Supplementary Materials

Belonging to the manuscript

Syntheses of 1-Alkyl-1,2,4-Triazoles and the Formation of Quaternary 1-Alkyl-4-Polyfluoroalkyl-1,2,4-Triazolium Salts Leading to Ionic Liquids

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Table 1. Crystal data and structure refinement for 1-Me-4 -CH₂CH₂CF₃-triazolium iodide.

Identification code	4a	
Empirical formula	C ₆ H ₉ F ₃ I N ₃	
Formula weight	307.06	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pccn	
Unit cell dimensions	a = 13.8289(9) Å	α = 90°.
	b = 17.3603(11) Å	β = 90°.
	c = 9.0587(6) Å	γ = 90°.
Volume	2174.8(2) Å ³	
Z	8	
Density (calculated)	1.876 Mg/m ³	
Absorption coefficient	2.949 mm ⁻¹	
F(000)	1168	
Crystal size	0.39 x 0.05 x 0.04 mm ³	
Crystal color and habit	colorless needle	
Diffractometer	Bruker SMART APEX	
Theta range for data collection	1.88 to 30.01°.	
Index ranges	-18 ≤ h ≤ 18, -24 ≤ k ≤ 23, -10 ≤ l ≤ 12	
Reflections collected	19067	
Independent reflections	3040 [R(int) = 0.0505]	
Completeness to theta = 30.01°	95.3 %	
Absorption correction	†Empirical	
Max. and min. transmission	0.8911 and 0.3925	
Solution method	SHELXS-97 (Sheldrick, 1990)	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3040 / 0 / 119	
Goodness-of-fit on F ²	1.130	
Final R indices [I > 2σ(I)]	R1 = 0.0484, wR2 = 0.0867	
R indices (all data)	R1 = 0.0725, wR2 = 0.0936	
Largest diff. peak and hole	0.762 and -1.099 e.Å ⁻³	

†**SADABS**: an empirical absorption correction program, Saint+ 6.22, Bruker AXS Inc., Madison, WI, 2001.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
I(1)	3722(1)	6142(1)	6939(1)	33(1)
C(1)	3526(3)	4144(3)	3976(6)	46(1)
C(2)	3763(3)	5482(3)	3031(5)	33(1)
C(3)	3782(3)	5210(2)	725(5)	37(1)
C(4)	3944(3)	6635(2)	1380(6)	38(1)
C(5)	4912(3)	6860(2)	762(5)	32(1)
C(6)	5740(3)	6757(2)	1787(5)	39(1)
F(1)	6545(2)	7078(2)	1240(4)	65(1)
F(2)	5959(2)	6005(2)	2034(3)	48(1)
F(3)	5582(3)	7057(2)	3121(3)	74(1)
N(1)	3644(2)	4740(2)	2844(4)	32(1)
N(2)	3651(3)	4549(2)	1381(4)	36(1)
N(3)	3866(2)	5794(2)	1711(4)	30(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **4a**.

C(1)-N(1)	1.465(6)	N(3)-C(4)-H(4A)	109.0
C(1)-H(1A)	0.9700	C(5)-C(4)-H(4A)	109.0
C(1)-H(1B)	0.9700	N(3)-C(4)-H(4B)	109.0
C(1)-H(1C)	0.9700	C(5)-C(4)-H(4B)	109.0
C(2)-N(1)	1.310(6)	H(4A)-C(4)-H(4B)	107.8
C(2)-N(3)	1.321(5)	C(6)-C(5)-C(4)	115.0(4)
C(2)-H(2A)	0.9400	C(6)-C(5)-H(5A)	108.5
C(3)-N(2)	1.305(6)	C(4)-C(5)-H(5A)	108.5
C(3)-N(3)	1.356(5)	C(6)-C(5)-H(5B)	108.5
C(3)-H(3A)	0.9400	C(4)-C(5)-H(5B)	108.5
C(4)-N(3)	1.495(5)	H(5A)-C(5)-H(5B)	107.5
C(4)-C(5)	1.503(6)	F(3)-C(6)-F(1)	108.0(4)
C(4)-H(4A)	0.9800	F(3)-C(6)-F(2)	105.3(4)
C(4)-H(4B)	0.9800	F(1)-C(6)-F(2)	106.0(4)
C(5)-C(6)	1.485(6)	F(3)-C(6)-C(5)	113.1(4)
C(5)-H(5A)	0.9800	F(1)-C(6)-C(5)	111.0(4)
C(5)-H(5B)	0.9800	F(2)-C(6)-C(5)	112.9(4)
C(6)-F(3)	1.334(5)	C(2)-N(1)-N(2)	111.3(4)
C(6)-F(1)	1.339(5)	C(2)-N(1)-C(1)	128.2(4)
C(6)-F(2)	1.359(5)	N(2)-N(1)-C(1)	120.6(4)
N(1)-N(2)	1.367(5)	C(3)-N(2)-N(1)	103.2(3)
		C(2)-N(3)-C(3)	106.3(3)
N(1)-C(1)-H(1A)	109.5	C(2)-N(3)-C(4)	126.2(4)
N(1)-C(1)-H(1B)	109.5	C(3)-N(3)-C(4)	127.2(4)
H(1A)-C(1)-H(1B)	109.5		
N(1)-C(1)-H(1C)	109.5		
H(1A)-C(1)-H(1C)	109.5		
H(1B)-C(1)-H(1C)	109.5		
N(1)-C(2)-N(3)	107.5(4)		
N(1)-C(2)-H(2A)	126.3		
N(3)-C(2)-H(2A)	126.3		
N(2)-C(3)-N(3)	111.7(4)		
N(2)-C(3)-H(3A)	124.1		
N(3)-C(3)-H(3A)	124.1		
N(3)-C(4)-C(5)	113.1(3)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	35(1)	38(1)	27(1)	1(1)	-2(1)	-4(1)
C(1)	42(3)	48(3)	46(3)	22(2)	8(2)	0(2)
C(2)	32(2)	39(2)	28(2)	-7(2)	-1(2)	-1(2)
C(3)	44(2)	37(2)	28(2)	-6(2)	-2(2)	1(2)
C(4)	38(2)	26(2)	51(3)	2(2)	8(2)	-2(2)
C(5)	39(2)	24(2)	34(2)	2(2)	4(2)	-2(2)
C(6)	40(2)	30(2)	46(3)	-7(2)	4(2)	-1(2)
F(1)	37(2)	49(2)	111(3)	9(2)	2(2)	-10(1)
F(2)	46(2)	34(1)	64(2)	7(1)	-5(1)	4(1)
F(3)	85(2)	88(2)	50(2)	-39(2)	-22(2)	30(2)
N(1)	28(2)	37(2)	32(2)	3(2)	1(2)	-1(2)
N(2)	41(2)	35(2)	33(2)	-5(2)	-2(2)	-2(2)
N(3)	33(2)	24(2)	32(2)	0(1)	2(2)	1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **4a**.

