

Supporting Information for  
**Copper-Promoted Direct C–H Alkoxylation of *S,S*-Functionalized Internal  
Olefins with Alcohols**

Zhuqing Liu,<sup>a,b</sup> Fei Huang,<sup>a,b</sup> Jiang Lou,<sup>a,b</sup> Quannan Wang<sup>a,b</sup> and Zhengkun Yu\*<sup>a</sup>

<sup>a</sup> Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian,  
Liaoning 116023, People's Republic of China.

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China.

**Experimental procedures and analytical data**

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## 1. General considerations

The solvents were dried and distilled prior to use by the literature methods.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a 400 MHz spectrometer and all chemical shift values refer to  $\text{CDCl}_3$  ( $\delta(^1\text{H})$ , 7.26 ppm;  $\delta(^{13}\text{C})$ , 77.16 ppm). The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. All the melting points were uncorrected. X-ray Crystallographic analysis was achieved by the Analysis Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Analytical TLC plates were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Substrates  $\alpha$ -oxo ketene dithioacetals **1** were prepared by the reported procedures.<sup>1-19</sup> 1-Methoxy-1,2-benziodoxol-3-(1H)-one (**6**) was prepared as reported.<sup>20</sup>

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## 2. Experimental procedures



### 2.1 C–H alkoxylation of $\alpha$ -oxo ketene dithioacetals **1** with alcohols **2**

**Screening of the reaction conditions:** By means of the alkoxylation reaction of  $\alpha$ -oxo ketene dithioacetal **1a** with EtOH (**2a**) as the model reaction, the reaction conditions were optimized as follows.

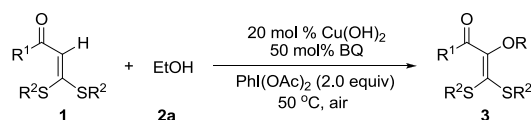
**Table 1.** Screening of the reaction conditions.<sup>a</sup>



Entry	Catalyst (20 mol%)	PhI(OAc) <sub>2</sub> (equiv)	Additive	Solvent	Temp (°C)	Yield <sup>b</sup> (%)
1	Cu(OH) <sub>2</sub>	1.5		EtOH	25	35
2	Cu(OH) <sub>2</sub>	1.5	BQ (0.2)	EtOH	25	40
3	Cu(OH) <sub>2</sub>	1.5	BQ (0.5)	EtOH	25	50
4	Cu(OH) <sub>2</sub>	1.5	BQ (1.0)	EtOH	25	44
5	Cu(OH) <sub>2</sub>	1.5	BQ (2.0)	EtOH	25	43
6	Cu(OH) <sub>2</sub>	1.5	O <sub>2</sub> (1 atm)	EtOH	25	11
7	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	EtOH	25	56

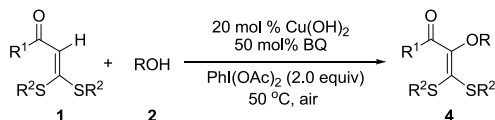
8	Cu(OH) <sub>2</sub>	2.1	BQ (0.5)	EtOH	25	55
9	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	EtOH	50	79 (71) <sup>d</sup>
10 <sup>c</sup>	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	EtOH	50	79 (72) <sup>d</sup>
11	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	EtOH	80	63
12	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	EtOH	100	53
13 <sup>e</sup>	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	THF	50	34
14 <sup>e</sup>	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	DMF	50	36
15 <sup>e</sup>	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	DCE	50	56
16 <sup>e</sup>	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	toluene	50	63
17 <sup>e</sup>	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	DMSO	50	23
18 <sup>f</sup>	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	toluene	50	50
19 <sup>g</sup>	Cu(OH) <sub>2</sub>	2.0	BQ (0.5)	toluene	50	36
20	CuCl <sub>2</sub>	1.5		EtOH	25	21
21	CuBr <sub>2</sub>	1.5		EtOH	25	23
22	CuI	1.5		EtOH	25	20
23	Cu(OAc)	1.5		EtOH	25	19
24	Cu(OTf) <sub>2</sub>	1.5		EtOH	25	11
25		PhI(OCOPh) <sub>2</sub> 3a, 42%	PhI(OCOCF <sub>3</sub> ) <sub>2</sub> 3a' 32%	PhIO 3a' 10%		3a, 12% 3a/3a', 0%

<sup>a</sup> Conditions: **1a** (0.3 mmol), Cu(OH)<sub>2</sub> (0.06 mmol), solvent (3 mL), air, 24 h. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. <sup>c</sup> Under argon atmosphere. <sup>d</sup> Isolated yield given in parathenses. <sup>e</sup> Using 10 equiv EtOH. <sup>f</sup> Using 5 equiv EtOH. <sup>g</sup> Using 2 equiv EtOH.



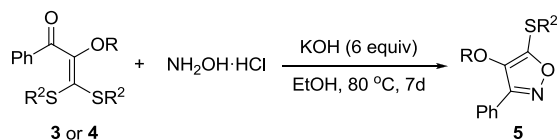
**A typical procedure for the alkoxylation of 1 with EtOH – Synthesis of 3,3-bis(methylthio)-2-ethoxyl-1-phenylprop-2-en-1-one (3a):** A mixture of  $\alpha$ -oxoketene dithioacetal **1a** (112 mg, 0.5 mmol), Cu(OH)<sub>2</sub> (10 mg, 0.1 mmol), PhI(OAc)<sub>2</sub> (322 mg, 1.0 mmol), and BQ (27 mg, 0.25 mmol) in 5 mL EtOH was stirred at 50 °C for 24 h. After cooled to ambient temperature, the resulting mixture was evaporated all the

volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/ethyl acetate = 200:1, v/v) to afford **3a** as a yellow liquid (95 mg, 71%).



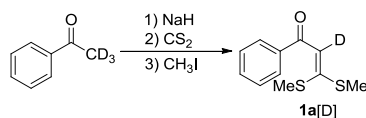
**A typical procedure for the alkoxylation of 1 with benzyl alcohols – Synthesis of 3,3-bis(methylthio)-2-benzyloxy-1-phenylprop-2-en-1-one (4i):** A mixture of  $\alpha$ -oxo ketene dithioacetal **1a** (112 mg, 0.5 mmol),  $\text{Cu(OH)}_2$  (10 mg, 0.1 mmol),  $\text{PhI(OAc)}_2$  (322 mg, 1.0 mmol), BQ (27 mg, 0.25 mmol), and BnOH (517  $\mu\text{L}$ , 5 mmol) in 5 mL toluene was stirred at 50 °C for 24 h. After cooled to ambient temperature, the resulting mixture was evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/ethyl acetate = 300:1, v/v) to afford **4i** as a yellow solid (104 mg, 63%).

## 2.2 Derivation of the C-H alkoxylation products 3 or 4 with hydroxylamine



**A typical procedure for the reactions of 3 or 4 with hydroxylamine hydrochloride – Synthesis of 5-(methylthio)-3-phenyl-4-(ethoxyl)-oxazole (5a):** A mixture of **3a** (134 mg, 0.5 mmol), hydroxylamine hydrochloride (208 mg, 3.0 mmol), and KOH (168 mg, 3.0 mmol) in ethanol (5 mL) was refluxed for 7 days. After cooled to ambient temperature, all the volatiles were removed under reduced pressure. The resulting residue was dissolved in ethyl acetate (10 mL), and washed with water (2 $\times$ 10 mL), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The filtrate was evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/ethyl acetate = 100:1, v/v) to afford **6a** as a colourless liquid (62 mg, 53%).

### 2.3 Preparation of deuterated $\alpha$ -oxo ketene dithioacetal **1a**[D]<sup>14</sup>



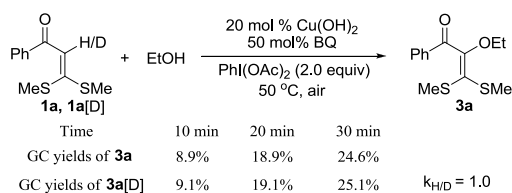
**Preparation of deuterated  $\alpha$ -oxo ketene dithioacetal **1a**[D]:** Iodomethane (1.57 g, 11 mmol) was added dropwise to a stirred mixture of aceto-D<sub>3</sub>-phenone (1.23 g, 10 mmol), NaH (0.80 g, 60% in oil, 20 mmol), CS<sub>2</sub> (1.20 g, 15 mmol), and 1 mL DMF in 19 mL toluene at 0 °C. The reaction was complete within 24 h by TLC monitoring. The resulting mixture was poured into 20 g of ice water, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×15 mL). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. All the volatiles were removed under reduced pressure and the resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/ethyl acetate = 50:1, v/v), affording **1a**[D] (1.46 g, 65% yield, 96%D) as a yellow solid.

### 2.4 Synthesis of 1-methoxy-1,2-benziodoxol-3-(1H)-one (**6**)<sup>20</sup>

1-Acetoxy-1,2-benziodoxol-3-(1H)-one (7.0 g, 26.5 mmol) was heated to reflux for 1 h in MeOH (25 mL). After cooled to ambient temperature, crystallization was continued at -10 °C. The crystals were dried under vacuum for 20 h, affording **6** (5.6 g, 80%) as a white solid.

### 2.5 Kinetic isotope effect (KIE)

The C-H alkoxylation reactions of  $\alpha$ -oxo ketene dithioacetal **1a** and its deuterated form, i.e., **1a**[D], were carried out in a parallel manner under the optimized conditions. A mixture of  $\alpha$ -oxo ketene dithioacetal **1a** or **1a**[D] (112 mg, 0.5 mmol), Cu(OH)<sub>2</sub> (10 mg, 0.1 mmol), PhI(OAc)<sub>2</sub> (322 mg, 1.0 mmol), and BQ (27 mg, 0.25 mmol) in 5 mL EtOH was stirred at 50 °C. The GC yields from the reactions were carefully checked by the signal integration of the target product **3a** with 1,3,5-methoxybenzene as the internal standard. The  $k_H/k_D$  value was calculated according to the yields of **3a** from the reactions at 10 min, 20 min and 30 min.



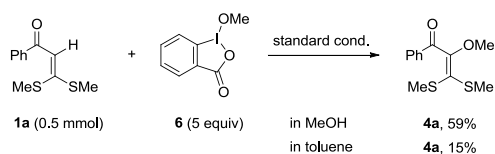
## 2.6 Radical trapping

**Radical trapping experiments:** A mixture of  $\alpha$ -oxo ketene dithioacetal **1a** (112 mg, 0.5 mmol), Cu(OH)<sub>2</sub> (10 mg, 0.1 mmol), TEMPO or BHT (1.0 mmol), PhI(OAc)<sub>2</sub> (322 mg, 1.0 mmol), and BQ (27 mg, 0.25 mmol) in 5 mL EtOH was stirred at 50 °C for 24 h. The resultant mixture was cooled to ambient temperature and subjected to GC analysis by using 1,3,5-methoxybenzene as the internal standard. No target product **3a** was found in the reaction mixture.



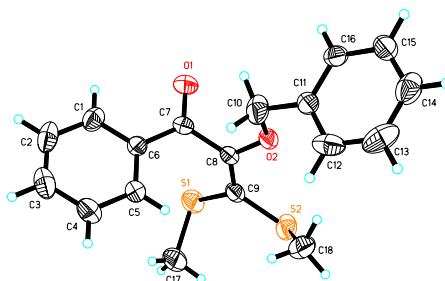
## 2.7 Mechanistic studies

In order to further verify the reaction mechanism PhI(OEt)<sub>2</sub> and PhI(OEt)(OAc) were tried to be prepared from the reaction of PhI(OAc)<sub>2</sub> with EtOH using a literature method.<sup>16</sup> Unfortunately, both PhI(OEt)<sub>2</sub> and PhI(OEt)(OAc) could not be successfully obtained due to their high susceptibility to thermal and moisture conditions. Alternatively, stable cyclic methoxyiodo(III) compound, that is, 1-methoxy-1,2-benziodoxol-3-(1H)-one (**6**)<sup>17</sup> was prepared and applied to react with **1a** in both methanol and toluene as solvents under the standard conditions, forming **4a** in 59% and 15% yields (Eq. 5), respectively. By increasing temperature to 110 °C in a sealed tube the yields could be improved to 71% and 19%, respectively. This result suggests the involvement of alkoxy-iodo(III) species in the C–H alkoxylation of **1** with alcohols.



### 3. X-Ray crystallographic studies

The X-ray diffraction studies for compound **4i** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$ . All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1469553 for **4i**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).



**Figure 1.** Molecular structure of compound **4i**.

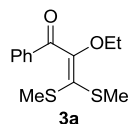
**Table 2.** Crystal data and structure refinement for compound **4i**.

Identification code	LZQ-443
Empirical formula	C <sub>18</sub> H <sub>18</sub> O <sub>2</sub> S <sub>2</sub>
Formula weight	330.44
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 <sub>1</sub> /c
Unit cell dimensions	a = 16.7723(14) Å = 90 ° b = 5.6960(4) Å = 113.699(10) °

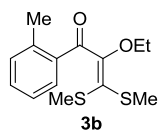


	$c = 19.6942(15) \text{ \AA}$	$= 90^\circ$
Volume	$1722.8(3) \text{ \AA}^3$	
Z, Density (calculated)	4, $1.274 \text{ Mg/m}^3$	
Absorption coefficient	$0.313 \text{ mm}^{-1}$	
F(000)	696	
Crystal size	$0.220 \times 0.170 \times 0.130 \text{ mm}^3$	
Theta range for data collection	$3.045 \text{ to } 25.999^\circ$	
Index ranges	$-20 \leq h \leq 14, -7 \leq k \leq 7, -20 \leq l \leq 24$	
Reflections collected	7944	
Independent reflections	3362 $R(\text{int}) = 0.0263$	
Completeness to $\theta = 25.242^\circ$	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.81096	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	3362 / 0 / 202	
Goodness-of-fit on $F^2$	1.036	
Final R indices $I > 2\sigma(I)$	$R1 = 0.0428, wR2 = 0.0956$	
R indices (all data)	$R1 = 0.0737, wR2 = 0.1144$	
Extinction coefficient	0.0160(14)	
Largest diff. peak and hole	0.138 and $-0.201 \text{ e.\AA}^{-3}$	

#### 4. Analytical data

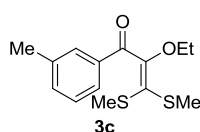


**3,3-Bis(methylthio)-2-ethoxy-1-phenylprop-2-en-1-one (3a):** 95 mg, 71% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.2$  Hz, 2H, aromatic CH), 7.59 (t,  $J = 7.4$  Hz, 1H, aromatic CH), 7.48 (t,  $J = 7.6$  Hz, 2H, aromatic CH), 3.85 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 2.40 (s, 3H, SMe), 2.05 (s, 3H, SMe), 1.26 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.8 (Cq, C=O), 154.0 (Cq, CSMe), 136.7 (Cq of Ph), 133.8, 129.2 and 128.8 (aromatic CH), 117.7 (Cq, COEt), 67.1 ( $\text{OCH}_2\text{CH}_3$ ), 18.0 (SMe), 16.0 (SMe), 15.5 ( $\text{OCH}_2\text{CH}_3$ ). HRMS Calcd for  $\text{C}_{13}\text{H}_{16}\text{O}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 269.0670; Found: 269.0672.

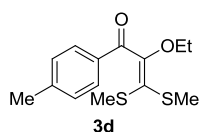


**3,3-Bis(methylthio)-2-ethoxy-1-(2-methylphenyl)prop-2-en-1-one (3b):** 99 mg,

70% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 7.6$  Hz, 1H, aromatic CH), 7.42 (t,  $J = 7.5$  Hz, 1H, aromatic CH), 7.30 (m, 2H, aromatic CH), 3.96 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 2.64 (s, 3H, SMe), 2.43 (s, 3H, SMe), 1.94 (s, 3H, Ph- $\text{CH}_3$ ), 1.33 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.5 (Cq, C=O), 155.0 (Cq, CSMe), 139.6 (Cq of Ph), 137.2, 131.9, 129.9 and 125.3 (aromatic CH), 120.6 (Cq, COEt), 67.0 ( $\text{OCH}_2\text{CH}_3$ ), 21.1 (Ph- $\text{CH}_3$ ), 17.4 (SMe), 16.1 (SMe), 15.5 ( $\text{OCH}_2\text{CH}_3$ ). HRMS Calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 283.0826; Found: 283.0826.

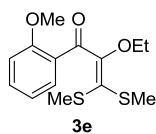


**3,3-Bis(methylthio)-2-ethoxy-1-(3-methylphenyl)prop-2-en-1-one (3c):** 101 mg, 70% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J = 7.5$  Hz, 1H, aromatic CH), 7.38 (t,  $J = 7.4$  Hz, 1H, aromatic CH), 7.24 (m, 2H, aromatic CH), 3.91 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 2.59 (s, 3H, SMe), 2.38 (s, 3H, SMe), 1.90 (s, 3H, Ph- $\text{CH}_3$ ), 1.28 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.6 (Cq, C=O), 155.1 (Cq, CSMe), 139.8 and 137.3 (Cq of Ph), 131.9, 130.1 and 125.3 (aromatic CH), 120.6 (Cq, COEt), 67.1 ( $\text{OCH}_2\text{CH}_3$ ), 21.2 (Ph- $\text{CH}_3$ ), 17.4 (SMe), 16.2 (SMe), 15.6 ( $\text{OCH}_2\text{CH}_3$ ). HRMS Calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 283.0826; Found: 283.0827.

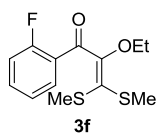


**3,3-Bis(methylthio)-2-ethoxy-1-(4-methylphenyl)prop-2-en-1-one (3d):** 96 mg, 68% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.1$  Hz, 2H, aromatic CH), 7.28 (m, 2H, aromatic CH), 3.84 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 2.41 (s, 3H, SMe), 2.38 (s, 3H, SMe), 2.06 (s, 3H, Ph- $\text{CH}_3$ ), 1.25 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.5 (Cq, C=O), 154.4 (Cq, CSMe), 144.9 and 134.1 (Cq of Ph), 129.6 and 129.4 (aromatic CH), 116.4 (Cq, COEt), 66.9 ( $\text{OCH}_2\text{CH}_3$ ), 21.9 (Ph- $\text{CH}_3$ ), 18.0 (SMe), 15.9 (SMe), 15.5 ( $\text{OCH}_2\text{CH}_3$ ). HRMS Calcd

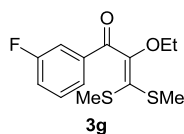
for  $C_{14}H_{18}O_2S_2$   $M+H^+$ : 283.0826; Found: 283.0826.



**3,3-Bis(methylthio)-2-ethoxy-1-(2-methoxyphenyl)prop-2-en-1-one (3e)**: 111 mg, 74% yield, yellow liquid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.71 (m, 1H, aromatic CH), 7.50 (m, 1H, aromatic CH), 7.01 (m, 1H, aromatic CH), 6.95 (m, 1H, aromatic CH), 3.89 (Ph- $OCH_3$ ), 3.86 ( $J = 7.0$  Hz, 2H,  $OCH_2CH_3$ ), 2.36 (s, 3H, SMe), 1.93 (s, 3H, SMe), 1.26 (t,  $J = 7.0$  Hz, 3H,  $OCH_2CH_3$ ).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ ).  $\delta$  191.0 (Cq, C=O), 158.9 (Cq, CSMe), 156.5 and 128.1 (Cq of Ph), 134.0, 131.4, 120.7 and 111.9 (aromatic CH), 117.5 (Cq, COEt), 66.9 ( $OCH_2CH_3$ ), 55.8 (Ph- $OCH_3$ ), 17.7 (SMe), 16.3 (SMe), 15.5 ( $OCH_2CH_3$ ). HRMS Calcd for  $C_{14}H_{18}O_3S_2$   $M+H^+$ : 299.0776; Found: 299.0777.

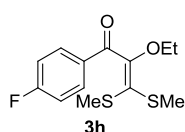


**3,3-Bis(methylthio)-2-ethoxy-1-(2-fluorophenyl)prop-2-en-1-one (3f)**: 104 mg, 72% yield, yellow liquid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.76 (m, 1H, aromatic CH), 7.49 (m, 1H, aromatic CH), 7.23 (m, 1H, aromatic CH), 7.10 (m, 1H, aromatic CH), 3.88 (q,  $J = 7.0$  Hz, 2H,  $OCH_2CH_3$ ), 2.39 (s, 3H, SMe), 2.02 (s, 3H, SMe), 1.26 (t,  $J = 7.0$  Hz, 3H,  $OCH_2CH_3$ ).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  188.30 (Cq, C=O), 161.07 (d,  $J = 256.0$  Hz, Cq of Ph), 154.4 (Cq, CSMe), 134.3 (d,  $J = 8.7$  Hz, aromatic CH), 131.08 (d,  $J = 1.4$  Hz, aromatic CH), 127.0 (d,  $J = 10.7$  Hz, Cq of Ph), 124.4 (d,  $J = 3.7$  Hz, aromatic CH), 123.6 (d,  $J = 3.3$  Hz, Cq, COEt), 116.5 (d,  $J = 22.1$  Hz, aromatic CH), 67.3 ( $OCH_2CH_3$ ), 17.8 (SMe), 16.4 (SMe), 15.4 ( $OCH_2CH_3$ ). HRMS Calcd for  $C_{13}H_{15}O_2S_2F$   $M+H^+$ : 287.0576; Found: 287.0579.

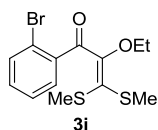


**3,3-Bis(methylthio)-2-ethoxy-1-(3-fluorophenyl)prop-2-en-1-one (3g)**: 106 mg, 74% yield, yellow liquid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$

7.71 (m, 1H, aromatic CH), 7.63 (m, 1H, aromatic CH), 7.45 (m, 1H, aromatic CH), 7.27 (m, 1H, aromatic CH), 3.84 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 2.39 (s, 3H, SMe), 2.05 (s, 3H, SMe), 1.25 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  190.4 (Cq, C=O), 162.9 (d,  $J = 248.4$  Hz, Cq of Ph), 153.1 (Cq, CSMe), 138.9 (d,  $J = 6.3$  Hz, Cq of Ph), 130.4 (d,  $J = 7.6$  Hz, aromatic CH), 124.9 (d,  $J = 3.0$  Hz, aromatic CH), 120.6 (d,  $J = 21.5$  Hz, aromatic CH), 119.9 (Cq, COEt), 115.5 (d,  $J = 22.5$  Hz, aromatic CH), 67.3 ( $\text{OCH}_2\text{CH}_3$ ), 17.9 (SMe), 16.0 (SMe), 15.4 ( $\text{OCH}_2\text{CH}_3$ ). HRMS Calcd for  $\text{C}_{13}\text{H}_{15}\text{O}_2\text{S}_2\text{F M}+\text{H}^+$ : 287.0576; Found: 287.0578.

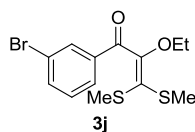


**3,3-Bis(methylthio)-2-ethoxy-1-(4-fluorophenyl)prop-2-en-1-one (3h):** 109 mg, 76% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.0 (m, 2H, aromatic CH), 7.15 (m, 2H, aromatic CH), 3.83 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 2.40 (s, 3H, SMe), 2.08 (s, 3H, SMe), 1.26 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  190.2 (Cq, C=O), 166.2 (d,  $J = 255.9$  Hz, Cq of Ph), 153.6 (Cq, CSMe), 133.0 (d,  $J = 2.9$  Hz, aromatic CH, Cq of Ph), 131.9 (d,  $J = 9.5$  Hz, aromatic CH), 118.7 (Cq, COEt), 116.1 (d,  $J = 22.1$  Hz, aromatic CH), 67.2 ( $\text{OCH}_2\text{CH}_3$ ), 18.1 (SMe), 15.9 (SMe), 15.5 ( $\text{OCH}_2\text{CH}_3$ ). HRMS Calcd for  $\text{C}_{13}\text{H}_{15}\text{O}_2\text{S}_2\text{F M}+\text{H}^+$ : 287.0576; Found: 287.0576.

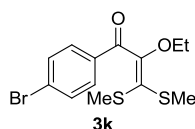


**3,3-Bis(methylthio)-2-ethoxy-1-(2-bromophenyl)prop-2-en-1-one (3i):** 125 mg, 72% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (m, 1H, aromatic CH), 7.44 (m, 1H, aromatic CH), 7.29 (m, 1H, aromatic CH), 7.20 (m, 1H, aromatic CH), 3.86 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 2.36 (s, 3H, SMe), 1.95 (s, 3H, SMe), 1.19 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  190.4 (Cq, C=O), 152.4 (Cq, CSMe), 140.5 and 132.1 (Cq of Ph), 133.82, 131.8, 130.3 and 127.0 (aromatic CH), 120.8 (Cq, COEt), 67.6 ( $\text{OCH}_2\text{CH}_3$ ), 17.9 (SMe), 16.5 (SMe), 15.5 ( $\text{OCH}_2\text{CH}_3$ ).

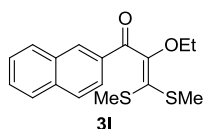
HRMS Calcd for C<sub>13</sub>H<sub>15</sub>O<sub>2</sub>S<sub>2</sub>Br M+H<sup>+</sup>: 346.9775; Found: 346.9776.



**3,3-Bis(methylthio)-2-ethoxy-1-(3-bromophenyl)prop-2-en-1-one (3j):** 138 mg, 79% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (s, 1H, aromatic CH), 7.83 (m, 1H, aromatic CH), 7.67 (m, 1H, aromatic CH), 7.34 (m, 1H, aromatic CH), 3.83 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.38 (s, 3H, SMe), 2.05 (s, 3H, SMe), 1.25 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 190.1 (Cq, C=O), 152.8 (Cq, CSMe), 138.6 and 122.9 (Cq of Ph), 136.3, 131.8, 130.3 and 127.7 (aromatic CH), 120.6 (Cq, COEt), 67.3 (OCH<sub>2</sub>CH<sub>3</sub>), 17.9 (SMe), 16.0 (SMe), 15.4 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>13</sub>H<sub>15</sub>O<sub>2</sub>S<sub>2</sub>Br M+H<sup>+</sup>: 346.9775; Found: 346.9777.

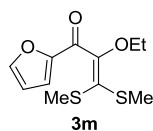


**3,3-Bis(methylthio)-2-ethoxy-1-(2-bromophenyl)prop-2-en-1-one (3k):** 140 mg, 81% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 8.4 Hz, 2H, aromatic CH), 7.61 (d, *J* = 8.4 Hz, 2H, aromatic CH), 3.82 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.38 (s, 3H, SMe), 2.06 (s, 3H, SMe), 1.24 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 190.6 (Cq, C=O), 153.2 (Cq, CSMe), 135.5 and 128.9 (Cq of Ph), 132.1, 130.6 (aromatic CH), 119.6 (Cq, COEt), 67.2 (OCH<sub>2</sub>CH<sub>3</sub>), 18.0 (SMe), 15.9 (SMe), 15.4 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>13</sub>H<sub>15</sub>O<sub>2</sub>S<sub>2</sub>Br M+H<sup>+</sup>: 346.9775; Found: 346.9778.

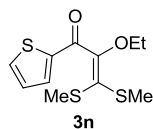


**3,3-Bis(methylthio)-2-ethoxy-1-(2-naphthyl)prop-2-en-1-one (3l):** 93 mg, 64% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.47 (s, 1H, naphthyl CH), 8.05 (m, 1H, naphthyl CH), 7.98 (m, 1H, naphthyl CH), 7.92 (m, 1H, naphthyl CH), 7.89 (m, 1H, naphthyl CH), 3.90 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.44 (s, 3H, SMe), 2.05 (s, 3H, SMe), 1.28 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ

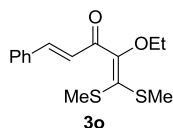
191.8 (Cq, C=O), 154.2 (Cq, CSMe), 136.0, 134.0, 132.6 (Cq of naphthalene), 131.4 (s), 129.8, 128.9, 128.8, 127.9, 127.0 and 124.3 (naphthyl CH), 117.6 (Cq, COEt), 67.2 (OCH<sub>2</sub>CH<sub>3</sub>), 18.1 (SMe), 15.9 (SMe), 15.5 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 319.0826; Found: 319.0823.



**3,3-Bis(methylthio)-2-ethoxy-1-(2-furyl)prop-2-en-1-one (3m):** 91 mg, 71% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (m, 1H, furyl CH), 7.22 (m, 1H, furyl CH), 6.50 (m, 1H, furyl CH), 3.86 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.37 (s, 3H, SMe), 2.14 (s, 3H, SMe), 1.26 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 178.4 (Cq, C=O), 152.5 (Cq, CSMe), 147.5 and 119.6 (furyl CH), , 123.2 (Cq of furan), 112.5 (Cq, COEt), 67.4 (OCH<sub>2</sub>CH<sub>3</sub>), 18.2 (SMe), 16.2 (SMe), 15.4 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>S<sub>2</sub> M+H<sup>+</sup>: 259.0463; Found: 259.0463.

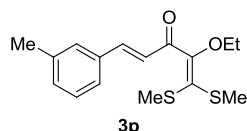


**3,3-Bis(methylthio)-2-ethoxy-1-(2-thienyl)prop-2-en-1-one (3n):** 82 mg, 60% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (m, 1H, thienyl CH), 7.68 (m, 1H, thienyl CH), 7.12 (m, thienyl CH), 3.87 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.39 (s, 3H, SMe), 2.15 (s, 3H, SMe), 1.28 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 183.2 (Cq, C=O), 153.3 (Cq, CSMe), 143.6 (Cq of thiophene), 134.9, 134.1 and 128.3 (thienyl CH), 122.1 (Cq, COEt), 67.5 (OCH<sub>2</sub>CH<sub>3</sub>), 18.3 (SMe), 16.2 (SMe), 15.4 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>S<sub>3</sub> M+H<sup>+</sup>: 275.0234; Found: 275.0235.



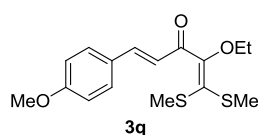
**(E)-3,3-bis(methylthio)-2-ethoxy-5-phenylpenta-1,4-dien-1-one (3o):** 90 mg, 64% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 16.0 Hz, 1H, CH=CH-Ph), 7.57 (m, 2H, aromatic CH), 7.40 (m, 3H, aromatic CH), 7.09 (d, *J* =

16.0 Hz, 1H, CH=CH-CO), 3.89 (q,  $J = 7.0$  Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.42 (s, 3H, SMe), 2.28 (s, 3H, SMe), 1.32 (dd,  $J = 9.0, 5.0$  Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 188.9 (Cq, C=O), 153.8 (Cq, CSMe), 144.1 (CH=CH-Ph), 134.8 (Cq of Ph), 130.7, 129.1 and 128.6 (aromatic CH), 126.9 (Cq, COEt), 125.3 (CH=CH-CO), 67.6 (OCH<sub>2</sub>CH<sub>3</sub>), 18.5 (SMe), 16.7 (SMe), 15.5 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 295.0826; Found: 295.0825.



**(E)-3,3-bis(methylthio)-2-ethoxy-5-(3-methylphenyl)penta-1,4-dien-1-one (3p):**

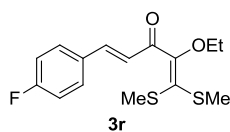
92 mg, 60% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 (d,  $J = 16.0$  Hz, 1H, CH=CH-Ph), 7.31 (d,  $J = 5.9$  Hz, 2H, aromatic CH), 7.20 (dd,  $J = 6.9, 3.1$  Hz, 1H, aromatic CH), 7.14 (d,  $J = 7.5$  Hz, 1H, aromatic CH), 6.99 (d,  $J = 16.0$  Hz, 1H, CH=CH-CO), 3.82 (q,  $J = 7.0$  Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.35 (s, 3H), 2.30 (s, 3H), 2.20 (s, 3H), 1.25 (t,  $J = 7.0$  Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 189.2 (Cq, C=O), 153.9 (Cq, CSMe), 144.4 (CH=CH-Ph), 138.8 and 134.7 (Cq of Ph), 131.6, 129.3, 128.9 and 125.7 (aromatic CH), 126.3 (Cq, COEt), 125.1 (CH=CH-CO), 67.5 (OCH<sub>2</sub>CH<sub>3</sub>), 21.4 (Ph-CH<sub>3</sub>), 18.5 (SMe), 16.6 (SMe), 15.5 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>16</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 309.0983; Found: 309.0986.



**(E)-3,3-bis(methylthio)-2-ethoxy-5-(4-methoxyphenyl)penta-1,4-dien-1-one (3q):**

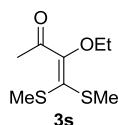
102 mg, 63% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (d,  $J = 15.9$  Hz, 1H, CH=CH-Ph), 7.51 (m, 2H, aromatic CH), 6.95 (15.9, 1H, CH=CH-C=O), 6.90 (m, 2H, aromatic CH), 3.87 (q,  $J = 7.0$  Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 3.81 (s, 3H, Ph-OCH<sub>3</sub>), 2.39 (s, 3H, SMe), 2.24 (s, 3H, SMe), 1.30 (t,  $J = 7.0$  Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 189.1 (Cq, C=O), 161.8 and 127.2 (Cq of Ph), 154.0 (Cq, CSMe), 144.1 (CH=CH-Ph), 130.2 and 114.4 (aromatic CH), 124.8 (Cq, COEt), 122.9 (CH=CH-C=O), 67.2 (OCH<sub>2</sub>CH<sub>3</sub>), 55.4 (Ph-OCH<sub>3</sub>), 18.3 (SMe), 16.4 (SMe),

15.4 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>16</sub>H<sub>20</sub>O<sub>3</sub>S<sub>2</sub> M+H<sup>+</sup>: 325.0932; Found: 325.0936.



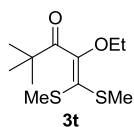
**(E)-3,3-bis(methylthio)-2-ethoxy-5-(4-fluorophenyl)penta-1,4-dien-1-one (3r):**

105 mg, 67% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 16.1 Hz, 1H, CH=CH-Ph), 7.50 (m, 2H, aromatic CH), 7.07 (m, 2H, aromatic CH), 7.01 (d, *J* = 16.0 Hz, 1H, CH=CH-C=O), 3.87 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.41 (s, 3H, SMe), 2.27 (s, 3H, SMe), 1.31 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 188.6 (Cq, C=O), 164.1 (d, *J* = 252.1 Hz, Cq of Ph), 153.6 (Cq, CSMe), 142.6 (CH=CH-C=O), 131.0 (d, *J* = 3.3 Hz, Cq of Ph), 130.4 (d, *J* = 8.6 Hz, aromatic CH), 127.9 (Cq, COEt), 124.8 (d, *J* = 2.2 Hz, CH=CH-Ph), 116.2 (d, *J* = 21.9 Hz, aromatic CH), 67.6 (OCH<sub>2</sub>CH<sub>3</sub>), 18.5 (SMe), 16.7 (SMe), 15.5 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>15</sub>H<sub>17</sub>FO<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 313.0732; Found: 313.0733.



**4,4-Bis(methylthio)-3-ethoxybut-3-en-2-one (3s):** 65 mg, 63% yield, yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.83 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.40 (s, 3H, SMe), 2.34 (s, 3H, SMe), 2.32 (s, 3H, SMe), 1.33 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 196.3 (Cq, C=O), 152.4 (Cq, CSMe), 134.0 (Cq, COEt), 67.7 (OCH<sub>2</sub>CH<sub>3</sub>), 28.7 (C=OCH<sub>3</sub>), 18.4 (SMe), 17.2 (SMe), 15.5 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 207.0513; Found: 207.0514.

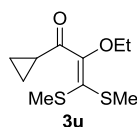


**3,3-Bis(methylthio)-2-ethoxy-1-tert-butylprop-2-en-1-one (3t):** 52 mg, 56% yield,

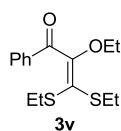
yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.79 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.29 (s, 3H, SMe), 2.16 (s, 3H, SMe), 1.27 (d, *J* = 7.1 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 1.20 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 208.6 (Cq, C=O), 155.5 (Cq, CSMe), 117.8 (Cq, COEt), 67.8 (OCH<sub>2</sub>CH<sub>3</sub>), 43.7 ((CH<sub>3</sub>)<sub>3</sub>C), 27.1 (C=OCH<sub>3</sub>), 17.9 (SMe),



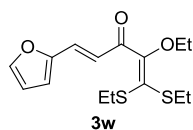
15.7 (OCH<sub>2</sub>CH<sub>3</sub>), 15.1 ((CH<sub>3</sub>)<sub>3</sub>C). HRMS Calcd for C<sub>11</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 249.0983; Found: 249.1006.



**3,3-Bis(methylthio)-2-ethoxy-1-cyclopropylprop-2-en-1-one (3u):** 65 mg, 56% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.86 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.45 (m, 1H, cyclopropyl CH), 2.35(s, 3H, SMe) 2.29 (s, 3H, SMe), 1.32 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 1.14 (m, 2H, cyclopropyl CH<sub>2</sub>), 0.95 (m, 2H, cyclopropyl CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 198.7 (Cq, C=O), 153.4 (Cq, CSMe), 130.0 (Cq, COEt), 67.7 (OCH<sub>2</sub>CH<sub>3</sub>), 19.9 (cyclopropyl CH), 18.4 (SMe), 16.9 (SMe), 15.5 (OCH<sub>2</sub>CH<sub>3</sub>), 12.3 (cyclopropyl CH<sub>2</sub>). HRMS Calcd for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 233.0670; Found: 233.0670.

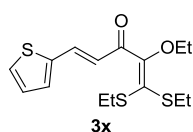


**3,3-Bis(ethylthio)-2-ethoxy-1-phenylprop-2-en-1-one (3v):** 111 mg, 75% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (m, 2H, aromatic CH), 7.56 (t, *J* = 7.4 Hz, 1H, aromatic CH), 7.45 (t, *J* = 7.6 Hz, 2H, aromatic CH), 3.83 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.88 (q, *J* = 7.3 Hz, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 2.57 (q, *J* = 7.4 Hz, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 1.30 (t, *J* = 7.3 Hz, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 1.23 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 1.04 (t, *J* = 7.4 Hz, 3H, SCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.9 (Cq, C=O), 155.6 (Cq, CSMe), 136.5 (Cq of Ph), 133.7, 129.3 and 128.8 (aromatic CH), 114.6 (Cq, COEt), 67.1 (OCH<sub>2</sub>CH<sub>3</sub>), 28.4 (SCH<sub>2</sub>CH<sub>3</sub>), 26.7 (SCH<sub>2</sub>CH<sub>3</sub>), 15.4 (SCH<sub>2</sub>CH<sub>3</sub>), 15.3 (SCH<sub>2</sub>CH<sub>3</sub>), 14.0 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 297.0983; Found: 297.0986.

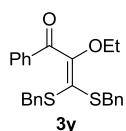


**(E)-3,3-bis(ethylthio)-2-ethoxy-5-(2-furyl)penta-1,4-dien-1-one (3w):** 111 mg, 71% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (s, 1H, furyl CH), 7.39

(d,  $J = 15.7$  Hz, 1H, CH=CH-furan), 6.96 (d,  $J = 15.7$  Hz, 1H, CH=CH-C=O), 6.68 (m, 1H, furyl CH), 6.50 (m, 1H, furyl CH), 3.88 (q,  $J = 7.0$  Hz, 2H,  $_3$  OCH<sub>2</sub>CH), 2.91 (q,  $J = 7.3$  Hz, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 2.78 (q,  $J = 7.4$  Hz, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 1.26 (m, 9H, OCH<sub>2</sub>CH<sub>3</sub> and SCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 188.8 (Cq, C=O), 155.4 (Cq, CSM<sub>e</sub>), 151.6 (Cq of furan), 145.3, 129.9, 123.1, 116.3 (furyl CH or CH=CH), 112.8 (Cq, COEt), 67.5 (OCH<sub>2</sub>CH<sub>3</sub>), 28.8 (SCH<sub>2</sub>CH<sub>3</sub>), 27.5 (SCH<sub>2</sub>CH<sub>3</sub>), 15.5 (SCH<sub>2</sub>CH<sub>3</sub>), 15.2 (SCH<sub>2</sub>CH<sub>3</sub>), 14.4 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>15</sub>H<sub>20</sub>O<sub>3</sub>S<sub>2</sub> M+H<sup>+</sup>: 313.0932; Found: 313.0931.

