Electronic Supplementary Information

Ru Catalyzed Methanol Homologation with CO_2 and H_2 in Ionic Liquid

Bernard Baffour Asare Bediako,[a,d] Qingli Qian,*[a,b] Jingjing Zhang,[a,d] Ying Wang,[a,d] Xiaojun Shen,[a,d] Jinbiao Shi,[a,d] Meng Cui,[a,d] Guanying Yang,[a,b] Zhen Wang [c,d], Shengrui Tong [c], Buxing Han* [a,b,d,e]

[a] *Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.*

[b] *Physical Science Laboratory, Huairou National Comprehensive Science Center, No. 5 Yanqi East Second Street, Beijing 101400, China*

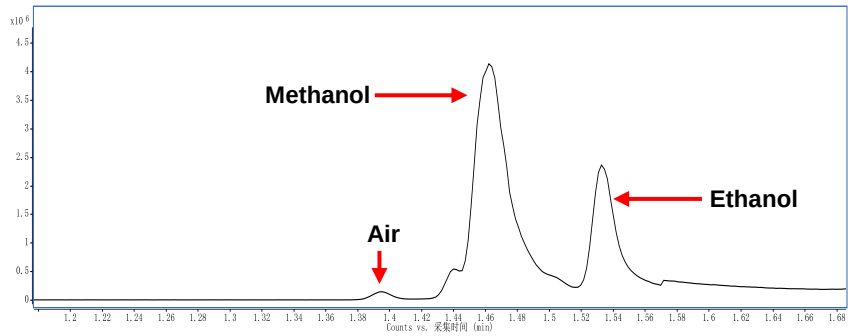
[c] *State Key Laboratory for Structural Chemistry of Unstable and Stable Species, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China*

[d] *School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

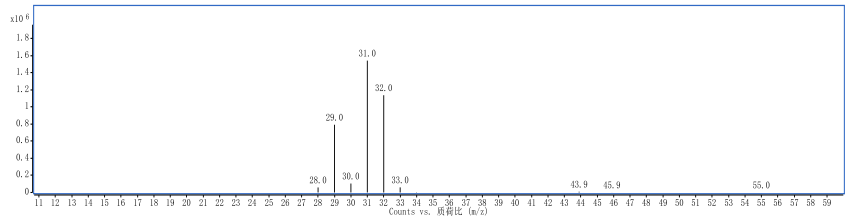
[e] *Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China*

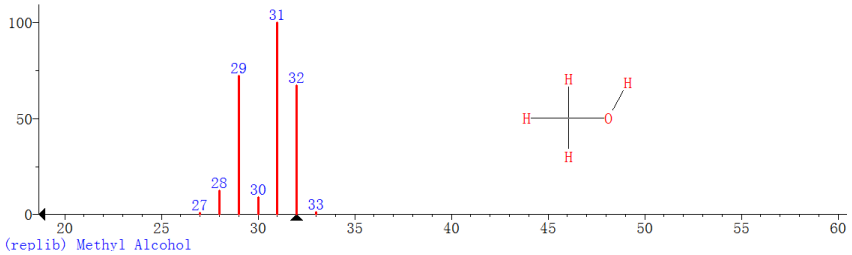
Correspondence to: Q. Q. (email: qianql@iccas.ac.cn); B. H. (email: hanbx@iccas.ac.cn).

Figures

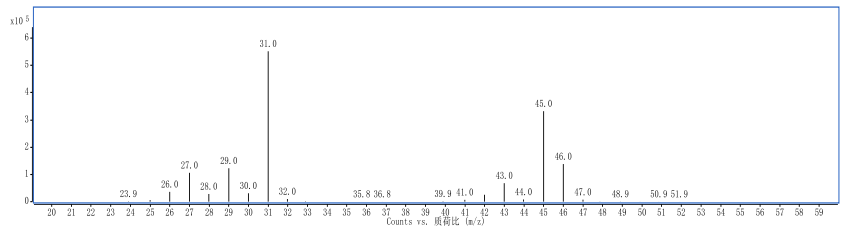


Methanol





Ethanol



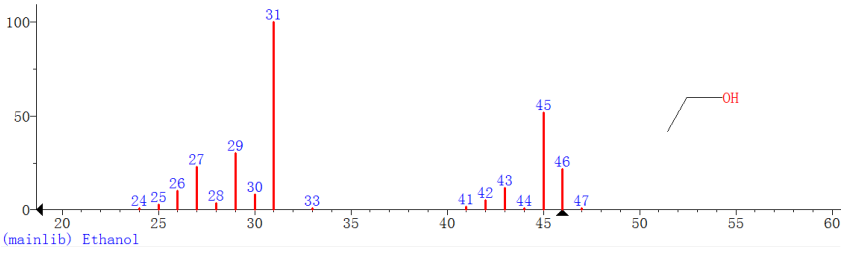


Fig. S1 GC-MS spectra of the liquid sample after methanol homologation with CO_2 and H_2. Reaction condition was the same as that of entry 1 in Table 1.

