Electronic Supplementary Information

Deep eutectic solvents choline chloride·2$CrCl_3$·6H_2O: an efficient catalyst for esterification of formic and acetic acid at room temperature

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1.Experimental section

Materials. All reagents and solvents for syntheses were purchased from commercial sources and used without further purification.

Measurements. The analysis of the reaction mixture was carried out on a gas chromatograph (sp-6890) equipped with a flame ionization detector (FID) and a capillary column (HP-5, 30 m×0.25 mm×0.25 mm). The column temperature was 80 ℃. The temperatures of the injector and detector were maintained at 320 ℃ and 320 ℃, respectively. The products were further identified by GC (varian 3900)–MS (varian saturn 2100 T) quipped with a flame ionization detector (FID) and a capillary column (DB-5, 30 m×0.25 mm×0.25 mm). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400MHz NMR spectrometer at 298K. The chemical shifts (δ) were given in part per million relative to internal tetramethylsilane (TMS, 0 ppm for ^{1}H), $CDCl_3$ (77.3 ppm for ^{13}C).

Preparation of deep eutectic solvent [ChCl][$CrCl_3 \cdot 6H_2O$]$_2$. A mixture of the chromium(iii) chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) and choline chloride in a molar ratio of 2:1 was heated to 70℃ with gentle stirring until a green liquid formed.

Preparation of deep eutectic solvent [ChCl][$FeCl_3$]$_2$. A mixture of the ferric chloride ($FeCl_3$) and choline chloride in a molar ratio of 2:1 was heated to 100℃ with gentle stirring until a dark brown liquid formed.

Preparation of deep eutectic solvent [ChCl][$AlCl_3 \cdot 6H_2O$]$_2$. A mixture of the aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$) and choline chloride in a molar ratio of 2:1 was heated to 70℃ with gentle stirring until a colorless liquid formed.

Preparation of deep eutectic solvent [ChCl][$MgCl_2 \cdot 6H_2O$]$_2$. A mixture of the magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and choline chloride in a molar ratio of 2:1 was heated to 70℃ with gentle stirring until a green clear liquid formed.

Preparation of deep eutectic solvent [ChCl][$MnCl_2 \cdot 4H_2O$]$_2$. A mixture of the manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) and choline chloride in a molar ratio of 2:1 was heated to 70℃ with gentle stirring until a pink liquid formed.

Preparation of deep eutectic solvent [ChCl][$CoCl_2 \cdot 6H_2O$]$_2$. A mixture of the cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and choline chloride in a molar ratio of 2:1 was heated to 70℃ with gentle stirring until a blue liquid formed.

Preparation of deep eutectic solvent [ChCl][$NiCl_2 \cdot 6H_2O$]$_2$. A mixture of the nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) and choline chloride in a molar ratio of 2:1 was heated to 70℃ with gentle stirring until a green liquid formed.

Preparation of deep eutectic solvent [ChCl][$CuCl_2 \cdot 2H_2O$]$_2$. A mixture of the cupric chloride ($CuCl_2 \cdot 2H_2O$) and choline chloride in a molar ratio of 2:1 was heated to 70℃ with gentle stirring until a brown liquid formed.

Preparation of deep eutectic solvent [ChCl][$ZnCl_2$]$_2$. A mixture of the Zinc chloride ($ZnCl_2$) and choline chloride in a molar ratio of 2:1 was heated to 100℃ with gentle stirring until a colorless liquid formed.

Preparation of deep eutectic solvent [ChCl][$SnCl_2$]$_2$. A mixture of the anhydrous stannous chloride ($SnCl_2$) and choline chloride in a molar ratio of 2:1 was heated to 100℃ with gentle stirring until a colorless liquid formed.

The synthesis process of n-butyl acetate. Carboxylic acids (0.10 mol 6.00g) and n-butanol (0.02 mol 1.48g) without solvent were added, and then the deep eutectic solvent [ChCl][$CrCl_3 \cdot 6H_2O$]$_2$ (0.5mmol 0.3365g) was added to initiate the reaction. The reaction mixture was stirred at 25℃ for 24h. After the reaction was completed, two clearly separated phases are formed, the upper liquid layer was spilled off with a Pasteur pipette, the lower layer formed by DES, water and excess starting material was extracted with diethyl ether three times. The combined organic layers were washed with saturated aqueous $NaHCO_3$ three times and dried over anhydrous Mg_2SO_4, filtered, and then the solvent was removed by rotary evaporation to obtain n-butyl acetate 1.99g (isolated yield=85.7%).

Recycle process of DES. After the reaction was completed, two clearly separated phases are formed, the upper liquid layer was spilled off with a Pasteur pipette, the lower layer formed by DES, water and excess starting material was extracted with diethyl ether three times. A drying in vacuo at 60℃ overnight was carried out on DES for further cycles.

2.The calculation of the yield n-butyl acetate by GC

The yield of esters and the selectivity to esters was calculated using equations (1-2), via GC with 1,4-dimethyl-benzene as intemal standard, in which the number of moles was determined by Internal Standard Method from the chromatographic analysis (BA-n-butyl acetate, PX-1,4-dimethyl-benzene) (n-butyl acetate's standard curve: $y=1.9754x-0.0500$ with $R^2=0.9997$, where $y=m_{BA}/m_{PX}$ and $x=A_{BA}/A_{PX}$ with A being the integral area of GC).

$$m_{BA}=m_{PX}\times(1.9754\times A_{BA}/A_{PX}-0.0500) \quad (1)$$

$$Yield_{BA}=(m_{BA}/116)/(m_{butanol}/74)\times 100\% \quad (2)$$

After the reaction was completed, liquid samples were analyzed on a gas chromatograph after addition of the internal standard. The yield of n-butyl acetate was calculated using equations (1-2).

3.Representative examples of GC chromatograms from reaction mixtures

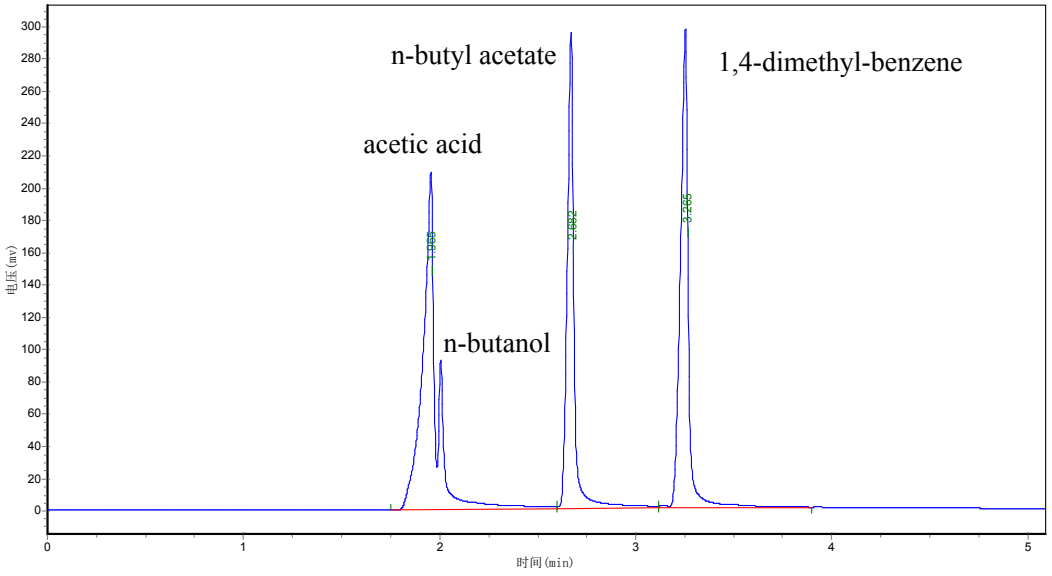

Fig S1 Representative examples of GC chromatograms from reaction mixtures

4.Characterization data and spectra for n-butyl acetate

δ_H (400 MHz, $CDCl_3$) 4.01, 1.99, 1.56, 1.34, 0.89. δ_C (101 MHz, $CDCl_3$) 171.33, 64.37, 30.57, 20.87, 19.05, 13.60.

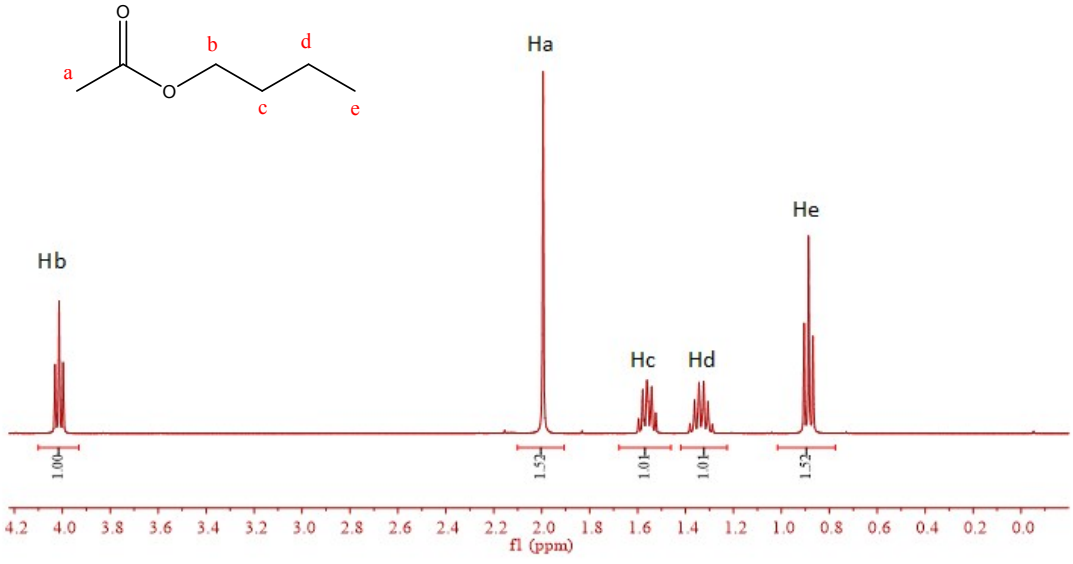

Fig S2 ^{1}H NMR spectrum of n-butyl acetate ($CDCl_3$; 400MHz).

