

Electronic Supplementary Information

***para*-Aminobenzoic acid-capped Hematite as an Efficient Nanocatalyst for Solvent-free CO₂ Fixation under Atmospheric Pressure**

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1. EXPERIMENTAL SECTION

1.1. Materials. Iron nitrate nonahydrate [Fe(NO₃)₃·9H₂O], *para*-Aminobenzoic acid (PABA), sodium acetate [CH₃COONa·3H₂O], urea [CO(NH₂)₂] and all the epoxides were purchased from Sigma Aldrich. Tetra-*n*-butylammonium iodide (TBAI), tetra-*n*-butylammonium bromide (TBAB) and ethanol were purchased from Merck. All chemicals were used without any further purification.

1.2. Catalyst Synthesis.

Preparation of PABA@ α -Fe₂O₃. In a 100 mL beaker Fe(NO₃)₃·9H₂O (2 mmol, 0.808 g) was dissolved in 40 mL distilled water. Then CH₃COONa·3H₂O (6 mmol, 0.816 g) was added to it and stirred for 5 minutes. In another 100 mL beaker PABA (6 mmol, 0.823 g) was dissolved in 40 mL of ethanol and transferred into the first reaction mixture under stirring condition. Next, urea (10 mmol, 0.6 g) was added to the reaction mixture and stirred for 5 minutes. The reaction mixture was then transferred to a 200 mL Teflon lined autoclave, and put for solvothermal reaction at 180 °C for 12 hours. The obtained reddish-brown solid product was washed with distilled water and methanol thrice, and collected by centrifugation with 4000 rpm for 10 min. The material was then dried in oven at 65 °C. The other catalysts were prepared following the same synthesis procedure by taking appropriate amount of precursors as mentioned in **Table S1**.

Table S1. Details of reagents used and corresponding sample IDs.

| S/No. | Details of Reagents | Sample ID |
|-------|--|--|
| 1 | Fe(NO ₃) ₃ ·9H ₂ O (2 mmol), CH ₃ COONa·3H ₂ O, urea | α -Fe ₂ O ₃ |
| 2 | Fe(NO ₃) ₃ ·9H ₂ O (2 mmol), PABA (6 mmol), CH ₃ COONa·3H ₂ O, urea | PABA@ α -Fe ₂ O ₃ |
| 3 | Fe(NO ₃) ₃ ·9H ₂ O (2 mmol), Benzoic acid (6 mmol, 0.733 g), CH ₃ COONa·3H ₂ O, urea | Benzoic acid@ α -Fe ₂ O ₃ |
| 4 | Fe(NO ₃) ₃ ·9H ₂ O (2 mmol), Aniline (6 mmol, 0.54 mL), CH ₃ COONa·3H ₂ O, urea | Aniline@ α -Fe ₂ O ₃ |

1.3. Characterization Techniques. The PXRD patterns were recorded using a Rigaku-MiniFlex diffractometer attached with a D/tex ultradetector and Cu K α source operating at 15 mA and 40 kV. The scan range was set from 5 to 80° 2 θ with a step size of 0.02° and a count time of 2 s. FT-IR measurements were performed in a Perkin Elmer Spectrum instrument. Field emission SEM

images and EDAX were acquired on a SUPRA 55-VP instrument with patented GEMINI column technology. Prior to loading the samples into the chamber, they were coated with a thin layer of gold-palladium in order to avoid charging effects. TEM images were acquired on a JEM 2100F field emission transmission electron microscope operating at 200 kV. Nitrogen adsorption–desorption measurements were conducted at 77 K with a Micromeritics Gemini VII-2390t instrument. The powders were outgassed in vacuum at 180 °C for 2 h prior to measurements. The surface chemistry of the samples was analyzed using X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II, ULVAC-PHI Inc.,USA) equipped with micro-focused (200 μm, 15 KV) monochromatic Al-Kα X-Ray source (hν = 1486.6 eV). ¹H and ¹³C NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer and on a Bruker AVANCE Ultrashield Plus 500 MHz spectrometer.

1.4. Average crystallite size calculation. The average crystallite size of the prepared catalysts was determined using the Scherrer equation:

$$D = \frac{K \lambda}{\beta \cos\theta}$$

where, D is the average crystallite size, β is the full-width half maximum (FWHM) of the X-ray diffraction peaks, θ is the Bragg angle, λ is the wavelength of an incident X-ray source (0.15418 nm) and the constant K is related to the crystallite shape (0.94 for spherical crystals with cubic symmetry).

1.5. General catalytic reaction procedure. In a 50 mL Schlenk round bottom flask the required amount of epoxides, catalyst and TBAI were taken with a small magnetic stirrer. One glass tube was fixed as condenser above the round bottom flask. The CO₂ filled balloon attached with the glass stopcock was fitted on top of the glass tube condenser. All the glass joints were properly sealed with the grease and Teflon tape to avoid any gas leakage. The set up was kept under vacuum

and backfilled with CO₂ gas thrice to make the set up air/ moisture free. Subsequently, the reaction was heated at 105 °C for 20 hours under CO₂ environment (1.02 atm pressure). After completion of the reaction small amount of aliquot was taken out and centrifuged for complete separation of the catalyst from the reaction mixture. The solution part was then dissolved in CDCl₃ solvent and characterized by ¹H and ¹³C NMR experiments.

1.6. Turnover number (TON) and Turnover frequency (TOF) calculation.

The turnover number (TON) and turnover frequency (TOF) have been evaluated considering the metal centers present in the PABA@α-Fe₂O₃ catalyst. For the catalytic studies, 50 mg of catalyst was used to convert 23 mmol of epoxides into corresponding cyclic carbonates.

50 mg of PABA@α-Fe₂O₃ catalyst contains 0.56 mmol of Fe centers.

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

For 100 % conversion of 23 mmol epoxides, TON = 1 x 23/0.56 = **41.07**

Hence, 98 % conversion of 23 mmol epichlorohydrin, TON= 0.98 x 41.07= 40.25

Turnover Frequency= TON/ time

Therefore, for 98 % conversion of 23 mmol epichlorohydrin, TOF= 40.25/ 20 h= 2.01 h⁻¹

In a similar way, the TON and TOF for all the conversions can be evaluated.

1.7. Recyclability study. For the recyclability study, the PABA@α-Fe₂O₃ nanocatalyst was recovered from reaction mixture after each catalytic cycle by centrifugation with 10000 rpm, for 10 minutes. Subsequently, it was washed with ethyl acetate and methanol followed by drying in oven, and used in next catalytic cycle.

Table S2. Nitrogen adsorption-desorption analysis data.

| Sample | Surface Area (m ² /g) | Pore diameter (nm) | Pore volume (cm ³ /g) |
|--|----------------------------------|--------------------|----------------------------------|
| α -Fe ₂ O ₃ | 26 | 27 | 0.22 |
| PABA@ α -Fe ₂ O ₃ | 35 | 18.6 | 0.19 |

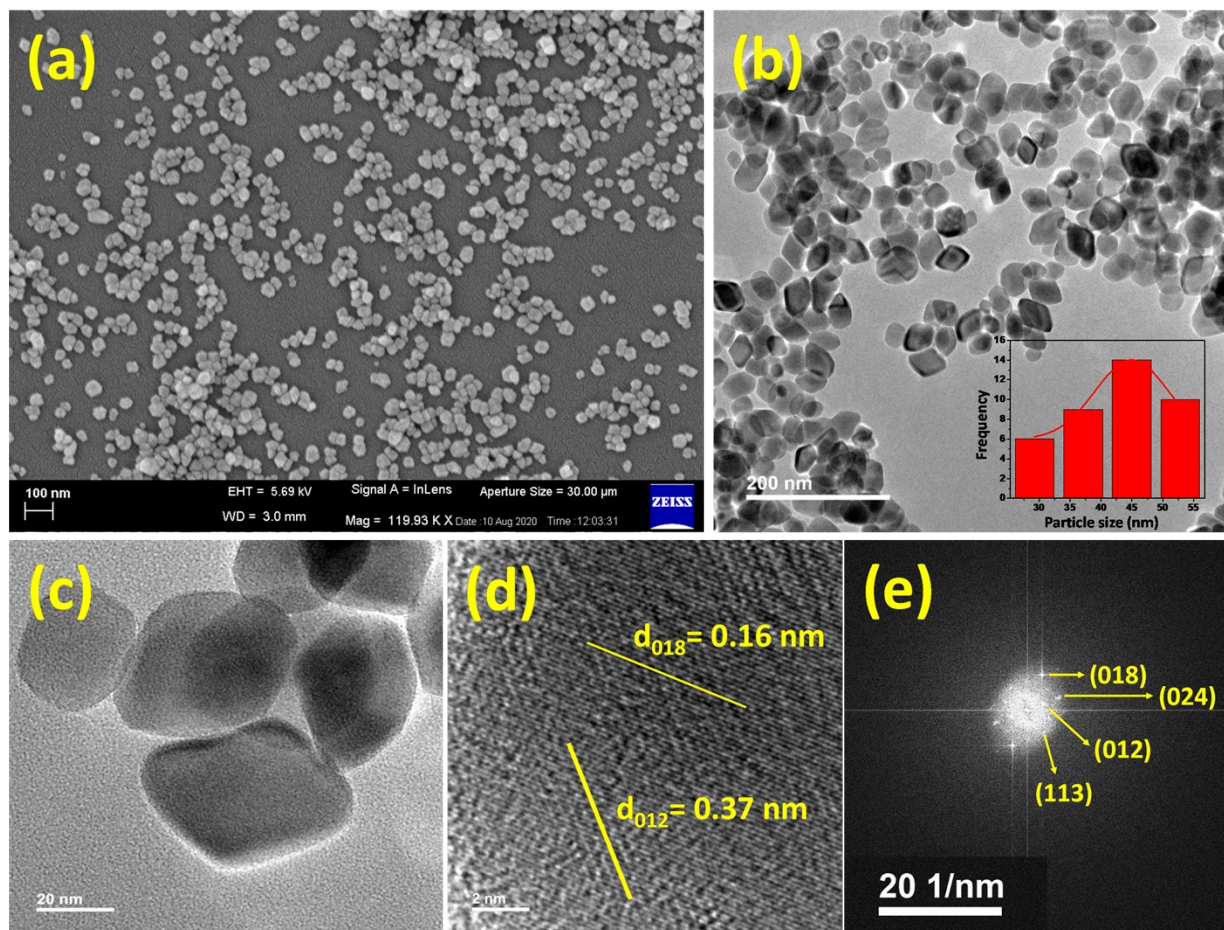


Figure S1. Morphology analysis of α -Fe₂O₃: (a) FESEM image, (b, c) TEM images, inset of b: particle size distribution, and (d, e) HRTEM image and corresponding FFT, respectively.

