

## Low Melting *N*-4-Functionalized-1-alkyl or Polyfluoroalkyl-1,2,4-triazolium Salts

Yousef R. Mirzaei, Hong Xue, and Jean'ne M. Shreeve\*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

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Butane sulfobetaines **2a,b**, zwitterionic oxo perfluorocarboxylates **3a,b**, and functionalized triazolium bromides **4b,c** and **5a–c** have been synthesized and subsequently reacted to give a series of hydrophilic and hydrophobic fluorinated and nonfluorinated *N*-1-alkyl-*N*-4-functionalized-triazolium compounds (**6a–11b**). With the exception of **11b** (mp 41 °C), all are liquids at room temperature. Metathesis of the fluorinated quaternary triazolium halides with other anions led to the formation of a new class of compounds, namely, [(R)(R<sub>func</sub>)-Taz]<sup>+</sup>Y<sup>-</sup>, Y = PF<sub>6</sub>, (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, and CF<sub>3</sub>SO<sub>3</sub>, in good isolated yields. All of the new compounds were characterized by <sup>1</sup>H, <sup>19</sup>F, and <sup>13</sup>C NMR, and MS spectral and elemental analyses. Thermal analyses indicate that high temperatures are attainable prior to decomposition. DSC studies show glass transitions for several samples, and all functionalized compounds, **5–11**, have *T*<sub>g</sub>s or *T*<sub>m</sub>s < 100 °C. Densities range between 1.4 and 1.61 g cm<sup>-3</sup>. 1-Heptyl-4-(butyl-4-sulfonic acid) triazolium trifluoromethanesulfonate, **6b**, in its role as a Brønsted acid, is an effective solvent/catalyst for high yield esterification and hetero-Michael addition reactions and may be recycled for repetitive use.

### Introduction

Because of their unique properties, such as low volatility, noncombustibility, and good solvent characteristics,<sup>1–3</sup> low melting salts are promising candidates as recyclable reaction media for organic and inorganic syntheses. The increasing number of publications is indicative of their potential as solvents for various chemical reactions. These include, for example, Friedel–Crafts reactions,<sup>4–6</sup> enzyme-catalyzed reactions,<sup>7,8</sup> hydrogenations,<sup>9,10</sup> Heck reactions,<sup>11</sup> Fischer

indole synthesis,<sup>12</sup> benzylation,<sup>13a</sup> and preparation of extended coordination networks.<sup>13b</sup> Recent work suggests that the potential for preparing a broad array of such liquids with ions incorporating functional groups is high,<sup>14</sup> and certain of these new compounds will have a wide variety of applications.<sup>15–19</sup>

Although both the cation and anion in these liquid salts are likely targets for structural modification, in this work

\* Author to whom correspondence should be addressed. E-mail: jshreeve@uidaho.edu.

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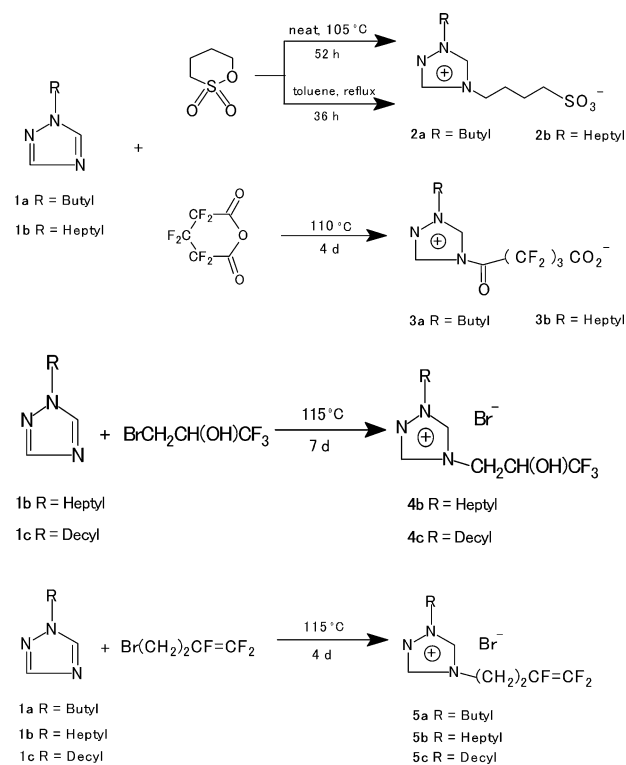
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focus is on cation modification by introducing substituents with functional groups onto a triazole core. To accomplish this requires the identification of a substrate that contains two functional groups with different reactivities that will allow attachment of the substrate to the core. The other remaining at the terminus is the functional group of interest or is modifiable to the group of interest. In some cases, we have used functionalized polyfluoroalkyl halides. For others, we have chosen different strategies, e.g., an alkane sulfonic acid group is covalently tethered to the cation by the reaction of the neutral nucleophile *N*-alkyl-1,2,4-triazole with 1,4-butane sultone, since zwitterionic-type salts have both cation and anion in intramolecular form. The appended functional groups provide versatile reactive sites that lend themselves to conversion into a variety of derivative functionalities. Since the anion exercises a significant amount of control over solubility and melting point,<sup>20</sup> the choice of the anion is also critical.

Some of the most important reactions in industrial chemistry including, e.g., alkylation, acylation and carbonylation of aromatic compounds, are catalyzed by highly acidic moieties. The use of mineral acids is often fraught with difficulties because of their inherent volatilities, lack of solubility of the substrate, need to use excessive amounts, etc. While the use of highly acidic Brønsted liquids with chloroaluminate anions has been known for nearly 15 years, the synthesis and utilization of highly acidic, but hydrolytically stable, liquid salts have only been reported recently.<sup>21,22</sup> These Brønsted acid systems were composed either of an imidazolium cation with an acidic anion, e.g.,  $\text{HSO}_4^-$ , or  $\text{SO}_4^{2-}$ <sup>21</sup> or with an acidic cation made up of an imidazole ring bonded to an alkane sulfonic acid group.<sup>22</sup> These systems were demonstrated to be useful, e.g., in the Friedel–Crafts alkylation of benzene with 1-decene, in Fischer esterification, in alcohol dehydrodimerization, in the pinacol/benzopinacol rearrangement, or as proton-conducting nonaqueous electrolytes.<sup>22,23</sup> Such liquids have great potential for being easily recyclable and tunable and for playing the role of good solvent systems for many organic and inorganic substances.<sup>24</sup>

We report the first triazolium (Taz) based liquid salts that are designed to be Brønsted strong acids. In these zwitterion liquids, an alkane sulfonic acid group is covalently tethered