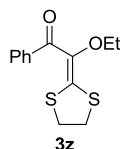


**(E)-3,3-bis(methylthio)-2-ethoxy-5-(2-thienyl)penta-1,4-dien-1-one (3x):** 115 mg, 70% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (d,  $J = 15.7$  Hz, 1H, CH=CH-thiophene), 7.40 (m, 1H, thienyl CH), 7.29 (m, 1H, thienyl CH), 7.06 (m, 1H, thienyl CH), 6.87 (d,  $J = 15.7$  Hz, 1H, CH=CH-C=O), 3.88 (q,  $J = 6.9$  Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.91 (q,  $J = 7.3$  Hz, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 2.78 (q,  $J = 7.3$  Hz, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 1.29 (m, 6H, OCH<sub>2</sub>CH<sub>3</sub> and SCH<sub>2</sub>CH<sub>3</sub>), 1.23 (t,  $J = 7.3$  Hz, 3H, SCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 188.7 (Cq, C=O), 155.3 (Cq, CSM<sub>e</sub>), 140.4 (Cq of thiophene), 136.4, 131.9, 129.2, 128.5, 124.5 (thienyl CH or CH=CH), 123.4 (Cq, COEt), 67.5 (OCH<sub>2</sub>CH<sub>3</sub>), 28.8 (SCH<sub>2</sub>CH<sub>3</sub>), 27.5 (SCH<sub>2</sub>CH<sub>3</sub>), 15.5 (SCH<sub>2</sub>CH<sub>3</sub>), 15.2 (SCH<sub>2</sub>CH<sub>3</sub>), 14.5 (OCH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>S<sub>3</sub> M+H<sup>+</sup>: 329.0704; Found: 329.0702.

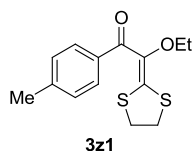


**3,3-Bis(benzylthio)-2-ethoxy-1-phenylprop-2-en-1-one (3y):** 141 mg, 67% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (m, 2H, aromatic CH), 7.53 (t,  $J = 7.4$  Hz, 1H, aromatic CH), 7.42 (m, 2H, aromatic CH), 7.35 (t,  $J = 7.6$  Hz, 4H, aromatic CH), 7.30 (m, 1H, aromatic CH), 7.18 (m, 3H, aromatic CH), 7.03 (dd,  $J = 6.6, 2.9$  Hz, 2H, aromatic CH), 4.10 (s, 2H, PhCH<sub>2</sub>S), 3.73 (s, 2H, PhCH<sub>2</sub>S), 3.68 (q,

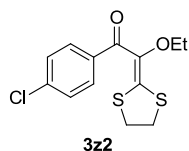
$J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 1.15 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.5 (Cq, C=O), 157.6 (Cq, CSMe), 138.4, 136.8 and 136.1 (Cq of Ph), 133.5, 129.3, 129.2, 129.1, 128.7, 128.5, 128.4 and 127.1 (aromatic CH), 112.3 (Cq, COEt), 67.11 ( $\text{OCH}_2\text{CH}_3$ ), 39.17 ( $\text{PhCH}_2\text{S}$ ), 37.02 ( $\text{PhCH}_2\text{S}$ ), 15.24 ( $\text{OCH}_2\text{CH}_3$ ). HRMS Calcd for  $\text{C}_{25}\text{H}_{24}\text{O}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 421.1296; Found: 421.1290.



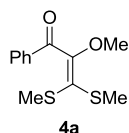
**2-(1,3-dithiolan-2-ylidene)-2-ethoxy-1-phenylethanone (3z):** 70 mg, 53% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 7.8$  Hz, 2H, aromatic CH), 7.48 (t,  $J = 7.0$  Hz, 1H, aromatic CH), 7.40 (t,  $J = 7.5$  Hz, 2H, aromatic CH), 3.60 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 3.45 (m, 2H,  $\text{SCH}_2$ ), 3.37 (m, 2H,  $\text{SCH}_2$ ), 1.16 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  187.1 (Cq, C=O), 154.3 (Cq, CSMe), 142.6 (Cq, COEt), 137.5 (Cq of Ph), 131.9, 129.2 and 128.1 (aromatic CH), 68.8 ( $\text{OCH}_2\text{CH}_3$ ), 40.0 ( $\text{SCH}_2$ ), 35.9 ( $\text{SCH}_2$ ), 15.5 ( $\text{OCH}_2\text{CH}_3$ ). HRMS Calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 267.0513; Found: 267.0510.



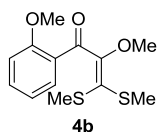
**2-(1,3-dithiolan-2-ylidene)-2-ethoxy-1-(p-tolyl)ethanone (3z1):** 78 mg, 56% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.1$  Hz, 2H, aromatic CH), 7.21 (d,  $J = 8.0$  Hz, 2H, aromatic CH), 3.61 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 3.44 (m, 2H,  $\text{SCH}_2$ ), 3.47 (m, 2H,  $\text{SCH}_2$ ), 2.39 (s, 3H, Ph- $\text{CH}_3$ ), 1.19 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.7 (Cq, C=O), 153.7 (Cq, CSMe), 142.8 (Cq of Ph), 142.6 (Cq, COEt), 134.8 (Cq of Ph), 129.4 and 128.9 (aromatic CH), 68.7 ( $\text{OCH}_2\text{CH}_3$ ), 39.9 ( $\text{SCH}_2$ ), 35.9 ( $\text{SCH}_2$ ), 21.8 (Ph- $\text{CH}_3$ ), 15.6 ( $\text{OCH}_2\text{CH}_3$ ). HRMS Calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 281.0670; Found: 281.0670.



**1-(4-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-ethoxyethanone (3z2):** 81 mg, 54% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (m, 2H, aromatic CH), 7.38 (m, 2H, aromatic CH), 3.59 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 3.45 (m, 2H,  $\text{SCH}_2$ ), 3.36 (dd,  $J = 7.1, 4.9$  Hz, 2H,  $\text{SCH}_2$ ), 1.17 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  185.5 (s), 155.4 (Cq,  $\text{CSMe}$ ), 142.3 (Cq,  $\text{COEt}$ ), 138.1 and 135.7 (Cq of Ph), 130.7 and 128.4 (aromatic CH), 68.8 ( $\text{OCH}_2\text{CH}_3$ ), 44.0 ( $\text{SCH}_2$ ), 36.0 ( $\text{SCH}_2$ ), 15.5 ( $\text{OCH}_2\text{CH}_3$ ). HRMS Calcd for  $\text{C}_{13}\text{H}_{13}\text{ClO}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 301.0124; Found: 301.0122.

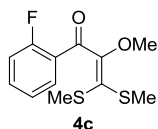


**3,3-Bis(methylthio)-2-methoxy-1-phenylprop-2-en-1-one (4a):** 91 mg, 72% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.94 (m, 2H, aromatic CH), 7.58 (m, 1H, aromatic CH), 7.48 (m, 2H, aromatic CH), 3.63 (s, 3H, OMe), 2.38 (s, 3H, SMe), 2.02 (s, 3H, SMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.5 (Cq,  $\text{C}=\text{O}$ ), 154.6 (Cq,  $\text{CSMe}$ ), 136.7 (Cq of Ph), 133.8, 129.1 and 128.8 (aromatic CH), 116.7 (Cq,  $\text{COMe}$ ), 58.3 (OMe), 17.8 (SMe), 16.0 (SMe). HRMS Calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 255.0513; Found: 255.0515.

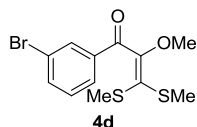


**3,3-Bis(methylthio)-2-methoxy-1-(2-methoxyphenyl)prop-2-en-1-one (4b):** 88 mg, 62% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (dd,  $J = 7.7, 1.5$  Hz, 1H, aromatic CH), 7.41 (m, 1H, aromatic CH), 6.97 (t,  $J = 7.5$  Hz, 1H, aromatic CH), 6.90 (d,  $J = 8.4$  Hz, 1H, aromatic CH), 3.80 (s, 3H, OMe), 3.63 (s, 3H, OMe), 2.29 (s, 3H, SMe), 1.83 (s, 3H, SMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  190.8 (Cq,  $\text{C}=\text{O}$ ), 158.9 (Cq,  $\text{CSMe}$ ), 157.3, 128.2 and 115.8 (Cq), 134.2, 131.4, 120.9 and 111.9 (aromatic

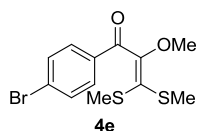
CH), 58.2 and 55.7 (OMe), 17.5 (SMe), 16.3 (SMe). HRMS Calcd for C<sub>12</sub>H<sub>16</sub>O<sub>3</sub>S<sub>2</sub> M+H<sup>+</sup>: 285.0619; Found: 285.0617.



**3,3-Bis(methylthio)-2-methoxy-1-(2-fluorophenyl)prop-2-en-1-one (4c):** 94 mg, 69% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 (m, 1H, aromatic CH), 7.44 (m, 1H, aromatic CH), 7.19 (m, 1H, aromatic CH), 7.05 (m, 1H, aromatic CH), 3.62 (s, 3H, OMe), 2.32 (s, 3H, SMe), 1.93 (s, 3H, SMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 188.0 (Cq, C=O), 160.9 (d, *J* = 255.7 Hz, Cq), 155.1 (Cq, CSMe), 134.31 (d, *J* = 8.8 Hz, aromatic CH), 130.9 (d, *J* = 1.3 Hz, aromatic CH), 127.1 (d, *J* = 10.7 Hz, Cq), 124.5 (d, *J* = 3.7 Hz, aromatic CH), 122.7 (d, *J* = 3.6 Hz, Cq), 116.5 (d, *J* = 22.0 Hz, aromatic CH), 58.5 (OMe), 17.6 (SMe), 16.4 (SMe). HRMS Calcd for C<sub>12</sub>H<sub>13</sub>FO<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 273.0419; Found: 273.0418.

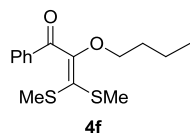


**3,3-Bis(methylthio)-2-methoxy-1-(3-bromophenyl)prop-2-en-1-one (4d):** 116.6 mg, 70% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (s, 1H, aromatic CH), 7.84 (d, *J* = 7.8 Hz, 1H, aromatic CH), 7.68 (m, 1H, aromatic CH), 7.36 (t, *J* = 7.9 Hz, 1H, aromatic CH), 3.64 (s, 3H, OMe), 2.39 (s, 3H, SMe), 2.04 (s, 3H, SMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 189.9 (Cq, C=O), 153.5 (Cq, CSMe), 138.7, 123.08 and 119.61 (Cq), 136.5, 131.8, 130.4 and 127.6 (aromatic CH), 58.6 (OMe), 17.8 (SMe), 16.1 (SMe). HRMS Calcd for C<sub>12</sub>H<sub>13</sub>BrO<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 332.9619; Found: 332.9621.

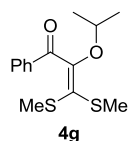


**3,3-Bis(methylthio)-2-methoxy-1-(4-bromophenyl)prop-2-en-1-one (4e):** 123 mg, 74% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.6 Hz, 2H, aromatic CH), 7.63 (d, *J* = 8.6 Hz, 2H, aromatic CH), 3.63 (s, 3H, OMe), 2.39 (s, 3H, SMe), 2.05 (s, 3H, SMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 190.44 (Cq, C=O),

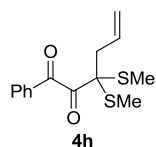
153.8 (Cq, CSMe), 135.6, 129.0 and 118.6 (Cq), 132.2 and 130.6 (aromatic CH), 58.5 (OMe), 17.9 (SMe), 16.0 (SMe). HRMS Calcd for C<sub>12</sub>H<sub>13</sub>BrO<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 332.9619; Found: 332.9619.



**3,3-Bis(methylthio)-2-butoxy-1-phenylprop-2-en-1-one (4f):** 92 mg, 62% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (m, 2H, aromatic CH), 7.58 (m, 1H, aromatic CH), 7.48 m, 2H, aromatic CH), 3.75 (m, 2H, OCH<sub>2</sub>), 2.36 (s, 3H, SMe), 2.07 (s, 3H, SMe), 1.60 (m, 2H, butyl CH<sub>2</sub>), 1.36 (m, 2H, butyl CH<sub>2</sub>), 0.86 (m, 3H, butyl CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.9 (Cq, C=O), 154.2 (Cq, CSMe), 136.7 (Cq of Ph), 133.7, 129.2 and 128.8 (aromatic CH), 117.4 (Cq, COCH<sub>2</sub>), 71.0 (OCH<sub>2</sub>), 31.9 (OCH<sub>2</sub>CH<sub>2</sub>), 19.0 (SMe), 18.0 (SMe), 15.9 (butyl CH<sub>2</sub>), 13.8 (butyl CH<sub>3</sub>). HRMS Calcd for C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 297.0983; Found: 297.0985.

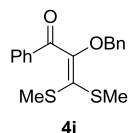


**3,3-Bis(methylthio)-2-isopropoxy-1-phenylprop-2-en-1-one (4g):** 95 mg, 67% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (m, 2H, aromatic CH), 7.58 m, 1H, aromatic CH), 7.47 (m, 2H, aromatic CH), 4.07 (m, 1H, OCH), 2.39 (s, 3H, SMe), 2.08 (s, 3H, SMe), 1.22 (m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.9 (Cq, C=O), 153.4 (Cq, CSMe), 136.5 (Cq of Ph), 133.7, 129.4 and 128.7 (aromatic CH), 119.8 (Cq, COCH), 74.4 (OCH), 22.7 (SMe), 18.3 (SMe), 15.8 (CH(CH<sub>3</sub>)<sub>2</sub>). HRMS Calcd for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 283.0826; Found: 283.0826.

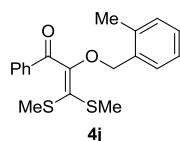


**3,3-Bis(methylthio)-1-phenylhex-5-ene-1,2-dione (4h):** 74 mg, 53% yield, colourless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (m, 2H, aromatic CH), 7.64 (m, 1H, aromatic CH), 7.48 (m, 2H, aromatic CH), 5.95 (m, 1H, CH=CH<sub>2</sub>), 5.21 (m, 2H, CH=CH<sub>2</sub>), 2.92 (d, *J* = 6.8 Hz, 2H, CH<sub>2</sub>), 2.05 (s, 6H, SMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100

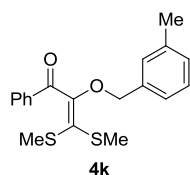
MHz, CDCl<sub>3</sub>) δ 193.7(Cq, C=O), 192.3 (Cq, C=O), 134.6 (CH=CH<sub>2</sub>), 133.5 (Cq of Ph), 132.0, 129.6, 128.8 (aromatic CH), 119.4 (CH=CH<sub>2</sub>), 67.5 (CSMe), 38.4 (CH<sub>2</sub>), 12.1 (SMe). HRMS Calcd for C<sub>14</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 281.0670; Found: 281.0669.



**3,3-Bis(methylthio)-2-(benzyloxy)-1-phenylprop-2-en-1-one (4i):** 104 mg, 63% yield, yellow solid, m.p.: 55-57 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (m, 2H, aromatic CH), 7.44 (m, 1H, aromatic CH), 7.32 (m, 2H, aromatic CH), 7.17 (m, 5H, aromatic CH), 4.77 (s, 2H, OCH<sub>2</sub>), 2.26 (s, 3H, SMe), 1.92 (s, 3H, SMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.5 (Cq, C=O), 152.9 (Cq, CSMe), 136.9 and 136.2 (Cq of Ph), 133.4, 129.1, 128.5, 128.4, 128.3 and 128.2 (aromatic CH), 121.0 (Cq, COCH), 72.8 (OCH<sub>2</sub>), 17.8 (SMe), 15.9 (SMe). HRMS Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 331.0826; Found: 331.0828.

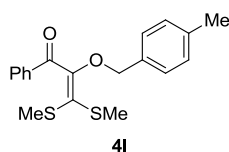


**3,3-Bis(methylthio)-2-((2-methylbenzyl)oxy)-1-phenylprop-2-en-1-one (4j):** 130 mg, 76% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (m, 2H, aromatic CH), 7.62 (m, 1H, aromatic CH), 7.50 (m, 2H, aromatic CH), 7.31 (m, 1H, aromatic CH), 7.24 (m, 1H, aromatic CH), 7.16 (m, 2H, aromatic CH), 4.93 (s, 2H, OCH<sub>2</sub>), 2.42 (s, 3H, SMe), 2.35 (s, 3H, SMe), 2.10 (s, 3H, Ph-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.7 (Cq, C=O), 153.2 (Cq, CSMe), 137.3, 136.9 and 134.3 (Cq of Ph), 133.5, 130.4, 129.6, 129.2, 128.7, 128.6 and 125.9 (aromatic CH), 120.7 (Cq, COCH), 71.2 (OCH<sub>2</sub>), 18.9 (Ph-CH<sub>3</sub>), 17.8 (SMe), 15.9 (SMe). HRMS Calcd for C<sub>19</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 345.0983; Found: 345.0983.

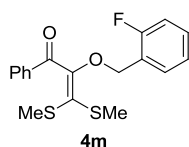


**3,3-Bis(methylthio)-2-((3-methylbenzyl)oxy)-1-phenylprop-2-en-1-one (4k):** 120

mg, 70% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (m, 2H, aromatic CH), 7.55 (m, 1H, aromatic CH), 7.42 (m, 2H, aromatic CH), 7.19 (m, 2H, aromatic CH), 7.09 (m, 2H, aromatic CH), 4.84 (s, 2H,  $\text{OCH}_2$ ), 2.37 (s, 3H, SMe), 2.31 (s, 3H, SMe), 2.03 (s, 3H, Ph- $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.6 (Cq, C=O), 153.1 (Cq, CSMe), 138.1, 136.9 and 133.2 (Cq of Ph), 133.4, 129.1, 128.5 and 128.3 (aromatic CH), 120.8 (Cq, COCH), 72.8 ( $\text{OCH}_2$ ), 21.3 (Ph- $\text{CH}_3$ ), 17.8 (SMe), 16.0 (SMe). HRMS Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 345.0983; Found: 345.0983.



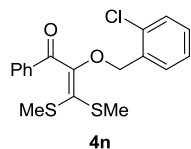
**3,3-Bis(methylthio)-2-((4-methylbenzyl)oxy)-1-phenylprop-2-en-1-one (4l):** 130 mg, 76% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (m, 2H, aromatic CH), 7.55 (m, 1H, aromatic CH), 7.43 (m, 2H, aromatic CH), 7.17 (m, 1H, aromatic CH), 7.12 (m, 1H, aromatic CH), 7.07 (m, 2H, aromatic CH), 4.84 (s, 2H,  $\text{OCH}_2$ ), 2.38 (s, 3H, SMe), 2.27 (s, 3H, SMe), 2.03 (s, 3H, Ph- $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.7 (Cq, C=O), 153.1 (Cq, CSMe), 138.1, 136.9 and 136.2 (Cq of Ph), 133.5, 129.3, 129.2, 129.01, 128.6, 128.4 and 125.41 (aromatic CH), 121.0 (Cq, COCH), 72.9 ( $\text{OCH}_2$ ), 21.4 (Ph- $\text{CH}_3$ ), 17.8 (SMe), 16.0 (SMe). HRMS Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 345.0983; Found: 345.0980.



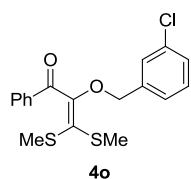
**3,3-Bis(methylthio)-2-((2-fluorobenzyl)oxy)-1-phenylprop-2-en-1-one (4m):** 108 mg, yield 62%, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (m, 2H, aromatic CH), 7.48 (m, 1H, aromatic CH), 7.37 (m, 3H, aromatic CH), 7.17 (m, 1H, aromatic CH), 7.01 (m, 1H, aromatic CH), 6.89 (m, 1H, aromatic CH), 4.85 (s, 2H,  $\text{OCH}_2$ ), 2.28 (s, 3H, SMe), 1.97 (s, 3H, SMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.4 (Cq, C=O), 161.7 (d,  $J = 248.4$  Hz, Cq of Ph), 152.8 (Cq, CSMe), 136.9 (Cq of Ph), 133.6 (aromatic CH), 130.6 (d,  $J = 3.7$  Hz, aromatic CH), 130.3 (d,  $J = 8.2$  Hz, aromatic CH), 129.2 (aromatic CH), 128.7 (aromatic CH), 124.2 (d,  $J = 3.7$  Hz), 123.6 (d,  $J = 14.4$



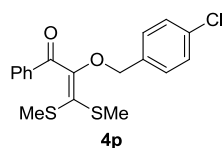
Hz, Cq of Ph), 121.8 (Cq, COCH<sub>2</sub>), 115.5 (s), 115.4 (d, *J* = 21.1 Hz, aromatic CH), 66.6 (d, *J* = 4.1 Hz, OCH<sub>2</sub>), 17.9 (SMe), 16.0 (SMe). HRMS Calcd for C<sub>18</sub>H<sub>17</sub>FO<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 349.0742; Found: 349.0740.



**3,3-Bis(methylthio)-2-((2-chlorobenzyl)oxy)-1-phenylprop-2-en-1-one (4n):** 128 mg, 70% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 7.6 Hz, 2H, aromatic CH), 7.55 (m, 2H, aromatic CH), 7.45 (m, 2H, aromatic CH), 7.29 (m, 1H, aromatic CH), 7.22 (m, 2H, aromatic CH), 4.97 (s, 2H, OCH<sub>2</sub>), 2.37 (s, 3H, SMe), 2.06 (s, 3H, SMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.4 (Cq, C=O), 152.8 (Cq, CSMe), 136.8, 134.1 and 133.2 (Cq of Ph), 133.6, 129.8, 129.5, 129.4, 129.2, 128.7 and 126.9 (aromatic CH), 121.3 (Cq, COCH<sub>2</sub>), 69.9 (OCH<sub>2</sub>), 17.8 (SMe), 16.0 (SMe). HRMS Calcd for C<sub>18</sub>H<sub>17</sub>O<sub>2</sub>S<sub>2</sub>Cl M+H<sup>+</sup>: 365.0437; Found: 365.0440.

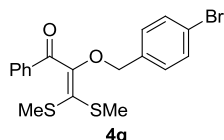


**3,3-Bis(methylthio)-2-((3-chlorobenzyl)oxy)-1-phenylprop-2-en-1-one (4o):** 133 mg, 73% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (m, 2H, aromatic CH), 7.56 (m, 1H, aromatic CH), 7.44 (m, 2H, aromatic CH), 7.32 (s, 1H, aromatic CH), 7.21 (m, 3H, aromatic CH), 4.83 (s, 2H, OCH<sub>2</sub>), 2.38 (s, 3H, SMe), 2.04 (s, 3H, SMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.5 (Cq, C=O), 152.5 (Cq, CSMe), 138.3, 136.8 and 134.4 (Cq of Ph), 133.7, 129.8, 129.2, 128.7, 128.5, 128.3 and 126.2 (aromatic CH), 122.0 (Cq, COCH<sub>2</sub>), 72.1 (OCH<sub>2</sub>), 17.8 (SMe), 15.9 (SMe). HRMS Calcd for C<sub>18</sub>H<sub>17</sub>O<sub>2</sub>S<sub>2</sub>Cl M+H<sup>+</sup>: 365.0437; Found: 365.0438.

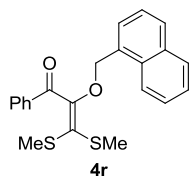


**3,3-Bis(methylthio)-2-((4-chlorobenzyl)oxy)-1-phenylprop-2-en-1-one (4p):** 139 mg, yield 76%, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (m, 2H, aromatic

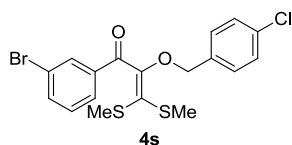
CH), 7.56 (m, 1H, aromatic CH), 7.43 (m, 2H, aromatic CH), 7.25 (m, 4H, aromatic CH), 4.83 (s, 2H, OCH<sub>2</sub>), 2.36 (s, 3H, SMe), 2.03 (s, 3H, SMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.5 (Cq, C=O), 152.6 (Cq, CSMe), 136.9, 134.8 and 134.3 (Cq of Ph), 133.6, 129.7, 129.2 and 128.7 (aromatic CH), 121.8 (Cq, COCH<sub>2</sub>), 72.1 (OCH<sub>2</sub>), 17.8 (SMe), 15.9 (SMe). HRMS Calcd for C<sub>18</sub>H<sub>17</sub>O<sub>2</sub>S<sub>2</sub>Cl M+H<sup>+</sup>: 365.0437; Found: 365.0439.



**3,3-Bis(methylthio)-2-((4-bromobenzyl)oxy)-1-phenylprop-2-en-1-one (4q):** 143 mg, 70% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 7.2 Hz, 2H, aromatic CH), 7.56 (m, 1H, aromatic CH), 7.43 (m, 4H, aromatic CH), 7.18 (d, *J* = 8.3 Hz, 2H, aromatic CH), 4.81 (s, 2H, OCH<sub>2</sub>), 2.37 (s, 3H, SMe), 2.03 (s, 3H, SMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.5 (Cq, C=O), 152.6 (Cq, CSMe), 136.9, 135.4 and 122.4 (Cq of Ph) 133.6, 131.7, 129.9, 129.2 and 128.7 (aromatic CH), 121.8 (Cq, COCH<sub>2</sub>), 72.1 (OCH<sub>2</sub>), 17.9 (SMe), 15.9 (SMe). HRMS Calcd for C<sub>18</sub>H<sub>17</sub>O<sub>2</sub>S<sub>2</sub>Br M+H<sup>+</sup>: 408.9932; Found: 408.9935.

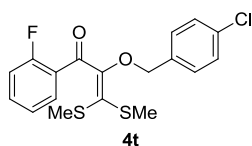


**3,3-bis(methylthio)-2-(naphthalen-1-ylmethoxy)-1-phenylprop-2-en-1-one (4r):** 123 mg, 64% yield, yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 7.6 Hz, 1H, aromatic CH), 7.83 (d, *J* = 8.2 Hz, 3H, aromatic CH), 7.78 (d, *J* = 8.2 Hz, 1H, aromatic CH), 7.52 (m, 4H, aromatic CH), 7.39 (d, *J* = 8.1 Hz, 2H, aromatic CH), 7.31 (m, 1H, aromatic CH), 5.35 (s, 2H, OCH<sub>2</sub>), 2.33 (s, 3H, SMe), 2.03 (s, 3H, SMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.7 (Cq, C=O), 152.9 (Cq, CSMe), 137.0, 133.7 and 131.8, 131.7 (Cq of Ph), 133.4, 129.5, 129.1, 128.5, 127.8, 126.5, 125.9, 125.1 and 124.2 (aromatic CH), 121.8 (COCH<sub>2</sub>), 71.3 (OCH<sub>2</sub>), 17.8 (SMe), 16.1 (SMe). HRMS Calcd for C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 381.0983; Found: 381.0983.



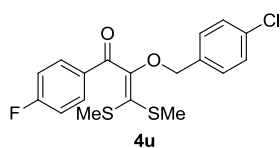
**3,3-Bis(methylthio)-2-((4-chlorobenzyl)oxy)-1-(3-bromophenyl)prop-2-en-1-one**

**(4s):** 169 mg, 76% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (m, 1H, aromatic CH), 7.62 (m, 2H, aromatic CH), 7.22 (m, 5H, aromatic CH), 4.80 (s, 2H,  $\text{OCH}_2$ ), 2.33 (s, 3H, SMe), 1.98 (s, 3H, SMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  189.7 (Cq, C=O), 151.4 (Cq, CSMe), 138.9, 134.6, 134.4, 124.5 and 122.7 (Cq), 136.0, 131.8, 130.1, 129.7, 128.7 and 127.4 (aromatic CH), 72.1 ( $\text{OCH}_2$ ), 17.6 (SMe), 15.9 (SMe). HRMS Calcd for  $\text{C}_{18}\text{H}_{16}\text{BrClO}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 442.9542; Found: 442.9540.



**3,3-Bis(methylthio)-2-((4-chlorobenzyl)oxy)-1-(2-fluorophenyl)prop-2-en-1-one**

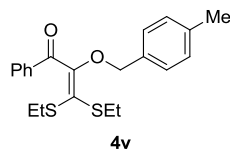
**(4t):** 134 mg, 70% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (m, 2H, aromatic CH), 7.19 (m, 4H, aromatic CH), 7.03 (m, 2H, aromatic CH), 4.74 (s, 2H,  $\text{OCH}_2$ ), 2.29 (s, 3H, SMe), 1.98 (s, 3H, SMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  189.9 (Cq, C=O), 166.0 (d,  $J = 255.8$  Hz, Cq), 152.2 (Cq, CSMe), 134.7, 134.4 and 122.7 (Cq), 133.3 (d,  $J = 2.8$  Hz, Cq), 131.9 (d,  $J = 9.4$  Hz, aromatic CH), 129.7 and 128.7 (aromatic CH), 115.9 (d,  $J = 22.0$  Hz, aromatic CH), 72.2 ( $\text{OCH}_2$ ), 17.9 (SMe), 15.9 (SMe). HRMS Calcd for  $\text{C}_{18}\text{H}_{16}\text{FClO}_2\text{S}_2$   $\text{M}+\text{H}^+$ : 383.0343; Found: 383.0345.



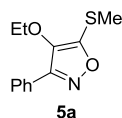
**3,3-Bis(methylthio)-2-((4-chlorobenzyl)oxy)-1-(4-fluorophenyl)prop-2-en-1-one**

**(4u):** 125 mg, 65% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (m, 1H, aromatic CH), 7.39 (m, 1H, aromatic CH), 7.20 (m, 5H, aromatic CH), 7.11 (m, 1H, aromatic CH), 7.00 (m, 1H, aromatic CH), 4.75 (s, 2H,  $\text{OCH}_2$ ), 2.29 (s, 3H, SMe), 1.96 (s, 3H, SMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  187.9 (C=O), 160.9 (d,  $J = 255.7$  Hz, Cq), 153.0 (Cq, CSMe), 134.9 134.2 and 130.9 (Cq), 134.1 (d,  $J = 8.7$  Hz, aromatic CH), 129.8, 128.7 and 127.3 (aromatic CH), 124.4 (d,  $J = 3.7$  Hz, aromatic

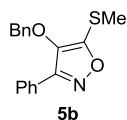
CH), 116.5 (d,  $J = 22.0$  Hz, aromatic CH), 72.4 (OCH<sub>2</sub>), 17.8 (SMe), 16.5 (SMe).  
HRMS Calcd for C<sub>18</sub>H<sub>16</sub>FCIO<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 383.0343; Found: 383.0340.



**3,3-Bis(ethylthio)-2-((4-methylbenzyl)oxy)-1-phenylprop-2-en-1-one (4v):** 147 mg, 79% yield, yellow solid, m.p.: 57-58 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (d,  $J = 7.4$  Hz, 2H, aromatic CH), 7.42 (t,  $J = 7.4$  Hz, 1H, aromatic CH), 7.29 (t,  $J = 7.7$  Hz, 2H, aromatic CH), 7.08 (d,  $J = 7.9$  Hz, 2H, aromatic CH), 6.96 (d,  $J = 7.8$  Hz, 2H, aromatic CH), 4.70 (s, 2H, OCH<sub>2</sub>), 2.75 (q,  $J = 7.3$  Hz, 2H, SCH<sub>2</sub>), 2.46 (q,  $J = 7.4$  Hz, 2H, SCH<sub>2</sub>), 2.18 (s, 3H, Ph-CH<sub>3</sub>), 1.17 (t,  $J = 7.3$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.91 (t,  $J = 7.4$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.6 (Cq, C=O), 154.8 (Cq, CSM<sub>e</sub>), 137.9 (s), 136.7 and 133.1 (s), 133.4 (s), 129.2, 129.0, 128.5 and 128.3 (aromatic CH), 117.5 (Cq, COCH<sub>2</sub>), 72.8 (OCH<sub>2</sub>), 28.3 (SCH<sub>2</sub>), 26.6 (SCH<sub>2</sub>), 21.2 (Ph-CH<sub>3</sub>), 15.3 (CH<sub>2</sub>CH<sub>3</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>S<sub>2</sub> M+H<sup>+</sup>: 373.1296; Found: 373.1294.

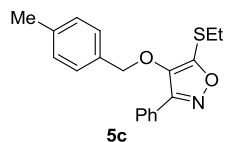


**5-(Methylthio)-4-ethoxy-3-phenylisoxazole (5a):** 62 mg, 53% yield, colourless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (m, 2H, aromatic CH), 7.45 (dd,  $J = 3.0, 2.2$  Hz, 3H, aromatic CH), 4.15 (q,  $J = 7.0$  Hz, 2H, OCH<sub>2</sub>), 2.56 (s, 3H, SMe), 1.35 (t,  $J = 7.0$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 156.6 (Cq, CSM<sub>e</sub>), 152.4 (Cq, C=N), 139.3 (Cq of Ph), 130.0, 128.8 and 127.3 (aromatic CH), 128.3 (Cq, COCH<sub>2</sub>), 69.7 (OCH<sub>2</sub>), 16.9 (SMe), 15.4 (CH<sub>2</sub>CH<sub>3</sub>). HRMS Calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>S M+H<sup>+</sup>: 236.0745; Found: 236.0743.



**5-(Methylthio)-4-(benzyloxy)-3-phenylisoxazole (5b):** 93 mg, 62% yield, colourless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d,  $J = 3.4$  Hz, 2H, aromatic CH), 7.47 (m, 3H, aromatic CH), 7.35 (s, 5H, aromatic CH), 5.10 (s, 2H, OCH<sub>2</sub>), 2.50

(s, 3H, SMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9 (Cq,  $\text{C}=\text{SMe}$ ), 153.2 (Cq,  $\text{C}=\text{N}$ ), 138.8 and 136.0 (Cq of Ph), 128.2 (Cq,  $\text{COCH}_2$ ), 130.1, 128.9, 128.7, 128.6, 128.4 and 127.4 (aromatic CH), 75.4 ( $\text{OCH}_2$ ), 16.8 (SMe). HRMS Calcd for  $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{S}$   $\text{M}+\text{H}^+$ : 298.0902; Found: 298.0900.

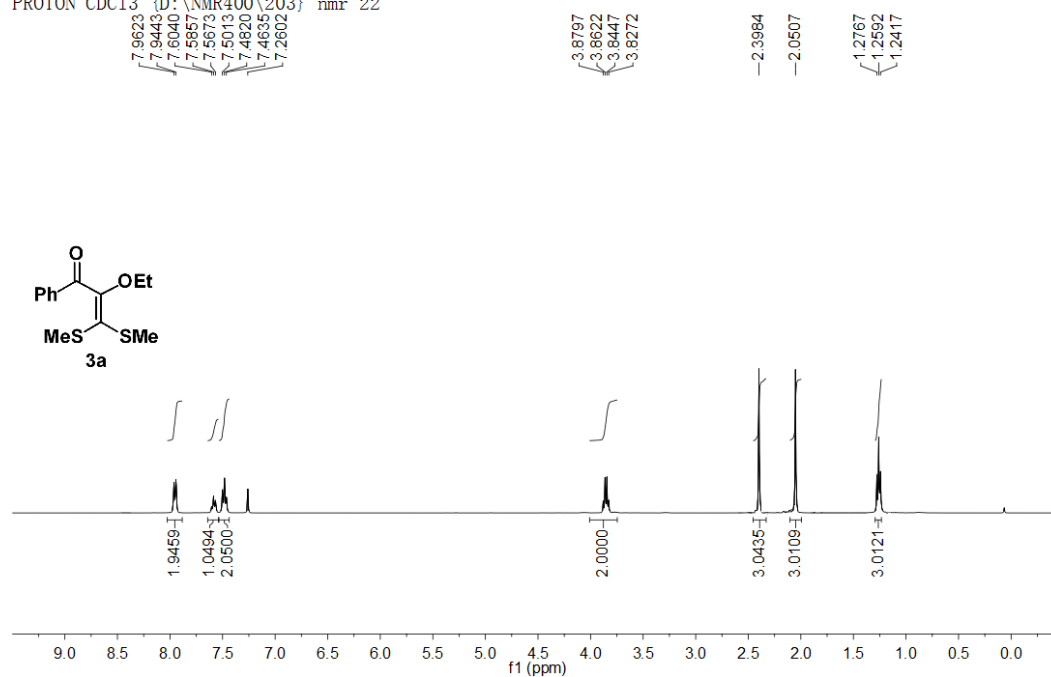


**5-(Ethylthio)-4-((4-methylbenzyl)oxy)-3-phenylisoxazole (5c):** 88 mg, 54% yield, colourless liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (m, 2H, aromatic CH), 7.35 (m, 3H, aromatic CH), 7.14 (d,  $J = 7.6$  Hz, 2H, aromatic CH), 7.05 (d,  $J = 7.7$  Hz, 2H, aromatic CH), 4.98 (s, 2H,  $\text{OCH}_2$ ), 2.86 (q,  $J = 7.3$  Hz, 2H,  $\text{SCH}_2$ ), 2.25 (s, 3H,  $\text{Ph-CH}_3$ ), 1.25 (t,  $J = 7.4$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7 (Cq,  $\text{C}=\text{SMe}$ ), 152.2 (Cq,  $\text{C}=\text{N}$ ), 140.2, 138.3 and 132.9 (Cq of Ph), 128.2 (Cq,  $\text{COCH}_2$ ), 129.9, 129.2, 128.7, 128.5 and 127.3 (aromatic CH), 75.4 ( $\text{OCH}_2$ ), 29.0 ( $\text{SCH}_2$ ), 21.3 ( $\text{Ph-CH}_3$ ), 15.5 ( $\text{CH}_2\text{CH}_3$ ). HRMS Calcd for  $\text{C}_{19}\text{H}_{19}\text{NO}_2\text{S}$   $\text{M}+\text{H}^+$ : 326.1215; Found: 326.1213.

