Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Synthesis of Ethanol via Reaction of Dimethyl Ether with CO_2 and H_2

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1. Figures and Tables

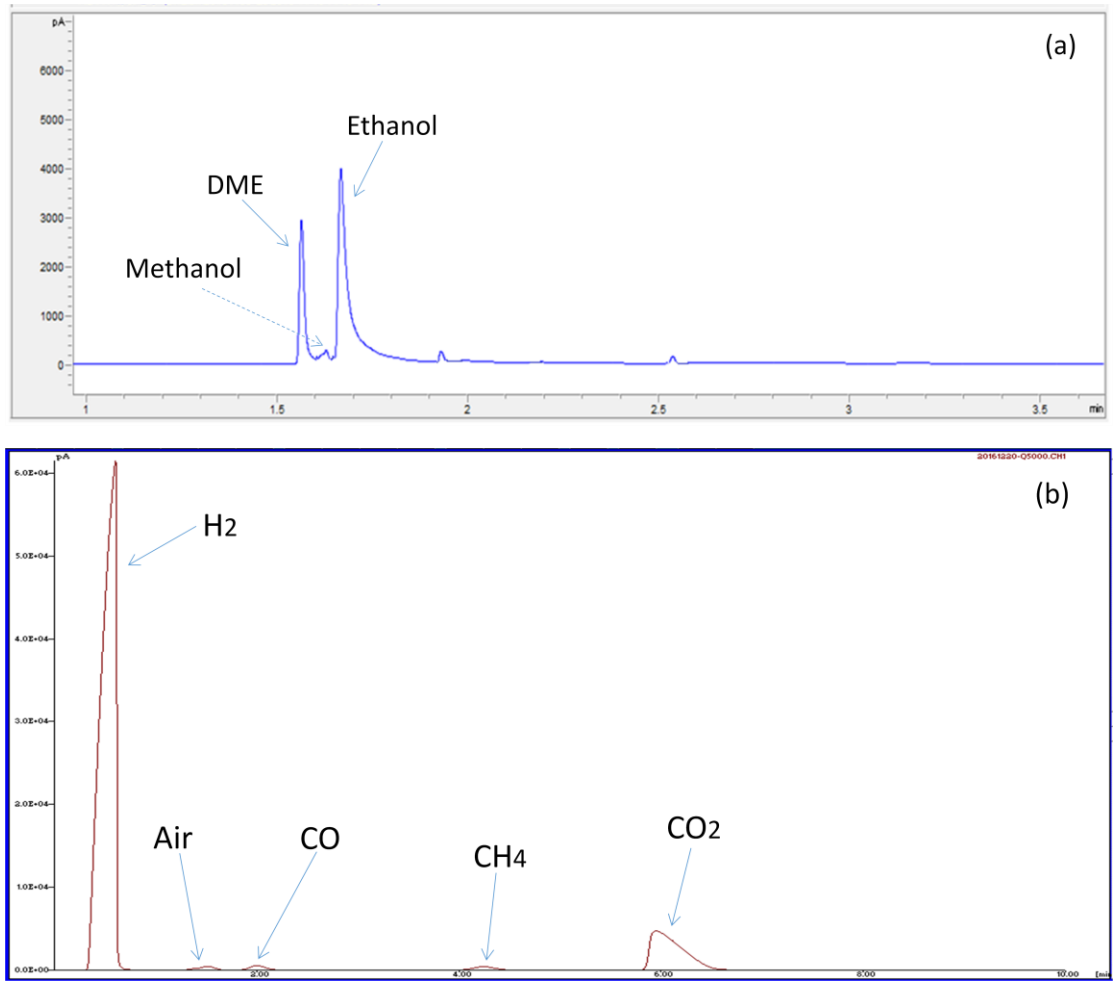


Figure S1. The GC traces of the liquid sample (a) and gaseous sample (b) at the reaction condition of Entry 1 in Table 1.

Note:

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

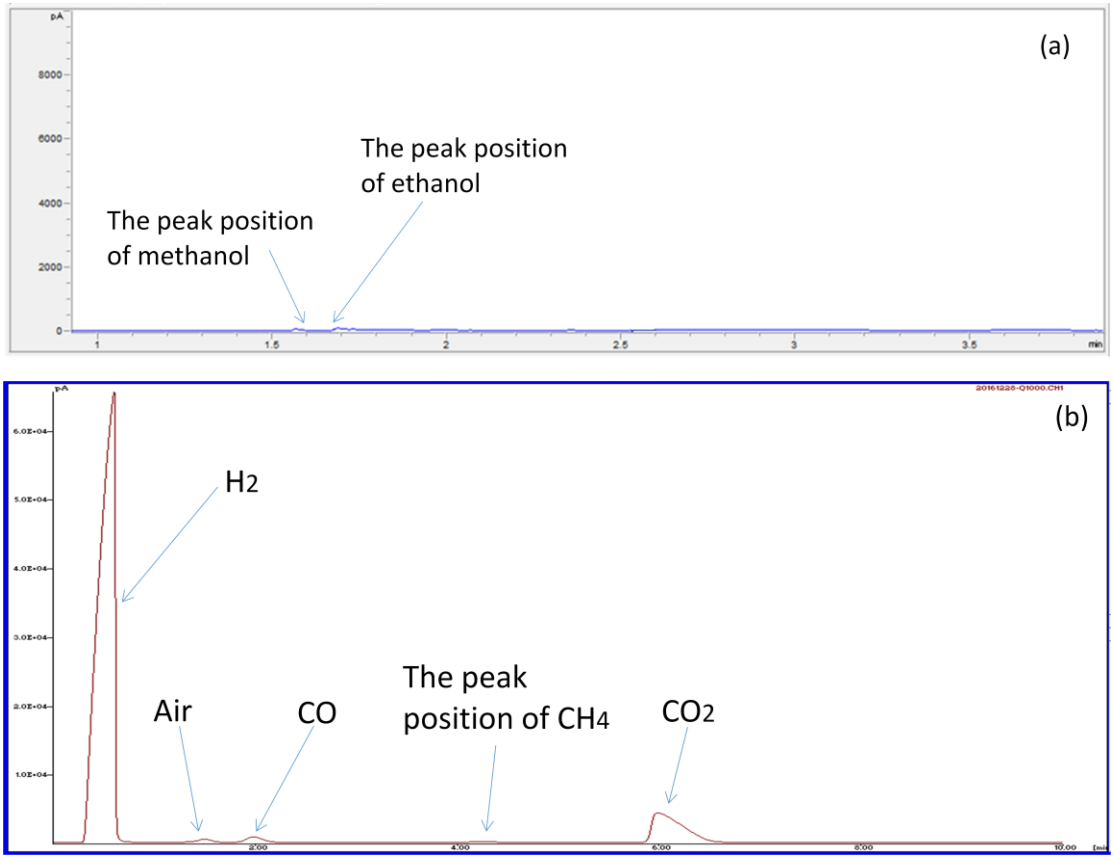


Figure S2. The GC traces of the liquid sample (a) and gaseous sample (b) after reaction of CO_2 and H_2. Reaction condition is given in Entry 17 of Table 2.

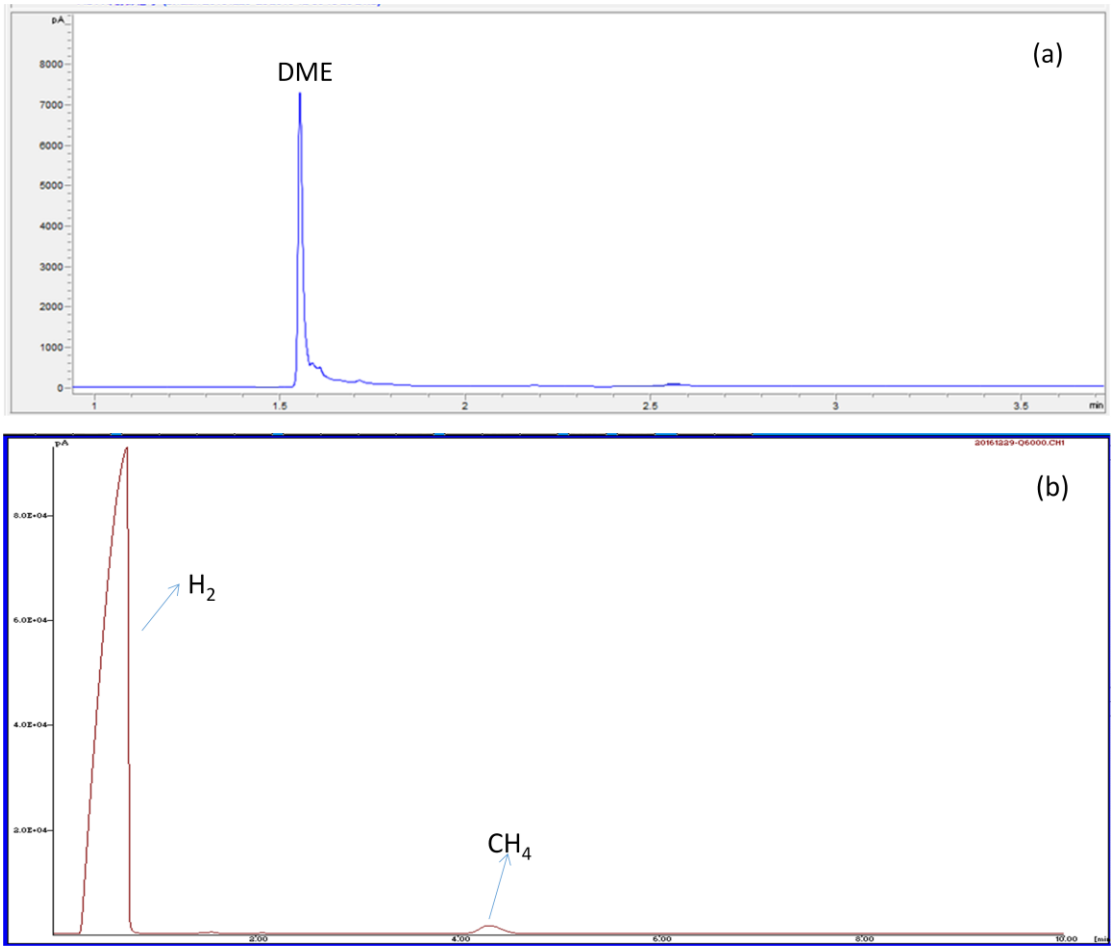


Figure S3. The GC traces of the liquid sample (a) and gaseous sample (b) after the reaction of DME and H_2. Reaction condition is given in Entry 8 of Table 2.

