JOC Notes

Methimazole-Based Ionic Liquids

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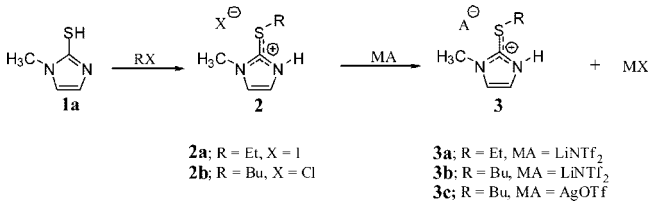


The alkylation reaction of 2-mercapto-1-methylimidazole **1a** with iodoethane and chlorobutane produced *S*-alkylmethimazole halides **2a** and **2b** which were subjected to anion metathesis with two different metal salts (MA) to afford methimazole-based room-temperature ionic liquids **3a**, **3b**, and **3c** in 82%, 85%, and 87% yields, respectively. S-Alkylation giving **2a** and **2b** suggests that methimazole reacts through the thione tautomer.

Ionic liquids have attracted considerable attention during the past few years due, in some cases, to their very low vapor pressure, wide liquid temperature range, good ionic conductivity, excellent electrochemical properties, and potential as solvents for liquid−liquid extraction.[1] While all of these properties are not necessarily always present, a number of well characterized ionic liquids exhibiting many of them are now available. Nevertheless, highly efficient and convenient syntheses of new ionic liquids are still required to broaden the applications.

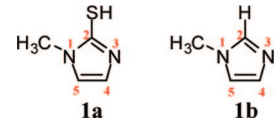


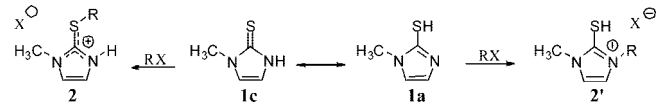
FIGURE 1. 2-Mercapto-1-methylimidazole (**1a**) and 1-methylimidazole (**1b**).

Methimazole **1a** (2-mercapto-1-methylimidazole) (Figure 1) is a molecule of considerable current interest in the fields of inorganic and organometallic chemistry, by virtue of its prolific use as a precursor of a range of novel poly(azolyl)borate ligands, in which the sulfur atom, often termed a "tame thiolate", acts as a soft donor toward a variety of transition metals.[2] Moreover, this thiolate binding has been utilized in efforts to model the active binding site of a variety of zinc-based proteins.[2b,c,3]

In the context of ionic liquids, the importance of methimazole lies with its direct analogy to the ubiquitous 1-methylimidazole **1b**, though with the distinction that the highly acidic C2 proton is replaced by a thiol linkage **1a**.

Methimazole exists in a tautomeric equilibrium between the 2-thiol **1a** and 2-thione **1c** forms (Scheme 1) and has been observed to react in both guises, depending upon the conditions and substrates employed.[2e,4] Thus, in seeking to 'alkylate' this molecule by addition of an alkyl halide (RX), two possible scenarios (Scheme 1) are immediately obvious, *viz.* (i) alkylation of methimazole at sulfur to afford the 2-alkylthiolonium imidazole **2**; and (ii) alkylation of methimazole at nitrogen to afford the imidazolium thiol **2′**.

SCHEME 1. Tautomer Equilibrium between the 2-Thiol 1a and 2-Thione 1c Forms



Moreover, both cations have extensive potential for tautomerism and might conceivably exist as a resonance hybrid or as one discrete canonical form. Metzger et al. reported the reaction of methimazole with MeI to afford 2-methylthiolonium

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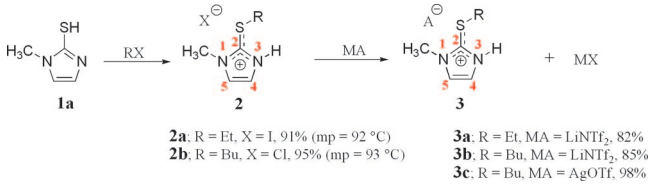
imidazole.[5] However, details of the reaction are limited in scope and the structure was not established.

Recently, the synthesis of various heterocyclic-based ionic liquids has been described.[6] However, no methimazolium-based ionic liquids have yet been reported. In this communication, we report on the synthesis and characterization of five members of this family of ionic liquids. Since electrochemical use of ionic liquids based on the structurally related **1b** has been of importance, a preliminary study of their potential windows is provided for comparative purpose.

