Electronic Supplementary Material (ESI) for ChemComm.

Zn(II) assisted synthesis of porous salen as an efficient heterogeneous scaffold for capture and conversion of CO_2

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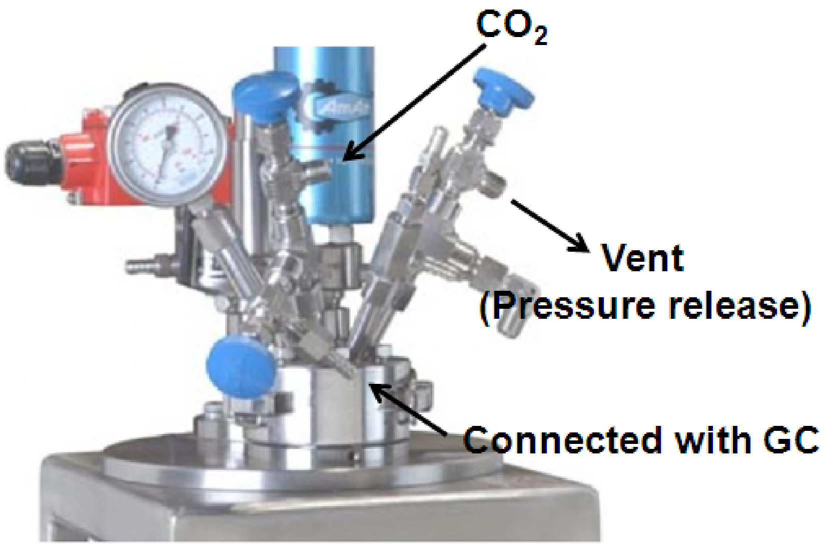
Section S1

Chemicals

3,3′diaminobenzidine (sigma aldrich, 99%); phloroglucinol anhydrous (spectrochem, +98%); anhydrous N,N-dimethyl formamide (DMF) (spectrochem, +99%); phosphorous oxychloride (Spectrochem, +99%); 1,4 dioxane (Merck, +99%); terminal epoxides: styrene oxide (Alfa Aesar , +98%), (±)-epichlorohydrin (Alfa Aesar , +98%), ,(±)-propylene oxide, 99+%; 1,2-epoxy-3 phenoxypropane (sigma Aldrich ,99%); butyl glycidyl ether (Alfa Aesar, 95%); allyl glycidyl ether (spectrochem, +99%); (S)- (-)glycidol (Alfa Aesar,ee +99%) was used as recieved.2,4,6-trihydroxyisophthalaldehyde was synthesized by the previously reported procedure.[1]

Characterizations

^{1}H and^{13}C NMR experiments (liquid state) were carried out on a Bruker DPX-300 NMR spectrometer. Carbon, hydrogen and nitrogen contents of Zn@SBMMPwas analyzed using a Perkin Elmer 2400 Series II CHN analyzer. X-Ray diffraction patterns of the powder samples were obtained with a Bruker AXS D_8 Advanced SWAX diffractometer using Cu Kα (= 0.15406 nm) radiation. Nitrogen sorption experiments and micropore analysis was conducted at 77 K using Autosorb 1 (quantachrome,USA). Prior to adsorption measurement the samples were degassed in vacuum at 150^{0}C for about 10 h. NLDFT pore-size distributions were determined from the sorption isotherms by using the carbon/slit-cylindrical pore model. The ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectrum was obtained on a500MHz BrukerAvance II spectrometer at a mass frequency of 8 kHz. Thermogravimetry (TG) and differential thermal analyses (DTA) of the samples are carried out in a TGA Instruments thermal analyzer TA-SDT Q-600. A Hitachi S-5200 field-emission scanning electron microscope was used for the determination of the morphology of the particles. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. The samples were prepared by dropping a colloidal solution onto the carbon-coated copper grids followed by drying under high vacuum. For the bulk elemental analysis the Zn@SBMMPwas digested with acid to dissolved them into clear liquid and then Zncontent were analyzed by using a Shimadzu AA-6300 atomic absorption spectrophotometer (AAS) fitted with a double beam monochromator.The reaction mixtures of the catalytic reactions wereanalyzed by capillary gas chromatography (Agilent Model 4890D,using a gas chromatograph equipped with a flame ionization detection(FID) device).Synthesis of cyclic carbonate was carried out by 100 ml stainless steel autoclave fitted with high pressure reactor (Amar equipments, Mumbai, India).

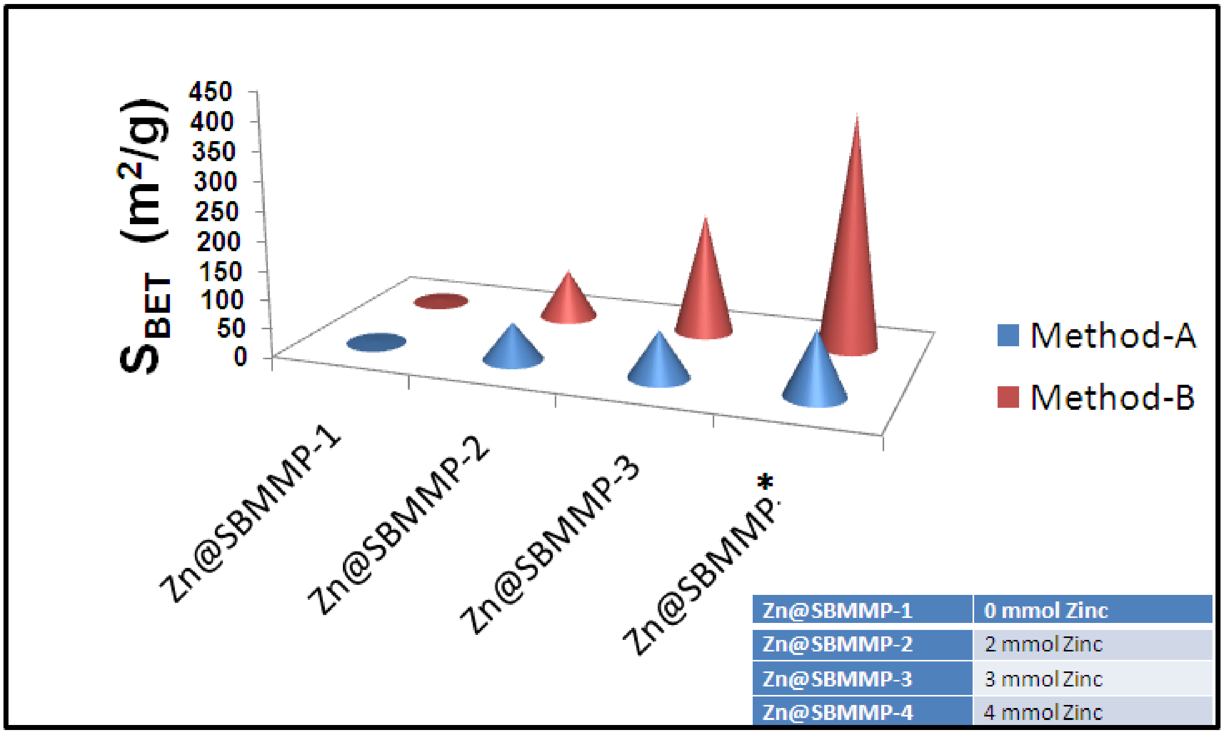


Experimental procedure for synthesis of Zn@SBMMP catalyst

A schlenk flask was charged with 0.025 mmol 3,3'diaminobenzidine (36 mg), 0.5 mmolphloroglucinol-dialdehyde (344 mg), $Zn(Oac)_2,2H_2O$ (1.0 mmol) and 100 ml anhydrous DMF under N_2 atmosphere and stirred for 24 h. Then the dark red sol was transferred to a Teflon lined stainless steel autoclave and heated at 180 ^{0}C for 3 days continuously. Then the reaction mixture was poured into large amount of acetone and filtered. The red solid has been designated as Zn@SBMMP and dried in an air oven overnight.

