Electronic Supplementary Information

New crown ether complex cation ionic liquids with N-heterocycle anion: preparation and application in the CO_2 fixation

Jinyuan Wang,[a] Yatao Liang,[a] Dagang Zhou,[a] Jiangping Ma,[a] Huanwang Jing*[a,b]

[a] *State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, PR China*

[b] *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, P.R. China*

Corresponding author E-mail: hwjing@lzu.edu.cn

Table of contents

1. ^{1}H, FT-IR, TGA-DSC of ionic liquids.....S2-S11

2. ^{1}H NMR of the substrates, products and catalysts.....S12-S15

3. The reusability of the catalytic system……..…….S16

4. ^{1}H NMR of CO_2 coupling with PGE under different temperature……S17

5. Kinetic data by [18-C-6K][Im] on cycloaddition of CO_2 and PGE.....S17-S20

6. Kinetic data by [15-C-5Na][Im] on cycloaddition of CO_2 and PGE.....S20-S22

7. The DFT calculation of [15-C-5Na][Im] for the formation of CPE……..S23

8. Tables of atom coordinates of reactions, product, intermediates and transition states obtained by DFT calculation……...……..……...……...…….S23-S37

9. References……..…….S37

1. ^{1}H, FT-IR, TGA-DSC of ionic liquids.

1.1 ^{1}H of ionic liquids.

[18-C-6K][Im]

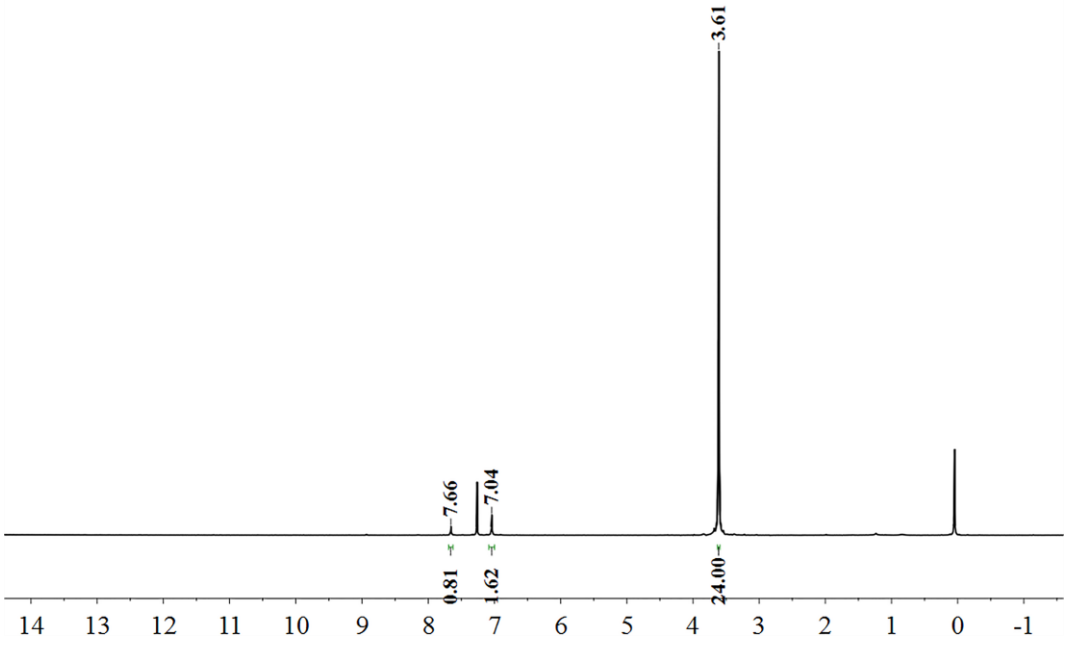


Fig. S1 ^{1}H of [18-C-6K][Im]

[18-C-6K][Pyr]

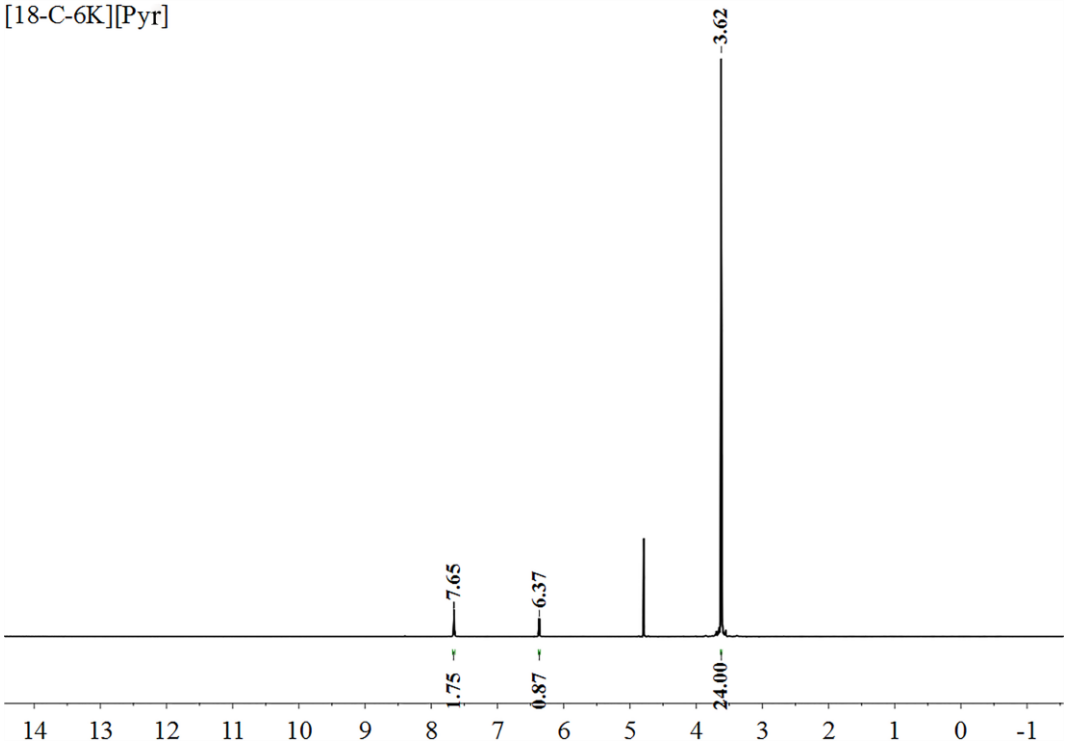


Fig. S2 ^{1}H of [18-C-6K][Pyr]

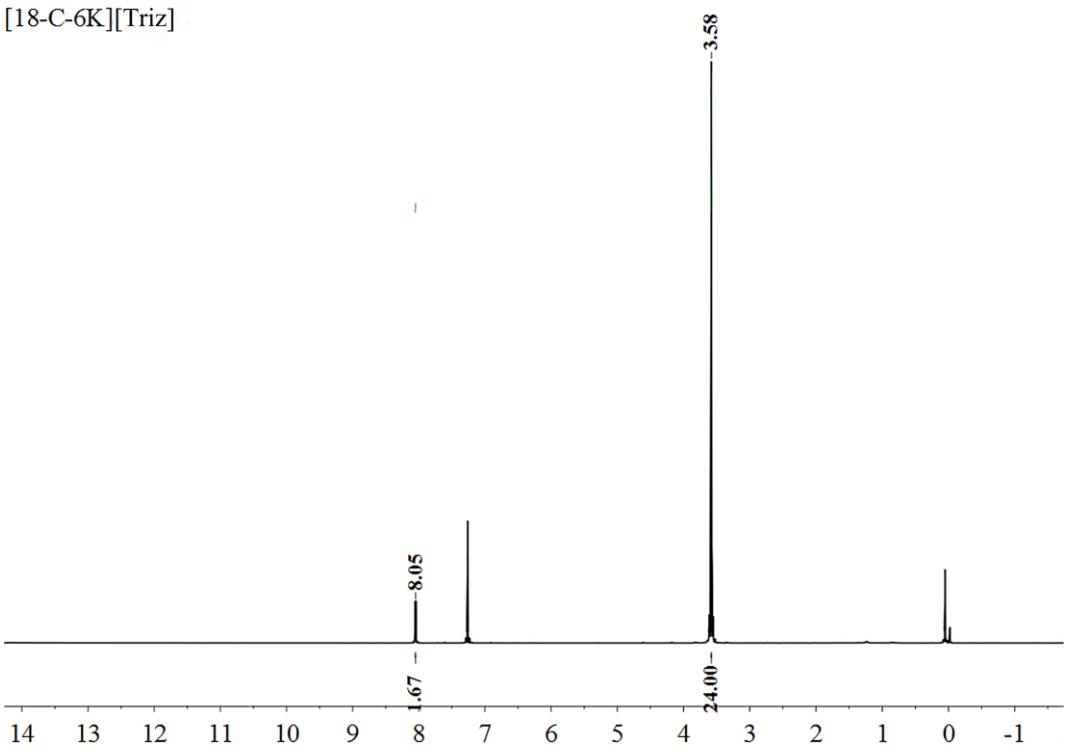


Fig. S3 ^{1}H of [18-C-6K][Triz]

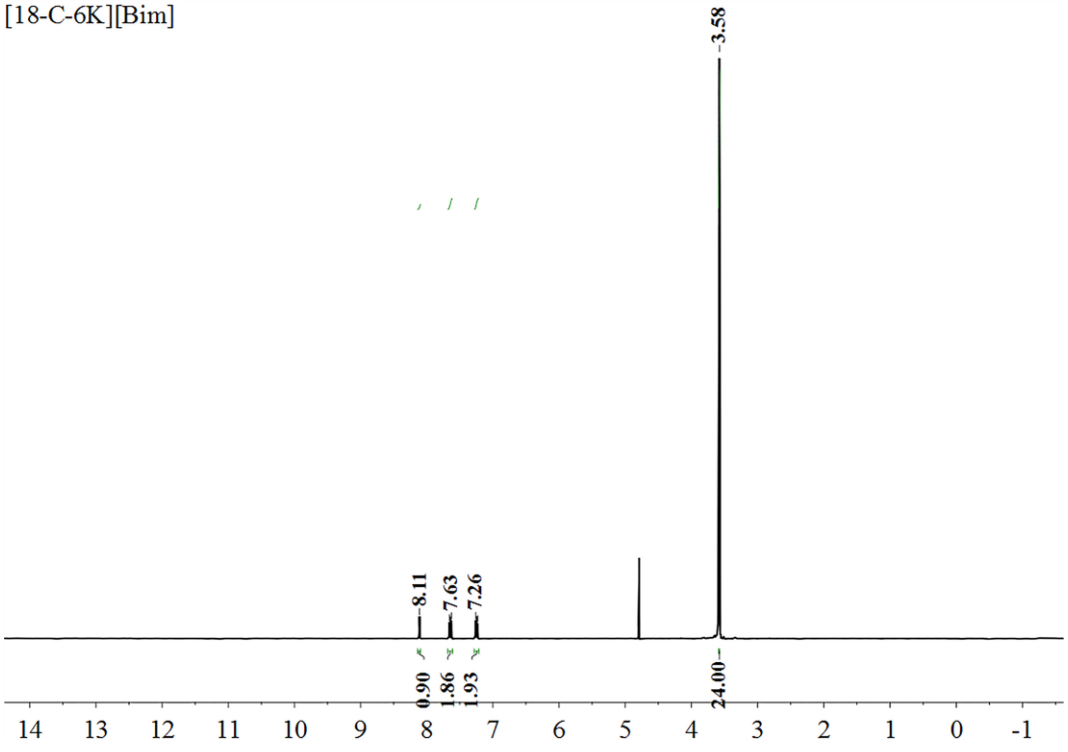


Fig. S4 ^{1}H of [18-C-6K][Bim]

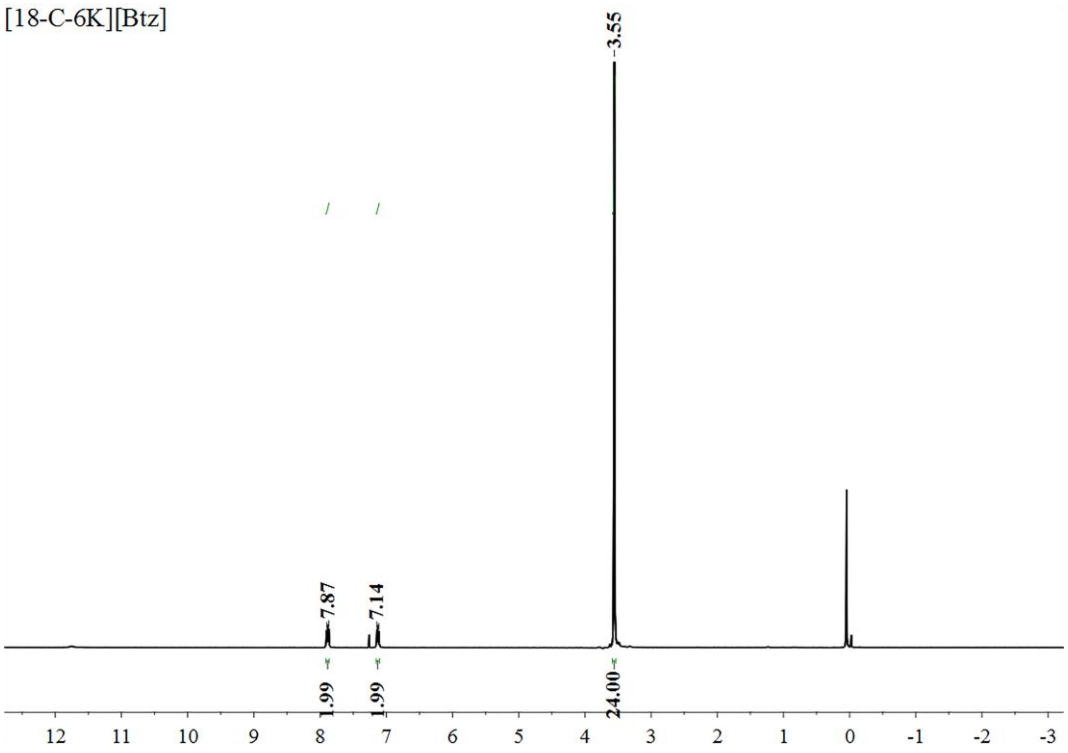


Fig. S5 ^{1}H of [18-C-6K][Btz]

