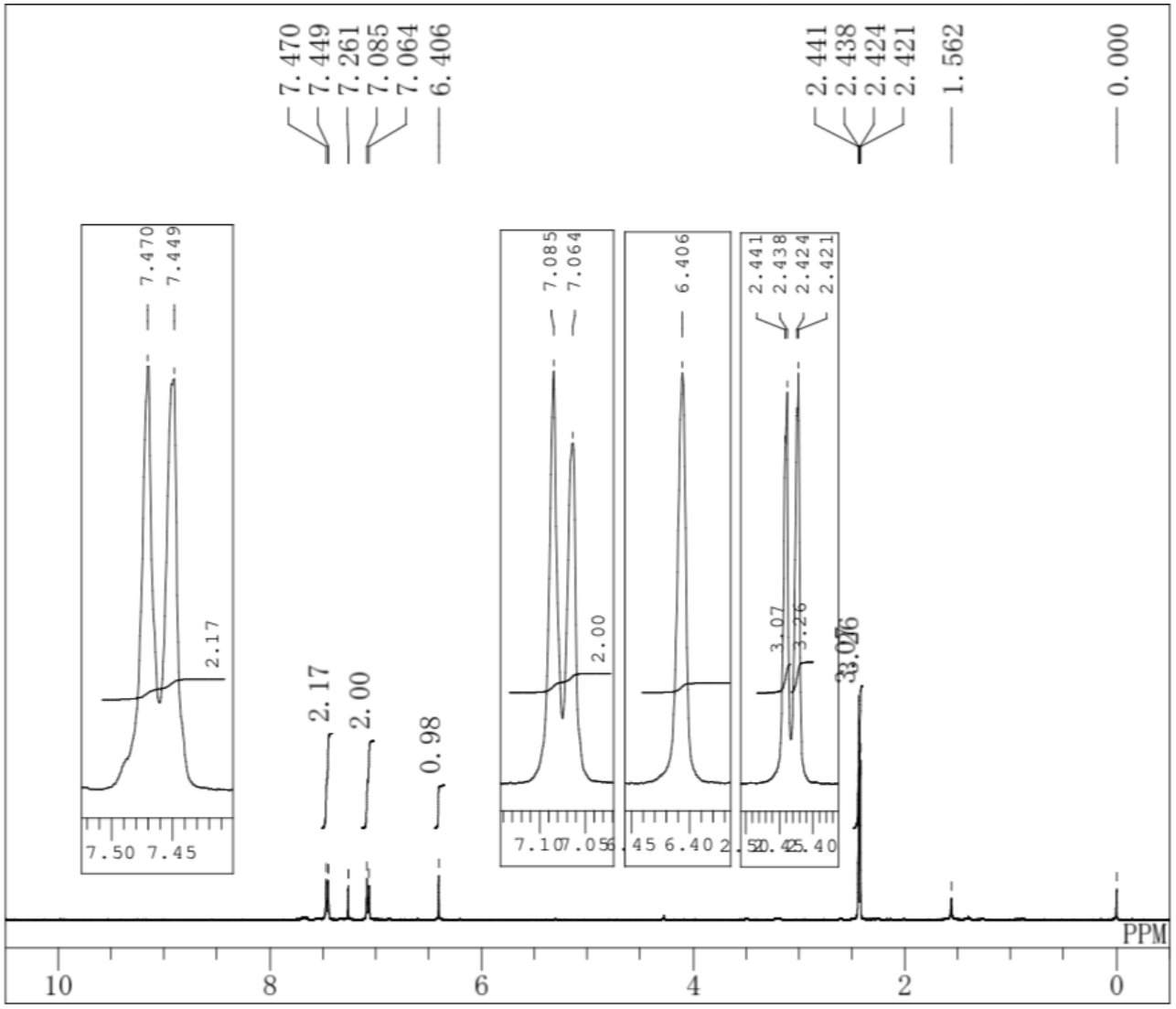


DFILE 4_4-PhSMeEBDT-TTF ar
COMNT 4-PhSMeEBDT-TTF aryl
DATIM /prog/mod/proc1d /op
OBNUC 1H
EXMOD zg30
OBFRQ 400.13 MHz
OBSET 2.47 KHz
OBFIN 0.97 Hz
POINT 32768
FREQU 8278.15 Hz
SCANS 16
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 22.7 c
SLVNT C6D6
EXREF 0.00 ppm
BF 0.00 Hz
RGAIN 362

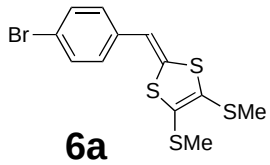


4

^{1}H NMR of **6a**

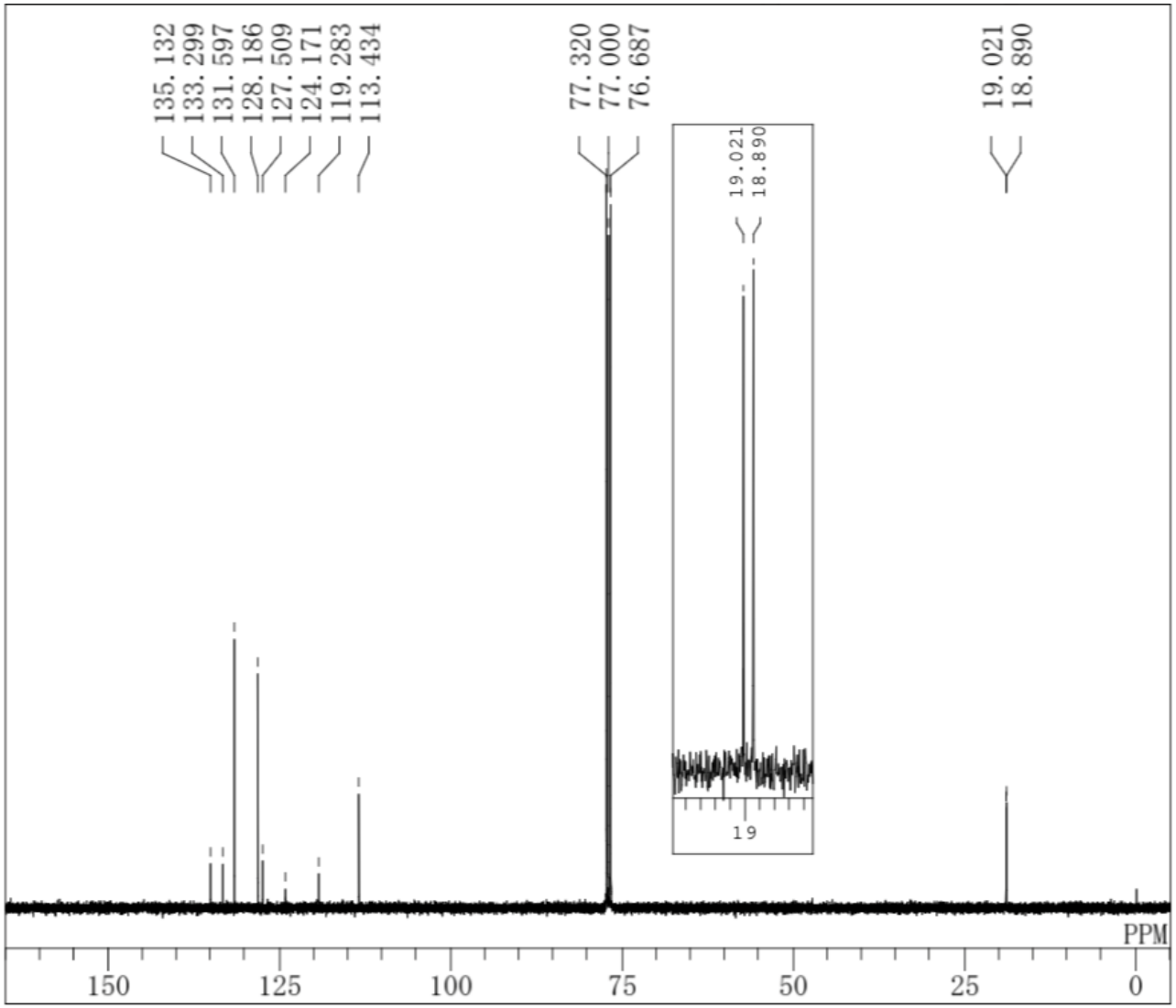


DFILE	04_4-PhBr-SMeDT H.al
COMNT	SMeDTBr
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.5 c
SLVNT	CDC13
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	322

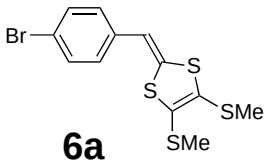


6a

^{13}C NMR of **6a**

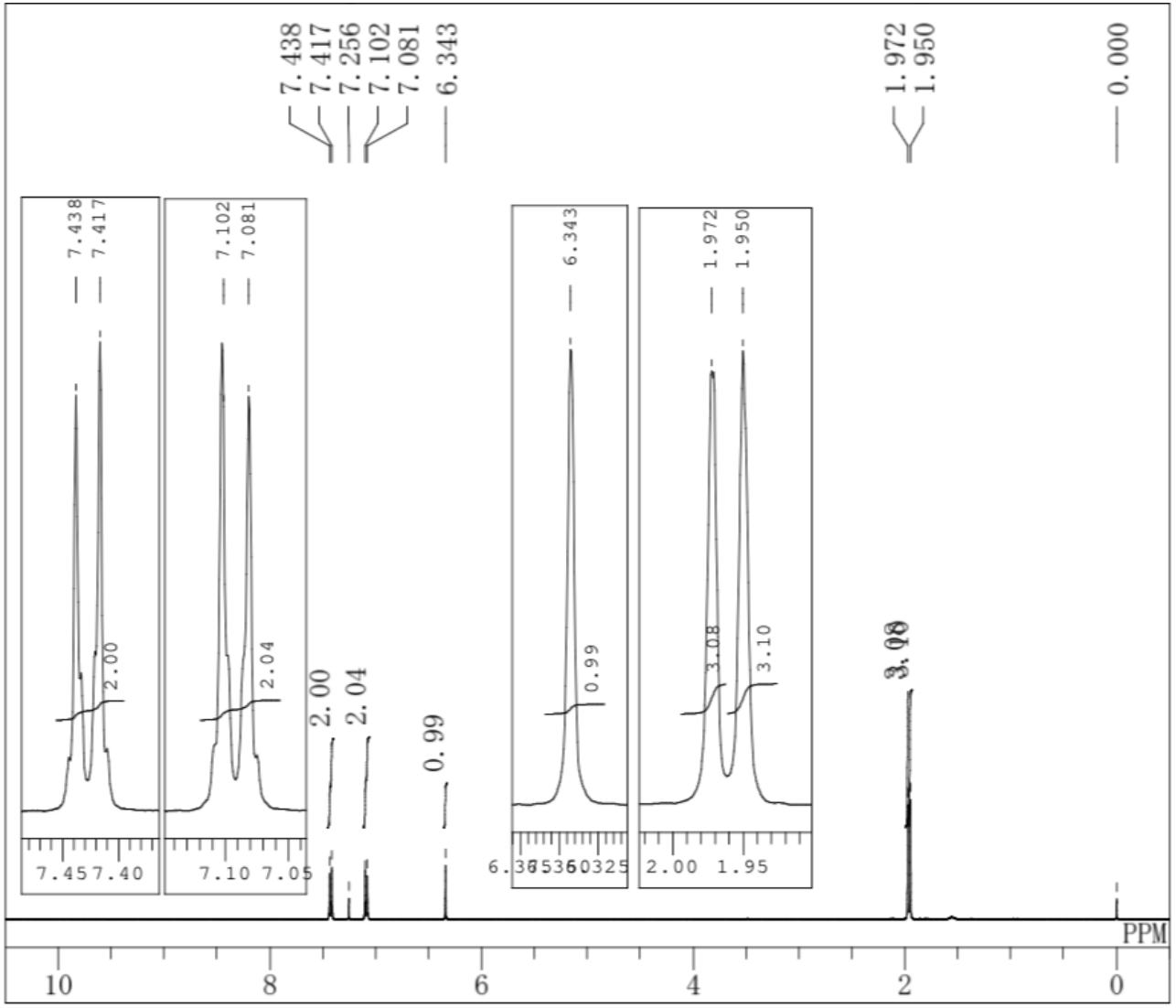



```
DFILE   04_4-PhBr-SMeDT C.al
COMNT   4-PhSMeDTBr
DATIM   /prog/mod/proc1d /op
OBNUC   13C
EXMOD   zgpg30
OBFRQ         100.62 MHz
OBSET           2.82 KHz
OBFIN           9.80 Hz
POINT          32768
FREQU       23980.81 Hz
SCANS            787
ACQTM         0.0000 sec
PD            0.0000 sec
PW1            10.00 usec
IRNUC
CTEMP           23.4 c
SLVNT   CDC13
EXREF          77.00 ppm
BF              0.00 Hz
RGAIN          20642
```