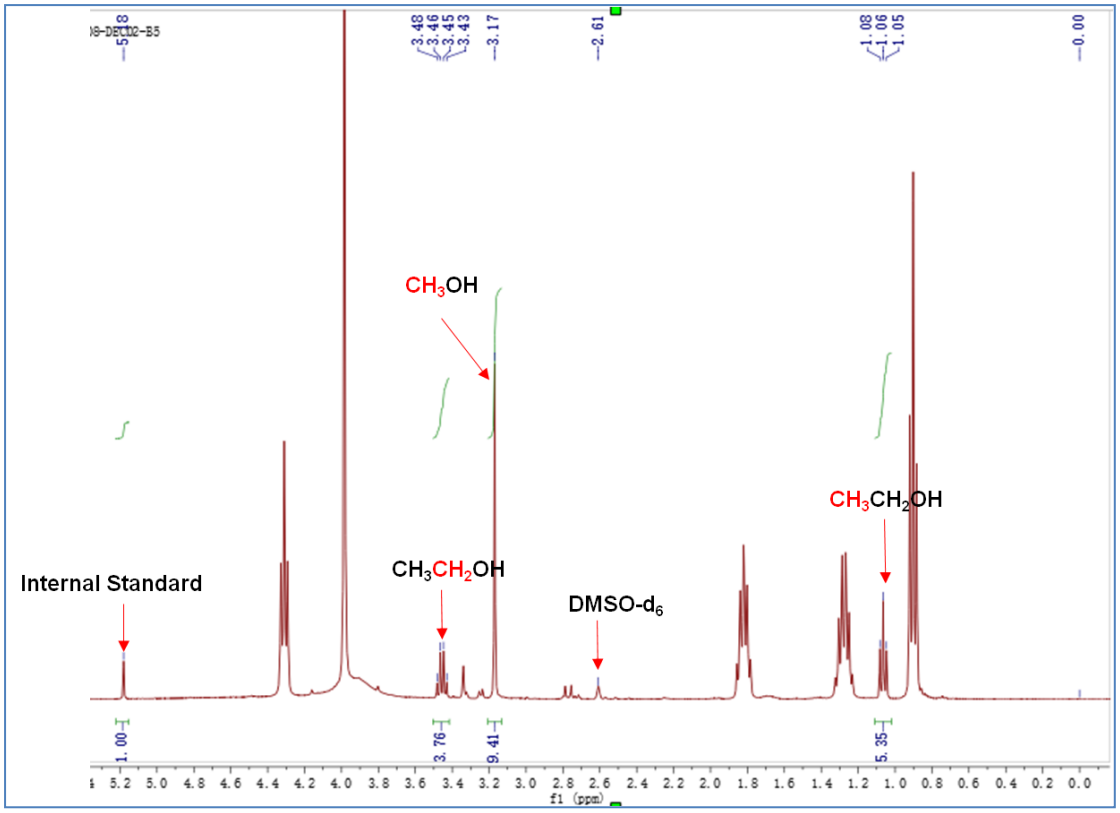


Fig. S2 ^{1}H NMR spectra of the liquid sample after methanol homologation with CO_2 and H_2 (with trioxane as the internal standard). Chemical shifts (ppm) are given relative to TMS. Reaction condition was the same as that of entry 1 in Table 1.

