Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

Sustainable, Highly Selective, and Metal-free Thermal Depolymerization of Poly-(3-hydroxybutyrate) to Crotonic acid in Recoverable Ionic Liquids

Piotr Jablonski, Dariush Nikjoo, Johan Warna, Knut Irgum, Jyri-Pekka Mikkola, Santosh Govind Khokarale

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Experimental Procedure. Synthesis of [DMEIM][AcO] and [BMIM][AcO] ionic liquids.

The synthesis of [DMEIM][AcO] IL was carried out in a two-step reaction. Initially, a mixture of 1, 2-dimethyl imidazole (4 g, 0.042 mol) and ethyl iodide (13.1 g, 0.084 mol) in 75 ml dichloromethane was prepared in a 250 ml of round bottom flask and refluxed at 60 °C for 6 h in a water bath. A biphasic system was formed in the reaction mixture, with a less dense dark brown liquid on top of the dichloromethane phase. The solvent was removed using a rotation evaporator, after which the remaining viscous brown colored liquid was mixed with 75 ml ethyl acetate. A pale yellow colored solid then precipitated and settled slowly at the bottom of the reaction flask. The ethyl acetate was removed by decantation and the obtained solid was further washed three times with 20 ml portions of ethyl acetate. The recovered solid material was dissolved in a minimum amount of methanol (≈ 5 ml) and recrystallized by addition of ethyl acetate, followed by additional washes with ethyl acetate. The obtained pale yellow colored solid was dried *in vacuo* and its purity confirmed by NMR. The pure form of the solid, *i.e.*, 1, 2-dimethyl-3-ethyl iodide was converted to the acetate analogue using anion exchange. To this end, 15 g of Amberlite IRN-78 ion exchange resin in the OH^- form (DuPont, Wilmington, DE, USA) was suspended in deionized water and loaded in a 25 ml glass column. The resin in the column was further washed with deionized water until neutral pH. One hundred milliliters of 1 M aqueous sodium acetate was flushed slowly through the column at ≈ 2 drops/second, whereby a change in the eluate pH from 14 to 8 was monitored. The column was further washed thoroughly with 100 ml of deionized water to remove excess of sodium acetate solution. An aqueous solution prepared from 2.5 g of the 1,2-dimethyl-3-ethyl iodide in 25 ml deionized water was eluted slowly (≈ 2 drops/second) through the ion exchange column into a 100 ml round bottom flask, followed by 50 ml of deionized water collected in the same flask. The water was thereafter separated from the recovered aqueous solution by rotation evaporation and the pale brown colored residual liquid was analyzed by NMR to identify its purity.

The synthesis of [BMIM][AcO] IL was carried using an anion exchange technique similar to that applied for the synthesis of [DMEIM][AcO] IL. In this case commercially available [BMIM][Cl] IL was used for the synthesis of [BMIM][AcO] IL and the viscous and pale yellow colored liquid obtained after the anion exchange process was analyzed by NMR to determine its purity (S1).