## 5. Copies of NMR spectra

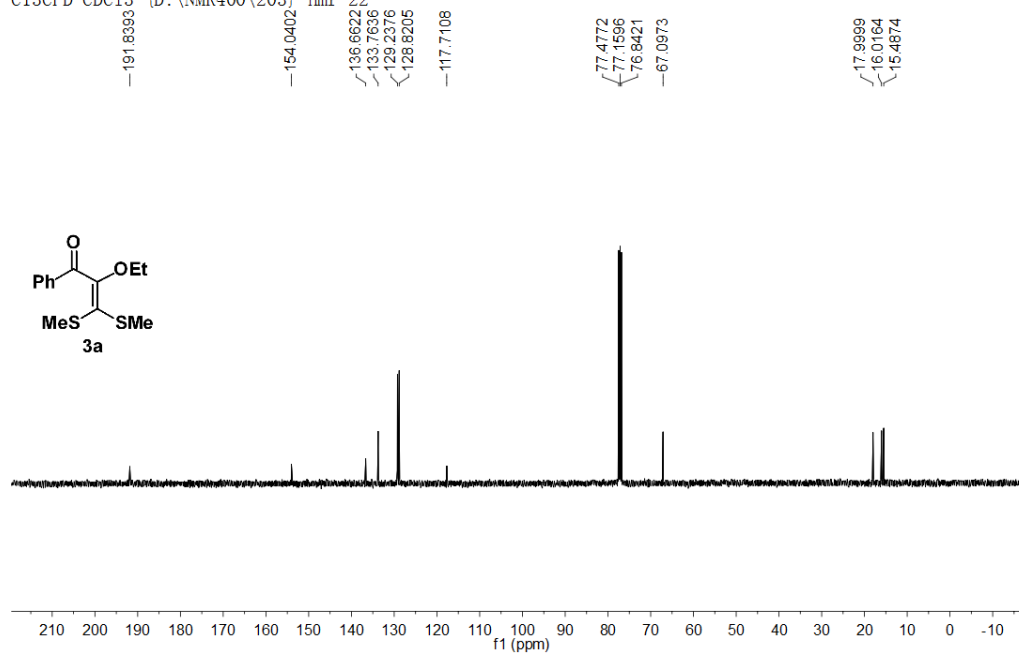
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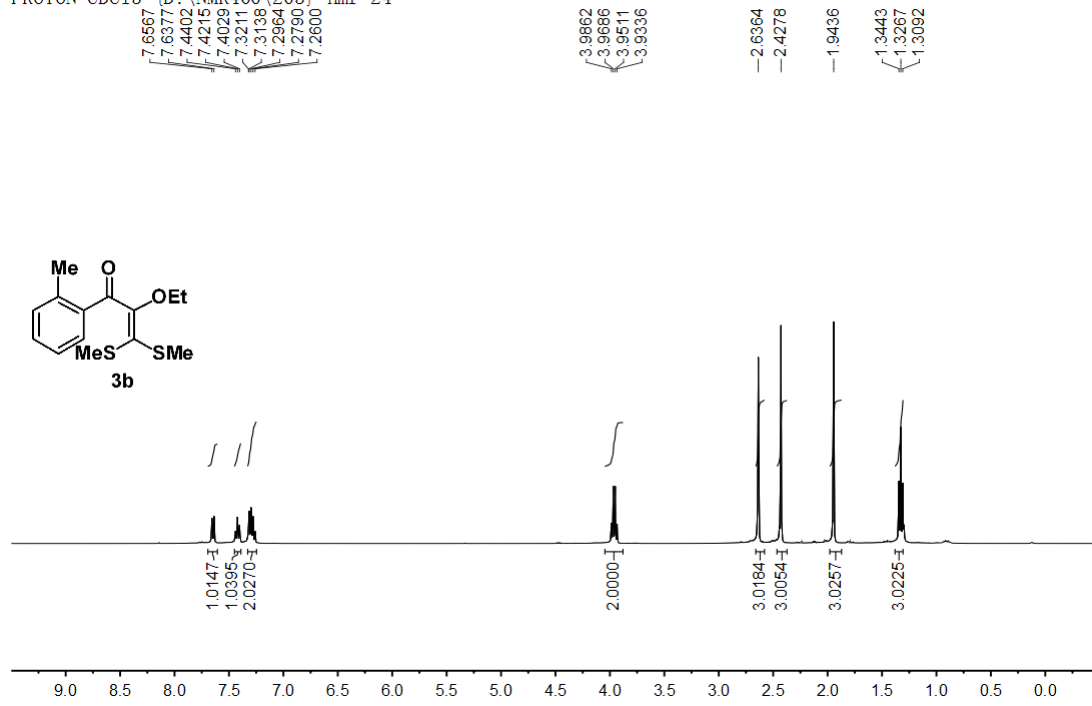
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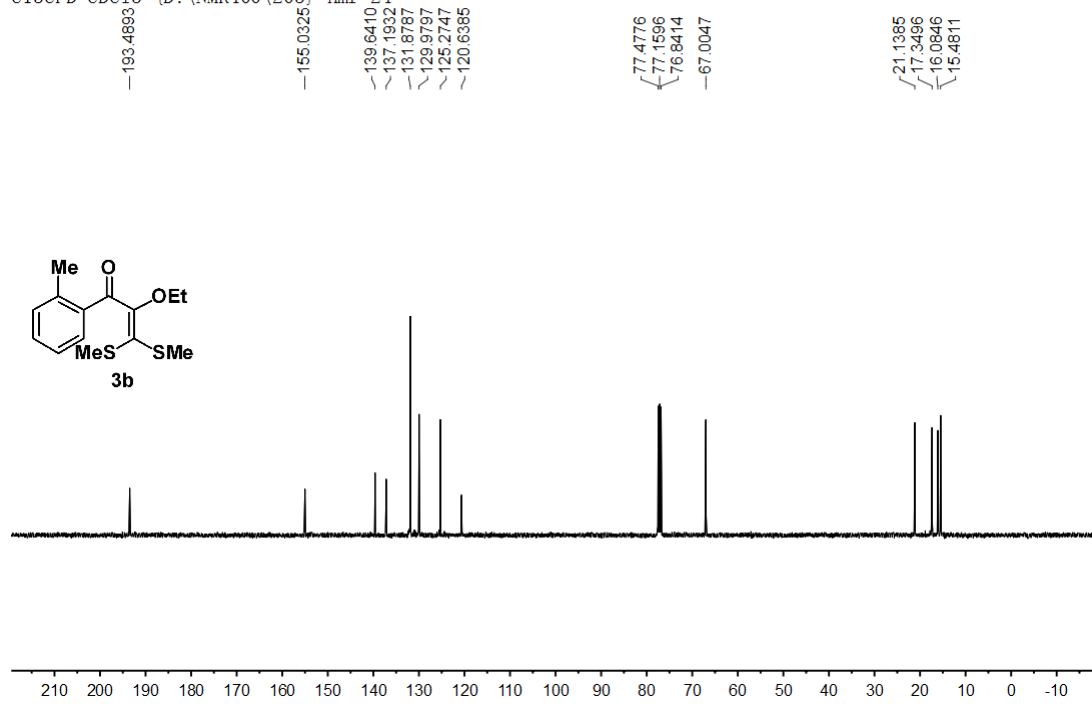
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lzq-758

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LZQ-394

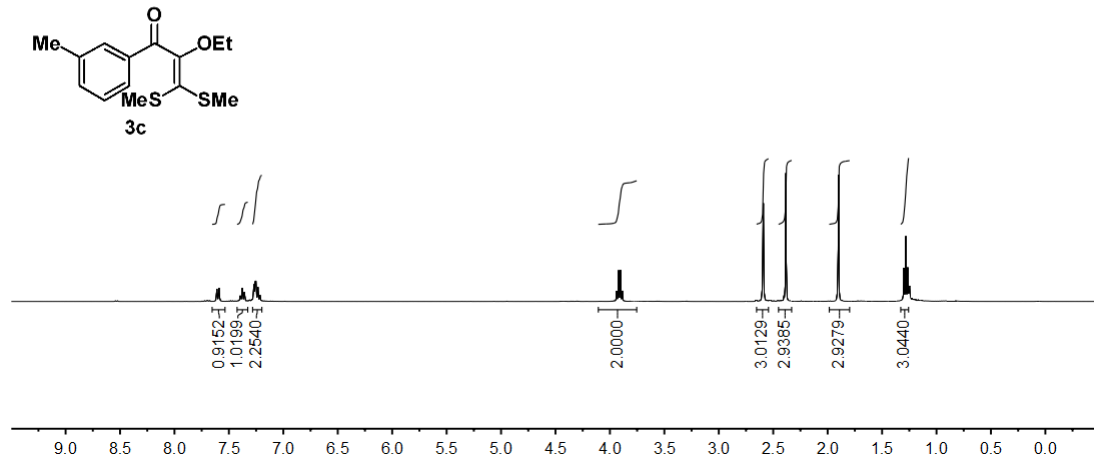
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7.6099  
7.5911  
7.3961  
7.3774  
7.3689  
7.2894  
7.2598  
7.2515  
7.2330  
7.2141

3.9383  
3.9207  
3.9032  
3.8857

2.5906  
2.3831  
1.8996

1.2890  
1.2815  
1.2639



LZQ-394

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193.5816

155.1258

139.7580

137.2480

131.9579

130.0647

125.3439

120.6282

77.4780

77.1601

76.8423

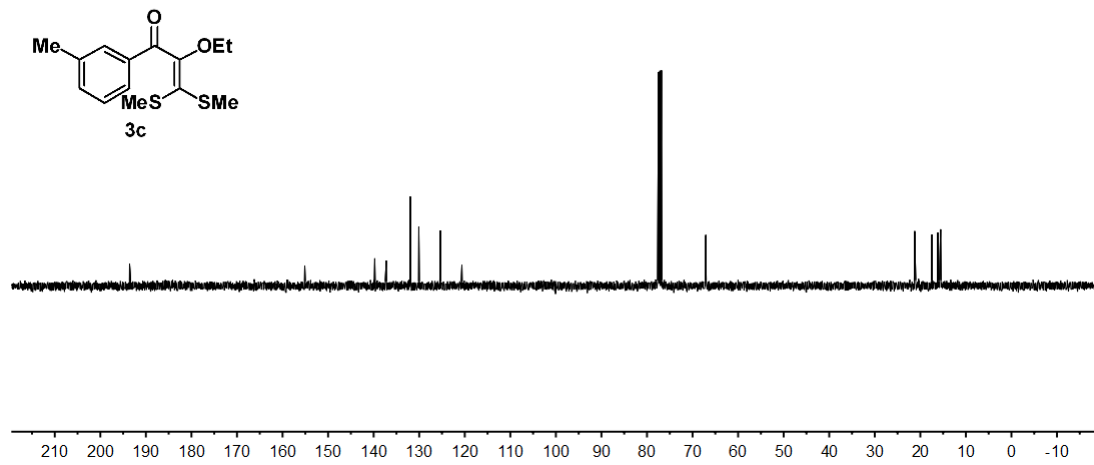
67.0884

21.2290

17.4319

16.1567

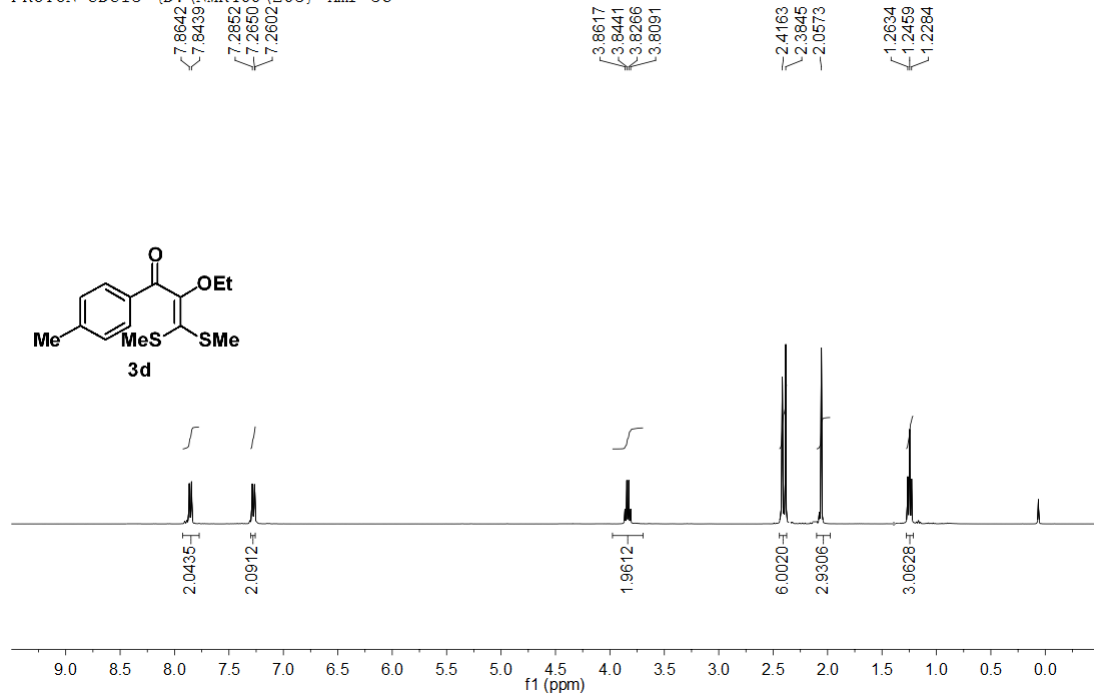
15.5538





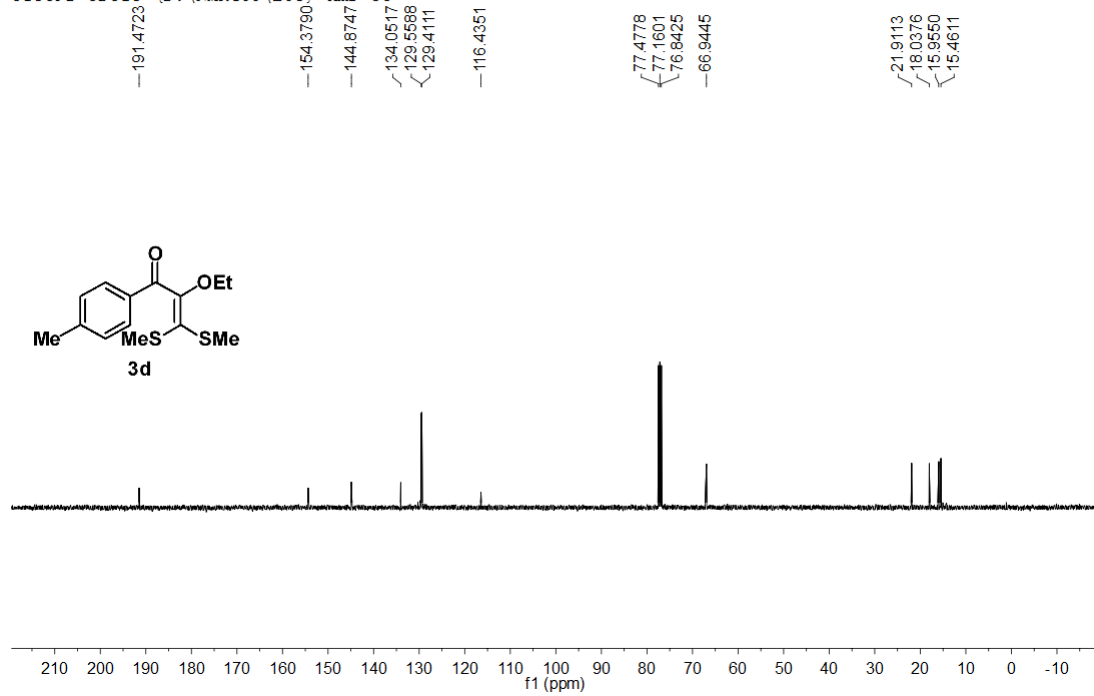
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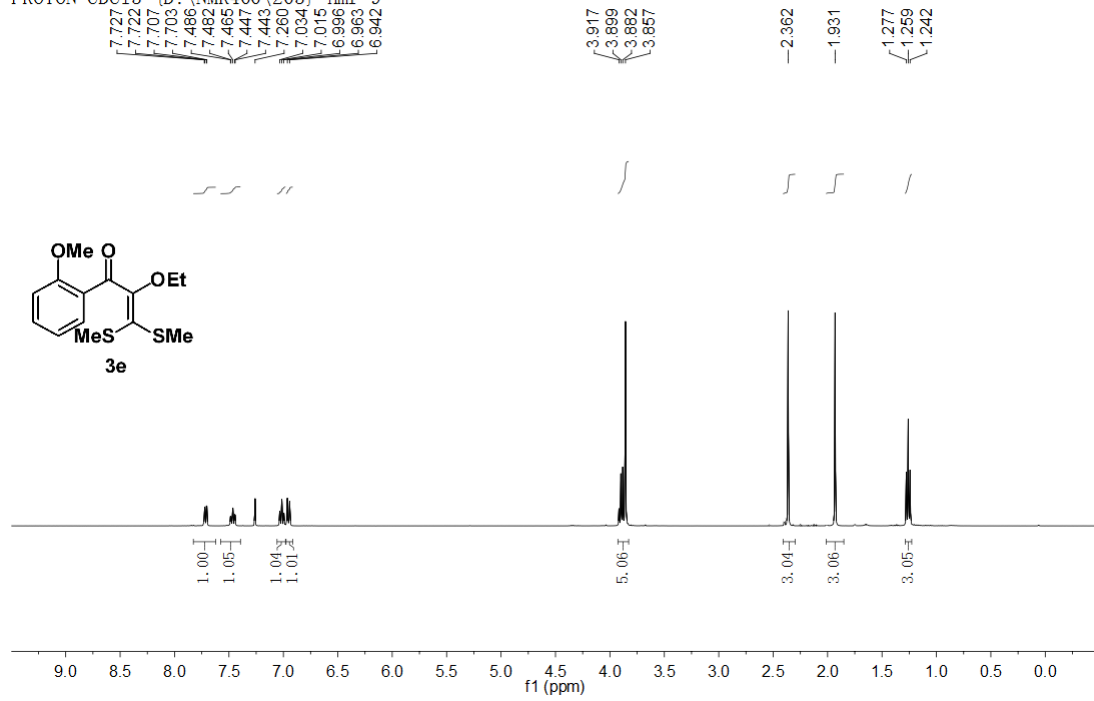
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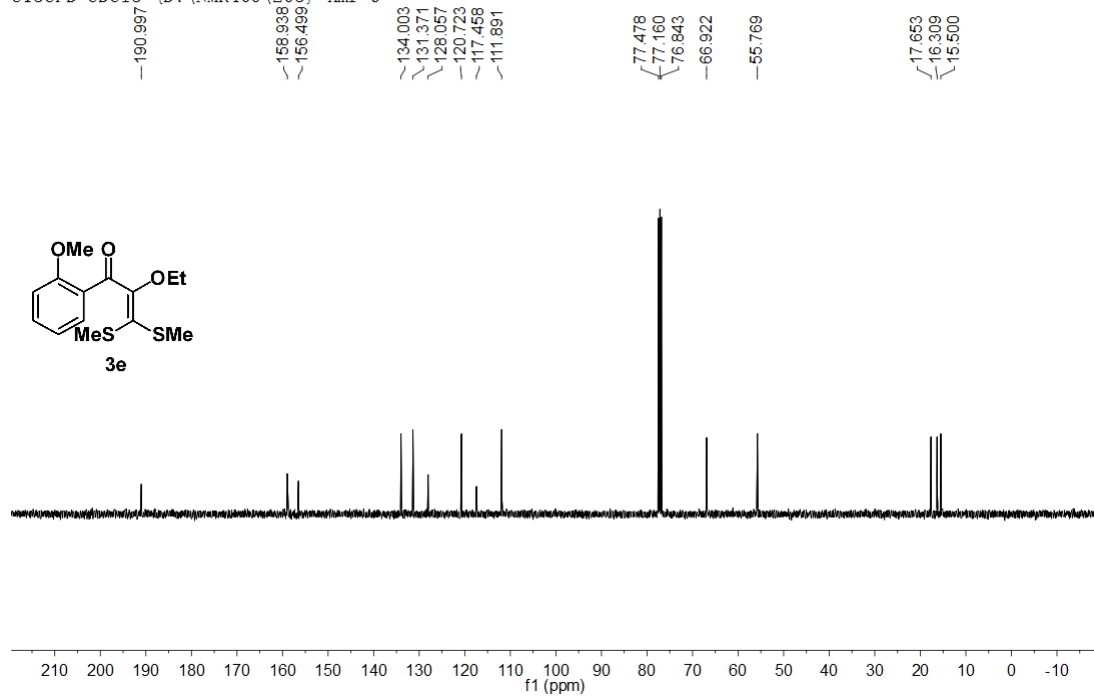
LZQ-414

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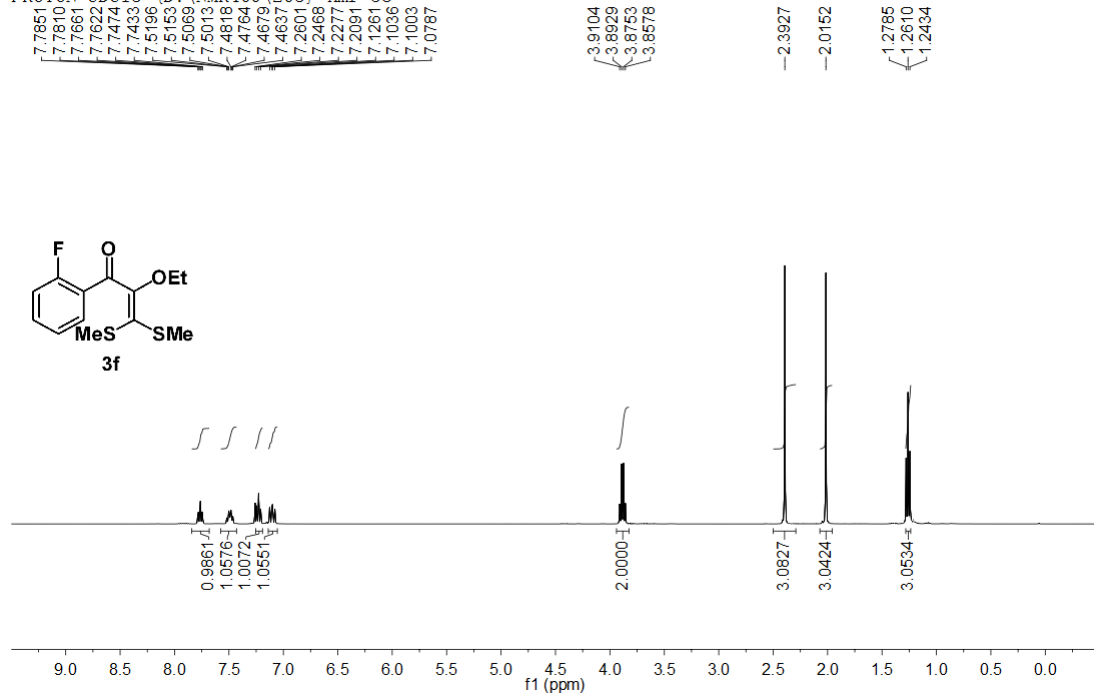
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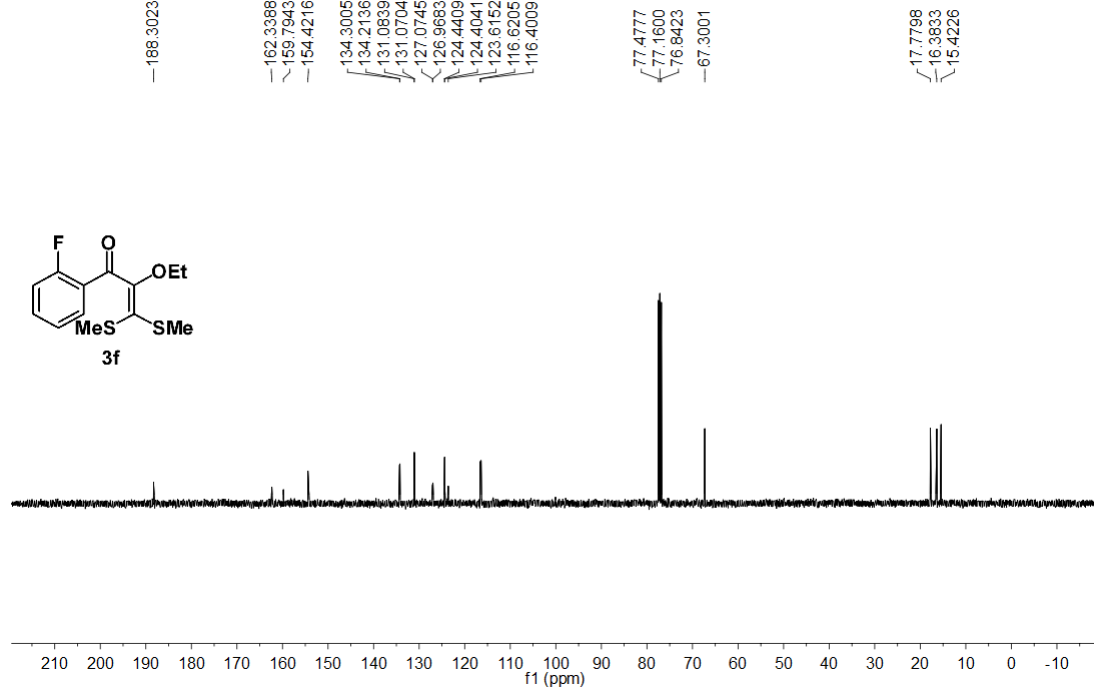
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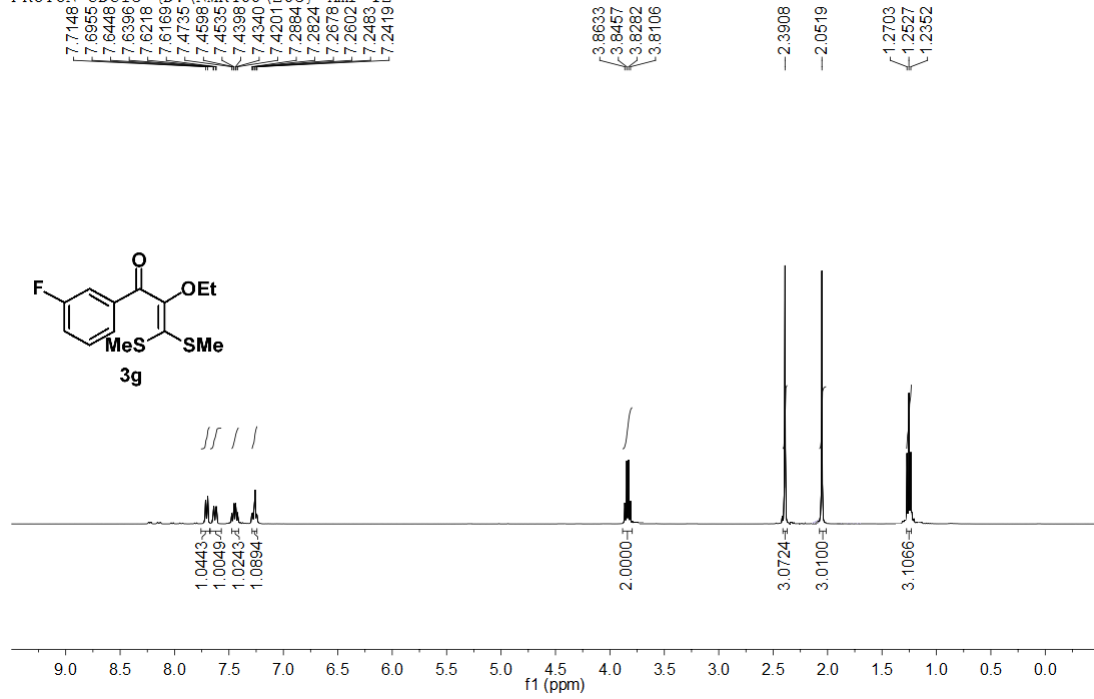
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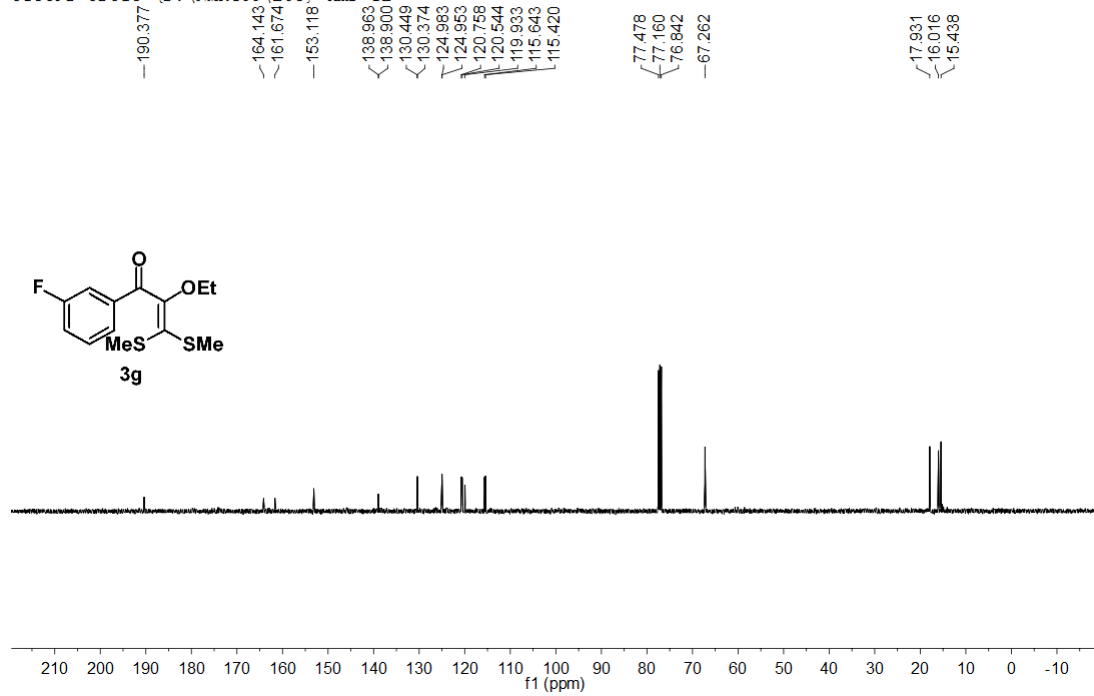
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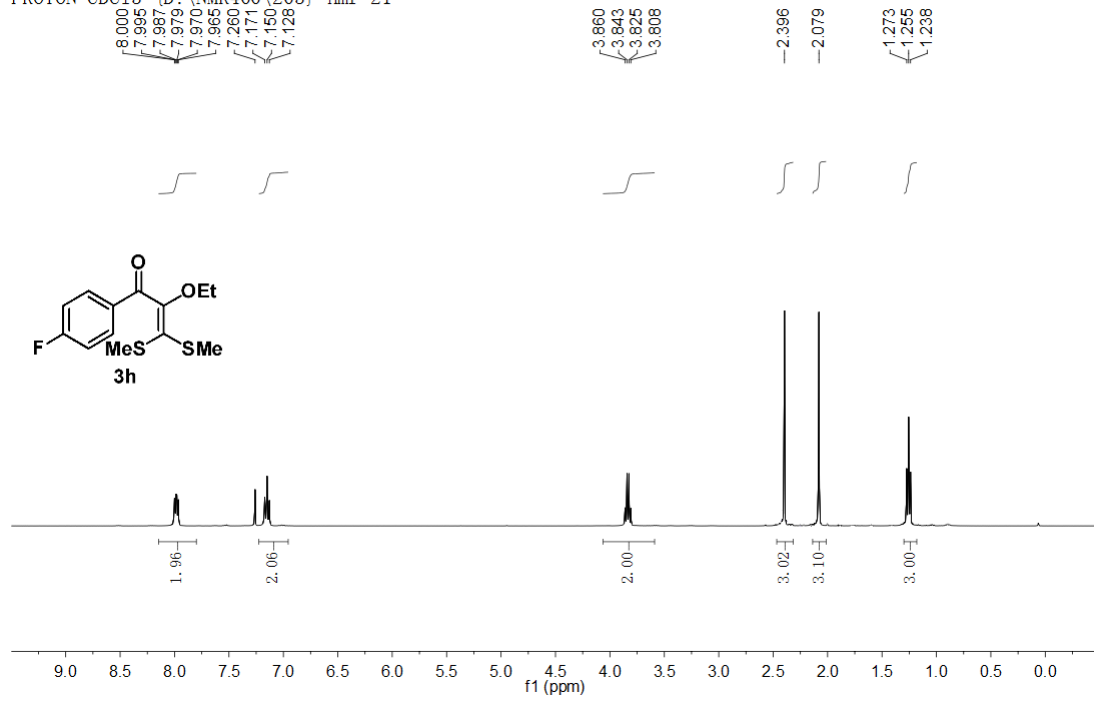
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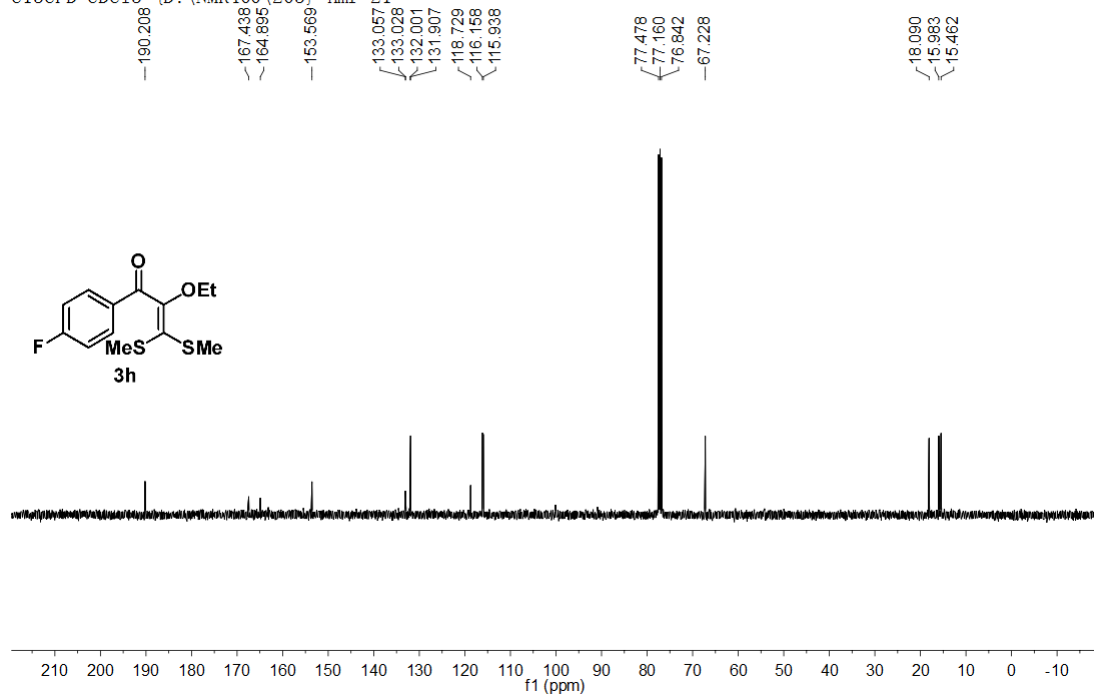
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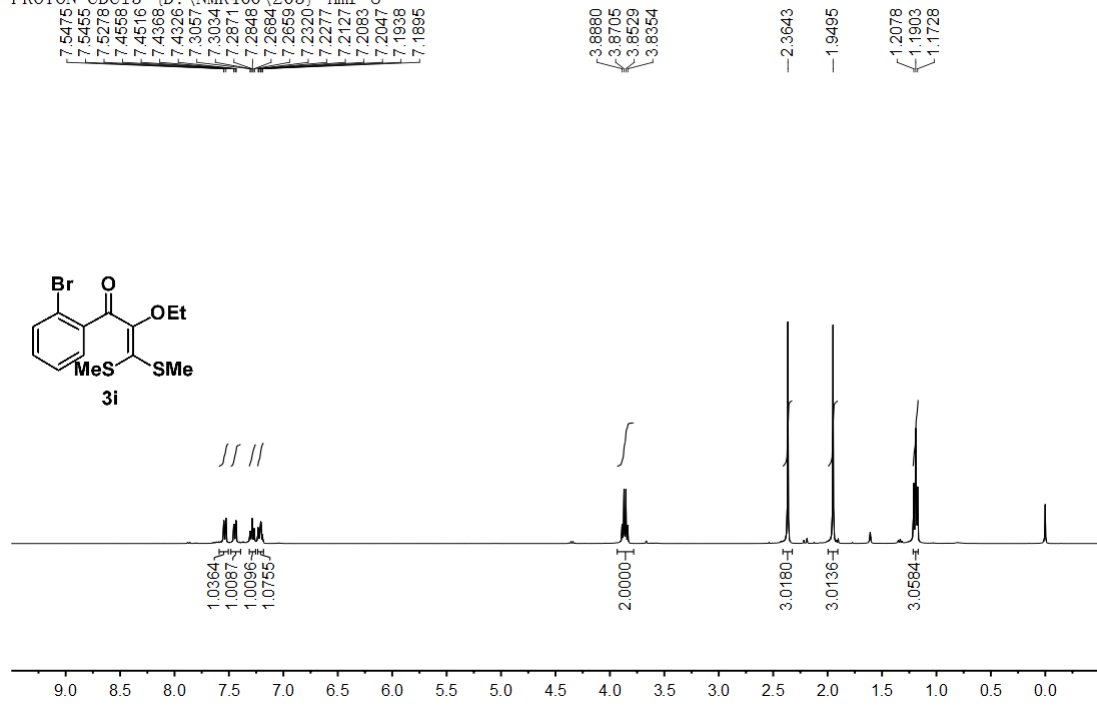
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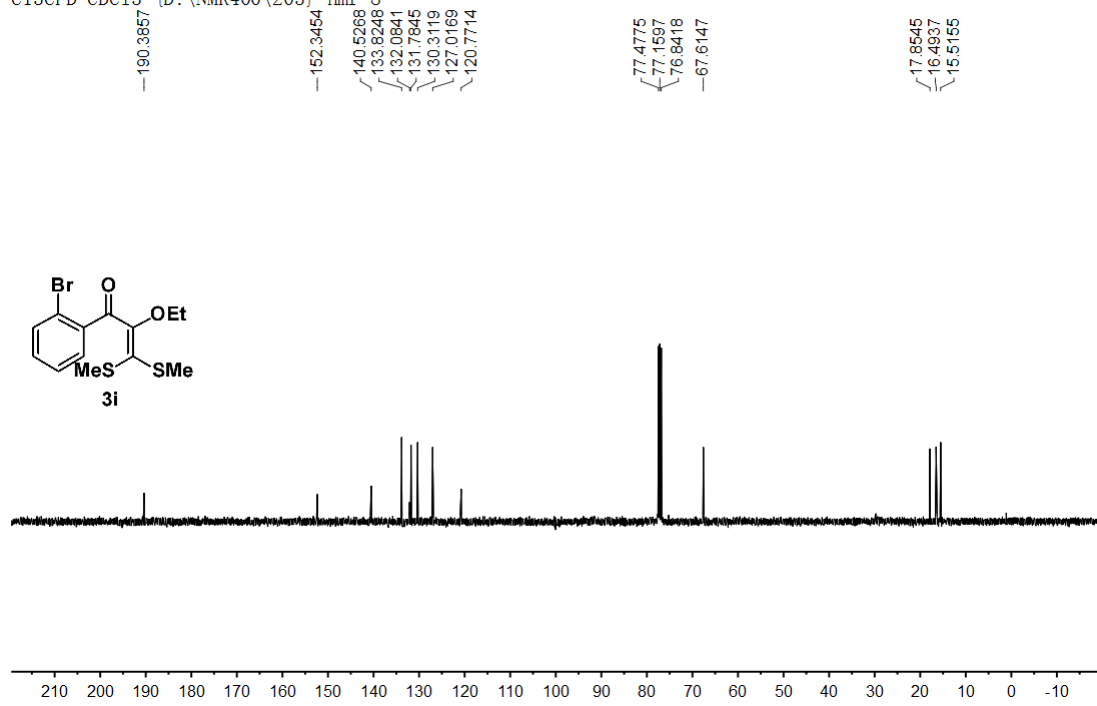
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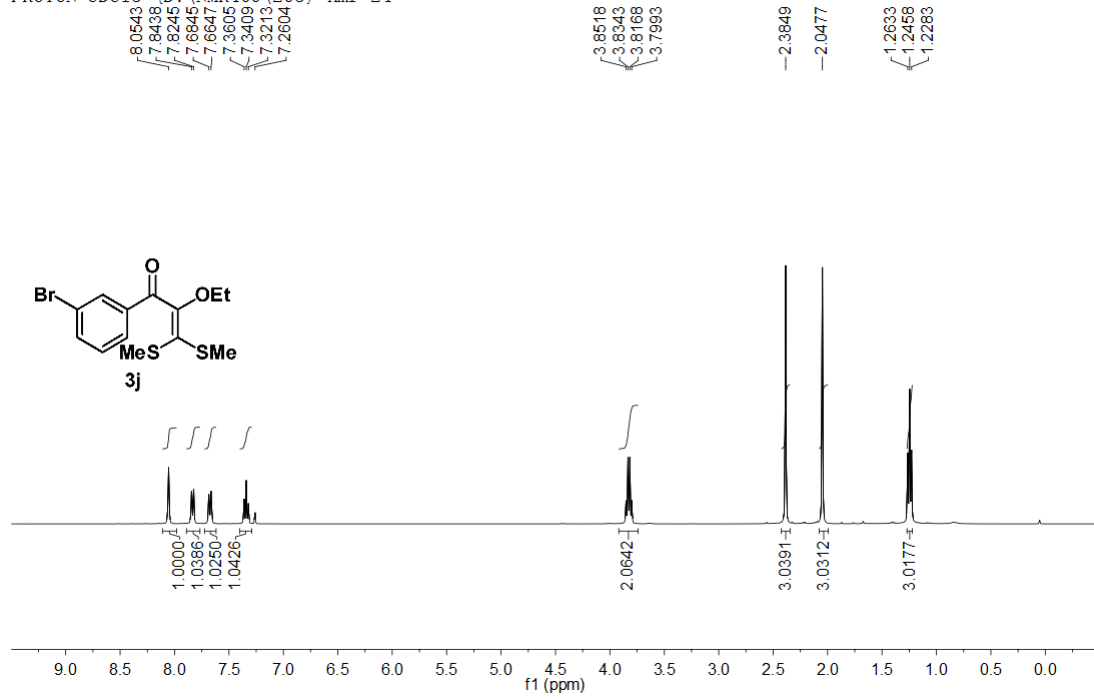
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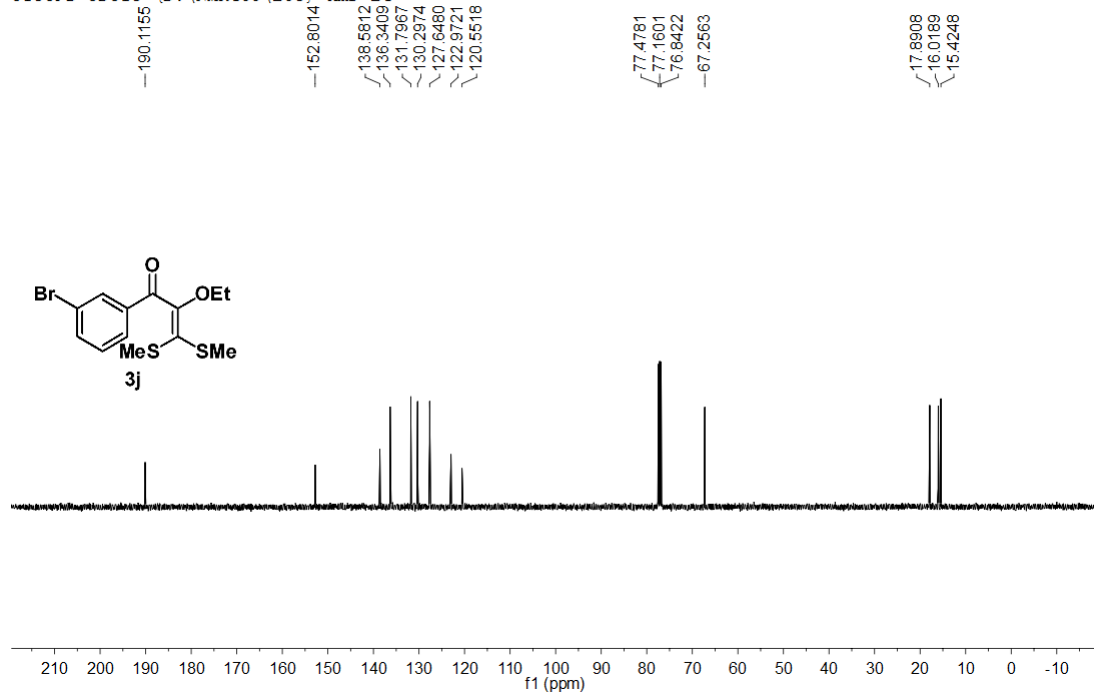
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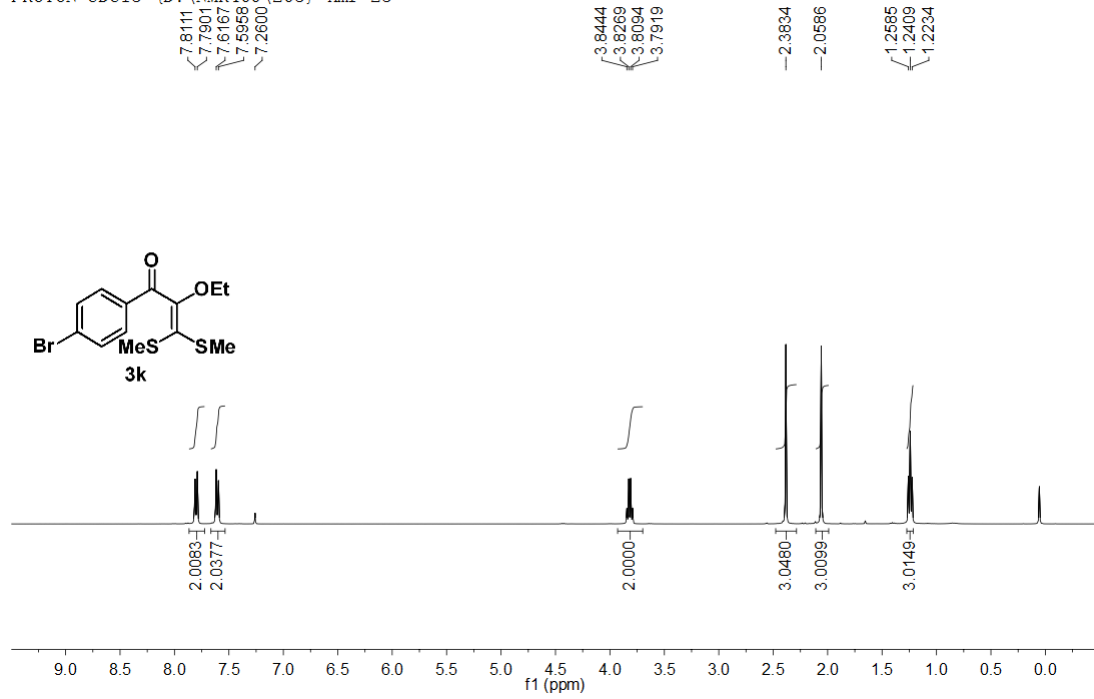
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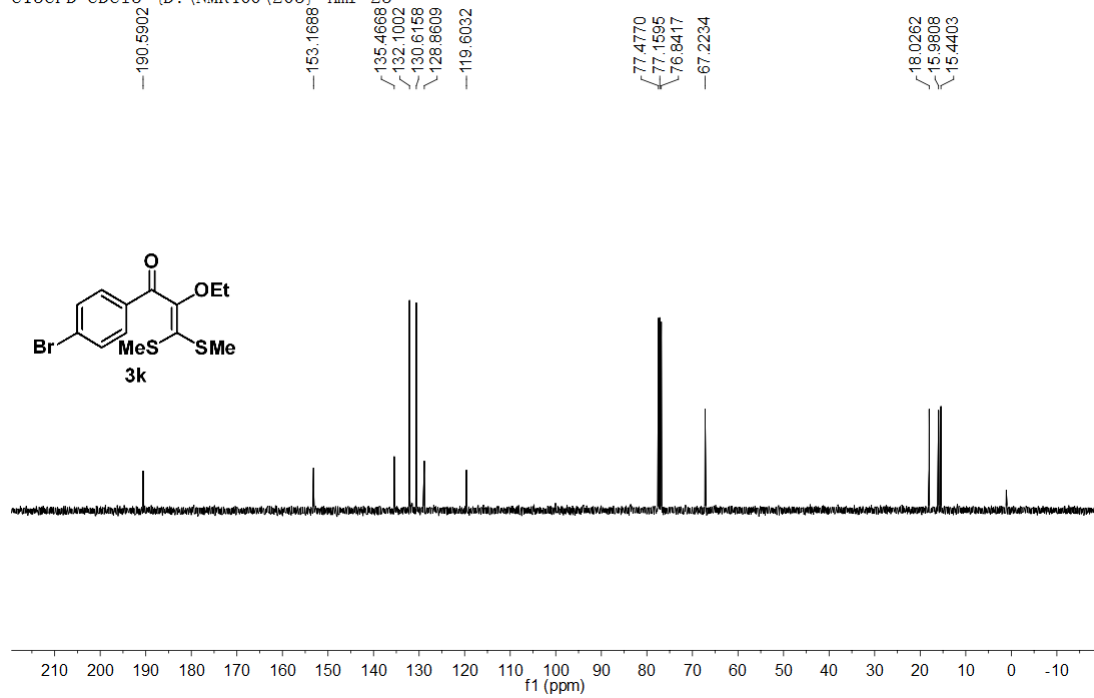
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LZQ-508

