

Brønsted acidic ionic liquids catalyzed high-yield production of diphenolic acid/esters from renewable levulinic acid

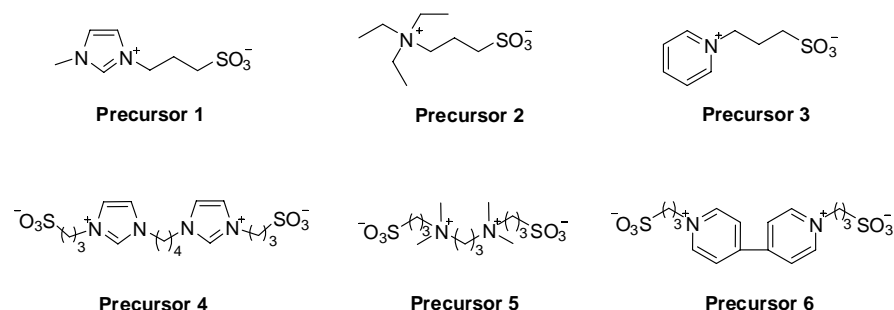
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Electronic Supplementary Information

1. Brønsted acidic ionic liquids (BAILs) preparation¹

To synthesis zwitterionic **precursors 1, 2, 3, 5 and 6**, 0.3 mol N-methylimidazole (0.3 mol triethylamine, 0.3 mol pyridine, 0.15 mol N,N,N',N'-tetramethyl-1,3-propyldiamine or 0.15 mol 4,4'-bipyridine) was dissolved in 100 mL acetonitrile and 0.3 mol 1,3-propyl sultone in 20 mL toluene was added slowly with stirring in ice bath. Then the mixture was heated to 50 °C for 2 h and filtrated after cooled down. The precipitate was washed with 50 mL diethyl ether for 3 times, giving yields over 80 mol%. ¹H NMR (400 MHz, D₂O) for **Precursor 1**: δ = 2.21(m, 2H), 2.81(t, 2H), 3.79(s, 3H), 4.26(t, 2H), 7.35(s, 1H), 7.42(s, 1H), 8.65(s, 1H); for **Precursor 2**: δ = 1.16(t, 9H), 2.01(m, 2H), 2.86(t, 2H), 3.22(m, 8H); for **Precursor 3**: δ = 2.38(m, 2H), 2.88(t, 2H), 4.67(t, 2H), 7.98(t, 2H), 8.46(t, 1H), 8.78(d, 2H); for **Precursor 5**: δ = 2.15(m, 2H), 2.25(m, 1H), 2.91(t, 2H), 3.08(s, 6H), 3.35(t, 2H), 3.46(t, 2H); for **Precursor 6**: δ = 2.45(m, 1H), 2.95(t, 1H), 4.81(t, 1H), 8.48(d, 1H), 9.08(d, 1H).

For **Precursor 4**, 0.4 mole imidazole was dissolved in 100 ml toluene/DMSO mixture (1 : 1) under N₂ atmosphere in a 250 mL flask and 40 mL 10M NaOH aqueous solution was added. After removal all water by gradually heating the mixture to 170 °C, the flask was cooled down and 0.2 mol 1,4-dibromobutane was added dropwisely, affording yellow solid mixture of 1, 4-diimidazol-1-yl butane and NaBr. Then mixture was dissolved by 150 mL chloroform to remove NaBr and purified 1, 4-diimidazol-1-yl butane was obtained by precipitation in water after evaporating chloroform. To prepare **Precursor 4**, 1, 4-diimidazol-1-yl butane reacted with 1,3-propyl sultone as above mentioned procedure. ¹H NMR (400 MHz, D₂O) for **Precursor 4**: δ = 1.85 (s, 2H), 2.26(m, 2H), 2.84(t, 2H), 4.20(s, 2H), 4.31(t, 2H), 7.45(s, 1H), 7.50(s, 1H), 8.79(s, 1H).



Scheme S1. Structures of zwitterionic precursors.

After the successful synthesis of zwitterionic precursors, stoichiometric amount of acid aqueous solution was added into it and stirred at 90 °C for 5 h. The BAILs were obtained by rotary distillation and vacuum drying with yields over 99 mol%.

2. Determination of acidity

The acidity of BAILs was evaluated by determination of Hammett acidity functions using UV-vis spectrometer (Shimadzu 2500) with *p*-nitroaniline as indicator.² Figure S1 shows the maximum absorbance of unprotonated indicator in UV-vis spectra at 371 nm and table S1 summarizes the Hammett acidity functions of ionic liquids in methanol.

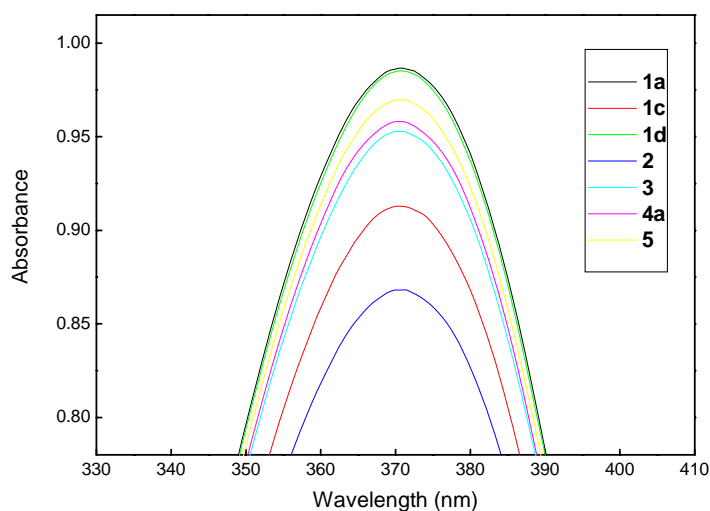


Figure S1. Absorption spectra of *p*-nitroaniline in the presence of ionic liquids in methanol.

