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Study on the reactions of fluoroalkanesulfonyl azides with pyrazine and its derivatives

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ABSTRACT

The thermal reactions of fluoroalkanesulfonyl azides $R_fSO_2N_3$ with pyrazine and its derivatives are studied in detail. All the reactions involved the fluoroalkanesulfonyl nitrene intermediates R_fSO_3N: which was captured by pyrazine to give the pyrazinium *N*-fluoroalkanesulfonyl ylides $C_4NH_4N^+-{}^-NSO_2R_f$ and hydrogen abstraction product $R_fSO_2NH_2$, but no corresponding *N*-pyrazinyl fluoroalkanesulfonyl amide derivatives $R_fSO_2NHC_4N_2H_3$ were isolated. Excess azides did not afford the bis*N*-ylide product $R_fSO_2N^-{}^-{}^+NC_4H_4N^+-{}^-NSO_2R_f$.

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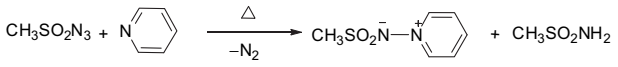
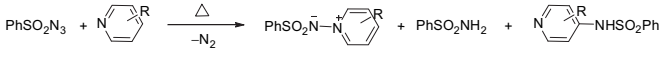
1. Introduction

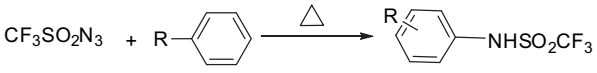
The reaction of fluoroalkanesulfonyl azides with aromatic compounds, such as benzene, pyridine and their derivatives were studied very early by Curtius et al.[1] Later, Abramovitch et al.[2] reinvestigated these reactions and found that the reaction product of sulfonyl azide with pyridine was pyridinium *N*-sulfonylimide ylide and no 2-, 3-, or 4-amino pyridine as reported by Curtius et al., the reaction gave three products in the case of sulfonyl azide reacted with methyl substituted pyridine.





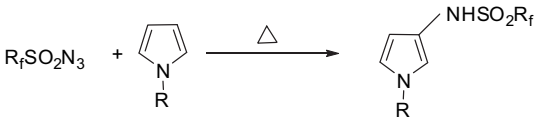
R=Me

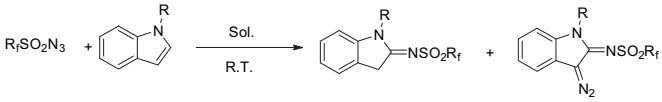
Comparing with the hydrocarbon analogues, the reactions of fluorinated sulfonyl azides $R_fSO_2N_3$ have been studied rarely. In 1984 Kamigate et al.[3] first reported the thermal reactions of $CF_3SO_2N_3$ with benzene, toluene, and anisole.



R=H, CH_3, OCH_3

During the course of our continuous study on the fluoroalkanesulfonyl azides since 1994, we have reported their reactions with alkene, triphenylphosphine, DMSO, pyridine, benzene, indole, pyrrole, and their derivatives.[4] For example:





As an extension of the exploration of the fluoroalkanesulfonyl nitrenes, recently we systematically investigated the thermal reaction of **1** with pyrazine and its derivatives and found that the products of all reactions were pyrazinium *N*-fluoroalkanesulfonyl imides $C_4NH_4N^+-{}^-NSO_2R_f$. We postulated that the electron-deficient singlet

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nitrene intermediate R_fSO_2N: formed by thermal decomposition of **1** was captured by pyrazine in the donor-acceptor fashion.

Herein we wish to report these results.

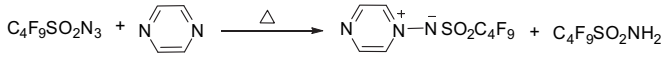
2. Results and discussion

The reaction of perfluorobutanesulfonyl azide **1a** (2.2 mmol) with pyrazine **2a** (2.0 mmol) was first carried out at 80 °C without solvent, after stirring for 4 h, TLC analysis showed that no reaction occurred. Then the reaction temperature was increased to 120 °C, the gas emission was observed, the reaction mixture was stirred for another 8 h, the releasing of gas stopped and TLC analysis indicated that the reaction was completed. Two products **3aa** and **4a** were separated and purified by column chromatography easily using petroleum ether and ethyl acetate (2:1, v/v) as elute. The more polar product pyrazinium *N*-fluoroalkanesulfonylimino ylide **3aa** was obtained in 34% yield.

