Electronic Supplementary Material (ESI) for New Journal of Chemistry.

New Journal of Chemistry

Supporting Information

An efficient CO_2 fixation reaction with epoxides catalysed by *in situ* formed blue vanadium catalyst from dioxovanadium(+5) complex: Moisture enhanced and atmospheric oxygen retarded catalytic activity

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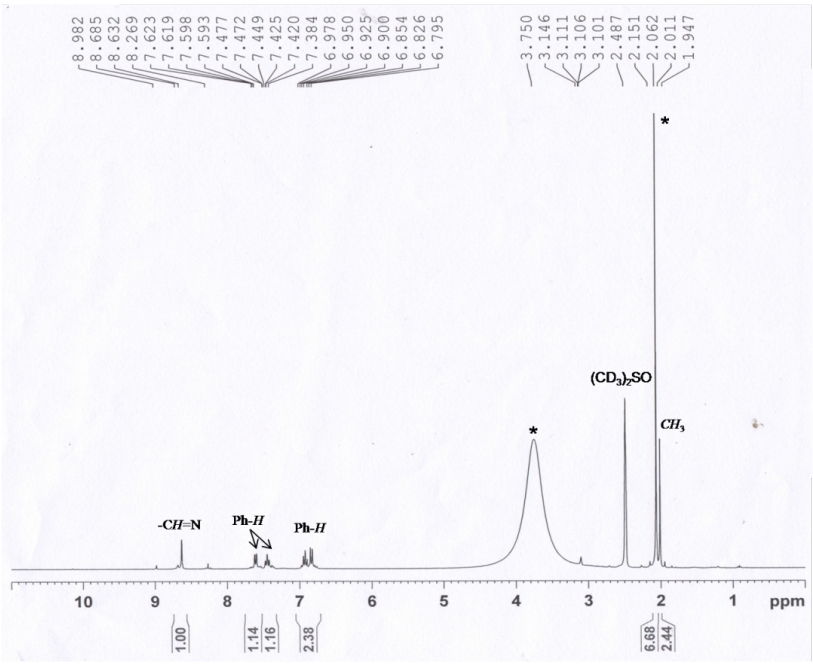

Fig. S1 ^{1}H NMR spectrum of [VO_2(HSal-ac)], **2** in DMSO-d_6 + 2 drops of methanol-d_4 (Asterisks represents solvent impurities).

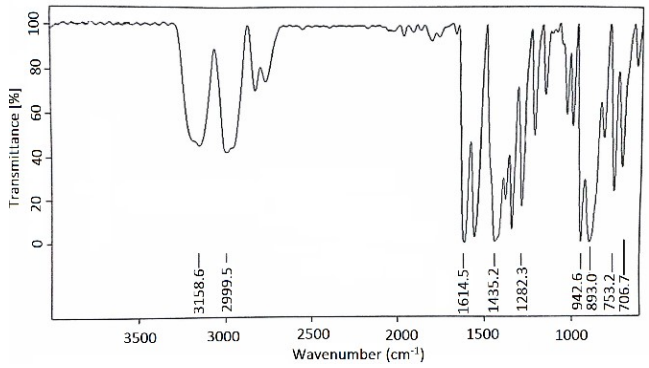

Fig. S2 FT-IR spectrum of [NH_4][VO_2(Sal-ac)], **1**.

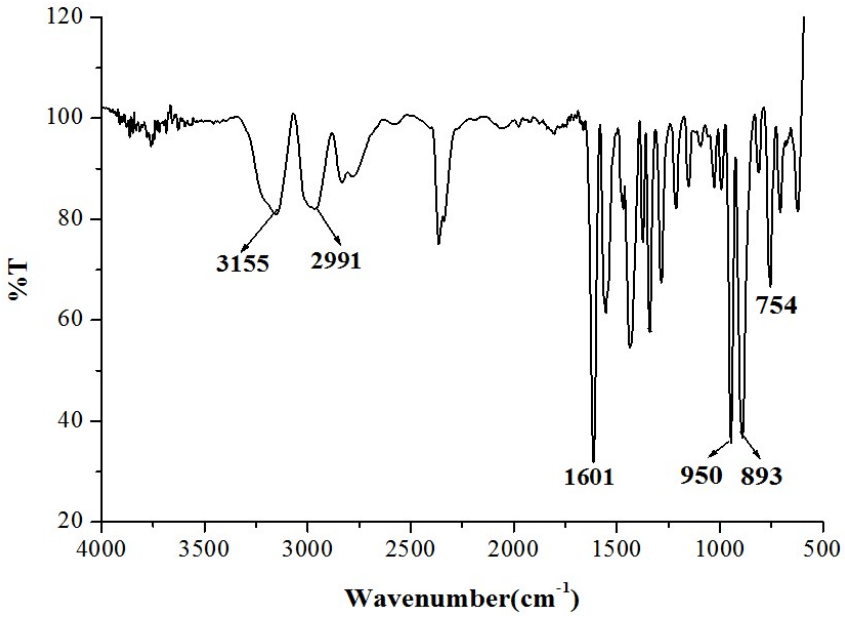

Fig. S3 FT-IR spectrum of [VO_2(HSal-ac)], **2**.

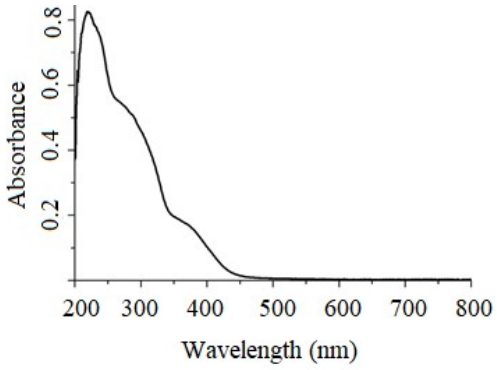

Fig. S4 UV/Vis spectrum of NH_4[VO_2(Sal-ac)], **1** in methanol.

