Electronic Supplementary information for

Investigation of thermal decomposition mechanism of glycerol: the combination of theoretical study based on Minnesota functional and experimental support

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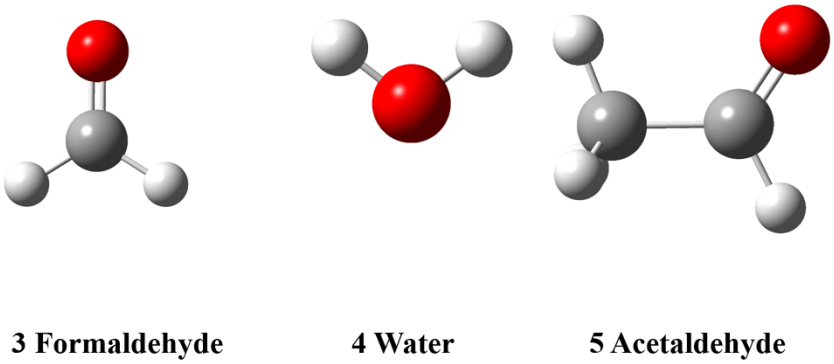
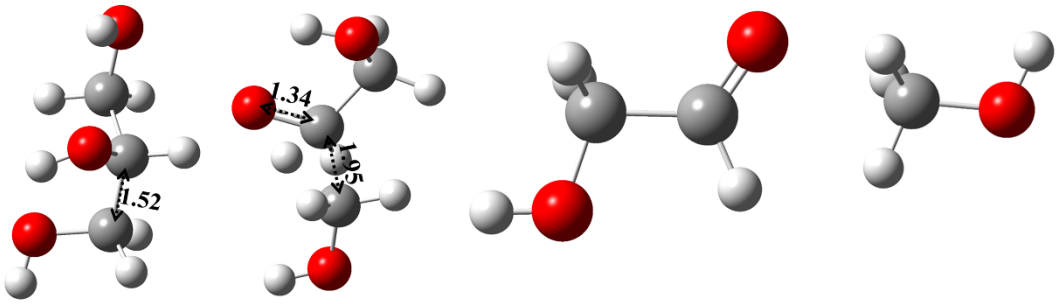
Contents

1. Optimized structures for glycerol, intermediates and transition states.

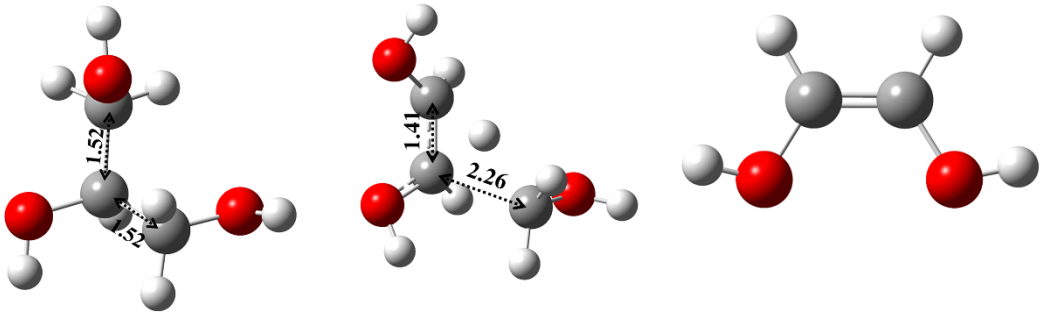


3 Formaldehyde **4 Water** **5 Acetaldehyde**

Figure S1.Part of the product of reaction (1) and its subsequent reaction.



Gly′ **TS3** **6 Glycolaldehyde** **7 Methanol**



Gly″ **TS4** **8 1,2-ethenediol**

Figure S2.The optimized results of the reactants and transition states of reactions (2) (3).

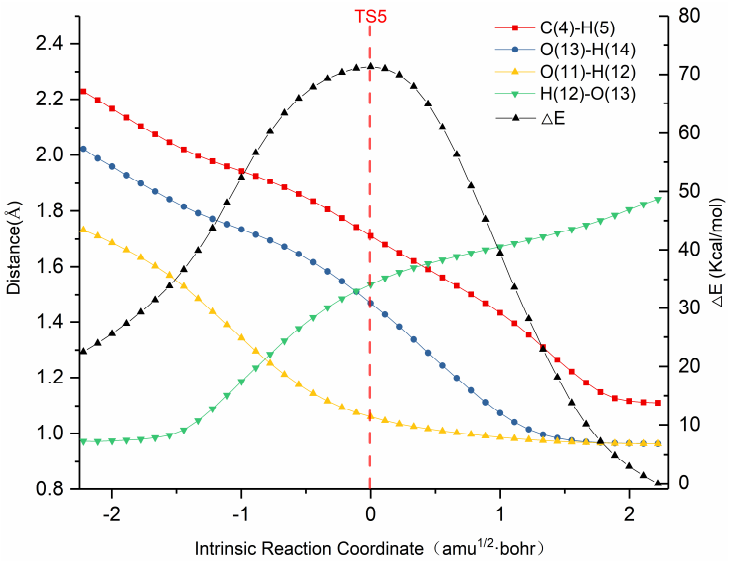


Figure S3. Bond length and ΔE under IRC method of the TS5.

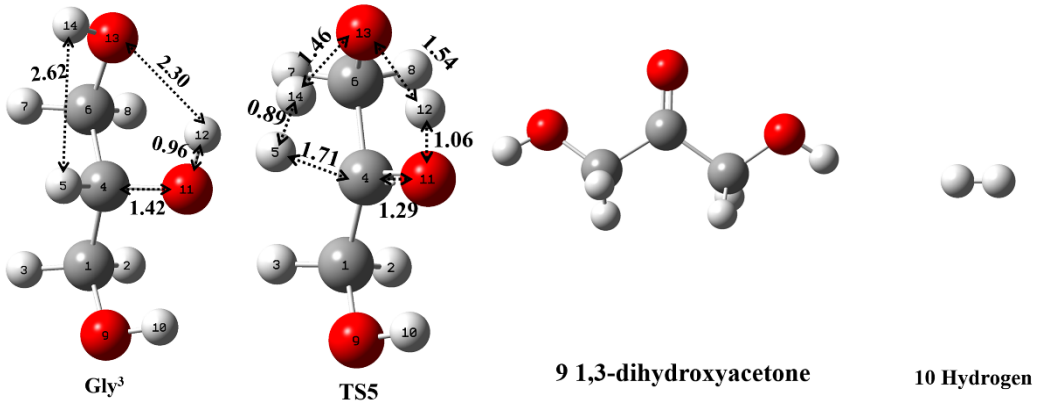


Figure S4.The optimized structure of the dehydrogenation path.

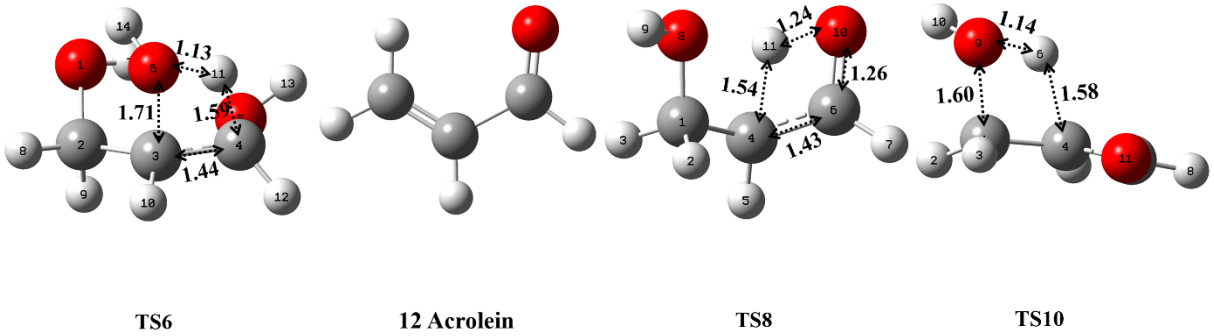
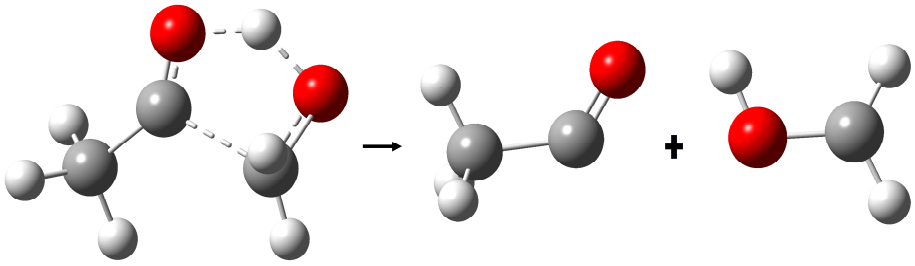


Figure S5.The optimized structure of the reaction (5) and its subsequent reactions.



TS13 O-H-O hydrogen bridge structure → double radical

Figure S6. O-H-O hydrogen bridge radical structure.