Scheme 1



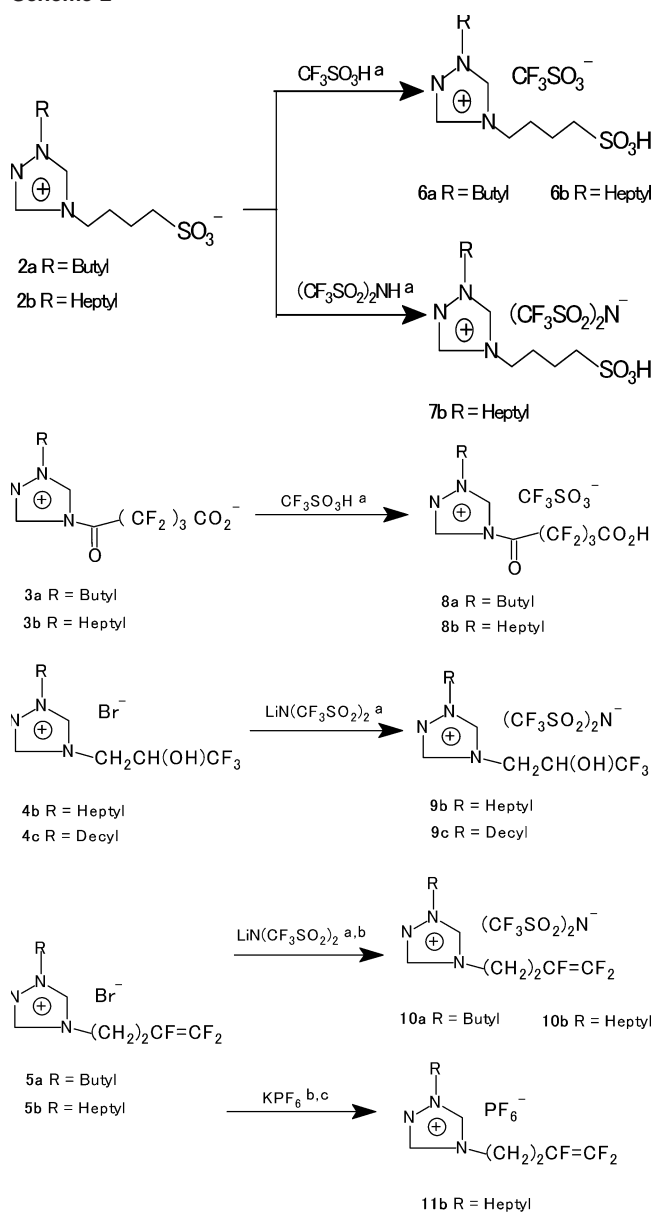
to the cation by the reaction of neutral nucleophiles *N*-alkyl-1,2,4-triazole with 1,4-butane sultone in excellent yields.<sup>25</sup> These zwitterionic triazolium salts were found to form liquids similar to ordinary triazolium salts.<sup>20</sup> In this work our results also describe the preparation of new hydrophilic and hydrophobic liquid-phases on which fluoroalkenyl units are grafted to alkyl triazoles under solvent free reaction conditions.<sup>20</sup> The applications for these types of compounds may extend from solvents meeting chemically inert or catalyst/solvent requirements to oxidatively stable lubricants and beyond.

## Results and Discussion

In view of our general interest in solvent free synthesis, we explored the preparation of (1) butane sulfobetaines **2a,b** by reacting the corresponding *N*-1-alkyl-1,2,4-triazole with 1,4-butane sultone, (2) zwitterionic oxo perfluorocarboxylates **3a,b**, by reacting *N*-1-alkyl-1,2,4-triazole with hexafluoroglutaric anhydride, and (3) functionalized triazolium bromides **4b,c** and **5a–c** by reacting the corresponding *N*-1-alkyl-1,2,4-triazole with the appropriate bromide under neat reaction conditions. When hexafluoroglutaric anhydride was used as the electrophile in addition to the *N*-4 isomer (major), some *N*-2-isomer was formed (as detected by NMR). The yield of the minor isomer can be diminished by increasing the length of the *N*-1-alkyl group (Scheme 1). The formation of these zwitterionic triazolium salts (**2a,b**, **3a,b**) in high yields was also observed for similar imidazolium salts.<sup>22b,25</sup>

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Scheme 2<sup>a</sup>

However, there appear to be no imidazolium salts with fluorine-containing substituents that have fluorovinyl or hydroxy functionalities, so comparison of properties and characteristics with our triazolium compounds is not possible.

Metathesis of zwitterionic compounds **2** and **3** and of fluorine-containing triazolium bromides **4** and **5** led to the formation of a new class of low melting salts **6–11**, namely, [(R)(R<sub>funct</sub>)-Taz]<sup>+</sup>Y<sup>-</sup> (Y = PF<sub>6</sub><sup>-</sup>, (CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>N<sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>), in excellent isolated yields without need for further purification (Scheme 2). Interaction of zwitterionic **2a,b**, **3a,b** with either triflic acid or bis(trifluorosulfonyl)amine resulted in high yields of new thermally stable liquids with glass transition temperatures hovering between -22 to -68 °C.

The thermal stability of the zwitterionic salts is reflected in these quaternary liquids. Although **6a** is essentially analogous to the 3-butyl-1-(butyl-4-sulfonyl)imidazolium

triflate,<sup>22b</sup> no physical properties are provided for the latter and therefore no comparisons are possible.

The decomposition (*T<sub>d</sub>*) and phase transition temperatures (*T<sub>g</sub>*s and *T<sub>m</sub>*s, midpoints of glass transitions and/or melting points) for compounds [(R)(R<sub>funct</sub>)-Taz]<sup>+</sup>Y<sup>-</sup> **2–11**, as determined by differential scanning calorimetry (DSC), and densities are presented in Table 1. Features discussed for cations of low-melting salts include low symmetry,<sup>1</sup> weak intermolecular interactions (such as little or no hydrogen bonding),<sup>16,17</sup> and a good distribution of charge in the cation.<sup>18</sup> Comparison of the melting points of different hexafluorophosphate, trifluoromethanesulfonate, and bis(trifluoromethylsulfonyl) amide triazolium salts illustrates clearly the influence of the cation. In comparison of salts where trifluoromethanesulfonate is the anion, e.g., *N*-4 butane sulfonic acid, as the *N*-1 alkyl groups were elongated from butyl to heptyl, the *T<sub>g</sub>*s remain constant but the decomposition temperatures increase and densities are decreased (**6a,b**). However, in the case of **8a,b**, the decomposition temperature is unchanged, but the *T<sub>g</sub>*s are increased and densities are decreased. Comparison of **6a,b** with **7b** shows that changing the anion from trifluoromethanesulfonate to bis(trifluoromethylsulfonyl)amide reduces the *T<sub>g</sub>* and increases density and the *T<sub>d</sub>*. The same pattern was also observed for **10** and **11**: changing the anion from bis(trifluoromethylsulfonyl)amide to hexafluorophosphate increases the *T<sub>g</sub>*/*T<sub>m</sub>* but has no effect on the *T<sub>d</sub>*. This suggested poorer packing in the crystalline lattice as the alkyl group was elongated. DSC studies show that compounds **8a,b** are stable at 250 °C whereas **7b** is stable to 408 °C. Thus, it is expected that the thermal stability of dialkyltriazolium cations will be relatively high and the choice of the anions often determines the decomposition temperature.