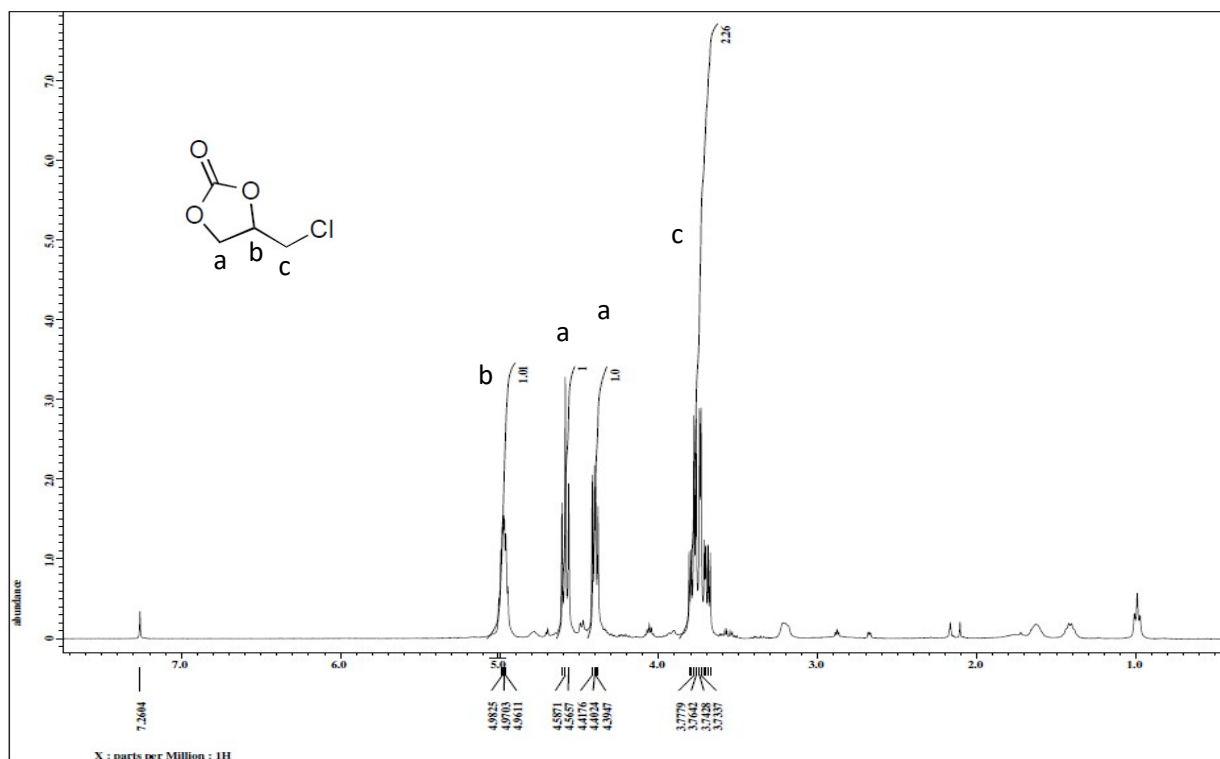


Figure S2. ^1H NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (CDCl_3 , 400 MHz).

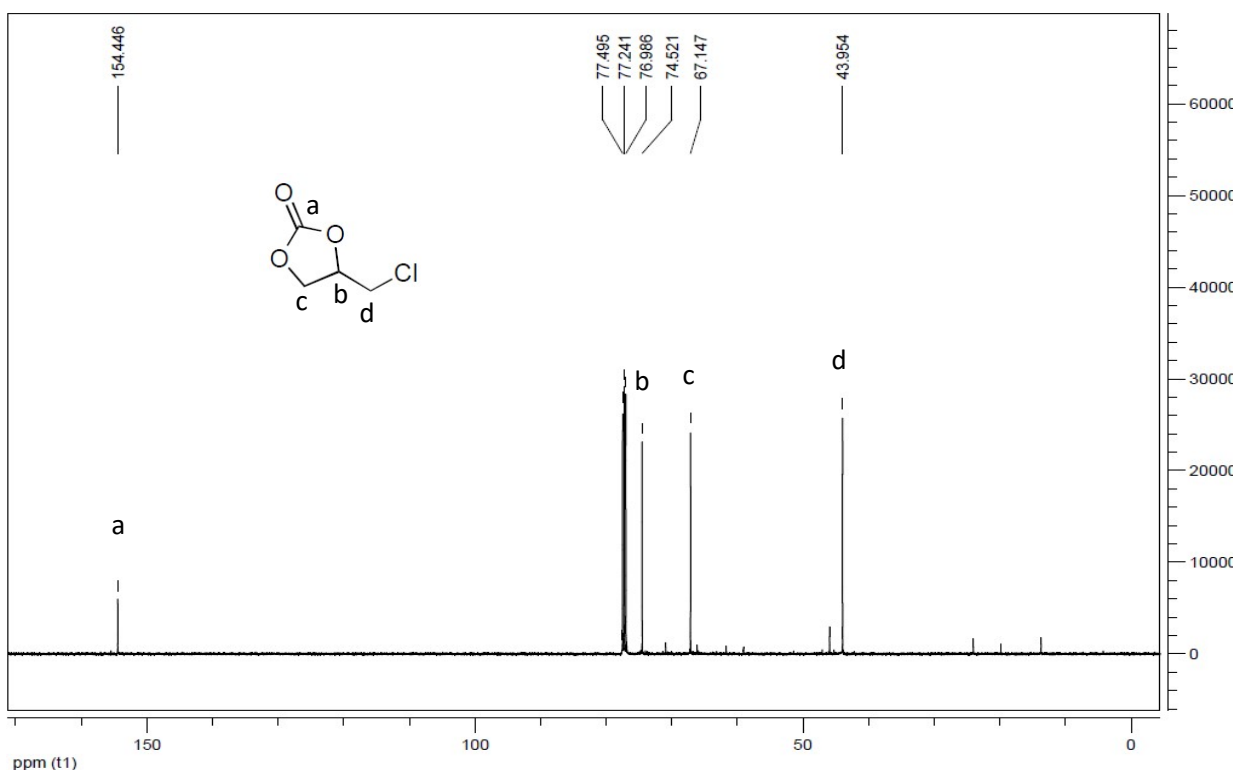


Figure S3. ^{13}C NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (CDCl_3 , 500 MHz).

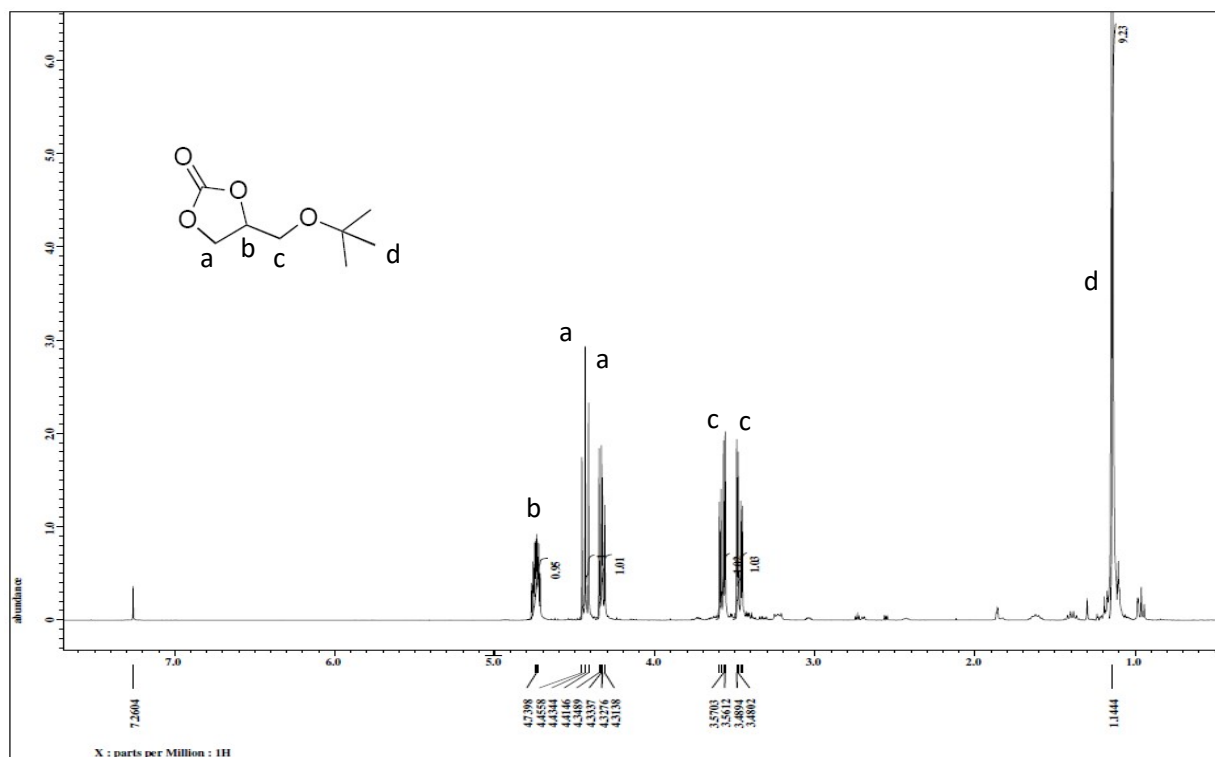


Figure S4. ¹H NMR spectrum of 4-(tert-butoxymethyl)-1,3-dioxolan-2-one (CDCl₃, 400 MHz).

