Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information

Efficient synthesis of ethanol by methanol homologation using CO_2 at lower temperature

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Figures

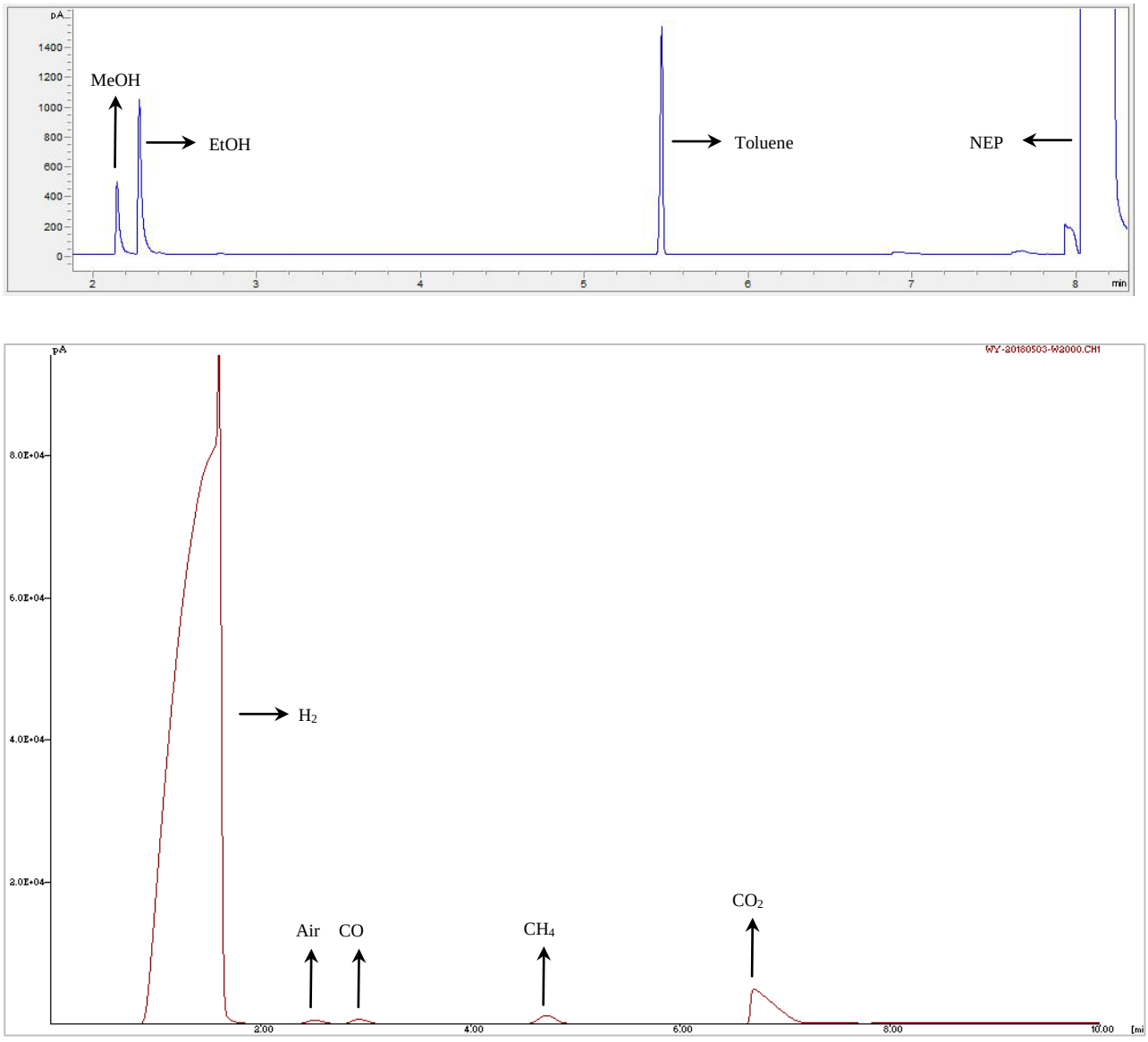
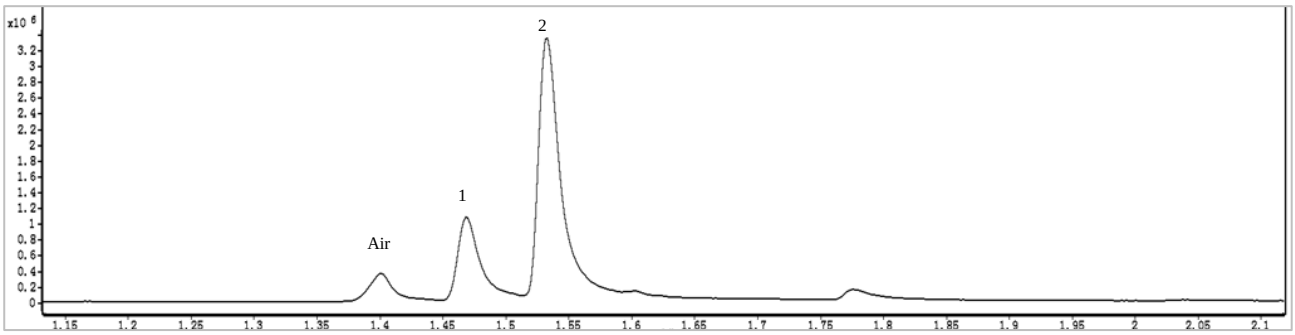
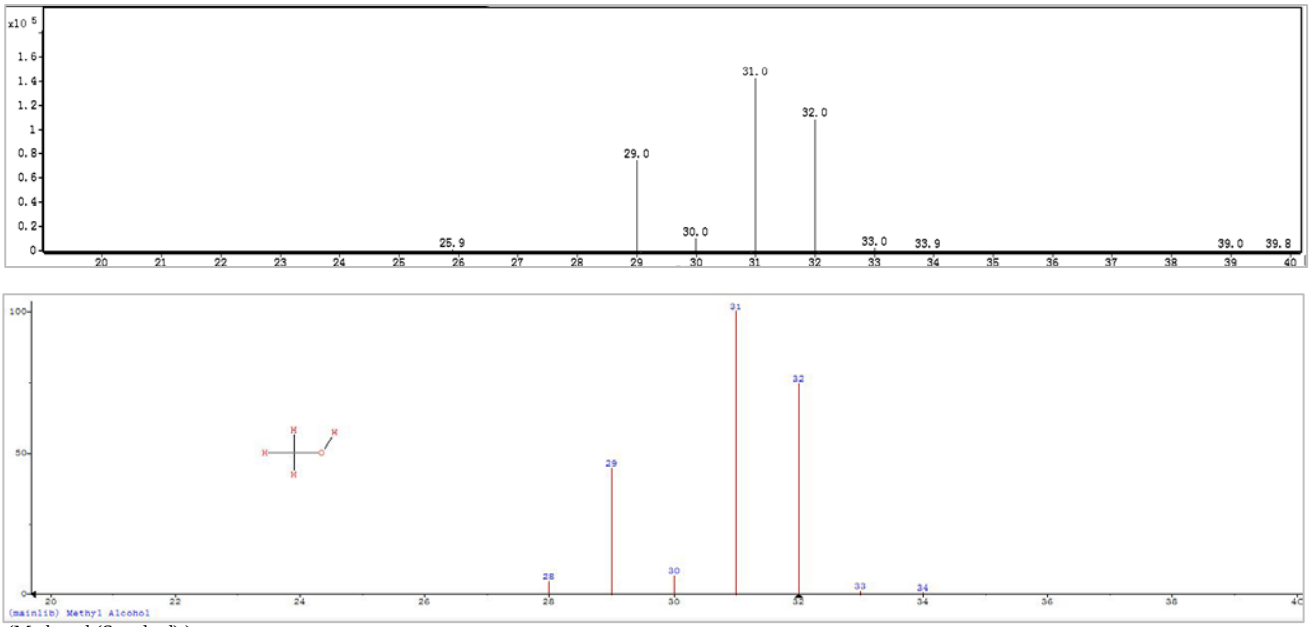


Fig. S1 The representative GC spectra of liquid sample with internal standard toluene (a) and gaseous sample (b) after methanol homologation with CO_2 and H_2. Reaction conditions were the same as that of entry 1 of Table 1.

