

# Supporting Information

## **CeO<sub>2</sub>-ZrO<sub>2</sub> Solid Solution Catalyzed and Moderate Acidic-Basic Sites Dominated Cycloaddition of CO<sub>2</sub> with Epoxides: Halogen-free Synthesis of Cyclic Carbonates**

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# 1. Experimental

## 1.1 Chemicals

Cerium(III) nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.9%, AR), zirconyl nitrate ( $\text{ZrO}(\text{NO}_3)_2$ , 99.0%, AR) and sodium hydroxide (NaOH, 99%, AR) were purchased from Beijing Innochem Chemical Reagent Co, Ltd. The 1,2-butylene carbonate (98%(w/w)) and epoxides including 1,2-butylene oxide (99.5%(w/w)), propylene oxide (99%(w/w)), 3-hydroxy-1,2-propenoxide (97%(w/w)), epichlorohydrin (99%(w/w)), styrene oxide (98%(w/w)), 2-((propenyloxy)methyl)oxirane (99%(w/w)), and cyclohexene oxide (98%(w/w)) were received from Shanghai TCI Chemical Reagent Co, Ltd. Dimethylformamide (DMF, 97%(w/w)), Dimethylacetamide (DMA, 97%(w/w)), Tetrahydrofuran (THF, 98%(w/w)), cyclohexane (98%(w/w)), methanol (99.8%, AR) and biphenyl (99.5%(w/w)) were bought from Beijing J&K Chemical Co, Ltd. All reagents were used as received without further purification.

## 1.2 Characterization techniques

XRD analysis was performed on a Rigaku D/MAX-2550 diffractometer equipped with a Cu  $K\alpha$  radiation source. The catalysts were scanned from  $10^\circ$  to  $90^\circ$  at a scan rate of  $10^\circ/\text{min}$ . TEM and HRTEM were performed on JEOL JEM-F200 transmission electron microscope at an accelerating voltage of 200 kV. Before TEM analysis, the powder catalysts were dispersed in ethanol and then deposited on a carbon film coated on a copper grid. Specific surface area measurement was carried out on Micromeritics ASAP 2460 using nitrogen adsorption at liquid-nitrogen temperature (77 K). The surface areas of the catalysts were estimated by the BET method and the pore size distributions were calculated from analysis of the desorption branch of the isotherm via the conventional the Barrett-Joyner-Halenda (BJH) model. XPS data were obtained by an ESCALab-250Xi electron spectrometer (VG, UK) using 300 W Al  $K\alpha$  radiation to investigate the surface chemical constitution. The binding energies were calibrated referenced to the carbonaceous C 1s at 284.6 eV. The bulk composition of the catalysts was determined with VISTA-MPX ICP-AES spectrometer. The acidic and basic properties were measured by Autochem 2920 TPD instrument (Micromeritics) by 10% v/v  $\text{NH}_3$ -He and 10% v/v  $\text{CO}_2$ -He, respectively. Approximately 100 mg of sample was pretreated at 200  $^\circ\text{C}$  for 1 h.  $\text{NH}_3$  ( $\text{CO}_2$ ) adsorption was performed at 100  $^\circ\text{C}$  by switching He flow to a stream of 10% v/v  $\text{NH}_3$  ( $\text{CO}_2$ )-He and maintaining the temperature for 1h. The sample was purged with He for 1 h in order to remove the physically adsorbed  $\text{NH}_3$  ( $\text{CO}_2$ ). TPD test was carried out under the condition of a constant flow of He from 100 to 800  $^\circ\text{C}$  at a heating rate of 20  $^\circ\text{C}/\text{min}$ . The concentration of  $\text{NH}_3$  ( $\text{CO}_2$ ) was continuously monitored by a TCD detector.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance III 500 M spectrometer.

## 2. Supplementary figures of characterization for $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts

## 2.1 TEM

As shown in Figure S1 (a) and (b), number of agglomerates appeared in  $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  and  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ , leading to morphology irregular. According to the HRTEM images, the rod  $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  and  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  exhibited (111), (200) and (220) lattice planes of  $\text{CeO}_2$  (Figure S1 (c) and (d)).

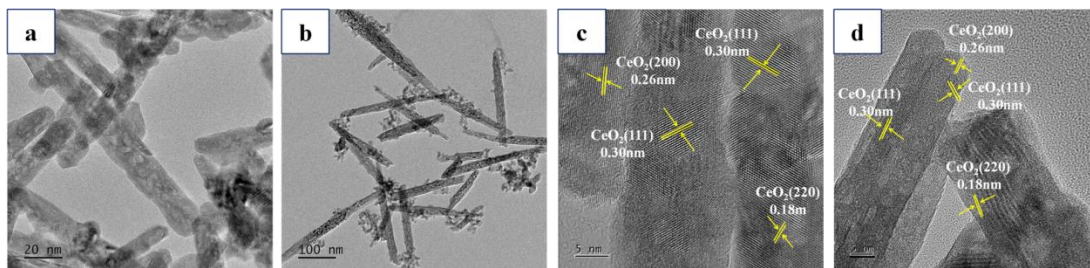


Figure S1. TEM images: a)  $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ , b)  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ ; HRTEM images: c)  $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ , d)  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$

In Figure S2, EDS characterization of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  indicated the agglomerated particle was  $\text{ZrO}_2$ .

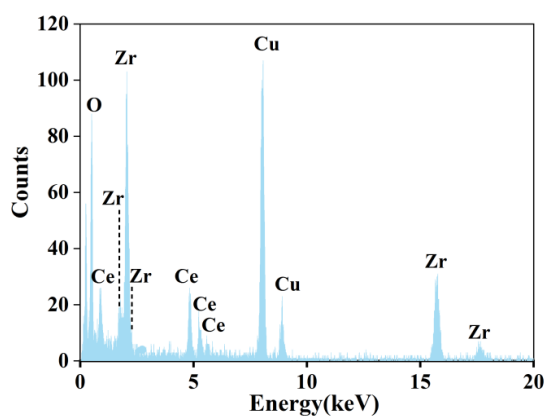


Figure S2. EDS spectrum of agglomerating particles in  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$

Figure S3 displayed EDS-Mapping characterization of  $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ . The element analysis demonstrated all the constituent elements, i.e. Ce, Zr and O, presented a homogeneous distribution in the solid solution.