Table S1. Crystal data and data collection parameters for complexes **1, 2** and **3**.

Crystal data	$NH_4[VO_2(Sal\text{-}ac)]$, **1**	$VO_2(HSal\text{-}ac)$, **2**	$VO_2(HSal\text{-}ac)$, **3**
Formula	$C_9H_{12}N_3O_4V$	$C_9H_9N_2O_4V$	$C_9H_9N_2O_4V$
T, (K)	296(2)	296(2)	273(2)
Formula weight	277.16	260.12	260.12
Color	Yellow	Brown	Yellow
Crystal system	Orthorombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P\ 2_1/n$
a, Å	6.4268(4)	7.4612(9)	7.3510(4)
b, Å	13.3674(10)	11.9060(14)	11.8967(7)
c, Å	13.5577(10)	11.1849(13)	11.1856(6)
α , deg	90	90	90
β, deg	90	99.077(7)	99.047(2)
γ, deg	90	90	90
V, $Å^3$	1164.74(14)	981.1(2)	966.04(9)
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
Z	4	4	4
d_{calcd}, $g.cm^{-3}$	1.581	1.761	1.789
F(000)	568	528	528
μ, mm^{-1}	0.858	1.010	1.026
No. of unique data	2274	1924	1896
No. of parameters, refined	162	146	141
GOF on F^2	1.059	1.086	1.116
$R1^a$ [$I > 2\sigma(I)$]	0.0241	0.0364	0.0449
$R1^a$ (all data)	0.0246	0.0406	0.0568
$wR2^b$ (all data)	0.0693	0.1088	0.1039
Largest diff. peak and hole, e. $Å^{-3}$	0.267 and -0.247	0.387 and -0.507	0.785 and -0.446
a $R1 = \frac{\sum \lvert\lvert Fo\rvert - \lvert Fc\rvert\rvert}{\sum \lvert Fo\rvert}$; b $wR2 = \sqrt{\frac{\sum \left[w\left(Fo^2 - Fc^2\right)^2\right]}{\sum \left[w\left(Fo^2\right)^2\right]}}$			

Table S2. Selected bond lengths (Å) and bond angles (°) for $NH_4[VO_2(Sal\text{-}ac)]$, **1**, $[VO_2(HSal\text{-}ac)]$, **2** and $[VO_2(HSal\text{-}ac)]$, **3** (**obtained from the blue reaction mixture after reaction**).

Bond distance (Å)	$NH_4[VO_2(Sal\text{-}ac)]$, **1**	$[VO_2(HSal\text{-}ac)]$, **2**	$[VO_2(HSal\text{-}ac)]$, **3**
V-O(3)	1.619(2)	1.6315(19)	1.639(2)
V-O(4)	1.646(2)	1.601(2)	1.614(2)
V-O(1)	1.9714(19)	2.0181(18)	2.019(2)
V-O(2)	1.893(2)	1.8742(17)	1.879(2)
V-N(1)	2.128(2)	2.1682(19)	2.169(3)
O(1)-C(1)	1.305(3)	1.260(3)	1.258(4)
N(2)-C(1)	1.296(3)	1.312(3)	1.322(4)
N(1)-C(3)	1.297(4)	1.295(3)	1.300(4)
N(1)-N(2)	1.406(3)	1.379(3)	1.386(3)
Bond angle (˚)			
O(3)-V-O(4)	109.54(13)	109.37(13)	109.23(13)
O(1)-V-O(2)	150.56(9)	150.81(8)	151.05(9)

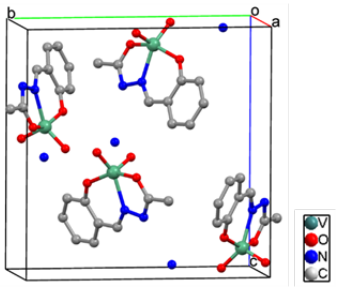

Fig. S5 Crystal packing diagram of $NH_4[VO_2(Sal\text{-}ac)]$, **1**. (H atoms are excluded for clarity).

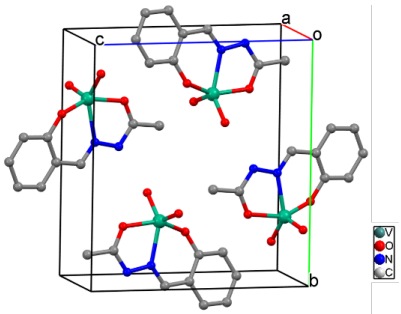

Fig. S6 Crystal packing diagram of $VO_2(HSal\text{-}ac)$, **2**. (H atoms are excluded for clarity).

General procedure for catalytic reactions

A mixture of epoxide, Vanadium catalyst, **1** (1 mol %) and Tetrabutylammonium bromide (2 mol %) were loaded into a 100 mL stainless steel autoclave equipped with a magnetic stirring bar. The appropriate pressure of CO_2 was then dosed into the reactor, and heating and stirring were started to achieve the desired temperature. After the desired time, the autoclave was vented carefully and a sample was taken immediately for the determination of conversion by ^{1}H NMR spectroscopy.

