Electronic Supplementary Information

Integration process of CO_2 capture and *in situ* hydrogenation to formate with tunable ethoxyl-functionalized amidine and Rh/bisphosphine 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. The absorbent materials were synthesized according to the references.[1-7]

Instruments

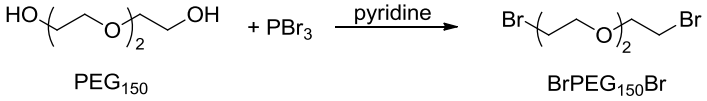
^{1}H NMR spectra was recorded at Bruker 400 or Varian Mercury-Plus 400 spectrometer in $CDCl_3$, D_2O or d_6-DMSO and TMS (0 ppm) was used as internal reference. ^{13}C NMR was recorded at 100.6 MHz in $CDCl_3$ or D_2O and $CDCl_3$ (77.0 ppm) was used as internal reference. ^{31}P NMR (162 MHz, $CDCl_3$) chemical shifts were measured relative to an external orthophosphoric acid standard. Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectropho-tometer with KBr pellets. *In situ* FTIR was collected on a Mettler Toledo React IR ic10, inner silicon probe, using ic IR analysis system. The probe is placed at the bottom of the autoclave, which is constantly stirred by mechanical stirring, and the spectra are collected in situ during the whole process. ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. GC analyses were performed on Shimadzu GC-2014, equipped with a capillary column (RTX-17, 30 m × 0.25 μm) using a flame ionization detector. GC-MS analyses were performed on SHIMADZU GCMS-QP2010 SE and GC equipped with a capillary column (Rxi-5MS, 30 m × 0.25 μm). TGA was performed on a PTC-10A TG-DTA analyzer (Japan, Rigaku) under air flow from room temperature to 700 ^{o}C with a heating rate of 10 ^{o}C/min. Elementary analysis was performed on vario ELCUBE analyzer. The scanning electron micros copy (SEM) images were taken with a JEOLJSM-6700F field emission scanning electron microscope (15 kV). The surface area was calculated using a multipoint Brunauer eEmmett e Teller (BET) model. The total pore volume was estimated at a relative pressure of 0.99, assuming full surface saturation with

nitrogen.

All of the theoretical calculations here were carried out using the GAUSSIAN 09 packages. The geometries were completely optimized by the B3LYP method in conjunction with 6-31+G(d) basis set. All the final structures were confirmed by frequency calculation to be the real minima without any imaginary frequency using the same level of theory. The solvent effect using the Conductor-like Polarizable Continuum Model (CPCM) in each case was carried out at the M06-2X/6-311++G(d,p) level. Solute-solvent interactions can have dramatic effects on molecular energies, structures, and properties, and ethanol was chosen as solvent environment. All the bond lengths are in angstroms (Å). Structures were generated using GaussView 5.0.

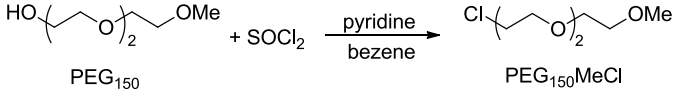
Synthesis of amidine derivatives

Synthesis of 1,2-bis(2-bromoethoxy)ethane (BrPEG$_{150}$Br)



To a stirred mixture of triethylene glycol (PEG_{150}) (0.13 mol) and pyridine (0.51 mol) at 0 ^{o}C, phosphorus tribromide (0.103 mol, distilled) was added dropwise over 30 min. The resulting suspension was heated at 60 ^{o}C for 4 h, and then the mixture was poured into ice-water (30 mL). The lower organic layer was washed with water (5×20 mL), and then it was dried with $MgSO_4$. Finally, the target compound $BrPEG_{150}Br$ was purified through distillation under reduced pressure as a light yellow liquid.[1]

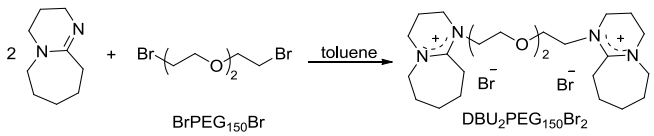
Synthesis of PEG$_{150}$MeCl



A solution of thionyl chloride (0.45 mol) in $CHCl_3$ (90 mL) was added slowly over 60 min to a stirred solution of triethylene glycol monomethyl ether (0.3 mol) and pyridine (0.3 mol) in $CHCl_3$ (200 mL), followed by refluxing the above reaction mixture at 100 ^{o}C for 4 h, and then a yellow liquid mixture is obtained, which was

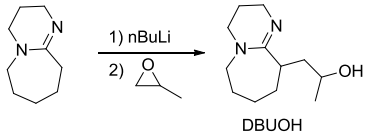
washed with water (4×125 mL), dried with $MgSO_4$, and concentrated under reduced pressure at 60 °C to remove $CHCl_3$. The crude product was purified under reduced pressure to give $PEG_{150}MeCl$ as a light yellow liquid.[2]

Synthesis of ionic liquids $DBU_2PEG_{150}Br_2$



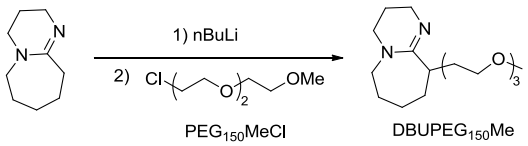
Under N_2, DBU (20 mmol) and $BrPEG_{150}Br$ (34.4 mmol) were added to dry toluene (2 mL) in a round-bottomed flask. The mixture was heated under reflux under N_2 for 24 h, upon which two layers had formed. The flask was allowed to cool to room temperature and was then cooled to -10 °C overnight, during which time white solid or yellow oil were formed. The excess toluene was decanted, while N_2 was being passed over the product layer. The resulting product was washed with dry Et_2O and then dried in vacuo for 24 h to obtain $DBU_2PEG_{150}Br_2$ as brown oil.[1]

Synthesis of DBUOH



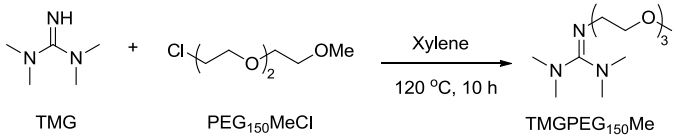
The reaction was carried out on a scale of 10 g under Ar atmosphere. DBU (1.0 equiv.) was added to the dry THF (50 mL) and it was cooled to -78 °C by liquid nitrogen-acetone bath. n-BuLi (1.6 M in hexane) (1.05 equiv.) was added dropwise into the solution at -78 °C for 20 min. After stirring for 2 h at -78 °C and for 1 h at -20 °C, a solution of propylene oxide (0.5 equiv.) in THF was added dropwise for 20 min at -10 °C. After stirring for 1 h at -10 °C, the solution was warmed up to room temperature slowly. The mixture was stirred for 2 h and hydrolyzed by deionized water (1.05 equiv.) for 30 min. The mixture was filtered and evaporated. DBUOH was obtained by fractional vacuum distillation.[3]

Synthesis of DBUPEG$_{150}$Me



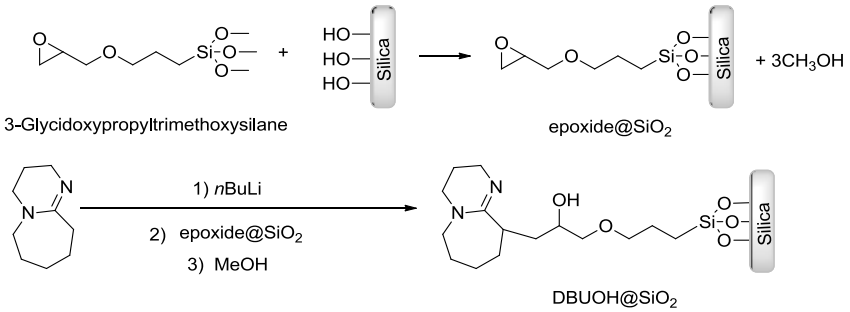
The reaction was carried out under Ar atmosphere. DBU (45 mmol, 6.84 g) was added to the dry THF (50 mL) and it was cooled to -78 °C by liquid nitrogen-acetone bath. n-BuLi (1.6 M in hexane) (47.3 mmol, 30 mL) was added dropwise into the solution at -78 °C for 20 min. After stirring for 2 h at -78 °C and for 1 h at -20 °C, a solution of PEG$_{150}$MeCl (45 mmol, 8.22 g) in THF was added dropwise for 20 min at -10 °C. After stirring for 1 h at -10 °C, the solution was warmed up to room temperature slowly. The mixture was stirred for 2 h and hydrolyzed by deionized water for 30 min. The mixture was filtered and evaporated. DBUPEG$_{150}$Me was obtained by column chromatography.[4]

Synthesis of TMGPEG$_{150}$Me



In a dry flask under N_2 atmosphere, 1,1,3,3-tetramethylguanidine (20 mmol, 2.30 g) and xylene (0.3 mL) were mixed together, and the system was heated up to 120 ^{o}C and maintained at this temperature for 2 h, and then PEG$_{150}$MeCl (10 mmol, 1.83 g) was added dropwise over 2 h. After being stirred at 120 ^{o}C for 7 h under N_2 atmosphere, the resulting mixture was allowed to cool down to room temperature. The formed salt precipitates 1,1,3,3-tetramethylguanidine·HCl was filtrated out. The filtrate liquid was distilled under reduced pressure and TMGPEG$_{150}$Me was thus obtained.[5]

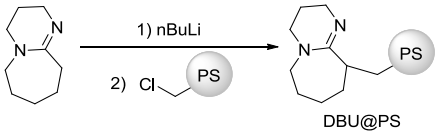
Synthesis of DBUOH@Silica



In a typical surface modification process, activated HG/T2354-92 H silica (8 g, 150 ^{o}C, under vacuum) was first treated with a refluxing anhydrous toluene solution (50 mL) of 3-glycidoxypropyltrimethoxysilane (25 mmol, 6 g). The solution was refluxed for 24 h at 120 ^{o}C under an inert N_2 atmosphere. The solution was filtered and the solid was washed subsequently with toluene, dichloromethane, and methanol, and dried under reduced pressure at 80 ^{o}C for 10 h to obtain epoxide@Silica as white powder, which was analyzed by IR spectroscopy.[6]

Then, the reaction was carried out under Ar atmosphere. DBU (30 mmol, 4.56 g) was added to the dry THF (50 mL) and it was cooled to -78 °C by liquid nitrogen-acetone bath. n-BuLi (1.6 M in hexane) (40 mmol, 25 mL) was added dropwise into the solution at -78 °C for 20 min. After stirring for 2 h at -78 °C and for 1 h at -20 °C, epoxide@Silica (13 g) was added in batches under inert atmosphere. Then, after stirring for 1 h at -10 °C, the solution was warmed up to room temperature slowly. The mixture was stirred overnight and hydrolyzed by methanol for 30 min. The mixture was filtered and evaporated to give the DBUOH@Silica as white powder, which was analyzed by IR spectroscopy and CHN elemental analysis.[3]

Synthesis of DBU@PS



The reaction was carried out under Ar atmosphere. DBU (30 mmol, 4.56 g) was added to the dry THF (50 mL) and it was cooled to -78 °C by liquid nitrogen-acetone bath. n-BuLi (1.6 M in hexane) (32 mmol, 20 mL) was added dropwise into the solution at -78 °C for 20 min. After stirring for 2 h at -78 °C and for 1 h at -20 °C,

activated chloromethylated polystyrene resin (18-19% Cl) was added to the solution under Ar atmosphere. Then, after stirring for 1 h at -10 °C, the solution was warmed up to room temperature slowly. The mixture was stirred overnight and hydrolyzed by methanol for 30 min. The mixture was filtered and evaporated to give the DBU@PS, which was analyzed by IR spectroscopy.[7]

2. *Table S1 and Figures S1-S10*

Table S1 Parameters of solid amidine derivatives.[a]

Amidine derivative	Surface area (S_{BET}) (m^2 g^{-1})	V_{total} ($cm^3 \cdot g^{-1}$)[a]	Base loading (wt %)[b]
DBU@PS	27.3	0.09	20.0%
DBUOH@Silica	98.5	0.07	11.3%

[a] Total volume calculated at P/P_0 = 0.99. [b] Measured by Elemental Analysis.

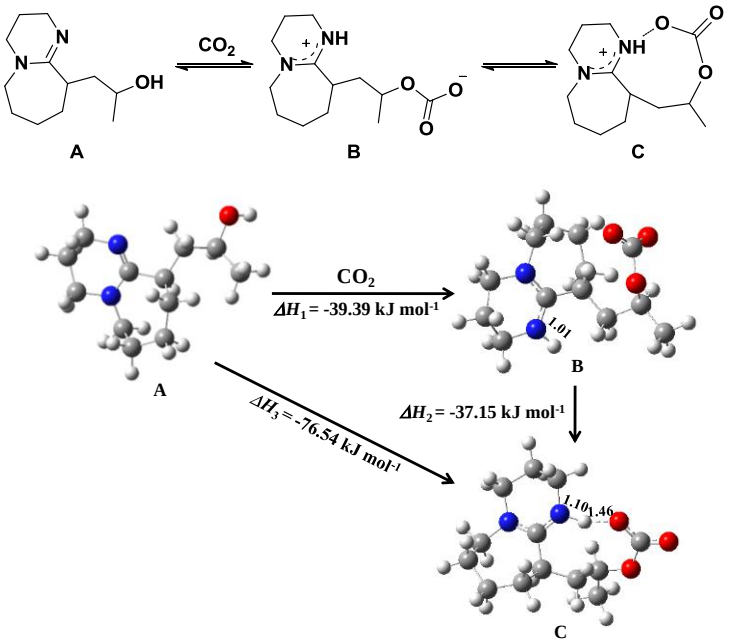


Figure S1 CO_2 capture/activation by alkanolamidine with enthalpy changes. (Calculated by M06-2X/6-311++G(d,p)//B3LYP/6-31+G(d)/CPCM method in ethanol.) **A**: DBUOH; **B**: $DBUH^+OCO_2$; **C**: $DBUH^+OCO_2^-$ with intramolecular hydrogen bond. H: white, C: gray, N: blue, O: red. N-H bond (1.10 Å) and O-H bond (1.46 Å) in the cyclic capture product **C**.

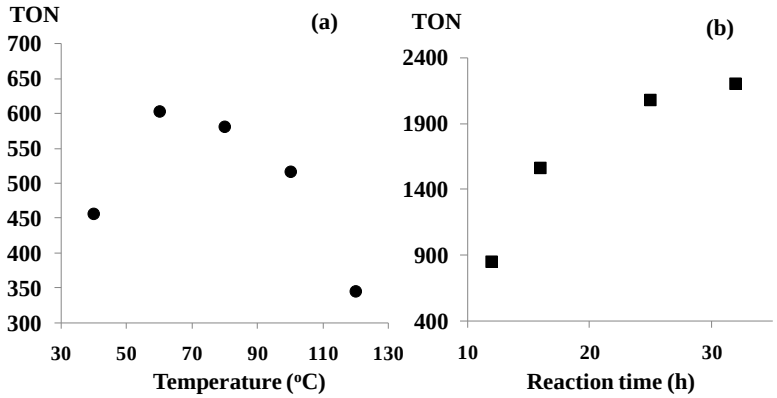


Figure S2 Temperature and time effect under CO_2 (4 MPa) and H_2 (4 MPa) pressure. Reaction conditions: (a) $RhCl_3 \cdot 3H_2O$ (0.01 mmol, 2.6 mg), DPEphos (0.01 mmol, 27 mg), DBU (3.3 mmol), methanol (3 mL), 16 h. (b) $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg), DPEphos (0.025 mmol, 13.5 mg), DBU (6.6 mmol), methanol (3 mL), 60 ^oC.

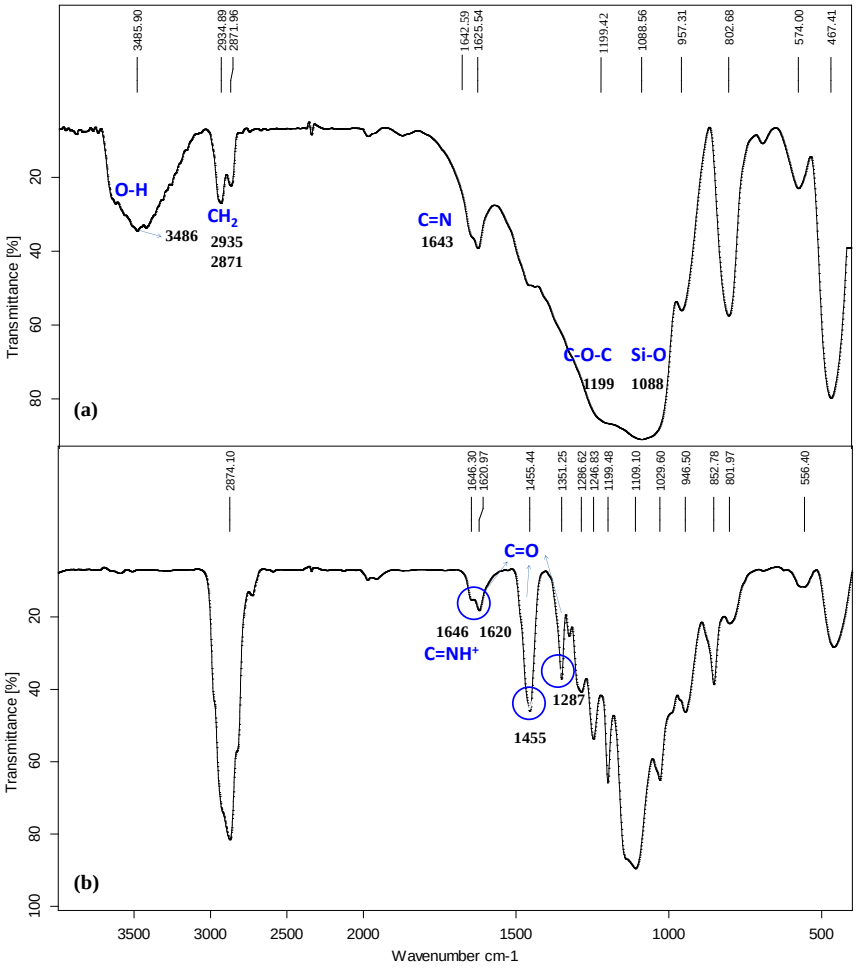


Figure S3 FT-IR spectra of the recovered DBUOH@Silica (a) and recovered DBUOH@Silica + CO_2 (b).

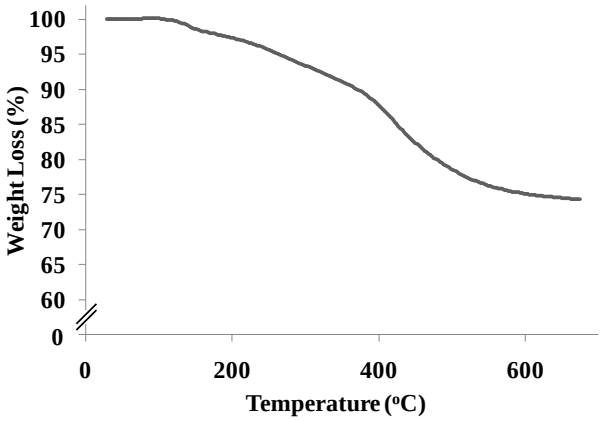


Figure S4 TGA of DBUOH@Silica. N_2, 10 ^oC min^{-1}, temperature range: 0-700 ^oC. The weight loss did not appear until heating to 189 ^oC.