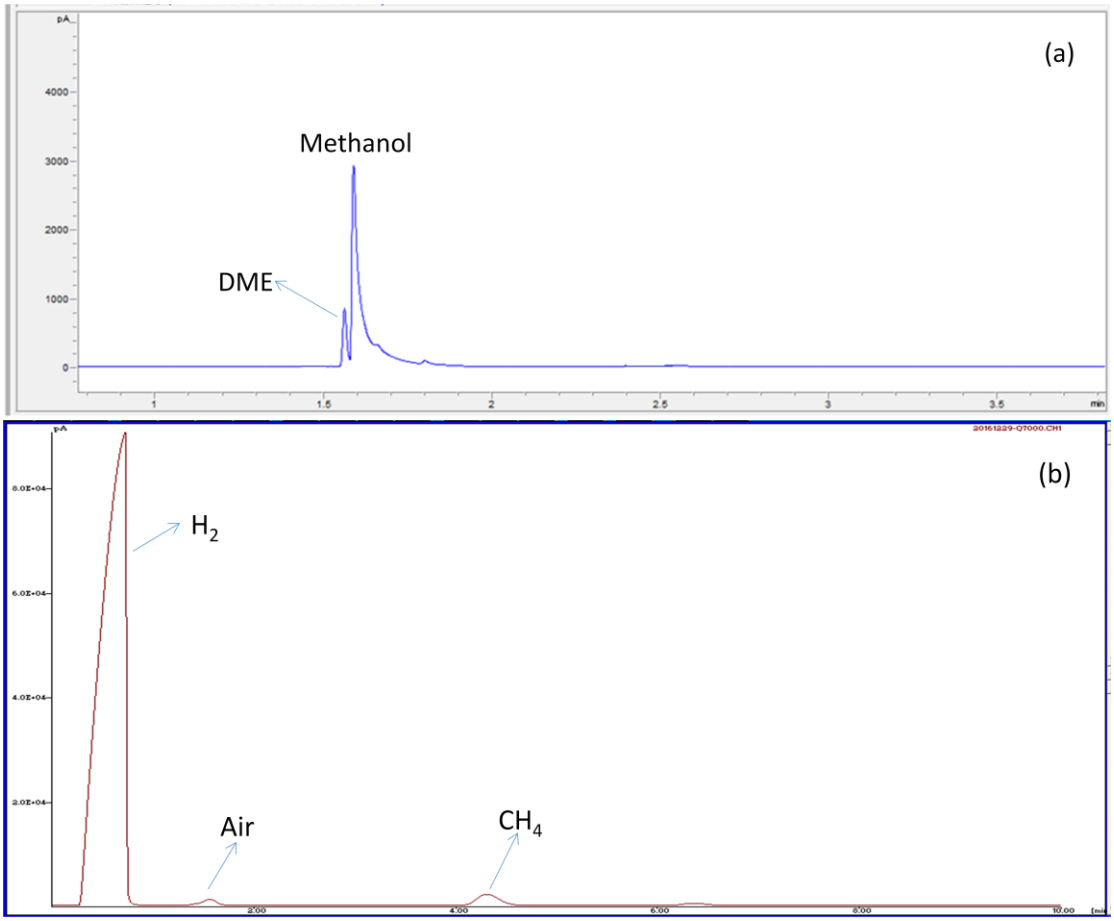


Figure S4. The GC traces of the liquid sample (a) and gaseous sample (b) after the reaction of methanol and H_2. Reaction condition: 30 μmol $Ru(PPh_3)_3Cl_2$ and 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 4 mmol methanol and 4 MPa H_2 (at room temperature), 180 ^oC and 12 h.

Note:
The amount of methanol (in mole) was the same as that of DME in Entry 1 of Table 1.

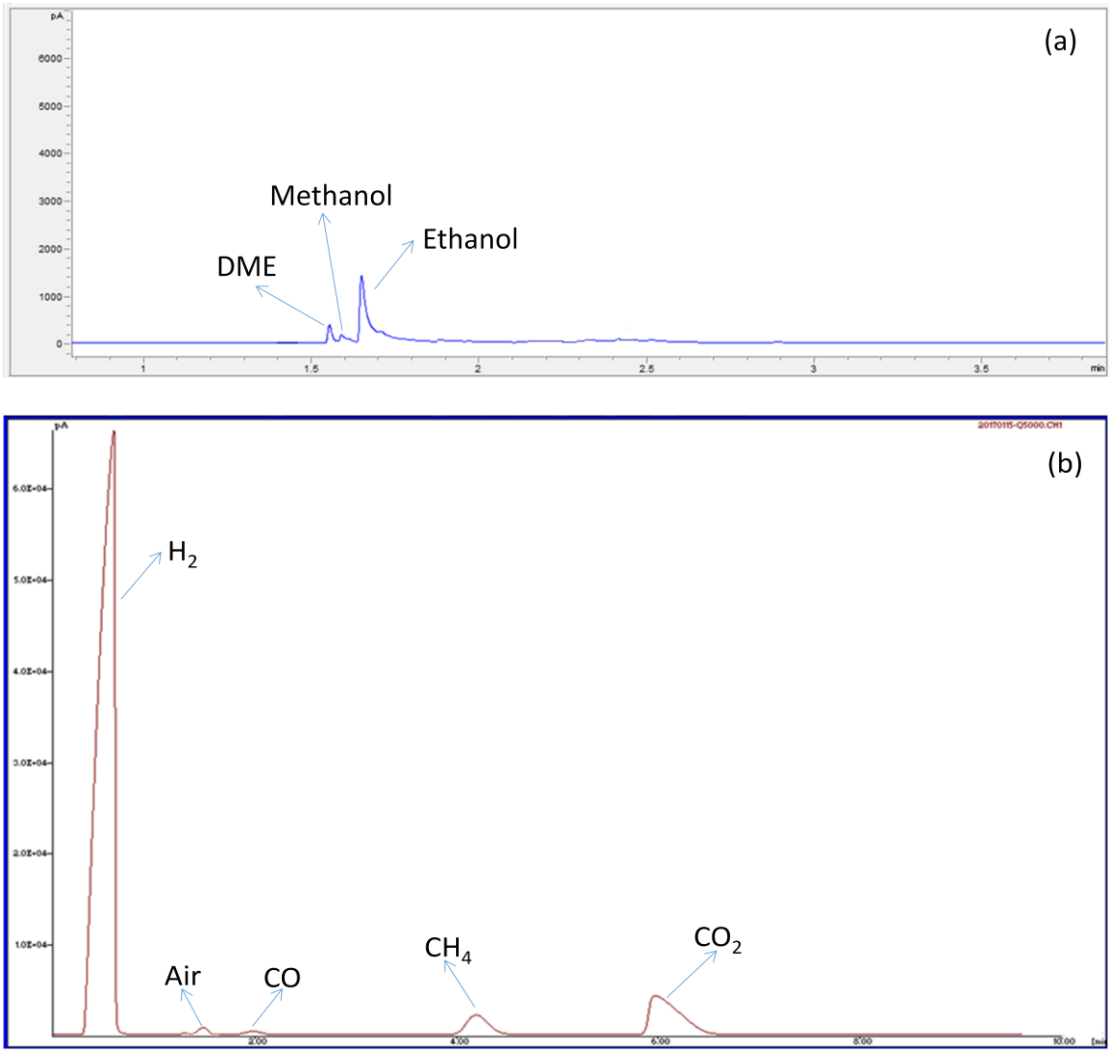


Figure S5. The GC traces of the liquid sample (a) and gaseous sample (b) after the reaction of methanol, CO_2 and H_2. Reaction conditions: 30 μmol $Ru(PPh_3)_3Cl_2$ and 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 4 mmol methanol, 4 MPa CO_2 and 4 MPa H_2 (at room temperature), 180 ^oC and 12 h.

Note:
The selectivity of ethanol in total products was only 35.6 C-mol% because considerable amount of methane was produced.

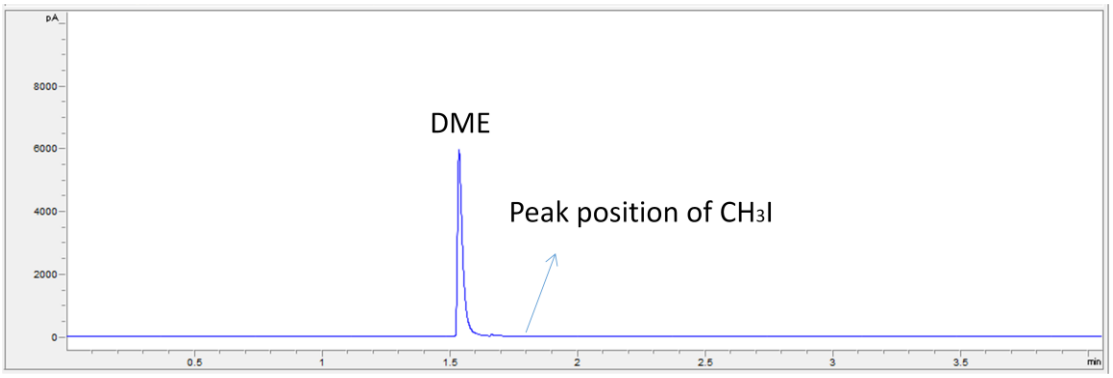


Figure S6. The GC traces of the liquid sample after reaction of DME and LiI. Reaction condition: 2.3 mmol LiI, 0.5 MPa DME, 2 mL DMI, 180 ^{o}C and 12 h.

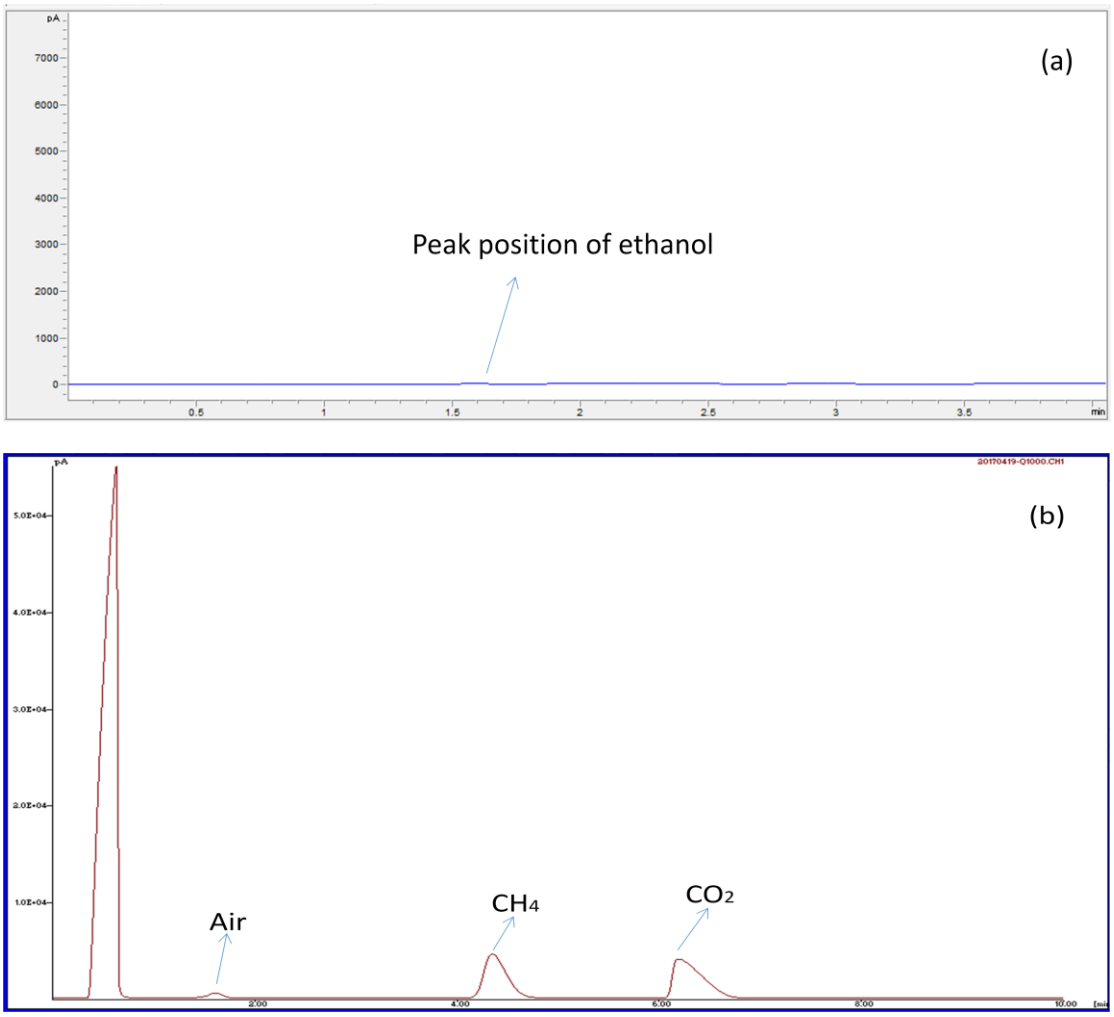


Figure S7. The GC traces ofthe liquid sample (a) and gaseous sample (b) after the reaction of CH_3I, CO_2 and H_2. Reaction conditions: 30 μmol $Ru(PPh_3)_3Cl_2$ and 70 μmolCoI_2, 2.3 mmol LiI, 2 mL DMI, 2 mmol CH_3I, 4 MPa CO_2 and 4 MPa H_2 (at room temperature), 180 ^oC and 12 h.