Note:
The peak of air resulted from the operation of sampling and injection.

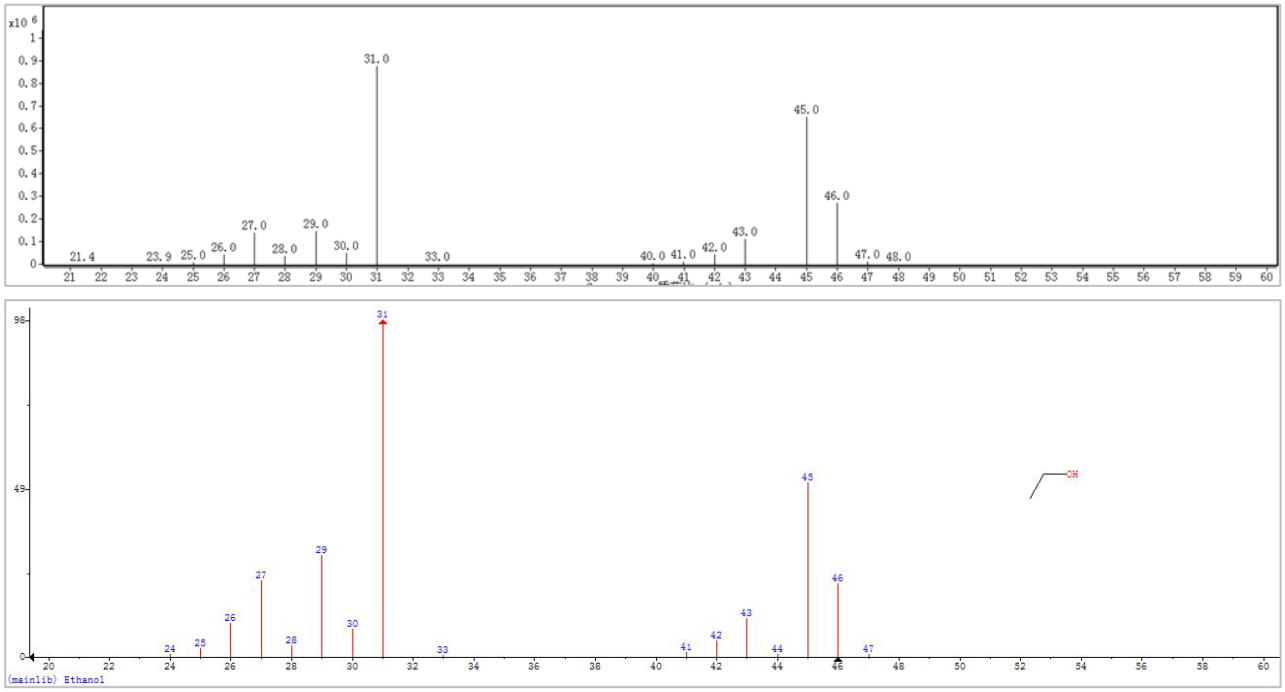


Peak 1



(Methanol (Standard))

Peak 2



(Ethanol (Standard))

Fig. S2 The representative GC-MS spectra of the liquid product after the reaction of methanol with CO_2 and H_2. Reaction conditions were the same as that of entry 1 in Table 1.

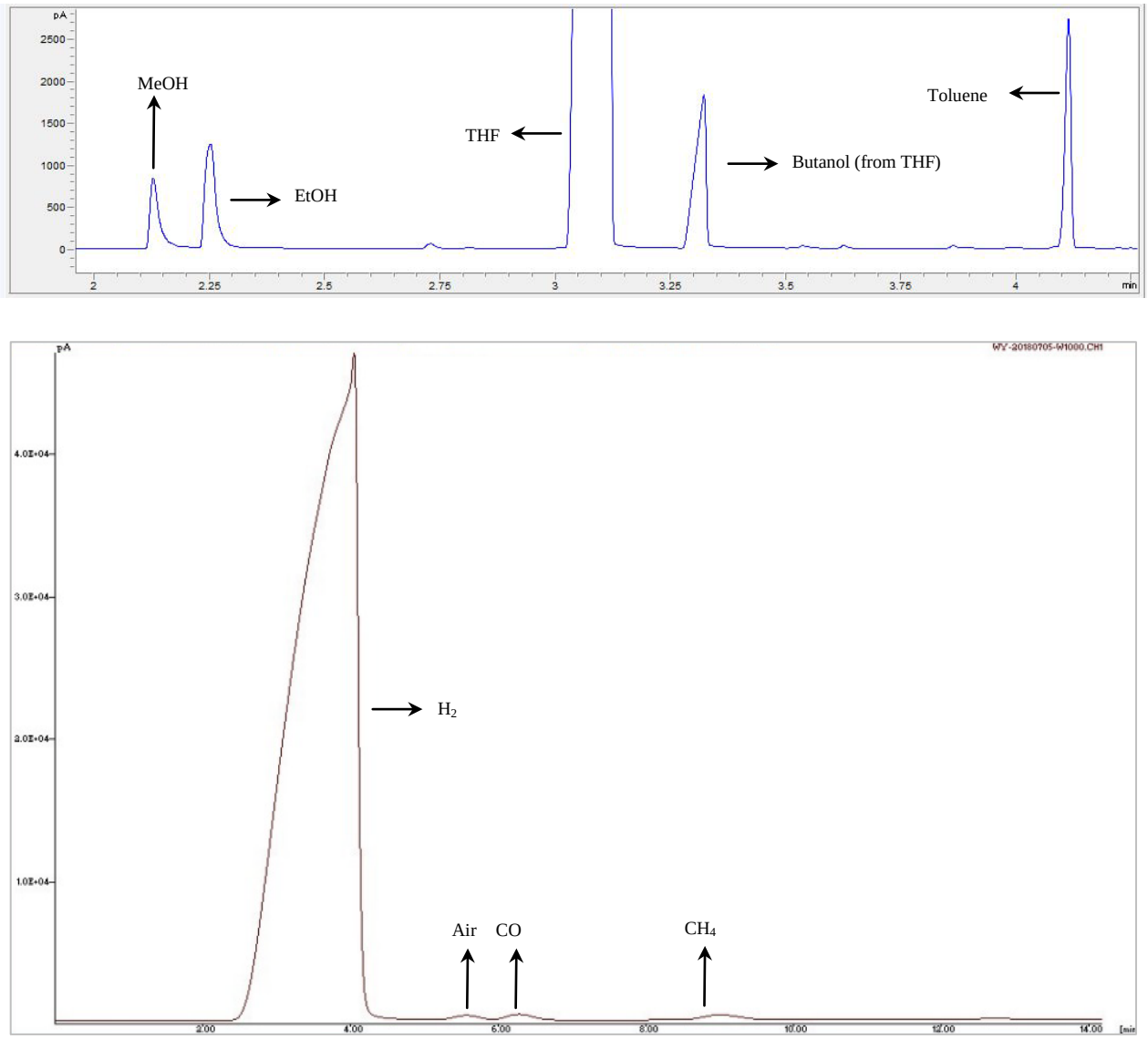
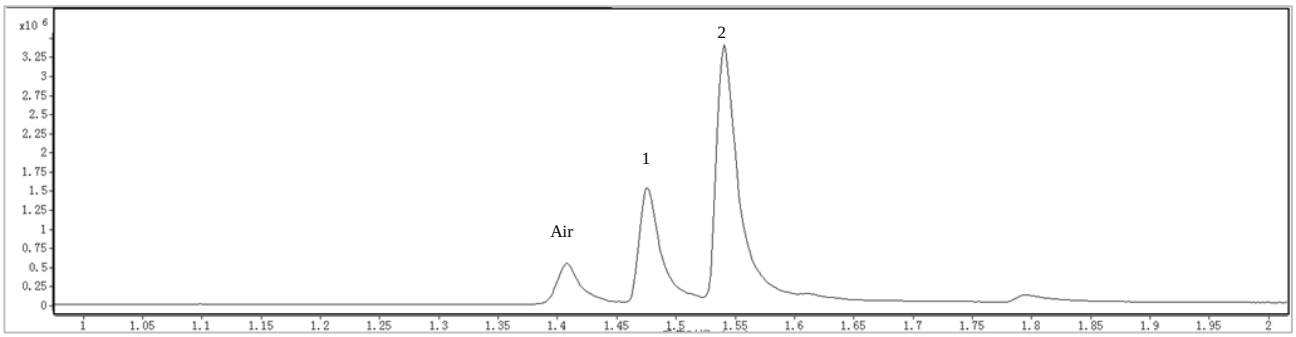


Fig. S3 The GC spectra of liquid products with internal standard toluene after the reaction of methanol with CO and H_2 using THF as solvent. Reaction conditions: 10 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_4(CO)_{12}$ (based on the metal), 2.5 mmol LiI, 2 mL THF, 2.6 mmol methanol, 0.5 MPa CO and 6 MPa H_2 (at room temperature), 160 ^oC, 15 h.



