

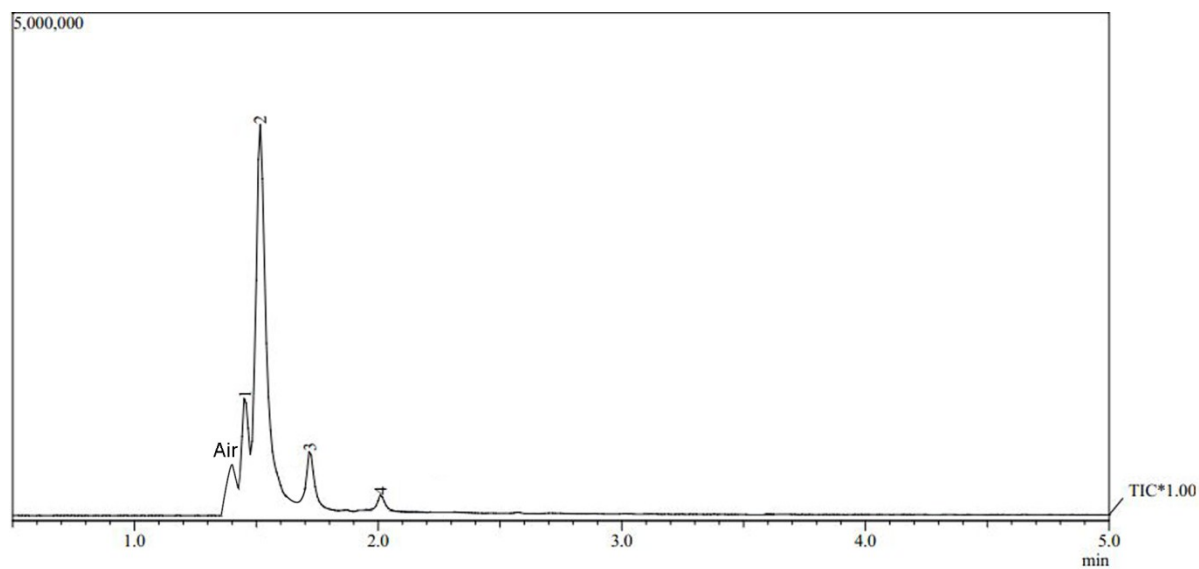
Electronic Supplementary Information

Bromide promoted hydrogenation of CO₂ to higher alcohols using Ru-Co homogeneous catalyst

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Figures

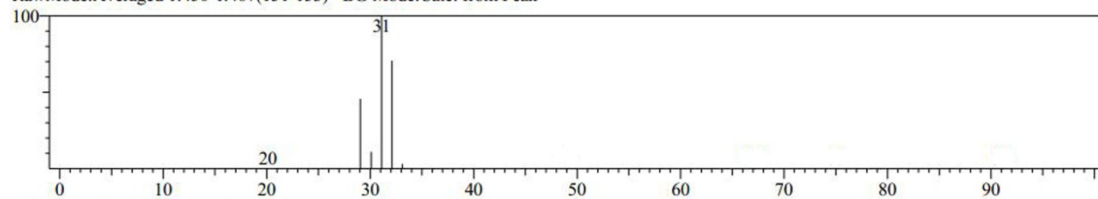


Library

<< Target >>

Line#:1 R.Time:1.458(Scan#:152) MassPeaks:21 BasePeak:31.10(228322)

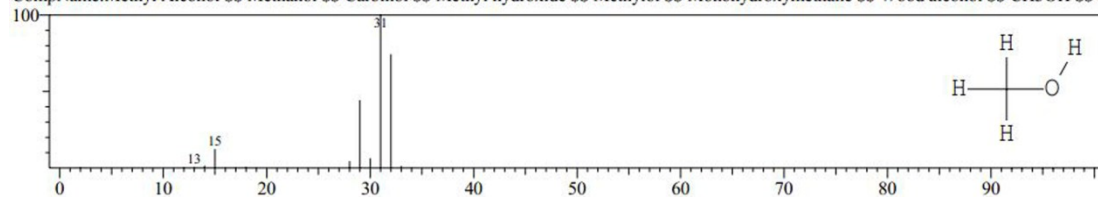
RawMode:Averaged 1.450-1.467(151-153) BG Mode:Calc. from Peak



