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# 1 One-pot sustainable synthesis of tetrabutylammonium 2 bis(trifluoromethanesulfonyl)imide ionic liquid

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6

## 7 **Abstract**

8 Tetrabutylammonium bis(trifluoromethanesulfonyl)imide (TBA TFSI) and  
9 tetrafluoroborate-based anion ionic liquids (ILs) were obtained simultaneously by using a  
10 fast, versatile, cheap, low cost, and one-pot process. The process relies on dissolving  
11 tetrabutylammonium tetrafluoroborate salt, an organic-based  
12 bis(trifluoromethanesulfonyl)imide, ILs, such as 1-ethyl-3-methylimidazolium, N-  
13 trimethyl-N-butylammonium, 1-butyl-1-methylpyrrolidinium, 1-methyl-1-  
14 propylpiperidinium derivatives in dimethylformamide. A further extraction process using  
15 water and ether allows the selective recovery of the TBA TFSI in the organic phase, and  
16 the organic-based tetrafluoroborate IL in the aqueous phase. All the ionic liquids  
17 synthesized were characterized using Infrared Spectroscopy and Nuclear Magnetic  
18 Resonance, and compared with commercially available samples.

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## 21 **Graphical Abstract**

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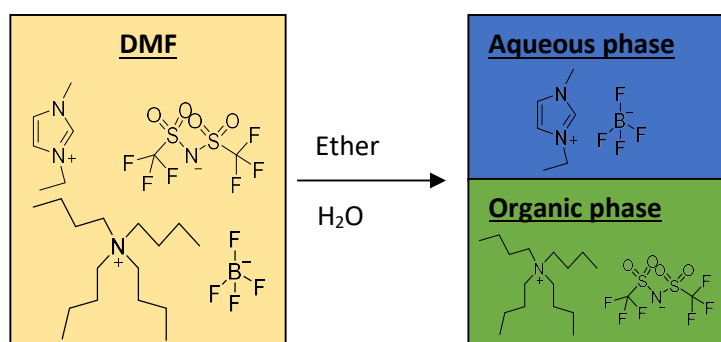
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## 32 1. Introduction

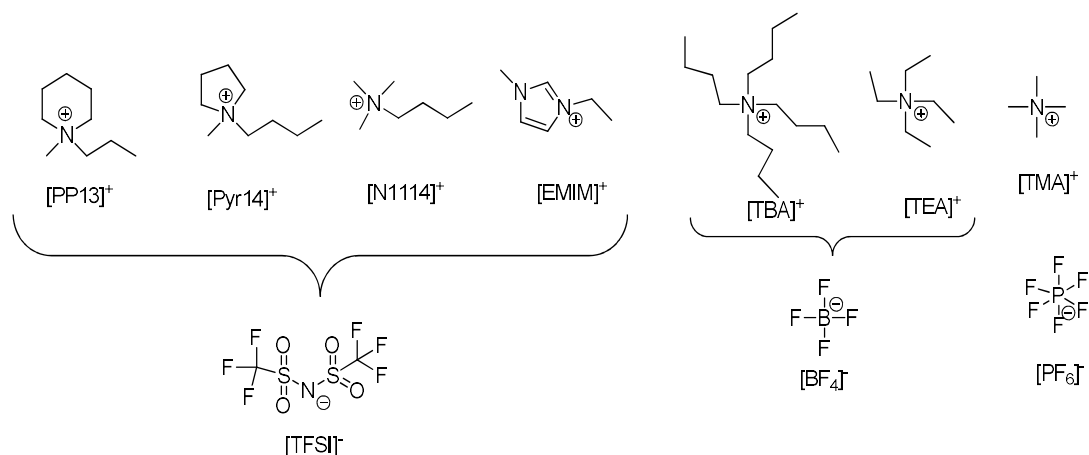
33 Solvents define a major part of the performance of processes in the chemical  
34 industry, and have an impact on cost, safety, and health issues. The use of alternative  
35 solvents represents a major entry in the general green chemistry toolkit, and is the subject  
36 of an enormous research effort<sup>[1–8]</sup>. In this sense, an attractive alternative to conventional  
37 organic solvents is the use of ionic liquids, ILs, due to both their benign chemical features  
38 (non-flammable, non-volatile, and thermally stable over a wide range of temperatures)<sup>[9–</sup>  
39 <sup>15]</sup> and their electrochemical characteristics. ILs have from moderate to high  
40 conductivities because they are liquids consisting of only ions and have good  
41 electrochemical stability (stable from -3.00 V to +1.7 V vs. Saturated Calomel Electrode  
42 (SCE) for reduction-oxidation processes)<sup>[16–20]</sup>. However, the processes and the reactant  
43 used for synthesizing ILs require a critical analysis from an environmental point of view.  
44 In most of the cases, it is not possible to obtain the IL with the desired anion in one single  
45 step, so two main different reaction pathways are used: 1) Lewis-acid-base reaction, or 2)  
46 anion metathesis<sup>[21–25]</sup>. Both types of reactions are performed from the halide salts of ionic  
47 liquids, producing a considerable amount of non-desired byproducts. In this regard, one  
48 important drawback associated with synthetic routes is to remove the impurities or  
49 byproducts of the ILs, which is a hard and tedious task (Scheme 1). Note that pure ILs  
50 are specially required for homogeneous catalysis, supporting electrolyte and electronic  
51 applications, such as gating in transistors<sup>[26,27]</sup>.



