Supporting Information

Efficient Synthesis of 6-Membered Cyclic Monothiocarbonates from Halohydrin and Carbonyl Sulfide

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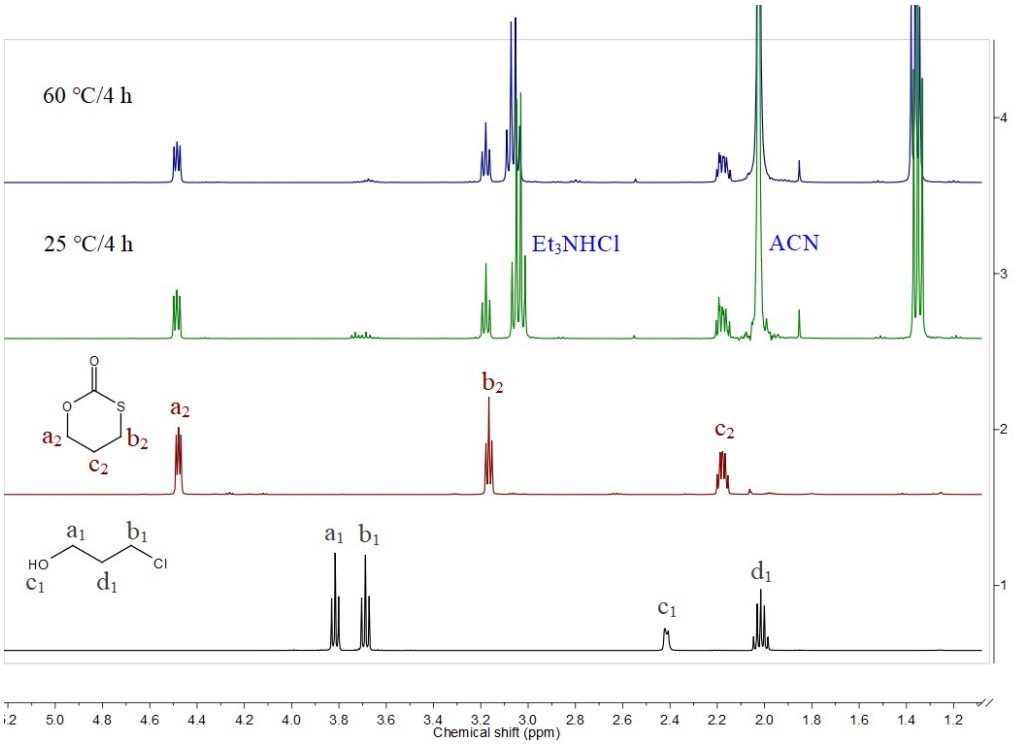


Fig. S1 Stacked partial ^{1}H NMR spectra of 3-chloro-1-propanol, 1,3-oxathian-2-one (**1b**), crude products of Table 1 entries 1 and 3 in $CDCl_3$.

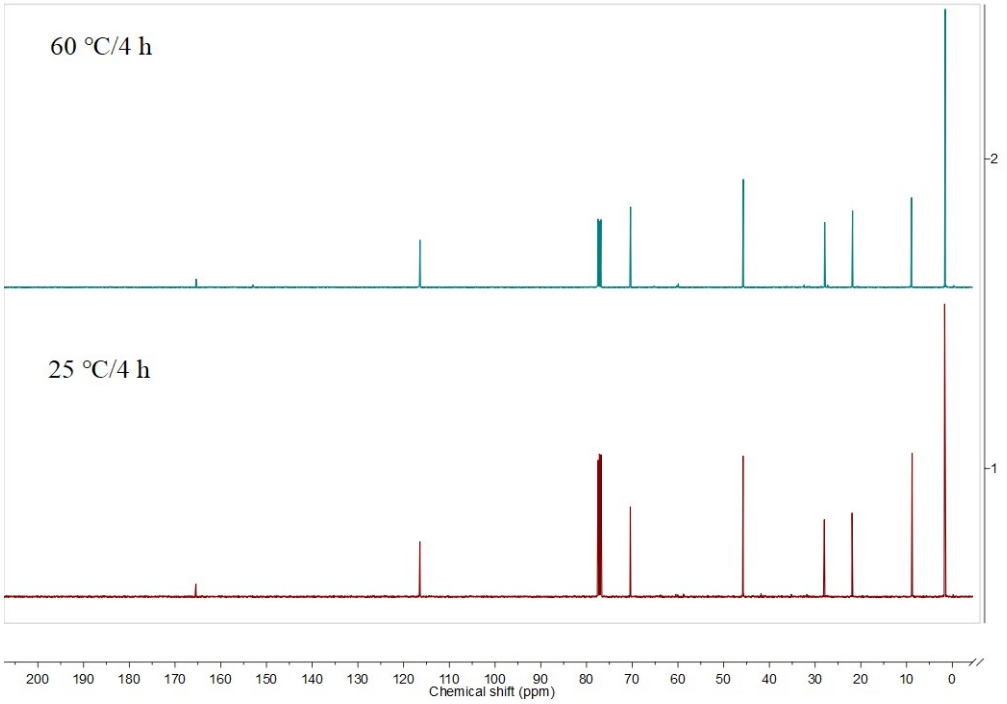


Fig. S2 Stacked ^{13}C NMR spectra of the crude products of Table 1 entries 1 and 3 in $CDCl_3$.

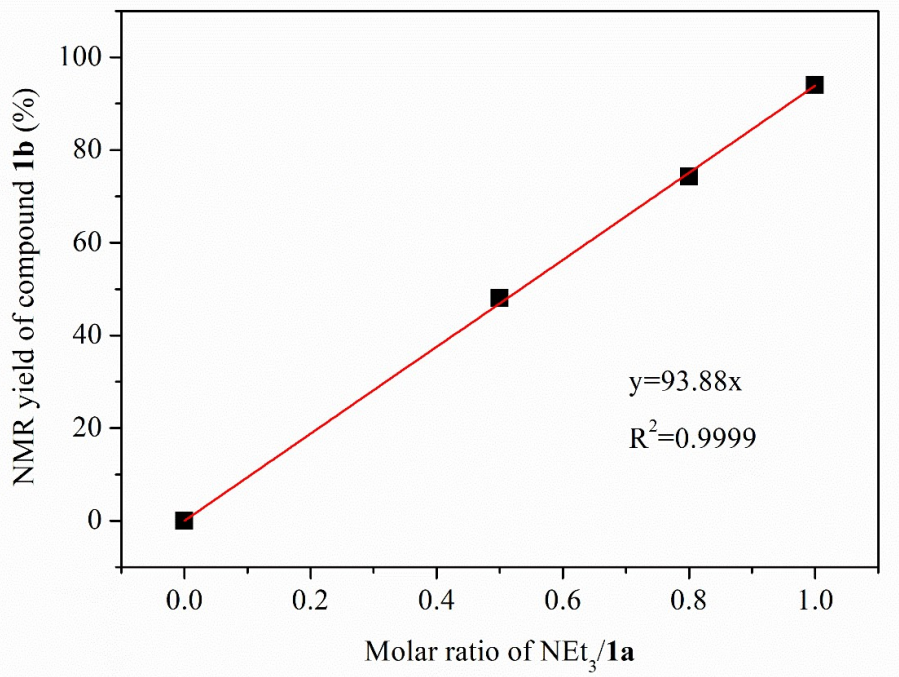


Fig. S3 The relationship between the yield of **1b** and the amount of NEt_3.

General Information

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AVANCE III 600M spectrometer with chloroform-*d* (CDCl3) as solvent. The peaks were internally referenced to TMS (0.00 ppm). IR spectra were obtained using a ThermoFisher iS50 spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (Agilent 6545 Q-TOF LC/MS). Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification.