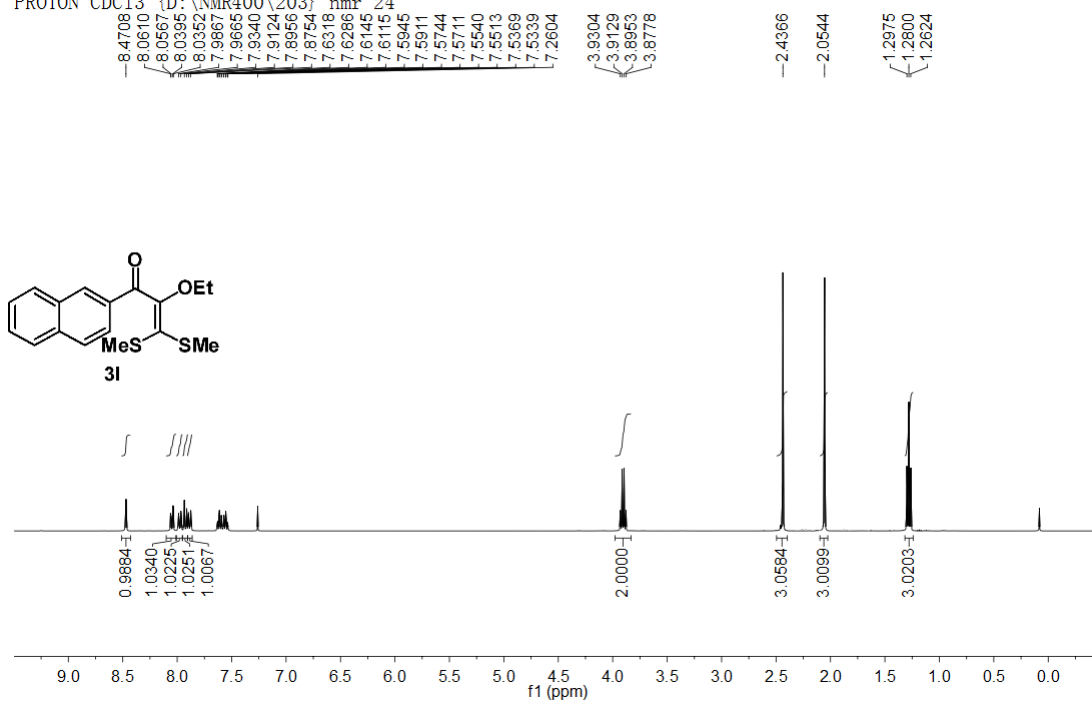
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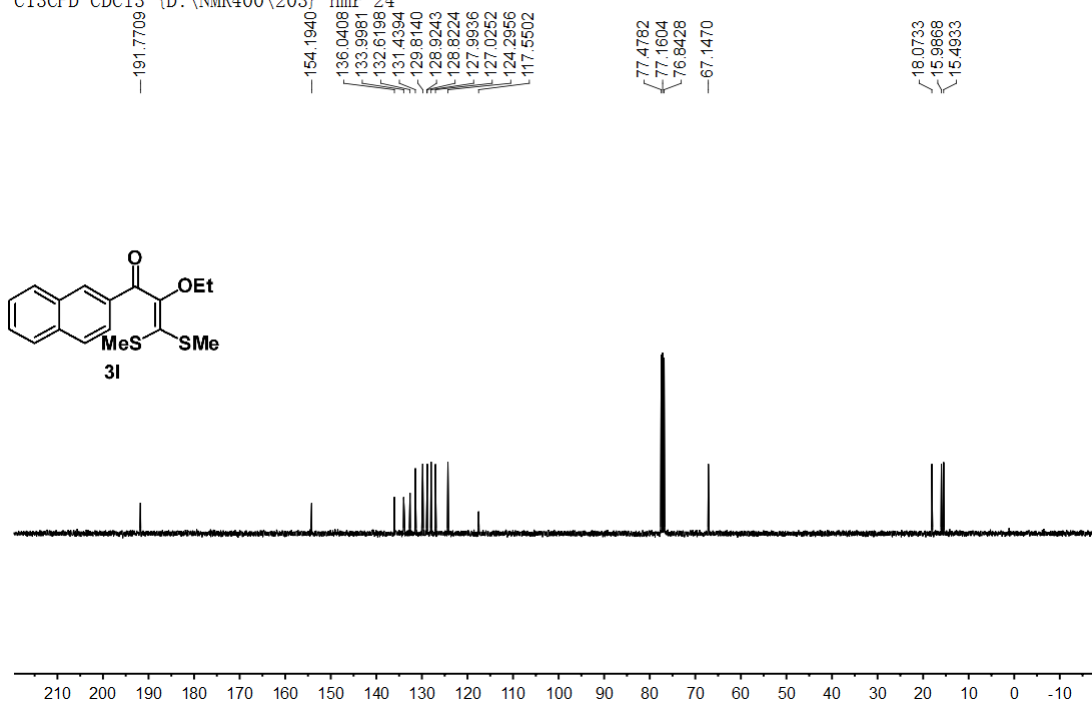
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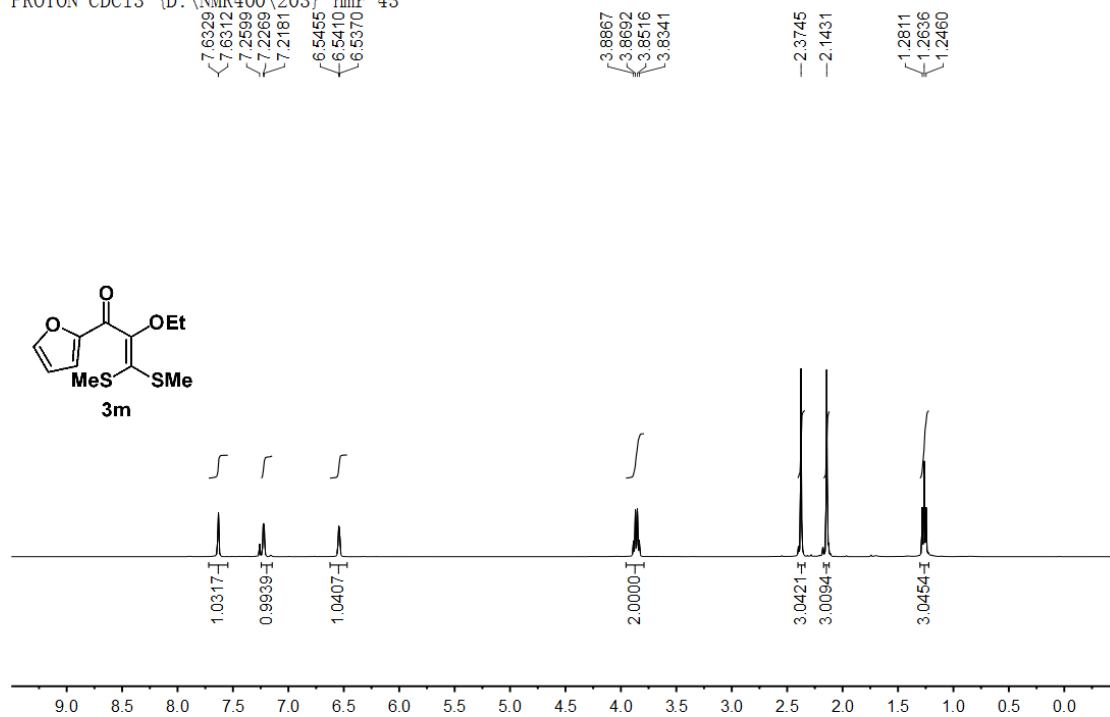
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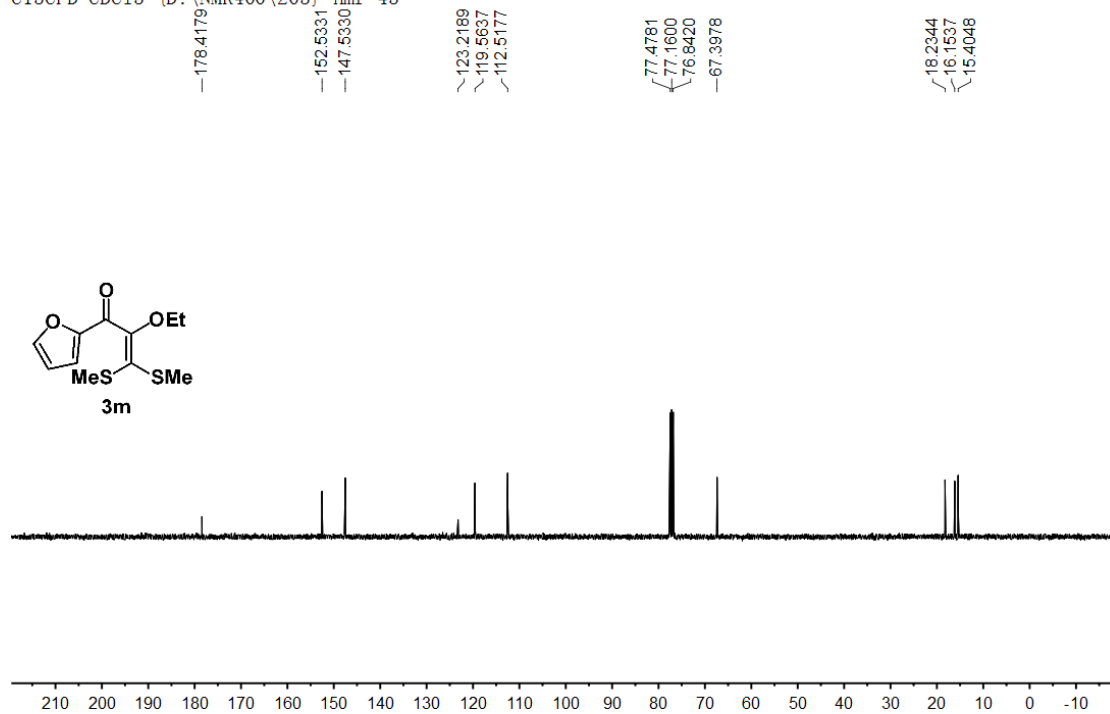
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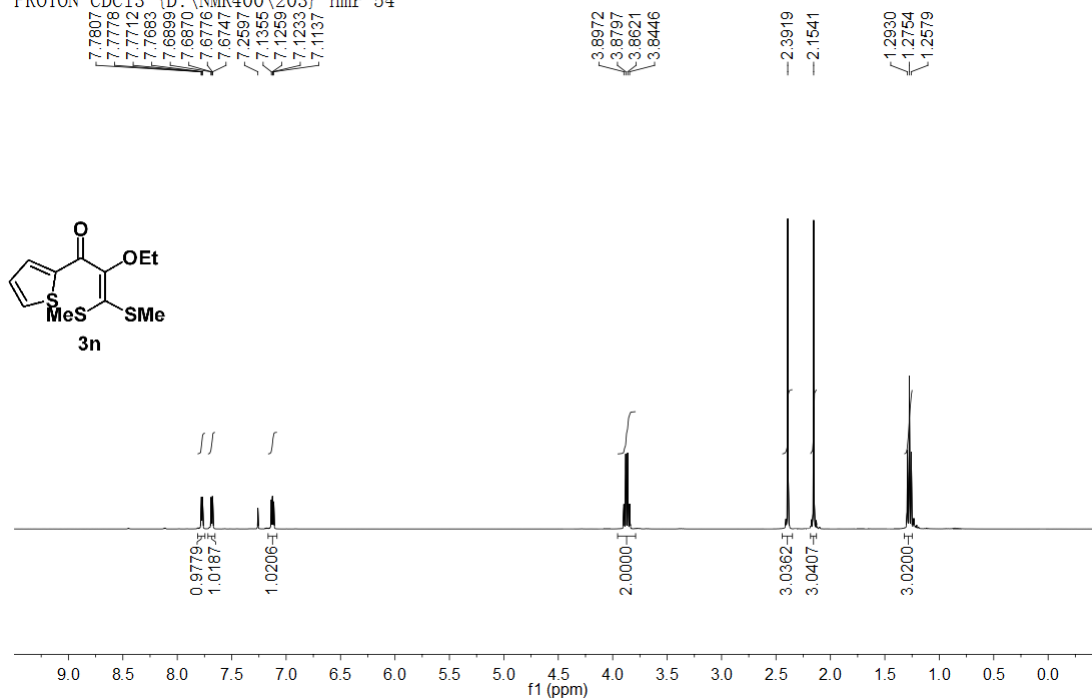
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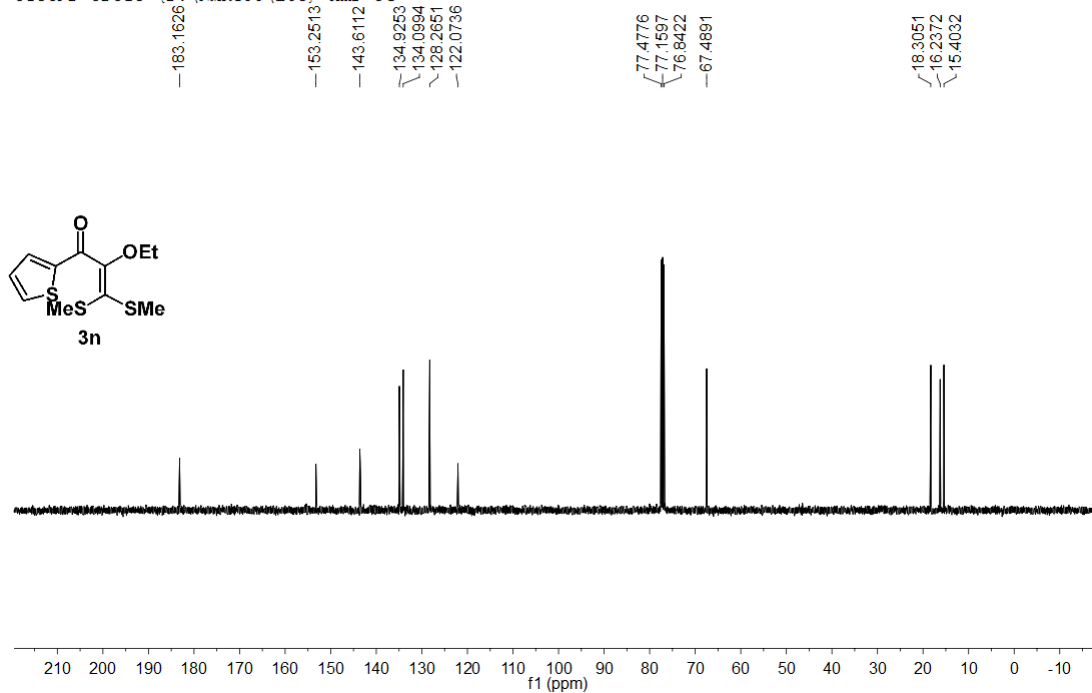
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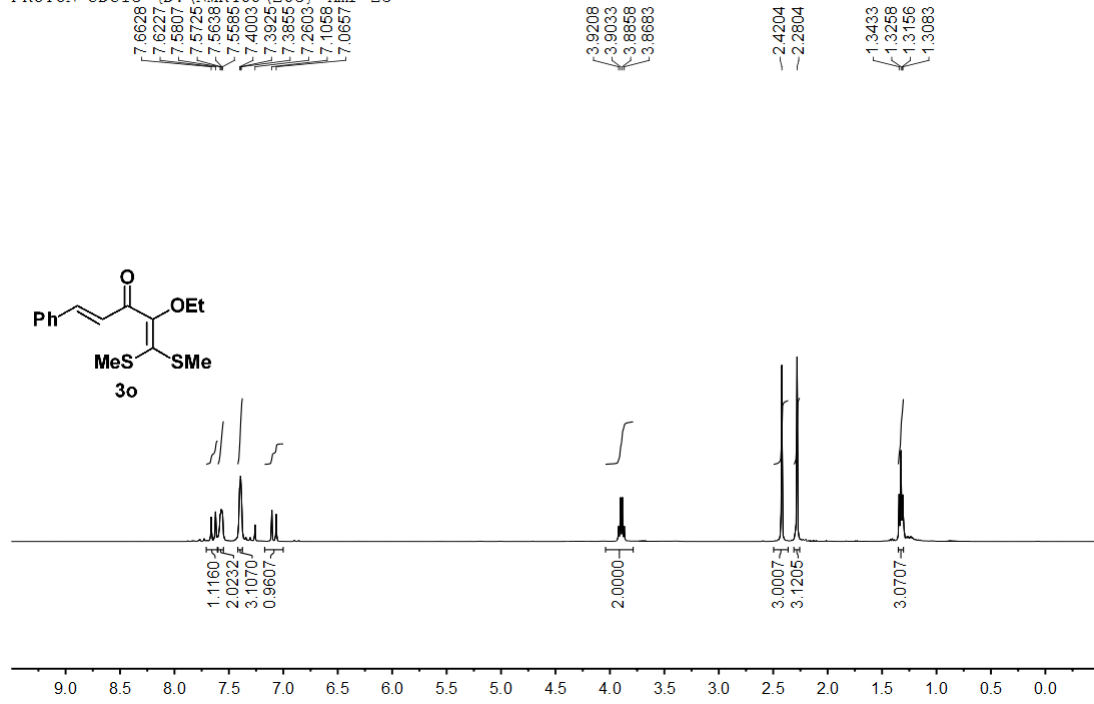
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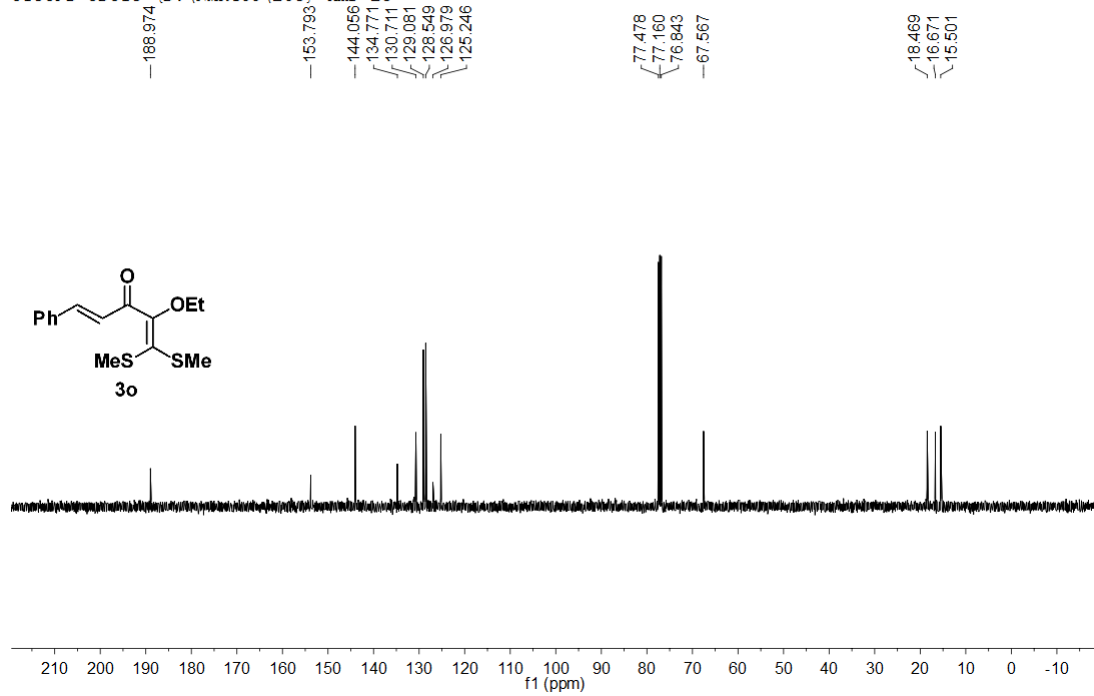
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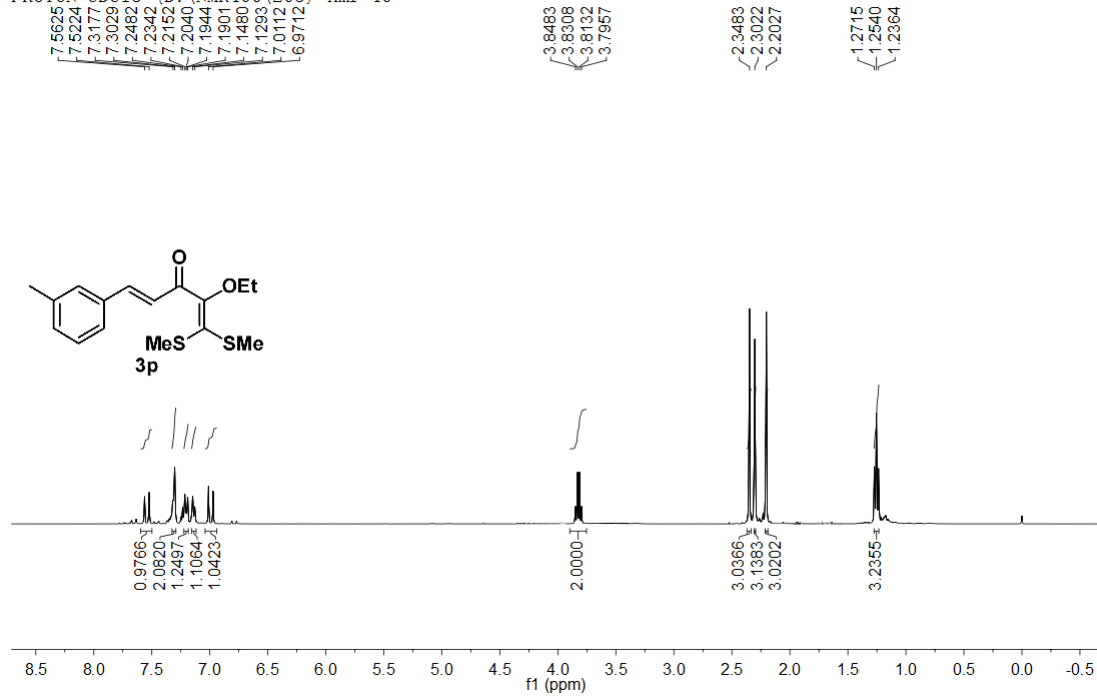
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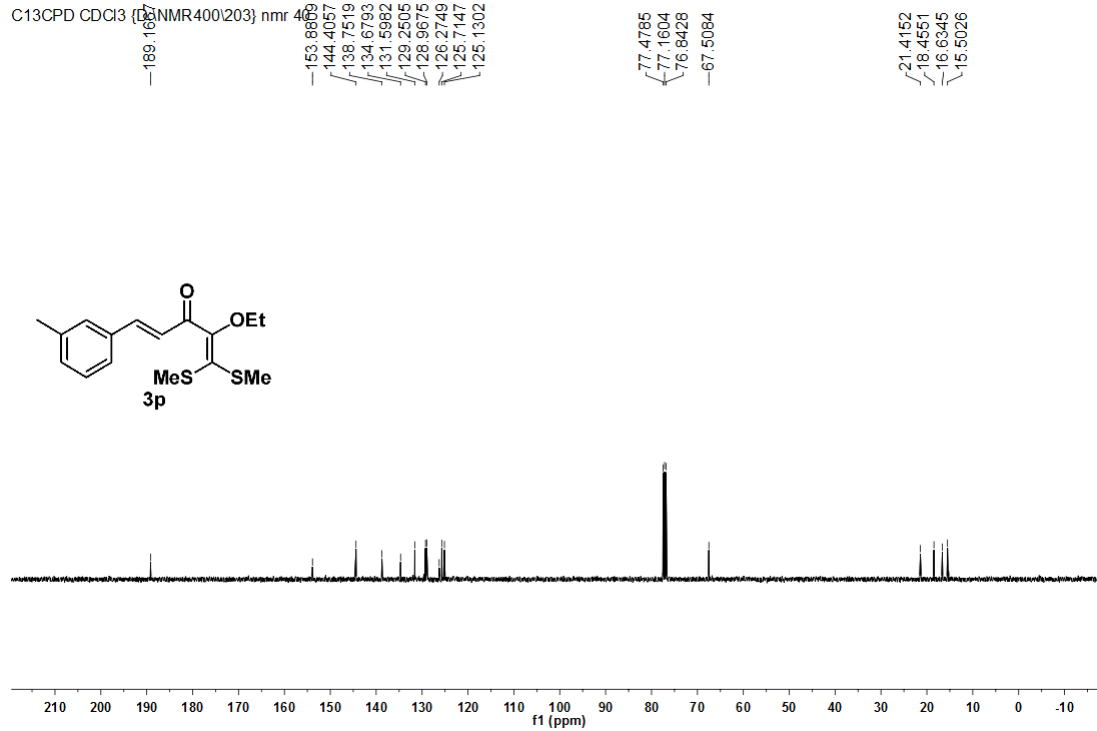
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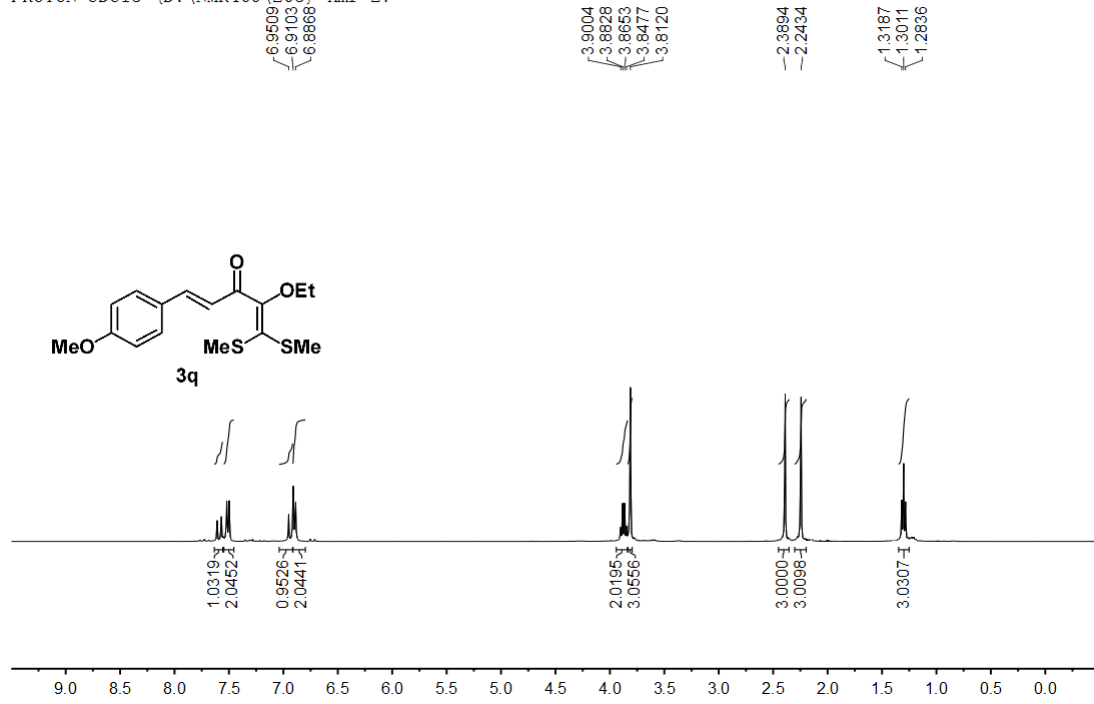
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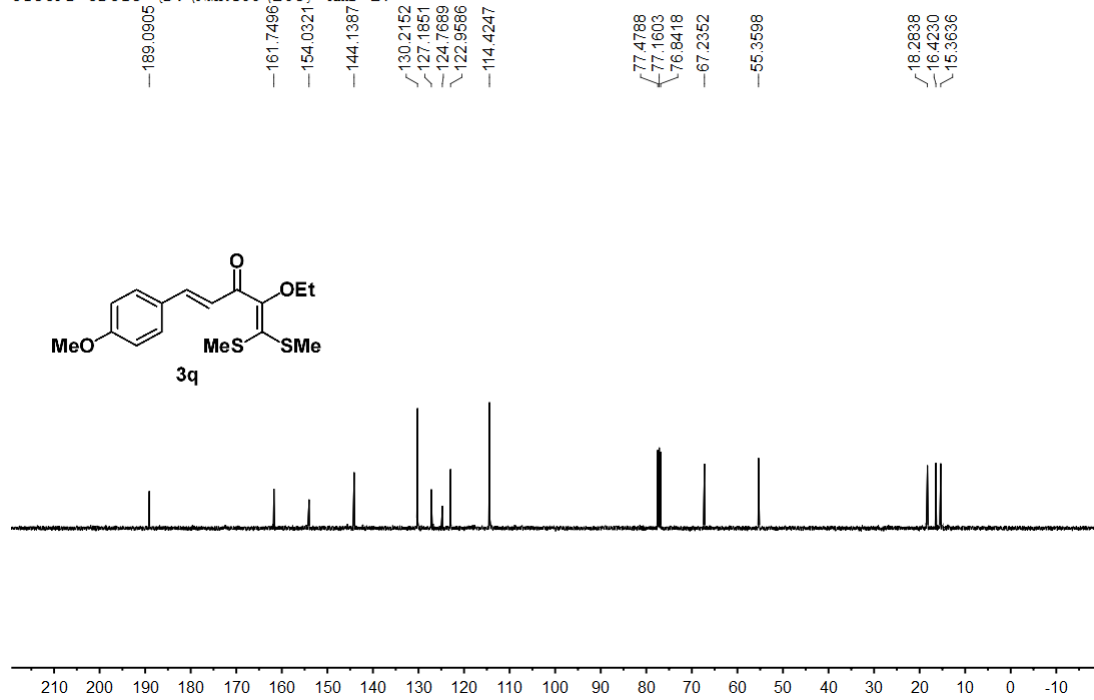
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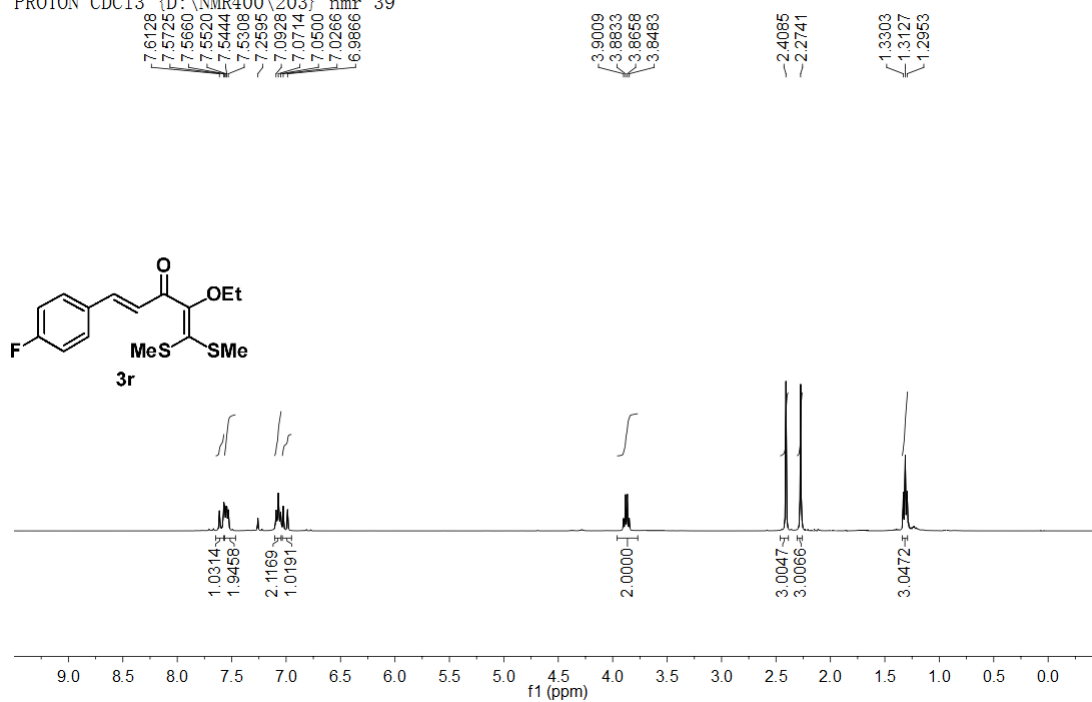
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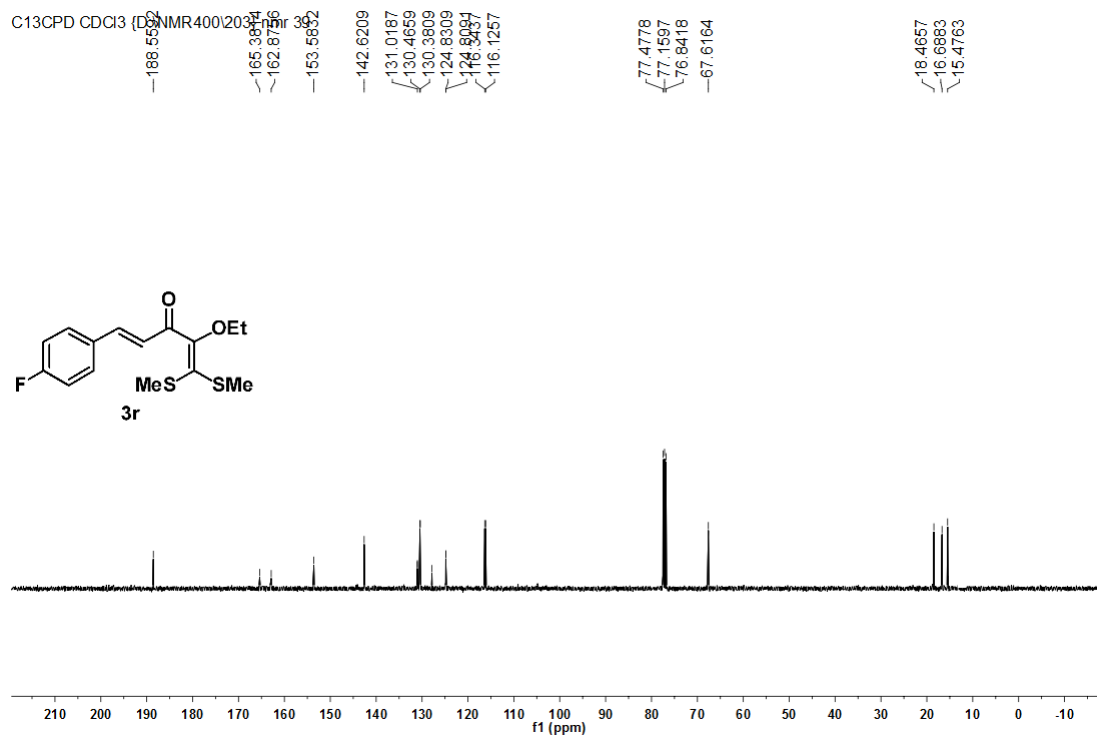
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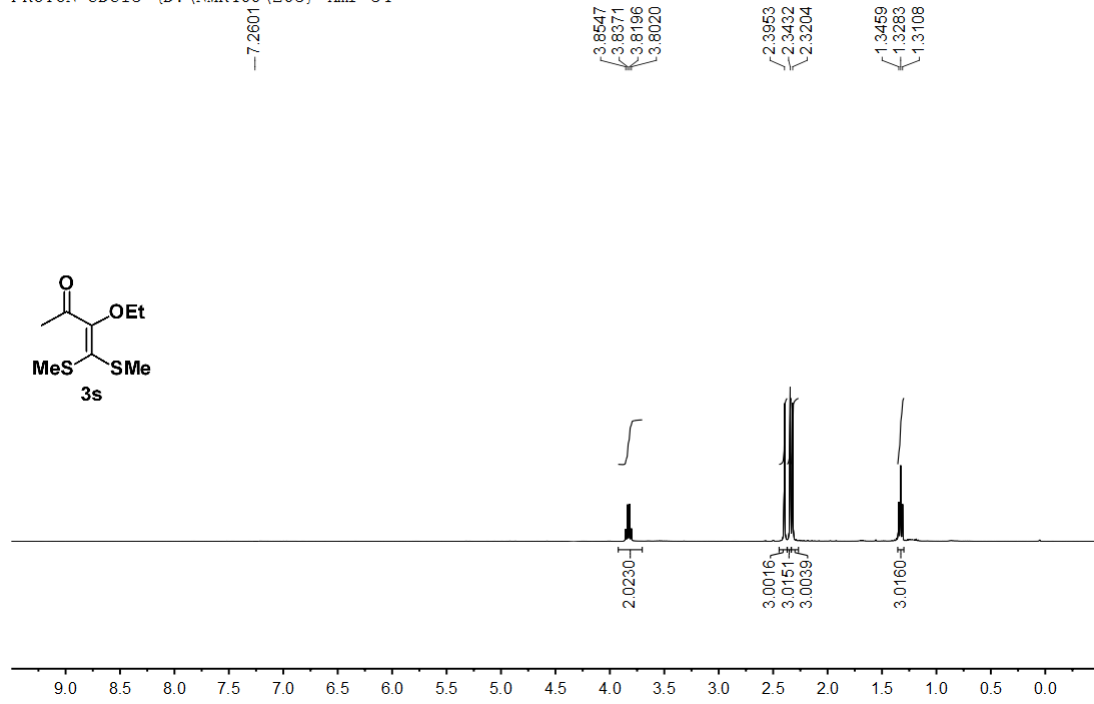
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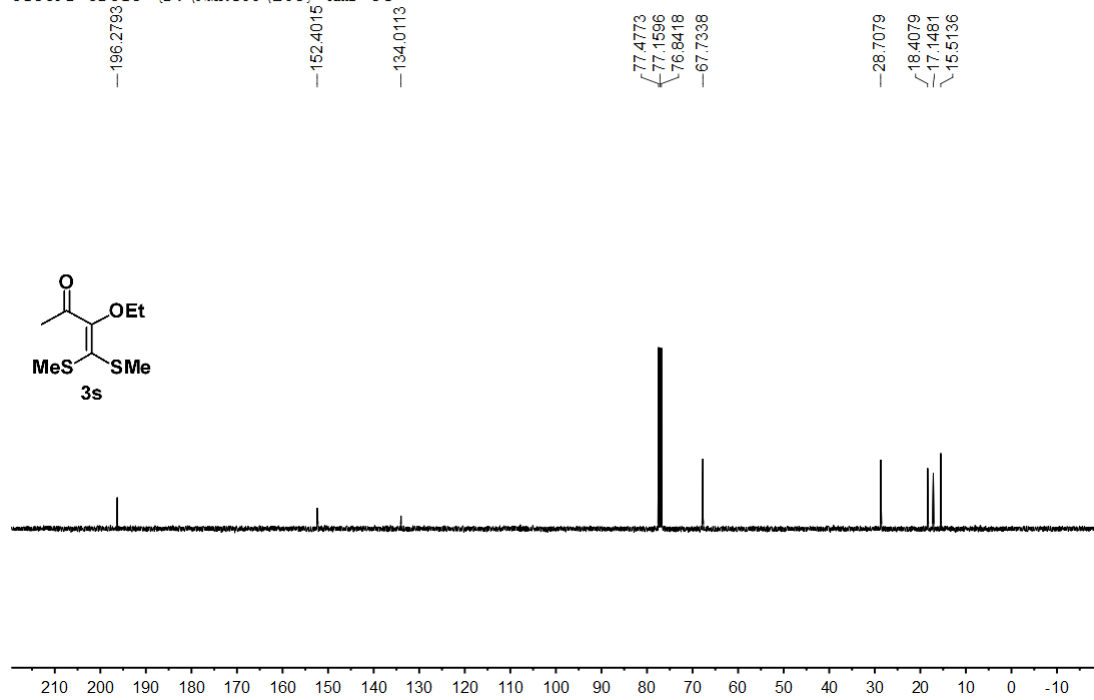
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LZQB-805