	x	y	z	U(eq)
H(1A)	2921	3874	3816	69
H(1B)	3520	4383	4945	69
H(1C)	4059	3783	3916	69
H(2A)	3774	5744	3939	40
H(3A)	3813	5274	-304	44
H(4A)	3828	6927	2288	46
H(4B)	3440	6776	669	46
H(5A)	5033	6554	-128	39
H(5B)	4885	7402	464	39

Figure 1. ORTEP drawing of **4a**

B. Experimental Data for Compounds 3a-c, 4b-f, 4k-m, 5a, c,d, f-i, l,m, o, q, s.

1-Methyl-1,2,4-triazole (3a): (4.80 g; 86% yield) colorless oil (bp 38-39 °C, 0.27-0.28 Torr, bath temperature 80 °C, lit.¹² bp 177 °C); $d_{240C} = 1.150 \text{ g/cm}^3$; IR (neat) 311, 2921, 2880, 1648, 1509, 1270, 1011 cm^{-1} ; ^1H NMR (500 MHz, D_2O) δ 3.72 (s, 3H), 7.75 (s, 1H), 8.15 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 151.86, 142.78, 39.77; GC-MS (CI) m/z (%) 85 ($\text{M}^+ + 1 + \text{H}$, 57), 84 ($\text{M}^+ + \text{H}$, 100).

1-Butyl-1,2,4-triazole (3b): (11.81 g; 86% yield) colorless oil (bp 46-48 °C, 0.26-0.27 Torr, bath temperature 80 °C); $d_{240C} = 1.006 \text{ g/cm}^3$; IR (neat) 3112, 2918, 2875, 1748, 1645, 1506, 1273, 1209, 1141, 1015, 873 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.89 (t, $J = 7.39 \text{ Hz}$, 3H), 1.25 (m, $J = 7.28 \text{ Hz}$, 2H), 1.80 (m, $J = 7.13 \text{ Hz}$, 2H), 4.10 (t, $J = 7.03 \text{ Hz}$, 2H), 7.87 (s, 1H, H-3), 7.99 (s, 1H, H-5); ^{13}C NMR (125 MHz, CDCl_3) δ 151.83, 142.77, 49.39, 31.73, 19.63, 13.42; GC-MS (CI) m/z (%) 126 ($\text{M}^+ + \text{H}$, 100), 125 (M^+ , 4). Anal Calcd for $\text{C}_6\text{H}_{11}\text{N}_3$: C, 57.57; H, 8.86. Found: C, 57.42; H, 8.68.

1-Heptyl-1,2,4-triazole (3c): (14.17 g; 84% yield) colorless oil (bp 89-90 °C, 0.38 Torr, bath temperature 120 °C); $d_{240C} = 0.980 \text{ g/cm}^3$; IR (neat) 3113, 2928, 2857, 1744, 1655, 1507, 1272, 1010 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.81 (t, $J = 6.89 \text{ Hz}$, 3H), 1.22 (m, $J = 5.70 \text{ Hz}$, 8H), 1.81 (p, $J = 7.35 \text{ Hz}$, 2H), 4.09 (t, $J = 7.13 \text{ Hz}$, 2H), 7.87 (s, 1H, H-3), 7.99 (s, 1H, H-5); ^{13}C NMR (125 MHz, CDCl_3) δ 151.87, 142.78, 49.73, 31.56, 29.78, 28.66, 26.41, 22.51, 14.00; GC-MS (CI) m/z (%) 169 ($\text{M}^+ + \text{H} + 1$, 12), 168 ($\text{M}^+ + 1$, 100). Anal Calcd for $\text{C}_9\text{H}_{17}\text{N}_3$: C, 64.63; H, 10.25; N, 25.12. Found: C, 64.32; H, 10.24; N, 25.34.

