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A simple access to metallic or onium bistrifluoromethanesulfonimide salts

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ABSTRACT

Numerous salts of the $(CF_3SO_2)_2N^-$ anion, called TFSI, were prepared according to an original one-pot procedure. First, *N*-benzyl trifluoromethanesulfonimide (*N*-benzyl triflimide) was treated with ethanol to form an oxonium intermediate, which was then neutralized by various bases to provide metallic or trialkylammonium triflimides salts. Alternatively, *N*-benzyl triflimide was directly treated with trialkyl sulfonium, quaternary ammonium or phosphonium halides to deliver the corresponding triflimide derivatives. *N*-Benzyl triflimide can be also reacted with di- or tri-alkylamines and phosphines to get benzyl onium salts. Analogous reactions can be carried out with *N*-allyl triflimide. Therefore, the TFSI anion can be very easily and expediently associated with a wide range of metallic or organic cations. Such salts can find applications as electrolytes for batteries and fuel cells, ionic liquids or Lewis acids.

1. Introduction

Since its first synthesis,[1] the $(CF_3SO_2)_2N^-$ anion was intensively studied for several applications, which, actually, are dependent on the nature of the associated cation: associated with lithium, the corresponding salt is used as electrolyte for lithium-polymer batteries,[2] while associated with protic ammonium, it is a promising electrolyte for fuel cells.[3] Moreover, several ionic liquids are constituted by this anion associated with tetraalkylammonium, *N*-alkylimidazolium, *N*-alkylpyridinium or alkylphosphonium cations.[4] Neutral derivatives of TFSI have also been prepared and have found application in synthetic chemistry. For example, $(CF_3SO_2)_2N–H$ (TFSIH) is a strong Brønsted acid, useful as catalyst,[5] whereas its *N*-fluoro derivative $(CF_3SO_2)_2N–F$ is one of the most powerful reagent for electrophilic fluorination.[6] Salts of TFSI and derivatives have also been considered as intermediates for agricultural chemicals[7] or as ligand for metals.[8]

In all these cases, the interest of TFSI salts or derivatives is mainly due to the properties induced by the presence of the two CF_3SO_2 groups.[1a] Their strong electron-withdrawing effect enhances the acidity of the hydrogen in TFSIH while, by enhancing the dispersion (and eventually the delocalization) of the negative charge, it stabilizes the conjugated base $(CF_3SO_2)_2N^-$, which, therefore, is a poor base and a poor nucleophile. An additional consequence is that $(CF_3SO_2)_2N^-$ M^+ also presents a high ionic conductivity and a huge resistance to oxidation.

With such a wide range of application, the synthesis of TFSI salts obviously received considerable attention. The first synthesis, reported by DesMarteau et al. in 1984, was based on the reaction of trifluoromethanesulfonyl fluoride with the sodium salt of *N*-trimethylsilyl-trifluoromethanesulfonamide.[1] Other research groups prepared TFSI salts by coupling trifluoromethanesulfonyl fluoride with trifluoromethanesulfonamide in the presence of a base.[9] A simpler method is the direct reaction of trifluoromethanesulfonyl fluoride with liquid ammonia.[10] The reaction of trifluoromethanesulfonyl fluoride with silazanes[11] [such as $LiN(SiMe_3)_2$] or trifluoroacetamides[12] has been also reported. However, all these methods use gaseous trifluoromethanesulfonyl fluoride and, most of the time, harsh conditions such as high

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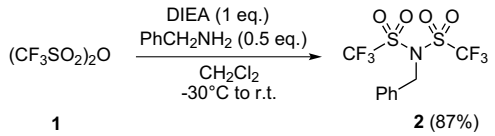
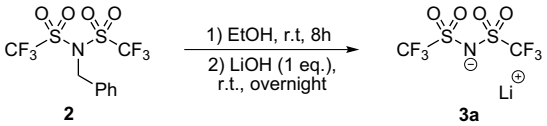


Scheme 1. Preparation of *N*-benzyl trifluoromethanesulfonimide.



Scheme 2. Preparation of LiTFSI.

pressure and high thermal level. Moreover, the reagents opposed to CF_3SO_2F are often very moisture sensitive and require special handling procedures.

Here, we wish to report a new, mild and expedient method, based on solid *N*-benzyl trifluoromethanesulfonimide as key intermediate, to prepare a wide range of TFSI salts.

2. Results

As we have already described,[14] the benzyl group of some fluorinated *N*-benzylsulfonimides can be easily cleaved by alcohols. Therefore, we decided to apply this deprotection method to *N*-benzyl trifluoromethanesulfonimide **2**, which can be obtained in very good yields from triflic anhydride **1** and benzylamine in the presence of diisopropylethylamine (DIEA) as base (Scheme 1).[13]

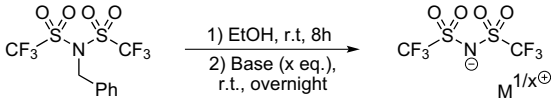
The first goal was to prepare lithium trifluoromethanesulfonimide (LiTFSI), which is a promising electrolyte, already commercially available, for lithium batteries. Indeed, the expected reaction occurred after treatment of **2** with ethanol at room temperature, followed by neutralization with lithium hydroxide (Scheme 2).

Here again, the strong electron-withdrawing effect of the fluorinated moieties explains such an unusual reactivity: in fact, the deprotection step is a very mild nucleophilic substitution around the benzylic carbon, which is strongly favoured by the very good leaving ability of the TFSI anion. It leads to an oxonium triflimide **4**, which has to be neutralized by a base to offer the expected lithium salt (Scheme 3). Moreover, its purification is really simple since the only formed by-product is benzyl ether, a non-ionic compound, which can be easily eliminated.

We can notice that such a reactivity has already been observed.[13,15] However, as the purpose of the corresponding works was to prepare benzylated compounds, no attention was paid to the isolation of the sulfonimide by-product.

As suggested in Scheme 3, the transformation of **2** into **3a** can be considered as a two-step reaction: first, deprotection of the benzyl group in ethanol (indicated by complete dissolution of **2** in ethanol and confirmed by ^{19}F NMR analysis), then neutralization of the resulting oxonium triflimide **4** by a base. It must be underlined that

Table 1
Synthesis of various sulfonimides by a two-step one-pot procedure



Entry	Base (*x* equiv)	Sulfonimide salt	M^+	Isolated yields
1	$LiOH·H_2O$ (1 equiv)	**3a**	Li^+	82%
2	$NaHCO_3$ (1 equiv)	**3b**	Na^+	89%
3	KOH (1 equiv)	**3c**	K^+	84%
4	$Ca(OH)_2$ (0.5 equiv)	**3d**	Ca^{2+}	77%
5	$MgCO_3$ (0.5 equiv)	**3e**	Mg^{2+}	76%
6	$Zn(OH)_2$ (0.5 equiv)	**3f**	Zn^{2+}	71%
7	Sc_2O_3 (0.3 equiv)	**3g**	Sc^{3+}	70%[a]
8	$Me_4N^+OH^-·5H_2O$ (1 equiv)	**3h**	Me_4N^+	79%
9	Et_3N (1 equiv)	**3i**	Et_3NH^+	85%
10	$^iPr_2EtN$ (1 equiv)	**3j**	$^iPr_2EtNH^+$	87%

[a] Reaction in refluxing $EtOH/H_2O$.