General Experimental Procedure

General procedure for the preparation of 1,3-halohydrins

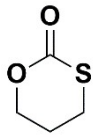
The halogenating reaction of 1,3-diols were performed in a flask using gaseous HCl in the presence of adipic acid. In a typical experiment: 2-methylpropane-1,3-diol (100.0 g) and adipic acid (5.0 g) were added into a 250 mL three-necked flask with a magnetic stirrer. The flask was placed in an oil bath and heated to 120 ^{o}C. Then gaseous HCl produced by adding concentrated sulfuric acid dropwise to sodium chloride (15~20 drops per minute) was introduced into the flask for 10 hours. After reaction, the mixture was cooled to room temperature and neutralized with sodium carbonate, and was filtered. The filtrate was then distillated in vacuum to give the target product 3-chloro-2-methyl-1-propanol (**3a**, collecting fractions at 70~75 ^{o}C, 42.1 g, 35% yield).

General procedure for the reaction of COS with 1,3-halohydrins

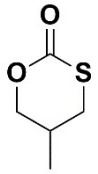
The coupling reactions of carbonyl sulfide (COS) and 1,3-halohydrins were performed in a 10 mL autoclave equipped with a magnetic stirrer and a pressure gauge. In a typical experiment, 3-chrolo-1-propanol (0.47 g, 5 mmol), triethylamine (0.56 g, 5.5 mmol), and acetonitrile (3.5 mL, [**1a**] ~1 M) were added into the autoclave. Then COS (0.6 g, 10 mmol) was purged into the sealed autoclave and quantified by weighting. The reaction was carried out at 25 °C for 10 h with continuous stirring. Then, the autoclave was cooled, and excess COS was released. The residue was purified by

fractional distillation or column chromatography to give the corresponding 6-membered cyclic thiocarbonates.

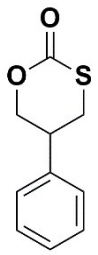
Characterization Data for All Products



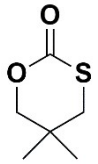
1,3-oxathian-2-one (**1b/2b**). White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.50-4.45 (m, 2H), 3.16 (t, J = 6.3 Hz, 2H), 2.21-2.14 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.5, 70.5, 28.2, 22.2. IR: 1686, 1660, 1434, 1396, 1215, 1120, 1071, 999, 857, 640 cm^{-1}. HRMS (ESI): $[M + Na]^+$ calcd for $C_4H_6O_2S$: 140.9981; found: 140.9981.



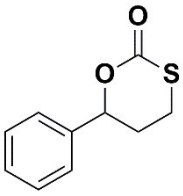
5-methyl-1,3-oxathian-2-one (**3b**). Colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.36 (s, 1H), 4.17 (s, 1H), 3.12 (d, J = 11.6 Hz, 1H), 2.93 (s, 1H), 2.34 (s, 1H), 1.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.7, 75.3, 34.5, 26.9, 15.7. IR: 1671, 1457, 1439, 1109, 1022, 999, 945, 869, 745, 701 cm^{-1}. HRMS (ESI): $[M + Na]^+$ calcd. for $C_5H_8O_2S$: 155.0137; found: 155.0136.



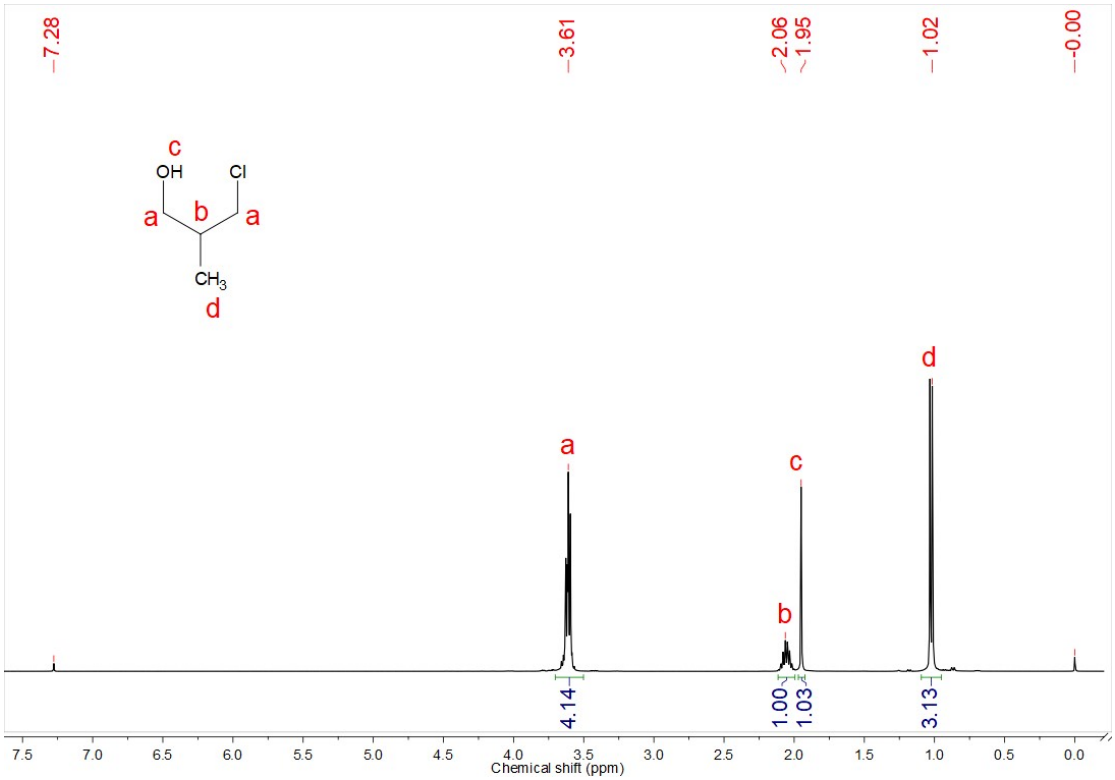
5-phenyl-1,3-oxathian-2-one (**4b**). White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (dd, J = 8.4, 6.8 Hz, 2H), 7.36-7.31 (m, 1H), 7.25 (dd, J = 8.2, 6.4 Hz, 2H), 4.59-4.48 (m, 2H), 3.49 (t, J = 11.4 Hz, 1H), 3.42 (tt, J = 11.3, 9.9, 3.8 Hz, 1H), 3.20 (ddd, J = 11.4, 4.5, 2.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.3, 137.9, 129.4, 128.4, 127.2, 74.3, 38.8, 33.8. IR: 1666, 1454, 1289, 1119, 1048, 1011, 850, 773, 729, 692 cm^{-1}. HRMS (ESI): $[M + Na]^+$ calcd for $C_{10}H_{10}O_2S$: 217.0294; found: 217.0296.



5,5-dimethyl-1,3-oxathian-2-one (**5b**). White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.09 (s, 2H), 2.94 (s, 2H), 1.20 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.8, 79.0, 40.3, 28.4, 23.7. IR: 1666, 1465, 1439, 1379, 1309, 1283, 1125, 1107, 1016, 919 cm^{-1}. HRMS (ESI): $[M + Na]^+$ calcd for $C_6H_{10}O_2S$: 169.0294; found: 169.0294.