Table S1. Hammett acidity functions (H_0) of ionic liquids

Entry	Ionic Liquids	H_0
1	1a	1.83
2	1c	1.63
3	1d	1.83
4	2	1.51
5	3	1.74
6	4a	1.74
7	5	1.80

3. Thermal stability of ionic liquids

The TGA tests of ionic liquids were performed on a Netzsch TG209 thermal gravity analyzer (Figure S2) under N_2 atmosphere. The temperature program is conducted from room temperature to 800°C with the rate of 10°C min⁻¹.

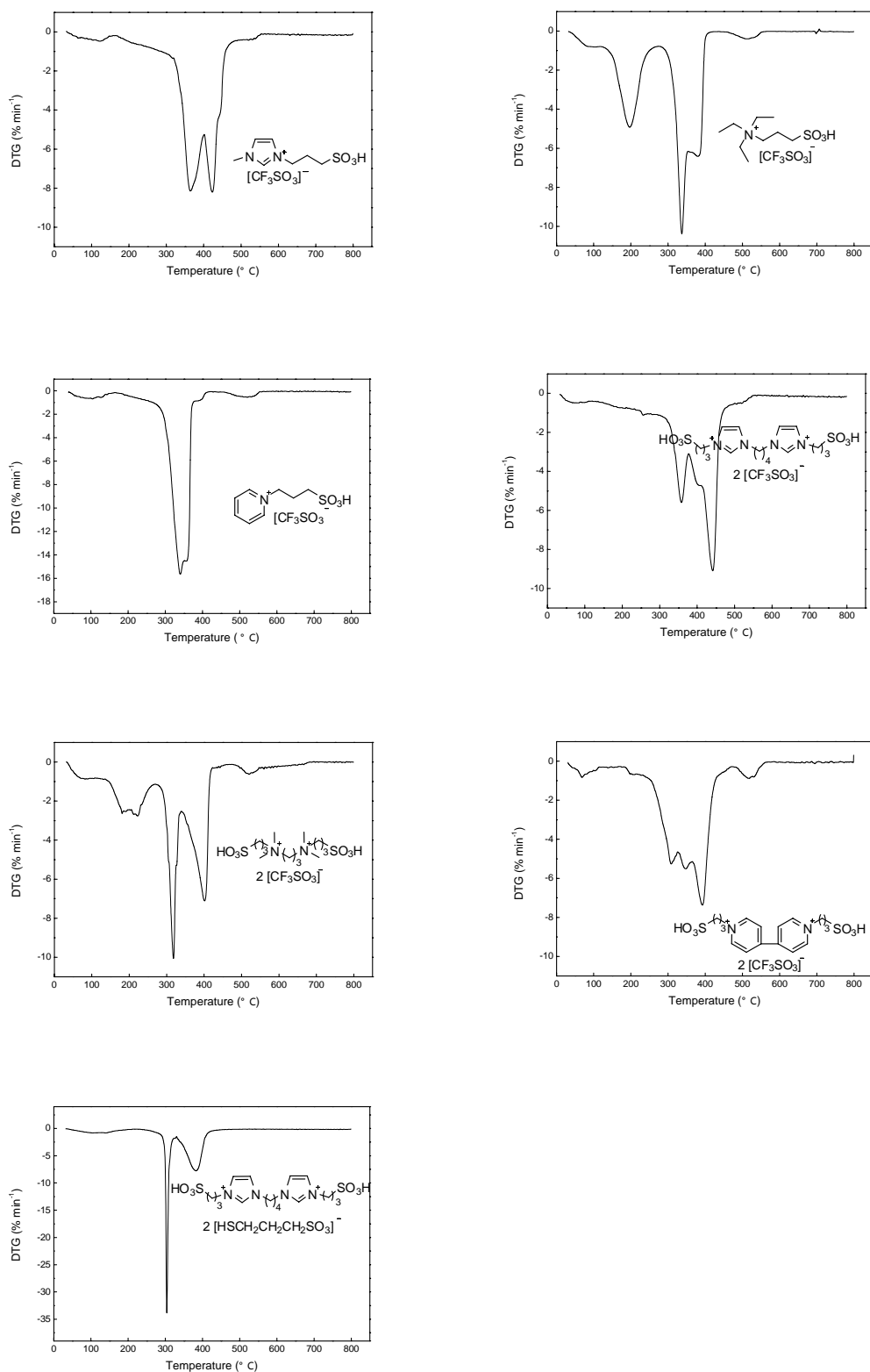


Figure S2. DTG curves of ionic liquids.

4. Catalytic tests

4.1 Synthesis of DPA

Phenol and levulinates were obtained commercially and used without further purification. For a typical procedure for DPA synthesis, 2 mmol **1a** was added with 16 mmol phenol and 4 mmol levulinic acid into a sealed tube equipped with magnetic stirrer and the tube was degassed and charged with Ar with schlenk line technique. Then mixture was heated to 60 °C for 48 h. After reaction the resulting mixture was sampled and analyzed by a HPLC system consisting of a C8 column (6.5 mm × 250 mm), a P200 II pump and a UV detector (wavelength at 270 nm) using acetonitrile-water (45 : 55) mixture as mobile phase at a flow rate of 1 mL min⁻¹.