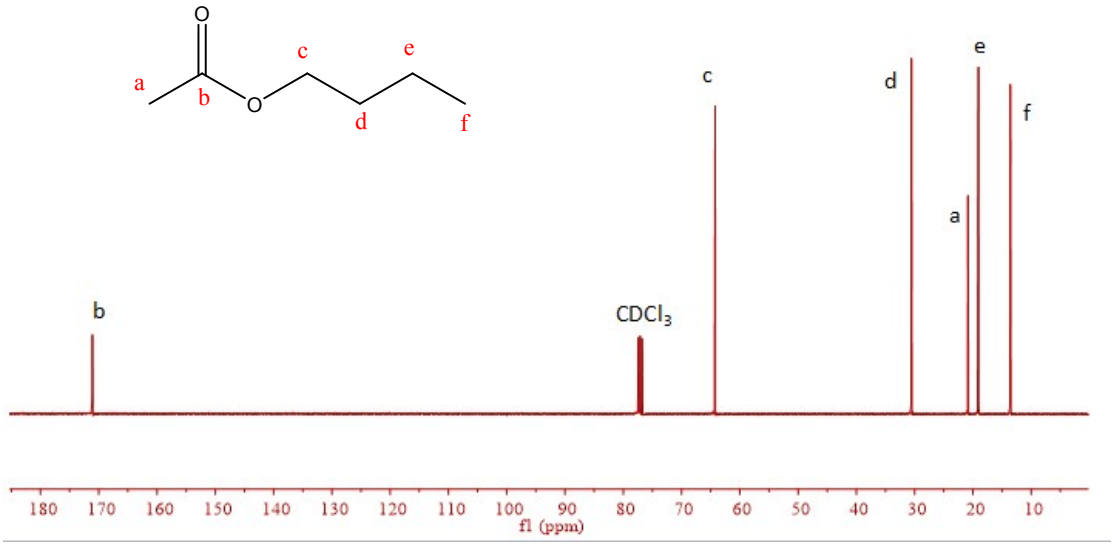

Fig S3 ^{13}C NMR spectrum of n-butyl acetate ($CDCl_3$; 100MHz).

5.The effect of temperature on the esterification reaction with [ChCl] $[FeCl_3]_2$

Table S1 The effect of temperature on the esterification reaction with [ChCl] $[FeCl_3]_2$ [a]

Entry	Temperature	Yield of n-butyl acetate [b]
1	25℃	64.5%
2	30℃	66.9%
3	40℃	71.3%
4	50℃	78.4%
5	60℃	79.9%
6	70℃	79.5%
7	80℃	78.5%

a Reaction conditions: n-butanol (0.01 mol), acetic acid (0.05 mol), and DES (0.25 mmol) for 24h
b Yield are based on GC. 1,4-dimethyl-benzene as intemal standard

6.The GC-MS spectra of esters （Table 4）

(1) The GC-MS spectra of ethyl acetate

Chromatogram Plot 1 - 9/7/2015 7:57 AM

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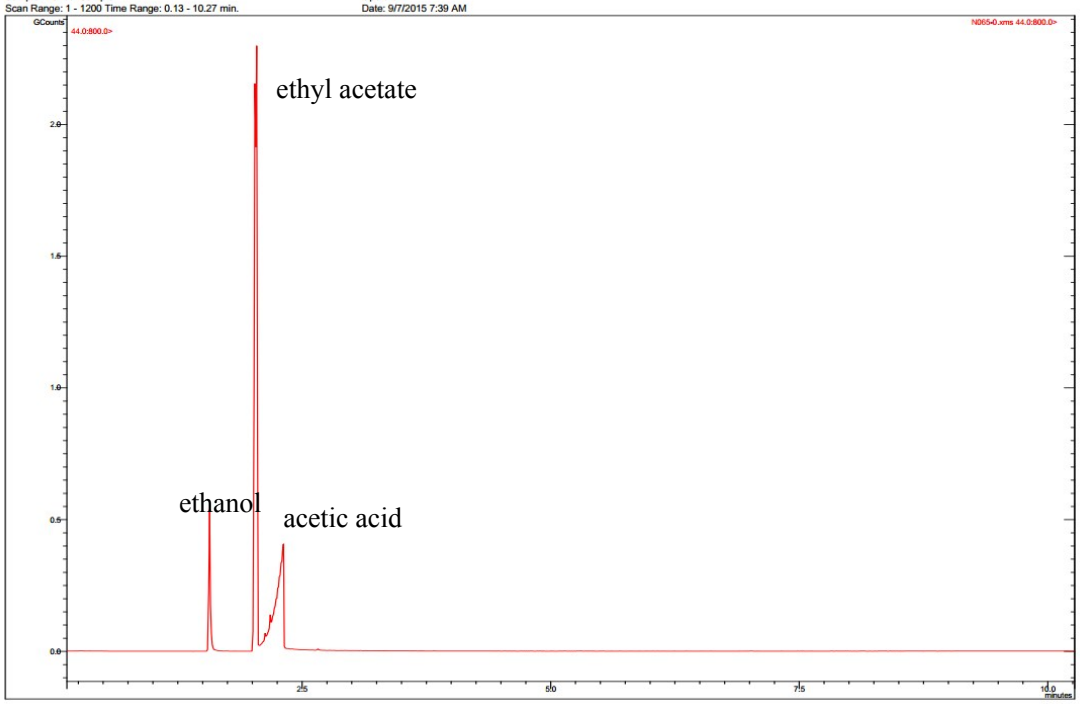
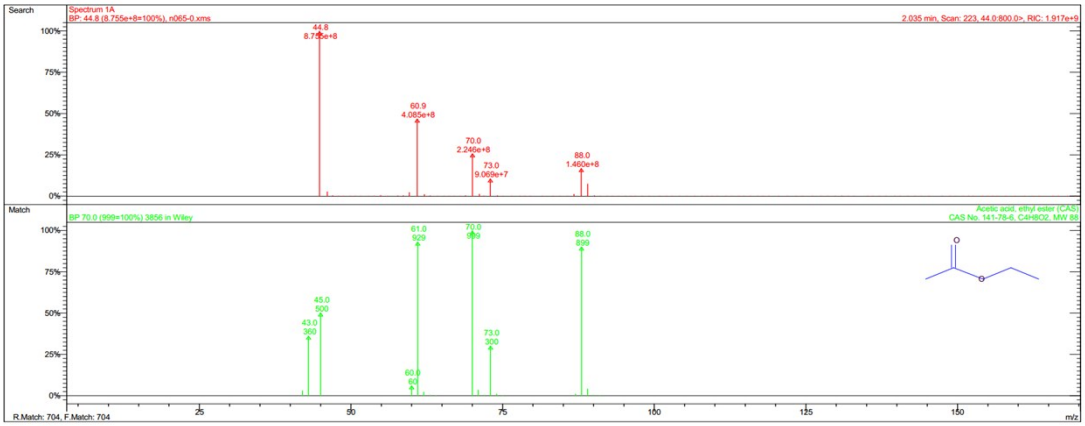
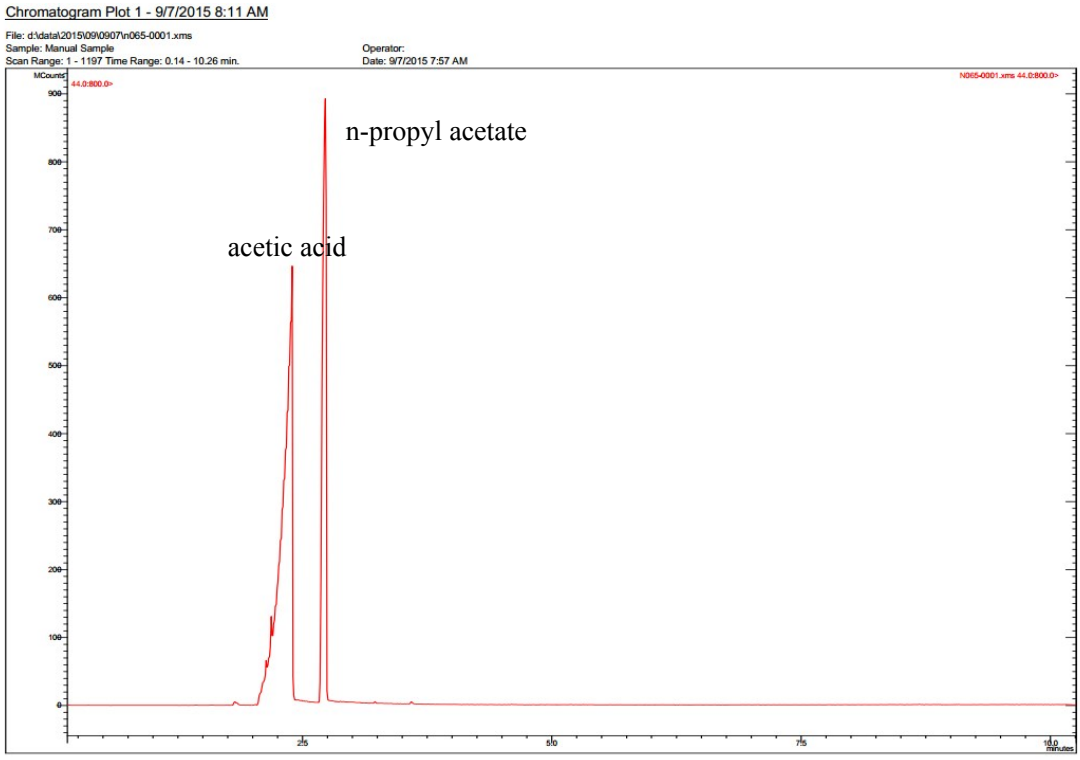
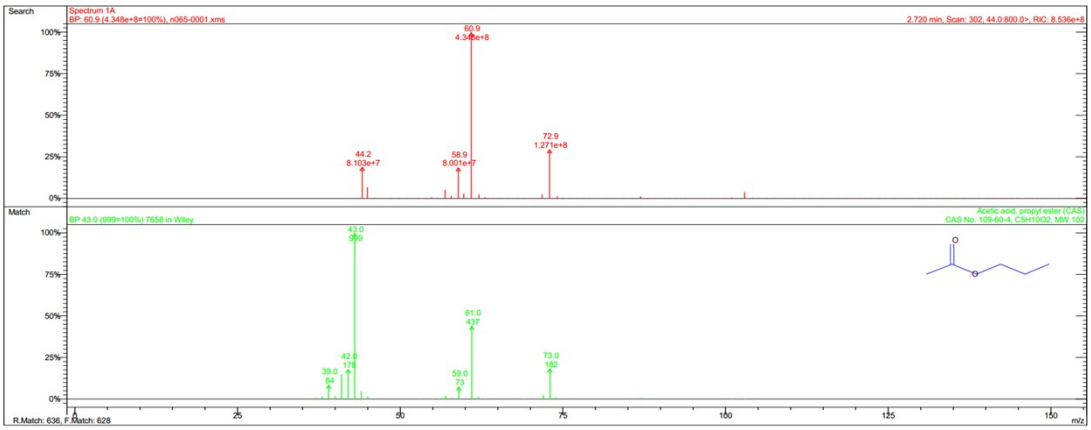