1-Butyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium iodide (4b): (1.09 g, 97% yield) tan solid, mp 123 °C; IR (KBr) 3106, 3026, 2969, 2880, 2824, 1779, 1579, 1528, 1466, 1443, 1418, 1389, 1335, 1256, 1226 1155, 1077, 1002, 857 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.96 (t, $J = 7.43 \text{ Hz}$, 3H), 1.43 (m, $J = 7.39 \text{ Hz}$, 2H), 2.02 (m, $J = 7.58 \text{ Hz}$, 2H), 3.30 (m, $J = 7.43 \text{ Hz}$, 2H), 4.59 (t, $J_{\text{HH}} = 7.17 \text{ Hz}$, 2H), 4.96 (t, $J_{\text{HH}} = 7.18 \text{ Hz}$, 2H), 9.45 (s, 1H), 11.00 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ

144.82, 143.28, 125.95 (q, $J_{\text{C-F}} = 276$ Hz), 52.36, 41.82, 33.57 (q, $J_{\text{C-C-F}} = 29.42$ Hz), 30.35, 19.07, 12.83; ^{19}F NMR (470 MHz, acetone- d_6) δ -66.09 (m, $J_{\text{H-F}} = 10.35$ Hz, $J_{\text{H-H-F}} = 4.23$, 3F); MS (solid probe) (EI) m/z (%) 222 (M^+ , 100). Anal Calcd for $\text{C}_9\text{H}_{15}\text{F}_3\text{I}_1\text{N}_3$: C, 30.96; H, 4.33; F, 16.32; N, 12.04. Found: C, 31.01; H, 4.20; F, 16.03; N, 12.08.

1-Heptyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium iodide (4c): (1.11 g, 92% yield) white solid, mp 174 °C; IR (KBr) 3124, 3028, 2932, 2860, 1578, 1505, 1462, 1256, 1154, 999 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.87 (t, $J = 7.09$ Hz, 3H), 1.29 (m, $J = 3.88$ Hz, 4H), 1.39 (m, $J = 6.53$ Hz, 4H), 2.00 (m, 2H), 3.28 (m, $J = 6.94$ Hz, 2H), 4.59 (t, $J_{\text{HH}} = 7.23$ Hz, 2H), 4.96 (t, $J_{\text{HH}} = 7.14$ Hz, 2H), 9.43 (s, 1H), 11.00 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 144.81, 143.27, 126.65 (q, $J_{\text{CF}} = 277$ Hz), 52.62, 41.81, 33.57 (d, $J = 28.9$ Hz), 31.43, 28.47, 28.42, 25.80, 22.31, 13.44; ^{19}F NMR (470 MHz, acetone- d_6) δ -66.08 (m, $J_{\text{H-F}} = 10.81$ Hz, $J_{\text{H-H-F}} = 1.41$, 3F); MS (solid probe) (EI) m/z (%) 264, 166 ($\text{M}^+ - \text{CF}_3\text{CH}_2\text{CH}_2 - \text{H}$, 100). Anal Calcd for $\text{C}_{12}\text{H}_{21}\text{F}_3\text{I}_1\text{N}_3$: C, 36.84; H, 5.41; F, 14.57. Found: C, 36.54; H, 5.39; F, 14.42.

1-Decyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium iodide (4d): (0.93 g, 98% yield) tan solid, mp 192 °C; IR (KBr) 3109, 3038, 2959, 2926, 2859, 1580, 1531, 1468, 1387, 1257, 1220, 1152, 1075, 1001, 859 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.87 (t, $J = 7.09$ Hz, 3H), 1.29 (m, 8H), 1.42 (m, $J = 4.55$ Hz, 4H), 2.00 (m, 2H), 3.29 (m, $J = 7.19$ Hz, 2H), 4.59 (t, $J_{\text{HH}} = 7.24$ Hz, 2H), 4.96 (t, $J_{\text{HH}} = 7.16$ Hz, 2H), 9.45 (s, 1H), 11.00 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 144.81, 143.27, 125.96 (q, $J_{\text{C-F}} = 276$ Hz), 52.63, 41.83 (m), 33.67 (q, $J_{\text{C-C-F}} = 29.21$ Hz), 31.74, 29.34, 29.25, 29.15, 28.80, 28.42, 25.86, 22.45, 13.49; ^{19}F NMR (470 MHz, acetone- d_6) δ -66.07 (m, $J_{\text{H-F}} = 10.35$ Hz, $J_{\text{H-H-F}} = 1.88$, 3F); MS (solid probe) (EI) m/z 306 (M^+ , 100). Anal Calcd for $\text{C}_{15}\text{H}_{27}\text{F}_3\text{I}_1\text{N}_3$: C, 41.58; H, 6.28; N, 9.70; F, 13.15. Found: C, 41.27; H, 6.17; N, 9.69; F, 12.96.

1-Butyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium iodide (4e): (1.98 g, 99% yield) white solid, mp 277 °C; IR (KBr) 3060, 3018, 2971, 2881, 1697, 1636, 1578, 1466, 1225, 1136, 996, 881, 733 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆) δ 0.96 (t, *J* = 7.39 Hz, 3H), 1.43 (hext, *J* = 7.66, 2H), 1.99 (m, *J* = 7.39 Hz, 2H), 3.31 (m, *J* = 7.39 Hz, 2H), 4.59 (t, *J*_{HH} = 7.15 Hz, 2H), 5.05 (t, *J*_{HH} = 7.46 Hz, 2H), 9.45 (s, 1H), 10.96 (s, 1H); ¹³C NMR (125 MHz, acetone-d₆) δ 144.91, 143.34, 106.52-120.26 (m, *J*_{C-F} = 243, *J*_{C-C-F} = 32.79, *J*_{C-C-C-F} = 8.3 Hz), 52.35, 40.73 (t, *J* = 5.13 Hz), 30.74 (t, *J* = 21.23 Hz), 30.37, 19.07, 12.83; ¹⁹F NMR (470 MHz, acetone-d₆) δ -82.37 (tt, *J*_{H-F} = 9.88 Hz, *J*_{H-H-F} = 2.82, 3F), -114.86 (m, ³*J*_{H-F} = 14.12 Hz, 2F), -125.31 (s, 2F), -127.10 (m, ³*J*_{F-F} = 9.5 Hz, 4.76 Hz, 2F); MS (solid probe) (EI) *m/z* (%) 372 (M⁺, 100). Anal Calcd for C₁₂H₁₅F₉I₁N₃: C, 28.87; H, 3.03; N, 8.42; F, 34.25. Found: C, 28.91; H, 3.07; N, 8.46; F, 34.52.