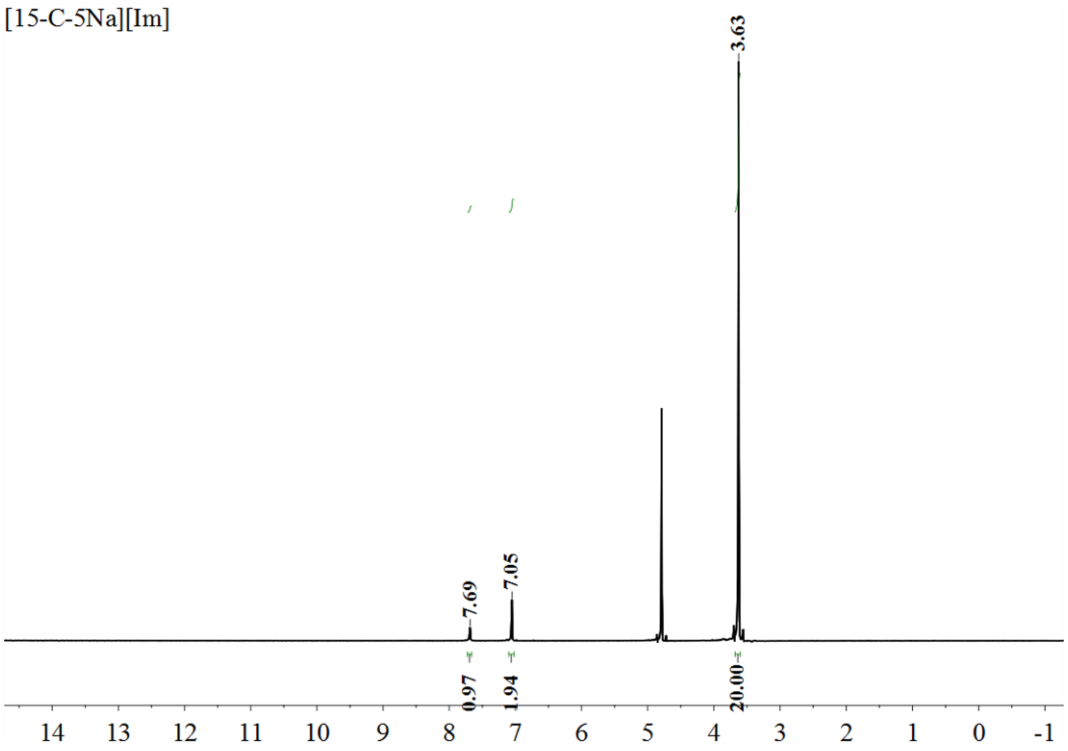


Fig. S6 ^{1}H of [15-C-5Na][Im]

1.2. FT-IR of ionic liquids.

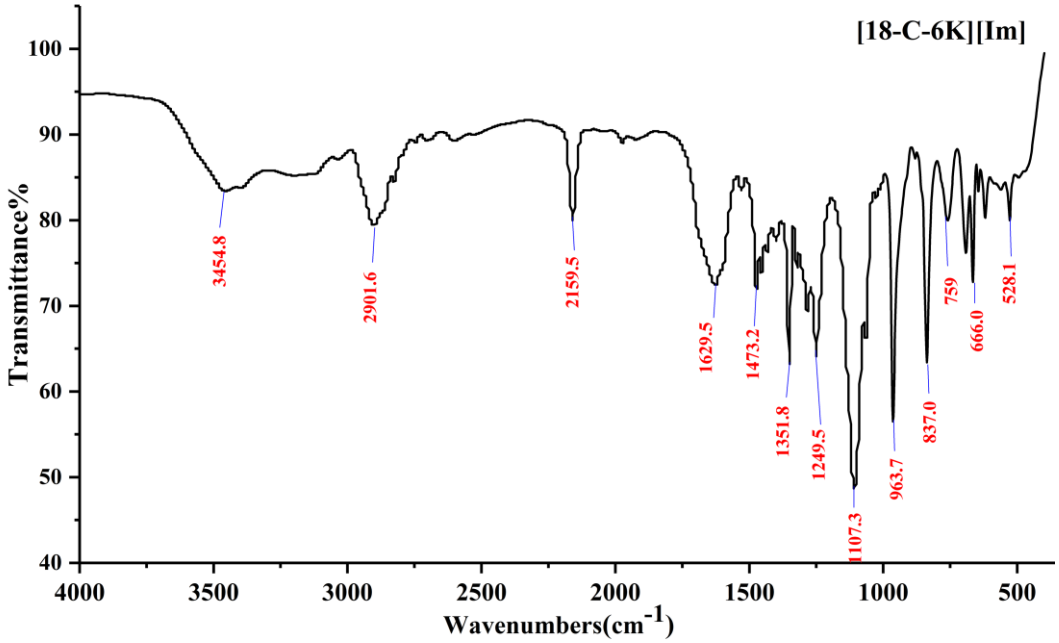


Fig. S7 FT-IR of [18-C-6K][Im]

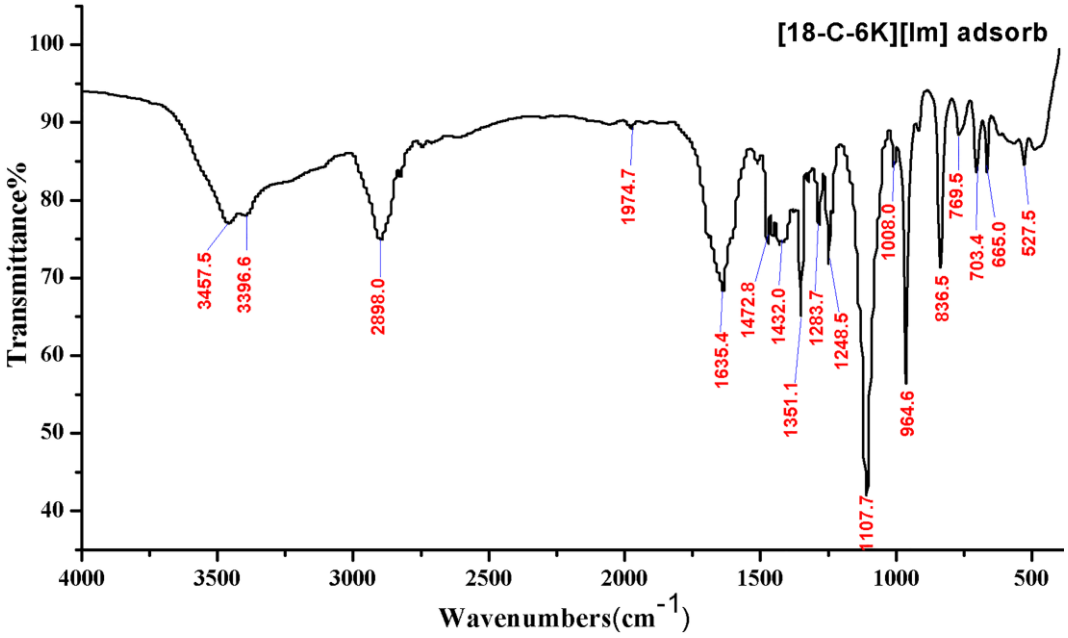


Fig. S8 FT-IR of [18-C-6K][Im] absorbed with CO_2

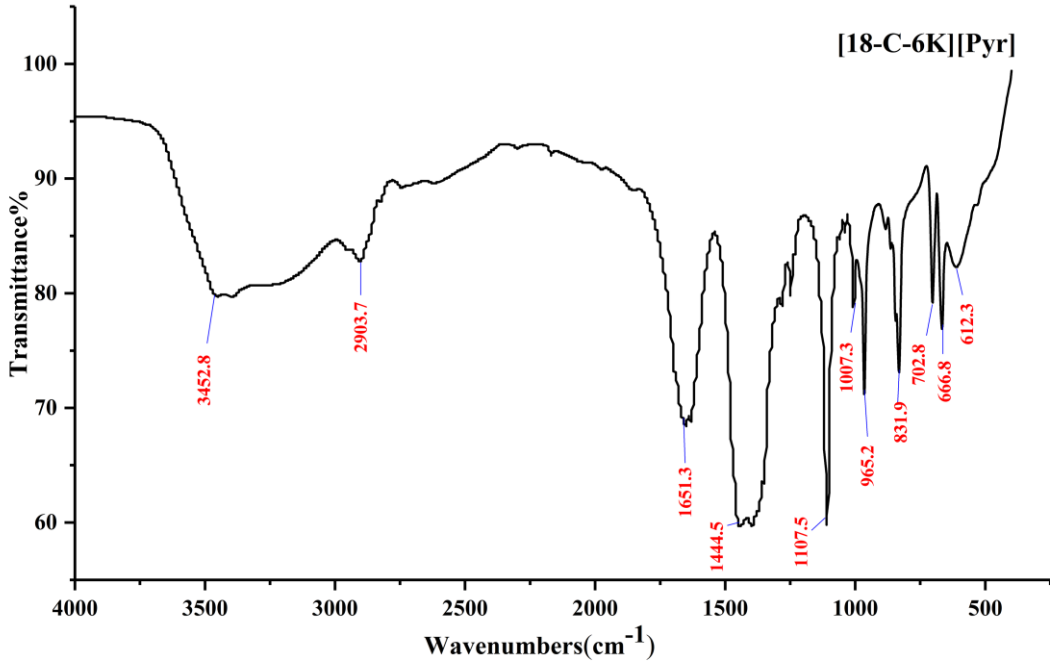


Fig. S9 FT-IR of [18-C-6K][Pyr]

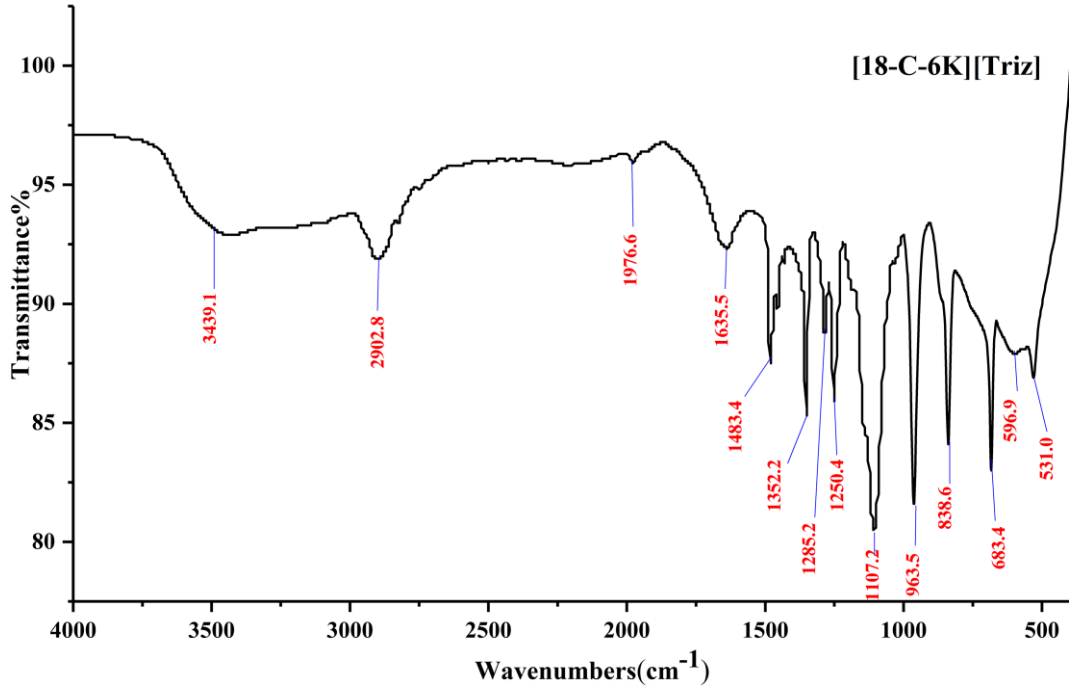


Fig. S10 FT-IR of [18-C-6K][Triz]

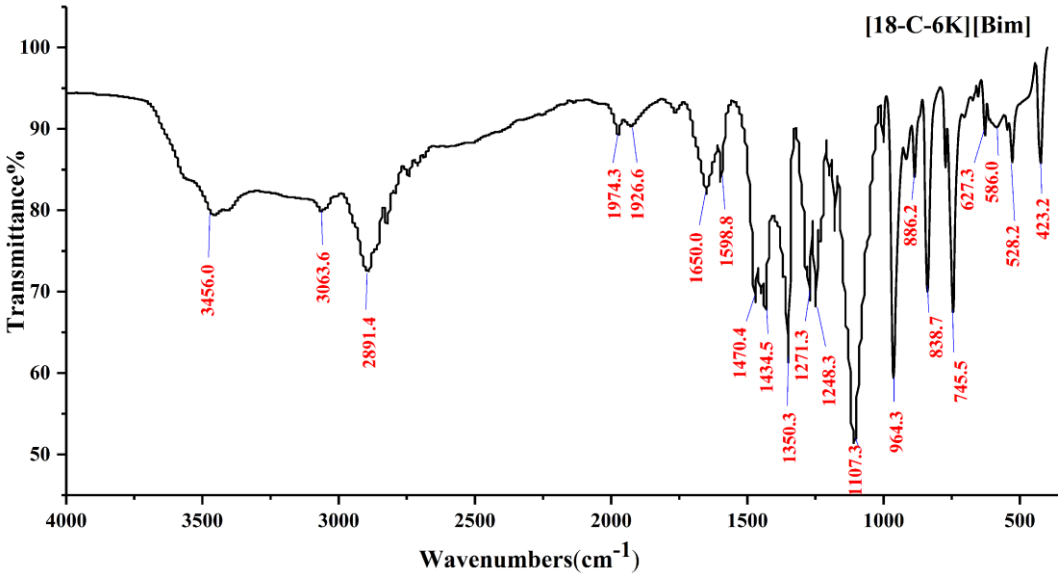


Fig. S11 FT-IR of [18-C-6K][Bim]

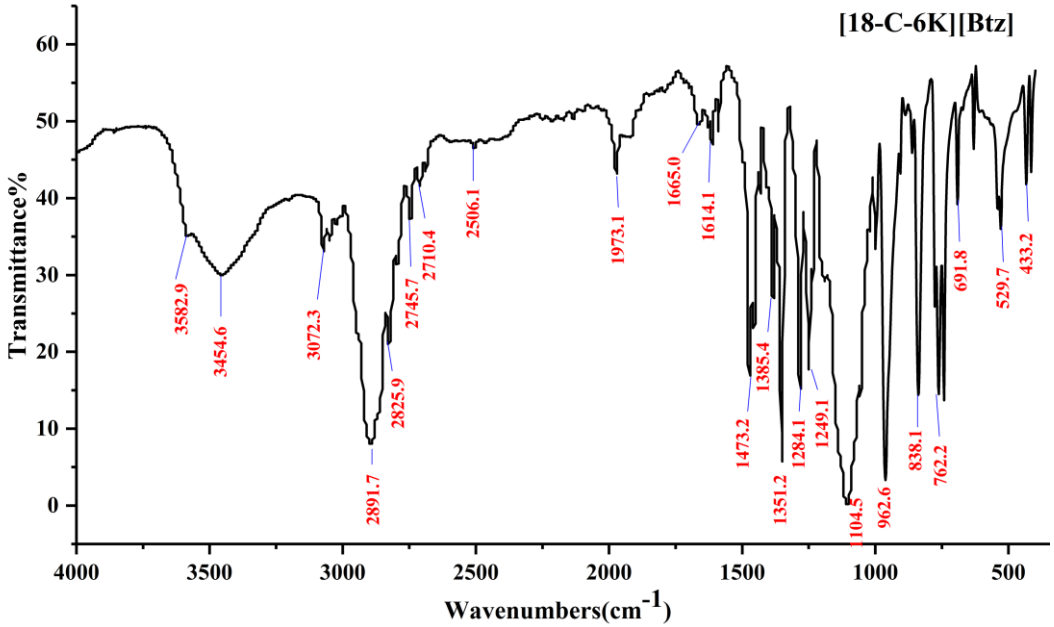


Fig. S12 FT-IR of [18-C-6K][Btz]

