

Mechanistic Insights into Lignin Depolymerisation in Acidic Ionic Liquids

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Supplementary Information

Experimental

1. Materials for kinetic studies

Guaiacylglycerol- β -guaiacol ether (Compound **I** 99%) was purchased from Tokyo Chemical Industry (Japan), 3,4,5-trimethoxybenzaldehyde (98%) was purchased from Sigma Aldrich and guaiacol purchased from VWR and were all used as received. The ionic liquids included in this investigation were synthesised following standard protocols involving either the acid-base neutralisation or alkylation of the amine with dimethylsulfate, followed by acid-catalysed hydrolysis. All amine starting materials were dried over potassium hydroxide and dimethyl sulfate dried over calcium oxide for 24 hours and distilled before use. 95-98% sulfuric acid was purchased from VWR and titrated before use using a TitroLine easy titrator. Deionised water was purchased from VWR and used as received.

2. Kinetic Data Analysis

High performance liquid chromatography (HPLC) analysis was performed on a Shimadzu Prominence HPLC with a Photodiode Array (PDA) detector. Detection was carried out at 280 nm using a Purospher STAR RP-18 end-capped column. A 10 minute isocratic method (20% acetonitrile, 80% deionised water) was employed, with column temperature at 40 °C and 2 μ L injection volume. 3,4,5-trimethoxybenzaldehyde was used as an internal standard for quantitative calculations of guaiacol yield after calibration. Conversion is defined as the molar ratio of guaiacol obtained to the initial molar amount of compound **I**.

3. NMR Procedures.

HSQC data were recorded on Bruker Avance-400 NMR spectrometers at 25 °C. Chemical shifts are reported downfield of tetramethylsilane, in units of ppm (referenced against the CDCl₃ residual peak at 7.26 ppm).

4. Materials and methods for Hammett acidity studies of [C₄C₁im][HSO₄]

The [C₄C₁im][HSO₄] ionic liquid used for the Hammett acidity study was synthesised in the same way as described in section **5h** of this ESI. The IL-acid-water systems were prepared using a sulfuric acid solution described in section 4.1., distilled water and the dry IL (water \leq 600 ppm using a Mettler Toledo V20 volumetric KF titrator). In cases where the water content was measured on an acidic sample, the buffer Hydranal® buffer-acid was used. The dyes used were 3-nitroaniline, 4-nitroaniline and 4-nitrotoluene which

were all purchased from Sigma-Aldrich and used without any further purification. Further information regarding these dyes can be found elsewhere.¹

4.1. Sulfuric acid preparation

The H₂SO₄ was prepared from fuming sulfuric acid (60% SO₃) and concentrated sulfuric acid (95-98 wt%) both purchased from Sigma Aldrich. Fuming sulfuric acid was added to the concentrated acid solution until a high acid concentration could be detected. This was achieved by allowing the mixture to stir for a few minutes and then adding a drop of water. If fumes arise from the sample that indicates that some SO₃ was still present. At this point the Hammett acidity of the mixture was measured using the probe 4-nitrotoluene. The acidity of the mixture was then adjusted by the addition of fuming sulfuric acid or water until a high accurate acid concentration could be reached (± 0.01 wt% done in triplicate). The concentrated acid solution was then diluted to around 60 wt% resulting in a highly accurate low concentration sulfuric acid solution.

4.2. Sample preparation of [C₄C₁im][HSO₄]_{10% acid} in a 5 (wt/wt) % excess water concentration.

Dry [C₄C₁im][HSO₄] (178.37 g) was placed in a 500 ml round bottled flask and the sulfuric acid solution (61.41 wt%, 12.06 g) was slowly added under stirring. After a few minutes the IL-Acid system was heated to 80 °C and put under vacuum until dried resulting in a 10.00 mol % excess acid system ((9.09 mol% acid and 90.91 mol% IL). The dry IL-acid system (18.1095 g) was then diluted with distilled water (0.9082 g) resulting in a [C₄C₁im][HSO₄]_{10% acid} 5.02 wt% excess water system (4.78 wt% water and 95.22 wt % [C₄C₁im][HSO₄]_{10% acid}). All other samples were prepared in the same way.

4.3. Hammett acidity measurements on [C₄C₁im][HSO₄]_{10% acid} with a 5 (wt/wt) % excess water concentration.

Hammett acidity (H₀) is determined by measuring the partial protonation of a specific dye. The pK_a of these dyes may vary therefore affecting the region of acidity that can be measured. The full protocol, a list of dyes and the theory behind the methods used when measuring the Hammett acidity of these IL-Acid systems have previously been published by our group and can be found elsewhere.¹ This includes a modification to the Hammett equation (Equation 1) that allows measurement of acidity for a system where the protonated peak cannot be detected. This is unfortunately necessary when measuring acidity on IL systems since ILs tend to interfere in the wavelength region where the protonated peak is usually found.

$$H_0 = pK_{BH^+} - \log\left(\frac{\epsilon_0 - \epsilon}{\epsilon}\right)$$

Equation S1: A modified version of the Hammett equation that allows the measurement of H₀ without the detection of the protonated peak.

The extinction coefficient (ϵ_0) and the pK_{BH⁺} is specific for the dye used and are already known.¹ The effective extinction coefficient (ϵ) however is dependent on the acidity of the system. To measure the effective extinction

coefficient (ϵ) for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]_{10\% \text{ acid}}$ in a 5 (wt/wt) % excess water concentration, ten samples of said system with different concentrations of the dye were prepared. In this case, the dye 4-nitroaniline was used. According to Beer-Lambert law ($A = \epsilon cl$) when plotting the absorption against the dye concentration multiplied by the path length for any given system, the gradient between the different dye concentrations is equal to the effective extinction coefficient (ϵ) for the said system (**Fig. S1**).

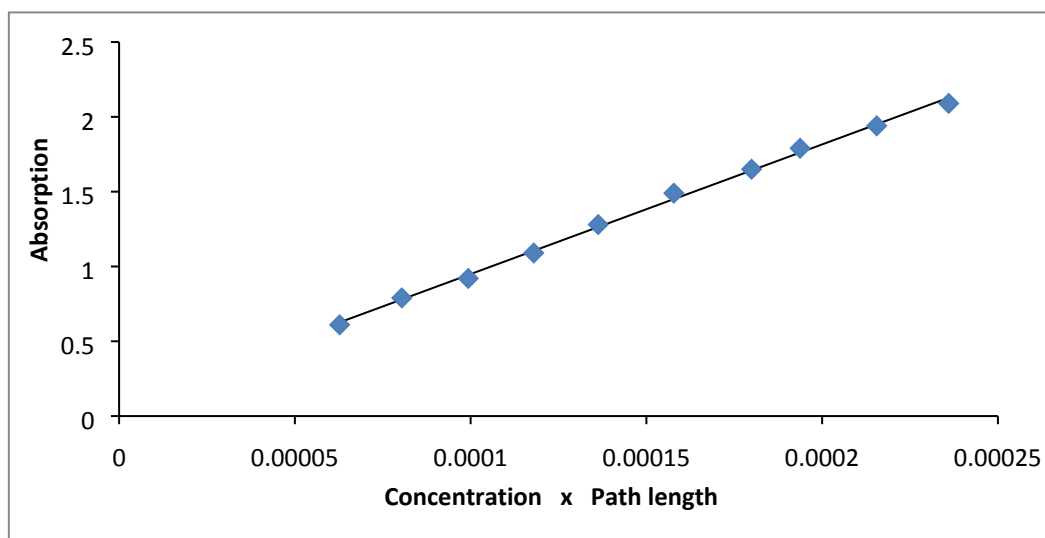
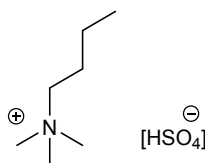


Fig. S1. Absorbance against the concentration \times path length for the dye 4-nitroaniline in the $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]_{10\% \text{ acid}}$ in a 5 (wt/wt) % excess water system. The equation of the trend line shows an effective extinction coefficient (ϵ) of 8666.