1-Heptyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium iodide (4f): (1.60 g, 99% yield) tan solid, mp 270 °C; IR (KBr) 3108, 3024, 2962, 2934, 2861, 1576, 1530, 1462, 1417, 1382, 1356, 1233, 1172, 1136, 1061, 1013, 997, 881, 831, 738 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆) δ 0.87 (t, *J* = 7.00 Hz, 3H), 1.27-1.43 (m, *J* = 6.10, 4.25 Hz, 8H), 2.02 (m, *J* = 7.50, 3.85 Hz, 2H), 3.35 (m, *J* = 7.46 Hz, 2H), 4.58 (t, *J*_{H-H} = 7.20 Hz, 2H), 5.06 (t, *J*_{H-H} = 7.30 Hz, 2H), 9.57 (s, 1H), 11.05 (s, 1H); ¹³C NMR (125 MHz, acetone-d₆) δ 144.88, 143.45, 120.15-106.78 (m, *J*_{C-F} = 254.76, 84.51, 32.57 Hz), 52.64, 40.81 (t, *J* = 4.78 Hz), 31.44, 30.82 (t, *J*_{C-C-F} = 20.79 Hz), 28.48, 28.37; ¹⁹F NMR (470 MHz, acetone-d₆) δ -82.37 (tt, *J*_{H-F} = 9.41 Hz, *J*_{H-H-F} = 3.29, 3F), -114.82 (m, *J* = 9.41, 4.59 Hz, 2F), -125.34 (m, *J* = 4.59 Hz, 2F), -127.04 (m, ³*J*_{FF} = 9.42 Hz, 2F); MS (solid probe) (EI) *m/z* (%) 414 (M⁺, 100). Anal Calcd for C₁₅H₂₁F₉I₁N₃: C, 33.29; H, 3.91; N, 7.76; F, 31.59. Found: C, 33.19; H, 3.91; N, 7.79; F, 32.07.

1-Butyl-4-(1-fluoroethyl)-1,2,4-triazolium bromide (4k): (0.57 g, 87% yield) tan solid, mp 167 °C; IR (KBr) 3118, 3030, 2956, 2930, 2857, 1460, 1387, 1248, 1157, 1023, 866 cm⁻¹; ¹H NMR (500 MHz,

DMSO- d_6) δ 0.90 (t, J = 7.35 Hz, 3H), 1.31 (m, J = 7.55 Hz, 2H), 1.84 (m, J = 7.46 Hz, 2H), 3.33 (m, J = 15.30 Hz, 2H), 4.38 (t, J = 7.10 Hz, 2H), 4.84 (m, 2H), 9.20 (s, 1H), 10.20 (s, 1H); ^{13}C NMR (125 MHz, DMSO- d_6) δ 145.29, 143.39, 80.02 (d, $J_{\text{C-F}}$ = 169 Hz), 52.03, 47.04, 40.66, 30.46, 29.38, 19.23, 13.79; ^{19}F NMR (470 MHz, DMSO- d_6) δ -223.23 (tt, $J_{\text{H-F}}$ = 47.06, $J_{\text{H-F}}$ = 28.23, 1F); MS (solid probe) (EI) m/z (%) 172 (M^+ , 6), 170 ($\text{M}^+ - 2$, 68), 86 (100). Anal Calcd for $\text{C}_8\text{H}_{15}\text{Br}_1\text{F}_1\text{N}_3$: C, 38.11; H, 6.00. Found: C, 38.16; H, 5.68.

1-Heptyl-4-(1-fluoroethyl)-1,2,4-triazolium bromide (4l): (1.06 g; 97% yield) tan solid, mp 125 °C; IR (KBr) 3030, 2956, 2927, 2853, 1813, 1574, 1462, 1265, 1158, 1027 cm^{-1} ; ^1H NMR (500 MHz, DMSO- d_6) δ 0.84 (t, J = 6.8 Hz, 3H), 1.26 (m, J = 2.4 Hz, 8H), 1.84 (p, J = 4.3 Hz, 2H), 4.39 (t, J = 7.1 Hz, 2H), 4.63 (dt, J_{HH} = 4.5, J_{HF} = 23.4 Hz, 2H), 4.84 (dt, J_{HH} = 4.9 Hz, J_{HF} = 46.8 Hz, 2H), 9.22 (s, 1H), 10.16 (s, 1H); ^{13}C NMR (125 MHz, DMSO- d_6) δ 145.4, 143.3, 81.6 (d, J = 176 Hz), 52.3 (d, 24 Hz), 48.7 (d, 19.6 Hz), 31.4, 28.5, 28.4, 25.9, 22.3, 14.3; ^{19}F NMR (470 MHz, DMSO- d_6) δ -223 (tt, $J_{\text{H-F}}$ = 47.1, $J_{\text{H-F}}$ = 28.2, 1F); MS (solid probe) (EI) m/z (%) 214 (M^+ , 100). Anal Calcd for $\text{C}_{11}\text{H}_{21}\text{Br}_1\text{F}_1\text{N}_3$: C, 44.91; H, 7.19; F, 6.46. Found: C, 44.80; H, 7.07; F, 6.32.

