## **Electronic Supporting Information (ESI)**

## Ionic liquids catalyzed lignin liquefaction: Mechanistic studies using TPO-MS, FT-IR, RAMAN and 1D, 2D-HSQC/NOSEY NMR

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## Section S1. Types of linkage present in lignin:

Type of linkages	Abundance,	Bond dissociation enthalpy
	<b>(%)</b> <sup>1-2</sup>	(kJ mol <sup>-1</sup> ) <sup>3-7</sup>
β-Ο-4	46-60	290-335
α-Ο-4	6-8	215-270
4-O-5	3-7	330
α-Ο-γ'	-	270
5-5'	4-11	490
β-β	2-3	335
β-1	7	270-289
α-1	-	360-390
-OCH <sub>3</sub>	-	255-275
others	5-13	-

Table S1. Linkage in lignin, their abundance & bond dissociation enthalpy (BDE; kJ mol<sup>-1</sup>)



Fig. S1 Various types of linkages in lignin.

## Section S2. Synthesis and characterisation of Brønsted acidic ionic liquids (BAILs)

## S2.1) Materials

1-methylimidazole (Sigma Aldrich USA,  $\geq 99\%$ ), 1,3-propanesultone (Alfa Aesar India, 99%), *p*-toluenesulfonic acid monohydrate (Sigma Aldrich USA, 98.5%), dealkaline lignin (TCI Japan with 28.6% of moisture + ignition residue),<sup>8</sup> toluene (Thomas Baker India, 99.5%), methanol (Merck India, 99.9%), tetrahydrofuran (THF, Thomas Baker India, 99.57%), hydrochloric acid (Merck India, 35%), sulphuric acid (Merck India, 98%), vanillin (Aldrich USA, 99%) Guaiacol glyceryl ether (Sigma USA, 98%), cumene (Acros organics USA, 98%) DMSO-d<sub>6</sub> (Aldrich USA, 99.9%) were used as received.

## S2.2) Synthesis procedure of BAILs and IL

Various imidazolium based BAILs such as, 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate,  $[C_3SO_3HMIM][HSO_4]$ ; 1-methyl-3-(3-sulfopropyl)-imidazolium *p*-toluenesulfonate,  $[C_3SO_3HMIM][PTS]$ ; and 1-methyl-3-(3-sulfopropyl)-imidazolium chloride,  $[C_3SO_3HMIM][Cl]$  were synthesized in a two-step method. Along with BAILs, neutral IL, 1-butyl-3-methylimidazolium chloride [BMIM][Cl] was also synthesized (ESI, Scheme S1).<sup>9</sup>

In a typical procedure, under slow stirring (100 rpm), to a solution of 1, 3-propanesultone (4.46 g, 36.58 mmol) dissolved in toluene (50 mL) was drop wise added 1-methylimidazole (3.00 g, 36.58 mmol) at 0 °C (ice bath) under inert atmosphere (N<sub>2</sub>). The solution was slowly warmed to reflux temperature and stirred (600 rpm) for 12 h. The resulting mixture was filtered to obtain the zwitterions as white solid. The solid was washed with toluene (25 mL) to remove any unreacted substrates. Next, this solid was dried in vacuum oven at 80 °C for 4 h. In the next step; to a zwitterion, [C<sub>3</sub>SO<sub>3</sub>MIM] a stoichiometric amount of acid (HCl, H<sub>2</sub>SO<sub>4</sub> or *p*-toluenesulfonic acid monohydrate) was added and the mixture was stirred at 100 °C for 12 h to obtain highly viscous transparent liquid. This liquid was washed 3 times with diethyl ether (50 mL) to remove any impurities and further dried under vacuum oven at 80 °C for 4 h.



I: 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate, X=  $HSO_4$ , [C<sub>3</sub>SO<sub>3</sub>HMIM][HSO<sub>4</sub>] II: 1-methyl-3-(3-sulfopropyl)-imidazolium *p*-toluenesulfonate, X= CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>, [ $\overline{C}_3SO_3$ HMIM][PTS] III: 1-methyl-3-(3-sulfopropyl)-imidazolium chloride, X=CI, [C<sub>3</sub>SO<sub>3</sub>HMIM][CI]

Scheme S1 Schematic representation of the synthesis of BAILs

HSO₄ SO<sub>3</sub>H

1-methyl-3-(3-sulfopropyl)imidazolium hydrogensulphate

CI SO<sub>2</sub>H

1-methyl-3-(3-sulfopropyl)imidazolium chloride

SO<sub>3</sub>H

1-methyl-3-(3-sulfopropyl)imidazolium *p*-toluenesulphonate

CI

3-butyl-1-methylimidazolium chloride

Fig. S2 Structures of BAILs and IL used for lignin depolymerization

## S2.3) Characterization of BAILs and IL

The synthesized ILs were characterized by various techniques to check their purity.

The C, H and N percentage values obtained from CHNS elemental analysis of ILs reveal that those match well with the theoretical values. The NMR ( $^{1}$ H,  $^{13}$ C) (Fig. S3) and FT-IR characterizations disclose that all the ILs are obtained in pure form. The TGA study carried out under air atmosphere reveals that ILs are stable until 250 °C (Fig. S4).

## S2.3.a) Elemental analysis, NMR (<sup>1</sup>H and <sup>13</sup>C) and FT-IR:

S2.3a.i) 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogensulphate, [C<sub>3</sub>SO<sub>3</sub>HMIM][HSO<sub>4</sub>]:

 $\begin{array}{l} \underline{Elemental\ analysis\ (\%):}\\ \hline C,\ 28.01;\ H,\ 4.35;\ N,\ 9.39;\ S,\ 20.90.\\ \underline{NMR}\\ \delta_{H}\ (200.13\ MHz,\ D_{2}O):\ 8.66\ (s,\ 1H),\ 7.42\ (s,\ 1H),\ 7.35\ (s,\ 1H),\ 4.26\ (t,\ 2H),\ 3.79\ (s,\ 3H),\ 2.82\ (t,\ 2H),\\ and\ 2.21\ (m,\ 2H)\\ \delta_{C}\ (50.32\ MHz,\ D_{2}O):\ 136.16,\ 123.74,\ 122,\ 47.69,\ 47.19,\ 35.66\ and\ 25.\\ \underline{FT-IR}\\ (v_{max}/cm^{-1}):\ 3440,\ 3155,\ 3105,\ 2955,\ 2870,\ 2600,\ 2480,\ 2220,\ 1650,\ 1575,\ 1460,\ 1330,\ 1215,\ 1180, \end{array}$ 

1040, 860, 745, 650 and 610.