It is well known that copper ion could catalyze the nitrene formation.[5] In our case, it was also found that when CuI (10 mol %) was added to the reaction mixture the nitrogen emitted at 100 °C (oil bath) and the reaction was completed in 6 h, however, the yield of **3aa** decreased a little.

When two equivalence amount of pyrazine was used, the thermal reaction time was unchanged (Table 1, entry 4), that means this reaction rate is independent on the concentration of pyrazine. Also,

Table 1
Reaction results of the azides **1a** with pyrazines **2a** under different conditions



1a **2a** **3aa** **4a**

Entry	Cat.	Mole ratio[a]	Temp (°C)	Time (h)	Product and yield (%)[b]	
					3aa	**4a**
1	—	1.1:1	80	4	N.R	
2	—	1.1:1	120	8	34	33
3	CuI (10 mol %)	1.1:1	100	6	31	33
4	—	1:2	120	8	28[c]	38
5	—	2:1	120	10	35	62

[a] Mole ratio of **1a**:**2a**.
[b] Isolated yield based on **2a**.
[c] Yield based on **1a**.

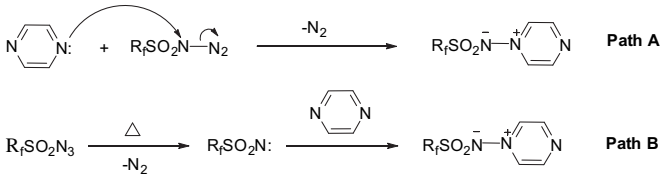
using excess azide **1a** (2 equiv) and prolonged the reaction time (10 h) did not afford the bis*N*-ylide product.

All the results were illustrated in Table 1.

The product **3aa** is stable yellow solid, when heated to melt (>110 °C) it did not decompose. Its structure was fully characterized by spectral methods and element analysis. For example, the ^{1}H NMR spectrum of **3aa** shows two doublet peaks at 9.13 and 8.73 ppm, both are down field comparing with the starting pyrazine, which is one singlet at 8.63 ppm. The ^{19}F NMR spectrum of **3aa** is very similar with the starting azide **1a**. Its MS (ESI) has a strong molecular ion peak (*m*/*z* 378). Another product $C_4F_9SO_2NH_2$ obtained in 33% yield and was confirmed with author's sample.

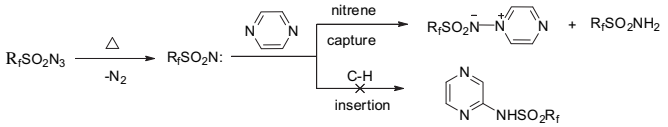
Under the same reaction condition (Table 1, entry 2) other fluoroalkanesulfonyl azides **(1b,1c)** reacted with **2a** and its derivatives **(2b–e)** gave similar results. It was noticed that in all these reactions no *N*-pyrazinyl fluoroalkanesulfonyl amide R_fSO_2NHAr was isolated.

There are two possible reaction pathways for this reaction, i.e., a simultaneous attack of the pyrazine nitrogen atom on the azide

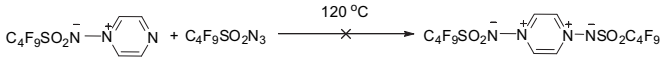


with the release of N_2 (Path A) or a direct trapping of electrophilic nitrene by pyrazine (Path B).

As mentioned above, the thermal reaction rate is independent on the concentration of pyrazine (Table 1, entry 4) and can be promoted by catalytic amount of CuI (Table 1, entry 3), it is clear that in the reaction the fluoroalkanesulfonyl nitrene intermediate should be involved (Path B). Because of the strong electro-withdrawing ability of R_fSO_2 group, the very electrophilic nitrene R_fSO_2N: was readily captured by pyrazine and did not give the nitrene insertion product amide.