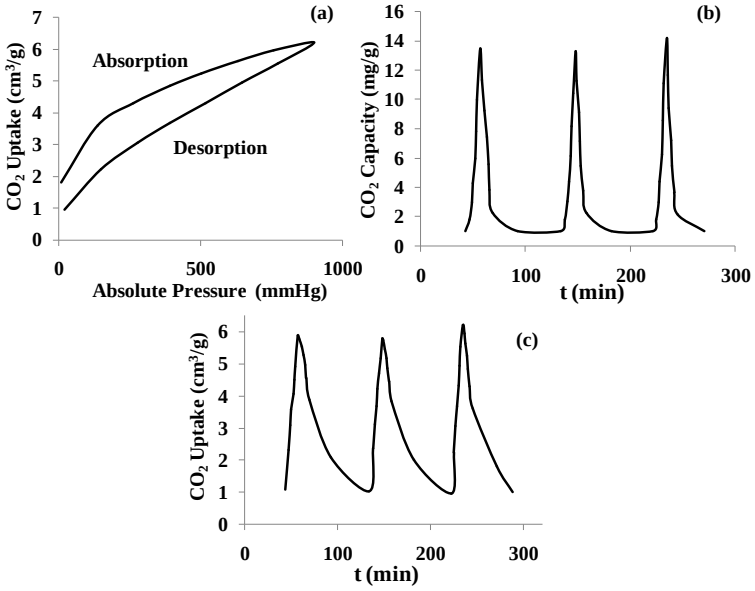


Figure S5 Reversible CO_2 absorption and desorption (a) and three consecutive cycles (b, c) by DBUOH@Silica with amidine content of 11.3% at 25 ^oC.

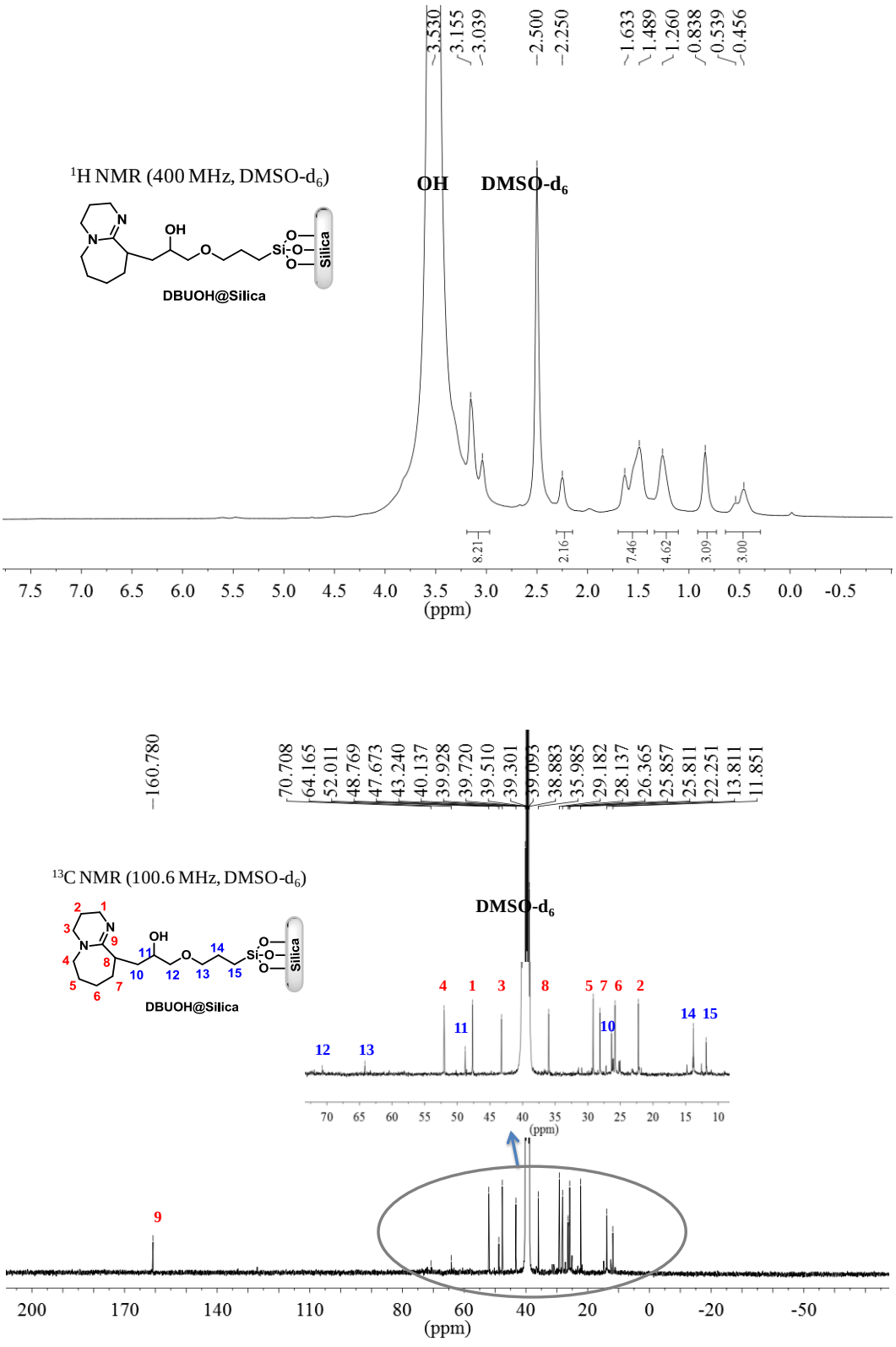


Figure S6 [1]H (400 MHz, DMSO-d$_6$) and [13]C NMR (100.6 MHz, DMSO-d$_6$) spectra of DBUOH@Silica.

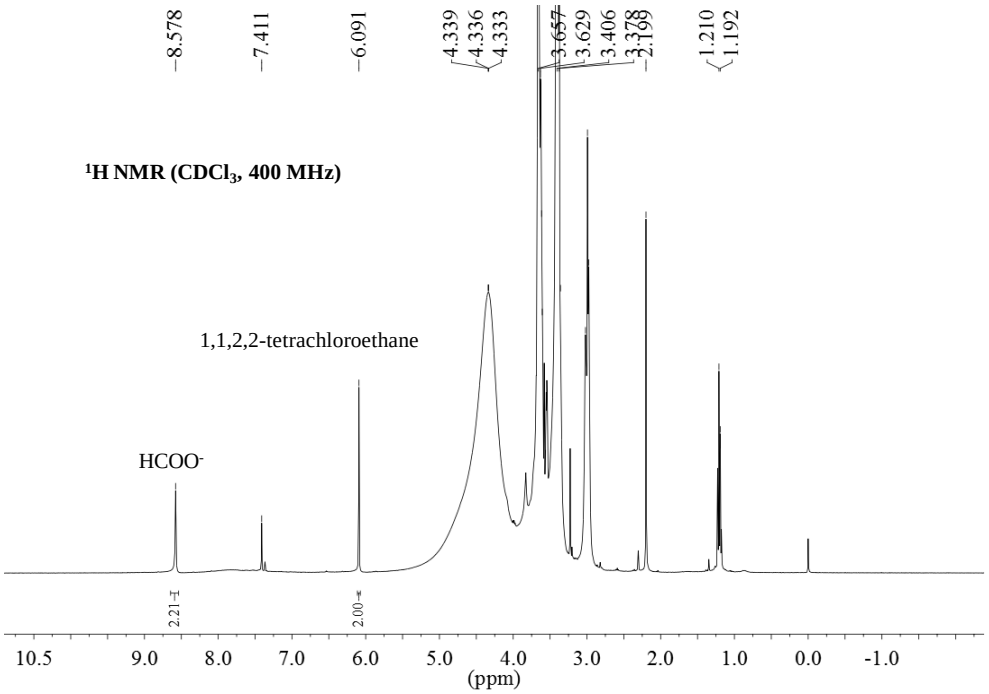


Figure S7 ^{1}H NMR spectrum for reaction mixture of CO_2 gas hydrogenation. Conditions: $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg), DPEphos (0.025 mmol, 13.5 mg), DBUOH (3 mmol, 0.64 g), methanol (3 mL), H_2 (4 MPa), CO_2 (4 MPa), 60 ^{o}C, 16 h.

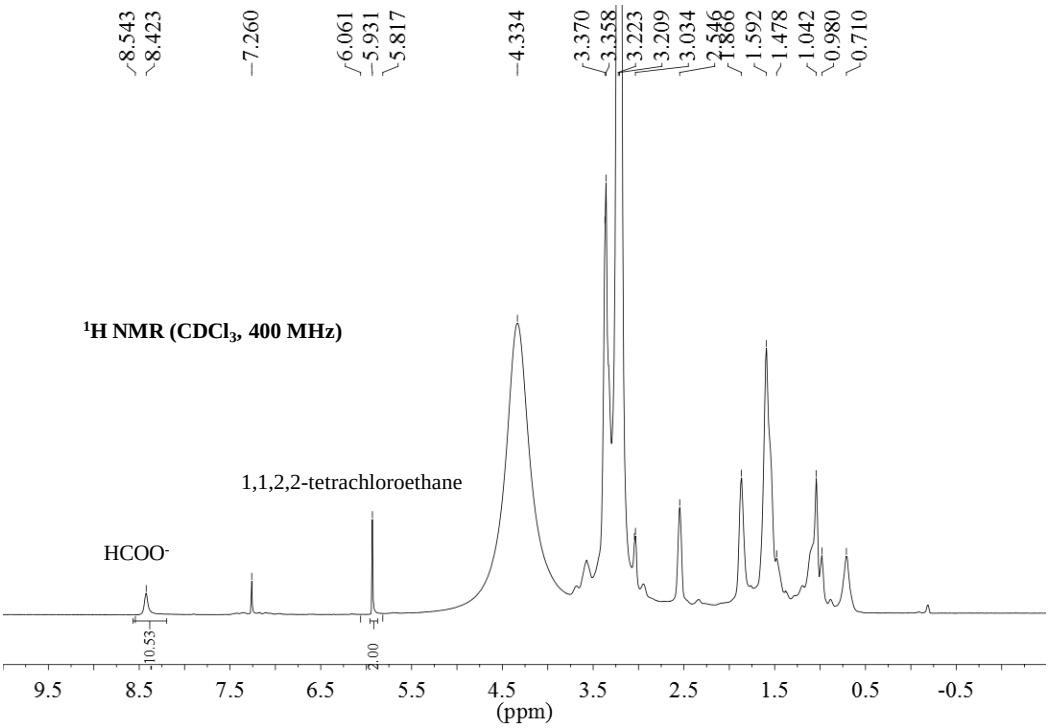


Figure S8 ^{1}H NMR spectrum for reaction mixture of captured CO_2 hydrogenation. $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg), DPEphos (0.05 mmol, 13 mg), DBUOH + CO_2 in tetraethylene glycol dimethyl ether (3 mmol : 2.85 mmol : 5 mmol), methanol (3 mL), H_2 (4 MPa), 60 ^{o}C, 16 h.

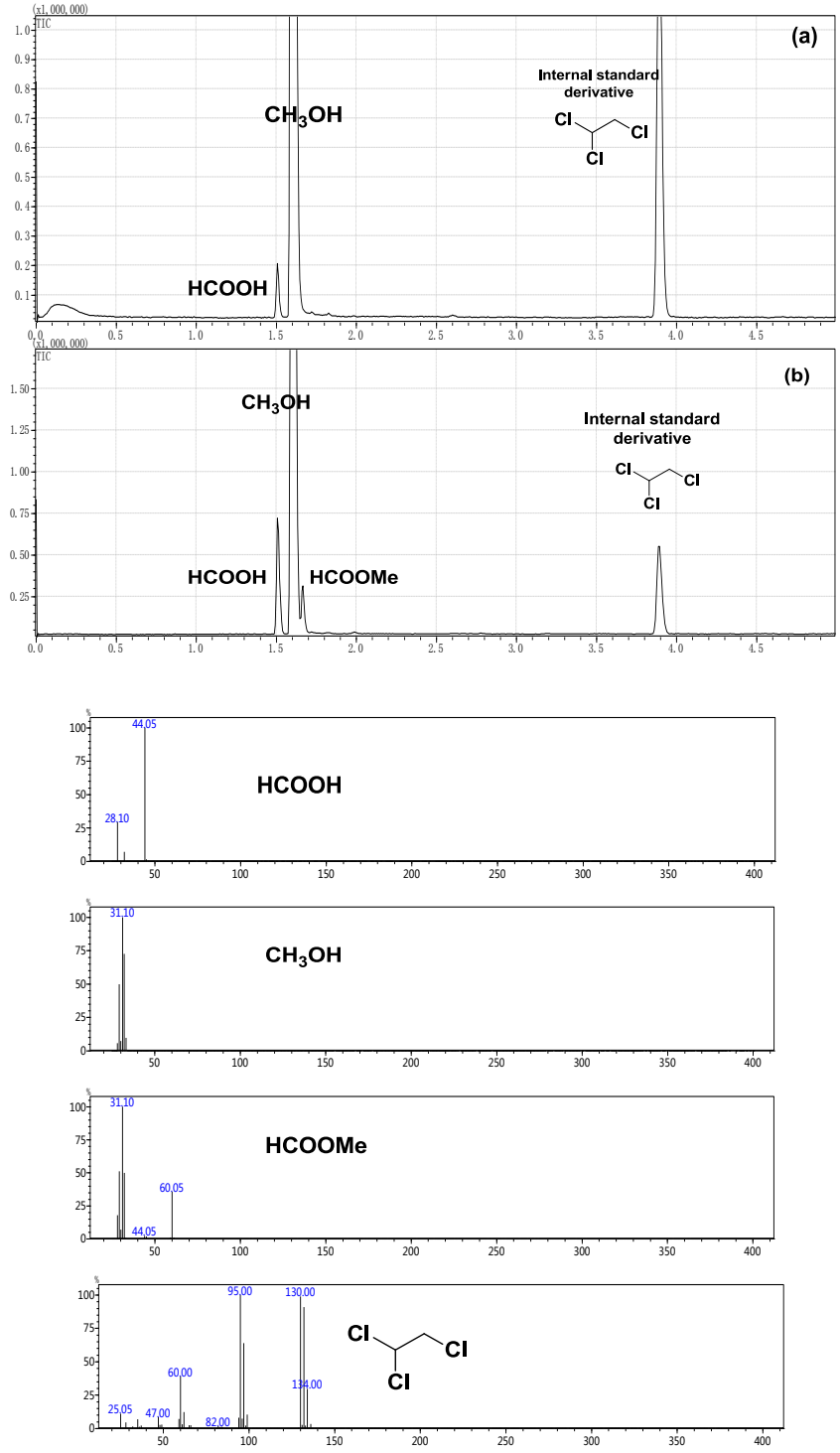


Figure S9 CG-MS analysis for reaction mixture of captured CO_2 hydrogenation (a) and gaseous CO_2 hydrogenation (b). Conditions: (a) $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg), DPEphos (0.05 mmol, 13 mg), DBUOH + CO_2 in tetraethylene glycol dimethyl ether (3 mmol : 2.85 mmol : 5 mmol), methanol (3 mL), H_2 (4 MPa), 60 ^oC, 16 h; (b) $RhCl_3 \cdot 3H_2O$ (0.005 mmol, 1.3 mg), DPEphos (0.05 mmol, 13 mg), DBUOH (3 mmol, 0.64 g), methanol (3 mL), CO_2 (4 MPa), H_2 (4 MPa), 60 ^oC, 16 h.

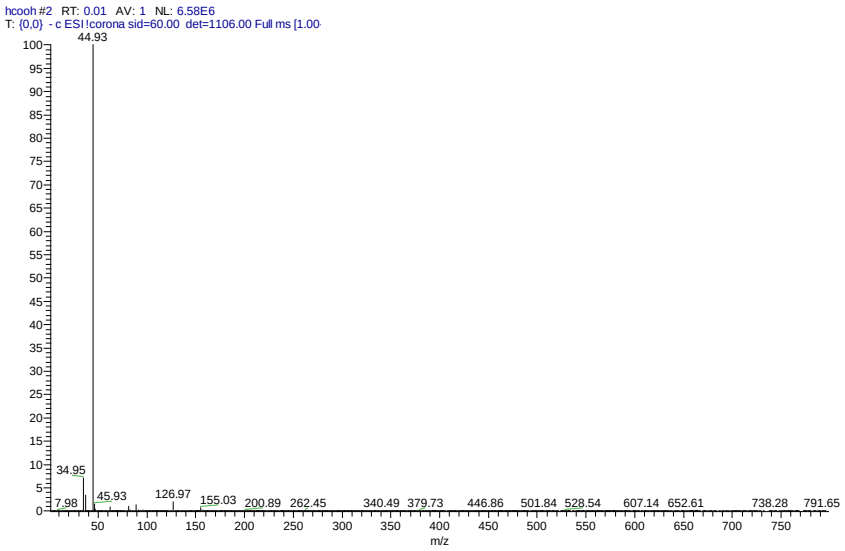


Figure S10 ESI-MS (4.8 kV) spectra of separated HCOOH (m/z (%) = 44.93 (100) $[M-H]^+$).

3. The Characterization data for the absorption mixture

PEG_{150} (triethylene glycol, MW = 150 Da)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (t, ^3J = 4.8 Hz, 4 H), 3.65 (s, 4 H), 3.59 (t, ^3J = 4.8 Hz, 4 H), 3.40 (s, 2 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 72.62, 70.25, 61.50.

$PEG_{150}MeCl$

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35 (s, 3H), 3.52 (s, 2H), 3.62-3.64 (m, 8H), 3.72 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 42.60, 58.93, 70.50, 70.54, 71.24, 71.82; GC-MS: m/z (%):183.02 (100), 185.03 (33) $[M^+]$, 151.08 (26), 153.07 (8) $[M^+-CH_3O]$, 103.13 (61) $[M^+-C_2H_4OCl]$.

$BrPEG_{150}Br$

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44-3.45 (m, 4H), 3.67 (d, ^3J = 2.8 Hz, 4H), 3. 78-3.81 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 30.30, 70.38, 71.11.

DBU

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 (t, ^3J = 5.6 Hz, 2H), 3.07-3.12 (m, 4H), 2.27 (d, ^3J = 6.4 Hz, 2H), 1.66-1.18 (m, 2H), 1.55 (t, ^3J = 2.4 Hz, 4H), 1.47 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 161.30, 52.60, 48.14, 44.04, 37.21, 29.56, 28.32, 25.80, 22.29.

$HOCH_2CH_2OH$ (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.

$DBU_2PEG_{150}Br_2$

^{1}H NMR (400 MHz, D_2O) δ 3.67-3.73 (m, 12H), 3.60-3.62 (m, 4H), 3.49-3.51 (m, 8H), 2.83 (d, ^3J = 8.8 Hz, 4H), 2.04 (t, ^3J = 5.2 Hz, 4H), 1.68-1.71 (m, 12H); ^{13}C NMR (100.6 MHz, D_2O) δ 167.2, 70.1, 68.0, 54.8, 52.5, 48.9, 47.2, 28.0, 25.4, 22.6, 19.6; ESI-MS calcd for $C_{24}H_{44}Br_2N_4O_2$ 578.18, found 210.5 $[(M-2Br)/2]^+$, 499.4, 501.4 $[M-Br]^+$.

$DBUPEG_{150}Me$

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68-3.47 (m, 13H), 3.32-3.29 (m, 3H), 3.16-3.12 (s, 5H), 2.31 (s, 1H), 1.71-1.49 (m, 8H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 165.04, 71.73, 71.16, 70.45, 70.40, 58.87, 53.94, 48.50, 42.58, 39.13, 33.12, 29.03, 27.06, 24.32, 20.03. ESI-MS: m/z 299.4 [$M+H^+$].

