

Supplementary Materials: Highly Efficient Acetalization and Ketalization Catalyzed by Cobaloxime under Solvent-Free Condition

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1. Typical experimental procedure

1.1. General Isolation Procedure for Products

The isolation procedure for products was conducted as follows: The reaction was stopped when GC showed that the reaction ran completely. After cooled to room temperature, the reaction mixture was transferred into a separating funnel. 15 mL CH_2Cl_2 was used to wash the reaction flask and poured into the funnel. The combined mixture was washed with saturated sodium carbonate solution (4×5 mL) and dried by anhydrous Na_2SO_4 . Then the mixture was distilled under vacuum to give the acetal (or ketal) product.

The reaction of cyclohexanone and propane-1,2-diol gave 97% yield of the corresponding ketal (the ^1H -NMR spectrum see Figure S16).

The reaction of benzaldehyde and propane-1,2-diol gave 95% yield of the corresponding acetal (the ^1H -NMR spectrum see Figure S17).

The reaction of cyclohexanone and glycerol gave 94% yield of the corresponding ketal (the ^1H -NMR spectrum see Figure S18).

1.2. The Procedure of the Additional Experiment Which Used HCl Gas Instead of CoCl_2 and DH_2

HCl gas was passed into the mixture of cyclohexanone (51.3 mmol) and propane-1,2-diol (76.9 mmol) in a flask until HCl gas was saturated. After that, the system was maintained under 5 KPa by a vacuum pump and was heated to 70 °C along with stirring for 3 h.

GC analysis showed that there was no desired product generated in the system.

2. GC-MS Spectra of Reactions

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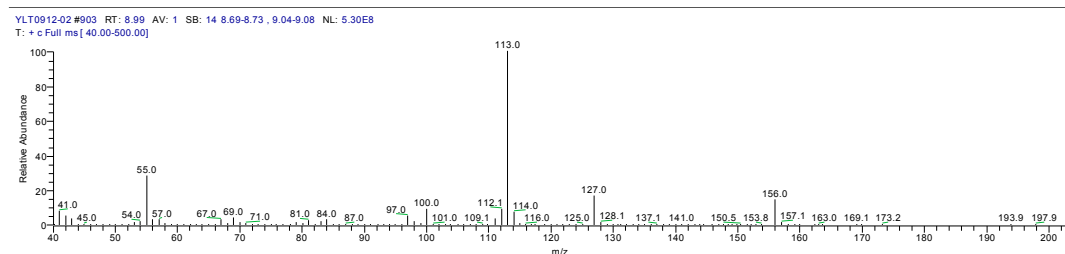
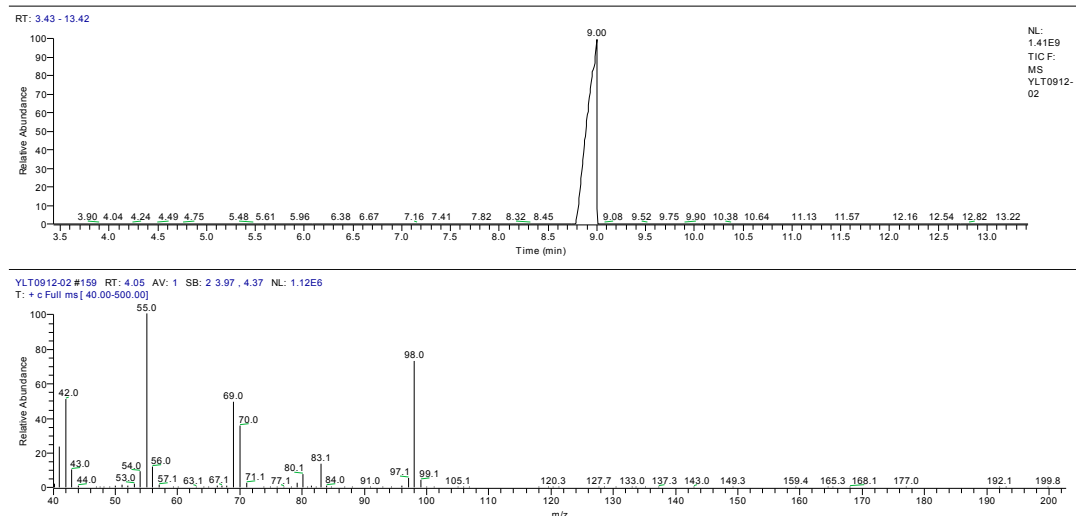


Figure S1. GC-MS spectrum of the reaction of cyclohexanone and propane-1,2-diol.

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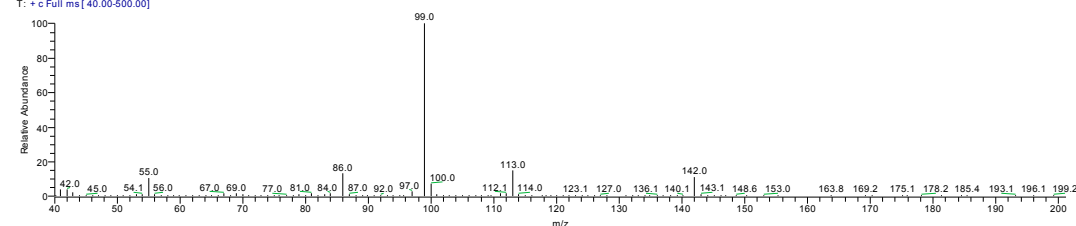
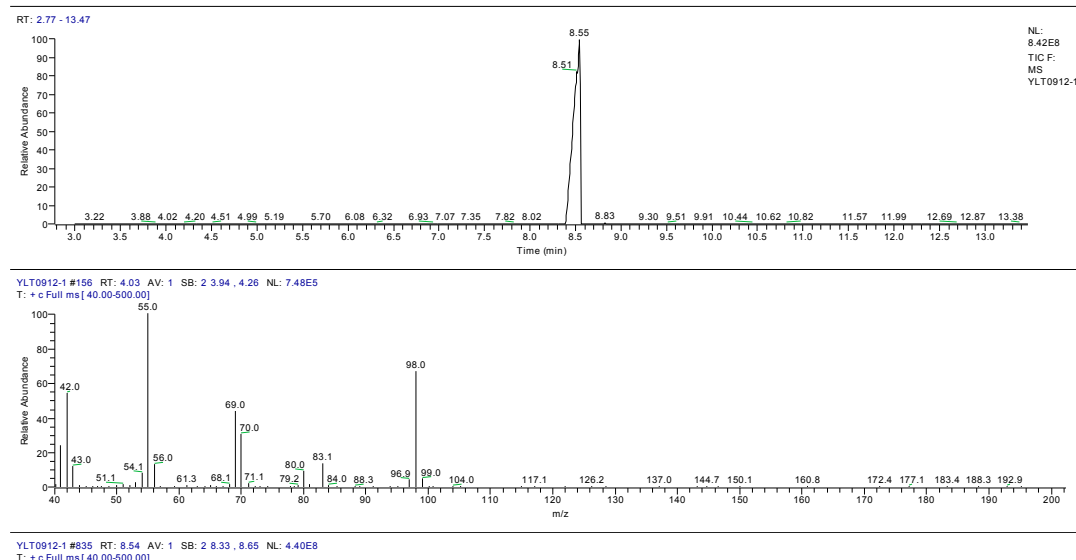


Figure S2. GC-MS spectrum of the reaction of cyclohexanone and ethane-1,2-diol.