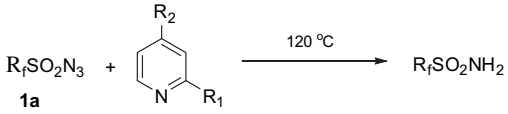


Due to the positively charged pyrazine ring of the *N*-ylide product **3aa** decreased its trapping ability as electron donor, the reaction did not afford bis*N*-ylide even excess azide was further heated with **3aa.**



3aa

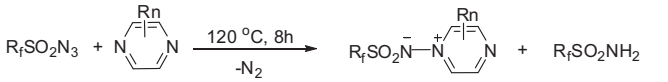
As we have previously reported that the reaction of **1** with 2- or 4-picoline gave fluoroalkanesulfonyl amide as the sole product:



1a

R_1=CH_3, R_2=H; R_1=H, R_2=CH_3

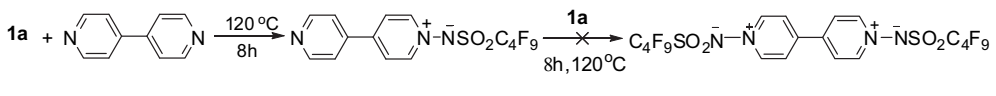
However, for the pyrazine derivatives, such as methyl pyrazine (**2b**), 2,5-dimethyl pyrazine (**2d**), and 2,3-dimethyl pyrazine (**2e**), they all gave corresponding *N*-ylide products when heated with the azide **1**.



1 **2** **3** **4**

R_f = C_4F_9 **(1a)** $HC_2F_4OC_2F_4$ **(1b)** $IC_2F_4OC_2F_4$ **(1c)** R=CH_3, n=1, 2

The structure of **3ad** was further confirmed by single crystal X-ray diffraction analysis, its molecular structure was shown in



5g **6ag**

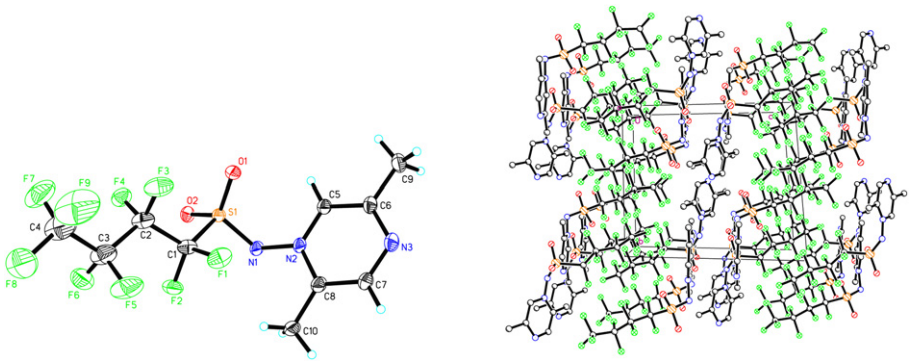


Fig. 1. The molecular structure and packing map of **3ad**.

Fig. 1. The bond length of N_1–N_2 (1.407 Å) indicated its single bond character.

Using two equivalence amount of **1a** and prolonged the reaction time (up to 16 h), the 2,5-dimethyl pyrazine (**2d**), which has two electron-donating groups on the *ortho* position of the nitrogen atom of the pyrazine ring did not afford the bis*N*-ylide.

Similarly, treatment of 4,4-dipyridine (**5g**) with **1a** gave corresponding *N*-ylide **6ag** in 28% yield. However, we also failed to obtain its bis*N*-ylide product, when **6ag** was further reacted with 1.1 equiv of **1a**.

2-Cyanopyrazine (**2f**), which has an electron-withdrawing group on the pyrazine ring did not afford the *N*-ylide product.

All the results are summarized in Table 2.

3. Conclusion

In summary, the thermolysis reaction of fluoroalkanesulfonyl azides with pyrazine and its derivatives gave a new kind of pyrazinium *N*-ylide via the fluoroalkanesulfonyl nitrene intermediate. It is notable that the chemical behavior of fluoroalkanesulfonyl azides $R_fSO_2N_3$ **1** is different to the hydrocarbon analogies $R_fSO_2N_3$, in all reactions of **1** with pyrazine or its derivatives, no corresponding C–H insertion product R_fSO_2NHAr are formed. The electron-poor nitrene intermediate R_fSO_2N: is more favored to combine with an electron donor affording the pyrazinium *N*-fluoroalkanesulfonyl imides.

