Quaternization of Pyrazine, Pyridazine, and Pyrimidine with Alkyl and Polyfluoroalkyl Halides: Formation of Low Melting Salts

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Abstract: Pyridazine (1a), pyrazine (1b), pyrimidine (1c) and 1,4-dimethylpiperazine (1d) were quaternized at N-1 with alkyl iodides and polyfluoroalkyl halides under either neat or solvent conditions at 10–110 °C to form N1CH2CH2CmF2m+1 (m = 0, 1, 6, 10) diazinium and polyfluoroalkyl halides under either neat or solvent conditions. Dimethylpiperazine (6d) was quaternized at N-1 with alkyl iodides and polyfluoroalkyl halides in moderate to high yields. Metathesis of these alkyl and monopolyfluoroalkyl substituted diazinium halides with other salts led to the formation of new quaternary compounds, some of which fall into the ionic liquid class (mp <100 °C), where [N1(RCH2CH2)2]+Y− (Y = NTf2, PF6, OTf, NO3, ClO4). 1,4-Dimethylpiperazine with 2.5 equivalents of 1-bromo-2-fluoroethane in DMSO gave the diaquaternized N1,N1′(CH2CH2F)2 product. All compounds were characterized by 1H, 13C, 19F NMR, MS, elemental analyses, and density measurements (for liquids). The phase transition and decomposition temperatures of the quaternized compounds were determined by DSC.

Key words: quaternization, ionic liquids, diazine, fluoroalkyl, polyfluoroalkyl

The field of low melting salts currently is predominately one of imidazolium salts.1–17 However, there are very few six-membered diazine compounds that have been shown to exhibit properties associated with ionic liquids (mp <100 °C). Apparently there has not been an extensive study on the preparation of quaternary salts from unsubstituted diazines. Of this small number, there is none that contains polyfluoroalkyl substituents.18–20 Therefore, it was of interest to synthesize a variety of mono polyfluoroalkyl diazinum derivatives in order to determine the impact of increasing degree of fluorination of the substituent (longer polyfluoroalkyl chain) on the physical properties of the quaternary salts. For comparison purposes, methyl and propyl substituted diazinium salts were also synthesized and characterized.

The ease with which the six-membered 1,2-, 1,3-, and 1,4-diazines undergo quaternization reactions increases as a function of the increasing nucleophilicity of the ring system, that is, pyridazine > pyrimidine > pyrazine.21,22 Both pyridine and imidazole are considerably more nucleophilic which accounts for the successful interactions with a greater variety of electrophiles that has led to a significantly larger number of quaternary salts with these two species.23

While monoquaternization at N1 proceeds quite readily in the diazine ring system,21 diquaternization of these diazines is extremely difficult and reportedly only occurs with the highly electrophilic oxonium salts, particularly Me3O+BF4−.23,24 Since the two nitrogen atoms are in identical environments in the parent ring system, many studies have emphasized the impact of ring substituents on the position at which quaternization occurred.25,26 Many of the reported diazine quaternary salts decompose at their melting points and are hygroscopic or deliquescent.18–20 Quaternization of the nitrogen in pyrimidines reportedly enhances ease of ring transformation.27

Relative to diazines, piperazines form diquaternary salts more readily since the ring is not conjugated and the electron pair associated with each nitrogen atom is essentially independent of the other. The two nitrogen atoms are active and as a result can form ionic polymers with other bifunctional monomers.28,29 However, as with diazines, many piperazine quaternary salts decompose at their melting points and are hygroscopic or deliquescent.30,31 The quaternary salts of diazine derivatives have many applications in industry,32 agriculture,33 and medicine.34 Piperazines are widely used in medicine35–37 and industry.38 In this paper, we report the quaternization of six-membered diazines and dimethylpiperazine with alkyl iodides and polyfluoroalkyl halides and their subsequent metathesis reactions to form the first examples of fluorine-containing compounds of this class that are low melting salts. Considerable attention is devoted to the change in the properties of the quaternary salts as a function of the ring structure, the fluoroalkyl chain length, and the impact of a variety of anions. It is interesting to note that in certain cases the six-membered diazinum salts are stable in contrast with similarly substituted imidazolium compounds.

Pyridazine (1a), pyrazine (1b), pyrimidine (1c), and 1,4-dimethylpiperazine (1d) were quaternized at N-1 by reaction with a slight molar excess of alkyl iodides or polyfluoroalkyl halides (Scheme 1). When the halides are liquids, a solvent is not necessary, since the polyfluorocarbon halide serves the purpose conveniently. However, when the polyfluoroalkyl halide is solid, a small volume of acetone is necessary to bring the reactants into a homogeneous phase. The rates of reaction vary widely, some reactions proceed at 10 °C (e.g., quaternization of 1a) to form 2a and 2b) while others are still incomplete after 48 hours at 110 °C (e.g., quaternization of 1c to form 6c and 6d). Some yields approaching theoretical are obtained. In
most cases, while analytically pure samples were obtained simply by washing the solid products with solvent (e.g., acetone or dichloromethane), a few products 2b, 3i were purified via recrystallization from acetone. Although the monoquaternary compounds formed reasonably well, attempts to prepare diquaternary salts of the diazines were unsuccessful. These failures apparently arise from the concomitant reduction in nucleophilicity of the second nitrogen brought about by quaternization of the first.

Under neat reaction conditions, only the monoquaternary salt was obtained from the reaction of 1,4-dimethylpiperazine with excess 1-bromo-2-fluoroethane. However, when 1,4-dimethylpiperazine was reacted with 2.5 mmol 1-bromo-2-fluoroethane in DMSO at 65 °C for 7 days, a diquaternary salt was obtained in >95% isolated yield (Scheme 1). The color of these halide salts ranged from white to orange or brown.

Scheme 1

Metathesis of alkyl and polyfluoroalkyl diazine halides with other salts led to the formation of new quaternary salts, namely, \([\text{N}_1(\text{RfCH}_2\text{CH}_2)^+\text{Y}^-](\text{Y} = \text{NTf}_2, \text{PF}_6, \text{OTf}, \text{NO}_3, \text{ClO}_4)\) in excellent yields. Some of the salts have \(T_{mp} < 100 \, ^\circ\text{C}\) (melting point), and therefore may be considered as ionic liquids (Table 1).