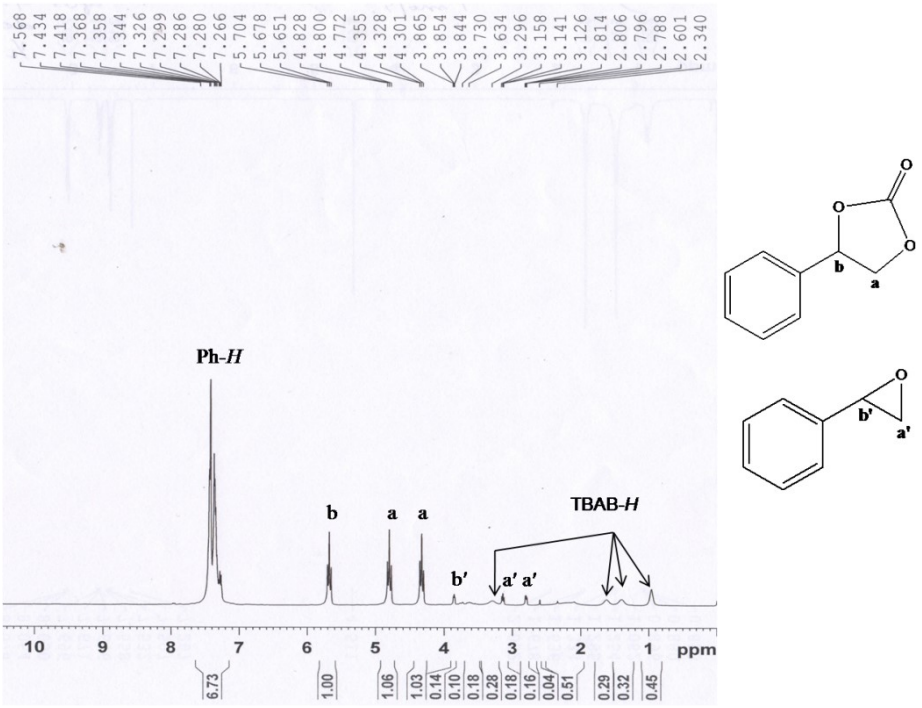

Fig. S7 ^{1}H NMR spectrum of reaction mixture in $CDCl_3$. [Catalyst **1** (1 mol%); **moistened** TBAB (2 mol%); Temperature, 60 °C; Pressure (CO_2), 5 bar; Time, 4 hours; ^{1}H NMR yield, 91%]

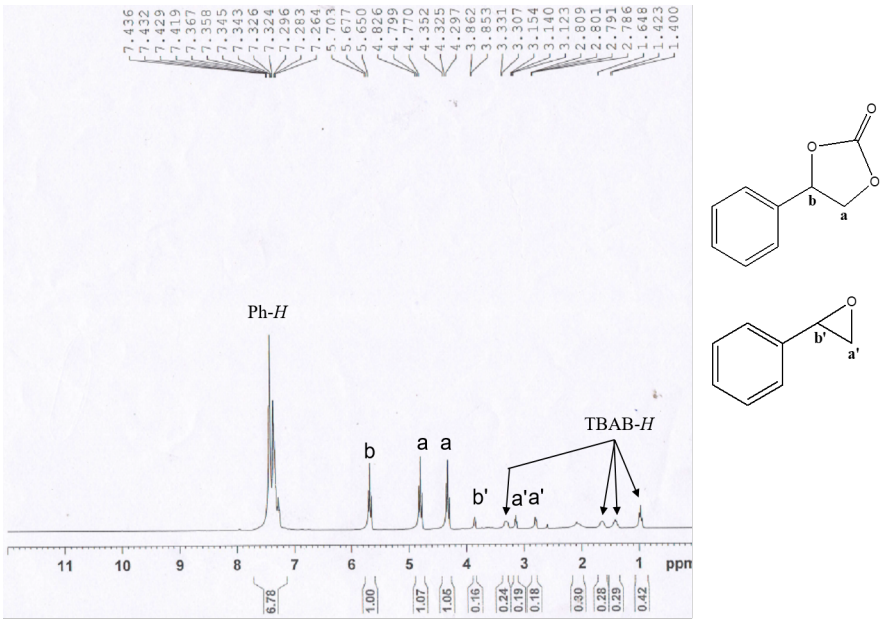

Fig. S8 ^{1}H NMR spectrum of reaction mixture in $CDCl_3$. [Catalyst **1** (1 mol%); **moistened** TBAB (2 mol%); Temperature, 60 °C; Pressure (CO_2), 5 bar; Time, 2 hours; ^{1}H NMR yield, 86%].