S2.3a.ii) 1-methyl-3(3-sulfopropyl)-imidazolium p-toluenesulphonate, [C<sub>3</sub>SO<sub>3</sub>HMIM][PTS]:

Elemental analysis (%): C, 44.27; H, 5.38; N, 7.44; S, 17.32.

## <u>NMR</u>:

 $\delta_{H}$  (200.13 MHz, D<sub>2</sub>O): 8.59 (s, 2H) 7.55 (d, 2H), 7.36 (s, 1H), 7.30 (s, 1H), 7.27 (d, 2H), 4.11 (t, 2H), 3.76 (s, 3H), 2.83 (t, 2H) 2.28 (s, 3H), and 1.90 (m, 2H).

 $\delta_C$  (50.32 MHz,  $D_2O$ ): 142.42, 139.43, 136.09, 129.40, 125.31, 123.72, 122.14, 47.69, 47.17, 35.66, 25.05, and 20.44.

<u>FT-IR</u>

(*v*<sub>max</sub>/cm<sup>-1</sup>): 3440, 3165, 3126, 2970, 2900, 2152, 1700, 1631, 1553, 1518, 1386, 1243, 1184, 1095, 1071, 874, 800, 746 and 623.

S2.3a.iii) 1-methyl-3-(3-sulfopropyl)-imidazolium chloride [C<sub>3</sub>SO<sub>3</sub>HMIM][Cl]:

 $\label{eq:spectral_$ 

*S2.3a.iv)* 1-butyl-3-methylimidazolium chloride [BMIM][Cl]:

Elemental analysis (%): C, 54.82; H, 8.32; N, 15.6. <u>NMR</u>:  $\delta_{\rm H}$  (200.13 MHz, D<sub>2</sub>O): 7.33 (s, 1H), 7.32 (s, 1H), 4.24 (t, 2H), 3.75 (s, 3H), 1.77 (qui, 2H), 1.35 (sex, 2H), and 0.57 (t, 3H);  $\delta_{\rm C}$  (50.32 MHz, D<sub>2</sub>O): 123.76, 122.18, 49.32, 35.7, 31.2, 19.12 and 12.34. <u>FT-IR</u>: ( $v_{\rm max}/{\rm cm}^{-1}$ ): 3381, 3139, 3047, 2955, 2936, 2873, 2124, 1771, 1645, 1568, 1466, 1384, 1336, 1166, 1113, 1021, 949, 867, 750, 654 and 625.

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**Fig. S3** <sup>1</sup>H and <sup>13</sup>C NMR. Of fresh, (a) [C<sub>3</sub>SO<sub>3</sub>HMIM][HSO<sub>4</sub>], (b) [C<sub>3</sub>SO<sub>3</sub>HMIM][PTS], (c) [C<sub>3</sub>SO<sub>3</sub>HMIM][C1] and (d) [BMIM][C1] (\* indicate the solvent peak)



Fig. S4 TGA spectra. Of fresh ILs in the presence of air (a)  $[C_3SO_3HMIM][HSO_4]$ , (b)  $[C_3SO_3HMIM][PTS]$ , (c)  $[C_3SO_3HMIM][C1]$  and (d) [BMIM][C1].

#### S2.3.b) Hammett acidity measurement

The acid strength reflects the extent of ease with which a catalyst can liberate/donate proton. For the determination of the acid strength in BAILs/IL and mineral acid, Hammett acidity function ( $H_0$ ) was calculated using UV-Vis spectroscopy. The purpose of this study was to draw a correlation between catalytic activity between BAILs/IL and minerals acid with their acid strength. The determination of Hammett acidity was carried out with the use of a basic indicator, *p*-nitroaniline. It is known that with an increase in acid strength in sample, the absorbance of the un-protonated form of basic indicator decreases. Whereas the protonated form of indicator could not be observed because of its small molar absorptivity. With higher acid strength, absorbance coefficient value will be low and  $H_0$  will be more at 380 nm due to less resonance between amine and nitro group present in the basic indicator that will stabilise the molecules via protonation (Fig. S5). The Hammett acidity function was calculated under the same concentration of *p*-nitroaniline (2mg/litre *pKa*=0.99) with 50 mmol of BAILs/IL and mineral acid (in distilled water) solution. Hammett acidity function has been calculated based on the following equation (1)

$$H_0 = pka + \log\frac{[I]}{[HI]} \tag{1}$$

Where, [I] and [HI] are the molar concentration of deprotonated and protonated form of indicator in solvent, respectively. The calculated  $H_0$  value of the BAILs and mineral acid are summarised in the Table S2.

Sr. No.	Indicator, BAILs/IL and mineral acid	Absorbance	[1]	[HI]	$H_{0}$
1	<i>p</i> - nitroaniline	0.1968	100	-	-
2	[BMIM][Cl]	0.2000	-	-	-
3	[C <sub>3</sub> SO <sub>3</sub> HMIM][Cl]	0.1549	78.7	21.29	1.56
4	[C <sub>3</sub> SO <sub>3</sub> HMIM][PTS]	0.1479	75.15	24.85	1.47
5	[C <sub>3</sub> SO <sub>3</sub> HMIM][HSO <sub>4</sub> ]	0.1369	69.56	30.44	1.35
6	[H <sub>2</sub> SO <sub>4</sub> ]	0.1230	62.5	37.5	1.21

Table S2. Hammett acidity function (Ho) of mineral acid and ionic liquids.



Fig. S5 UV-Vis spectra of indicator, BAILs, IL and mineral acid

BAILs and mineral acid ( $H_2SO_4$ ) were analyzed for their acidic strength by UV-Vis technique (Fig. S5). The calculation of Hammett acidity function (*Ho*, Table S2) revealed that, among all the BAILs, [C<sub>3</sub>SO<sub>3</sub>HMIM][HSO<sub>4</sub>] has more acid strength.