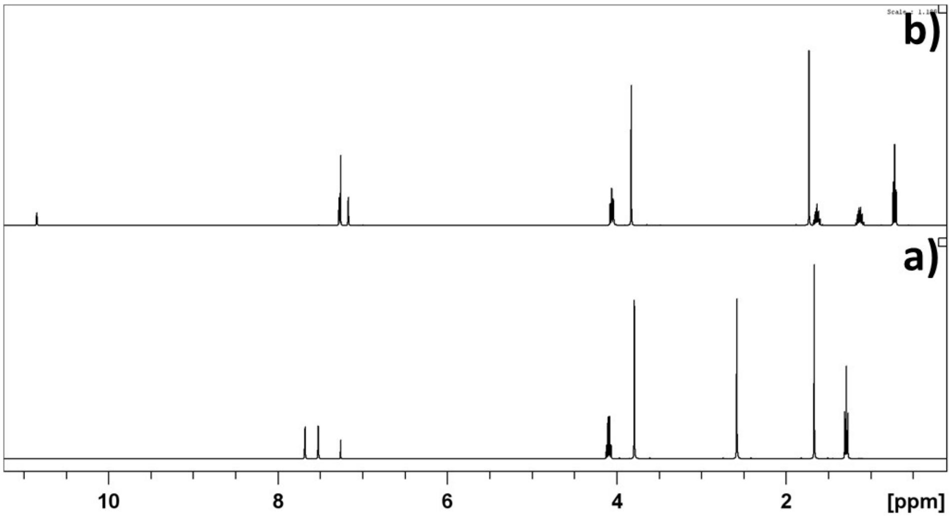

Figure S1. ^{1}H NMR spectra for a) [DMEIM][AcO] and b) [BMIM][AcO] ILs

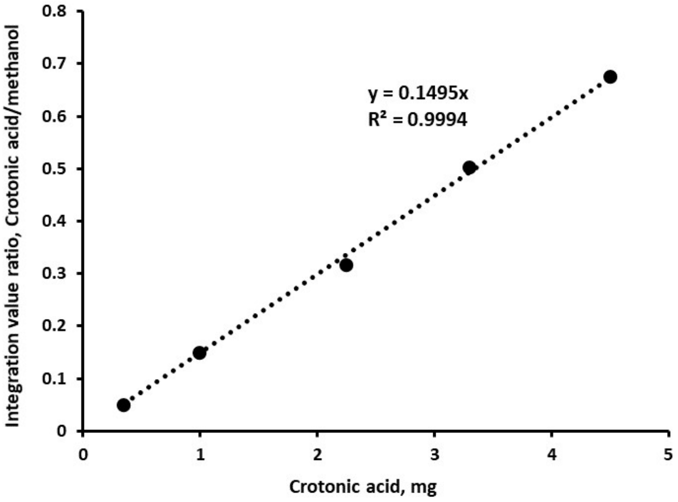

Figure S2. Calibration curve for the quantification of crotonic acid.

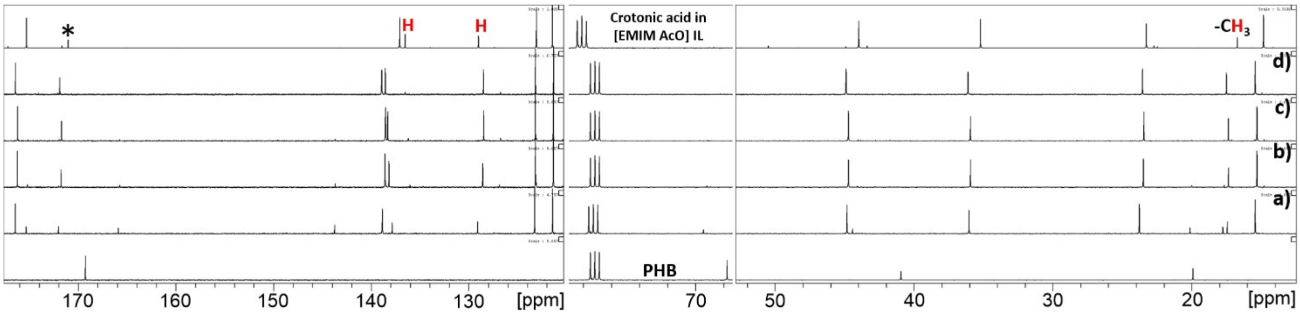

Figure S3. ^{13}C NMR spectra for the conversion of PHB to crotonic acid in [EMIM][AcO] IL at 120 °C for a) 30 min, b) 90 min, c) 3 h and d) 5 h, PHB = 20 wt.% in IL.

