Electronic supplementary material for

Transformation of cellulosic saccharides into alkyl glucosides catalyzed by bifunctional ionic liquids

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Experimental

General preparation of the hydrophobic Brösted acidic ILs

BFIL**1** was synthesized as follows: Under reflux condition, bis(1-imidazolyl)methane (0.10 mol) was dissolved in 1-bromobutane (0.11 mol) with 3 mL acetone and stirred for 16 h at 60 oC under an argon atmosphere. A white crystalline solid ([BIm(CH_2)Im][Br]) formed, which was filtered, washed with ethyl acetate (10 mL×3), then dried in a vacuum. [BIm(CH_2)Im][Br] (0.09 mol) was added to an aqueous solution of lithium bis(trifluoromethanesulfonyl)imide (0.09 mol) and stirred at room temperature for 2 h. The [BIm(CH_2)Im][NTf_2] automatically separated from the water. The bottom product layer was separated and washed with distilled water (20 mL×3), then dried under vacuum. The obtained 0.088 mol [BIm(CH_2)Im][NTf_2] was dissolved in 30 mL acetonitrile. Under vigorous stirring, 0.088 mol 1,3-propanesultone was dissolved in 20 mL acetonitrile and then added drop by drop into the above solution. After addition, the solution was further agitated at 40 ^oC for 4 h, then 0.088 mol methanesulfonic acid was added under agitation. After agitation for another 4 h, the resultant mixture was treated in vacuum to remove acetonitrile; a sticky liquid, BFIL**1**, was obtained and washed with distilled water (20 mL×3), then dried in vacuum and characterized by H and C NMR, FT-IR spectroscopy, MS, and TGA. BFIL**2** and BFIL**3** were prepared by a similar method.

Typical procedure for transformation of cellobiose into alkyl glucosides

0.1 g cellobiose, 0.02 g catalyst, and 5 mL alcohol were added into a 10 mL reactor and sealed. The reactor was heated to 368K and kept for 4 h under vigorous agitation. After the reaction, 10 mL distilled water was added at room temperature, the upper aqueous layer which dissolved products and the bottom catalyst separated automatically, after separation, the catalyst can be reused by treatment in vacuum, and the product was analyzed by HPLC equipped with a Shedox Sugar Column (SH1011) and a refractive index detector (50 ^oC). The product were separated by SH1011 at 60 ^oC using 0.05 g/L H_2SO_4 as mobile phase with a fow rate of 0.5 mL/min. The injection volume for the HPLC analysis was 80 μL. Ethylene glycol(~0.5 g/L) was used as an internal standard.

Characterization Section

NMR

NMR measurements were recorded on a Brüker AV-400 Fourier transform NMR spectrometer using an inner capillary filled with CD_3OD for ^1H, ^{13}C, and ^{19}F NMR. Chemical shifts were reported in parts per million (ppm, δ).

BFIL**1** ($[NTf_2][BIm(CH_2)Im(CH_2)_3SO_3H][CH_3SO_3]$):
^1H NMR (CD_3OD): 0.98(t, 3H), 1.37(m, 2H), 1.77(m, 2H), 1.97(s, 1H), 2.31(m, 2H), 2.84(s, 3H), 3.30(t, 2H), 3.65(t, 4H), 6.41(s, 1H), 6.77 (d, 2H), 6.83(d, 2H), 7.52(s, 2H). ^{13}C NMR (CD_3OD): 12.8, 19.1, 24.1, 38.8, 43.6, 49.6, 51.7, 55.7, 65.6, 117.4(4), 136.9, 137.0, 137.1, 137.2. ^{19}F NMR (CD_3OD): -80.5 (s, $CF_3SO_2^-$)

BFIL**2** ($[NTf_2][BPyPy(CH_2)_3SO_3H][CH_3SO_3]$):

^1H NMR (CD_3OD): 0.96 (t, 3H), 1.14(t, 6H), 1.20(m, 2H), 1.97(m, 2H), 2.30 (s, 1H), 3.30 (s, 3H), 3.80(t, 2H), 8.90(d, 4H), 9.2(d, 4H). ^{13}C NMR (CD_3OD): 12.7, 19.0, 20.9, 31.3, 40.7, 50.0, 60.3, 61.4, 117.4(4), 136.8(2), 146.9(4), 148.3(2). ^{19}F NMR (CD_3OD): -80.5 (s, $CF_3SO_2^-$)

BFIL**3** ($[NTf_2][B(CH_3)_2N(CH_2)_2N(CH_3)_2(CH_2)_3SO_3H][CH_3SO_3]$):

^1H NMR (CD_3OD): 1.05(t, 3H), 1.49(m, 2H), 2.09(quint, 2H), 2.73(s, 1H), 2.94(quint, 2H), 3.08(s, 3H), 3.28(t, 4H), 3.32(s, 12H), 3.50(t, 2H), 3.67(t, 4H). ^{13}C NMR (CD_3OD): 12.5, 15.8, 19.2, 24.1, 43.1, 50.4, 57.0, 60.4, 61.1, 65.4, 121.0. ^{19}F NMR (CD_3OD): -80.5 (s, $CF_3SO_2^-$)

NMR spectra of BFILs

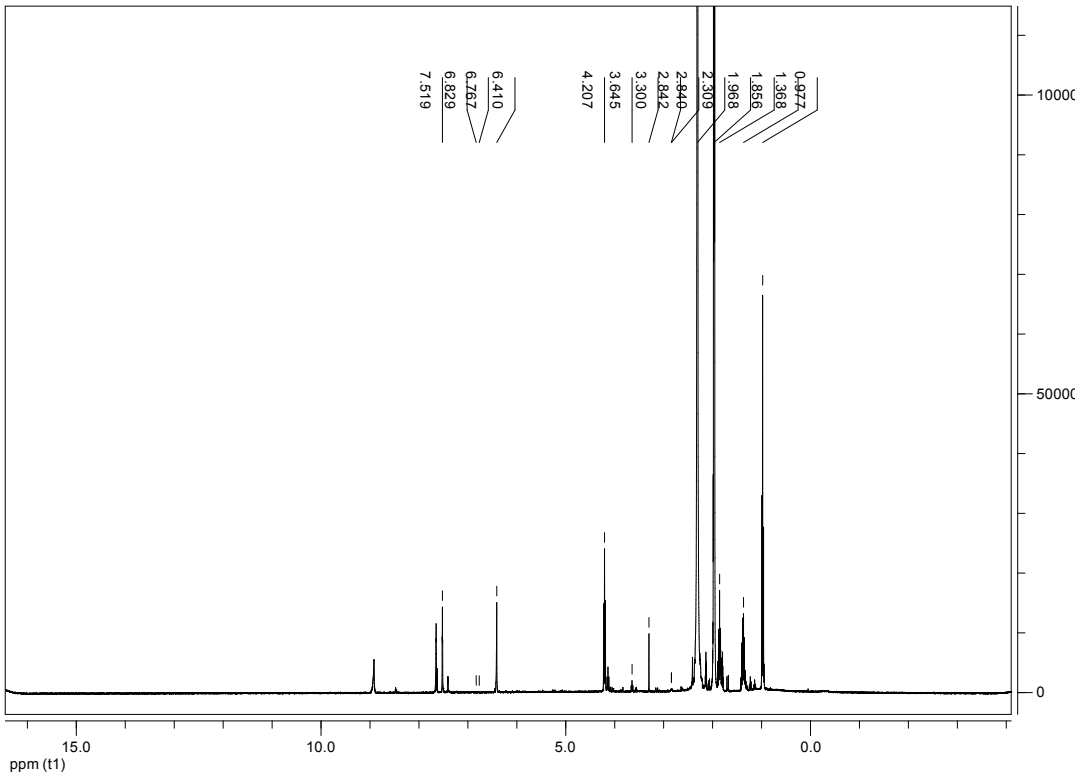

Fig. *S1* ^{1}H spectrum of BFIL**1**.

