Supporting Information

for

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

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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 100–210µm) 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$_6$D$_6$-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$_6$D$_6$: 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 $n$Bu$_4$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), PrBu$_3$-HBF$_4$ (26.3 mg, 0.0906 mmol), and Cs$_2$CO$_3$ (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 dichloromethane three times. The combined organic layer was washed with H$_2$O, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by silica gel chromatography with a mixture of dichloromethane/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 (CDCl$_3$, 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$_{20}$: 1331.7857; found: 1331.7732.

1b: Red brown powder; $^1$H NMR (CD$_6$-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 (CD$_6$-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$_{12}$: 817.8663; found: 817.8531.

2b: Red powder; $^1$H NMR (CD$_6$-CS$_2$, 400 MHz) δ 1.82 (s 6H), 1.84 (s 6H), 6.18 (s, 2H), 6.92-6.96 (m, 6H), 7.03-7.08 (m, 6H); $^{13}$C NMR (CD$_6$-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 dichloromethane 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 ^1^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:**

![Chemical structure](attachment:image.png)

**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); ^1^C NMR (CDCl_3, 100 MHz) δ 18.9, 19.0, 113.4,
was added. The mixture was heated at 110 °C 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) 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 1H 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•H2O (244.0 mg, 0.602 mmol) 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 H₂O, sat. NaHCO₃ aq., and sat. NaCl aq., dried over anhydrous Na₂SO₄, 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:**

![Reaction Scheme](image)

**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 12 h. After removal of solvent and excess P(OEt)₃, The residue was washed by methanol in 80% yield.

12: Yellow powder; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₁₈H₁₇Br₈S₈: 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 POCl₃ (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 dichloromethane. The combined organic layers were washed with H₂O and sat. NaCl aq. three times, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The product was obtained by suction filtration with dichloromethane 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 POCl₃ (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 dichloromethane. The combined organic layers were washed with H₂O and sat. NaCl aq. Three by suction filtration with dichloromethane and hexane in 77% yield.
21: Yellow powder; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 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) $\delta$ 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°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**

<table>
<thead>
<tr>
<th>Angle</th>
<th>1a</th>
<th>3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>A–A’</td>
<td>155.5°</td>
<td>155.7°</td>
</tr>
<tr>
<td>A–B</td>
<td>137.9°</td>
<td>51.0°</td>
</tr>
<tr>
<td>A–B’</td>
<td>48.5°</td>
<td>146.6°</td>
</tr>
<tr>
<td>A’–C</td>
<td>48.6°</td>
<td>52.1°</td>
</tr>
<tr>
<td>A’–C’</td>
<td>136.6°</td>
<td>143.8°</td>
</tr>
<tr>
<td>B–D</td>
<td>1.5°</td>
<td>9.4°</td>
</tr>
<tr>
<td>B’–D’</td>
<td>21.8°</td>
<td>6.7°</td>
</tr>
<tr>
<td>C–E</td>
<td>156.1°</td>
<td>8.0°</td>
</tr>
<tr>
<td>C’–E’</td>
<td>12.3°</td>
<td>9.5°</td>
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<tr>
<td>A–D</td>
<td>156.1°</td>
<td>42.2°</td>
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<tr>
<td>A–D’</td>
<td>68.6°</td>
<td>149.7°</td>
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<td>A’–E</td>
<td>31.1°</td>
<td>44.2°</td>
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<tr>
<td>A’–E’</td>
<td>157.5°</td>
<td>152.9°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<tr>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>( A' - A )</td>
<td>164.3(^\circ)</td>
<td>( B - E )</td>
</tr>
<tr>
<td>( A - B )</td>
<td>142.5(^\circ)</td>
<td>( B' - E' )</td>
</tr>
<tr>
<td>( A - B' )</td>
<td>54.4(^\circ)</td>
<td>( C - G )</td>
</tr>
<tr>
<td>( A - C )</td>
<td>92.7(^\circ)</td>
<td>( C' - G' )</td>
</tr>
<tr>
<td>( A - C' )</td>
<td>99.9(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( B - D )</td>
<td>50.3(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( B' - D' )</td>
<td>48.4(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( C - F )</td>
<td>50.0(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( C' - F' )</td>
<td>129.4(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( D - E )</td>
<td>111.6(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( D' - E' )</td>
<td>50.1(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( F - G )</td>
<td>110.5(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( F' - G' )</td>
<td>111.7(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( A - D )</td>
<td>92.7(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( A - D' )</td>
<td>99.9(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( A' - F )</td>
<td>11.0(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( A' - F' )</td>
<td>9.1(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( B - E )</td>
<td>94.7(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( B' - E' )</td>
<td>84.7(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( C - F )</td>
<td>50.0(^\circ)</td>
<td></td>
</tr>
<tr>
<td>( C' - F' )</td>
<td>129.4(^\circ)</td>
<td></td>
</tr>
</tbody>
</table>
Cyclic Voltammograms

Figure S2. Cyclic voltammograms of (a) 2a and (b) 3a in PhCN/CS₂ (1/1, V/V) (0.3 mM) solution in designated solvent containing 0.1 m nBu₄NPF₆.

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

<table>
<thead>
<tr>
<th></th>
<th>E₁/V</th>
<th>E₂/V</th>
<th>E₃/V</th>
<th>E₄/V</th>
<th>E₅/V</th>
<th>E₆/V</th>
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</thead>
<tbody>
<tr>
<td>2a</td>
<td>-0.05</td>
<td>+0.09</td>
<td>+0.49</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>+0.14</td>
<td></td>
<td></td>
<td>+0.25</td>
<td></td>
<td>+0.52</td>
</tr>
<tr>
<td>5b</td>
<td>-0.01</td>
<td>+0.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10b</td>
<td>-0.25</td>
<td>+0.60</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>22b</td>
<td>+0.00</td>
<td>+0.47</td>
<td></td>
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</tbody>
</table>

*In PhCN/CS₂ (1/1, V/V) containing 0.1 M nBu₄NPF₆, all potentials measured against Ag/Ag⁺ reference electrode and converted to vs. Fc/Fc⁺.

