Electronic Supplementary Information for

The effect of ring size on the selective carboxylation of cycloalkene oxides

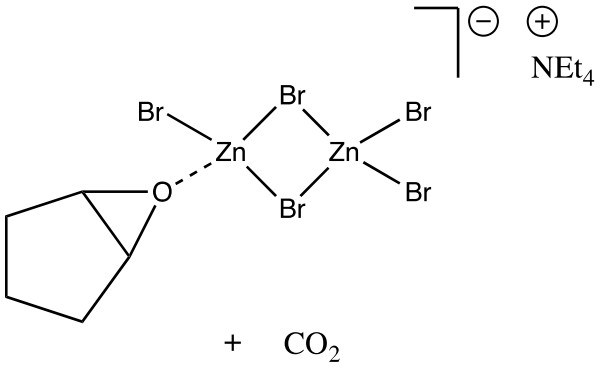
Raiedhah Alsaiari[a], Luke T. Perrott[a], Ewa Nowicka[a], Rebecca V. Engel[a], Peter J. Miedziak[a], Simon A. Kondrat[a], Jennifer K. Edwards[a], David J. Willock[a]* and Graham J. Hutchings[a]*

[a].Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK.
* Correspondence to Graham J. Hutchings or David J. Willock
Tel: +44 29 2087 4059, Fax: (+44) 2920-874-030, E-mail: hutch@cardiff.ac.uk
Tel: +44 29 2087 4779, Fax: (+44) 2920-874-030, E-mail: willockdj@cardiff.ac.uk

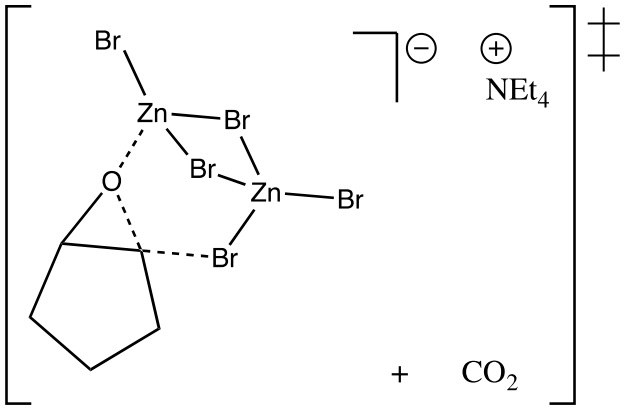
Calculated structures

Co-ordinates for all optimised structures and transition states have been uploaded as Car_Files.rar along side this Supplementary Information document.

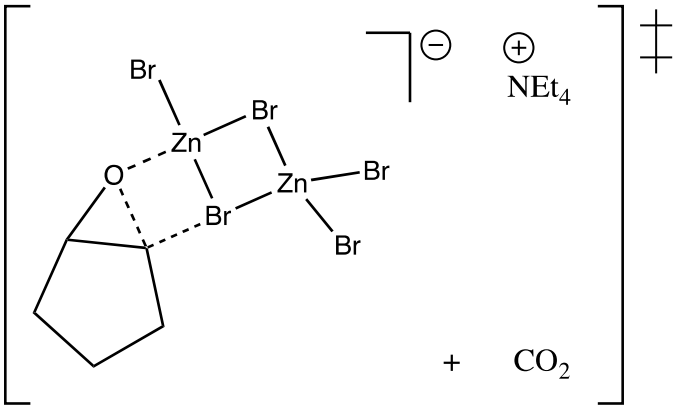
The associated research data can be found at http://doi.org/10.17035/d.2017.0038069018**.**



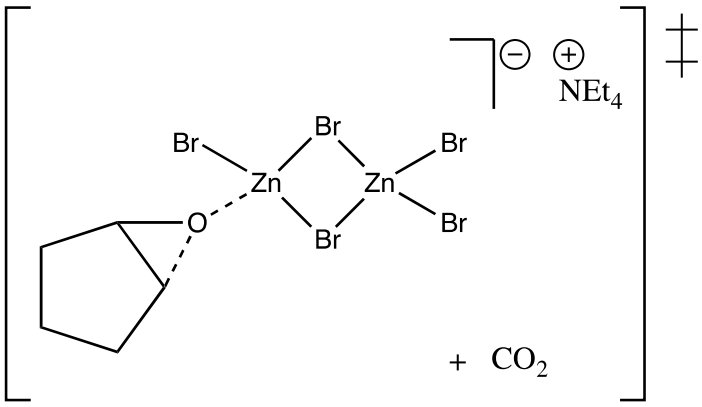
Int. 1



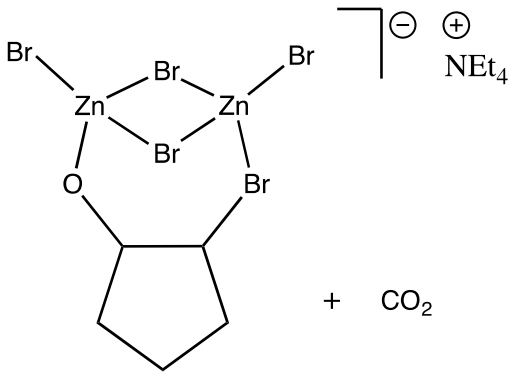
S_N2 TS-1t'



S_N2 TS-1b

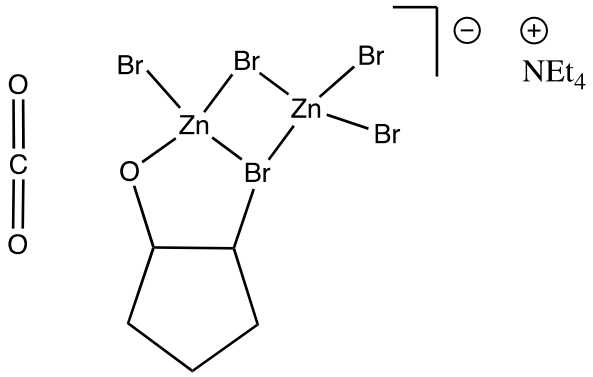


S_N1 TS-1t
S_N1 TS-1b



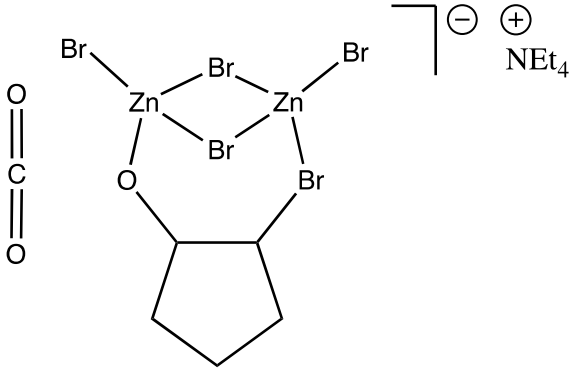
Int. 2t

Int. 2t'



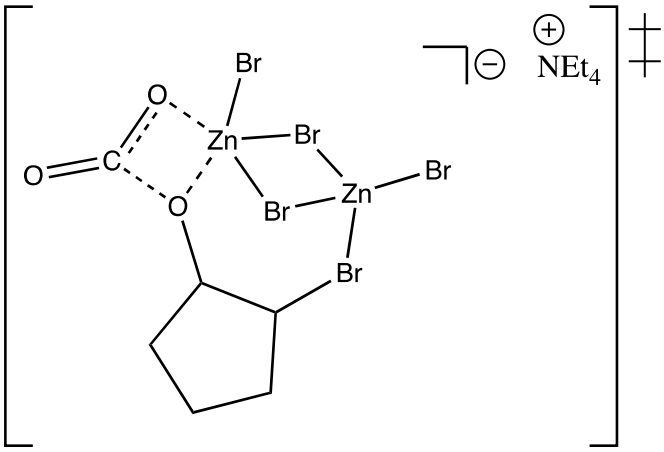
Int. 3b

Int. 3b'

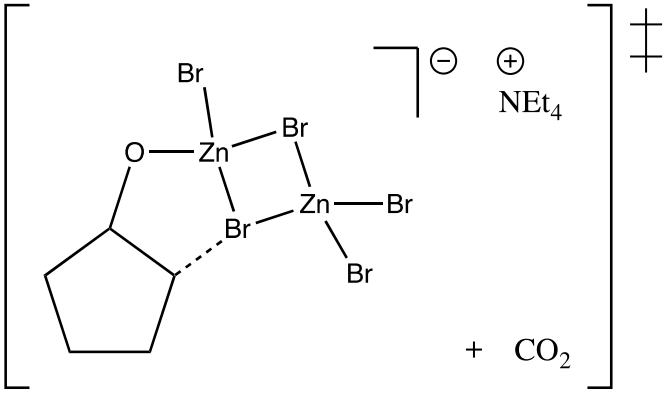


Int. 3t

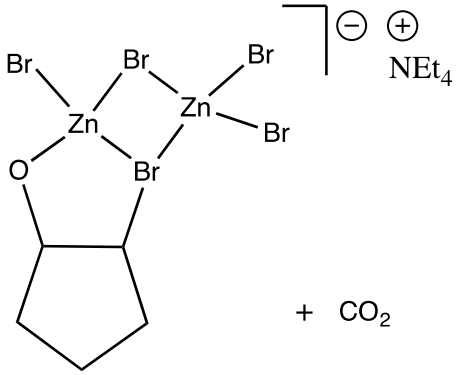
Int. 3t'



Int. 3t'

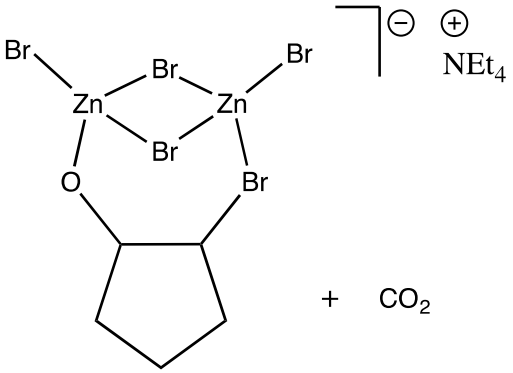


S_N1 TS-1b'



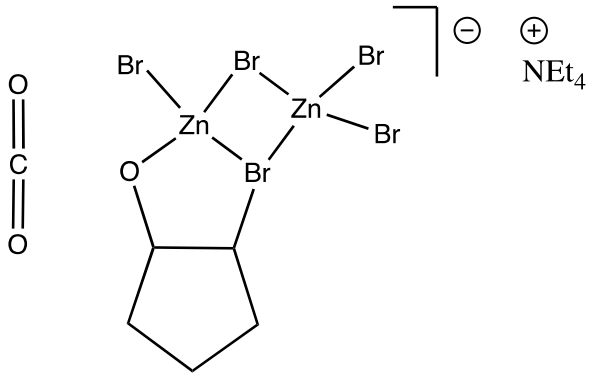
Int. 2b

Int. 2b'



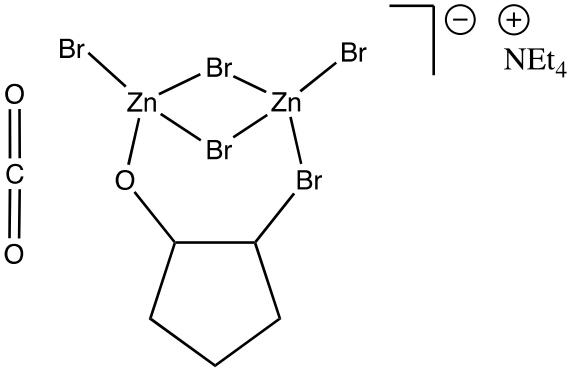
Int. 2t

Int. 2t'