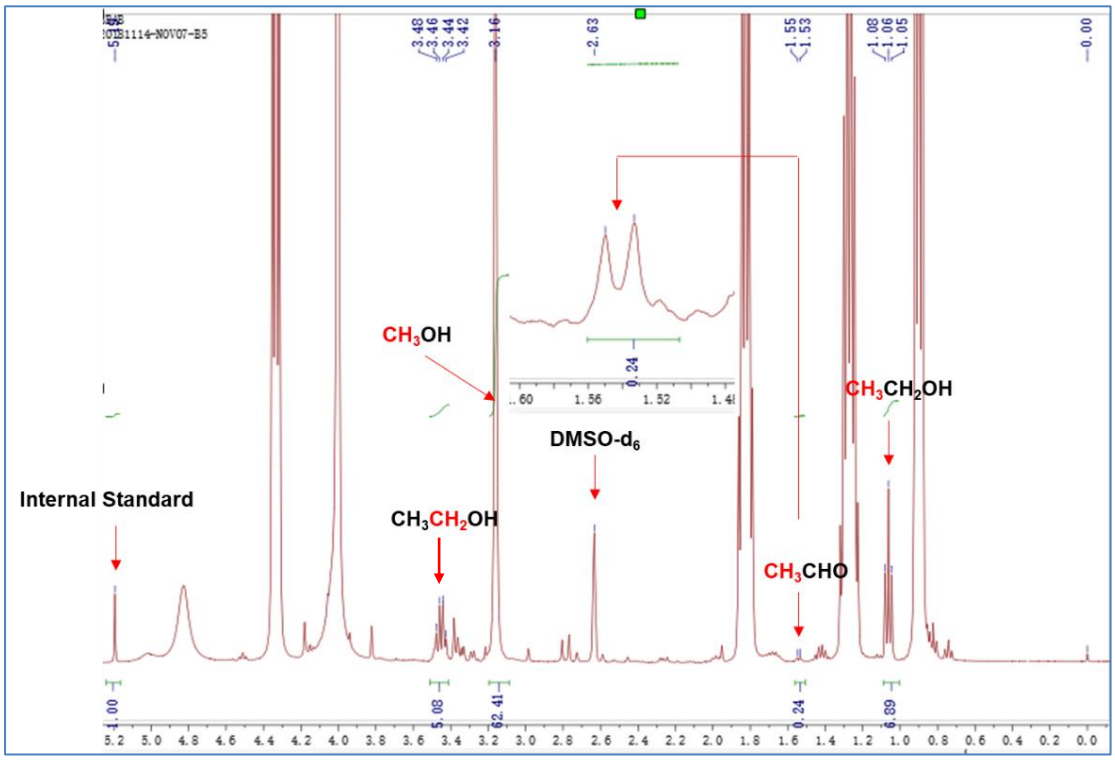


Fig. S3 ^{1}H NMR spectra of the liquid sample after the reaction of methanol with CO and H_2. Reaction condition was the same as that of entry 1 in Table 1 except that 3 MPa of CO was used instead of CO_2.

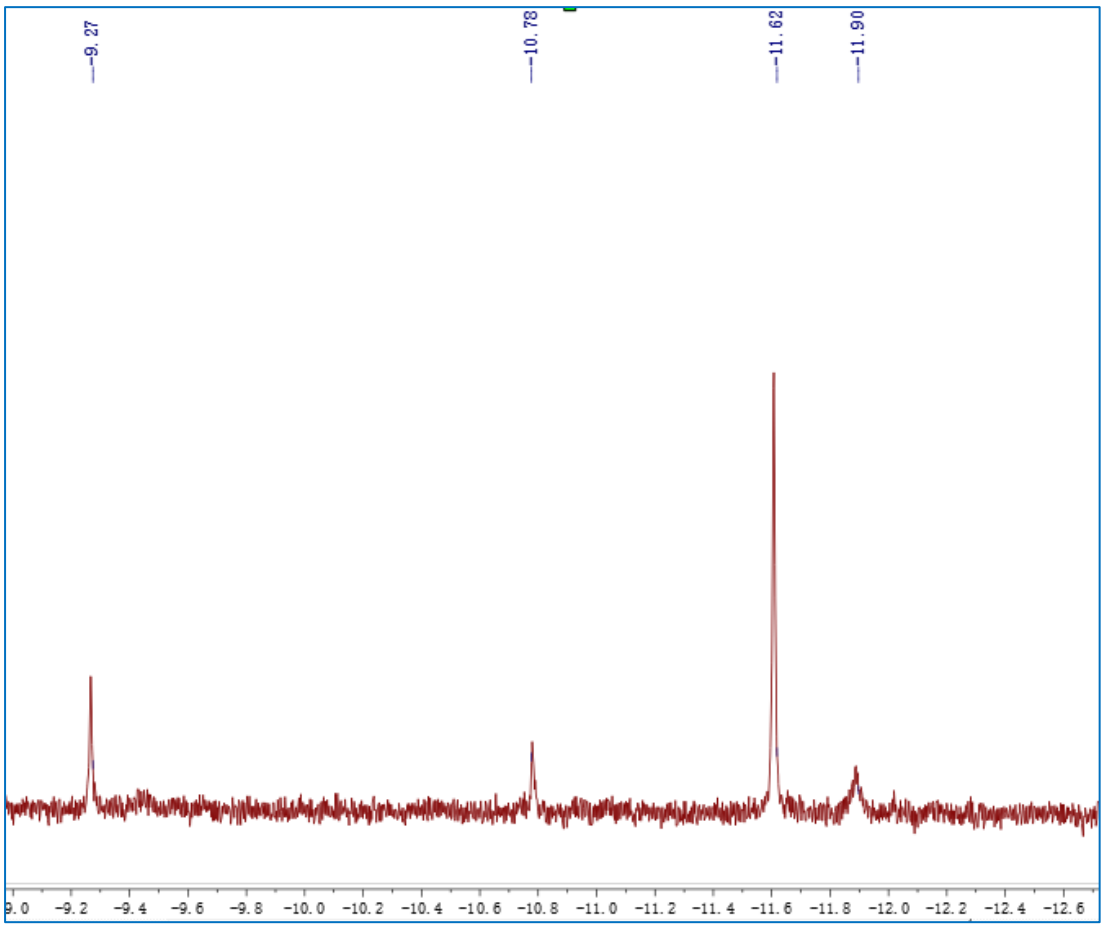


Fig. S4 ^{1}H NMR spectra of the liquid sample after the reaction of methanol, CO_2 and H_2. $CDCl_3$ instead of DMSO-d_6 was used as solvent to prepare the NMR sample, and chemical shifts (ppm) are given relative to TMS. Reaction condition was the same as that of entry 1 in Table 1.