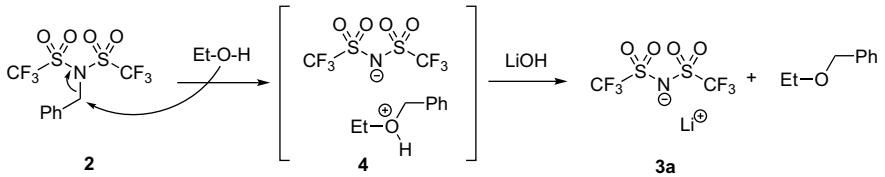
the preliminary ethanolic treatment is necessary to avoid the side-reactions observed when *N*-benzyl sulfonimide **2** was directly treated with LiOH. Actually, these undesired reactions were due to the abstraction of a benzylic proton by such a strong base and also by the presence of the sulfur(VI) sites of the triflyl groups, which are a hard electrophiles, able to be attacked by a hard nucleophile such as HO^-. In contrast, ethanol is a less basic and softer nucleophile, and thus, only nucleophilic substitution was observed. Consequently, selective debenzylation occurred.

As the lithium cation associated with $(CF_3SO_2)_2N^-$ was brought by the base used to deprotonate the oxonium salt, a wide range of cations can be expected to be associated with this triflimide anion by simply varying the base. Thus, different metallic hydroxides [LiOH, KOH, $Ca(OH)_2$, $Zn(OH)_2$], hydrogenocarbonates ($NaHCO_3$), carbonates ($MgCO_3$) or oxides (Sc_2O_3) were used to neutralize ethanolic solutions of **2** and the corresponding triflimide salts **3a–g** were obtained in good to excellent yields (Table 1). Tetramethylammonium hydroxide worked as well and provided a quaternary ammonium triflimide **3h**. Alternatively, the oxonium triflimide **4** can be neutralized by tertiary amines to get protonic ammonium triflimides **3i,j** (Table 1).

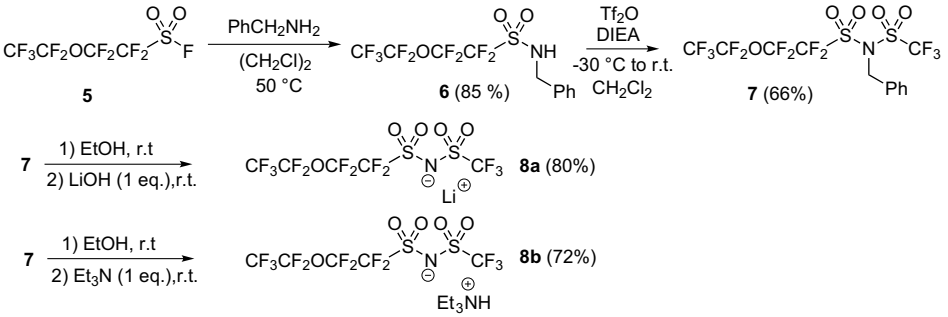
If alkaline triflimides (**3a–c**, M=Li, Na, K) and calcium triflimide (**3d**) can be used in present or future batteries, magnesium, zinc and scandium triflimides (**3e–g**, M=Mg, Zn, Sc) constitute very potent Lewis acids since these salts are probably very dissociated in solution. On the other hand, proton-containing ammonium triflimides **3i,j** are good candidates for proton exchange membrane fuel cells (PEMFCs).[3]

The method has been extended to the manufacture of other lithium and triethylammonium perfluoroalkanesulfonimide starting from commercially available 2-(pentafluoroethoxy)tetrafluoroethanesulfonyl fluoride (Scheme 4).

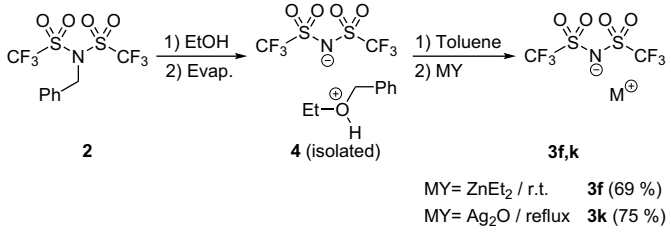
By analogy with the synthesis of the scandium salt **3g**, silver oxide was also reacted with **2** in refluxing ethanol, in order to prepare another potent Lewis acid. Unfortunately, under these conditions, silver oxide was reduced by ethanol into a silver



Scheme 3. Proposed mechanism.



Scheme 4. Synthesis of sulfonimides **8a** and **8b**.



Scheme 5. Synthesis of Zn(II) and Ag(I) triflimides.

mirror. Thus, the process was modified: after complete reaction between **2** and ethanol, the latter was evaporated and the crude oxonium triflimide **4** was dissolved in toluene, brought to reflux then reacted with silver oxide. In such a way, silver triflimide **3k** was obtained in a good yield (Scheme 5). The same process was applied to the preparation of zinc triflimide **3f** from diethyl zinc except that the reaction was carried out at room temperature (Scheme 5).

As stated above, that, if *N*-benzyl triflimide **2** can be cleanly debenzylated by ethanol, the triflimide moiety cannot be directly and selectively substituted from **2** by the basic and hard nucleophile HO^-. Nevertheless, it was anticipated that less basic and softer nucleophiles could cleanly perform a nucleophilic substitution on the benzylic centre. Indeed, when reacted with **2**, *n*-tetrabutylammonium bromide, trimethylsulfonium iodide or methyltriphenylphosphonium bromide provided the corresponding triflimide salts in good yield (Table 2).

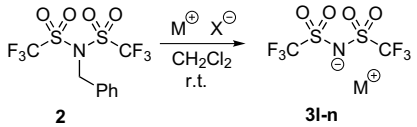
This method looks efficient for preparing onium triflimides, since onium halides are generally more accessible than onium hydroxides, but its scope is not so wide as that of the ethanol-mediated one as far as metallic salts are concerned. For example, no reaction was observed between **2** and silver iodide or cupric bromide in toluene at room temperature and decomposition of the substrate occurred when heating the mixtures up to 70 °C and 110 °C, respectively. Maybe such metallic halides, which contain an oxophilic cation, could add onto the S=O bond and deliver trifluoromethanesulfonyl iodide or bromide, which are known to be thermally unstable[16] and cannot be detected (CF_3SO_2I decomposes spontaneously into CF_3I and SO_2 at room temperature).[16a] This hypothesis is consistent with the fact that silver fluoride and tetramethylammonium fluoride reacted with **2** to deliver trifluoromethanesulfonyl fluoride, a thermally stable product, which was detected by ^{19}F NMR. The latter product obviously resulted from the attack of the hard nucleophile F^- on the hardest electrophilic site of **2** that is the sulfur(VI) moiety.

