Supporting Information

for

Synthesis and Properties of Tetrathiafulvalenes Bearing 6-Aryl-1,4-dithiafulvenes

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CONTENTS

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 100–210μm) or alumina gel (Merck Ltd., Alumina 90, Activated, Neutral, Activity I, 63–200 μm) column chromatography. ^{1}H, 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 solvent. The chemical shifts were referenced to tetramethylsilane for ^{1}H and ^{13}C NMR or the solvent resonances for ^{13}C NMR as internal standards ($CDCl_3$: 77.0 ppm, C_6D_6: 128.0 ppm). MS spectra were determined on JEOL JMS-S3000. Melting points were determined with a Yanaco MP-500D. Cyclic voltammetries (CV) were recorded on ALS/chi 617B Electrochemical analyzer. The CV cell consisted of Pt working electrode, Pt wire counter electrode, and an $Ag/AgNO_3$ reference electrode. The measurements were carried out in benzonitrile with a concentrate 0.1 M nBu$_4$N$^+$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 synthesis of 1, 2, and 4: $Pd(OAc)_2$ (6.8 mg, 0.0124 mmol), P*t*Bu$_3$•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) was added. The mixture heated at 110 °C for 36 h. The organic compounds were extracted with dichlorometane 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 an eluent to yield **1a** as an 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).

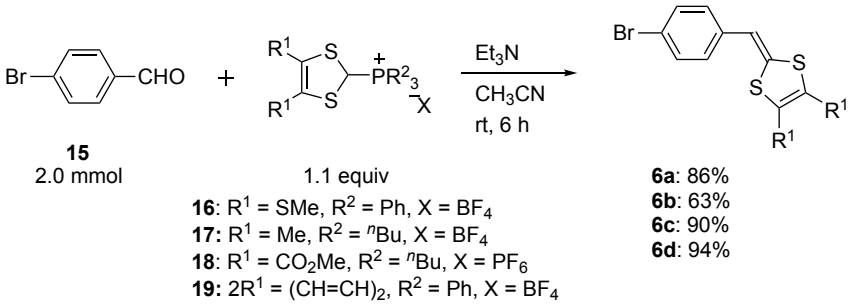
Typical procedure for synthesis of 3: Compound **10** (15.1 mg, ca. 0.0233 mmol), **11** (43.0 mg, 0.186 mmol), dry-toluene (0.9 mL), and $P(OEt)_3$ (0.9 mL) were placed in a 50-mL

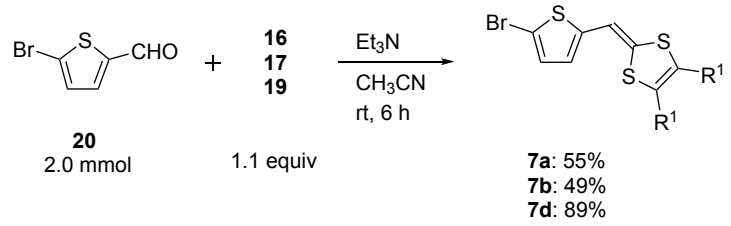
reaction flask under an argon atmosphere. The mixture heated at reflux for 12 h. After removal of solvent and excess $P(OEt)_3$, the residue was purified by silica gel chromatography with dichlorometane as an eluent. The product **3** was obtained by suction filtration with methanol and hexane in 29% 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 °C. 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 heated at reflux for 12 h. After removal of solvent and excess $P(OEt)_3$, the residue was washed by methanol, hexane, and acetone in 44% yield from **1a**.

Compounds 6 and 7 were synthesized as below;





Typical procedure for 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) was added triethylamine (2.5 mL) at 0 °C under an argon atmosphere and the mixture was stirred for 6 h at room temperature. After removal of 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).

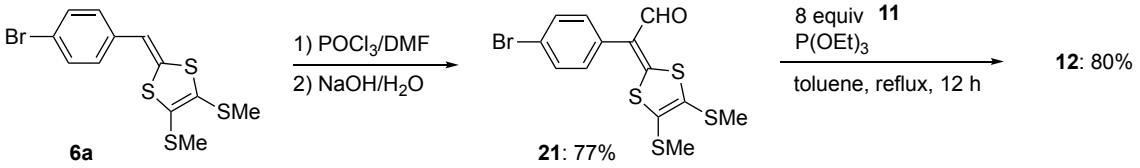
7d: White powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.64 (s 1H), 6.68 (d , *J* = 4.0 Hz, 1H), 6.99 (d , *J* = 4.0 Hz, 1H), 7.12-7.17 (m, 2H), 7.23-7.25 (m, 1H) , 7.28-7.32 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 107.4, 110.8, 121.2, 122.0, 124.0, 125.7, 126.2, 130.0, 132.0, 135.2, 136.2, 142.2; Mp 68–69 °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 (2mL) and TTF (38.4 mg, 0.188 mmol) was added. The mixture heated at 110 °C for 72 h. The obtained solid was washed by dichlorometane and methanol to yield **9** as a 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) was added PTSA•H_2O (244.0 mg, 0.602 mmol) at room temperature and the mixture was

stirred for 1 h. The organic compounds were extracted with dichlorometane three times. The combined organic layer was washed with H_2O, sat. $NaHCO_3$ aq., and sat. NaCl aq., dried over anhydrous Na_2SO_4, and concentrated in vacuo. The obtained solid was washed by methanol and hexane to yield **10** as a black solid. Being identified by ^1H NMR, this compound was used for the next step without further purification.

Compound 12 was synthesized as 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 heated at reflux for h. After removal of solvent and excess $P(OEt)_3$, The residue was washed by methanol in 80% yield.

12: Yellow powder; ^1H 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 °C; 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) was added $POCl_3$ (74 μL, 0.79 mmol) at 0 °C and the mixture was warmed to room temperature and stirred for 2 h. After the reaction, 1M 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 dichlorometane. The combined organic layers were washed with H_2O and sat. NaCl aq. three times, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The product was obtained by suction filtration with dichlorometane and hexane in 44% yield from **1a**. Being identified by ^1H NMR, this compound was used for the next step without further purification.

Synthesis of 21: Compound **6a** (1.150 g, 3.16 mmol) in DMF (20 mL) was added $POCl_3$ (1.2 mL, 12.7 mmol) at 0 °C and the mixture was warmed to room temperature and stirred for 2 h. After the reaction, 1M 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 sat. NaCl aq. Three 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 compound **3a, 4** was carried out based on t density functional theory (DFT) using spin-restricted B3LYP/6-31G(d,p) level of theory.

(a) **3a** (b) **4**

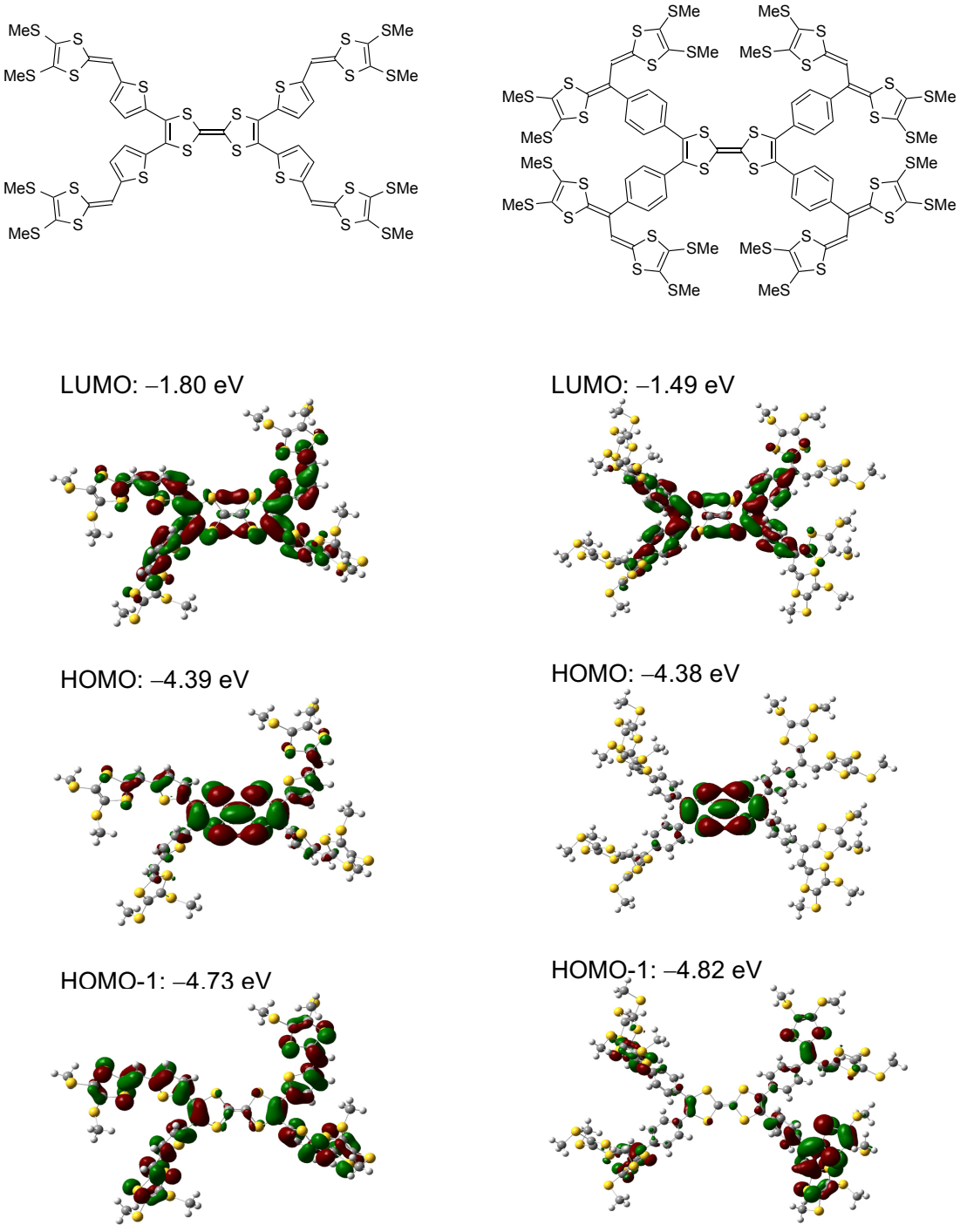
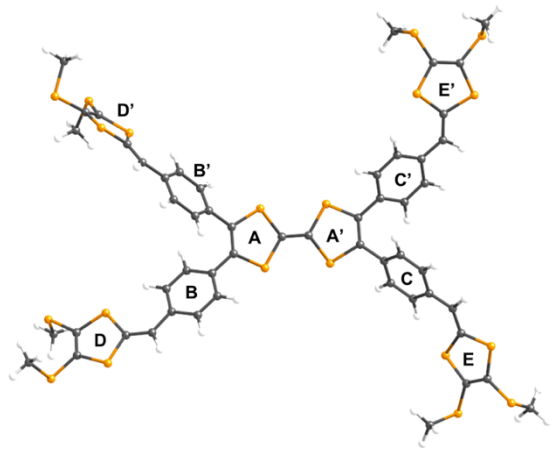
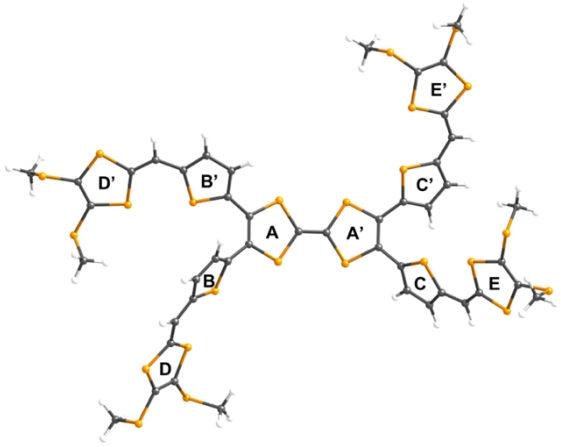
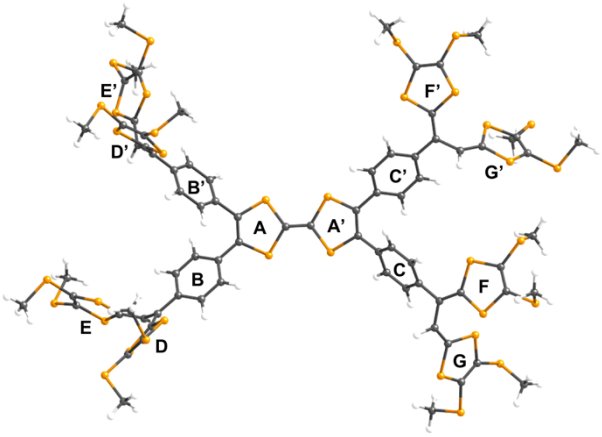


Figure S1. (a) Molecular orbitals of **3a** and (b) **4**.

The dihedral angles

Table S1. The dihedral angles of **1a**, **3a**, **4**

 **1a**		 **3a**	
A–A’	155.5º	A–A’	155.7º
A–B	137.9º	A–B	51.0º
A–B’	48.5º	A–B’	146.6º
A’–C	48.6º	A’–C	52.1º
A’–C’	136.6º	A’–C’	143.8º
B–D	1.5º	B–D	9.4º
B’–D’	21.8º	B’–D’	6.7º
C–E	156.1º	C–E	8.0º
C’–E’	12.3º	C’–E’	9.5º
A–D	156.1º	A–D	42.2º
A–D’	68.6º	A–D’	149.7º
A’–E	31.1º	A’–E	44.2º
A’–E’	157.5º	A’–E’	152.9º



4

A'–A	164.3°	B–E	94.7°
A–B	142.5°	B'–E'	84.7°
A–B'	54.4°	C–G	117.0°
A–C	92.7°	C'–G'	81.8°
A–C'	99.9°		
B–D	50.3°		
B'–D'	48.4°		
C–F	50.0°		
C'–F'	129.4°		
D–E	111.6°		
D'–E'	50.1°		
F–G	110.5°		
F'–G'	111.7°		
A–D	92.7°		
A–D'	99.9°		
A'–F	11.0°		
A'–F'	9.1°		
B–E	94.7°		
B'–E'	84.7°		
C–F	50.0°		
C'–F'	129.4°		

Cyclic Voltammograms

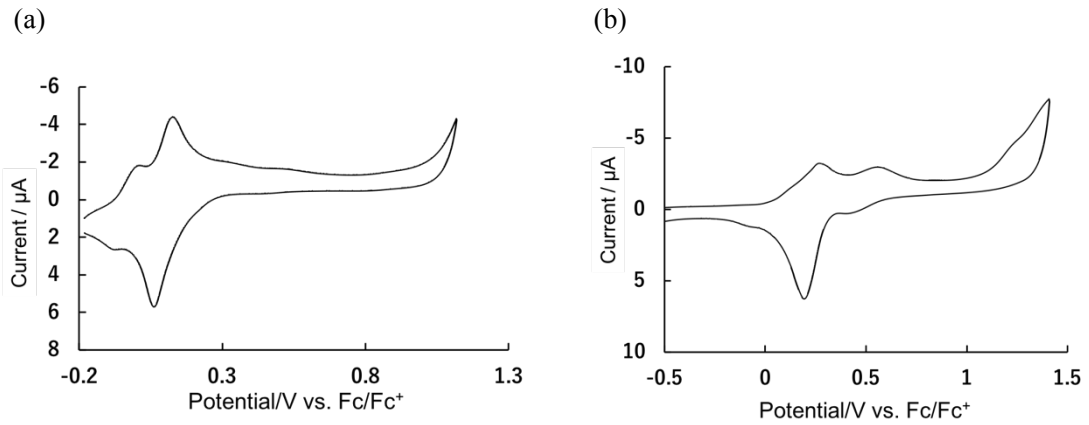


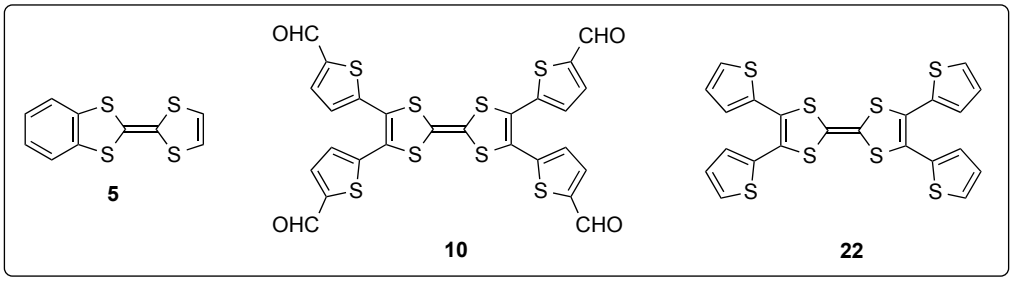
Figure S2. Cyclic voltammograms of (a) **2a** and (b) **3a** in PhCN/CS_2 (1/1, V/V) (0.3 mM) solution in designated solvent containing 0.1 m *n*Bu_4NPF_6.

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

	E_1/V	E_2/V	E_3/V	E_4/V	E_5/V	E_6/V
2a	–0.05	+0.09		+0.49		
3a	+0.14		+0.25			+0.52
5[b]	–0.01	+0.42				
10[b]	–0.25	+0.60				
22[b]	+0.00	+0.47				

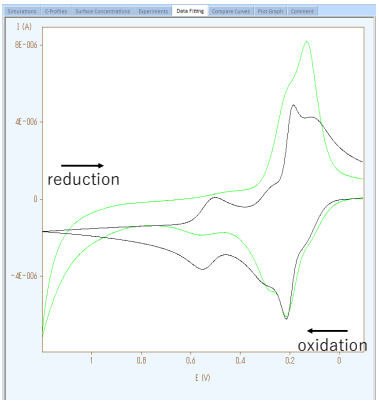
[a]In PhCN/CS_2 (1/1, V/V) containing 0.1 M ^{n}Bu_4NPF_6, all potentials measured against Ag/Ag^+ reference electrode and converted to vs. Fc/Fc^+.

[b]In PhCN containing 0.1 M ^{n}Bu_4NPF_6, all potentials measured against Ag/Ag^+ reference electrode and converted to vs. Fc/Fc^+.



The results of a digital simulation technique of 1a and 4

(a) **1a**



(b) **4**

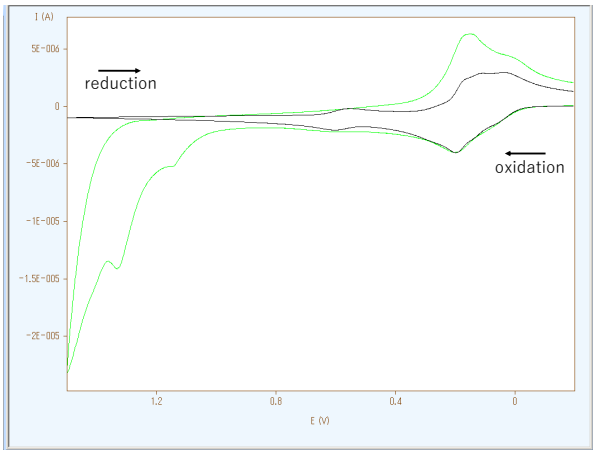


Figure S3. The results of a digital simulations of (a) **1a** and (b) **4**. Black line; disital simulated wave. Green line; observed wave.

