

Electronic supplementary information

Efficient synthesis of cyclic carbonate from carbon dioxide using polymer anchored diol functionalized ionic liquids as a highly active heterogeneous catalyst

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1. Experimental Section

1.1 Materials

All chemicals were purchased from firms of repute with their highest purity available and used without further purification/pre-treatments. Polymer supported diol functionalised ionic liquid were prepared according to the procedure reported in literature with modification.²

1.2 General procedure for preparation of polymer-supported diol functionalised ionic liquids

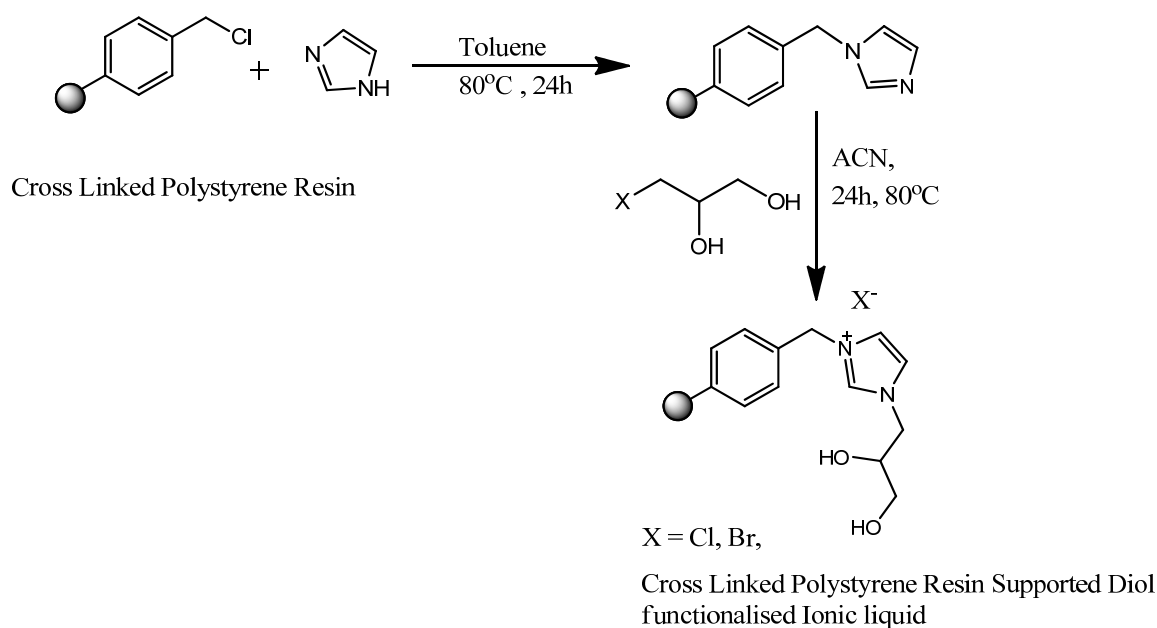
Step-1 Preparation method of imidazolium-loaded polymeric support (PS-IM)

Merrifield peptide resin (2% cross linked, 2.3 mmol Cl/g, Aldrich) (10.0 g, 53.4 mmol), imidazole (53.5 mmol) and toluene (70 mL) were added to round bottom flask (100 mL) and refluxed for time period of 24 h (Scheme 1). On completion of reaction, the mixture was cooled to room temperature (25 °C). The resulting reaction mixture was then filtered and residue obtained was washed with toluene, 10% HCl, water and methanol sequentially, followed by drying under reduced pressure to give the supported IL catalyst PS-IM (loading of IL was determined by elemental analysis) (Scheme 1). The catalyst was further characterized by FT-IR analysis to ensure the attachment of IL.

