

The First 1-Alkyl-3-perfluoroalkyl-4,5dimethyl-1,2,4-triazolium Salts

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Abstract: Syntheses of guaternary 1-alkyl-3-perfluoroalkyl-4,5-dimethyl-1,2,4-triazolium iodides have led to a variety of new quaternary salts via metathesis reactions. 1,4,5-Trimethyl-3-trifluoro-methyl-1,2,4-triazolium iodide (6) with LiN(SO₂CF₃)₂, KSO₃CF₃, AgClO₄, AgBF₄; 1-(3-fluoropropyl)-3-trifluoromethyl-4,5-dimethyl-1,2,4-triazolium iodide (7) with LiN(SO₂CF₃)₂; and 1,4,5-trimethyl-3-perfluorooctyl-1,2,4-triazolium iodide (8) with $LiN(SO_2CF_3)_2$, $AgClO_4$, AgBF₄ gave excellent yields of new thermally stable and relatively low melting quaternary salts. The structure of 1,4,5-trimethyl-3-perfluorooctyl-1,2,4-triazolium tetrafluoroborate (11c) was confirmed by single-crystal X-ray analysis. Although the molecular weight of **11c** (cation) is 3-fold greater than that of the 3-trifluoromethyl derivative 9d, its melting point is 32 °C lower.

There is growing interest in triazoles as high-energy propellants, herbicides, and fungicides and as components of drugs for a variety of clinical conditions.^{1,2} The parent triazoles and their derivatives, especially trifluoromethylated nitrogen-containing heterocycles, have been of great interest in medicinal and agricultural fields as well as in materials sciences and fluorine chemistry.³ Substitution at the carbon atoms of 1,2,4-triazole is difficult to accomplish directly and is often more efficiently accomplished by construction of the triazole with the required substituent in place.⁴ Despite the versatility of perfluoroalkylated azoles, most of the existing methodologies for the introduction of these fluorine-containing moieties require multistep manipulations involving expensive starting materials, and often result in low yields.⁵ However, recently two viable general synthetic routes to perfluoroalkylated 1,2,4-triazoles were reported. Hydrazinolysis of 5-perfluoralkyl-1,2,4-oxadiazoles^{4a} and the one-pot condensation reaction of ethyl trifluoroacetate, hydrazine, and amidines^{4b} gave 5-perfluoroalkyl-1,2,4triazoles and 3-trifluoromethyl-1,2,4-triazoles, respectively. The latter straightforward chemistry provides a route to precursors required for the syntheses of the perfluoroalkyl triazolium quaternary salts realized in this work.

Until recently, there were very few triazolium quaternary salts with melting points <100 °C, especially polyfluoroalkylated or perfluoroalkylated triazolium compounds.^{6,7} We have found that 1-alkyl-1,2,4-triazoles can be quaternized at N-4 by reaction with equivalent amounts of polyfluoroalkyl iodides or bromides under neat reaction conditions to produce polyfluoroalkyl-substituted quaternary salts in >98% isolated yields. Metathesis of these halides with other salts led to the formation of new liquid 1,2,4-triazolium quaternary salts.⁸ However, the analogous perfluoroalkylated-1,2,4-triazolium salts do not exist. Quaternization of triazoles with perfluoroalkyl iodides or bromides is not a viable route because of the electron-withdrawing effect of the α and β fluorine atoms in decreasing the S_N2 reactivity of the perfluoroalkyl halides.

We now report the syntheses of several new 3-perfluoroalkyl-1,5-dimethyl-1,2,4-triazoles or 3-perfluoroalkyl-1-(3-fluoropropyl)-5-methyl-1,2,4-triazoles, their subsequent quaternization to 1-methyl[1-(3-fluoropropyl)]-3perfluoroalkyl-4,5-dimethyl-1,2,4-triazolium iodides, and their conversion to new stable, relatively low melting (<100 °C) salts. Salts with long liquid ranges (low melting and thermal stability at high temperature) are attracting considerable attention for applications as solvents, highenergy materials, lubricants, and reaction catalysts to name a few. There is an expanding interest in developing more convenient synthetic procedures for such target molecules.9 In this respect, in addition to the direct introduction of fluorine or a fluorinated group into a given heterocycle, the construction of a heterocyclic ring from fluorine-containing noncyclic species through conventional heterocyclization reactions is a widely exploitable procedure. We have used this direct and general access to 5-methyl-3-perfluoroalkyl-1,2,4-triazoles, which consists of the three-component condensation reaction of ethyl trifluoroacetate (or ethyl perfluorononanoate), hydrazine, and acetamidine.⁴ (Scheme 1).