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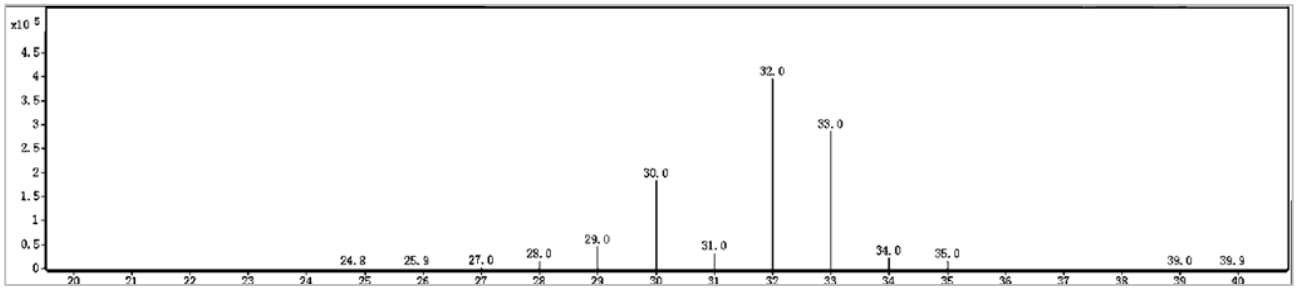
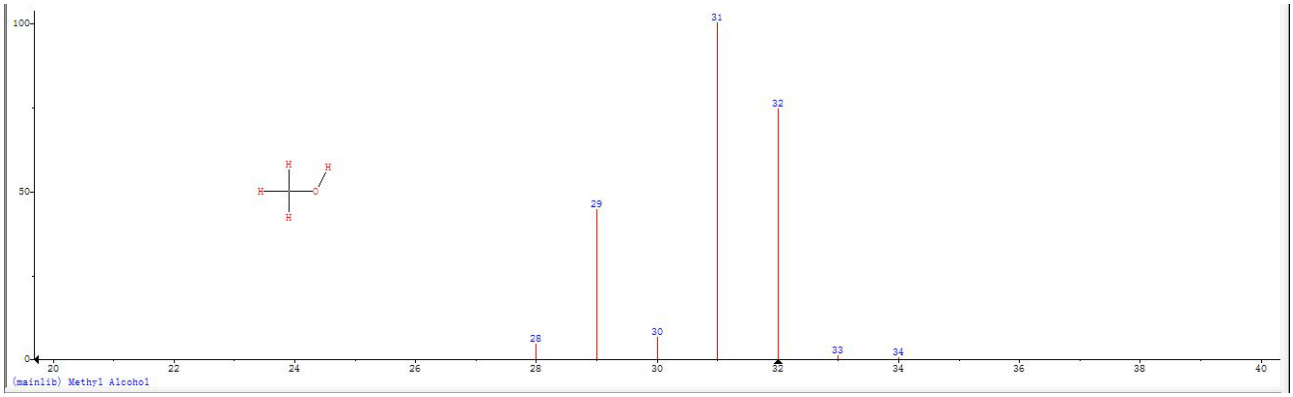
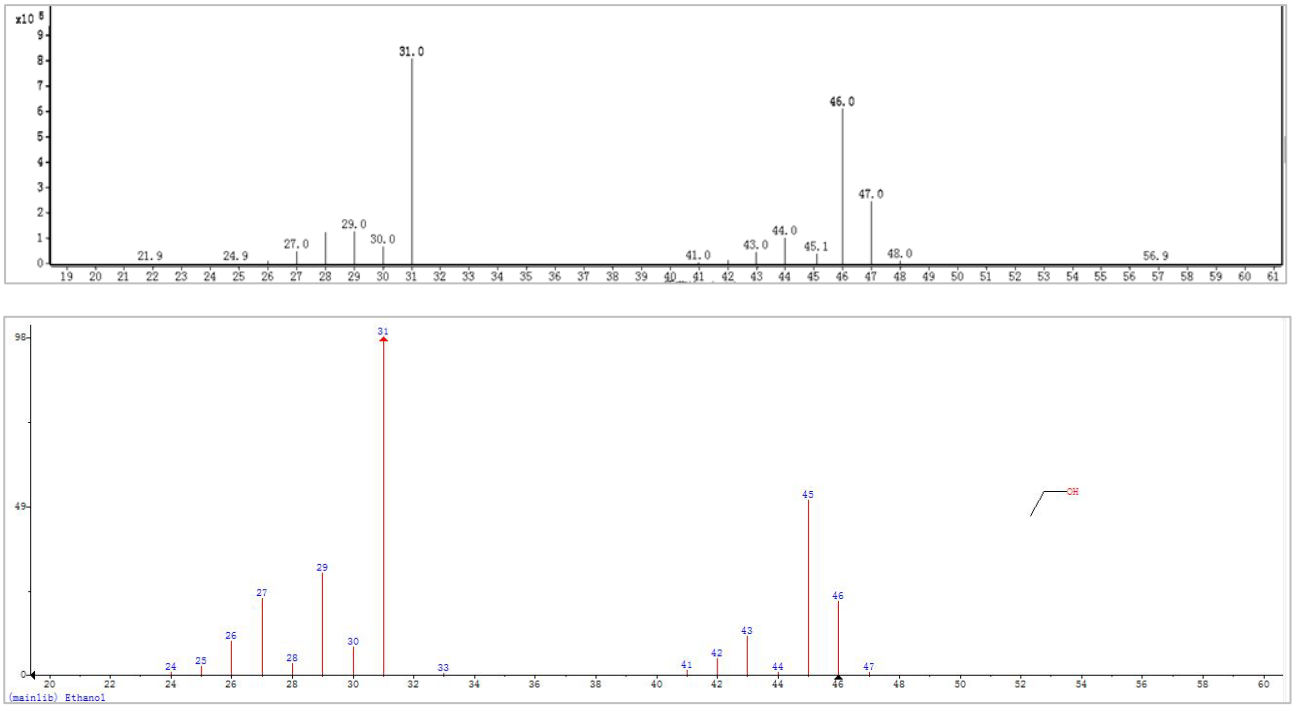




(Methanol (Standard))

Peak 2



(Ethanol (Standard))

Fig. S4 The GC-MS spectra of reaction solution using $^{13}CH_3OH$ instead of methanol. Other reaction conditions were the same as that of entry 1 in Table 1.

Note: The molecular weight of ethanol formed in the reaction was 47 Daltons. This demonstrates that the two C atoms in the ethanol product were from ^{13}C of $^{13}CH_3OH$ and C of CO_2, respectively. In addition, the methyl group of $^{13}CH_3OH$ was transferred to the methyl group of $^{13}CH_3CH_2OH$ molecule.