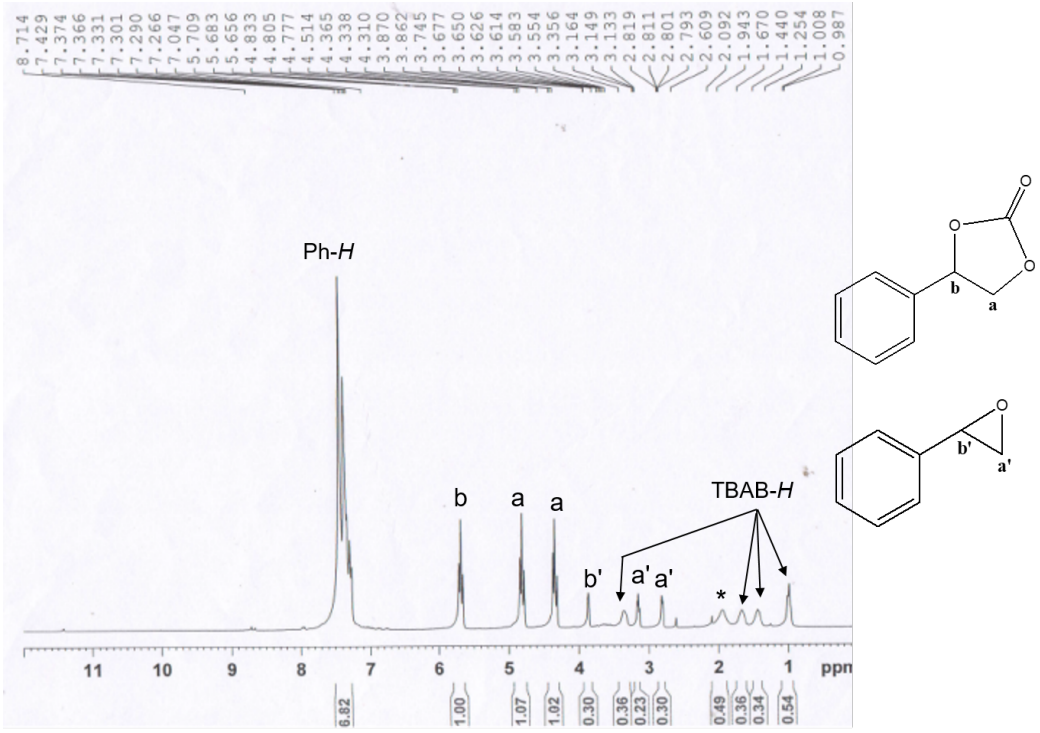

Fig. S9 ^{1}H NMR spectrum of reaction mixture in $CDCl_3$. [Catalyst **2** (1 mol%); **moistened** TBAB (2 mol%); Temperature, 60 °C; Pressure (CO_2), 5 bar; Time, 2 hours; ^{1}H NMR yield, 77%].

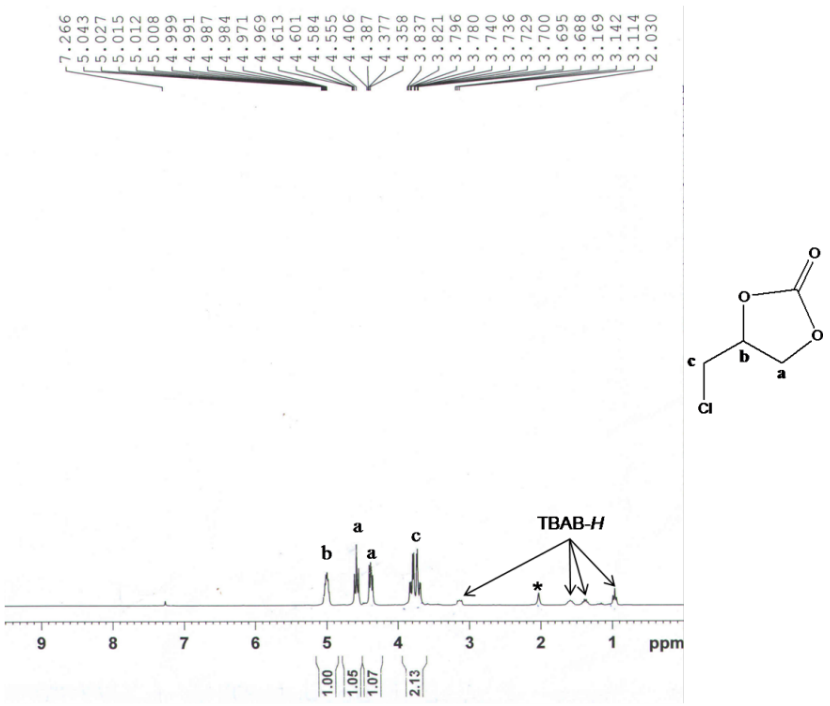

Fig. S10 ^{1}H NMR spectrum of reaction mixture in $CDCl_3$. [Catalyst **1** (1 mol%); **moistened** TBAB (2 mol%); Temperature, 45 °C; Pressure (CO_2), 5 bar; Time, 14 hours; ^{1}H NMR yield, 99 %] (Asterik represents solvent impurity).

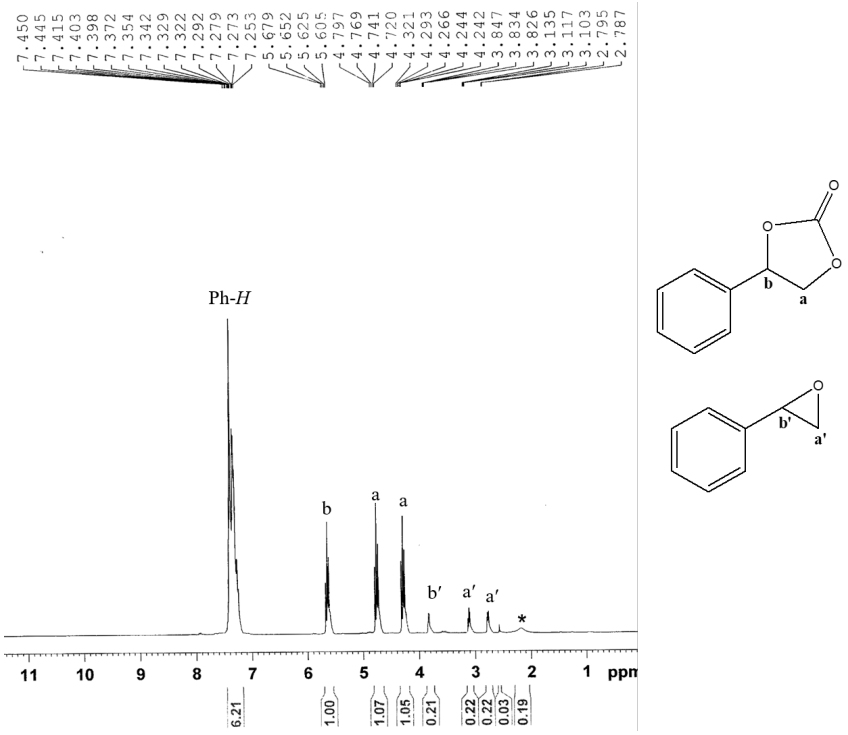

Fig. S11 ^{1}H NMR spectrum of reaction mixture in $CDCl_3$. [Catalyst **1** (1 mol%); **moistened** TBAB (2 mol%); Temperature, 45 °C; Pressure (CO_2), 5 bar; Time, 14 hours; ^{1}H NMR yield, 83 %] (Asterik represents solvent impurity).

