

Pd-catalyzed Ethylene Methoxycarbonylation with Brønsted Acid Ionic Liquids as Promoter and Phase-separable Reaction Media

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S1. Synthesis of Brønsted acid ionic liquids (BAILs)

1-(4-sulfonylbutyl)-3-methylimidazolium methanesulfonate: An equimolar mixture of 1-(4-sulfonylbutyl)-3-methylimidazolium and MeSO_3H (x%) was heated with stirring at 60 °C overnight. During this period the solid liquefied resulting in the formation of the desired ILs as a slightly yellow sticky oil, which was washed with ethyl acetate and dried under vacuum at 65 °C overnight (Yield 93%).

^1H NMR (D_2O , 300MHz) δ /ppm: 1.69 (m, 2H), 1.97 (m, 2H), 2.76 (s, 3H), 2.90 (^3J (HH) = 7.5 Hz, t, 2H), 3.84 (s, 3H), 4.20 (^3J (HH) = 7.5 Hz, t, 2H), 7.39 (m, 1H), 7.45 (m, 1H), 8.70 (s, 1H).

1-(4-sulfonylbutyl)-3-methylimidazolium hydrogensulfate: An equimolar mixture of 1-(4-sulfonylbutyl)-3-methylimidazolium and H_2SO_4 (98%) was heated with stirring at 60 °C overnight. During this period the solid liquefied resulting in the formation of the desired ILs as a slightly yellow sticky oil, which was washed with ethyl acetate and dried under vacuum at 65 °C overnight (Yield 95%).

^1H NMR (D_2O , 300MHz) δ /ppm: 1.70 (m, 2H), 1.95 (m, 2H), 2.89 (^3J (HH) = 7.5 Hz, t, 2H), 3.84 (s, 3H), 4.19 (^3J (HH) = 7.5 Hz, t, 2H), 7.38 (m, 1H), 7.44 (m, 1H), 8.69 (s, 1H).

1-(4-sulfonylbutyl)-3-methylimidazolium p-toluenesulfonate: An equimolar mixture of 1-(4-sulfonylbutyl)-3-methylimidazolium and *p*-TsOH were grounded in a mortar until the two white solids turned into a viscous liquid. The latter was washed three times with ethyl acetate and dried under vacuum at 65 °C overnight (Yield 92%).

^1H NMR (D_2O , 300MHz) δ /ppm: 1.68 (m, 2H), 1.96 (m, 2H), 2.34 (s, 3H), 2.89 (^3J (HH) = 7.5 Hz, t, 2H), 3.82 (s, 3H), 4.18 (^3J (HH) = 7.5 Hz, t, 2H), 7.32 (^3J (HH) = 7.5 Hz, d, 2H), 7.37 (m, 1H), 7.43 (m, 1H), 7.63 (^3J (HH) = 7.5 Hz, d, 2H), 8.67 (s, 1H).

1-(4-sulfonylbutyl)pyridinium p-toluenesulfonate: An equimolar mixture of 1-(4-sulfonylbutyl)pyridinium and *p*-TsOH were grounded in a mortar until the two white solids turned

into a viscous liquid. The latter was washed three times with ethyl acetate and dried under vacuum at 65 °C overnight (Yield 88%).

^1H NMR (D_2O , 300MHz) δ /ppm: 1.76 (m, 2H), 2.14 (m, 2H), 2.34 (s, 3H), 2.92 (^3J (HH) = 7.5 Hz, t, 2H), 4.60 (^3J (HH) = 7.5 Hz, t, 2H), 7.31 (^3J (HH) = 7.5 Hz, d, 2H), 7.63 (^3J (HH) = 7.5 Hz, d, 2H), 8.02 (^3J (HH) = 7.5 Hz, t, 2H), 8.49 (^3J (HH) = 7.5 Hz, t, 1H), 8.81 (^3J (HH) = 7.5 Hz, d, 2H).