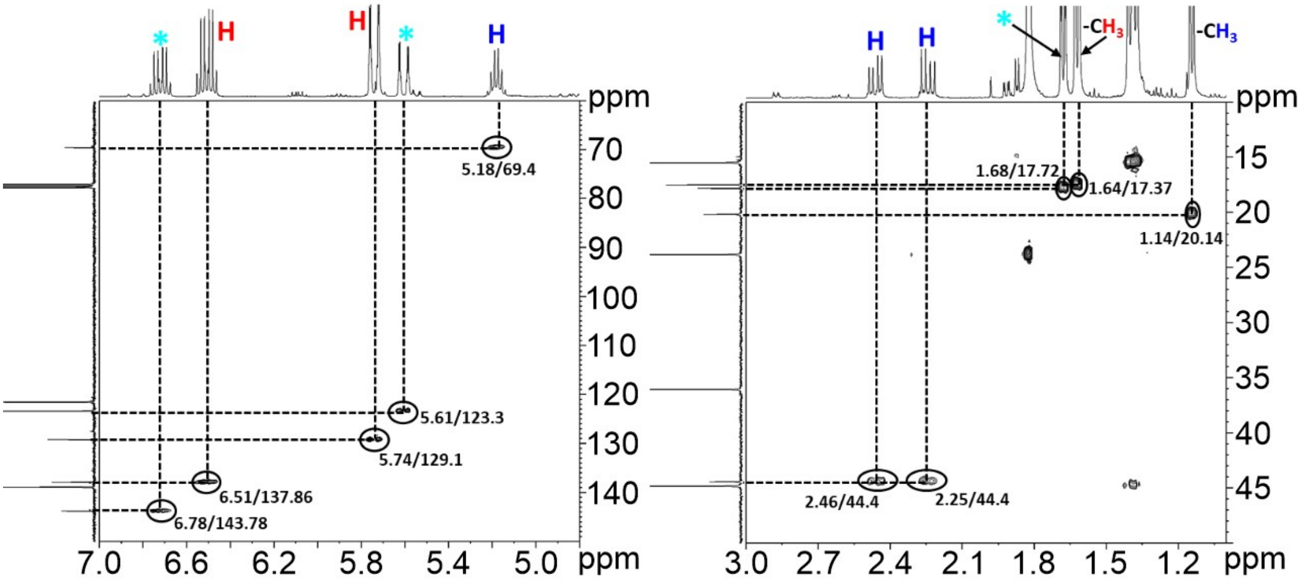

Figure S4. ^{1}H-^{13}C HSQC spectra for reaction mixture comprised of 20 wt.% of PHB in [EMIM][AcO] IL. Temperature = 120 °C, time= 30 min, PHB = 0.4 g, IL= 1.60 g.

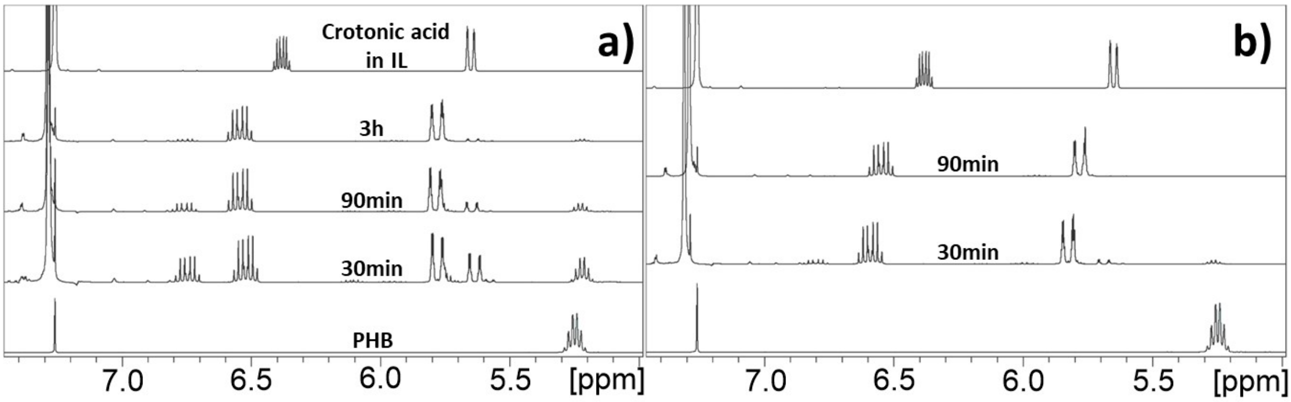

Figure S5. ^{1}H NMR spectra of the conversion of PHB to CA in [EMIM][AcO] IL at a) 120 °C and b) 140 °C, PHB = 20 wt.% in IL.