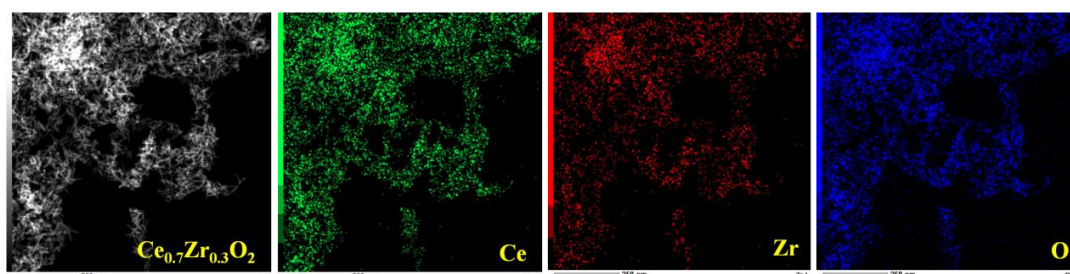


Figure S3. EDS-Mapping images of  $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$

## 2.2 BET

N<sub>2</sub> adsorption-desorption isotherm and BJH pore size distribution of different catalysts were recorded in Figure S4 (a) and Figure S4 (b). The Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> samples all showed type IV adsorption isotherm. It can be seen from the pore distribution curve that the materials mainly have one-dimensional pore structure.

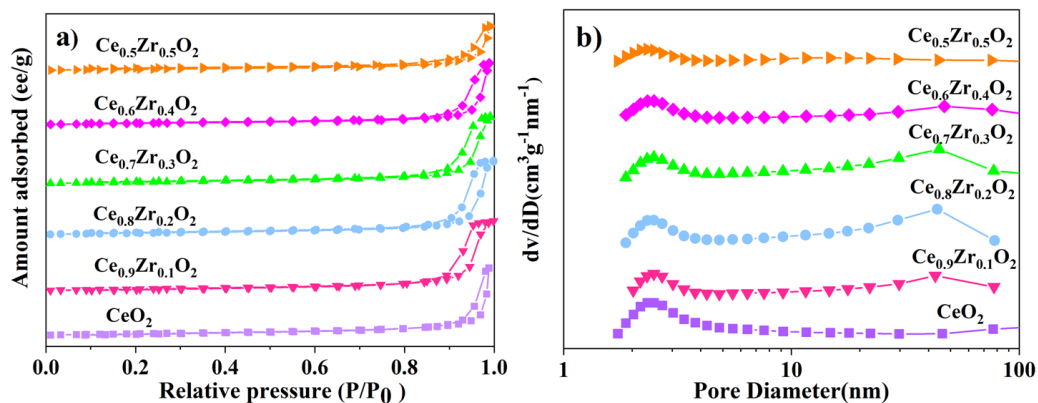


Figure S4. a) N<sub>2</sub> adsorption-desorption isotherm, b) BJH pore size distribution of CeO<sub>2</sub> and Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> nanorods

### 3. Effect of the solvent and weight of catalyst

Various solvents were screened for the cycloaddition of CO<sub>2</sub> with **1a** (Table S1, entries 1-4). When the non-polar solvent of cyclohexane was used, only 45% yield of **2a** was produced (entry 1). The yield of **2a** was improved when a polar solvent was replaced (entry 2-4). Amines had a positive effect on the reaction, and DMF gave the best catalytic activity with 96% yield of **2a** (entry 4). As the adding amount of the catalyst increased, the yield of **2a** gradually enhanced to 96% (entry 4-8). Table S1. Effect of the solvents and catalyst amount on the cycloaddition of CO<sub>2</sub> with **1a**<sup>a</sup>

$  \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{Et} + \text{CO}_2 \xrightarrow{\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2} \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \text{---} \text{C} \text{---} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{Et}  $					
Entry	Solvent	Amount of catalyst/g	Conv. <sup>b</sup> /%	Sel. <sup>b</sup> /%	Yield <sup>b</sup> /%
1	cyclohexane	1	50 ± 2	90 ± 0	45 ± 2
2	THF	1	71 ± 3	94 ± 2	67 ± 4
3	DMA	1	91 ± 1	96 ± 1	87 ± 2
4	DMF	1	96 ± 1	> 99	96 ± 1
5	DMF	0.3	56 ± 2	96 ± 0	54 ± 2
6	DMF	0.5	73 ± 4	99 ± 1	72 ± 3
7	DMF	0.8	86 ± 2	99 ± 0	85 ± 2
8	DMF	1.2	96 ± 1	> 99	96 ± 2

<sup>a</sup> Reaction conditions: 1 mL (11.42 mmol) **1a**, Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub>, 6 MPa CO<sub>2</sub> at 150 °C, 24 h. <sup>b</sup> Determined by GC using biphenyl as internal standard, the disparity values were calculated from the results of three parallel experiments.

## 4. Evaluation for the reaction time

Figure S5 showed conversion of 1,2-butylene oxide catalyzed by Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> within different times under conditions of 150 °C, 6 MPa, 3mL DMF. The reaction rate increased first and then decreased, finally the conversion of 1,2-butylene oxide reached 96% in 24h.

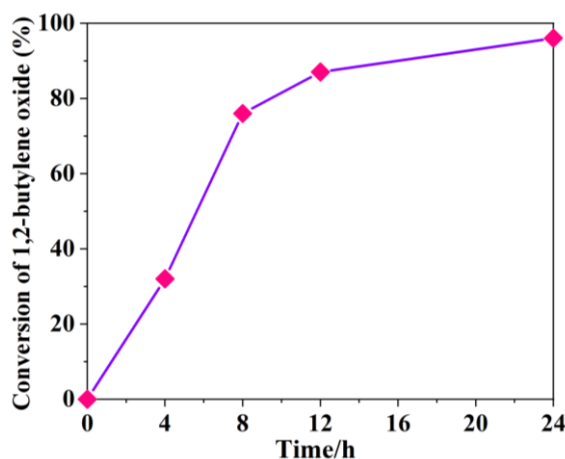


Figure S5. Effect of time on the activity of Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub>

## 5. Activity evaluation of different catalysts at 6 h

In order to clarify the correlation between acidity/basicity and catalytic activity, we evaluated the catalytic activity at 6 h. The data of conversion, selectivity, and the amount of acidic/basic sites of catalysts are listed in Table S2.

