

## Supporting Information

### Palladium-Catalyzed Oxidative C–O Cross-Coupling of Ketene Dithioacetals and Carboxylic Acids

Deqiang Liang,<sup>a,b</sup> Mang Wang,\*<sup>a</sup> Ying Dong,<sup>a</sup> Yaru Guo,<sup>a</sup> and Qun Liu\*<sup>a</sup>

<sup>a</sup> Department of Chemistry, Northeast Normal University, Changchun 130024, China

<sup>b</sup> Department of Chemistry, Kunming University, Kunming 650214, China

E-mail: wangm452@nenu.edu.cn; liuqun@nenu.edu.cn.

#### Table of Contents

<b>I. General</b> .....	S2
<b>II. Acetoxylation of Ketene Dithioacetals 1</b> .....	S2
<b>III. Spectral Data of 2</b> .....	S2
<b>IV. Cross-Coupling of 1a with Carboxylic Acids</b> .....	S6
<b>V. Spectral Data of 3 and 4</b> .....	S6
<b>VI. Copies of NMR spectra of all new compounds</b> .....	S8
<b>VII. ESI/MS Experiment and Copies of ESI/MS Spectra for E</b> .....	S28

## I. General

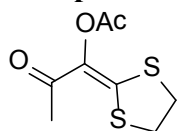
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. Compounds **1** were prepared according to the reported procedure.<sup>1</sup> <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at 25°C on a Varian 500 MHz and 125 MHz, respectively, and TMS as internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

## II. Acetoxylation of Ketene Dithioacetals **1**

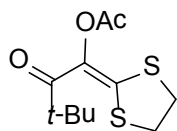
**General Procedure for Cross-Coupling Reactions of Ketene Dithioacetals **1** with Carboxylic Acids (**1a** as Example):** A 25 mL flask, equipped with a magnetic-stirring bar, was charged with ketene dithioacetal **1a** (160 mg, 1.0 mmol), PhI(OAc)<sub>2</sub> (387 mg, 1.2 mmol), and Pd(OAc)<sub>2</sub> (23 mg, 0.1 mmol), followed by addition of 9.1 mL acetic acid and 0.91 mL water. The reaction mixture was stirred at 50 °C for 1 h. Then it was cooled to room temperature and poured into 50 mL ice-water under stirring. After neutralized by saturated aqueous K<sub>2</sub>CO<sub>3</sub> solution, the resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The extract was dried over anhydrous MgSO<sub>4</sub>. After removal of solvents, the residue was purified by column chromatography on silica gel (petroleum ether : diethyl ether = 7 : 1, V/V) to afford the desired product **2a** as a white solid (213 mg, 98 % yield).

In the cases of **1i-p**, 20 mol % of Pd(OAc)<sub>2</sub> was used.

## III. Spectral Data of **2**

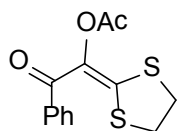


*1-(1,3-dithiolan-2-ylidene)-2-oxopropyl acetate **2a***, white solid: mp 93-94 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 2.13 (s, 3H), 2.29 (s, 3H), 3.36 (t, *J* = 6.5 Hz, 2H), 3.49 (t, *J* = 6.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 189.9, 168.8, 153.2, 134.0, 40.1, 36.3, 25.1, 20.4; HRMS (ESI-TOF) Calcd for C<sub>8</sub>H<sub>11</sub>O<sub>3</sub>S<sub>2</sub><sup>+</sup> ([M+H]<sup>+</sup>) 219.0144. Found 219.0160.

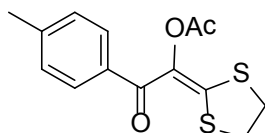


*1-(1,3-dithiolan-2-ylidene)-3,3-dimethyl-2-oxobutyl acetate **2b***, colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 1.19 (s, 9H), 2.28 (s, 3H), 3.35 (t, *J* = 6.5 Hz, 2H), 3.44 (t, *J* = 6.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 196.7, 168.2, 156.0, 133.8, 42.1, 39.8, 36.3, 26.4 (3C), 20.9; HRMS (ESI-TOF) Calcd for C<sub>11</sub>H<sub>17</sub>O<sub>3</sub>S<sub>2</sub><sup>+</sup> ([M+H]<sup>+</sup>) 261.0614. Found 261.0611.

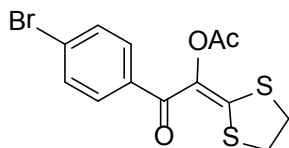
1 H. Yu, W. Jin, C. Sun, J. Chen, W. Du, S. He, Z. Yu, *Angew. Chem. Int. Ed.* **2010**, *49*, 5792–5797, and references therein.



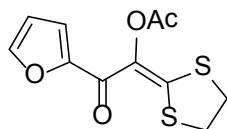
*1-(1,3-dithiolan-2-ylidene)-2-oxo-2-phenylethyl acetate 2c*, yellow solid: mp 99-100 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.06 (s, 3H), 3.40-3.43 (m, 2H), 3.50-3.52 (m, 2H), 7.39 (dd,  $J$  = 7.5, 7.5 Hz, 2H), 7.47 (dd,  $J$  = 7.5, 7.5 Hz, 1H), 7.73-7.74 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 185.5, 168.3, 156.0, 137.0, 133.3, 131.4, 127.90 (2C), 127.95 (2C), 39.9, 36.3, 20.3; HRMS (ESI-TOF) Calcd for  $\text{C}_{13}\text{H}_{13}\text{O}_3\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 281.0301. Found 281.0309.



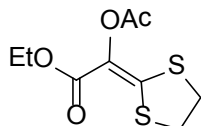
*1-(1,3-dithiolan-2-ylidene)-2-oxo-2-(p-tolyl)ethyl acetate 2d*, yellow solid: mp 171-172 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.08 (s, 3H), 2.38 (s, 3H), 3.40 (t,  $J$  = 6.5 Hz, 2H), 3.49 (t,  $J$  = 6.5 Hz, 2H), 7.19 (d,  $J$  = 8.0 Hz, 2H), 7.66 (d,  $J$  = 8.0 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 185.2, 168.4, 155.4, 142.0, 134.3, 133.6, 128.7 (2C), 128.1 (2C), 39.8, 36.3, 21.4, 20.4; HRMS (ESI-TOF) Calcd for  $\text{C}_{14}\text{H}_{15}\text{O}_3\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 295.0457. Found 295.0459.



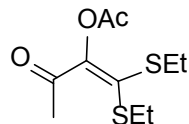
*2-(4-bromophenyl)-1-(1,3-dithiolan-2-ylidene)-2-oxoethyl acetate 2e*, light yellow solid: mp 177-178 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.08 (s, 3H), 3.41 (t,  $J$  = 6.0 Hz, 2H), 3.51 (t,  $J$  = 6.0 Hz, 2H), 7.54 (d,  $J$  = 8.5 Hz, 2H), 7.62 (d,  $J$  = 8.5 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 184.4, 168.4, 157.0, 136.1, 133.3, 131.5 (2C), 129.8 (2C), 126.4, 40.1, 36.6, 20.5; HRMS (ESI-TOF) Calcd for  $\text{C}_{13}\text{H}_{12}\text{BrO}_3\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 358.9406. Found 358.9421.



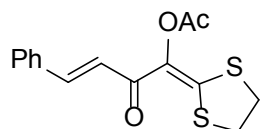
*1-(1,3-dithiolan-2-ylidene)-2-(furan-2-yl)-2-oxoethyl acetate 2f*, yellow solid: mp 159-161 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.32 (s, 3H), 3.39 (t,  $J$  = 6.5 Hz, 2H), 3.50 (t,  $J$  = 6.5 Hz, 2H), 6.50 (dd,  $J$  = 1.5, 3.5 Hz, 1H), 7.20 (d,  $J$  = 3.5 Hz, 1H), 7.56 (d,  $J$  = 1.5 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 171.4, 168.8, 157.3, 151.4, 146.1, 132.5, 118.0, 112.0, 40.1, 36.3, 20.7; HRMS (ESI-TOF) Calcd for  $\text{C}_{11}\text{H}_{11}\text{O}_4\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 271.0093. Found 271.0079.



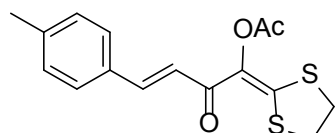
*ethyl 2-acetoxy-2-(1,3-dithiolan-2-ylidene)acetate 2g*, white solid: mp 66-67 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.29 (t,  $J$  = 7.0 Hz, 3H), 2.24 (s, 3H), 3.39 (t,  $J$  = 6.0 Hz, 2H), 3.50 (t,  $J$  = 6.0 Hz, 2H), 4.24 (q,  $J$  = 7.0 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 168.4, 161.2, 152.3, 125.1, 61.1, 39.9, 36.9, 20.2, 14.2; HRMS (ESI-TOF) Calcd for  $\text{C}_9\text{H}_{13}\text{O}_4\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 249.0250. Found 249.0254.



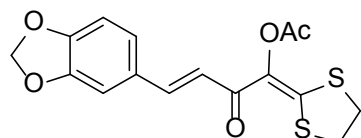
*1,1-bis(ethylthio)-3-oxobut-1-en-2-yl acetate 2h*, brown liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.24-1.29 (m, 6H), 2.19 (s, 3H), 2.29 (s, 3H), 2.71 (q,  $J$  = 7.5 Hz, 2H), 2.85 (q,  $J$  = 7.5 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.8, 168.1, 157.4, 121.6, 29.5, 24.4, 20.9, 20.5, 14.5, 14.3; HRMS (ESI-TOF) Calcd for  $\text{C}_{10}\text{H}_{17}\text{O}_3\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 249.0614. Found 249.0615.



*(E)-1-(1,3-dithiolan-2-ylidene)-2-oxo-4-phenylbut-3-en-1-yl acetate 2i*, yellow solid: mp 128-129 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.36 (s, 3H), 3.40 (t,  $J$  = 6.5 Hz, 2H), 3.52 (t,  $J$  = 6.5 Hz, 2H), 6.94 (d,  $J$  = 15.5 Hz, 1H), 7.37-7.39 (m, 3H), 7.54 (dd,  $J$  = 3.0, 6.0 Hz, 2H), 7.76 (d,  $J$  = 15.5 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 180.6, 168.6, 155.1, 143.6, 134.8, 134.2, 130.2, 128.7 (2C), 128.2 (2C), 119.7, 40.0, 36.3, 20.3; HRMS (ESI-TOF) Calcd for  $\text{C}_{15}\text{H}_{15}\text{O}_3\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 307.0457. Found 307.0455.

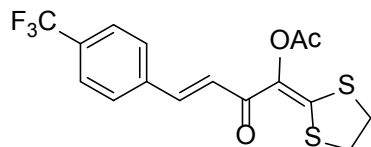


*(E)-1-(1,3-dithiolan-2-ylidene)-2-oxo-4-(p-tolyl)but-3-en-1-yl acetate 2j*, yellow solid: mp 147-148 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.35 (s, 3H), 2.36 (s, 3H), 3.36-3.39 (m, 2H), 3.48-3.51 (m, 2H), 6.89 (d,  $J$  = 15.5 Hz, 1H), 7.18 (d,  $J$  = 8.0 Hz, 2H), 7.43 (d,  $J$  = 8.0 Hz, 2H), 7.73 (d,  $J$  = 15.5 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 180.9, 168.7, 154.7, 143.9, 140.8, 134.3, 132.2, 129.5 (2C), 128.3 (2C), 118.6, 40.1, 36.4, 21.5, 20.5; HRMS (ESI-TOF) Calcd for  $\text{C}_{16}\text{H}_{17}\text{O}_3\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 321.0614. Found 321.0629.

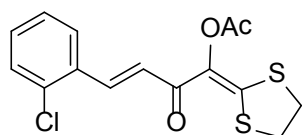


*(E)-4-(benzo[d][1,3]dioxol-5-yl)-1-(1,3-dithiolan-2-ylidene)-2-oxobut-3-en-1-yl acetate 2k*, yellow solid: mp 199-200 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.36 (s, 3H), 3.39 (t,  $J$  = 6.0 Hz, 2H), 3.51 (t,  $J$  = 6.0 Hz, 2H), 6.01 (s, 2H), 6.76 (d,  $J$  = 16.0 Hz, 1H), 6.81 (d,  $J$  = 8.5 Hz, 1H), 7.03-7.04 (m, 2H), 7.67 (d,  $J$  = 16.0 Hz, 1H);  $^{13}\text{C}$

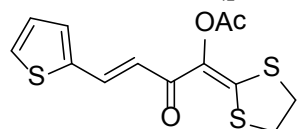
NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 180.8, 168.8, 154.6, 149.7, 148.2, 143.8, 134.4, 129.5, 125.1, 117.7, 108.6, 106.5, 101.5, 40.1, 36.4, 20.5; HRMS (ESI-TOF) Calcd for C<sub>16</sub>H<sub>15</sub>O<sub>5</sub>S<sub>2</sub><sup>+</sup> ([M+H]<sup>+</sup>) 351.0355. Found 351.0356.



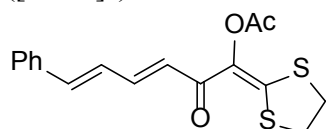
*(E)*-1-(1,3-dithiolan-2-ylidene)-2-oxo-4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl acetate **2l**, yellow solid: mp 233-234 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.36 (s, 3H), 3.41 (t, *J* = 6.5 Hz, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 6.99 (d, *J* = 15.5 Hz, 1H), 7.63 (s, 4H), 7.74 (d, *J* = 15.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 180.3, 168.8, 156.3, 141.7, 138.4, 134.2, 131.5 (q, <sup>2</sup>*J*<sub>(C-F)</sub> = 32.5 Hz), 128.4 (2C), 125.7 (d, <sup>3</sup>*J*<sub>(C-F)</sub> = 3.4 Hz, 2C), 124.9 (q, <sup>1</sup>*J*<sub>(C-F)</sub> = 270.4 Hz), 122.0, 40.1, 36.5, 20.5; HRMS (ESI-TOF) Calcd for C<sub>16</sub>H<sub>14</sub>F<sub>3</sub>O<sub>3</sub>S<sub>2</sub><sup>+</sup> ([M+H]<sup>+</sup>) 375.0331. Found 375.0327.