Table S2. The following charge-transfer reaction and redox potentials were used for a digital simulation of **1a** and **4**

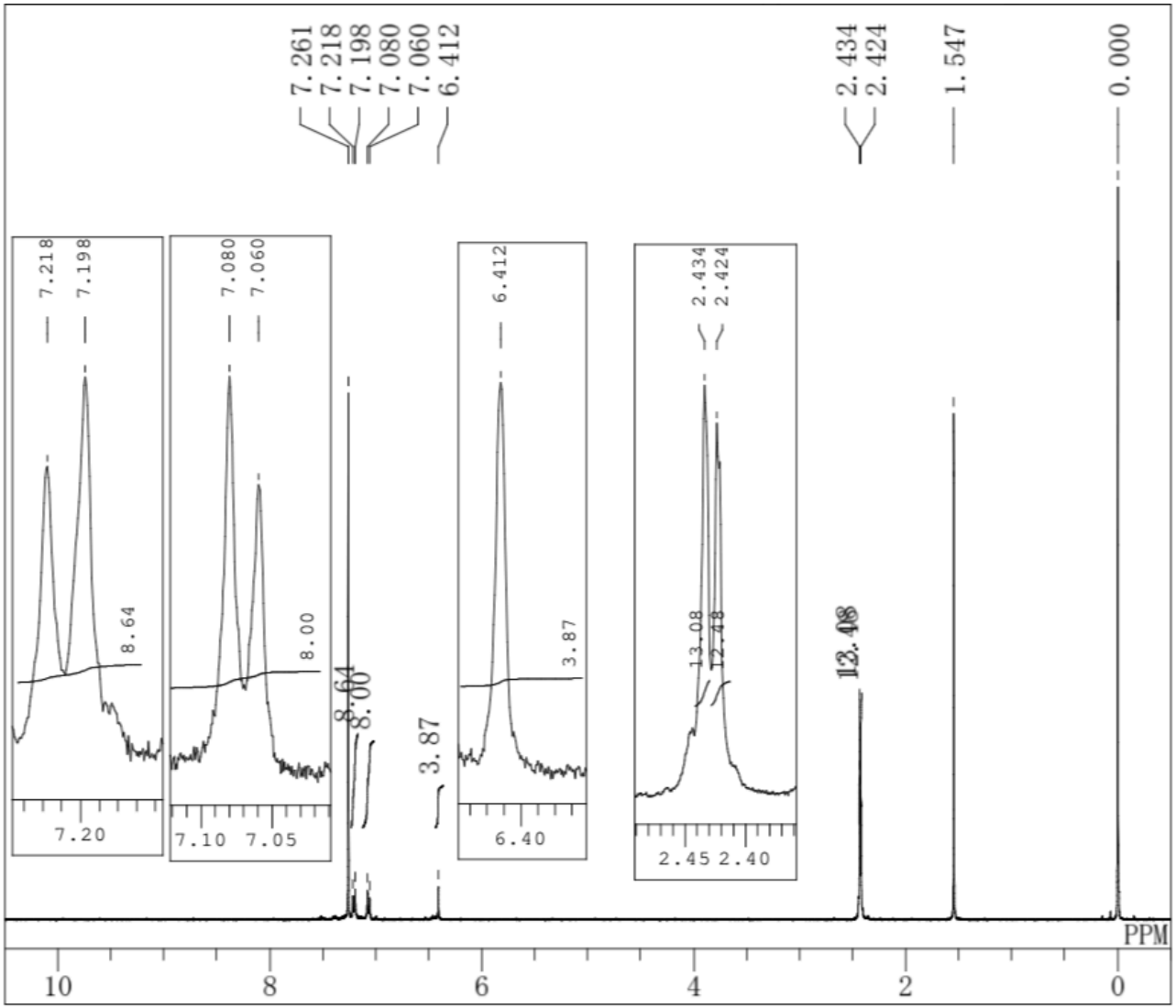
(a) **1a**

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**

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OBSET            2.47 KHz
OBFIN            0.97 Hz
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FREQU         8278.15 Hz
SCANS              16
ACQTM          0.0000 sec
PD             0.0000 sec
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EXREF            0.00 ppm
BF               0.12 Hz
RGAIN             362
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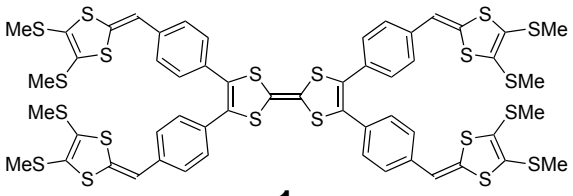
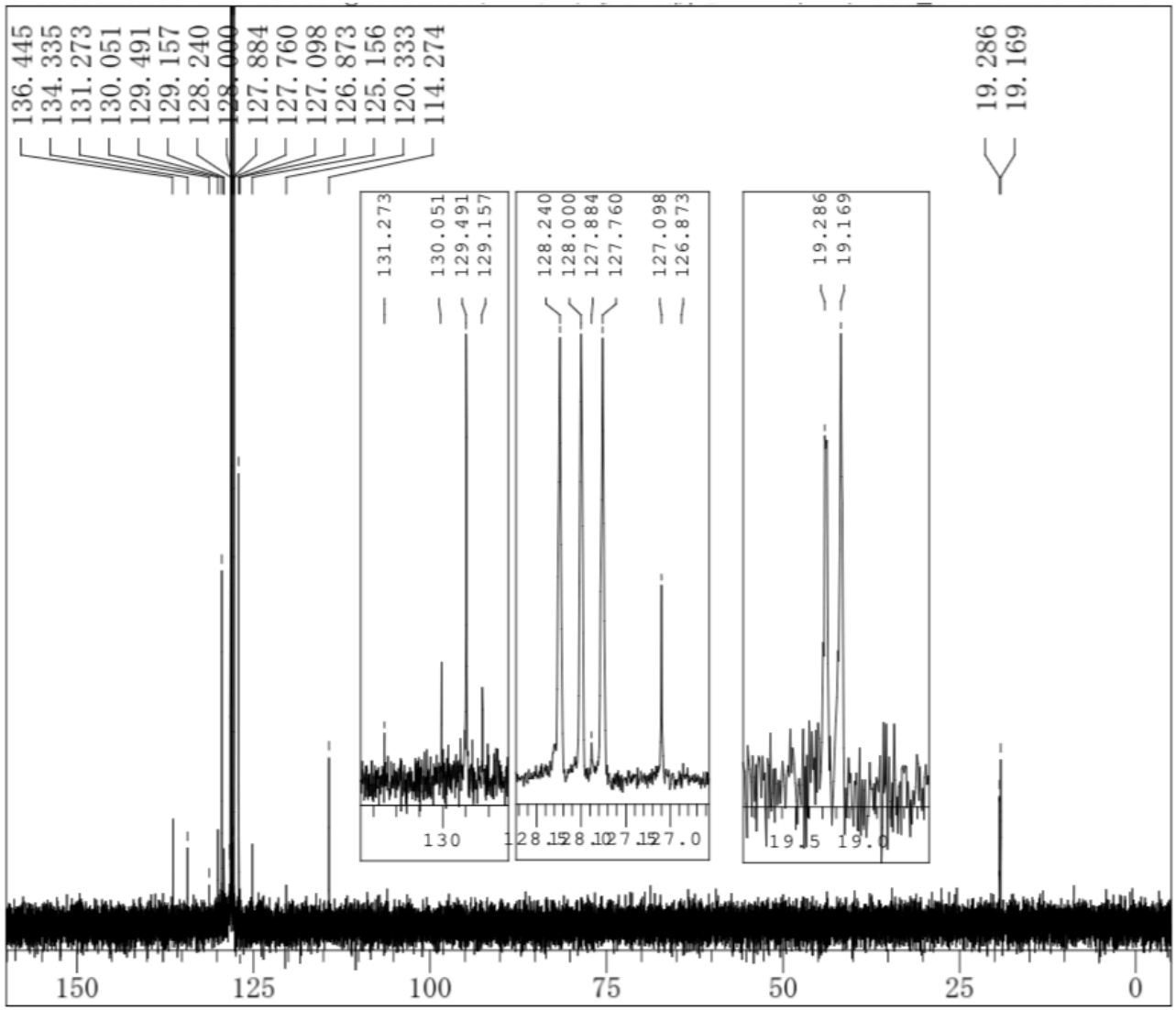


1a

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

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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
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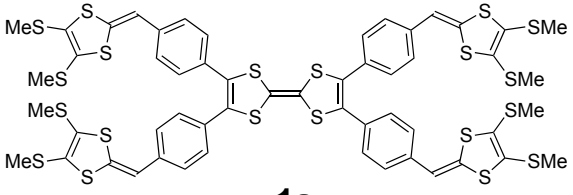
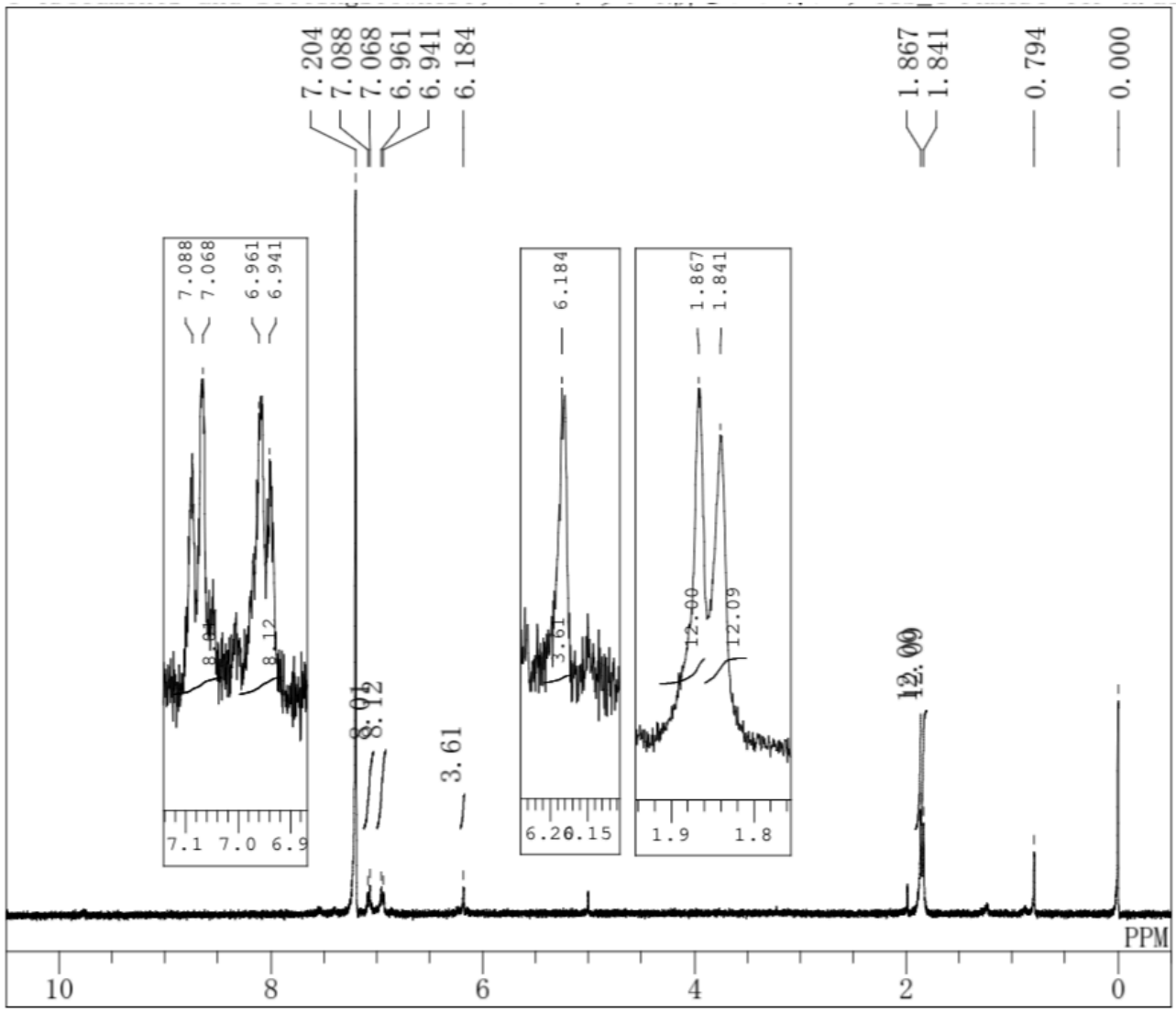
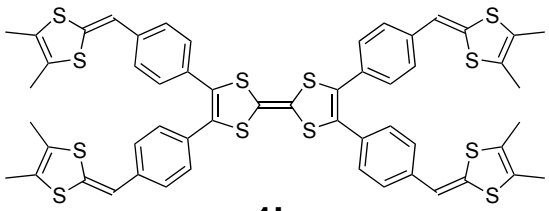


1a

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

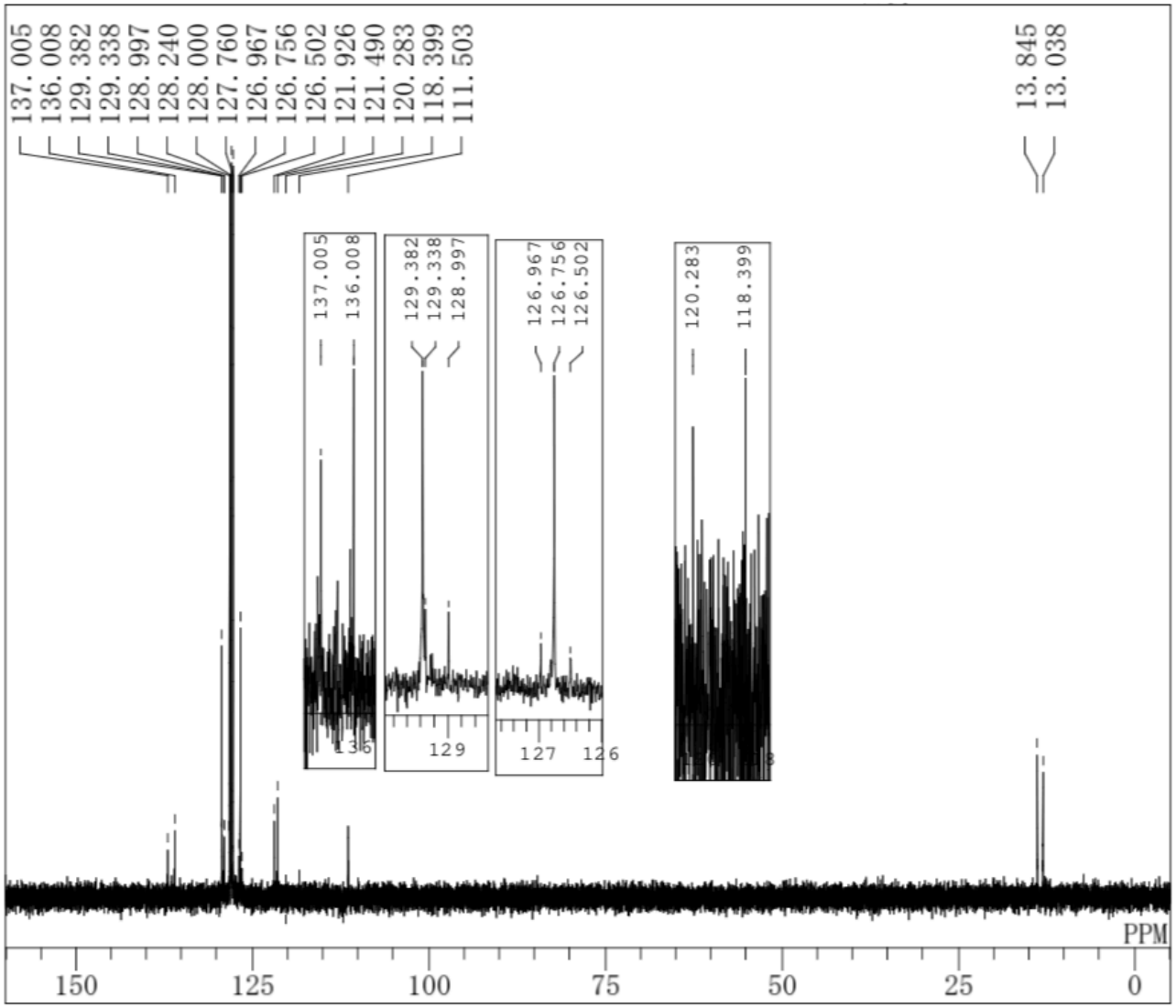


DFILE 1b_4-PhMeDT-TTF H.al
COMNT Me
DATIM /prog/mod/proc1d /op
OBNUC 1H
EXMOD zg30
OBFRQ 400.13 MHz
OBSET 2.47 KHz
OBFIN 0.97 Hz
POINT 32768
FREQU 8278.15 Hz
SCANS 16
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 22.4 c
SLVNT C6D6
EXREF 0.00 ppm
BF 0.00 Hz
RGAIN 456

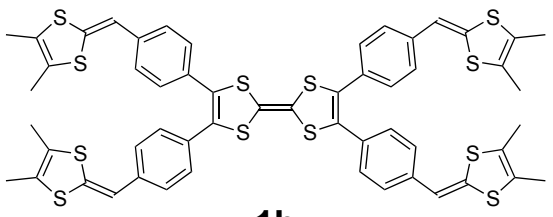


1b

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

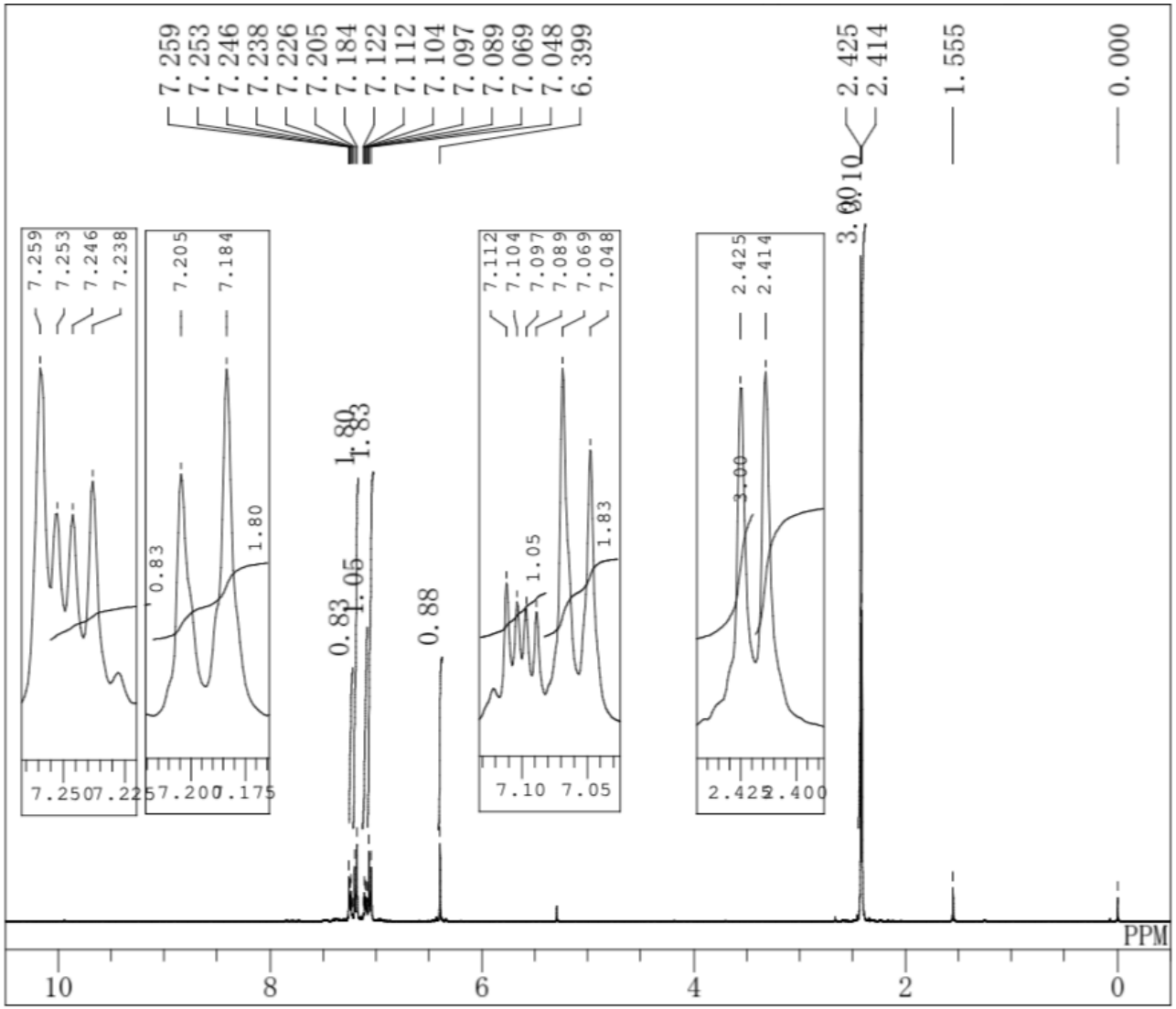


DFILE fid
COMNT 4-PhMeDT-TTF C
DATIM /prog/mod/proc1d /op
OBNUC 13C
EXMOD zgpg30
OBFRQ 100.62 MHz
OBSET 2.82 KHz
OBFIN 9.80 Hz
POINT 32768
FREQU 23980.81 Hz
SCANS 1024
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 23.9 c
SLVNT C6D6
EXREF 128.00 ppm
BF 0.00 Hz
RGAIN 20642