Alkylation, arylation, and acylation reactions at nitrogen in triazole have been extensively explored, and a wide range of reagents has been used.¹ Both protonated and deprotonated nitrogen substrates have been used. N-Alkylation of triazole occurs preferentially at N-1 rather than N-4. With 3- and 5-substituted triazoles, the prediction of substitution between N-1 and N-2 is more difficult. Both products are obtained, the ratio depending on the

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SCHEME 1



 $R_f = CF_3, C_8F_{17}$

a NH₂NH₂·H₂O, THF, reflux

b CH₃C(=NH)NH₂·HCl, NaOH, THF, reflux

SCHEME 2



^a Melting point. ^bThermal degradation.

alkylating agent.^{1,10} In this work, we have alkylated at the N-1 position of 3,5-substituted triazoles by treatment with sodium hydride followed by electrophilic attack with CH₃I or CH₂FCH₂CH₂I (Scheme 2). 1,3,5-Substituted triazoles (**3**–**5**) were subsequently quaternized at N-4 by reaction with an equivalent amount of CH₃I under neat reaction conditions to produce salts **6–8** (Scheme 2). Single-crystal structure determinations of **9b** and **11c**

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TABLE 1. Miscibility of Various Ionic Salts in OrganicSolvents^a with Dielectric Constant ϵ^b

compd	hexane	CH_2Cl_2	EtOAc	acetone	H ₂ O
6	nm	m	m	m	m
7	nm	m	m	m	m
8	nm	nm	nm	pm	pm
9a	nm	m	m	m	nm
9b	nm	pm	pm	m	m
9c	nm	pm	pm	m	m
9d	nm	pm	pm	m	m
10	nm	m	m	m	nm
11a	nm	pm	m	m	nm
11b	nm	pm	pm	m	m
11c	nm	pm	pm	m	m
$a_{\rm m}$ — missible, $m_{\rm m}$ — nonmissible, $m_{\rm m}$ — nontially missible					

^{*a*} m = miscible; nm = nonmiscible; pm = partially miscible. ^{*b*} Dielectric constant ϵ at 25 °C: hexane = 1.89/20 °C; CH₂Cl₂ = 8.93; EtOAc = 6.02; acetone = 20.7; H₂O = 78.54.

clearly show methyl substitution at N-4; See crystal structure data.

Metathesis of compounds 6–8 with several metal salts led to the formation of new quaternary salts 9-11 in excellent isolated yields. Melting points and decomposition points for 5-11 as determined by differential scanning calorimetry (DSC) are given in Scheme 2. Salts 9a, **10**, and **11a**–**c** have melting points <100 °C. Comparison of the melting points of different salts clearly illustrates the influence of the cation and anion. For example, with bis(trifluoromethanesulfonyl)amide (NTf₂) as the common anion, perfluorooctyl or trifluoromethyl at N-3, methyl or 3-fluoropropyl at N-1, the melting points decreased from 81 (11a) to 70 (9a) to 49 (10) °C, respectively. The anion appears to exhibit a major influence on the melting point in a more predictable manner. For example, when triflate (OTf), tetrafluoroborate (BF₄), perchlorate (ClO₄), and NTf₂ were the anions for compounds **9b**, **9d**, **9c**, and 9a, respectively, the melting point decreased from 137 to 130 to 128 to 70 °C. Compounds 11c, 11b, and 11a behaved similarly where the melting points decreased from 98 to 90 to 81 °C, respectively. In addition, after metathesis with other salts, the variation of melting point for the iodide 8 with C₈F₁₇ at N-3 is greater than that for the analogous iodide $\boldsymbol{6}$ with $C\bar{F}_3$ at N-3. When metathesis reactions were carried out with silver perchlorate, the melting point for 6 decreased from 165 to 128 °C (9c), while 8 decreased from 211 to 90 °C (11b). However, particularly striking is the decrease in the melting point of 9d (CF₃/BF₄) at 130 °C when compared with **11c** (C_8F_{17}/BF_4) at 98 °C when note is taken of the fact that the molecular weight of the cation has increased by 3-fold from 180 to 530!

