

## Electronic Supporting Information

### Controllable preparation of phosphonium-based polymeric ionic liquids as highly selective nanocatalysts for the chemical conversion of CO<sub>2</sub> with epoxides

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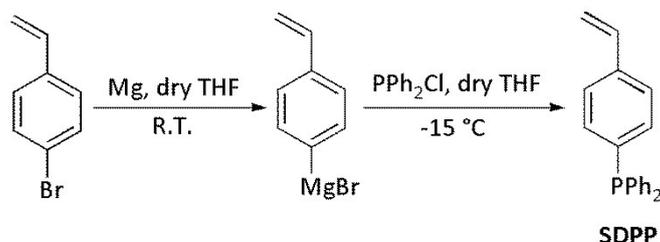
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## 1. General information

All reagents were purchased from commercial sources and directly used without any purification except special states. The manipulation on the synthesis of SDPP complex was performed in the standard Schlenk technique under dry nitrogen atmosphere, and THF was distilled from sodium/benzophenone under N<sub>2</sub> atmosphere. All cycloaddition reactions were respectively completed in the high pressure stainless reactor.

## 2. Synthesis and NMR Spectra of 4-diphenylphosphinostyrene

**Scheme S1.** Synthesis route for 4-diphenylphosphinostyrene



4-Diphenylphosphinostyrene was synthesized as the literature reported<sup>[1,2]</sup>. The preparation procedure was described as below. To a solution of Grignard reagent prepared by the reaction of 4-bromostyrene (18.3 g, 100 mmol) with Mg (4.8 g, 200 mmol) in dry THF (200 mL), chlorodiphenylphosphine (22 g, 100 mmol) was slowly dropwised at -15 °C under nitrogen atmosphere. After the addition was complete, the reaction mixture was stirred for 3 h. Then, 10% aqueous NH<sub>4</sub>Cl (20 mL) was added at the temperature of 0 °C. Finally, the mixture was extracted with EtOAc (2×100 mL), sequentially washed with saturated aqueous NaHCO<sub>3</sub> (2×100 mL) solution and brine (2×100 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and excess solvent removed by vacuum. The crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/EtOAc to afford a white solid product (21.8 g, 76 mmol, 78%, m.p.77-80 °C). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 600 MHz) δ = 7.38 (d, J=8.0 Hz, 2H, *p*-Ar-H), 7.24 (m, 8H, Ar-H), 7.27 (t, J= 8.0 Hz, 2H, *m*-Ar-H), 6.70 (dd, J=10.9 Hz, 18.0 Hz, 1H, =CH<sub>2</sub>), 5.78 (d, J= 18.0 Hz, 1H, =CH<sub>2</sub>), 5.28 (d, J= 10.9 Hz, 1H, =CH<sub>2</sub>); <sup>31</sup>P NMR (CDCl<sub>2</sub>, 240 MHz) δ = -5.29.

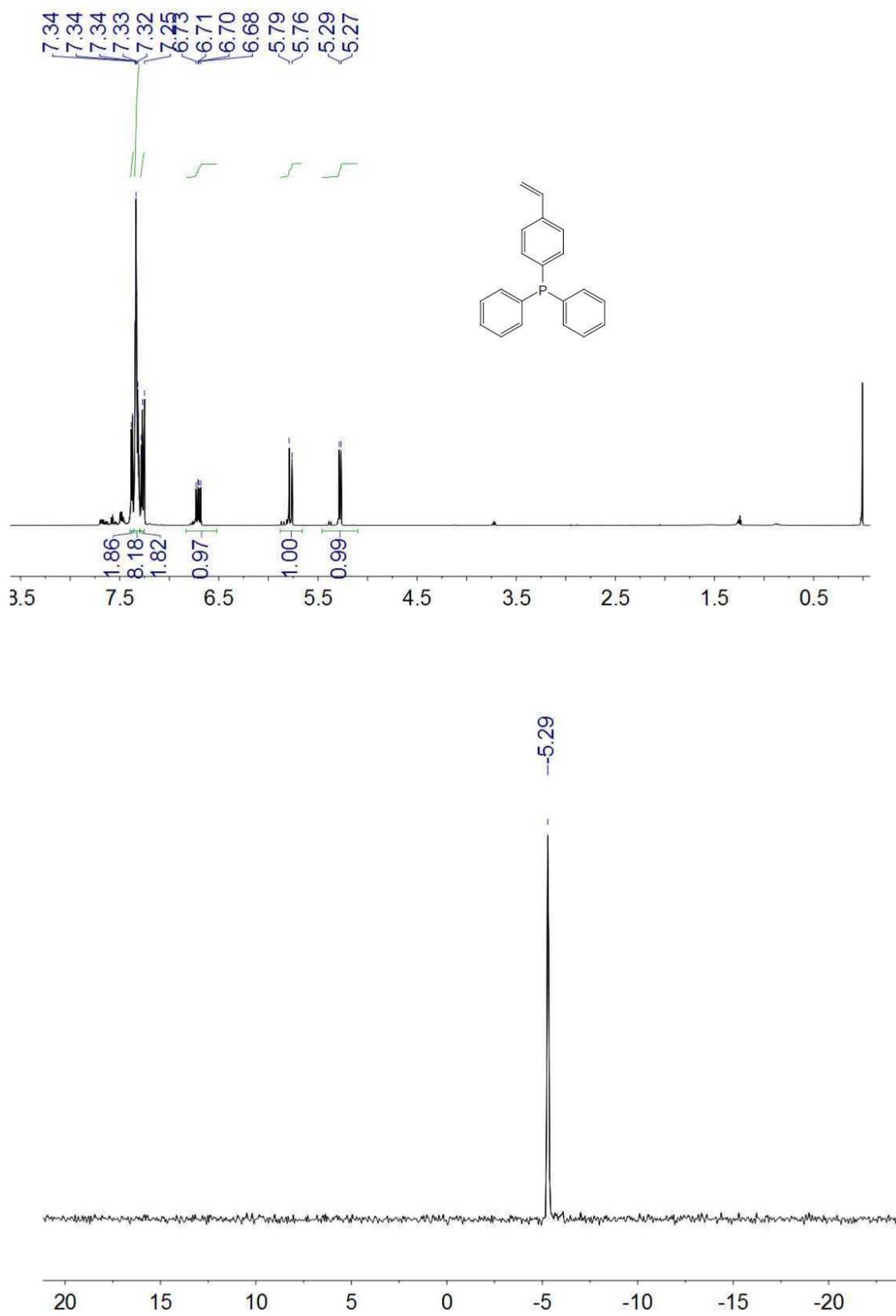
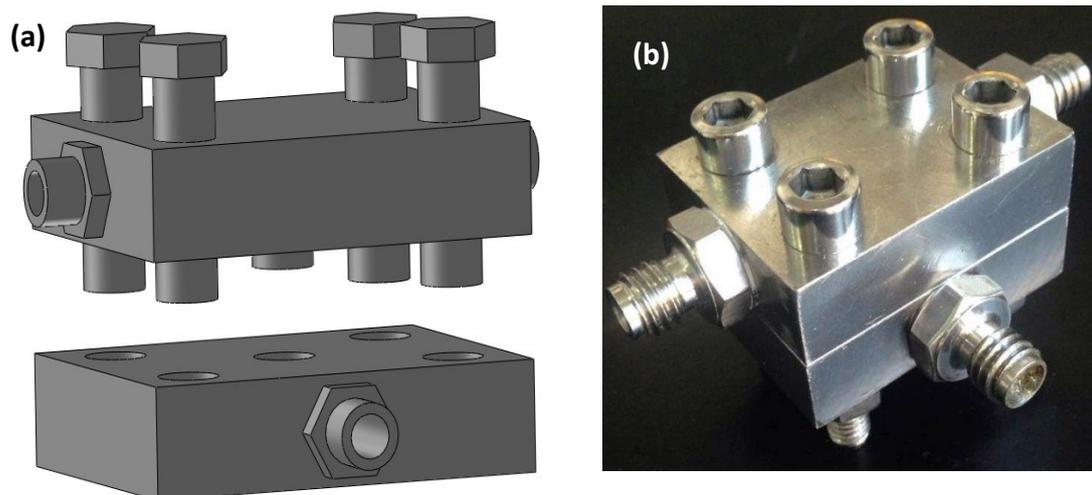
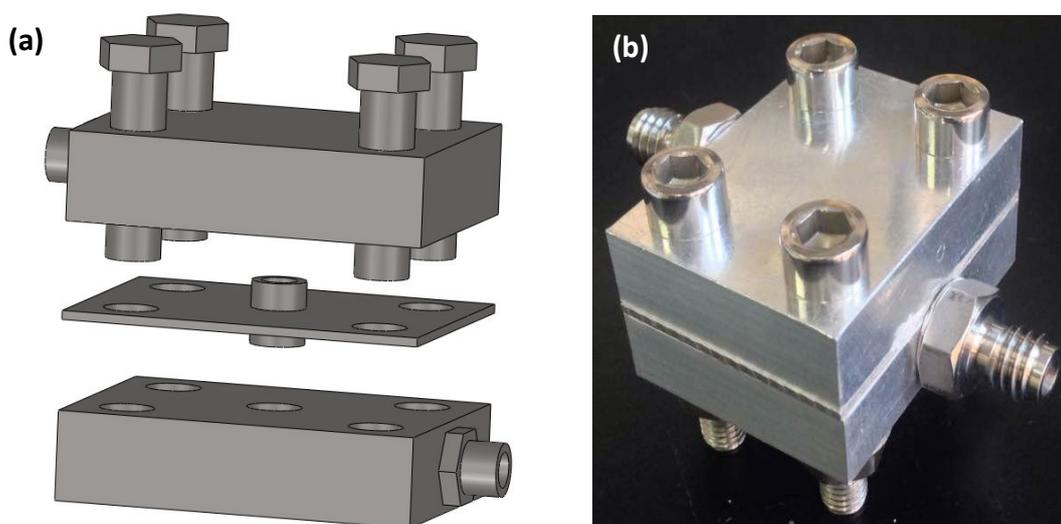