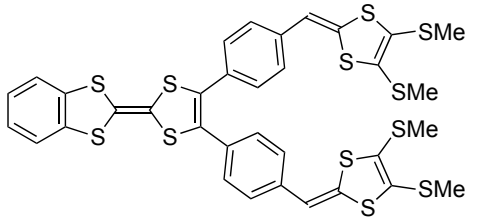


1b

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

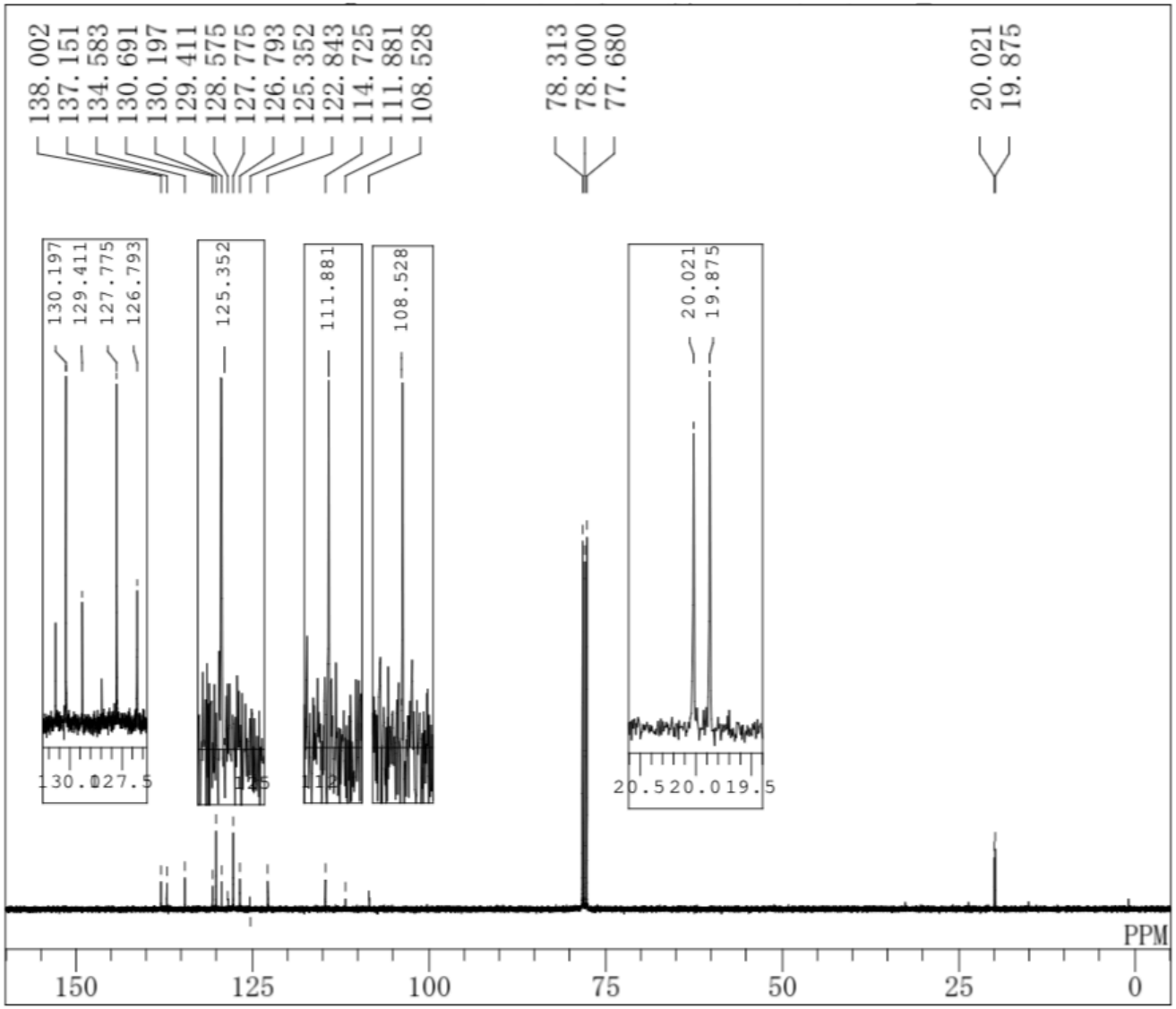



```
DFILE   21_4-PhSMeDT-BzTTF H
COMNT   4-PhSMeDT-BzTTF
DATIM   /prog/mod/proc1d /op
OBNUC   1H
EXMOD   zg30
OBFRQ          400.13 MHz
OBSET            2.47 KHz
OBFIN            0.97 Hz
POINT           32768
FREQU         8278.15 Hz
SCANS              16
ACQTM          0.0000 sec
PD             0.0000 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**

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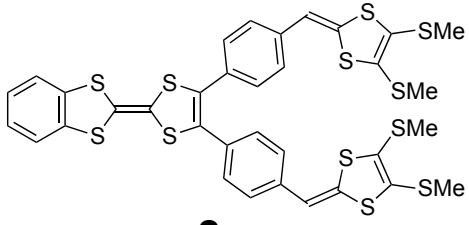
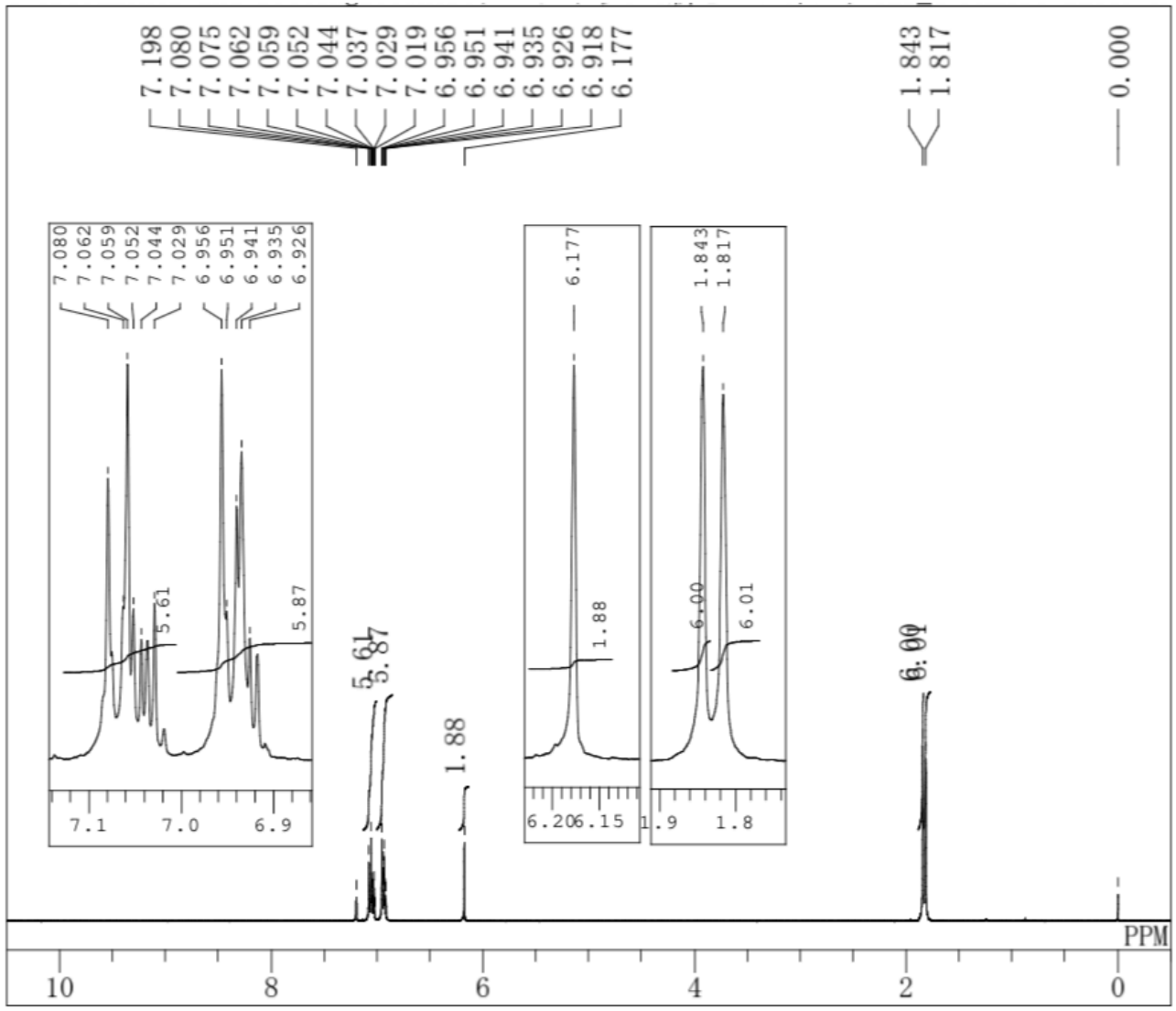
DFILE  2a_4-PhSMeDT-BzTTF C.
COMNT  4-PhSMeDT-BzTTF
DATIM  /prog/mod/proc1d /op
OBNUC  13C
EXMOD  zgpg30
OBFRQ        100.62 MHz
OBSET          2.82 KHz
OBFIN          9.80 Hz
POINT         32768
FREQU      23980.81 Hz
SCANS           912
ACQTM        0.0000 sec
PD           0.0000 sec
PW1          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

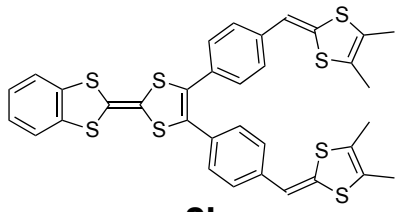


2a

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

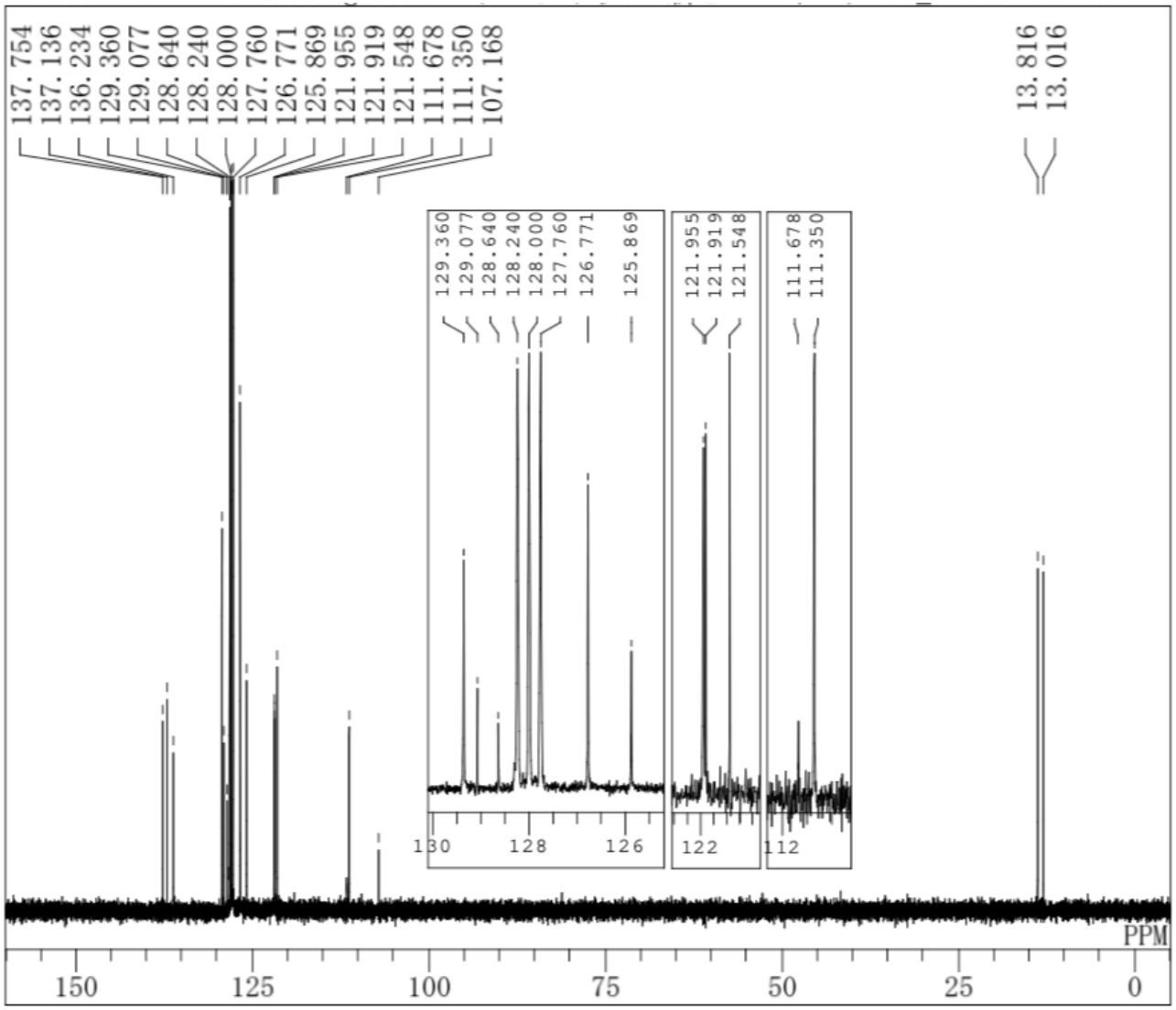


DFILE 2b_4-PhMeDT-BzTTF H
COMNT 4-PhMeDT-BzTTF H
DATIM /prog/mod/proc1d /op
OBNUC 1H
EXMOD zg30
OBFRQ 400.13 MHz
OBSET 2.47 KHz
OBFIN 0.97 Hz
POINT 32768
FREQU 8278.15 Hz
SCANS 16
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 23.2 c
SLVNT C6D6
EXREF 0.00 ppm
BF 0.00 Hz
RGAIN 228

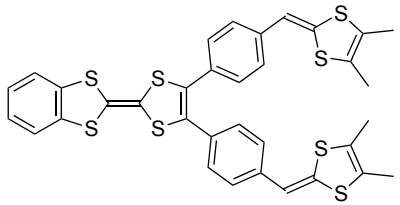


2b

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

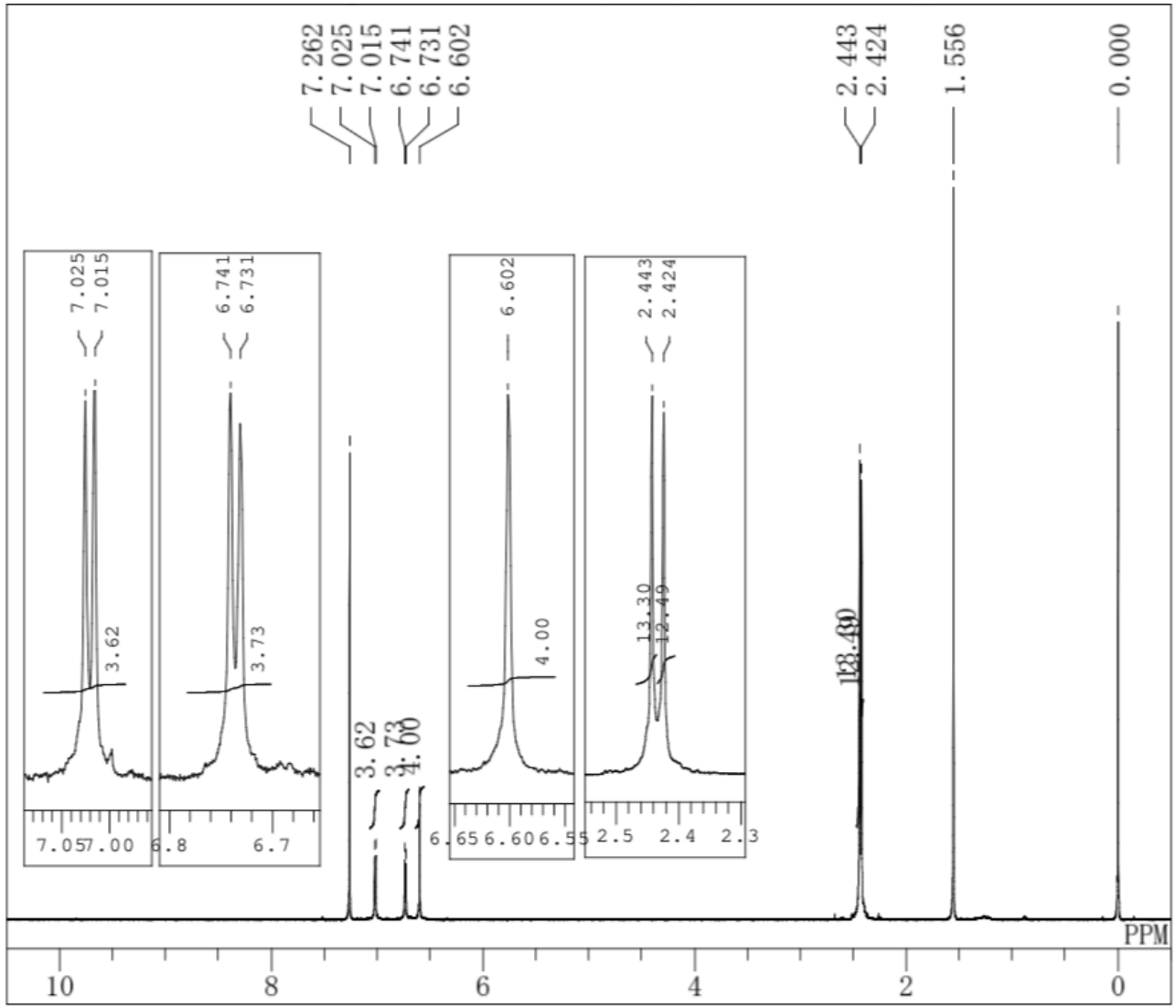


DFILE 2b_4-PhMeDT-BzTTF C.
COMNT 4-PhMeDT-BzTTF C
DATIM /prog/mod/proc1d /op
OBNUC 13C
EXMOD zgpg30
OBFRQ 100.62 MHz
OBSET 2.82 KHz
OBFIN 9.80 Hz
POINT 32768
FREQU 23980.81 Hz
SCANS 1024
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 23.5 c
SLVNT C6D6
EXREF 128.00 ppm
BF 0.00 Hz
RGAIN 20642

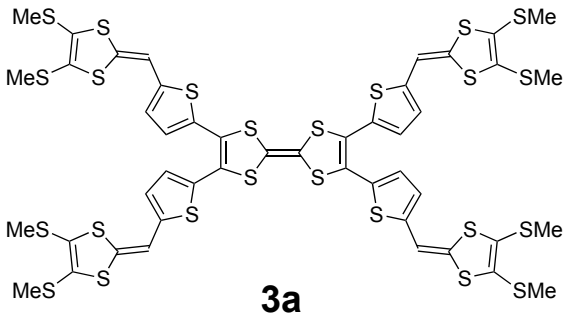


2b

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

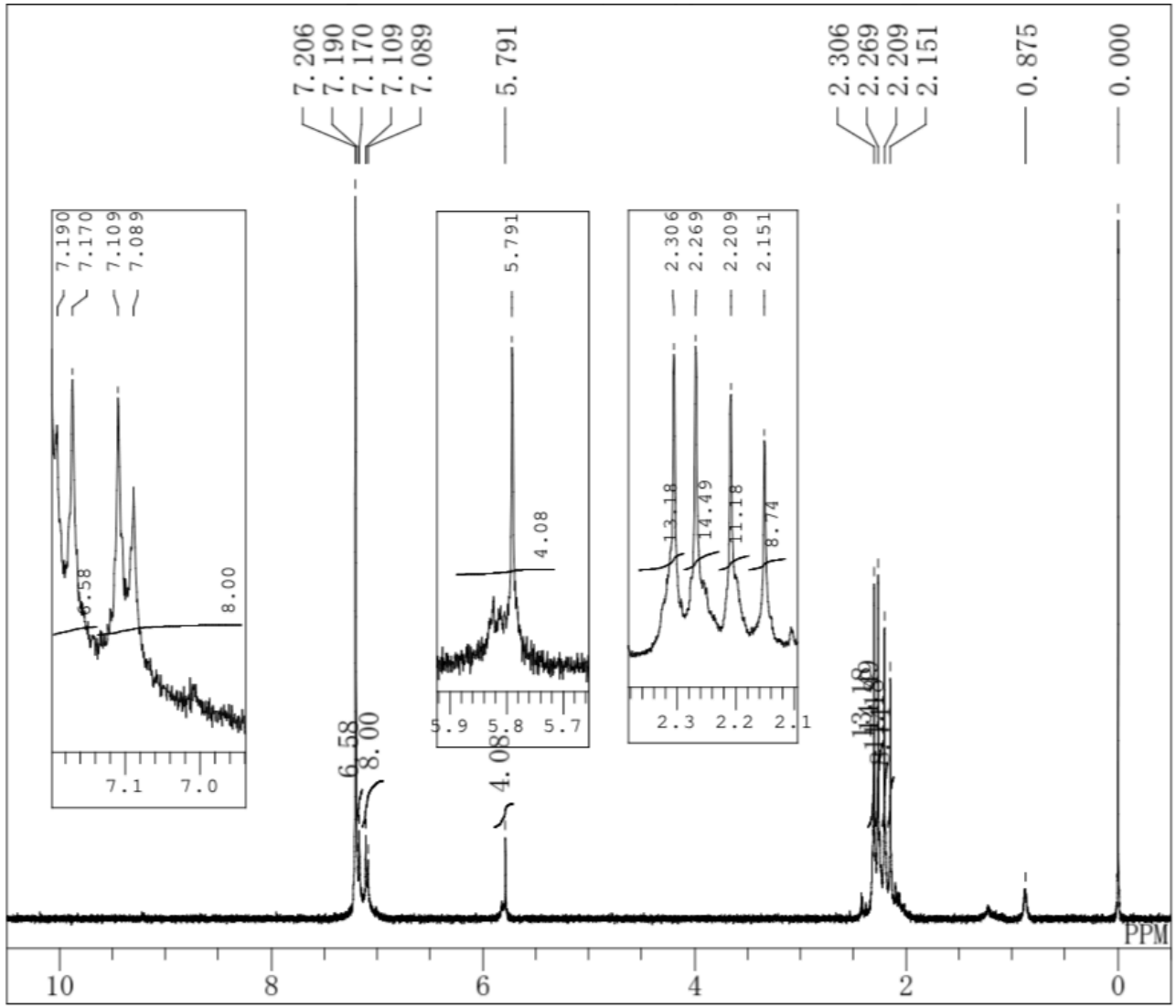