6-phenyl-1,3-oxathian-2-one (**6b**). White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43-7.39 (m, 2H), 7.39-7.34 (m, 3H), 5.43 (dd, J = 9.9, 2.0 Hz, 1H), 3.31 (td, J = 11.5, 4.7 Hz, 1H), 3.08 (dt, J = 11.9, 4.5 Hz, 1H), 2.43 (dtd, J = 14.7, 4.5, 2.0 Hz, 1H), 2.31-2.17 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.9, 138.4, 128.9, 125.9, 82.8, 29.3, 27.0. IR: 1668, 1450, 1417, 1301, 1223, 1137, 1007, 923, 910, 749, 698 cm^{-1}. HRMS (ESI): [M + Na]$^{+}$ calcd for $C_{10}H_{10}O_2S$: 217.0294; found: 217.0295.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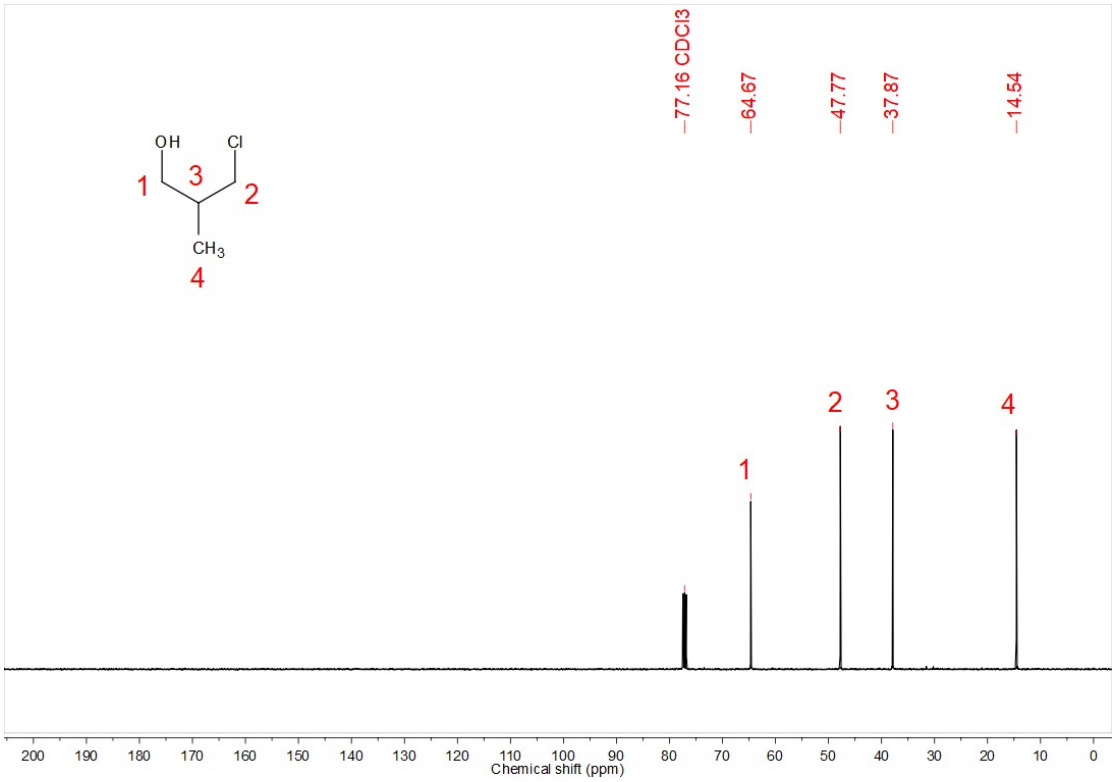
3.61
2.06
1.95
1.02
0.00
c
OH
Cl
a
b
a
CH3
d
d
a
c
b
4.14
1.00
1.03
3.13
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)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47.77
37.87
14.54
OH
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3
2
CH3
4
2
3
4
1
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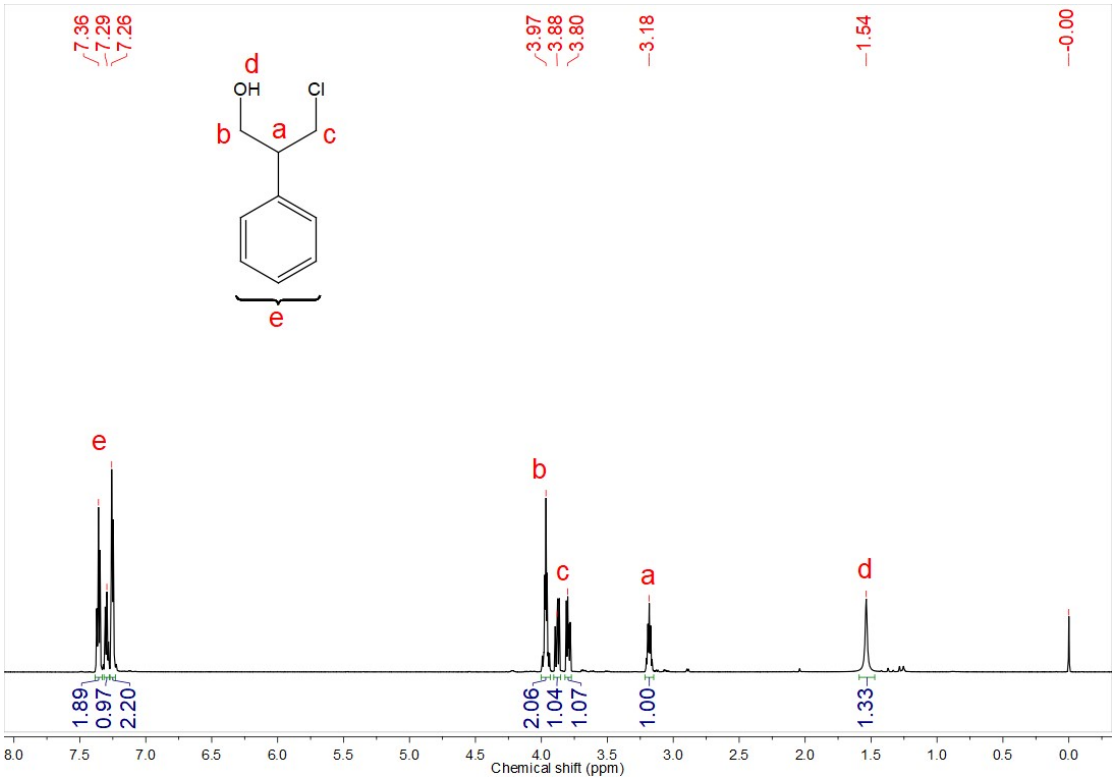
Chemical shift (ppm)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3.88
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1.54
0.00
d
OH
Cl
b
a
c
e
e
b
c
a
d
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2.20
2.06
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1.07
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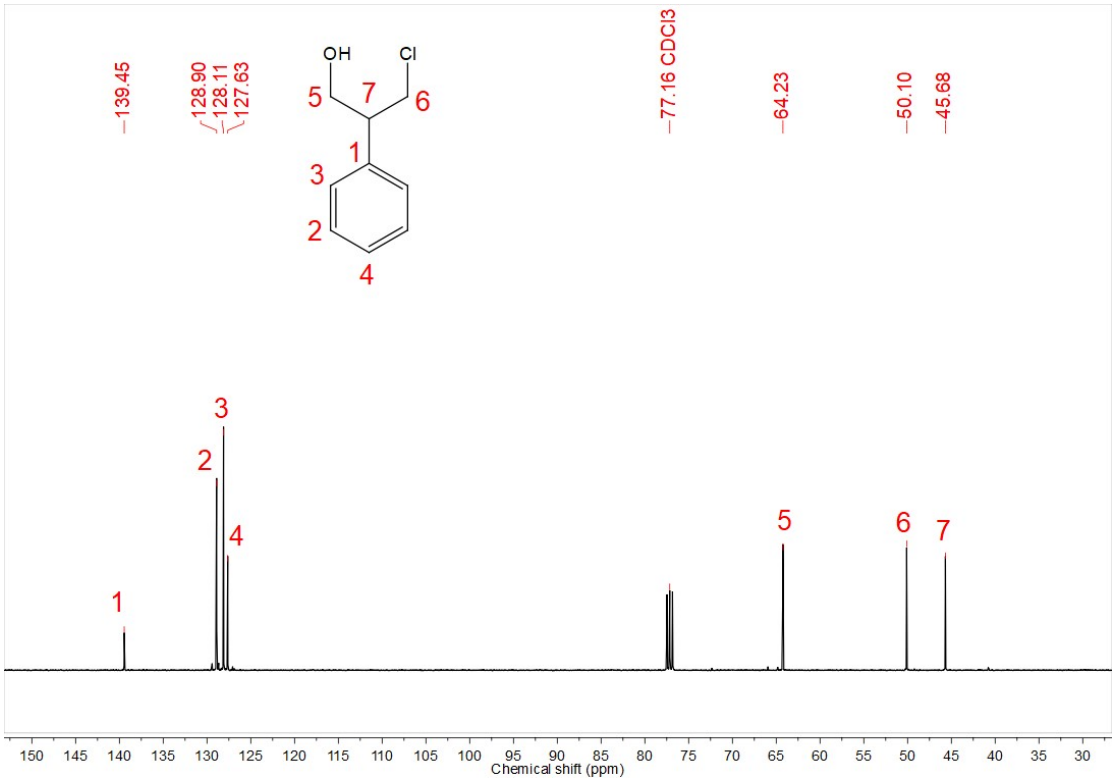
1.33
Chemical shift (ppm)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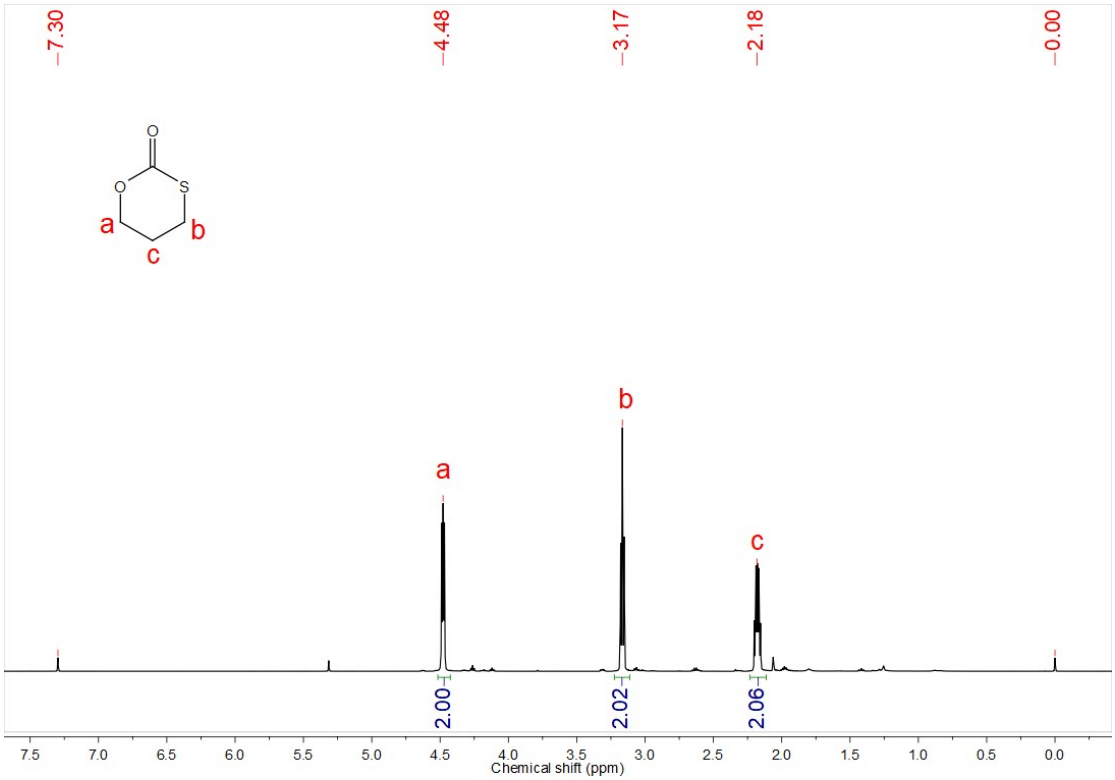
4
3
2
4
1
5
6
7
Chemical shift (ppm)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O
S
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b
c
a
b
c
2.00
2.02
2.06
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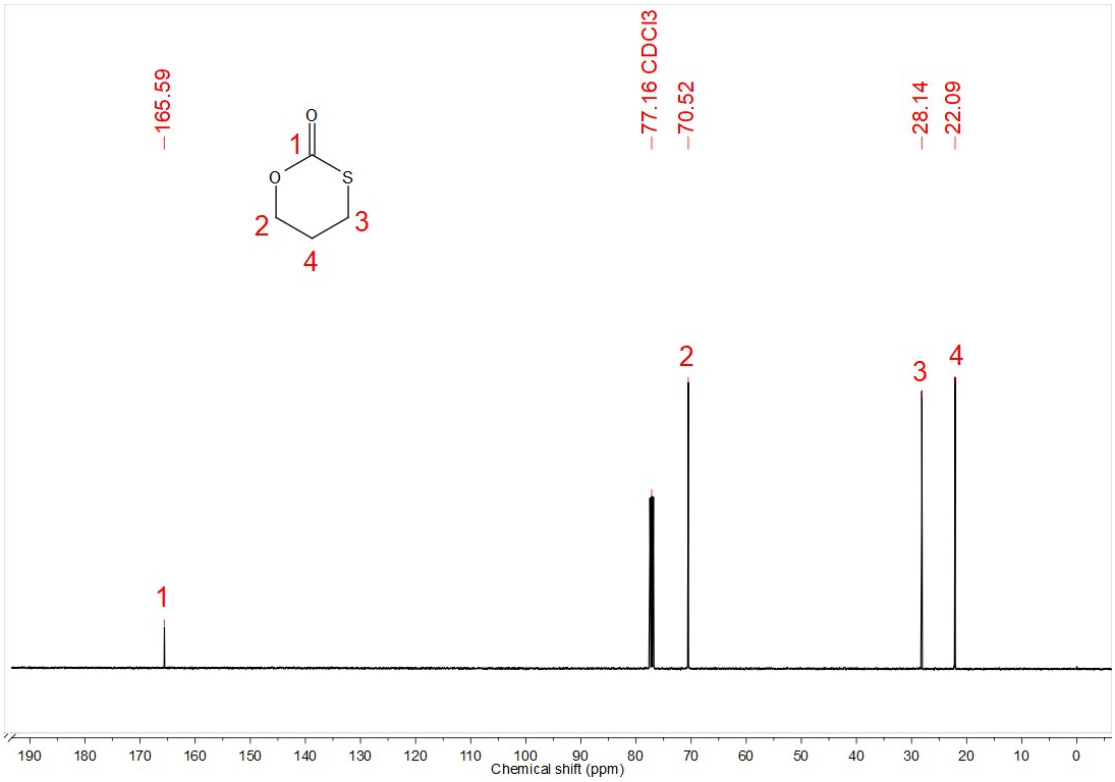
Chemical shift (ppm)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28.14
22.09
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1
O
S
2
3
4
1
2
3
4
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Chemical shift (ppm)