Although **9b,c**, not unexpectedly, undergo phase transitions at higher temperatures than their CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> (in lieu of CF<sub>3</sub>-CH(OH)CH<sub>2</sub>) counterparts,<sup>20a</sup> their thermal decomposition temperatures occur 80 degrees lower than those of the 3,3,3-trifluoropropyl derivatives (395 vs 325 °C, 400 vs 320 °C). Interestingly, the latter derivatives were about 6–7% more dense. Compounds **10a,b** also are less thermally stable than the 3,3,3-trifluoropropyl derivatives by ~50 °C.<sup>20a</sup>

Most of the quaternary salts discussed here are moisture stable. Some of them are prepared from aqueous solutions. Compounds **10a,b** containing <sup>-</sup>N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> and **11b** containing PF<sub>6</sub><sup>-</sup> are immiscible with water, reflecting the absence of hydrogen bonding.<sup>26</sup> While PF<sub>6</sub><sup>-</sup>-containing ionic liquids are reputed to hydrolyze upon heating to form HF, we have not observed this phenomenon. Also, although containing a hydroxyl group, compounds **9b,c** with the bis(trifluorosulfonyl)amide anion are immiscible with water.<sup>27</sup>

In our work, the application of the new compound **6b** as a solvent/catalyst was demonstrated successfully in esterification reactions (25 to 170 °C) (Table 2). We also found that compound **6b** was also useful for hetero-Michael

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**Table 1.** Phase Transition and Decomposition Temperatures and Densities of Quaternary Salts [(R)(R<sub>func</sub>)Taz]<sup>+</sup>Y<sup>-</sup>

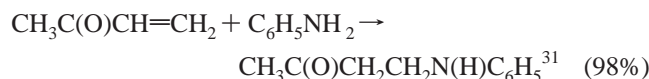
compd	phase transition temp/°C				dec temp/°C <i>T<sub>d</sub></i>	<i>d</i> <sub>24 °C</sub> (g/cm <sup>3</sup> )
	<i>T<sub>g1</sub></i>	<i>T<sub>g2</sub></i>	<i>T<sub>m1</sub></i>	<i>T<sub>m2</sub></i>		
<b>2a</b>	51.2		164.3	293	374	
<b>2b</b>			225.0	303	363	
<b>4b</b>			98.3	210.9	299	
<b>4c</b>		153	102.7	220.8	290	
<b>5a</b>	68.5	144.6	79.1	155.3		
<b>5b</b>			51.6	196.1	271	
<b>5c</b>			58.5	212.3	286	
<b>6a</b>	-41.0		-16.9		333	1.48
<b>6b</b>	-41.0				361	1.43
<b>7b</b>	-44.4				408	1.52
<b>8a</b>	-67.7				254	1.63
<b>8b</b>	-39.0				254	1.46
<b>9b</b>	-51.7				315	1.43
<b>9c</b>	-47.2				320	1.40
<b>10a</b>	-22.4		-71.2		359	1.57
<b>10b</b>	-56.4				350	1.44
<b>11b</b>			41.1	109.6	350	

**Table 2.** Esterification Reactions in **6b**

RC(O)OH + R'OH → RC(O)OR'			
R	R'	time, h	yield, % (GC)
CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	0.75	96.5 <sup>a</sup>
CH <sub>3</sub>	CF <sub>3</sub> CH <sub>2</sub>	0.75	90.3 <sup>b</sup>
CH <sub>3</sub>	HCF <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub>	3.0	94.5 <sup>c</sup>
CF <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	1.3	92.8 <sup>d</sup>

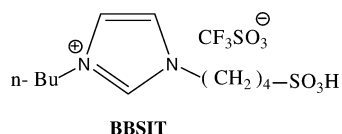
<sup>a</sup> Reference 22b. <sup>b</sup> Reference 28. <sup>c</sup> Reference 29. <sup>d</sup> Reference 30.

reactions (25 °C, 1 h) resulting in high product yields, e.g.,



The latter reaction is particularly interesting and should be extendable to a large number of alcohol, thiol, and carbamate additions to acrylamides, alkylidene malonates, and  $\alpha,\beta$ -unsaturated ketones with these Brønsted acid ionic liquids replacing the Lewis acids normally employed.<sup>28–31</sup>

Comparison with similar reactions in 3-butyl-1-(butyl-1-sulfonyl)imidazolium trifluoromethanesulfonate, BBSIT, or



triphenyl(propyl-3-sulfonyl)phosphonium tolenesulfonate systems is difficult since few if any fluorine-containing alcohols or acids have been run in either system. However, when acetic acid was condensed with ethanol in BBSIT, and was heated at 175 °C for 45 min, ethyl acetate was obtained in 96% yield.<sup>22b</sup> In our studies, the reaction of the same two

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**Table 3.** Recycling of **6b** in the Synthesis of Ethyl Acetate

cycle	<b>6b</b> (%) <sup>a</sup>	BBSIT <sup>b</sup> (%) <sup>c</sup>
1	96	82
2	96	91
3	94	96
4	92	81
5	93	87

<sup>a</sup> This work, GC yield. <sup>b</sup> Reference 22b. <sup>c</sup> Isolated yield.

moieties in **6b** gave essentially the same yield. When BBSIT was used as a solvent/catalyst to study the reaction of CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>H with CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>OH, the ester was isolated in 82% yield after 48 h at 22 °C.

As was carried out with BBSIT,<sup>22b</sup> we then examined the yield of ethyl acetate obtained when **6b** was recycled several times. The yields for the two systems are compared in Table 3. While the yields reported for BBSIT are isolated yields, the results for **6b** are percentages obtained from GC analyses. It is difficult to compare and thus predict which of these two systems would be more utilitarian, since no physical properties, other than spectral, are reported for BBSIT. Both systems appear to have considerable potential.

## Conclusion

An efficient procedure for the syntheses of new families of functionalized alkyl/fluoroalkyl-containing triazolium quaternary salts and triazolium liquids in good isolated yields is described. This series of triazolium cations that contain covalently bound anionic sites, such as sulfonate, fluoro homoallylic, fluoro carboxy, and fluoroalkanol groups, was converted by metathesis with fluorine-containing salts to new low melting salts. The functionalized triazolium salts possess many characteristics of excellent liquids with respect to air, water, and thermal stability. Compounds **6–10** are liquids at 25 °C with high decomposition temperatures and densities between 1.45 and 1.61 gm<sup>-3</sup>. The successful role of **6b** as a recyclable Brønsted acid solvent/catalyst in reactions that are normally promoted by Lewis acids suggests further applications in similar systems.

## Experimental Section

**General Methods.** <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded in acetone-*d*<sub>6</sub> unless otherwise stated on a 500 MHz spectrometer (Bruker AVANCE) operating at 500, 125, and 470 MHz, respectively. The 500 MHz instrument was rarely utilized for <sup>19</sup>F NMR spectra. Chemical shifts are reported in ppm relative to the appropriate standard. GC/MS spectra were determined on a Shimadzu QP5050A spectrometer. Mass spectra for ionic compounds were determined by insertion using a solid probe. Masses for the cation species are reported. M<sup>+</sup> refers to the cation only. *T<sub>m</sub>*s and *T<sub>g</sub>*s were recorded on a differential scanning calorimeter at a scan rate of 10 °C per minute. IR spectra were obtained using NaCl plates for neat liquids and KBr pellets for solids. Densities were measured at 24 °C using a pycnometer.