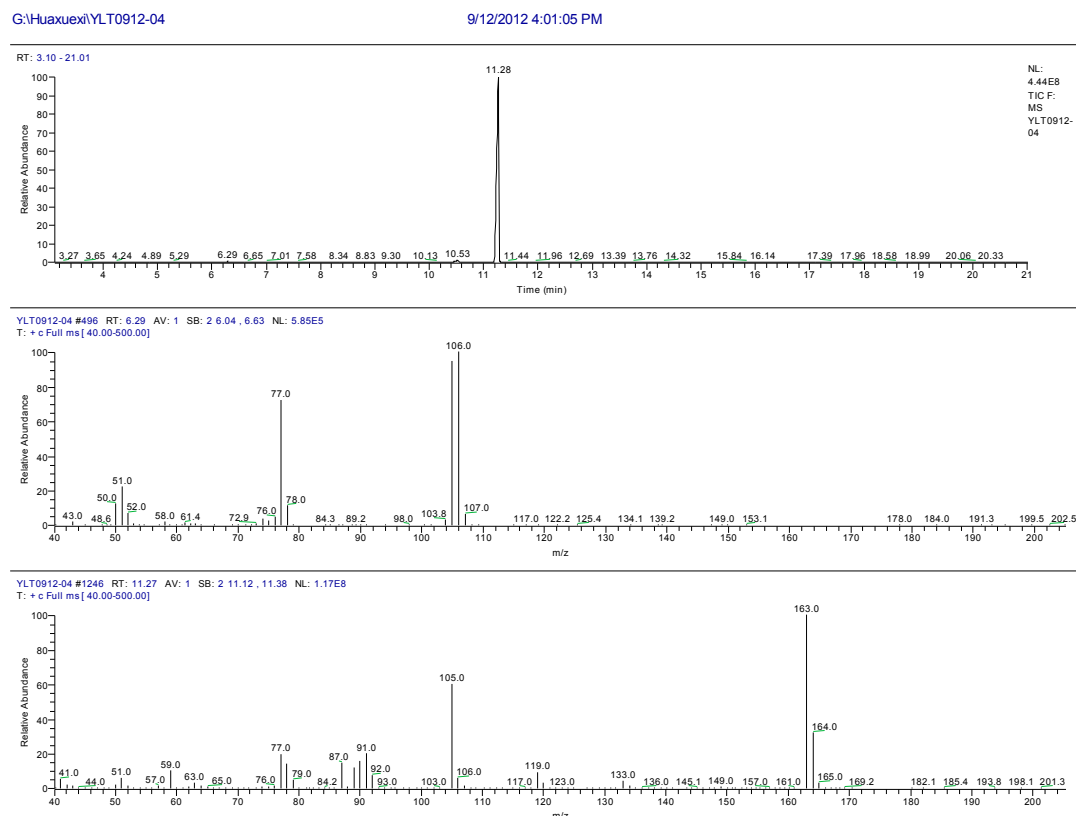


Figure S3. GC-MS spectrum of the reaction of benzaldehyde and propane-1,2-diol.

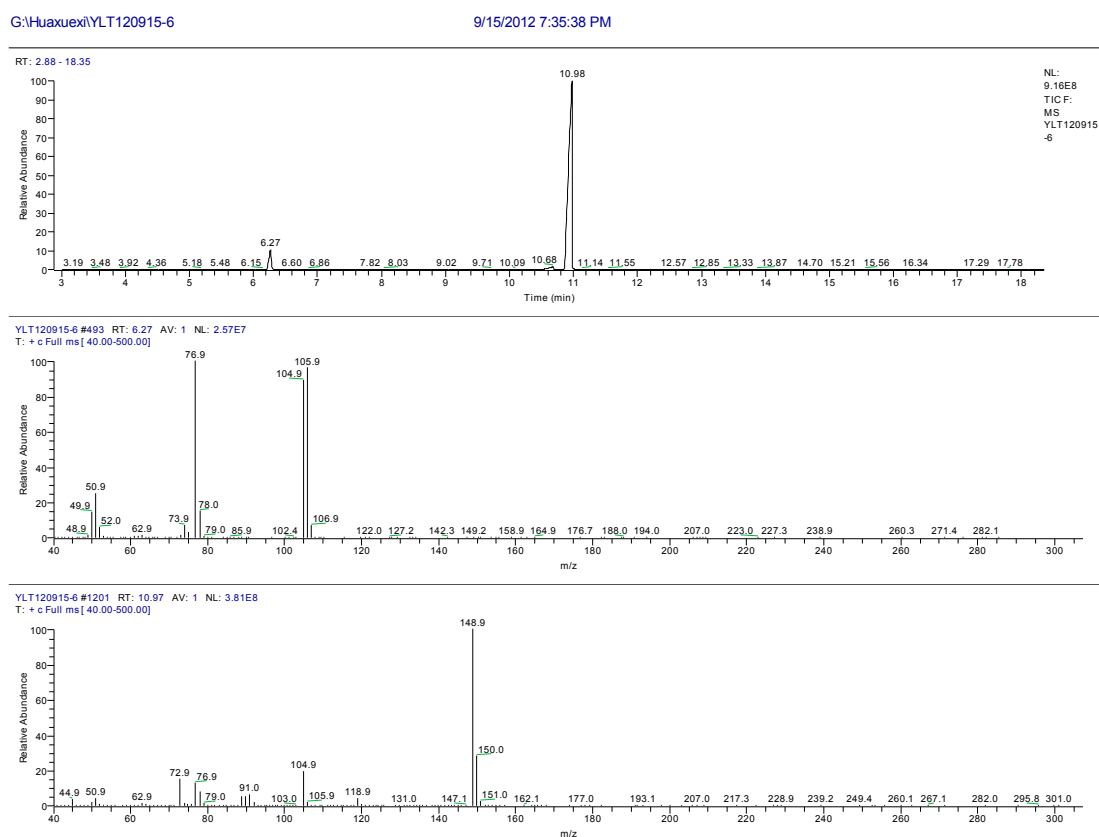
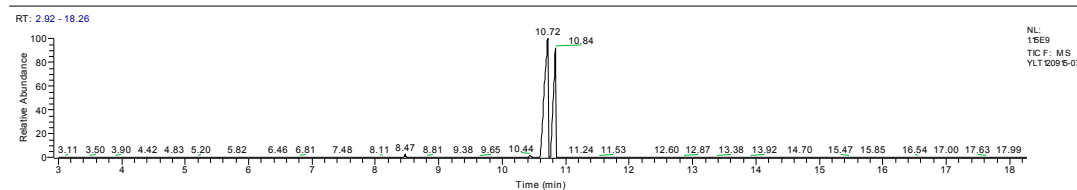