The cation appears to exhibit a major influence on chemical stability in water and in methanol (polar protic solvent). Pyrazinium and pyridazinium compounds were stable in water, while pyrimidinium compounds were unstable in water or methanol. Quaternized pyrimidinium salts readily undergo ring-modifying processes with carbanions and other nucleophiles.27 In our experience, the pyrimidinium cations were modified in solution, regardless of the cation substituent or of the anion. The cation was more stable when a shorter polyfluoroalkyl chain was present. When 6b (RfCH2CH2 = trifluoropropyl) and 6c

\[
\begin{align*}
\text{H}_3\text{C} &- \text{N} - \text{CH}_3 + \text{BrCH}_2\text{CH}_2\text{F} \\
\text{DMSO} &\rightarrow \\
\text{neat} &\rightarrow
\end{align*}
\]

(RfCH2CH2 = fluoropropyl) were dissolved in water, and an aqueous solution of LiN(SO2CF3)2 was added quickly, pure 7a and 7b were isolated in a straightforward manner. However, aqueous solutions of KSO3CF3, KPF6 or AgClO4, which require longer reaction times for the metathesis reactions to occur resulted in marked changes in the cations even in 15 minutes. Compound 6e [Rf = (CH2CH2(CF2)9CF3] was modified even in the presence of traces of water in DMSO-d6. Compound 6g (R = Pr) changed more slowly than 6b and 6c.

When the behavior of 2a and 4a in D2O was compared with that of the methyl imidazolium salt, 10a, the exchange of the hydrogen at C-2 in the latter was complete after 12 hours at 25 °C while for the former two, no hydro-

<table>
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<tr>
<th>Compound</th>
<th>Ringa</th>
<th>R(CH2)b/R</th>
<th>X</th>
<th>Tm [Td]b</th>
<th>Compound</th>
<th>Y</th>
<th>Tm(Tg)c [Td]b</th>
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<tr>
<td>2a</td>
<td>1a</td>
<td>(CH2)bF</td>
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<td>3a</td>
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<td>3b</td>
<td>SO2CF3</td>
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<td>140 [207]</td>
<td>3c</td>
<td>ClO4</td>
<td>58 [262]</td>
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<tr>
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<td>I</td>
<td>146 [274]</td>
<td>3d</td>
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<td>3f</td>
<td>NO3</td>
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<td>Br</td>
<td>139 [147]</td>
<td>5a</td>
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<td>Br</td>
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<td>(–50) [199]</td>
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<tr>
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<td>1d</td>
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<td>Br</td>
<td>168 [172]</td>
<td>9b</td>
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<td>1e</td>
<td>(CH2)eF</td>
<td>Br</td>
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<td>11a</td>
<td>N(SO2CF3)2</td>
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</table>

a 1a = pyridazine, 1b = pyrazine, 1c = pyrimidine, 1d = 1,4-dimethylpiperazine, 1e = 1-methylimidazol e.

b Melting point (°C); [Thermal degradation temperature (°C)].

c Phase transition temperature (°C).
gen-deuterium exchange had occurred after one month. Similarly we observed that the C-2 hydrogen in the known salts, 1,3-dimethylimidazolium iodide and 1-butyl-3-methylimidazolium iodide was 98% (0.5 h) and 35% (12 h) exchanged with deuterium of D2O at 25 °C, respectively. Exchange of the acidic C-2 hydrogen in 1,3-dialkylimidazolium compounds has been observed by others.\(^{39}\) This phenomenon may argue against the use of imidazolium liquid salts and for 6-member diazolium compounds in systems where such exchanges may occur.

As evidenced by a shift in the fluorine resonance from \(\delta = -218\) to \(-120\) in the \(^{19}\)F NMR spectrum, the carbon–fluorine bond in N1-CH2CH2F-1,4-dimethylpiperazinium bromide (8a) is cleaved in the presence of water. The \(^1\)H NMR spectrum contains only two CH singlets in the ratio of 1:2. The former is assigned to CH3 compared to the initial quaternized salt that displays six CH resonances. The identity of the product is uncertain, but NMR supports the likelihood of the formation of a 1,4-diazabicyclo[2.2.2]octane ring. The diquaternized salt, 8b, was not changed in water.

Phase transition temperatures (midpoints of melting points) for all of the quaternized compounds as determined by differential scanning calorimetry (DSC) are given in Table 1. The key criterion for evaluation of an ionic liquid is, by definition, its melting point. Features discussed for cations of low-melting salts include low symmetry, weak intermolecular interactions (such as little or no hydrogen bonding), and a good distribution of charge in the cation. Therefore, the relationship between the structure and chemical composition of an ionic liquid and its melting point is of particular interest. Quaternary salts of pyridazine\(^{18,19}\) and pyrazine\(^{20}\) were reported to likely decompose at their melting points. In contrast, we now report that with the exception of 4a and 8a where the phase transition and decomposition temperatures differ by only 8 and 4 °C, respectively, all of the alkyl and polyfluoroalkyl-containing quaternary salts decompose thermally beyond their transition points.

For example, the \(T_m\) (melting temperature) and \(T_d\) (decomposition temperature) values for the iodopolyfluoroalkyl pyridazines, 2b–d, and the iodopolyfluoroalkyl pyrimidines, 6b, 6d, 6e (with the exception of \(T_m\) for 6e), increase directly as a function of the length of the polyfluoroalkyl chain. Comparing the bromopolyfluoroalkyl, 2a, 4a, 6a, and the iodopolyfluoroalkyl compounds, 2b, 6b, where the polyfluoroalkyl group is constant in each group, the diazine ring (whether pyridazine, pyrazine, or pyrimidine) apparently has essentially no impact on the melting point. But when all compounds are compared, the pyridazine-containing compounds exhibited higher thermal stability.

The anion appears to exhibit a major influence on the melting point in a more predictable manner. When Br– or I– was exchanged with \(\text{NTf}_2^–, \text{OTf}^–, \text{PF}_6^–, \text{ClO}_4^–, \text{NO}_3^–\), the melting points of the resulting compounds were all decreased to some degree (except for derivatives of 4b).

This is especially noticeable for compounds that contain the nonpolarizable \(\text{NTf}_2^–\) species where \(T_m\) decreases quite dramatically. With the exception of the nitrate derivatives, all metathetical products exhibited greater thermal stability than the halide compounds. Thus, the liquid ranges of these salts are markedly expanded.

