

## **Diaspore as Efficient Halide-free Catalysts for the Conversion of CO<sub>2</sub> into Cyclic Carbonates**

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Electronic Supplementary Information (ESI) available:

## **MATERIALS AND INSTRUMENTATION**

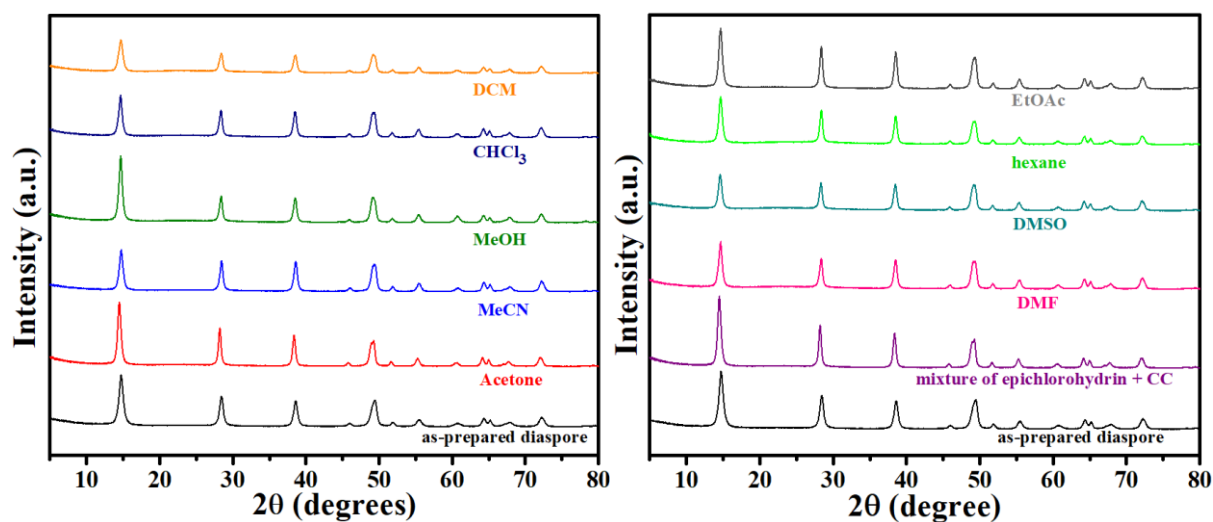
Epichlorohydrin and other epoxides (TCI and Sigma Aldrich),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck) and organic solvents DMF, methanol and acetone (Merck), NMR solvents,  $\text{CDCl}_3$  (Sigma Aldrich) are used as obtained.

PXRD measurements are carried out in a Rigaku MiniFlex600 diffractometer attached with a D/tex ultradetector and  $\text{Cu K}\alpha$  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.  $^1\text{H}$  spectra are recorded on a Bruker AVANCE Ultrashield Plus 500 MHz spectrometer.

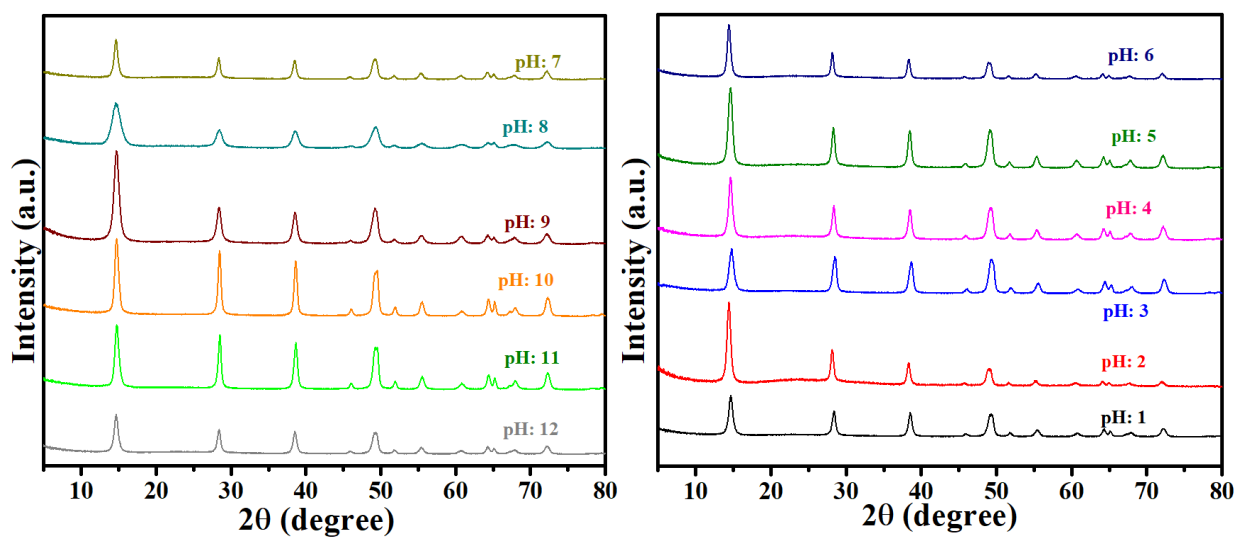
### **Solvent stability and pH stability**

The robustness of the as-prepared diaspore, its stability was checked in common solvents and pH. Solvents like ethanol, ethyl acetate, chloroform, *N,N'*-dimethyl formamide (DMF), dimethyl sulphoxide, acetone, etc were added in different glass vials containing 30 mg of the materials and kept in those solvents for 12 hours. Later the solvents were decanted and after drying, the PXRD patterns of the samples are recorded.

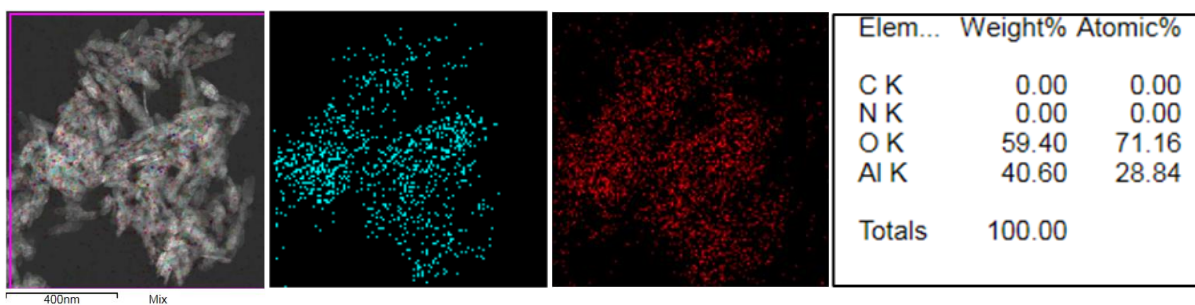
In a similar way 50 mg of the material is taken in 12 different vials. 10 ml solutions of different pH ranging from 1 to 12 were added to it and kept for 12 hours. The solvents were decanted and after drying, the PXRD patterns were recorded.



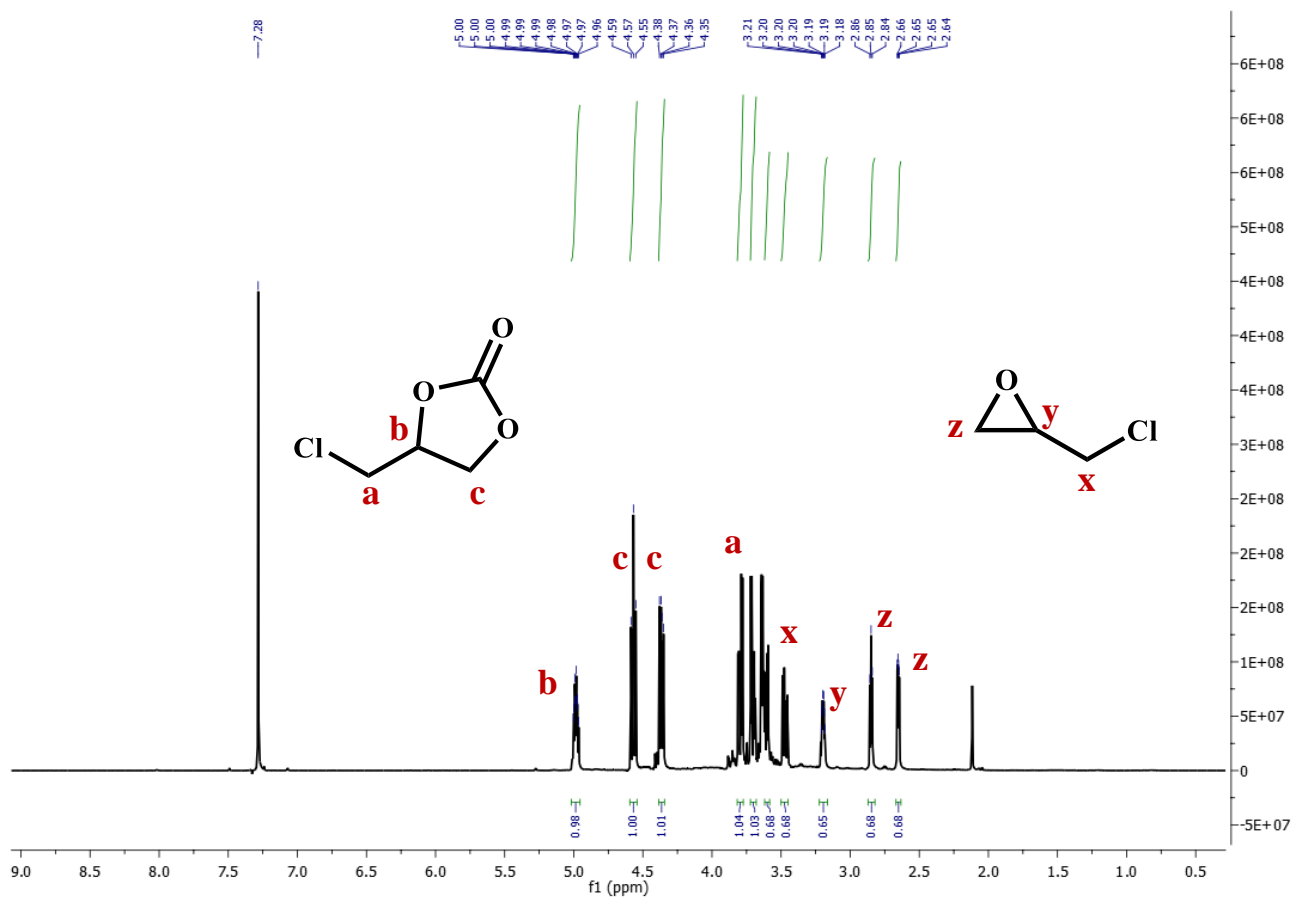
**Figure S1.** PXR D patterns of dias pore recorded after stirring in the above solvents for twelve hours.