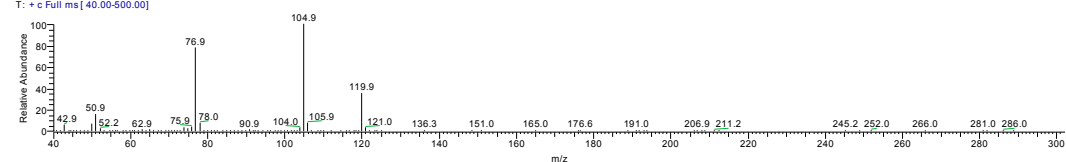
Figure S4. GC-MS spectrum of the reaction of benzaldehyde and ethane-1,2-diol.

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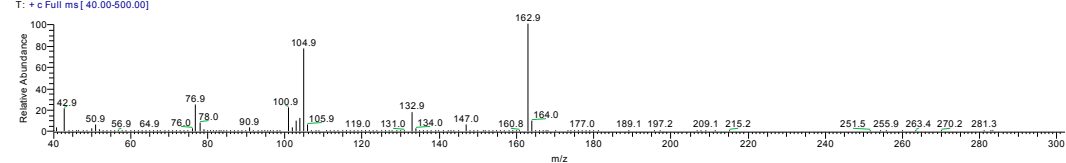
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YLT120915-07 #1164 RT: 10.72 AV: 1 NL: 3.32E8
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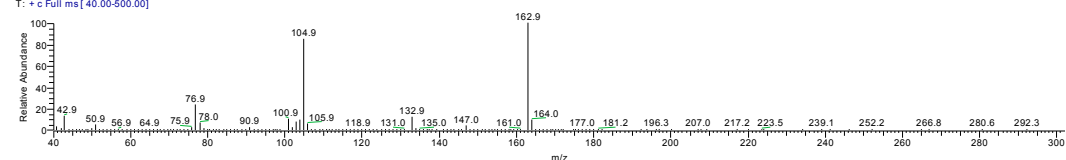
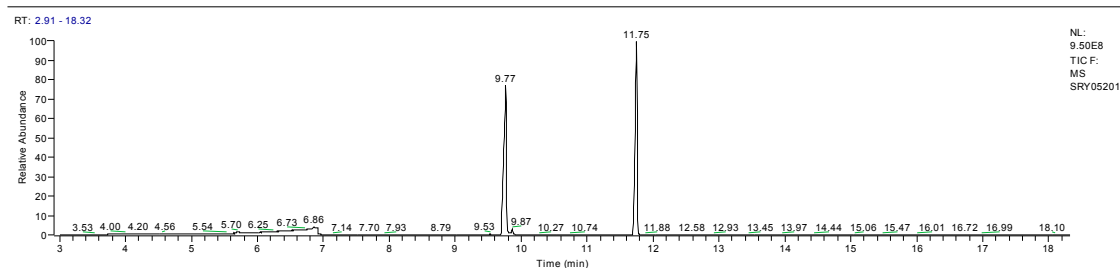


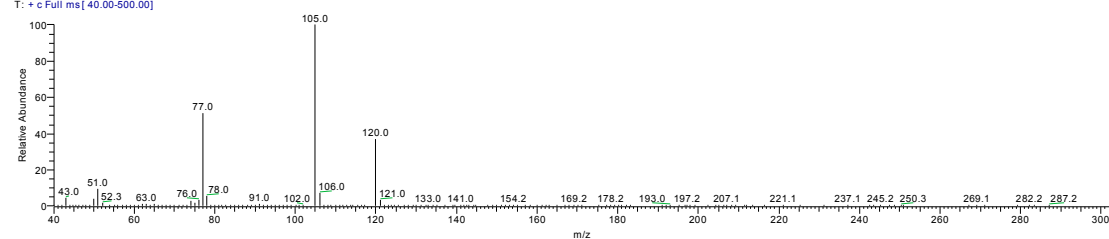
Figure S5. GC-MS spectrum of the reaction of acetophenone and propane-1,2-diol.

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SR05201 #1319 RT: 11.75 AV: 1 NL: 4.20E8
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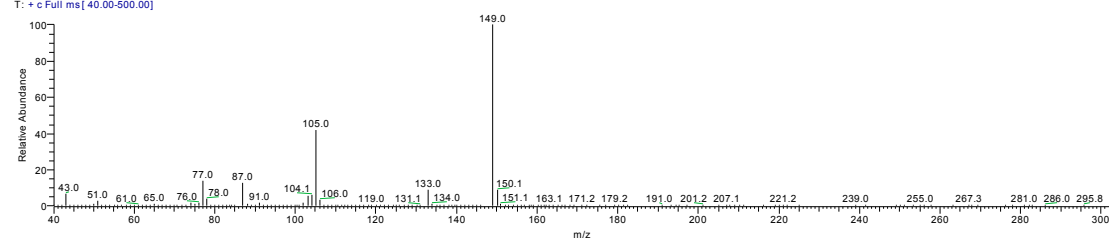


Figure S6. GC-MS spectrum of the reaction of acetophenone and ethane-1,2-diol.