Figure S1

Optimization of BET surface area with varying amount of zinc acetate



Zn@SBMMP-1	0 mmol Zinc
Zn@SBMMP-2	2 mmol Zinc
Zn@SBMMP-3	3 mmol Zinc
Zn@SBMMP-4	4 mmol Zinc

Figure S1. Method A. Zn@SBMMP was synthesized by one step process.

Method B. Zn@SBMMP was synthesized by two step process.

*This material is optimized material and each characterization had been studied using this material.

Figure S2

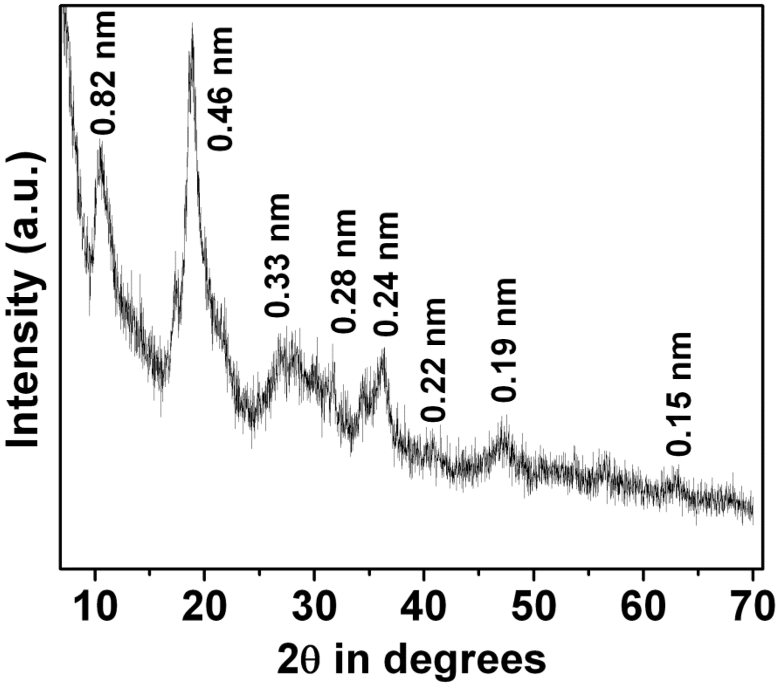


Figure S2. Wide angle XRD pattern of Zn@SBMMP

Figure S3

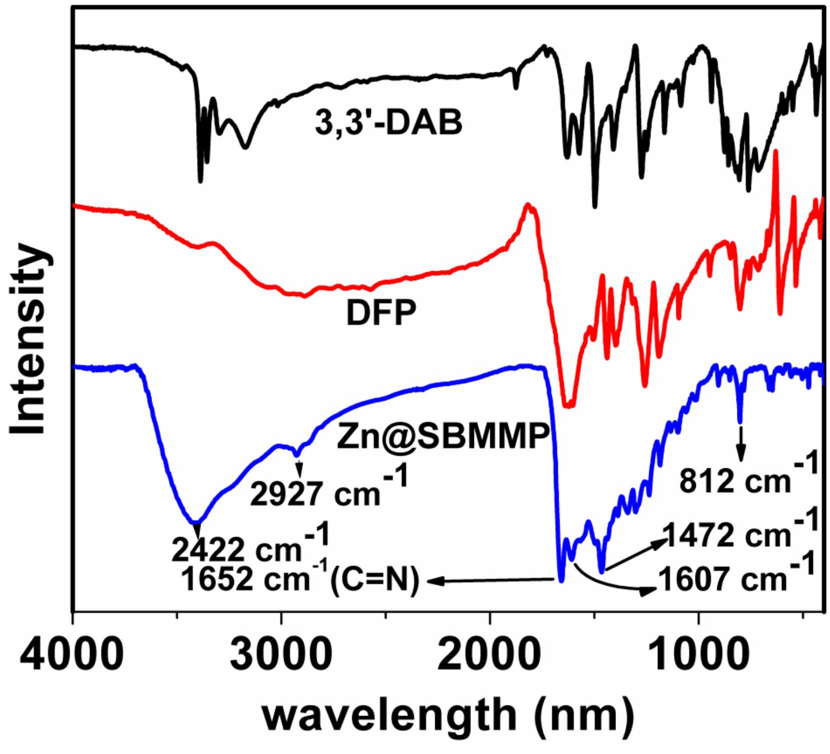


Figure S3. IR- spectra of 3,3′ diaminobenzidine (3,3′ DAB), Diformyl Phloroglucinol (DFP) & Zn@SBMMP material

Figure S4

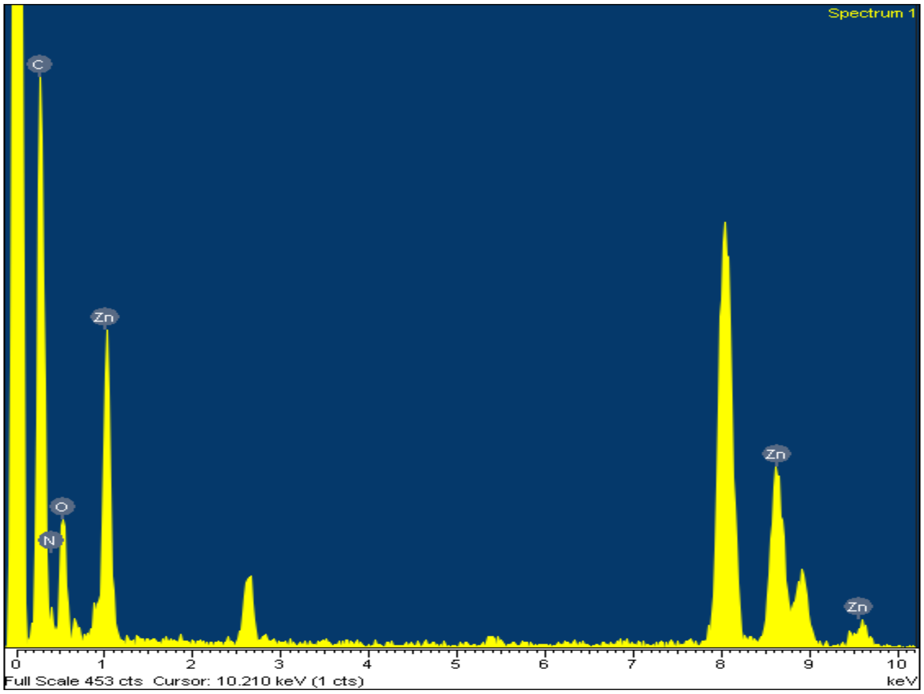


Figure S4. Energy dispersive X-ray(EDX) analysis data obtained from TEM analysis of Zn@SBMMP.