Figure S1. NMR spectra of SDPP.

### 3. Experimental set-up for synthesizing NP particles



**Figure S2.** Premix microdevice. (a) 3D schematic diagram; (b) physical device. Length×width×height=40mm×30mm×20mm.



**Figure S3.** Modified double membranes' microdevice. (a) 3D schematic diagram; (b) physical device. Length×width×height=40mm×30mm×21mm.

#### 4. Particle sized distribution (CV)

The Particle sized distribution is expressed by the coefficient of variance (CV), defined as

$$CV = \sqrt{\frac{\sum (d_i - d_n)^2}{Nd_n^2}}$$

Where  $d_i$  is the particle size,  $d_n$  is the average diameter size, and  $N$  is the number of particles.

## 5. Elemental analysis result and EDS spectra of NP and NPILs

**Table S1.** Elemental analysis of NP and NPILs by using EDS spectroscopy.

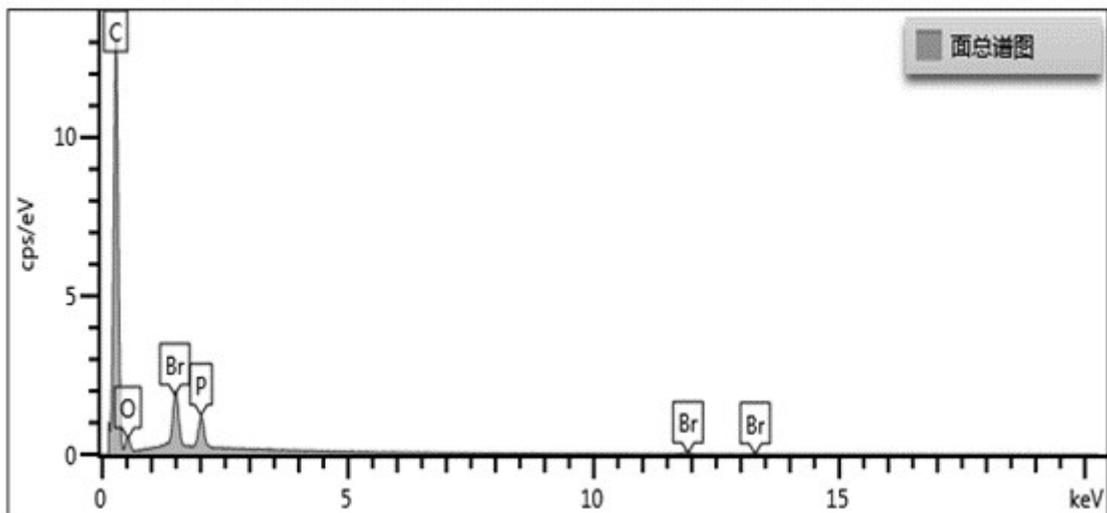
Entry	Sample	Weight%				At%			
		C	O	P	Br	C	O	P	Br
1	NP <sup>a</sup>	98.78	—	1.22	—	99.52	—	0.48	—
2	NPILs-BPA <sup>a</sup>	79.33	8.66	2.18	9.83	89.99	7.37	0.96	1.68
3	NPILs-BBA <sup>a</sup>	85.62	9.22	0.86	4.30	91.55	7.40	0.35	0.69
4	NPILs-BPA <sup>b</sup>	87.19	7.03	1.52	4.25	93.05	5.64	0.63	0.68
5	NPILs-BPA <sup>c</sup>	87.06	7.20	1.35	4.40	92.97	5.77	0.56	0.71

<sup>a</sup>67 nm of particle sizes; <sup>b</sup> 271 nm of particle sizes; <sup>c</sup> 375 nm of particle sizes.