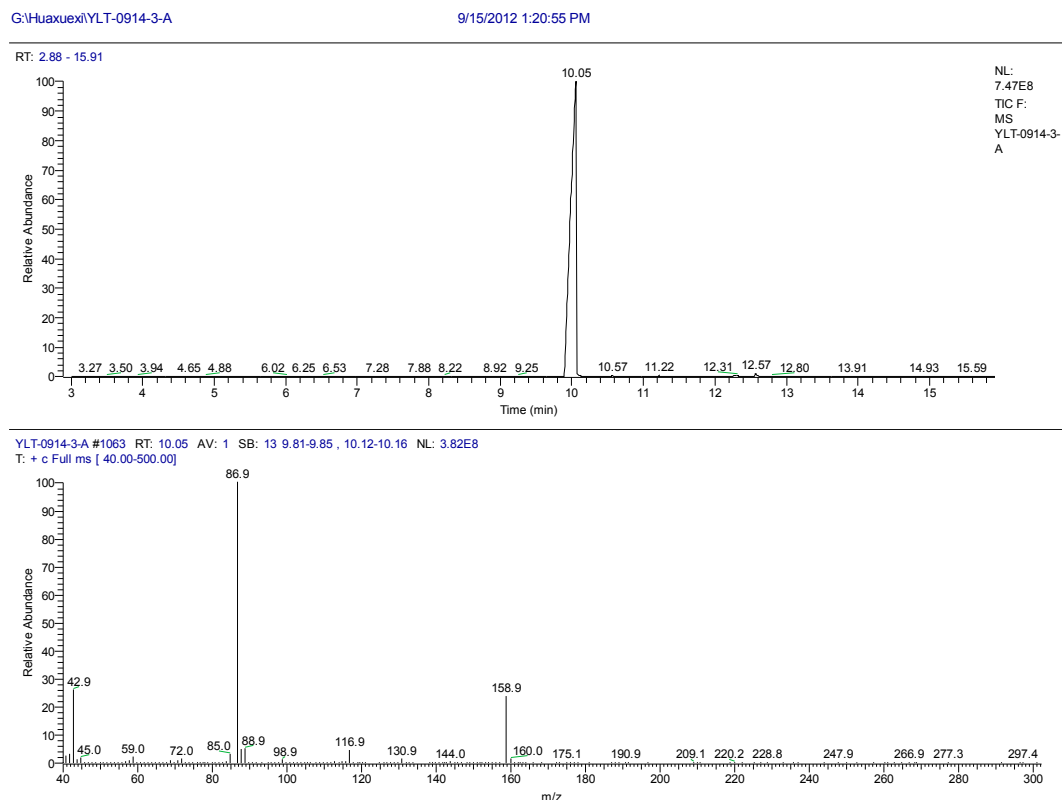


Figure S7. GC-MS spectrum of the reaction of ethyl acetoacetate and ethane-1,2-diol.

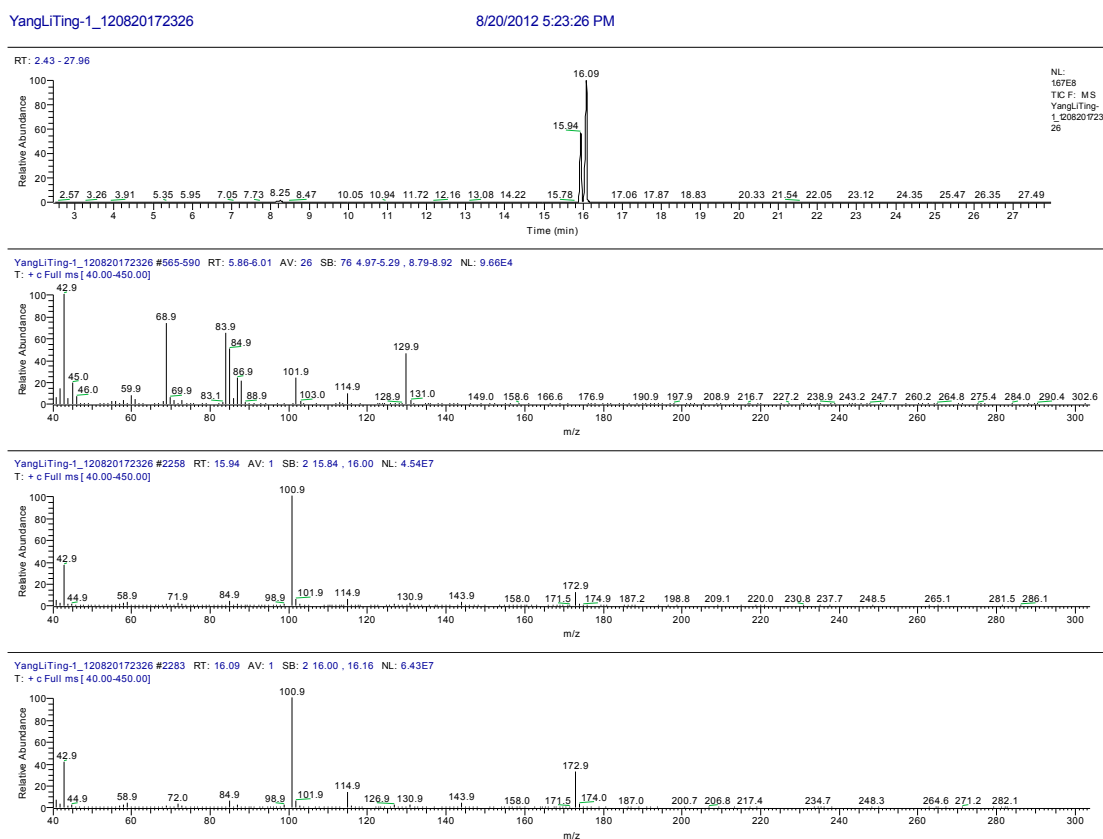


Figure S8. GC-MS spectrum of the reaction of ethyl acetoacetate and propane-1,2-diol.

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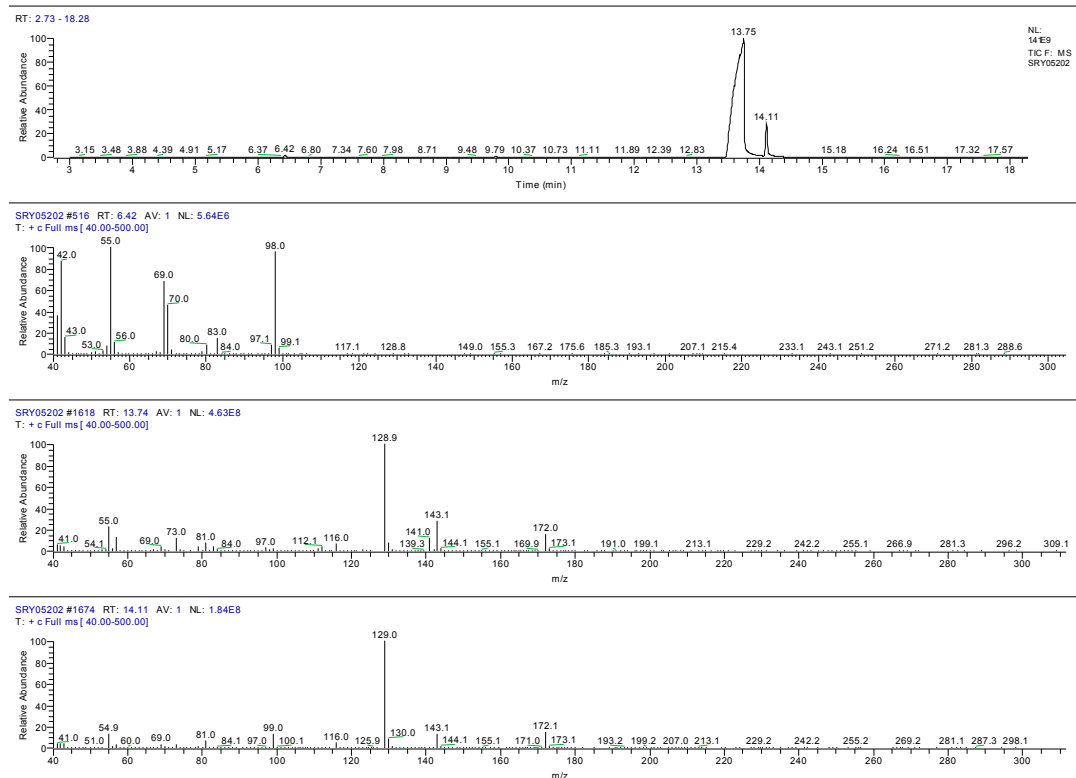


Figure S9. GC-MS spectrum of the reaction of cyclohexanone and glycerol.