The solubility properties of these new ionic salts are shown in Table 1. The ionic salts do not dissolve in hexane, but their solubilities increase directly with the dielectric constant of the solvents. Most of them can be dissolved in acetone and water. However, **8** is only partially dissolved in acetone and water, but it does dissolve in dimethyl sulfoxide (DMSO) and mixture of N,Ndimethylformamide (DMF) and water (1:1). Invariably when NTf₂ was used as anion, the compounds were not soluble in water. This provides a simple method to purify such ionic compounds. The solubility of **11b** and **11c** in both acetone and water is somewhat surprising given the presence of the perfluoroalkyl group, C₈F₁₇.

X-ray Crystal Structure of 11c. To confirm whether the alkylation occurred at N-2 or N-4 in 3-5, a singlecrystal X-ray structure was determined for 11c. The crystal structure shows the complete molecular ion pair in the asymmetric unit. Atypically this long fluorinated chain is not disordered. There are only a few other crystallographically determined long chain fluorinated molecules in the Cambridge Database¹¹ [chain length = C_7F_{15} , ¹² (C_7F_{15})₂, ^{13,14} (C_8F_{17})¹³], the majority being disordered. This is not unexpected given the waxy nature of this group. Compound 11c was very difficult to crystallize and the crystals could not be cut, as they would then lose crystallinity. The molecules pack in an interesting manner in the solid state with a head to head triazole arrangement with the fluorinated tails aligned. These also arrange tail to tail. The BF₄⁻ anions lie between the triazole rings. This leaves a void of ca. 2.5 Å between the triazole heads of this extended bilayer system. The structure confirms that the initial alkylation occurred at N-1 and the second alkylation at N-4. Both the structure of compound 11c and details of data collection are given in Supporting Information.

An efficient procedure for the syntheses of a family of new perfluoroalkyl-containing triazolium quaternary salts has been developed. When there is a longer fluoroalkyl substituent at N-3, the variation of melting point is greater after metathesis with other salts. Regardless of the cation, when the anion is iodide, the melting points are high. However, introduction of other anions, particularly NTf₂, reduces the melting point drastically.

Experimental Section

X-ray Crystallographic Studies. Crystals of compound 11c were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.¹⁵ Data for **11c** were collected at 83(2) K using a Bruker/Siemens SMART APEX instrument (Mo K α radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using ω scans of 0.3° per frame for 20 s, and a full sphere of data was collected. A total of 2132 frames were collected with a final resolution of 0.73 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART¹⁶ software and refined using SAINTPlus¹⁷ on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.¹⁸ The structure was solved by direct methods and refined by least-squares method on F⁵ using the SHELXTL program package. All atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are provided in Supporting Information.

(16) . *SMART*: version 5.625; Bruker Molecular Analysis Research Tool; Bruker AXS: Madison, WI, 2001.

(17) SAINTPlus: version 6.22, Data Reduction and Correction Program; Bruker AXS: Madison, WI, 2001.

Compounds 1 and 2 were prepared by a literature procedure of K. Funabiki. $^{\rm 4b}$

