

# **A Novel Base Recycling Process for Effective Hydrogenation of CO<sub>2</sub> to Formic Acid**

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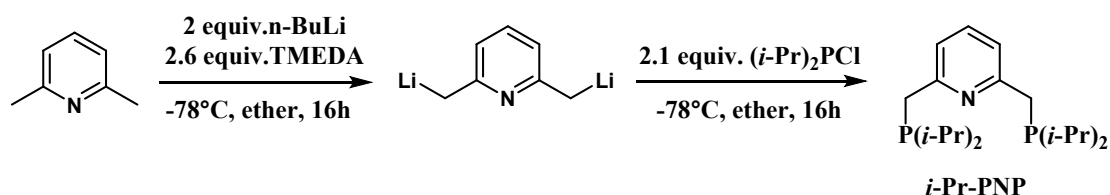
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## 1. General information

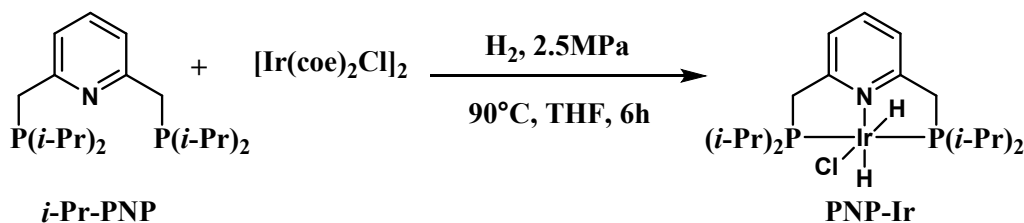
The manipulations which are sensitive to moisture or air were performed in a nitrogen-filled glove box (JMS-1X) or using standard Schlenk techniques unless stated otherwise. NMR spectra were recorded on a Bruker AV 500 (or Bruker AV 400) spectrometer. The NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts are given in ppm and referenced to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C). H<sub>2</sub> (99.999 vt.%) and CO<sub>2</sub> (99.99 vt.%) were purchased from Nanjing Tianze Gas Center, Nanjing. Part of the solvent used for catalyst synthesis is distilled after drying with an appropriate desiccant. Commercially available reagents were purchased from TCI Chemical.

## 2. Synthesis and characterization of PNP-Ir catalyst



PNP-Ir was synthesized following the procedure reported in references.<sup>[S1, S2]</sup> In a nitrogen-filled glovebox, a thick walled glass vessel was charged with dry tetramethylethylenediamine (2.49 g, 21.4 mmol) and 40 mL of dry diethyl ether. The glass vessel was taken out of the glovebox and purged with argon for 5 minutes before addition of 2,6- dimethylpyridine (8.84 mmol) via syringe. A 2.5 M solution of *n*-BuLi (16.5 mmol), additionally diluted with 10 mL of diethyl ether, was then added to the resulting pale yellow solution using a cannula at -78 °C under a positive pressure of argon. The reaction vessel was warmed to room temperature and then heated to 40 °C in an oil bath overnight (16 h). The resulting brown solution was cooled to room temperature before diisopropylchlorophosphine (2.64 g, 17.3 mmol), diluted with 10 mL of diethyl ether, was added to the stirring solution using a cannula under a positive pressure of argon at -78 °C. A color change from brown to cloudy yellow was observed upon the addition of the chlorophosphine. The mixture was stirred at room temperature overnight (16 h). The reaction was cooled to 0 °C and degassed water was added to the

mixture using a cannula under a positive pressure of argon with vigorous stirring. The glass vessel was sealed and the contents were mixed vigorously before the aqueous layer was removed using a cannula. The extraction procedure was repeated 4 times. Anhydrous MgSO<sub>4</sub> was added to the organic layer. The glass vessel was brought inside the glovebox and the mixture was filtered through sand core funnel to remove the MgSO<sub>4</sub>. Evaporation of the solvent in vacuo yielded crude (*i*-Pr-PNP) as a yellow oil (1.86 g, 62% yield). This material was carried through the next step without any further purification. Characterization of *i*-Pr-PNP: <sup>1</sup>H NMR (400 MHz, Chloroform-*d*), δ 7.45 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 14.2 Hz, 2H), 2.97 (dd, *J* = 10.0, 2.3 Hz, 4H), 1.80 (dtd, *J* = 14.2, 7.0, 2.1 Hz, 4H), 1.09 – 1.01 (m, 24H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*), δ 159.80 (d, *J* = 8.8 Hz), 136.13, 120.44, 32.52, 32.31, 23.58, 23.44, 19.78, 19.63, 19.16, 19.05.



To a 50 mL stainless autoclave, [Ir(coe)<sub>2</sub>Cl]<sub>2</sub> (170 mg, 190 μmol), *i*-Pr-PNP (212 mg, 625 μmol), and THF (15 mL) were charged under argon atmosphere. The mixture was pressurized by hydrogen (3 MPa) and stirred at 90 °C for 6 h. The solvent was removed in vacuo and the resulting residue was washed with hexane. The volatiles were removed under vacuum and the products were isolated by flash chromatography on silica gel (eluent: ethyl acetate). The result is a solid white powder of PNP-Ir (84 mg, 52% yield). Characterization of PNP-Ir: <sup>1</sup>H NMR (400 MHz, Chloroform-*d*), δ 7.49 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 3.78 (dt, *J* = 16.8, 4.2 Hz, 2H), 3.49 (dt, *J* = 16.8, 3.9 Hz, 2H), 2.81 (dtp, *J* = 10.6, 7.2, 3.6 Hz, 2H), 2.06 (dtt, *J* = 13.6, 6.7, 3.3 Hz, 2H), 1.49 – 1.38 (m, 6H), 1.33 (q, *J* = 6.9 Hz, 6H), 1.13 (dt, *J* = 8.5, 7.0 Hz, 6H), 0.87 (q, *J* = 7.2 Hz, 6H), -19.72 (td, *J* = 13.2, 7.7 Hz, 1H), -23.31 (td, *J* = 15.0, 7.7 Hz, 1H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*), δ 162.95, 135.26, 119.27, 119.22, 119.18, 43.34, 43.22, 43.10, 24.83, 24.70, 24.56, 24.48, 24.33, 24.31, 24.15, 20.79, 20.76, 20.73, 20.68, 20.65, 20.61, 18.88, 17.15.

### 3. Synthesis and characterization of $[R_1R_2ImR_3][HCO_3]$

**Synthesis:** Typically, a mixture of  $[C_1C_4Im][Br]$  (0.05 mmol) and  $KHCO_3$  (1.1 equiv) was dried at 50 °C under vacuum for 18 h. Then, dry methanol (30 mL) was added to the mixture, which was stirred for 48 h at RT. After the KBr suspension was filtered, the solvent was evaporated under vacuum to afford a clear liquid. Then, the liquid was dried at 60 °C under vacuum for 12 h.  $[C_1C_4ImH][HCO_3]$  was obtained in 83% yield.  $[C_1C_2ImH][HCO_3]$ 、 $[C_1C_6ImH][HCO_3]$ 、 $[C_4C_4ImH][HCO_3]$  and  $[C_1C_4ImCH_3][HCO_3]$  were synthesized and purified by this method.

#### **Characterization of $[R_1R_2ImR_3][HCO_3]$ :**

**In each  $[R_1R_2ImH][HCO_3]$ , carbene- $CO_2$  adduct, a coexistence compound in equilibrium, can be observed.** <sup>[S3, S4]</sup>

$^1H$ -NMR, (400 MHz, DMSO- $d_6$ )

$[C_1C_2ImH][HCO_3]$ :  $\delta$  1.41-1.38 (t, 3H, -CH<sub>3</sub>), 3.88 (s, 3H, N-CH<sub>3</sub>), 4.26-4.20 (q, 2H, N-CH<sub>2</sub>-), 7.80 (d, 1H, -CH=C-), 7.91 (d, 1H, -C=CH-), 9.44 (s, 1H, N-CH-N)

$C_1C_2Im-CO_2$ :  $\delta$  1.33-1.29 (t, 3H, -CH<sub>3</sub>), 3.95 (s, 3H, N-CH<sub>3</sub>), 4.49-4.44 (q, 2H, N-CH<sub>2</sub>-), 7.68 (d, 1H, -CH=C-), 7.76 (d, 1H, -C=CH-)

$^{13}C$ -NMR, (100 MHz, DMSO- $d_6$ )

$[C_1C_2ImH][HCO_3]$ :  $\delta$  15.66 (-CH<sub>3</sub>), 36.22 (N-CH<sub>3</sub>), 44.46 (N-CH<sub>2</sub>-), 122.42 (-CH=), 123.95 (=CH-), 136.80 (N-CH-N)

$C_1C_2Im-CO_2$ :  $\delta$  16.44 (-CH<sub>3</sub>), 36.94 (N-CH<sub>3</sub>), 44.55 (N-CH<sub>2</sub>-), 120.99 (-CH=), 122.85 (=CH-), 142.05 (N-C-N), 154.72 (CO<sub>2</sub>)

$^1H$ -NMR, (400 MHz, DMSO- $d_6$ )

$[C_1C_4ImH][HCO_3]$ :  $\delta$  0.88-0.86 (t, 3H, -CH<sub>3</sub>), 1.28-1.21 (m, 2H, -CH<sub>2</sub>-), 1.80-1.72 (m, 2H, -CH<sub>2</sub>-), 3.89 (s, 3H, N-CH<sub>3</sub>), 4.23-4.19 (t, 2H, N-CH<sub>2</sub>-), 7.87 (d, 1H, -CH=C-), 7.97 (d, 1H, -C=CH-), 9.59 (s, 1H, N-CH-N)

$C_1C_4Im-CO_2$ :  $\delta$  0.85-0.82 (t, 3H, -CH<sub>3</sub>), 1.20-1.16 (m, 2H, -CH<sub>2</sub>-), 1.71-1.65 (m, 2H, -CH<sub>2</sub>-), 3.96 (s, 3H, N-CH<sub>3</sub>), 4.48-4.44 (t, 2H, N-CH<sub>2</sub>-), 7.66 (d, 1H, -CH=C-), 7.73 (d, 1H, -C=CH-).

<sup>13</sup>C-NMR, (100 MHz, DMSO-d<sub>6</sub>)

[C<sub>1</sub>C<sub>4</sub>ImH][HCO<sub>3</sub>]: δ 13.73 (-CH<sub>3</sub>), 19.20 (-CH<sub>2</sub>-), 31.85 (-CH<sub>2</sub>-), 36.24 (N-CH<sub>3</sub>), 48.88 (N-CH<sub>2</sub>-), 122.73 (-CH=), 124.00 (=CH-), 137.17 (N-CH-N), 159.39 (HCO<sub>3</sub><sup>-</sup>)

C<sub>1</sub>C<sub>4</sub>Im-CO<sub>2</sub>: δ 13.82 (-CH<sub>3</sub>), 19.38 (-CH<sub>2</sub>-), 32.60 (-CH<sub>2</sub>-), 36.94 (N-CH<sub>3</sub>), 48.66 (N-CH<sub>2</sub>-), 121.39 (-CH=), 122.73 (=CH-), 142.07 (N-C-N), 154.92 (CO<sub>2</sub>)

<sup>1</sup>H-NMR, (400 MHz, DMSO-d<sub>6</sub>)

[C<sub>1</sub>C<sub>6</sub>ImH][HCO<sub>3</sub>]: δ 0.76-0.73 (t, 3H, -CH<sub>3</sub>), 1.17 (br, 6H, -C<sub>3</sub>H<sub>6</sub>-), 1.76-1.73 (m, 2H, -CH<sub>2</sub>-), 3.91 (s, 3H, N-CH<sub>3</sub>), 4.25-4.21 (t, 2H, N-CH<sub>2</sub>-), 7.92 (d, 1H, -CH=C-), 8.02 (d, 1H, -C=CH-), 9.64 (s, 1H, N-CH-N)

C<sub>1</sub>C<sub>6</sub>Im-CO<sub>2</sub>: δ 0.76-0.73 (t, 3H, -CH<sub>3</sub>), 1.17 (br, 6H, -C<sub>3</sub>H<sub>6</sub>-), 1.68-1.65 (m, 2H, -CH<sub>2</sub>-), 3.97 (s, 3H, N-CH<sub>3</sub>), 4.49-4.45 (t, 2H, N-CH<sub>2</sub>-), 7.83 (d, 1H, -CH=C-), 7.90 (d, 1H, -C=CH-)

<sup>13</sup>C-NMR, (100 MHz, DMSO-d<sub>6</sub>)

[C<sub>1</sub>C<sub>6</sub>ImH][HCO<sub>3</sub>]: δ 14.15 (-CH<sub>3</sub>), 22.29 (-CH<sub>2</sub>-), 25.54 (-CH<sub>2</sub>-), 29.92 (-CH<sub>2</sub>-), 30.98 (-CH<sub>2</sub>-), 36.25 (N-CH<sub>3</sub>), 49.06 (N-CH<sub>2</sub>-), 122.69 (-CH=), 123.88 (=CH-), 137.12 (N-CH-N), 159.48 (HCO<sub>3</sub><sup>-</sup>)

C<sub>1</sub>C<sub>6</sub>Im-CO: δ 14.15 (-CH<sub>3</sub>), 22.31 (-CH<sub>2</sub>-), 25.71 (-CH<sub>2</sub>-), 30.61 (-CH<sub>2</sub>-), 31.07 (-CH<sub>2</sub>-), 37.03 (N-CH<sub>3</sub>), 48.91 (N-CH<sub>2</sub>-), 121.57 (-CH=), 122.81 (=CH-), 141.94 (N-C-N), 154.95 (CO<sub>2</sub>)

<sup>1</sup>H-NMR, (400 MHz, DMSO-d<sub>6</sub>)

[C<sub>4</sub>C<sub>4</sub>ImH][HCO<sub>3</sub>]: δ 0.86-0.84 (t, 6H, -CH<sub>3</sub>), 1.27-1.22 (m, 4H, -CH<sub>2</sub>-), 1.81-1.73 (m, 4H, -CH<sub>2</sub>-), 4.24-4.20 (t, 4H, N-CH<sub>2</sub>-), 7.92 (d, 2H, -CH=C-), 9.62 (s, 1H, N-CH-N)

C<sub>1</sub>C<sub>4</sub>Im-CO<sub>2</sub>: δ 0.83-0.81 (t, 6H, -CH<sub>3</sub>), 1.20-1.15 (m, 4H, -CH<sub>2</sub>-), 1.71-1.67 (m, 4H, -CH<sub>2</sub>-), 4.46-4.42 (t, 4H, N-CH<sub>2</sub>-), 7.76 (d, 2H, -CH=C-).