Step-2 Preparation of PS-DFILX

Secondly, polymer supported diol functionalized ionic liquids (PS-DFIL) were prepared from PS-IM and corresponding halide substituted diol (Scheme 1). To 125 mL three-necked flask equipped with a magnetic stirrer, 3-bromopropane-1, 2-diol (54 mmol), PS-IM (10 g) and acetonitrile (70 mL) were added and was then heated at 80°C for 24 h with vigorous stirring. The reaction mixture was cooled to room temperature, after completion of reaction. The upper phase was decanted carefully and the residue was washed with ethyl acetate (3 × 20 mL). Further, the solid was dried under vacuum at 80°C for 12 h to afford the polymer supported 1-(2, 3-dihydroxypropyl)-imidazolium bromide (PS-DHPIMBr) (Scheme 1).

Based on the similar procedure, the polymer supported 1-(2, 3-dihydroxyl-propyl)-imidazolium chloride (PS-DHPIMCl) was synthesized.



Scheme 1. Preparation of polymer-supported diol functionalised ionic liquids (PS-DFILX)

1.3 Characterization of polymer-supported ionic liquids

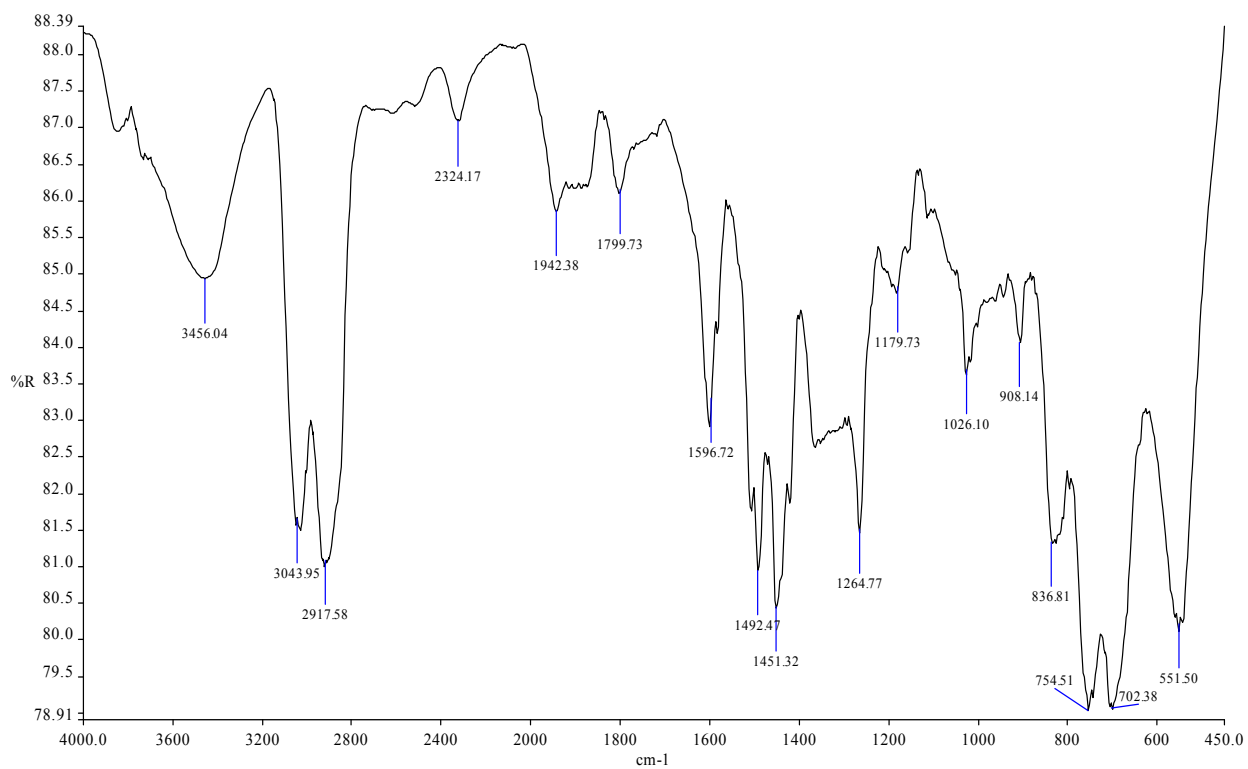
The immobilization of DHPIMBr on a polymer was examined by Fourier Transform Infrared (FT-IR) spectra (Perkin-Elmer FT-IR spectrophotometer) with anhydrous KBr as standard (Thermo Electron Co.). To measure the amount of diol functionalised ILs loaded on the polymeric support (chloromethyl polystyrene resin) CMPS was determined by elemental analysis (Thermo finnigan) PS-DHPIMBr (loading, 3.2 mmol/g), PS-DHEIMCl (loading, 2.8 mmol/g). Solid-state NMR for ¹³C nuclei was carried out. Thermo gravimetric analysis (TGA) of prepared catalyst was carried out using TGA-SDT (Q600 V8.2 Build 100) in a nitrogen atmosphere between 25°C and 600°C at a heating rate 5°C/min.