$TMGPEG_{150}Me$

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 6H), 2.69 (s, 6H), 3.27 (t, ^{3}J = 6.4 Hz, 2H), 3.32 (s, 3H), 3.58-3.50 (m, 4H), 3.60 (s, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 161.00, 73.23, 71.80, 70.50, 70.33, 70.22, 58.87, 49.30, 39.48, 38.68. ESI-MS: m/z 262.2 [$M+H^+$].

DBUOH

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01-1.07 (m, 3H), 1.69-1.56 (m, 7H), 1.94 (s, 1H), 2.35-2.45 (m, 3H), 2.49-2.61 (m, 2H), 3.25-3.27 (m, 2H), 3.30-3.48 (m, 2H), 3.57 (s, OH), 3.68-3.79 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.19, 64.75, 56.60, 49.35, 45.72, 45.30, 36.92, 29.73, 28.31, 27.57, 23.23, 20.42; ESI-MS: m/z 211.4 [$M+H^+$].

3-Glycidoxypropyltrimethoxysilane

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64-3.67 (m, 2H), 3.51 (s, 9H), 3.38-3.44 (m, 1H), 3.30-3.34 (m, 1H), 3.08 (s, 1H), 2.73 (s, 1H), 2.55 (s, 1H), 1.64 (t, ^{3}J = 8.0 Hz, 2H), 0.617 (t, ^{3}J = 8.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 73.37, 71.24, 50.71, 50.35, 44.17, 22.66, 5.08.

DBUOH@Silica

^{1}H NMR (400 MHz, DMSO-d_6) δ 3.53 (s, OH), 3.04-3.16 (m, 8H), 2.25 (s, 2H), 1.26-1.63 (m, 11H), 0.84 (s, 3H), 0.46-0.54 (m, 3H); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 160.78, 70.71, 64.17, 52.01, 48.77, 47.67, 43.24, 35.99, 29.18, 28.14, 26.37, 25.81, 22.25, 13.81, 11.85.

$DBUPEG_{150}Me$ /Glycol (1:2)+CO_2

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.57-1.65 (m, 6H), 1.86-1.95 (m, 1H), 2.68-2.76 (m, 2H), 3.18-3.28 (m, 7H), 3.28-3.56 (m, 22H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 165.76, 151.29, 71.47, 70.90, 70.13, 63.40, 58.61, 54.13, 48.36, 42.47, 37.76, 32.11, 28.58, 26.32, 23.57, 19.08.

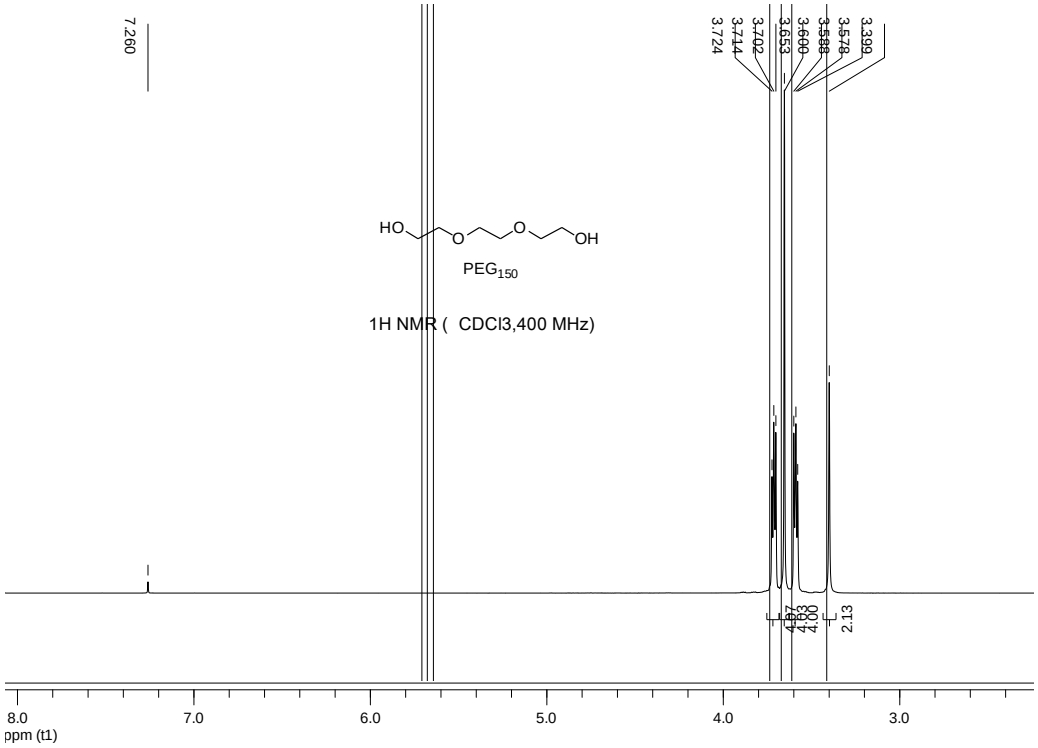
$TMGPEG_{150}Me$ /Glycol (1:5)+CO_2

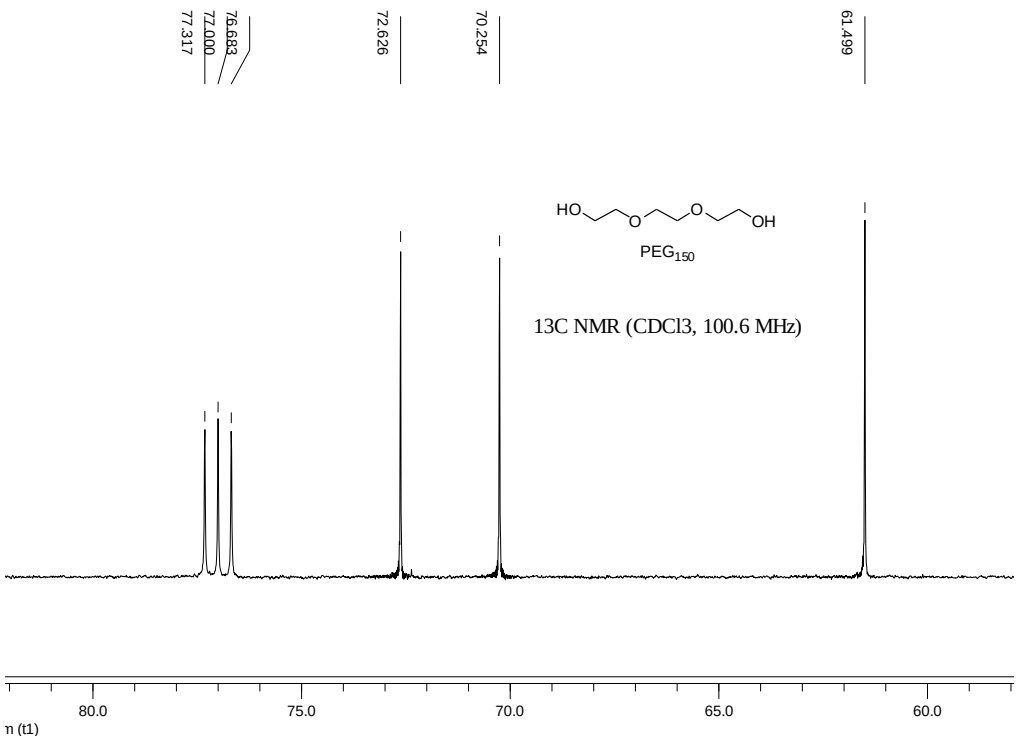
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (t, ^{3}J = 8.0 Hz, 9H), 3.16 (t, ^{3}J = 6.8 Hz, 4H), 3.33 (s, 2H), 3.41-3.45 (m, 30H), 3.77 (s, 2H), 5.0 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 162.17, 158.73, 71.27, 69.83, 69.70, 69.03, 66.66, 63.00, 61.12, 58.31, 44.26, 39.25.

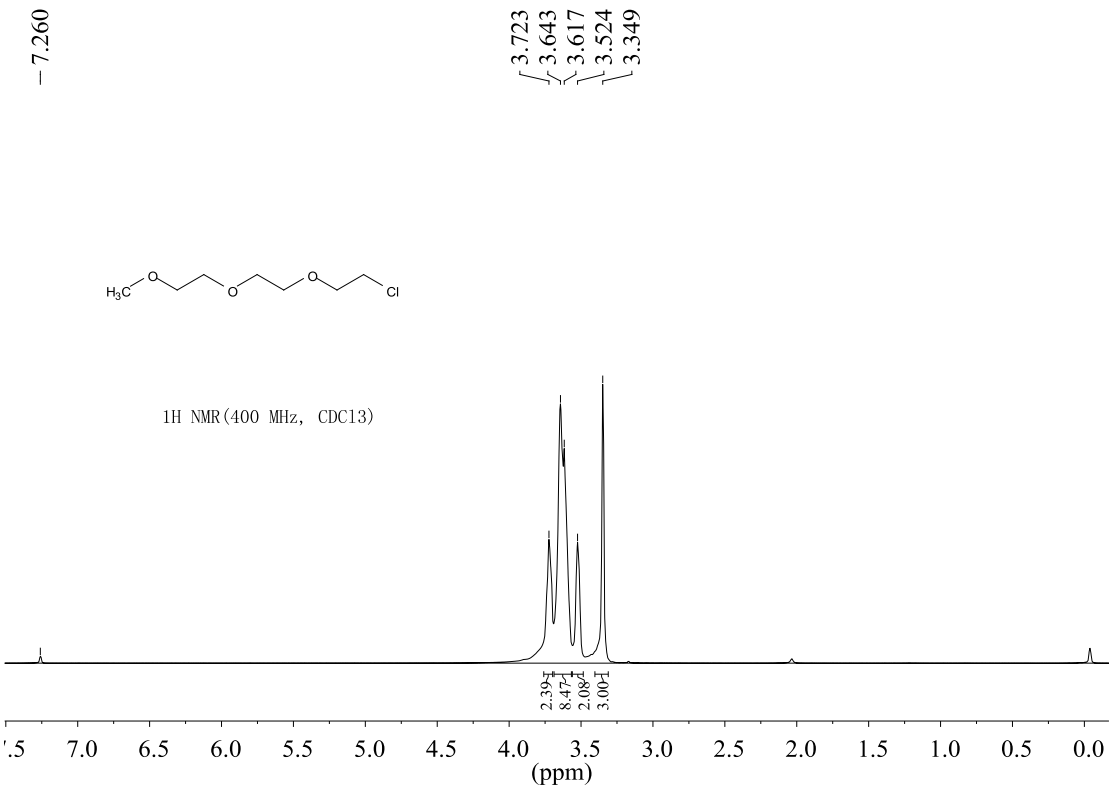
DBUOH+CO_2

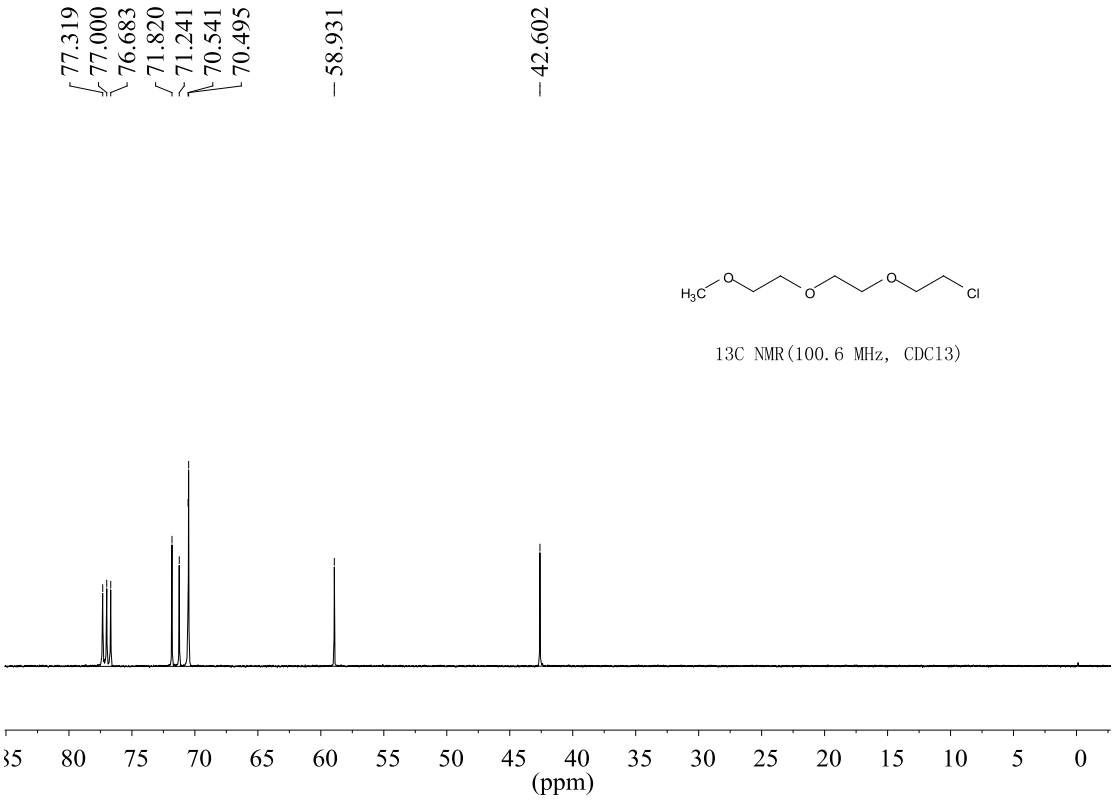
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92-1.00 (m, 3H), 1.47-1.67 (m, 8H), 2.34-2.43 (m, 3H), 2.51-2.58 (m, 2H), 3.18-3.31 (m, 4H), 3.61 (s, 0.5H), 3.79 (s, 0.5H), 5.21 (s, OH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.19, 164.25, 63.90, 55.93, 49.19, 45.36, 45.01, 36.64, 29.48, 28.04, 26.44, 23.00, 20.41.

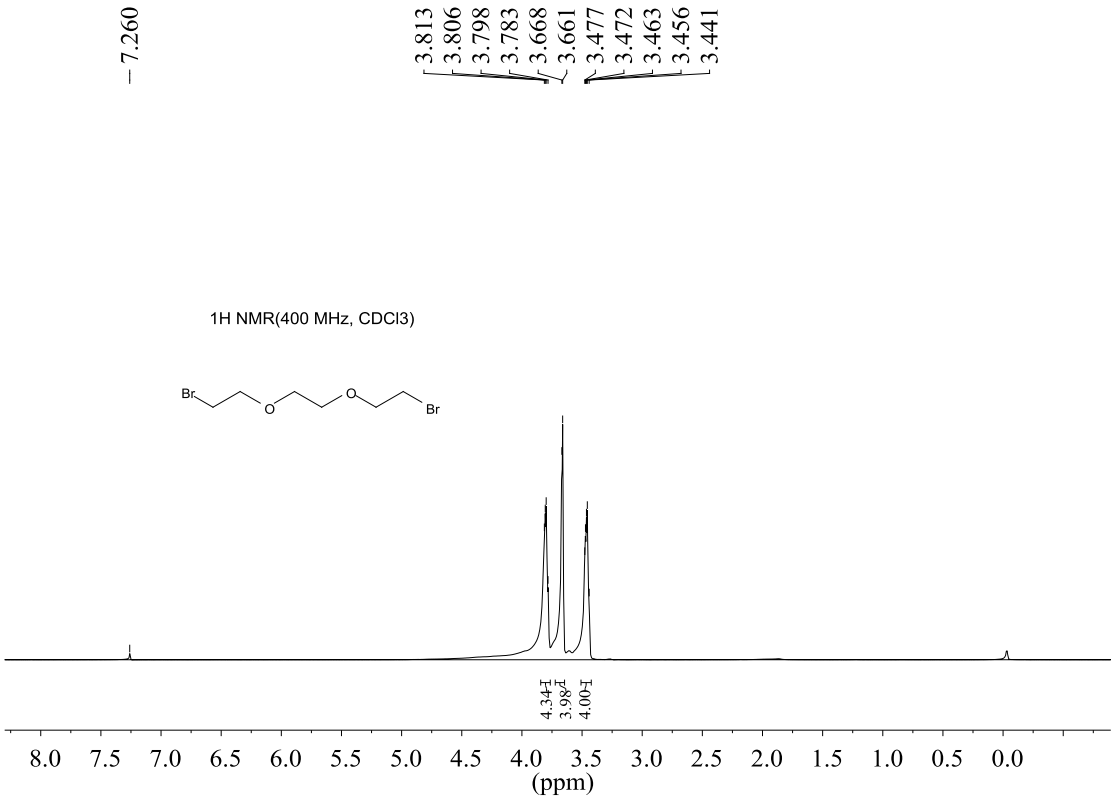
4. ^{1}H NMR and ^{13}C NMR Charts

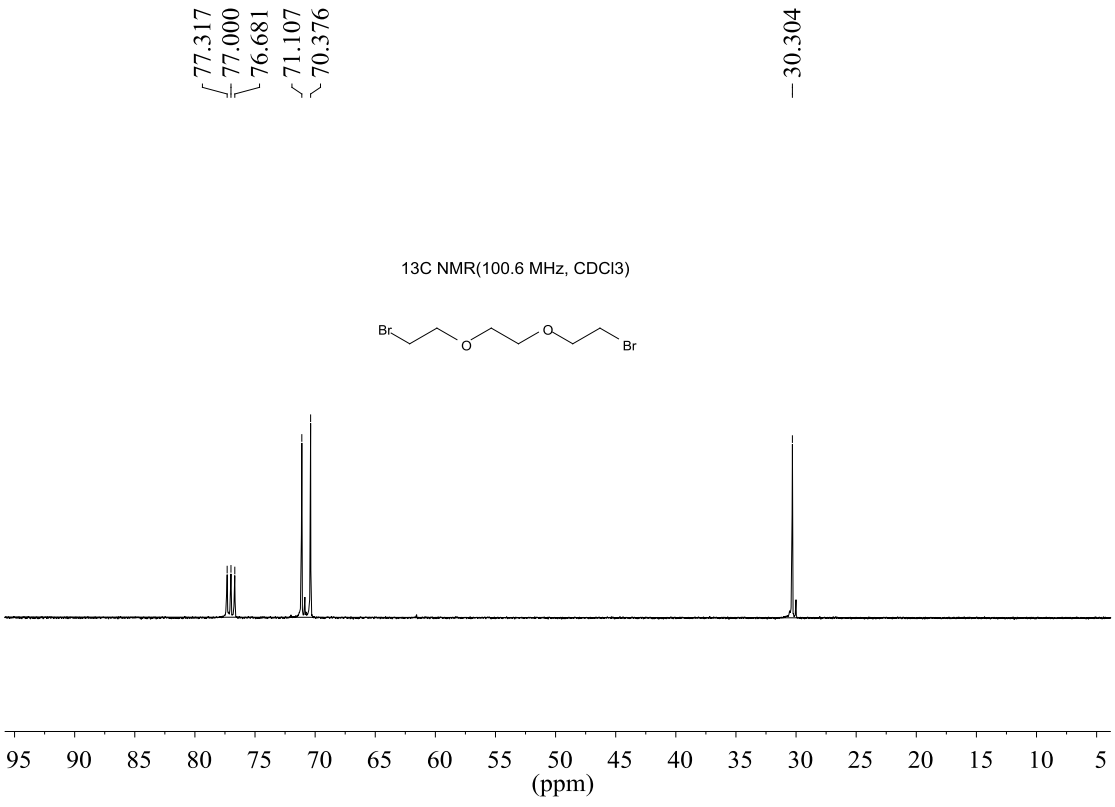


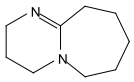



7.260
3.723
3.643
3.617
3.524
3.349
H3C
O
O
O
Cl
1H NMR(400 MHz, CDC13)
2.39
8.47
2.08
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

