

ESI

## **Cellulose Dissolution with Polar Ionic Liquids Under Mild Conditions: Required Factors for Anions**

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### **EXPERIMENTAL SECTION**

#### **MATERIALS AND INSTRUMENTS**

THF was purified using solvent dispensing system before use. *N*-Ethylimidazole was purchased from Tokyo Chemical Ind. Co., Ltd, and dried over KOH and distilled before use. Trimethylphosphate, dimethyl methylphosphonate and dimethyl phosphite were purchased from Tokyo Chemical Ind. Co., Ltd, and were dried over K<sub>2</sub>CO<sub>3</sub> and CaCl<sub>2</sub> and distilled before use. Other commercially available solvents were used as received.

The measurements of <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were carried out on a JEOL ECX-400. Electrospray ionization-time-of-flight-mass (ESI-TOF-MAS) spectrometry was made on JEOL JMS-T100LC. Elemental analysis was performed by Elementar vario EL III. Ion chromatography was performed with DIONEX ICS-3000 equipped with a DIONEX IonPac CS17 column (for cation) and a SHODEX SI-90 4E column (for anion). The amount of water was

confirmed by Karl Fischer coulometric titration (Kyoto Electronics MKC-510N). The differential scanning calorimetry (DSC) measurements were carried out using DSC-6200 (SEIKO Instruments) at a scanning rate for both heating and cooling of  $1^{\circ}\text{Cmin}^{-1}$  in the temperature range  $-100^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ . The thermogravimetric analysis (TGA) was made on SEIKO TG/DTA 220 instrument with heating rate of  $10^{\circ}\text{Cmin}^{-1}$  from  $25^{\circ}\text{C}$  to  $400^{\circ}\text{C}$  under nitrogen. Visible spectrum was measured using SHIMAZU UV 2450. The viscosity measurement was carried out with Brookfield DV-I + viscometer from  $25^{\circ}\text{C}$  to  $95^{\circ}\text{C}$  at interval of  $5^{\circ}\text{C}$  under nitrogen gas.