Fragmentor Voltage	Collision Energy	Ionization Mode
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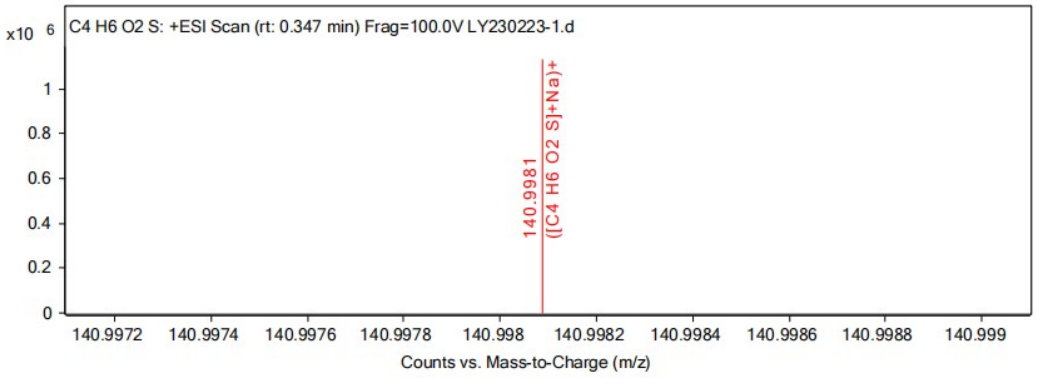