Figure S5

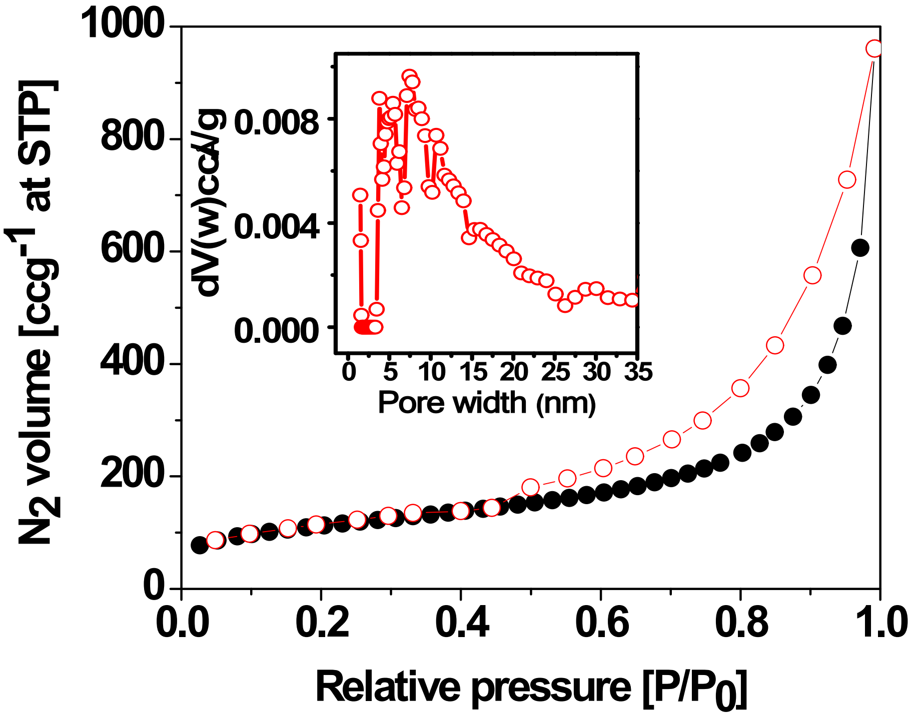


Figure S5. N_2 adsorption/desorption isotherms of Zn@SBMMP. Adsorption points are marked by filled circles and desorption points by empty circles. Pore sized distribution of Zn@SBMMP is shown in the inset.

Figure S6

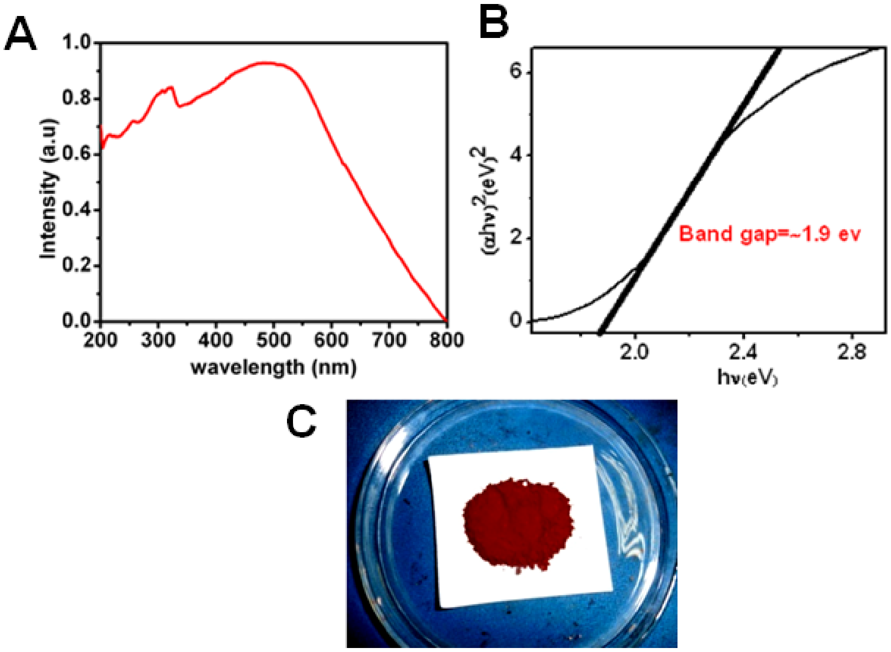


Figure S6. Solid state UV-Visible spectra(A) of Zn@SBMMP and band gap (B) and photograph of dark red colored powdered material(C).

Figure S7

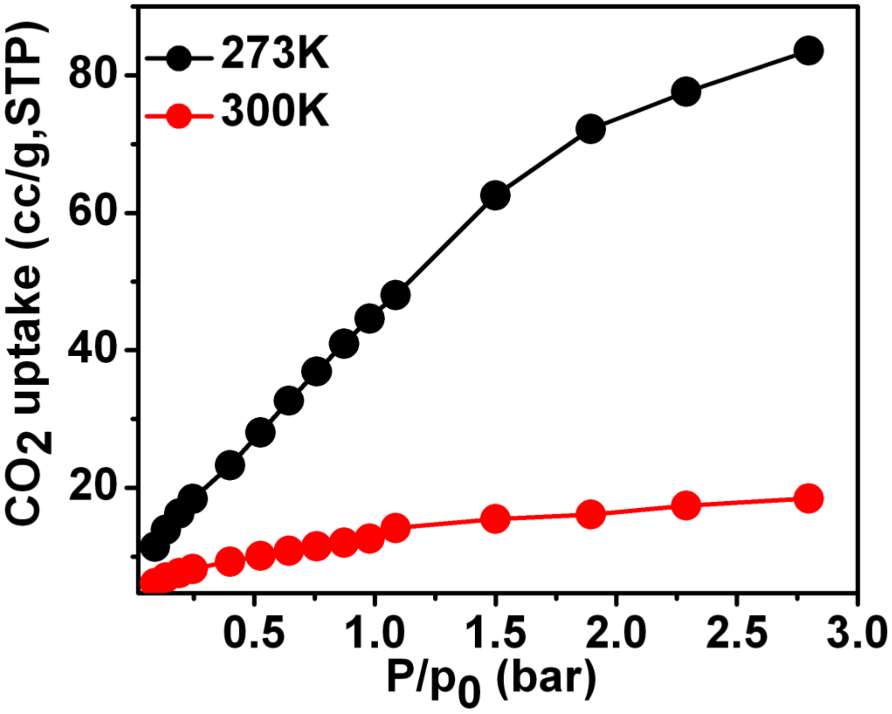


Figure S7.CO_2 adsorption isotherm at 273 K and 300 K by Zn@SBMMP upto 3 bar.