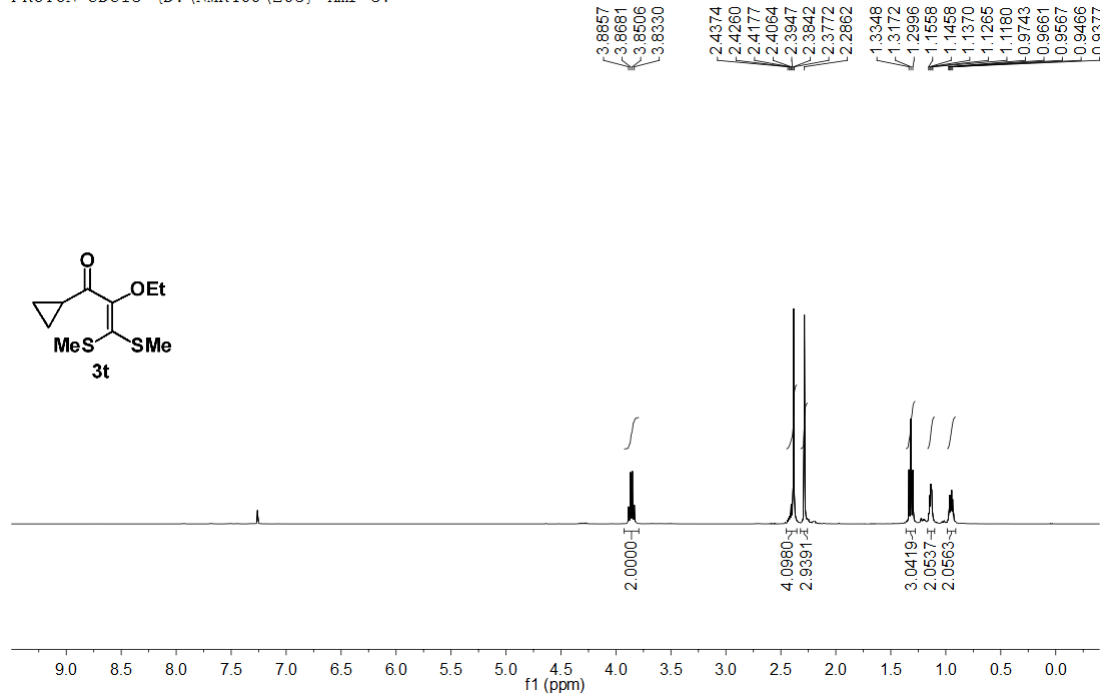
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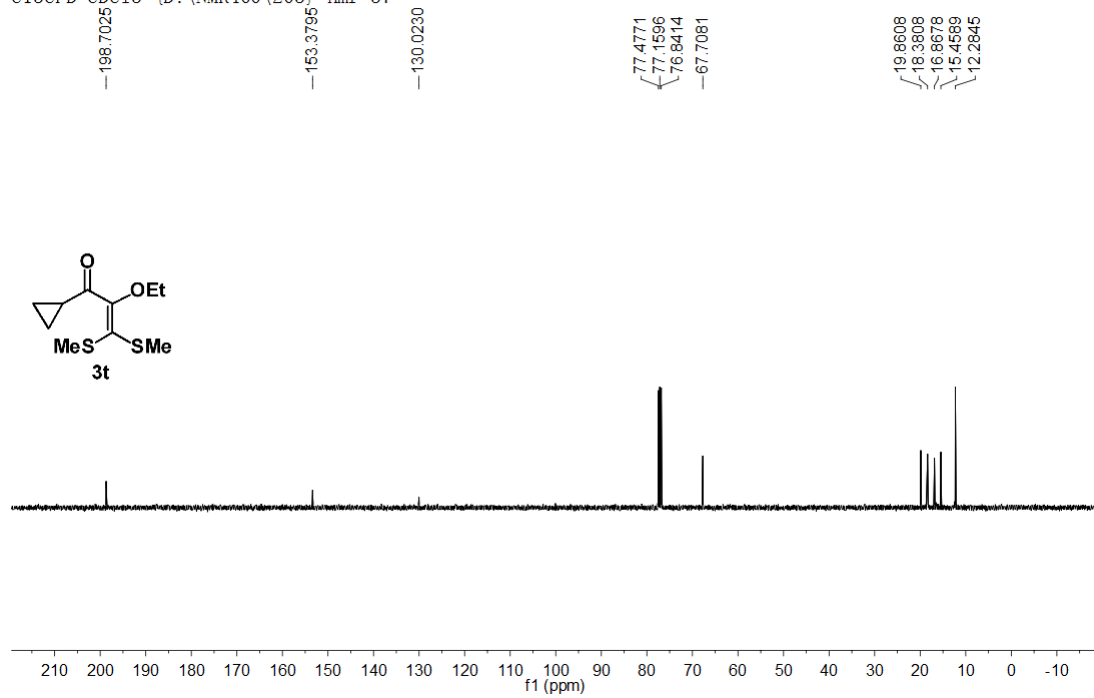
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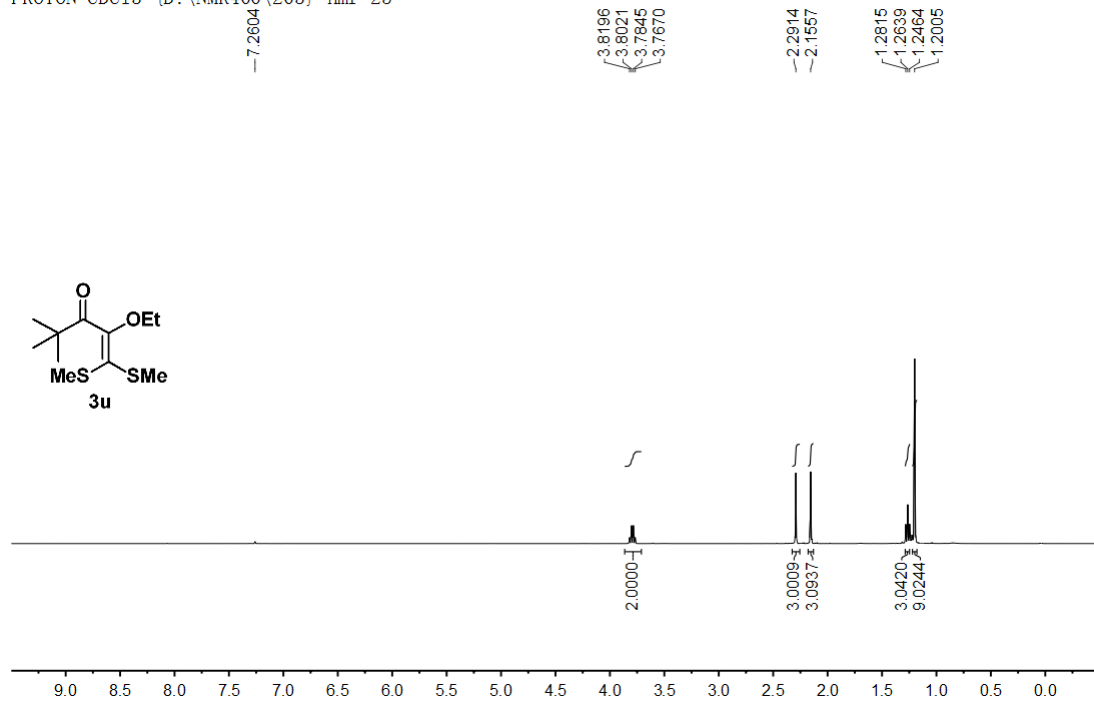
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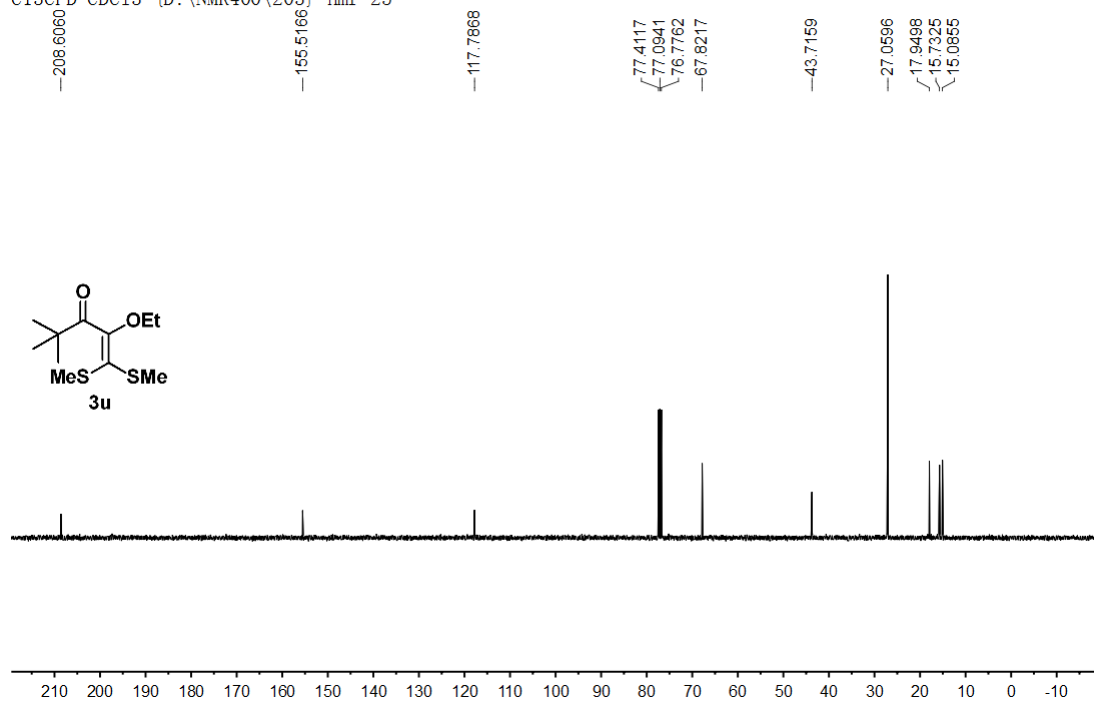
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PROTON CDC13 {D:\NMR400\203} nmr 25



lzq-757

C13CPD CDC13 {D:\NMR400\203} nmr 25

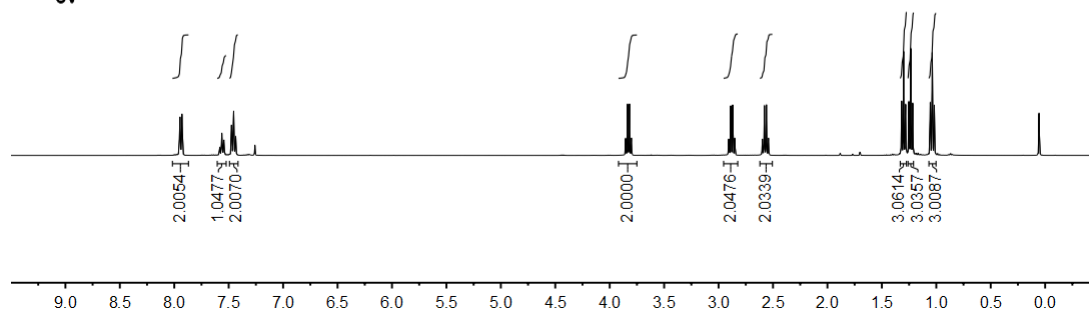
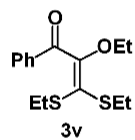


LZQ-426

PROTON CDC13 {D:\NMR400\203} nmr 11

7.9482  
7.9300  
7.9271  
7.5616  
7.5633  
7.5449  
7.4739  
7.4544  
7.4358  
7.2596

3.8539  
3.8364  
3.8189  
3.8013  
2.9065  
2.8882  
2.8699  
2.8515  
2.5976  
2.5791  
2.5606  
2.5421  
1.3185  
1.3002  
1.2819  
1.2518  
1.2343  
1.2167  
1.0553  
1.0368  
1.0182



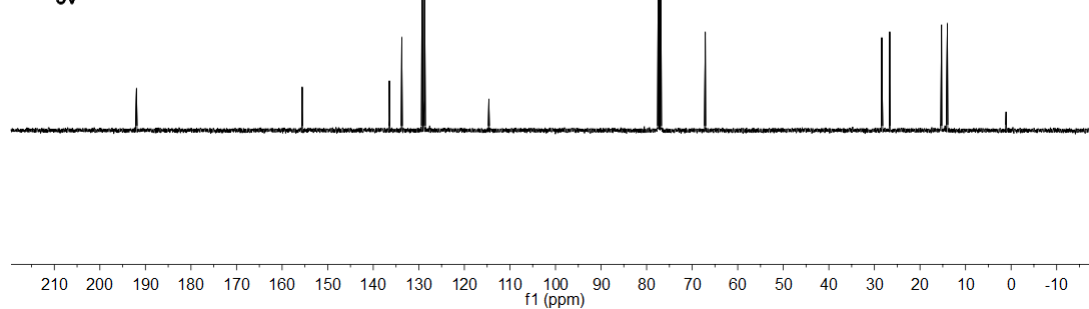
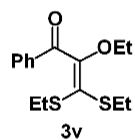
LZQ-426

C13CPD CDC13 {D:\NMR400\203} nmr 11

191.9635  
155.6066  
136.4550  
133.7338  
129.2889  
128.7567  
114.6193

77.4775  
77.4598  
76.8416  
67.1247

28.3824  
26.6625  
15.3886  
15.2780  
13.9898

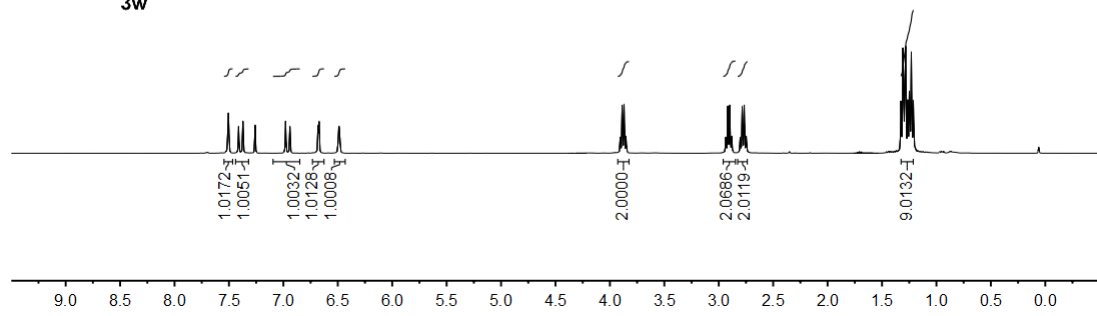
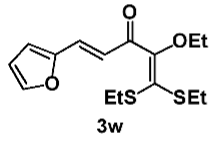


LZQ-438

PROTON CDC13 {D:\NMR400\203} nmr 39

7.5046  
7.4114  
7.3722  
7.2596  
6.9796  
6.9403  
6.6807  
6.6725  
6.4903  
6.4868  
6.4827

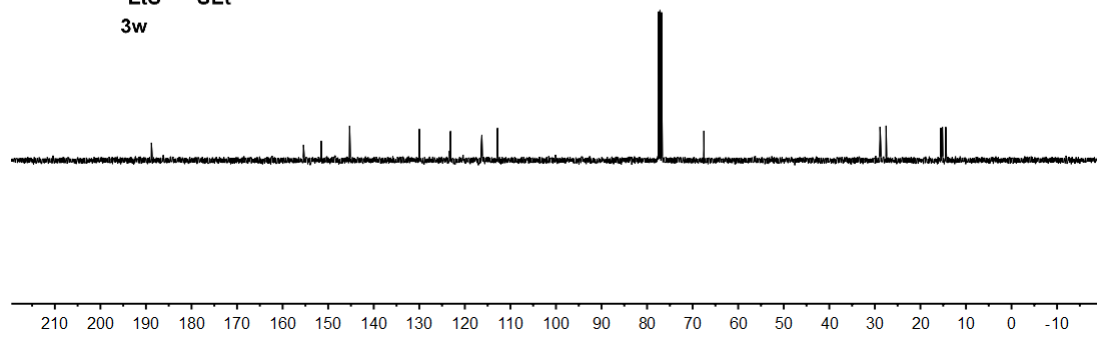
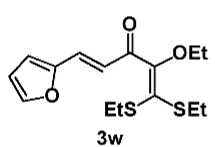
3.9050  
3.8874  
3.8699  
3.8524  
2.9353  
2.9169  
2.8986  
2.8802  
2.8629  
2.7845  
2.7660  
2.7476  
1.3257  
1.3081  
1.3016  
1.2905  
1.2829  
1.2644  
1.2490  
1.2307  
1.2123



LZQ-438

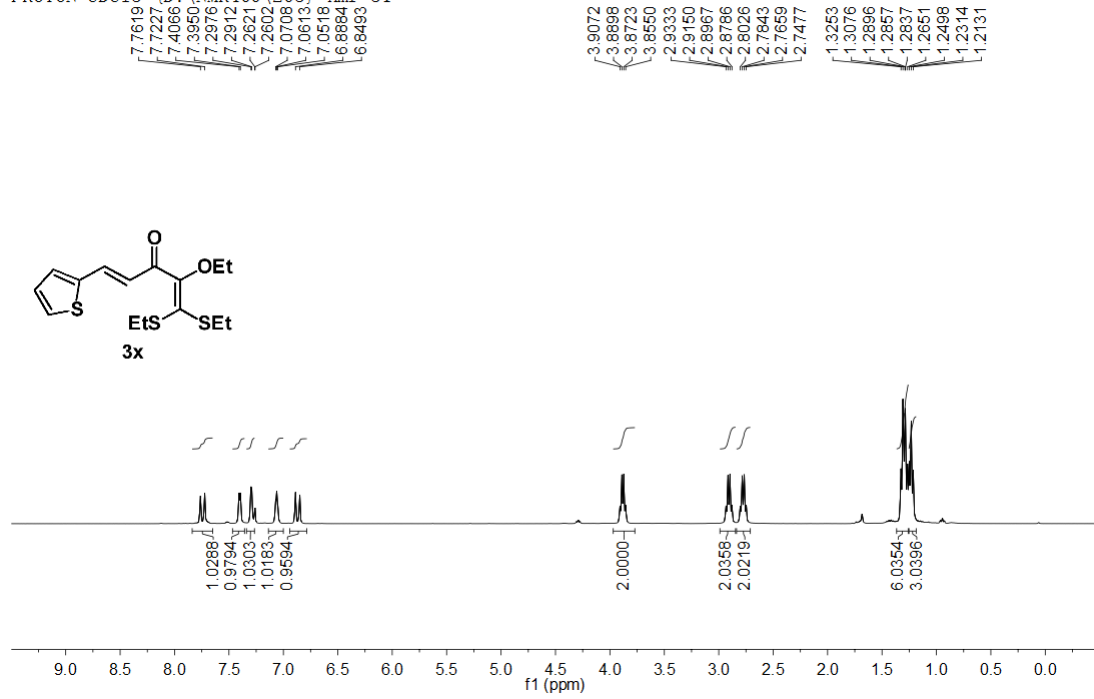
C13CPD CDC13 {D:\NMR400\203} nmr 39

188.7878  
155.3994  
151.5633  
145.2763  
129.9882  
123.1388  
116.2623  
112.8214  
77.4779  
77.1605  
76.8426  
67.5073  
28.8390  
27.5108  
15.5050  
15.1628  
14.4426



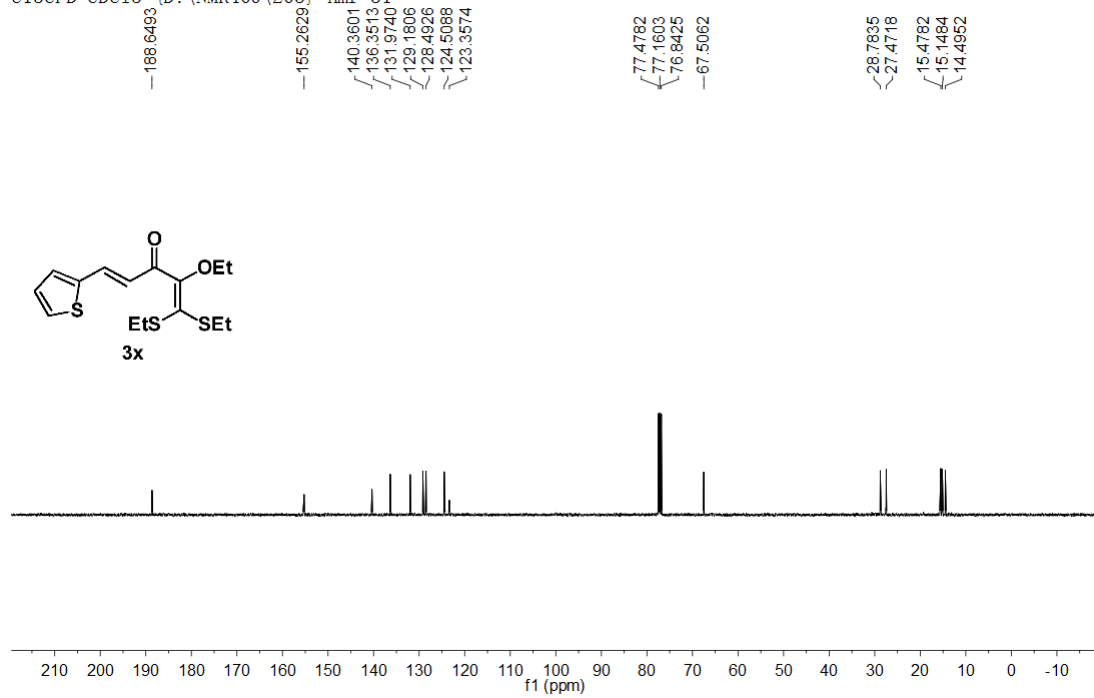
LZQ-439

PROTON CDC13 {D:\NMR400\203} nmr 31



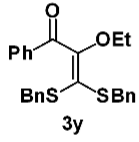
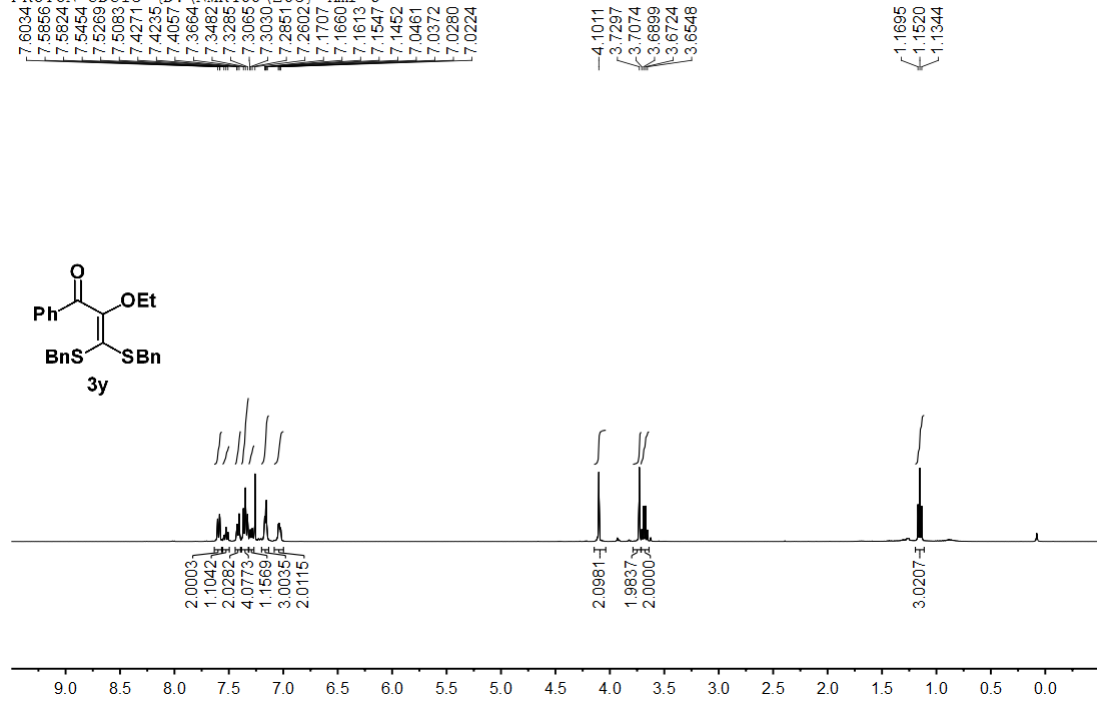
LZQ-439

C13CPD CDC13 {D:\NMR400\203} nmr 31



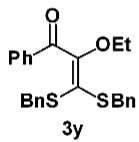
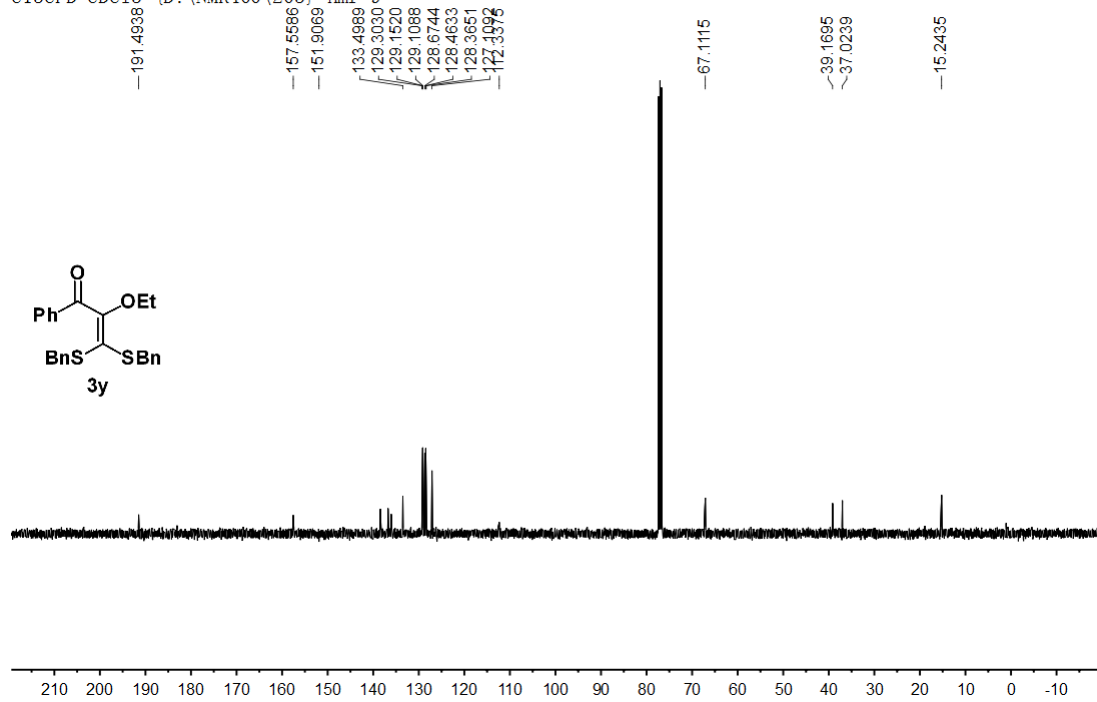
LZQ-462

PROTON CDC13 {D:\NMR400\203} nmr 9



LZQ-462

C13CPD CDC13 {D:\NMR400\203} nmr 9



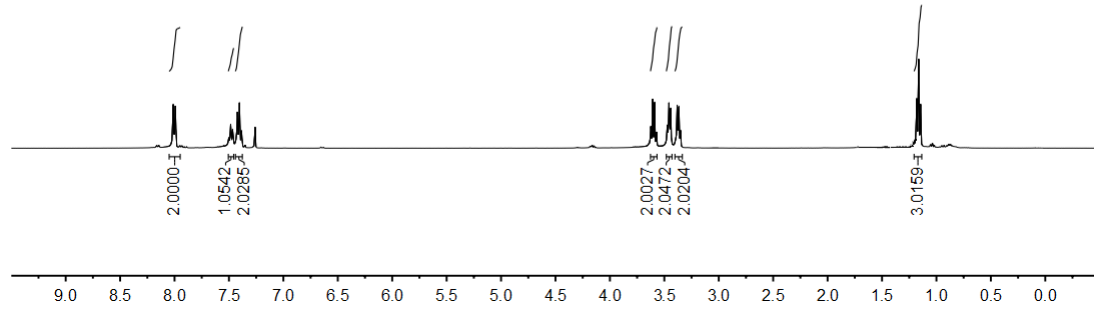
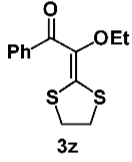
LZQ-B-2

PROTON CDC13 {D:\NMR400\203} nmr 42

8.0121  
7.9926  
7.5016  
7.4842  
7.4666  
7.4221  
7.4034  
7.3846  
7.2597

3.6241  
3.6066  
3.5890  
3.5716  
3.4717  
3.4574  
3.4409  
3.3822  
3.3658  
3.3515

1.1804  
1.1629  
1.1454



LZQ-B-2

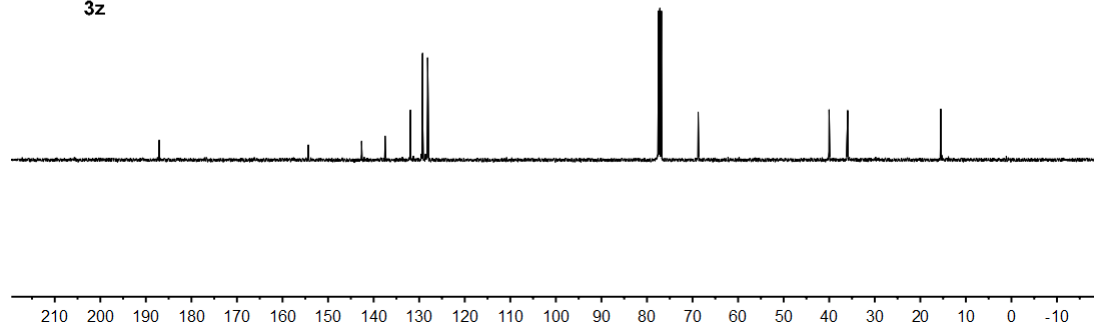
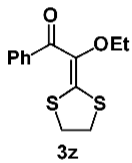
C13CPD CDC13 {D:\NMR400\203} nmr 42