Formula Calculator Element Limits

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O	0	10
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S	1	1

Formula Calculator Results

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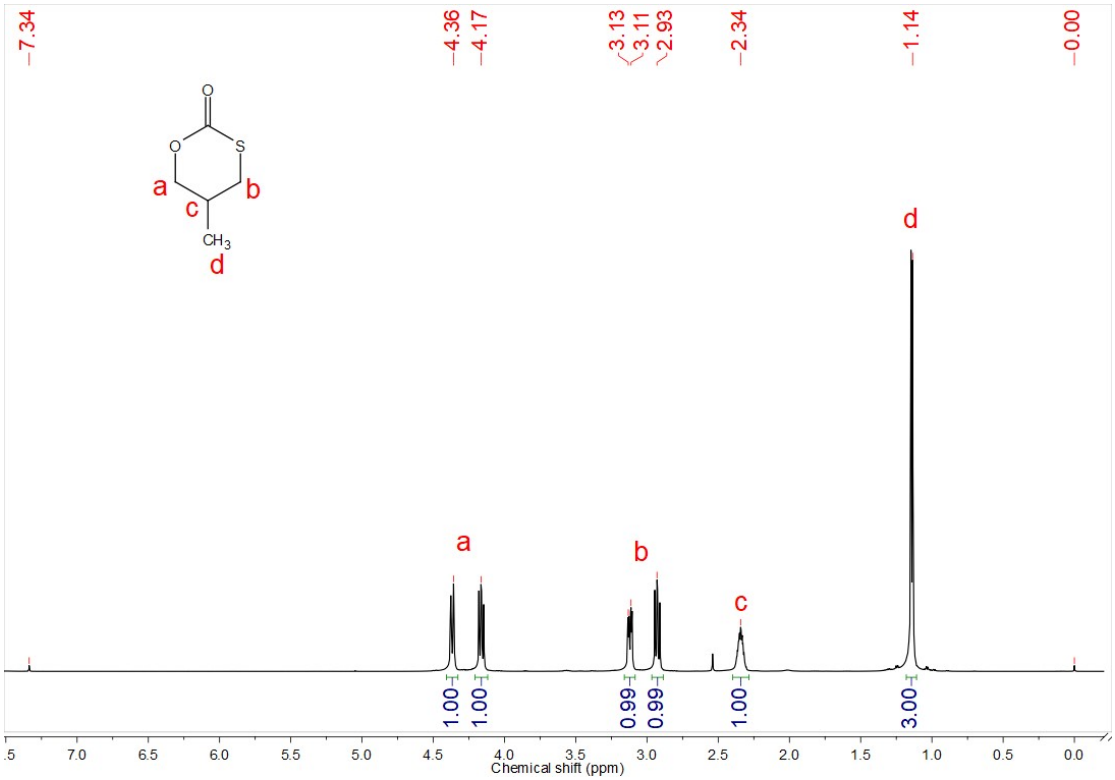
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4.17
3.13
3.11
2.93
2.34
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a
b
c
d
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1.00
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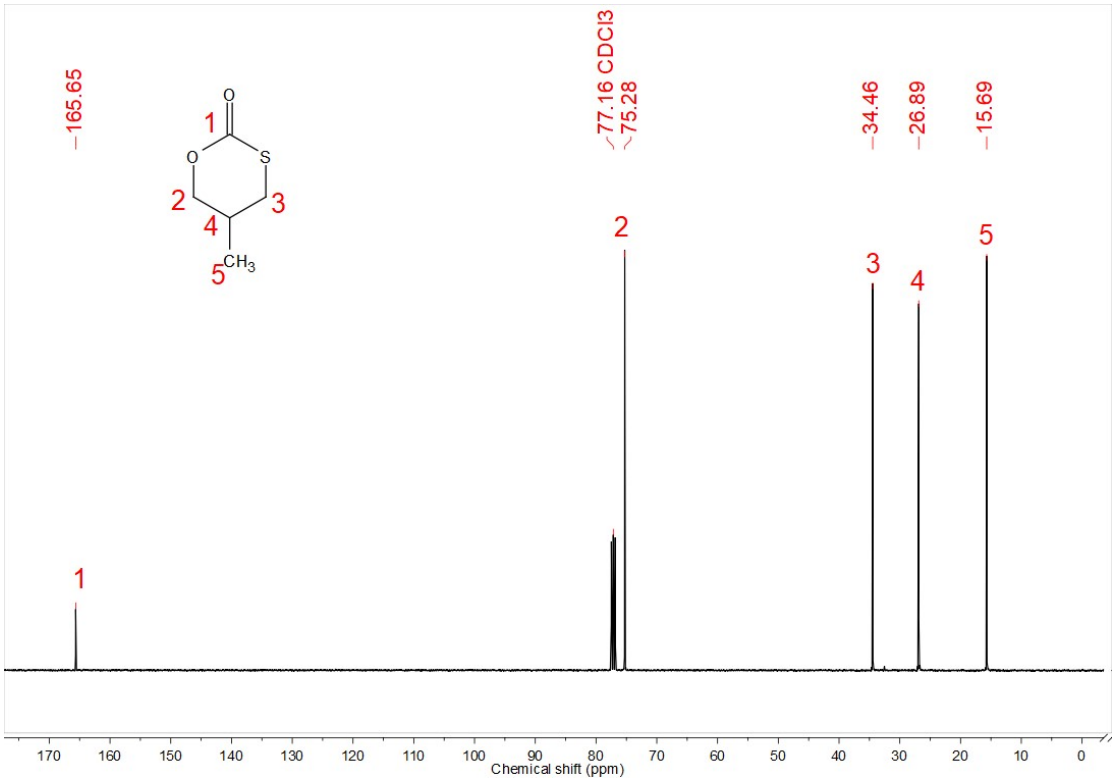
0.99
1.00
3.00
Chemical shift (ppm)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4
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Chemical shift (ppm)

Fragmentor Voltage	Collision Energy	Ionization Mode
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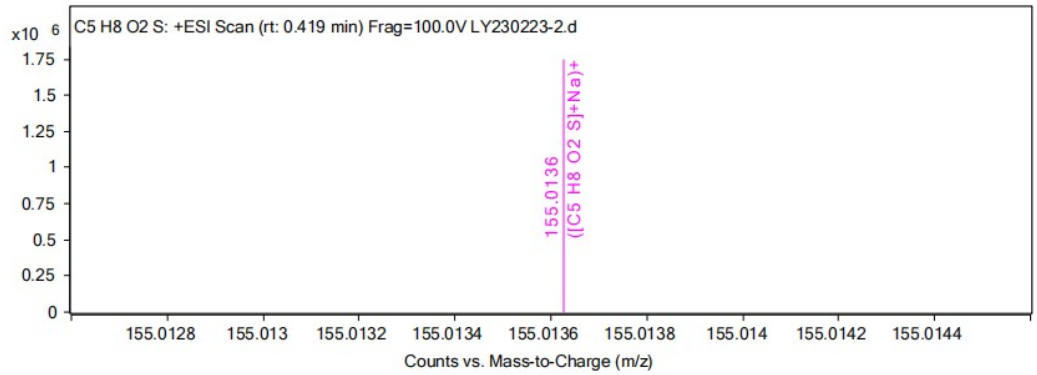

