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Divergent Preparation of Fluoroalkylated Sulfilimine and Sulfilimino Iminium Salts

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Abstract: We have successfully extended our previously described methodology for the preparation of trifluoromethyl *N*-acyl sulfilimines to the case of bromodifluoro- and dichlorofluoromethyl derivatives. Attempts to convert such *N*-acyl sulfilimines to free NH-sulfilimines failed. However, a strategy based on the reaction of their direct ditriflyl ketal precursor with amines allows the isolation of either original sulfilimino iminium salts using secondary amines or of free NH-sulfilimines using primary amines. The latter were further easily *N*-functionalized with electron-withdrawing groups giving structures close to those of efficient perfluoroalkylating agents. Preliminary experiments showed that these new sulfilimine-based compounds have poor perfluoroalkylating abilities, demonstrating that the sulfilimine function is not sufficiently activating for that purpose, contrary to sulfur(VI) reagents.

Keywords: electron-deficient compounds; fluorine; sulfilimines; sulfilimino iminium salts; synthetic methods

Introduction

The introduction of fluorine into organic substrates is a subject of great interest. Numerous studies in this field have been stimulated by the unrivalled properties brought about by the presence of this atom.[1] Its incorporation into molecules has allowed for progress in life sciences (medicinal chemistry and agrochemistry), material sciences, energy and also in catalysis.[2] Despite all these improvements, there are many challenges still remaining for organic chemists, in particular the introduction of perfluoroalkyl groups. The family of sulfur(IV) and sulfur(VI) derivatives appears to be flexible for this purpose because it has furnished either nucleophilic or electrophilic reagents (Figure 1). Perfluoroalkyl sulfoxides and sulfones have indeed been described as efficient nucleophilic perfluoroalkylating reagents,[3] yet recent innovative research in this area has highlighted the importance of the perfluoroalkyl sulfoximine structures as new electrophilic perfluoroalkylating agents.[4] Interestingly, it is important to notice that the replacement of an oxygen by a nitrogen atom reverses the behaviour of the reagent.

However, until our publication concerning the preparation under very mild conditions of sulfilimines and sulfoximines, access to compounds **2** and **4** was somewhat limited. We disclosed a Ritter-like reaction, between nitriles and sulfoxides activated by trifluoromethanesulfonic anhydride, giving rise to a wide

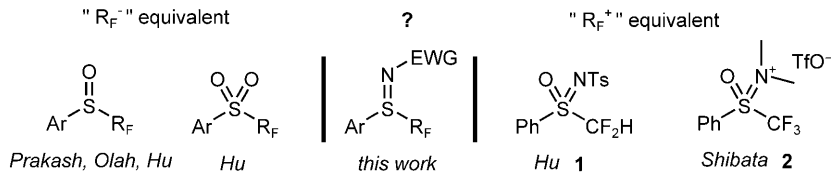
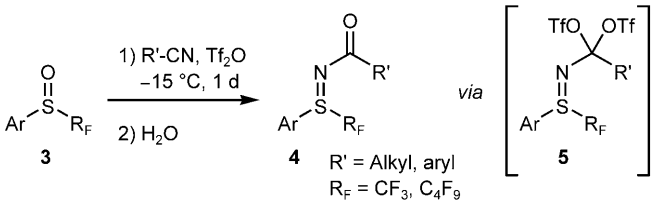


Figure 1. Sulfoxide, sulfone and sulfoximine perfluoroalkylating reagents.



Scheme 1. General preparation of fluorinated acyl sulfilimines.

range of acyl sulfilimines **4** after hydrolysis of a ditriflyl ketal **5** intermediate (Scheme 1).[5] In the same work, we also described the facile synthesis of perfluorinated sulfoximines either by oxidation of pure sulfilimines **4** or directly in a one-pot process from sulfoxides.

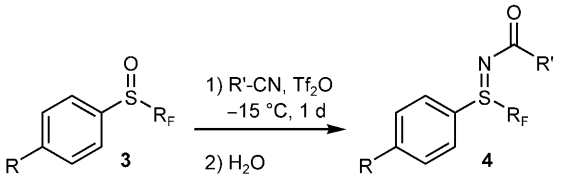
Recently, Hu and co-workers described the preparation of a difluoromethyl sulfoximine **1** by copper-catalyzed nitrene transfer reaction onto the corresponding sulfoxide.[4a] This publication prompted us to firstly extend our methodology to aryl mono- and difluoromethyl *N*-functionalized sulfilimines. Secondly, we wanted to probe the behaviour of a wide range of fluorinated sulfilimines including newly synthesized ones under both nucleophilic and electrophilic perfluoroalkylation conditions.

Results and Discussion

As a prerequisite we started by studying the preparation of aryl bromodifluoro- and dichlorofluoromethyl sulfilimines (Table 1). Selected examples of bromodifluoromethyl sulfoxides clearly demonstrated the efficiency of our approach (entry 1). For these the substitution of the aromatic ring was tolerated (entries 2 and 3) as well as the variation of the nitrile (entry 4) including one derivative bearing a terminal bromine allowing a further post-functionalization (entry 5). Similar results were obtained with dichlorofluoromethyl sulfoxides with somewhat lower yields especially with nitriles other than acetonitrile (entries 6–10). The isolation of aryl difluoromethyl acylsulfilimines ($R_F = CF_2H$) **4** was not really successful. In spite of a total conversion of the corresponding aryl difluoromethyl sulfoxide, we were unable to isolate, in both an acceptable and reproducible yield, the target molecule because of its degradation during the purification on silica gel. For the further synthesis of sulfoximines, our work hence appears to be complementary to the copper-based methodology of Hu and co-workers.[4a]

We next focused our attention on the preparation of "free sulfilimines". The isolation of these target compounds would be of interest, with one of the first and most important challenges envisioned being the

Table 1. Preparation of mono- and difluoromethyl acyl sulfilimines.



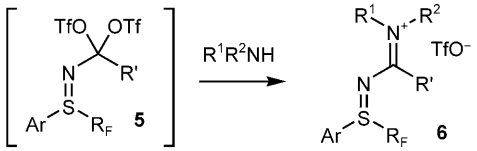
Entry[a]	R	R′	R_F		Yield [%]
1	H	Me	CF_2Br	**4a**	81
2	Me	Me	CF_2Br	**4b**	83
3	Br	Me	CF_2Br	**4c**	78
4	H	Ph	CF_2Br	**4d**	72
5	H	$(CH_2)_2Br$	CF_2Br	**4e**	55
6	H	Me	$CFCl_2$	**4f**	73
7	Me	Me	$CFCl_2$	**4g**	67
8	Br	Me	$CFCl_2$	**4h**	64
9	H	Ph	$CFCl_2$	**4i**	31
10	H	$(CH_2)_2Br$	$CFCl_2$	**4j**	18

[a] See ref.[6] for the preparation of starting sulfoxides.

functionalization of the nitrogen. The main purpose is the preparation of new perfluoroalkylating reagents based on enhanced activation of the perfluoroalkyl part by the nitrogen substituent. Numerous attempts at hydrolysis (or reduction) of acylsulfilimines **4** proved, however, to be unsuccessful and only led either to the parent sulfoxides or to non-fluorinated products.

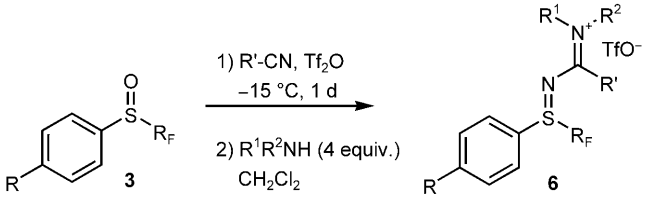
We thought that a clue to this problem could be found in the synthetic intermediate **5**. The challenge was to switch from a simple hydrolysis of **5** (giving rise to acyl sulfilimine **4)** to the preparation of derivatives which are more amenable to deprotection by the choice of a suitable nucleophile able to selectively replace the trifluoromethanesulfonic groups in **5**.