```
DFILE   12_2-ThioSMeDT-TTF.a
COMNT   Thio-SMe-fr2
DATIM   /prog/mod/proc1d /op
OBNUC   1H
EXMOD   zg30
OBFRQ          400.13 MHz
OBSET            2.47 KHz
OBFIN            0.97 Hz
POINT           32768
FREQU         8278.15 Hz
SCANS              16
ACQTM          0.0000 sec
PD             0.0000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

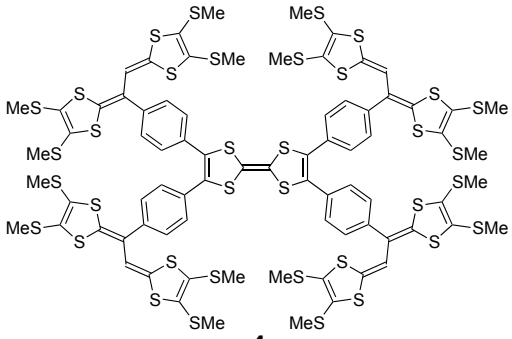


3a

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

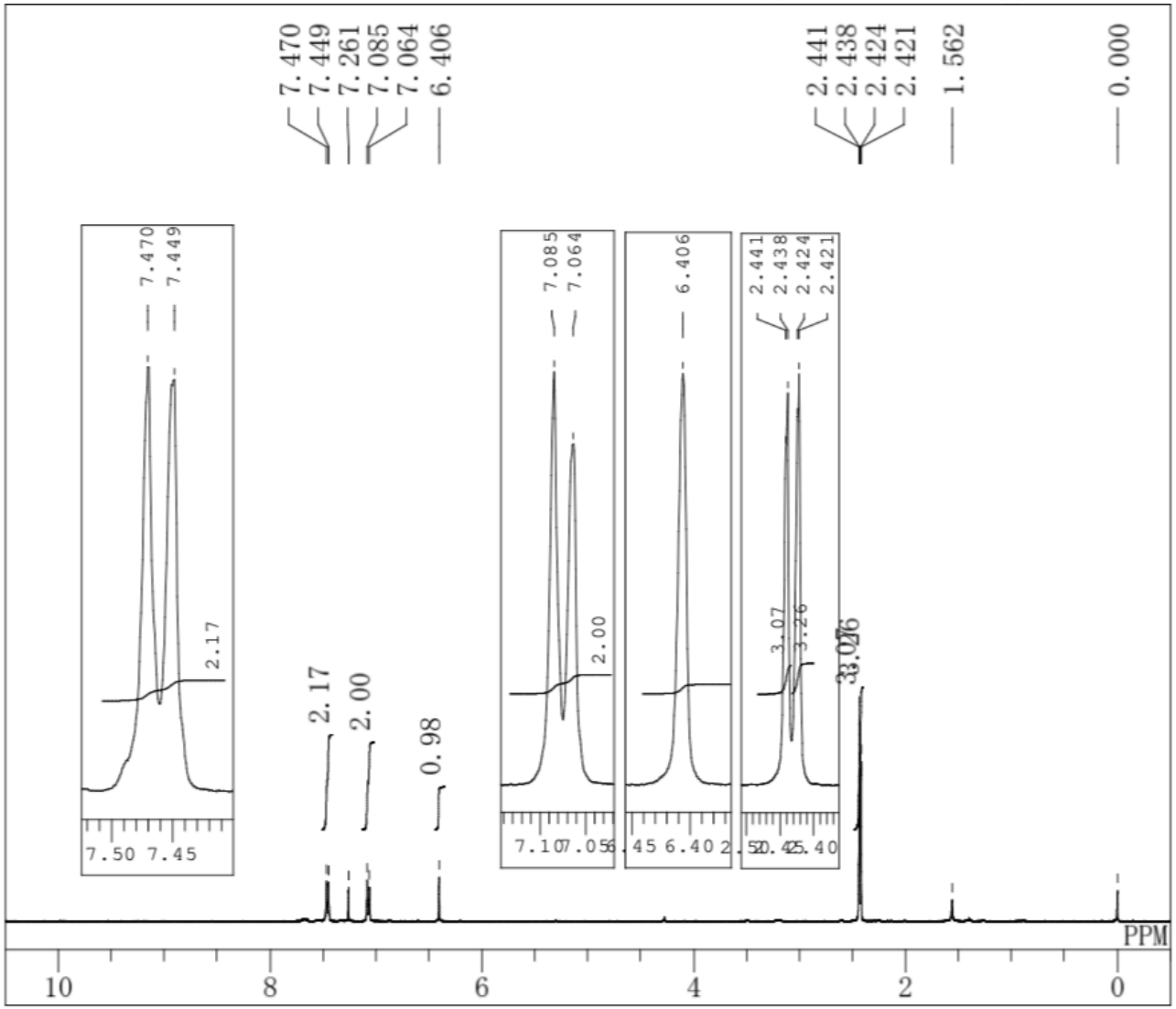


DFILE 4_4-PhSMeEBDT-TTF ar
COMNT 4-PhSMeEBDT-TTF aryl
DATIM /prog/mod/proc1d /op
OBNUC 1H
EXMOD zg30
OBFRQ 400.13 MHz
OBSET 2.47 KHz
OBFIN 0.97 Hz
POINT 32768
FREQU 8278.15 Hz
SCANS 16
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 22.7 c
SLVNT C6D6
EXREF 0.00 ppm
BF 0.00 Hz
RGAIN 362

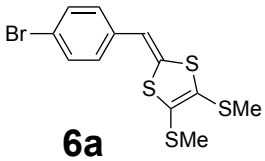


4

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

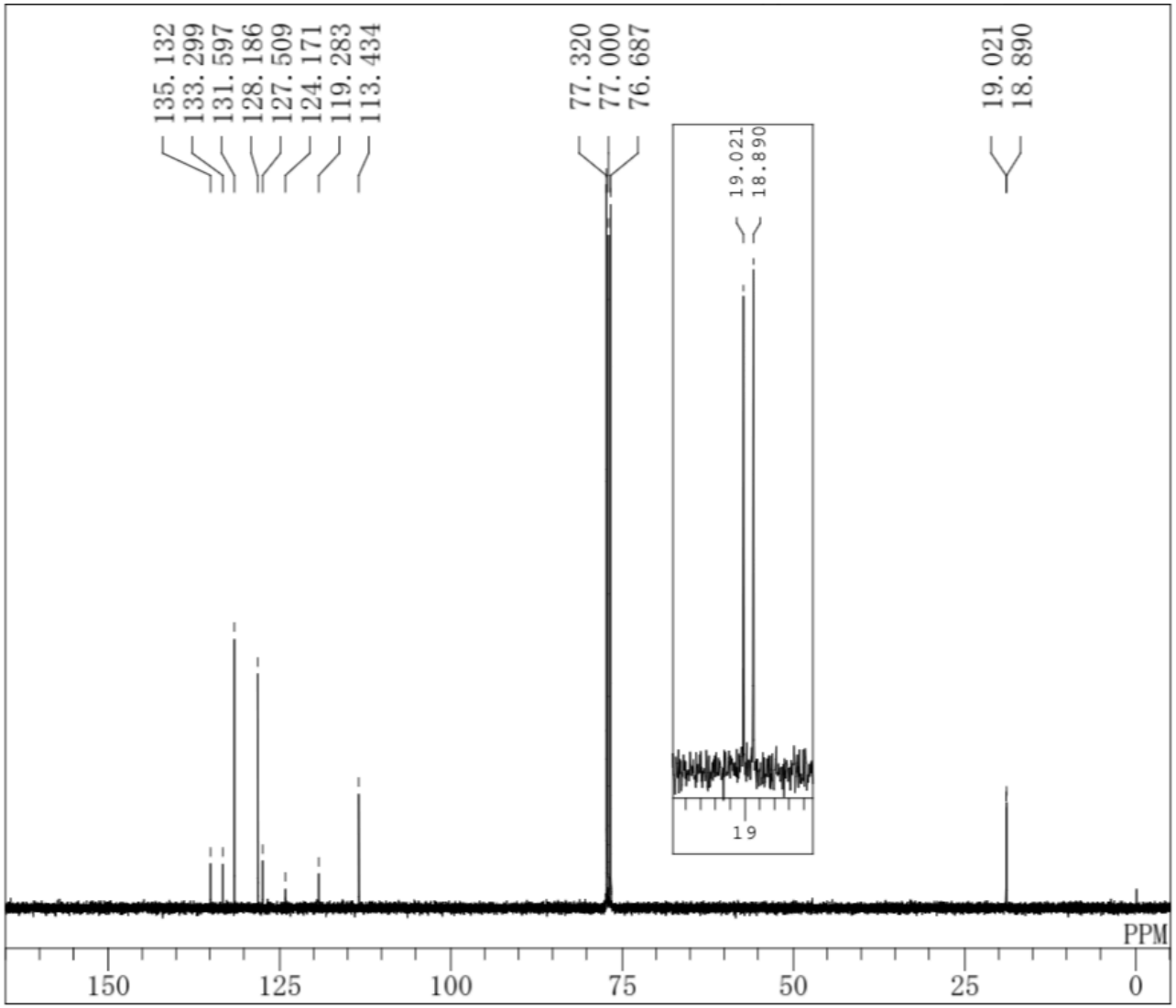


DFILE 04_4-PhBr-SMeDT H.al
COMNT SMeDTBr
DATIM /prog/mod/proc1d /op
OBNUC 1H
EXMOD zg30
OBFRQ 400.13 MHz
OBSET 2.47 KHz
OBFIN 0.97 Hz
POINT 32768
FREQU 8278.15 Hz
SCANS 16
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 22.5 c
SLVNT CDC13
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 322

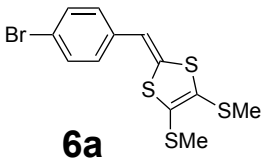


6a

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

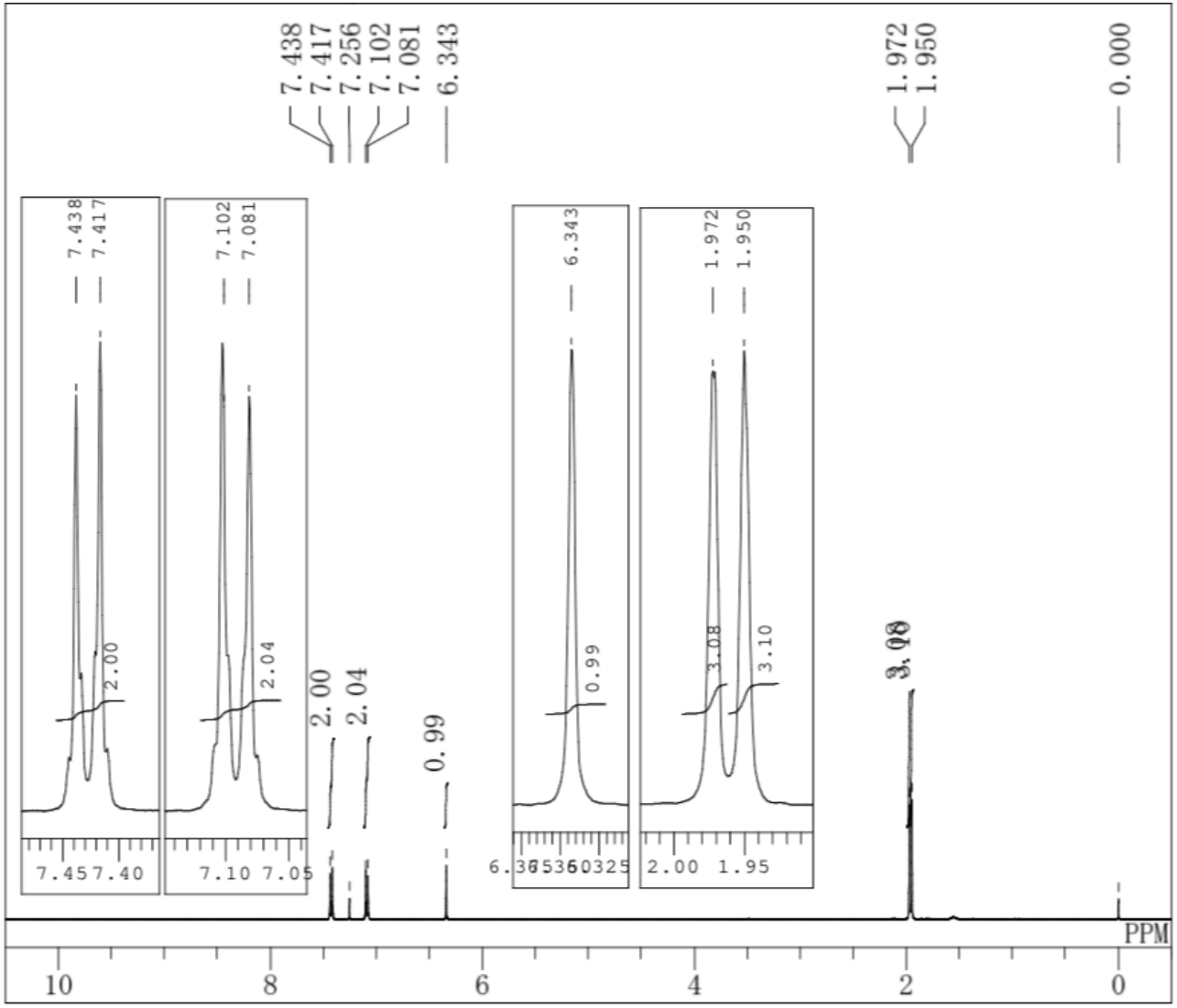


DFILE	04_4-PhBr-SMeDT C.al
COMNT	4-PhSMeDTBr
DATIM	/prog/mod/proc1d /op
OBNUC	13C
EXMOD	zgpg30
OBFRQ	100.62 MHz
OBSET	2.82 KHz
OBFIN	9.80 Hz
POINT	32768
FREQU	23980.81 Hz
SCANS	787
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	23.4 c
SLVNT	CDC13
EXREF	77.00 ppm
BF	0.00 Hz
RGAIN	20642

