SUPPORTING INFORMATION

In situ hydrogenation of the captured CO_2 to formate with polyethyleneimine and Rh/monophosphine system

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1. General experimental methods

Materials

Metal salts and ligands were obtained commercially from J&K Chemical and Aladdin without further purification. The solvents of chromatographically purity were obtained commercially and distilled prior to use.

Procedure of CO_2 capture

CO_2 capture was carried out in a 10 mL glass tube. The absorbents were charged into the reactor at room temperature. Then, the air in the flask was replaced by CO_2 and a needle was used for CO_2 bubbling, which was inserted in the bottom of the glass. The absorption reaction was conducted with a CO_2 bubbling rate of 0.1 L/min. The amount of CO_2 absorbed was determined by an Analytical Balance within an accuracy of ±0.0001 g every five minutes.

Procedure of CO_2 hydrogenation

The manipulations were performed in a recirculating mBraun MBio compact inert atmosphere (Ar) drybox at 20 ºC. The reaction was carried out in a 50 mL stainless-steel autoclave reactor with an inner glass and a magnetic stirrer. The reaction mixture consisting of methanol (3 mL), $RhCl_3 \cdot 3H_2O$ and the ligand was transferred to the inner glass and stirred for 10 min. PEI_{600} (0.5 mmol, 0.3 g) was added dropwise to the mixture as stirring. After sealing the autoclave reactor cover, H_2 and CO_2 were introduced to the system with the initial pressure of 4 MPa and 4 MPa, respectively. The reactive mixture was stirred for 16 h-32 h at 60 ^oC. After the reaction was completed, the reactor was cooled to room temperature. The excess gas was depressurized very slowly in ice water. The resultant mixture was analyzed by NMR spectroscopy with 1,1,2,2-tetrachloromethane as the internal standard, and the formic acid can be separated by distillation.

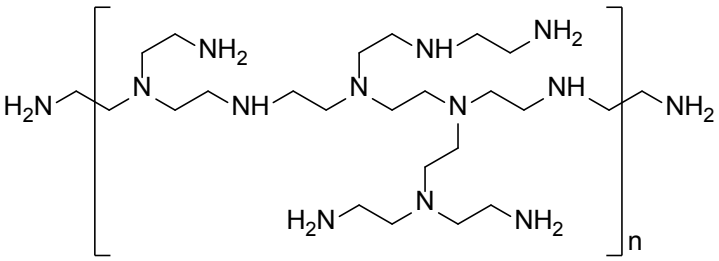
Procedure of CO_2 capture and subsequent hydrogenation

CO_2 capture was carried out in a 10 mL glass tube initially. The absorbents were charged into the reactor at room temperature. Then, the air in the flask was replaced by CO_2 and a needle was used for CO_2 bubbling, which was inserted in the bottom of the glass. The absorption reaction was conducted with a CO_2 bubbling rate of 0.1 L/min. The amount of CO_2 absorbed was determined by an Analytical Balance within an accuracy of ±0.0001 g every five minutes. Then, the manipulations were performed under Ar atmosphere. The product of CO_2 capture was dissolved in methanol, $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg) and $CyPPh_2$ (0.05 mmol, 13 mg) were transferred to the glass tube. The tube was placed into the 50 mL stainless-steel autoclave. After sealing the autoclave reactor cover, H_2 was led into the system with the initial pressure of 4 MPa. The reactive mixture was stirred for 16 h at 60 ^oC, and with the same post-processing and analysis method as obove.

Instruments

^1H NMR spectra was recorded at Bruker 400 or Varian Mercury-Plus 400 spectrometer in $CDCl_3$, D_2O or CD_3OD and TMS (0 ppm) was used as internal reference. ^{13}C NMR was recorded at 100.6 MHz in $CDCl_3$ or D_2O and $CDCl_3$ (77.0 ppm) was used as internal reference. ^{31}P NMR (162 MHz, $CDCl_3$) chemical shifts were measured relative to an external orthophosphoric acid standard. *In situ* FTIR was collected on a Mettler Toledo React IR ic10, Diamond ATR probe, using ic IR analysis system. The probe is placed in the middle of the reaction mixture, which is constantly stirred by magnetic whisk, and the spectra are collected *in situ* during the whole process. GC-MS analyses were performed on SHIMADZU GCMS-QP2010 SE and GC equipped with a capillary column (Rxi-5MS, 30 m × 0.25 μm). ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. Infrared (IR) spectra were recorded on a Bruker Tensor27 FT-IR spectropho-tometer with KBr pellets.

2. *Scheme 1, Table S1-S2 and Figures S1-S12*

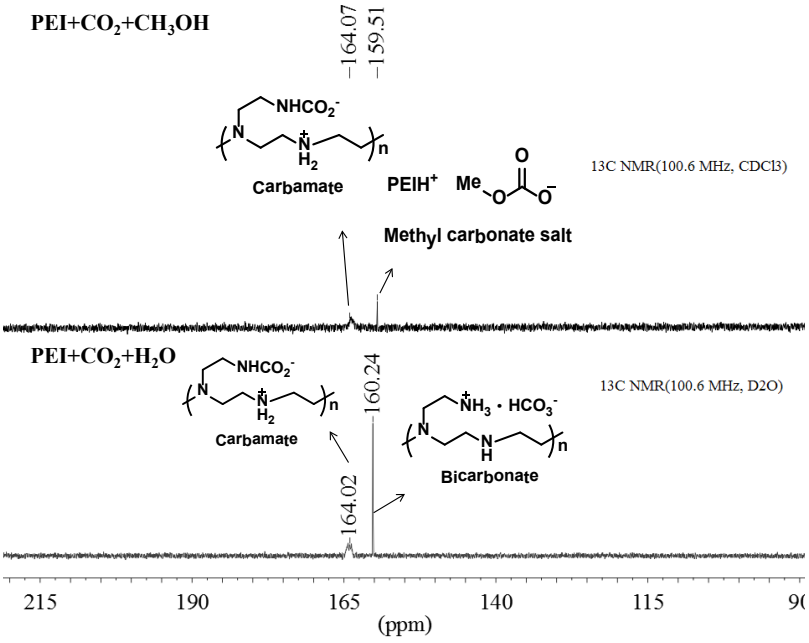


Scheme S1 Structure of PEI ($H_2NCH_2[C_{22}H_{56}N_{11}]_nCH_2NH_2$).

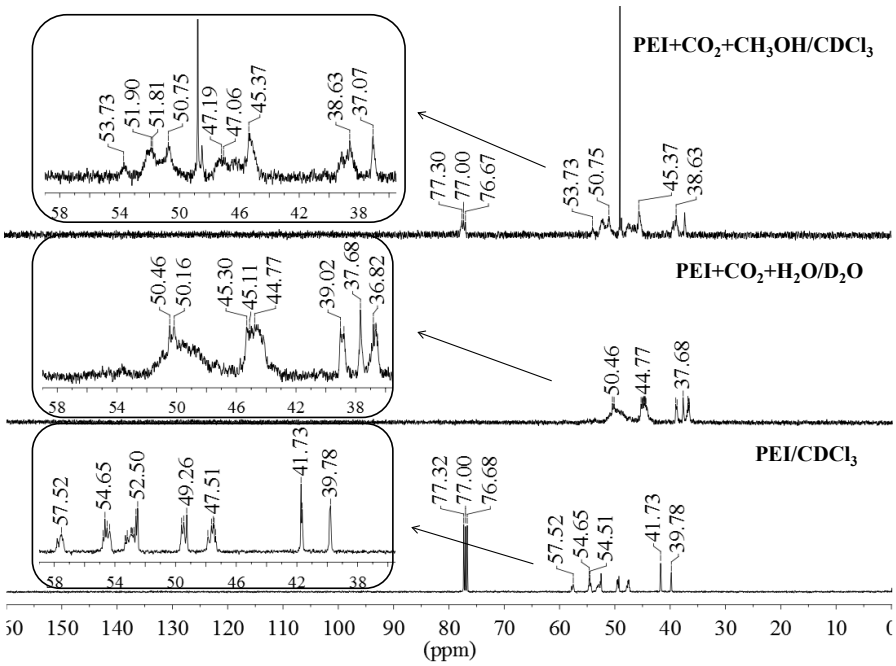
Table S1 Metal salts effect.[a]

Entry	Metal salt	TON[b]	$HCOO^-PEIH^+$ N(mmol)[b]
1	$RhCl_3 \cdot 3H_2O$	852	4.26
2	$RuCl_3 \cdot 6H_2O$	278	1.39
3	$NiCl_2 \cdot 6H_2O$	n.d.	n.d.
4	$PdCl_2$	23	0.115
5	$Fe(BF_4)_2 \cdot 6H_2O$	n.d.	n.d.
6	$Rh(acac)_3$	19	0.095

[a]Conditions (50 mL autoclave): metal salt (0.005 mmol, 1.3 mg), $CyPPh_2$ (0.05 mmol, 13 mg), PEI_{600} (0.5 mmol, 0.3 g), methanol (3 mL), CO_2 (4 MPa), H_2 (4 MPa), 60 °C, 16 h; [b]Calculated by ^1H NMR using 1,1,2,2-tetrachloromethane as internal standard, TON = turnover number (moles of formate per mole of transition metal catalyst).

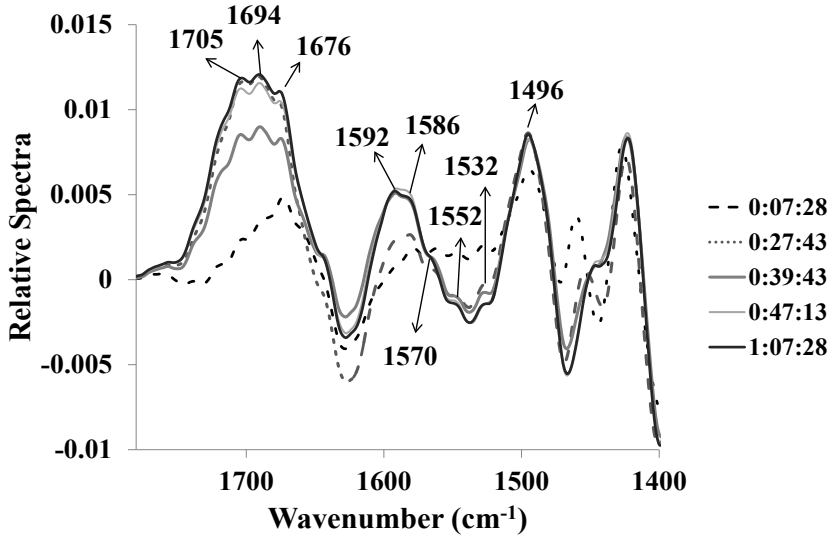


(a)



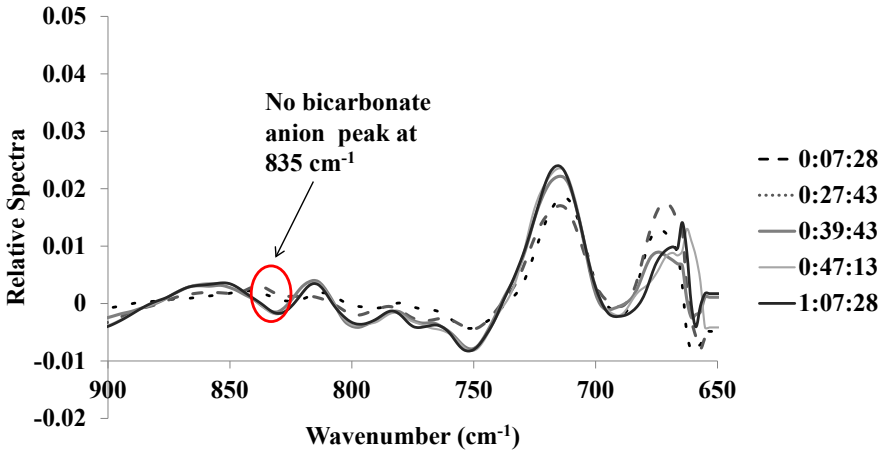
(b)

Figure S1 ^{13}C NMR spectrum of CO_2 capture by PEI_{600} in methanol or H_2O (100.6 MHz). Conditions: PEI_{600} (0.5 mmol, 0.3 g), H_2O (3 mL) or methanol (3 mL), CO_2 was bubbled to the solution.



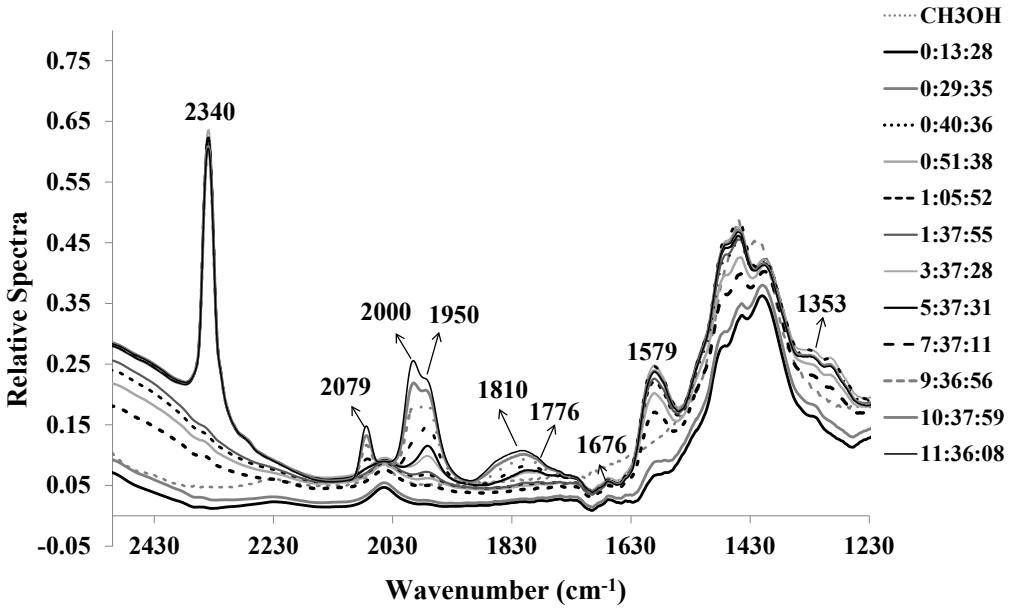
(a)

Wavenumber (cm $^{-1}$)	Assignment	Species	Wavenumber (cm $^{-1}$) in Ref.
1676-1705	C=O stretching	$RNHCOO^-$	1666 [1], 1672 [2]
1570	C=O stretching vibration	$MeOCO_2^-$	1572 [3]
1592-1586	N-H asymmetric deformation	RNH_3^+, $RR'NH_2^+$	1600 [4]
1552-1523	N-H symmetric deformation	RNH_3^+, $RR'NH_2^+$	1539 [5]
1496	N-H bending vibration	$NHCOO^-$	1496 [2]



(b)

Figure S2 *In situ* FT-IR 2nd derivative spectrum of CO_2 capture by PEI_{600}. Conditions: PEI_{600} (0.5 mmol, 0.3 g), methanol (3 mL), CO_2 (4 MPa), 1.5 h. The spectrum of methanol was subtracted.