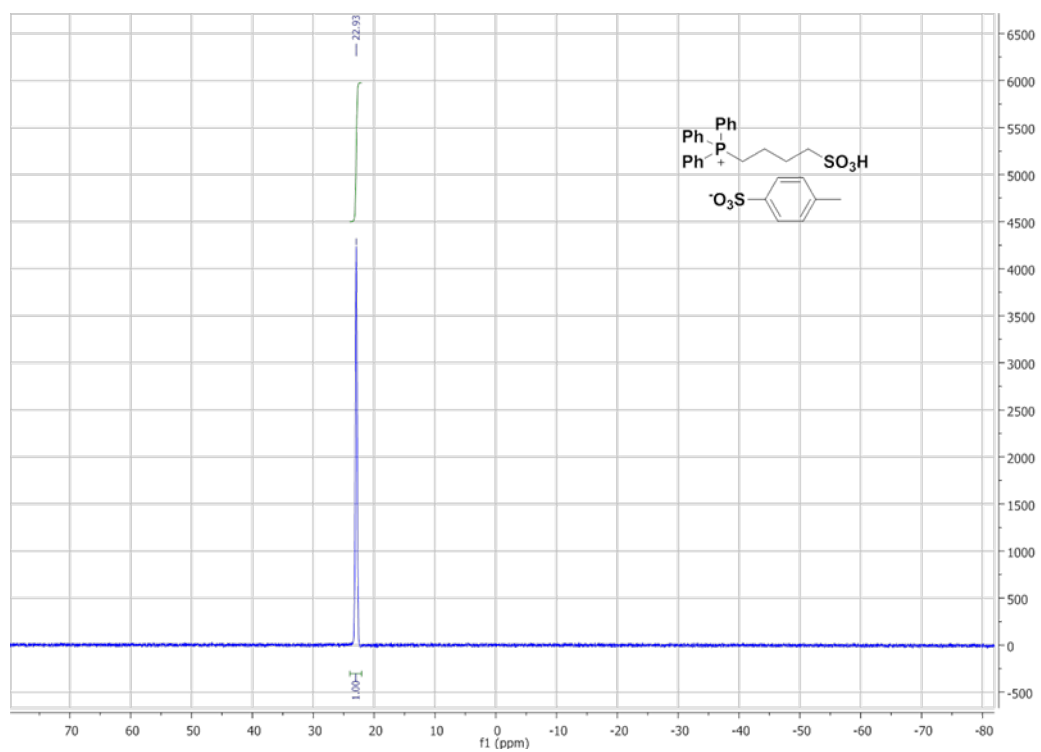
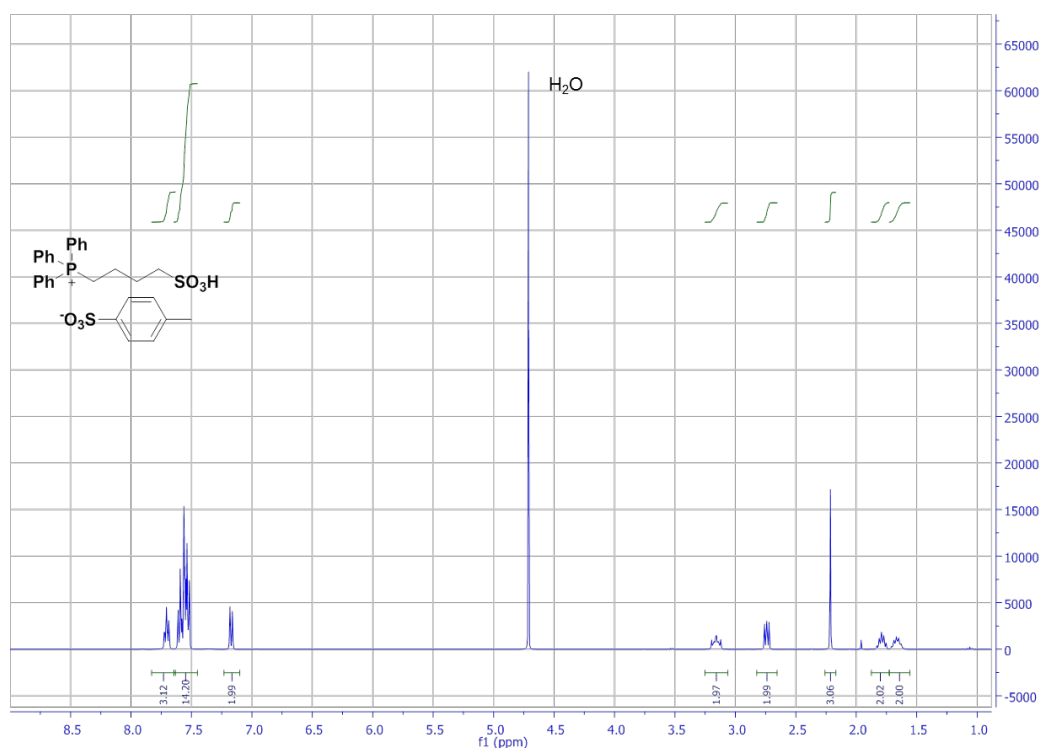
1-(4-sulfonylbutyl)triethylammonium, p-toluenesulfonate: An equimolar mixture of 1-(4-sulfonylbutyl)triethylammonium and *p*-TsOH were grounded in a mortar until the two white solids turned into a viscous liquid. The latter was washed three times with ethyl acetate and dried under vacuum at 65°C overnight (Yield 84%).