<sup>13</sup>C-NMR, (100 MHz, DMSO-d<sub>6</sub>)

[C<sub>4</sub>C<sub>4</sub>ImH][HCO<sub>3</sub>]: δ 13.70 (-CH<sub>3</sub>), 19.22 (-CH<sub>2</sub>-), 31.83 (-CH<sub>2</sub>-), 48.93 (N-CH<sub>2</sub>-), 122.89 (-CH=), 136.69 (N-CH-N), 159.16 (HCO<sub>3</sub><sup>-</sup>)

C<sub>1</sub>C<sub>4</sub>Im-CO<sub>2</sub>: δ 13.80 (-CH<sub>3</sub>), 19.37 (-CH<sub>2</sub>-), 32.58 (-CH<sub>2</sub>-), 48.62 (N-CH<sub>2</sub>-), 121.56 (-

CH=), 142.42 (N-C-N), 154.77 (CO<sub>2</sub>)

[C<sub>1</sub>C<sub>4</sub>ImHCH<sub>3</sub>][HCO<sub>3</sub>]:

<sup>1</sup>H-NMR, (400 MHz, DMSO-d<sub>6</sub>)

δ 0.91-0.87 (t, 3H, -CH<sub>3</sub>), 1.32-1.23 (m, 2H, -CH<sub>2</sub>-), 1.72-1.64 (m, 2H, -CH<sub>2</sub>-), 2.60 (s, 3H, N-C(CH<sub>3</sub>)-N), 3.77 (s, 3H, N-CH<sub>3</sub>), 4.14-4.11 (t, 2H, N-CH<sub>2</sub>-), 7.68 (d, 1H, -CH=C-), 7.70 (d, 1H, -C=CH-)

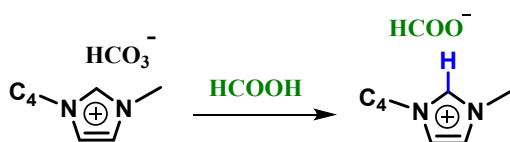
C<sub>1</sub>C<sub>4</sub>ImCH<sub>3</sub>-CO<sub>2</sub>: Not exist

<sup>13</sup>C-NMR, (100 MHz, DMSO-d<sub>6</sub>)

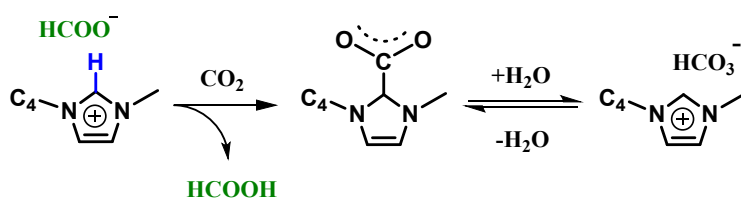
δ 9.72 (-CH<sub>3</sub>), 13.88 (-CH<sub>2</sub>-), 19.33 (-CH<sub>2</sub>-), 31.67 (-CH<sub>3</sub>), 35.17 (N-CH<sub>3</sub>), 47.74 (N-CH<sub>2</sub>-), 121.34 (-CH=), 122.77 (=CH-), 144.63 (N-C-N), 155.68 (HCO<sub>3</sub><sup>-</sup>)

C<sub>1</sub>C<sub>4</sub>ImCH<sub>3</sub>-CO<sub>2</sub>: Not exist

#### 4. Process for the transformation between [C<sub>1</sub>C<sub>4</sub>Im][HCO<sub>3</sub>] and [C<sub>1</sub>C<sub>4</sub>Im][HCOO]

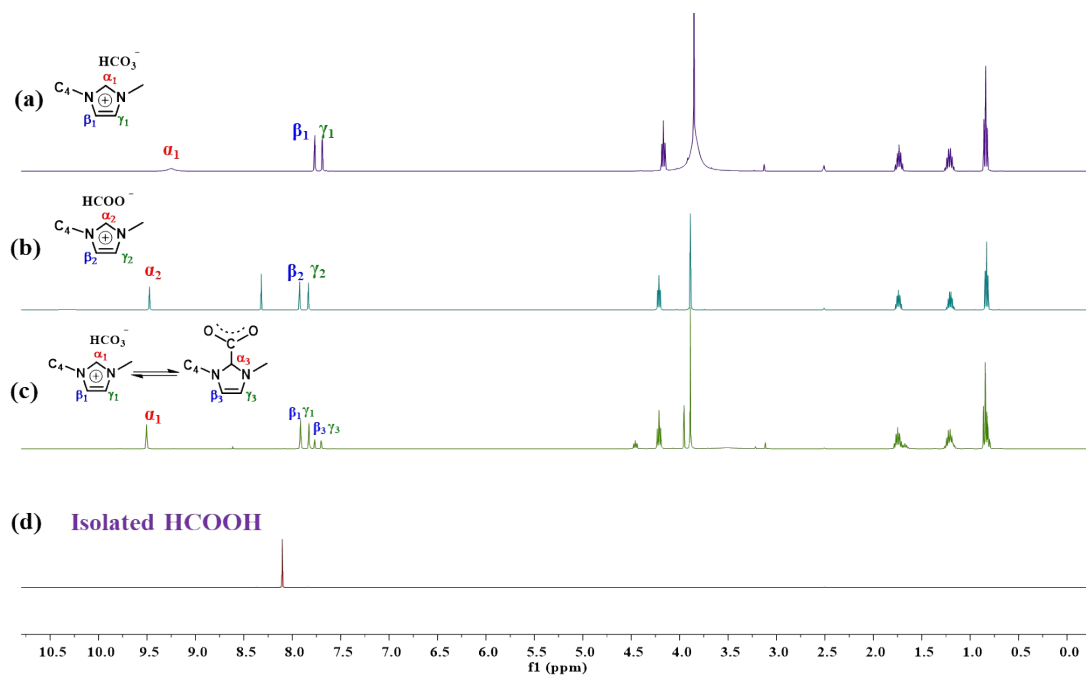


5g [C<sub>1</sub>C<sub>4</sub>ImH][HCO<sub>3</sub>] was putted into a 100mL round bottom flask. Then, 1.1 equiv formic acid was added, and a large number of bubbles were released. After full stirring for 10 minutes, the generated water and excess formic acid were vacuumed out at 60°C under vacuum to obtain a colorless transparent liquid [C<sub>1</sub>C<sub>4</sub>ImH][HCOO] (yield 92%).

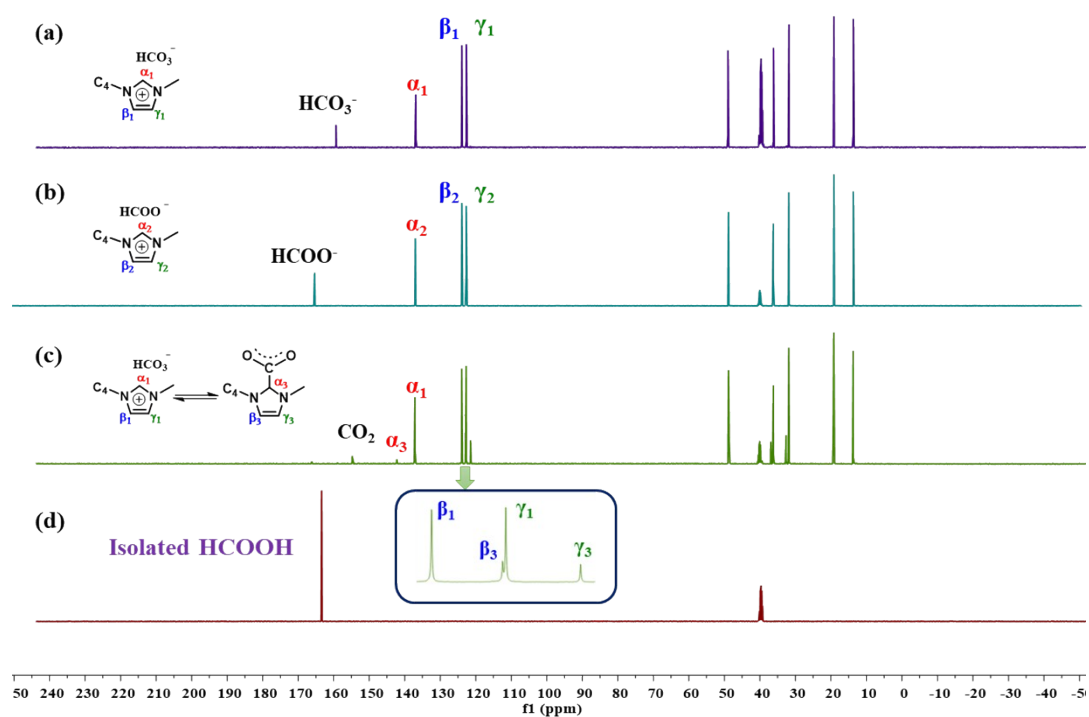


At room temperature, 2g [C<sub>1</sub>C<sub>4</sub>ImH][HCOO] and 5 mL H<sub>2</sub>O were added into a 50ml high-pressure reaction kettle, and 3MPa carbon dioxide was filled. The mixture was stirred at 120°C for 12h. During this process, CO<sub>2</sub> was released and reloaded every

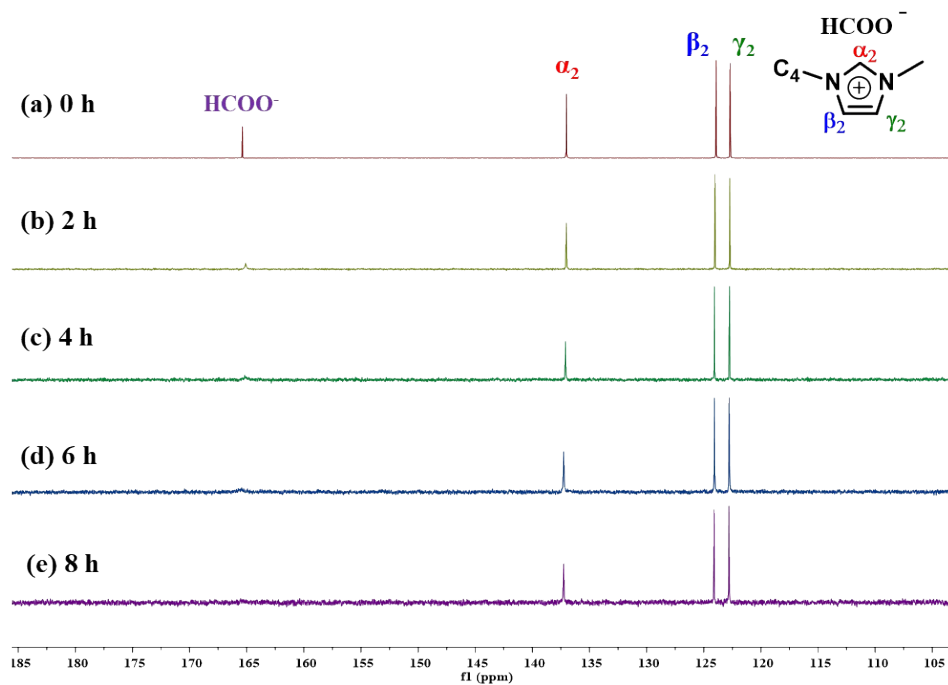
2 hours to replace HCOOH. At the same time, the released CO<sub>2</sub> was collected with a cold trap at low temperature, and colorless droplets on the bottle wall was collected and characterized by NMR as pure formic acid. After the reaction, open the reaction kettle and transfer the colorless solution into a 50mL round-bottom flask. The solvent water is removed by vacuum at 70°C. The liquid in the flask appears white precipitation and the solution becomes sticky ([C<sub>1</sub>C<sub>4</sub>ImH][HCO<sub>3</sub>] and NHC-CO<sub>2</sub>).



**Figure S1.** <sup>1</sup>H NMR spectra (in DMSO-d<sub>6</sub>) of the transformation between [C<sub>1</sub>C<sub>4</sub>ImH][HCOO] and [C<sub>1</sub>C<sub>4</sub>ImH][HCO<sub>3</sub>] listed in Figure 2(A).



**Figure S2.**  $^{13}\text{C}$  NMR spectra (in DMSO- $d_6$ ) of the transformation between  $[\text{C}_1\text{C}_4\text{ImH}][\text{HCOO}^-]$  and  $[\text{C}_1\text{C}_4\text{ImH}][\text{HCO}_3^-]$  listed in Figure 2(A).



**Figure S3.**  $^{13}\text{C}$  NMR of the amount of  $\text{HCOO}^-$  during  $\text{HCOOH}$  release, in DMSO- $d_6$ .

## 5. Isolation of formic acid and $[\text{C}_1\text{C}_4\text{ImH}][\text{HCOO}^-]$ decomposition



### 5.1 Isolation of formic acid

At room temperature, 5g [C<sub>1</sub>C<sub>4</sub>ImH][HCOO] and catalyst PNP-Ir (0.01 μmol) [solution of THF (4×10<sup>-4</sup> mol/L)] were added into a 50ml high-pressure reaction kettle, and 3MPa CO<sub>2</sub> was filled. The mixture was stirred at 120°C for 12 h. During this process, vacuum distillation was carried out every 2 h, CO<sub>2</sub> was released and reloaded every 2 h. At the same time, the released CO<sub>2</sub> was collected with a cold trap at low temperature, and colorless droplets (HCOOH) on the bottle wall was collected.

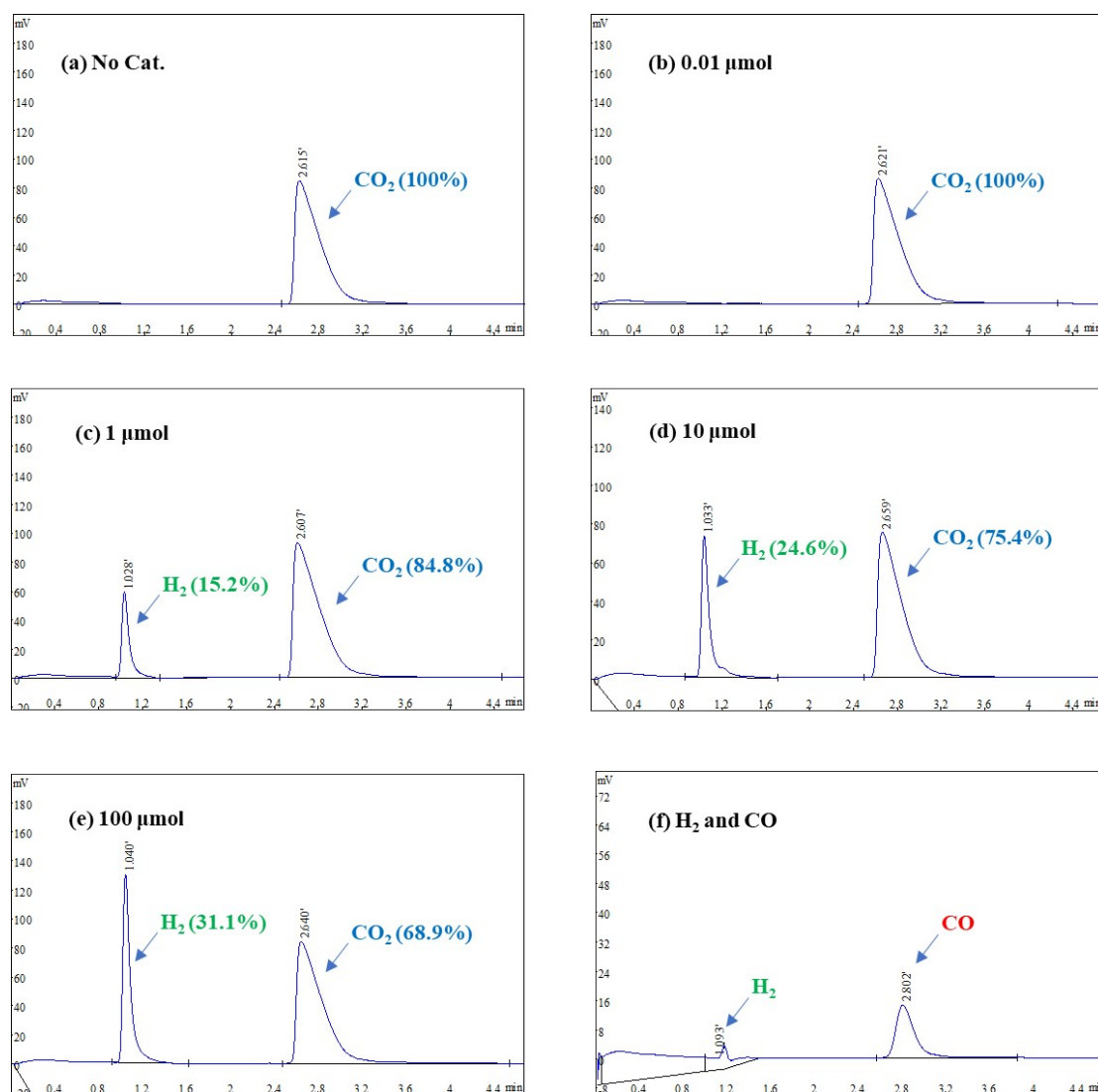
**Table S1.** The Separation yield of formic acid under different conditions.

