Biomass-derived metal-organic hybrids for CO_2 transformation under ambient conditions

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1. Materials and methods.

1.1 Materials

Chitosan, $ZnCl_2$ (99%) $AlCl_3 \cdot 6H_2O$ were acquired from Sinopharm Chemical Reagent. Phytic acid (45 wt% in water), $MnCl_2$ (99%), $CuCl_2$ (99%), tetrabutylammonium bromide (99%), propylene oxide (99%), epichlorohydrin (99%) and epibromohydrin (99%) were purchased from J&K Scientific Ltd.. Allyl glycidyl ether (99%), 2-(chloromethyl)-2-methyloxirane (98%), styrene oxide (98%), cyclohexene oxide (98%) and 1,2-epoxyoctane (97%) were purchased from Adamas Reagent Co., Ltd.. CO_2 was supplied by Beijing Analytical Instrument Factory with purity of 99.99%. All above chemicals were used without further purification.

1.2 Methods

Field emission scanning electron microscope (SEM, S-4800, Hitachi, Japan) and transmission electron microscope (TEM, JEM2100F, JEOL, Japan) equipped with energy dispersive spectroscopy (EDS) were applied to observe the morphology of the samples. The specific surface area (SSA) and pore structure of the resultant materials were investigated by means of a Quantachrome Quadrasorb SI-MP porosimeter using nitrogen as the adsorbate at 77 K. Prior to determination of the isotherm, the MOHs samples were degassed at 120 °C under vacuum for at least 6 h. The value of the total pore volume was determined from the NLDFT kernel at the relative pressure $P/P_0 = 0.99$. The total SSA was calculated using the Brunauer-Emmett-Teller (BET) method from the nitrogen adsorption data in the relative pressure (P/P_0) of 0.03-0.30. X-Ray photoelectron spectroscopy (XPS) data were collected on an ESCALab220i-XL electron spectrometer using 300 W Al-Kα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. FT-IR analyses of the samples were detected using a Bruker Optic TENSOR-37. All samples were determined in the range of 400-4000 cm^{-1} wavenumbers mixed with KBr. The elemental contents of the samples were determined using Flash EA1112 from Thermo. TGA analysis was carried out with a Perkin Elmer thermoanalyzer (model: Diamond TG/DTA). The weight loss was recorded in the range of 100–800 ^oC. Inductively coupled plasma (ICP) analysis was performed on a Jarrel-AshJ-A1100 spectrometer. X-ray diffraction (XRD) measurements were carried out on D/max 2500. NMR analysis was performed on a Bruker Avance 400 MHz spectrometer. X-ray absorption (XAS) experiments were operated at the 1W1B beam line at Beijing Synchrotron Radiation Facility. Temperature-programmed desorption of carbon dioxide (CO_2-TPD) was performed on Micromeritics' AutoChem 2950 HP Chemisorption Analyzer. The CO_2 adsorption isotherms were measured at 273 K and 298 K by Autosorb-1-C Quantachrome analyzer.

2. Characterization for the synthesis of materials, Figure. S1-S7, Table. S1-S3.

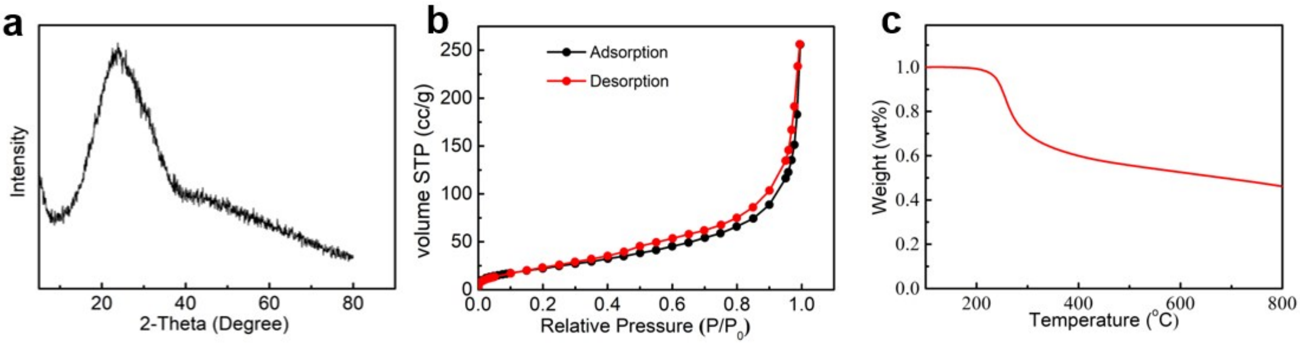

Figure S1. Characterization for MOH-Zn: (a) Powder XRD pattern, (b) N_2-sorption isotherms and (c) TGA plot.

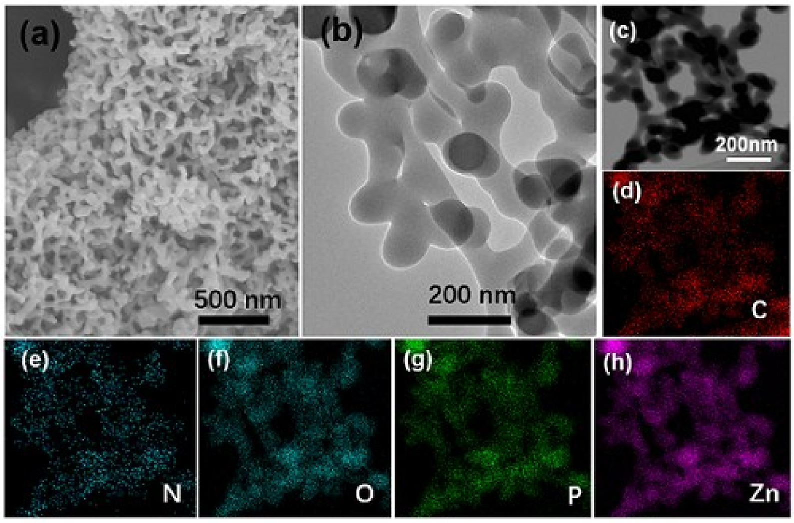

Figure S2. (a) SEM image of MOH-Cu, (b-c) TEM images of MOH-Cu and (d-h) EDS mapping images.