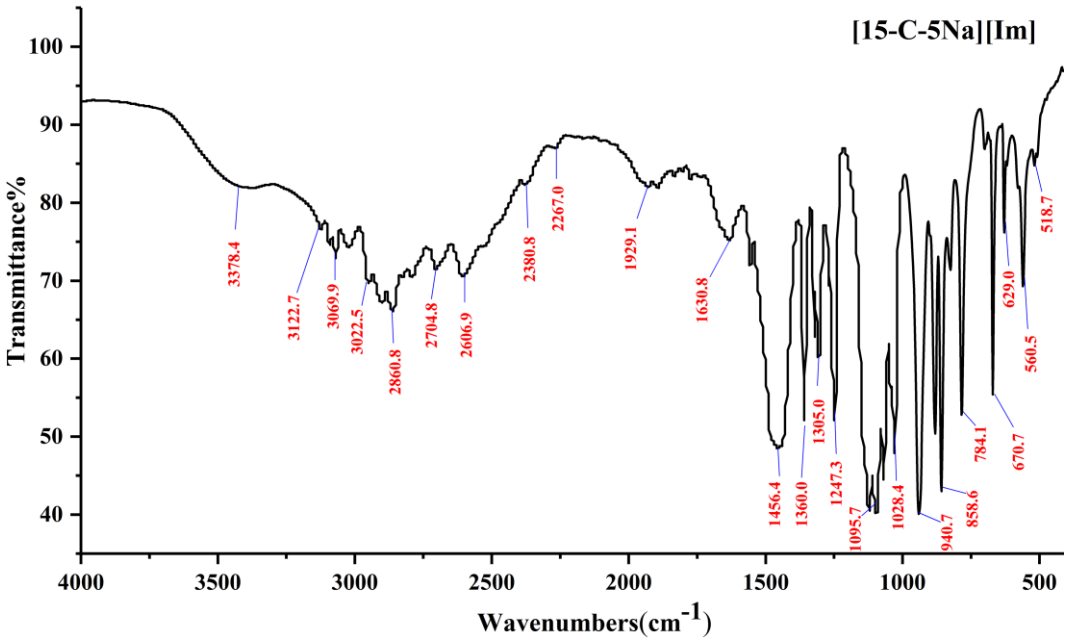


Fig. S13 FT-IR of [15-C-5Na][Im]

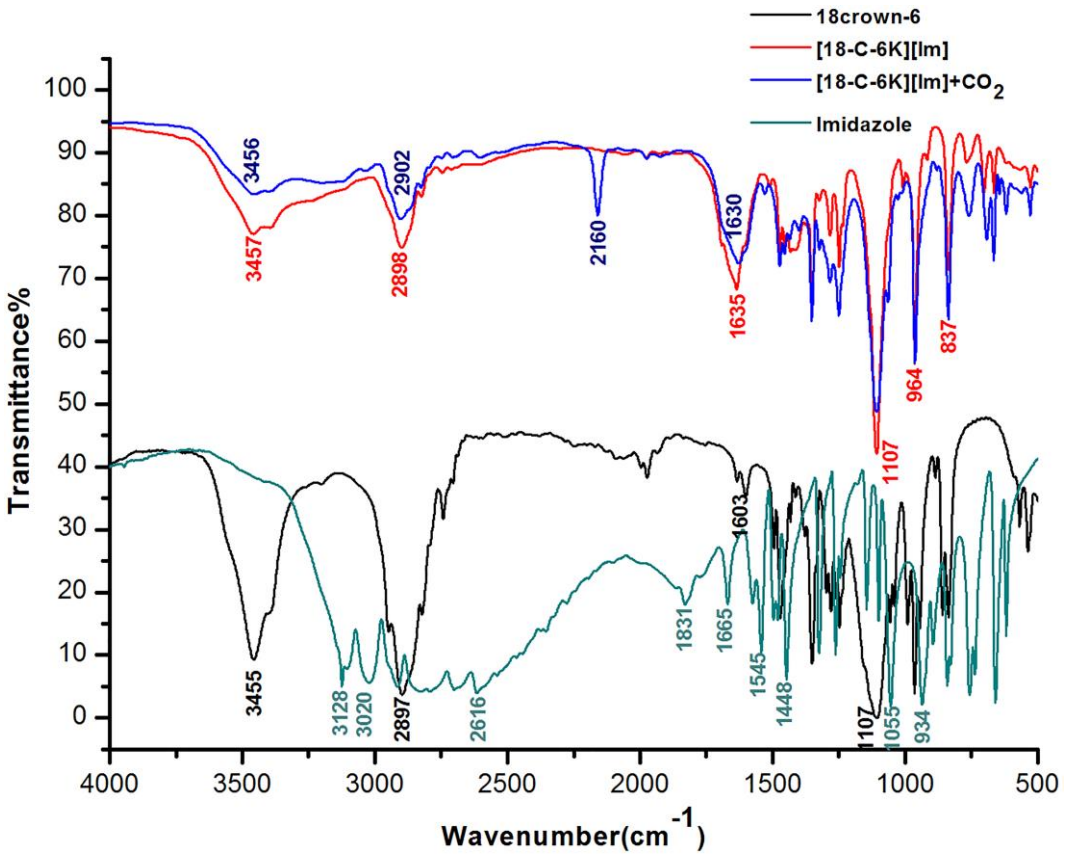


Fig. S14 FT-IR of 18crown-6, [18-C-6K][Im], [18-C-6K][Im] + CO_2 and Imidazole

1.3. TGA-DSC of ionic liquids

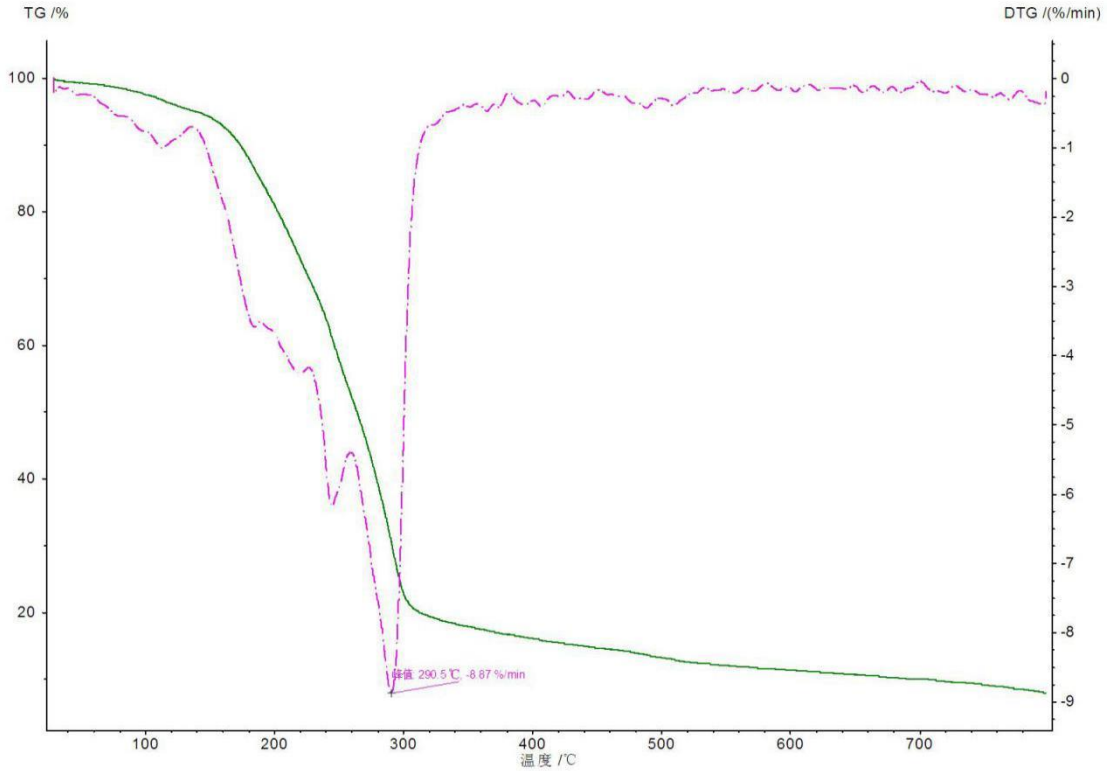


Fig. S15 TGA-DSC of [18-C-6K][Im]

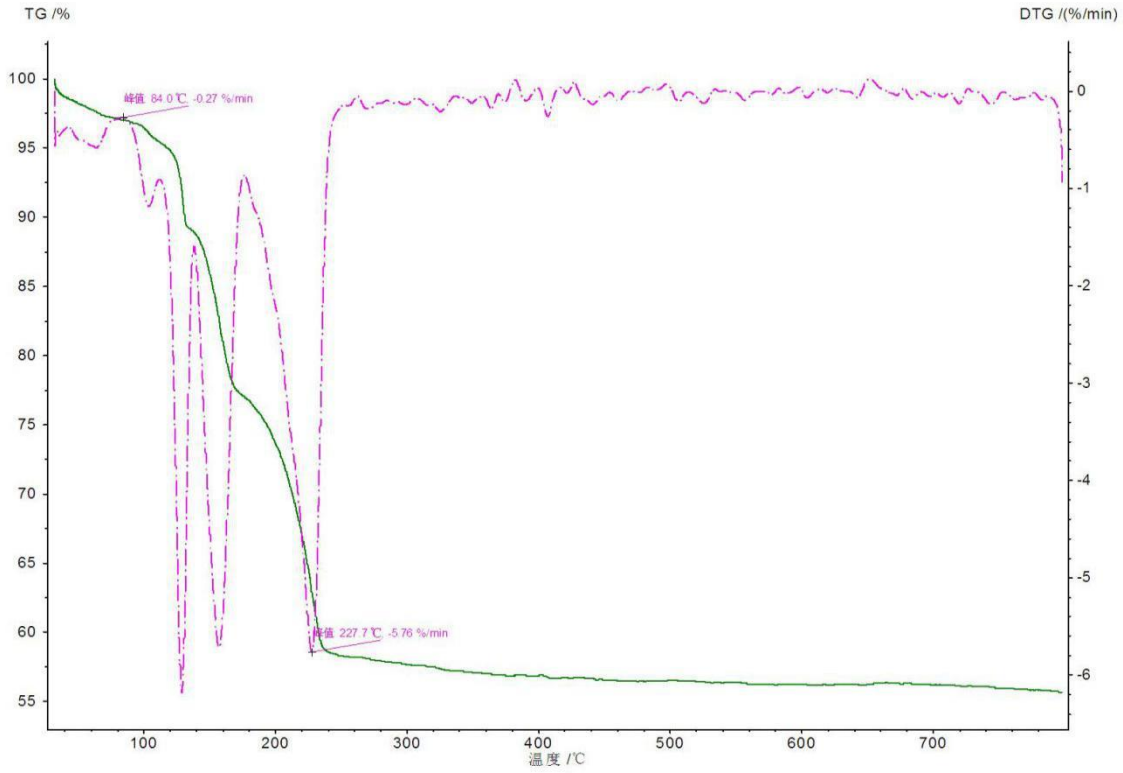


Fig. S16 TGA-DSC of [18-C-6K][Pyr]

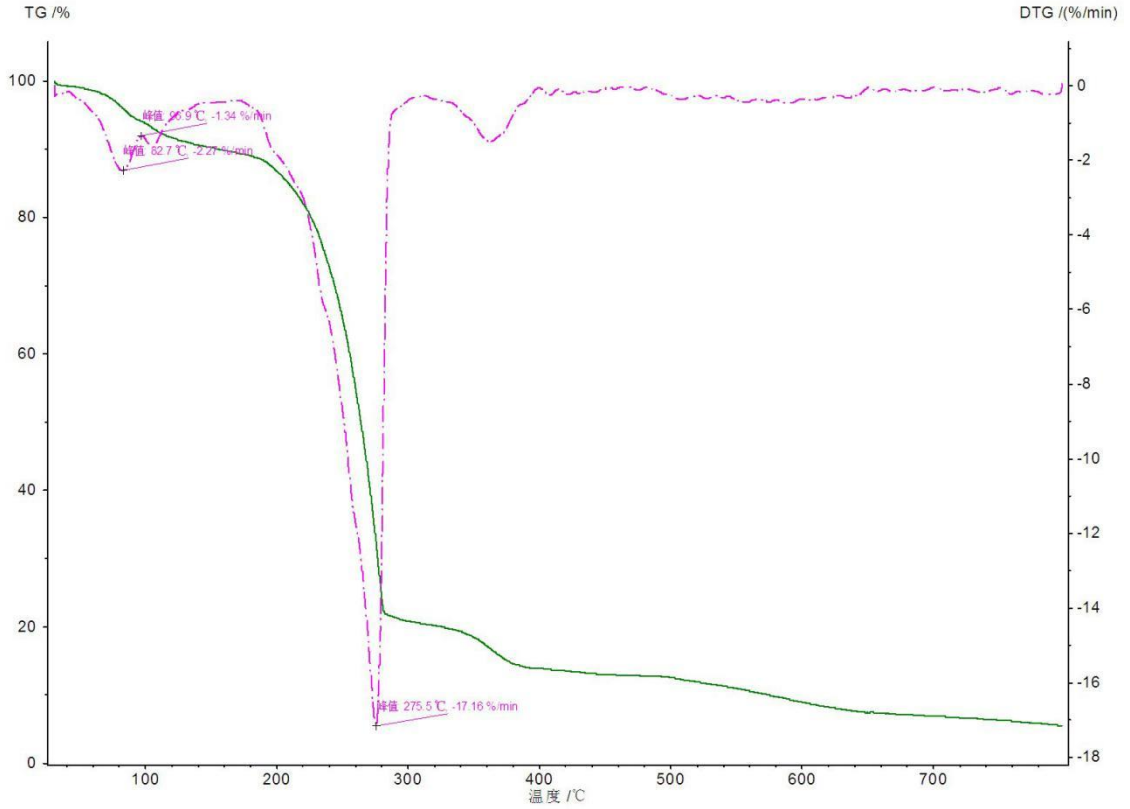


Fig. S17 TGA-DSC of [18-C-6K][Triz]