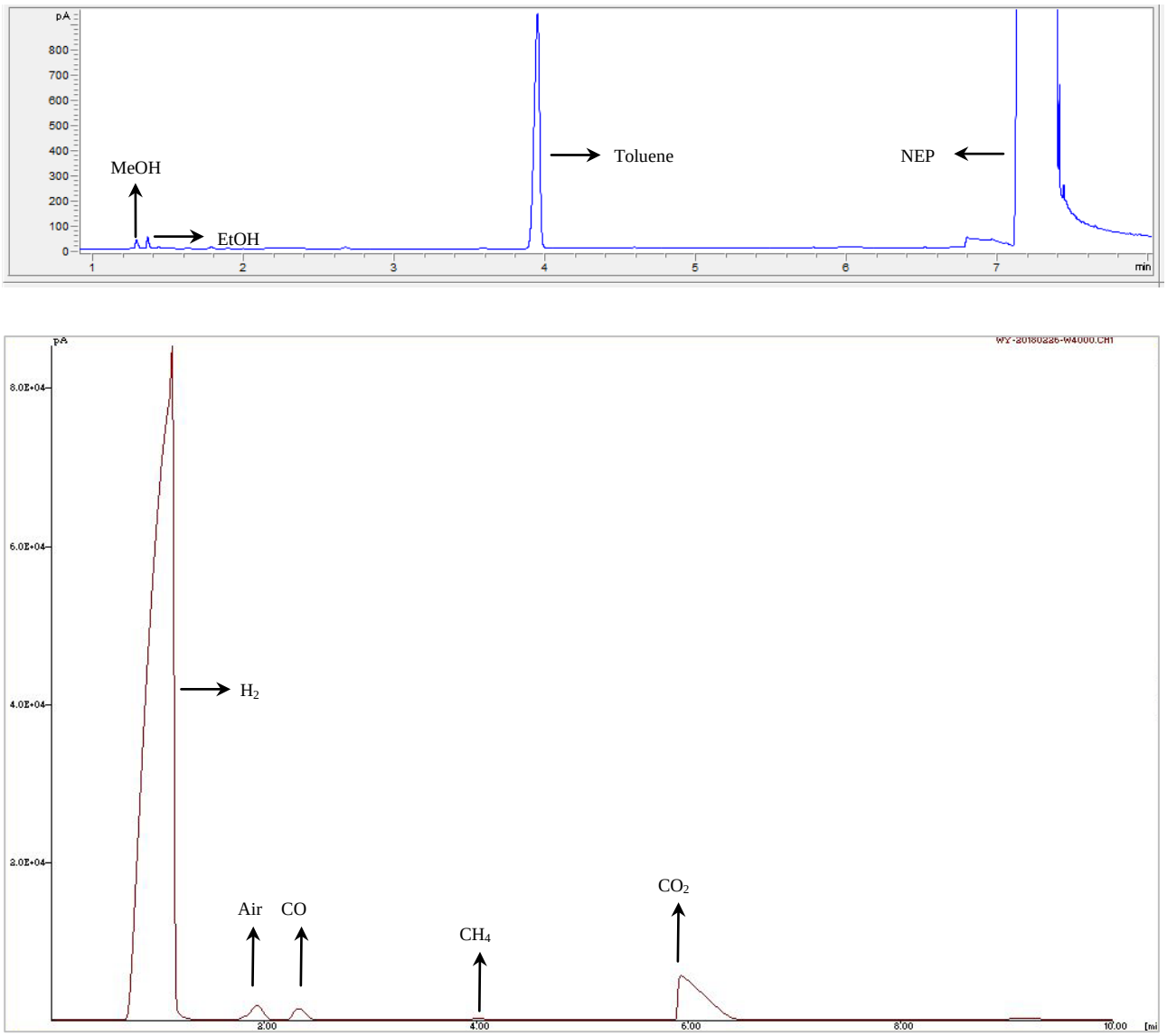


Fig. S5 The GC spectra of liquid products with internal standard toluene (a) and gaseous products (b) after direct CO_2 hydrogenation. Reaction conditions: 10 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_4(CO)_{12}$ (based on the metal), 2.5 mmol LiI, 2 mL NEP, 2 MPa CO_2 and 6 MPa H_2 (at room temperature), 160 ^{o} C, 15 h.

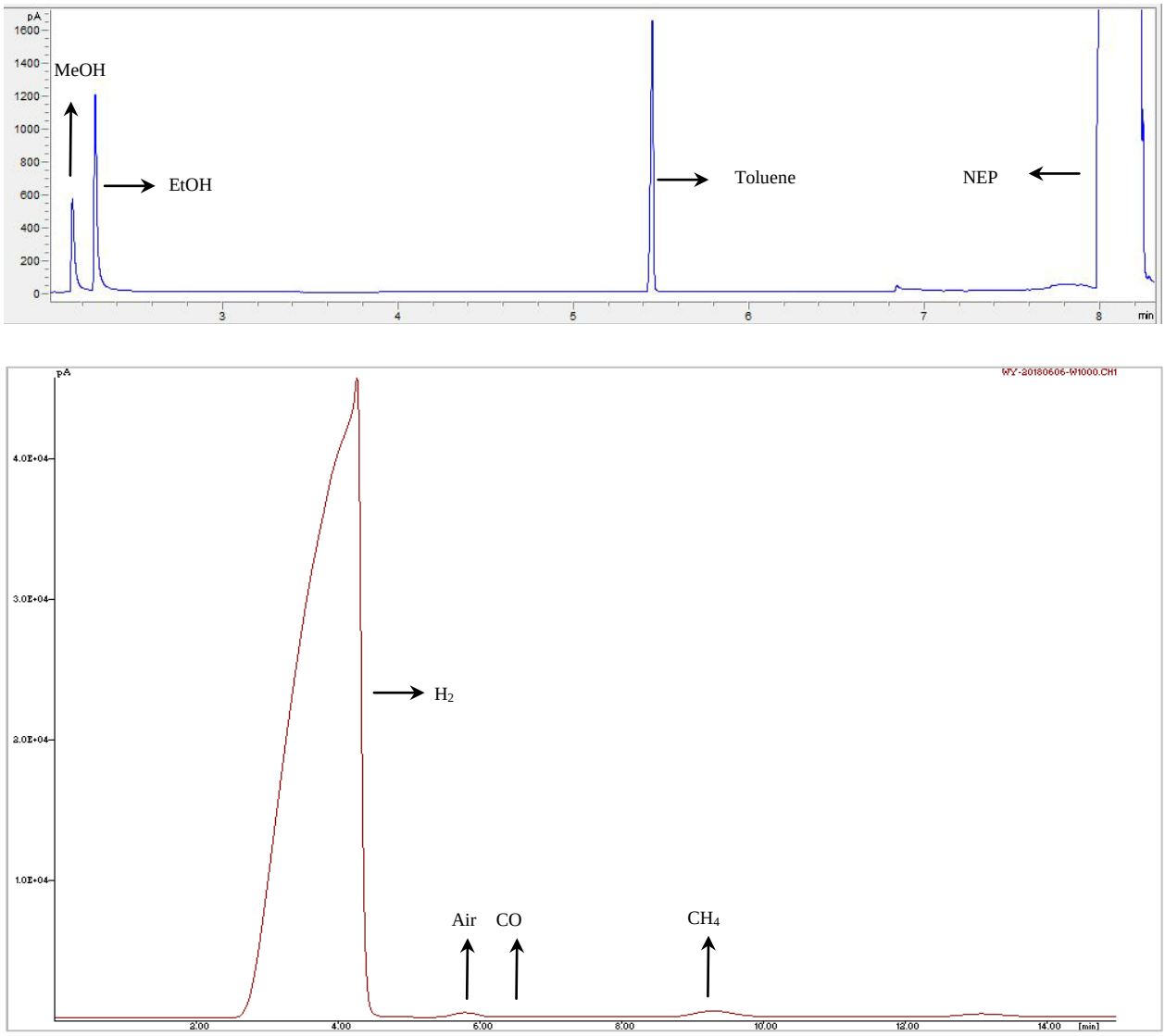
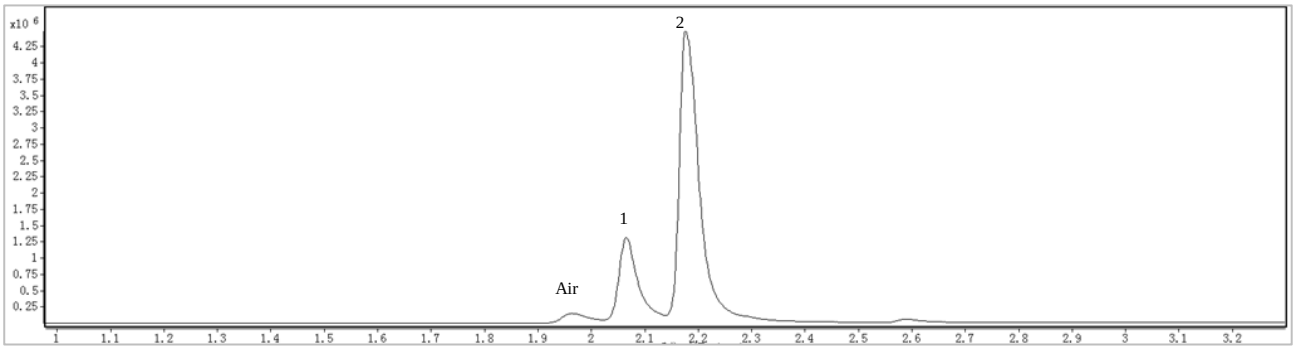


Fig. S6 The GC spectra of liquid products with internal standard toluene after the reaction of methanol with CO and H_2 using NEP as solvent. Reaction conditions: 10 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_4(CO)_{12}$ (based on the metal), 2.5 mmol LiI, 2 mL NEP, 2.6 mmol methanol, 0.5 MPa CO and 6 MPa H_2 (at room temperature), 160 ^{o} C, 15 h.