187.0724  
154.3285  
142.6316  
137.5064  
131.9019  
129.2446  
128.1333

77.4779  
77.1603  
76.8425  
68.7619

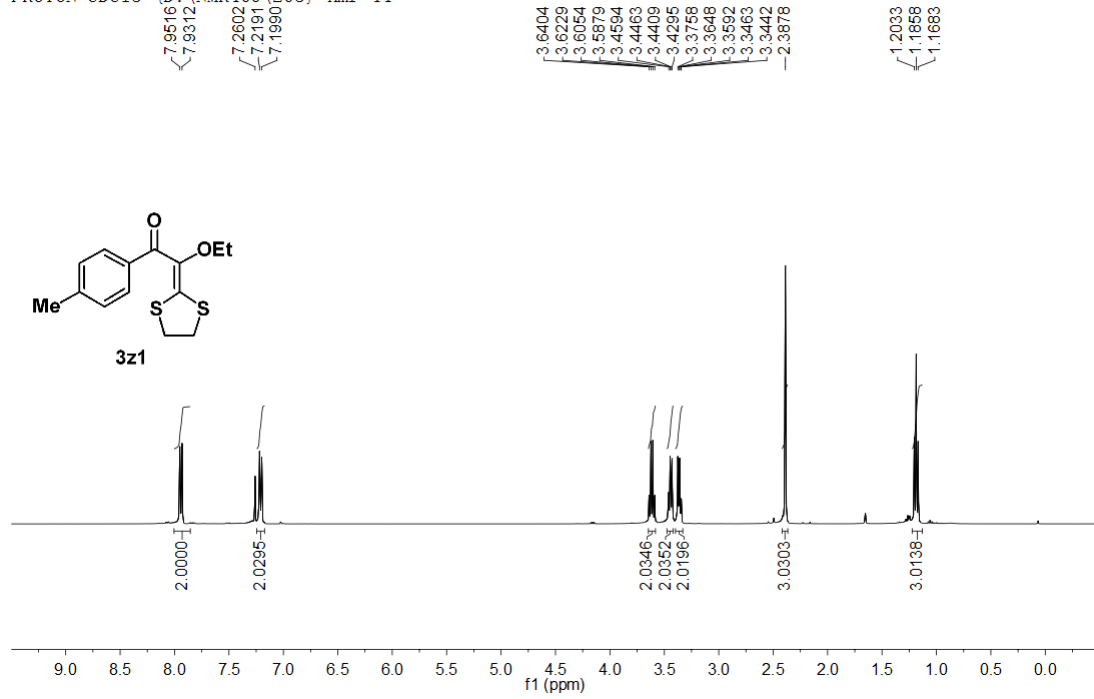
40.0105  
35.9441

15.5137



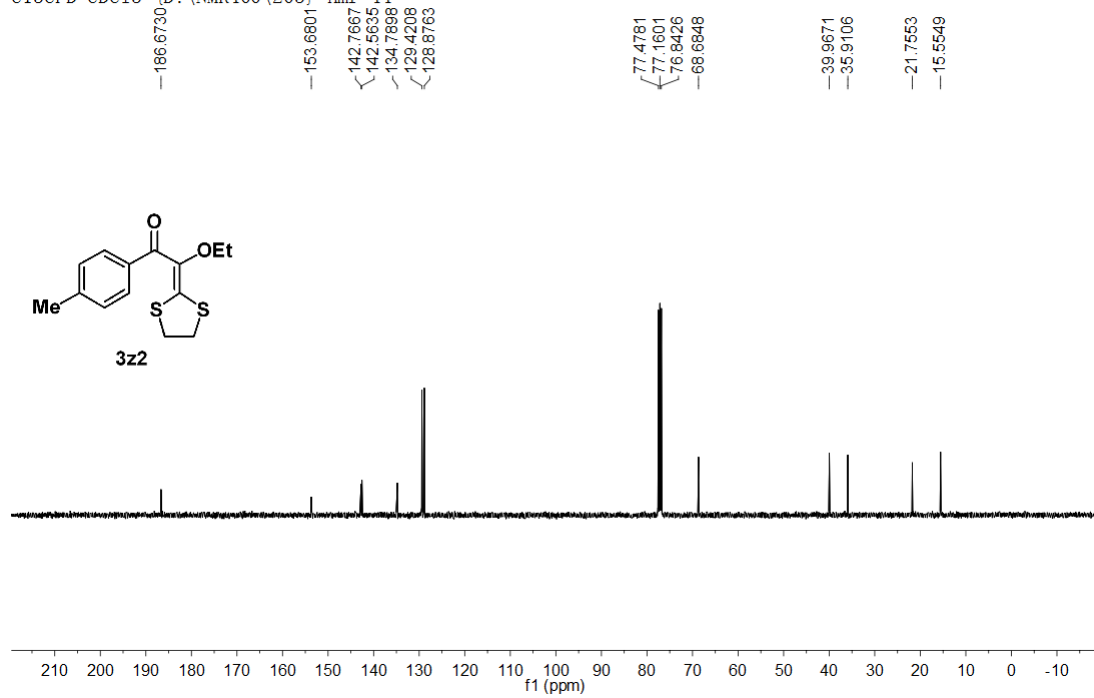
LZQ-449

PROTON CDC13 {D:\NMR400\203} nmr 44



LZQ-449

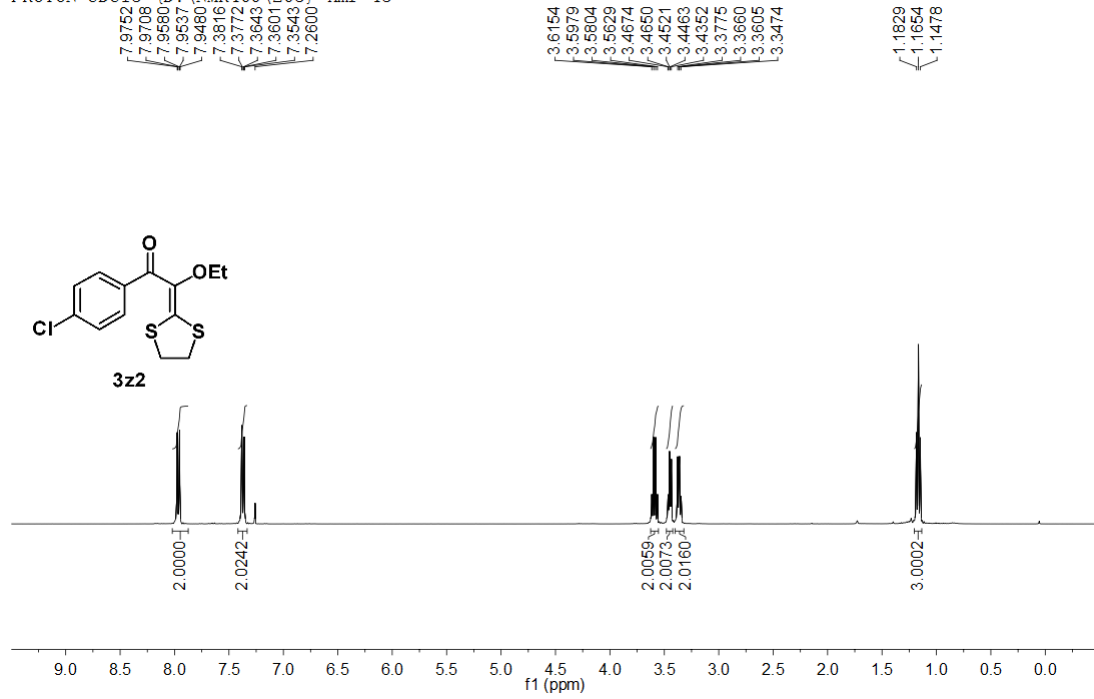
C13CPD CDC13 {D:\NMR400\203} nmr 44





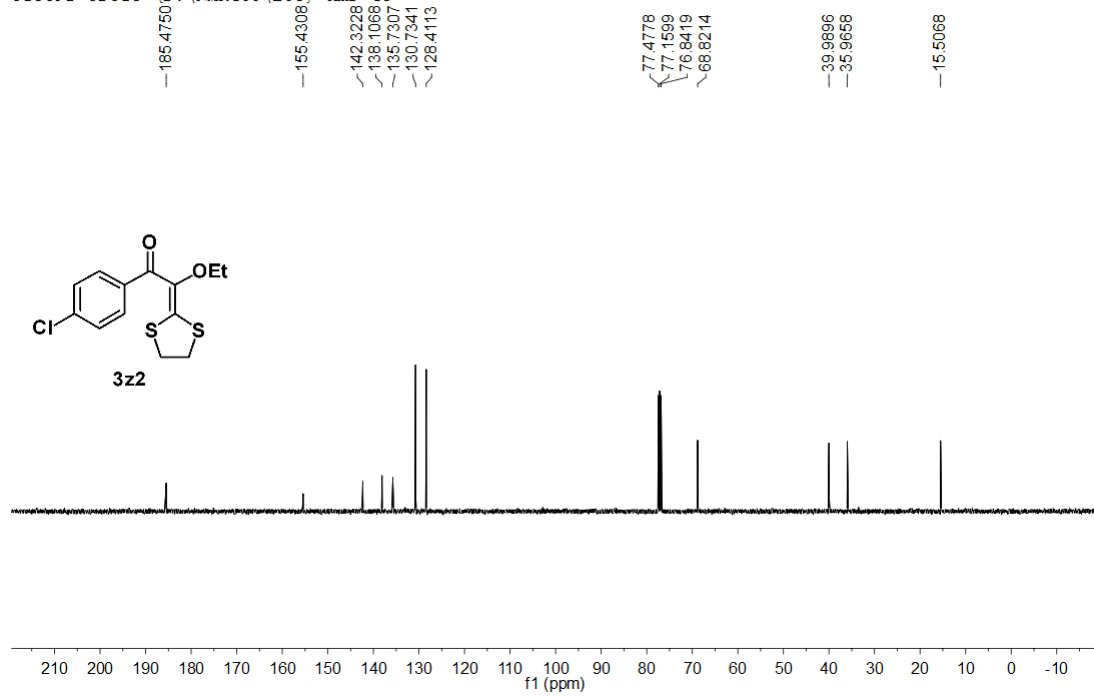
LZQ-448

PROTON CDC13 (D:\NMR400\203} nmr: 43



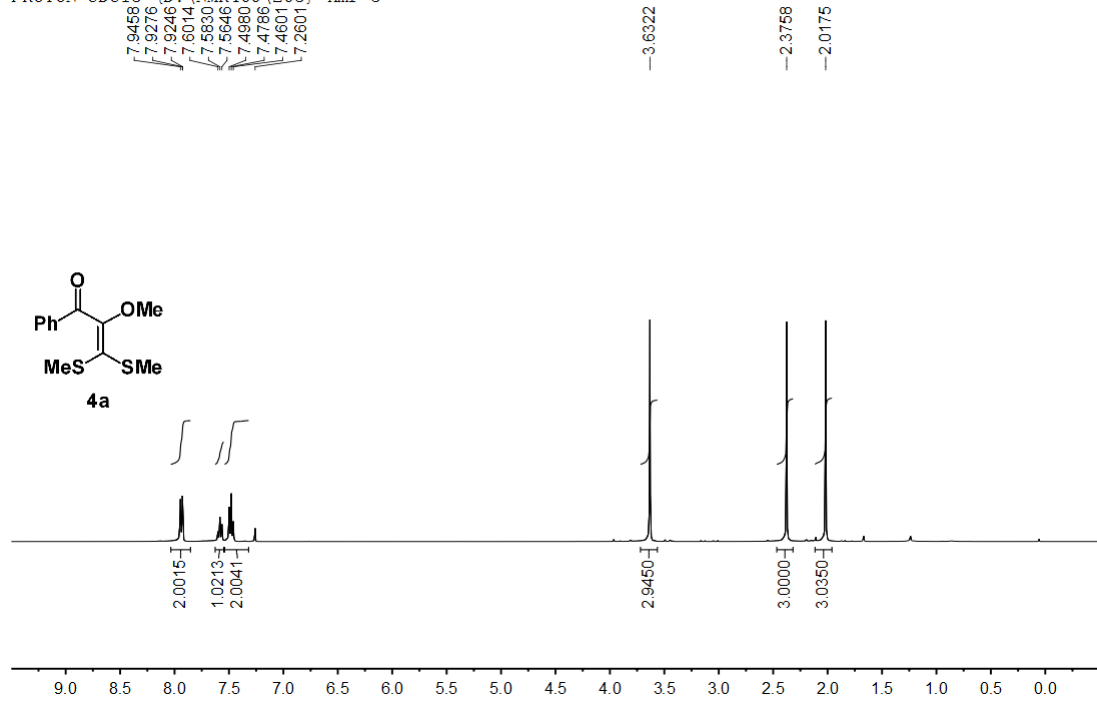
LZQ-448

C13CPD CDC13 (D:\NMR400\203} nmr: 43



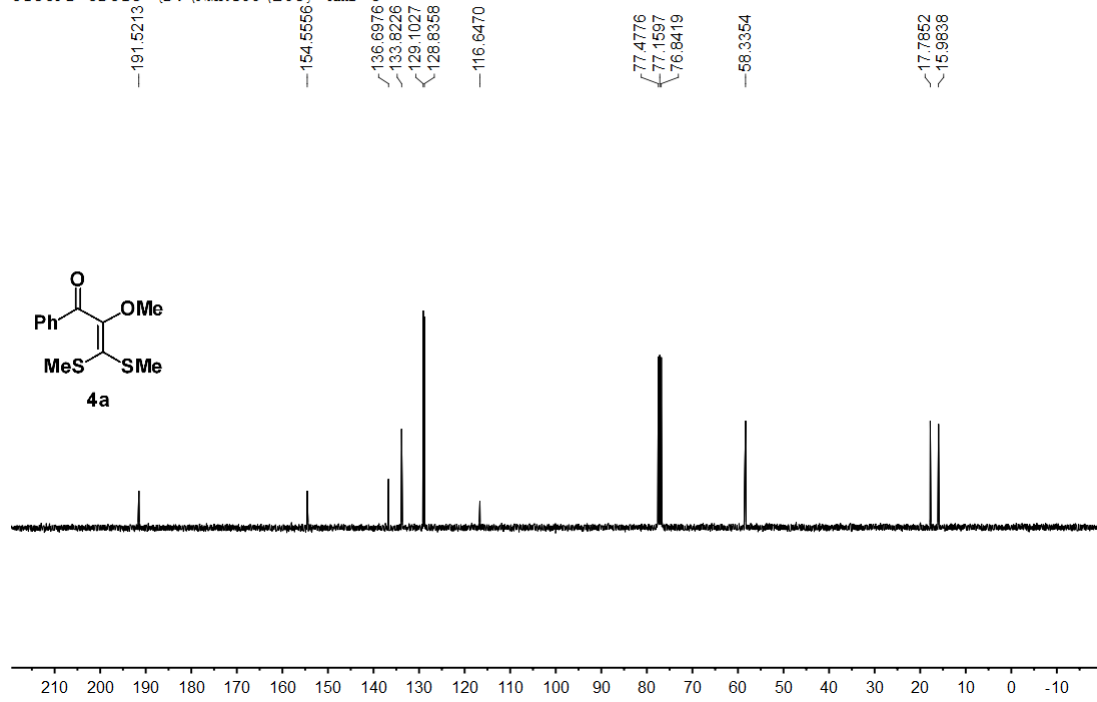
LZQ-380-7

PROTON CDC13 {D:\NMR400\203} nmr 5



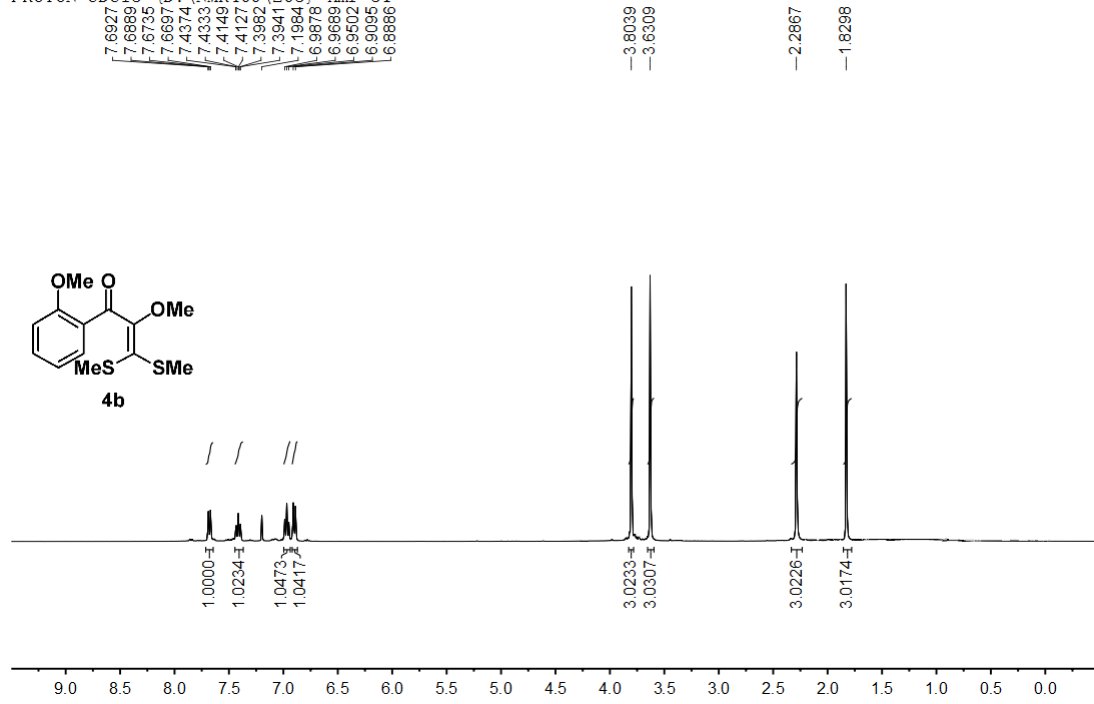
LZQ-380-7

C13CPD CDC13 {D:\NMR400\203} nmr 51



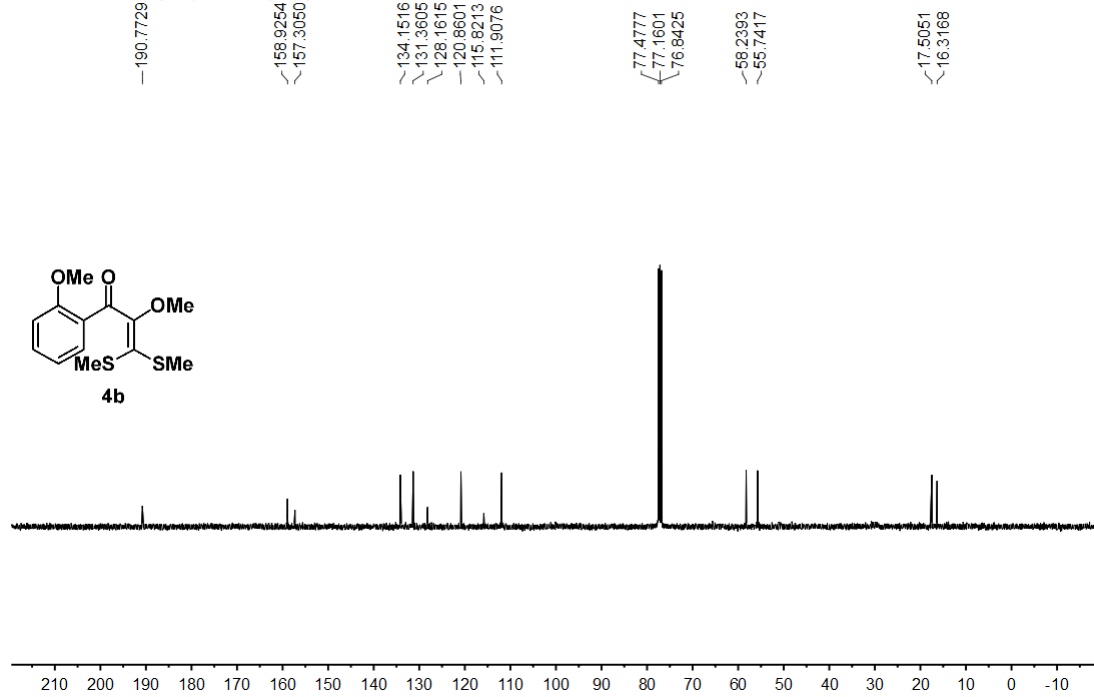
LZQ-869

PROTON CDC13 {D:\NMR400\203} nmr 31



LZQ-869

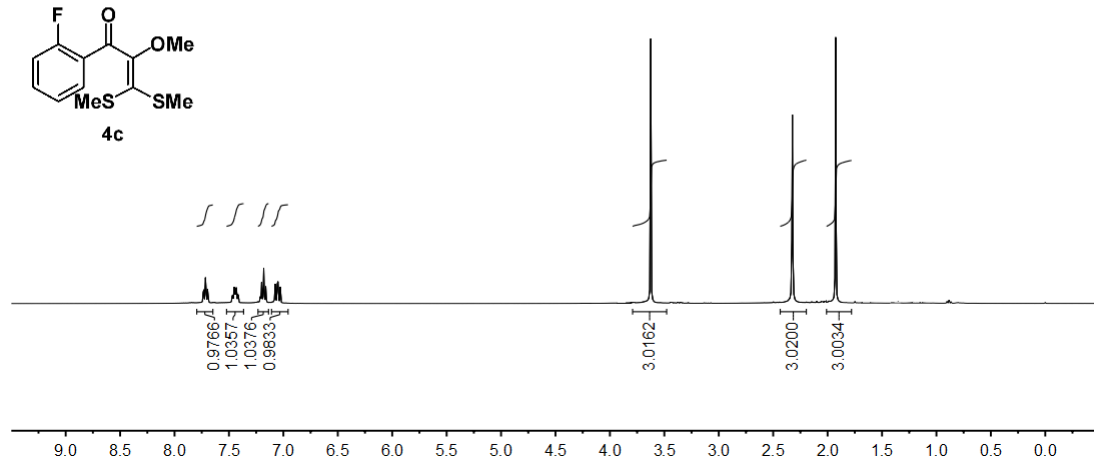
C13CPD CDC13 {D:\NMR400\203} nmr 31



LZQ-868

PROTON CDC13 {D:\NMR400\203} nmr 33

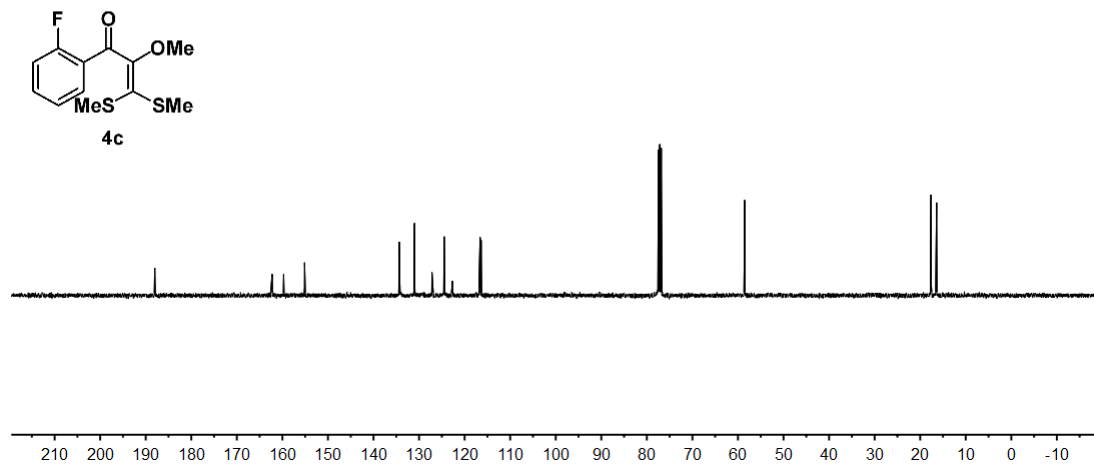
7.7344  
7.7304  
7.7155  
7.7116  
7.6867  
7.6826  
7.4697  
7.4655  
7.4569  
7.4516  
7.4321  
7.4266  
7.4181  
7.4139  
7.2092  
7.1997  
7.1806  
7.1619  
7.0759  
7.0527  
7.0498  
7.0286



LZQ-868

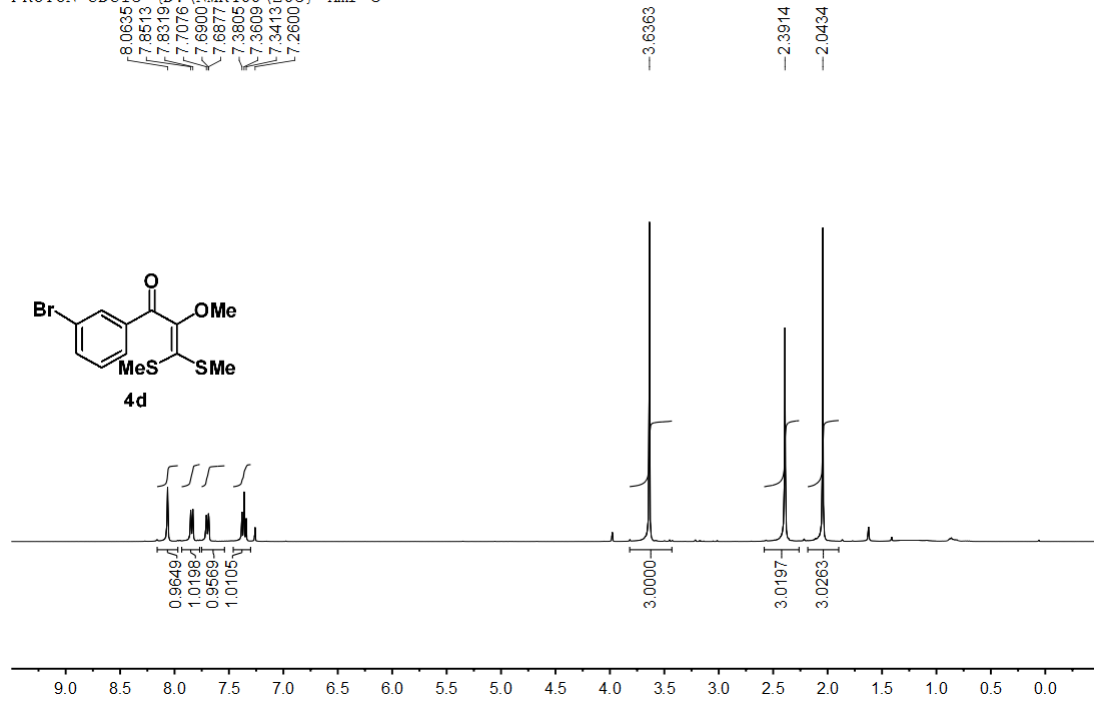
C13CPD CDC13 {D:\NMR400\203} nmr 33

188.0277  
162.2642  
159.7229  
155.1214  
134.3578  
134.2705  
131.0005  
130.9880  
127.1728  
127.0666  
124.5000  
124.4636  
122.6497  
116.6045  
116.3855  
77.4780  
77.1600  
76.8421  
58.5218  
17.6074  
16.4044



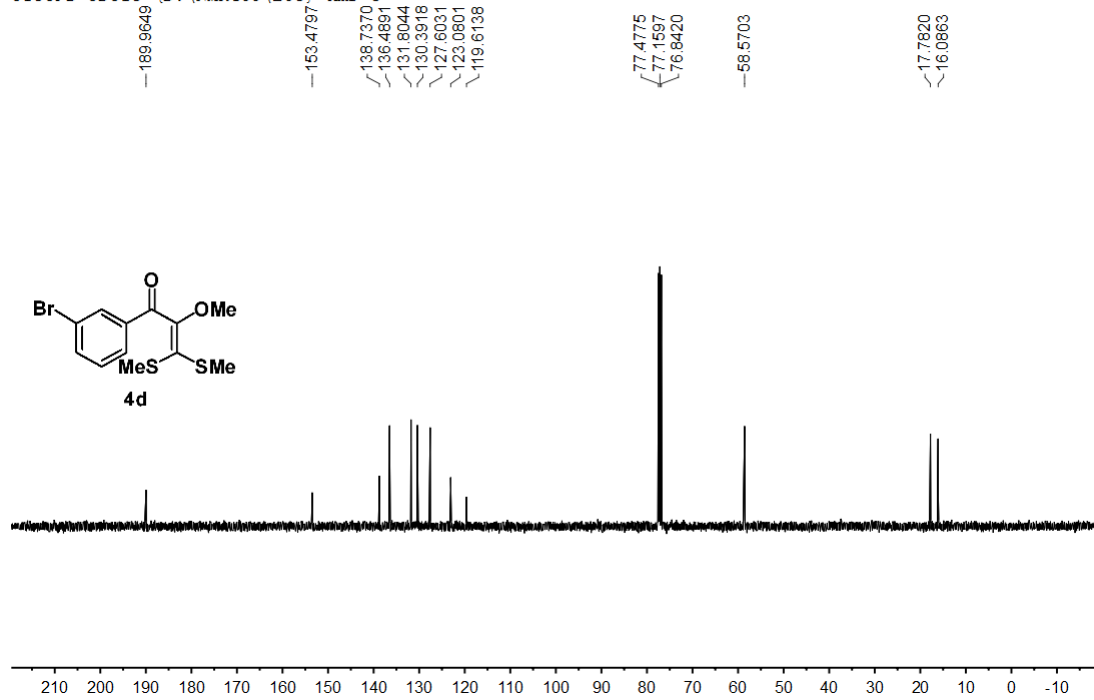
LZQ-862

PROTON CDC13 {D:\NMR400\203} nmr 8



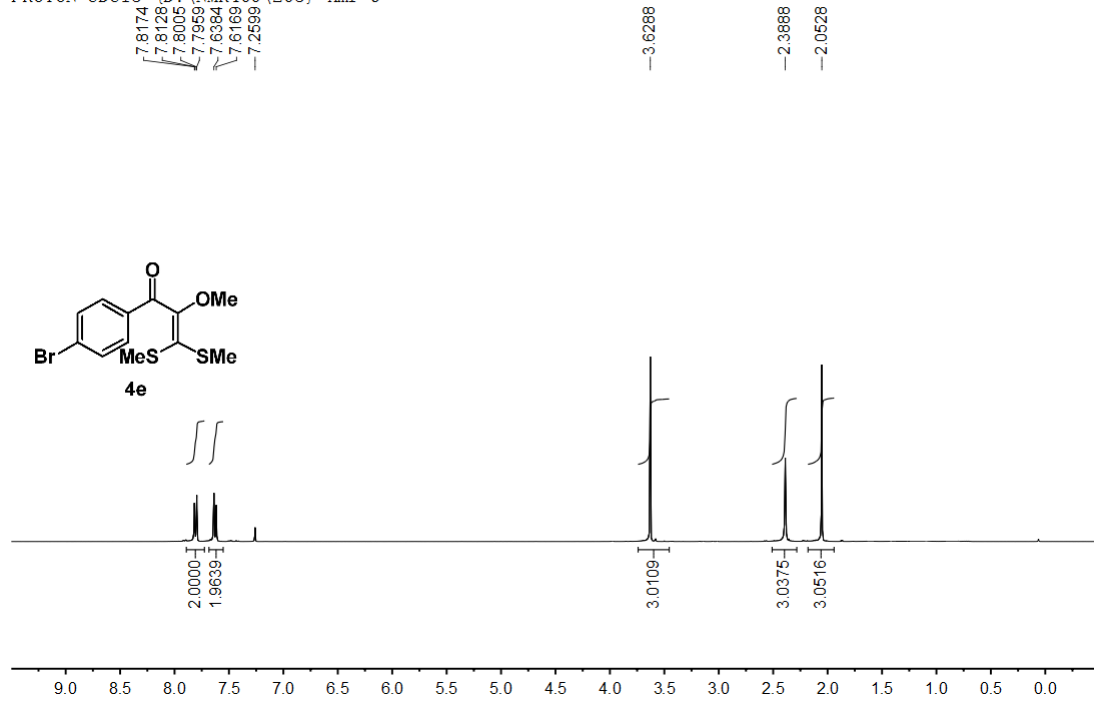
LZQ-862

C13CPD CDC13 {D:\NMR400\203} nmr 8



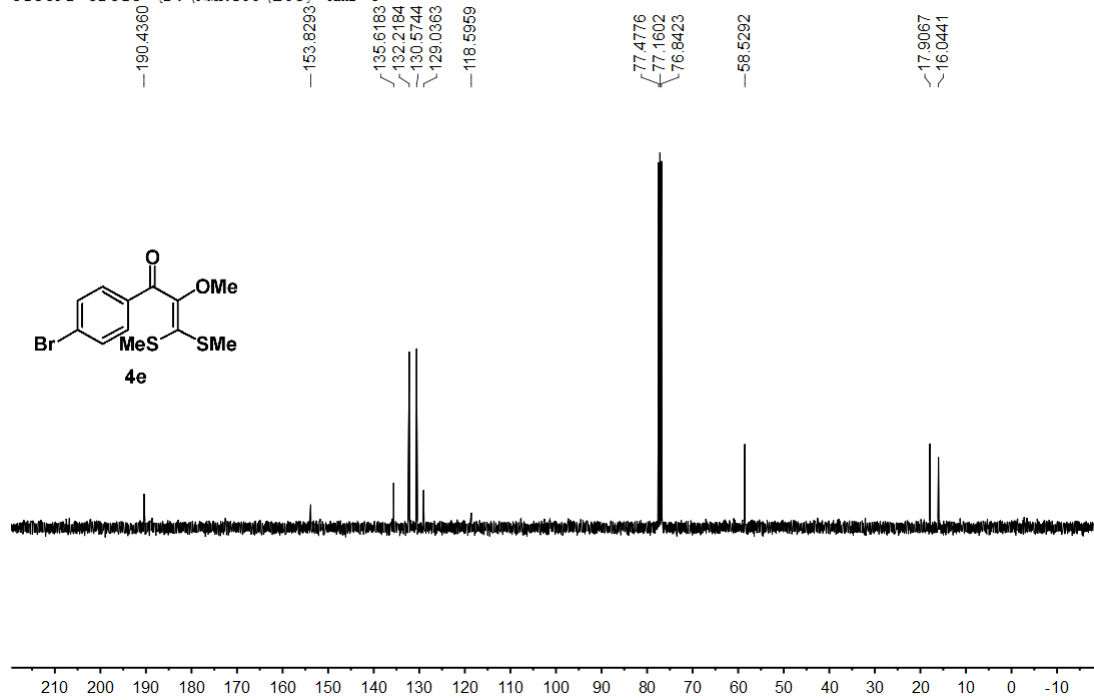
LZQ-863

PROTON CDC13 {D:\NMR400\203} nmr 9



LZQ-863

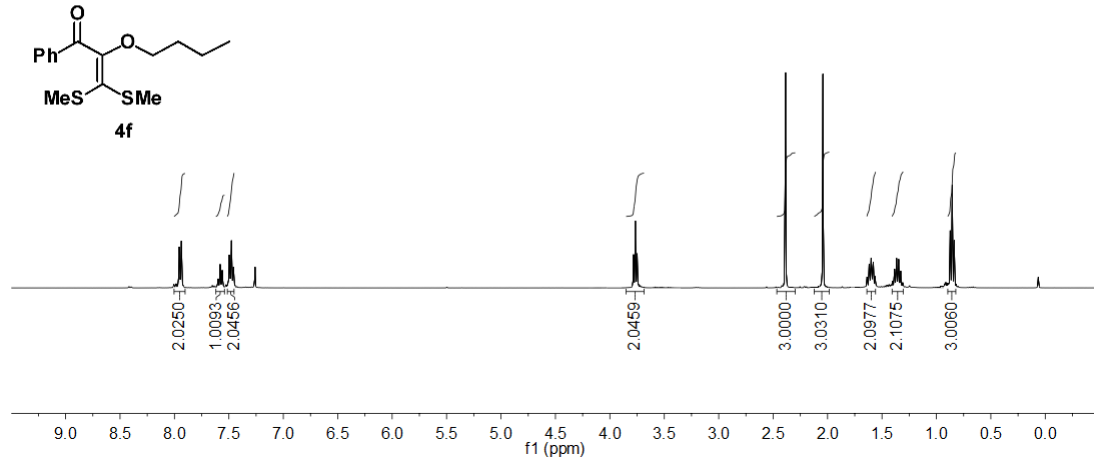
C13CPD CDC13 {D:\NMR400\203} nmr 9



LZQ-490

PROTON CDC13 {D:\NMR400\203} nmr 22

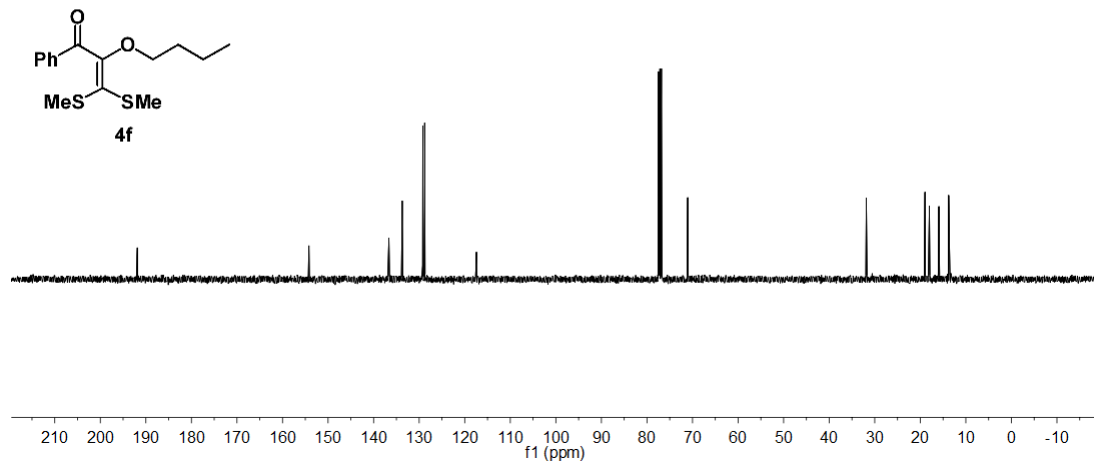
7.9558  
7.9366  
7.5981  
7.5802  
7.5612  
7.4960  
7.4764  
7.4577  
7.2597



LZQ-490

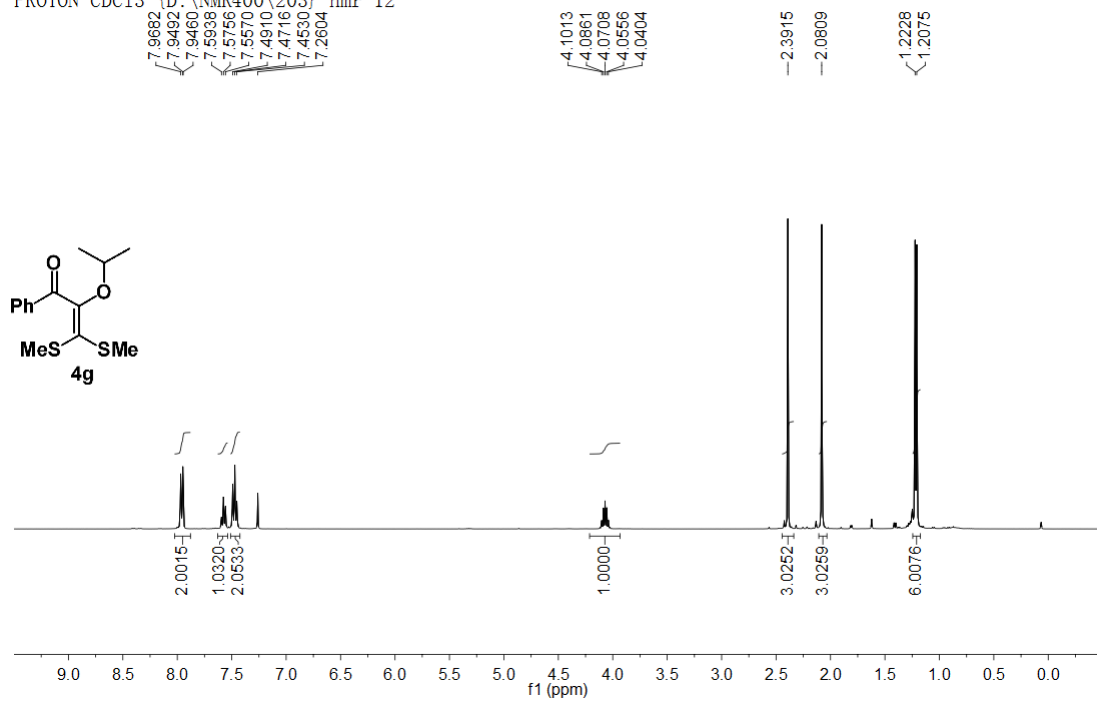
C13CPD CDC13 {D:\NMR400\203} nmr 22

191.8579  
154.2099  
136.6468  
133.7355  
129.2089  
128.7869  
117.4294  
77.4779  
77.1601  
76.8422  
71.0410  
31.8556  
18.9544  
18.0066  
15.9095  
13.7839