## NMR SPECTRA OF IONIC LIQUIDS

### i) IL **3**; *N*-Ethyl-*N*'-methylimidazolium dimethylphosphate ([C2mim][[(MeO)<sub>2</sub>PO<sub>2</sub>]])

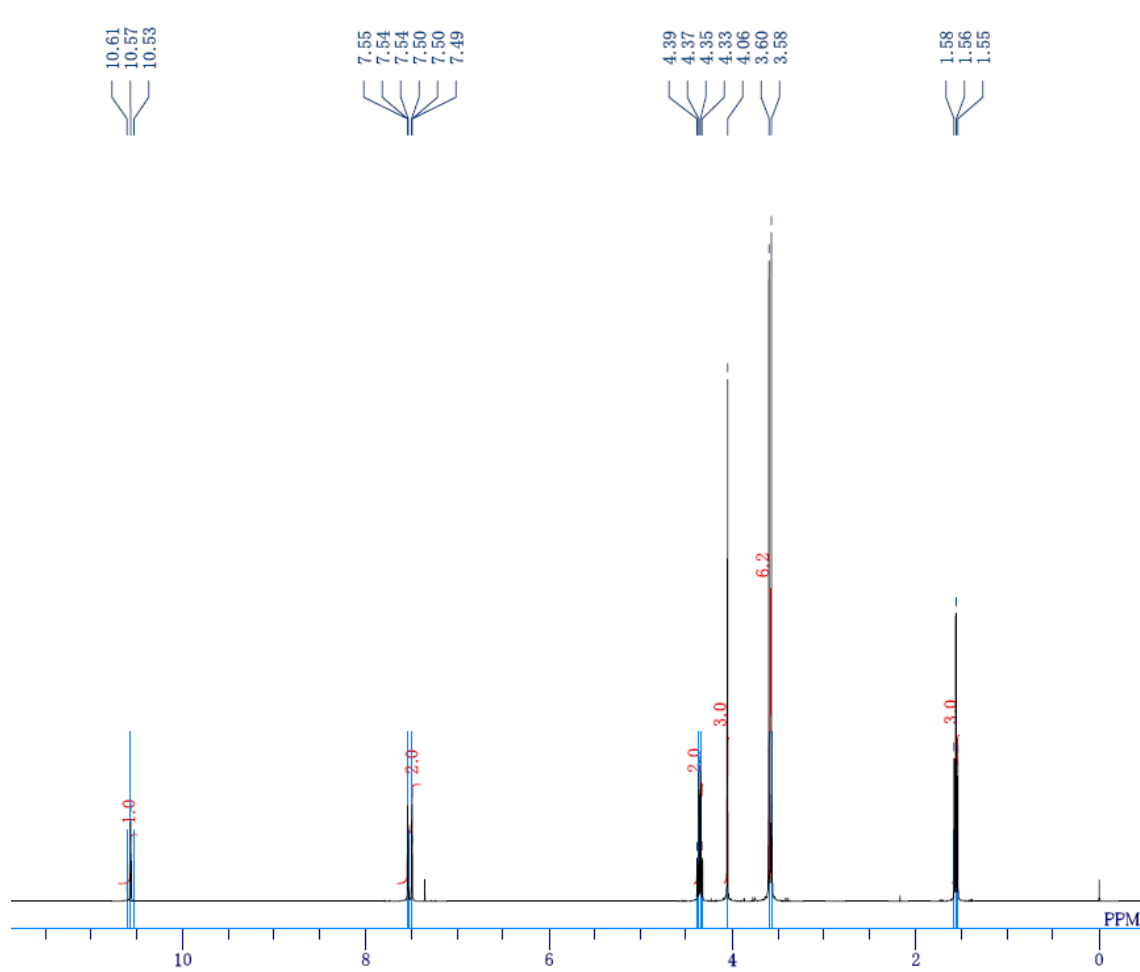
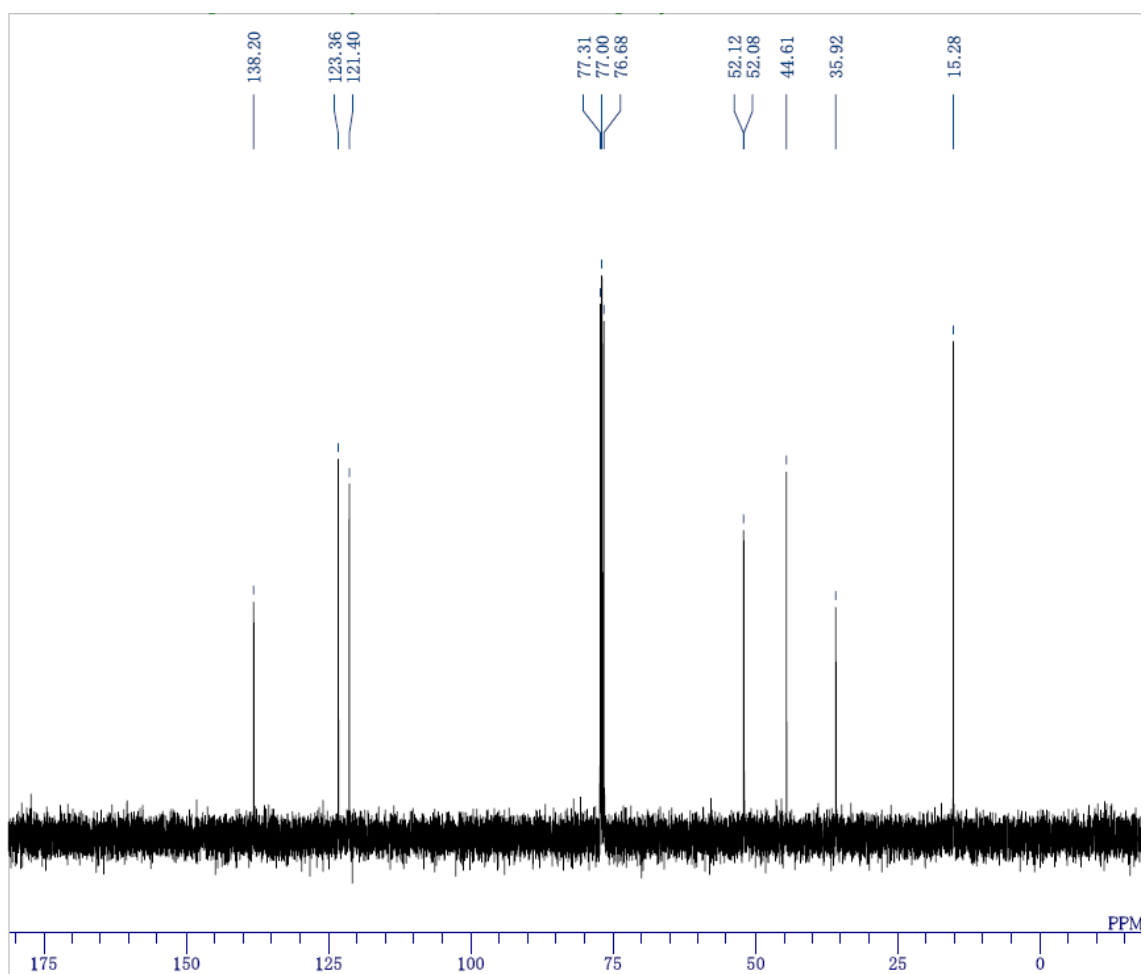