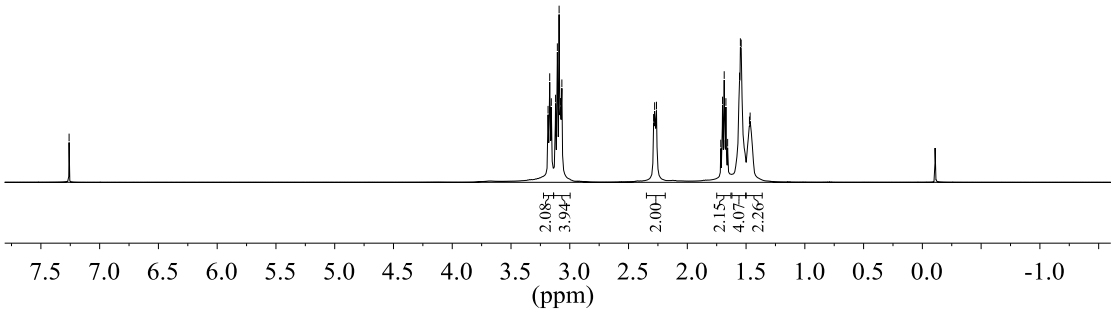

77.319
77.000
76.683
71.820
71.241
70.541
70.495
58.931
42.602
H3C
O
O
O
Cl
13C NMR(100.6 MHz, CDC13)
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
(ppm)

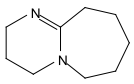

7.260
3.813
3.806
3.798
3.783
3.668
3.661
3.477
3.472
3.463
3.456
3.441
1H NMR(400 MHz, CDCl3)
Br
O
O
Br
4.34
3.98
4.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


77.317
77.000
76.681
71.107
70.376
30.304
13C NMR(100.6 MHz, CDCl3)
Br
O
O
Br
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
(ppm)

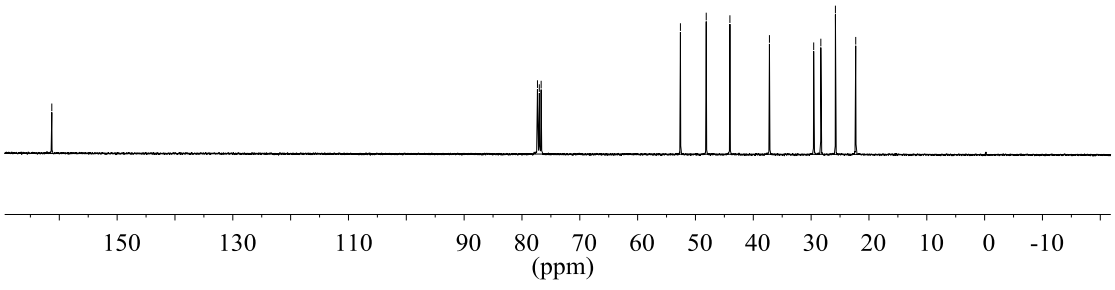


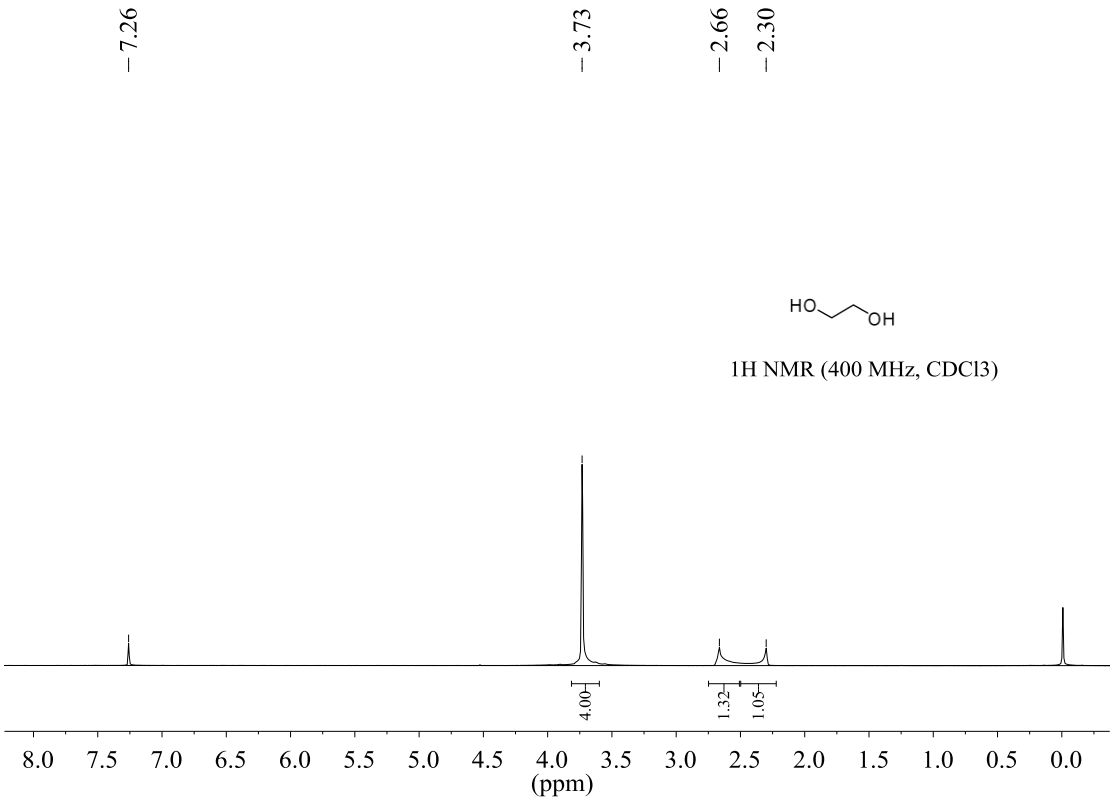
1H NMR (400 MHz, CDCl3)

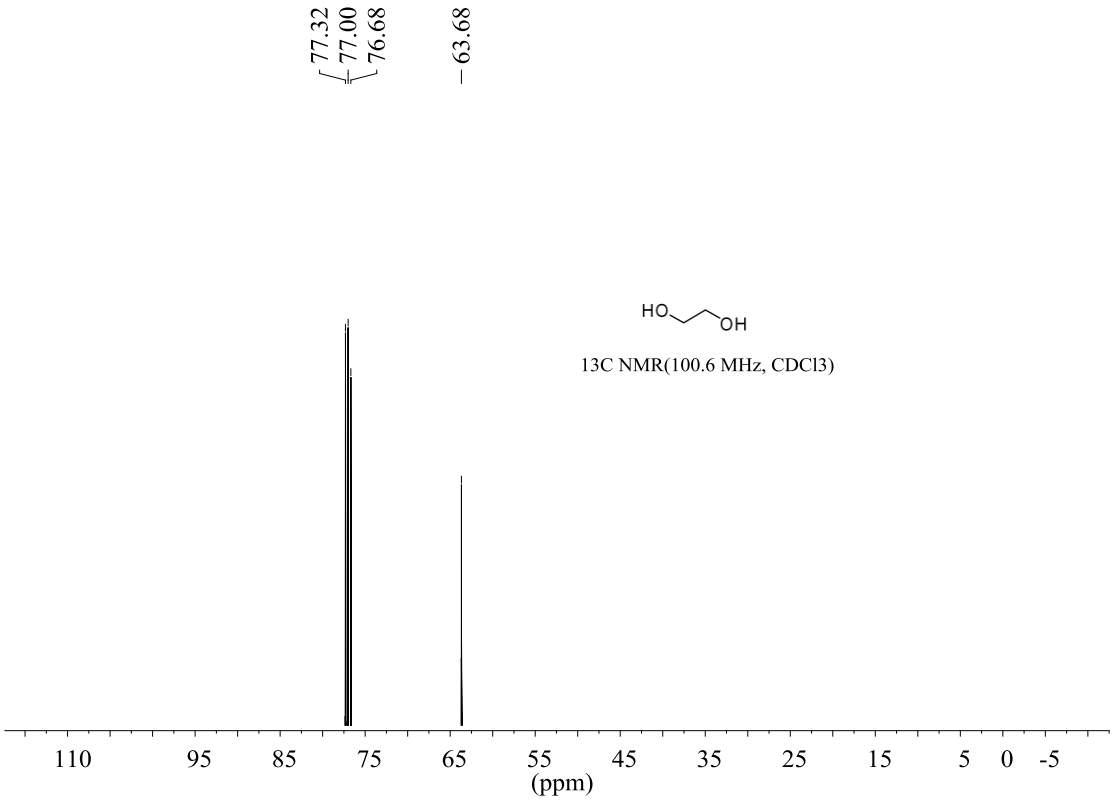


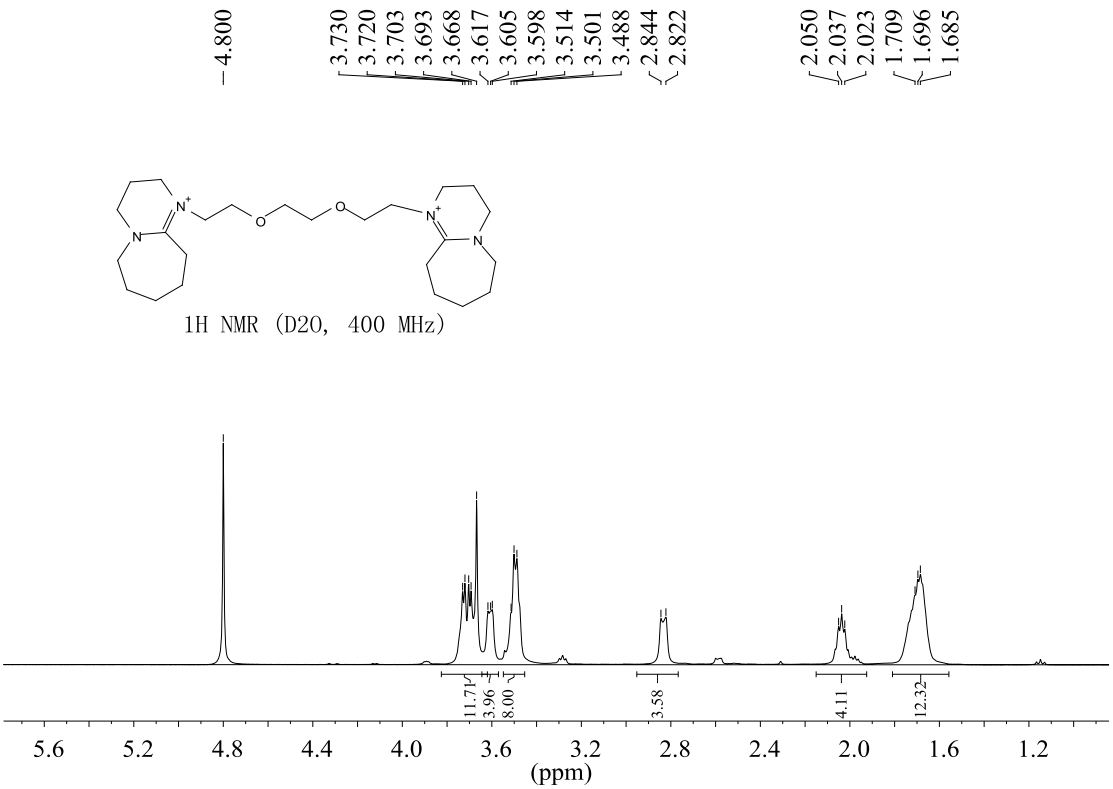


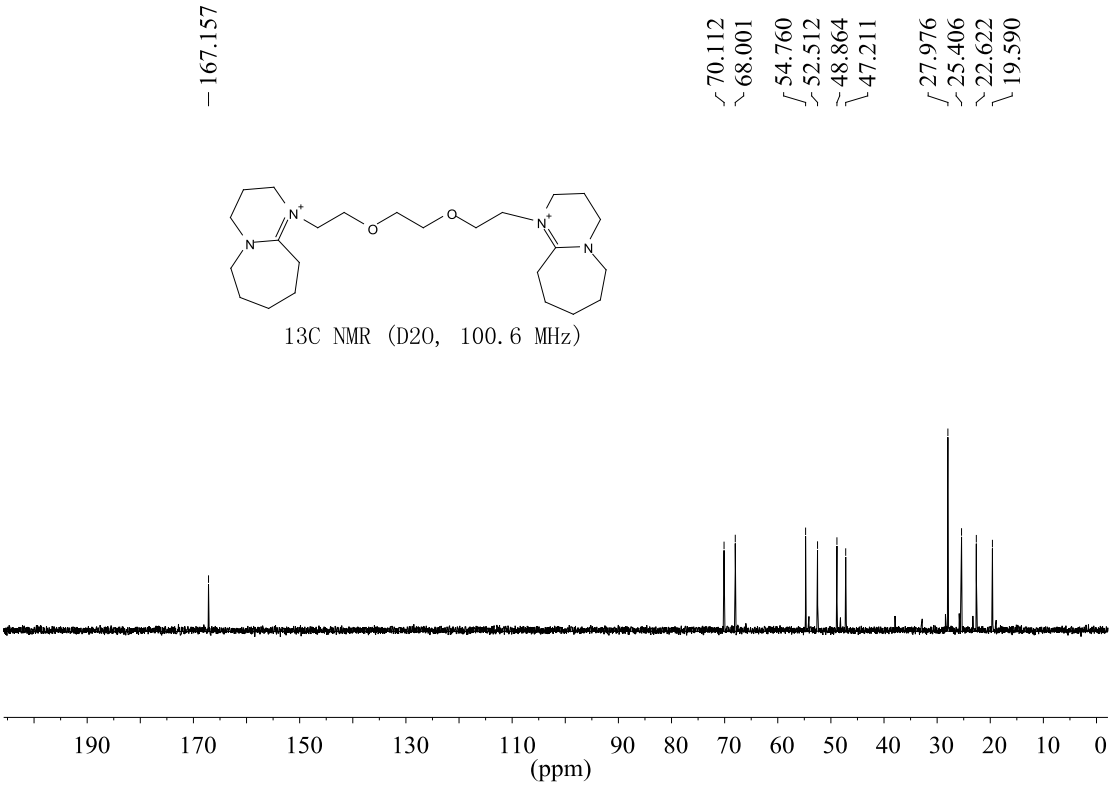
13C NMR (100.6 MHz, CDCl3)

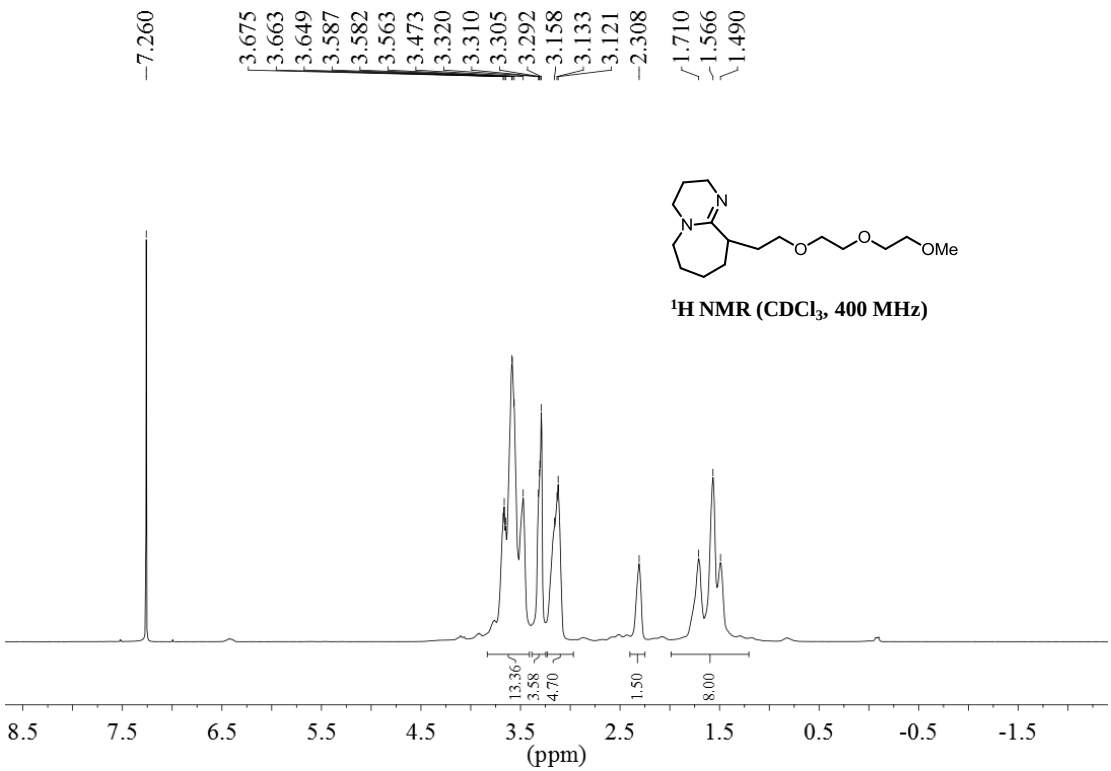



7.26
3.73
2.66
2.30
HO
OH
1H NMR (400 MHz, CDCl3)
4.00
1.32
1.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

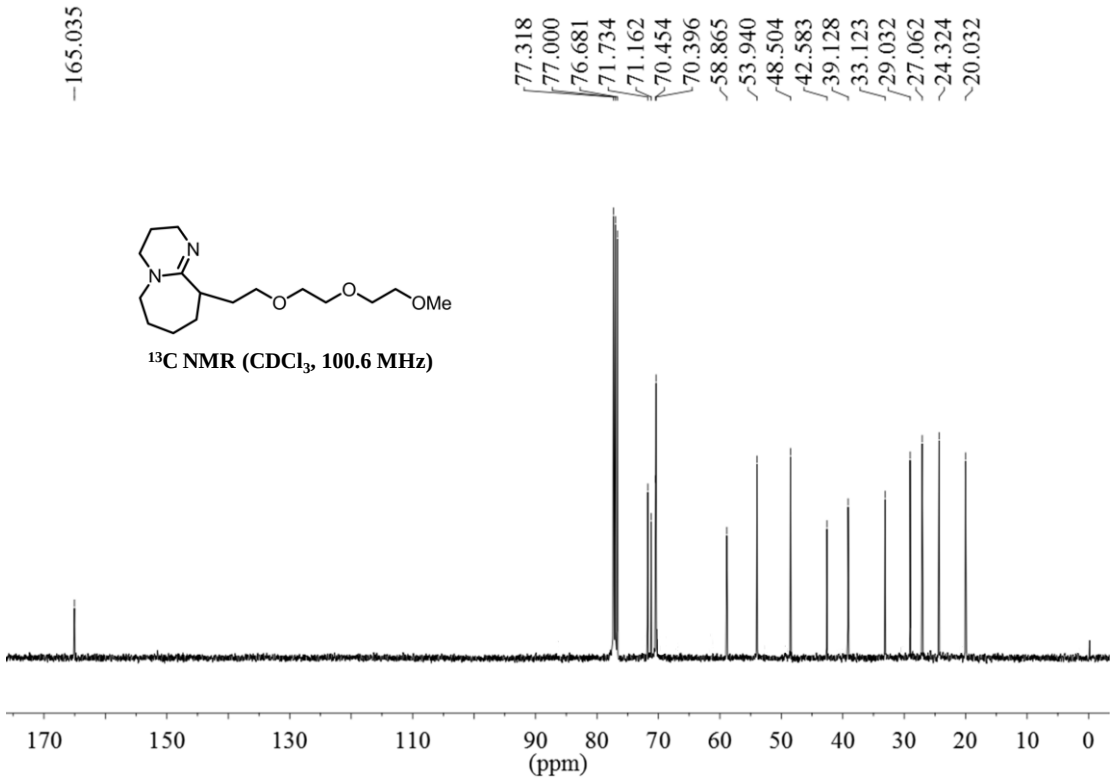

77.32
77.00
76.68
63.68
HO
OH
13C NMR(100.6 MHz, CDCl3)
110 95 85 75 65 55 45 35 25 15 5 0 -5
(ppm)