1.4 Typical procedure for the synthesis of cyclic carbonate from epoxide and CO₂

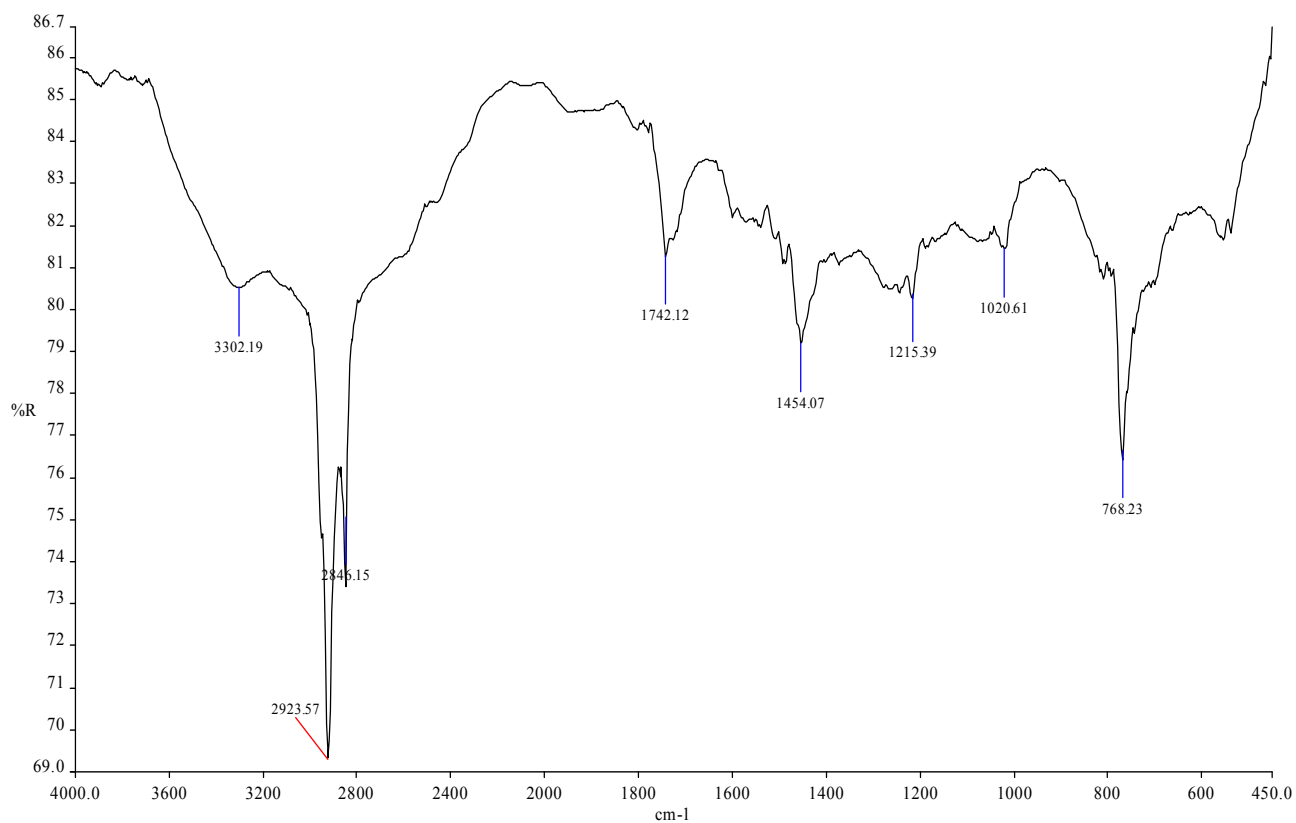
The cyclic carbonate was synthesized by coupling reaction of CO₂ with epoxide in presence of PS-DHPIMBr as catalyst. All the reactions were carried out in a 100 mL stainless-steel autoclave with stirring speed of 650 rpm and equipped with automatic temperature control system. In a typical reaction procedure, 0.2 g of catalyst was introduced into a reactor containing propylene oxide (25 mmol) at room temperature and then pressurized to 5 MPa of CO₂ pressure and heated to a specified temperature. After completion of the reaction, the reactor was cooled in an ice-cold water bath and then CO₂ was released slowly. Product was separated from the reaction mixture by simple filtration and analysed by GC analysis (Perkin Elmer, Clarus 400) (BP-10 GC column, 30 m × 0.32 mm ID, film thickness 0.25 mm). The products were confirmed by ¹H spectra recorded on NMR spectrometer using TMS as internal standard and by GC-MS (Shimadzu QP 2010) analysis.