*(E)*-4-(2-chlorophenyl)-1-(1,3-dithiolan-2-ylidene)-2-oxobut-3-en-1-yl acetate **2m**, yellow solid: mp 165-166 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.34 (s, 3H), 3.39 (t, *J* = 6.5 Hz, 2H), 3.51 (t, *J* = 6.5 Hz, 2H), 6.92 (d, *J* = 15.5 Hz, 1H), 7.24-7.31 (m, 2H), 7.40 (dd, *J* = 2.0, 7.5 Hz, 1H), 7.60 (dd, *J* = 2.0, 7.5 Hz, 1H), 8.13 (d, *J* = 15.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 180.5, 168.7, 155.8, 139.4, 135.4, 134.2, 133.3, 130.9, 130.2, 127.7, 126.9, 122.5, 40.1, 36.4, 20.5; HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>14</sub>ClO<sub>3</sub>S<sub>2</sub><sup>+</sup> ([M+H]<sup>+</sup>) 341.0067. Found 341.0053.

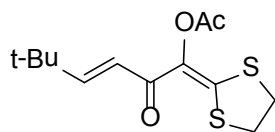


*(E)*-1-(1,3-dithiolan-2-ylidene)-2-oxo-4-(thiophen-2-yl)but-3-en-1-yl acetate **2n**, yellow solid: mp 104-105 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.35 (s, 3H), 3.38 (t, *J* = 6.0 Hz, 2H), 3.50 (t, *J* = 6.0 Hz, 2H), 6.72 (d, *J* = 15.5 Hz, 1H), 7.05 (dd, *J* = 3.5, 4.5 Hz, 1H), 7.28 (d, *J* = 3.5 Hz, 1H), 7.37 (d, *J* = 4.5 Hz, 1H), 7.85 (d, *J* = 15.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 180.4, 168.7, 154.9, 140.5, 136.2, 134.2, 131.7, 128.4, 128.2, 118.7, 40.1, 36.4, 20.4; HRMS (ESI-TOF) Calcd for C<sub>13</sub>H<sub>13</sub>O<sub>3</sub>S<sub>3</sub><sup>+</sup> ([M+H]<sup>+</sup>) 313.0021. Found 313.0024.



*(3E,5E)*-1-(1,3-dithiolan-2-ylidene)-2-oxo-6-phenylhexa-3,5-dien-1-yl acetate **2o**, semisolid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.35 (s, 3H), 3.37-3.40 (m, 2H), 3.49-3.52 (m, 2H), 6.49 (d, *J* = 15.0 Hz, 1H), 6.93-6.95 (m, 2H), 7.30 (dd, *J* = 7.0, 7.5 Hz, 1H),

7.35 (dd,  $J = 7.0, 7.5$  Hz, 2H), 7.47 (d,  $J = 7.5$  Hz, 2H), 7.54 (dd,  $J = 9.5, 15.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta = 180.8, 168.8, 154.6, 143.9, 141.5, 136.1, 134.4, 129.0, 128.7$  (2C), 127.2 (2C), 127.1, 123.1, 40.1, 36.3, 20.5; HRMS (ESI-TOF) Calcd for  $\text{C}_{17}\text{H}_{17}\text{O}_3\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 333.0614. Found 333.0612.



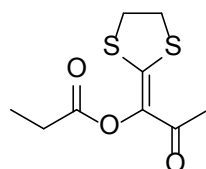
(*E*)-1-(1,3-dithiolan-2-ylidene)-5,5-dimethyl-2-oxohex-3-en-1-yl acetate **2p**, white solid: mp 73-74 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta = 1.01$  (s, 9H), 2.30 (s, 3H), 3.37 (t,  $J = 6.5$  Hz, 2H), 3.49 (t,  $J = 6.5$  Hz, 2H), 6.21 (d,  $J = 15.5$  Hz, 1H), 7.01 (d,  $J = 15.5$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta = 181.7, 168.6, 158.5, 154.3, 134.1, 118.2, 40.2, 36.3, 33.9, 28.6$  (3C), 20.4; HRMS (ESI-TOF) Calcd for  $\text{C}_{13}\text{H}_{19}\text{O}_3\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 287.0770. Found 287.0774.

#### IV. Cross-Coupling of **1a** with Carboxylic Acids

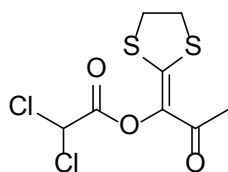
**Cross-Coupling Reactions of Ketene Dithioacetal **1a** with Carboxylic Acids, Affording **3** and/or **4** (Propionic Acid as Example):** A 25 mL flask, equipped with a magnetic-stirring bar, was charged with ketene dithioacetal **1a** (160 mg, 1.0 mmol),  $\text{PhI}(\text{OAc})_2$  (387 mg, 1.2 mmol), and  $\text{Pd}(\text{OAc})_2$  (23 mg, 0.1 mmol), followed by addition of 9.1 mL propionic acid and 0.91 mL water. The reaction mixture was stirred at 50 °C for 3 h. Then it was cooled to room temperature and poured into 50 mL ice-water under stirring. After neutralized by saturated aqueous  $\text{K}_2\text{CO}_3$  solution, the resulting mixture was extracted with  $\text{CH}_2\text{Cl}_2$  three times. The extract was dried over anhydrous  $\text{MgSO}_4$ . After removal of solvents, the residue was purified by column chromatography on silica gel (petroleum ether : diethyl ether = 7 : 1, V/V) to afford the desired product **3a** as a white solid (116 mg, 50 % yield).

In the case of TFA, anhydrous TFA was used as solvent, and 400 mg 4 Å MS was added.

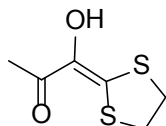
#### V. Spectral Data of **3** and **4**



1-(1,3-dithiolan-2-ylidene)-2-oxopropyl propionate **3a**, white solid: mp 61-62 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta = 1.29$  (t,  $J = 7.5$  Hz, 3H), 2.12 (s, 3H), 2.58 (q,  $J = 7.5$  Hz, 2H), 3.35 (t,  $J = 6.0$  Hz, 2H), 3.48 (t,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta = 189.9, 172.2, 152.9, 133.9, 40.1, 36.3, 27.3, 25.1, 9.0$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_9\text{H}_{13}\text{O}_3\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 233.0301. Found 233.0304.



*1-(1,3-dithiolan-2-ylidene)-2-oxopropyl 2,2-dichloroacetate 3b*, white solid: mp 93-94 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.17 (s, 3H), 3.39-3.42 (m, 2H), 3.50-3.53 (m, 2H), 6.16 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 188.7, 162.2, 155.3, 133.2, 63.6, 40.1, 36.7, 29.6, 25.2; HRMS (ESI-TOF) Calcd for  $\text{C}_8\text{H}_9\text{Cl}_2\text{O}_3\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 286.9365. Found 286.9365.



*1-(1,3-dithiolan-2-ylidene)-1-hydroxypropan-2-one 4*, light yellow solid: mp 159-160 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.51 (s, 3H), 3.42-3.44 (m, 2H), 3.54-3.57 (m, 2H), 6.68 (s, exchanges with  $\text{D}_2\text{O}$ , 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 188.2, 139.1, 135.5, 40.4, 36.9, 27.3; HRMS (ESI-TOF) Calcd for  $\text{C}_6\text{H}_9\text{O}_2\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 177.0038. Found 177.0051.

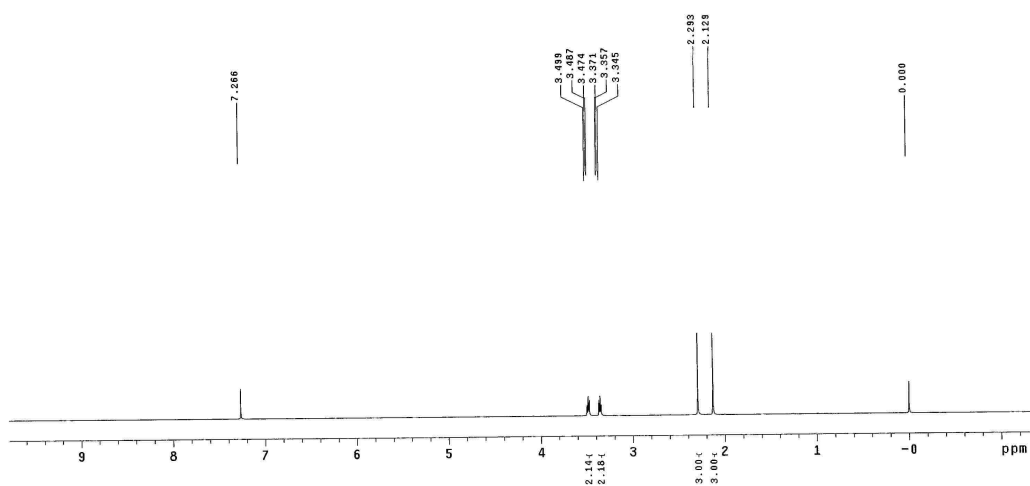
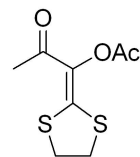
## VI. Copies of NMR Spectra of All New Compounds

### 2a

#### STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrSYS/data  
Sample directory:  
Pulse Sequence: s2pul  
Solvent: CDCl3  
Ambient temperature  
File: w319  
INOVA-500 "NENU500"

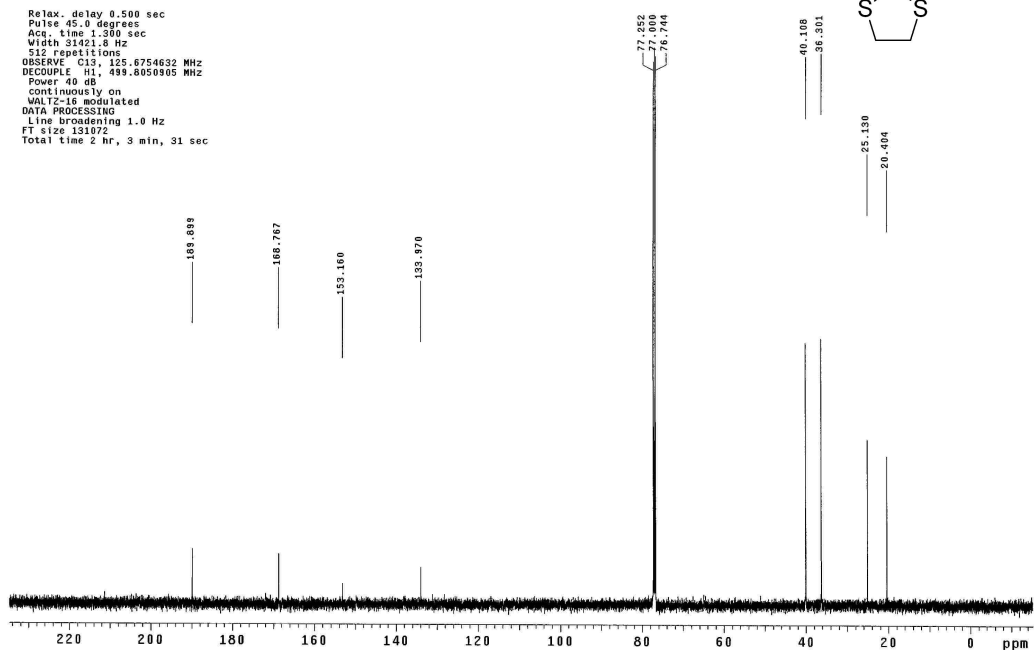
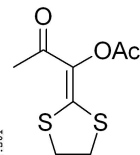
Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.852 sec  
Width 7356.8 Hz  
8 repetitions  
OBSERVE H1, 499.802587 MHz  
DATA PROCESSING  
F1 size 65536  
Total time 0 min, 23 sec



#### STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrSYS/data  
Sample directory:  
Pulse Sequence: s2pul  
Solvent: CDCl3  
Ambient temperature  
User: 1-14-87  
File: p249  
INOVA-500 "NENU500"

Relax. delay 0.500 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 31421.8 Hz  
512 repetitions  
OBSERVE C13, 125.6754632 MHz  
DECOUPLE H1, 499.8050905 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
F1 size 131072  
Total time 2 hr, 3 min, 31 sec





2b

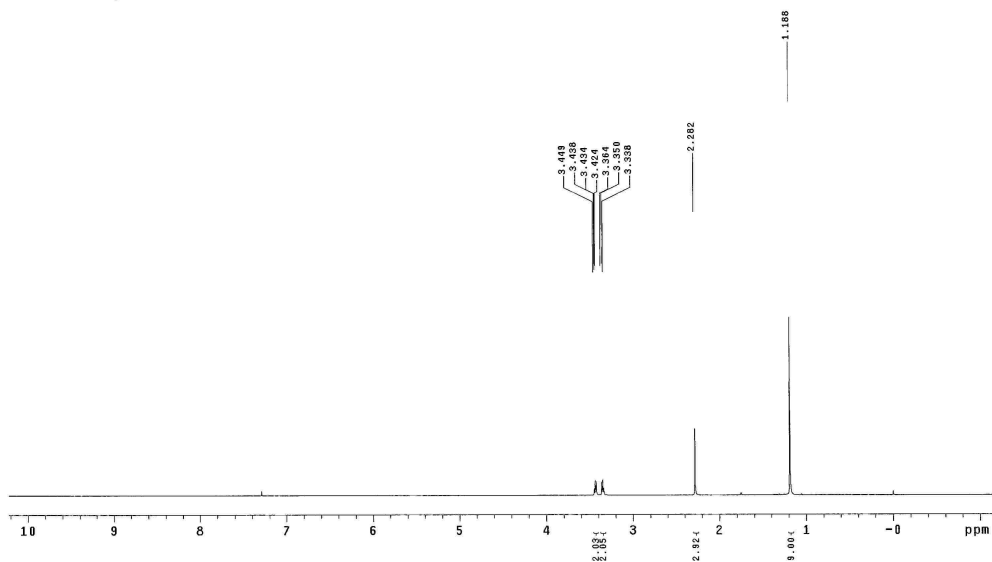
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl3  
Ambient temperature  
File: w561  
INOVA-500 "NENU500"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.692 sec  
Width 7996.8 Hz  
S repetitions  
OBSERVE H1, 499.8025753 MHz  
DATA PROCESSING  
FT size 65536  
Total time 0 min, 23 sec