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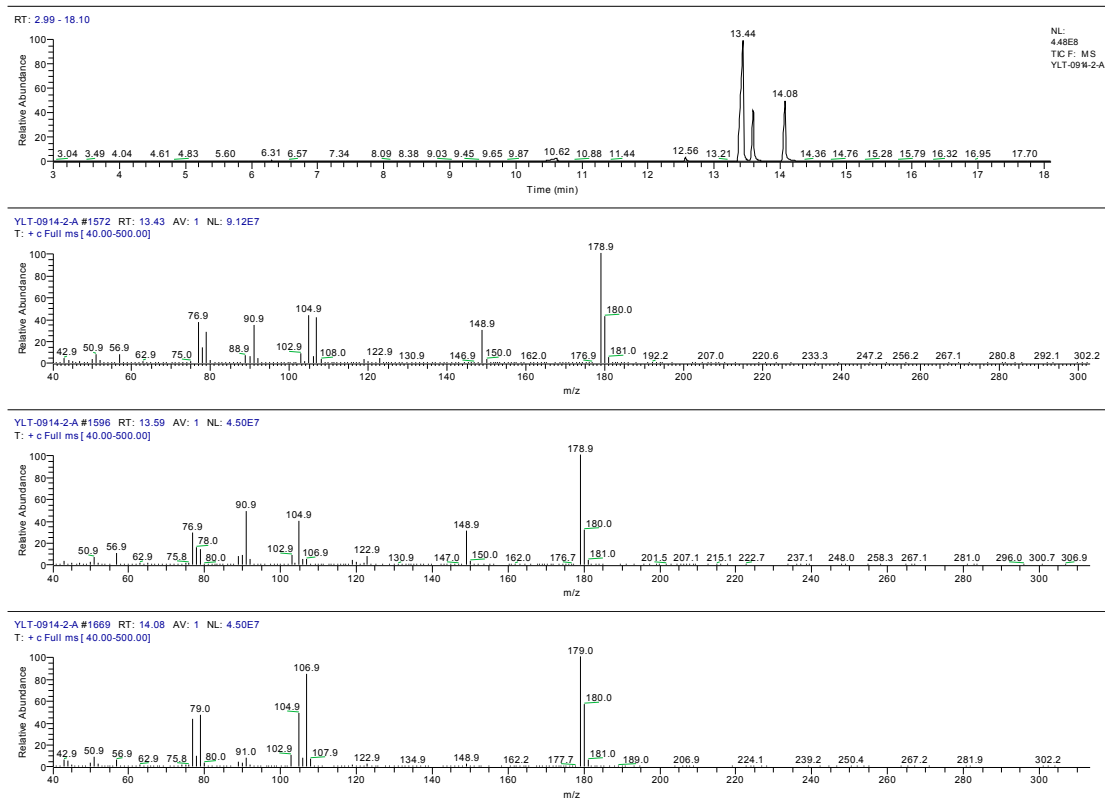
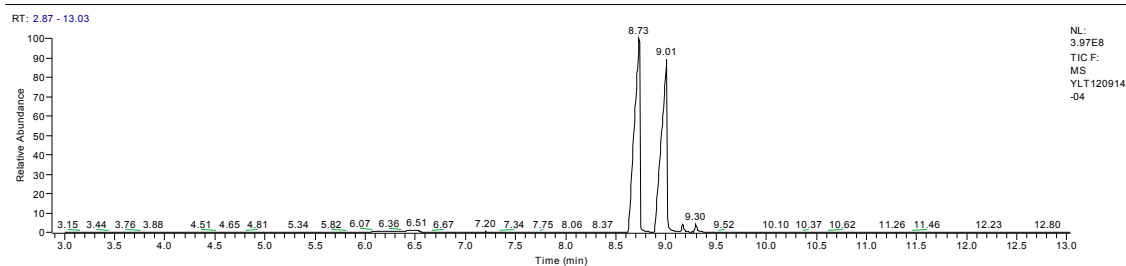


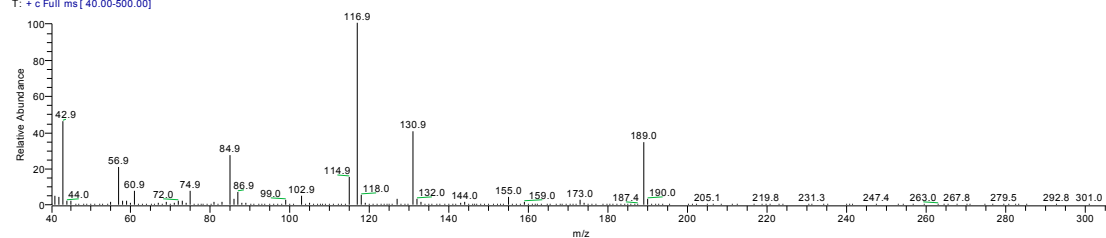
Figure S10. GC-MS spectrum of the reaction of benzaldehyde and glycerol.