4. Experimental

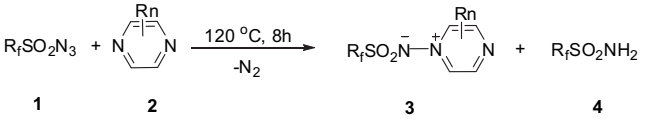
4.1. General

Melting point are measured on a Temp-Melt apparatus and are uncorrected. ^1H (300 MHz) and ^{19}F NMR(282 MHz) spectra were recorded on a Bruker AM-300 ultra shield spectrometer with Me_4Si and $CFCl_3$ as the internal and external standards. FT-IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low resolution mass spectra (LRMS) and high resolution mass spectra (HRMS) were obtained on a Finnigan GC-MS 4021 and a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 eV) or electrospray ionization. Elemental analyses were performed by this institute.

4.2. General procedure

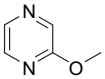
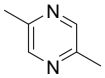
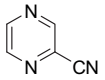
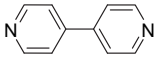
Perfluorobutanesulfonyl azides **1a** (715 mg, 2.2 mmol) and pyrazine **2a** (2.0 mmol) was mixed without solvent at room temperature, this reaction mixture stirred for 8 h at 120 °C, TLC analysis showed the reaction was completed. The product **3aa** was obtained by flash column chromatography (using petroleum ether/ethyl acetate=2:1 as eluant) as a yellow solid in 34% yield (234 mg). The product **4a** (179 mg, 33%) was confirmed with author's sample.

Table 2
Reaction results of azides **1** with pyrazine and its derivatives[a]



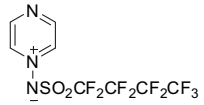
1 **2** **3** **4**

R_f = C_4F_9 (**1a**) $HC_2F_4OC_2F_4$ (**1b**) $IC_2F_4OC_2F_4$ (**1c**) R=CH_3, n=1, 2

Entry	Azide **1**	Pyrazine **2**		Product and yield (%)
1	**1a**	 (**2a**)	**3aa(34)**	**4a(33)**
2	**1b**		**3ba(23)**	**4b(34)**
3	**1c**		**3ca(20)**	**4c(33)**
4	**1a**	 (**2b**)	**3ab(31)**	**4a(35)**
5	**1b**		**3bb(28)**	**4b(37)**
6	**1c**		**3cb(21)**	**4c(36)**
7	**1a**	 (**2c**)	**3ac(35)**	**4a(33)**
8	**1b**		**3bc(30)**	**4b(35)**
9	**1a**	 (**2d**)	**3ad(36)**	**4a(35)**
10	**1b**		**3bd(30)**	**4b(34)**
11	**1c**		**3cd(24)**	**4c(37)**
12	**1a**	 (**2e**)	**3ae(28)**	**4a(36)**
13	**1b**		**3be(26)**	**4b(34)**
14	**1c**		**3ce(21)**	**4c(33)**
15	**1a**	 (**2f**)	**3af(0)**	**4a(62)**
16	**1a**	 (**6g**)	**6ag(28)**	**4a(35)**

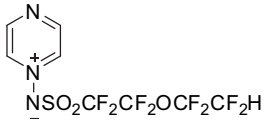
[a] Reaction carried out at 120 °C. Mole ratio of **1:2**=1.1:1. Reaction time: 8 h.

*4.2.1. N-Perfluorobutanesulfonylpyrazinium imide (**3aa**)*



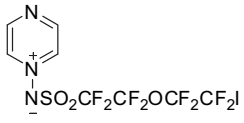
Yellow solid, mp 106–108 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.13 (2H, d, J=3.9 Hz), 8.73 (2H, d, J=3.9 Hz) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.8 (3F, t, J=10.3 Hz, CF_3), −111.0 (2F, t, J=14.9 Hz, CF_2S), −121.4 (2F, s, CF_2), −126.0 (2F, t, J=14.1 Hz, CF_2) ppm. IR (KBr) cm^{-1}: 3103, 3077, 3036, 1608, 1484, 1439, 1357, 1133, 1035. MS (ESI) m/z: 378.0 ([M+H]$^+$), 395.2 ([M+NH$_4$]$^+$). Anal. Calcd for $C_8H_4F_9N_3O_2S$: C, 25.47; H, 1.07; N, 11.14%. Found: C, 25.61; H, 1.27; N, 11.15%.