Entry <sup>[a]</sup>	Cat. (μmol)	Formate	Formate (g)	HCOOH (g)	Yield of HCOOH
1	-	[C <sub>1</sub> C <sub>4</sub> ImH][HCOO]	5.00	1.11	88.5%
2	0.01	[C <sub>1</sub> C <sub>2</sub> ImH][HCOO]	5.01	1.22	82.6%
3	0.01	[C <sub>1</sub> C <sub>4</sub> ImH][HCOO]	5.02	1.07	85.3%
4	0.01	[C <sub>1</sub> C <sub>6</sub> ImH][HCOO]	4.99	0.94	86.8%
5	0.01	[C <sub>1</sub> C <sub>4</sub> ImCH <sub>3</sub> ][HCOO]	2.03	trace	-
6	1	[C <sub>1</sub> C <sub>4</sub> ImH][HCOO]	5.02	0.62	49.6%
7	10	[C <sub>1</sub> C <sub>4</sub> ImH][HCOO]	5.01	0.11	8.8%
8	100	[C <sub>1</sub> C <sub>4</sub> ImH][HCOO]	4.99	trace	-

[a] Standard conditions: Cat: PNP-Ir. Temperature (120 °C). Pressure: 3MPa CO<sub>2</sub>. Reaction time: 12h.

### 5.2 [C<sub>1</sub>C<sub>4</sub>ImH][HCOO] decomposition

At room temperature, 5g [C<sub>1</sub>C<sub>4</sub>ImH][HCOO] and catalyst PNP-Ir was added into a 50ml high-pressure reaction kettle, and 3MPa CO<sub>2</sub> was filled. The mixture was stirred at 120°C for 12 h. After the reaction, a small amount of gas was collected for GC analysis with TCD detector.



**Figure S4.** The GC chromatogram of  $[C_1C_4ImH][HCOO]$  decomposition with (a) 0  $\mu\text{mol}$  catalyst, (b) 0.01  $\mu\text{mol}$  catalyst, (c) 1  $\mu\text{mol}$  catalyst, (d) 10  $\mu\text{mol}$  catalyst, and (e) 100  $\mu\text{mol}$  catalyst. (f) The GC chromatogram of H<sub>2</sub> and CO mixture.

## 6. Typical procedure for the hydrogenation of CO<sub>2</sub> with H<sub>2</sub>

The catalyst PNP-Ir (0.01 or 0.001  $\mu\text{mol}$ ) [solution of THF ( $4 \times 10^{-4}$  mol/L or  $4 \times 10^{-5}$  mol/L)], 5 mL H<sub>2</sub>O and 5 mmol base were added into the 50 mL high pressure reaction kettle. Then, 20 bar CO<sub>2</sub> and 50 bar H<sub>2</sub> were introduced at room temperature and reacted at 120°C for 12 or 24 h. After the reaction, the reactor was cooled to room temperature and the pressure was vented laxly. 0.2 g isopropanol was added into the reaction kettle as internal standard, and 100  $\mu\text{L}$  reaction solution was taken out and

mixed with 400 $\mu$ L D<sub>2</sub>O for <sup>1</sup>H NMR analysis to determine the amount of formate.

**Table S2.** Supplementary data for hydrogenation of CO<sub>2</sub> to formic acid under different conditions.

Entry <sup>[a]</sup>	Cat. ( $\mu$ mol)	Base	Base (mmol)	TON	Utilization of base
1 <sup>[b]</sup>	0.01	[C <sub>1</sub> C <sub>4</sub> Im][HCO <sub>3</sub> ]	5	972	0.19%
2	0.01	[C <sub>1</sub> C <sub>2</sub> Im][HCO <sub>3</sub> ]	5	20466	4.09%
3	0.001	[C <sub>1</sub> C <sub>2</sub> Im][HCO <sub>3</sub> ]	5	56019	1.12%
4	0.01	[C <sub>1</sub> C <sub>6</sub> Im][HCO <sub>3</sub> ]	5	22803	4.56%
5	0.001	[C <sub>1</sub> C <sub>6</sub> Im][HCO <sub>3</sub> ]	5	113047	2.26%
6	0.01	[C <sub>4</sub> C <sub>4</sub> Im][HCO <sub>3</sub> ]	5	16903	3.38%
7	0.001	[C <sub>4</sub> C <sub>4</sub> Im][HCO <sub>3</sub> ]	5	69371	1.39%
8	0.01	[C <sub>1</sub> C <sub>4</sub> ImCH <sub>3</sub> ][HCO <sub>3</sub> ]	5	31372	6.27%
9	0.001	[C <sub>1</sub> C <sub>4</sub> ImCH <sub>3</sub> ][HCO <sub>3</sub> ]	5	65867	1.32%
10 <sup>[c]</sup>	0.01	TMG	5	23694	4.68%
11 <sup>[c]</sup>	0.01	DBN	5	41276	8.36%
12	0.01	NaOH	5	20681	4.15%
13	0.01	KOH	5	32469	6.46%

[a] Standard conditions: Cat: PNP-Ir. Solvent (5mL). Temperature (120 °C). CO<sub>2</sub>:H<sub>2</sub> (bar) (20:50). The amount of formate and TON was determined by <sup>1</sup>H NMR with isopropanol as the internal standard. Reaction time (12h); [b] Solvent(5mL THF); [c] TMG: 1,1,3,3-Tetramethylguanidine; DBN: 1,5-Diazabicyclo[4.3.0]non-5-ene.

**Base and catalyst recycling experiment in Figure 6:** The catalyst PNP-Ir (0.01 $\mu$ mol), 5 mL water and 0.5 mmol base [R<sub>1</sub>R<sub>2</sub>ImR<sub>3</sub>][HCO<sub>3</sub>] were added into the 50 mL high pressure reaction kettle. CO<sub>2</sub> of 20 bar and H<sub>2</sub> of 50 bar were then filled at room temperature and reacted at 120°C for 12h. After the reaction, the reactor was cooled to room temperature and the pressure was vented laxly. 100  $\mu$ L reaction solution in 400  $\mu$ L D<sub>2</sub>O, 15mg isopropyl alcohol as internal standard for <sup>1</sup>H NMR analysis to determine the content of formate. 30 bar of CO<sub>2</sub> was then filled and stirred at 120°C for

another 12 hours. During this process, CO<sub>2</sub> was released and reloaded every 2 hours to replace HCOOH. The catalyst was remained in the solution throughout the regeneration of base. No additional treatment is needed for the reusing of catalyst. The above NMR quantitative operation was repeated and the conversion rates of formate and TON were calculated.

**Table S3.** Cyclic experiments of [C<sub>1</sub>C<sub>4</sub>ImH][HCO<sub>3</sub>] on hydrogenation of CO<sub>2</sub>

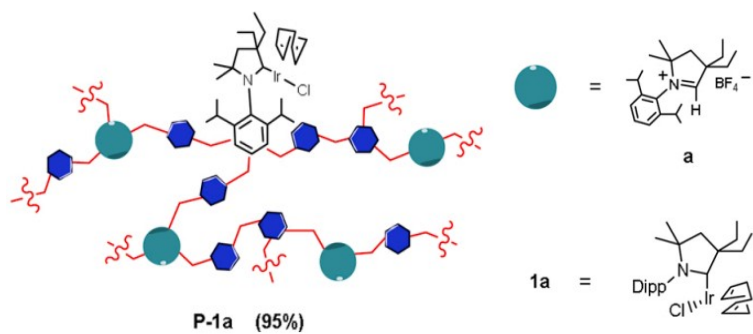
Runs	Base(mol)	Total amount of HCOO <sup>-</sup> (mmol)	Rest amount of HCOO <sup>-</sup> (mmol)	Conv.( HCOO <sup>-</sup> )	TON
1	0.5	0.218	-	-	21795
2	0.5	0.243	0.038	84.36%	20504
3	0.5	0.219	0.024	89.04%	19472
4	0.5	0.214	0.023	89.25%	19131
5	0.5	0.207	0.014	93.24%	19289

**Table S4. Hydrogenation of CO<sub>2</sub> with P-CAAC-Ir**

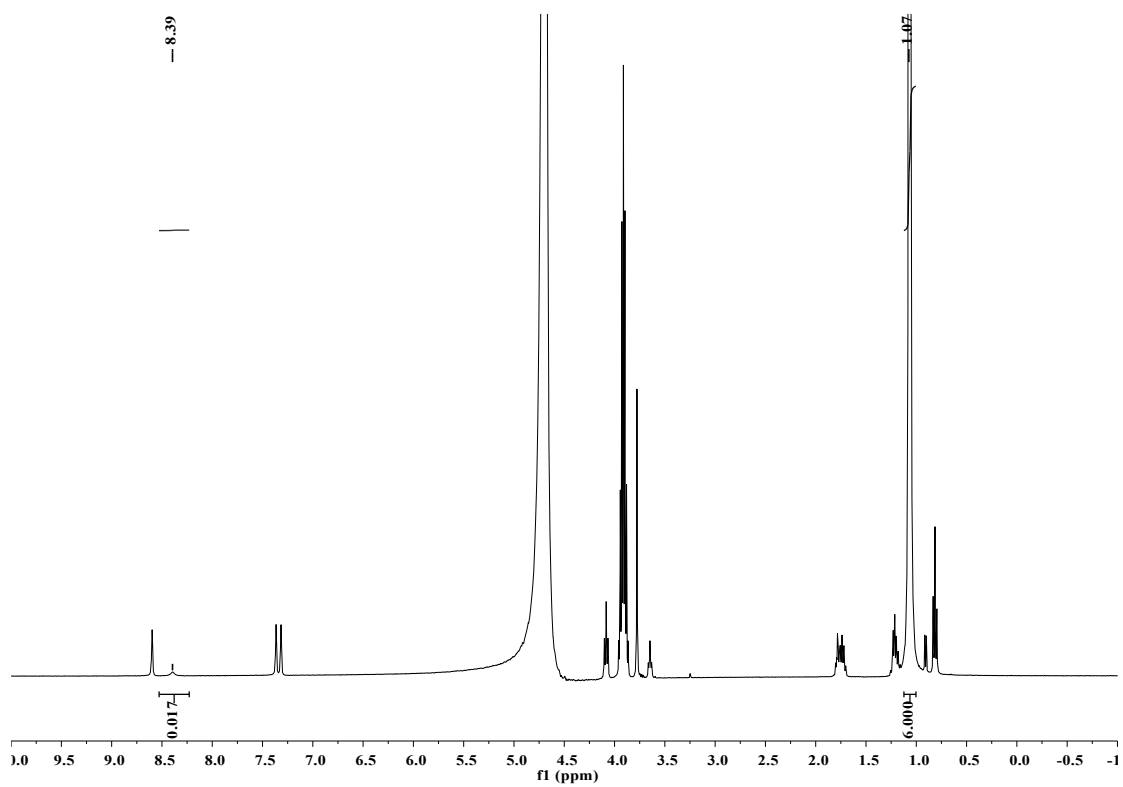
Entry <sup>[a]</sup>	Cat.	Base	Base (mmol)	TON
1	P-CAAC-Ir	[C <sub>1</sub> C <sub>2</sub> Im][HCO <sub>3</sub> ]	5	22597
2	P-CAAC-Ir	[C <sub>1</sub> C <sub>4</sub> Im][HCO <sub>3</sub> ]	5	51378
3	P-CAAC-Ir	[C <sub>1</sub> C <sub>6</sub> Im][HCO <sub>3</sub> ]	5	17348
4	P-CAAC-Ir	[C <sub>4</sub> C <sub>4</sub> Im][HCO <sub>3</sub> ]	5	24865

[a] Standard conditions: Ir content in catalyst is 0.00002 mmol, H<sub>2</sub>/CO<sub>2</sub> = 50/20 bar, solvent 5 mL H<sub>2</sub>O, Temperature (120 °C), 24 h. The amount of formate and TON was determined by <sup>1</sup>H NMR with isopropanol as the internal standard.