4.800
3.730
3.720
3.703
3.693
3.668
3.617
3.605
3.598
3.514
3.501
3.488
2.844
2.822
2.050
2.037
2.023
1.709
1.696
1.685
1H NMR (D2O, 400 MHz)
11.71
3.96
8.00
3.58
4.11
12.32
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
(ppm)

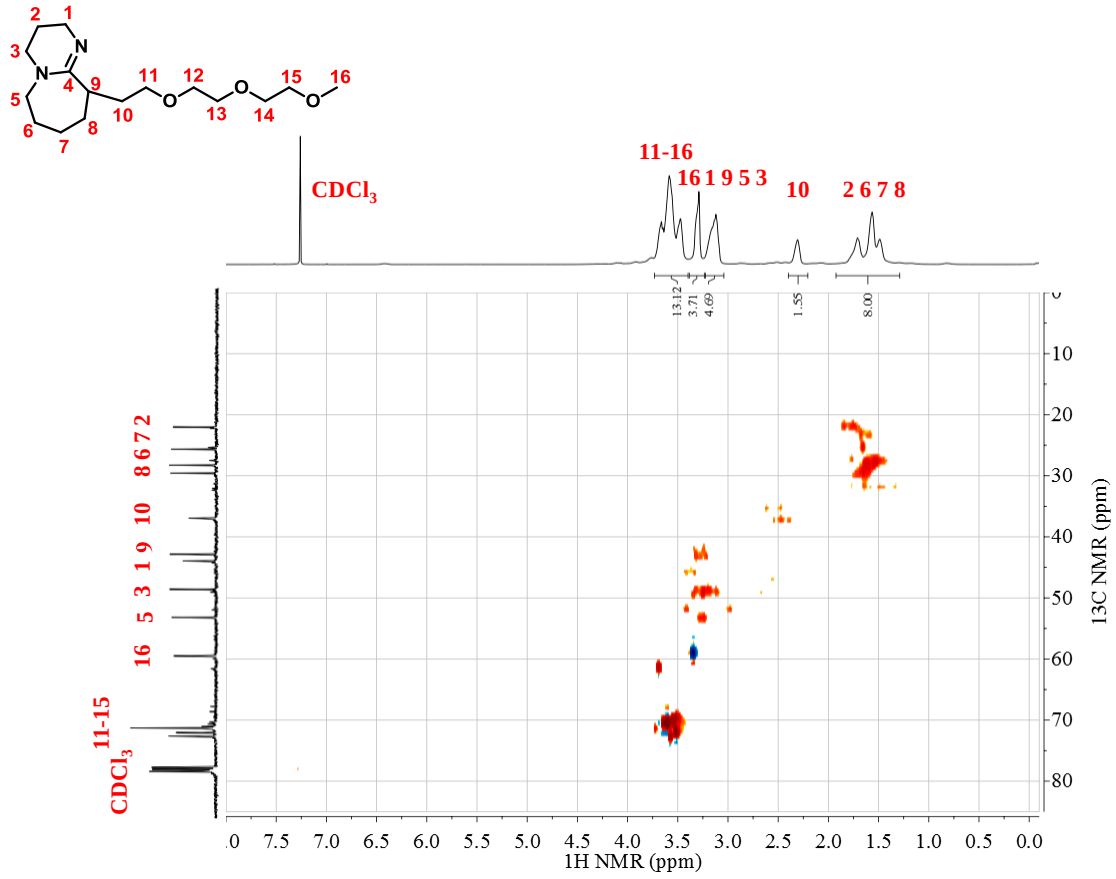

167.157
70.112
68.001
54.760
52.512
48.864
47.211
27.976
25.406
22.622
19.590
13C NMR (D2O, 100.6 MHz)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)

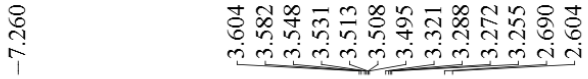


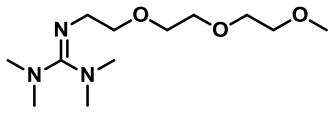
^{1}H NMR ($CDCl_3$, 400 MHz)



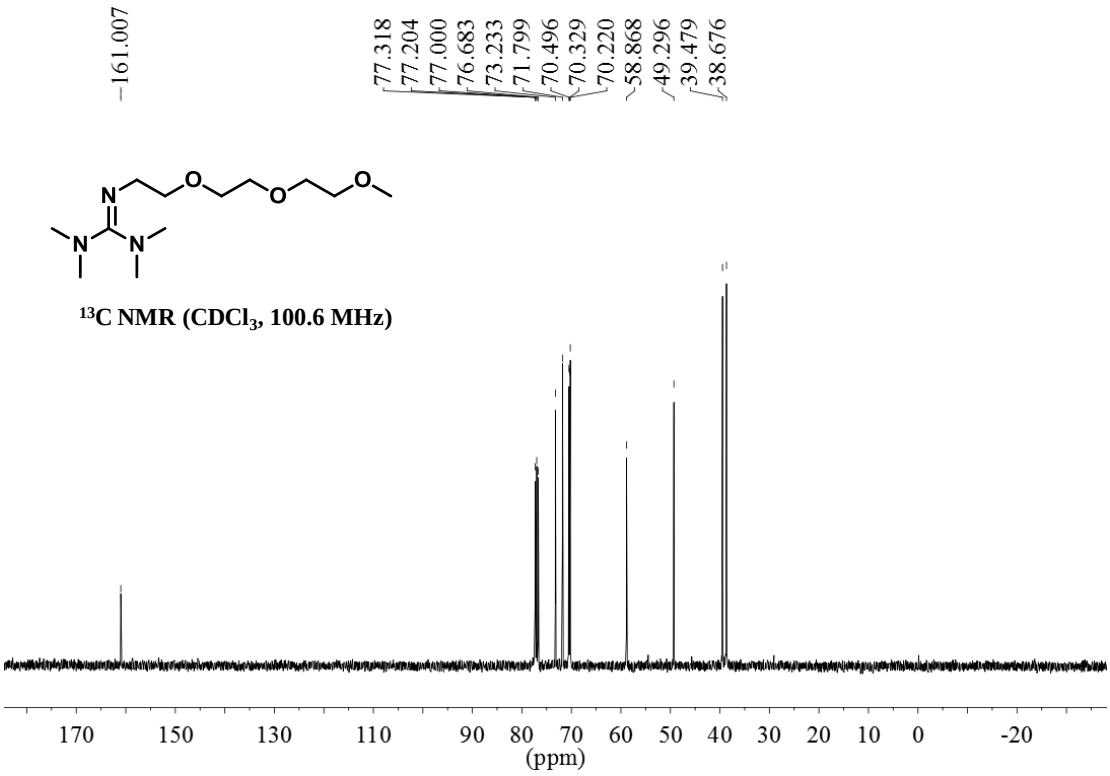
^{13}C NMR ($CDCl_3$, 100.6 MHz)

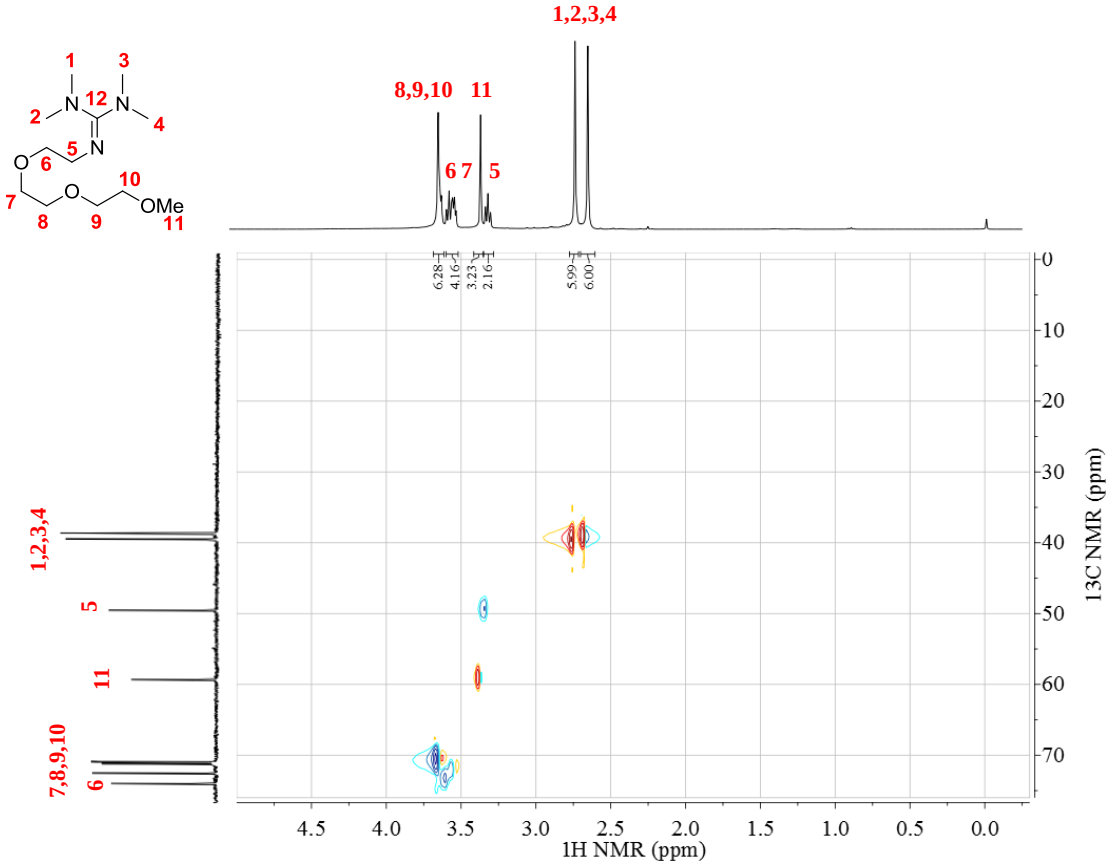


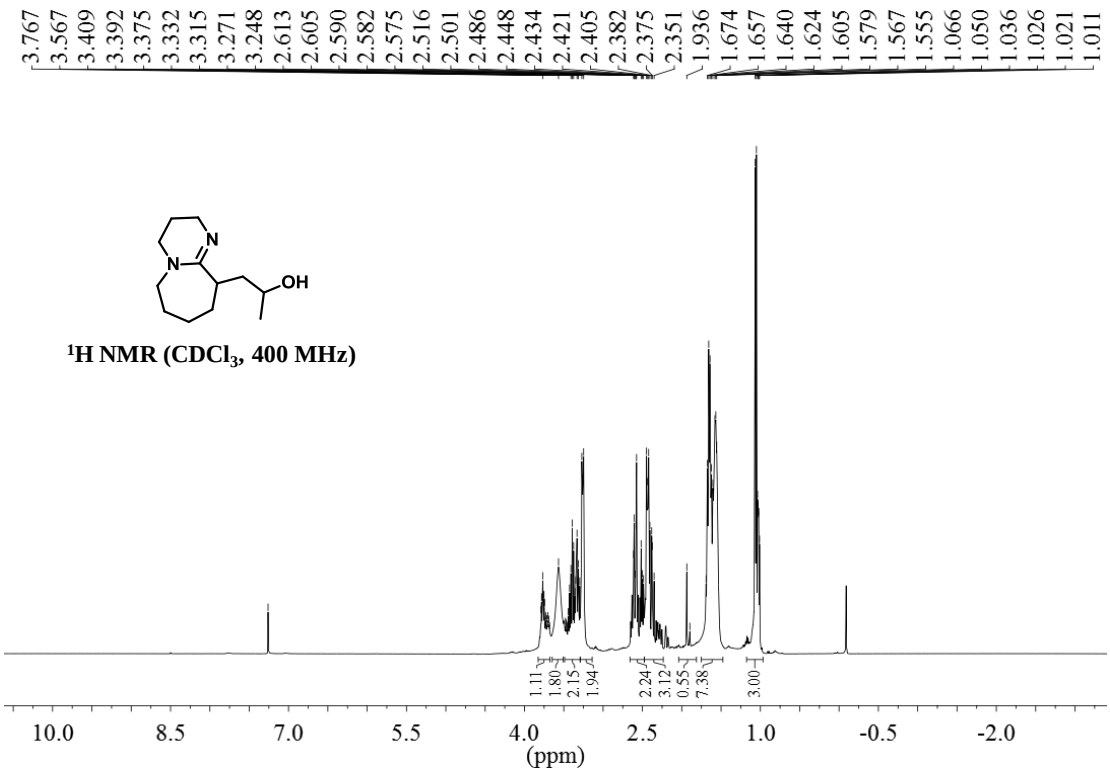




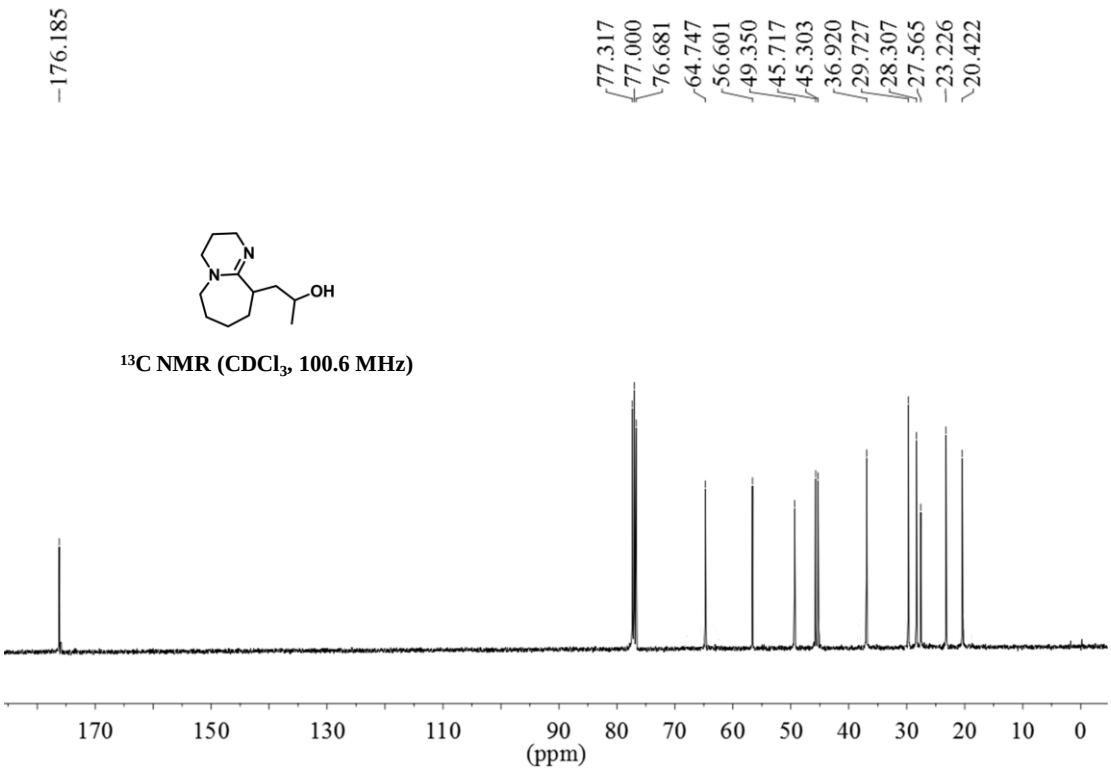
^{1}H NMR ($CDCl_3$, 400 MHz)


161.007
77.318
77.204
77.000
76.683
73.233
71.799
70.496
70.329
70.220
58.868
49.296
39.479
38.676
N
O
O
O
N
N
N
13C NMR (CDCl3, 100.6 MHz)
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
(ppm)

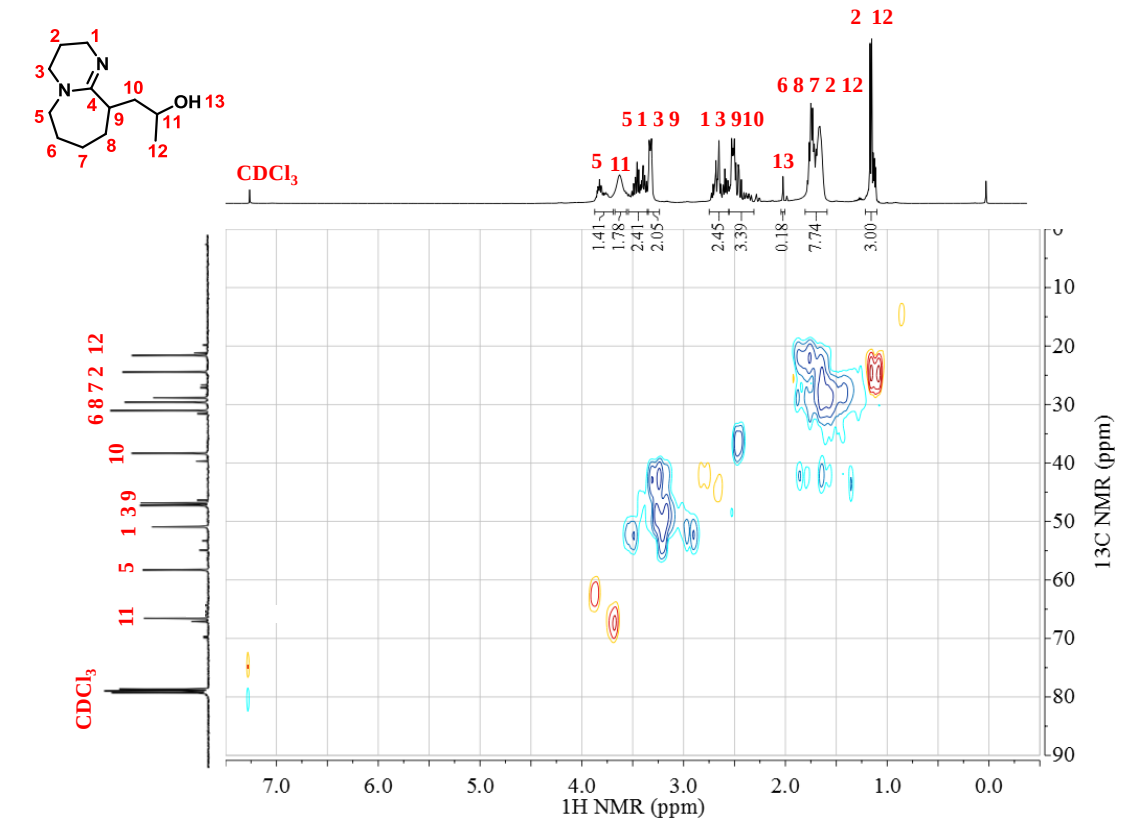

1
3
2
N
12
N
4
5
N
O
6
10
7
O
OMe
8
9
11
1,2,3,4
8,9,10
11
6 7
5
6.28
4.16
3.23
2.16
5.99
6.00
1,2,3,4
5
11
7,8,9,10
6
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (ppm)
0
10
20
30
40
50
60
70
13C NMR (ppm)