Table S2. Effect of different catalysts on the cycloaddition of CO<sub>2</sub> with 1,2-butylene oxide at 6 h<sup>a</sup>

<div style="text-align: center;"> </div>						
Entry	Catalyst	Moderate acidic sites (mmol/g)	Moderate basic sites (mmol/g)	Conv. <sup>b</sup> /%	Sel. <sup>b</sup> /%	Yield <sup>b</sup> /%
1	CeO <sub>2</sub> -rod	0.198	0.200	36 ± 3	99 ± 1	36 ± 4
2	Ce <sub>0.9</sub> Zr <sub>0.1</sub> O <sub>2</sub>	0.240	0.237	42 ± 2	99 ± 1	42 ± 1
3	Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub>	0.302	0.276	51 ± 4	99 ± 3	50 ± 1
4	Ce <sub>0.7</sub> Zr <sub>0.3</sub> O <sub>2</sub>	0.339	0.337	65 ± 3	> 00	65 ± 2
5	Ce <sub>0.6</sub> Zr <sub>0.4</sub> O <sub>2</sub>	0.325	0.313	60 ± 2	99 ± 2	59 ± 3

6	Ce <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub>	0.321	0.307	56 ± 2	99 ± 1	55 ± 1
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<sup>a</sup> Reaction conditions: 1 mL (11.42 mmol) **1a**, 1 g catalyst, 3 mL DMF, 6 MPa CO<sub>2</sub> at 150 °C, 6 h. <sup>b</sup> Determined by GC using biphenyl as internal standard, the disparity values were calculated from the results of three parallel experiments.

## 6. XRD spectra of reused Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub>

The nature of the reused catalyst after each run was monitored by XRD (Figure S6), which illustrated no significant difference between the fresh and reused catalyst.

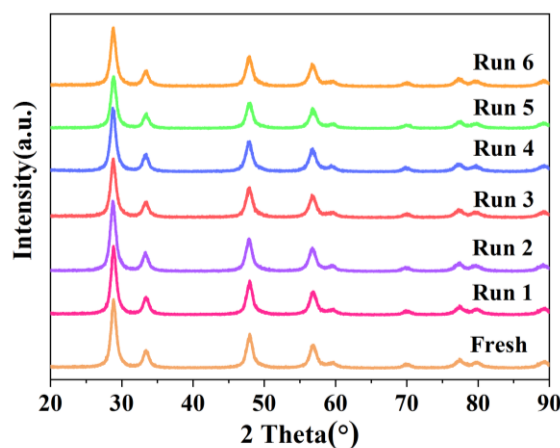
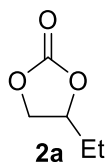


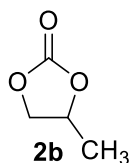
Figure S6. The XRD patterns of reused Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub>

## 7. <sup>1</sup>H and <sup>13</sup>C NMR data of the resultant cyclic carbonates

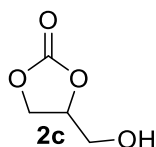


1,2-Butylene carbonate (**2a**): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.56 (dt, *J* = 13.8, 6.9 Hz, 1H), 4.41 (t, *J* = 8.2 Hz, 1H), 3.96 (dd, *J* = 8.5, 6.9 Hz, 1H), 1.73-1.53 (m, 2H), 0.87 (d, *J* = 7.5 Hz, 3H) ppm.

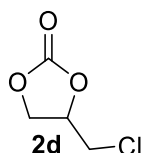
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.18, 78.10, 69.01, 26.57, 8.18 ppm.



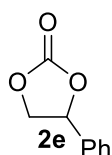
Propylene carbonate (**2b**): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.78 (dd, *J* = 14.3, 5.7 Hz, 1H), 4.52-4.42 (m, 1H), 3.97-3.88 (m, 1H), 1.37 (d, *J* = 6.3 Hz, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.51, 74.68, 70.96, 18.96 ppm.



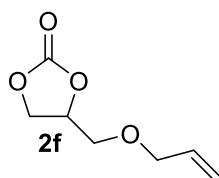
3-Hydroxy-1,2-propylene carbonate (**2c**):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.83 (ddt,  $J = 8.5, 6.5, 3.2$  Hz, 1H), 4.54 (dd,  $J = 10.4, 6.2$  Hz, 1H), 4.48 (dd,  $J = 8.4, 6.6$  Hz, 1H), 4.00 (dd,  $J = 12.9, 2.9$  Hz, 1H), 3.72 (dd,  $J = 12.9, 3.4$  Hz, 1H), 2.90 (m, 1H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  154.78, 76.69, 65.83, 60.02 ppm.



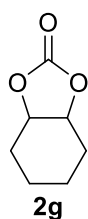
3-Chloro-1,2-propylene carbonate (**2d**):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.02-4.94 (m, 1H), 4.54 (t,  $J = 8.7$  Hz, 1H), 4.33 (dd,  $J = 8.9, 5.7$  Hz, 1H), 3.80 (dd,  $J = 12.5, 4.2$  Hz, 1H), 3.68 (dd,  $J = 12.4, 3.6$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.54, 74.97, 68.21, 44.68 ppm.



Styrene carbonate (**2e**):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48-7.18 (m, 5H), 5.65 (d,  $J = 8.0$  Hz, 1H), 4.76 (d,  $J = 8.4$  Hz, 1H), 4.29 (d,  $J = 8.2$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.95, 136.14, 129.68, 129.21, 126.00, 78.11, 71.23 ppm.



