Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Efficient CO_2 fixation under ambient pressure using Poly(Ionic liquid)s based heterogeneous catalysts

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Characterization techniques:

^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS400 MHz spectrometer and on a Bruker Avance III 500 MHz spectrometer. The X-Ray diffraction (XRD) patterns were collected using the Rigaku-Smart Lab diffractometer attached with a D/tex ultra-detector and a Cu-Kα source operating at 35 kV and 70 mA. The scan range was set from 05-60^o (2θ) with a scanning rate 2^o min^{-1}. The samples were well powdered and spread evenly on a quartz slide. Thermogravimetric analysis (TGA) was performed using Mettler Toledo TGA 851 instrument under N_2 atmosphere at a heating rate of 10 °C min^{-1}. For TEM imaging, ethanolic dispersions of the as-prepared samples were ultrasonicated to obtain a stable dispersion of the particles. One drop of this solution was drop casted onto the carbon coated Cu-based grid (Ted Pella, Inc., 300 mesh Cu) and images were recorded with a JEOL, JEM-2100F microscope using a 200 kV electron source at the DST-FIST facility, IISER. Field emission scanning electron microscopy (FESEM) images were collected on The SUPRA 55-VP JSM-With patented GEMINI column technology. Prior to loading the samples into the chamber, they were coated with a thin film of gold in order to avoid charging effects. The elemental analyses were performed on a Perkin Elmer Inc. EA 2400 CHNS series. The Fourier transform infrared (FTIR) spectra were recorded using Perkin Elmer Spectrometer RX1 spectrophotometer with KBr disk technique in the range of 4000-400 cm^{-1}. For recording the FTIR spectra 5 mg of the samples were mixed with ~200 mg of KBr to make the pellets.

Experimental Section:

Materials:

Vinyl imidazole and trithiocyanuric acid were purchased from Alfa Aesar. All dibromoalkanes were purchased from Sigma Aldrich. AIBN was purchased from Spectrochem. All epoxides used here were purchased from Sigma Aldrich. Chloroform-d was purchased from sigma and chloroform was used as internal standard. All chemicals were used as received.

Preparation of the dicationic ionic liquid:

62.5 mmol of N-vinyl imidazole and 25 mmol of 1,n-dihalo alkanes were taken in 20 ml methanol (40 ml for 1,10-dibromodecane) inside a high-pressure tube. The reaction mixture was heated at 70 ^{o}C for 16 h on an oil bath. After the completion of the reaction, the solvent was evaporated to obtain a highly viscous liquid. Ethyl acetate was added to the viscous liquid and stirred. It resulted in the formation of a white precipitate. The precipitates were centrifuged and washed again for next two times with ethyl acetate followed by dried under vacuum. The NMR spectra of the products were checked in D_2O (Figure. S3-S12). The yield of the materials was varied from 50% to 65%.

Preparation of the polymer:

8 mmol of dicationic ionic liquid and 5 mmol of trithiocyanuric acid (TTCA) was taken together in a 50 ml round bottom (RB) flask. 25 ml methanol and 200 mg AIBN were added to the RB flask and nitrogen gas was purged for 15 min to remove the residual air from the reaction mixture.

Subsequently, the reaction mixture was heated at 60 ^{o}C for 12 h on an oil bath. A white jelly type material appeared. This material was washed 3 times with dimethyl sulfoxide (DMSO) followed by 3 times methanol and dried under vacuum. Depending upon the ionic liquid chain length the polymer will be represented as 1,n-IL-TTCA. The yield of these materials were 1,2-IL-TTCA 2 gm, 1,4-IL-TTCA 2.6 gm, 1,6-IL-TTCA 2.9 gm, 1,8-IL-TTCA 3.2 gm and 1,10-IL-TTCA 3.4 gm. For poly-1,6-IL preparation, all the conditions were same expect TTCA. The yield of this material was 2.0 gm.

General scheme for the polymer preparation:

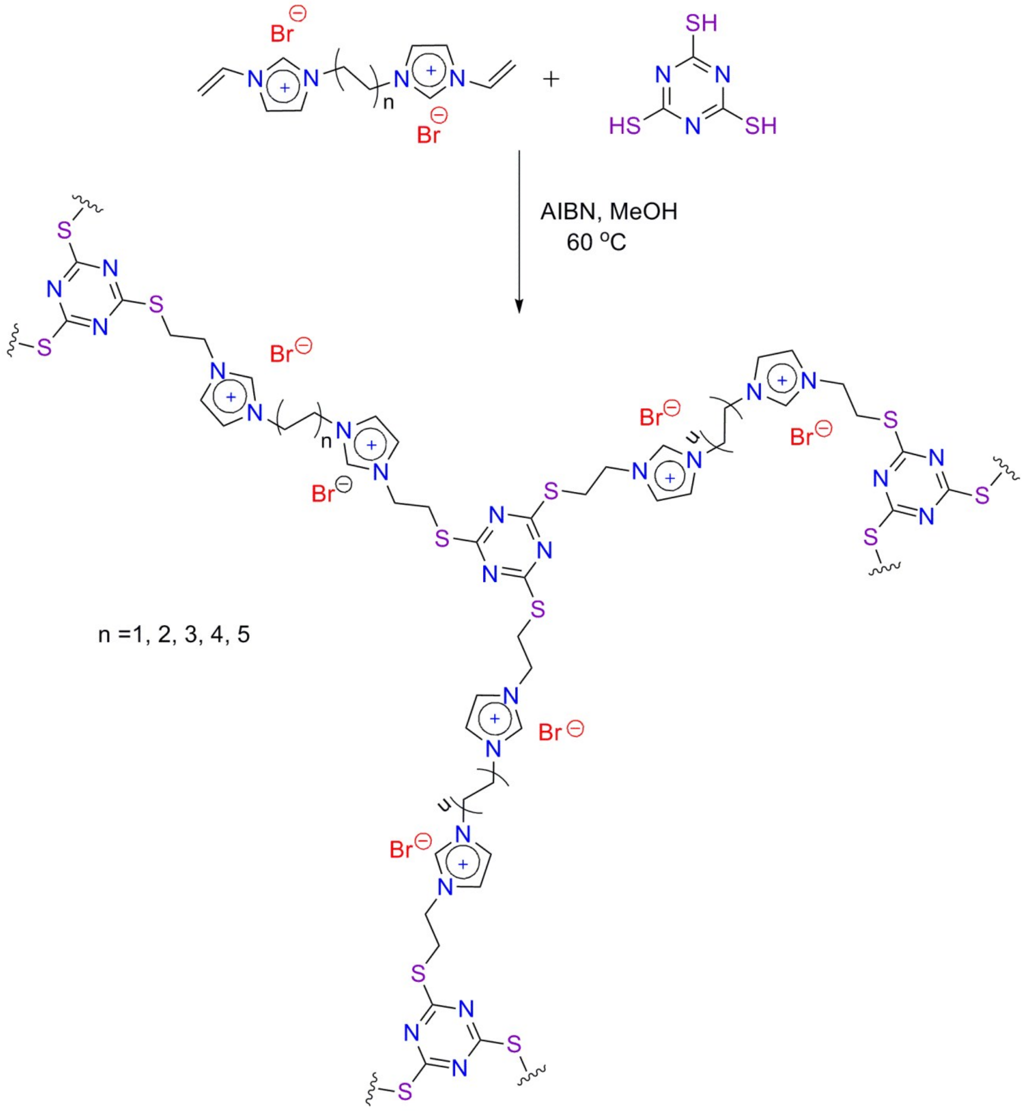

Figure. S1(a): Probable structure of the thiol-ene polymers.

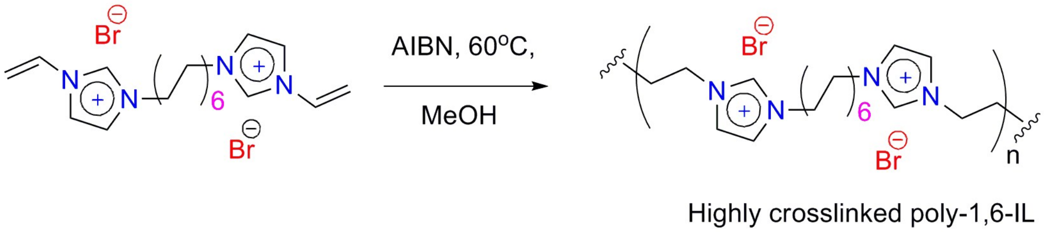

Figure. S1(b): Probable structure of the homo polymer (poly-1,6-IL).

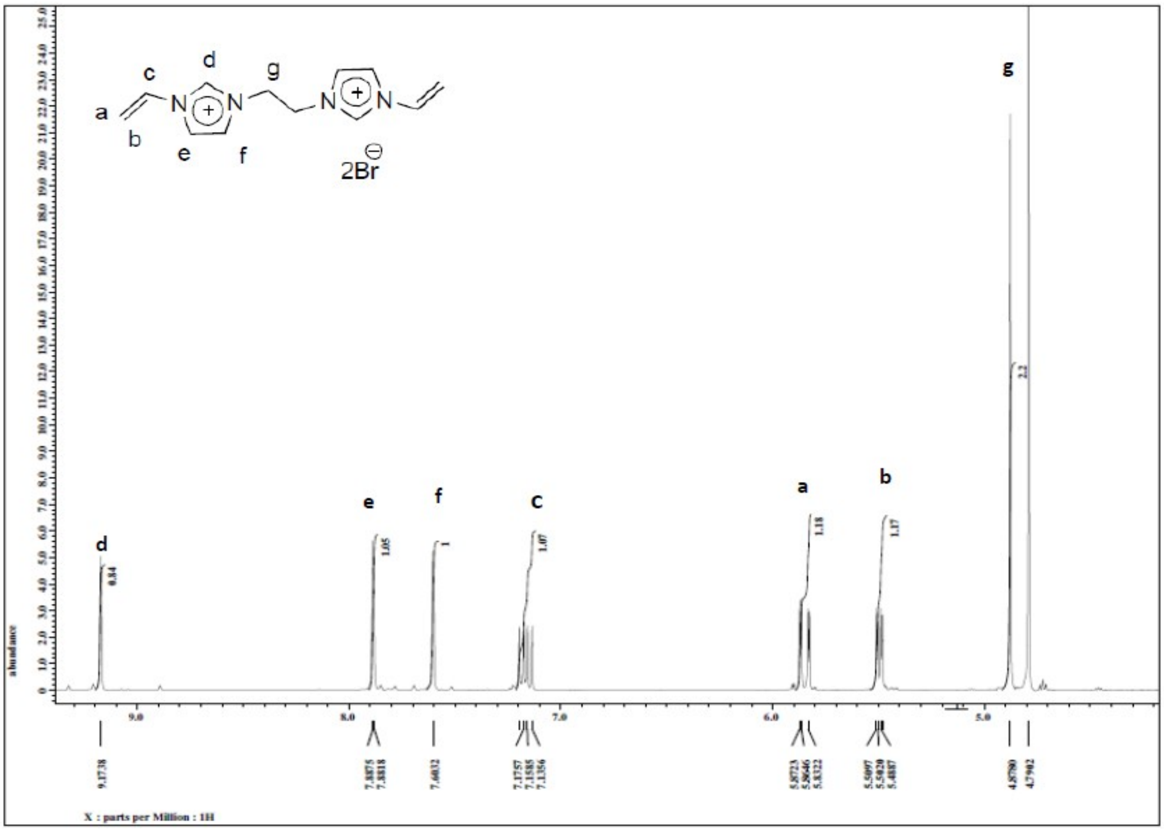

Figure. S2: ^{1}H NMR spectrum of 2-divinyl imidazolium bromide (D_2O, 400 MHz).

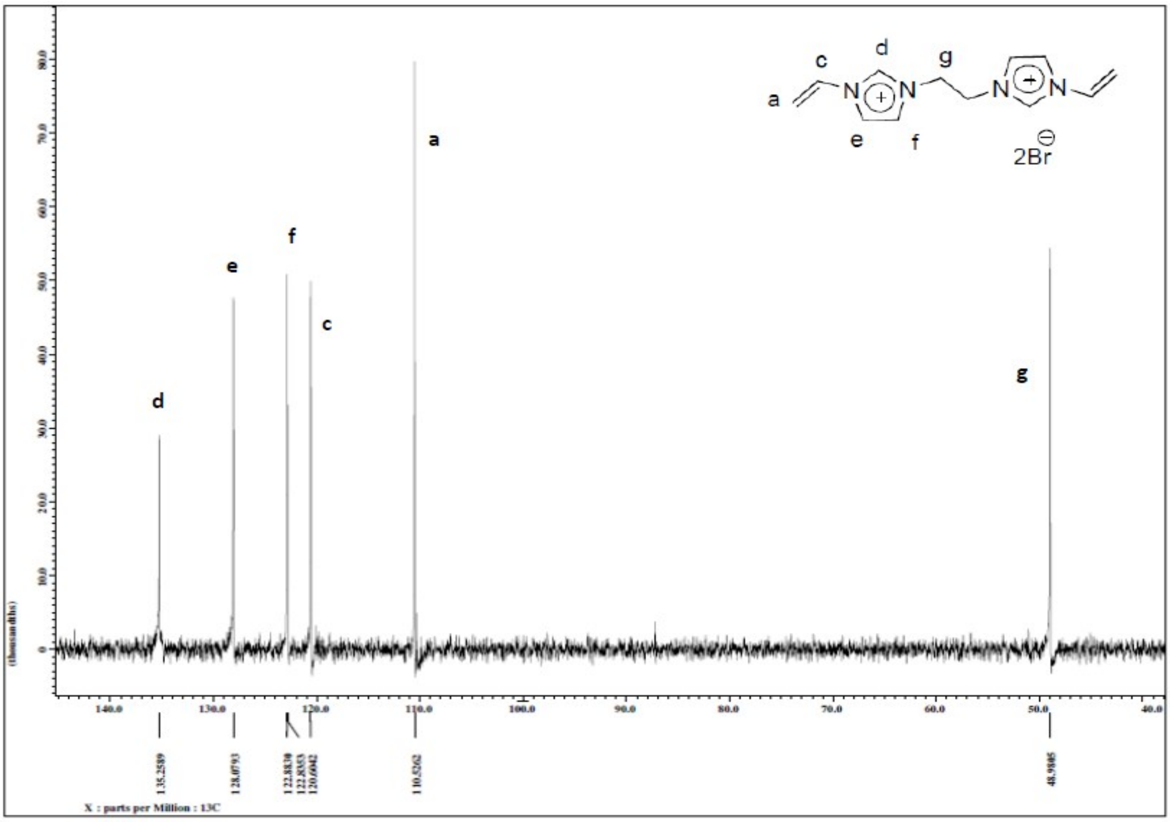

Figure. S3: ^{13}C NMR spectrum of 1,2-divinyl imidazolium bromide (D_2O, 400 MHz).