4.2 Synthesis of diphenolic esters

Strategy 1 for diphenolic esters synthesis: For a typical procedure for ethyl diphenolic ester synthesis, (0.9 mmol) **4a** and 0.1 mmol **4b** were added with 16 mmol phenol and 4 mmol ethyl levulinate into a sealed tube equipped with magnetic stirrer and the tube was degassed and charged with Ar with schlenk line technique. Then mixture was heated to 60 °C for 48 h. After reaction the resulting mixture was sampled and analyzed by a HPLC system consisting of a C8 column (6.5 mm × 250 mm), a P200 II pump and a UV detector (wavelength at 270 nm) using acetonitrile-water (45 : 55) mixture as mobile phase at a flow rate of 1 mL min⁻¹.

Strategy 2 for diphenolic esters synthesis: For a typical procedure for ethyl diphenolic ester synthesis, (0.9 mmol) **4a** and 0.1 mmol **4b** were added with 16 mmol phenol and 4 mmol levulinic acid into a sealed tube equipped with magnetic stirrer and the tube was degassed and charged with Ar with schlenk line technique. Then mixture was heated to 60 °C for 48 h. 2 mL alcohols was added and reacted at 40 °C for another 8 h. After reaction the resulting mixture was sampled and analyzed by a HPLC system consisting of a C8 column (6.5 mm × 250 mm), a P200 II pump and a UV detector (wavelength at 270 nm) using acetonitrile-water (45 : 55) mixture as mobile phase at a flow rate of 1 mL min⁻¹.

¹H NMR (400 MHz, DCCl₃) for ethyl diphenolic ester: δ = 1.20(t, 3H), 1.53(s, 1H), 2.08 (t, 2H), 2.36(t, 2H), 4.06(m, 2H), 6.70(d, 4H), 7.01(d, 4H).

4.3 Recycle experiment

The scale of recycle catalytic run was 5-fold enlarged using 4.5 mmol **4a**, 0.5 mmol **4b**, 20 mmol levulinic acid, 80 mmol phenol and 10 mL ethanol. After reaction, the mixture was extracted with 25 mL ethyl acetate for 3 times. The extract was sampled and analyzed by a HPLC system consisting of a C8 column (6.5 mm × 250 mm), a P200 II pump and a UV detector (wavelength at 270 nm) using acetonitrile-water (45 : 55) mixture as mobile phase at a flow rate of 1 mL min⁻¹. The ionic liquids were regenerated simply by removal residual extract under vacuum.

5. Temperature effect on yield and ratio of DPA

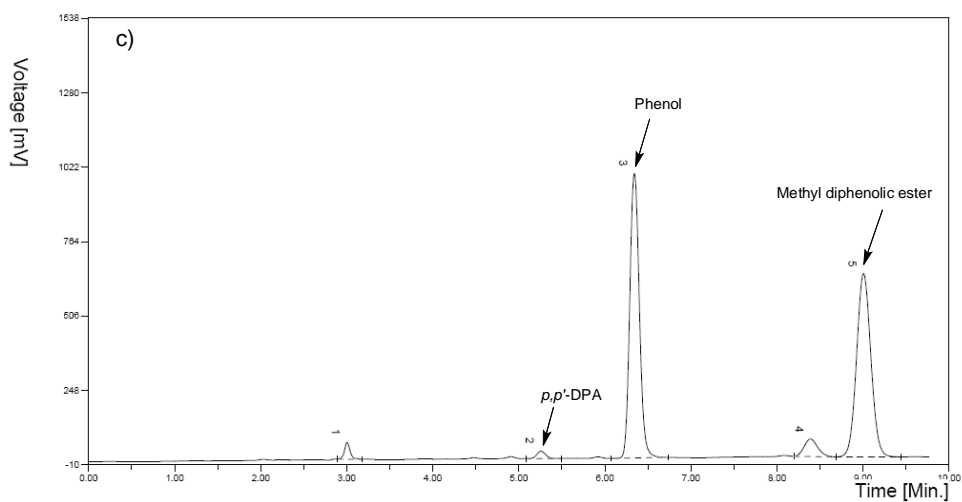
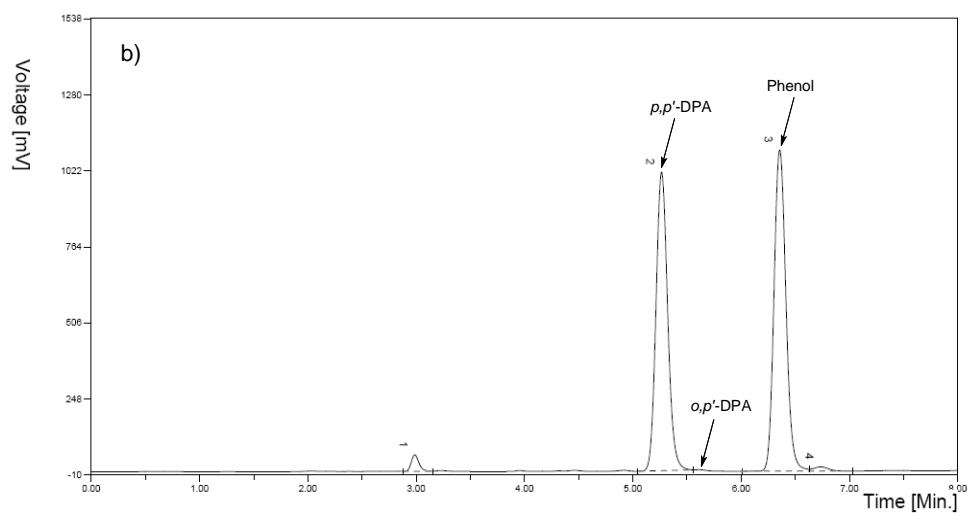
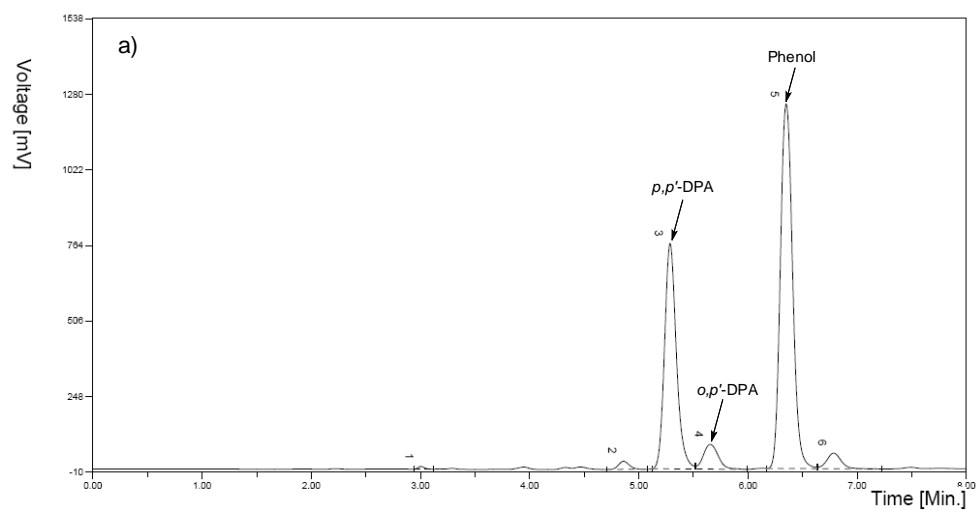
The table S2 shows the results of DPA synthesis with lower ionic liquids loading at elevated temperature.