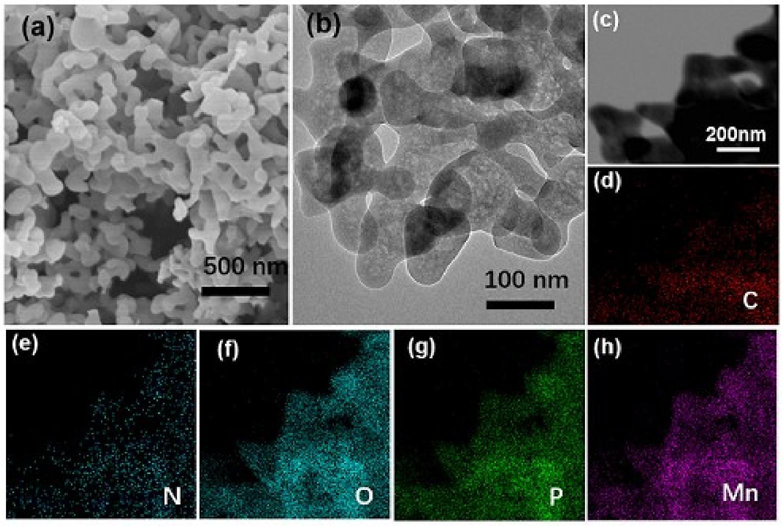

Figure S3. (a) SEM image of MOH-Mn, (b-c), TEM images of MOH-Mn and (d-h) EDS mapping images.

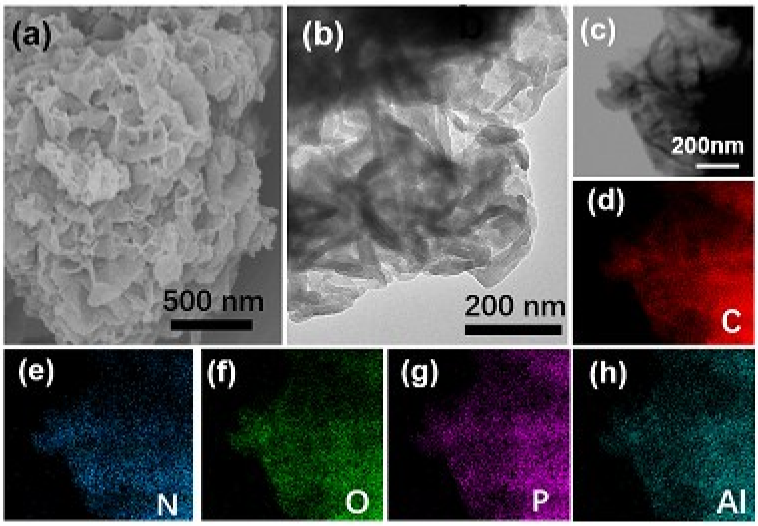

Figure S4. (a) SEM image of MOH-Al, (b-c) TEM images of MOH-Al, (d-h) EDS mapping images.

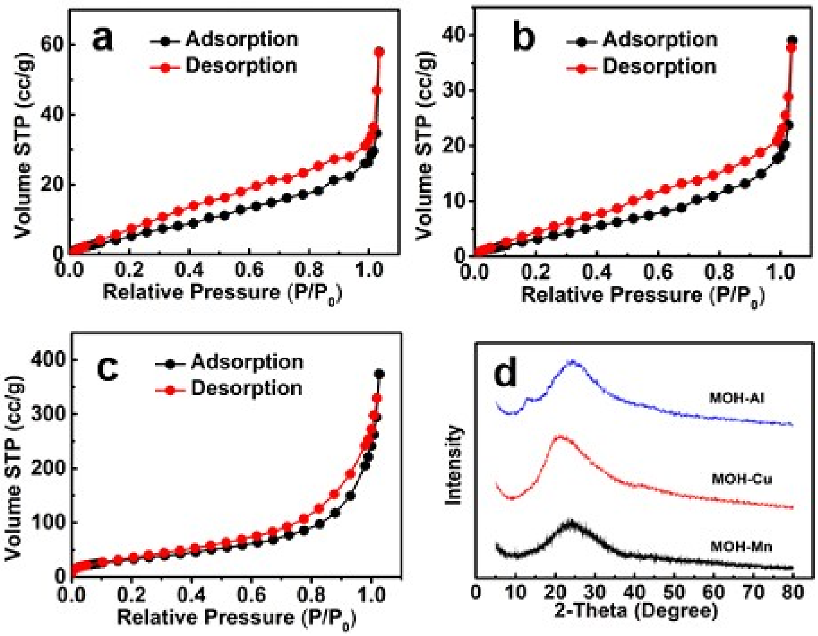

Figure S5. N_2-sorption isotherms for (a) MOH-Cu, (b) MOH-Mn and (c) MOH-Al; (d) XRD patterns for synthesized MOH-M.

