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

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Abstract: Syntheses of quaternary 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 $LiN(SO_2CF_3)_2$, KSO_3CF_3, $AgClO_4$, $AgBF_4$; 1-(3-fluoropropyl)-3-trifluoromethyl-4,5-dimethyl-1,2,4-triazolium iodide (**7**) with $LiN(SO_2CF_3)_2$; and 1,4,5-trimethyl-3-perfluorooctyl-1,2,4-triazolium iodide (**8**) with $LiN(SO_2CF_3)_2$, $AgClO_4$, $AgBF_4$ 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-1,2,4-triazoles 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)]-3-perfluoroalkyl-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, high-energy 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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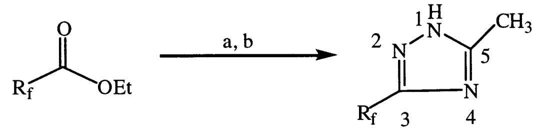
SCHEME 1

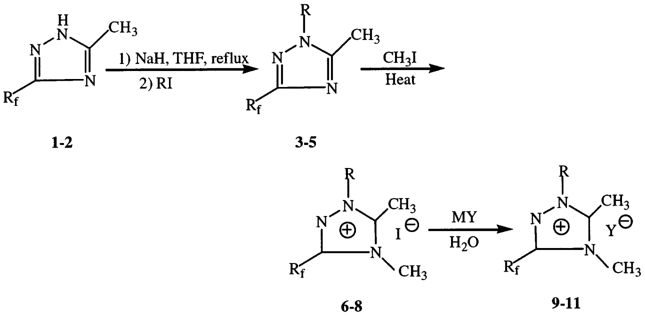


R_f = CF_3, C_8F_{17}

a $NH_2NH_2 \cdot H_2O$, THF, reflux

b $CH_3C(=NH)NH_2 \cdot HCl$, NaOH, THF, reflux

SCHEME 2



Compd	R_f	R	MY	T_m (°C)[a]	T_d (°C)[b]
1	CF_3	-	-	144	-
2	C_8F_{17}	-	-	125	-
3	CF_3	CH_3	-	-	-
4	CF_3	$CH_2CH_2CH_2F$	-	-	-
5	C_8F_{17}	CH_3	-	60	-
6	CF_3	CH_3	-	165	>450
7	CF_3	$CH_2CH_2CH_2F$	-	115	250
8	C_8F_{17}	CH_3	-	211	>450
9a	CF_3	CH_3	$LiNTf_2$	70	368
9b	CF_3	CH_3	KOTf	137	324
9c	CF_3	CH_3	$AgClO_4$	128	270
9d	CF_3	CH_3	$AgBF_4$	130	326
10	CF_3	$CH_2CH_2CH_2F$	$LiNTf_2$	49	323
11a	C_8F_{17}	CH_3	$LiNTf_2$	81	313
11b	C_8F_{17}	CH_3	$AgClO_4$	90	294
11c	C_8F_{17}	CH_3	$AgBF_4$	98	306

[a] Melting point. [b]Thermal 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 CH_3I or $CH_2FCH_2CH_2I$ (Scheme 2). 1,3,5-Substituted triazoles (**3**−**5**) were subsequently quaternized at N-4 by reaction with an equivalent amount of CH_3I under neat reaction conditions to produce salts **6**−**8** (Scheme 2). Single-crystal structure determinations of **9b** and **11c** clearly show methyl substitution at N-4; See crystal structure data.

TABLE 1. Miscibility of Various Ionic Salts in Organic Solvents[a] with Dielectric Constant ϵ[b]

compd	hexane	CH_2Cl_2	EtOAc	acetone	H_2O
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] m = miscible; nm = nonmiscible; pm = partially miscible. [b] Dielectric constant ϵ at 25 °C: hexane = 1.89/20 °C; CH_2Cl_2 = 8.93; EtOAc = 6.02; acetone = 20.7; H_2O = 78.54.

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 (NTf_2) 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 (BF_4), perchlorate (ClO_4), and NTf_2 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 C_8F_{17} at N-3 is greater than that for the analogous iodide **6** with CF_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** (CF_3/BF_4) 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*,*N*-dimethylformamide (DMF) and water (1:1). Invariably when NTf_2 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, C_8F_{17}.

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X-ray Crystal Structure of 11c. To confirm whether the alkylation occurred at N-2 or N-4 in **3**−**5**, a single-crystal 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 Database[11] [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 BF_4^- 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 NTf_2, 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 Kα 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 SMART[16] software and refined using SAINTPlus[17] 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 F^5 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.