**General Procedure for the Preparation of 1-Alkyl-1,2,4-triazoles 1.** These compounds were synthesized by a modification of the procedure of Atkinson and Polya.<sup>18,20,32</sup>

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**General Procedure for the Preparation of Quaternary Salts**

**2. 1-Heptyl-triazolium-4-(butyl-4-sulfonate) 2b.** 1,4-Butanesultone (0.644 g, 4.70 mmol) and 1-heptyl-1,2,4-triazole (0.72 g, 4.299 mmol) were placed in a Pyrex glass tube, which was evacuated, sealed, and heated at 105 °C for 52 h. The white residue was washed repeatedly with diethyl ether and toluene and dried under reduced pressure at ~50 °C. The product was obtained in 90% yield (1.17 g) and in high purity as a water miscible white solid:  $T_{m1}$  225.02 °C,  $T_{m2}$  303 °C; IR (KBr) 3111, 3063, 3029, 2926, 2857, 1577, 1536, 1467, 1415, 1387, 1258, 1182, 1124 1038, 890, 789  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  0.73 (t,  $J = 6.74$  Hz, 3H), 1.20 (m, 8H), 1.68 (m,  $J = 7.39$  Hz, 2H), 1.84 (m,  $J = 6.93$  Hz, 2H), 1.97 (m,  $J = 7.66$  Hz, 2H), 2.84 (t,  $J = 7.39$  Hz, 2H), 4.25 (t,  $J_{\text{HH}} = 7.19$  Hz, 2H), 4.30 (t,  $J_{\text{HH}} = 7.01$  Hz, 2H), 8.79 (s, 1H), 9.76 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  144.6, 141.7, 52.6, 49.9, 47.7, 30.8, 27.8 (m), 25.2, 21.9, 20.9, 13.3; GC-MS (EI)  $m/z$  (%) 302.75 ( $\text{M}^+$ , 100), 301.90 ( $\text{M}^+ - 1$ , 30), 300.85 ( $\text{M}^+ - 2$ , 100). Anal. Calcd for  $\text{C}_{13}\text{H}_{25}\text{N}_3\text{O}_3\text{S}$ : C, 51.46; H, 8.30; N, 13.85. Found: C, 51.00; H, 8.30; N, 13.47.

**1-Butyl-triazolium-4-(butyl-4-sulfonate) 2a:** 1.28 g, 86% yield; water miscible white solid;  $T_g$  51.17 °C,  $T_m$  164.31 °C; IR (KBr) 3113, 3026, 2957, 2933, 2869, 1577, 1535, 1464, 1414, 1387, 1289, 1220, 1186, 1124, 1038, 1000, 894, 789  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$  0.81 (t,  $J = 7.34$  Hz, 3H), 1.22 (m,  $J = 7.55$  Hz, 2H), 1.65 (m,  $J = 7.34$  Hz, 2H), 1.81 (m,  $J = 7.42$  Hz, 2H), 1.99 (m,  $J = 7.57$  Hz, 2H), 2.85 (t,  $J = 7.59$  Hz, 2H), 4.26 (t,  $J_{\text{HH}} = 7.28$  Hz, 2H), 4.32 (t,  $J_{\text{HH}} = 7.08$  Hz, 2H), 8.79 (s, 1H), 9.76 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  144.6, 141.7, 52.3, 49.9, 47.7, 30.0, 27.8, 20.9, 18.7, 12.6; MS (ES $^-$ )  $m/z$  (%) 260.01 ( $\text{M}^+$ , 15), 260.06 ( $\text{M}^+ - 1$ , 100), 233 ( $\text{M}^+ - 2\text{CH}_2$ , 63), 180 ( $\text{M}^+ - \text{SO}_3 - \text{H}$ , <6); MS (ES $^+$ )  $m/z$  (%) 262.08 ( $\text{M}^+ + 2$ , 52). Anal. Calcd for  $\text{C}_{10}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$ : C, 45.96; H, 7.33; N, 16.08. Found: C, 45.86; H, 7.61; N, 15.74.

**1-Heptyl-4-(3,3,3-trifluoro-2-propanol)triazolium bromide 4b.** 1-Heptyl-1,2,4-triazole (0.44 g, 2.63 mmol) and 3-bromo-1,1,1-trifluoro-2-propanol (0.55 g, 2.76 mmol) were placed in a Pyrex glass tube, which was evacuated, sealed, and heated at 115 °C for 7 days. The residue was washed repeatedly with dichloromethane and hexane and dried under reduced pressure at ~50 °C (0.93 g, 96% yield): pale pink solid,  $T_{m1}$  98.30 °C,  $T_{m2}$  210.93 °C; IR (KBr) 3647, 3156, 3113, 3043, 2967, 2957, 2929, 2859, 1796, 1617, 1576, 1530, 1449, 1415, 1391, 1326, 1267, 1238, 1181, 1135, 1113, 1076, 1049, 989, 901, 860  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.87 (t,  $J = 7.15$  Hz, 3H), 1.30 (m,  $J = 3.81$  Hz, 4H), 1.44 (m,  $J = 6.69$  Hz,  $J = 3.57$  Hz, 4H), 2.09 (m,  $J = 2.69$  Hz, 2H), 4.54 (t,  $J_{\text{HH}} = 7.31$  Hz, 2H), 4.69 (dd,  $J_{\text{HH}} = 13.92$  Hz,  $J_{\text{HH}} = 10.58$  Hz, 1H), 4.85 (m,  $J_{\text{HH}} = 6.97$  Hz, 1H), 4.97 (dd,  $J_{\text{HH}} = 13.92$  Hz,  $J_{\text{HH}} = 2.84$  Hz, 1H), 9.27 (s, 1H), 10.65 (s, 1H);  $^{13}\text{C}$  NMR  $\delta$  146.0, 144.2, 125.3 (q,  $J_{\text{C-F}} = 281.58$  Hz), 67.5 ( $J_{\text{C-F}} = 31.44$  Hz), 53.4, 48.5, 32.2, 30.3, 30.1, 26.7, 23.1, 14.2;  $^{19}\text{F}$  NMR (282 MHz)  $\delta$  -78.42 (d,  $J_{\text{H-F}} = 7.06$  Hz, 3F); MS (EI)  $m/z$  (%) 280.30 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{12}\text{H}_{21}\text{BrF}_3\text{N}_3\text{O}$ : C, 40.01; H, 5.88; N, 11.67; F, 15.82. Found: C, 39.87; H, 5.86; N, 11.65; F, 16.00.

**1-Decyl-4-(3,3,3-trifluoro-2-propanol)triazolium bromide 4c:** 0.72 g, 97% yield; white solid,  $T_{m1}$  102.66 °C,  $T_{g1}$  153 °C,  $T_{m2}$  220.72 °C; IR (KBr) 3220, 3134, 3033, 2926, 2940, 2857, 1578, 1528, 1456, 1334, 1270, 1114, 1051, 993  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.88 (t,  $J = 6.90$  Hz, 3H), 1.28 (m, 10H), 1.38 (m, 6H), 2.81 (br. s, 1H), 4.55 (t,  $J_{\text{HH}} = 7.30$  Hz, 2H), 4.81 (m, 1H), 4.84 (m, 2H), 9.22 (s, 1H), 10.56 (s, 1H);  $^{13}\text{C}$  NMR  $\delta$  146.0, 144.2, 125.2 (q,  $J_{\text{C-F}} = 282$  Hz), 67.58 (q,  $J_{\text{C-F}} = 31.31$  Hz), 53.4, 48.5, 32.2, 30.0, 29.3, 26.7, 23.1, 14.2;  $^{19}\text{F}$  NMR (282 MHz)  $\delta$  -78.44 (td,  $J_{\text{H-F}} = 7.06$  Hz,  $J_{\text{H-F}} = 1.88$  Hz, 3F); MS (EI)  $m/z$  (%) 322.25 ( $\text{M}^+$ , 100).