53 **Scheme 1.** Reaction pathways

54 In this sense the tetrabutylammonium bis(trifluoromethylsulfonyl)imide (TBA TFSI) is  
55 one of the most promising IL for electronic applications, more exactly, for transistor  
56 design. However, up until now, there are only three synthetic routes for obtaining TBA  
57 TFSI IL, and all of them generate a considerably amount of lithium salts or other  
58 byproducts<sup>[9,10,21,28]</sup>. The aim of this work is to design a cleaner strategy for obtaining  
59 TBA TFSI by mixing an organic TFSI ionic liquid and a tetrabutylammonium  
60 tetrafluoroborate salt (TBA BF<sub>4</sub>) in dimethylformamide (DMF). This new synthetic route

61 will potentially allow two different ionic liquids, TBA TFSI and organic cation,  $C^+ BF_4^-$   
 62 to be produced after an ion exchange process. It is important to highlight that following  
 63 this new approach, then main product (TBA TFSI) and the byproducts formed in the ion  
 64 exchange process are also ILs, which will potentially have their own market. Finally, it is  
 65 remarkable there is the higher recyclability of the solvents involved in the chemical  
 66 process.



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**Scheme 2.** Chart of structures

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## 70 2. Experimental

### 71 2.1 Chemicals

72 Ionic liquids (1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIM  
 73 TFSI), N-Trimethyl-N-butylammonium bis(trifluoromethanesulfonyl)imide (N<sub>1114</sub>  
 74 TFSI), 1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr14 TFSI),  
 75 1-Methyl-1-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13 TFSI)) were  
 76 purchased from Solvionic and used without further purification. Tetrabutylammonium  
 77 tetrafluoroborate (TBA BF<sub>4</sub>), Tetraethylammonium tetrafluoroborate (TEA BF<sub>4</sub>),  
 78 Tetramethylammonium hexafluorophosphate (TMA PF<sub>6</sub>), Tetrabutylammonium bis  
 79 (trifluoromethanesulfonyl)imide (TBA TFSI) and N,N-dimethylformamide (DMF),  
 80 99.8%, were supplied by Sigma-Aldrich and used as received (Scheme 2).

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### 82 2.2 Analysis and Product Characterization

83 Products obtained were characterized by Nuclear Magnetic Resonance and Near Infrared  
 84 Spectroscopy and compared with commercially available samples.

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### 2.2.1 Nuclear Magnetic Resonance (NMR)

87 Synthetized ionic liquids and commercially available samples of the synthesized ionic  
88 liquids were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR. Measurements were  
89 performed in a Bruker DPX360 (360 MHz) (Billerica, MA, USA) spectrometer, and  
90 Bruker DPX250 (250 MHz) with a Quattro Nucleus Probe (QNP). Proton chemical shifts  
91 were reported in ppm ( $\delta$ ) ( $\text{CDCl}_3$ ,  $\delta = 7.26$  or  $\text{CD}_3\text{CN}$ ,  $\delta = 1.94$ ). Carbon chemical shifts  
92 are reported in ppm ( $\delta$ ) ( $\text{CDCl}_3$ ,  $\delta = 77.2$  or  $\text{CD}_3\text{CN}$ ,  $\delta = 1.32$ ). The J values are reported  
93 in Hz. Fluor chemical shifts are reported in ppm ( $\delta$ ) ( $\text{CDCl}_3$ ).

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### 2.2.2 Infrared Spectroscopy (IR)

96 Near infrared spectra were recorded in attenuated total reflectance (ATR) mode on a  
97 Model Tensor 27 spectrophotometer from Bruker that was governed via the software  
98 OPUS 5.5, also from Bruker.

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## 101 3. Results and discussion

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103 Scheme 3 describes the simple ionic exchange process between TBA  $\text{BF}_4$  (organic salt)  
104 and EMIM TFSI (ionic liquid). An equimolar amount of the above-mentioned salt and  
105 IL are dissolved in dimethylformamide (DMF) by stirring the mixture for five minutes at  
106 room temperature. After that the DMF solution was poured into a separator funnel, which  
107 contained the same amount of water and ether. Due to the fact that neither EMIM TFSI  
108 nor TBA  $\text{BF}_4$  is soluble in water, an ion exchange process takes place. Hence, in the  
109 organic phase, after washing and drying this phase with water and anhydrous sodium  
110 sulphate, the desired IL (tetrabutylammonium bis(trifluoromethanesulfonyl)imide) is  
111 obtained with an 89% yield. Moreover, the byproduct of the ion exchange between  
112 tetrabutylammonium tetrafluoroborate and 1-ethyl-3-methylimidazolium  
113 bis(trifluoromethanesulfonyl)imide, EMIM  $\text{BF}_4$ , is easily recovered from the aqueous  
114 phase after several washings with dichloromethane. Distillation of dichloromethane  
115 enables EMIM  $\text{BF}_4$  to be obtained in a 66.7% yield. It is important to highlight that the  
116 one-pot synthetic process above described enables two highly pure ionic liquids to be  
117 obtained following several principles of Green Chemistry, such as high atom economy,

118 the utilization of by-products, recovery of the solvents, as well as recyclability of the  
119 reactants.

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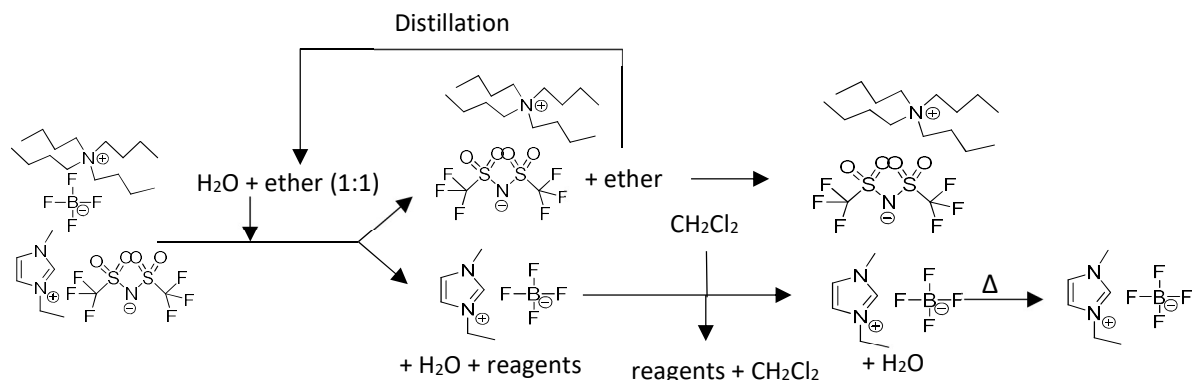
130 **Scheme 3.** Ionic exchange for EMIM TFSI and TBA BF<sub>4</sub>