Figure S1. <sup>1</sup>H-NMR spectrum of [C2mim][[(MeO)<sub>2</sub>PO<sub>2</sub>]]



**Figure S2.**  $^{13}\text{C}$ -NMR spectrum of [C2mim][(MeO)<sub>2</sub>PO<sub>2</sub>]

ii) IL 2; *N*-Ethyl-*N*'-methylimidazolium methyl methylphosphonate  
([C2mim][(MeO)(Me)PO<sub>2</sub>])

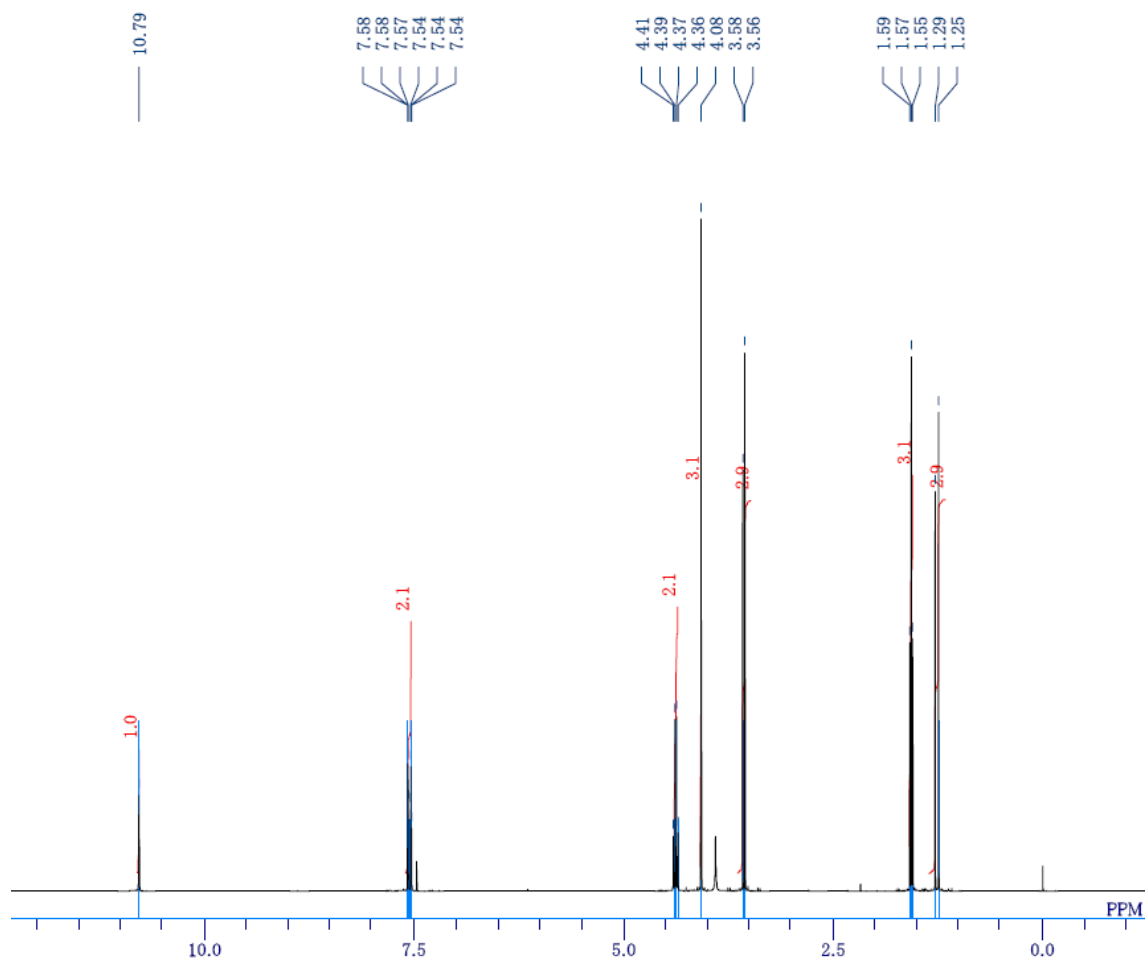
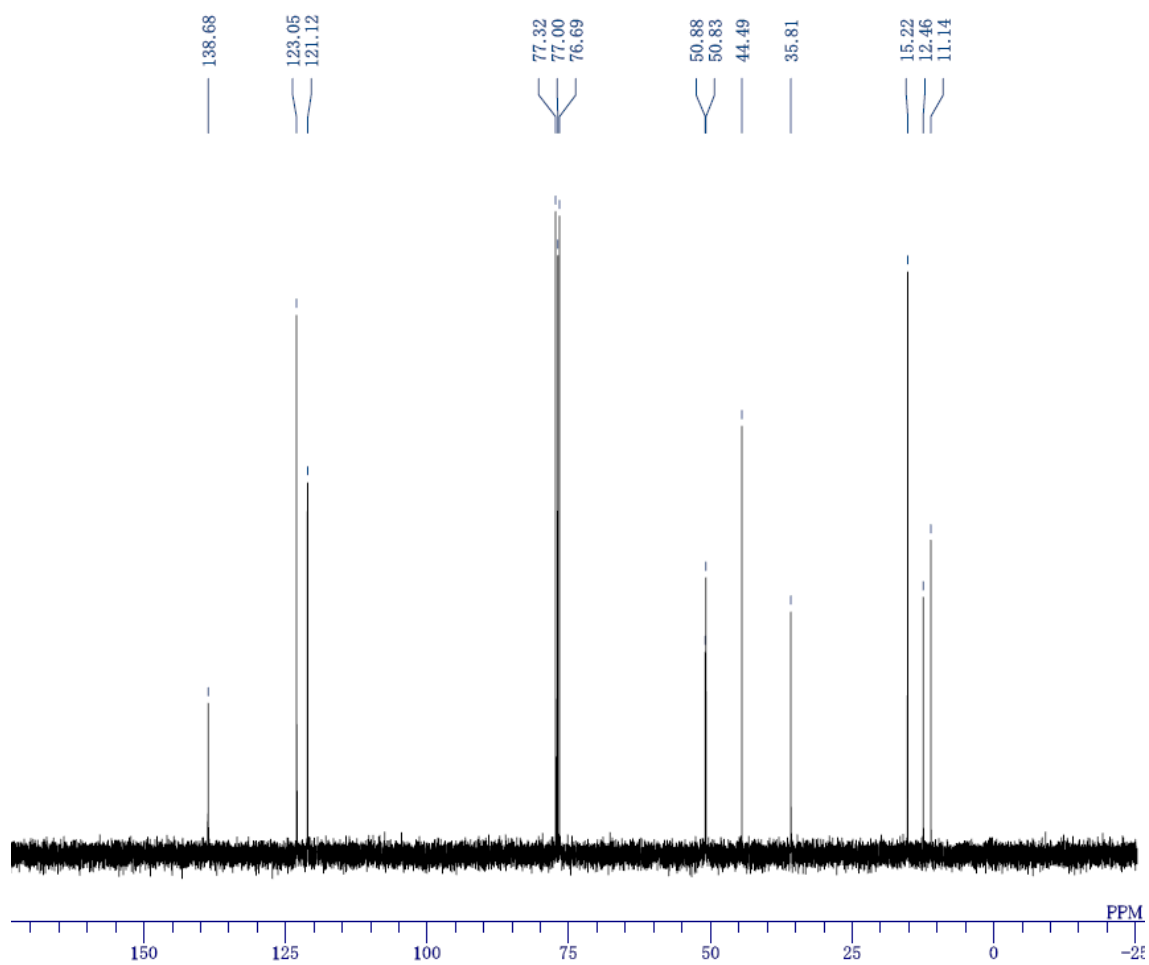