Amongst the possible reagents, amines were first considered as candidates for such a purpose. Interestingly, we found that the compounds formed using primary amines were totally different from those obtained with secondary amines. In this latter case, we were pleased to find that addition of amines to the crude reaction mixture allowed the formation of stable and original sulfilimino iminium salts **6**, thus achieving our first goal: the substitution of the bis triflate moieties (Scheme 2).



Scheme 2. Treatment with secondary amines.

Table 2. Preparation of sulfilimino iminium salts.

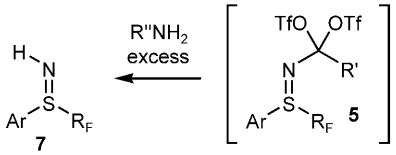


Entry	R	R′	R^1	R^2	R_F		Yield [%]
1	H	Me	Et	Et	$CFCl_2$	**6a**	76
2	H	Me	Et	Et	CF_2Br	**6b**	83
3	H	Me	H	Pr	CF_3	**6c**	79[a]
4	H	Me	Me	Me	CF_3	**6d**	98
5	Me	Me	Me	Me	CF_3	**6e**	76
6	Me	Me	Et	Et	CF_3	**6f**	91
7	Me	Ph	Et	Et	CF_3	**6g**	82
8	Me	Ph	Ph	Ph	CF_3	**6h**	85
9	Br	Me	Et	Et	C_4F_9	**6i**	89

[a] Only three equivalents of amine were used.

In the case of secondary amines a short study showed that at least 4 equivalents of amine relative to the starting sulfoxide were needed in order to ensure good yields of salts **6**, but that a large excess of amine was not detrimental to the yield. The reaction appears very flexible to numerous possible structural variations: substitution of the aromatic ring, the length of the fluorinated chain (from mono to perfluoralkyl), the nature of the nitrile and of the secondary amine (Table 2). All these new compounds were stable, isolated in very good yields and fully characterized. The examples depicted in Table 2 are representative of the versatility and the flexibility of this one-pot reaction. This as yet unknown and original family of molecules can thus be easily synthesized on demand and may find useful applications. For instance aryl sulfilimino iminium salts such as **6h** (entry 8) exhibiting many highly delocalized π electrons, and a high polarity could be interesting in molecular electronics with emphasis in fluorescence.

Interestingly, the use of a primary amine in a 3:1 stoichiometry also led to the isolation of an iminium salt **6c** (entry 3). However, contrary to the case of secondary amines and to our delight, when an excess of primary amine was used a free sulfilimine **7** was isolated instead of a salt **6** (Scheme 3).

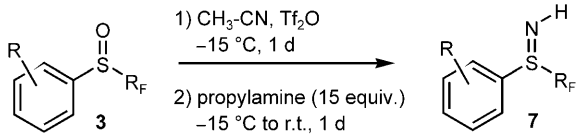


Scheme 3. Treatment with an excess of primary amines.

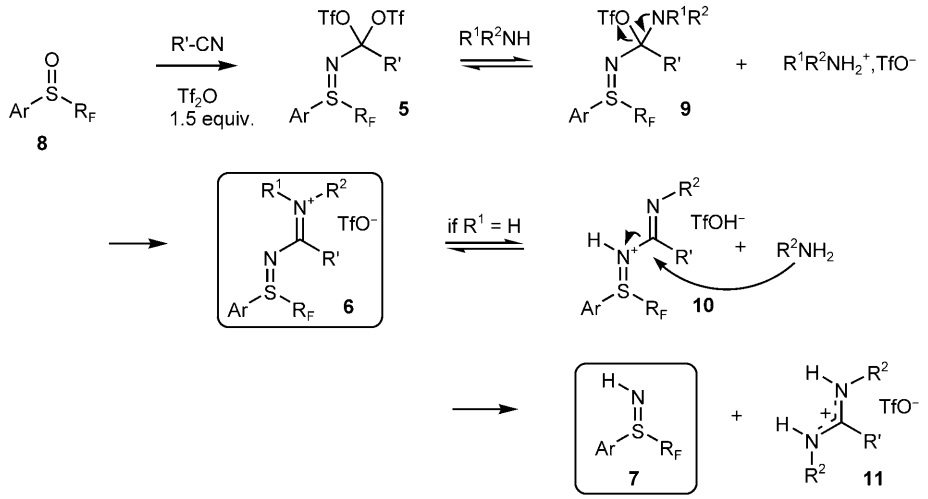
This latter reaction was then optimized. Ideally, the primary amine should be introduced in a dry form (to avoid formation of acylsulfilimines **4** by competing hydrolysis), should be inexpensive and have a low boiling point (because the amine is used in excess). Good results were obtained with ammonia and ethylamine but these were later discarded because their volatility was too high.

Propylamine met the above criteria and hence appeared to be the best candidate. The number of equivalents needed for the reaction was then studied. Below a critical value of 15 equivalents, we were not able to reach total completion of the reaction. This amount was considered as our standard for the studies devoted to the scope of this transformation (Table 3). The reaction was then conducted on a wide range of aryl fluoroalkyl sulfoxides. Two types of structural variations were examined: the nature and length of the fluorinated chains and the substitution of the aromatic ring. The gram-scale synthesis of NH-sulfilimines occurred in good to quantitative yields with mono- (entries 1–3), di- (entries 4–6), trifluoromethyl (entries 7–14) and higher perfluoroalkyl chains. In spite of a total conversion, the slightly lower yields observed for mono- and difluorinated groups may be explained by the fact that compounds **7a–f** are relatively unstable and partially decomposed during the purification step on silica gel. The presence of a methyl substituent on the aromatic group is beneficial to the yield whereas the attachment of a halogen decreased slightly the yield. All these new compounds

Table 3. Preparation of "free sulfilimines".



Entry	R	R_F		Yield [%]
1	H	$CFCl_2$	**7a**	54
2	*p*-Me	$CFCl_2$	**7b**	46
3	*p*-Br	$CFCl_2$	**7c**	48
4	H	CF_2Br	**7d**	59
5	*p*-Me	CF_2Br	**7e**	64
6	*p*-Br	CF_2Br	**7f**	57
7	H	CF_3	**7g**	91
8	*o*-Me	CF_3	**7h**	99
9	*m*-Me	CF_3	**7i**	99
10	*p*-Me	CF_3	**7j**	99
11	*p*-Br	CF_3	**7k**	88
12	*o*-Cl	CF_3	**7l**	90
13	*m*-Cl	CF_3	**7m**	77
14	*p*-Cl	CF_3	**7n**	79
15	H	C_4F_9	**7o**	70
16	*p*-Me	C_4F_9	**7p**	94
17	*p*-Br	C_4F_9	**7q**	70



Scheme 4. Mechanism proposal with either primary or secondary amines.

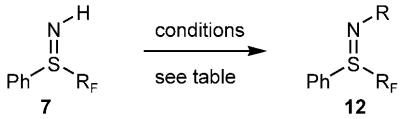
are stable once isolated and can be kept for weeks in the refrigerator.