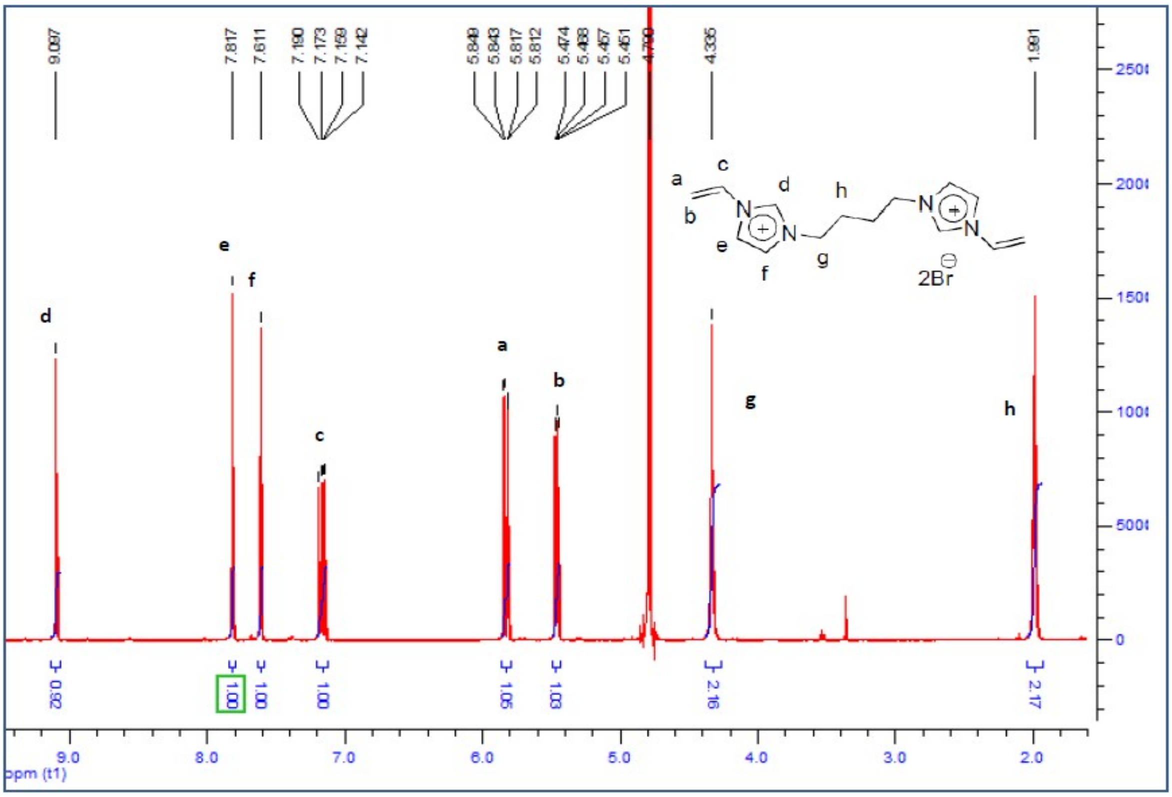

Figure. S4: ^{1}H NMR spectrum of 1,4-divinyl imidazolium bromide (D_2O, 500 MHz).

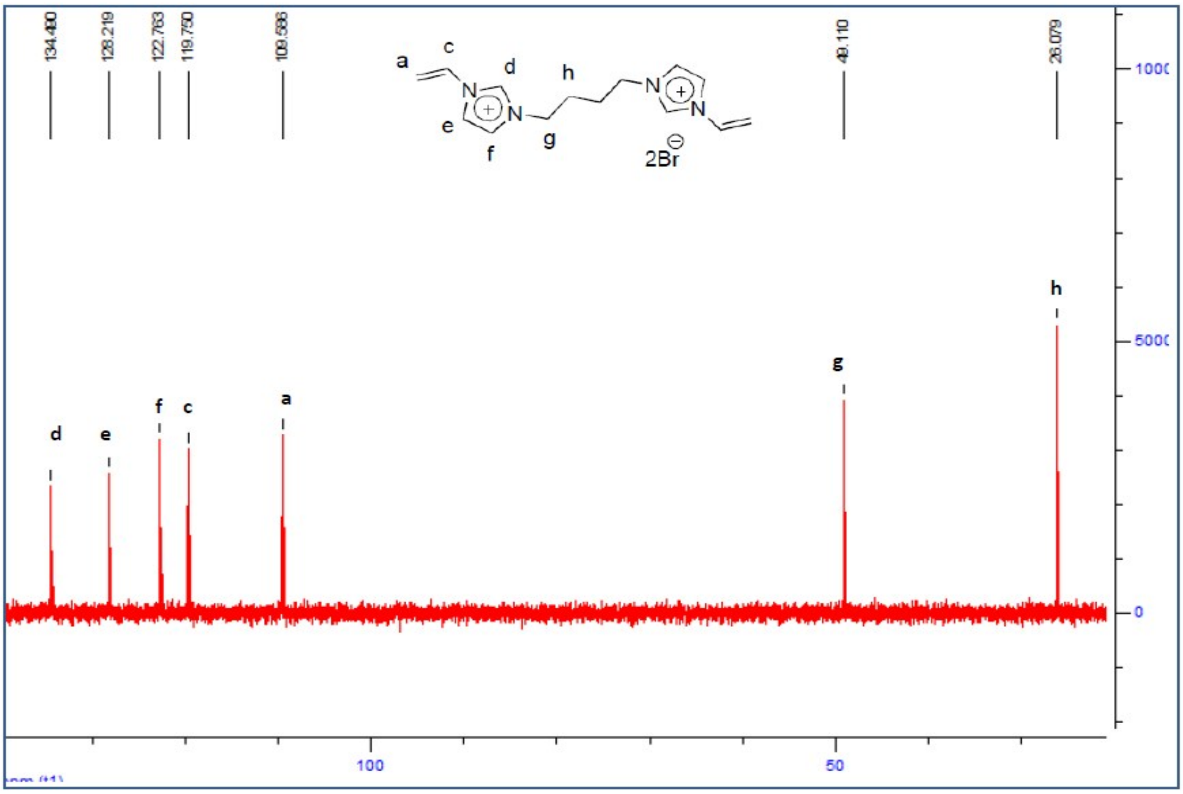

Figure. S5: ^{13}C NMR spectrum of 1,4-divinyl imidazolium bromide (D_2O, 500 MHz).

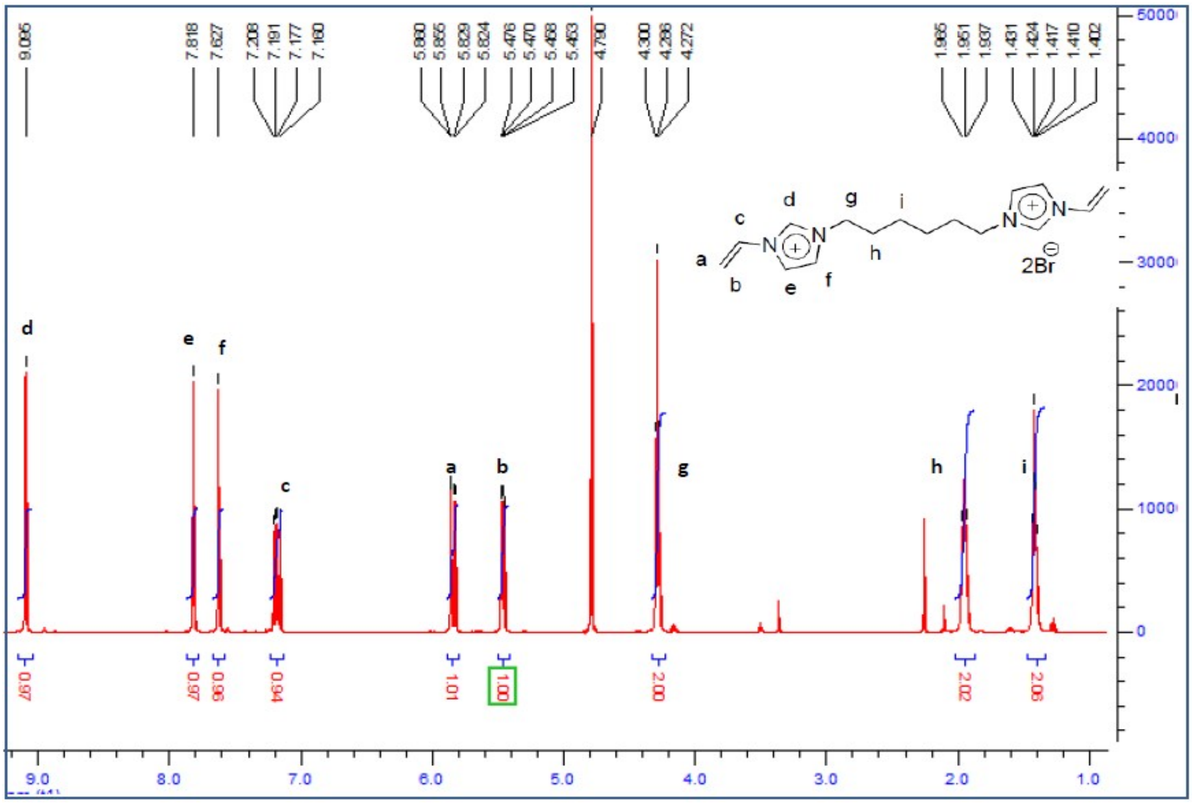

Figure. S6: ^{1}H NMR spectrum of 1,6-divinyl imidazolium bromide (D_2O, 500 MHz).

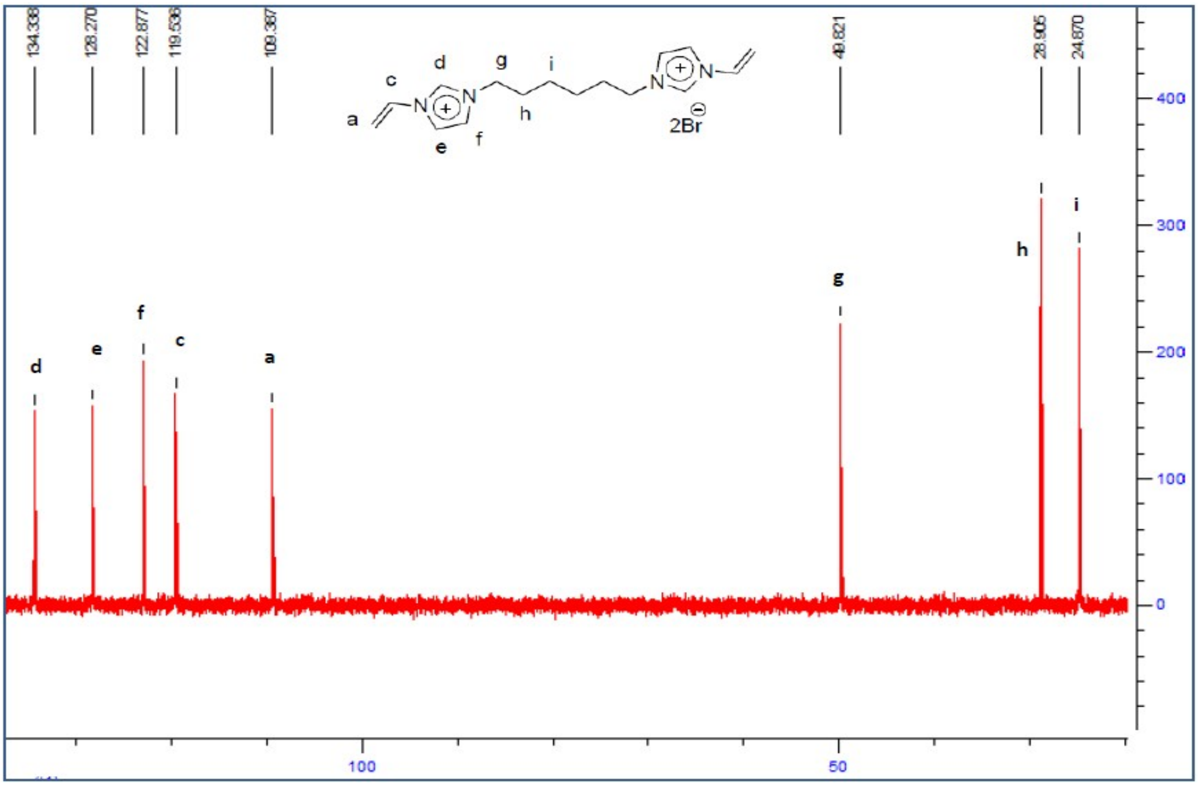

Figure. S7: ^{13}C NMR spectrum of 1,6-divinyl imidazolium bromide (D_2O, 500 MHz).

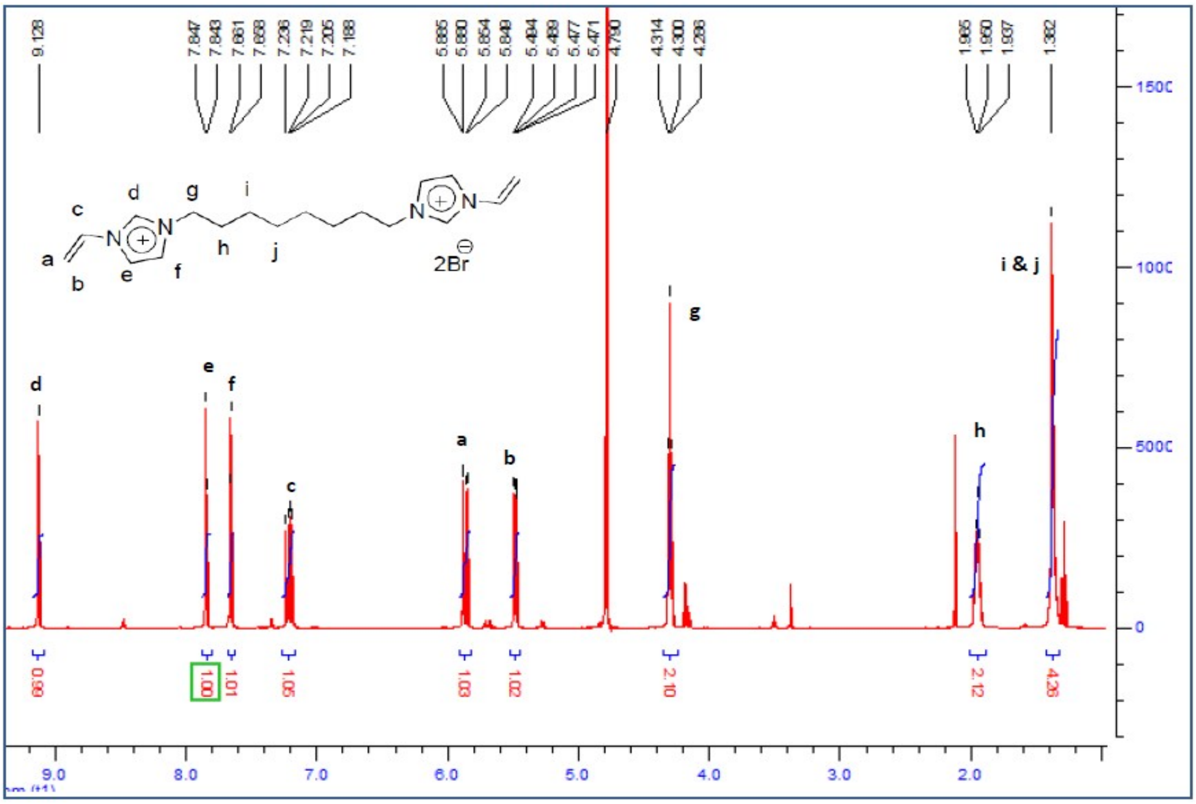

Figure. S8: ^{1}H NMR spectrum of 1,8-divinyl imidazolium bromide (D_2O, 500 MHz).

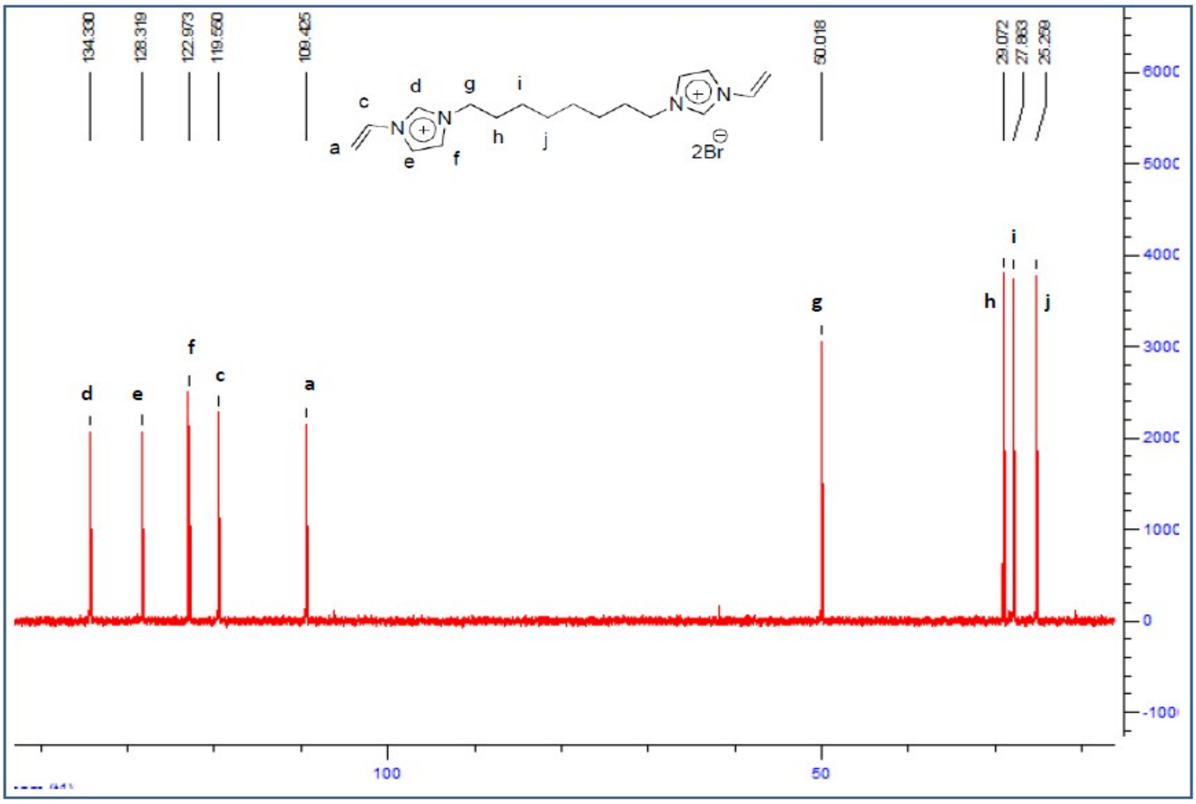

Figure. S9: ^{13}C NMR spectrum of 1,8-divinyl imidazolium bromide (D_2O, 500 MHz).