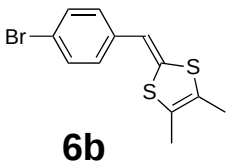


6a

^{1}H NMR of **6b**

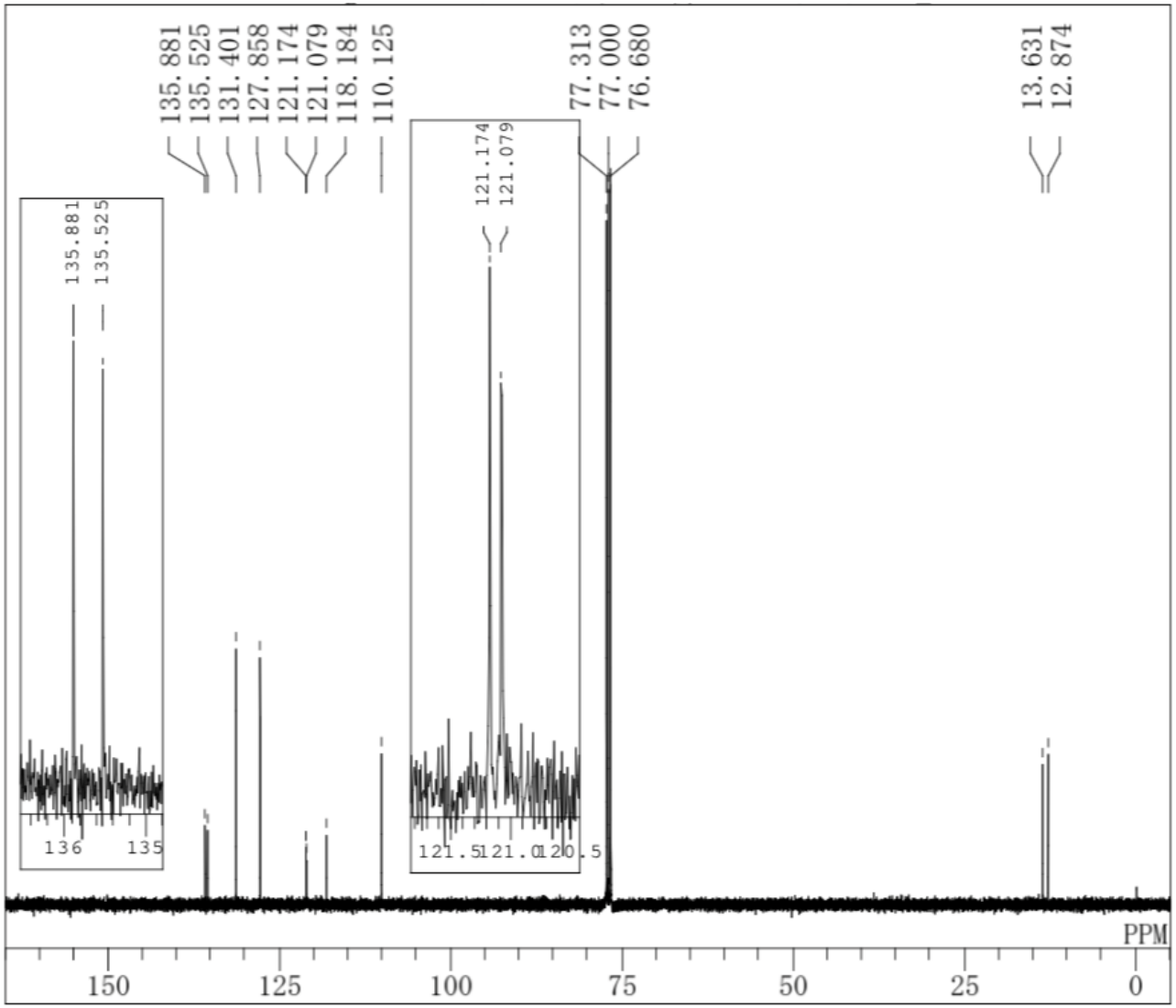


DFILE 6b_4-PhBr-MeDT H.als
COMNT 4-PhMeDT-Br
DATIM /prog/mod/proc1d /op
OBNUC 1H
EXMOD zg30
OBFRQ 400.13 MHz
OBSET 2.47 KHz
OBFIN 0.97 Hz
POINT 32768
FREQU 8278.15 Hz
SCANS 16
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 22.8 c
SLVNT CDC13
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 181

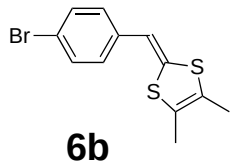


6b

^{13}C NMR of **6b**

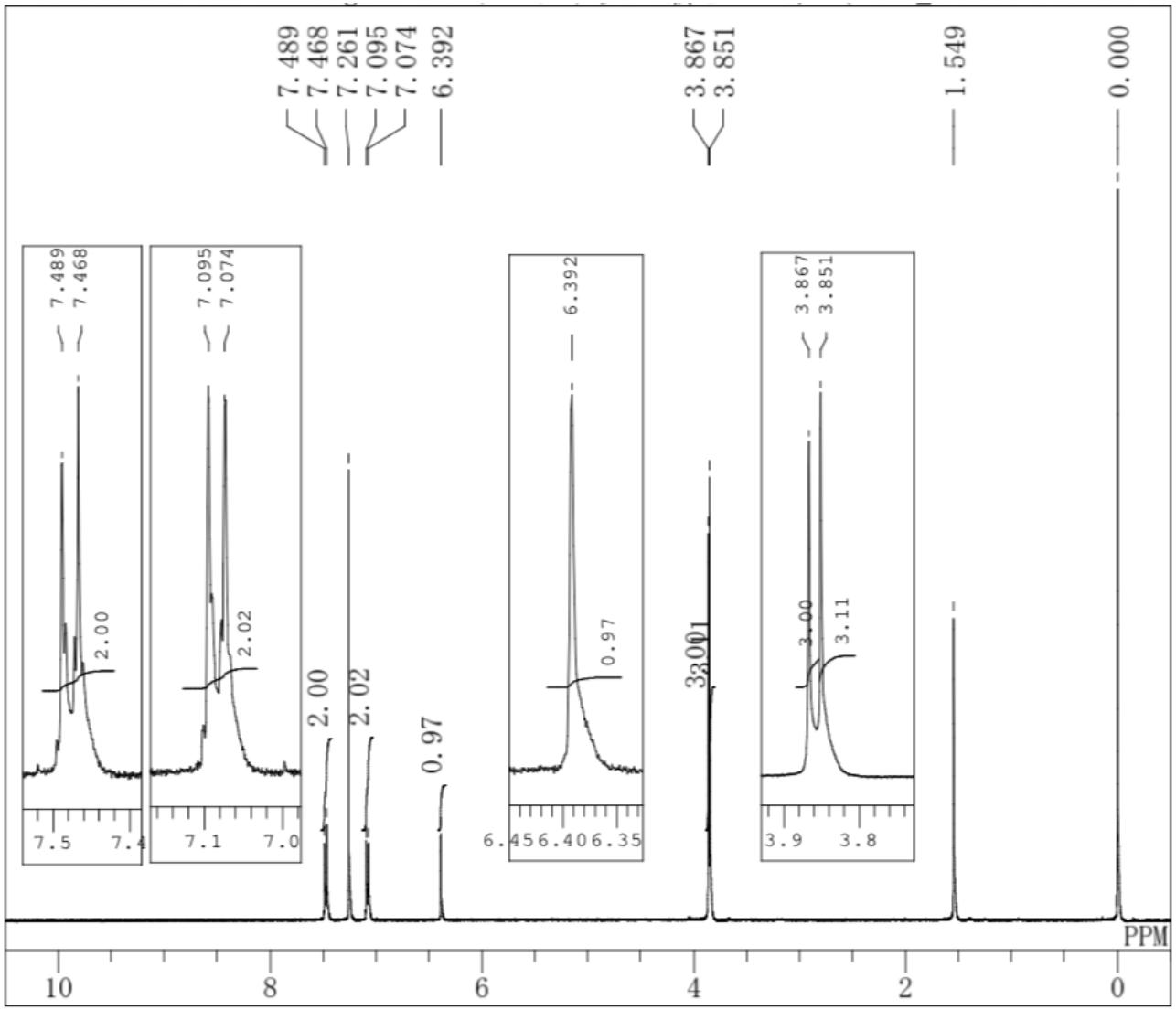


DFILE	6b_4-PhBr-MeDT C.als
COMNT	4-PhMeDTBr
DATIM	/prog/mod/proc1d /op
OBNUC	13C
EXMOD	zgpg30
OBFRQ	100.62 MHz
OBSET	2.82 KHz
OBFIN	9.80 Hz
POINT	32768
FREQU	23980.81 Hz
SCANS	844
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	23.5 c
SLVNT	CDC13
EXREF	77.00 ppm
BF	0.00 Hz
RGAIN	18390