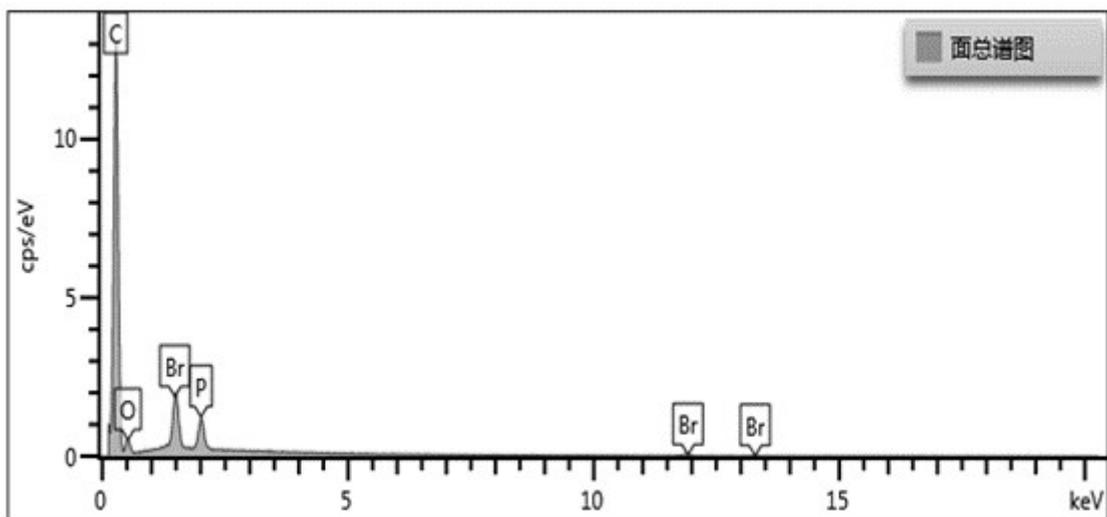
**Table S2.** Phosphor content of nanocatalysts precisely determined by using ICP spectrometer

Entry	Sample	P weight%
1	NPILs-BPA <sup>a</sup>	1.98
2	NPILs-BPA <sup>b</sup>	1.41
3	NPILs-BPA <sup>c</sup>	1.32

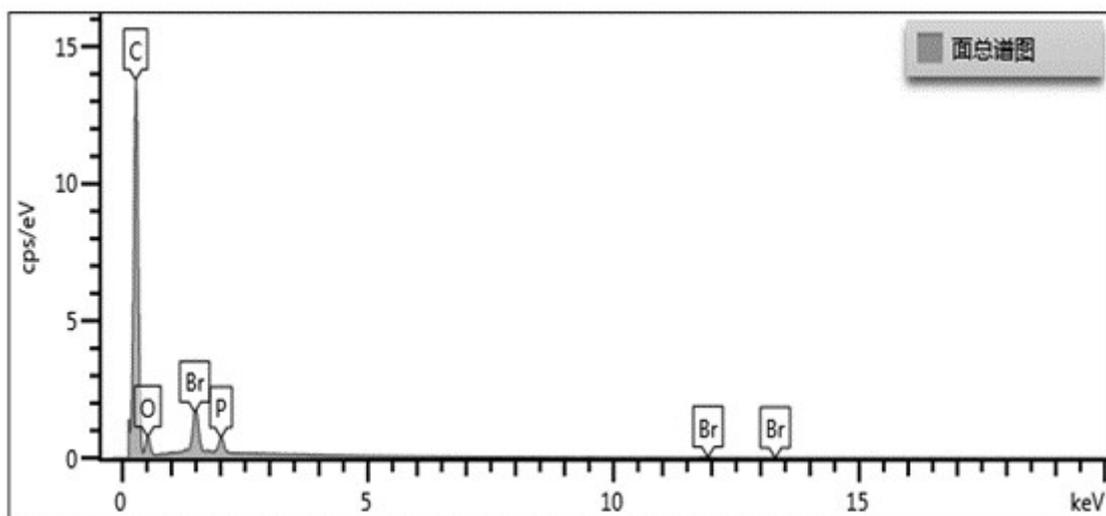
<sup>a</sup>67 nm of particle sizes; <sup>b</sup> 271 nm of particle sizes; <sup>c</sup> 375 nm of particle sizes.