Hit#:1 Entry:16 Library:NIST08.LIB

SI:97 Formula:CH4O CAS:67-56-1 MolWeight:32 RetIndex:0

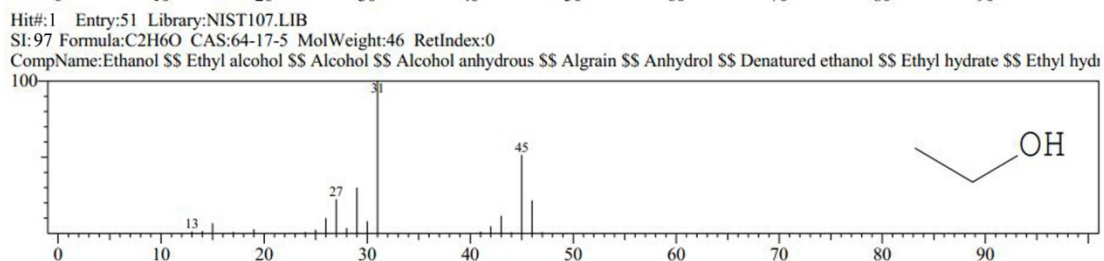
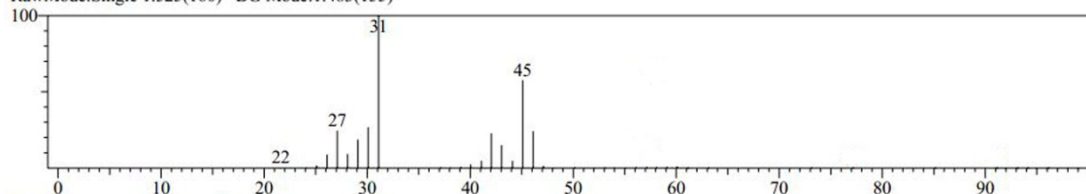
CompName:Methyl Alcohol \$\$ Methanol \$\$ Carbinol \$\$ Methyl hydroxide \$\$ Methylol \$\$ Monohydroxymethane \$\$ Wood alcohol \$\$ CH3OH \$\$ C



<< Target >>

Line#:2 R.Time:1.525(Scan#:160) MassPeaks:42 BasePeak:31.10(675208)

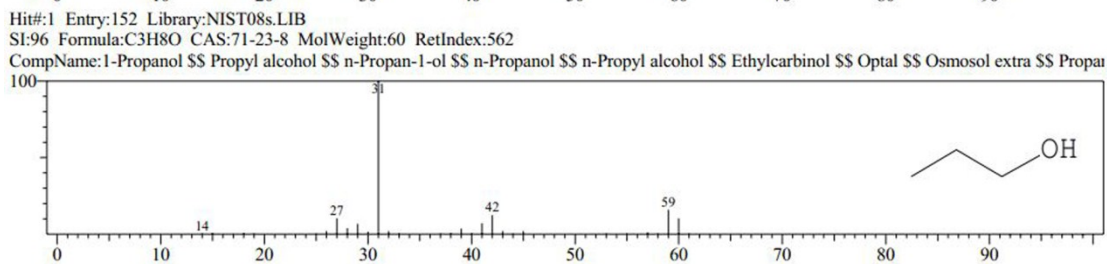
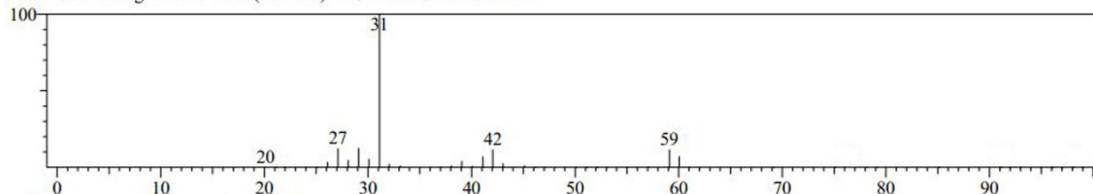
RawMode:Single 1.525(160) BG Mode:1.483(155)



<< Target >>

Line#:3 R.Time:1.725(Scan#:184) MassPeaks:44 BasePeak:31.10(139438)

RawMode:Averaged 1.717-1.733(183-185) BG Mode:Calc. from Peak



<< Target >>

Line#:4 R.Time:2.017(Scan#:219) MassPeaks:45 BasePeak:43.10(20648)