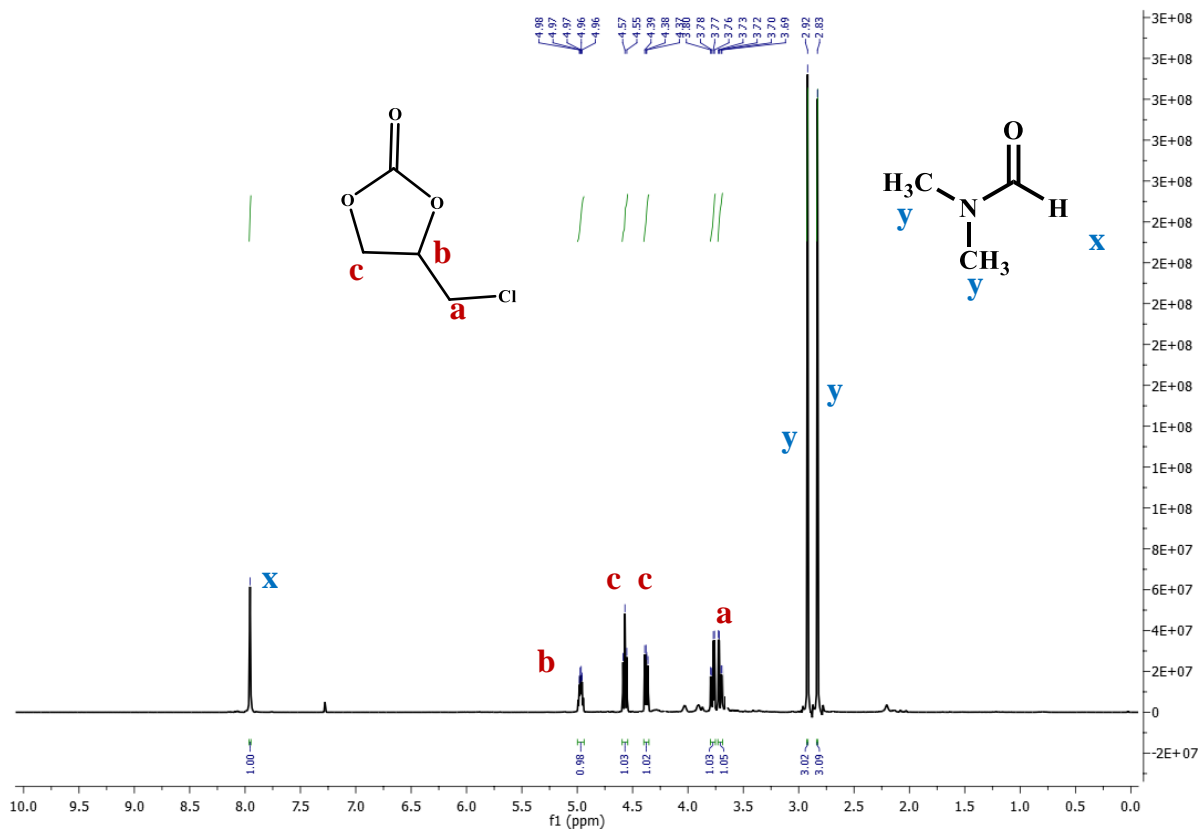
**Figure S2.** PXR D patterns of dias pore recorded after it is stirred in solutions of different pH (1 to 12)



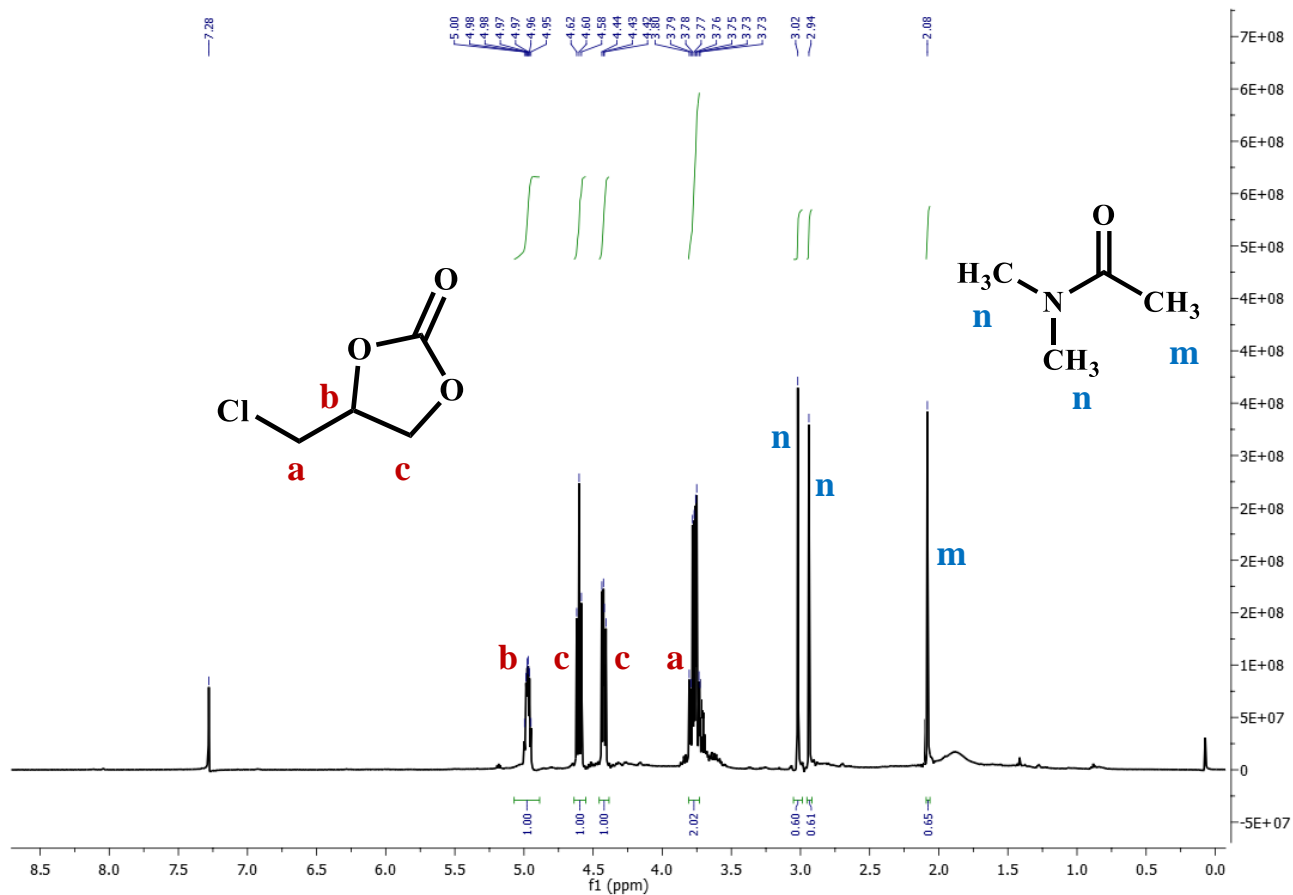
**Figure S3.** Elemental mapping and EDS of diaspore showing the presence of oxygen and aluminium only.



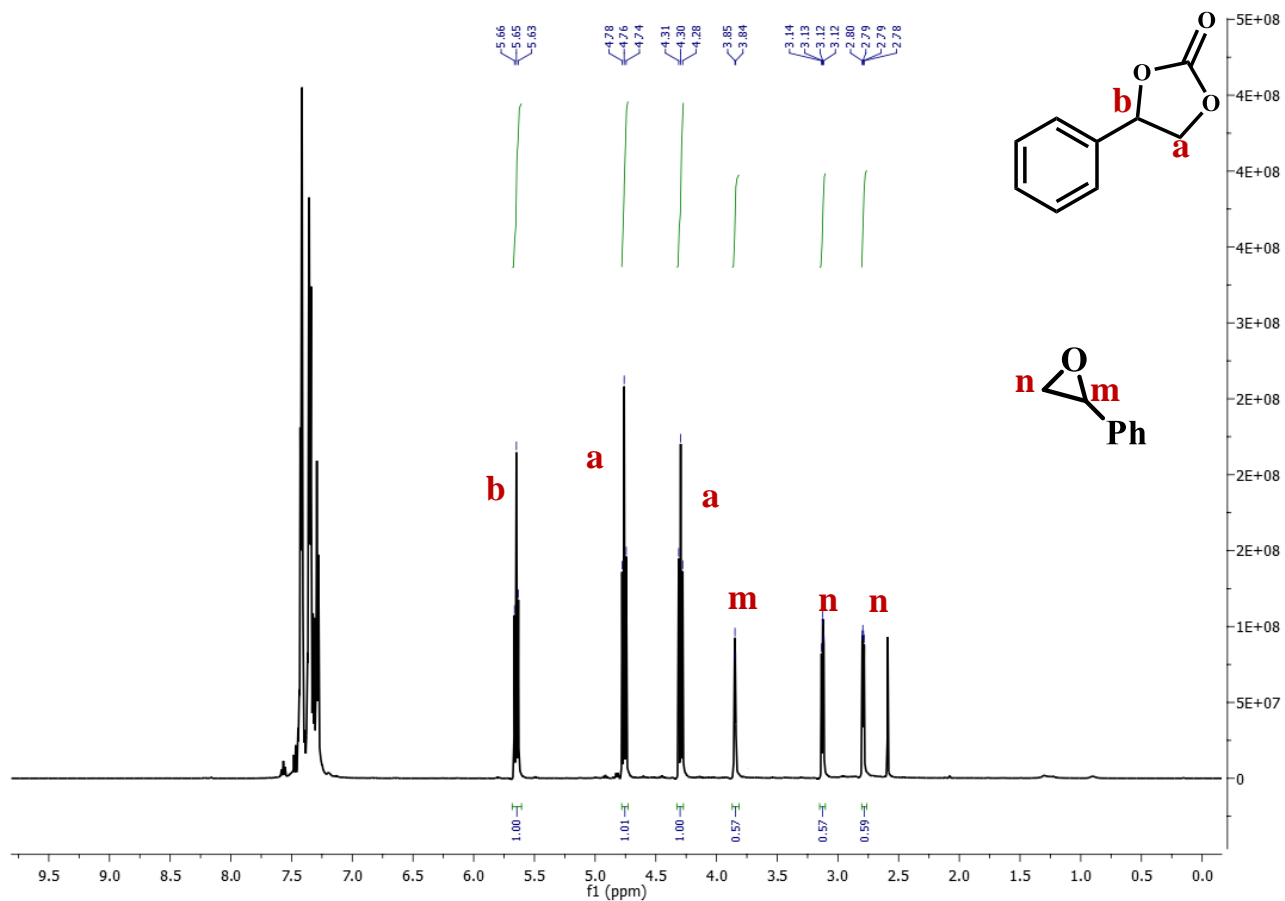
**Figure S4.**  $^1\text{H-NMR}$  spectrum of the reaction mixture of epichlorohydrin and 4-(chloromethyl)-1,3-dioxolan-2-one using diaspore as catalyst (58% conversion, 500 MHz,  $\text{CDCl}_3$ )



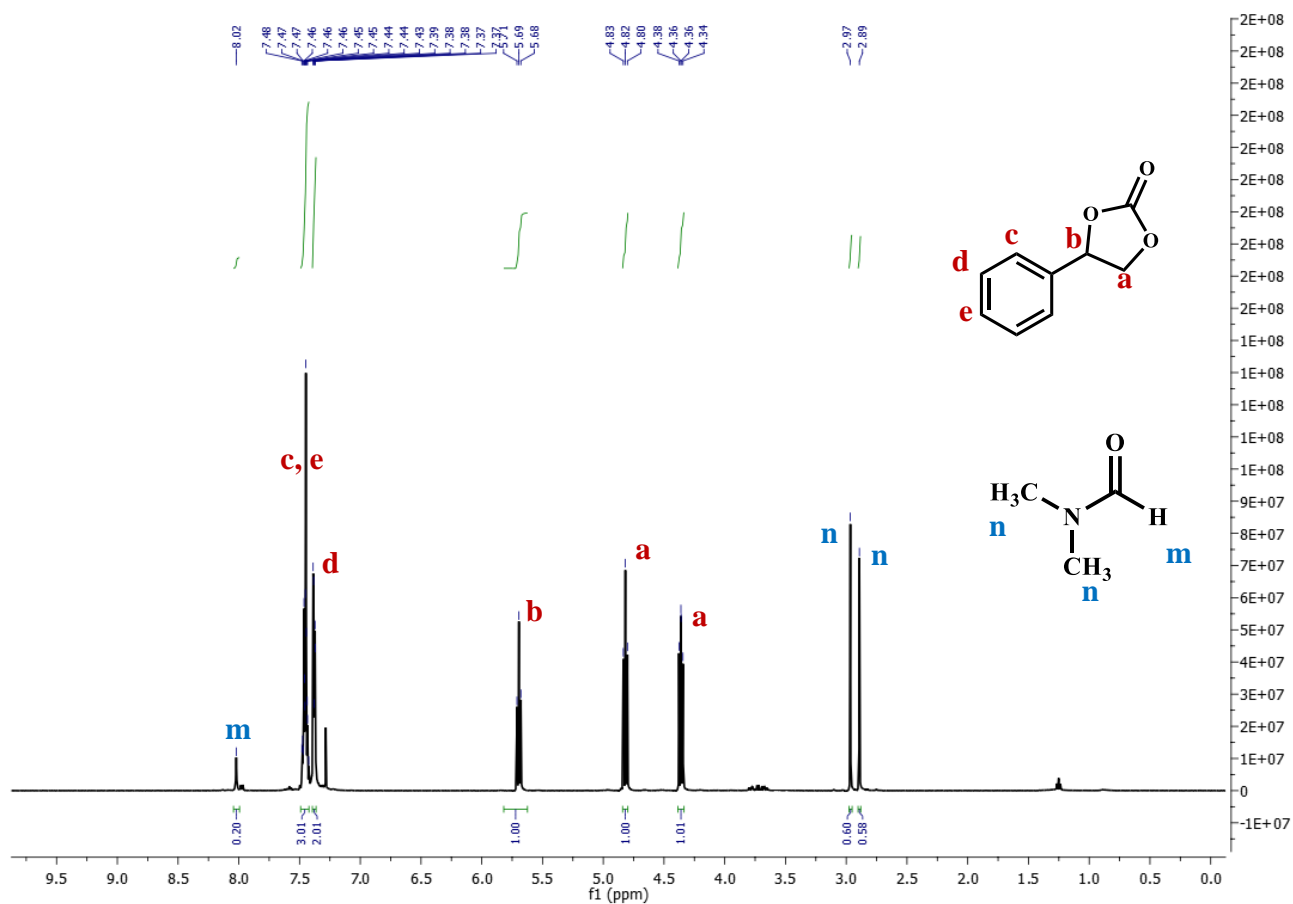
**Figure S5.**  $^1\text{H-NMR}$  spectrum of the reaction mixture of epichlorohydrin and 4-(chloromethyl)-1,3-dioxolan-2-one using diaspore and DMF (12.75 mmol) as catalyst (>99% conversion, 500 MHz,  $\text{CDCl}_3$ )