With $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]_{10\% \text{ acid}}$ in a 5 wt% excess water system the effective extinction coefficient (ϵ) is $8666 \text{ Mol}^{-1} \text{ L cm}^{-1}$ (**Fig. S1**). By combining this value with the dye specific data for 4-nitroaniline ($\text{pK}_{\text{BH}^+} = 1.00$ and $\epsilon_0 = 15447 \text{ Mol}^{-1} \text{ L cm}^{-1}$), **Equation S1** gives us a Hammett acidity of 1.11. The Hammett acidity (H_0) for all the other systems was measured in the same way.

5. Synthesis and Characterisation of Acidic Ionic Liquids

a. Butyltrimethylammonium hydrogensulfate $[\text{N}_{4111}][\text{HSO}_4]$



Butyltrimethylamine (48.14 g, 476 mmol) was mixed with 100 mL of toluene and the mixture was cooled to 0 °C. Dimethyl sulfate was added dropwise to the stirred solution (50 g, 396 mmol). The reaction was left to stir

for one hour until the reaction mixture warmed to room temperature; a white solid was then seen to form. The top phase was decanted and the lower phase washed with toluene (3 × 50 mL). The ionic liquid was dried under vacuum yielding butyltrimethylammonium methylsulfate as a white solid (81.24 g, 90%).

Butyltrimethylammonium methylsulfate (76.61 g, 337 mmol) was diluted with deionized water (100 mL) in an open-topped three-necked round-bottomed flask fitted with dropping funnel and thermometer. Sulfuric acid (2 drops) was added. The solution was heated at 180 °C for 5 h with vigorous stirring, allowing water and generated methanol to boil off. Deionized water was dispensed dropwise from the dropping funnel. The solution was then allowed to cool to room temperature. Water was removed under reduced pressure at 65 °C. When cooled to room temperature the product yielded a white solid (68.7 g, 96 %, mpt 139.2 °C).

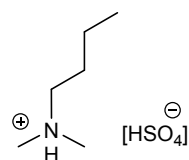
¹H: (400MHz, DMSO)/ppm, 3.28 (2H, m, NCH₂CH₂CH₂CH₃), 3.04 (9H, s, -NCH₃), 1.65 (2H, quintet, *J* = 8 Hz, -CH₂CH₂CH₂CH₃), 1.28 (2H, sextet, *J* = 7.2 Hz, -CH₂CH₂CH₂CH₃) and 0.93 (3H, t, *J* = 7.2 Hz, -CH₂CH₂CH₂CH₃).

¹³C: (100 MHz, DMSO-d₆)/ppm, 65.03, 52.10, 24.07, 19.17 and 13.54

m/z (FAB+) 116 (100%) ([N₄₁₁₁]⁺), 58 (45%),

m/z (FAB-) 97 (100%) ([HSO₄]⁻).

b. Butyldimethylammonium hydrogensulfate [N₄₁₁₀][HSO₄]



96% sulfuric acid (29.53 g, 289 mmol) was added dropwise to a solution of dimethylbutylamine (29.29 g, 289 mmol) in distilled water (50 mL) under stirring at 0 °C. After addition, the mixture was left to reach room temperature over an hour. The mixture was then heated to 60 °C and dried under vacuum yielding a viscous clear liquid (55.76 g, 97 %).

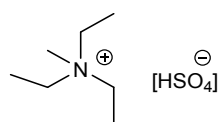
¹H: (400MHz, DMSO)/ppm, 3.02 (2H, m, NCH₂CH₂CH₂CH₃), 2.76 (6H, d, *J* = 5.2 Hz, NCH₃), 1.57 (2H, m, NCH₂CH₂CH₂CH₃), 1.30 (2H, sextet, *J* = 7.4 Hz, NCH₂CH₂CH₂CH₃) and 0.89 (3H, t, *J* = 7.2 Hz, NCH₂CH₂CH₂CH₃).

¹³C: (100 MHz, DMSO-d₆)/ppm 56.49, 42.29, 25.77, 19.24 and 13.54

m/z (FAB+) 102 (100%), ([N₄₁₁₀]⁺)

m/z (FAB-) 97 (100%) ([HSO₄]⁻)

c. Triethylmethylammonium hydrogensulfate [N₂₂₂₁][HSO₄]



Triethylamine (48.14 g, 476 mmol) was mixed with 100 mL of toluene and the mixture was cooled to 0 °C. Dimethyl sulfate was added dropwise to the stirred solution (50 g, 396 mmol). The reaction was left stirring for 1 h until the reaction mixture warmed to room temperature. The top phase was decanted and the lower phase washed with toluene (3 × 50 mL). The ionic liquid was dried under vacuum and yielded Triethylmethylammonium methylsulfate as a white hygroscopic solid (78.01 g, 89 %).

Triethylmethylammonium methylsulfate (78.01 g, 343 mmol) was diluted with deionized water (100 mL) in an open-topped three-necked round-bottomed flask fitted with dropping funnel and thermometer. Sulfuric acid (2 drops) was added. The solution was heated at 180 °C for 5 h with vigorous stirring, allowing water and generated methanol to boil off. Deionized water was dispensed dropwise from the dropping funnel, in order to maintain the temperature at 180 °C. The solution was allowed to cool to room temperature. Water was removed under reduced pressure at 65 °C. When cooled to room temperature the product yielded a white hygroscopic solid (74.01 g, 99 %).

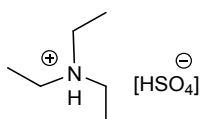
¹H: (400MHz, DMSO)/ppm, 3.25 (6H, q, $J = 7.2$ Hz, $-CH_2CH_3$), 2.88 (3H, s, $-NCH_3$) and 1.19 (9H, tt, $J = 7.2$, 2.0 Hz, $-CH_2CH_3$).

¹³C: (100 MHz, DMSO- d_6)/ppm, 54.90, 52.81, 45.97 and 7.42

m/z (FAB+) 116 (100%), ($[N_{2111}]^+$)

m/z (FAB-) 97 (100%) ($[HSO_4]^-$)

d. Triethylammonium hydrogensulfate $[N_{2220}][HSO_4]$



96 % sulfuric acid (29.89 g, 293 mmol) was added dropwise to a solution of triethylamine (29.60 g, 293 mmol) in distilled water (50 mL) under stirring at 0 °C. After addition, the mixture was left to reach room temperature over an hour. The mixture was then heated to 65 °C and dried under vacuum yielding a white solid (58.7 g, 99 %).