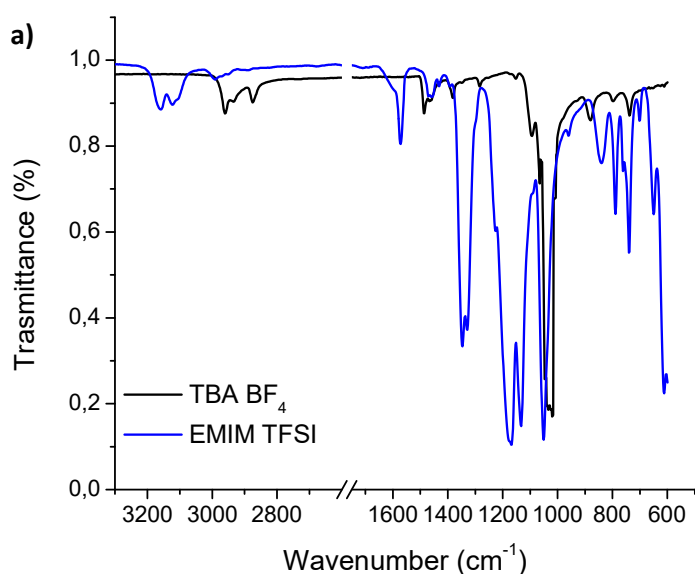
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132 Standard spectroscopy techniques were used as useful tools to identify and characterize  
133 the products formed. Quick comparisons between the spectroscopic features of pure  
134 reactants, compounds obtained, and pure commercial available samples of the compounds  
135 obtained verified the exchange process. [28–30] Figure 1 (a-b) shows the different IR spectra  
136 for the TBA BF<sub>4</sub> and EMIM TFSI reagents, and the synthesized ionic liquids, TBA TFSI  
137 and EMIM BF<sub>4</sub>. All frequencies described in IR for the EMIM<sup>+</sup>, TBA<sup>+</sup> cations, and TFSI<sup>-</sup>,  
138 BF<sub>4</sub><sup>-</sup> anions are summarized in Table S1. The stretching/bending vibrations for the cation  
139 part could be distinguished, focusing between 2880 - 2970 cm<sup>-1</sup> for TBA<sup>+</sup> cation and  
140 between 2950 - 3165 cm<sup>-1</sup> for EMIM<sup>+</sup>. Furthermore, the imidazolium ring of EMIM<sup>+</sup>  
141 shows characteristic vibrations between 1300 – 1600 cm<sup>-1</sup>. In the anion part, the spectra  
142 for BF<sub>4</sub><sup>-</sup> is easily described as it shows a huge peak at 1050 cm<sup>-1</sup>; however, in the case of  
143 the TFSI<sup>-</sup> anion the spectra show four different peaks that describe the stretching and  
144 bending for CF<sub>3</sub>, SO<sub>2</sub>, and S-N-S bonds.