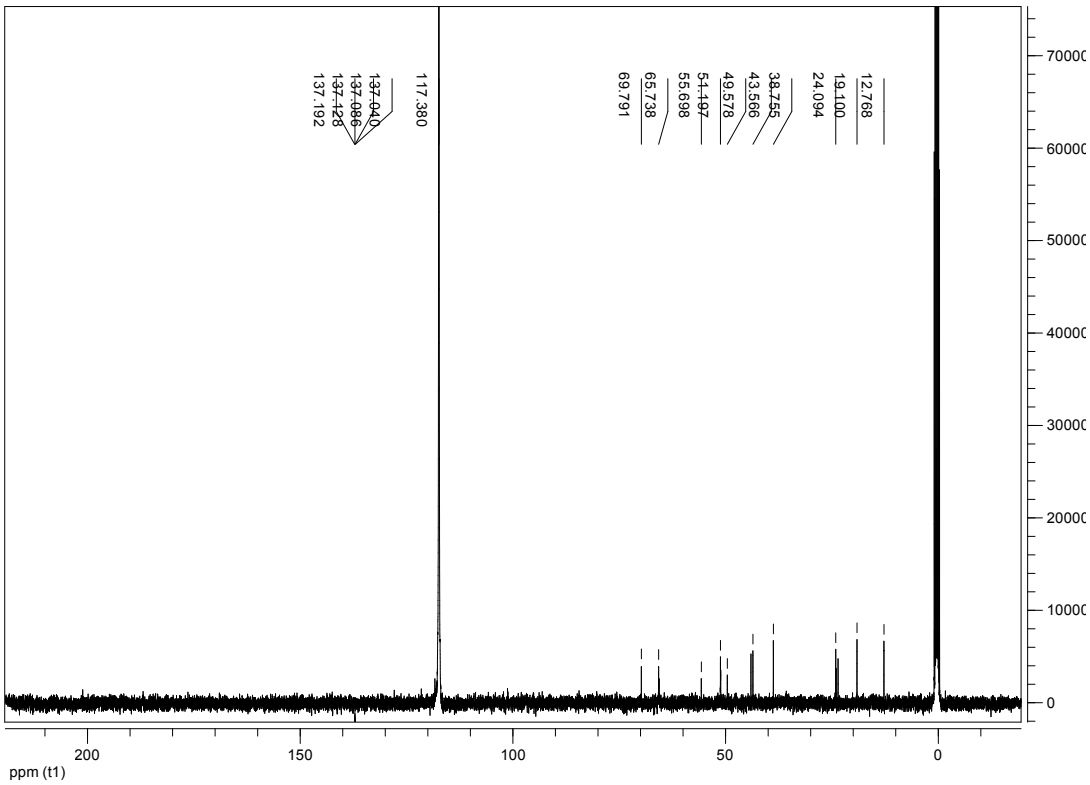

Fig. *S2* ^{13}C spectra of BFIL**1**.

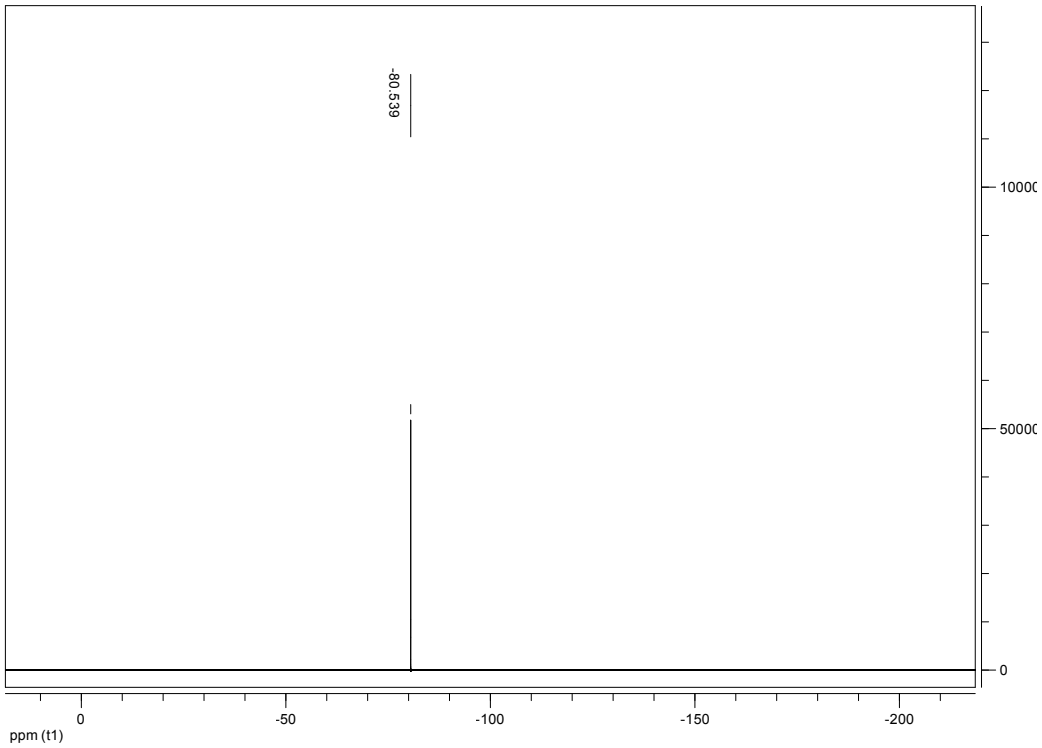

Fig. *S3* ^{19}F spectrum of BFIL**1**.