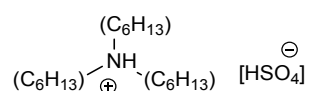
¹H: (400MHz, DMSO)/ppm, 3.08 (6H, q, $J = 7.6$ Hz, NCH_2CH_3) and 1.17 (9H, t, $J = 7.6$ Hz, NCH_2CH_3)

¹³C: (100 MHz, DMSO- d_6)/ppm, 45.87 and 8.65

m/z (FAB+) 102 (100%), ([N₂₂₂₀]⁺)

m/z (FAB-) 196 (100%) (2[HSO₄]⁻), 97 (55%) ([HSO₄]⁻)

e. Trihexylmethylammonium hydrogensulfate [N₆₆₆₁][HSO₄]



Trihexylamine (34.55 g, 128 mmol) was mixed with 100 mL of toluene and the mixture was cooled to 0 °C. Dimethyl sulfate was added dropwise to the stirred solution (14.70 g, 112 mmol). The reaction was left stirring for 1 h until the reaction mixture warmed to room temperature. The top phase was decanted and the lower phase washed with diethyl ether (3 × 50 mL). The ionic liquid was dried under vacuum and yielded Trihexylmethylammonium methylsulfate as a viscous colourless liquid (44.15 g, 99%).

Trihexylmethylammonium methylsulfate (42.09 g, 106 mmol) was diluted with deionized water (100 mL) in an open-topped three-necked round-bottomed flask fitted with dropping funnel and thermometer. Sulfuric acid (2 drops) was added. The solution was heated at 180 °C for 5 h with vigorous stirring, allowing water and generated methanol to boil off. Deionized water was dispensed dropwise from the dropping funnel in order to maintain the temperature of 180 °C. The solution was allowed to cool to room temperature. Water was removed under reduced pressure at 65 °C. When cooled to room temperature the product yielded a clear solid (40.13 g, 99 %)

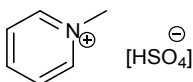
¹H: (400MHz, DMSO)/ppm, 3.21 (6H, m, (NCH₂CH₂CH₂CH₂CH₂CH₃)₃), 2.94 (3H, s, NCH₃), 1.61 (6H, br, N(CH₂CH₂CH₂CH₂CH₂CH₃)₃), 1.29 (18H, br, (NCH₂CH₂CH₂CH₂CH₂CH₃)₃) and 0.88 (9H, t, J = 6.8 Hz, (NCH₂CH₂CH₂CH₂CH₂CH₃)₃).

¹³C: (100 MHz, DMSO-d₆)/ppm = 60.53, 47.47, 30.63, 25.44, 21.88, 21.31 and 13.81.

m/z (FAB+) 284 (100%), ([N₆₆₆₁]⁺) and 128 (25%),

m/z (FAB-) 97 (100%) ([HSO₄]⁻)

f. N-Methylpyridinium hydrogensulfate [N-MePyr][HSO₄]



Pyridine (49.56 g, 627 mmol) was mixed with 100 mL of toluene and the mixture was cooled to 0 °C. Dimethyl sulfate was added dropwise to the stirred solution (61.85 g, 490 mmol). The reaction was left stirring for one hour until the reaction mixture warmed to room temperature. The top phase was decanted and the lower phase washed three times with toluene (3 × 50 mL). The ionic liquid was dried under vacuum and yielded *N*-methylpyridinium methylsulfate as a yellow liquid (111.4 g, 83 %).

N-Methylpyridinium methylsulfate (111.44 g, 543 mmol) was diluted with deionized water (100 mL) in an open-topped three-necked round-bottomed flask fitted with dropping funnel and thermometer. Sulfuric acid (2 drops) was added. The solution was heated at 180 °C for 5 h with vigorous stirring, allowing water and generated methanol to boil off. Deionized water was dispensed dropwise from the dropping funnel, in order to maintain the temperature of 180 °C. The solution was allowed to cool to room temperature. Water was removed under reduced pressure at 65 °C. When cooled to room temperature the product yielded a yellow solid (97.96 g, 93 %).

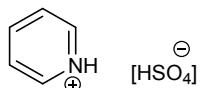
¹H: (400MHz, DMSO)/ppm, 8.98 (2H, d, *J* = 5.6 Hz, Ar-H), 8.58 (1H, t, *J* = 7.6 Hz, Ar-H), 8.13 (2H, t, *J* = 6.8 Hz, Ar-H) and 4.35 (3H, s, N-CH₃).

¹³C: (100 MHz, DMSO-d₆)/ppm = 145.6, 145.08, 127.72 and 47.92

m/z (FAB+) 94 (100%), ([*N*-MePyr]⁺)

m/z (FAB-) 196 (100%), (2[HSO₄]⁻) and 97 (65%) ([HSO₄]⁻)

g. Pyridinium hydrogensulfate [HPyr][HSO₄]



97.05 % sulfuric acid (39.24 g, 388 mmol) was added dropwise to a solution of pyridine (30.71 g, 388 mmol) in distilled water (50 mL) under stirring at 0 °C. After addition, the solution became highly viscous and the mixture was left to reach room temperature over an hour. The mixture was then heated to 65 °C and dried under vacuum yielding a white solid (69.42 g, 99 %).

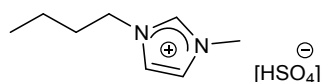
¹H: (400MHz, DMSO)/ppm, 8.95 (2H, d, *J* = 5.6 Hz, Ar-H), 8.64 (1H, tt, *J* = 8 Hz, 1.2 Hz, Ar-H) and 8.12 (2H, t, *J* = 6.4 Hz, Ar-H).

¹³C: (100 MHz, DMSO-d₆)/ppm = 145.6, 145.08, 127.72 and 47.92

m/z (FAB+) 83 (100%), ([*H*pyr]⁺), 109 (57%),

m/z (FAB-) 97 (100%) ([HSO₄]⁻)

h. 1-Butyl-3-methylimidazolium hydrogensulfate [C₄C₁im][HSO₄]



N-Butylimidazole (54.24 g, 437 mmol) was mixed with toluene (70 mL) and the mixture was cooled to 0 °C. Dimethylsulfate (55.09 g, 437 mmol) was added dropwise to the stirred solution over 1 h until the reaction mixture warmed to room temperature. The top phase was then decanted and the lower phase washed three times with toluene (3 × 50 mL). Residual toluene was removed under reduced pressure at 65 °C overnight and yielded 1-butyl-3-methylimidazolium methylsulfate as a colourless viscous liquid (105.68 g, 97%).

1-Butyl-3-methylimidazolium methylsulfate (30 g, 119.87 mmol) was diluted with deionized water (50 mL) in an open-topped three-necked round-bottomed flask fitted with dropping funnel and thermometer. Sulfuric acid (2 drops) was added. The solution was heated at 180 °C for 3 h with vigorous stirring, allowing water and generated methanol to boil off. Deionized water was dispensed dropwise from the dropping funnel. The solution was allowed to cool to room temperature. Water was removed under reduced pressure at 65 °C overnight. When cooled to room temperature the product yielded a transparent yellow liquid (57.45 g, 97 %).

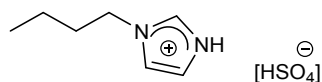
¹H: (400MHz, DMSO)/ppm, 9.11 (1H, s, -N-CH-N-), 7.78 (1H, s, -N-CHCH-N-), 7.71 (1H, s, -N-CHCH-N-), 4.16 (2H, t, *J* = 8 Hz, CH₂CH₂CH₂CH₃), 3.85 (3H, s, N-CH₃), 1.76 (2H, m, CH₂CH₂CH₂CH₃), 1.23 (2H, m, CH₂CH₂CH₂CH₃), 0.9 (3H, t, *J* = 8 Hz, CH₂CH₂CH₂CH₃).