Table S2.

Entry ^a	Reaction Temperature (°C)	Yield of DPA (mol%)	TOF (h ⁻¹) ^b	Ratio of <i>p</i> , <i>p'</i> -DPA : <i>o</i> , <i>p'</i> -DPA
1	80	6.5	1.3	24
2	90	14.5	2.9	16
3	100	20.7	4.1	12

^a Reaction conditions: levulinic acid (0.46 g, 4 mmol), phenol (1.5 g, 16 mmol), **6** (0.04 mmol) for 5 h. ^b Calculated as the total number of DPA per acid site per hour.

6. HPLC of DPA and diphenolic esters



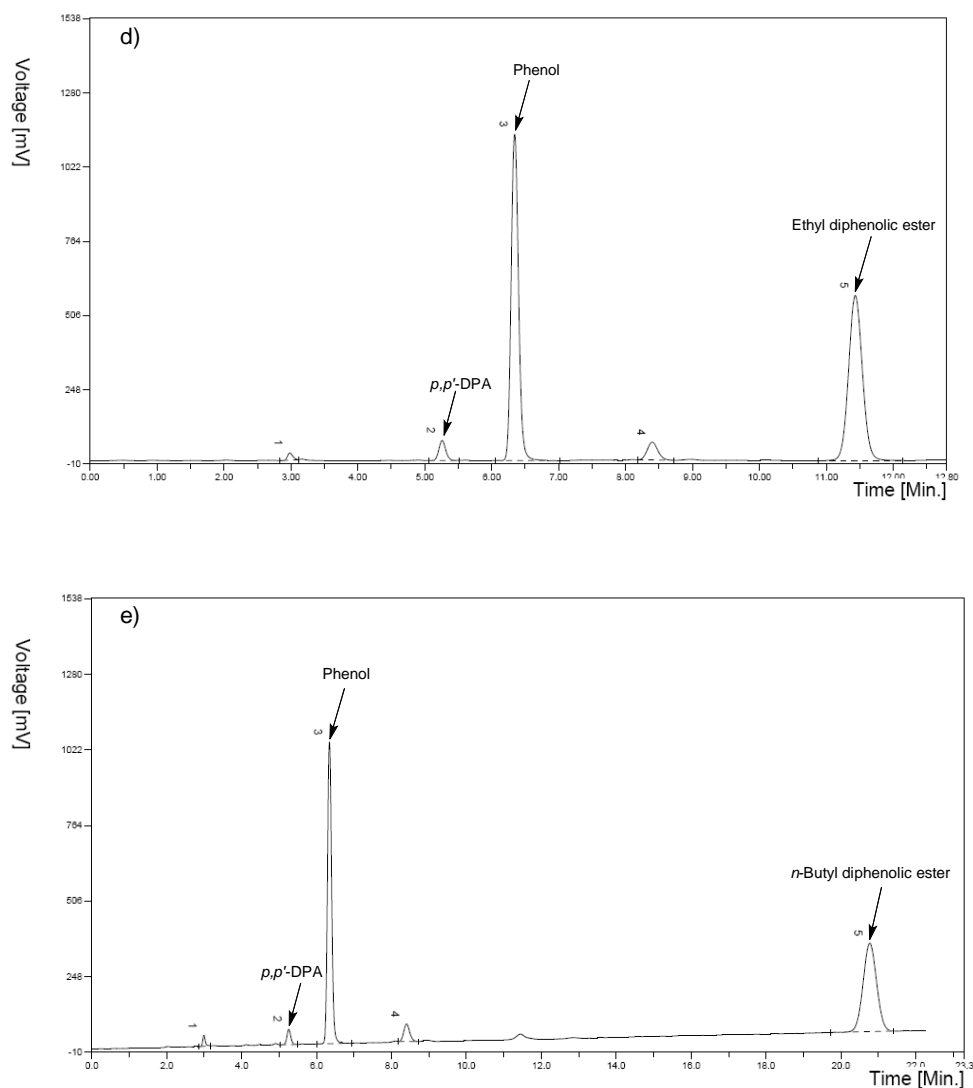
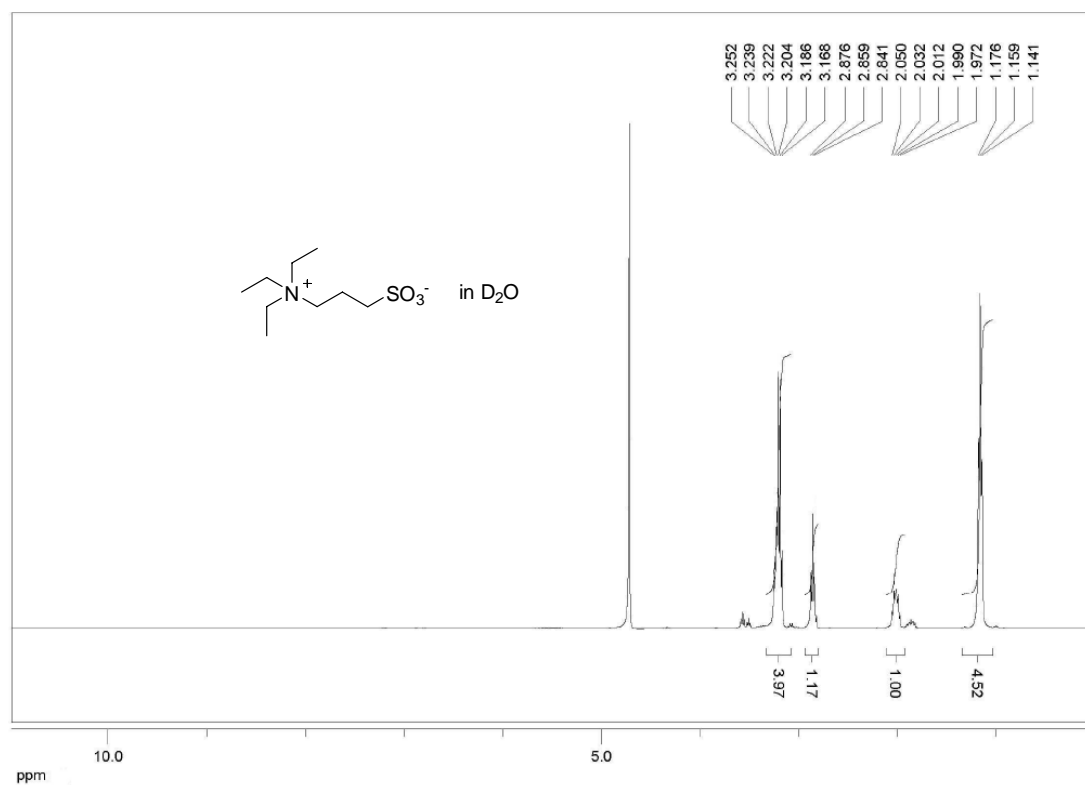
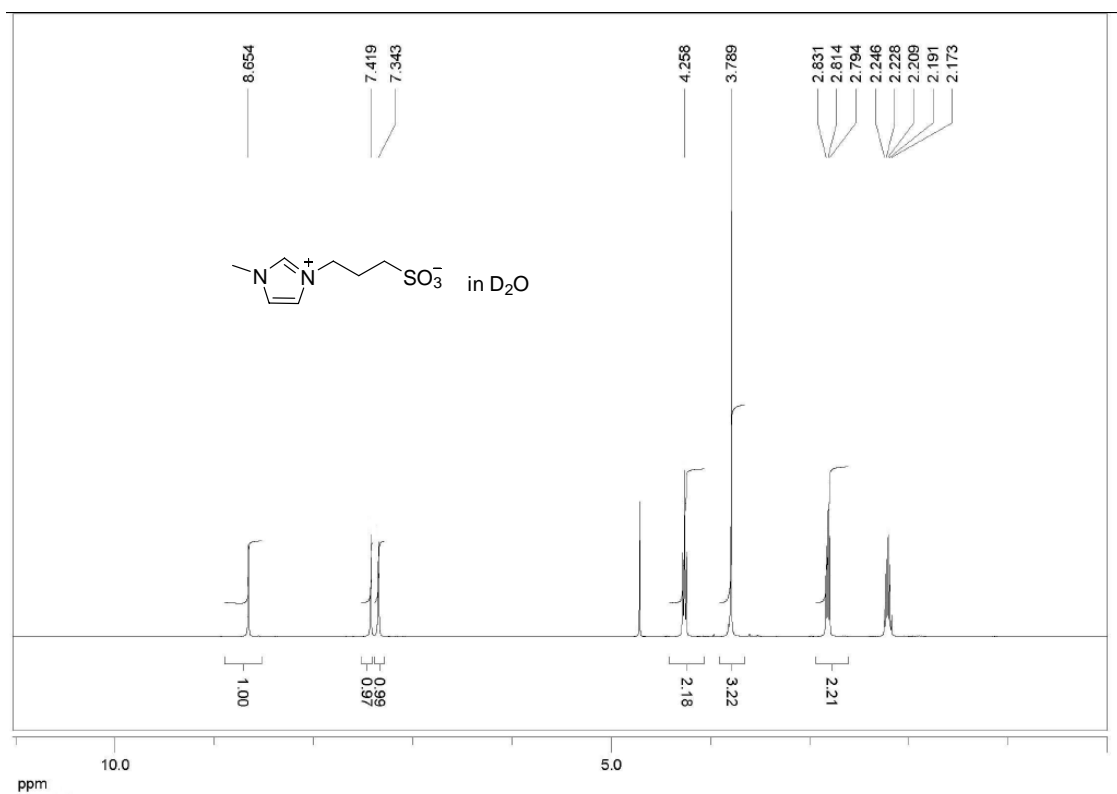
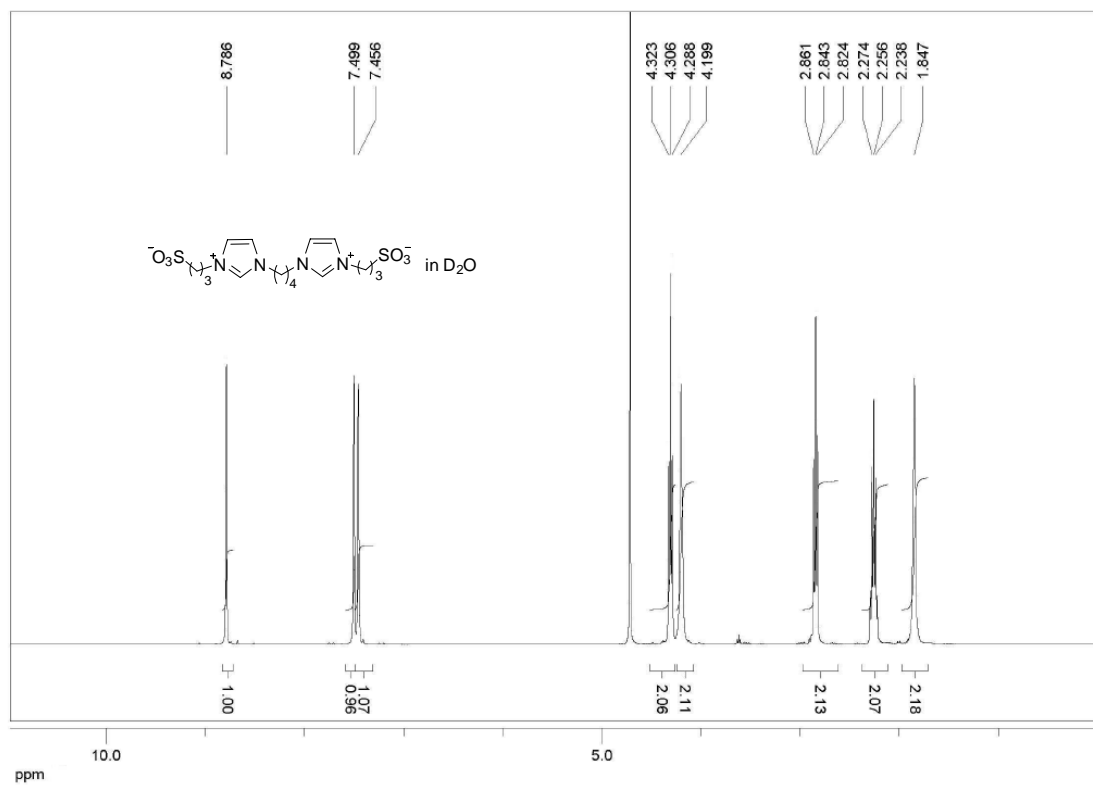
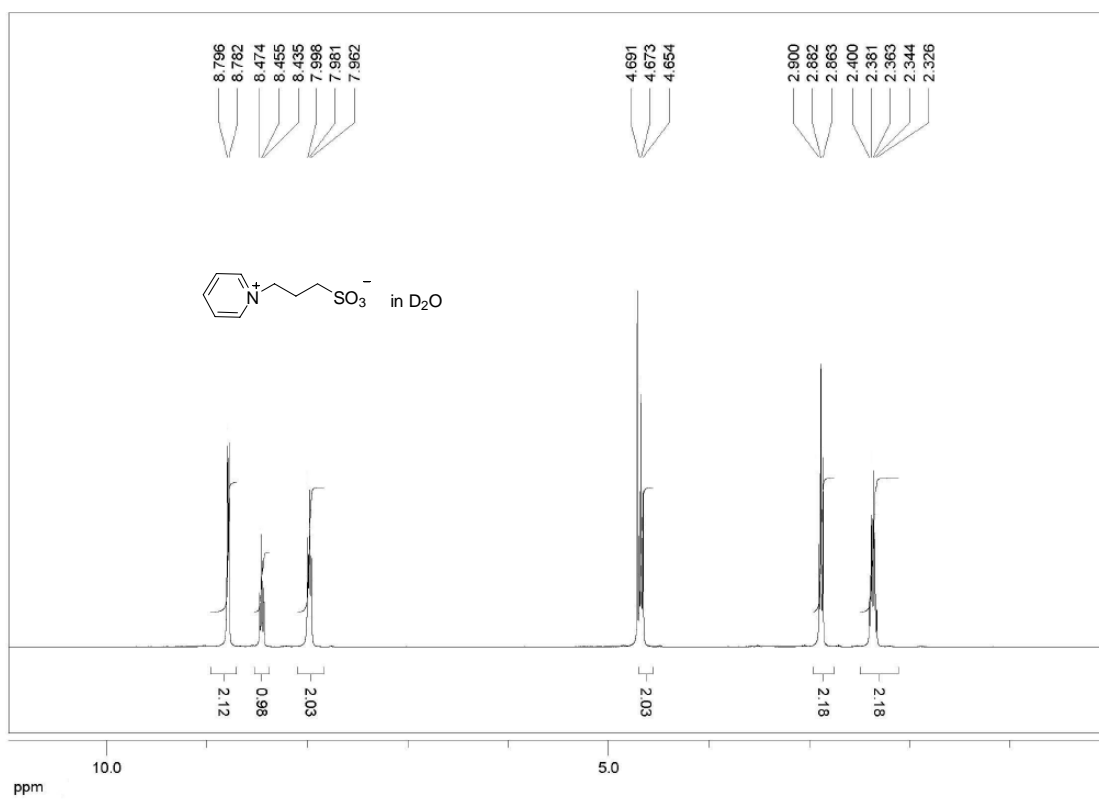