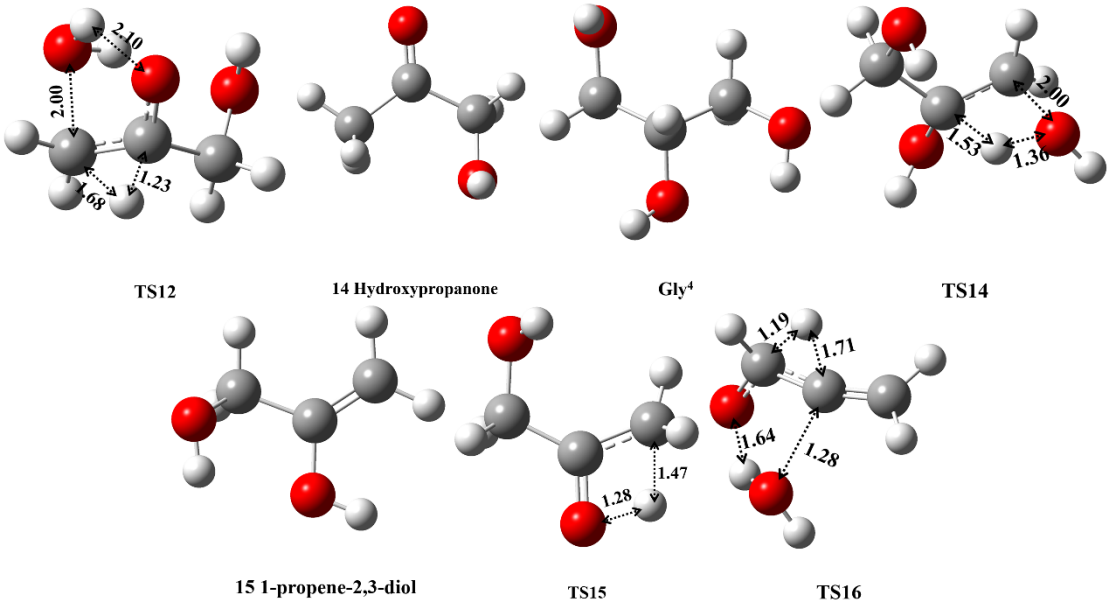


Figure S7.The optimized structure of the reactions (7), reaction (8) and their subsequent reactions.

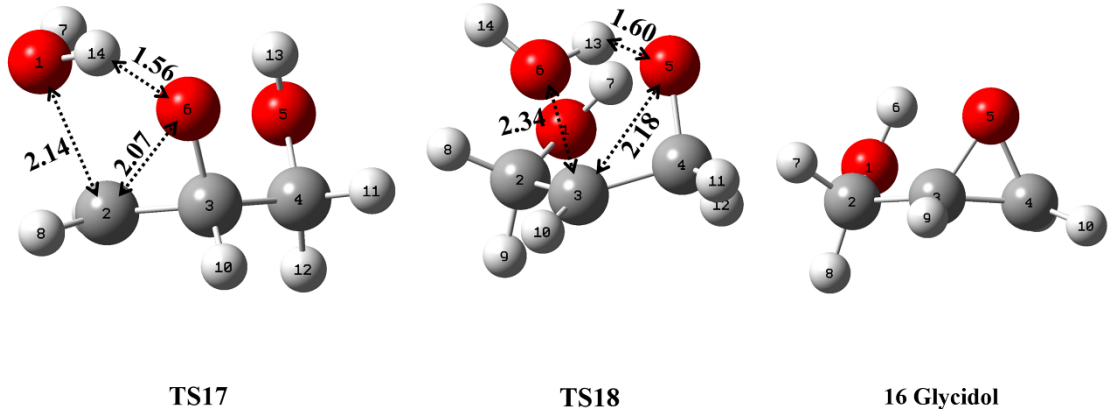
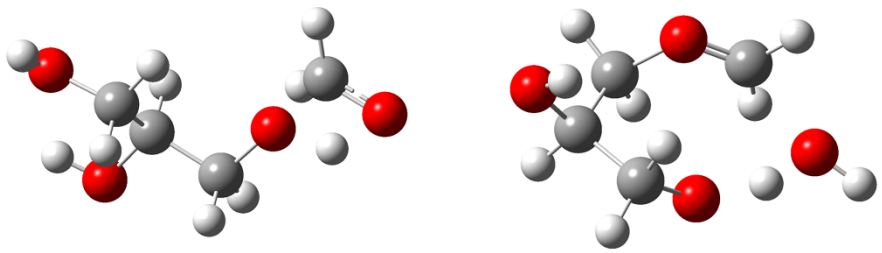


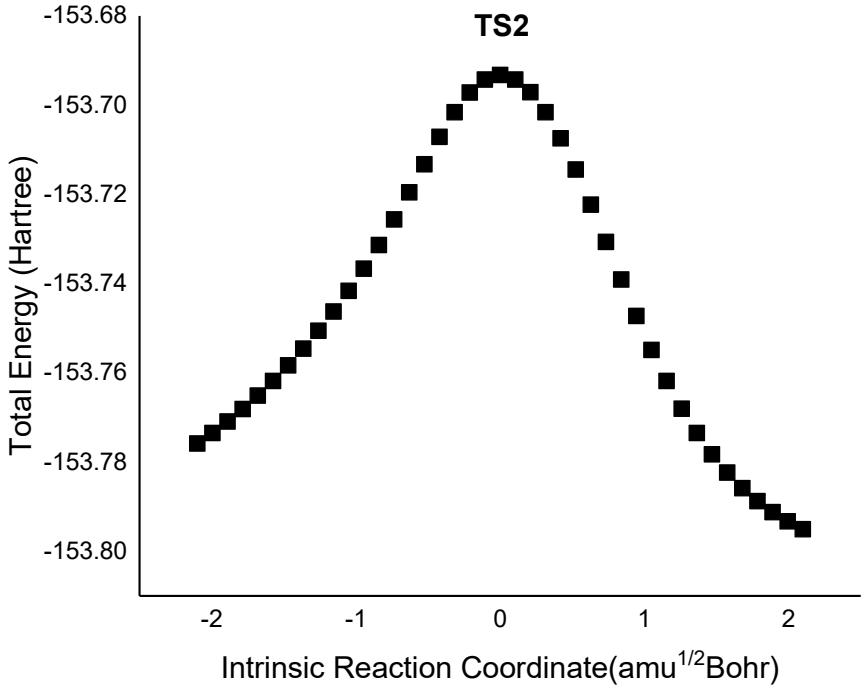
Figure S8. The optimized structure of the reactions (9) and reaction (10)