Figure S8

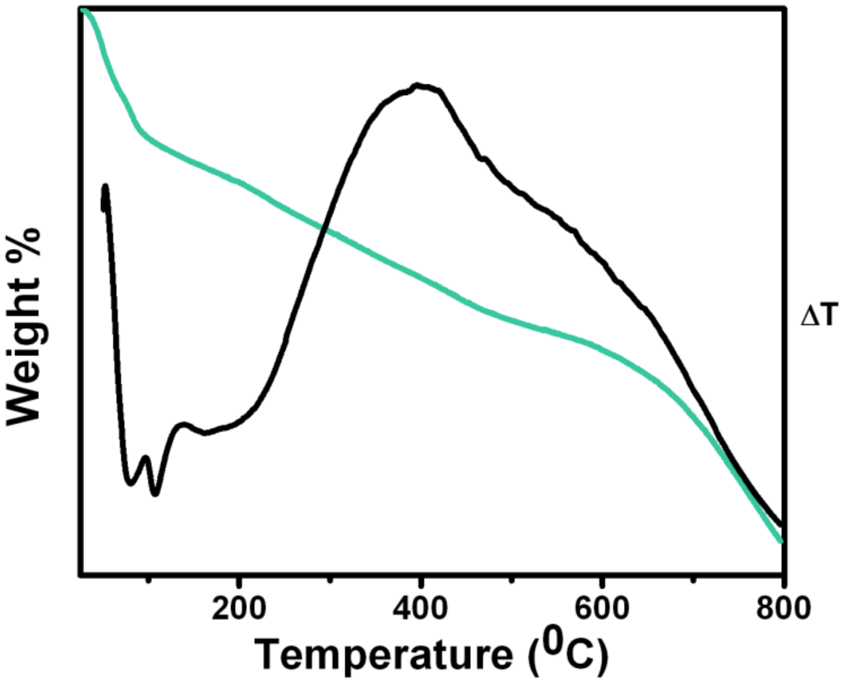


Figure S8 Thermogravimetric analysis of of Zn@SBMMP.

Section S2, Table-S1

Optimization of CO_2 capture and conversion efficiency of Zn@SBMMP using Styrene oxide (SO)

The CO_2 conversion efficiency of Zn@SBMMP material was confirmed by the conversion of styrene oxide to styrene carbonate(SC). The high density of Zn-Salen unit was utilized for this cycloaddition reaction of CO_2 with epoxide under moderately mild condition without any solvent. The performance of this Zn@SBMMP catalyst was competitive with other zinc based homogenous and heterogeneous catalysts or catalytic system. This reaction had been done using only Zn(salen) complex afforded 27% SC using $^{n}Bu_4N^+Br^-$(TBAB) as a co-catalyst at 1.5 MPa and 70^0C, 53% at 2 MPa and 90^0C using dichloromethane as a solvent. The yield raised to 85% in presence of $^{n}Bu_4N^+I^-$(TBAI)as a co-catalyst expected. High conversion in milder conditions are very attracting for homogenous catalyst but these catalysis are associated with poor turn over number (TON) (ESI Sec. S3) value and no scope of reusability. Zn@SBMMP afforded 97% conversion at 2MPa and 100^0C without using any solvent and 93% at initial pressure 1.5 MPa at 80^0C in presence of solvent (25 ml) for SO(styrene oxide)/CO_2 coupling reaction(Table S1). In the absence of co-catalyst Zn@SBMMP gives 18% SC (styrene carbonate) and the co-catalyst. TBAB alone gives 35% .

Entry	Catalyst (mg)	Co-catalyst	CO_2 Pressure (MPa)ʃ	Temperature (^{0}C)	Time(h)	Yield¶(%)
1.	Zn-Salen complex (80)	TBAB	1.5	70	2	27
2.	Zn-Salen complex (80)	TBAB	2	90	4	53
3.	Zn-Salen complex(80)	TBAI	2	90	4	85
4.	Zn@SBMMP (20)	-	2	80	4	18
5.	-	TBAB	2	80	4	35
6.	Zn@SBMMP(20)	TBAB	1.5	80	5	93
7.	Zn@SBMMP(20)	TBAB	2	80	4	97
8.	KI(25)	-	0.1	30	40	5
9.	KI(25)	-	3	100	4	11
10.	KI/β-CD(25+150)	-	0.1	30	40	~6
11.	KI/β-CD(25+150)	-	3	100	4	~12
12	ZIF-8(100)	-	0.7	80	4	60

Table S1 □Experimental condition- Styrene oxide (10 mmol), Zn@SBMMP (20mg, Zn: 0.04 mmol) or Zn-salen complex (80.0 mg, Zn: 0.122 mmol) or KI (20.3 mg, 0.15 mmol), dichloromethane (20 ml), unless otherwise noted.

ʃInitial pressure

¶Yield was calculated by GC-MS.

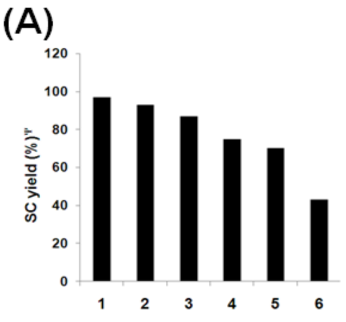
Section S3, Figure S9

Catalytic experimental procedure

A pre-dried 100-ml autoclave was charged with Zn@SBMMP (10- 30 mg) and Styrene Carbonate (1.2 g, 10 mmol), TBAB (1.8 mol%) in 20 ml dichloromethane at atmospheric pressure. Next, the assembled autoclave was purged of air three times with CO_2. After the CO_2 (20 bar) was introduced, the reaction mixture was stirred at 80 °C for 4 h. The autoclave was cooled to room temperature and CO_2 was released. The reaction mixture was then dissolved with ethyl acetate (30 ml) and the insoluble solid material was filtered. Removing the solvent from the filtrate yielded a pale yellow oil substance. Further purification of the crude product was carried out by column chromatography (yield: 85–97%).

Recycliclibility test with or without solvent

After each reaction the catalyst was filtered and dried in oven the further used for next cycle. The catalytic reaction was carried out in presence of solvent (DCM). The catalyst can be recycled atleast 10 times (Fig. S9B) and maximum 6 times without solvent ((Fig. S9A).



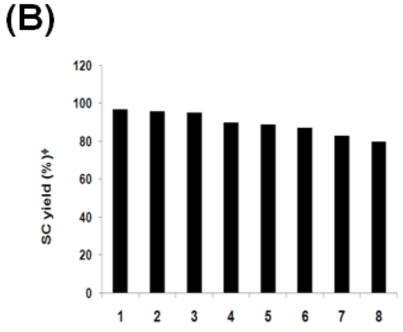


Figure S9A. $^{\Psi}$ reaction condition:2 MPa and 80^0C without Solvent

Figure S9B.$^{\Phi}$ reaction condition: 2 MPa and 80^0C using dichloromethane as a Solvent.

