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Low Melting Inorganic Salts of Alkyl-, Fluoroalkyl-, Alkyl Ether-, and Fluoroalkyl Ether-Substituted Oxazolidine and Morpholine

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N-Alkyl- and *N*-fluoroalkyl-substituted oxazolidinium- and morpholinium-based quaternary salts and ionic liquids have been synthesized and characterized. Reactions of *N*-methyloxazolidine (**1**) or *N*-methylmorpholine (**2**) with 3-fluoropropyl bromide or iodopropane in THF at 25 °C gave the quaternary salts (**3a,b**, **4a,b**). These salts were metathesized with various metal salts to yield the corresponding ionic liquids (**5a**–**h**, **6a**–**i**). *N*-Alkoxyethyl- and *N*-(fluoroalkoxy)ethyl-substituted morpholines (**8**–**11**) were prepared and quaternized with methyl iodide (**8a**–**11a**). Their corresponding ionic liquids (**12**–**18**) were obtained by anion exchange and characterized. For both series of compounds, nitrate, hexafluorophosphate, perchlorate, triflate, and bis(trifluoromethanesulfonyl)amide were utilized. Most of the final products are liquids at 25 °C and are thermally stable with long liquid ranges as determined by thermal gravimetric analyses. For compounds **12**, **16**, and **18**, thermal stabilities of ≥400 °C were observed. All the new compounds were characterized by spectroscopic and elemental analyses. Their densities and viscosities were also determined.

Introduction

Since the discovery of the first ambient-temperature molten salt in 1914,[1] many classes of molten salts have been investigated. In recent years, ionic liquids have been recognized as "green solvents" due to their negligible vapor pressure, wide liquid range, high thermal stability, high ionic conductivity, and potential for being recycled more easily than organic solvents.[2] The properties of these materials are optimizable and can be modified as need arises. Because of these unusual characteristics, they have promise as solvents for a wide range of inorganic and organic reactions and may be the key to clean processes and green chemistry.[3,4] Such properties allow these extraordinary liquids, many of which possess nitrogen-containing heteroatom rings as the cationic cores, to have potential useful applications far beyond acting strictly as solvents.[4−17]

Early during our study of *N*-methyloxazolidine and *N*-methylmorpholine as possible precursors to ionic liquids, two limited reports appeared that describe (a) *N*-butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)amide as a low melting solid,[18] (b) X-ray crystallographic studies of novel ionic liquids based on *N*-alkylmorpholinium salts,[19] and (c) *N*-butyl-*N*-methyloxazolidinium bis(trifluoromethanesulfonyl)amide (butylmethyloxazolium bis(trifluoromethanesulfonyl)amide [sic]).[18] Quaternized oxazolidinium and morpholinium halo, perchlorate, and other salts are known, and some

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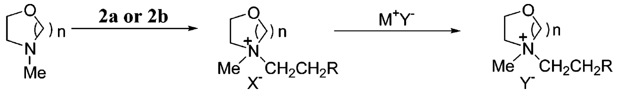
applications have been suggested.[20,21] None of these compounds is classified as an ionic liquid. Recently we synthesized a variety of fluorinated imidazolium-, pyridinium-, bipyridinium-, and triazolium-based ionic liquids.[22−26] Now we report the syntheses and characterization of several new *N*-methyloxazolidinium- and *N*-methylmorpholinium-based ionic liquids where the cations contain either *N*-propyl or *N*-fluoropropyl substitutents. Also, *N*-alkoxyethyl- and *N*-(fluoroalkoxy)ethyl-substituted *N*-methylmorpholinium-centered ionic liquids are described. These are the first samples of quaternary salts that, with the exception of one or two thiazolium compounds,[27] contain two different heteroatoms in the cationic ring and which exhibit properties normally associated with ionic liquids (e.g., mp < 100 °C)[18,19] and, in some cases, unusually high thermal stabilities.

Results

A large fraction of the known ionic liquids are composed of alkylammonium, alkylphosphonium, *N*,*N*′-dialkylimidazolium, and *N*-alkylpyridinium cations.[8] Recently, quaternary triazolium salts have also been demonstrated to exhibit ionic liquid characteristics.[28−30] All of these systems are either acyclic or the cation ring has at least some aromatic character. In this work we have prepared both alkyl- and fluoroalkyl-substituted oxazolidinium and morpholinium ionic salts formed by quaternization with alkyl or polyfluoroalkyl halides as well as ionic liquids derived from quaternized alkoxyethyl and (fluoralkoxy)ethyl *N*-methylmorpholine compounds. The corresponding final ionic liquids were prepared by metathesis reactions of the quaternary salts with appropriate metal salts to form nitrate, hexafluorophosphate, perchlorate, triflate, and bis(trifluoromethanesulfonyl)amide salts using water or water/acetone mixture as solvent.

Scheme 1



1 (n=1), **2** (n=2)   **3a, 3b** (n=1)   **5a-5h** (n=1)

2a = $FCH_2CH_2CH_2Br$ **4a, 4b** (n=2)   **6a-6i** (n=2)

2b = $CH_3CH_2CH_2I$

Y = Tf_2N, PF_6, NO_3, ClO_4, TfO
M = Li, K, Ag, Ag, K

Table 1. Yields, Densities, and Viscosities of Alkyl- and Fluoroalkyl-Substituted Oxazolidinium (**5a−h**) and Morpholinium (**6a−i**) Based Ionic Liquids

compd	CH_2CH_2R	Y	yield (%)	density[a]	viscosity[b]
5a	CH_2F	Tf_2N	45	1.63	287
5b	CH_2F	PF_6	35	[c]	
5c	CH_2F	NO_3	90	1.49	
5d	CH_2F	ClO_4	85	1.46	
5e	CH_2F	TfO	50	[c]	
5f	CH_3	Tf_2N	55	1.55	340
5g	CH_3	PF_6	40	[d]	
5h	CH_3	NO_3	90	[c]	
6a	CH_2F	Tf_2N	50	1.69	
6b	CH_2F	PF_6	40	[d]	
6c	CH_2F	NO_3	90	[d]	
6d	CH_2F	ClO_4	90	1.50	
6e	CH_2F	TfO	40	d	
6f	CH_3	Tf_2N	50	1.54	
6g	CH_3	PF_6	40	[d]	
6h	CH_3	NO_3	90	[d]	
6i	CH_3	ClO_4	90	[d]	

[a] g/cm^3, 25 °C, pycnometer, 30 °C. [b] cP. [c] Not determined. [d] Solid.

Synthesis of Alkyl- and Fluoroalkyl-Substituted Oxazolidinium- and Morpholinium-Based Quaternary Salts and Their Ionic Liquids. *N*-Methyloxazolidine (**1**) was prepared by modification of the earlier methodology[31] and utilized for quaternization studies without further purification. Initially the reactions of **1** with 3,3,3-trifluoropropyl iodide without solvent or in THF were attempted at 40 and 60 °C, and while small amounts of the quaternized product were obtained, it was impossible to purify the salt even after exchanging with other anionic species. However, when 3-fluoropropyl bromide (**2a**) or 1-iodopropane (**2b**) was used either under neat conditions or in THF at 25 °C, **3a**,**b** were isolated in 75% yields (Scheme 1).

N-Methylmorpholine (**2**) did not react with 3,3,3-trifluoropropyl iodide but was quaternized with 3-fluoropropyl bromide (**2a**) and 1-iodopropane (**2b**) under analogous conditions to form **4a**,**b** in about 50% yields. Modifying reaction conditions by increasing reaction time or raising the temperature did not impact the product yields. Metathesis reactions of the quaternary salts (**3a,b**, **4a,b**) with metal salts (M^+Y^-) containing the desired anions were normally performed in water/acetone mixtures at 25 °C to prepare the ionic liquids **5a−h** and **6a−i** in varying yields (Scheme 1, Table 1).