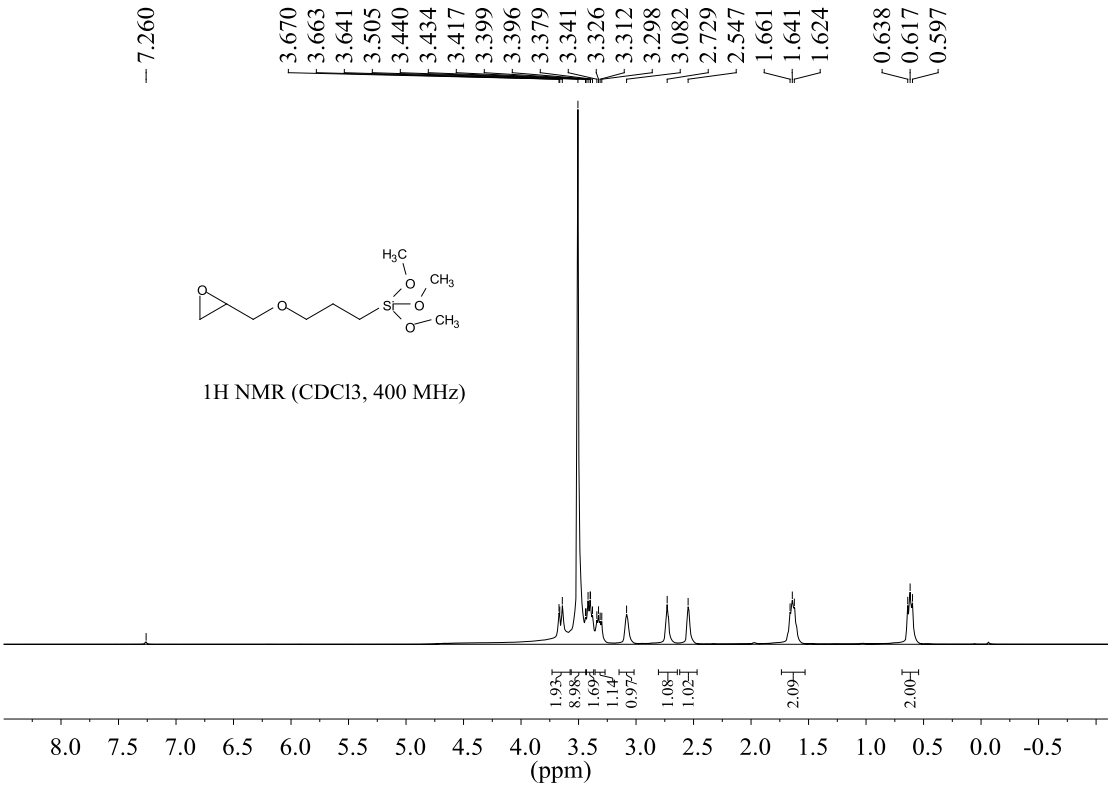


^{1}H NMR ($CDCl_3$, 400 MHz)

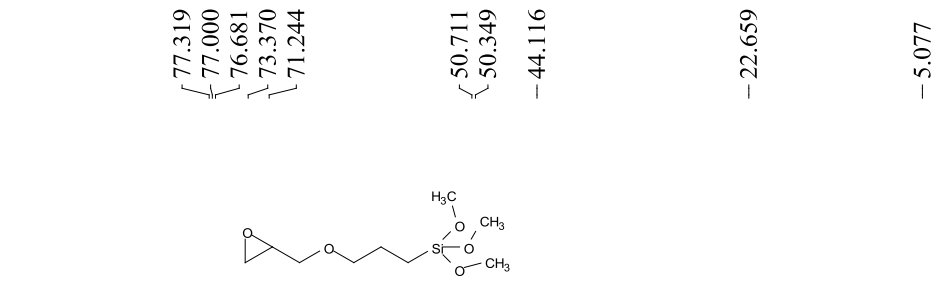


^{13}C NMR ($CDCl_3$, 100.6 MHz)

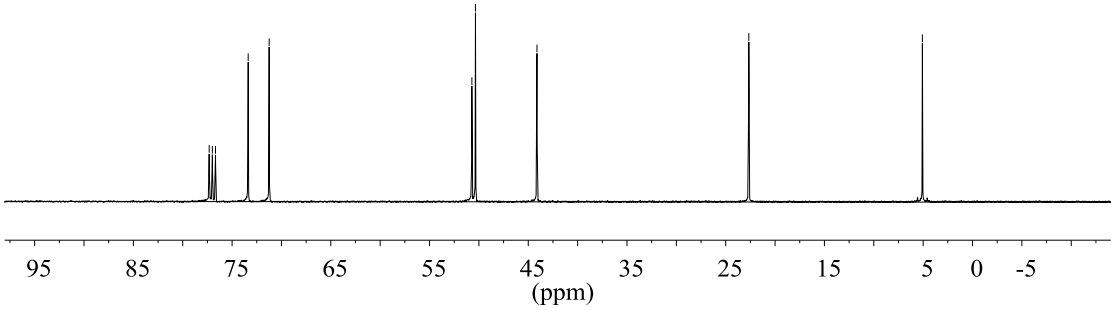




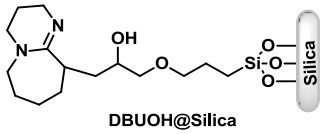
1H NMR (CDCl3, 400 MHz)



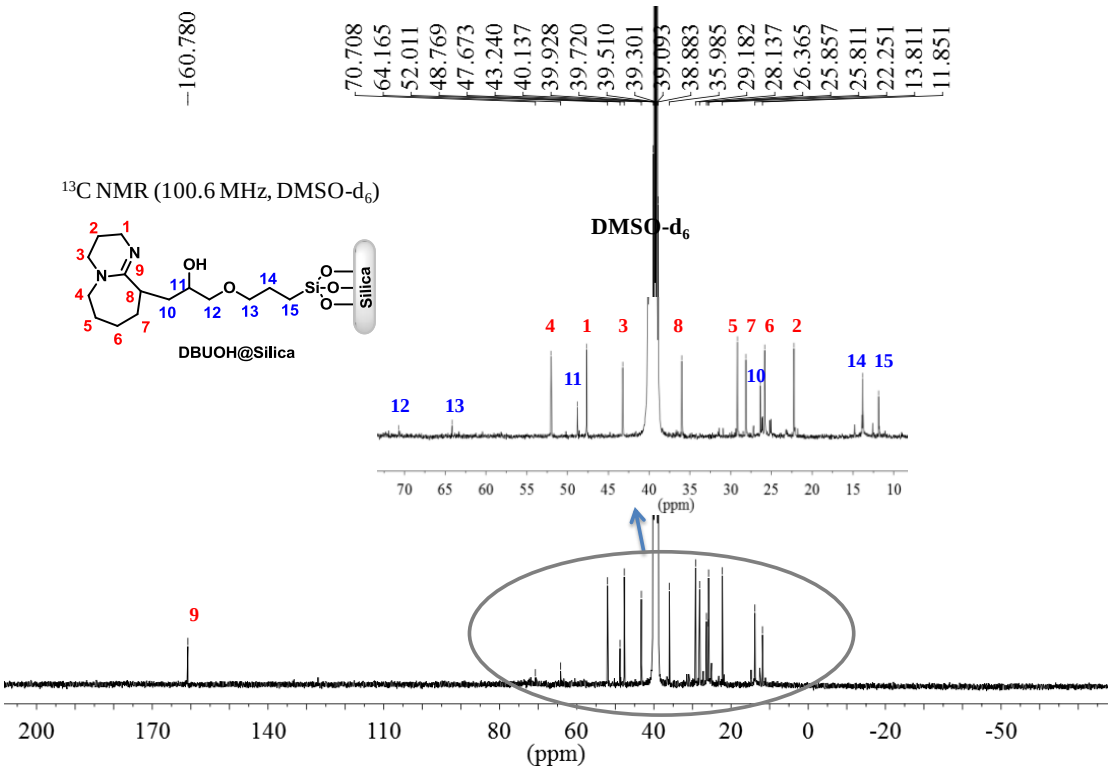
13C NMR(CDCl3, 100.6 MHz)

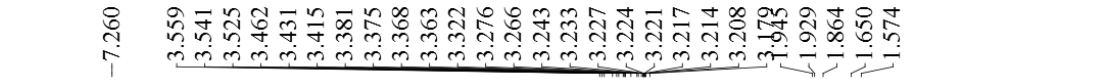


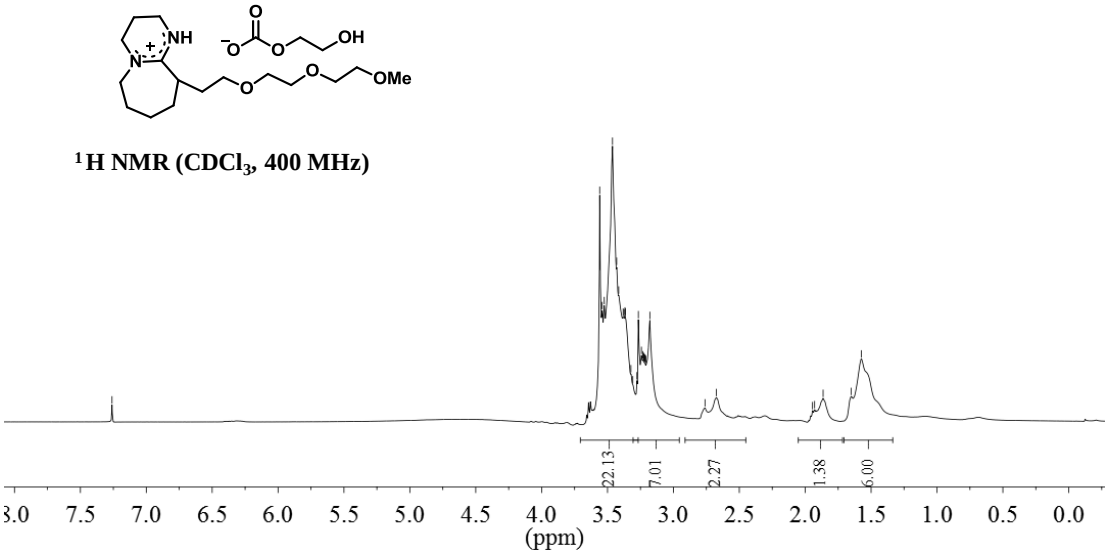
^{1}H NMR (400 MHz, DMSO-d$_6$)

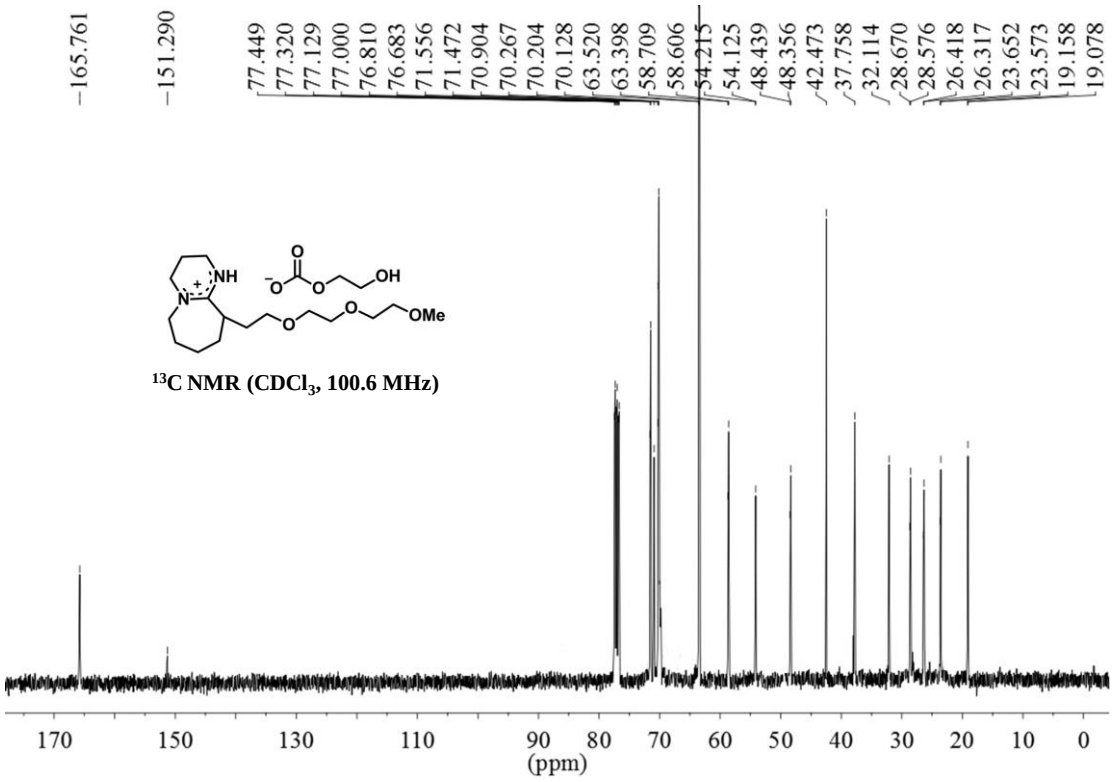


DBUOH@Silica

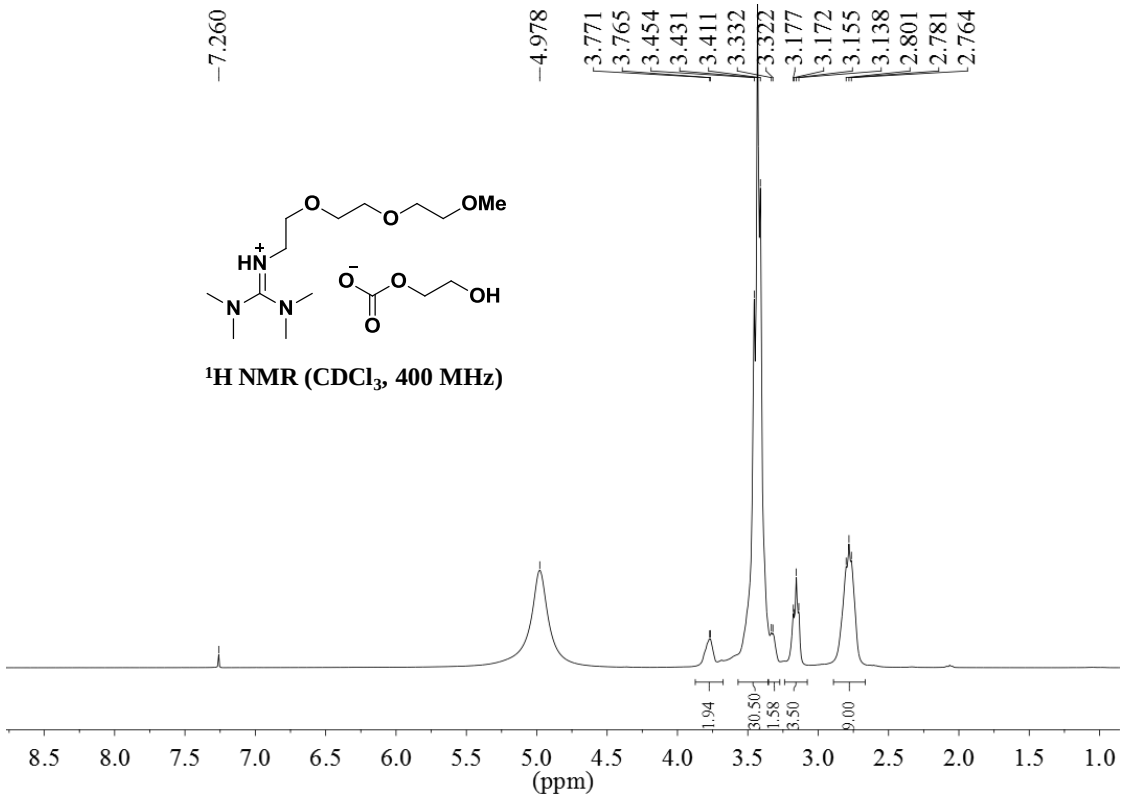

160.780
70.708
64.165
52.011
48.769
47.673
43.240
40.137
39.928
39.720
39.510
39.301
39.095
38.883
35.985
29.182
28.137
26.365
25.857
25.811
22.251
13.811
11.851
13C NMR (100.6 MHz, DMSO-d6)
DMSO-d6
DBUOH@Silica
Silica
(ppm)


7.260
3.559
3.541
3.525
3.462
3.431
3.415
3.381
3.375
3.368
3.363
3.322
3.276
3.266
3.243
3.233
3.227
3.224
3.221
3.217
3.214
3.208
3.179
1.945
1.929
1.864
1.650
1.574

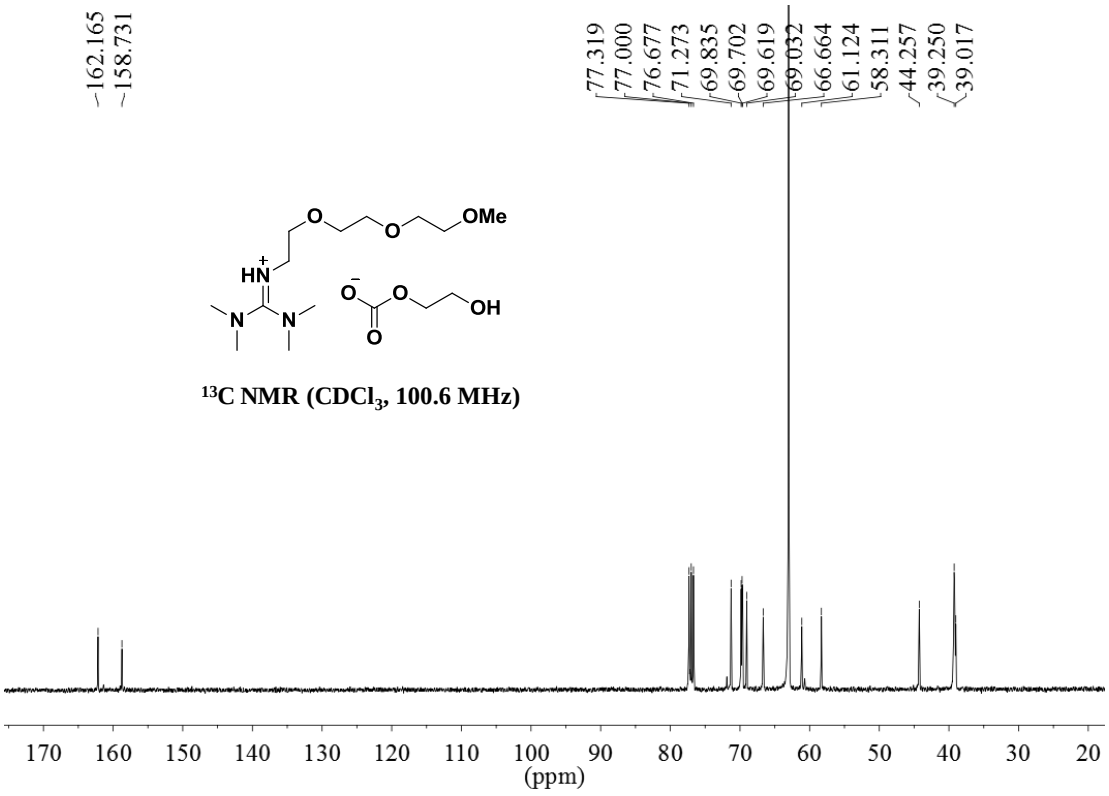

1H NMR (CDCl3, 400 MHz)
22.13
7.01
2.27
1.38
6.00
(ppm)