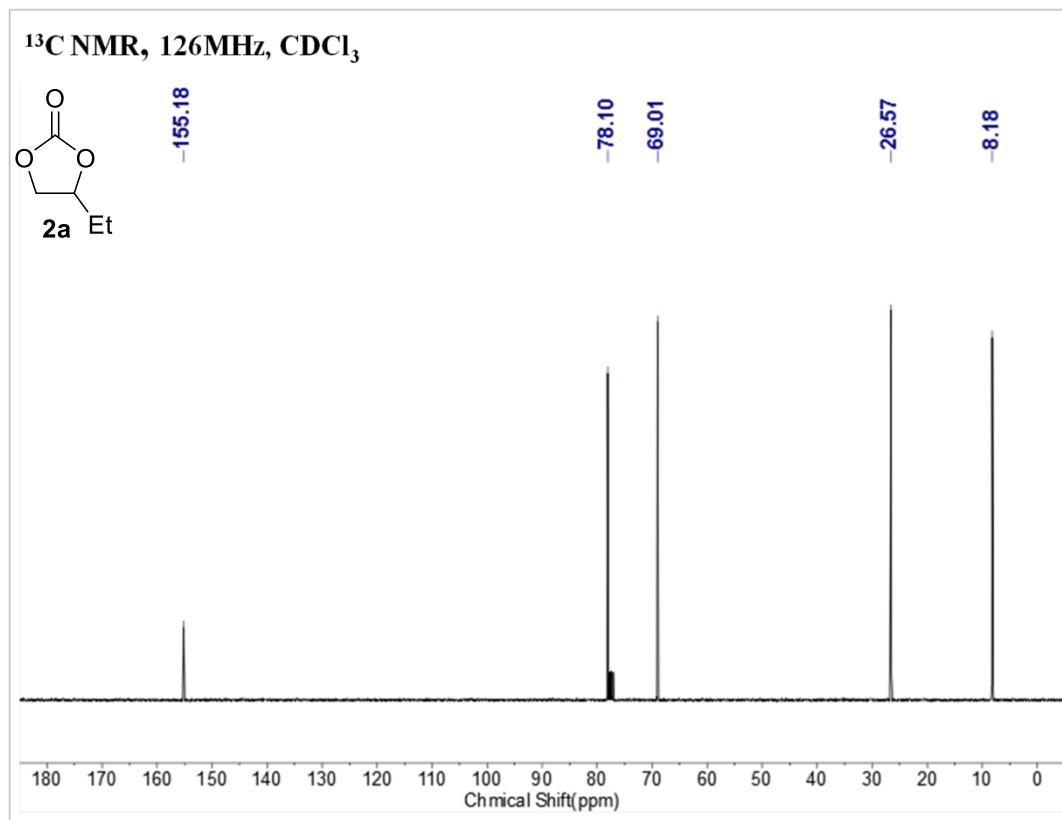
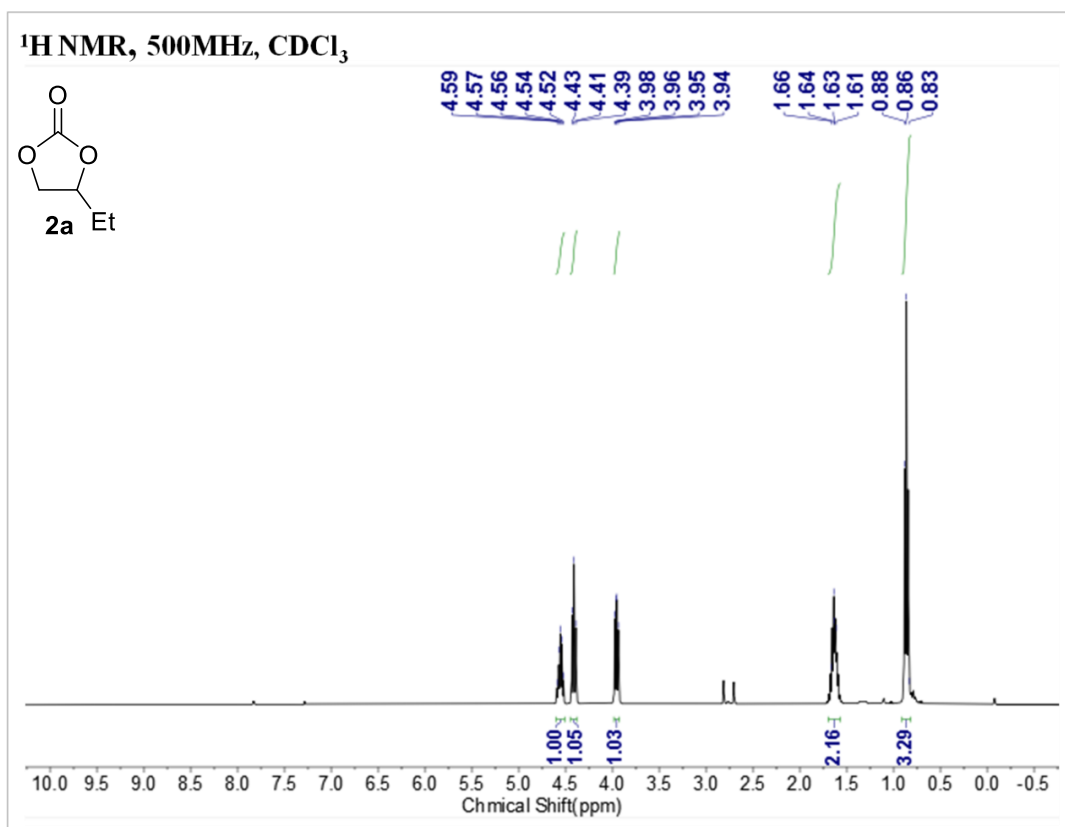
2-((Propenyloxy)methyl)-ethylene carbonate (**2f**):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.88-5.75 (m, 1H), 5.29-5.09 (m, 2H), 4.80 (td,  $J = 9.6, 3.8$  Hz, 1H), 4.46 (t,  $J = 8.4$  Hz, 1H), 4.36-4.30 (m, 1H), 3.99 (dd,  $J = 2.9, 1.4$  Hz, 2H), 3.65 (dd,  $J = 11.2, 3.4$  Hz, 1H), 3.55 (dd,  $J = 11.2, 3.7$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.39, 133.63, 117.37, 75.51, 72.65, 68.72, 66.48 ppm.