**Figure S6.** <sup>1</sup>H-NMR spectrum of reaction mixture consisting dimethyl acetamide (DMAc, 0.25 mmol), epichlorohydrin and 4-(chloromethyl)-1,3-dioxolan-2-one (>99% conversion, CDCl<sub>3</sub>, 500 MHz)

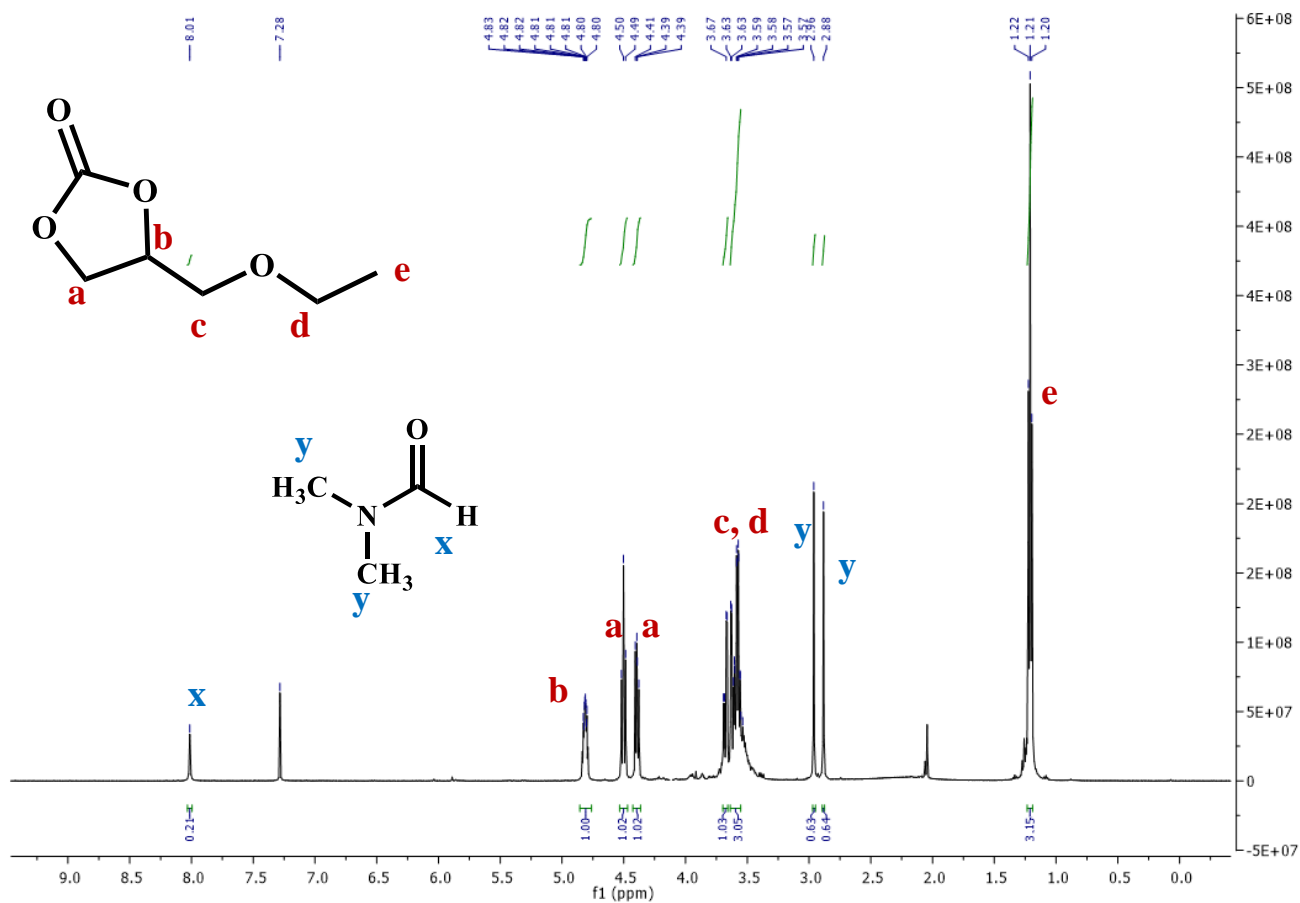


**Figure S7.** <sup>1</sup>H-NMR spectrum of reaction mixture, containing styrene oxide and 4-(phenyl)-1,3-dioxolan-2-one (64% conversion, DMSO-d<sub>6</sub>, 500 MHz)

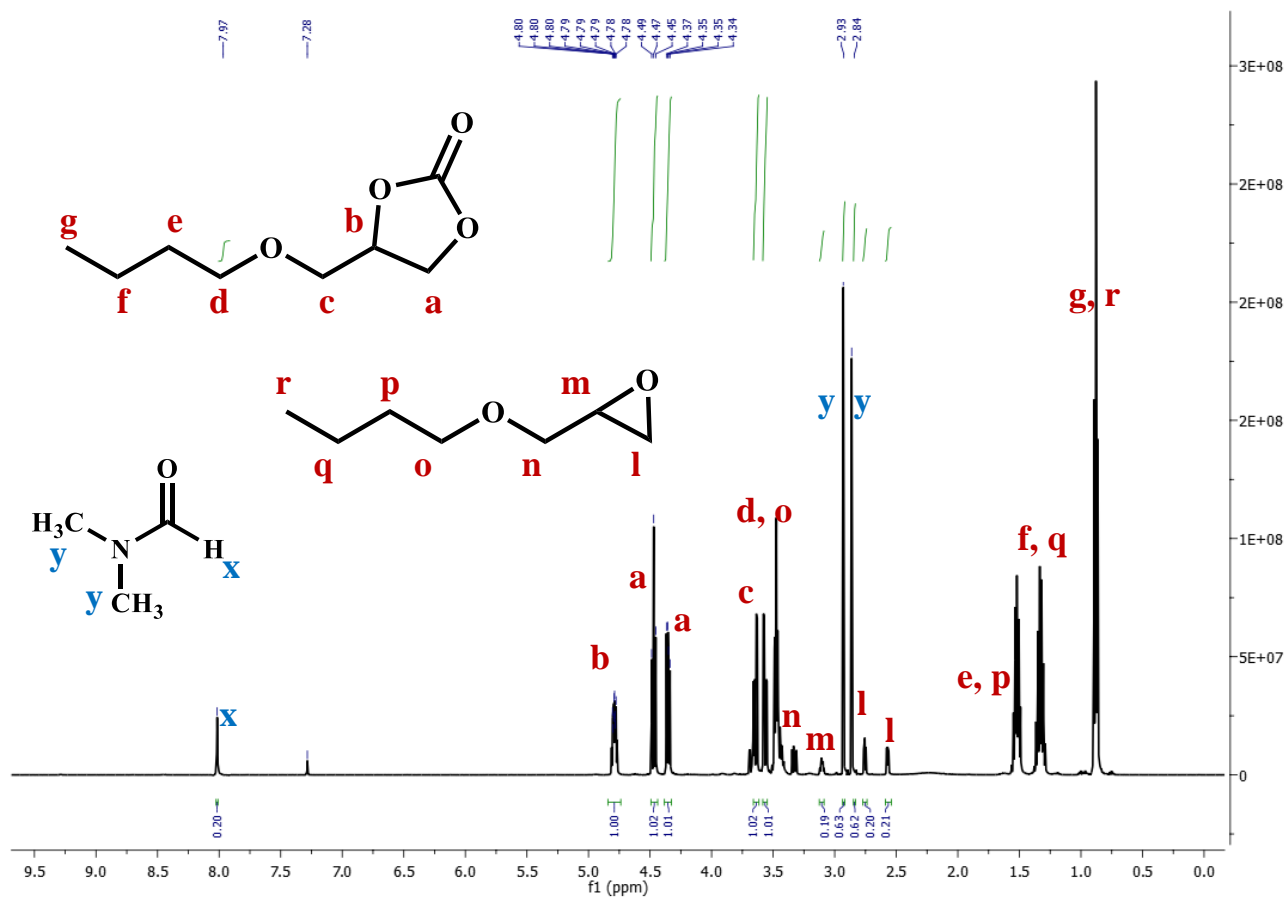


**Figure S8.** <sup>1</sup>H-NMR spectrum of reaction DMF (0.25 mmol), styrene oxide and 4-(phenyl)-1,3-dioxolan-2-one (complete conversion, CDCl<sub>3</sub>, 500 MHz)