Wavenumber (cm $^{-1}$)	Assignment	Wavenumber (cm $^{-1}$) in Ref.
2340	CO_2	2380-2400 [1]
2079-1950	Rh-H stretching vibration	1900-2150 [6]
1810-1776	C=O stretching vibration in formic acid and derivatives	1725 [6]
1676	C=O stretching in $RNHCOO^-$	1666 [1], 1672 [2]
1579, 1353	C=O vibration in formato-Rh complexes	1567, 1361 [6]

Figure S3 Monitoring of the reaction process by *in situ* FT-IR under CO_2 pressure. Conditions: $RhCl_3 \cdot 3H_2O$ (0.03 mmol, 7.9 mg), $CyPPh_2$ (0.3 mmol, 80 mg), PEI_{600} (1.5 mmol, 0.9 g), methanol (9 mL), H_2 (4 MPa), CO_2 (4 MPa), 60 ^oC, 13 h. The spectrum of PEI_{600} was subtracted.

2340 cm^{-1} can be assigned to gaseous CO_2 peak.

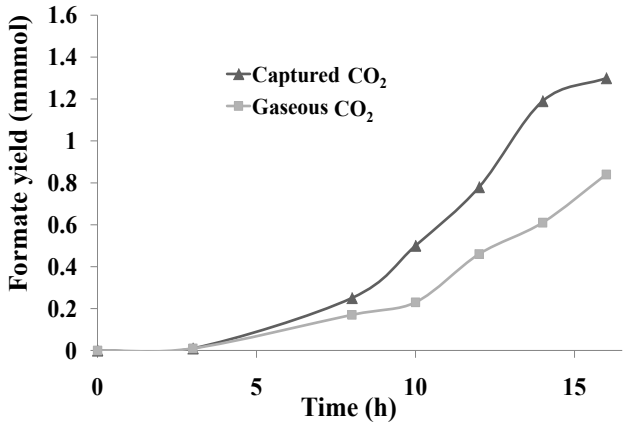


Figure S4 Formate yield comparison between hydrogenation of the captured CO_2 and equivalent gaseous CO_2. Conditions: $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg), $CyPPh_2$ (0.05 mmol, 13 mg), methanol (2 mL), H_2 (4 MPa), 60 ^{o}C, Captured CO_2 (3.6 mmol) by PEI_{600}/glycol (0.5/18 mmol), or Gaseous CO_2 (0.2 MPa, 3.6 mmol) with glycol (18 mmol, 1 mL) and PEI_{600} (0.5 mmol, 0.3 g).

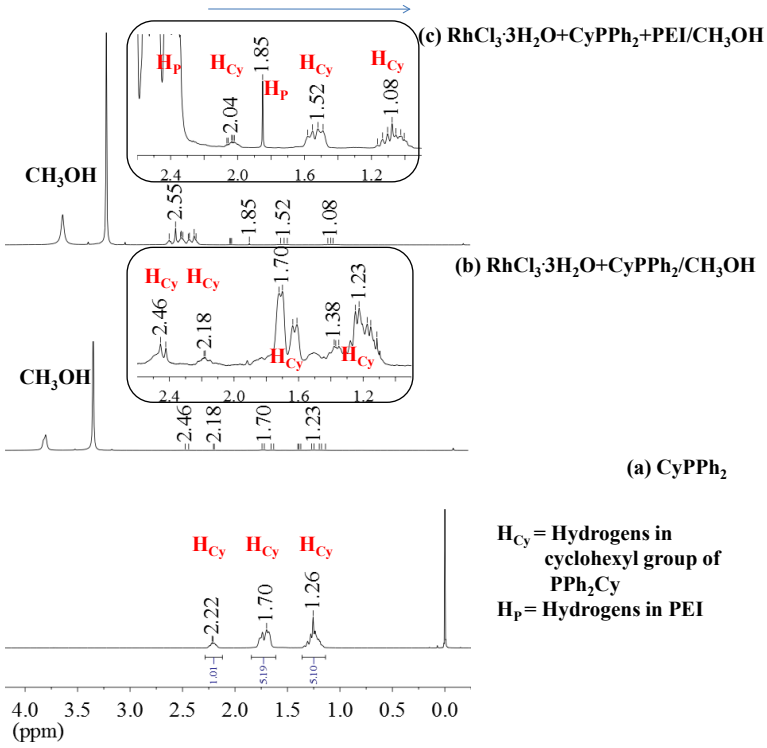


Figure S5 Comparison of ^{1}H NMR spectrums shifts of $CyPPh_2$ in different catalytic solutions (400 MHz, $CDCl_3$). Conditions: $RhCl_3 \cdot 3H_2O$ (0.01 mmol, 2.6 mg), $CyPPh_2$ (0.1 mmol, 26 mg), PEI_{600} (0.5 mmol, 0.3 g), methanol (3 mL).

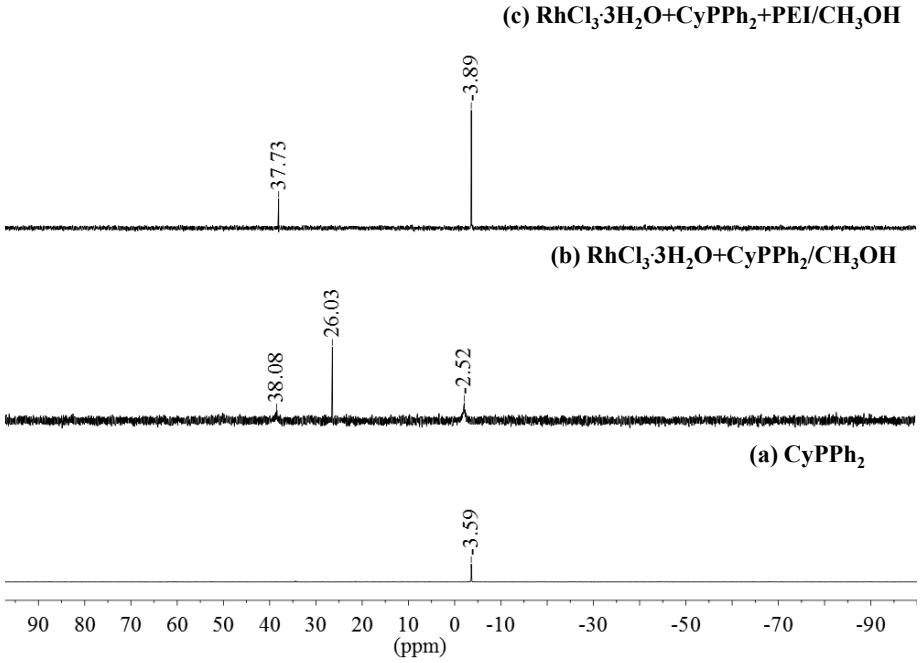
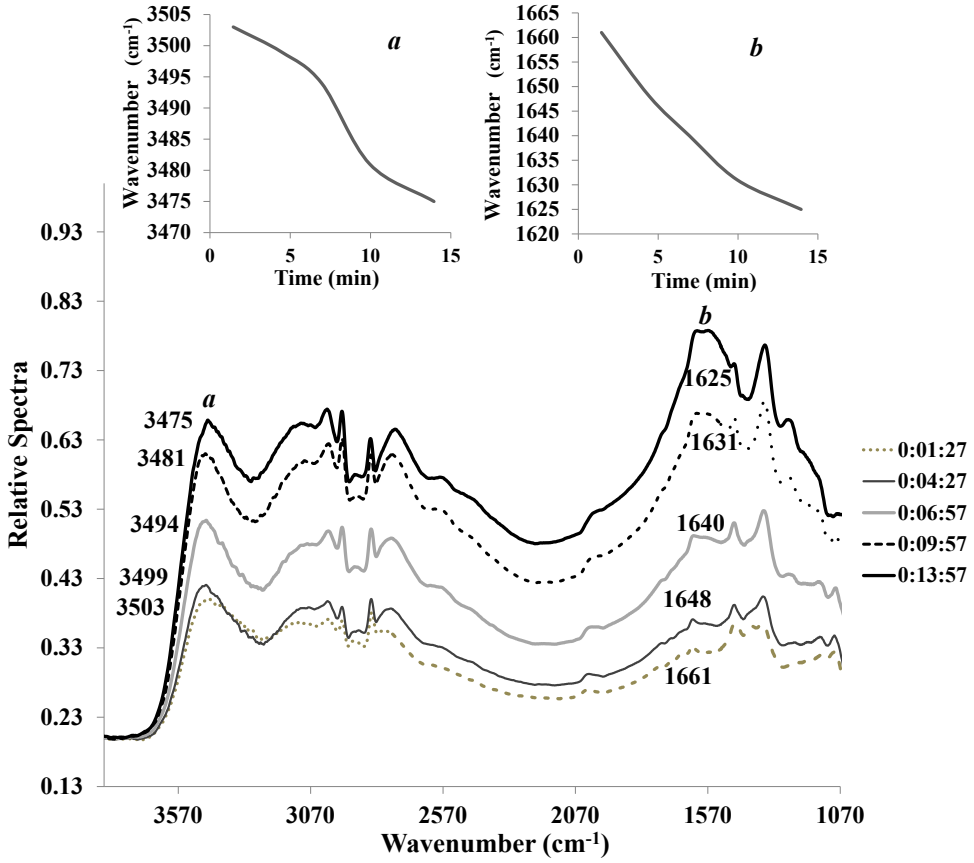
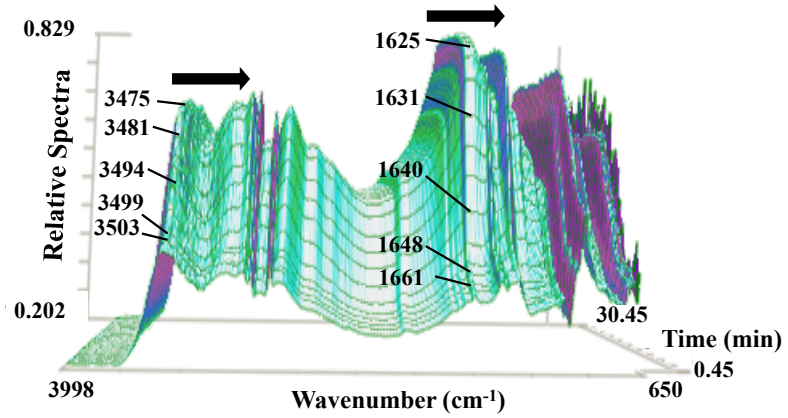


Figure S6 ^{31}P NMR spectrums comparison using $CyPPh_2$ (162 MHz, $CDCl_3$). Conditions: $RhCl_3 \cdot 3H_2O$ (0.01 mmol, 2.6 mg), $CyPPh_2$ (0.1 mmol, 26 mg), PEI_{600} (0.5 mmol, 0.3 g), methanol (3 mL).

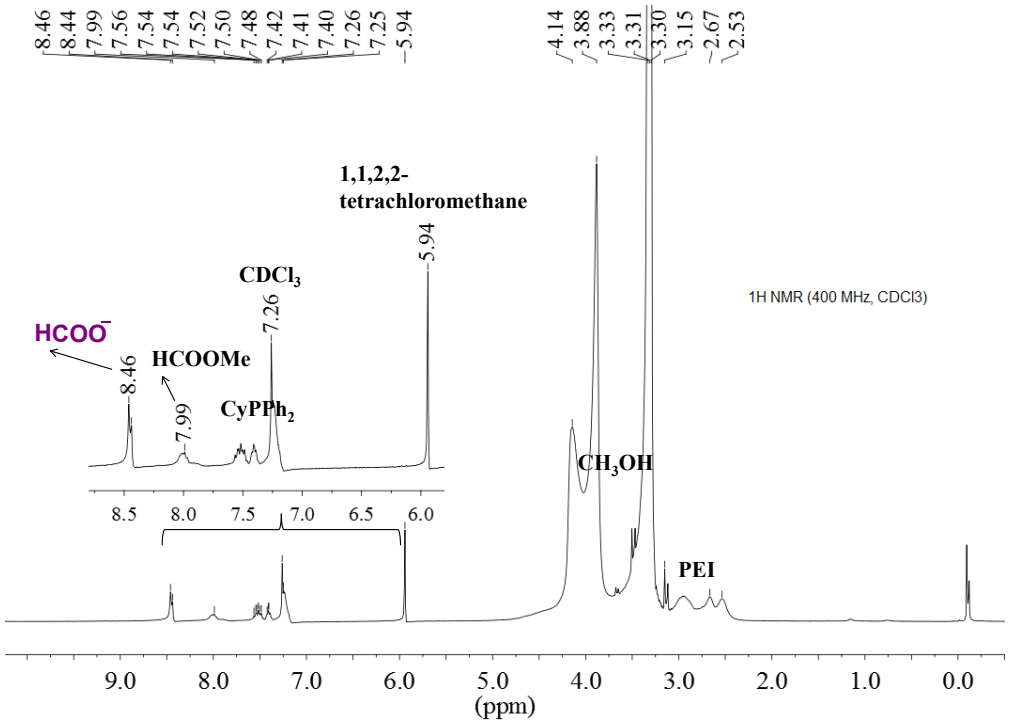


(a)



(b)

Figure S7 *In situ* FT-IR spectrum of the mixture in the absence of CO_2 and hydrogen. Conditions: $RhCl_3 \cdot 3H_2O$ (0.02 mmol, 5.2 mg), $CyPPh_2$ (0.2 mmol, 53 mg), PEI_{600} (1 mmol, 0.6 g), methanol (6 mL), 1.5 h. The spectrum of the mixture of $CyPPh_2$ and CH_3OH was subtracted.