¹³C: (100 MHz, DMSO-d₆)/ppm = 137.07, 124.06, 122.73, 48.92, 39.16, 31.82, 19.23 and 13.74.

m/z (FAB+) 139 (100%), ([C₄C₁im]⁺),

m/z (FAB-) 97 (100%) ([HSO₄]⁻).

i. 1-Butylimidazolium hydrogensulfate [HC₄im][HSO₄]



96% sulfuric acid (79.33 g, 638 mmol) was added dropwise to 1-butylimidazole (79.33 g, 638 mmol) under stirring at 0 °C. After addition, the solution became highly viscous and the mixture was left to reach room temperature over an hour. The light brown ionic liquid was passed through a C18 silica column in order to remove the colour. Water was removed under reduced pressure 65 °C overnight. When cooled to room temperature, the product yielded a clear viscous liquid (141.69 g, 96 %).

¹H: (400MHz, DMSO)/ppm, 9.15 (1H, s, -N-CH-N-), 7.80 (1H, s, -N-CHCH-N-), 7.68 (1H, s, -N-CHCH-N-), 4.20 (2H, t, *J* = 7.2 Hz, NCH₂CH₂CH₂CH₃), 1.77 (2H, quintet, *J* = 7.6 Hz, NCH₂CH₂CH₂CH₃), 1.24 (2H, quintet, *J* = 7.6 Hz, NCH₂CH₂CH₂CH₃) and 0.90 (3H, t, *J* = 7.2 Hz, NCH₂CH₂CH₂CH₃).

¹³C: (100 MHz, DMSO-d₆)/ppm, 135.73, 122.49, 120.42, 48.68, 31.92, 19.28 and 13.75.

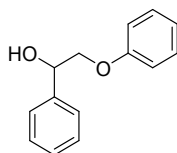
m/z (FAB+) 125 (100%), ([HC₄im]⁺)

m/z (FAB-) 97 (100%), ([HSO₄]⁻).

6. Synthesis and Characterisation of Lignin Model Compounds

The model compounds 2-phenoxy-1-phenylethanol (**II**), 2-(2-methoxyphenoxy)-1-phenylethanol (**III**), 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (**IV**) and erythro-1-(3-methoxy-4-*O*-benzylphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**V**) were synthesised using protocols reported in literature.^{2,3}

a) 2-phenoxy-1-phenylethanol



A 250 mL round bottom flask equipped with a reflux condenser and dropping funnel was charged with phenol (1.18 g, 12.6 mmol) and K_2CO_3 (2.07 g, 15 mmol) in acetone (50 mL) and stirred at room temperature. To this solution, 2-bromoacetophenone (2 g, 10 mmol) in acetone (50 mL) was added dropwise over 30 min at room temperature. The resulting suspension was stirred at reflux for 4h (during the reaction course the colour changed to clear yellow), after which the suspension was filtered and concentrated in *vacuo*. The crude product was purified by recrystallization from ethanol to give 2-phenoxy-1-phenylethanol as a white solid (2.09 g, 9.84 mmol, 98 %).

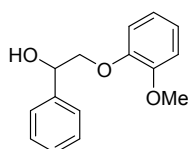
A 100 mL round bottom flask was charged with 2-phenoxy-1-phenylethanol (1.03 g, 4.9 mmol) along with a THF-water mixture (28:5 mL). $NaBH_4$ (0.36 g, 9.41 mmol) was added in one portion at room temperature. The flask was equipped with a reflux condenser and the reaction was left stirring under reflux for 2 h. After cooling to room temperature an excess of NH_4Cl was added (until pH 5-6) and the reaction mixture was stirred for 1 h. The crude product was extracted with diethyl ether (3×50 mL). The combined organic extracts were washed with brine (100 mL) and dried over anhydrous Na_2SO_4 . The crude product was then purified via column chromatography producing a white solid (0.84 g, 81 %, 62.4 – 63.3 °C mpt).

1H : (400MHz, $CDCl_3$)/ppm. 7.48-7.30 (7H, m, ArH), 7.00-6.94 (3H, m, ArH), 5.13 (1H, dd, $J = 8.8, 3.2$ Hz, $ArCH_a$), 4.12 (1H, dd, $J = 9.6, 3.2$ Hz, $ArCH_b$) and 4.02 (1H, t, $J = 9.2$ Hz, OH-CH-).

^{13}C : (100 MHz, $CDCl_3$)/ppm, 158.50, 139.78, 129.68, 128.69, 128.30, 126.41, 121.43, 114.76, 73.40 and 73.70

m/z (CI^+), 232 ($[M]^+NH_4$, 100%), 197 (48%)

b) 2-(2-methoxyphenoxy)-1-phenylethanol



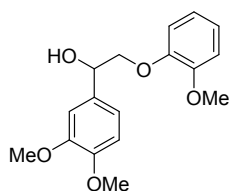
Synthesis followed the same protocol as 2-phenoxy-1-phenylethanone with the addition of 2-methoxyphenol instead of phenol to form 2-(2-methoxyphenoxy)-1-phenylethanone as a yellow crystalline solid (6.41 g, 35 %). Reduction of 2-(2-methoxyphenoxy)-1-phenylethanone followed the same protocol as above producing the 2-(2-methoxyphenoxy)-1-phenylethanol product as white solid (1.4 g, 93 %, 49.2 – 50.4 °C mpt).

^1H : (400MHz, CDCl_3)/ppm. 7.45-7.30 (5H, m, ArH), 7.02-6.88 (4H, m, ArH), 5.12 (1H, dd, $J = 9.6, 2.8$ Hz, ArCH_{a-}), 4.19 (1H, dd, $J = 9.6, 2.8$ Hz, ArCH_{b-}), 4.01 (1H, t, $J = 10$ Hz, OH-CH-) and 3.89 (3H, s, $-\text{OCH}_3$).

^{13}C : (100 MHz, CDCl_3)/ppm, 150.30, 148.10, 139.63, 128.62, 128.15, 126.42, 122.73, 121.23, 116.23, 112.15, 72.46 and 55.99.

m/z (EI^+), 244, ($[\text{M}]^+$, 28%), 202, (75%) and 124 (100%)

c) 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol



Synthesis followed the same protocol as 2-phenoxy-1-phenylethanol with the addition of 2-bromo-(3,4-dimethoxy)acetophenone replacing bromoacetophenone and 2-methoxyphenol replacing phenol to produce 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone (0.52 g, 45 %).

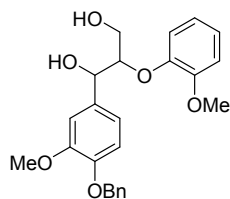
Reduction of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone followed the same protocol as above producing the 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol product as a white solid (0.16 g, 55 %, 131.4 – 132.8 °C mpt).

^1H : (400MHz, CDCl_3)/ppm. 7.01-6.83 (7H, m, ArH), 5.06 (1H, dd, $J = 9.2, 2.4$ Hz, $-\text{OCH}_{a-}\text{H}$), 4.17 (1H, dd, $J = 9.2, 2.4$ Hz $-\text{OCH}_{b-}\text{H}$), 3.97 (1H, t, $J = 9.6$ Hz, OH-CH-), 3.90 (3H, s, $-\text{OCH}_3$), 3.89 (3H, s, $-\text{OCH}_3$) and 3.88 (3H, s, $-\text{OCH}_3$).