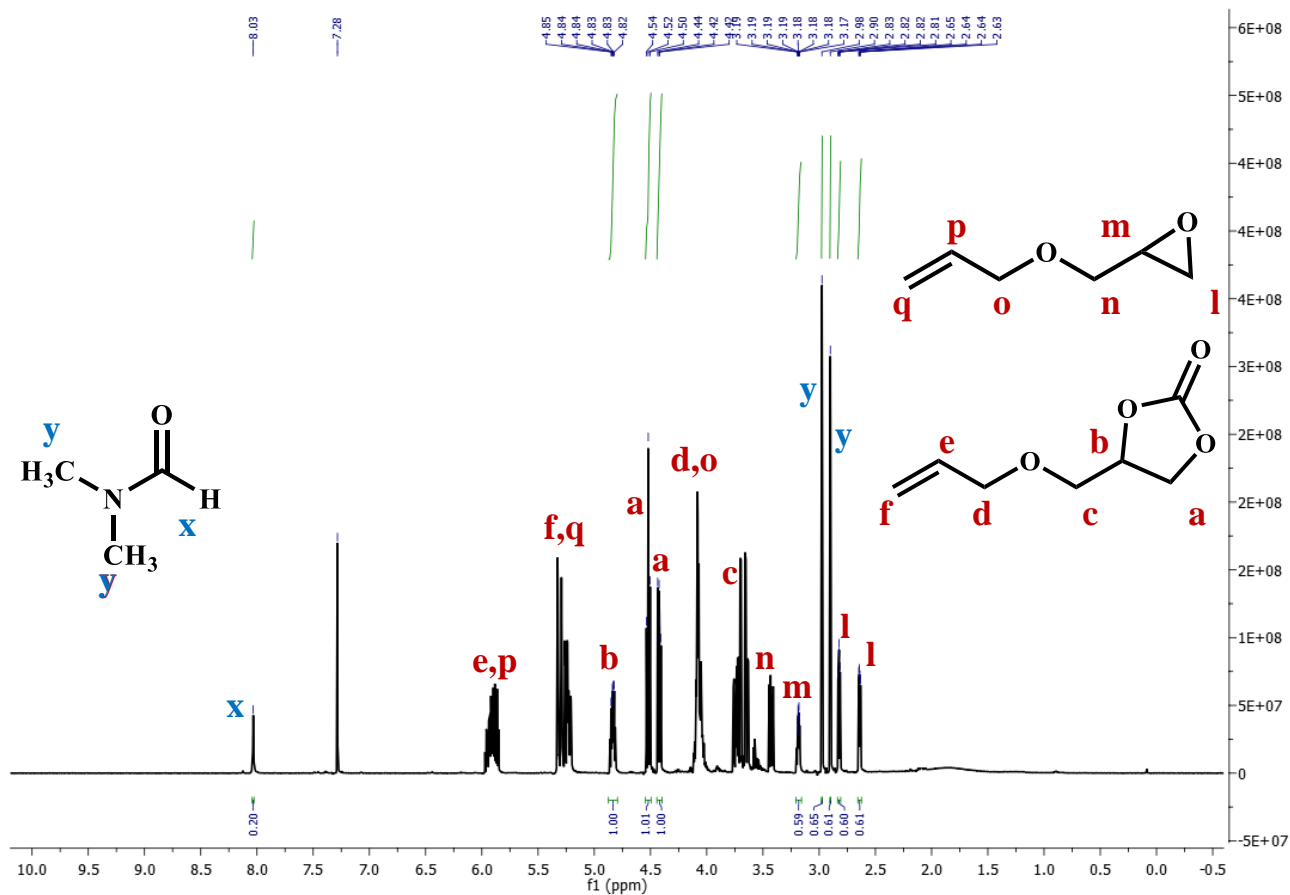




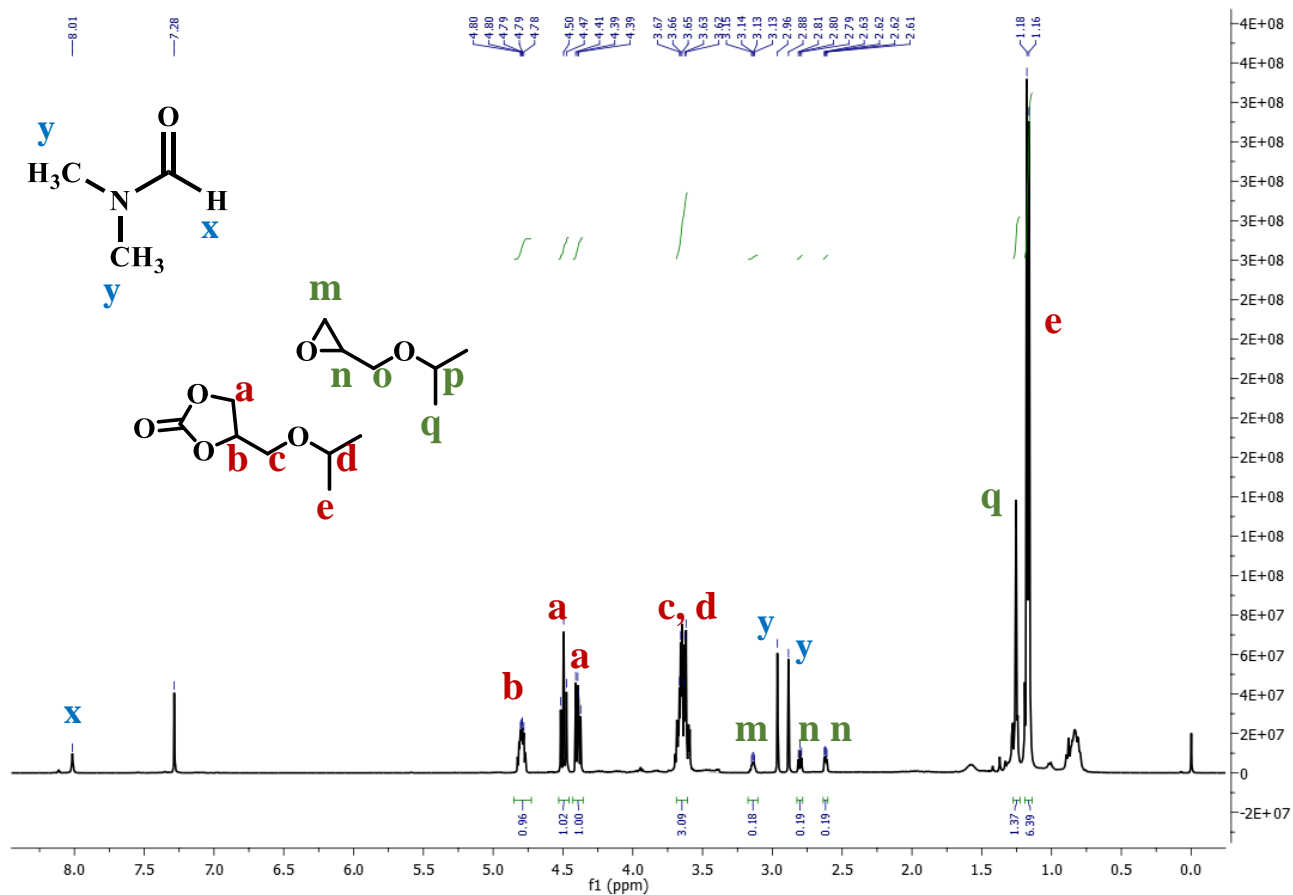
**Figure S9.** <sup>1</sup>H-NMR spectrum of reaction mixture consisting dimethyl acetamide (DMF, 0.25 mmol), ethyl glycidyl ether and 4-(ethoxymethyl)-1,3-dioxolan-2-one (>99% conversion, CDCl<sub>3</sub>, 500 MHz)



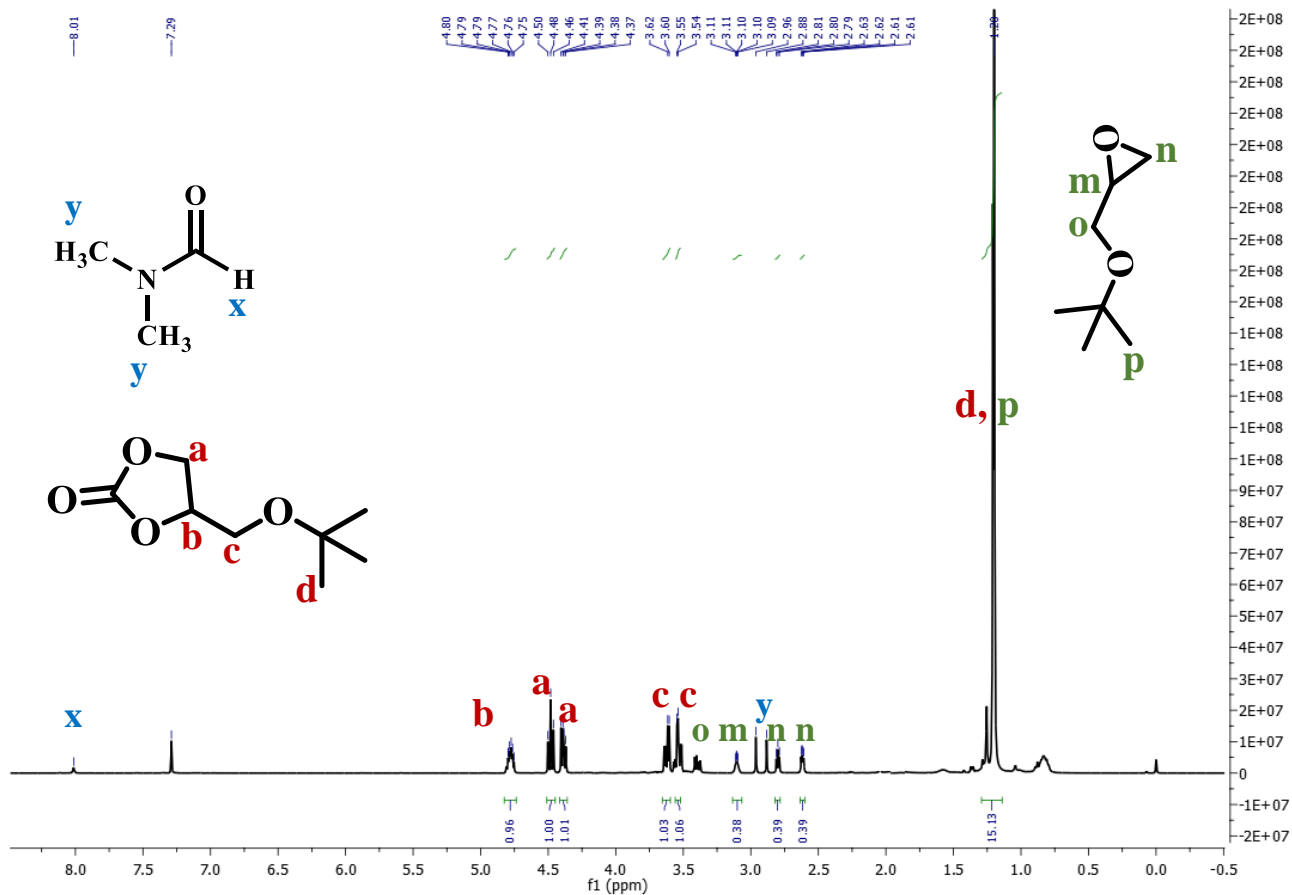
**Figure S10.** <sup>1</sup>H-NMR spectrum of reaction mixture consisting DMF (0.25 mmol), n-butyl glycidyl ether and 4-(n-butyloxymethyl)-1,3-dioxolan-2-one (>83% conversion, CDCl<sub>3</sub>, 500 MHz)



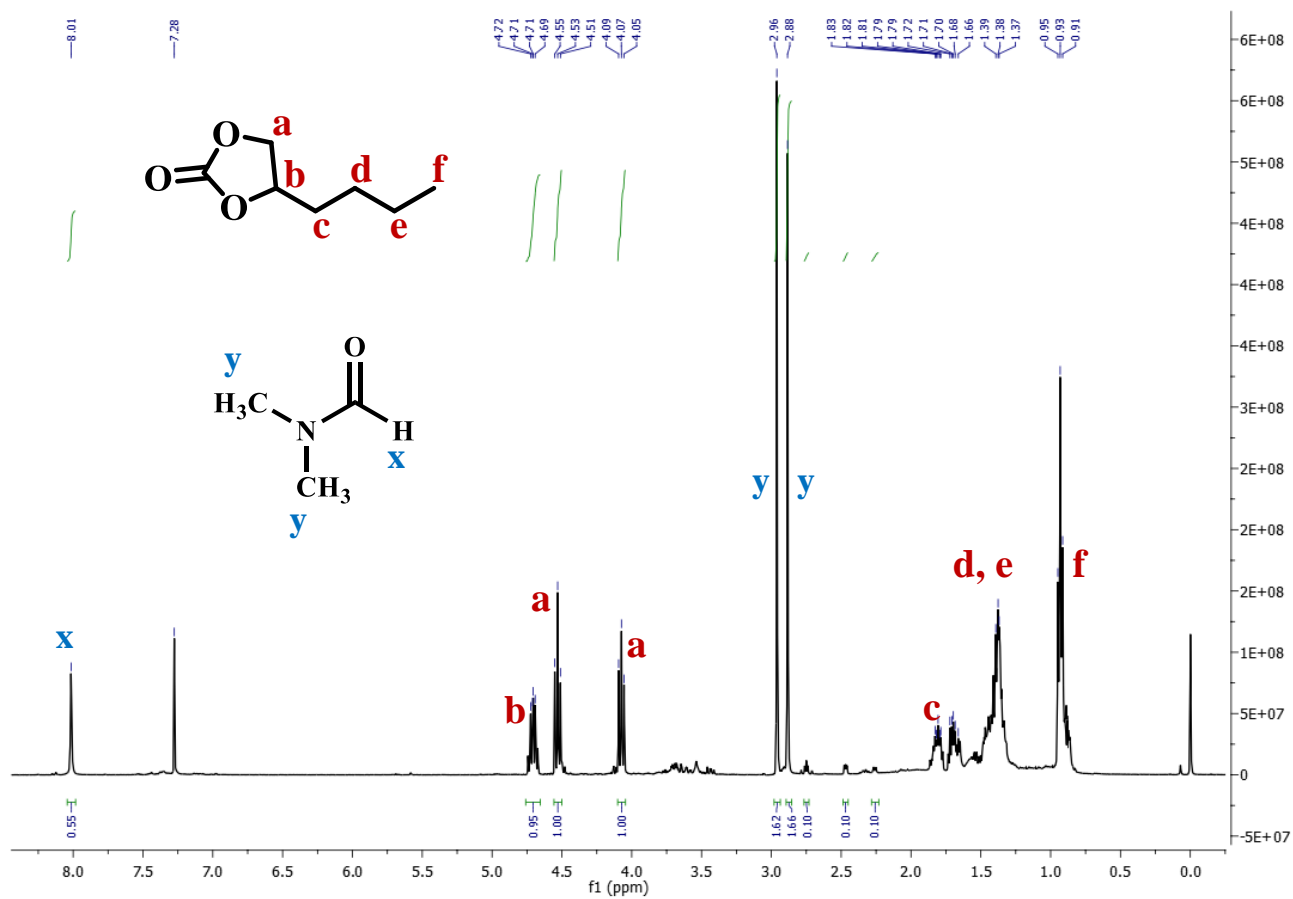
**Figure S11.**  $^1\text{H-NMR}$  spectrum of reaction mixture consisting DMF (0.25 mmol), allyl glycidyl ether and 4-(allyloxymethyl)-1,3-dioxolan-2-one (>62% conversion,  $\text{CDCl}_3$ , 500 MHz)