2. FTIR analysis of PS-DHPIMX

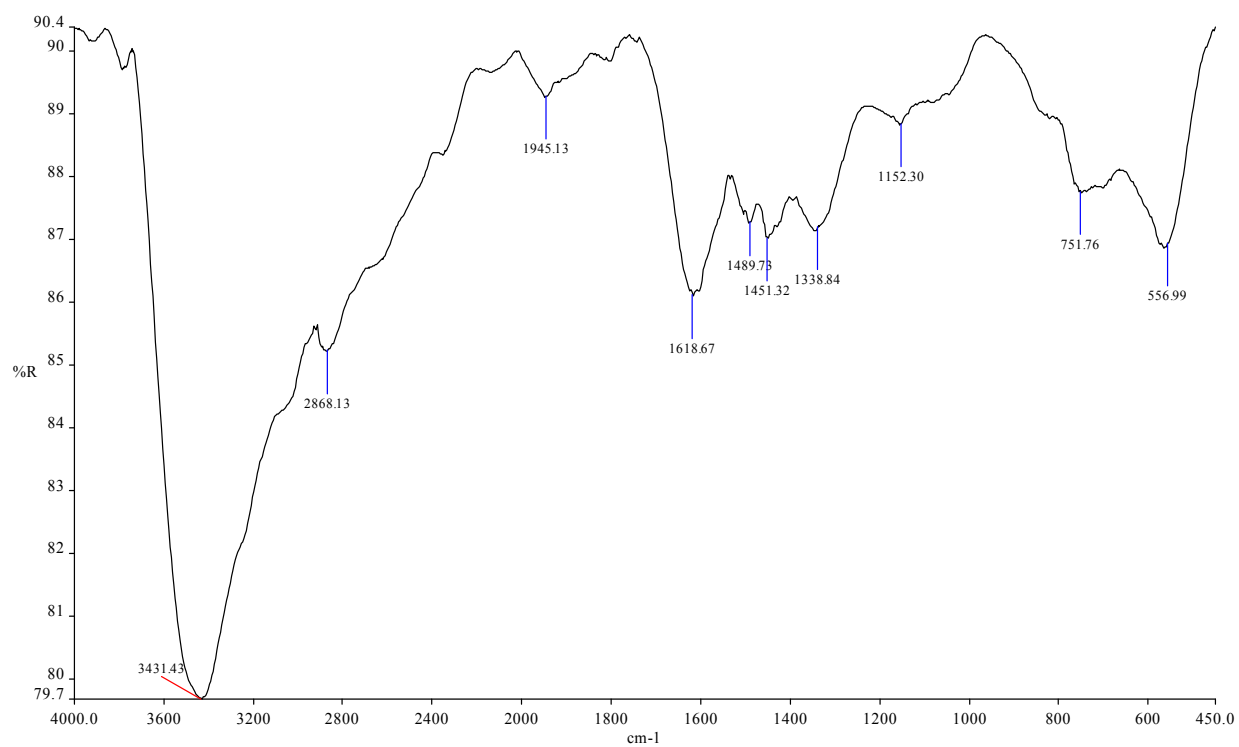
2.1 FTIR of PS-CH₂Cl (Figure S1.1a)