3-Trifluoromethyl-5-methyl-1,2,4-triazole (1). A mixture of ethyl trifluoroacetate (0.71 g, 5.0 mmol), hydrazine monohydrate (0.2 g, 4.0 mmol), and THF (25 mL) was stirred for 1 h at reflux temperature and then cooled to room temperature. After the addition of acetamidine hydrochloride (0.52 g, 5.5 mmol) and NaOH (0.22 g, 5.5 mmol), the resultant mixture was stirred for another 3 h at reflux temperature. The mixture was quenched with a cold saturated NaHCO₃ solution (250 mL) and extracted with ethyl acetate (50 mL \times 3). The extracts were dried with Na₂SO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel using hexane/ethyl acetate (2:1) to give 3-trifluoromethyl-5-methyl-1,2,4-triazole (0.57 g, 94.4% yield, white solid): $R_f 0.46$ (hexane/ethyl acetate 2:1); mp 144 °C; IR (KBr) 3449, 3150, 3055, 3013, 2924, 2856, 2815, 2722, 2629, 1708, 1522, 1418, 1367, 1188, 1127, 1059, 1022, 878, 761, 692 cm^-1; $^1\!\mathrm{H}$ NMR δ 2.52 (s, 3H), 11.30 (br, s, 1H); $^{13}\!\mathrm{C}$ NMR δ 156.21, 154.25 (q, $J_{C-C-F} = 37.80$ Hz), 120.71 (q, $J_{C-F} = 266.70$ Hz), 11.74; ¹⁹F NMR δ –65.90 (s, 3F); GC–MS (ÉI) m/z 151 (M⁺, 54), 142 (6), 132 (17), 110 (14), 100 (4), 82 (5), 69 (30), 56 (19), 42 (100). Anal. Calcd for C₄H₄F₃N₃: C, 31.80; H, 2.67. Found: C, 31.84; H, 2.73.

3-Perfluorooctyl-5-methyl-1,2,4-triazole (2). Ethyl perfluorononanoate (2.46 g, 5 mmol) gave **2** (1.40 g) 70% yield, white solid: R_f 0.34 (hexane/ethyl acetate 2:1); mp 125 °C; IR (KBr) 3481, 3063, 2857, 1702, 1566, 1420, 1364, 1218, 1150, 1055, 954 cm⁻¹, ¹H NMR δ 2.53 (s, 3H), 11.32 (br, s, 1H); ¹³C NMR δ 156.35, 153.62 (t, $J_{C-C-F} = 27.67$ Hz), 119.08–108.95 (m), 11.75; ¹⁹F NMR δ –76.94 (tt, 3F, J = 10.17 Hz, J = 2.26 Hz), –122.03 to –107.60 (m, 14F); GC–MS (EI) m/z 501 (M⁺, 5), 482 (6), 142 (36), 132 (100), 119 (9), 100 (27), 91 (8), 69 (19), 57 (9), 40 (61). Anal. Calcd for C₁₁H₄N₃F₁₇: C, 26.36; H, 0.80. Found: C, 26.11; H, 0.93.

General Procedure for Preparation of 3-5. 3-Trifluoromethyl-1,5-dimethyl-1,2,4-triazole (3). A mixture of 1 (0.30 g, 2 mmol) and NaH (0.048 g, 2 mmol) in anhydrous THF (10 mL) was refluxed for 7 h and then cooled to room temperature. After the addition of CH₃I (0.284 g, 2 mmol), the mixture was refluxed for 20 h. After removal of the solvent, the residue was treated with water and then extracted with EtOAc. The organic layers were dried over Na₂SO₄ and evaporated. The residue was chromotographed on silica gel using hexane/ethyl acetate (2/1) to give 3-trifluoromethyl-1,5-dimethyl-1,2,4-triazole (3) (0.29 g, 88% yield, oil): Rf 0.80 (hexane/ethyl acetate 2:1); IR (NaCl) 2960, 1525, 1475, 1420, 1375, 1180, 1139, 1037, 1001, 781, 659 cm⁻¹; ¹H NMR δ 2.53 (s, 3H), 3.94 (s, 3H); ¹³C NMR δ 155.69, 152.25 (q, $J_{\rm C-C-F}$ = 38.25 Hz), 120.68 (q, $J_{\rm C-F}$ = 266.25 Hz), 36.11, 11.70; ¹⁹F NMR δ -65.85 (s, 3F); GC-MS (EI) m/z 165 (M⁺, 100), 146 (13), 124 (78), 96 (20), 69 (19), 42 (21). Anal. Calcd for C₅H₆F₃N₃: C, 36.37; H, 3.66. Found: C, 36.54; H, 3.80.