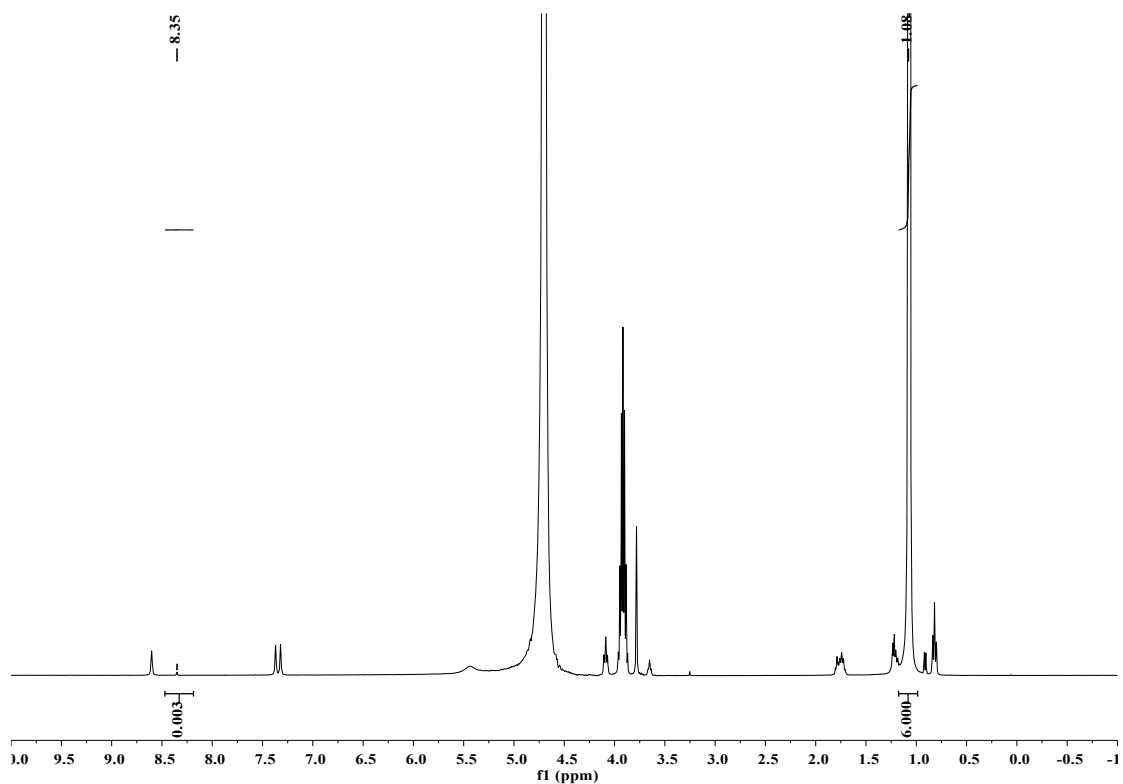
**The structure of P-CAAC-Ir<sup>[SS]</sup>:**



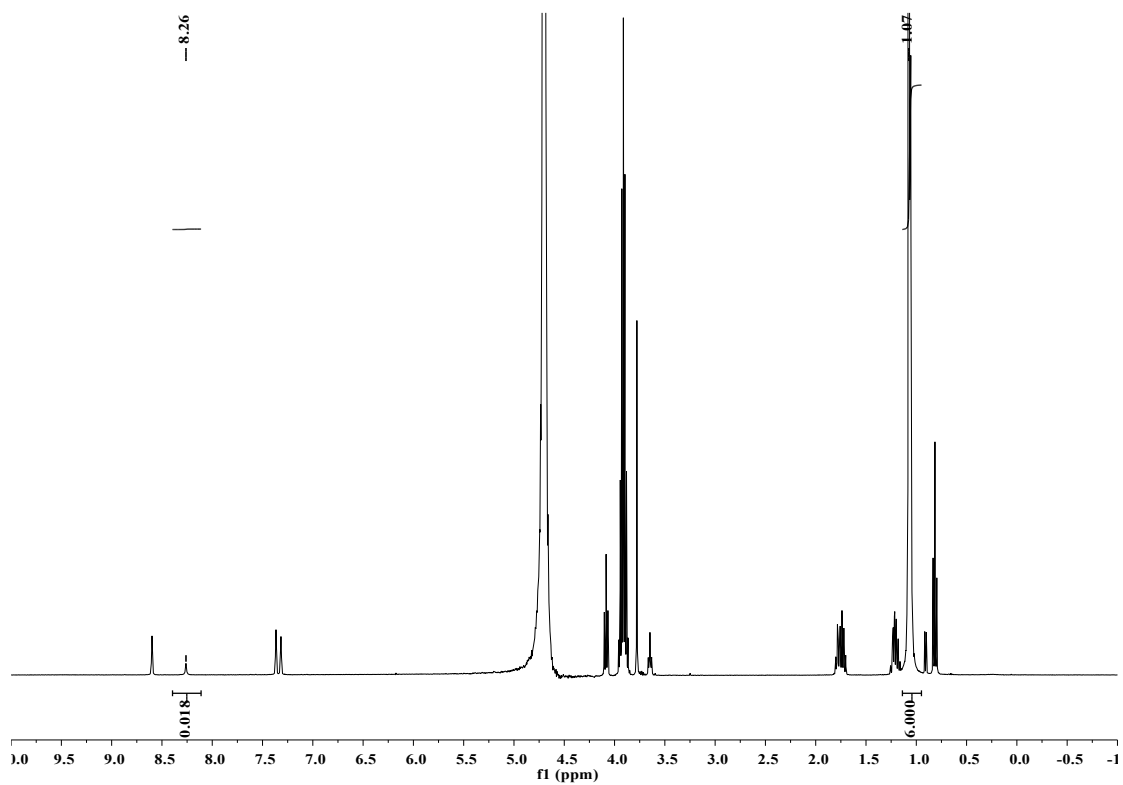
## 7. The NMR spectra of the recycled system experiments



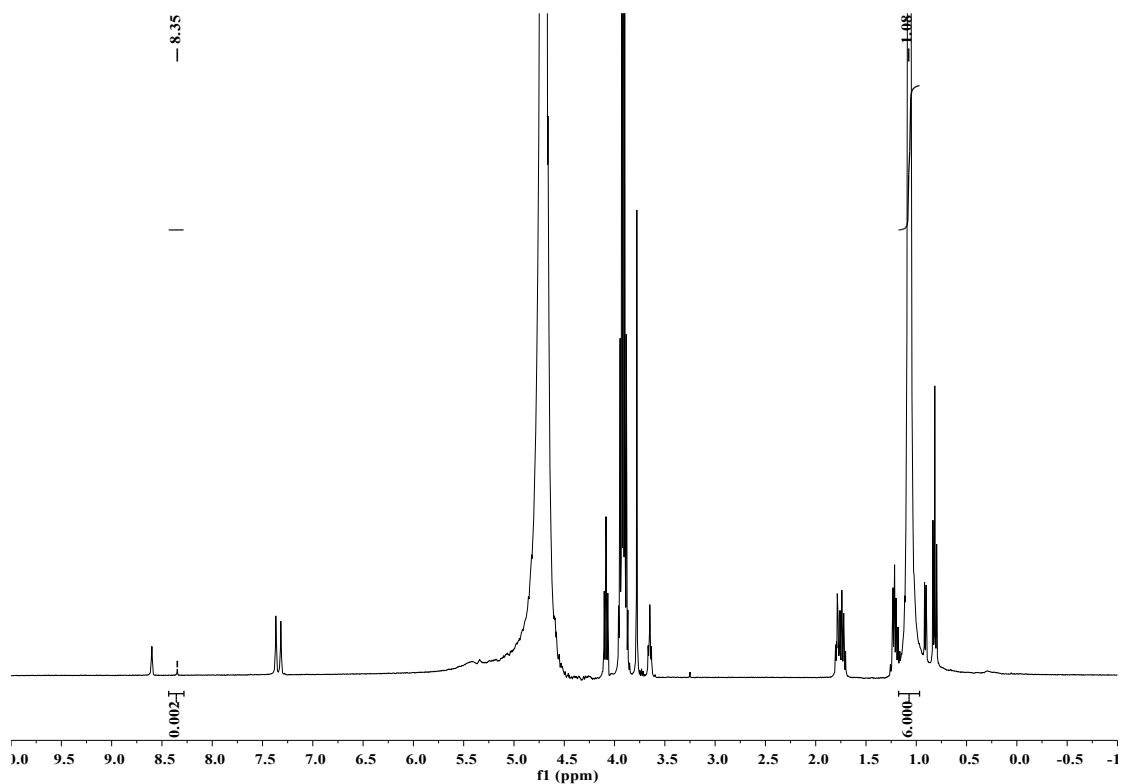
**Figure S5.**  $[C_1C_4ImH][HCO_3]$ : before the first recycle ( $CO_2$  hydrogenation result).



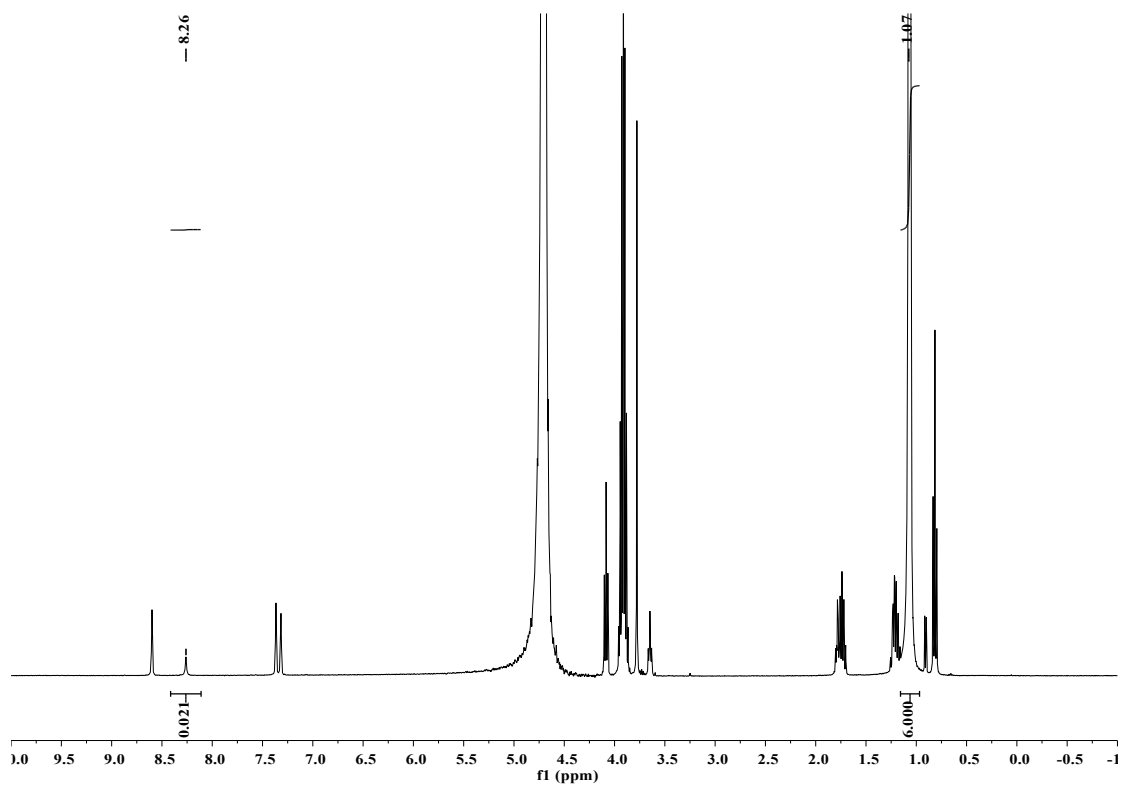
**Figure S6.**  $[\text{C}_1\text{C}_4\text{ImH}][\text{HCO}_3]$ : after the first recycle (base recycled result).



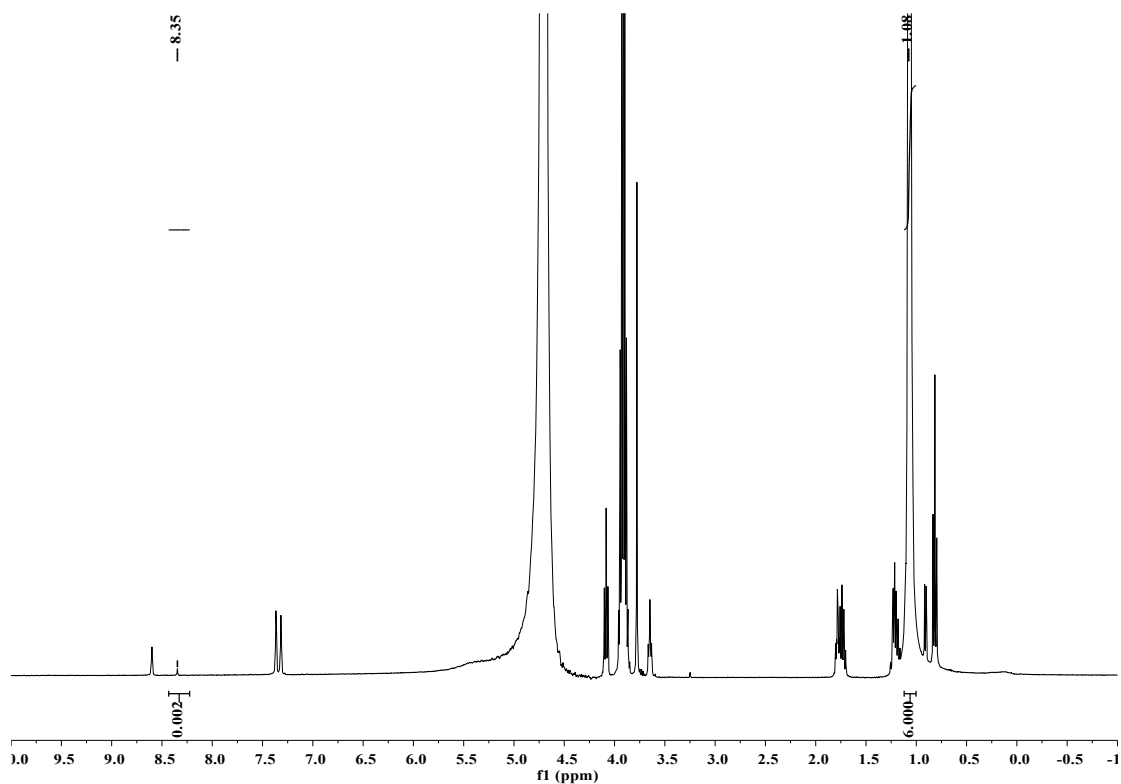
**Figure S7.**  $[\text{C}_1\text{C}_4\text{ImH}][\text{HCO}_3]$ : before the second recycle ( $\text{CO}_2$  hydrogenation result).



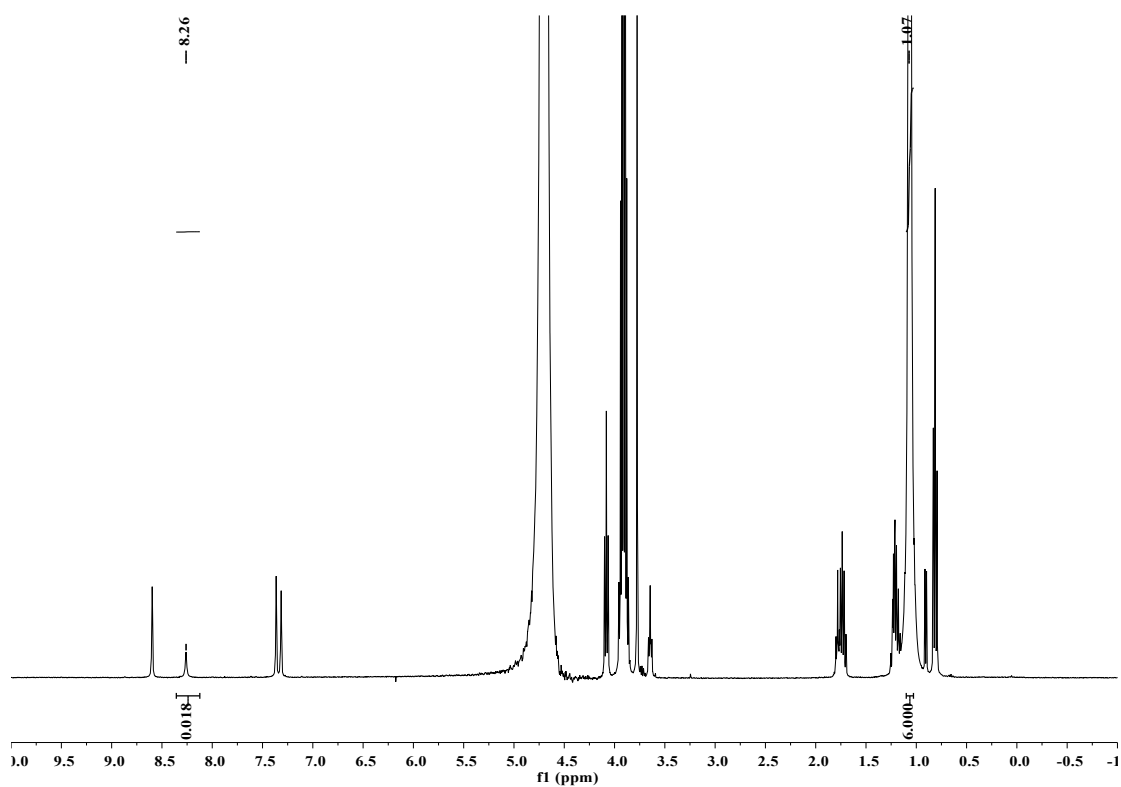
**Figure S8.**  $[\text{C}_1\text{C}_4\text{ImH}][\text{HCO}_3]$ : after the second recycle (base recycled result).