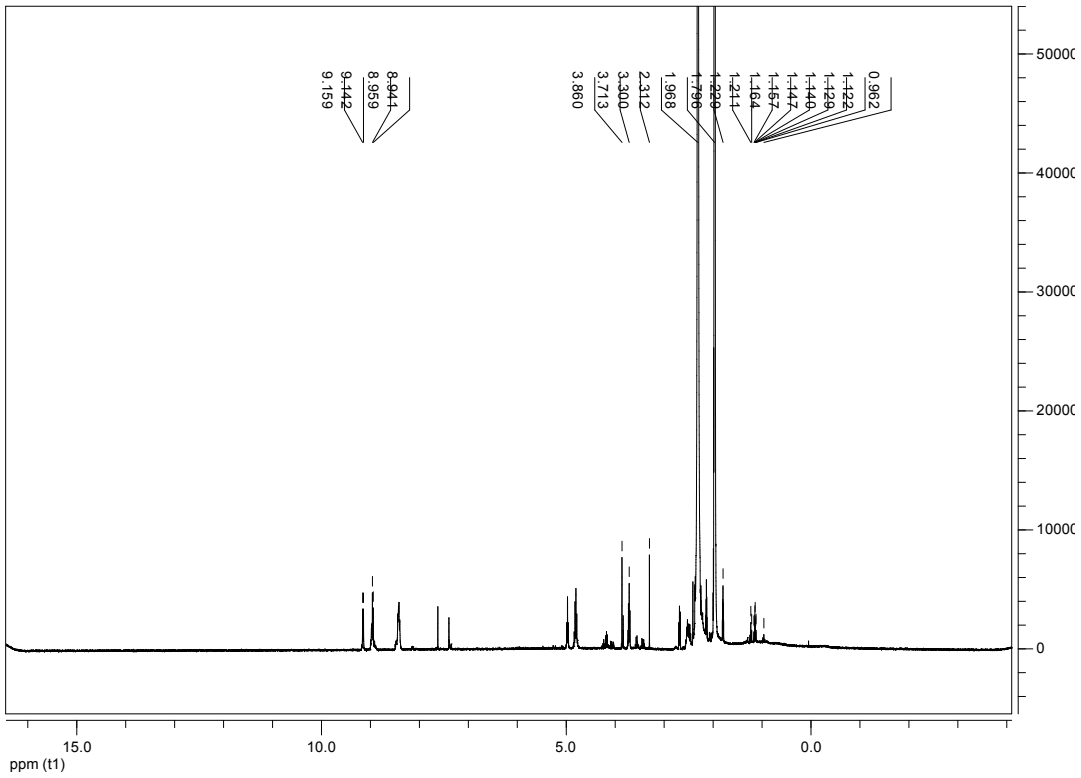

Fig. *S4* ^{1}H spectrum of BFIL**2**

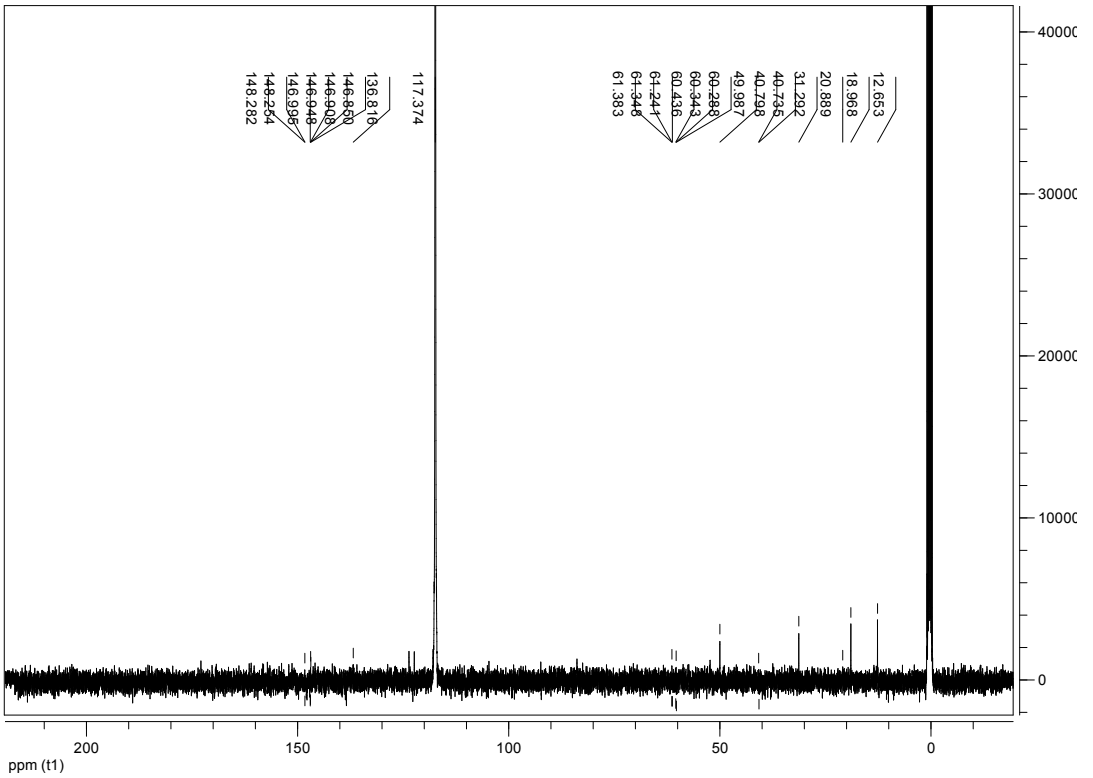

Fig. *S5* ^{13}C spectrum of BFIL**2**

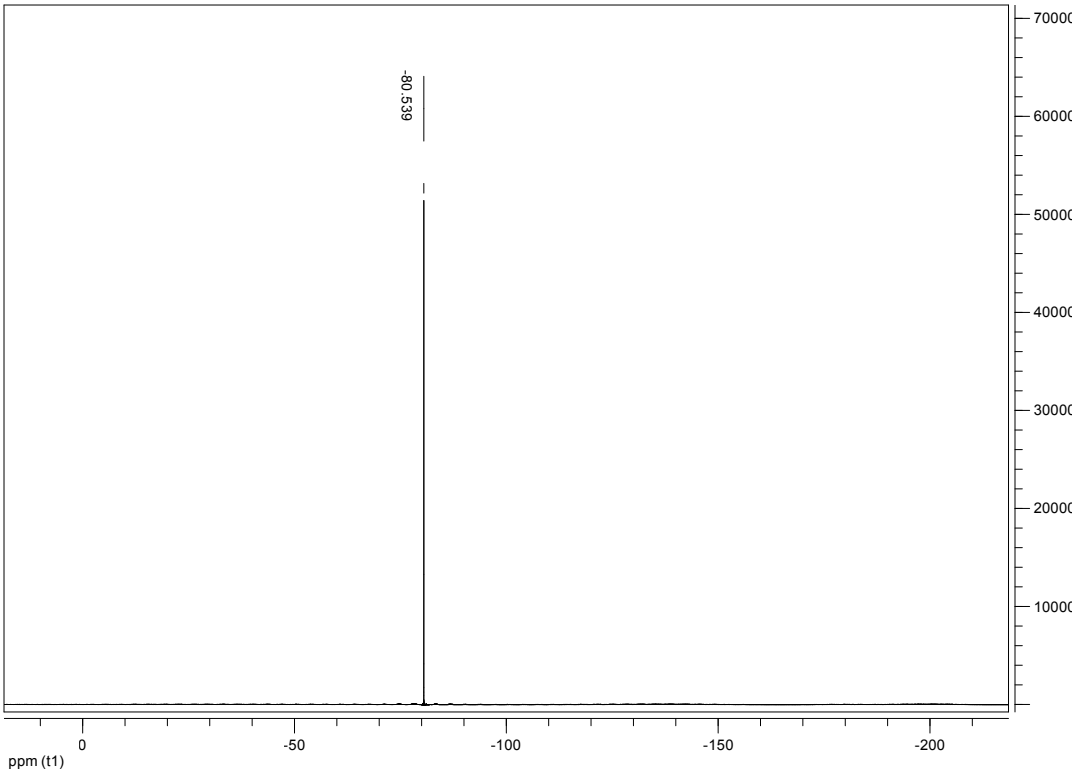

Fig. *S6* ^{19}F spectrum of BFIL**2**

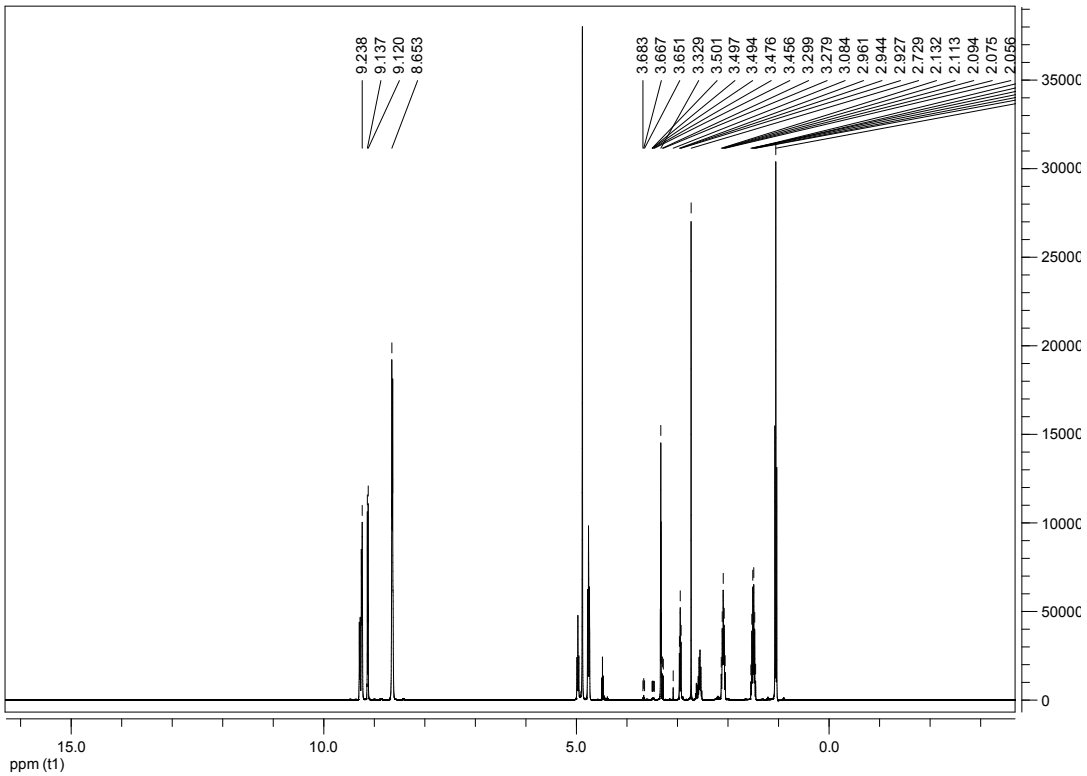

Fig. *S7* ^{1}H spectrum of BFIL**3**

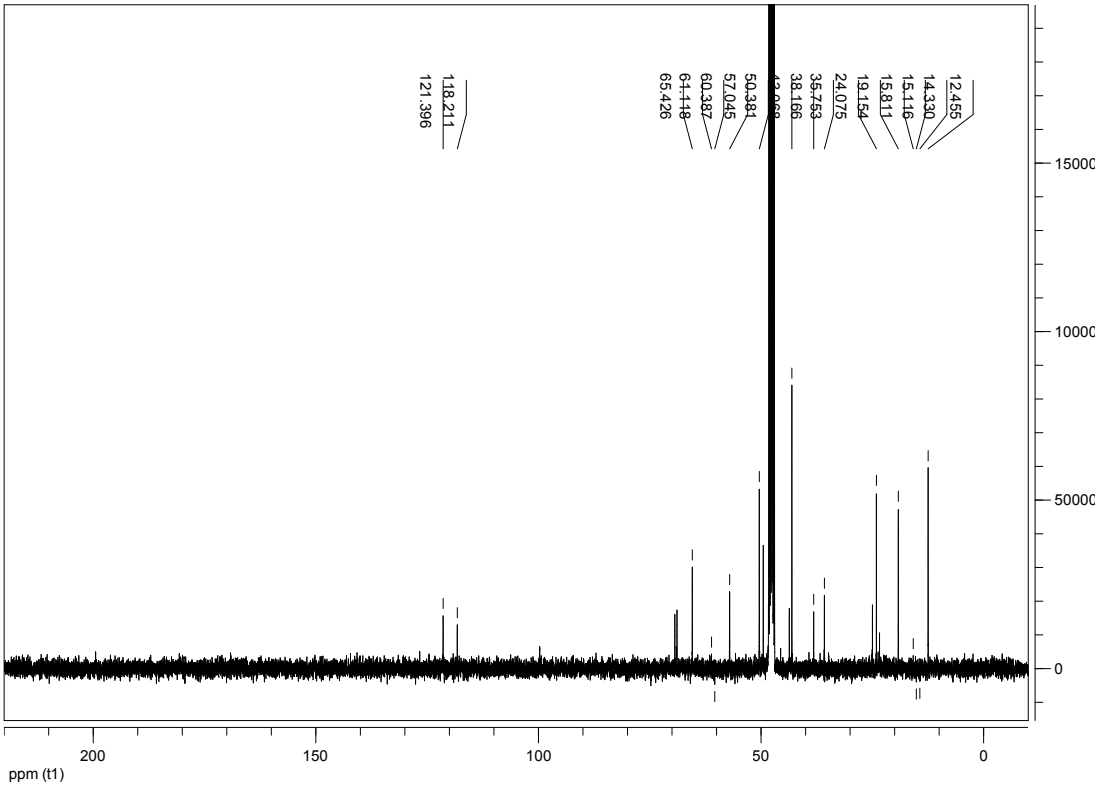

Fig. *S8* ^{13}C spectrum of BFIL**3**

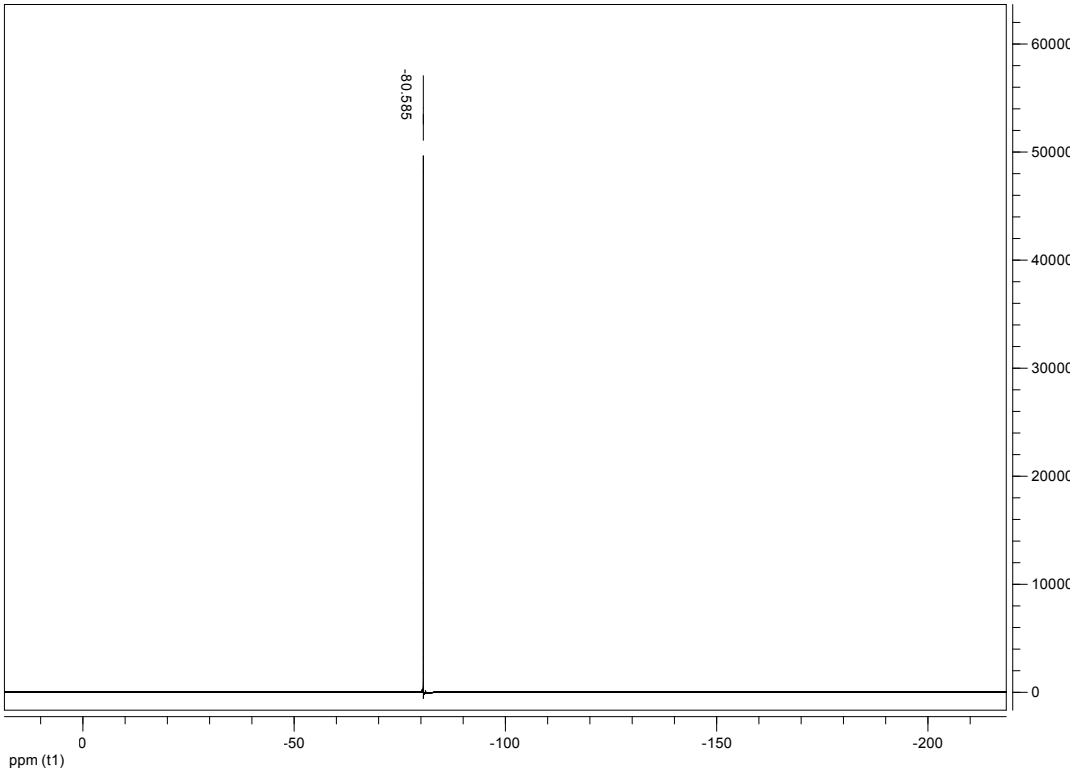

Fig. *S9* ^{19}F spectrum of BFIL**3**

FTIR

Fourier transform infrared spectra (FTIR) were obtained using Thermo Scientific Nicolet 6700 spectroscopy. The sample was coated on the surface of the pressed dry KBr sheet for measurement.