Anal. Calcd for  $\text{C}_{15}\text{H}_{27}\text{BrF}_3\text{N}_3\text{O}$ : C, 44.78; H, 6.76; N, 10.45; F, 14.17. Found: C, 44.77; H, 6.85; N, 10.68; F, 14.29.

**1-Butyl-4-(3,4,4-trifluoro-3-butenyl)triazolium bromide 5a.** 1-Butyl-1,2,4-triazole (0.62 g, 4.95 mmol) and 4-bromo-1,1,2-trifluoro-1-butene (1.01 g, 5.2 mmol) were placed in a Pyrex glass tube, which was evacuated, sealed, and heated at 115 °C for 4 days. The residue was washed repeatedly with dichloromethane and hexane and dried under reduced pressure at ~40 °C (1.53 g, 98% yield): white solid,  $T_{g1}$  68.47 °C,  $T_{m1}$  79.08 °C,  $T_{g2}$  144.56 °C,  $T_{m2}$  155.34 °C; IR (KBr) 3108, 3010, 2964, 2941, 2879, 1799, 1702, 1630, 1576, 1528, 1461, 1385, 1304, 1248, 1162, 1115, 1032, 953, 910  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz)  $\delta$  0.97 (t,  $J = 7.36$  Hz, 3H), 1.42 (hex,  $J = 7.46$  Hz, 2H), 1.99 (m, 2H), 3.34 (m, 2H), 4.61 (t,  $J_{\text{HH}} = 7.09$  Hz, 2H), 4.95 (t,  $J_{\text{HH}} = 6.94$  Hz, 2H), 9.70 (s, 1H), 11.74 (s, 1H);  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  154.6, 145.7, 144.5, 127.4, 52.9, 45.2, 31.3, 27.4 (dd,  $J_{\text{C,F}} = 21.26$ ,  $J_{\text{C,F}} = 2.45$  Hz), 19.86, 13.63;  $^{19}\text{F}$  NMR (282 MHz)  $\delta$  -104.08 (ddt,  $J_{\text{FF}} = 81.89$  Hz,  $J_{\text{FF}} = 33.89$  Hz,  $J_{\text{FF}} = 2.82$  Hz, 1F), -122.88 (ddm,  $^2J_{\text{FF}} = 114.96$  Hz,  $^3J_{\text{FF}} = 86.13$  Hz, 1F), -175.54 (m, 1F); MS (EI)  $m/z$  (%) 234.25 ( $\text{M}^+$ , 80). Anal. Calcd for  $\text{C}_{10}\text{H}_{15}\text{BrF}_3\text{N}_3$ : C, 38.23; H, 4.81; N, 13.38; F, 18.14. Found: C, 38.02; H, 4.84; N, 12.99; F, 17.96.

**1-Heptyl-4-(3,4,4-trifluoro-3-butenyl)triazolium bromide 5b:** 1.43 g, 98% yield; white solid,  $T_{m1}$  51.59 °C,  $T_{m2}$  196.06 °C; IR (KBr) 3108, 3011, 3071, 2959, 2932, 2860, 1799, 1630, 1577, 1529, 1462, 1380, 1304, 1249, 1177, 1161, 1007, 953  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.87 (t,  $J = 6.95$  Hz, 3H), 1.29 (m, 4H), 1.39 (m, 4H), 2.97 (m, 2H), 3.31 (d,  $J = 19.95$  Hz, 2H), 4.59 (t,  $J_{\text{HH}} = 7.10$  Hz, 2H), 4.95 (t,  $J_{\text{HH}} = 6.50$  Hz, 2H), 9.83 (s, 1H), 11.75 (s, 1H);  $^{13}\text{C}$  NMR  $\delta$  145.6, 144.5, 53.13, 45.1, 32.2, 29.3, 27.5, 27.3, 26.6, 23.1, 14.21;  $^{19}\text{F}$  NMR (282 MHz)  $\delta$  -104.56 (dd,  $J_{\text{FF}} = 84.71$  Hz,  $J_{\text{FF}} = 32.94$  Hz, 1F), -123.33 (dd,  $^2J_{\text{FF}} = 117.65$  Hz,  $^3J_{\text{FF}} = 89.41$  Hz, 1F), -176.17 (d,  $^2J_{\text{FF}} = 104$  Hz, 1F); MS (EI)  $m/z$  (%) 276.25 ( $\text{M}^+$ , 68). Anal. Calcd for  $\text{C}_{13}\text{H}_{21}\text{BrF}_3\text{N}_3$ : C, 43.83; H, 5.94; N, 11.80; F, 16.00. Found: C, 43.59; H, 5.94; N, 11.95; F, 16.18.

**1-Decyl-4-(3,4,4-trifluoro-3-butenyl)triazolium bromide 5c:** 1.68 g, 97% yield; white solid,  $T_{m1}$  58.59 °C,  $T_{m2}$  212.29 °C; IR (KBr) 3109, 3015, 2958, 2925, 2854, 1800, 1582, 1530, 1466, 1377, 1304, 1251, 1122, 1073, 812  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.86 (t,  $J = 6.9$  Hz, 3H), 1.36 (m, 14H), 2.83 (2H), 3.30 (d,  $J = 21.91$  Hz, 2H), 4.59 (t,  $J_{\text{HH}} = 7.15$  Hz, 2H), 4.92 (t,  $J_{\text{HH}} = 6.75$  Hz, 2H), 9.57 (s, 1H), 11.71 (s, 1H);  $^{13}\text{C}$  NMR  $\delta$  145.5, 144.5, 53.2, 45.1 (t), 32.5, 30.1, 30.0, 29.8, 27.5, 27.5, 27.3, 26.6, 23.2, 14.3;  $^{19}\text{F}$  NMR (282 MHz)  $\delta$  -104.45 (dd,  $J_{\text{FF}} = 82.36$  Hz,  $J_{\text{FF}} = 33$  Hz, 1F), -123.38 (dd,  $^2J_{\text{FF}} = 113$  Hz,  $^3J_{\text{FF}} = 85$  Hz,  $^4J_{\text{HF}} = 4.7$  Hz, 1F), -176.17 (dm,  $^2J_{\text{FF}} = 113$  Hz,  $^3J_{\text{HF}} = 23$  Hz, 1F); MS (EI)  $m/z$  (%) 318.30 ( $\text{M}^+$ , 62). Anal. Calcd for  $\text{C}_{16}\text{H}_{27}\text{BrF}_3\text{N}_3$ : C, 48.25; H, 6.83; N, 10.55; F, 14.31. Found: C, 47.87; H, 6.99; N, 10.46; F, 14.37.