**Figure S9.**  $[\text{C}_1\text{C}_4\text{ImH}][\text{HCO}_3]$ : before the third recycle ( $\text{CO}_2$  hydrogenation result).

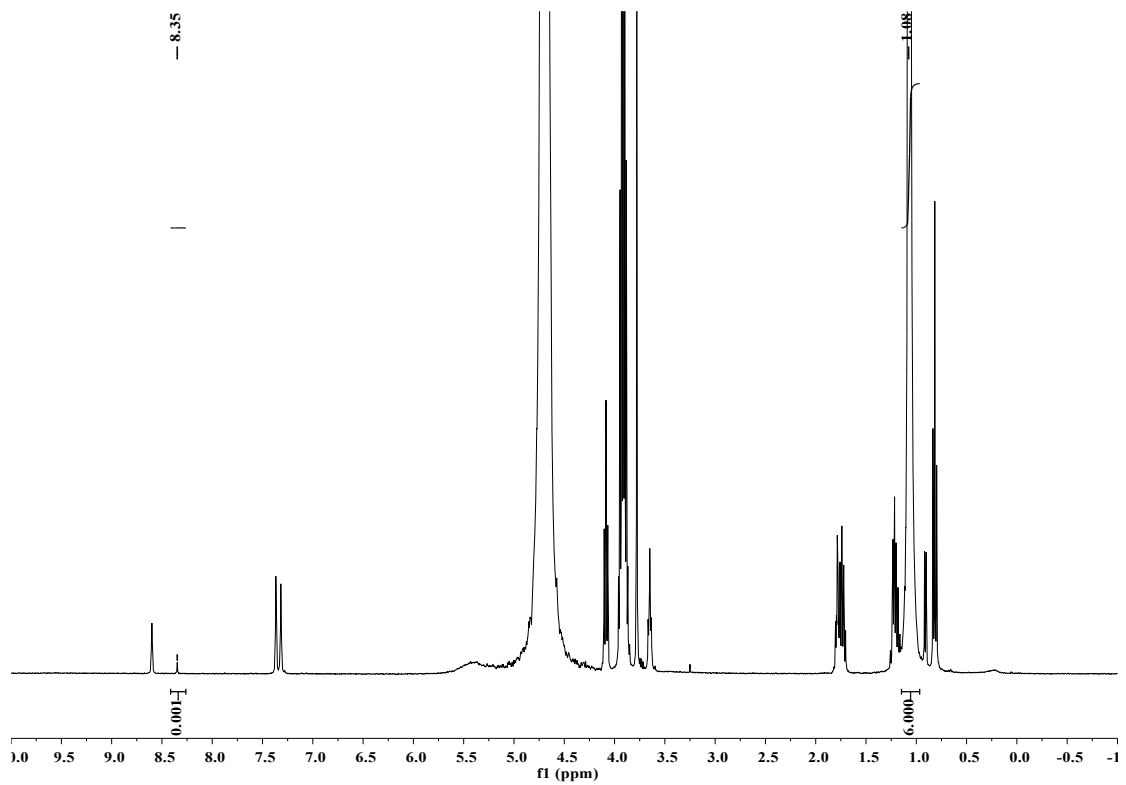


**Figure S10.**  $[\text{C}_1\text{C}_4\text{ImH}][\text{HCO}_3]$ : after the third recycle (base recycled result).

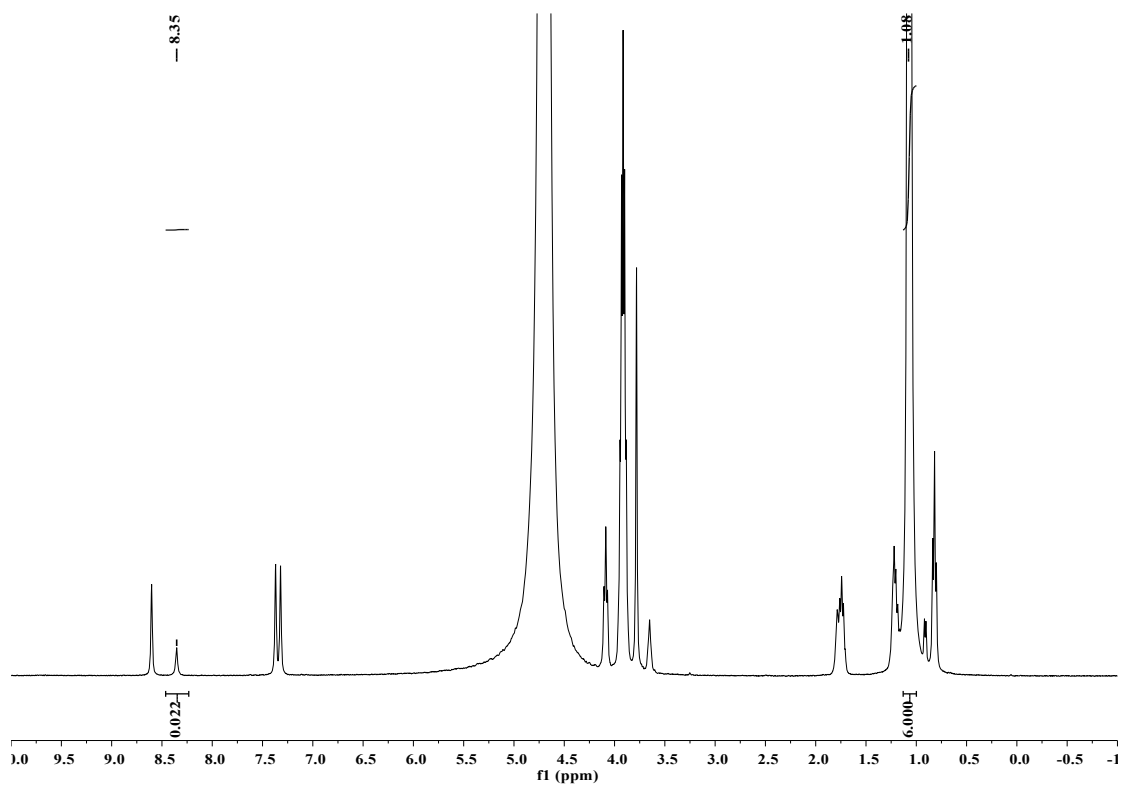


**Figure S11.**  $[\text{C}_1\text{C}_4\text{ImH}][\text{HCO}_3]$ : before the fourth recycle ( $\text{CO}_2$  hydrogenation result).





**Figure S12.**  $[\text{C}_1\text{C}_4\text{ImH}][\text{HCO}_3]$ : after the fourth recycle (base recycled result).



**Figure S13.**  $[\text{C}_1\text{C}_4\text{ImH}][\text{HCO}_3]$ : before the fifth recycle ( $\text{CO}_2$  hydrogenation result).

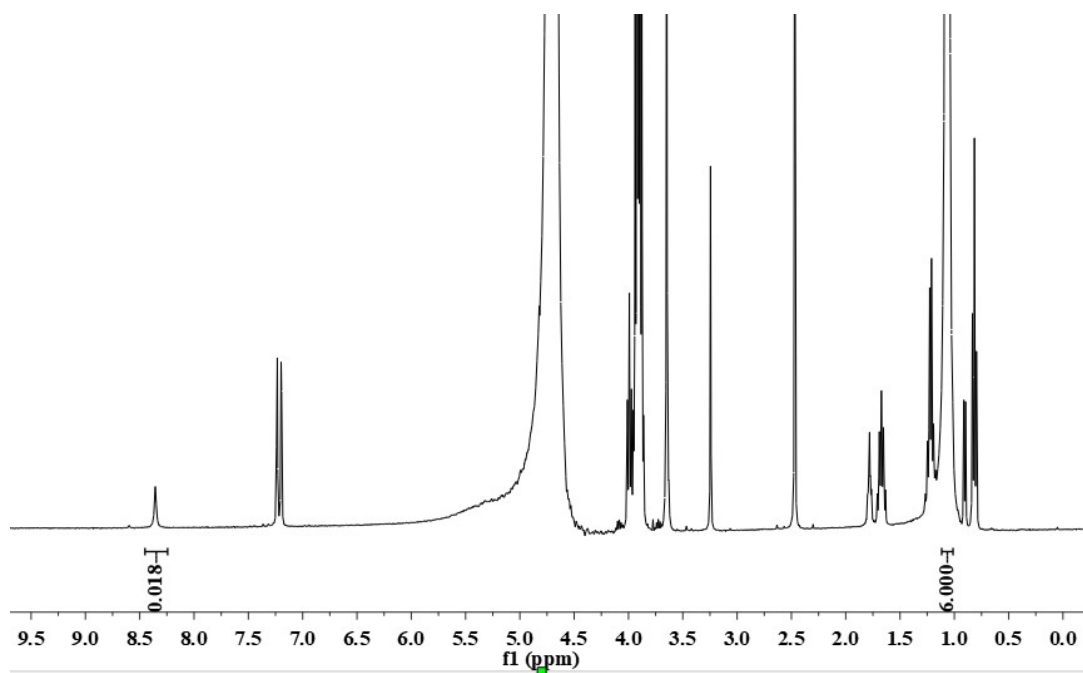


Figure S14.  $[\text{C}_1\text{C}_4\text{ImCH}_3][\text{HCO}_3]$ : before the first recycle ( $\text{CO}_2$  hydrogenation result).

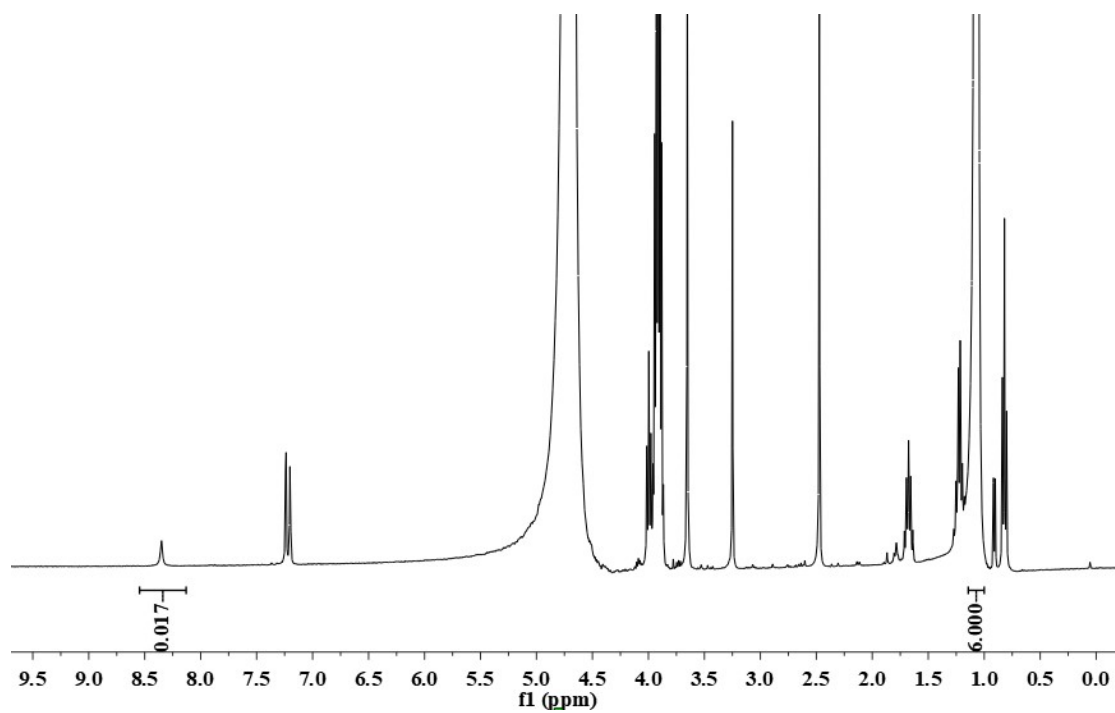
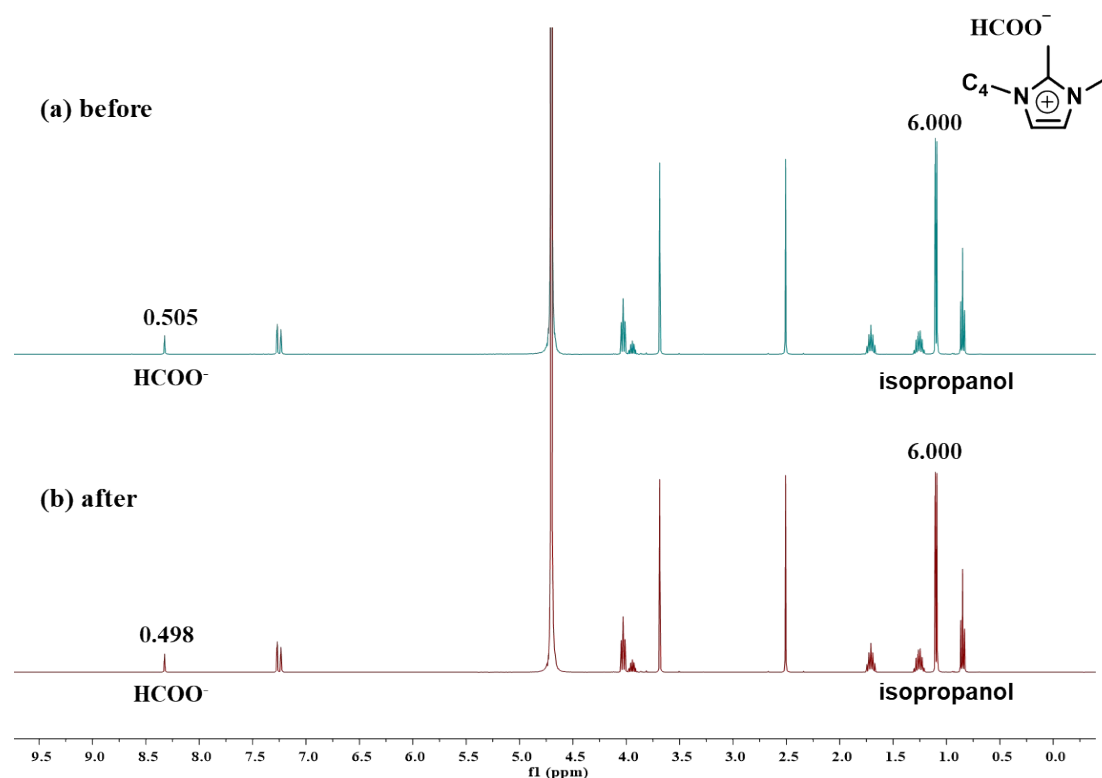


Figure S15.  $[\text{C}_1\text{C}_4\text{ImCH}_3][\text{HCO}_3]$ : after the first recycle (base recycled result).