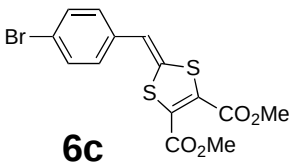


6b

^{1}H NMR of **6c**

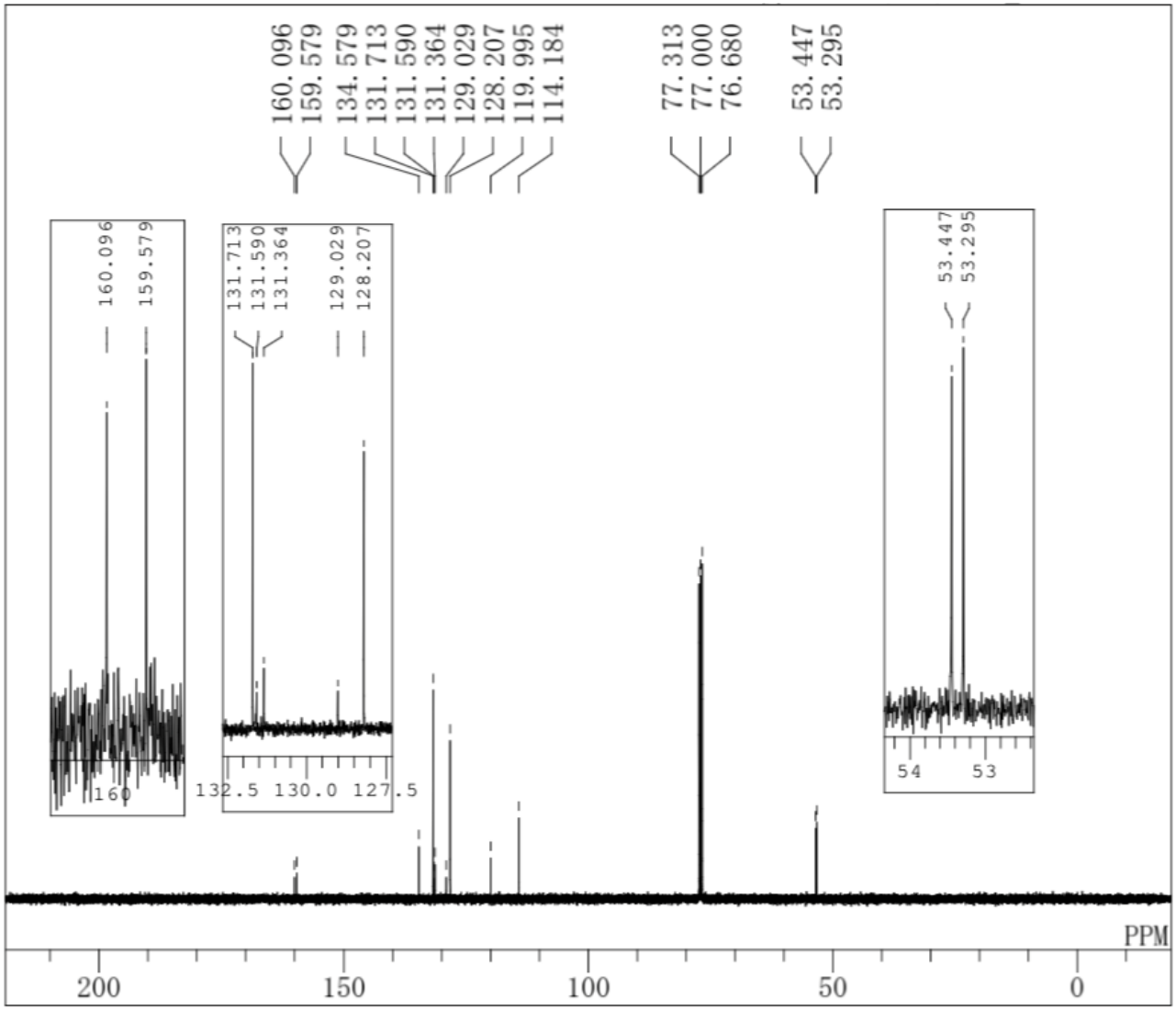


DFILE	6c_4-PhBr-CO2MeDT H.
COMNT	BrBzDTCO2Me-1
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	23.3 c
SLVNT	CDC13
EXREF	0.00 ppm
BF	0.00 Hz
RGAIN	456

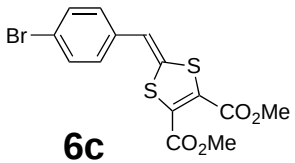


6c

^{13}C NMR of **6c**

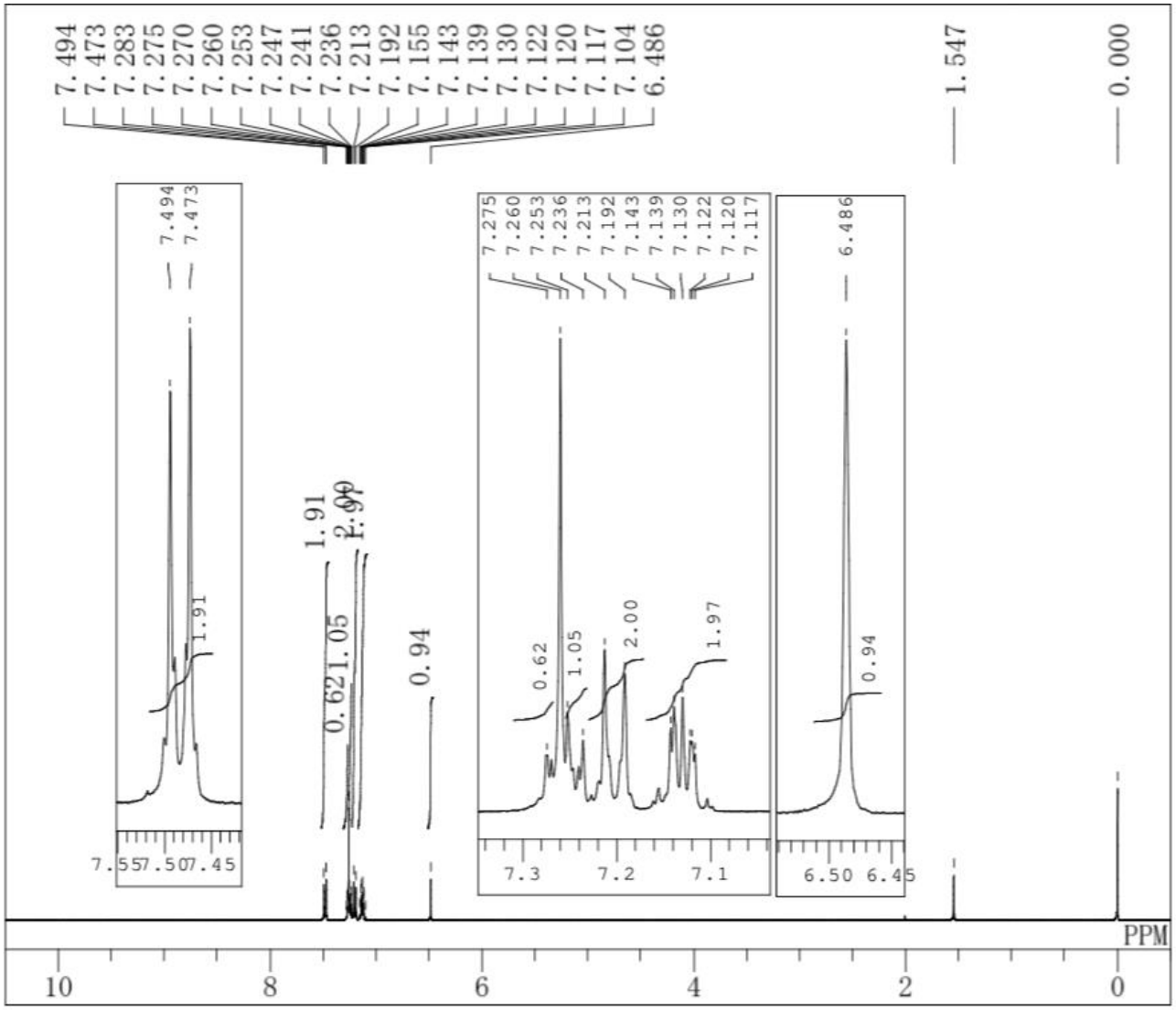



```
DFILE   07_4-PhBr-CO2MeDT C.a
COMNT   4-PhBr-CO2MeDT C
DATIM   /prog/mod/proc1d /opt
OBNUC   13C
EXMOD   zgpg30
OBFRQ         100.62 MHz
OBSET           2.82 KHz
OBFIN           9.80 Hz
POINT          32768
FREQU       23980.81 Hz
SCANS            347
ACQTM         0.0000 sec
PD            0.0000 sec
PW1            10.00 usec
IRNUC
CTEMP           23.6 c
SLVNT   CDC13
EXREF          77.00 ppm
BF              0.00 Hz
RGAIN          20642
```

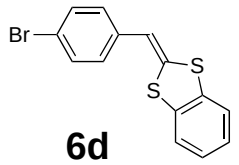


6c

^{1}H NMR of **6d**

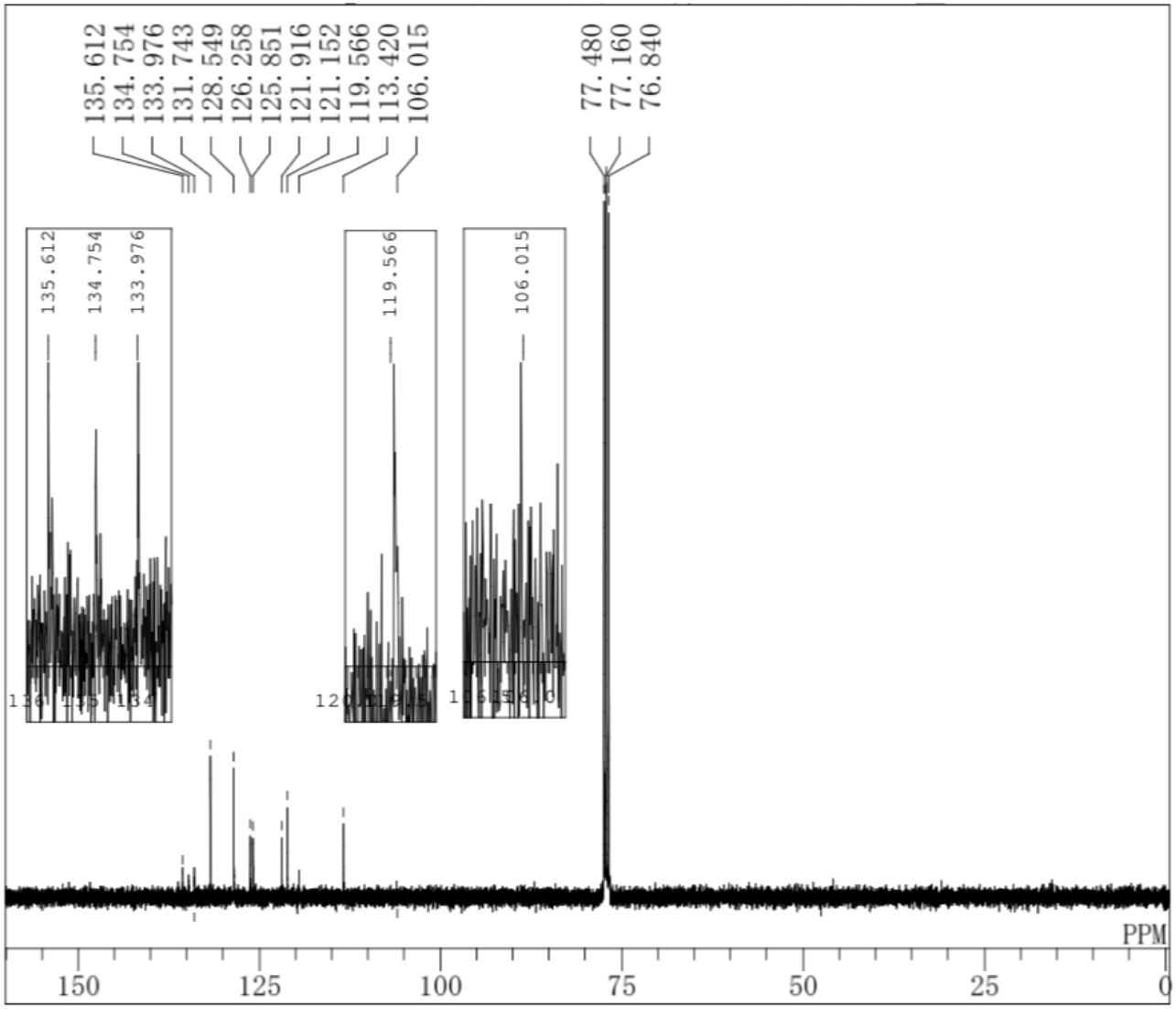


DFILE	06_4-PhBr-BzDT H.als
COMNT	BzDT-BzBr
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.4 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	362