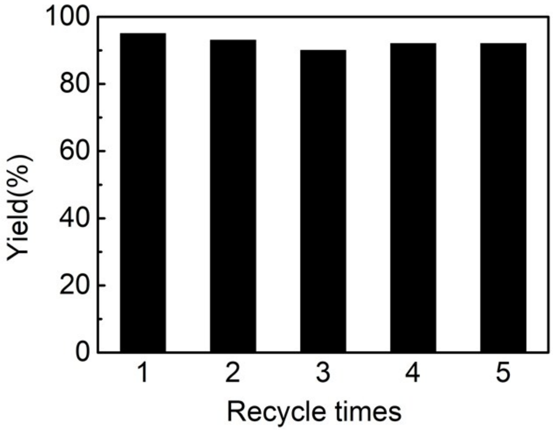

Figure S6. The results of the recycling test for the reaction of CO_2 with propylene oxide. Reaction condition: 1a (10 mmol), TBAB (7.2 mol%), content of Zn: 0.5 mol%, 30 ^{o}C, CO_2 (1 atm).

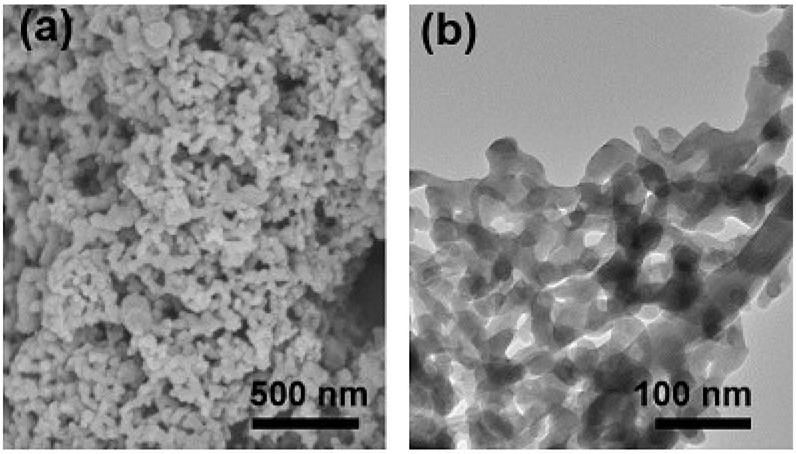

Figure S7. (a) SEM and (b) TEM images of MOH-Zn after 5 runs.

Table S1. Structural parameters extracted from the EXAFS fitting.

Sample	Shell	N	R(Å)	σ^2(Å^2)	R-factor(%)
Zn foil	Zn-Zn	6	2.638±0.006	0.0111±0.0007	0.5
Sample	Zn-N/O	4.001±0.023	1.988±0.004	0.0038	0.5
	Zn-P	1.203±0.023	2.301±0.007	0.0030	

Fitting range: 2.521≤k (/Å)≤10.996 and 1.25≤R (Å)≤2.8

Table S2. Element contents of the as-synthesized MOHs based on ICP analysis.

Sample	N (wt%)	P (wt%)	M (wt%)
MOH-Zn	4.79	5.05	8.24
MOH-Cu	5.63	7.89	6.63
MOH-Mn	4.33	12.37	9.82
MOH-Al	4.57	15.28	4.43

Table S3. Specific surface area, volume and average pore size of the as-synthesized MOHs.

Sample	Specific surface area (m^2/g)	Volume (cm^3/g)	Average pore size (nm)
MOH-Zn	90	0.40	9
MOH-Cu	30	0.09	6
MOH-Mn	17	0.06	7
MOH-Al	127	0.57	9

3. NMR spectra for products, Figure. S8-S21.

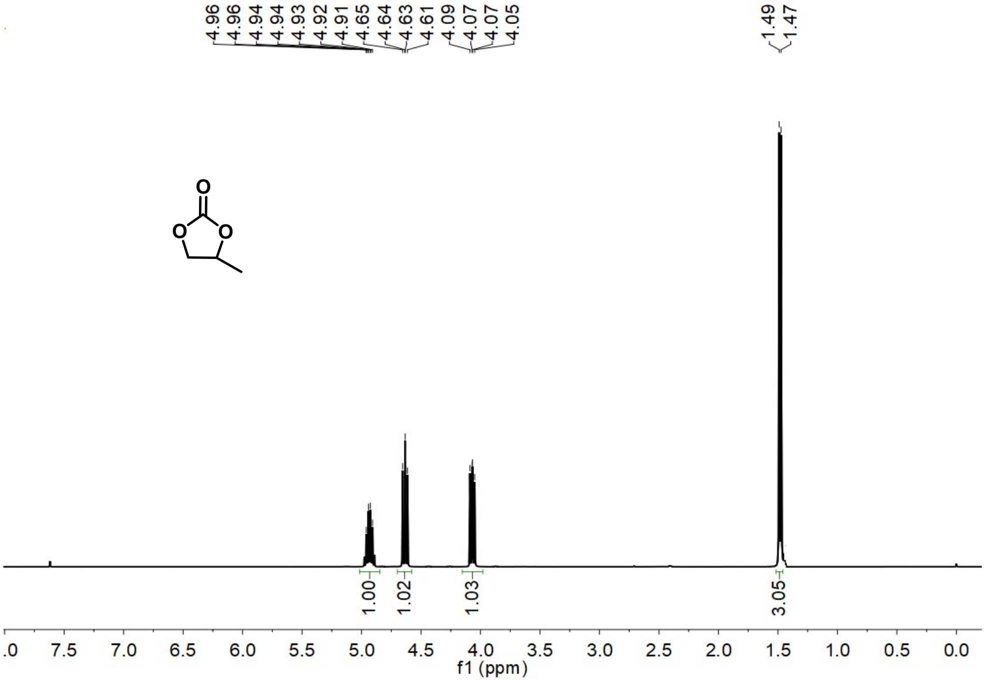

Figure S8. ^{1}H NMR spectrum for **2a**.