Note: The ^{1}H NMR spectra demonstrated signals in the hydride region at δ = -9.27, -10.78, -11.62 and -11.90 ppm. This affirmed the formation of the Ru-H under the reaction conditions. Related Ru-H species is reported elsewhere.[1]

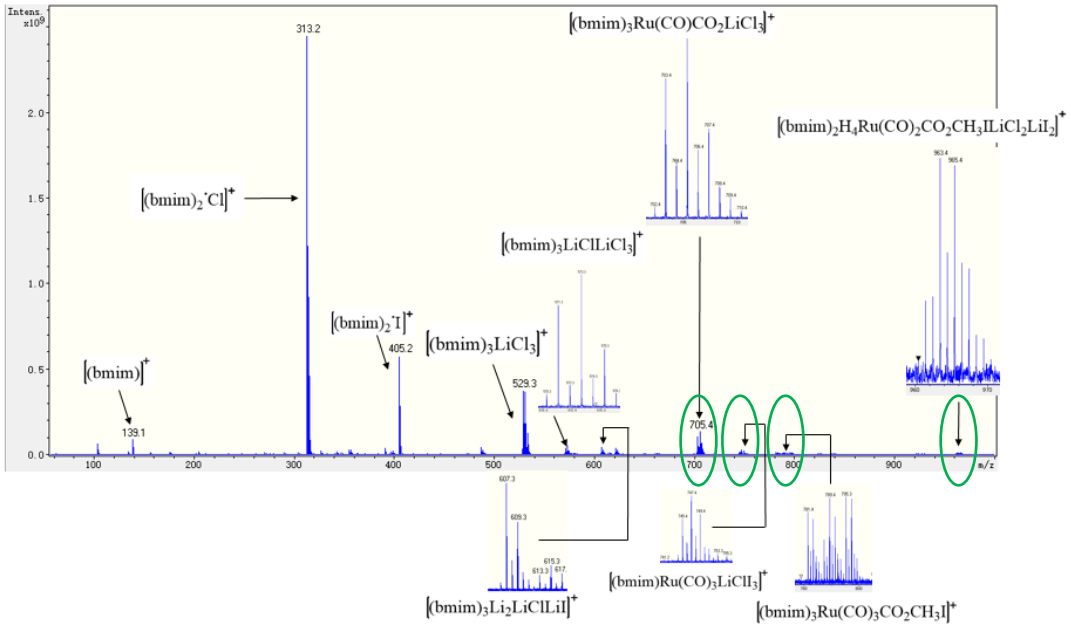


Fig. S5: HR-ESI-MS spectra of the reaction solution after 2 h of reaction at condition of Fig. 2b.