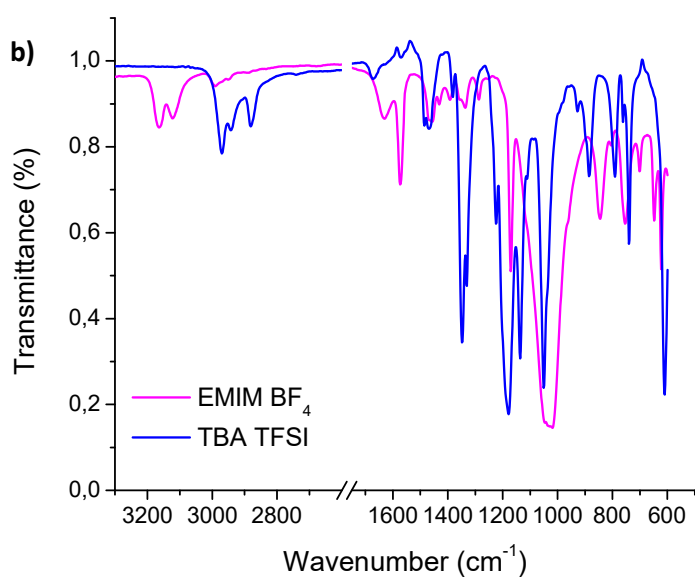
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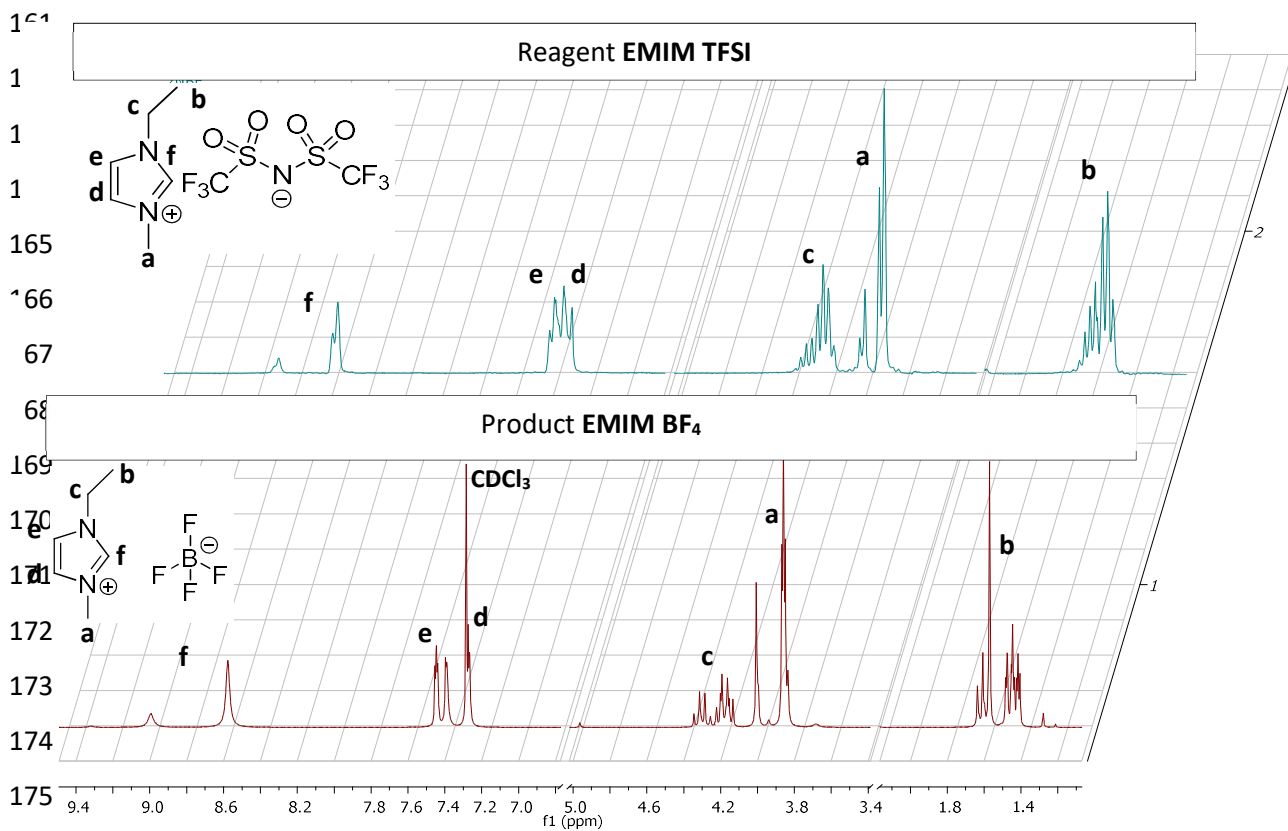
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149 **Figure 1.** IR spectra of ionic exchange process between TBA BF<sub>4</sub> and EMIM TFSI a) before mixing and b) after a  
 150 mixing and a purification process

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152 On the other hand, figure 2 and 3 show the <sup>1</sup>H-NMR spectrum for EMIM BF<sub>4</sub>, EMIM  
 153 TFSI, TBA BF<sub>4</sub> and TBA TFSI. It is easy to distinguish between cation EMIM<sup>+</sup> and TBA<sup>+</sup>  
 154 because they have very different kind of protons in their structure; TBA<sup>+</sup> presents 4  
 155 different signals of its alkyl protons, whereas EMIM<sup>+</sup> has 6 different proton types, which  
 156 appear at a higher chemical shift because of the resonance of the imidazolium ring.  
 157 Moreover, the EMIM<sup>+</sup> cation described an ion-pair formation equilibrium with BF<sub>4</sub><sup>-</sup> and  
 158 TFSI<sup>-</sup> anions in dilute low dielectric solutions, such as chloroform<sup>[31]</sup>. Hence, <sup>1</sup>H-NMR

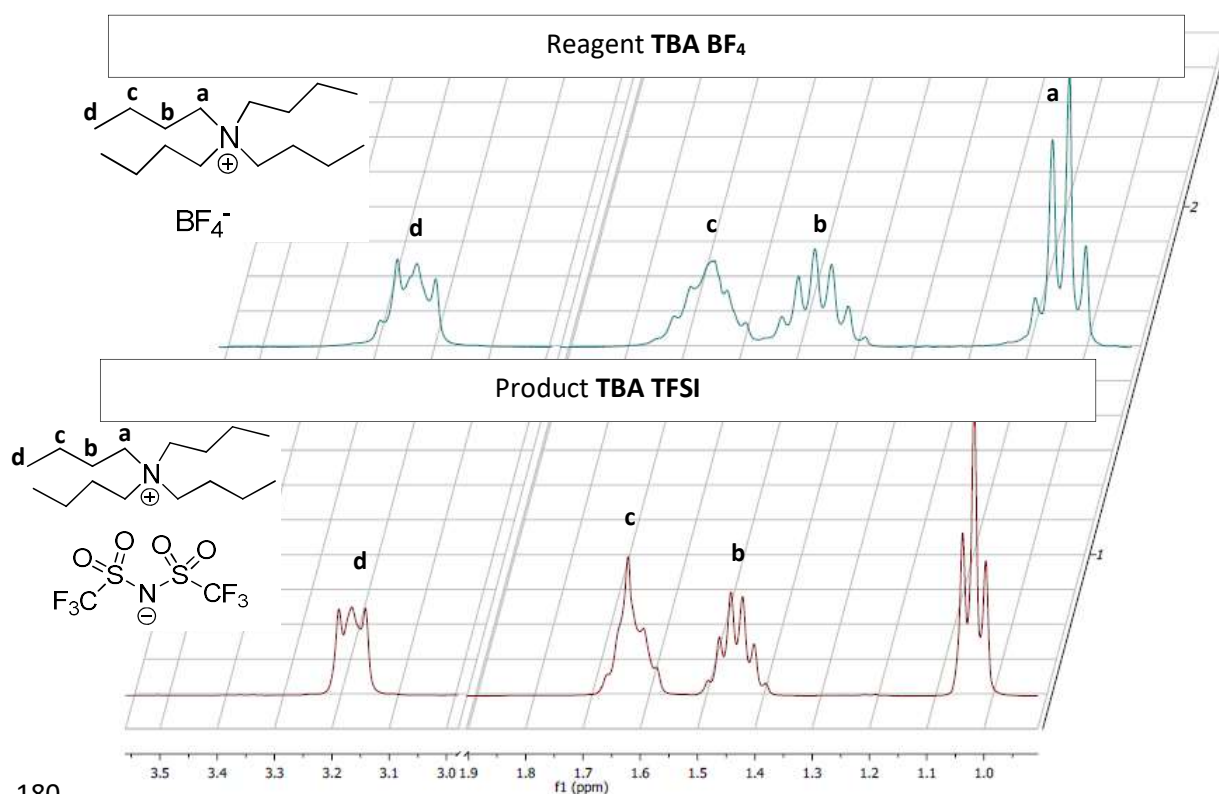
159 describes two concurrent sets of signals due to the presence in the sample of freely  
160 dissolved ions and ion-pair aggregates, these signals are different depending on anion.