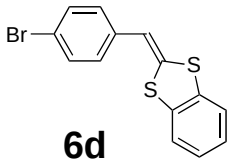


6d

^{13}C NMR of **6d**

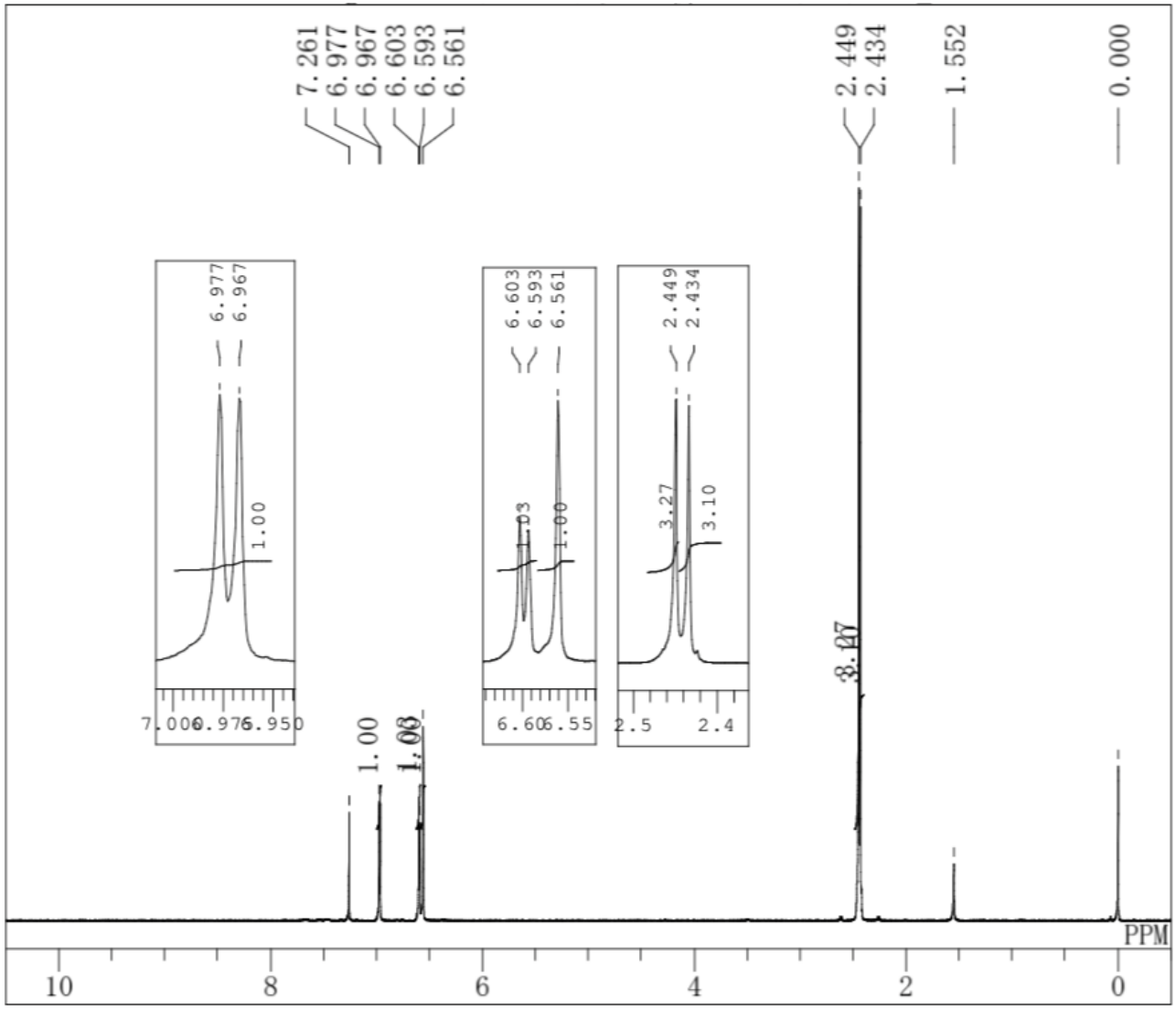



```
DFILE   6d__4-PhBr-BzDT C.al
COMNT   2-ThioBr-BzDT reverc
DATIM   /prog/mod/procld /op
OBNUC   13C
EXMOD   zgpg30
OBFRQ         100.62 MHz
OBSET           2.82 KHz
OBFIN           9.80 Hz
POINT          32768
FREQU       23980.81 Hz
SCANS           1024
ACQTM         0.0000 sec
PD            0.0000 sec
PW1            10.00 usec
IRNUC
CTEMP           23.8 c
SLVNT   CDC13
EXREF          77.16 ppm
BF              0.12 Hz
RGAIN          20642
```

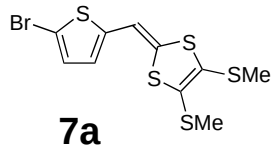


6d

^{1}H NMR of **7a**

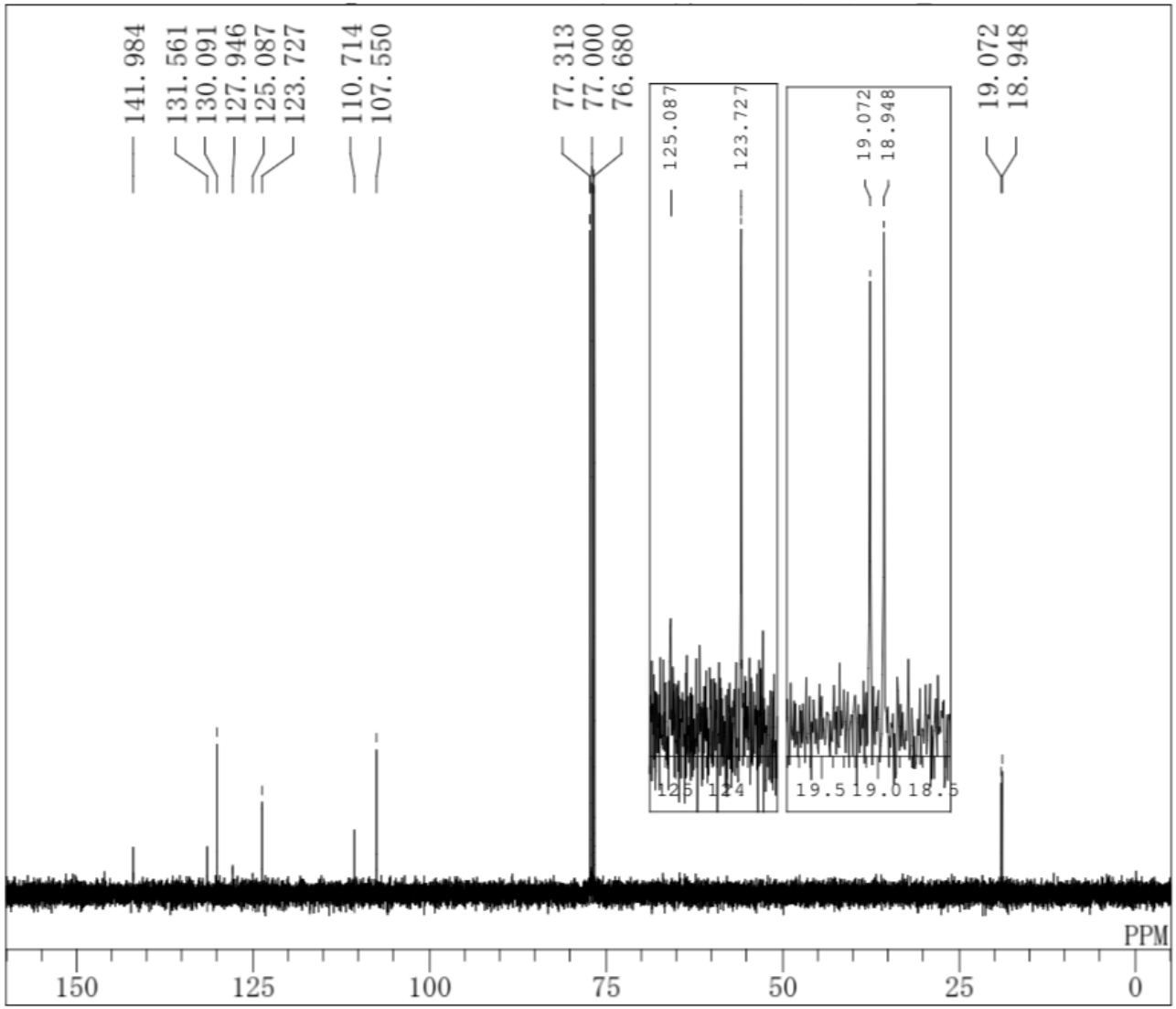



```
DFILE   7a_2-ThioBr-SMeDT H.
COMNT   Br-thio-SMeDT
DATIM   /prog/mod/proc1d /op
OBNUC   1H
EXMOD   zg30
OBFRQ         400.13 MHz
OBSET           2.47 KHz
OBFIN           0.97 Hz
POINT          32768
FREQU        8278.15 Hz
SCANS            16
ACQTM         0.0000 sec
PD            0.0000 sec
PW1            10.00 usec
IRNUC
CTEMP           22.6 c
SLVNT   CDC13
EXREF          0.00 ppm
BF             0.00 Hz
RGAIN           322
```

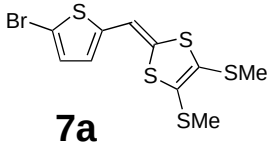


7a

^{13}C NMR of **7a**

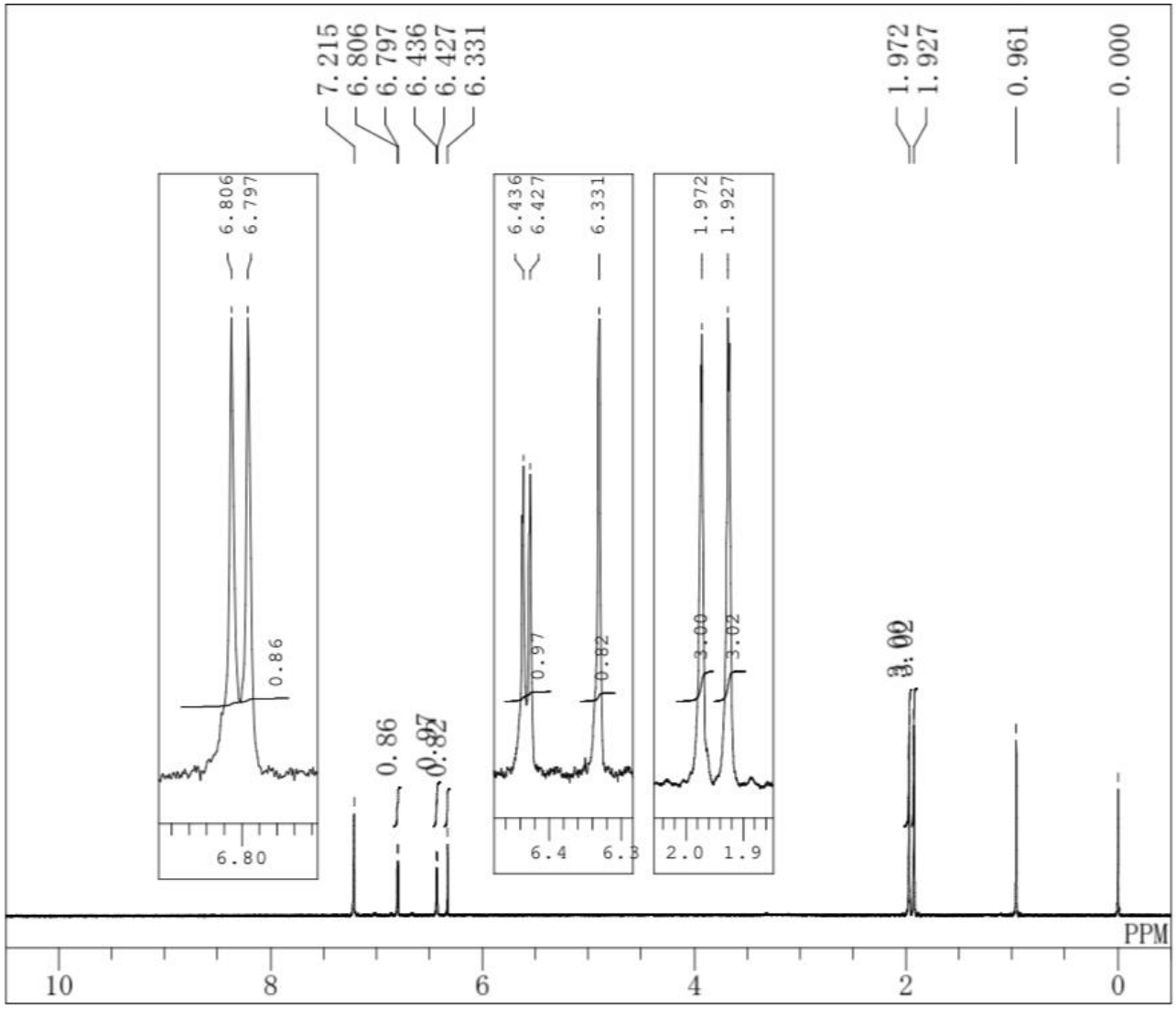



```
DFILE   7a_2-ThioBr-SMeDT C.
COMNT   Br-thio-SMeDT-C
DATIM   /prog/mod/proc1d /op
OBNUC   13C
EXMOD   zgpg30
OBFRQ         100.62 MHz
OBSET           2.82 KHz
OBFIN           9.80 Hz
POINT          32768
FREQU       23980.81 Hz
SCANS            214
ACQTM         0.0000 sec
PD            0.0000 sec
PW1            10.00 usec
IRNUC
CTEMP           23.7 c
SLVNT   CDC13
EXREF          77.00 ppm
BF              0.00 Hz
RGAIN          20642
```