Figure S3. <sup>1</sup>H-NMR spectrum of [C2mim][(MeO)(Me)PO<sub>2</sub>]



**Figure S4.**  $^{13}\text{C}$ -NMR spectrum of [C2mim][(MeO)(Me)PO<sub>2</sub>]

iii) IL 1: *N*-Ethyl-*N*'-methylimidazolium methylphosphonate ([C2mim][[(MeO)(H)PO<sub>2</sub>])

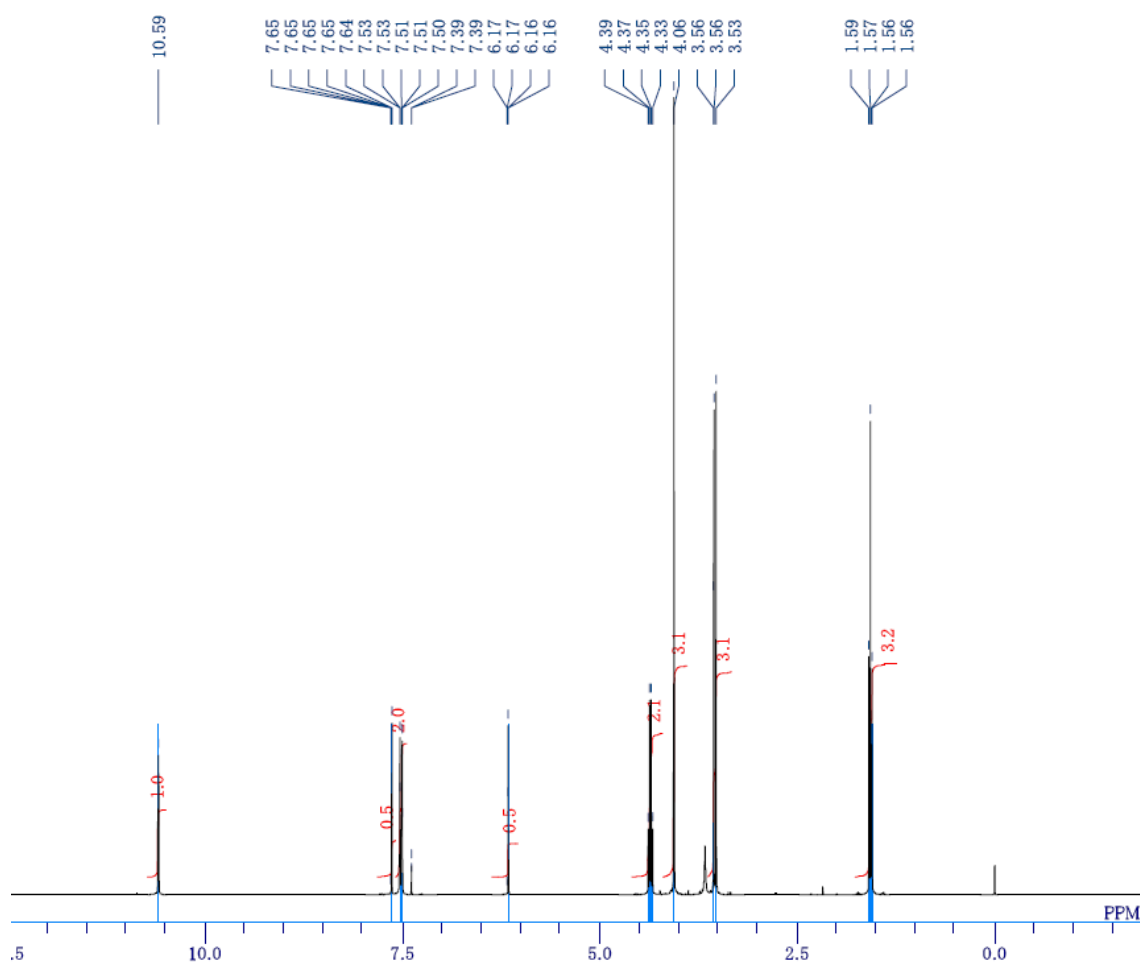
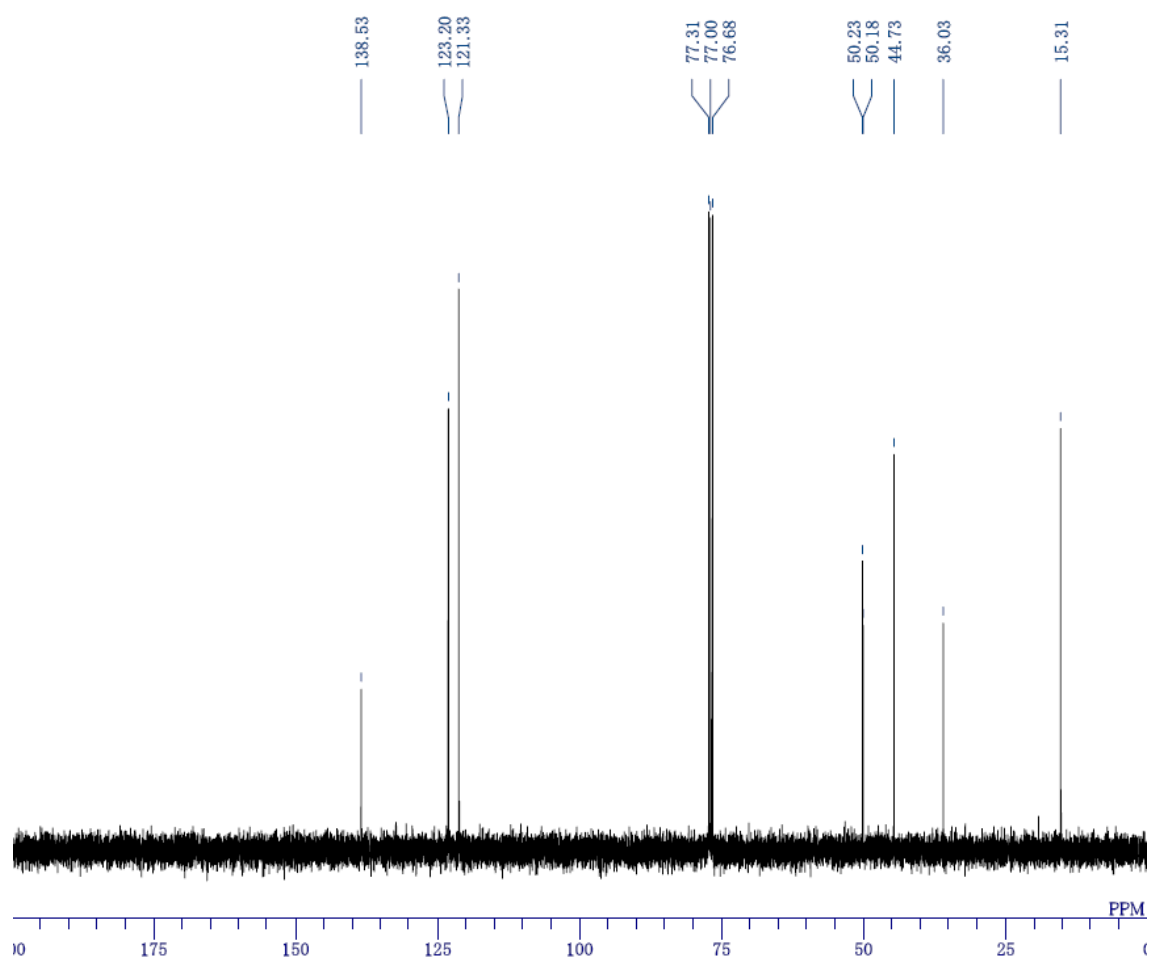