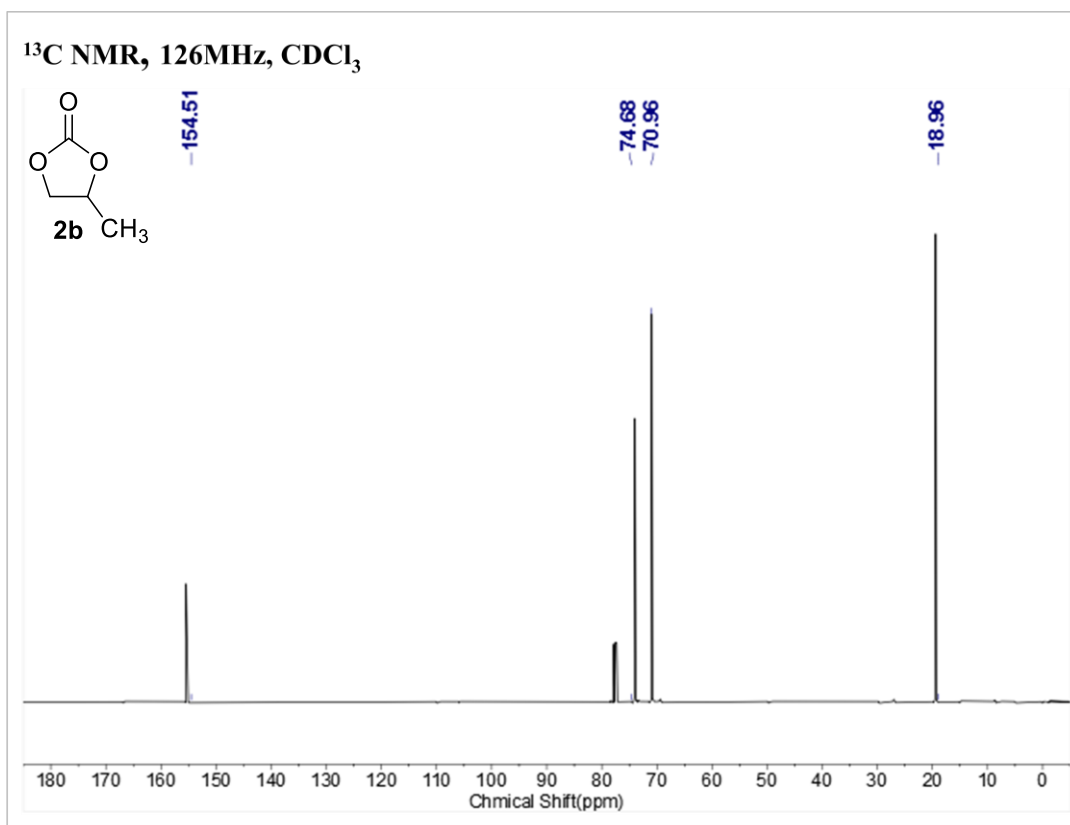
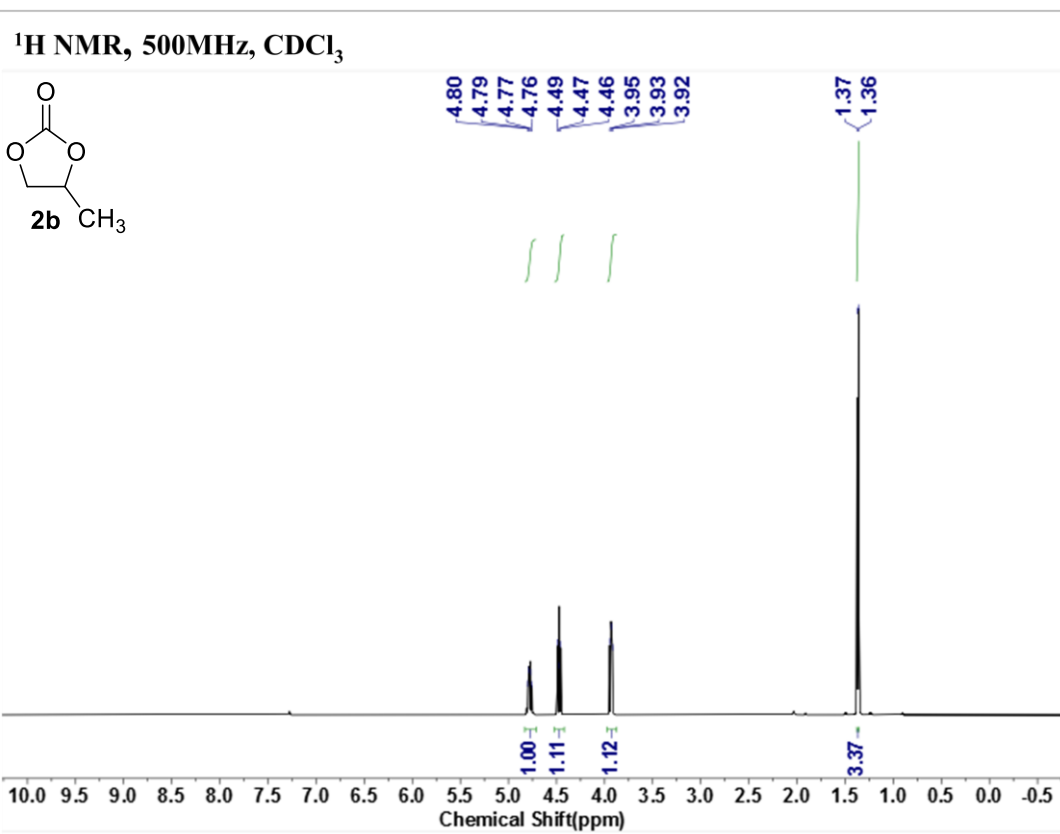