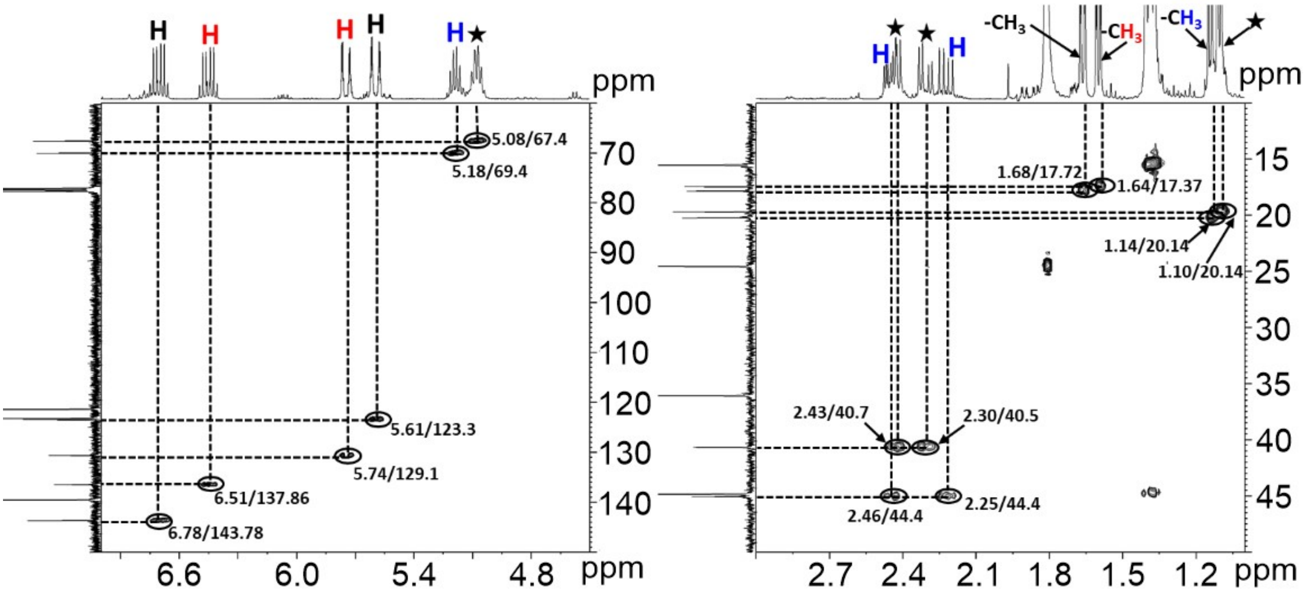

Figure S6. ^{1}H-^{13}C HSQC spectra for reaction mixture comprised of 20 wt.% of PHB in [EMIM][AcO] IL. Temperature = 80 °C, time = 3 h, PHB = 0.4 g, IL = 1.60 g.