Reactions with both secondary and primary amines can be rationalized by the following mechanism proposal (Scheme 4). We assume that a first equivalent of amine displaces a trifluoromethanesulfonate of the ketal **5**[7] (trapped by a second equivalent of amine) to produce the intermediate **9** which quickly evolves into the key iminium salt **6**. The first part of this transformation pathway requires at least three equivalents of amine: two for the main process and a third being consumed by the slight excess of trifluoromethanesulfonic anhydride remaining in the reaction medium. Addition of an amine in this precise amount then gives rise to the sole isolation of salt **6** whatever its substitution degree (primary or secondary). On the other hand, the addition of an amine in a large excess showed the greatly diverging behaviour of primary and secondary amines. With secondary amines, even in excess, nothing else happens and salt **6** is still the major product. The use of a primary amine allows the formation of free sulfilimines **7**. As a matter of fact, when R^1 and R^2 are not hydrogens, compound **6** seems to be stable in the reaction medium and would not evolve further. If however R^1 is a hydrogen, a prototropic equilibrium can generate molecule **10**. The latter can further react with another equivalent of amine to yield sulfilimine **7** and amidinium **11**. This mechanism is supported by the isolation and full characterization of **11a** (R = Ph and R^2 = Pr, see Experimental Section), whose structure is in agreement with those of previously described analogues.[8] Moreover, when the pure isolated salt **6c** was treated again with an excess of propylamine it was fully converted into the corresponding free sulfilimine **7g**.

With free sulfilimines in hand, different possibilities for their *N*-functionalization were then envisioned. All attempts at alkylation by direct nucleophilic substitution failed, thus preventing the introduction of methyl, benzyl or allyl groups. With all these experiments, the conversion of the starting sulfilimines was almost quantitative but no fluorinated compound has been observed. We assume therefore that *N*-alkylated sulfilimines are not stable enough to be isolated. Metal-catalyzed (Pd and Cu) arylation at nitrogen under the conditions described for sulfoximines proved unsuccessful.[9] No reaction occurred in the different conditions tested and the starting materials was entirely recovered. Fortunately, the introduction of an electron-withdrawing group was efficient for sulfilimine stabilization, as shown by the results summarized in Table 4. Mild conditions allowed the synthesis of sulfilimines bearing a trifluoromethanesulfonyl group in good (for CF_3 series) to acceptable yields (for mono- and difluoromethyl series) (entries 1–3). We next concentrated our efforts on trifluoromethyl derivatives. Tosyl and nosyl derivatives as well as nitro, cyano and Boc substituted derivatives were readily obtained (entries 4–8). We also envisioned functionalization of the nitrogen by an aza-Michael addition. However, reactions attempted with classic Michael acceptors (acrylonitriles or acrylates) met with poor success even under harsh conditions (no solvent, high temperature). By contrast, vinyl tridecafluorohexyl sulfone showed again its very high reactivity[10] and the Michael adduct **12i** (entry 9) was obtained within a very short time and in an excellent yield. These latter results highlighted the poor nucleophilicity of perfluoroalkyl free sulfilimines.

As mentioned in the introduction, the structures of some of the compounds described in this work are reminiscent of those of efficient fluoroalkylating reagents described either by Shibata or Hu.[4] It was thus tempting to test the fluoroalkylating ability of our compounds toward nucleophilic (thiolate, acetylide, enolate, phenolate) or also electrophilic (ketone,

Table 4. Functionalization of "free sulfilimines".



Entry	Reactant	Conditions	R		Yield [%]
1	**7a**	Tf_2O, pyridine, CH_2Cl_2	Tf	**12a**	47
2	**7d**	Tf_2O, pyridine, CH_2Cl_2	Tf	**12b**	38
3	**7g**	Tf_2O, pyridine, CH_2Cl_2	Tf	**12c**	84
4	**7g**	TsCl, pyridine, CH_2Cl_2	Ts	**12d**	100
5	**7g**	NsCl, pyridine, CH_2Cl_2	Ns	**12e**	83
6	**7g**	HNO_3, H_2SO_4, Ac_2O, CH_2Cl_2	NO_2	**12f**	66
7	**7g**	BrCN, Et_3N, CH_2Cl_2	CN	**12g**	38
8	**7g**	Boc_2O, Et_3N, CH_2Cl_2	Boc	**12h**	70
9	**7g**	CH_2=CH–$SO_2C_6F_{13}$, CH_2Cl_2	$(CH_2)_2SO_2C_6F_{13}$	**12i**	83

aldehyde, alkene) species. In both cases, the attempts with the acyl sulfilimines **4**, with iminium salts **6** as well as with free sulfilimines **7** afforded only at best traces amounts of fluoroalkylated products. Although some encouraging results were obtained with trifluoromethanesulfonyl sulfilimines **12a–c**, they were not sufficiently clear-cut or high-yielding to warrant further extensive study. The best results were achieved upon condensation of lithium phenylacetylide with acylsulfilimine **4a** affording bromodifluoromethylphenylacetylene in only 23% conversion, or of lithium 6-methoxy-2-naphthylacetylide with triflyl sulfilimine **12b** giving the corresponding bromodifluoromethyl derivative in a 22% estimated yield but hardly separable from the starting material.

Conclusions

We have demonstrated the efficiency of amine trapping for the functionalization of the bis triflate intermediate **5**. The great molecular diversity offered by the judicious choice of the nitrogen derivative allowed either original sulfilimino iminium salts **6** or free sulfilimines **7** to be obtained as needed. Further *N*-substitution of sulfilimines **7** by electron-withdrawing groups afforded stable sulfilimines. Preliminary experiments showed that these sulfilimine-based compounds showed poor efficiency regarding perfluoroalkyl transfer reactions. Nevertheless, the important variety of sulfilimines described here opens the way, by simple oxidation, to a wide range of sulfoximines as new and promising perfluoroalkylating reagents. These studies are currently under development in our laboratory. Furthermore, many other applications are envisioned for these new and original structures. Non-fluorinated sulfoximines have been extensively described as efficient ligands for catalysis[11] and also more rarely non-fluorinated sulfilimines.[12] We assume that these compounds could be used as novel ligands for organometallic purposes. Besides, the free sulfilimines will be studied as new organocatalysts. Lastly, these new sulfilimine derivatives will be evaluated as new pharmacophores for medicinal and agrochemistry purposes.

Experimental Section

General Procedure for the Preparation of Sulfilimine, as Exemplified by the Reaction of Difluorobromomethyl Phenyl Sulfoxide with Acetonitrile

Trifluoromethanesulfonic anhydride (1.7 mL, 9.5 mmol, 1.5 equiv.) was added to a precooled (−15 °C) mixture of phenyl bromodifluoromethyl sulfoxide (1.6 g, 6.4 mmol, 1 equiv.) and acetonitrile (0.5 mL, 9.5 mmol, 1.5 equiv.). The reaction mixture was stirred for one day at −15 °C, then hydrolyzed with water (20 mL), and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water (3 × 50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, pentane/Et_2O 4/6) to give ***N*-(acetyl) bromodifluoromethyl phenyl sulfilimine (4a)** as an orange powder; yield: 1.5 g (81%); mp 56–58 °C; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −47.1 and −46.1 (AB syst, J = 136 Hz); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21 (3H, s), 7.55–7.61 (2H, m), 7.68 (1H, tt, J = 7.5 Hz, J = 1.6 Hz), 7.87–7.91 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.6, 123.4 (CF_2, dd, J = 352 Hz, J = 348 Hz), 128.0, 129.2, 129.7, 134.2, 183.3; anal. calcd. for $C_9H_8BrF_2NOS$: C 36.50, H 2.72, N 4.73; found: C 36.59, H 2.73, N 4.73.

***N*-(Acetyl) bromodifluoromethyl *p*-tolyl sulfilimine (4b):** White powder; mp 58–60 °C; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −47.4 and −46.4 (AB syst, J = 135 Hz); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.19 (3H, s), 2.41 (3H, s), 7.36 (2H, d, J = 8.2 Hz), 7.77 (2H, d, J = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 24.7, 123.6 (CF_2, dd, J = 352 Hz, J = 348 Hz), 124.6, 129.3, 130.5, 145.5, 183.3; MS (pos. ESI, for ^{79}Br): m/z = 332 (M + Na)$^+$, 641 (2M + Na)$^+$; HR-MS: m/z =

331.9517, calcd. for $C_{10}H_{10}{}^{79}BrF_2NOSNa$: 331.9532 ($\delta$ = 4.5 ppm).