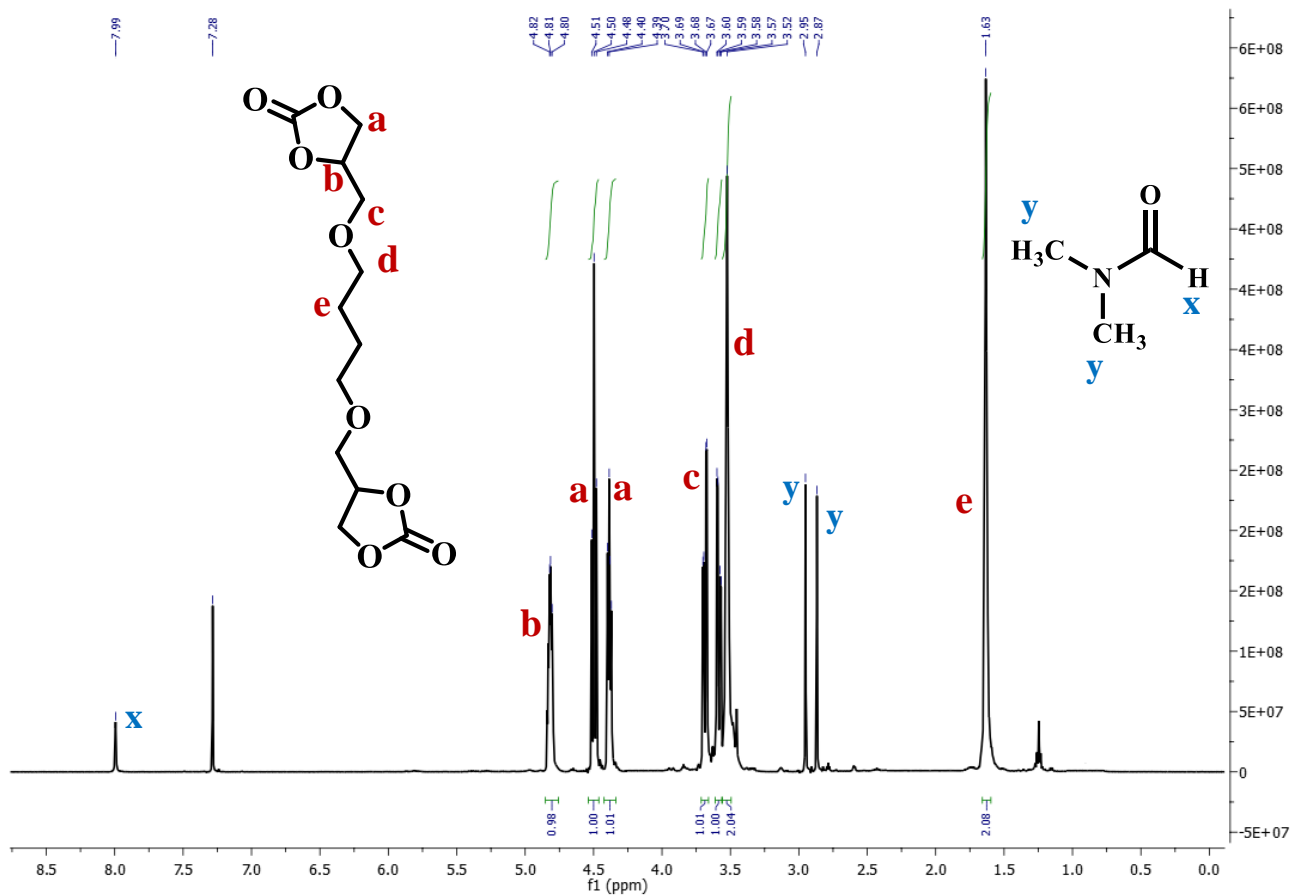
**Figure S12.** <sup>1</sup>H-NMR spectrum of reaction mixture consisting DMF (0.25 mmol), isopropoxy glycidyl ether and 4-(n-isopropoxymethyl)-1,3-dioxolan-2-one (>84% conversion, CDCl<sub>3</sub>, 500 MHz)



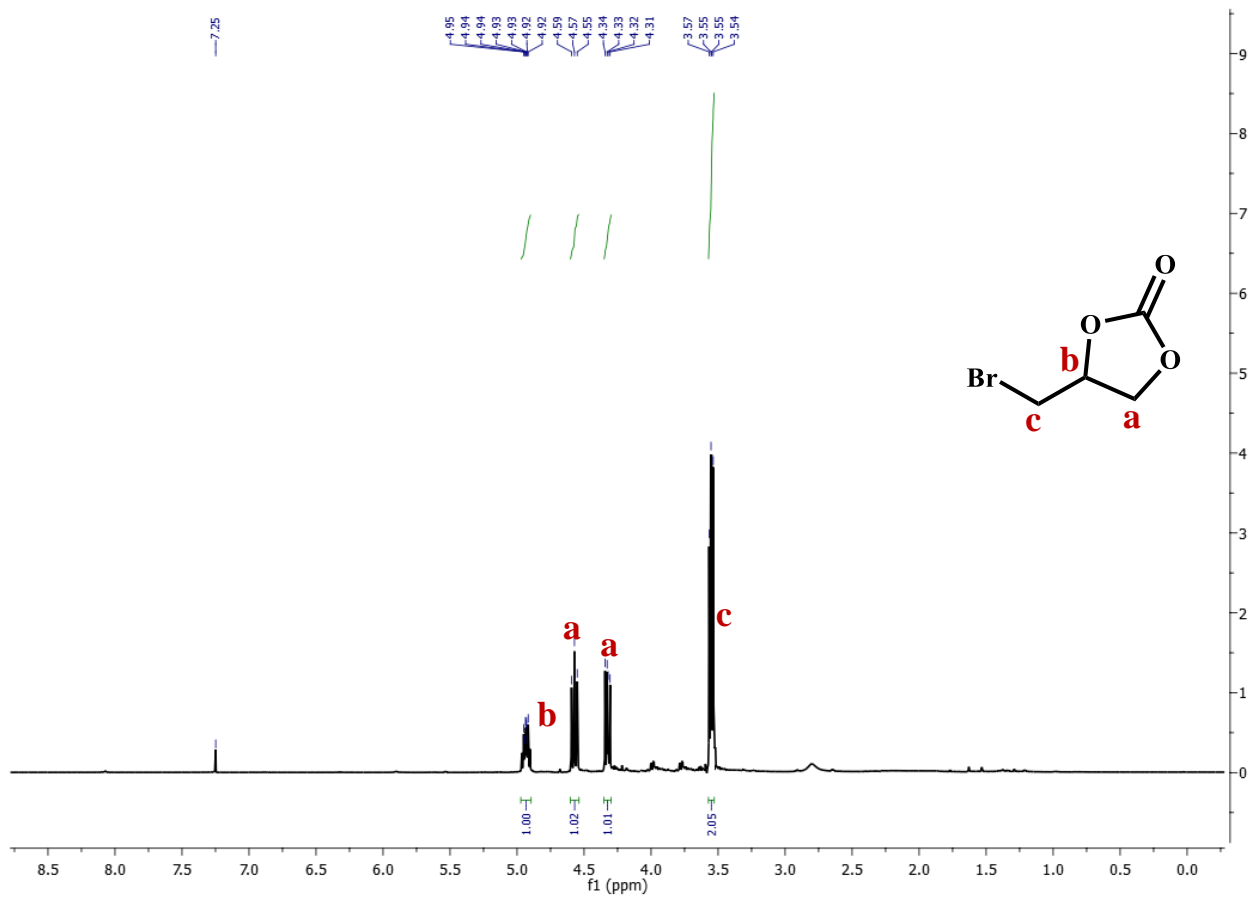
**Figure S13.**  $^1\text{H}$ -NMR spectrum of reaction mixture consisting DMF (0.25 mmol), t-butyl glycidyl ether and 4-(t-butoxymethyl)-1,3-dioxolan-2-one (>72% conversion,  $\text{CDCl}_3$ , 500 MHz)



**Figure S14.**  $^1\text{H-NMR}$  spectrum of reaction mixture consisting DMF (0.63 mmol), 1,2-epoxy hexane and 4-(butyl)-1,3-dioxolan-2-one and (91% conversion,  $\text{CDCl}_3$ , 500 MHz)

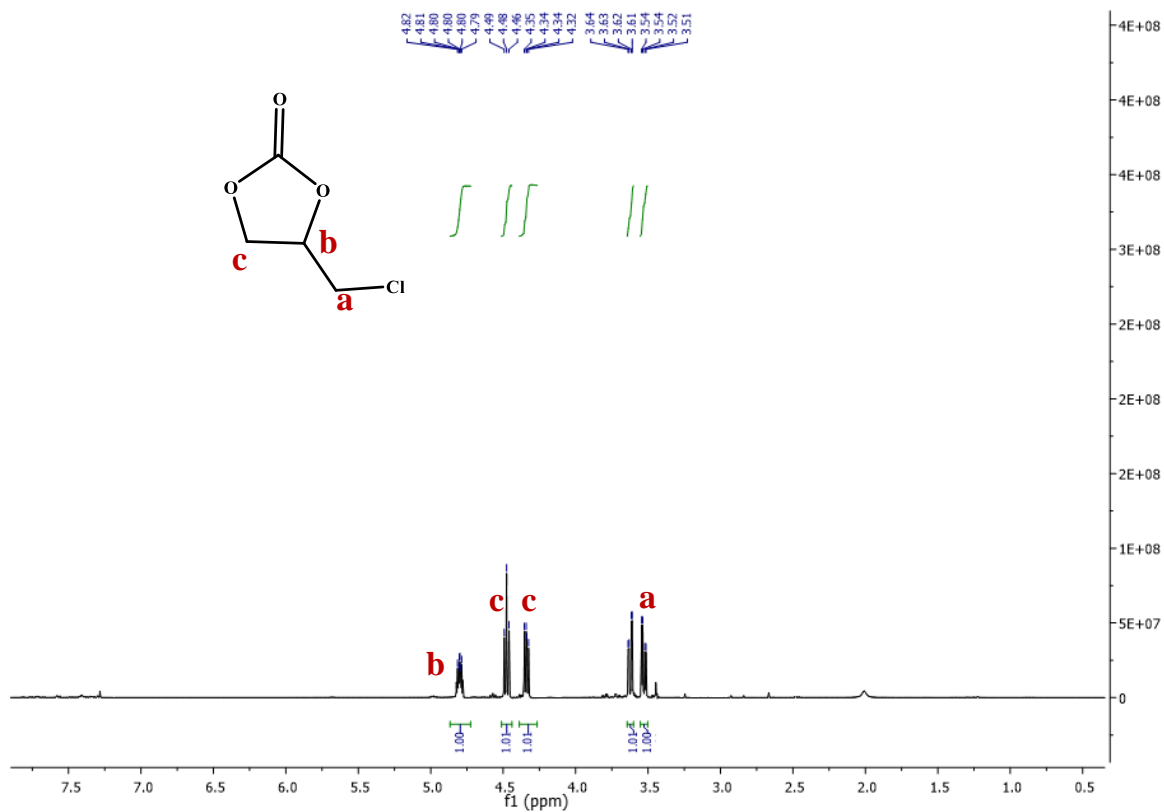


**Figure S15.**  $^1\text{H-NMR}$  spectrum of reaction mixture consisting DMF (0.25 mmol), 4,4'-(butane-1,4-diylbis(oxy)) bis(methylene)bis(1,3-dioxolan2-one) (complete conversion,  $\text{CDCl}_3$ , 500 MHz)