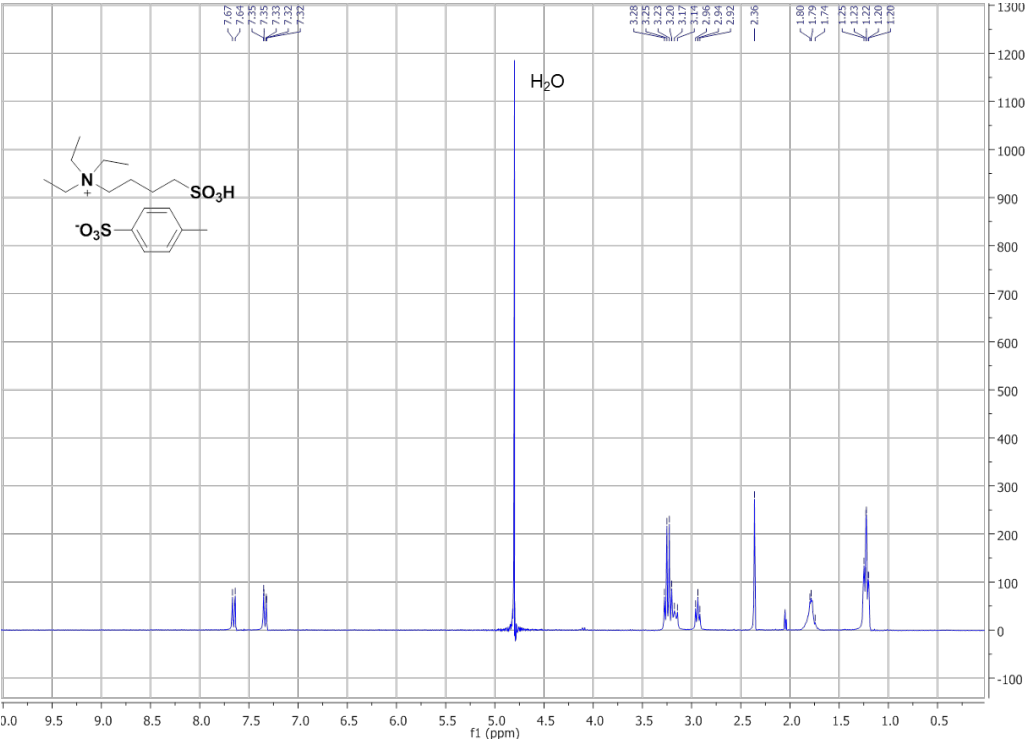
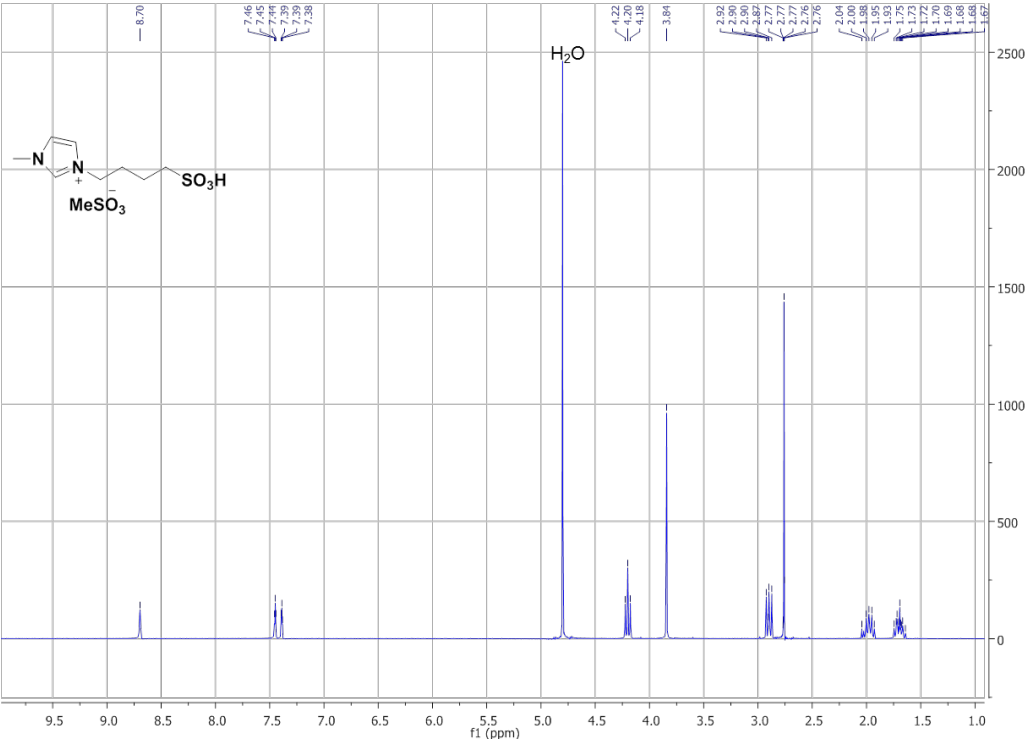
^1H NMR (D_2O , 300MHz) δ (ppm) 1.24 (^3J (HH) = 7.5 Hz, t, 9H), 1.79 (m, 4H), 2.37 (s, 3H), 2.94 (^3J (HH) = 7.5 Hz, t, 2H), 3.18 (m, 2H), 3.24 (^3J (HH) = 7.5 Hz, q, 6H), 7.34 (^3J (HH) = 7.5 Hz, d, 2H), 7.67 (^3J (HH) = 7.5 Hz, d, 2H).