*In PhCN containing 0.1 M nBu₄NPF₆, 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; digital 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

<table>
<thead>
<tr>
<th>charge-transfer reaction</th>
<th>redox potentials (V)</th>
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<tr>
<td>A + e = B</td>
<td>0.502</td>
</tr>
<tr>
<td>B + e = C1</td>
<td>0.285</td>
</tr>
<tr>
<td>C + 2e = D1</td>
<td>0.2</td>
</tr>
<tr>
<td>D1 + e = D2</td>
<td>0.15</td>
</tr>
<tr>
<td>D2 + e = D3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

(b) 4

<table>
<thead>
<tr>
<th>charge-transfer reaction</th>
<th>redox potentials (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + e = B</td>
<td>0.582</td>
</tr>
<tr>
<td>B + e = C1</td>
<td>0.26</td>
</tr>
<tr>
<td>C1 + e = C2</td>
<td>0.19</td>
</tr>
<tr>
<td>C2 + e = C3</td>
<td>0.184</td>
</tr>
<tr>
<td>C3 + e = C4</td>
<td>0.18</td>
</tr>
<tr>
<td>C4 + e = D</td>
<td>0.133</td>
</tr>
<tr>
<td>D + e = E1</td>
<td>0.129</td>
</tr>
<tr>
<td>E1 + e = E2</td>
<td>0.088</td>
</tr>
<tr>
<td>E2 + e = E3</td>
<td>0.05</td>
</tr>
<tr>
<td>E3 + e = F</td>
<td>0.02</td>
</tr>
</tbody>
</table>
$^1$H NMR of 1a
$^{13}$C NMR of 1a
$^1$H NMR of 1b

[Image of NMR spectrum]

S17
$^{13}$C NMR of 1b

**Spectrum Details**
- **DFILE**: fid
- **COMNT**: 4-PhMeDT-TTF C
- **DATIM**: /prog/mod/procld /op
- **OBNUC**: 13C
- **EXMOD**: zgpg30
- **OBFQR**: 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

**Chemical Structure**

![Chemical Structure](image)
$^1$H NMR of 2a

[Image of a NMR spectrum with peaks labeled and chemical structure of 2a]
$^{13}$C NMR of 2a
$^1$H NMR of 2b

![NMR Spectrum of 2b]
$^{13}$C NMR of 2b
$^1$H NMR of 3a
\(^1\)H NMR of 4

\begin{align*}
\text{DFILE: } & 4.4 - \text{PhMeEBDT-TTF aryl} \\
\text{COMNT: } & 4 - \text{PhMeEBDT-TTF aryl} \\
\text{DATIM: } & /prog/mod/proclage/op \\
\text{OBNUC: } & 1H \\
\text{EXMOD: } & zg30 \\
\text{OBFBQ: } & 400.13 \text{ MHz} \\
\text{OBSET: } & 2.47 \text{ KHz} \\
\text{OBFIN: } & 0.97 \text{ Hz} \\
\text{POINT: } & 32768 \\
\text{FREQU: } & 8278.15 \text{ Hz} \\
\text{SCANS: } & 16 \\
\text{ACQTM: } & 0.0000 \text{ sec} \\
\text{PD: } & 0.0000 \text{ sec} \\
\text{PW1: } & 10.00 \text{ usec} \\
\text{IRNUC: } & 22.7 \text{ c} \\
\text{CTEMP: } & C6D6 \\
\text{EXREF: } & 0.00 \text{ ppm} \\
\text{BF: } & 0.00 \text{ Hz} \\
\text{RGAIN: } & 362
\end{align*}

\[ \text{MeS} \quad \text{SMe} \quad \text{MeS} \quad \text{SMe} \]

4
$^1$H NMR of 6a

DFILE 04_4-PhBr-SMeDT H.al
COMNT SMeDBr
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

PPM

S25
$^{13}$C NMR of $6a$
1H NMR of 6b
$^{13}\text{C NMR of 6b}$

Br

S

S

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
$^1$H NMR of 6c
$^{13}$C NMR of 6c
$^1$H NMR of 6d

![NMR Spectrum](image)

**Parameters**
- **DFILE**: 06_4-PhBr-BzDT H.als
- **COMNT**: BzDT-BzBr
- **DATIM**: /prog/mod/proclid /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 $^\circ$C
- **SLVNT**: CDC13
- **EXREF**: 0.00 ppm
- **BF**: 0.12 ppm
- **RGAIN**: 362

**Structure**

![Chemical Structure](image)
$^{13}$C NMR of $6d$
$^1$H NMR of 7a

\[
\text{Br}_2\text{S-SMe}_2
\]
$^{13}$C NMR of 7a
$^1$H NMR of 7b

[Diagram of NMR spectrum with peaks at various ppm values]
$^{13}$C NMR of 7b

![13C NMR spectrum of 7b](image)

**Parameters:**
- **DFILE:** 02_2-ThioBr-MeDT C.a
- **COMINT:** 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
$^1$H NMR of 7d
$^{13}$C NMR of 7d
$^{1}H$ NMR of 9
$^{1}H$ NMR of 10
$^1$H NMR of 12
$^{13}$C NMR of 12
$^{1}H$ NMR of 13
$^1$H NMR of 21

[Diagram of 1H NMR spectrum]

S44
$^{13}$C NMR of 21

![C NMR spectrum](image)

**S45**