RawMode:Averaged 2.008-2.025(218-220) BG Mode:Calc. from Peak

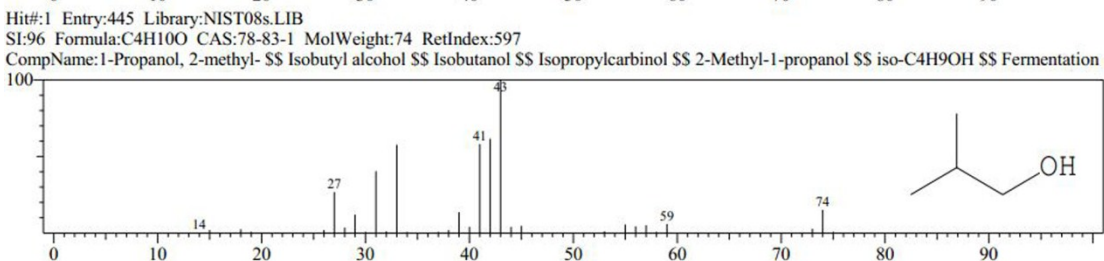
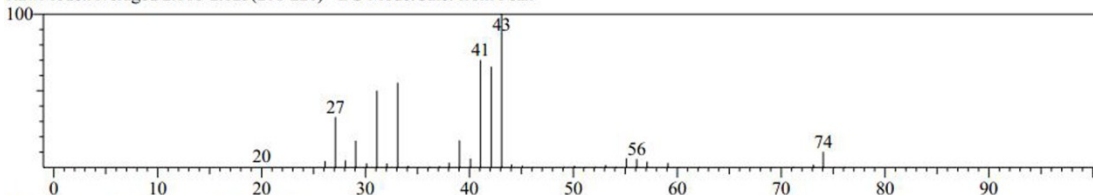


Fig. S1 GC-MS spectra of the products. Reaction conditions were the same as that of entry 1 in Table 1.

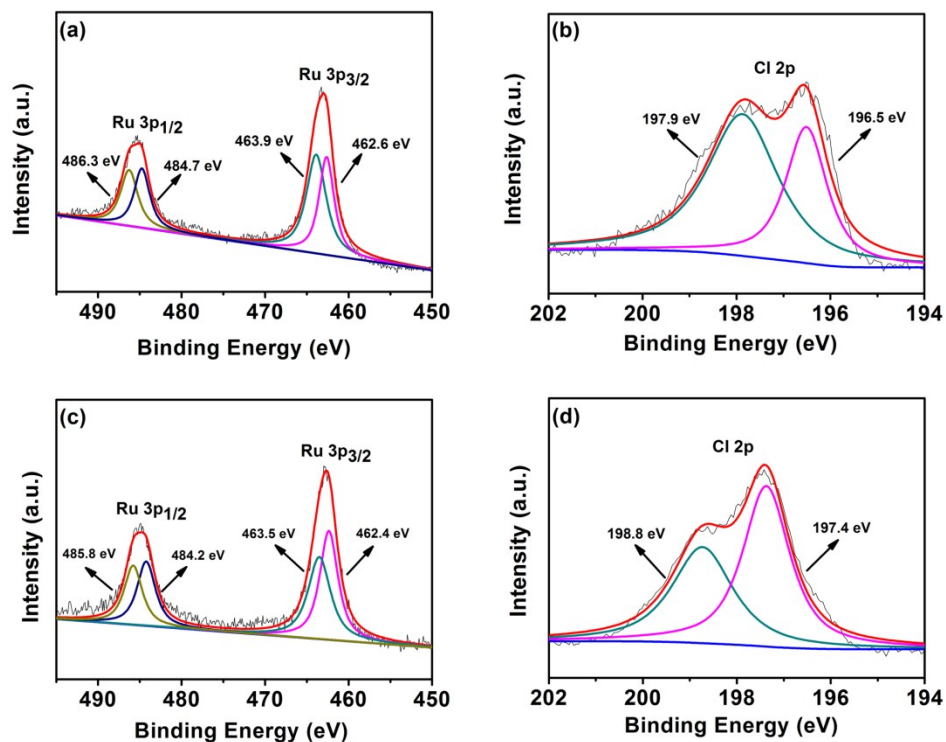
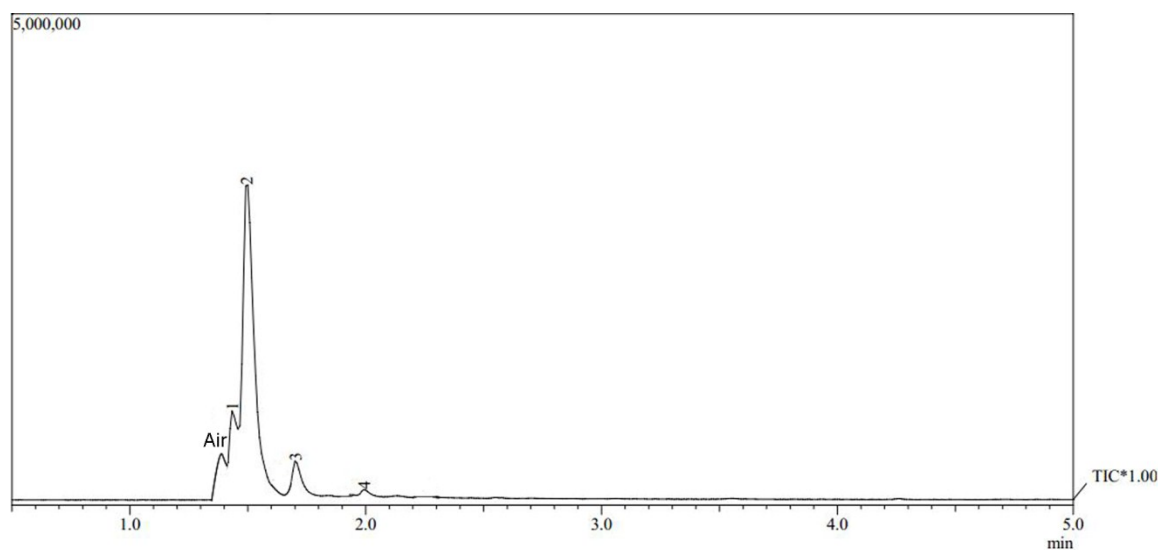