The alkylation reaction of **1a** with iodoethane gave methimazolium iodide **2a** in 91% yield. Likewise, the reaction of methimazole with chlorobutane afforded **2b** in 95% yield. The metathesis reaction of the methimazolium halides **2** with metal salts (MA) gave the room-temperature methimazolium-based ionic liquids **3a**, **3b**, and **3c** in good to high yields (Scheme 2).

SCHEME 2. Metathesis Reactions of Methimazole Halides 2 with Metal Salts



The metathesis reaction of the methimazolium halide **2a** with lithium bis(trifluoromethanesulfonyl)amide, $LiNTf_2$, (also known as LiTFSA) proceeded smoothly at room temperature (20 ± 2 °C) in water to give the corresponding ionic liquid[mimSEt]-$[NTf_2]$ **3a** (mimSEt = 2-Ethylthiolonium). Likewise, the reaction of **2b** afforded[mimSBu]$[NTf_2]$ **3b**. The alkylation reaction of **2b** with silver trifluoromethanesulfonate (AgOTf) proceeded cleanly to give[mimSBu][OTf] **3c**.

All the ionic liquids were dried at 70 °C under high vacuum for 2 days and then characterized by NMR spectroscopy, microanalysis, IR, ESI mass spectrometry, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and viscosity. Data obtained showed that the isolated materials were pure, free from methimazole and metal salt starting materials. The water content of dried samples of **3a**, **3b**, and **3c**, determined with a Karl Fischer coulometer, was <100 ppm. [mimSEt][I] **2a** and [mimSBu][Cl] **2b** salts are solids at room temperature. The DSC traces showed that **2a** and **2b** melt at temperatures of 92 and 93 °C, respectively, thereby being ionic liquids, according to the classification scheme based on a mp <100 °C.[7] Also, glass transition temperatures (T_g) of these ionic salts **2a** and **2b** were found at −23 and −22 °C, respectively. DSC measurements on the room-temperature ionic liquids (RTILs) **3a**, **3b**, and **3c** provided no evidence of a melting point (T_m), but glass transition temperatures were detected at −79 °C, −79 °C, and −77 °C, respectively. The viscosities of ionic liquids **3a**, **3b**, and **3c** were 110 mPa s, 115 mPa s, and 184 mPa s at 20 °C, respectively.

The thermogravimetric analyses for thoroughly dried compounds [mimSEt]$[NTf_2]$ and [mimSBu]$[NTf_2]$ showed no weight loss at temperatures up to at least 350 °C, and hence they can be classified as highly thermally stable ILs, providing a large, stable liquid range. [mimSBu][OTf] decomposed at 314 °C. This is in contrast to, for example, methimazolium iodide[mimSEt][I] and methimazolium chloride [mimSBu][Cl] ionic liquids that decompose at much lower temperatures (∼210 °C).