Compounds **1** and **2** were prepared by a literature procedure of K. Funabiki.[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 $NaHCO_3$ solution (250 mL) and extracted with ethyl acetate (50 mL × 3). The extracts were dried with Na_2SO_4, 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}; ^1H NMR δ 2.52 (s, 3H), 11.30 (br, s, 1H); ^{13}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; ^{19}F NMR δ −65.90 (s, 3F); GC−MS (EI) *m/z* 151 (M^+, 54), 142 (6), 132 (17), 110 (14), 100 (4), 82 (5), 69 (30), 56 (19), 42 (100). Anal. Calcd for $C_4H_4F_3N_3$: 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); ^{13}C NMR δ 156.35, 153.62 (t, $J_{C-C-F} = 27.67$ Hz), 119.08−108.95 (m), 11.75; ^{19}F 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 $C_{11}H_4N_3F_{17}$: 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 CH_3I (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 Na_2SO_4 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): R_f 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); ^{13}C NMR δ 155.69, 152.25 (q, $J_{C-C-F} = 38.25$ Hz), 120.68 (q, $J_{C-F} = 266.25$ Hz), 36.11, 11.70; ^{19}F 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 $C_5H_6F_3N_3$: 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-3-fluoropropane (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); ^{13}C 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; ^{19}F 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 $C_7H_9F_4H_3$: 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); ^{13}C NMR δ 155.88, 151.50 (t, $J_{C-C-F} = 27.67$ Hz), 119.08−110.70 (m), 36.21, 11.69; ^{19}F 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}; ^{1}H NMR δ 3.14 (s, 3H), 4.17 (s, 3H), 4.28 (s, 3H); ^{13}C 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; ^{19}F NMR δ −64.56 (s, 3F); MS (solid probe) (EI) *m/z* 180 (M$^+$, 100). Anal. Calcd for $C_6H_9F_3N_3I$: 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 CH_3I (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}; ^{1}H NMR δ 2.42−2.56 (m, 2H), 3.16 (s, 3H), 4.16 (s, 3H), 4.69 (dt, 2H, $J = 45.02$ Hz, $J = 6.0$ Hz); 4.76 (t, 2H, $J = 9.0$ Hz); ^{13}C 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; ^{19}F NMR δ −59.81 (s, 3F), −218.74 (tt, 1F, $J = 48.1$ Hz, $J = 25.4$ Hz); MS (solid probe) (EI) *m/z* 226 (M$^+$, 100). Anal. Calcd for $C_8H_{12}F_4N_3I$: 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 CH_3I (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}; ^{1}H NMR (DMSO-d_6) δ 2.82 (s, 3H), 3.90 (s, 3H), 4.12 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 157.45, 141.48 (t, $J_{C-C-F} = 30.18$ Hz), 118.32−108.70 (m), 39.05, 35.55, 11.41; ^{19}F NMR (DMSO-d_6) 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 $C_{13}H_9F_{17}N_3I$: 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 ($LiNTf_2$, 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}; ^{1}H NMR δ 3.11 (s, 3H), 4.20 (s, 3H), 4.32 (s, 3H); ^{13}C 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; ^{19}F NMR δ −64.71 (s, 3F); −79.92 (s, 6F); MS (solid probe) (EI) *m/z* 180 (M$^+$, 100). Anal. Calcd for $C_8H_9F_9N_4S_2O_4$: 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 KSO_3CF_3 (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}; ^{1}H NMR δ 3.07 (s, 3H), 4.16 (s, 3H), 4.29 (s, 3H); ^{13}C 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; ^{19}F NMR δ −59.97 (s, 3F), −74.35 (s, 3F); MS (solid probe) (EI) *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 $AgClO_4$ (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}; ^{1}H NMR δ 3.01 (s, 3H), 4.11 (s, 3H), 4.23 (s, 3H); ^{13}C NMR 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; ^{19}F NMR δ −64.65 (s, 3F); MS (solid probe) (EI) *m/z* 180 (M$^+$, 100). Anal. Calcd for $C_6H_9F_3N_3$-ClO_4: 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 $AgBF_4$ (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}; ^{1}H NMR δ 3.01 (s, 3H), 4.13 (s, 3H), 4.26 (s, 3H); ^{13}C 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; ^{19}F NMR δ −64.71 (s, 3F), −153.11 (s, 4F); MS (solid probe) (EI) *m/z* 180 (M$^+$, 100). Anal. Calcd for $C_6H_9F_7N_3B$: 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 $LiNTf_2$ (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}; ^{1}H 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); ^{13}C 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; ^{19}F 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 $C_{10}H_{12}F_{10}N_4S_2O_4$: 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 $LiNTf_2$ (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}; ^{1}H NMR δ 3.12 (s, 3H), 4.23 (s, 3H), 4.36 (s, 3H); ^{13}C 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; ^{19}F 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 $C_{15}H_9F_{23}N_4S_2O_4$: 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 $AgClO_4$ (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}; ^{1}H NMR δ 3.07 (s, 3H), 4.18 (s, 3H), 4.31 (s, 3H); ^{13}C 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; ^{19}F 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 $C_{13}H_9F_{17}N_3ClO_4$: 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 $AgBF_4$ (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}; ^{1}H NMR δ 3.06 (s, 3H), 4.17 (s, 3H), 4.31 (s, 3H); ^{13}C 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; ^{19}F 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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