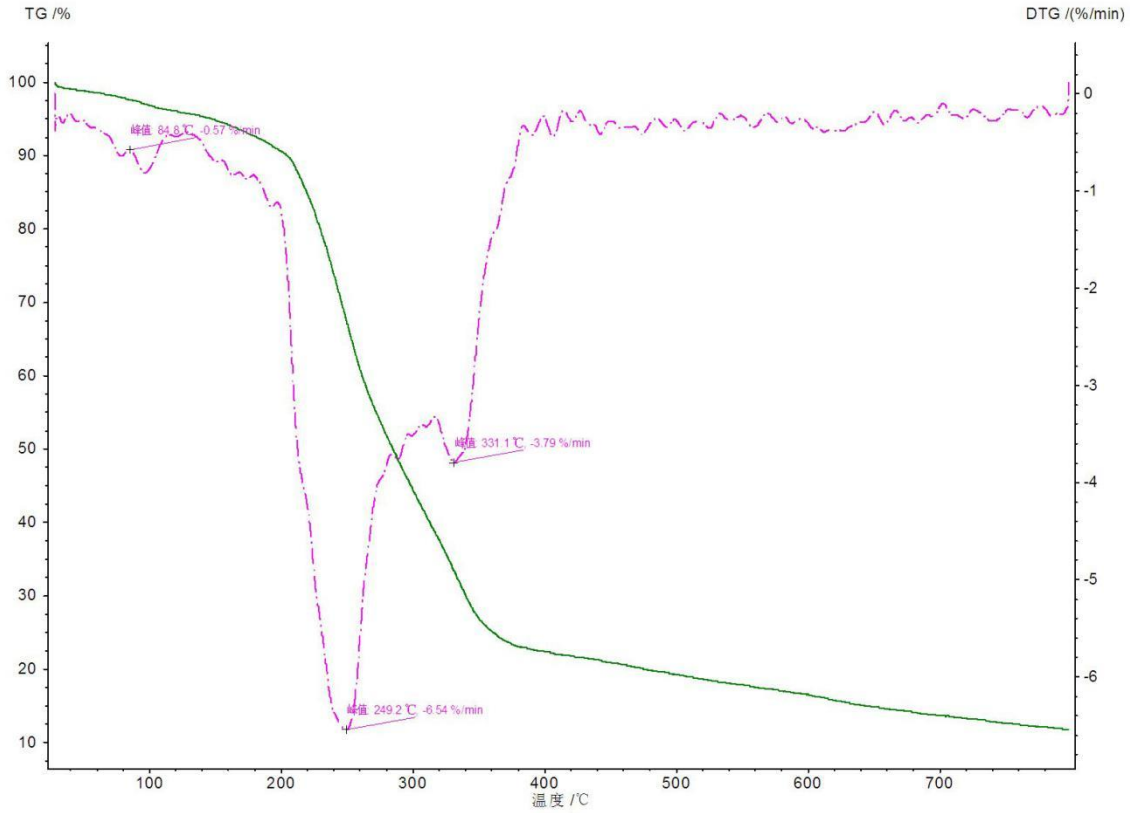


Fig. S18 TGA-DSC of [18-C-6K][Bim]

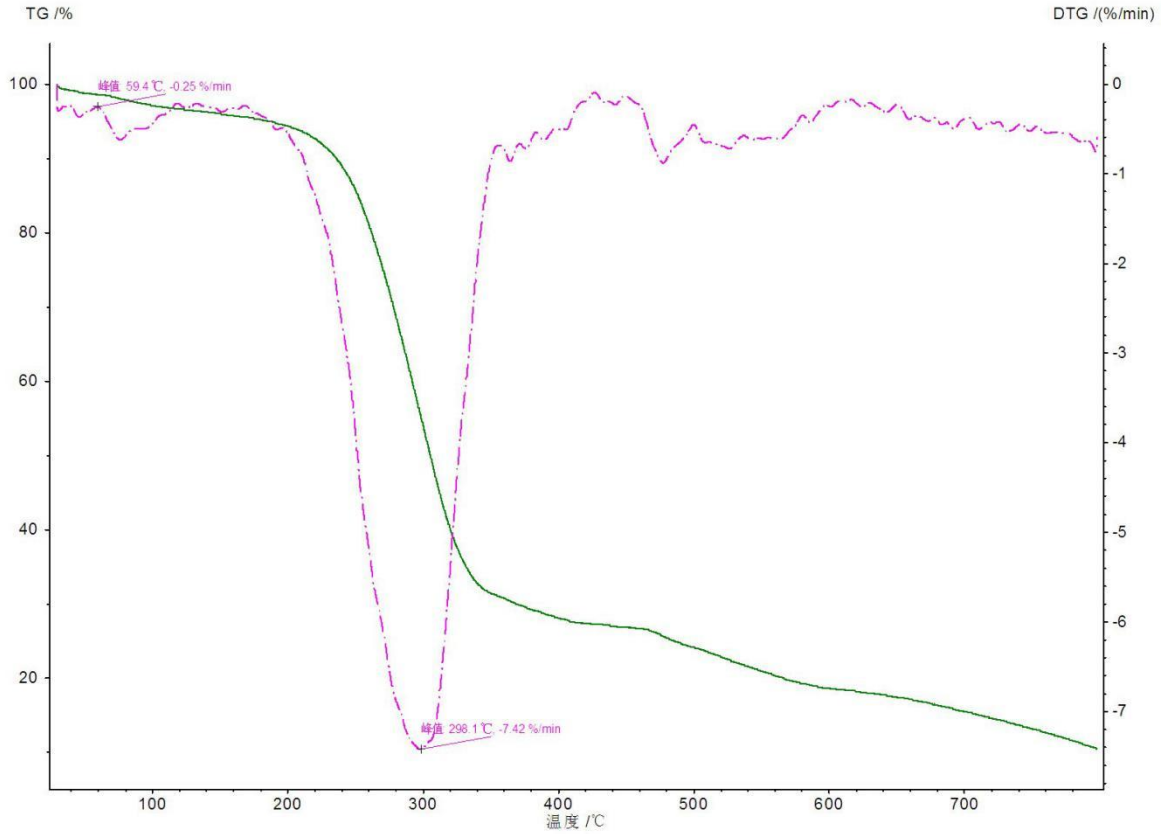


Fig. S19 TGA-DSC of [18-C-6K][Btz]

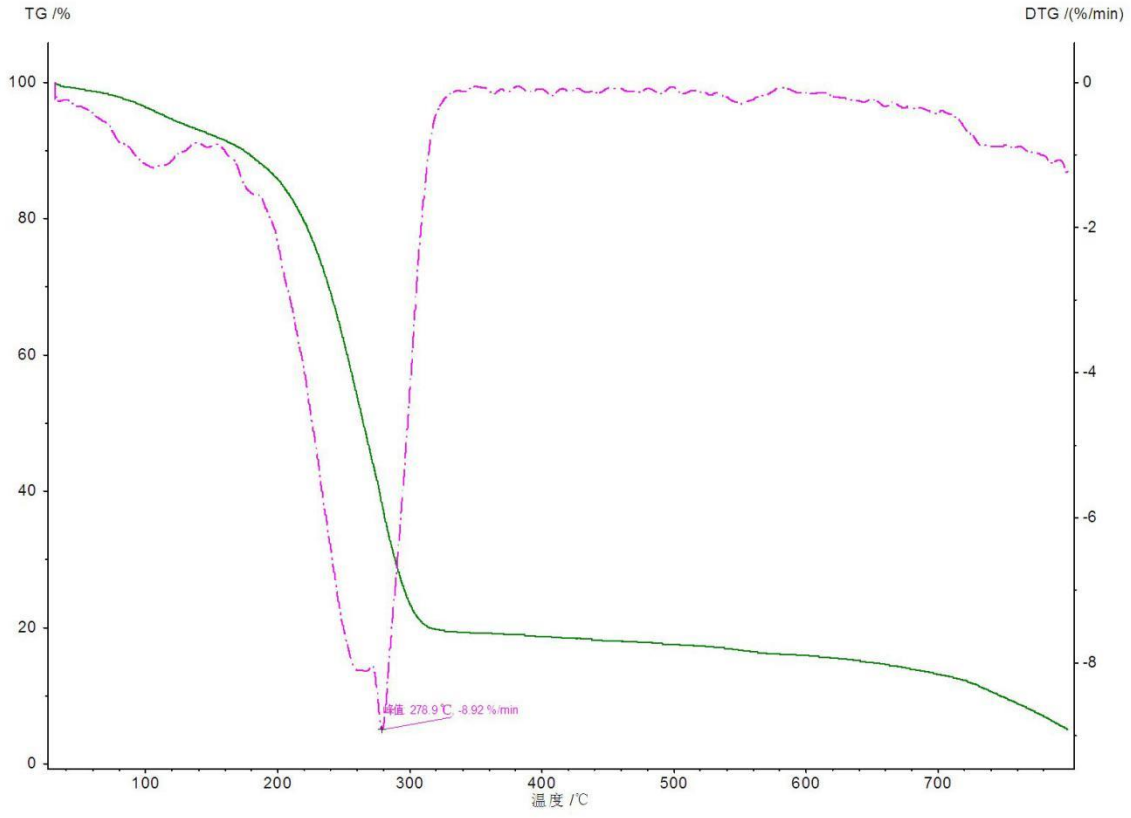
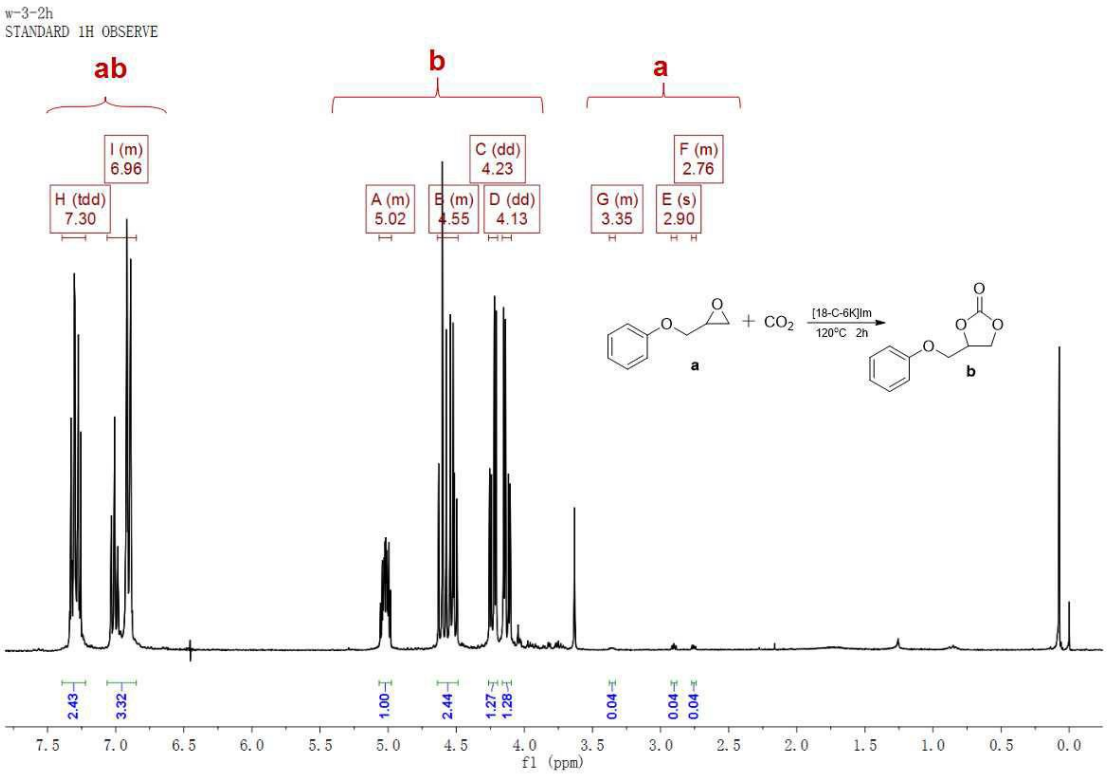
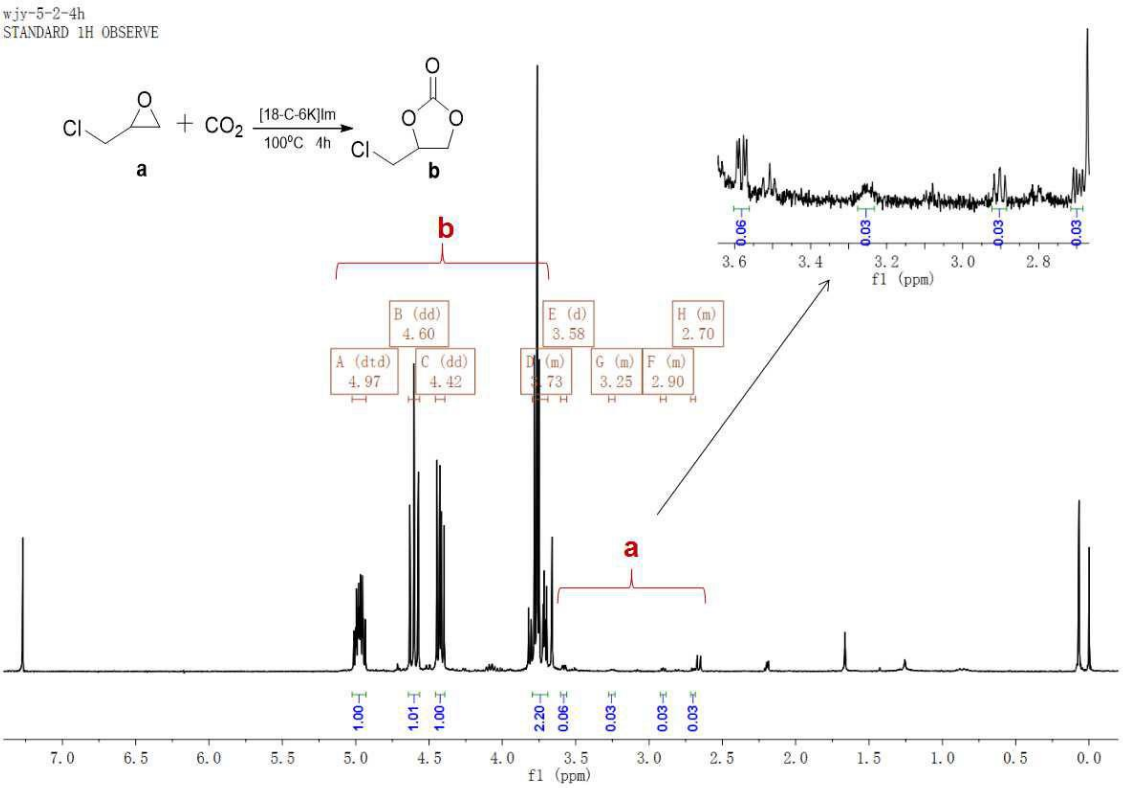
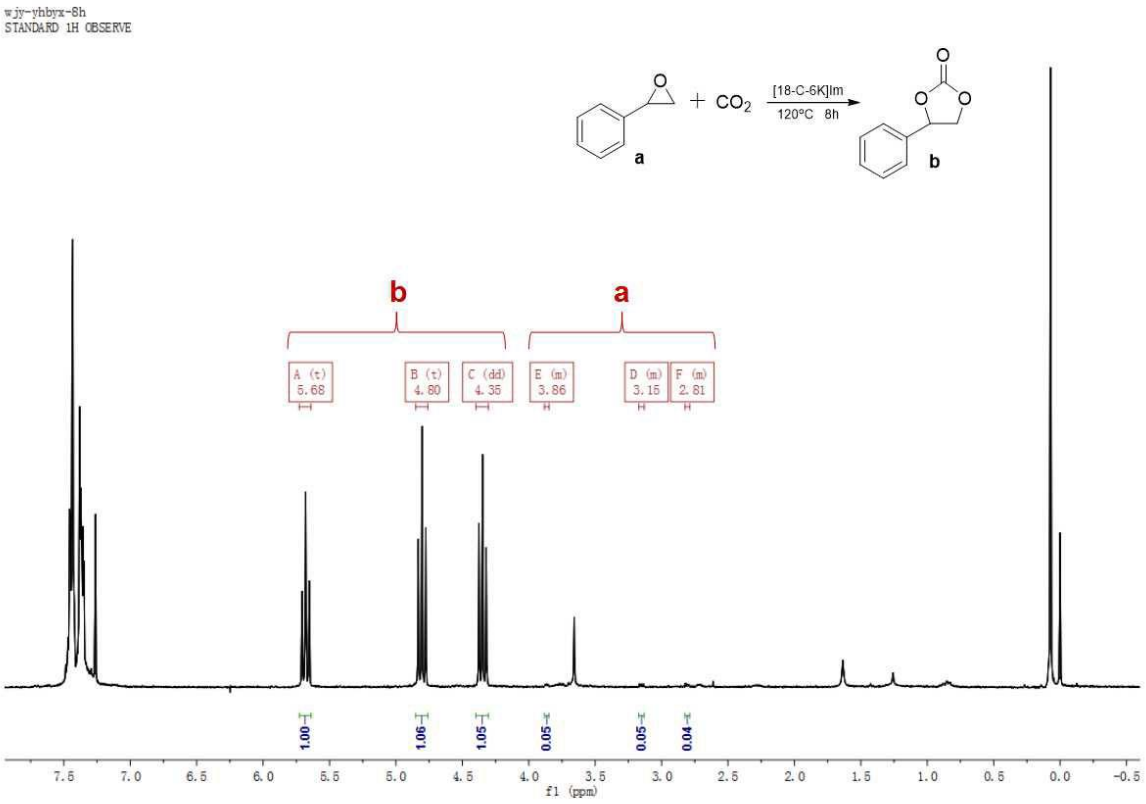