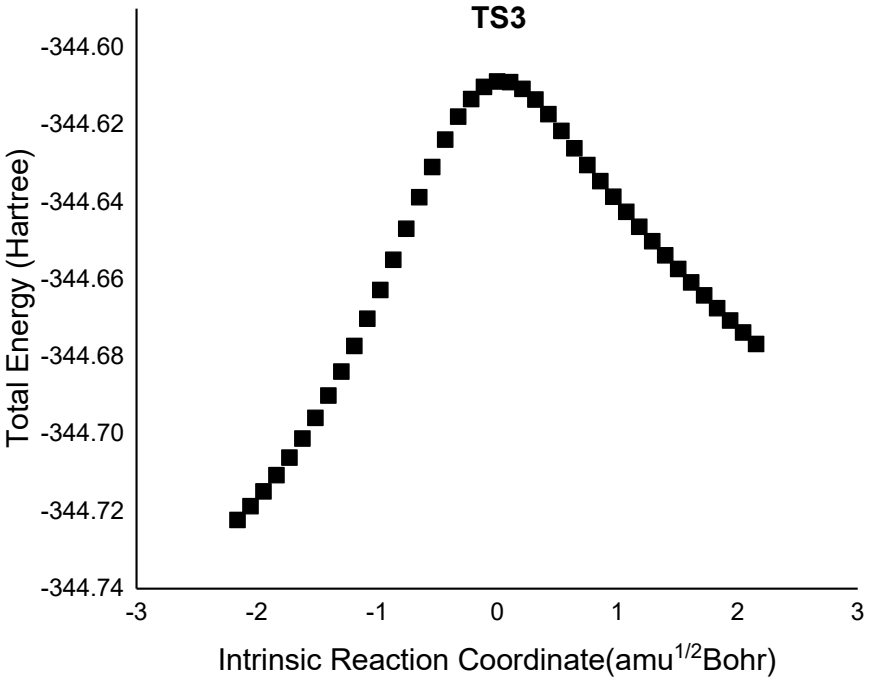


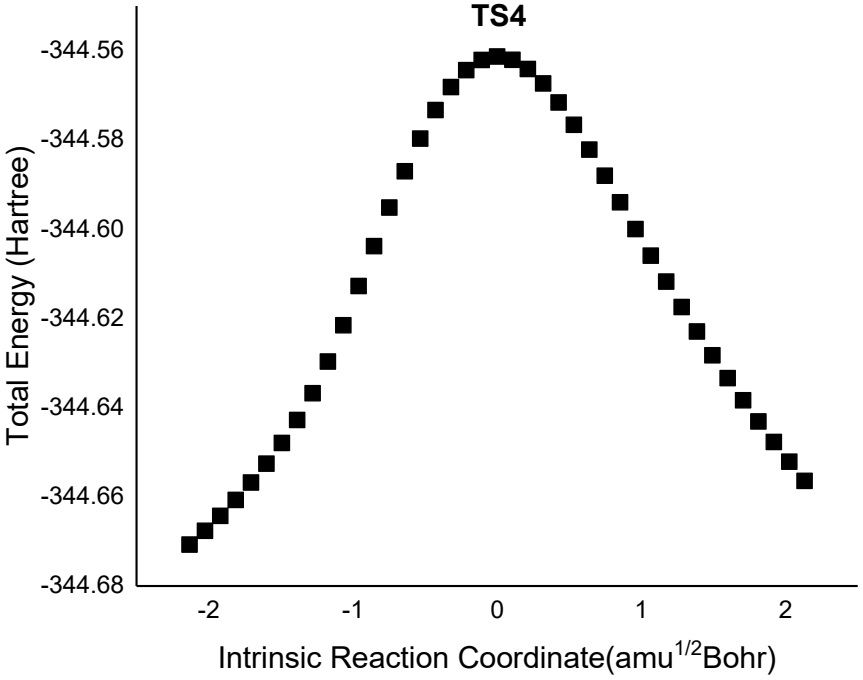
TS19 **TS20**

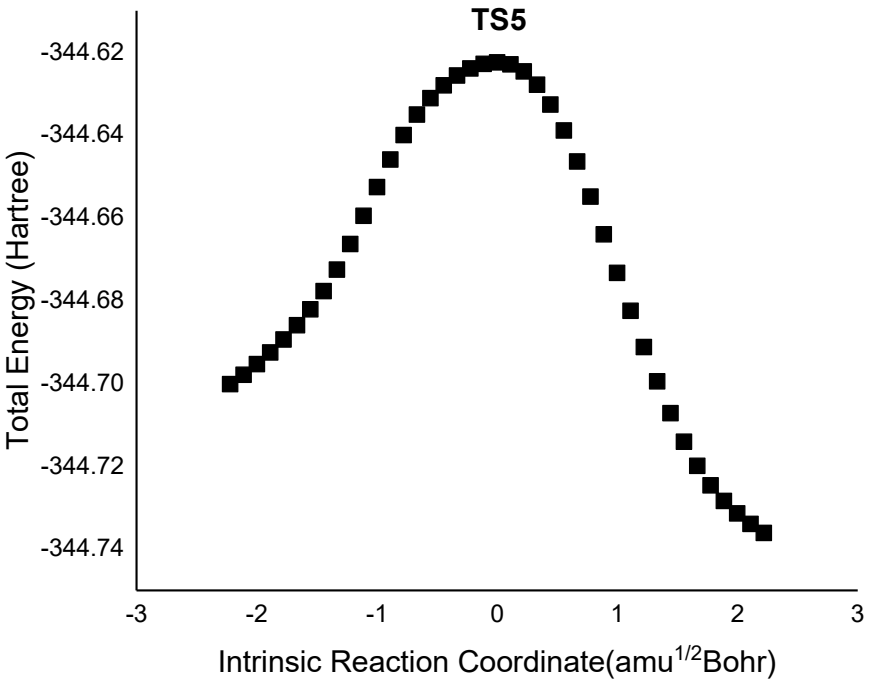
Figure S9. Transition state TS19 and TS20 during the formation of glycerol formal

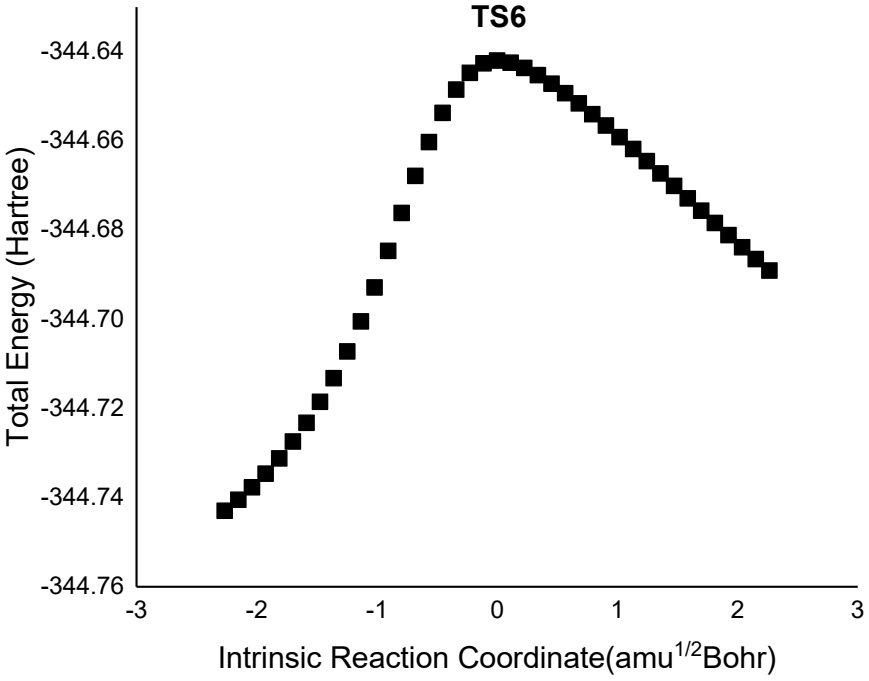
2. Intrinsic reaction coordinate results of transition-states.

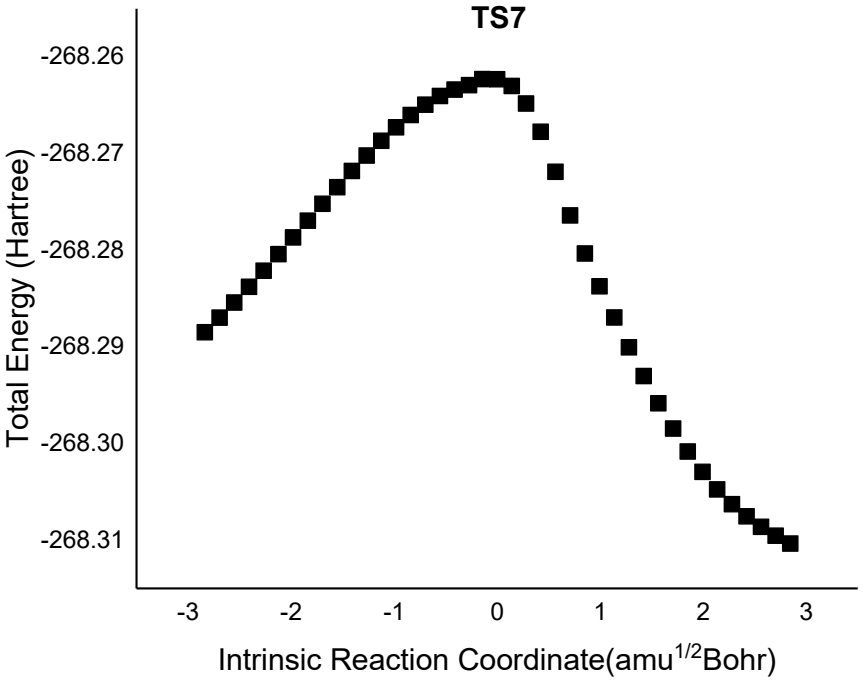


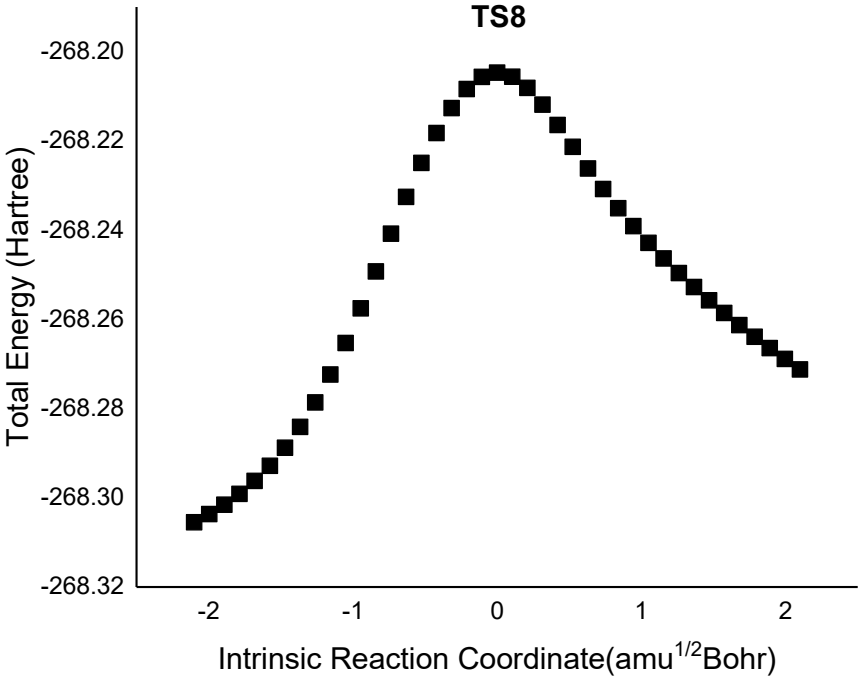

TS3
-344.60
-344.62
-344.64
-344.66
-344.68
-344.70
-344.72
-344.74
Total Energy (Hartree)
-3
-2
-1
0
1
2
3
Intrinsic Reaction Coordinate(amu1/2Bohr)

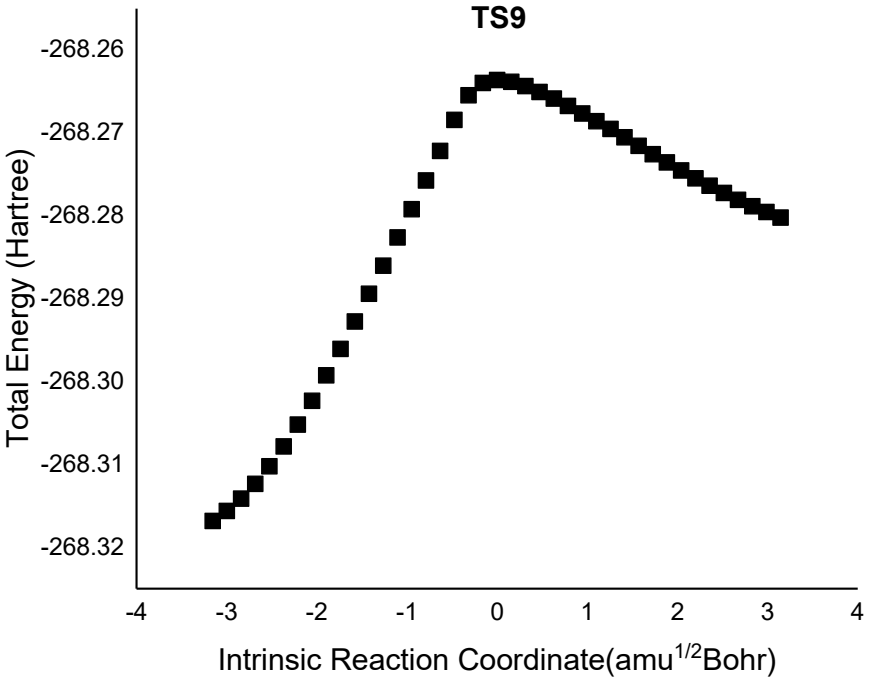

TS4
-344.56
-344.58
-344.60
-344.62
-344.64
-344.66
-344.68
Total Energy (Hartree)
-2
-1
0
1
2
Intrinsic Reaction Coordinate(amu1/2Bohr)