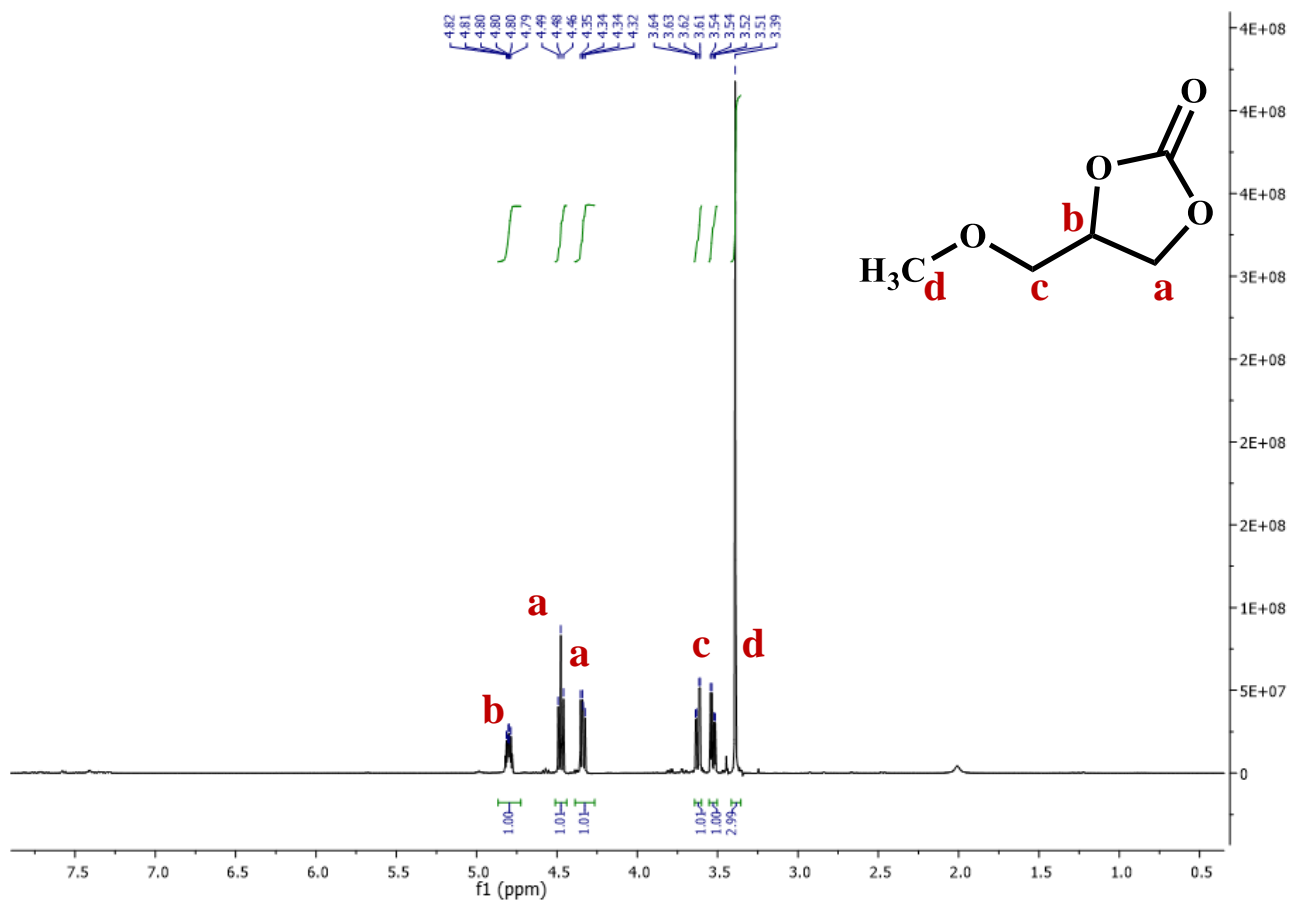


**Figure S16.** <sup>1</sup>H-NMR spectrum of 4-(bromomethyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 500 MHz)

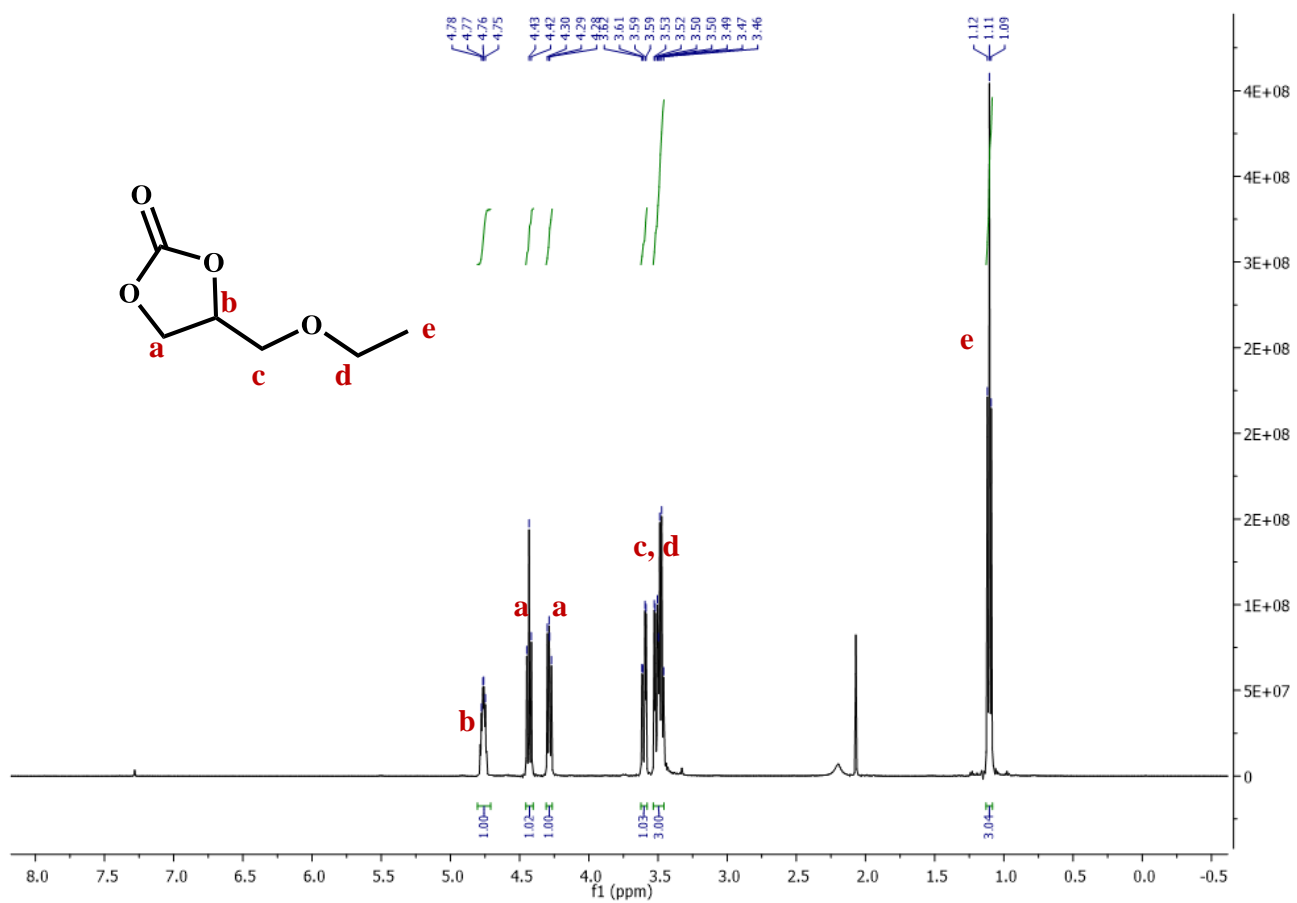




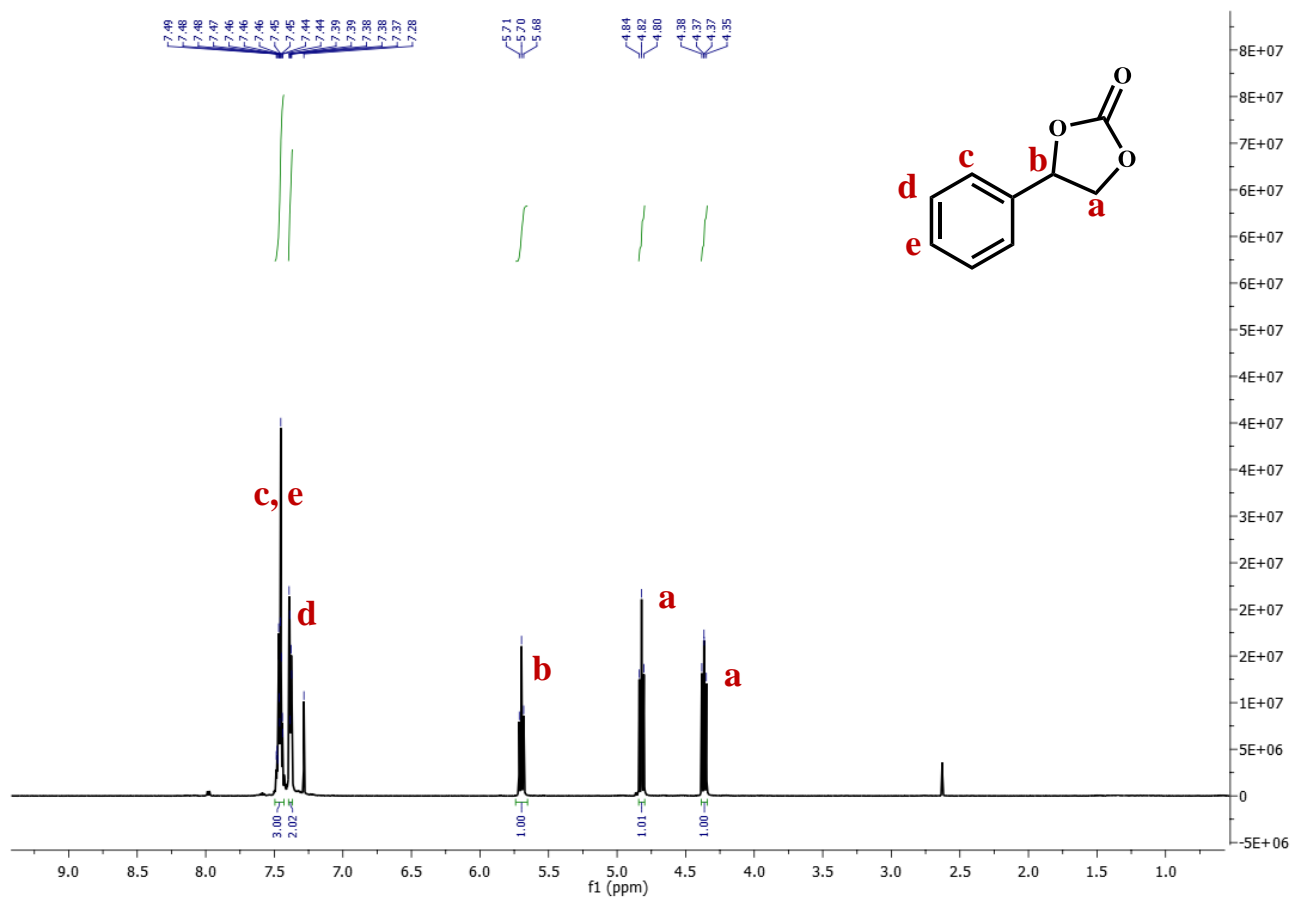
**Figure S17.**  $^1\text{H}$ -NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one ( $\text{CDCl}_3$ , 500 MHz)