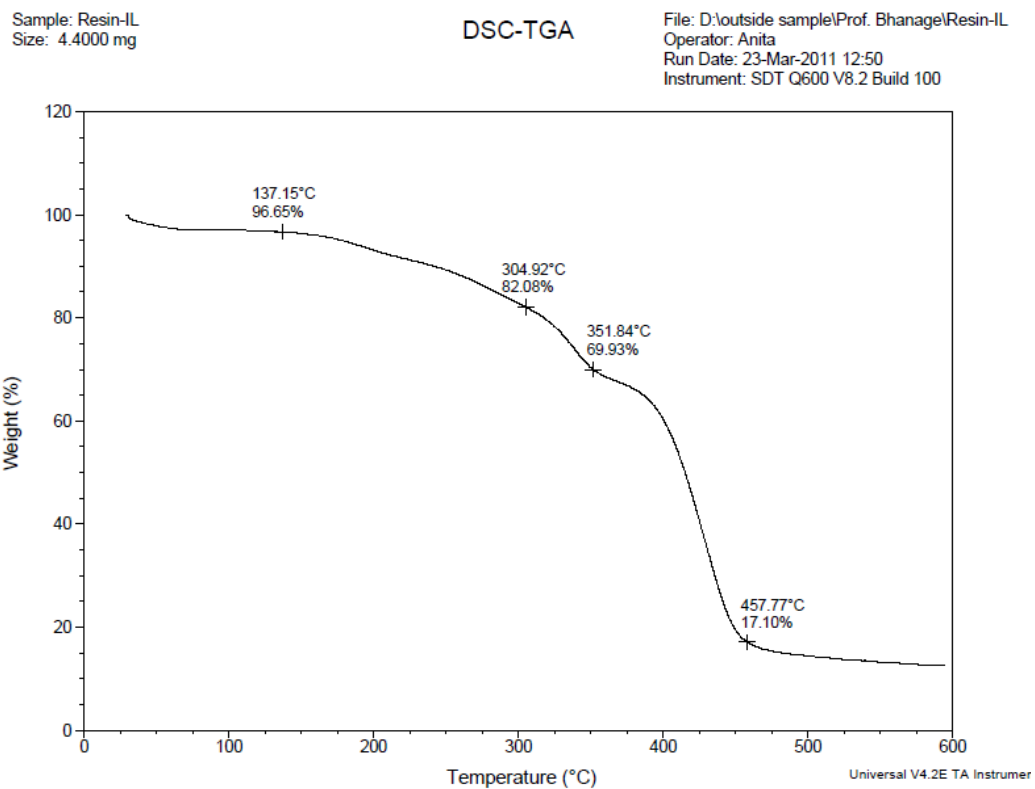
2.2 FTIR of PS-DHPIMBr (Figure S1, 1b)