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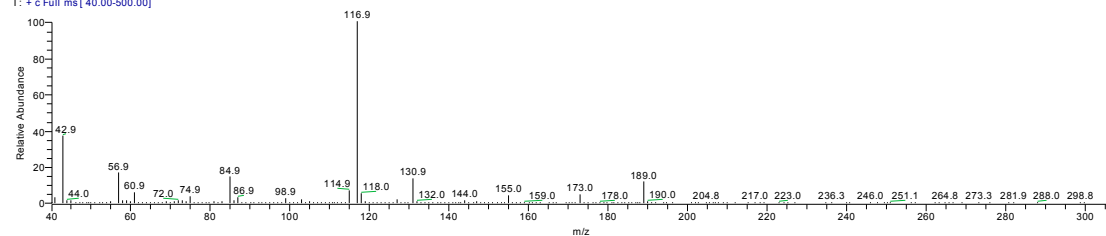
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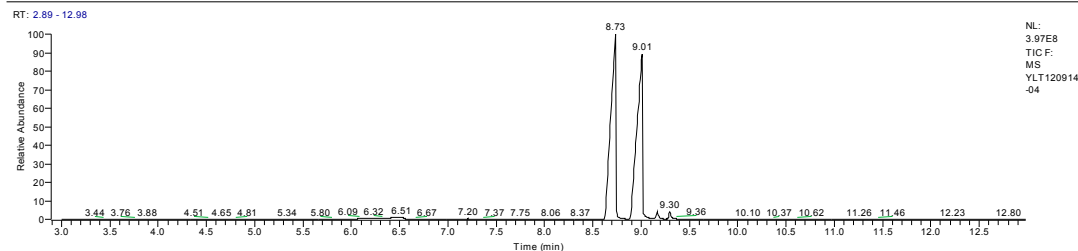
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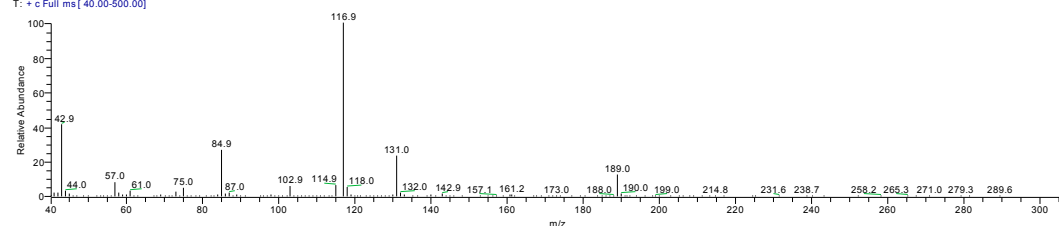
(a)

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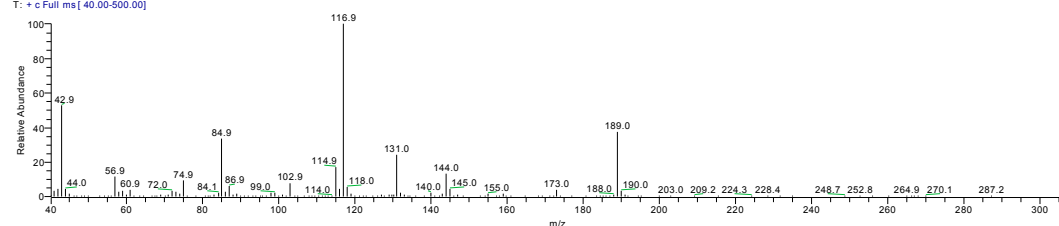
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T: + c Full ms [40.00-500.00]



YLT120914-04 #949 RT: 9.30 AV: 1 SB: 2 9.25, 9.38 NL: 3.88E6
T: + c Full ms [40.00-500.00]



(b)

Figure S11. (a,b) GC-MS spectrum of the reaction of ethyl acetoacetate and glycerol.

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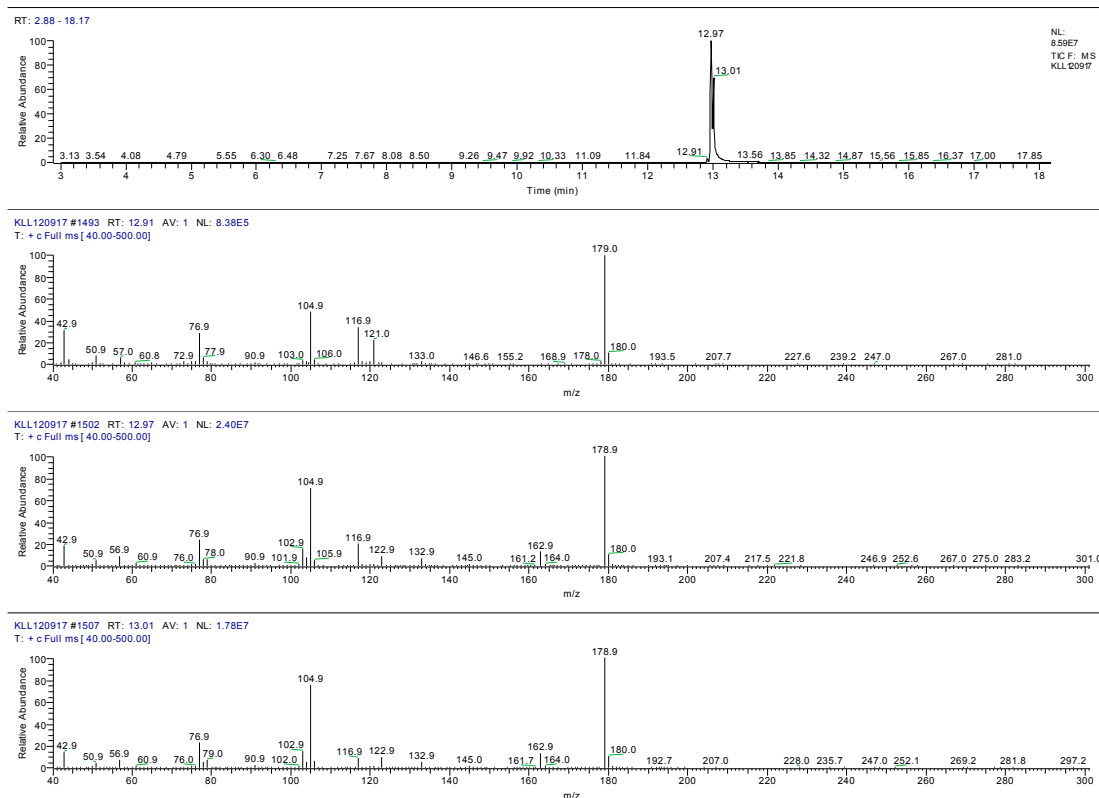


Figure S12. GC-MS spectrum of the reaction of acetophenone and glycerol.