As **2** reacted cleanly at the benzylic site with ethanol and ionic nucleophiles such as onium halides, it was also opposed to amines and phosphines. The reaction worked very well and delivered onium triflimides in which the cation contained a benzyl substituent (Table 3). Depending on the substitution pattern of the cation, these onium triflimides can be useful as ionic liquids[17] or can behave as new electrolytes for fuel cells. Of note, DesMarteau et al. recently used a similar method to prepare *N*-methyl-imidazole from *N*-methyl-trifluorosulfonimide.[18]

Finally, owing to the fact that allylic substitution is as easy as benzylic substitution, *N*-allyl triflimide **9** was also prepared in a similar way as **2** (Scheme 6).

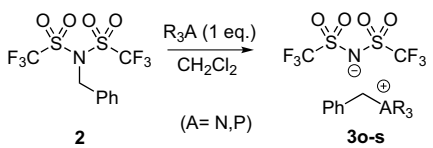
Then, reactions of **9** with amines, phosphines and sulfides were examined. As expected, these reaction delivered good to very good yields (Table 4), though **9** seemed a little bit less reactive than **2**: for example, diisopropylamine reacted nicely with **2** at room temperature whereas heating to 70 °C was necessary with **9**. Allylation of tetrahydrothiophene proceeded smoothly but allylation of dibenzothiophene or benzo[*b*]thiophene was not observed, even after heating at 70 °C, since these conjugated substrates are poorer nucleophile. Obviously, the cation of the resulting onium triflimide contained an allyl substituent.

Table 2
Synthesis of sulfonimides through direct debenzylation with salts



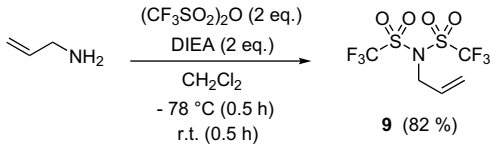
Entry	MX (*x* equiv)	Sulfonimide salt	M^+	Isolated yield
1	*n*-$Bu_4N^+Br^-$ (1 equiv)	**3l**	Bu_4N^+	73%
2	$Me_3S^+I^-$ (1 equiv)	**3m**	Me_3S^+	59%
3	$MePh_3P^+Br^-$ (1 equiv)	**3n**	$MePh_3P^+$	81%

Table 3
Synthesis of sulfonimides through direct debenzylation with amines and phosphines



Entry	R_3A	Sulfonimide salt	M^+	Isolated yields
1	Et_3N[a]	**3o**	$BnEt_3N^+$	84%
2	$^iPr_2NH$[a]	**3p**	$Bn^iPr_2NH^+$	88%
3	DIEA[b]	**3q**	$Bn^iPr_2EtN^+$	59%
4	*N*-Me imidazole[a]	**3r**	*N*-Me-*N*′-Bn-Im^+	85%
5	Ph_3P[b]	**3s**	$BnPh_3P^+$	78%

[a] Reaction at rt.
[b] Reaction at 70 °C under autogeneous pressure.



Scheme 6. Synthesis of *N*-allyl triflimide **9**.

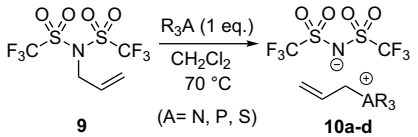
In conclusion, we have developed a new and versatile method to synthesize trifluoromethanesulfonimide salts, based on the easy deprotection of *N*-benzyl- or *N*-allyl trifluoromethanesulfonimide (**2** and **9**, respectively) without using any hydrogen or noble metal as catalyst.[19] This process was carried out either by two steps in one-pot, that is ethanolysis followed by neutralization, or by a single substitution step, provided that, in this case, the incoming nucleophile is not too basic and hard. The two-step one-pot method exhibits the largest scope but a suitable combination of the two techniques allows the synthesis of a very wide range of salts with varied cations. These methods are very simple since the reagents and reactants are easy to handle, the intermediates are moderately moisture sensitive and the required conditions are mild. The triflimide salts thus obtained could find various applications as electrolytes for batteries and fuel cells, as ionic liquids or as acid catalysts.

3. Experimental

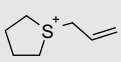
3.1. General

Prior to use, solvents were distilled and stored over 4 Å molecular sieves under nitrogen atmosphere. Amines and $Ti(O^iPr)_4$ were freshly distilled prior to use. Other commercially available reagents were used as received. Ag_2O was freshly prepared by precipitation from 1 M aq $AgNO_3$ with 1 equiv of 1 M aq NaOH followed by washing with demineralized water to pH=7 and drying at 80 °C. All reactions were carried out under nitrogen atmosphere in screw caped thick glassware that allowed reactions in dichloromethane at 70 °C under autogeneous pressure. TLC analyses were carried out on silica gel (Merck Kieselgel $60F_{254}$) deposited on aluminium plates, detection being done by UV (254 nm). NMR spectra were recorded in $CDCl_3$, DMSO-d_6, acetone-d_6 or CD_3CN as stated for each experiment. ^1H NMR spectra were recorded at 200 or 300 MHz and ^{13}C NMR spectra at 100; 75 or 50 MHz, respectively. ^{19}F NMR spectra were recorded at 282 MHz and ^{31}P NMR spectra at 121 MHz. Chemical shifts (δ) are given in parts per million versus TMS (^1H, ^{13}C); $CFCl_3$ (^{19}F) or H_3PO_4 (^{31}P) used as internal references. Coupling constants are given in hertz.

Table 4
Synthesis of sulfonimides through direct deallylation with amines, phosphines and sulfides



9 **10a-d**

Entry	R_3A	Sulfonimide salt	$[CH_2{=}CHCH_2AR_3]^+$	Isolated yields
1	$^iPr_2NH$	**10a**	Allyl$^iPr_2NH^+$	78%
2	DIEA	**10b**	Allyl$^iPr_2EtN^+$	76%
3	Ph_3P	**10c**	AllylPh_3P^+	86%
4		**10d**		95%[a]

[a] Reaction at rt.

The substitution pattern of the different carbons was determined by a 'DEPT 135' sequence. Elemental analyses were determined by the 'Laboratoire Central d'Analyses du CNRS' at Vernaison (France). As the different salts are highly hygroscopic, their melting points were not determined.

3.2. Synthesis of *N*-benzyl trifluoromethanesulfonimide 2

RN: [35034-08-3][13]

DIEA (0.515 g, 4 mmol) was added, under inert atmosphere, to a solution of a freshly distilled benzylamine (0.215 g, 2 mmol) in anhydrous dichloromethane (20 mL). The reaction mixture was cooled down to −78 °C, then triflic anhydride (1.41 g, 5 mmol) was added dropwise. The reaction mixture was slowly warmed up to room temperature during 1 h and stirred at this temperature for 1 h. Then, aqueous HCl (3%) was added. The aqueous phase was extracted with dichloromethane and the combined organic layers were dried over $MgSO_4$. Filtration and evaporation of the solvent left a crude mixture, which was refluxed in pentane. Before cooling down to room temperature, the pentane phases were collected. This operation was repeated several times. Evaporation of the combined pentane fractions left *N*-benzyl sulfonimide **2** as a pale brown solid (0.65 g, 87%).