176  
177 **Figure 2.** <sup>1</sup>H NMR of EMIM BF<sub>4</sub> and EMIM TFSI ILs

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181 **Figure 3.** <sup>1</sup>H NMR of TBA BF<sub>4</sub> salt and TBA TFSI IL

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183 Furthermore, the combined use of <sup>13</sup>C NMR and <sup>19</sup>F NMR allow the nature of the counter  
 184 anion present to be identified in the ILs formed. Figure 4 shows the <sup>13</sup>C NMR for the  
 185 TBA<sup>+</sup> cation paired with TFSI<sup>-</sup> and BF<sub>4</sub><sup>-</sup>. An extra signal (C5) TBA TFSI, which is related  
 186 to CF<sub>3</sub> group. Table S2 summarizes the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR signals for TBA TFSI.  
 187 <sup>19</sup>F NMR data are reported in Figure S1, according to previously published data<sup>32-34</sup>)  
 188 two different signals are observed for BF<sub>4</sub><sup>-</sup> and TFSI<sup>-</sup> anions at 152.4 and 79.9 ppm,  
 189 respectively.

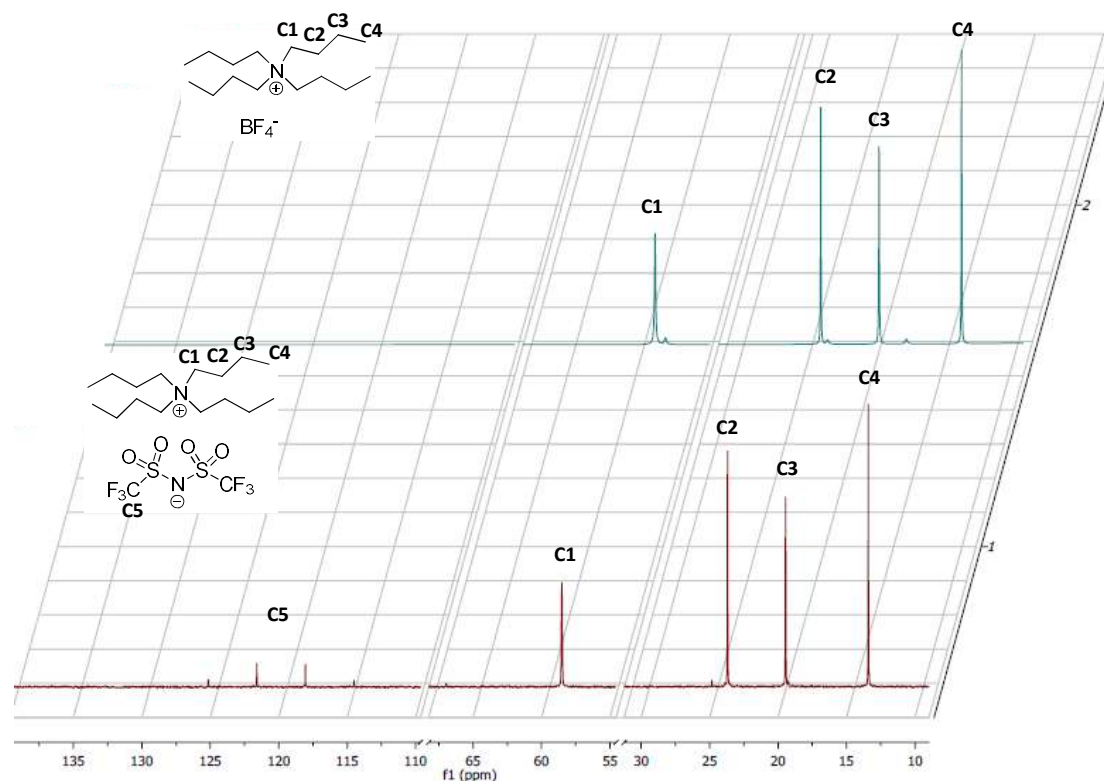
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196 **Figure 4.** <sup>13</sup>C NMR for TBA BF<sub>4</sub> and TBA TFSI