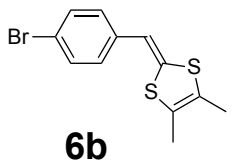


6a

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

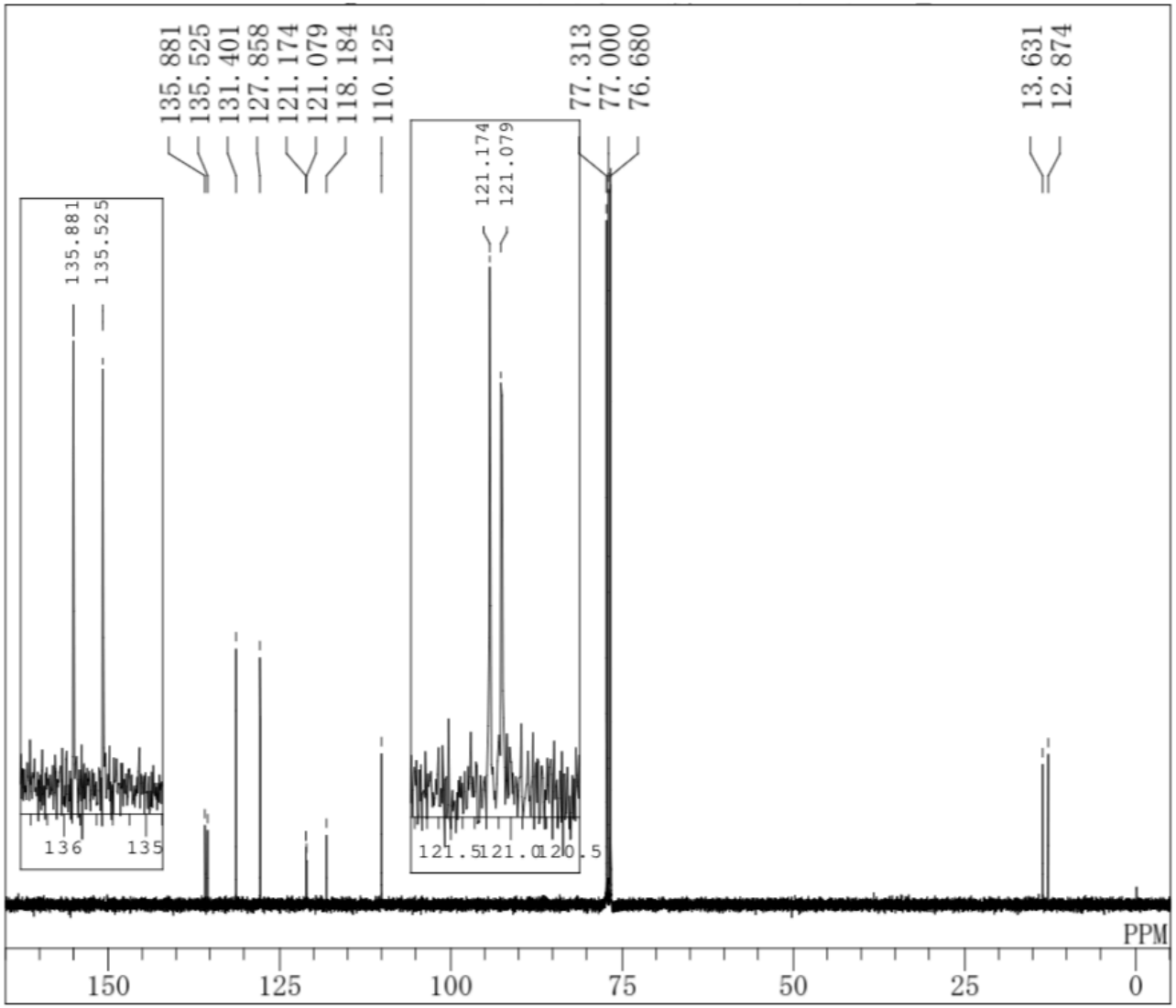


DFILE	6b_4-PhBr-MeDT H.als
COMNT	4-PhMeDT-Br
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.8 c
SLVNT	CDC13
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	181

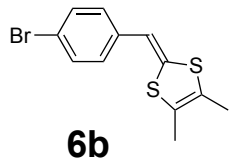


6b

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

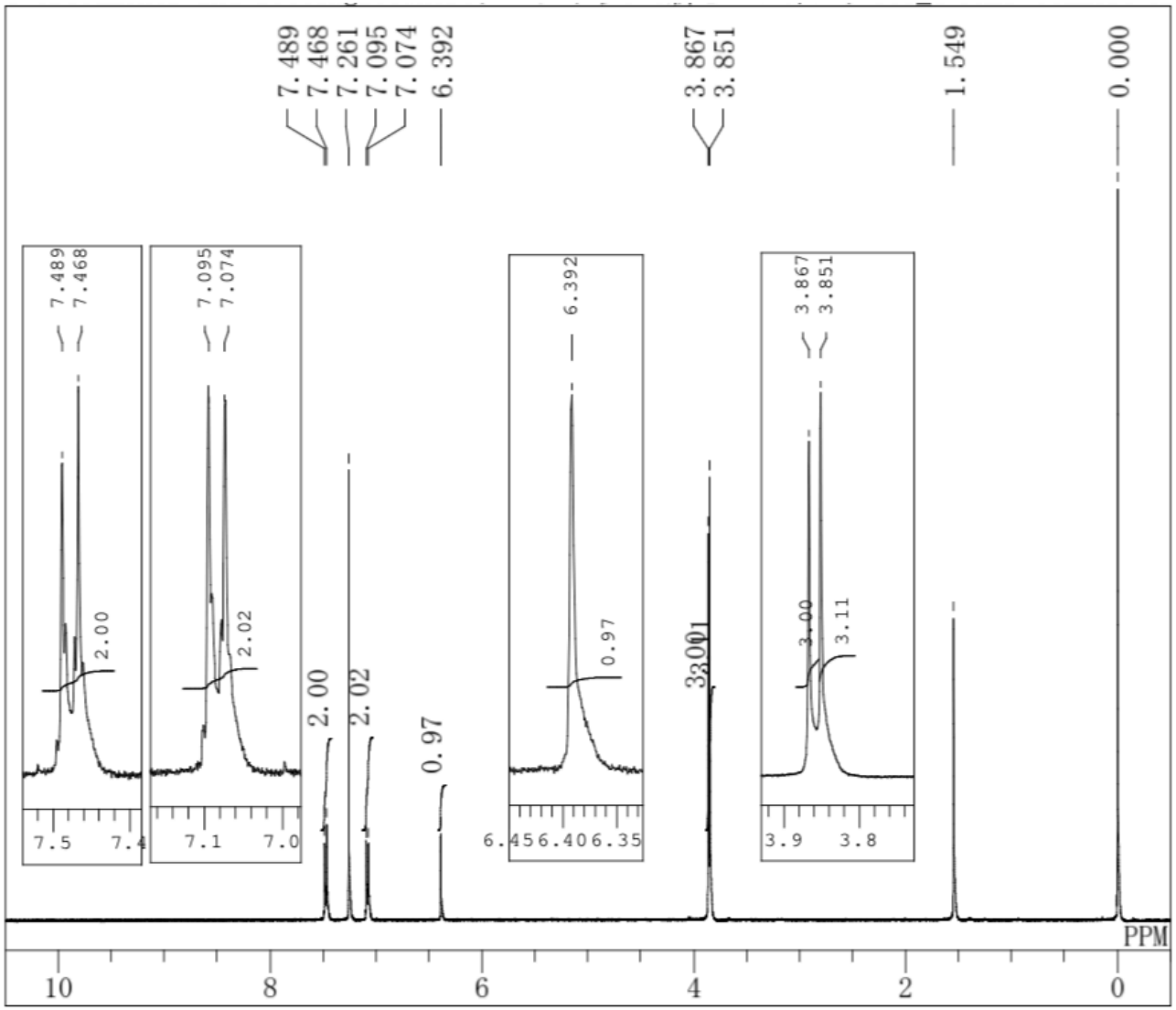


DFILE	6b_4-PhBr-MeDT C.als
COMNT	4-PhMeDTBr
DATIM	/prog/mod/proc1d /op
OBNUC	13C
EXMOD	zgpg30
OBFRQ	100.62 MHz
OBSET	2.82 KHz
OBFIN	9.80 Hz
POINT	32768
FREQU	23980.81 Hz
SCANS	844
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	23.5 c
SLVNT	CDC13
EXREF	77.00 ppm
BF	0.00 Hz
RGAIN	18390

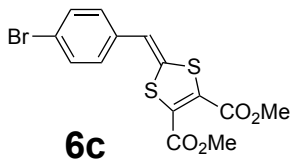


6b

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

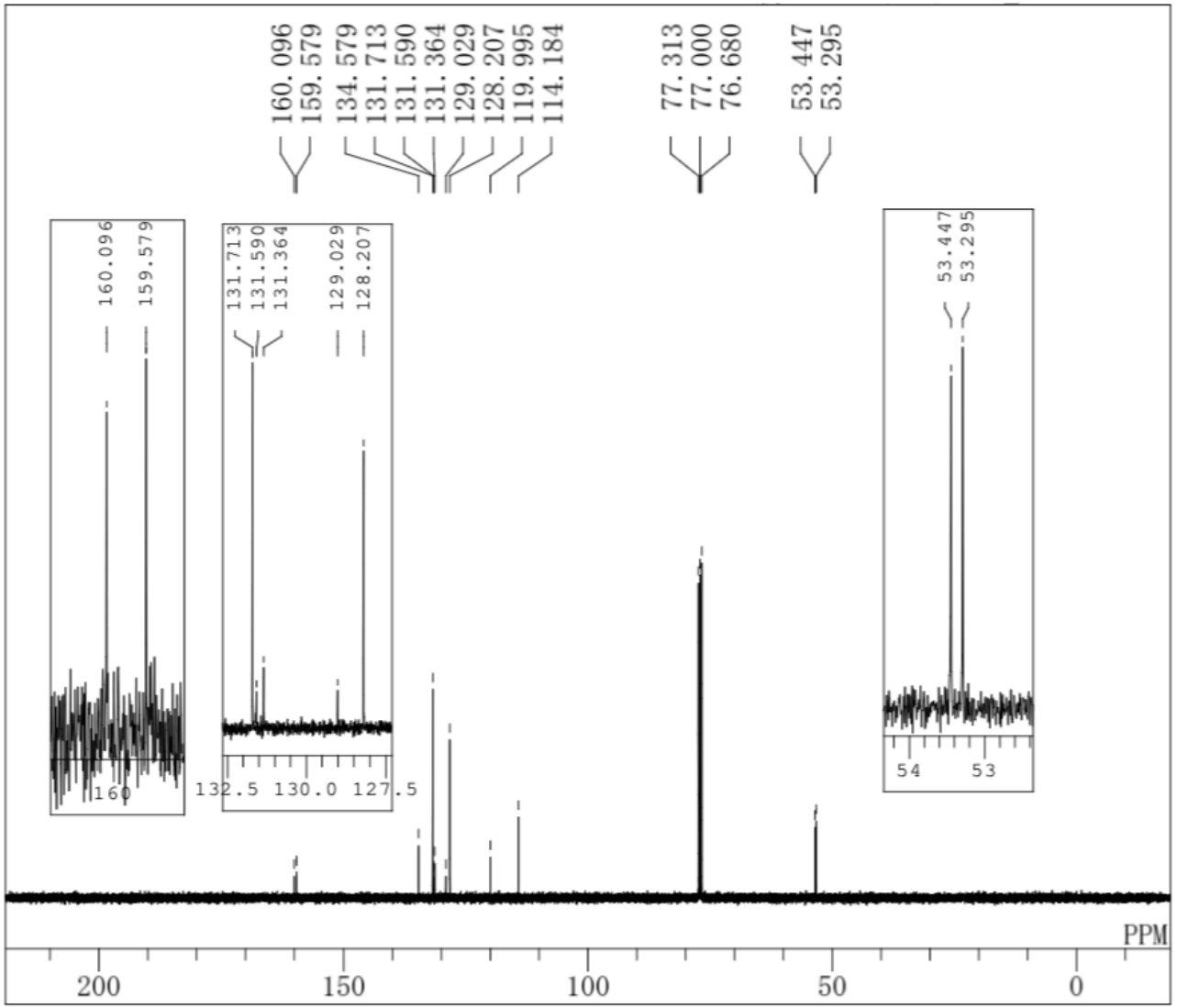



```
DFILE   6c_4-PhBr-CO2MeDT H.
COMNT   BrBzDTCO2Me-1
DATIM   /prog/mod/proc1d /op
OBNUC   1H
EXMOD   zg30
OBFRQ          400.13 MHz
OBSET            2.47 KHz
OBFIN            0.97 Hz
POINT           32768
FREQU         8278.15 Hz
SCANS              16
ACQTM          0.0000 sec
PD             0.0000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

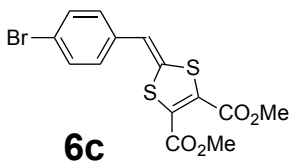


6c

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

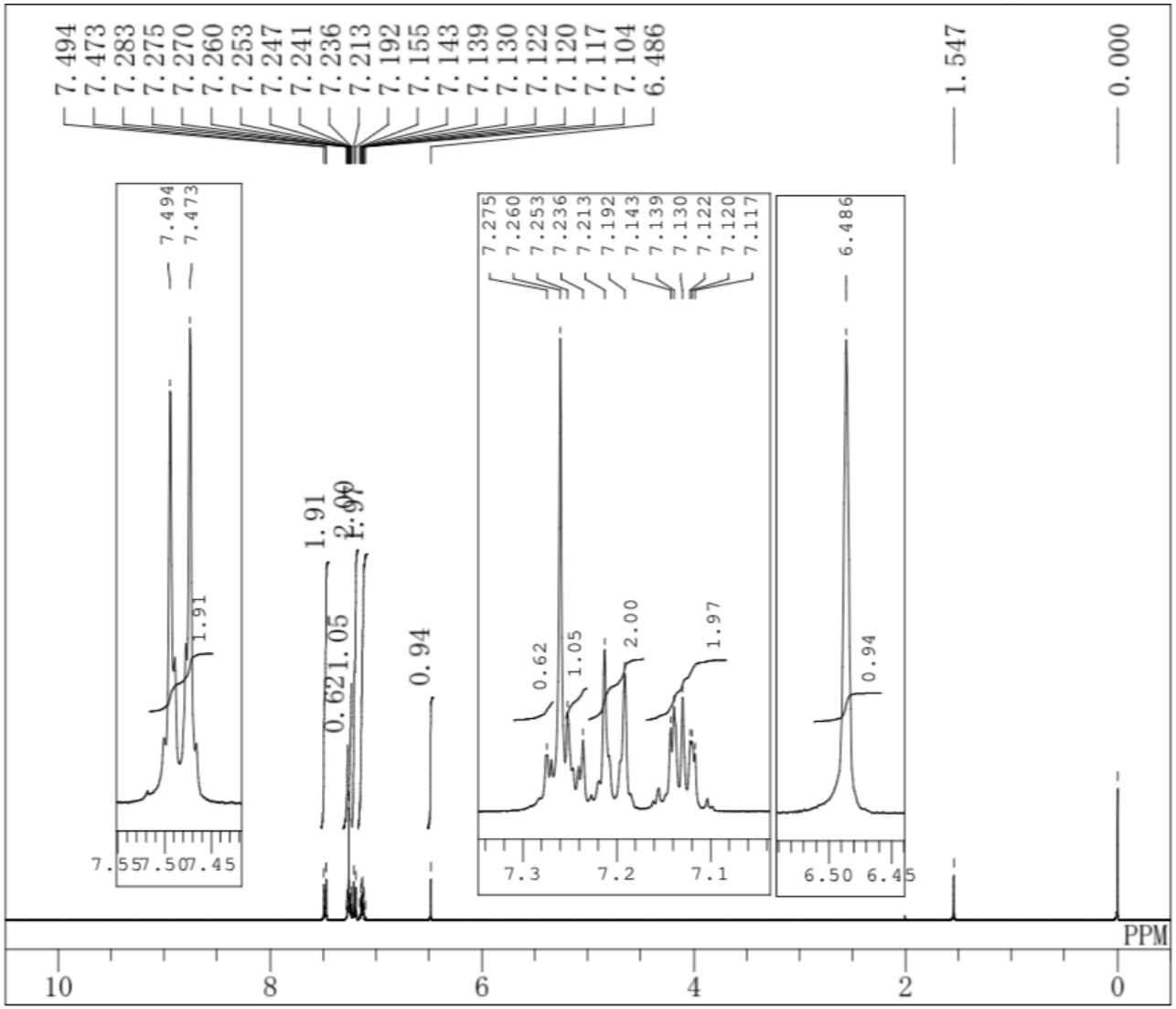


DFILE	07_4-PhBr-CO2MeDT C.a
COMNT	4-PhBr-CO2MeDT C
DATIM	/prog/mod/proc1d /opt
OBNUC	13C
EXMOD	zgpg30
OBFRQ	100.62 MHz
OBSET	2.82 KHz
OBFIN	9.80 Hz
POINT	32768
FREQU	23980.81 Hz
SCANS	347
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	23.6 c
SLVNT	CDC13
EXREF	77.00 ppm
BF	0.00 Hz
RGAIN	20642

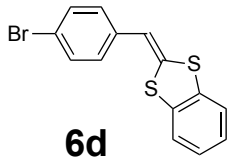


6c

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

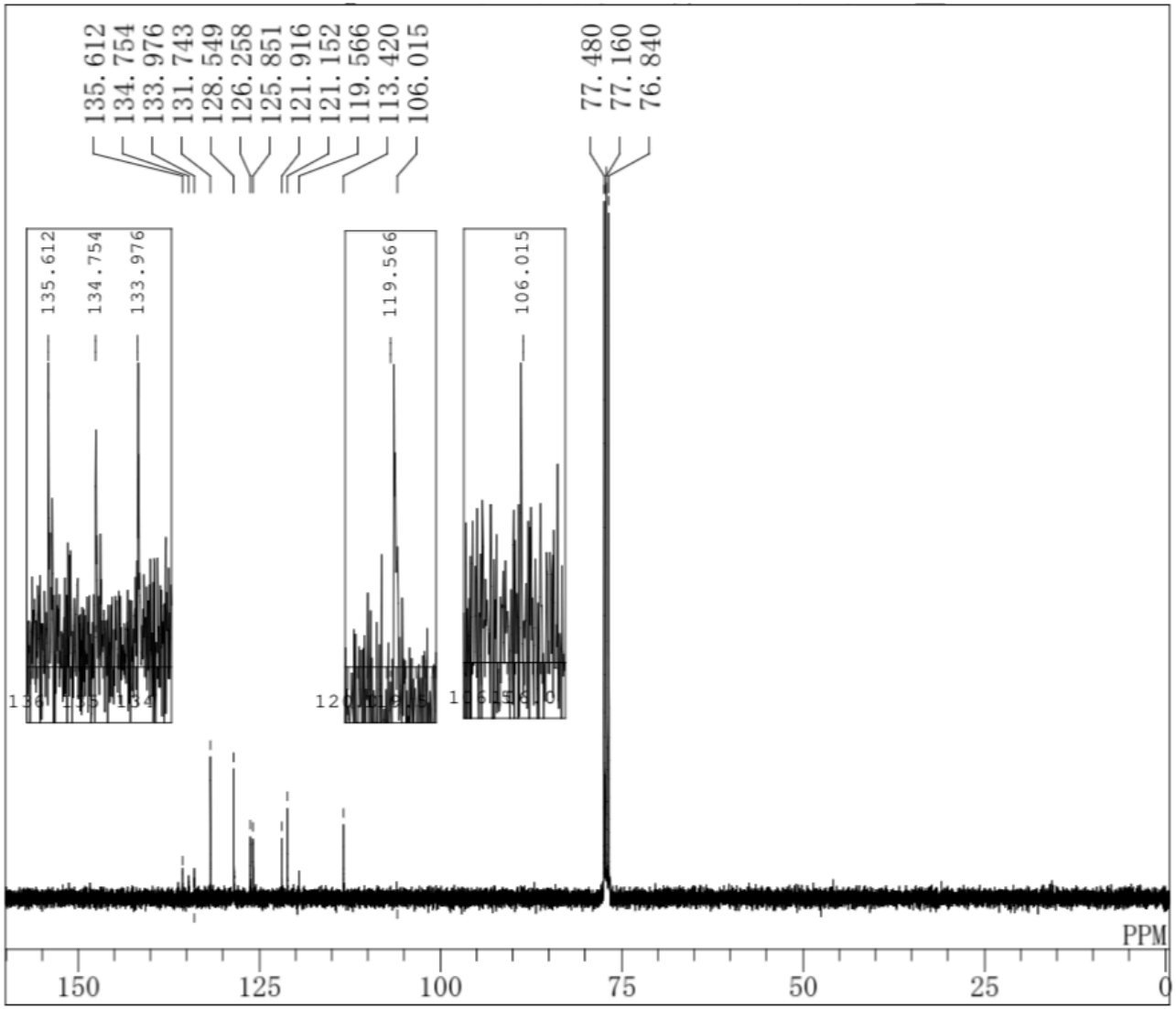


DFILE	06_4-PhBr-BzDT H.als
COMNT	BzDT-BzBr
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.4 c
SLVNT	CDC13
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	362

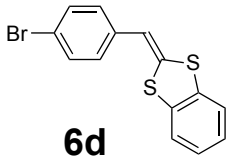


6d

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

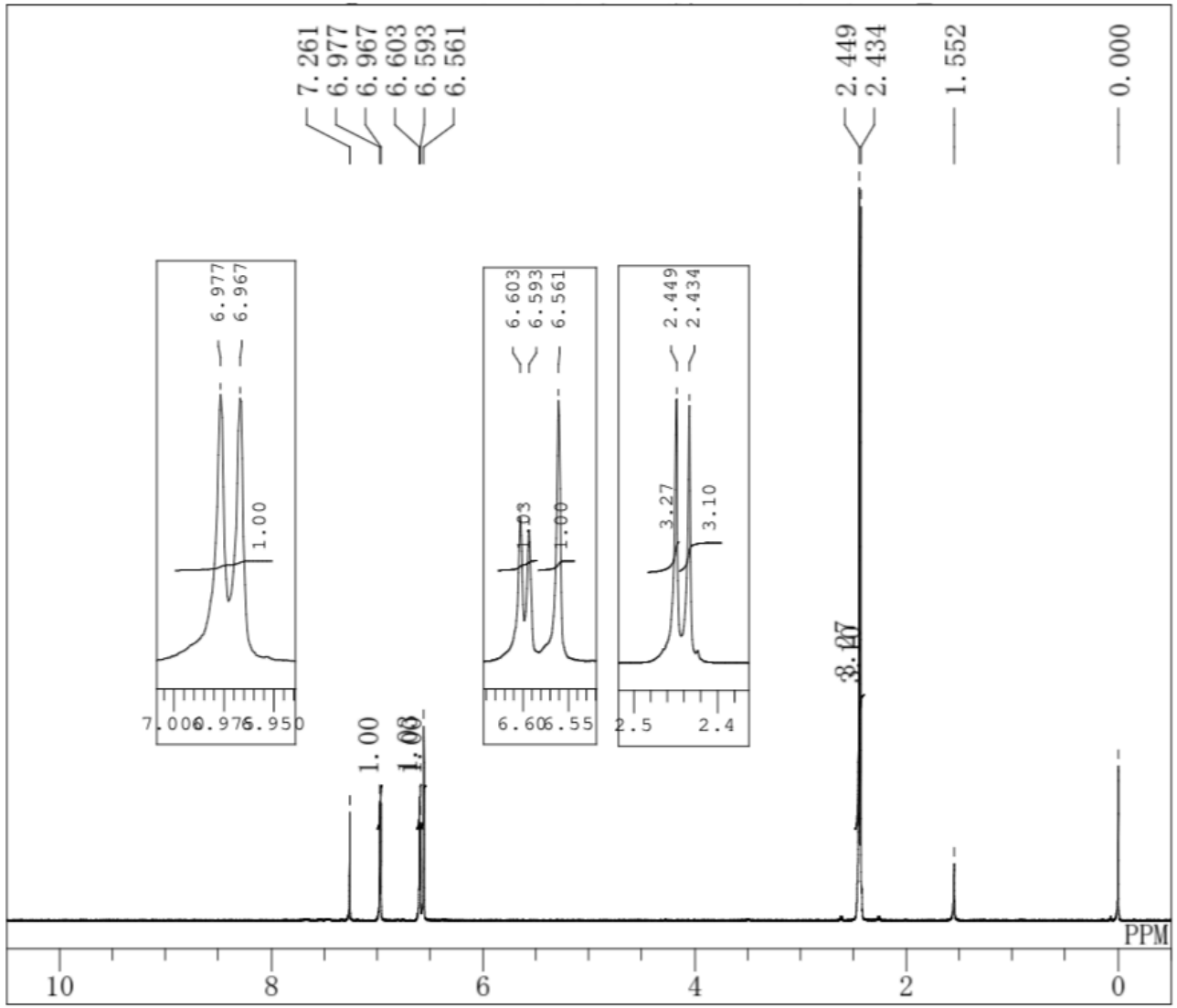