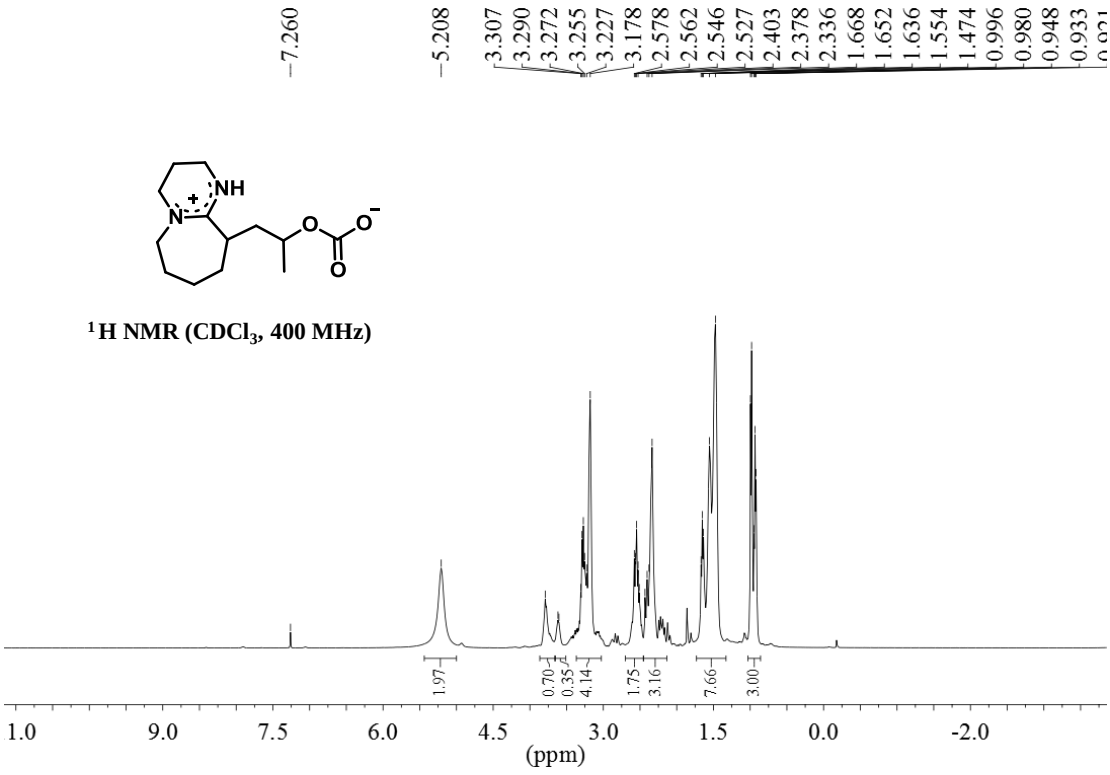
^{13}C NMR ($CDCl_3$, 100.6 MHz)



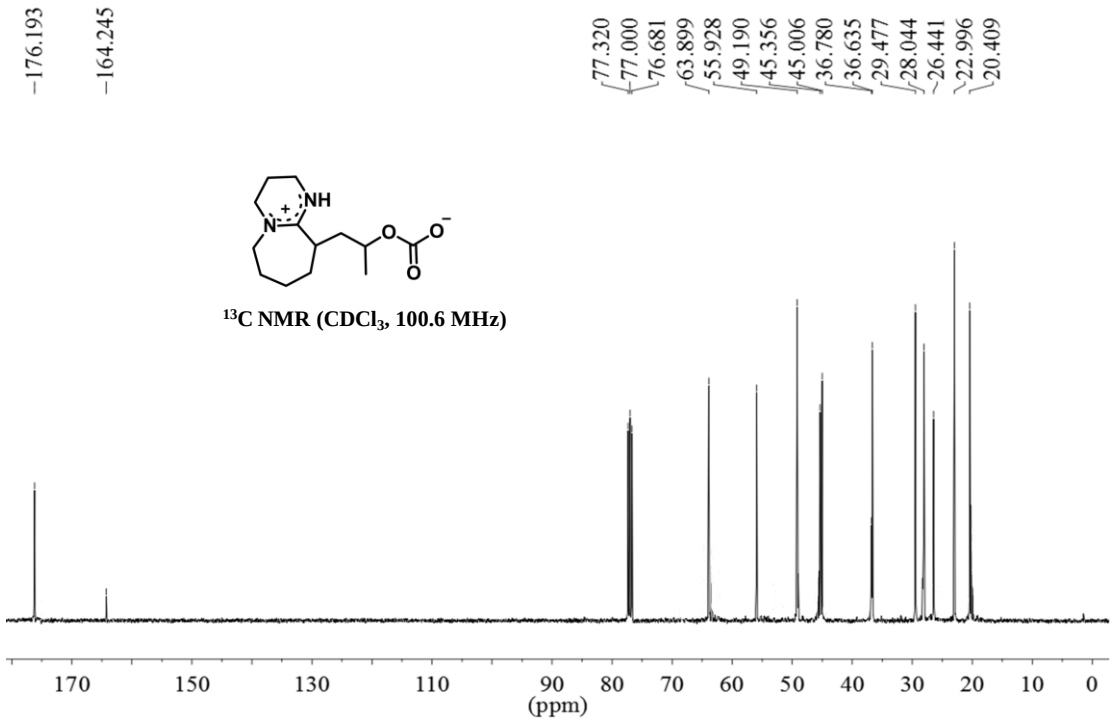
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 100.6 MHz)



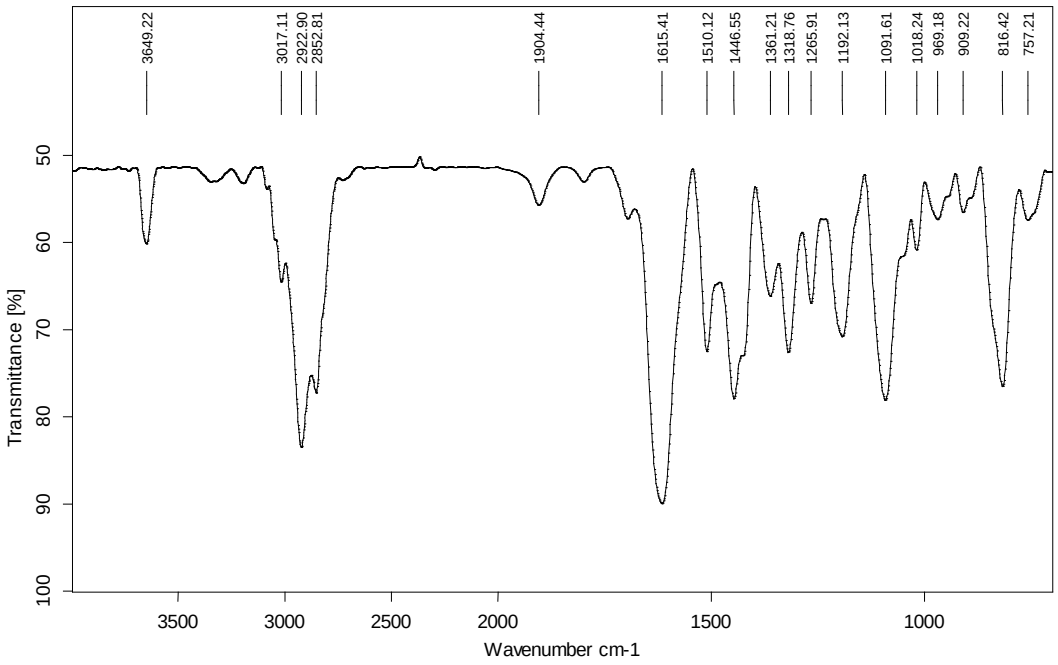
^{1}H NMR ($CDCl_3$, 400 MHz)



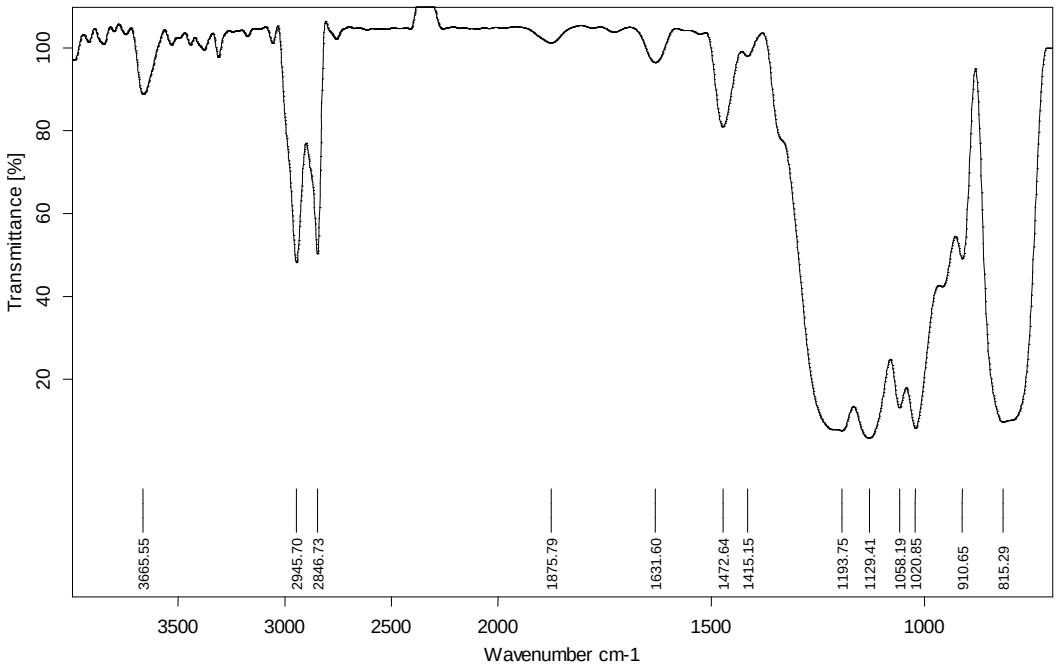
^{13}C NMR ($CDCl_3$, 100.6 MHz)