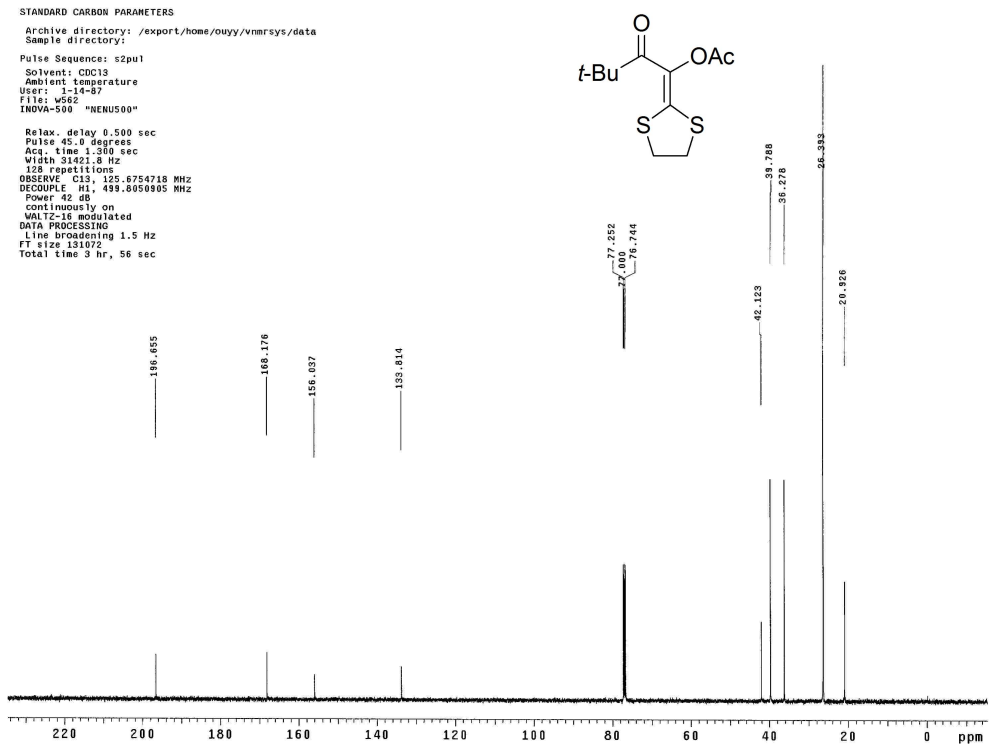
STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl3  
Ambient temperature  
User: 1-14-07  
File: w562  
INOVA-500 "NENU500"

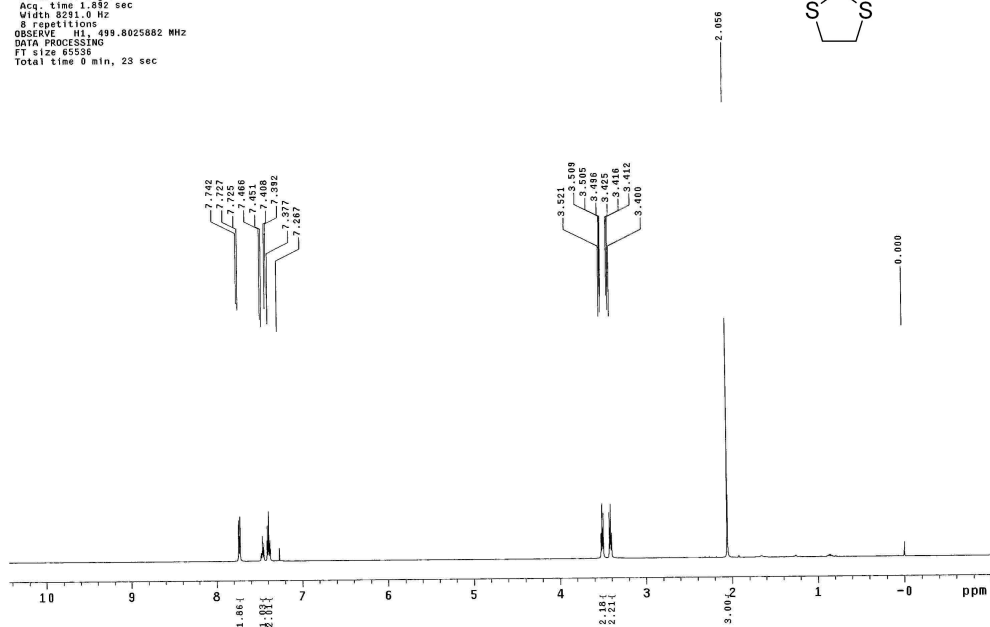
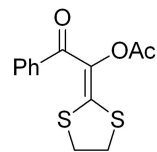
Relax. delay 0.500 sec  
Pulse 45.0 degrees  
Acq. time 1.380 sec  
Width 31421.8 Hz  
128 repetitions  
OBSERVE C13, 125.6754718 MHz  
DECOUPLE H1, 499.8050905 MHz  
Power 42 dB  
Continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.5 Hz  
FT size 131072  
Total time 3 hr, 56 sec



2c

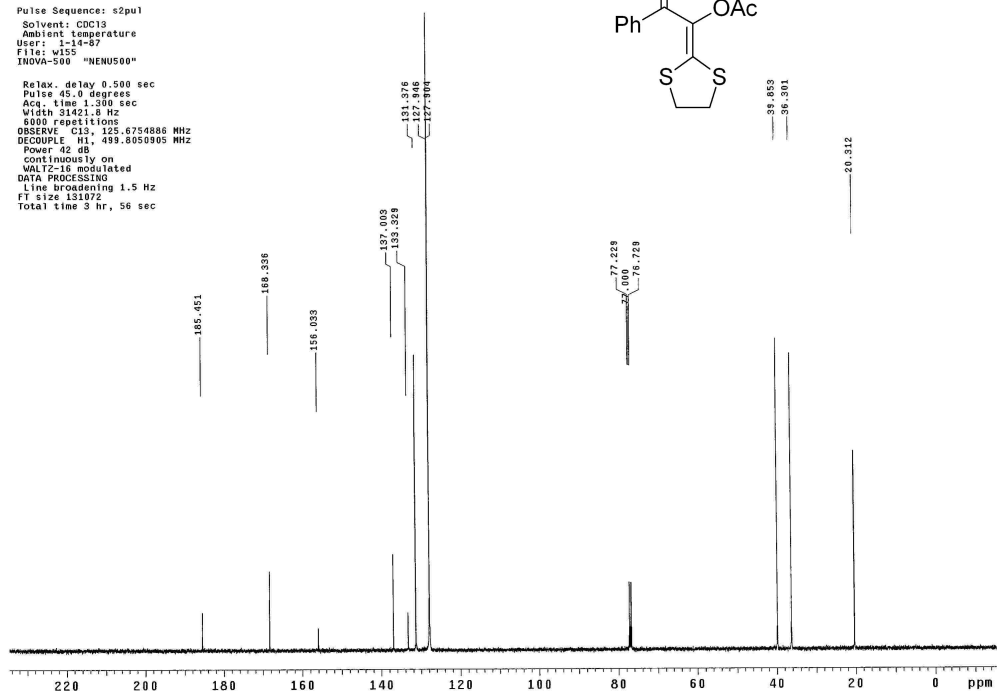
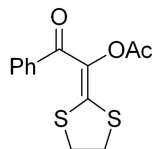
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 File: w145  
 INOVA-500 "NENUS00"  
 Relax. delay 1.000 sec  
 Pulse 45.0 degrees  
 Acq. time 1.892 sec  
 Width 8291.0 Hz  
 8 repetitions  
 OBSERVE H1, 499.8025882 MHz  
 DATA PROCESSING  
 FT size 65536  
 Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

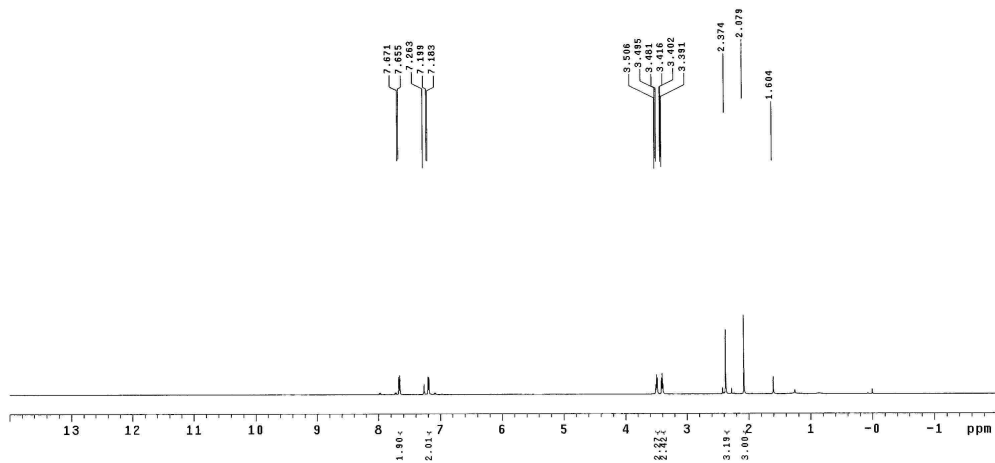
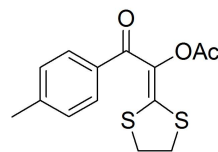
Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 User: 1-14-87  
 File: w155  
 INOVA-500 "NENUS00"  
 Relax. delay 0.500 sec  
 Pulse 45.0 degrees  
 Acq. time 1.300 sec  
 Width 31421.8 Hz  
 6000 repetitions  
 OBSERVE C13, 125.6754886 MHz  
 DECOUPLE H1, 499.8050305 MHz  
 Power 42 dB  
 continuous ly on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.5 Hz  
 FT size 131072  
 Total time 3 hr, 56 sec



2d

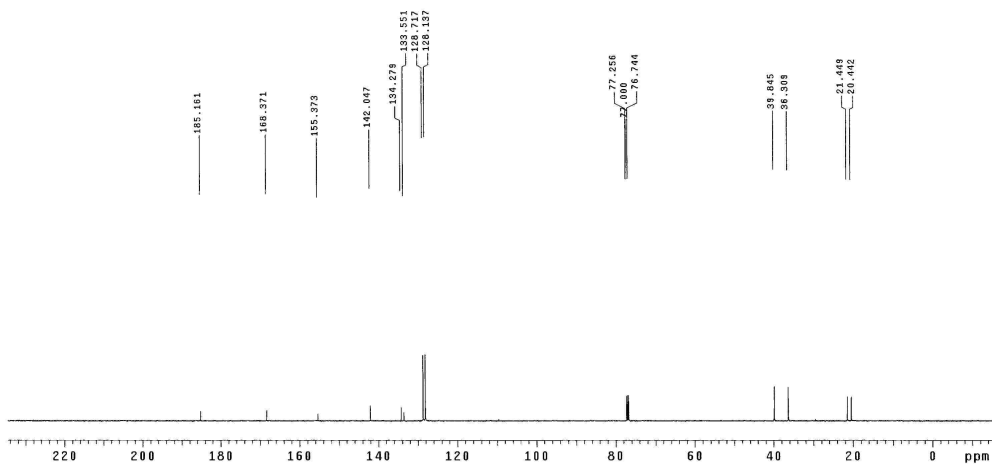
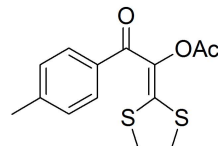
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 File: w464  
 INOVA-500 "NENU500"  
 Relax. delay 1.000 sec  
 Pulse 45.0 degrees  
 Acq. time 1.852 sec  
 Width 7996.8 Hz  
 8 repetitions  
 OBSERVE H1, 499.8025904 MHz  
 DATA PROCESSING  
 FT size 65526  
 Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

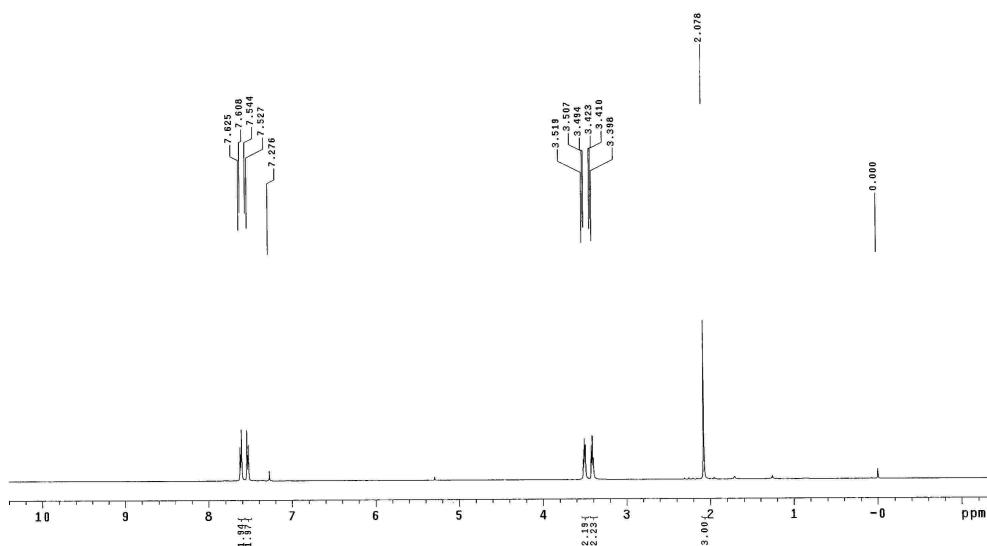
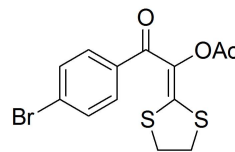
Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: cdcl3  
 Ambient temperature  
 User: 1-14-67  
 File: d223  
 INOVA-500 "NENU500"  
 Relax. delay 0.500 sec  
 Pulse 45.0 degrees  
 Acq. time 1.300 sec  
 Width 31423.8 Hz  
 64 repetitions  
 OBSERVE C13, 125.675829 MHz  
 DECOUPLE H1, 499.8050905 MHz  
 Power 42 dB  
 continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.5 Hz  
 FT size 131072  
 Total time 2 hr, 3 min, 31 sec



