

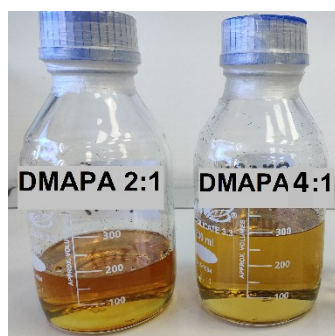
Supplementary Information

Protic ionic liquids from di- or triamines: even cheaper Brønsted acidic catalysts

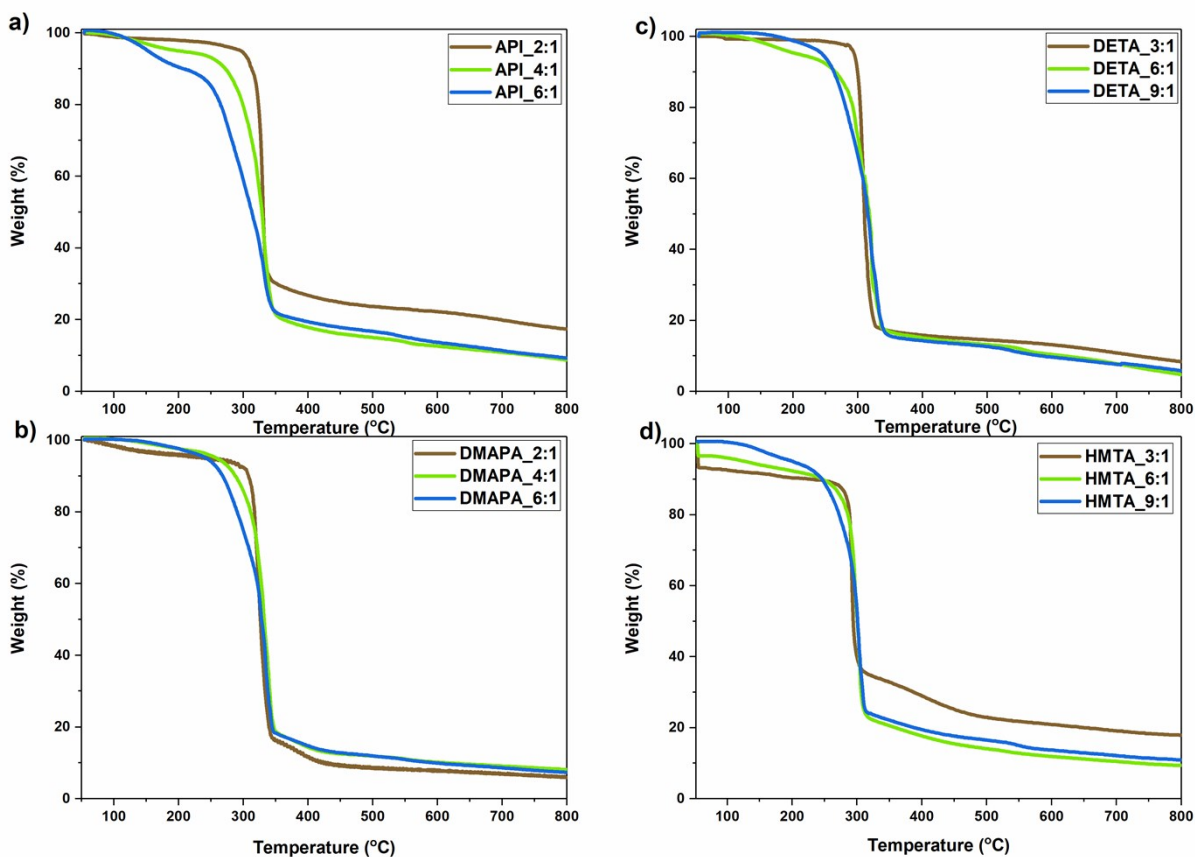
Alina Brzęczek-Szafran,^{*a} Justyna Więclawik,^a Natalia Barteczko,^a Anna Szelwicka,^a Emily Byrne,^b Anna Kolanowska,^a Małgorzata Swadźba Kwaśny,^{*b} Anna Chrobok^a

^a Faculty of Chemistry, Silesian University of Technology, Krzywoustego 4, Gliwice, 44-100, Poland