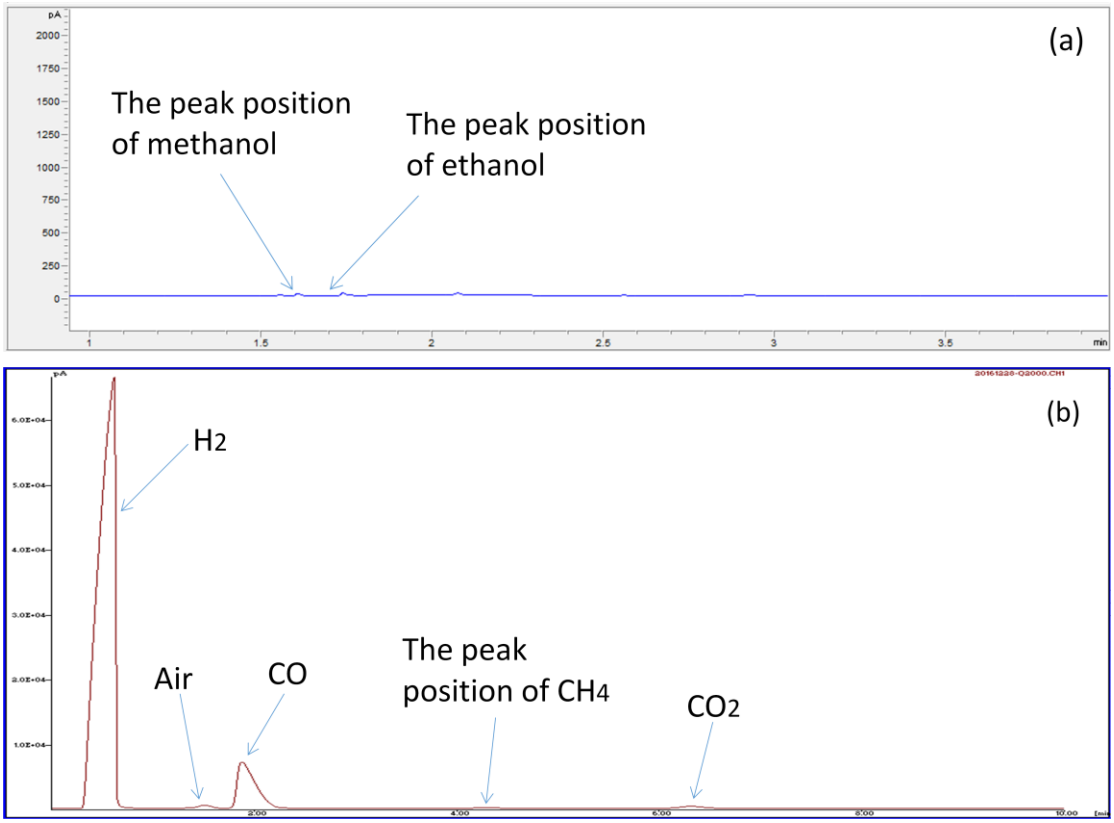


Figure S8. The GC traces of the liquid sample (a) and gaseous sample (b) after the reaction of CO and H_2. Reaction condition is given in Entry 22 of Table 2.

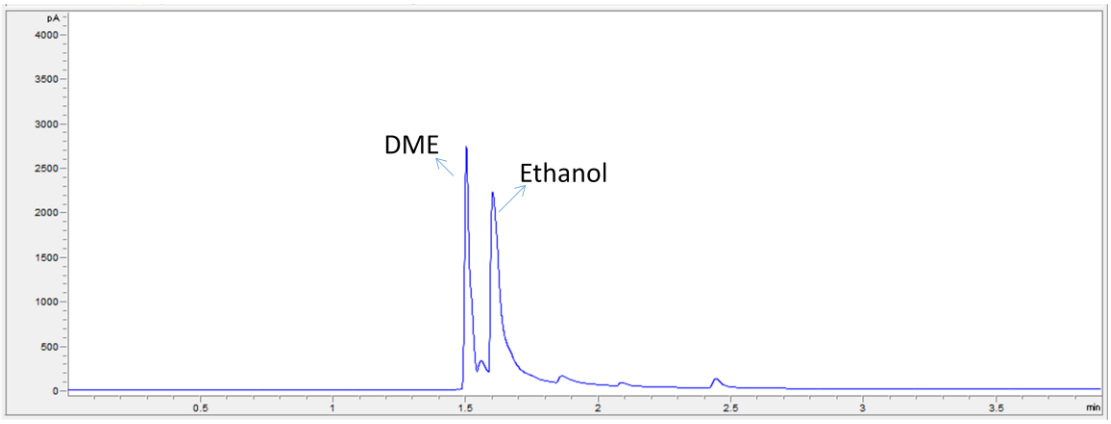


Figure S9. The GC traces of the liquid sample after reaction of DME with CO and H_2. Reaction conditions: 30 μmol $Ru(PPh_3)_3Cl_2$ and 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 50 μL H_2O, 0.5 MPa DME, 0.5 MPa CO and 4 MPa H_2 (at room temperature), 180 ^oC and 12 h.

Note: the amount of water was equimolar to that of CO.

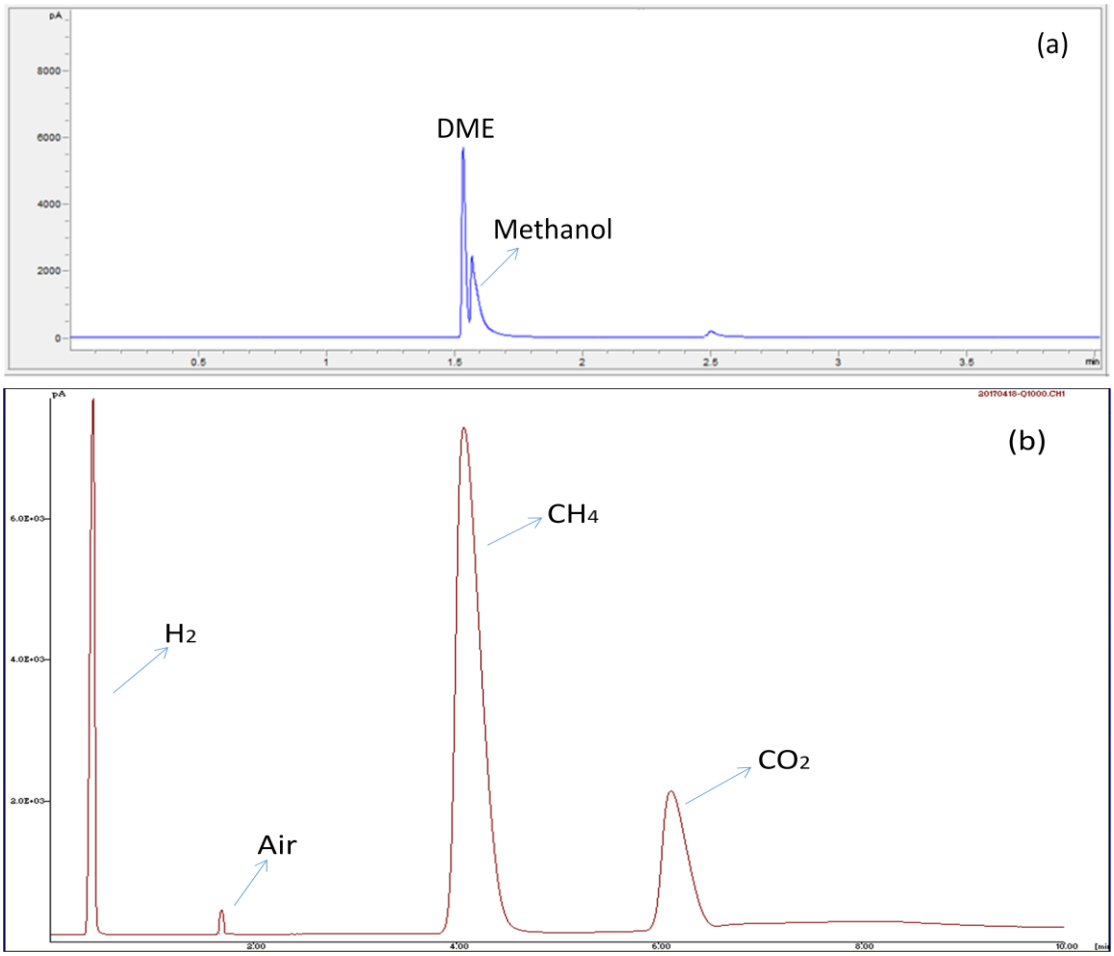


Figure S10. The GC traces of the liquid sample (a) and gaseous sample (b) after the reaction of DME and formaldehyde. Reaction condition: 30 μmol $Ru(PPh_3)_3Cl_2$ and 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 2 mmol formaldehyde, 0.5 MPa DME (at room temperature), 180 ^oC and 12 h.