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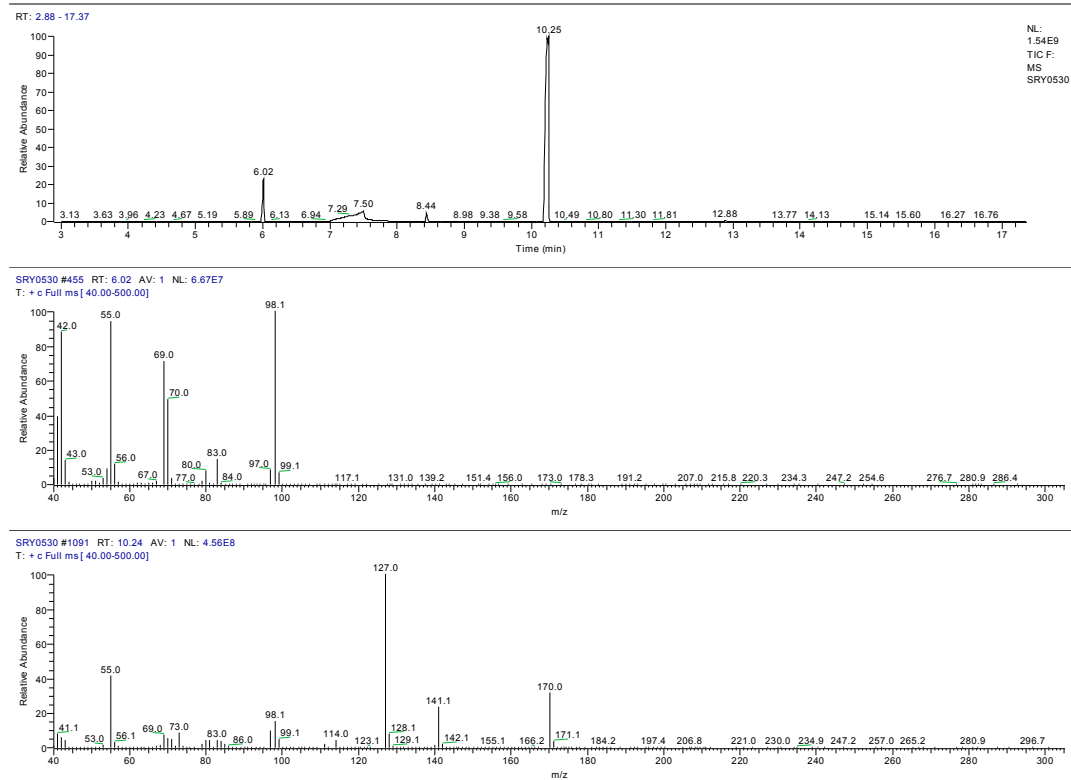


Figure S13. GC-MS spectrum of the reaction of cyclohexanone and butane-1,4-diol.

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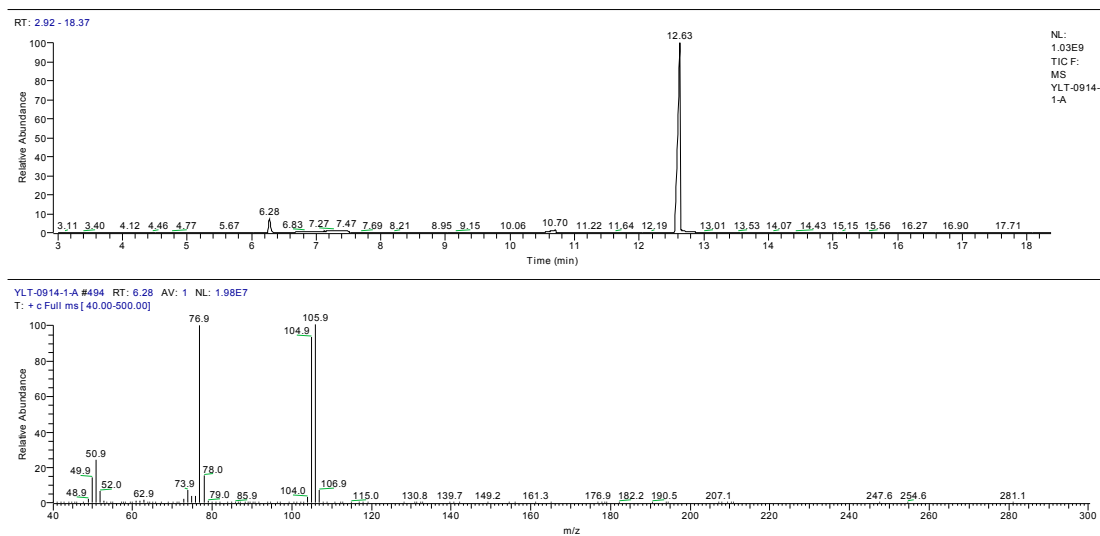


Figure S14. GC-MS spectrum of the reaction of benzaldehyde and butane-1,4-diol.

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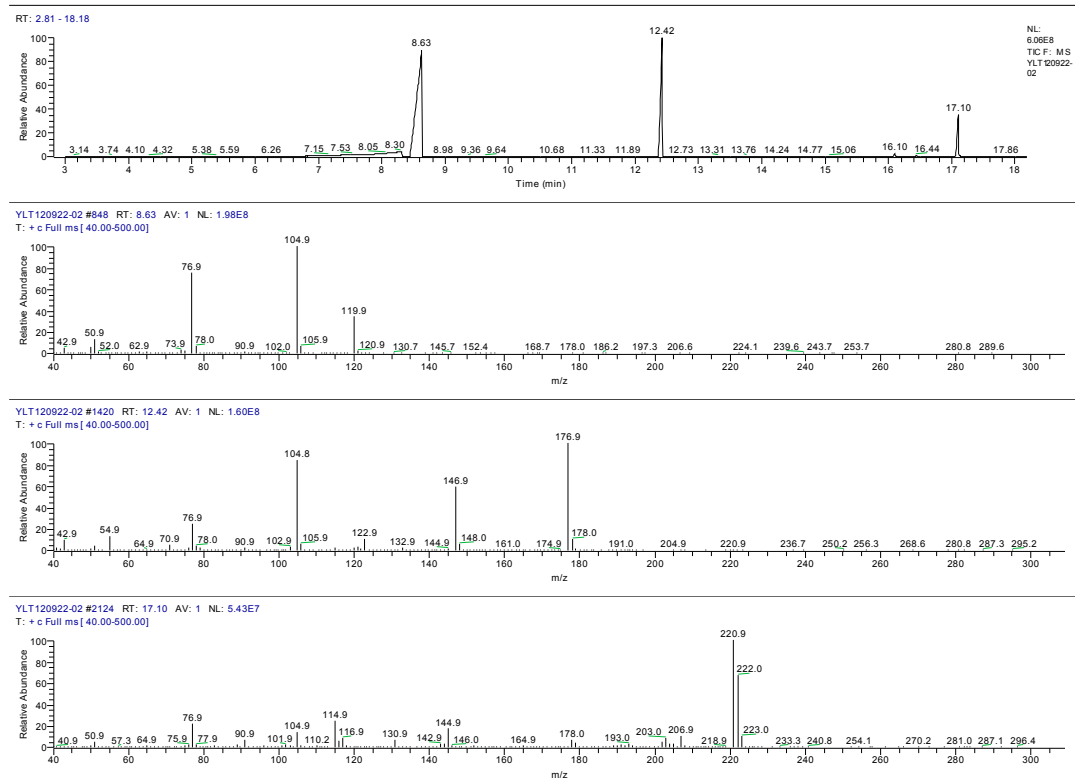


Figure S15. GC-MS spectrum of the reaction of acetophenone and butane-1,4-diol.