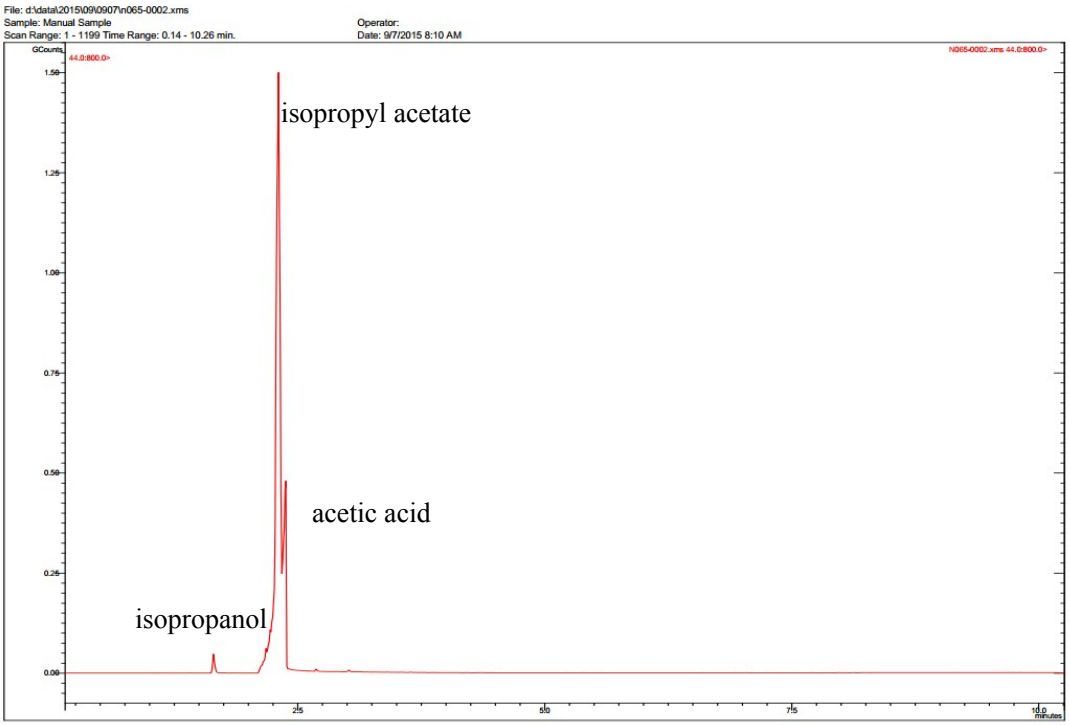


（2）The GC-MS spectra of n-propyl acetate

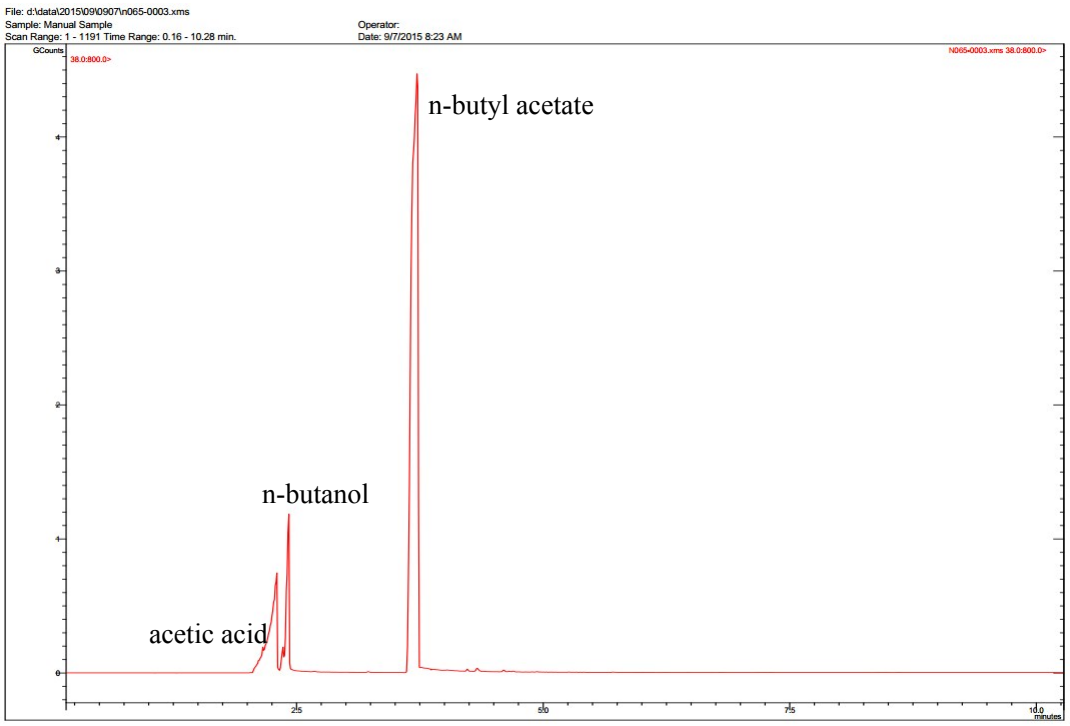




□3□The GC-MS spectra of isopropyl acetate



□4□The GC-MS spectra of n-butyl acetate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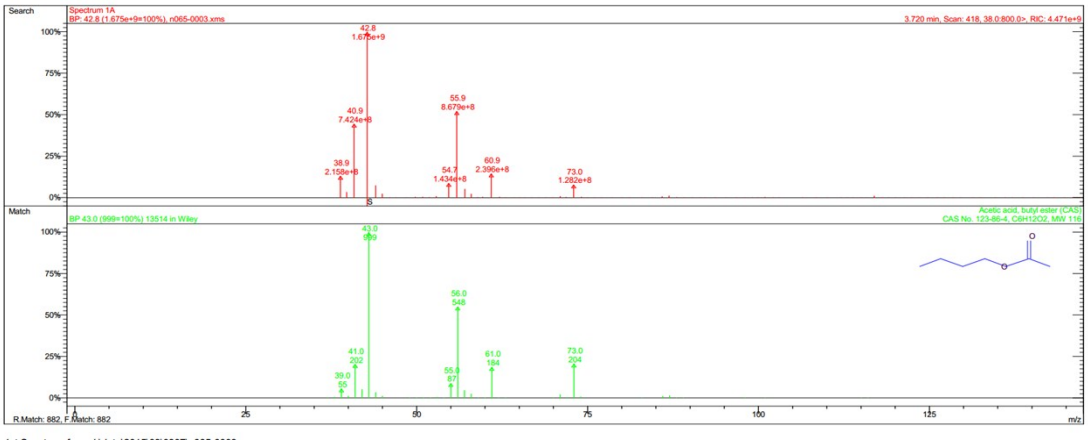
n-butanol
acetic acid
minutes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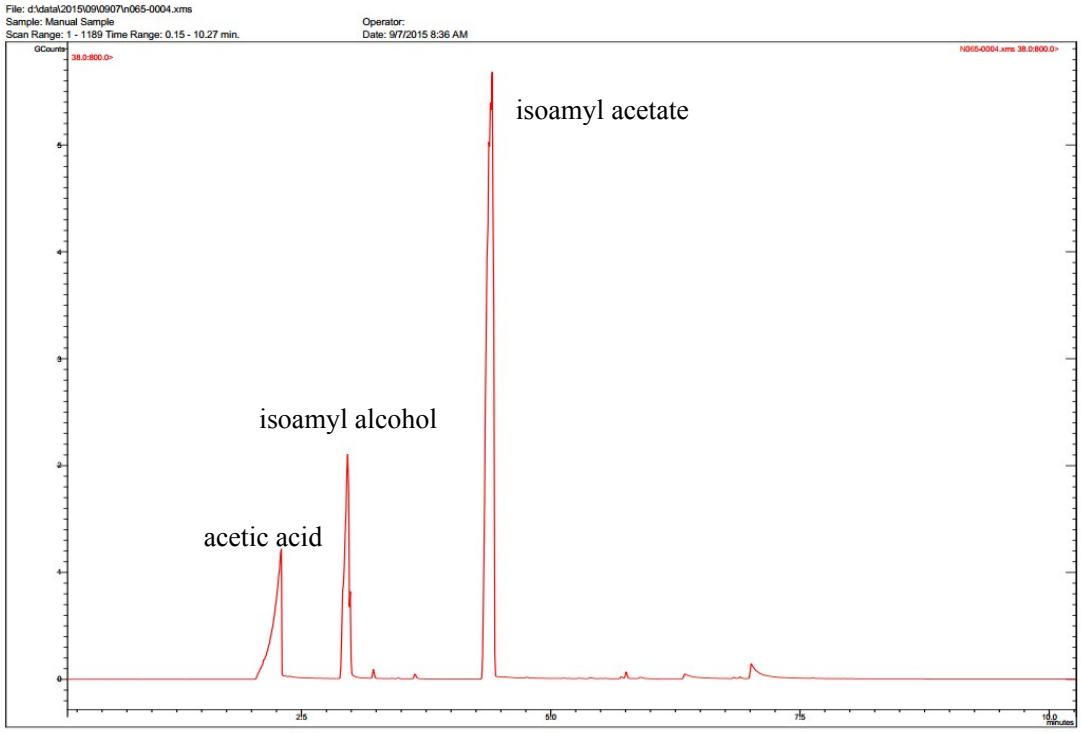
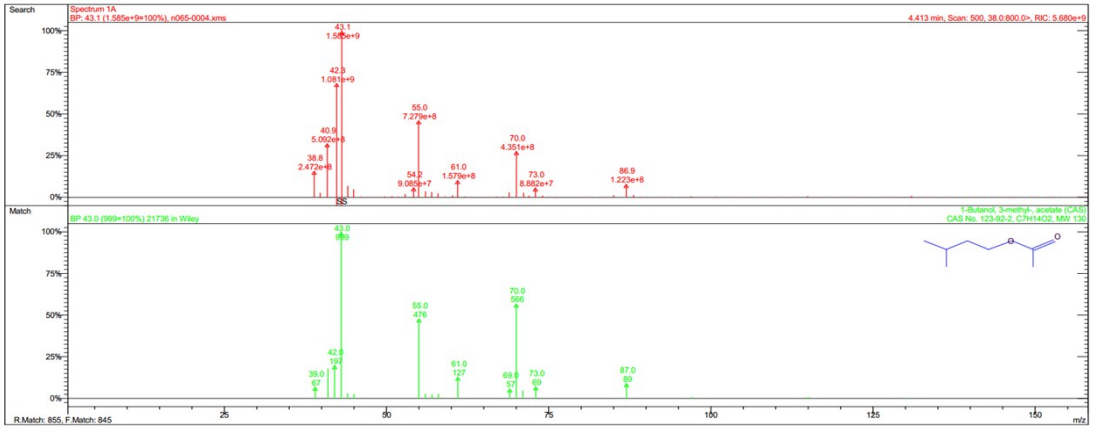
（5）The GC-MS spectra of isoamyl acetate