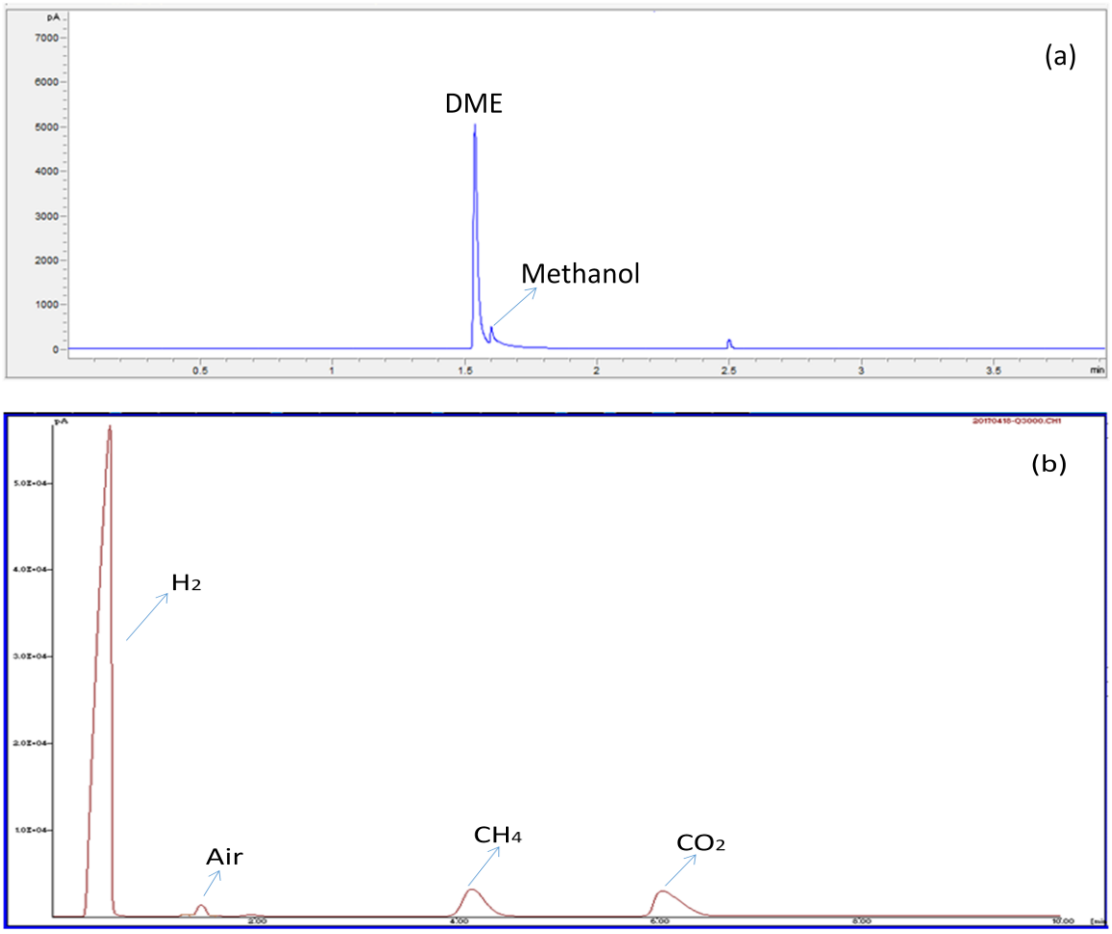
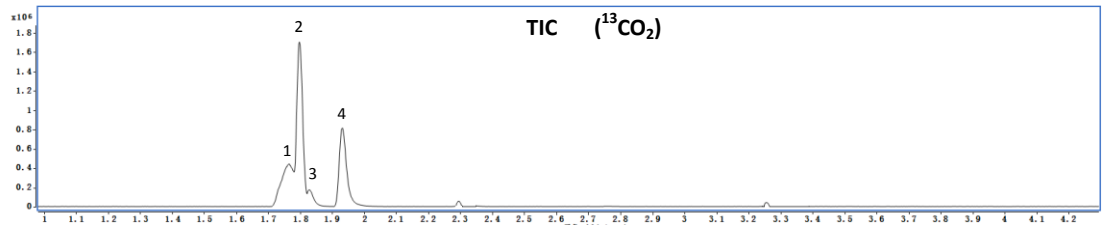
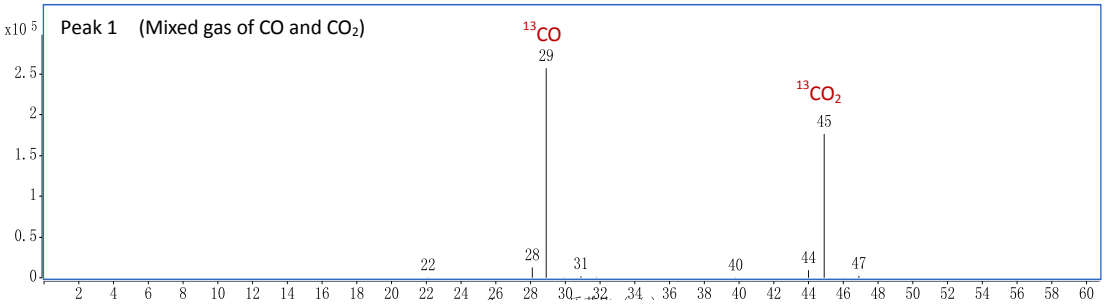
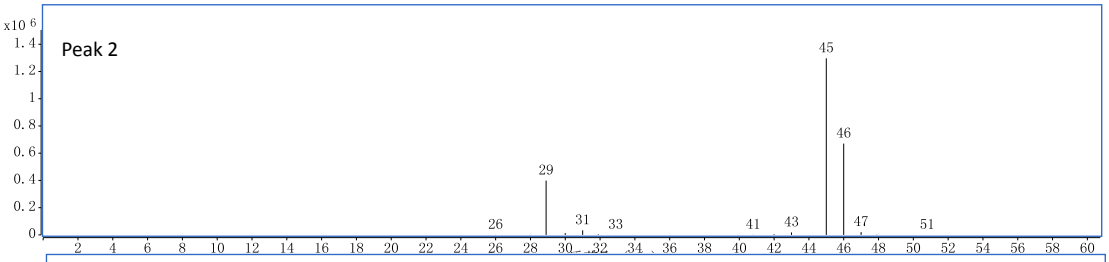
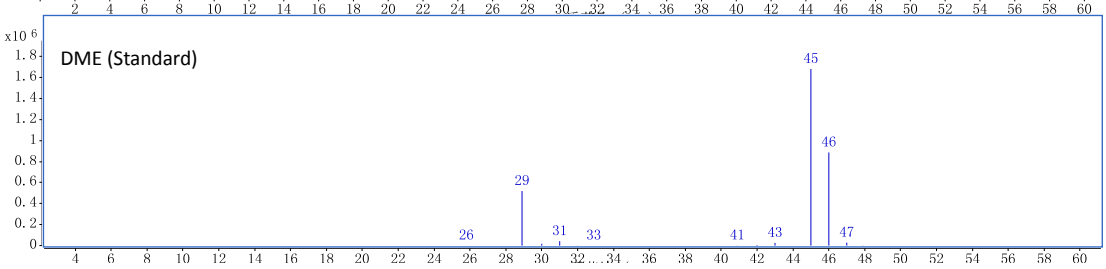


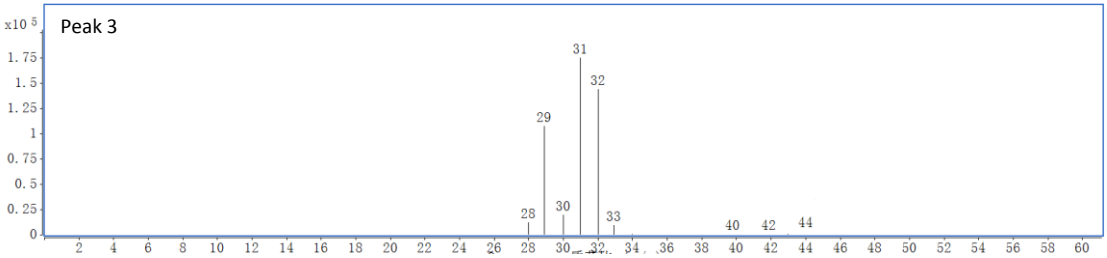
Figure S11. The GC traces of the liquid sample (a) and gaseous sample (b) after the reaction of DME and formic acid. Reaction condition: 30 μmol $Ru(PPh_3)_3Cl_2$ and 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 2 mmol formic acid, 0.5 MPa DME (at room temperature), 180 ^oC and 12 h.

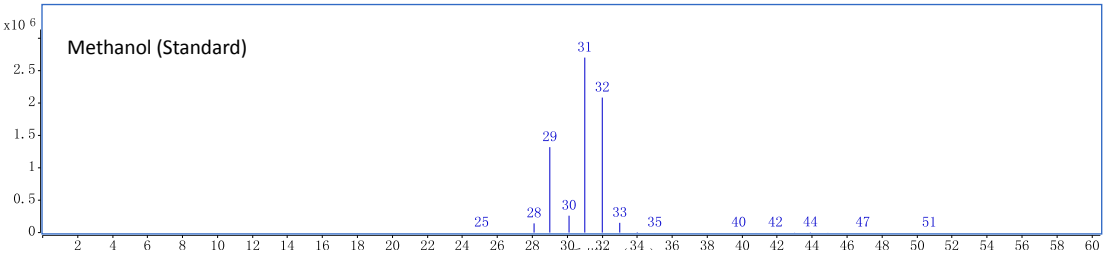

TIC ($^{13}CO_2$)
1
2
3
4


Peak 1 (Mixed gas of CO and CO_2)
^{13}CO
$^{13}CO_2$


Peak 2


DME (Standard)


Peak 3


Methanol (Standard)

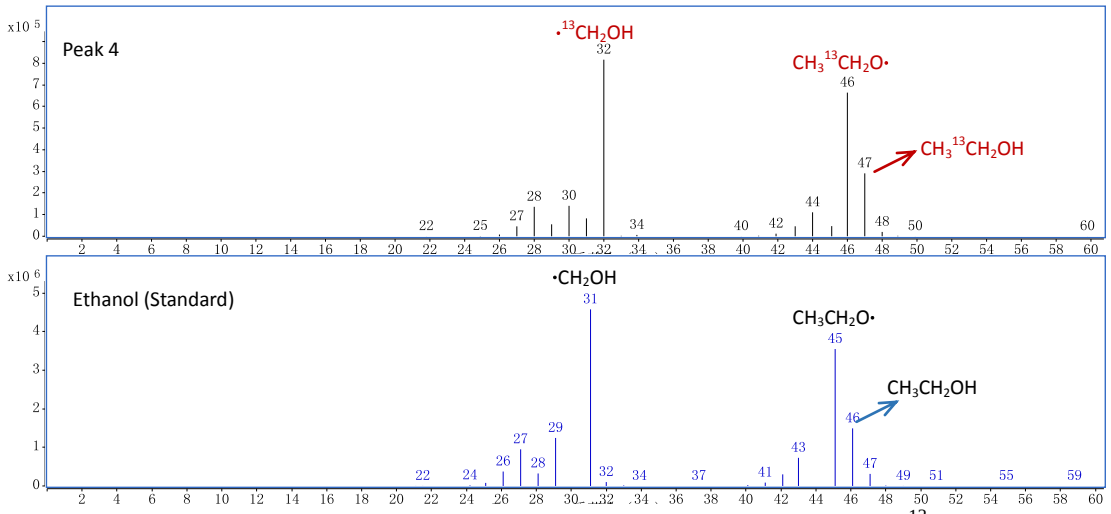
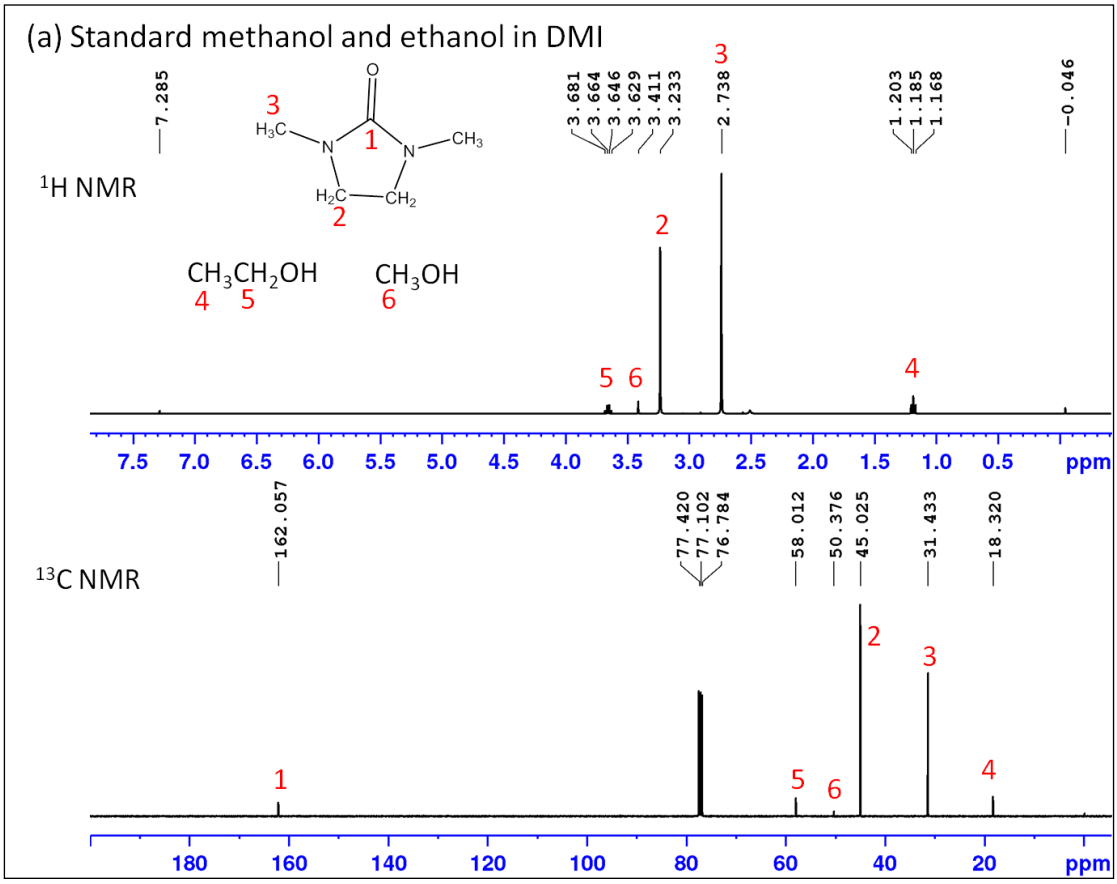