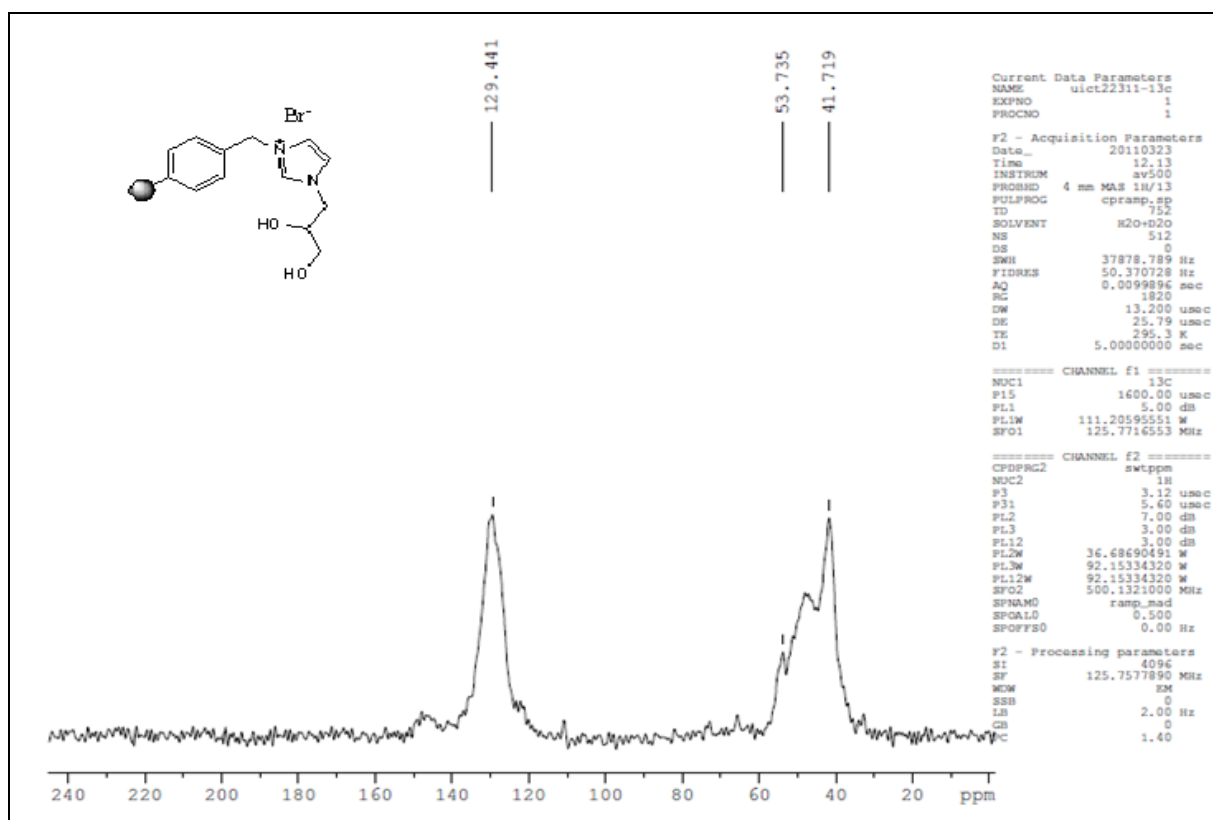
2.3 FTIR of PS-DHPIMCl (Figure S1, 1c)