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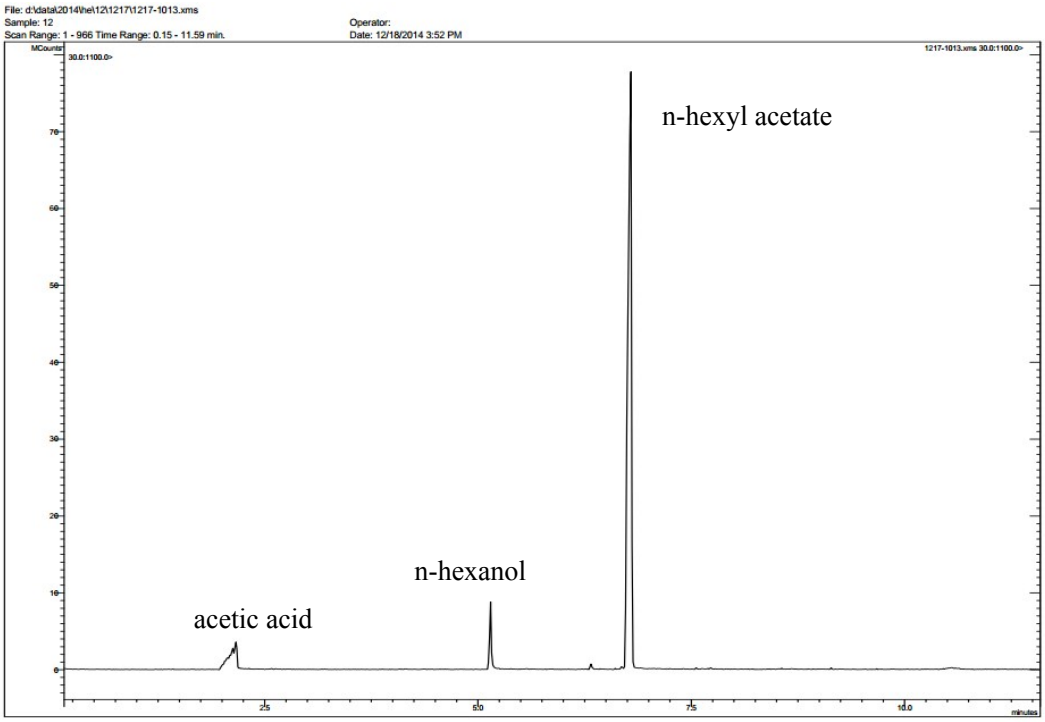

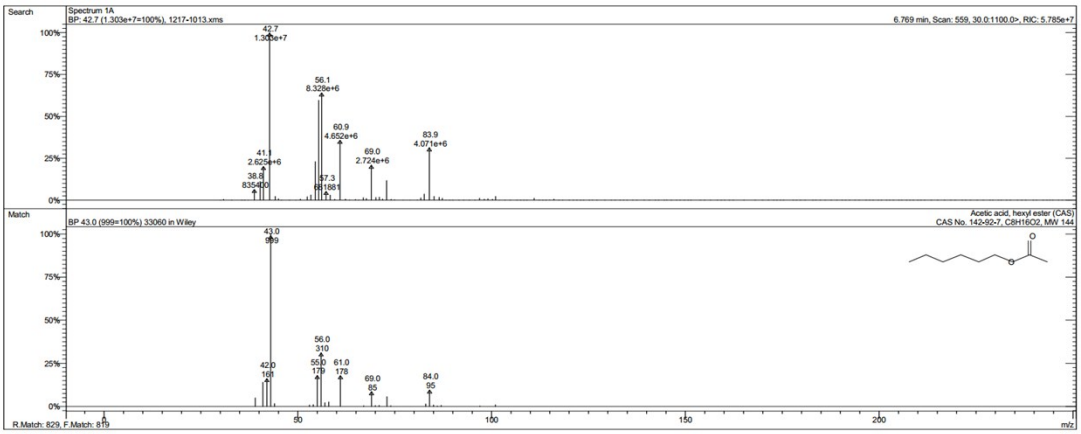

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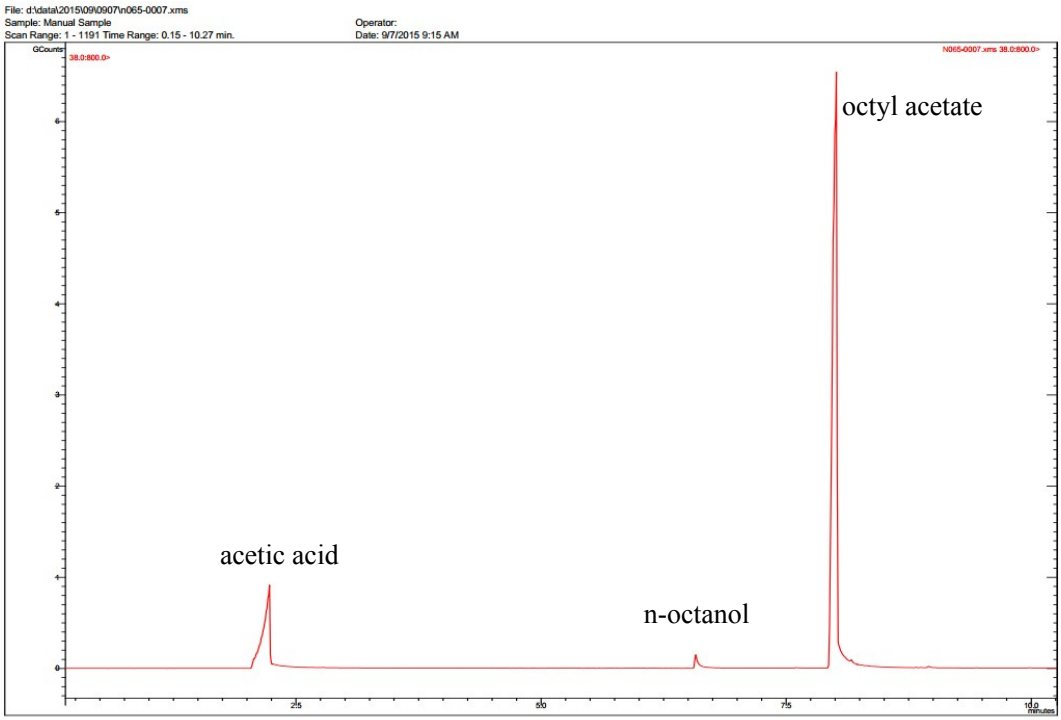