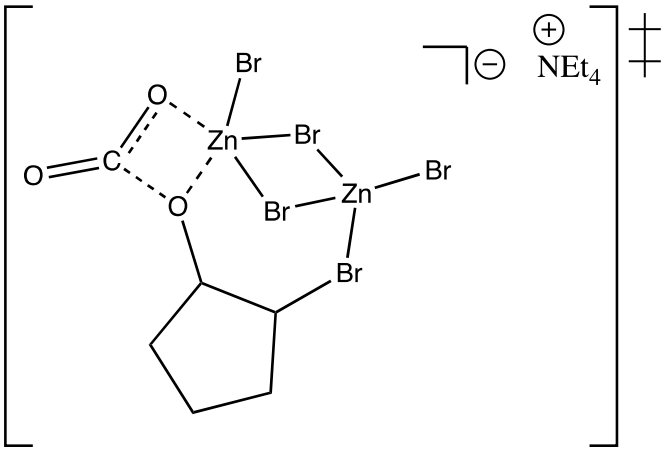
Int. 3b

Int. 3b'

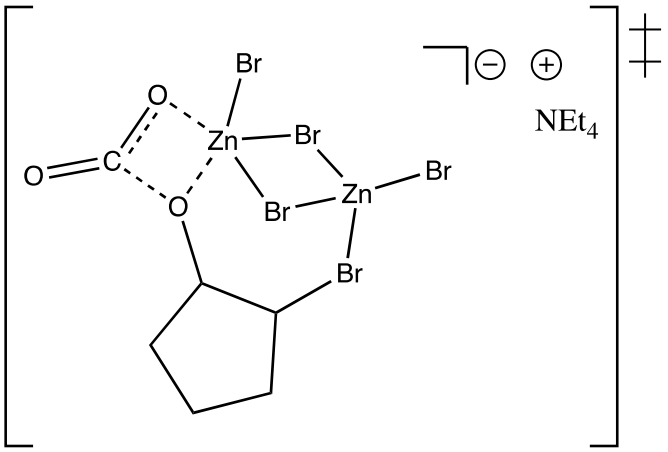


Int. 3t

Int. 3t'

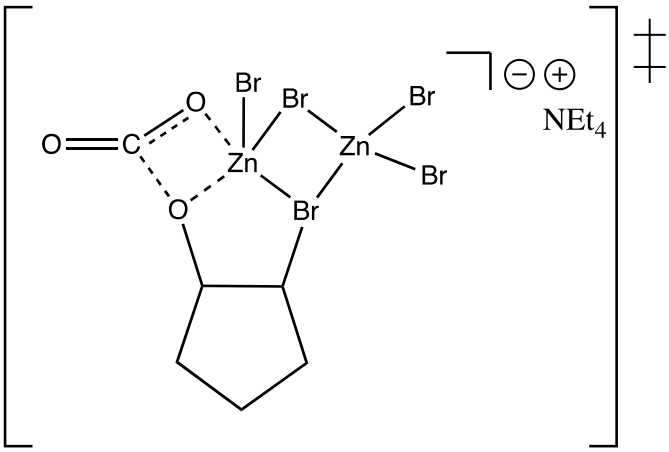


Int. 3t'

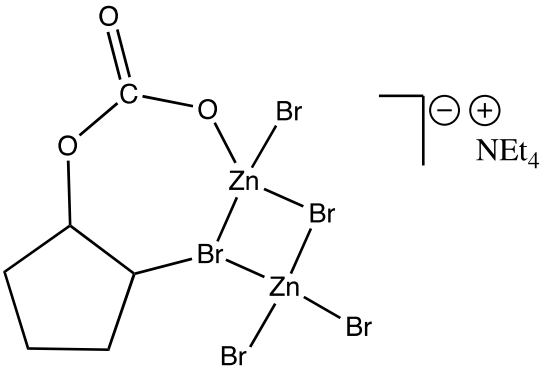


TS-2t

TS-2t'

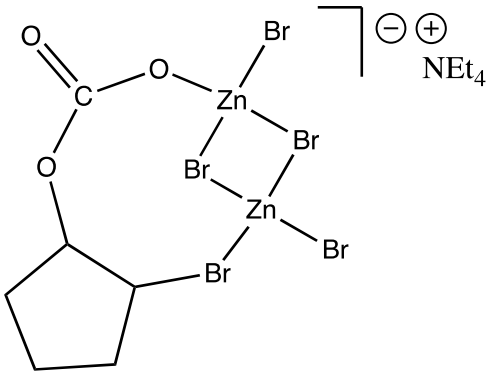


TS-2b



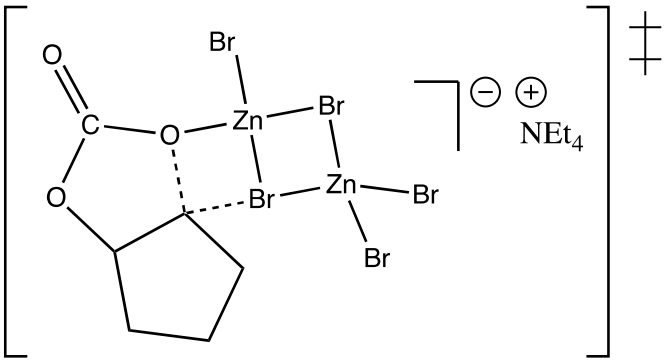
Int. 4b

Int. 4b'

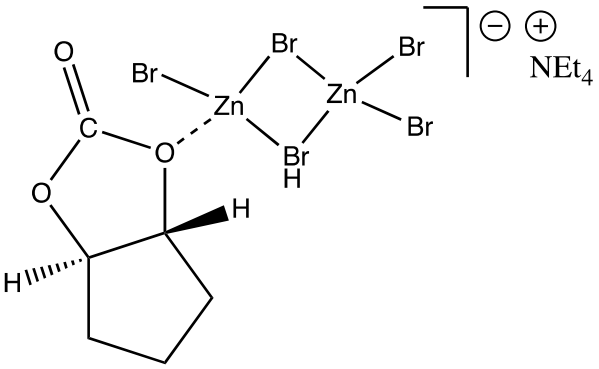


Int. 4t

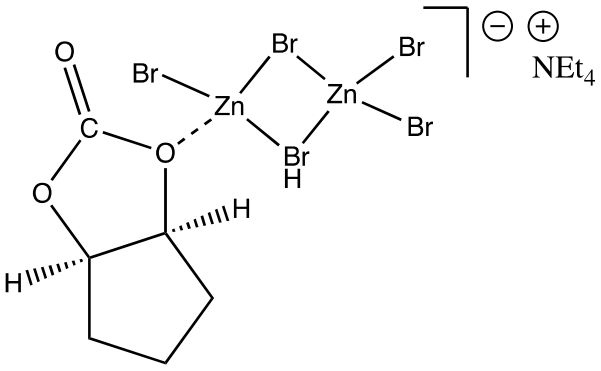
Int. 4t'



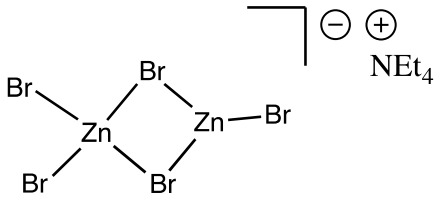
TS-3 (all)