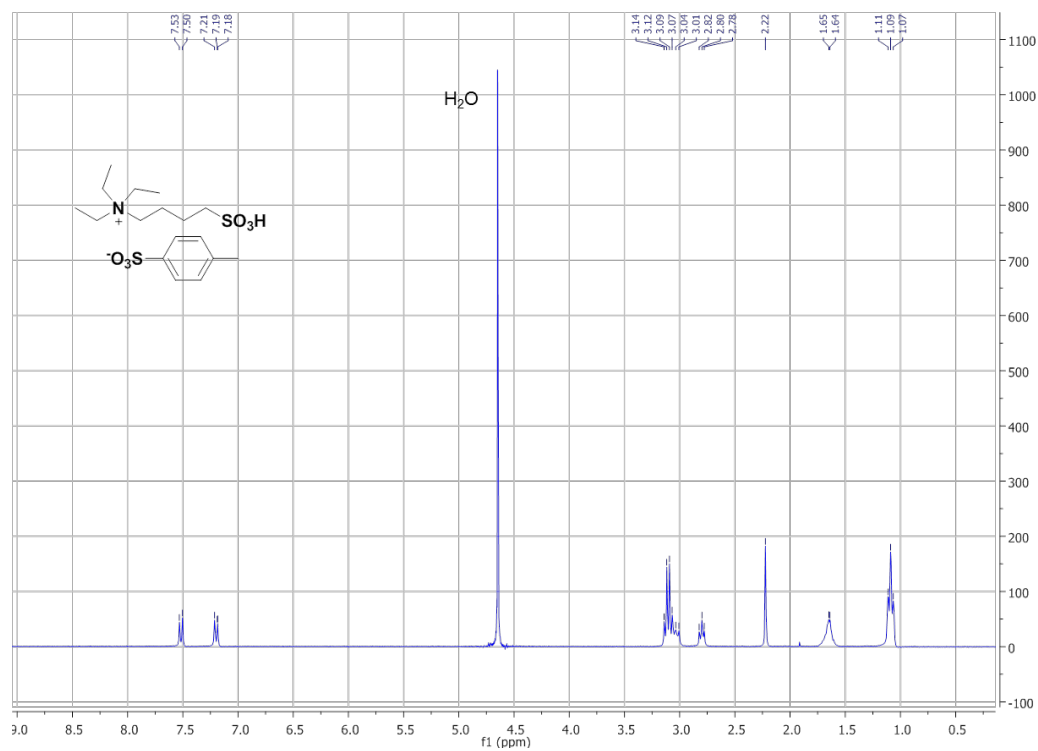
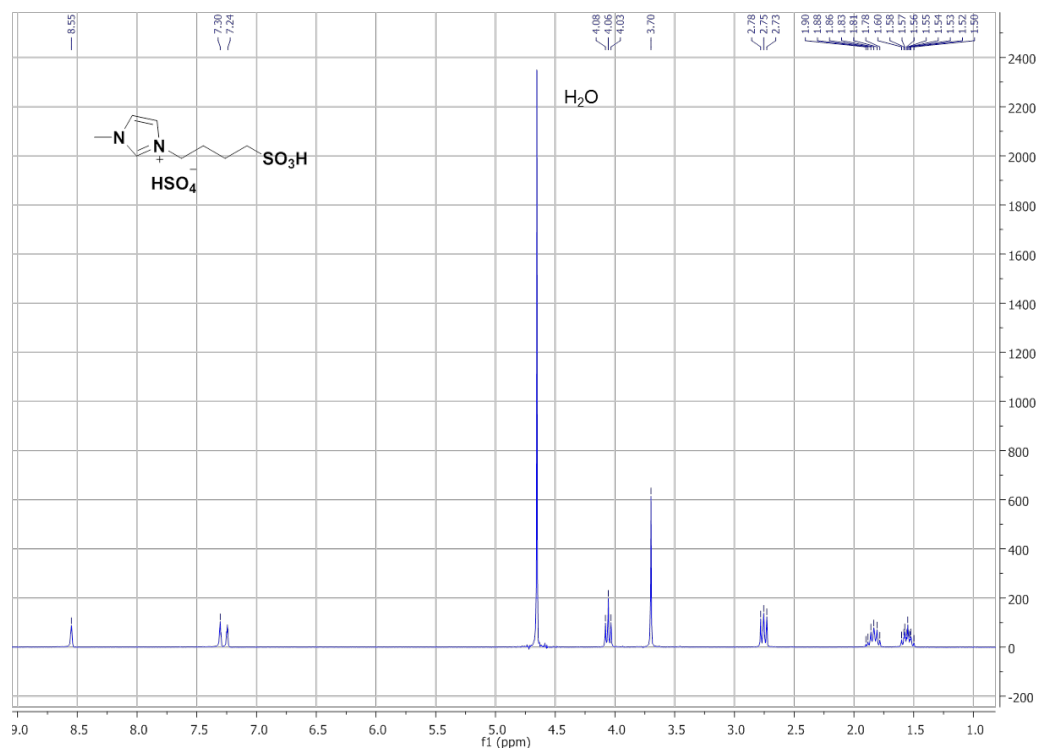
1-(4-sulfonylbutyl)triphenylphosphonium p-toluenesulfonate: An equimolar mixture 1-(4-sulfonylbutyl)triphenylphosphonium and *p*-TsOH were grounded in a mortar until the two white solids turned into a viscous liquid. The latter was washed three times with ethyl acetate and dried under vacuum at 65 °C overnight (Yield 93%).