^{13}C : (100 MHz, CDCl_3)/ppm, 132.12, 122.59, 121.12, 118.64, 116.04, 111.99, 111.03, 109.38, 76.40, 72.13, 55.96, 55.91 and 55.87.

m/z (EI^+), 368 ($[\text{M}]^+ + \text{CH}_3\text{CN} + \text{Na}$, 100% and 327 ($[\text{M}]^+ + \text{Na}$, 22%).

d) *Erythro*-1-(3-methoxy-4-O-benzylphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol



A dry and argon flushed 250 mL three-necked flask equipped with a magnetic stirrer, a low temperature thermometer, an argon inlet and an addition funnel was charged with diisopropylamine (3.643 g, 36 mmol, 1.2 equiv) and THF (50 mL). The reaction mixture was cooled to 0 °C and a solution of commercial *n*-butyllithium in hexanes (21.9 mL, 1.6 M, 34.5 mmol, 1.15 equiv) was added dropwise in 15 min. After stirring for 30 min at 0 °C the reaction mixture was cooled to -78 °C, and a solution of ethyl (2-methoxyphenoxy)acetate (6.3 g, 30 mmol, 1 equiv) in THF (60 mL) was added dropwise over a period of 1 h. After stirring for additional 10 min, a solution of 3,4-dimethoxybenzaldehyde (7.99 g, 33 mmol, 1.1 equiv) in THF (60 mL) was added in 30 min at -78 °C. At the end of the addition, stirring was continued for 90 min at -78 °C and then distilled water (100 mL) was added. The aqueous phase was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with a 1M aqueous HCl solution (80 mL), water (80 mL) and brine (80 mL), then dried with MgSO₄, filtered, and concentrated under reduced pressure. The crude solid was recrystallized in ethyl acetate (2.5 mL of AcOEt for 4 g of crude material; diethyl ether was used to wash the recrystallized solid) to obtain *erythro*-ethyl-3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate (5.59 g, 41%, *erythro/threo* >98:2) as a white solid.

A dry and argon flushed 250 mL three-necked flask equipped with a magnetic stirrer, a reflux condenser, an argon inlet and an addition funnel was charged with LiAlH₄ in THF (11.05 mL, 1.6 M, 11.05 mmol, 2.5 equiv). The reaction mixture was cooled to 0 °C and a solution of 3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate (2 g, 4.42 mmol, 1 equiv) in THF (20 mL) was added dropwise in 15 min. The heterogeneous reaction mixture was then stirred at 60 °C for 3 h and cooled to 0 °C. The reaction mixture was carefully quenched via the addition of ethyl acetate (20 mL) and the dropwise addition of half saturated potassium sodium tartrate solution (20 mL). The reaction mixture was then stirred for 30 min at ambient temperature. The filtrate was dried over MgSO₄ and evaporated under reduced pressure. The crude residue was purified by flash chromatography (CH₂Cl₂/MeOH 99:1 → 97:3). The resulting pure diol was dried by azeotropic distillation with toluene under reduced pressure, and then dried overnight yielding *Erythro*-1-(3-methoxy-4-O-benzylphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (1.0 g, 55%) as a viscous oil.

¹H: (400MHz, CDCl₃)/ppm. 7.44-7.26 (5H, m, ArH), 7.06 (1H, ddd, *J* = 8.0, 7.2, 1.6 Hz, ArH), 6.99 – 6.83 (6H, m, ArH), 5.14 (2H, s, ArCH₂), 4.96 (1H, d, *J* = 4.8 Hz, OH-CH-), 4.17-4.13 (1H, m, O-CH-), 3.88 (3H, s, -OCH₃), 3.88 (3H, s, -OCH₃), 3.92 (1H, m, CH_aHOH), 3.65 (1H, m, CH_bHOH).

¹³C: (100 MHz, CDCl₃)/ppm, 151.68, 149.84, 147.68, 146.97, 137.22, 133.19, 128.64, 127.94, 127.39, 124.32, , 11.74, 121.06, 118.47, 114.04, 112.27, 109.88, 87.45, 72.81, 71.17, 60.8 56.15 and 55.98.

m/z (EI⁺), 433 ([M]⁺Na, 100%) and 343 (15%).

7. Reactivity of Model compounds: HSQC analysis

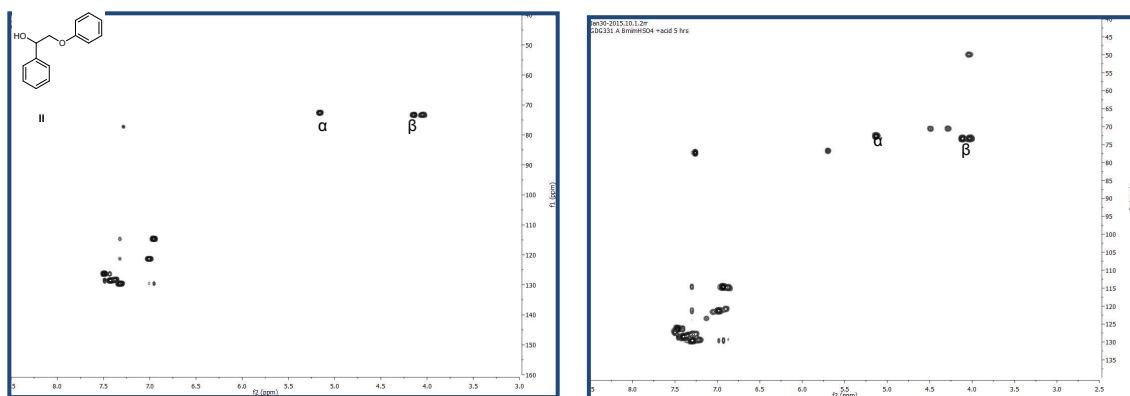


Fig S2. HSQC of II and after reaction in $[C_4C_1im][HSO_4]_{10\%}$ acid and 16.67 (wt/wt) % water

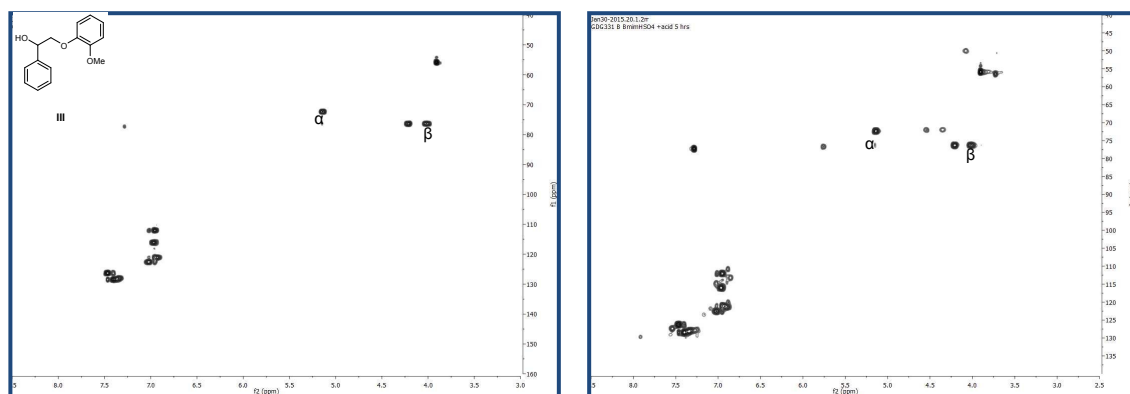


Fig. S3. HSQC of III and after reaction in $[C_4C_1im][HSO_4]_{10\%}$ acid and 16.67 (wt/wt) % water