The pyridazinium bis(trifluoromethanesulfonyl) amide salts, 3a, 3d and 3g, exhibit relatively high densities at 1.81, 1.85, and 2.13 g cm\(^{-3}\), respectively, the latter is the most dense ionic liquid yet (excluding the hydrolytically unstable metal salts) even exceeding the SF\(_5\)-containing polyfluoroalkyl derivatives.\(^{40}\) The propyl analogue, 3k, is less dense at 1.60 g cm\(^{-3}\).

The solution properties of an ionic salt can be modified by careful choice of cation and anion. When the dielectric constants of the organic solvents (THF, ethyl acetate, acetonitrile, dichloromethane) exceed a characteristic limit, the diazine compounds are completely miscible. This limit appears to be specific for each cation/anion combination. The influence of the cation, for example, is shown by investigation of the solubility of 2b, 2c, 2d, 6b, 6d, 6e, 3b, 3h, 3j. In each of these triads with common anion and with increasing length of the fluoroalkyl substituents (and thus an increasing number of fluorine atoms) on the cation, the solubility of the ionic compounds decreases not surprisingly in all of the solvents tried. This suggests that the stepwise variation of the solubility property achieved by changing the fluoroalkyl group of the cation can be taken advantage of to design ionic salts with specific solubility characteristics.

The influence of the anion on the solubility characteristics of the ionic compounds can be demonstrated by example of the solubility of different salts containing the \(\text{NTf}_2^–, \text{OTf}^–, \text{Br}^–, \text{I}^–, \text{PF}_6^–, \text{ClO}_4^–, \text{NO}_3^–\) anions. In general, with short fluoroalkyl chains (minimum fluorine concentration), the bromide- and iodide-containing quaternary salts were readily soluble in water but had limited solubility in organic solvents. The salts with the bis(trifluoromethanesulfonyl)amide anion were invariably insoluble in water, but, with the exception of hexane, were readily soluble in organic solvents. With \(\text{PF}_6^–\)-containing salts, a biphasic mixture is formed. Diazine quaternary salts that do not contain fluorine are reported to be hygroscopic.\(^{35}\) In our work, only 4a and 6b were obviously hygroscopic.

Since imidazolium salts appear to be the reference family for these low melting salts, 1-(1-fluoroethyl)-3-methylimidazolium bromide (10a) leading to 1-(1-fluoroethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (11a) were prepared for comparison with the compounds described in this work. Each of the 1-fluoroethyl derivatives (NTf\(_2^–\)) of imidazole (11a), pyridazine (3a), and pyrazine (5a) exhibit either \(T_m\) or \(T_d\) considerably below 0 °C, and while the latter compounds are significantly more dense (\(d = 1.81\) g cm\(^{-3}\) compared to 11a at 1.57 g cm\(^{-3}\)), 11a is markedly more thermally stable (compare \(T_d = 398\) °C with 318 and 251 °C for 3a and 5a, respectively). While the 3,3,3-trifluoropropyl derivatives (NTf\(_2^–\)) of imi-
Other NMR solvents used were D2O and DMSO-
otherwise indicated, on a 300 (500) MHz spectrometer operating at
for applications of the former liquid salts where the latter
the analogous imidazolium compounds which may allow
stable with respect to hydrogen/deuterium exchange than
points, and were prepared under the mildest reaction con-
ing the most stable. They also have the lowest melting
zine,15,16 and pyridazine (3d) melt or have a Tg well be-
 below 0 °C, the pyrazine (5d), and pyrimidine (7a) salts melt
at 55 and 95 °C, respectively. However, this places all
four compounds in the ionic liquid class. Although the Tg
for the imidazolium compound was not determined, 3d is
markedly more stable at 376 °C than 5d at 269 °C and 7a
at 199 °C. The thermally stable 3d has a density of 1.85 g/
cm3 compared to 1.44 g/cm3 for the imidazolium salt.

In conclusion, a variety of new quaternized salts of py-
razine, pyrazine, pyrimidine and 1,4-dimethyl pipera-
zeine, usually bis(trifluoromethanesulfonyl)amide but
sometimes perchlorate and nitrate, many of these quater-
nary salts melt below 100 °C and therefore fall into the
ionic liquid class. The thermal stability is largely depend-
ent on the cation with the pyridazinium compounds be-
ing the most stable. They also have the lowest melting
points, and were prepared under the mildest reaction con-

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Anal. Calcd for C6H8BrFN2: C, 34.81; H, 3.89. Found: C, 34.76; H,
melting point was 140.1 °C. The thermally stable
has a density of 1.85 g/
cm3 compared to 1.44 g/cm3 for the imidazolium salt.

IR (KBr): 3046, 2978, 1588, 1429, 1277, 1219, 1148, cm–1.
1H NMR (500 MHz, DMSO-d6): δ = 3.35–3.28 (m, 2 H),
5.19–5.24 (m, 2 H), 8.64–8.67 (m, 1 H), 8.73–8.78 (m, 1 H),
9.63–9.65 (m, 1 H), 10.04–10.08 (m, 1 H).
13C NMR (125 MHz, DMSO-d6): δ = 155.1, 151.6 (d,
J = 4.9 Hz, 13C), 136.6–136.7 (m, 2 H), 108.8–120.2 (m),
57.45 (t, J = 4.8 Hz), 30.58 (t, J = 21.3 Hz).
19F NMR (470 MHz, DMSO-d6, 100 °C): δ = –80.69 (tt,
j = 2.8 Hz, J2 = 9.9 Hz, 3 F), –121.0 to –121.2 (m, 2 F),
–121.1 to –121.4 (m, 2 F), –122.2 (br s, 2 F), –122.9 (br s, 2 F),
–125.6 (br s, 2 F).
MS (EL, solid probe): m/z (%) = 627 (M+*, 100).
Anal. Calcd for C8H12F6I2N2: C, 25.48; H, 1.07. Found: C, 25.56; H,
1.02.
1-Propylpyridazinium Iodide (2e)
The same procedure was followed as that described for 2a ex-
cept the product was washed with acetone–hexane; yield: 0.48 g
(96%); brown solid; mp 66.7 °C.