The structure of **2a** was established by NMR spectrometry. The resonance associated with the isolated proton ($^+$NH) was initially elusive, being heavily broadened and appearing at an unexpectedly high frequency (δ_H 11.09 ppm), thus implying its involvement in strong intermolecular associations and/or interior intramolecular site exchange. Indeed, this notion is supported by the observation of appreciable concentration dependence for this resonance; {δ_H α[**2a**]}. A comparable series of data were obtained for the salt **2b**. The site of alkylation can be clearly established on the basis of proton-detected long-range $^1H-^{13}C$ heteronuclear correlation (HMBC) experiments which indicate, for the *N*-methyl protons, significant spin−spin coupling interactions with both the quaternary (C2 of **2a**) and proximal alkenic carbon centers (C4, C5 of **2a**) (Scheme 2). In contrast, the S-bound CH_2R (**2a**, R = CH_3) protons interact only with the quaternary (C2 of **2a**) center, thus indicating that the alkyl chain resides upon the sulfur atom of **2a**. However, location of the isolated proton is more difficult, since for neither **2a** nor **2b** is any HMBC response observed. A further notable feature is the observation of an appreciable shift to lower frequency (0.46 ppm) of the proton resonance associated with the S-bound CH_2 unit of the alkyl chain[**2a**, δ_H 3.53 ppm (SCH_2CH_3); **3a**, δ_H 3.07 ppm ($SCH_2CH_2CH_2CH_3$)] upon replacing the halide anion **2a** with$[NTf_2]^-$ anion **3a**. While this clearly implies some delocalization of charge on to the sulfur center, delocalization of charge between S and N is both possible and likely. In seeking to resolve this issue, and more confidently assign the location of the isolated proton and the interactions in which it is involved, the neat liquids **3a** and **3b** were the subject of multinuclear NMR investigation. Unsurprisingly, the heavy deshielding of the isolated proton ($^+$NH) proved also to be a feature of the neat IL[**3a**, δ_H ($CDCl_3$) 10.69 ppm][**3a**, δ_H (neat) 11.39 ppm], consistent with the concentration dependence previously observed. More significantly, it was found that for neither liquid (**3a** or **3b**) can an interaction be resolved between this proton ($^+$NH) and any nitrogen nucleus on the NMR time scale, the ^{15}N and ^{15}N {1H} spectra showing no distinction in intensity or multiplicity for either IL. It should also be noted that these experiments have also failed to demonstrate a resolvable interaction of the isolated proton ($^+$NH) with the imide nitrogen of $[NTf_2]^-$ anion. Thus, association with the ^{15}N nucleus of the $[NTf_2]^-$ anion is no greater than with those of the $[mimSEt]^+$ cation. Perhaps one of the most striking features to emerge from these studies is the observation for **3b** of a single ^{15}N NMR resonance (δ_N 166.5 ppm) corresponding to the two imidazole ^{15}N nuclei [apparent magnetic equivalence despite clear chemical inequivalence]. This is particularly perplexing given that for the ethyl analogue **3a** the two nuclei give rise to separate resonances (δ_N 167.2 ppm, 165.4 ppm) as expected, albeit that their magnetic environments are perhaps more similar than one might intuitively anticipate. Possibly the *N*-methyl substituent can delocalize between the two nitrogen centers, which would contribute to some level of magnetic equivalence. The infrared spectrum of **3b** was recorded and a weak, broad intensity absorption is apparent 3573 cm^{-1}, assigned to the N−H stretching mode, albeit slightly high in energy. Therefore, it is

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TABLE 1. Potential Window Data Obtained from Cyclic Voltametry for 3a, 3b, and 3c

ionic liquid	E_W (V)[a]	cathodic limit (V)	anodic limit (V)
3a	3.77	−2.13[b]	1.64[b]
3b	3.78	−2.24[b]	1.54[b]
3c	3.07	−1.91[c]	1.16[c]

[a] Potential window data obtained from cyclic voltammetry at a glassy carbon working electrode using a scan rate of 0.1 V s^{-1}; E_W: Potential window as determined using procedures described in ref 10c; T: 20 ± 1 °C. [b] Potentials are vs the $Fc^{0/+}$ reference scale. [c] Potentials are vs Ag wire.

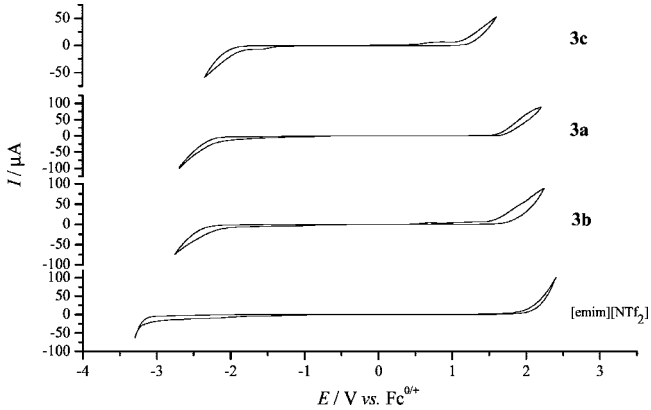

FIGURE 2. Potential windows obtained from cyclic voltammetry at a glassy carbon electrode (1 mm diameter) for **3a**, **3b**, and **3c** and [emim][NTf_2]. v: 0.1 V s^{-1}; T: 20 ± 1 °C; Potentials are vs the $Fc^{0/+}$ reference scale, except for **3c** where Ag wire was used as a quasireference electrode since **3c** slowly reacts with Fc.

highly probable that the alkylation reaction proceeds through the 2-thione form **1c**.

