ESI For

Design and preparation of polymer resin-supported organoselenium catalyst with industrial potential

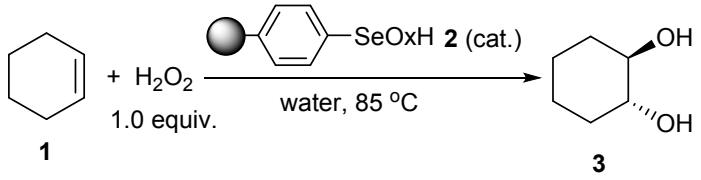
Yuguang Wang,[a] Lihua Yu,[a] Bingchun Zhu*[ab] and Lei Yu*[c]

[a] Key Laboratory of Bioorganic Synthesis of Zhejiang Province, College of Biotechnology and Bioengineering,Zhejiang University of Technology, Hangzhou, Zhejiang310014, China. E-mail: zhumelta@163.com.
[b] Zhejiang Research Institute of Chemical Industry, Hangzhou, Zhejiang 310023, China.
[c] Jiangsu Co-Innovation Centre for Prevention and Control of Important Animal Infectious Diseases and Zoonoses, Jiangsu Key Laboratory of Zoonosis, School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, China. E-mail: yulei@yzu.edu.cn.

CONTENTS

1. Detailed Table

Table S1 Test of catalyst loadings.[a]



Entry	**2**/%[b]	t (h)	**3**/%[c]
1	25	1	90
2	25	3	99
3	25	5	99
4	25	8	99
5	25	10	99
6	25	20	99
7	25	27	99
8	10	1	71
9	10	3	99
10	10	5	99
11	10	8	99
12	10	10	99
13	10	20	99
14	10	27	99
15	5	1	52
16	5	3	70
17	5	5	99
18	5	8	99
19	5	10	99
20	5	20	99
21	5	27	99
22	2	1	24
23	2	3	59
24	2	5	65
25	2	8	75
26	2	10	80
27	2	20	98
28	2	27	98
29	1	1	9
30	1	3	39
31	1	5	44
32	1	8	56

33	1	10	62
34	1	20	98
35	1	27	98

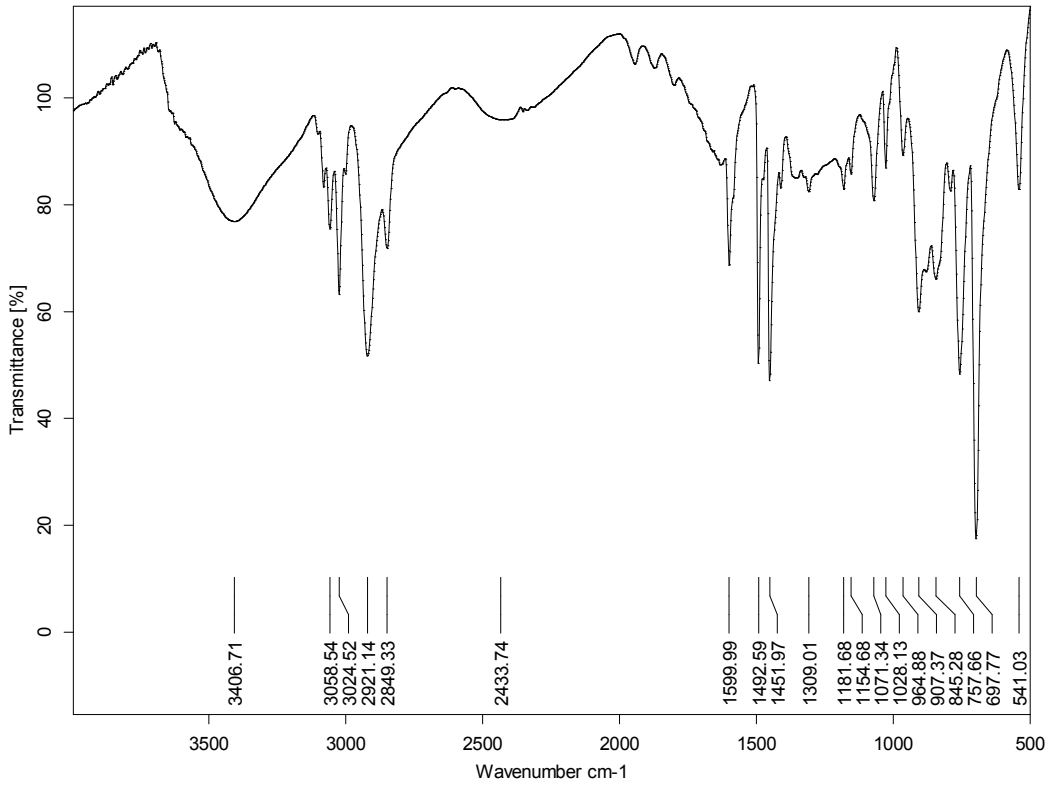
[a] 1mmol of **1**, 1 mmol of H_2O_2 (30 w/w %) and 5 mL of solvent were heat at 85 ^oC. [b] Catalyst loadings based on **1**. [c] GC yield of **3** based on **1**.

Table S2 Detailed XPS analysis result of the catalysts

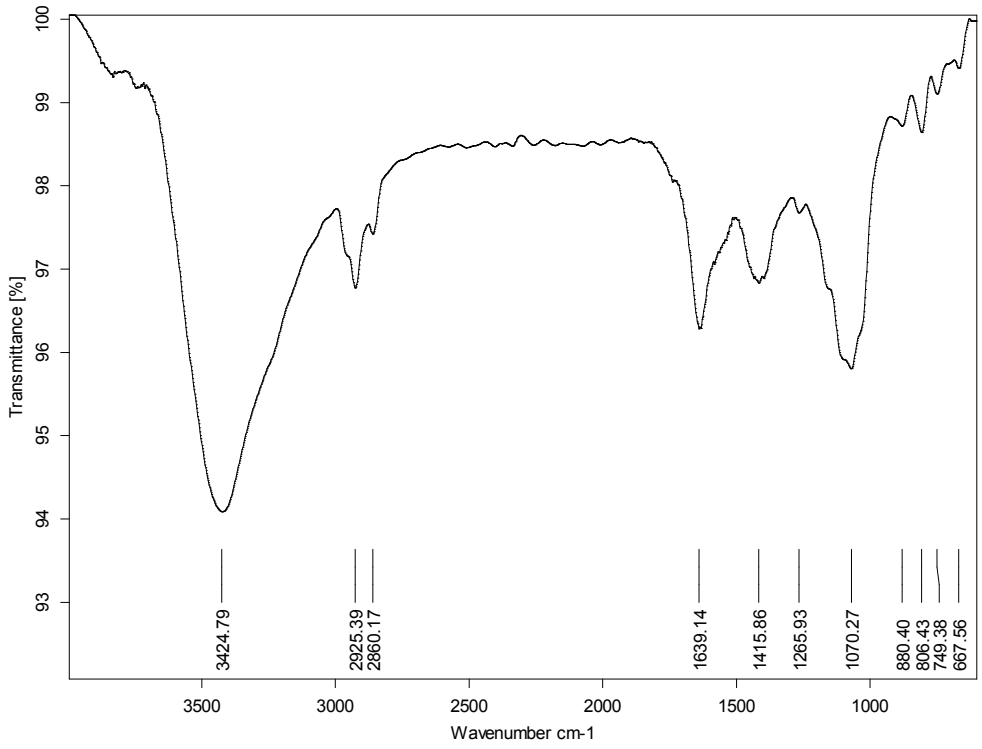
Figure in text	Se^{6+}3d (BE 60 ev), %	Se^{4+}3d (BE 59.5 ev), %	Se^{2+}3d (BE 56 ev), %
Fig. 2	65±1	35±1	0
Fig. 5	21±1	0	79±1