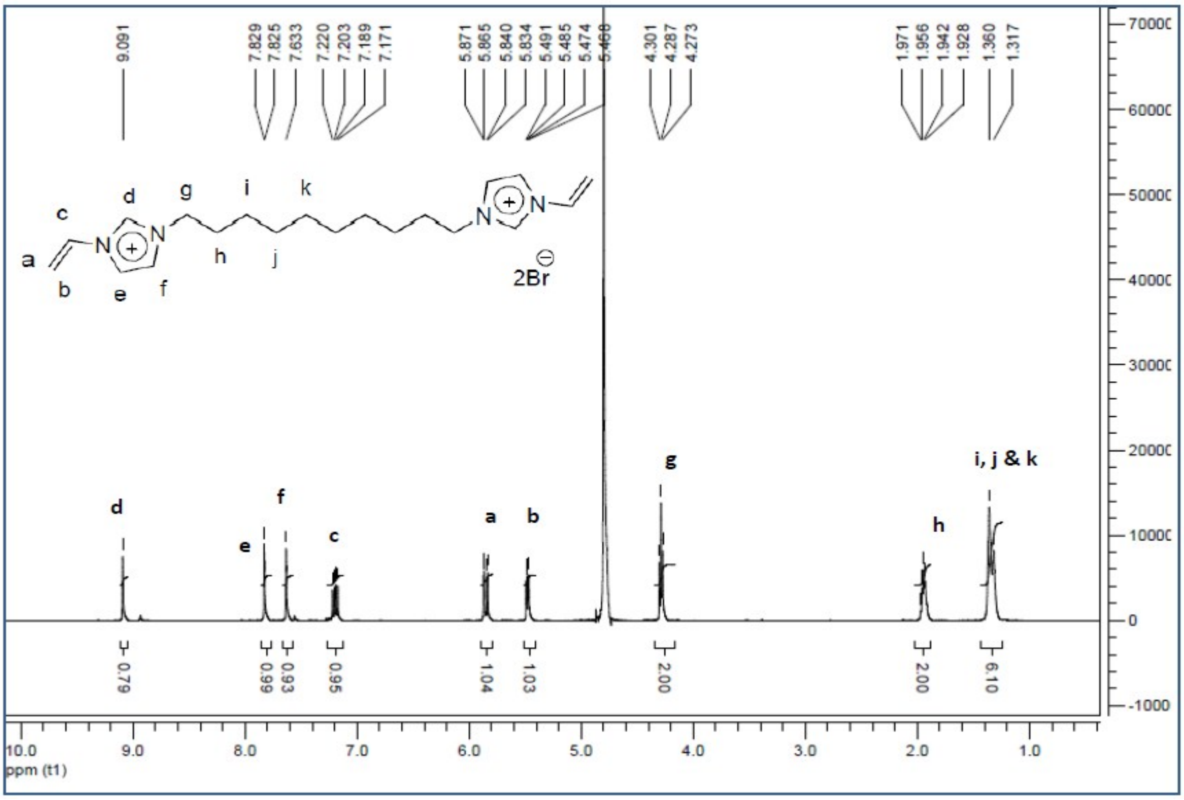

Figure. S10: ^{1}H NMR spectrum of 1,10-divinyl imidazolium bromide (D_2O, 400 MHz).

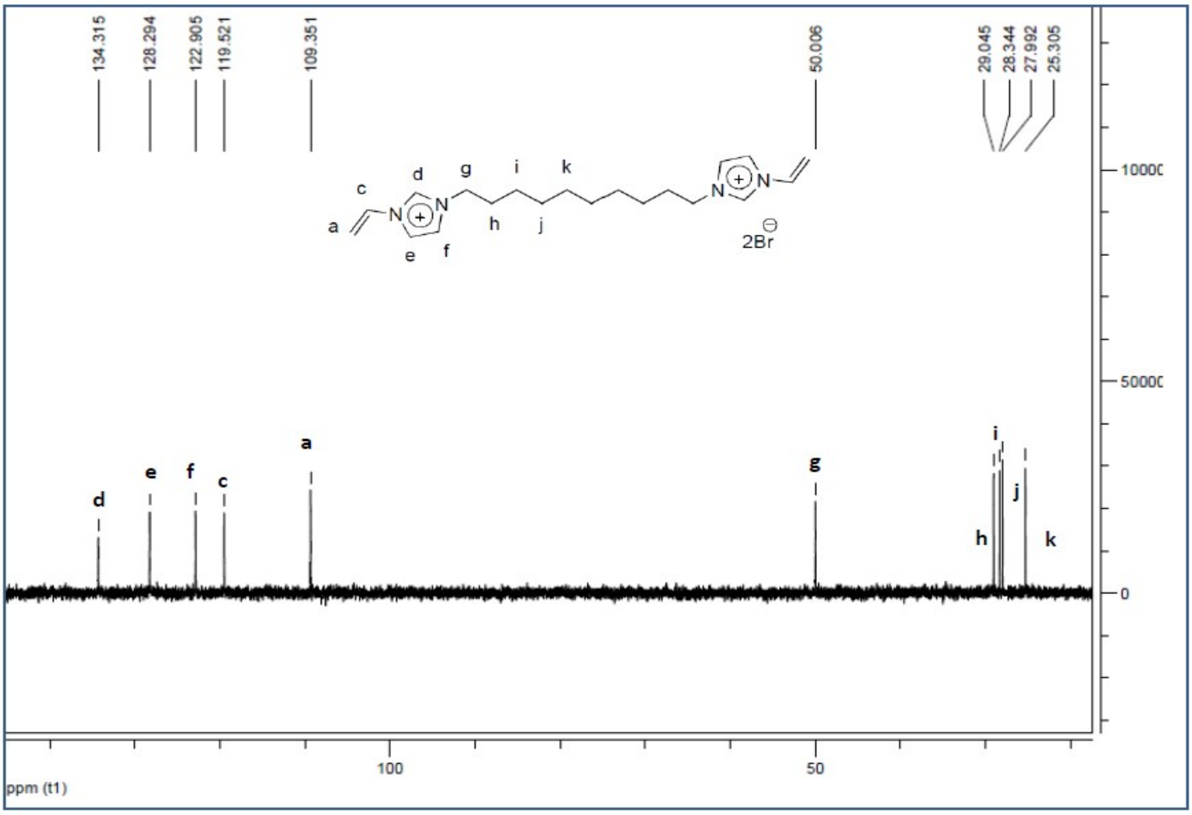

Figure. S11: ^{13}C NMR spectrum of 1,10-divinyl imidazolium bromide (D_2O, 400 MHz).

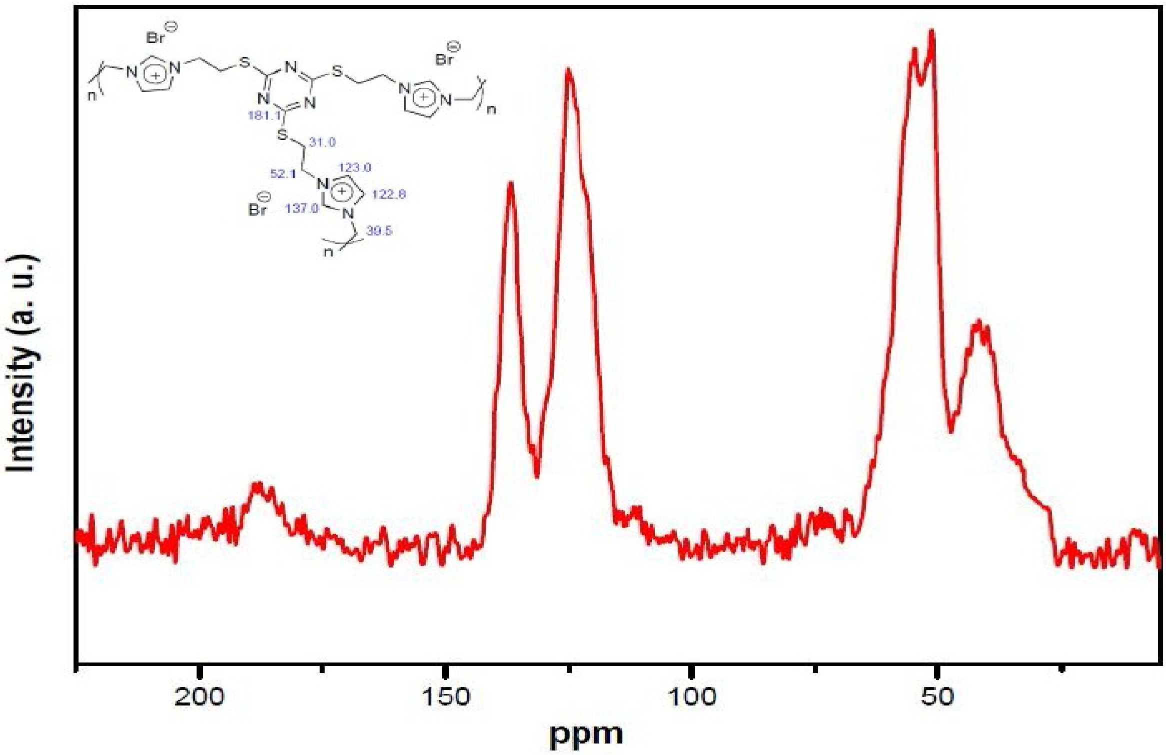

Figure. S12: **^{13}C CP-MAS spectrum of 1,2-IL-TTCA (500 MHz).**

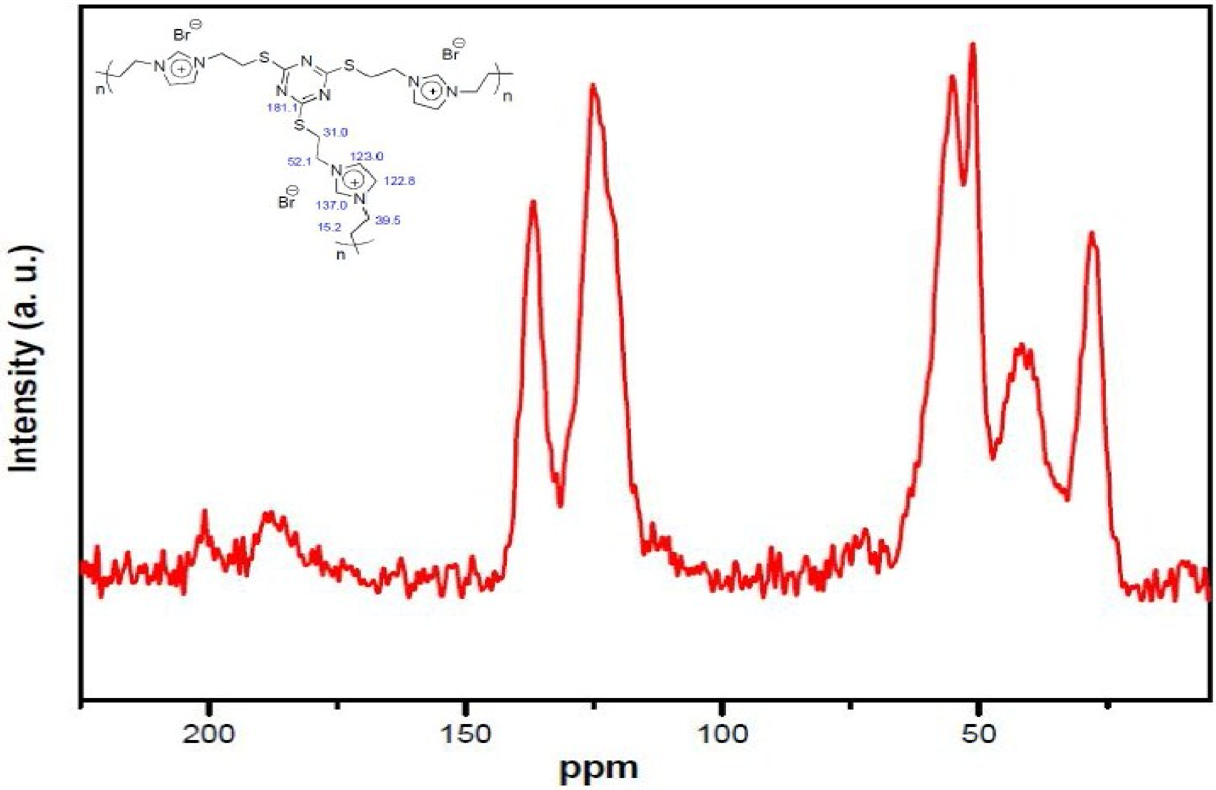

Figure. S13: **^{13}C CP-MAS spectrum of 1,4- IL-TTCA (500 MHz).**

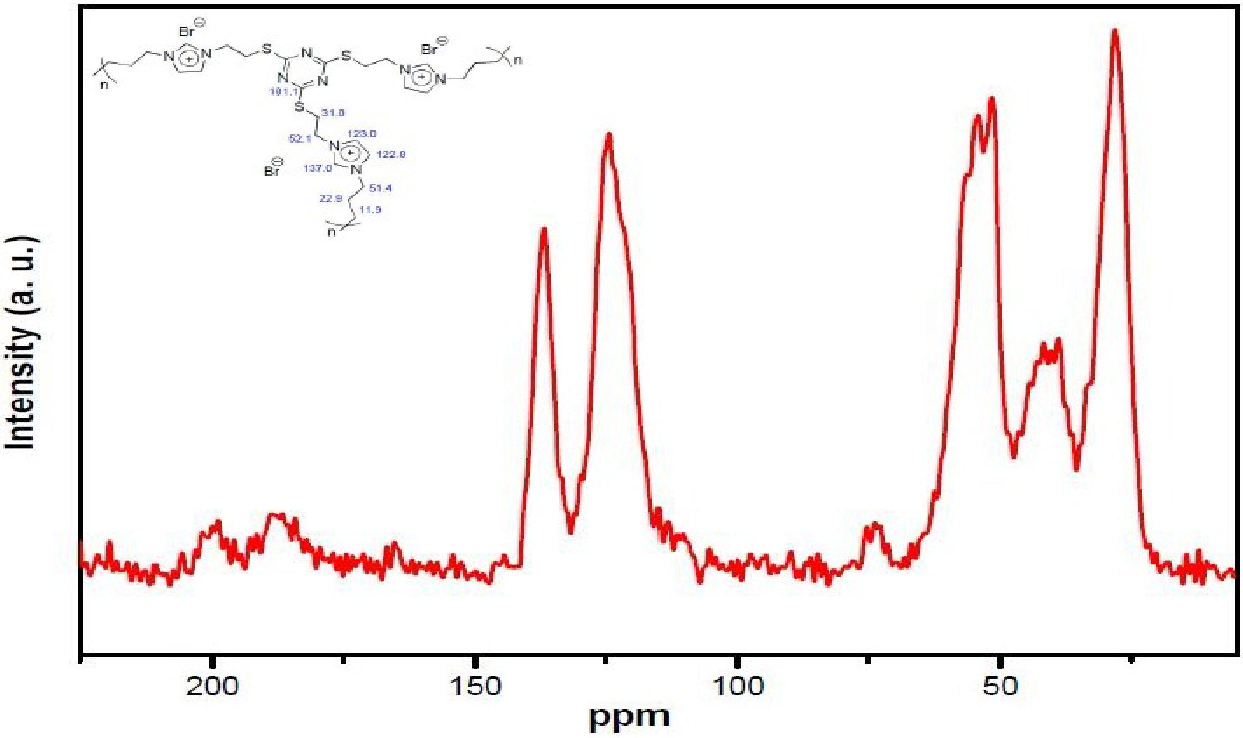

Figure. S14: ^{13}C CP-MAS spectrum of 1,6- IL-TTCA (500 MHz).