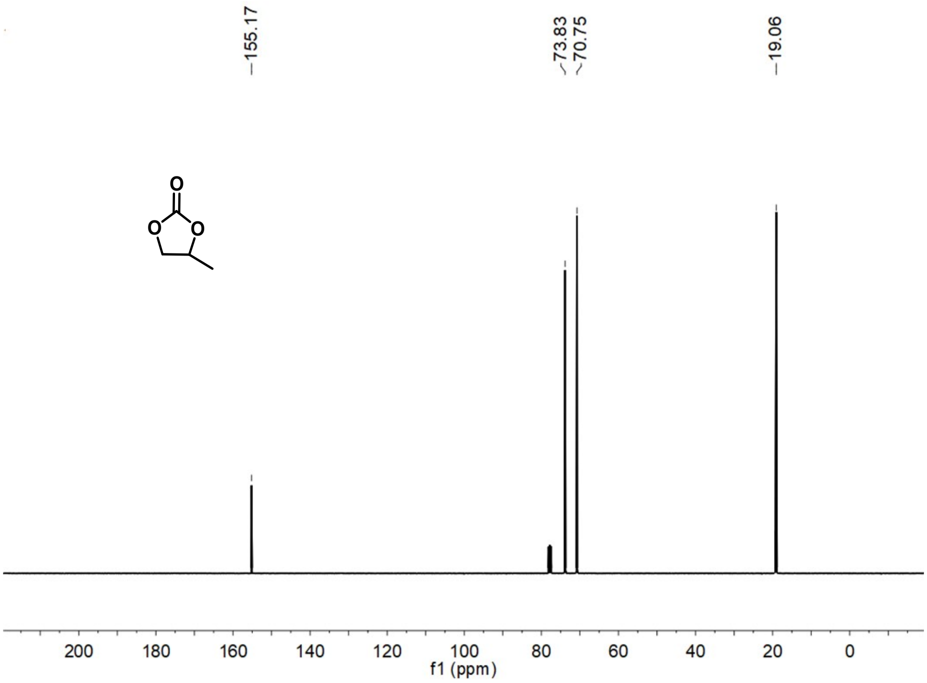

Figure S9. ^{13}C NMR spectrum for **2a**.

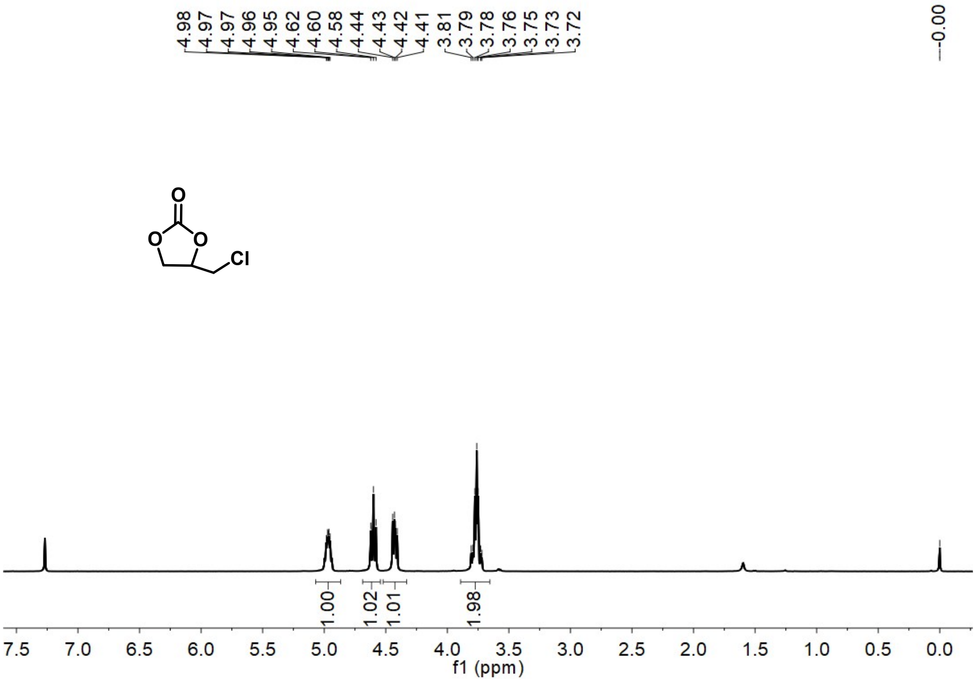

Figure S10. ^{1}H NMR spectrum for **2b**.

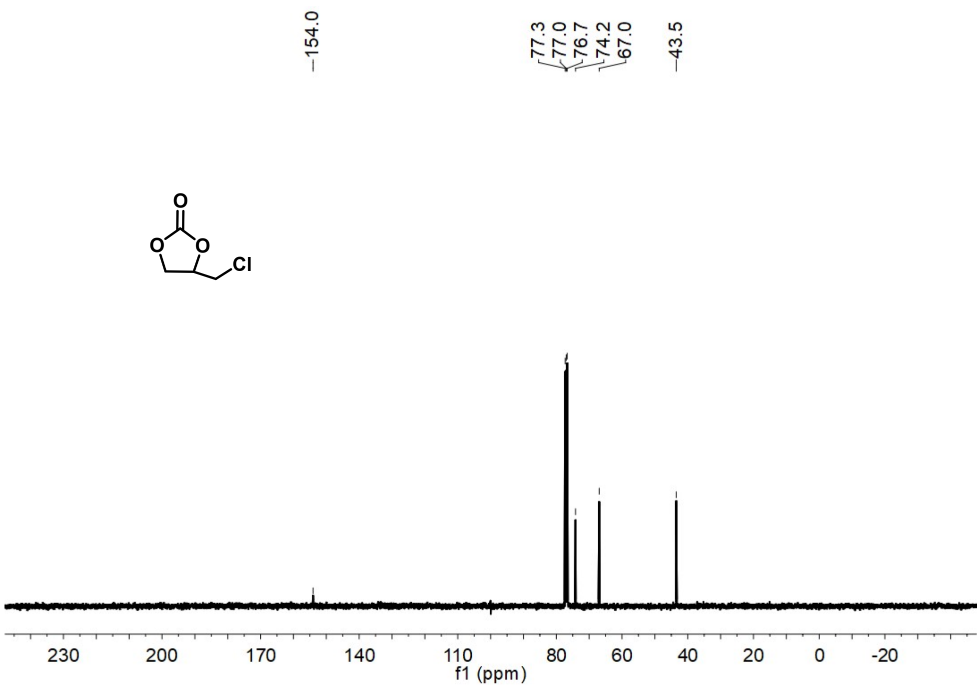

Figure S11. ^{13}C NMR spectrum for **2b**.