***N*-(Acetyl) bromodifluoromethyl *p*-bromophenyl sulfilimine (4c):** White powder; mp 88–90 °C; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −47.0 and −46.0 (AB syst, J = 136 Hz); ^1H NMR (200 MHz, $CDCl_3$): δ = 2.21 (3 H, s), 7.69–7.79 (4 H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.6, 123.2 (CF_2, dd, J = 353 Hz, J = 349 Hz), 127.1, 129.6, 130.5, 133.1, 183.3; MS (pos. ESI, for ^{79}Br): m/z = 396 $(M+Na)^+$, 769 $(2M+Na)^+$; HR-MS: m/z = 395.8481, calcd. for $C_9H_7{}^{79}Br_2F_2NOSNa$: 395.8481 ($\delta$ = 0 ppm).

Bromodifluoromethyl phenyl *N*-(phenylacetyl) sulfilimine (4d): Yellow powder; mp 98–100 °C; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −46.8 and −45.5 (AB syst, J = 135 Hz); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.49 (2 H, m), 7.50–7.55 (1 H, m), 7.60–7.66 (2 H, m), 7.70–7.77 (1 H, m), 8.02 (2 H, d, J = 7.7 Hz), 8.26–8.30 (2 H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.0, 128.6 (CF_2, dd, J = 348 Hz, J = 347 Hz), 129.3, 129.4, 129.9, 131.7, 134.3, 135.2, 177.4; anal. calcd. for $C_{14}H_{10}BrF_2NOS$: C 46.94, H 2.81, N 3.91; found: C 47.03, H 2.94, N 3.86.

Bromodifluoromethyl *N*-(bromopropylacetyl) phenyl sulfilimine (4e): Yellow powder; mp 56–58 °C; ^{19}F NMR (188 MHz, $CDCl_3$): δ = -47.0 and −45.8 (AB syst, J = 136 Hz); ^1H NMR (200 MHz, $CDCl_3$): δ = 3.07 (2 H, t, J = 7 Hz), 3.71 (2 H, t, J = 7.1 Hz), 7.56–7.76 (3 H, m), 7.93 (2 H, d, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.4, 41.1, 123.4 (CF_2, dd, J = 352 Hz, J = 347 Hz), 127.7, 129.3, 129.8, 134.4, 181.9; MS (pos. ESI, for ^{79}Br): m/z = 410 $(M+Na)^+$, 797 $(2M+Na)^+$; HR-MS: m/z = 409.8642, calcd. for $C_{10}H_9{}^{79}Br_2F_2NOSNa$ 409.8637 (δ = 1.2 ppm).

***N*-(Acetyl) dichlorofluoromethyl phenyl sulfilimine (4f):** White powder; mp 84–86 °C; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −54.3 (1 F, d, J = 1.4 Hz); ^1H NMR (200 MHz, $CDCl_3$): δ = 2.23 (3 H, s), 7.53–7.74 (3 H, m), 7.94–8.00 (2 H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.2, 124.9 (CF, d, J = 340 Hz), 129.1, 129.5, 129.8, 134.4, 183.6; anal. calcd. for $C_9H_8Cl_2FNOS$: C 40.31, H 3.01, N 5.22; found: C 39.92, H 2.94, N 5.02.

***N*-(Acetyl) dichlorofluoromethyl *p*-tolyl sulfilimine (4g):** Yellow powder; mp 68–70 °C; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −54.7 (1 F, d, J = 1.4 Hz); ^1H NMR (200 MHz, $CDCl_3$): δ = 2.21 (3 H, s), 2.43 (3 H, s), 7.36 (2 H, d, J = 8.1 Hz), 7.83 (2 H, d, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 25.1, 124.9 (CF, d, J = 340 Hz), 125.5, 129.7, 130.2, 145.6, 183.3; anal. calcd. for $C_{10}H_{10}Cl_2FNOS$: C 42.57, H 3.57, N 4.96; found: C 42.65, H 3.68, N 4.89.

***N*-(Acetyl) *p*-bromophenyl dichlorofluoromethyl sulfilimine (4h):** Brown powder; mp 90–92 °C; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −54.3 (1 F, s); ^1H NMR (200 MHz, $CDCl_3$): δ = 2.21 (3 H, s), 7.68–7.74 (2 H, m), 7.79–7.86 (2 H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0, 124.6 (CF, d, J = 341 Hz), 128.0, 129.8, 131.0, 132.8, 183.4; MS (pos. ESI, for ^{79}Br, ^{35}Cl): m/z = 346 $(M+H)^+$, 368 $(M+Na)^+$, 691 $(2M+H)^+$; HR-MS: m/z = 345.8880, calcd. for $C_9H_8{}^{79}Br^{35}Cl_2FNOS$: 345.8871 ($\delta$ = 2.6 ppm).

Dichlorofluoromethyl phenyl *N*-(phenylacetyl) sulfilimine (4i): ^{19}F NMR (188 MHz, $CDCl_3$): δ = −54.0 (1 F, s); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.48 (2 H, m), 7.49–7.55 (1 H, m), 7.59–7.66 (2 H, m), 7.70–7.76 (1 H, m), 8.07–8.11 (2 H, m), 8.28–8.32 (2 H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 125.4 (CF, d, J = 340 Hz), 127.9, 129.4, 129.5, 129.6, 129.8, 131.7, 134.4, 135.5, 137.7, 177.5; MS (pos. ESI for ^{35}Cl): m/z = 352 $(M+Na)^+$, 681 $(2M+Na)^+$; HR-MS: m/z = 351.9741, calcd. for $C_{14}H_{10}{}^{35}Cl_2FNOSNa$: 351.9742 ($\delta$ = 0.3 ppm).

***N*-(Bromopropylacetyl) dichlorofluoromethyl phenyl sulfilimine (4j):** ^{19}F NMR (188 MHz, $CDCl_3$): δ = −54.3 (1 F, d, J = 1.4 Hz); ^1H NMR (300 MHz, $CDCl_3$): δ = 3.09 (2 H, t, J = 7.1 Hz), 3.72 (1 H, t, J = 7.1 Hz), 7.59–7.64 (2 H, m), 7.70–7.76 (1 H, m), 7.99 (2 H, d, J = 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.5, 41.5, 124.9 (CF, d, J = 340 Hz), 128.7, 129.6, 129.9, 134.6, 182.1; MS (pos. ESI, for ^{79}Br, ^{35}Cl): m/z = 360 $(M+H)^+$, 382 $(M+Na)^+$, 741 $(2M+Na)^+$; HR-MS: m/z = 359.9036, calcd. for $C_{10}H_{10}{}^{79}Br^{35}Cl_2FNOS$: 359.9028 ($\delta$ = 2.2 ppm).