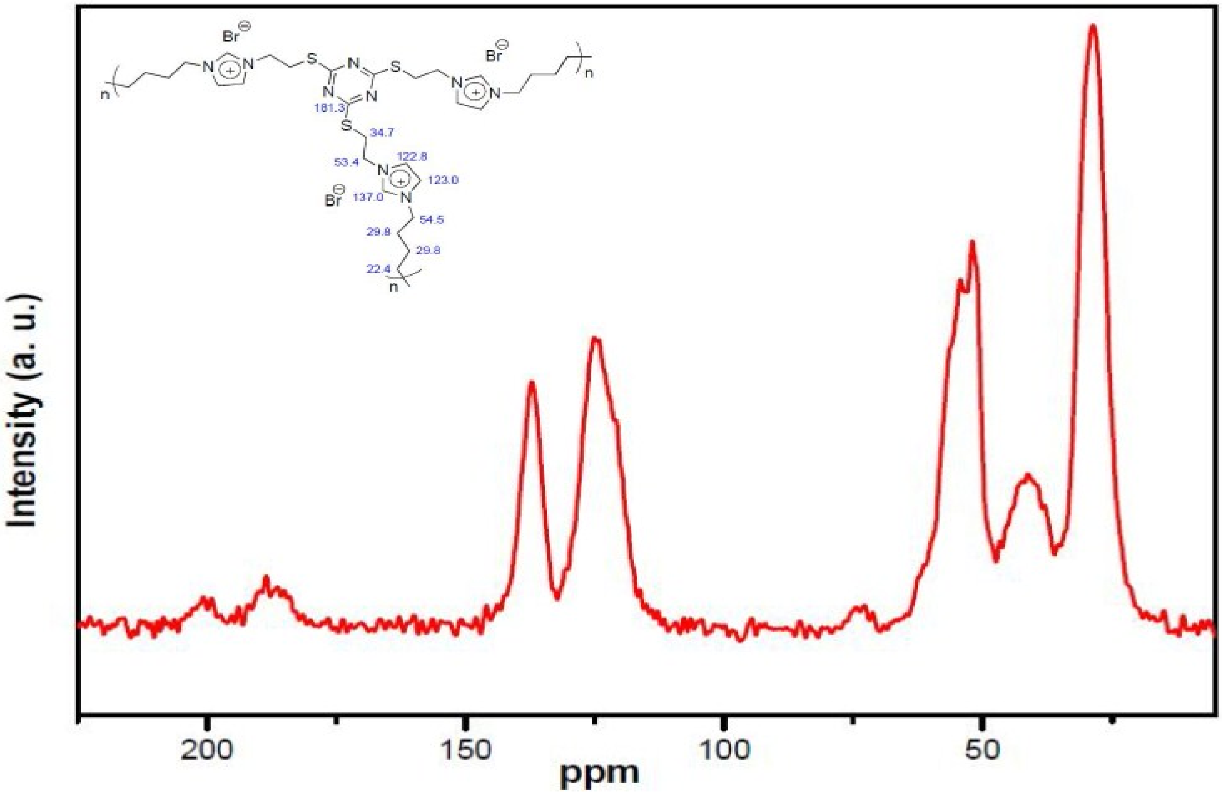

Figure. S15: ^{13}C CP-MAS spectrum of 1,8- IL-TTCA (500 MHz).

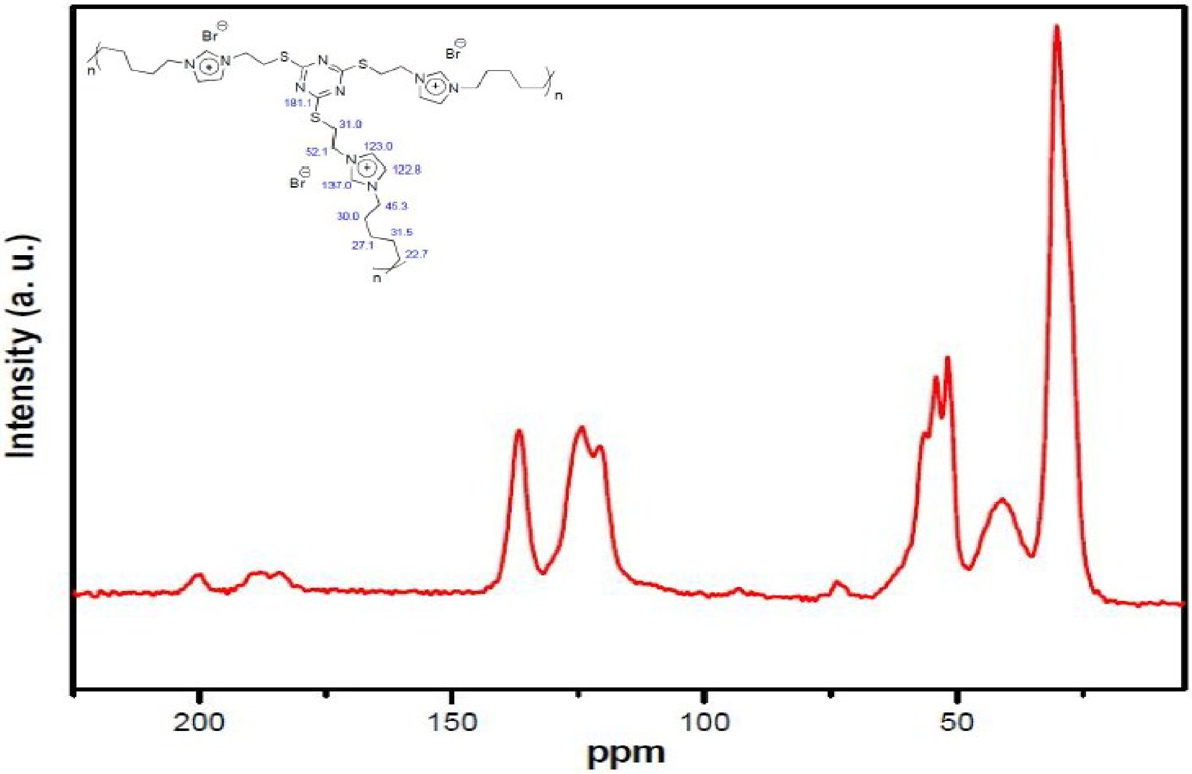

Figure. S16: ^{13}C CP-MAS spectrum of 1,10- IL-TTCA (500 MHz).

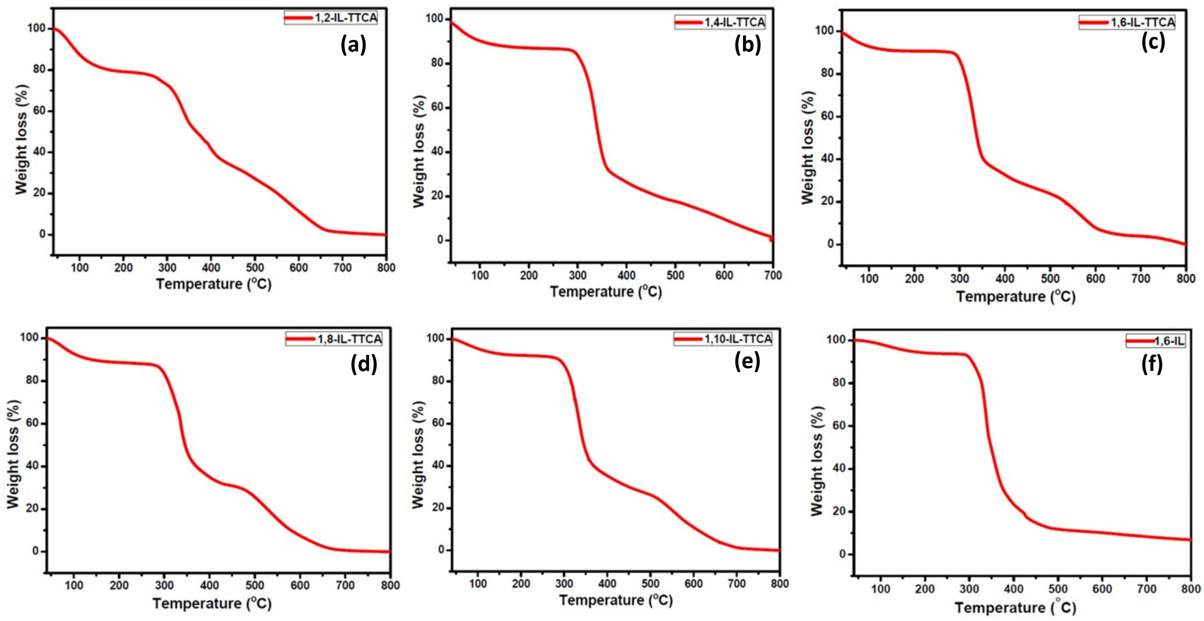

Figure. S17: TGA spectra of all the polymeric catalysts. Figure. (a) to (e) are the five thiol congaing polymeric catalyst and Figure. (f) is the homopolymer of 1,6-IL (poly-1,6-IL).

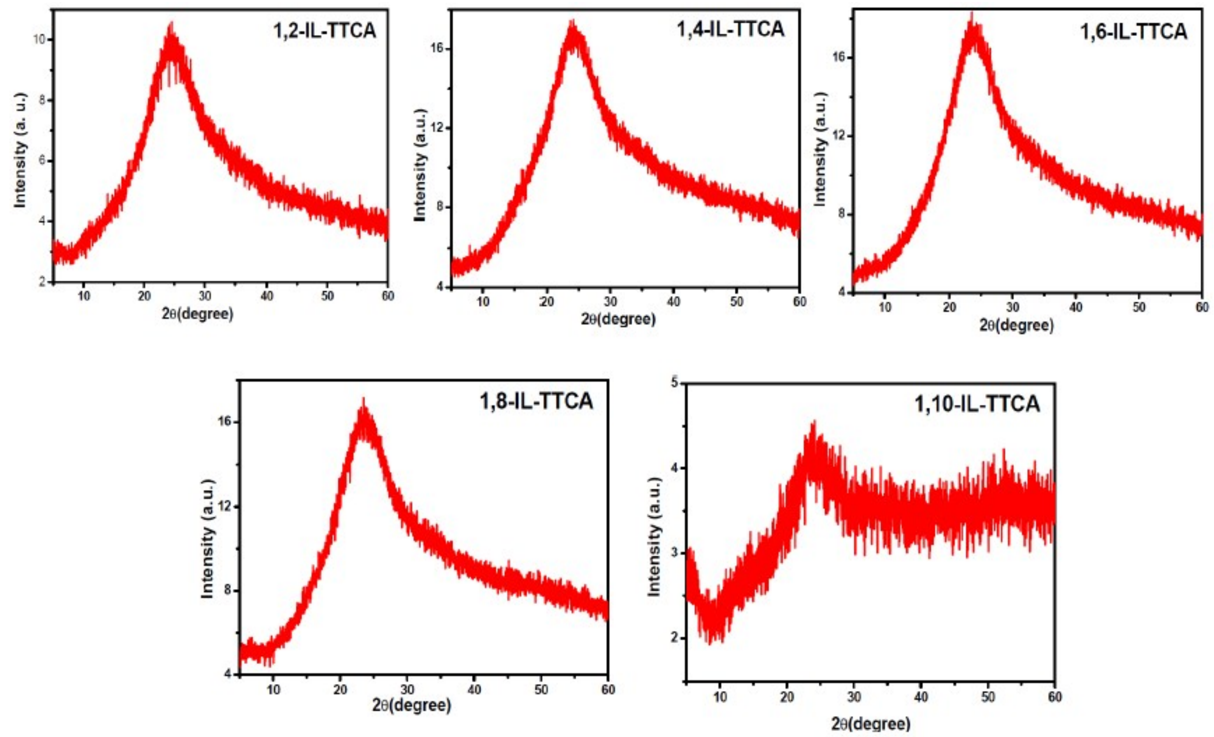

Fig: S18: PXRD analysis of all five polymeric catalysts.

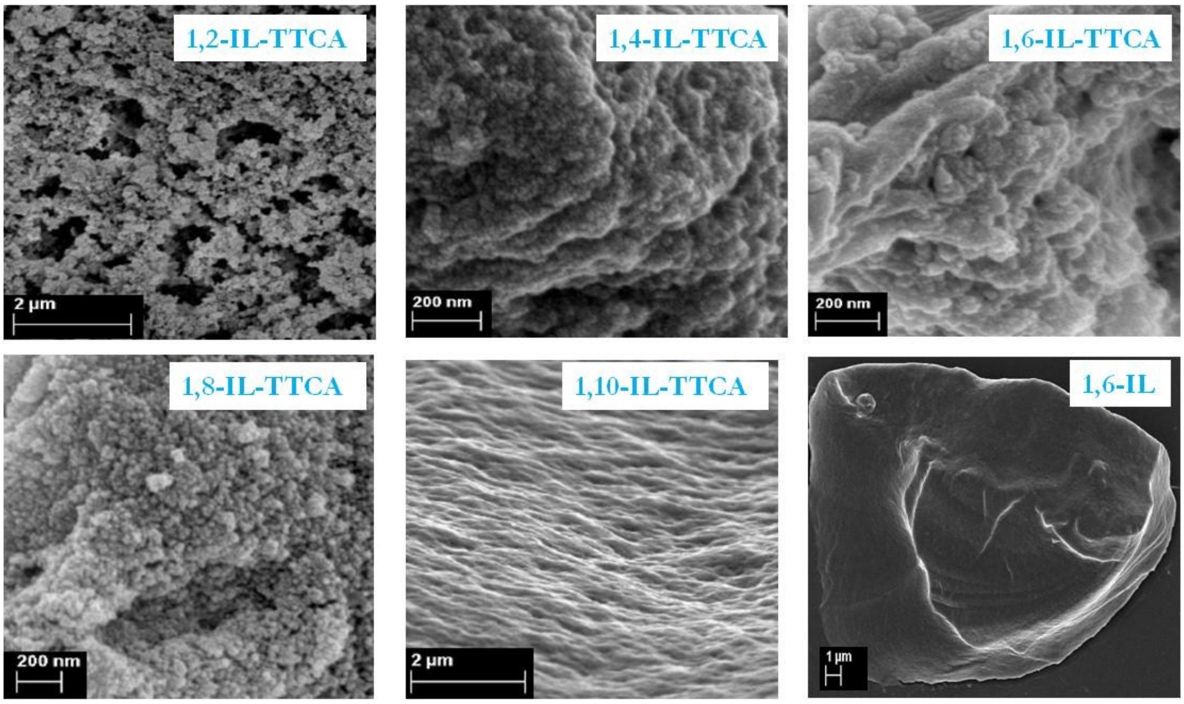

Figure. S19: SEM analysis of all five thiol congaing polymer and one thiol free polymer catalysts.