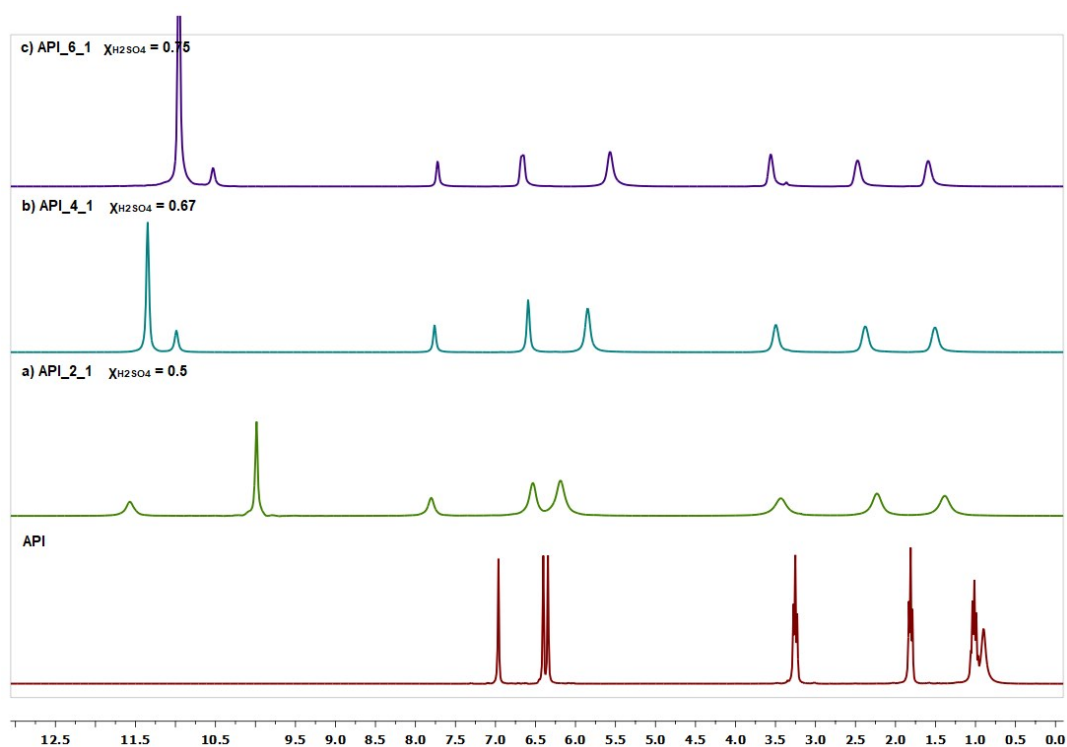
^b QUILL, School of Chemistry and Chemical Engineering, Queen's University Belfast



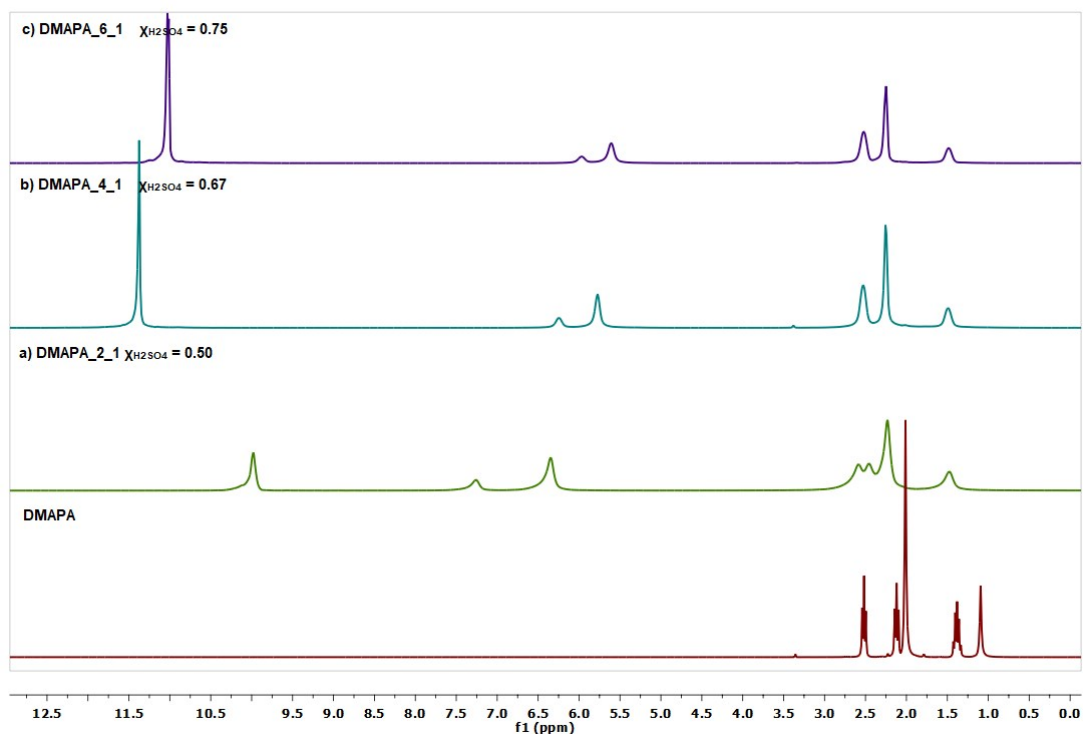
S1. Physical appearance of dicationic DMAPA_2_1 and DMAPA_4_1 ILs based on sulfuric acid synthesized by adding an acid to an amine.