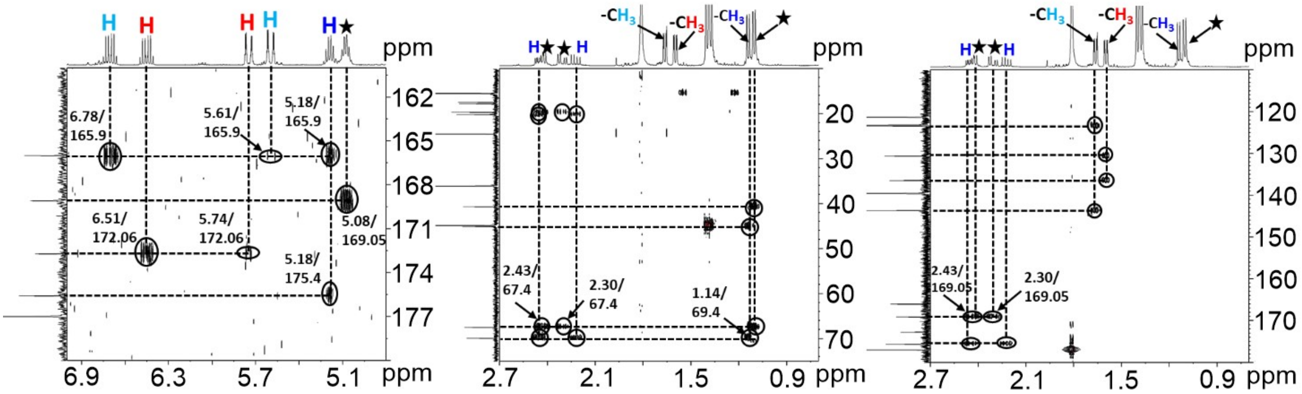

Figure S7. ^{1}H-^{13}C HMBC NMR spectra for the conversion of PHB to CA in [EMIM][AcO] IL at 80 °C for 3 h, PHB = 20 wt.% in IL. For colour coding, see Figure 3 in the main text.

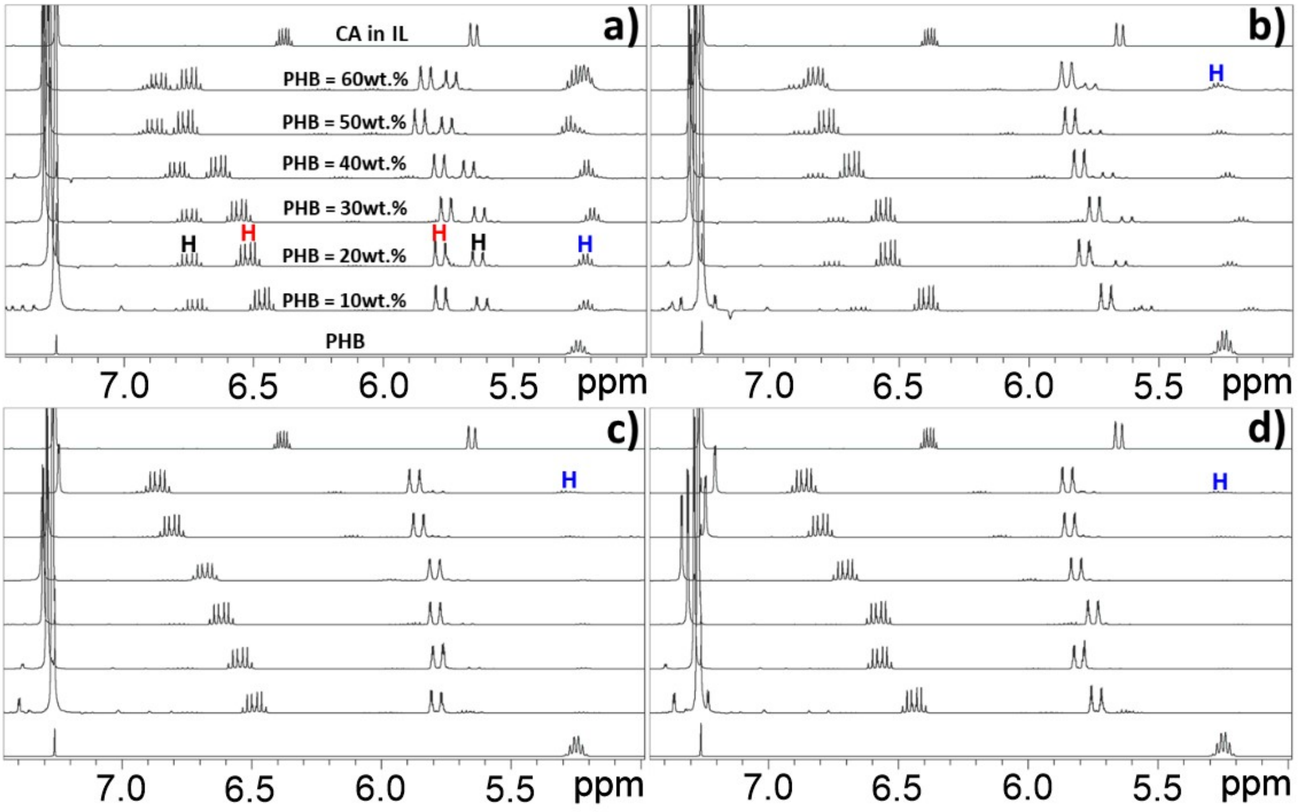

Figure S8. ^{1}H NMR spectra of the conversion of PHB to crotonic acid in [EMIM][AcO] IL with different amounts of PHB at 120 °C for a) 30 min, b) 90 min, c) 3 h and d) 5 h.