**Figure S4.** EDS spectrum of NPILs-BPA with the average diameter size of 271 nm.

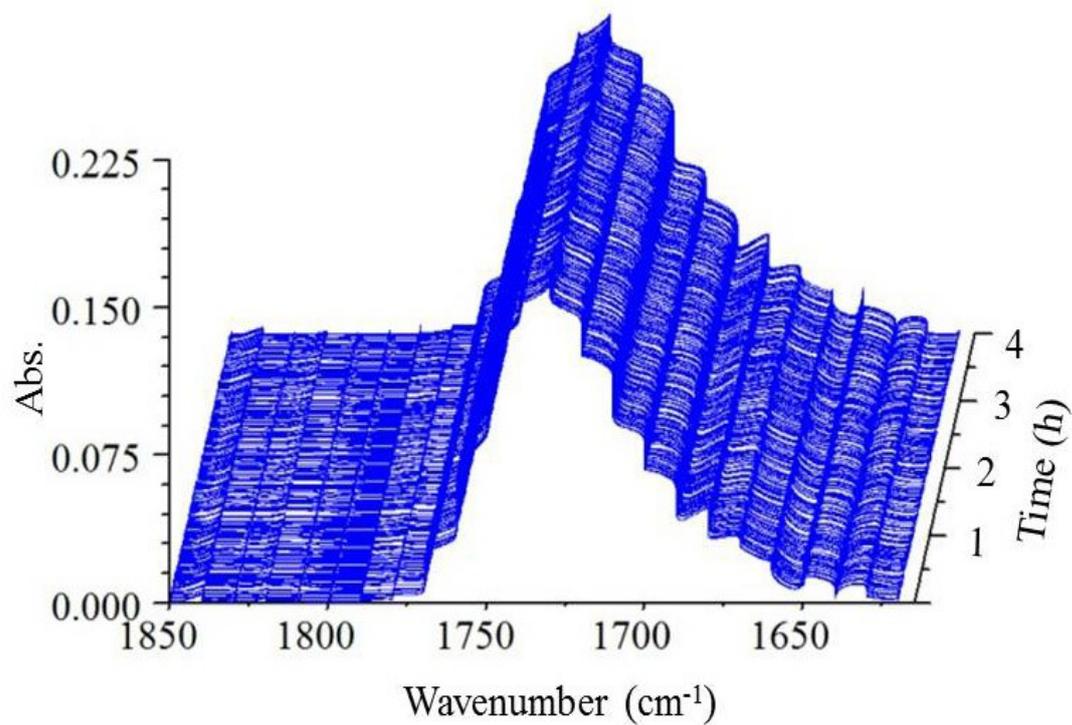


**Figure S5.** EDS spectrum of NPILs-BPA with the average diameter size of 375 nm.



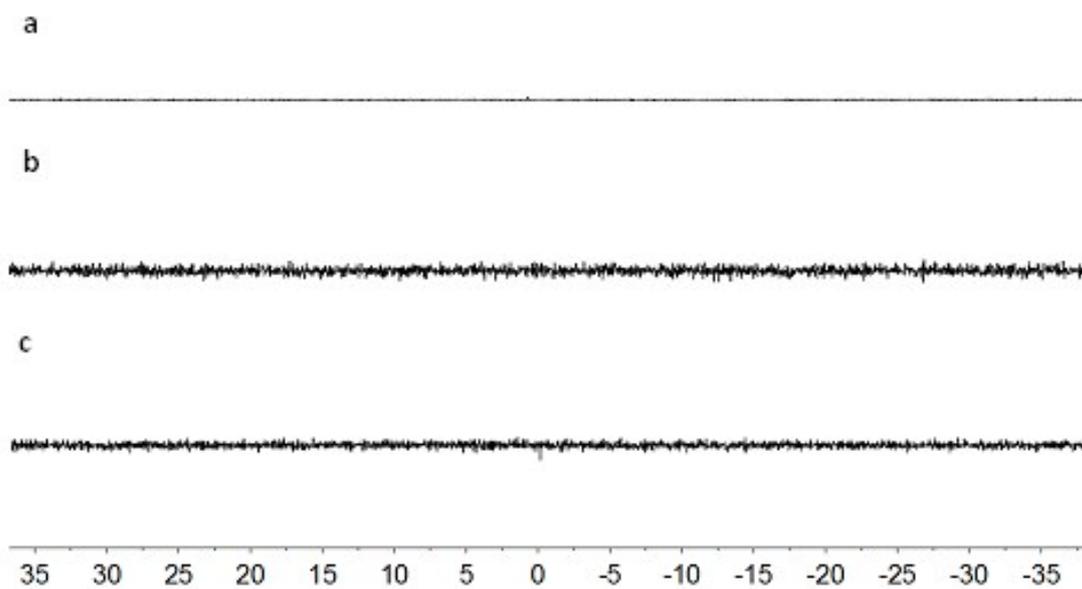
**Figure S6.** EDS spectrum of NPILs-BBA.

**6. *In-situ* FTIR characterization of NPILs-BPA under CO<sub>2</sub> atmosphere**



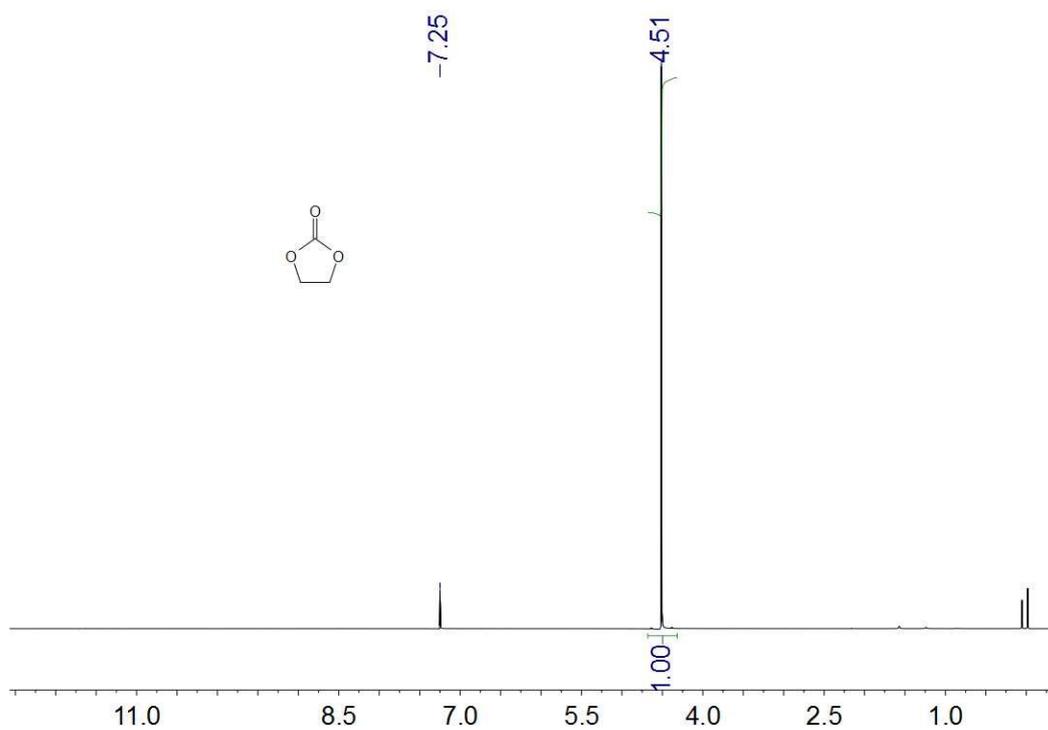
**Figure S7.** In-situ spectrum of NPILs-BPA under CO<sub>2</sub> atmosphere.