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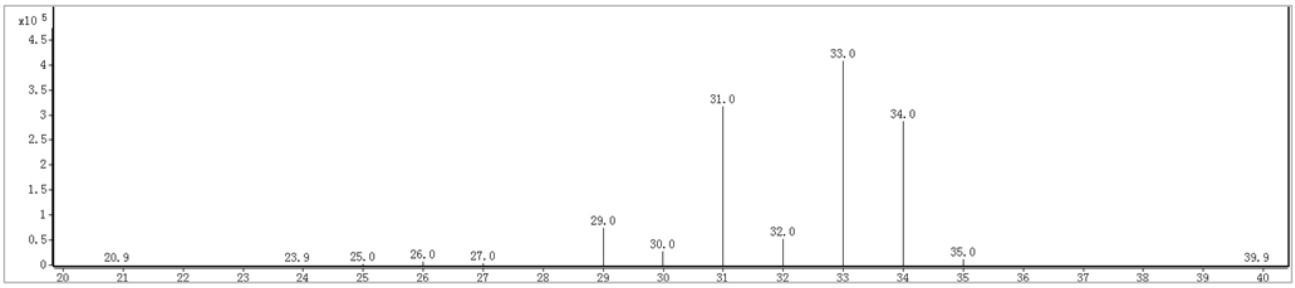
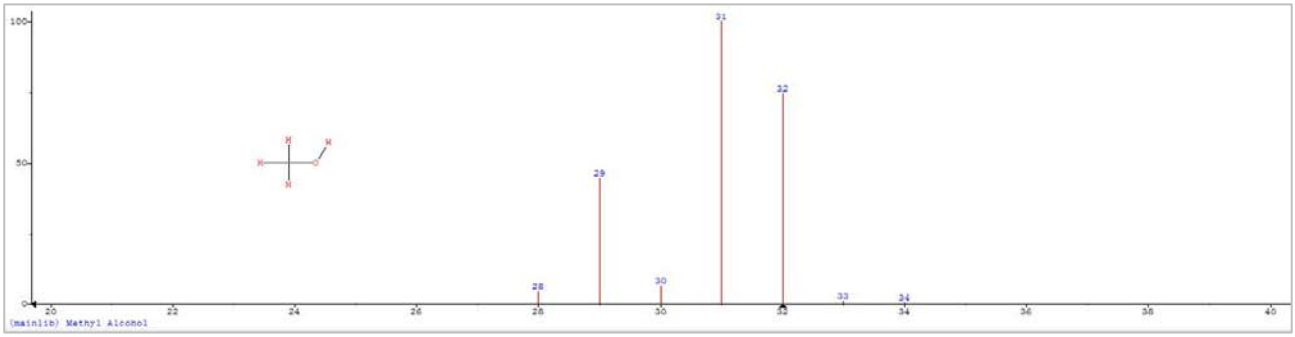
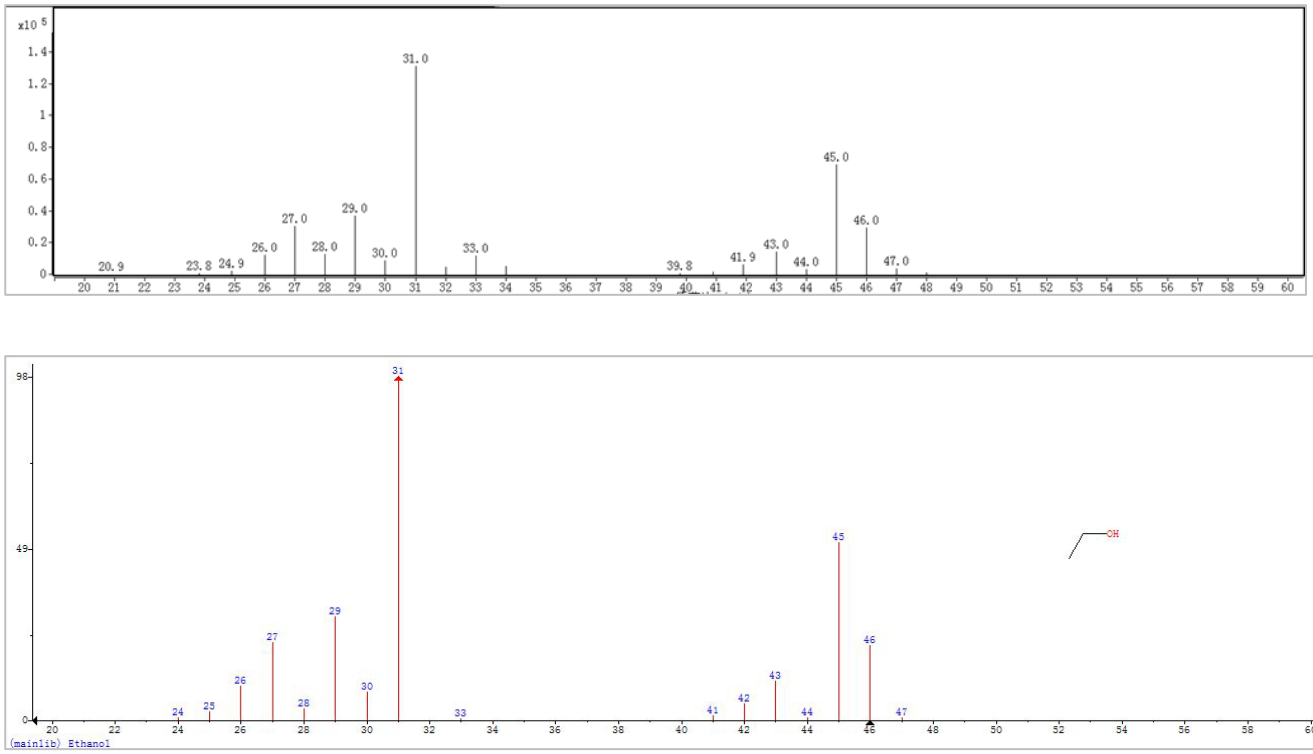




(Methanol (Standard))