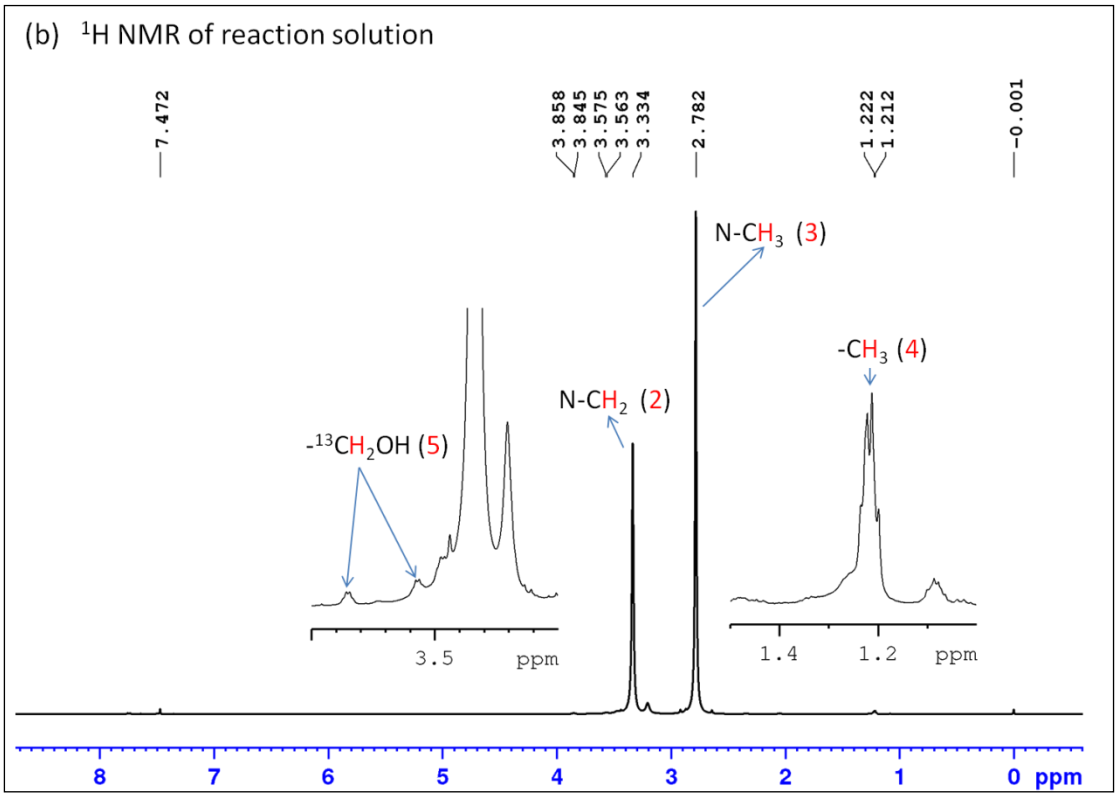
Figure S12. The GC-MS spectra of the liquid sample after reaction using 2 MPa $^{13}CO_2$ and 6 MPa H_2. Other reaction condition is the same as that given in Entry 1 of Table 1.

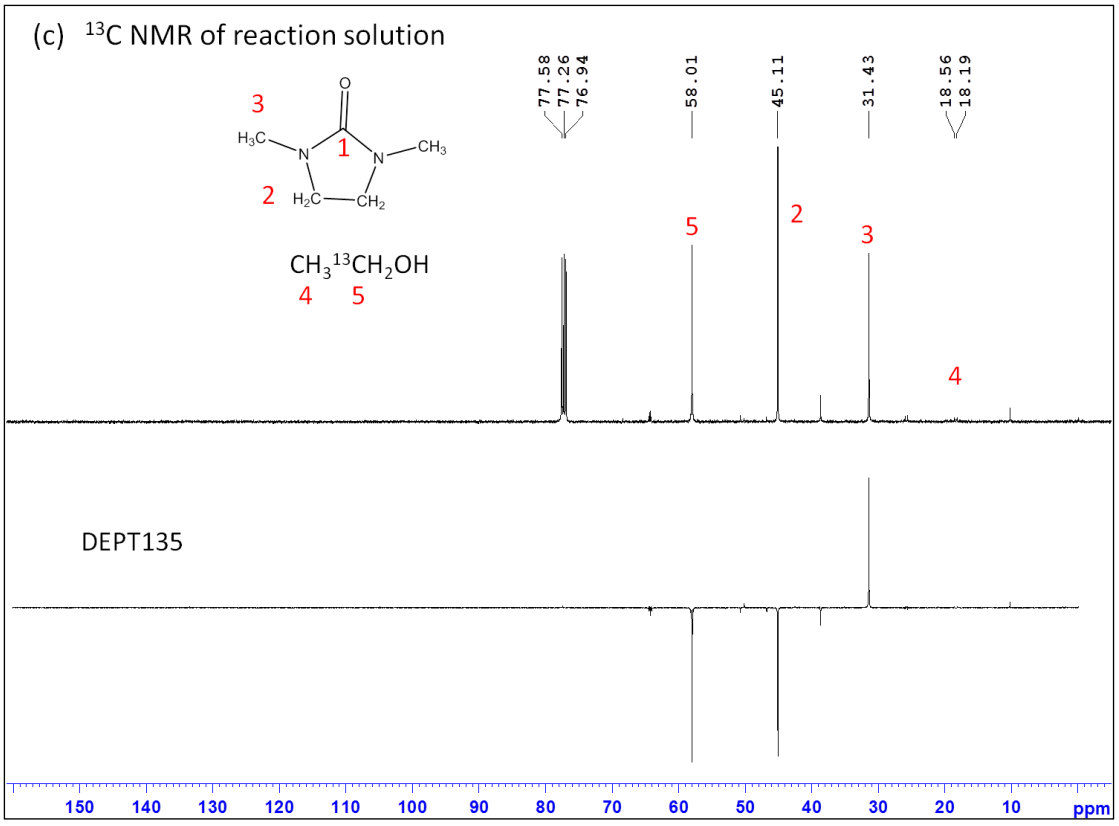
Note:

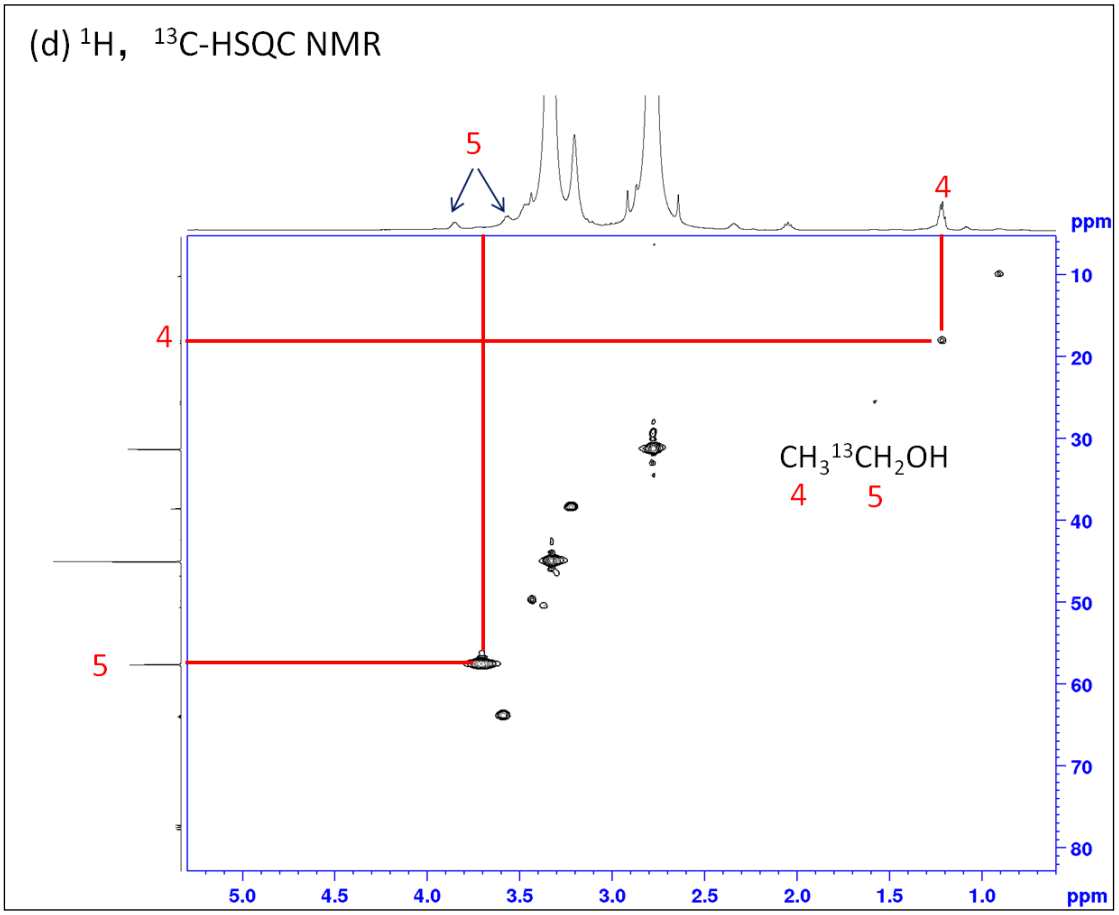
The following conclusions can be made according to $^{13}CO_2$ tracer test.

1. The C atoms in the unreacted DME molecules were intact.
2. The CO generated in the reaction was from CO_2.
3. The C atom of the methanol generated in the reaction was from DME.
4. In the ethanol generated in the reaction, the C atom of the CH_3 group was from DME, and the C atom of CH_2OH group was from CO_2.


(a) Standard methanol and ethanol in DMI
^{1}H NMR
^{13}C NMR
CH_3CH_2OH
CH_3OH
7.285
3.681
3.664
3.646
3.629
3.411
3.233
2.738
1.203
1.185
1.168
0.046
162.057
77.420
77.102
76.784
58.012
50.376
45.025
31.433
18.320
ppm


(b) ^{1}H NMR of reaction solution
7.472
3.858
3.845
3.575
3.563
3.334
2.782
1.222
1.212
0.001
N-CH_3 (3)
-CH_3 (4)
N-CH_2 (2)
-$^{13}CH_2OH$ (5)
3.5 ppm
1.4 1.2 ppm
ppm


(c) ^{13}C NMR of reaction solution
77.58
77.26
76.94
58.01
45.11
31.43
18.56
18.19
$CH_3{}^{13}CH_2OH$
DEPT135
ppm


(d) ^{1}H, ^{13}C-HSQC NMR
$CH_3{}^{13}CH_2OH$
ppm

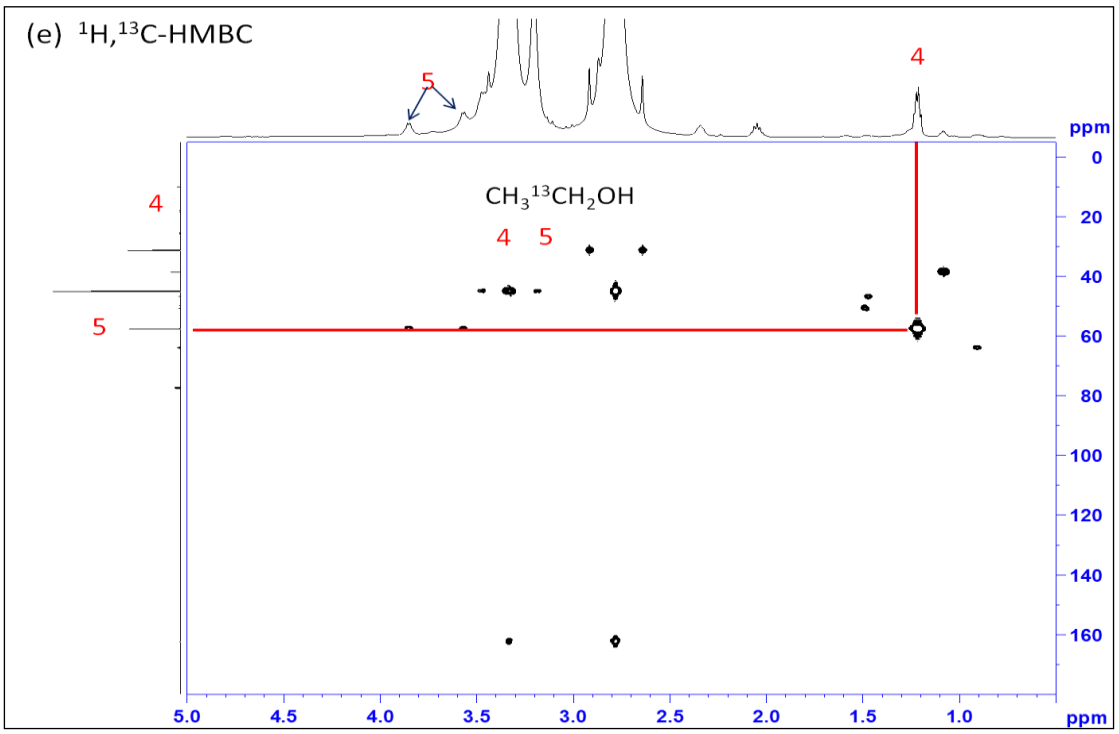


Figure S13. The standard NMR spectra of methanol and ethanol in DMI *(a)* and NMR spectra of the reaction solution *(b-e)* using 2 MPa $^{13}CO_2$ and 6 MPa H_2. Other reaction condition is the same as that given in Entry 1 of Table 1.