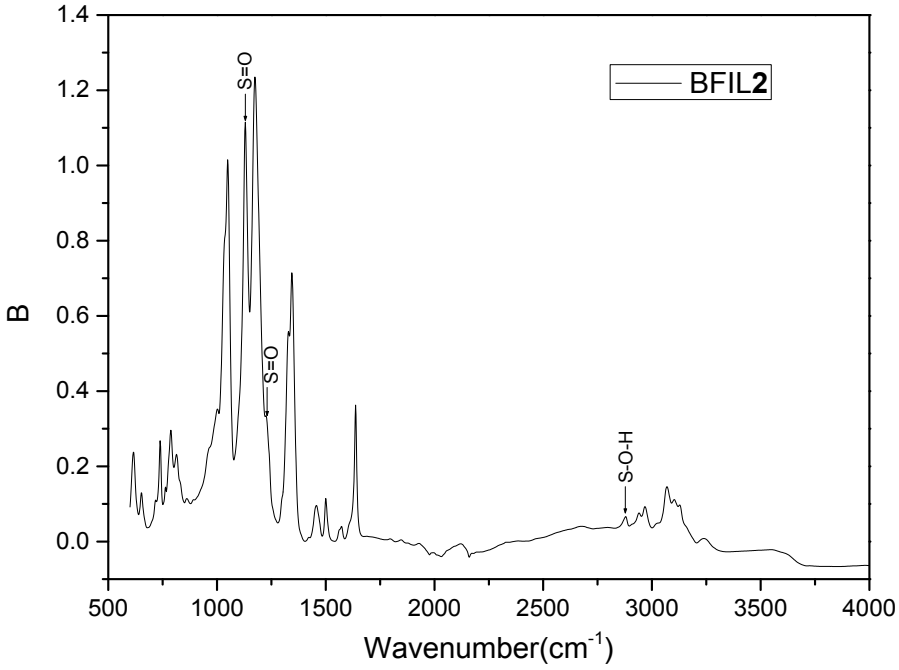

Fig. *S10* IR spectrogram of BFIL**2**.

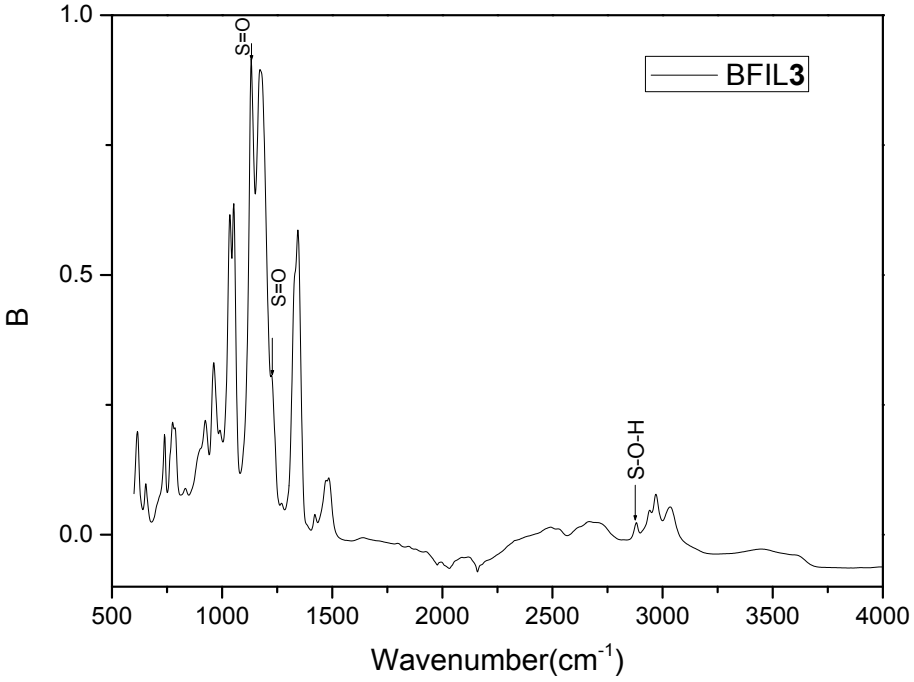

Fig. *S11* IR spectrogram of BFIL**3**.

TGA

Thermal gravimetric analysis (TGA) was performed with Simultaneous Thermal Analysis-STA 409EP. The samples for TGA were placed in an aluminium crucible, thermal analysis and temperature-dependent mass changes were examined in the range of 30 to 600 ºC. The thermal decomposition temperature (T_d) was recorded with 10% of mass loss of BFILs with scan rate of 10 ºC/min under N_2 atmosphere.