3. ^1H -NMR Spectra of Representative Products

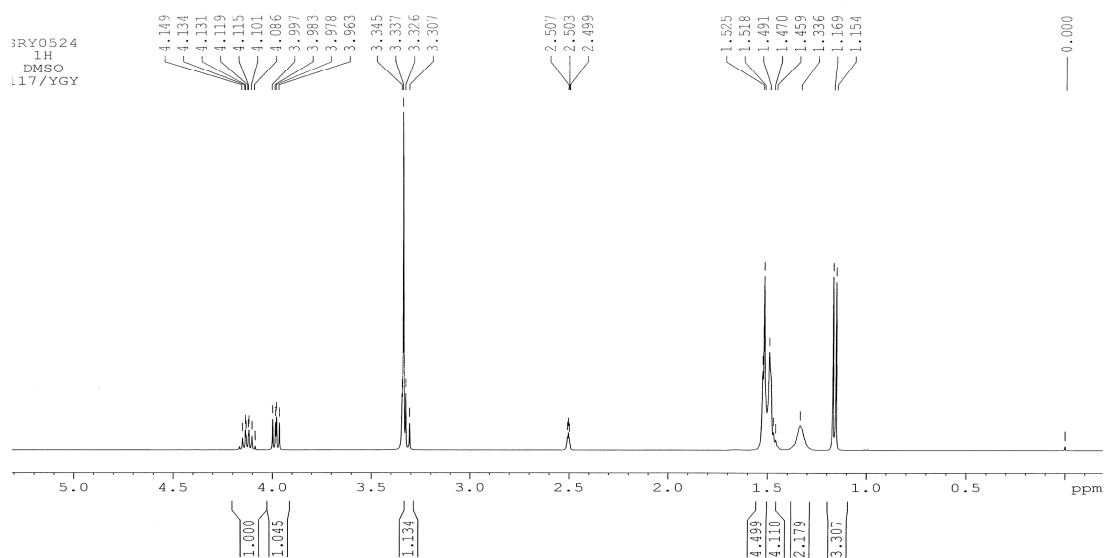


Figure S16. ^1H -NMR spectrum of the reaction product of cyclohexanone and propane-1,2-diol.

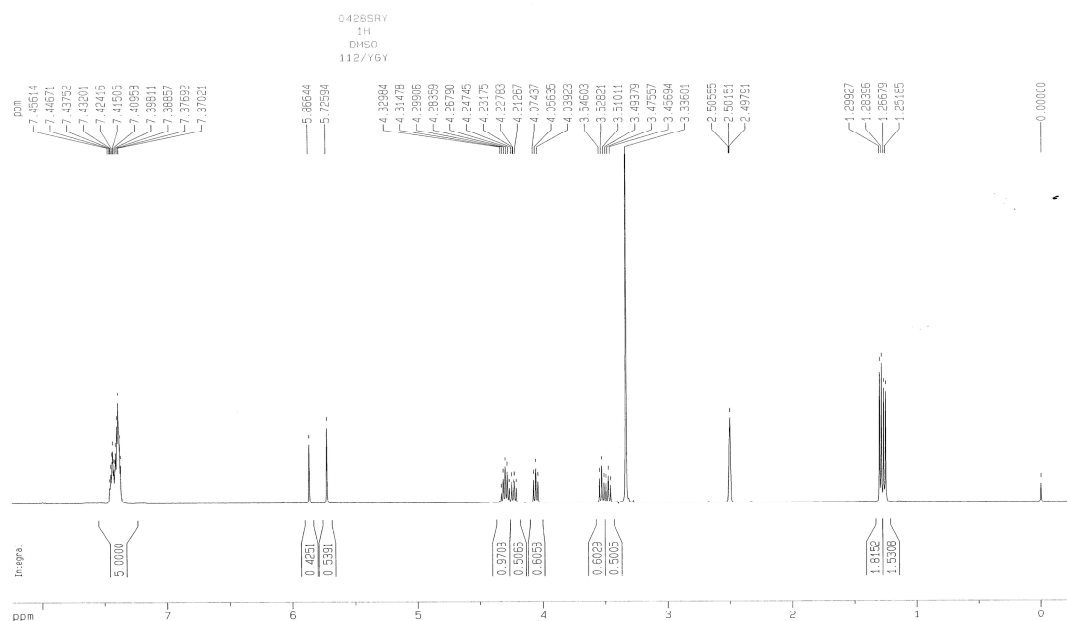


Figure S17. ^1H -NMR spectrum of the reaction product of benzaldehyde and propane-1,2-diol.

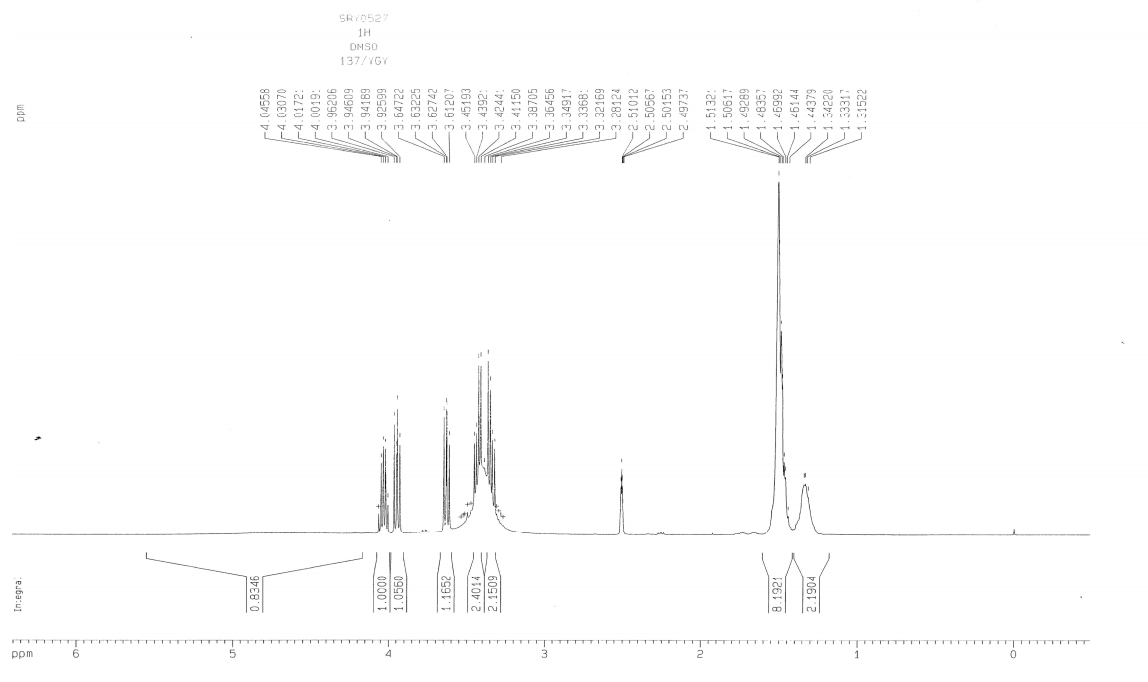


Figure S18. ^1H -NMR spectrum of the main product of reaction of cyclohexanone and glycerol.



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