

### Supporting Information

#### **Halide-free catalytic carbon dioxide fixation of epoxides to cyclic carbonates under atmospheric pressure**

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## **MATERIALS AND INSTRUMENTATION**

2,5-pyridine dicarboxylic acid (TCI), Terephthalic acid (Sigma Aldrich), epichlorohydrin and other epoxides (TCI and Sigma Aldrich),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck),  $\text{AlCl}_3$  (Merck) and organic solvents DMF, methanol and acetone (Merck), NMR solvents,  $\text{CDCl}_3$  (Sigma Aldrich) are used as obtained

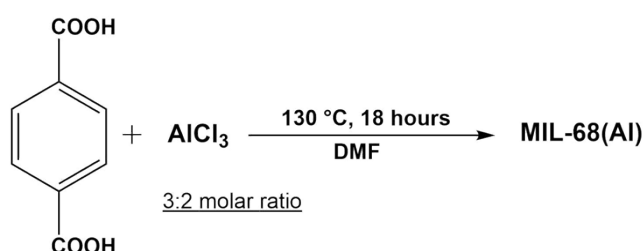
PXRD measurements are carried out in a Rigaku MiniFlex600 diffractometer attached with a D/tex ultradetector and Cu  $K\alpha$  source operating at 15 mA and 40 kV. FT-IR measurements are performed in a Perkin Elmer Spectrum instrument. Field emission SEM images and EDS are acquired on a SUPRA 55-VP instrument with patented GEMINI column technology. Prior to measurements, the samples are coated with a thin layer of gold-palladium to avoid charging effects. The TEM images and EDS are collected on a JEM 2100F field emission transmission electron microscope operating at 200 kV. Thermo-gravimetric analysis (TGA) was carried out on a Mettler-Toledo TG50 and SDT Q600 TG-DTA analyser under  $\text{N}_2$  atmosphere from  $30^\circ\text{C}$  to  $900^\circ\text{C}$  along with a ramp rate of  $10^\circ\text{C min}^{-1}$ . The surface chemistry of the samples are analyzed using X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II, ULVAC-PHI Inc., USA) equipped with micro-focused ( $200\ \mu\text{m}$ , 15 KV) monochromatic Al- $K\alpha$  X-Ray source ( $h\nu = 1486.6\ \text{eV}$ ).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are recorded on a JEOL ECS 400 MHz spectrometer and on a Bruker AVANCE Ultrashield Plus 500 MHz spectrometer.

### **Synthesis of Al-PDC**

The synthesis involved the reaction of 2,5-pyridine dicarboxylic acid (8 mmol, 1.34 g) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (8 mmol, 3.00 g). The reactants were dissolved in 30 ml *N,N'*-dimethyl formamide (DMF) and placed in a 50 ml Teflon lined autoclave and heated for 24 hours at  $115^\circ\text{C}$ . The autoclave was allowed to cool and the white solid precipitate (Al-PDC) was collected

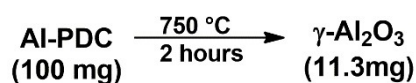
by centrifugation. Then the precipitate was washed with DMF and methanol to wash off the unreacted starting materials followed by washing with acetone. The precipitate was finally placed in a hot air oven overnight at 60 °C and then dried in a vacuum desiccator for further characterization and catalysis.

### Synthesis of MIL-68(Al)



To make MIL-68(Al), terephthalic acid (6 mmol, 1000 mg) and Aluminium Chloride (4 mmol, 533 mg) was used as per report in patent BASF. The mixture was dissolved in 20 ml *N,N*-dimethylformamide and heated at 130 °C for 18 hours in a round bottomed flask. After completion of the reaction, the solid white product was washed with DMF, methanol and acetone. Then it was placed overnight at 60 °C in a hot air oven for further characterization and catalysis.

### Calculation of Turnover Number



100 mg of Al-PDC was calcined at 750 °C and 11.3 mg  $\gamma\text{-Al}_2\text{O}_3$  was formed. In 1 equivalent  $\gamma\text{-Al}_2\text{O}_3$  is composed of almost 52.9% Al by mass.

Therefore, 11.3 mg  $\gamma\text{-Al}_2\text{O}_3$  has around 5.98 mg Al in it.

5.98 mg Al equals (5.98/26.98) mmol Al, which is equal to 0.22 mmol of Al. Here, we used 0.22 mmol Al(III) to convert 20 mmol epoxides.

So, we can conclude,

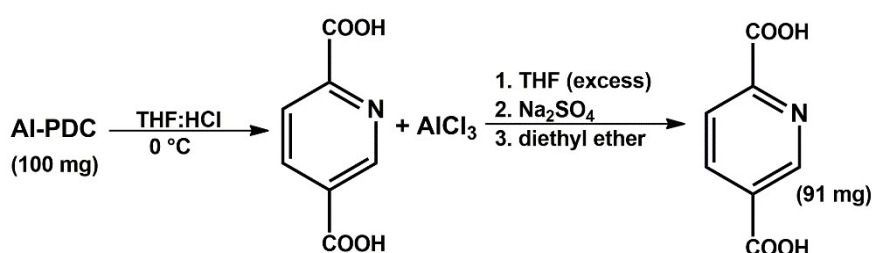
100 mg of Al-PDC contains 0.1 mmol of Al(III):  $(0.22/20) \times 100 = 1.1 \text{ mol\% w.r.t. Al(III)}$

Turnover Number = (moles of reactant consumed)/ (moles of catalyst).

For 100 % conversion of 20 mmol epoxides, TON =  $20/0.22$

So, **93 % conversion of epichlorohydrin:  $0.93 \times (20/0.22) = 85.4$**

### Quantification of 2,5-PDCA in Al-PDC



A solution of 0.5 ml conc. HCl and 5.5 ml THF was added to 100 mg as-prepared Al-PDC at 0 °C and stirred. This led to leaching of the Al(III) ion from Al-PDC and resulted in degradation of the polymeric framework. To the resulting solution excess THF (20 ml) was added. Anhydrous Na<sub>2</sub>SO<sub>4</sub> was added to the solution to absorb water. The resulting mixture was filtered to remove the solid Na<sub>2</sub>SO<sub>4</sub> and the THF was dried in rotavapor. The solid white precipitate was washed multiple times with diethyl ether and dried in a vacuum desiccator. The solid precipitate weighed 91 mg and the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the material confirmed it to be 2,5-PDCA. Hence, the stoichiometry of the ligand (91 mg) in 100 mg AL-PDC was determined.

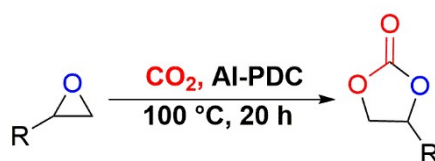
**Table S1.** Effect of reaction parameters on the coupling of CO<sub>2</sub> and epichlorohydrin

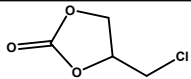
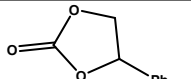
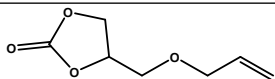
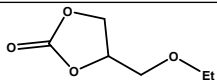
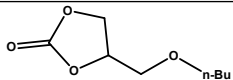
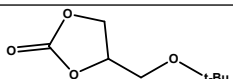
Entry	Catalysts Used	Temperature	Time	Conversion
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		(°C)	(hours)	(%)
1.	No Catalyst	100	20	ZERO
2.	2,5-PDCA	100	20	12
3.	Al(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	100	20	2
4.	Physical mixture of 2,5-PDCA and Al(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	100	20	25
5.	Diaspore [ $\alpha$ -AlO(OH)]	100	20	33
6.	$\gamma$ -Alumina	100	20	<1
7.	<b>Al-PDC</b>	<b>100</b>	<b>20</b>	<b>93</b>
8.	Al-PDC	55	20	20
9.	Al-PDC	70	20	33
10.	Al-PDC	85	20	72
11.	Al-PDC	100	20	93
12.	Al-PDC	115	20	100
13.	Al-PDC	100	8	52
14.	Al-PDC	100	12	66
15.	Al-PDC	100	16	78
16.	Al-PDC	100	20	93
17.	Al-PDC	100	24	95
18.	Al-PDC (post 180 °C calcination)	100	20	92
19.	Al-PDC (post 250 °C calcination)	100	20	44
20.	Al-PDC (post 350 °C calcination)	100	20	5
21.	Al-PDC (post 450 °C calcination)	100	20	<1
22.	MIL-68(Al)	100	20	15

Conditions: epoxide 20 mmol; 100 mg Al-PDC (or other mentioned substances like 100 mg diaspore, 100 mg 2,5-PDCA etc.); 1 atm. CO<sub>2</sub>; Conversion was measured using <sup>1</sup>H-NMR spectroscopy

**Table S2.** Isolated yield of six synthesized cyclic carbonates.



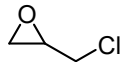
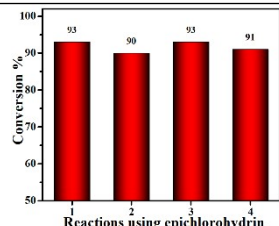
Cyclic Carbonate	Molecular weight (Cyclic carbonate)	Weight obtained	Yield (%)
	136.53	2477 mg	91
	<b>164.16</b>	<b>23.36 g<sup>a</sup></b>	<b>95</b>
	158.15	2943 mg	93
	146.14	2576 mg	88
	174.20	2231 mg	64
	174.20	1603 mg	46

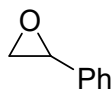
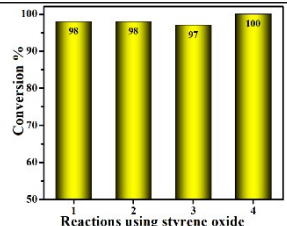
Conditions: epoxide 20 mmol; 100 mg Al-PDC as catalyst; 1 atm. CO<sub>2</sub>; 100 °C; 20 h. a: 150 mmol styrene oxide, 750 mg Al-PDC.