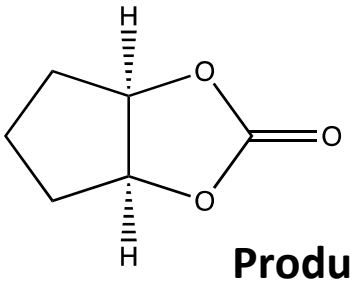
Int.5 - Trans



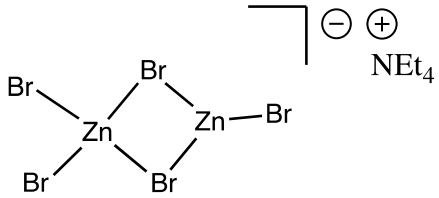
Int.5 – Cis



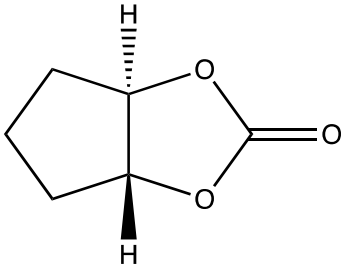
+



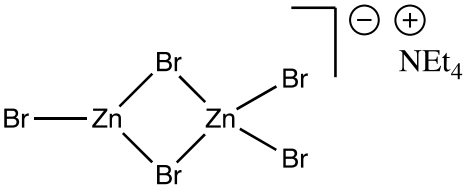
Product – Cis



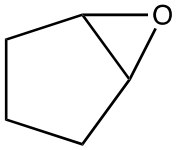
+



Product – Trans



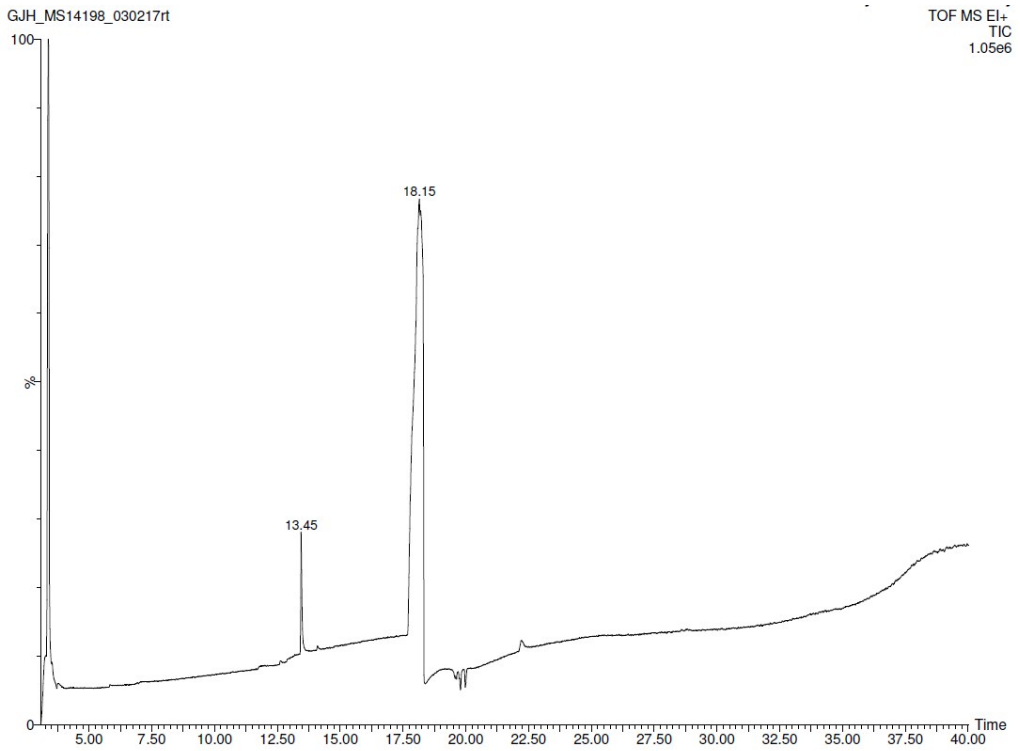
+ CO_2 +

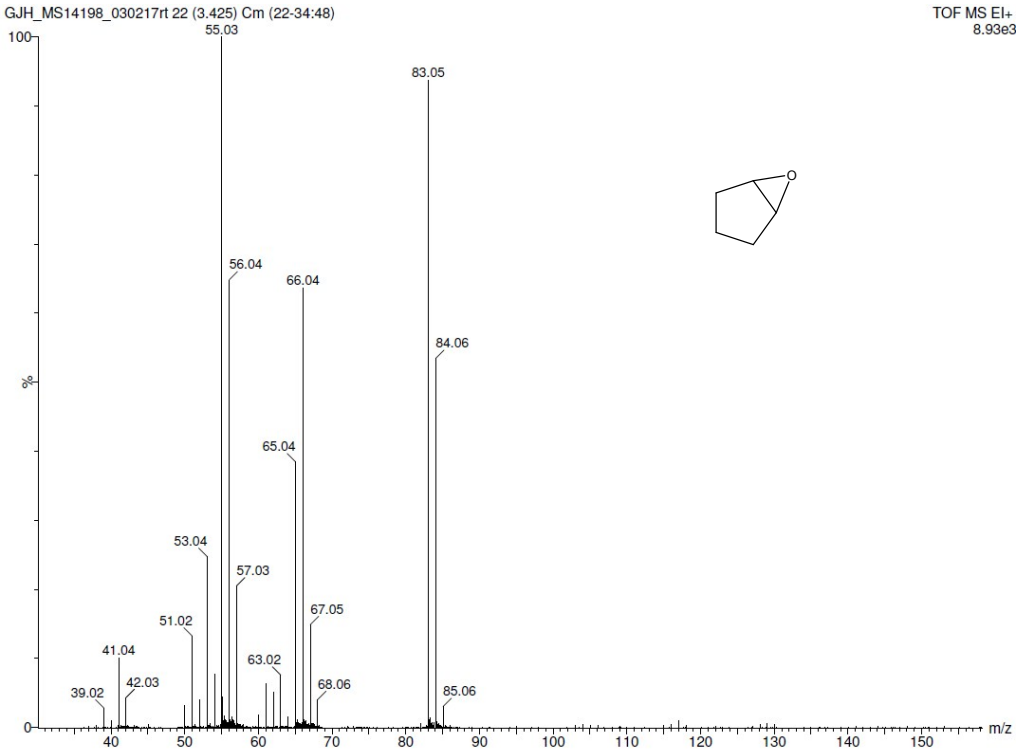


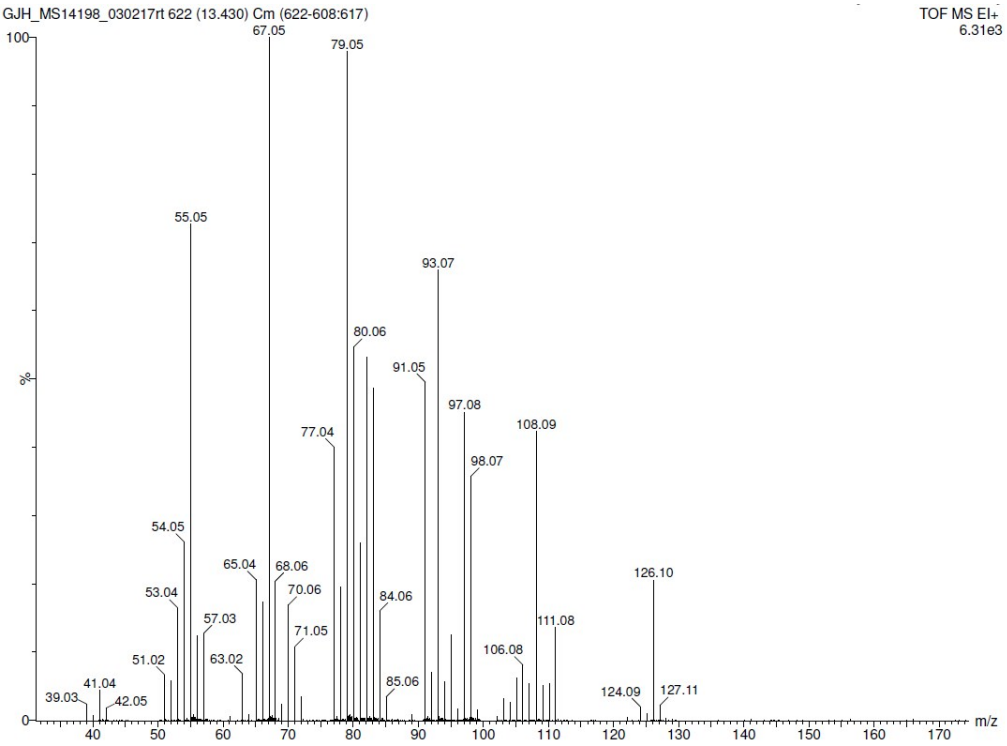
Isolated Reagents

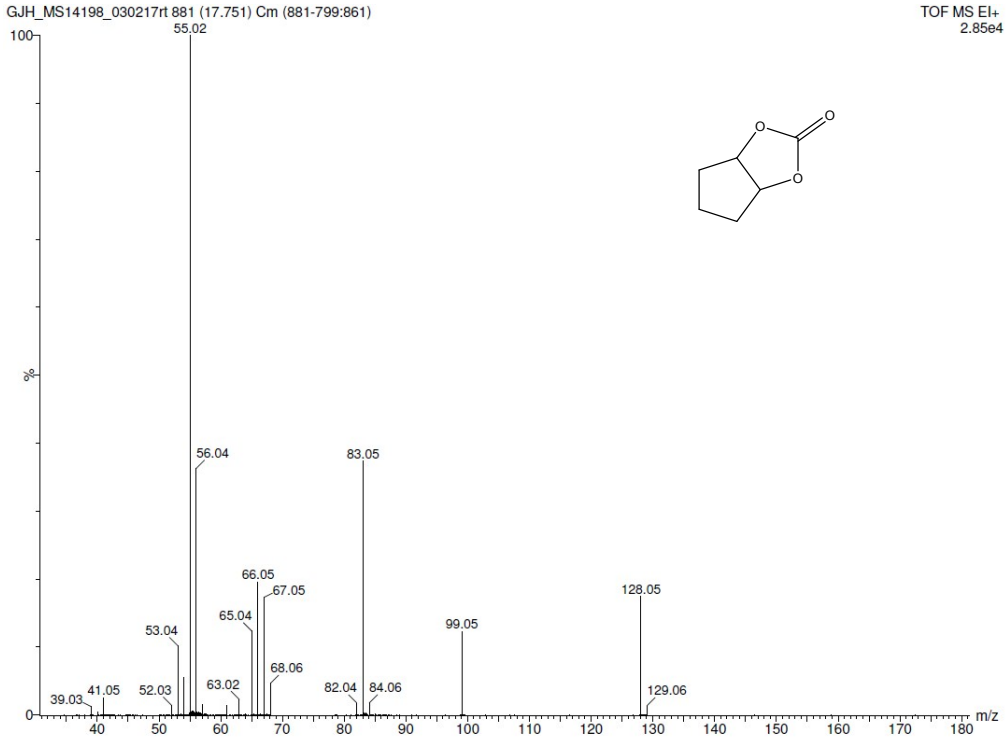
Spectroscopic Data: Suggested assignments of products are shown on the spectra where it was possible.

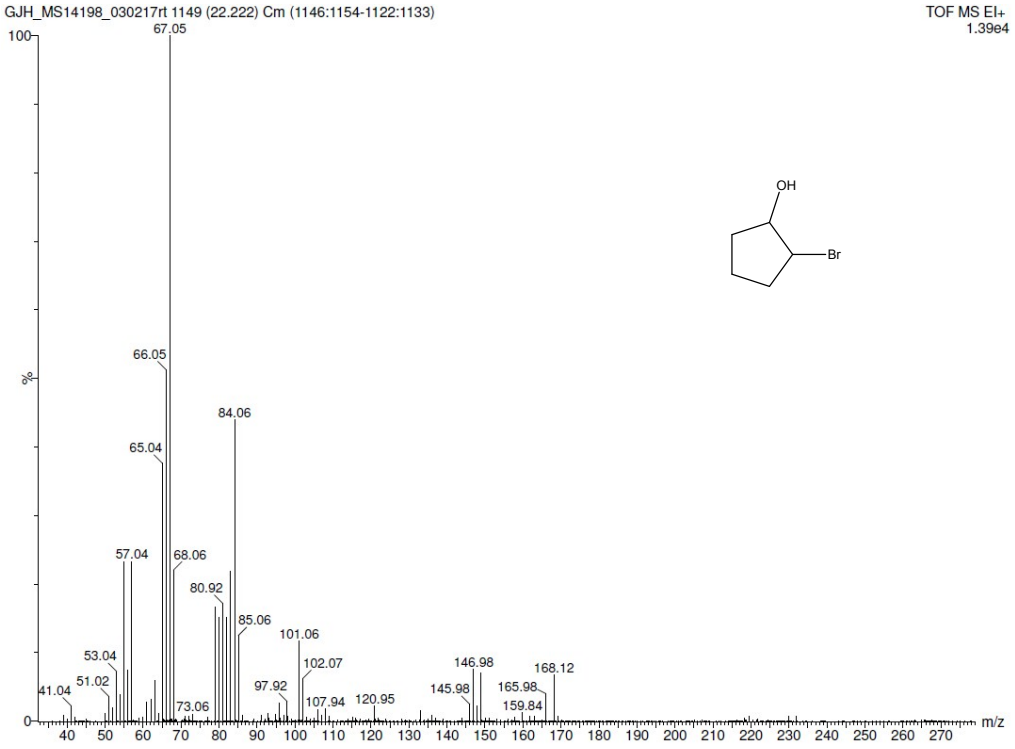
Cyclopentene oxide experiment (90 °C, 20 bar CO_2, 4 h)