Fig. S2 XPS spectra of Ru (a), Cl (b) before the coordination of $\text{Ru}_3(\text{CO})_{12}$ with PPNCI and Ru (c), Cl (d) after the coordination of $\text{Ru}_3(\text{CO})_{12}$ with PPNCI.

Notes: The coordination of $\text{Ru}_3(\text{CO})_{12}$ and PPNCI was conducted as follows: 8.5 mg $\text{Ru}_3(\text{CO})_{12}$ (40 μmol Ru) was dissolved in 20 mL THF, 86.1 mg PPNCI (0.15 mmol) was dissolved in 20 mL methanol, the above solutions were mixed under stirring and the color of the mixed solution changed gradually from orange to bright yellow. After the mixture was stirred for 5 hrs at 40 $^{\circ}\text{C}$, the solvent was removed using rotary evaporator. The precipitate was dried in vacuum at room temperature for 12 hrs before the XPS analysis. The X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCA Lab 220i-XL electron spectrometer from VG Scientific using 300 W $\text{AlK}\alpha$ radiation. The base pressure was about 3×10^{-9} mbar. The binding energy was referenced to the C_{1s} line at 284.8 eV from adventitious carbon.

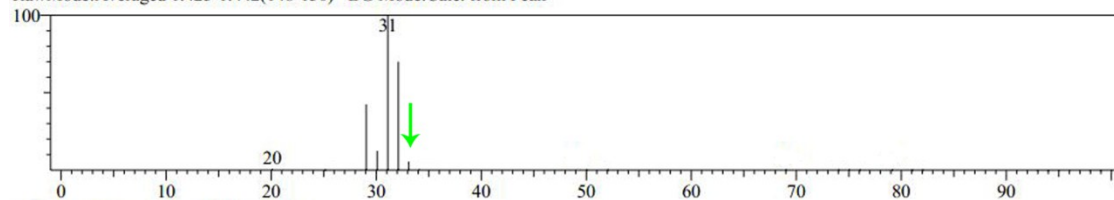


Library

<< Target >>

Line#1 R.Time:1.433(Scan#:149) MassPeaks:21 BasePeak:31.10(167434)

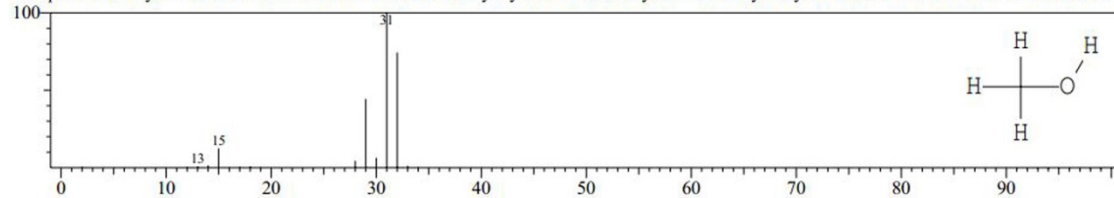
RawMode:Averaged 1.425-1.442(148-150) BG Mode:Calc. from Peak



Hit#1 Entry:15 Library:NIST147.LIB

SI:96 Formula:CH4O CAS:67-56-1 MolWeight:32 RetIndex:0

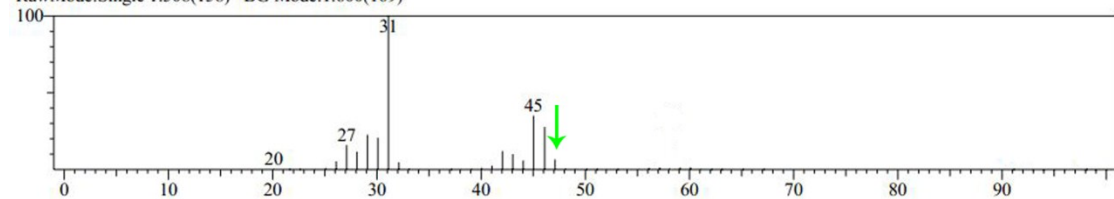
CompName:Methyl Alcohol SS Methanol SS Carbinol SS Methyl hydroxide SS Methylol SS Monohydroxymethane SS Wood alcohol SS CH3OH SS C