## Section S3. Liquefaction of lignin and work-up procedures

## **S3.1)** Liquefaction of lignin

Depolymerisation reactions of lignin were conducted at desired temperature for required time in a batch mode reactor of 100 mL capacity (Parr Autoclave, USA). Unless specified, in all the reactions, lignin (2 wt.% solution H<sub>2</sub>O:CH<sub>3</sub>OH, 1:5 v/v) & catalyst (0.5g) were charged and the reactor was heated to desired temperature under slow stirring (100 rpm). After attaining the desired temperature, stirring was increased to 1000 rpm and this time was considered as starting time of reaction. At this temperature the pressure generated in the autoclave is 0.35 MPa due to water and methanol. After completion of reaction, reactor was allowed to cool to room temperature under the flow of air and slow stirring (100 rpm) (Section S3).

## S3.2) Solubility of lignin

**Table S3.** Solubility, Hansen solubility parameter and polarity index of various solvents for lignin solubility and extraction of liquefied products from the reaction mixture;

Solvent/mixture/	Hansen Solubility	<b>Polarity Index</b>	Solubility*
aromatic monomers	parameter (δ; MPa <sup>1/2</sup> ) <sup>10-12</sup>		$(mg mL^{-1})$
Water	48.0	9.0	22
Methanol	29.7	5.1	37
Ethanol	26.2	5.2	IS
Propanol	23.5	5.1	IS
Butanol	23.3	1	IS
Acetone	19.7	5.1	IS
Ethyl acetate	18.1	4.4	IS
Chloroform	18.94	4.1	IS
THF	19.4	4.0	IS
DCM	20.79	3.1	IS
Diethyl ether	15.8	2.8	IS
Glycerol	34.12	-	21
Ethylene glycol	33.7	-	32
1,2-propylene glycol	29.52	-	24

Binary mixtures			
Water: Methanol (1:5 $v/v$ )	-	-	50
Water:Methanol	32.42	-	
Water:ethanol	27.92	-	
Water:n-propanol	25.09	-	
Water:i-propanol	25.3	-	
Water:acetone	21.5	-	
Water:THF	20.20	-	
Water:1,4-dioxane	21.78	-	
	Aromatic o	compounds	
<i>p</i> -cresol	22.7	-	
Phenol	24.1	-	
Vanillin	25.24	-	
Eugenol	22.75	-	
Resorcinol	29.0	-	
Benzene	18.7	-	
Toluene	18.3	-	
Xylene	18.2	-	
Styrene	19.0	-	
Acetophenone	19.6	-	
Benzaldehyde	22.5	-	
Benzylalcohol	25.18	-	
Lignin	28.63	-	
[*] dealkaline lignin 50	mg, solubilized in solvent	$t^{1}$ 1 mL, at RT (25±3 $^{0}$ C	). IS: Insoluble

### S3.3) Work-up procedure

After completion of reaction, reactor was allowed to cool to room temperature under the flow of air and slow stirring (100 rpm). Reaction mixture was collected and solvent (water and methanol) was evaporated using rotary vacuum evaporator (Fig. S6). The care was taken to trap all the low volatile products by arranging 3 ice traps in series before vacuum pump. The analysis of any collected solvent in these traps revealed no loss of products. The reaction mass (ILs + products + unreacted lignin) obtained after removing solvent was dried at 55 °C for 16 h and further under vacuum at 80 °C for 4 h. The weight of this dried mass was taken to check the mass balance. To the dried mass, 30 mL of THF was added to dissolve the products. THF was chosen to extract the products because it does not dissolve lignin (for more details please refer lignin characterization section in SI). Similarly, we also observed that ILs are not soluble in THF (Fig. S6) and hence solvent will only extract aromatic products. Similar to THF extraction, products were also extracted using ethyl acetate (EtOAc) and diethyl ether (DEE).



a: depolymerised, repolymerized, unconverted lignin BAILs and IL

- b: THF soluble products, lower molecular weight aromatic products (analysed by GC, GC-MS, LC-MS, GPC, FT-IR, DSC, 2D (HSQC) NMR and TGA.
- c: lignin, repolymerized lignin, ionic liquids and inorganic ash and
- d: repolymerised lignin and ash

Fig. S6 Extraction of organic solvent soluble products from reaction mixture

## S3.3.a) Solubility of BAIL in THF

0.5 g BAIL was mixed with 30 mL THF and stirred for 1 h at room temperature. It was observed that IL and THF form separate layers. Afterwards, upper layer, THF was pipette out and this THF was evaporated using rotary evaporator. To the RB water was added and it was injected on HPLC but no peak for IL was observed. Moreover, weight of empty RB and after evaporation of THF was same. These studies confirm that IL has not dissolved in THF and hence it is not contributing to the weight of THF soluble products. Additionally, we did not observe any peak for BAIL when samples were injected on LC-MS.

## S3.3.b) Recovery of BAIL

After extraction of products, IL was recovered by solvomorphic separation process and it was reused after acid treatment. For more details, please refer recycle experiment section (ESI, S3.6.e).

## **S3.4)** Analytical methods for the identification of products

The organic solvent (THF, EtOAc, DEE) soluble products were analysed using gas chromatography (GC), gas chromatography-mass spectroscopy (GC-MS), liquid chromatography-mass spectroscopy (LC-MS) and gel permeation chromatography (GPC) techniques.

## S3.4.a) Gas chromatography

GC (Varian CP 3800) attached with flame ionization detector (FID) and CPSIL 8CB capillary column (5 % phenyl 95 % dimethyl polysiloxane) (30 m x 0.25 mm x 0.32  $\mu$ m) was used. N<sub>2</sub> (30 mL min<sup>-1</sup>) was used as a carrier gas. The column oven program; 100 °C (4 min.)  $\rightarrow$  10 °C/min.  $\rightarrow$  280 °C (20 min.) was used along with injector temperature of 275 °C and detector temperature of 280 °C.

## S3.4.b) Gas chromatography-mass spectroscopy

The Varian 3800 GC-MS, (Saturn 2000MS) with the VF-5 capillary column (5 % phenyl 95 % dimethyl polysiloxane) (30 m x 0.25 mm x 0.25  $\mu$ m) was used. Helium (0.6 mL/min) was used as a carrier gas. The similar column oven program was used as used for GC (please see above). The formation of various compounds was confirmed by matching the fragmentation pattern(s) from NIST library and by injecting standards procured commercially.

## S3.4.c) Liquid chromatography-mass spectroscopy

The LC-MS (Thermo Finnigan Electro Spray Ionisation, Positive mode 40 volt) analysis of THF soluble products was carried out using Surveyor MSQ liquids chromatography.

For the details on 2D (HSQC) NMR, FT-IR, ICP-OES, CHNS, UV-Vis, GPC, MALDI and DSC analysis please refer lignin characterization section in main text.