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S	1	1

Formula Calculator Results

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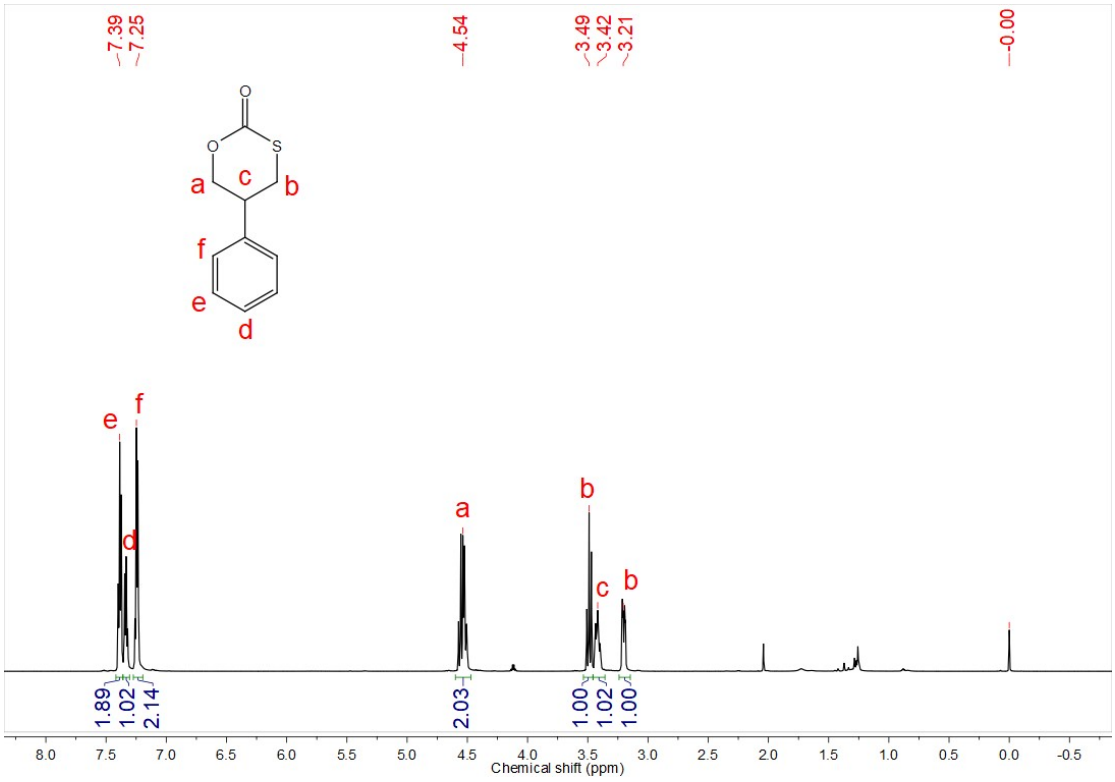
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3.42
3.21
0.00
O
O
S
a
c
b
f
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d
e
f
d
a
b
c
b
1.89
1.02
2.14
2.03
1.00
1.02
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
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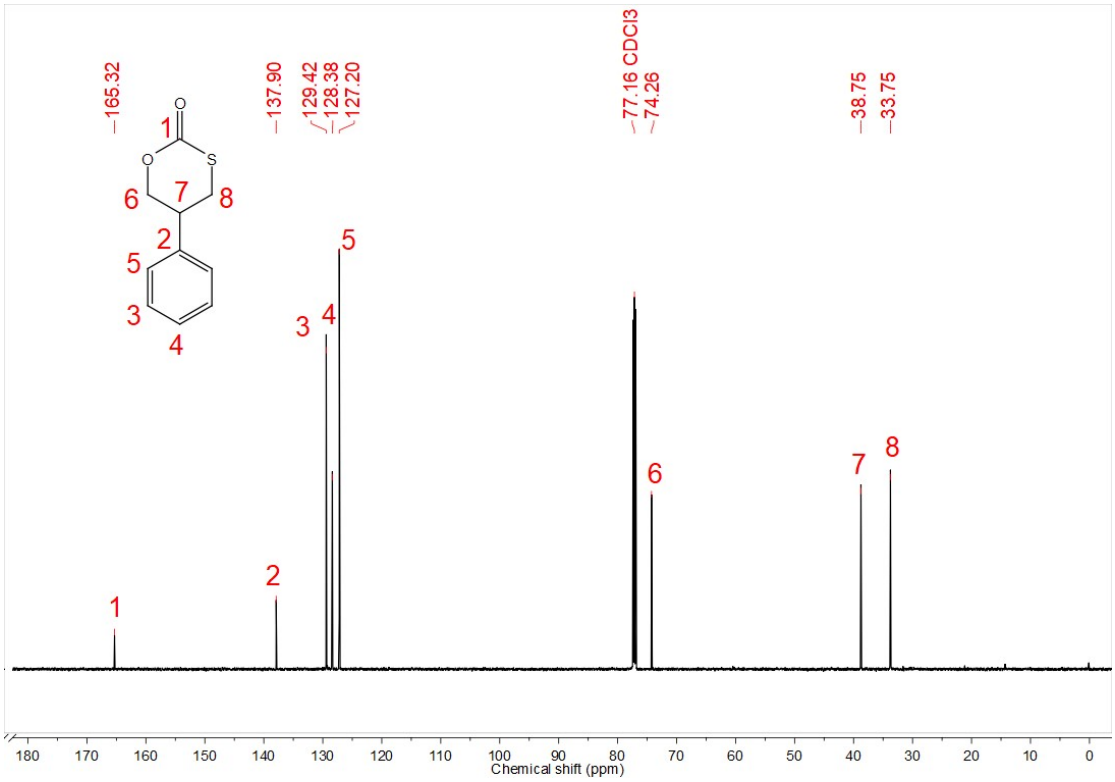
-0.5
Chemical shift (ppm)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127.20
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74.26
38.75
33.75
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7
8
2
5
3
4
1
2
3
4
5
6
7
8
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
20
10
0
Chemical shift (ppm)

Fragmentor Voltage	Collision Energy	Ionization Mode
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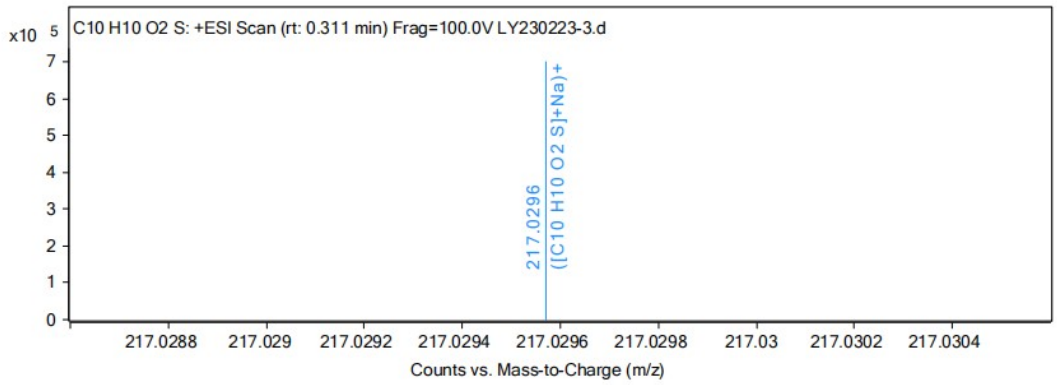