General Procedure for the Synthesis of Sulfilimino Iminium Salts, as Exemplified by the Reaction of Phenyl Trifluoromethyl Sulfoxide with Acetonitrile and Dimethylamine

Trifluoromethanesulfonic anhydride (0.3 mL, 1.9 mmol, 1.5 equiv.) was added under argon to a precooled (−15 °C) mixture of phenyl trifluoromethyl sulfoxide (0.25 g, 1.3 mmol, 1 equiv.) and acetonitrile (0.1 mL, 1.9 mmol, 1.5 equiv.). The reaction mixture was stirred for 1 d at −15 °C, then dimethylamine (0.35 mL, 5.2 mmol, 4 equiv.) diluted in 2 mL of CH_2Cl_2 was carefully added to the mixture. After 16 h the reaction was hydrolyzed with water (5 mL), extracted with CH_2Cl_2 (3 × 15 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by preparative chromatography (SiO_2, CH_2Cl_2/methanol, 95/5) to give **dimethyl-{1-[(phenyl(trifluoromethyl)-λ⁴-sulfanylidene)amino]ethylidene}ammonium trifluoromethanesulfonate (6d)**; yield: 0.52 g (98%); ^{19}F NMR (188 MHz, $CDCl_3$): δ = −79.0 (3 F, s), −67.3 (3 F, s); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.62 (3 H, s), 3.33 (3 H, s), 3.36 (3 H, s), 7.64–7.73 (2 H, m), 7.75–7.82 (1 H, m), 8.05 (2 H, d, J = 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2, 39.8, 41.6, 120.7 (CF_3, q, J = 321 Hz), 123.2 (CF_3, q, J = 329 Hz), 124.5, 129.1, 130.8, 135.9, 173.8; MS (pos. ESI): m/z = 194 $(M-CF_3)^+$, 263 $(M)^+$; HR-MS: m/z = 263.0816, calcd. for $C_{11}H_{14}F_3N_2S$: 263.0830 (δ = −5.3 ppm).

1-({[Dichloro(fluoro)methyl]-phenyl-λ⁴-sulfanylidene}amino)ethylidene-diethyl-ammonium trifluoromethanesulfonate (6a): Brown powder; mp 80–82 °C; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −78.8 (3 F, s), −56.3 (1 F, s); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15–1.32 (6 H, m), 2.64 (3 H, s), 3.43–3.72 (3 H, m), 3.79–3.96 (1 H, m), 7.56–7.68 (2 H, m), 7.70–7.80 (1 H, m), 8.01 (2 H, d, J = 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.8, 12.9, 18.4, 45.2, 46.7, 120.5 (CF_3, q, J = 320 Hz), 125.0 (CF, d, J = 344 Hz), 129.6, 126.0,130.0, 135.8, 172.1; MS (pos. ESI, for Cl^{35}): m/z = 222 $(M-CCl_2F)^+$, 323 $(M)^+$; HR-MS: m/z = 323.0562, calcd. for $C_{13}H_{18}{}^{35}Cl_2FN_2S$ 323.0552 (δ = 3.1 ppm).

1-({[Bromo(difluoro)methyl]-phenyl-λ⁴-sulfanylidene}amino)ethylidene-diethyl-ammonium trifluoromethanesulfonate (6b): Brown powder; mp 48–50 °C; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −78.8 (3 F, s), −49.5 and −48.5 (AB system, J = 198 Hz); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.22–1.33 (6 H, m), 3.47–3.72 (3 H, m), 2.65 (3 H, s), 3.81–3.95 (1 H, m), 7.61–7.70 (2 H, m), 7.74–7.81 (1 H, m), 8.01 (2 H, d, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.1, 13.2, 18.8,

45.4, 47.0, 120.7 (CF_3, q, $J=328$ Hz), 122.8 (CF_2, dd, $J=356$ Hz, $J=346$ Hz), 125.5, 129.4, 130.5, 135.9, 172.3; MS (pos. ESI, for ^{79}Br): $m/z=222$ $(M-CF_2Br)^+$, 351 $(M)^+$; anal. calcd. for $C_{14}H_{18}BrF_5N_2O_3S_2$: C 33.54, H 3.62, N 5.59; found: C 33.91, H 3.73, N 5.61.

Methyl-(1-{[phenyl(trifluoromethyl)-λ⁴-sulfanylidene]amino}ethylidene)ammonium trifluoromethanesulfonate (6c): ^{19}F NMR (188 MHz, $CDCl_3$) $\delta=-79.0$ (3F, s), −67.3 (3F, s); ^1H NMR (200 MHz, $CDCl_3$) $\delta=0.95$ (3H, t, $J=7.4$ Hz), 1.60–1.78 (2H, m), 2.61 (3H, s), 3.37–3.63 (2H, m), 7.68–7.88 (3H, m), 8.07 (2H, d, $J=7.6$ Hz), 9.42 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta=11.2$, 20.7, 21.1, 44.8, 120.4 (CF_3, q, $J=317$ Hz), 123.0 (CF_3, q, $J=326$ Hz), 124.1, 129.0, 130.8, 136.0, 173.7; MS (pos. ESI): $m/z=277$ $(M)^+$; HR-MS: $m/z=277.0996$, calcd. for $C_{12}H_{16}F_3N_2S$: 277.0986 ($\delta=3.6$ ppm).

Dimethyl-(1-{[*p*-tolyl(trifluoromethyl)-λ⁴-sulfanylidene]amino}ethylidene)ammonium trifluoromethanesulfonate (6e): ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-78.9$ (3F, s), −67.7 (3F, s); ^1H NMR (300 MHz, $CDCl_3$): $\delta=2.43$ (3H, s), 2.58 (3H, s), 3.30 (3H, s), 3.33 (3H, s), 7.45 (2H, d, $J=8.1$ Hz), 7.90 (2H, d, $J=8.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=19.0$, 21.8, 39.7, 41.4, 120.7 (CF_3, q, $J=321$ Hz), 120.8, 123.1 (CF_3, q, $J=328$ Hz), 129.1, 131.4, 147.6, 173.5; MS (pos. ESI): $m/z=208$ $(M-CF_3)^+$, 277 $(M)^+$; HR-MS: $m/z=277.0978$, calcd. for $C_{12}H_{16}F_3N_2S$: 277.0986 ($\delta=-2.9$ ppm).

Diethyl-(1-{[*p*-tolyl(trifluoromethyl)-λ⁴-sulfanylidene]amino}ethylidene)ammonium trifluoromethanesulfonate (6f): ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-78.8$ (3F, s), −67.5 (3F, s); ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.20$–1.30 (6H, m), 2.43 (3H, s), 2.62 (3H, s), 3.46–3.71 (3H, m), 3.73–3.87 (1H, m), 7.46 (2H, d, $J=8.7$ Hz), 7.91 (2H, d, $J=8.3$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=11.9$, 13.2, 18.6, 21.8, 45.3, 47.0, 120.7 (CF_3, q, $J=321$ Hz), 120.9, 123.1 (CF_3, q, $J=328$ Hz), 129.2, 131.5, 147.7, 172.4; MS (pos. ESI): $m/z=236$ $(M-CF_3)^+$, 305 $(M)^+$; HR-MS: $m/z=305.1293$, calcd. for $C_{14}H_{20}F_3N_2S$: 305.1299 ($\delta=-2.0$ ppm).

Diethyl-(phenyl-{[*p*-tolyl(trifluoromethyl)-λ⁴-sulfanylidene]amino}methylene)ammonium trifluoromethanesulfonate (6g): Brown powder; mp 109–111 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-78.7$ (3F, s), −66.2 (3F, s); ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.05$–1.16 (3H, m), 1.33–1.44 (3H, m), 2.41 (3H, s), 3.25–3.42 (2H, m), 3.71–3.86 (1H, m), 3.98–4.13 (1H, m), 6.96–7.04 (1H, m), 7.30–7.37 (1H, m), 7.38–7.51 (3H, m), 7.51–7.65 (2H, m), 7.65–7.72 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=11.9$, 13.4, 21.6, 44.4, 48.0, 120.6 (CF_3, q, $J=321$ Hz), 120.5, 122.7 (CF_3, q, $J=326$ Hz), 125.9, 126.1, 128.6, 129.7, 130.1, 130.2, 131.7, 132.0, 148.1, 173.7; MS (pos. ESI): $m/z=298$ $(M-CF_3)^+$, 367 $(M)^+$; HR-MS: $m/z=367.1438$, calcd. for $C_{19}H_{22}F_3N_2S$: 367.1450 ($\delta=3.5$ ppm).