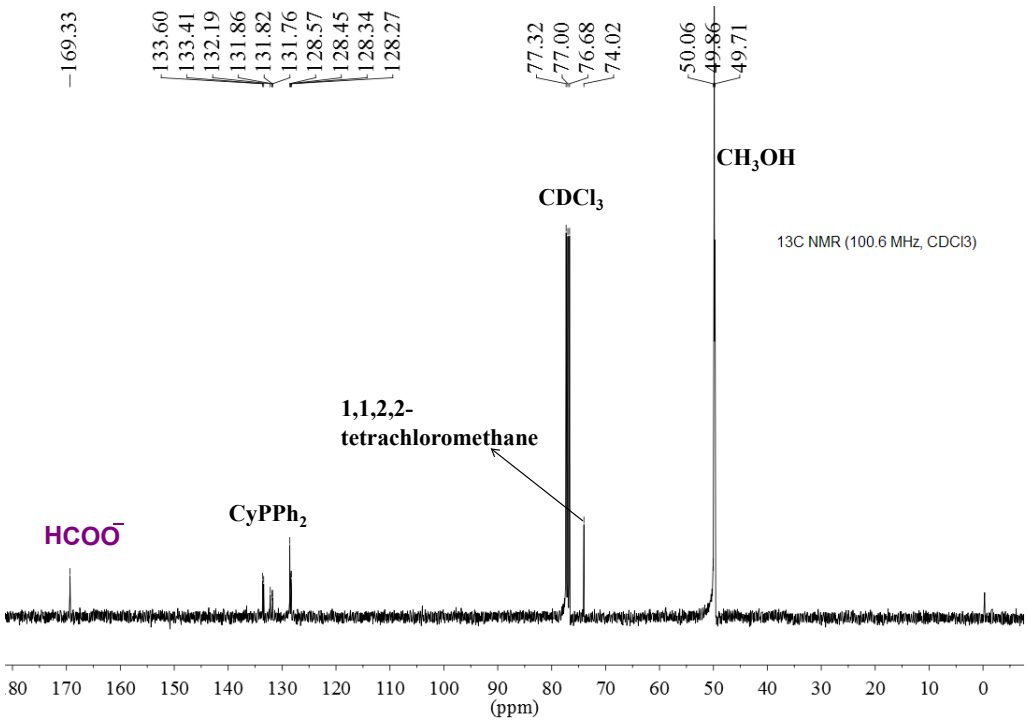
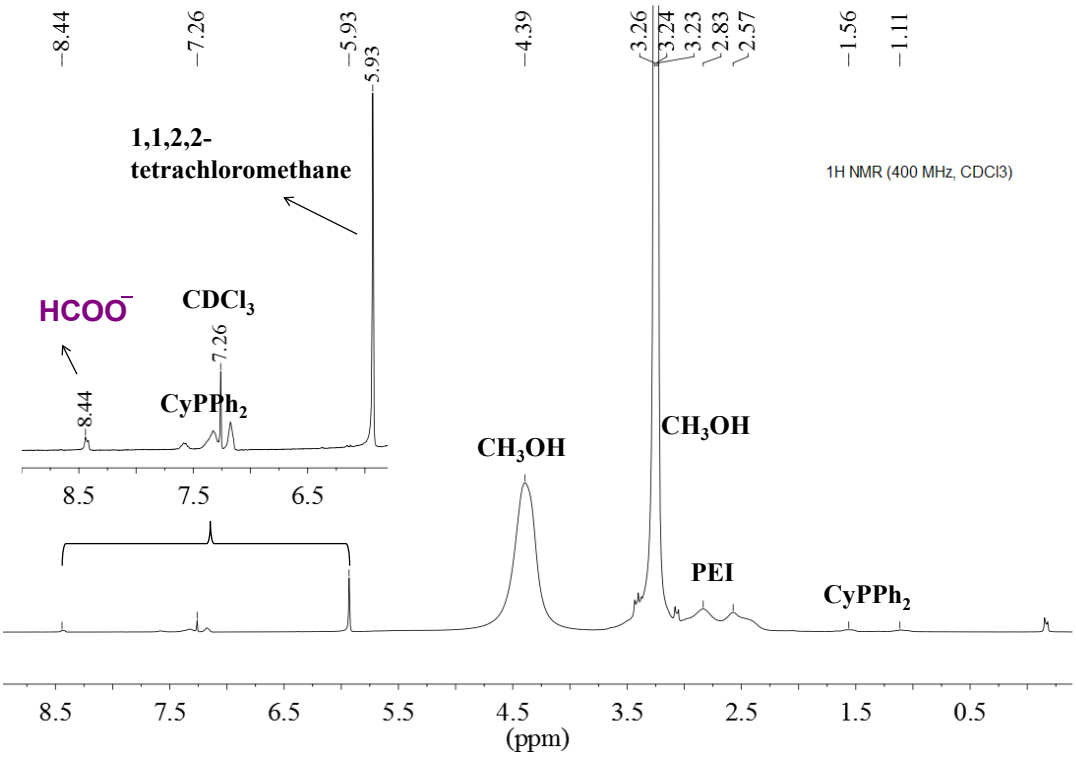


Figure S8 ^{1}H NMR and ^{13}C NMR spectrums for reaction mixture of gaseous CO_2 hydrogenation. Conditions: $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg), $CyPPh_2$ (0.05 mmol, 13 mg), PEI_{600} (0.5 mmol, 0.3 g), methanol (3 mL), H_2 (4 MPa), CO_2 (4 MPa), 60 °C, 16 h, internal standard: 1,1,2,2-tetrachloromethane as internal standard.



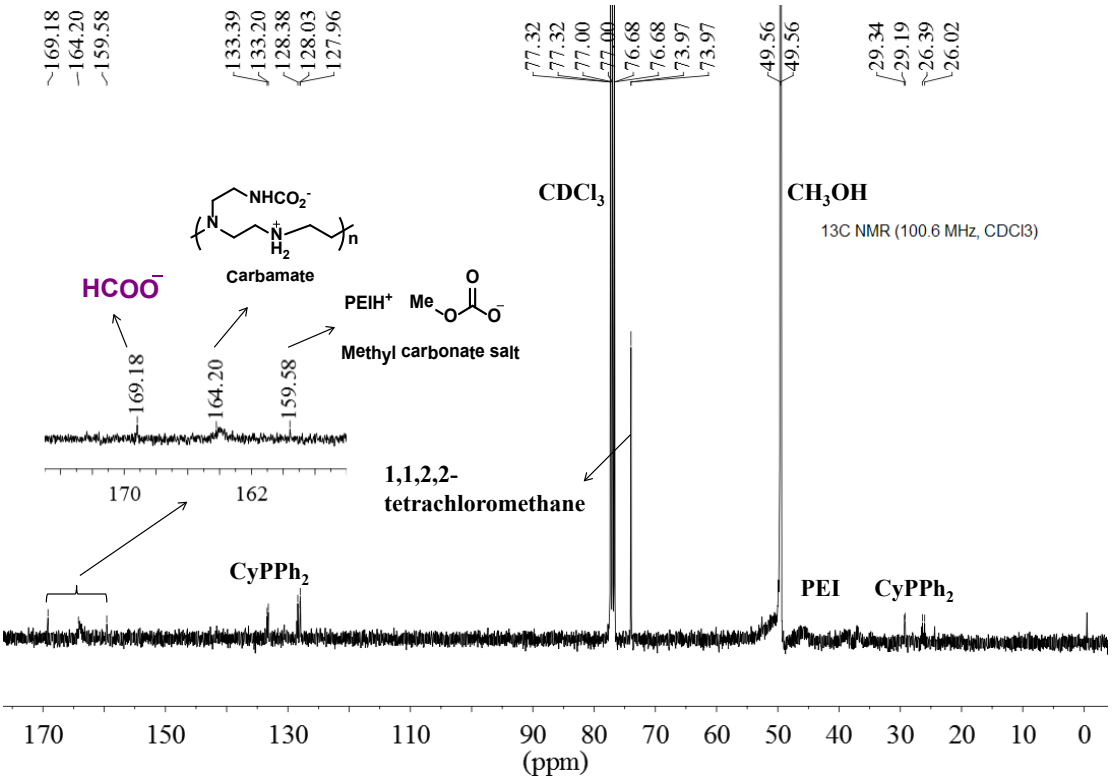
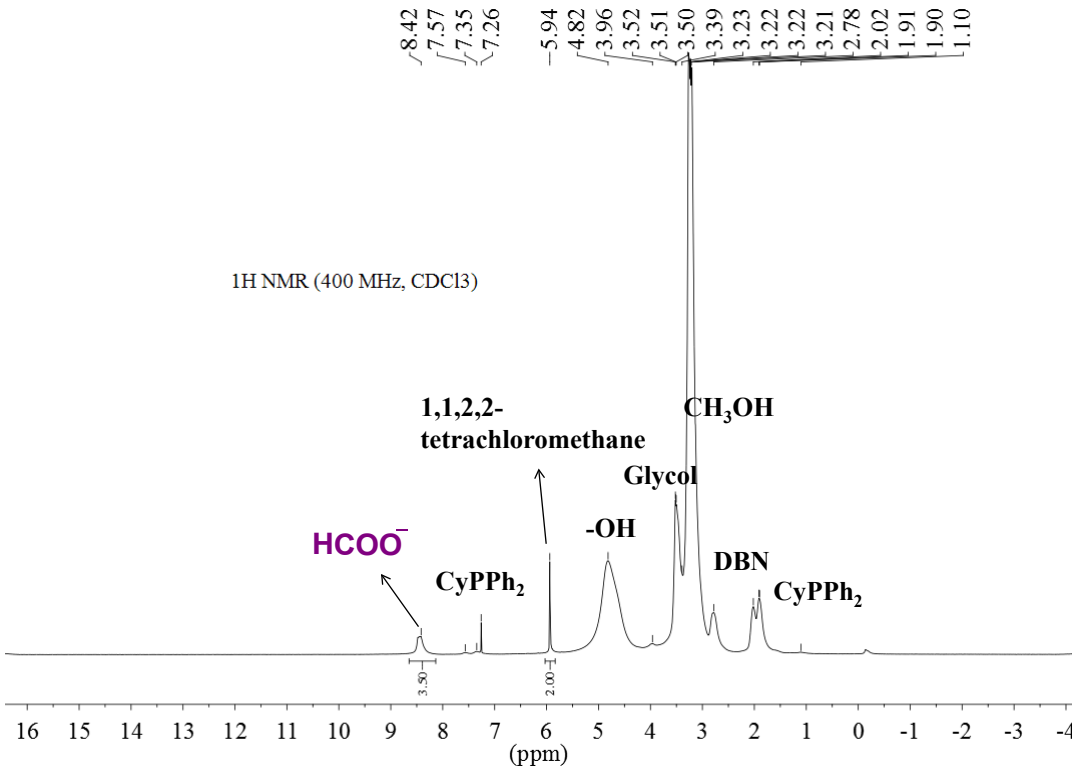


Figure S9 ^{1}H NMR and ^{13}C NMR spectrums for reaction mixture of captured CO_2 hydrogenation. $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg), $CyPPh_2$ (0.05 mmol, 13 mg), PEI_{600}/glycol + CO_2 (molar ratio 1:36:7.2) (0.5 mmol), methanol (2 mL), H_2 (4 MPa), 60 ^{o}C, 16 h, internal standard: 1,1,2,2-tetrachloromethane as internal standard.



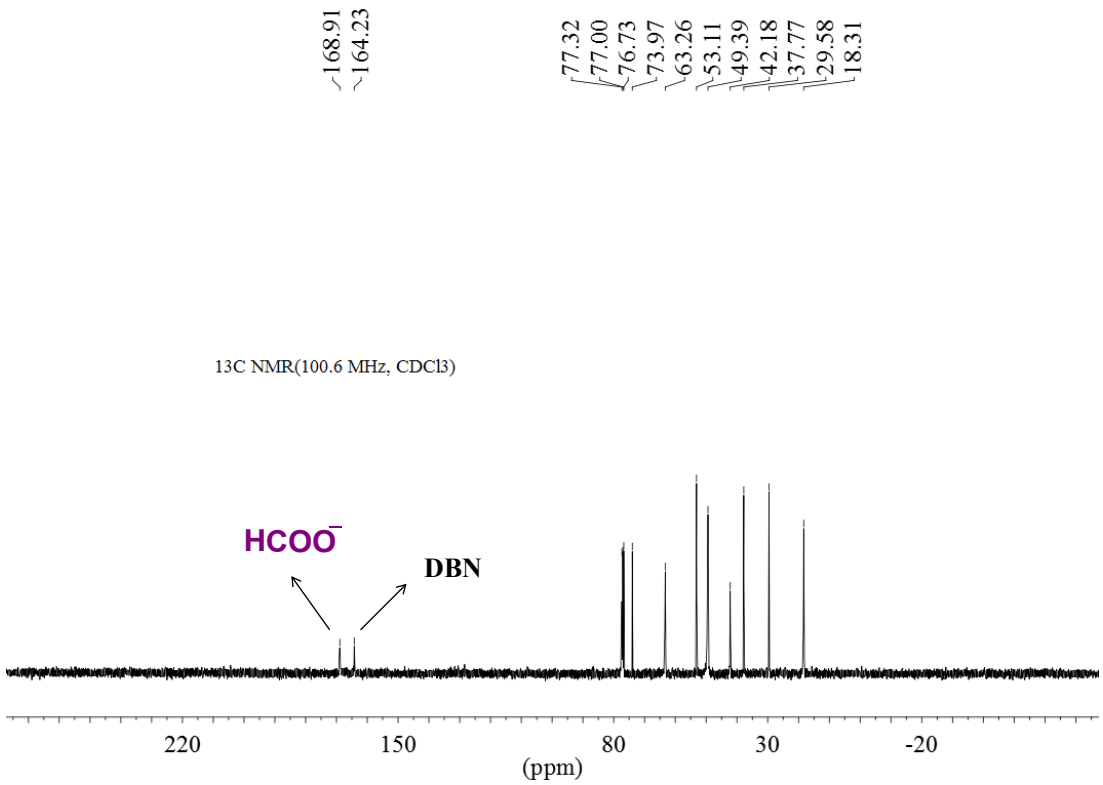
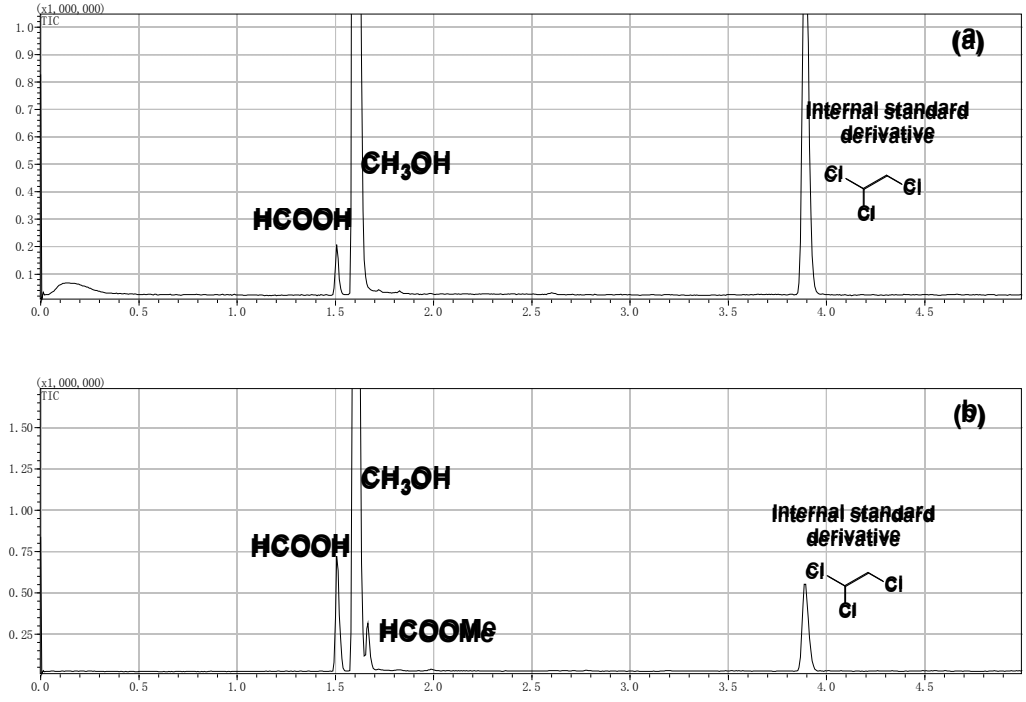


Figure S10 ^{1}H NMR and ^{13}C NMR spectrums for reaction mixture of captured CO_2 hydrogenation. $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg), $CyPPh_2$ (0.05 mmol, 13 mg), DBN/glycol + CO_2 (molar ratio 1:1.2:1.1) (5 mmol), methanol (3 mL), H_2 (4 MPa), 60 ^{o}C, 16 h, internal standard: 1,1,2,2-tetrachloromethane as internal standard.