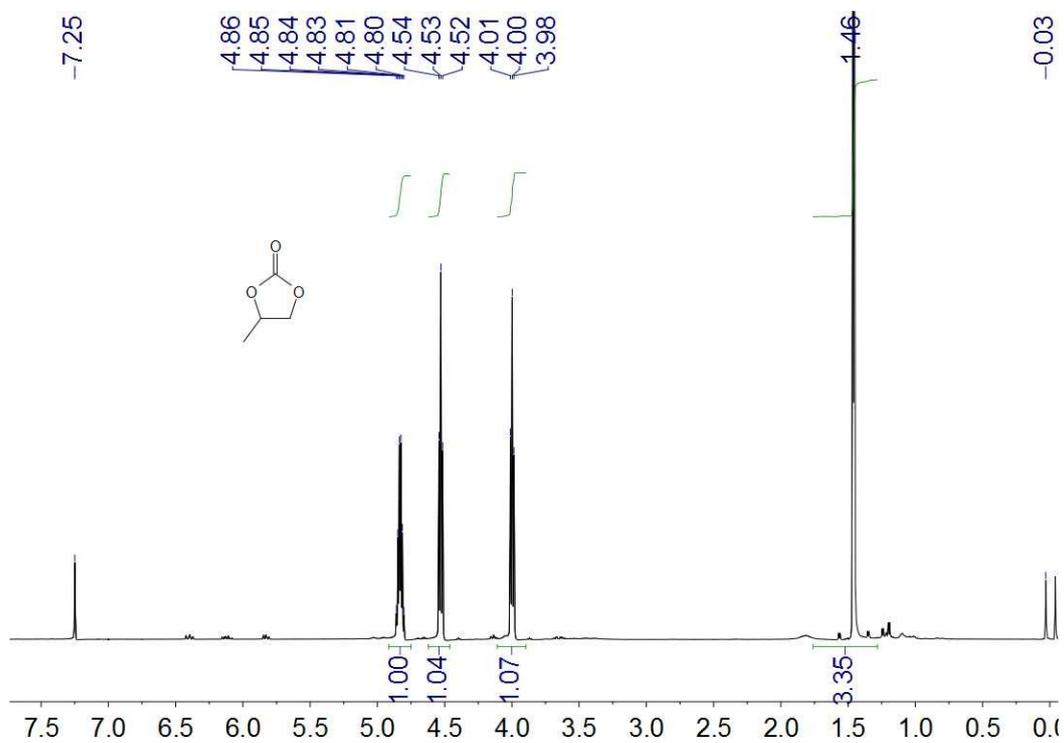
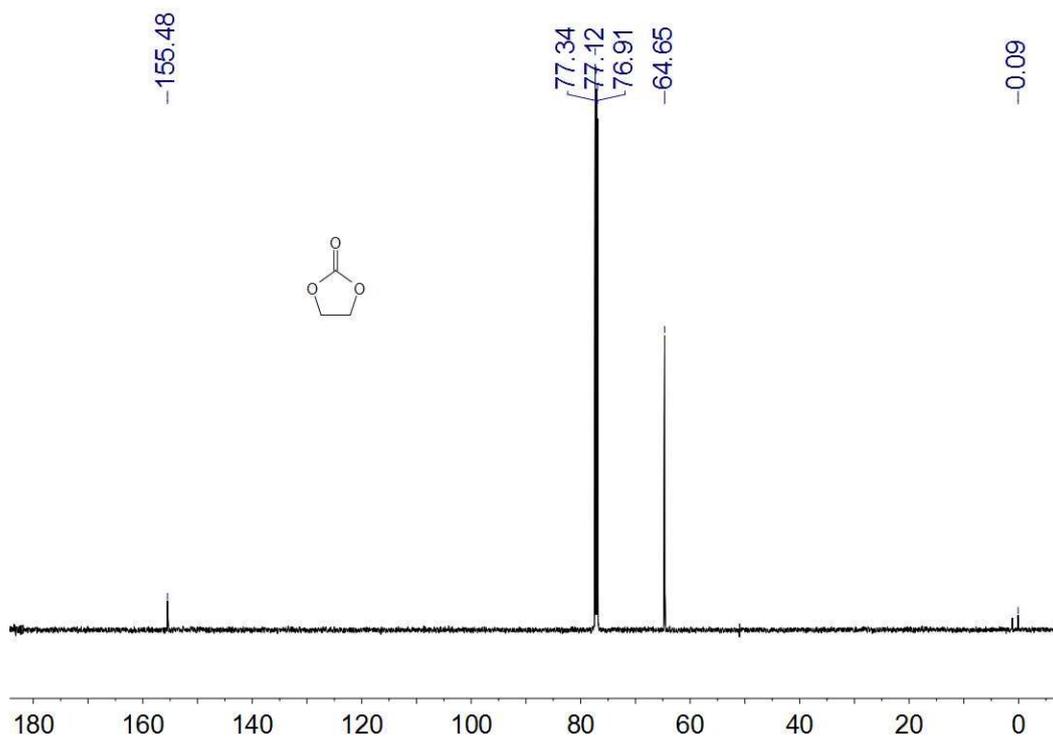
## 7. $^{31}\text{P}$ NMR analyse the leaching of phosphonium salts during recycling

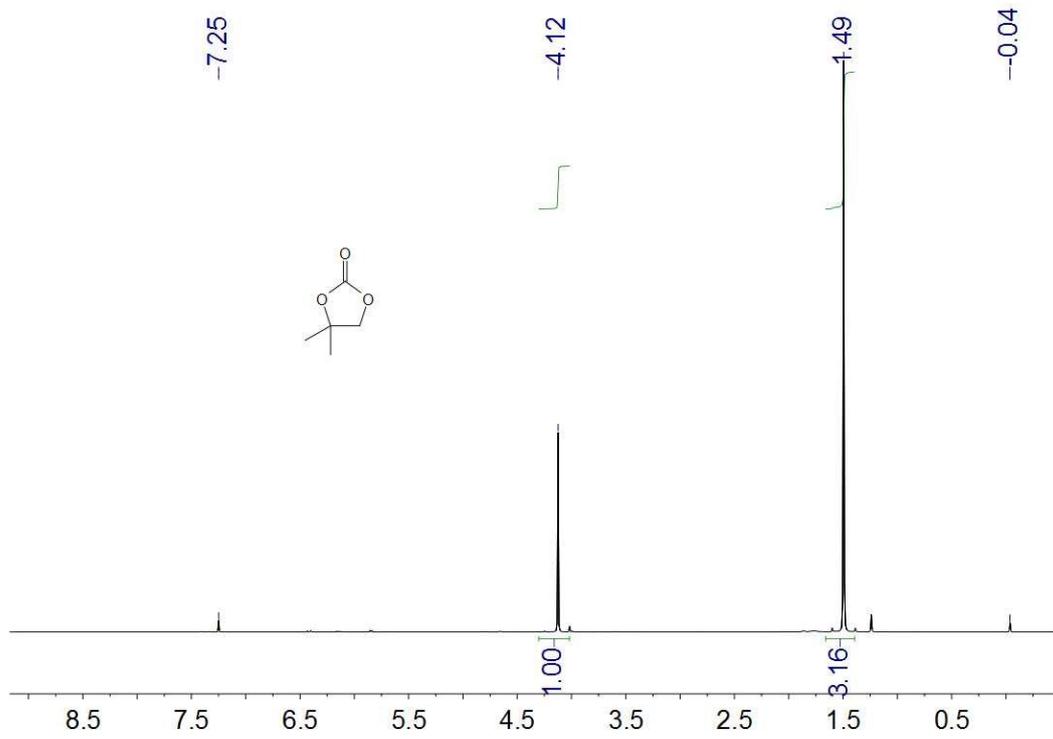
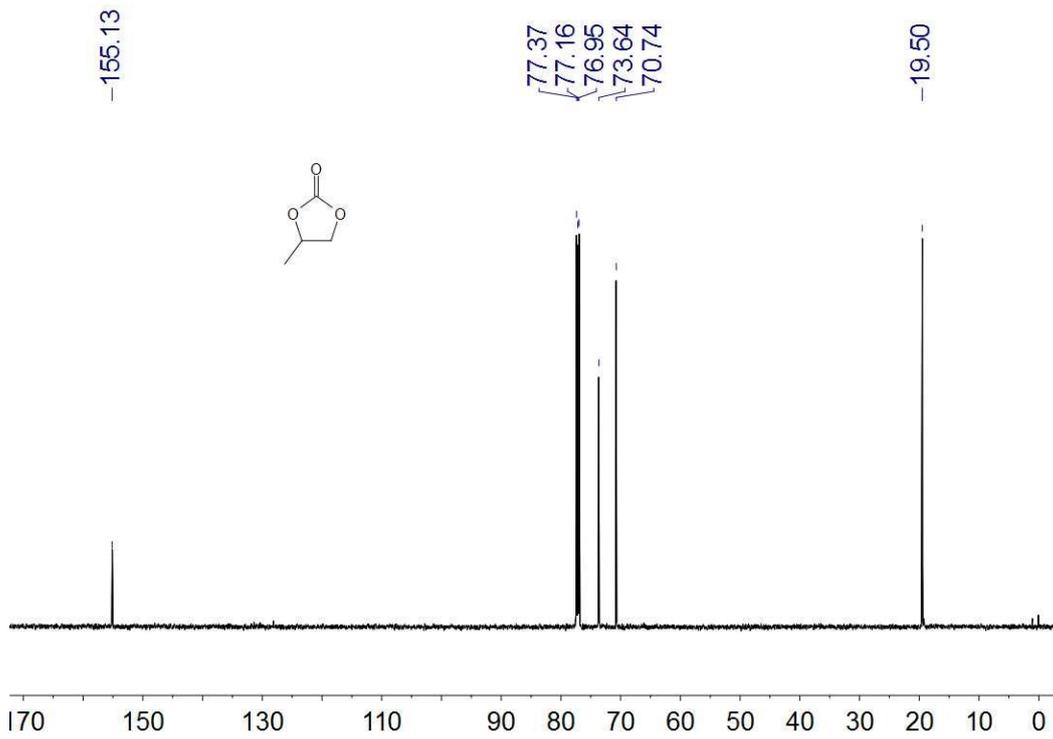