```
DFILE   6d__4-PhBr-BzDT C.al
COMNT   2-ThioBr-BzDT reverc
DATIM   /prog/mod/proc1d /op
OBNUC   13C
EXMOD   zgpg30
OBFRQ         100.62 MHz
OBSET           2.82 KHz
OBFIN           9.80 Hz
POINT          32768
FREQU       23980.81 Hz
SCANS           1024
ACQTM         0.0000 sec
PD            0.0000 sec
PW1             10.00 usec
IRNUC
CTEMP           23.8 c
SLVNT   CDC13
EXREF           77.16 ppm
BF              0.12 Hz
RGAIN          20642
```

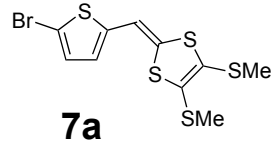


6d

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

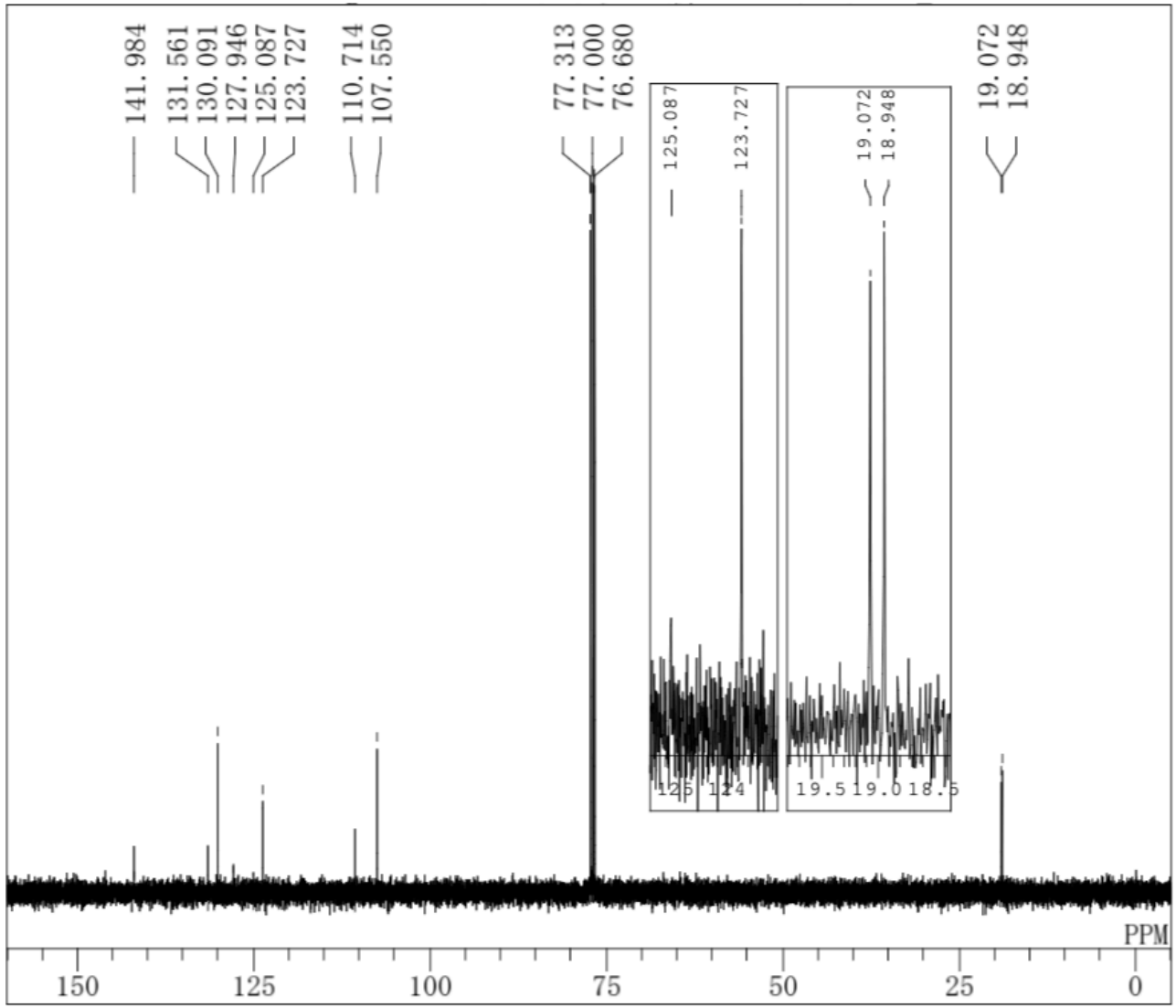



```
DFILE   7a_2-ThioBr-SMeDT H.
COMNT   Br-thio-SMeDT
DATIM   /prog/mod/proc1d /op
OBNUC   1H
EXMOD   zg30
OBFRQ         400.13 MHz
OBSET           2.47 KHz
OBFIN           0.97 Hz
POINT          32768
FREQU        8278.15 Hz
SCANS            16
ACQTM         0.0000 sec
PD            0.0000 sec
PW1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

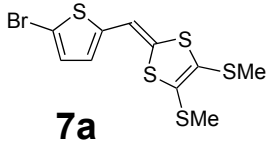


7a

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

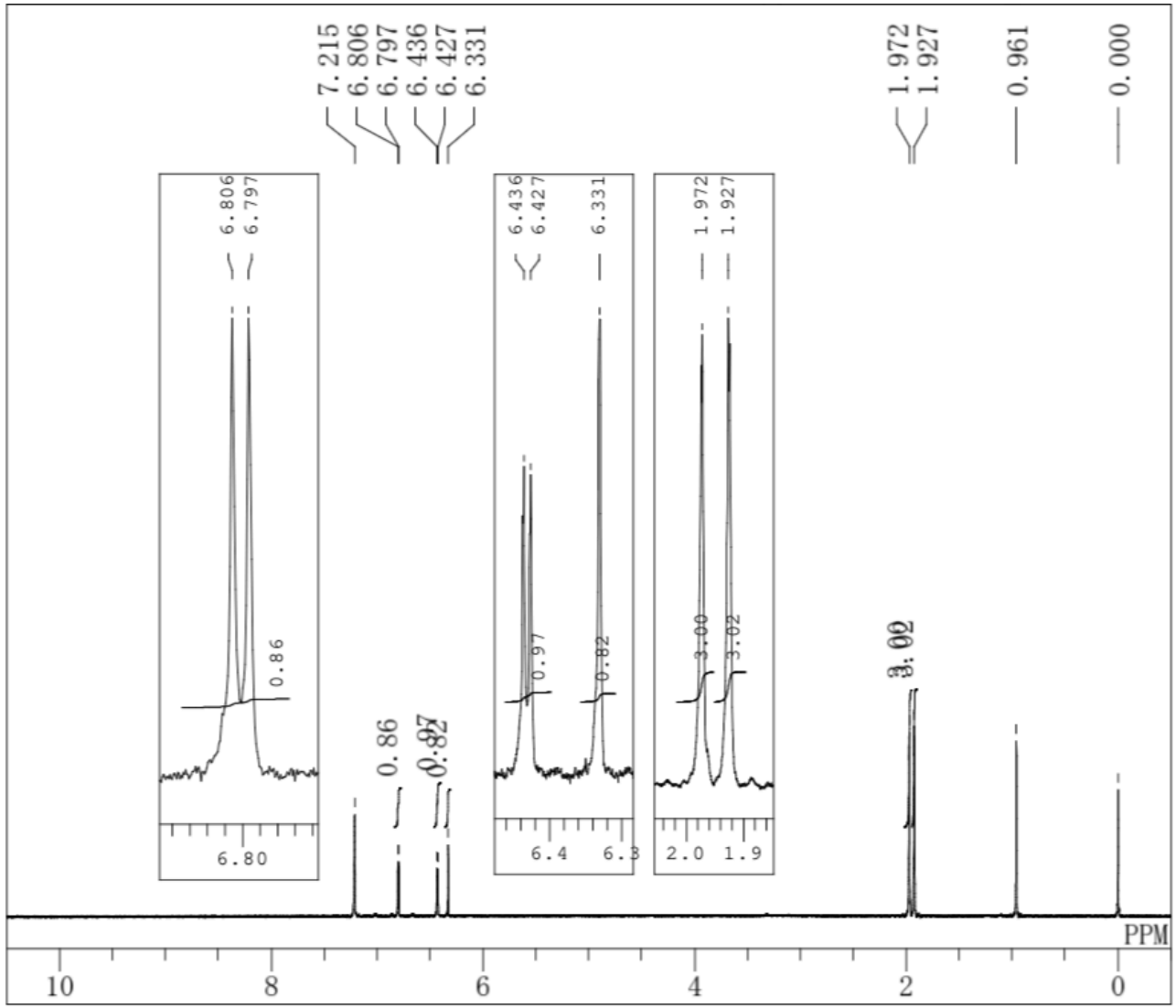


DFILE	7a_2-ThioBr-SMeDT C.
COMNT	Br-thio-SMeDT-C
DATIM	/prog/mod/proc1d /op
OBNUC	13C
EXMOD	zgpg30
OBFRQ	100.62 MHz
OBSET	2.82 KHz
OBFIN	9.80 Hz
POINT	32768
FREQU	23980.81 Hz
SCANS	214
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	23.7 c
SLVNT	CDC13
EXREF	77.00 ppm
BF	0.00 Hz
RGAIN	20642

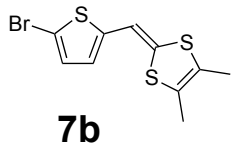


7a

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

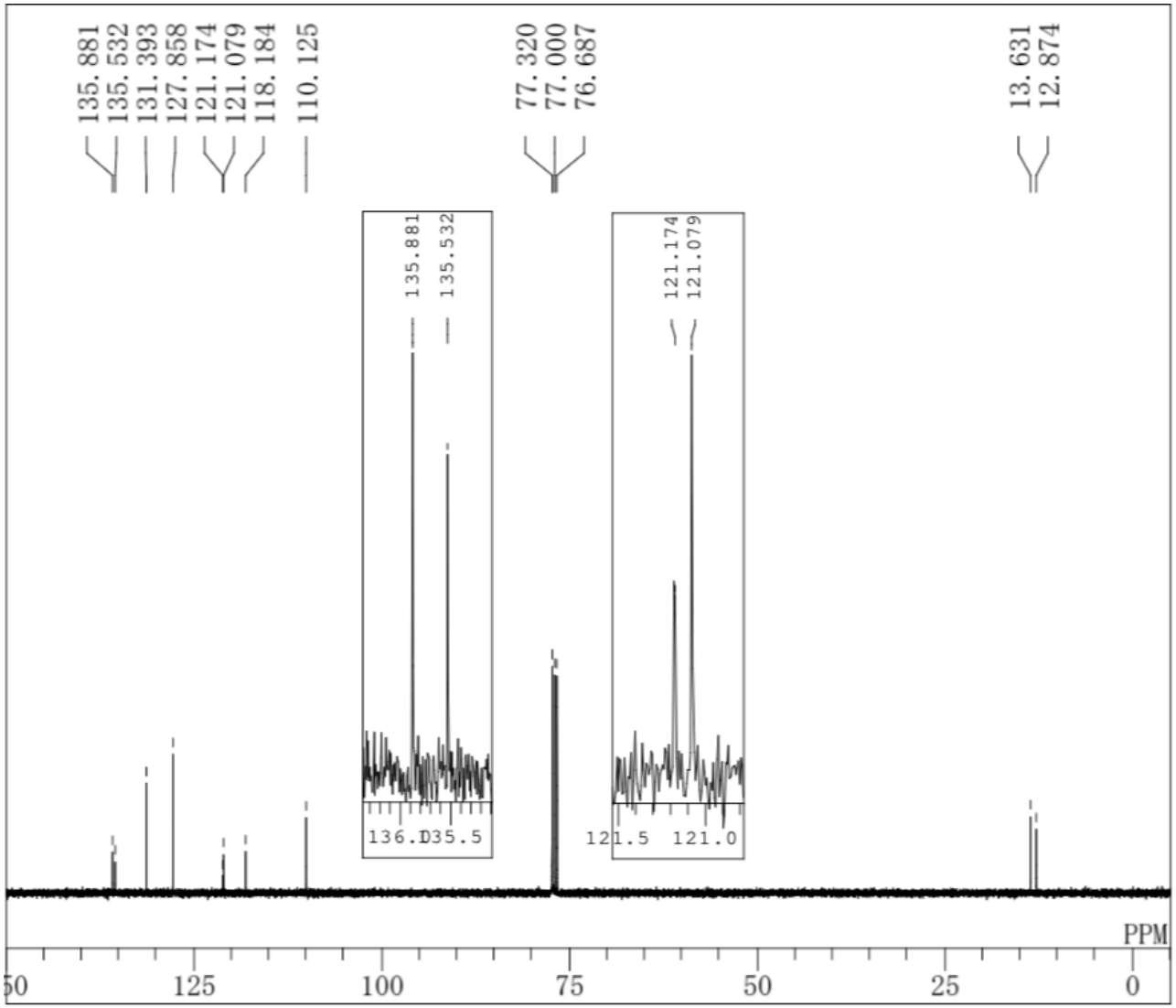


DFILE	02_2-ThioBr-MeDT H.a
COMNT	MeDT ThioBr
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	23.5 c
SLVNT	C6D6
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	574