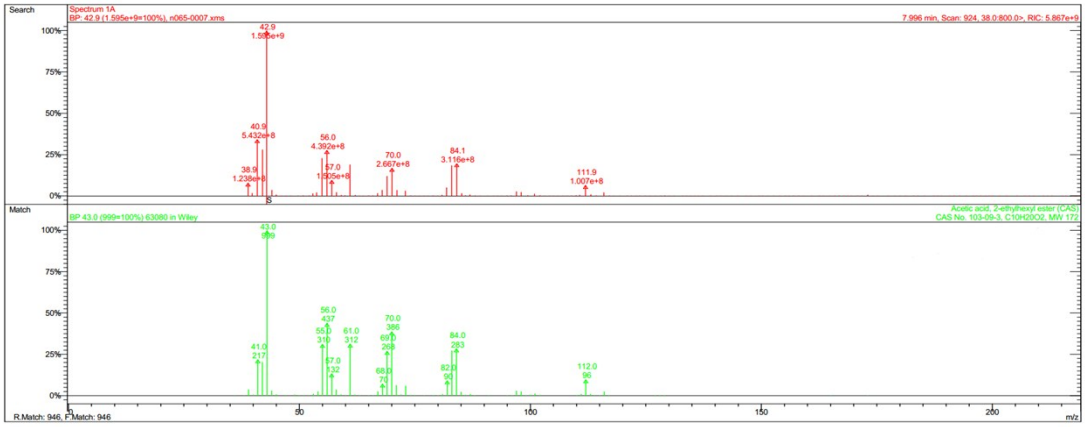

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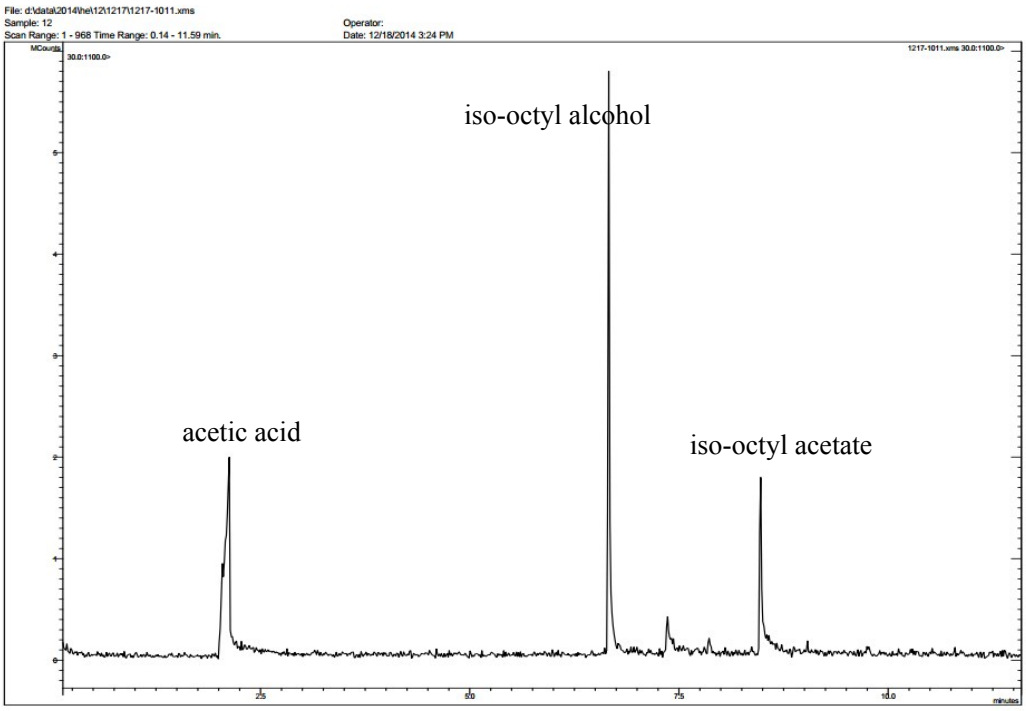
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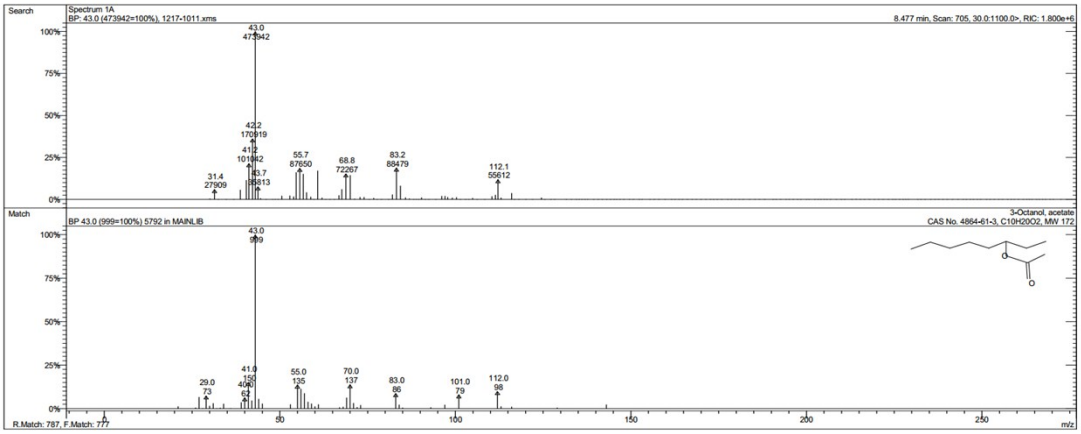
acetic acid
iso-octyl acetate
minutes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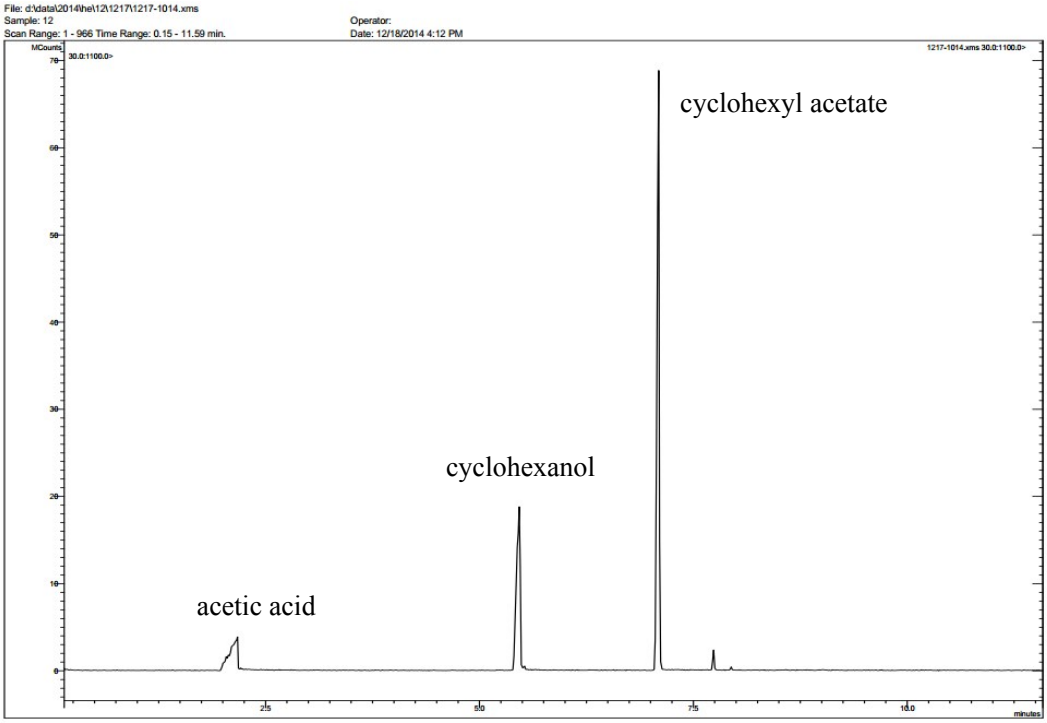

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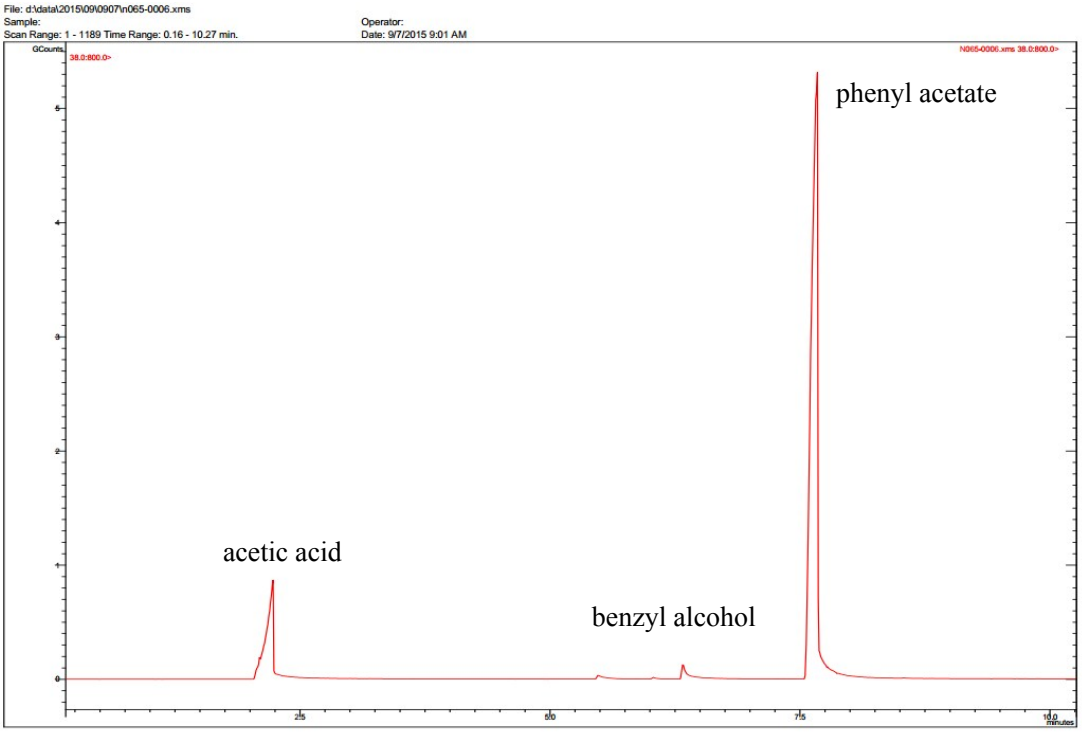

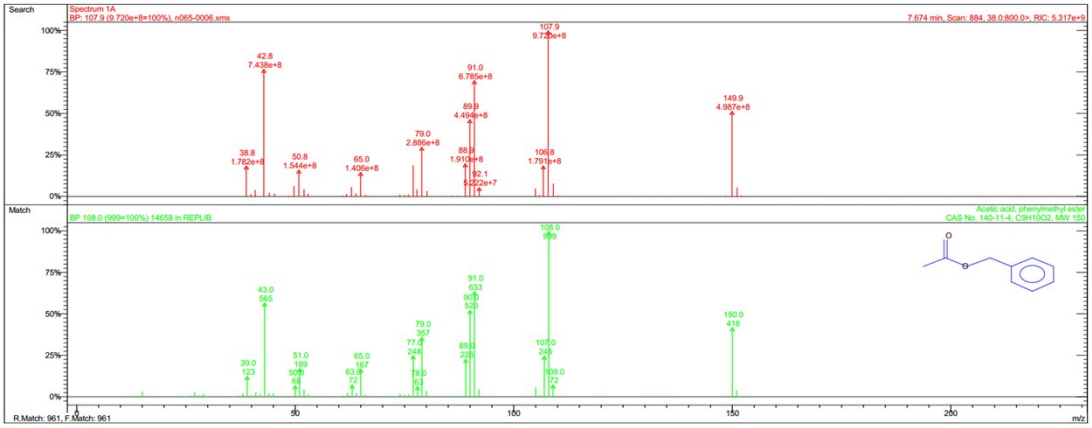

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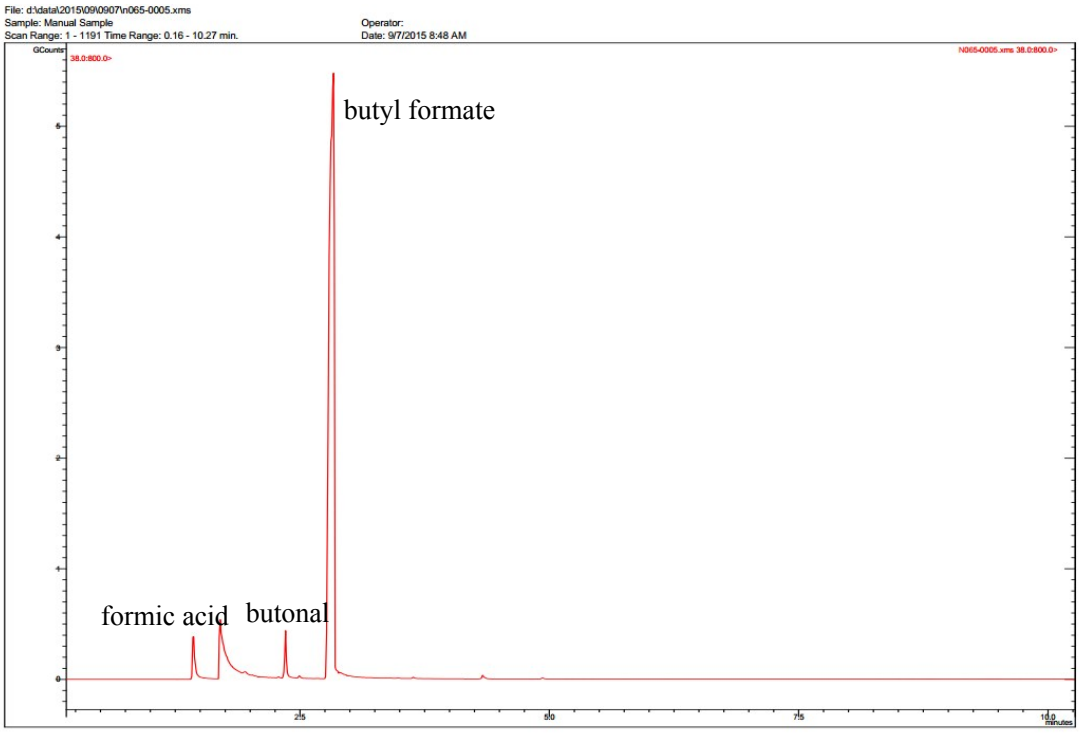