^1H NMR ($CDCl_3$, 300 MHz): δ 7.49–7.52 (m, 2H), 7.40–7.43 (m, 3H), 5.11 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 131.9, 130.0, 129.9, 129.1, 118.9 (q, $^1J_{C-F}$=324.8 Hz), 56.8; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −72.57.

3.3. General synthesis of trifluoromethanesulfonimide salts 3a–j[20]

A solution of **2** (1 equiv) in ethanol (0.2 M solution) was stirred at room temperature for 8 h. Then, a base (1 equiv) was added and the reaction mixture was stirred overnight. After evaporation of the solvent, the residue was dissolved in ether and filtrated over Celite®. Evaporation of the filtrate left a solid, which was washed several times with pentane to give the corresponding TFSI salt.

3.4. Lithium trifluoromethanesulfonimide 3a

RN: [90076-65-6][20a]

Prepared from $LiOH{\cdot}H_2O$ (35.7 mg, 0.85 mmol); white hygroscopic solid (0.20 g, 82%).

^{13}C NMR (acetone-d_6, 75 MHz): δ 120.9 (q, $^1J_{C-F}$=321.1 Hz); ^{19}F NMR (DMSO-d_6, 282 MHz): δ −79.16 (s, CF_3).

3.5. Sodium trifluoromethanesulfonimide 3b

RN: [91742-21-1][1a]

Prepared from $NaHCO_3$ (84.01 mg, 1 mmol); white hygroscopic solid (270 mg, 0.89 mmol, 89%).

^{13}C NMR (acetone-d_6, 75 MHz): δ 120.8 (q, $^1J_{C-F}$=321.1 Hz); ^{19}F NMR (DMSO-d_6, 282 MHz): δ −79.21 (s, CF_3).

3.6. Potassium trifluoromethanesulfonimide 3c

RN: [90076-67-8][20b]

Prepared from KOH (0.056 g, 1 mmol); white hygroscopic solid (0.268 g, 0.84 mmol, 84%).

^{13}C NMR (acetone-d_6, 75 MHz): δ 119.2 (q, $^1J_{C-F}$=319.8 Hz); ^{19}F NMR (acetone-d_6, 282 MHz): δ −80.56 (s, CF_3).

3.7. Calcium bis-(trifluoromethanesulfonimide) 3d

RN: [165324-09-4][20c]

Prepared from $Ca(OH)_2$ (37 mg, 0.5 mmol); white hygroscopic solid (231 mg, 0.39 mmol, 77%).

^{13}C NMR (acetone-d_6, 50 MHz): δ 120.0 (q, $^1J_{C-F}$=320.0 Hz); ^{19}F NMR (acetone-d_6, 282 MHz): δ −80.09 (s, CF_3).

3.8. Magnesium bis-(trifluoromethanesulfonimide) 3e

RN: [133395-16-1][20c]

Prepared from $MgCO_3$ (0.0357 g, 0.85 mmol); white hygroscopic solid (0.378 g, 0.65 mmol, 76%).

^{13}C NMR (acetone-d_6, 75 MHz): δ 120.3; ^{19}F NMR (acetone-d_6, 282 MHz): δ −77.31 (s, CF_3).

3.9. Zinc bis-(trifluoromethanesulfonimide) 3f

RN: [168106-25-0][20c]

Prepared from $Zn(OH)_2$ (0.099 g, 1 mmol); white hygroscopic solid (0.444 g, 0.71 mmol, 71%).

^{13}C NMR (acetone-d_6, 75 MHz): δ 120.9 (q, $^1J_{C-F}$=319.5 Hz); ^{19}F NMR (acetone-d_6, 282 MHz): δ −79.84 (s, CF_3).

3.10. Scandium tris-(trifluoromethanesulfonimide) 3g

RN: [176726-07-1][20d]

N-Benzyl sulfonimide **2** (0.371 g, 1 mmol) in ethanol (5 mL) was stirred at room temperature for 8 h. Then, the reaction mixture was diluted with water, scandium oxide (0.023 g, 0.167 mmol) was added and the reaction mixture was heated under reflux overnight. The reaction mixture was cooled down, extracted with diethyl ether. The ethereal solution was dried over $MgSO_4$, filtered and volatiles were evaporated. The residue was washed with pentane several times. The salt compound was obtained as a white hygroscopic solid (0.207 g, 0.233 mmol, 70%).

^{13}C NMR (acetone-d_6, 50 MHz): δ 120.4 (q, $^1J_{C-F}$=321.1 Hz); ^{19}F NMR (acetone-d_6, 282 MHz): δ −79.93 (s, CF_3).

3.11. Tetramethylammonium trifluoromethanesulfonimide 3h

RN: [161401-25-8][20e]

Prepared from $Me_4N^+OH^-\cdot 5H_2O$ (109 mg, 0.6 mmol); crystallized from dichloromethane/pentane to yield white solid (280 mg, 79%).

^{13}C NMR (CD_3CN, 50 MHz): δ 119.9 (q, J_{C-F}=320.1 Hz), 56.2; ^1H NMR (CD_3CN, 200 MHz): δ 3.09 (s, 12H); ^{19}F NMR (CD_3CN, 282 MHz): δ −80.01 (s, 3F).

Anal. Calcd for $C_6H_{12}F_6N_2O_4S_2$: C, 20.34; H, 3.41; N, 7.91; S, 18.10. Found: C, 20.31; H, 3.33; N, 7.84; S, 18.05.

3.12. Triethylammonium trifluoromethanesulfonimide 3i

RN: [192998-66-6][20f]

Prepared from Et_3N (0.14 mL, 1 mmol); white hygroscopic solid (325 mg, 0.85 mmol, 85%).

^1H NMR (acetone-d_6, 300 MHz): δ 7.09 (s, 1H), 3.31 (q, 6H, $^3J_{H-H}$=7.2 Hz), 1.35 (t, 9H, $^3J_{H-H}$=7.2 Hz); ^{13}C NMR (acetone-d_6, 75 MHz): δ 120.4 (q, CF_3, $^1J_{C-F}$=321.0 Hz), 48.2, 9.0; ^{19}F NMR (acetone-d_6, 282 MHz): δ −80.50 (s, 3F).

3.13. Diisopropylethylammonium trifluoromethanesulfonimide 3j

RN: [1000369-41-4][20g]

Prepared from DIEA (0.174 mL, 1 mmol); white hygroscopic solid (357 mg, 0.87 mmol, 87%).

^1H NMR ($CDCl_3$, 200 MHz): δ 7.18 (s, 1H), 3.55–3.43 (m, 2H), 3.07–2.94 (m, 2H), 1.28–1.21 (m, 15H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 120.2 (q, $^1J_{C-F}$=317.0 Hz, CF_3), 55.0, 43.1, 18.2, 16.7, 12.5; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.14 (s, 3F).