## S3.5) Yield and mass balance calculations

Dealkaline lignin contains 11% moisture<sup>8</sup> and 17% ignition residue.

So, if 0.5 g dealkaline lignin is charged in the reactor, then it contains 0.055 g moisture. The actual weight of dealkaline lignin charge is 0.445 g out of 0.5 g.

## **S3.5.a)** Yield calculation

The yield (%) for THF soluble products was calculated based on the solid recovered from the THF solvent.

THF soluble product yield (%) = (Weight of THF soluble products/weight of lignin charged)  $\times 100$ 

Most of the reactions are performed three times to check the reproducibility of results and the data presented in this report is average of these three reactions. Typically, we observed  $\pm 3\%$  error in yield in each reaction.

## S3.5.b) Mass balance calculation

Reaction conditions: Lignin (2 wt.% solution  $H_2O:CH_3OH$ , 1:5 v/v), BAILs / IL /  $H_2SO_4$  0.5 g, 120 °C, 1 h. Total charge of the reaction is 0.945 g (lignin 0.445 g (0.5-0.055 g) + BAILs, IL/ $H_2SO_4$  0.5 g). After following above mentioned work-up procedure, the weight of viscous mass at room temperature was 0.92 g.

$$Mass \ balanced = \frac{Weight \ of \ dried \ viscous \ mass}{Weight \ of \ actual \ charge} \times 100$$
$$Mass \ balanced = \frac{0.92g}{0.945g} \times 100$$
$$= 97\%$$

## **S3.6)** Results and discussions on lignin liquefaction reactions

## **S3.6.a)** Effect of H<sup>+</sup> concentration

Since, in all the experiments same quantity of catalyst (0.5g) was used, it was expected that due to disparity in  $H^+$  concentration at 0.5 g loading of catalyst (H<sub>2</sub>SO<sub>4</sub>, 10.2 mmol; [C<sub>3</sub>SO<sub>3</sub>HMIM][HSO<sub>4</sub>], 3.32 mmol; [C<sub>3</sub>SO<sub>3</sub>HMIM][PTS], 1.33 mmol) variation in activity was observed (98, 78 and 42% yield). To nullify this effect, reactions were performed using comparable  $H^+$  concentration (2.78 mmol) in the reaction mixture by altering the catalyst quantity and the following order of activity was seen,

 $[H_2SO_4] (96\%) > [C_3SO_3HMIM][HSO_4] (52\%) > [C_3SO_3HMIM][PTS] (49\%).$ 

This shows that if  $H^+$  concentration is kept constant, analogous activity (52, 49%) can be observed with all the ILs with varying anions.

### **S3.6.b)** Effect of temperature and time

To enhance the yields with  $[C_3SO_3HMIM][HSO_4]$ , reaction temperatures were varied from 80 to 170 °C and the results are presented in Fig. S7. When reaction was done at 120 °C for1 h, maximum yield of 78% was obtained. Since at lower temperatures (80°C), poor yield (33%) was observed after 1 h reaction, experiment was conducted for 2 h at 80 °C and 37% was seen. Since there was no improvement in yield at 80 °C, reaction was done at 120 °C for 2 h and 80% yield was seen. Subsequently, reactions were performed at higher temperatures but, inferior yields were seen (170 °C, 4%) due to the formation of black colour solid (char, THF insoluble). To understand this phenomenon, products stability study was performed. For more details on this study please refer product stability section in main text.



**Fig. S7** The effect of temperature on THF soluble product yields. Reaction condition: Lignin (2 wt.% solution H<sub>2</sub>O:CH<sub>3</sub>OH, 1:5  $\nu/\nu$ ) & catalyst [C<sub>3</sub>SO<sub>3</sub>HMIM][HSO<sub>4</sub>] (0.5 g) were charged, 80-170 °C, 1 h, 1000 rpm.









**Fig. S8** GC-MS of products. THF soluble products using (a)  $[C_3SO_3HMIM][HSO_4]$ , (b)  $[C_3SO_3HMIM][PTS]$ , (c)  $[C_3SO_3HMIM][C1]$  catalysts. GC-MS of organic solvent soluble products for  $[C_3SO_3HMIM][HSO_4]$  catalyzed reaction (d) ethyl acetate, (e) diethyl ether and (f) THF soluble products with  $H_2SO_4$  as a catalyst.



Fig. S9 LC-MS of THF soluble products in methanol obtained in  $[C_3SO_3HMIM][HSO_4]$  catalyzed reaction .



Fig. S10 GC-FID of THF soluble products obtained in  $[C_3SO_3HMIM][HSO_4]$  catalyzed reaction.

## **S3.6.d)** Gas chromatography-thermal conductivity detector (GC-TCD)

Samples were analysed in Chemito 8610 model GC attached with TCD detector and is equipped with Porapack Q column (9 feet, 2 mm diameter). The column oven program was used as 100 °C (4 min.)  $\rightarrow$  10 °C/min.  $\rightarrow$  180 °C (4 min.) along with injector temperature is 50 °C and detector temperature is 150 °C.

The GC-TCD confirmed lack of any gaseous products formation, which essentially gave higher yields of low molecular weight aromatic products.



Fig. S11 THF soluble products identified by GC-MS analysis.

#### S3.6.e) Recycle study of BAILs and IL

For reuse of the BAILs, after extracting the products in THF (in which BAIL is not soluble; For more information please see S3.3.a and S3.3.b), water was added to THF insoluble mass to separate unreacted lignin and water insoluble products from BAIL. The water soluble BAIL was again subjected to rotary evaporator and after evaporation of all the water, viscous mass was dried at 55 °C for 6 h and later dried in vacuum oven at 120 °C for 4 h. The recovered BAIL contained 603 ppm Na per 0.5 g of as determined by ICP-OES technique. To remove the contamination of Na from BAIL, HCl (2.94 mmol) was added to BAIL solution (1.0 g recovered BAIL in 20 mL water) to form NaCl salt. Again after evaporation of water, ethanol was added to the viscous mass and some white coloured solid (mostly NaCl) to separate BAIL from NaCl. This is possible since NaCl is insoluble in ethanol but BAIL is soluble. After separation of ethanol solution from solid (NaCl), ethanol was evaporated and the recovered BAIL was again subjected to ICP-OES technique. The analysis confirmed absence of Na and thus this BAIL was further used in recycle experiments. Moreover, to check the presence of Cl<sup>-</sup> in BAIL, silver chloride (mirror) test was done and the results illustrate that BAILs were not contaminated with any Cl<sup>-</sup>.