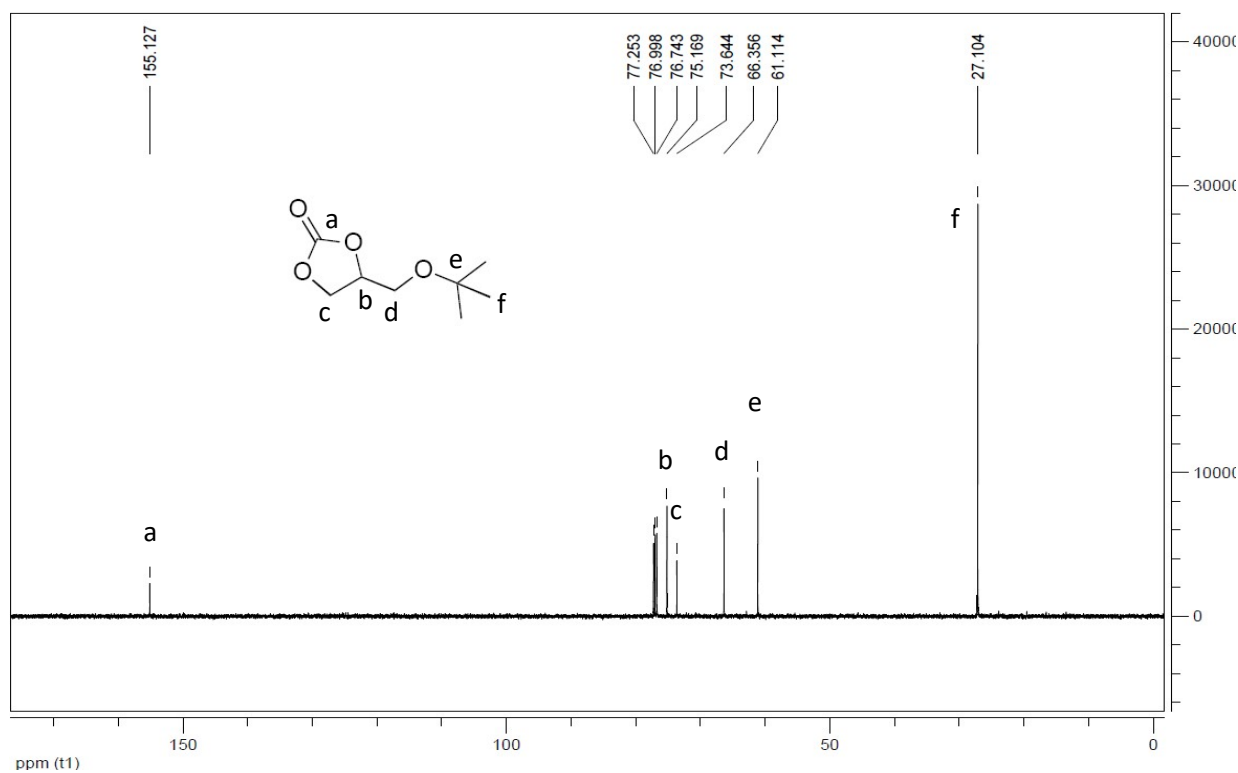


Figure S5. ¹³C NMR spectrum of 4-(tert-butoxymethyl)-1,3-dioxolan-2-one (CDCl₃, 500 MHz).

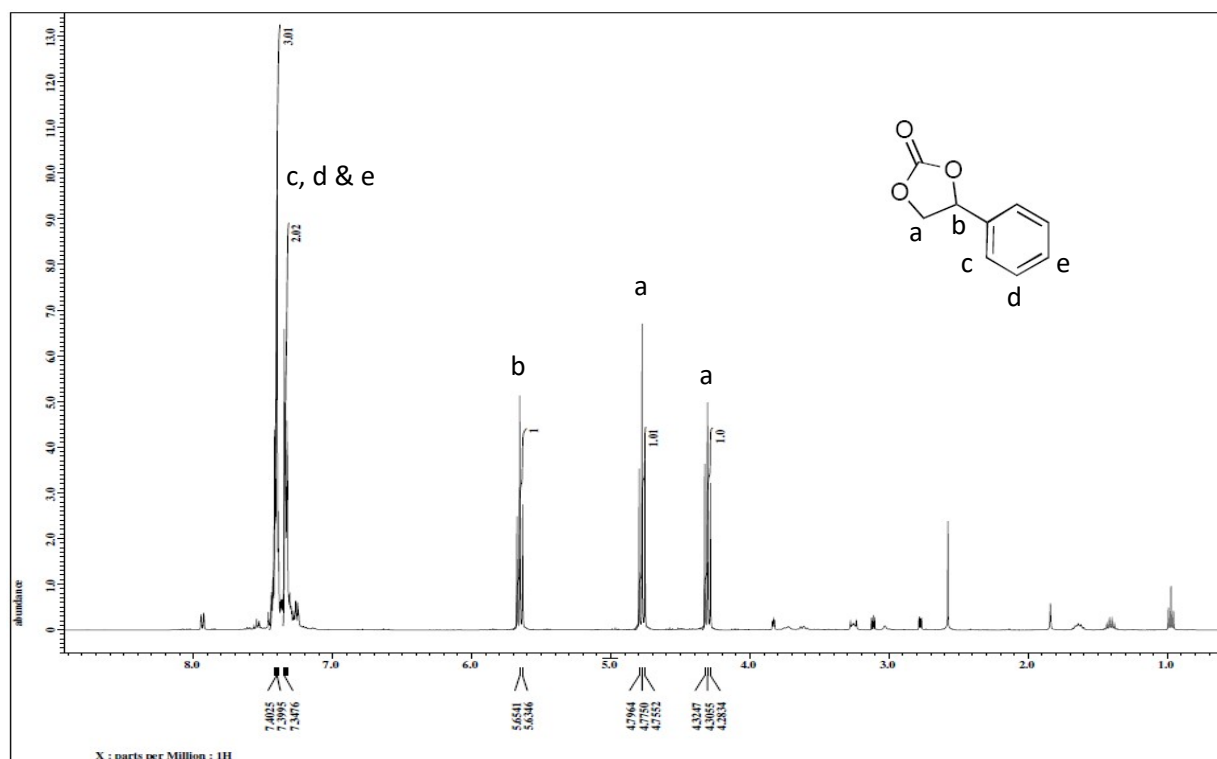


Figure S6. ^1H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one (CDCl₃, 400 MHz).

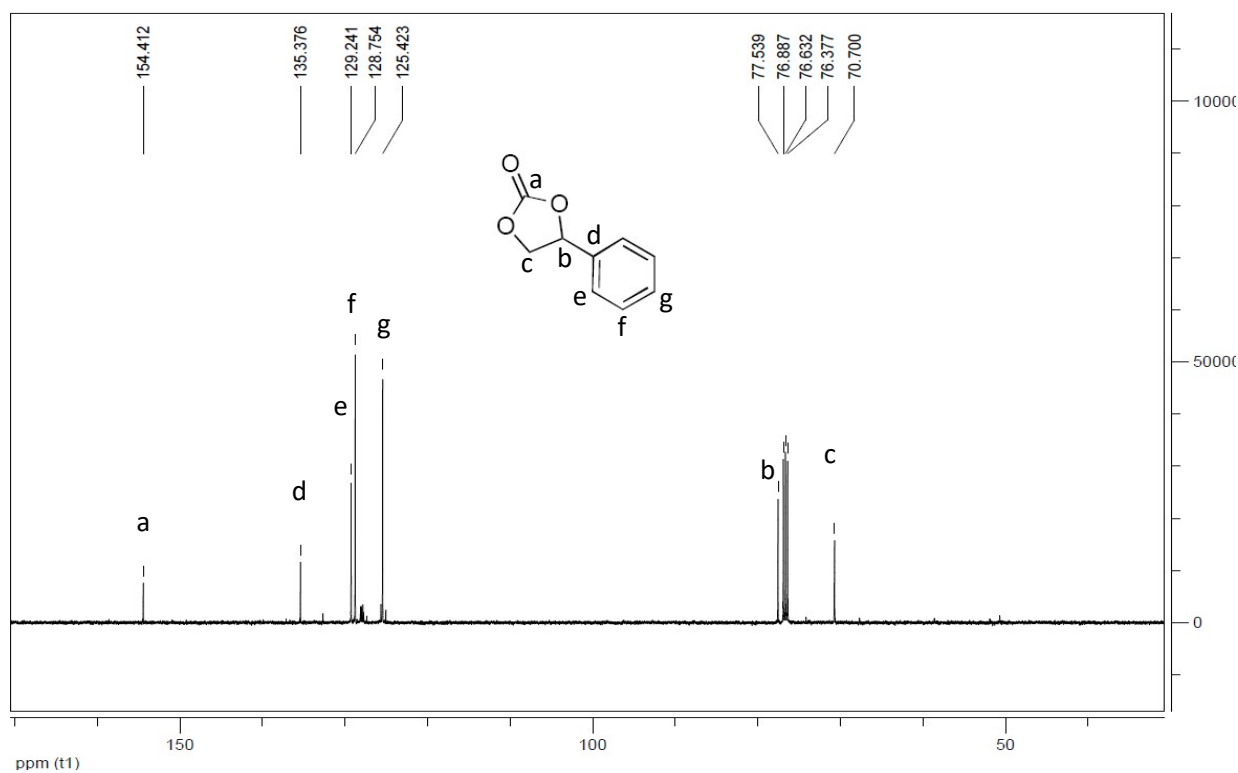


Figure S7. ^{13}C NMR spectrum of 4-phenyl-1,3-dioxolan-2-one (CDCl₃, 500 MHz).

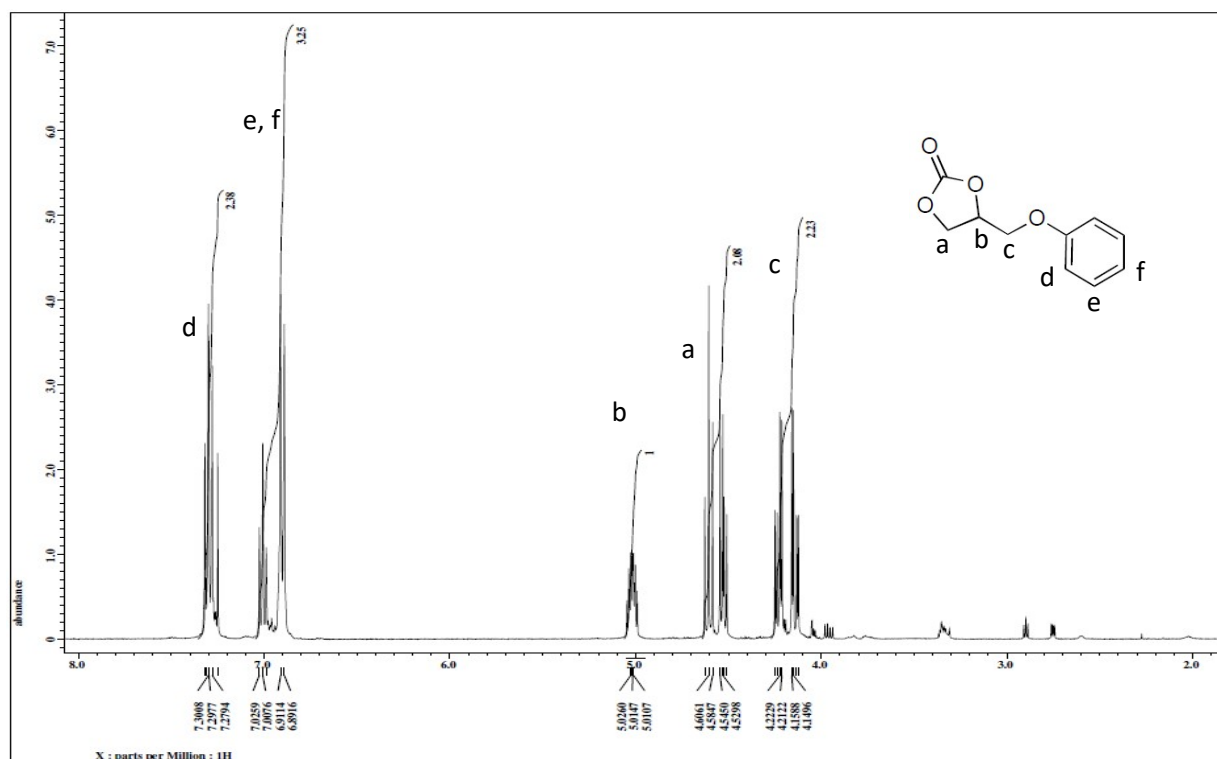


Figure S8. ¹H NMR spectrum of 4-(phoxymethyl)-1,3-dioxolan-2-one (CDCl₃, 400 MHz).