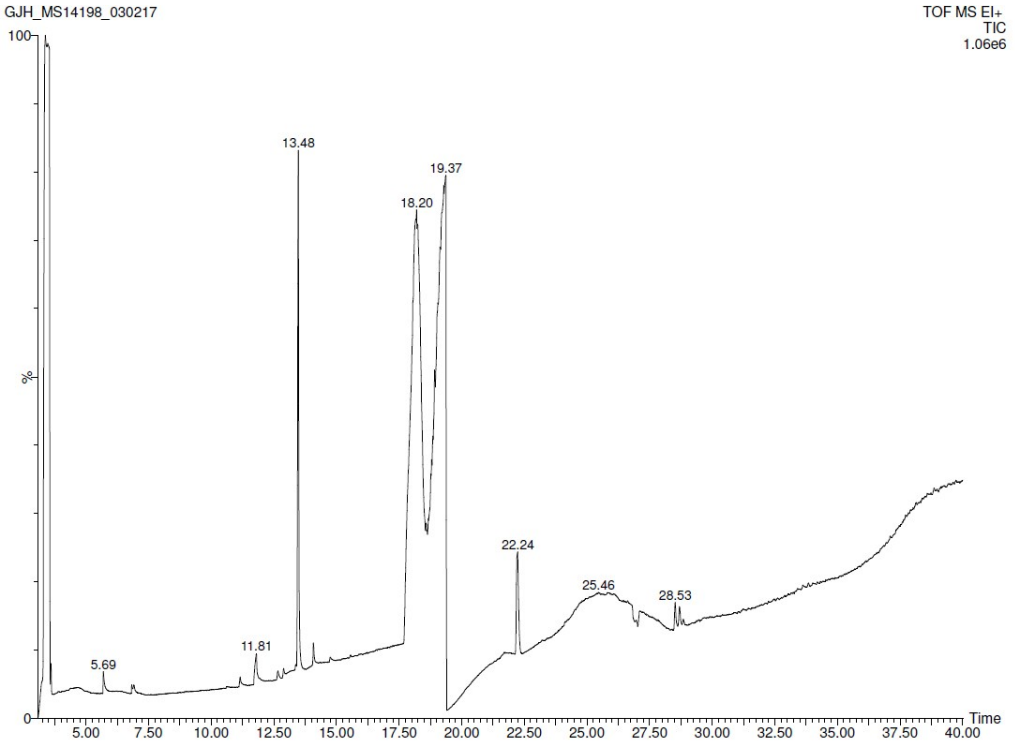


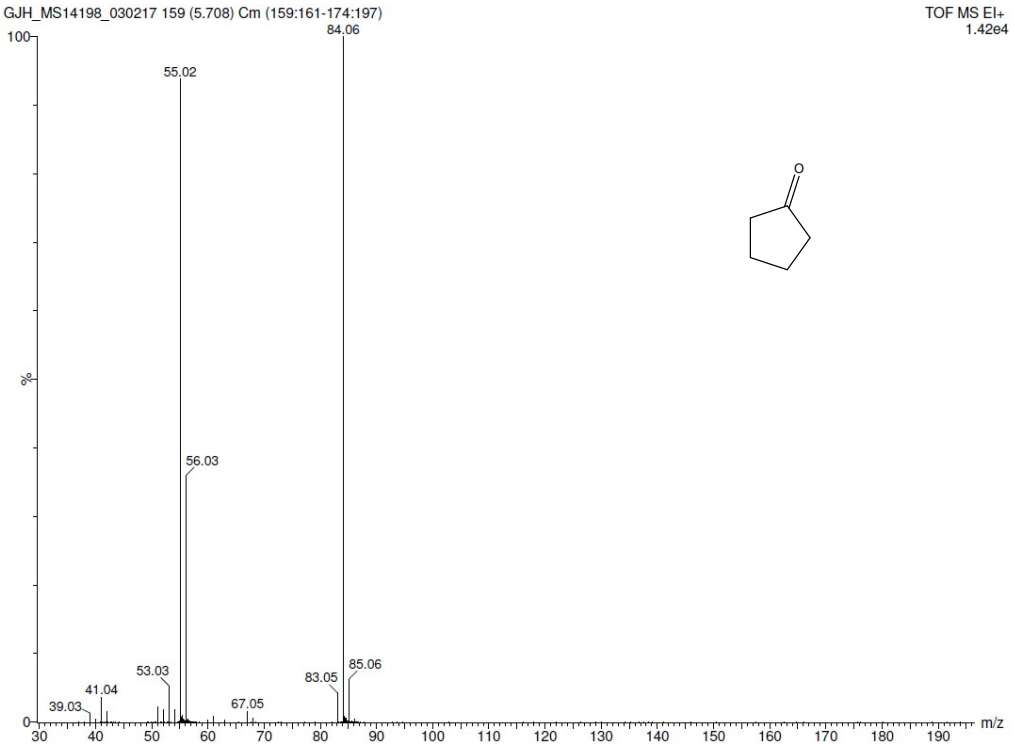

GJH_MS14198_030217rt 622 (13.430) Cm (622-608:617)
TOF MS EI+
6.31e3
100
%
0
67.05
79.05
55.05
93.07
80.06
91.05
97.08
108.09
77.04
98.07
54.05
65.04
68.06
126.10
53.04
70.06
84.06
57.03
111.08
71.05
106.08
51.02
63.02
41.04
85.06
39.03
42.05
124.09
127.11
40
50
60
70
80
90
100
110
120
130
140
150
160
170
m/z

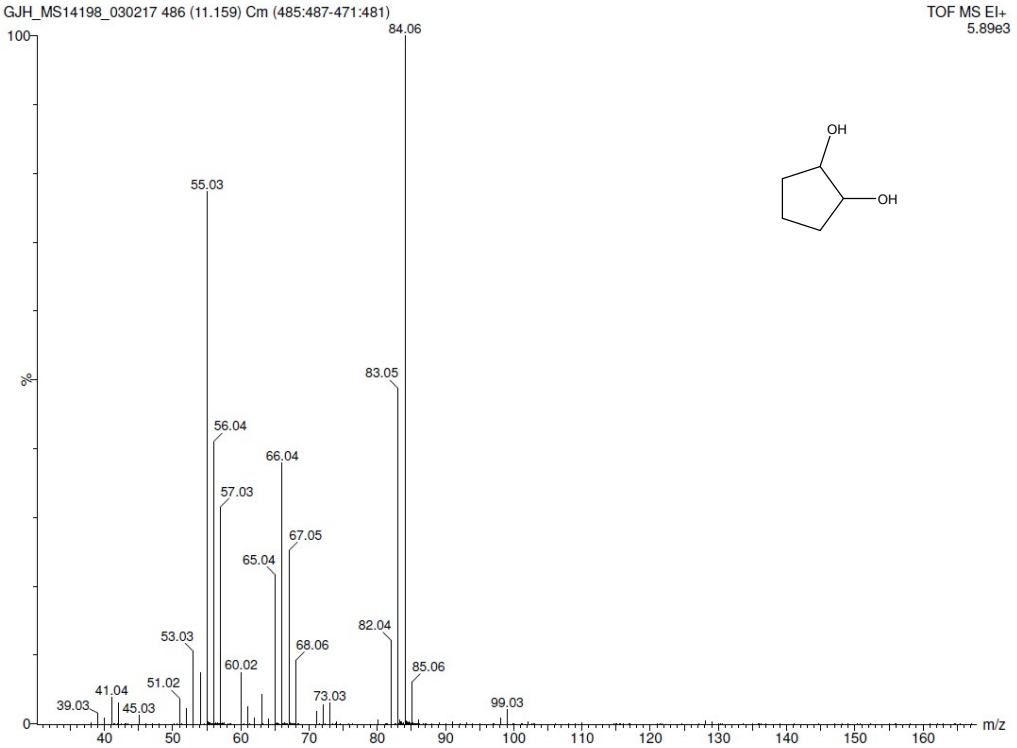

GJH_MS14198_030217rt 881 (17.751) Cm (881-799:861)
TOF MS EI+
2.85e4
100
%
0
55.02
56.04
83.05
66.05
67.05
128.05
65.04
99.05
53.04
68.06
63.02
82.04
84.06
129.06
39.03
41.05
52.03
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
m/z
O
O
O



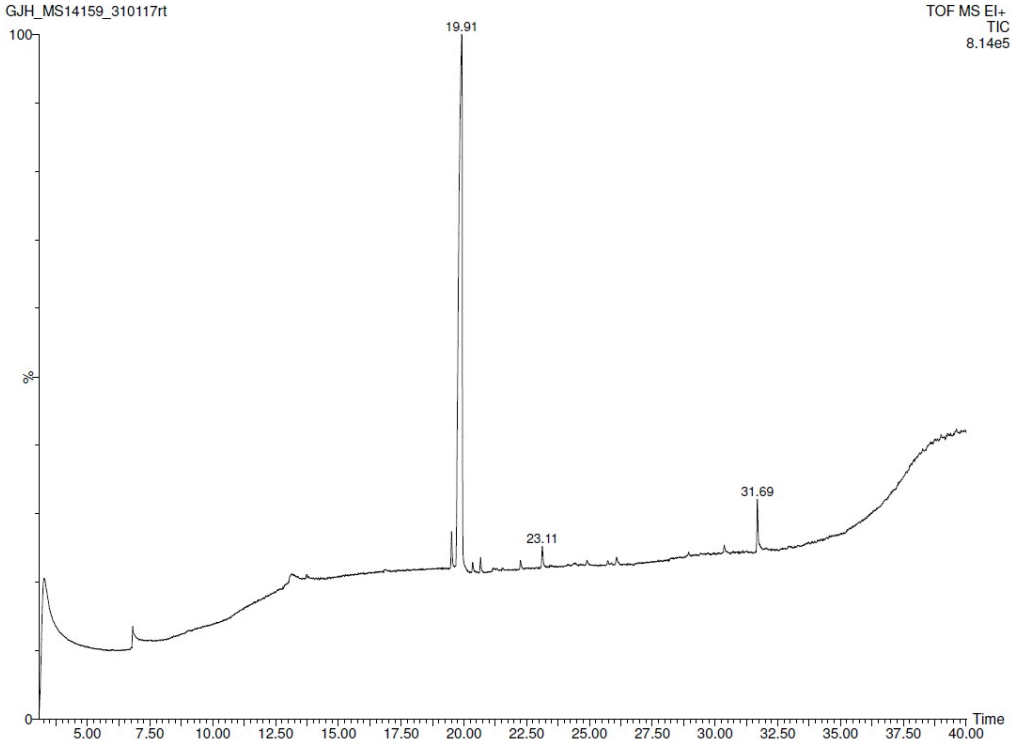
A more concentrated sample shows further side products:

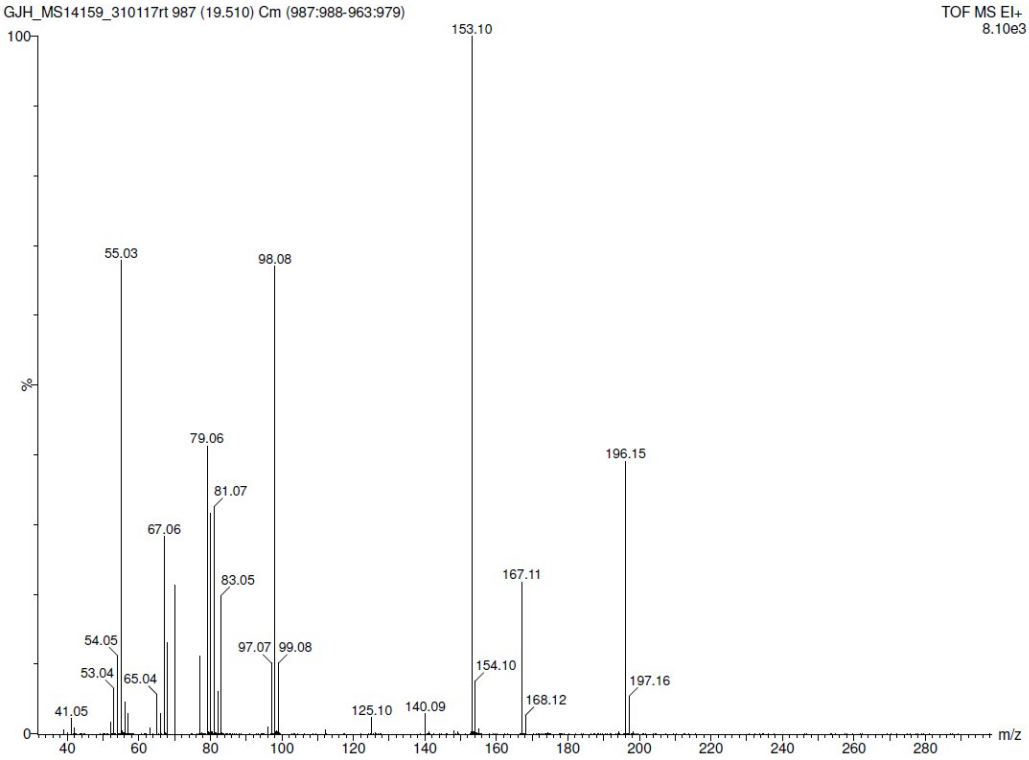


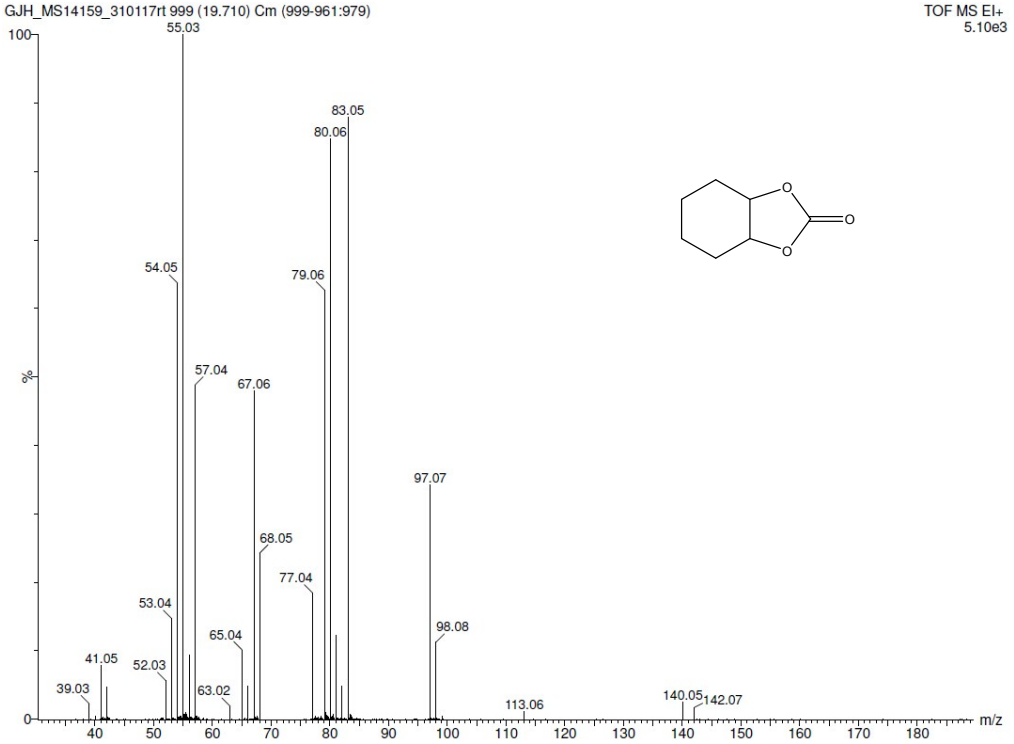


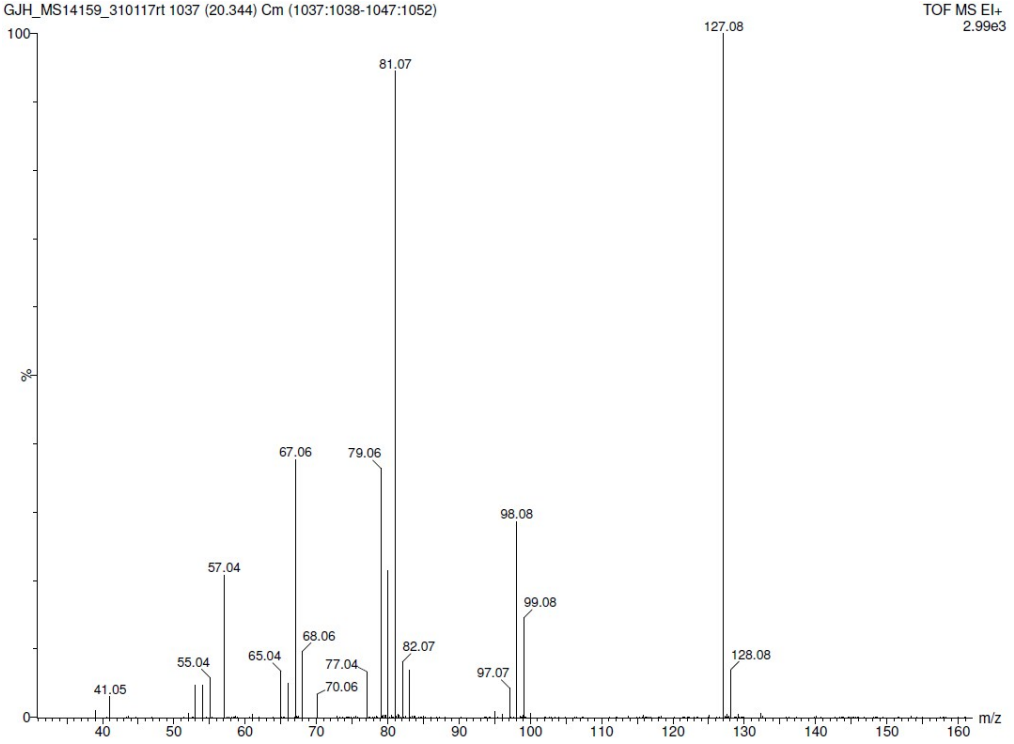


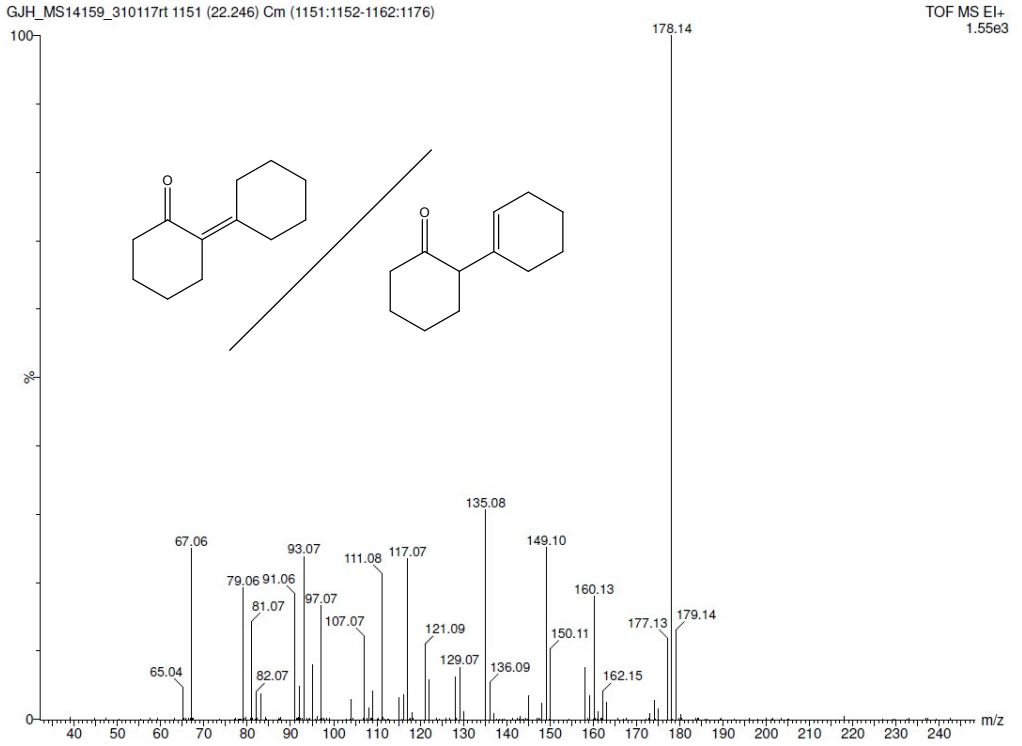
Cyclohexene oxide experiment (125 °C, 20 bar CO_2, 16 h)

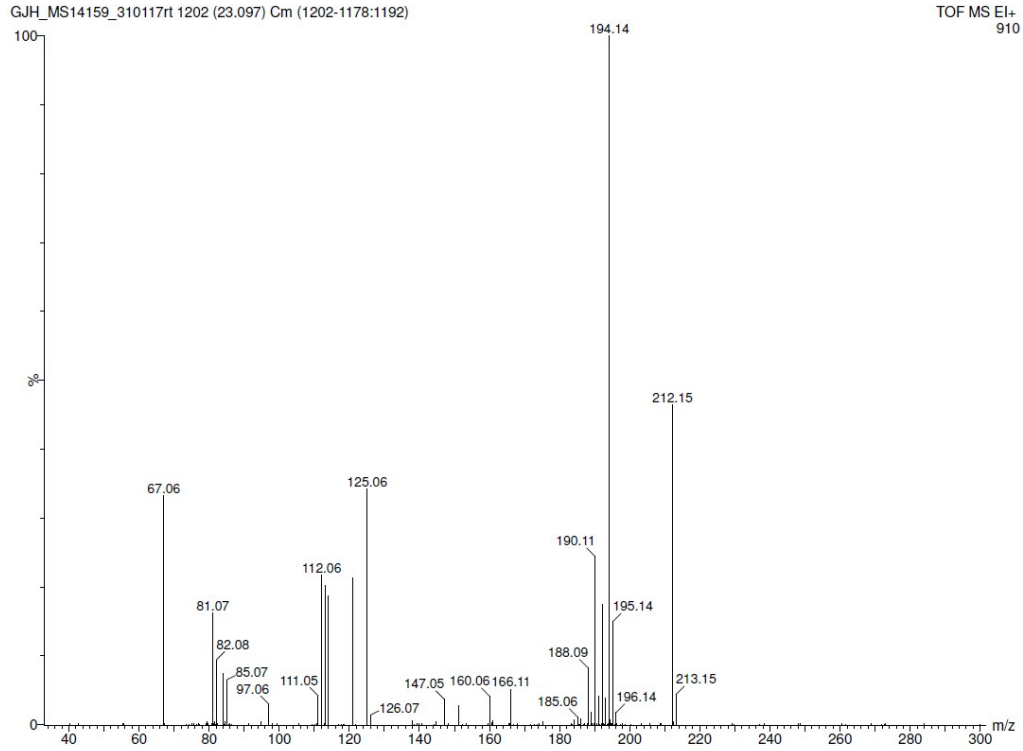

GJH_MS14159_310117rt
TOF MS EI+
TIC
8.14e5
100
%
0
19.91
31.69
23.11
5.00
7.50
10.00
12.50
15.00
17.50
20.00
22.50
25.00
27.50
30.00
32.50
35.00
37.50
40.00
Time