Cyclic voltammograms were obtained from **3a**, **3b**, and **3c** neat liquids and from **3b** dissolved in acetonitrile (0.1 M [Bu_4N][PF_6]). A separation of about 1.35 V in the E^0_f values (reversible formal potentials calculated as the average of the oxidation and reductive peak potentials) between the $Fc^{0/+}$ (Fc = Ferrocene) and the $Cc^{+/0}$ (Cc^+ = Cobalticinium) redox couple was found in all of the neat liquids as well as in acetonitrile. An irreversible oxidation process was observed with a peak potential of 1.53 V vs $Cc^{+/0}$ using a glassy carbon electrode at a scan rate of 100 mV s^{-1} when a 2 mM **1a** solution in acetonitrile was oxidized to methimazole disulfide via dimerization of a methimazole free-radical cation.[8] In contrast, 2 mM **3b** solution exhibits an irreversible oxidation reaction at the much more positive potential of 3.20 V vs $Cc^{+/0}$ under the same conditions, as expected for a predominantly thioether rather than thiol structure.

The potential windows[10c] for **3a**, **3b**, and **3c** (Table 1) as neat liquids and 1-ethyl-3-methylimidazolium NTf_2 {[emim][NTf_2]} have been measured by cyclic voltammetry at a scan rate of 100 mV s^{-1} using a glassy carbon working electrode (Figure 2). The magnitude of the potential windows lie in the order [emim][NTf_2] > **3a** = **3b** > **3c**. The oxidation potential limit of **3a**, **3b**, and **3c**, attributed to oxidation of the thioether (see above) occurs at less positive potentials that found with the [emim][NTf_2] ionic liquid.[9,10]

The negative potential limit for [emim][NTf_2] is attributed to the reduction of the emim cation,[11] although small processes also present at around −1.5 V have been reported by Howlett et al.[11] and Endres et al.[12] The relatively smaller negative potential limit for **3a**, **3b**, and probably **3c** are tentatively attributed to reduction of the proton present at the N(3) position (Scheme 2). The reason for the substantial difference in potential window for **3c** and **3b**, which have a common cation, is under investigation.

In summary, we have now reported five new ionic liquids based on methimazole cation and various anions in good to high yields. Three of the compounds are liquids at room temperature which have reasonably wide electrochemical windows. The full characterization of an exhaustive series of new methimazole-based ionic liquids and electrochemical studies in what are potentially coordinating solvents is now under active investigation in our laboratories.

Experimental Section

Synthesis of 2-Ethylthiolonium Iodide [mimSEt][I] (2a).[13,14] Under dinitrogen, a Schlenk flask was charged with methimazole (19.980 g, 175 mmol), suspended in acetonitrile (100 mL). To this suspension was added freshly distilled iodoethane (15.0 mL, 188 mmol), and then the mixture was stirred overnight, while shielded from light. After 12 h the solvent was removed under reduced pressure to afford a pale yellow precipitate, which was recrystallized from acetonitrile/ether to yield the pure title compound as an off-white solid that was dried *in vacuo*. Yield: 91%. IR (neat) 3384w (br), 3063, 3030, 2925, 2868, 1589, 1560, 1501, 1477, 1402, 1348, 1284, 1259, 1216, 1178, 1152, 1136, 1090, 1076, 1027, 1001, 985, 777, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ_H 11.09 (s, br, 1H, N*H*), 7.43 (m, 2H), 3.85 (s, 3H), 3.53 (q, J = 6.9 Hz, 2H), 1.38 (t, J = 7.3 Hz, 3H). ^1H NMR (neat, 300 MHz) δ_H 8.07, 8.01 (2 × NCH=), 4.03 (NCH_3), 3.36 (SCH_2CH_3), 1.40 (SCH_2CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 142.9 (CS), 123.9, 120.4 (2 × NCH=), 36.2 (NCH_3), 30.9 (SCH_2CH_3), 15.2 (SCH_2CH_3); Anal. Calcd for $C_6H_{11}IN_2S$: C, 26.68; H, 4.10; N, 10.37; S, 11.87; I, 46.98. Anal. Found: C, 26.83; H, 4.20; N, 10.35; S, 11.90; I, 47.20. MS (ESI) Calcd for "$C_6H_{11}N_2S^+$": m/z 143.1; Found: m/z 142.8; Calcd for "I^-": m/z 126.9; Found: m/z 126.7.