<< Target >>

Line#2 R.Time:1.508(Scan#:158) MassPeaks:45 BasePeak:31.10(800308)

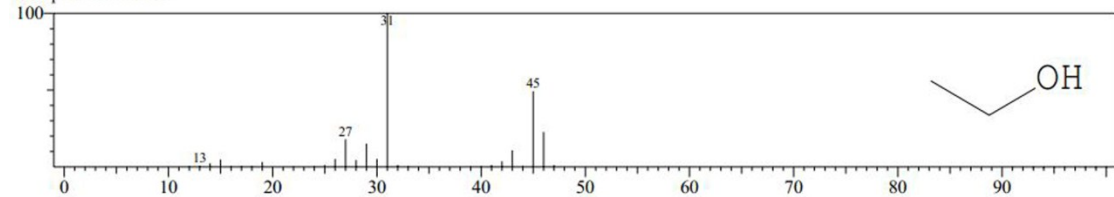
RawMode:Single 1.508(158) BG Mode:1.600(169)



Hit#1 Entry:60 Library:NIST21.LIB

SI:84 Formula:C2H6O CAS:64-17-5 MolWeight:46 RetIndex:0

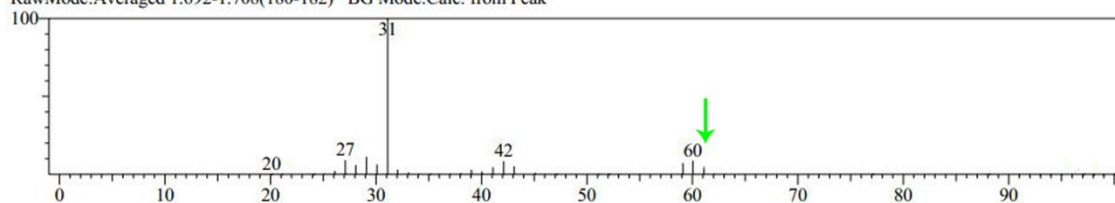
CompName:Ethanol



<< Target >>

Line#:3 R.Time:1.700(Scan#:181) MassPeaks:38 BasePeak:31.10(129421)

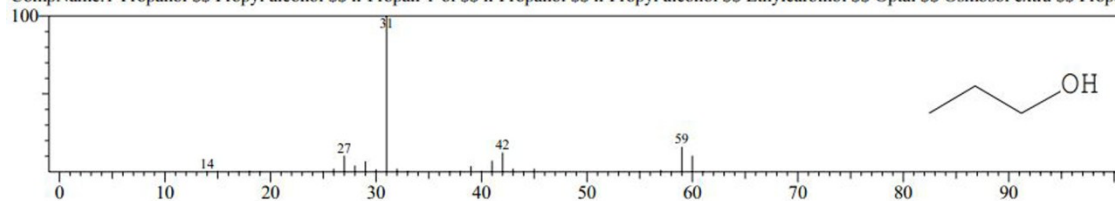
RawMode:Averaged 1.692-1.708(180-182) BG Mode:Calc. from Peak



Hit#:1 Entry:152 Library:NIST08s.LIB

SI:94 Formula:C₃H₈O CAS:71-23-8 MolWeight:60 RetIndex:562

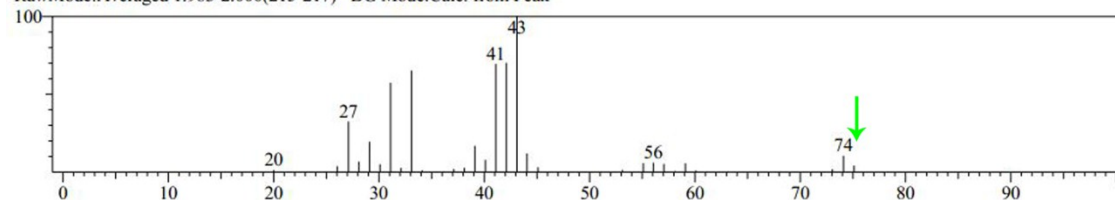
CompName:1-Propanol \$\$ Propyl alcohol \$\$ n-Propan-1-ol \$\$ n-Propanol \$\$ n-Propyl alcohol \$\$ Ethylcarbinol \$\$ Optal \$\$ Osmosol extra \$\$ Propa



<< Target >>

Line#:4 R.Time:1.992(Scan#:216) MassPeaks:43 BasePeak:43.10(8782)