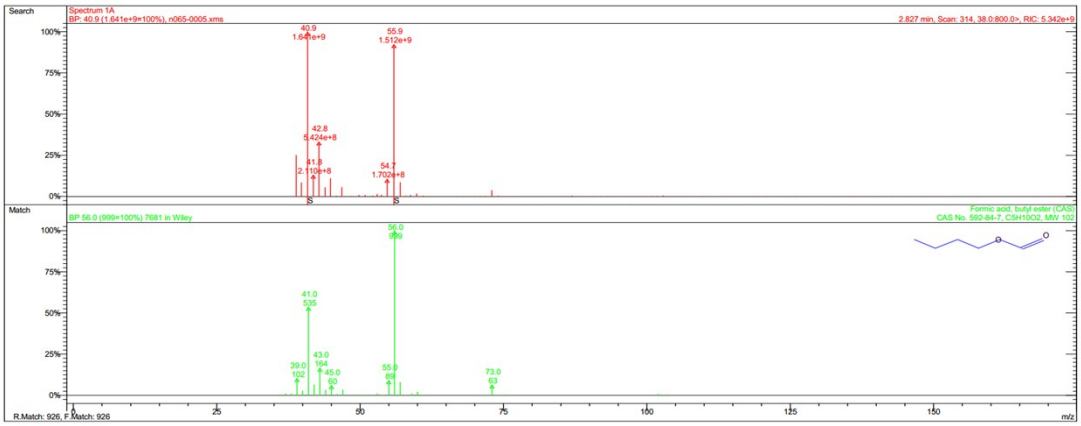

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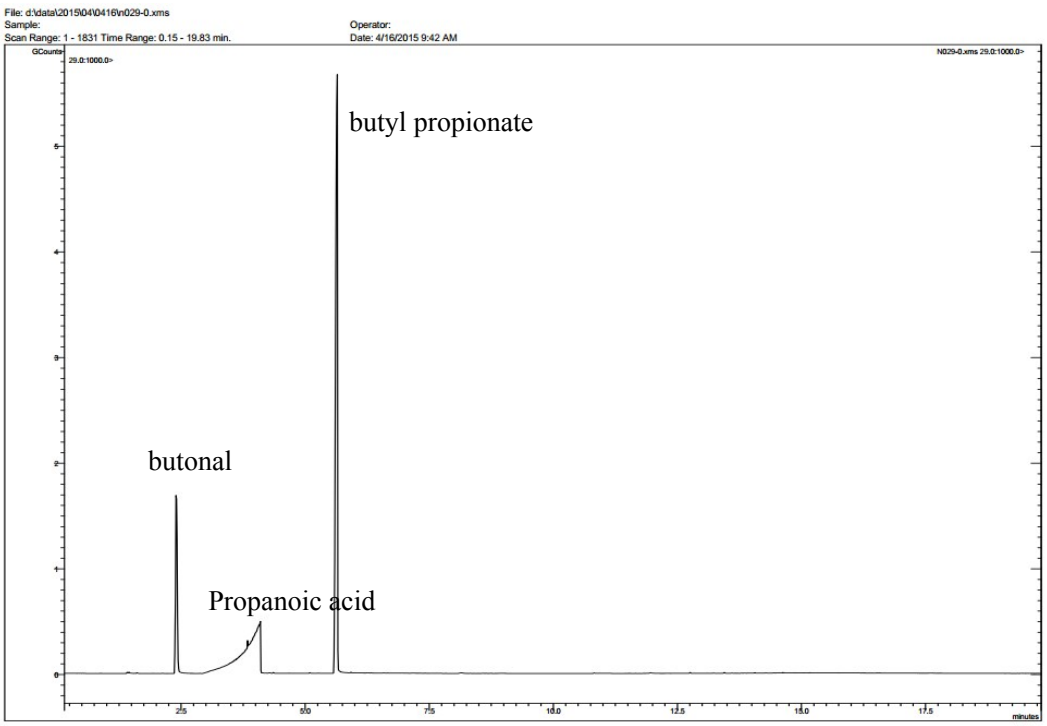
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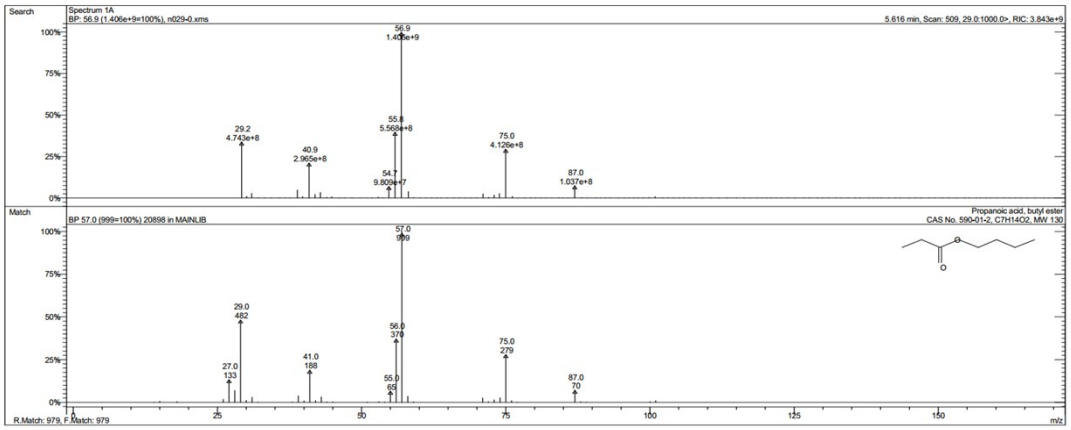
butonal
Propanoic acid
minutes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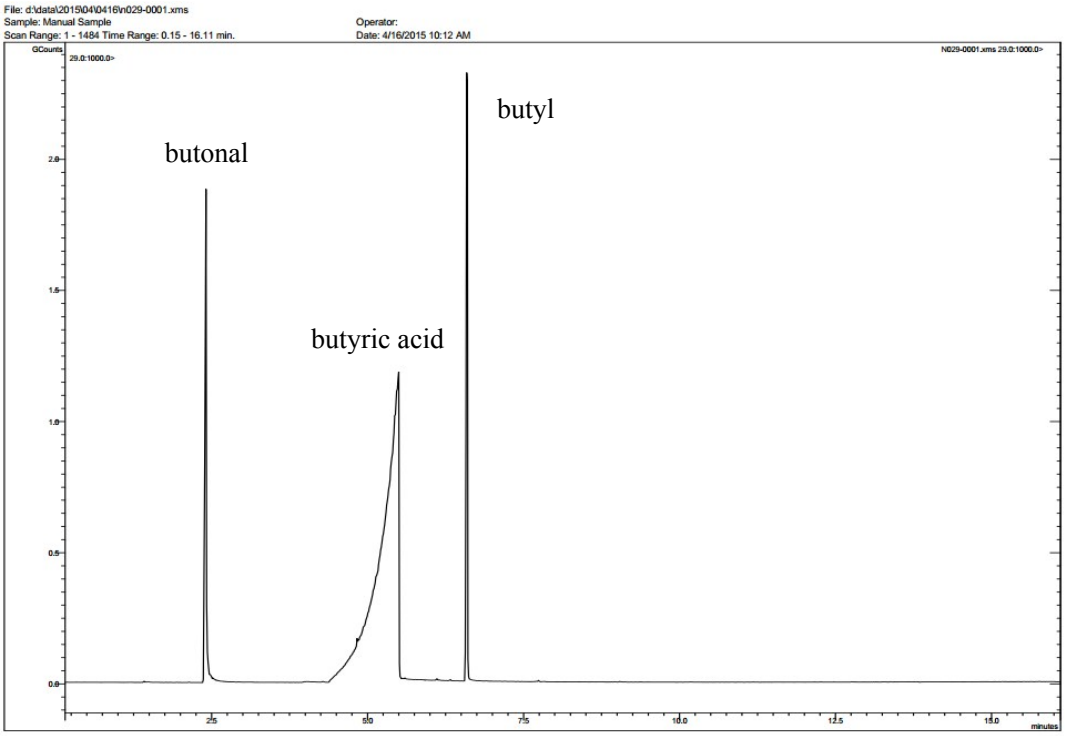

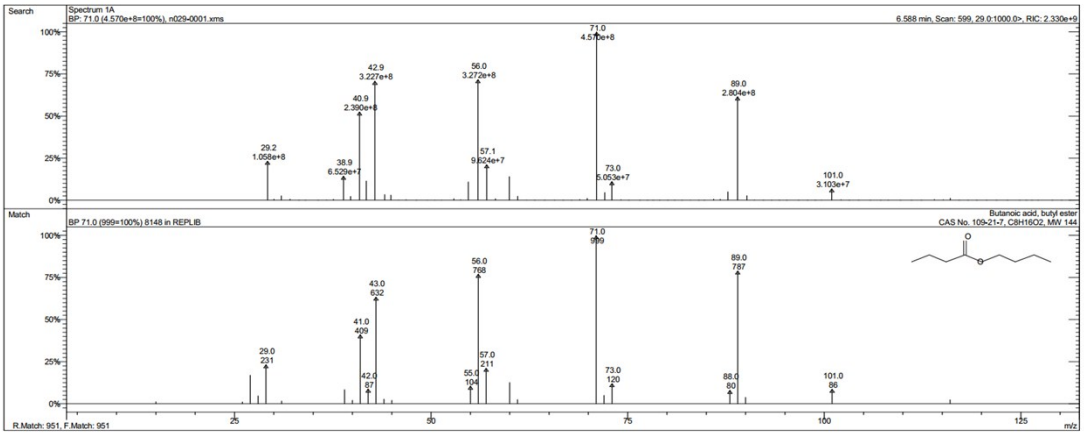

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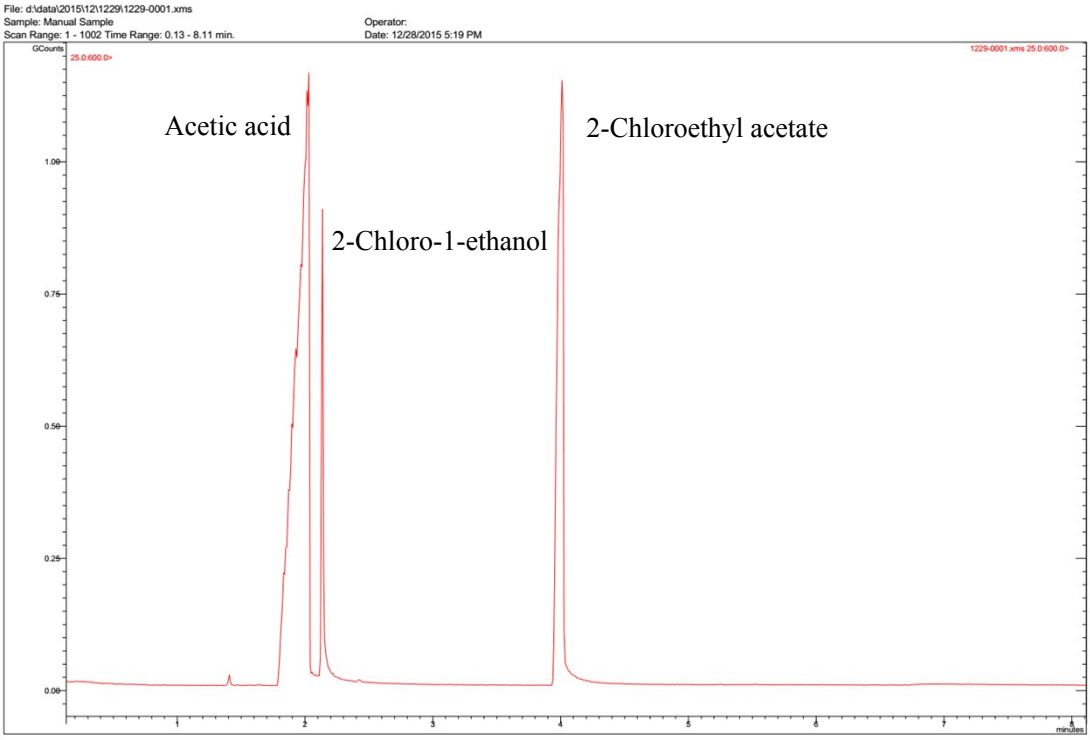