Synthesis of *N*-Alkoxy- and *N*-Fluoroalkoxy-Substituted Morpholines and Their Quaternary Salts and Ionic Liquids. To prepare ether-containing morpholine species with longer chain, more flexible substitutents, 4-(2-chloro-

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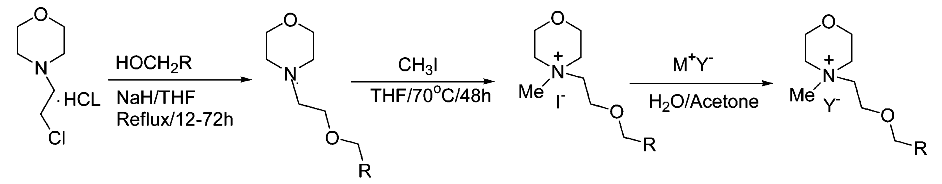
Scheme 2



7 **8 - 11** **8a - 11a** **12 - 18**

$M^+Y^- = Li^+NTf_2^-, K^+PF_6^-$

Table 2. Yields, Densities, and Viscosities of *N*-Alkoxy (**15**, **18**) and *N*-Fluoroalkoxy (**12**−**14**, **16**, **17**) Substituted Morpholinium-Based Ionic Liquids

compd	$C_2H_4OCH_2R$	Y	yield (%)	density[a]	viscosity[b]
12	CF_3	Tf_2N	90	1.69	
13	CF_3	PF_6	98	[c]	
14	CF_3	NO_3	95	[d]	
15	CH_3	Tf_2N	95	1.54	
16	$(CF_3)_3CHF_2$	Tf_2N	95	1.86	970
17	$(CF_3)_3CHF_2$	PF_6	95	[c]	
18	$(CH_2)_3CH_3$	Tf_2N	95	1.38	223

[a] g/cm^3, 25 °C, pycnometer. [b] cP, 30 °C. [c] Solid. [d] Not determined.

Table 3. Phase Transition Temperatures T_m (T_g) (°C) of the Quaternary Salts As Determined by DSC

	Tf_2N^-	PF_6^-	NO_3^-	ClO_4^-	TfO^-
		N−Me Oxazolidinium			
$N{-}(CH_2)_2CH_2F$	[a]	(−56)	[a]	[a]	[a]
$N{-}(CH_2)_2CH_3$	44	41	(−60)		
		N−Me Morpholinium			
$N{-}(CH_2)_2CH_2F$	(−51)	80	58	[a]	68
$N{-}(CH_2)_2CH_3$	(−38)	86	58	91	
$N{-}(CH_2)_2OCH_2CF_3$	(−53)	72			
$N{-}(CH_2)_2OCH_2CH_3$	(−53)				
$N{-}(CH_2)_2OCH_2(CF_2)_3CHF_2$	(−53)	62			
$N{-}(CH_2)_2O(CH_2)_4CH_3$	(−54)				

[a] < −78 °C (T_g).

Table 4. Thermal Decomposition Temperatures (°C) of Oxazolidinum and Morpholinium Salts As Determined by TGA

	Tf_2N^-	PF_6^-	NO_3^-	ClO_4^-	TfO^-
		N−Me Oxazolidinum			
$N{-}(CH_2)_2CH_2F$	330	191	245	268	283
$N{-}(CH_2)_2CH_3$	347	239	183		
		N−Me Morpholinium			
$N{-}(CH_2)_2CH_2F$	342	196	289	276	293
$N{-}(CH_2)_2CH_3$	200	200	285	312	
$N{-}(CH_2)_2OCH_2CF_3$	412	268	277		
$N{-}(CH_2)_2OCH_2CH_3$	389				
$N{-}(CH_2)_2OCH_2(CF_2)_3CHF_2$	400	260			
$N{-}(CH_2)_2O(CH_2)_4CH_3$	410				

ethyl)morpholine hydrochloride (**7**) was reacted with alkyl and fluoroalkyl alcohols using a modified literature procedure[32] to form *N*-alkoxyethyl- or *N*-((fluoroalkoxy)ethyl)-morpholine derivatives (**8**−**11**) (Scheme 2). The introduction of an oxygen-containing substitutent was anticipated to have considerable impact on the physical properties of the quaternized morpholinium salts compared to their alkyl- and polyfluoroalkyl-substituted analogues. Each of the morpholine ethers was quaternized with methyl iodide in THF as solvent at 70 °C to form the respective quaternary salts (**8a**−**11a**). The iodide ion was subsequently exchanged with other metal salts to form several new ionic liquids, **12**−**18**, in excellent yields (Table 2).

The thermal properties of these new quaternary salts were examined using differential scanning calorimetry (DSC, Table 3) and thermogravimetric analysis (TGA, Table 4). Viscosity data are presented in Tables 1 and 2.

Discussion

With the exception of *N*-methyl-*N*-propyloxazolidinium nitrate (**5h**), which decomposes at 183 °C, all of the quaternary salts (excluding bromides or iodides) are thermally stable over a range between 196 °C (*N*-methyl-*N*-fluoropropylmorpholinium hexafluorophosphate (**6b**)) to 400 °C and beyond. While the substituted *N*-methylmorpholinium (**6a**,**f**, **12**, **15**, **16**, **18)** and *N*-methyloxazolidinium (**5a**,**f**) Tf_2N salts are more stable by >100 °C than any of the others, even the nitrate and perchlorate (fluoropropyl and propyl) derivatives are remarkably stable over a range between 250 and 312 °C (excepting **5h**). Interestingly, while propyl *N*-morpholinium $(Tf)_2N$ (**6f**) is considerably less stable thermally than its pyrazinium analogue (T_d = 216 vs 316 °C), the fluoropropyl *N*-methylmorpholinium (**6a**) salt is markedly more stable than the analogous saturated fluoroethyl 1,4-dimethylpiperazinium or the fluoroethyl pyrazinium compound (T_d = 342 vs 199 vs 251 °C). In general, there appears to be little difference in the thermal stabilities of the *N*-propyl and *N*-fluoropropyl N−Me oxazolidinium Tf_2N derivatives in contrast with the analogous morpholinium compounds. Regardless of substituent, the morpholinium ether derivatives (Tf_2N) have remarkable thermal stability, comparable to bis(fluoroethyl)-1,4-dimethylpiperazine.

While all of the *N*-(fluoropropyl)-*N*-methyloxazolidinium quaternary salts are liquids with low T_g's (Table 3), it is surprising that the *N*-(fluoropropyl)hexafluorophosphate (**5b**) is liquid. Supercooling may play a role, but in our hands it was not possible to cause the compound to solidify and to remain solid at 25 °C. This phenomenon may also explain the low T_g of the propyl oxazolidinium nitrate (**5h**). All of the substituted *N*-methylmorpholinium Tf_2N salts (**6a**,**f**, **12**, **15**, **16**, **18)** are liquids with T_g's ranging between −38 and −54 °C. These values are somewhat lower than those for several substituted 3-Me imidazolium Tf_2N salts.[16,23,33−36]

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However, when the hexafluorophosphates are compared, the imidazolium derivatives are lower melting by several tens of degrees, but all are solids at 25 °C.

Perhaps most unexpected is the lack of influence on any of the physical properties (except thermal) of the N−Me morpholinium salts (with Tf$_2$N) formed when ether-containing moieties are substituted on the ring. While less efficient packing would be expected as the substitutent chain increases in length or becomes more flexible as occurs with oxygen in the chain (e.g., the case where lower melting points are observed for butyl-substituted imidazoles compared to methyl), essentially no difference in the T_g is observed when changing from propyl (**6f**) to 2,2,3,3,4,4,5,5,-octafluoropentoxyethyl (**16**) to pentoxyethyl (**18**) among the bis(trifluoromethanesulfonyl)amide salts. Although the density of **16** is relatively high at 1.86 g/cm^3, the densities of all the liquid salts fall between 1.38 and 1.69 g/cm^3. With the exception of the 1-Me-(trifluoroethyl)imidazolium salt[16] whose viscosity approximates the oxazolidinium salt (**5a**) and the (pentoxyethyl)morpholinium salt (**18**), the viscosities of the oxazolidinium and the morpholinium Tf$_2$N compounds are in some cases more than 1 order of magnitude greater than the similar imidazolium and pyrrolidinium counterparts.[18,37] (Octafluoropentoxy)ethyl)morpholinium Tf$_2$N (**16**) is significantly more viscous than is its nonfluorinated analogue **18**.