#### S3.6. f) Characterisation of recovered BAILs

S3.5f.i)<sup>1</sup>H and <sup>13</sup>C-NMR spectra of fresh and recovered [C<sub>3</sub>SO<sub>3</sub>HMIM][HSO<sub>4</sub>].BAIL



**Fig. S12** <sup>1</sup>H and <sup>13</sup>C NMR. Of fresh (a) and recovered (b) up to 5<sup>th</sup> run of [C<sub>3</sub>SO<sub>3</sub>HMIM][HSO<sub>4</sub>] BAIL

*S3.5f. ii) FT-IR transmittance spectra and TGA study of fresh and recovered* [*C*<sub>3</sub>*SO*<sub>3</sub>*H MIM*][*HSO*<sub>4</sub>] *BAIL* 



Fig. S13 FT-IR and TGA. Of fresh (a) and recovered (b) up to 5<sup>th</sup> run of [C<sub>3</sub>SO<sub>3</sub>HMIM][HSO<sub>4</sub>] BAIL

The observed shift in baseline for spent IL in TGA is may be ascribed to the trace of water or low molecular weight aromatic products.

BAILs and IL	Fresh (%)		Recovered (%)			)		
	С	Н	N	S	С	Н	N	S
[C <sub>3</sub> SO <sub>3</sub> HMIM][HSO <sub>4</sub> ]	28.01	4.35	9.39	20.90	27.78	4.20	8.96	21.01
[C <sub>3</sub> SO <sub>3</sub> HMIM][PTS]	44.27	5.38	7.44	17.32	43.85	5.62	7.63	16.90
[C <sub>3</sub> SO <sub>3</sub> HMIM][Cl]	34.97	5.70	7.44	13.80	35.04	5.80	7.32	13.57
[BMIM][Cl]	54.82	8.37	15.6	-	54.97	7.97	15.23	-

**Table S4.** Elemental analysis of fresh and revcoverd BAILs and IL

## Section S4. Mechanistic studies

## S4.1) Characterisation of lignin and products

As properties of lignins differ based on the type/age of plant and isolations procedures, it becomes important to understand those before depolymerisation and hence commercially procured lignin<sup>8</sup> was systematically characterized by various techniques.

## S4.1.a) Physical properties

Table S5. Physical properties of dealkaline lignin

Properties	Contents
Moisture, (%)	11.20
Inorganic residue, (%)	16.97
Calcination	600 <sup>o</sup> C
ICP-OES,* Na (PPM)	2686
TGA (N <sub>2</sub> )	35.72
TGA (Air)	16.97
рН	4.16
colour	Dark brown
Elemental composition, (%)	
C	65.92
Н	7.02
0	25.87
S	0.98

Total, CHNO	99.79
O/C, ratio	0.39
H/C, ratio	0.12
Monomers molecular formula <sup>†</sup>	$C_{10}H_{13}O_3S_{0.09}$
Higher heat value, <sup>13</sup> (HHV, MJ/kg) <sup>≠</sup>	27.76
Molecular weight	~60 kDa

Note; \*ICP-OES results for 1.0 g of lignin, <sup>†</sup> monomers molecular formula based on elemental analysis, <sup>≠</sup> HHV have been calculated using "Dulong formula"

HHV (MJ/kg) =  $0.3383 \times C + 1.442 \times (H-O/8)$  (1)

## S4.1.b) Elemental analysis

Elemental analysis was done in Thermo Finnigan, Italy; model EA1112 Series Flash Elemental Analyzer. The amount of C, H, N and S in samples was determined by rapid combustion of small amounts (10-15 mg) of the sample in pure  $O_2$  (Dumas method or "flash combustion").

Based on the CHNS analysis (C,66%; H,7%; S,1%), molecular formula for lignin was calculated as,  $C_{10}H_{13}O_3S_{0.09}$  which matches well with the literature.<sup>14-15</sup>

## S4.1.c) MALDI-TOF mass spectroscopy

MALDI-TOF for lignin samples were recorded using Voyager DE-STR instrument. It was equipped with a N<sub>2</sub> laser (337 nm, 3 ns pulse, 20 Hz maximum firing rate). The matrix compound used was 2, 5-dihydroxy benzoic acid (DHB). Lignin was dissolved in methanol with a concentration of 1 mg/ml. Lignin samples (1  $\mu$ l) were overlaid onto the matrix (1  $\mu$ l) placed on the golden MALDI target plate. Plate was then kept for drying until the solvent was evaporated and then subjected for the analysis.

The lignin had a high molecular weight in the range of 10-100 kDa (average 60 kDa). This result is in good correlation with GPC data.

## S4.1.d) SEM-EDAX spectra of lignin

The SEM micrographs of the samples were obtained on a Leo Leica Cambridge UK Model Stereoscan 440 scanning electron microscope, with an electron beam of 5-50 eV. Non-uniform morphology of lignin with particle size ranging from  $<1 \mu m$  to  $30\mu m$  in the SEM spectra is seen from Fig. S14a. The elemental composition of the sample was determined using the EDAX (Fig. S14b), attached with the SEM instrument. It is clearly indicate that carbon, oxygen, sodium and sulphur are present in the lignin sample.



Fig. S14 (a) SEM image and (b) EDAX spectra of lignin

## S4.1.e) Inductively coupled plasma – optical electron spectroscopy (ICP-OES)

Samples were analysed in SPECTRO ARCOS Germany, FHS 12 ICP-OES instrument. The sample was prepared as follows;

To prepare the sample for ICP-OES analysis, 1 g lignin was first calcined at 700 °C for 6 h under air. After burning all the C, H and O as gaseous products (for details please refer TPO-MS analysis), 0.170 g ash was obtained (for details please refer TGA analysis). The elemental analysis of this ash revealed that it does not contain any organic matter (C, H, O, N). The XRD analysis of ash showed peaks for only  $Na_2SO_4$  (for more details please refer XRD analysis). Later, 0.05 g ash was weighed in the polypropylene bottle and to this ca. 400 µL of HF was added followed by 2 mL of water. The mixture was heated at 80 °C to remove the excess HF. The resulting mixture is then diluted and made to 50 mL. The solution was filtered using 0.22 micron filter and filtered solution was analysed by ICP-OES.