**1-Heptyl-4-(butyl-4-sulfonic acid)triazolium Trifluoromethanesulfonate 6b.** 1,4-Butane sultone (1.09 g, 8.01 mmol), 1-heptyl-1,2,4-triazole (1.22 g, 7.28 mmol), and toluene (20 mL) were placed in a two-necked reaction flask and stirred at 115 °C for 4 days. The white salt was washed repeatedly with diethyl ether and toluene to remove any unreacted starting materials. After the solid was dried in vacuo at ~50 °C, a stoichiometric amount of trifluoromethane sulfonic acid was added (1.086 g, 7.094 mmol) and the mixture stirred under nitrogen for 4 h at 40 °C. During this time the zwitterions dissolved/liquefied, and the resulting ionic liquid phase was washed repeatedly with diethyl ether and toluene to remove any unreacted starting materials. This resulted in the formation of a colorless viscous oil:  $d_{24}^{\text{C}} = 1.43$   $\text{g}/\text{cm}^3$  (2.63 g, 95% yield);  $T_g$  -41.05 °C; IR (KBr) 3438, 3130, 3075, 2930, 2860, 1695, 1578, 1530, 1466, 1380, 1226, 1031, 902  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.95 (t,  $J = 7.42$  Hz, 3H), 1.42 (hex,  $J = 7.68$  Hz, 2H), 1.99 (m, 2H), 3.23 (m,

2H), 4.60 (t,  $J_{\text{HH}} = 7.2$  Hz, 2H), 5.02 (t,  $J_{\text{HH}} = 7.4$  Hz, 2H), 9.29 (s, 1H), 10.22 (s, 1H);  $^{13}\text{C}$  NMR  $\delta$  144.7, 142.5, 121.1 (q,  $J_{\text{C-F}} = 322$  Hz), 52.5, 50.7, 47.7, 31.4, 28.5, 28.5, 28.49, 28.47, 28.0, 25.8, 22.3, 20.7, 13.4;  $^{19}\text{F}$  NMR (282 MHz)  $\delta$  -79.52 (s, 3F); MS (EI)  $m/z$  (%) 303.55 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{14}\text{H}_{26}\text{F}_3\text{N}_3\text{O}_6\text{S}_2$ : C, 37.08; H, 5.78; F, 12.57. Found: C, 36.76; H, 6.01; F, 12.51.

**1-Butyl-4-(butyl-4-sulfonic acid)triazolium trifluoromethanesulfonate 6a:** 1.08 g, 88% yield; colorless viscous oil,  $d_{24}^{\circ\text{C}} = 1.48$  g/cm $^3$ ,  $T_g$  -41.02 °C,  $T_m$  -16.87 °C; IR (KBr) 3440, 3128, 3080, 2934, 2860, 1576, 1537, 1468, 1387, 1288, 1189, 1040, 900 cm $^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.95 (t,  $J = 7.43$  Hz, 3H), 1.43 (hex,  $J = 7.67$  Hz, 2H), 1.92 (m,  $J_{\text{HH}} = 5.60$  Hz, 2H), 1.99 (m, 2H), 2.26 (m,  $J_{\text{HH}} = 7.48$  Hz, 2H), 3.23 (t,  $J_{\text{HH}} = 7.54$  Hz, 2H), 4.55 (t,  $J_{\text{HH}} = 7.21$  Hz, 2H), 4.60 (t,  $J_{\text{HH}} = 7.29$  Hz, 2H), 9.17 (s, 1H), 10.11 (s, 1H);  $^{13}\text{C}$  NMR  $\delta$  144.7, 142.5, 121.3 (q,  $J_{\text{CF}} = 325$  Hz), 52.3, 50.6, 47.7, 30.5, 29.5, 28.0, 20.7, 19.1, 12.8;  $^{19}\text{F}$  NMR (282 MHz)  $\delta$  -79.48 (s, 3F); MS (EI)  $m/z$  (%) 262.25 ( $\text{M}^+$ , <3). Anal. Calcd for  $\text{C}_{11}\text{H}_{20}\text{F}_3\text{N}_3\text{O}_6\text{S}_2$ : C, 32.11; H, 4.90; F, 13.85. Found: C, 32.24; H, 5.25; F, 13.98.

**1-Heptyl-4-(butyl-4-sulfonic acid)triazolium Bis(trifluoromethanesulfonyl)amide 7b.** Compound **2a** (0.86 g, 2.834 mmol) and trifluoromethane sulfonimide (0.881 g of 95%, 2.976 mmol) were placed together and stirred under nitrogen for 4 h at 40 °C. The zwitterions dissolved/liqefied to form a colorless viscous oil (1.08 g, 88% yield):  $d_{24}^{\circ\text{C}} = 1.52$  g/cm $^3$ ,  $T_g$  -44.40 °C; IR (KBr) 3416, 3137, 3084, 2959, 2932, 2861, 1695, 1578, 1528, 1466, 1387, 1350, 1195, 1135, 1058, 896 cm $^{-1}$ ;  $^1\text{H}$  NMR (300 MHz)  $\delta$  0.85 (t,  $J = 6.87$  Hz, 3H), 1.33 (m, 8H), 1.91 (m,  $J_{\text{HH}} = 7.20$  Hz, 4H), 2.19 (m,  $J_{\text{HH}} = 7.44$  Hz, 2H), 3.14 (t,  $J_{\text{HH}} = 7.41$  Hz, 2H), 4.55 (t,  $J_{\text{HH}} = 7.21$  Hz, 2H), 4.57 (t,  $J_{\text{HH}} = 6.75$  Hz, 2H), 9.14 (s, 1H), 10.07 (s, 1H);  $^{13}\text{C}$  NMR  $\delta$  144.7, 142.4, 120.1 (q,  $J_{\text{C-F}} = 321$  Hz), 52.6, 50.5, 47.8, 31.4, 30.5, 29.5, 28.0, 25.8, 22.3, 20.7, 19.1, 13.4;  $^{19}\text{F}$  NMR (282 MHz)  $\delta$  -80.32 (s, 3F); MS (EI)  $m/z$  (%) 303.85 ( $\text{M}^+$ , <1). Anal. Calcd for  $\text{C}_{15}\text{H}_{26}\text{F}_6\text{N}_4\text{O}_7\text{S}_3$ : C, 30.82; H, 4.48; F, 19.50. Found: C, 31.13; H, 4.75; F, 19.67.

**1-Butyl-4-(2,2,3,3,4,4-hexafluoro-5-oxo-pentanoic acid)triazolium Trifluoromethanesulfonate 8a.** 1-Butyl-1,2,4-triazole (0.53 g, 4.23 mmol) and hexafluoroglutaric anhydride (1.02 g, 4.44 mmol) were placed in a Pyrex glass tube, which was evacuated, sealed, and heated at 115 °C for 5 days to give **3a** (1.55 g, 99%). The latter was washed repeatedly with diethyl ether and toluene and dried at reduced pressure, after which a stoichiometric amount of trifluoromethane sulfonic acid was added (0.48 g, 3.16 mmol). The mixture was stirred under nitrogen for 4 h at 40 °C and then washed repeatedly with diethyl ether and toluene to remove any unreacted starting materials, to leave a red-brown viscous oil (1.50 g, 95% yield):  $d_{24}^{\circ\text{C}} = 1.61$  g/cm $^3$ ,  $T_g$  -67.74 °C; IR (KBr) 3472, 3144, 3071, 2967, 2940, 2879, 1776, 1702, 1568, 1443, 1377, 1253, 1177, 1032, 812 cm $^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.94 (t,  $J = 7.35$  Hz, 3H), 1.40 (m,  $J = 7.60$  Hz, 2H), 1.98 (m, 2H), 4.61 (t,  $J_{\text{HH}} = 6.77$  Hz, 2H), 9.08 (s, 1H), 10.01 (s, 1H), 10.98 (br s, 1H);  $^{13}\text{C}$  NMR  $\delta$  210.19, 198.63, 143.96, 142.27, 124.60 (t,  $J = 23.39$  Hz), 121.58 (q,  $J_{\text{C-F}} = 320$  Hz), 52.98, 31.38, 19.80, 13.69;  $^{19}\text{F}$  NMR (282 MHz)  $\delta$  -79.61 (s, 3F), -119.56 (m, 2F), -120.84 (m, 2F), -122.56 (m, 2F); MS (EI)  $m/z$  (%) 348.25 ( $\text{M}^+$ , 9). Anal. Calcd for  $\text{C}_{12}\text{H}_{12}\text{F}_9\text{N}_3\text{O}_6\text{S}$ : C, 28.98; H, 2.43; F, 34.38. Found: C, 29.03; H, 2.51; F, 34.62.