1-(3-Fluoropropyl)-3-trifluoromethyl-5-methyl-1,2,4-triazole (4). Compound **1** (0.30 g, 2 mmol) and 1-bromo-3fluoropropane (0.28 g, 2 mmol) gave **4** (0.35 g, 84.1% yield, colorless oil): R_f 0.78 (hexane/ethyl acetate 2:1); IR (NaCl) 2977, 2398, 2280, 1522, 1470, 1426, 1388, 1190, 1140, 1038, 1005, 933, 765, 647 cm⁻¹; ¹H NMR δ 2.22–2.39 (m, 2H), 2.53 (s, 3H), 4.39 (t, 2H, J = 9.0 Hz), 4.76 (dt, 2H, J = 48.02 Hz, J = 6.0 Hz); ¹³C NMR δ 155.68, 152.75 (q, J_{C-C-F} = 38.48 Hz), 120.65 (q, J_{C-F} = 268.67 Hz), 81.55 (d, J_{C-F} = 163.77 Hz), 45.84, 30.78 (d, J_{C-C-F} = 20.37 Hz), 11.70; ¹⁹F NMR δ -65.90 (s, 3F), -223.03 (tt, 1F, J = 48.0 Hz, J = 25.41 Hz); GC–MS (EI) m/z 211 (M⁺, 10), 192 (11), 165 (31), 142 (91), 123 (19), 100 (61), 69 (14), 58 (15), 40 (100). Anal. Calcd for C₇H₉F₄H₃: C, 39.82; H, 4.30. Found: 39.46; H, 4.32.

3-Perfluorooctyl-1,5-dimethyl-1,2,4-triazole (5). Compound **2** (1.0 g, 2 mmol) gave **5** (0.84 g, 81.6% yield, white solid): R_f 0.59 (hexane/ethyl acetate 2:1); mp 60 °C; IR (KBr) 3414, 2910, 1715, 1458, 1366, 1197, 1148, 1037, 942, 656 cm⁻¹; ¹H NMR δ 2.53 (s, 3H), 3.97 (s, 3H); ¹³C NMR δ 155.88, 151.50 (t, $J_{C-C-F} = 27.67$ Hz), 119.08–110.70 (m), 36.21, 11.69; ¹⁹F NMR δ -76.96 (tt, 3F, J = 10.17 Hz, J = 2.26 Hz), -107.65- -122.03 (m, 14F); GC–MS (EI) m/z 515 (M⁺, 2), 496 (6), 169 (2), 146 (100),

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10 5(16), 69 (8), 56 (3), 40 (23). Anal. Calcd for $C_{12}H_6F_{17}N_3:\ C,$ 27.98; H, 1.17. Found: C, 28.02; H, 1.22.

General Procedure for Preparation of 6–8. 1,4,5-Trimethyl-3-trifluoromethyl-1,2,4-triazolium Iodide (6). Compound 3 (0.20 g, 1.21 mmol) and iodomethane (0.17 g, 1.21 mmol) were placed into a Pyrex glass tube that was evacuated, sealed, and heated at 80 °C for 24 h. The brown residue was dissolved in methylene chloride and recrystallized (EtOAc–hexane) to give a white solid (0.36 g, 98% yield): mp 165 °C; IR (KBr) 3006, 2282, 1568, 1527, 1454, 1373, 1278, 1191, 1167, 1107, 1032, 812, 747 cm⁻¹; ¹H NMR δ 3.14 (s, 3H), 4.17 (s, 3H), 4.28 (s, 3H); ¹³C NMR δ 157.68, 143.38 (q, $J_{C-C-F} = 40.0$ Hz), 117.70 (q, $J_{C-F} = 270.0$ Hz), 39.95, 35.33, 13.15; ¹⁹F NMR δ –64.56 (s, 3F); MS (solid probe) (EI) m/z 180 (M⁺, 100). Anal. Calcd for C₆H₉F₃N₃I: C, 23.47; H, 2.95. Found: C, 23.46; H, 2.91.