2e

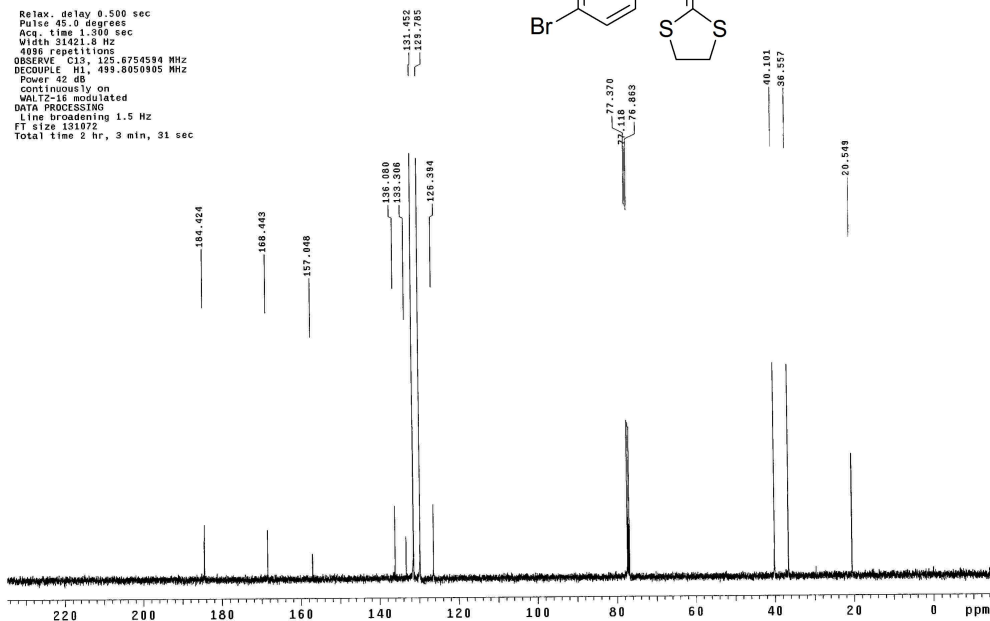
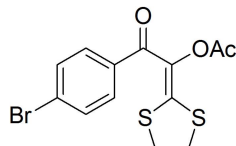
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrSYS/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 File: x531  
 INOVA-500 "NENU500"  
 Relax. delay 1.000 sec  
 Pulse 45.0 degrees  
 Acq. time 1.682 sec  
 Width 7986.8 Hz  
 8 repetitions  
 OBSERVE H1, 499.8025831 MHz  
 DATA PROCESSING  
 FT size 65536  
 Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

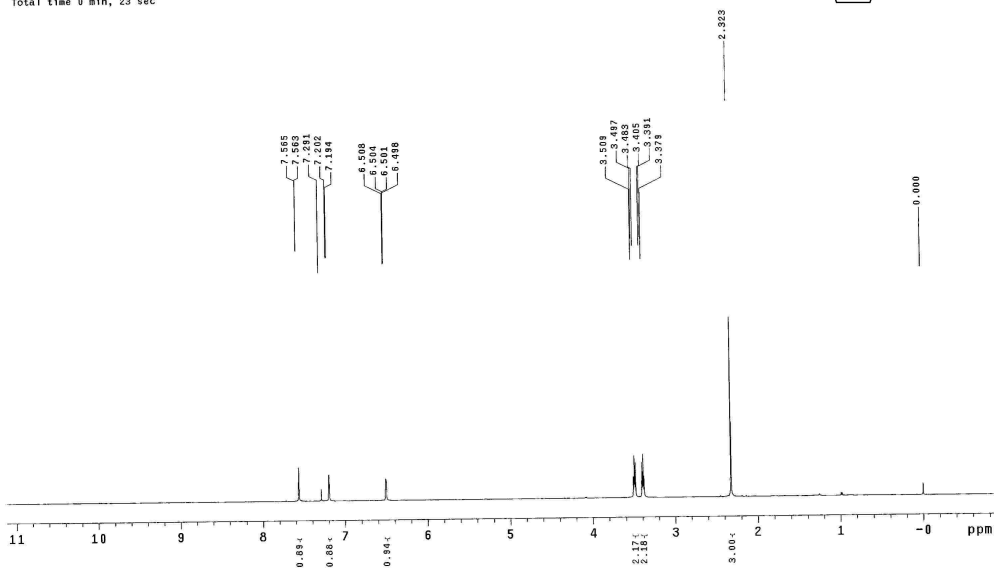
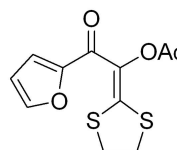
Archive directory: /export/home/ouyy/vnmrSYS/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 User: 1-14-87  
 File: x532  
 INOVA-500 "NENU500"  
 Relax. delay 0.500 sec  
 Pulse 45.0 degrees  
 Acq. time 1.300 sec  
 Width 31421.6 Hz  
 4056 repetitions  
 OBSERVE C13, 125.6754594 MHz  
 DECOUPLE H1, 499.8050905 MHz  
 Power 42 dB  
 continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.5 Hz  
 FT size 131072  
 Total time 2 hr, 3 min, 31 sec



2f

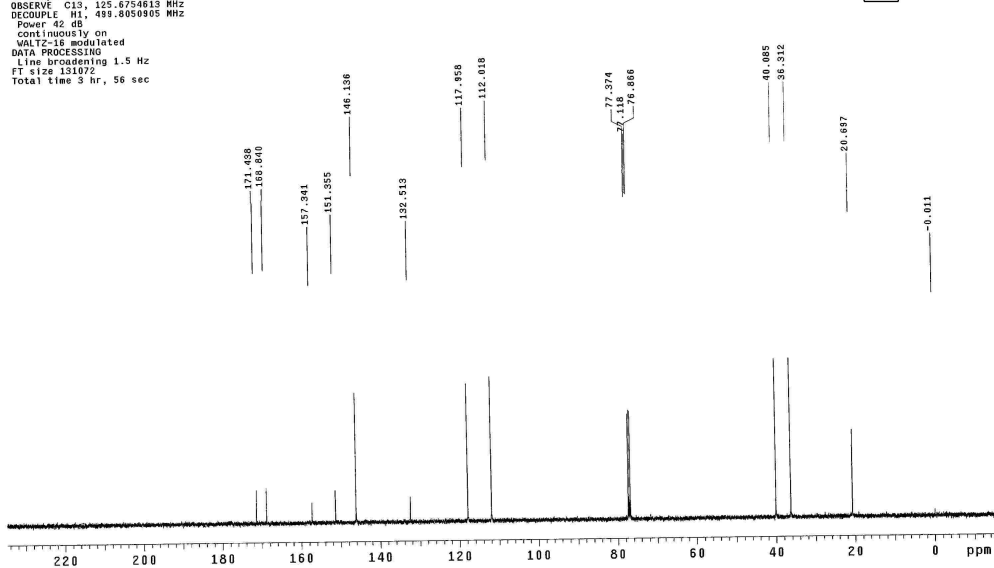
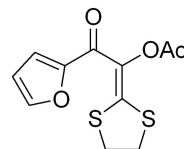
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 File: x403  
 INOVA-500 "NENU500"  
 Relax. delay 1.000 sec  
 Pulse 45.0 degrees  
 Acq. time 1.892 sec  
 Width 7896.8 Hz  
 8 repetitions  
 OBSERVE H1, 499.8025753 MHz  
 DATA PROCESSING  
 FT size 65536  
 Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

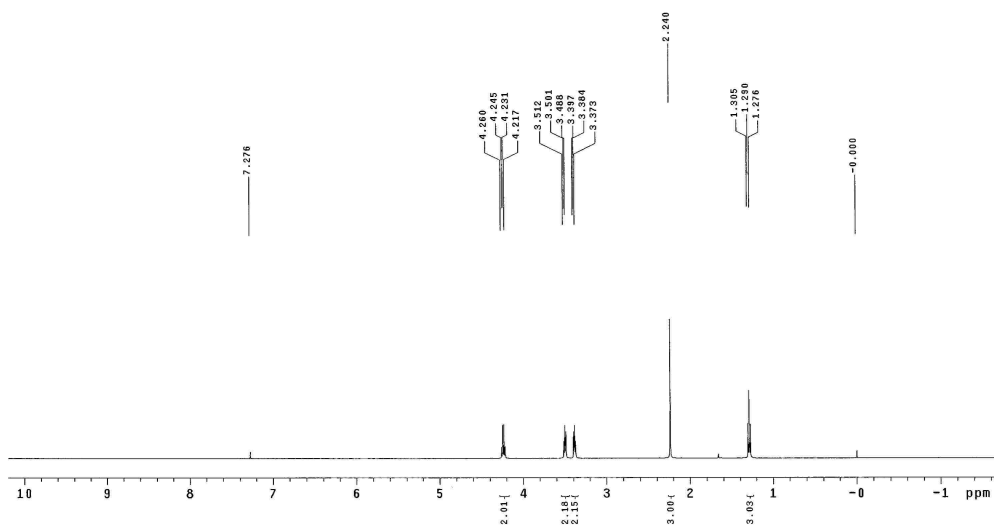
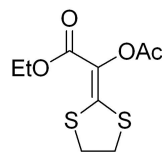
Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 User: 1-14-97  
 File: x404  
 INOVA-500 "NENU500"  
 Relax. delay 0.500 sec  
 Pulse 45.0 degrees  
 Acq. time 1.300 sec  
 Width 31421.8 Hz  
 64 repetitions  
 OBSERVE C13, 125.6754813 MHz  
 DECOUPLE H1, 499.8050865 MHz  
 Power 42 dB  
 Continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.5 Hz  
 FT size 131072  
 Total time 3 hr, 56 sec



## 2g

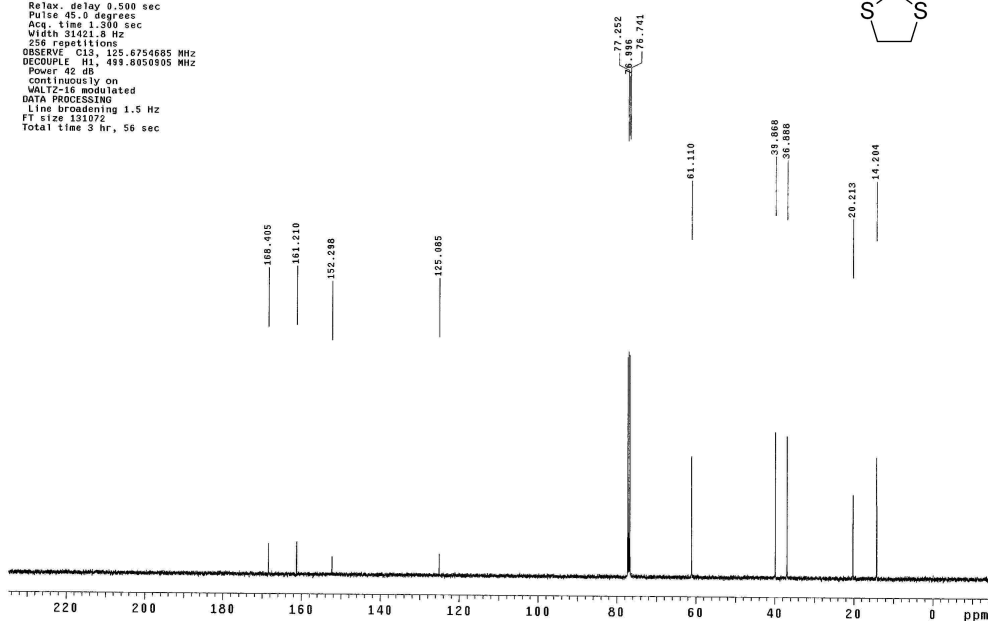
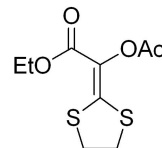
### STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouy/vnmrsys/data  
Sample directory:  
Pulse Sequence: s2pu1  
Solvent: CDCl3  
Ambient temperature  
Files: w180  
INOVA-500 "NENUS00"  
Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 8281.0 Hz  
8 repetitions  
OBSERVE H1: 499.8025836 MHz  
DATA PROCESSING  
FT size 65536  
Total time 0 min, 23 sec



### STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouy/vnmrsys/data  
Sample directory:  
Pulse Sequence: s2pu1  
Solvent: CDCl3  
Ambient temperature  
User: 1-14-87  
Files: w180  
INOVA-500 "NENUS00"  
Relax. delay 0.500 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 31421.8 Hz  
258 repetitions  
OBSERVE C13: 125.6754685 MHz  
DECOUPLE H1: 499.8050905 MHz  
Power 32 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.5 Hz  
FT size 131072  
Total time 3 hr, 56 sec



2h

STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: w208

INOVA-500 "NENU500"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.492 sec

Width 8291.0 Hz

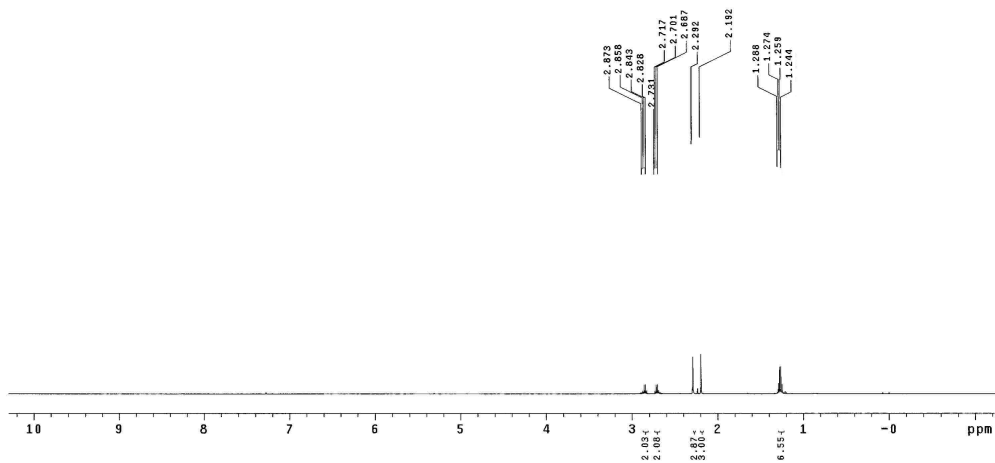
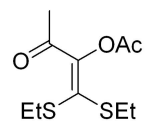
8 repetitions

OBSERVE H1, 499.8025836 MHz

DATA PROCESSING

FT size 65536

Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: w209

INOVA-500 "NENU500"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 1.308 sec