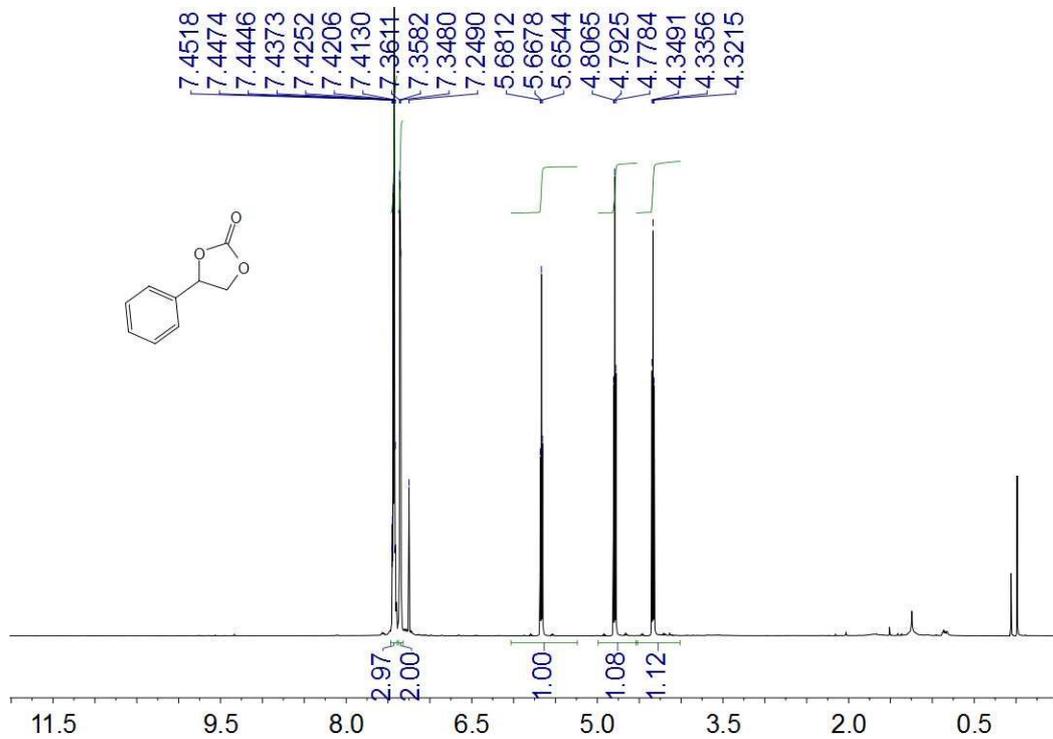
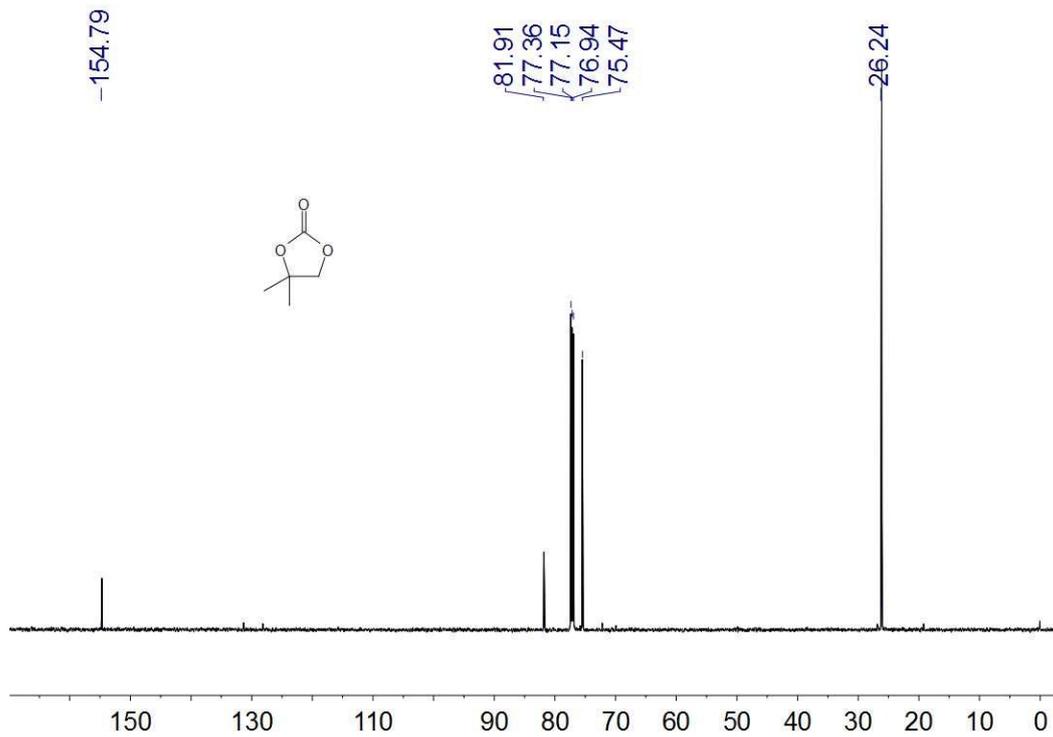
**Figure S8.**  $^{31}\text{P}$  NMR (240 MHz,  $\text{CDCl}_3$ ): (a) the filtrate after the third run; (b) the filtrate after the fifth run and (c) the filtrate after the seventh run.