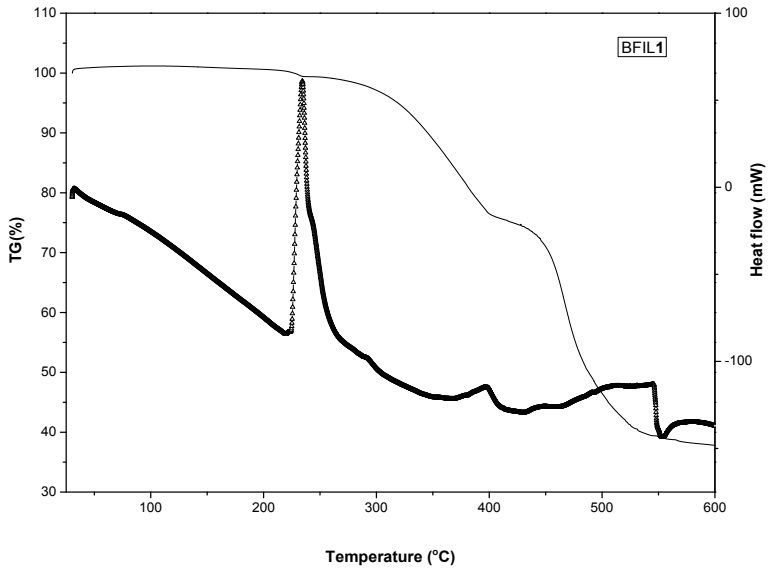

Fig. *S12* TGA spectrogram of BFIL**1**.

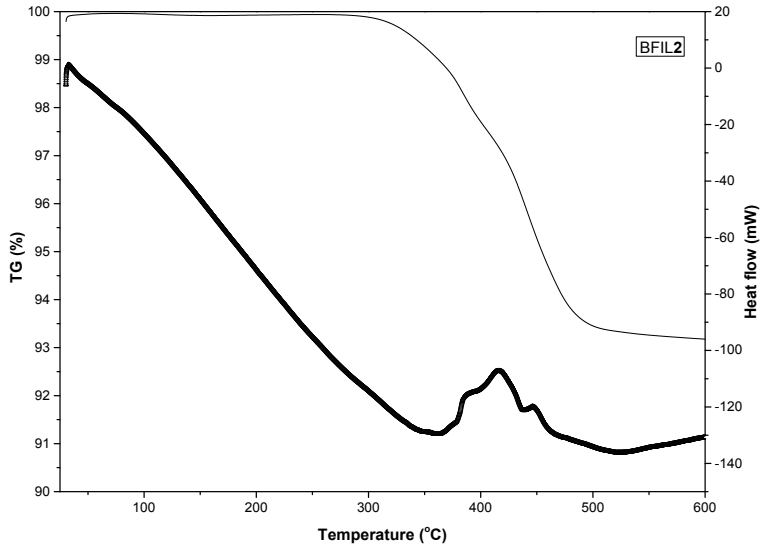

Fig. *S13* TGA spectrogram of BFIL**2**.

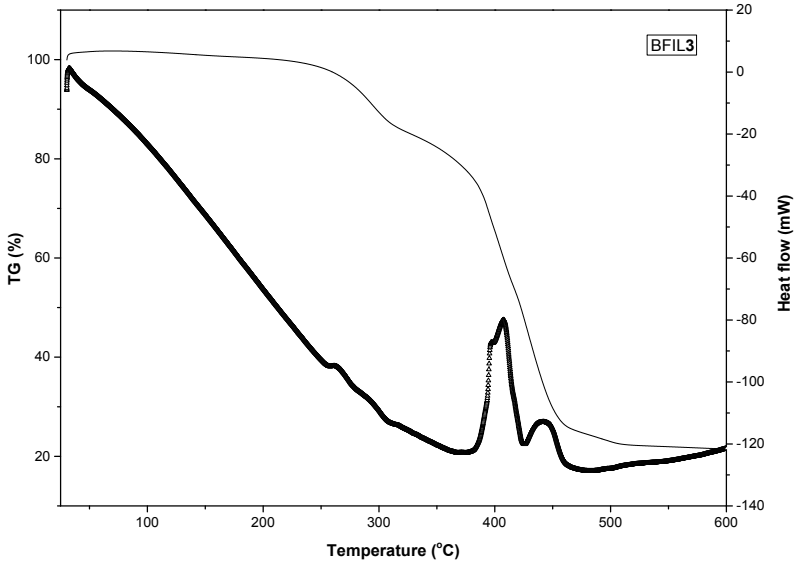

Fig. *S14* TGA spectrogram of BFIL**3**.

Contact Angles measurement

Contact angles were measured using a Drop Shape Analyzer (Phoenix-300 Touch, SEO, Korea) at 298.2 K. The sessile drop fitting method was used for flat surface. The ionic liquid drops were placed using a micro-syringe pointed vertically downward onto the flat glass surfaces.

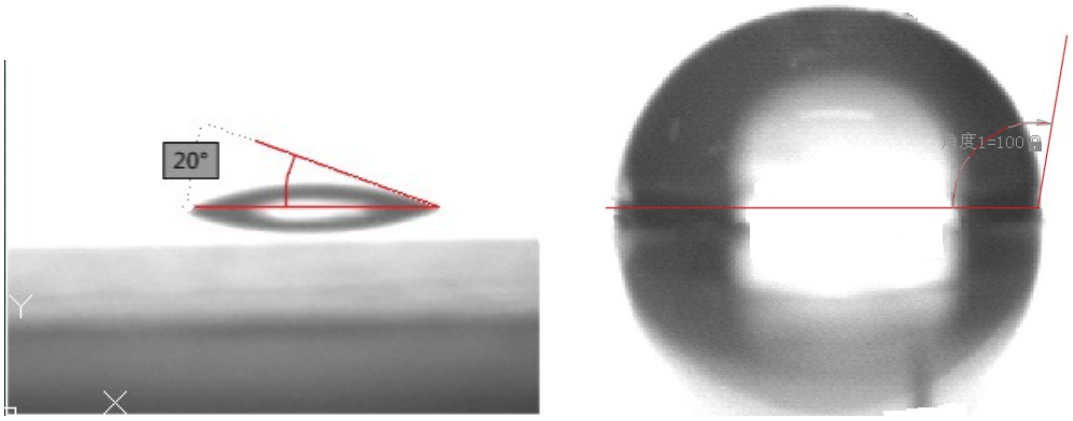

Fig. *S15* Contact angles of the precursor and BFIL**1** on the flat glass surface.

Mass Spectra

A GC model 6890N (Agilent Technologies, Waldbrom, Germay) fitted with a split/splitless injector and equipped with a MSD model 5975B (Agilent Technilogies, Tokyo, Japan) has been used in this work. One microlitre IL/Methanol solutions were injected in each case automatically by an autosampler model 7683 (Agilent).