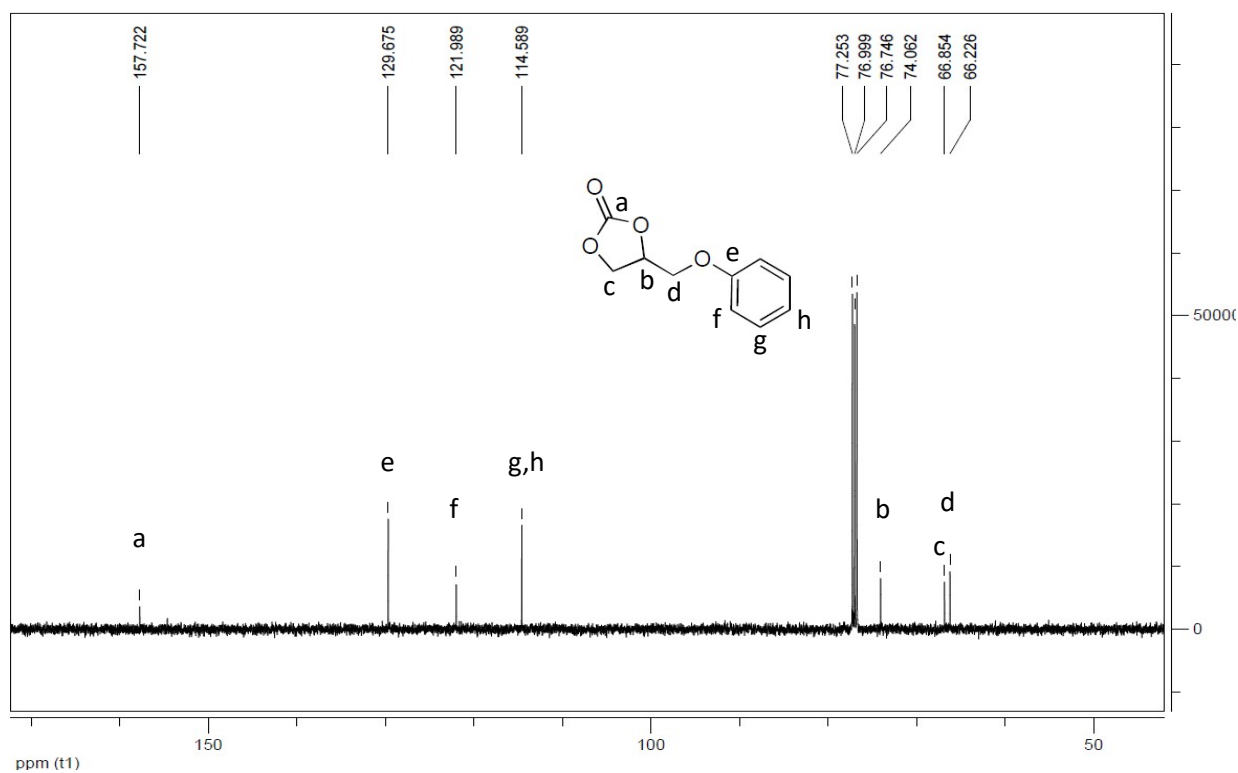


Figure S9. ¹³C NMR spectrum of 4-(phoxymethyl)-1,3-dioxolan-2-one (CDCl₃, 500 MHz).

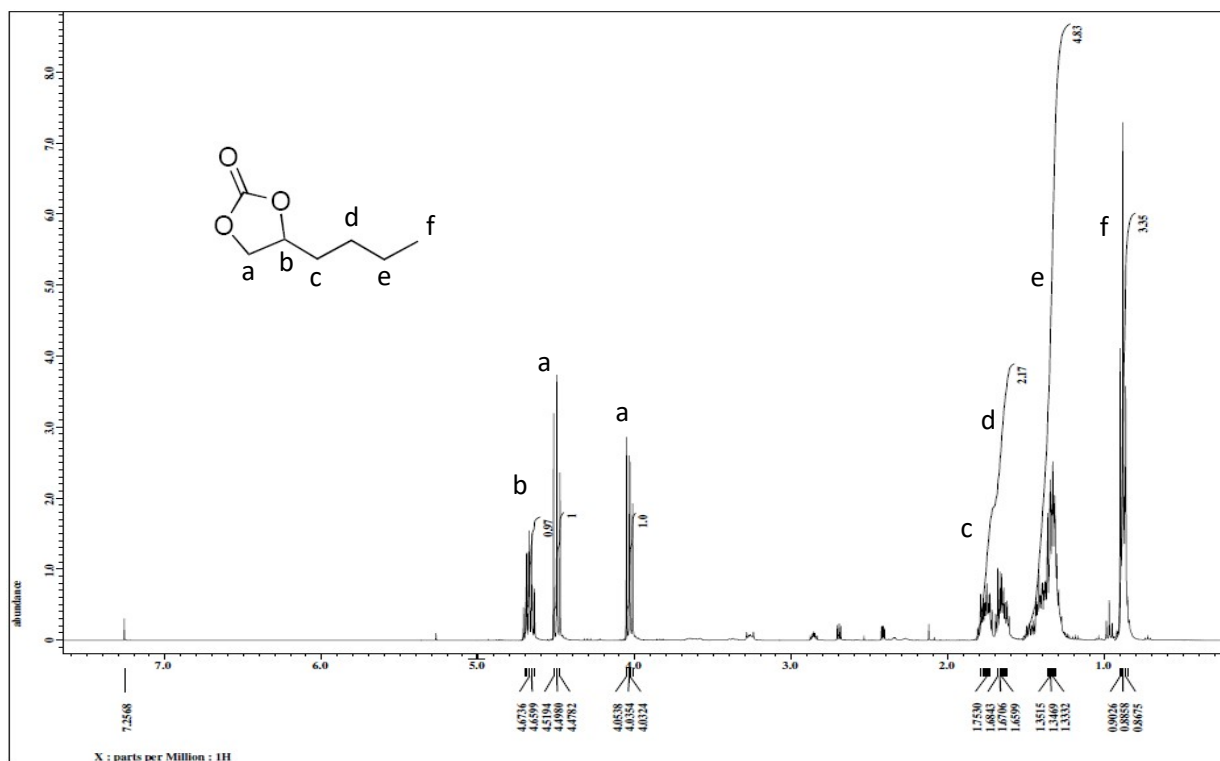


Figure S10. ^1H NMR spectrum of 4-butyl-1,3-dioxolan-2-one (CDCl_3 , 400 MHz).

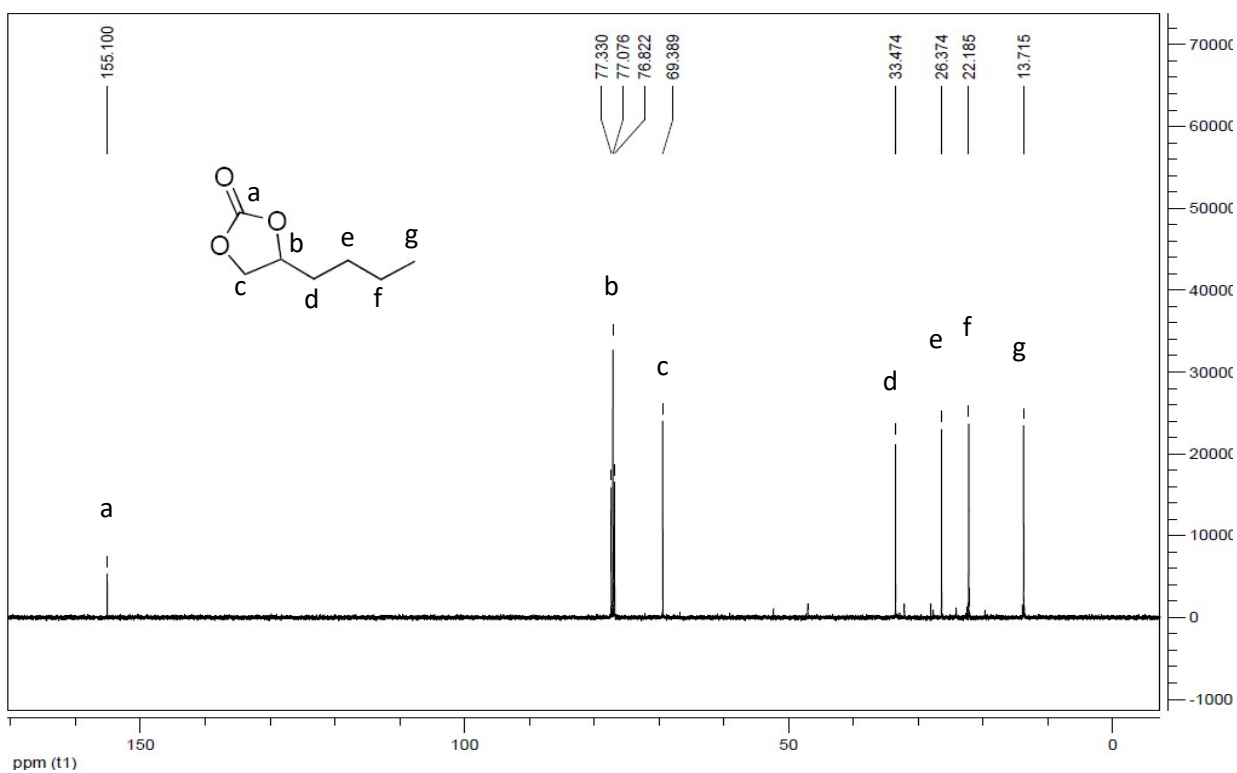


Figure S11. ^{13}C NMR spectrum of 4-butyl-1,3-dioxolan-2-one (CDCl_3 , 500 MHz).