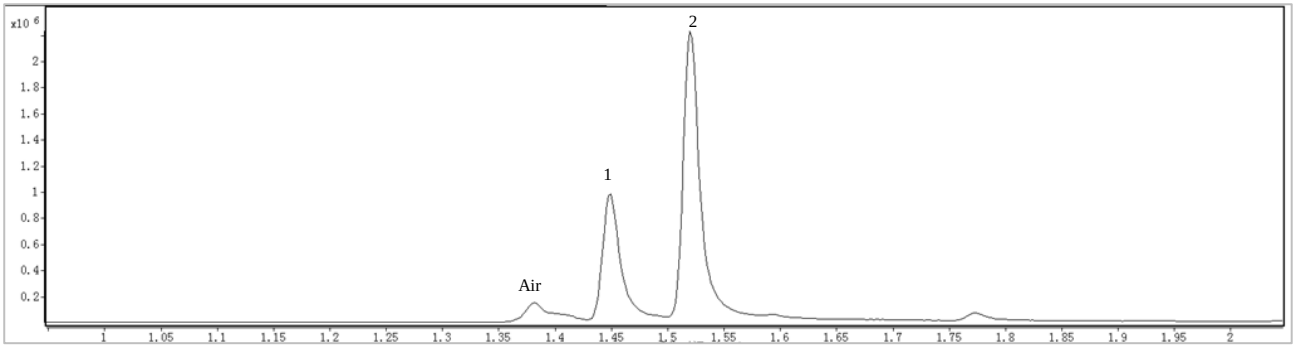
Peak 2



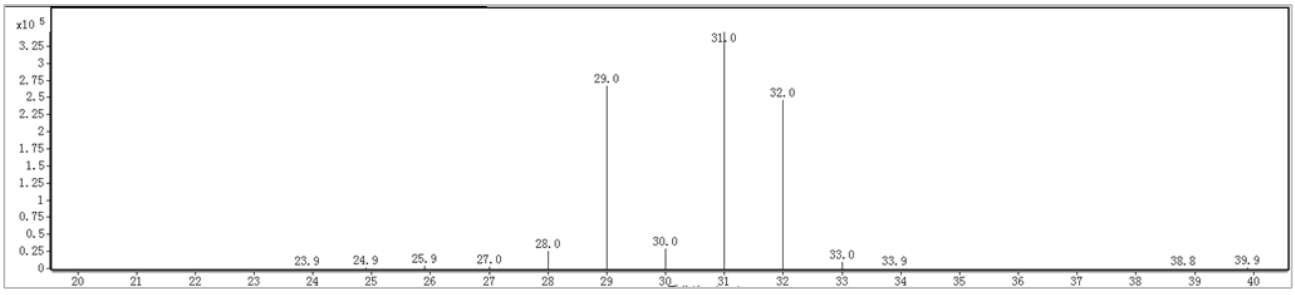
(Ethanol (Standard))

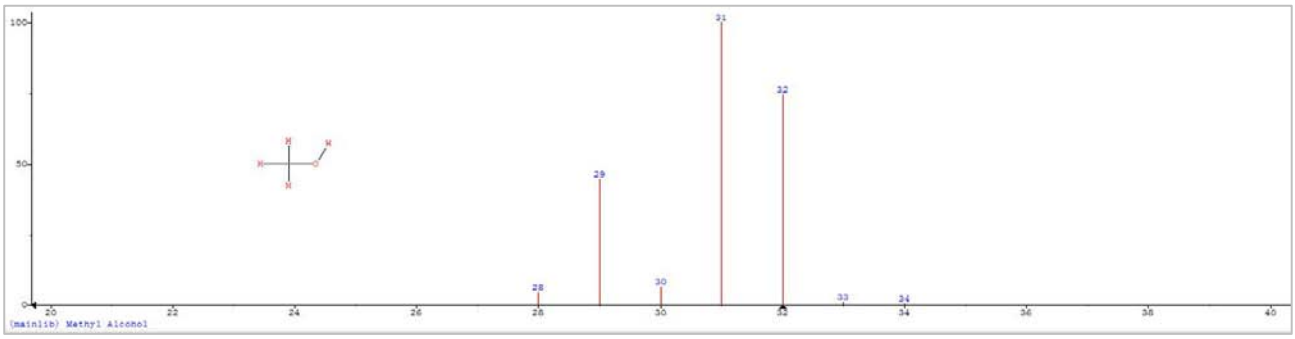
Fig. S7 The GC-MS spectra of reaction solution using $CH_3{}^{18}OH$ instead of methanol. Other reaction conditions were the same as that of entry 1 in Table 1.

Notes: The molecular weight of ethanol synthesized was still 46 Daltons. This result supports that the CH_3 and ^{18}OH group broke away during the reaction. Otherwise, the molecular weight of ethanol should be 48 Daltons.



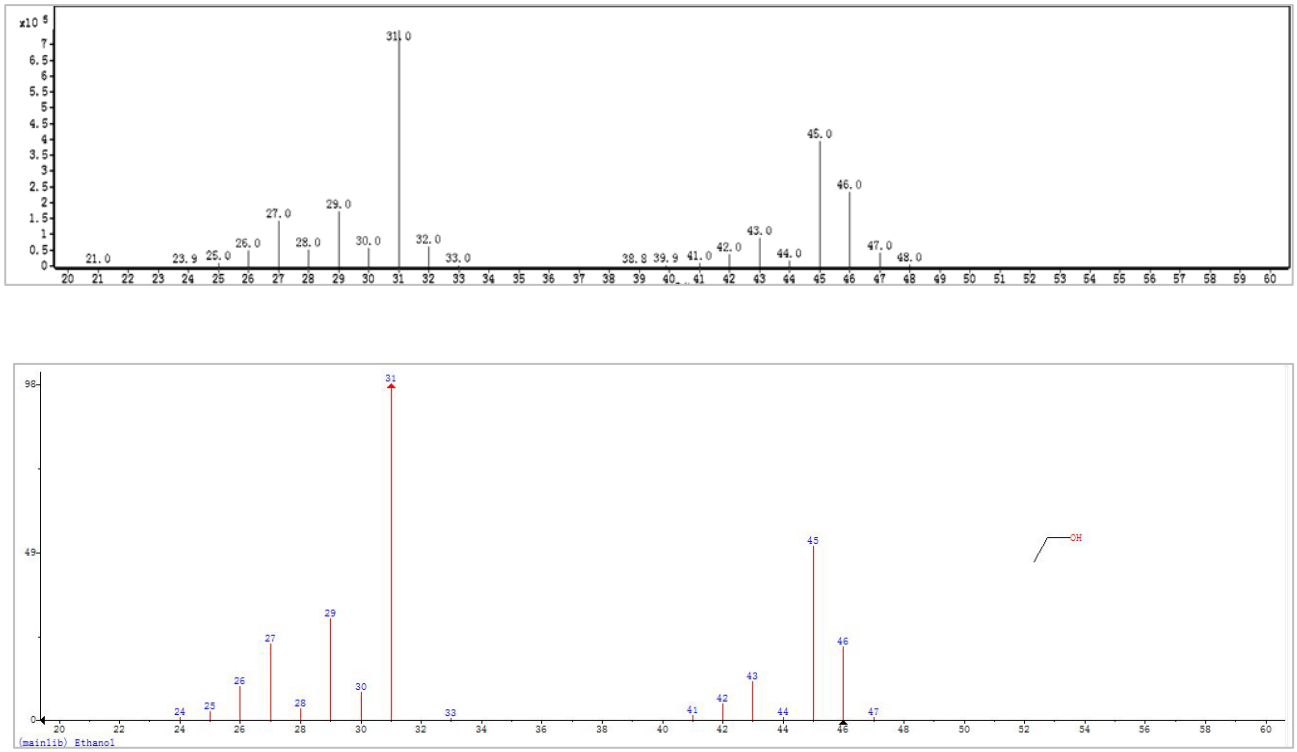
Peak 1





(Methanol (Standard))

Peak 2



(Ethanol (Standard))

Fig. S8 The GC-MS spectra of reaction solution using CH_3OD instead of methanol. Other reaction conditions were the same as that of entry 1 in Table 1.

Notes: The molecular weight of ethanol generated in the reaction was still 46 Daltons. This result supports two deductions.

1. The CH_3 and OD group broke away during the reaction. Otherwise, the molecular weight of ethanol should be 47 Daltons.
2. H atom in the OH group of ethanol was from H_2. Otherwise, the molecular weight of ethanol should be 47 Daltons.