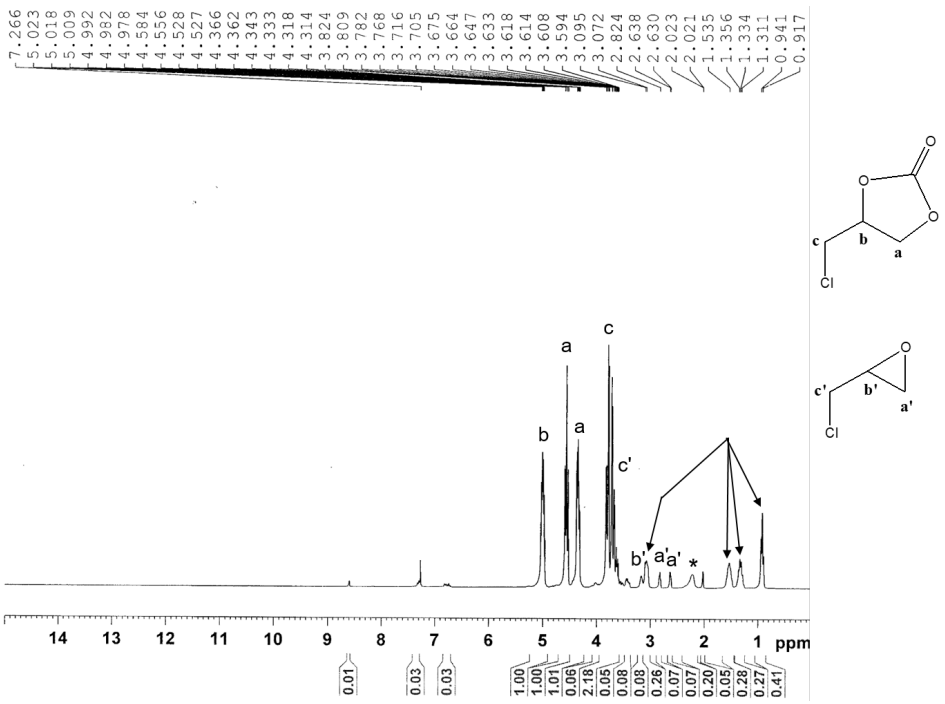

Fig. S12 ^{1}H NMR spectrum of reaction mixture in $CDCl_3$. [Catalyst **1** (1 mol%); **moistened** TBAB (2 mol%); Temperature, 60 °C; Pressure (CO_2), 5 bar; Time, 4 hours; ^{1}H NMR yield, 95 %] (Asterik represents solvent impurity).

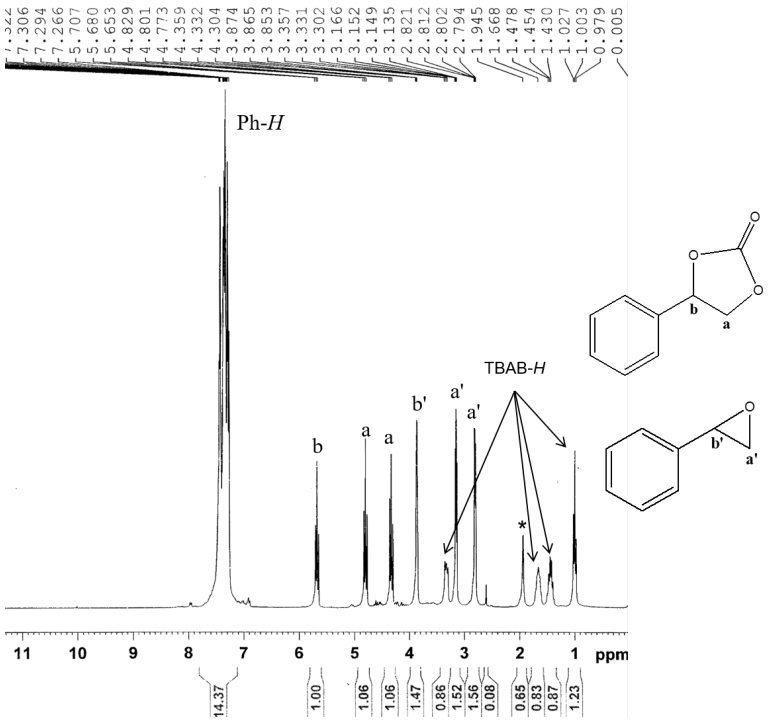

Fig. S13 ^{1}H NMR spectrum of reaction mixture in $CDCl_3$. [Catalyst (0 mol%); **moistened TBAB** (2 mol%); Temperature, 45 °C; Pressure (CO_2), 5 bar; Time, 15 hours; ^{1}H NMR yield, 40%].