**Table S3.** Comparison of the Catalytic Activity of different materials that performed CO<sub>2</sub> fixation with epoxides under halide free conditions.

Catalyst (Conversion %)	Pressure	Temp (°C)	Time (h)	Nature	Reference
Pyridyl Salicylimines (99 %)	1 atm	100	24	Heterogeneous	ACS Appl. Mater. Interfaces 2018, 10, 9478-9484
Bifunctional organic catalyst (99 %)	2 MPa	150	24	Homogeneous	Green Chem., 2021, 23, 1147–1153
Zn MOFs (99 %)	1 bar	100	24	Heterogeneous	Chem. – Eur. J. 2019, 25, 11474– 11480.
Salophen (100 %)	10 bar	120	3.5, 24	Homogeneous	ACS Catal. 2019, 9, 1895-1906
Polyurethane (99 %)	9 MPa	150	16	Heterogeneous	ACS Sustainable Chem. Eng. 2020, 8, 4337–4340
Schiff Base (99 %)	1 MPa	110	4, 12	Homogeneous	Appl. Catal. Gen. 2020, 601, 117646
Salophen	10 bar	100		Homogeneous	Catal. Sci. Technol., 2021,11, 2529-2539
<b>Co-ordination polymers (93% for EPCH and 98% for S.O.)</b>	<b>1 atm.</b>	<b>100</b>	<b>20</b>	<b>Heterogeneous</b>	<b>This Work</b>

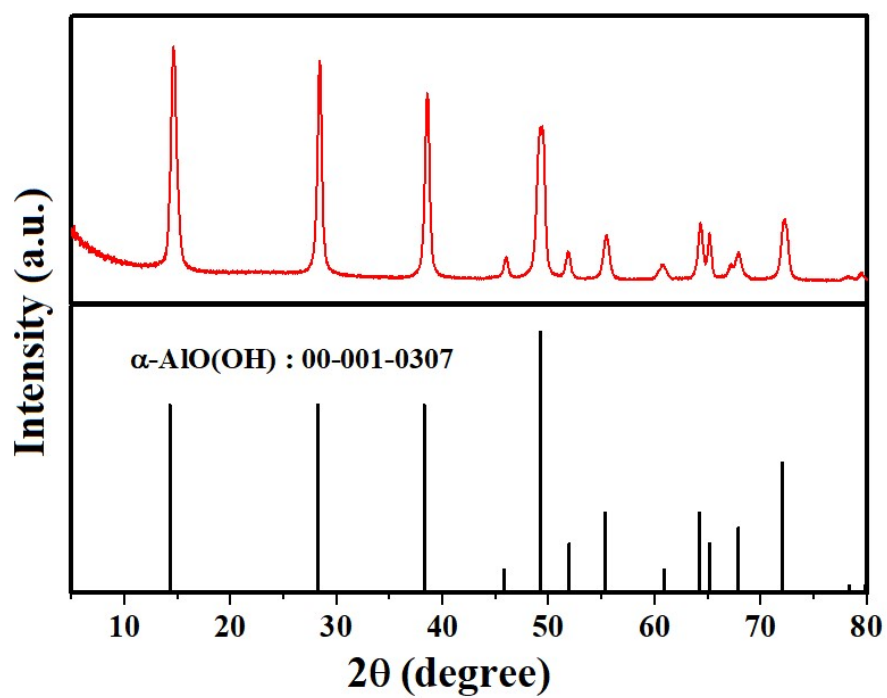
**Table S4.** Precision of the catalytic activity of Al-PDC to carryout CO<sub>2</sub> fixation using two different catalysts under optimized conditions.

Entry	Epoxide used	Conversion upon multiple reactions	Standard Deviation	Bar Diagram
1.		a. 93 b. 90 c. 93 d. 91	1.5	

2.		a. 98	1.26	
		b. 98		
		c. 97		
		d. 100		

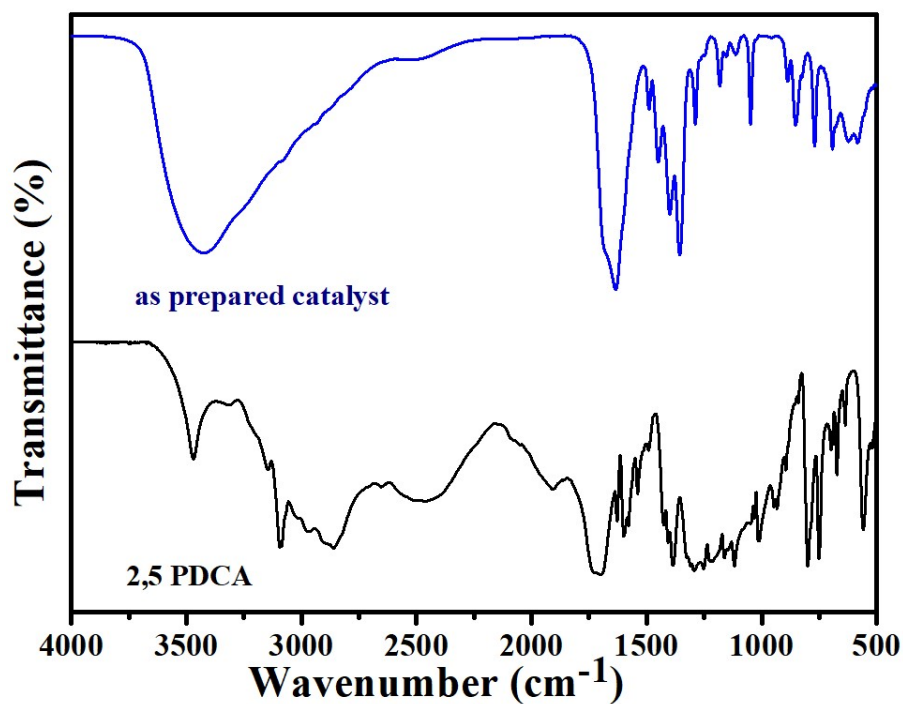
Conditions: epoxide 20 mmol; 100 mg Al-PDC as catalyst; 1 atm. CO<sub>2</sub>; 100 °C; 20 h.

Conversion was measured using <sup>1</sup>H-NMR spectroscopy

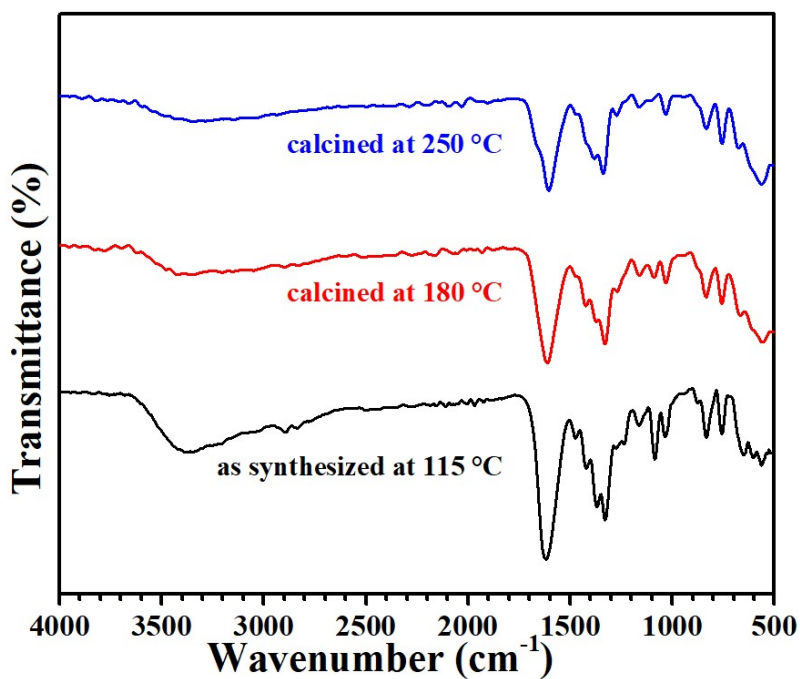




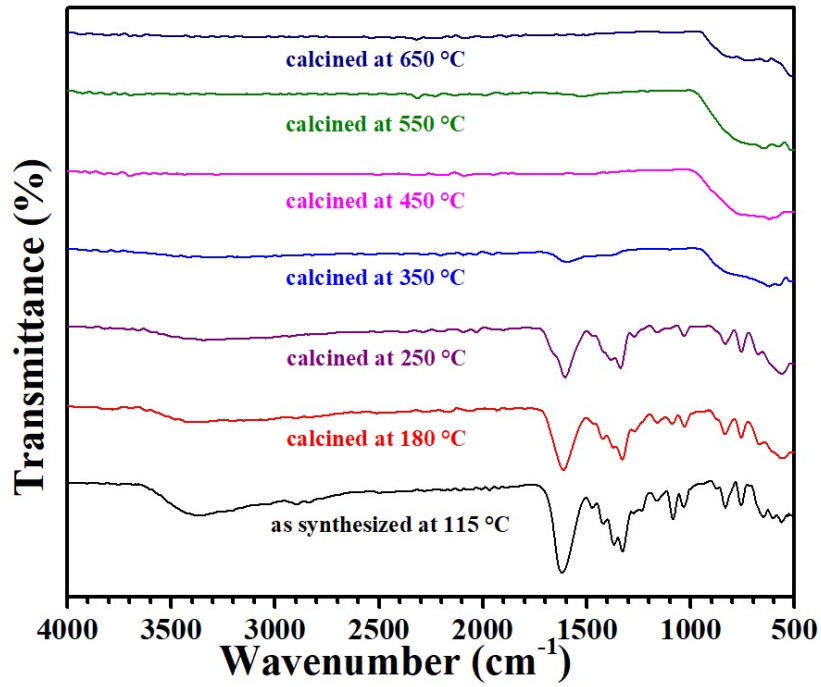
**Fig S1.** PXRD pattern of Diaspore [AlO(OH)]