The ICP-OES analysis confirmed presence of Na (1343 ppm) and S (940 ppm) in lignin (0.5 g or 0.085 g ash). The contamination of Na and S is not much surprising since lignin might have been isolated by Kraft process which uses  $Na_2S$  and NaOH as reagents.

## S4.1.f) X-ray diffraction of lignin

The morphology of lignin was characterised using Powder XRD. Rigaku Miniflex 600, with duel goniometer diffractor instrument was used for the analysis. The source of X-ray used was Cu K $\alpha$  (1.5418 Å radiation) with Ni filter. The sample was scanned from a 20 value of 5 to 80 ° at the rate of 4 °/min.

XRD analysis of lignin (Fig. S15) showed broad peak for the amorphous nature of the sample at  $21^{\circ}$ . Besides this broad peak, few extra peaks were seen at 2 $\theta$  value of 18.8, 28, 29, 32, 34 and 49° showing the presence some crystalline impurities in the sample. These peaks are matched well with XRD of Na<sub>2</sub>SO<sub>4</sub> (JCPDS file No. 36 0397). The presence of Na and S is also confirmed from elemental, SEM-EDAX and ICP-OES analysis of lignin samples.



# S4.1.g) Thermal gravimetric analysis (TGA) and temperature programme oxidation-mass spectroscopy (TPO-MS)

The TGA and TPO-MS for decomposition of lignin in presence and absence of oxygen (5% v/v) TGA experiments were conducted using METTLER TOLEDO TGA / SDTA851 series, USA; instrument. The following program is used for the analysis;

50 °C  $\rightarrow$  10 °C/min  $\rightarrow$  700 °C under air.

The graphs obtained for lignin are presented in Fig. S16.





As seen (Fig. S16), lignin is stable until 250 °C. Even after heating lignin upto 700 °C, some amount of lignin remains unburnt. This is due to presence of inorganic residue (ash) in lignin. This inorganic residue is mostly  $Na_2SO_4$  as is evident from CHNS (main text) and ICP analysis (main text) that Na and S are present in lignin. Moreover, XRD analysis (Fig. S15) of lignin shows the characteristic peaks for  $Na_2SO_4$ . Based on the results obtained in TGA and understanding the structure of lignin ( $C_{10}H_{13}O_3S_{0.09}$ ) it is predicted that lignin may decompose as CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>. To understand this TPO-MS experiments were performed.

TPO-MS (Micromeritics autochem II chemisorption analyzer-fiefer instrument) attached with thermal conductivity detector (TCD) and mass-spectroscopy was used for the study. The experiments were performed uner 5%  $O_2$  (95% He v/v) or 100% He to understand the effect of environment on the lignin decomposition product formation. For the experiments ca. 30 mg lignin sample was taken in a sample tube. The following TPO program was used;

a) Pre-treatment for removal of moisture: RT  $\rightarrow$  5 °C/min  $\rightarrow$  120 °C (hold time: 2 h)  $\rightarrow$  Cooling (50 °C)

b) Analysis:  $50 \,^{\circ}\text{C} \rightarrow 5 \,^{\circ}\text{C/min} \rightarrow 800^{\circ}\text{C}$  (hold time: 10 min)  $\rightarrow$  Cooling (RT) (oxidation/decomposition in the presence of 5% O<sub>2</sub> + 95% He (*v/v*) *OR* 100% He)

The lignin sample was selected in order to study their thermal conversion behaviour. Heats of decomposition for each sample were measured during continuous heating at a prescribed heating rate. The decomposition generally started in lignin sample in case of 100% He, at 200 °C to 770 °C; while in case of 5%  $O_2 + 95\%$  He decomposition started at ca.300 °C and was completed at 550 °C in a series of endo and exothermic reactions influenced by its lignin.

As seen from Fig. 3 (main text), lignin showed decomposition over a broad range of temperatures due to presence of various types of linkages (Fig. S1), functional groups and bond dissociation enthalpies on lignin (ESI, Section S1 Table S1, Fig. S1). As listed in Tables S1 and S6 depending on the temperature, cleavage of aryl-aryl/alkyl (C-C) or aryl-ether (C-O-C) linkages is possible.<sup>16-17</sup> It is worth noting here that when experiment was done with 5% O<sub>2</sub>, highly intense peaks for gaseous products (CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub> etc. Table S6, equations S1-16) were observed, while formation of these products was less under inert atmosphere (100% He). Importantly, observance of ozone under both the conditions informs possibility of radical mechanism in the depolymerisation of lignin under thermal conditions.

Based on these observations following equations are proposed;

RH	>	R' + H'	(S1)
$R' + O_2$		R-OO'	(S2)
R-OO' + RH		$R-OOH + R^{\bullet}$	(S3)
2H <b>'</b>		$H_2$	(S4)
ROOH		RO' + 'OH	(S5)
2ROOH		RO' + ROO'	(S6)
RO'		CO + R'	(S7)
ROO'		$CO_2 + R^{\bullet}$	(S8)
$Na_2SO_4$		$Na' + SO_4'$	(S9)

$SO_4$		$SO_2 + OO^{\bullet}$	(S10)
$O_2 + OO'$	>	$O_3 + O^{\bullet}$	(S11)
RCH <sub>3</sub>	>	$R' + CH_3'$	(S12)
$CH_3$ + H	>	$CH_4$	(S13)
R-O-CH <sub>3</sub>		$RO' + CH_3'$	(S14)
ROO' + O'		$O_2 + R-O'$	(S15)
$R' + CH_3'$	>	RCH <sub>3</sub>	(S16)

Table S6. Decomposition of lignin into various products in TPO-MS experiment.

Sr.	Molecules (m/z, g/mol)	Temperature (°C)	Temperature (°C)		
No.		100% He	5% O <sub>2</sub> + 95% He		
1	Carbon monoxide (28)	310	370, 475		
2	Carbon dioxide (44)	445	370, 475		
3	Benzene (78)	558, 675	345, 475		
4	Sulphur dioxide (64)	240, 355, 690	310		
5	Methane (16)	225	(-310, -510)*, 425		
6	Hydrogen (2)	690	350, 475		
7	Ozone (48)	225	310, 340		
8	Oxygen (32)	(-235)*, 290	(-375, -490)*		
9	Toluene (92)	(-225)*, 280, 440, 700	-		
10	Water (18)	-	(-210, -410)*, 350		
Notes:	Notes: *: energy consumed during decomposition, - value indicates endothermic process				

The similar experiments were also done using following substrates to calibrate the system and to understand the effect of conditions on decomposition products formation.