Recently it has been pointed out that the *N*-pentyl/*C*-ethyl- or *N*-methyl/*C*-ethyl-substituted oxazolinium cation has low stability with concomitant ring opening under acidic conditions although the hexafluorophosphate salts were prepared under aqueous acid conditions in 91% yield![38] Our metathetical syntheses of oxazolidinium and morpholinium salts are accomplished using water or water/acetone solutions for anion exchange. Under these conditions no evidence was found for ring opening; however, stability or lack of stability of the latter salts under strongly acidic conditions has not been determined.

Conclusion

In summary, we have synthesized and characterized *N*-alkyl- and *N*-fluoroalkyl-substituted oxazolinium- and morpholinium-based quaternary salts and their corresponding ionic liquids as well as ionic liquids obtained from quaternization of alkoxyethyl- and (fluoroalkoxy)ethyl-substituted morpholine compounds. All of the bis(trifluoromethanesulfonyl)amide morpholinium products are liquids at 25 °C and have interesting physical properties. Each of the new quaternary salts (not bromide or iodide) has been confirmed via elemental analysis. They are stable thermally and have long liquid ranges. Overall these ionic liquids with saturated core rings tend to exhibit greater thermal stabilities than those composed of unsaturated rings. This property plus the concomitant higher viscosities suggests higher temperature fluids applications.

Experimental Section

General Methods. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded in acetone-d_6 (unless otherwise stated) on a 300 MHz spectrometer operating at 300, 76, 282, and 121 MHz, respectively. Deuterium oxide was frequently added to enhance solubility. Chemical shifts are reported in ppm relative to the appropriate standard. GC/MS spectra were determined by insertion using the solid probe. M$^+$ is the mass of cation. IR spectra were recorded using NaCl plates for neat liquids and KBr pellets for solids. T_m and T_g were recorded on a differential scanning calorimeter at a scan rate of 10 °C/min. Thermal stability were determined by thermogravimetric analysis (TGA). Density and viscosity were measured using a pycnometer and a viscometer (Minivis II, Grabner Instruments), respectively. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry.

General Procedure for the Preparation of Quaternary Salts (3a,b, 4a,b). In a typical reaction, *N*-methyloxazolidine (10 mmol) was taken in a 50 mL flask and dissolved in 6 mL of THF. RY (Y = Br or I) (11 mmol) was added under nitrogen at 25 °C. The reaction mixture was stirred for 3 days at 25 °C. All volatile materials were removed at reduced pressure, and the residue was subjected to dynamic vacuum for 1day leaving the pure quaternary salt.

***N*-(3-Fluoropropyl)-*N*-methyloxazolidinium bromide (3a):** 75% yield, yellow viscous liquid; IR (KBr) 3425, 2978, 2912, 2068, 1630, 1466, 1388, 1341, 1126, 1043, 1190, 900 cm^{-1}; ^{1}H NMR (300 MHz, D$_2$O) δ 2.20 (dm, 2H), 3.15 (s, 3H), 3.71 (m, 2H), 3.58 (m, 2H), 4.55 (dt, $J_{H-F} = 46.72$ Hz, $J_{H-H} = 5.37$ Hz, 2H), 4.85 (dd, $J = 19.45$ Hz, $J = 5.77$ Hz, 2H); ^{13}C NMR (125 MHz, D$_2$O) δ 93.91 (t, $J = 1.91$ Hz), 82.28 (d, $J_{C-F} = 162.54$ Hz), 67.28, 61.12 (t, $J = 3.73$ Hz), 60.01 (br m), 48.57 (t, $J = 3.68$ Hz), 25.55 (d, $J_{C-C-F} = 19.94$ Hz); ^{19}F NMR (282 MHz, D$_2$O) δ −218.76 (sept, $J_{H-F} = 48.01$ Hz, $J_{H-F} = 28.24$ Hz, 1F); MS (solid probe) (EI) *m*/*z* (%) 148 (M$^+$, 6), 104 (M$^+$ − C$_3$H$_8$, 100).

***N*-Propyl-*N*-methyloxazolidinum iodide (3b):** 75% yield, wax; IR (KBr) 3450, 2970, 2360, 1463, 1093, 948, 915, 875, 756 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.04 (t, $J = 7.32$ Hz, 3H), 1.97 (m, 2H), 3.48 (s, 3H), 3.84 (m, 2H), 4.13 (dm, 2H),4.52 (m, 2H), 5.28 (dd, $J = 14.21$ Hz, $J = 5.38$ Hz, 2H); ^{13}C NMR (125 MHz) δ 93.78, 67.21, 63.78, 60.76, 48.54 (t, $J = 12.90$ Hz), 17.99, 10.97; MS (solid probe) (EI) *m*/*z* (%) 128 (M$^+$ − 2, 3).

***N*-(3-Fluoropropyl)-*N*-methylmorpholinium bromide (4a):** 50% yield, white solid; IR (KBr) 3433, 2360, 2076, 1635, 1477, 1350, 1124, 1043, 891 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6 + 1 drop of D$_2$O) δ 2.23 (dm, 2H), 3.17 (s, 3H), 3.49 (m, 4H), 3.63 (m, 2H), 4.03 (br s, 4H), 4.60 (dt, $J_{H-F} = 46.70$ Hz, $J_{H-H} = 5.44$ Hz, 2H); ^{13}C NMR (125 MHz, acetone-d_6 + 1 drop of D$_2$O) δ 82.22 (d, $J_{C-F} = 162.67$ Hz), 62.97, 61.29, 60.70 (t, $J = 2.77$ Hz), 60.01 (br m), 47.69 (t, $J = 3.45$ Hz), 23.56 (d, $J_{C-C-F} = 19.92$ Hz); ^{19}F NMR (282 MHz, acetone-d_6 + 1 drop of D$_2$O) δ −220.58 (tt, $J_{H-F} = 48.00$ Hz, $J_{H-F} = 25.42$ Hz, 1F); MS (solid probe) (EI) *m*/*z* (%) 148 (M$^+$ − CH$_2$, 6); 58 (OC$_2$H$_4$N$^+$, 100).

***N*-Propyl-*N*-methylmorpholinium iodide (4b):** 50% yield, white solid; IR (KBr) 3457, 2971, 2879, 2360, 1471, 1624, 1346, 1112, 1019, 972, 939, 885 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6 + 1 drop of D$_2$O) δ 0.91 (t, $J = 7.31$ Hz, 3H), 1.74 (m, 2H), 3.11 (s, 3H), 3.35 (m, 2H), 3.40 (m, 4H), 3.97 (brs, 4H); ^{13}C NMR (125 MHz, acetone-d_6 + 1 drop of D$_2$O) δ 67.36, 61.27, 60.41 (t, $J = 2.66$ Hz), 47.82, 15.59, 10.73; MS (solid probe) (EI) *m*/*z* (%) 142 (M$^+$ − 2, 48), 100 (M$^+$ − CH$_3$ − CH$_2$CH$_3$, 100).

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***N*-(3-Fluoropropyl)-*N*-methyloxazolidinium bis(trifluoromethanesulfonyl)amide (5a):** 45% yield, viscous liquid; IR (KBr) 3560, 3049, 2987, 2918, 2360, 1798, 1627, 1472, 1192,1056, 906, 740 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.41 (dm, 2H), 3.45 (s, 3H), 3.85 (m, 2H), 4.02 (m, 2H), 4.51 (m, 2H), 4.65 (dt, $J_{\mathrm{H-F}} = 47.08$ Hz, $J_{\mathrm{H-H}} = 5.52$ Hz, 2H), 5.15 (dd, $J = 13.20$ Hz, $J = 5.69$ Hz, 2H); ^{13}C NMR (125 MHz) δ 120.94 (q, $J = 321.16$ Hz), 94.21, 81.56 (d, $J_{\mathrm{C-F}} = 160.82$ Hz), 80.50, 61.29 (t, $J = 3.68$ Hz), 60.11 (m), 48.43 (t, $J = 3.73$ Hz), 25.79 (d, $J_{\mathrm{C-C-F}} = 20.13$ Hz); ^{19}F NMR (282 MHz, D_2O) δ -79.885 (s, 6F), -222.09(tt, $J_{\mathrm{H-F}} = 42.36$ Hz, $J_{\mathrm{H-F}} = 25.79$ Hz, 1F); MS (solid probe) (EI) *m/z* (%) 148 (M$^+$, 100). Anal. Calcd for $C_9H_{15}F_7N_2O_5S_2$: C, 25.23; H, 3.50. Found: C, 25.35; H, 3.68.