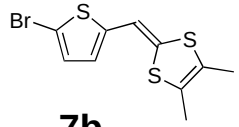


7a

^{1}H NMR of **7b**

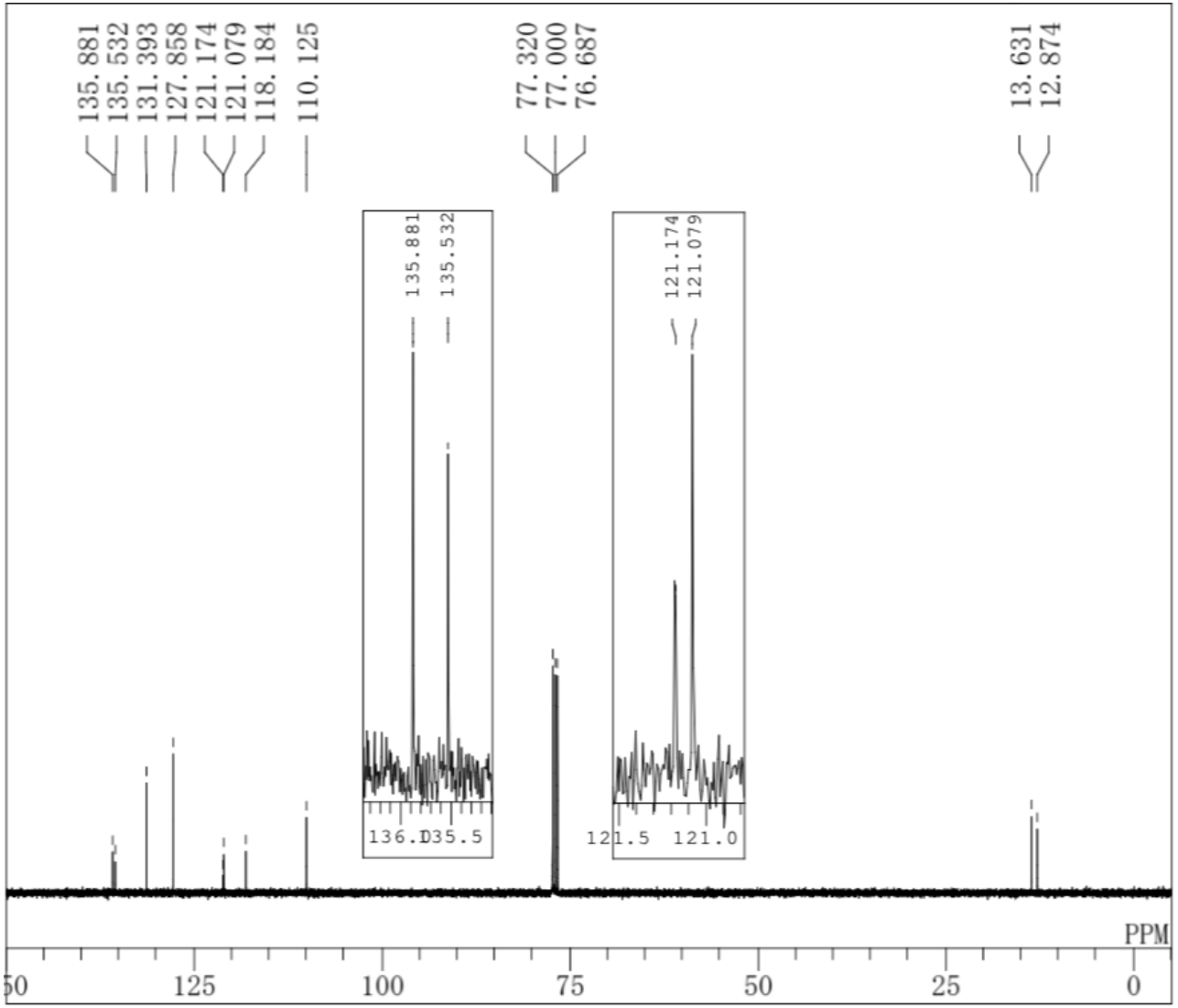



```
DFILE   02_2-ThioBr-MeDT H.a
COMNT   MeDT ThioBr
DATIM   /prog/mod/proc1d /op
OBNUC   1H
EXMOD   zg30
OBFRQ         400.13 MHz
OBSET           2.47 KHz
OBFIN           0.97 Hz
POINT          32768
FREQU        8278.15 Hz
SCANS            16
ACQTM         0.0000 sec
PD            0.0000 sec
PW1            10.00 usec
IRNUC
CTEMP           23.5 c
SLVNT   C6D6
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           574
```

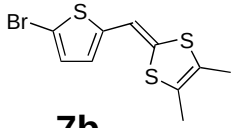


7b

^{13}C NMR of **7b**

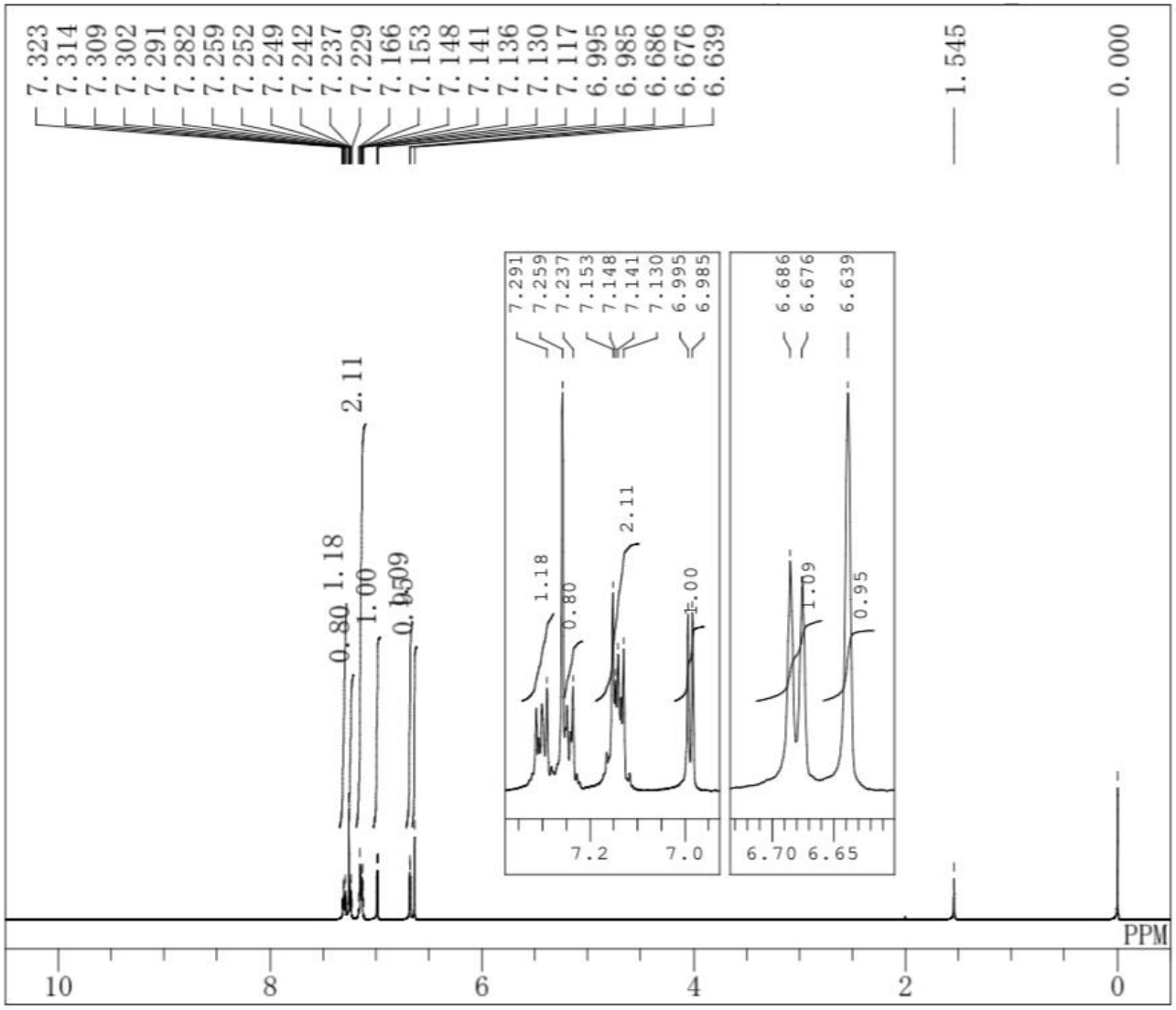


DFILE	02_2-ThioBr-MeDT C.a
COMNT	2-ThioMeDT-Br2
DATIM	/prog/mod/proc1d /op
OBNUC	13C
EXMOD	zgpg30
OBFRQ	100.62 MHz
OBSET	2.82 KHz
OBFIN	9.80 Hz
POINT	32768
FREQU	23980.81 Hz
SCANS	211
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	23.6 c
SLVNT	CDC13
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	32768