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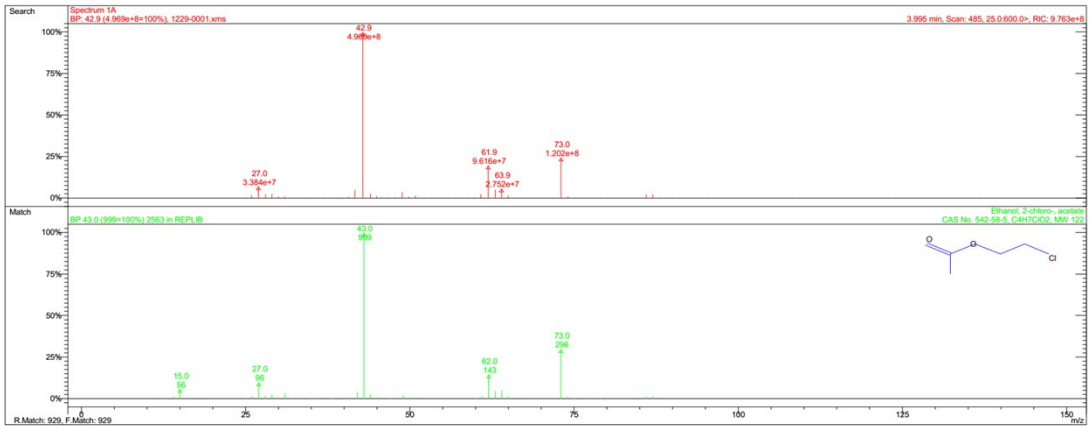

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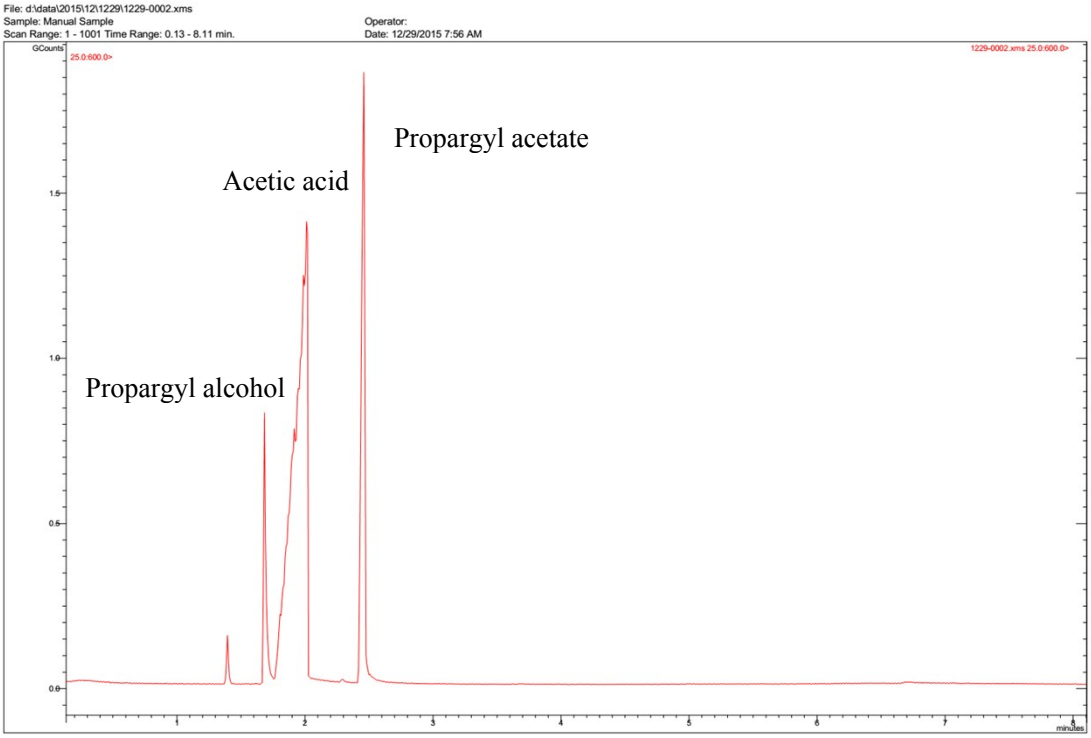

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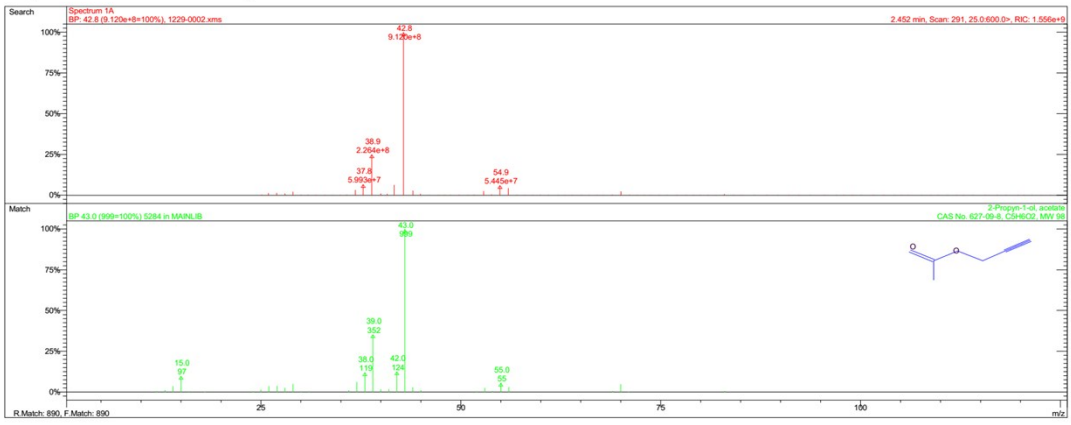
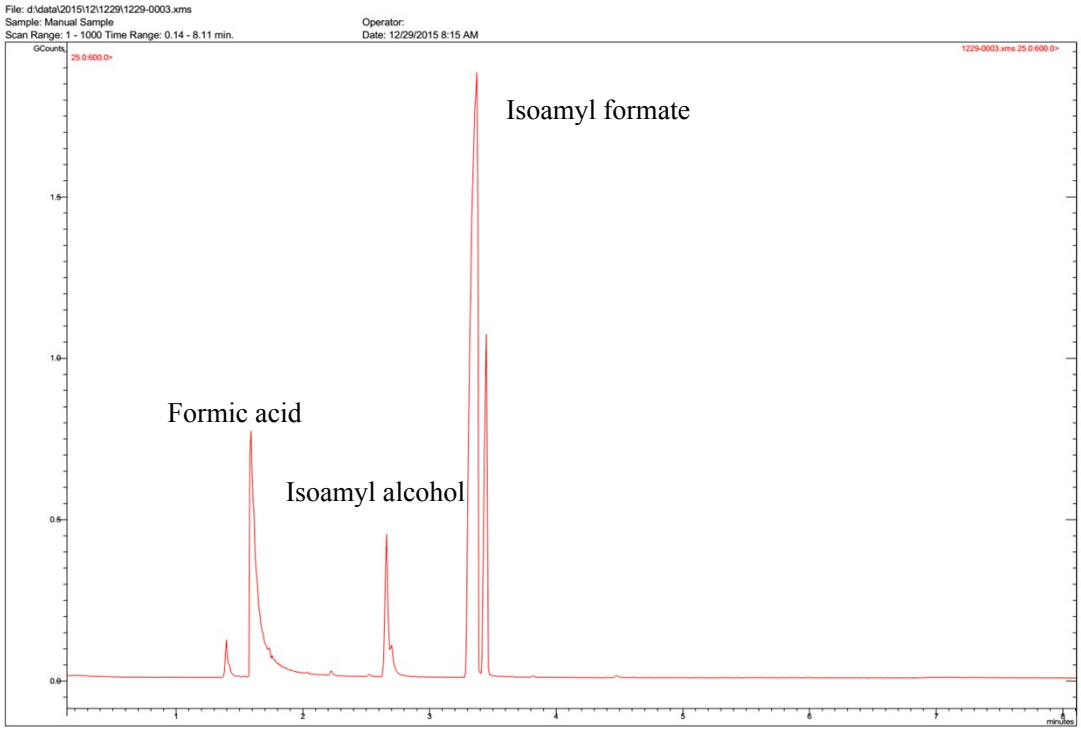


（16）The GC-MS spectra of isoamyl formate



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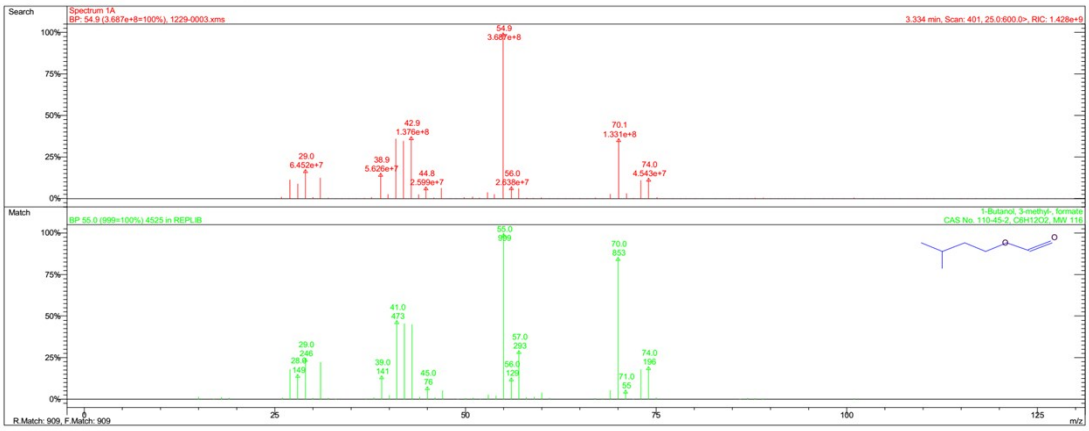