**1-Heptyl-4-(2,2,3,3,4,4-hexafluoro-5-oxo-pentanoic acid)triazolium Trifluoromethanesulfonate 8b.** 1-Heptyl-1,2,4-triazole (0.44 g, 2.63 mmol) and hexafluoroglutaric anhydride (0.63 g, 2.76 mmol) were put in a Pyrex glass tube, which was evacuated, sealed, and heated at 115 °C for 2 days to give **3b** (1.13 g, 99%). The latter was washed repeatedly with diethyl ether and toluene and dried at reduced pressure, after which a stoichiometric amount of

trifluoromethane sulfonic acid was added (0.73 g, 4.65 mmol). The mixture was stirred under nitrogen for 4 h at 40 °C and then washed repeatedly with diethyl ether and toluene to remove any unreacted starting materials, to leave a red-brown viscous oil (1.13 g, 96% yield): red-brown oil,  $d_{24}^{\circ\text{C}} = 1.46$  g/cm $^3$ ,  $T_g$  -38.98 °C; IR (KBr) 3472, 3144, 3071, 2967, 2940, 2879, 1776, 1702, 1568, 1443, 1377, 1253, 1177, 1032, 812 cm $^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.86 (t,  $J = 6.81$  Hz, 3H), 1.34 (m,  $J = 7.60$  Hz, 8H), 1.98 (m, 2H), 4.60 (t,  $J_{\text{HH}} = 7.29$  Hz, 2H), 9.09 (s, 1H), 10.02 (s, 1H), 11.04 (br s, 1H);  $^{13}\text{C}$  NMR  $\delta$  210.16, 198.71, 143.79, 141.96, 124.59 (t,  $J = 24.52$  Hz), 121.55 (q,  $J_{\text{CF}} = 320$  Hz), 52.98, 32.19, 29.22, 26.63, 26.52, 22.07, 14.22;  $^{19}\text{F}$  NMR (282 MHz)  $\delta$  -79.69 (s, 3F), -119.58 (m, 2F), -120.84 (t, 2F), -122.57 (m, 2F); MS (EI)  $m/z$  (%) 391.40 ( $\text{M}^+$ , 2). Anal. Calcd for  $\text{C}_{15}\text{H}_{18}\text{F}_9\text{N}_3\text{O}_6\text{S}$ : C, 33.40; H, 3.36; F, 31.70. Found: C, 33.57; H, 3.49; F, 31.93.

**General Procedure for the Preparation of 9–11.** To a magnetically stirred solution of bromide **4** (1.09 mmol) in water (5 mL) was added lithium bis(trifluoromethylsulfonyl) amide (1.09 mmol). After 8 h at 40 °C, the lower liquid layer was separated and dissolved in dichloromethane (8 mL). The dichloromethane solution was washed with water ( $2 \times 15$  mL) and evaporated in vacuo. Benzene was added to the residue and the solution dried using a Dean–Stark apparatus. After removal of the benzene in vacuo, the residue was dried in vacuo (0.3 mmHg) at 40 °C.

**1-Heptyl-4-(3,3,3-trifluoro-2-propanol)triazolium bis(trifluoromethanesulfonyl) amide 9b:** 0.92 g, 98.6% yield; water immiscible, colorless oil,  $d_{24}^{\circ\text{C}} = 1.43$  g/cm $^3$ ,  $T_g$  -51.65 °C; IR (KBr) 3474, 3149, 3089, 2933, 2862 1578, 1532, 1454, 1352, 1276, 1199, 1137, 1058, 990, 905 cm $^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 6.94$  Hz, 3H), 1.29 (m, 4H), 1.35 (m, 4H), 1.98 (m, 2H), 4.37 (t,  $J_{\text{HH}} = 7.39$  Hz, 2H), 4.46 (dd,  $J = 14.29$  Hz, 7.21 Hz, 1H), 4.55 (m, 2H), 4.68 (dd,  $J = 14.38$  Hz, 2.82 Hz, 1H), 8.52 (s, 1H), 9.57 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  145.3, 142.9, 124.1 (q,  $J_{\text{C-F}} = 282.33$  Hz), 120.4 (q,  $J_{\text{C-F}} = 320.56$  Hz), 68.2 (q,  $J_{\text{C-F}} = 32.70$  Hz), 54.1, 48.2, 32.2, 29.4, 29.2, 26.7, 23.2, 14.7;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.59 (d,  $J_{\text{H-F}} = 5.65$ , 3F), -79.49 (s, 3F); MS (EI)  $m/z$  (%) 280.25 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{14}\text{H}_{21}\text{F}_9\text{N}_4\text{O}_5\text{S}_2$ : C, 30.00; H, 3.78; N, 10.00; F, 30.51. Found: C, 30.11; H, 3.76; N, 9.91; F, 30.26.

**1-Decyl-4-(3,3,3-trifluoro-2-propanol)triazolium bis(trifluoromethanesulfonyl) amide 9c:** 0.41 g, 98% yield; water immiscible, yellow oil,  $d_{24}^{\circ\text{C}} = 1.40$  g/cm $^3$ ,  $T_g$  -47.19 °C; IR (KBr) 3478, 3146, 3089, 2957, 2928, 2958, 1578, 1533, 1456, 1351, 1275, 1198, 1141, 1057, 994 cm $^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 7.15$  Hz, 3H), 1.29–1.34 (m, 15H), 1.97 (m, 2H), 4.37 (t,  $J_{\text{HH}} = 7.35$  Hz, 2H), 4.53 (m, 2H), 4.70 (m, 1H), 8.54 (s, 1H), 9.60 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  145.3, 142.9, 124.2 (q,  $J_{\text{C-F}} = 282.33$  Hz), 120.3 (q,  $J_{\text{C-F}} = 320.81$  Hz), 68.1 (q,  $J_{\text{C-F}} = 32.32$  Hz), 54.1, 48.3, 32.6, 30.2, 30.0, 30.0, 29.6, 29.4, 26.9, 23.4, 14.8;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.44 (d,  $J_{\text{H-F}} = 6.12$ , 3F), -79.48 (s, 3F); MS (EI)  $m/z$  (%) 322.25 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{17}\text{H}_{27}\text{F}_9\text{N}_4\text{O}_5\text{S}_2$ : H, 4.52; N, 9.30; F, 28.38. Found: H, 4.81; N, 9.68; F, 27.77.