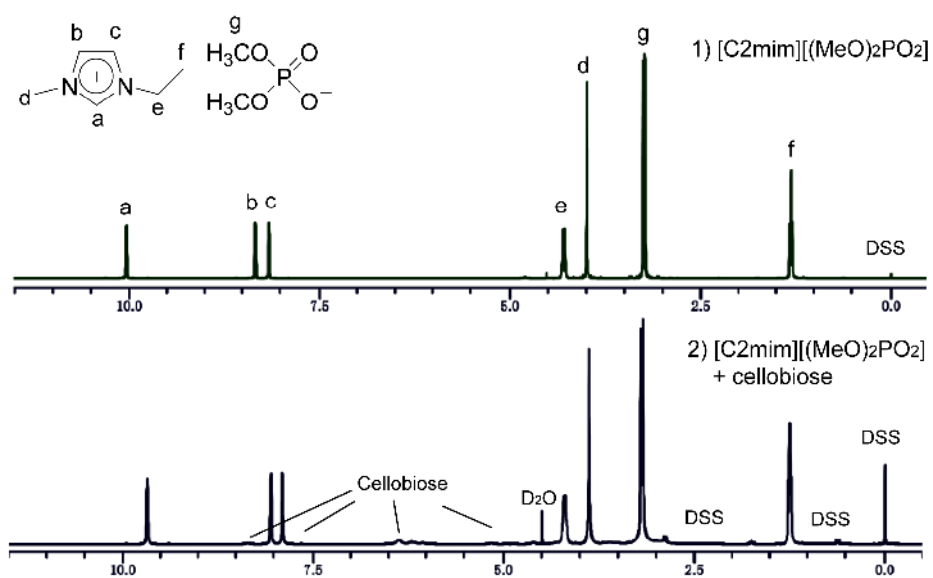
Figure S5. <sup>1</sup>H-NMR spectrum of [C2mim][[(MeO)(H)PO<sub>2</sub>]