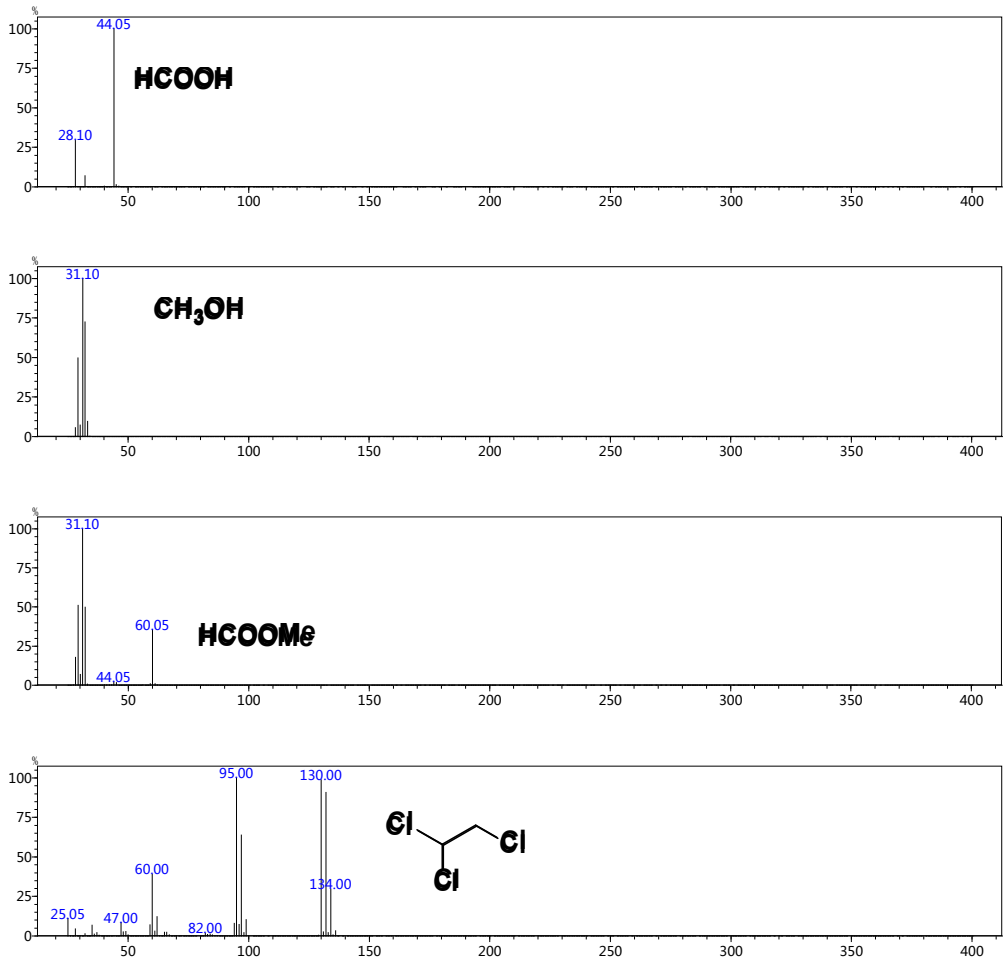


Figure S11 CG-MS analysis for reaction mixture of captured CO_2 hydrogenation (a) and gaseous CO_2 hydrogenation (b). Conditions: (a) $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg), $CyPPh_2$ (0.05 mmol, 13 mg), PEI_{600}/glycol + CO_2 (molar ratio 1:36:7.2) (0.5 mmol), methanol (2 mL), H_2 (4 MPa), 60 ^oC, 16 h; (b) $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg), $CyPPh_2$ (0.05 mmol, 13 mg), PEI_{600} (0.5 mmol, 0.3 g), methanol (3 mL), CO_2 (4 MPa), H_2 (4 MPa), 60 ^oC, 16 h.

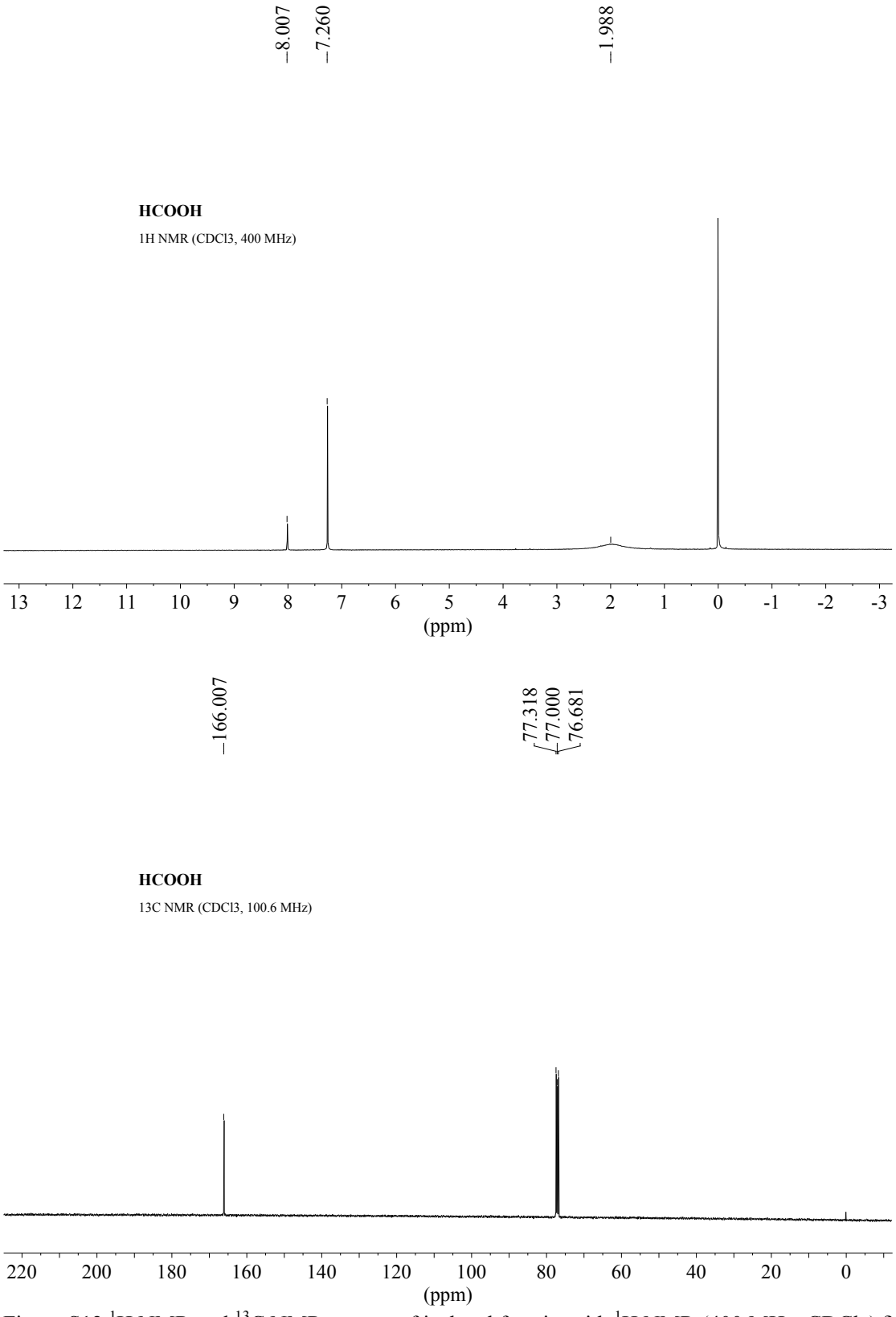


Figure S12 ^{1}H NMR and ^{13}C NMR spectra of isolated formic acid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.007 (s, 1H), 1.988 (s, OH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 166.007.

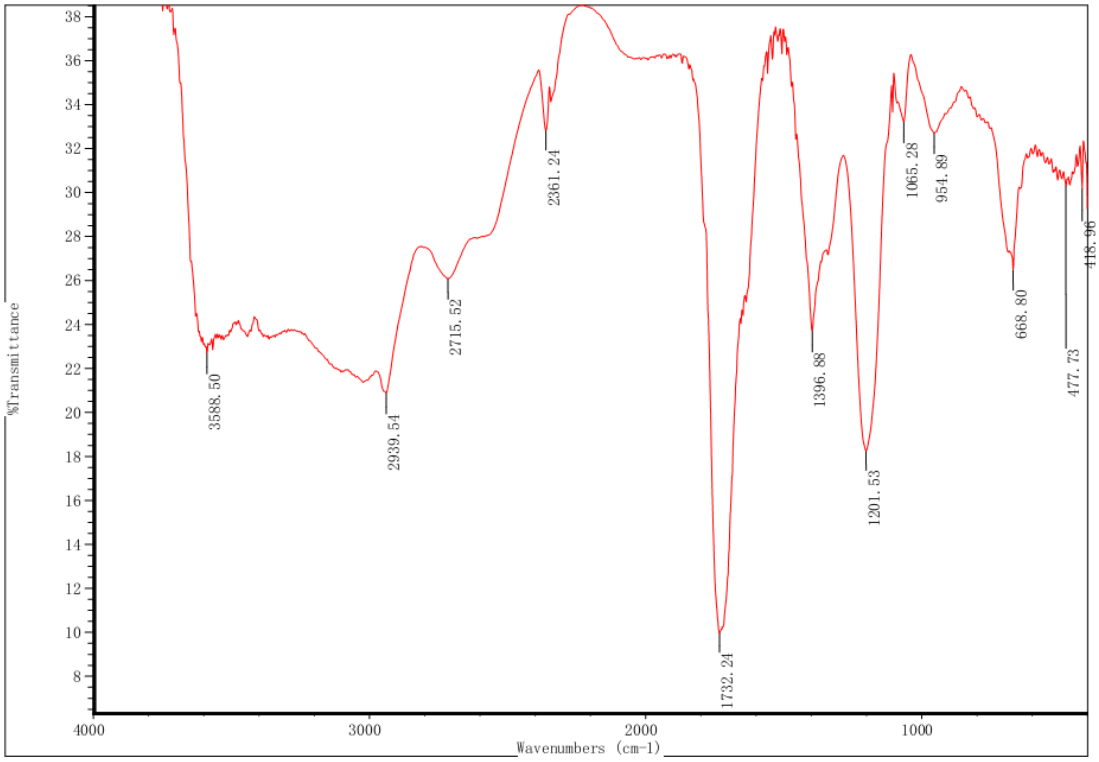


Figure S13 IR spectrum of isolated formic acid. (2939.54 cm^{-1} can be assigned to O-H stretching vibration absorption of HCOOH, and 1732.24 cm^{-1} can be suggestive of C=O stretching vibration.)

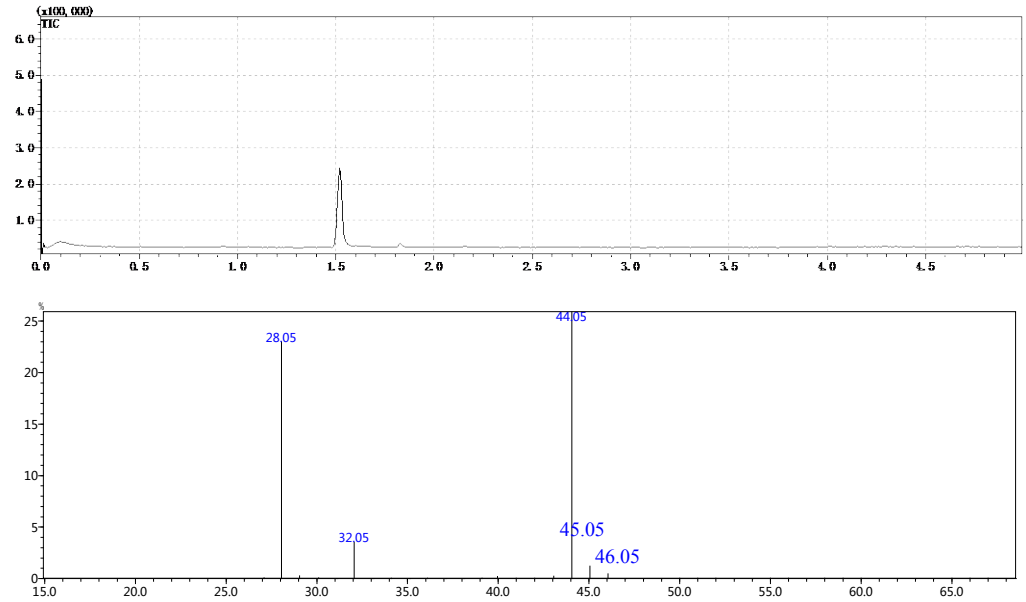


Figure S14 GC-MS spectrum of isolated formic acid. GC-MS (EI, 70 eV), m/z = 46.05 (M^+, 0.44), 45.05 [$(M-H)^+$, 1.22], 44.05 [$(M-2H)^+$, 100], 32.05 [$(M-CH_2)^+$, 3.52], 28.05 [$(M-H_2O)^+$, 22.98].