1-(3-Fluoropropyl)-3-trifluoromethyl-4,5-dimethyl-1,2,4-triazolium Iodide (7). After reaction at 100 °C for 5 days, **4** (0.26 g, 1.21 mmol) and CH₃I (0.17 g, 1.21 mmol) gave **7** (0.048 g, 11.2% yield, white solid): mp 115 °C; IR (KBr) 3468, 2974, 1560, 1520, 1415, 1209, 1167, 1105, 1032, 925, 739 cm⁻¹; ¹H NMR δ 2.42–2.56 (m, 2H), 3.16 (s, 3H), 4.16 (s, 3H), 4.69 (dt, 2H, J = 45.02 Hz, J = 60 Hz); 4.76 (t, 2H, J = 90 Hz); ¹³C NMR δ 157.64, 143.93 (q, $J_{C-C-F} = 42.76$ Hz), 117.63 (q, $J_{C-F} = 271.64$ Hz), 81.37 (d, $J_{C-F} = 163.49$ Hz), 49.22, 35.15, 29.78 (d, $J_{C-C-F} = 20.12$ Hz), 12.27; ¹⁹F NMR δ –59.81 (s, 3F), –218.74 (tt, 1F, J = 48.1 Hz, J = 25.4 Hz); MS (solid probe) (EI) *mlz* 226 (M⁺, 100). Anal. Calcd for C₈H₁₂F₄N₃I: C, 27.21; H, 3.43. Found: C, 27.38; H, 3.34.

1,4,5-Trimethyl-3-perfluorooctyl-1,2,4-triazolium Iodide (8). After reaction at 100 °C for 7 days, **5** (0.62 g, 1.21 mmol) and CH₃I (0.17 g, 1.21 mmol) gave **8** (0.16 g, 20% yield, white solid): mp 211 °C; IR (KBr) 3590, 3003, 2144, 1713, 1420, 1361, 1221, 1153, 1092, 903 cm⁻¹; ¹H NMR (DMSO- d_{θ}) δ 2.82 (s, 3H), 3.90 (s, 3H), 4.12 (s, 3H); ¹³C NMR (DMSO- d_{θ}) δ 157.45, 141.48 (t, $J_{C-C-F} = 30.18$ Hz), 118.32–108.70 (m), 39.05, 35.55, 11.41; ¹⁹F NMR (DMSO- d_{θ}) δ –75.89 (tt, 3F, J = 10.17 Hz, J = 2.26 Hz), -105.69 to -121.42 (m, 14F); MS (solid probe) (EI) *m*/*z* 530 (M⁺, 100). Anal. Calcd for C₁₃H₉F₁₇N₃I: C, 23.76; H, 1.38. Found: C, 23.57; H, 1.44.

General Procedure for Preparation of Ionic Salts 9a–d, 10, 11a–c. 1,4,5-Trimethyl-3-trifluoromethyl-1,2,4-triazolium Bis(trifluoromethanesulfonyl)amide (9a). To a magnetically stirred solution of 6 (0.15 g, 0.5 mmol) in water (3 mL) was added lithium bis(trifluoromethanesulfonyl)amide (LiNTf₂, 0.14 g, 0.5 mmol). After 2 h at 40 °C, the salt was separated and washed with water, and the residue was dried in vacuo to give 9a (0.22 g, 96% yield, white solid): mp 70 °C; IR (KBr) 2397, 2278, 1570, 1521, 1354, 1277, 1196, 1161, 1052, 1107, 795, 741, 618 cm⁻¹; ¹H NMR δ 3.11 (s, 3H), 4.20 (s, 3H), 4.32 (s, 3H); ¹³C NMR δ 157.44, 143.73 (q, $J_{C-C-F} = 42.5$ Hz), 120.82 (q, $J_{C-F} = 320.0$ Hz), 117.59 (q, $J_{C-F} = 271.62$ Hz), 39.23, 34.46, 10.31; ¹⁹F NMR δ –64.71 (s, 3F); –79.92 (s, 6F); MS (solid probe) (EI) *m*/z 180 (M⁺, 100). Anal. Calcd for C₈H₉F₉N₄S₂O₄: C, 20.87; H, 1.97. Found: C, 20.71; H, 2.07.