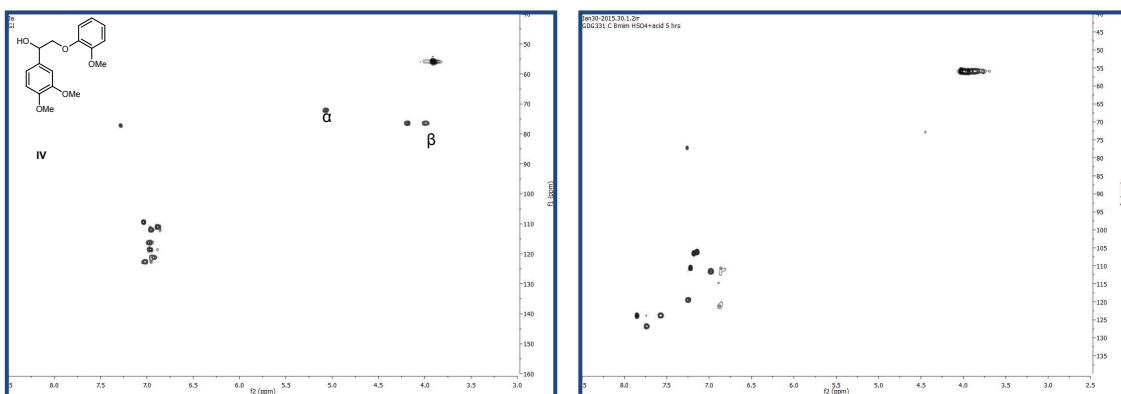


Fig. S4. HSQC of IV and after reaction in $[C_4C_1im][HSO_4]_{10\% \text{ acid}}$ and 16.67 (wt/wt) % water

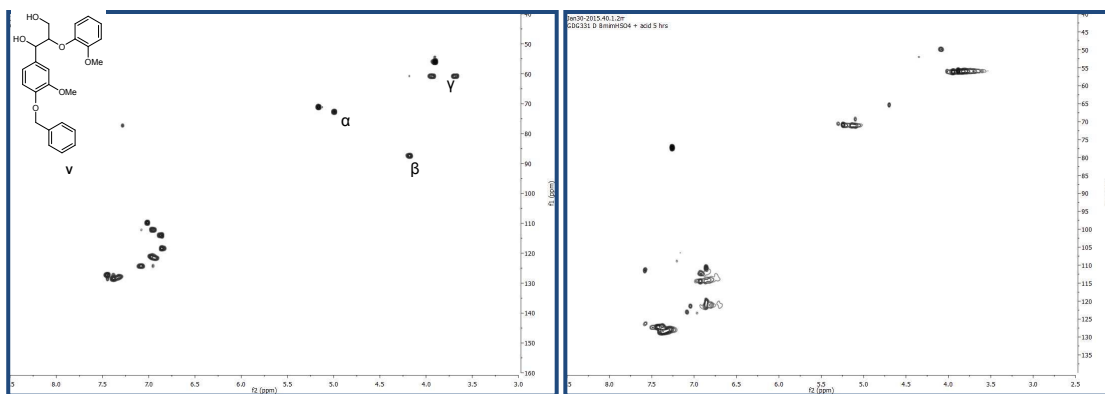


Fig. S5. HSQC of compound V and after reaction in $[C_4C_1im][HSO_4]_{10\% \text{ acid}}$ and 16.67 (wt/wt) % water

8. Reaction profile

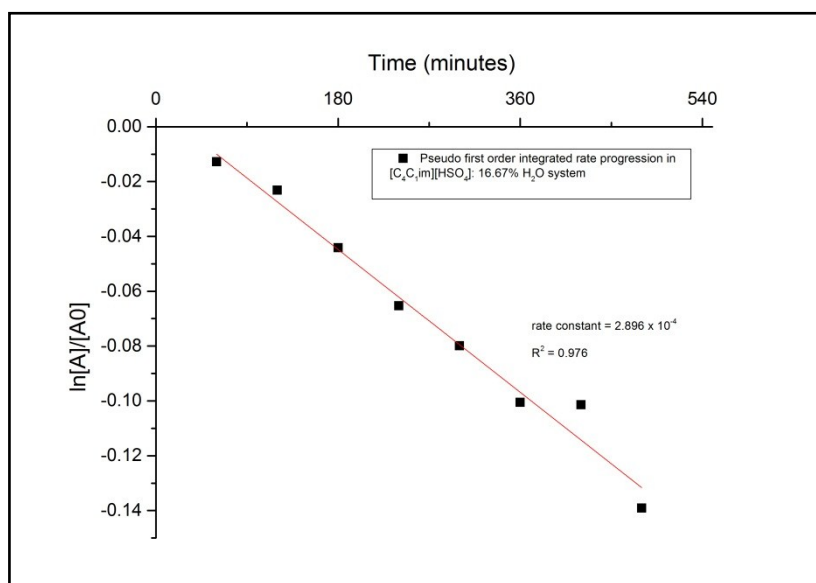


Fig. S6. Reaction profile of guaiacol yield within $[C_4C_1im][HSO_4]_{10\% \text{ acid}}$ and 16.67 (wt/wt) % water at 100 °C, where A is the remaining concentration of compound I determined from the concentration of guaiacol produced and A_0 being the initial concentration of compound I.

9. Eyring Plots.

Eyring plots were generated with at least four data points between 90 °C and 120 °C.