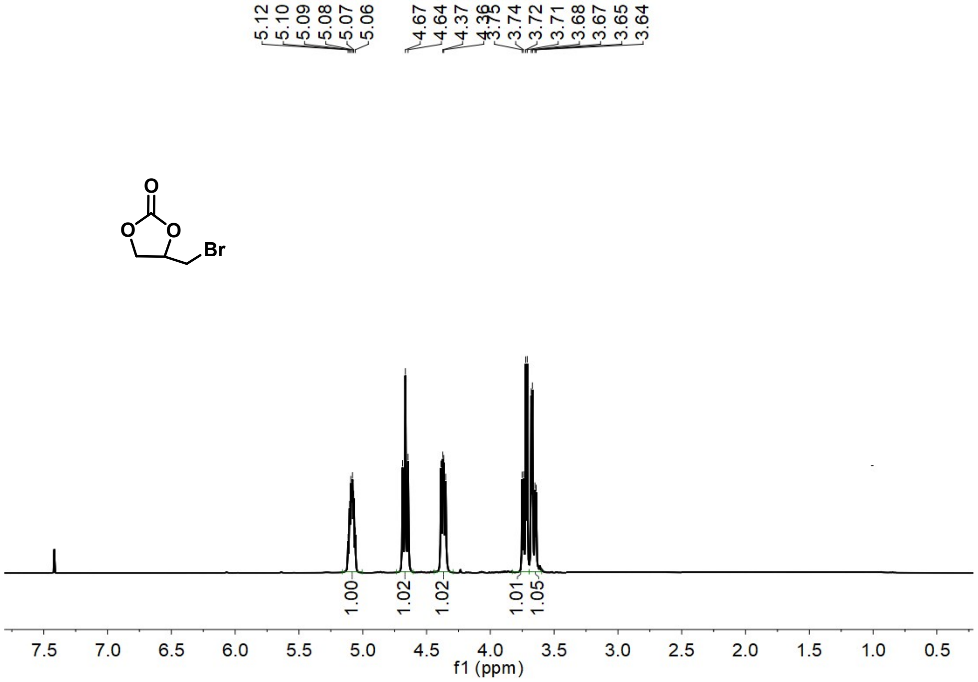

Figure S12. ^{1}H NMR spectrum for **2c**.

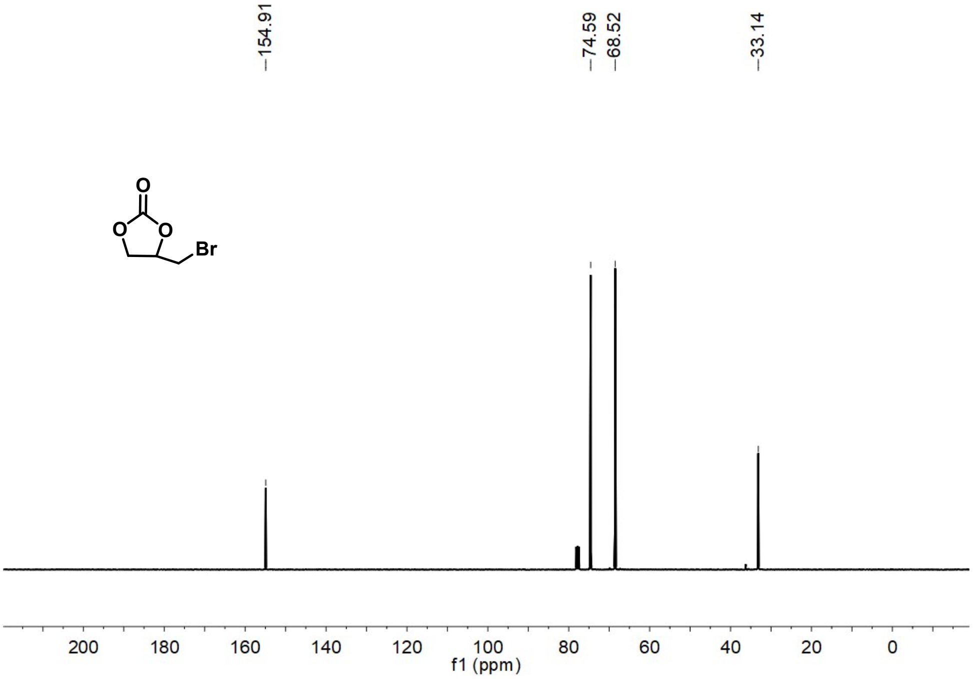

Figure S13. ^{13}C NMR spectrum for **2c**.