1-((1H,1H,2H,2H)-Perfluorooctyl)pyridazinium Iodide (2c)
1-iodo-1H,1H,2H,2H-perfluorooctane (0.52 g, 1.1 mmol) and
pyridazine (0.08 g, 1 mmol) were placed in a 15 mL Pyrex glass tube
that was evacuated, sealed, and heated at 65 °C for 2 days. The gold-
en residue was washed with acetone; yield: 0.44 g (80%); mp 171.3
°C.
IR (KBr): 3067, 2978, 1588, 1429, 1277, 1219, 1148, cm–1.
1H NMR (300 MHz, DMSO-d6): δ = 3.23 (tt, J1 = 7.1 Hz, J2 = 19.6
Hz, 2 H), 5.23 (t, J = 7.1 Hz, 2 H), 8.67–8.71 (m, 1 H), 8.80–8.83
(m, 1 H), 9.69 (d, J = 4.1 Hz, 1 H), 10.1 (d, J = 5.8 Hz, 1 H).
13C NMR (125 MHz, DMSO-d6): δ = 155.1, 151.6 (d, J = 9.1 Hz,
137.9–138.0 (m), 136.6–136.7 (m), 108.3–120.2 (m), 57.08 (t,
J = 4.0 Hz), 30.18 (t, J = 20.6 Hz).
19F NMR (282 MHz, DMSO-d6): δ = –80.44 (t, J = 9.9 Hz, 3 F),
–112.6 to –112.7 (m, 2 F), –121.7 (br s, 2 F), –122.7 (br s, 2 F),
–123.1 to –123.2 (m, 2 F), –125.8 to –125.9 (m, 2 F).
MS (EL, solid probe): m/z (%) = 427 (M+, 100).
Anal. Calcd for C21H22F26I2N2: C, 26.01; H, 1.46. Found: C, 26.05; H,
1.44.
1-(1H,1H,2H,2H)-Perfluorododecyl)pyridazinium Iodide (2d)
1-iodo-1H,1H,2H,2H-perfluorododecane (0.68 g, 1.0 mmol) and
pyridazine (0.16 g, 2 mmol) were dissolved in acetone (3 mL)
and the solution was placed in a 15 mL Pyrex glass tube that was evac-
uated, sealed, and heated at 65 °C for 3 days. The golden residue
was washed with acetone; yield: 0.49 g (65%); mp 204.5
°C.
IR (KBr): 3067, 2978, 1588, 1429, 1277, 1219, 1148, cm–1.
1H NMR (500 MHz, DMSO-d6, 100 °C): δ = 3.15–3.28 (m, 2 H),
5.19–5.24 (m, 2 H), 8.64–8.67 (m, 1 H), 8.73–8.78 (m, 1 H),
9.63–9.65 (m, 1 H), 10.04–10.08 (m, 1 H).
13C NMR (125 MHz, DMSO-d6, 100 °C): δ = 155.1, 151.6 (d,
J = 4.9 Hz, 13C), 136.6–136.7 (m, 2 H), 108.8–120.2 (m),
57.45 (t, J = 4.8 Hz), 30.58 (t, J = 21.3 Hz).
19F NMR (470 MHz, DMSO-d6, 100 °C): δ = –80.69 (tt,
j = 2.8 Hz, J2 = 9.9 Hz, 3 F), –121.0 to –121.2 (m, 2 F),
–121.1 to –121.4 (m, 2 F), –122.2 (br s, 2 F), –122.9 (br s, 2 F),
–125.6 (br s, 2 F).
MS (EL, solid probe): m/z (%) = 627 (M+, 100).
Anal. Calcd for C8H12F6I2N2: C, 25.48; H, 1.07. Found: C, 25.56; H,
1.02.
1-Propylpyridazinium Iodide (2e)
The same procedure was followed as that described for 2a ex-
cept the product was washed with acetone–hexane; yield: 0.48 g
(96%); brown solid; mp 66.7 °C.
IR (KBr): 3061, 2968, 1586, 1431, 1283, 1182, 984, cm\(^{-1}\).

\(^1\)H NMR (300 MHz, D\(_2\)O): \(\delta = 0.87\) (t, \(J = 7.4\) Hz, 3 H), 2.04 (tq, \(J_1 = 7.4\) Hz, \(J_2 = 7.3\) Hz, 2 H), 4.72 (t, \(J = 7.2\) Hz, 2 H), 8.40–8.43 (m, 1 H), 8.48–8.51 (m, 1 H), 9.40 (d, \(J = 3.6\) Hz, 1 H), 9.61 (d, \(J = 5.8\) Hz, 1 H).

\(^1\)C NMR (75 MHz, D\(_2\)O): \(\delta = 155.5, 150.1, 137.5, 136.8, 68.12, 24.15, 10.76\).

MS (EI, solid probe): \(m/z\) (%) = 123 (M\(^+\), 100).


I-(1-Fluoroethy1)pyrazinium Bromide (4a)

1-Bromo-2-fluoroethane (0.28 g, 2.2 mmol) and pyrazine (0.16 g, 2 mmol) were placed in a 10 mL Pyrex glass tube that was evacuated, sealed, and heated at 60 °C for 7 days. The residue was washed with acetone to leave a brown solid; yield: 0.37 g (93%); mp 139.0 °C.

The same procedure was followed as that described for 4a.

IR (KBr): 3007, 1448, 1181, 1159, 1113, 1032, 868 cm\(^{-1}\).

1H NMR (300 MHz, D\(_2\)O): \(\delta = 4.95–5.00\) (m, 1 H), 5.10–5.16 (m, 2 H), 5.19–5.22 (m, 1 H), 9.13 (d, \(J = 2.3\) Hz, 2 H), 9.53–9.56 (m, 2 H).

\(^1\)C NMR (75 MHz, D\(_2\)O): \(\delta = 26.2, 70.1, 125.0, 127.9, 128.7, 134.3, 147.8, 150.5\), 151.7, 155.2, 166.1, 196.6.

I-(1-Fluoroethy1)pyrimidinium Iodide (6b)

The same procedure was followed as for 4a; yield: 0.58 g (95%); brown solid; mp 130.7 °C.

IR (KBr): 3451, 3032, 2969, 1622, 1563, 1494, 1440, 1400, 1255, 1169, 1146, 1105, 1057, 998, 687 cm\(^{-1}\).

1H NMR (300 MHz, D\(_2\)O): \(\delta = 5.39\) (t, \(J = 7.3\) Hz, 2 H), 8.53 (t, \(J = 5.8\) Hz, 1 H), 7.74 (dd, \(J_1 = 4.9\) Hz, \(J_2 = 1.9\) Hz, 1 H), 10.13 (d, \(J = 6.3\) Hz, 1 H), 10.31 (s, 1 H).