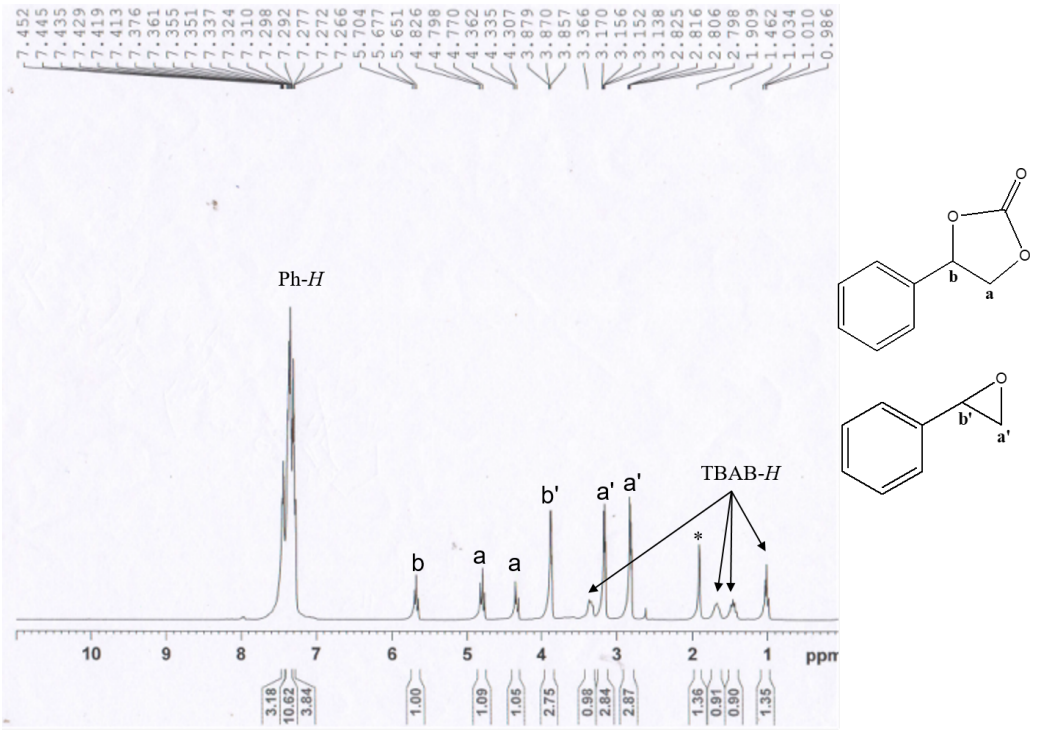

Fig. S14 ^{1}H NMR spectrum of reaction mixture in $CDCl_3$. [Catalyst (0 mol%); **unmoistened TBAB** (2 mol%); Temperature, 60 °C; Pressure (CO_2), 5 bar; Time, 4 hours; ^{1}H NMR yield, 24%].

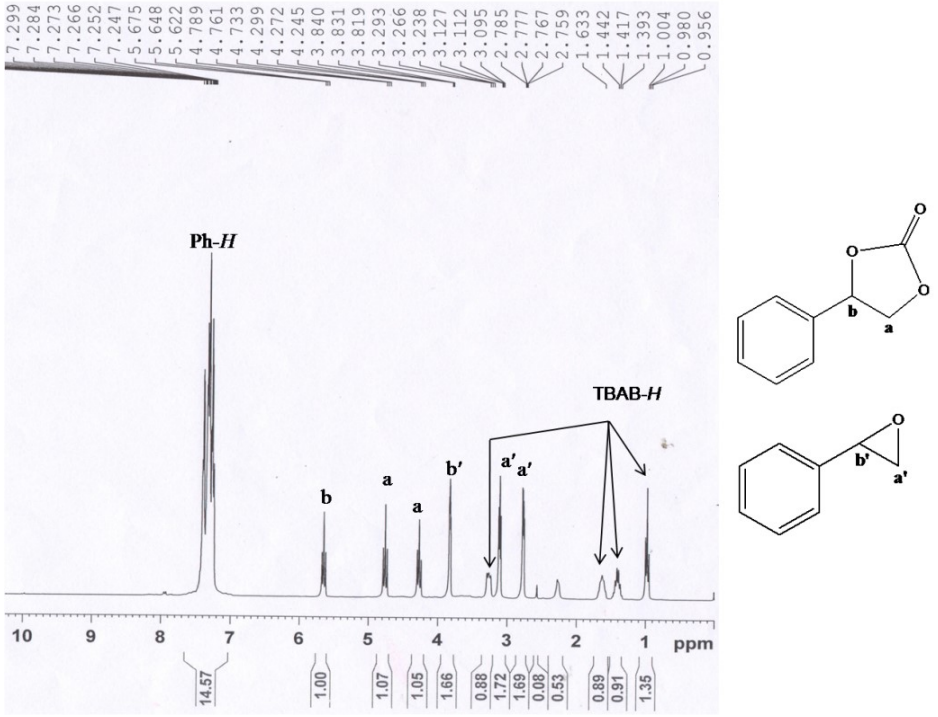

Fig. S15 ^{1}H NMR spectrum of reaction mixture in $CDCl_3$. [Catalyst (0 mol%); **moistened** TBAB (2 mol%); Temperature, 60 °C; Pressure (CO_2), 5 bar; Time, 4 hours; ^{1}H NMR yield, 37%]. (Asterik represents solvent impurity).