Fig. S20 TGA-DSC of [15-C-5Na][Im]

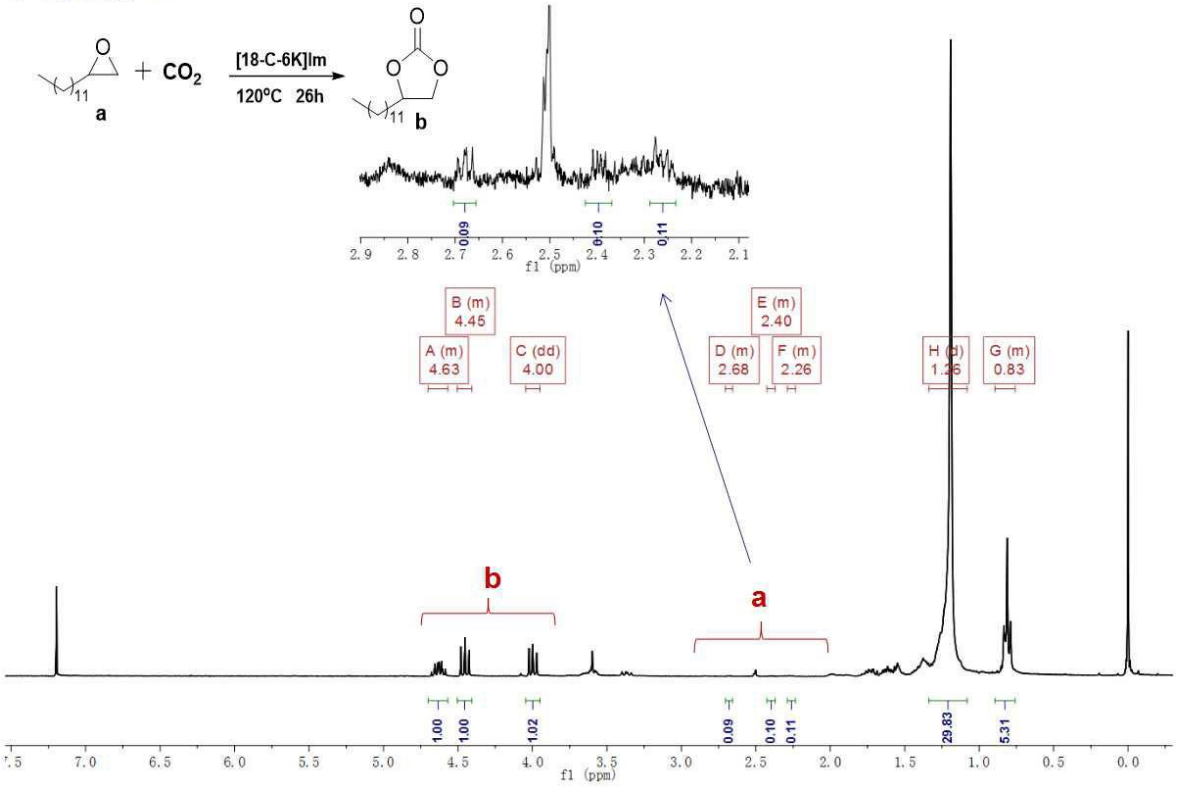
2. ^{1}H NMR of the substrates, products and catalysts.



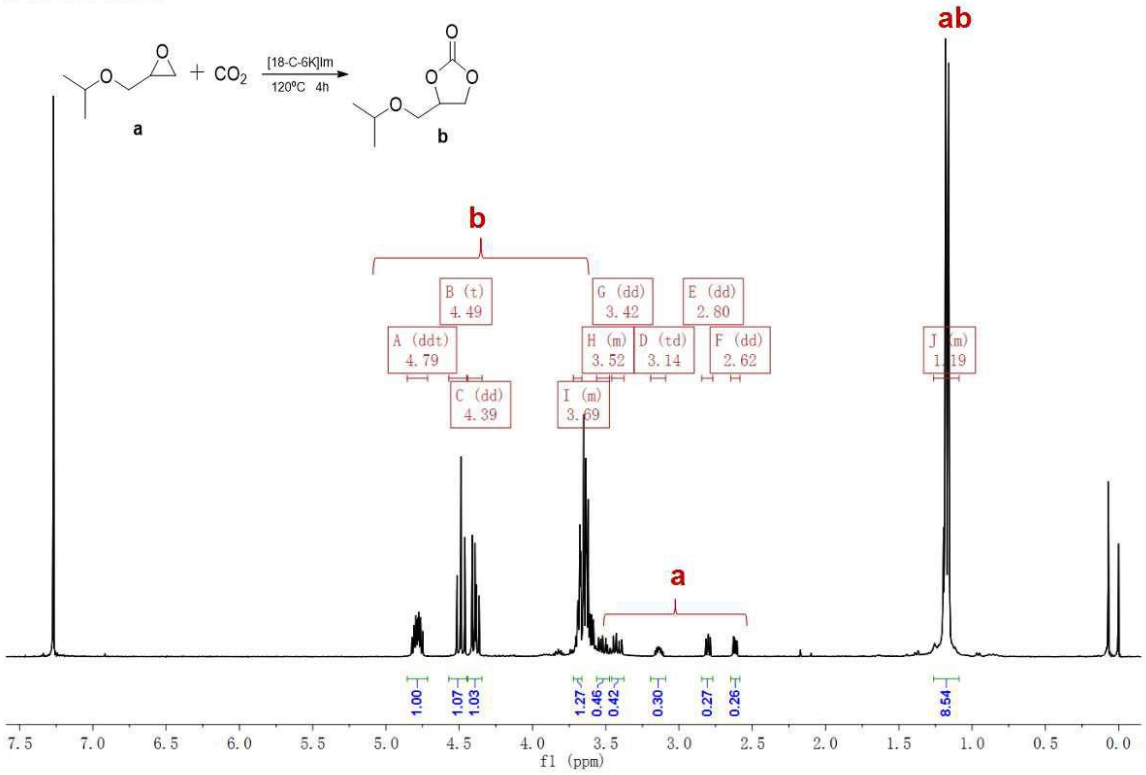



wjy-yhbyx-8h
STANDARD 1H OBSERVE
+ CO2
[18-C-6K]Im
120°C 8h
a
b
b
a
A (t) 5.68
B (t) 4.80
C (dd) 4.35
E (m) 3.86
D (m) 3.15
F (m) 2.81
1.00
1.06
1.05
0.05
0.05
0.04
f1 (ppm)

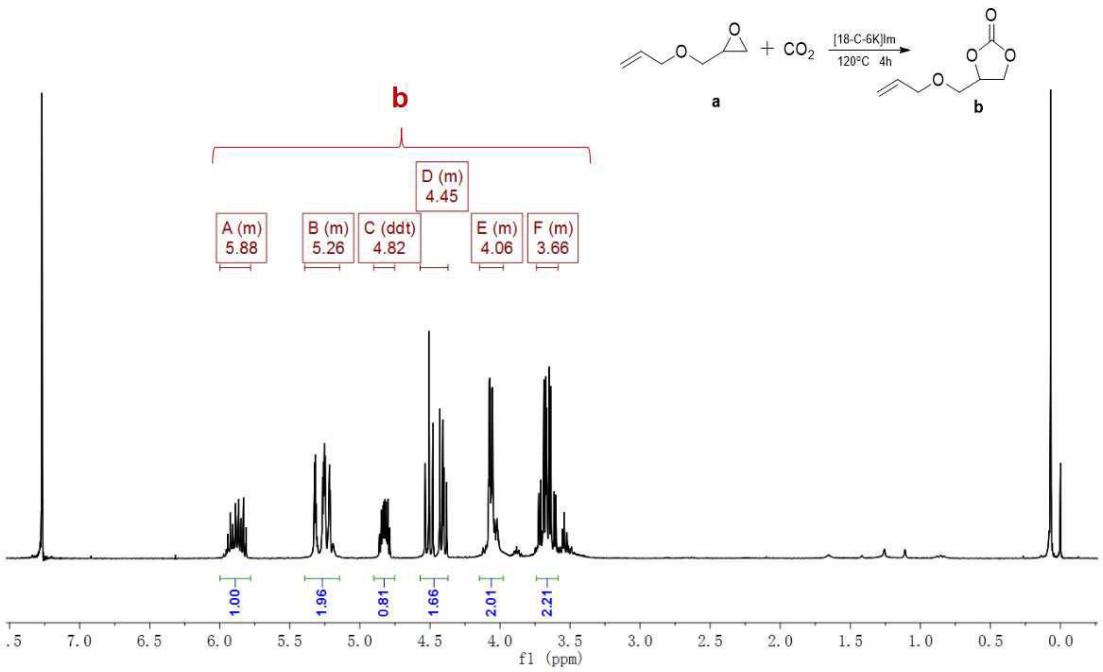
1,2环氧十四烷-26h

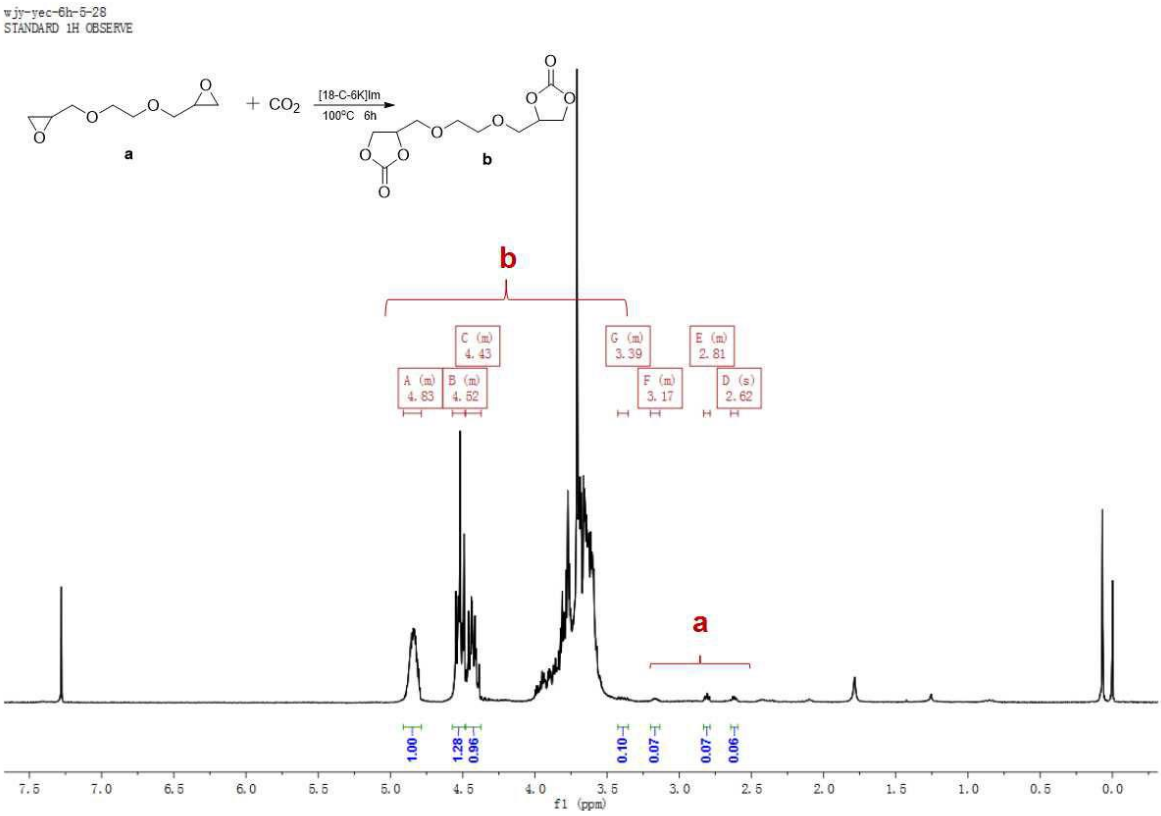

+ CO2
[18-C-6K]Im
120°C 26h
a
b
0.09
0.10
0.11
f1 (ppm)
B (m) 4.45
A (m) 4.63
C (dd) 4.00
E (m) 2.40
D (m) 2.68
F (m) 2.26
H (d) 1.26
G (m) 0.83
b
a
1.00
1.00
1.02
0.09
0.10
0.11
29.83
5.31
f1 (ppm)