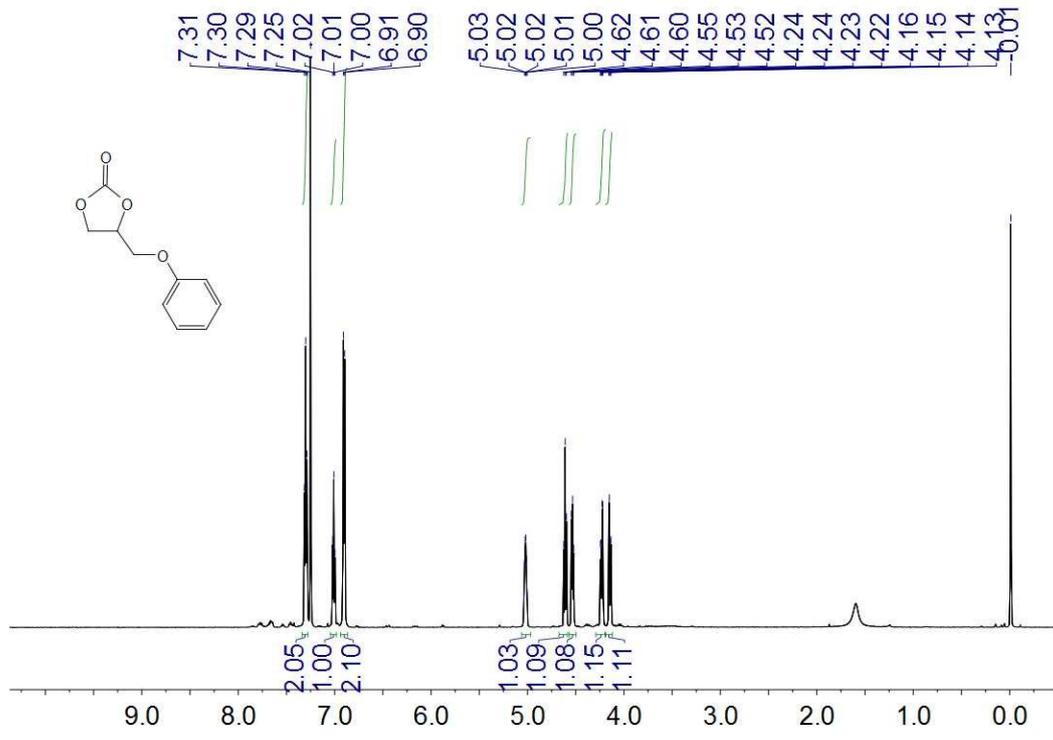
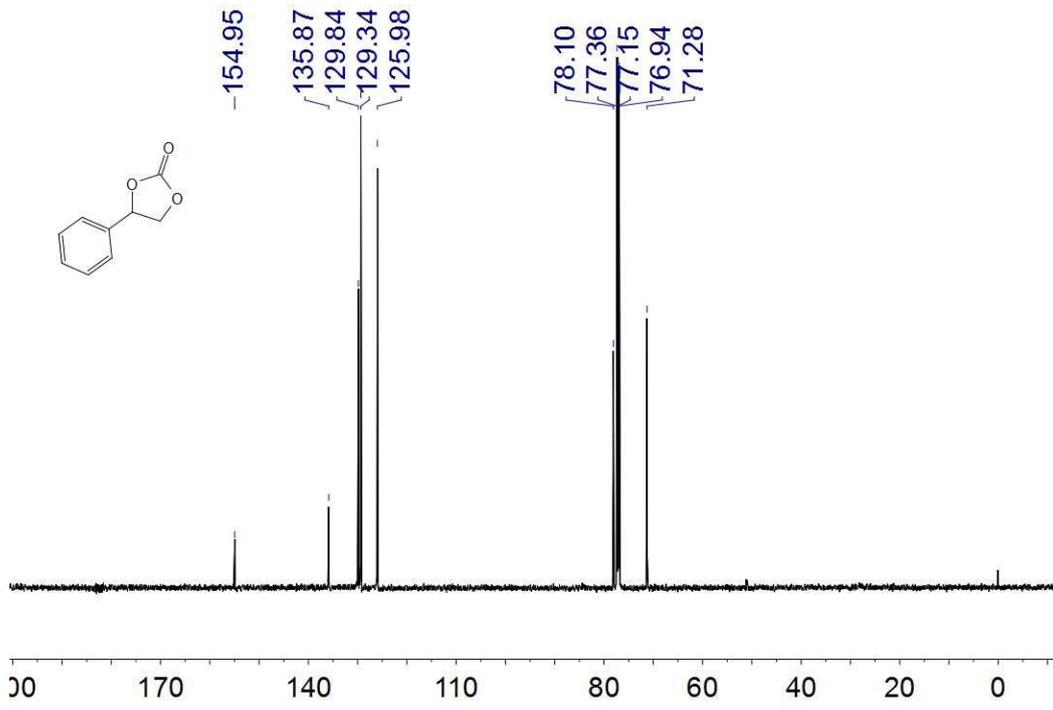
## 8. NMR spectra of the carbonate products