Note:

The NMR spectra of the reaction solution using $^{13}CO_2$ as tracer indicate that the secondary carbon (in -CH_2-) in the ethanol molecule was from $^{13}CO_2$. The evidences are as follows:

(1) In the ^{1}H NMR spectrum *(b)*, the proton signal of the methylene group (-CH_2-) in the ethanol molecule produced in the reaction splits into two peaks by the coupling with the ^{13}C atom.

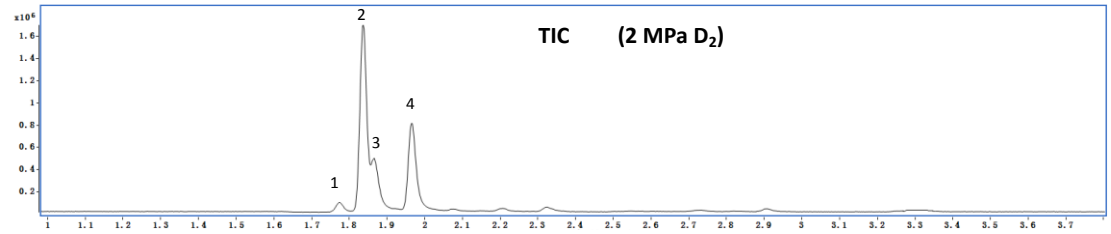
(2) In the ^{13}C NMR spectrum*(c)*, the signal of methylene group (-CH_2-) in ethanol produced in the reaction was abnormally high compared with the standard spectra *(a)*, which is due to the ^{13}C-labled reaction. The ^{13}C signal of methyl group (CH_3-) becomes weaker and splits into two peaks, which is caused by the coupling with the adjacent ^{13}C atom in the -CH_2- group. In addition, the group containing the ^{13}C tracer atom has a minus signal in the DEPT135 spectrum, indicating that it is the methylene group (-CH_2-). These confirm that the C atom of -CH_2- group was from $^{13}CO_2$. The $^1J_{CC}$ value is 37 Hz and coincides well with that of ethanol in the literature.

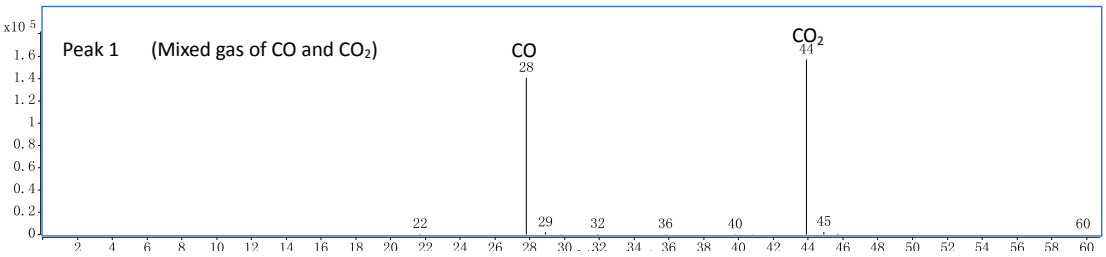
(3) The ^{1}H, ^{13}C-HSQC NMR spectrum *(d)* demonstrates the linkage between the protons and corresponding C atoms in the ethanol molecule. The ^{1}H, ^{13}C-HMBC NMR spectrum *(e)* illustrates the linkage between protons in the methyl group (CH_3-) and C atom in the methylene (-CH_2-) group.

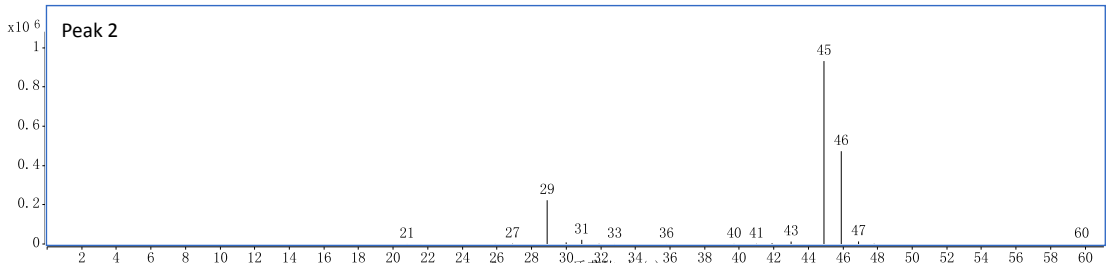
References

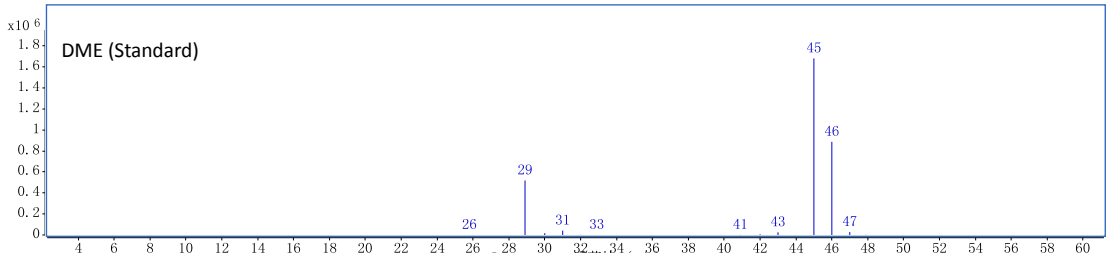
[1] E. Pretsch, P. Buhlmann, C. Affolter, Structure determination of organic compounds, Tables of spectral data, 3rd, Springer, 2000

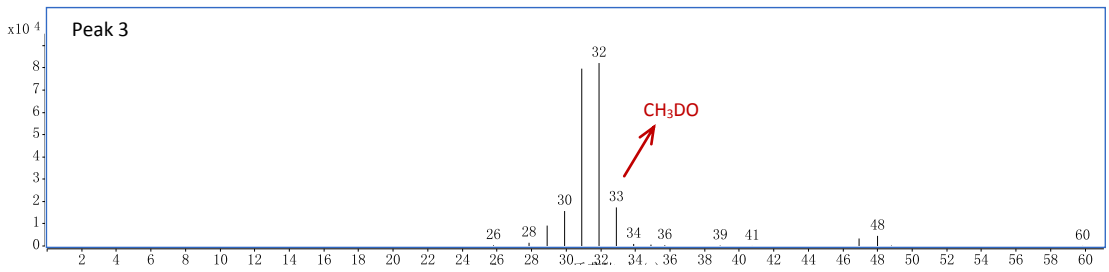
[2] E. Breitmaier, W. Voelter, Carbon-13 NMR spectroscopy, High-Resolution Methods and Applications in Organic Chemistry and Biochemistry, 3rd, VCH, 1987

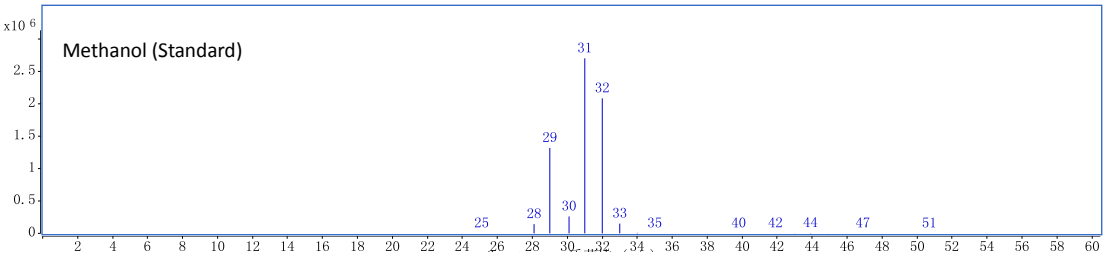

TIC (2 MPa D2)
1
2
3
4


Peak 1 (Mixed gas of CO and CO2)
CO
CO2


Peak 2


DME (Standard)


Peak 3
CH3DO


Methanol (Standard)

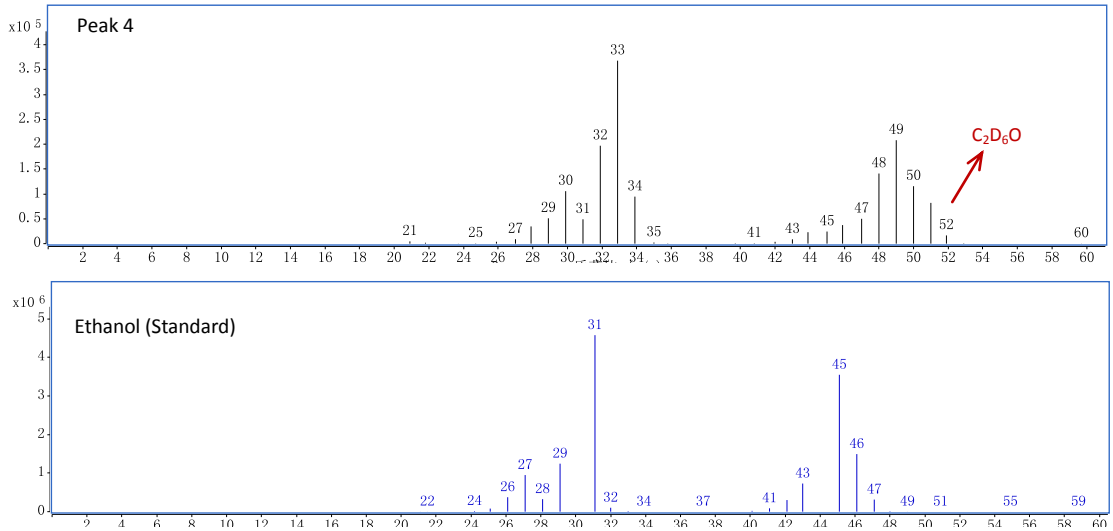


Figure S14. The GC-MS spectra of liquid sample of the reaction using 2 MPa D_2 instead of H_2. Other reaction condition is the same as that given in Entry 1 of Table 1.