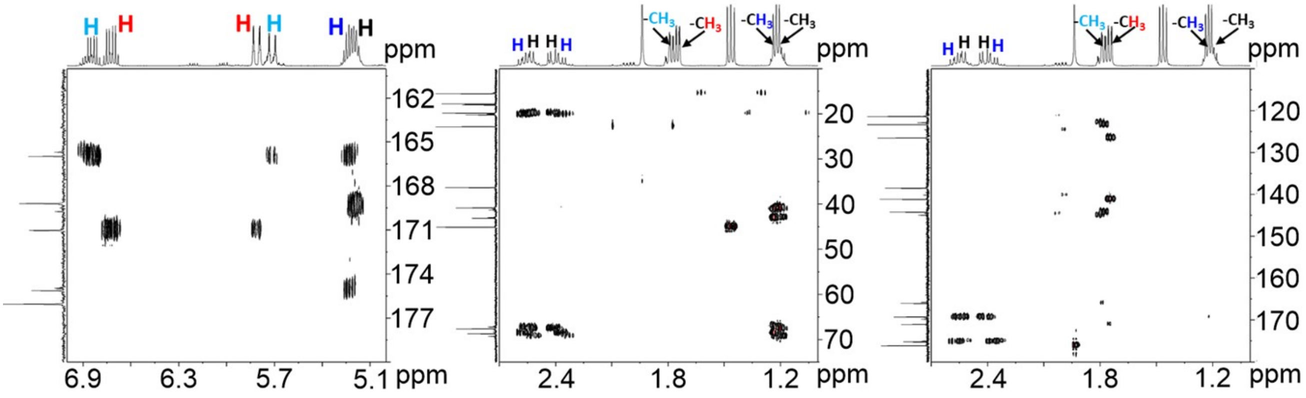

Figure S9. ^{1}H-^{13}C HMBC spectra for reaction mixture comprised of 60 wt. % of PHB in [EMIM][AcO] IL. Temperature = 120 °C, time = 30 min, PHB = 1.2g, IL = 0.8g. Black color protons: unreacted PHB.

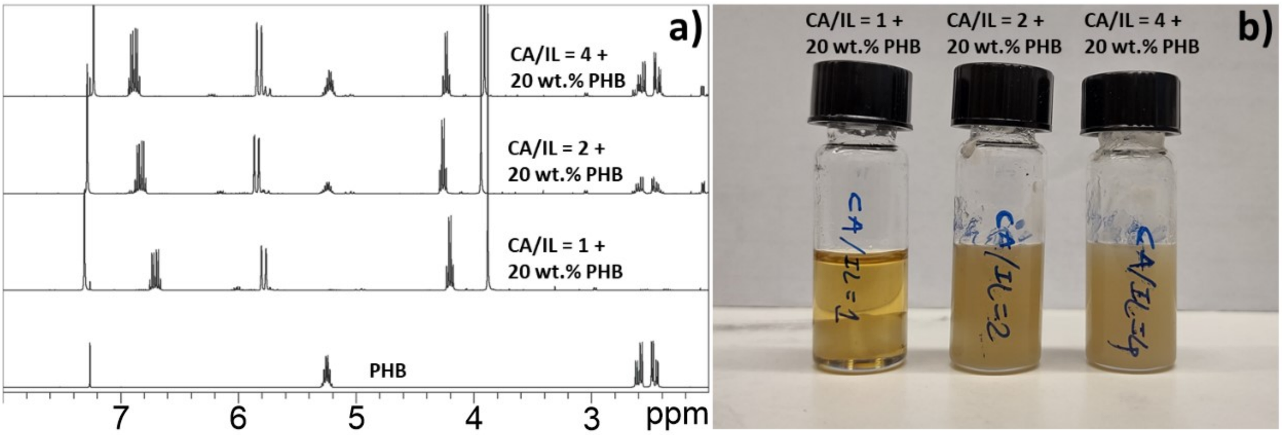

Figure S10. ^{1}H NMR spectra of the conversion of PHB to crotonic acid in [EMIM][AcO] IL and CA mixtures with different CA/IL molar ratios at 120 °C for 3 h. b) Their corresponding reaction mixtures obtained after 3 h.