3.14. Silver trifluoromethanesulfonimide 3k

RN: [189114-61-2][20h]

N-Benzyl sulfonimide **2** (0.371 g, 1 mmol) in ethanol (5 mL) was stirred at room temperature for 8 h. The volatiles were evaporated from the reaction mixture under reduced pressure at 60 °C. The oily residue was dissolved in dry oxygen-free toluene (7 mL). Then, silver oxide (0.116 g, 0.5 mmol) was added and the light protected reaction mixture was heated under reflux for 3 h, after which complete dissolution of the solid was observed. The reaction mixture was cooled down, filtered over Celite® and concentrated to 1:3 of the volume. Then, the product was precipitated with pentane. The title compound was obtained as a yellow hygroscopic solid (0.291 g, 0.75 mmol, 75%).

^{13}C NMR (CD_3CN, 50 MHz): δ 120.1 (q, J_{C-F}=319.7 Hz); ^{19}F NMR (CD_3CN, 282 MHz): δ −80.13 (s, CF_3).

3.15. *N*-Benzyl-1,1,2,2-tetrafluoro-2-pentafluoroethoxy-ethanesulfonamide 6

In a Pyrex round bottom screw-cap flask, freshly distilled benzylamine (29.6 mL, 271.45 mmol) was added, under inert atmosphere, to a solution of a 1,1,2,2-tetrafluoro-2-pentafluoroethoxy-ethanesulfonyl fluoride (17.28 g, 54.29 mmol) in anhydrous dichloromethane (30 mL). The reaction mixture was heated to 50 °C overnight in the closed flask (the reaction was followed by ^{19}F NMR). The reaction mixture was cooled down to room temperature and then aqueous HCl (10%) was added. The aqueous phase was extracted with dichloromethane and the combined organic layers dried over $MgSO_4$. Filtration and solvent evaporation left a crude mixture, which was purified by filtration over a 2 cm layer of silica gel, then washed with dichloromethane. Evaporation of the solvent left the title compound **6** as an oil in 85% yield (18.67 g, 46.15 mmol) and was used to prepare **7** without further purification.

^1H NMR ($CDCl_3$, 300 MHz): δ 7.42–7.30 (m, 5H), 5.34 (s, 1H), 4.44 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 135.4 (C), 129.2, 128.8, 128.0 (CH), 116.4 (tt, CF_2, $^{1,2}J_{C-F}$=289.2, 31.5 Hz), 116.1 (qt, CF_2, $^{1,2}J_{C-F}$=285.4, 41.0 Hz), 114.3 (tq, CF_2, $^{1,2}J_{C-F}$=286.9, 44.1 Hz), 113.1 (tt, CF_3, $^{1,2}J_{C-F}$=295.8, 36.8 Hz), 48.7 (CH_2); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −82.01 (m, 2F), −86.99 (s, 3F), −88.63 (m, 2F), −116, 36 (s, 2F).

3.16. *N*-Benzyl-*N*-(1,1,2,2-tetrafluoro-2-pentafluoroethoxy-ethanesulfonyl)-trifluoromethanesulfonamide 7

DIEA (8.03 mL, 46.6 mmol) was added, under inert atmosphere, to a solution of imide **6** (11.8 g, 29.13 mmol) in anhydrous dichloromethane (29 mL). The reaction mixture was cooled down to 0 °C, then triflic anhydride (7.25 mL, 43.7 mmol) was added dropwise. The reaction mixture was stirred at this temperature for 30 min then warmed up to room temperature. Stirring continued for 1 h. Evaporation of the solvent left a crude product, which was refluxed in pentane. Before cooling down to room temperature, the pentane phase was collected. This operation was repeated several times. Evaporation of the combined pentane fractions left the crude sulfonimide **7** as a brownish solid in 66% yield (10.33 g, 19.23 mmol), and was used to prepare **8a**,**b** without further purification.

^{19}F NMR ($CDCl_3$, 282 MHz): δ −72.79 (s, 3F), −81.60 (m, 2F), −87.07 (s, 3F), −88.68 (m, 2F), −109.40 (m, 2F).

3.17. Lithium *N*-(1,1,2,2-tetrafluoro-2-pentafluoroethoxy-ethanesulfonyl)-trifluoromethanesulfonamide 8a

A suspension of *N*-benzyl sulfonimide **7** (3.91 g, 7.27 mmol) in ethanol (40 mL) was stirred at room temperature for 8 h. Then, $LiOH \cdot H_2O$ (0.306 g, 7.27 mmol) was added and the reaction mixture was stirred overnight. After evaporation of the solvent, the residue was dissolved in ether and filtrated over Celite®. Evaporation of the filtrate left a solid, which was washed several times by pentane to give the lithium sulfonimide **8a** as oil in 80% yield (2.63 g, 5.82 mmol).

^{13}C NMR (acetone-d_6, 75 MHz): δ 120.9 (q, CF_3, $^1J_{C-F}$=321.1 Hz), 117.8 (tt, CF_2, $^{1,2}J_{C-F}$=289.3, 32.6 Hz), 116.7 (qt, CF_3, $^{1,2}J_{C-F}$=284.7, 41.6 Hz), 114.7 (tq, CF_2, $^{1,2}J_{C-F}$=284.5, 43.8 Hz), 112.8 (tt, CF_2, $^{1,2}J_{C-F}$=294.4, 34.8 Hz); ^{19}F NMR (acetone-d_6, 282 MHz): δ −80.40 (s, 3F), −82.48 (m, 2F), −87.91 (s, 3F), −89.44 (m, 2F), −118.11 (s, 2F).

Anal. Calcd for $C_5F_{12}NO_5S_2Li$: C, 13.25; N, 3.09; S, 14.15. Found: C, 13.40; N, 2.83; S, 14.36.

3.18. Triethylammonium *N*-(1,1,2,2-tetrafluoro-2-pentafluoroethoxy-ethanesulfonyl)-trifluoromethanesulfonamide 8b

A suspension of *N*-benzyl sulfonimide **7** (3.91 g, 7.27 mmol) in ethanol (40 mL) was stirred at room temperature for 8 h. Then, triethylamine (1.01 mL) was added and the reaction mixture was stirred overnight. Evaporation of the volatiles left a residue, which was washed several times with pentane to give triethylammonium sulfonimide **8b** as a white oil in 72% yield (2.87 g, 5.23 mmol). ^1H NMR (acetone-d_6, 300 MHz): δ 7.10 (s, 1H), 3.39 (q, 6H, $^3J_{H-H}$=7.3 Hz), 1.37 (t, 9H, $^3J_{H-H}$=7.3 Hz); ^{13}C NMR (acetone-d_6, 75 MHz): δ 120.9 (q, CF_3, $^1J_{C-F}$=320.9 Hz), 117.8 (tt, CF_2, $^{1,2}J_{C-F}$=288.8, 32.7 Hz), 116.8 (qt, CF_3, $^{1,2}J_{C-F}$=284.7, 41.6 Hz), 114.8 (tq, CF_2, $^{1,2}J_{C-F}$=284.2, 43.8 Hz), 112.8 (tt, CF_2, $^{1,2}J_{C-F}$=294.7, 35.0 Hz), 48.1 (CH_2), 9.1 (CH_3); ^{19}F NMR (acetone-d_6, 282 MHz): δ −80.50 (s, 3F), −82.53 (t, 2F, $^3J_{F-F}$=11.3 Hz), −88.06 (s, 3F), −89.55 (t, 2F, $^3J_{F-F}$=12.6 Hz), −118.07 (s, 2F).