3 *The Characterization data for the absorption mixture*

$HOCH_2CH_2OH$ (Glycol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 4H), 2.66 (s, 1H), 2.30 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 63.68.

PEI_{600} (Polyethyleneimine, MW = 600 Da)
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46-2.75 (m, 48H), 1.47 (s, 15H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ57.80, 57.63, 57.58, 57.51, 54.67, 54.53, 54.33, 53.20, 53.15, 53.01, 52.90, 52.85, 52.76, 52.64, 52.53, 49.64, 49.50, 49.45, 49.30, 47.65, 47.52, 41.76, 41.68, 39.85, 39.80.

$PEI_{600}/CH_3OH + CO_2$
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (s, 1H), 2.60-3.69 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 164.07, 159.51, 52.57, 49.5.

$PEI_{600}/HOCH_2CH_2OH + CO_2$
^{1}H NMR (400 MHz, CD_3OD) δ 5.32 (s, 2H), 3.77-3.97 (m, 1H), 3.63 (s, 4H), 2.81-3.46 (m, 1H); ^{13}C NMR (100.6 MHz, CD_3OD) δ 165.77, 165.71, 165.64, 165.57, 165.51, 165.42, 165.30, 165.25, 160.43, 64.19.

DBN (1,5-diazabicyclo[4.3.0]non-5-ene)
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (t, ^{3}J = 4.8 Hz, 2H), 3.21 (t, ^{3}J = 6.8 Hz, 2H), 3.13 (t, ^{3}J = 6 Hz, 2H), 2.38 (t, ^{3}J = 7.6 Hz, 2H), 1.83-1.91 (m, 2H), 1.70-1.76 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 160.47, 51.19, 43.84, 42.85, 31.25, 20.60, 19.45.

PEG_{150} (triethylene glycol, MW = 150 Da)
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (t, ^{3}J = 4.8 Hz, 4 H), 3.65 (s, 4 H), 3.59 (t, ^{3}J = 4.8 Hz, 4 H), 3.40 (s, 2 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 72.63, 70.25, 61.50.

DBN/PEG_{150} (1:1)+ CO_2
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (t, ^{3}J = 8.0 Hz, 2H), 3.50-3.63 (m, 10H), 3.36 (t, ^{3}J = 7.0 Hz, 2H), 3.28 (t, ^{3}J = 5.4 Hz, 2H), 3.20 (t, ^{3}J = 6.0 Hz, 2H), 2.65 (t, ^{3}J = 8.0 Hz, 2H), 1.90-1.97 (m, 2H), 1.77-1.83 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 162.43, 158.24, 77.20, 72.52, 70.14, 63.93, 60.93, 52.06, 42.53, 40.69, 30.34, 19.55, 19.02.

DBN/$HOCH_2CH_2OH$ (1:2)+ CO_2
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.375 (s, 4H, OH), 3.34-3.38 (m, 4H), 3.30 (s, 4H), 3.12 (d, ^{3}J = 2.2 Hz, 2H), 2.64 (t, ^{3}J = 7.8 Hz, 2H), 1.80-1.88 (m, 2H), 1.70-1.73 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 163.47, 158.37, 77.2, 66.24, 63.05, 61.23, 52.48, 41.74, 37.70, 29.26, 18.03.

DETA (diethylenetriamine)
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70-2.44 (s, 8H), 0.97-1.09 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 52.16, 41.55.

DETA + CO_2

^{1}H NMR (400 MHz, CD_3OD) δ 2.80 (d, ^{3}J = 10.2 Hz, 8H); ^{13}C NMR (100.6 MHz, CD_3OD) δ 165.82, 52.33, 51.07, 41.88.

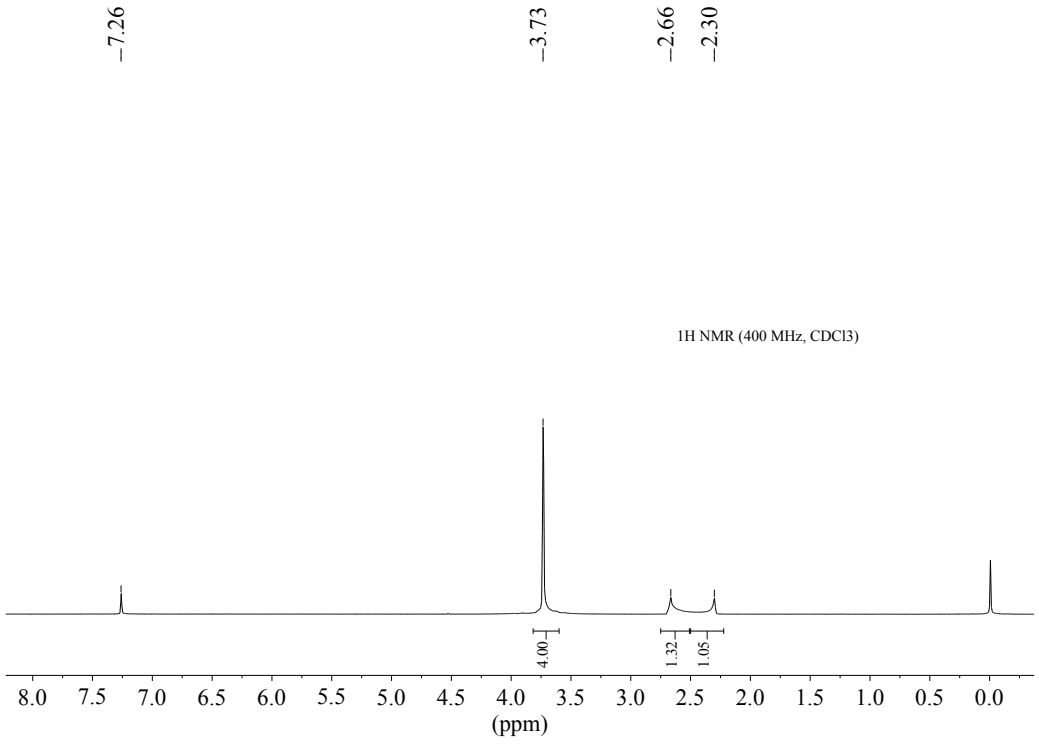
Aniline

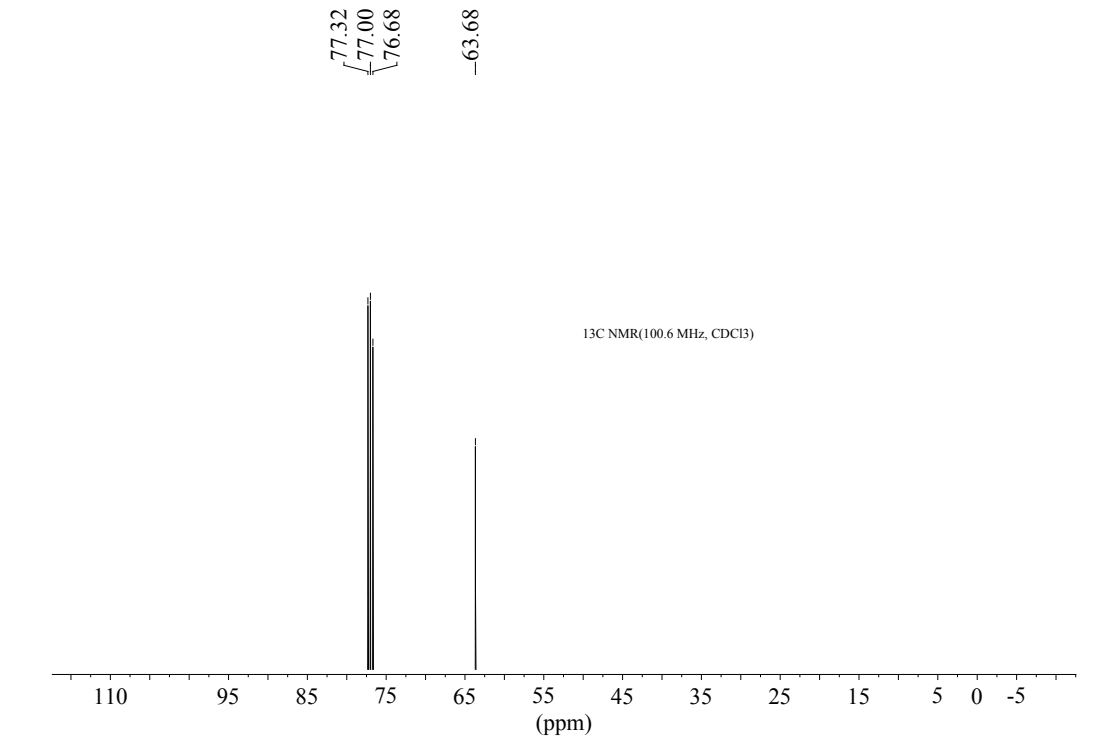
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, ^{3}J = 7.6 Hz, 2H), 6.79 (t, ^{3}J = 7.2 Hz, 1H), 6.71 (d, ^{3}J = 3.6 Hz, 2H), 3.61 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 146.29, 129.22, 118.22, 115.03.

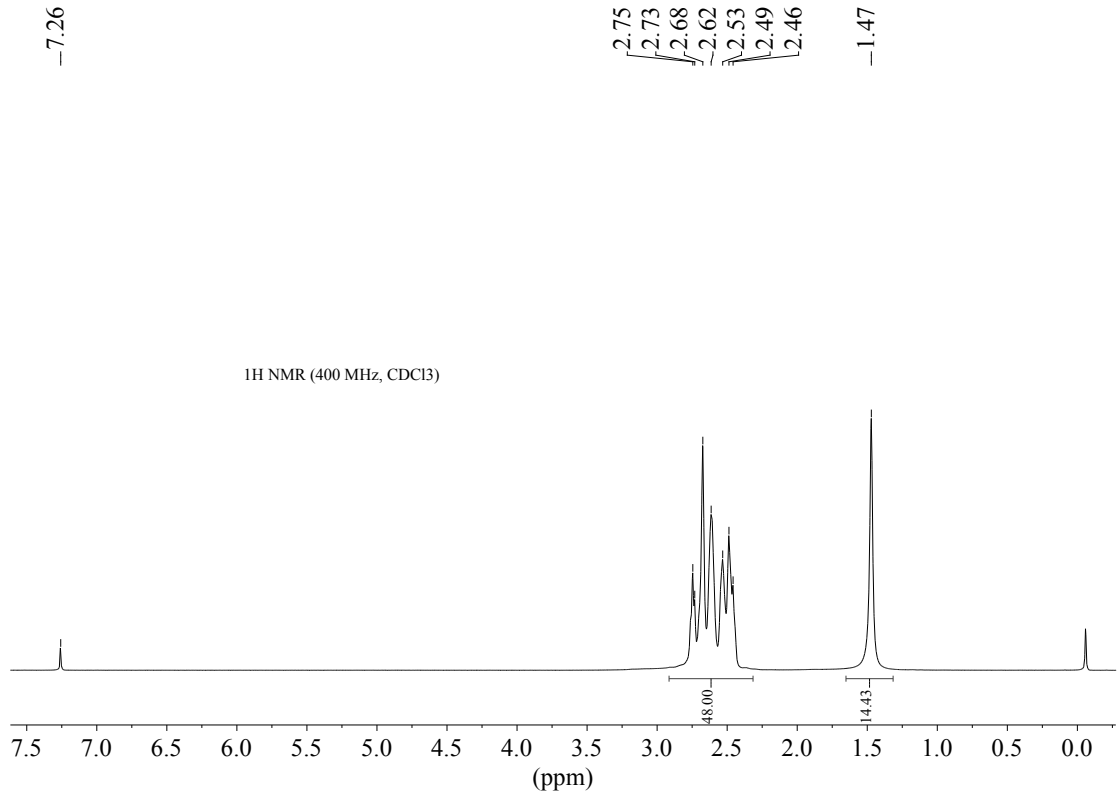
Aniline/H_2O + CO_2

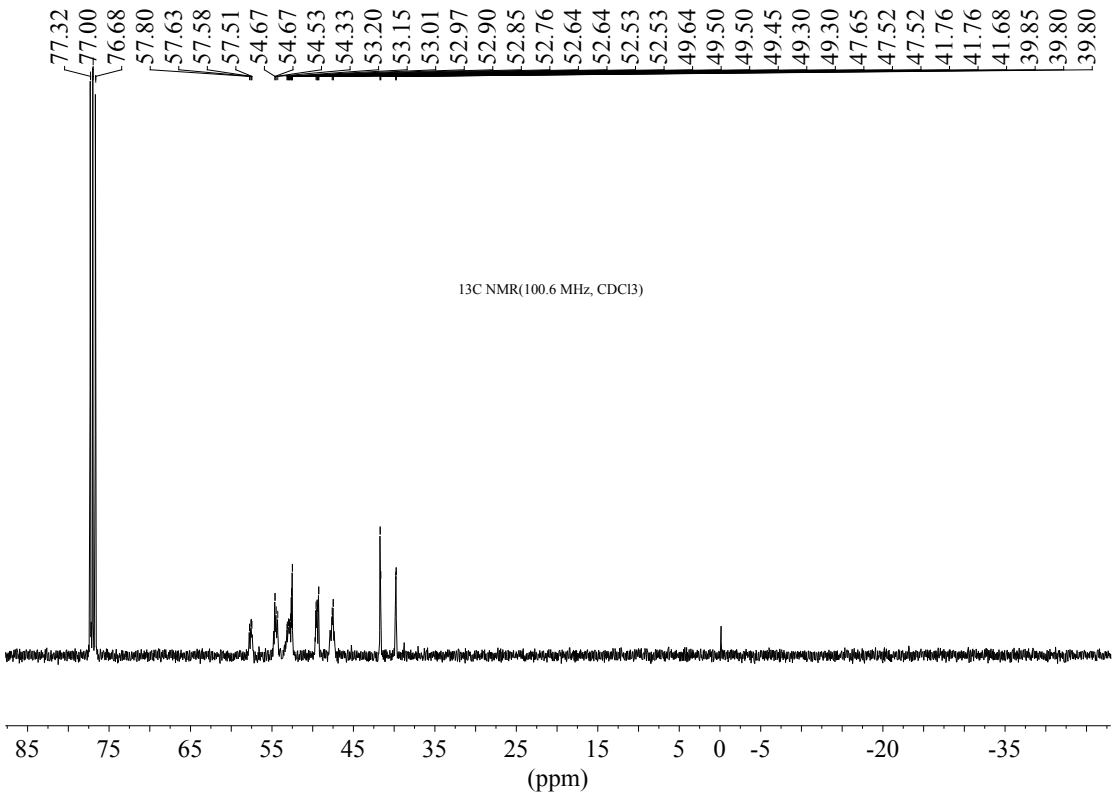
^{1}H NMR (400 MHz, D_2O) δ 7.11-7.15 (m, 2H), 6.73-6.78 (m, 3H); ^{13}C NMR (100.6 MHz, D_2O) δ 160.22, 146.73, 145.77, 129.49, 129.13, 119.69, 118.10, 116.54, 115.19.