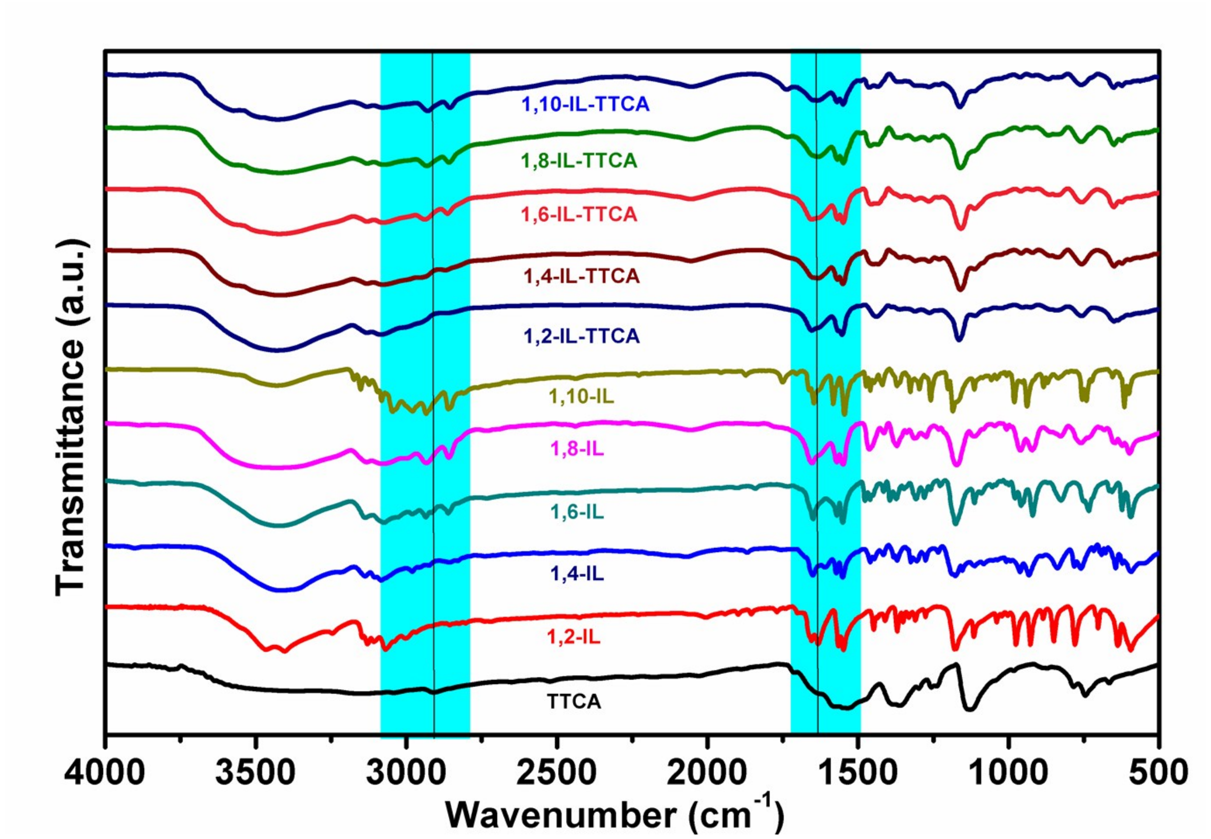

Figure. S20(a): FTIR analysis of TTCA, all five dicationic ionic liquid and all five polymers.

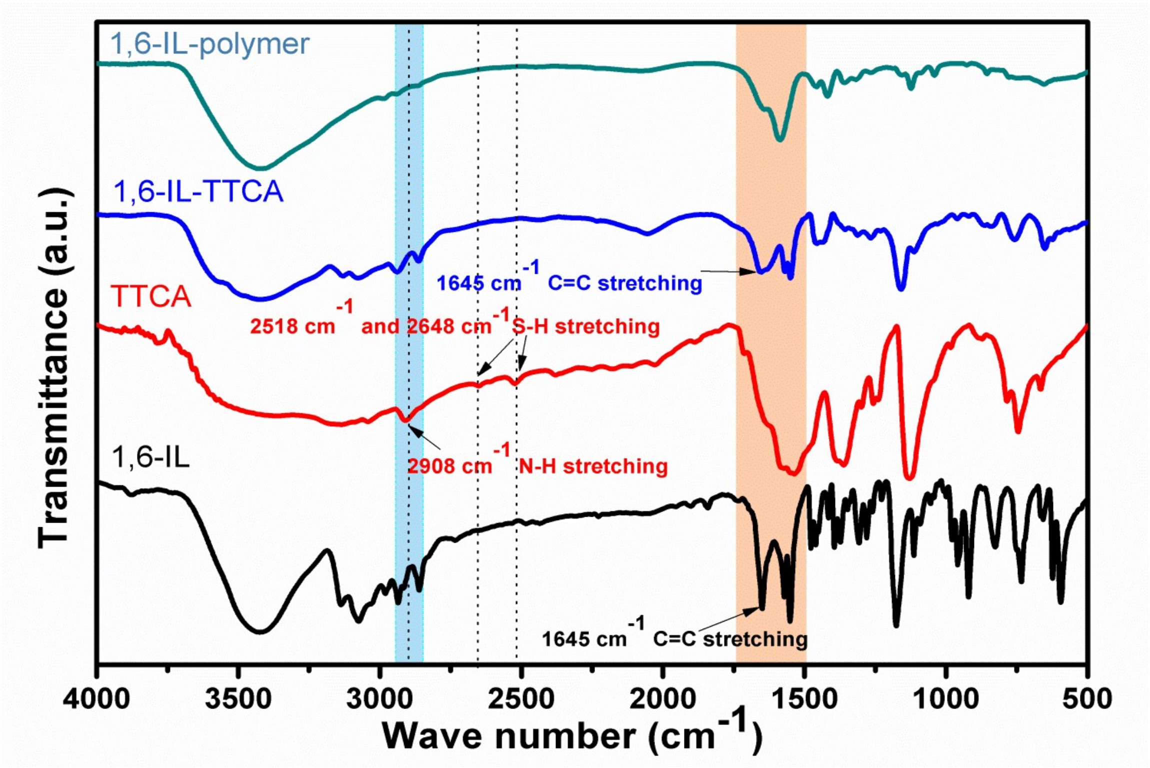

Figure. S20(b): FTIR analysis of TTCA, 1,6-IL, poly-1,6-IL and 1,6-IL-TTCA.

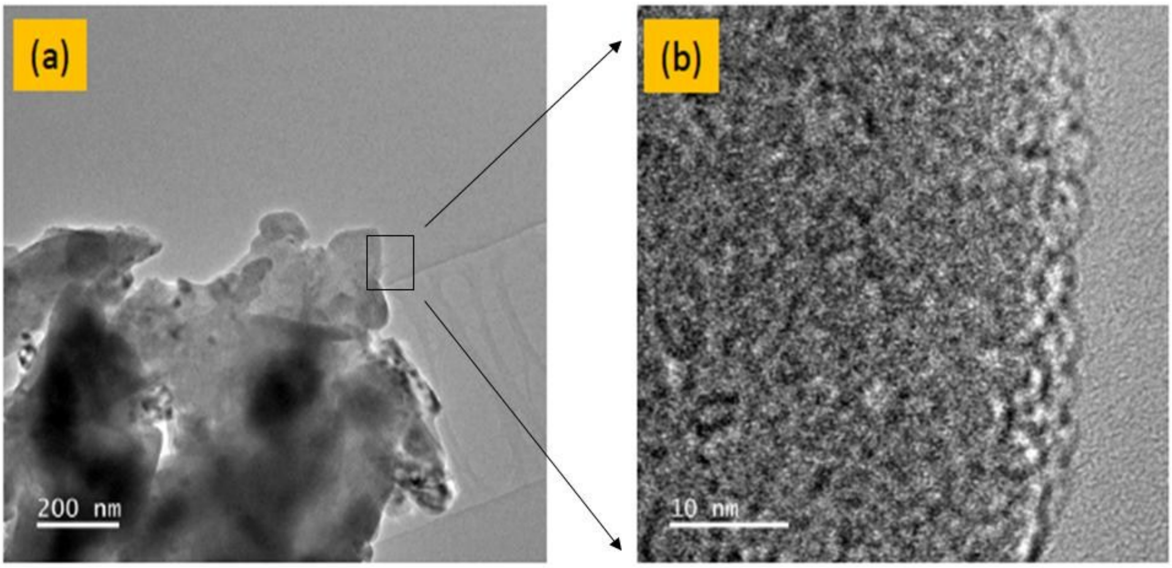

Figure. S21. TEM images of 1,6-ILTTCA (a) and the enlarged portion (b).

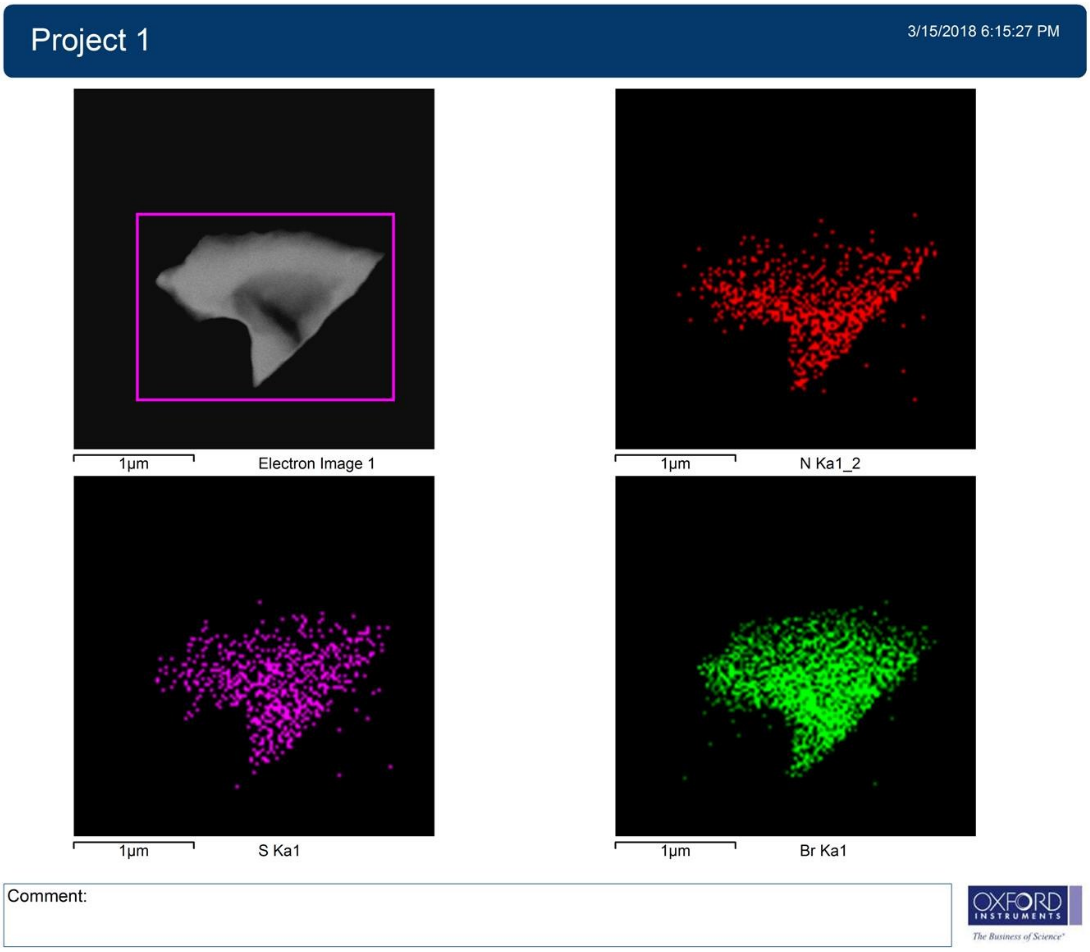

Figure. S22: Elemental mapping of the elements nitrogen, sulphur and bromine of 1,6-IL-TTCA from Transmission electron microscopy.

Table S1. **Elemental analysis from TEM (average of five different spots)**

Element	Weight (%)	Atomic (%)
N	32.0	64.2
S	11.9	9.0
Br	56.1	26.7

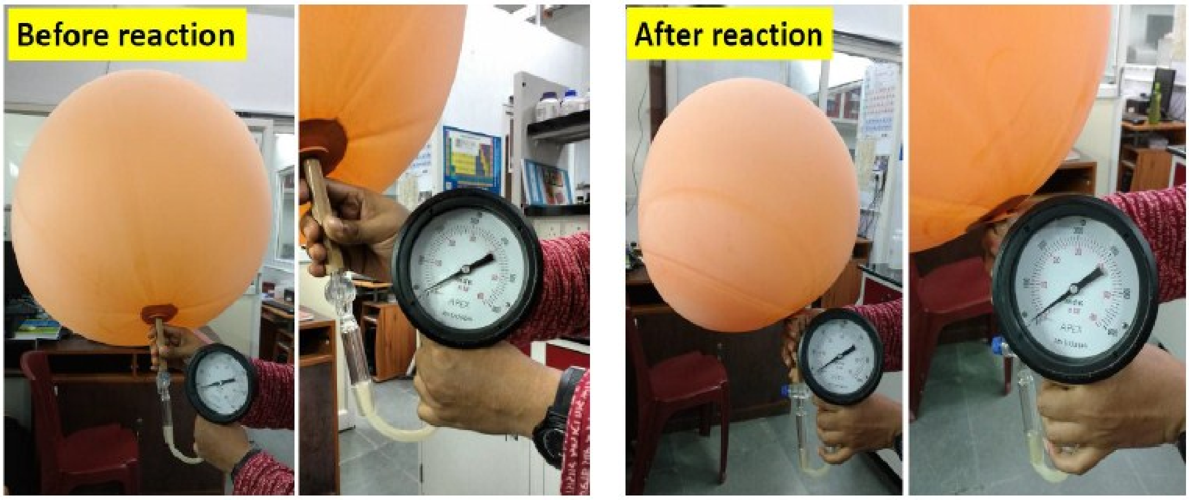

Figure.S23: Digital images showing the measurement of balloon pressure before and after the reaction

Figure. S24: Digital image of the experimental setup used for the conversion of epoxides to cyclic carbonates under CO_2 filled balloon condition.

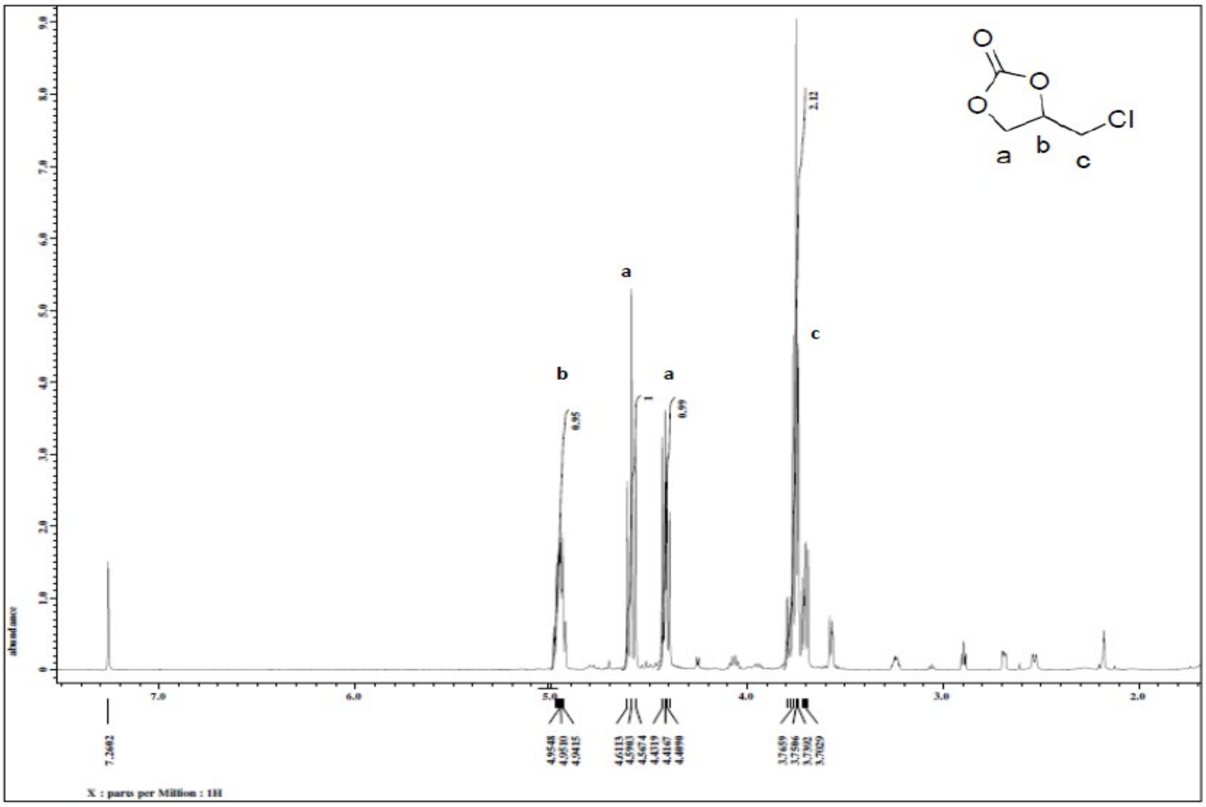

Figure. S25: ^{1}H NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (CDCl3, 400 MHz).