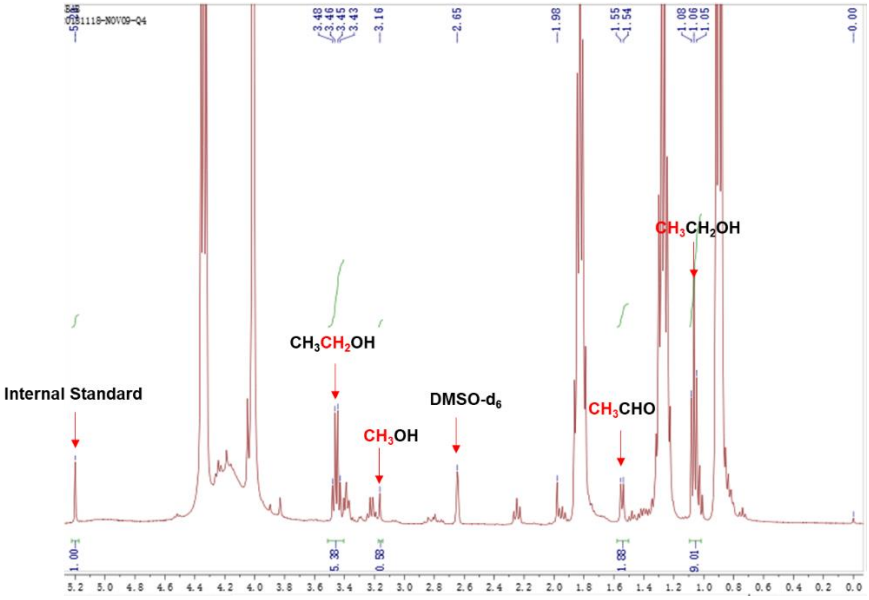
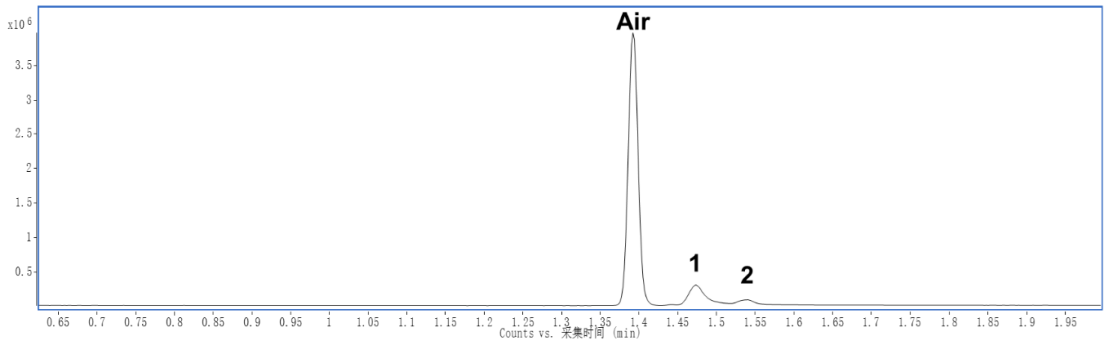
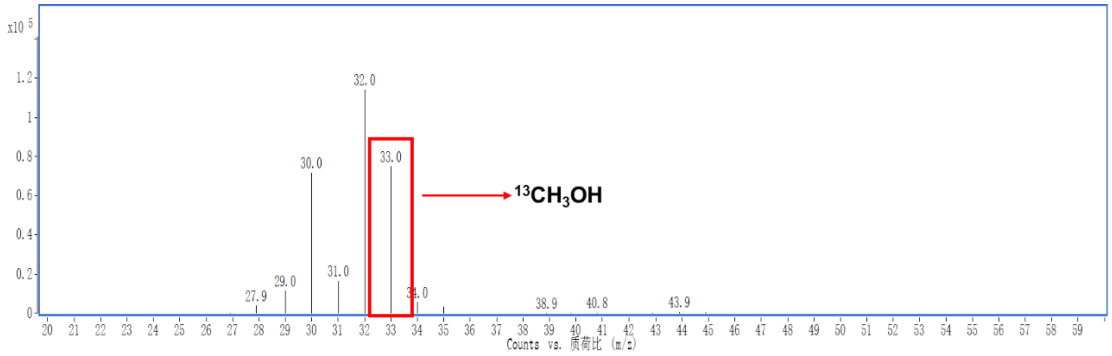
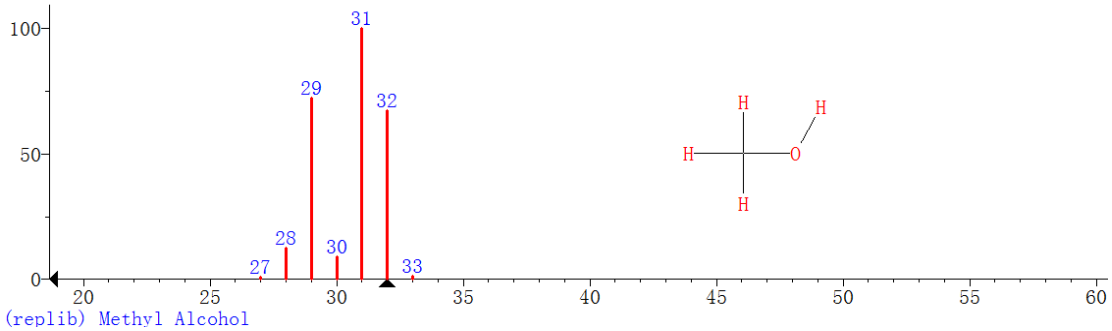


Fig. S6 The ^{1}H NMR spectra of liquid sample after the reaction of acetaldehyde and H_2. Reaction conditions: 32.1 μmol $Ru_3(CO)_{12}$ (based on the metal), 2.1 mmol LiI, 1.9 mmol LiCl, 11.5 mmol [bmim]Cl, 2 mmol acetaldehyde, 6 MPa H_2 (at room temperature), 160 °C, 15 h.

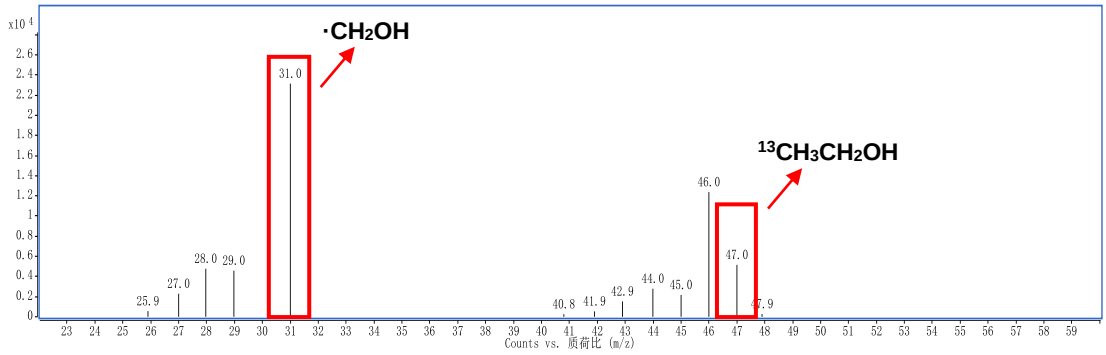

Air
1
2
Counts vs. 采集时间 (min)