2. Spectra

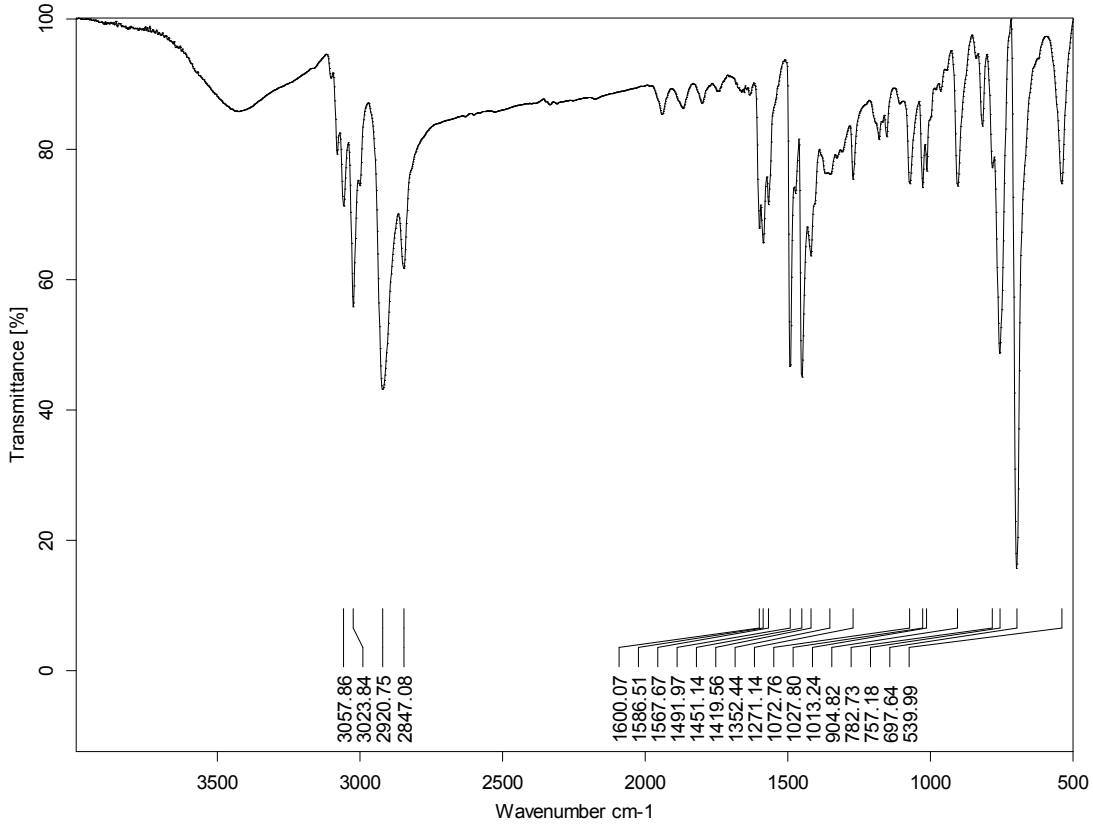
FT-IR Spectra of Polymer 2



FT-IR Spectra of Polymer 7

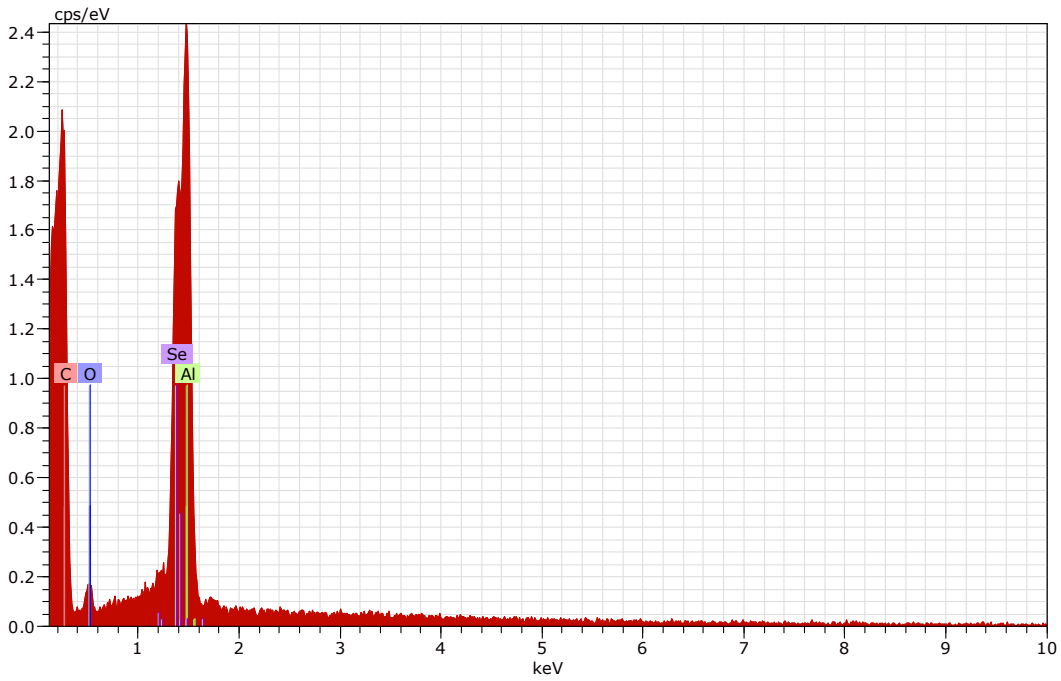


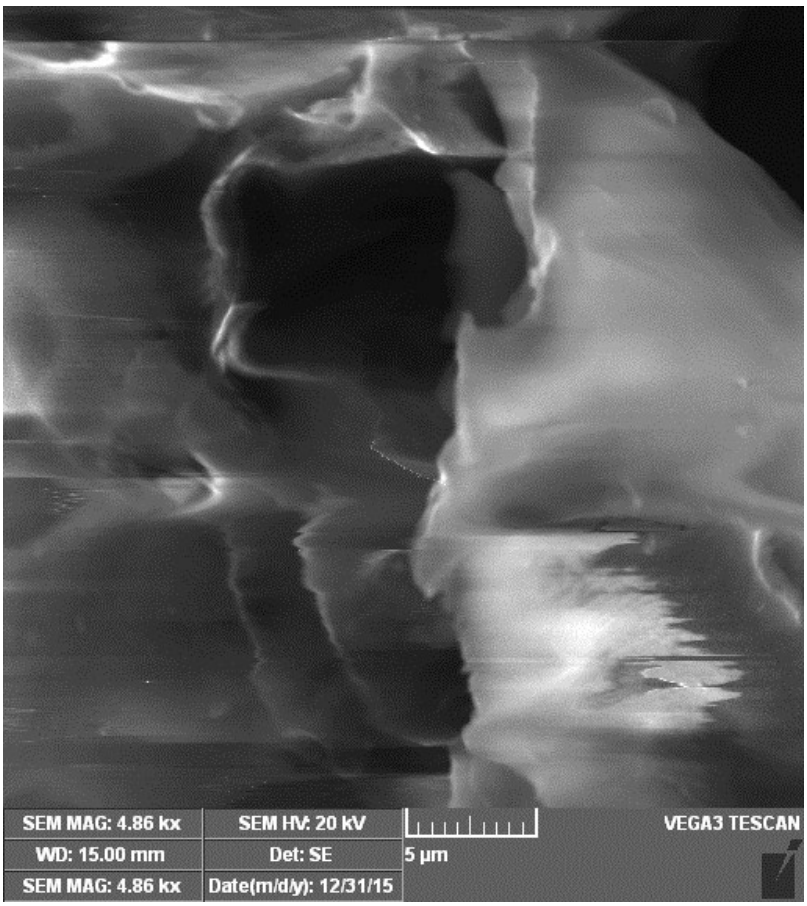
FT-IR Spectra of Polymer 6



EDS Spectra of Catalyst

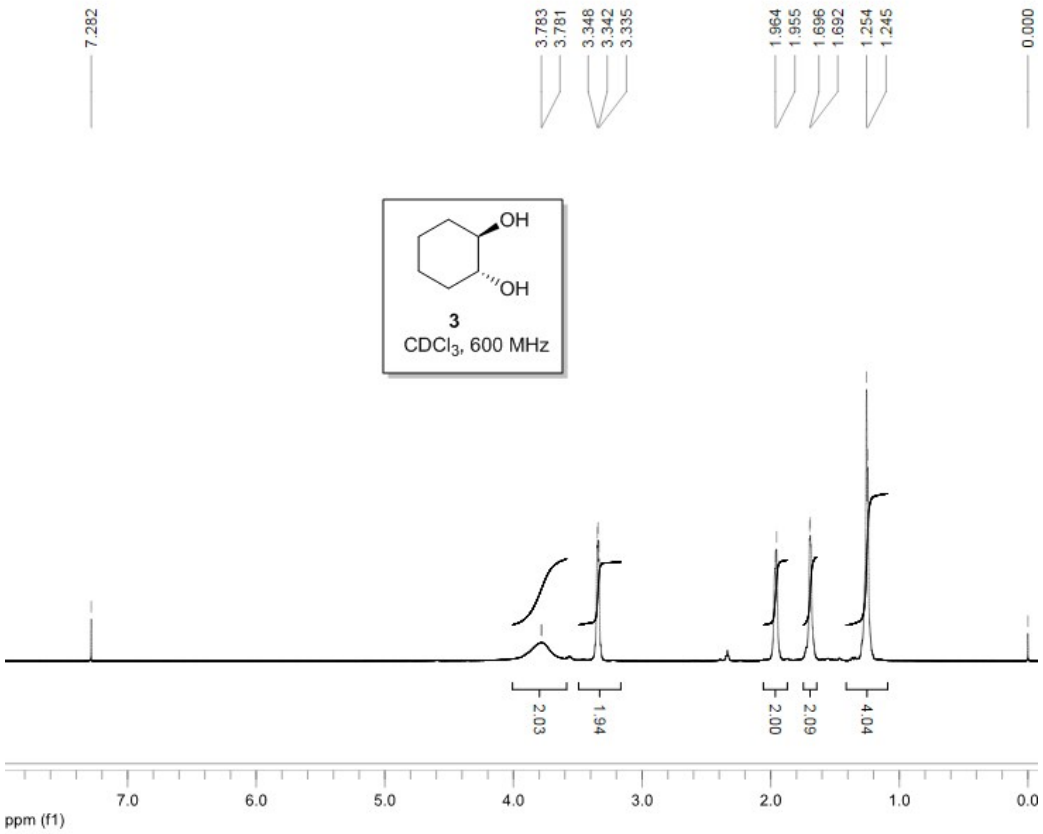
EDS Spectra of Polymer 2



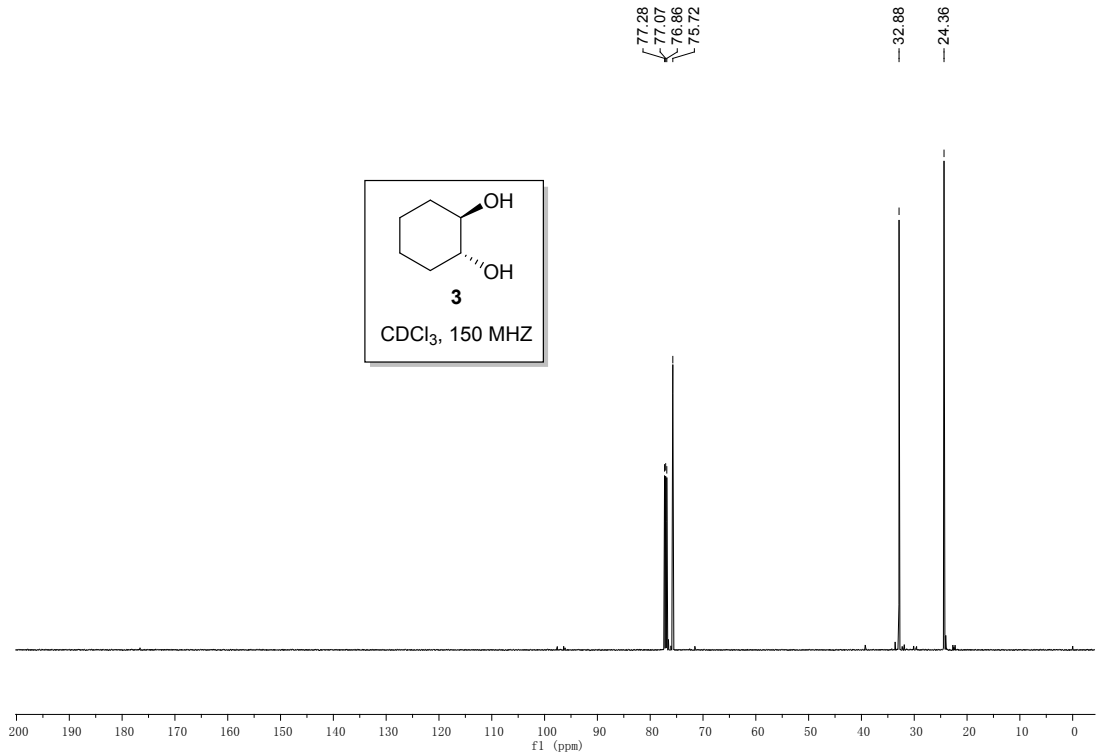


Characterization Spectra of Product 3

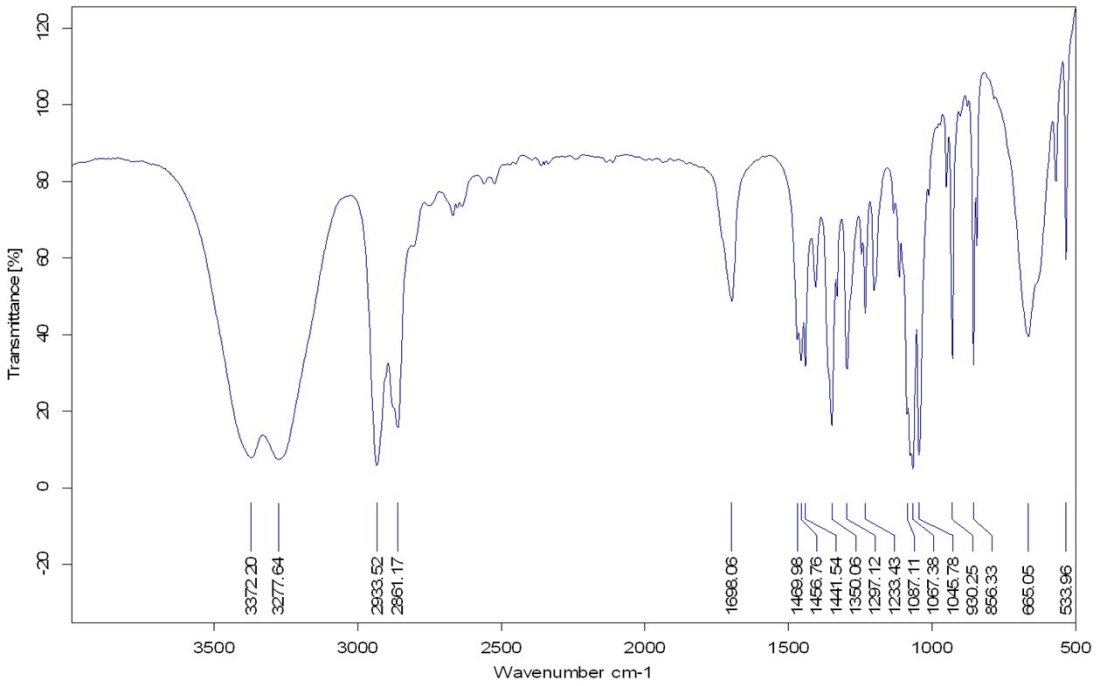
^{1}H NMR



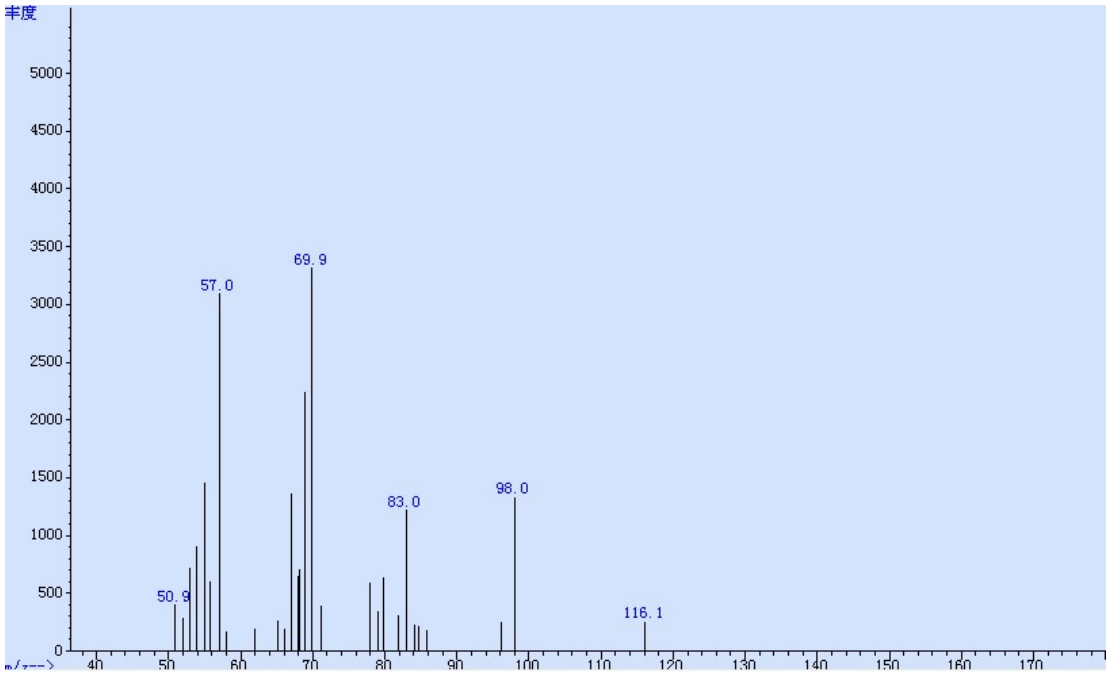