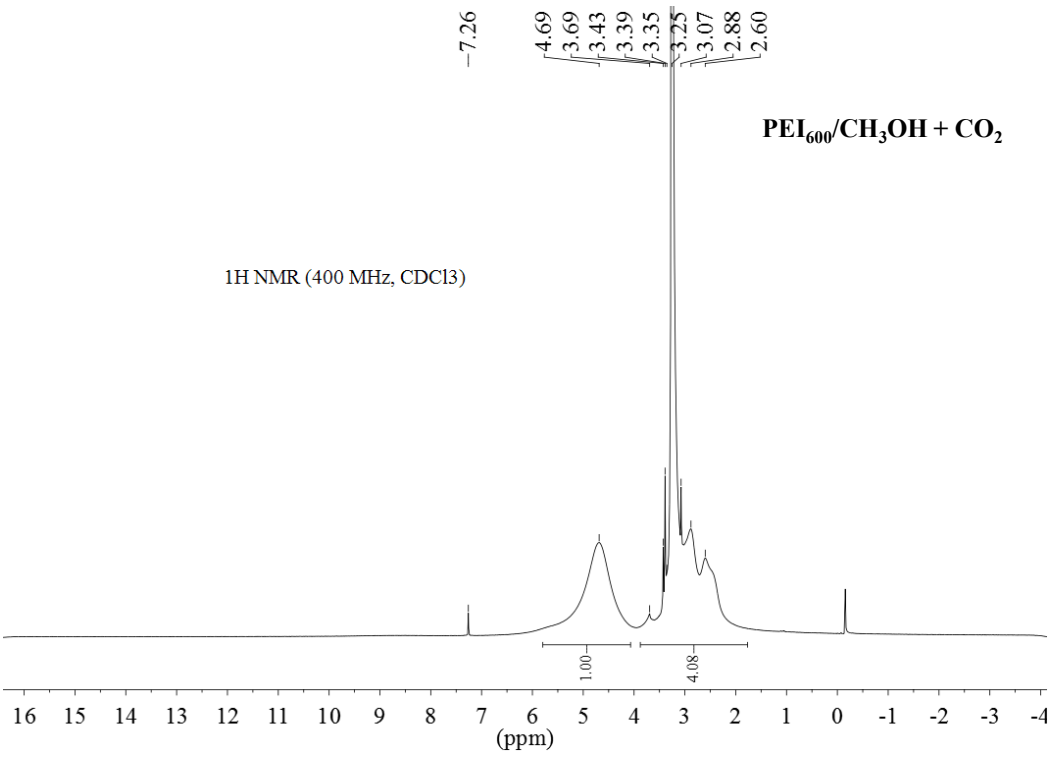
4 *^{1}H NMR and ^{13}C NMR Charts for the absorption mixture*

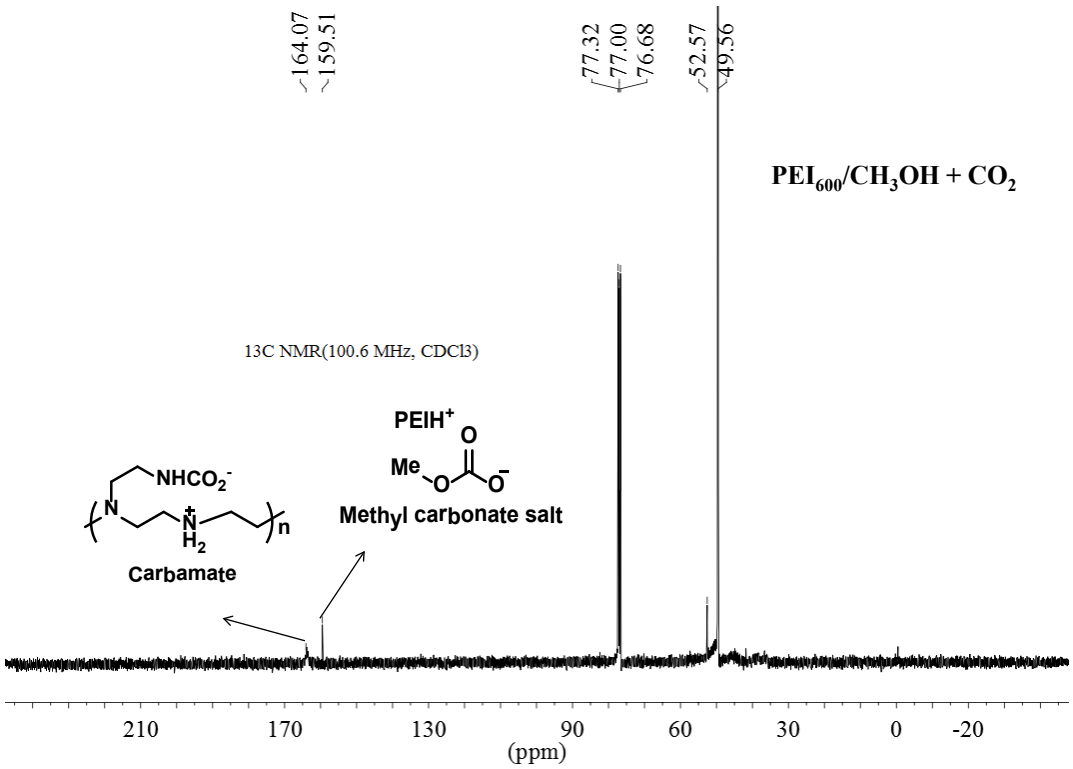


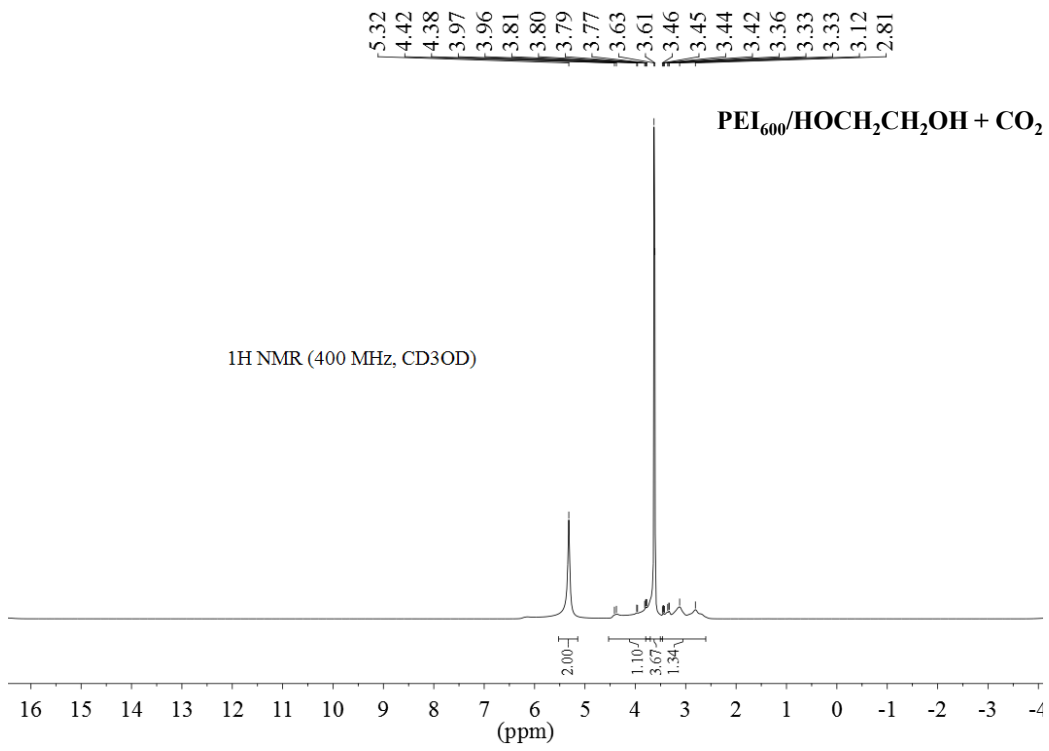

77.32
77.00
76.68
63.68
13C NMR(100.6 MHz, CDCl3)
110
95
85
75
65
55
45
35
25
15
5
0
-5
(ppm)

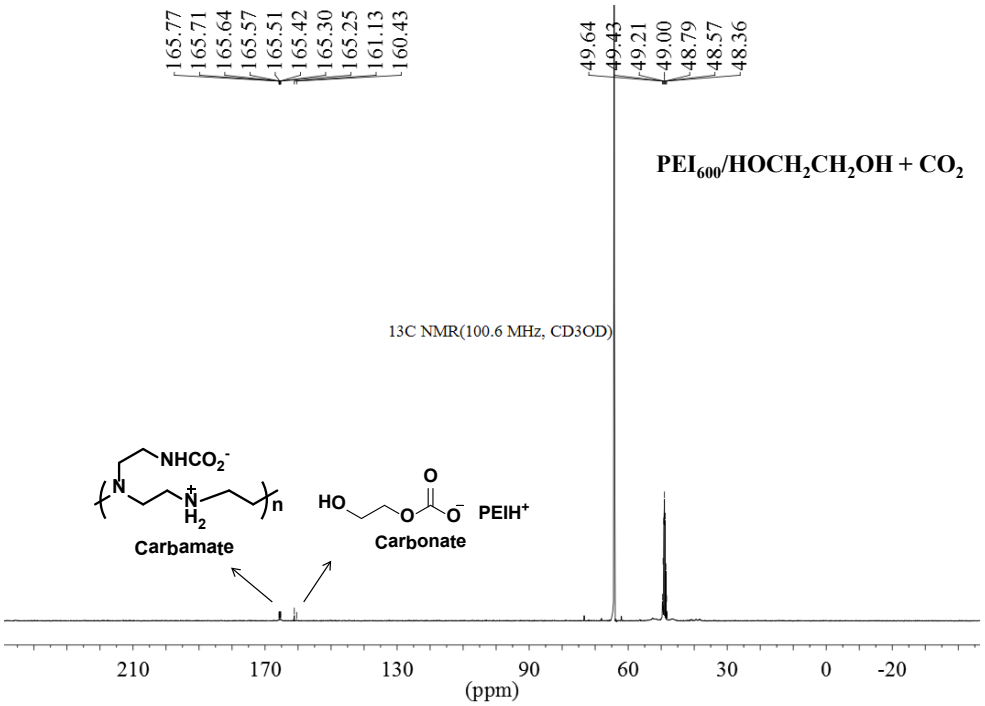

7.26
2.75
2.73
2.68
2.62
2.53
2.49
2.46
1.47
1H NMR (400 MHz, CDCl3)
48.00
14.43
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


77.32
77.00
76.68
57.80
57.63
57.58
57.51
54.67
54.67
54.53
54.33
53.20
53.15
53.01
52.97
52.90
52.85
52.76
52.64
52.64
52.53
52.53
49.64
49.50
49.50
49.45
49.30
49.30
47.65
47.52
47.52
41.76
41.76
41.68
39.85
39.80
39.80
13C NMR(100.6 MHz, CDCl3)
85
75
65
55
45
35
25
15
5
0
-5
-20
-35
(ppm)

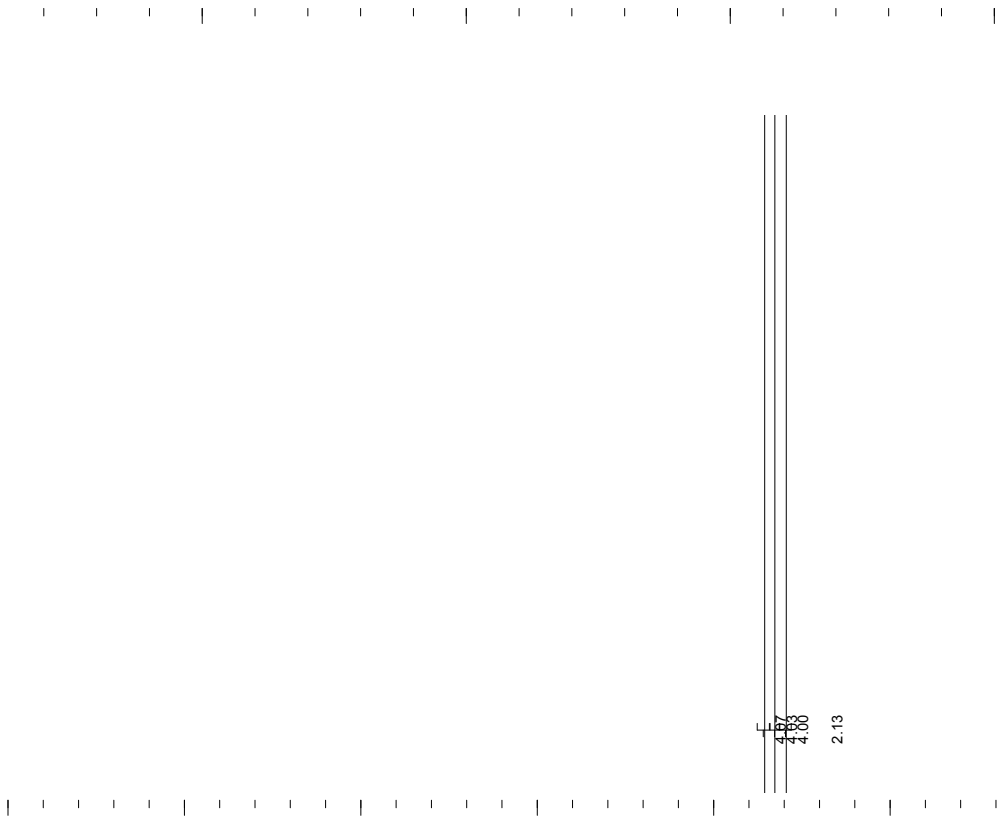

7.26
4.69
3.69
3.43
3.39
3.35
3.25
3.07
2.88
2.60
PEI600/CH3OH + CO2
1H NMR (400 MHz, CDCl3)
1.00
4.08
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
(ppm)