异丙基缩水甘油醚-4h

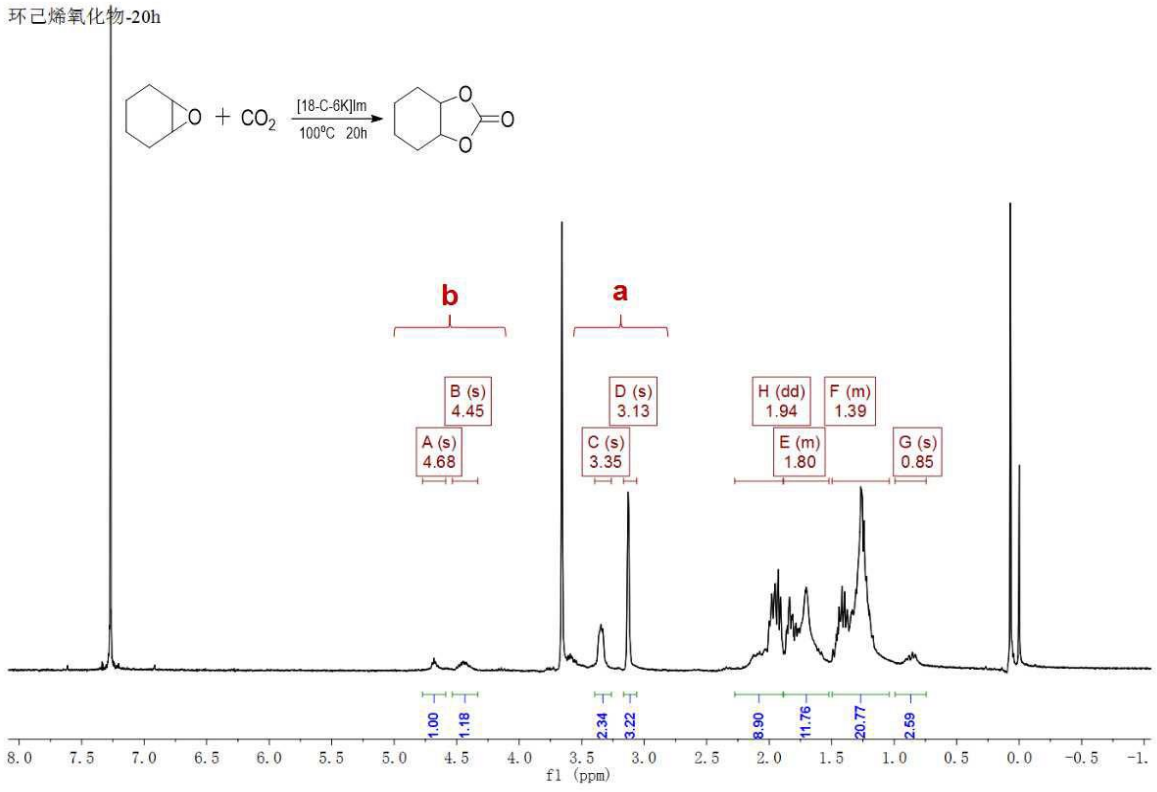


wjy-xbj-4h
STANDARD 1H OBSERVE




wjy-yec-6h-5-28
STANDARD 1H OBSERVE
a
+ CO2
[18-C-6K]Im
100°C 6h
b
b
C (m) 4.43
A (m) 4.83
B (m) 4.52
G (m) 3.39
E (m) 2.81
F (m) 3.17
D (s) 2.62
a
1.00
1.28
0.96
0.10
0.07
0.07
0.06
f1 (ppm)

环己烯氧化物-20h


+ CO2
[18-C-6K]Im
100°C 20h
b
a
B (s) 4.45
A (s) 4.68
D (s) 3.13
C (s) 3.35
H (dd) 1.94
F (m) 1.39
E (m) 1.80
G (s) 0.85
1.00
1.18
2.34
3.22
8.90
11.76
20.77
2.59
f1 (ppm)

3. The reusability of the catalytic system.

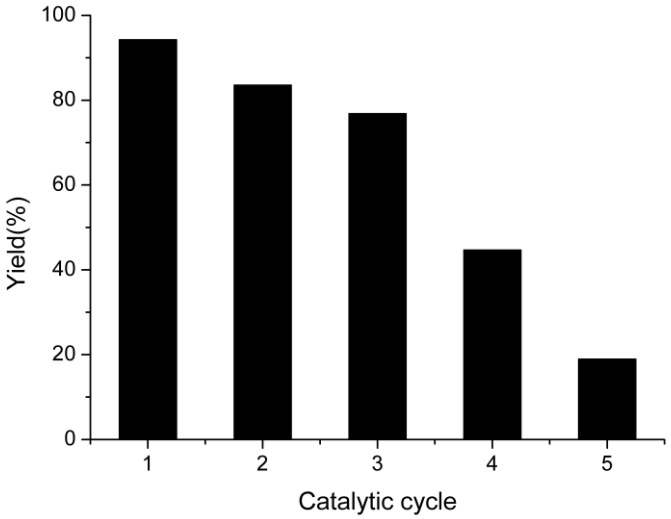


Fig. S21 Recycling of the catalyst [18-C-6K][Im] in the coupling reaction of epichlorohydrin and CO_2: epichlorohydrin (100mmol), catalyst amount (1 mol%), CO_2 (0.1 Mpa), 100 °C, 4 h.

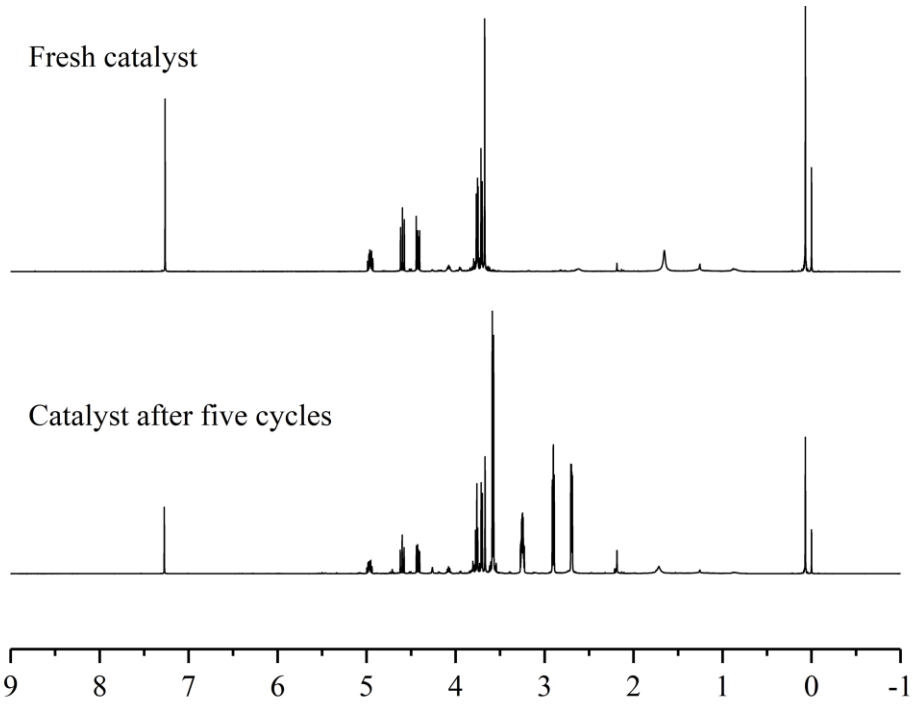


Fig. S22 ^{1}H NMR of recycling system.

4. ^{1}H NMR of CO_2 coupling with PGE under different temperature.

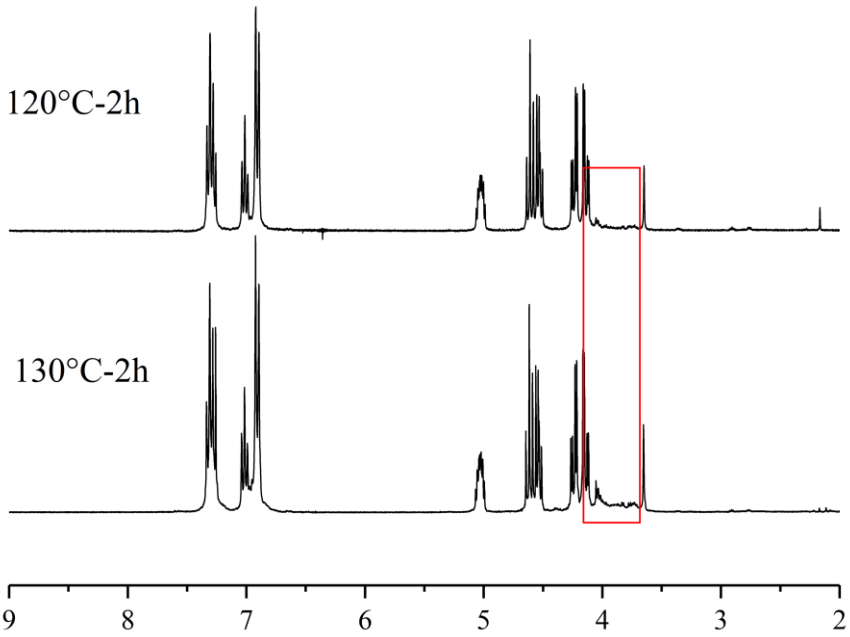


Fig. S23 ^{1}H NMR of CO_2 coupling with PGE under different temperature.

5. Kinetic data by [18-C-6K][Im] on cycloaddition of CO_2 and PGE.[1-3]

Table S1. Effects of the reaction time on cycloaddition of CO_2 and PGE by [18-C-6K][Im] at 90 ^{o}C [a].

Entry	Time (h)	Yield[b] (%)	Selectivity[b] (%)
1	0.5	14.6	>99
2	1.0	28.2	>99
3	1.5	37.2	>99
4	2.0	47.2	>99

[a] Reaction conditions: catalyst (0.20 mmol), [18-C-6K]Im$_0$/[PGE]$_0$ = 1/100, no solvent, 0.1 MPa, T = 90 ± 1^{o}C. [b] Yields and selectivities were determined by ^{1}H NMR spectrum of the reaction mixture.

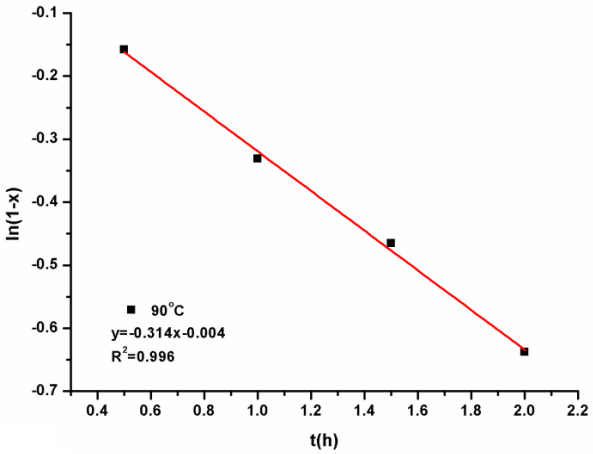


Fig. S24 Logarithmic plots of (1 – *x*) versus time by [18-C-6K][Im] at 90 °C (*x* = [CPE]).

Table S2. Effects of the reaction time on cycloaddition of CO_2 and PGE by [18-C-6K][Im] at 100 °C[a].

Entry	Time (h)	Yield[b] (%)	Selectivity[b] (%)
1	0.5	23.5	>99
2	1.0	45.5	>99
3	1.5	60.2	>99
4	2.0	73.0	>99

[a] Reaction conditions: catalyst (0.20mmol), $[18\text{-C-6K}][Im]_0/[PGE]_0$ = 1/100, no solvent, 0.1 MPa, T = 100 ± 1 °C. [b] Yields and selectivities were determined by ^{1}H NMR spectrum of the reaction mixture.

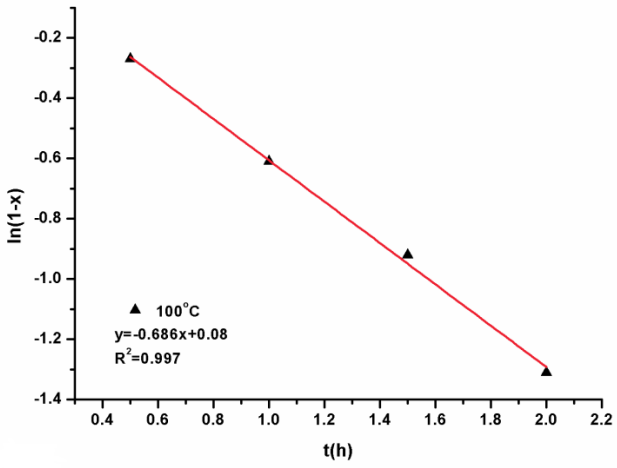


Fig. S25 Logarithmic plots of (1 – x) versus time by [18-C-6K][Im] at 100 °C (x = [CPE]).

Table S3. Effects of the reaction time on cycloaddition of CO_2 and PGE by [18-C-6K][Im] at 110 °C[a].

Entry	Time (h)	Yield[b] (%)	Selectivity[b] (%)
1	0.5	28.1	>99
2	1.0	52.1	>99
3	1.5	67.6	>99
4	2.0	79.4	>99

[a] Reaction conditions: catalyst (0.20mmol), $[18\text{-C-6K}][Im]_0/[PGE]_0$ = 1/100, no solvent, 0.1 MPa, T = 110±1°C. [b] Yields and selectivities were determined by ^{1}H NMR spectrum of the reaction mixture.

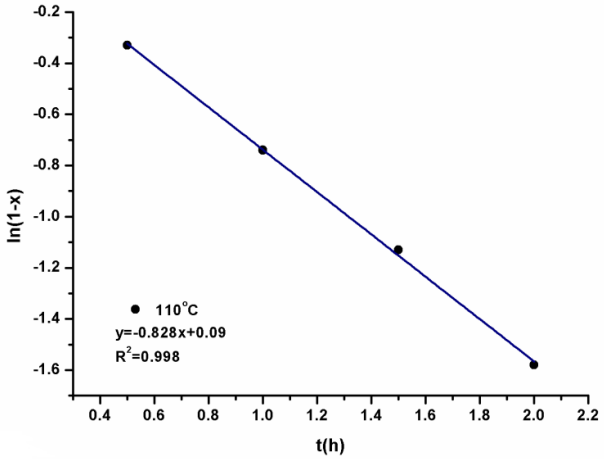


Fig. S26 Logarithmic plots of $(1 - x)$ versus time by [18-C-6K][Im] at 110 °C (x = [CPE]).

Table S4. Effects of the reaction time on cycloaddition of CO_2 and PGE by [18-C-6K][Im] at 120 °C[a].

Entry	Time (h)	Yield[b] (%)	Selectivity[b] (%)
1	0.5	40.3	>99
2	1.0	68.5	>99
3	1.5	89.3	>99
4	2.0	96.2	>99

[a] Reaction conditions: catalyst (0.20mmol), $[18\text{-C-6K}][Im]_0/[PGE]_0$ = 1/100, no solvent, 0.1 MPa, T = 120±1°C. [b] Yields and selectivities were determined by ^{1}H NMR spectrum of the reaction mixture.