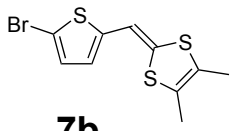


7b

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

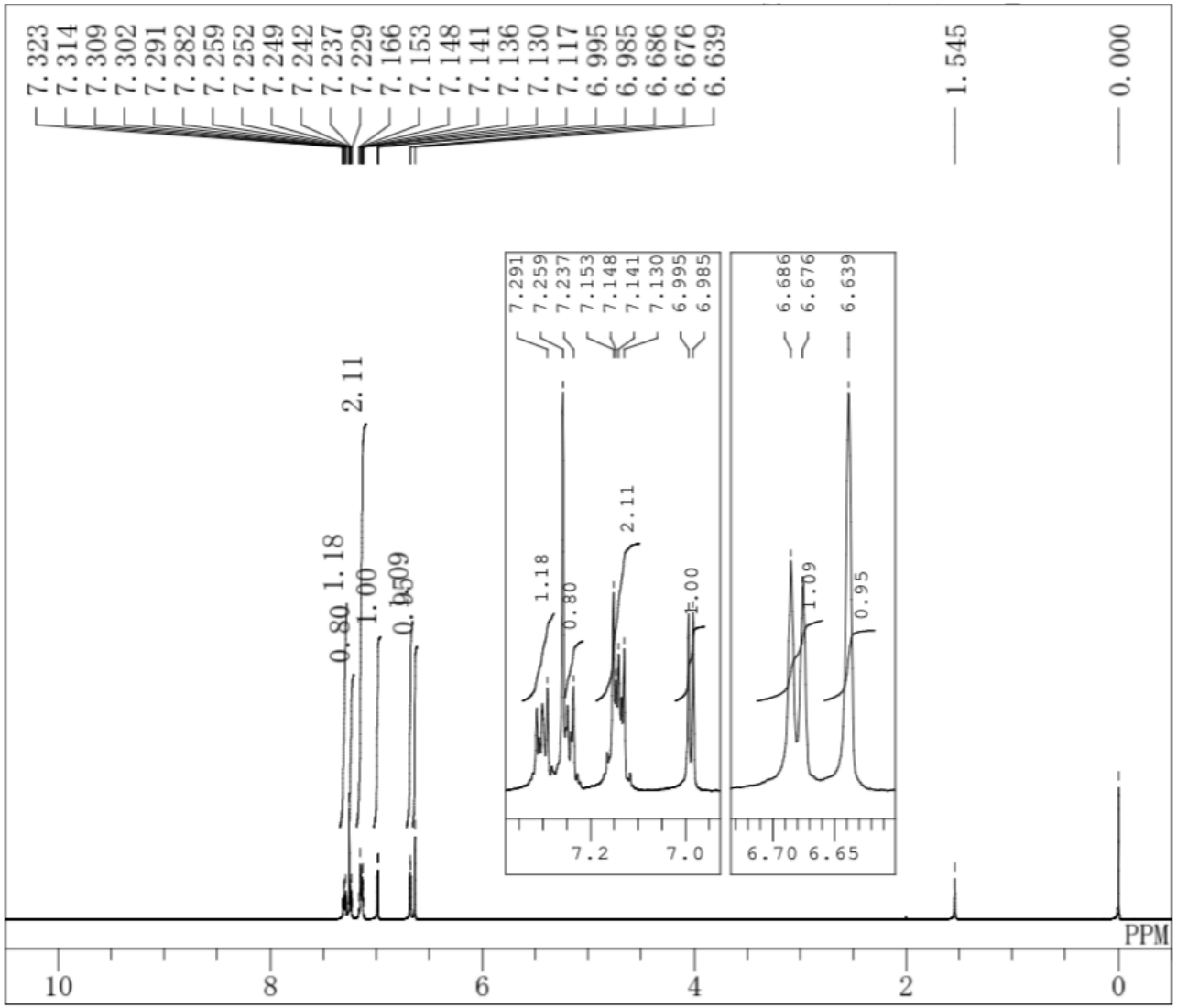



```
DFILE   02_2-ThioBr-MeDT C.a
COMNT   2-ThioMeDT-Br2
DATIM   /prog/mod/proc1d /op
OBNUC   13C
EXMOD   zgpg30
OBFRQ         100.62 MHz
OBSET           2.82 KHz
OBFIN           9.80 Hz
POINT          32768
FREQU       23980.81 Hz
SCANS            211
ACQTM         0.0000 sec
PD            0.0000 sec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

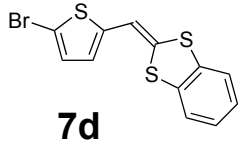


7b

[1]H NMR of **7d**

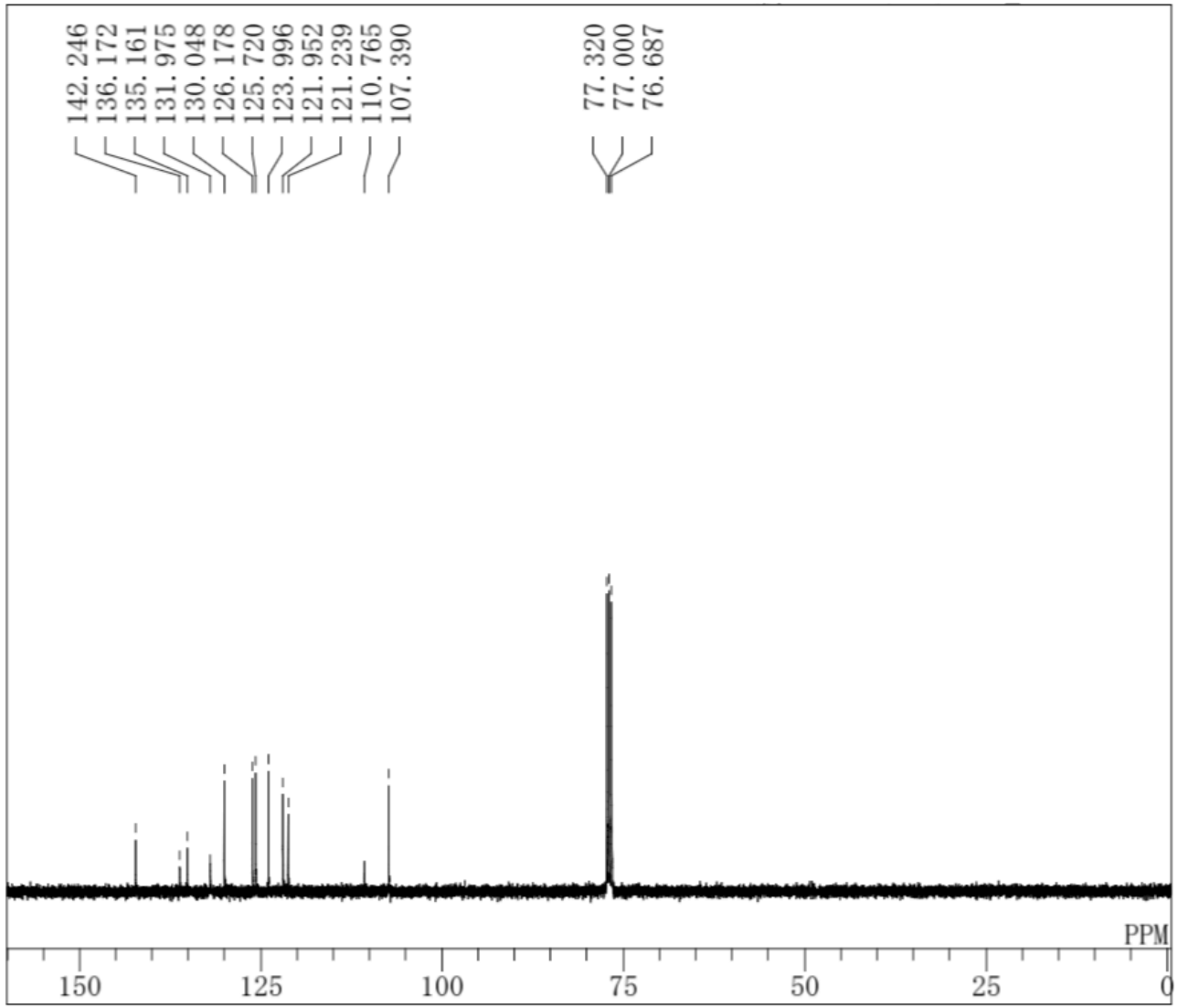



```
DFILE   03_2-ThioBr-BzDT H.a
COMNT   BzDT-BzBr
DATIM   /prog/mod/proc1d /op
OBNUC   1H
EXMOD   zg30
OBFRQ          400.13 MHz
OBSET            2.47 KHz
OBFIN            0.97 Hz
POINT           32768
FREQU         8278.15 Hz
SCANS              16
ACQTM          0.0000 sec
PD             0.0000 sec
PW1              10.00 usec
IRNUC
CTEMP            22.4 c
SLVNT   CDC13
EXREF             0.00 ppm
BF                0.12 Hz
RGAIN              362
```

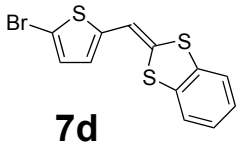


7d

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

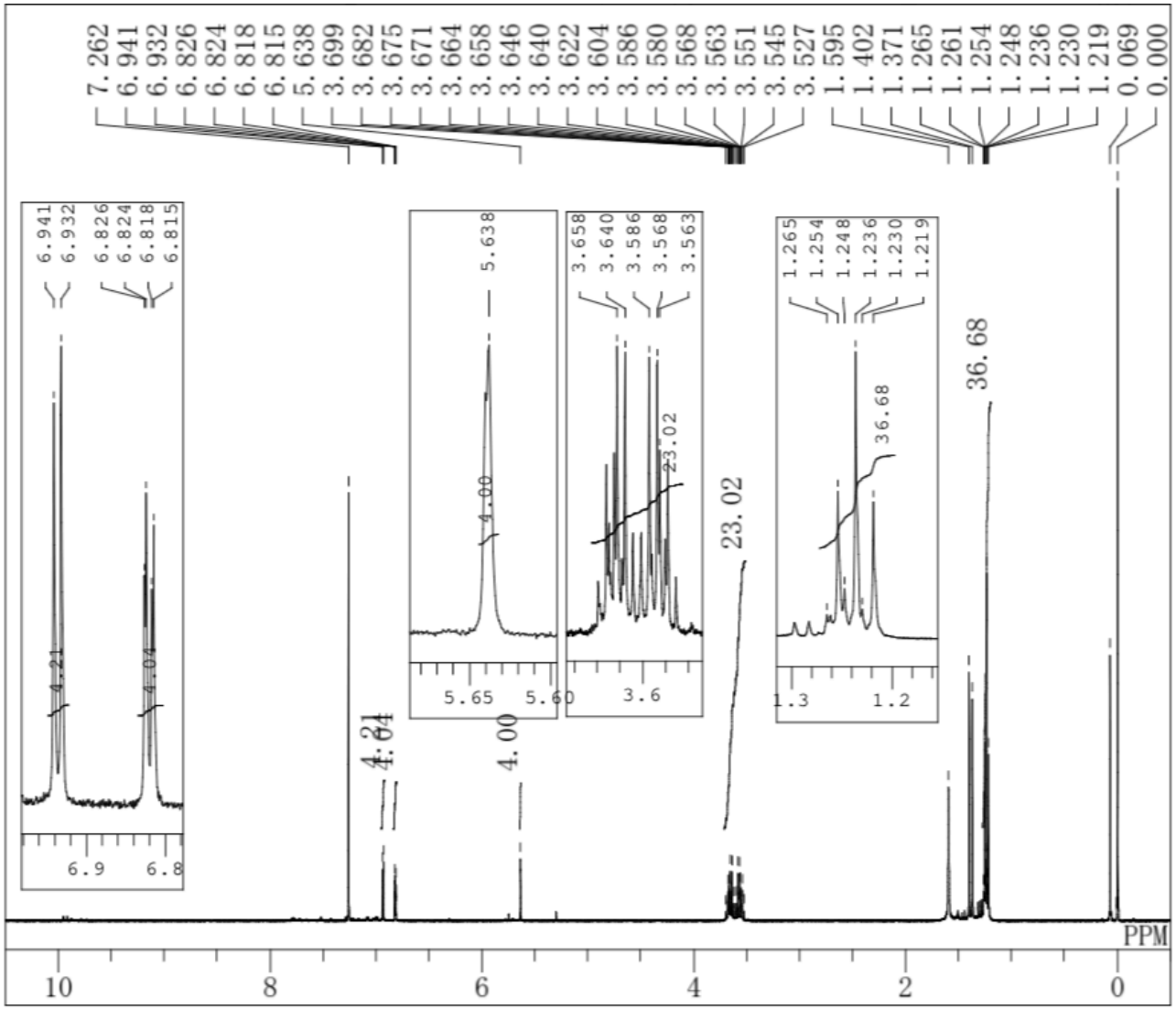



```
DFILE   03_2-ThioBr-BzDT C.a
COMNT   4-PhBr-BzDT
DATIM   /prog/mod/proc1d /op
OBNUC   13C
EXMOD   zgpg30
OBFRQ         100.62 MHz
OBSET           2.82 KHz
OBFIN           9.80 Hz
POINT          32768
FREQU       23980.81 Hz
SCANS            518
ACQTM         0.0000 sec
PD            0.0000 sec
PW1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

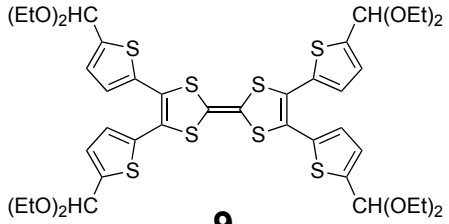


7d

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

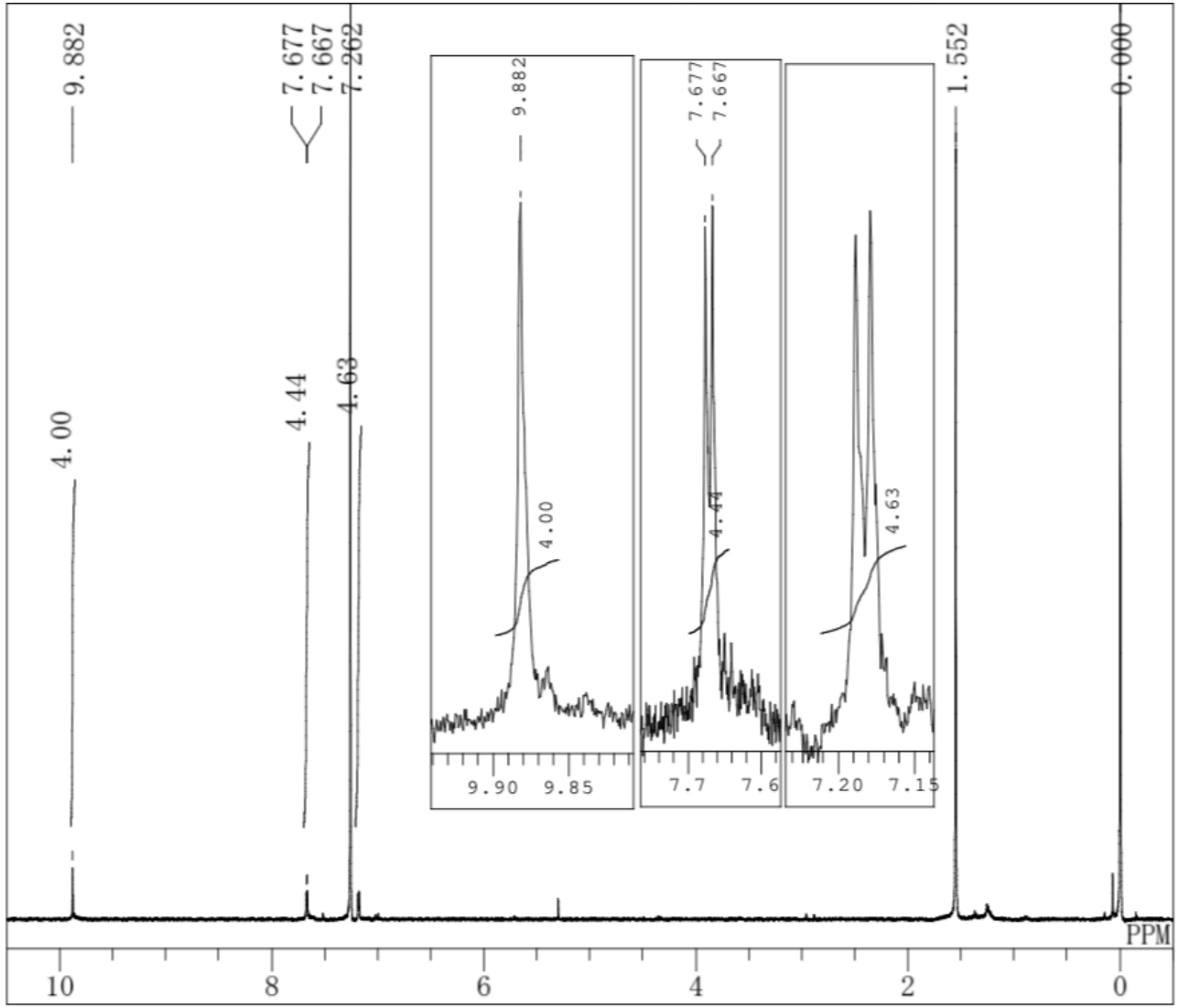


DFILE	9_2-ThioCHOEt2精製せ
COMNT	TTF-4Ar-thio-CH(OEt)2
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.2 c
SLVNT	CDC13
EXREF	0.00 ppm
BF	0.00 Hz
RGAIN	362

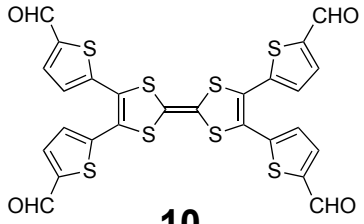


9

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

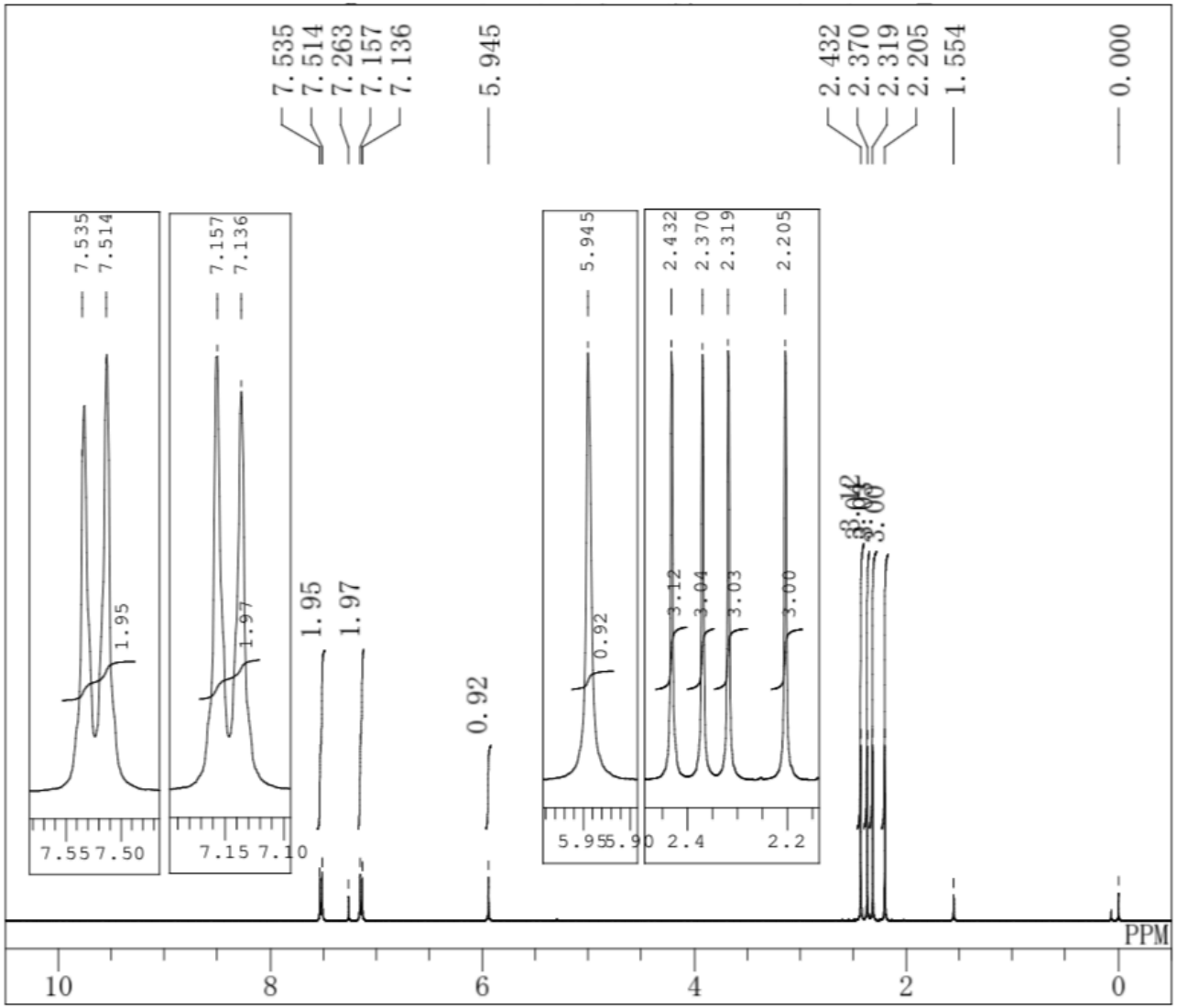


DFILE	10_2-ThioCHO-TTF.als
COMNT	TTF-Thio-CHO
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.1 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	362