1-Decyl-4-(1-fluoroethyl)-1,2,4-triazolium bromide (4m): (1.01 g, 96% yield) tan solid, mp 129 °C; IR (KBr) 3111, 3030, 2954, 2922, 2847, 1464, 1385, 1248, 1159, 1026, 864 cm^{-1} ; ^1H NMR (500 MHz, DMSO- d_6) δ 0.84 (t, J = 6.96 Hz, 3H), 1.25 (m, 14H), 1.84 (m, 2H), 4.38 (t, J = 7.2 Hz, 2H), 4.63 (dt, J_{HH} = 4.46, J_{HF} = 27.5 Hz, 2H), 4.84 (dt, J_{HH} = 4.47 Hz, J_{HF} = 46.7 Hz, 2H), 9.24 (s, 1H), 10.20 (s, 1H); ^{13}C NMR (125 MHz, DMSO- d_6) δ 145.45, 143.26, 81.70 (d, $J_{\text{C-F}}$ = 167 Hz), 52.3, 48.60 (d, $J_{\text{C-C-F}}$ = 19.24 Hz), 31.77, 29.38, 29.29, 29.17, 28.83, 28.55, 28.39, 25.90, 22.59, 14.46; ^{19}F NMR (470 MHz, DMSO- d_6) -223.23 (tt, $J_{\text{H-F}}$ = 47.06, $J_{\text{H-F}}$ = 28.23, 1F); MS (solid probe) (EI) m/z (%) 256 (M^+ , 46), 168 (HepTaz $^+$ -1, 100). Anal Calcd for $\text{C}_{14}\text{H}_{27}\text{Br}_1\text{F}_1\text{N}_3$: C, 50.00; H, 8.09; N, 12.50; F, 5.56. Found: C, 49.69; H, 7.95; N, 12.61; F, 5.11.

1-Methyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium bis(trifluoromethane- sulfonyl)amide (5a):

(0.16 g, 68% yield) colorless viscous oil, mp -58°C , $d_{240\text{C}} = 1.663$; IR (KBr): 3146, 3097, 2986, 1585, 1349, 1258, 1191, 1131, 1053, 883, 791 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 3.17 (m, $J = 3.43$ Hz, 2H), 4.30 (s, 3H), 4.93 (m, $J_{\text{HH}} = 7.06$ Hz, 4H), 9.24 (s, 1H), 10.16 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 144.9, 143.4, 122.91 (q, $J_{\text{C-F}} = 419$ Hz), 41.73 (q, $J_{\text{C-C-C-F}} = 4.17$ Hz), 38.97 (s, Me), 33.35 (q, $J_{\text{C-C-F}} = 29.5$ Hz); ^{19}F NMR (470 MHz, acetone- d_6) δ -66.34 (t, $J_{\text{H-F}} = 7.05$ Hz, 3F), -80.41 (s, 3F) MS (solid probe) (EI) m/z (%) 180 (M^+ , 100). Anal Calcd for $\text{C}_8\text{H}_9\text{F}_9\text{N}_4\text{O}_4\text{S}_2$: C, 20.87; H, 1.97; N, 12.17. Found: C, 20.73; H, 2.46; N, 12.15.

1-Heptyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium bis(trifluoromethane- sulfonyl)amide (5c):

(0.71 g, 98% yield) colorless oil, mp -67°C , $d_{240\text{C}} = 1.522 \text{ g/cm}^3$; IR (KBr): 3146, 3097, 2986, 1585, 1349, 1258, 1191, 1131, 1053, 883, 791 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.85 (t, $J = 7.15$ Hz, 3H), 1.28 (m, 4H), 1.37 (m, 4H), 1.99 (m, 2H), 3.17 (m, $J = 3.50$ Hz, 2H), 4.58 (t, $J = 7.21$ Hz, 2H), 4.90 (t, $J_{\text{HH}} = 7.09$ Hz, 2H), 9.24 (s, 1H), 10.17 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 144.99, 142.73, 125.87 (q, $J_{\text{CF}} = 276$ Hz), 120.11 (q, $J_{\text{CF}} = 321$ Hz), 52.72, 41.79 (q, $J_{\text{C-C-C-F}} = 3.97$ Hz), 33.31 (q, $J_{\text{C-C-F}} = 29.5$ Hz), 28.51, 28.41, 25.74, 25.73, 22.27, 13.82; ^{19}F NMR (500 MHz, acetone- d_6) δ -66.35 (t, $J_{\text{HF}} = 10.35$ Hz, 3F), -80.4 (d, $J = 1.88$ Hz, 3F); MS (solid probe) (EI) m/z (%) 264 (M^+ , 100). Anal Calcd for $\text{C}_{14}\text{H}_{21}\text{F}_9\text{N}_4\text{O}_4\text{S}_2$: C, 30.88; H, 3.89; N, 10.29; F, 31.4. Found: C, 30.99; H, 4.22; N, 10.39; F, 31.58.