**1-Butyl-4-(3,4,4-trifluoro-3-butenyl)triazolium bis(trifluoromethanesulfonyl) amide 10a:** 0.77 g, 96% yield; water immiscible, colorless oil,  $d_{24}^{\circ\text{C}} = 1.57$  g/cm $^3$ ;  $T_g$  -22.43 °C,  $T_m$  -71.20 °C; IR (KBr) 3140, 3088, 2969, 2941, 2882, 1800, 1576, 1531, 1464, 1352, 1111, 1057, 954, 889 cm $^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.94 (t,  $J = 7.42$  Hz, 3H), 1.40 (sext,  $J = 7.54$  Hz, 2H), 1.97 (m, 2H), 3.19 (m, 2H), 4.55 (t,  $J_{\text{HH}} = 6.84$  Hz, 2H), 4.78 (t,  $J_{\text{HH}} = 6.84$  Hz, 2H), 9.18 (s, 1H), 10.08 (s, 1H), 11.04 (br s, 1H);  $^{13}\text{C}$  NMR  $\delta$  156.7 (d,  $J_{\text{CF}} = 45.90$  Hz), 154.7 (dd,  $J_{\text{CF}} = 45.78$  Hz,  $J_{\text{CF}} = 11.12$  Hz), 152.5 (d,  $J_{\text{CF}} = 45.90$  Hz), 145.6, 143.3, 127.5 (dd,

$J_{C,F} = 53.58$  Hz,  $J_{C,F} = 17.98$  Hz), 125.7 (dd,  $J_{C,F} = 53.26$  Hz,  $J_{C,F} = 15.60$  Hz), 120.9 (q,  $J_{C-F} = 321$  Hz), 53.3, 45.3, 31.2, 27.2, 27.0, 19.8, 13.5;  $^{19}\text{F}$  NMR  $\delta$  -80.39 (s, 6F), -104.15 (dd,  $J_{F,F} = 80.0$  Hz,  $J_{F,F} = 32.94$  Hz, 1F), -123.44 (dd,  $J_{F,F} = 82.35$  Hz,  $J_{F,F} = 84.70$  Hz,  $J = 9.40$  Hz, 1F), -176.76 (md,  $J_{F,F} = 84.70$  Hz, 1F), -122.57 (m, 2F); MS (EI)  $m/z$  (%) 234.10 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{12}\text{H}_{15}\text{F}_9\text{N}_4\text{O}_4\text{S}_2$ : C, 28.02; H, 2.94; N, 10.89; F, 33.24. Found: C, 27.71; H, 2.85; N, 10.88; F, 33.50.

**1-Heptyl-4-(3,4,4-trifluoro-3-butenyl)triazolium bis(trifluoromethanesulfonyl) amide 10b:** 0.79 g, 99% yield; water immiscible, colorless oil,  $d_{24}^{\circ\text{C}} = 1.44$  g/cm $^3$ ;  $T_g = -56.39$  °C; IR (KBr) 3138, 3083, 2932, 2932, 2862, 1800, 1578, 1529, 1462, 1352, 1191, 1057, 1011, 890  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz)  $\delta$  0.88 (t,  $J = 6.80$  Hz, 3H), 1.29 (m, 4H), 1.37 (m, 4H), 2.05 (m, 2H), 3.27 (dm,  $J = 18.01$  Hz, 2H), 4.62 (t,  $J_{\text{HH}} = 7.18$  Hz, 2H), 4.88 (t,  $J_{\text{HH}} = 6.89$  Hz, 2H), 9.28 (s, 1H), 10.22 (s, 1H);  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  145.7, 143.4, 120.0 (q,  $J_{C-F} = 321.81$  Hz), 53.6, 45.4, 32.2, 29.4, 27.3 (d,  $J = 2.56$ ), 27.0 (d,  $J = 2.32$ ), 26.6, 23.7, 14.2;  $^{19}\text{F}$  NMR (282 MHz)  $\delta$  -79.90 (s, 6F), -103.57 (tdd,  $J_{\text{FF}} = 84.72$  Hz,  $J_{\text{FF}} = 32.48$  Hz,  $J_{\text{FH}} = 2.82$  Hz, 1F), -122.98 (tdd,  $J_{\text{FF}} = 114.37$  Hz,  $J_{\text{FF}} = 84.72$  Hz,  $J_{\text{FH}} = 2.82$  Hz, 1F), -176.23 (tdd,  $J_{\text{FF}} = 112.96$  Hz,  $J_{\text{FF}} = 32.48$  Hz,  $J_{\text{FH}} = 19.77$  Hz, 1F); MS (EI)  $m/z$  (%) 276.20 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{15}\text{H}_{21}\text{F}_9\text{N}_4\text{O}_4\text{S}_2$ : C, 32.38; H, 3.80; N, 10.07; F, 30.73. Found: C, 32.28; H, 3.77; N, 9.94; F, 31.12.

**1-Heptyl-4-(3,4,4-trifluoro-3-butenyl)triazolium hexafluorophosphate 11b:** 0.77 g, 93% yield; water immiscible, white solid,  $T_{\text{m}1} 41.10$  °C,  $T_{\text{m}2} 109.60$  °C; IR (KBr) 3165, 3133, 3105, 2960, 2931, 2862, 1802, 1770, 1584, 1535, 1469, 1392, 1382, 1302, 1252, 1194, 1165, 1004, 957  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.87 (t,  $J = 6.93$  Hz, 3H), 1.29 (m, 4H), 1.38 (m, 4H), 2.97 (m, 2H), 3.32 (dm,  $J =$

21.28 Hz, 1.4 Hz, 2H), 4.58 (m, 2H), 4.83 (m, 2H), 9.23 (br s, 1H), 10.10 (br s, 1H);  $^{13}\text{C}$  NMR  $\delta$  145.6, 143.4, 53.5, 45.3, 32.2, 30.2, 29.2, 27.2, 27.0, 26.5, 23.1, 14.2;  $^{19}\text{F}$  NMR  $\delta$  -72.31 (d,  $J_{\text{PF}} = 705.89$  Hz, 6F), -104.56 (dd,  $J_{\text{FF}} = 84.71$  Hz,  $J_{\text{FF}} = 32.94$  Hz, 1F), -123.45 (tdd,  $J_{\text{FF}} = 112.94$  Hz,  $J_{\text{FF}} = 82.35$  Hz,  $J_{\text{FH}} = 4.71$  Hz, 1F), -176.69 (tdd,  $J_{\text{FF}} = 112.94$  Hz,  $J_{\text{FF}} = 32.94$  Hz,  $J_{\text{FH}} = 4.71$  Hz, 1F);  $^{31}\text{P}$  NMR (202.46 MHz)  $\delta$  -143.05 (sept,  $J_{\text{PF}} = 706.58$  Hz MS (EI)  $m/z$  (%) 276.25 ( $\text{M}^+$ , 7). Anal. Calcd for  $\text{C}_{13}\text{H}_{21}\text{F}_9\text{N}_3\text{P}_1$ : C, 37.06; H, 5.02; N, 9.97. Found: C, 37.19; H, 4.91; N, 9.60.

**General Procedure for Utilizing 6b as a Brønsted Acid Catalyst/Solvent.** In a typical case, a 10 mL Schlenk tube was charged with 1.04 g (2.30 mmol) of **6b**, acetic acid (0.57 mL, 10 mmol) (added by syringe), and an equal molar amount of ethanol. The reaction mixture was warmed to 170 °C over a period of 45 min and was analyzed by GC-MS. In the case where **6b** was recycled in the ethyl acetate reaction, the volatile materials (including water) were removed by subjecting the reaction mixture to dynamic vacuum at 70 °C for 12 h for each cycle. New portions of the reactants were then added to nonvolatile **6b**.

The single cycle esterification reactions and the hetero-Michael reaction were carried out in a similar manner by using equimolar amounts of reactants (10 mmol) and by varying the reaction times as detailed in Table 2 for the former reactions, and at 25 °C after 1 h for the latter.

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