^{13}C NMR



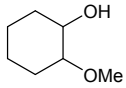
IR



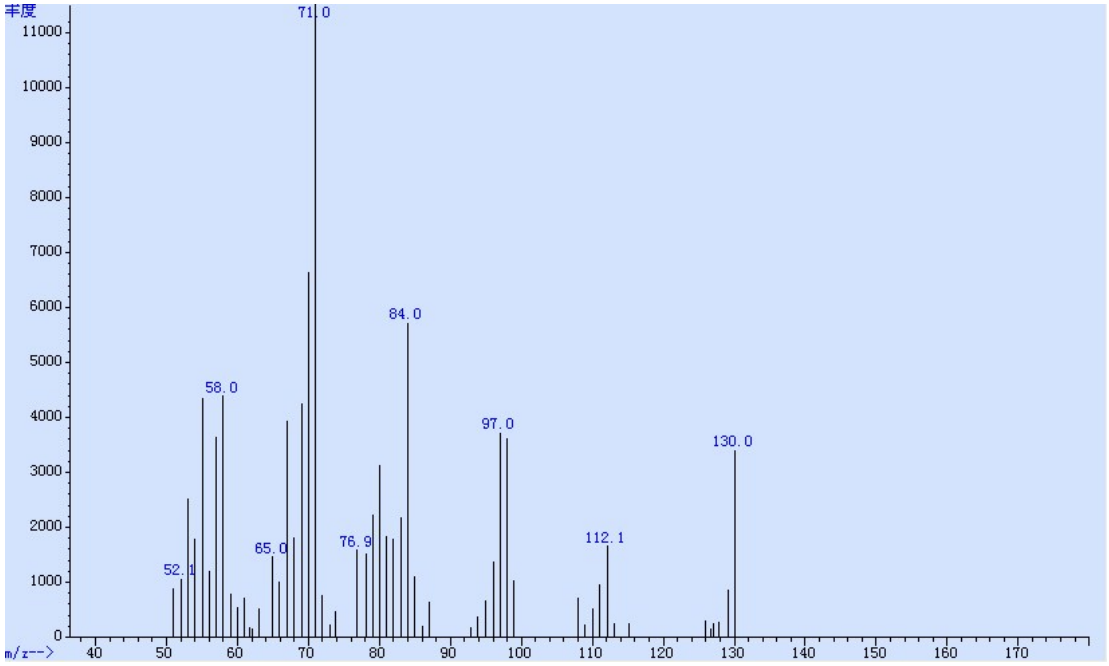
GC-MS (EI): m/z 116 [M$^+$]

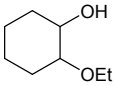


GC-MS of the by-products 8-10

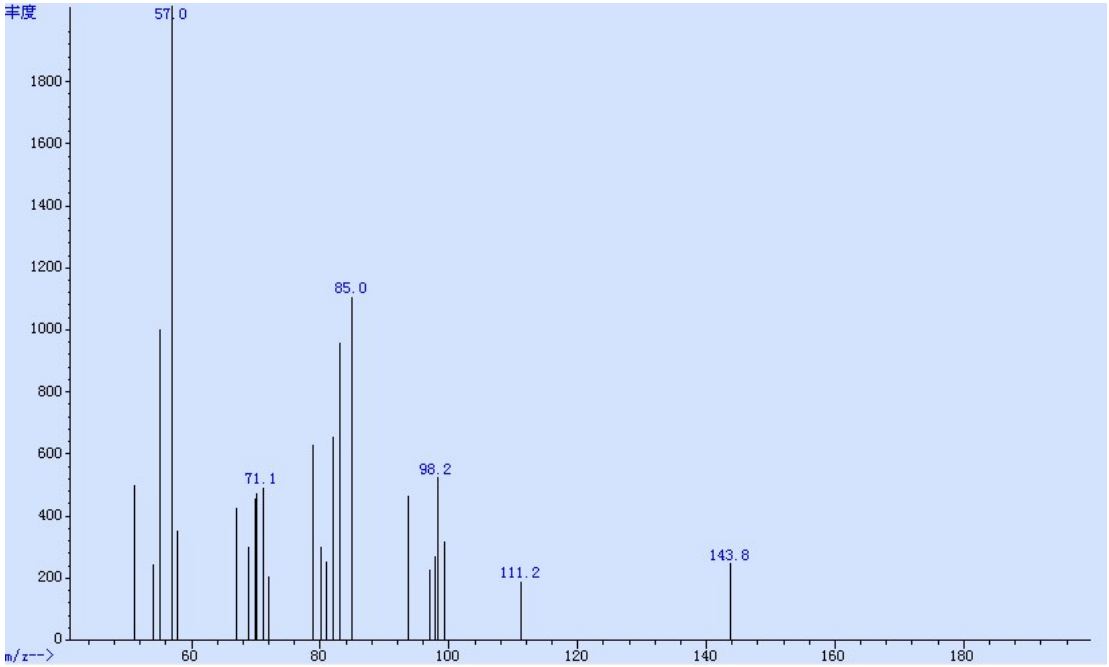


2-Methoxycyclohexanol 3. GC-MS (EI): m/z 130 [M^+]. Known compound (2979-24-0).

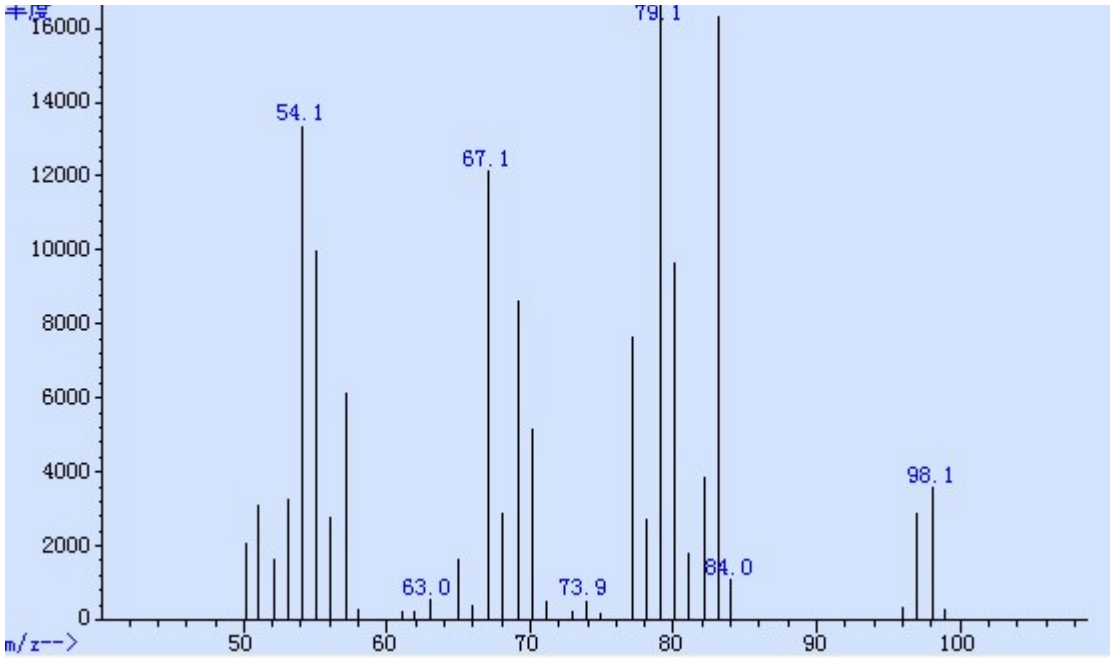




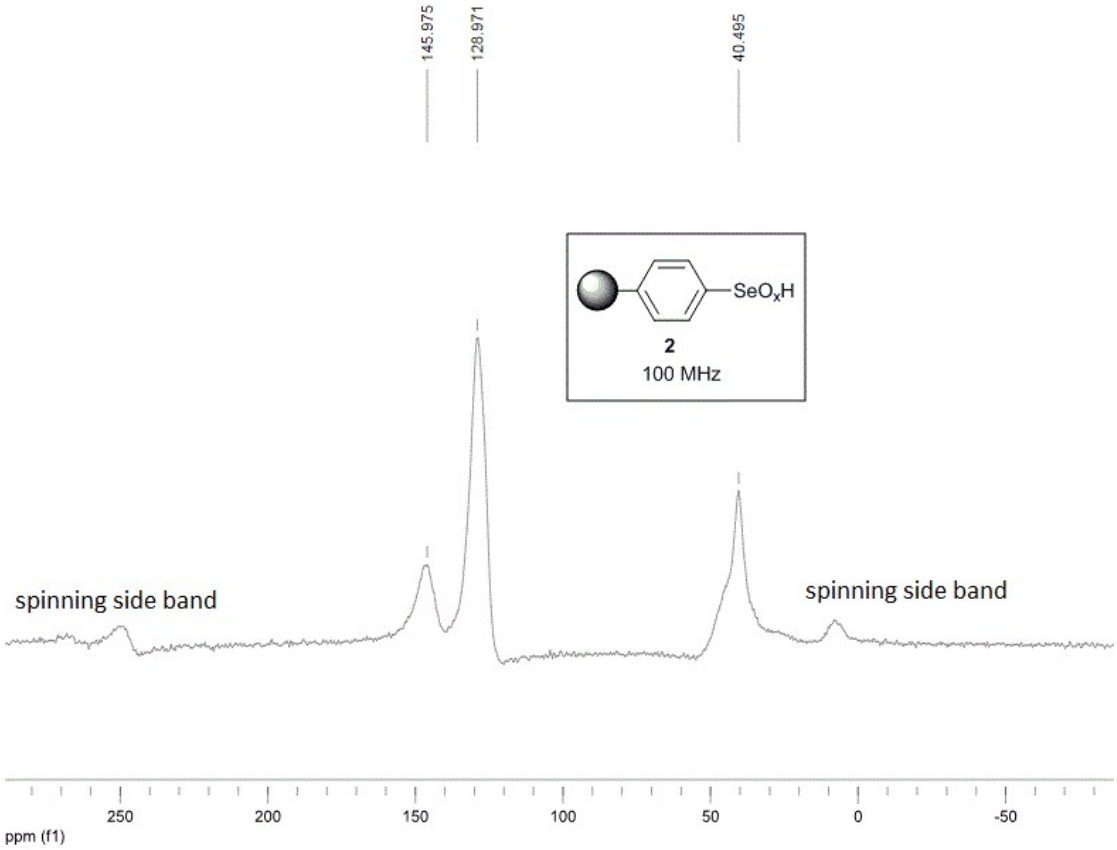
2- Ethoxycyclohexanol 4. GC-MS (EI): m/z 144 [M^+]. Known compound (2979-26-2).