Anal. Calcd for $C_{11}H_{16}F_{12}N_2O_5S_2$: C, 24.09; H, 2.94; N, 5.11; S, 11.69. Found: C, 24.58; H, 2.93; N, 5.14; S, 12.10.

3.19. General synthesis of salts 3l–n via nucleophilic substitution on the benzylic centre of 2

Into a solution (0.2 M) of *N*-benzyl trifluoromethanesulfonimide **2** (1 equiv) in dry dichlomethane was added the corresponding salt and the solution was stirred overnight at rt. The volatiles were evaporated and the residue was washed repeatedly by pentane.

3.20. Tetrabutylammonium trifluoromethanesulfonimide 3l

RN: [210230-40-3][20i]

Prepared from $nBu_4N^+Br^-$ (0.322 g, 1 mmol); colourless oil (0.382 g, 0.73 mmol, 73%).

^1H NMR ($CDCl_3$, 300 MHz): δ 3.19–3.13 (m, 8H), 1.60–1.55 (m, 8H), 1.45–1.35 (m, 8H), 1.02–0.96 (m, 12H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 119.9 (q, $^1J_{C-F}$=319.0 Hz), 58.5, 23.7, 19.4, 12.6; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.24 (s, 1F).

3.21. Trimethylsulfonium trifluoromethanesulfonimide 3m

RN: [321746-48-9][20j]

Prepared from $Me_3S^+I^-$ (0.204 g, 1 mmol); yellow oil (0.211 g, 0.59 mmol, 59%).

^1H NMR (CD_3CN, 200 MHz): δ 2.81 (s, 9H); ^{13}C NMR (CD_3CN, 50 MHz): δ 120.9 (q, $^1J_{C-F}$=319 Hz), 27.4; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.02 (s, 1F).

3.22. Methyltriphenylphosphonium trifluoromethanesulfonimide 3n

Prepared from $MePh_3P^+Br^-$ (0.277 g, 1 mmol); yellow oil (0.452 g, 0.81 mmol, 81%).

^1H NMR ($CDCl_3$, 200 MHz): δ 7.79–7.58 (m, 15H), 2.83 (d, J_{H-P}=8.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 135.3, 132.9 (d, J_{C-P}=10.5 Hz), 130.6 (d, J_{C-P}=13 Hz), 118.7 (d, J_{C-P}=88.5 Hz), 9.3 (d, J_{C-P}=59 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.48 (s, 1F), ^{31}P NMR ($CDCl_3$, 121 MHz): δ 20.26 (s, 1P).

Anal. Calcd for $C_{21}H_{18}F_6NO_4PS_2$: C, 45.24; H, 3.25; N, 2.51; S, 11.50. Found: C, 45.46; H, 3.39; N, 2.65; S, 11.54.

3.23. General synthesis of salts 3o–s and 10a–d

Into a solution (0.2 M) of *N*-benzyl trifluoromethanesulfonimide **2** (1 equiv) or *N*-allyl trifluoromethanesulfonimide **9** (1 equiv) in dry dichlomethane was added the corresponding base and the solution was stirred overnight at rt. Salts **3q**, **3s** and **10b–d** were prepared by heating the reaction mixture to 70 °C in a closed Pyrex screw-cap flask overnight. The volatiles were evaporated and the residue was washed repeatedly by pentane. The solid residues were crystallized from a dichloromethane/pentane mixture.

3.24. Benzyltriethylammonium trifluoromethanesulfonimide 3o

RN: [950207-89-3][17]

Prepared from Et_3N (0.139 mL, 1 mmol); yellow oil (0.397 g, 0.84 mmol, 84%).

^1H NMR ($CDCl_3$, 300 MHz): δ 7.44–7.34 (m, 5H), 4.24 (s, 2H), 3.13 (q, ^2J=7.4 Hz, 6H), 1.33 (t, ^2J=7.4 Hz, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 132.0, 131.1, 129.7, 120.7 (q, $^1J_{C-F}$=319 Hz), 60.7, 52.5, 7.6; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.41 (s, 1F).

Anal. Calcd for $C_{15}H_{22}F_6N_2O_4S_2$: C, 38.13; H, 4.69; N, 5.93; S, 13.55. Found: C, 38.40; H, 4.65; N, 5.64; S, 13.58.

3.25. Benzyldiisopropylammonium trifluoromethanesulfonimide 3p

Prepared from $^iPr_2NH$ (0.14 mL, 1 mmol); yellow oil (0.88 mmol, 88%).

^1H NMR (DMSO-d_6, 300 MHz): δ 8.51 (br s, 1H), 7.59–7.55 (m, 2H), 7.47–7.43 (m, 3H), 4.34 (d, ^2J=5.2 Hz, 2H), 3.70–3.63 (m, 2H), 1.36 (d, ^2J=6.6 Hz, 6H), 1.30 (d, ^2J=6.6 Hz, 6H); ^{13}C NMR (DMSO-d_6, 50 MHz): δ 131.5, 130.4, 129.0, 119.8 (q, $^1J_{C-F}$=320.0 Hz), 54.2, 49.8, 28.5, 18.0, 17.4; ^{19}F NMR (DMSO-d_6, 282 MHz): δ −79.09 (s, 1F).

Anal. Calcd for $C_{15}H_{22}F_6N_2O_4S_2 \cdot 0.5H_2O$: C, 37.42; H, 4.81; N, 5.82; S, 13.32. Found: C, 37.63; H, 4.72; N, 6.01; S, 13.65.

3.26. Benzylethyldiisopropylammonium trifluoromethanesulfonimide 3q

Prepared from DIEA (0.172 mL, 1 mmol); yellow oil (0.295 g, 0.59 mmol, 59%).

^1H NMR ($CDCl_3$, 300 MHz): δ 7.52–7.37 (m, 5H), 4.28 (s, 2H), 4.07–3.99 (m, 2H), 3.42 (q, J=7.2 Hz, 2H), 1.45–1.27 (m, 15H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 133.7, 130.7, 129.4, 128.2, 120.0 (q, $^1J_{C-F}$=319.1 Hz), 62.4, 62.2, 51.2, 18.8, 18.4, 9.6; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.28 (s, 1F).

Anal. Calcd for $C_{17}H_{26}F_6N_2O_4S_2$: C, 40.79; H, 5.24; N, 5.60; S, 12.81. Found: C, 40.79; H, 5.25; N, 5.63; S, 12.52.