Peak 1


32.0
33.0
30.0
31.0
29.0
27.9
34.0
38.9
40.8
43.9
$^{13}CH_3OH$
Counts vs. 质荷比 (m/z)


31
29
32
28
30
27
33
(replib) Methyl Alcohol

Peak 2


·CH2OH
31.0
$^{13}CH_3CH_2OH$
46.0
47.0
28.0
29.0
27.0
25.9
44.0
45.0
42.9
40.8
41.9
Counts vs. 质荷比 (m/z)

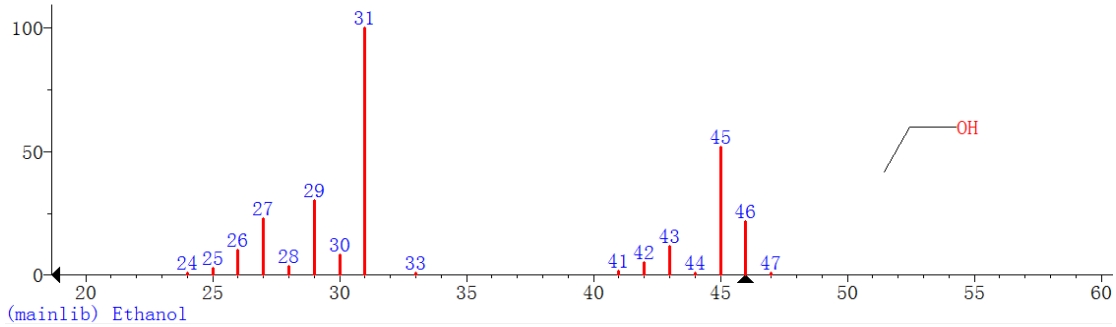
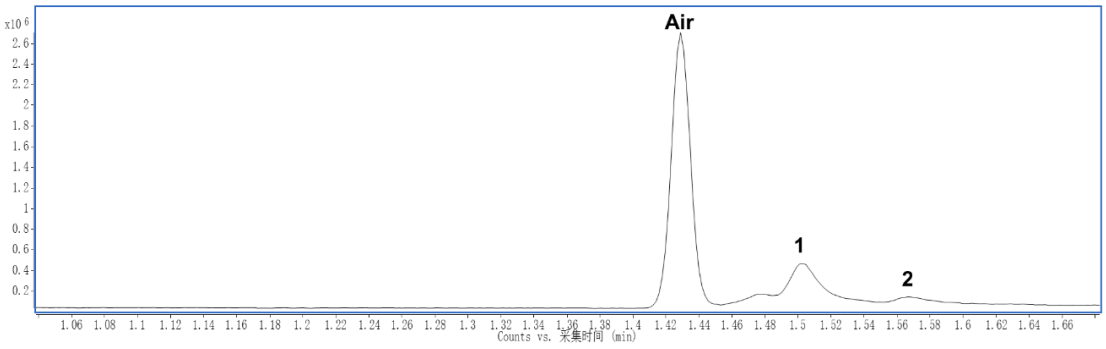
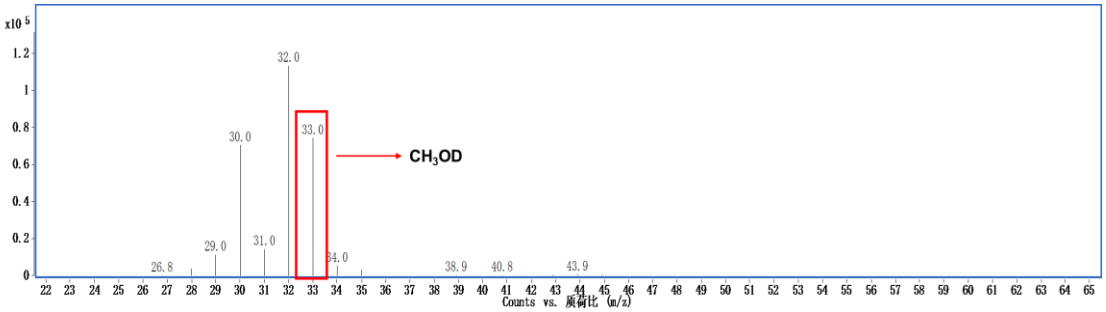
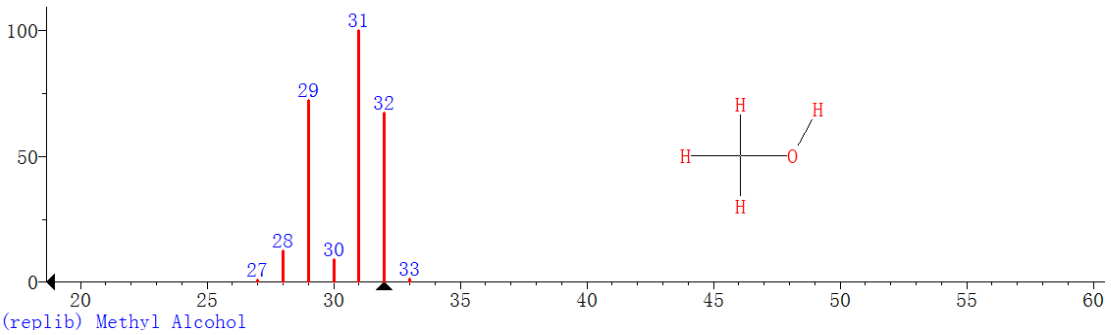