\(^1\)C NMR (75 MHz, D\(_2\)O): \(\delta = 126.4, 155.5, 154.0, 125.1, 82.83\) (d, \(J = 168.6\) Hz), 59.40 (d, \(J = 18.6\) Hz).

\(^19\)F NMR (282 MHz, DMSO-d\(_6\)):

\(\delta = -219.0\) to \(-219.5\) (1 F).

MS (EI, solid probe): \(m/z\) (%) = 127 (M\(^+\), 100).

1-(3,3,3-Trifluoropropyl)pyrimidinium Iodide (6b)

The same procedure was followed as for 4a; yield: 0.58 g (95%); brown solid; mp 130.7 °C.

IR (KBr): 3061, 2968, 1586, 1431, 1283, 1182, 984, cm\(^{-1}\).

1H NMR (300 MHz, D\(_2\)O): \(\delta = 2.43\) (dtt, \(J_1 = 7.2\) Hz, \(J_2 = 7.0\) Hz, \(J_3 = 5.7\) Hz, 2 H), 4.63 (dt, \(J_1 = 47.1\) Hz, \(J_2 = 5.5\) Hz, 2 H), 4.79 (t, \(J = 7.2\) Hz, 2 H), 8.35 (t, \(J = 5.6\) Hz, 1 H), 9.50 (dd, \(J_1 = 5.0\) Hz, \(J_2 = 1.8\) Hz, 1 H), 9.62 (dt, \(J_1 = 6.3\) Hz, \(J_2 = 1.7\) Hz, 1 H), 10.02 (s, 1 H).

\(^1\)C NMR (75 MHz, DMSO-d\(_6\)):

\(\delta = 165.9, 155.4, 153.7, 125.0, 84.84\) (d, \(J = 161.7\) Hz), 56.70 (d, \(J = 4.0\) Hz), 31.97 (d, \(J = 19.3\) Hz).

\(^19\)F NMR (282 MHz, DMSO-d\(_6\)):

\(\delta = -215.5\) (t, \(J = 46.6\) Hz, \(J_1 = 26.8\) Hz, 1 F).

MS (EI, solid probe): \(m/z\) (%) = 141 (M\(^+\), 100%).

1-(1-Fluoroethyl)pyrimidinium Bromide (6a)

The same procedure was followed as for 2f, except the mixture was heated at 80 °C for 48 h; yield: 0.40 g (97%); yellow solid; mp 138.3 °C.

IR (KBr): 3012, 2964, 1624, 1566, 1493, 1433, 1354, 1209, 1136, 1051, 1025, 972, 856 cm\(^{-1}\).

1H NMR (300 MHz, DMSO-d\(_6\)):

\(\delta = 9.99\) (t, \(J = 4.3\) Hz, 3 F), 32.07 (t, \(J = 21.0\) Hz).

\(^19\)F NMR (282 MHz, DMSO-d\(_6\)):

\(\delta = -76.96\) (t, \(J = 9.9\) Hz, 3 F), \(-108.9\) to \(-109.0\) (m, 2 F), \(-117.7\) (br s, 2 F), \(-118.7\) (br s, 2 F), \(-119.1\) to \(-119.2\) (m, 2 F), \(-122.1\) to \(-122.2\) (m, 2 F).

MS (EI, solid probe): \(m/z\) (%) = 427 (M\(^+\), 100%).

1,1-(1H,2H,3H,2H-Perfluorododecyl)pyrimidinium Iodide (6e)
The same procedure was followed as for 2e except the mixture was maintained at 110 °C for 48 h. It was washed with acetone to give a yellow solid; yield: 0.38 g (50%); mp 214.1 °C.

1H NMR (300 MHz, DMSO-d6): δ = 7.82–7.84 (m, 1 H), 7.62–7.67 (m, 1 H), 7.53 (d, J = 1.7 Hz, 1 H), 7.51 (t, J = 4.5 Hz, 2 H), 7.48 (t, J = 4.5 Hz, 2 H), 7.41 (t, J = 4.5 Hz, 2 H), 7.27 (d, J = 1.7 Hz, 1 H), 7.25 (d, J = 1.7 Hz, 1 H), 7.21 (d, J = 1.7 Hz, 1 H), 7.19 (d, J = 1.7 Hz, 1 H), 6.87 (s, 1 H).

IR (KBr): 3151, 3096, 1631, 1565, 1448, 1171, 1044, 858 cm⁻¹.

1H NMR (300 MHz, D2O): δ = 3.88 (s, 3 H), 4.53 (dt, J = 28.2 Hz, J1 = 4.5 Hz, 2 H), 4.79 (dt, J = 46.7 Hz, J2 = 4.5 Hz, 2 H), 7.45 (t, J = 1.7 Hz, 1 H), 7.51 (t, J = 1.7 Hz, 1 H), 8.77 (s, 1 H).

13C NMR (75 MHz, D2O): δ = 167.5, 153.1, 152.5, 78.03 (d, J = 156.0 Hz), 137.2, 124.6, 123.4, 82.77 (d, J = 151.7 Hz), 66.6 (q, J = 156.0 Hz), 138.6, 120.9 (q, J = 137.5 Hz), 124.6, 123.4, 82.77 (d, J = 151.7 Hz), 66.6 (q, J = 156.0 Hz).

Low Melting Solids 3, 5, 7, 9, 11; 1-(1-Fluoroethyl)pyridazinium Bis(trifluoromethanesulfonyl)amide (3a); Typical Procedure
To a magnetically stirred solution of 2a (0.5 mmol) in H2O (2 mL) in a 15 mL flask (3g–3k) were run in 0.25 mmol, others were run in 0.5 mmol scale) was added LiNH2 (0.6 mmol). After 8 h at 40 °C, the lower liquid layer was separated and dissolved in EtOAc (10 mL). The latter was washed with H2O (2 × 5 mL) and evaporated in vacuo. After removal of the solvent, the residue was dried in vacuo (0.3 Torr) at 40 °C for 24 h; yield: 0.20 g (98%); yellow liquid; d = 1.81 g/cm³.

IR (KBr): 3115, 3050, 1591, 1477, 1440, 1351, 1190, 1137, 1056, 789 cm⁻¹.