*4.2.2. N-(1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy) ethylsulfonyl) pyrazinium imide (**3ba**)*



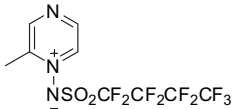
Yellow solid, mp 48–50 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.11 (2H, d, J=3.0 Hz), 8.71 (2H, d, J=3.0 Hz), 5.86 (1H, tt, J=52.8, 3.0 Hz HCF_2) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): −81.7 (2F, t, J=12.7 Hz, CF_2O), −88.7 (2F, s, OCF_2), −114.5 (2F, s, CF_2S), −137.4 (2F, d, J=51.9 Hz, CF_2H) ppm. IR (KBr) cm^{-1}: 3122, 3015, 1596, 1477, 1430, 1353, 1283, 1130, 1015. MS (ESI) m/z: 376.0 ([M+H]$^+$), 393.0 ([M+NH$_4$]$^+$). Anal. Calcd for $C_8H_5F_8N_3O_3S$: C, 25.61; H, 1.34; N, 11.20%. Found: C, 25.79; H, 1.43; N, 11.54%.

*4.2.3. N-(1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy) ethylsulfonyl) pyrazinium imide (**3ca**)*



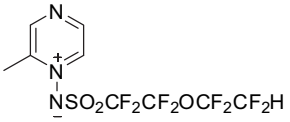
Yellow solid, mp 108–109 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.11 (2H, d, J=4.5 Hz), 8.71 (2H, d, J=4.5 Hz) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −64.9 (2F, s, ICF_2), −82.0 (2F, t, J=11.8 Hz, CF_2O), −85.6 (2F, t, J=9.7 Hz, OCF_2), −114.4 (2F, s, CF_2S) ppm. IR (KBr) cm^{-1}: 3114, 3055, 2988, 2306, 1947, 1715, 1595, 1429, 1354, 1294, 1220. MS (ESI) m/z: 501.8 ([M+H]$^+$), 519.0 ([M+NH$_4$]$^+$). Anal. Calcd for $C_8H_4F_8I$-N_3O_3S: C, 19.18; H, 0.80; N, 8.39%. Found: C, 19.13; H, 0.80; N, 8.30%.

*4.2.4. 1-Perfluorobutanesulfonyl-2-methylpyrazinium imide (**3ab**)*



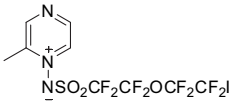
Yellow solid, mp 110–112 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.98 (1H, d, J=3.9 Hz), 8.55 (1H, s), 8.52 (1H, d, J=3.9 Hz), 2.81 (3H, s, $ArCH_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.9 (3F, t, J=8.7 Hz, CF_3), −111.1 (2F, t, J=13.1 Hz, CF_2S), −121.4 (2F, s, CF_2), −126.1 (2F, t, J=13.1 Hz, CF_2) ppm. IR (KBr) cm^{-1}: 3128, 2935, 1599, 1489, 1349, 1292, 1264, 1218, 1017. MS (ESI) m/z: 390.0 ([M−H]$^-$). Anal. Calcd for $C_9H_6F_9N_3O_2S$: C, 27.63; H, 1.55; N, 10.74%. Found: C, 27.85; H, 1.36; N, 10.70%.

*4.2.5. 1-(1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)ethylsulfonyl) -2-methylpyrazinium imide (**3bb**)*



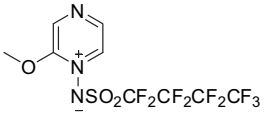
Yellow solid, mp 78–80 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.96 (1H, d, J=3.9 Hz), 8.52 (1H, s), 8.50 (1H, d, J=3.9 Hz), 5.87 (1H, tt, J=52.5, 3.0 Hz, HCF_2), 2.80 (3H, s, $ArCH_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.7 (2F, t, J=12.5 Hz, CF_2O), −88.7 (2F, s, OCF_2), −114.4 (2F, s, CF_2S), −137.4 (2F, d, J=51.6 Hz, CF_2H) ppm. IR (KBr) cm^{-1}: 3116, 3041, 1597, 1473, 1351, 1284, 1209, 1018. MS (ESI) m/z: 390.2 ([M+H]$^+$). Anal. Calcd for $C_9H_7F_8N_3O_3S$: C, 27.77; H, 1.81; N, 10.80%. Found: C, 27.78; H, 1.81; N, 10.75%.