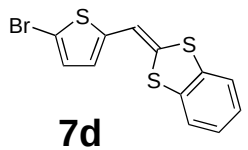


7b

^{1}H NMR of **7d**

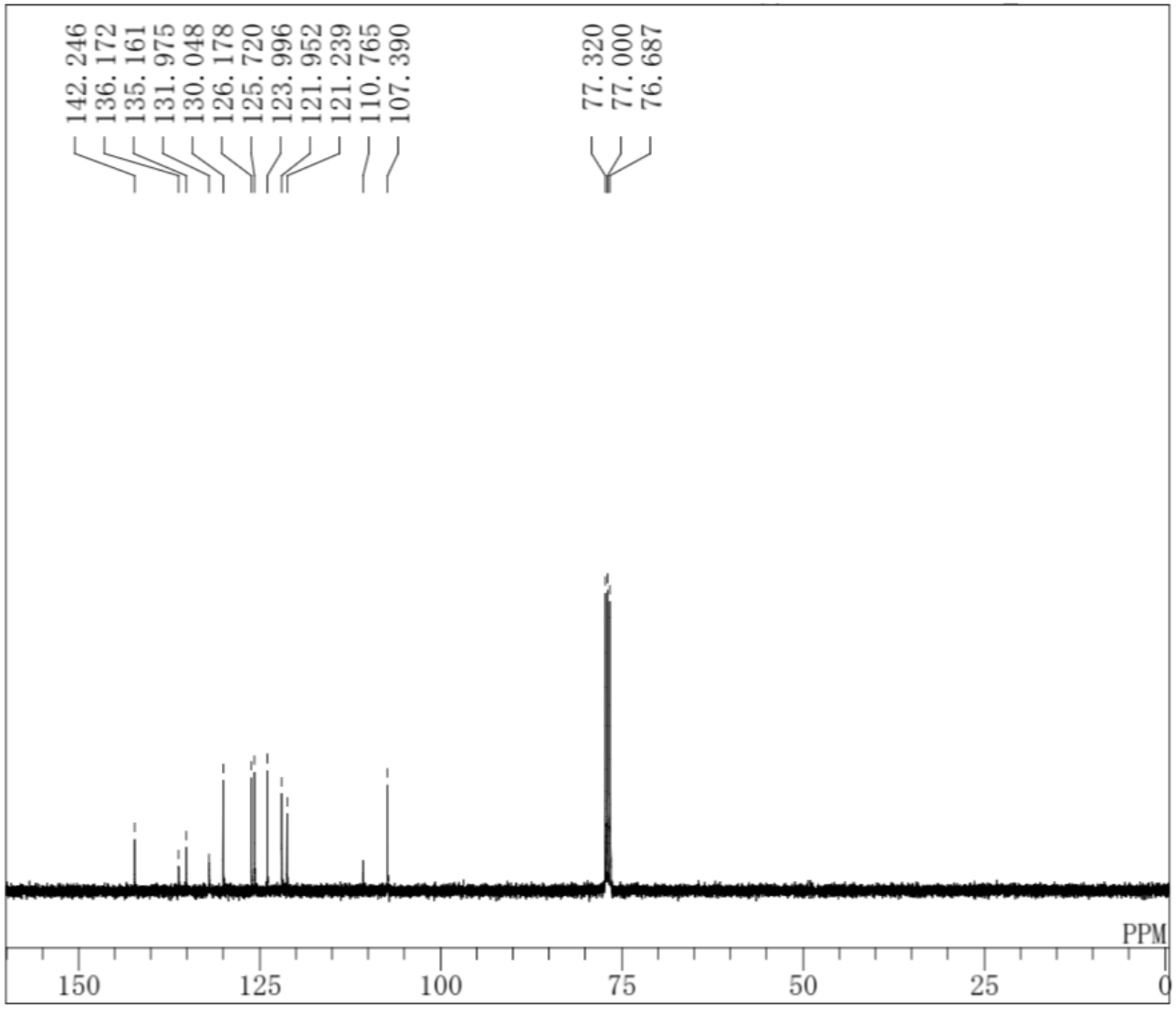


DFILE	03_2-ThioBr-BzDT H.a
COMNT	BzDT-BzBr
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.4 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	362

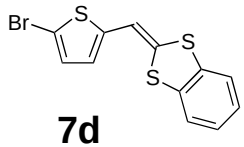


7d

^{13}C NMR of **7d**

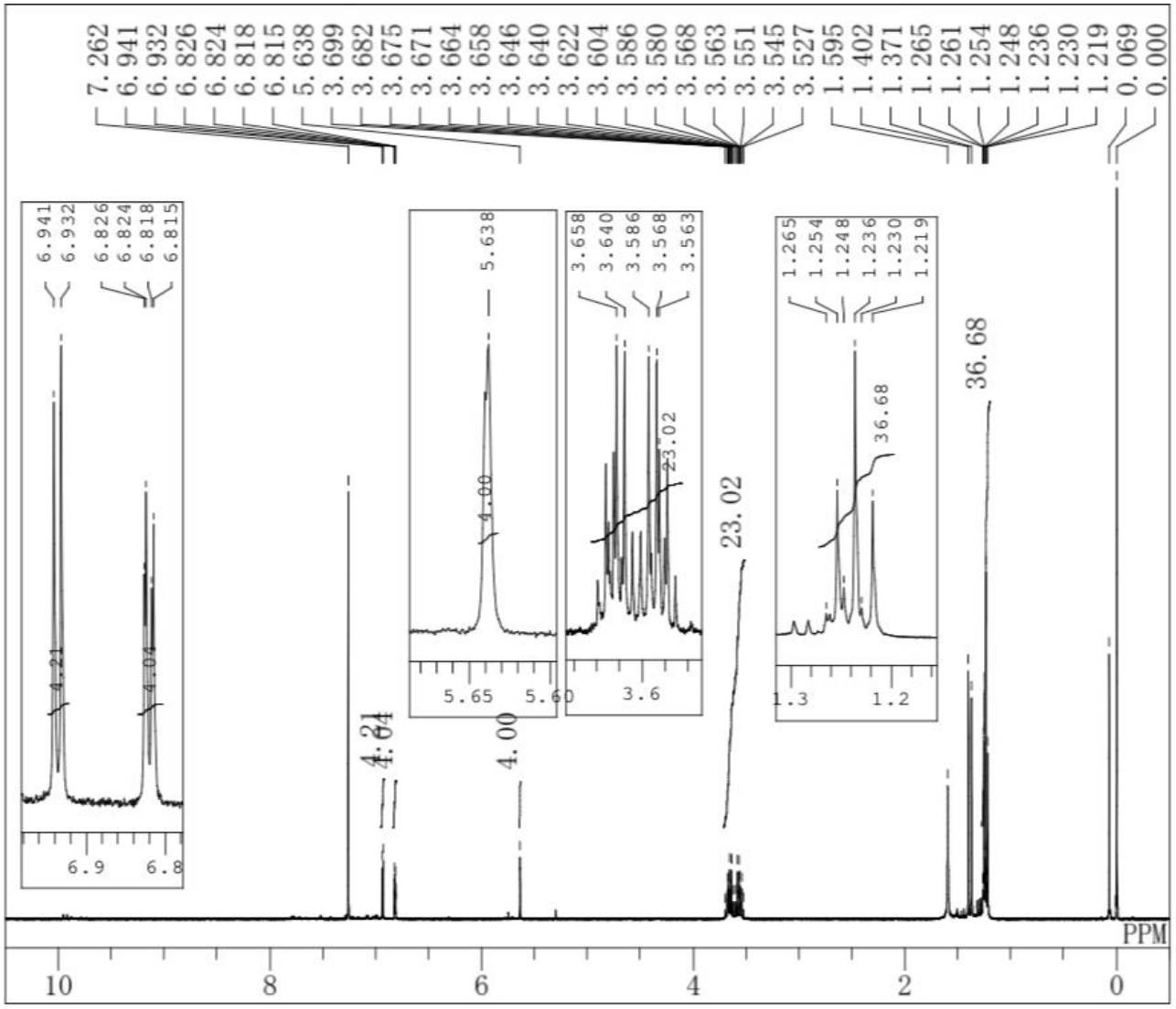


DFILE	03_2-ThioBr-BzDT C.a
COMNT	4-PhBr-BzDT
DATIM	/prog/mod/proc1d /op
OBNUC	13C
EXMOD	zgpg30
OBFRQ	100.62 MHz
OBSET	2.82 KHz
OBFIN	9.80 Hz
POINT	32768
FREQU	23980.81 Hz
SCANS	518
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	23.9 c
SLVNT	CDC13
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	20642

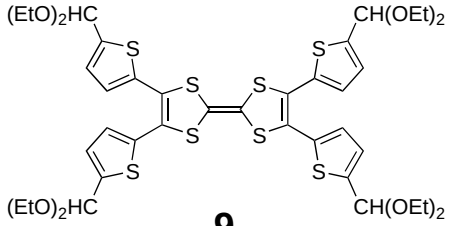


7d

^{1}H NMR of **9**

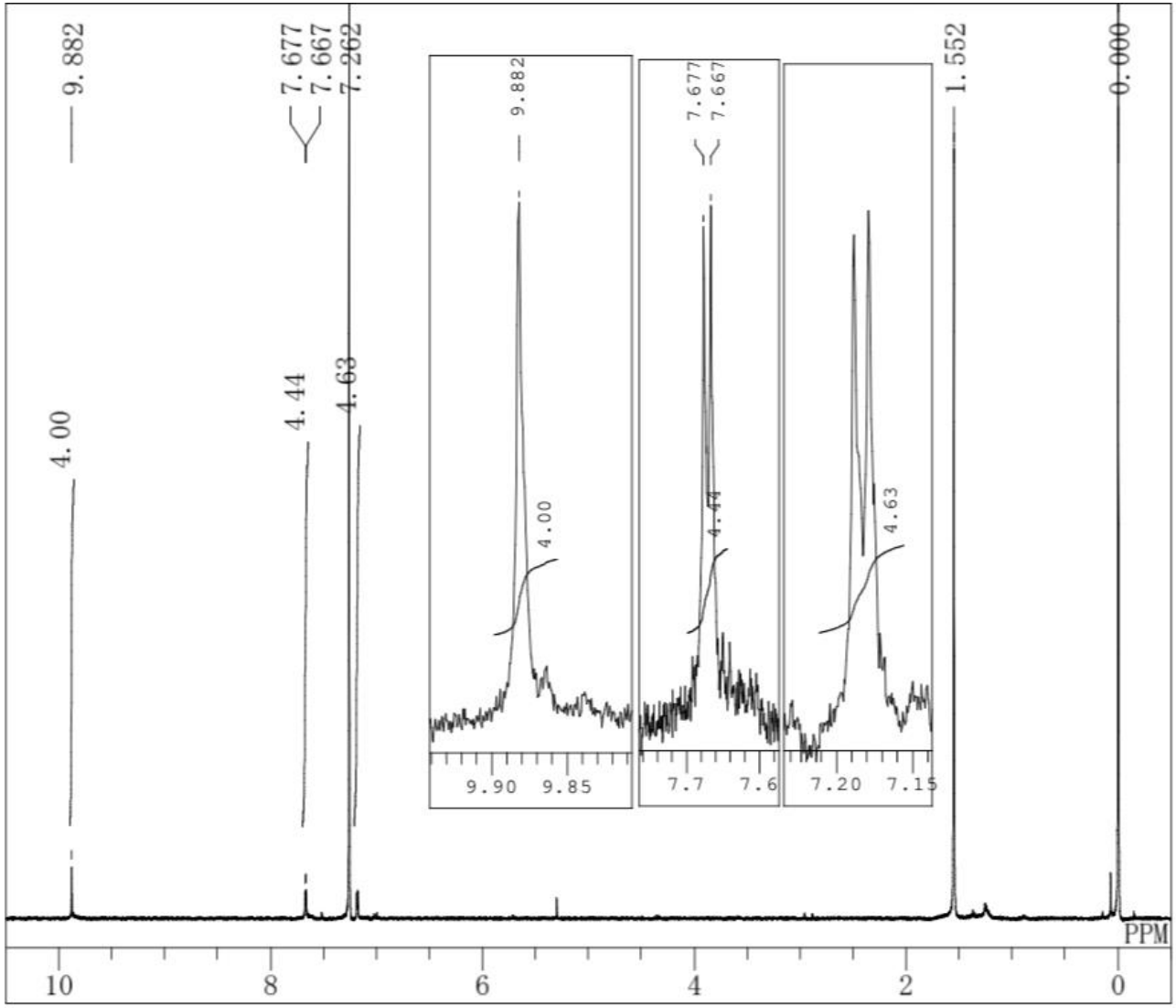


DFILE 9_2-ThioCHOEt2精製せ
COMNT TTF-4Ar-thio-CH(OEt)
DATIM /prog/mod/procld /op
OBNUC 1H
EXMOD zg30
OBFRQ 400.13 MHz
OBSET 2.47 KHz
OBFIN 0.97 Hz
POINT 32768
FREQU 8278.15 Hz
SCANS 16
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 22.2 c
SLVNT CDC13
EXREF 0.00 ppm
BF 0.00 Hz
RGAIN 362