1H NMR (300 MHz, D2O): δ = 5.43 (dt, J1 = 25.9 Hz, J2 = 4.5 Hz, 2 H), 4.41 (d, J = 46.7 Hz, J1 = 4.5 Hz, 2 H), 7.89–8.93 (m, 2 H), 9.77 (t, J = 3.8 Hz, 1 H), 10.03 (d, J = 5.8 Hz, 1 H).

13C NMR (75 MHz, D2O): δ = 150.6, 151.7, 138.6, 137.2, 120.9 (q, J = 321.2 Hz), 81.6 (q, J = 171.4 Hz), 66.6 (q, J = 19.3 Hz).

19F NMR (282 MHz, D2O): δ = –223.0 (tt, J1 = 4.6 Hz, J2 = 27.8 Hz, 1 F).

MS (EI, solid probe): m/z (%) = 129 (M⁺, 100).

Anal. Calcd for C14H12F2N2Br: C, 44.7; H, 4.82. Found: C, 43.95; H, 4.93.

1,4-Dimethyl-1-(1-fluoroethyl)piperazine Bromide (8a)
The same procedure was followed as for 2e except the mixture was maintained at 60 °C for 12 h; yield: 0.47 g (98%); white solid; mp 167.7 °C.

1H NMR (300 MHz, DMSO-d6): δ = 3.26 (s, 3 H), 2.60–2.74 (m, 4 H), 3.14 (s, 3 H), 2.50 (t, J = 9.0 Hz, 4 H), 3.88 (dd, J1 = 29.4 Hz, J2 = 3.9 Hz, 2 H), 4.97 (dt, J1 = 47.0 Hz, J2 = 3.9 Hz, 2 H).

13C NMR (125 MHz, DMSO-d6): δ = 78.66 (d, J = 166.2 Hz), 64.48, 61.27, 48.73, 48.23, 45.69.

19F NMR (470 MHz, DMSO-d6): δ = –211.81 (br s, 1 F).

1-(1-Fluoroethyl)pyridazinium Trifluoromethanesulfonate (3b)

Yield: 0.11 g (96%); light yellow solid; d = 1.50 g/cm³.

IR (KBr): 3133, 3048, 1591, 1479, 1437, 1362, 1290, 1092, 987, 866 cm⁻¹.

1H NMR (300 MHz): δ = 5.18 (dt, J = 46.6 Hz, J = 4.5 Hz, 2 H), 5.40 (dt, J = 26.2 Hz, J = 4.5 Hz, 2 H), 8.78–8.81 (m, 1 H), 8.84–8.90 (m, 1 H), 9.74 (d, J = 4.1 Hz, 1 H), 9.96 (d, J = 5.8 Hz, 1 H).

13C NMR (75 MHz): δ = 156.0, 151.9, 138.6, 137.3, 121.1 (q, J = 321.4 Hz), 81.71 (d, J = 171.1 Hz), 66.47 (d, J = 19.4 Hz).

19F NMR (282 MHz): δ = −79.84 (s, 3 F), −225.1 (tt, J, J = 155.8, 152.1, 138.7, 137.4, 126.7 (q, J = 276.1 Hz), 59.60 (q, J = 276.1 Hz), 59.38 (q, J = 276.1 Hz), 9.77 (d, J = 10.5 Hz, 3 F).

MS (EI, solid probe): m/z (%) = 177 (M⁺, 100).

Anal. Calcd for C₁₄H₁₂F₁₉N₃O₈S₂: C, 23.77; H, 1.84. Found: C, 23.77; H, 1.92.

[(H₂H₂)₂(Perfluorooctyl)pyridazinium Bis(trifluoromethanesulfonamide) (3g)]

The same procedure was followed as for 3g; yield: 0.14 g (97%); white solid; mp 68.0 °C.

IR (KBr): 3109, 3040, 1592, 1437, 1257, 1200, 1146, 1031, 1005 cm⁻¹.

1H NMR (300 MHz): δ = 3.40 (tt, J = 7.1 Hz, J = 18.7 Hz, 2 H), 5.53 (t, J = 7.2 Hz, 2 H), 8.82–8.86 (m, 1 H), 8.92–8.96 (m, 1 H), 9.80 (d, J = 4.2 Hz, 1 H), 10.2 (d, J = 5.7 Hz, 1 H).

13C NMR (125 MHz): δ = 155.2 (d, J = 2.3 Hz), 151.3 (d, J = 13.8 Hz), 137.9–138.0 (m), 136.5–136.7 (m), 120.1 (q, J = 321.1 Hz), 108.4–119.9 (m), 57.73 (t, J = 4.3 Hz, 30.45 (t, J = 21.2 Hz).

19F NMR (282 MHz): δ = −79.94 (s, 6 F), −81.72 (t, J = 2.5 Hz, J = 10.0 Hz, 3 F), −113.7 to −113.9 (m, 2 F), −123.3 (br s, 2 F), −123.4 (br s, 2 F), −124.0 (br s, 2 F), −126.7 to −126.8 (m, 2 F).

MS (EI, solid probe): m/z (%) = 427 (M⁺, 100).


[(H,1H,2H,2F-Perfluoroctyl)pyridazinium Trifluoromethanesulfonate (3h)]

The same procedure was followed as for 3g; yield: 0.14 g (97%); white solid; mp 68.0 °C.

IR (KBr): 3109, 3040, 1592, 1437, 1257, 1200, 1146, 1031, 1005 cm⁻¹.

1H NMR (300 MHz): δ = 3.40 (tt, J = 7.1 Hz, J = 18.7 Hz, 2 H), 5.53 (t, J = 7.2 Hz, 2 H), 8.82–8.86 (m, 1 H), 8.92–8.96 (m, 1 H), 9.80 (d, J = 4.2 Hz, 1 H), 10.2 (d, J = 5.7 Hz, 1 H).

13C NMR (125 MHz): δ = 155.2 (d, J = 2.3 Hz), 151.3 (d, J = 13.8 Hz), 137.9–138.0 (m), 136.5–136.7 (m), 120.1 (q, J = 321.1 Hz), 108.4–119.9 (m), 57.73 (t, J = 4.3 Hz, 30.45 (t, J = 21.2 Hz).

19F NMR (282 MHz): δ = −79.94 (s, 6 F), −81.72 (t, J = 2.5 Hz, J = 10.0 Hz, 3 F), −113.7 to −113.9 (m, 2 F), −123.3 (br s, 2 F), −123.4 (br s, 2 F), −124.0 (br s, 2 F), −126.7 to −126.8 (m, 2 F).