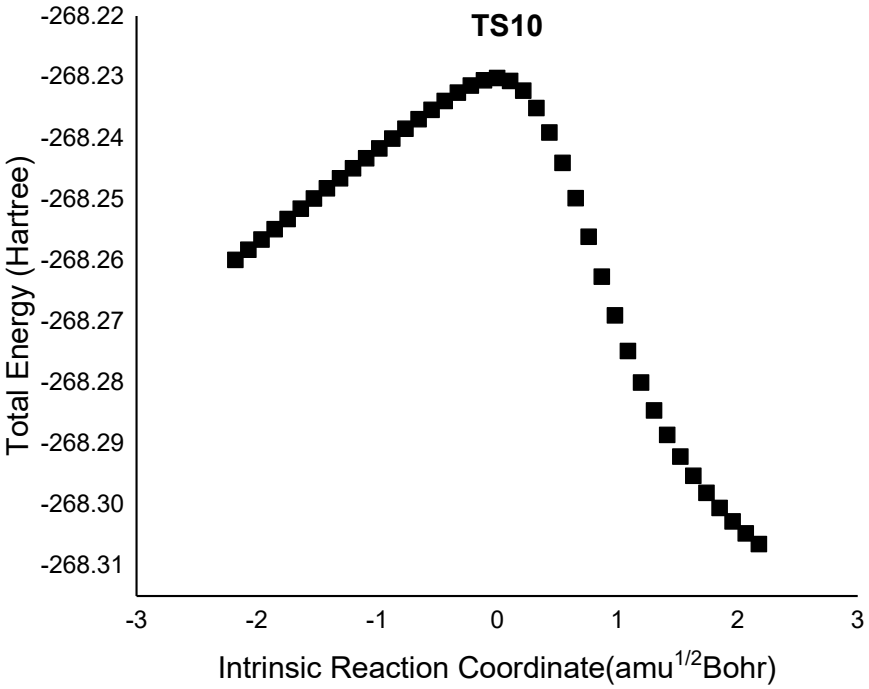

TS5
-344.62
-344.64
-344.66
-344.68
-344.70
-344.72
-344.74
Total Energy (Hartree)
-3
-2
-1
0
1
2
3
Intrinsic Reaction Coordinate(amu1/2Bohr)

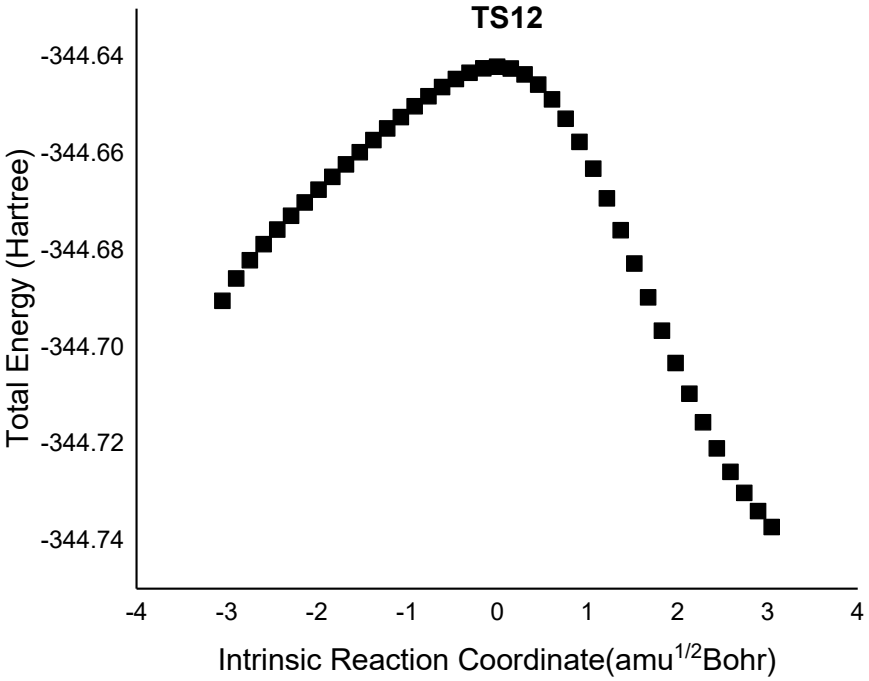

TS6
-344.64
-344.66
-344.68
-344.70
-344.72
-344.74
-344.76
Total Energy (Hartree)
-3
-2
-1
0
1
2
3
Intrinsic Reaction Coordinate(amu1/2Bohr)

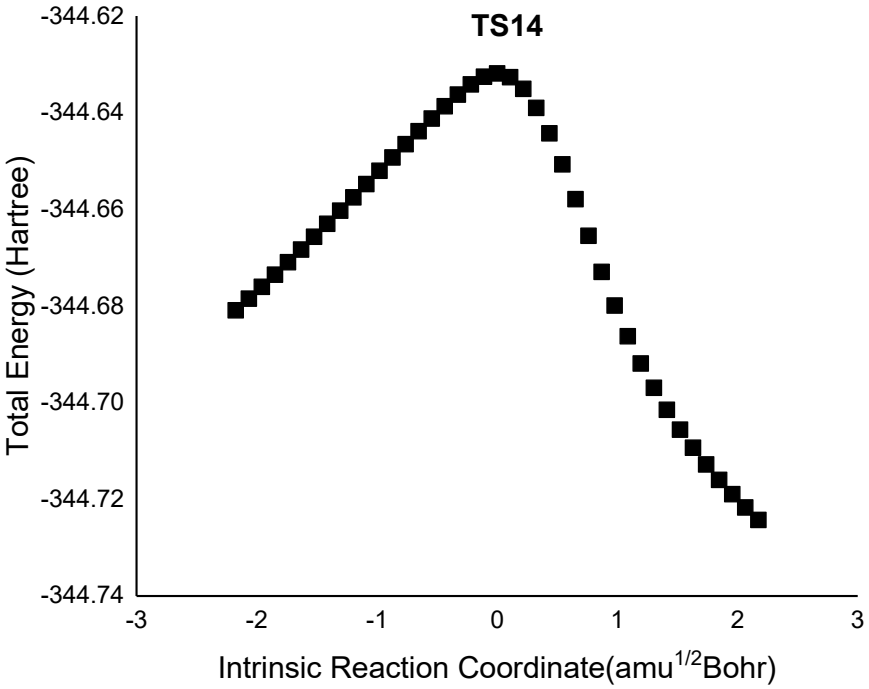

TS7
-268.26
-268.27
-268.28
-268.29
-268.30
-268.31
Total Energy (Hartree)
-3
-2
-1
0
1
2
3
Intrinsic Reaction Coordinate(amu1/2Bohr)

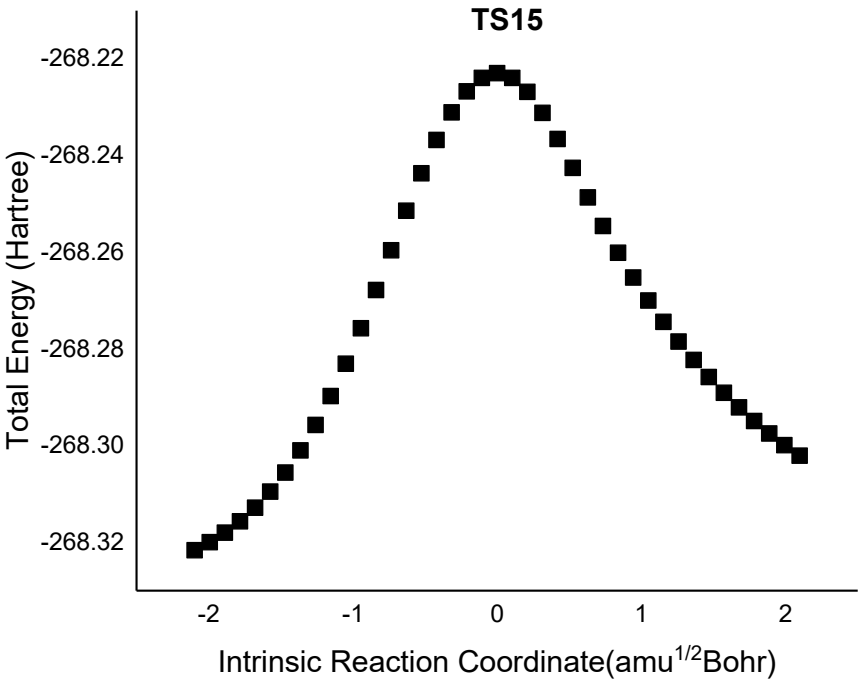

TS8
-268.20
-268.22
-268.24
-268.26
-268.28
-268.30
-268.32
Total Energy (Hartree)
-2
-1
0
1
2
Intrinsic Reaction Coordinate(amu1/2Bohr)