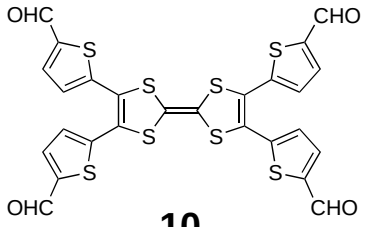


9

^{1}H NMR of **10**

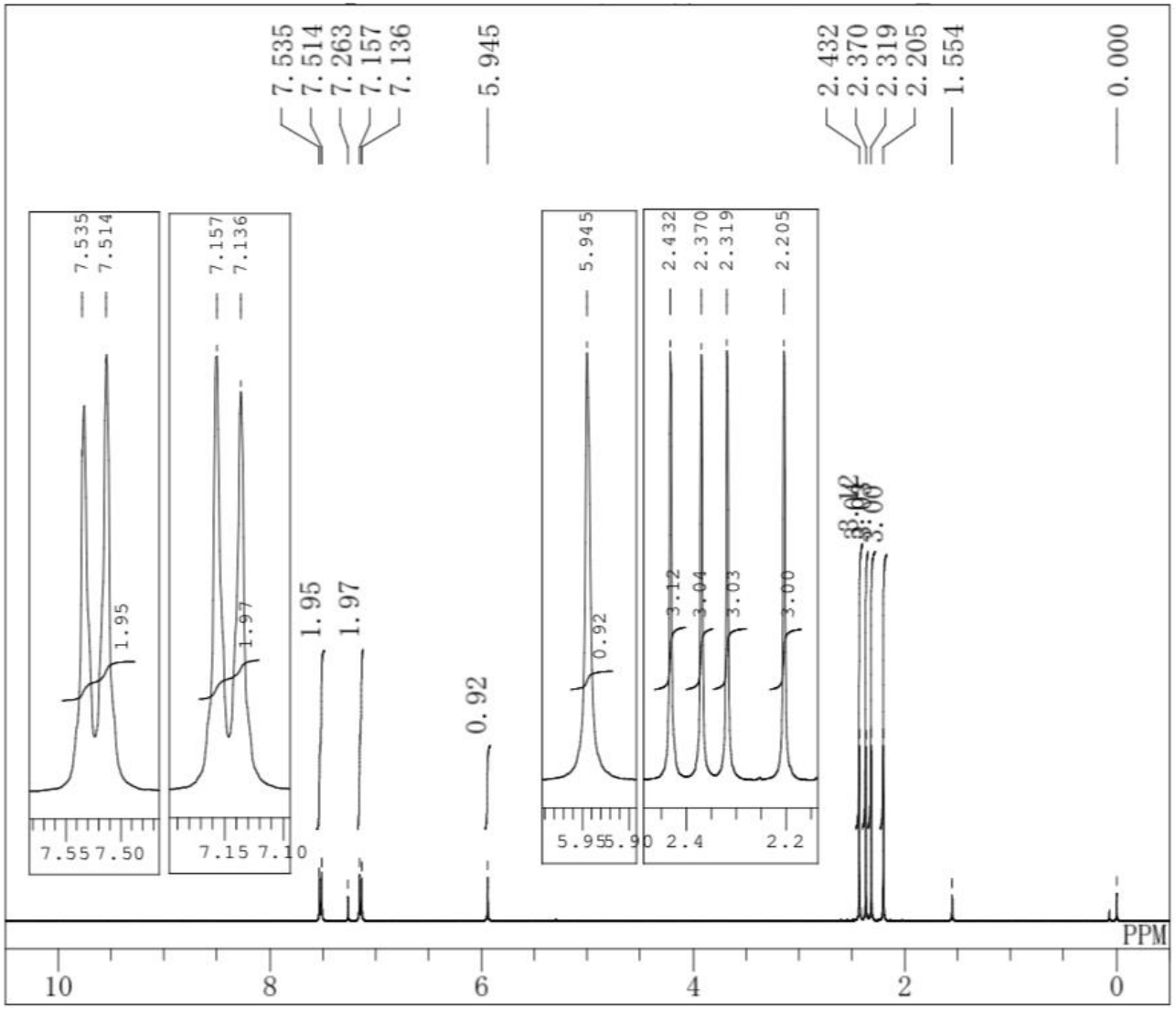


DFILE	10_2-ThioCHO-TTF.als
COMNT	TTF-Thio-CHO
DATIM	/prog/mod/procld /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.1 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	362

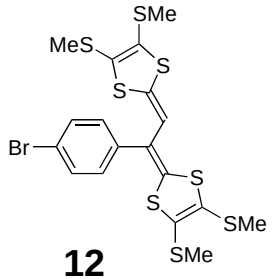


10

^{1}H NMR of **12**

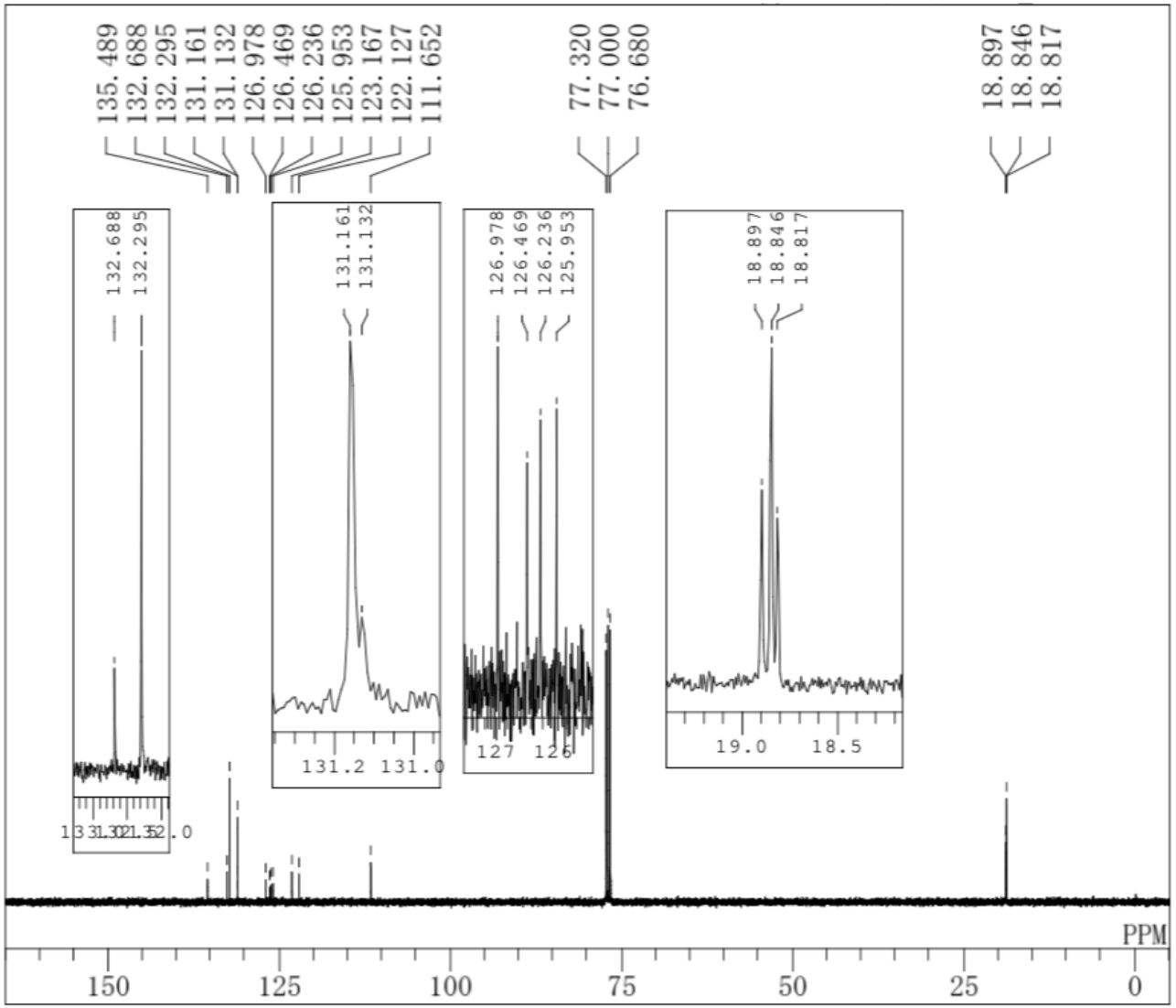


DFILE 12_4-PhBr-SMeEBDT H.
COMNT 4-PhBr-SMeDT-SMeDT
DATIM /prog/mod/proc1d /op
OBNUC 1H
EXMOD zg30
OBFRQ 400.13 MHz
OBSET 2.47 KHz
OBFIN 0.97 Hz
POINT 32768
FREQU 8278.15 Hz
SCANS 16
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 22.7 c
SLVNT CDC13
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 228