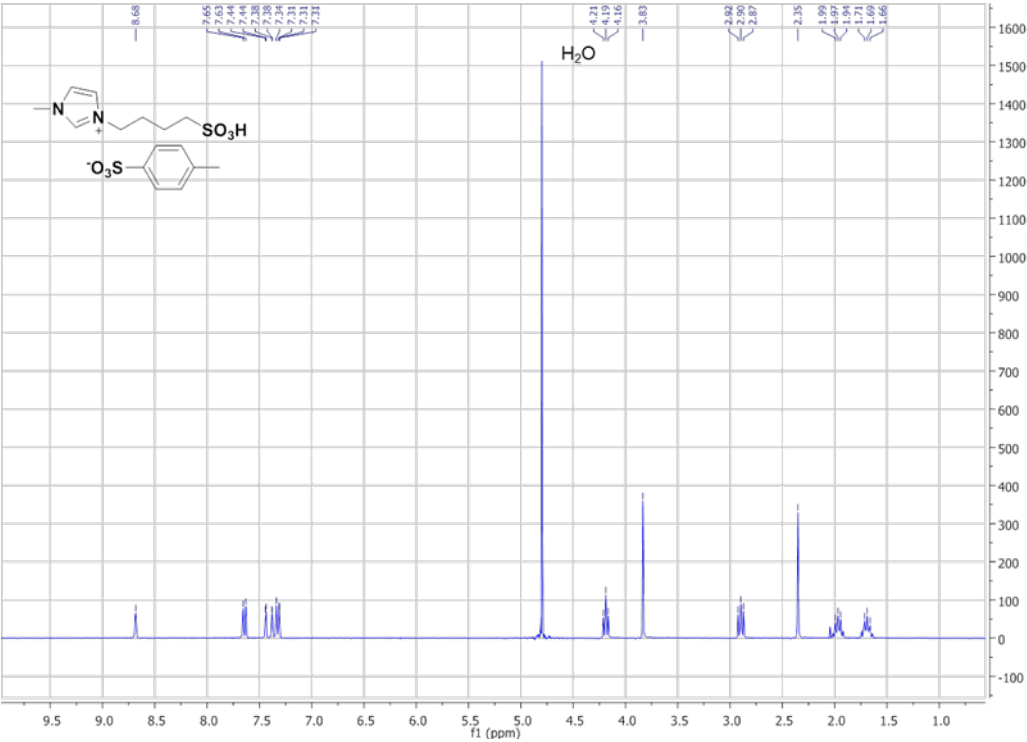
^1H NMR (D_2O , 300MHz) δ /ppm: 1.75 (m, 2H), 1.86 (m, 2H), 2.29 (s, 3H), 2.82 (^3J (HH) = 7.5 Hz, t, 2H), 3.23 (m, 2H), 7.26 (^3J (HH) = 7.5 Hz, d, 2H), 7.64 (m, 14H), 7.89 (m, 3H). $^{31}\text{P}\{^1\text{H}\}$ NMR (D_2O , 202MHz) δ /ppm: 22.93.