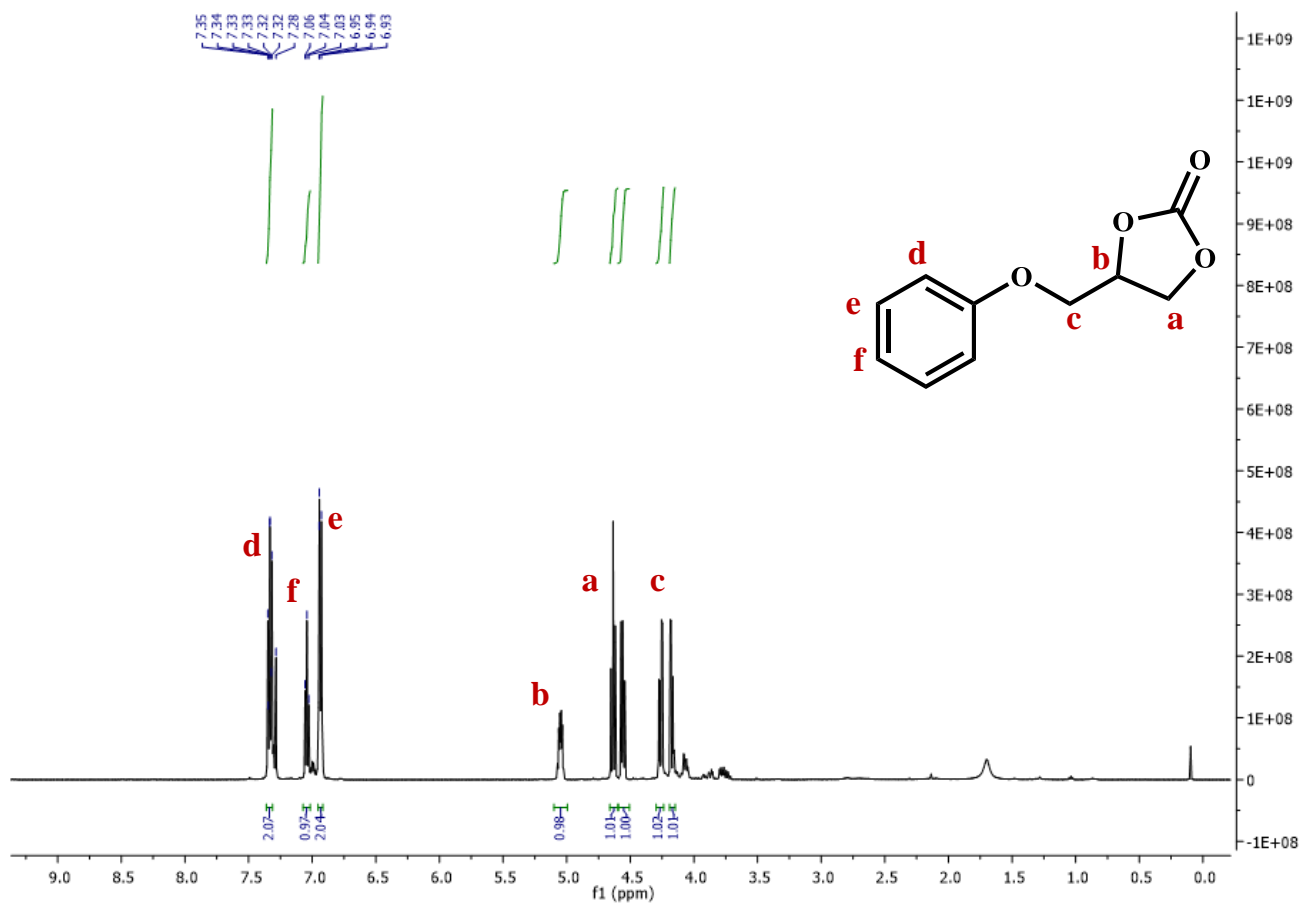
**Figure S18.**  $^1\text{H-NMR}$  of 4-(methoxymethyl)-1,3-dioxolan-2-one ( $\text{CDCl}_3$ , 500 MHz)



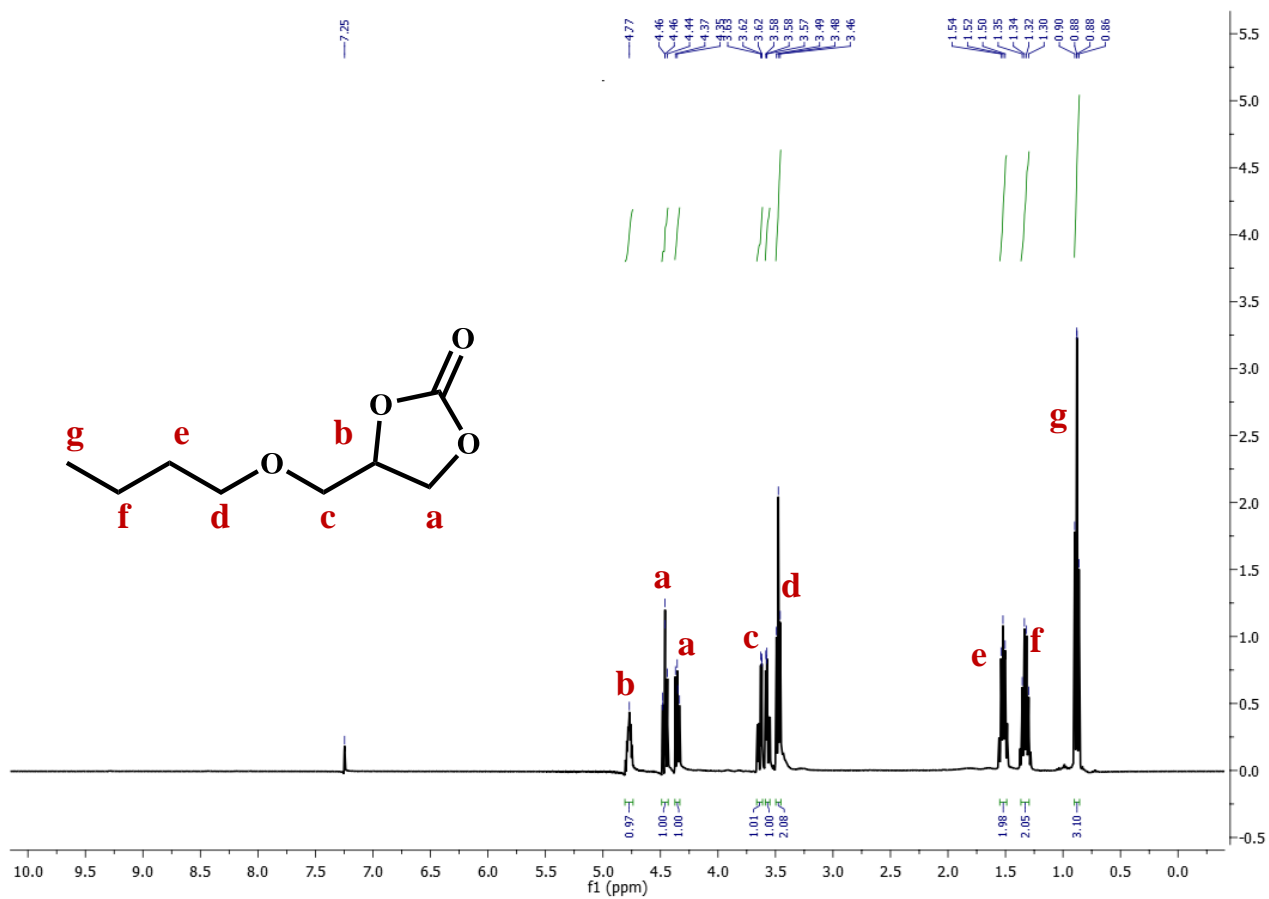
**Figure S19.** <sup>1</sup>H-NMR of 4-(ethoxymethyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 500 MHz)



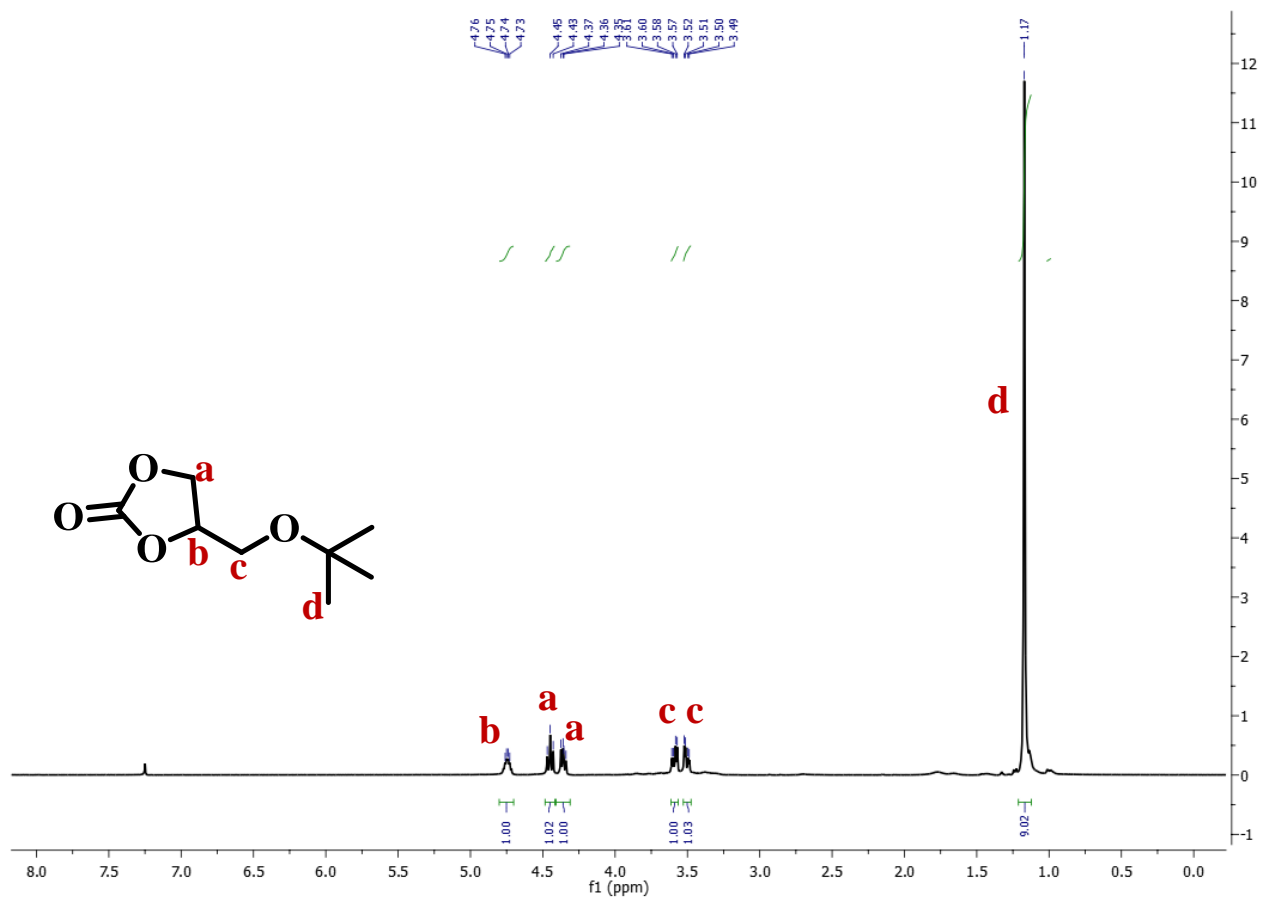
**Figure S20.** <sup>1</sup>H-NMR spectrum of 4-(phenyl)-1,3-dioxolan-2-one (DMSO-d<sub>6</sub>, 500 MHz)



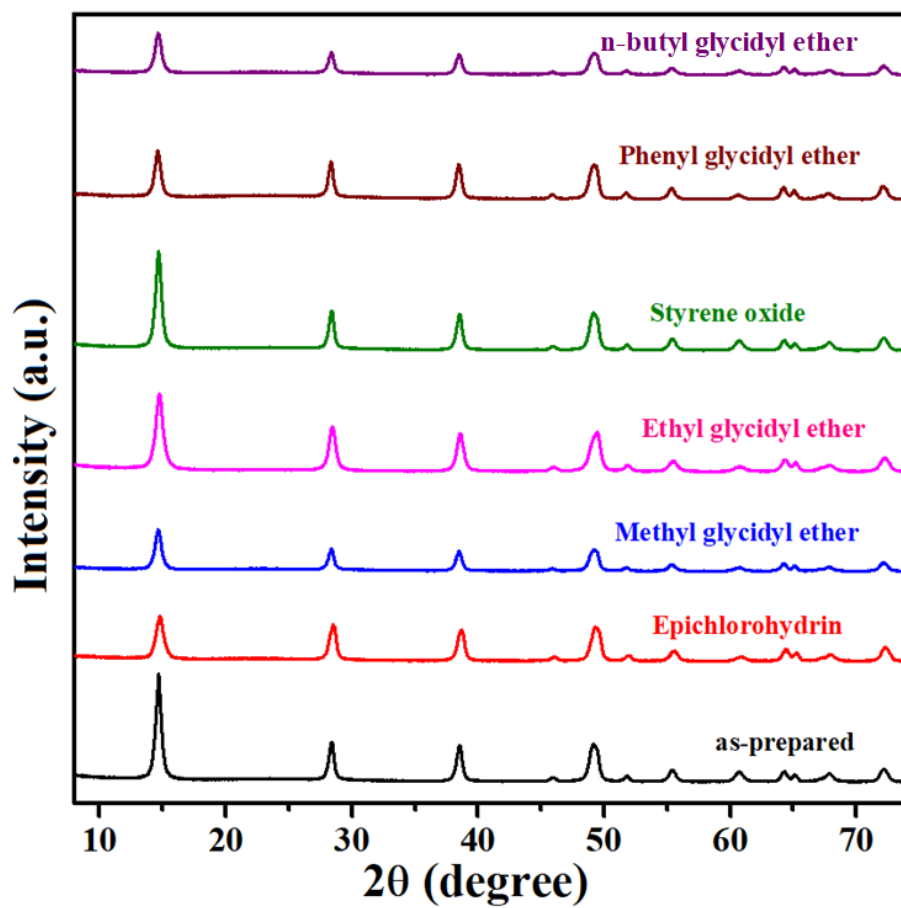
**Figure S21.** <sup>1</sup>H-NMR spectrum 4-(phenoxy methyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 500 MHz)