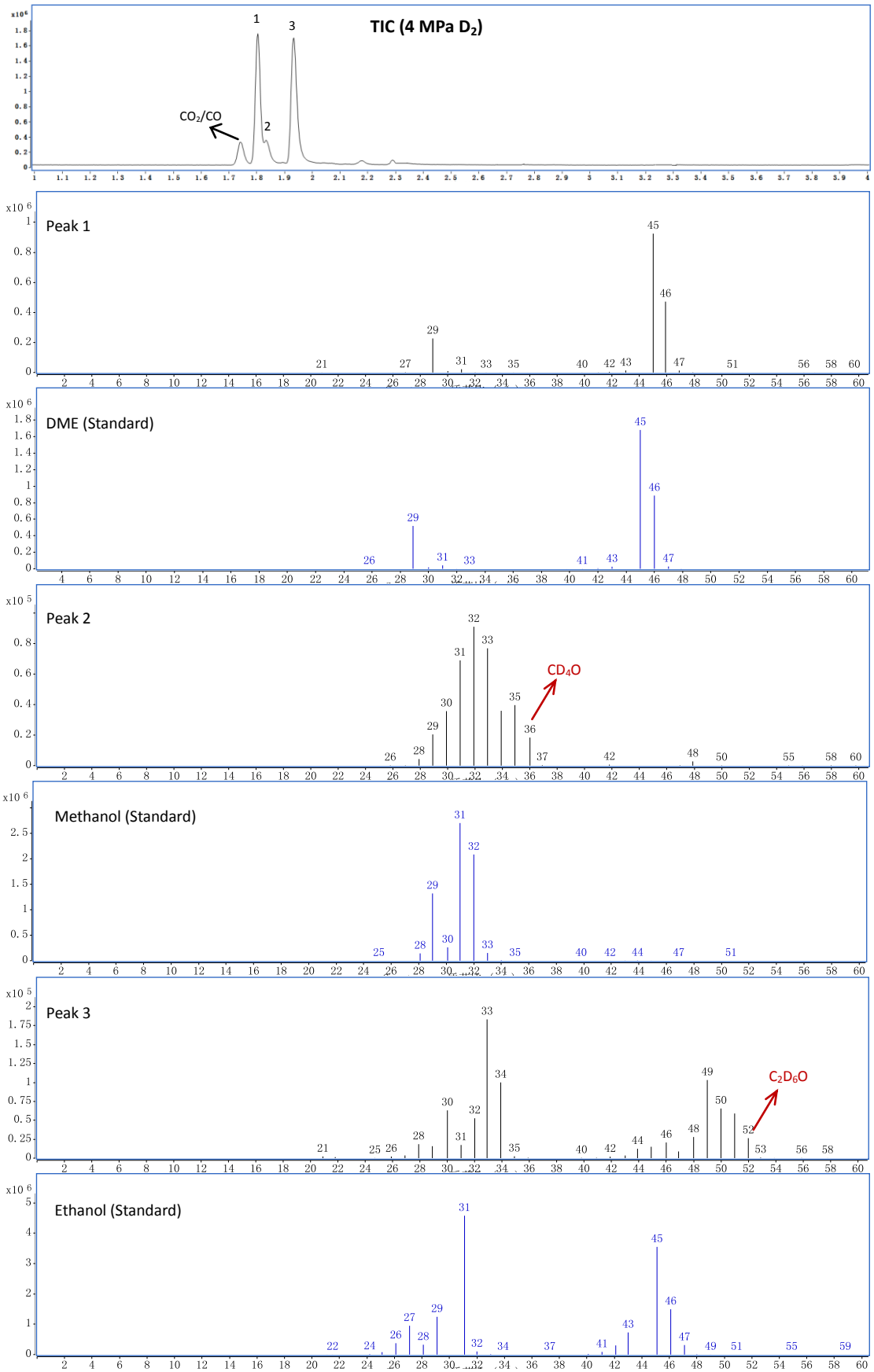


Figure S15. The GC-MS spectra of liquid sample of the reaction using 4 MPa D_2 instead of H_2. Other reaction condition is the same as that given in Entry 1 of Table 1.

The following conclusions can be obtained from D_2 tracer test.

1. The H atoms in the unreacted DME molecules were intact.
2. The D atoms could enter the methanol generated in the reaction. When the D_2 pressure was 2 MPa, only one D atom entered into a methanol molecule. When the D_2 pressure was elevated to 4 MPa, four D atoms could enter into a methanol molecule.
3. The D atoms could enter the ethanol generated in the reaction. Six D atoms could enter into one ethanol molecule, and the ratio of ethanol molecules with 6 D atoms increased when the D_2 pressure was elevated from 2 MPa to 4 MPa.

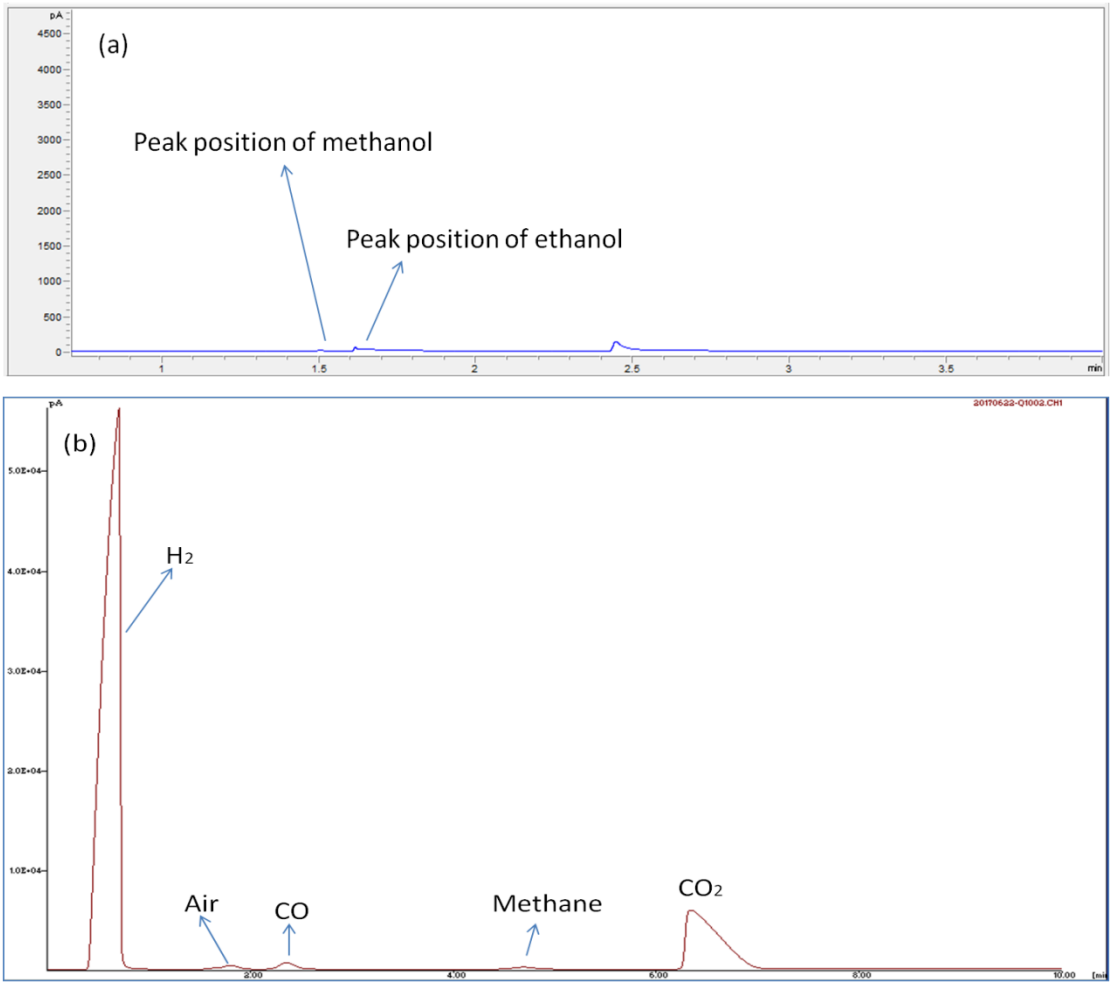


Figure S16. The GC traces of the liquid sample (a) and gaseous sample (b) after reaction of CO_2 and H_2 catalyzed by Ru catalyst. Reaction conditions: 30 μmol $Ru(PPh_3)_3Cl_2$, 2.3 mmol LiI, 2 mL DMI, 4 MPa CO_2 and 4 MPa H_2 (at room temperature), 180 ^oC, 12 h.

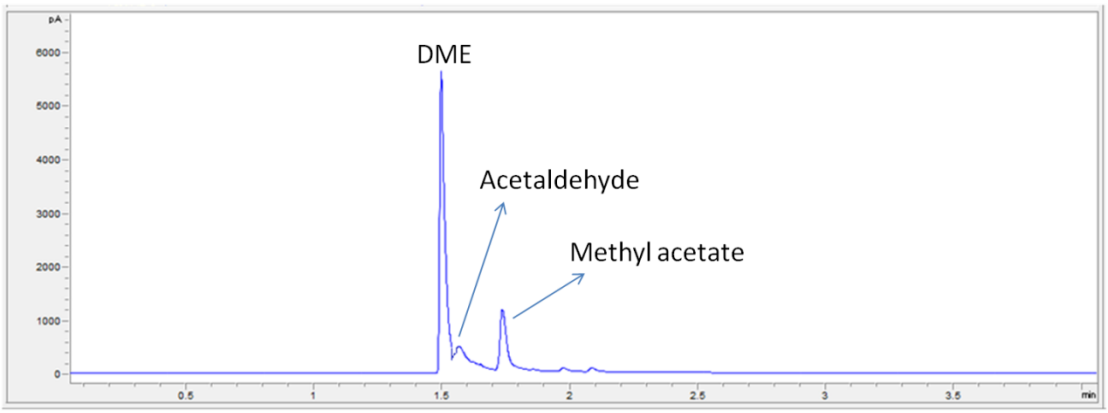


Figure S17. The GC traces of the liquid sample after reaction of DME with CO and H_2. Reaction conditions: 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 0.5 MPa DME, 0.5 MPa CO and 4 MPa H_2 (at room temperature), 180 ^{o}C, 12 h.

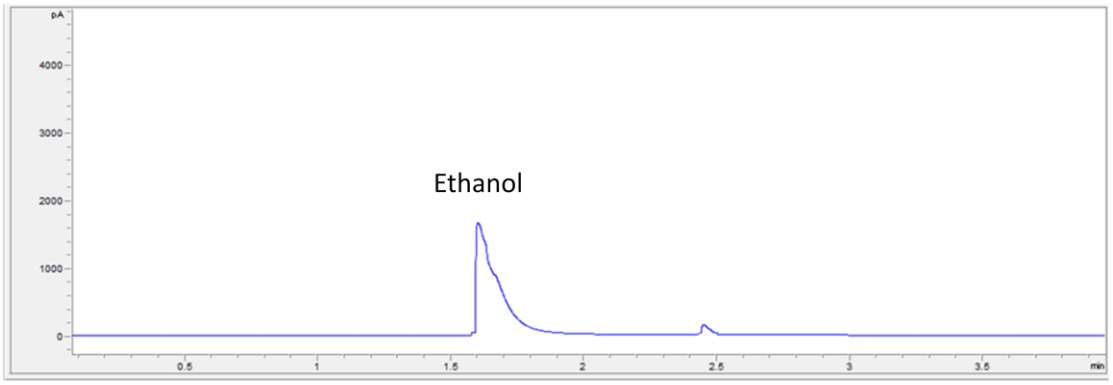


Figure S18. The GC traces of the liquid sample after the reaction of acetaldehyde and H_2 catalyzed by $Ru(PPh_3)_3Cl_2$. Reaction condition: 30 μmol $Ru(PPh_3)_3Cl_2$, 2.3 mmol LiI, 2 mL DMI, 2 mmol acetaldehyde, 4 MPa H_2 (at room temperature), 140 ^oC, 30 min.