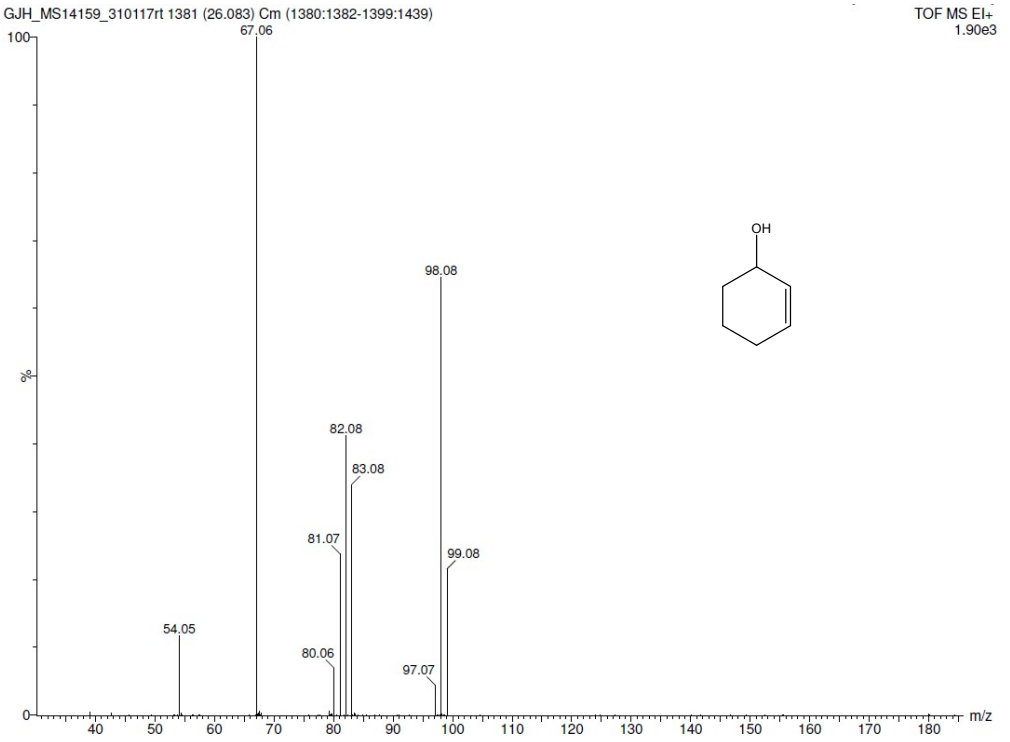

GJH_MS14159_310117rt 987 (19.510) Cm (987:988-963:979)
TOF MS EI+
8.10e3
100
%
0
153.10
55.03
98.08
79.06
196.15
81.07
67.06
167.11
83.05
54.05
97.07
99.08
154.10
53.04
65.04
197.16
168.12
41.05
125.10
140.09
40
60
80
100
120
140
160
180
200
220
240
260
280
m/z

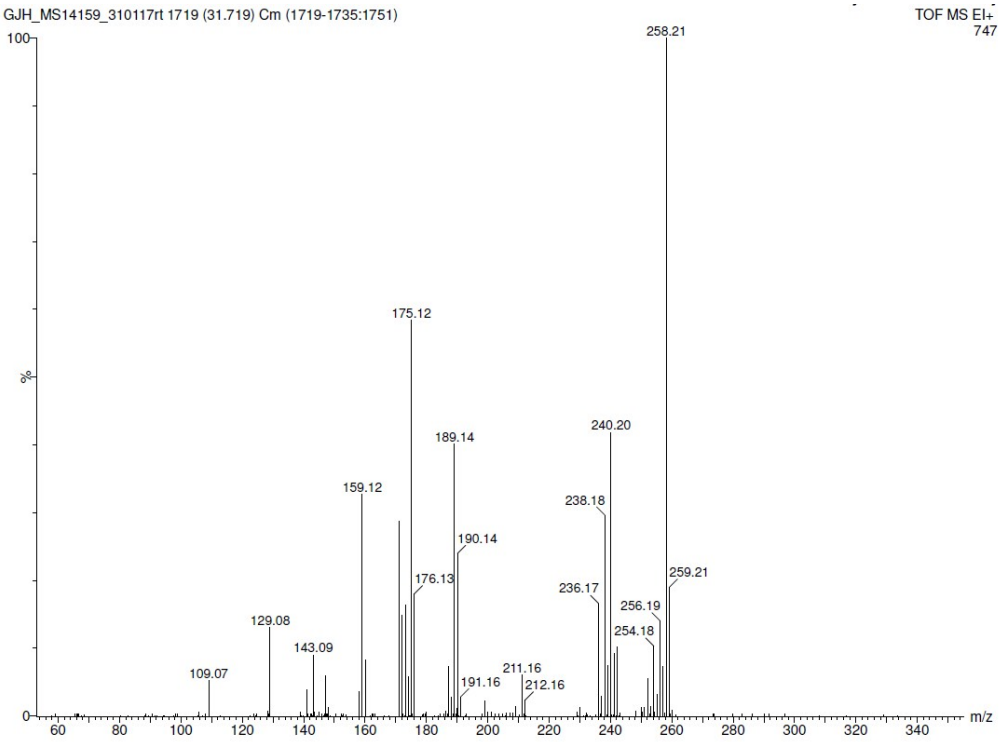

GJH_MS14159_310117rt 999 (19.710) Cm (999-961:979)
TOF MS EI+
5.10e3
100
%
0
55.03
83.05
80.06
54.05
79.06
57.04
67.06
97.07
68.05
77.04
53.04
98.08
65.04
41.05
52.03
39.03
63.02
113.06
140.05
142.07
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
m/z
O
O
O


GJH_MS14159_310117rt 1037 (20.344) Cm (1037:1038-1047:1052)
TOF MS EI+
2.99e3
100
%
0
127.08
81.07
67.06
79.06
98.08
57.04
99.08
68.06
65.04
82.07
55.04
77.04
97.07
128.08
41.05
70.06
40 50 60 70 80 90 100 110 120 130 140 150 160
m/z

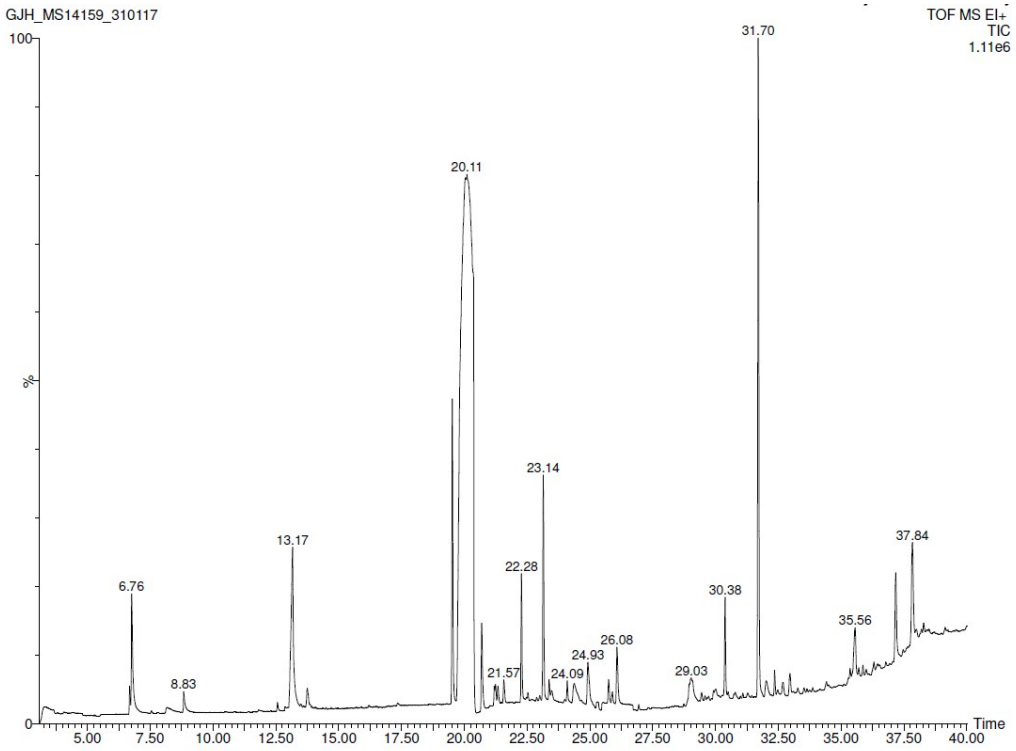

GJH_MS14159_310117rt 1151 (22.246) Cm (1151:1152-1162:1176)
TOF MS EI+
1.55e3
100
%
0
178.14
135.08
67.06
93.07
111.08
117.07
149.10
79.06
91.06
97.07
81.07
107.07
160.13
177.13
179.14
121.09
150.11
129.07
136.09
65.04
82.07
162.15
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240
m/z

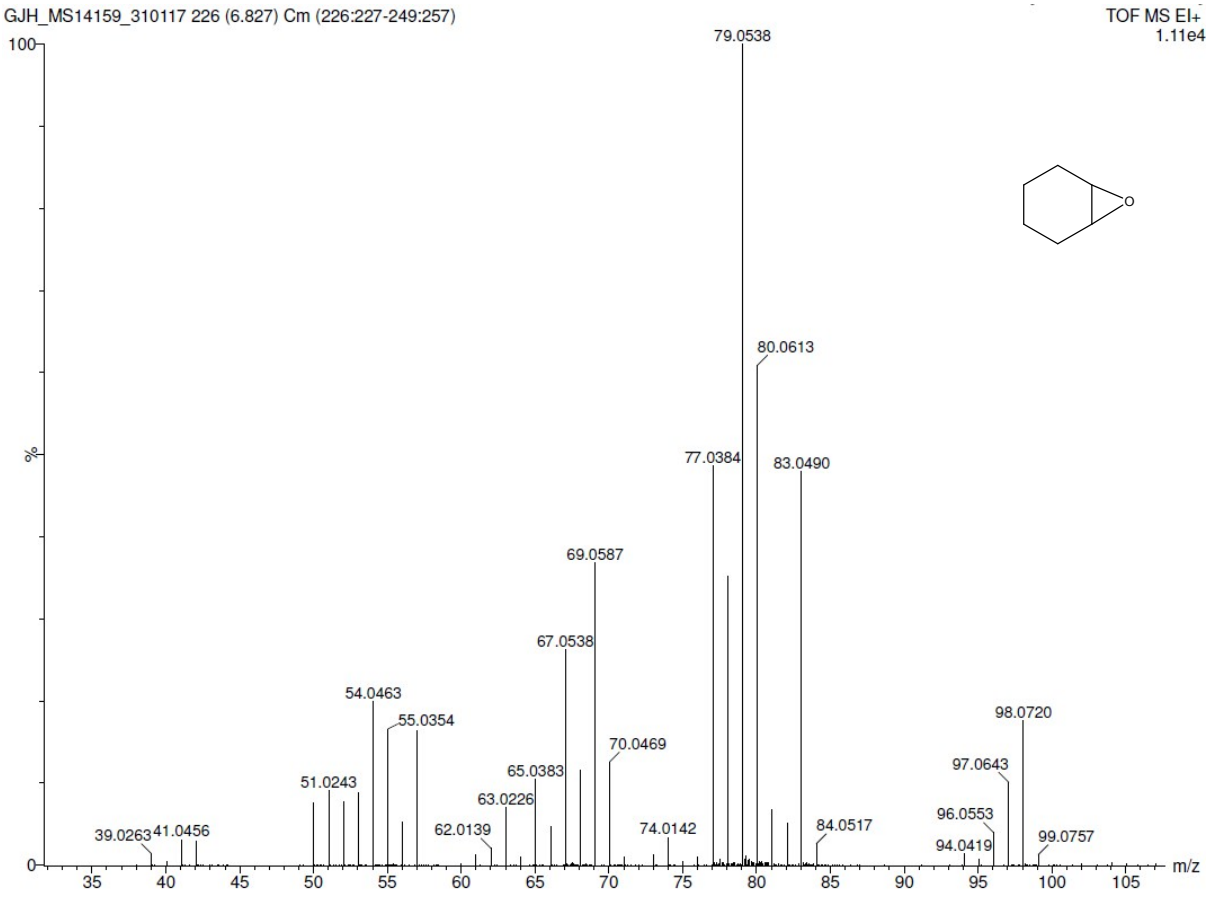

GJH_MS14159_310117rt 1202 (23.097) Cm (1202-1178:1192)
TOF MS EI+
910
100
%
0
194.14
212.15
67.06
125.06
190.11
112.06
81.07
195.14
82.08
188.09
85.07
111.05
147.05
160.06
166.11
213.15
97.06
126.07
185.06
196.14
40 60 80 100 120 140 160 180 200 220 240 260 280 300
m/z