Synthesis of 2-Butylthiolonium Chloride [mimSBu][Cl] (2b).[14] Under dinitrogen, a Schlenk flask was charged with methimazole (10.960 g, 96 mmol) and pumped *in vacuo* for 30 min. To this was added an excess of freshly distilled chlorobutane (29.6 mL, 281 mmol), and then the mixture was brought to reflux for 24 h. The solvent was then removed under reduced pressure to afford an off-white solid, which was dried *in vacuo*. Yield: 95%. IR (neat) 3429w (br), 3092, 2958, 2931, 2870, 2851, 1577, 1494, 1473, 1307, 1294, 1283, 1102, 859 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ_H 16.28 (s, br, 1H, N*H*), 7.34 (m, 2H, 2 × NC*H*=), 3.78 (s, 3H, NCH_3), 3.56 (t, 2H, J = 7.2 Hz, $SCH_2CH_2CH_2CH_3$), 1.41−1.65 (m, 4H, $SCH_2CH_2CH_2CH_3$), 0.89 (t, 3H, J = 7.2 Hz, $S(CH_2)_3CH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 143.2 (CS), 123.3, 121.1 (2 × NCH=), 35.4 (SCH_2CH_3), 35.2 (NCH_3), 31.6 ($SCH_2CH_2CH_2CH_3$), 21.6 ($SCH_2CH_2CH_2CH_3$), 13.7[$S(CH_2)_3CH_3$]; Anal. Calcd for $C_8H_{15}ClN_2S$: C, 46.48; H, 7.31; N, 13.55; S, 15.51; Cl, 17.15. Anal. Found: C, 46.61; H, 7.22; N, 13.83; S, 15.51; Cl, 17.15. MS (ESI)

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Calcd for "$C_8H_{15}N_2S^+$": *m*/*z* 171.1; Found: *m*/*z* 170.8; Calcd for "Cl^-": *m*/*z* 35.0; Found: *m*/*z* 34.9.

Synthesis of 2-Ethylthiolonium Bis(trifluoromethanesulfonyl)-amide [mimSEt][NTf$_2$] (3a).[13] The salt **2a** [mimSEt][I] (15.127 g, 56 mmol) was dissolved in water (100 mL). With vigorous stirring, an aqueous solution (150 mL) of $LiNTf_2$ (16.938 g, 59 mmol) was added, resulting in immediate formation of a colloidal suspension. The mixture was screened from light and stirred overnight. After 15 h, the mixture was transferred to a separating funnel and allowed to settle. The ionic liquid (IL) layer (bottom) was separated and washed several times with 30 mL aliquots of hot water. The IL was then taken into acetone and stirred over activated carbon at 50 °C for 20 h. After filtration through celite, followed by a plug of basic alumina, the solvent was removed at reduced pressure. Finally the liquid was passed through a 0.45 μm syringe filter and dried in vacuum at 120 °C. Yield: 82%. IR (neat) 3602w (br), 3235, 3184, 3154, 3061, 3005, 2980, 2880, 2847, 2749, 1582, 1487, 1455, 1418, 1346, 1328, 1276, 1226, 1178, 1131, 1051, 968, 924 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ_H 10.69 (s, br, 1H, N*H*), 7.29 (d, J = 8.1 Hz, 2H), 3.75 (s, 3H), 3.08 (q, J = 5.6 Hz, 2H), 1.25 (t, J = 5.2 Hz, 3H); ^{1}H NMR (neat, 300 MHz): δ_H 11.40 (N*H*), 7.52, 7.44 (2 × NC*H*═), 3.92 (NCH_3), 3.19 (SCH_2CH_3), 1.32 (SCH_2CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 142.2 (CS), 125.1, 121.1 (2 × N*C*H═), 119.9 (q, J_{CF} = 320 Hz, $N(SO_2CF_3)_2$), 35.6 (NCH_3), 29.8 (SCH_2CH_3), 14.6 (SCH_2CH_3); ^{15}N NMR (neat, 30 MHz) δ_N 167.2 (NH), 165.4 (NCH_3), 127.4 (NTf_2); Anal. Calcd for $C_8H_{11}F_6N_3O_4S_3$: C, 22.70; H, 2.62; N, 9.93; F, 26.92; S, 22.72. Anal. Found: C, 22.63; H, 2.79; N, 10.02; F, 26.78; S, 22.72; The Li content of **3a** was 2.2 ppm. MS (ESI) Calcd for "$C_6H_{11}N_2S^+$": *m*/*z* 143.1; Found: *m*/*z* 143.0; Calcd for "NTf_2^-": *m*/*z* 279.9; Found: *m*/*z* 280.0.