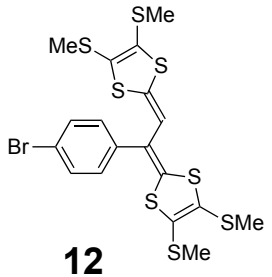


10

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

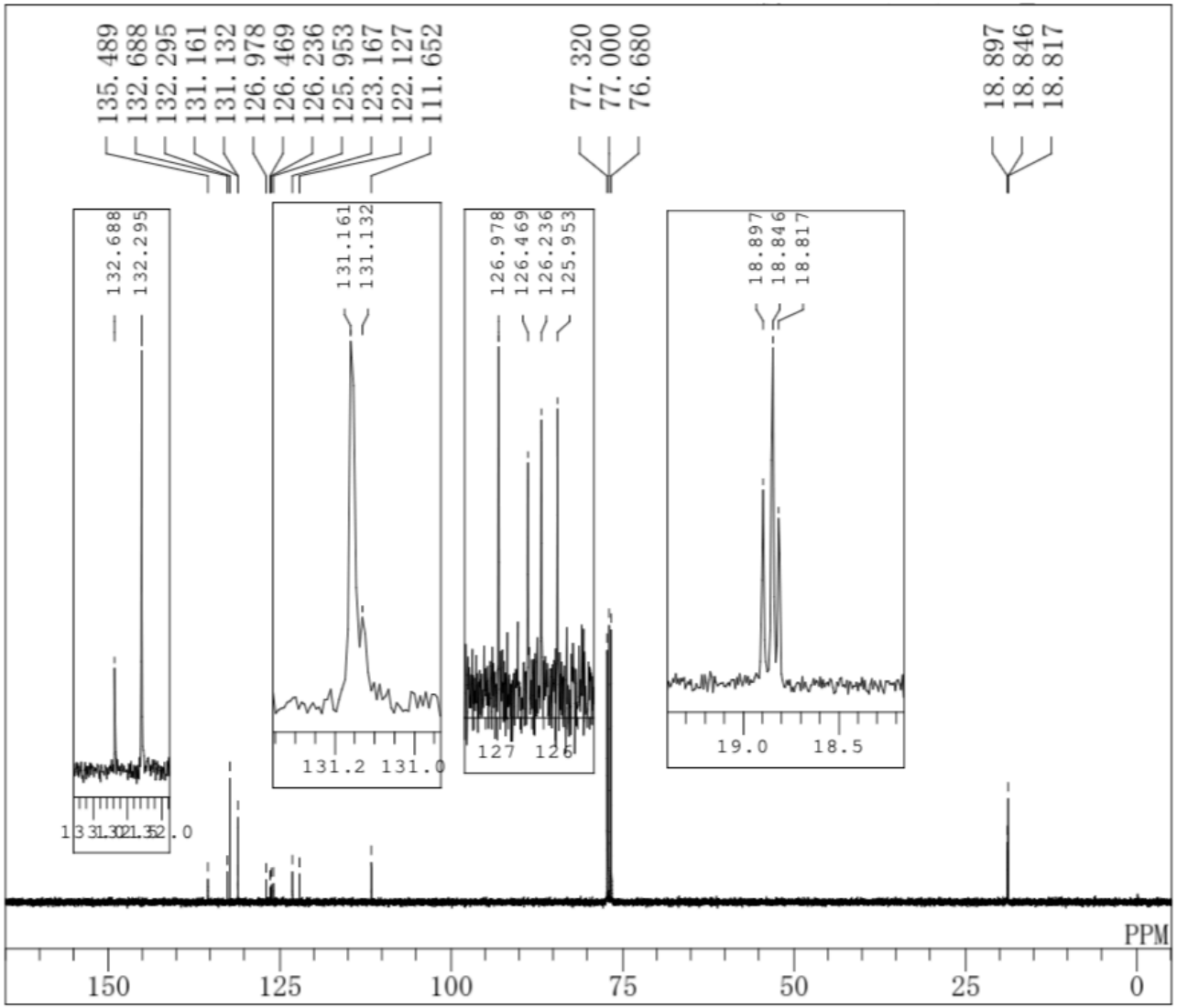


DFILE 12_4-PhBr-SMeEBDT H.
COMNT 4-PhBr-SMeDT-SMeDT
DATIM /prog/mod/proc1d /op
OBNUC 1H
EXMOD zg30
OBFRQ 400.13 MHz
OBSET 2.47 KHz
OBFIN 0.97 Hz
POINT 32768
FREQU 8278.15 Hz
SCANS 16
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 22.7 c
SLVNT CDC13
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 228

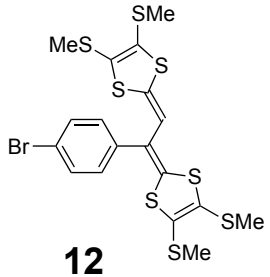


12

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

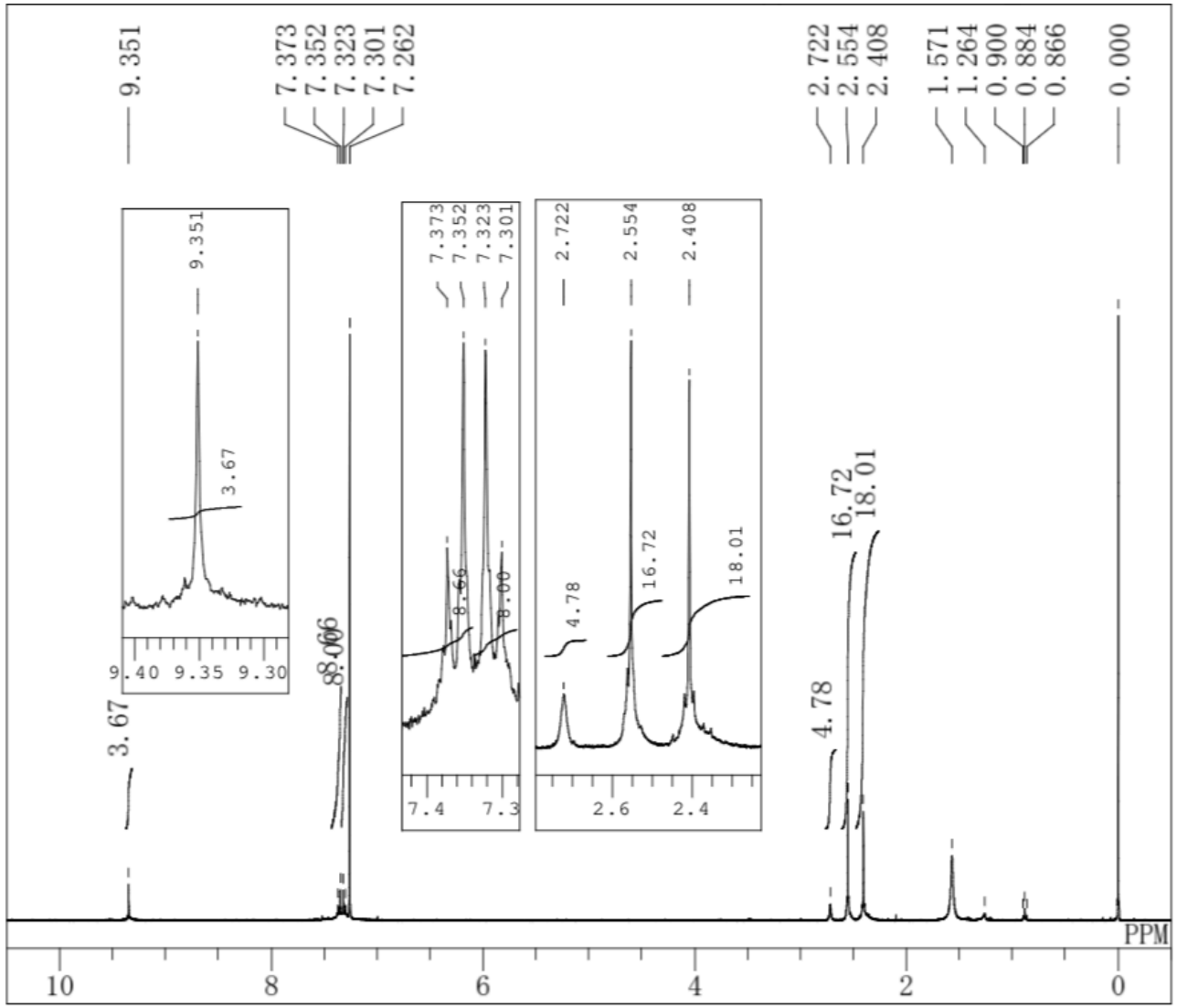


DFILE 009_4-PhBr-SMeEBDT C
COMNT 4-PhBr-SMeDT-SMeDT
DATIM /prog/mod/proc1d /op
OBNUC 13C
EXMOD zgpg30
OBFRQ 100.62 MHz
OBSET 2.82 KHz
OBFIN 9.80 Hz
POINT 32768
FREQU 23980.81 Hz
SCANS 538
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 23.9 c
SLVNT CDC13
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 20642

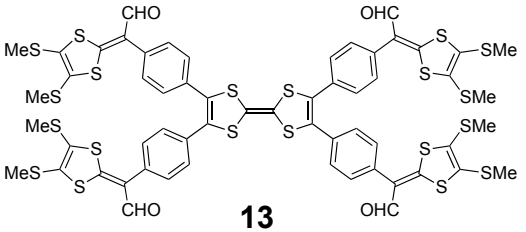


12

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

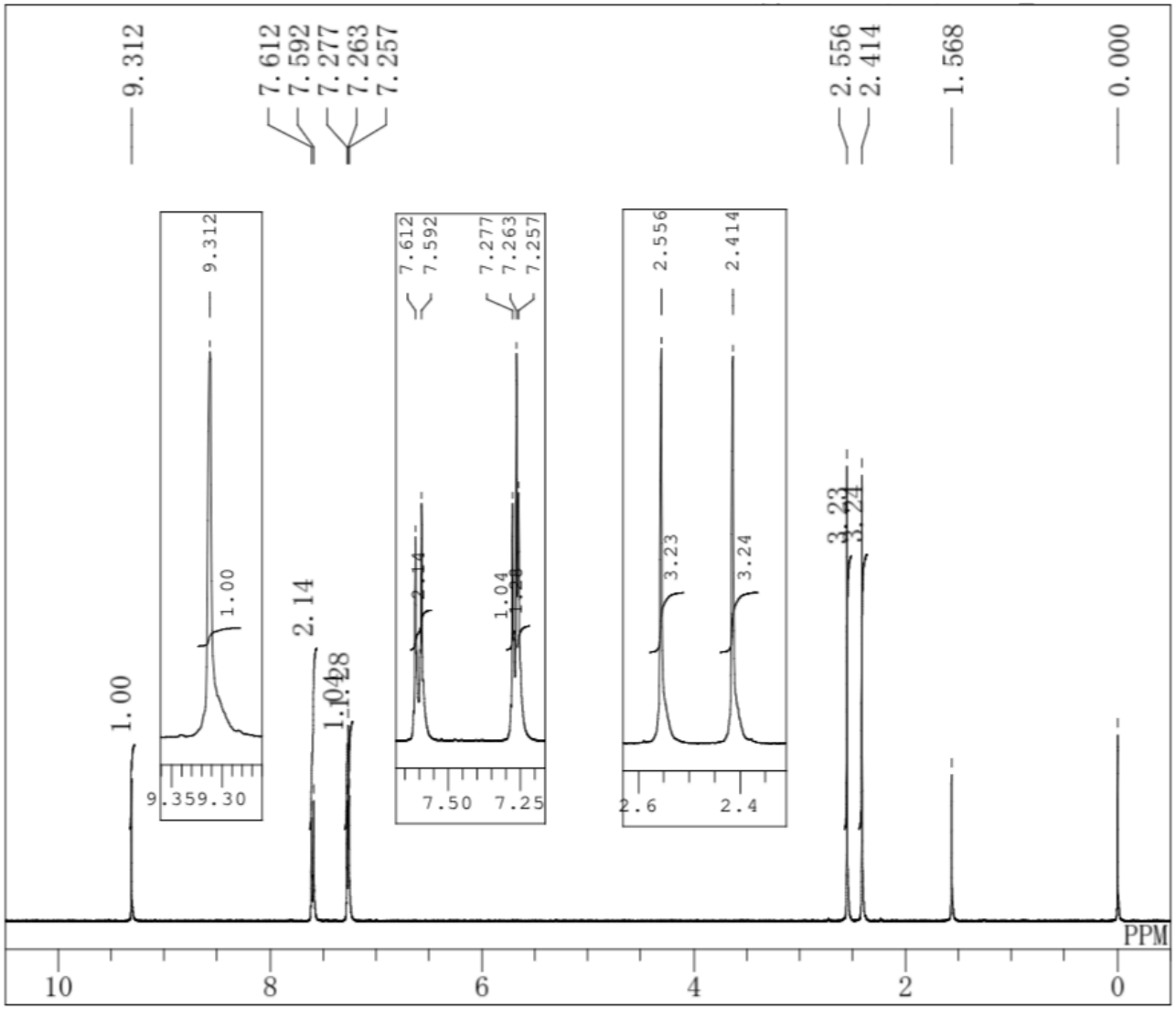


DFILE	00_4-PhSMeDT-TTF-CHO	
COMNT	4-PhSMeDT-TTF-CHO	
DATIM	/prog/mod/proc1d /op	
OBNUC	1H	
EXMOD	zg30	
OBFRQ	400.13	MHz
OBSET	2.47	KHz
OBFIN	0.97	Hz
POINT	32768	
FREQU	8278.15	Hz
SCANS	16	
ACQTM	0.0000	sec
PD	0.0000	sec
PW1	10.00	usec
IRNUC		
CTEMP	22.4	c
SLVNT	CDC13	
EXREF	0.00	ppm
BF	0.12	Hz
RGAIN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

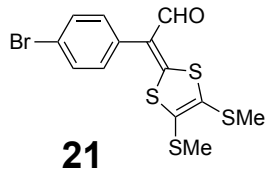


13

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

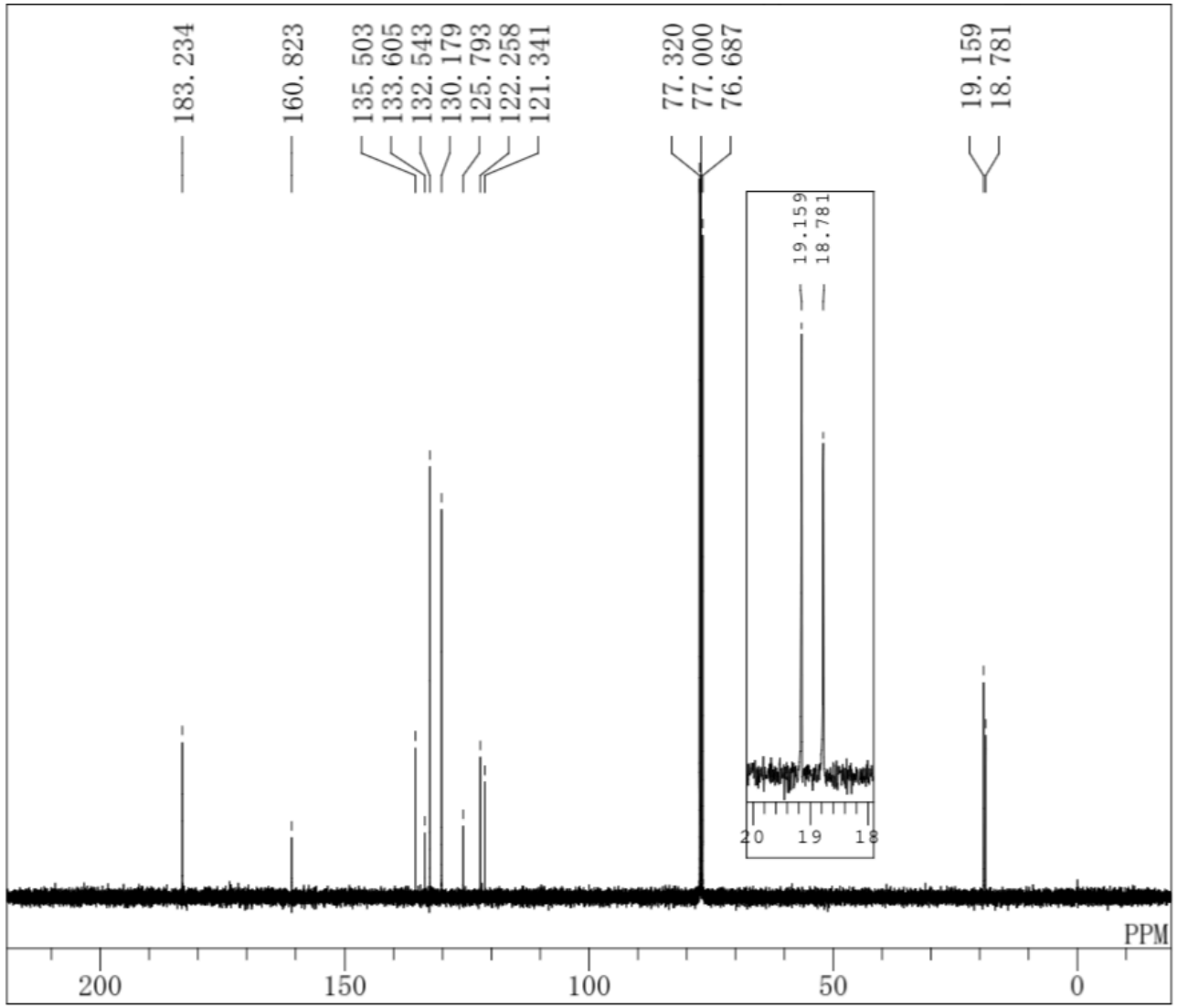


DFILE	008_4-PhBr-SMeDT-CHO
COMNT	4-PhSMeDT-CHO
DATIM	/prog/mod/proc1d /op
OBNUC	1H
EXMOD	zg30
OBFRQ	400.13 MHz
OBSET	2.47 KHz
OBFIN	0.97 Hz
POINT	32768
FREQU	8278.15 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	22.5 c
SLVNT	CDC13
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	362

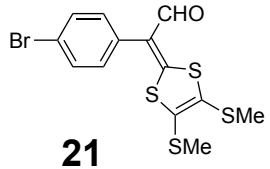


21

^{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