## 8. Regeneration experiments of other formats

At room temperature, 2 mmol  $[C_1C_4ImCH_3][HCOO]$  and 5 mL  $H_2O$  were added into a 50 ml high-pressure reaction kettle, and 3MPa  $CO_2$  was filled. The reaction was stirred at  $120^\circ C$  for 12 h. During this process,  $CO_2$  was released and reloaded every 2 hours. Then 0.2 g isopropanol was added into the reaction kettle as internal standard, and 100  $\mu L$  reaction solution was mixed with 400  $\mu L$   $D_2O$  for  $^1H$  NMR analysis to determine the amount of formate.

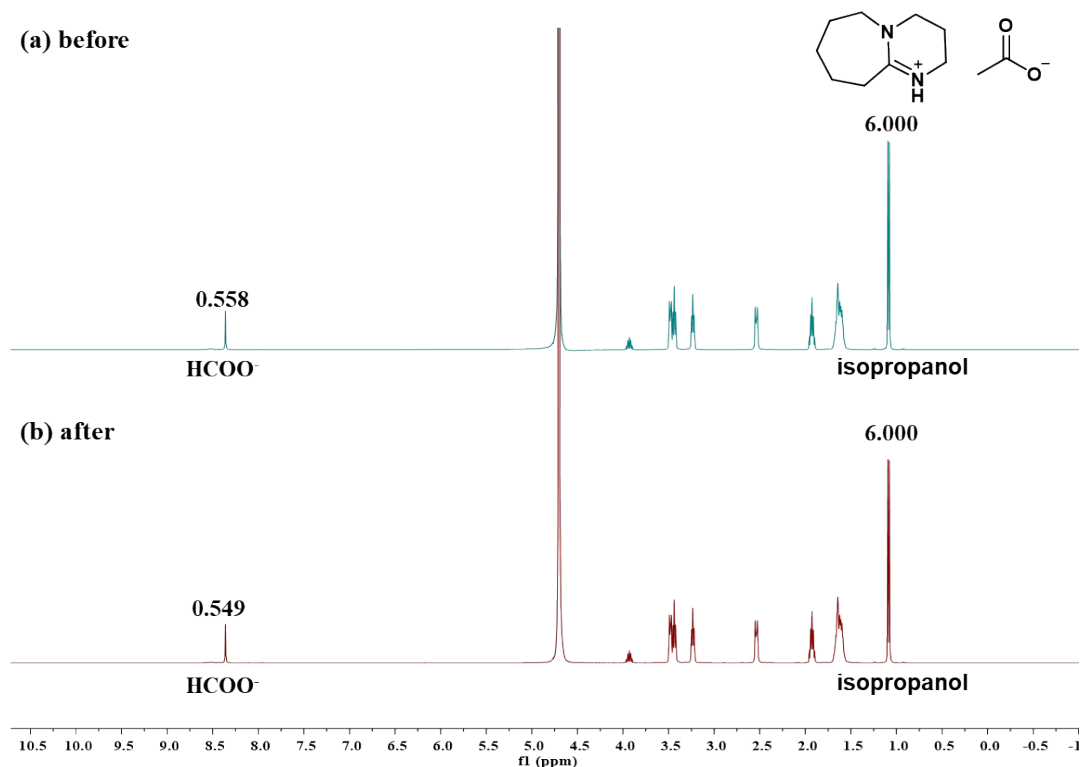
No notable change was observed for the  $^1H$  NMR spectra of  $[C_1C_4ImCH_3][HCOO]$  before and after regeneration (Figure S16).



**Figure S16.**  $^1H$  NMR spectra of  $[C_1C_4ImCH_3][HCOO]$  before and after regeneration, in  $D_2O$ .

At room temperature, 2 mmol  $[DBUH][HCOO]$  and 5 mL  $H_2O$  were added into a 50ml high-pressure reaction kettle, and 3MPa carbon dioxide was filled. The reaction was stirred at  $120^\circ C$  for 12h. During the process of reaction, the pressure relief and charging operation of  $CO_2$  should be carried out in the reaction kettle every 2h. Then 0.2 g isopropanol was added into the reaction kettle as internal standard, and 100 $\mu L$  reaction solution was taken into 400 $\mu L$   $D_2O$  for  $^1H$  NMR analysis to determine the amount of formate.

No notable change was observed for the  $^1\text{H}$  NMR spectra of  $[\text{DBUH}][\text{HCOO}]$  before and after regeneration (Figure S17).



**Figure S17.**  $^1\text{H}$  NMR spectra of  $[\text{DBUH}][\text{HCOO}]$  before and after regeneration, in  $\text{D}_2\text{O}$

At room temperature, 4 mmol  $[\text{TEAH}][\text{HCOO}]$  and 5 mL  $\text{H}_2\text{O}$  were added into a 50ml high-pressure reaction kettle, and 3MPa carbon dioxide was filled. The reaction was stirred at  $120^\circ\text{C}$  for 12h. During the process of reaction, the pressure relief and charging operation of  $\text{CO}_2$  should be carried out in the reaction kettle every 2h. Then 0.2 g isopropanol was added into the reaction kettle as internal standard, and  $100\mu\text{L}$  reaction solution was taken into  $400\mu\text{L}$   $\text{D}_2\text{O}$  for  $^1\text{H}$  NMR analysis to determine the amount of formate.

No notable change was observed for the  $^1\text{H}$  NMR spectra of  $[\text{TEAH}][\text{HCOO}]$  before and after regeneration (Figure S18).

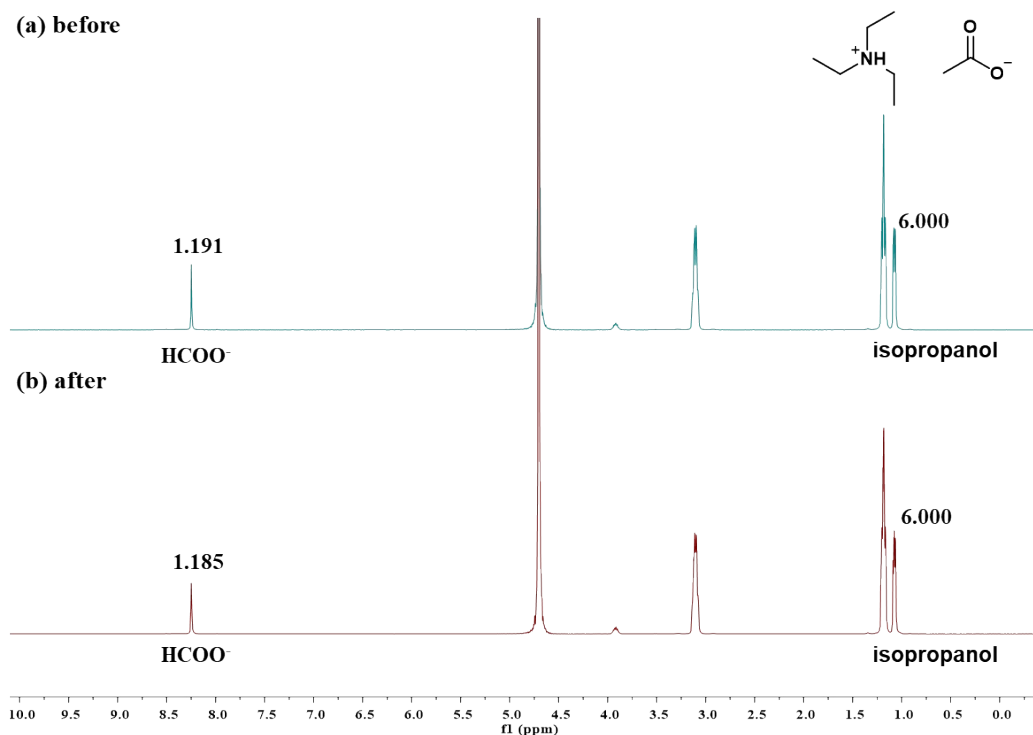
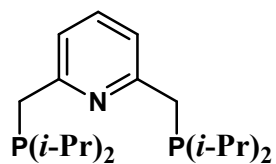
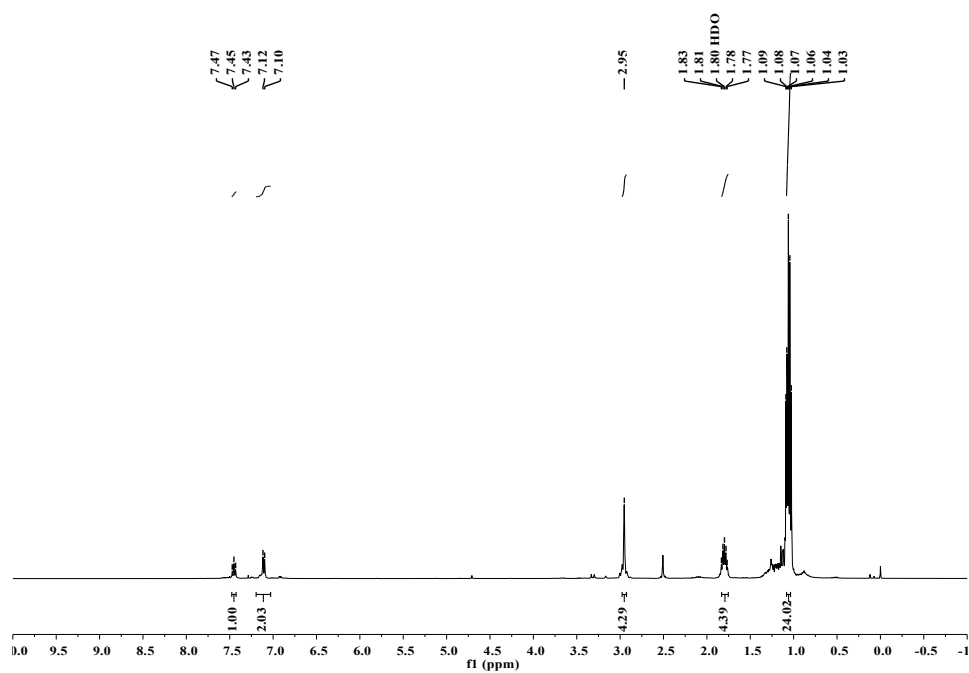


Figure S18. <sup>1</sup>H NMR spectra of [TEAH][HCOO] before and after regeneration, in D<sub>2</sub>O

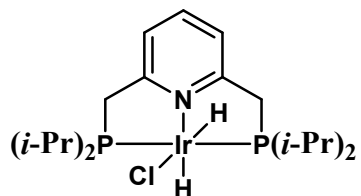
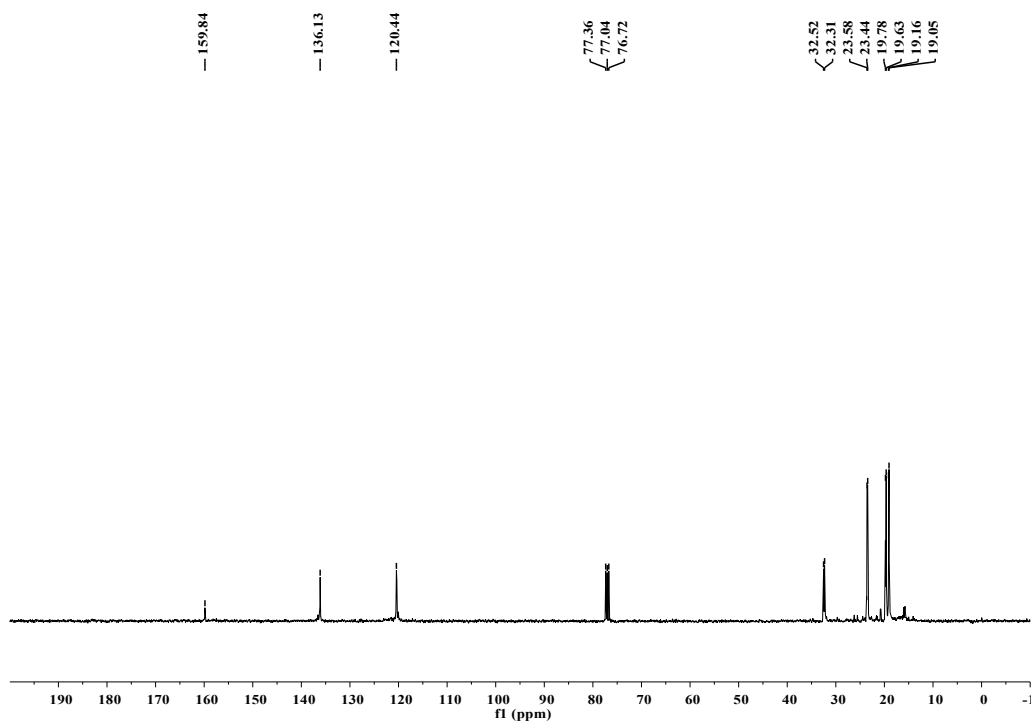
## 9. The original NMR spectra of [R<sub>1</sub>R<sub>2</sub>ImR<sub>3</sub>][HCO<sub>3</sub>] and PNP