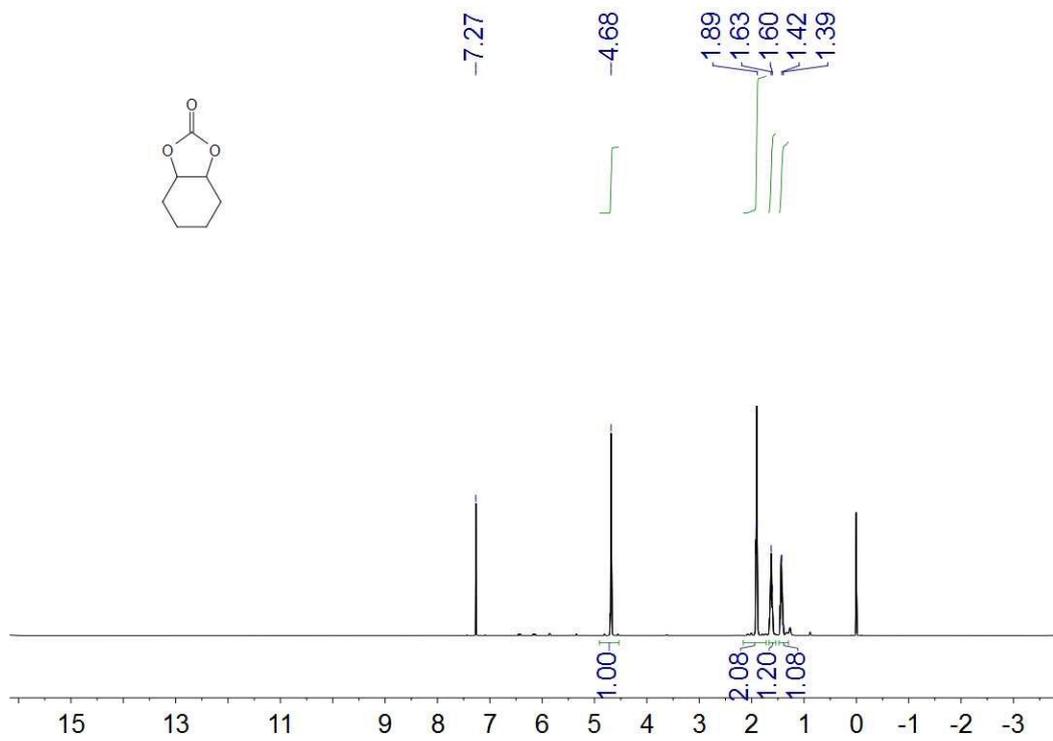
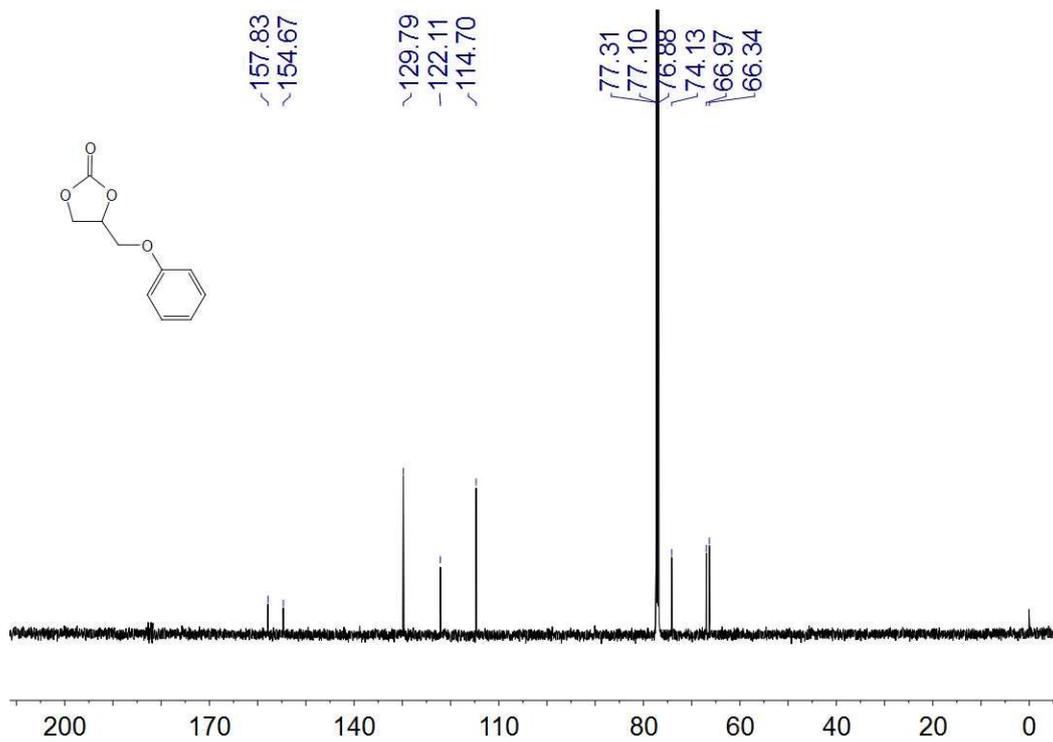


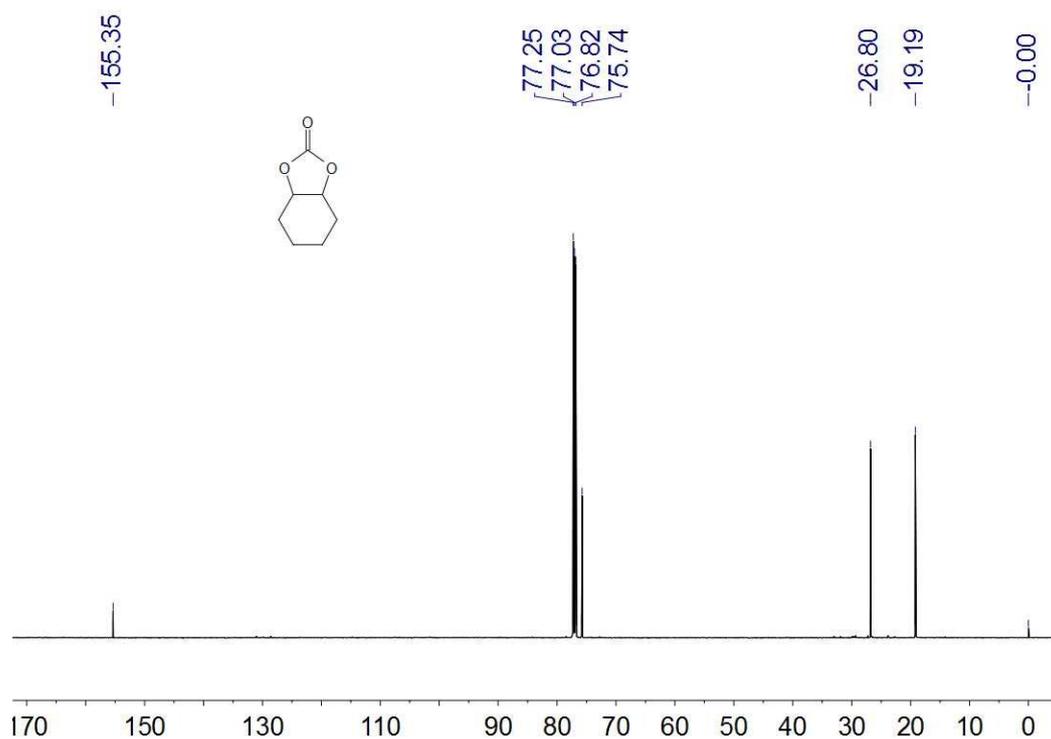












## 9. References

- [1] M.K.W. Choi, H.S. He and P.H. Toy, *J. Org. Chem.*, 2003, 68, 9831-9834.
- [2] Y. Liu, X.J. Feng, D.C. Bao, K.X. Li and M. Bao, *J. Mol. Catal. A: Chem.*, 2010, 323, 16-22.