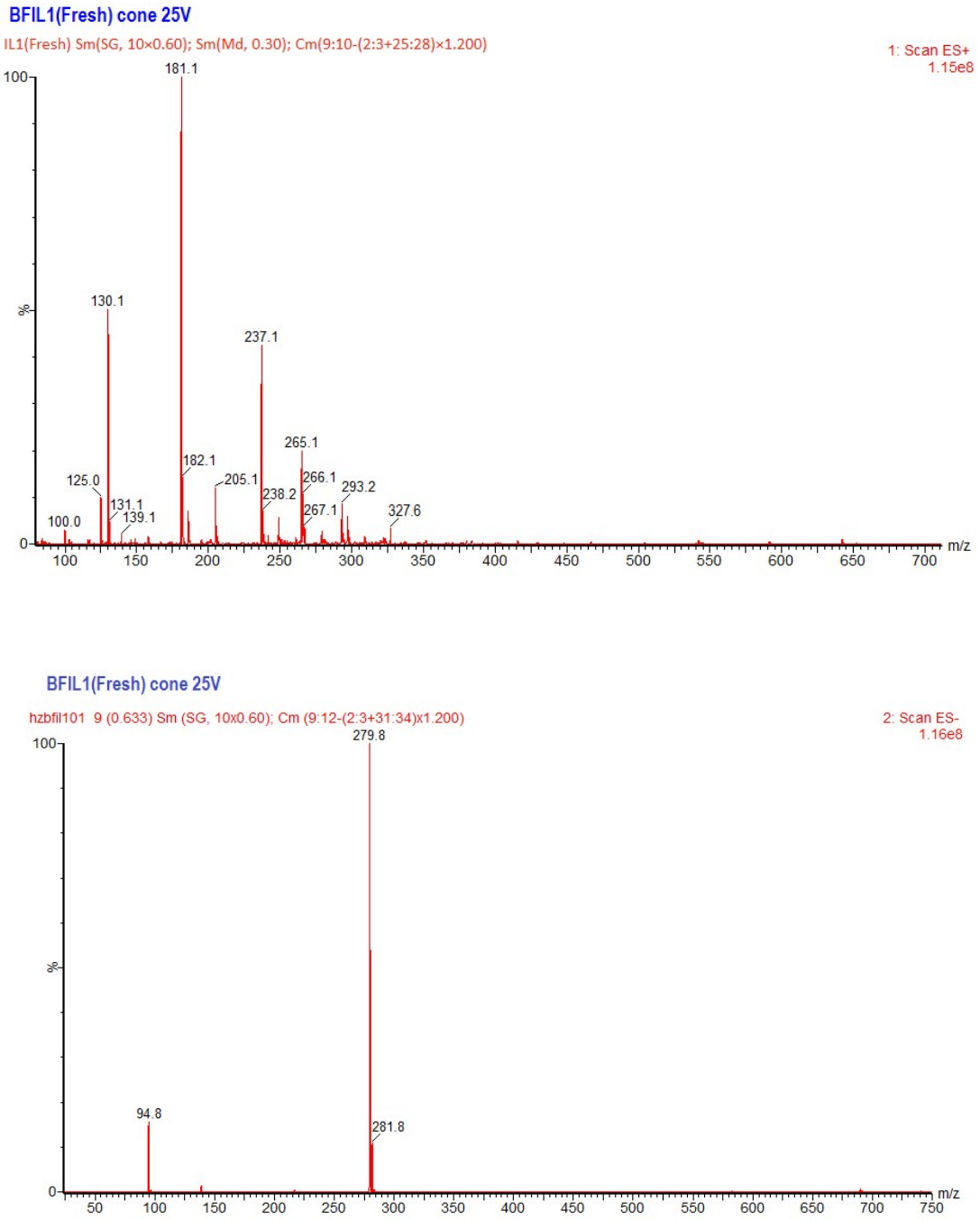

Fig. *S16* Mass spectra of the fresh BFIL**1**.

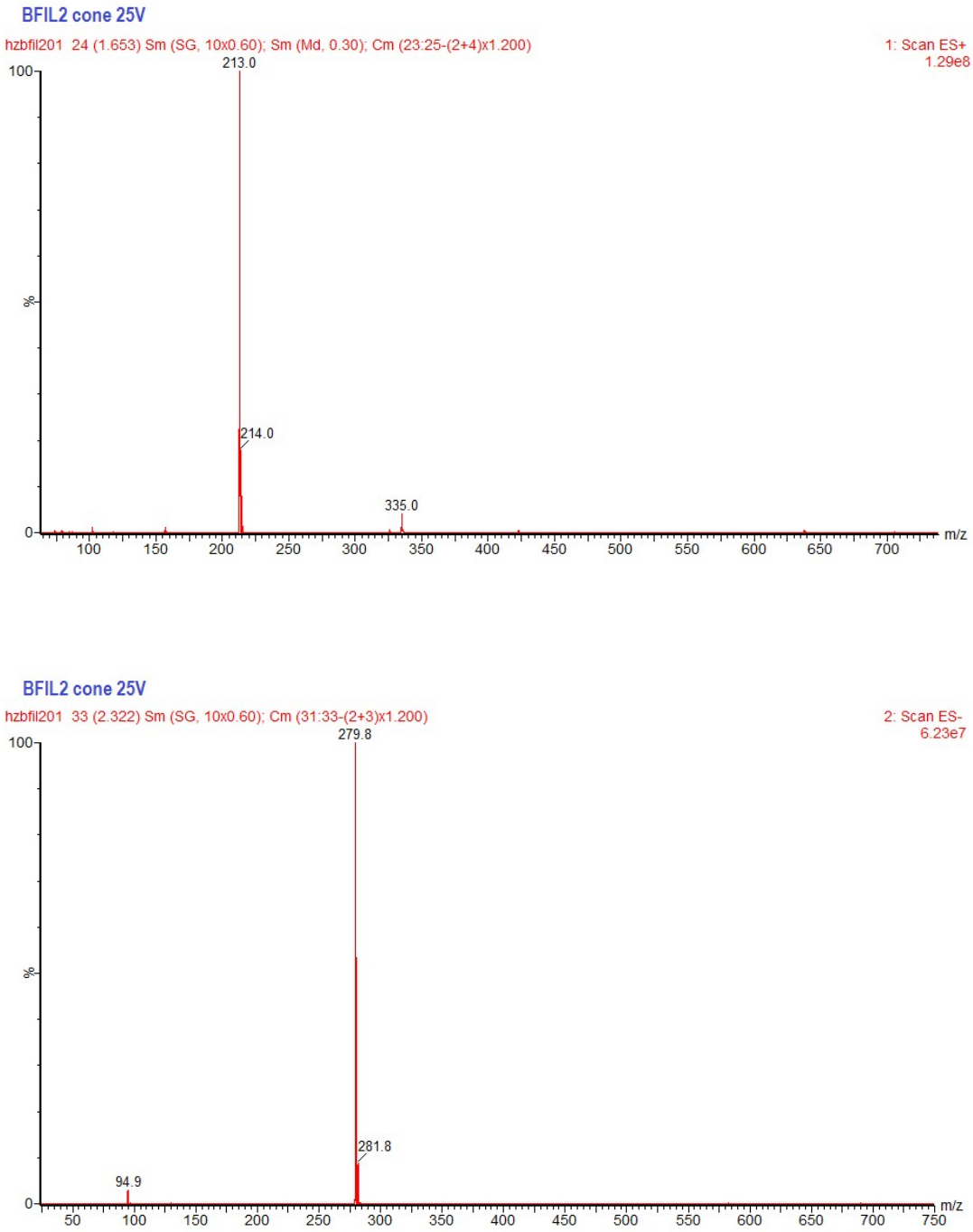

Fig. *S17* Mass spectra of the fresh BFIL**2**.

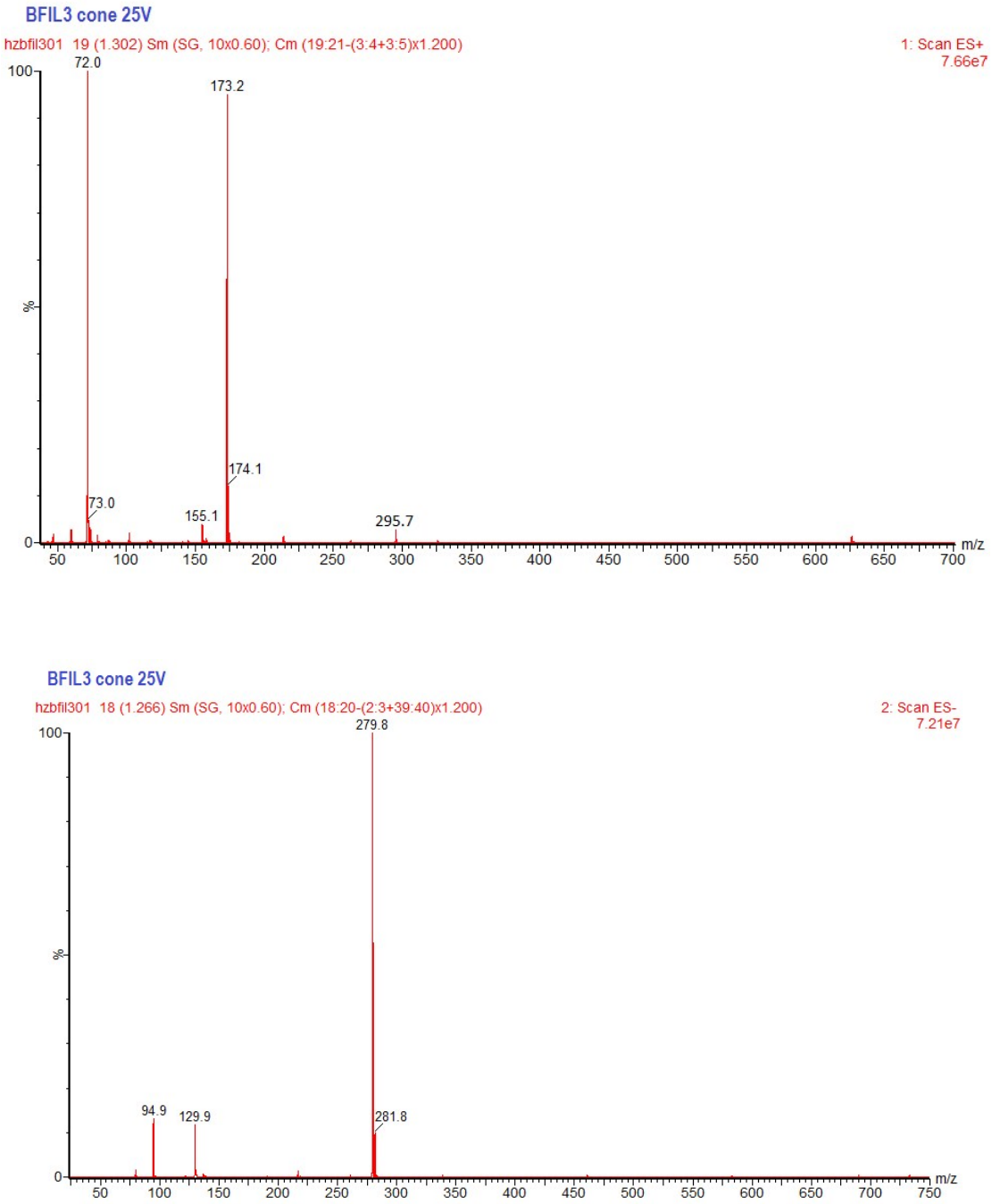

Fig. *S18* Mass spectra of the fresh BFIL**3**.