S2. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the prepared BAILs in D_2O

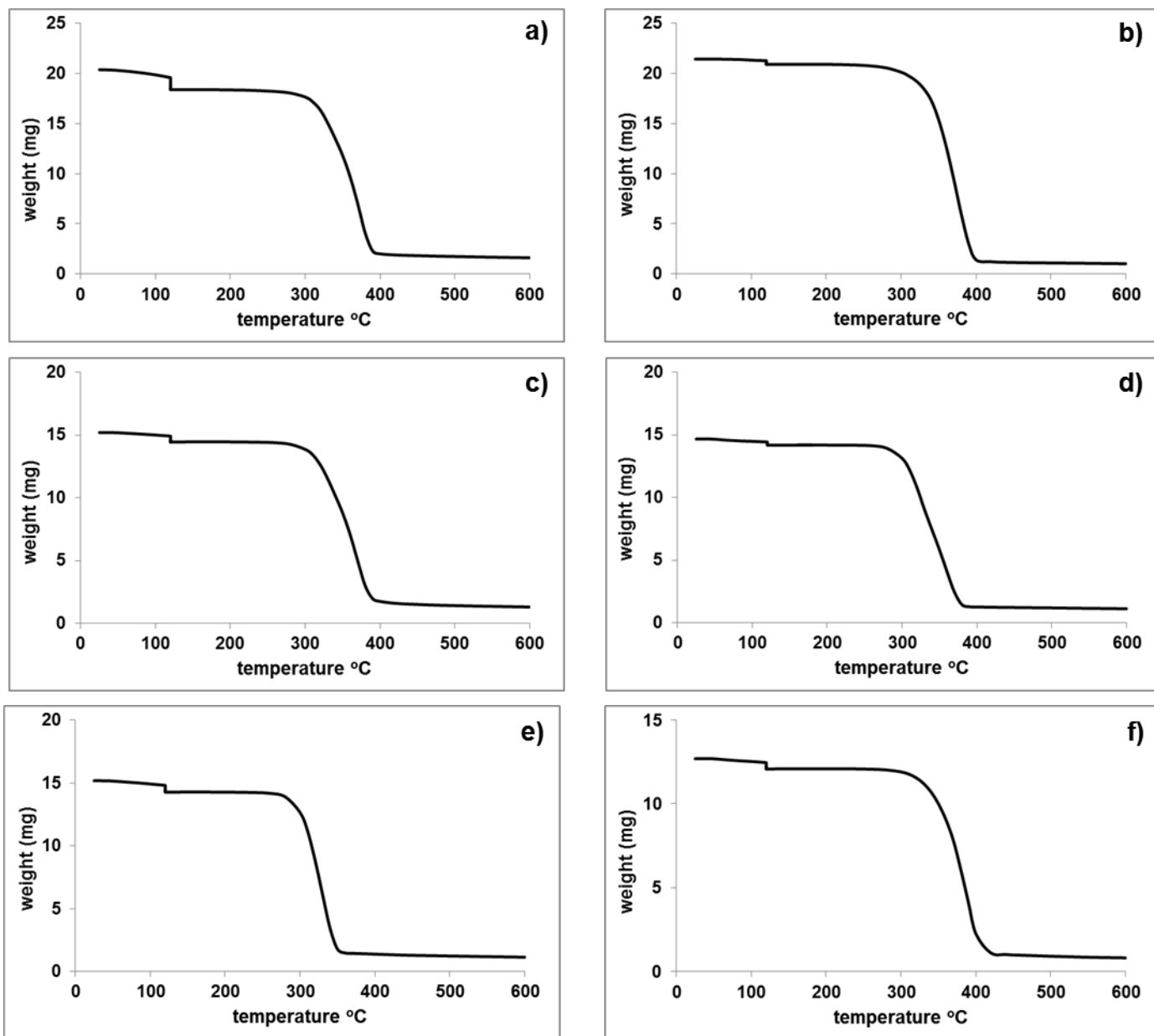








S2. TG profiles of the prepared BAILs and water content



a) 1-(4-sulfonylbutyl)-3-methylimidazolium hydrogensulfate, **b)** 1-(4-sulfonylbutyl)-3-methylimidazolium methanesulfonate, **c)** 1-(4-sulfonylbutyl)-3-methylimidazolium *p*-toluenesulfonate, **d)** 1-(4-sulfonylbutyl)triethylammonium *p*-toluenesulfonate, **e)** 1-(4-sulfonylbutyl)pyridinium *p*-toluenesulfonate, **f)** 1-(4-sulfonylbutyl)triphenylphosphonium *p*-toluenesulfonate.

Estimation of water content in the prepared BAILs from TGA analysis:

[SBMI][HSO₄] ~ 5.9 wt%, [SBMI][MeSO₃] ~ 0.9 wt%, [SBMI][*p*-TsO] ~ 1.9 wt%, [SBTA][*p*-TsO] ~ 0.7 wt%, [SBPP][*p*-TsO] ~ 2.6 wt%, [SBP][*p*-TsO] ~ 2.4 wt%.