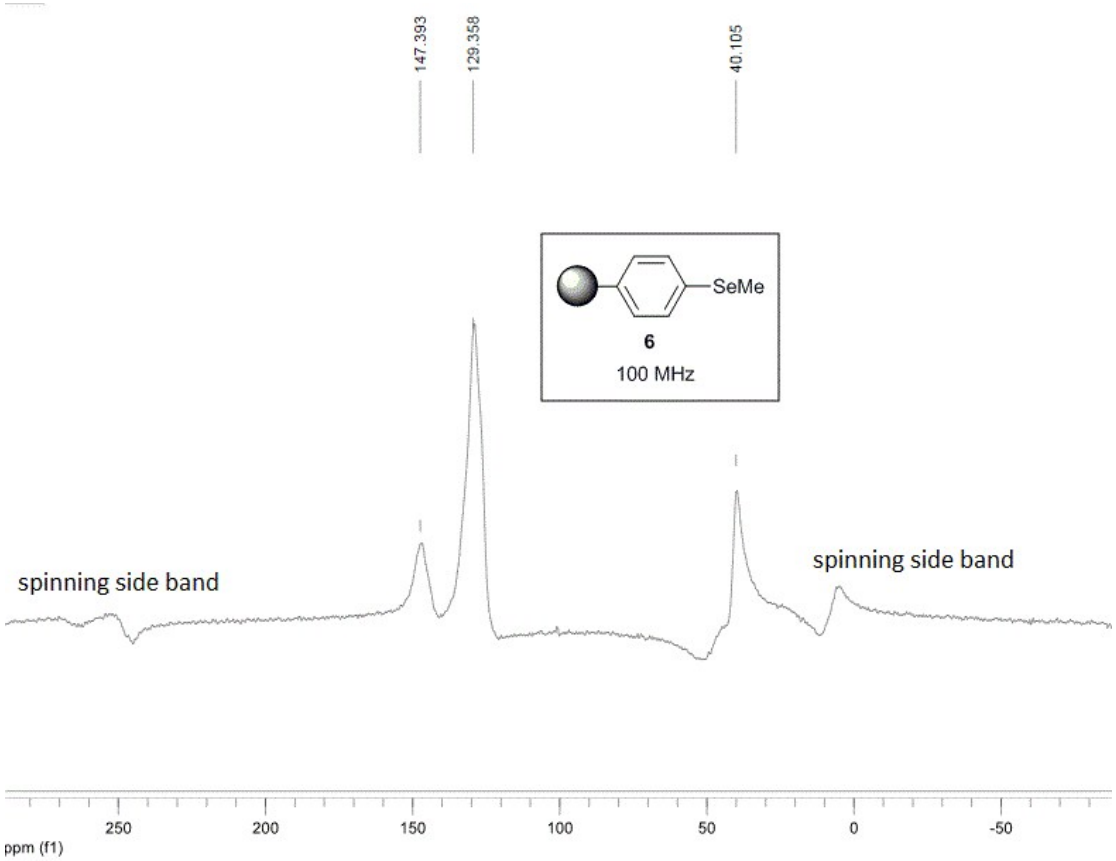


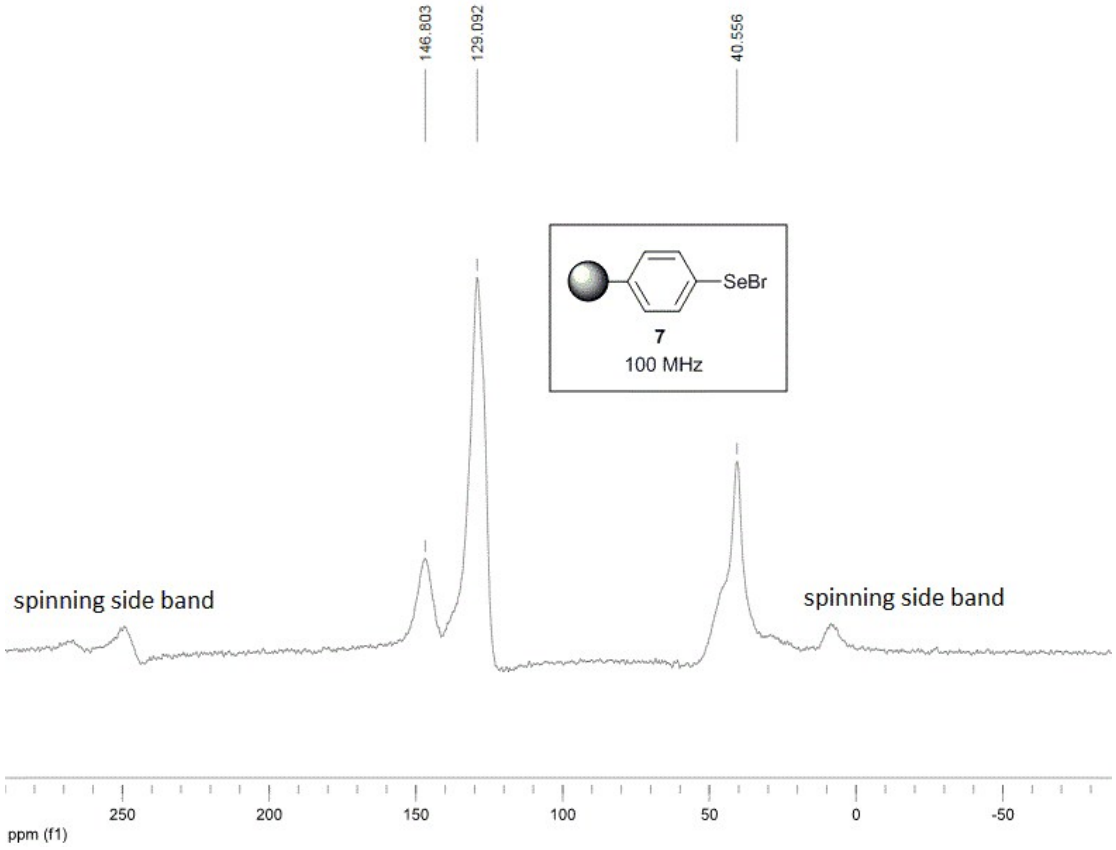
7-oxa-bicyclo[4.1.0]heptane 5. GC-MS (EI): m/z 98 [M^+]. Known compound (286-20-4).



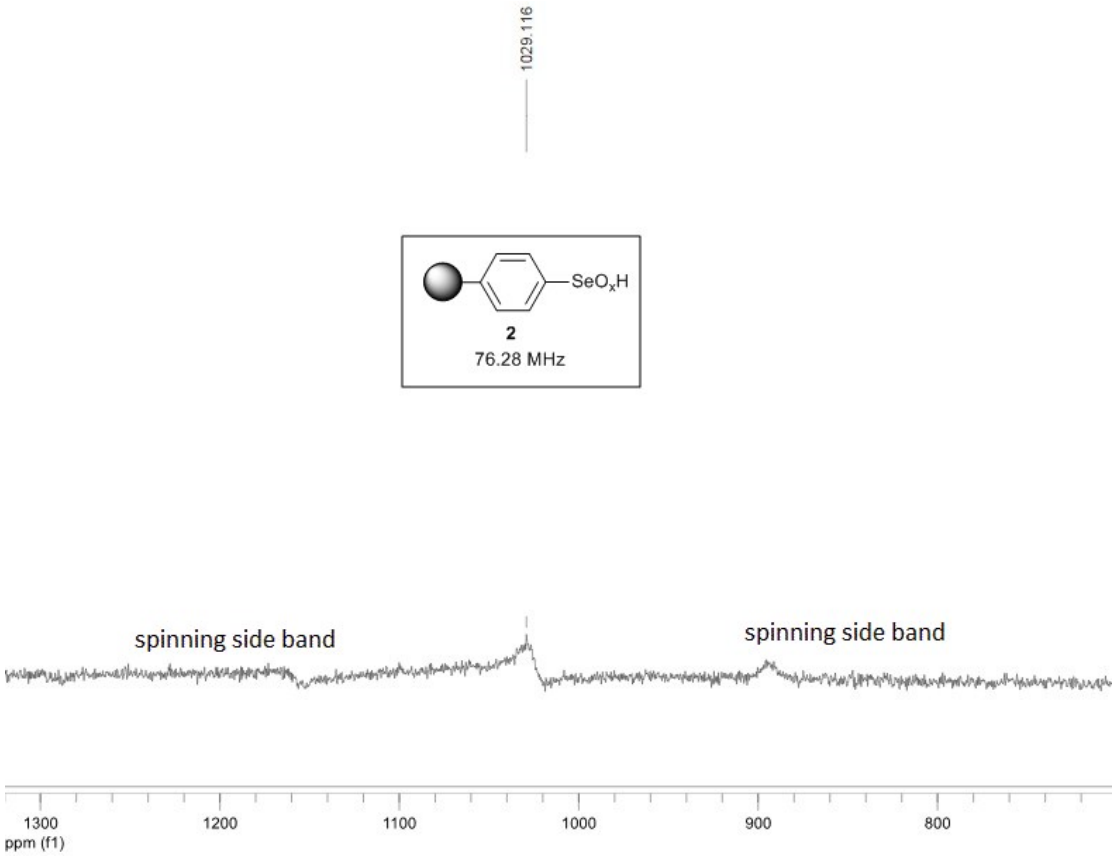
Solid state ^{13}C NMR spectra of resin 2, 6 and 7




147.393
129.358
40.105
SeMe
6
100 MHz
spinning side band
spinning side band
250
200
150
100
50
0
-50
ppm (f1)

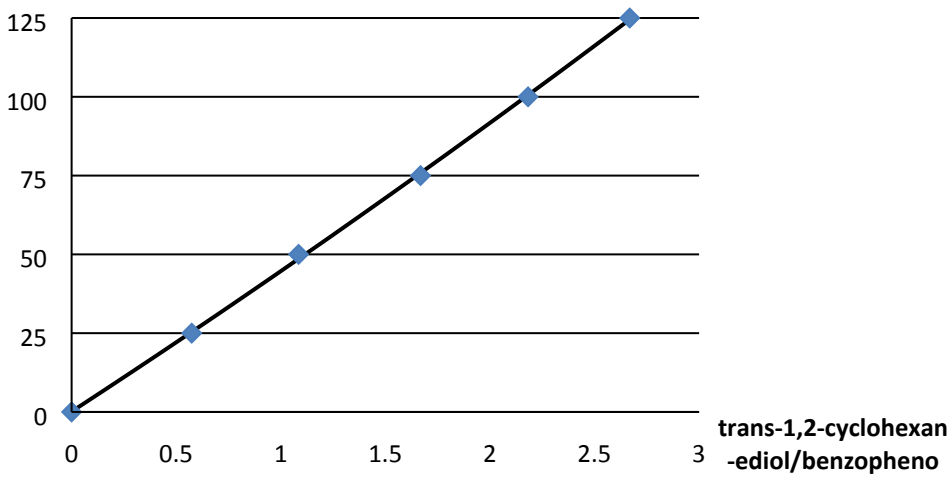

146.803
129.092
40.556
SeBr
7
100 MHz
spinning side band
spinning side band
250
200
150
100
50
0
-50
ppm (f1)

