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 MeSO₃H (x%) was heated with stirring at 60 ºC 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 ºC overnight (Yield 93%).

¹H NMR (D₂O, 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 H₂SO₄ (98%) was heated with stirring at 60 ºC 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 ºC overnight (Yield 95%).

¹H NMR (D₂O, 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 ºC overnight (Yield 92%).

¹H NMR (D₂O, 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 (D2O, 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 (D2O, 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 (D2O, 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). 31P{1H} NMR (D2O, 202MHz) δ/ppm: 22.93.
S2. \(^1\text{H}\) and \(^{31}\text{P}(^1\text{H})\) NMR spectra of the prepared BAILs in D\(_2\)O
**S2. TG profiles of the prepared BAILs and water content**

![Graphs of TG profiles](image)

- 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%