1,4,5-Trimethyl-3-trifluoromethyl-1,2,4-triazolium Trifluoromethanesulfonate (9b). Compound **6** (0.15 g, 0.5 mmol) and KSO₃CF₃ (0.094 g, 0.5 mmol) gave **9b** (0.16 g, 97% yield, white solid): mp 137 °C; IR (KBr) 2350, 1560, 1523, 1266, 1160, 1032, 743, 639 cm⁻¹; ¹H NMR δ 3.07 (s, 3H), 4.16 (s, 3H), 4.29 (s, 3H); ¹³C NMR δ 157.31, 143.49 (q, J_{C-C-F} = 42.76 Hz), 122.04 (q, J_{C-F} = 321.92 Hz), 117.65 (q, J_{C-F} = 271.62 Hz), 39.19, 34.48, 10.77; ¹⁹F NMR δ -59.97 (s, 3F), -74.35 (s, 3F); MS (solid probe) (E1) *m/z* 180 (M⁺, 100).

1,4,5-Trimethyl-3-trifluoromethyl-1,2,4-triazolium Perchlorate (9c). Compound **6** (0.15 g, 0.5 mmol) and AgClO₄ (0.10 g, 0.5 mmol) gave **9c** (0.14 g, 98% yield, white solid): mp 128 °C; IR (KBr) 2355, 1571, 1524, 1351, 1276, 1195, 1094, 810, 742, 623 cm⁻¹; ¹H NMR δ 3.01 (s, 3H), 4.11 (s, 3H), 4.23 (s, 3H); ¹CNMR δ 157.46, 143.44 (q, $J_{C-C-F} = 42.26$ Hz), 117.69 (q, $J_{C-F} = 270.94$ Hz), 39.08, 34.37, 10.53; ¹⁹F NMR δ -64.65 (s, 3F); MS (solid probe) (EI) m/z 180 (M⁺, 100). Anal. Calcd for C₆H₉F₃N₃-ClO₄: C, 25.80; H, 3.25. Found: C, 25.76; H, 3.42.

1,4,5-Trimethyl-3-trifluoromethyl-1,2,4-triazolium Tetrafluoroborate (9d). Compound 6 (0.15 g, 0.5 mmol) and AgBF₄ (0.10 g, 0.5 mmol) gave **9d** (0.13 g, 98% yield, white solid): mp 130 °C; IR (KBr) 3645, 2413, 2278, 1573, 1525, 1277, 1171, 1105, 1058, 810, 743 cm⁻¹; ¹H NMR δ 3.01 (s, 3H), 4.13 (s, 3H), 4.26 (s, 3H); ¹³C NMR δ 157.44, 143.55 (q, $J_{C-C-F} = 42.26$ Hz), 117.70 (q, $J_{C-F} = 270.94$ Hz), 38.99, 34.24, 10.18; ¹⁹F NMR δ -64.71 (s, 3F), -153.11 (s, 4F); MS (solid probe) (EI) *m*/*z* 180 (M⁺, 100). Anal. Calcd for C₆H₉F₇N₃B: C, 27.00; H, 3.40. Found: C, 27.55; H, 3.51.

1-(3-Fluoropropyl)-3-trifluoromethyl-4,5-dimethyl-1,2,4-triazolium Bis(trifluoromethanesulfonyl)amide (10). Compound 7 (0.18 g, 0.5 mmol) and LiNTf₂ (0.14 g, 0.5 mmol) gave **10** (0.25 g, 98% yield, white solid): mp 49 °C; IR (KBr) 2984, 2390, 1560, 1520, 1353, 1195, 1139, 1106, 930, 791, 741, 618 cm⁻¹; ¹H NMR δ 2.36–2.61 (m, 2H), 3.15 (s, 3H), 4.20 (s, 3H), 4.64 (dt, 2H, J = 48.02 Hz, J = 6.0 Hz), 4.80 (t, 2H, J = 6.0 Hz); ¹³C NMR δ 157.52, 144.20 (q, J_{C-C-F} = 42.26 Hz), 120.94 (q, J_{C-F} = 321.50 Hz), 117.61 (q, J_{C-F} = 271.69 Hz), 81.11 (d, J_{C-F} = 161.51 Hz), 49.16, 34.50, 29.83 (d, J_{C-C-F} = 20.38 Hz), 10.33; ¹⁹F NMR δ –64.74 (s, 3F), –79.95 (s, 6F), –223.49 (tt, 1F, J = 48.01 Hz, J = 25.42 Hz); MS (solid probe) (EI) m/z 226 (M⁺, 100). Anal. Calcd for C₁₀H₁₂F₁₀N₄S₂O₄: C, 23.71; H, 2.39. Found: C, 23.38; H, 2.38.