Solid state ^{77}Se NMR spectra of resin 2

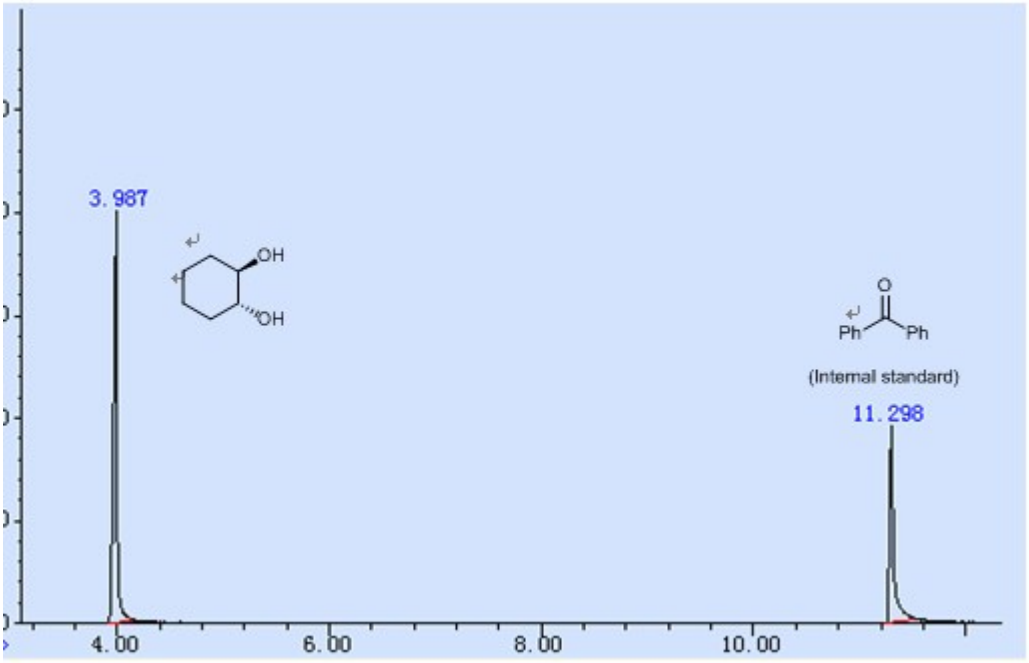


3. Detailed GC-yield Calculation Procedures

Internal standard curve



Example (Reaction in Table 1, entry 1 in text)

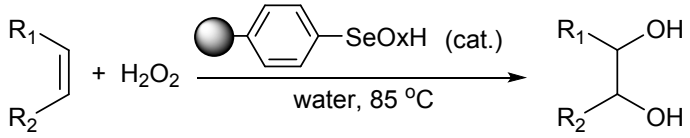


Peak	Ret. Time	Height	Area	Area%
1	3.987	1967077	45818465	64.097%
2	11.298	962755	25664853	35.903%

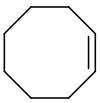
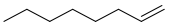
X= 45818465/25664853, Thus, Y = 81% according to internal standard curve.

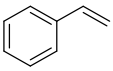
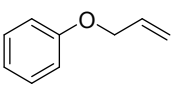
4. Oxidation of other olefins by using polymer 2 as catalyst

Table S3 Oxidation of olefins catalyzed by polymer 2[a]



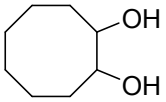
olefin

Entry	Olefin	Cat. amount (mol %)	H_2O_2 amount (equiv.)	Diol yield (%)[b]
1		5	1.0	94[b]
2		5	4.0	92[b]
3		5	1.0	95[b]

4		10	4.0	9[c]
5		10	2.0	18[c]
6		10	1.0	0

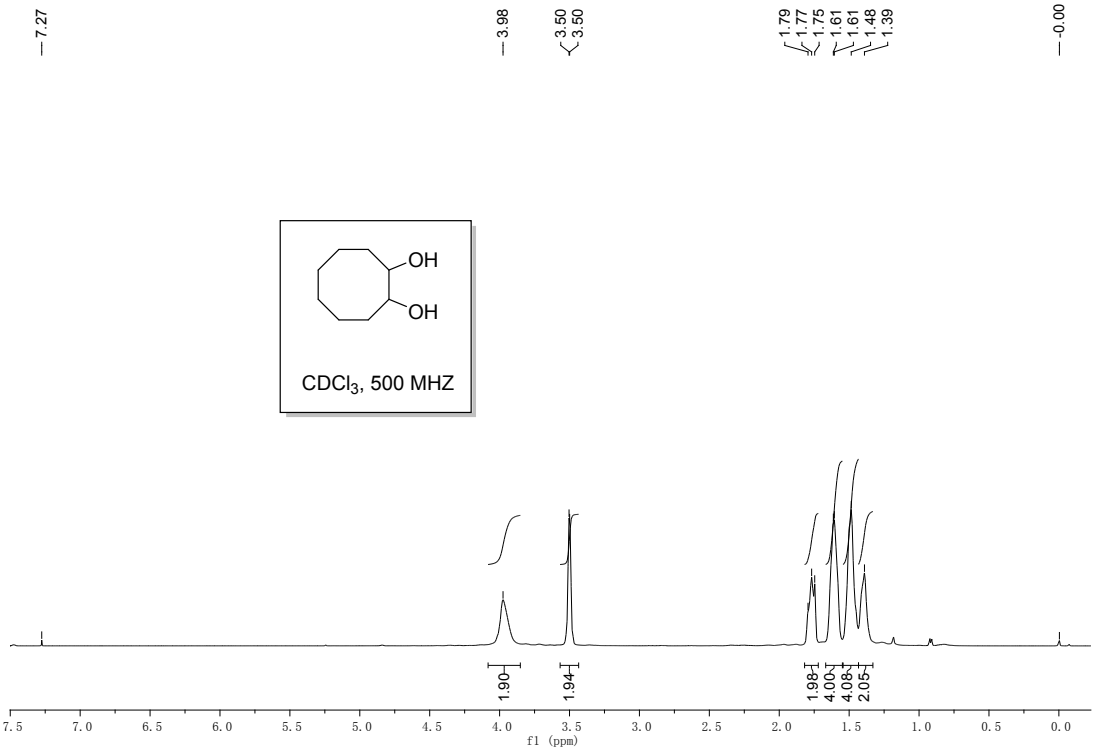
[a] 1 mmol of olefin was employed; [b] Isolated yield; [c] GC-yield.

Product spectra and characterization data.

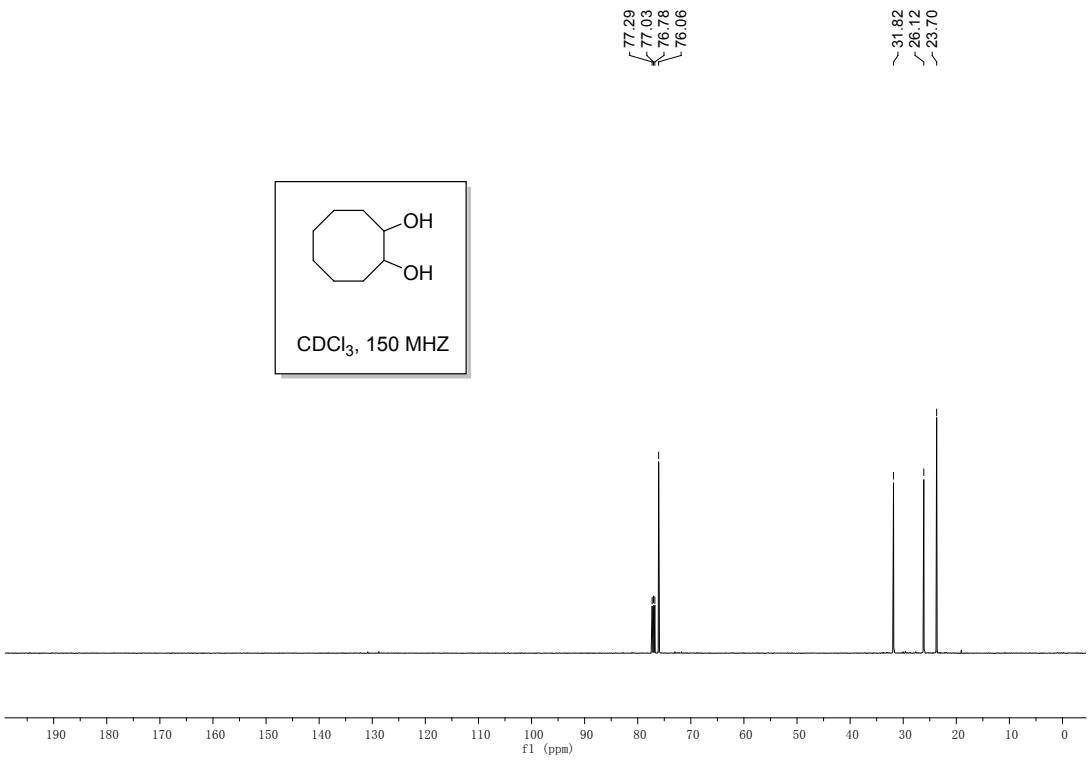


1,2-Cyclooctanediol. *Known compound* (4277-32-1). 92% yield. White solid. Melting point 31.1 - 32.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.98 (s, 2H), 3.50 (d, J = 2.2 Hz, 2H), 1.82 - 1.72 (m, 2H), 1.61 (d, J = 3.5 Hz, 4H), 1.48 (s, 4H), 1.39 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 76.06, 31.82, 26.12, 23.70. GC-MS (EI): *m/z* 144 [M^+]. IR ν_{max} (KBr): 3390, 2924, 2856, 2697, 1465, 1448, 1403, 1354, 1335, 1282, 1212, 1115, 1085, 1036, 984, 962, 902, 741, 576cm^{-1}.