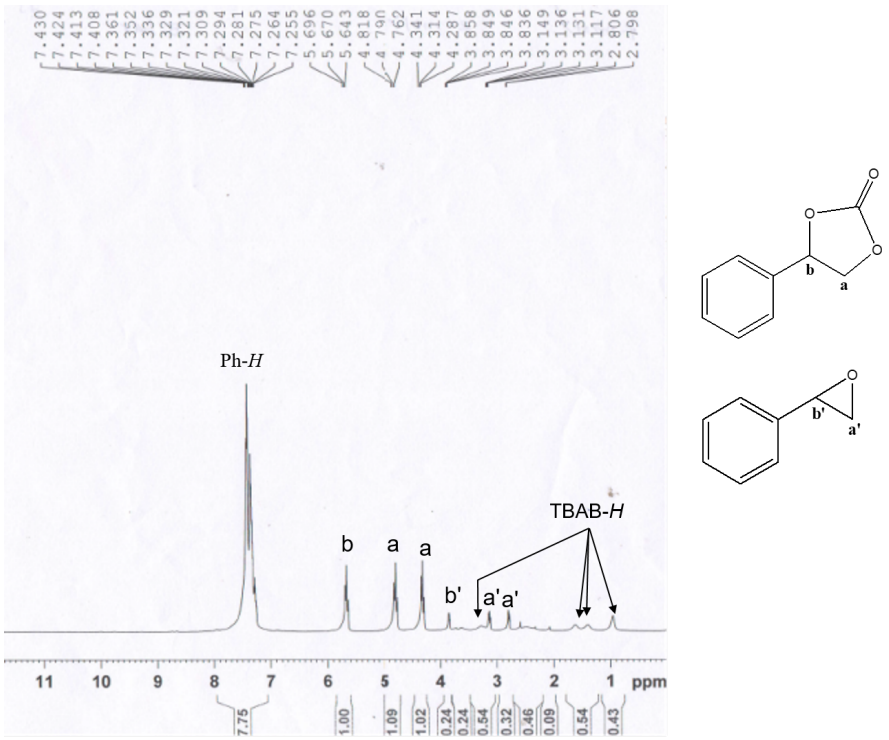

Fig. S16 ^{1}H NMR spectrum of reaction mixture in $CDCl_3$. [Catalyst **1** (1 mol%); **unmoistened** TBAB (2 mol%); Temperature, 60 °C; Pressure (CO_2), 5 bar; Time, 4 hours; ^{1}H NMR yield, 75%].

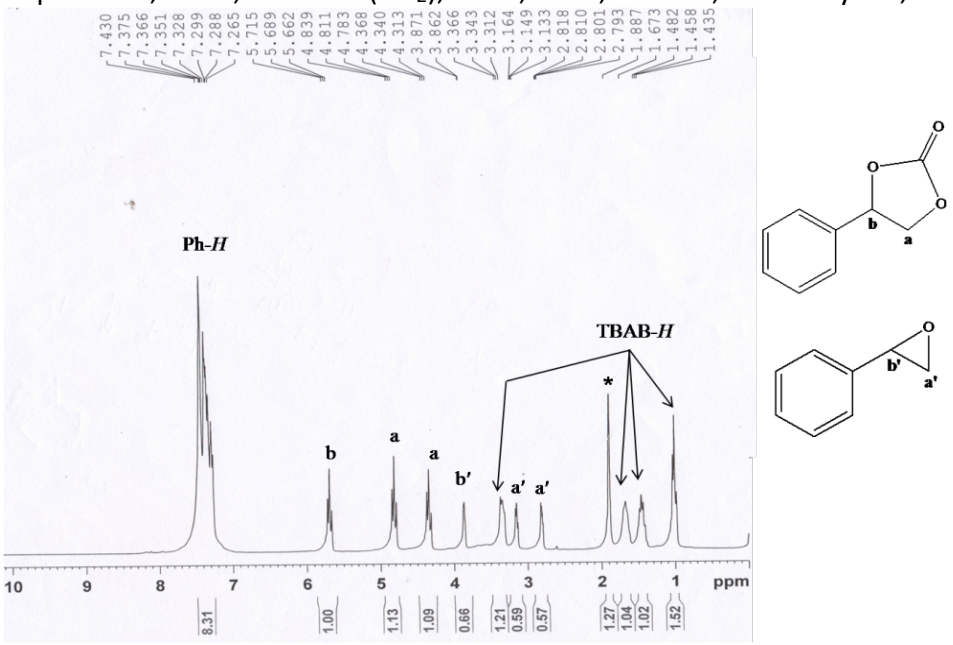

Fig. S17 ^{1}H NMR spectrum of reaction mixture in $CDCl_3$. [Catalyst **1** (1 mol%); moistened TBAB (2 mol%); Temperature, 60 °C; Pressure (CO_2), 5 bar; Time, 4 hours; ^{1}H NMR yield, 60%. Reaction was done without purging the reaction vessel with CO_2].

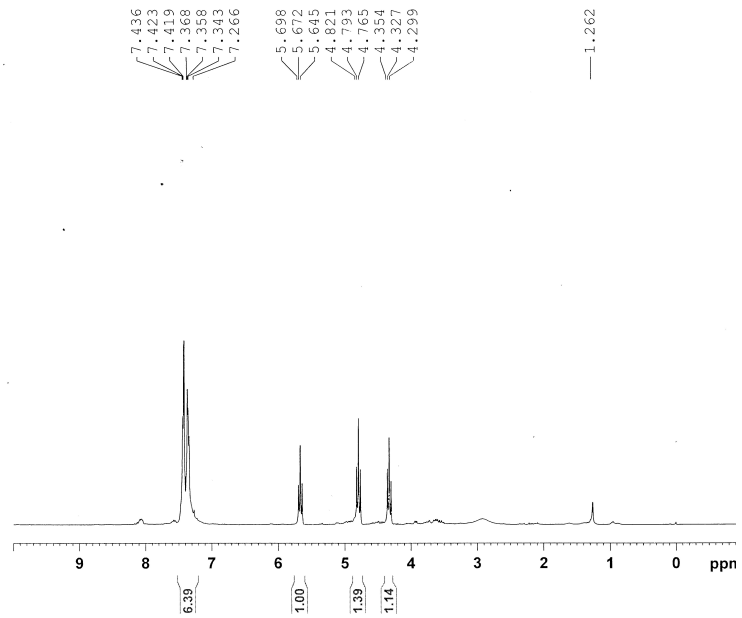

Fig. S18 ^{1}H NMR spectrum of styrene carbonate in $CDCl_3$ purified by column chromatography. [Catalyst **1** (1 mol%); moistened TBAB (2 mol%); Temperature, 60 °C; Pressure (CO_2), 5 bar; Time, 4 hours; yield, 86 %.