RawMode:Averaged 1.983-2.000(215-217) BG Mode:Calc. from Peak



Hit#:1 Entry:444 Library:NIST08s.LIB

SI:94 Formula:C₄H₁₀O CAS:78-83-1 MolWeight:74 RetIndex:597

CompName:1-Propanol, 2-methyl- \$\$ Isobutyl alcohol \$\$ Isobutanolol \$\$ Isopropylcarbinol \$\$ 2-Methyl-1-propanol \$\$ iso-C₄H₉OH \$\$ Fermentation

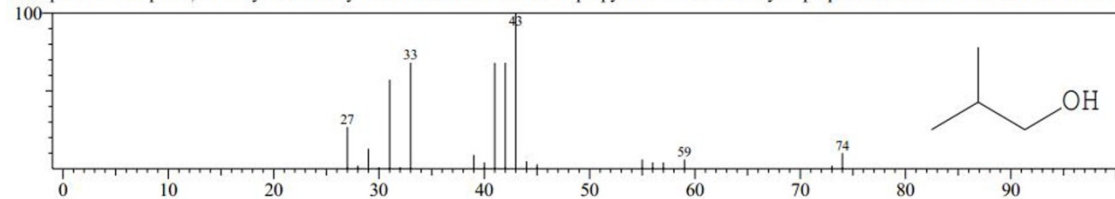
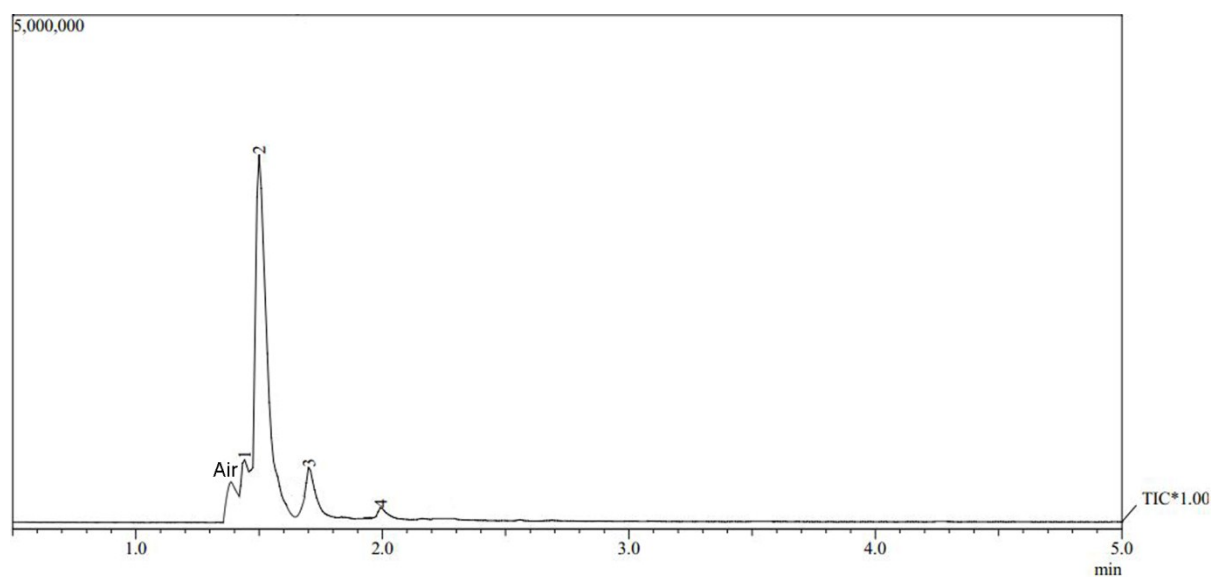


Fig. S3 GC-MS spectra of ¹³CH₃OH tracer experiment. 60 μL ¹³CH₃OH was used as tracer, other reaction conditions were the same as that of entry 1 in Table 1.

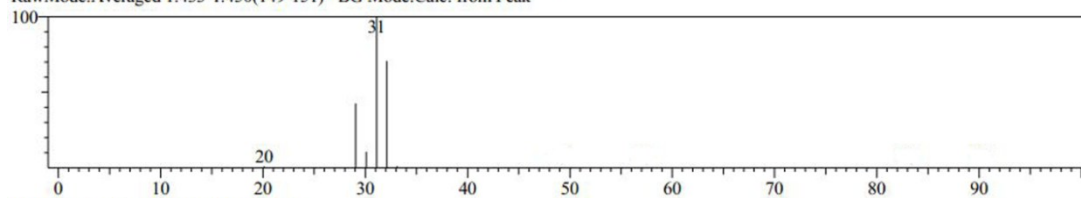


Library

<< Target >>

Line#1 R.Time:1.442(Scan#:150) MassPeaks:23 BasePeak:31.10(130043)