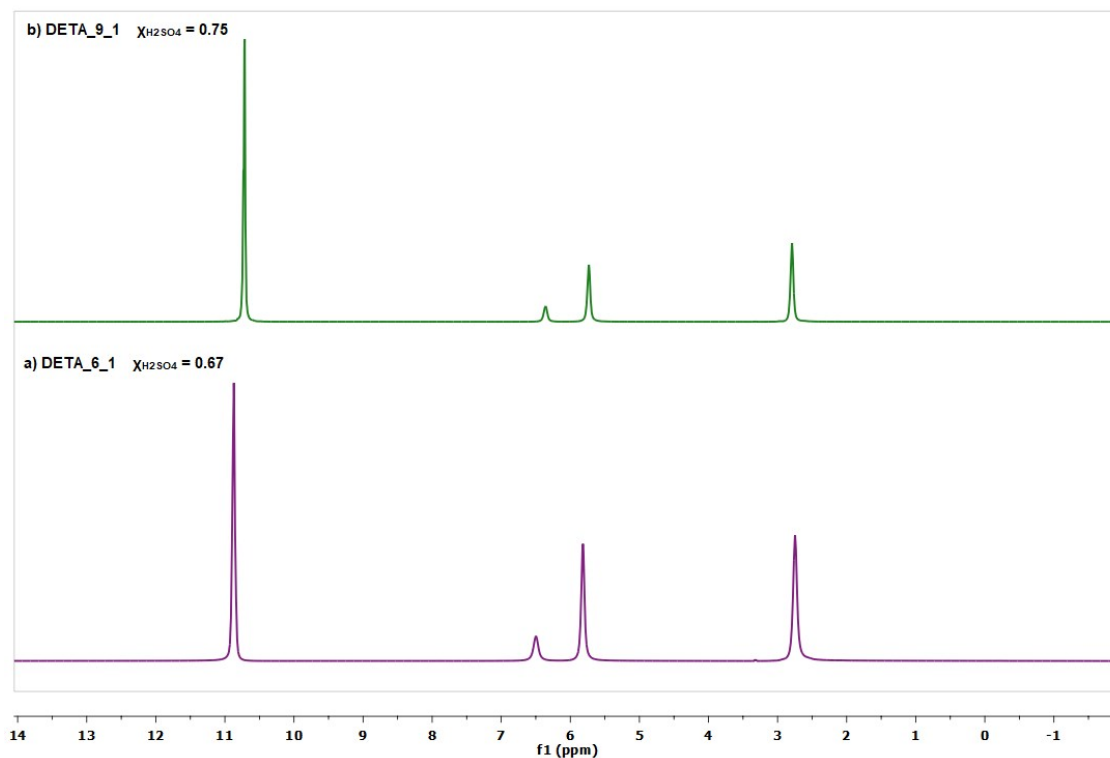
S2. Thermogravimetric analysis curves, depicting water loss and thermal decomposition of di- and three-cationic ILs as a function of temperature.