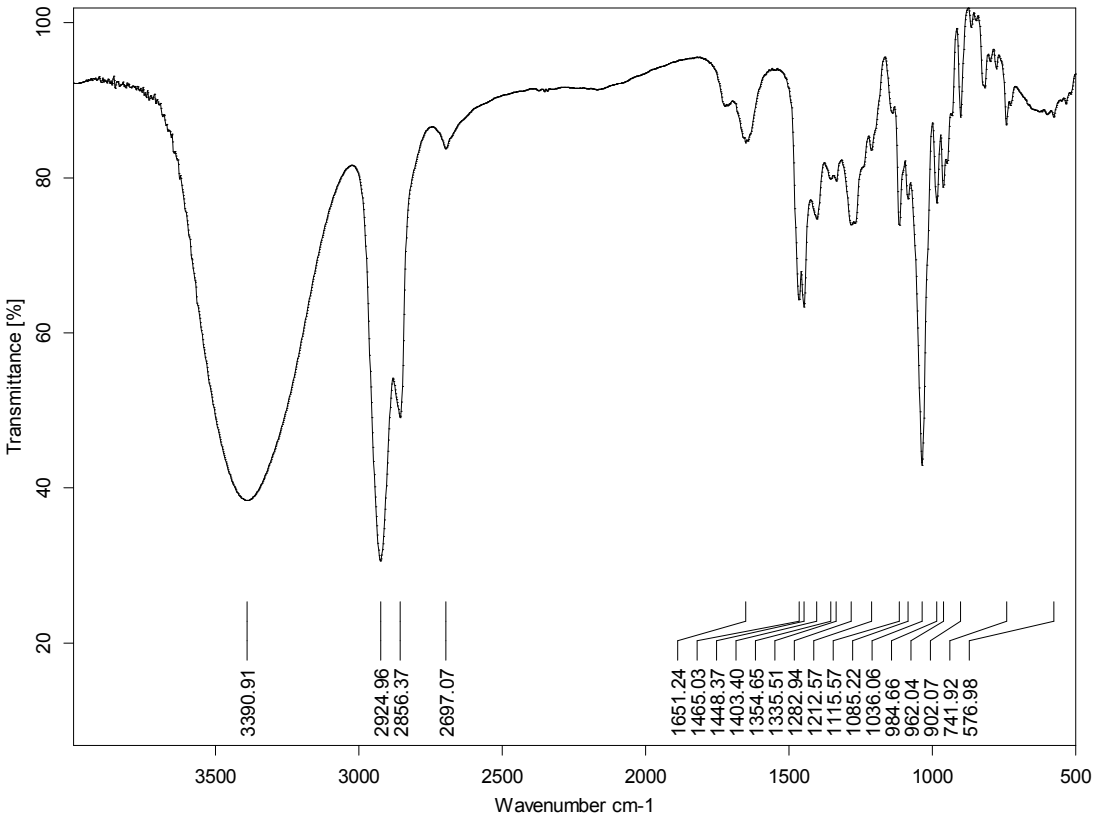
^{1}H NMR



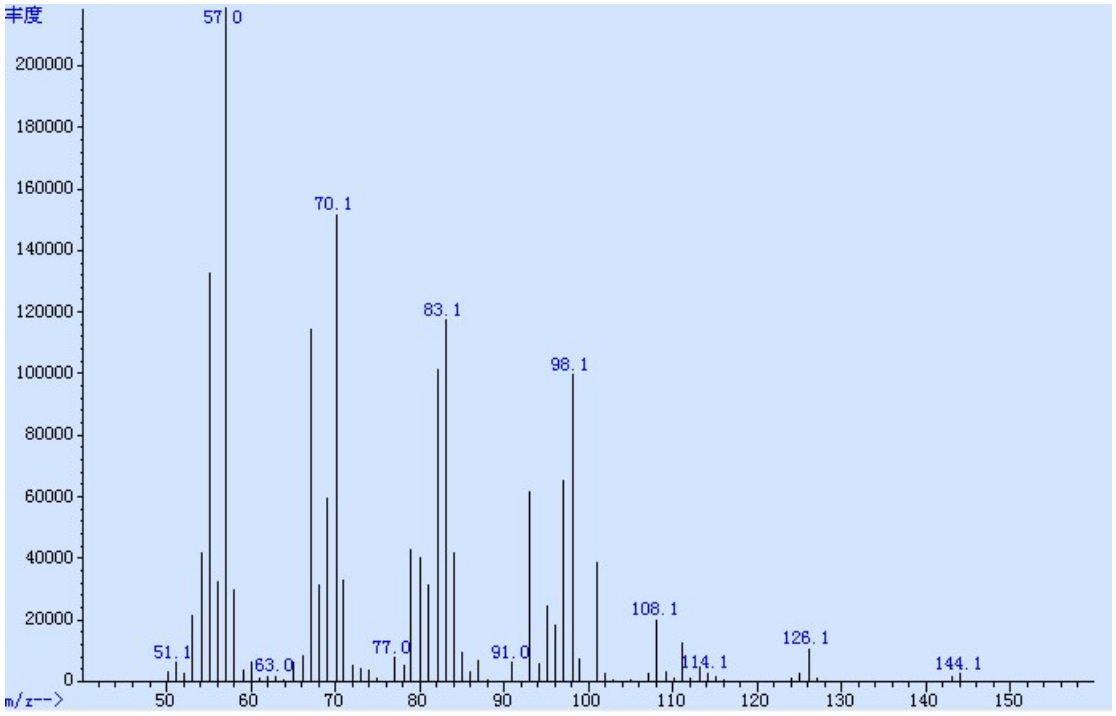
^{13}C NMR

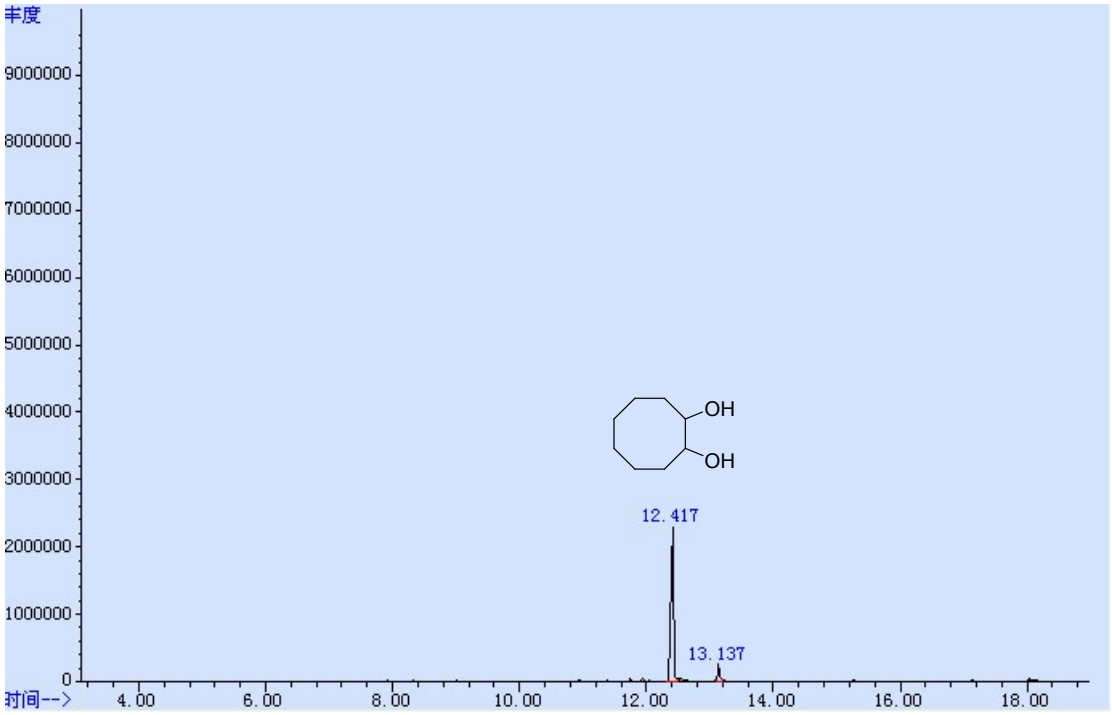

77.29
77.03
76.78
76.06
31.82
26.12
23.70
OH
OH
CDCl3, 150 MHZ
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

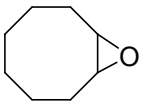
FT-IR


Transmittance [%]
100
80
60
40
20
3390.91
2924.96
2856.37
2697.07
1651.24
1465.03
1448.37
1403.40
1354.65
1335.51
1282.94
1212.57
1115.57
1085.22
1036.06
984.66
962.04
902.07
741.92
576.98
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

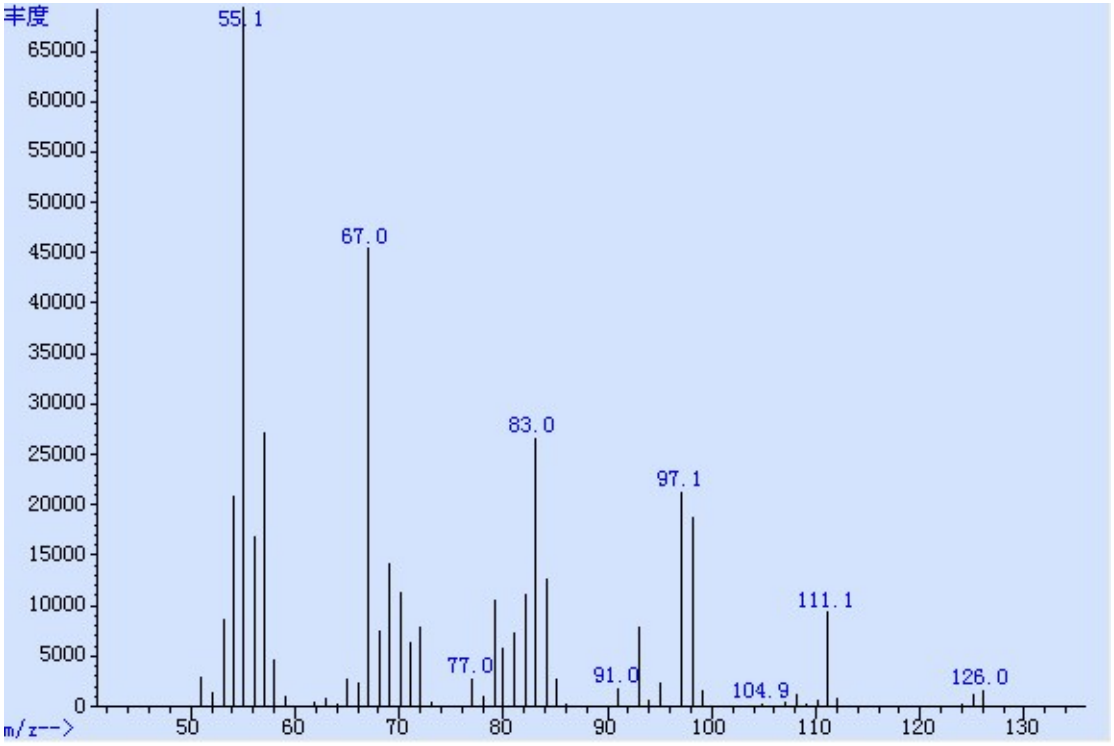
GC-MS (EI)

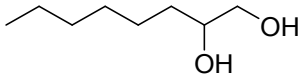

丰度
57.0
70.1
83.1
98.1
108.1
126.1
144.1
51.1
63.0
77.0
91.0
114.1
m/z-->
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
50
60
70
80
90
100
110
120
130
140
150



By-product: 

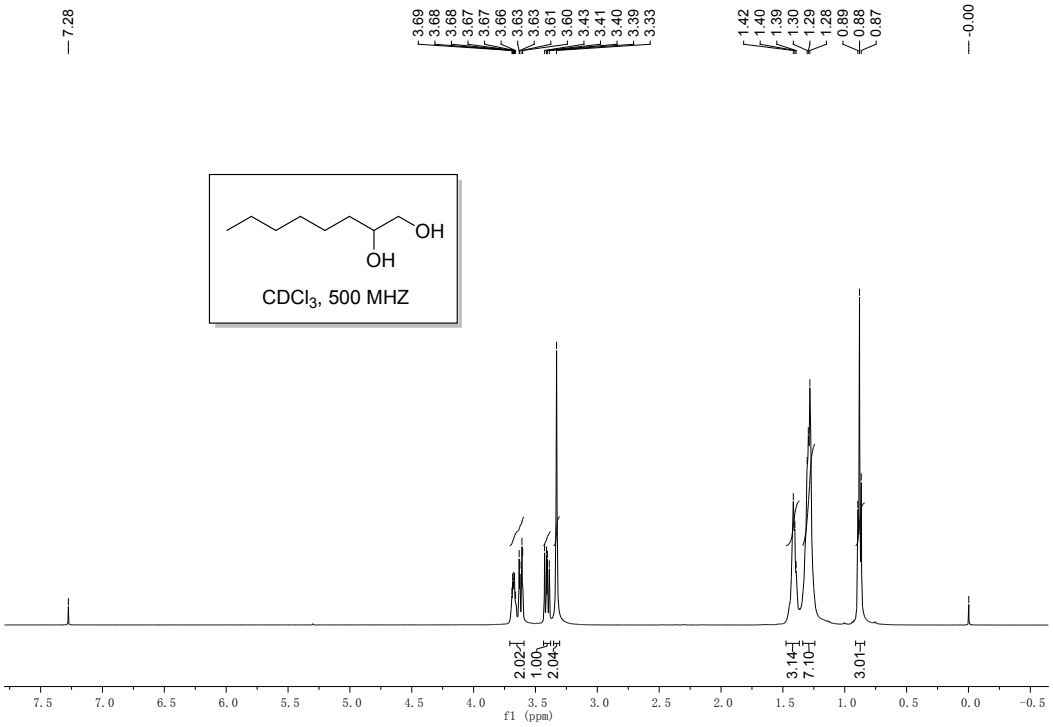
9-Oxabicyclo[6.1.0]nonane . *Known compound* (286-62-4). GC-MS (EI): *m/z* 126 [M^+].