Formula Calculator Element Limits

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O	0	10
N	0	5
S	1	1

Formula Calculator Results

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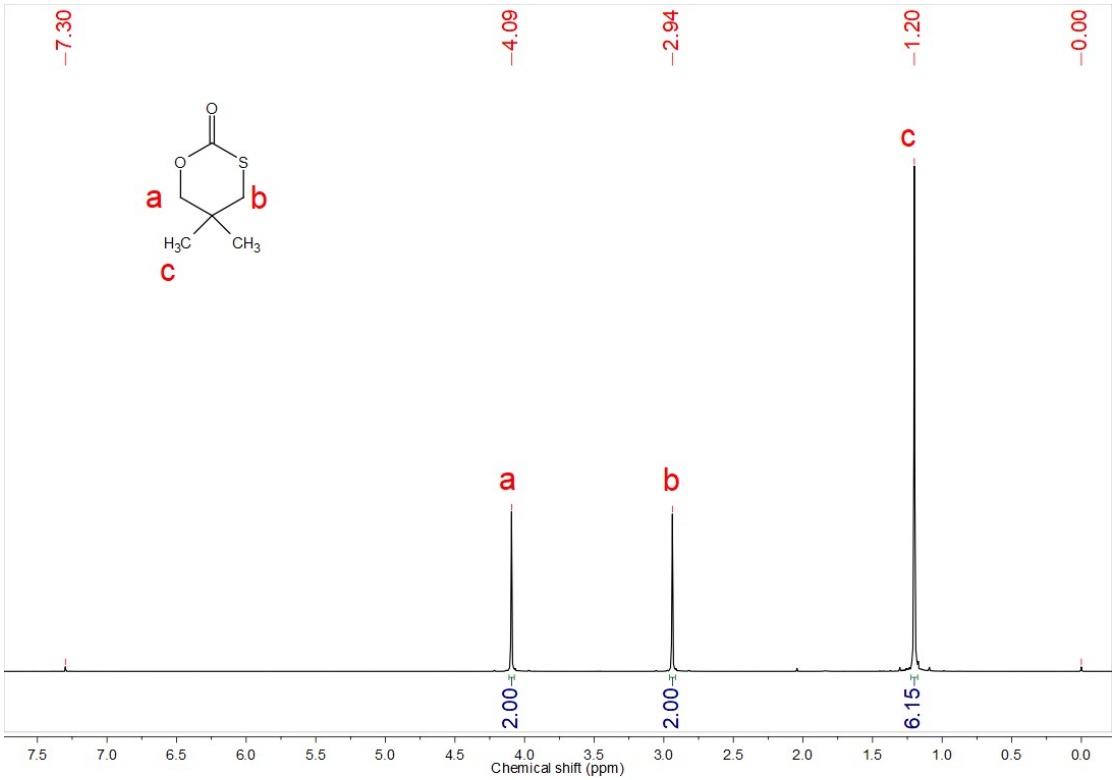
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O
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b
H3C
CH3
c
c
a
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2.00
6.15
7.5
7.0
6.5
6.0
5.5
5.0
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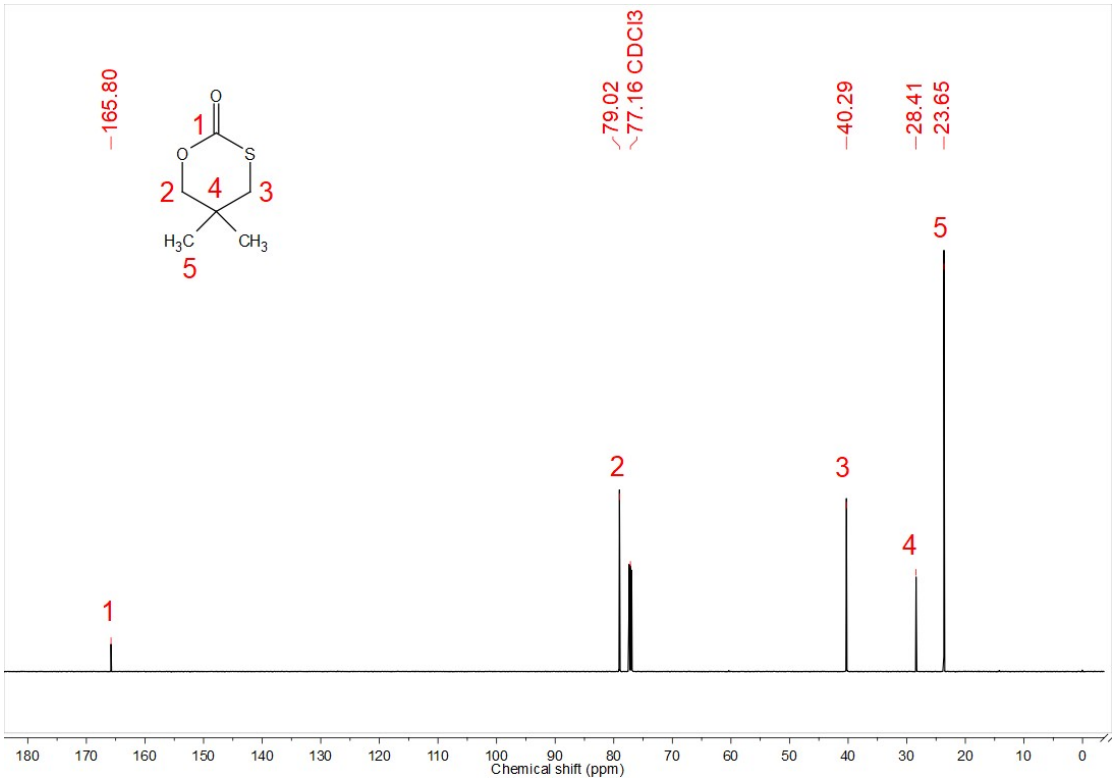
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)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40.29
28.41
23.65
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O
S
2
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H3C
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5
5
2
3
4
1
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Fragmentor Voltage	Collision Energy	Ionization Mode
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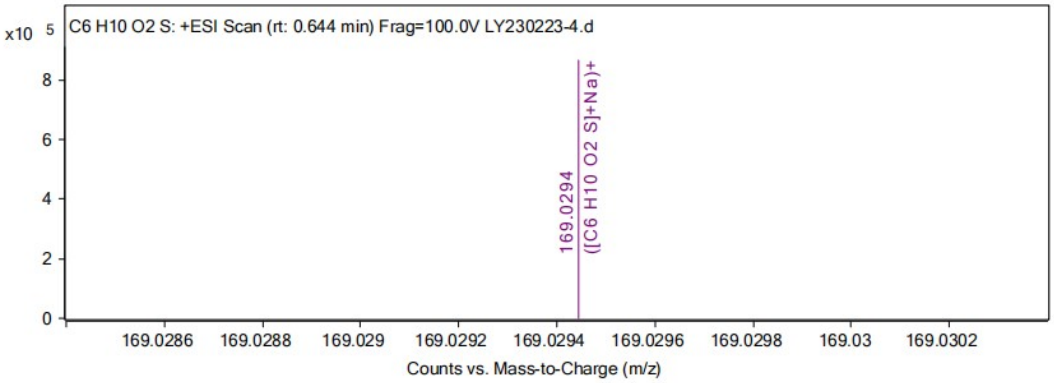