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198 The current methodology can be extended to other similar  
 199 bis(trifluoromethanesulfonyl)imide based ionic liquids by a simple mixture with TBA  
 200 BF<sub>4</sub>. Table 1 summarizes the yields obtained after the ionic exchange and phase  
 201 separation process described in Scheme 3, when N-Trimethyl-N-butylammonium  
 202 bis(trifluoromethanesulfonyl)imide (N<sub>1114</sub> TFSI), 1-Butyl-1-methylpyrrolidinium  
 203 bis(trifluoromethanesulfonyl)imide (Pyr14 TFSI), 1-Methyl-1-propylpiperidinium  
 204 bis(trifluoromethanesulfonyl)imide (PP13 TFSI) are used as reagents. Notice that in all  
 205 cases are obtained TBA TFSI is obtained a good yield, whereas the by-product (BF<sub>4</sub><sup>-</sup>  
 206 based ionic liquid) is obtained in moderate yields. However, the ionic exchange process  
 207 is strongly dependent on the length of the alkyl chain present in the tetraalkylammonium  
 208 salt, as it was previously described in the literature<sup>[9]</sup> Hence, no ionic exchange products  
 209 were obtained when Tetraethylammonium tetrafluoroborate (TEA BF<sub>4</sub>) or salt is used as  
 210 starting material. This fact can be rationalized by taking into account the different  
 211 hydrophobicity of both cations, TEA<sup>+</sup> and TBA<sup>+</sup>; therefore, it is soluble in aqueous phase.

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Reactive + TBA BF <sub>4</sub>	Products + TBA TFSI	TBA TFSI Yield (%)	C <sup>+</sup> BF <sub>4</sub> <sup>-</sup> Yield (%)
		73.4	31.2
		67.3	35.4
		71.2	41.4

215

216 **Table 1.** Ionic liquid yields obtained after ionic exchange and purification processes.

217

218 The purity of the ionic liquids synthesized following this methodology are determined  
 219 employing the <sup>1</sup>H NMR data using of <sup>13</sup>C satellites of imidazolium N-methyl group as  
 220 internal standard<sup>[35]</sup> as well as the integration of similar protons in non-imidazolium ILs.

221 In the case of TBA TFSI the purity of IL obtained was from 96.2% to 99.3 % depending  
 222 on the type of C<sup>+</sup>TFSI used as reagent. For the rest of the ILs obtained as a byproducts  
 223 purities obtained were the following: 99.2% for Pyr14 TFSI, 93.5% for PP13 TFSI, 98.0%  
 224 for N<sub>1114</sub> TFSI and 99.1% for EMIM TFSI. Finally, it is remarkable that a comparison in  
 225 terms of atom economy between our methodology and a classical one starting from  
 226 similar products reveals that are very similar in both cases (c.a. 80 %). However, the  
 227 byproducts obtained using our methodology are also ILs and the solvent used are  
 228 recyclable, whereas in the case the classical route the byproduct obtained is a salt (lithium  
 229 bromide).

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## 231 4. Conclusions

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233 In the current manuscript we have been able to design a new synthetic route for  
 234 synthesizing the tetrabutylammonium bis (trifluoromethanesulfonyl) imide ionic liquid  
 235 (TBA TFSI) following a sustainable one-pot methodology based on an ion exchange  
 236 process with purities from 96 to 99 %. It is important to highlight tetrafluoroborate based  
 237 ionic liquids are also obtained as a secondary product with purities from 98 to 99 %. In  
 238 terms of cost-effectiveness analysis, our exchange ionic approach is a low-cost alternative  
 239 since the products obtained at the end (ILs) have increased their value by ca 40% in  
 240 comparison with the starting IL and salt used. Moreover, ca 80% of the solvent and

241 reagents used can be recycled and reused at the end of the process. Hence, the above  
242 described methodology allows the previous synthetic methodologies reported in the  
243 literature to be improved, avoiding the use of multistep processes, non-desirable  
244 byproducts, as well as strong experimental conditions.

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## 248 **Acknowledgments**

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## 255 **References**

256

- 257 (1) Kamimura, A.; Murata, K.; Kawamoto, T. An Efficient and Selective Conversion of  
258 Sorbitol in Ionic Liquids: Use of Ion Exchange Resin as a Solid Acid Catalyst.  
259 *Tetrahedron Lett.* **2017**, *58* (37), 3616–3618. <https://doi.org/10.1016/j.tetlet.2017.07.105>.
- 260 (2) Takashima, Y.; Yokoyama, M.; Horikoshi, A.; Sato, Y.; Tsuruoka, T.; Akamatsu, K. Ionic  
261 Liquid/Metal–Organic Framework Hybrid Generated by Ion-Exchange Reaction:  
262 Synthesis and Unique Catalytic Activity. *New J. Chem.* **2017**, *41* (23), 14409–14413.  
263 <https://doi.org/10.1039/C7NJ03269B>.
- 264 (3) Mao, X.; Wu, M.; Xu, X.; Jiang, L.; Yan, J.; Du, Z.; Li, J.; Hou, S. Fabrication of an  
265 Electrochemical Sensor for NO<sub>x</sub> Based on Ionic Liquids and MoS<sub>2</sub>. *Int. J. Electrochem.*  
266 *Sci.* **2018**, *13* (11), 11038–11048. <https://doi.org/10.20964/2018.11.79>.
- 267 (4) Tahara, H.; Uranaka, K.; Hirano, M.; Ikeda, T.; Sagara, T.; Murakami, H.  
268 Electrochromism of Ferrocene- and Viologen-Based Redox-Active Ionic Liquids  
269 Composite. *ACS Appl. Mater. Interfaces* **2018**, *11*, 6–11.  
270 <https://doi.org/10.1021/acsami.8b16410>.
- 271 (5) Liu, R.; Zhang, P.; Zhang, S.; Yan, T.; Xin, J.; Zhang, X. Ionic Liquids and Supercritical  
272 Carbon Dioxide: Green and Alternative Reaction Media for Chemical Processes. *Rev.*  
273 *Chem. Eng.* **2016**, *32* (6), 587–609. <https://doi.org/10.1515/revce-2015-0078>.
- 274 (6) Seddon, K. R. Review Ionic Liquids for Clean Technology \*. **1997**, *50* (Iii), 1–6.