Sulphur dioxide, carbon monoxide, carbon dioxide, methane, hydrogen, oxygen etc. are used for the calibration of the TPO-MS instrument.

With all above substrates formation of decomposition products are obtained which were matched with the lignin sample and also with decomposed products (CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, O<sub>2</sub>).

#### S4.2) Product stability

For the product stability study following composition was used;

Vanillin: 80 mg, methyl vanillate: 20 mg, *m*-cresol: 60 mg, guaiacol: 60 mg, 1,4-dimethoxybenzene: 60 mg and eugenol: 80 mg.

To the above mixture of compounds, 0.5 g of  $[C_3SO_3HMIM][HSO_4]$  and water:methanol (1:5 v/v) was charged. Reactor was heated between 80-170 °C and after attaining the desired temperature, stirring (1000 rpm) was continued for 1 h. After completion of reaction the reactor was slowly cooled down to room temperature and sample were collected for GC analysis (program used was same as mentioned in Section S3). Similar experiment was also conducted without catalyst.





**Fig. S17** Products stability checked using GC-FID. (a) reaction mixture before reaction, (b) reaction mixture after 120 °C reaction and (c) reaction mixture after 170 °C reaction. All the reactions were performed with  $[C_3SO_3HMIM][HSO_4]$  as catalyst.

## S4.3) Correlation between lignin structure and products

## S4.3.a) Gel permeation chromatography

GPC (DMF) VISKOTEK TDA 305-040 Triple Detector Array refractive index (RI), viscometer (VISC), low angle light scattering (LALS), right angle light scattering (RALS) GPC/SEC MODULE was used. The separations were achieved by using different columns (T6000M, GENERAL MIXED ORG, 300 X 7.8 mm; TGAURD, ORG GUARD COL, 10 x 4.6 mm). DMF was used as mobile phase at 60 °C under a constant flow rate of 1 mL/min. GPC samples were prepared at concentrations of 10 mg/mL. The instrument was calibrated using polystyrene standards.



Fig. S18 GPC (DMF) analysis profiles for (a) DMF solvent, (b) lignin and (c) THF soluble products obtained with  $[C_3SO_3HMIM][HSO_4]$  as catalysts.

The lignin had a high molecular weight of ca. 60 kDa as determined from GPC study (Fig. S18).

## S4.3.b) Differential Scanning Calorimetric analysis (DSC)

Melting and crystalline temperature of lignin and THF soluble products were recorded on DSC Q-10 (TA instruments, USA) under N<sub>2</sub> atmosphere with a heating rate of 10 °C/min from 50 to 300 °C. For more details please see Fig. 4 (main text).

### S4.3.c) UV-Visible spectroscopy:

The chromophoric groups were identified with the help of UV-Vis absorption measurement of the sample using PerkinElmer spectrophotometer (model-Lambda 650). Sample (2 mg) was dissolved in methanol (10 mL) and analysed from a range of  $\lambda = 200-400$  nm.



Fig. S19 UV-Visible spectra of (a) lignin, (b) THF soluble products in methanol.

## S4.3.d) FT-IR spectra of dealkaline lignin and THF soluble product:

Presence of functional groups in lignin and THF soluble products were analysed using FT-IR (FT-IR-8300 Shimadzu) technique. For the analysis, pallets were made with KBr by maintaining 1wt% concentration. The normalization of intensities was performed based on the exact concentration used for making pallets.

The FT-IR spectrum (ESI, Fig. S20a) of lignin illustrates presence of various functional groups such as hydroxyl ( $\sim$ 3400 cm<sup>-1</sup>), methoxy C-H ( $\sim$ 2935 cm<sup>-1</sup>), and carbonyl ( $\sim$ 1730, 1770 cm<sup>-1</sup>). Multiple peaks for aromatic C=C (in ring) (1400-1600 cm<sup>-1</sup>), ether bonds (~1125, 1200-1270 cm<sup>-1</sup>), and primary alcohols (1040-1060 cm<sup>-1</sup>) etc. were also observed in the spectrum. The FT-IR study of products (Fig. S20b) demonstrate that besides peaks observed in parent lignin sample with similar or different intensities, emergence of few new peaks was seen. A new peak appeared at 1180 cm<sup>-1</sup> (s) was assigned to C-O (stretch) in phenol or to C-O (stretch) in lactone and acyl group. Another major peak visible at 1068 cm<sup>-1</sup> is assigned to (sp<sup>3</sup>) alkoxy C-O. Peaks at 850 and 885 cm<sup>-1</sup> are assigned for (sp<sup>2</sup>) C-H bending in substituted benzene and R<sub>2</sub>C=CH<sub>2</sub> (geminal disubstituted alkene). Twin peaks visible at 1730, 1770 cm<sup>-1</sup> are due to C=O stretch in acids/esters/aldehydes/ketones. The increase in peak intensity (2875 cm<sup>-1</sup>) in products implies that this contribution is primarily from aldehyde group (C-H stretch). Appearance of peak at 2945 cm<sup>-1</sup> because of C-H stretching in (sp<sup>3</sup>) alkanes is in line with multiple peaks observed for alkanes (1380-1460 cm<sup>-1</sup>) in products. An enhancement in intensity of broad peak in products at 3200-3500 cm<sup>-1</sup> due to RO-H (alcohol) implies that lignin undergoes depolymerisation. A decline in intensity for peaks at 1040 (aromatic) and 1125 cm<sup>-1</sup> (aliphatic) due to ether linkages in products compared with lignin again corroborate that lignin undergoes depolymerisation. This study reveals that most of the functionalities present in lignin are conserved in products and also some new functionalities are introduced because of cleavage of several bonds in lignin.



**Fig. S20** FT-IR spectra of (a) lignin and (b) THF soluble products. Reaction condition: lignin (2 wt.% solution  $H_2O:CH_3OH$ , 1:5 v/v), [C<sub>3</sub>SO<sub>3</sub>HMIM][HSO<sub>4</sub>] (0.5 g), 120 °C, 1 h, 1000 rpm.

## S4.4) Interaction studies

## S4.4.a) NMR analysis

S4.4a.i) 1D (<sup>1</sup>H) NMR

200.13 MHz and 500.13 MHz frequency Bruker Avance-200/500 NMR instrument were used for  ${}^{1}$ H spectra at 27.0 and 25.9 °C in DMSO-d<sub>6</sub> (2.5 ppm).