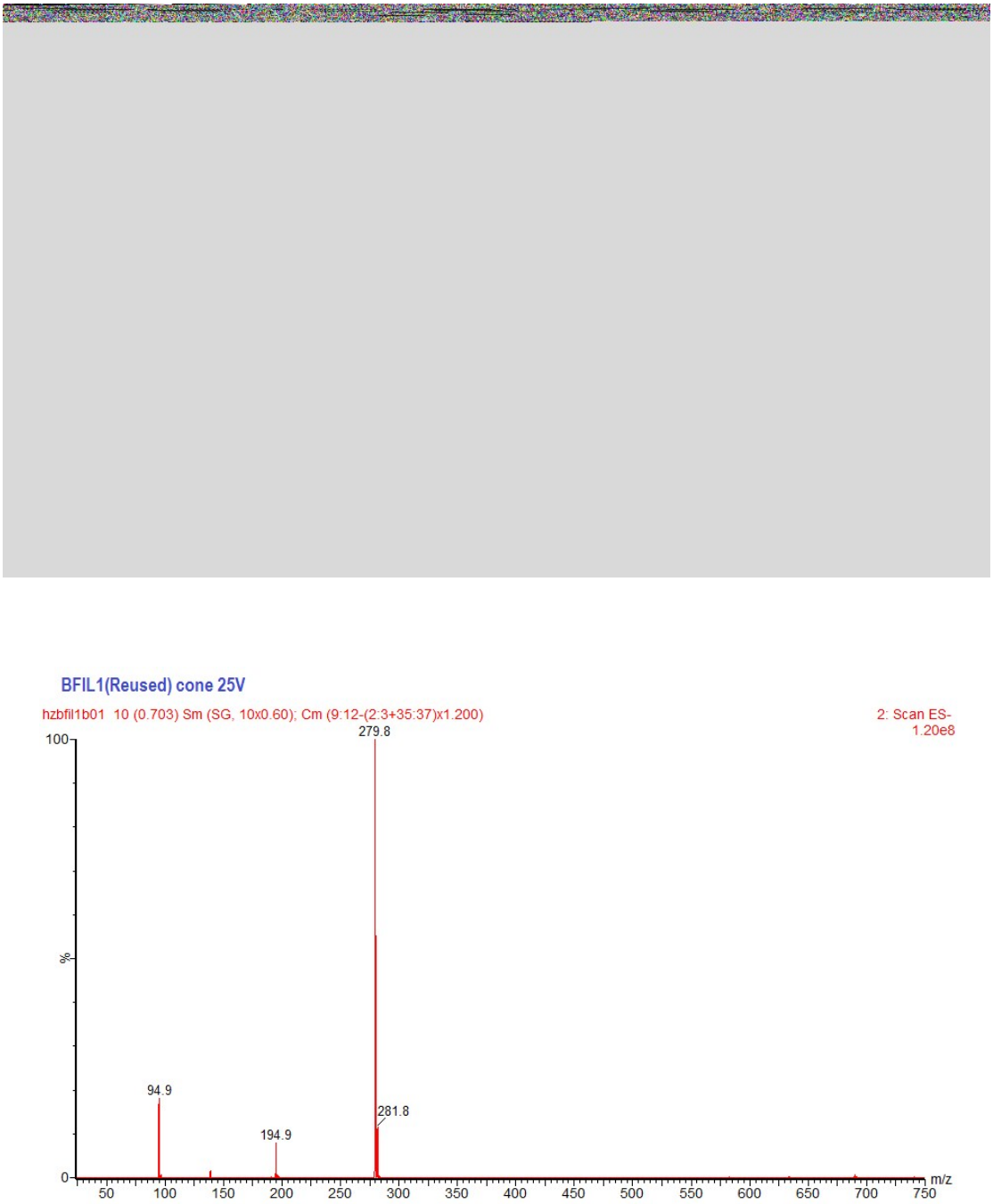

Fig. *S19* Mass spectra of the recovered BFIL**1** for the first time.

Acidity measurement

The acidic scales of the BFILs were measured by UV-vis spectra with basic indicators according to the procedure reported in the literature.[1] Based on eqn (1), where H_0 is the Hammett acidity function which represents the relative acidity of IL; [I] and [IH^+] are the molar concentrations of, respectively, the unprotonated and protonated forms of the indicator. Based on the Beer-Lambert law the absorption is proportional to the concentration of absorbing species in the material, and on condition of the same light path length, the ratio of [I]/[IH^+] can be calculated by the absorbance difference of basic indicator measured after addition of BFILs.

$$H_0 = pK(I) + \log([I]/[IH]^+) \qquad (1)$$

2-Nitrophenylamine (NPA) (8 mg L^{-1}, pK_a= - 0.2) in dichloromethane were chosen as the basic indicators. The concentration of each BFIL was set at 80 mmol L^{-1} in dichloromethane.

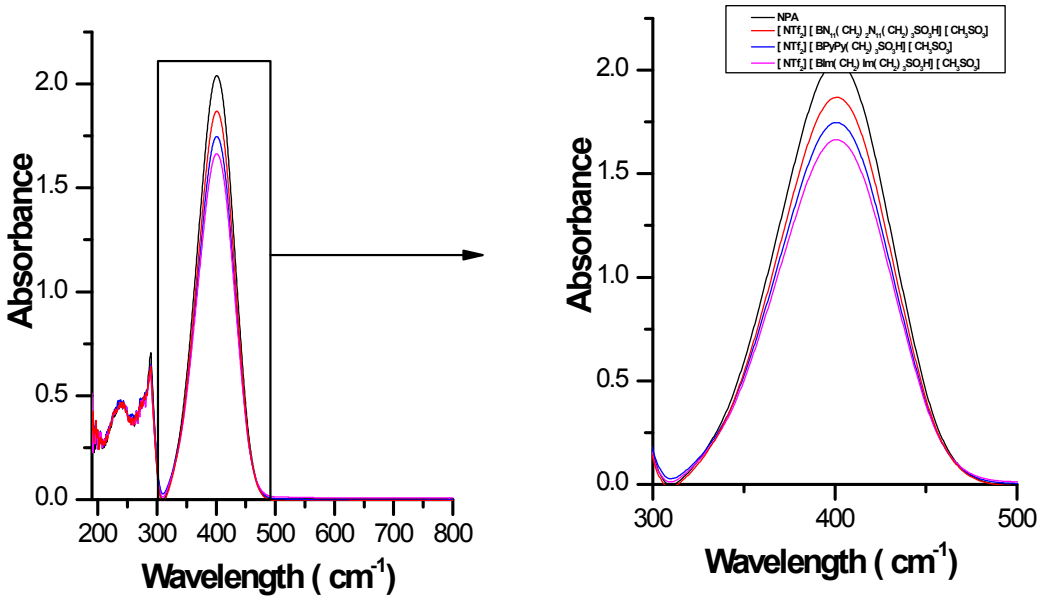

Fig. *S20* UV-Vis spectra of 2-nitrophenylamine basic indicators and after addition of the three BFILs.

XRD

X-ray powder diffraction measurement (XRD) was carried out using a PANalytical X'pert PRO equipped with Cu-Kαradiation (λ = 0.15418 nm). In a typical measurement, the ball-milled cellulose for different times was spread on a glass plate to form a thin film. Then the plate was moved into the platform. The scanning angle was between 10° and 50°, and the scanning step size was 0.01°.