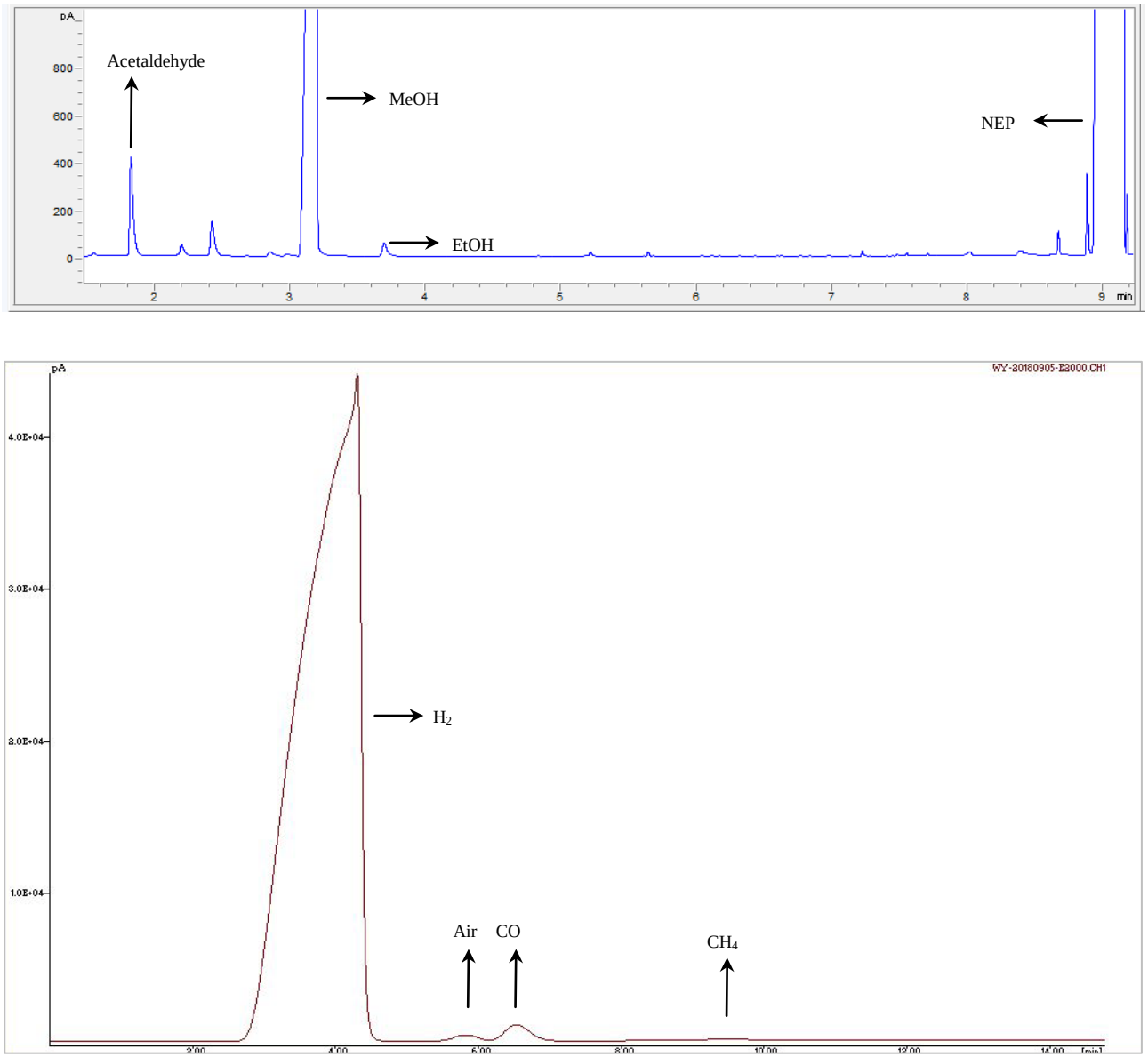


Fig. S9 The GC traces of the liquid sample (a) and gaseous sample (b) after the reaction of methanol, CO and H_2. Reaction conditions: 60 μmol $Co_4(CO)_{12}$ (based on the metal), 2.5 mmol LiI, 2 mL NEP, 2.6 mmol methanol, 0.5 MPa CO and 6 MPa H_2 (at room temperature), 160 ^oC, 10 h.

Notes: The liquid sample was analyzed by using a gas chromatograph (GC, Agilent 7890) equipped with a flame ionization detector (FID) and an HP-INNOWAX capillyary column with no internal standard.

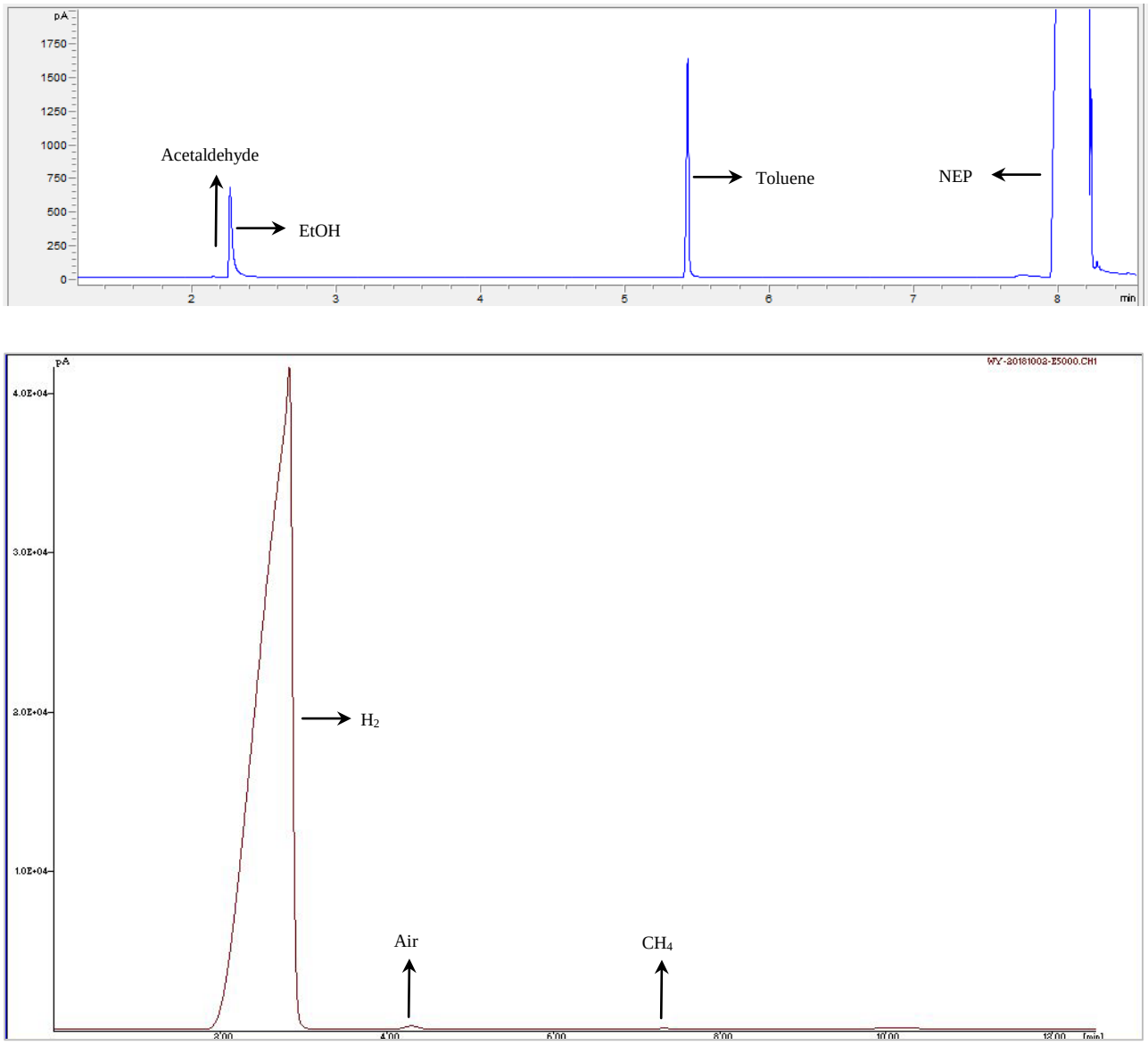
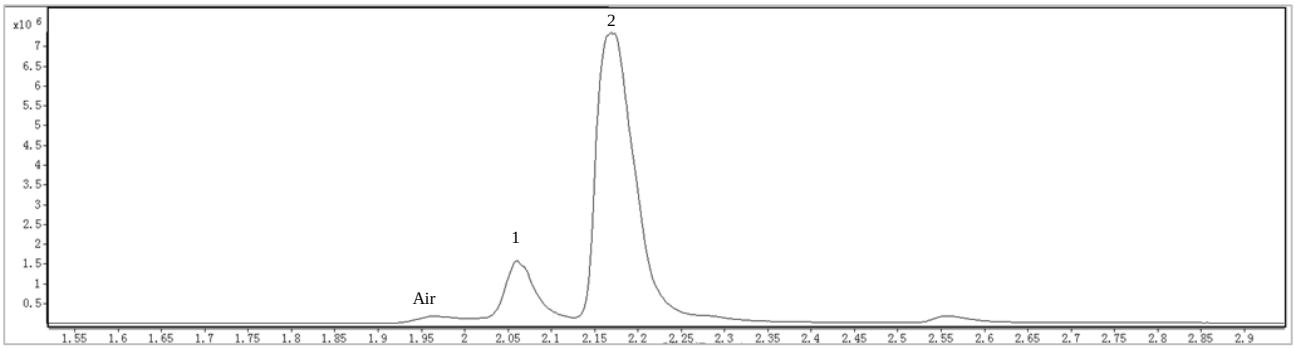
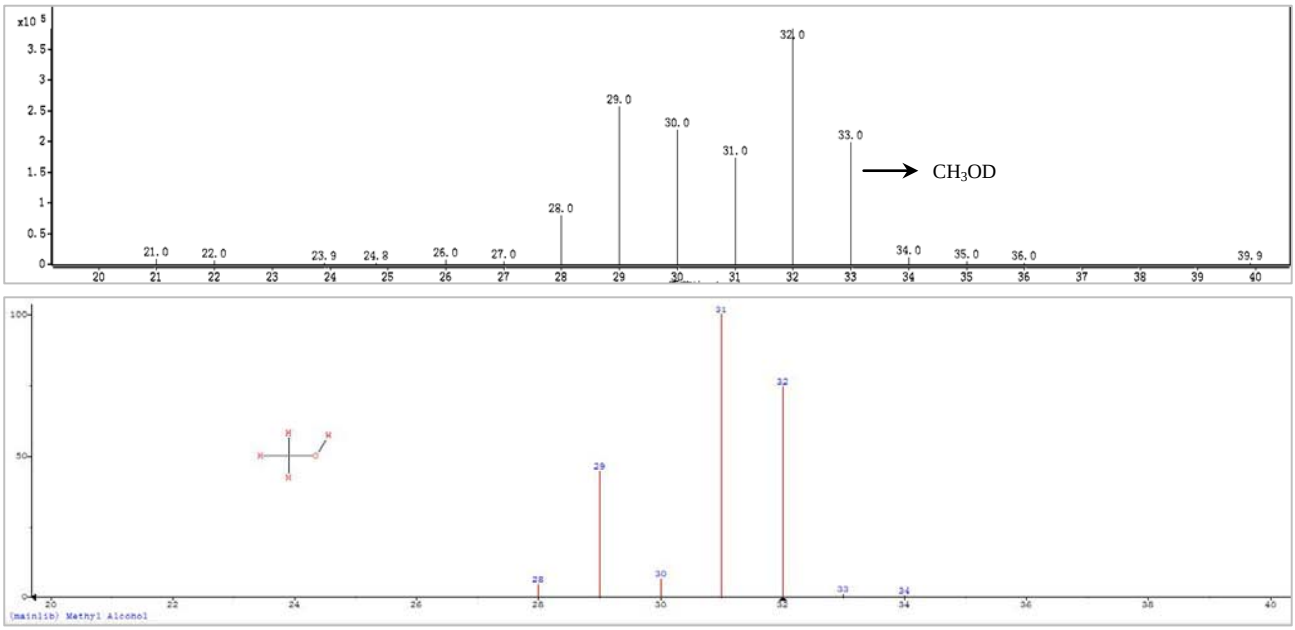