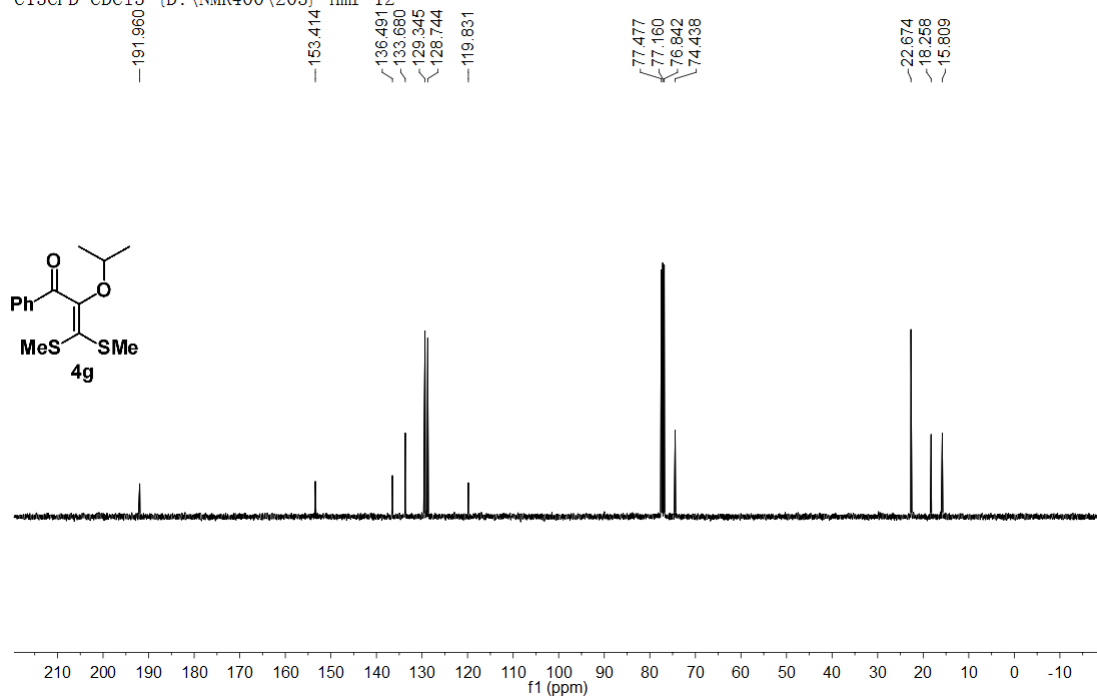
LZQ-430

PROTON CDC13 {D:\NMR400\203} nmr 12



LZQ-430

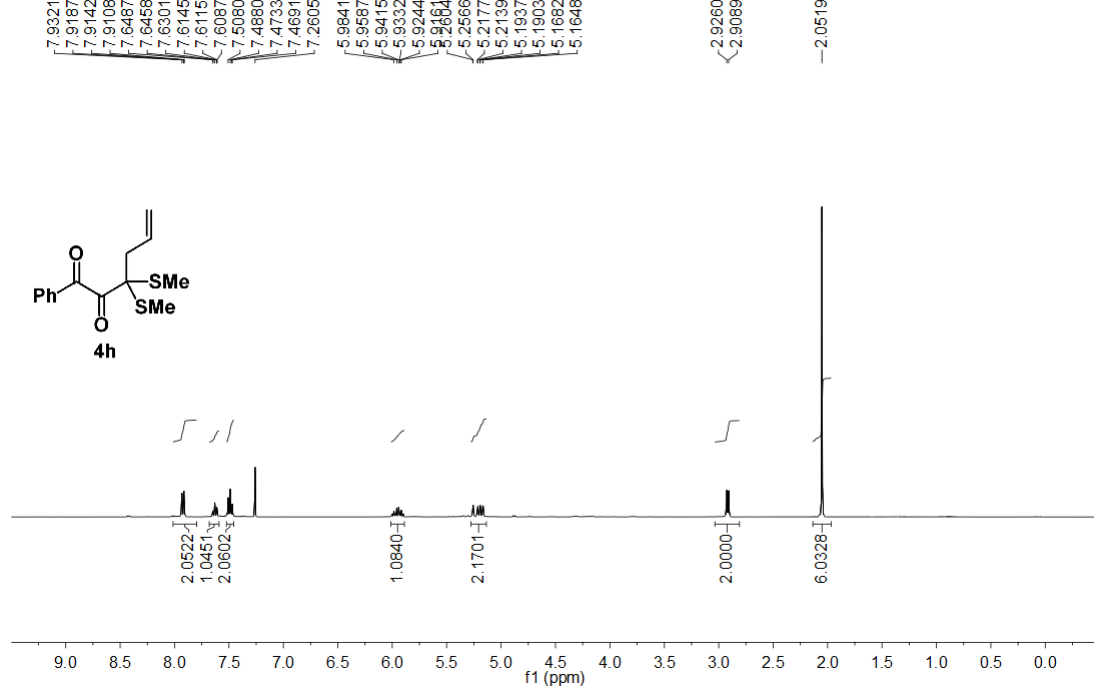
C13CPD CDC13 {D:\NMR400\203} nmr 12





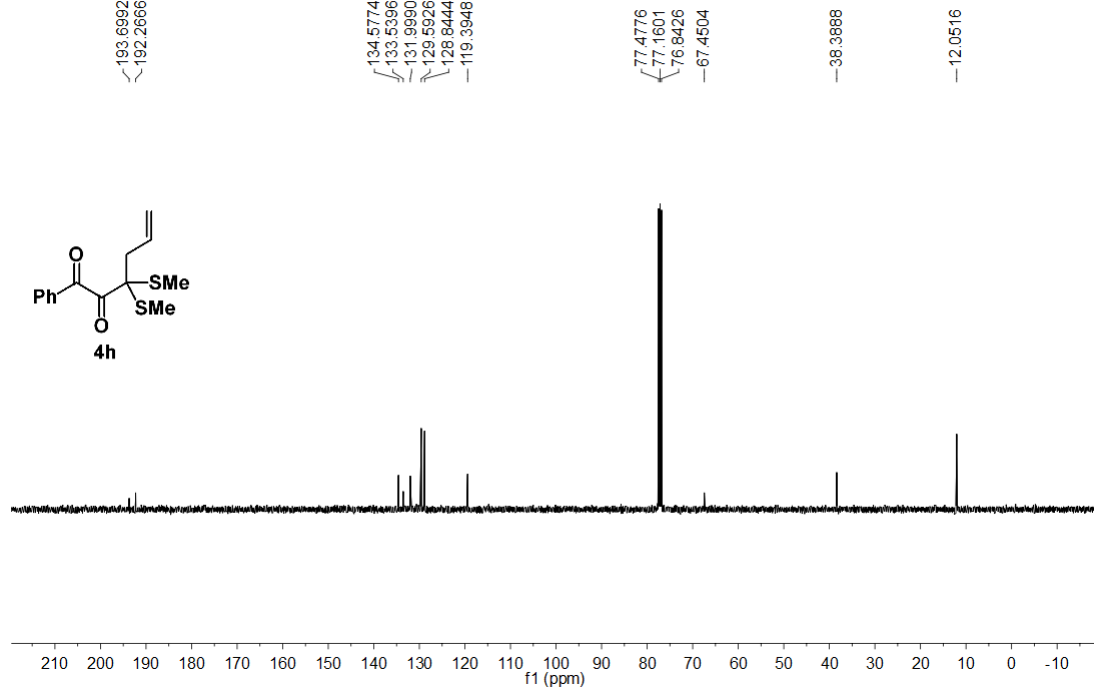
LZQ-424

PROTON CDC13 {D:\NMR400\203} nmr 11



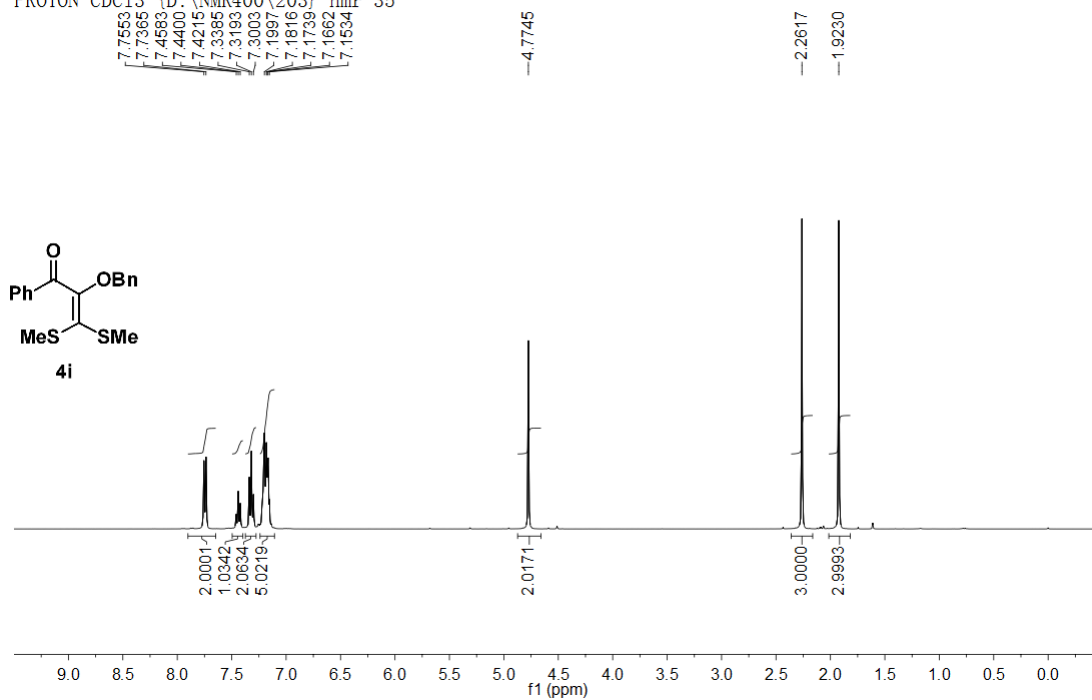
LZQ-424

C13CPD CDC13 {D:\NMR400\203} nmr 11



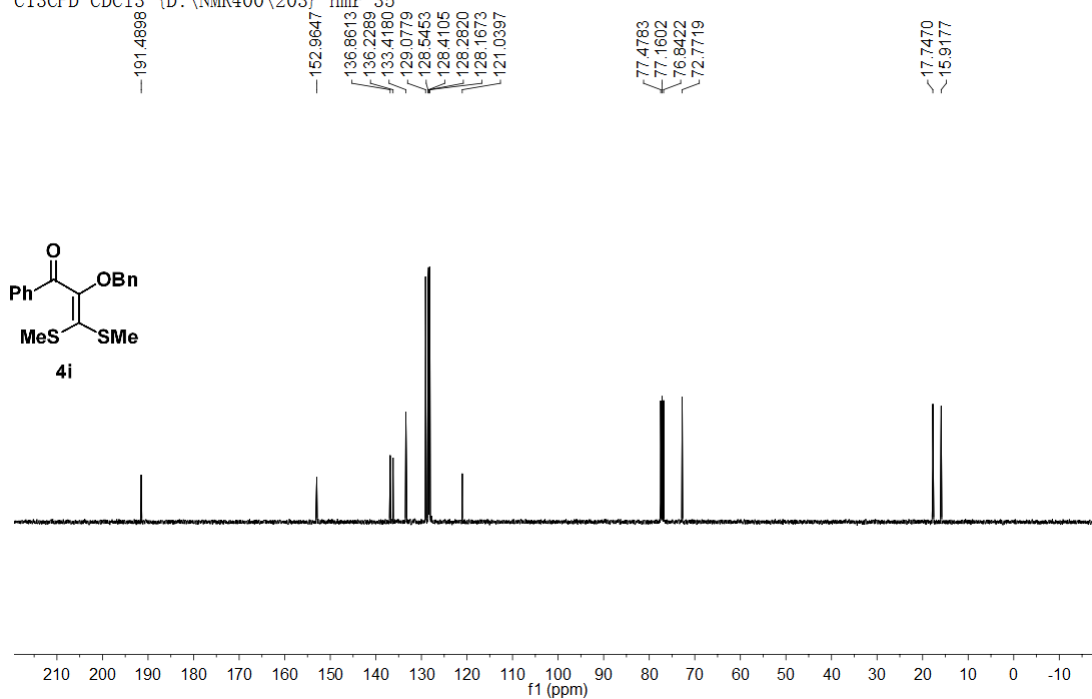
LZQ-443

PROTON CDC13 {D:\NMR400\203} nmr 35



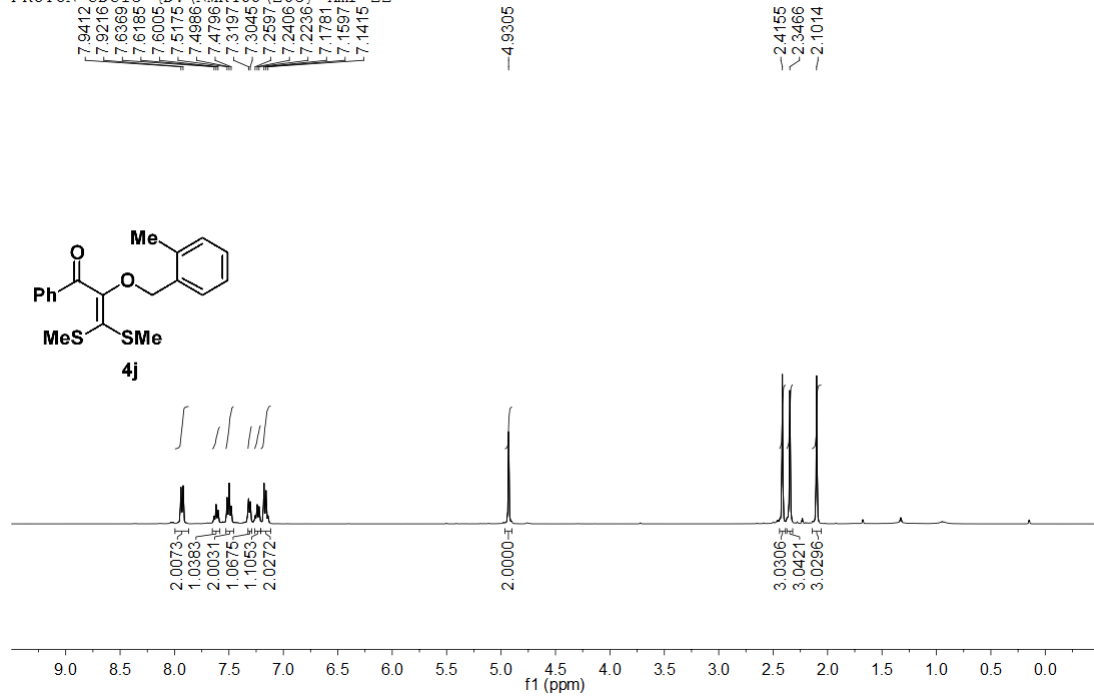
LZQ-443

C13CPD CDC13 {D:\NMR400\203} nmr 35



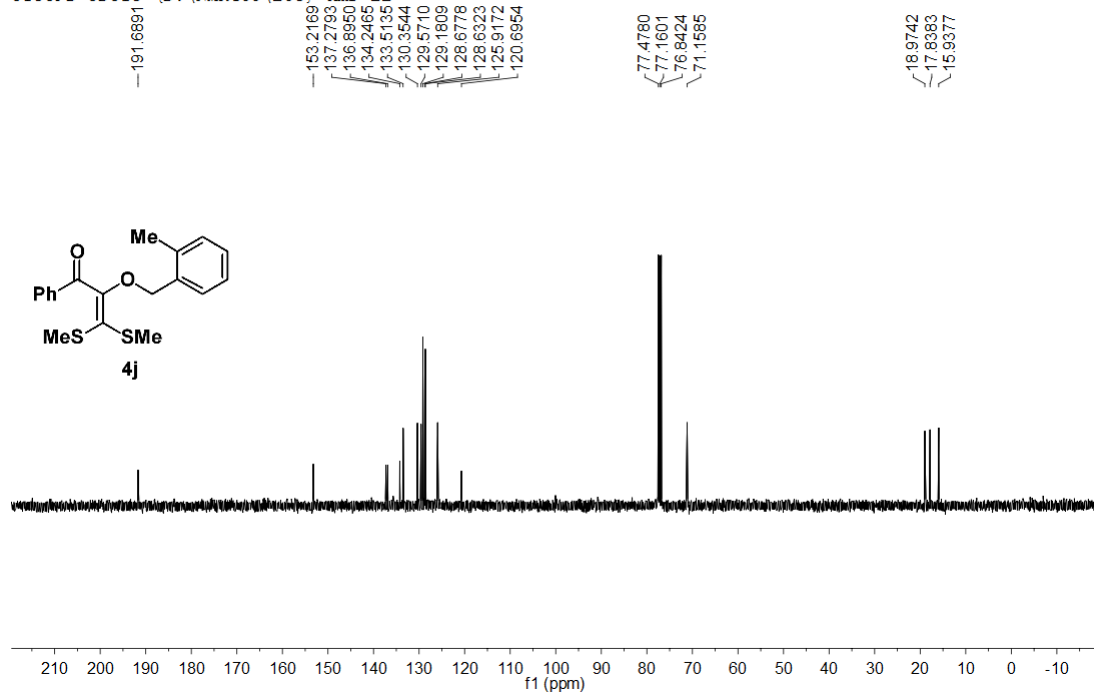
LZQ-509

PROTON CDC13 {D:\NMR400\203} nmr 22



LZQ-509

C13CPD CDC13 {D:\NMR400\203} nmr 22

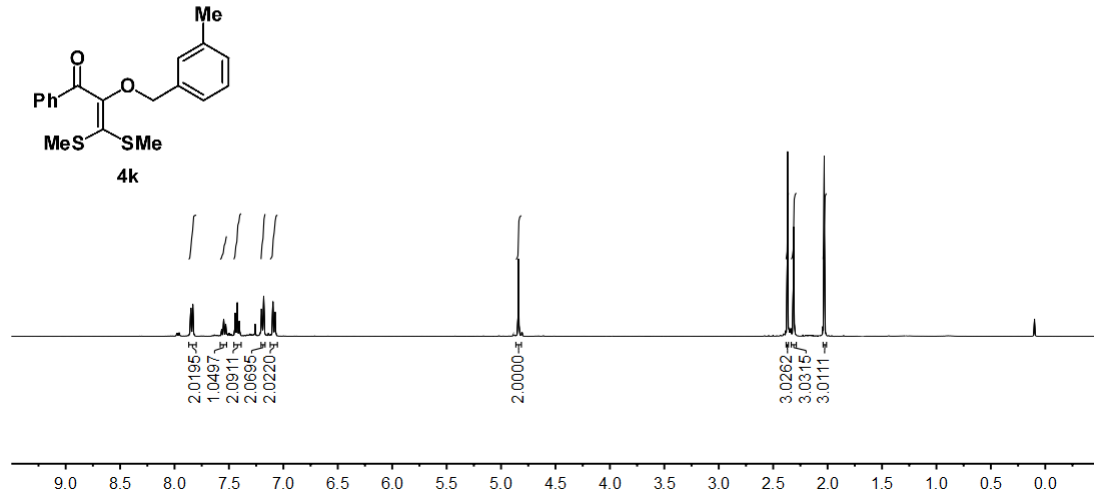


LZQ-487

PROTON CDC13 {D:\NMR400\203} nmr 24  
7.8602  
7.8370  
7.8325  
7.8291  
7.5667  
7.5482  
7.5328  
7.5297  
7.5267  
7.4431  
7.4235  
7.4087  
7.4048  
7.2603  
7.2006  
7.1807  
7.0963  
7.0766

-4.8401

-2.3685  
-2.3120  
-2.0307

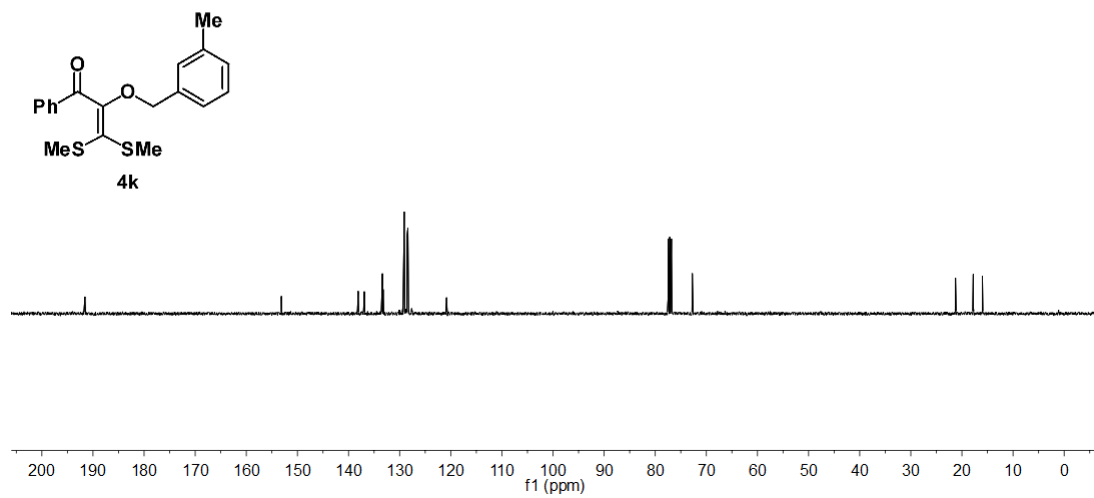


LZQ-487

C13CPD CDC13 {D:\NMR400\203} nmr 24  
-191.581  
-153.136  
138.117  
133.373  
133.233  
129.127  
129.114  
128.523  
128.383  
128.816

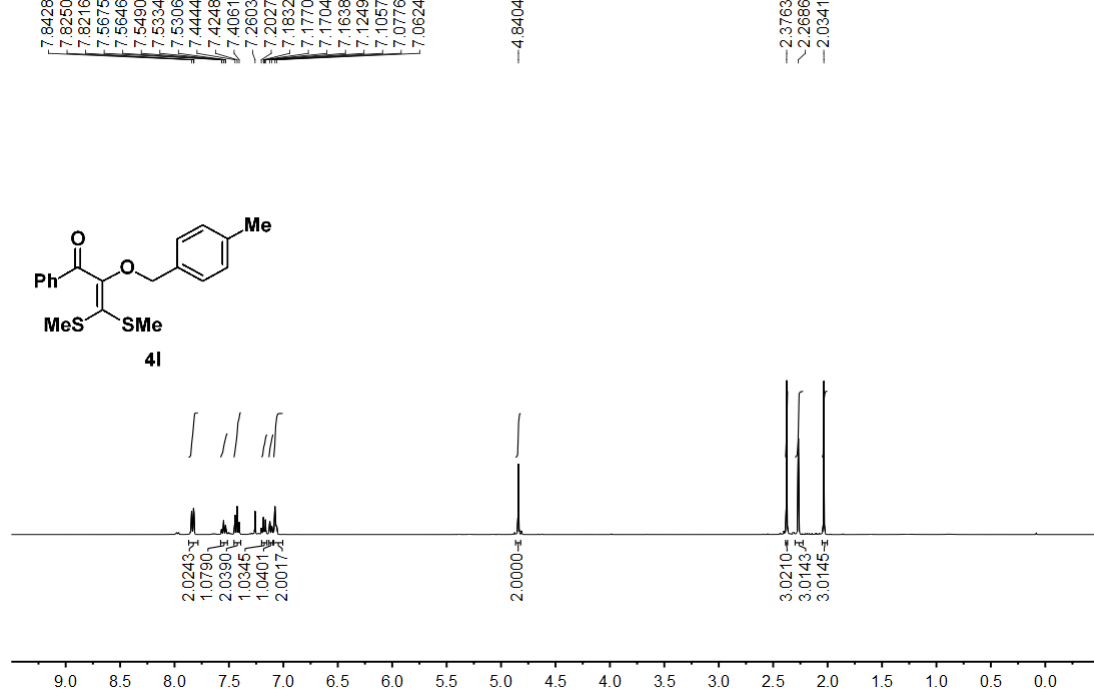
77.477  
77.160  
76.842  
72.751

21.254  
17.788  
15.992



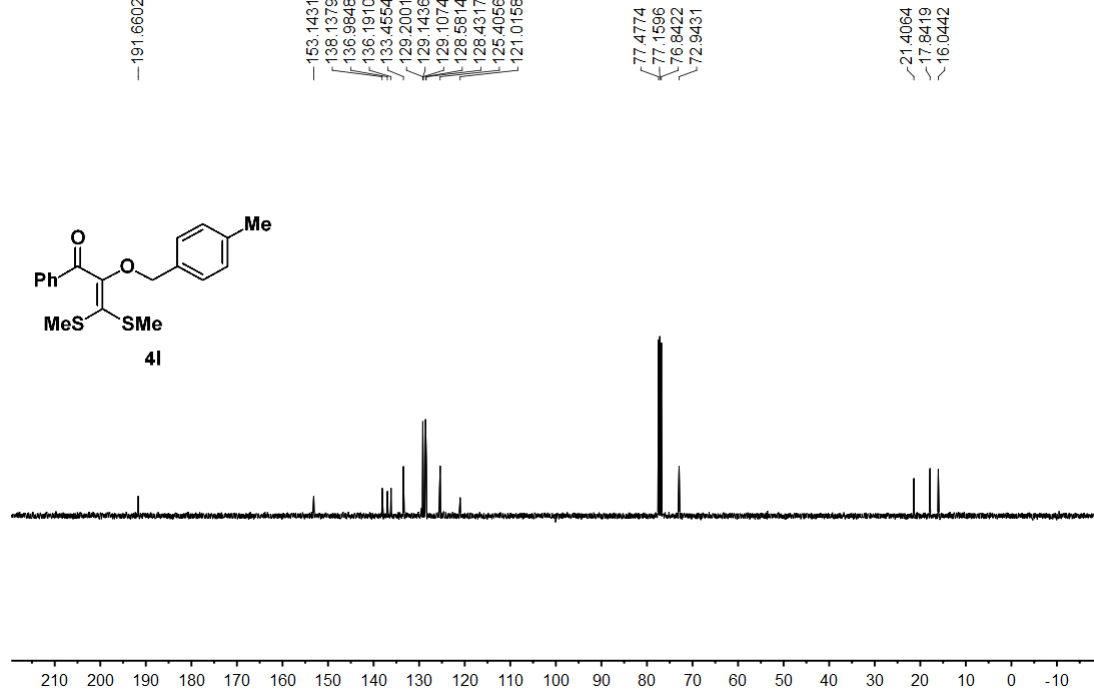
LZQ-488

PROTON CDC13 {D:\NMR400\203} nmr 25



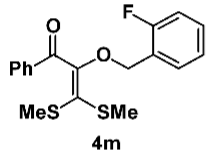
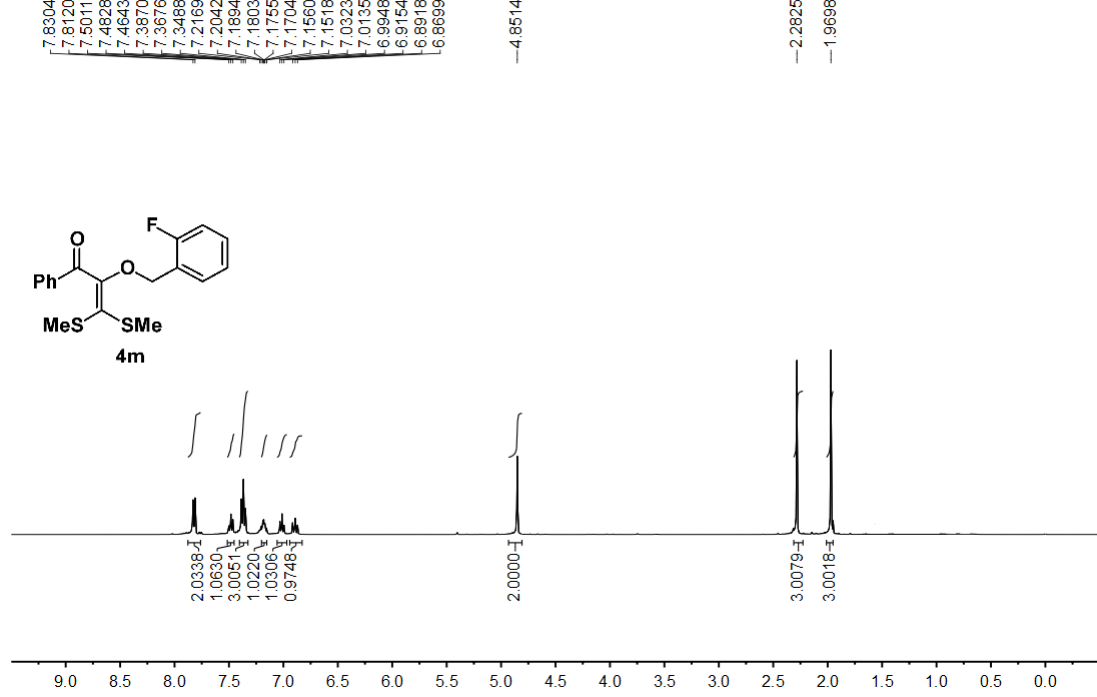
LZQ-488

PROTON CDC13 {D:\NMR400\203} nmr 25



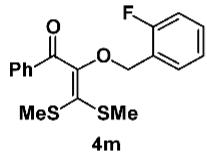
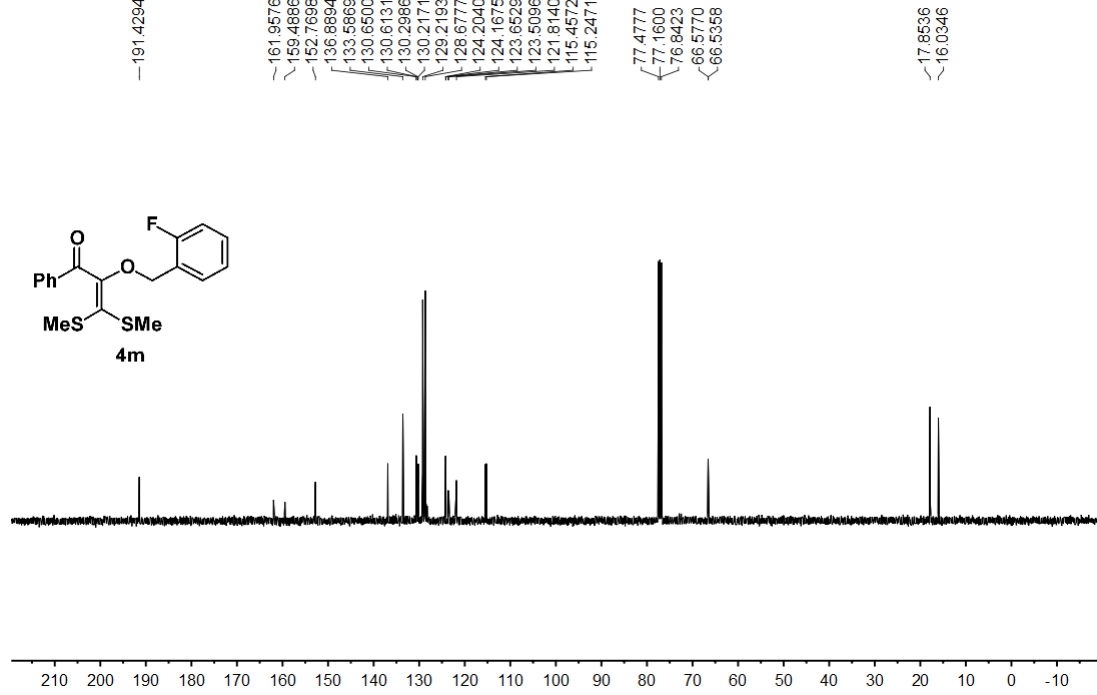
LZQ-767

PROTON CDC13 {D:\NMR400\203} nmr 56



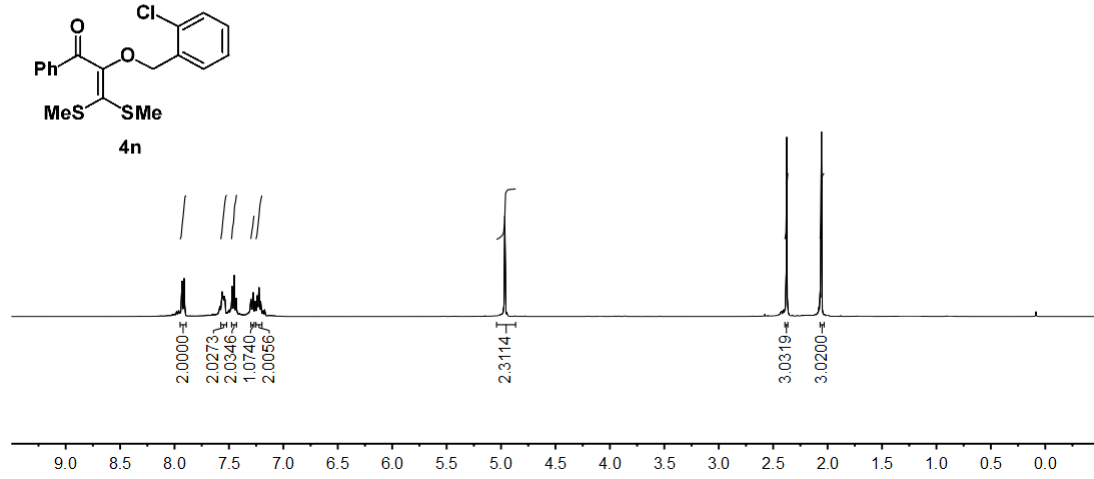
LZQ-767

C13CPD CDC13 {D:\NMR400\203} nmr 56



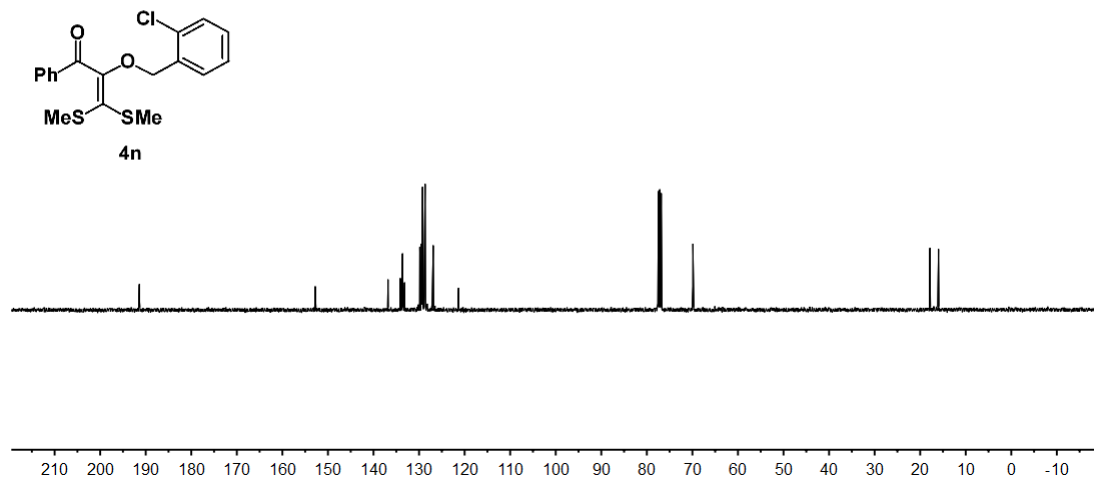
LZQ-775

PROTON CDC13 {D:\NMR400\203} nmr 55  
7.9313  
7.9123  
7.5822  
7.5639  
7.5588  
7.5523  
7.5451  
7.5416  
7.5356  
7.4712  
7.4518  
7.4328  
7.2988  
7.2946  
7.2809  
7.2761  
7.2604  
7.2410  
7.2369  
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7.2209  
7.2086  
7.2038  
-4.9651  
-2.3749  
-2.0568

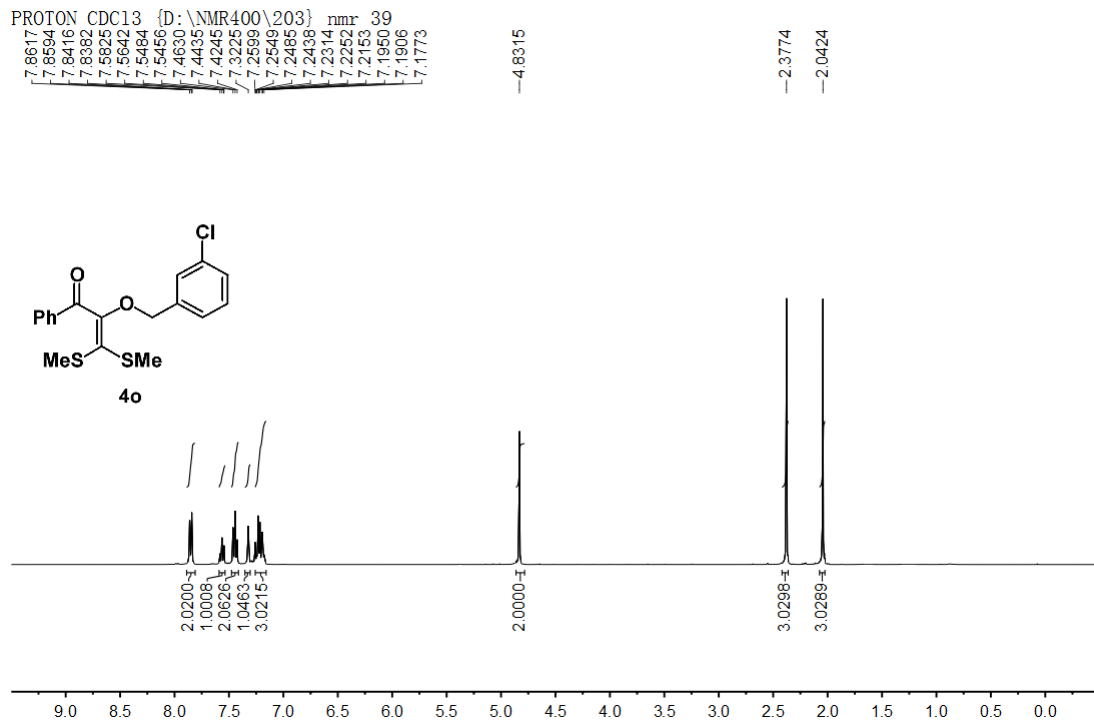


LZQ-775

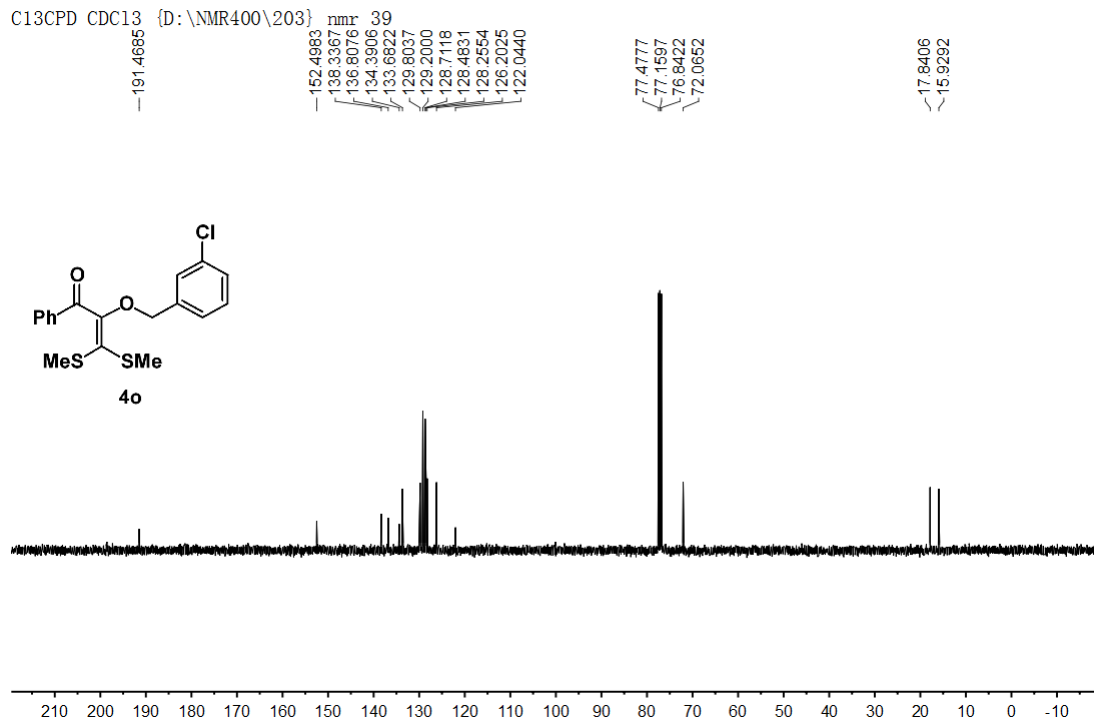
C13CPD CDC13 {D:\NMR400\203} nmr 55  
-191.3930  
-152.7944  
-136.8238  
-134.1221  
-133.6223  
-133.1763  
-129.8423  
-129.4537  
-129.3575  
-129.2193  
-128.6844  
-126.9120  
-121.3114  
77.4782  
77.1603  
76.8425  
69.8728  
17.8424  
15.9825



LZQ-766



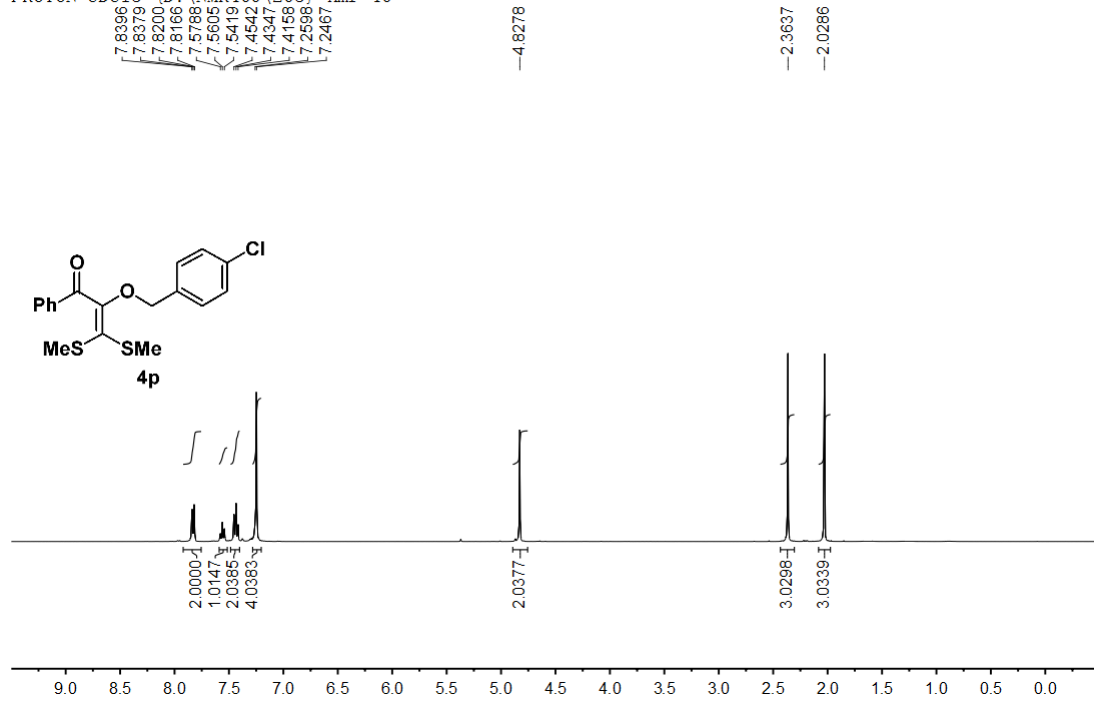
LZQ-766





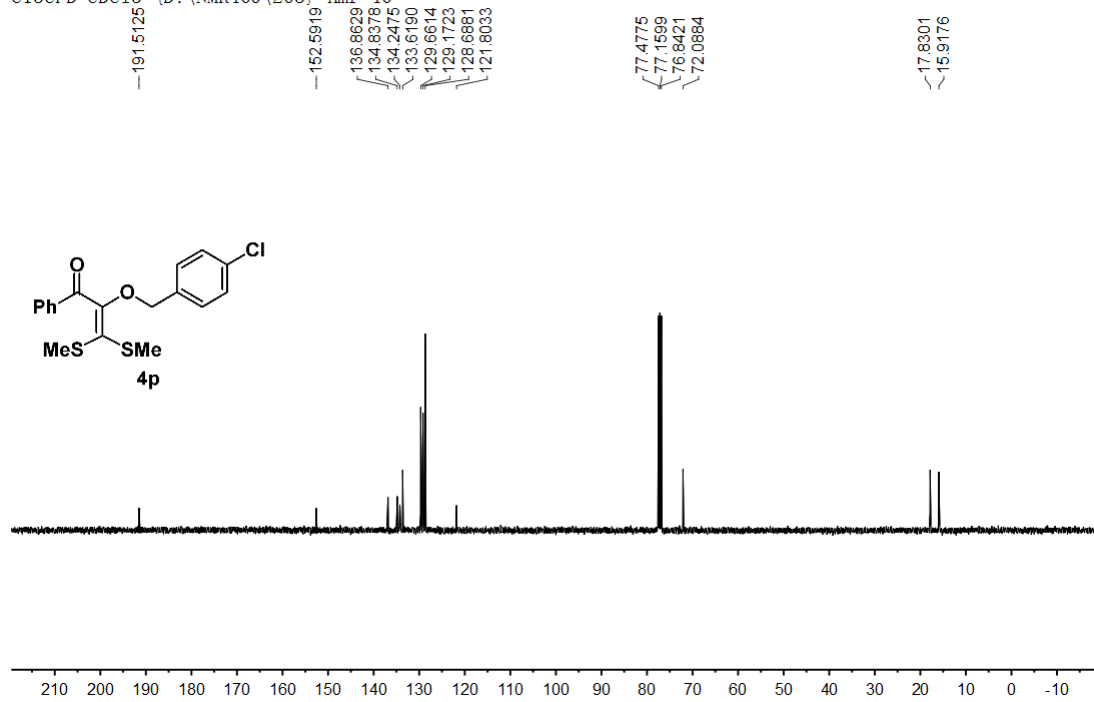
LZQ-765

PROTON CDC13 {D:\NMR400\203} nmr: 40



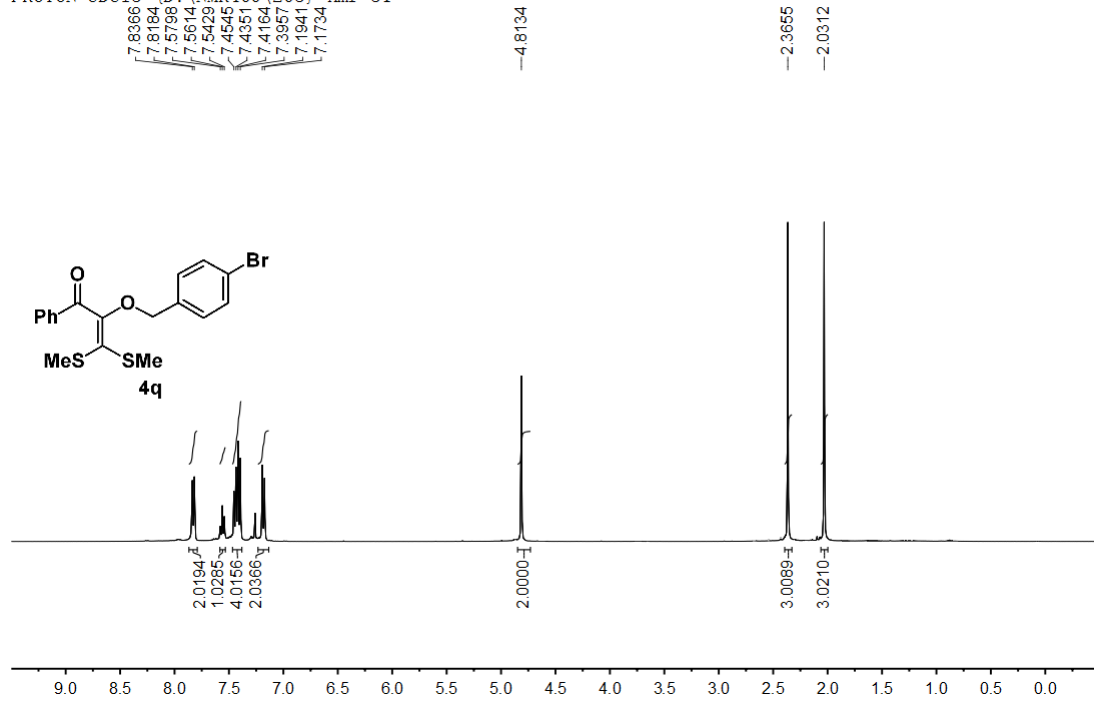
LZQ-765

C13CPD CDC13 {D:\NMR400\203} nmr: 40



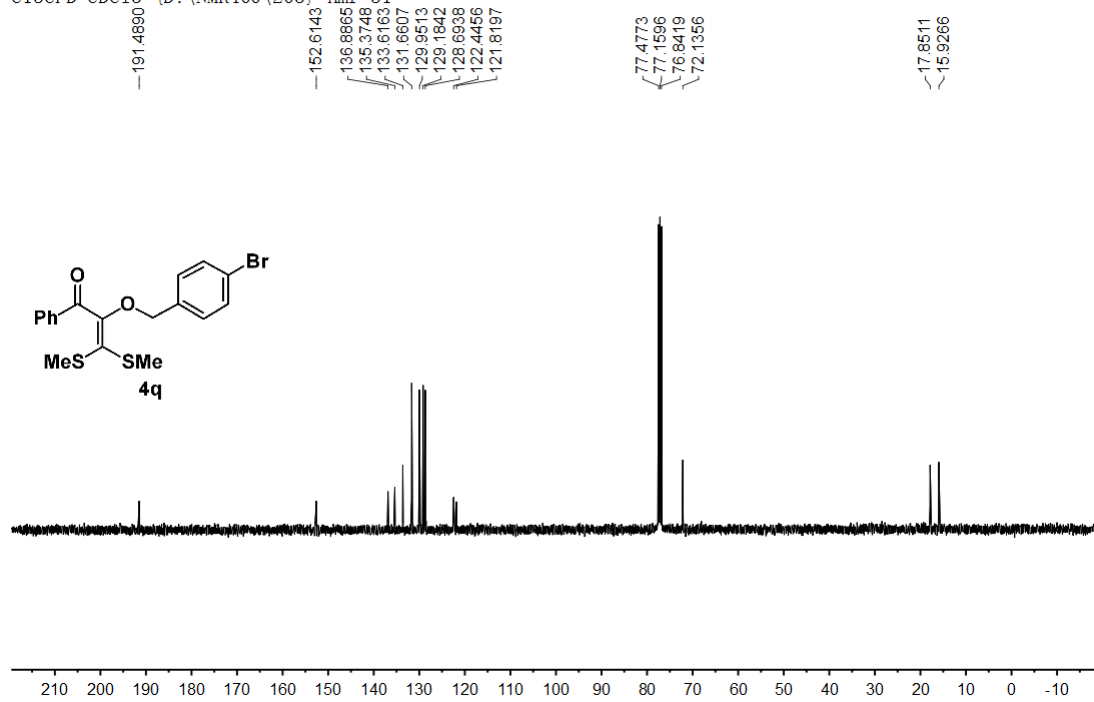
LZQ-776

PROTON CDC13 {D:\NMR400\203} nmr 31



LZQ-776

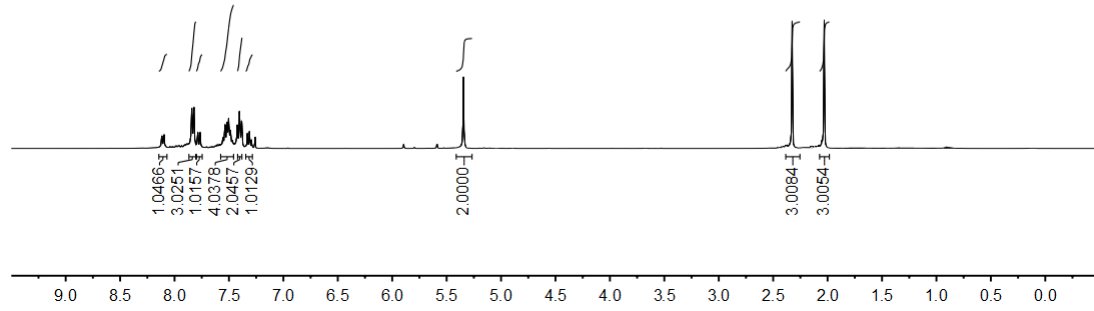
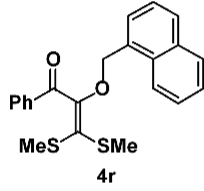
C13CPD CDC13 {D:\NMR400\203} nmr 31