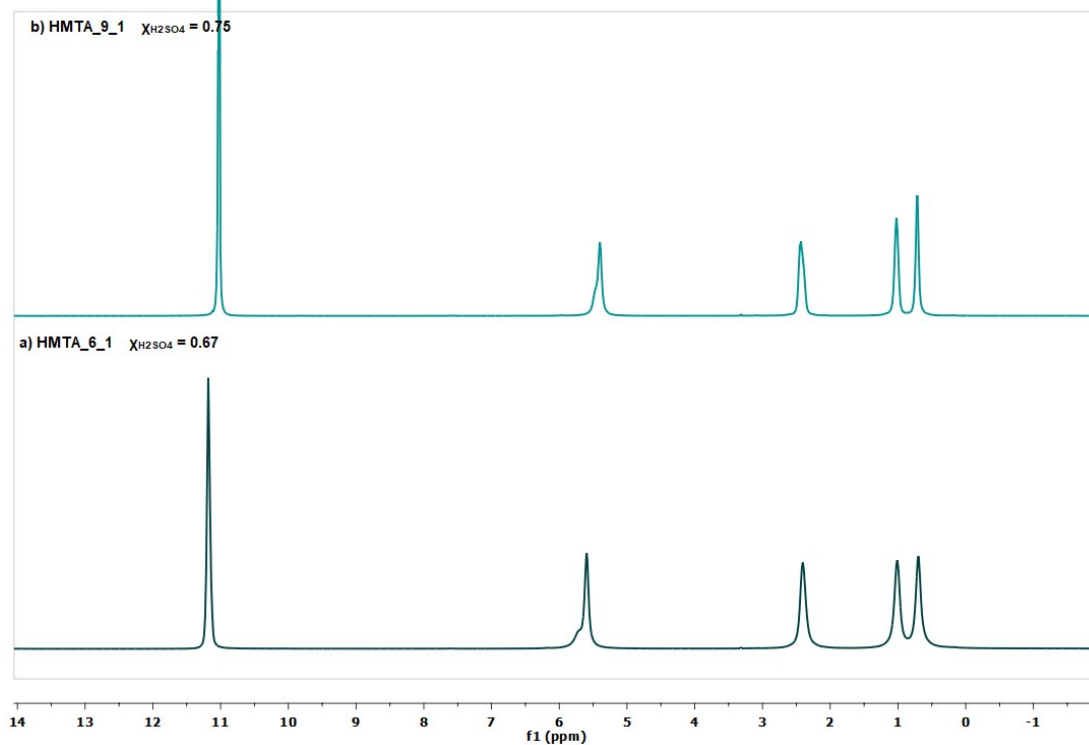
S3. ¹H NMR spectra (400.112 MHz, 25 °C, neat) of the systems based on 1-(3-aminopropyl)imidazole (API) and its sulfuric acid mixtures: API_2_1 (a), API_4_1 (b), API_6_1 (c).



S4. ¹H NMR spectra (400.112 MHz, 25 °C, neat) of the systems based on N,N-dimethylaminopropylamine (DMAPA) and its sulfuric acid mixtures: DMAPA_2_1 (a), DMAPA_4_1 (b), DMAPA_6_1 (c)



S5. 1H NMR spectra (400.112 MHz, 25 °C, neat) of the systems based on the mixtures of diethylenetriamine and sulfuric acid: DETA_6_1 (a), DETA_9_1 (b). The neat spectrum of diethylenetriamine was not registered due to the solid state of a base at RT.