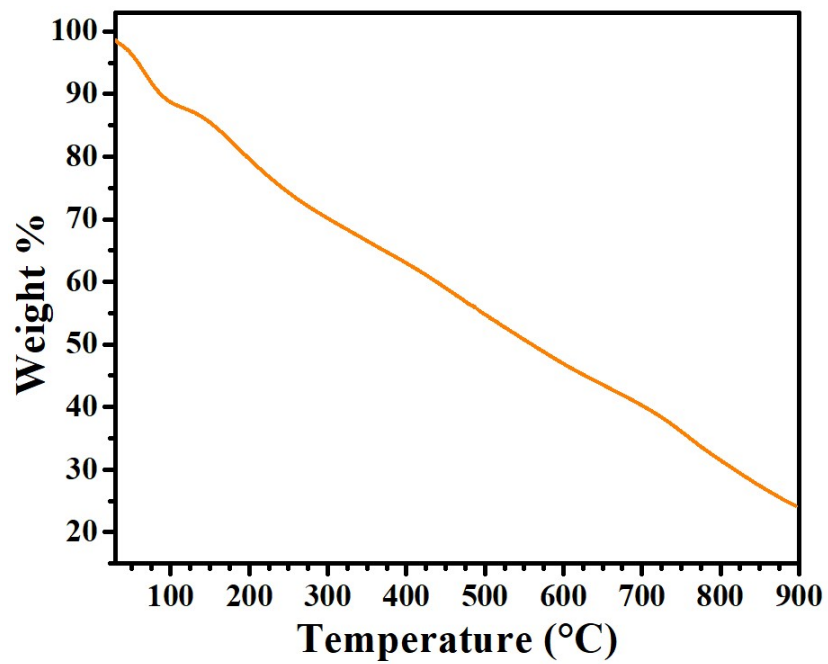
**Fig S2.** FT-IR spectra of 2,5-PDCA and as-prepared Al-PDC.



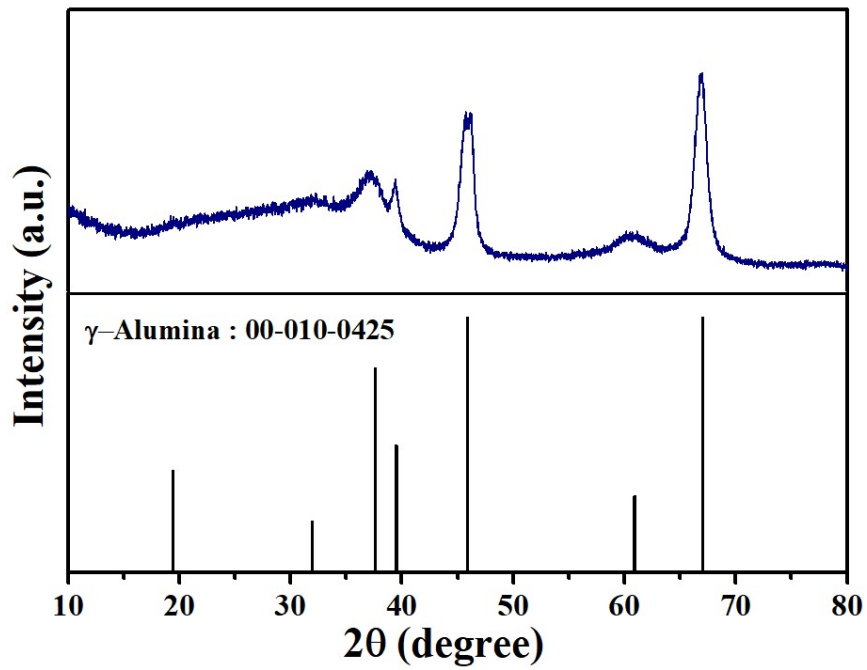
**Fig S3.** FT-IR spectra of as-prepared Al-PDC, calcined Al-PDC at 180 °C and 250 °C. The absence of wide peaks at around 3000-3500  $\text{cm}^{-1}$  is due to the evaporation of surface adsorbed water molecules upon calcination.



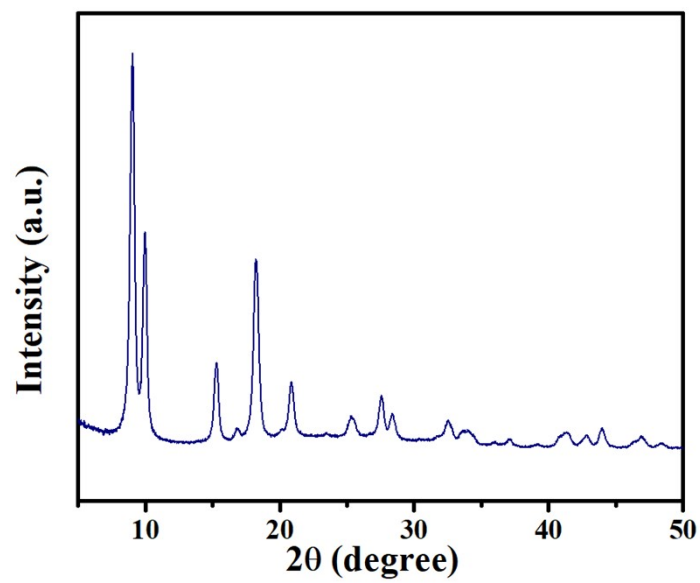
**Fig S4.** FT-IR spectra of the materials formed upon calcination of Al-PDC in different temperatures.



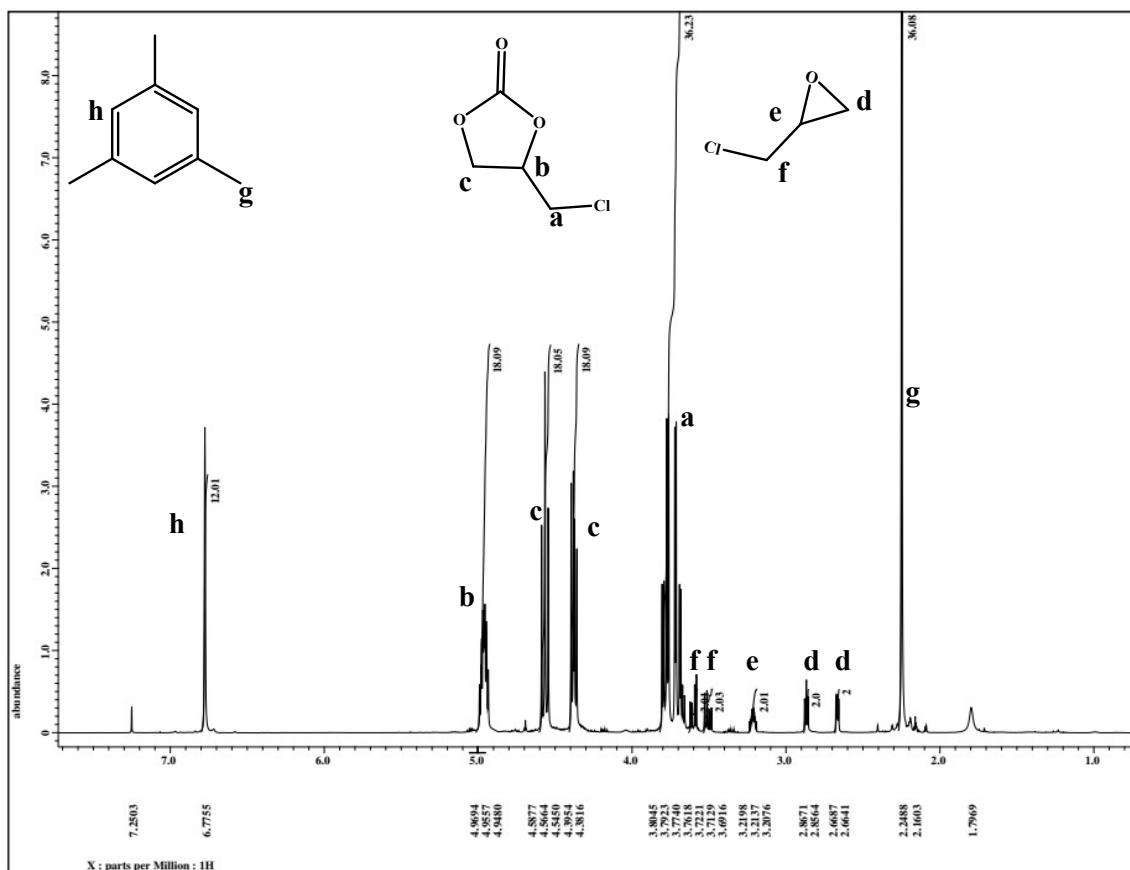
**Fig S5.** The TGA pattern of Al-PDC



**Fig S6.** PXRD pattern of  $\gamma\text{-Al}_2\text{O}_3$  formed upon calcination of Al-PDC at 750 °C along with the standard pattern of  $\gamma\text{-Al}_2\text{O}_3$



**Fig S7.** PXRD of MIL-68(Al)



**Fig S8.** <sup>1</sup>H-NMR spectrum of reaction mixture containing mesitylene as internal standard, epichlorohydrin and 4-(chloromethyl)-1,3-dioxolan-2-one (90% conversion). The mixture contains around 4 mmol mesitylene, >18 mmol 4-(chloromethyl)-1,3-dioxolan-2-one and 2 mmol epichlorohydrin.