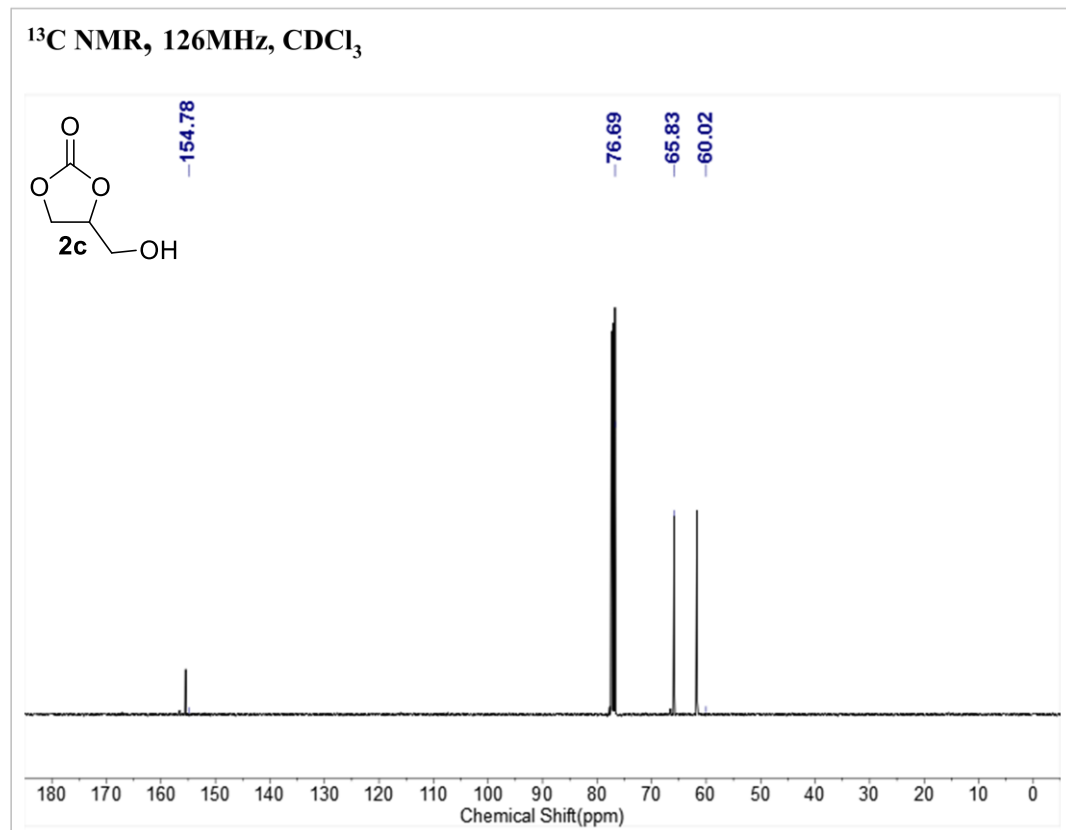
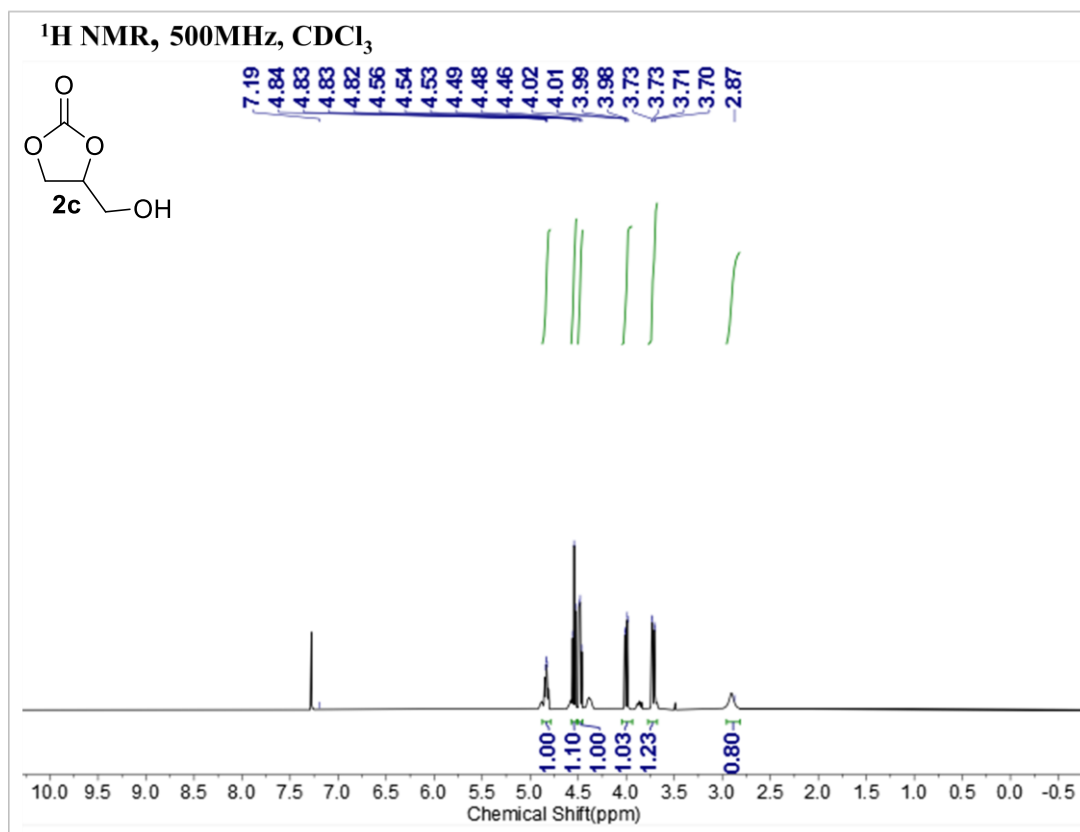
Cyclohexene carbonate (**2g**):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.52-4.46 (m, 2H), 1.95-1.89 (m, 4H), 1.66-1.57 (m, 2H), 1.50-1.41 (m, 2H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.34, 75.74, 26.76, 18.59 ppm.