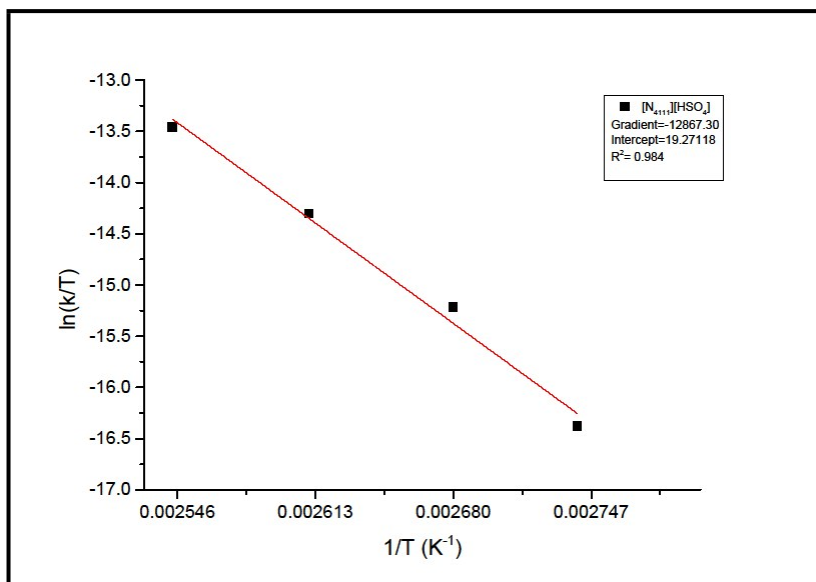


Fig. S7. Eyring plot for $[N_{4111}][HSO_4]$ with 16.67 % (wt/wt) water

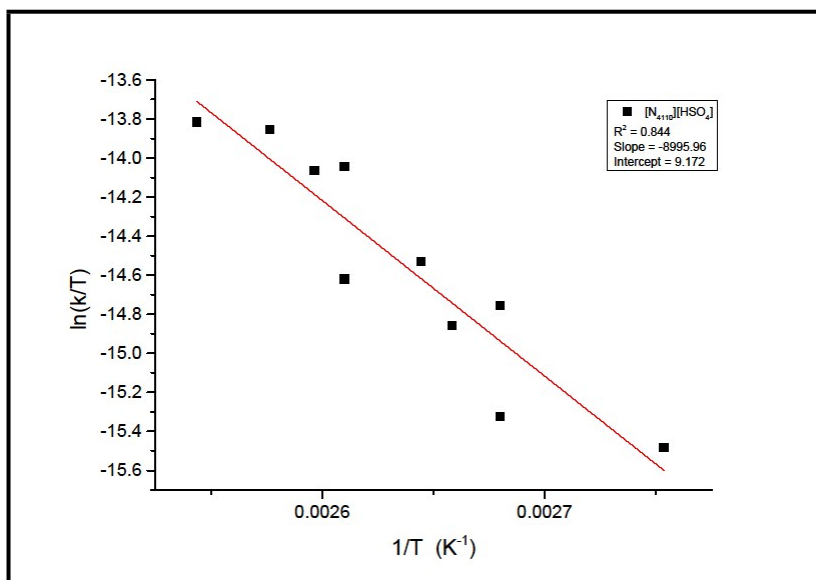


Fig. S8. Eyring plot for $[N_{4110}][HSO_4]$ with 16.67 % (wt/wt) water

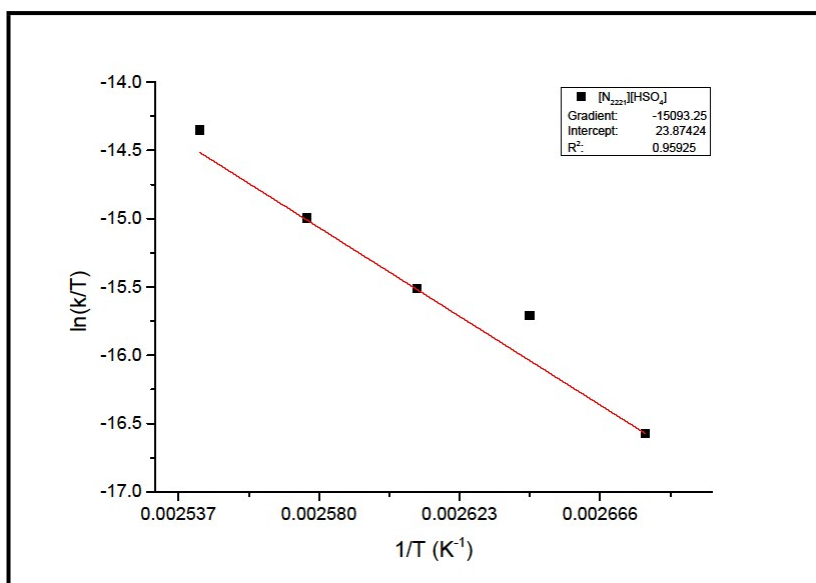


Fig. S9. Eyring plot for $[N_{2221}][HSO_4]$ with 16.67 % (wt/wt) water

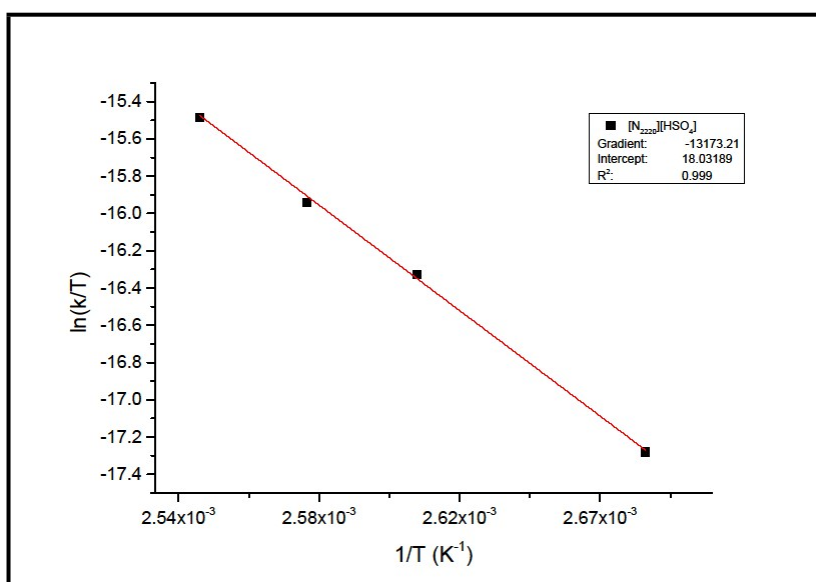


Fig. S10. Eyring plot for $[N_{2220}][HSO_4]$ with 16.67 % (wt/wt) water

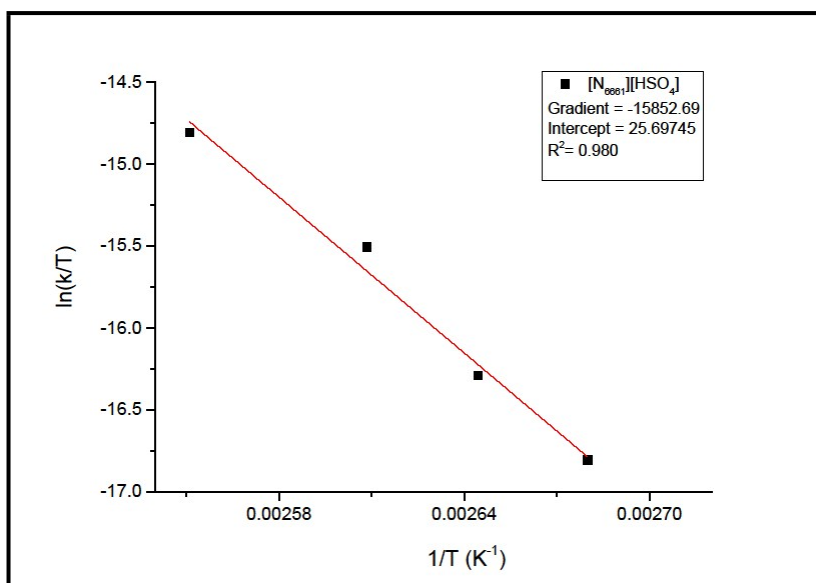


Fig. S11. Eyring plot for $[N_{661}][HSO_4]$ with 16.67 % (wt/wt) water

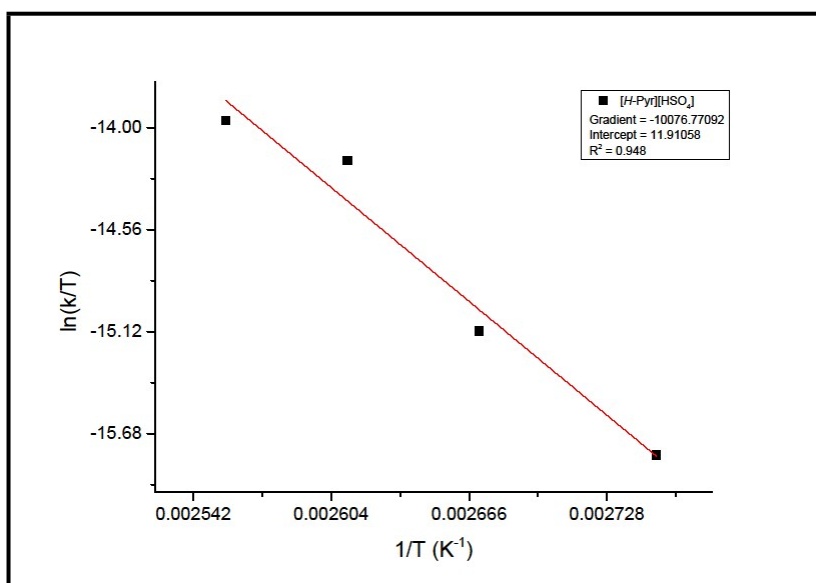


Fig. S12. Eyring plot for $[HPyr][HSO_4]$ with 16.67 % (wt/wt) water

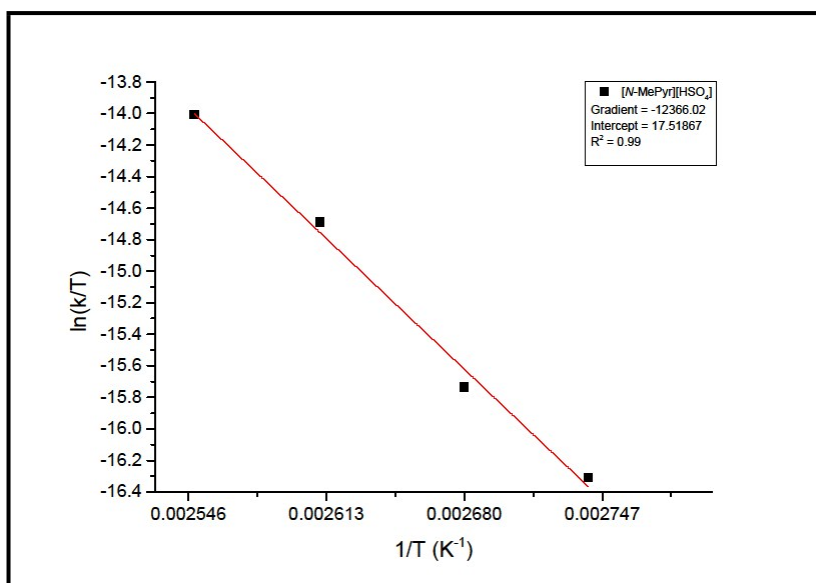


Fig. S13. Eyring plot for [N-MePyr][HSO₄] with 16.67 % (wt/wt) water

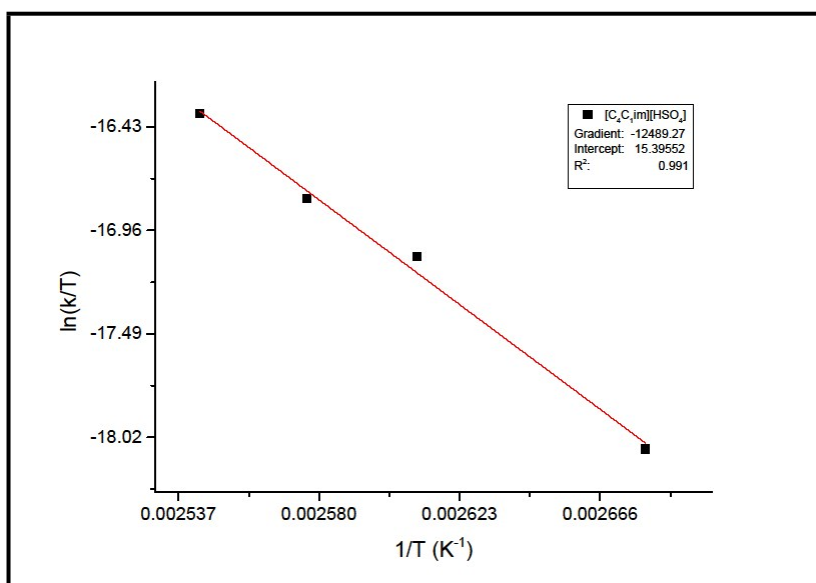