MS (EI, solid probe): m/z (%) = 427 (M⁺, 100).

1-(1H,1H,2H,2H-Perfluorododecyl)pyridazinium Bis(trifluoromethanesulfonat)(3j)
The same procedure was followed as for 3g; yield: 0.21 g (93%); yellow solid; mp 94.5 °C.

IR (KBr): 3096, 3023, 1590, 1433, 1346, 1202, 1148, 1054, 1001 cm⁻¹.

¹H NMR (300 MHz): δ = 3.40 (t, J = 7.3 Hz, 3 H), 5.52 (t, J = 7.2 Hz, 2 H), 8.82–8.86 (m, 1 H), 8.91–8.94 (m, 1 H), 9.80 (dd, J₁ = 0.9 Hz, J₂ = 4.0 Hz, 1 H), 10.2 (d, J = 5.8 Hz, 1 H).

¹C NMR (75 MHz): δ = 156.0, 152.1, 138.8, 137.4, 120.9 (q, J = 321.1 Hz), 105.5–123.0 (m), 58.54 (t, J = 4.7 Hz), 31.28 (t, J = 21.3 Hz).

¹⁹F NMR (282 MHz): δ = −79.99 (s, 6 F), –81.78 (t, J = 2.0 Hz, 3 F), –113.7 to −113.9 (m, 2 F), –122.3 (br s, 10 F), –123.3 (br s, 2 F), –124.0 (br s, 2 F), –126.8 (br s, 2 F).

MS (EI, solid probe): m/z (%) = 627 (M⁺, 100).

Anal. Calcd for C₁₉H₁₉F₂₂N₂O₃S: C, 27.91; H, 0.89. Found: C, 27.31; H, 0.73.

1-(1H,1H,2H,2H-Perfluorododecyl)pyridinium Trifluoromethanesulfonate (3j)
The same procedure was followed as for 3g; yield: 0.19 g (98%); yellow solid; mp 94.5 °C.

IR (KBr): 3119, 3028, 1594, 1437, 1259, 1206, 1150, 1032 cm⁻¹.

¹H NMR (300 MHz): δ = 3.41 (t, J = 7.2 Hz, 3 H), 18.9 Hz, 2 H), 5.50 (t, J = 7.1 Hz, 2 H), 8.81–8.85 (m, 1 H), 8.89–8.94 (m, 1 H), 9.78 (d, J = 4.0 Hz, 1 H), 10.22 (d, J = 5.5 Hz, 1 H).

¹C NMR (75 MHz): δ = 155.9, 152.4, 138.7, 137.4, 122.1 (q, J = 321.1 Hz), 108.1–124.3 (m), 58.46 (t, J = 4.8 Hz), 31.24 (t, J = 21.3 Hz).

¹⁹F NMR (282 MHz): δ = −79.04 (s, 3 F), –81.86 (t, J = 8.5 Hz, 3 F), –113.7 (br s, 2 F), –122.2 (br s, 10 F), –123.2 (br s, 2 F), –123.9 (br s, 2 F), –126.7 (br s, 2 F).

MS (EI, solid probe): m/z (%) = 627 (M⁺, 100).

Anal. Calcd for C₁₉H₁₉F₂₂N₂O₃S: C, 27.3; H, 0.84. Found: C, 23.71; H, 0.73.

1-Propylpyridazinium Bis(trifluoromethanesulfonat)amide (3k)
Yield: 0.19 g (95%); light yellow liquid; d = 1.60 g/cm³.

IR (KBr): 3113, 3046, 2980, 1590, 1435, 1347, 1190, 1136, 1058, 972, 969 cm⁻¹.

¹H NMR (300 MHz): δ = 1.04 (t, J = 7.4 Hz, 3 H), 2.24 (tq, J = 7.4 Hz, 7.4 Hz, 2 H), 5.01 (t, J = 7.3 Hz, 2 H), 8.71–8.75 (m, 1 H), 8.81–8.87 (m, 1 H), 9.72 (d, J = 3.8 Hz, 1 H), 9.99 (d, J = 5.7 Hz, 1 H).

¹C NMR (75 MHz): δ = 155.7, 150.7, 137.8, 137.1, 120.9 (q, J = 321.1 Hz), 68.03, 24.26, 10.66.

¹⁹F NMR (282 MHz): δ = −78.88 (s, 6 F).

MS (EI, solid probe): m/z (%) = 123 (M⁺, 100).


1-(1-Fluoroethyl)pyrazinium Hexafluorophosphate (5b)
Yield: 0.12 g (88%); colorless solid; mp 114.3 °C.

IR (KBr): 3126, 3054, 1448, 1157, 1118, 1054, 837 cm⁻¹.

¹H NMR (300 MHz): δ = 5.09–5.14 (m, 1 H), 5.25–5.30 (m, 1 H), 5.40 (dt, J = 26.2 Hz, J₂ = 4.2 Hz, 2 H), 9.33 (d, J = 2.1 Hz, 2 H), 9.72–9.76 (m, 2 H).

¹C NMR (75 MHz): δ = 152.4 (t, J = 1.4 Hz, 185.8 (d, J = 1.1 Hz, J₂ = 8.8 Hz, 82.23 (d, J = 171.6 Hz, J₂ = 0.9 Hz), 63.72 (dt, J = 18.8 Hz, J₂ = 4.5 Hz).

¹⁹F NMR (282 MHz): δ = −72.69 (d, J = 707.7 Hz, 6 F), –224.1 (tt, J₁ = 46.6 Hz, J₂ = 26.6 Hz, 1 F).

MS (EI, solid probe): m/z (%) = 127 (M⁺, 100).


1-(3,3,3-Trifluoropropyl)pyrazinium Bis(trifluoromethanesulfonat)amide (5d)
Yield: 0.22 g (96%); colorless solid; mp 94.7 °C.

IR (KBr): 3119, 3047, 1452, 1346, 1258, 1190, 1128, 1057, 1022, 793 cm⁻¹.

¹H NMR (300 MHz): δ = 3.39–3.48 (m, 2 H), 5.41 (t, J = 7.2 Hz, 2 H), 9.53 (d, J = 2.5 Hz, 2 H), 9.76–9.79 (m, 2 H).