Pressure and time variation

The influence of pressure and time on the styrene carbonate (SC) yield was monitored by conducting reaction at various pressure range between 0.3-6.0 MPa and time range between 1-8 h (Figure S9C). The temperature kept constant at 80^0C throughout whole experiment due to very low catalytic activity at low temparature. When the reaction was carried out at 0.3 MPa, after 4 h the yield of SC was 43% and then the yield was increasing with the pressure of CO_2. The yield was maximum 97% at 2.0 MPa. After that the yield was not varied significantly with the increment of pressure(6 MPa). The influence of reaction time on the SC yield has shown at Figure S9D is the reaction was conducted at 80^0C and 1.5MPa . The yield of SC yield increased with increasing time at the beginning and approached 95% after a reaction time of 5h.

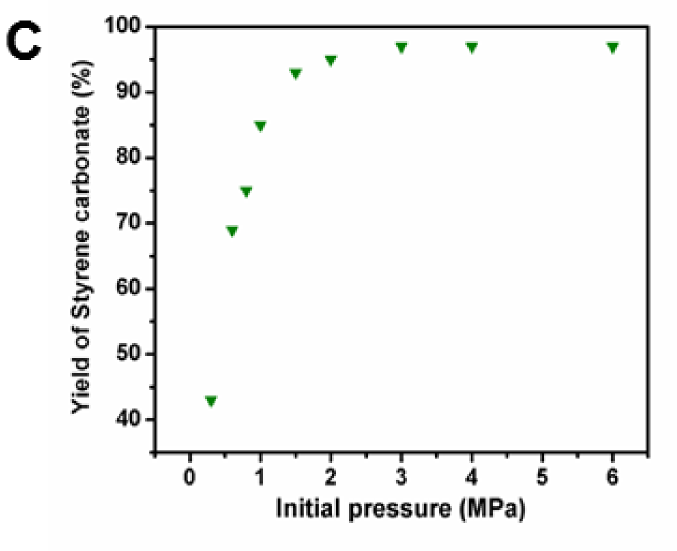


Figure S9C. Effect of the CO_2 pressure on the SC yield. Reaction conditions: 10 mmol SO with 1.8 mol% n-BuN_4Br, 0.030g Zn@SBMMP, 30ml DCM, reaction temperature 80 ◦C, reaction time 4 h.

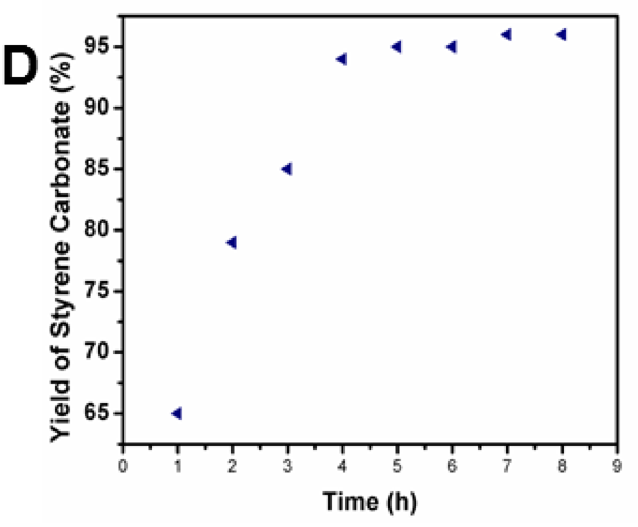
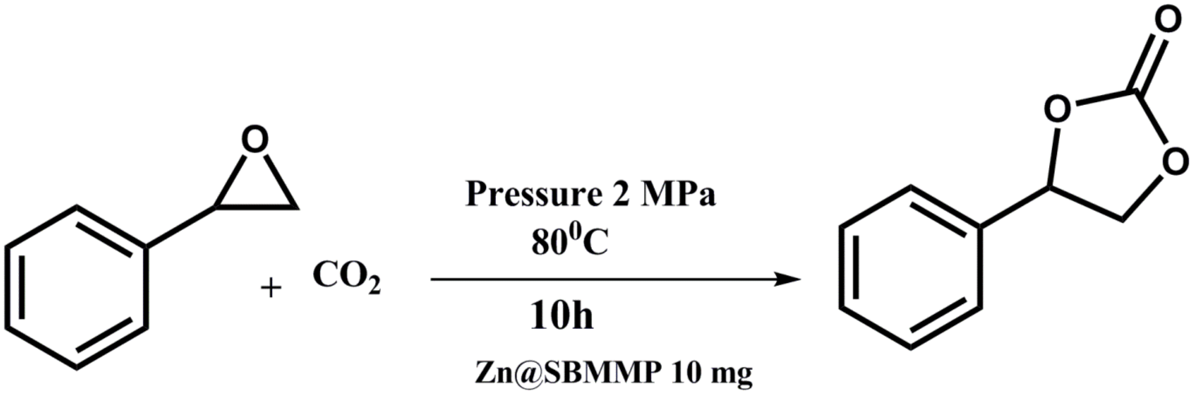


Figure S9D. The influence of the reaction time on the SC yield. Reactionconditions: 10 mmol SO with 1.8 mol% n-BuN_4Br,0.030gZn@SBMMP, CO_2pressure 1.5 MPa, reaction temperature 80 ◦C, 30ml DCM.