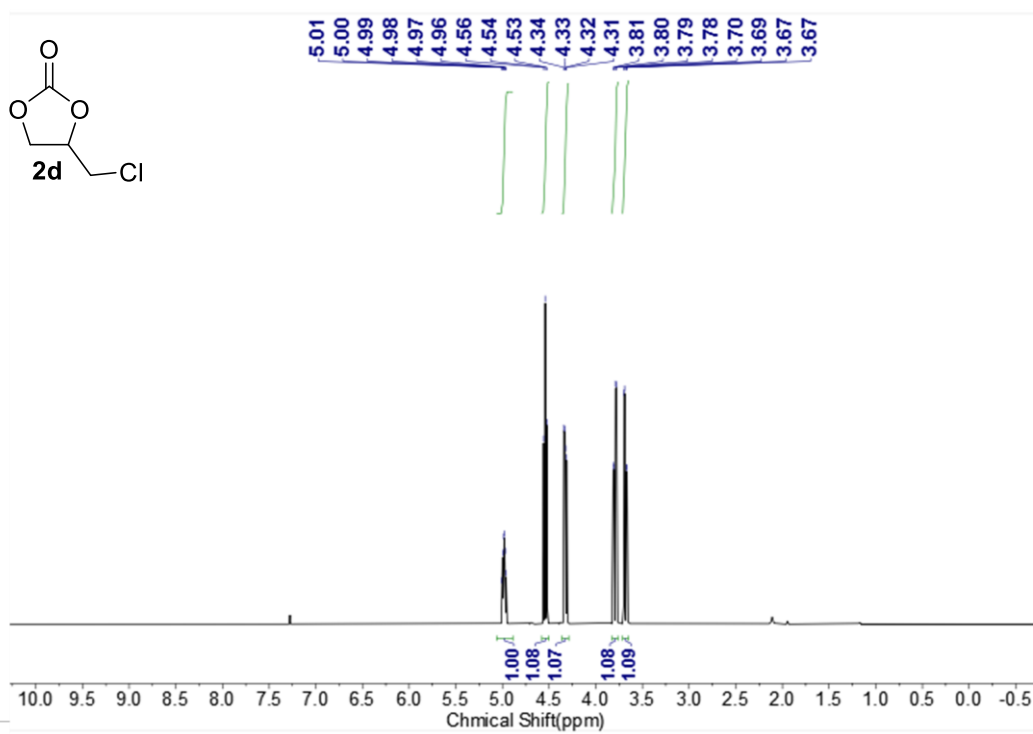
## 8. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of the resultant cyclic carbonates