1-Decyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium bis(trifluoromethane- sulfonyl)amide (5d):

(0.71 g, 98% yield) colorless oil, mp -67°C , $d_{240\text{C}} = 1.495 \text{ g/cm}^3$; IR (KBr): 3141, 3087, 2928, 2858, 1579, 1465, 1445, 1350, 1258, 1193, 1135, 1001, 959, 889, 791 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.87 (t, $J = 6.87$ Hz, 3H), 1.28 (m, 4H), 1.38 (m, 10H), 2.00 (m, 2H), 3.19 (m, 2H), 4.61 (t, $J = 7.11$ Hz, 2H), 4.92 (t, $J_{\text{H-H}} = 7.09$ Hz, 2H), 9.27 (s, 1H), 10.20 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ

145.05, 142.77, 125.00 (q, $J_{\text{C-F}} = 276$ Hz), 118.89 (q, $J_{\text{C-F}} = 321$ Hz), 52.76, 41.80 (q, $J_{\text{C-C-C-F}} = 3.72$ Hz), 33.31 (q, $J_{\text{C-C-F}} = 29.59$ Hz), 29.31, 29.21, 29.12, 28.76, 28.54, 25.80, 22.43, 13.46; ^{19}F NMR (500 MHz, acetone- d_6) δ -66.32 (t, $J_{\text{H-F}} = 10.35$ Hz, 3F), -80.4 (s, 3F); MS (solid probe) (EI) m/z (%) 306 (M^+ , 78). Anal Calcd for $\text{C}_{17}\text{H}_{27}\text{F}_9\text{N}_4\text{O}_4\text{S}_2$: C, 38.41; H, 4.64; N, 9.55; F, 29.15. Found: C, 35.08; H, 4.75; N, 9.90; F, 29.11.

1-Heptyl-4-(1H,1H,2H,2H-perfluorohexyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)amide (5f): (0.54 g, 96% yield) colorless wax, mp 55 °C; IR (KBr): 3142, 3089, 2933, 2864, 1580, 1470, 1350, 1227, 1199, 1138, 1059, 998, 883, 793, 742 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.87 (t, $J = 7.06$ Hz, 3H), 1.28 (m, 4H), 1.38 (m, 4H), 1.99 (m, 2H), 3.23 (m, $J = 11.75$ Hz, 2H), 4.62 (t, $J = 7.08$ Hz, 2H), 5.03 (t, $J_{\text{H-H}} = 5.78$ Hz, 2H), 9.31 (s, 1H), 10.25 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 145.16, 142.88, 100-125.87 (m), 52.75, 40.78 (d, $J_{\text{C-C-C-F}} = 4.65$ Hz), 31.45, 30.60 (t, $J_{\text{C-C-F}} = 20.14$ Hz), 28.56, 28.43, 25.76, 22.28, 13.38; ^{19}F NMR (470 MHz, acetone- d_6) δ -80.42 (m, $J_{\text{F-F}} = 4.71$ Hz, 3F), -82.38 (m, $J = 9.41$ Hz, 3F), -115.01 (t, $J = 22.15$ Hz, 2F), -125.47 (t, $J_{\text{F-F}} = 4.71$ Hz, 2F), -127.11 (t, $J_{\text{F-F}} = 4.71$ Hz, 2F); MS (solid probe) (EI) m/z (%) 414 (M^+ , 100). Anal Calcd for $\text{C}_{17}\text{H}_{21}\text{F}_{15}\text{N}_4\text{O}_4\text{S}_2$: C, 29.40; H, 3.05; N, 8.07; F, 41.03. Found: C, 29.25; H, 3.05; N, 8.07; F, 41.26.

1-Decyl-4-(1H,1H,2H,2H-perfluorohexyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)amide (5g): (0.53 g, 98% yield) colorless wax, mp 53 °C; IR (KBr): 3146, 3090, 2928, 2858, 1580, 1533, 1469, 1349, 1224, 1197, 1137, 1060, 997, 882, 792 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.87 (t, $J = 7.10$ Hz, 3H), 1.28-1.38 (m, 14H), 2.01 (m, 2H), 2.82 (m, 2H), 4.61 (t, $J = 7.20$ Hz, 2H), 5.03 (t, $J_{\text{H-H}} = 7.30$ Hz, 2H), 9.30 (s, 1H), 10.25 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 145.15, 142.87, 100-125.87 (m), 52.76, 40.74 (d, $J_{\text{C-C-C-F}} = 4.65$ Hz), 31.72, 30.59 (t, $J_{\text{C-C-F}} = 20.40$ Hz), 29.32, 29.23, 28.78, 28.56, 25.82, 22.43, 13.45; ^{19}F NMR (470 MHz, acetone- d_6) δ -80.42 (3F), -82.38 (tt, $J = 9.88, 5.17$ Hz, 3F), -115.01 (m, $J = 18.82, 4.71$ Hz, 2F), -125.47 (m, $J_{\text{F-F}} = 4.71$ Hz, 2F), -127.11 (m, $J_{\text{F-F}} = 9.40$,

4.71 Hz, 2F); MS (solid probe) (EI) m/z (%) 456 (M^+ , 100). Anal Calcd for $C_{20}H_{27}F_{15}N_4O_4S_2$: C, 32.61; H, 3.69; N, 7.61; F, 38.69. Found: C, 32.12; H, 3.59; N, 7.51; F, 38.60.

1-Methyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)amide

(5h): (0.34 g, 98% yield) colorless wax, mp 62 °C; IR (KBr): 3144, 3108, 3046, 3006, 2960, 2930, 2864, 1584, 1542, 1462, 1445, 1387, 1321, 1256, 1192, 1126, 1057, 848 cm^{-1} ; 1H NMR (500 MHz, acetone- d_6) δ 2.12 (sep, $J = 10.52, 7.92$ Hz, 2H), 4.31 (s, 3H), 5.03 (m, $J_{H-H} = 7.7$ Hz, 2H), 9.27 (s, 1H), 10.19 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 144.94, 143.44, 128.87 (q, $J_{C-F} = 302$ Hz), 119.97 (q, $J_{C-F} = 321.6$ Hz), 67.48, 52.72, 40.68 (t, $J_{C-C-C-F} = 5.13$ Hz), 38.95, 30.78 (t, $J_{C-C-F} = 20.93$ Hz); ^{19}F NMR (470 MHz, acetone- d_6) δ -80.48 (m, $J_{F-F} = 3.29$ Hz, 3F), -82.17 (m, $J = 7.52$ Hz, 3F), -114.75, -122.86, -123.89, -124.61, -127.24 (m, $J = 9.4$ Hz); MS (solid probe) (EI) m/z (%) 430 (M^+ , 100). Anal Calcd for $C_{13}H_9F_{19}N_4O_4S_2$: C, 21.98; H, 1.28; N, 7.89; F, 50.82. Found: C, 22.06; H, 1.60; N, 7.86; F, 50.77.