LZQ-430

PROTON CDC13 {D:\NMR400\203} nmr 47

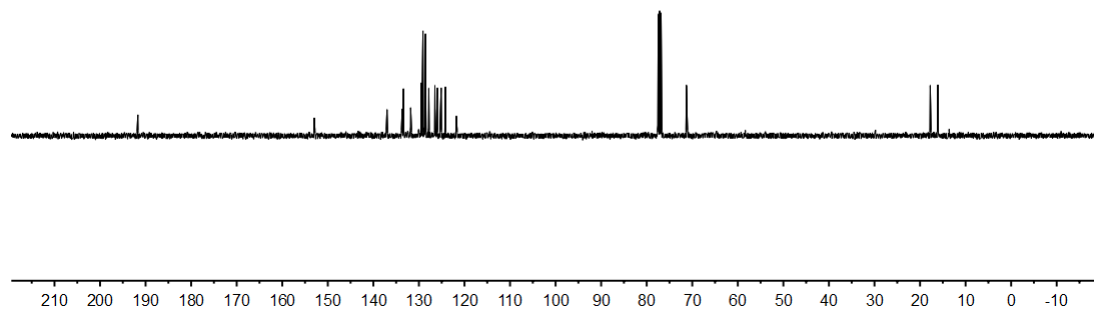
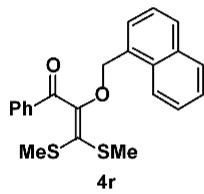
8.1152  
8.0962  
7.8416  
7.8212  
7.7856  
7.7651  
7.5642  
7.5359  
7.5175  
7.5031  
7.4857  
7.4712  
7.4236  
7.4040  
7.3837  
7.3309  
7.2930  
7.2596  
-5.3453  
-2.3254  
-2.0310



LZQ-430

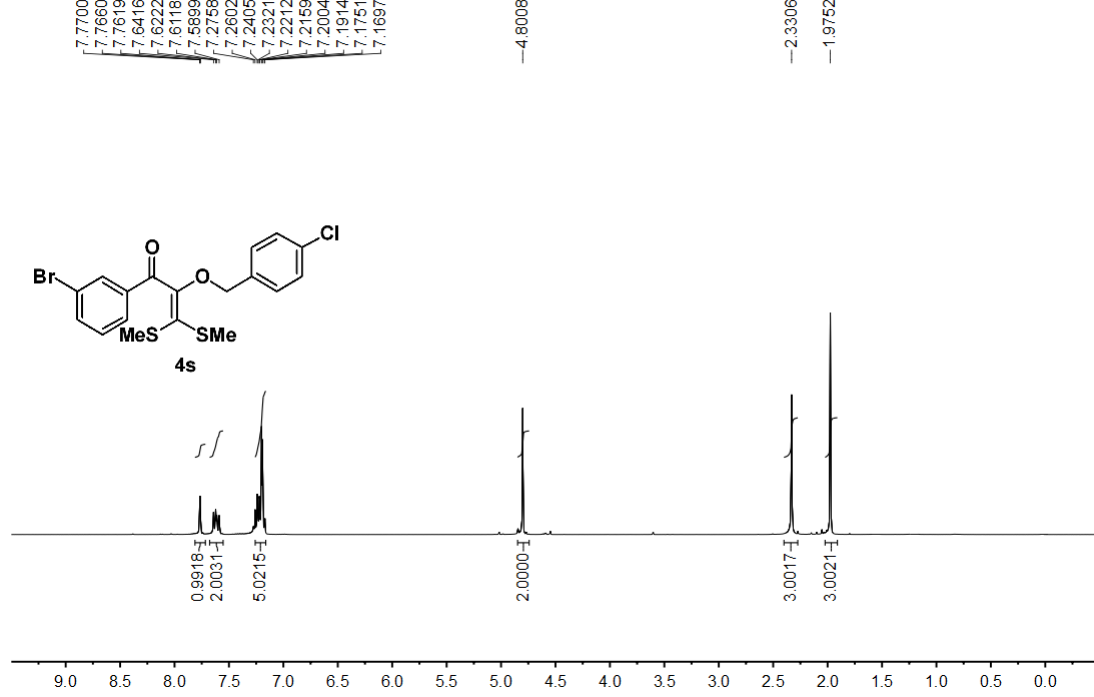
C13CPD CDC13 {D:\NMR400\203} nmr 47

-191.7185  
-152.9658  
-137.0160  
-133.6947  
-133.3777  
-131.7979  
-131.6818  
-129.4506  
-129.1184  
-128.5494  
-128.5122  
-127.8259  
-126.4985  
-125.9758  
-125.1342  
-124.1776  
-121.7803  
-77.4783  
-77.1605  
-76.8426  
-71.2971  
-17.7540  
-16.0653



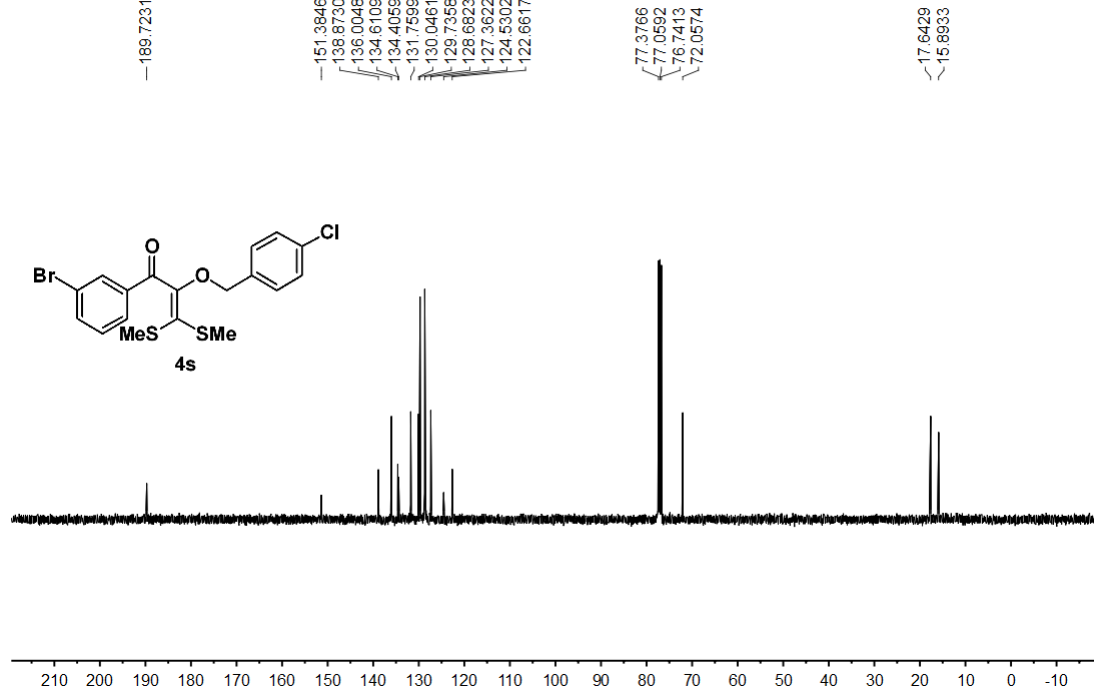
LZQ-884

PROTON CDC13 {D:\NMR400\203} nmr 34



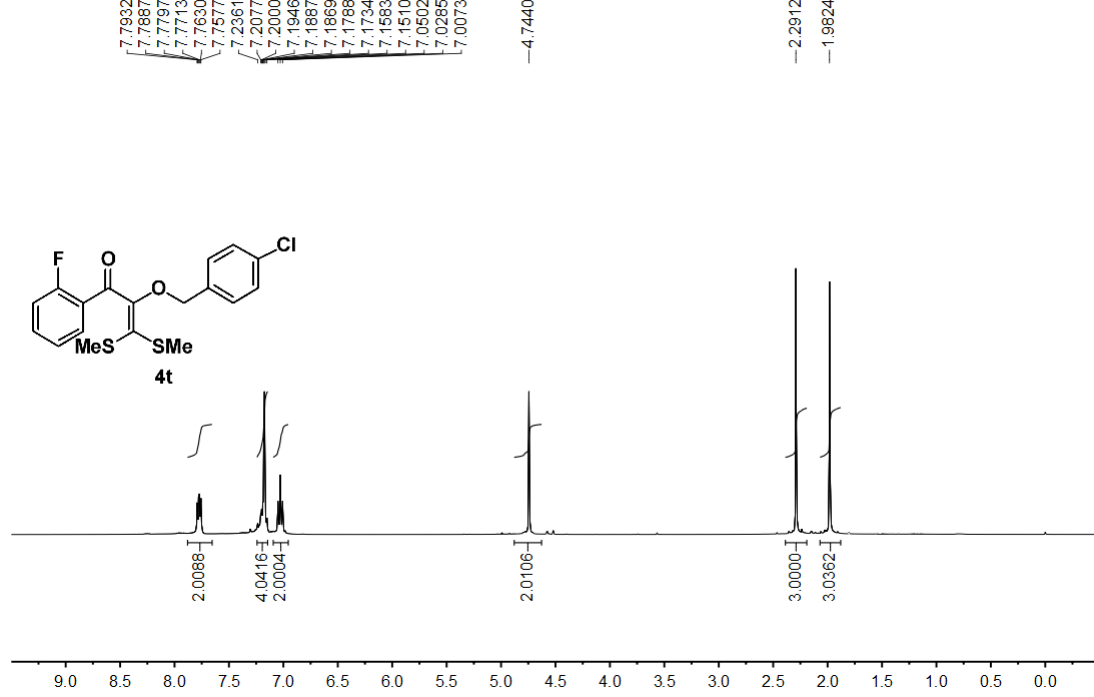
LZQ-884

C13CPD CDC13 {D:\NMR400\203} nmr 35



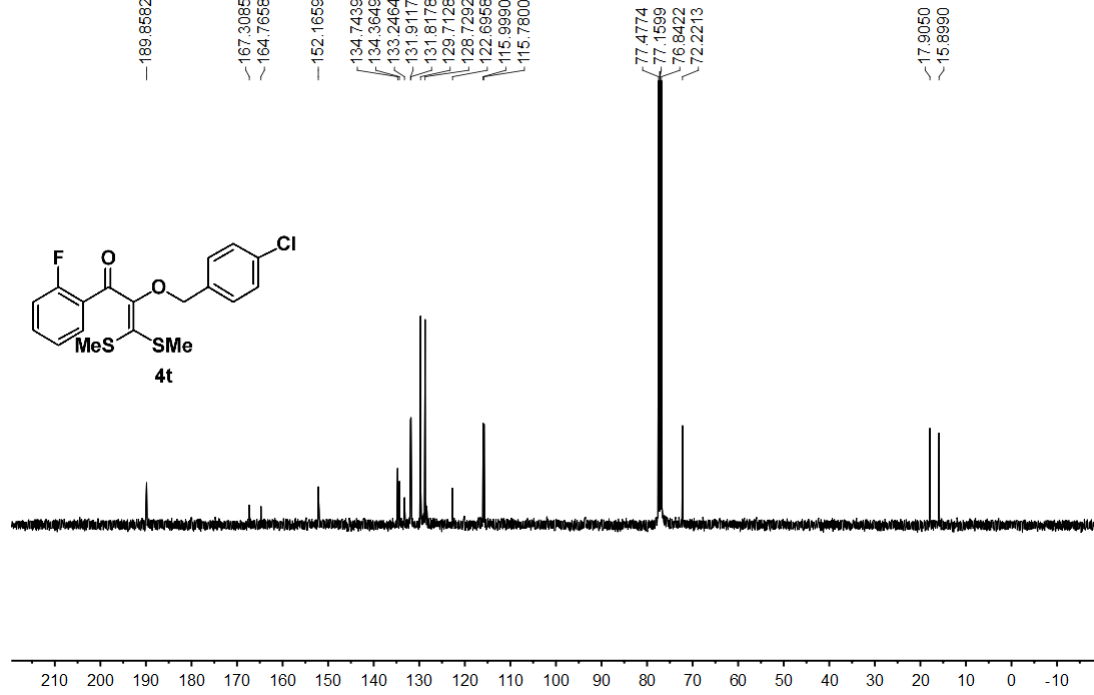
LZQ-841

PROTON CDC13 {D:\NMR400\203} nmr: 26



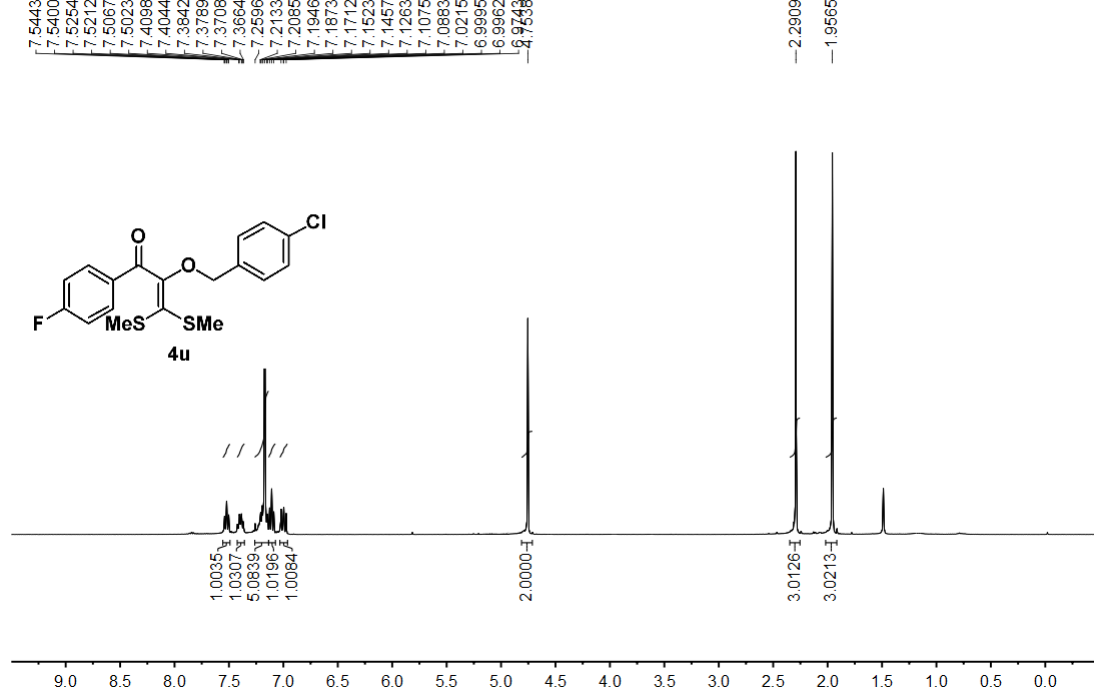
LZQ-841

C13CPD CDC13 {D:\NMR400\203} nmr: 18



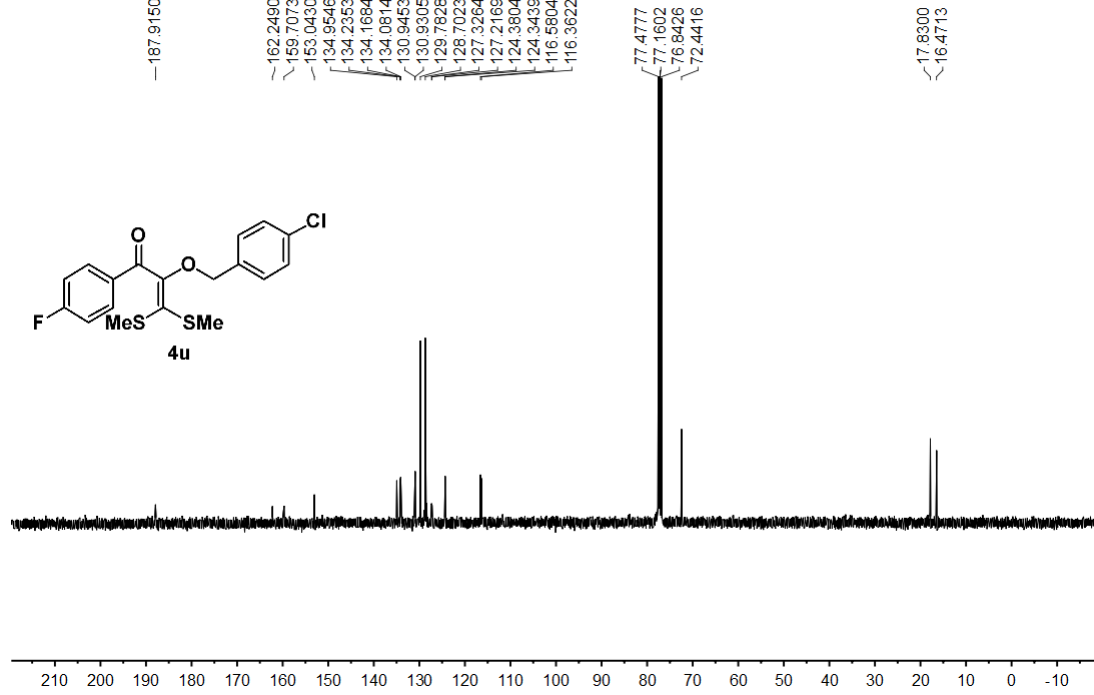
LZQ-885

PROTON CDC13 {D:\NMR400\203} 35



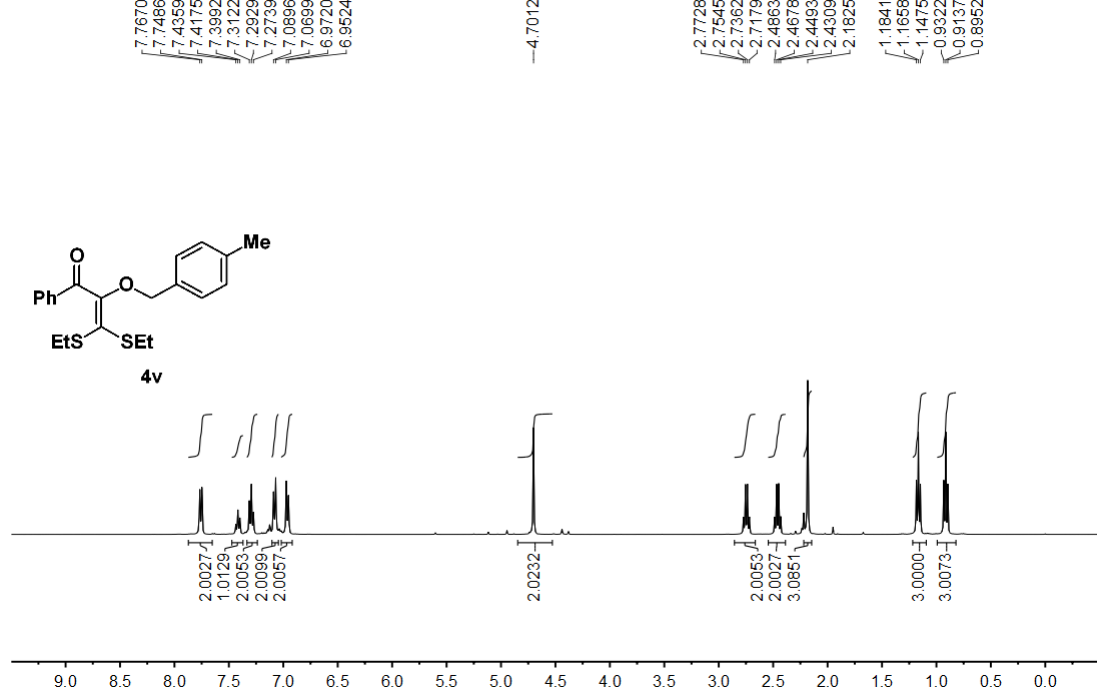
LZQ-885

C13CPD CDC13 {D:\NMR400\203} 36



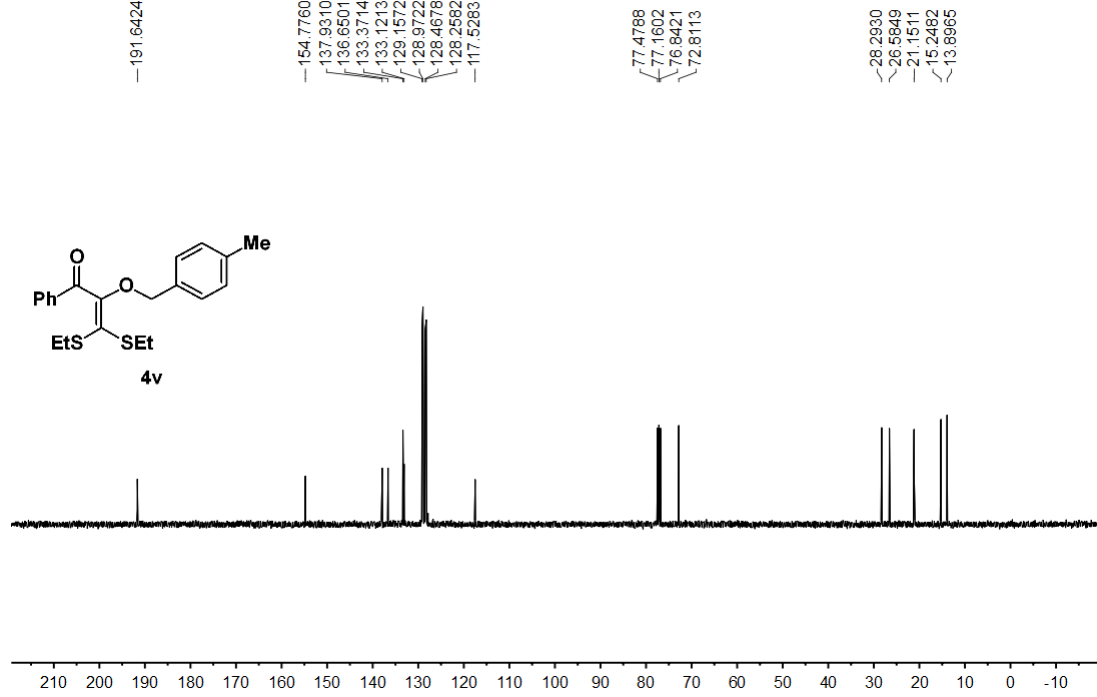
LZQ-469

PROTON CDC13 {D:\NMR400\203} nmr 45



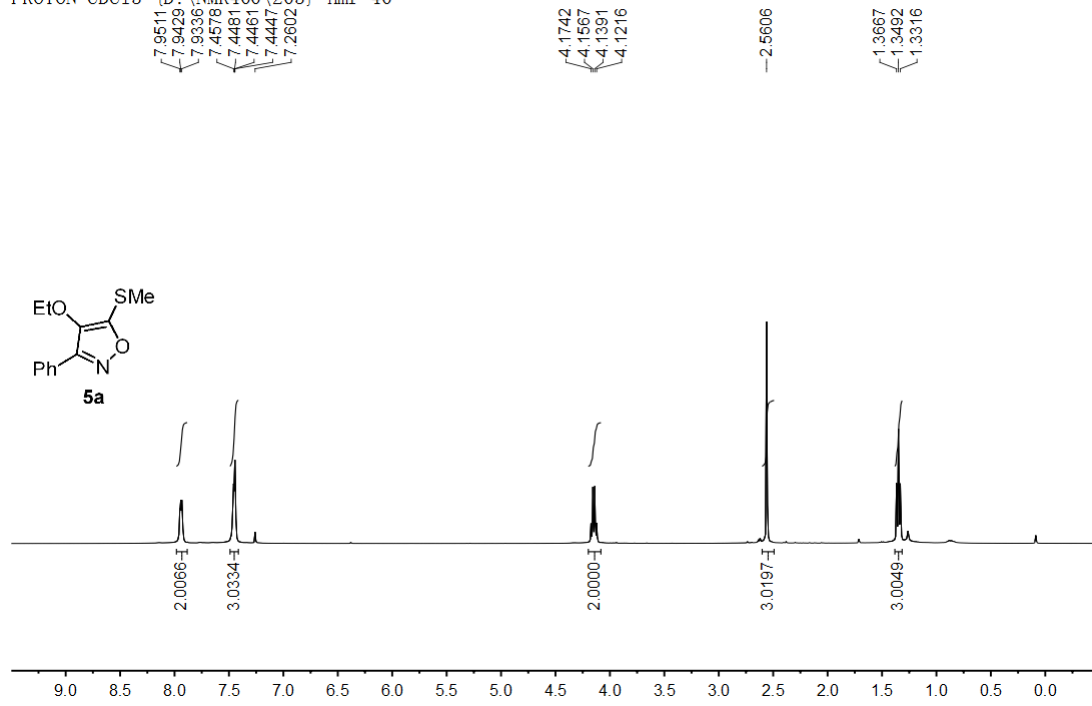
LZQ-469

C13CPD CDC13 {D:\NMR400\203} nmr 45



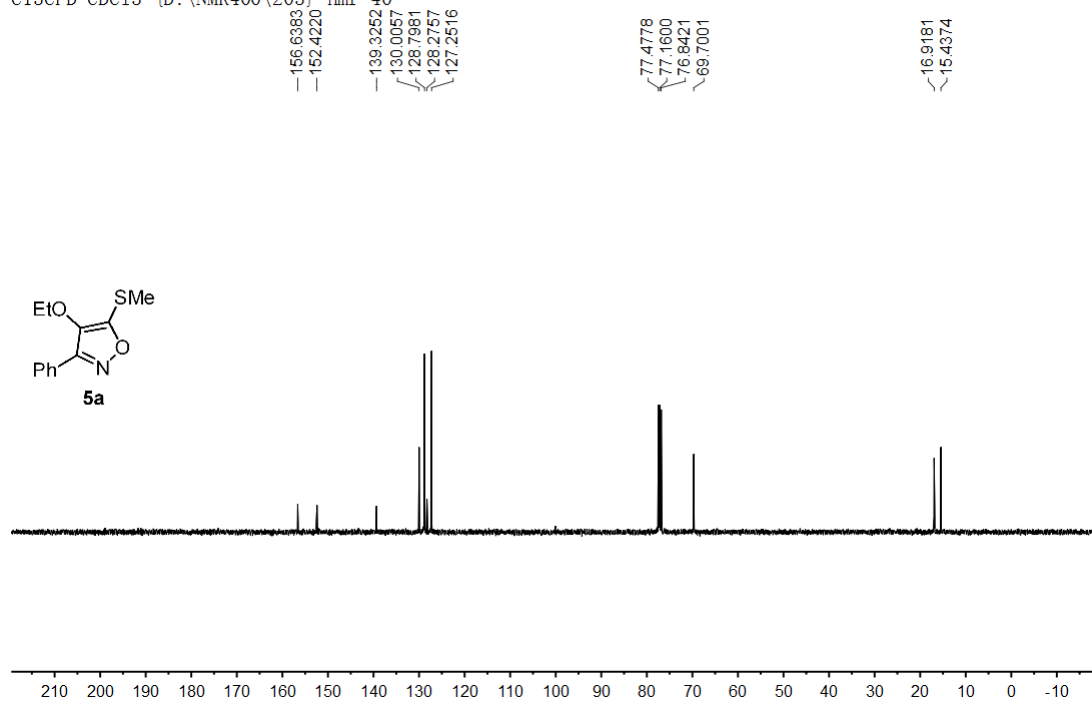
LZQ-512

PROTON CDC13 {D:\NMR400\203} nmr 40



LZQ-512

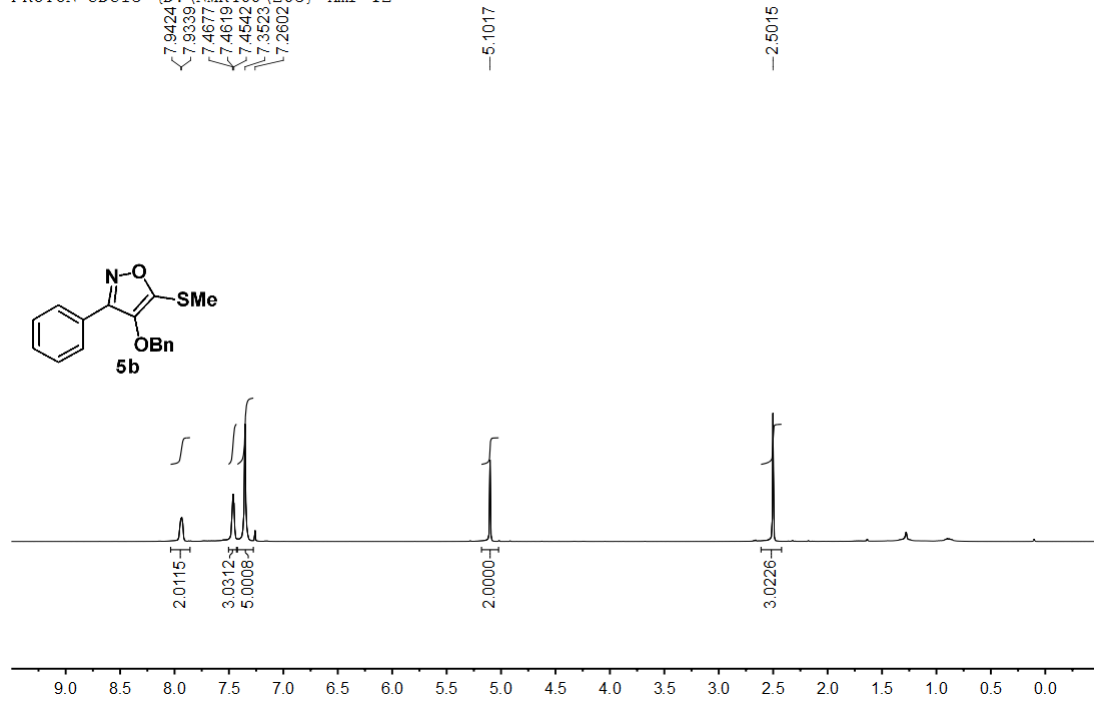
C13CPD CDC13 {D:\NMR400\203} nmr 40





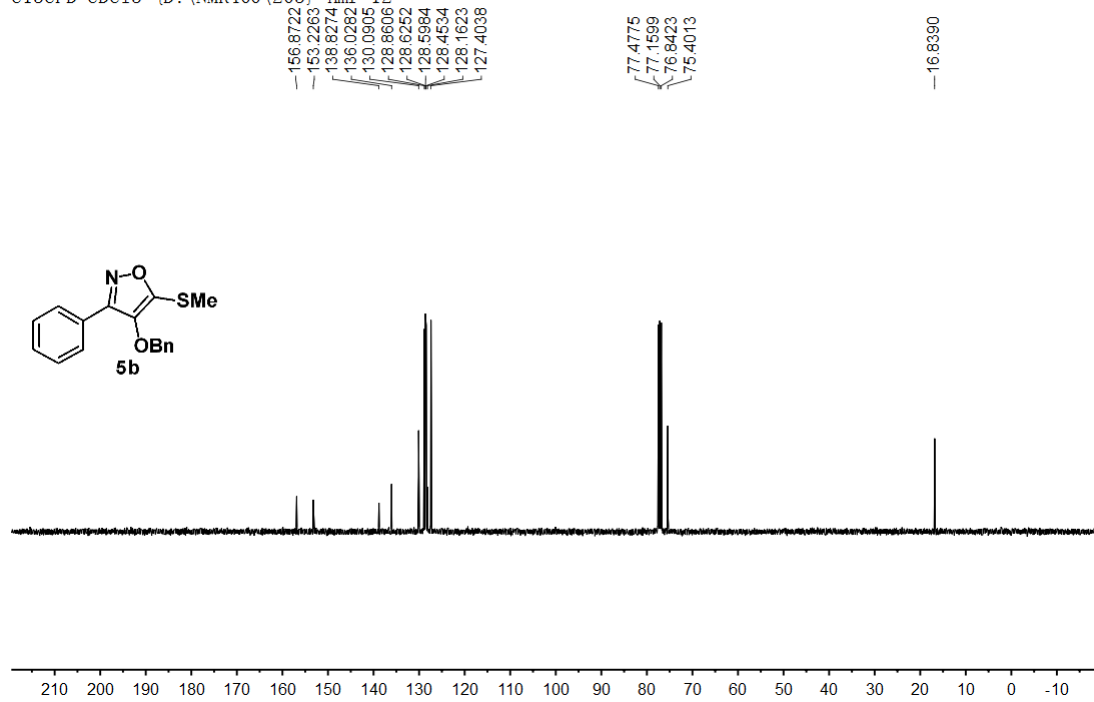
LZQ-513

PROTON CDC13 {D:\NMR400\203} nmr 12



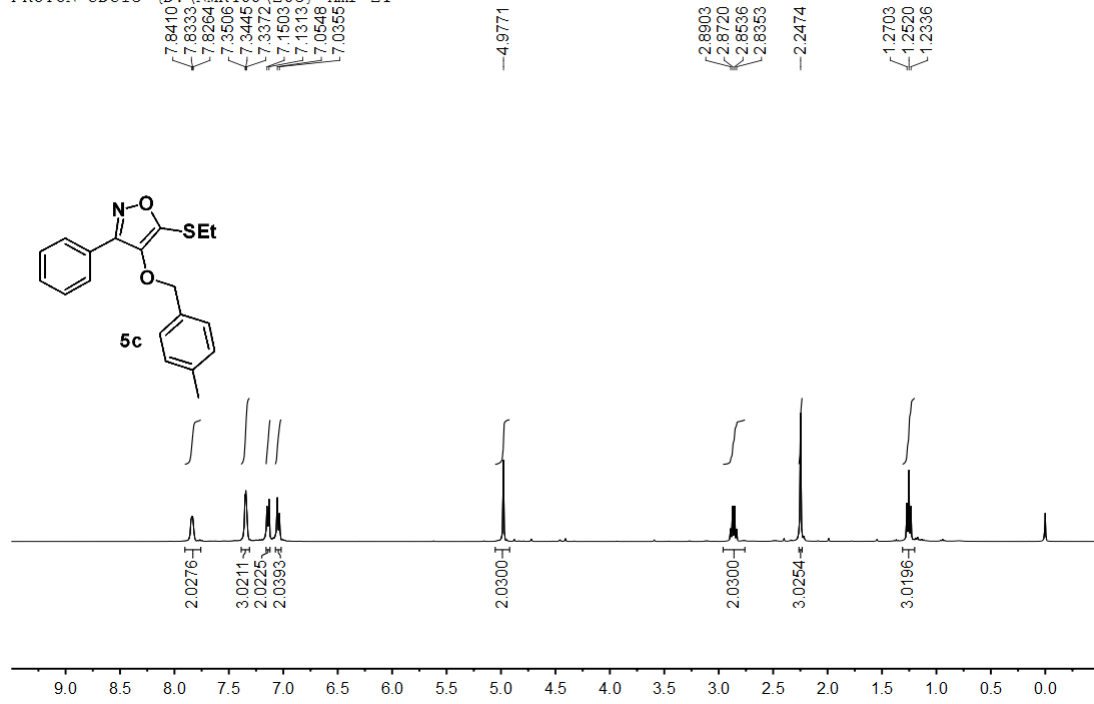
LZQ-513

C13CPD CDC13 {D:\NMR400\203} nmr 12



lzq-514-s

PROTON CDC13 {D:\NMR400\203} nmr 21



lzq-514-s

C13CPD CDC13 {D:\NMR400\203} nmr 21