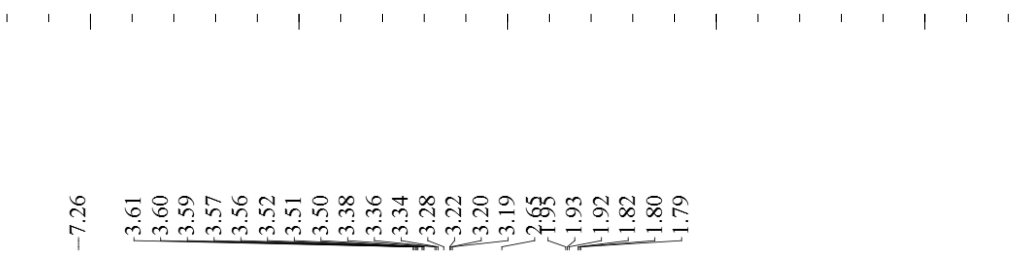




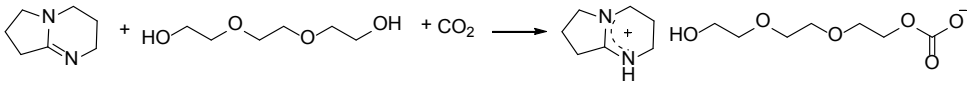

165.77
165.71
165.64
165.57
165.51
165.42
165.30
165.25
161.13
160.43
49.64
49.43
49.21
49.00
48.79
48.57
48.36
PEI600/HOCH2CH2OH + CO2
13C NMR(100.6 MHz, CD3OD)
NHCO2-
Carbamate
HO
O
O
PEIH+
Carbonate
210
170
130
90
60
30
0
-20
(ppm)


2.01
1.97
2.00
1.93
1.95
2.01

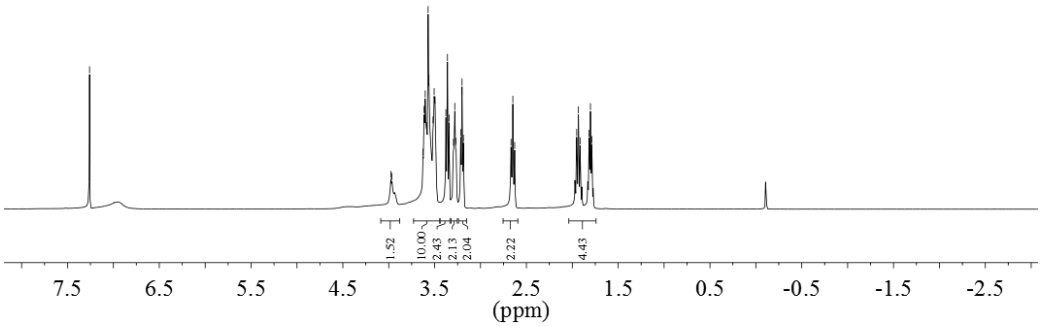




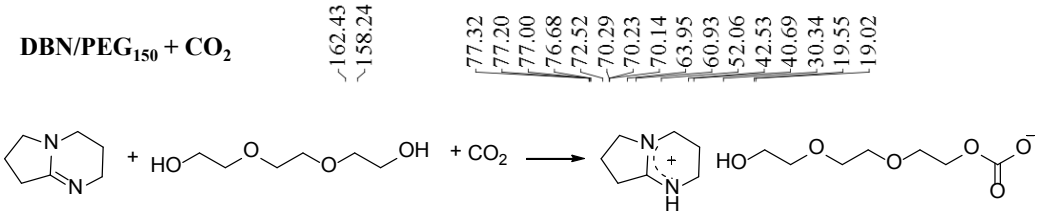
DBN/PEG$_{150}$ + CO$_2$

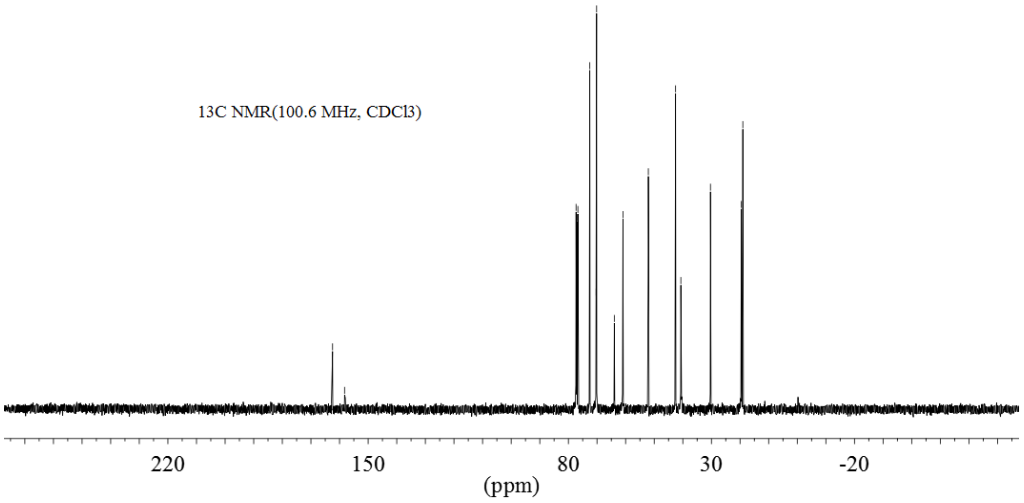


1H NMR (400 MHz, CDCl3)