***N*-(3-Fluoropropyl)-*N*-methyloxazolidinium hexafluorophosphate (5b):** 35% yield, viscous liquid; IR (KBr) 3430, 2357, 2084, 2088, 1637, 1464, 1394, 1190, 1078, 1044, 858 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6 + 1 drop of D_2O) δ 2.41 (dm, 2H), 3.40 (s, 3H), 3.80 (br t, 2H), 3.97 (m, 2H), 4.50 (m, 2H), 4.64 (dt, $J_{\mathrm{H-F}} = 47.08$ Hz, $J_{\mathrm{H-H}} = 5.54$ Hz, 2H), 4.85 (dd, $J = 12.06$ Hz, $J = 5.48$ Hz, 2H); ^{13}C NMR (125 MHz) δ 94.19 (t, $J = 1.91$ Hz), 81.60 (d, $J_{\mathrm{C-F}} = 164.19$ Hz), 67.34, 61.27 (t, $J = 3.81$ Hz), 60.02 (brm), 48.41 (t, $J = 3.81$ Hz), 25.76 (d, $J_{\mathrm{C-C-F}} = 20.18$ Hz); ^{19}F NMR (282 MHz) δ -72.40 (d, $J = 707.6$, 6F), -222.02 (tt, $J = 45.18$, $J = 28.24$, 1F); ^{31}P NMR (121 MHz) -138.95 (sept, $J_{\mathrm{P-F}} = 707.1$ Hz, 1P); MS (solid probe) (EI) *m/z* (%) 149 (M$^+$ + 1, 3), 42 ($CH_2CH_2N^+$, 100). Anal. Calcd for $C_7H_{15}F_7NOP$: C, 28.68; H, 5.16. Found: C, 29.08; H, 5.45.

***N*-(3-Fluoropropyl)-*N*-methyloxazolidinium nitrate (5c):** 90% yield, viscous liquid; IR (KBr) 3413, 2982, 2395, 2064, 1634, 1392, 1190, 1129, 1043, 947, 900, 826 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.43 (dm, 2H), 3.48 (s, 3H), 3.86 (m, 2H), 3.94 (m, 2H), 4.49 (m, 2H), 4.66 (dt, $J_{\mathrm{H-F}} = 48.00$ Hz, $J_{\mathrm{H-H}} = 5.89$ Hz, 2H), 5.24 (dd, $J = 16.57$ Hz, $J = 5.56$ Hz, 2H); ^{13}C NMR (125 MHz) δ 93.99, 82.03 (d, $J_{\mathrm{C-F}} = 164.05$ Hz), 67.31, 61.06 (t, $J = 3.41$ Hz), 59.77 (m), 48.43 (t, $J = 3.47$ Hz), 25.83 (d, $J_{\mathrm{C-C-F}} = 20.08$ Hz); ^{19}F NMR (282 MHz, D_2O) δ -221.21 (tt, $J_{\mathrm{H-F}} = 47.99$ Hz, $J_{\mathrm{H-F}} = 25.41$ Hz, 1F); MS (solid probe) (EI) *m/z* (%) 148 (M$^+$, 7), 104 (M$^+$ $-$ C_2H_4, 100). Anal. Calcd for $C_7H_{15}FN_2O_4{\cdot}H_2O$: C, 36.84; H, 7.46. Found, C, 36.78; H, 6.88.

***N*-(3-Fluoropropyl)-*N*-methyloxazolidinium perchlorate (5d):** 85% yield, viscous liquid; IR (KBr) 3428, 2979, 2913, 2360, 1635, 1469, 1392, 1361, 1093, 902, 767 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.43 (dm, 2H), 2.90 (s, 3H), 3.83 (m, 2H), 4.00 (m, 2H), 4.50 (m, 2H), 4.65 (dt, $J_{\mathrm{H-F}} = 47.11$ Hz, $J_{\mathrm{H-H}} = 5.56$ Hz, 2H), 5.13 (dd, $J = 14.17$ Hz, $J = 5.68$ Hz, 2H); ^{13}C NMR (125 MHz) δ 93.96, 81.88 (d, $J_{\mathrm{C-F}} = 164.64$ Hz), 67.29, 60.94 (t, $J = 3.45$ Hz), 59.62 (m), 48.31 (t, $J = 3.43$ Hz), 25.93 (d, $J_{\mathrm{C-C-F}} = 20.19$ Hz); ^{19}F NMR (282 MHz, D_2O) δ -221.21 (tt, $J_{\mathrm{H-F}} = 48.00$ Hz, $J_{\mathrm{H-F}} = 25.41$ Hz, 1F); MS (solid probe) (EI) *m/z* (%) 148 (M$^+$, 5), 104 (M$^+$ $-$ C_2H_4, 100). Anal. Calcd for $C_7H_{15}FNO_5Cl$: C, 33.95; H, 6.11. Found: C, 33.35; H, 6.07.

***N*-(3-Fluoropropyl)-*N*-methyloxazolidinium trifluoromethanesulfonate (5e):** 50% yield, viscous liquid; IR (KBr) 3558, 283, 2918, 2360, 1635, 1472, 1393, 1261, 1030, 905, 758 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.43 (dm, 2H), 3.45 (s, 3H), 3.86 (m, 2H), 4.04 (m, 2H), 4.49 (m, 2H), 4.65 (dt, $J_{\mathrm{H-F}} = 47.13$ Hz, $J_{\mathrm{H-F}} = 5.44$ Hz, 2H), 5.16 (dd, $J = 15.67$ Hz, $J = 5.51$ Hz, 2H); ^{13}C NMR (125 MHz) δ 122.18 (q, $J_{\mathrm{C-F}} = 321.54$ Hz), 94.18, 81.56 (d, $J_{\mathrm{C-F}} = 165.08$ Hz), 67.35, 61.23 (t, $J = 3.86$ Hz), 59.99 (m), 48.42 (t, $J = 3.70$ Hz), 25.82 (d, $J_{\mathrm{C-C-F}} = 20.22$ Hz); ^{19}F NMR (282 MHz, D_2O) δ -79.99 (s, 6F), -222.09 (tt, $J_{\mathrm{H-F}} = 48.00$ Hz, $J_{\mathrm{H-F}} = 25.41$ Hz, 1F); MS (solid probe) (EI) *m/z* (%) 148 (M$^+$, 100). Anal. Calcd for $C_8H_{15}F_4NO_4S$: C, 32.32; H, 5.09. Found: C, 33.75; H, 5.29.

***N*-Propyl-*N*-methyloxazolidinum bis(trifluoromethanesulfonyl)amide (5f):** 55% yield, viscous yellow liquid; IR (KBr) 2982, 1932, 1464, 1352, 1195, 1138, 1057, 975, 951, 916, 876, 790, 740 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.04 (t, $J = 7.32$ Hz, 3H), 1.99 (m, 2H), 3.38 (s, 3H), 3.62 (m, 2H), 3.96 (m, 2H), 4.47 (m, 2H), 5.08 (dd, $J = 18.10$ Hz, $J = 5.68$ Hz, 2H); ^{13}C NMR (125 MHz) δ 120.93 (q, $J_{\mathrm{C-F}} = 321.08$ Hz), 93.97, 67.23, 64.48, 61.11 (t, $J = 3.76$ Hz), 48.30 (t, $J = 3.71$ Hz), 17.81, 10.83; ^{19}F NMR (282 MHz) δ -79.88 (s, 6F); MS (solid probe) (EI) *m/z* (%) 130 (M$^+$, 100). Anal. Calcd for $C_9H_{16}F_6N_2O_5S_2$: C, 26.34; H, 3.93. Found: C, 26.42; H, 3.84.