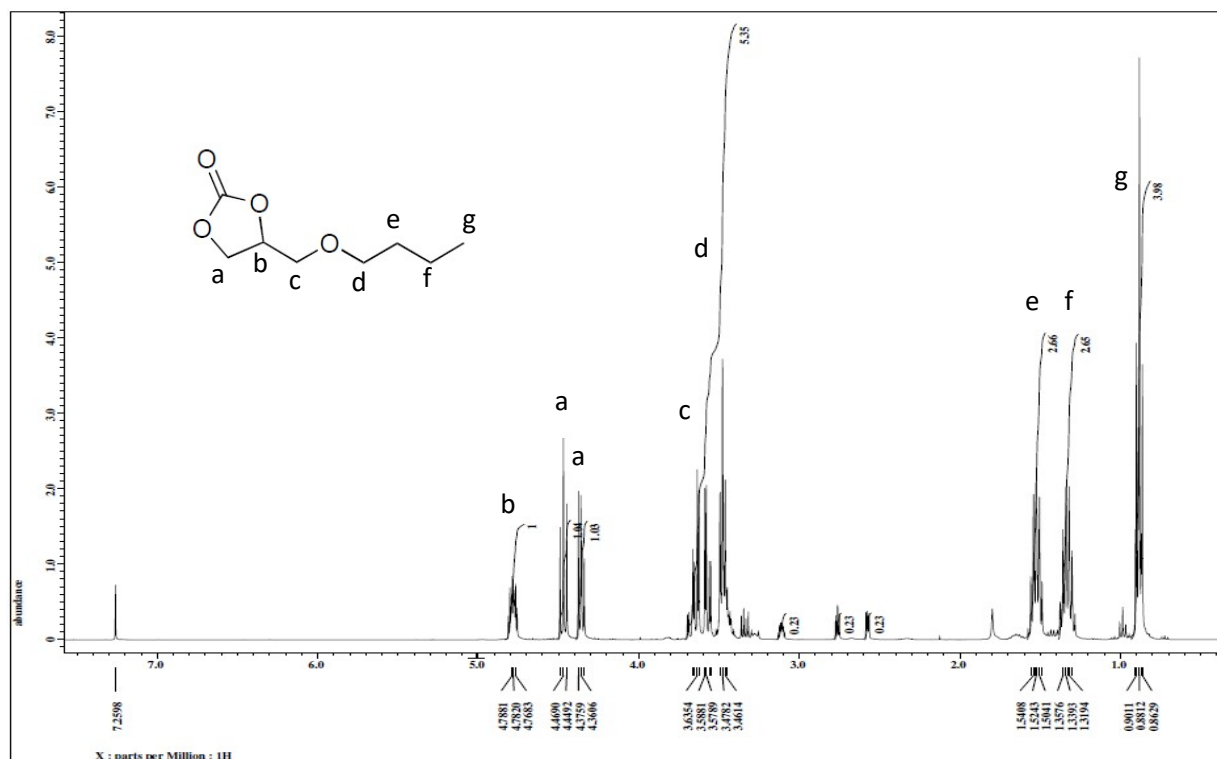


Figure S12. ^1H NMR spectrum of 4-(butoxymethyl)-1,3-dioxolan-2-one (CDCl_3 , 400 MHz).

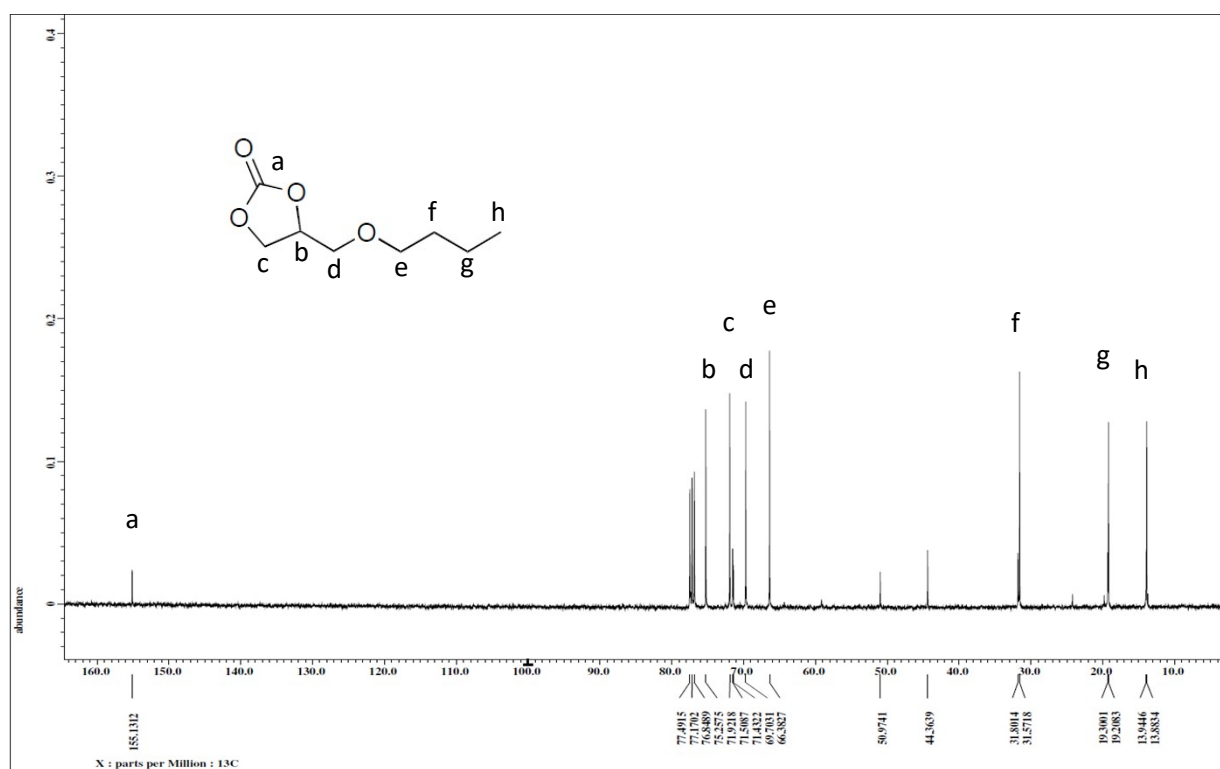


Figure S13. ^{13}C NMR spectrum of 4-(butoxymethyl)-1,3-dioxolan-2-one (CDCl_3 , 400 MHz).

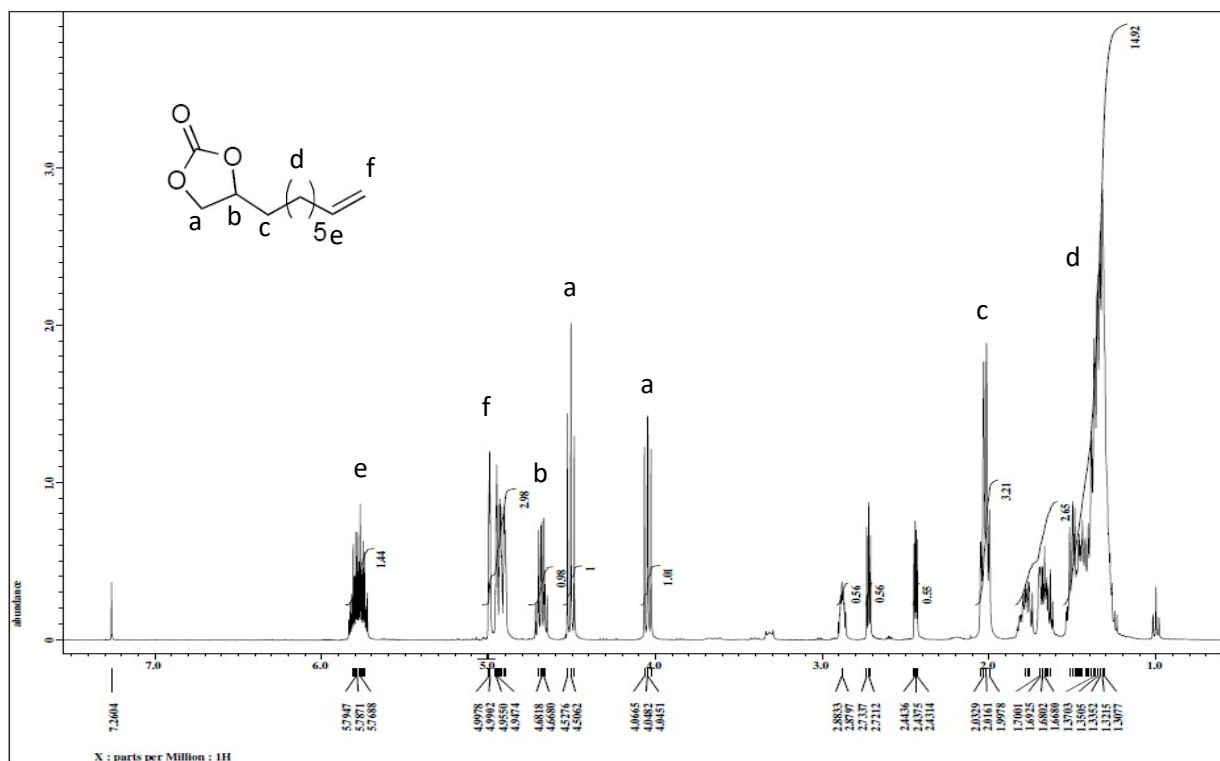


Figure S14. ¹H NMR spectrum of 4-(oct-7-enyl)-1,3-dioxolan-2-one (CDCl₃, 400 MHz).