({[*p*-Tolyl)(trifluoromethyl)-λ⁴-sulfanylidene]amino}-phenyl-methylene)-diphenyl-ammonium trifluoromethanesulfonate (6h): Brown powder; mp 174–176 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-78.7$ (3F, s), −65.0 (3F, s); ^1H NMR (300 MHz, $CDCl_3$): $\delta=2.46$ (3H, s), 7.03–7.29 (5H, m), 7.31–7.68 (14H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=21.8$, 120.4, 120.8 (CF_3, q, $J=321$ Hz), 122.9 (CF_3, q, $J=328$ Hz), 126.6, 127.5, 128.4, 128.7, 128.8, 129.1, 129.5, 129.5, 129.8, 130.3, 131.7, 132.2, 141.9, 148.1, 177.2; MS (pos. ESI): $m/z=394$ $(M-CF_3)^+$, 463 $(M)^+$; HR-MS: $m/z=463.1445$, calcd. for $C_{27}H_{22}F_3N_2S$: 463.1450 ($\delta=1.1$ ppm).

1-{[(4-Bromophenyl)(nonafluorobutyl)-λ⁴-sulfanylidene]-amino]ethylidene-diethyl-ammonium trifluoromethanesulfonate (6i): ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-126.2$ (2F, m), −119.8 (2F, m), −107.6 (2F, m), −81.0 (3F, t, $J=9.6$ Hz), −78.9 (3F, s); ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.23$–1.33 (6H, m), 2.67 (3H, s), 3.48–3.72 (3H, m), 3.77–3.94 (1H, m), 7.83 (2H, d, $J=9.1$ Hz), 7.96 (2H, d, $J=8.7$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=11.9$, 13.0, 18.7, 45.3, 47.1, 123.0, 131.2, 131.7, 133.8, 172.4; MS (pos. ESI, for ^{79}Br): $m/z=300$ $(M-C_4F_9)^+$, 519 $(M)^+$; anal. calcd. for $C_{17}H_{17}BrF_{12}N_2O_3S_2$: C 30.50, H 2.56, N 4.19; found: C 30.68, H 2.69, N 4.25.

General Procedure for the Preparation of Free Sulfilimines, as Exemplified by the Reaction of Phenyl Trifluoromethyl Sulfoxide with Acetonitrile

Trifluoromethanesulfonic anhydride (2.0 mL, 11.6 mmol, 1.5 equiv.) was added to a precooled (−15 °C) mixture of phenyl trifluoromethyl sulfoxide (1.5 g, 7.7 mmol, 1 equiv.) and acetonitrile (0.6 mL, 11.6 mmol, 1.5 equiv.). The reaction mixture was stirred for one day at −15 °C, diluted with CH_2Cl_2 (5 mL) then hydrolyzed by slow addition of propylamine (9.5 mL, 11.6 mmol, 15 equiv.). The reaction mixture was stirred for one day at room temperature, then water (10 mL) was added and the crude mixture extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with water (3×20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, pentane/Et_2O 4/6) to give **phenyl trifluoromethyl sulfilimine (7g)** as a white powder; yield: 1.4 g (91%); mp 48–50 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-74.4$ (3F, s); ^1H NMR (200 MHz, $CDCl_3$): $\delta=1.86$ (1H, br s), 7.53–7.66 (3H, m), 7.73–7.78 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=125.9$ (CF_3, q, $J=1.3$ Hz), 128.3 (CF_3, q, $J=337$ Hz), 129.5, 132.5, 135.2; anal. calcd. for $C_7H_6F_3NS$: C 43.52, H 3.13, N 7.25; found: C 43.71, H 3.12, N 7.21.

***N,N'*-Dipropylphenylamidinium trifluoromethanesulfonate (11a):** ^{19}F NMR (188 MHz, MeOD): $\delta=-87.7$; ^1H NMR (300 MHz, MeOD) $\delta=0.89$ (6H, t, $J=7.3$ Hz), 1.58 (4H, sextuplet, $J=7.3$ Hz), 3.15 (4H, t, $J=7.0$ Hz), 7.37–7.42 (2H, m), 7.46–7.53 (3H, m); ^{13}C NMR (50 MHz, CD_3CN) $\delta=11.6$, 24.2, 47.7, 128.4, 129.4, 130.4, 134.5, 161.8; MS (pos. ESI): $m/z=205$ $(M)^+$; HR-MS: $m/z=205.1693$, calcd. for $C_{13}H_{21}N_2$: 205.1705 ($\delta=-4.8$ ppm).

Dichlorofluoromethyl phenyl sulfilimine (7a): Yellow powder; mp 48–50 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-60.2$ (1F, d, $J=1.4$ Hz); ^1H NMR (200 MHz, $CDCl_3$): $\delta=2.47$ (1H, br s), 7.50–7.66 (3H, m), 7.79–7.84 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=127.0$, 129.0, 129.4 (CF, d, $J=348$ Hz), 132.7, 135.8; anal. calcd. for $C_7H_6Cl_2FNS$: C 37.19, H 2.67, N 6.19; found: C 37.42, H 2.78, N 6.19.

Dichlorofluoromethyl *p*-tolyl sulfilimine (7b) Yellow powder; mp 68–70 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-60.4$ (1F, d, $J=1.4$ Hz); ^1H NMR (200 MHz, $CDCl_3$): $\delta=2.42$ (3H, s), 2.50 (1H, br s), 7.34 (2H, d, $J=8.1$ Hz), 7.68 (2H, dd, $J=7.3$ Hz, $J=1.1$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=21.5$, 126.9, 129.5 (CF, d, $J=348$ Hz), 129.7, 132.7, 143.6; anal. calcd. for $C_8H_8BrF_2NS$: C 40.01, H 3.36, N 5.83; found: C 40.21, H 3.51, N 5.82.

***p*-Bromophenyl dichlorofluoromethyl sulfilimine (7c):** Orange powder; mp 64–66 °C; ^{19}F NMR (188 MHz, $CDCl_3$):

$\delta = -60.3$ (1F, s); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.49$ (1H, br s), 7.71 (4H, d, $J = 0.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 127.8$, 128.5, 129.2 (CF, d, $J = 349$ Hz), 132.3, 134.8; MS (pos. ESI, for ^{79}Br, ^{35}Cl): $m/z = 304$ $(M+H)^+$; HR-MS: $m/z = 303.8764$, calcd. for $C_7H_6{}^{79}Br^{35}Cl_2FNS$: 303.8765 ($\delta = 0.3$ ppm).

Bromodifluoromethyl phenyl sulfilimine (7d): ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -52.3$ and -51.2 (AB syst, $J = 135$ Hz); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.16$ (1H, br s), 7.52–7.68 (3H, m), 7.73–7.79 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 126.4$, 129.3, 131.5 (CF_2, dd, $J = 368$ Hz, $J = 366$ Hz), 132.6, 135.8. Due to its relative instability, full characterization of this compound was finalized *via* its derivative **12b**.

Bromodifluoromethyl *p*-tolyl sulfilimine (7e): ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -52.5$ and -51.5 (AB syst, $J = 135$ Hz); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.11$ (1H, br s), 2.44 (3H, s), 7.36 (2H, d, $J = 8.1$ Hz), 7.62 (2H, d, $J = 8.2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.5$, 126.3, 129.9, 131.5 (CF_2, dd, $J = 366$ Hz, $J = 357$ Hz), 132.6, 143.4; MS (pos. ESI, for ^{79}Br): $m/z = 268$ $(M+H)^+$; HR-MS: $m/z = 267.9606$, calcd. for $C_8H_9{}^{79}BrF_2NS$: 267.9607 ($\delta = 0.4$ ppm).