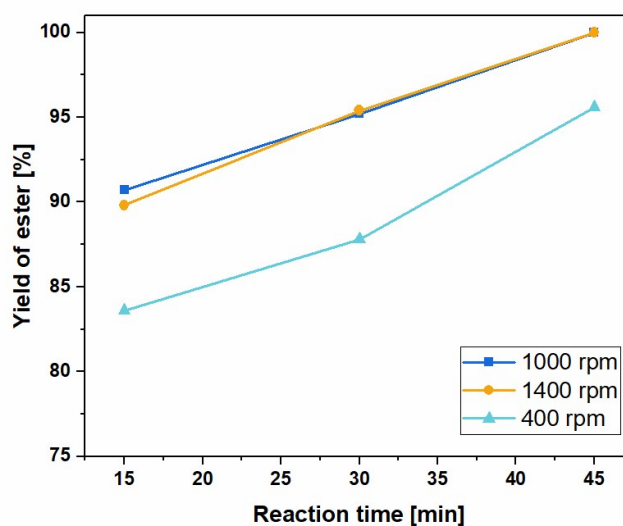


S6. 1H NMR spectra (400.112 MHz, 25 °C, neat) of the systems based on the mixtures of bis(hexamethylene)triamine and sulfuric acid: HMTA_6_1 (a), HMTA_9_1 (b). The neat spectrum of bis(hexamethylene)triamine was not registered due to the solid state of a base at RT.

S7. Viscosity and density values registered at 25, 50 and 80 °C for di- and three-cationic ILs.

Mixture	25 °C		50 °C		80 °C	
	η (mPa s)	ρ (kg/m ³)	η (mPa s)	ρ (kg/m ³)	η (mPa s)	ρ (kg/m ³)
DMAPA_2_1	16560*	1.5	3762	1.49	707	1.48
DMAPA_4_1	307	1.63	109	1.61	67	1.59
DMAPA_6_1	104	1.69	44	1.67	19	1.65
API_2_1	28914*	1.58	5051	1.57	614	1.55
API_4_1	385	1.68	133	1.88	50	1.64
API_6_1	120	1.72	49	1.71	22	1.68
DETA_3_1	-	-	-	-	-	-
DETA_6_1	875	1.82	245	1.80	78	1.78
DETA_9_1	206	1.84	77	1.82	30	1.79
HMTA_3_1	-	1.41	-	1.40	664	1.39
HMTA_6_1	1067	1.55	328	1.53	110	1.51
HMTA_9_1	245	1.62	93	1.60	38	1.58

*Estimated values, values beyond the measurement range.



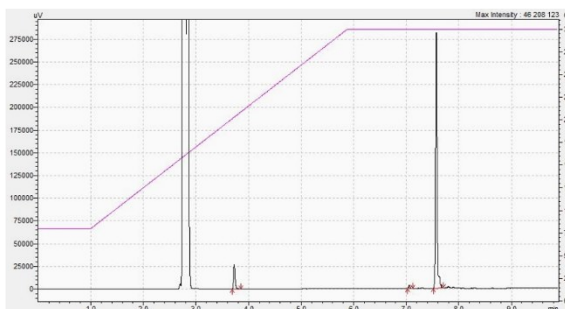
S8. Effect of a different stirring speed on the yield of methyl oleate using triamino protic ionic liquid mixture HMTA_9_1 as the catalyst. Reaction conditions: 60 °C, methanol/oleic acid molar ratio: 10:1, catalyst loading: 5 mol %.

S9. Retention times of investigated esters on GC analysis.

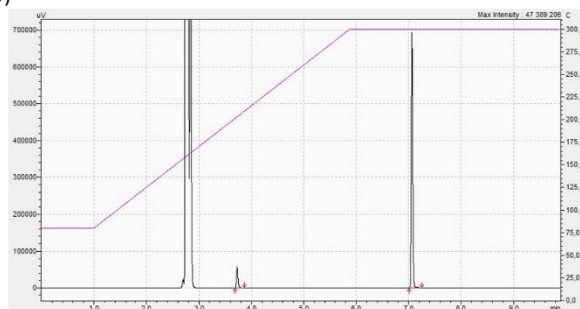
methyl oleate	7.57 min	a)
methyl palmitate	7.06 min	b)
methyl stearate	7.55 min	c)
methyl laureate	6.02 min	d)

Retention time of decane: 3.73

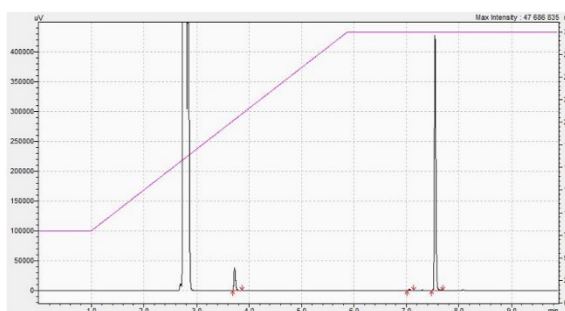
a)



b)



c)



d)