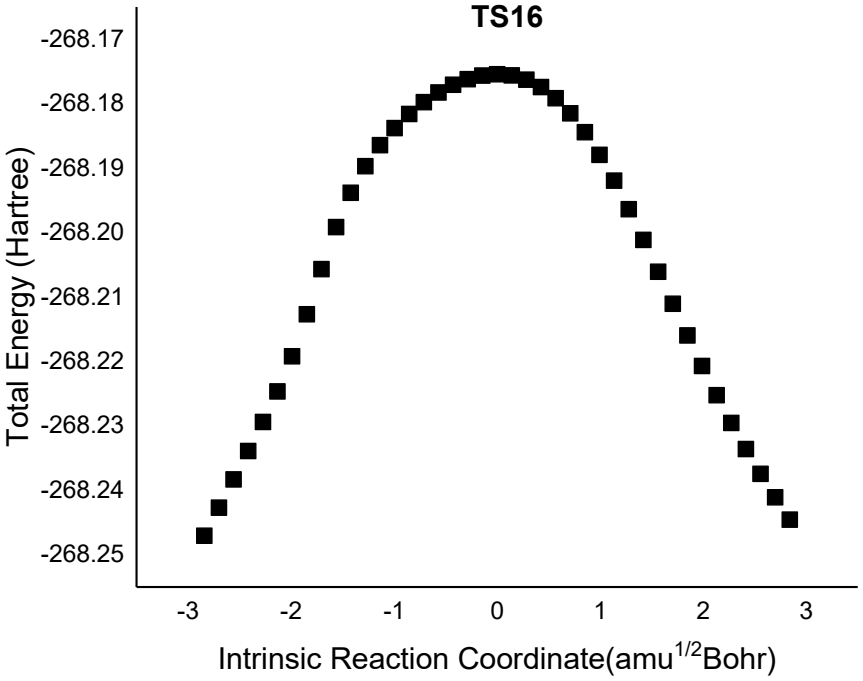

TS9
-268.26
-268.27
-268.28
-268.29
-268.30
-268.31
-268.32
Total Energy (Hartree)
-4
-3
-2
-1
0
1
2
3
4
Intrinsic Reaction Coordinate(amu1/2Bohr)

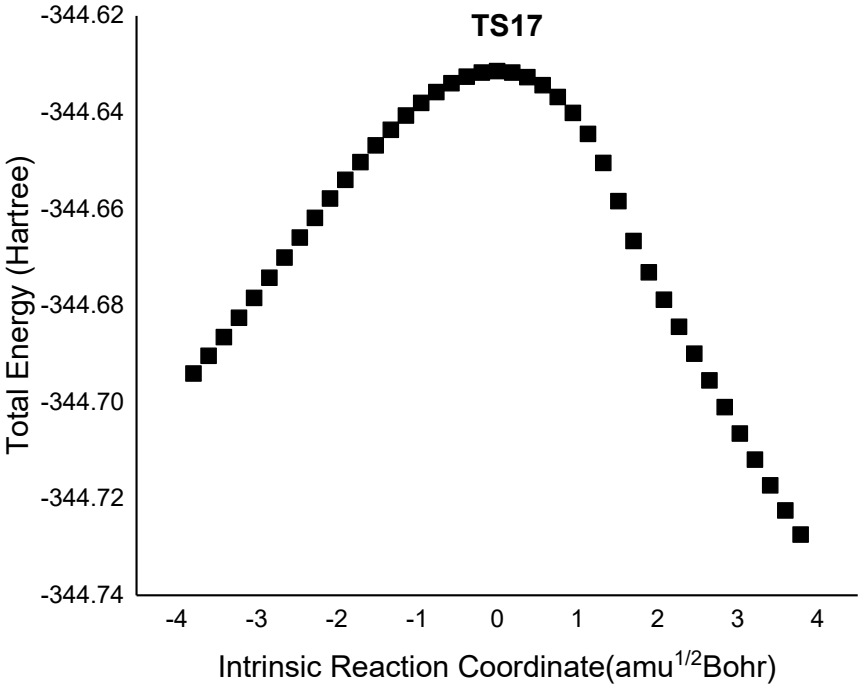

TS10
-268.22
-268.23
-268.24
-268.25
-268.26
-268.27
-268.28
-268.29
-268.30
-268.31
Total Energy (Hartree)
-3
-2
-1
0
1
2
3
Intrinsic Reaction Coordinate(amu1/2Bohr)

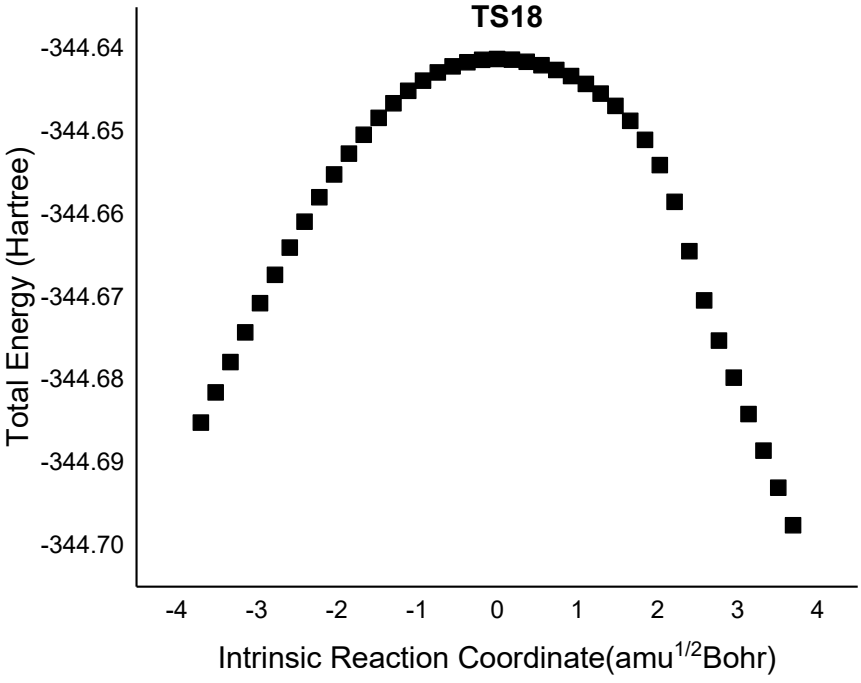

TS12
-344.64
-344.66
-344.68
-344.70
-344.72
-344.74
Total Energy (Hartree)
-4
-3
-2
-1
0
1
2
3
4
Intrinsic Reaction Coordinate(amu1/2Bohr)


TS14
-344.62
-344.64
-344.66
-344.68
-344.70
-344.72
-344.74
Total Energy (Hartree)
-3
-2
-1
0
1
2
3
Intrinsic Reaction Coordinate(amu1/2Bohr)


TS15
-268.22
-268.24
-268.26
-268.28
-268.30
-268.32
Total Energy (Hartree)
-2
-1
0
1
2
Intrinsic Reaction Coordinate(amu1/2Bohr)


TS16
-268.17
-268.18
-268.19
-268.20
-268.21
-268.22
-268.23
-268.24
-268.25
Total Energy (Hartree)
-3
-2
-1
0
1
2
3
Intrinsic Reaction Coordinate(amu1/2Bohr)


TS17
-344.62
-344.64
-344.66
-344.68
-344.70
-344.72
-344.74
Total Energy (Hartree)
-4
-3
-2
-1
0
1
2
3
4
Intrinsic Reaction Coordinate(amu1/2Bohr)


TS18
-344.64
-344.65
-344.66
-344.67
-344.68
-344.69
-344.70
Total Energy (Hartree)
-4
-3
-2
-1
0
1
2
3
4
Intrinsic Reaction Coordinate(amu1/2Bohr)

3. Tabular data.

Table S1. Gradient elution program of UPLC.

Time/min	Flow rate /(mL/min)	%A	%B
0.00	0.4	48	52
2.50	0.4	48	52
7.50	0.4	25	75
8.00	0.4	25	75
10.00	0.4	48	52

Table S2. Glycerol initial molecular conformation, TS1, TS2, and vinyl alcohol bond length optimization results.

Bond	1 γγ	TS1	2 ethenol	
R (O1,C2)	1.42	1.29	R (C1,H2)	1.08
R (O1,H7)	0.97	1.42	R (C1,H3)	1.08
R (C2,C3)	1.53	1.87	R (C1,C4)	1.33
R (C2,H8)	1.09	1.1	R (C4,H5)	1.08
R (C2,H9)	1.10	1.1	R (C4,O6)	1.36
R (C3,C4)	1.52	1.39	R (O6,H7)	0.96
R (C3,O6)	1.42	1.39	TS2	
R (C3,H10)	1.10	1.09	R (C1,H2)	1.08
R (C4,O5)	1.42	2.08	R (C1,H3)	1.09
R (C4,H11)	1.09	1.08	R (C1,C4)	1.41
R (C4,H12)	1.09	1.08	R (C1,H7)	1.48
R (O5,H7)	2.11	1.05	R (C4,H5)	1.09
R (O5,H13)	0.96	0.96	R (C4,O6)	1.27
R (O6,H14)	0.96	0.97	R (O6,H7)	1.28

Table S3. Glycerol initial molecular conformation and TS11 bond length optimization results.

Bond	1 γγ	TS11	Bond	1 γγ	TS11
R (O1,C2)	1.42	1.31	R (C3,H10)	1.1	1.09
R (O1,H7)	0.97	1.61	R (C4,O5)	1.42	1.41
R (C2,C3)	1.53	1.46	R (C4,H11)	1.09	1.09
R (C2,H8)	1.09	1.11	R (C4,H12)	1.09	1.1
R (C2,H9)	1.1	1.19	R (O5,H7)	2.12	1.02
R (C3,C4)	1.52	1.51	R (O5,H13)	0.96	1.83
R (C3,O6)	1.42	1.98	R (O6,H13)	2.57	0.98
R (C3,H9)	2.16	1.73	R (O6,H14)	0.96	0.96

Table S4. Electron energy and Gibbs free energy barrier of fierce competitive primary channels calculated under different methods.