Fig. S10 The GC traces of the liquid sample (a) and gaseous sample (b) after the reaction of CH_3CHO and H_2 catalyzed by Ru catalyst. Reaction conditions: 10 μmol $[RuCl_2(CO)_3]_2$ (based on the metal), CH_3CHO 1 mmol, and 6 MPa H_2 (at room temperature), 160 ^oC, 15 h.

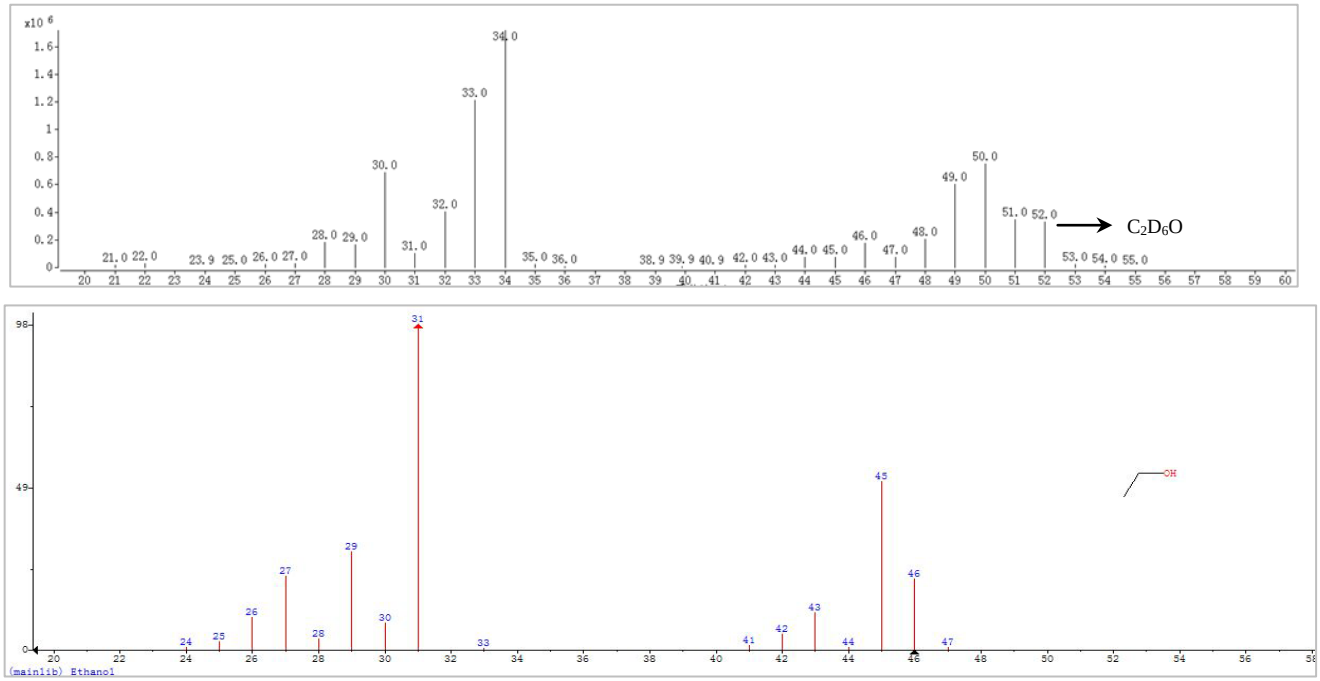


Peak 1



(Methanol (Standard))

Peak 2



(Ethanol (Standard))

Fig. S11 The GC-MS spectra of liquid products after reaction using D_2 instead of H_2 . Other reaction conditions were the same as that of entry 1 in Table 1.

Notes: This result supports two deductions.

1. Only one H atom of the unreacted methanol was substituted by D atom.
2. The D atoms could enter the ethanol generated in the reaction, and at most Six D atoms could enter into one ethanol molecule.

Table S1. Effect of NMP and NEP on methanol homologation with CO_2 and H_2 at different CO_2 pressures.

Entry	CO_2 /H_2 [MPa]	Solvent	TOF (h^{-1})	Selectivity (C-mol%)		
				Ethanol	CO	CH_4
1	2/6	NMP	7.0	57.5	27.7	14.9
2		NEP	7.5	65.0	21.2	13.8
3	3/5	NMP	6.7	53.0	33.6	13.4
4		NEP	7.2	57.9	27.3	14.8
5	4/4	NMP	6.2	47.8	41.1	11.2
6		NEP	6.8	53.5	34.0	12.5
7	5/3	NMP	5.2	39.0	47.9	13.1
8		NEP	6.2	47.8	35.4	16.9
9	6/2	NMP	4.3	35.3	47.2	17.5
10		NEP	5.6	45.8	34.6	19.6

Reaction conditions: 10 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_4(CO)_{12}$ (based on the metal), 2.5 mmol LiI, 2 mL solvent, 2.6 mmol methanol, different pressure of CO_2 and H_2 (at room temperature), 160 ^{o} C, 15 h.