***N*-Propyl-*N*-methyloxazolidinum hexafluorophosphate (5g):** 40% yield, wax; IR (KBr) 3429, 2981, 1629, 1469, 1197, 950, 916, 845 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.01 (t, $J = 7.31$, 3H), 1.94 (m, 2H), 3.35 (s, 3H), 3.56 (m, 2H), 3.90 (m, 2H), 4.44 (m, 2H), 5.03 (dd, $J = 19.67$ Hz, $J = 5.66$ Hz, 2H); ^{13}C NMR (125 MHz) δ 93.84, 67.15, 64.35, 60.97 (t, $J = 3.80$ Hz), 48.17 (t, $J = 3.67$ Hz), 17.99, 10.86; MS (solid probe) (EI) *m/z* (%) 130 (M$^+$, 21), 85 (M$^+$ $-$ C_2H_4, 100); ^{31}P MNR δ -144.21 (sept, $J = 708.28$, 1P). Anal. Calcd for $C_7H_{16}F_6NOP$: C, 30.55; H, 5.86. Found: C, 29.51; H, 6.11.

***N*-Propyl-*N*-methyloxazolidinum nitrate (5h):** 90% yield, wax; IR (KBr) 3434, 2978, 2360, 1645, 1377, 1202, 1128, 1095, 950 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.02 (t, $J = 3.66$ Hz, 3H), 1.96 (m, 2H), 3.67 (m, 2H), 4.00 (m, 2H), 4.45 (m, 2H), 5.14 (dd, $J = 21.12$ Hz, $J = 5.56$ Hz, 2H); ^{13}C NMR (125 MHz) δ 93.70, 67.22, 64.00, 60.76 (t, $J = 3.40$ Hz), 47.93 (t, $J = 3.57$ Hz), 17.85, 11.05; MS (solid probe) (EI) *m/z* (%) 130 (M$^+$, 36), 85 (M$^+$ $-$ C_2H_4, 100). Anal. Calcd for $C_7H_{16}N_2O_4$: C, 43.74; H, 8.39. Found: C, 43.67; H, 8.90.

***N*-(3-Fluoropropyl)-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)amide (6a):** 50% yield, viscous solid; IR (KBr) 2982, 1478, 1196, 1134, 1056, 894, 790 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.43 (dm, 2H), 3.48 (s, 3H), 3.75 (m, 4H), 3.88 (m, 2H), 4.15 (m, 4H), 4.67 (dt, $J_{\mathrm{H-F}} = 47.06$ Hz, $J_{\mathrm{H-H}} = 5.51$ Hz, 2H); ^{13}C NMR (125 MHz) δ 120.96 (q, $J_{\mathrm{C-F}} = 321.23$ Hz), 81.53 (d, $J_{\mathrm{C-F}} = 165.63$ Hz), 63.01, 61.17, 61.00 (t, $J = 2.67$ Hz), 47.55, 23.82 (d, $J_{\mathrm{C-C-F}} = 20.28$ Hz); ^{19}F NMR (282 MHz) δ -79.89 (s, 6F), -221.91 (tt, $J_{\mathrm{H-F}} = 48.00$ Hz, $J_{\mathrm{H-F}} = 25.41$ Hz, 1F); MS (solid probe) (EI) *m/z* (%) 162 (M$^+$, 100). Anal. Calcd for $C_{10}H_{17}F_7N_2O_5S_2$: C, 27.15; H, 3.87. Found: C, 27.24; H, 4.01.

***N*-(3-Fluoropropyl)-*N*-methylmorpholinium hexafluorophosphate (6b):** 40% yield, pink solid; IR (KBr) 2360, 1479, 1128, 1045, 837 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.28 (dm, 2H), 3.24 (s, 3H), 3.56 (m, 4H), 3.67 (m, 2H), 4.08 (br s, 4H), 4.61 (dt, $J_{\mathrm{H-F}} = 47.02$ Hz, $J_{\mathrm{H-H}} = 5.55$ Hz, 2H); ^{13}C NMR (125 MHz) δ 82.28 (d, $J_{\mathrm{C-F}} = 162.61$ Hz), 63.00, 61.32, 60.73 (t, $J = 2.75$ Hz), 47.73 (t, $J = 3.31$ Hz), 23.59 (d, $J_{\mathrm{C-C-F}} = 19.93$ Hz); ^{19}F NMR (282 MHz, acetone-d_6) δ -220.46 (tt, $J_{\mathrm{H-F}} = 45.00$ Hz, $J_{\mathrm{H-F}} = 28.24$ Hz, 1F); ^{31}P NMR (121 MHz, acetone-d_6); MS (solid probe) (EI) *m/z* (%) 162 (M$^+$, 3), 58 ($OC_2H_4N^+$, 100). Anal. Calcd for $C_8H_{17}F_7NOP{\cdot}0.5H_2O$: C, 30.37; H, 5.69. Found: C, 30.07; H, 5.53.

***N*-(3-Fluoropropyl)-*N*-methylmorpholinium nitrate (6c):** 90% yield, yellow solid; IR (KBr) 3429, 2980, 2067, 1638, 1475, 1379, 1238, 1126, 1043, 893, 826 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.17 (dm, 2H), 3.12 (s, 3H), 3.44 (m, 4H), 3.56 (m, 2H), 3.97 (brs, 4H), 4.54 (dt, $J_{\mathrm{H-F}} = 46.66$ Hz, $J_{\mathrm{H-H}} = 5.43$ Hz, 2H); ^{13}C NMR (125 MHz) δ 81.91 (d, $J_{\mathrm{C-F}} = 164.35$ Hz), 62.90, 61.24, 60.80 (t, $J = 2.41$ Hz), 47.23, 23.80 (d, $J_{\mathrm{C-C-F}} = 20.14$ Hz); ^{19}F NMR (282 MHz) δ -218.69 (tt, $J_{\mathrm{H-F}} = 45.18$ Hz, $J_{\mathrm{H-F}} = 25.41$ Hz, 1F); MS (solid probe) (EI) *m/z* (%) 100 (M$^+$ $-$ $CH_2CH_2CH_2F$, 31), 58 ($OC_2H_4N^+$, 100). Anal. Calcd for $C_8H_{17}FN_2O_4{\cdot}0.5H_2O$: C, 41.20; H, 7.72. Found: C, 41.27; H, 7.73.

***N*-(3-Fluoropropyl)-*N*-methylmorpholinium perchlorate (6d):** 90% yield, solid; IR (KBr) 3433, 2979, 1635, 1477, 1388, 1103, 893 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.40 (dm, 2H), 3.45 (s, 3H), 3.71 (brt, 4H), 3.84 (m, 2H), 4.14 (br s, 4H), 4.66 (dt, $J_{H-F} = 47.10$ Hz, $J_{H-H} = 5.59$ Hz, 2H); ^{13}C NMR (125 MHz) δ 81.77 (d, $J_{C-F} = 164.88$ Hz), 62.84, 61.20, 60.84 (t, $J = 2.52$ Hz), 47.31 (br s), 23.84 (d, $J_{C-C-F} = 20.22$ Hz); ^{19}F NMR (282 MHz) δ -78.95 (s, 6F), -221.52 (tt, $J_{H-F} = 45.18$ Hz, $J_{H-H} = 25.41$ Hz, 1F); MS (solid probe) (EI) *m/z* (%) 142 ($M^+ - F$, 1), 43 ($C_3H_7^+$, 100). Anal. Calcd for $C_8H_{17}FNO_5Cl{\cdot}0.5H_2O$: C, 35.55; H, 6.66. Found: C, 35.74; H, 6.54.