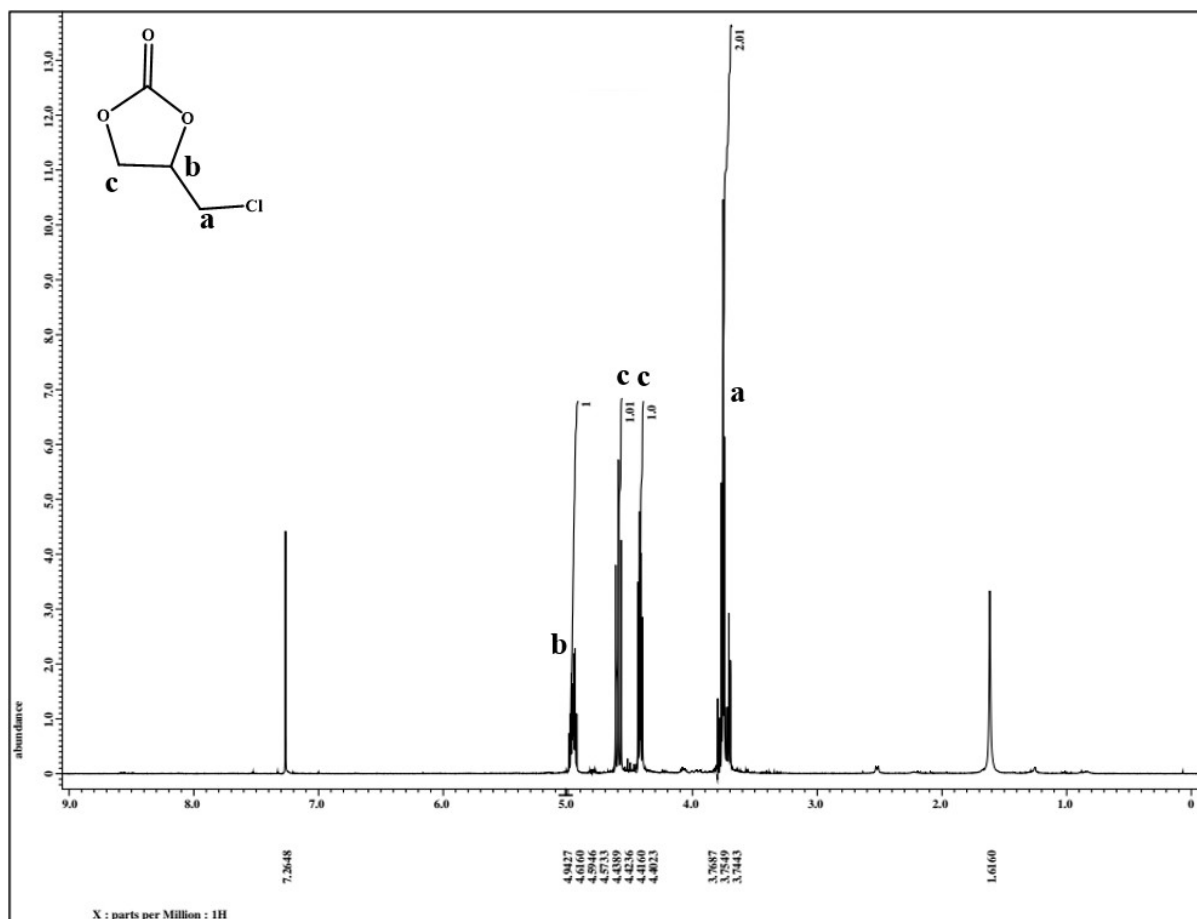
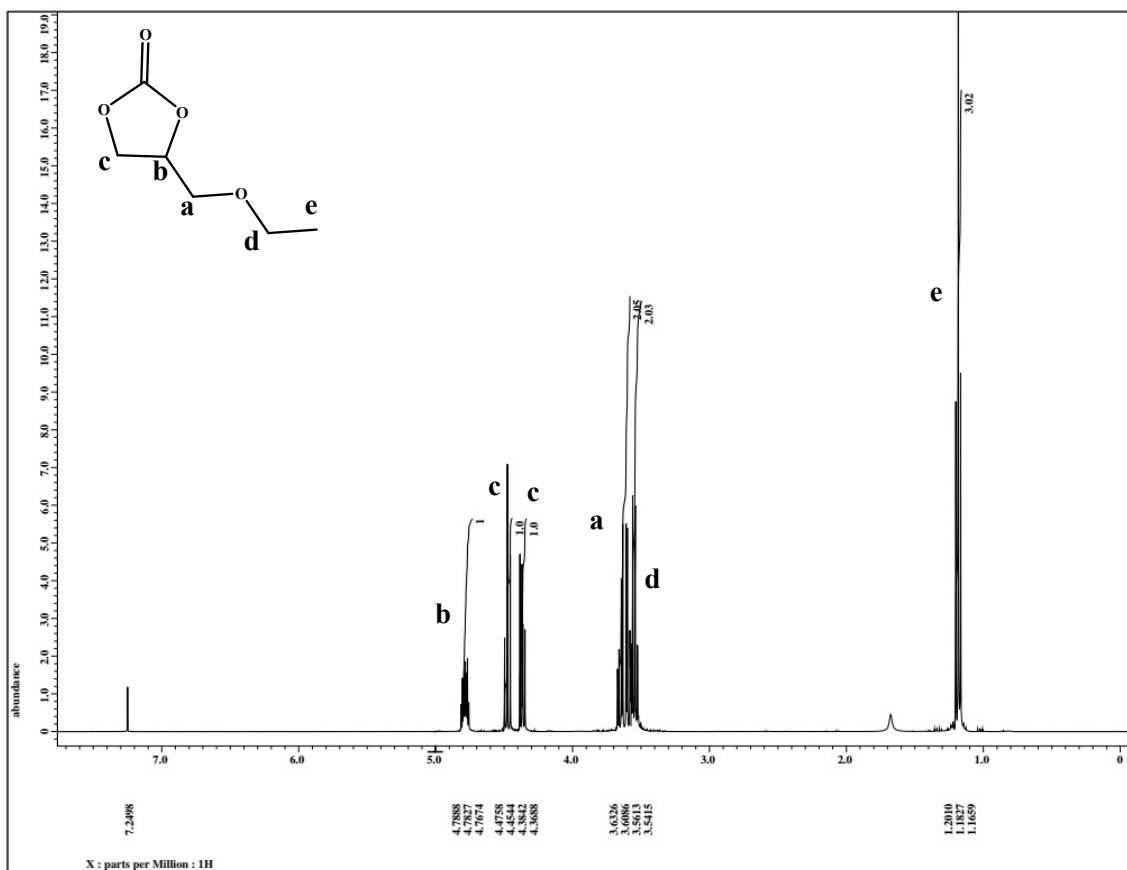
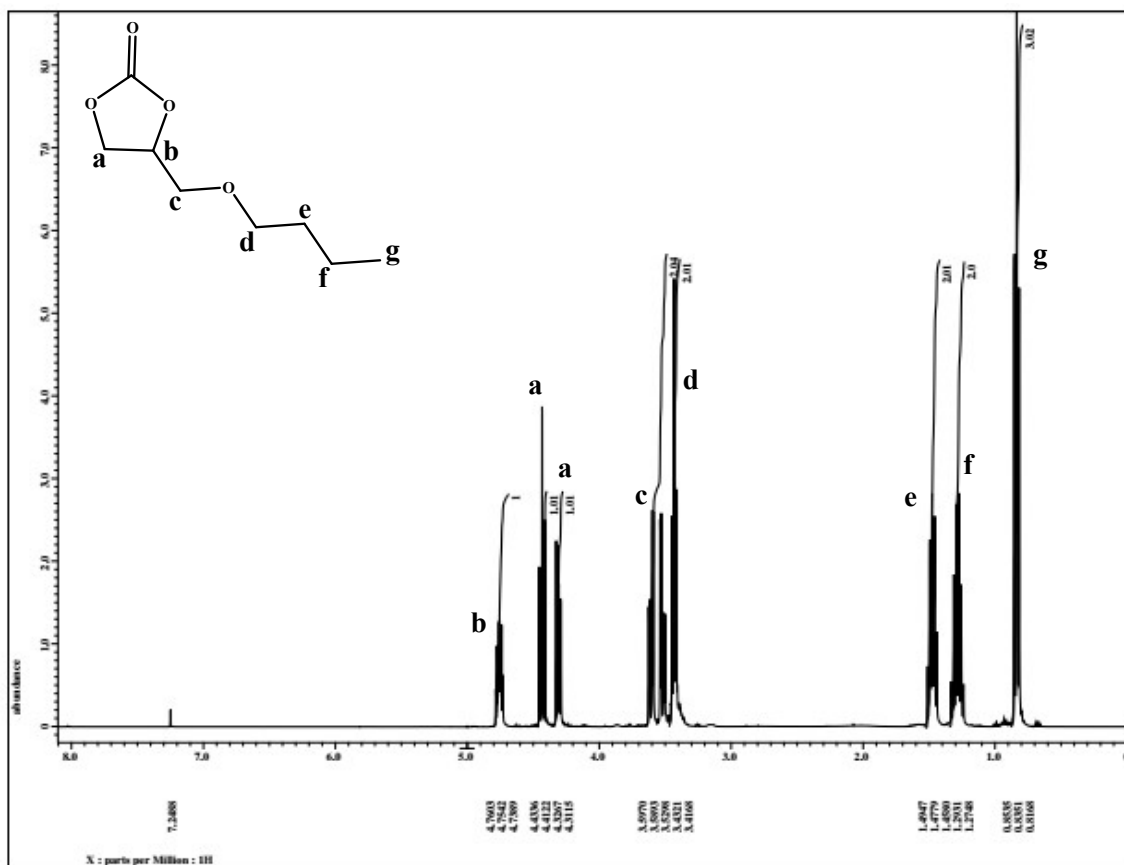