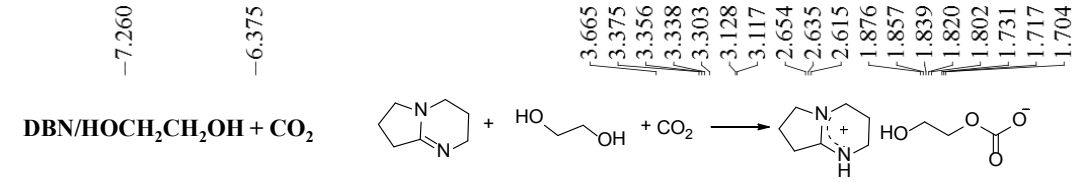


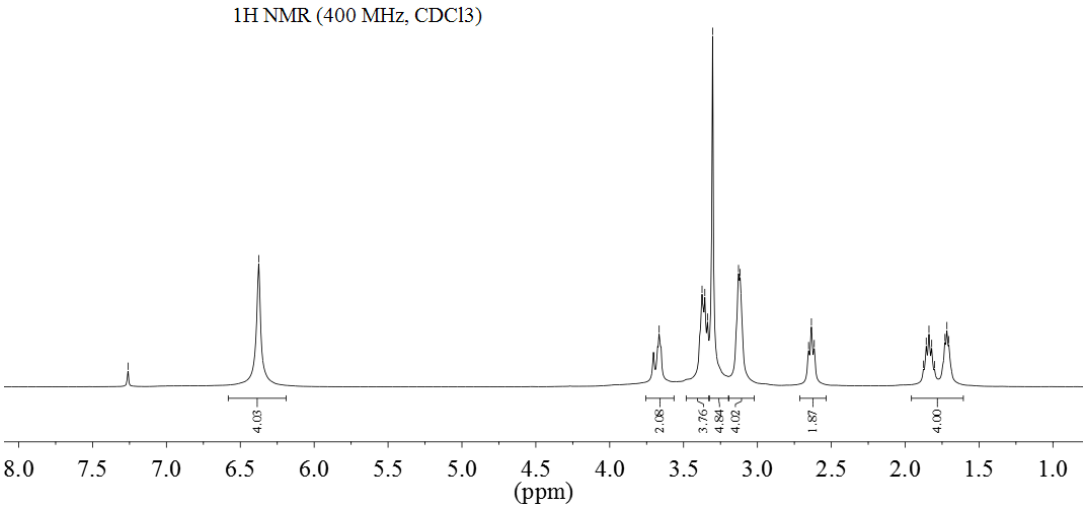
DBN/PEG$_{150}$ + CO$_2$

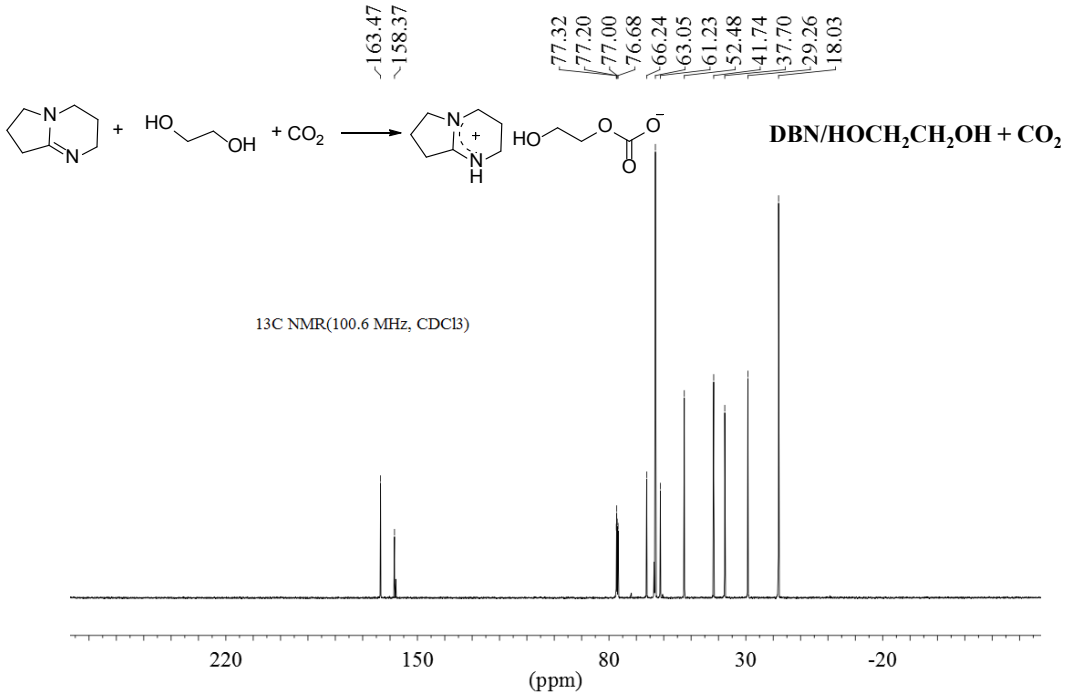


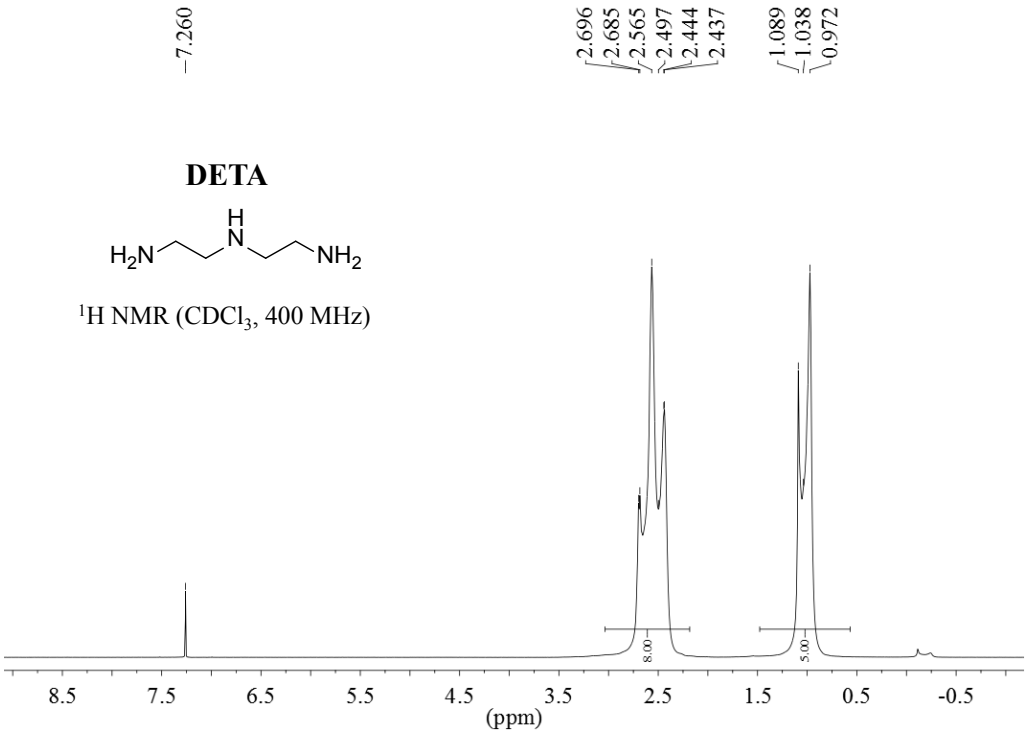


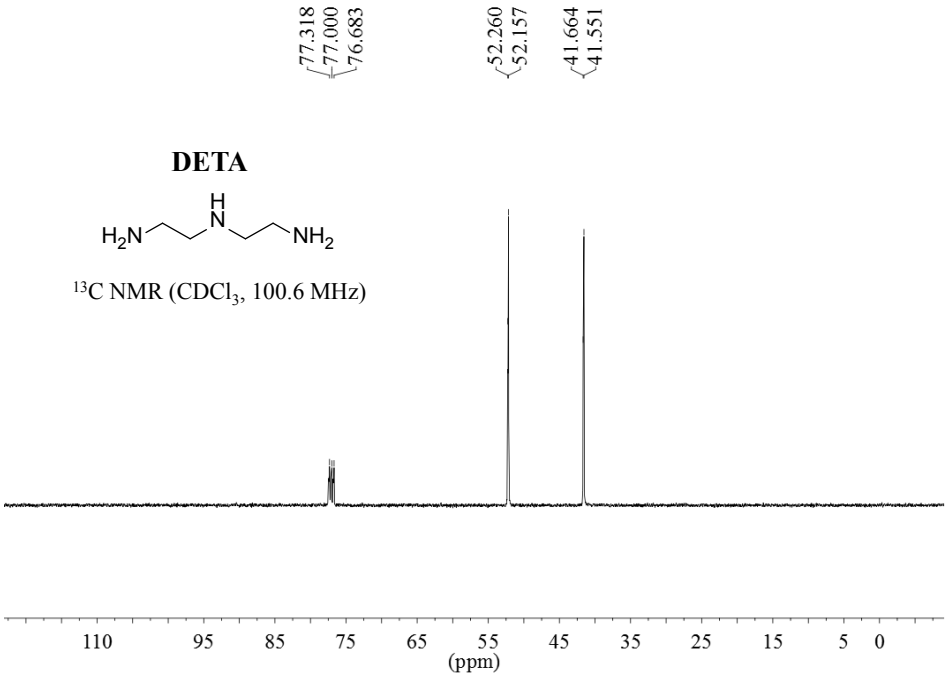
DBN/HOCH$_2$CH$_2$OH + CO$_2$

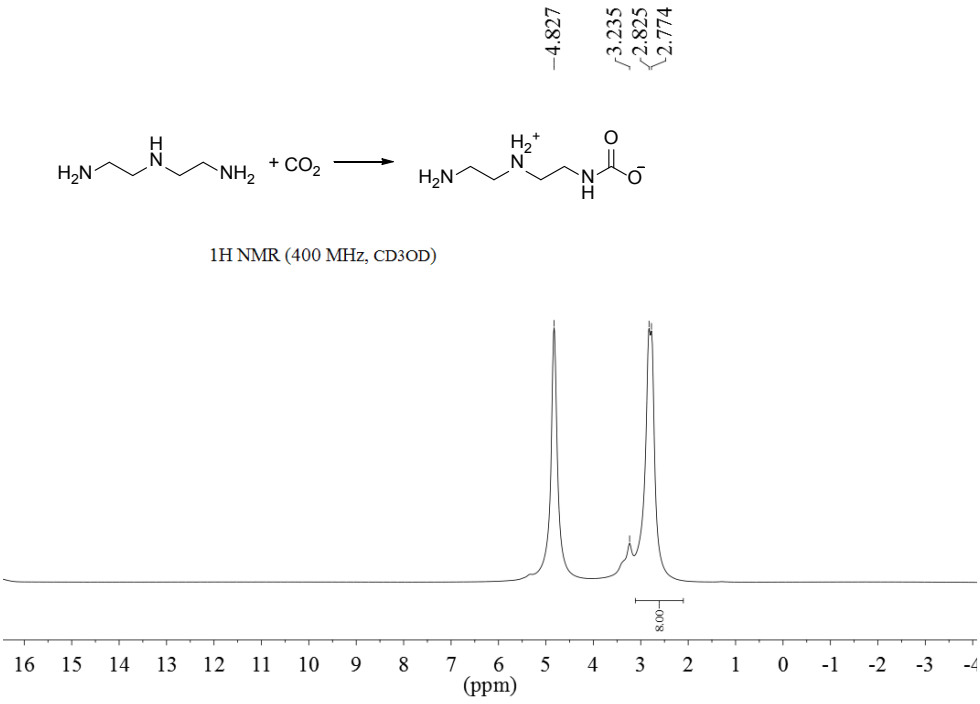


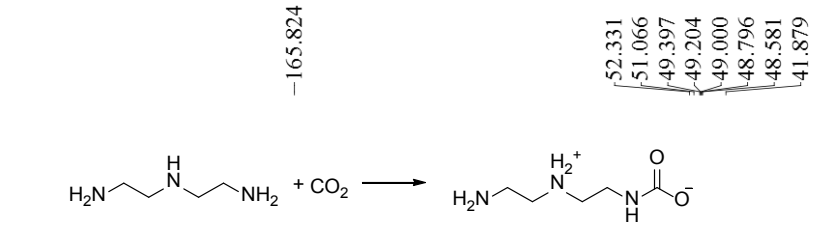



163.47
158.37
77.32
77.20
77.00
76.68
66.24
63.05
61.23
52.48
41.74
37.70
29.26
18.03
HO
OH
+ CO2
HO
DBN/HOCH2CH2OH + CO2
13C NMR(100.6 MHz, CDCl3)
220
150
80
30
-20
(ppm)

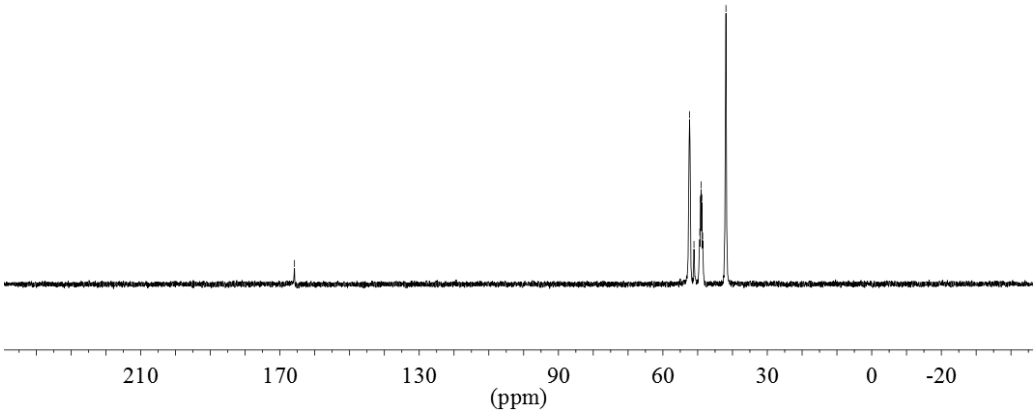

7.260
2.696
2.685
2.565
2.497
2.444
2.437
1.089
1.038
0.972
DETA
H2N
NH2
1H NMR (CDCl3, 400 MHz)
8.00
5.00
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)

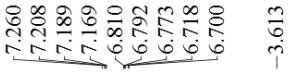

77.318
77.000
76.683
52.260
52.157
41.664
41.551
DETA
H
N
H2N
NH2
13C NMR (CDCl3, 100.6 MHz)
110
95
85
75
65
55
45
35
25
15
5
0
(ppm)

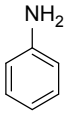

4.827
3.235
2.825
2.774
H
N
H2N
NH2
+ CO2
H2+
N
O
O-
N
H
1H NMR (400 MHz, CD3OD)
8.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
(ppm)



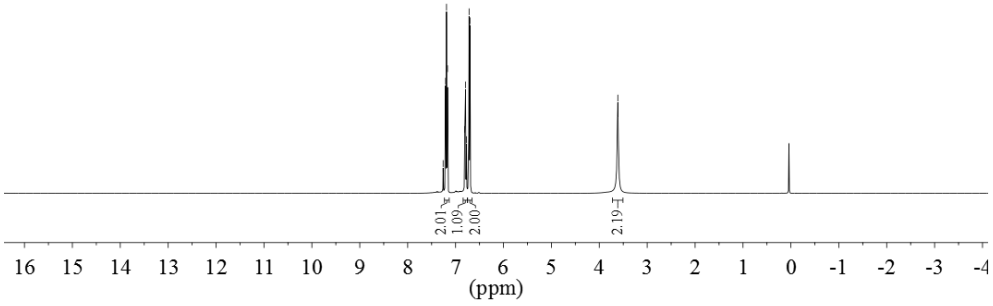
13C NMR(100.6 MHz, CD3OD)

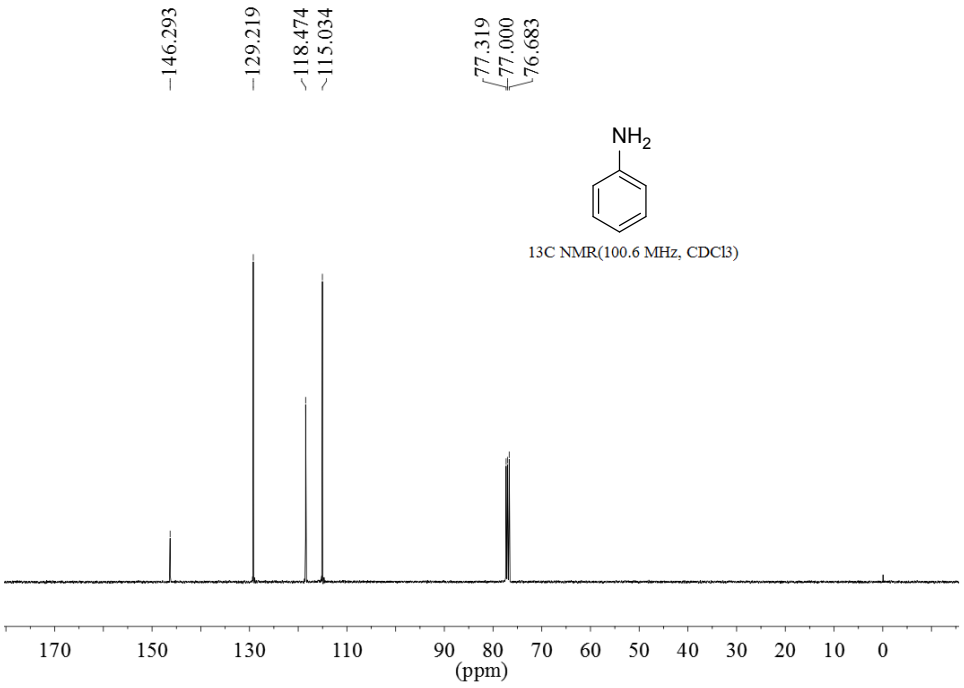


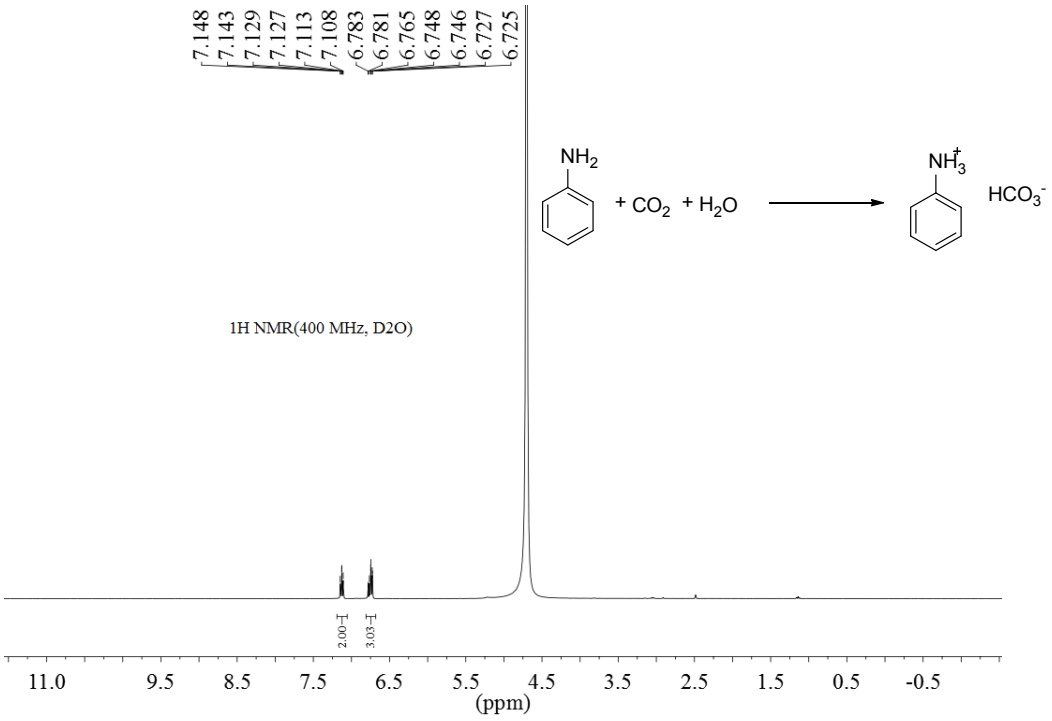


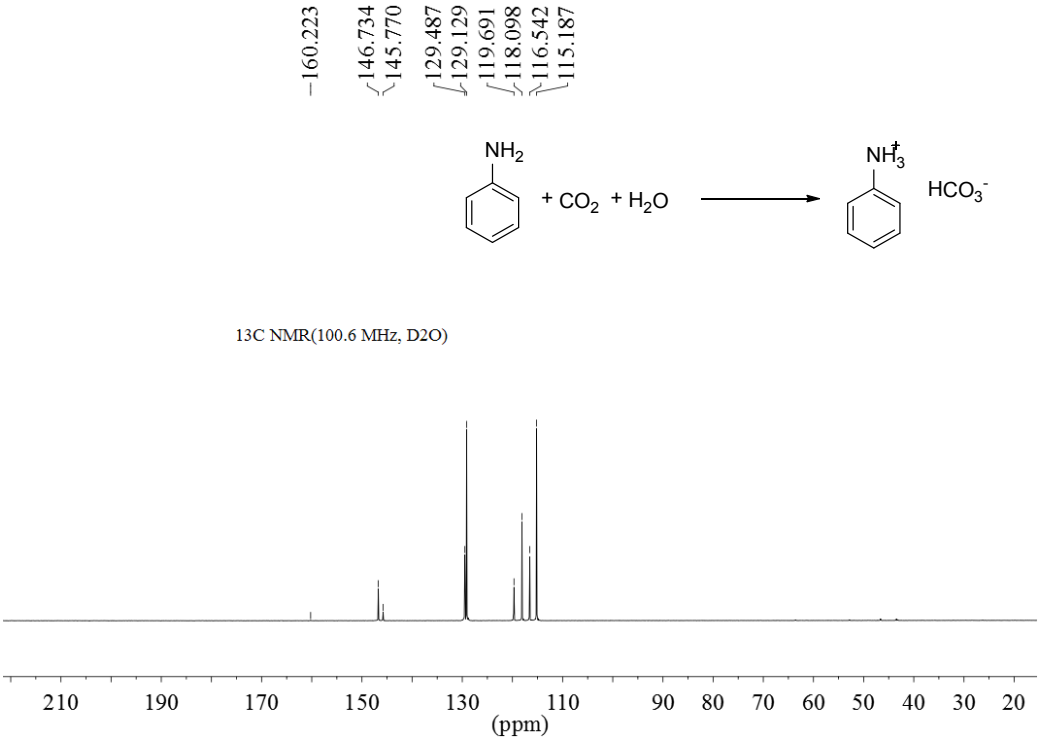


1H NMR (400 MHz, CDCl3)




146.293
129.219
118.474
115.034
77.319
77.000
76.683
NH2
13C NMR(100.6 MHz, CDCl3)
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)


7.148
7.143
7.129
7.127
7.113
7.108
6.783
6.781
6.765
6.748
6.746
6.727
6.725
NH2
+ CO2 + H2O
NH3+
HCO3-
1H NMR(400 MHz, D2O)
2.00
3.03
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)



5. References

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(3) (a) Yang, Z.-Z.; He, L.-N.; Zhao, Y.-N.; Li, B.; Yu, B. *Energy Environ. Sci.* **2011**, *4*, 3971-3975. (b) Wang, C.; Mahurin, S. M.; Luo, H.; Baker, G. A.; Li, H.; Dai, S. *Green Chem.* **2010**, *12*, 870-874.

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(5) Huang, H. Y.; Yang, R. T.; Chinn, D.; Munson, C. L. *Ind. Eng. Chem. Res.* **2003**, *42*, 2427-2433.

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