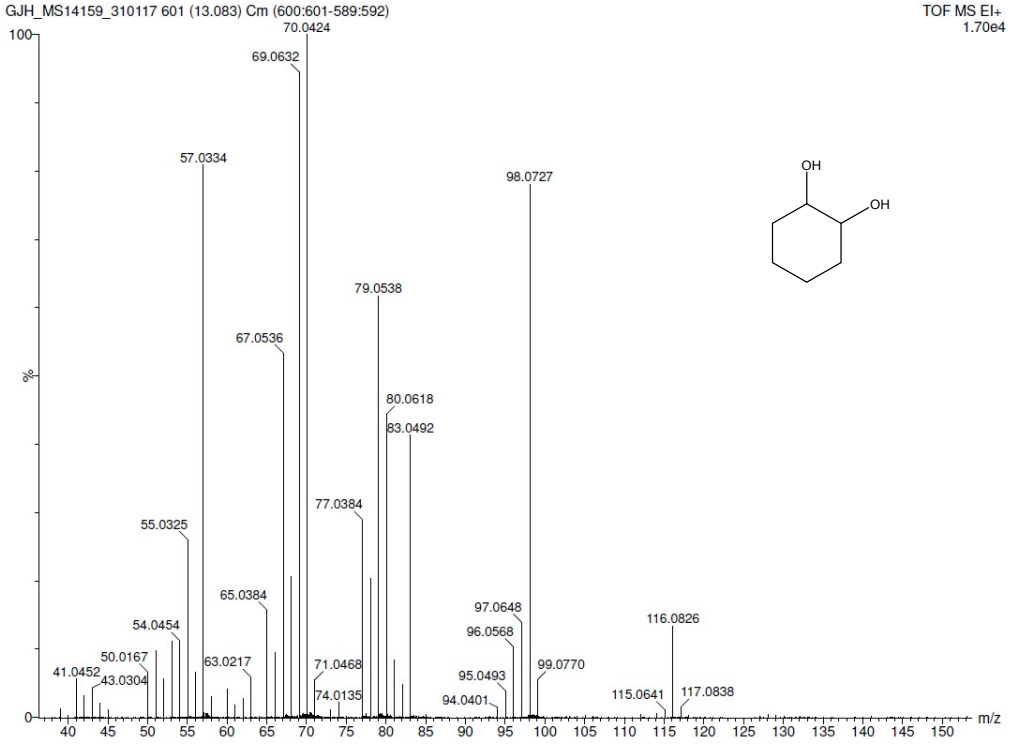




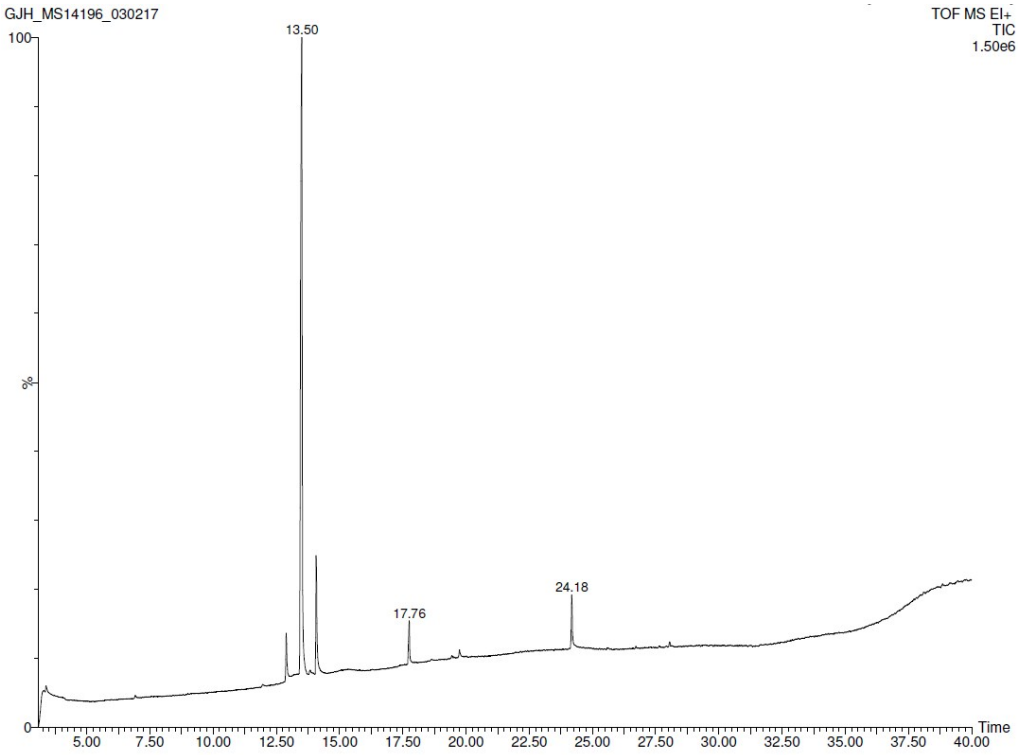
A more concentrated sample shows further side products and the starting material:


GJH_MS14159_310117
TOF MS EI+
TIC
1.11e6
100
%
0
31.70
20.11
23.14
13.17
37.84
22.28
6.76
30.38
35.56
26.08
24.93
21.57
24.09
29.03
8.83
Time
5.00
7.50
10.00
12.50
15.00
17.50
20.00
22.50
25.00
27.50
30.00
32.50
35.00
37.50
40.00

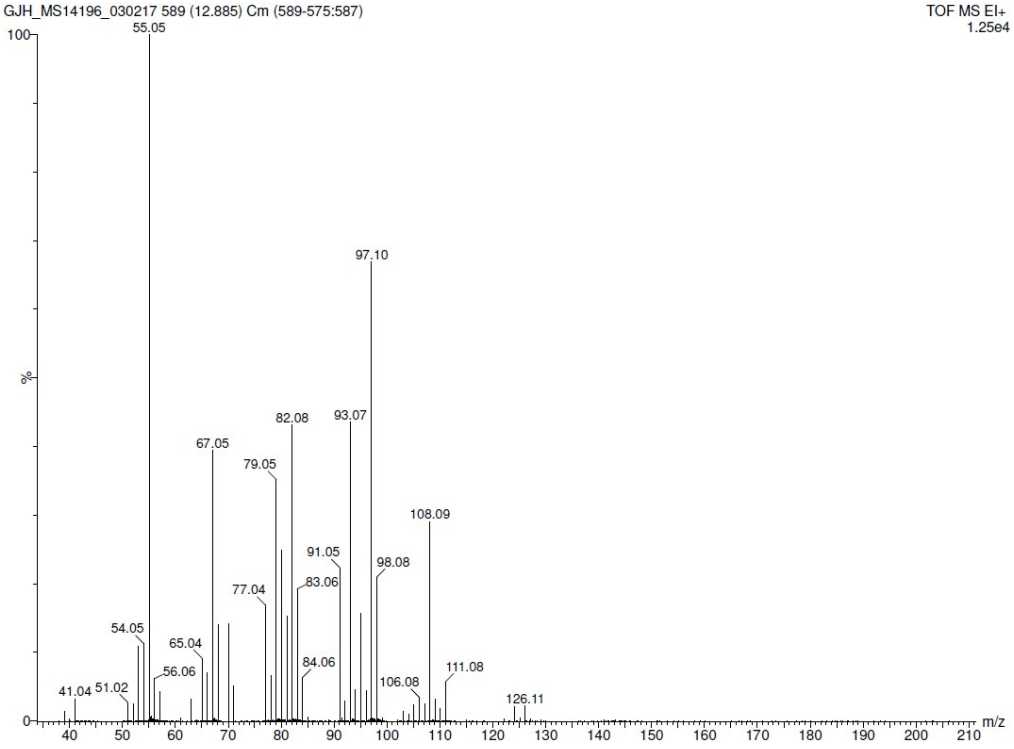

GJH_MS14159_310117 226 (6.827) Cm (226:227-249:257)
TOF MS EI+
1.11e4
100
%
0
79.0538
80.0613
77.0384
83.0490
69.0587
67.0538
54.0463
55.0354
98.0720
70.0469
97.0643
65.0383
51.0243
63.0226
96.0553
39.0263
41.0456
62.0139
74.0142
84.0517
94.0419
99.0757
m/z
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105