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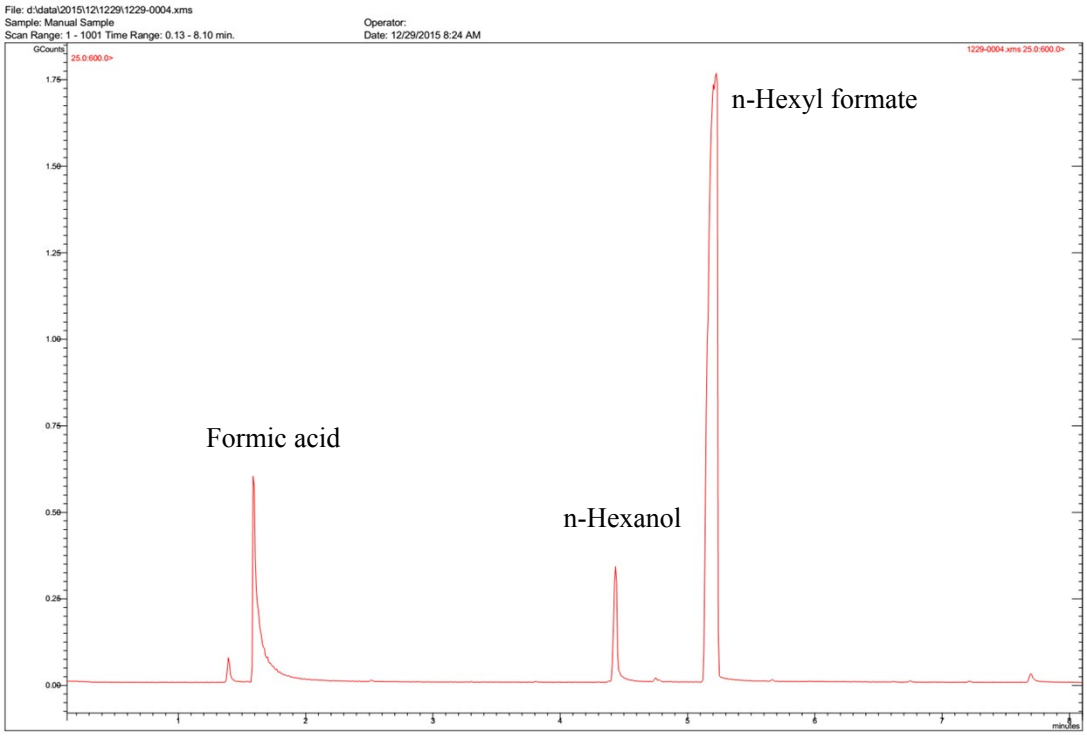

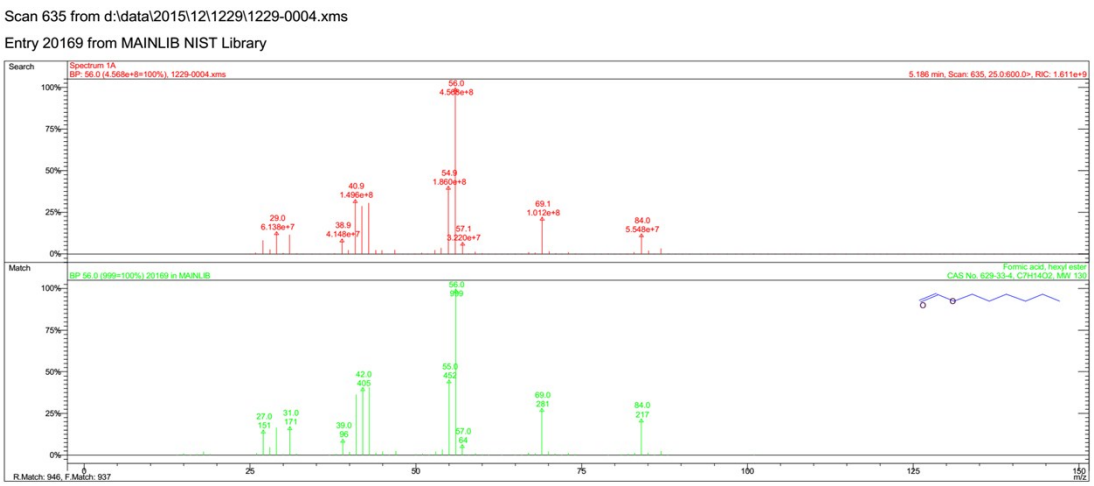

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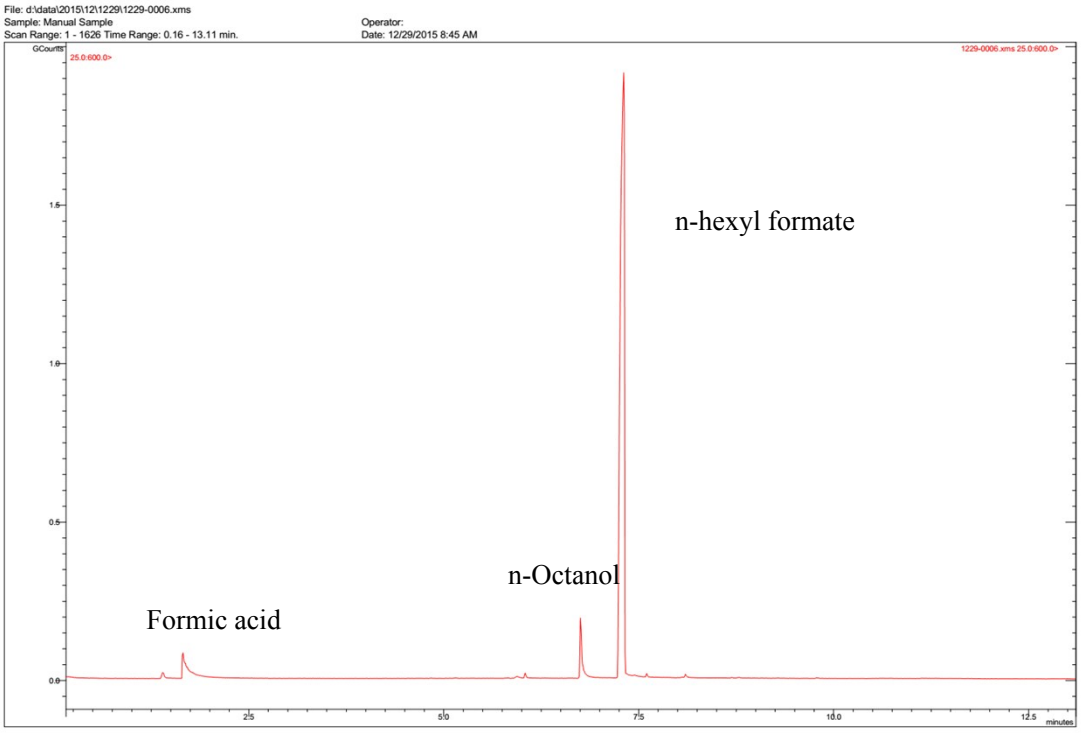

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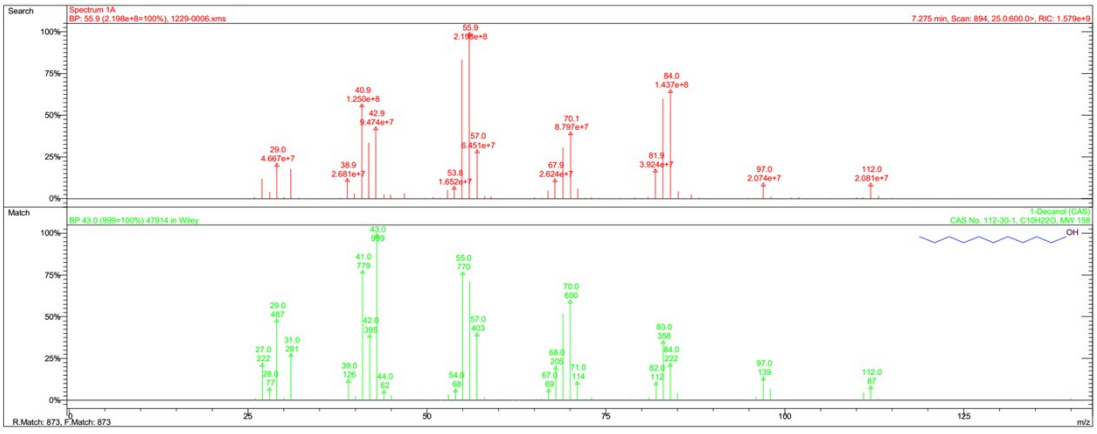
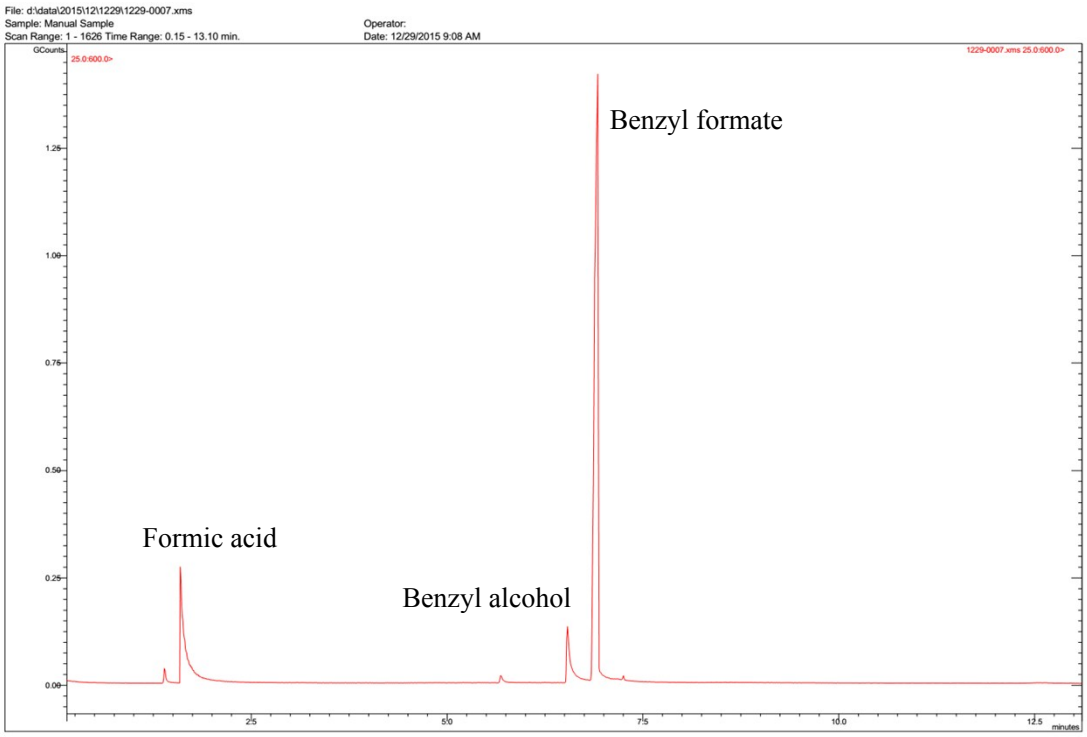


（19）The GC-MS spectra of benzyl formate



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