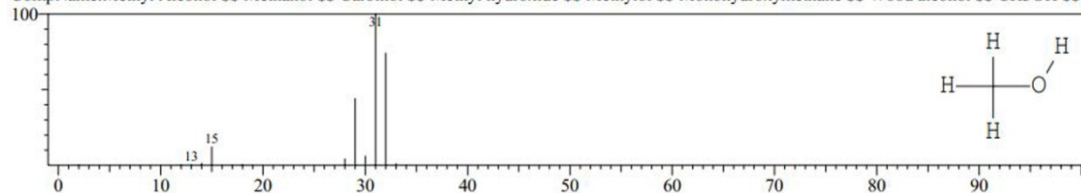
RawMode:Averaged 1.433-1.450(149-151) BG Mode:Calc. from Peak



Hit#1 Entry:15 Library:NIST147.LIB

SI:97 Formula:CH4O CAS:67-56-1 MolWeight:32 RetIndex:0

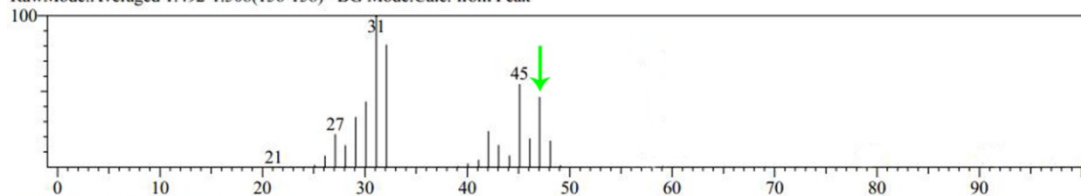
CompName:Methyl Alcohol \$\$ Methanol \$\$ Carbinol \$\$ Methyl hydroxide \$\$ Methylol \$\$ Monohydroxymethane \$\$ Wood alcohol \$\$ CH3OH \$\$ C



<< Target >>

Line#2 R.Time:1.500(Scan#:157) MassPeaks:48 BasePeak:31.10(480053)

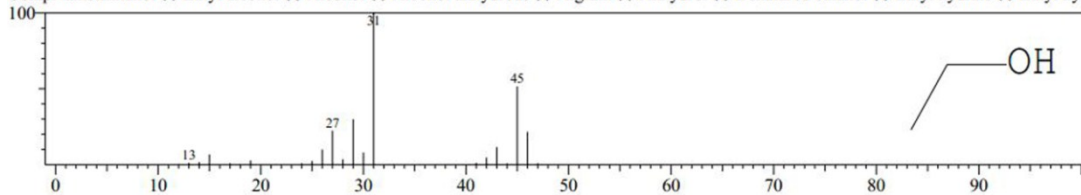
RawMode:Averaged 1.492-1.508(156-158) BG Mode:Calc. from Peak



Hit#1 Entry:56 Library:NIST08.LIB

SI: Formula:C2H6O CAS:64-17-5 MolWeight:46 RetIndex:463

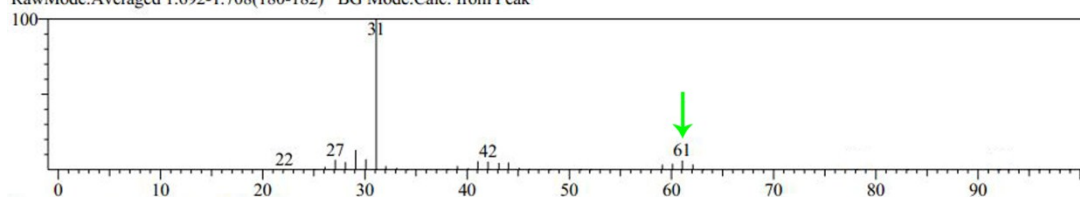
CompName:Ethanol \$\$ Ethyl alcohol \$\$ Alcohol \$\$ Alcohol anhydrous \$\$ Algrain \$\$ Anhydrol \$\$ Denatured ethanol \$\$ Ethyl hydrate \$\$ Ethyl hyd



<< Target >>

Line#:3 R.Time:1.700(Scan#:181) MassPeaks:35 BasePeak:31.10(154725)

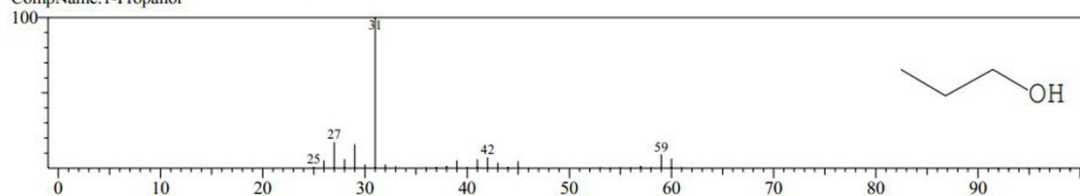
RawMode:Averaged 1.692-1.708(180-182) BG Mode:Calc. from Peak