1,4,5-Trimethyl-3-perfluorooctyl-1,2,4-triazolium Bis-(**trifluoromethanesulfonyl)amide (11a).** Compound **8** (0.33 g, 0.5 mmol) and LiNTf₂ (0,14 g, 0.5 mmol) gave **11a** (0.40 g, 98% yield, white solid): mp 81 °C; IR (KBr) 2 950, 1708, 1557, 1509, 1445, 1352, 1200, 1145, 1055, 953, 864, 788, 736, 654 cm⁻¹; ¹H NMR δ 3.12 (s, 3H), 4.23 (s, 3H), 4.36 (s, 3H); ¹³C NMR δ 158.05, 142.67 (q, $J_{C-C-F} = 30.94$ Hz), 120.94 (q, $J_{C-F} = 321.50$ Hz), 120.25–108.16 (m), 39.48, 35.23, 10.62; ¹⁹F NMR δ –79.91 (s, 6F), –81.59 (tt, 3F, J = 10.17 Hz, J = 2.26 Hz), -110.53 to –126.63 (m, 14F); MS (solid probe) (EI) m/z 530(M⁺, 100). Anal. Calcd for C₁₅H₉F₂₃N₄S₂O₄: C, 22.22; H, 1.12. Found: C, 22.73; H, 1.37.

1,4,5-Trimethyl-3-perfluorooctyl-1,2,4-triazolium Perchlorate (11b). Compound **8** (0.33 g, 0.5 mmol) and AgClO₄ (0.10 g, 0.5 mmol) gave **11b** (0.31 g, 98% yield, white solid): mp 90 °C; IR (KBr) 3528, 2254, 1702, 1425, 1248, 1088, 1034, 960, 625 cm⁻¹; ¹H NMR δ 3.07 (s, 3H), 4.18 (s, 3H), 4.31 (s, 3H); ¹³⁰ NMR δ 158.04, 142.65 (q, $J_{C-C-F} = 30.92$ Hz), 120.88 (q, $J_{C-F} = 321.50$ Hz), 120.21–108.14 (m), 39.35, 35.15, 10.64; ¹⁹F NMR δ -81.59 (tt, 3F, J = 10.17 Hz, J = 2.26 Hz), -110.76 to -126.73 (m, 14F); MS (solid probe) (EI) m/z 530 (M⁺, 100). Anal. Calcd for C₁₃H₉F₁₇N₃ClO₄: C, 24.80; H, 1.44. Found: C, 23.80; H, 1.81.

1,4,5-Trimethyl-3-perfluorooctyl-1,2,4-triazolium Tetrafluoroborate (11c). Compound **8** (0.33 g, 0.5 mmol) and AgBF₄ (0.10 g, 0.5 mmol) gave **11c** (0.30 g, 98% yield, white solid): mp 98 °C; IR (KBr) 3590, 1703, 1421, 1364, 1220, 1150, 1135, 530 cm⁻¹; ¹H NMR δ 3.06 (s, 3H), 4.17 (s, 3H), 4.31 (s, 3H); ¹³C NMR δ 158.05, 142.65 (q, $J_{C-C-F} = 30.90$ Hz), 120.91 (q, $J_{C-F} = 321.50$ Hz), 120.20–108.17 (m), 39.30, 35.06, 10.45; ¹⁹F NMR δ –81.58 (tt, 3F, J = 10.17 Hz, J = 2.26 Hz), -110.54 to -126.65 (m, 14F), -152.19 (s, 4F); MS (solid probe) (EI) *m*/*z* 530 (M⁺, 100).

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Supporting Information Available: Tables of data collection parameters, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and ORTEP drawing of **11c**, and general experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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