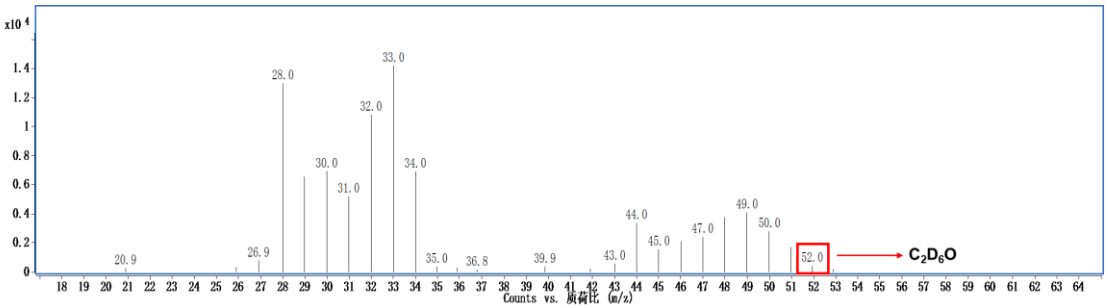
Fig. S7 GC-MS spectra of the liquid sample after the reaction of $^{13}CH_3OH$, CO_2 and H_2. Reaction condition was the same as that of entry 1 in Table 1 except that 30 μL $^{13}CH_3OH$ was used instead of methanol.







(replib) Methyl Alcohol



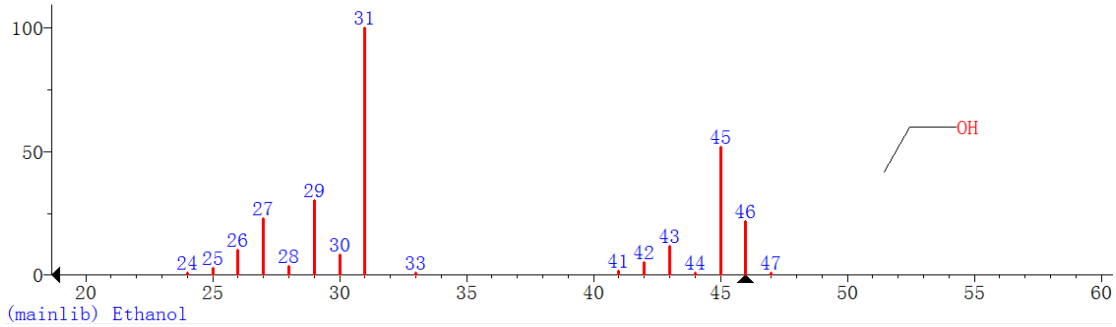


Fig. S8 The GC-MS spectra of liquid sample after the reaction of methanol, CO_2 and D_2. Reaction condition was the same as that of entry 1 in Table 1 except that D_2 was used instead of H_2.

Notes: Two deductions can be formed based on the results.

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.

Tables

Table S1. Some representative works on synthesis of ethanol using CO_2 and H_2.

Entry	Catalyst/Temperature	Catalytic activity	Monometallic metal	Reference
1	$Ru_3(CO)_{12}$, 160 °C	36.8 (TON based on Ru)		This work
2	$[Ru(CO)_4Cl_2]_2$-$Co_2(CO)_8$, 160 °C	7.5 (TOF based on Ru)	Ru, 0.5 (TOF based on Ru) Co, no ethanol product.	*Green Chem*., 2019, **21**, 589-596
3	$CoAlO_x$, 140 °C	0.444 mmol $g^{-1}h^{-1}$	Co, 0.01 mmol $g^{-1}h^{-1}$ Al, 0 mmol $g^{-1}h^{-1}$	*Angew. Chem. Int. Ed*., 2018, **57**, 6104 -6108
4	Pd_2Cu/TiO_2 (P25), 200 °C	359.0 h^{-1} (TOF based on Pd)	Pd/TiO_2, 80 (TOF based on Pd) Cu, not applicable	*J. Am. Chem. Soc*., 2017, **139**, 6827-683019
5	Pt/Co_3O_4, 200 °C	0.51 mmol g_{cat}^{-1} h^{-1} (alcohols)	Pt, not applicable Co_3O_4, 0.004 mmol g_{cat}^{-1} h^{-1} (alcohols)	*Angew. Chem. Int. Ed*., 2016, **55**, 737-741

Table S2: Influence of reaction parameter on methanol homologation with CO_2/H_2.