3. DSC -TGA of PS-DHPIMBr (Figure S2)

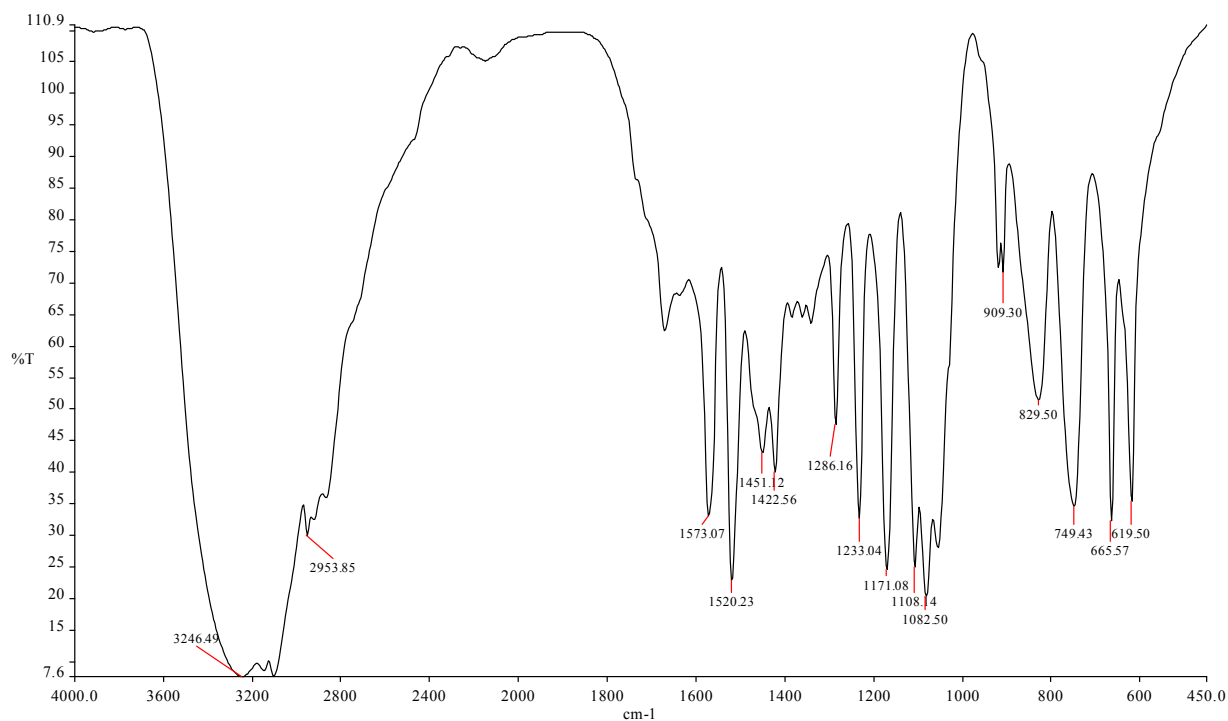


4. Solid state ^{13}C NMR of PS-DHPIMBr catalyst. (Figure S3)



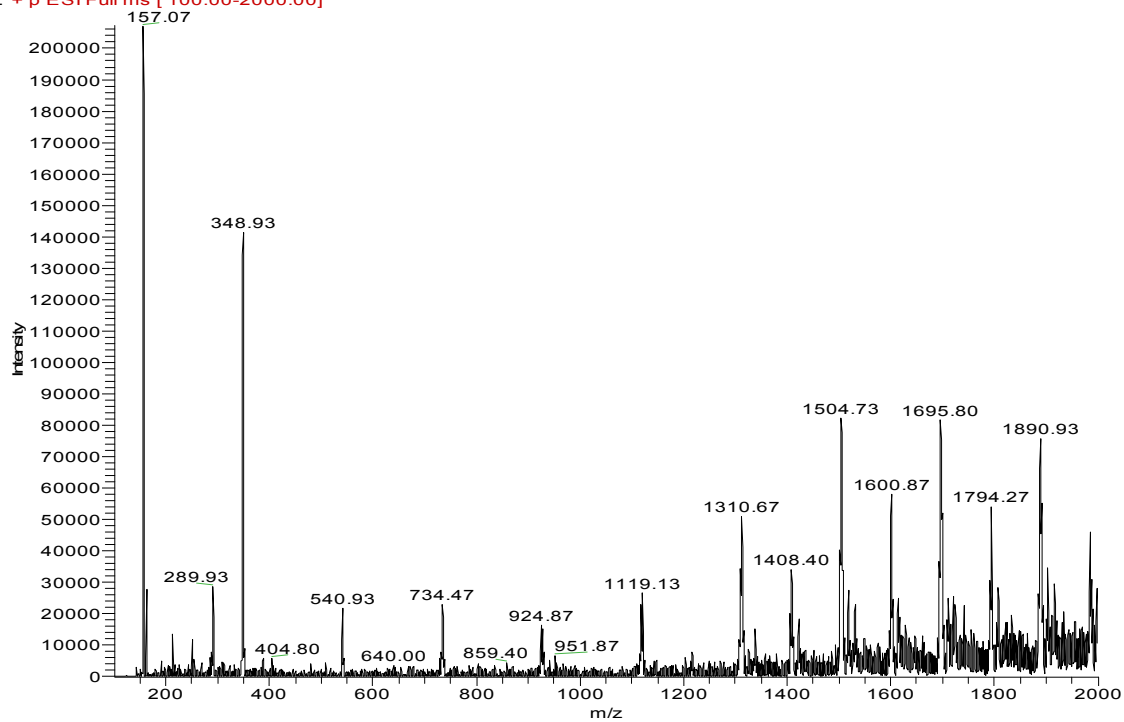
5. Characterization of DHPMIMBr (homogeneous diol functionalised ionic liquid)