Hit#:1 Entry:162 Library:NIST21.LIB

SI:91 Formula:C₃H₈O CAS:71-23-8 MolWeight:60 RetIndex:0

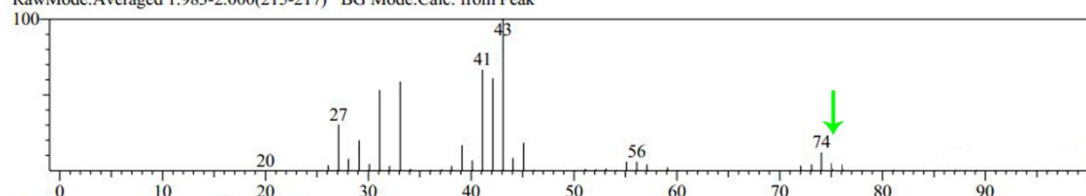
CompName:1-Propanol



<< Target >>

Line#:4 R.Time:1.992(Scan#:216) MassPeaks:53 BasePeak:43.10(15600)

RawMode:Averaged 1.983-2.000(215-217) BG Mode:Calc. from Peak



Hit#:1 Entry:445 Library:NIST08s.LIB

SI:95 Formula:C₄H₁₀O CAS:78-83-1 MolWeight:74 RetIndex:597

CompName:1-Propanol, 2-methyl- \$\$ Isobutyl alcohol \$\$ Isobutanol \$\$ Isopropylcarbinol \$\$ 2-Methyl-1-propanol \$\$ iso-C₄H₉OH \$\$ Fermentation

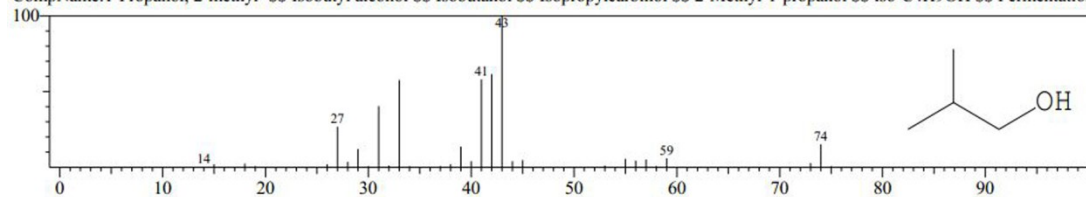


Fig. S4 GC-MS spectra of $^{13}\text{C}_2\text{H}_5\text{OH}$ tracer experiment. 25 μL $^{13}\text{C}_2\text{H}_5\text{OH}$ was used as tracer, other reaction conditions were the same as that of entry 1 in Table 1.

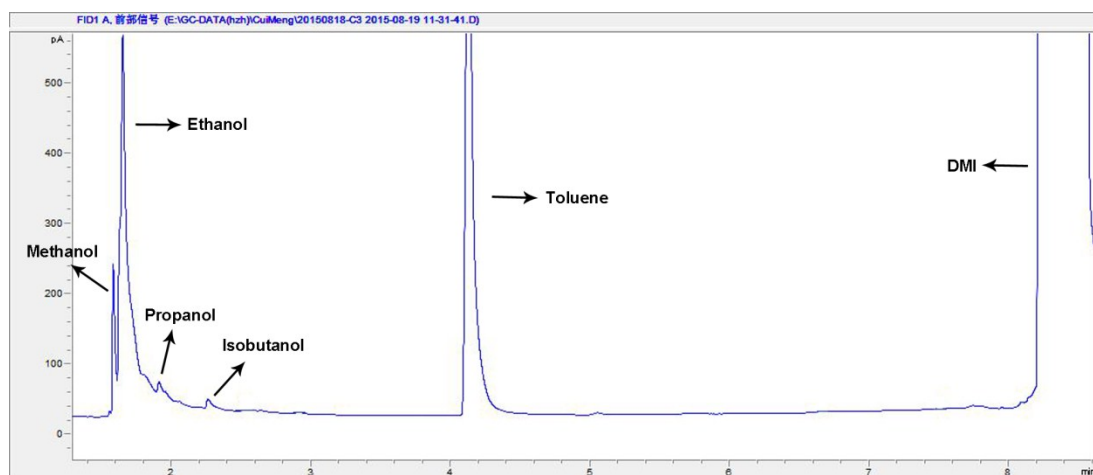


Fig. S5 Representative GC spectra of reaction solution after CO₂ hydrogenation with internal standard toluene. Reaction conditions were the same as that of entry 1 in Table 1.