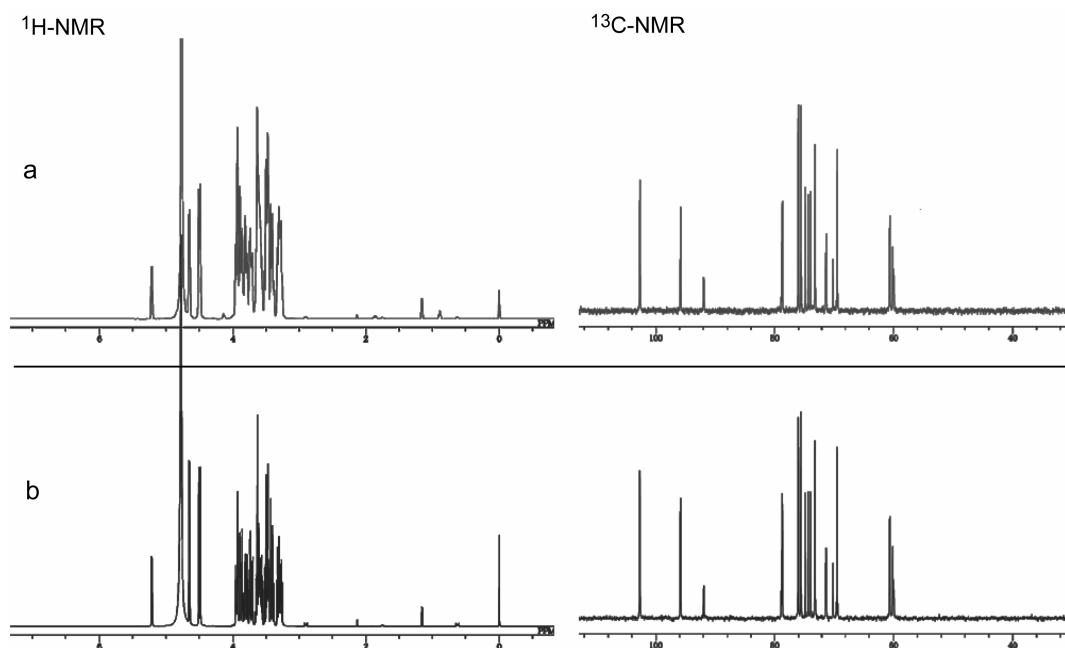
**Figure S6.**  $^{13}\text{C}$ -NMR spectrum of [C2mim][(MeO)(H)PO<sub>2</sub>]



**$^1\text{H}$  AND  $^{13}\text{C}$ -NMR SPECTRA OF IONIC LIQUID (NEAT AND CELLOBIOSE SOLUTION ) AND CELLOBIOSE**



**Figure S8.**  $^1\text{H}$ -NMR spectra of [C2mim][(MeO)<sub>2</sub>PO<sub>2</sub>](1) and [C2mim][(MeO)<sub>2</sub>PO<sub>2</sub>] with cellobiose (2)



**Figure S9.**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra of cellobiose; a) original cellobiose, b) regenerated cellobiose