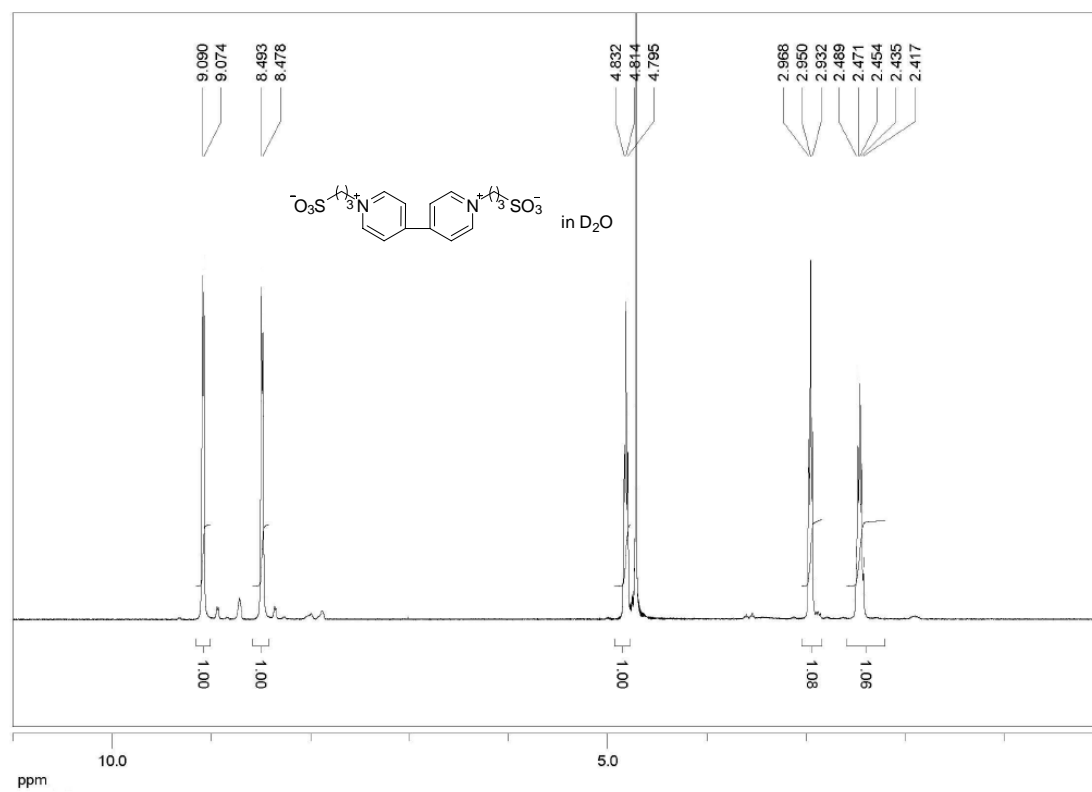
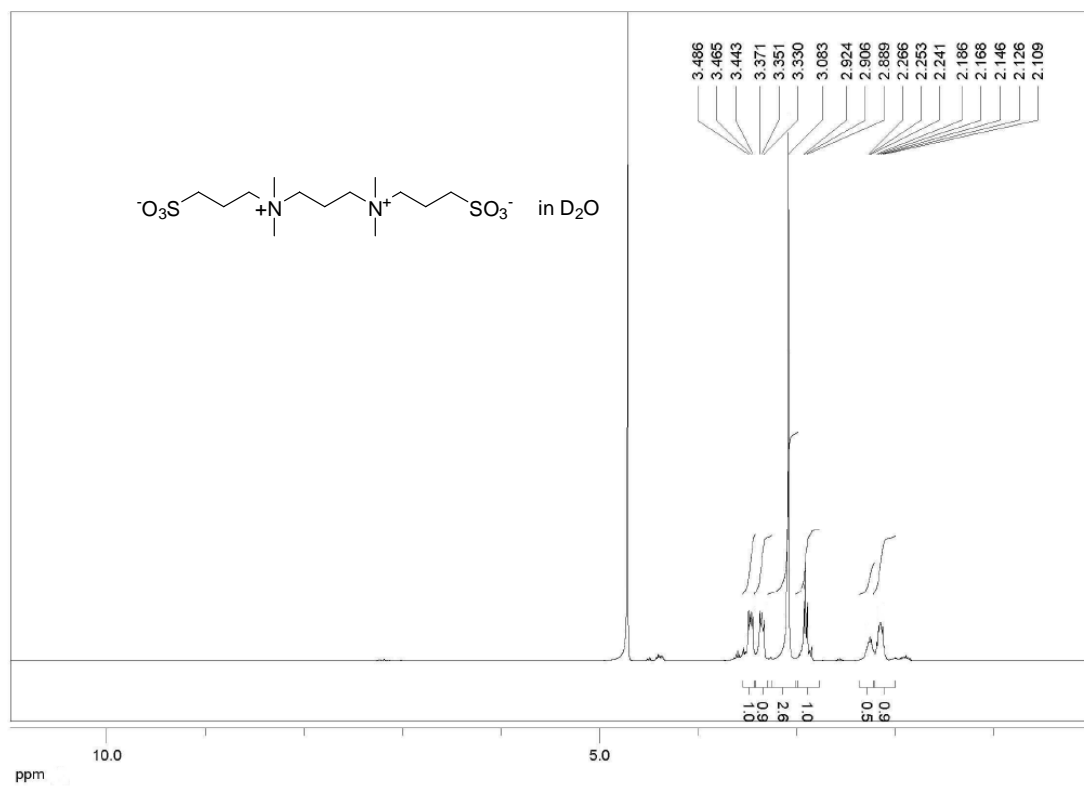
Figure S3. HPLC spectra of DPA/diphenolic esters prepared in the presence of ionic liquids.

