Elaboration of phase diagrams

According to the procedure described in the experimental section of the article, immiscible mixtures were prepared, stirred and allowed to split into phases in thermodynamic equilibrium. At this point, one sample of each phase was taken, dissolved in deuterated solvent and placed in NMR tube, then running ^{1}H NMR experiments for both samples and integrating in the spectra the selected areas for the compositional analysis. Figures S.1 and S.2 show the spectra corresponding to the samples of two phases in equilibrium.

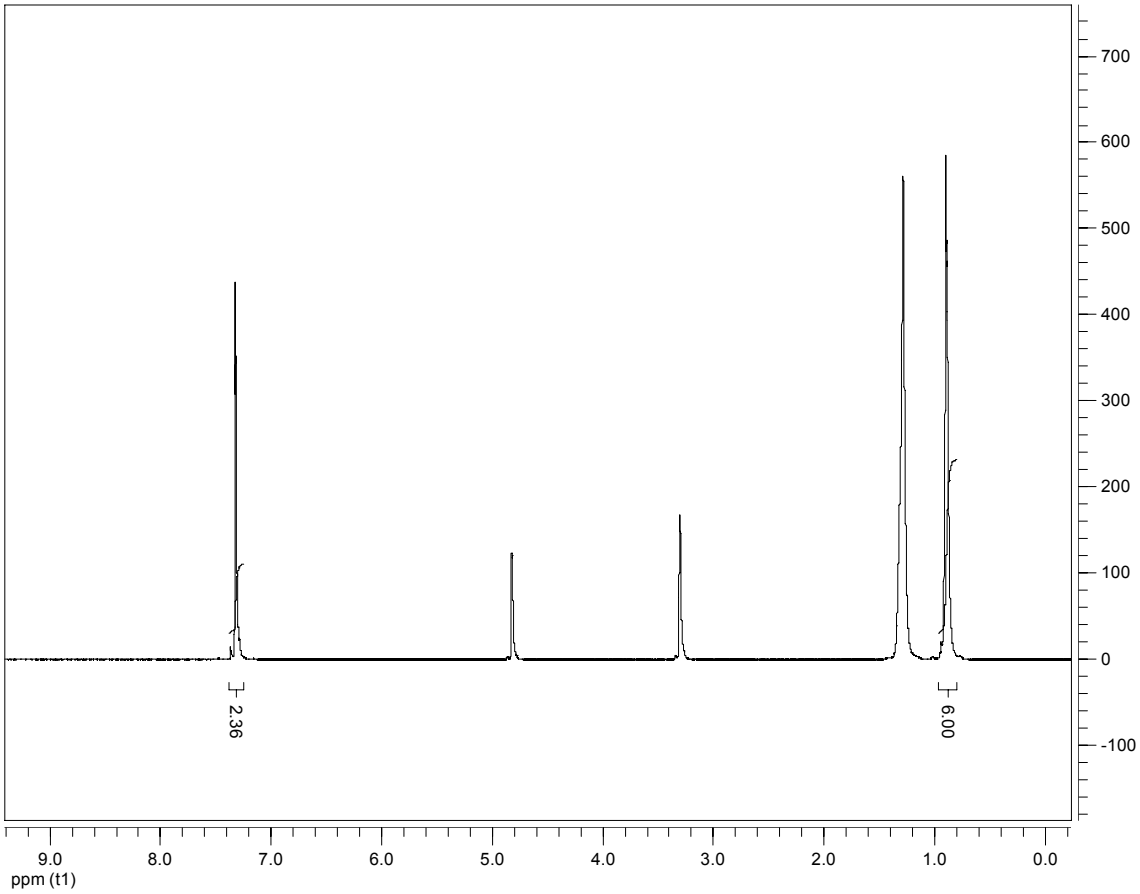

Figure S.1. Integrated ^{1}H NMR spectrum for an equilibrium top phase.