*4.2.6. 1-(1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy) ethylsulfonyl)-2-methylpyrazinium imide (**3cb**)*



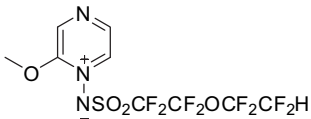
Yellow solid, mp 118–120 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.89 (1H, d, J=3.6 Hz), 8.53 (1H, s), 8.51 (1H, d, J=3.6 Hz), 2.80 (3H, s, $ArCH_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −64.9 (2F, d, J=12.4 Hz, ICF_2), −82.0 (2F, t, J=11.7 Hz, CF_2O), −85.6 (2F, t, J=10.7 Hz, OCF_2), −114.3 (2F, s, CF_2S) ppm. IR (KBr) cm^{-1}: 3101, 3073, 3035, 1603, 1483, 1454, 1355, 1297, 1220, 1022. MS (ESI) m/z: 516.0 ([M+H]$^+$), 538.0 ([M+Na]$^+$). Anal. Calcd for $C_9H_6F_8IN_3O_3S$: C, 20.98; H, 1.17; N, 8.16%. Found: C, 21.08; H, 1.20; N, 8.45%.

*4.2.7. 1-Perfluorobutanesulfonyl-2-methoxylpyrazinium imide (**3ac**)*



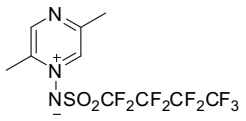
Yellow solid, mp 146–148 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.55 (1H, d, J=3.6 Hz), 8.35 (1H, s), 8.22 (1H, d, J=3.6 Hz), 4.16 (3H, s, OCH_3) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.9 (3F, t, J=9.7 Hz, CF_3), −111.1 (2F, t, J=15.7 Hz, CF_2S), −121.4 (2F, s, CF_2), −126.1 (2F, t, J=11.3 Hz, CF_2) ppm. IR (KBr) cm^{-1}: 3092, 3035, 1612, 1535, 1486, 1414, 1351, 1132, 1052, 1007. MS (ESI) m/z: 408.2 ([M+H]$^+$). Anal. Calcd for $C_9H_6F_9N_3O_3S$: C, 26.55; H, 1.49; N, 10.32%. Found: C, 26.61; H, 1.59; N, 10.13%.

*4.2.8. 1-(1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrofluoroethoxy) ethylsulfonyl)-2-methoxypyraziniumimide (**3bc**)*



Yellow solid, mp 85–87 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.53 (1H, d, J=3.6 Hz), 8.34 (1H, s), 8.21 (1H, d, J=3.6 Hz), 5.86 (1H, tt, J=52.5, 3.3 Hz, HCF_2), 4.15 (3H, s, OCH_3) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.7 (2F, t, J=11.8 Hz, CF_2O), −88.8 (2F, s, OCF_2), −114.5 (2F, s, CF_2S), −137.5 (2F, d, J=55.8 Hz, CF_2H) ppm. IR (KBr) cm^{-1}: 3128, 2958, 1605, 1537, 1487, 1411, 1351, 1156. MS (ESI) m/z: 406.0 ([M+H]$^+$). Anal. Calcd for $C_9H_7F_8N_3O_4S$: C, 26.68; H, 1.74; N, 10.37%. Found: C, 26.69; H, 1.78; N, 10.65%.