1-Butyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)amide

(5i): (0.23 g, 92% yield) colorless solid, mp 28 °C; IR (KBr): 3080, 2966, 2883, 1934, 1707, 1579, 1532, 1467, 1411, 1351, 1259, 1192, 1121, 879, 793, 701, 569 cm^{-1} ; 1H NMR (500 MHz, acetone- d_6) δ 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, $J_{H-H} = 7.2$ Hz, 2H), 5.02 (t, $J_{H-H} = 7.4$ Hz, 2H), 9.29 (s, 1H), 10.22 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 145.14, 142.87, 120.14 (q, $J_{C-F} = 321$ Hz), 114.0-116.0 (m), 52.47, 40.75 (t, $J_{C-C-C-F} = 5.16$ Hz), 30.60 (t, $J_{C-C-F} = 21.25$ Hz), 30.48, 19.01, 12.72; ^{19}F NMR (470 MHz, acetone- d_6) δ -80.48 (t, $J_{FF} = 4.71$ Hz, 3F), -82.15 (tt, $J = 10.35$ Hz, 2.8 Hz, 3F), -114.76 (m, $J_{F-F} = 4.71$ Hz, $J_{H-F} = 18.82$ Hz, 2F), -122.85 (m, $J_{F-F} = 4.71$ Hz, $J_{H-F} = 9.41$ Hz, 2F), -123.89, -124.53, -127.22 (m, $J = 9.4$ Hz); MS (solid probe) (EI) m/z (%) 472 (M^+ , 100). Anal Calcd for $C_{16}H_{15}F_{19}N_4O_4S_2$: C, 25.54; H, 2.01; N, 7.45; F, 47.97. Found: C, 25.71; H, 2.46; N, 7.50; F, 48.08.

1-Decyl-4-(1-fluoroethyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)amide (5l): (0.21 g, 91% yield) pale yellow oil, mp -62 °C, $d_{240C} = 1.366 \text{ g/cm}^3$; IR (KBr) 3140, 3084, 2961, 2927, 2857, 1576, 1582, 1531, 1466, 1447, 1412, 1350, 1260, 1193, 1134, 1057, 864 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.87 (t, $J = 7.10 \text{ Hz}$, 3H), 1.25-1.44 (m, 14H), 1.99 (m, 2H), 4.69 (t, $J = 7.23 \text{ Hz}$, 2H), 4.91-5.05 (m, 4H), 9.16 (s, 1H), 10.14 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 145.05, 143.76, 120.15 (q, $J_{\text{C-F}} = 321 \text{ Hz}$), 81.17 (d, $J_{\text{CF}} = 169 \text{ Hz}$), 52.85, 48.80 (d, $J_{\text{C-C-F}} = 19.50 \text{ Hz}$), 47.26, 31.72, 29.32, 29.22, 28.78, 28.57, 25.86, 22.44, 13.47; ^{19}F NMR (470 MHz, acetone- d_6) δ -80.37 (2CF_3), -224.78 (tt, $J_{\text{H-F}} = 47.06$, $J_{\text{H-F}} = 28.23$, 1F); MS (solid probe) (EI) m/z (%) 256 (M^+ , 8), 236 ($\text{M}^+ - \text{HF}$, 100). Anal Calcd for $\text{C}_{16}\text{H}_{27}\text{F}_7\text{N}_4\text{O}_4\text{S}_2$: C, 35.82; H, 5.07; N, 10.44. Found: C, 35.91; H, 5.11; N, 10.47.

1-Decyl-4-(1-fluoroethyl)-1,2,4-triazolium trifluoromethanesulfonate (5m): (0.16 g, 88% yield) colorless solid, mp 46 °C; IR (KBr) 3177, 3137, 3092, 2959, 2920, 2852, 1580, 1582, 1536, 1468, 1442, 1412, 1390, 1269, 1154, 1069, 1032, 997, 904, 858 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.86 (t, $J = 7.08 \text{ Hz}$, 3H), 1.29-1.43 (m, $J = 3.27 \text{ Hz}$, 16H), 4.57 (t, $J = 6.95 \text{ Hz}$, 2H), 4.87 (dt, $J_{\text{H-H}} = 3.08$, $J_{\text{H-F}} = 27.78$, 2H), 5.11 (dt, $J_{\text{H-H}} = 3.52$, $J_{\text{H-F}} = 46.85$, 2H), 9.15 (s, 1H), 10.11 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 144.96, 142.89, 117.41-125.08 (q, $J_{\text{C-F}} = 321.22 \text{ Hz}$, CF_3), 80.73 (d, $J_{\text{C-F}} = 168.35 \text{ Hz}$), 52.54, 48.65 (d, $J_{\text{C-C-F}} = 18.99 \text{ Hz}$), 31.74, 29.35, 29.24, 29.14, 28.82, 28.53, 28.47, 25.87, 22.45, 13.50; ^{19}F NMR (470 MHz, acetone- d_6) δ -79.53 (m, $J_{\text{F-F}} = 4.7$), -224.99 (tt, $J_{\text{H-F}} = 42.35$, $J_{\text{H-F}} = 28.23$, 1F); MS (solid probe) (EI) m/z (%) 256 (M^+ , 100). Anal Calcd for $\text{C}_{15}\text{H}_{27}\text{F}_4\text{N}_3\text{S}_1$: C, 44.43; H, 6.71; N, 10.36; F, 18.74. Found: C, 44.45; H, 6.05; N, 10.39; F, 18.80.