Fig. S14. Eyring plot for [C₄C₁im][HSO₄] with 16.67 % (wt/wt) water

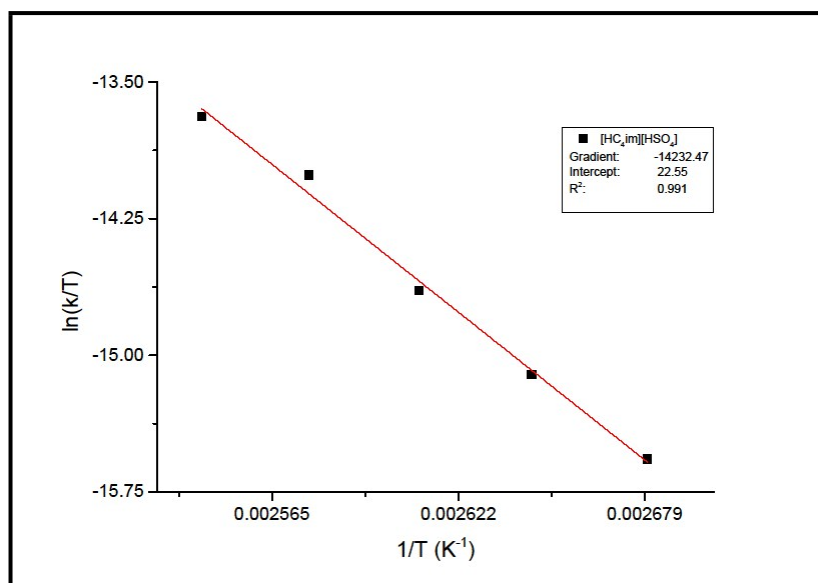


Fig. S15. Eyring plot for [HC₄im][HSO₄] with 16.67 % (wt/wt) water

10. Extrapolated Rate Constants for Ether Cleavage of compound I in Ionic Liquids

Ionic Liquid	Rate Constant at 85 °C (s ⁻¹ × 10 ⁻⁶)	Rate Constant at 150 °C (s ⁻¹ × 10 ⁻⁴)
[C ₄ C ₁ im][HSO ₄]	1.12	2.83
[HC ₄ im][HSO ₄]	13.8	72.0
[N-MePyr][HSO ₄]	13.6	32.7
[HPyr][HSO ₄]	28.3	25.4
[N ₄₁₁₁][HSO ₄]	16.8	102
[N ₄₁₁₀][HSO ₄]	41.2	23.3
[N ₂₂₂₁][HSO ₄]	5.08	39.9
[N ₂₂₂₀][HSO ₄]	2.31	7.56
[N ₆₆₆₁][HSO ₄]	2.87	30.7

References

- (1) Gräsvik, J.; Hallett, J. P.; To, T. Q.; Welton, T. *Chem. Commun.* **2014**, 50, 7258.
- (2) Galkin, M. V.; Sawadjoon, S.; Rohde, V.; Dawange, M.; Samec, J. S. M. *ChemCatChem* **2014**, 6 (1), 179.
- (3) Buendia, J.; Mottweiler, J.; Bolm, C. *Chem. Eur. J.* **2011**, 17 (49), 13877.