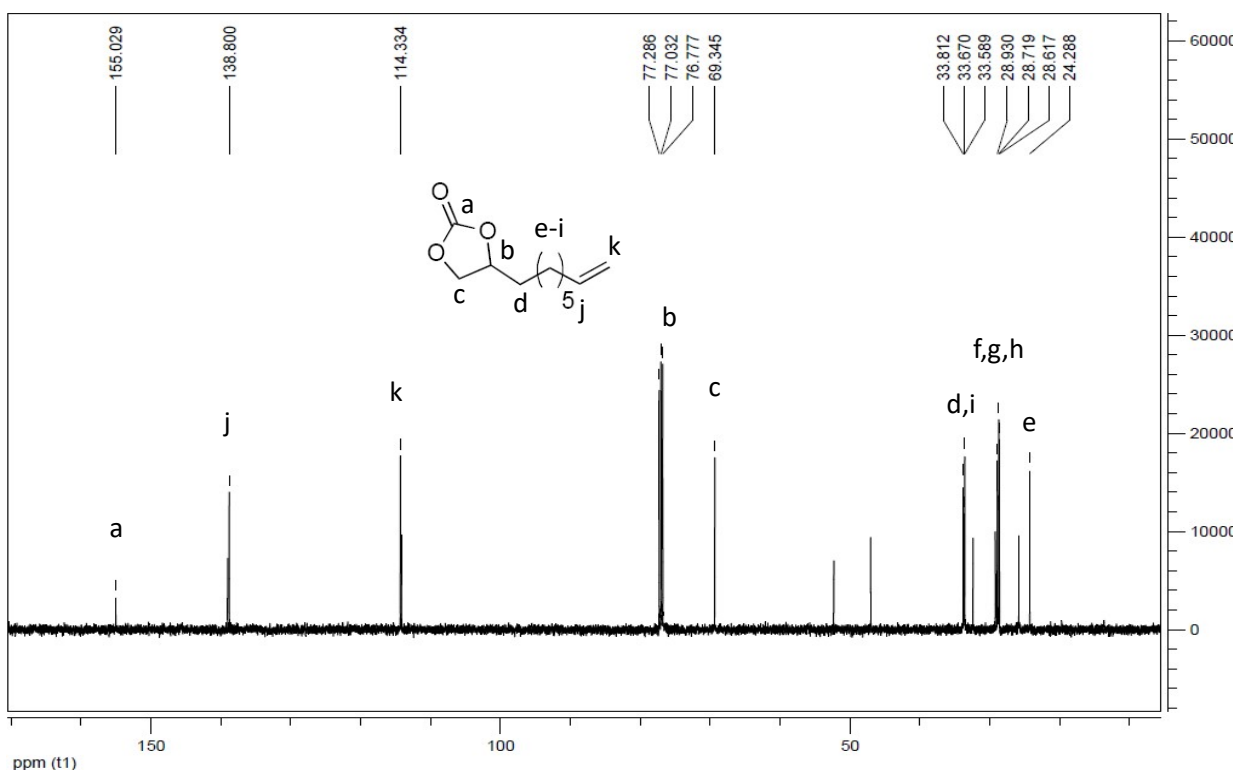


Figure S15. ¹³C NMR spectrum of 4-(oct-7-enyl)-1,3-dioxolan-2-one (CDCl₃, 500 MHz).

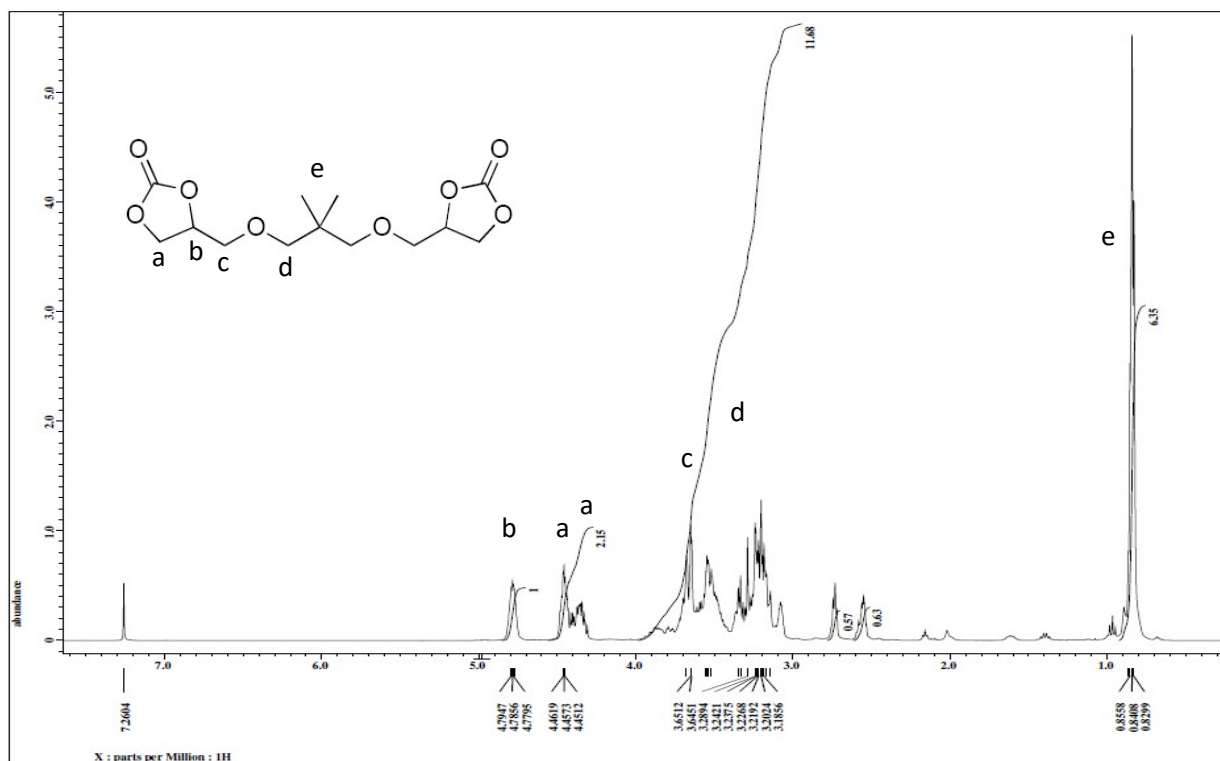


Figure S16. ^1H NMR spectrum of 4,4'-(2,2-dimethylpropane-1,3-diyl)bis(oxy)bis(methylene)bis(1,3-dioxolan-2-one) (CDCl₃, 400 MHz).

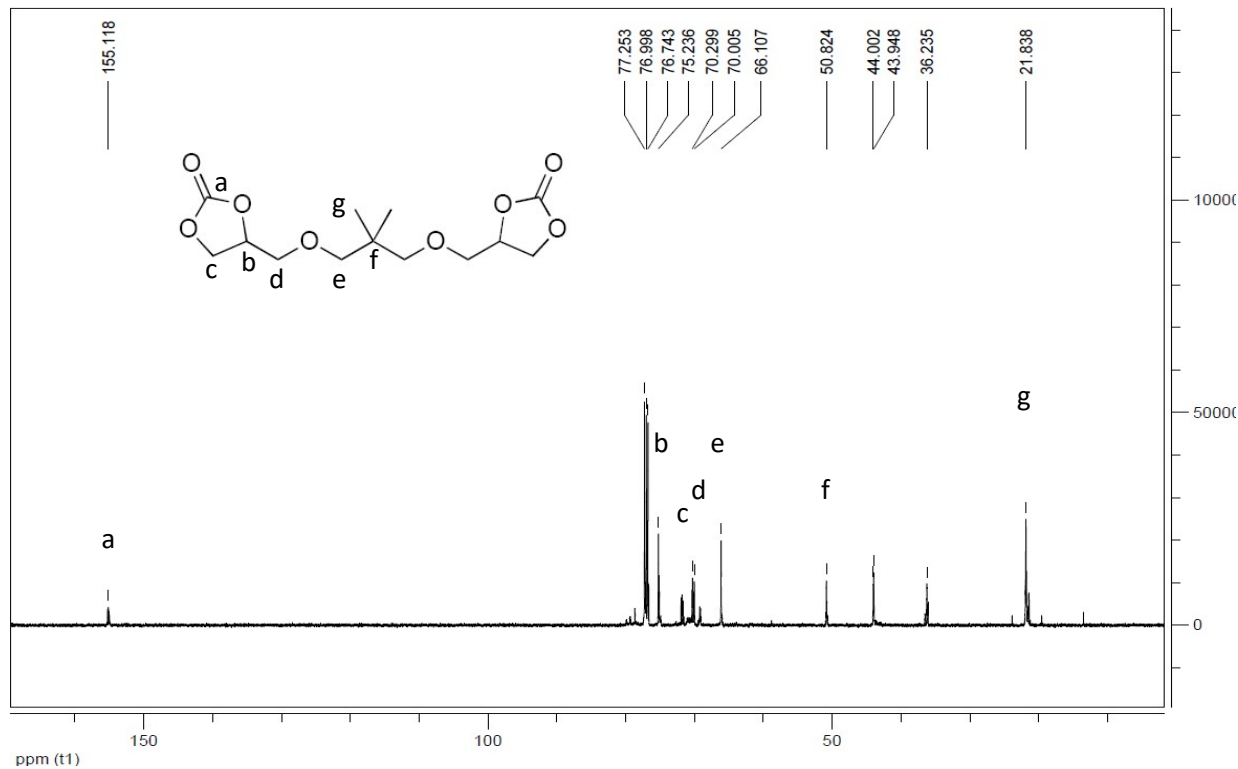


Figure S17. ^{13}C NMR spectrum of 4,4'-(2,2-dimethylpropane-1,3-diyl)bis(oxy)bis(methylene)bis(1,3-dioxolan-2-one) (CDCl₃, 500 MHz).