**Figure S22.**  $^1\text{H-NMR}$  spectrum 4-(n-butyloxymethyl)-1,3-dioxolan-2-one ( $\text{CDCl}_3$ , 500 MHz)

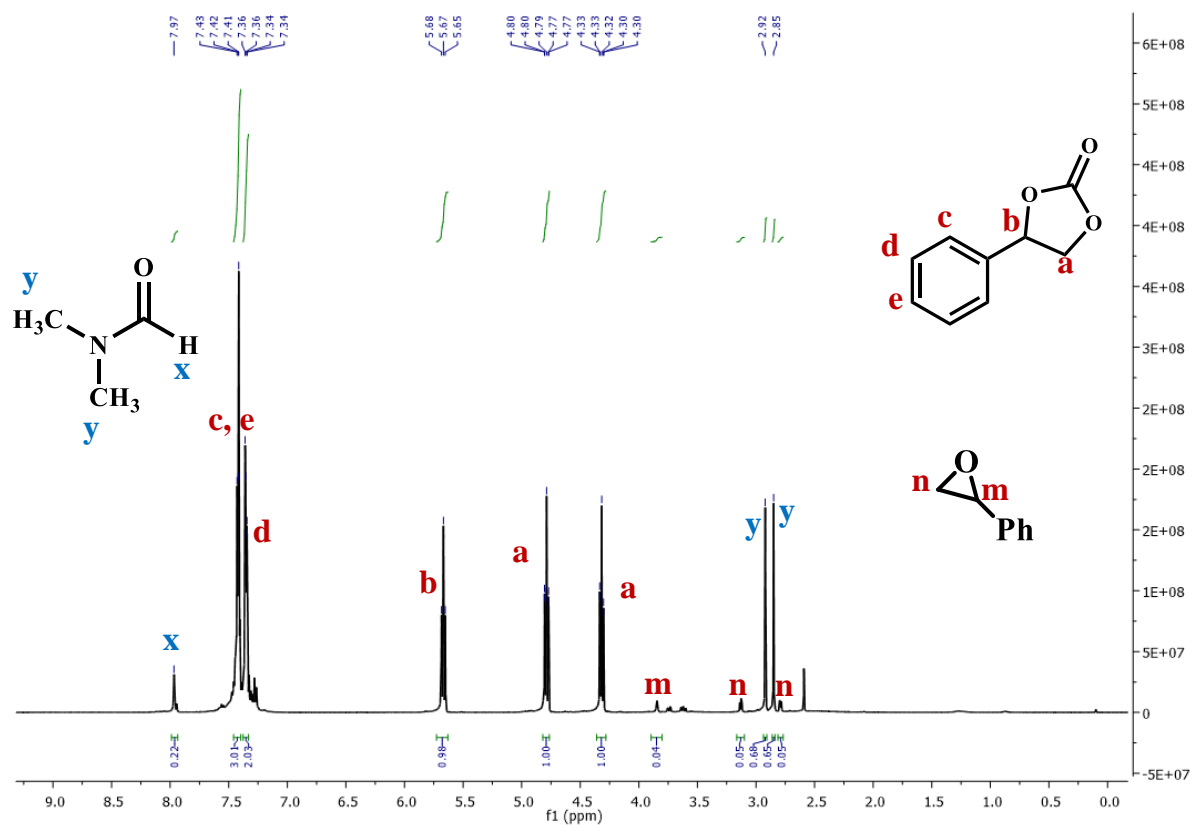


**Figure S23.** <sup>1</sup>H-NMR spectrum 4-(tert-butoxymethyl)-1,3-dioxolan-2-one (CDCl<sub>3</sub>, 500 MHz)

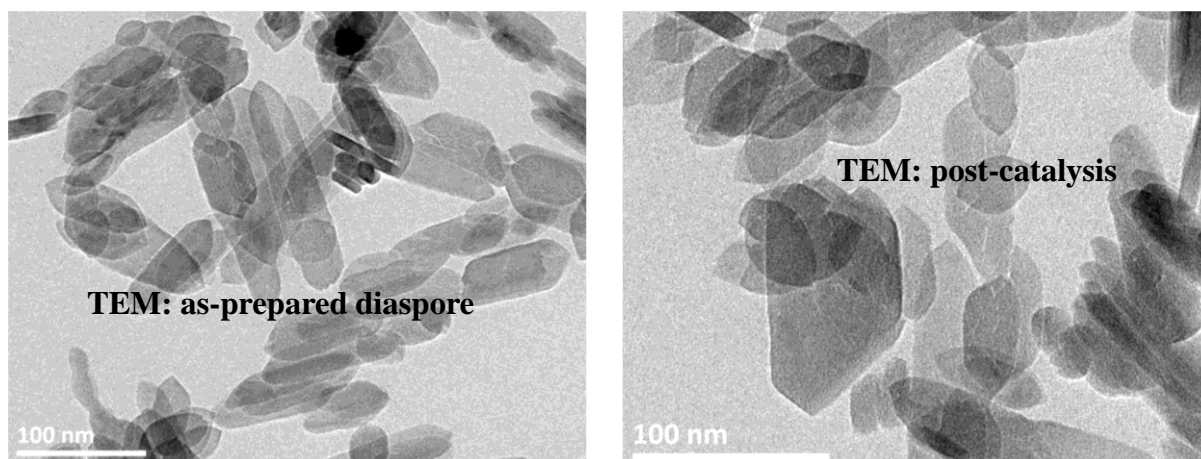


**Figure S24.** PXRD patterns of diaspora recovered after reaction with different epoxides

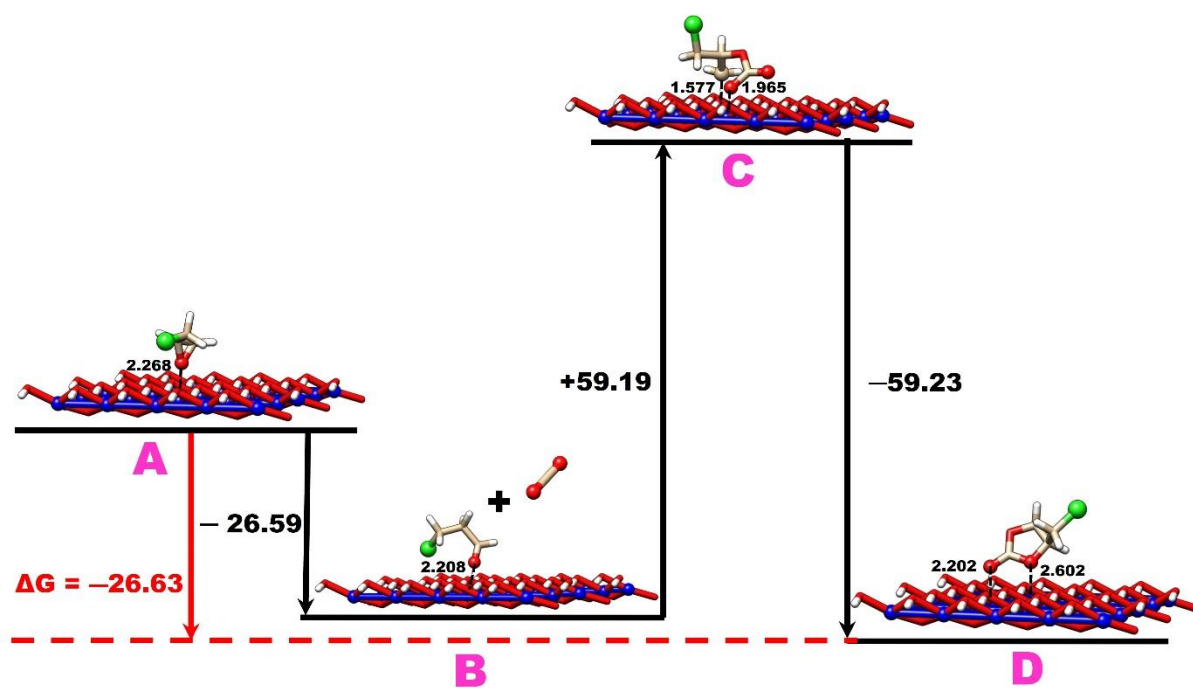




**Figure S25.** <sup>1</sup>H-NMR spectrum of reaction mixture after 4<sup>th</sup> cycle of catalysis consisting DMF (0.25 mmol), styrene oxide and 4-(phenyl)-1,3-dioxolan-2-one (96% conversion, DMSO-d<sub>6</sub>, 500 MHz)

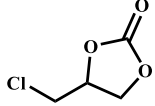
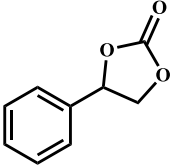
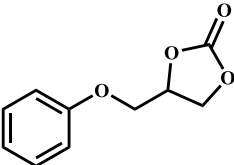
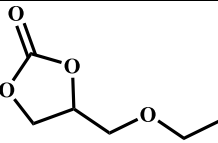
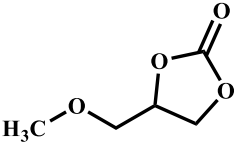
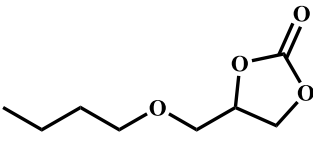
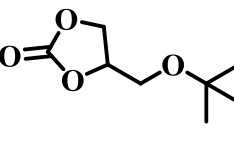


**Figure S26.** TEM images of as-prepared catalyst and post-catalytic sample.



**Figure S27.** Representation of the minima geometries on the diaspore [0 4 0] surface for the DMF free mechanism. The interactions between the oxygen atoms and aluminium on the sheet are indicated, along with the corresponding bond distances marked in the inset. The relative energies of the structures in the mechanism are provided along with the net free energy change for the entire reaction.

**Table S1.** Isolated yield of seven synthesized cyclic carbonates.

Cyclic Carbonate	Molecular weight (Cyclic carbonate)	<sup>1</sup> H NMR conversion	Isolated Yield
	136.53	>99%	98%
	164.16	>99%	97%
	194.17	>99%	96%
	146.14	>99%	97%
	132.14	>99%	99%
	174.20	83%	80%
	174.20	72%	70%

**Table S2.** Comparison of the activities of different halide-free catalysts for CO<sub>2</sub> fixation. In the table homogenous catalysts are marked with \*, other catalysts are heterogenous catalysts.

(Here 1 MPa = 10 bar pressure; 1 atm = 1.01 bar pressure)

Catalyst	Pressure	Temp (°C)	Time (h)	No. of epoxides converted	Reference
Pyridyl Salicylimines	1 atm. <b>(0.1 MPa)</b>	100	24	5	S1
Bifunctional catalyst*	2 MPa	150	24	6	S2
Nanoporous polymer	4 bar <b>(0.4 MPa)</b>	100	20	5	S3
Salophen*	10 bar <b>(1 MPa)</b>	120	3.5	7	S4
Polyurethane	9 MPa	150	16	10	S5
Schiff Base*	1 MPa	110	4, 12	9	S6
Calcium alginate	5 bar <b>(0.5 MPa)</b>	80	12	5	S7
Graphene oxide	1 atm <b>(0.1 MPa)</b>	140	9	5	S8
CeO <sub>2</sub> -ZrO <sub>2</sub> solid solution	6 MPa	150	-	7	S9
Ionic organic polymer	1 atm <b>(0.1 MPa)</b>	60, 80, 100	48, 72	8	S10
Organocatalyst	1 MPa	120	12	9	S11
Zn MOFs	1 atm <b>(0.1 MPa)</b>	100	24	6	S12
Ionic liquids*	2 MPa	120	6	12	S13
Zn-Adenine MOFs	1 atm <b>(0.1 MPa)</b>	100	24	4	S14
<b>Diaspore [<math>\alpha</math>-AlO(OH)]</b>	<b>1 atm. (0.1 MPa)</b>	<b>100</b>	<b>16</b>	<b>12</b>	<b>This work</b>

**Table S3.** Inductively coupled plasma atomic emission spectroscopy (ICP-AES) data.

Entry	Composition of reaction mixture	Concentration of Al <sup>3+</sup> from ICP-AES (ppm)
1	4-(chloromethyl)-1,3-dioxolan-2-one, diaspore, DMF and epichlorohydrin	0.00
2	4-(phoxymethyl)-1,3-dioxolan-2-one, diaspore, DMF and styrene oxide	0.00

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