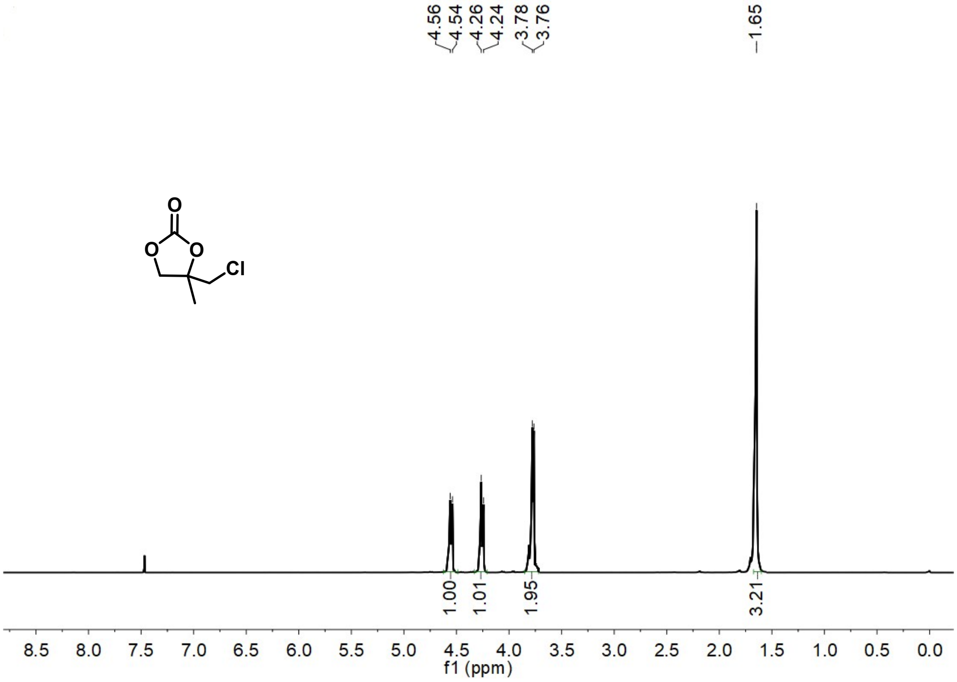

Figure S14. ^{1}H NMR spectrum for **2d**.

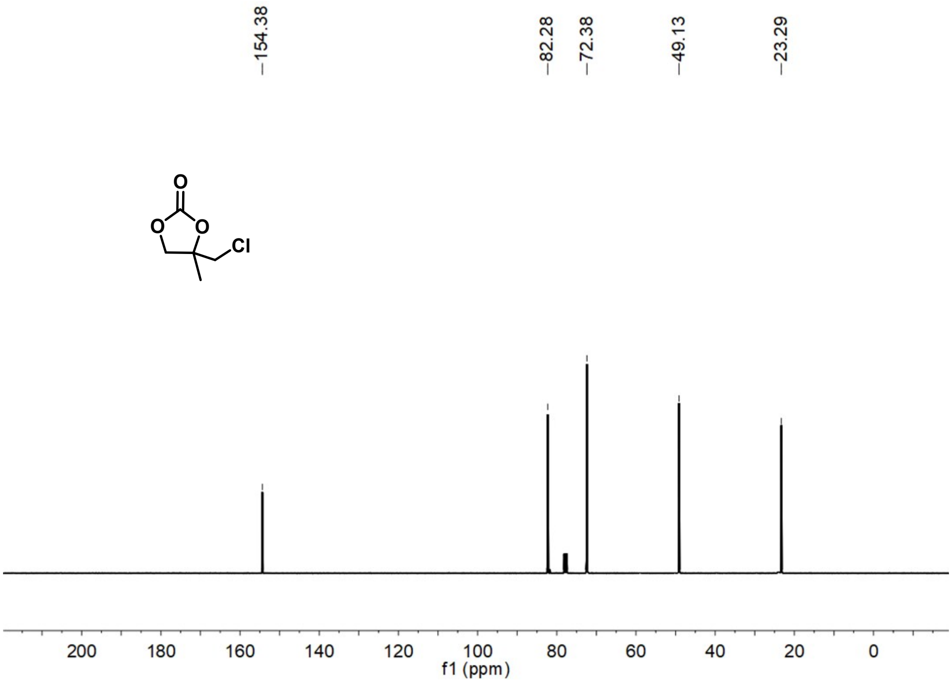

Figure S15. ^{13}C NMR spectrum for **2d**.

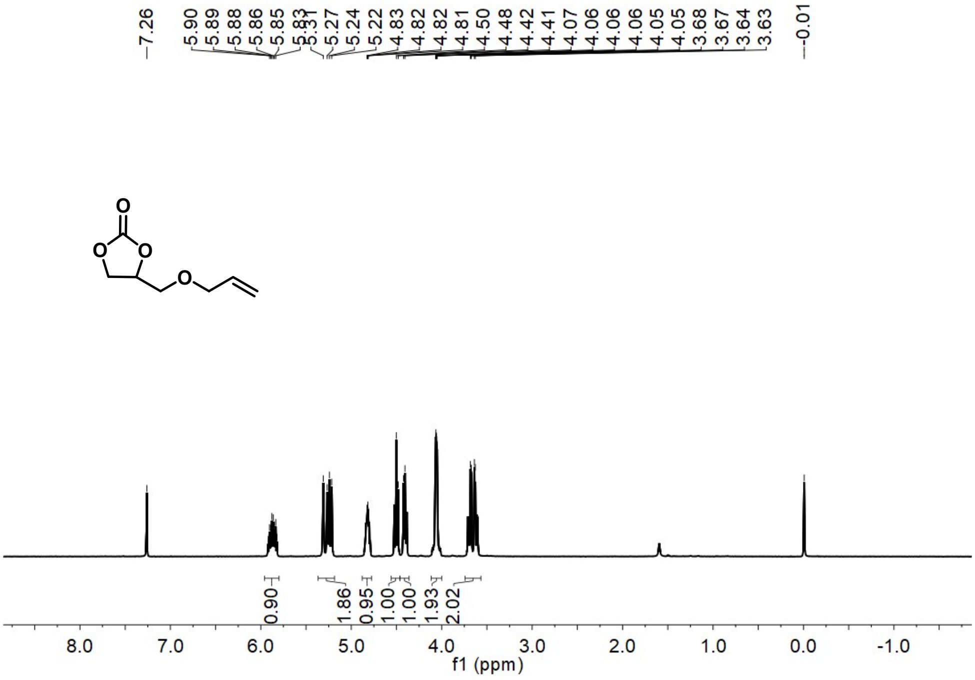

Figure S16. ^{1}H NMR spectrum for **2e**.