5.1 FTIR of DHPMIMBr (Figure S4, 4a)

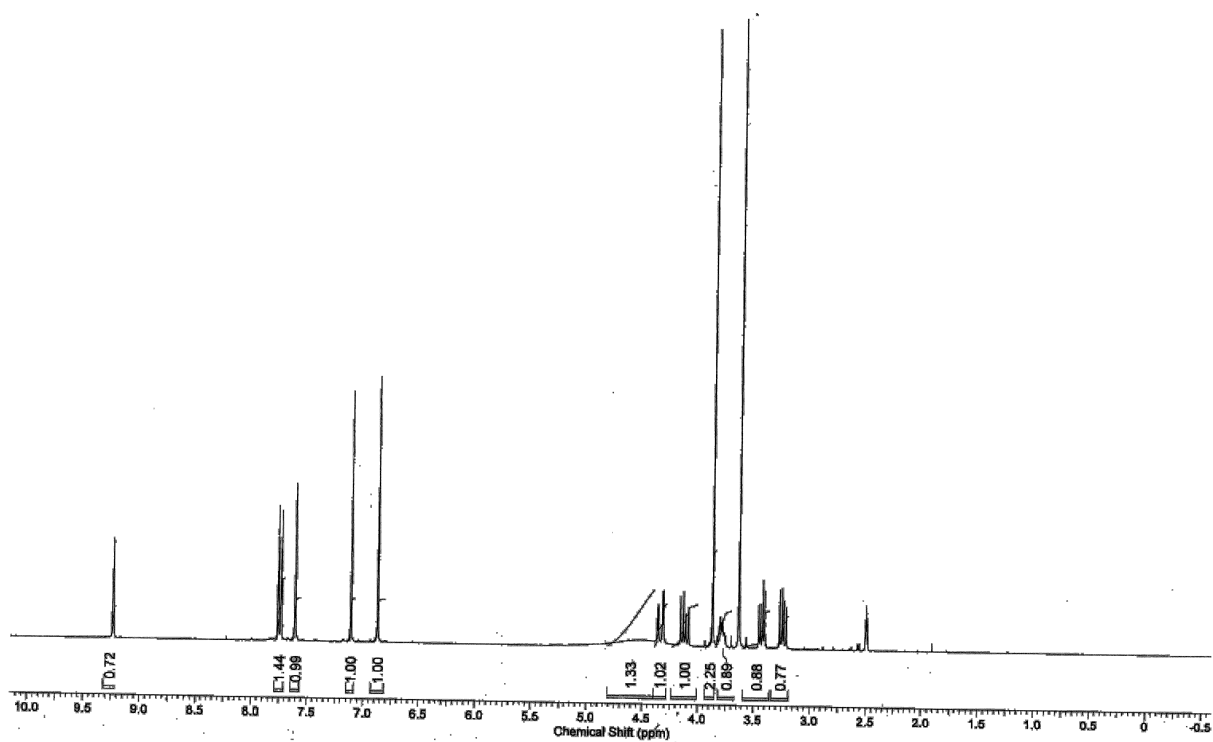


5.2 GC-MS of DHPMIMBr (Figure S4, 4b)

MS_192_170311 #5 RT: 0.16 AV: 1 NL: 2.07E5
F: +p ESI Full ms [100.00-2000.00]



5.3 ^1H NMR spectra of DHPMIMBr (Figure S4, 4c)



6. Reference

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2. J. Sun, W. Cheng, W. Fan, Y. Wang, Z. Meng, and S. Zhang, *Catal. Today*, 2009, **148**, 361
3. H. Zhou, Y. M. Wang, W. Z. Zhang, J. Qu and X. B. Lu, *Green Chem.*, 2011, **13**, 644.