## S4.4a.ii) 1D (<sup>13</sup>C) NMR

50.23 MHz and 125.76 MHz frequency Bruker Avance-200/500 NMR instrument were used for  ${}^{13}C$  spectra at 27.05 and 26.1 °C in DMSO-d<sub>6</sub> (39.52 ppm) was taken as reference.

## S4.4a.iii) 2D HSQC NMR

2D (HSQC) NMR were also recorded at 25 °C using Bruker Avance-500 MHz (operating at a frequency of 500.13 MHz) spectrometer for lignin and [BMIM][Cl] samples in DMSO-d<sub>6</sub> (2.5 ppm) was taken as reference.

## S4.4a.iV) 2D NOSEY NMR

2D (NOSEY) NMR were also recorded at 25  $^{\circ}$ C using Bruker Avance-400 MHz (operating at a frequency of 400.13 MHz) spectrometer for vanillin and [BMIM][Cl] samples in DMSO-d<sub>6</sub> (2.5 ppm) was taken as reference.

All the samples were prepared by keeping same quantity of DMSO-d<sub>6</sub> of 700  $\mu$ L. As shown in Table S7 quantities of cumene, vanillin, guaiacol glyceryl ether and [BMIM][Cl] were taken for analysis in DMSO-d<sub>6</sub>.

Sr. No.	Compound	Quantity ( ±0.02 mg)		
For neat samples				
1	Cumene	15.8		
2	Vanillin	20		
3	Guaiacol glyceryl ether	26.06		
4	Lignin	70		
5	[BMIM][Cl]	22.97 mg for monomer and		
		dimer, in case lignin 48.5 mg		
For mixtures	'	'		
6	Cumene	15.8		
	[BMIM][Cl]	22.97		
7	Vanillin	20		
	[BMIM][Cl]	22.97		
8	Guaiacol glyceryl ether	26.06		
	[BMIM][Cl]	22.97		
9	Lignin	70		
	[BMIM][Cl]	48.5		
For concentration study				
10	For 0.5 molar ratio			
	Vanillin	10		
	[BMIM][Cl]	22.97		
11	For 1 molar ratio			
	Vanillin	20		
	[BMIM][Cl]	22.97		
12	For 1.5 molar ratio			
	Vanillin	30		
	[BMIM][Cl]	22.97		
13	For 3.0 molar ratio			
	Vanillin	60		
	[BMIM][Cl]	22.97		
14	For 5.0 molar ratio			

Table S7a. Summary on the concentrations used for NMR studies.\*

Vanillin	100
[BMIM][Cl]	22.97

**Table 7b.** Summary on the concentrations, data points and scans used for HSQC and NOSEY NMR studies.\*

Sr.	Compound	Quantity (±0.02 mg)	Data points	Number of scans
No.				
For neat samples				
1	Vanillin	20	1024	128
2	Lignin	70	1024	88
3	[BMIM][Cl]	22.97	1024	160
For mixtures				
4	Vanillin	20	1024	128
	[BMIM][Cl]	22.97		
5	Lignin	70	1024	128
	[BMIM][Cl]	48.5		
NOSEY spectra of vanillin and [BMIM][Cl]				
6	Vanillin + [BMIM][Cl]	20 + 22.97	1024	16

**HSQC:** From 0 to 10 p.p.m. in F2 (<sup>1</sup>H) with 1,024 data points, 0 to 200 p.p.m. in F1 (<sup>13</sup>C) with 256 increments of 128 scans for Vanillin, 88 scans for lignin, 160 scans for [BMIM][Cl], 128 scans for Vanillin & [BMIM][Cl] and 128 scans for lignin & [BMIM][Cl].

**NOSEY:** From 0 to 10 p.p.m. in F2 (<sup>1</sup>H) with 1,024 data points, 0 to 10 p.p.m. in F1 (<sup>1</sup>H) with 256 increments of 16 scans for Vanillin & [BMIM][C1].

\* All the samples were prepared in 700  $\mu$ L DMSO-d<sub>6</sub>.

## S4.4.b) Molar concentration study on chemical shift

In a vanillin concentration study (Figs. S21a, b), maximum ( $^{1}$ H) chemical shift was observed at 0.5 and 1 molar ratio (vanillin/IL) for vanillin (Fig. S21a) and later at higher molar ratios (1.5, 3 and 5) it declined. Nevertheless, at the same time continuous increase in chemical shift in IL was seen (Fig. S21b). These contrasting results were exhibited due to change of concentration of both vanillin and IL in DMSO-d6. Until reaching stoichiometric amount of vanillin to IL, increase in chemical shift was observed but when surplus (above stoichiometric >1 molar ratio) vanillin  $^{1}$ H 1D NMR studies (Fig. 6b in the main text).



**Fig. S21.** (a) Effect of molar concentration on chemical shift of vanillin for mixture of [BMIM][Cl] & vanillin; and (b) Effect of molar concentration on chemical shift of [BMIM][Cl] for mixture of [BMIM][Cl] & vanillin. All the spectra were recorded in DMSO-d<sub>6</sub>.

#### S4.4.c) Proposed mechanism

As change in concentration of  $H^+$  in the solution showed difference in the products yields it is expected that this mechanism is credible (Fig. 8, main text). Moreover, BAILs may not be able to catalyze cracking reactions at 120 °C and therefore solitary possibility is the hydrolysis reaction under the reaction conditions. Additionally, it is projected that since with alteration in BAIL, no distinction in product formation is seen, the foremost role of BAIL is to contribute the  $H^+$  to the reaction solution and carry out the hydrolysis reaction. While, this role is major, the attachment of BAIL with substrate molecule enhances its probability for depolymerisation because even if same concentration of  $H^+$  was present when  $H_2SO_4$  was used as catalyst still, most of the products formed were not low molecular weight aromatic monomers as is seen from GC-MS analysis (ESI, Fig. S8).

#### S4.4.d) RAMAN analysis

Vanillin, Ionic liquids and mixture of vanillin and ionic liquids were subjected for Raman shift analysis using LabRAM HR Evolution instrument (HORIBA Scientific) using monochromatic radiation emitted by an  $Ar^+$  laser (514.5 nm) operating at 100 mW.



Fig. S22 Raman spectra of (a) [BMIM][Cl], (b) vanillin and (c) [BMIM][Cl] + vanillin at room temperature.



Fig. S23 Possible mode of interaction between IL and vanillin. (a) Parallel (b) Perpendicular

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