Turn over no. calculation



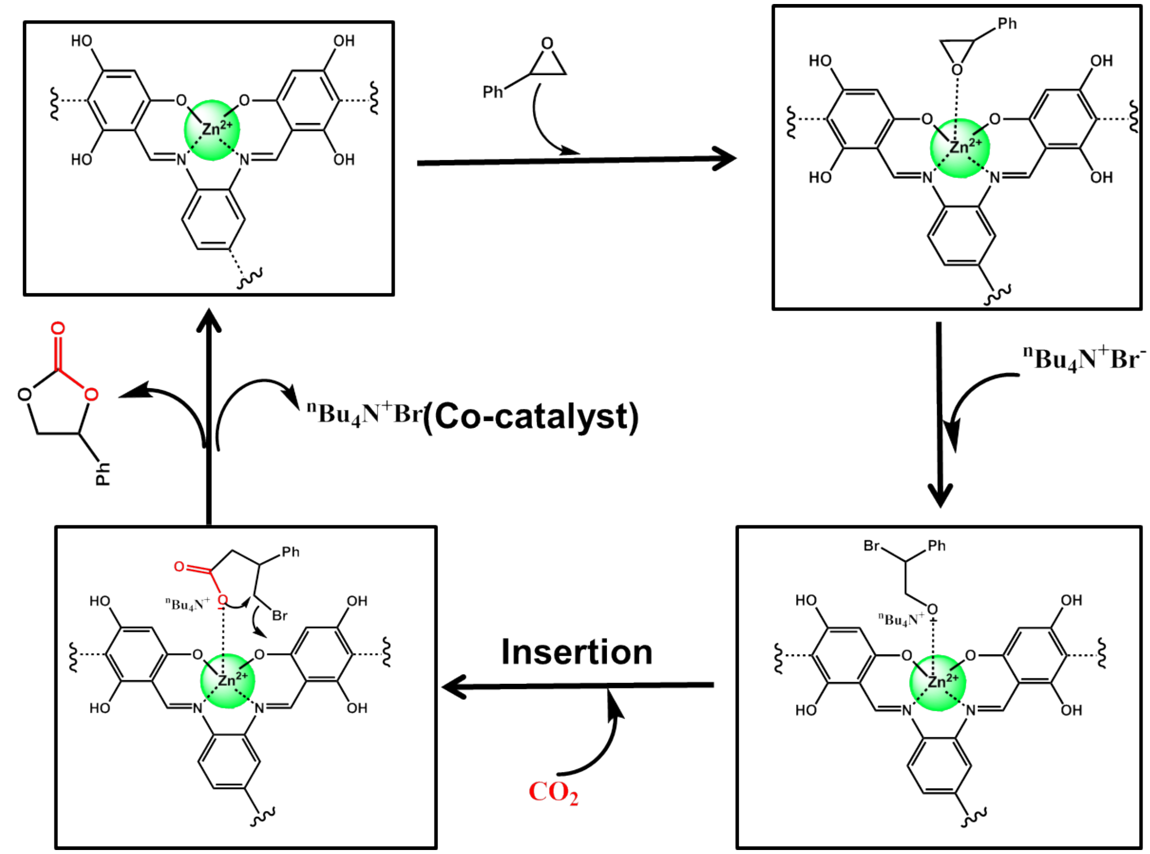
The Zinc content of Zn@SBMMP is 15.3 wt%

10 mg Zn@SBMMP contains 1.5×10^{-3} g = 2.3×10^{-5} Mol Zn.

Turn over number (TON) = $\frac{Mols\ of\ Styrene\ carbonate\ obtained}{mols\ of\ Zinc}$ **= (**9.5×10^{-3})/ (2.3×10^{-5})= **413**.

Figure S10

Proposed catalytic pathway



Section S4, Figure S11

TON value comperison with some homogeneous and heterogeneous catalyst

Entry	Pressure (Mpa)	Temparature(^{0}C)	Time (h)	TON	Ref.
binaphthyldiamino salenZn N(II) complex **(homogeneous)**	3.5	100	2	30-901	[2]
Re(CO)$_5$Br**(homogeneous)**	6	110		850	[3]
PVP-SupportedZnBr$_2$ Catalyst**(Heterogeneous)**	3.5	100	1	201	[4]
Al(salen)/PEA**(Heterogeneous)**	10	80	6	47	[5]
Al(salen)/PS**(Heterogeneous)**	10	80	6	7	[5]
Co-CMP**(Heterogeneous)**	3	100	1	201	[6]
Al-CMP**(Heterogeneous)**	3	100	1	187	[6]
Zn@SBMMP**(Heterogeneous)**	2	80	10	413	This work

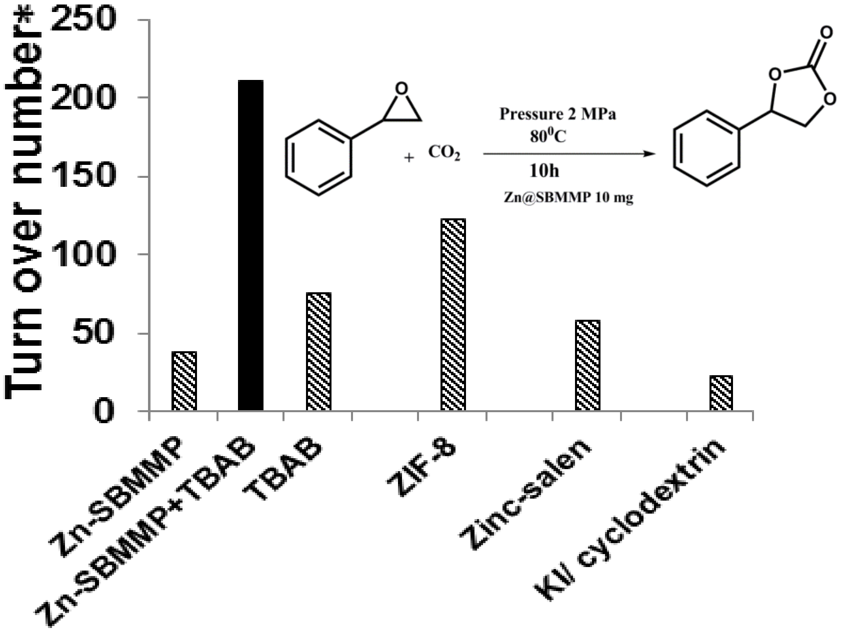
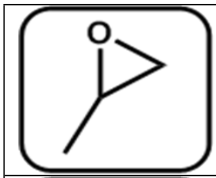
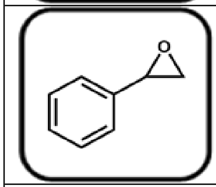
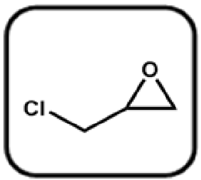
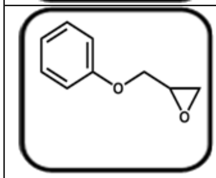
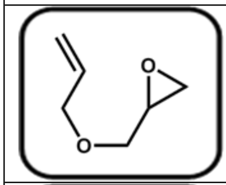
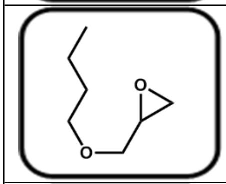
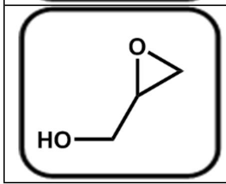


Figure S11. Catalytic efficiency of Zn@SBMMP vis-a-vis other Zn-catalysts in the CO$_2$ fixation reaction on styrene oxide.