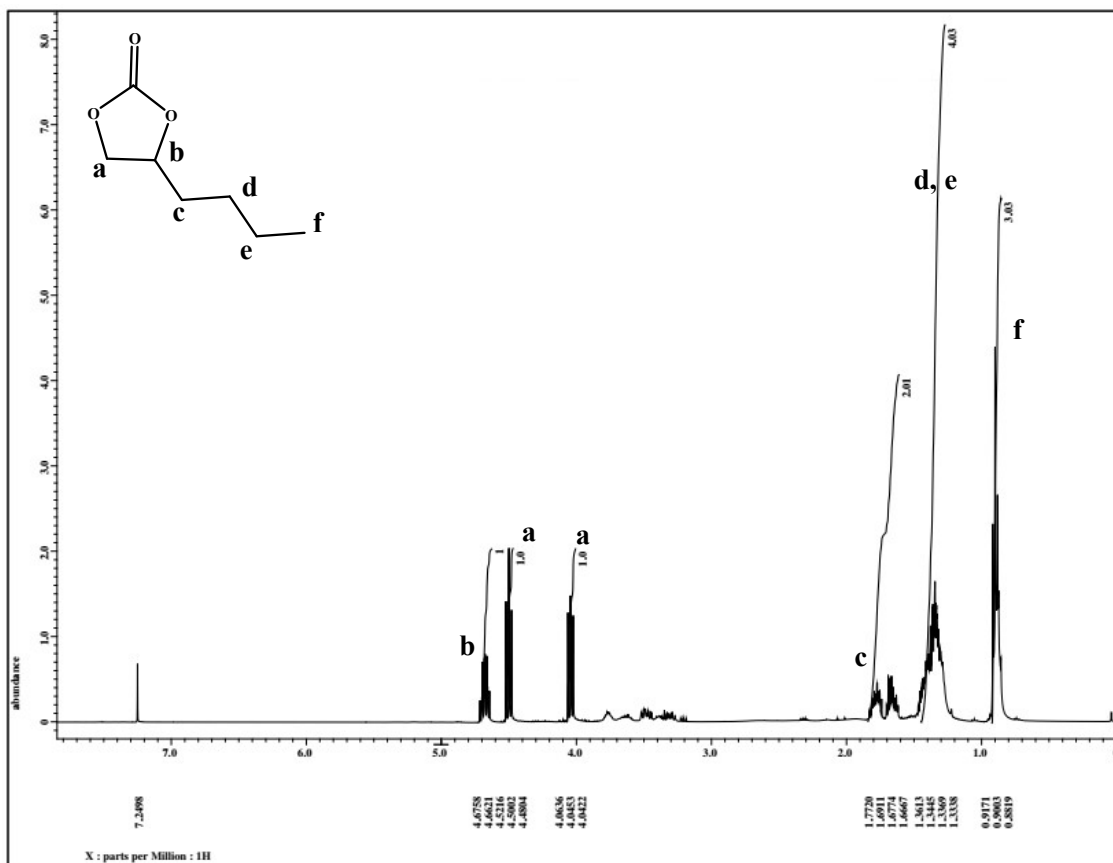
Fig S9. <sup>1</sup>H-NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 400 MHz)



**Fig S10.** <sup>1</sup>H-NMR of 4-(ethoxymethyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 400 MHz)

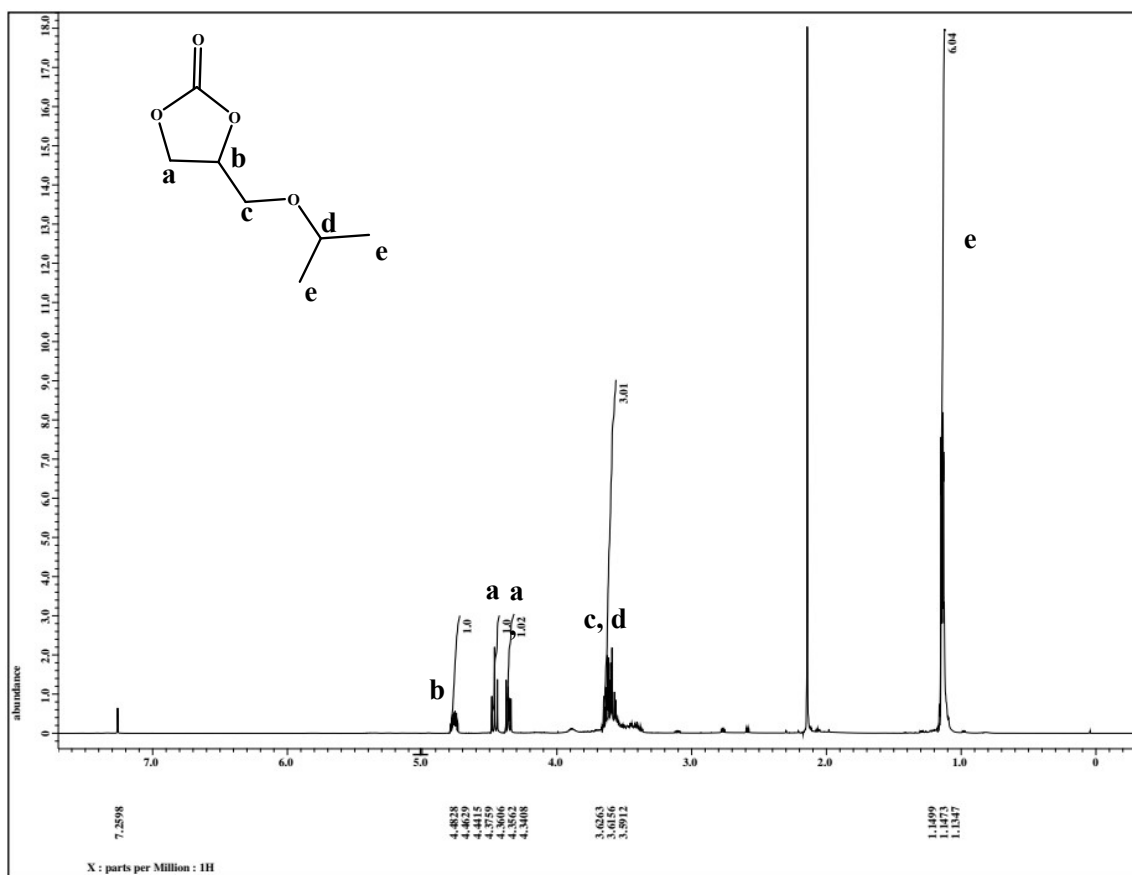


**Fig S11.** <sup>1</sup>H-NMR spectrum 4-(n-butoxymethyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 400 MHz)

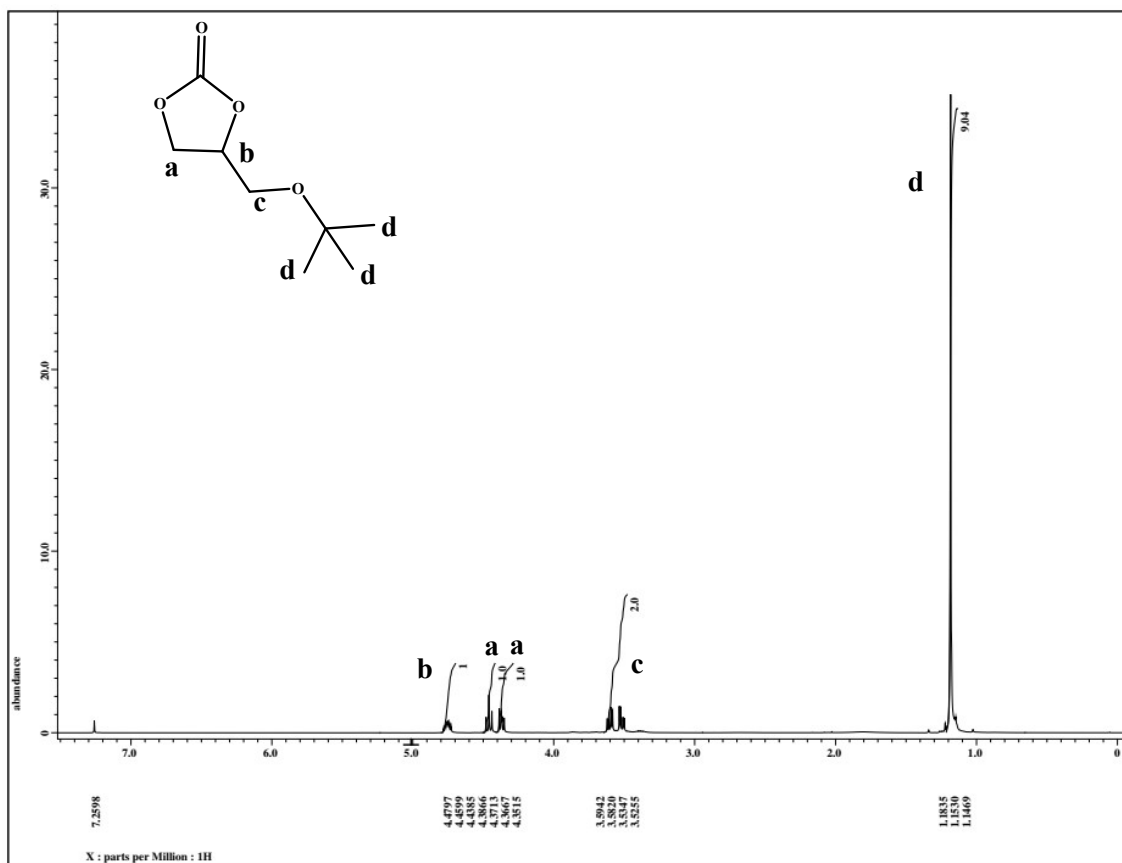


**Fig S12.** <sup>1</sup>H-NMR spectrum 4-(butyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 400 MHz)





**Fig S13.** <sup>1</sup>H-NMR spectrum 4-(isopropoxymethyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 400 MHz)



**Fig S14.** <sup>1</sup>H-NMR spectrum 4-(tert-butoxymethyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 400 MHz)