¹C NMR (75 MHz, acetone-d₆): δ = 152.6 (t, J = 1.3 Hz, 183.6 (t, J = 8.9 Hz, 126.4 (q, J₁ = 1.5 Hz, J₂ = 274.6 Hz), 121.0 (q, J = 321.2 Hz), 56.88 (q, J = 4.5 Hz), 34.88 (q, J = 30.3 Hz).

¹⁹F NMR (282 MHz): δ = −65.46 (d, J = 10.5 Hz, 3 F), –79.90 (s, 6 F).

MS (EI, solid probe): m/z (%) = 177 (M⁺, 100).


1-(3,3,3-Trifluoropropyl)pyrazinium Hexafluorophosphate (5e)
Yield: 0.14 g (87%); colorless solid; mp 127.6 °C.

IR (KBr): 3126, 1435, 1403, 1255, 1182, 1130, 841, 809 cm⁻¹.

1H NMR (300 MHz): \( \delta = 3.37–3.47 \) (m, 2 H), 5.37 (t, \( J = 7.1 \) Hz, 2 H), 9.47 (s, 2 H), 9.74–9.77 (m, 2 H).

13C NMR (75 MHz): \( \delta = 152.5 \) (t, \( J = 1.2 \) Hz), 138.5 (t, \( J = 8.9 \) Hz), 126.4 (qq, \( J = 1.7 \) Hz, \( J = 72.6 \) Hz), 56.85 (q, \( J = 4.5 \) Hz), 34.81 (q, \( J = 30.2 \) Hz).

19F NMR (282 MHz): \( \delta = -65.46 \) (t, \( J = 10.4 \) Hz, 3 F), –72.61 (d, \( J = 706.4 \) Hz, 6 F).

MS (EI, solid probe): m/z (%) = 177 (M+*, 100).

Anal. Calcd for C7H8F3N3O4S: C, 33.70; H, 2.89. Found: C, 33.28; H, 2.74.

1-Propylpyrazinium Bis(trifluoromethanesulfonyl)amide (5c)

Yield: 0.18 g (90%); yellow solid; mp 102.4 °C.

IR (KBr): 3080, 1626, 1568, 1445, 1349, 1194, 1139, 1057, 792 cm–1.

1H NMR (300 MHz): \( \delta = 3.29–3.42 \) (m, 2 H), 5.27 (t, \( J = 7.4 \) Hz, 2 H), 9.41 (d, \( J = 3.3 \) Hz, 2 H), 9.64–9.68 (m, 2 H).

13C NMR (125 MHz): \( \delta = 152.5 \) (t, \( J = 1.3 \) Hz), 139.3 (t, \( J = 8.9 \) Hz), 126.4 (qq, \( J = 1.6 \) Hz, \( J = 72.6 \) Hz), 56.90 (q, \( J = 4.5 \) Hz), 34.62 (q, \( J = 30.2 \) Hz).

19F NMR (282 MHz): \( \delta = -60.60 \) (t, \( J = 11.2 \) Hz, 3 F).

MS (EI, solid probe): m/z (%) = 177 (M+*, 100).

Anal. Calcd for C7H8F3N3O4S: C, 33.70; H, 2.89. Found: C, 33.28; H, 2.74.

1-Propylpyrazinium Bis(trifluoromethanesulfonyl)amide (5g)

Yield: 0.18 g (90%); yellow solid; mp 102.4 °C.

IR (KBr): 3080, 1626, 1568, 1445, 1349, 1194, 1139, 1057, 792 cm–1.

1H NMR (300 MHz): \( \delta = 3.29–3.42 \) (m, 2 H), 5.27 (t, \( J = 7.4 \) Hz, 2 H), 9.41 (d, \( J = 3.3 \) Hz, 2 H), 9.64–9.68 (m, 2 H).

13C NMR (125 MHz): \( \delta = 152.5 \) (t, \( J = 1.3 \) Hz), 139.3 (t, \( J = 8.9 \) Hz), 126.4 (qq, \( J = 1.6 \) Hz, \( J = 72.6 \) Hz), 56.90 (q, \( J = 4.5 \) Hz), 34.62 (q, \( J = 30.2 \) Hz).

19F NMR (282 MHz): \( \delta = -60.60 \) (t, \( J = 11.2 \) Hz, 3 F).

MS (EI, solid probe): m/z (%) = 177 (M+*, 100).

Anal. Calcd for C7H8F3N3O4S: C, 33.70; H, 2.89. Found: C, 33.28; H, 2.74.

1-Propylpyrazinium Bis(trifluoromethanesulfonyl)amide (5f)

Yield: 0.18 g (90%); yellow solid; mp 102.4 °C.

IR (KBr): 3080, 1626, 1568, 1445, 1349, 1194, 1139, 1057, 792 cm–1.

1H NMR (300 MHz): \( \delta = 3.29–3.42 \) (m, 2 H), 5.27 (t, \( J = 7.4 \) Hz, 2 H), 9.41 (d, \( J = 3.3 \) Hz, 2 H), 9.64–9.68 (m, 2 H).

13C NMR (125 MHz): \( \delta = 152.5 \) (t, \( J = 1.3 \) Hz), 139.3 (t, \( J = 8.9 \) Hz), 126.4 (qq, \( J = 1.6 \) Hz, \( J = 72.6 \) Hz), 56.90 (q, \( J = 4.5 \) Hz), 34.62 (q, \( J = 30.2 \) Hz).

19F NMR (282 MHz): \( \delta = -60.60 \) (t, \( J = 11.2 \) Hz, 3 F).

MS (EI, solid probe): m/z (%) = 177 (M+*, 100).

Anal. Calcd for C7H8F3N3O4S: C, 33.70; H, 2.89. Found: C, 33.28; H, 2.74.
1H NMR (300 MHz): & = 4.11 (s, 3 H), 4.76 (dt, J = 27.8 Hz, J2 = 4.4 Hz, 2 H), 4.92 (dt, J1 = 46.4 Hz, J2 = 4.4 Hz, 2 H), 7.76 (t, J = 1.7 Hz, 1 H), 7.78 (t, J = 1.7 Hz, 1 H), 9.06 (s, 1 H).
13C NMR (75 MHz): & = 137.9, 125.0, 123.8, 120.9 (q, J = 129.1 Hz), 82.43 (d, J = 169.1 Hz), 50.85 (d, J = 19.6 Hz), 36.75.
19F NMR (282 MHz): & = 28.2 Hz, 1 F).

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