***N*-(3-Fluoropropyl)-*N*-methylmorpholinium trifluoromethanesulfonate (6e):** 40% yield, solid; IR (KBr) 2980, 2360, 1635, 1479, 1261, 1162, 1030, 893, 758 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.40 (dm, 2H), 3.45 (s, 3H), 3.72 (br s, 4H), 3.85 (m, 2H), 4.13 (brs, 4H), 4.66 (dt, $J_{H-F} = 47.10$ Hz, $J_{H-H} = 5.57$ Hz, 2H); ^{13}C NMR (125 MHz) δ 122.19 (q, $J_{C-F} = 321.45$), 81.67 (d, $J_{C-F} = 164.95$ Hz), 62.86, 61.18, 60.87 (t, $J = 2.64$ Hz), 47.31, 23.84 (d, $J_{C-C-F} = 20.22$ Hz); ^{19}F NMR (282 MHz) δ -78.95 (s, 6F), -221.78 (tt, $J_{H-F} = 48.00$ Hz, $J_{H-F} = 25.41$ Hz, 1F); MS (solid probe) (EI) *m/z* (%) 142 ($M^+ - F$, 100), 43 ($C_3H_7^+$, 100). Anal. Calcd for $C_9H_{17}F_4NO_4S{\cdot}H_2O$: C, 33.75; H, 5.62. Found: C, 33.69; H, 5.30.

***N*-Propyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)amide (6f):** 50% yield, viscous liquid; IR (KBr) 3443, 2981, 2888, 1633, 1475, 1351, 1200, 1058, 973, 940, 887, 791, 740 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.04 (t, $J = 7.31$ Hz, 3H), 1.97 (m, 2H), 3.41 (s, 3H), 3.67 (m, 6H), 4.11 (br s, 4H); ^{13}C NMR (125 MHz) δ 120.98 (q, $J_{C-F} = 321.45$ Hz), 67.28, 61.17, 60.78 (t, $J = 2.75$ Hz), 47.62, 15.70, 10.72; ^{19}F NMR (282 MHz) δ -79.89 (s, 6F); MS (solid probe) (EI) *m/z* (%) 144 (M^+, 100). Anal. Calcd for $C_{10}H_{18}F_6N_2O_5S_2$: C, 28.30; H, 4.28. Found: C, 28.16; H, 4.27.

***N*-Propyl-*N*-methylmorpholinium hexafluorophosphate (6g):** 40% yield, white solid; IR (KBr) 3432, 2978, 2885, 2360, 2056, 1636, 1475, 1354, 1056, 1110, 973, 850 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.02 (t, $J = 7.30$ Hz, 3H), 1.94 (m, 2H), 3.40 (s, 3H), 3.67 (m, 6H), 4.08 (brs, 4H); ^{13}C NMR (125 MHz) δ 67.24, 61.23, 60.69 (t, $J = 2.72$ Hz), 47.67, 15.77, 10.80; ^{19}F NMR (282 MHz) δ -72.30 (d, $J = 707.85$ Hz, 6F); ^{31}P NMR (121 MHz) δ -144.22 (sept, $J_{P-F} = 708.28$ Hz); MS (solid probe) (EI) *m/z* (%) 142 ($M^+ - 2$, 4), 100 ($M^+ - C_3H_8$, 100). Anal. Calcd for $C_8H_{18}F_6NOP$: C, 33.22; H, 6.27. Found: C, 34.74; H, 6.54.

***N*-Propyl-*N*-methylmorpholinium nitrate (6h):** 90% yield, viscous liquid; IR (KBr) 3427, 2974, 2882, 2359, 1636, 1113, 1056, 940, 973, 825 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6 + 1 drop of D_2O) δ 0.89 (t, $J = 7.31$ Hz, 3H), 1.71 (m, 2H), 3.31 (m, 2H), 3.08 (s, 3H), 3.37 (m, 4H), 3.95 (brs, 4H); ^{13}C NMR (125 MHz, acetone-d_6 + 1 drop of D_2O) δ 67.37, 61.23, 60.36 (t, $J = 2.66$ Hz), 47.62, 15.50, 10.60; MS (solid probe) (EI) *m/z* (%) 129 ($M^+ - CH_3$, 3), 43 ($C_3H_7^+$, 100).

***N*-Propyl-*N*-methylmorpholinium perchlorate (6i):** 90% yield, colorless solid; IR (KBr) 3432, 2976, 2884, 2360, 1636, 1392, 1232, 1111, 1021, 973, 941, 887 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6 + 1 drop of D_2O) δ 0.91 (t, $J = 7.31$ Hz, 3H), 1.71 (m, 2H), 3.10 (s, 3H), 3.33 (m, 2H), 3.40 (m, 4H), 3.97 (s, 4H); ^{13}C NMR (125 MHz, acetone-d_6 + 1 drop of D_2O) δ 67.41, 61.25, 60.37 (t, $J = 2.69$ Hz), 47.64, 15.52, 10.64; MS (solid probe) (EI) *m/z* (%) 142 ($M^+ - 2$, 8), 43 ($C_3H_7^+$, 100). Anal. Calcd for $C_8H_{18}NO_5Cl$: C, 39.45; H, 7.45. Found: C, 39.39; H, 7.42.

General Procedure for the Preparation of 8−11. This synthesis is a modification of the procedure reported.[21] The entire process was performed under nitrogen. Sodium hydride (2.4 g, 100 mmol) was transferred into a 250 mL three-necked flask, and then 80 mL THF was added by syringe. Trifluoroethanol (8 g, 80 mmol) of was added slowly to the cooled reaction mixture and stirred for 1 h at ambient temperature. Finally, 14.5 g of 4-(2-chloroethyl)-morpholine hydrochloride was added to the reaction mixture, and the mixture was stirred for 1 h at 25 °C and then warmed at 78 °C for 8 h. The product was extracted with ether, and the solvent was removed by vacuum distillation. Flash column chromatography was used to purify the products.

***N*-((Trifluoroethoxy)ethyl)morpholine (8):** 70% yield, brown liquid; IR (KBr) 3423, 2961, 2858, 2812, 2361, 1638, 1454, 1358, 1278, 1157, 1117, 1007, 962, 916, 767, 734, 665 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.46 (brt, $J = 4.70$ Hz, 4H), 2.57 (t, $J = 5.72$ Hz, 2H), 3.60 (br t, $J = 4.63$ Hz, 4H), 3.77 (t, $J = 5.73$ Hz, 2H), 4.03 (q, $J_{H-F} = 9.17$ Hz, 2H); ^{13}C NMR (125 MHz) δ 125.43 (q, $J_{C-F} = 278.74$ Hz), 70.88, 68.63 (q, $J_{C-C-F} = 33.14$ Hz), 67.44, 58.75, 54.85; ^{19}F NMR (282 MHz) δ -70.30 (t, $J_{H-F} = 9.04$ Hz, 3F); MS (solid probe) (EI) *m/z* (%) 213 (M^+, 1), 100 ($M^+ - CH_2OCH_2CF_3$, 100).

***N*-((Trifluoroethoxy)ethyl)-*N*-methylmorpholinium iodide (8a):** 75% yield, brown solid; IR (KBr) 3495, 2360, 2071, 1636, 1457, 1357, 1352, 1123, 1042 cm^{-1}; ^{1}H NMR (300 MHz) δ 3.67 (s, 3H), 3.92 (br t, $J = 9.86$, 4H) 4.19 (br m, $J = 4.64$ Hz, 4H), 4.30 (br m, $J = 5.04$ Hz, 4H), 4.35 (q, $J_{H-F} = 9.06$ Hz, 2H), 4.41 (brs, 2H); ^{13}C NMR (125 MHz) δ 125.14 (q, $J_{C-F} = 278.07$ Hz), 68.69 (q, $J_{C-C-F} = 33.92$ Hz), 66.11, 64.14, 61.55, 61.25, 49.52; ^{19}F NMR (282 MHz) δ -74.66 (t, $J_{H-F} = 9.04$ Hz, 3F); MS (solid probe) (EI) *m/z* (%) 213 ($M^+ - CH_3$, 2), 100 ($M^+ - CH_2OCH_2CF_3 - CH_3$, 100).