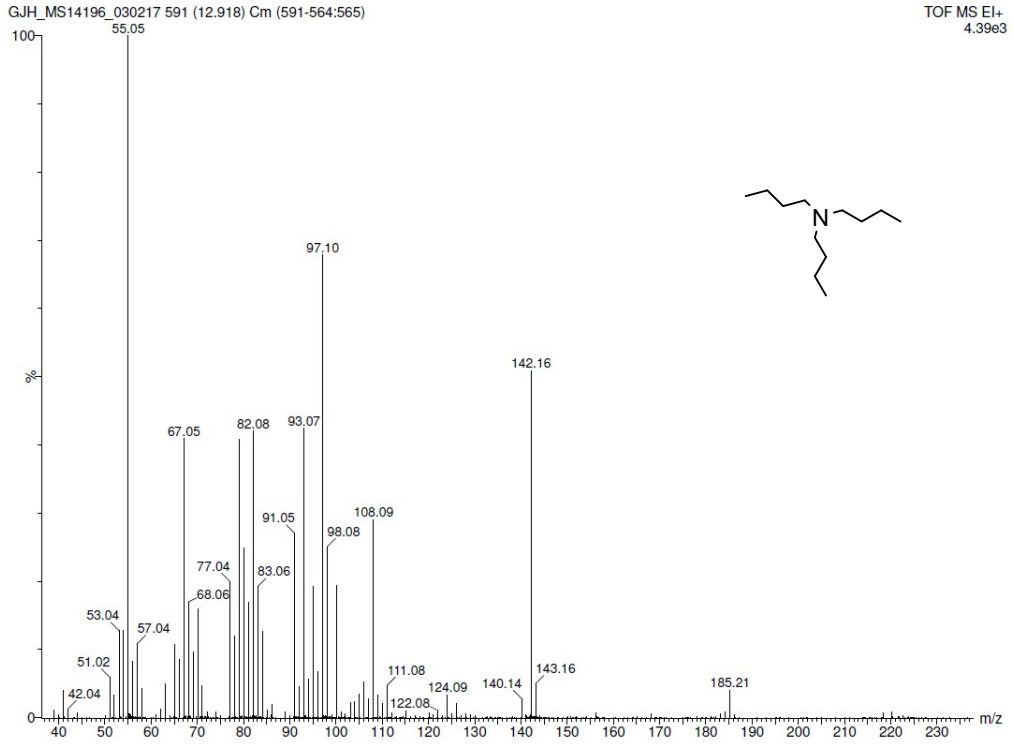


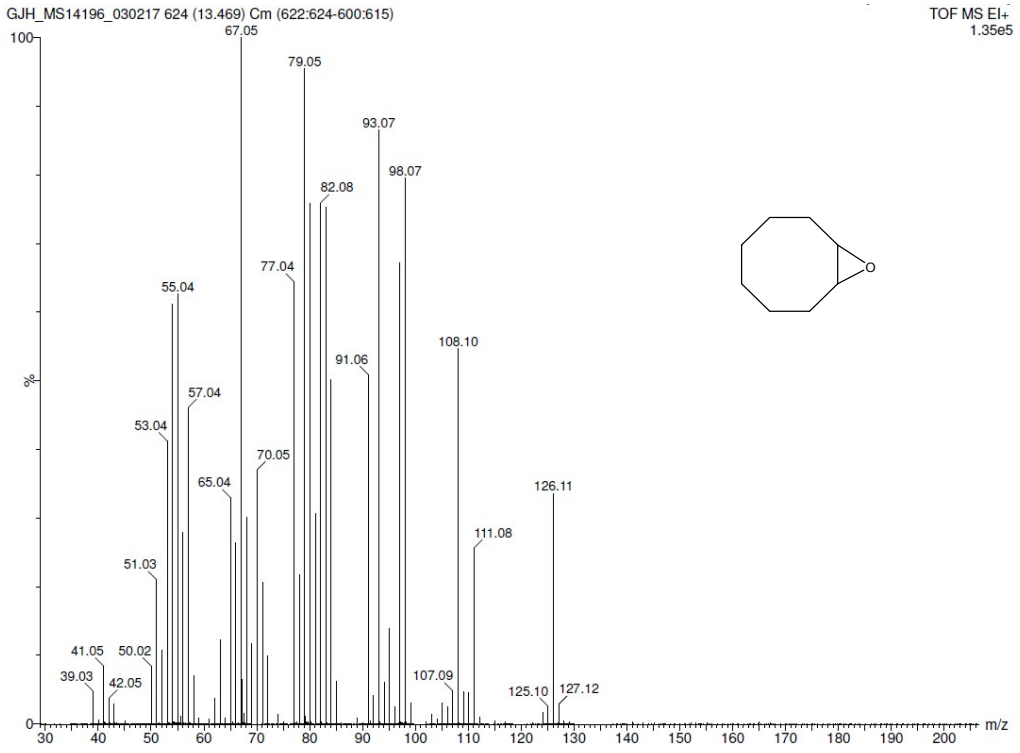
Cyclooctene oxide experiment (130 °C, 20 bar CO_2, 24 h)

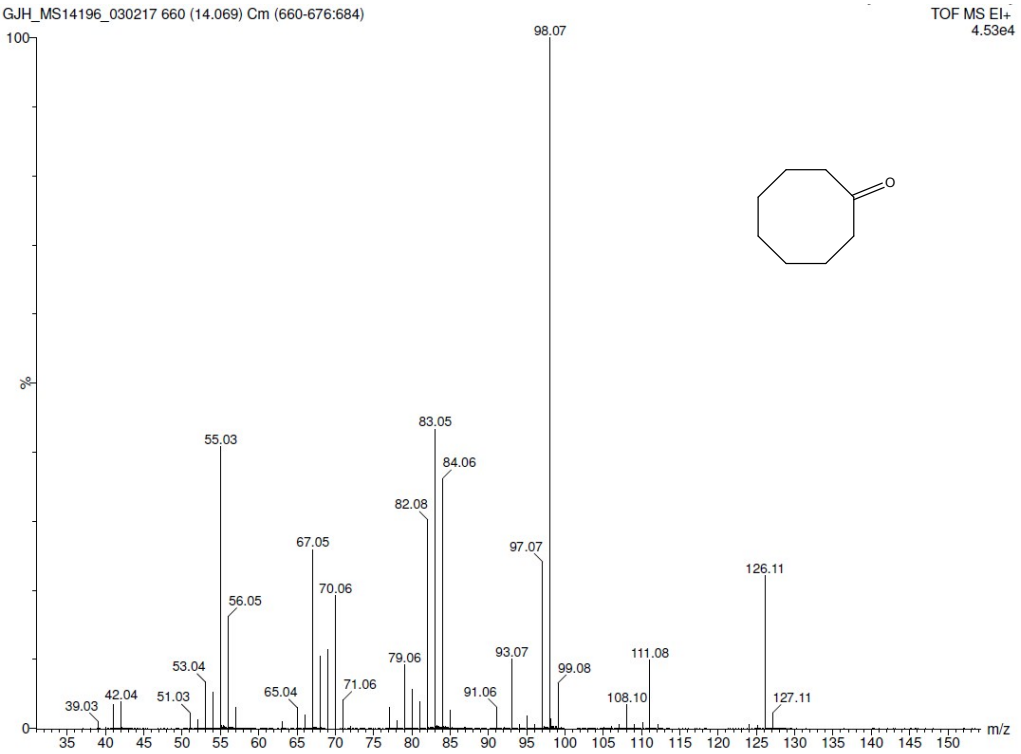


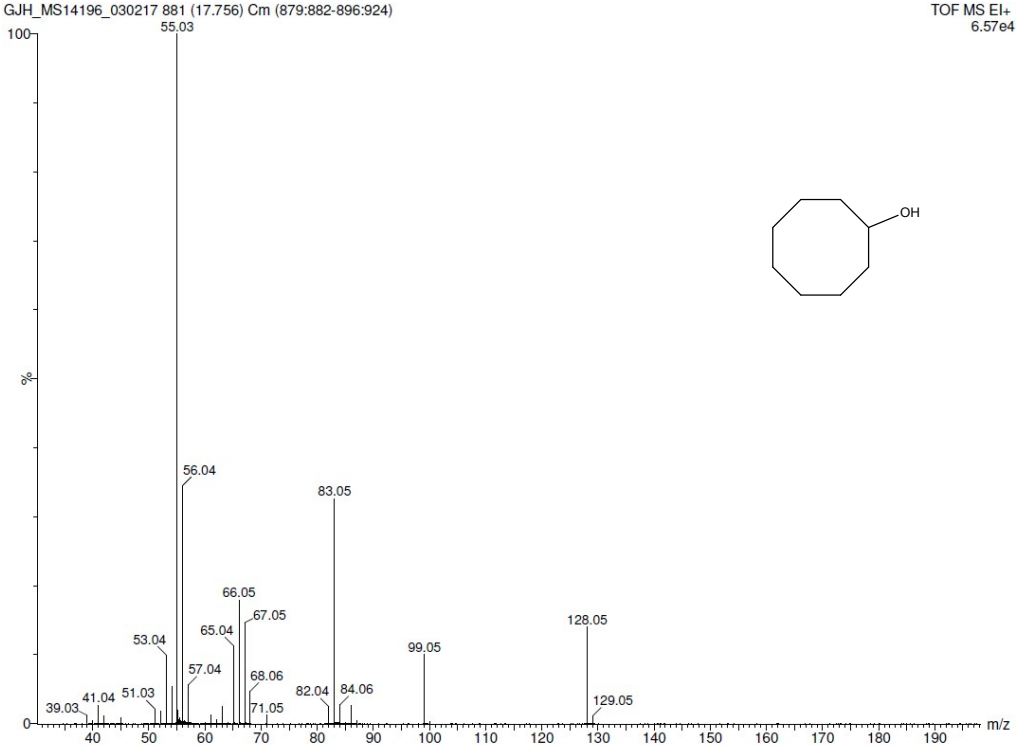
At 12.9 min two compounds are co-eluting, an isomer of the starting material and tributylamine.

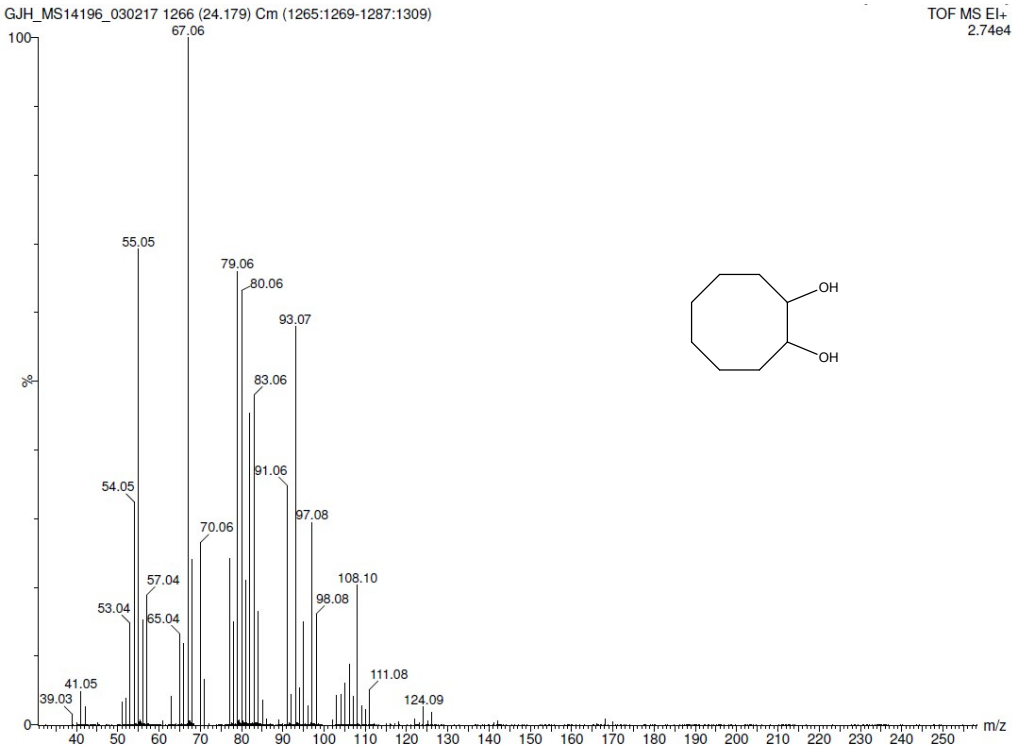

GJH_MS14196_030217 589 (12.885) Cm (589-575:587)
TOF MS EI+
1.25e4
100
%
0
55.05
97.10
82.08
93.07
67.05
79.05
108.09
91.05
98.08
83.06
77.04
54.05
65.04
84.06
56.06
111.08
41.04
51.02
106.08
126.11
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210
m/z


GJH_MS14196_030217 591 (12.918) Cm (591-564:565)
TOF MS EI+
4.39e3
100
%
0
55.05
97.10
142.16
67.05
82.08
93.07
91.05
108.09
98.08
77.04
83.06
68.06
53.04
57.04
51.02
111.08
143.16
124.09
140.14
185.21
42.04
122.08
N
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230
m/z


GJH_MS14196_030217 624 (13.469) Cm (622:624-600:615)
TOF MS EI+
1.35e5
100
%
0
67.05
79.05
93.07
98.07
82.08
77.04
55.04
91.06
108.10
57.04
53.04
70.05
65.04
126.11
111.08
51.03
41.05
50.02
39.03
42.05
107.09
125.10
127.12
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
m/z
O


GJH_MS14196_030217 660 (14.069) Cm (660-676:684)
TOF MS EI+
4.53e4
100
%
0
98.07
83.05
55.03
84.06
82.08
67.05
97.07
126.11
70.06
56.05
79.06
93.07
111.08
53.04
99.08
71.06
65.04
91.06
108.10
127.11
42.04
39.03
51.03
35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150
m/z
O


GJH_MS14196_030217 881 (17.756) Cm (879:882-896:924)
TOF MS EI+
6.57e4
100
%
0
55.03
56.04
83.05
66.05
67.05
65.04
53.04
57.04
68.06
71.05
82.04
84.06
99.05
128.05
129.05
39.03
41.04
51.03
OH
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190
m/z


GJH_MS14196_030217 1266 (24.179) Cm (1265:1269-1287:1309)
TOF MS EI+
2.74e4
100
%
0
67.06
55.05
79.06
80.06
93.07
83.06
91.06
54.05
97.08
70.06
57.04
108.10
98.08
53.04
65.04
111.08
41.05
39.03
124.09
OH
OH
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250
m/z