Synthesis of compounds **A1**, **A2**, **A5**, and **A6** involve refluxing 1 molar equiv of 1,3,5-tris(bromomethyl)benzene with 4 molar equiv 1-butylimidazole, 1-methylimidazole, 1-butylpyrrolidine, or tripropylphosphine respectively in isopropanol for 7 days. After removal of isopropanol with a rotary evaporator, the bromide salt was dissolved in water and purified by extraction with ethyl acetate. Water was removed by a rotary evaporator and the remaining salt was dried under vacuum.

Synthesis of compounds **B1**, **B4**, and **B6** involve refluxing 1 molar equiv of 2,4,6-tris(bromomethyl)mesitylene with 4 molar equiv of 1-butylimidazole, 1-benzylimidazole, or tripropylphosphine respectively in isopropanol for 7 days. After the reaction, the products were all purified by extraction with ethyl acetate and dried under vacuum. Compound **B2** was synthesized carrying out the same procedure using 1 molar equiv of 2,4,6-tris(bromomethyl)mesitylene with 4 molar equiv of 1-methylimidazole but using toluene as the solvent.

Compounds **C2**, **C3**, **C4**, and **C5** were synthesized by refluxing 1 molar equivalent of Tris(2-chloroethyl)amine hydrochloride in isopropyl alcohol with 6 molar equivalents of 1-methylimidazole, 1- benzylimidazole, 1-butylpyrrolidine, and 1-(2-hydroxyethyl)imidazole respectively. Rotoevaporation of the solvent yielded the crude hydrochloride salt. This was then dissolved in water with 2 molar equivalents of NaOH. NaOH is used to neutralize the hydrochloride salt. The excess starting material was extracted with ethyl acetate. Final products were synthesized through a metathesis reaction of the chloride salts with lithium trifluorlmethanesulfonimide (NTf_2^-). Specifically, 1 molar equivalent of the chloride salt was dissolved in water and treated with 4.5 molar equivalents of the lithium NTf_2^-. The resulting solution was stirred at room temperature for 24 hrs. After that, dichloromethane was added to

the solution to dissolve the tricationic NTf_2^- salt that has phase separated from the water. The lithium chloride, sodium chloride, excess sodium hydroxide and excess lithium NTf_2^- were removed from the dichloromethane phase with successive washing with water. Removal of dichloromethane through rotoevaportaiton followed by vacuum drying over phosphorous pentoxide at 80 ^{0}C for 24hrs resulted in the pure tricationic ILs with NTf_2^- counter ions.

Compounds **C1** was synthesized by refluxing 1 molar equivalent of Tris(2-chloroethyl)amine hydrochloride in isopropyl alcohol with 6 molar equivalents of 1-butylimidazole for 5 days. Rotoevaporation of the solvent yielded the crude hydrochloride salt. This was then dissolved in water and passed through anion exchange resin - Amberlite IRA-400(Cl) saturated with OH^- anion to obtain the hydroxide salt of the trication. The eluent was then titrated with tetrafluoroboric acid until pH 7. Evaporation of water under vacuum and drying under phosphorous pentoxide at 80^{0}C yield the pure TIL2 as the BF_4^- salt.

Synthesis of compound **C6** involves refluxing 1 molar equiv of tris(2-chloroethyl)amine hydrochloride with 4 equiv of tripropylphosphine in isopropanol. The product was purified by extraction with ethyl acetate and dried under vacuum. Purified chloride salt was converted to hydroxide form using an ion exchange resin. The metathesis of the hydroxide salt was then carried out using fluoroboric acid. Compound 9 was isolated by the subsequent removal of water using rotary evaporator.

Synthesis of compound **C7** involves refluxing 1 molar equivalent of tris(2-chloroethyl)amine hydrochloride with 4 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene in isopropanol. After removing isopropanol with a rotary evaporator, the salt was dissolved in water and excess 1,8-diazabicyclo[5.4.0]undec-7-ene was removed by carrying out extractions with ethyl acetate.

After addition of sodium hydroxide metathesis process was then carried out using lithium trifluoromethanesulfonimide to isolate compound **C7**.

Core **D** was not commercially available and therefore had to be synthesized. To a solution of tris(2-aminoethyl)amine (5 ml, 33.8 mmol) and triethylamine (23.2 ml, 166.7 mmol) in CH_2Cl_2 (100 ml) at -78 °C was added 6-bromohexanolychloride (16.5 ml, 107.8 mmol) through a syringe under a vigorous stream of N_2. The reaction mixture was stirred for 3h at -78 °C and allowed to stir at temperature for 12h. Then the reaction mixture was poured in to 100 ml of cold water and the aqueous layer was extracted with (3 × 50 ml) of CH_2Cl_2 and the combined organic layer was concentrated in vacuo to give a pale yellow liquid. This was further dried under high vacuum to give **1** in 90% yield as orange color solid.

For the synthesis of **D2**, methylimidazole (1.89 ml, 22.1 mmol) was added to a solution of core **D** (3g, 4.4 mmol) in dry THF and refluxed for 36 hr under N_2. Then the solvent was evaporated under vacuum and resulted thick brown colored liquid was dissolved in 100 ml of water and washed the aqueous layer with ethyl acetate (6 × 100 ml). The aqueous layer was evaporated to dryness and resulted ionic liquid was dried under vacuum for 24 hr to give **2** in 65 % yield.

For the synthesis of **D6**, tripropylphosphene (4.2 ml, 26.4 mmol) was added to a solution of core **D** (3g, 4.4 mmol) in *iso*-propanol and refluxed for 48 hr under a vigorous stream of N_2. Then the solvents were removed in vacuo and resulted light yellow coloured thick liquid was dissolved in 100 ml of water and washed with ethyl acetate (8 × 100 ml). The aqueous layer was then concentrated in vacuo and further dried under high vacuum to give **3** in 85 % yield as a yellow solid.