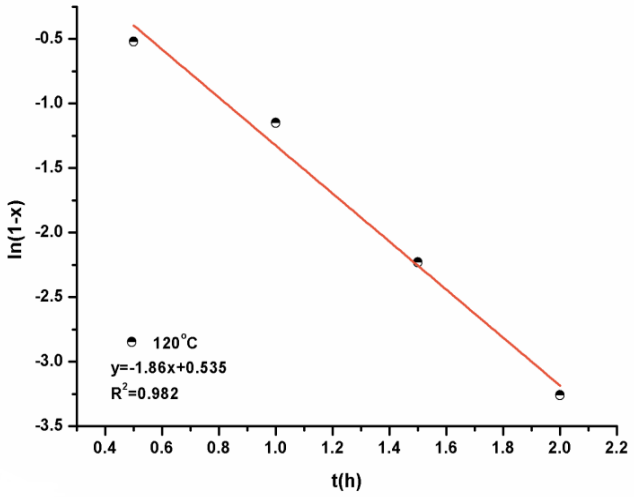


Fig. S27 Logarithmic plots of (1 – *x*) versus time by [18-C-6K][Im] at 120 °C (*x* = [CPE]).

6. Kinetic data by [15-C-5Na][Im] on cycloaddition of CO_2 and PGE.

Table S5. Effects of the reaction time on cycloaddition of CO_2 and PGE by [15-C-5Na][Im] at 90 °C[a].

Entry	Time (h)	Yield[b] (%)	Selectivity[b] (%)
1	0.5	0.0	>99
2	1.0	4.7	>99
3	1.5	11.1	>99
4	2.0	13.5	>99

[a] Reaction conditions: catalyst (0.20mmol), $[15\text{-C-5Na}][Im]_0/[PGE]_0$ = 1/100, no solvent, 0.1 MPa, T = 90 ± 1°C. [b] Yields and selectivities were determined by ^{1}H NMR spectrum of the reaction mixture.

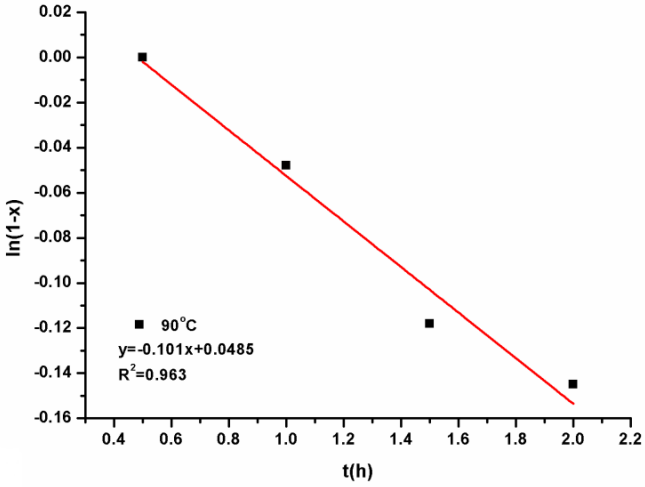


Fig. S28 Logarithmic plots of (1 – *x*) versus time by[15-C-5Na][Im] at 90 °C (*x* = [CPE]).

Table S6. Effects of the reaction time on cycloaddition of CO_2 and PGE by [15-C-5Na][Im] at 100 °C[a].

Entry	Time (h)	Yield[b] (%)	Selectivity[b] (%)
1	0.5	10.0	>99
2	1.0	14.2	>99
3	1.5	20.5	>99
4	2.0	30.1	>99

[a] Reaction conditions: catalyst (0.20mmol), $[15\text{-C-5Na}][Im]_0/[PGE]_0$ = 1/100, no solvent, 0.1 MPa, T = 100±1°C. [b] Yields and selectivities were determined by ^{1}H NMR spectrum of the reaction mixture.

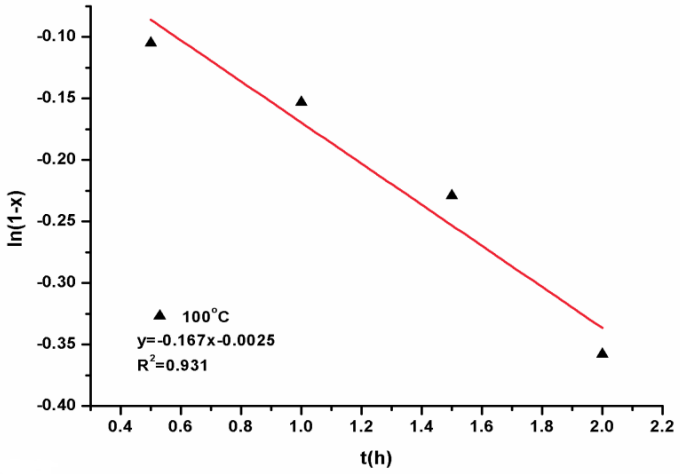


Fig. S29 Logarithmic plots of $(1 - x)$ versus time by[15-C-5Na][Im] at 100 °C (x = [CPE]).

Table S7. Effects of the reaction time on cycloaddition of CO_2 and PGE by [15-C-5Na][Im] at 110 °C[a].

Entry	Time (h)	Yield[b] (%)	Selectivity[b] (%)
1	0.5	16.6	>99
2	1.0	28.7	>99
3	1.5	38.3	>99
4	2.0	54.5	>99

[a] Reaction conditions: catalyst (0.20mmol), $[15\text{-C-5Na}]Im_0/[PGE]_0$ = 1/100, no solvent, 0.1 MPa, T = 110±1°C. [b] Yields and selectivities were determined by ^{1}H NMR spectrum of the reaction mixture.

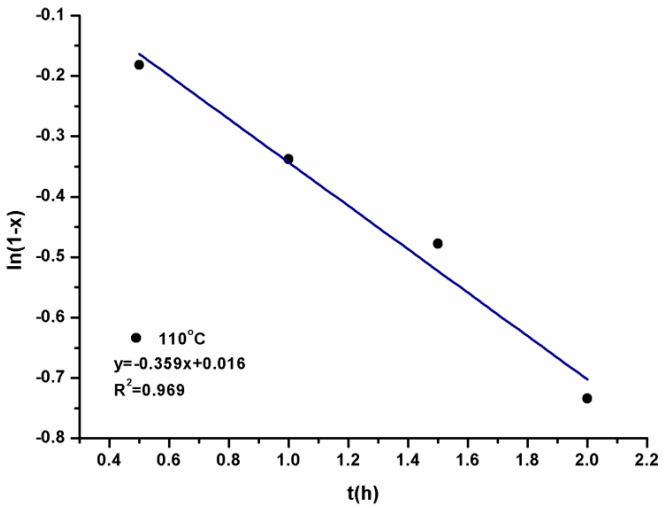


Fig. S30 Logarithmic plots of $(1 - x)$ versus time by[15-C-5Na][Im] at 110 °C (x = [CPE]).

Table S8. Effects of the reaction time on cycloaddition of CO_2 and PGE by [15-C-5Na][Im] at 120 °C[a].

Entry	Time (h)	Yield[b] (%)	Selectivity[b] (%)
1	0.5	19.8	>99
2	1.0	33.8	>99
3	1.5	58.9	>99
4	2.0	65.9	>99

[a] Reaction conditions: catalyst (0.20 mmol), $[15\text{-C-5Na}][Im]_0/[PGE]_0$ = 1/100, no solvent, 0.1 MPa, T = 120 ± 1°C. [b] Yields and selectivities were determined by ^{1}H NMR spectrum of the reaction mixture.

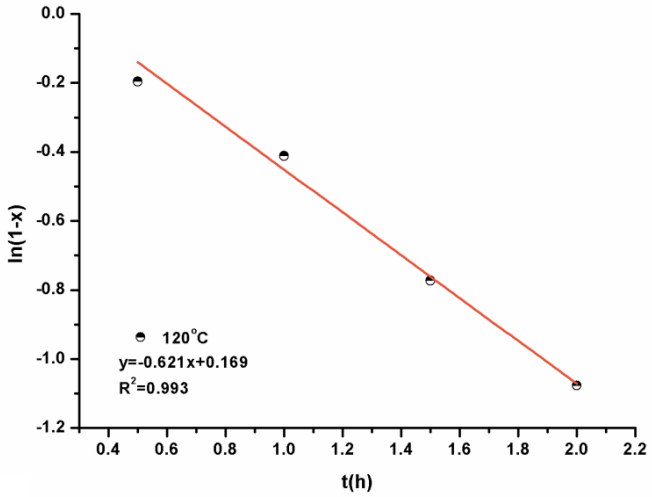


Fig. S31 Logarithmic plots of $(1 - x)$ versus time by[15-C-5Na][Im] at 120 °C (x = [CPE]).

7. The DFT calculation of [15-C-5Na][Im] for the formation of CPE

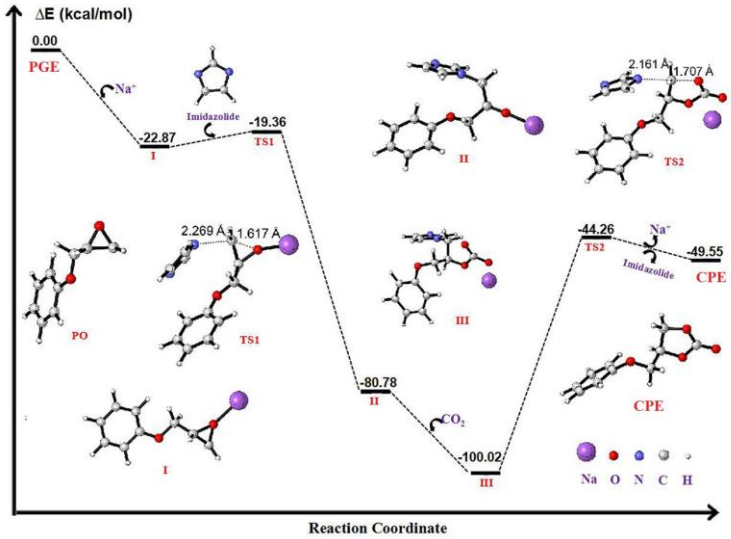


Figure S32. The potential energy surface from coupling PGE and CO_2 to CPE.

8. Tables of atom coordinates of reactions, product, intermediates and transition states obtained by DFT calculation

PO

C	-0.68832300	0.26170900	-0.21444100
C	-1.54949300	0.64989000	0.81288100
C	-2.59316200	1.53087500	0.53025100
C	-2.77161600	2.01211100	-0.77040700
C	-1.90831400	1.61536000	-1.77908900
C	-0.85796300	0.73661400	-1.50789200
H	0.12289900	-0.42347100	0.01094900
H	-1.39952500	0.26073700	1.81285400
H	-3.59267400	2.69559000	-0.95748600
H	-2.05406300	1.99585000	-2.78511200
H	-0.18282200	0.42781200	-2.29832100
O	-3.49320100	1.97536900	1.45123200
C	-3.31649200	1.57370900	2.79366100
H	-3.43206200	0.48664200	2.90703000
C	-4.37547100	2.27054300	3.60320100
C	-5.66092300	1.61388100	3.85831700
H	-4.33147700	3.35884400	3.60313100
O	-4.65055000	1.67220000	4.85571700
H	-2.31562100	1.85293100	3.15116700
H	-6.54301200	2.21848700	4.05393700

H	-5.84289100	0.62808300	3.43419800

Imidazolide

C	0.89346500	0.69607900	-0.00005100
C	0.89750500	-0.69150300	-0.00002000
C	-1.09291100	-0.00363100	0.00013200
N	-0.39532100	1.14642300	-0.00002600
H	1.73758700	1.38137300	-0.00009100
H	1.74585500	-1.37156500	-0.00002800
H	-2.18246300	-0.00473200	0.00021600
N	-0.38886900	-1.14795800	-0.00004000

I(K^+)

C	-0.68252600	0.26777300	-0.21698500
C	-1.54297200	0.64265600	0.81686800
C	-2.59301400	1.51300000	0.53886900
C	-2.78968000	2.00252000	-0.75272700
C	-1.92704800	1.61900600	-1.76811500
C	-0.86700700	0.74950100	-1.50558100
H	0.13664700	-0.41038600	-0.00164800
H	-1.38260700	0.24720000	1.81339600
H	-3.61818000	2.67852700	-0.93292400
H	-2.08105900	2.00248100	-2.77119000
H	-0.19394700	0.45215900	-2.30168600
O	-3.50051200	1.94423900	1.47692000
C	-3.29715100	1.55484500	2.80627600
H	-3.40664200	0.46762300	2.94026700
C	-4.36273700	2.26676400	3.59713500
C	-5.66346100	1.63493200	3.81446700
H	-4.30944300	3.35341800	3.60014600
O	-4.68188800	1.68528100	4.86724900
K	-4.28104800	1.31288600	7.36405500
H	-2.29610100	1.84632900	3.15752000
H	-6.54042100	2.25304400	3.98145000
H	-5.83700800	0.64285500	3.40606800

TS1(K^+)

C	-0.74523600	0.19650400	-0.30288400
C	-1.51436200	0.64170600	0.77527400
C	-2.47163200	1.63332900	0.56662700
C	-2.67645100	2.16546900	-0.71164700
C	-1.90178800	1.71262900	-1.76654600
C	-0.92651600	0.72934000	-1.57086200
H	0.00090600	-0.57526900	-0.13789700
H	-1.35998100	0.21272700	1.75912800
H	-3.48694200	2.87774500	-0.83679000
H	-2.06807600	2.12060200	-2.75890200
H	-0.32597000	0.37889800	-2.40387300
O	-3.23994000	2.16766100	1.55370300
C	-3.28159500	1.51235400	2.79047000
H	-3.57086300	0.45833500	2.66382500
C	-4.30345100	2.24497600	3.62584600
C	-5.61518800	1.67881200	3.82414500
H	-4.23303200	3.32847900	3.50096300
O	-4.43306900	1.79778800	4.96323600
H	-2.30385800	1.55401300	3.30138800
H	-6.44114300	2.30187500	4.13184200
H	-5.76739300	0.62110000	3.66792300
C	-5.75200500	1.18786500	-0.26906800
C	-6.10512700	0.68775400	0.96880700
C	-6.27732800	2.81018700	0.98052000
N	-5.86193300	2.55022600	-0.25987000
H	-5.42524300	0.65082700	-1.15192000
H	-6.15310900	-0.34092900	1.31278200
H	-6.45668100	3.82122400	1.33700100
N	-6.46435900	1.73687900	1.77420400
K	-4.44976900	1.04697400	7.23916300

II(K^+)

C	-0.70263600	0.19483100	-0.20096800
C	-1.49888400	0.63583100	0.85773100
C	-2.49440300	1.58487300	0.61746200
C	-2.69074700	2.07969600	-0.67853900
C	-1.89003900	1.63199000	-1.71623800
C	-0.88716200	0.68580200	-1.48630800
H	0.07073800	-0.54309300	-0.00807900
H	-1.33914600	0.24468700	1.85563900
H	-3.49262100	2.79528200	-0.83069000
H	-2.05154600	2.01949900	-2.71764700
H	-0.26348100	0.33697100	-2.30256100
O	-3.30823900	2.09476500	1.57011400
C	-3.32150400	1.49545800	2.85360400
H	-3.46075500	0.40475300	2.76388400
C	-4.44521500	2.10343500	3.70689800
C	-5.82599600	1.59685800	3.22367000
H	-4.41726500	3.19814000	3.48544900
O	-4.28618500	1.78748000	5.00942200
K	-3.84684800	1.37323100	7.23224700
H	-2.37140000	1.67937400	3.37579600
H	-6.60416100	2.12996200	3.77909000
H	-5.89473500	0.53549300	3.48436400
C	-6.05113400	1.35869200	-0.36071100
C	-5.94448000	0.73524900	0.85479600
C	-6.22671200	2.88620900	1.10907800
N	-6.22873300	2.70847800	-0.19352200
H	-6.00721200	0.91079600	-1.34320500
H	-5.79028100	-0.29489200	1.13761400
H	-6.32759500	3.83530600	1.61869700
N	-6.07503700	1.72570600	1.79599800