Bromodifluoromethyl *p*-bromophenyl sulfilimine (7f): Orange powder; mp 58–60 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -52.4$ and -51.3 (AB syst, $J = 136$ Hz); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.12$ (1H, br s), 7.68 (4H, dd, $J = 9.6$ Hz, $J = 8.6$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 127.6$, 127.9, 131.1 (CF_2, dd, $J = 362$ Hz, $J = 356$ Hz), 132.5, 134.8; MS (pos. ESI, for ^{79}Br): $m/z = 332$ $(M+H)^+$; HR-MS: $m/z = 331.8557$, calcd. for $C_7H_6{}^{79}Br_2F_2NS$: 331.8556 ($\delta = 0.3$ ppm).

***o*-Tolyl trifluoromethyl sulfilimine (7h):** Yellow powder; mp 56–58 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.1$ (3F, s); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.86$ (1H, br s), 2.52 (3H, s), 7.28–7.32 (1H, m), 7.48 (2H, t, $J = 4.5$ Hz), 7.90 (1H, t, $J = 4.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.8$, 125.3, 127.3, 129.7 (CF_3, q, $J = 295$ Hz), 131.2, 132.3, 134.5, 137.6; anal. calcd. for $C_8H_8F_3NS$: C 46.37, H 3.89, N 6.76; found: C 46.74, H 3.66, N 6.86.

***m*-Tolyl trifluoromethyl sulfilimine (7i):** ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.4$ (3F, s); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.85$ (1H, br s), 2.45 (3H, s), 7.32–7.55 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.3$, 123.1, 124.8 (CF_3, q, $J = 338$ Hz), 126.1, 129.3, 133.3, 135.2, 139.9; anal. calcd. for $C_8H_8F_3NS$: C 46.37, H 3.89, N 6.76; found: C 45.87, H 3.96, N 6.65.

***p*-Tolyl trifluoromethyl sulfilimine (7j):** Yellow powder; mp 58–62 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.7$ (3F, s); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.81$ (1H, br s), 2.41 (3H, s), 7.35 (2H, d, $J = 8.1$ Hz), 7.60 (2H, d, $J = 8$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.3$, 124.1 (CF_3, q, $J = 337$ Hz), 125.8, 130.1, 131.9, 143.3; MS (pos. ESI): $m/z = 230$ $(M+Na)^+$, 437 $(2M+Na)^+$; HR-MS: $m/z = 230.0251$, calcd. for $C_8H_8F_3NSNa$: 230.0227 ($\delta = 1.2$ ppm).

***p*-Bromophenyl trifluoromethyl sulfilimine (7k):** White powder; mp 72–74 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.4$ (3F, s); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.80$ (1H, br s), 7.64 (2H, d, $J = 8.5$ Hz), 7.74 (2H, d, $J = 8.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 124.5$ (CF_3, q, $J = 337$ Hz), 127.5, 127.6, 132.8, 134.4; anal. calcd. for $C_7H_5BrF_3NS$: C 30.90, H 1.85, N 5.15; found: C 31.21, H 1.51, N 5.22.

***o*-Chlorophenyl trifluoromethyl sulfilimine (7l):** White powder; mp 64–66 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.3$ (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.98$ (1H, br s for NH), 7.54 (2H, d, $J = 8.9$ Hz), 7.69 (2H, d, $J = 8.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 124.5$ (CF_3, q, $J = 340$ Hz), 127.3, 129.8, 133.5, 139.1; MS (pos. ESI, for ^{35}Cl isotope): $m/z = 228$ $(M+H)^+$, 250 $(M+Na)^+$, 477 $(2M+Na)^+$; HR-MS: $m/z = 227.9851$, calcd. for $C_7H_6{}^{35}ClF_3NS$: 227.9862 ($\delta = -4.8$ ppm).

***m*-Chlorophenyl trifluoromethyl sulfilimine (7m):** White powder; mp 48–50 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -73.9$ (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.23$ (1H, br s for NH), 7.44–7.60 (2H, m), 7.63 (1H, d, $J = 7.5$ Hz), 7.77 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 124.2$, 124.5 (CF_3, q, $J = 339$ Hz), 126.0, 130.7, 132.8, 136.0, 136.9; MS (pos. ESI, for ^{35}Cl isotope): $m/z = 228$ $(M+H)^+$, 250 $(M+Na)^+$, 477 $(2M+Na)^+$; HR-MS: $m/z = 227.9857$, calcd. for $C_7H_6{}^{35}ClF_3NS$: 227.9862 ($\delta = -2.2$ ppm).

***p*-Chlorophenyl trifluoromethyl sulfilimine (7n):** White powder; mp 59–60 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -73.2$ (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.22$ (1H, br s for NH), 7.46–7.59 (3H, m), 7.90–7.98 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 127.4$, 128.0, 130.5, 133.5, 133.7, 134.5; MS (pos. ESI, for ^{35}Cl isotope): $m/z = 228$ $(M+H)^+$, 250 $(M+Na)^+$, 477 $(2M+Na)^+$; HR-MS: $m/z = 227.9854$, calcd. for $C_7H_6{}^{35}ClF_3NS$: 227.9862 ($\delta = -3.5$ ppm).

Nonafluorobutyl phenyl sulfilimine (7o): Yellow powder; mp 48–50 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -126.6$ (2F, m), -121.3 (2F, m), -115.7 (2F, m), -81.3 (3F, tt, $J = 10$ Hz, $J = 2.4$ Hz); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.12$ (1H, br s), 7.52–7.66 (3H, m), 7.74 (2H, d, $J = 7.9$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 126.6$, 129.5, 132.8, 134.7; anal. calcd. for $C_{10}H_6F_9NS$: C 34.99, H 1.76, N 4.08; found: C 35.42, H 1.91, N 4.21.

Nonafluorobutyl tolyl sulfilimine (7p): White powder; mp 89–91 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -126.6$ (2F, m), -121.2 (2F, m), -115.6 (2F, m), -81.3 (3F, t, $J = 9.6$ Hz); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.45$ (3H, s), 2.48 (1H, br s for NH), 7.34 (2H, d, $J = 7.5$ Hz), 7.64 (2H, d, $J = 8.1$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.0$, 131.2, 130.3, 126.7, 21.5; MS (pos. ESI): $m/z = 139$ $(M-C_4F_9)^+$, 358 $(M+H)^+$; HR-MS: $m/z = 358.0304$, calcd. for $C_{11}H_9F_9NS$: 358.0307 ($\delta = 0.7$ ppm).

***p*-Bromophenyl nonafluorobutyl sulfilimine (7q):** White powder; mp 94–96 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -126.5$ (2F, m), -121.1 (2F, m), -115.2 (2F, m), -81.3 (3F, t, $J = 9.6$ Hz); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.47$ (1H, br s for NH), 7.62 (2H, d, $J = 8.3$ Hz), 7.72 (2H, d, $J = 8.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 127.9$, 128.1, 132.8, 133.4; MS (pos. ESI, for ^{79}Br isotope): $m/z = 202$ $(M-C_4F_9)^+$, 421 $(M+H)^+$; HR-MS: $m/z = 421.9245$, calcd. for $C_{10}H_6{}^{79}BrF_9NS$: 421.9255 ($\delta = 2.3$ ppm).