- 275 (7) Wasserscheid, P.; Welton, T. Ionic Liquids Ionic Liquids. *Top. Curr. Chem.* **2017**, *1*  
276 (December), 1–4.
- 277 (8) Picquet, M.; Tkatchenko, I.; Tommasi, I.; Wasserscheid, P.; Zimmermann, J. Ionic  
278 Liquids, 3. Synthesis and Utilisation of Protic Imidazolium Salts in Homogeneous  
279 Catalysis. *Adv. Synth. Catal.* **2003**, *345* (8), 959–962.  
280 <https://doi.org/10.1002/adsc.200303025>.
- 281 (9) Fagnant, D. P.; Desilva, M. A.; Brennecke, J. F. Solid-Liquid Equilibria Measurements of  
282 Mixtures of Lithium Bis(Trifluoromethanesulfonyl)Imide with Varying Alkyl Chain  
283 Length Ammonium Bis(Trifluoromethanesulfonyl)Imide Ionic Liquids. *J. Chem. Eng.*  
284 *Data* **2016**, *61* (2), 958–967. <https://doi.org/10.1021/acs.jced.5b00807>.
- 285 (10) Kohno, Y.; Arai, H.; Saita, S.; Ohno, H. Material Design of Ionic Liquids to Show  
286 Temperature-Sensitive Lcst-Type Phase Transition after Mixing with Water. *Aust. J.*  
287 *Chem.* **2011**, *64* (12), 1560–1567. <https://doi.org/10.1071/CH11278>.
- 288 (11) Marcilla, R.; Blazquez, J. A.; Rodriguez, J.; Pomposo, J. A.; Mecerreyes, D. Tuning the  
289 Solubility of Polymerized Ionic Liquids by Simple Anion-Exchange Reactions. *J. Polym.*  
290 *Sci. Part A Polym. Chem.* **2004**, *42* (1), 208–212. <https://doi.org/10.1002/pola.11015>.
- 291 (12) Thompson, M. W.; Matsumoto, R.; Sacci, R. L.; Sanders, N. C.; Cummings, P. T. Scalable  
292 Screening of Soft Matter: Case Study of Mixtures of Ionic Liquids and Organic Solvents.  
293 *J. Phys. Chem. B* **2019**, [acs.jpcc.8b11527](https://doi.org/10.1021/acs.jpcc.8b11527). <https://doi.org/10.1021/acs.jpcc.8b11527>.
- 294 (13) Zhou, F.; Liu, S.; Yang, B.; Wang, P.; Alshammari, A. S.; Deng, Y. Electrochemistry  
295 Communications Highly Selective and Stable Electro-Catalytic System with Ionic Liquids  
296 for the Reduction of Carbon Dioxide to Carbon Monoxide. *Electrochem. commun.* **2015**,  
297 *55*, 43–46.
- 298 (14) Deetlefs, M.; Seddon, K. R.; Shara, M. Predicting Physical Properties of Ionic Liquids.  
299 *Phys. Chem. Chem. Phys.* **2006**, *8* (5), 642–649. <https://doi.org/10.1039/b513453f>.
- 300 (15) Earle, M. J.; Esperança, J. M. S. S.; Gilea, M. A.; Lopes, J. N. C.; Rebelo, L. P. N.; Magee,  
301 J. W.; Seddon, K. R.; Widegren, J. A. The Distillation and Volatility of Ionic Liquids.  
302 *Nature* **2006**, *439* (7078), 831–834. <https://doi.org/10.1038/nature04451>.
- 303 (16) Cruz, H.; Gallardo, I.; Guirado, G. Electrochemically Promoted Nucleophilic Aromatic  
304 Substitution in Room Temperature Ionic Liquids - An Environmentally Benign Way to  
305 Functionalize Nitroaromatic Compounds. *Green Chem.* **2011**, *13* (9), 2531–2542.  
306 <https://doi.org/10.1039/c1gc15303j>.
- 307 (17) Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M.; Mei, T. X. Investigating the  
308 Electrochemical Windows of Ionic Liquids. *J. Ind. Eng. Chem.* **2013**, *19* (1), 106–112.  
309 <https://doi.org/10.1016/j.jiec.2012.07.011>.
- 310 (18) Pappenfus, T. M.; Lee, K.; Thoma, L. M.; Dukart, C. R. Wind to Ammonia:  
311 Electrochemical Processes in Room Temperature Ionic Liquids. *ECS Trans.* **2009**, *16* (49),