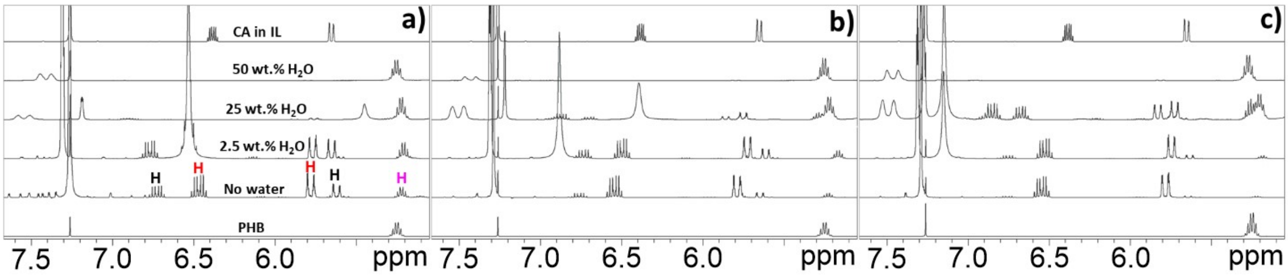

Figure S11. ^{1}H NMR spectra for the conversion of PHB to crotonic acid in [EMIM][AcO] IL with different amounts of H_2O at 120 °C for a) 30 min, b) 90 min and c) 3 h

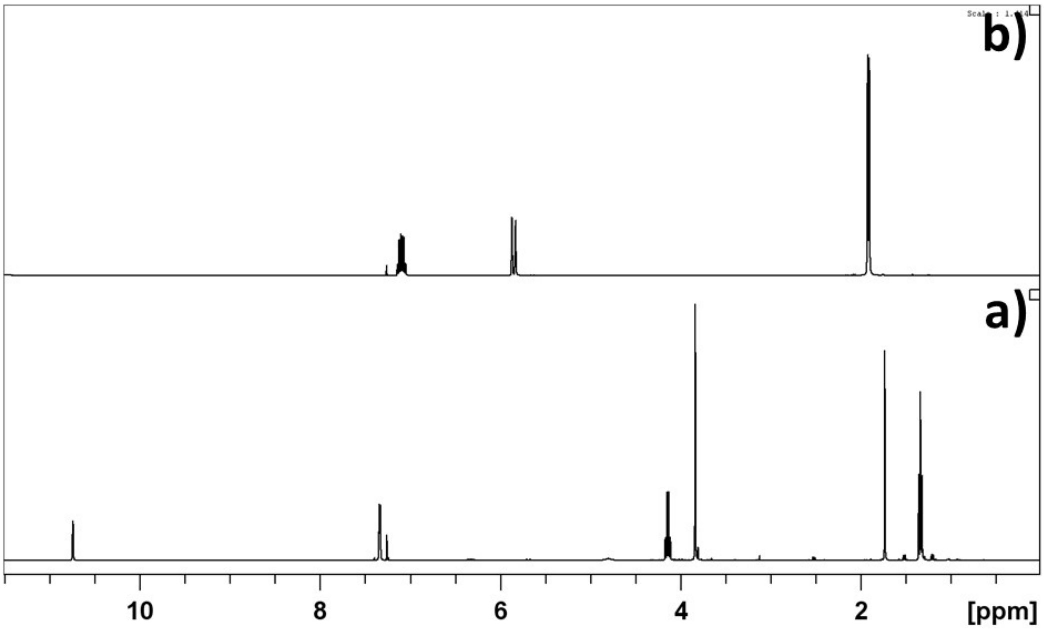

Figure S12. ^{1}H NMR spectra of the recovered a) [EMIM][AcO] IL and b) CA.