Reaction conditions: a) levulinic acid (0.46 g, 4 mmol), phenol (1.5 g, 16 mmol), **1a** (2 mmol) and HSCH₂COOH (0.2 mmol) at 60 °C for 48 h; b) levulinic acid (0.46 g, 4 mmol), phenol (1.5 g, 16 mmol), **4a** (0.9 mmol) and **4b** (0.1 mmol) at 60 °C for 48 h; c), d) and e) levulinic acid (0.46 g, 4 mmol), phenol (1.5 g, 16 mmol), **4a** (0.9 mmol) and **4b** (0.1 mmol) at 60 °C for 48 h and alcohols (2mL) at 40°C for 8 h.

7. ^1H NMR spectra of zwitterionic precursors







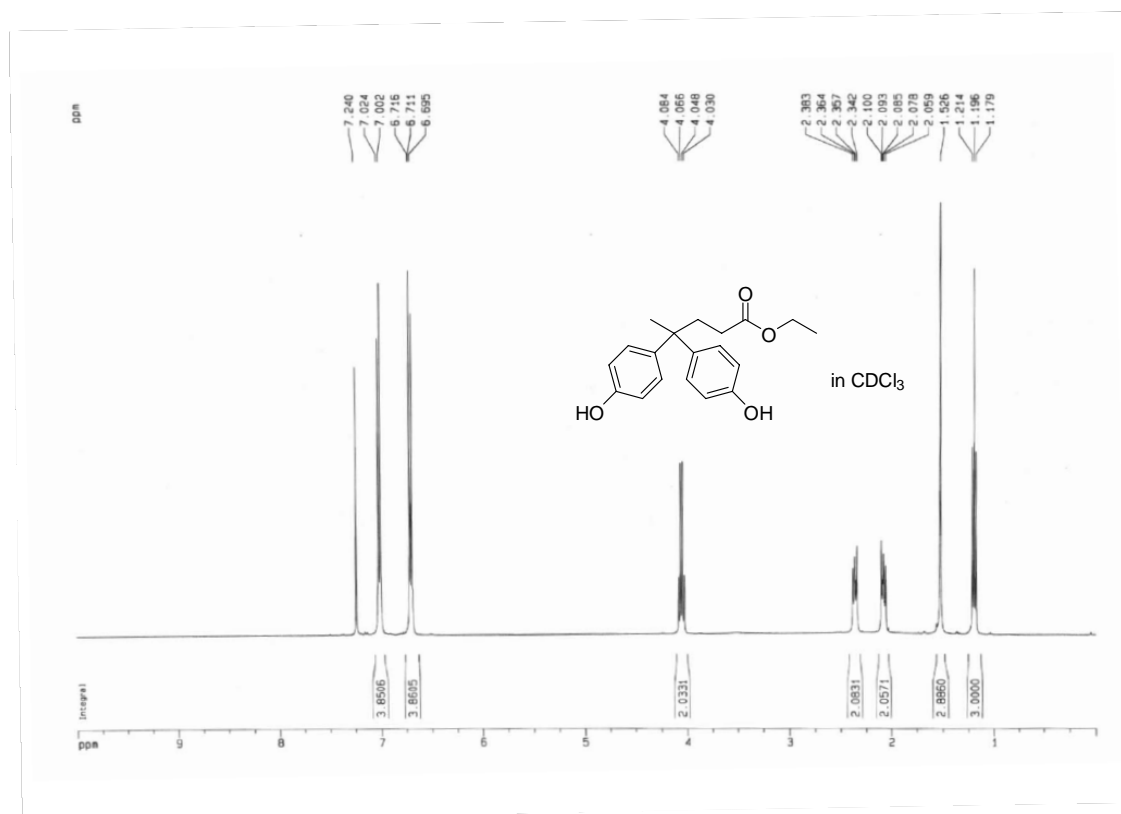


Figure S4. ¹H NMR spectra of zwitterionic precursors

Reference:

- 1 a) M. Yoshizawa, M. Hirao, K. Ito-Akita and H. Ohno, *J. Mater. Chem*, 2001, **11**, 1057; b) A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes and J. H. Davis, *J. Am. Chem. Soc.*, 2002, **124**, 5962.
- 2 a) C. Thomazeau, H. Olivier-Bourbigou, L. Magna, S. Luts, B. Gilbert, *J. Am. Chem. Soc* **2003**, *125*, 5264 ;b) Y. Wang, D. Jiang, L. Dai, *Catalysis Communications*, **2008**, *9*, 2475; c) H. Xing, T. Wang, Z. Zhou, Y. Dai, *J. Mol. Cata. A: Chem*, **2007**, *264*, 53