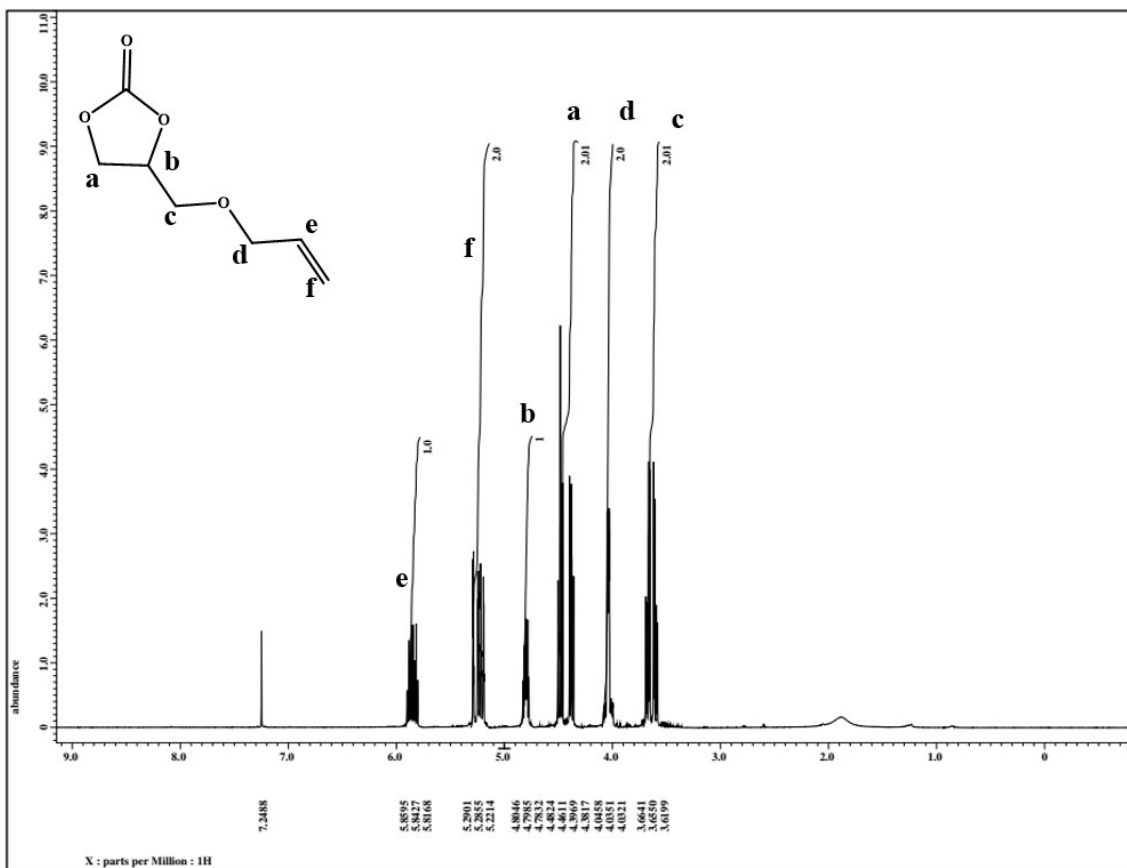
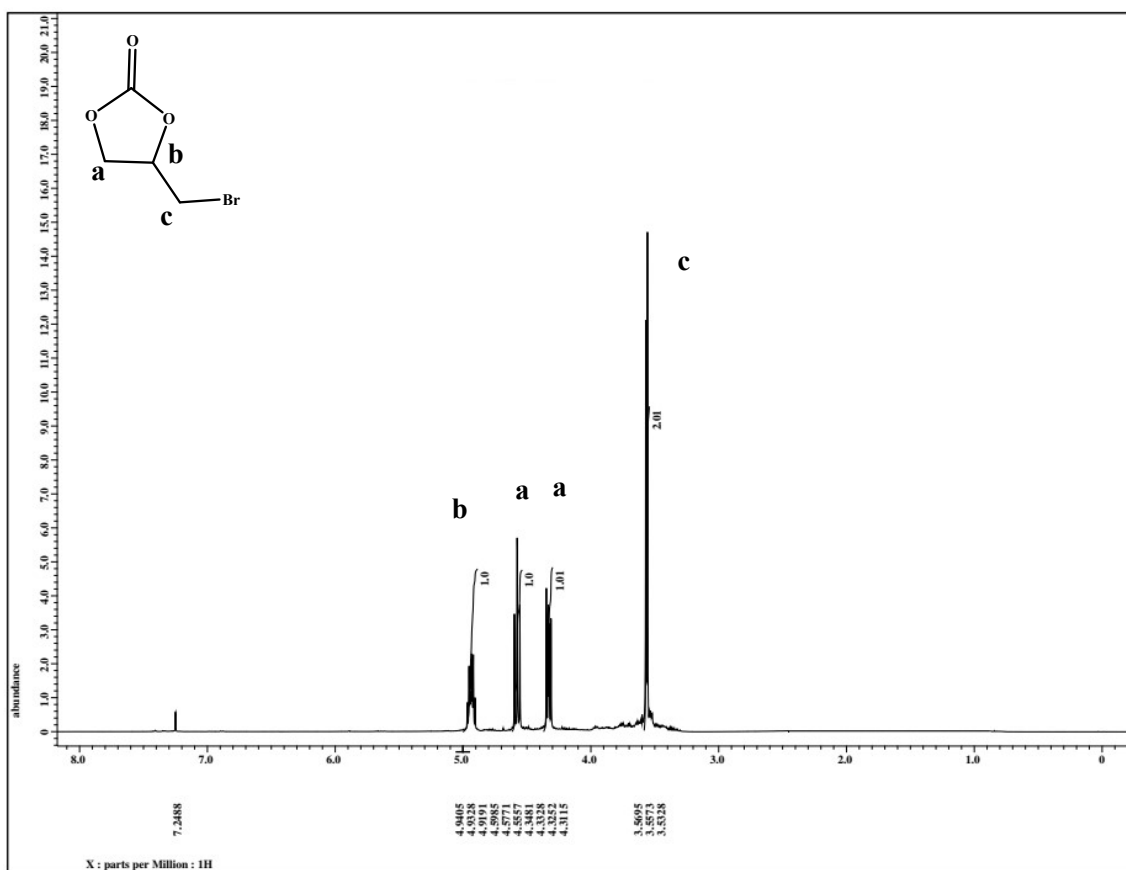
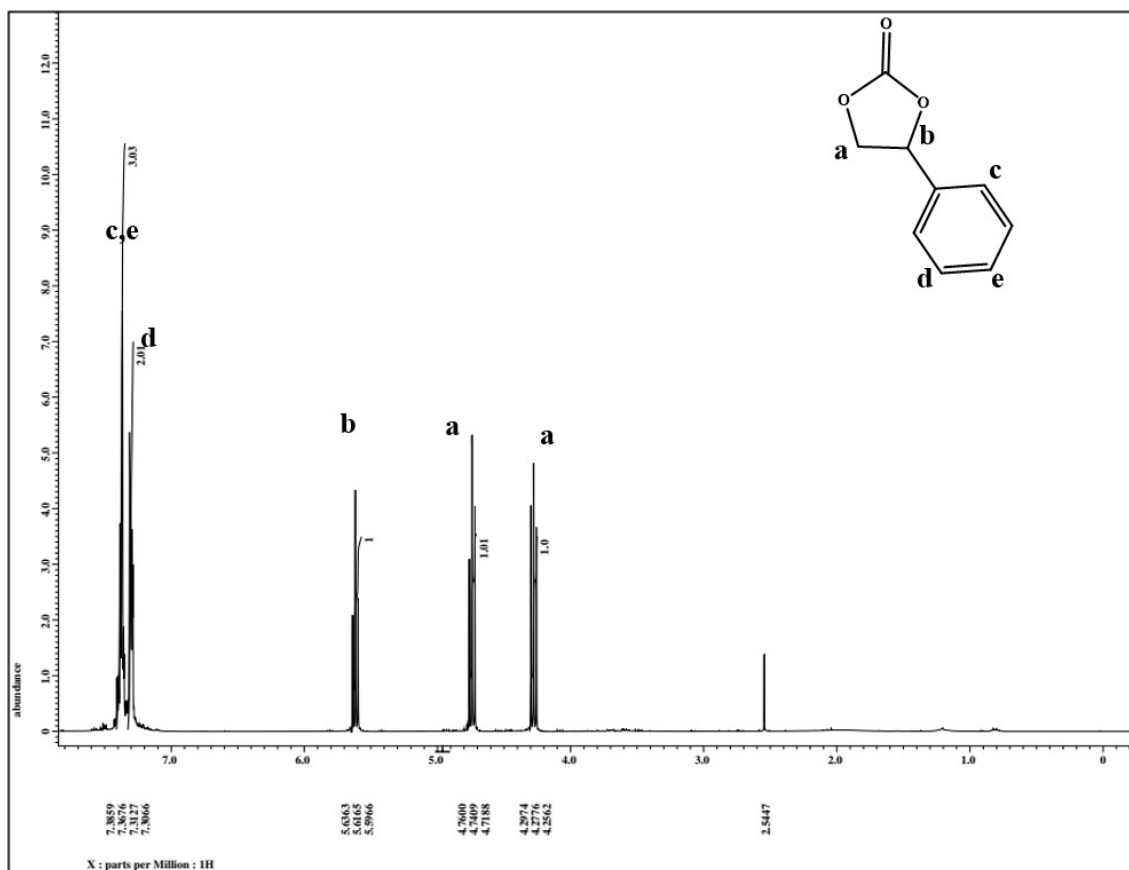