3.27. 1-Benzyl-3-methyl-3*H*-imidazol-1-ium trifluoromethanesulfonimide 3r

RN: [433337-24-7][20k]

Prepared from 1-methyl-1*H*-imidazole (0.079 mL, 1 mmol); yellow oil (0.385 g, 0.85 mmol, 85%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.68 (s, 1H), 7.37 (s, 5H), 7.29–7.28 (m, 1H), 7.24–7.23 (m, 1H), 5.27 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4, 132.3, 129.4, 129.2, 128.5, 123.7, 122.0, 119. 5 (q, $^1J_{C-F}$=319 Hz), 53.1, 35.9; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.58 (s, 1F).

Anal. Calcd for $C_{13}H_{13}F_6N_3O_4S_2$: C, 34.44; H, 2.89; N, 9.27; S, 14.14. Found: C, 34.36; H, 2.78; N, 9.24; S, 14.05.

3.28. Benzyltriphenylphosphonium trifluoromethanesulfonimide 3s

RN: [953415-83-3][20l]

Prepared from Ph_3P (0.873 mmol); colourless oil (0.431 g, 0.68 mmol, 78%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.81 (qt, J=7.5, 1.4 Hz, 3H), 7.65 (dt, J=7.8, 3.6 Hz, 6H), 7.53–7.46 (m, 6H), 7.31–7.26 (m, 1H), 7.16 (t, J=7.6 Hz, 2H), 6.88 (dd, J=7.4, 2.0 Hz, 2H), 4.57 (d, J=14.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 135.43 (d, J_{C-P}=3.0 Hz), 133.9 (d, J_{C-P}=10.0 Hz), 130.9 (d, J_{C-P}=5.5 Hz), 130.4 (d, J_{C-P}=12.5 Hz), 129.1 (d, J_{C-P}=3.5 Hz), 128.9 (d, J_{C-P}=4.0 Hz), 126.4 (d, J_{C-P}=8.5 Hz), 119. 7 (q, J_{C-F}=320 Hz), 117.0 (d, J_{C-P}=85.5 Hz), 30.7 (d, J_{C-P}=47.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.19 (s, 1F), ^{31}P NMR ($CDCl_3$, 121 MHz): 23.66 (s, 1P).

Anal. Calcd for $C_{27}H_{22}F_6NO_4PS_2$: C, 51.19; H, 3.50; N, 2.21; S, 10.12. Found: C, 51.44; H, 3.62; N, 2.37; S, 9.91.

3.29. *N*-Allyl trifluoromethanesulfonimide 9

RN: [70869-00-0][15c]

DIEA (8.14 mL, 46.8 mmol) was added, under inert atmosphere, to a solution of a freshly distilled allylamine (1.75 mL, 23.40 mmol) in anhydrous dichloromethane (40 mL). The reaction mixture was cooled down to −78 °C, then triflic anhydride (9.83 mL, 58.5 mmol) was added dropwise. The reaction mixture was slowly warmed up to room temperature (30 min) and stirred at this temperature for 30 min. Then, 3% aqueous HCl (50 mL) was added. The aqueous phase was extracted with dichloromethane and the combined organic layers dried over $MgSO_4$. Filtration and solvent evaporation left a crude mixture, which was refluxed in pentane. Before cooling down to room temperature, the pentane phase was collected. This operation was repeated several times. Evaporation of the combined pentane fractions left the allyl sulfonimide **9** as a brown oil (0.65 g, 87%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.98–5.84 (m, 1H), 5.49–5.42 (m, 2H), 4.53 (d, $^3J_{H-H}$=7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 129.3, 123.2, 118.8 (q, J_{C-F}=322.2 Hz), 55.8; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −72.60 (s, CF_3).

3.30. Allyldiisopropylammonium trifluoromethanesulfonimide 10a

Prepared from ^{i}Pr$_2$NH (0.140 mL, 1 mmol); colourless oil (0.329 g, 0.78 mmol, 78%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.71 (br s, 1H), 6.03–5.80 (m, 1H), 5.62–5.42 (m, 2H), 3.95–3.83 (m, 1H), 3.61–3.77 (m, 3H), 1.33 (d, $^3J_{H-H}$=6.8 Hz, 12H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 127.6, 124.5, 119.6 (q, $^1J_{C-F}$=318.5 Hz), 55.3, 50.2, 18.2, 17.1; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.55 (s, 1F).

Anal. Calcd for $C_{11}H_{20}F_6N_2O_4S_2$: C, 31.28; H, 4.77; N, 6.63; S, 15.18. Found: C, 31.46; H, 4.76; N, 6.64; S, 14.94.

3.31. Allylethyldiisopropylammonium trifluoromethanesulfonimide 10b

Prepared from DIEA (0.172 mL, 1 mmol); colourless oil (0.342 g, 0.76 mmol, 76%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.99–5.86 (m, 1H), 5.59–5.48 (m, 2H), 3.90–3.78 (m, 4H), 3.29 (q, $^3J_{H-H}$=6.0 Hz, 2H), 1.39 (d, $^3J_{H-H}$=6.8 Hz, 12H), 1.29 (t, $^3J_{H-H}$=6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 126.7, 126.3, 119.8 (q, $^1J_{C-F}$=319.5 Hz), 62.7, 60.1, 52.3, 18.2, 18.1, 9.8; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.48 (s, 1F).

Anal. Calcd for $C_{13}H_{24}F_6N_2O_4S_2\cdot 0.4H_2O$: C, 34.12; H, 5.46; N, 6.12; S, 14.01. Found: C, 34.21; H, 5.27; N, 6.12; S, 14.39.

3.32. Allyltriphenylphosphonium trifluoromethanesulfonimide 10c

Prepared from Ph_3P (1 mmol); colourless oil (0.484 g, 0.83 mmol, 83%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.82–7.76 (m, 3H), 7.70–7.58 (m, 12H), 5.73–5.58 (m, 1H), 5.41–5.33 (m, 2H), 4.04–3.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 135.4, 133.5 (d, J_{C-P}=10.0 Hz), 130.5 (d, J_{C-P}=12.5 Hz), 126.1 (d, J_{C-P}=13.0 Hz), 122.7 (d, J_{C-P}=9.5 Hz), 119.9 (q, $^1J_{C-F}$=320.0 Hz), 117.4 (d, J_{C-P}=86.0 Hz), 28.4 (d, J_{C-P}=51.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.32 (s, 1F); ^{31}P NMR ($CDCl_3$, 121 MHz): 21.62 (s, 1P).

Anal. Calcd for $C_{23}H_{20}F_6NO_4PS_2$: C, 47.34; H, 3.45; N, 2.40; S, 10.99. Found: C, 47.35; H, 3.54; N, 2.52; S, 10.69.

3.33. 1-Allyl-tetrahydrothiophenium trifluoromethanesulfonimide 10d

RN: [949155-08-2][20m]

Prepared from tetrahydrothiophene (1 mmol); yellow oil (0.358 g, 0.84 mmol, 84%).