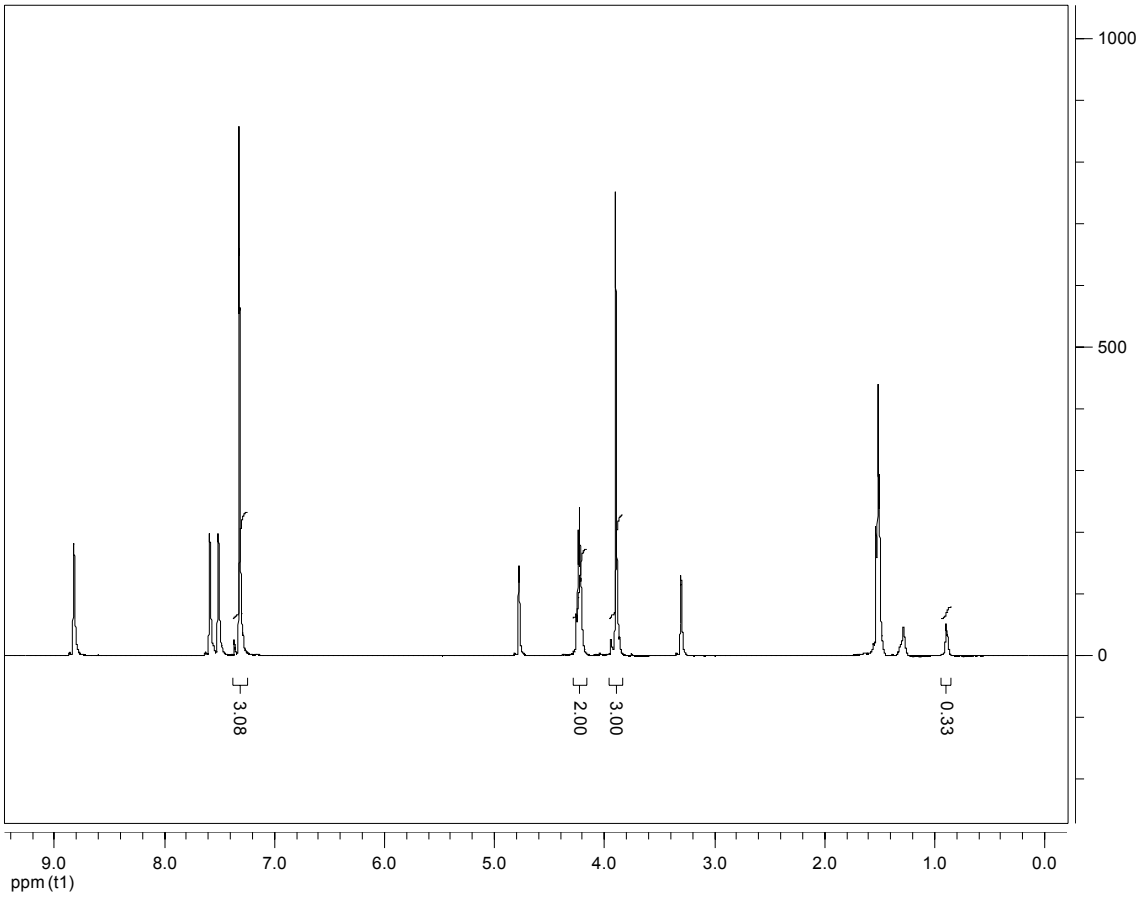

Figure S.2. Integrated ^{1}H NMR spectrum for the bottom phase in equilibrium with that one whose spectrum is shown in Figure S.1.