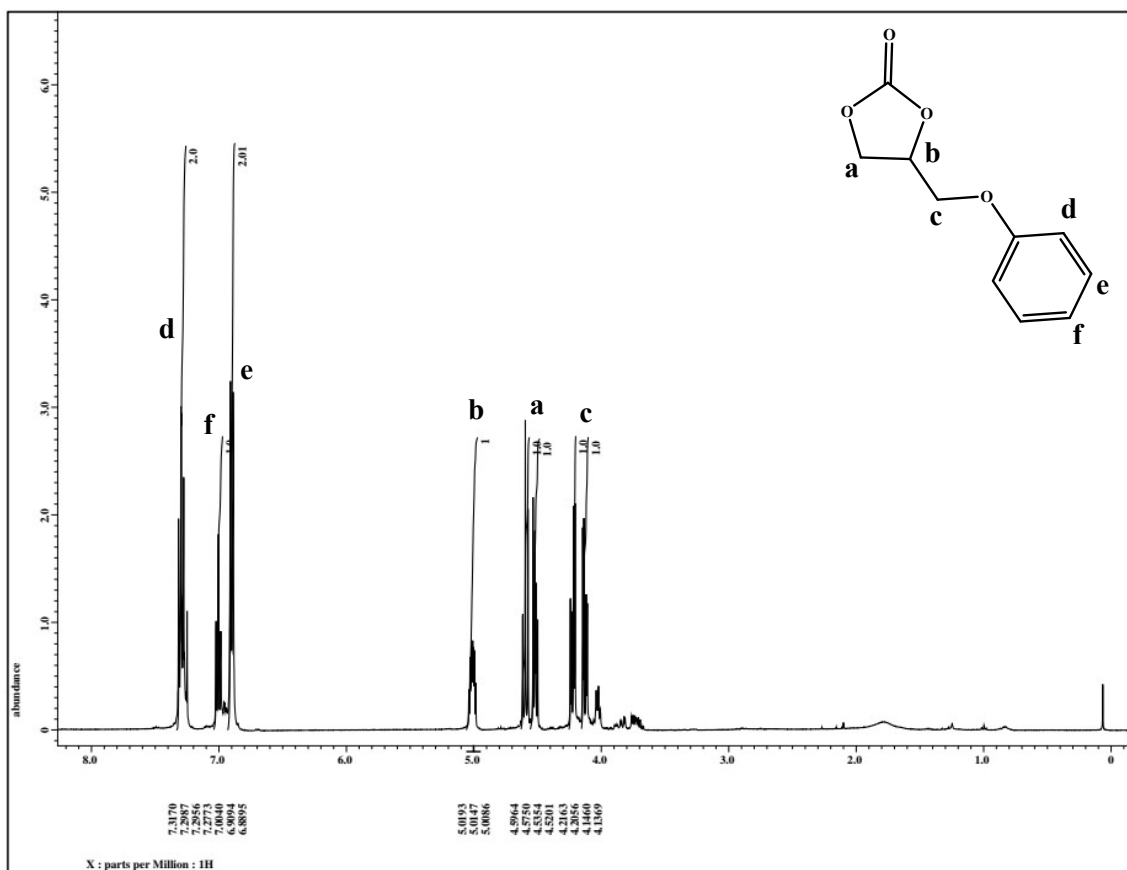
Fig S15.  $^1\text{H}$ -NMR spectrum 4-(allyloxymethyl)-1,3-dioxolan-2-one ( $\text{CDCl}_3$ , 400 MHz)



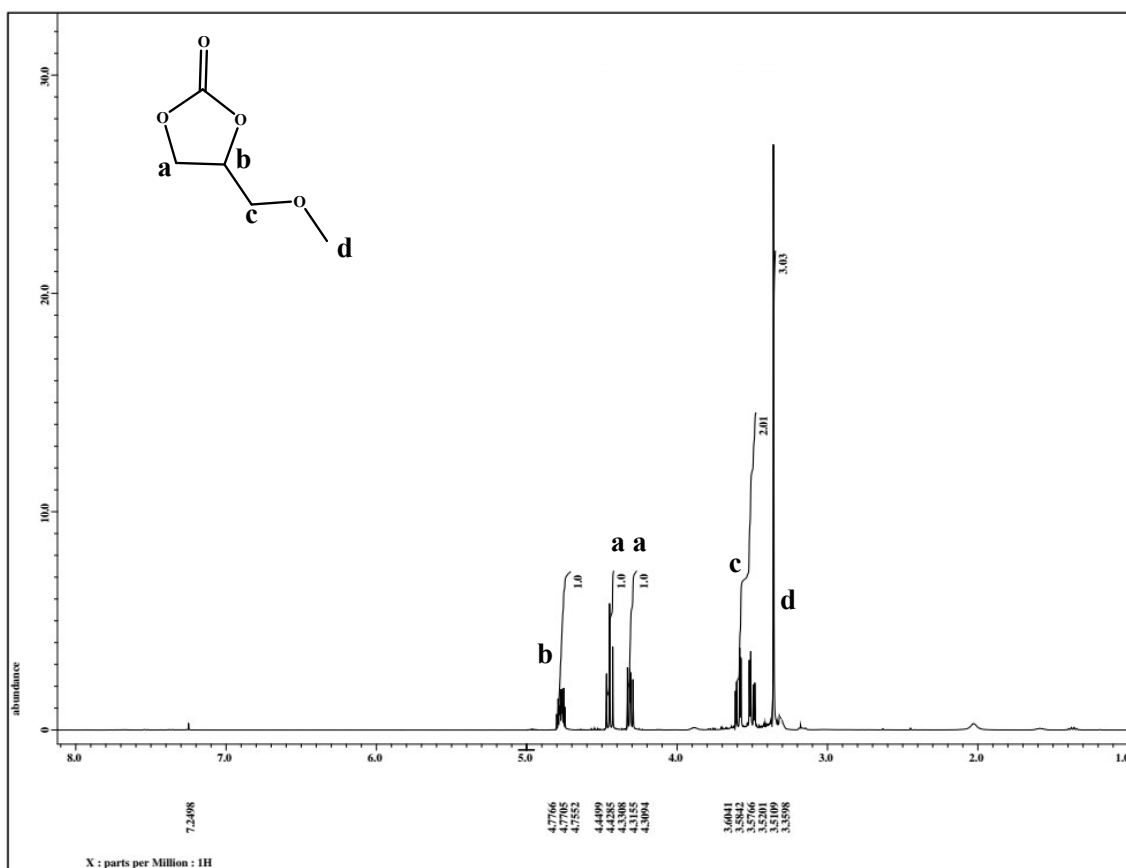
**Fig S16.** <sup>1</sup>H-NMR spectrum of 4-(bromomethyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 400 MHz)



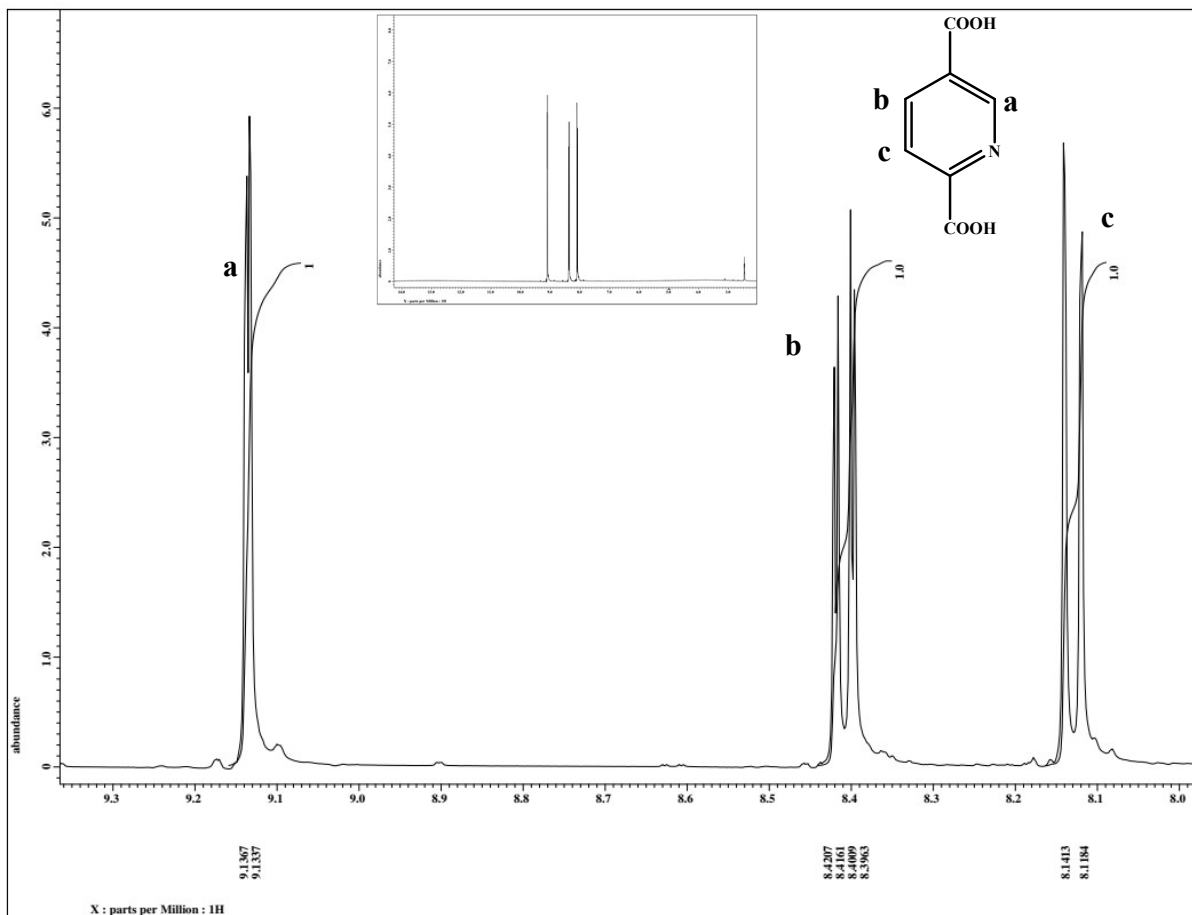
**Fig S17.**  $^1\text{H-NMR}$  spectrum of 4-(phenyl)-1,3-dioxolan-2-one (DMSO- $d_6$ , 400 MHz)