^{1}H NMR (CD_3CN, 200 MHz): δ 8.89–5.77, (m, 1H), 5.66–5.55 (m, 2H), 3.81 (d, J_{H-H}=8 Hz, 2H), 3.54–3.24 (m, 4H), 2.39–2.14 (m, 4H); ^{13}C NMR (CD_3CN, 50 MHz): δ 127.8, 126.0, 121.0 (q, $^1J_{C-F}$=318.5 Hz), 45.2, 43.2, 29.4; ^{19}F NMR (CD_3CN, 235 MHz): δ −79.93.

Anal. Calcd for $C_9H_{13}F_6NO_4S_3$: C, 26.40; H, 3.20; N, 3.42; S, 23.50. Found: C, 26.65; H, 3.10; N, 3.53; S, 23.11.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.04.068.

References and notes

1. (a) Foropoulos, J.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720–3723; (b) DesMarteau, D. D.; Witz, M. *J. Fluorine Chem.* **1991**, *52*, 7–12.
2. Xu, K. *Chem. Rev.* **2004**, *104*, 4303–4417.
3. (a) Belieres, J. P.; Gervasio, D.; Angell, C. A. *Chem. Commun.* **2006**, 4799–4801; (b) Susan, B. H.; Noda, A.; Mitsushima, S.; Watanabe, M. *Chem. Commun.* **2003**, 938–939.
4. Xue, H.; Verma, R.; Shreeve, J. M. *J. Fluorine Chem.* **2006**, *127*, 159–176.
5. Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; John Wiley: New York, NY, 1985.
6. (a) Singh, S.; DesMarteau, D. D.; Zuberi, S. S.; Witz, M.; Huang, H.-N. *J. Am. Chem. Soc.* **1987**, *109*, 7194–7196; (b) Zhang, J.; DesMarteau, D. D. *J. Fluorine Chem.* **2001**, *111*, 253–257; (c) Lal, G. S.; Pez, G. P.; Syvret, R. G. *Chem. Rev.* **1996**, *96*, 1737–1755.
7. Central Glass Co. Ltd, JP 070246338, 1995.
8. Hasegawa, Y.; Ohkubo, T.; Sogabe, K.; Kawamura, Y.; Wada, Y.; Nakashima, N.; Yanagida, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 357–360.
9. (a) Howells, R. D; Lamanna, W. M; Fanta, A. D; Waddell, J.E. WO 9723448 (to 3M), 1997; *Chem. Abstr.* **1997**, 03575; (b) Sakai, S; Takase, H; Sakauchi, H. EP 1029850 (to Central Glass Co. Ltd.), 2000; *Chem. Abstr.* **2000**, 592395.
10. (a) Sakaguchi, H; Fuji, K; Sakai, S; Kobayashi, Y; Kita, Y. FR 2724380 (to Central Glass Co. Ltd.), 1996; *Chem. Abstr.* **1996**, 311263; (b) Morizaki, K; Sasaki, M. JP 2000086617 (to Kanto Denka Kogyo KK), 2000; *Chem. Abstr.* **2000**, 198018.

11. (a) Armand, M. FR 2637284 (to Elf Aquitaine & Hydro Quebec), 1991; *Chem. Abstr.* **1990**, 531568; (b) Furuya, M; Nakajima, H. JP 9173856 (to Asahi Chemical Ind.), 1997.
12. (a) Sogabe, K. JP 2001233849 (to New Japan Chem. Co. Ltd.), 2001; *Chem. Abstr.* **2001**, 628706; (b) Sogabe, K.; Hasegawa, Y.; Wada, Y.; Kitamura, T.; Yanagida, S. *Chem. Lett.* **2000**, 944–945.
13. (a) Hendrickson, J. B.; Bergeron, R.; Giga, A.; Sternbach, D. *J. Am. Chem. Soc.* **1973**, *95*, 3412–3413; (b) Glass, R. S. *J. Chem. Soc., Chem. Commun.* **1971**, 1546–1547; (c) Müller, P.; Phuong, N. T. M. *Helv. Chim. Acta* **1979**, *62*, 1485–1492.
14. Toulgoat, F.; Langlois, B. R.; Médebielle, M.; Sanchez, J.-Y. *J. Org. Chem.* **2008**, *73*, 5613–5616.
15. (a) DeChristopher, P. J.; Adamek, J. P.; Klein, S. A.; Lyon, G. D.; Baumgarten, R. J. *J. Org. Chem.* **1975**, *40*, 3288–3291; (b) Glass, R. S.; Swedo, R. J. *J. Org. Chem.* **1978**, *43*, 2291–2294; (c) Müller, P.; Phuong, N. T. M. *Tetrahedron Lett.* **1978**, *47*, 4727–4730.
16. (a) Wakselman, C. Private communication. (b) Langlois, B. R; Forat, G. Unpublished work.
17. For example **3q** was already tested as ionic liquids: Williams, D. B. G.; Ajam, M.; Ranwell, A. *Organometallics* **2007**, *26*, 4692–4695.
18. Zhang, J.; Martin, G. R.; DesMarteau, D. D. *Chem. Commun.* **2003**, 2334–2335.
19. A method claimed in a Japanese patent seems to be similar to our, except that the transformations of **2** to sulfonimides salts are not 'one-pot'. However, no explanation of the transformation is available. Mogi, A; Morizaki, K; Funaki, M. JP 2004269491 (to Kanto Denka Kogyo KK), 2004; *Chem. Abstr.* **2004**, 798634.
20. (a) Prasad, P. S. S.; Munshi, M. Z. A.; Owens, B. B.; Smyrl, W. H. *Solid State Ionics* **1990**, *40–41*, 959–963; (b) Lascaud, S.; Perrier, M.; Vallee, A.; Besner, S.; Prud'homme, J.; Armand, M. *Macromolecules* **1994**, *27*, 7469–7477; (c) Kobayashi, H.; Nie, J.; Sonoda, T. *Chem. Lett.* **1995**, *4*, 307–308; (d) Ishihara, K.; Kubota, M.; Yamamoto, H. *Synlett* **1996**, 265–266; (e) Ue, M. *J. Electrochem. Soc.* **1994**, *141*, 3336–3342; (f) Susan, M. A. B. H.; Noda, A.; Mitsushima, S.; Watanabe, M. *Chem. Commun.* **2003**, 938–939; (g) Luo, H.; Yu, M.; Dai, S. *Z. Naturforsch., A: Phys. Sci.* **2007**, *62*, 281–291; (h) Vij, A.; Zheng, Y. Y.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1994**, *33*, 3281–3288; (i) Sun, J.; Forsyth, M.; MacFarlane, D. R. *J. Phys. Chem. B* **1998**, *102*, 8858–8864; (j) Matsumoto, H.; Matsuda, T.; Miyazaki, Y. *Chem. Lett.* **2000**, *12*, 1430–1431; (k) Dzyuba, S. V.; Bartsch, R. A. *ChemPhysChem* **2002**, *3*, 161–166; (l) Shiomi, Y. Pct WO 2007119631 (to Koei Chemical Co., Ltd.), 2007; *Chem. Abstr.* **2007**, 1204023; (m) Zhao, D.; Fei, Z.; Ang, W. H.; Dyson, P. J. *Int. J. Mol. Sci.* **2007**, *8*, 304–315.