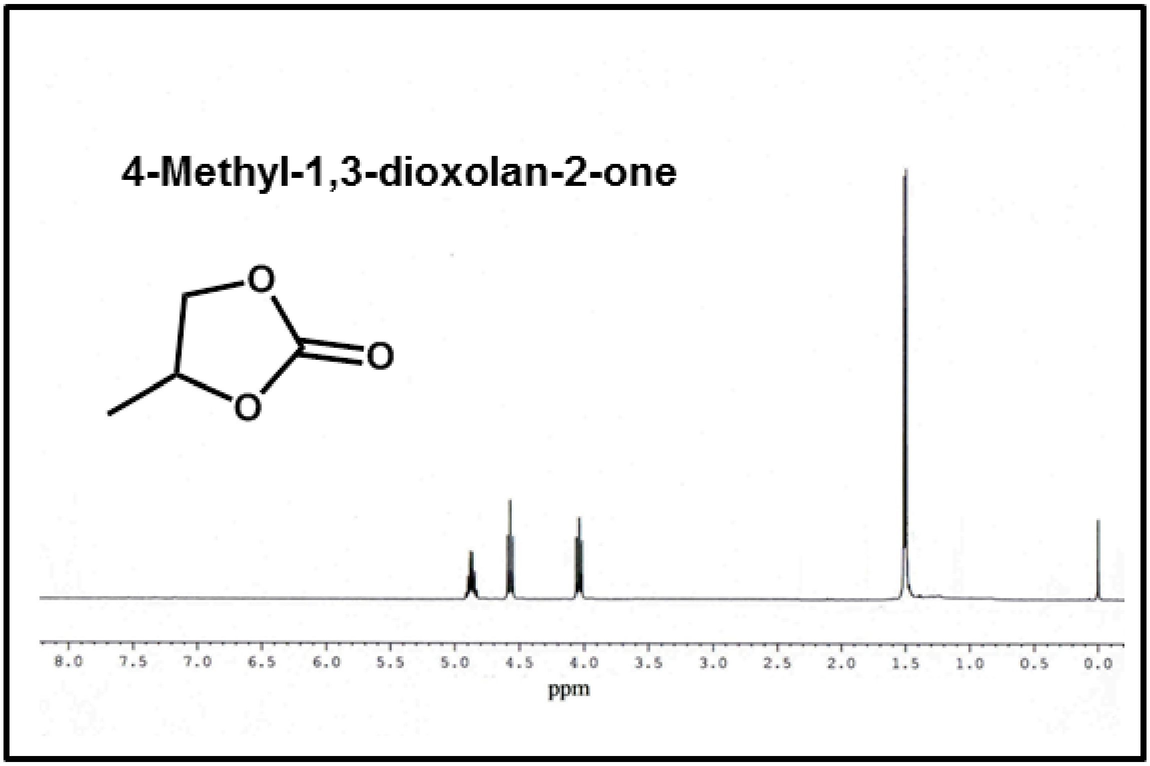
Section S5

^{1}H NMR data of cyclic carbonates

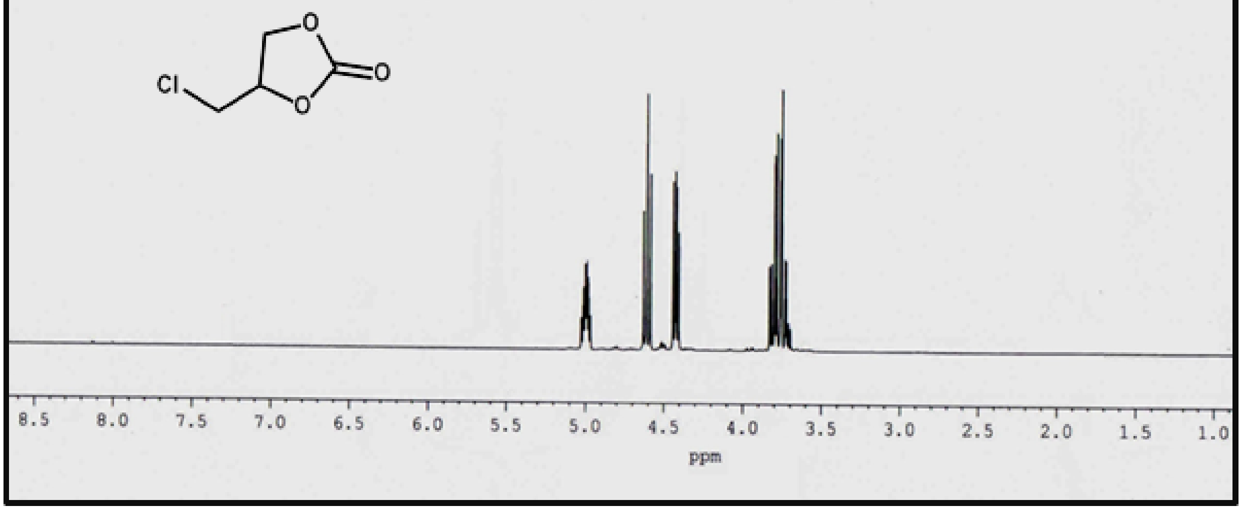
	**4-Methyl-1,3-dioxolan-2-one:**Colorless liquid,(hexane/ethyl acetate, 4:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.89–4.84 (m, 1H), 4.57 (dd, J=8.4, 7.8 Hz, 1H), 4.03 (dd, J=8.4, 7.2 Hz, 1 H), 1.42 (d, J=6.3 Hz, 3H).
	**4-Phenyl-1,3-dioxolan-2-one:**White solid, (hexane/ethyl acetate, 4:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.46–7.42 (m, 3H), 7.38–7.32 (m, 2H), 5.67 (t, J=8.1 Hz, 1H), 4.79 (dd, J=8.4, 8.1 Hz, 1H), 4.33 (dd, J=8.4, 8.1 Hz, 1H).
	**4-Chloromethyl-1,3-dioxolan-2-one:**Colorless liquid,(hexane/ethyl acetate, 7:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.02–4.96 (m, 1H), 4.611 (dd, J=9.0, 8.7 Hz, 1H), 4.43 (dd, J=8.7, 8.7 Hz, 1H), 3.83–3.72 (m, 2H).
	**4-Phenoxymethyl-1,3-dioxolan-2-one:**White solid, (hexane/ethyl acetate, 4:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.328 (t, J=7.2 Hz, 2H), 6.987 (dd, J=7.8, 7.2 Hz, 1H), 6.89 (d, J=7.8 Hz, 2H), 5.05–4.99 (m, 1H), 4.62 (dd, J=8.4, 7.8 Hz, 1H), 4.37 (dd, J=8.4, 6.3 Hz, 1H), 4.24(d, J=10.5 Hz, 1H), 4.16 (d, J=10.8 Hz, 1H)
	**4-Allyloxymethyl-1,3-dioxolan-2-one:**Colorless liquid, (hexane/ethyl acetate, 4:1 v/v); ^{1}H NMR (500 MHz, $CDCl_3$): δ=5.71 (ddt, J=17.4, 10.5, 5.7 Hz, 1H), 5.10(dd, J=17.4, 1.5 Hz, 1H), 5.03(dd, J=10.5, 1.5 Hz, 1H), 4.73–4.69 (m, 1H), 4.36 (t, J=8.4 Hz, 1H), 4.21 (t, J=8.4 Hz, 1H), 3.89 (d, J=5.7 Hz, 2H), 3.56–3.43 (m, 2H).
	**4-Butoxymethyl-1,3-dioxolan-2-one:**Colorless liquid, (hexane/ethyl acetate, 15:1 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.84–4.76 (m, 1H), 4.49 (dd, J=8.4, 8.1 Hz, 1H), 4.39 (dd, J=8.4, 8.4 Hz, 1H), 3.69–3.57 (m, 2H), 3.50 (t, J=6.6 Hz, 2H), 1.65–1.50 (m, 2H), 1.35 (dt, J=14.4, 7.2 Hz, 2H), 0.91 (dd, J=7.5, 7.2 Hz, 3H).
	**4-(hydroxymethyl)-1,3-dioxolan-2-one:**^{1}H NMR (300 MHz, $CDCl_3$) δ 4.82 (ddd, J = 11.3, 6.6, 3.2 Hz, 1 H), 4.59 – 4.43 (m, 2 H), 4.00 (ddd, J = 12.8, 5.0, 2.9 Hz, 1 H), 3.72 (ddd, J = 12.8, 6.6, 3.4 Hz, 1 H), 2.80 (br s, 1 H).