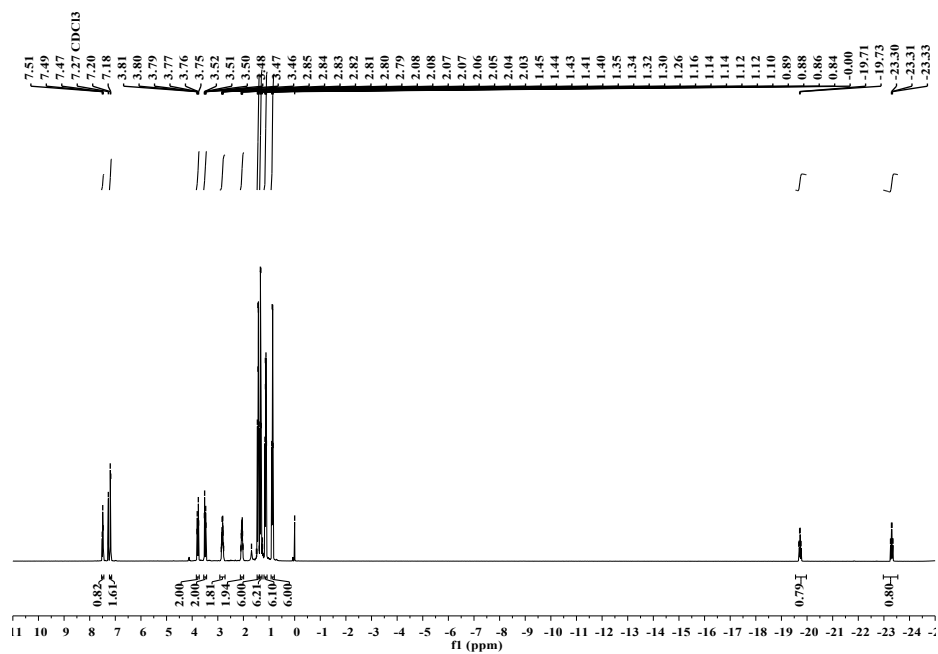
<sup>1</sup>H NMR spectrum



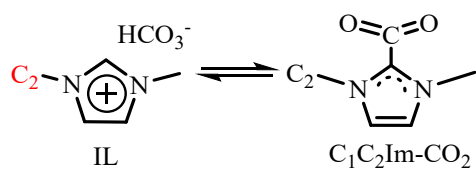
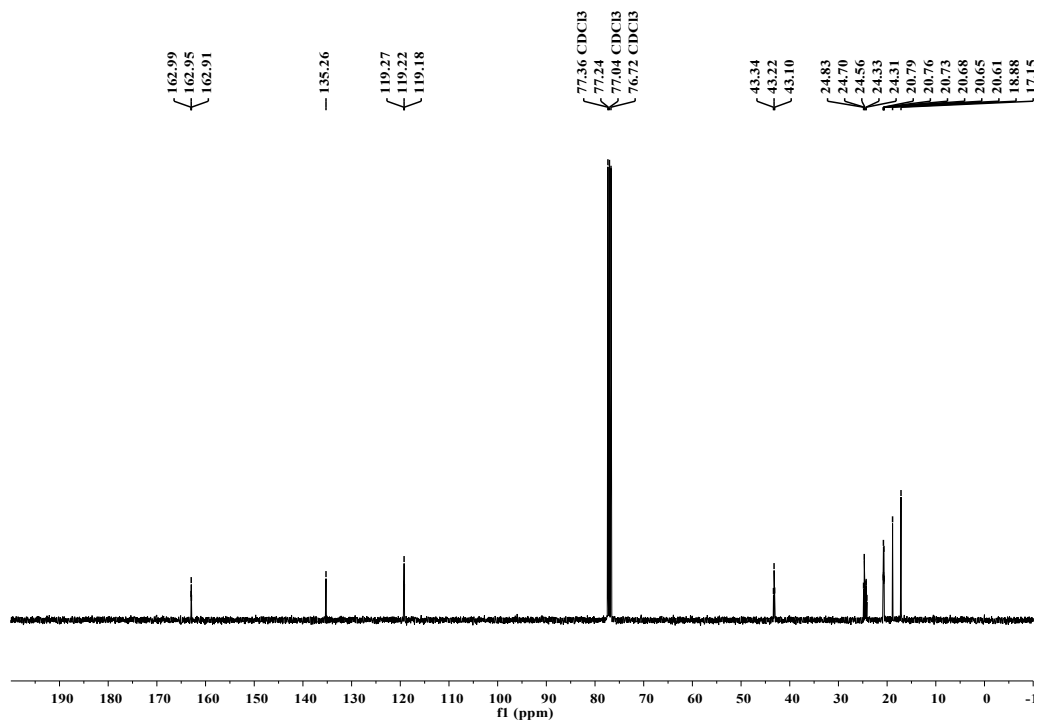
### <sup>13</sup>C NMR spectrum



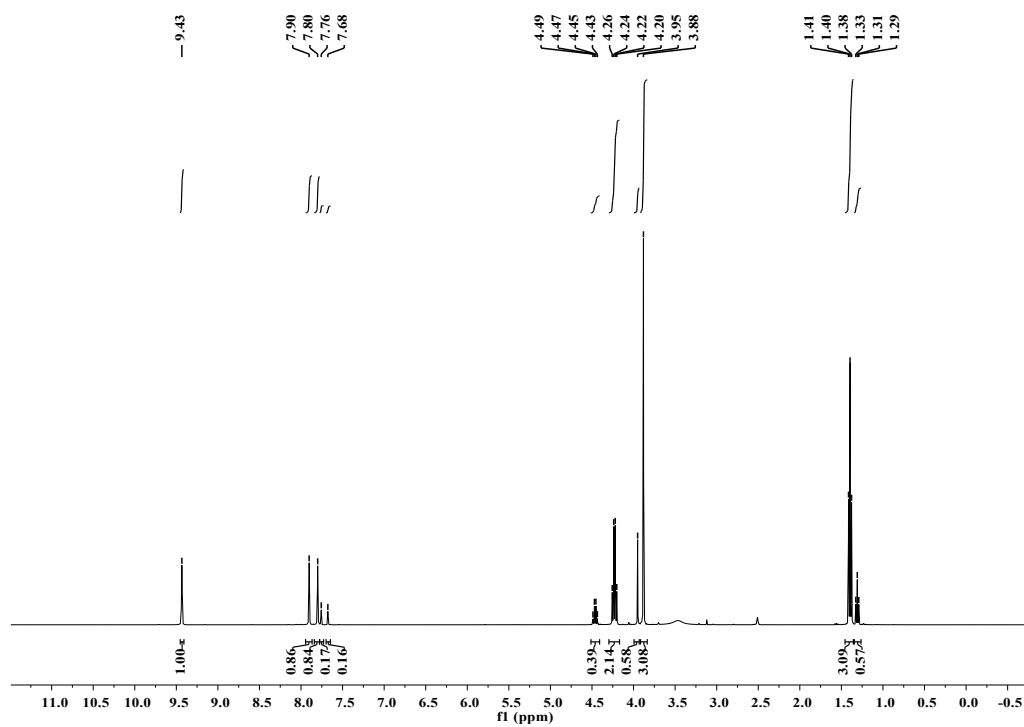
### <sup>1</sup>H NMR spectrum



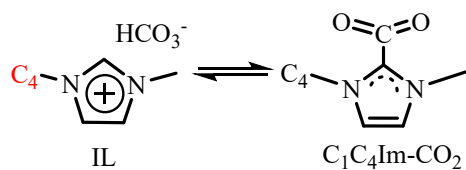
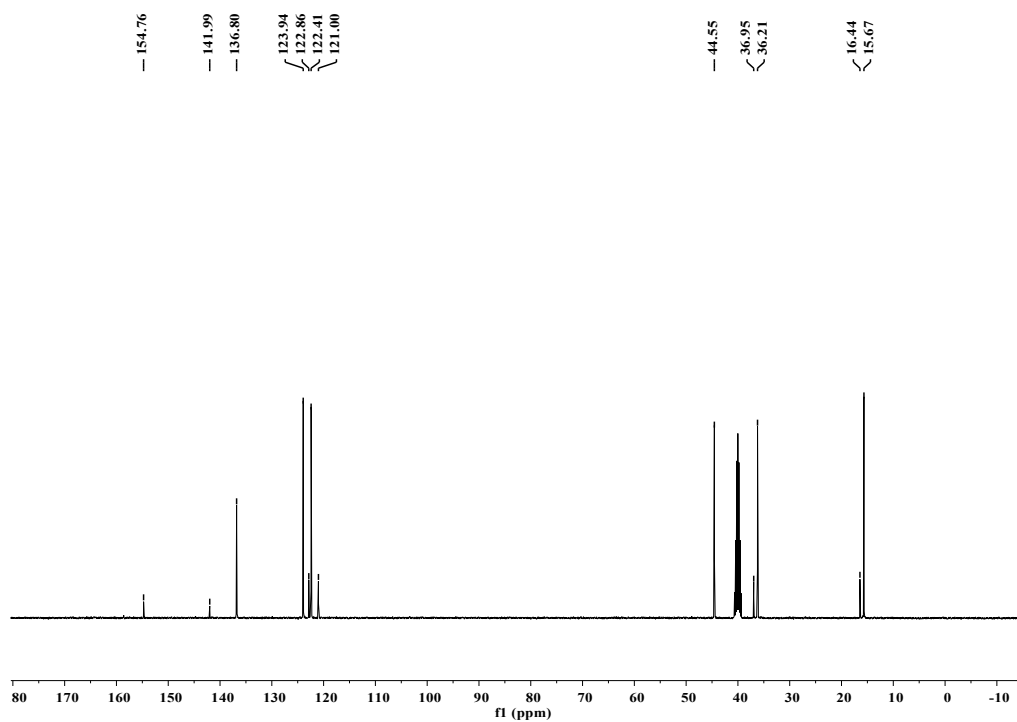
### <sup>13</sup>C NMR spectrum



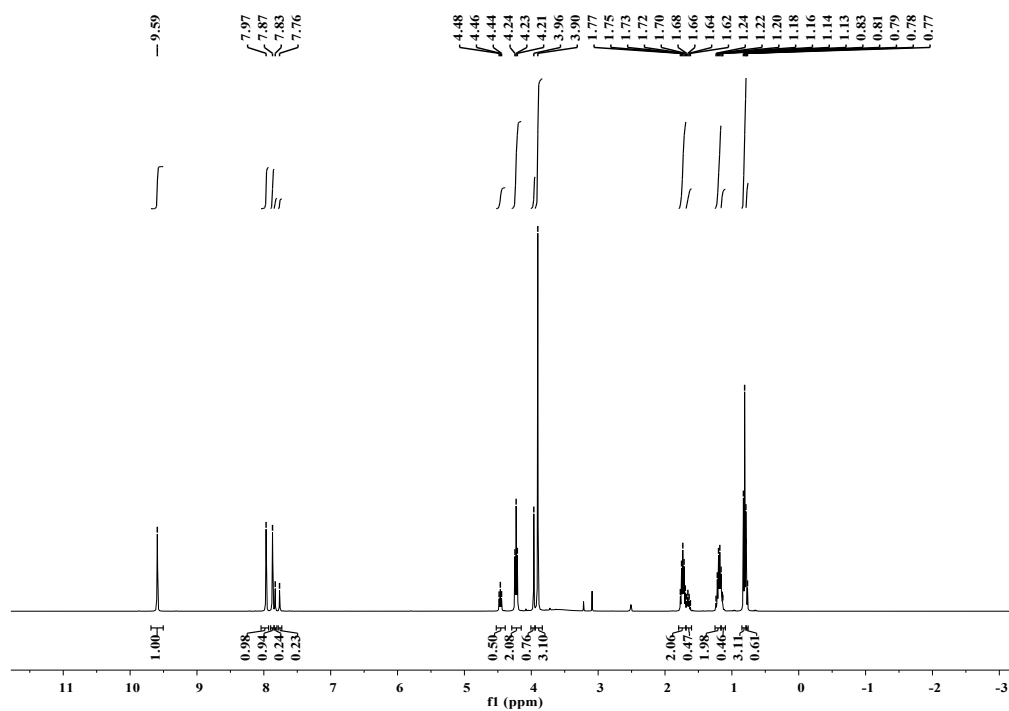
<sup>1</sup>H NMR spectrum (400 MHz, DMSO-d<sub>6</sub>)



**<sup>13</sup>C NMR spectrum (100 MHz, DMSO-d6)**

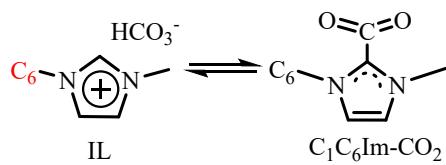
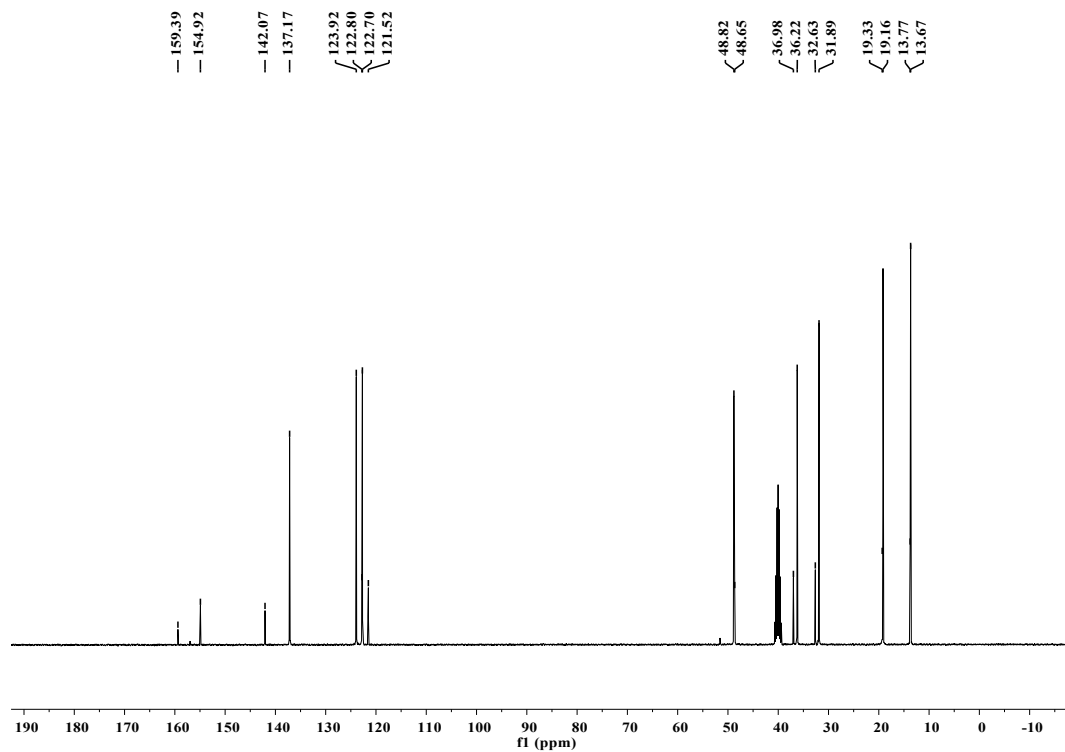