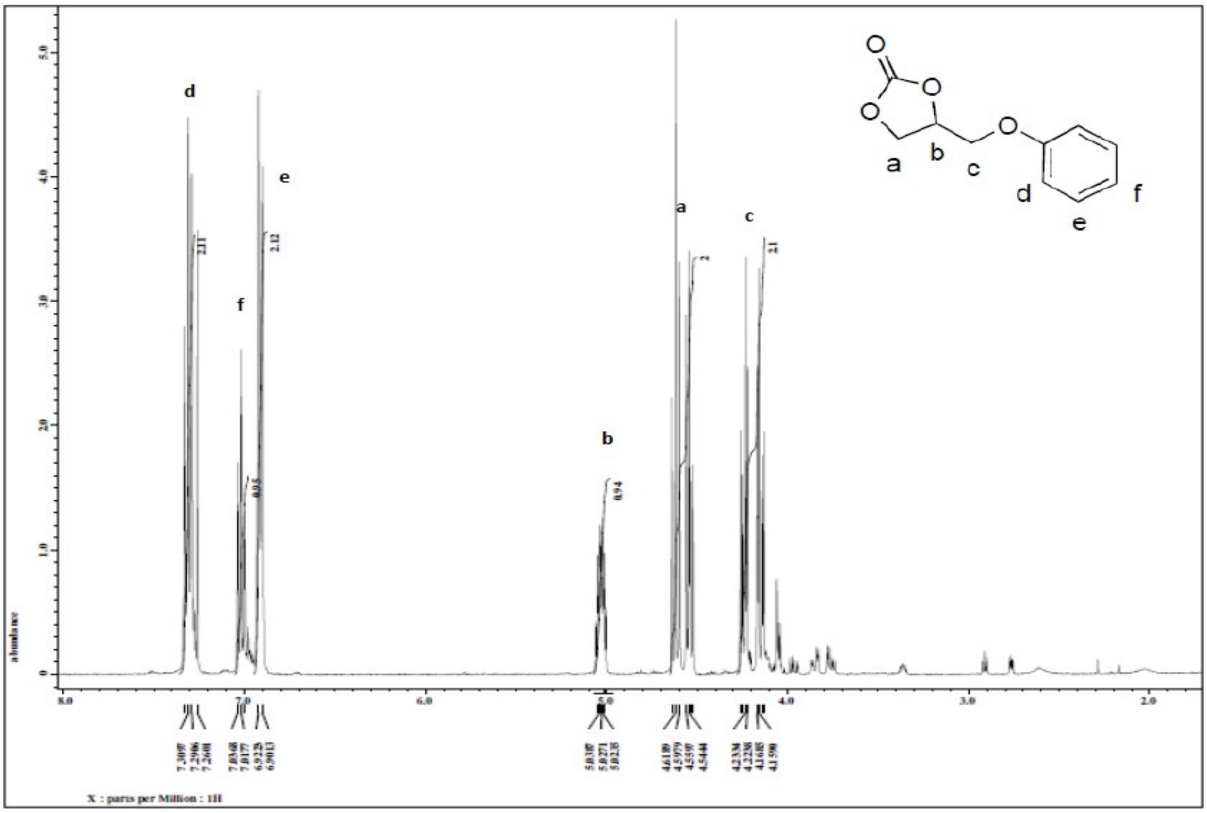

Figure. S26: ^{1}H NMR spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one ($CDCl_3$, 400 MHz).

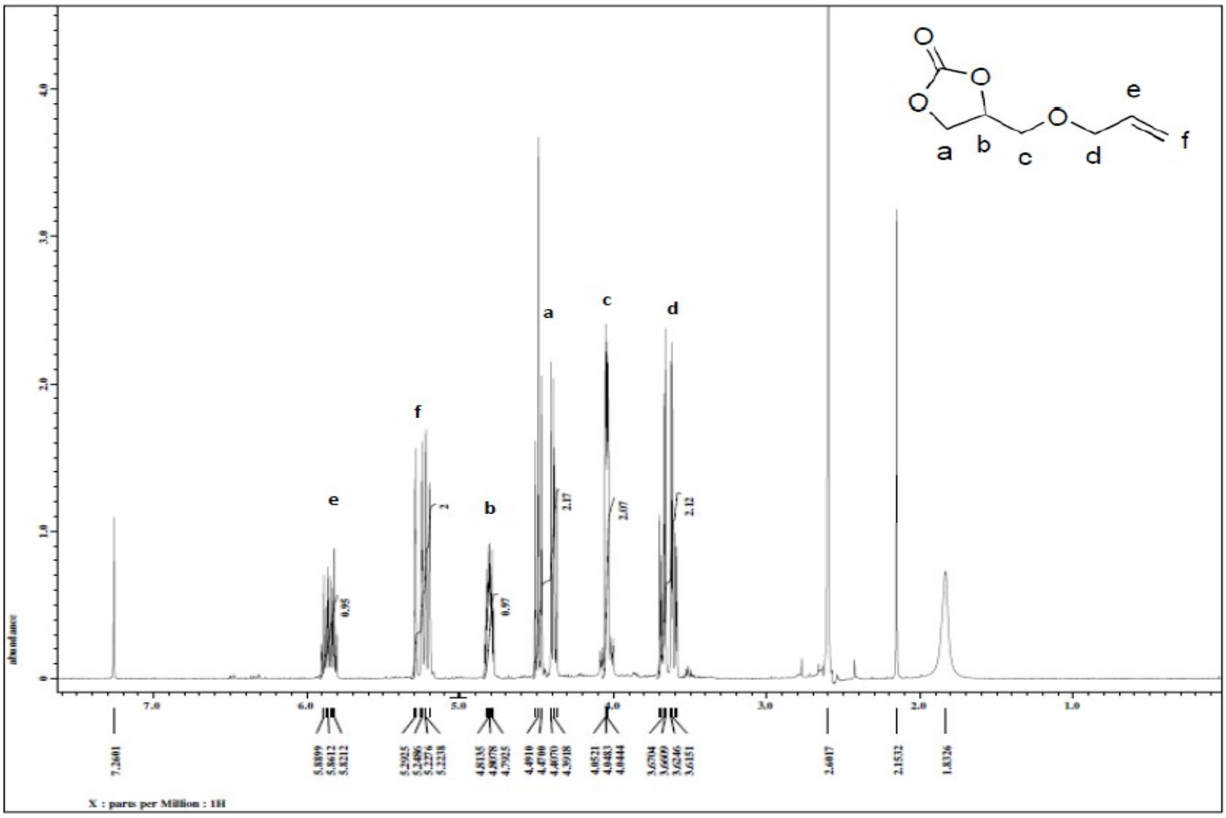

Figure. S27: ^{1}H NMR spectrum of 4-(allyloxymethyl)-1,3-dioxolan-2-one ($CDCl_3$, 400 MHz).

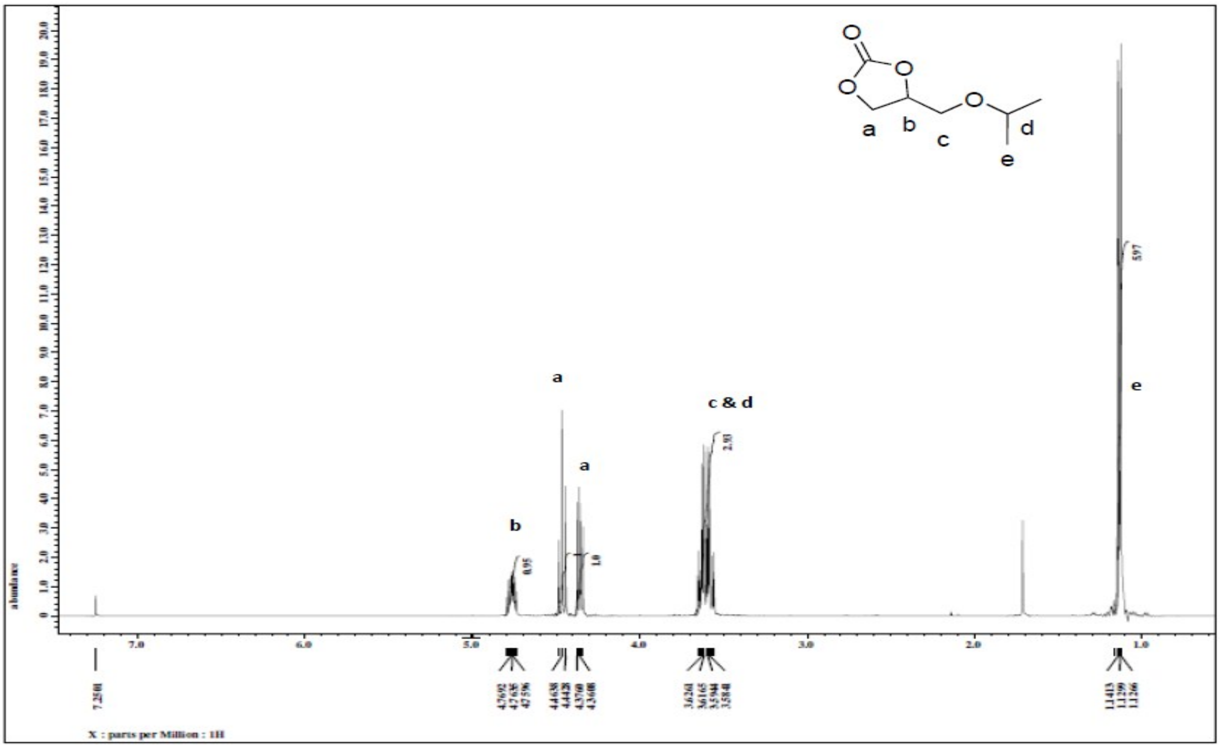

Figure. S28: ^{1}H NMR spectrum of (isopropoxymethyl)-1,3-dioxolan-2-one ($CDCl_3$, 400 MHz).

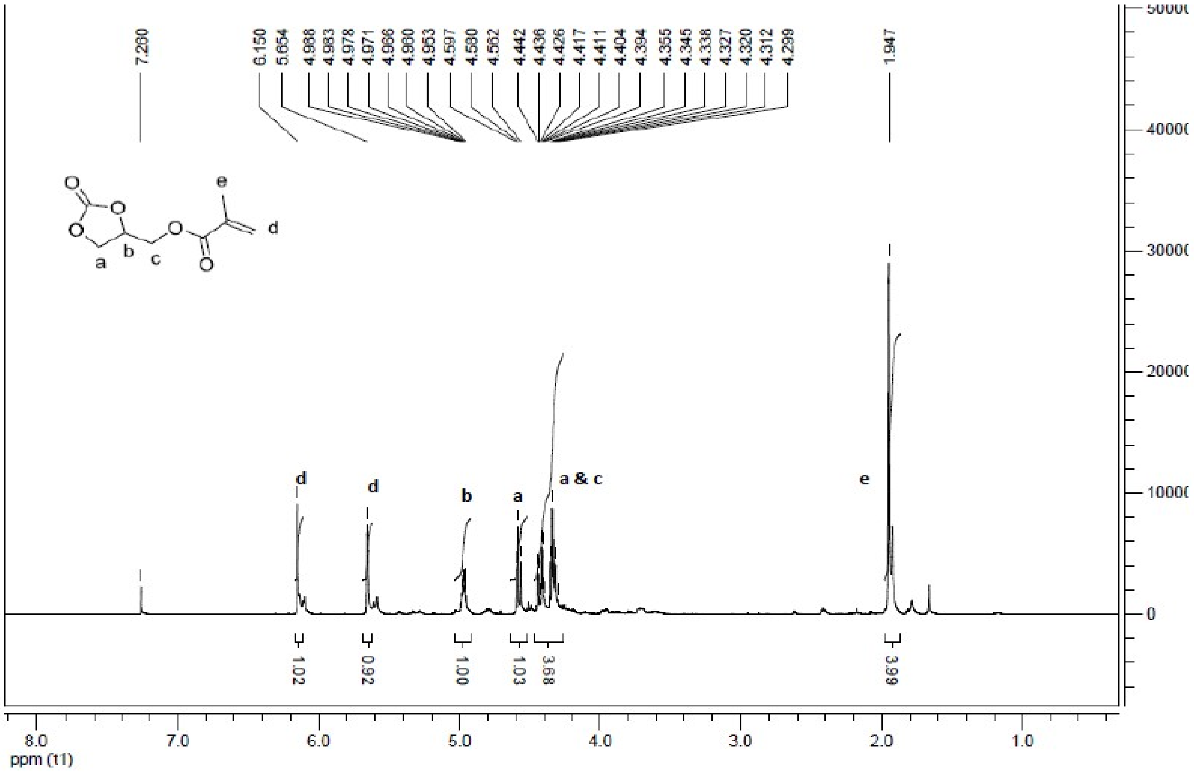

Figure. S29: ^{1}H NMR spectrum of (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate (CDCl$_3$, 500 MHz).

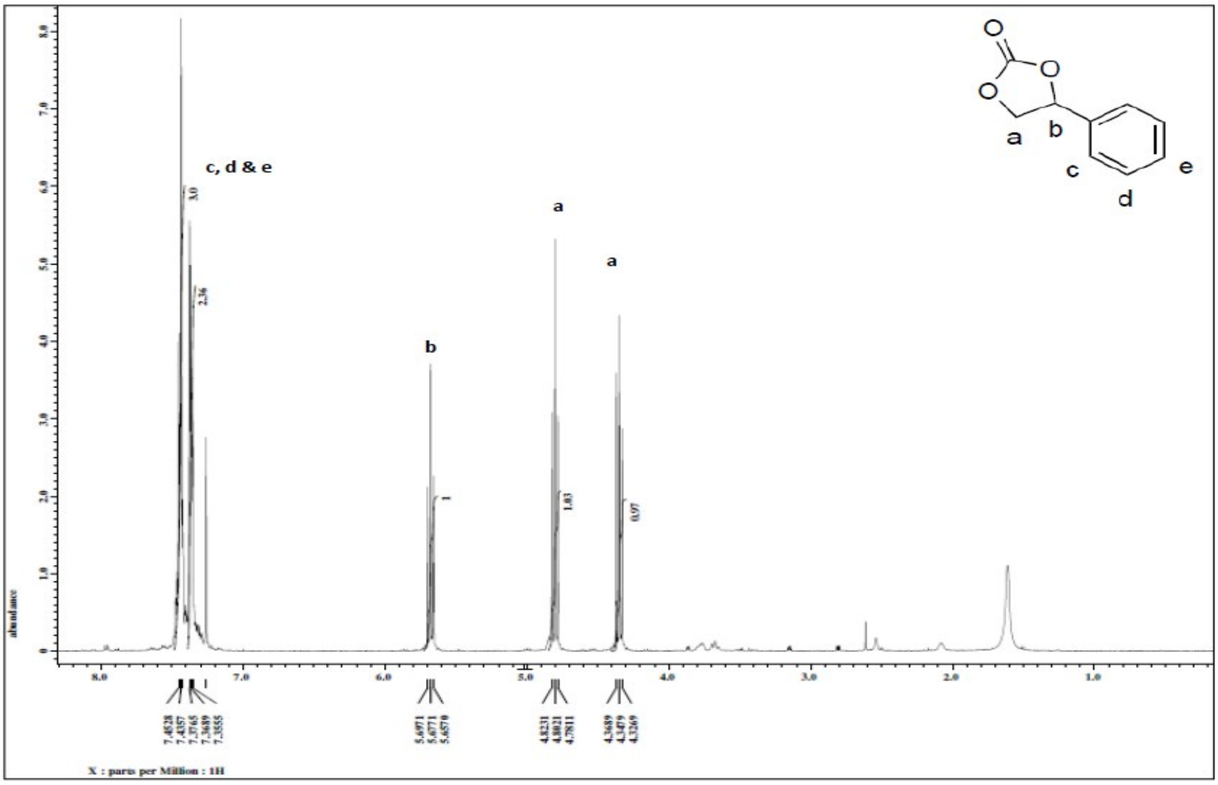

Figure. S30: ^{1}H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one (CDCl$_3$, 400 MHz).