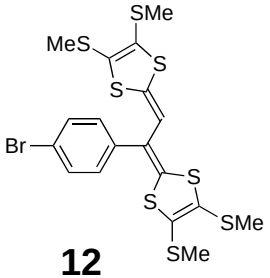


12

^{13}C NMR of **12**

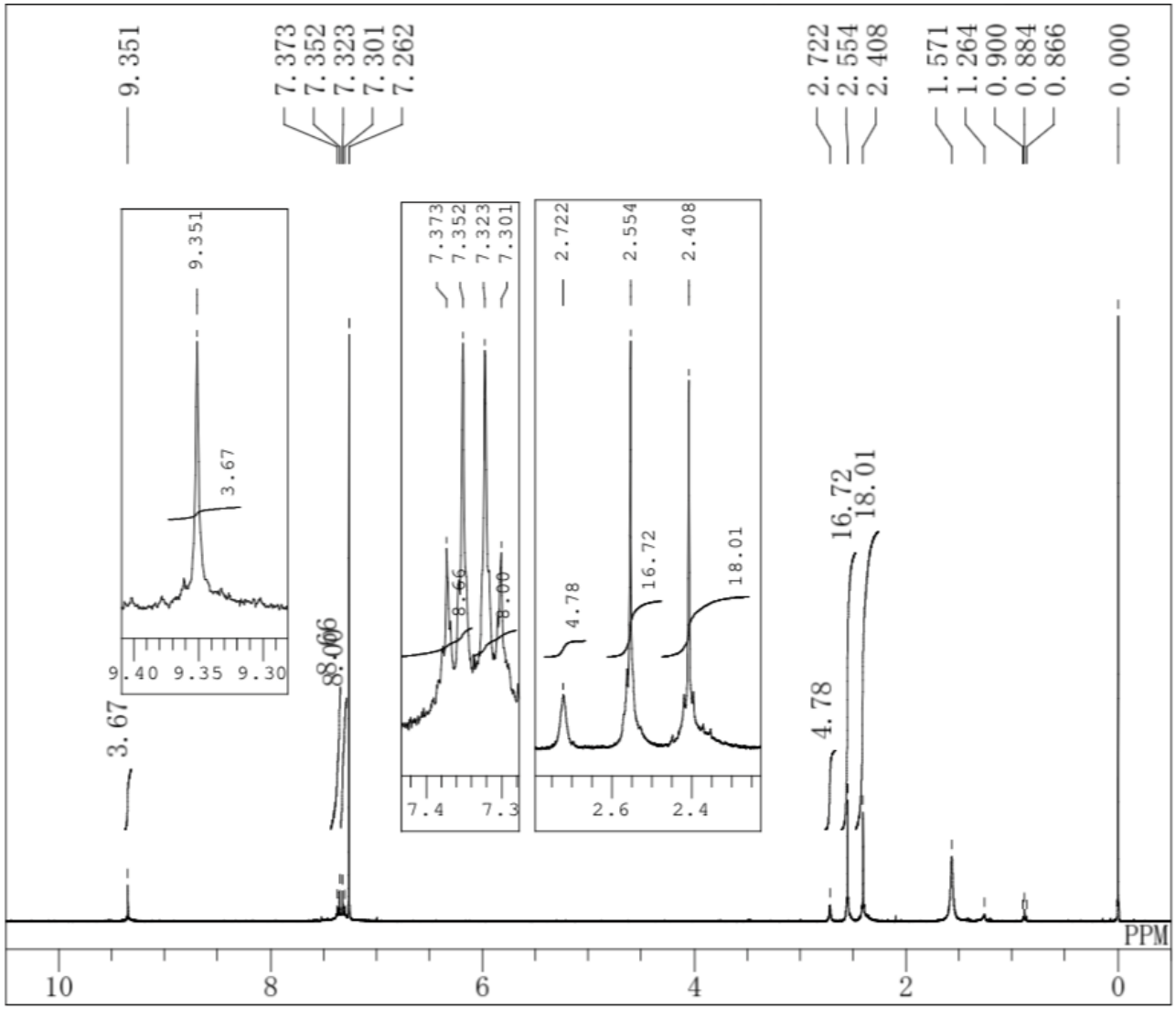


DFILE 009_4-PhBr-SMeEBDT C
COMNT 4-PhBr-SMeDT-SMeDT
DATIM /prog/mod/proc1d /op
OBNUC 13C
EXMOD zgpg30
OBFRQ 100.62 MHz
OBSET 2.82 KHz
OBFIN 9.80 Hz
POINT 32768
FREQU 23980.81 Hz
SCANS 538
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 23.9 c
SLVNT CDC13
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 20642

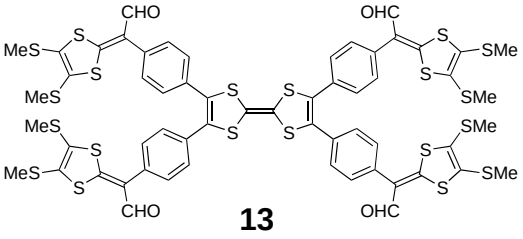


12

^{1}H NMR of **13**

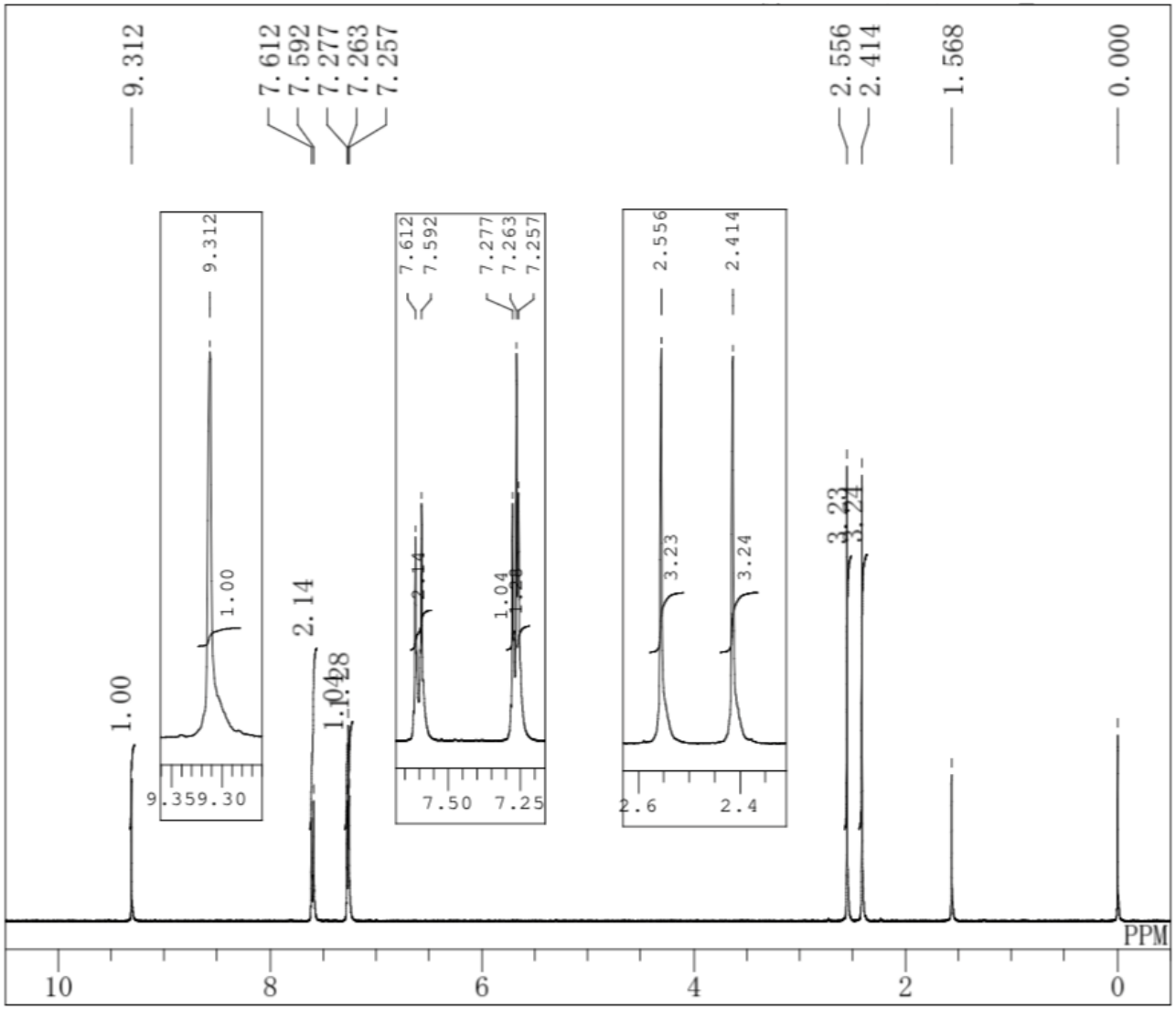


DFILE	00_4-PhSMeDT-TTF-CHO
COMNT	4-PhSMeDT-TTF-CHO
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.4 c
SLVNT	CDC13
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	362

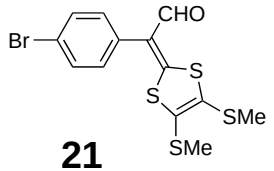


13

^{1}H NMR of **21**

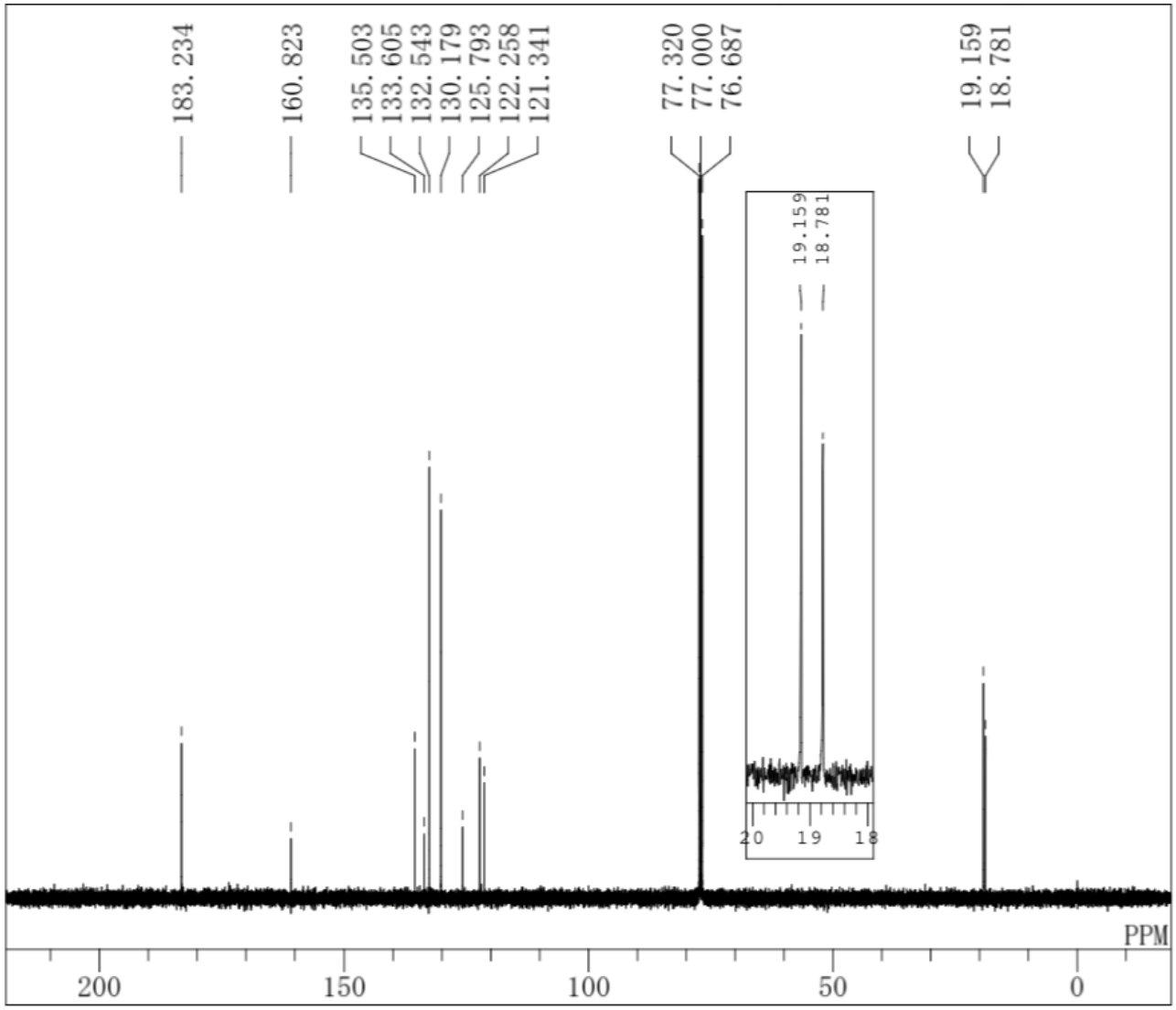


DFILE	008_4-PhBr-SMeDT-CHO
COMNT	4-PhSMeDT-CHO
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.5 c
SLVNT	CDC13
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	362

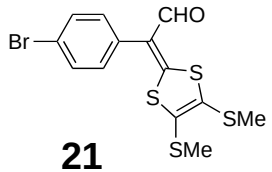


21

^{13}C NMR of **21**




```
DFILE   08_4-PhBr-SMeDT-CHO
COMNT   4-PhBr-SMeDT-CHO
DATIM   /prog/mod/proc1d /op
OBNUC   13C
EXMOD   zgpg30
OBFRQ          100.62 MHz
OBSET            2.82 KHz
OBFIN            9.80 Hz
POINT           32768
FREQU        23980.81 Hz
SCANS             529
ACQTM          0.0000 sec
PD             0.0000 sec
PW1              10.00 usec
IRNUC
CTEMP             24.3 c
SLVNT   CDC13
EXREF            77.00 ppm
BF                0.12 Hz
RGAIN            18390
```



21