***N*-(Ethoxyethyl)morpholine (9).** With vigorous stirring, 2.3 g of sodium was taken in a 25 mL three-necked flask under nitrogen and dissolved in 45 mL of ethanol at room temperature. After the ethoxide was formed completely, 14.5 g of 4-(2-chloroethyl)-morpholine hydrochloride was added to the reaction mixture and stirred at 78 °C for 40 h: 60% yield, brown liquid; IR (KBr) 3457, 2536, 2055, 1634, 1472, 1303, 1116, 955, 881 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.13 (t, $J = 7.00$ Hz, 3H), 2.44 (br t, $J = 4.59$ Hz, 4H), 2.49 (t, $J = 2.48$ Hz, 2H), 3.45 (q, $J = 7.00$ Hz, 2H), 3.52 (t, $J = 5.96$ Hz, 2H), 3.59 (br t, $J = 4.69$ Hz, 4H); ^{13}C NMR (125 MHz) δ 69.19, 67.45, 66.61, 59.06, 55.05, 15.55; MS (solid probe) (EI) *m/z* (%) 114 ($M^+ - OCH_2CH_3$, 1), 100 ($M^+ - CH_2OCH_2CH_3$, 100).

***N*-(Ethoxyethyl)-*N*-methylmorpholinium iodide (9a):** 90% yield, brown liquid; IR (KBr) 3457, 2058, 1637, 1473, 1459, 1305, 1235, 1116, 1047, 881 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ 1.17 (t, $J = 7.00$, 3H), 3.50 (s, 3H), 3.59 (q, $J = 7.00$ Hz, 2H), 3.77 (m, 4H), 4.02 (m, 4H), 4.10 (brt, $J = 1.97$ Hz, 4H); ^{13}C NMR (125 MHz, acetone-d_6) δ 67.16, 64.42, 64.35, 61.57 (t, $J = 2.47$), 61.30, 49.40, 15.28; MS (solid probe) (EI) *m/z* (%) 174 (M^+, 2), 100 ($M^+ - CH_2OCH_2CH_3 - CH_3$, 100).

***N*-(2,2,3,3,4,4,5,5-Octafluoro-1-pentoxyethyl)morpholine (10):** 75% yield, yellow liquid; IR (KBr) 3456, 2958, 2863, 2815, 1636, 1456, 1359, 1280, 1070, 1037, 974, 910, 859, 754, 704 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.46 (t, $J = 4.52$ Hz, 4H), 2.57 (t, $J = 5.59$ Hz, 2H), 3.60 (t, $J = 4.85$ Hz, 4H), 3.79 (t, $J = 5.56$ Hz, 2H), 4.16 (tt, $J_{H-F} = 14.24$ Hz, $J_{H-F} = 1.59$ Hz, 1H), 6.81 (tt, $J_{H-F} = 45.36$ Hz, $J_{H-F} = 5.74$ Hz, 1H); ^{13}C NMR (125 MHz) δ 116.00 (tt, $J_{C-F} = 255.00$ Hz, $J_{C-C-F} = 29.96$ Hz, 2F), 115.87−114.80 (m), 114 (tt, $J_{C-F} = 251.00$ Hz, $J_{C-C-F} = 30.18$ Hz, 2F), 108.00−107.49 (m), 70.84, 68.01 (t, $J_{C-C-F} = 25.66$ Hz), 67.34, 58.75, 54.76;^{19}F NMR (282 MHz) δ -120.75 (m, 2F), -126.65 (br t, 2F), -131.22 (m, 2F), -139.16 (m, 2F); MS (solid probe) (EI) *m/z* (%) 345 (M^+, 1), 100 ($M^+ - CH_2OCH_2CF_2\ CF_2CF_2CF_2H$, 100).

***N*-(2,2,3,3,4,4,5,5-Octafluoro-1-pentoxyethyl)-*N*-methylmorpholinium iodide (10a):** 75% yield, yellow liquid; IR (KBr) 3454, 2030, 1630, 1473, 1289, 1170, 1126, 1043, 956, 884, 807, 754 cm^{-1}; ^{1}H NMR (300 MHz) δ 3.62 (s, 3H), 3.88 (br m, 4H), 4.15 (br m, 4H), 4.24 (br m, 2H), 4.40 (br m, 4H), 6.88 (tt, $J_{HF} = 51.05$ Hz, $J_{HH} = 5.63$ Hz, 1H); ^{13}C NMR (125 MHz) δ 116.52 (tt, $J = 255.80$, $J = 30.64$), 116−111 (m), 109.06 (tt, $J = 252.34$, $J = 30.78$), 109−106 (m), 68.14 (t, $J = 25.27$), 66.45, 64.15, 61.55, 61.23, 49.50; ^{19}F NMR (282 MHz) δ −120.61 (m, 2F), −125.85 (br t, 2F), −130.96 (m, 2F), −139.16 (m, 2F); MS (solid probe) (EI) *m*/*z* (%) 360 (M$^+$, 77), 100 (M$^+$ − $CH_2OCH_2CF_2CF_2CF_2CF_2H$ − CH_3, 100).

***N*-(Pentoxyethyl)morpholine (11):** 75% yield, yellow liquid; IR (KBr) 2932, 2857, 2805, 2360, 1645, 1455, 1353, 1301, 1377, 1277, 1011, 945, 914 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.91 (m, 3H), 1.32 (m, 4H), 1.54 (m, 2H), 2.44 (t, $J = 4.52$ Hz, 4H), 2.50 (t, $J = 5.90$ Hz, 2H), 3.40 (t, $J = 6.50$ Hz, 2H), 3.52 (t, $J = 5.90$ Hz, 2H), 3.95 (br t, $J = 4.60$ Hz, 4H); ^{13}C NMR (125 MHz) δ 71.41, 69.53, 67.48, 59.07, 55.07, 30.22, 29.16, 23.15, 14.35; MS (solid probe) (EI) *m*/*z* (%) 201 (M$^+$, 2), 100 (M$^+$ − $CH_2OCH_2CH_2CH_2CH_2CH_3$, 100).

***N*-(Pentoxyethyl)-*N*-methylmorpholinium iodide (11a):** 75% yield, viscous liquid; IR (KBr) 3458, 2931, 2870, 2360, 2029, 1634, 1468, 1362, 1304, 1232, 1117, 1039, 953, 882 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.89 (m, 3H), 1.33 (m, 4H), 1.59 (m, 4H), 3.62 (s, 3H), 3.87 (m, 4H), 4.06 (br s, 2H), 4.17 (br m, 6H); ^{13}C NMR (125 MHz) δ 71.89, 64.74, 64.15, 61.49, 61.30, 49.61, 29.89, 29.01, 23.09, 14.31; MS (solid probe) (EI) *m*/*z* (%) 201 (M$^+$ − CH_3, 1), 100 (M$^+$ − $CH_2OCH_2CH_2CH_2CH_2CH_3$ − CH_3, 100).

***N*-((Trifluoroethoxy)ethyl)-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)amide (12):** 90% yield, viscous brown liquid; IR (KBr) 2953, 2889, 1474, 1351, 1280, 1190, 1133, 1055, 964, 789, 738, 655 cm^{-1}; ^{1}H NMR (300 MHz) δ 3.53 (s, 3H), 3.79 (m, 4H), 4.08 (br m, 2H), 4.14 (br s, 4H), 4.19 (q, $J_{H-F} = 8.93$, 2H), 4.36 (brs, 2H); ^{13}C NMR (125 MHz) δ 125.00 (q, $J_{C-F} = 277.96$ Hz), 120.97 (q, $J_{C-F} = 321.28$ Hz), 68.54 (q, $J_{C-C-F} = 34.17$ Hz), 66.03, 64.65, 61.74 (t, $J = 2.25$ Hz), 61.18, 49.09; ^{19}F NMR (282 MHz) δ −74.94 (t, $J_{H-F} = 9.04$ Hz, 3F), −79.87 (s, 6F); MS (solid probe) (EI) *m*/*z* (%) 228 (M$^+$, 100). Anal. Calcd for $C_{11}H_{17}F_9N_2O_6S_2$: C, 25.99; H, 3.37. Found: C, 25.96; H, 3.44.