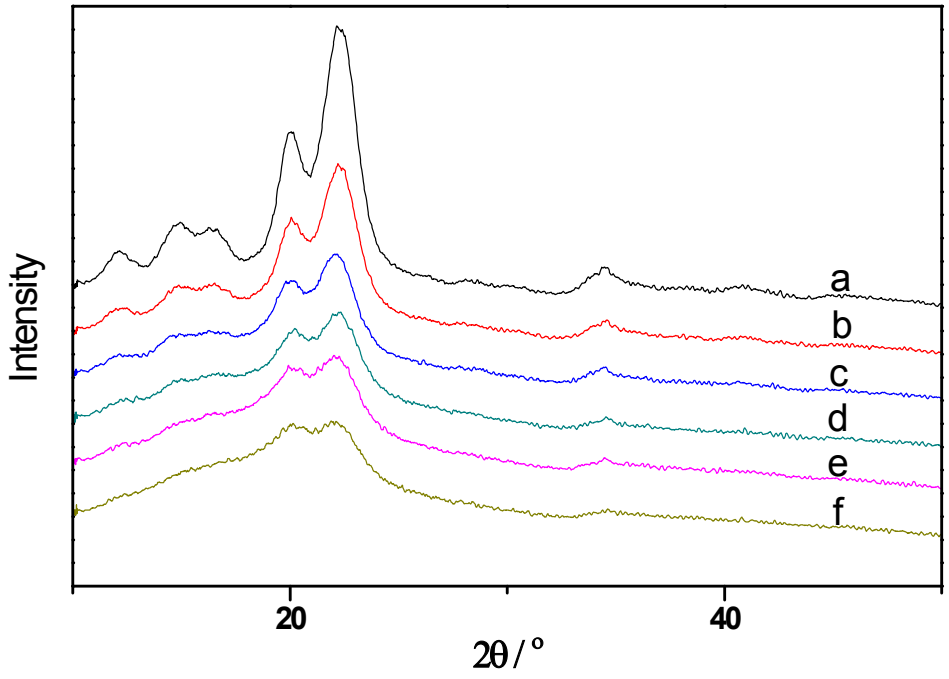

Fig. *S21* XRD spectra of ball-milled cellulose for different time. a). cellulose of 85% crystallinity; b) after ball-milled for 24h; c) after ball-milled for 48h; d) after ball-milled for 72h; e) after ball-milled for 96h; f) after ball-milled for 120h.

The recycle of BFIL1 in butanolysis of cellulose

After the reaction, the product was separated from resultant mixtures by simply adding distilled water. The BFIL**1** was recovered and recycled by removing part of the *n*-butanol and traces of water under vacuum and then reusing directly.

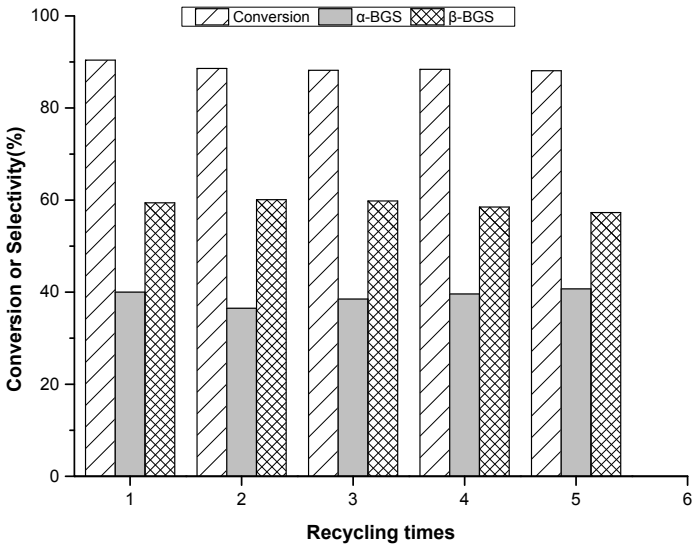

Fig. *S22* The recycle of BFIL**1** in butanolysis of cellulose

Solubility of BFIL1 in Different Alcohols at Room Temperature

Table *S1*. The solubility of BFIL**1** in different alcohols at 25 °C[a]

Ionic liquids	Methanol	*n*-Butanol	*n*-Octanol
BFIL**1**	0.21	0.036	0.025

[a]The unit of solubility is g/mL.

Optimization of the reaction conditions

Before investigating the catalytic performance of these BFILs in alcoholysis of cellulosic saccharides, BFIL**1** was selected to optimize the reaction conditions, and n-butanol was chosen as reaction media for it's modest length of carbon chain compared to methanol and ethanol and better solubility of BFIL1 in it. Fig. S23-25 showed the effect of reaction temperature and time, and the amount of catalyst in butanolysis of cellobiose. It is obvious that the optimised reaction condition are as follows: the mass ratio of cellobiose : butanol : catalyst is 10 : 405 : 2, the reaction time is 4 h at 368 K.

Similarily, according to the reaction conditions for butanolysis of cellulose reported in literatures (reference 16), after preliminary experiments, we chose 413 K, 4 h for cellulose conversion in different alcohol catalyzed by BFIL**1**.

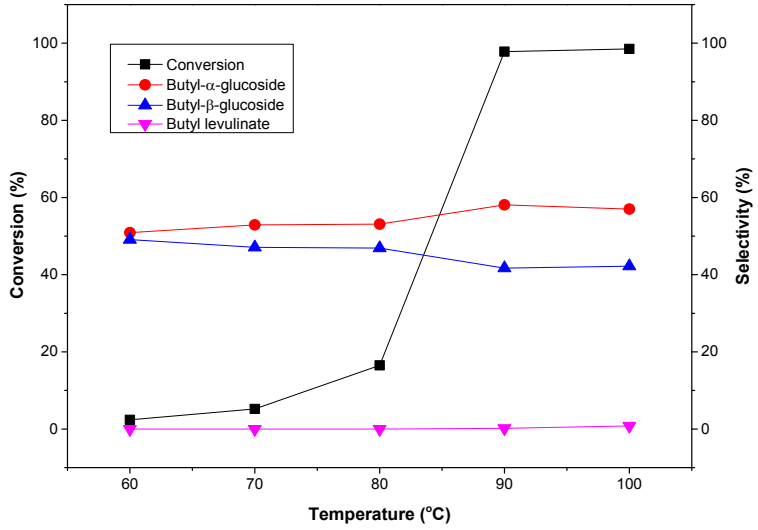

Fig. *S23* Influence of temperature on butanolysis of cellobiose catalyzed by BFIL**1**.

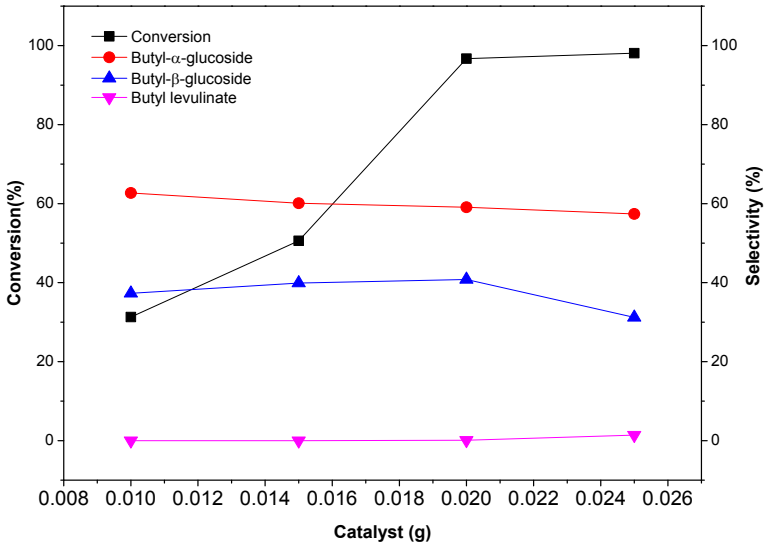

Fig. *S24* Effect of the amount of BFIL**1** on butanolysis of 0.50 g cellobiose at 363 K.

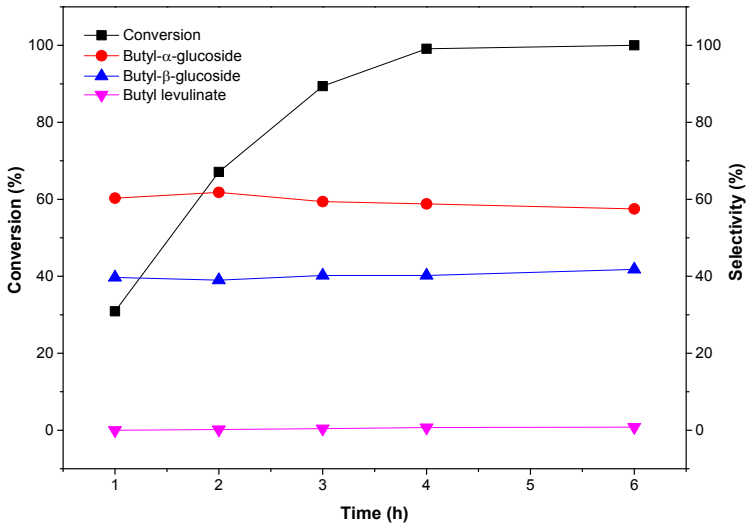

Fig. *S25* Influence of time on butanolysis of cellobiose catalyzed by BFIL**1**.