1-Butyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium hexafluorophosphate (5o): (0.27 g, 98% yield) white solid, mp 296 °C; IR (KBr): 3164, 3054, 2971, 2987, 2882, 1972, 1584, 1538, 1442, 1421, 1265, 1163, 1135, 1096, 1014, 895, 823, 745, 707 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.94 (t, $J = 7.36 \text{ Hz}$, 3H), 1.41 (hex, $J = 5.82 \text{ Hz}$, 2H), 1.97 (m, 2H), 3.21 (m, $J = 11.22 \text{ Hz}$, 7.44 Hz, 2H),

4.58 (t, $J_{\text{H-H}} = 3.07$ Hz, 2H), 4.98 (t, $J_{\text{H-H}} = 7.46$ Hz, 2H), 9.26 (s, 1H), 10.16 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 145.09, 142.88, 122 (m), 52.45 (d), 40.69 (t, $J_{\text{C-C-C-F}} = 5.35$ Hz), 30.53 (t, $J_{\text{C-C-F}} = 21.64$ Hz), 30.45, 19.01, 12.74; ^{19}F NMR (470 MHz, acetone- d_6) δ -73.04 (d, $J_{\text{P-F}} = 708$ Hz, 6F), -82.8 (tt, $J_{\text{F-F}} = 7.06, 2.82$ Hz, 3F), -115.03 (m, $J = 14.11, 4.73$ Hz, 2F), -122.46 (m, 2F), -127.10 (m, 2F); MS (solid probe) (EI) m/z (%) 372 (M^+ , 100). Anal Calcd for $\text{C}_{12}\text{H}_{15}\text{F}_{15}\text{N}_3\text{P}_1$: C, 27.87; H, 2.92; N, 8.12. Found: C, 28.03; H, 3.18; N, 7.96.

1-Butyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium hexafluorophosphate (5q): (0.38 g, 79% yield) white solid, mp 289 °C; IR (KBr): 3164, 2971, 2943, 2881, 1972, 1730, 1705, 1583, 1534, 1469, 1236, 1204, 1145, 999, 962, 882, 826, 736, 707 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.95 (t, $J = 7.40$ Hz, 3H), 1.42 (hex, $J = 7.49$ Hz, 2H), 1.99 (m, 2H), 3.21 (m, 2H), 4.57 (t, $J_{\text{H-H}} = 7.21$ Hz, 2H), 4.97 (t, $J_{\text{H-H}} = 7.50$ Hz, 2H), 9.24 (s, 1H), 10.14 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 145.00, 142.86, 114-122 (q, $J_{\text{C-F}} = 230$ Hz), 106-112 (m), 52.40 (d), 40.67 (t, $J_{\text{C-C-C-F}} = 5.35$ Hz), 30.60 (t, $J_{\text{C-C-F}} = 21.12$ Hz), 30.39, 30.38, 19.00, 12.73; ^{19}F NMR (470 MHz, acetone- d_6) δ -72.99 (d, $J_{\text{P-F}} = 708$ Hz, 6F), -82.17 (tt, $J_{\text{F-F}} = 9.88, 2.82$ Hz, 3F), -114.76 (m, 2F), -122.85 (m, 2F), -123.89 (m, 2F), -124.53 (m, 2F), -127.24 (m, $J = 9.4, 4.71$ Hz, 2F); MS (solid probe) (EI) m/z (%) 472 (M^+ , 46), 49 (100). Anal Calcd for $\text{C}_{14}\text{H}_{15}\text{F}_{19}\text{N}_3\text{P}_1$: C, 27.24; H, 2.45; N, 6.81. Found: C, 27.29; H, 2.66; N, 6.84.

1-Butyl-4-(1H,1H,2H,2H-perfluorohexyl)-1,2,4-triazolium trifluoromethane-sulfonate (5s): (0.35 g, 72% yield) pale yellow solid, mp 173 °C; IR (KBr): 3133, 3076, 2970, 2883, 1583, 1468, 1258, 1171, 1135, 1032, 882, 748 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 0.95 (t, $J = 7.40$ Hz, 3H), 1.43 (m, $J = 7.50$ Hz, 2H), 1.99 (m, $J = 7.40$, 2H), 3.22 (m, $J = 7.50$, Hz, 2H), 4.58 (t, $J_{\text{HH}} = 7.16$, Hz, 2H), 4.99 (t, $J_{\text{H-H}} = 7.30$ Hz, 2H), 9.29 (s, 1H), 10.32 (s, 1H); ^{13}C NMR (125 MHz, acetone- d_6) δ 145.05, 143.15, 121.28 (m), 52.48, 40.73 (t, $J_{\text{C-C-C-F}} = 5.15$ Hz), 30.53 (t, $J_{\text{C-C-F}} = 22.65$ Hz), 30.45, 19.02, 12.76; ^{19}F NMR (470 MHz, acetone- d_6) δ -79.53.30 (s, 3F), -82.39 (tt, $J = 3.29$ Hz, 12.70 Hz, 3F); MS (solid

probe) (EI) m/z (%) 372 (M^+ , 100). Anal. Calcd for $C_{13}H_{15}F_{12}N_3O_3S_1$: C, 29.95; H, 2.90; N, 8.06; F, 43.73. Found: C, 30.26; H, 3.17; N, 7.59; F, 43.02.