	Potential energy (in Hartree)		
	M06-2X-D3/6-311+G (d, p)	CAM-B3LYP/6-311+G (d, p)	ωB97X-D /6-311+G (d, p)
Glycerol	-344.7610099	-344.7650992	-344.7967163
TS1	-344.649088	-344.657772	-344.6882423
TS11	-344.6471591	-344.6576197	-344.688506
TS18	-344.6412631	-344.6545176	-344.6850361
	DLPNO-CCSD(T)/CBS// M06-2X-D3/6-311+G (d, p)	DLPNO-CCSD(T)/CBS// CAM-B3LYP/6-311+G (d, p)	DLPNO-CCSD(T)/CBS//ωB97X-D /6-311+G (d, p)
Glycerol	-344.465911072480	-344.465910867331	-344.465909831582
TS1	-344.353945877457	-344.354098176923	-344.354190384
TS11	-344.354361508854	-344.354160103823	-344.354204033
TS18	-344.350199823676	-344.350529521269	-344.350495935268

Table S5. The only imaginary frequency of the transition states under M06-2X-D3, CAM-B3LYP, ωB97X-D functionals, in which there is no transition state in the reaction 7-1 that generates two free radicals, and it is referred to as ''TS13''. (unit: cm^{-1}).

Transition state	M06-2X-D3	CAM-B3LYP	wB97XD
TS1	-783.54	-710.74	-660.25
TS2	-2208.11	-2232.76	-2228.44
TS3	-1853.82	-1970.55	-1963.25
TS4	-1854.87	-2060.88	-2029.73
TS5	-1362.28	-1220.19	-1163.82
TS6	-1505.61	-1890.49	-1944.12
TS7	-716.34	-883.4	-824.64
TS8	-2108.07	-2149.39	-2171.89
TS9	-756.13	-871.85	-801.65
TS10	-1358.95	-1534.67	-1539.35
TS11	-653.58	-510.73	-478.95
TS12	-893.78	-833.39	-802.25
TS14	-1793.68	-1692.51	-1715.87
TS15	-2187.72	-2212.81	-2196.32
TS16	-721.96	-591.41	-562.45
TS17	-665.94	-524.83	-534.53
TS18	-373.74	-373.53	-368.14

Table S6.The content of carbonyl compounds in glycerol pyrolysis products at different temperatures (unit: μg).

T/℃	Formaldehyde	Acetaldehyde	Acetone	Acrolein	Propionaldehyde
100	0.25	0.00	0.00	0.00	0.00
200	1.23	0.07	0.13	0.00	0.00
300	4.63	1.70	0.18	1.08	2.13
400	5.38	6.88	0.18	3.13	2.50
500	12.98	28.80	1.33	15.93	7.28
600	13.48	32.45	2.98	13.63	7.78
700	14.75	35.35	5.60	12.28	8.90
800	17.73	48.13	11.98	14.60	11.23
900	16.95	50.88	11.65	18.40	11.53
1000	17.43	47.00	12.30	14.75	11.55

4. The experimental results of UPLC.

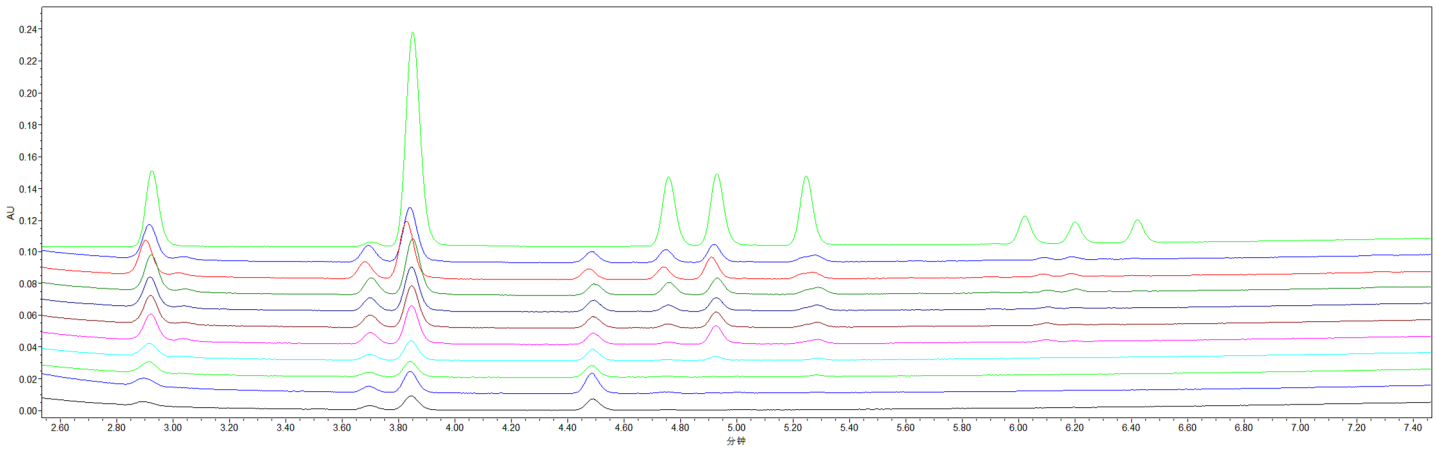


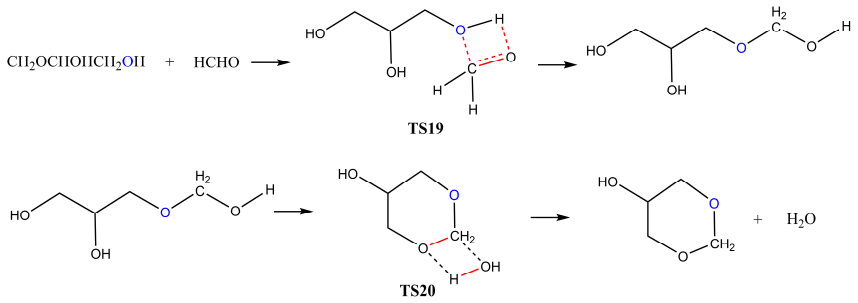
Figure S10. The experimental results of UPLC, bottom up, temperature range 100-1000℃ (interval 100), The top green peak is the standard sample. The abscissa: time (min), the ordinate: absorption (AU).

In the above figure, the top green peak is the standard sample. The corresponding carbonyl compound-DNPH from left to right are: formaldehyde-DNPH, acetaldehyde-DNPH, acetone-DNPH, acrolein-DNPH, propionaldehyde-DNPH, crotonaldehyde-DNPH, 2-butanone-DNPH, butyraldehyde-DNPH.

The bottom-up peaks are the carbonyl compounds produced by glycerol cracking at 100℃～1000℃(interval 100). Quantitative analysis by comparing the integral area.

Since UPLC relies on standard samples to achieve quantitative and qualitative purposes, it is inevitable that there will be omissions (such as peaks around 4.5min), so it is supplemented by GC/MS for qualitative testing.

5. Condensation reaction of glycerol and formaldehyde.

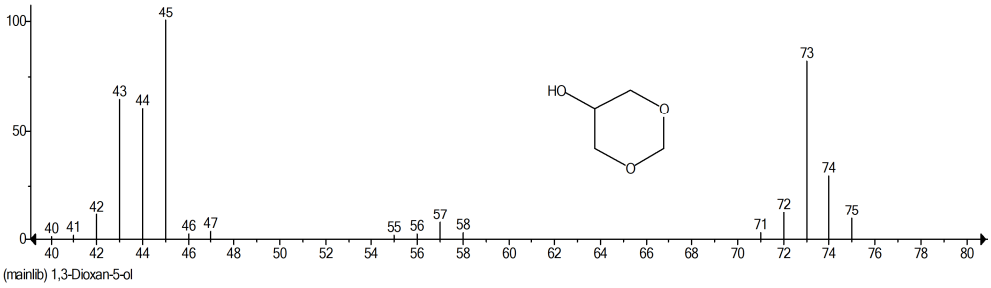


Scheme S1. A two-step reaction to form glycerol formal.

In the first step, glycerol and formaldehyde undergo a polycondensation reaction to form an intermediate product, and the free energy barrier of the reaction is 38.6 kcal mol^{-1}; in the second step, the hydroxyl groups at both ends of the intermediate product are dehydrated to form glycerol formal, the free energy barrier of the reaction is 55.5 kcal mol^{-1}, so the condensation energy barrier of glycerol and formaldehyde is 55.5 kcal mol^{-1}.