**Fig S18.** <sup>1</sup>H-NMR spectrum 4-(phenoxymethyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 400 MHz)



**Fig S19.** <sup>1</sup>H-NMR spectrum 4-(methoxymethyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 400 MHz)

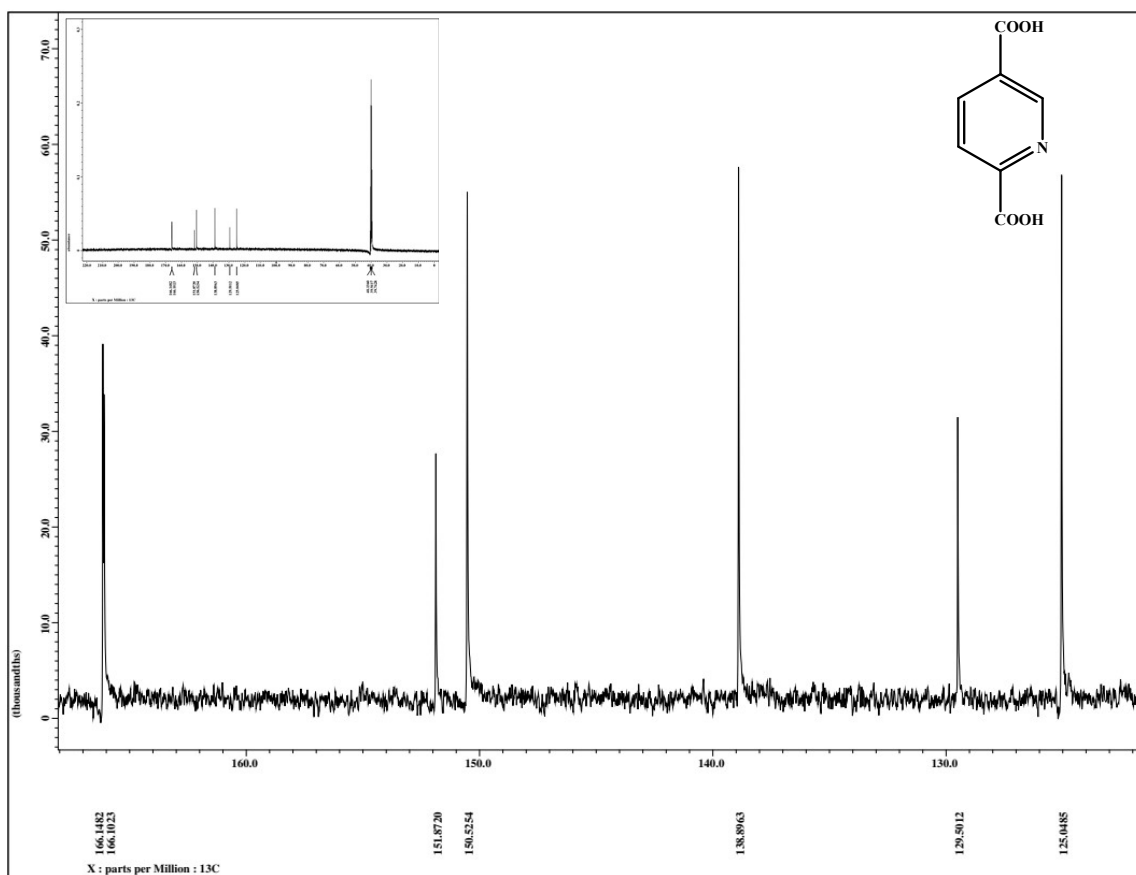


**Fig S20.**  $^1\text{H-NMR}$  spectrum commercially purchased 2,5-Pyridine dicarboxylic acid ( $\text{DMSO-d}_6$ , 400 MHz). Full spectrum is inset

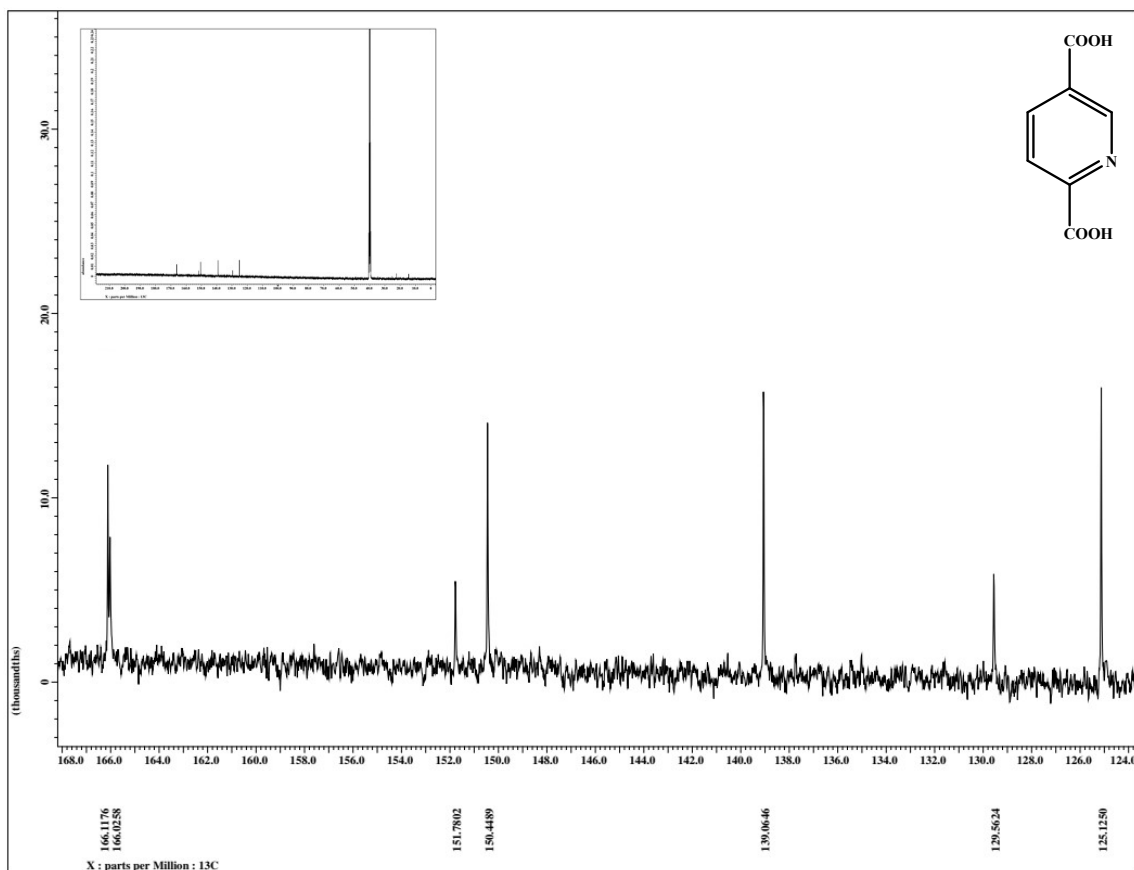




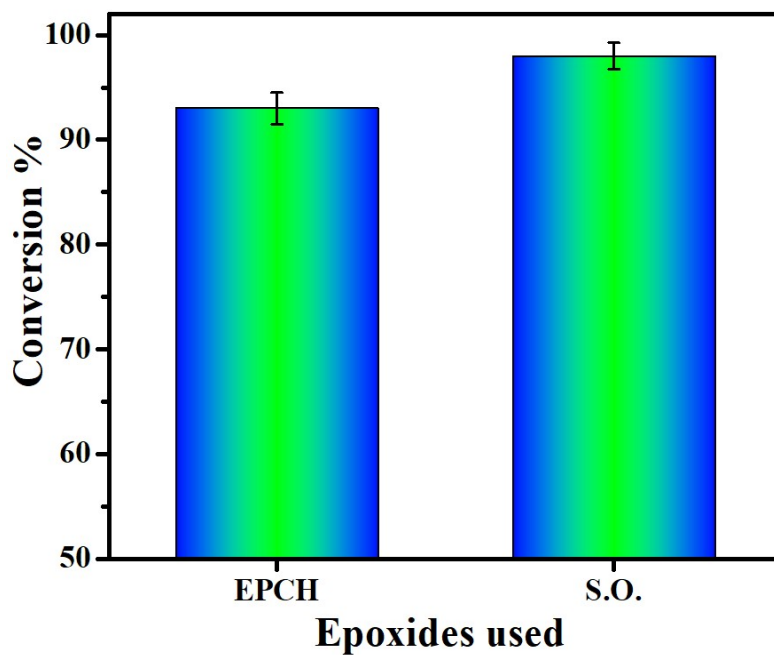
**Fig S21.**  $^1\text{H}$  NMR spectrum of 2,5-PDCA recovered digesting Al-PDC in conc. HCl. Full spectrum is inset



**Fig S22.**  $^{13}\text{C}$ -NMR spectrum commercially purchased 2,5-Pyridine dicarboxylic acid (DMSO- $d_6$ , 400 MHz). The full spectrum from 0 to 220 ppm is inset.



**Fig S23.** <sup>13</sup>C NMR spectrum of 2,5-PDCA recovered digesting Al-PDC in conc. HCl. Full spectrum is inset



**Fig. S24.** Conversion of epichlorohydrin (EPCH) and styrene oxide (S.O.) along with the error bar.