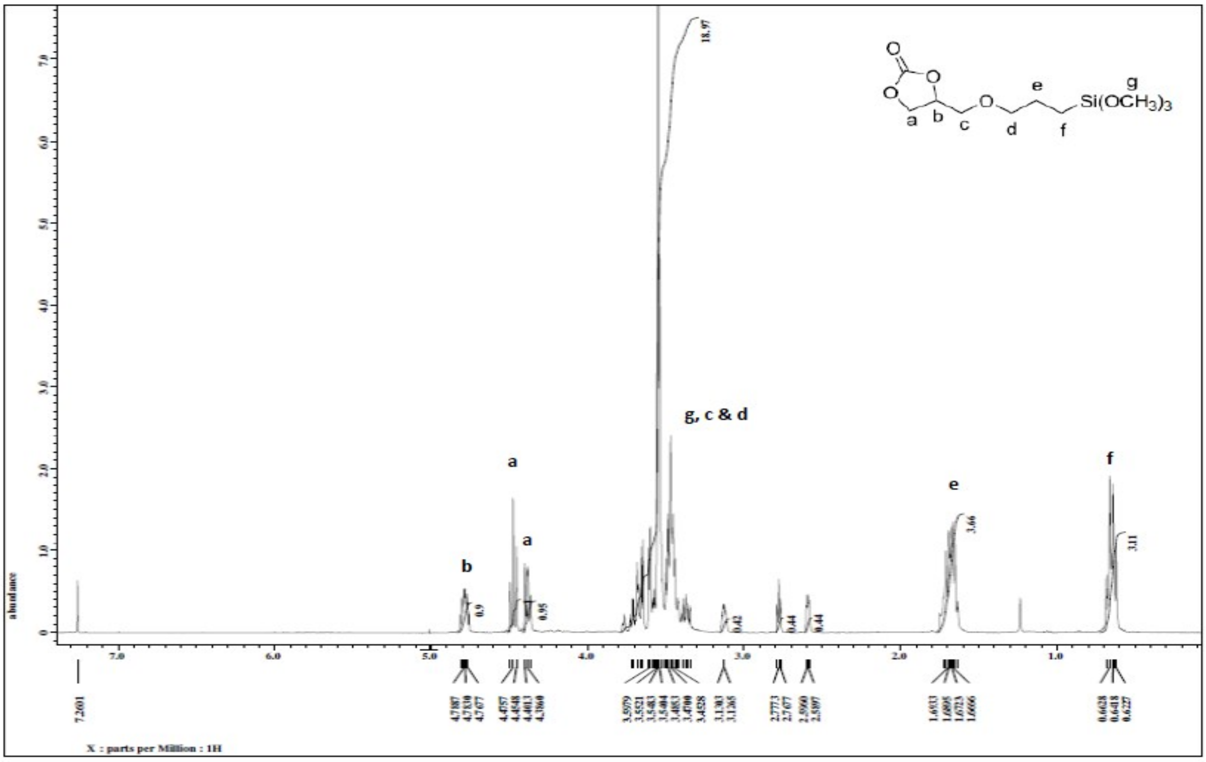

Figure. S31: ^{1}H NMR spectrum of 4-((3-(trimethoxysilyl)propoxy)methyl)-1,3-dioxolan-2-one ($CDCl_3$, 400 MHz).

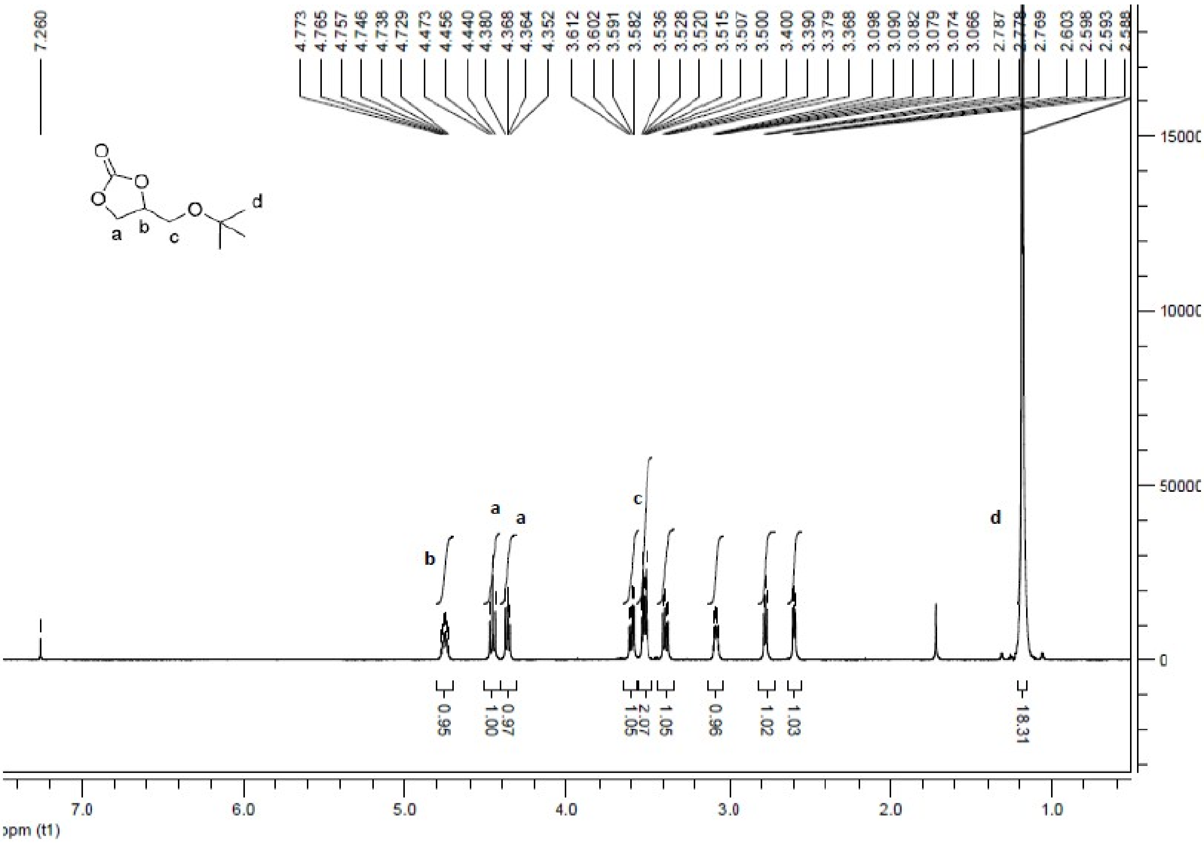

Figure. S32: ^{1}H NMR spectrum of 4-(tert-butoxymethyl)-1,3-dioxolan-2-one ($CDCl_3$, 500 MHz).

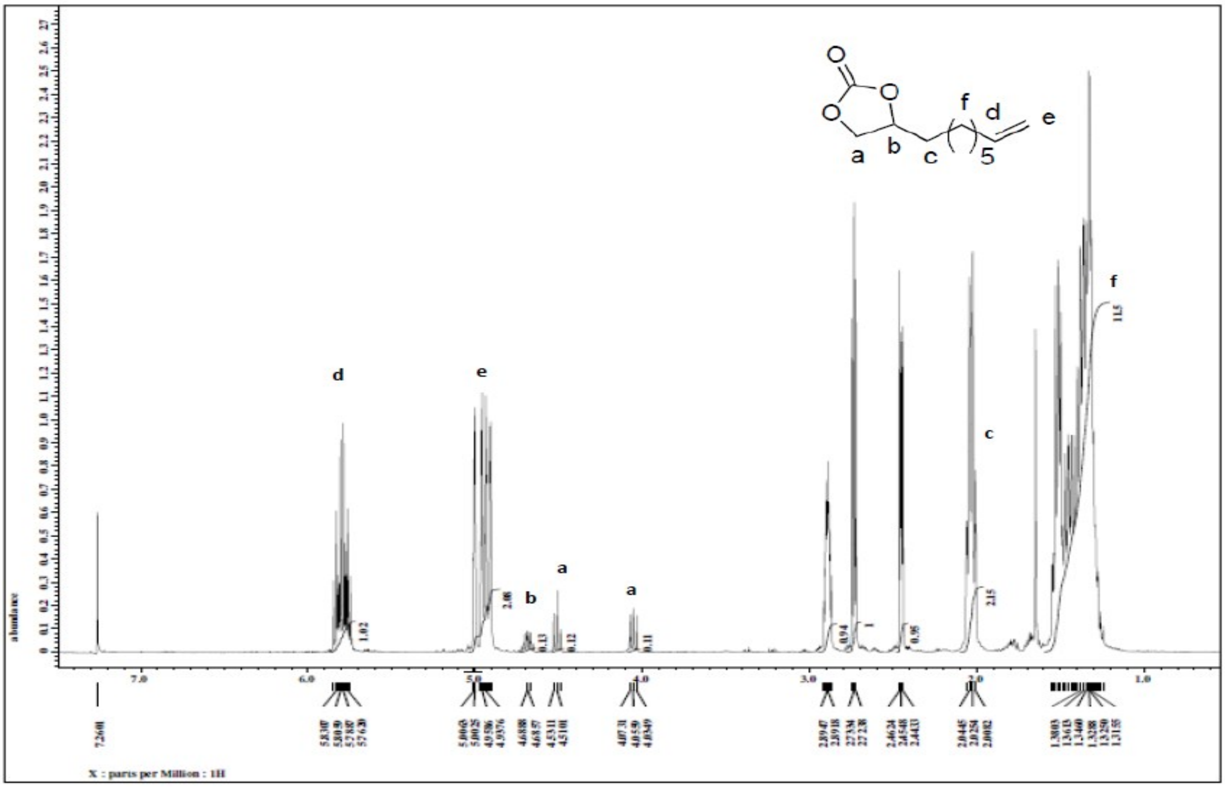

Figure. S33: ^{1}H NMR spectrum of 4-(oct-7-enyl)-1,3-dioxolan-2-one (CDCl$_3$, 400 MHz).

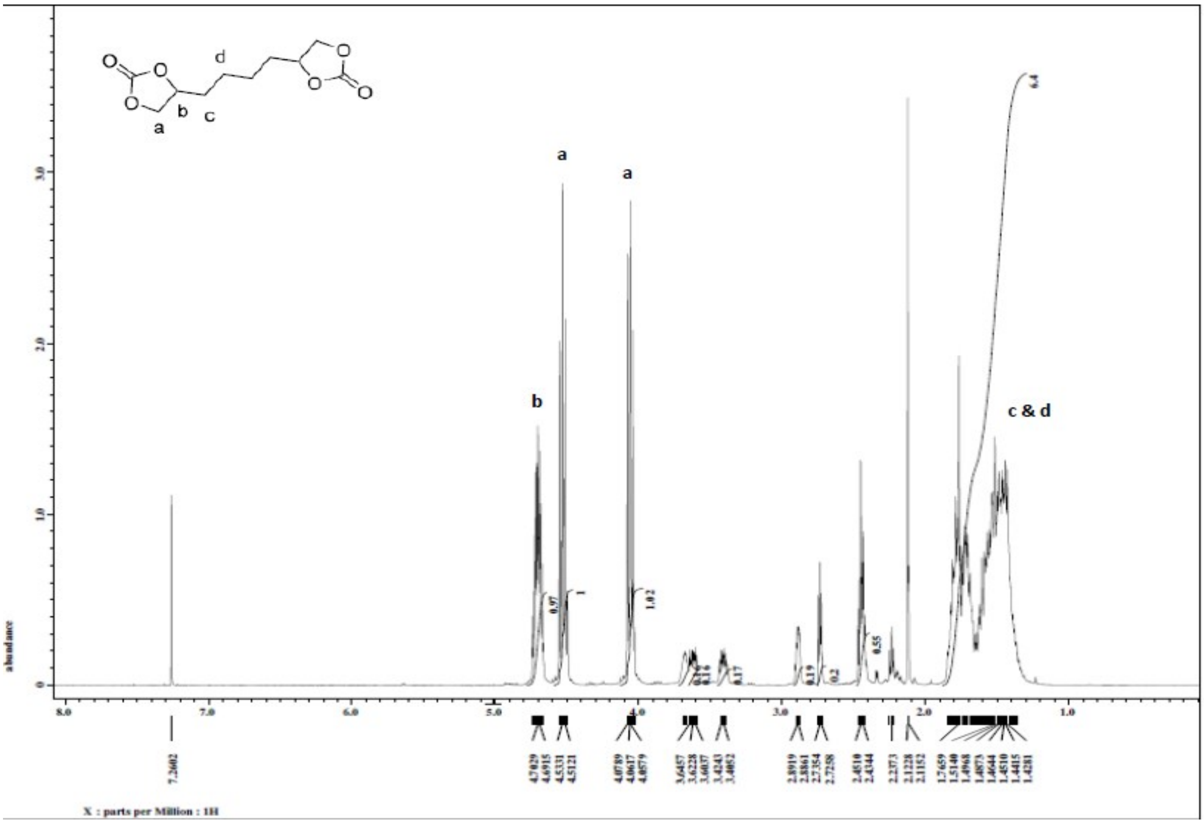

Figure. S34: ^{1}H NMR spectrum of 4,4'-(butane-1,4-diyl)bis(1,3-dioxolan-2-one) (CDCl$_3$, 400 MHz).

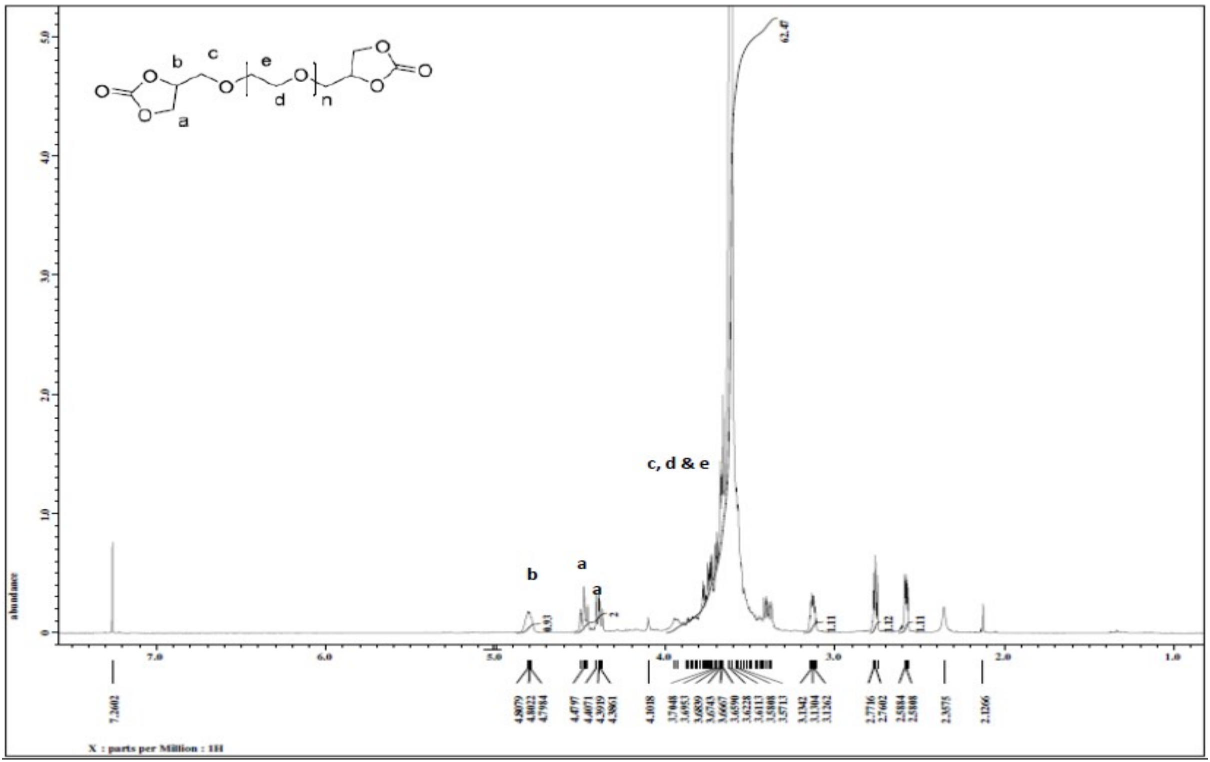

Figure. S35: ^{1}**H NMR spectrum of the cyclic carbonate of Poly(ethylene glycol) diglycidyl ether (n= 500) (CDCl$_3$, 400 MHz).**