*4.2.9. 1-Perfluorobutanesulfonyl-2,5-dimethylpyrazinium imide (**3ad**)*

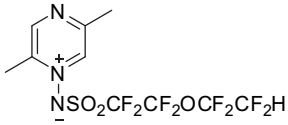


White solid, mp 109–111 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.86 (1H, s), 8.72 (1H, s), 2.80 (3H, s, $ArCH_3$), 2.73 (3H, s, $ArCH_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.9 (3F, t, J=11.0 Hz, CF_3), −113.2 (2F, t, J=15.7 Hz, CF_2S), −121.2 (2F, s, CF_2), −126.1 (2F, t, J=14.2 Hz, CF_2) ppm. IR (KBr) cm^{-1}: 3134, 3043, 1598, 1493, 1455, 1352, 1142, 1035, 1011. MS (ESI) m/z: 406.0 ([M+H]$^+$), 444.0 ([M+K]$^+$). Anal. Calcd for $C_{10}H_8F_9N_3O_2S$: C, 29.64; H, 1.99; N, 10.37%. Found: C, 29.52; H, 1.98; N, 10.60%.

Crystal data for $C_{10}H_8F_9N_3O_2S$: MW=405.26, triclinic, space group P-1, a=11.5617(18), b=11.5701(18), c=12.982(2) Å, α=80.724 (2), β=71.759(2), γ=68.074(2), V=1528.2(4) Å^3, Z=2, Dc=1.761 mg/m^3, F(000)=808, crystal dimension 0.45 mm×0.33 mm×0.27 mm, radiation Mo Kα (l=0.71073 Å), 5.30≤2θ≤50.48, intensity data were collected at 173 K with a Bruker APEX-II CCD diffractometer in the range of −14≤h≤14, −14≤k≤13, −14≤l≤16; The structure was solved by a direct method, all non-hydrogen atoms were positioned and anisotropic thermal parameters refined from 5795 observed reflections with R (int)=0.0344 by a full-matrix least-squares technique converged to R=0.0658 and Rw=0.2011.

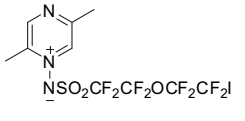
CCDC reference number is 802444.

*4.2.10. 1-(1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrofluoroethoxy)ethylsulfonyl)-2,5-dimethyl pyrazinium imide (**3bd**)*



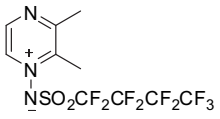
Yellow solid, mp 65–67 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.85 (1H, s), 8.71 (1H, s), 5.86 (1H, tt, J=52.5, 3.0 Hz, HCF_2), 2.80 (3H, s, $ArCH_3$), 2.72 (3H, s, $ArCH_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.4 (2F, t, J=12.1 Hz, CF_2O), −88.7 (2F, s, OCF_2), −116.6 (2F, s, CF_2S), −137.3 (2F, d, J=53.0 Hz, CF_2H) ppm. IR (KBr) cm^{-1}: 3141, 3061, 1600, 1493, 1449, 1342, 1280, 1212, 1019. MS (ESI) m/z: 404.0 ([M+H]$^+$), 442.0 ([M+K]$^+$). Anal. Calcd for $C_{10}H_9F_8N_3O_3S$: C, 29.78; H, 2.25; N, 10.42%. Found: C, 29.72; H, 2.28; N, 10.52%.

*4.2.11. 1-(1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy) ethylsulfonyl)-2,5-dimethylpyrazinium imide (**3cd**)*



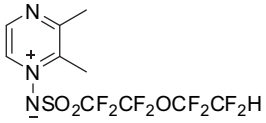
Yellow solid, mp 87–89 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.86 (1H, s), 8.72 (1H, s), 2.80 (3H, s, $ArCH_3$), 2.73 (3H, s, $ArCH_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −64.7 (2F, s, ICF_2), −81.6 (2F, t, J=12.1 Hz, CF_2O), −85.5 (2F, s, OCF_2), −116.3 (2F, s, CF_2S) ppm. IR (KBr) cm^{-1}: 3127, 3053, 2935, 1600, 1491, 1346, 1293, 1232. MS (ESI) m/z: 530.0 ([M+H]$^+$), 568.0 ([M+K]$^+$). Anal. Calcd for $C_{10}H_8F_8IN_3O_3S$: C, 22.70; H, 1.52; N, 7.94%. Found: C, 22.86; H, 1.33; N, 8.04%.