Synthesis of 2-Butylthiolonium Bis(trifluoromethanesulfonyl)-amide [mimSBu][NTf$_2$] (3b). IR (neat) 3573w (br), 3232, 3153, 2965, 2938, 2878, 1947, 1582, 1487, 1467, 1346, 1328, 1179, 1132, 1052, 923 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ_H 11.68 (s, br, 1H, N*H*), 7.37 (m, 2H, 2 × NC*H*═), 3.84 (s, 3H, NCH_3), 3.15 (t, J = 7.4 Hz, 2H, $SCH_2CH_2CH_2CH_3$), 1.63 (m, 2H, $SCH_2CH_2CH_2CH_3$), 1.44 (m, 2H, $SCH_2CH_2CH_2CH_3$), 0.90 (t, J = 7.1 Hz, 3H, $S(CH_2)_3CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 141.4 (s, CS), 123.7 (s, N*C*H═), 120.1 (s, N*C*H═), 119.6 (q, J_{CF} = 320 Hz, $N(SO_2CF_3)_2$), 34.4 (s, NCH_3), 33.8 (s, $SCH_2CH_2CH_2CH_3$), 30.2 (s, $SCH_2CH_2CH_2CH_3$), 20.7[s, $S(CH_2)_2CH_2CH_3$], 12.1 (s, $S(CH_2)_3CH_3$); ^{19}F NMR (282.4 MHz, $CDCl_3$) δ_F −78.3. ^{1}H NMR (neat, 10 mm tube, 300 MHz) δ_H 12.77 (N*H*), 8.34, 8.25 (2 × NC*H*═), 4.74 (NCH_3), 3.99 ($SCH_2CH_2CH_2CH_3$), 2.44 ($SCH_2CH_2CH_2CH_3$), 2.26[$S(CH_2)_2CH_2CH_3$], 1.72[$S(CH_2)_3CH_3$]; ^{13}C NMR (neat, 75 MHz) δ_C 144.3 (CS), 127.9, 123.2 (2 × N*C*H═), 122.4[q, J_{CF} = 320 Hz, $N(SO_2CF_3)_2$], 37.8 (NCH_3), 37.3 (SCH_2Pr), 33.9 ($SCH_2CH_2CH_2CH_3$), 23.7[$SCH_2CH_2CH_2CH_3$], 15.3[$S(CH_2)_3CH_3$]; ^{15}N NMR (neat, 30 MHz) δ_N 166.5 (2 × N(imid)), 127.6[NTf_2]; Anal. Calcd for $C_{10}H_{15}F_6N_3O_4S_3$: C, 26.61; H, 3.35; N, 9.31; F, 25.25; S, 21.31. Anal. Found: C, 26.30; H, 3.59; N, 9.28; F, 24.99; S, 21.40; Cl, 0.24; The Li content of **3b** was 2.7 ppm. MS (ESI) Calcd for "$C_8H_{15}N_2S^+$": *m*/*z* 171.1; Found: *m*/*z* 170.0; Calcd for "NTf_2^-": *m*/*z* 279.9; Found: *m*/*z* 279.9.

Synthesis of 2-Butylthiolonium TrifluoromethaneSulfonate [mimSBu][OTf] (3c).[15] Under dinitrogen, a Schlenk flask was charged with **2b** [mimSBu][Cl] (3.916 g, 14.5 mmol) dissolved in dry dichloromethane (60 mL). To this was added AgOTf (3.854 g, 15 mmol), which after several minutes began to dissipate and give rise to a precipitate. The mixture was stirred in the dark for 8 h and then filtered, and the solvent was removed under reduced pressure to afford a vivid pink liquid. Yield: 92%. IR (neat) 3493w (br), 3137, 3056, 2979, 2933, 2877, 2754, 1583, 1491, 1454, 1381, 1275, 1235, 1221, 1155, 1060, 1025, 968, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ_H 13.54 (s, br, 1H, N*H*), 7.34 (m, 2H), 3.82 (s, 3H), 3.22 (t, J = 3.9 Hz, 2H), 1.37−1.69 (m, 4H), (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 143.0, 124.5, 121.2, 120.6 (q, J = 319 Hz), 35.5, 34.6, 21.6, 13.5; Anal. Calcd for $C_9H_{15}F_3N_2O_3S_2$: C, 33.74; H, 4.72; N, 8.74; F, 17.79; S, 20.02. Anal. Found: C, 33.92; H, 4.52; N, 9.05; F, 17.49; S, 20.09; Cl, 0.21; No Ag^+ was detected electrochemically. MS (ESI) Calcd for "$C_8H_{15}N_2S^+$": *m*/*z* 171.1; Found: *m*/*z* 171.0; Calcd for "OTf^-": *m*/*z* 149.0; Found: *m*/*z* 148.9.

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Supporting Information Available: Instrumental details and spectral data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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