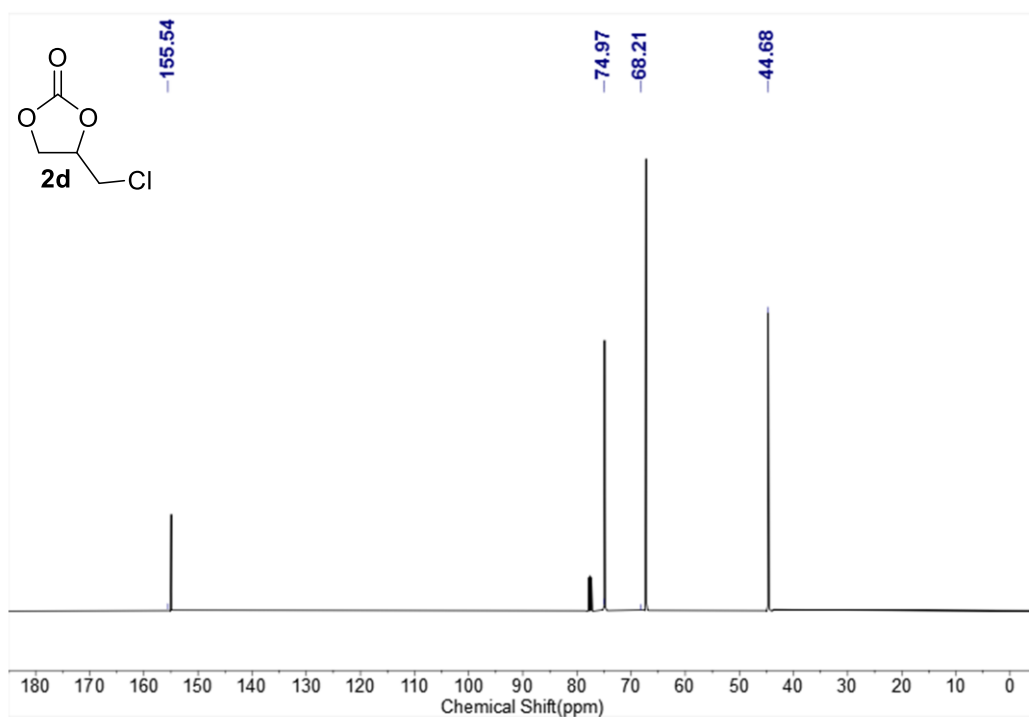


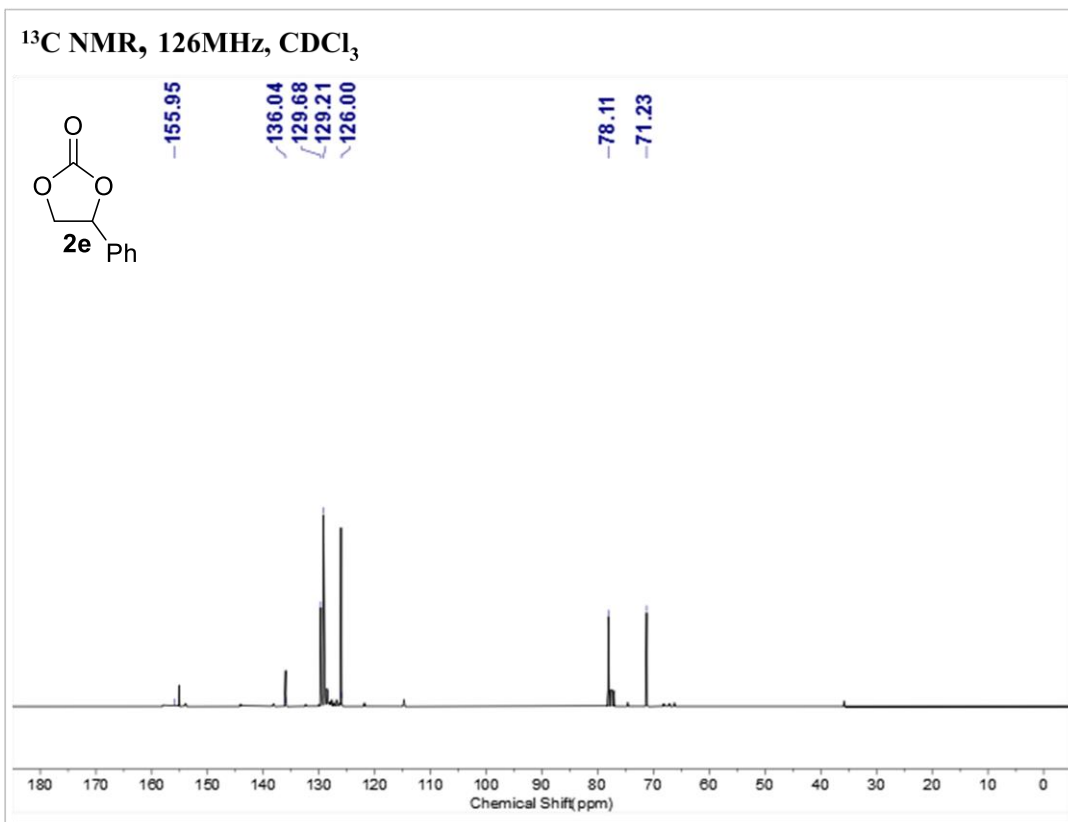
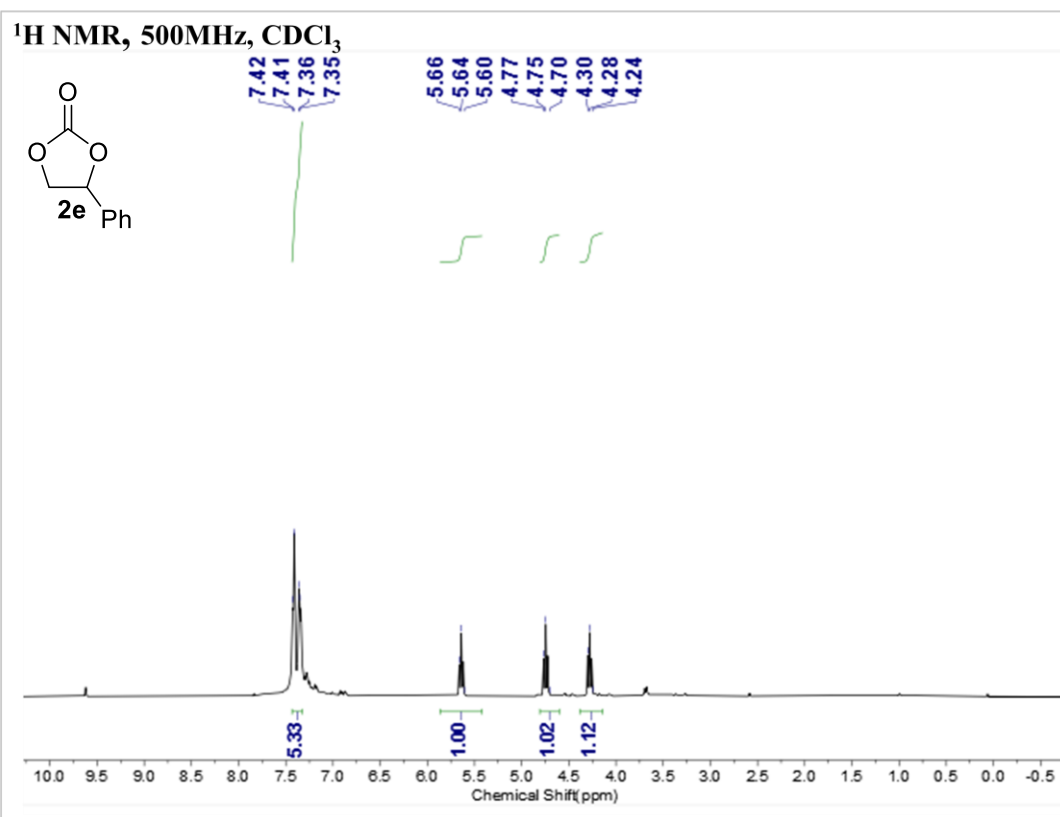


**<sup>1</sup>H NMR, 500MHz, CDCl<sub>3</sub>**

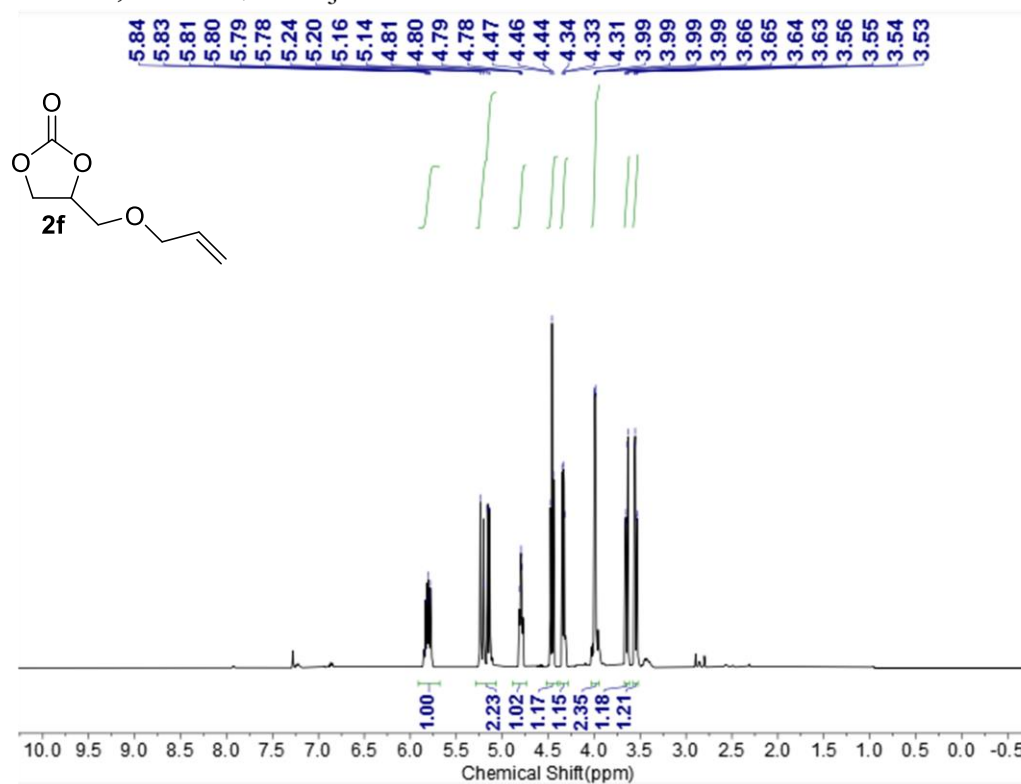


**<sup>13</sup>C NMR, 126MHz, CDCl<sub>3</sub>**





<sup>1</sup>H NMR, 500MHz, CDCl<sub>3</sub>



<sup>13</sup>C NMR, 126MHz, CDCl<sub>3</sub>