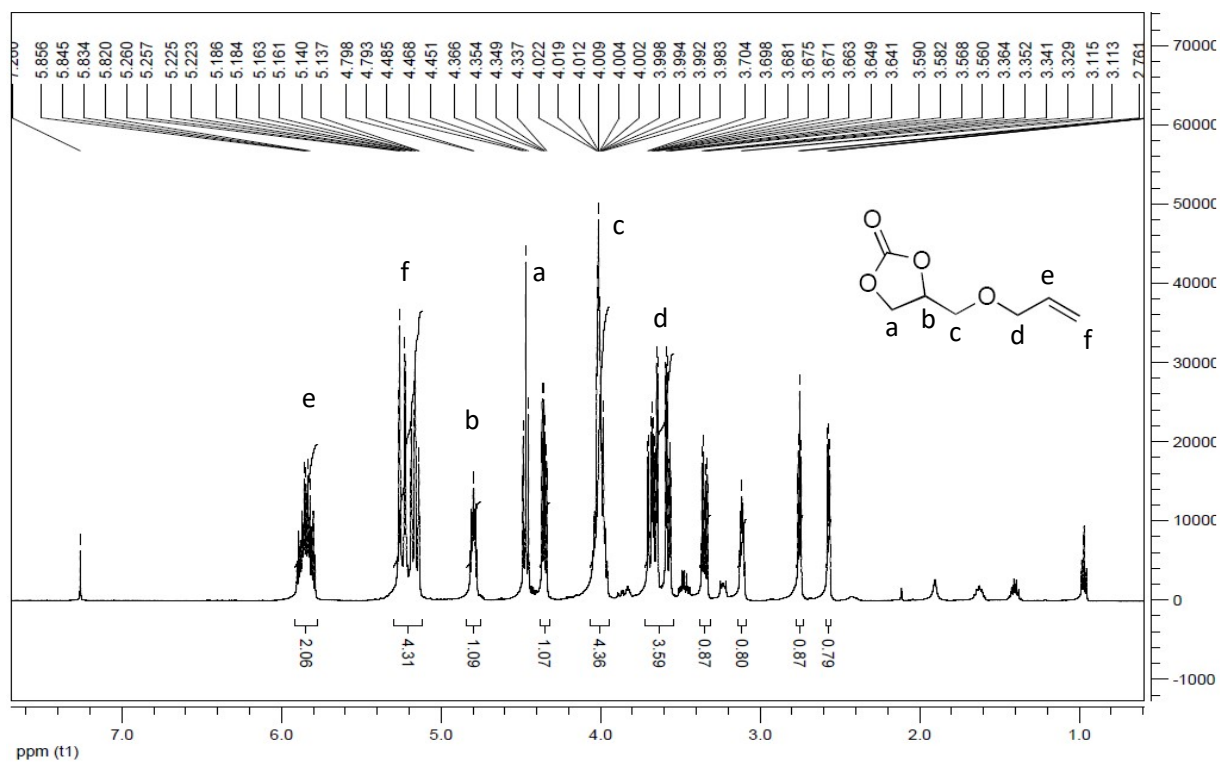


Figure S18. ^1H NMR spectrum of 4-(allyloxymethyl)-1,3-dioxolan-2-one (CDCl_3 , 500 MHz).

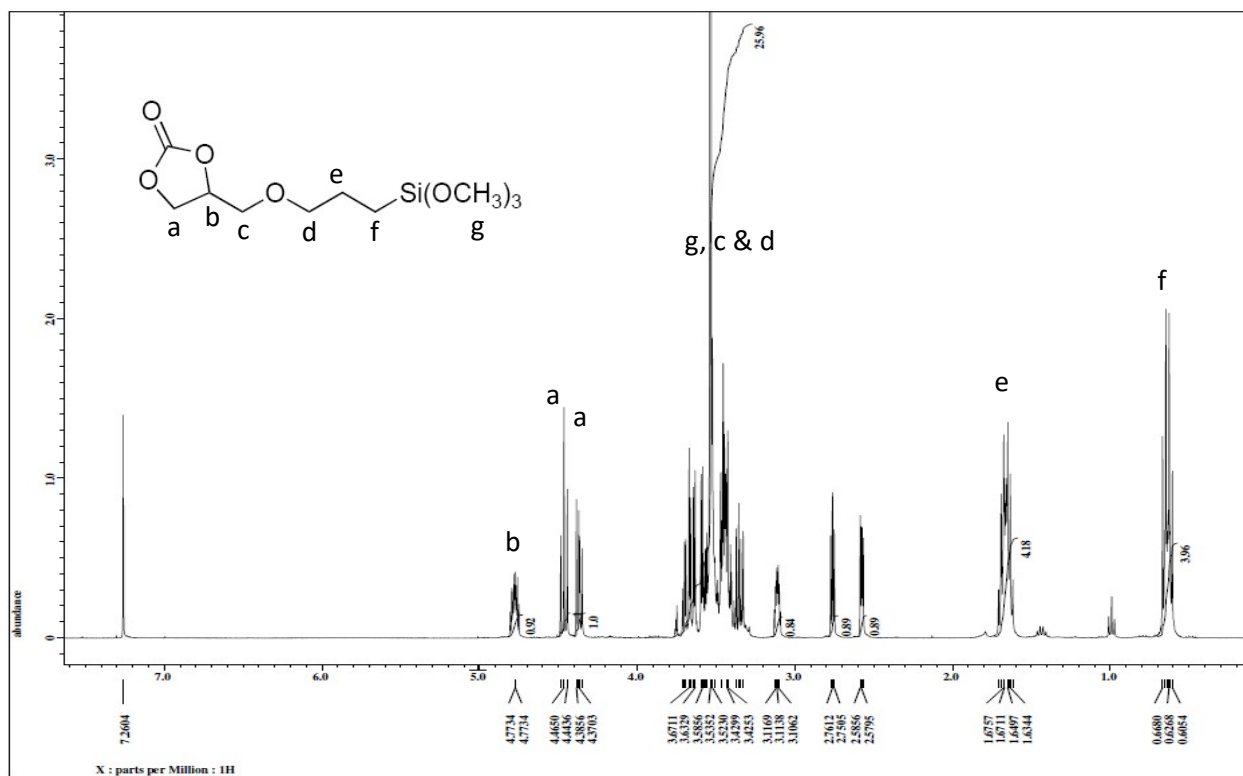


Figure S19. ¹H NMR spectrum of 4-((3-(trimethoxysilyl)propoxy)methyl)-1,3-dioxolan-2-one (CDCl₃, 400 MHz).

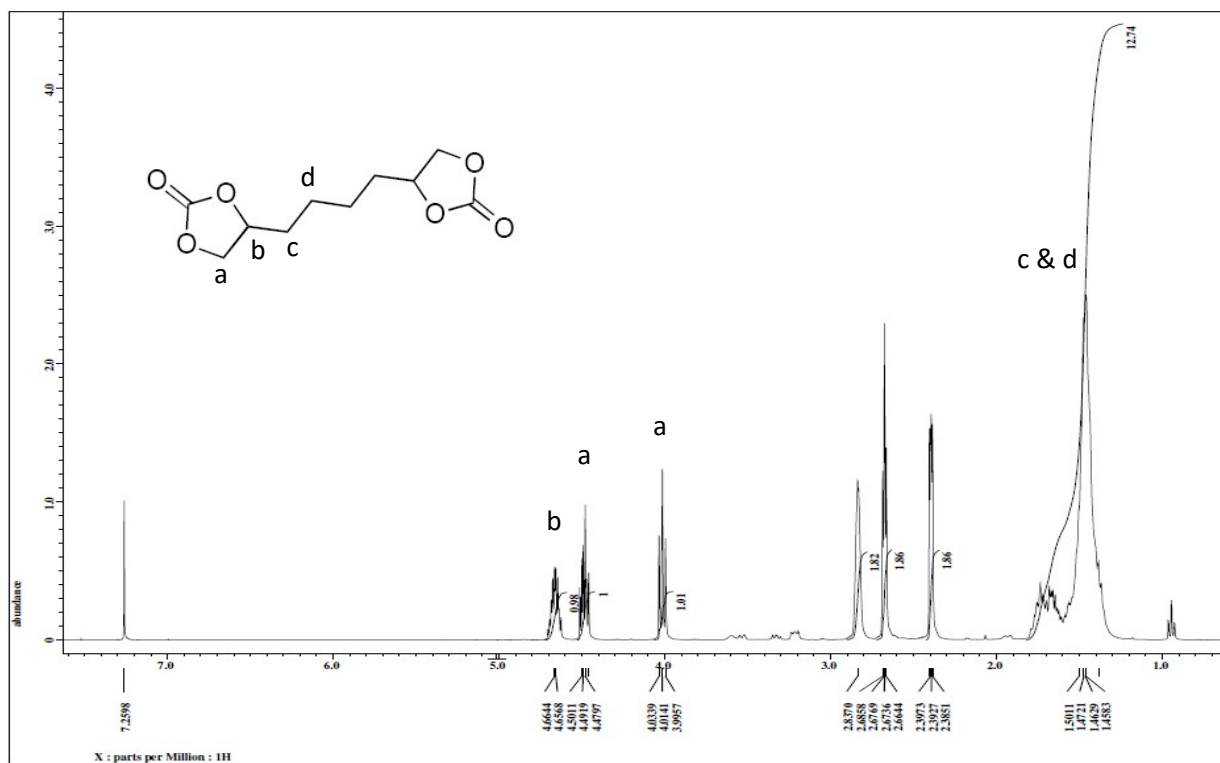


Figure S20. ¹H NMR spectrum of 4,4'-(butane-1,4-diyl)bis(1,3-dioxolan-2-one) (CDCl₃, 400 MHz).

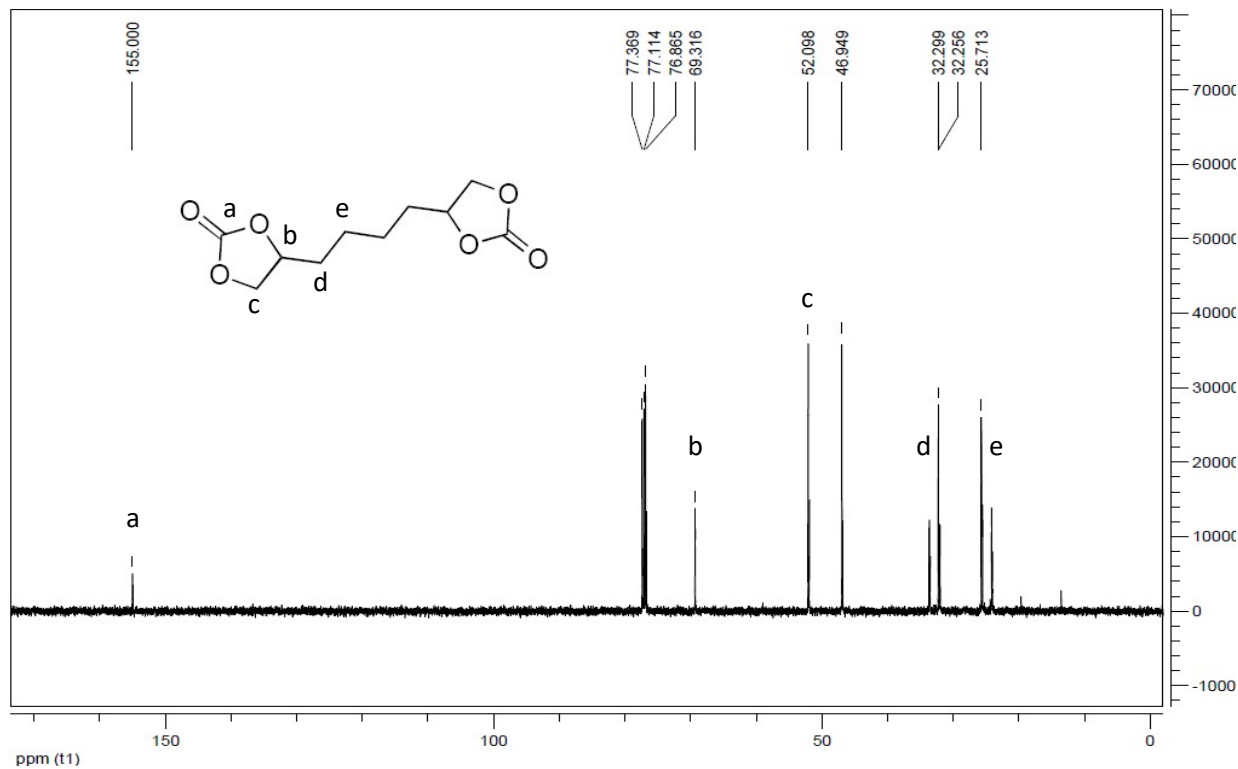


Figure S21. ¹³C NMR spectrum of 4,4'-(butane-1,4-diyl)bis(1,3-dioxolan-2-one) (CDCl₃, 500 MHz).