Width 31421.8 Hz

64 repetitions

OBSERVE C13, 125.0754632 MHz

DECOUPLE H1, 499.8059905 MHz

Power 42 dB

continuously on

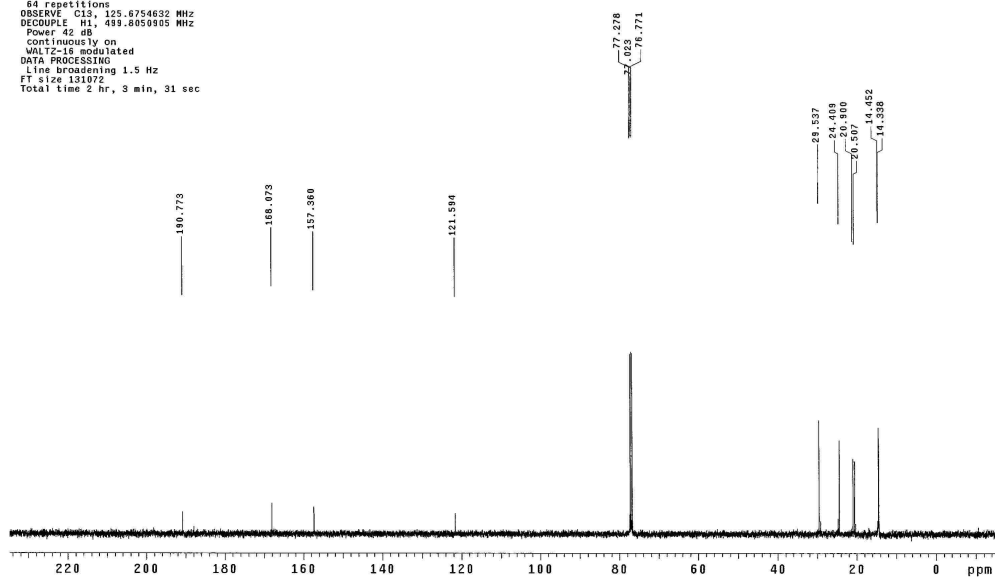
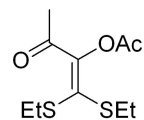
WALTZ-16 modulated

DATA PROCESSING

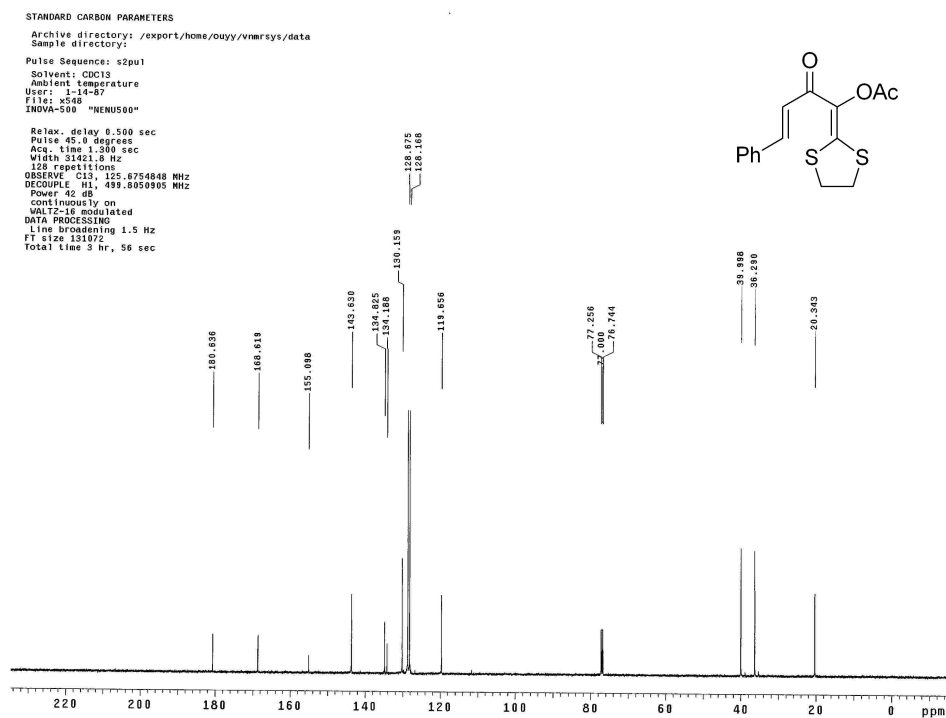
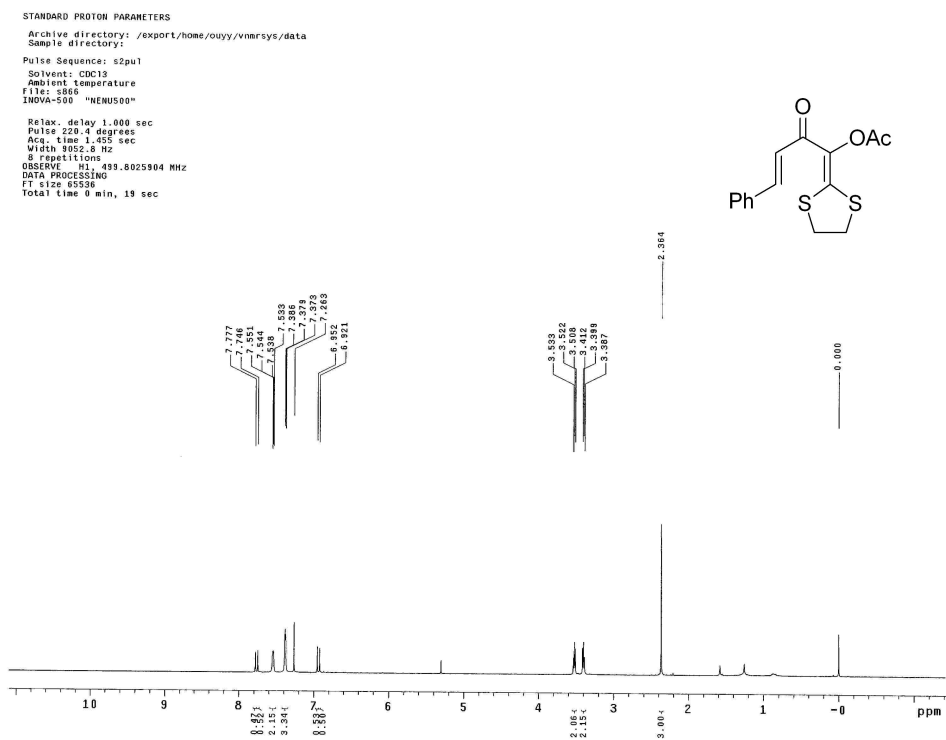
Line broadening 1.5 Hz

FT size 133672

Total time 2 hr, 3 min, 31 sec

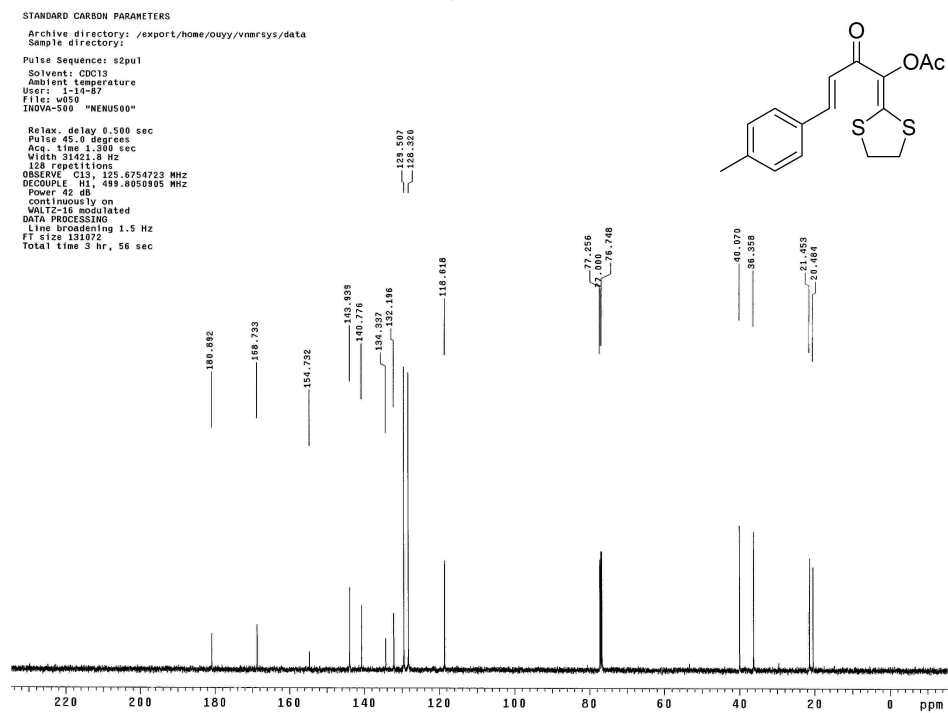
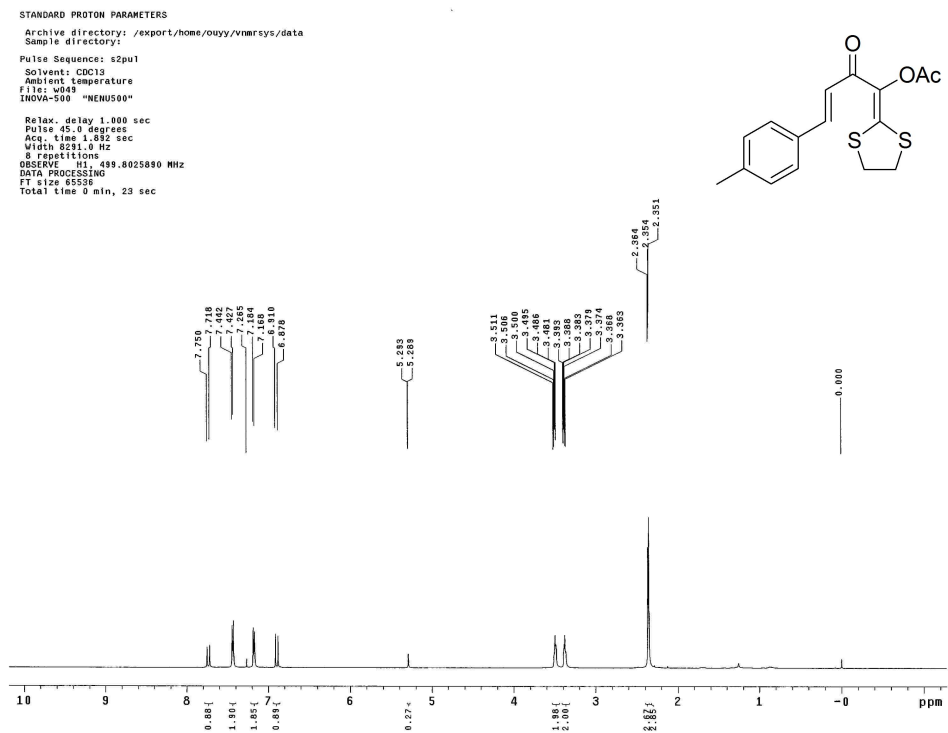


2i

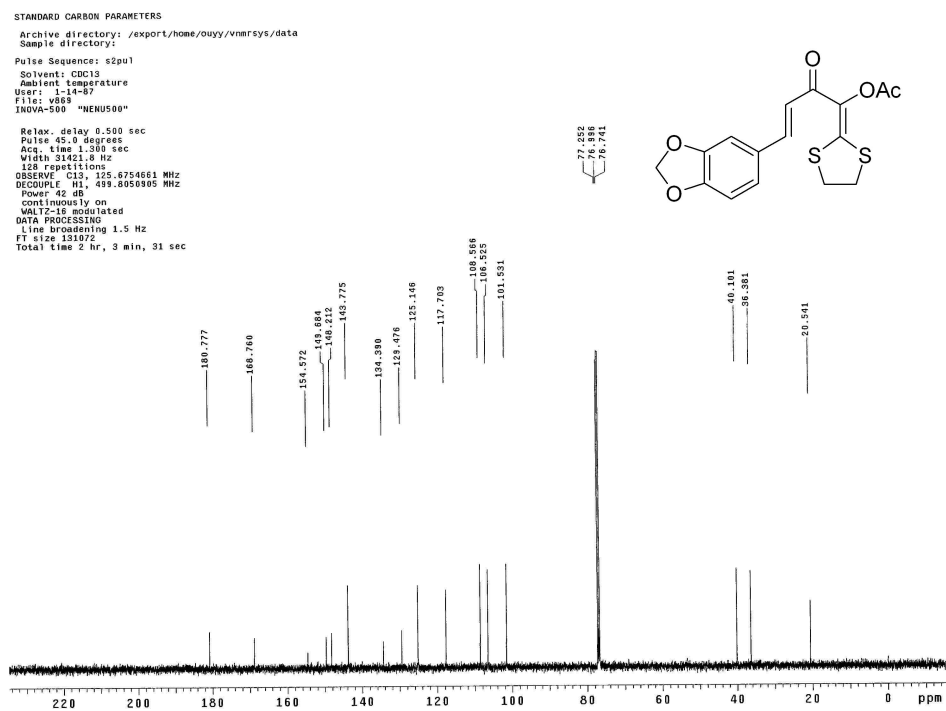
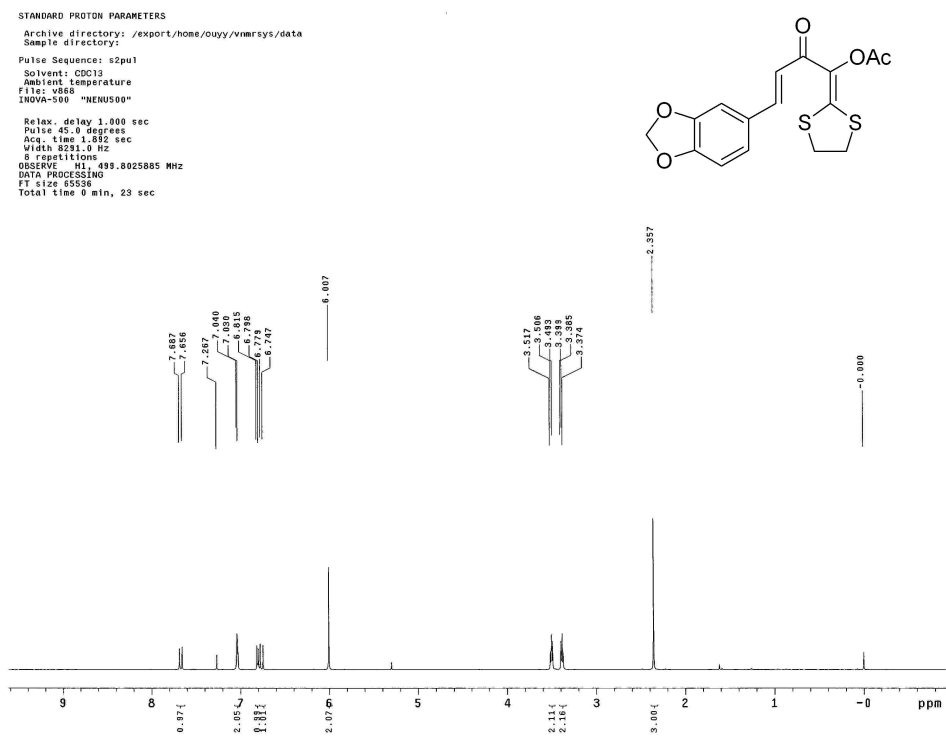