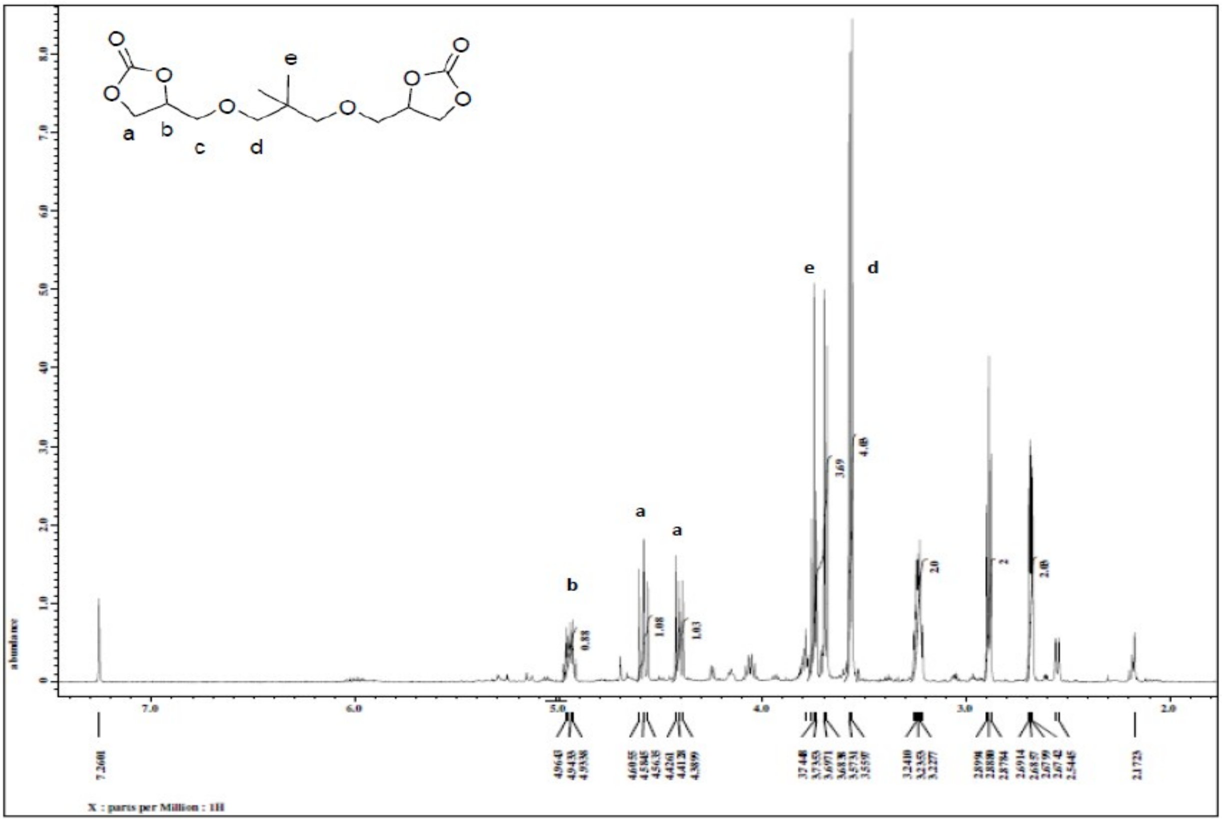

Figure. S36: ^{1}**H NMR spectrum of 4,4'-(2,2-dimethylpropane-1,3-diyl)bis(oxy)bis(methylene)bis(1,3-dioxolan-2-one) (CDCl$_3$, 400 MHz).**

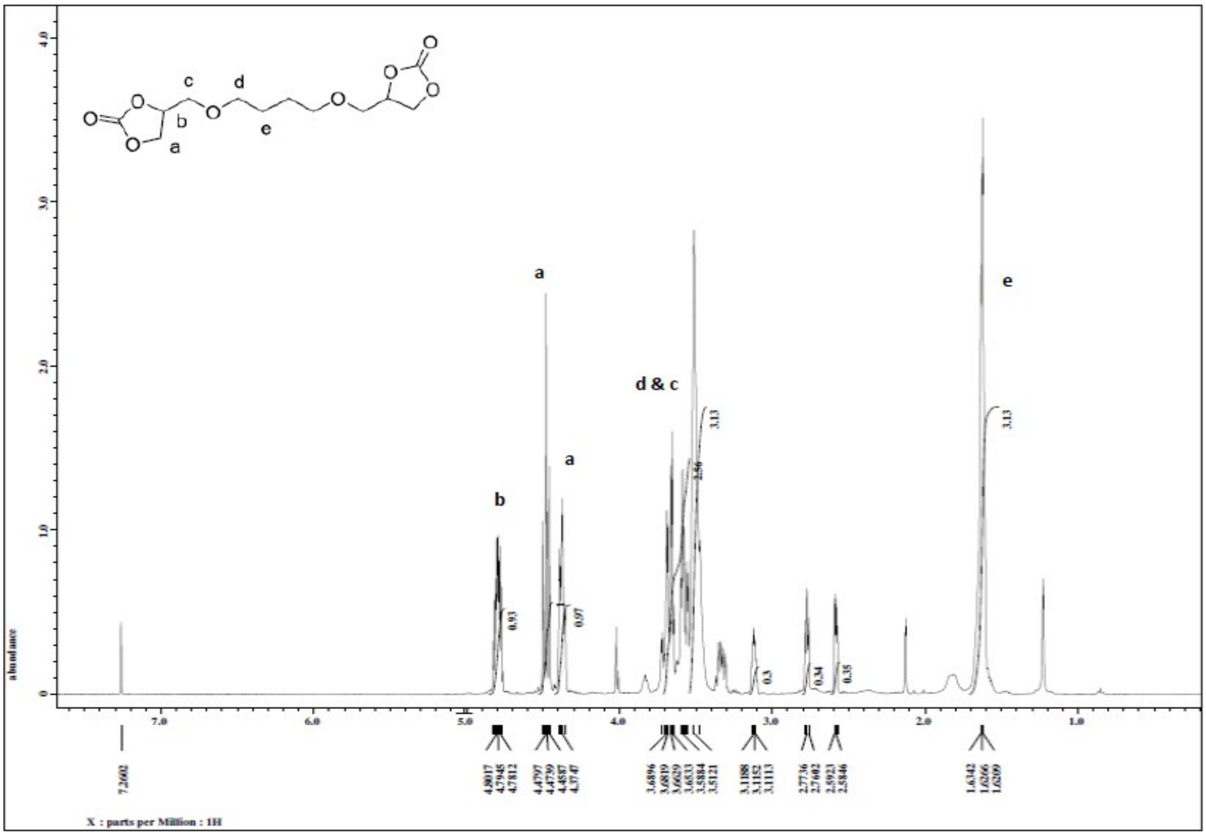

Figure. S37: ^{1}H NMR spectrum of 4,4'-(butane-1,4-diylbis(oxy))bis(methylene)bis(1,3-dioxolan-2-one) (CDCl$_3$, 400 MHz).

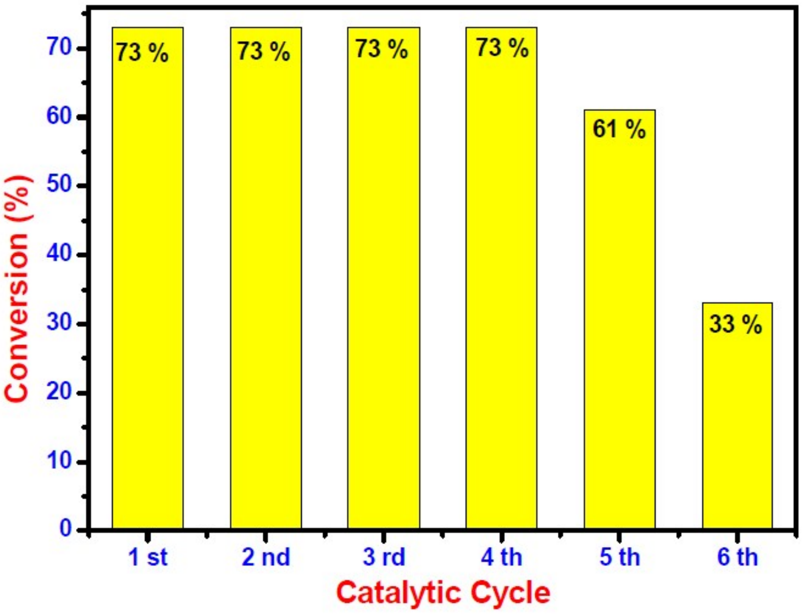

Figure.S38. Bar diagram showing the recyclability of the catalyst: Condition, substrate: epichlorohydrin 15 mmol, CO$_2$ filled balloon (1.02 atm, 99.5% pure), time 20 h and temp. 105 ^{o}C. Conversion was measured using ^{1}H NMR spectroscopy. After each cycle the catalyst was washed with ethyl acetate twice and dried inside a 60^{o}C oven and reused for next step reaction.

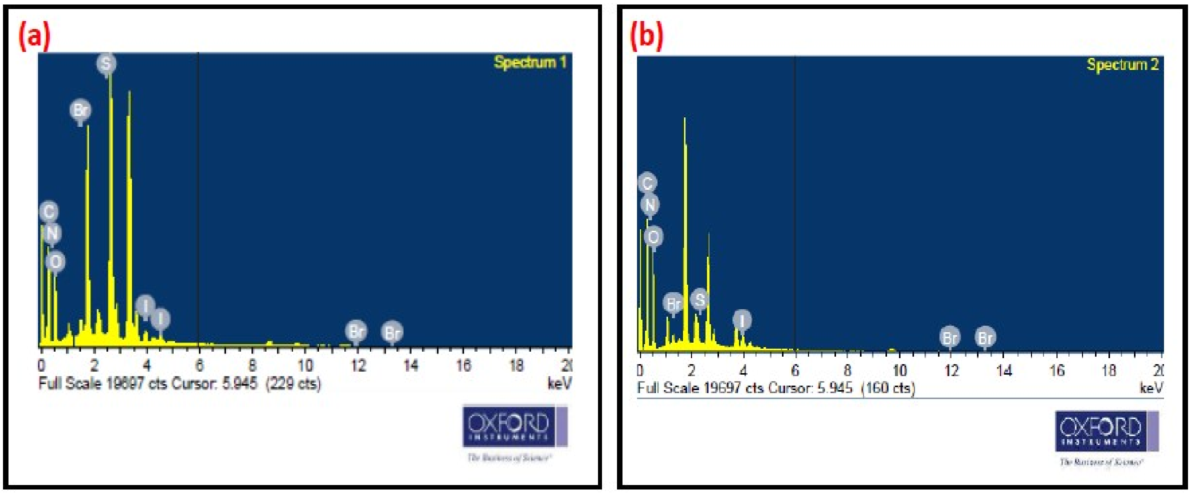

Figure.S39: EDAX analysis of the samples after 6th cycle. (a) Before water wash and (b) after water wash.

Table S2: EDAX analysis results of the sample obtained after 6th cycle (average value of five spots).

Element	**Percentage of atom before water wash**	**Percentage of atom after water wash**
Bromine	1.059%	0.206%
Iodine	0.667%	0.626%.

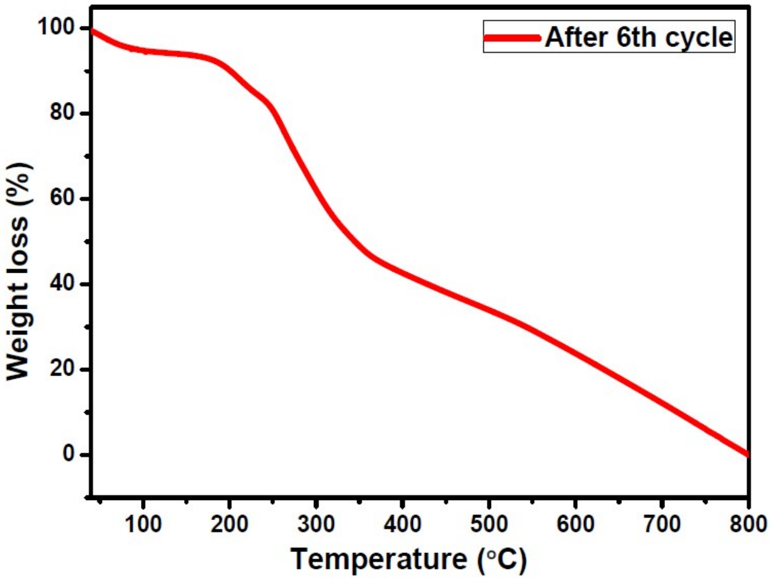

Figure. S40: TGA spectrum of the polymeric catalyst retained after the sixth cycle.

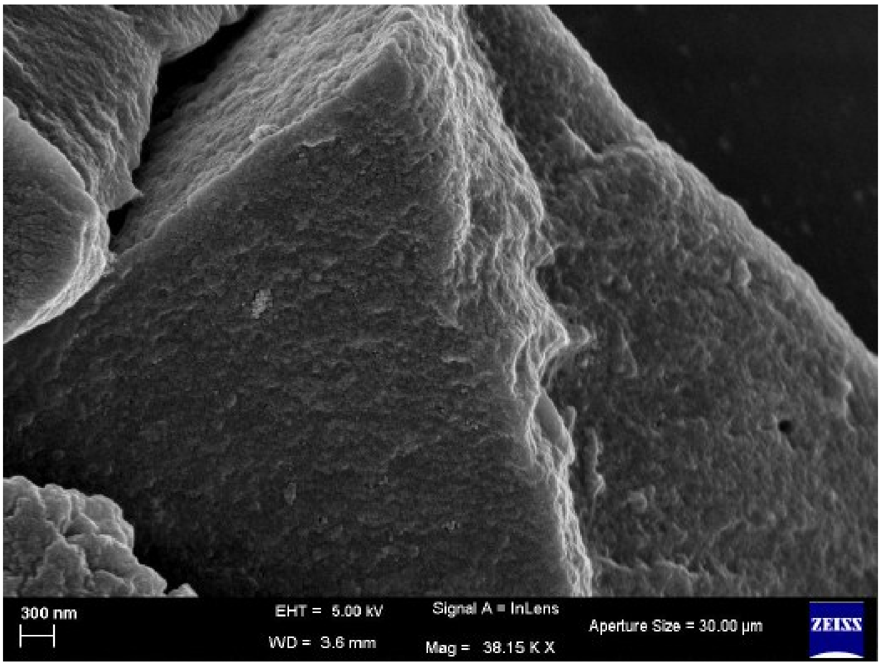

Figure. S41: SEM image of the polymeric catalyst obtained after the 6th cycle.

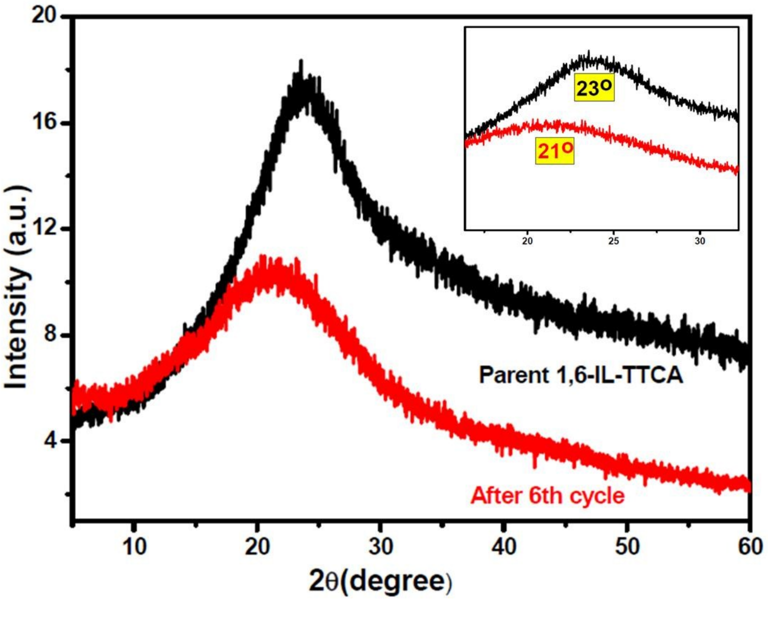

Figure. S42: Comparison of PXRD spectrum between the parent polymeric catalyst (1,6-IL-TTCA) and the same recovered after the 6th cycle.