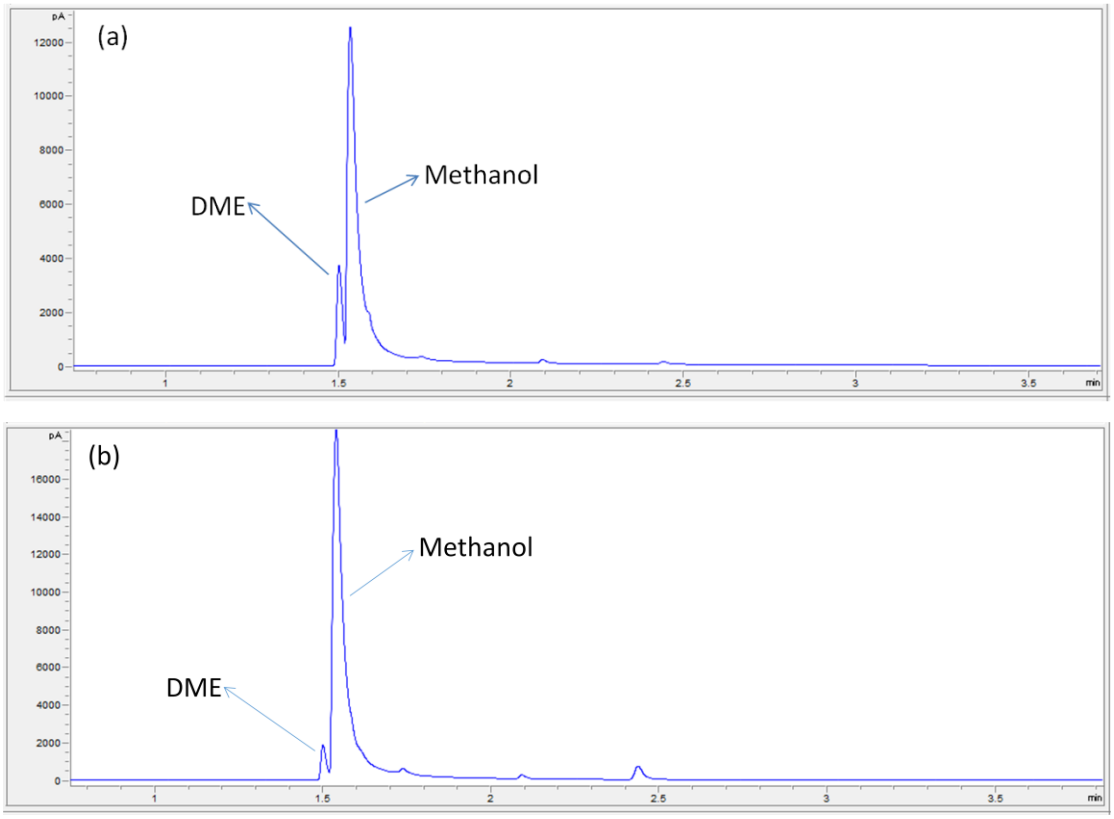


Figure S19. The GC traces of the liquid sample after reaction of methanol itself catalyzed by 30 μmol $Ru(PPh_3)_3Cl_2$ (a) and 70 μmol CoI_2 (b) respectively. Other reaction conditions: 2.3 mmol LiI, 2 mL DMI, 12 mmol methanol, 180 ^oC, 5 h.

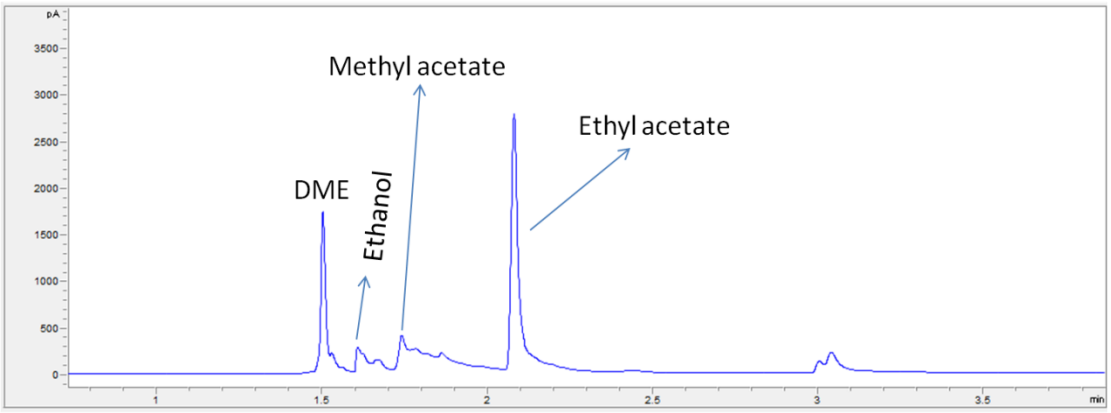


Figure S20. The GC traces of the liquid sample after reaction of DME with CO and H_2. Reaction conditions: 30 μmol $Ru(PPh_3)_3Cl_2$ and 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 0.5 MPa DME, 2 MPa CO and 4 MPa H_2 (at room temperature), 180 ^oC, 12 h.

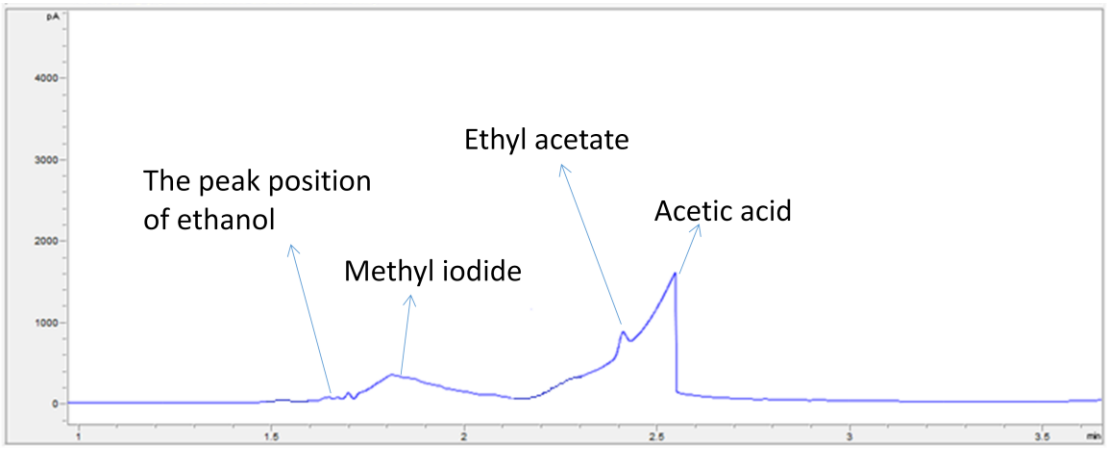


Figure S21. The GC traces of the liquid sample after reaction of DME with CO and H_2. Reaction conditions: 30 μmol $Ru(PPh_3)_3Cl_2$ and 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 0.5 MPa DME, 4 MPa CO and 4 MPa H_2 (at room temperature), 180 ^oC, 12 h.

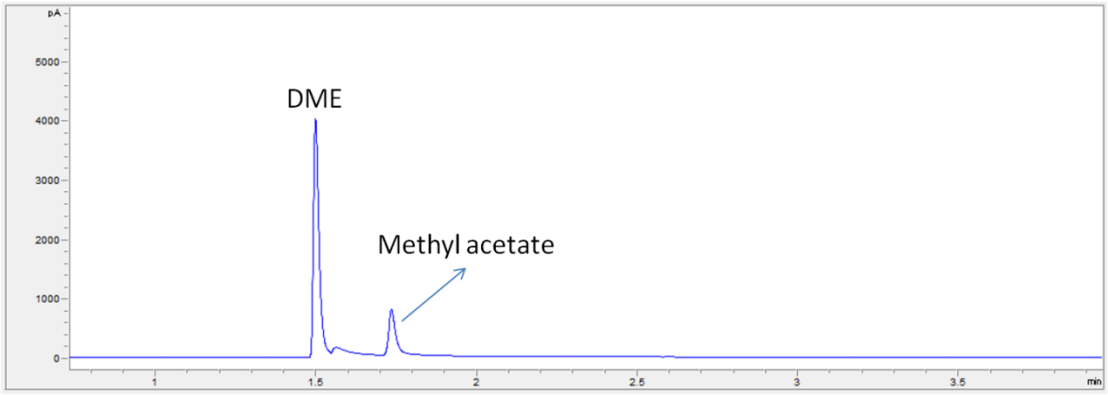


Figure S22. The GC traces of the liquid sample after reaction of DME and CO. Reaction conditions: 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 0.5 MPa DME, 1 MPa CO (at room temperature), 180 ^{o}C, 12 h.

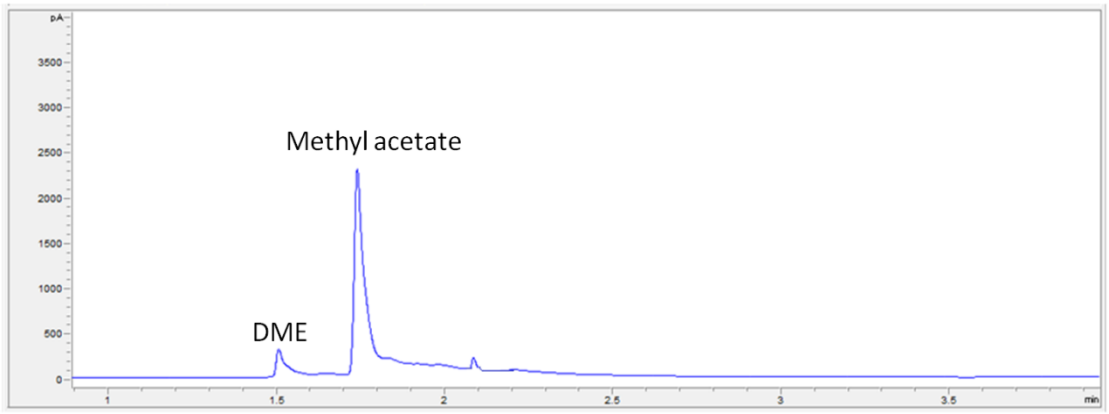


Figure S23. The GC traces of the liquid sample after reaction of methyl acetate itself. Reaction conditions: 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 2 mmol methyl acetate, 180 ^{o}C, 12 h.

Table S1. The performance of some reported catalysts for CO_2 hydrogenation to ethanol.

Entry	Catalyst	Temp (^oC)	Activity (based on CO_2)	Ethanol Sel. (C-mol%)	Ref.
1	Rh-Fe/SiO_2	260	4.3 mol $g_{cat}^{-1}h^{-1}$	16.0	7
2	Li/RhY	250	35.1 mmol $g_{cat}^{-1}h^{-1}$	2.7	8
3	$Rh_{10}Se/TiO_2$	250	2.3 mmol $g_{cat}^{-1}h^{-1}$	83.0	9
4	Fe:Cu:Al:K + Cu:Zn:Al:K (mixed catalyst)	330	173.0 mol $L^{-1}h^{-1}$	14.8	10
5	Rh/silicate + Fe:Cu:Al:K (mixed catalyst)	350	229.7 mol $L^{-1}h^{-1}$	9.3	11
6	CoMoS	340	121 g $kg_{cat}^{-1}h^{-1}$	5.5	12
7	$CuZnFe_{0.5}K_{0.15}$	300	0.17 g $mL^{-1}h^{-1}$ (alcohols)	19.1	13
8	PPNCl-$Ru_3(CO)_{12}$-$Co_4(CO)_{12}$ -LiBr	200	33.7 mmol $L^{-1}h^{-1}$ (alcohols)	87.5 (in alcohols)	14
9	$Ru_3(CO)_{12}$-$Rh_2(CO)_4Cl_2$-LiI	200	12.9 mmol $L^{-1}h^{-1}$ (alcohols)	41.9 (in alcohols)	15
10	$Ru_3(CO)_{12}$-$Co_2(CO)_8$-KI	200	0.7 h^{-1} (ethanol, Ru)	15.0	16
11	Pt/Co_3O_4	200	0.5 mmol $g_{cat}^{-1}h^{-1}$ (alcohols)	57.0 (in alcohols)	17
12	$Ru_3(CO)_{12}$-$Co_2(CO)_8$-LiI (methanol substrate)	180	1.1 h^{-1} (ethanol, Ru)	34.2	18a
13	$Ru(acac)_3$-$CoBr_2$,-LiI (paraformaldehyde substrate)	180	17.9 h^{-1} (ethanol, Ru)	50.9	18b
14	Pd_2Cu	200	359.0 h^{-1} (Pd)	92.0	20

2. Calculation of the space time yield (STY):

The STY is defined as mmol of C in reaction products per liter of solvent per hour. Taking the experiment in Entry 1 of table 1 as an example: The products (ethanol, methanol, CO and methane) generated in the reaction were 1.14mmol, 0.13mmol, 0.45mmol and 0.32mmol respectively, and total mmols of C in the products was $2 \times 1.14 + 0.13 + 0.45 + 0.32 = 3.18$ C mmol. The reaction time was 12 h and the solvent volume was 2 mL (0.002 L). The STY of this experiment = $3.18/(0.002 \times 12) = 132.5$C-mmol$L^{-1}h^{-1}$.