***N*-((Trifluoroethoxy)ethyl)-*N*-methylmorpholinium hexafluorophosphate (13):** 98% yield, brown solid; IR (KBr) 2954, 2360, 1475, 1280, 1165, 1131, 964 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ 3.56 (s, 3H), 3.81 (m, 4H), 4.11 (br m, 2H), 4.16 (br s, 4H), 4.21 (q, $J = 8.97$, 2H), 4.38 (br s, 2H); ^{13}C NMR (125 MHz) δ 125.04 (q, $J_{C-F} = 278.07$ Hz), 68.50 (q, $J_{C-C-F} = 34.16$ Hz), 66.03, 64.59, 61.70 (t, $J = 2.36$ Hz), 61.18, 49.04; ^{19}F NMR (282 MHz) δ −72.38 (d, $J_{P-F} = 707.69$ Hz, 6F), −74.90 (t, $J_{H-F} = 9.04$ Hz, 3F); ^{31}P NMR (121 MHz) δ −144.15 (sept, $J_{P-F} = 707.07$ Hz, 1P); MS (solid probe) (EI) *m*/*z* (%) 100 (M$^+$ − $CH_2OCH_2CF_3$ − CH_3, 63), 43 (C_3H_7, 100). Anal. Calcd for $C_9H_{17}F_9NO_2P$: C, 28.97; H, 4.59. Found: C, 28.77; H, 4.47.

***N*-((Trifluoroethoxy)ethyl)-*N*-methylmorpholinium nitrate (14):** 95% yield, viscous brown liquid; IR (KBr) 3442, 2956, 2360, 1337, 1279, 1164, 1127, 1043, 964, 884, 829 cm^{-1}; ^{1}H NMR (300 MHz) δ 3.54 (s, 3H), 3.79 (m, 4H), 4.08 (br m, 2H), 4.14 (br s, 4H), 4.19 (q, $J_{H-F} = 8.97$ Hz, 2H), 4.37 (brs, 2H); ^{13}C NMR (125 MHz) δ 125.18 (q, $J_{C-F} = 277.85$ Hz), 68.31 (q, $J_{C-C-F} = 33.99$ Hz), 66.10, 64.25, 61.44, 61.23, 48.73; ^{19}F NMR (282 MHz) δ −74.80 (t, $J_{H-F} = 9.04$ Hz, 3F); MS (solid probe) (EI) *m*/*z* (%) 228 (M$^+$, 10), 100 (M$^+$ − $CHCH_2OCH_2CF_3$ − H, 100). Anal. Calcd for $C_9H_{17}F_3N_2O_5{\cdot}H_2O$: C, 35.06; H, 6.16. Found: C, 34.79; H, 6.12.

***N*-(Ethoxyethyl)-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)amide (15):** 95% yield, viscous brown liquid; IR (KBr) 3453, 2981, 2885, 2068, 1634, 1474, 1195, 1352, 1135, 1057, 985, 882, 790, 738 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.19 (t, $J = 7.01$, 3H), 3.54 (s, 3H), 3.60 (q, $J = 7.00$ Hz, 2H), 3.78 (m, 4H), 3.99 (m, 2H), 4.06 (m, 2H), 4.14 (br t, $J = 1.99$ Hz, 4H); ^{13}C NMR (125 MHz) δ 120.96 (q, $J = 321.23$ Hz), 67.18, 64.63, 64.19, 61.67 (t, $J = 2.34$ Hz), 61.22, 49.21, 15.17; ^{19}F NMR (282 MHz) δ −79.90 (s, 6F); MS (solid probe) (EI) *m*/*z* (%) 174 (M$^+$, 100). Anal. Calcd for $C_{11}H_{17}F_6N_2O_6S_2{\cdot}H_2O$: C, 28.14; H, 4.05. Found: C, 28.37; H, 4.27.

***N*-(2,2,3,3,4,4,5,5-Octafluoro-1-pentoxyethyl)-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)amide (16):** 95% yield, viscous liquid; IR (KBr) 3449, 2958, 2936, 2873,2360, 1847, 1471, 1354, 1213, 1058, 957, 883, 790 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.88 (m, 3H), 1.32 (m, 4H), 1.59 (m, 2H), 3.49 (s, 3H), 3.53 (m, $J = 6.52$ Hz, 2H), 3.76 (m, 4H), 3.97 (m, 2H), 4.05 (brs, 2H), 4.12 (br m, 4H); ^{13}C NMR (125 MHz) δ 120.97 (q, $J = 321.33$ Hz), 71.93, 64.59, 64.47, 61.67, 61.23, 49.36, 29.80, 28.97, 23.02, 14.21; ^{19}F NMR (282 MHz) δ −79.86 (s, 6F); MS (solid probe) (EI) *m*/*z* (%) 360 (M$^+$, 100). Anal. Calcd for $C_{12}H_{18}F_{14}N_2O_6S_2$; C, 26.25; H, 2.81. Found: C, 25.89; H, 2.90.

***N*-(2,2,3,3,4,4,5,5-Octafluoro-1-pentoxyethyl)-*N*-methylmorpholinium hexafluorophosphate (17):** 95% yield, yellow liquid; IR (KBr) 2356, 1475, 1284, 1172, 1128, 956, 845, 740 cm^{-1}; ^{1}H NMR (300 MHz) δ 3.52 (s, 3H), 3.78 (m, 4H), 4.07 (m, 2H), 4.13 (br s, 4H), 4.30 (t, $J = 14.50$ Hz, 2H), 4.37 (br s, 2H), 6.74 (tt, $J_{C-F} = 51.00$, $J = 5.56$, 1H); ^{13}C NMR (125 MHz) δ 116.47 (tt, $J_{C-F} = 255.51$, $J_{C-C-F} = 30.71$), 116.40−111.00 (m), 109.44 (tt, $J_{C-F} = 251.36$, $J_{C-C-F} = 30.71$), 109.00−106.00 (m), 67.94 (t, $J_{C-F} = 25.30$ Hz), 66.24, 64.34, 61.59, 61.14, 49.07; ^{19}F NMR (282 MHz) δ −72.33 (d, $J = 706.00$ Hz, 6F), −120.66 (m, 2F), −130.86 (m, 2F), −134.62 (dm, 2F); ^{31}P NMR (121 MHz, acetone-d_6) δ −144.15 (sept, $J_{P-F} = 5.83$, 1P); MS (solid probe) (EI) *m*/*z* (%) 360 (M$^+$, 44), 100 (M$^+$ − $C_2H_4OC_4F_8H$ − H, 100). Anal. Calcd for $C_{12}H_{18}NF_{14}O_2P$: C, 28.53; H, 3.59. Found: C, 27.93; H, 3.23.

***N*-(Pentoxyethyl)-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)amide (18)**: 95% yield, viscous liquid; IR (KBr) 3449, 2958, 2936, 2873, 2360, 1847, 1627, 1471, 1354, 1213, 1058, 957, 883, 790 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.88 (m, 3H), 1.32 (m, 4H), 1.59 (m, 2H), 3.49 (s, 3H), 3.53 (m, $J = 6.52$ Hz, 2H), 3.76 (m, 4H), 3.97 (m, 2H), 4.05 (br s, 2H), 4.12 (br m, 4H); ^{13}C NMR (125 MHz) δ 120.97 (q, $J = 321.33$ Hz), 71.93, 64.59, 64.47, 61.67, 61.23, 49.36, 29.80, 28.97, 23.02, 14.21; ^{19}F NMR (282 MHz) δ −79.86 (s, 6F); MS (solid probe) (EI) *m*/*z* (%) 216 (M$^+$, 32), 100 (M$^+$ − $CH_2OCH_2CH_2CH_2CH_2CH_3$ − CH_3), 100). Anal. Calcd for $C_{12}H_{18}F_{14}N_2O_6S_2$; C, 30.39; H, 5.53. Found: C, 30.88; H, 5.02.

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