*4.2.12. 1-Perfluorobutanesulfonyl-2,3-dimethylpyrazinium imide (**3ae**)*



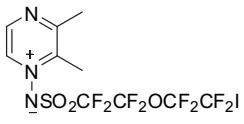
Yellow solid, mp 106–108 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.73 (1H, d, J=3.9 Hz) 8.69 (1H, d, J=3.9 Hz), 2.88 (3H, s, $ArCH_3$), 2.82 (3H, s, $ArCH_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.9 (3F, t, J=10.4 Hz, CF_3), −112.9 (2F, t, J=13.3 Hz, CF_2S), −121.2 (2F, s, CF_2), −126.1 (2F, t, J=13.3 Hz, CF_2) ppm. IR (KBr) cm^{-1}: 3133, 1667, 1586, 1447, 1349, 1166, 1135, 1074, 1031. MS (ESI) m/z: 406.0 ([M+H]$^+$). Anal. Calcd for $C_{10}H_8F_9N_3O_2S$: C, 29.64; H, 1.99; N, 10.37%. Found: C, 29.68; H, 2.19; N, 10.09%.

*4.2.13. 1-(1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrofluoroethoxy)ethylsulfonyl)-2,3-dimethlpyrazinium imide (**5be**)*



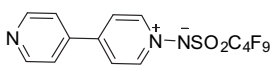
Yellow solid, mp 76–78 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.71 (1H, d, J=3.9), 8.67 (1H, d, J=3.9 Hz), 5.85 (1H, tt, J=52.5, 3.0 Hz, HCF_2), 2.88 (3H, s, $ArCH_3$), 2.80 (3H, s, $ArCH_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.4 (2F, t, J=12.7 Hz, CF_2O), −88.6 (2F, s, OCF_2), −116.2 (2F, s, CF_2S), −137.3 (2F, d, J=52.2 Hz, CF_2H) ppm. IR (KBr) cm^{-1}: 3135, 3013, 1587, 1447, 1344, 1282, 1131, 1075. MS (ESI) m/z: 404.0 ([M+H]$^+$). Anal. Calcd for $C_{10}H_9F_8N_3O_3S$: C, 29.78; H, 2.25; N, 10.42%. Found: C, 29.70; H, 2.20; N, 10.31%.

*4.2.14. 1-(1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy) ethylsulfonyl)-2,3-dimethylpyrazinium imide (**3ce**)*



Yellow solid, mp 108–110 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.72 (1H, s), 8.69 (1H, s) 2.89 (3H, s, $ArCH_3$), 2.81 (3H, s, $ArCH_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −64.6 (2F, s, ICF_2), −81.7 (2F, t, J=13.8 Hz, CF_2O), −85.4 (2F, m, OCF_2), −116.0 (2F, s, CF_2S) ppm. IR (KBr) cm^{-1}: 3097, 3027, 1448, 1349, 1300, 1219, 1141, 1093. MS (ESI) m/z: 530.0 ([M+H]$^+$). Anal. Calcd for $C_{10}H_8F_8IN_3O_3S$: C, 22.70; H, 1.52; N, 7.94%. Found: C, 22.37; H, 1.61; N, 7.74%.

*4.2.15. N-Perfluorobutanesulfonyl-4,4-dipyradine imide (**6ag**)*



Yellow solid, mp 140–142 °C. ^{1}H NMR (acetone-d_6, 300 MHz): δ 8.98 (2H, d, J=7.2 Hz), 8.89 (2H, d, J=7.2 Hz), 8.50 (2H, d, J=6.0 Hz), 8.02 (2H, d, J=6.0 Hz) ppm. ^{13}C NMR (acetone-d_6, 100 MHz): δ 151.6, 150.8, 146.4, 142.2, 125.7, 122.2. ^{19}F NMR (acetone-d_6, 282 MHz): δ −81.1 (3F, t, J=8.2 Hz, CF_3), −111.6 (2F, t, J=14.4 Hz, CF_2S), −121.1 (2F, s, CF_2), −126.0 (2F, t, J=13.3 Hz, CF_2) ppm. IR (KBr) cm^{-1}: 3126, 3046, 1627, 1600, 1485, 1114, 1033. MS (ESI) m/z: 453.8 ([M+H]$^+$). HRMS (ESI) m/z 476.0101 ([M+Na]$^+$), $C_{14}H_8F_9N_3O_2SNa$ required 476.0086).

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.01.077.

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