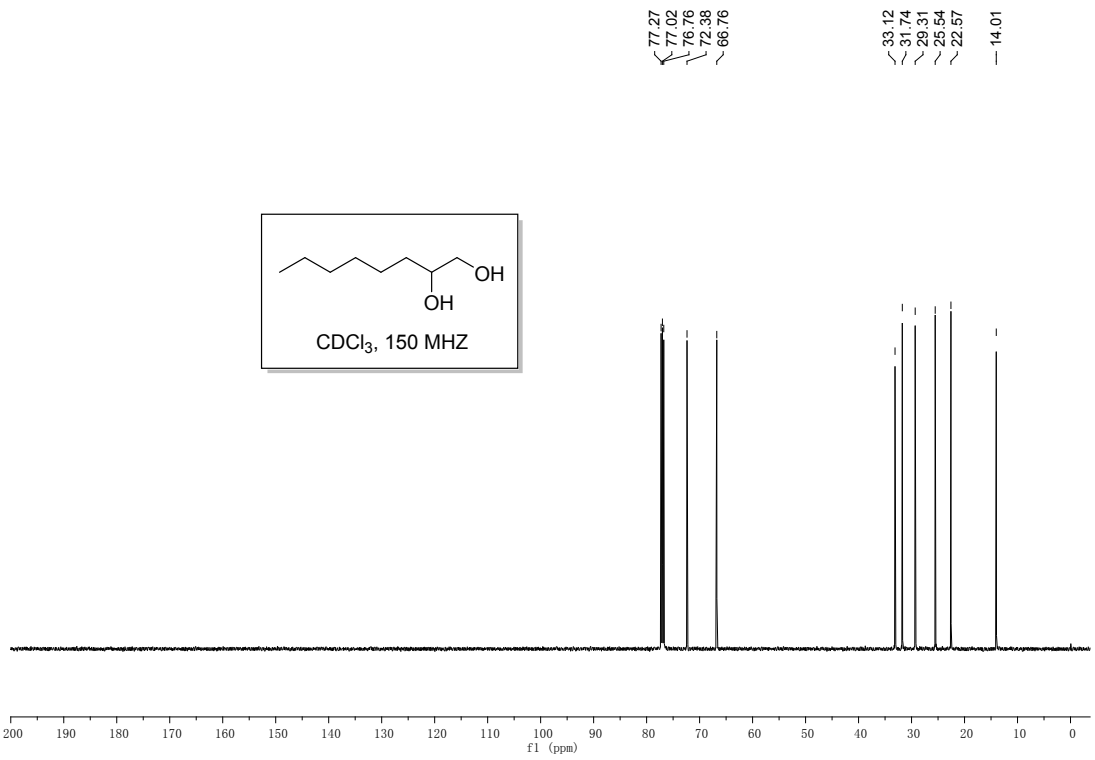


1,2-Octanediol. *Known compound* (1117-86-8). 95% yield. White solid. Melting point 36.1 – 37.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.71 - 3.59 (m, 2H), 3.41 (dd, *J* = 11.3, 7.9 Hz, 1H), 3.33 (s, 2H), 1.47 - 1.37 (m, 3H), 1.34 - 1.24 (m, 7H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 72.38, 66.76, 33.12, 31.74, 29.31, 25.54, 22.57, 14.01. GC-MS (EI): *m/z* 145 [M^+]. IR ν_{max} (KBr): 3381, 2957, 2928, 2857, 1650, 1467, 1378, 1133, 1072, 860, 724, 668, 578cm^{-1}.

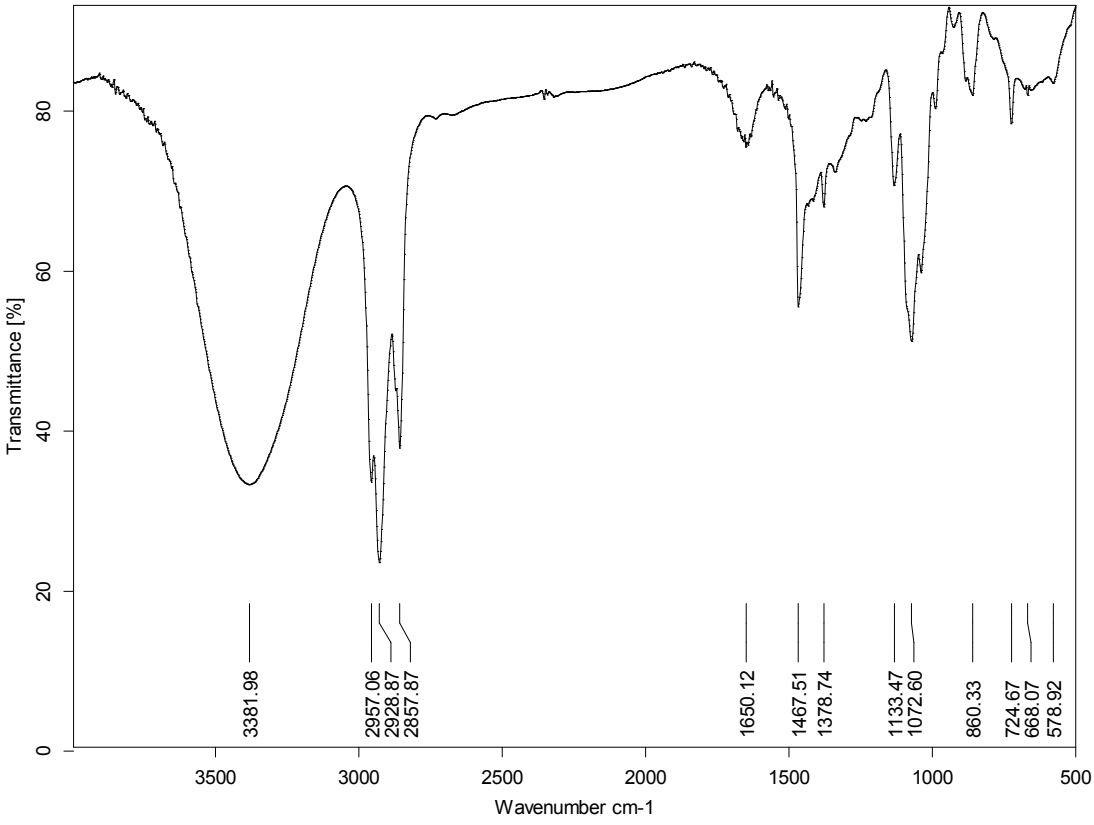
^{1}H NMR



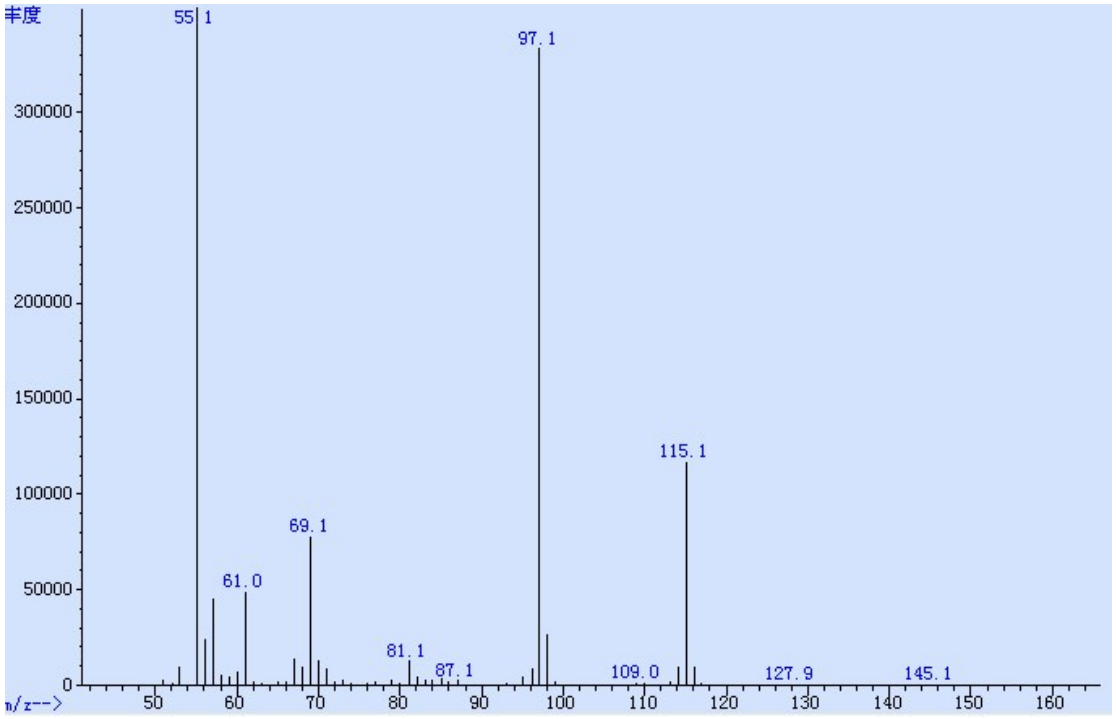
^{13}C NMR

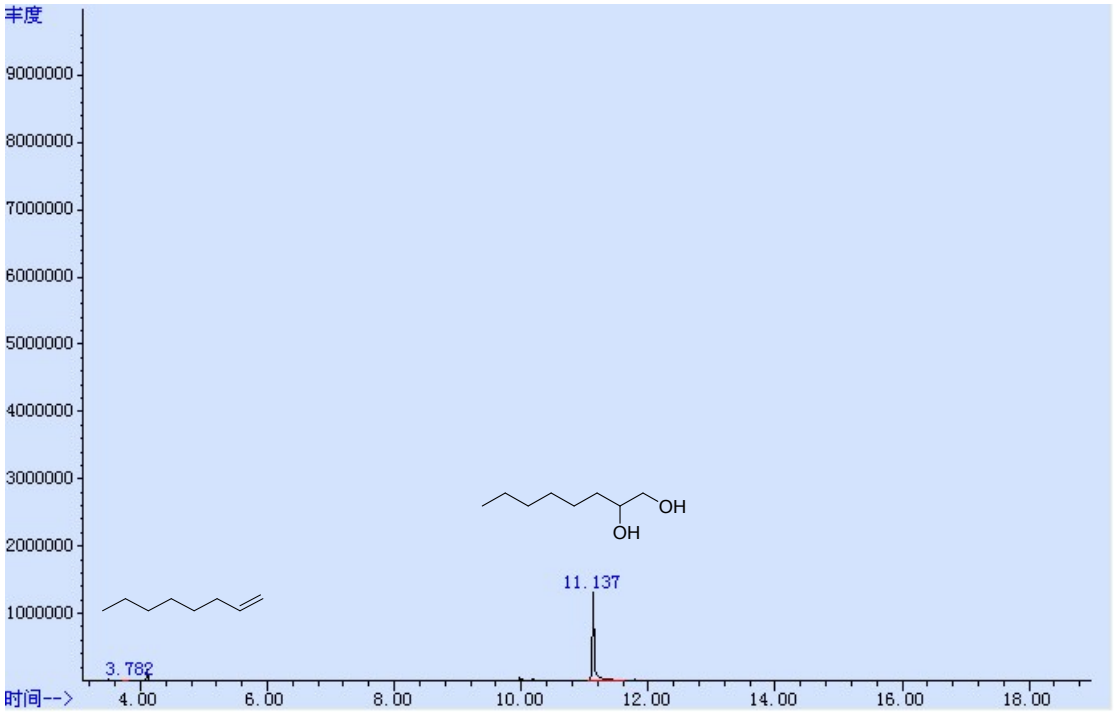

77.27
77.02
76.76
72.38
66.76
33.12
31.74
29.31
25.54
22.57
14.01
OH
OH
CDCl3, 150 MHZ
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

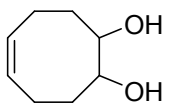
FT-IR


Transmittance [%]
0
20
40
60
80
3381.98
2957.06
2928.87
2857.87
1650.12
1467.51
1378.74
1133.47
1072.60
860.33
724.67
668.07
578.92
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

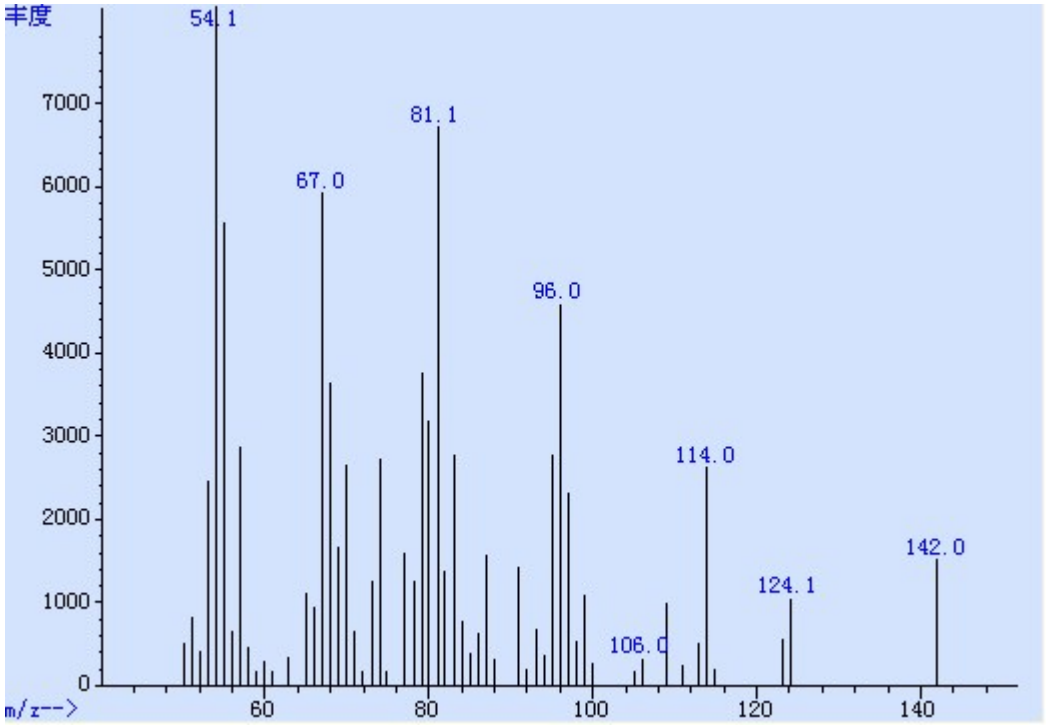
GC-MS (EI)