Section S6

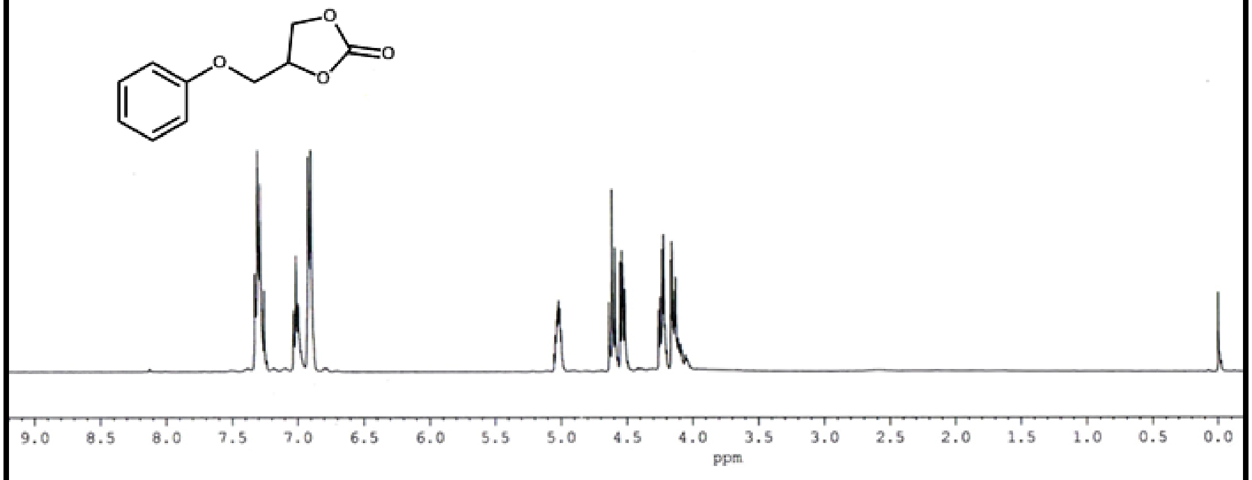
Some representative ^{1}H NMR spectra of cyclic carbonates.



4-Chloromethyl-1,3-dioxolan-2-one



4-Phenoxymethyl-1,3-dioxolan-2-one



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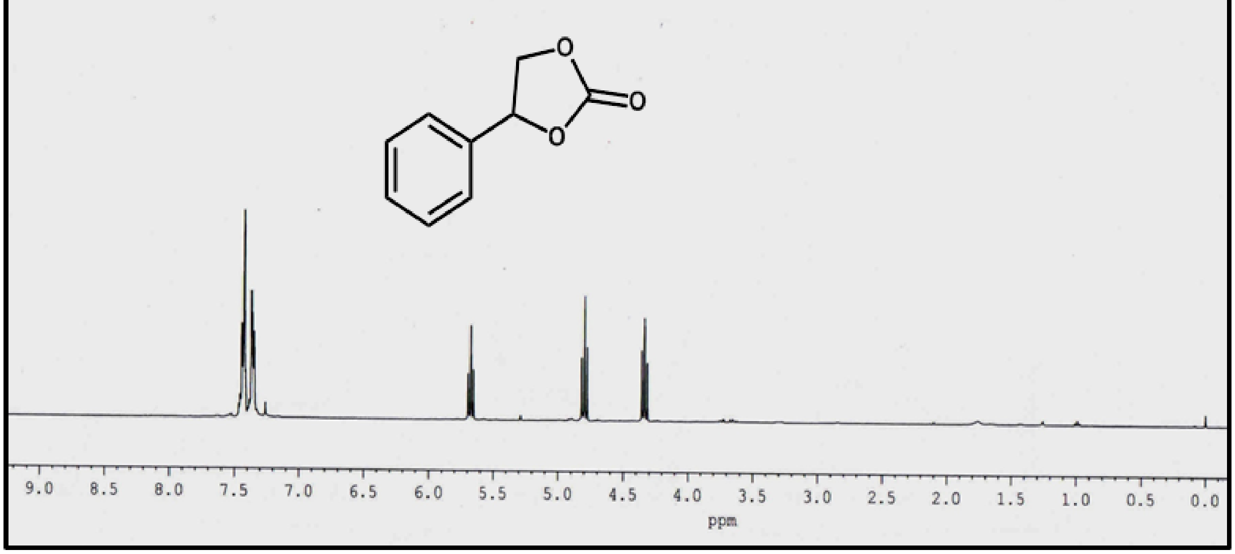

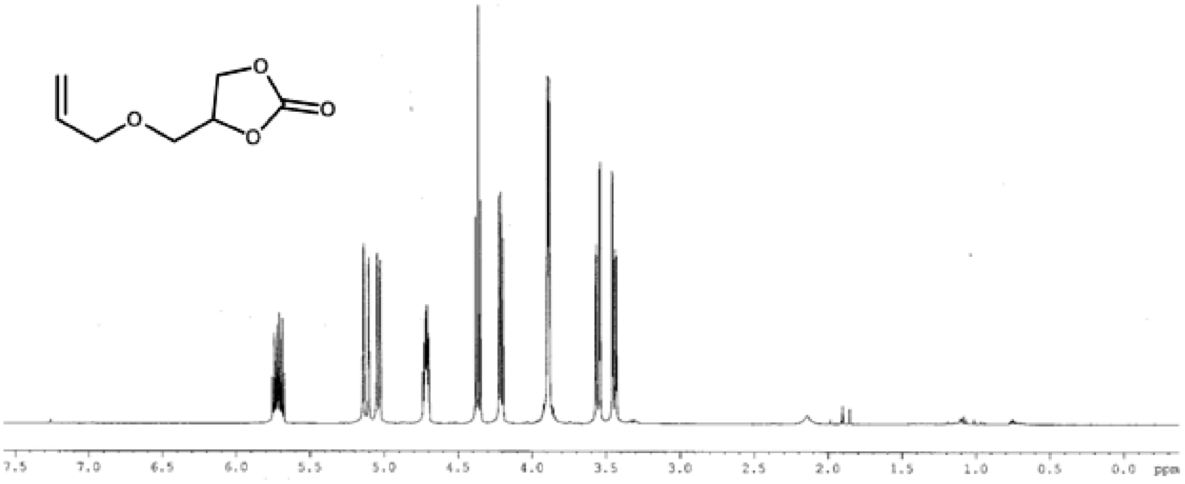

4-Allyloxymethyl-1,3-dioxolan-2-one

Section S7

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