6. The experimental results of GC/MS.

(a)



(b)

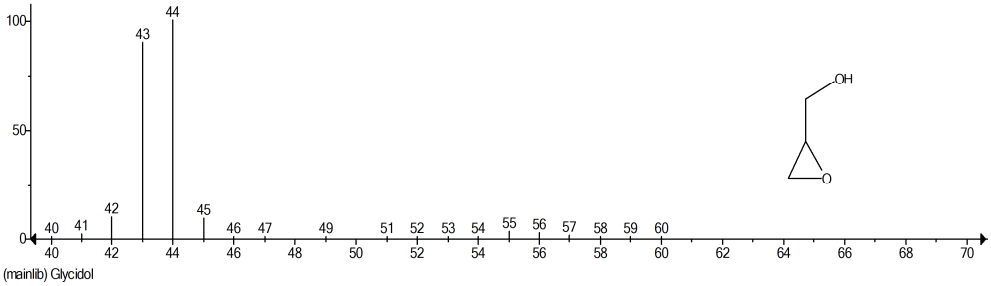
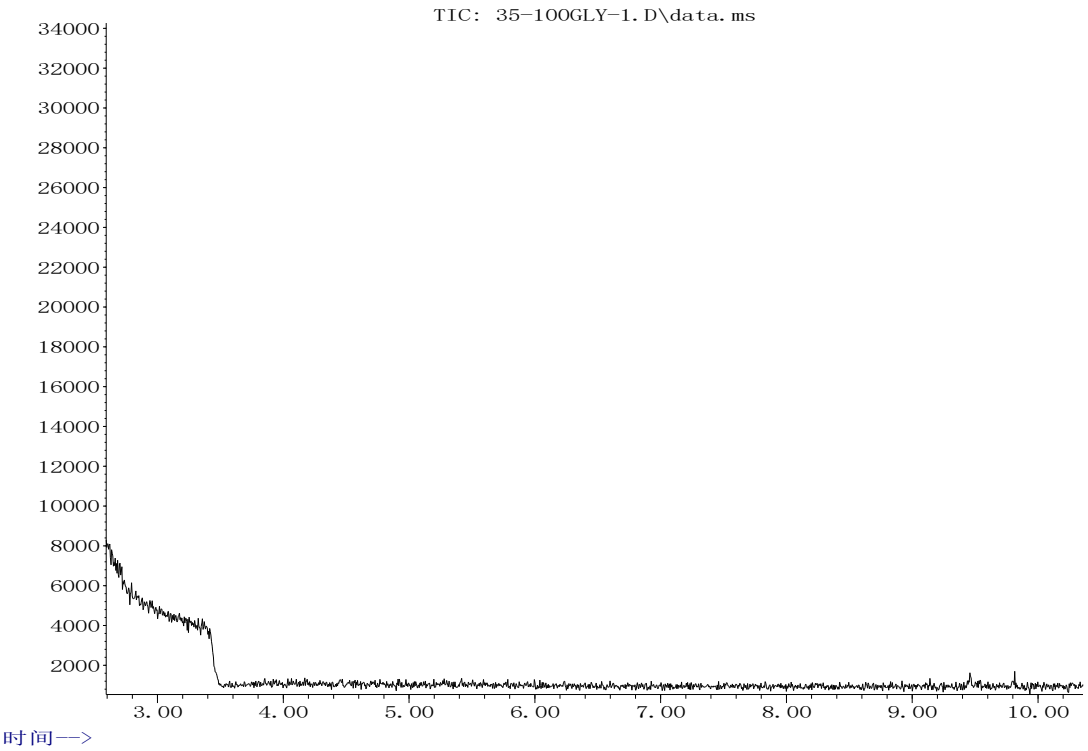


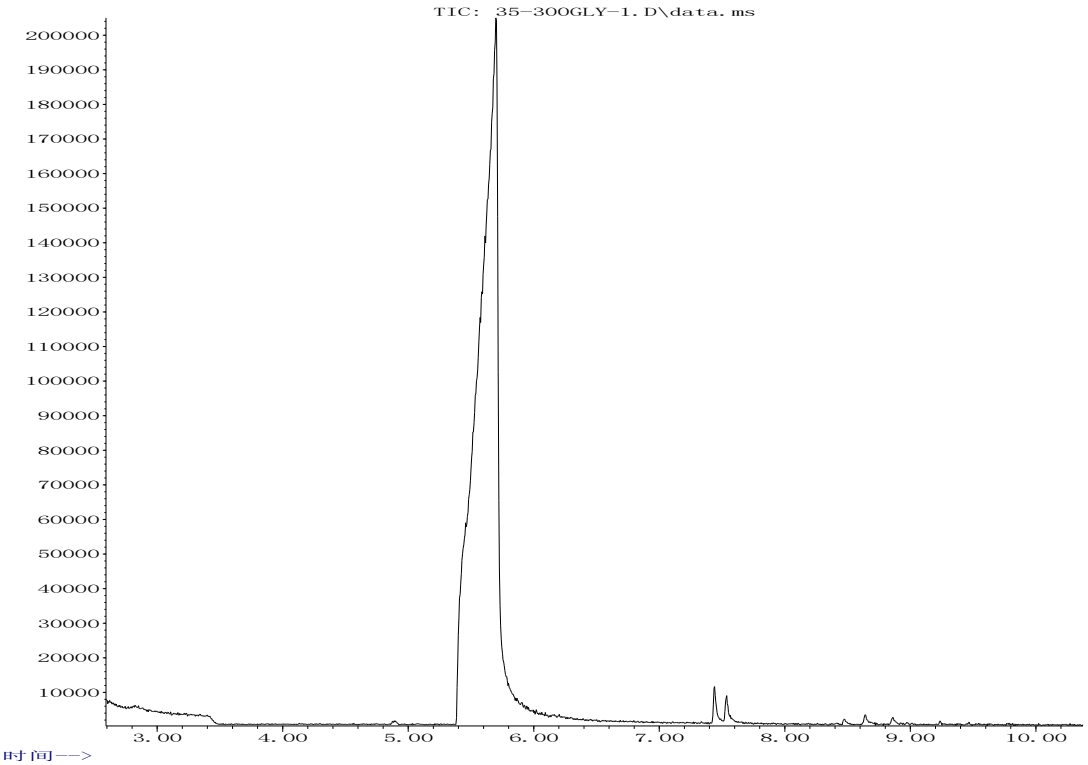
Figure S11. Standard samples: (a) glycerol formal; (b) glycidol.

Total Ion Chromatogram (TIC):

100℃(Abscissa: time/Ordinate: abundance, Same below.)

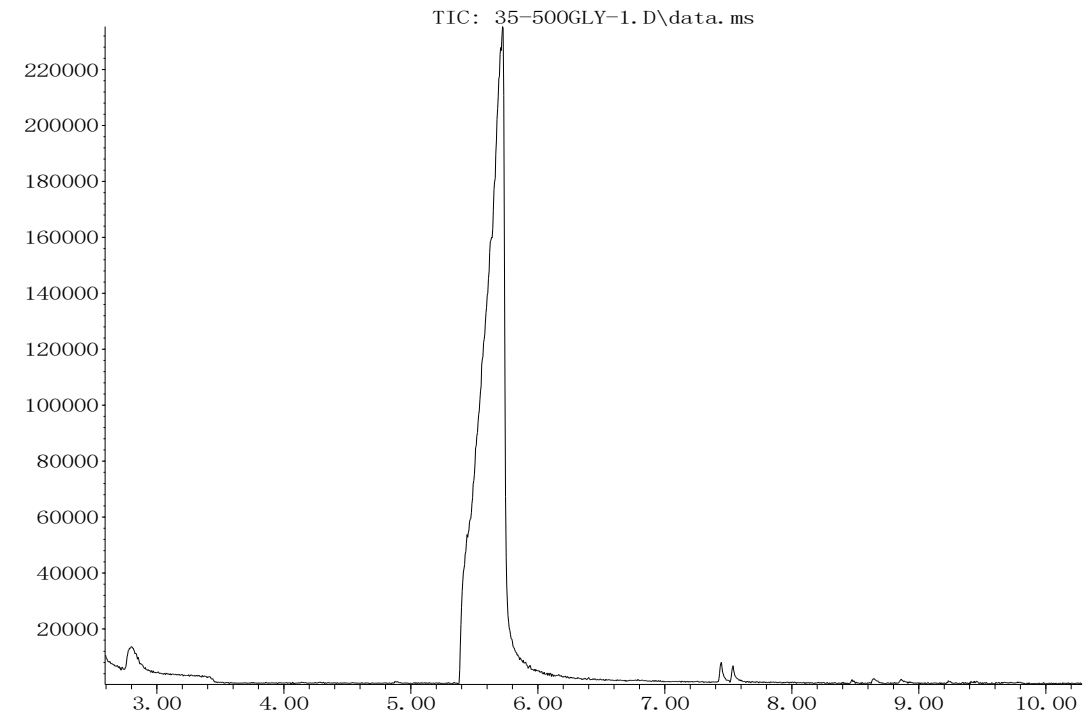


300℃


丰度
TIC: 35-300GLY-1.D\data.ms
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
时间-->
400℃
丰度
TIC: 35-400GLY-1.D\data.ms
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
时间-->