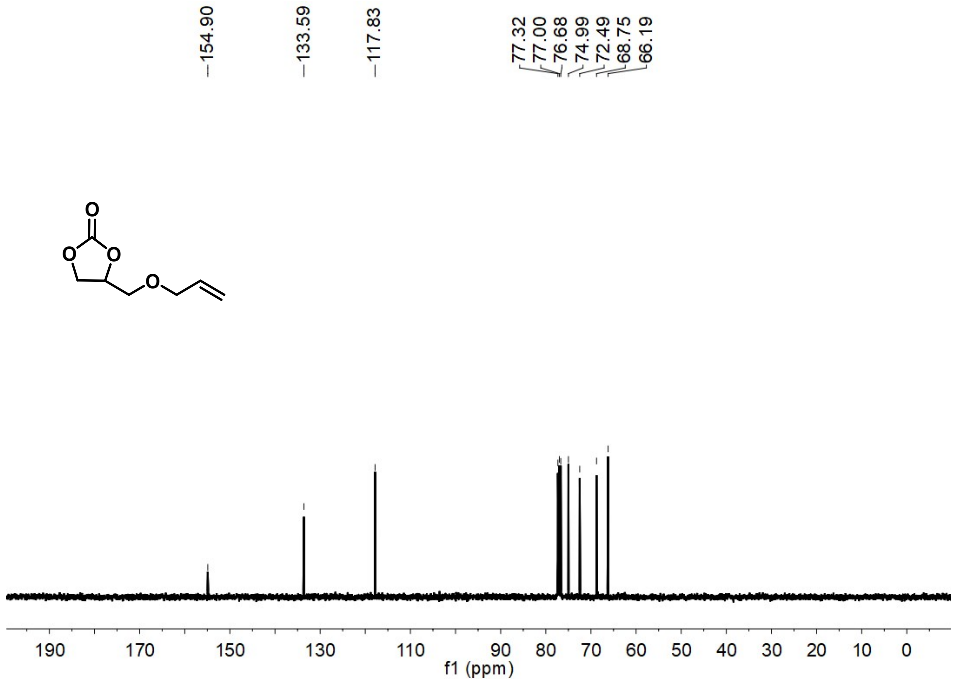

Figure S17. ^{13}C NMR spectrum for **2e**.

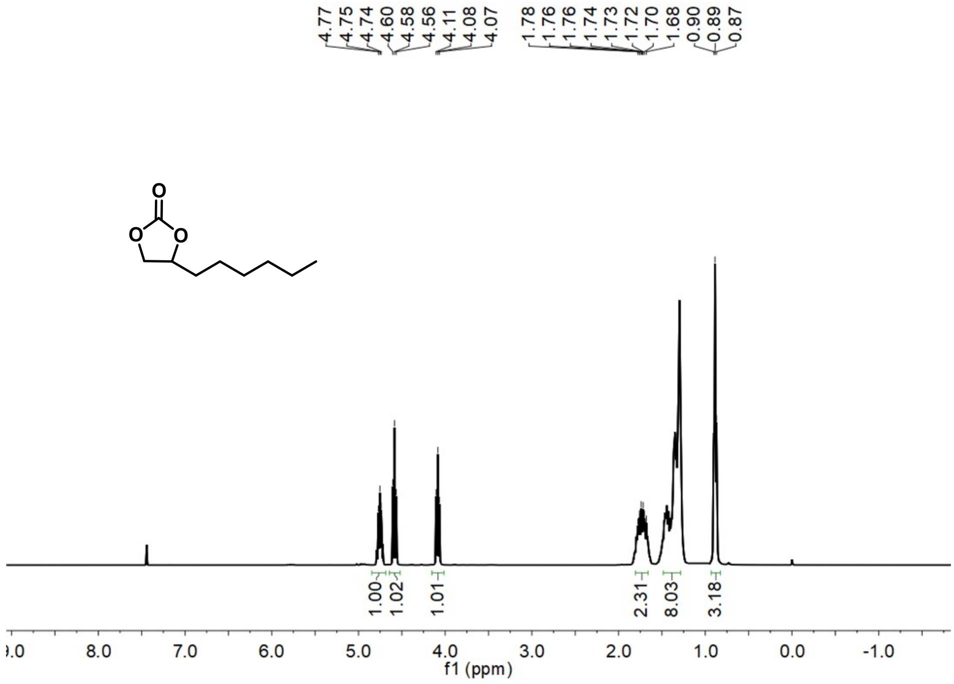

Figure S18. ^{1}H NMR spectrum for **2f**.