5. IR spectra

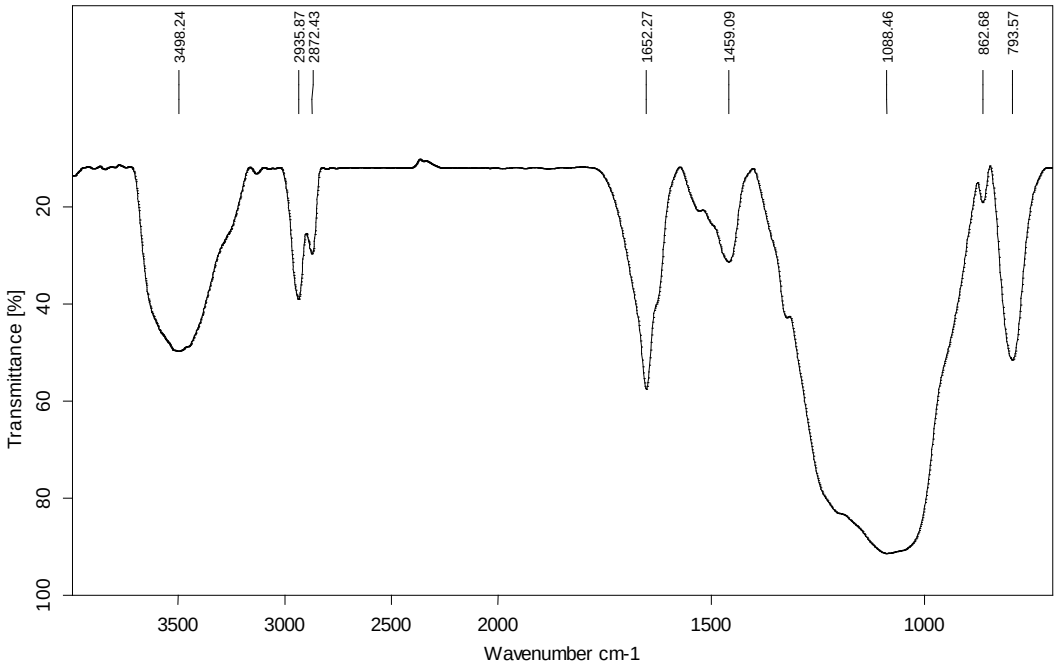
DBU@PS



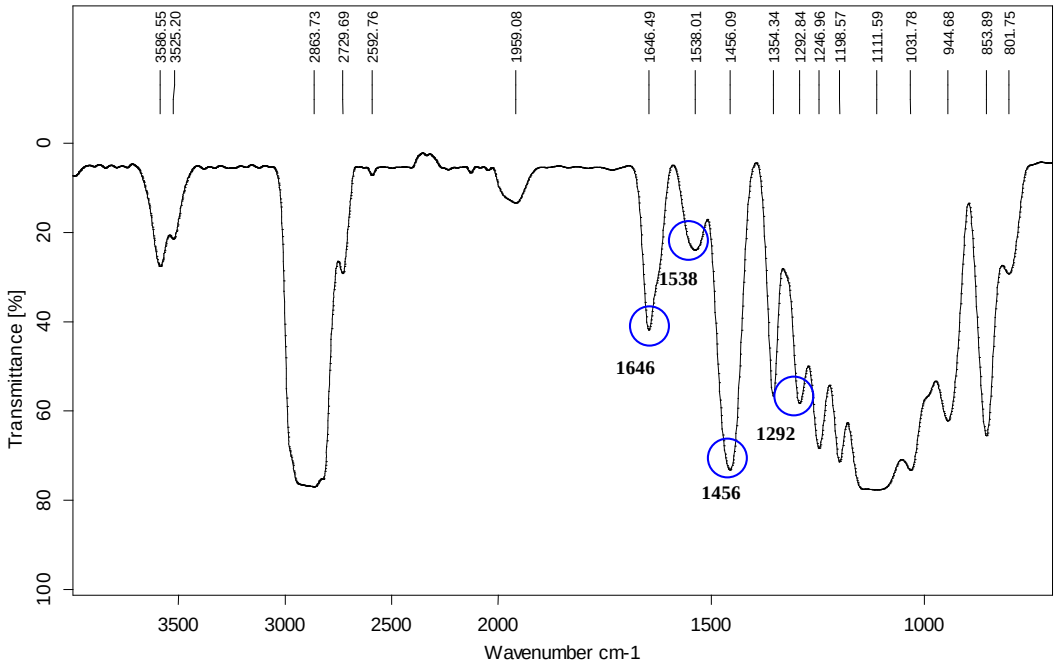
Epoxide@Silica



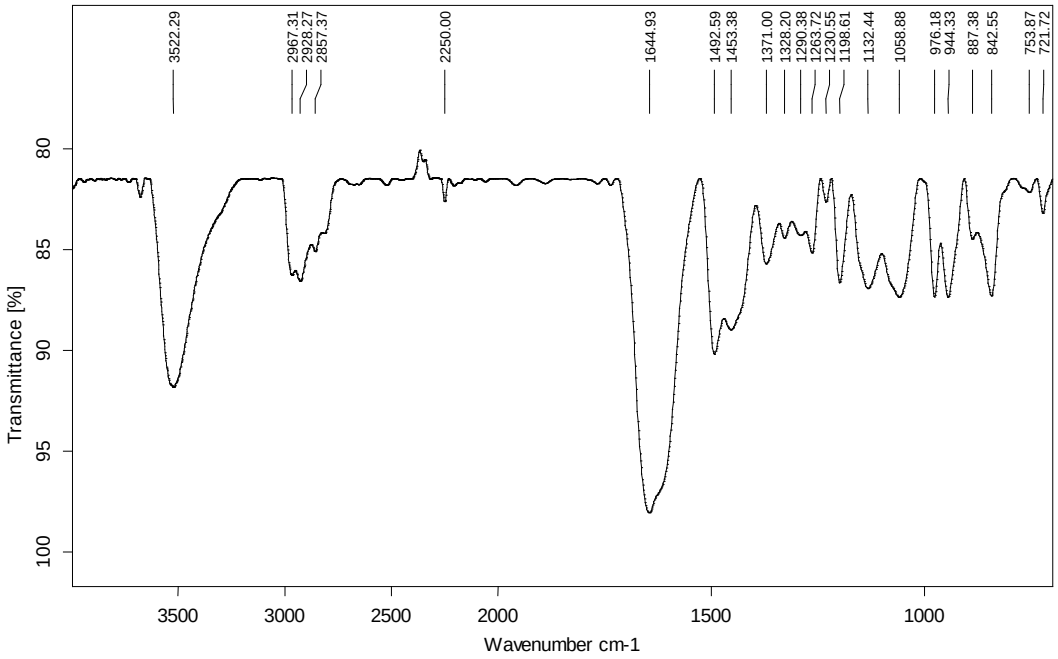
DBUOH@Silica



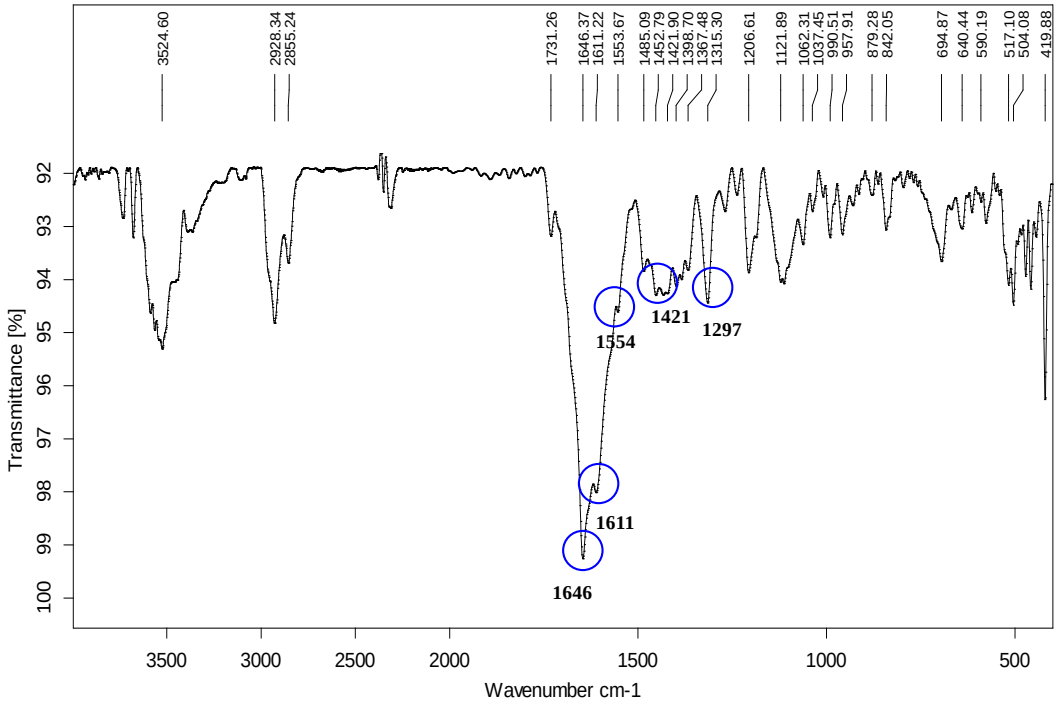
DBUOH@Silica+CO_2



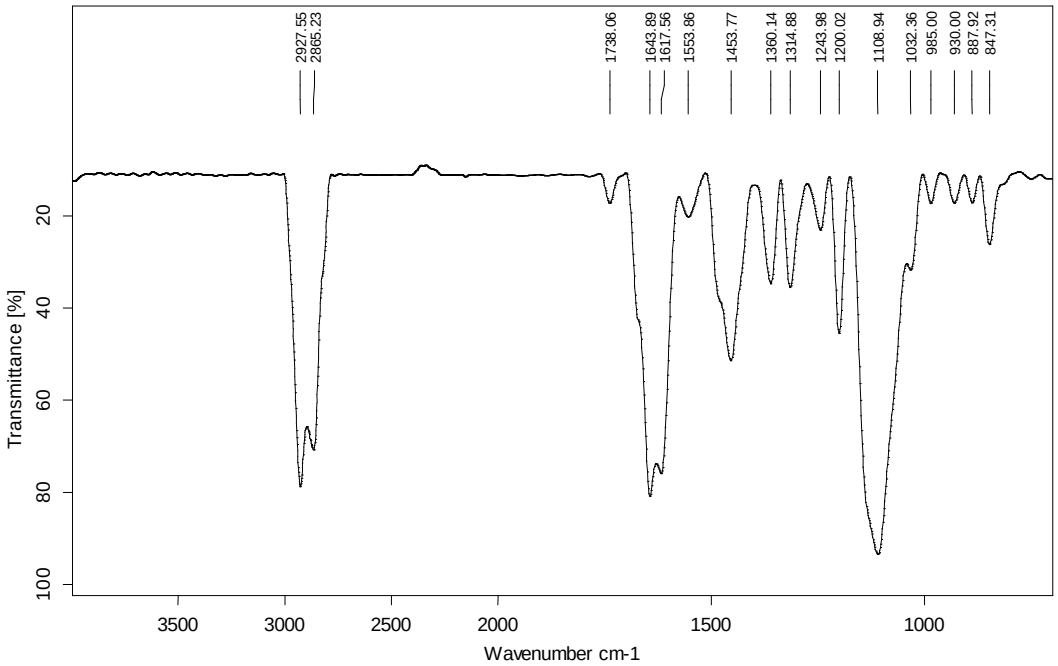
DBUOH



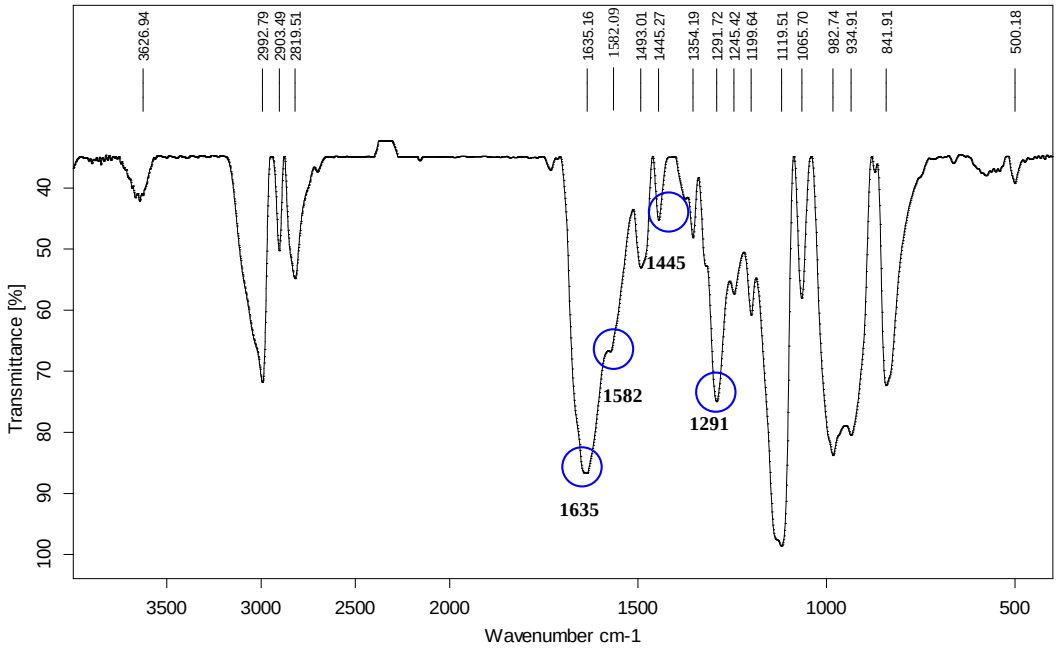
DBUOH+CO_2



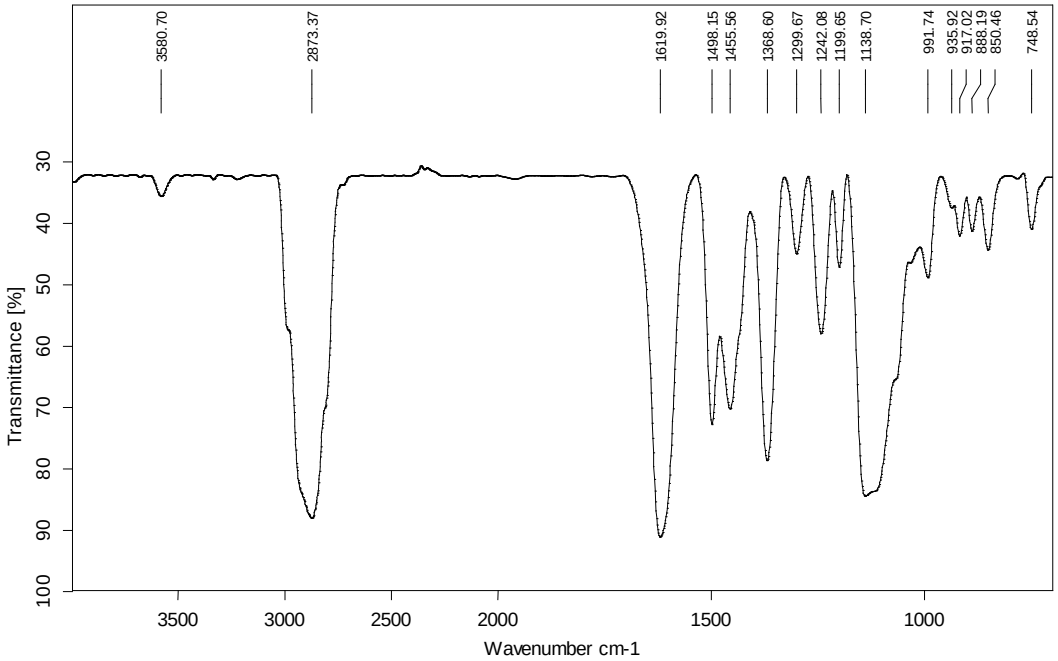
DBUPEG$_{150}$Me



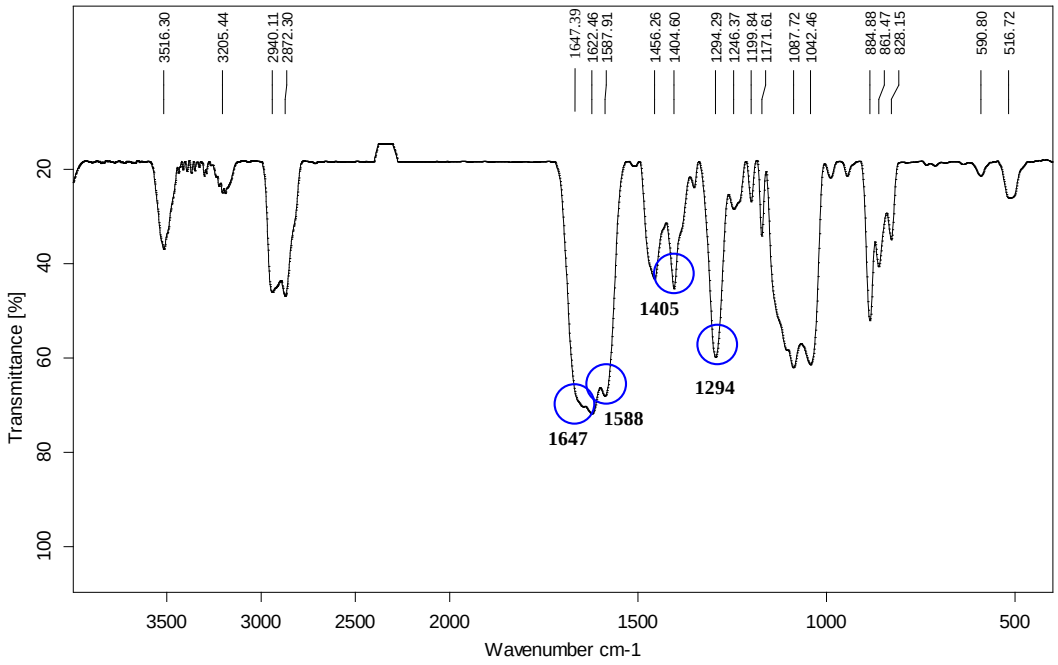
DBUPEG$_{150}$Me+Glycol+CO_2



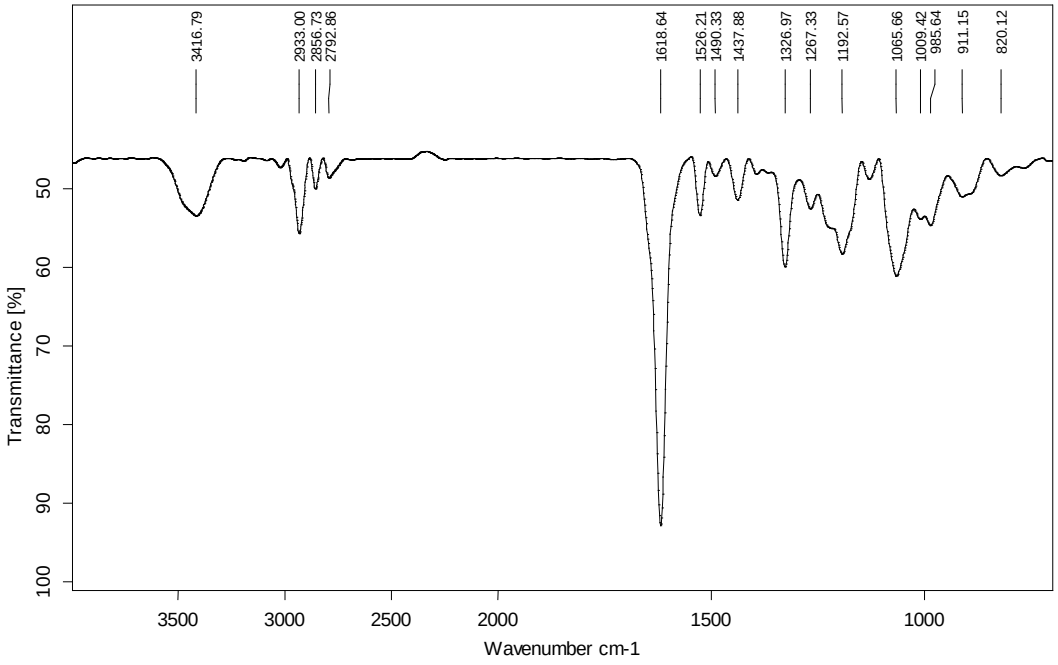
TMGPEG$_{150}$Me



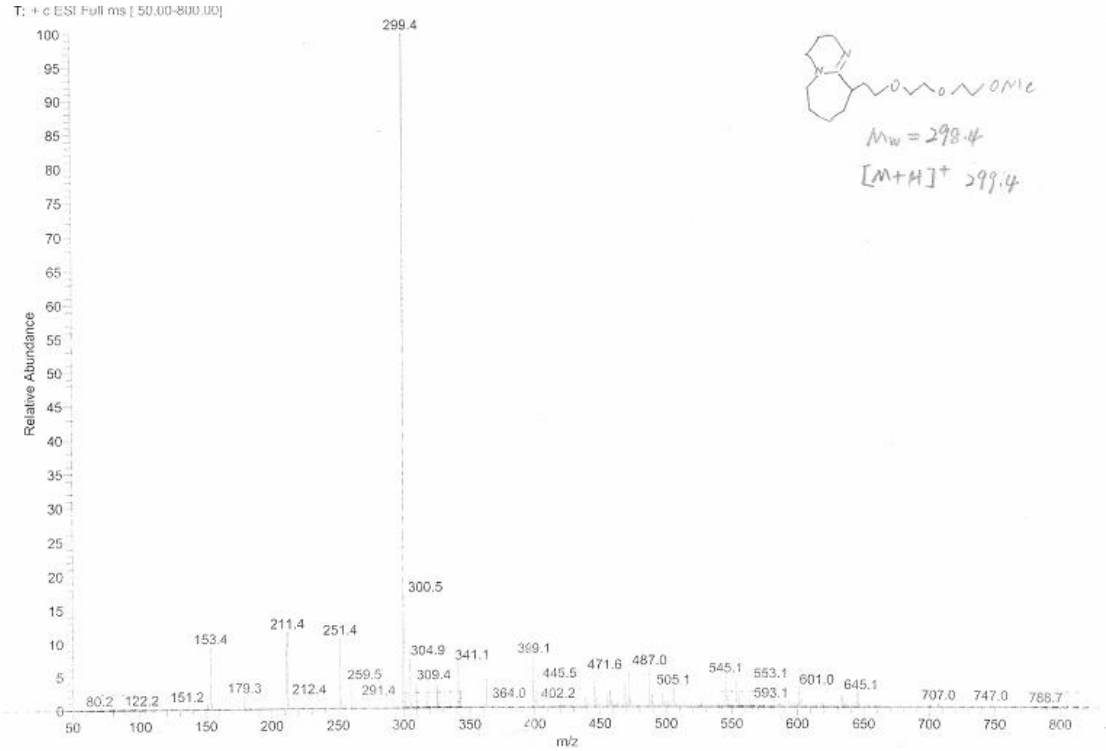
TMGPEG$_{150}$Me+Glycol+CO$_2$

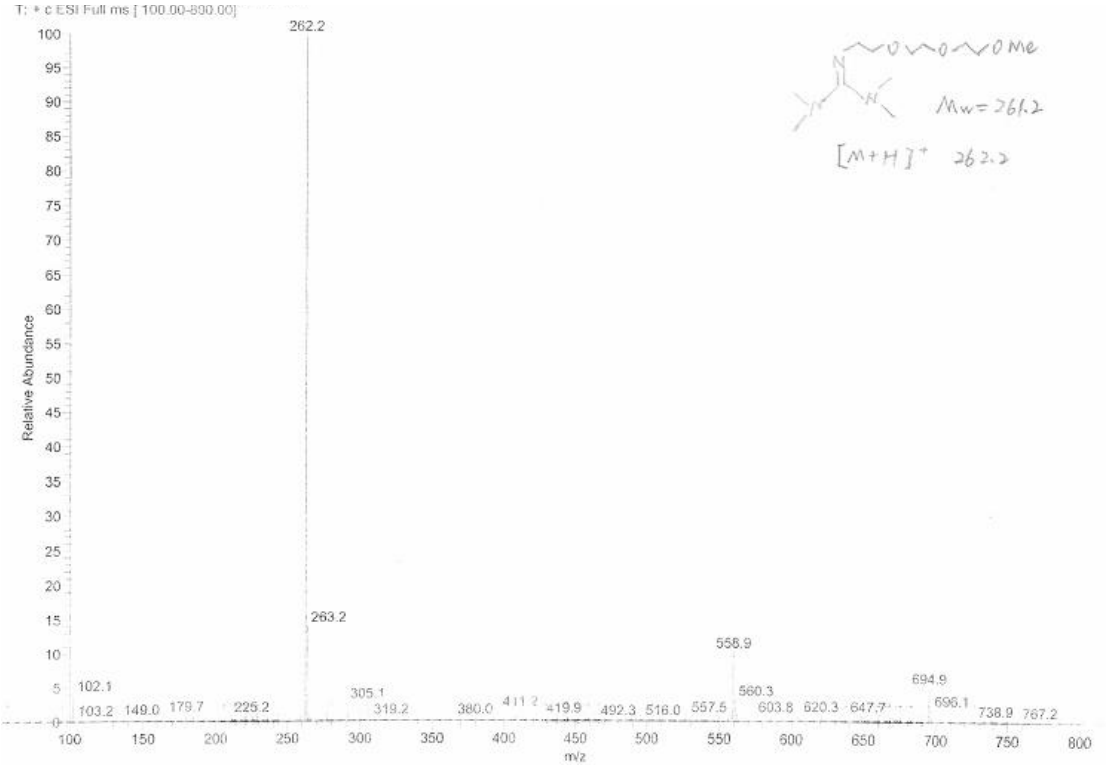


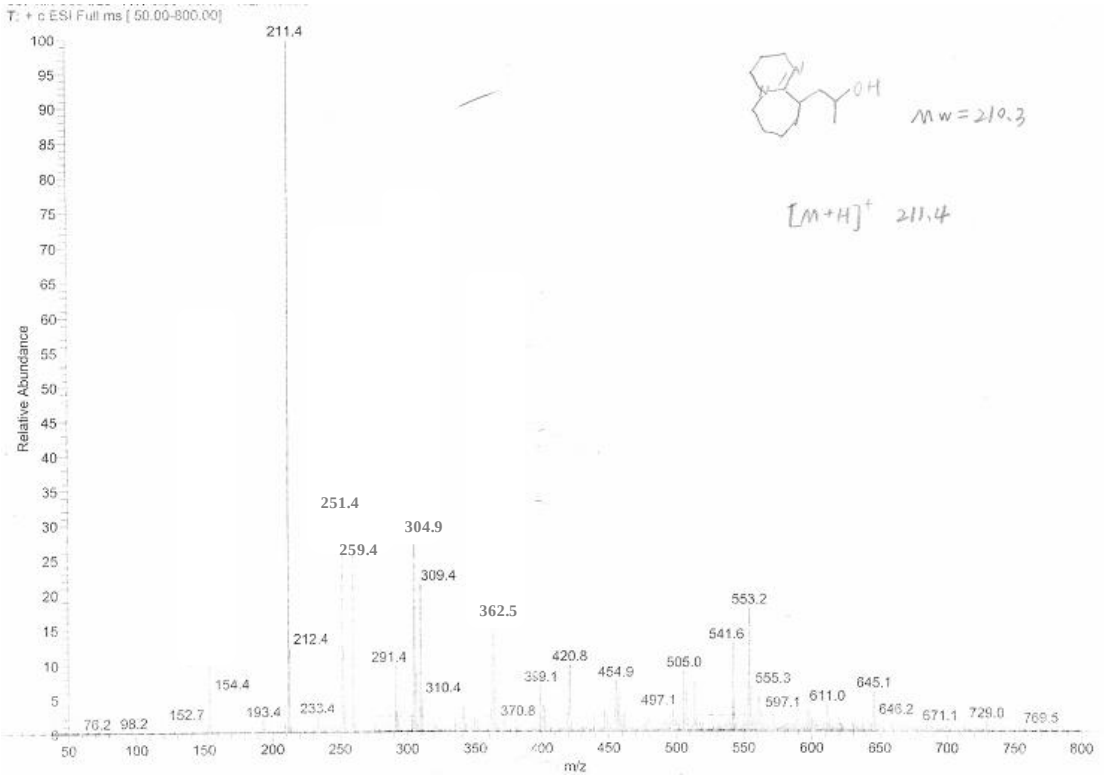
$DBU_2PEG_{150}Br_2$



6. ESI-MS


T: + c ESI Full ms [50.00-800.00]
Relative Abundance
m/z
299.4
300.5
211.4
251.4
153.4
304.9
341.1
369.1
471.6
487.0
545.1
553.1
601.0
645.1
707.0
747.0
788.7
OMe
Mw = 298.4
[M+H]+ 299.4


T: + c ESI Full ms [100.00-800.00]
Relative Abundance
m/z
262.2
263.2
102.1
558.9
560.3
694.9
696.1
OMe
Mw = 261.2
[M+H]+ 262.2



7. References

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