III(K^+)

C	-0.11719700	0.58732400	1.53466800
C	-1.49731200	0.53043200	1.34136900
C	-2.10727800	1.43346700	0.45940300
C	-1.31577100	2.37209500	-0.22258000
C	0.06032500	2.41406700	-0.02025300
C	0.67246300	1.52591300	0.86964900
H	0.33414700	-0.10807200	2.23564800
H	-2.08187100	-0.17944200	1.91634000
H	-1.80820900	3.04614000	-0.91609200
H	0.65751300	3.13613500	-0.56921500
H	1.74580000	1.55097000	1.02424700
O	-3.42761600	1.48526100	0.18032700
C	-4.37759900	0.88890500	1.06373200
H	-5.27008500	0.73077000	0.45263900
C	-4.70857900	1.84760900	2.20452500
C	-5.92661900	1.37615400	3.01693800
H	-4.97795200	2.80776000	1.74324700
O	-3.58641100	2.13997100	3.01589800
K	-1.13788500	3.20685600	2.92011100
H	-4.03476400	-0.07089800	1.45541400
H	-5.99175700	1.98878200	3.92133000
H	-5.81006500	0.33808400	3.32439700
C	-8.84476600	1.13863600	0.91376500
C	-7.79135700	0.52365000	1.53848100
C	-7.84879000	2.66086100	2.01754500
N	-8.87399100	2.47508200	1.22058700
H	-9.58558800	0.69169500	0.26652200
H	-7.44599900	-0.49893800	1.56148500
H	-7.55874300	3.59905100	2.47373100
N	-7.15441400	1.51328300	2.25075100
C	-3.05436000	1.07753100	3.87082900
O	-3.63093600	-0.00505200	3.80928200
O	-2.05648400	1.48345800	4.48326600

TS2(K^+)

C	-0.21063400	0.45625100	1.36529100
C	-1.59899000	0.57144700	1.28100200
C	-2.16640500	1.58315500	0.49210300
C	-1.31886300	2.46925700	-0.19482100
C	0.06290900	2.34628000	-0.09548500
C	0.63222400	1.34079200	0.69332800
H	0.20895400	-0.33483800	1.97920800
H	-2.21570100	-0.11701600	1.84541000
H	-1.77894500	3.23443000	-0.81172000
H	0.69866000	3.03097900	-0.64906100
H	1.70954300	1.23333900	0.75908500
O	-3.48435100	1.80955300	0.32520700
C	-4.44665500	1.13505500	1.12871900
H	-5.37286000	1.10527100	0.55377900
C	-4.70077900	1.90511700	2.42348200
C	-5.47431800	1.06102300	3.43047900
H	-5.21803800	2.83707300	2.20741300
O	-3.44522300	2.26910200	3.02794300
K	-0.89519700	3.14142500	2.91097200
H	-4.13593700	0.10546300	1.33813200
H	-6.01886900	1.54870100	4.22544100
H	-5.74453800	0.03945600	3.20485000
C	-8.70137200	1.03111100	0.65949500
C	-7.77778200	0.43424100	1.49594200
C	-7.79305700	2.55298900	1.81339300
N	-8.70856800	2.38060400	0.86429200
H	-9.35840600	0.56447400	-0.06363000
H	-7.51155700	-0.61001300	1.61652700
H	-7.54579400	3.52686800	2.22745300
N	-7.19468100	1.42144900	2.24273700
C	-3.13511600	1.42649000	4.07541400
O	-4.08369300	0.62434300	4.35700900
O	-2.02651100	1.54027200	4.57899900

IV(K^+)

C	-3.75531400	-1.65115900	-0.78218200
C	-2.57175800	-1.16249600	-0.22461900
C	-2.60298700	0.03156200	0.49133900
C	-3.79776700	0.73432000	0.64604100
C	-4.96382100	0.23665000	0.08396800
C	-4.94966500	-0.96025200	-0.63331500
H	-3.73158200	-2.58378900	-1.33584500
H	-1.65607400	-1.72947400	-0.35151200
H	-3.78755300	1.65708000	1.21525500
H	-5.89195100	0.78369400	0.21068500
H	-5.86373200	-1.34849800	-1.06758100
O	-1.50723900	0.61122600	1.09791900
C	-0.26149100	-0.02041800	0.99711300
H	0.36146400	0.39780600	1.79606600
C	0.37090800	0.31836400	-0.35197400
C	0.62040400	1.82263200	-0.50541400
H	-0.19880200	-0.09996700	-1.18355900
O	1.71115200	-0.22030600	-0.39800000
K	4.23929500	-1.96008300	-0.41944900
H	-0.32696600	-1.10480800	1.14288700
H	0.51883900	2.18039500	-1.53133900
H	0.00655800	2.41874200	0.16950400
C	2.59763400	0.78097100	-0.16669600
O	2.00290600	1.95586000	-0.11915400
O	3.77531700	0.56334900	-0.03333900

I(Na^+)

C	-0.67946700	0.26934500	-0.21914700
C	-1.54264300	0.64125100	0.81351900
C	-2.59388900	1.50894700	0.53342500
C	-2.79075400	1.99944500	-0.75722700
C	-1.92524000	1.61875400	-1.77142000
C	-0.86349400	0.75183900	-1.50753300
H	0.14112700	-0.40674800	-0.00301100
H	-1.38267400	0.24505100	1.80987400
H	-3.62062100	2.67348200	-0.93841900
H	-2.07842200	2.00254000	-2.77445600
H	-0.18834000	0.45692500	-2.30275200
O	-3.50541800	1.93725600	1.47184400
C	-3.29787900	1.55260600	2.80043800
H	-3.40676500	0.46593400	2.94037300
C	-4.36537900	2.26937800	3.58498700
C	-5.66988400	1.64282600	3.79753200
H	-4.30882700	3.35551600	3.59267700
O	-4.69094600	1.68837200	4.85798800
H	-2.29802200	1.84787600	3.15154600
H	-6.54401100	2.26403500	3.96562100
H	-5.84400000	0.64946900	3.39341800
Na	-4.34004700	1.36482400	7.00600100

TS1(Na^+)

C	-0.76769400	0.18864400	-0.25296600
C	-1.54239800	0.65826200	0.81067000
C	-2.47246500	1.66981100	0.58133200
C	-2.64758300	2.19926100	-0.70139100
C	-1.86811900	1.72227700	-1.74220500
C	-0.91848300	0.71871200	-1.52606600
H	-0.04202400	-0.59900200	-0.07316200
H	-1.41231000	0.23127600	1.79911400
H	-3.44583500	2.92168400	-0.84348400
H	-2.01254300	2.12595100	-2.73952600
H	-0.31458300	0.34898200	-2.34812100
O	-3.24007100	2.23054400	1.55853400
C	-3.36742800	1.54768800	2.77018200
H	-3.69866700	0.51161100	2.60008200
C	-4.38628600	2.30395600	3.58884400
C	-5.69111300	1.74325100	3.83903500
H	-4.30997100	3.38456600	3.45904200
O	-4.51724900	1.87565000	4.94357600
H	-2.40995700	1.53454200	3.32587900
H	-6.51659900	2.37426200	4.12947000
H	-5.85973600	0.68906900	3.67720200
C	-5.69437800	1.13549200	-0.25065900
C	-6.12133700	0.68037800	0.98264800
C	-6.29119900	2.80018300	0.90786100
N	-5.80347400	2.49612900	-0.29661000
H	-5.32001400	0.56702000	-1.09413400
H	-6.20046700	-0.33666000	1.35543900
H	-6.49455100	3.82332300	1.21281400
N	-6.52512200	1.75718900	1.72887200
Na	-3.71578700	0.80217000	6.56564100

II(Na^+)

C	-3.09068900	-2.36709600	0.58750100
C	-1.76620500	-2.00694100	0.33138600
C	-1.49977100	-0.80905700	-0.33279200
C	-2.55409200	0.02298300	-0.73018200
C	-3.86191600	-0.35200400	-0.47008700
C	-4.14160100	-1.55124600	0.19080600
H	-3.29282700	-3.30107100	1.10357200
H	-0.95754300	-2.65756300	0.64311900
H	-2.30282300	0.96005600	-1.21756400
H	-4.67382300	0.29972800	-0.77826300
H	-5.16739500	-1.83904700	0.39533300
O	-0.25784200	-0.36936400	-0.64636300
C	0.86406100	-1.02598900	-0.08821100
H	0.75141900	-1.11728500	1.00512900
C	2.13761400	-0.24033600	-0.42673500
C	2.22207100	1.06002200	0.40527000
H	2.02071300	0.06568500	-1.49088400
O	3.24168500	-0.98734700	-0.18646600
H	0.97378200	-2.03583900	-0.50867700
H	3.09073800	1.63257600	0.06485900
H	2.39711800	0.77450200	1.44772300
C	-0.96305100	2.69787400	0.74233900
C	0.03865700	1.94905400	1.30112300
C	0.58431600	2.59555300	-0.71397800
N	-0.61365700	3.10015900	-0.52172600
H	-1.91345400	2.96806400	1.17995200
H	0.13840300	1.45718000	2.25669900
H	1.17657400	2.69309200	-1.61433600
N	1.03814800	1.90185900	0.36164200
Na	4.82732400	-2.17249300	0.04708400

III(Na^+)

C	-7.89297500	3.58090400	-0.80622600
C	-6.93368600	2.65439300	-0.39528400
C	-7.27988000	1.30423000	-0.30246800
C	-8.58421600	0.89830100	-0.60428000
C	-9.52632500	1.83206200	-1.00670100
C	-9.18713100	3.18202000	-1.11407500
H	-7.61547500	4.62814800	-0.88450600
H	-5.93160800	2.98921200	-0.15141300
H	-8.82801800	-0.15511600	-0.51542300
H	-10.53512500	1.50506500	-1.23891000
H	-9.92572200	3.91012600	-1.43168800
O	-6.42101000	0.30956800	0.05579900
C	-5.13452500	0.66382800	0.53902800
H	-4.55192000	-0.25615300	0.54384900
C	-5.22891700	1.26761100	1.95140000
C	-5.22745600	0.20438300	3.06958900
H	-6.17871200	1.81092500	2.02098100
O	-4.22846800	2.25583900	2.16021800
H	-4.63695900	1.36926600	-0.13752200
H	-4.70517600	0.61168900	3.94037900
H	-4.68772700	-0.69152500	2.75700100
C	-8.63331200	-0.86513700	3.57121100
C	-7.52409800	-0.82156900	2.76733000
C	-7.15336100	0.18268200	4.68068700
N	-8.39275500	-0.23433400	4.76585100
H	-9.59044300	-1.31778400	3.35536700
H	-7.32394400	-1.17463300	1.76796700
H	-6.60691300	0.71471600	5.44899300
N	-6.57203600	-0.14536000	3.49337300
C	-2.83662600	1.78566900	2.12043300
O	-2.68561600	0.60316300	1.87770300
O	-2.06929500	2.74075100	2.36513100
Na	-3.53223600	4.29016100	2.78400300

TS2(Na^+)

C	-7.37542500	0.31807900	-2.81741500
C	-6.98519800	1.04420800	-1.70240400
C	-5.89414800	0.60380500	-0.94974000
C	-5.21639100	-0.56307400	-1.29455900
C	-5.62712000	-1.28499600	-2.41604300
C	-6.69675900	-0.84681200	-3.18494100
H	-8.23191400	0.65160300	-3.39505200
H	-7.53591600	1.90934500	-1.34673500
H	-4.37854700	-0.91595100	-0.70289400
H	-5.09963100	-2.19569100	-2.68273700
H	-7.01228900	-1.41259700	-4.05507700
O	-5.52579100	1.39707400	0.10140400
C	-4.85304000	0.78031300	1.17073800
H	-5.35337800	-0.15785700	1.43444700
C	-4.87624900	1.76252300	2.34397400
C	-5.42587200	1.18733900	3.65116700
H	-5.43447400	2.64677200	2.04718600
O	-3.51740000	2.20694900	2.62052000
H	-3.80290500	0.56833100	0.91098200
H	-5.93931800	1.84023600	4.34015400
H	-5.65162400	0.13353700	3.72566000
C	-8.74723700	0.43393100	1.07604300
C	-7.83975200	0.04614800	2.04051000
C	-7.93368800	2.18121800	1.94605200
N	-8.80473700	1.79816100	1.01700400
H	-9.35296400	-0.18809100	0.42909300
H	-7.55296600	-0.94621100	2.37038200
H	-7.73006700	3.22592600	2.16699300
N	-7.31878700	1.17883000	2.60866000
C	-3.06391100	1.74616000	3.83478800
O	-3.94213600	1.11459300	4.49257900
O	-1.89386000	2.00633600	4.11195500
Na	-1.44558200	3.10573800	2.22528100

PC

C	-7.56778200	5.06157800	0.81589800
C	-6.90092800	3.87202500	1.11180100
C	-7.64393300	2.73963100	1.44633700
C	-9.03908200	2.80324000	1.48527200
C	-9.68572200	3.99358000	1.18990500
C	-8.95379100	5.13300300	0.85314900
H	-6.98417900	5.93890500	0.55582400
H	-5.81794400	3.85002300	1.07359300
H	-9.58817700	1.90478700	1.74514300
H	-10.76991100	4.03228100	1.22147000
H	-9.46136400	6.06313600	0.62346200
O	-7.10882000	1.51453700	1.74806800
C	-5.70562700	1.37249400	1.75247600
H	-5.50838500	0.29724800	1.68993600
C	-5.12256700	1.90980400	3.05687400
C	-5.51432800	1.05091300	4.26039900
H	-5.36536200	2.96540100	3.19495500
O	-3.70555300	1.76283400	3.02012100
H	-5.23731400	1.85567900	0.88857400
H	-5.57654800	1.62595100	5.18799900
H	-6.44119500	0.49951400	4.09653000
C	-3.34952300	0.64440900	3.70680900
O	-4.42484600	0.13455900	4.35054900
O	-2.25415200	0.18548500	3.73099000

References

[1] X. Jiang, F. Gou and H. Jing, *J. Catal*., 2014, **313**, 159.

[2] B. Li, L. Zhang, Y. Song, D. Bai and H. Jing, *J. Mol. Catal. A: Chem*., 2012, **26**, 363–364.

[3]. X. Jiang, F. L. Gou, F. J. Chen and H. W. Jing, *Green Chem*., 2016, **18**, 3567–3576.