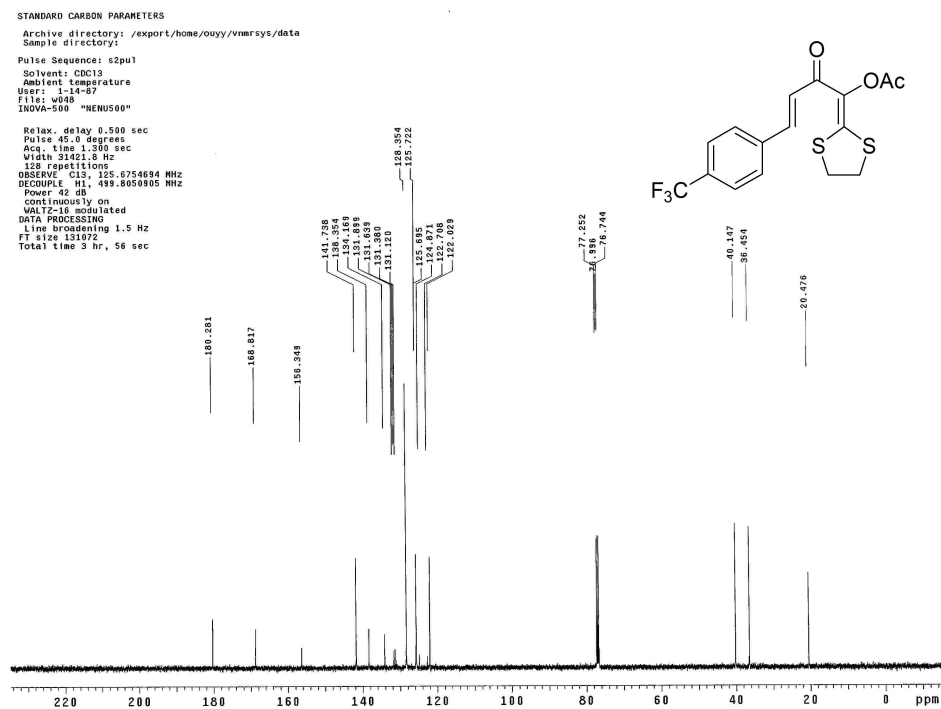
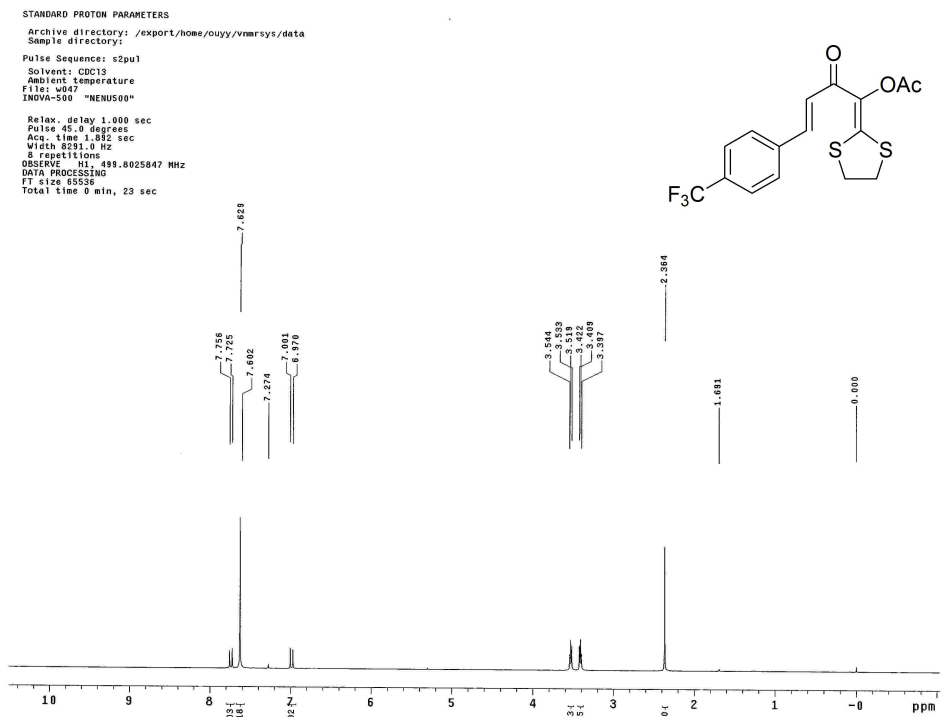
2j



2k



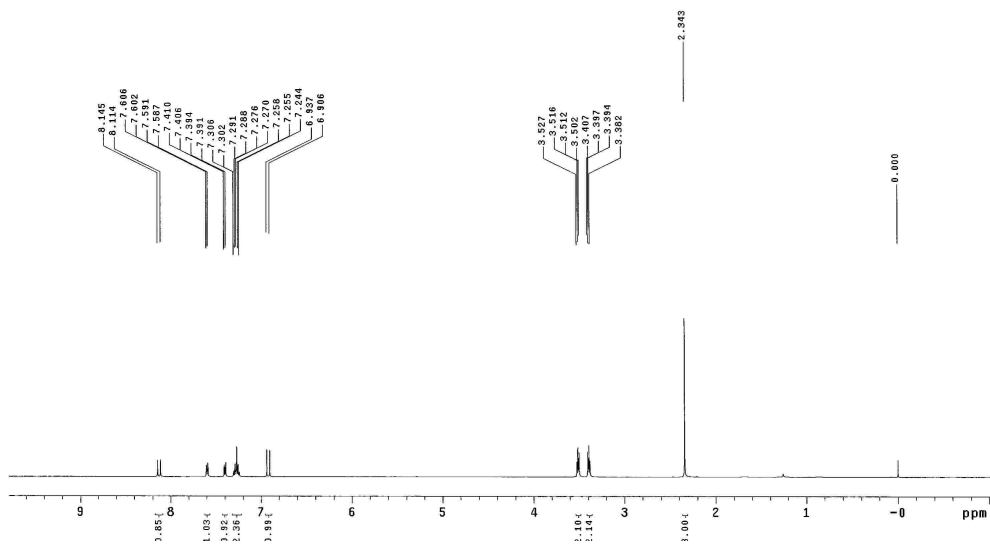
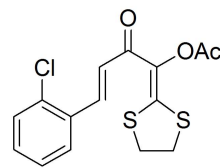
21



2m

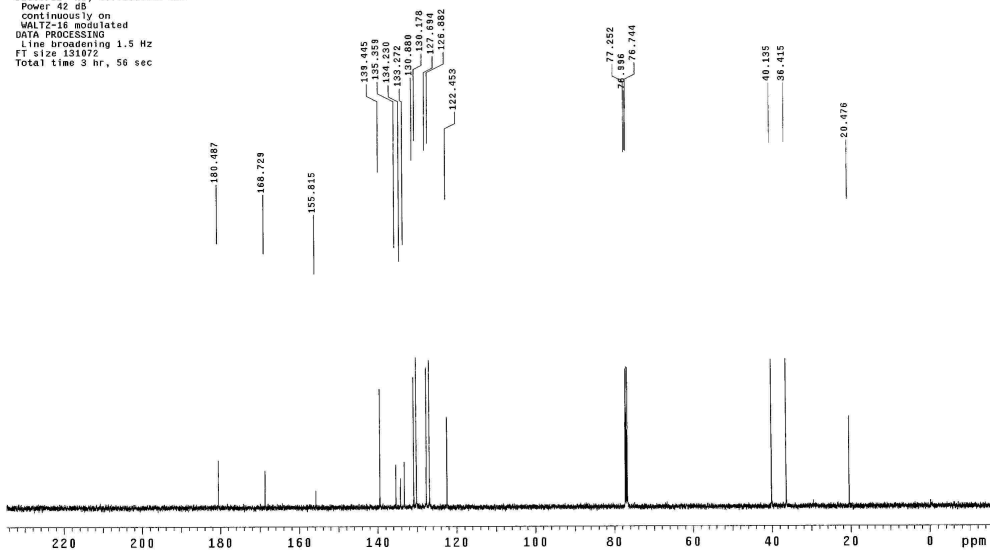
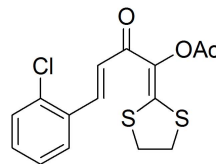
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 File: x408  
 INOVA-500 "NENUS00"  
 Relax. delay 1.000 sec  
 Pulse 45.0 degrees  
 Acq. time 1.833 sec  
 Width 7956.8 Hz  
 S repetitions  
 OBSERVE H1, 499.8025860 MHz  
 DATA PROCESSING  
 FT size 85336  
 Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

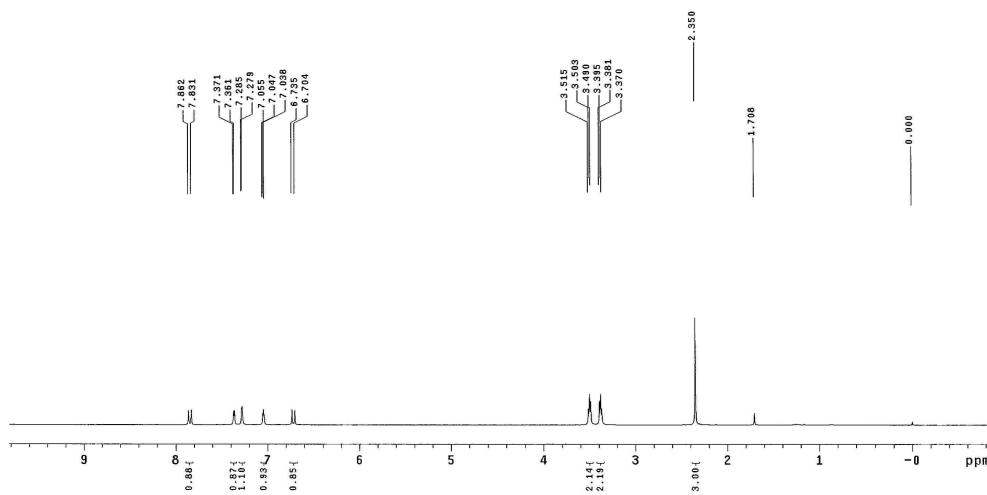
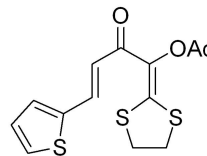
Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 User: 114-87  
 File: x408  
 INOVA-500 "NENUS00"  
 Relax. delay 0.500 sec  
 Pulse 45.0 degrees  
 Acq. time 1.300 sec  
 Width 31421.8 Hz  
 128 repetitions  
 OBSERVE C13, 125.6754704 MHz  
 DECOUPLE H1, 499.8050305 MHz  
 Power 42 dB  
 Continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.5 Hz  
 FT size 131072  
 Total time 3 hr, 56 sec



2n

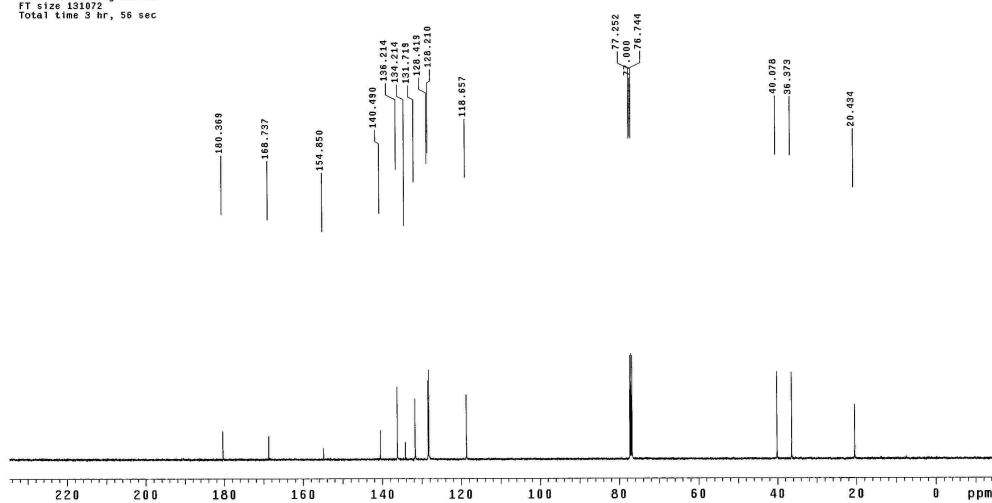
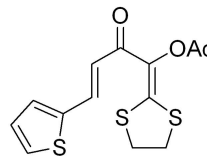
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 File: w496  
 INOVA-500 "NENUS00"  
 Relax. delay 1.000 sec  
 Pulse 45.0 degree  
 Acq. time 1.892 sec  
 Width 7896.8 Hz  
 8 repetitions  
 OBSERVE H1, 499.8025858 MHz  
 DATA PROCESSING  
 FT size 65536  
 Total time 0 min, 23 sec