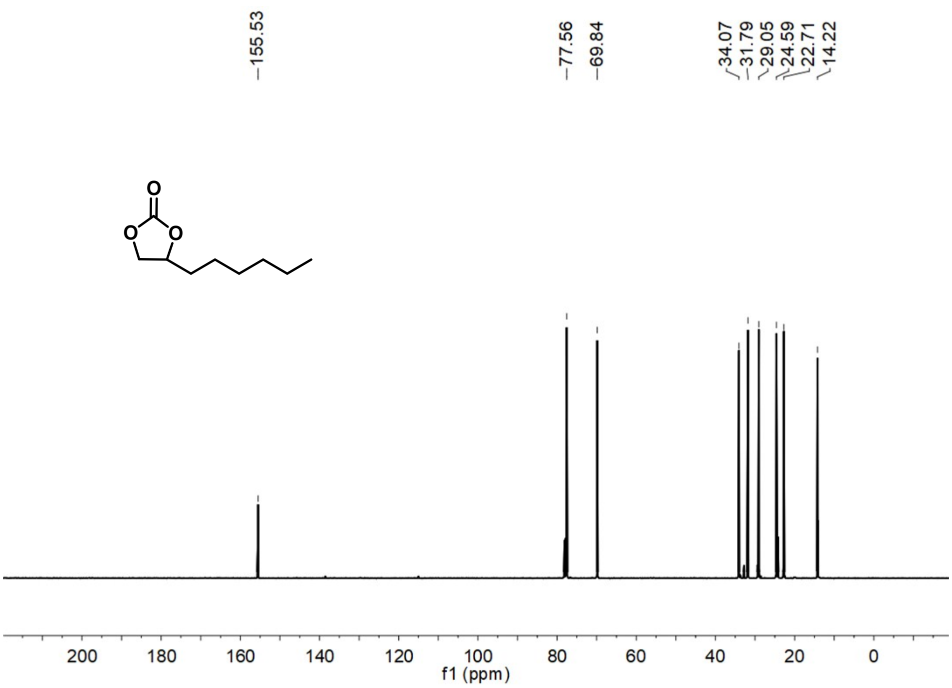

Figure S19. ^{13}C NMR spectrum for **2f**.

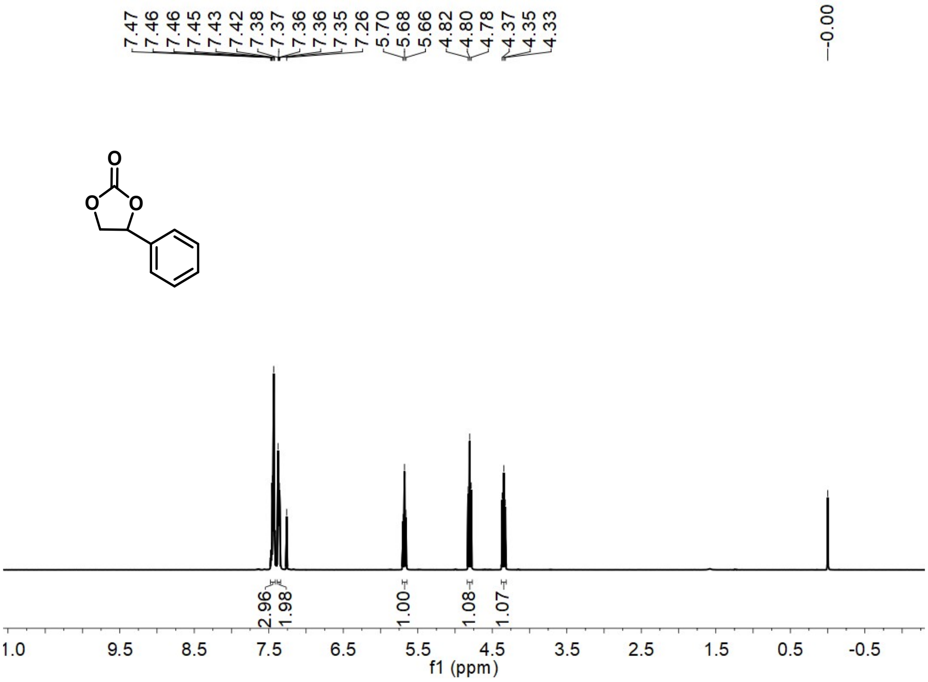

Figure S20. ^{1}H NMR spectrum for **2g**.

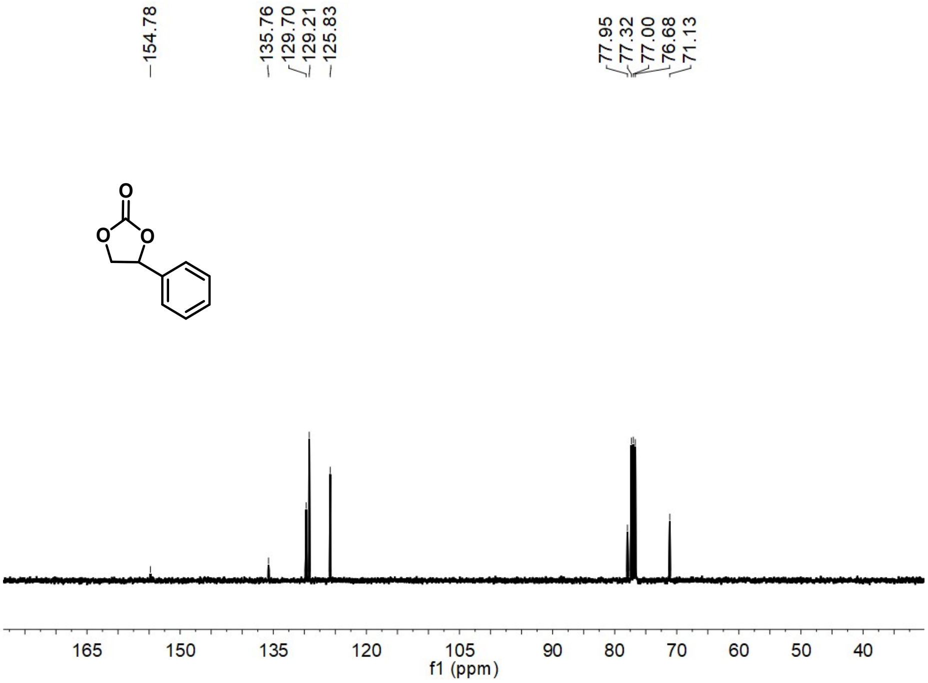

Figure S21. ^{13}C NMR spectrum for **2g**.