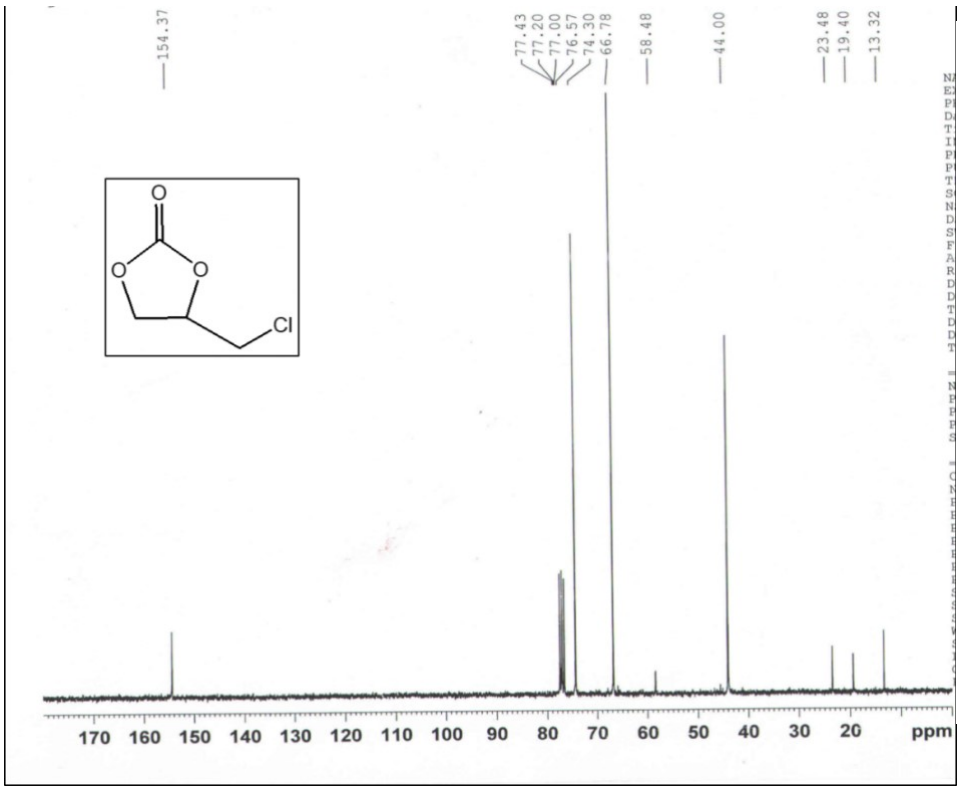

Fig. S19 ^{13}C NMR spectrum of chloropropylene carbonate in $CDCl_3$.

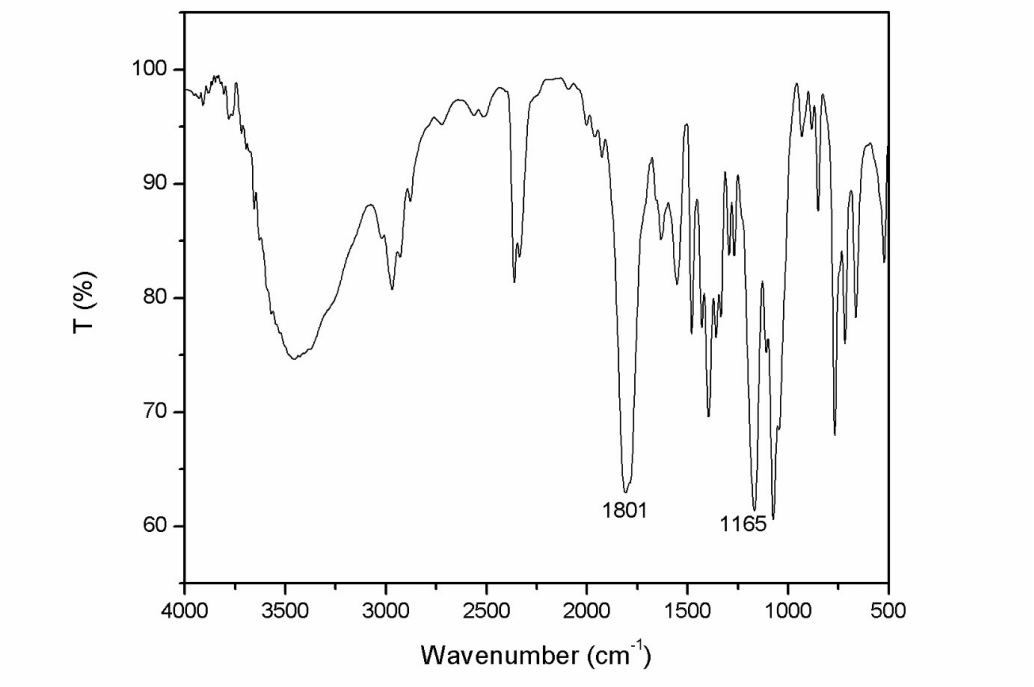

Fig. S20 IR spectrum of Chloropropylene Carbonate in KBr.

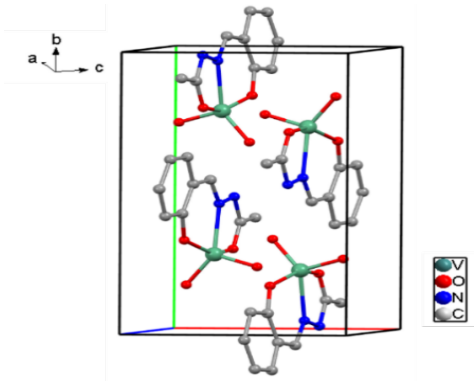

Fig. S21 Crystal packing diagram of VO_2(HSal-ac), **3**. (H atoms are excluded for clarity).