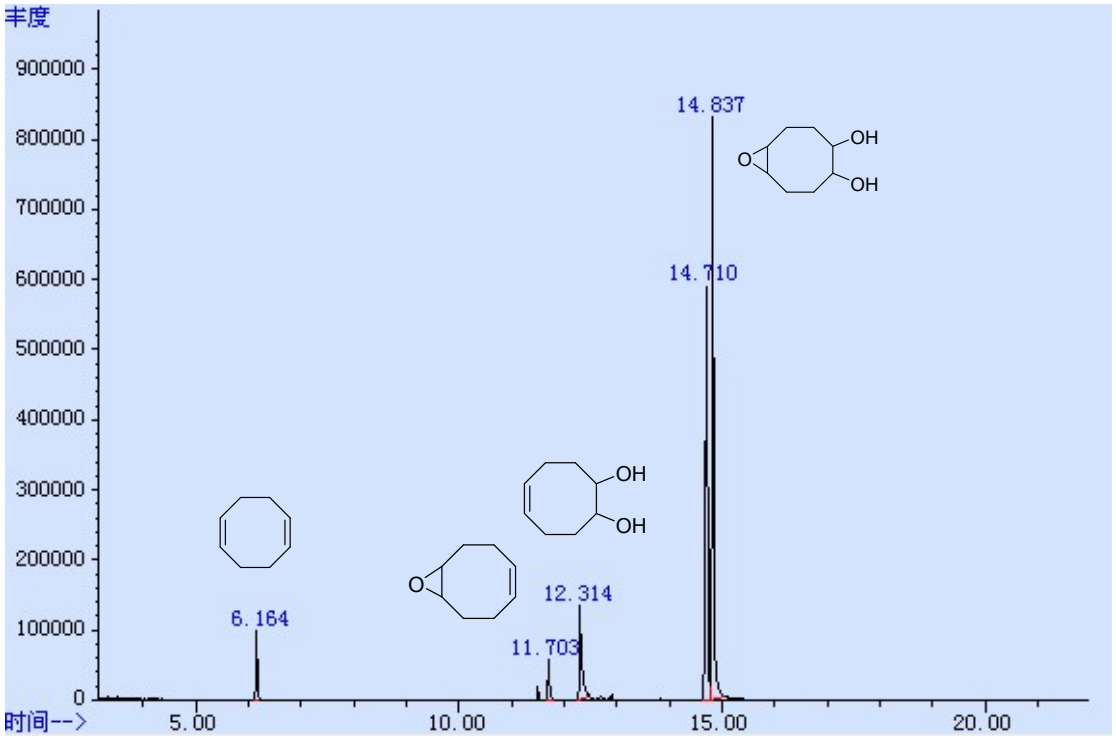


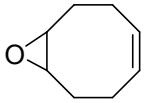




5-Cyclooctene-1,2-diol. *Known compound* (55519-21-6). 9% yield. GC-MS (EI): *m/z* 142 [M^+].

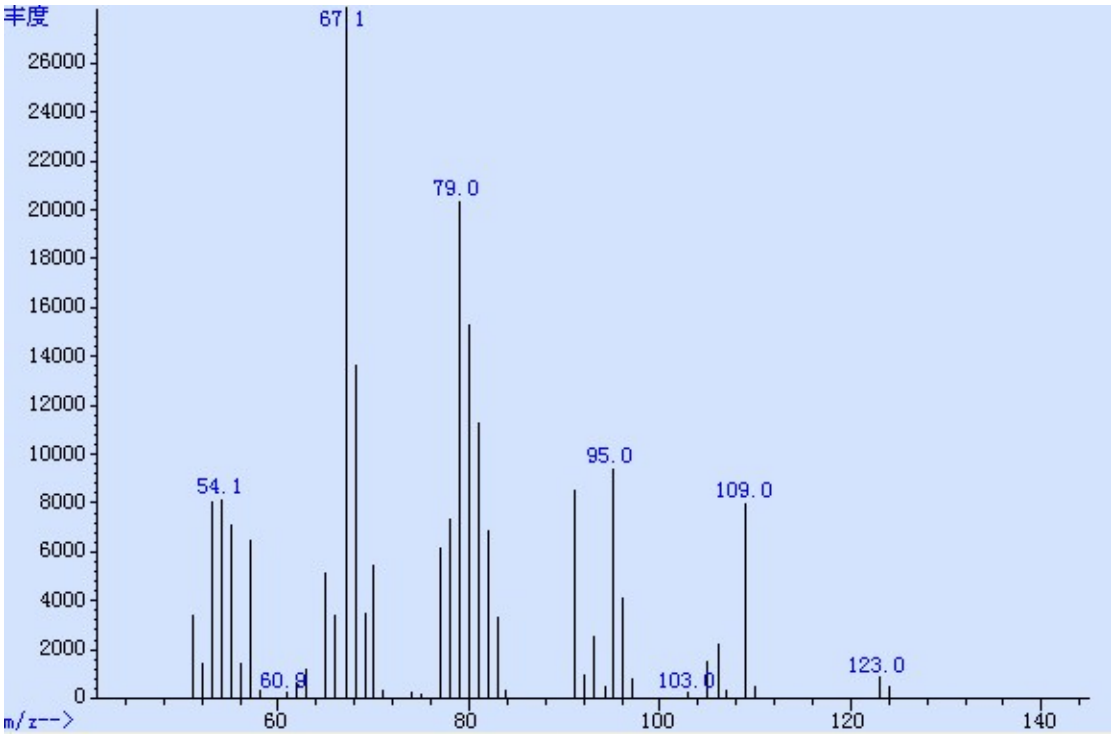


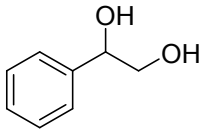




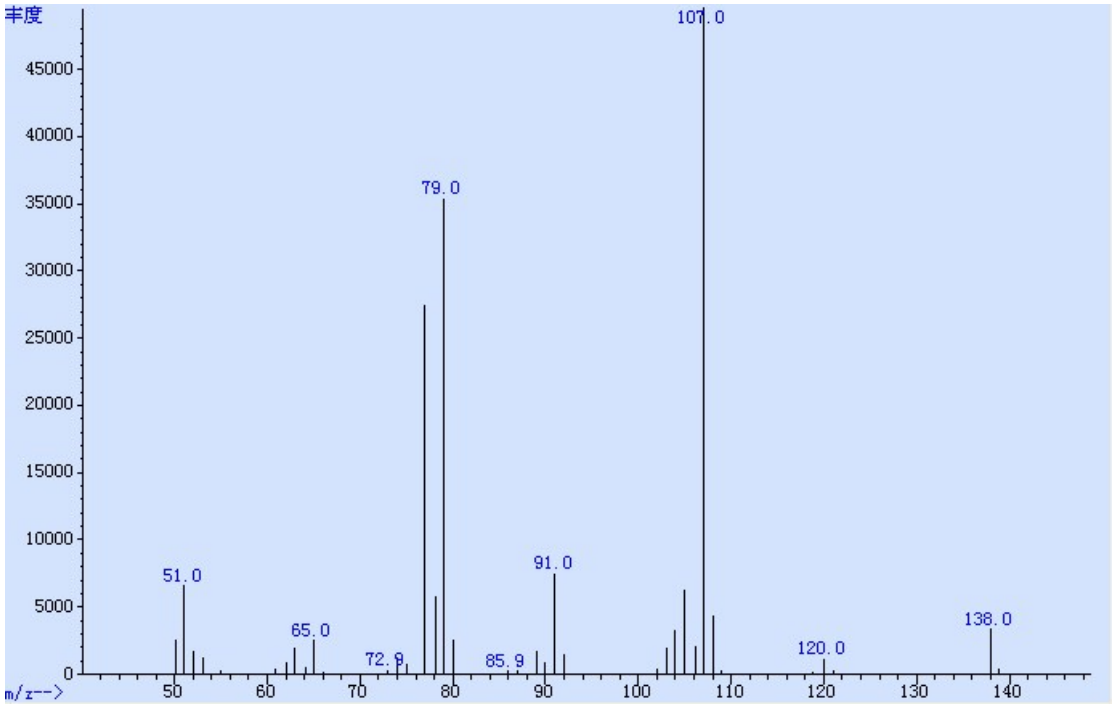
By-product:

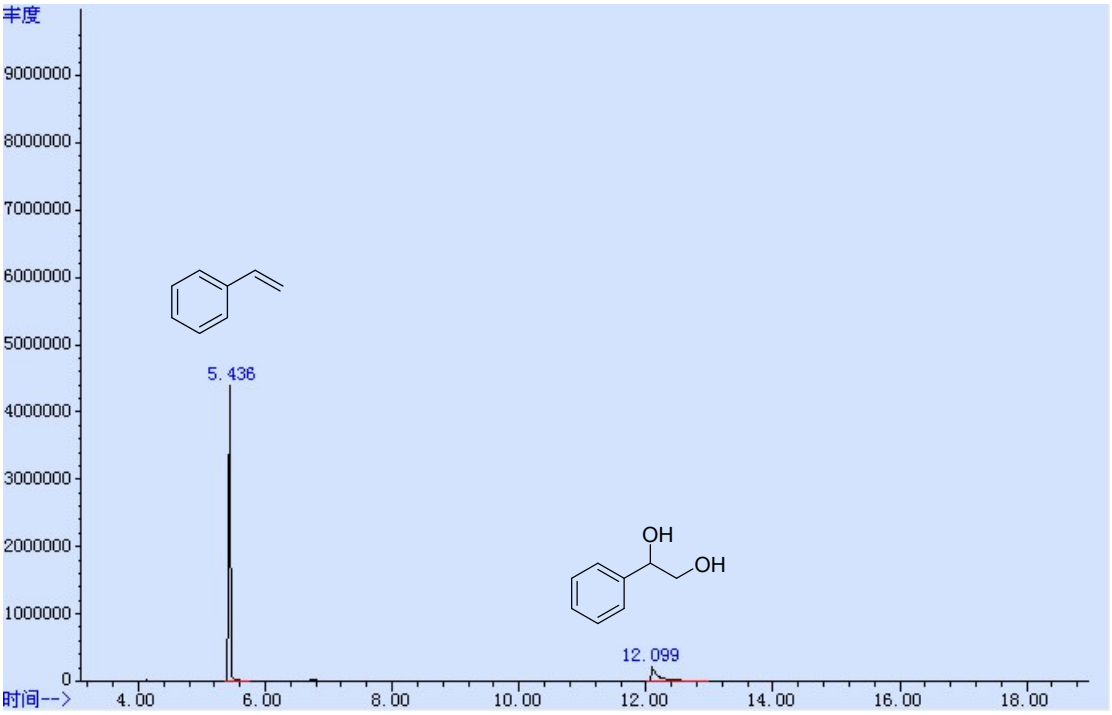
9-Oxabicyclo[6.1.0]non-4-ene. *Known compound* (637-90-1). GC-MS (EI): *m/z* 124 [M^+].





1-Phenyl-1,2-ethanediol. *Known compound* (93-56-1). 18% yield. GC-MS (EI): *m/z* 138 [M^+].




丰度
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
5.436
OH
OH
12.099
时间-->
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00