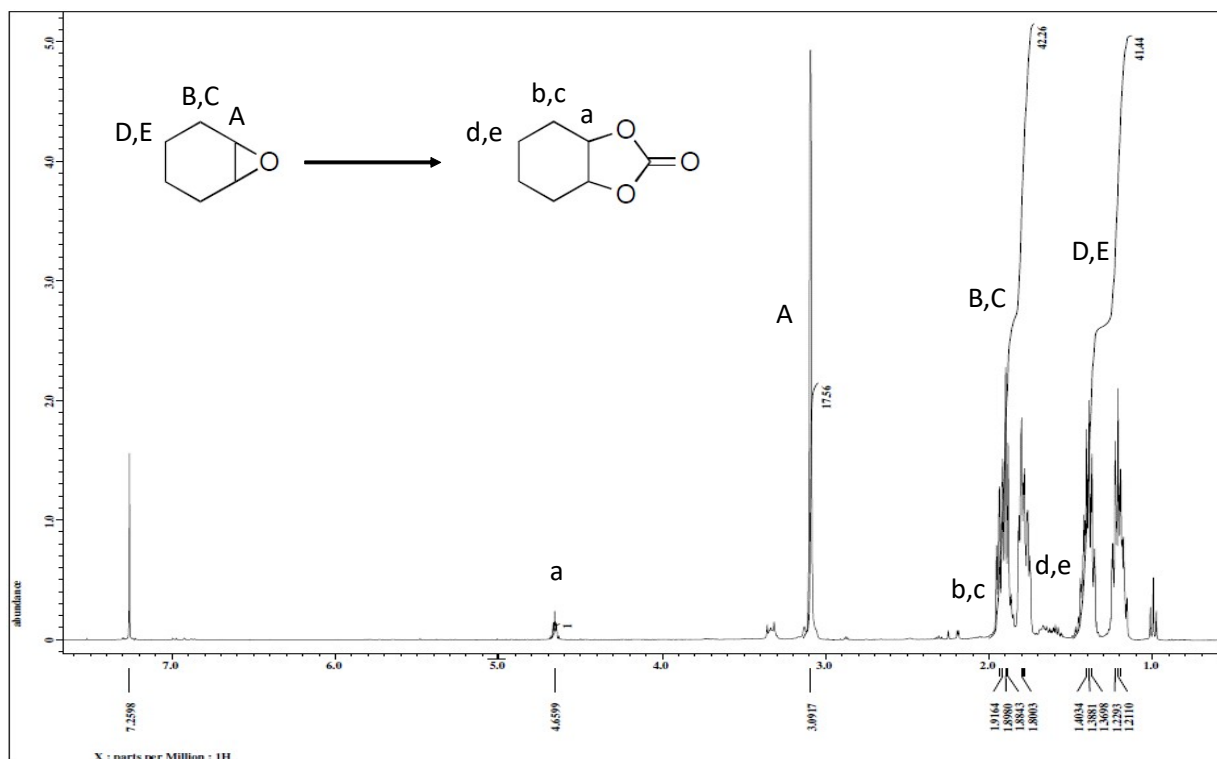


Figure S22. ^1H NMR spectrum of epoxycyclohexane to hexahydro-1,3-benzodioxol-2-one conversion (CDCl_3 , 400 MHz).

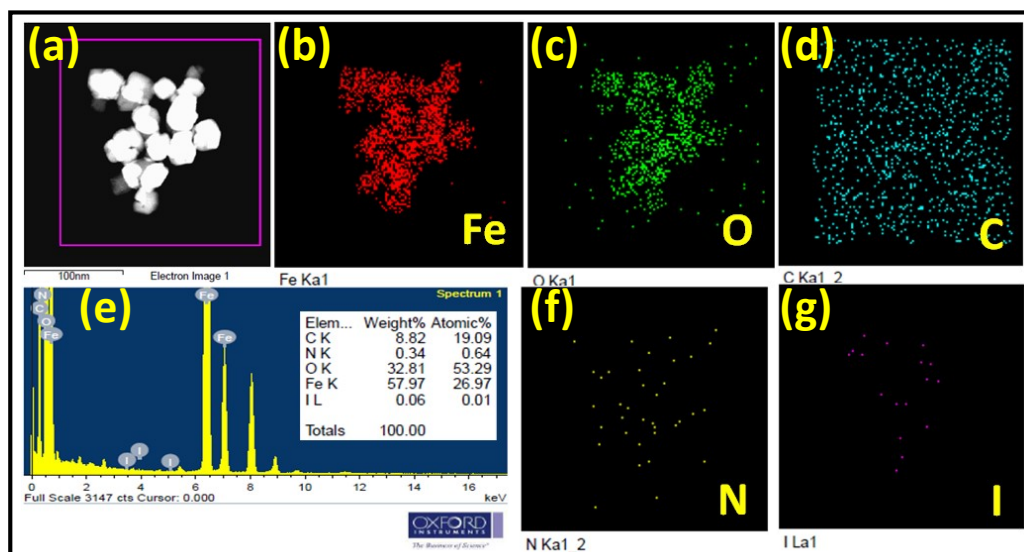


Figure S23. Elemental mapping and corresponding EDS data of PABA@ α - Fe_2O_3 nanocatalyst after the recyclability study.

Table S3. Comparison of PABA@ α -Fe₂O₃ nanocatalyst with the reported heterogeneous catalysts for cycloaddition of CO₂ into epoxide to synthesize cyclic carbonate

| Catalyst (amount) | Cocatalyst (amount) | Epoxide (amount) | Reaction conditions (temperature, pressure, time) | Conversion (%) | Reference |
|---|---|------------------|---|----------------|--|
| PABA@ α -Fe ₂ O ₃ (50 mg) | TBAI (0.25 mmol) | 23 mmol | 105°C, 1 atm, 20 h | 98 | This work |
| Au/ α -Fe ₂ O ₃ (50 mg) | TBAI (0.25 mmol) | 23 mmol | 105°C, 1 atm, 20 h | 91 | <i>New J. Chem.</i> 2020 , 44, 11887-11894 |
| Microporous Zn(II)-MOF (0.5 mol%) | TBAB (0.5 mol%) | 2 mmol | 40°C, 1 atm, 24 h | 99 | <i>Inorg. Chem.</i> 2020 , 59 (7), 4273-4281 |
| Cage-like Zn-MOF (0.2 mol%) | TBAB (2 mol%) | 20 mmol | 80°C, 2.0 MPa, 4 h | 97 | <i>Inorg. Chem. Front.</i> 2020 , 7(3), 746-755 |
| (3,3',5,5'-tetrakisphenylbiphenyl) TPBP-COFs (0.01 mmol) | TBAB (0.05 mmol) | 1 mmol | 40°C, 0.1 MPa, 24 h | 91 | <i>Chem. Eur. J.</i> 2020 , 26, 4510-4514 |
| COF1/ZnBr ₂ [0.7: 0.1: 2.5(TBAB) mol%] | TBAB [catalyst: TBAI= 0.7: 0.1: 2.5 mol%] | 10 mmol | 80°C, 0.1 MPa, 12 h | 99 | <i>Microporous Mesoporous Mater.</i> 2020 , 308, 110314 |
| Benzimidazole-based hyper-crosslinked poly(ionic liquids) (20 mg) | TBAB (1 mmol) | 4 mmol | 70°C, 0.1 MPa, 9 h | 99 | <i>Chem. Eng. J.</i> 2020 , 385, 123973 |
| Zn-Salen based conjugated microporous polymers (0.1 mmol) | TBAB (600 mg) | 50 | 120°C, 3.0 MPa, 1 h | 89 | <i>ChemistrySelect.</i> 2020 , 5, 10516-10520 |

| Catalyst (amount) | Cocatalyst (amount) | Epoxide (amount) | Reaction conditions (temperature, pressure, time) | Conversion (%) | Reference |
|---|--|-----------------------------------|---|----------------|--|
| porous carbon/silica nanocomposites supported ionic liquids (ILs loading, 1.07 mmol g ⁻¹) | -- | propylene oxide (2 mL) | 100°C, 1.0 MPa, 3 h | 73 | <i>Microporous Mesoporous Mater.</i> 2020 , 293, 109768 |
| Graphene oxide (3.2 wt.%) | TBAB [TBAB: epoxide ratio (1/40 mole %)] | TBAB: epoxide ratio (1/40 mole %) | 80°C, 1 bar, 12 h | 95 | <i>J. Environ. Chem. Eng.</i> 2020 , 8, 104568 |
| Pyridyl Salicylimines (30 mg) | -- | 5 mmol | 100°C, 1 atm, 24 h | 99 | <i>ACS Appl. Mater. Interfaces</i> 2018 , 10, 9478-9484 |
| Polyurethane (20 mol %) | -- | 5 mmol | 150°C, 9 MPa, 16 h | 99 | <i>ACS Sustainable Chem. Eng.</i> 2020 , 8, 4337-4340 |
| Cu-based magnetic nanocatalyst (50 mg) | DBU (4 mol%) | 5 mmol | 80°C, 1 atm, 12 h | 92 | <i>Sci. Rep.</i> , 2018 , 8, 1901 |
| Palladium NP/ mesoporous TiO ₂ (20 mg) | TBAB (5 mmol) | 5 mmol | 80°C, 1 atm, 2 h | 98 | <i>New J. Chem.</i> , 2017 , 41, 12937-12946 |
| Amine-Functionalized Graphene Oxide (30 mg) | TBAI (0.1 mmol) | 10 mmol | 70 °C, 1 MPa, 12 h | 95 | <i>ChemSusChem</i> 2016 , 9, 644-650 |