- 312 89–93. <https://doi.org/10.1149/1.3159311>.
- 313 (19) Cruz, H.; Gallardo, I.; Guirado, G. Understanding Specific Effects on the Standard  
314 Potential Shifts of Electrogenerated Species in 1-Butyl-3-Methylimidazolium Ionic  
315 Liquids. *Electrochim. Acta* **2008**, *53* (20), 5968–5976.  
316 <https://doi.org/10.1016/j.electacta.2008.03.062>.
- 317 (20) Reche, I.; Gallardo, I.; Guirado, G. The Role of Cations in the Reduction of 9-Fluorenone  
318 in Bis(Trifluoromethylsulfonyl)Imide Room Temperature Ionic Liquids. *New J. Chem.*  
319 **2014**, *38* (10), 5030–5036. <https://doi.org/10.1039/c4nj01200c>.
- 320 (21) Arvai, R.; Toulgoat, F.; Langlois, B. R.; Sanchez, J. Y.; Médebielle, M. A Simple Access  
321 to Metallic or Onium Bistrifluoromethanesulfonimide Salts. *Tetrahedron* **2009**, *65* (27),  
322 5361–5368. <https://doi.org/10.1016/j.tet.2009.04.068>.
- 323 (22) BHATT, V. D.; GOHIL, K. Ion Exchange Synthesis and Thermal Characteristics of Some  
324 [N2222]<sup>+</sup> Based Ionic Liquids. *Bull. Mater. Sci.* **2013**, *36* (6), 1121–1125.  
325 <https://doi.org/10.1007/s12034-013-0557-x>.
- 326 (23) Dietz, M. L.; Dzielawa, J. A. Ion-Exchange as a Mode of Cation Transfer into Room-  
327 Temperature Ionic Liquids Containing Crown Ethers: Implications for the “greenness” of  
328 Ionic Liquids as Diluents in Liquid–Liquid Extraction. *Chem. Commun.* **2001**, 2124–2125.  
329 <https://doi.org/10.1039/b104349h>.
- 330 (24) Jensen, M. P.; Neufeind, J.; Beitz, J. V.; Skanthakumar, S.; Soderholm, L. Mechanisms  
331 of Metal Ion Transfer into Room-Temperature Ionic Liquids: The Role of Anion  
332 Exchange. *J. Am. Chem. Soc.* **2003**, *125* (50), 15466–15473.  
333 <https://doi.org/10.1021/ja037577b>.
- 334 (25) Keil, P.; Schwiertz, M.; König, A. Metathesis of Ionic Liquids: Continuous Ion Exchange  
335 by Donnan Dialysis. *Chem. Eng. Technol.* **2014**, *37* (6), 919–926.  
336 <https://doi.org/10.1002/ceat.201200322>.
- 337 (26) Zhang, D.; Ronson, T. K.; Mosquera, J.; Martinez, A.; Nitschke, J. R. Selective Anion  
338 Extraction and Recovery Using a Fe II<sub>4</sub> L<sub>4</sub> Cage. *Angew. Chemie - Int. Ed.* **2018**, *57* (14),  
339 3717–3721. <https://doi.org/10.1002/anie.201800459>.
- 340 (27) Kuroboshi, M.; Shiba, T.; Tanaka, H. Viologen as Catalytic Organic Reductant: Electro-  
341 Reductive Dimerization of Aryl Bromides in a Pd/Viologen Double Mediator System.  
342 *Tetrahedron Lett.* **2013**, *54* (28), 3666–3668. <https://doi.org/10.1016/j.tetlet.2013.04.127>.
- 343 (28) Nishi, N.; Minami, K.; Motobayashi, K.; Osawa, M.; Sakka, T. Interfacial Structure at the  
344 Quaternary Ammonium-Based Ionic Liquids|gold Electrode Interface Probed by Surface-  
345 Enhanced Infrared Absorption Spectroscopy: Anion Dependence of the Cationic  
346 Behavior. *J. Phys. Chem. C* **2017**, *121* (3), 1658–1666.  
347 <https://doi.org/10.1021/acs.jpcc.6b10826>.
- 348 (29) Buffeteau, T.; Grondin, J.; Lassègues, J.-C. Infrared Spectroscopy of Ionic Liquids:

- 349 Quantitative Aspects and Determination of Optical Constants. *Appl. Spectrosc.* **2010**, *64*  
350 (1), 112–119. <https://doi.org/10.1366/000370210790572089>.
- 351 (30) Mozhzhukhina, N.; Tesio, A. Y.; Mendez De Leo, L. P.; Calvo, E. J. In Situ Infrared  
352 Spectroscopy Study of PYR14TFSI Ionic Liquid Stability for Li–O<sub>2</sub> Battery. *J.*  
353 *Electrochem. Soc.* **2017**, *164* (2), A518–A523. <https://doi.org/10.1149/2.1391702jes>.
- 354 (31) Tubbs, J. D.; Hoffmann, M. M. Ion-Pair Formation of the Ionic Liquid 1-Ethyl-3-  
355 Methylimidazolium Bis ( Trifyl ) Imide in Low Dielectric Media. *J. Solution Chem.* **2004**,  
356 *33* (4), 381–394. <https://doi.org/10.1023/B:JOSL.0000036308.36052.01>.
- 357 (32) De Diego, T.; Lozano, P.; Gmouh, S.; Vaultier, M.; Iborra, J. L. Fluorescence and CD  
358 Spectroscopic Analysis of the  $\alpha$ -Chymotrypsin Stabilization by the Ionic Liquid, 1-Ethyl-  
359 3-Methylimidazolium Bis[(Trifluoromethyl)Sulfonyl]Amide. *Biotechnol. Bioeng.* **2004**,  
360 *88* (7), 916–924. <https://doi.org/10.1002/bit.20330>.
- 361 (33) Su, B.-M.; Zhang, S.; Zhang, Z. C. Structural Elucidation of Thiophene Interaction with  
362 Ionic Liquids by Multinuclear NMR Spectroscopy. *J. Phys. Chem. B* **2004**, *108* (50),  
363 19510–19517. <https://doi.org/10.1021/jp0490271>.
- 364 (34) Hartman, J. S.; Schrobilgen, G. J. Mixed Tetrahaloborate Ions. Detection and Study by  
365 Nuclear Magnetic Resonance. *Inorg. Chem.* **1972**, *11* (5), 940–951.  
366 <https://doi.org/10.1021/ic50111a005>.
- 367 (35) Cassol, C. C.; Ebeling, G.; Ferrera, B.; Dupont, J. A Simple and Practical Method for the  
368 Preparation and Purity Determination of Halide-Free Imidazolium Ionic Liquids. *Adv.*  
369 *Synth. Catal.* **2006**, *348* (1–2), 243–248. <https://doi.org/10.1002/adsc.200505295>.
- 370  
371  
372  
373