500℃

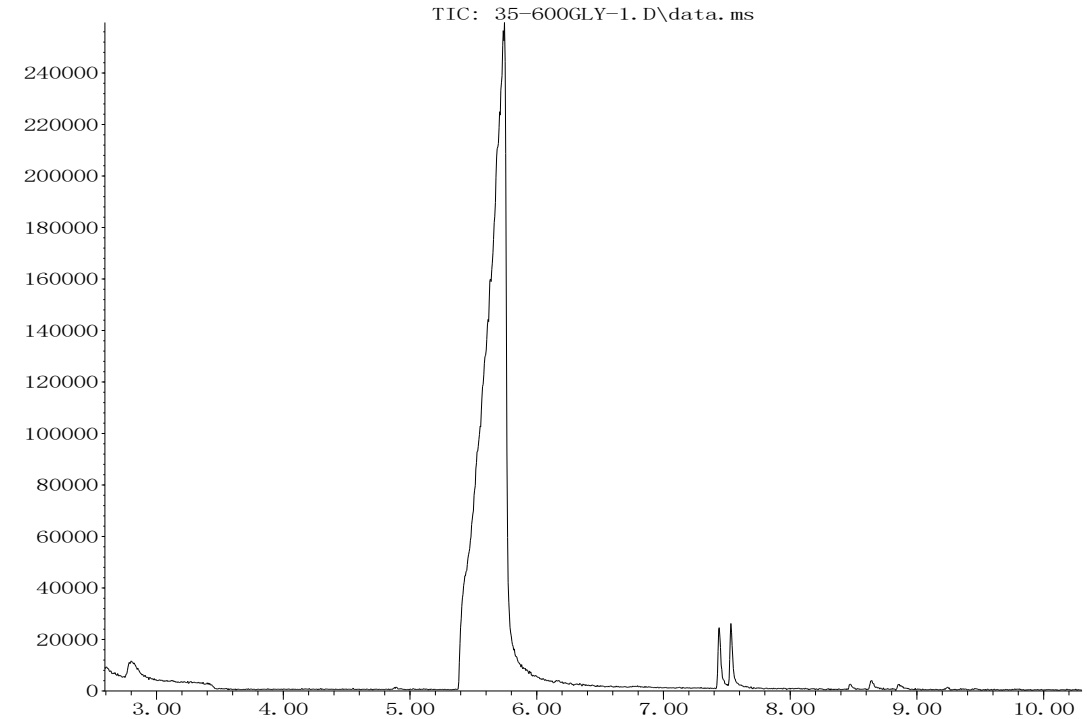
丰度



时间—>

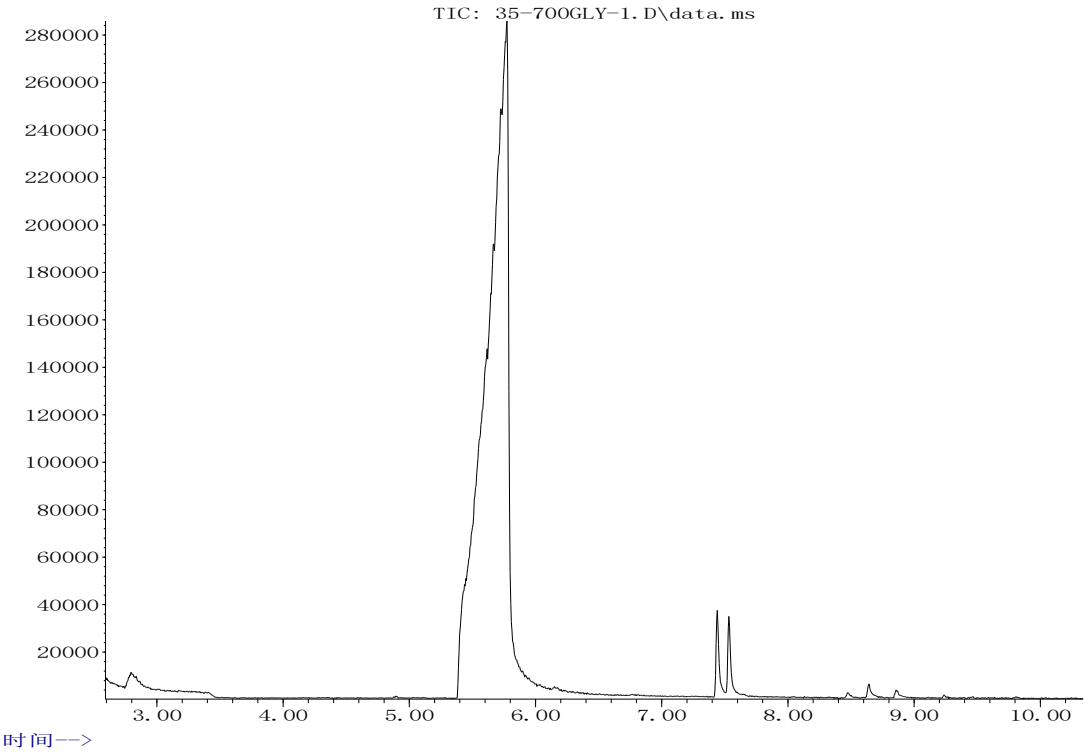
600℃

丰度

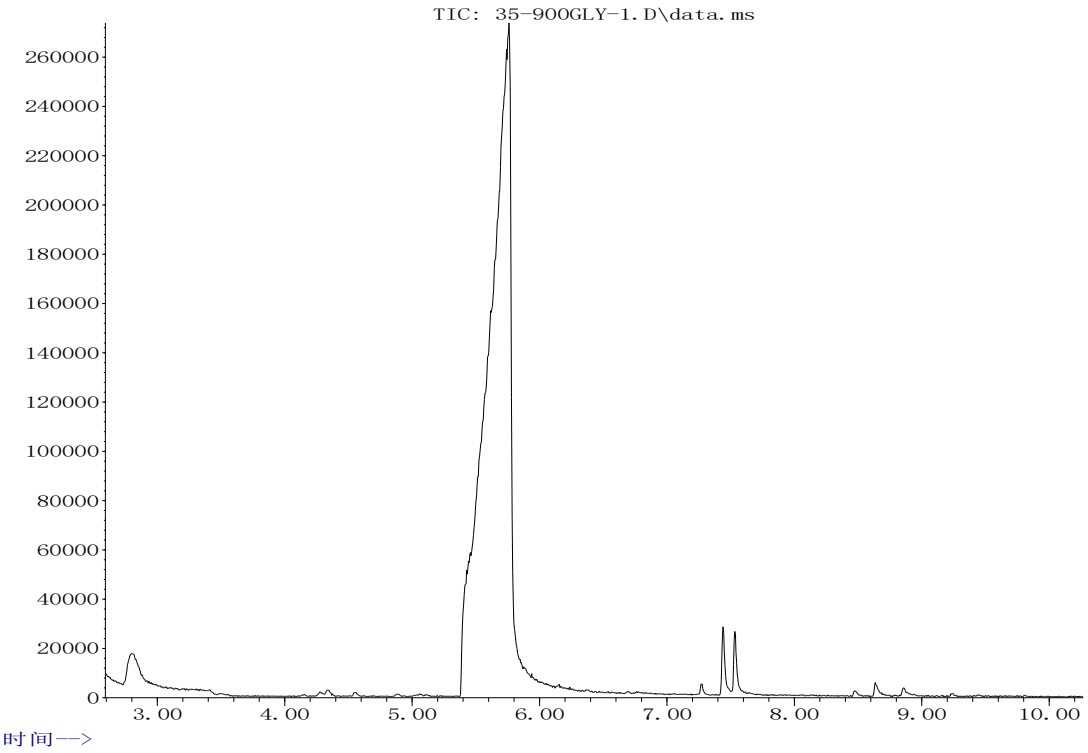


时间—>

700℃

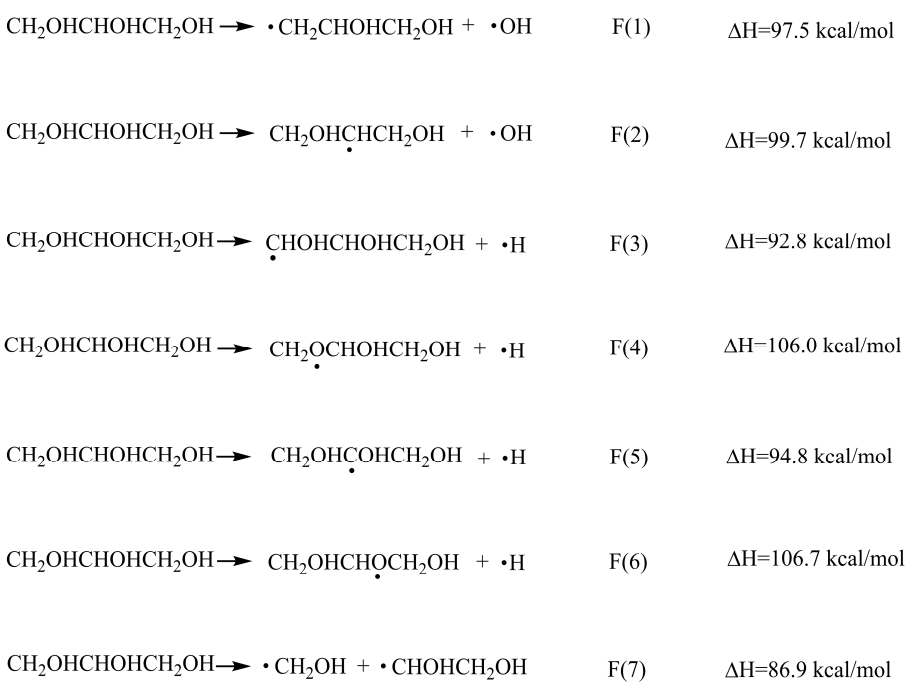

TIC: 35-700GLY-1.D\data.ms
丰度
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
时间-->
800℃
丰度
TIC: 35-800GLY-1.D\data.ms
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
时间-->

900℃


TIC: 35-900GLY-1.D\data.ms
丰度
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
时间-->
1000℃
丰度
TIC: 35-1000GLY-1.D\data.ms
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
时间-->

The corresponding substance of the chromatographic peak at 2.8min is glycidol, and the corresponding substance of the chromatographic peak at 4.3min is glycerol formal. The big peak around 5.4min is glycerol, the two peaks at 7.441min and 7.537min are identified as one substance (may be isomers), which is 1,4-dioxane-2,5-dimethanol (CAS: 14236-12-5). It is inferred that they are the product of the intermolecular dehydration of two glycerol molecules, which is another work we are pushing forward.

7. Radical decomposition channels.



Scheme S2. Radical decomposition channels of glycerol under anaerobic at 101 kPa and 298 K，the enthalpies are calculated under M06-2X-D3/6-311+G (d, p) level.

Radical decomposition reactions F (1), F (2) will produce 1,2-propanediol and 1,3-propanediol free radicals, respectively, which will combine with H free radicals to produce 1,2-propanediol and 1,3-propanediol. The decomposition of propylene glycol will produce propionaldehyde and acetone.

A follow-up work that we are advancing includes this aspect.