With the values of the areas under the selected peaks, and taking into consideration the number of protons assigned to each peak, it was possible to calculate the mole fractions of the components in both phases. For the sample in Figure S.2, for instance, the integrated areas are, from left to right: 53309.20 for the 6H peak of benzene, 34667.24 and 52002.32 for the 2H and 3H peaks of [C_2mim][NTf_2], and 5758.39 for the 6H peak of hexane. The calculation of the composition of the sample would be as follows:

$$x_{hexane} = \frac{\dfrac{5758.39}{6}}{\dfrac{5758.39}{6} + \dfrac{53309.20}{6} + \dfrac{1}{2}\cdot\left(\dfrac{34667.24}{2} + \dfrac{52002.32}{3}\right)} = 0.035$$

$$x_{benzene} = \frac{\dfrac{53309.20}{6}}{\dfrac{5758.39}{6} + \dfrac{53309.20}{6} + \dfrac{1}{2}\cdot\left(\dfrac{34667.24}{2} + \dfrac{52002.32}{3}\right)} = 0.327$$

$$x_{[C_2mim][NTf_2]} = \frac{\frac{1}{2}\cdot\left(\frac{34667.24}{2}+\frac{52002.32}{3}\right)}{\frac{5758.39}{6}+\frac{53309.20}{6}+\frac{1}{2}\cdot\left(\frac{34667.24}{2}+\frac{52002.32}{3}\right)} = 0.638$$

A ternary mixture can be represented by one point in a triangular diagram. The calculated compositions of the equilibrium phases correspond to the ends of a tie-line in the immiscibility region of the ternary system. Figure S.3 shows the tie-line derived from the example samples.

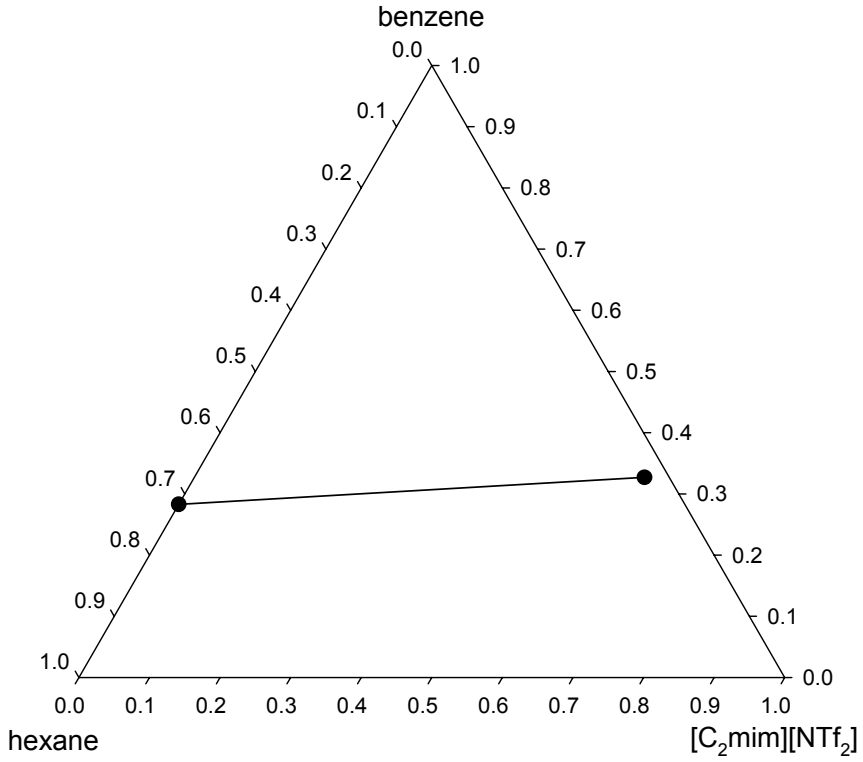

Figure S.3. Example of plotting of a liquid-liquid equilibrium tie-line in a triangular diagram.

By repeating the procedure for other initial immiscible mixtures of the three components, with an appropriate global composition, tie-lines are gradually obtained in order to cover the whole immiscibility region of the ternary system. Examples of final diagrams, including the totality of the tie-lines experimentally determined, are presented as figures in the paper.