Formula Calculator Element Limits

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O	0	10
N	0	5
S	1	1

Formula Calculator Results

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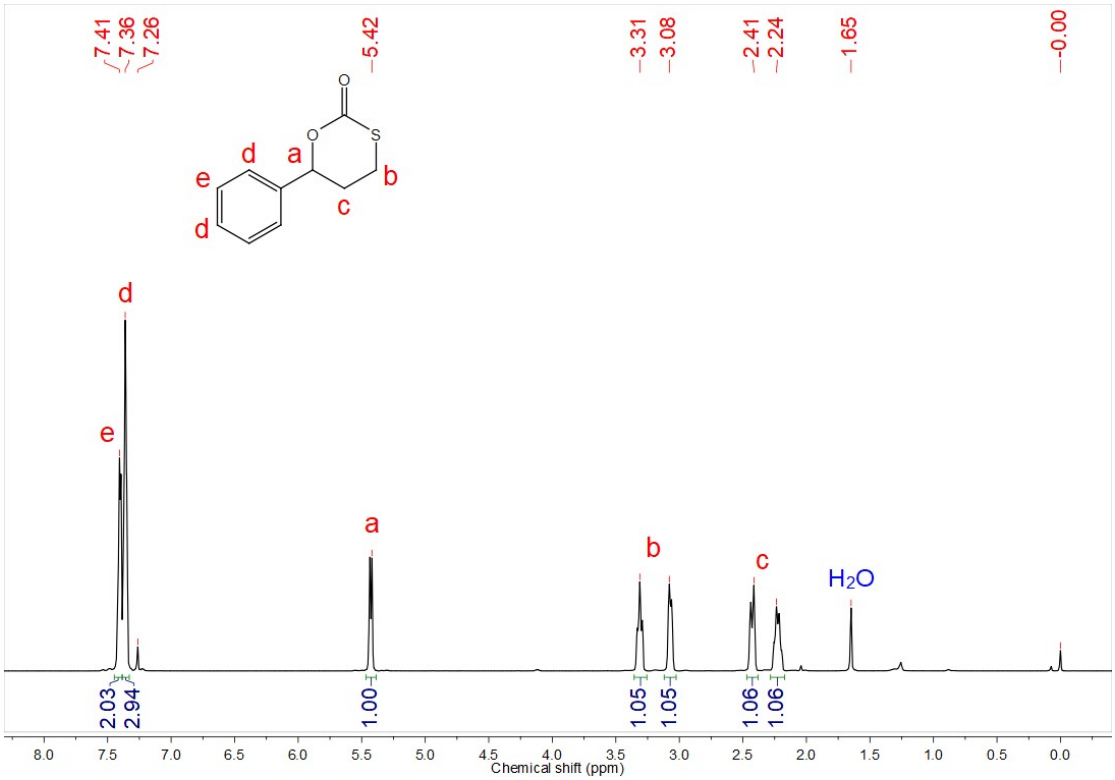
--- End Of Report ---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5.42
3.31
3.08
2.41
2.24
1.65
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O
S
d
a
b
c
e
d
d
e
a
b
c
H2O
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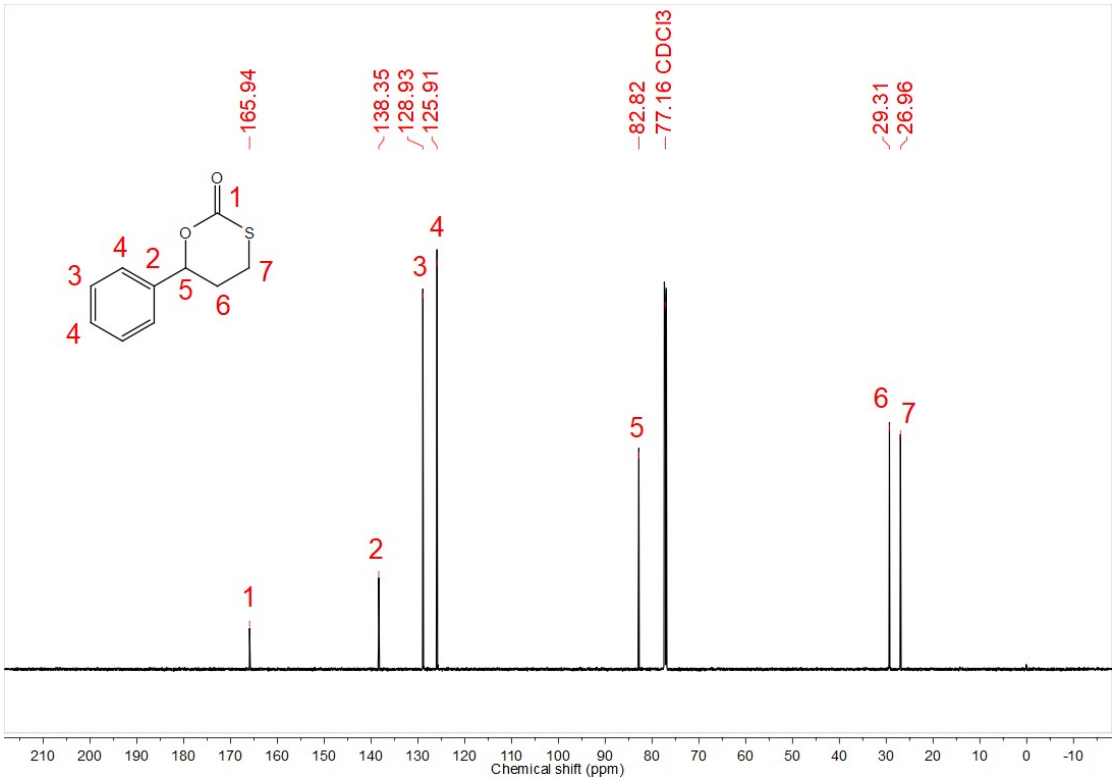
2.94
1.00
1.05
1.05
1.06
1.06
Chemical shift (ppm)


165.94
138.35
128.93
125.91
82.82
77.16 CDCl3
29.31
26.96
O
O
S
1
2
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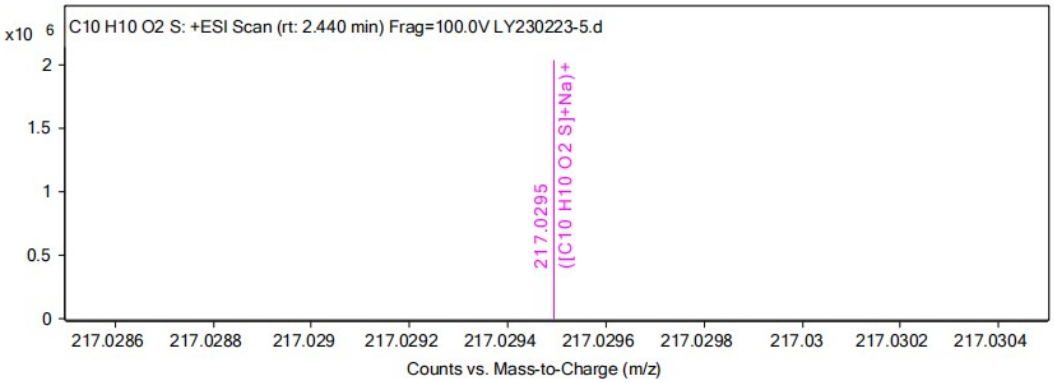
5
6
7
4
3
4
1
2
3
4
5
6
7
Chemical shift (ppm)

Fragmentor Voltage	Collision Energy	Ionization Mode
100	0	ESI



Formula Calculator Element Limits

Element	Min	Max
C	0	50
H	0	100
O	0	10
N	0	5
S	1	1

Formula Calculator Results

Formula	Best	Measured Mass	Tgt Mass	Diff (ppm)	Score
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--- End Of Report ---