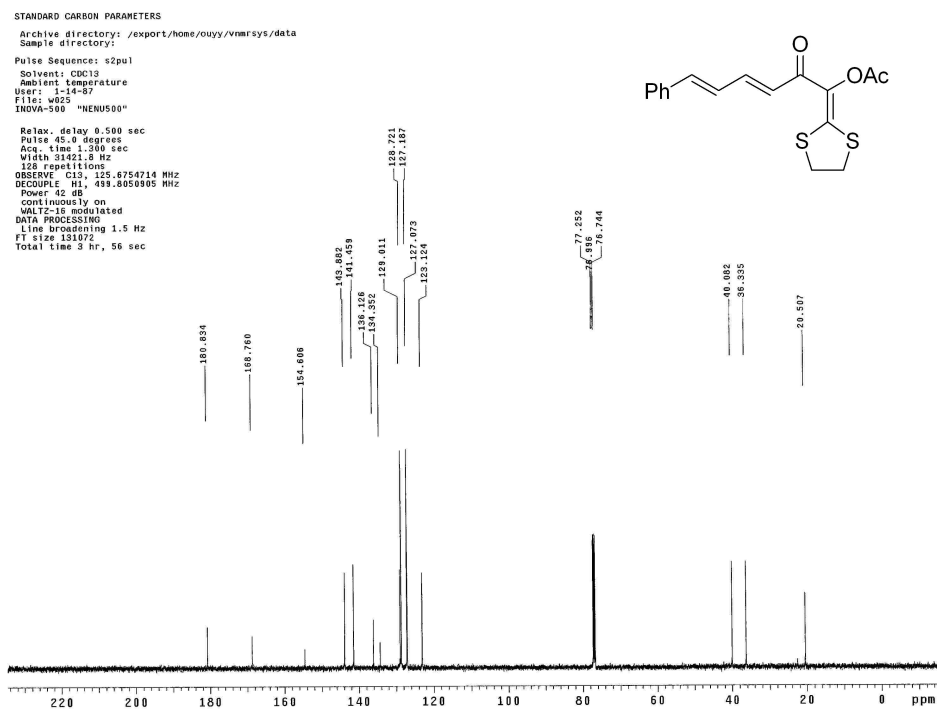
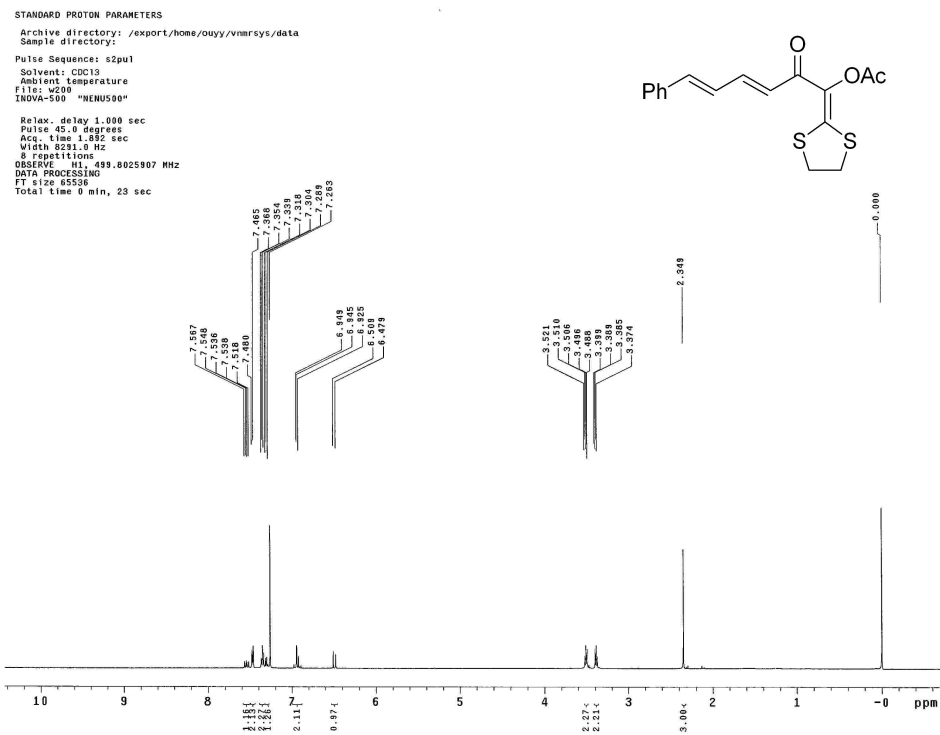


STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 User: 1-14-87  
 File: w497  
 INOVA-500 "NENUS00"  
 Relax. delay 0.500 sec  
 Pulse 45.0 degree  
 Acq. time 1.300 sec  
 Width 21421.8 Hz  
 448 repetitions  
 OBSERVE C13, 125.6754704 MHz  
 DECOUPLE H1, 499.8050905 MHz  
 Power 42 dB  
 continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.5 Hz  
 FT size 121072  
 Total time 3 hr, 56 sec



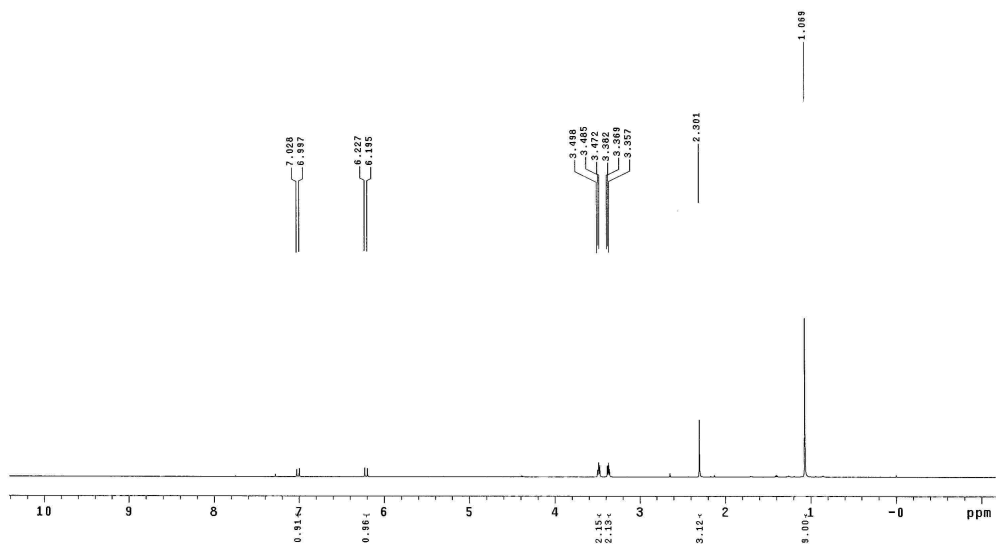
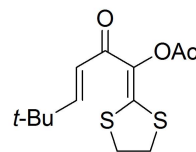
20



2p

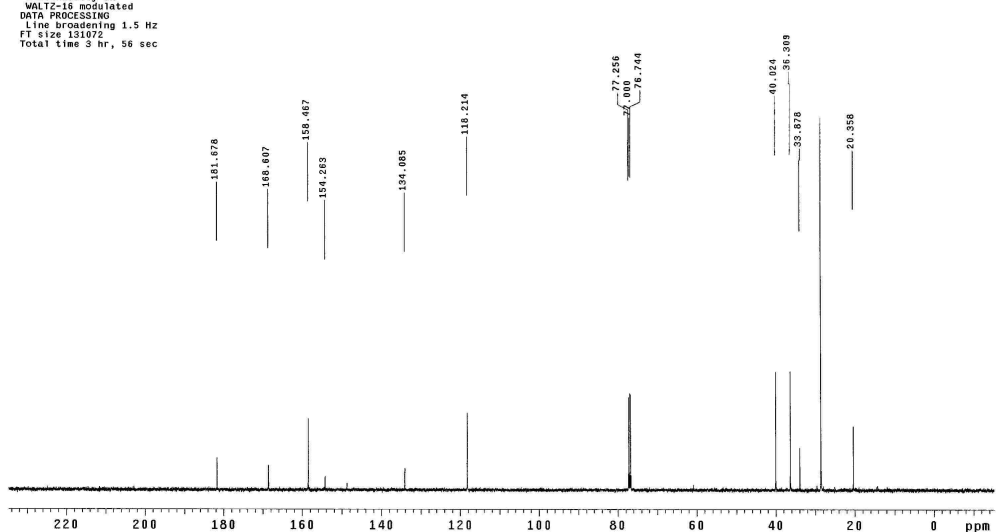
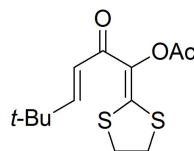
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 File: w415  
 INOVA-500 "MENU500"  
 Relax. delay 1.000 sec  
 Pulse 45.0 degrees  
 Acq. time 1.882 sec  
 Width 7386.8 Hz  
 8 repetitions  
 OBSERVE H1, 499.8025814 MHz  
 DATA PROCESSING  
 FT size 65586  
 Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

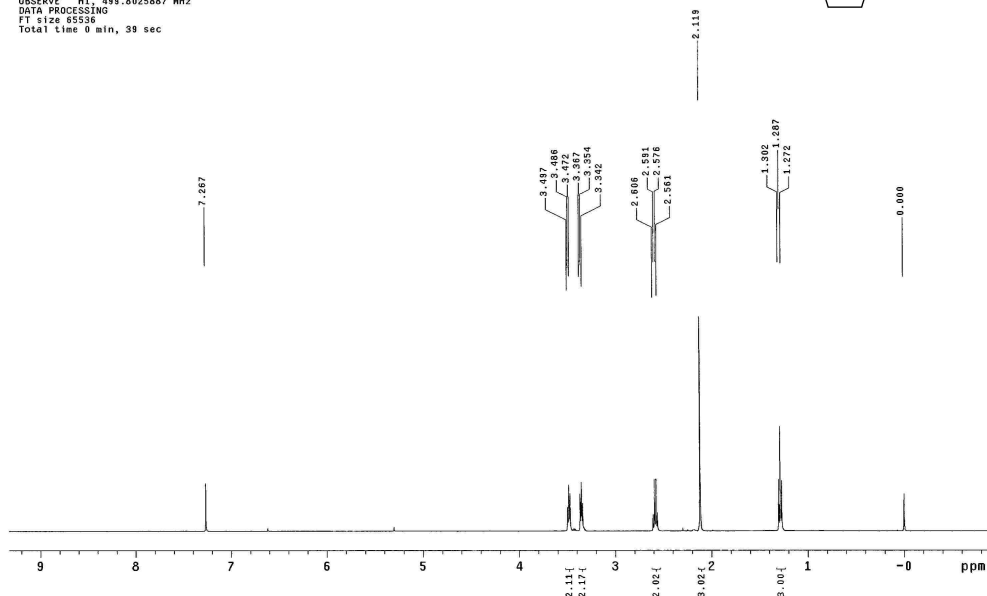
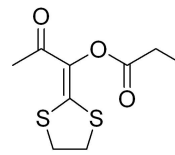
Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 User: 1-19-87  
 File: w447  
 INOVA-500 "MENU500"  
 Relax. delay 0.500 sec  
 Pulse 45.0 degrees  
 Acq. time 1.300 sec  
 Width 31421.8 Hz  
 152 repetitions  
 OBSERVE C13, 125.6754680 MHz  
 DECOUPLE H1, 499.8050905 MHz  
 Power 42 dB  
 Continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.5 Hz  
 FT size 131072  
 Total time 3 hr, 56 sec



### 3a

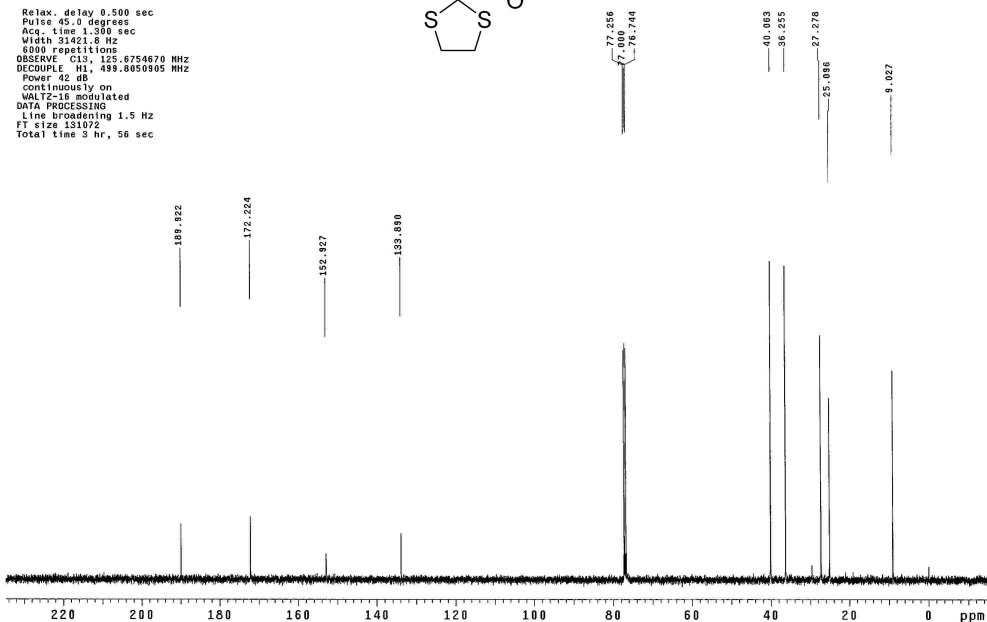
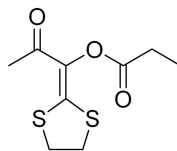
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 File: s105  
 INOVA-500 "NENU500"  
 Relax. delay 1.000 sec  
 Pulse 220.4 degrees  
 Acq. time 1.455 sec  
 Width 9052.8 Hz  
 16 repetitions  
 OBSERVE H1, 499.8025887 MHz  
 DATA PROCESSING  
 FT size 65539  
 Total time 0 min, 39 sec



STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
 Sample directory:  
 Pulse Sequence: s2pu1  
 Solvent: CDCl3  
 Ambient temperature  
 User: j-14-87  
 File: x547  
 INOVA-500 "NENU500"  
 Relax. delay 0.500 sec  
 Pulse 45.0 degrees  
 Acq. time 1.300 sec  
 Width 31421.8 Hz  
 6000 repetitions  
 OBSERVE C13, 125.6754670 MHz  
 DECOUPLE H1, 499.8050305 MHz  
 Power 42 dB  
 Continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.5 Hz  
 FT size 131072  
 Total time 3 hr, 56 sec





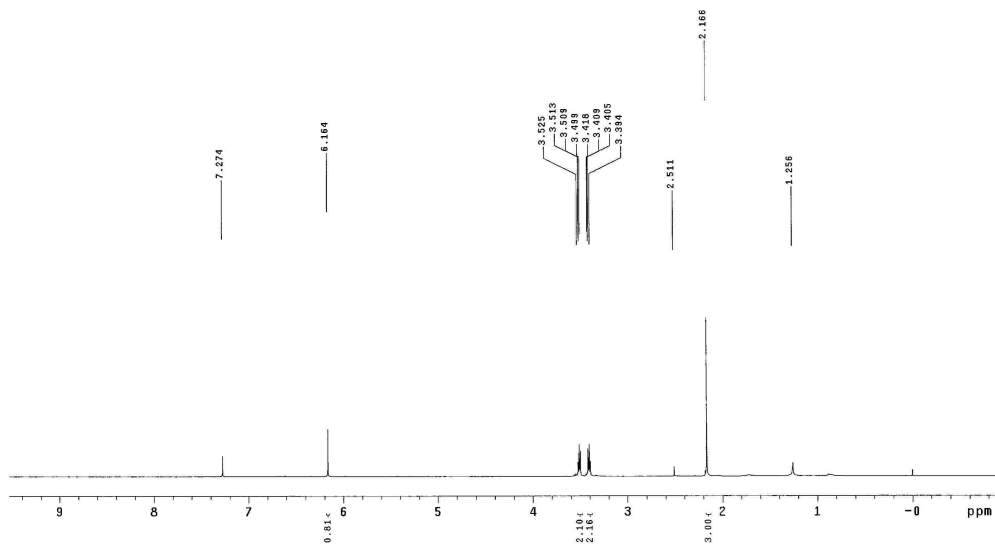
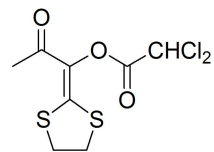
### 3b

#### STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data  
Sample directory:

Pulse Sequence: s2pul  
Solvent: CDCl<sub>3</sub>  
Ambient temperature  
File: x394  
INOVA-500 "NENU500"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.492 sec  
Width 7996.8 Hz  
8 repetitions  
OBSERVE H1, 499.8025841 MHz  
DATA PROCESSING  
FT size 65536  
Total time 0 min, 23 sec

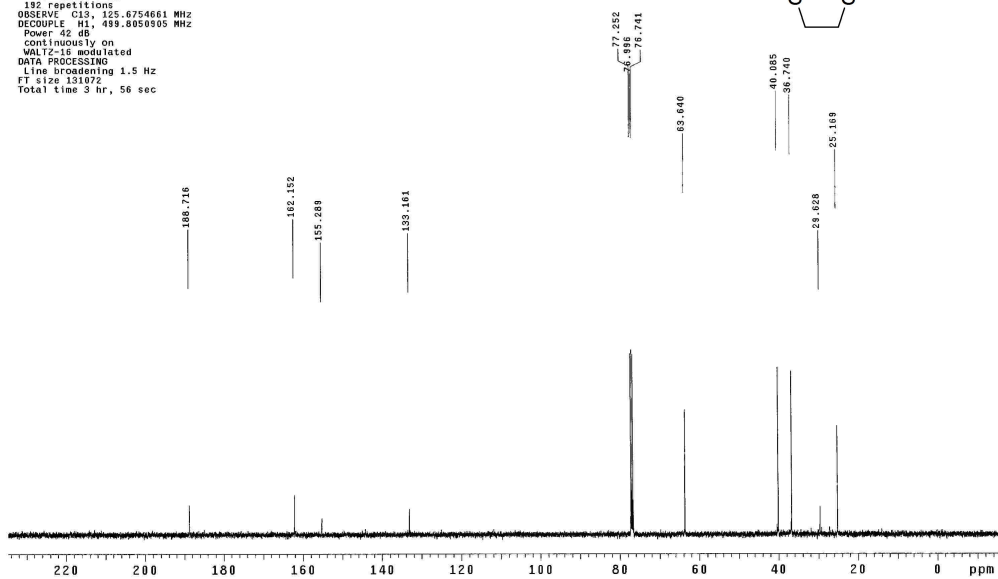
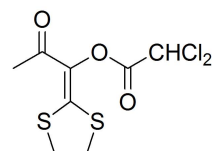


#### STANDARD CARBON PARAMETERS

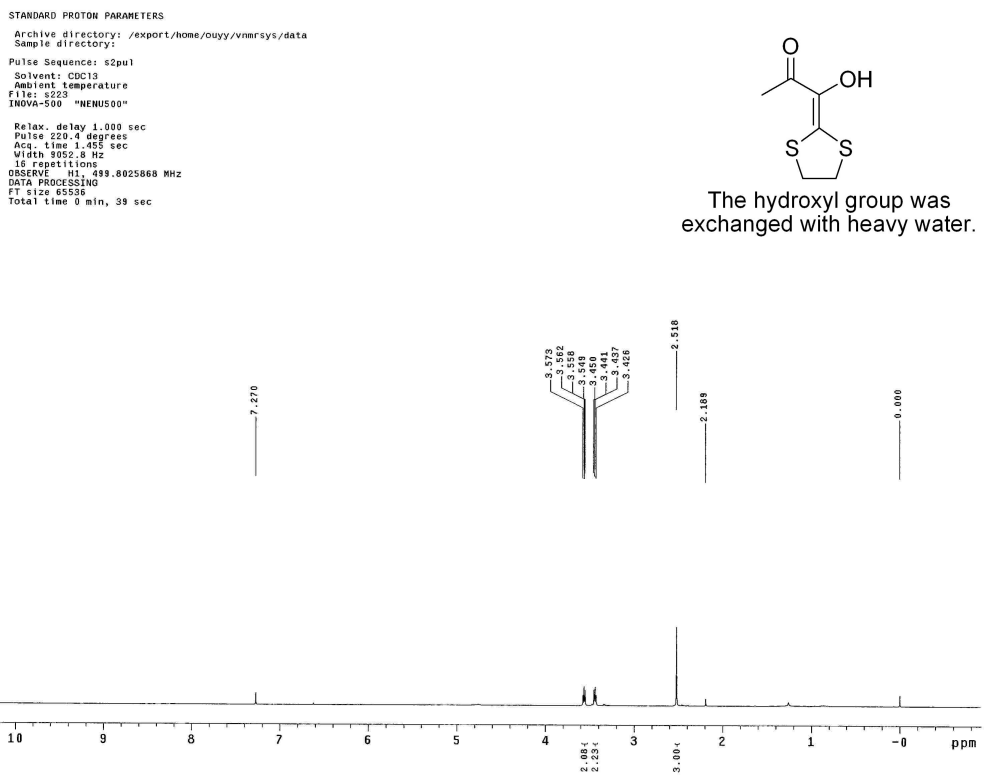
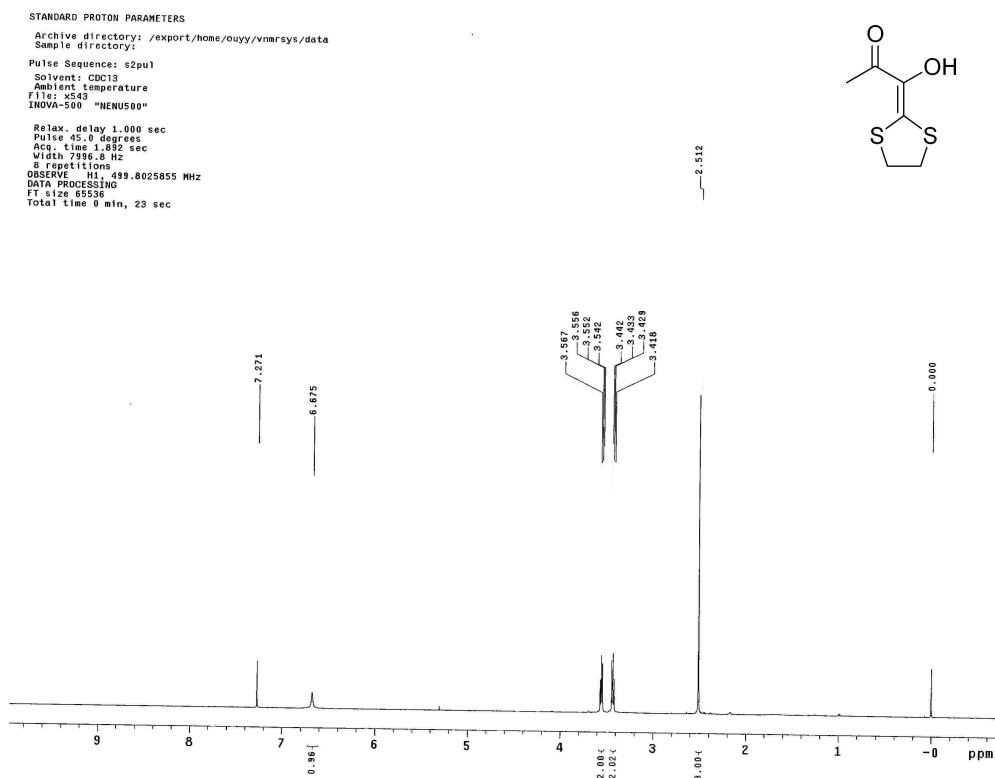
Archive directory: /export/home/ouyy/vnmrsys/data  
Sample directory:

Pulse Sequence: s2pul  
Solvent: CDCl<sub>3</sub>  
Ambient temperature  
User: i-14-87  
File: x317  
INOVA-500 "NENU500"

Relax. delay 0.500 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 31921.8 Hz  
192 repetitions  
OBSERVE C13, 125.6754661 MHz  
DECOUPLE H1, 499.8050905 MHz  
Power 02 dB  
continuously on  
MULTI-16 modulated  
DATA PROCESSING  
Line broadening 1.5 Hz  
FT size 131072  
Total time 3 hr, 56 sec



4



STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsws/data  
Sample directory:

Pulse Sequence: s2pul

Solvents: CDCl3

Ambient temperature

User: 1-14-87

File: 9235

INOVA-500 "MENV500"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Width 31421.8 Hz

128 repetitions

OBSERVE C13, 125.6754704 MHz

DECOUPLE H1, 499.8050905 MHz

Power 40 db

continuously on

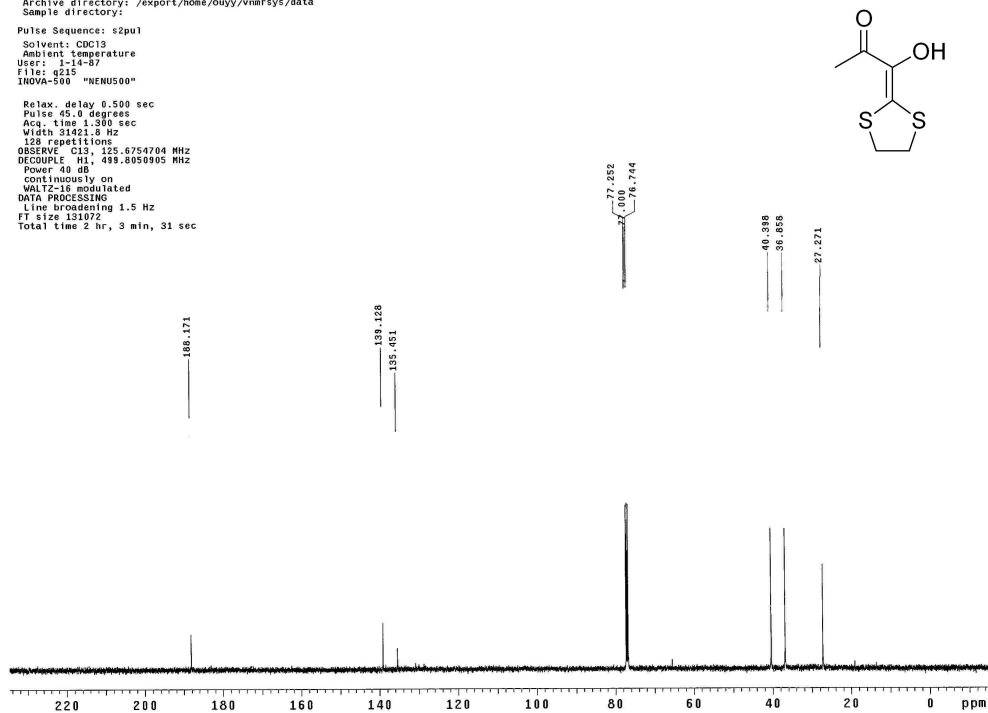
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.5 Hz

FT size 321072

Total time 2 hr, 3 min, 31 sec

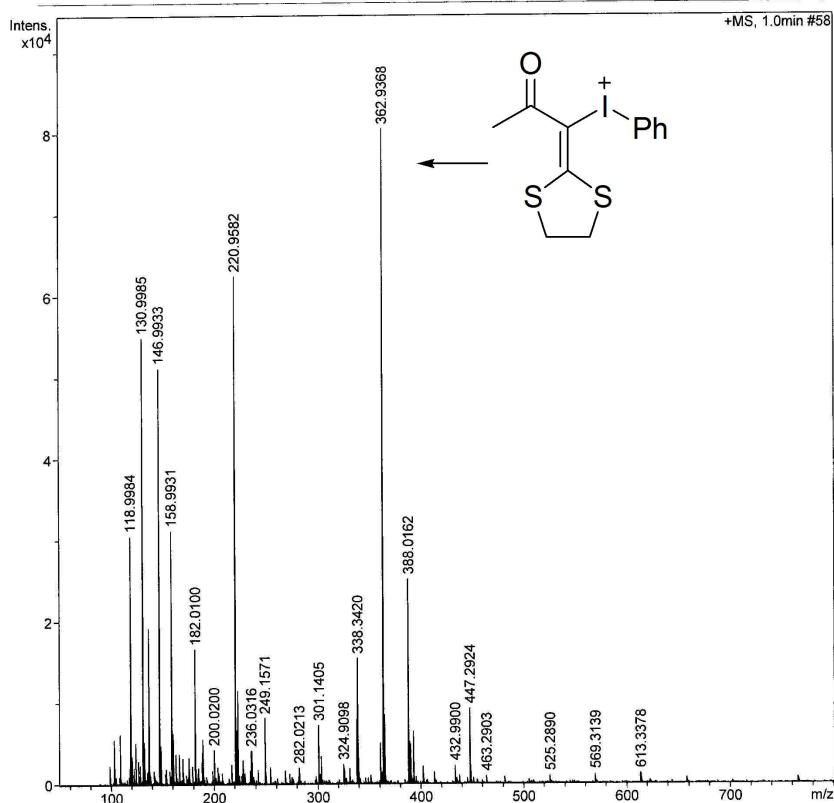


## VII. ESI/MS Experiment and Copies of ESI/MS Spectra for E

A 25 mL flask, equipped with a magnetic-stirring bar, was charged with ketene dithioacetal **1a** (160 mg, 1.0 mmol) and  $\text{PhI}(\text{OAc})_2$  (387 mg, 1.2 mmol), followed by addition of 9.1 mL acetic acid and 0.91 mL water. The reaction mixture was stirred at 50 °C for 1 h and monitored by ESI-MS spectroscopy.

<b>Analysis Info</b>	Acquisition Date	9/9/2013 10:40:36 AM	
Analysis Name	D:\Data\user\E2013\Ea699_79_01_4295.d	Operator	
Method	Sample 5 min.m	Instrument / Ser#	micrOTOF 10328
Sample Name	Ea699	Comment	

<b>Acquisition Parameter</b>	Ion Polarity	Positive	Set Nebulizer	1.5 Bar	
Source Type	ESI		Set Dry Heater	180 °C	
Focus	Not active		Set Dry Gas	8.0 l/min	
Scan Begin	50 m/z	Set Capillary	4500 V		
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSig ma	rdb	e <sup>-</sup> Conf	N-R uler
362.9368	1	C 12 H 12 I O S 2	100.00	362.9369	0.2	0.3	4.6	6.5	even	ok

The ESI-MS spectrum showed a major ion at 362.9368 (**E**).