**<sup>1</sup>H NMR spectrum (400 MHz, DMSO-d6)**

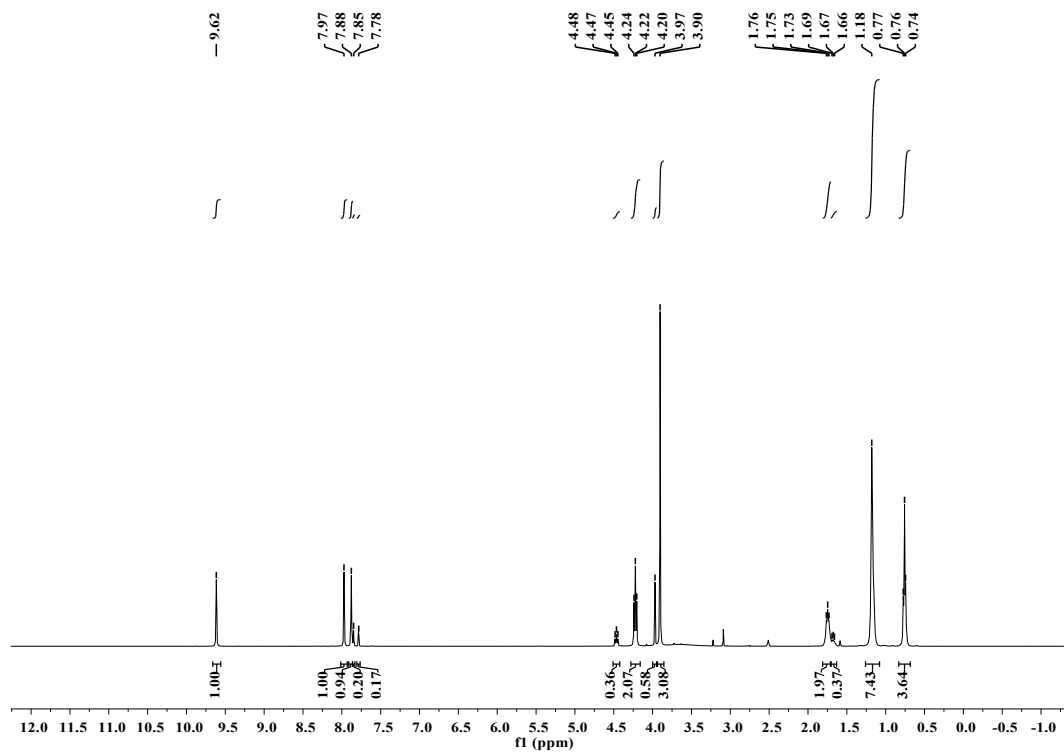


**<sup>13</sup>C NMR spectrum (100 MHz, DMSO-d6)**

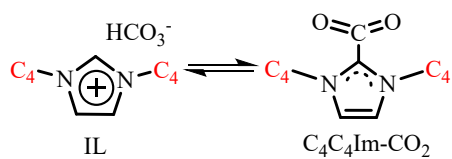
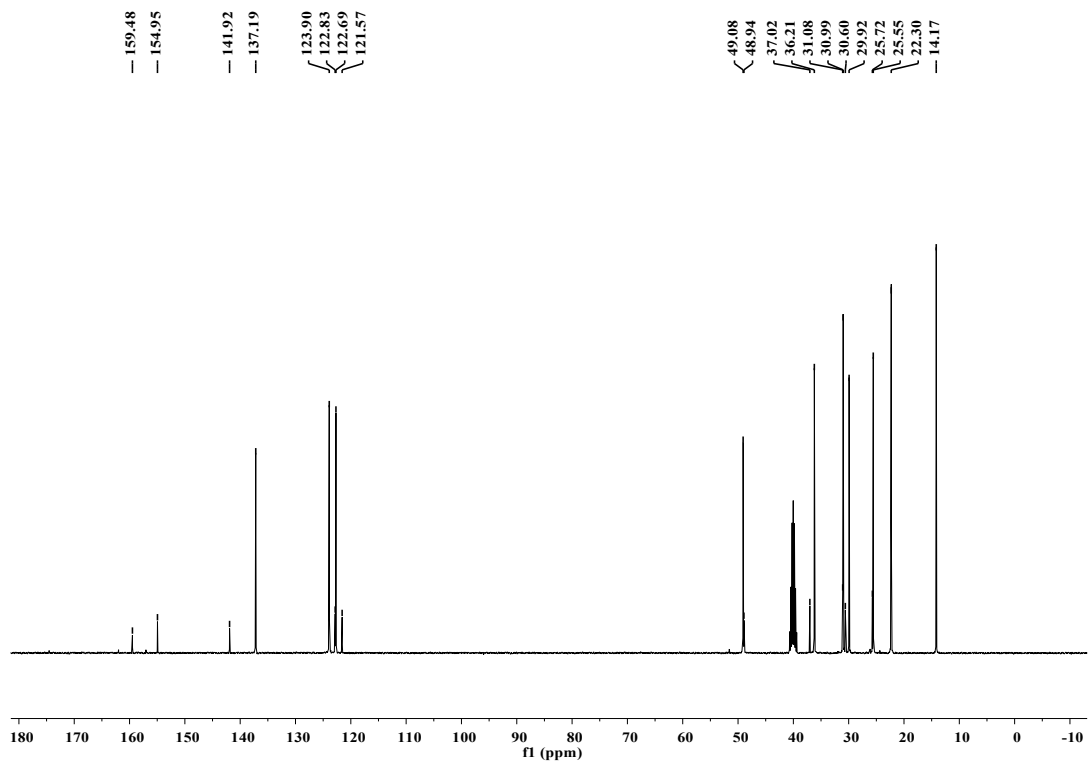




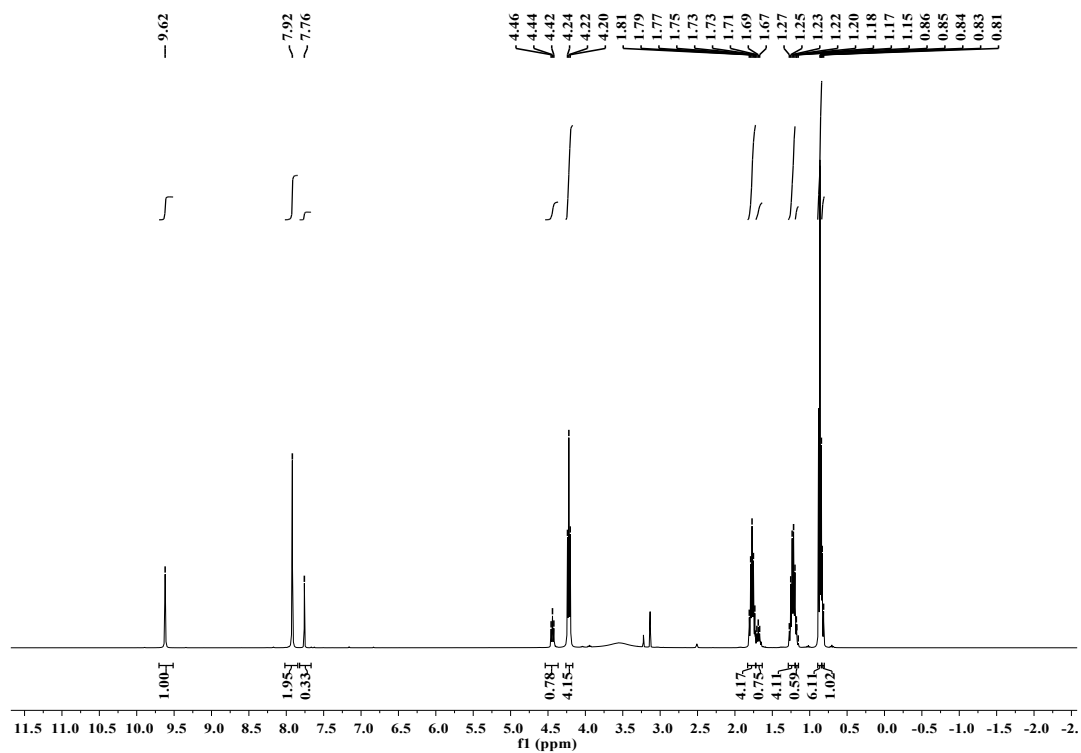
**$^1\text{H}$  NMR spectrum (400 MHz, DMSO-d<sub>6</sub>)**



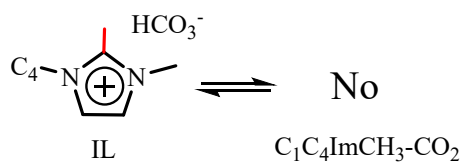
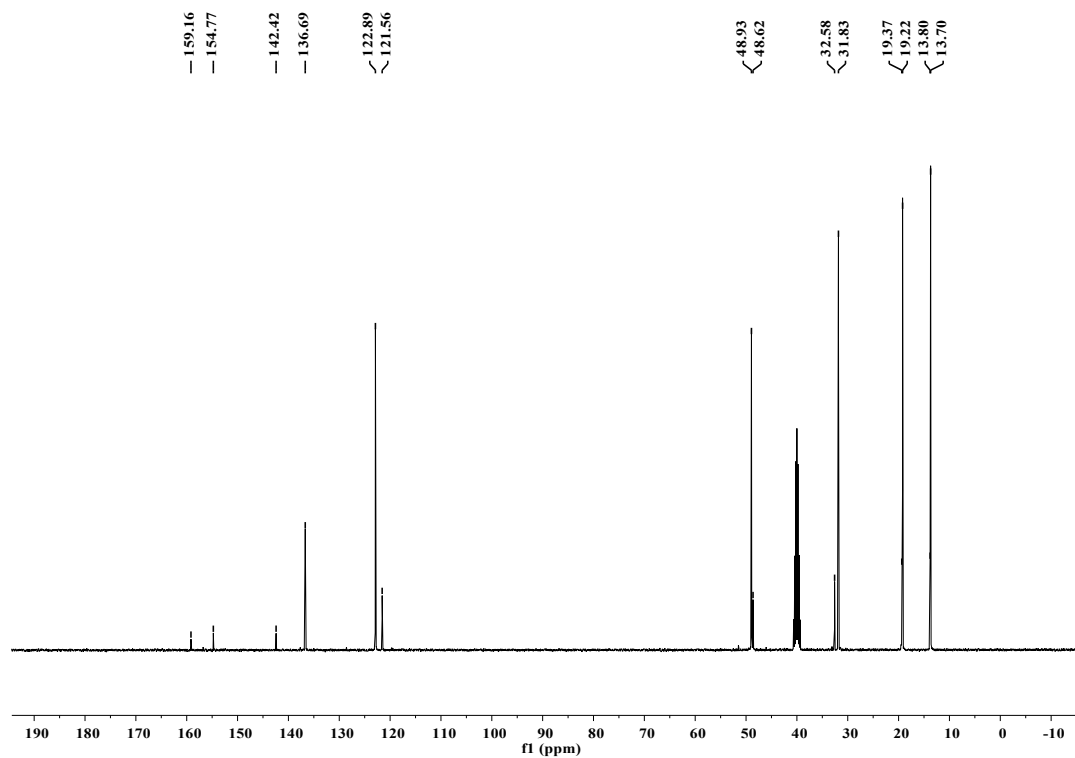
**$^{13}\text{C}$  NMR spectrum (100 MHz, DMSO-d<sub>6</sub>)**



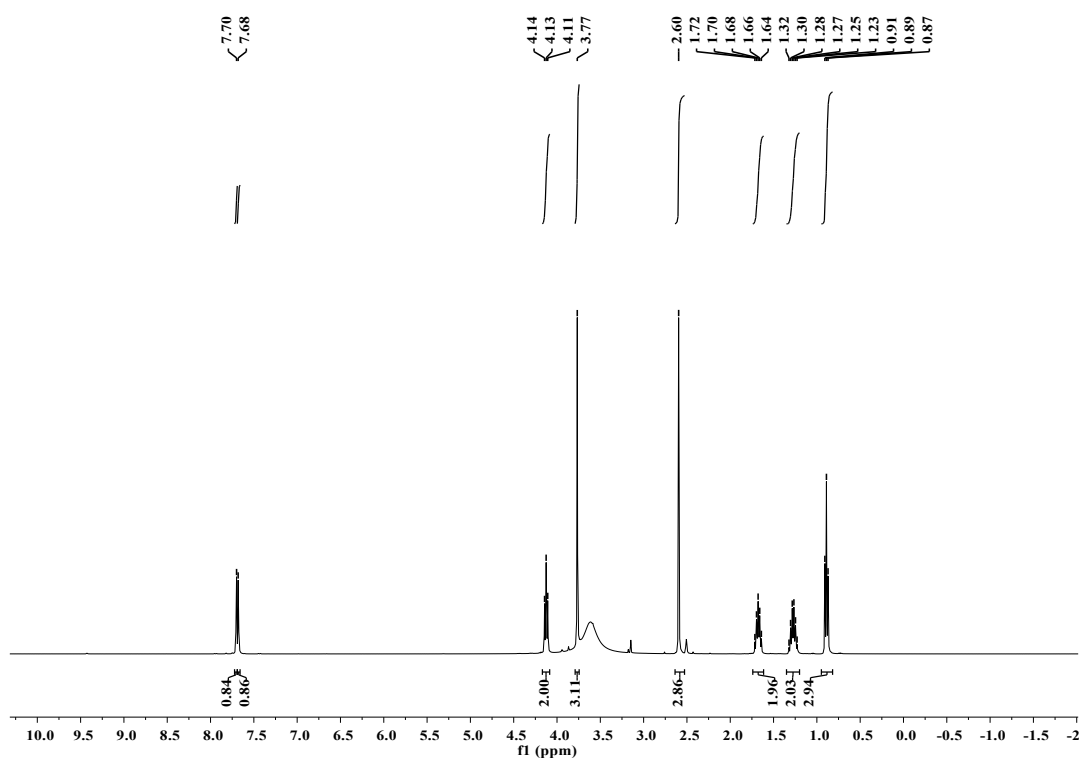
**<sup>1</sup>H NMR spectrum (400 MHz, DMSO-d<sub>6</sub>)**



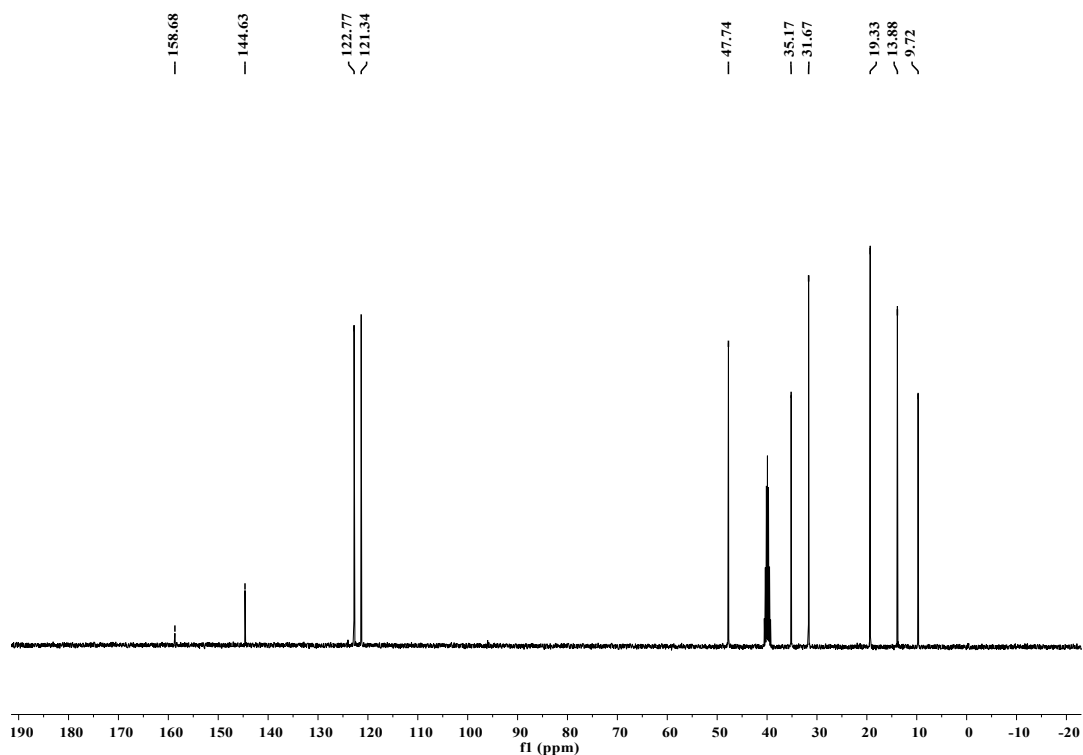
**<sup>13</sup>C NMR spectrum (100 MHz, DMSO-d6)**



**<sup>1</sup>H NMR spectrum (400 MHz, DMSO-d6)**



### <sup>13</sup>C NMR spectrum (100 MHz, DMSO-d6)



## 10. Theoretical calculation method

All the structures were fully optimized with M06-2X method.<sup>S6-S8</sup> 6-311++G\*\* basis set was used for all atoms. Energy calculations as well as Zero-point energy (ZPE) correction have been done by using the same level of theory. The influence of solvent was investigated in condensed phase using the Polarizable Continuum Model (PCM) with a dielectric constant of 24.85.

The computed stationary points have been characterized as minima or transition states by diagonalizing the Hessian matrix and analyzing the vibrational normal modes. In this way, the stationary points can be classified as minima if no imaginary frequencies are shown or as transition states if only one imaginary frequency is obtained. The particular nature of the transition states has been determined by analyzing the motion described by the eigenvector associated with the imaginary frequency. All calculations were performed with the Gaussian 09 suite of programs<sup>S9</sup>.

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