Entry	Ru (μmol)	LiI (mmol)	LiCl (mmol)	[bmim]Cl (mmol)	H_2/CO_2 (MPa)	TON	Selectivity (C-mmol%)		
							EtOH	CO	CH_4
1	27.1	2.1	1.9	11.5	6/3	31.2	53.9	39.0	7.1
2	32.1	2.1	1.9	11.5	6/3	36.8	51.5	39.1	9.4
3	37.1	2.1	1.9	11.5	6/3	38.3	50.0	38.5	11.5
4	42.1	2.1	1.9	11.5	6/3	40.8	49.1	34.3	16.6
5	32.1	1.1	1.9	11.5	6/3	28.0	50.1	42.9	7.0
6	32.1	3.6	1.9	11.5	6/3	37.7	50.6	29.7	19.7
7	32.1	2.1	0.8	11.5	6/3	29.6	48.5	42.6	8.9
8	32.1	2.1	2.7	11.5	6/3	18.7	32.6	46.7	20.7
9	32.1	2.1	1.9	3.4	6/3	22.7	34.7	27.3	38.0
10	32.1	2.1	1.9	8.6	6/3	27.1	41.8	36.8	21.4
11	32.1	2.1	1.9	14.3	6/3	29.0	45.3	41.5	13.2
12	32.1	2.1	1.9	11.5	7/2	30.2	50.3	33.9	15.8
13	32.1	2.1	1.9	11.5	4/5	29.6	54.5	25.1	20.4
14	32.1	2.1	1.9	11.5	3/1.5	6.5	16.7	47.2	36.1
15	32.1	2.1	1.9	11.5	6.75/3.25	39.6	49.7	36.8	13.5
16	32.1	2.1	1.9	11.5	0/6	0	0	0	0
17	32.1	2.1	1.9	11.5	6/0	0	0	0	0
18	32.1	2.1	1.9	11.5	0/0	0	0	0	0
19[b]	32.1	2.1	1.9	11.5	6/3	1.9	5.4	89.5	5.1
20[b]	0	0	0	11.5	6/3	0	0	38.7	61.3
21[b]	0	2.1	1.9	11.5	6/3	0	0	86.3	13.7

[a]Reaction conditions: $Ru_3(CO)_{12}$ was used as the catalyst (based on the metal), LiI and LiCl were used as the promoters, [bmim]Cl was used as the reaction solvent, 3.7 mmol methanol, 160 °C, 15 h. CO_2 and H_2 were the reactants and charged into reactor at room temperature.

[b]No methanol was added before the reaction.

Notes: The dosage of catalytic components affected the catalytic performance. With elevating Ru dosage, the TON increased and ethanol selectivity decreased (entries 1-4). At 32.1 μmol Ru, the TON reached 36.8 and the increase became slower when the Ru dosage was further enhanced. Similarly, the TON rose with the increasing LiI dosage, but it became minor when the amount of LiI was higher than 2.1 mmol (entries 1, 5, 6). In addition, the ethanol selectivity using 2.1 mmol LiI was better than those obtained at other LiI dosages. The dosage of LiCl also affected the catalytic performance. With the increase of LiCl amount, Both TON and ethanol selectivity were enhanced firstly and then reduced (entries 1, 7, 8). The best result was achieved at 1.9 mmol LiCl. The impact of [bmim]Cl dosage was similar to that of LiCl, and the appropriate amount of [bmim]Cl was 11.5 mmol (entries 1, 9-11). We also conducted the reaction at different H_2/CO_2 ratio and different total pressure, respectively. The results indicated that 6 MPa H_2 and 3 MPa CO_2 were suitable for the reaction (entries 1, 12-15). Both CO_2 and H_2 were required for the reaction, because no product was observed without CO_2 and/or H_2 (entries 16-18). In short, 32.1 μmol Ru, 2.1 mmol LiI, 1.9 mmol LiCl, 11.5 mmol [bmim]Cl, 3 MPa CO_2 and 6 MPa H_2 were the optimal reaction condition.

Reference

[1] M. H. G. Prechtl, Y. Ben-David, D. Giunta, S. Busch, Y. Taniguchi, W. Wisniewski, H. Görls, R. J. Mynott, N. Theyssen, D. Milstein and W. Leitner, *Chem. Eur. J.*, 2007, **13**, 1539-1546.