General Procedure for the Preparation of Trifluoromethanesulfonyl Sulfilimines, as Exemplified by the Reaction with 7a

To a solution of dichlorofluoromethyl phenyl sulfilimine **7a** (0.28 g, 1.2 mmol, 1.0 equiv.) and pyridine (0.30 mL, 3.7 mmol, 3.0 equiv.) in CH_2Cl_2 (15 mL) was added trifluoromethanesulfonic anhydride (0.31 mL, 1.9 mmol, 1.5 equiv.) at 0 °C. The mixture was stirred overnight at room temperature. CH_2Cl_2 (10 mL) and 1M hydrochloric acid solution (20 mL) were then added. The phases were separated and

the aqueous layer extracted with CH_2Cl_2 (2×20 mL). The combined organic phases were dried over magnesium sulfate and evaporated under vacuum. Purification by a silica gel preparative plate (SiO_2, pentane/Et_2O, 8/2) afforded **dichlorofluoromethyl phenyl *N*-trifluoromethanesulfonyl sulfilimine (12a)** as a white solid; yield: 0.21 g (47%); mp 76–78 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -78.3$ (3F, s), −56.6 (1F, s); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.68$–7.73 (2H, m), 7.81–7.87 (1H, m), 7.99–8.02 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 119.7$ (CF_3, q, $J = 322$ Hz), 124.9 (CF, d, $J = 343$ Hz), 127.5, 129.3, 130.3, 135.9; anal. calcd. for $C_8H_5Cl_2F_4NO_2S_2$: C 26.83, H 1.41, N 3.91; found: C 26.51, H 1.39, N 3.81.

Bromodifluoromethyl phenyl *N*-trifluoromethanesulfonyl sulfilimine (12b): Pale yellow solid; mp 67–69 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -78.3$ (3F, s), −49.1 and −48.7 (AB system, $J = 132$ Hz); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.69$–7.75 (2H, m), 7.82–7.88 (1H, m), 7.97–8.00 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 119.7$ (CF_3, q, $J = 322$ Hz), 123.1 (CF_2, *app.* t, $J = 354$ Hz), 126.8, 128.8, 130.5, 135.8; anal. calcd. for $C_8H_5BrF_5NO_2S_2$: C 24.88, H 1.31, N 3.63; found: C 25.23, H 1.32, N 3.57.

Phenyl *N*-(trifluoromethane sulfonyl) trifluoromethyl sulfilimine (12c): Yellow powder; mp 48–50 °C; ^{19}F NMR (188 MHz, $CDCl_3$) $\delta = -78.4$ (3F, d, $J = 2.0$ Hz), −67.5 (3F, d, $J = 2.0$ Hz); ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.71$–7.77 (2H, m) 7.86 (1H, tt, $J = 7.4$ Hz, $J = 2.0$ Hz), 7.97–8.00 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 119.7$ (CF_3, q, $J = 320$ Hz), 123.0 (CF_3, q, $J = 325$ Hz), 125.4, 128.3, 130.8, 135.9; anal. calcd. for $C_8H_5F_6NO_2S_2$: C 29.54, H 1.55, N 4.31; found: C 29.91, H 1.42, N 4.28.

Phenyl *N*-*p*-toluenesulfonyl trifluoromethyl sulfilimine (12d): To a solution of trifluoromethyl phenyl sulfilimine **7g** (0.65 g, 3.4 mmol, 1.0 equiv.) and pyridine (0.5 mL, 10.1 mmol, 3.0 equiv.) in CH_2Cl_2 (8 mL) was added *p*-toluenesulfonyl chloride (0.96 g, 5.1 mmol, 1.5 equiv.) at room temperature. The mixture was heated under reflux and stirred overnight. CH_2Cl_2 (20 mL) and 1 M of hydrochloric acid solution (20 mL) were then added. The phases were separated and the aqueous layer extracted with CH_2Cl_2 (2× 20 mL). The combined organic phases were dried over magnesium sulfate and evaporated under vacuum. Purification by silica gel flash chromatography (SiO_2, pentane/Et_2O, 4/6) afforded the corresponding sulfilimine as a white solid; yield: 1.2 g (100%); mp 101–103 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -68.2$ (3F, s); ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 2.38 (3H, s), 7.25 (2H, d, $J = 7.9$ Hz), 7.60–7.66 (2H, m), 7.71–7.73 (1H, m), 7.81 (2H, d, $J = 8.3$ Hz), 7.90–7.93 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.4$, 123.4 (CF_3, q, $J =$ 330 Hz), 126.2, 127.2, 128.0, 129.4, 130.3, 134.7, 140.1, 142.6; anal. calcd. for $C_{14}H_{12}F_3NO_2S_2$: C 48.41, H 3.48, N 4.03; found: C 48.48, H 3.48, N 3.94.

***N*-*o*-Nitrobenzenesulfonyl phenyl trifluoromethyl sulfilimine (12e):** To a solution of trifluoromethyl phenyl sulfilimine **7g** (30 mg, 0.16 mmol, 1.0 equiv.) and pyridine (38 μL, 0.47 mmol, 3.0 equiv.) in CH_2Cl_2 (1 mL) was added *o*-nitrobenzenesulfonyl chloride (52 mg, 0.23 mmol, 1.5 equiv.). The mixture was stirred overnight at room temperature. CH_2Cl_2 (20 mL) and 1 M hydrochloric acid solution (20 mL) were then added. The phases were separated and the aqueous layer extracted with CH_2Cl_2 (2×20 mL). The combined organic phases were dried over magnesium sulfate and evaporated under vacuum. Purification on a silica gel preparative plate (SiO_2, pentane/Et_2O 7/3) afforded the corresponding sulfilimine **12e** as a white solid; yield: 49 mg (83%); mp 87–89 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -68.4$ (3F, s); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.58$–7.74 (6H, m), 7.92–7.96 (2H, m), 8.24–8.29 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 123.4$ (CF_3, q, $J = 329$ Hz), 124.2, 126.7, 128.2, 130.3, 130.7, 132.3, 132.9, 134.9, 136.2, 147.2; anal. calcd. for $C_{13}H_9F_3N_2O_4S_2$: C 41.27, H 2.40, N 7.40; found: C 41.31, H 2.49, N 7.24.

***N*-Nitro phenyl trifluoromethyl sulfilimine (12f):** To a solution of trifluoromethyl phenyl sulfilimine **7g** (47 mg, 0.24 mmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added fuming nitric acid (10 μL) at 0 °C. After 15 min, sulfuric acid (1 drop) and acetic anhydride (0.5 mL) were added to the mixture, which was stirred overnight at room temperature. CH_2Cl_2 (20 mL) and a saturated aqueous solution of sodium bicarbonate (20 mL) were then added. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (2× 20 mL). The combined organic phases were dried over magnesium sulfate and evaporated under vacuum. Purification on a silica gel preparative plate (SiO_2, pentane/Et_2O, 4:6) afforded **12f** as a white solid; yield: 38 mg (66%); mp 87–89 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -60.8$ (3F, s); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.68$–7.73 (2H, m), 7.81–7.83 (1H, m), 7.95–7.98 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 123.2$ (CF_3, q, $J = 328$ Hz), 123.3, 129.7, 130.8, 135.9; anal. calcd. for $C_7H_5F_3N_2O_2S$: C 35.30, H 2.12, N 11.76; found: C 35.38, H 2.21, N 11.61.

***N*-Cyanophenyl trifluoromethyl sulfilimine (12g):** To a solution of trifluoromethyl phenyl sulfilimine **7g** (50 mg, 0.26 mmol, 1.0 equiv.) and triethylamine (73 μL, 0.52 mmol, 2.0 equiv.) in CH_2Cl_2 (1 mL) was added cyanogen bromide (41 mg, 0.39 mmol, 1.5 equiv.). The mixture was stirred overnight at room temperature. CH_2Cl_2 (20 mL) and 1 M hydrochloric acid solution (20 mL) were then added. The phases were separated and the aqueous layer extracted with CH_2Cl_2 (2×20 mL). The combined organic phases were dried over magnesium sulfate and evaporated under vacuum. Purification on a silica gel preparative plate (SiO_2, pentane/Et_2O, 4/6) afforded **12g** as a white solid; yield: 22 mg (38%); mp 97–99 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -67.5$ (3F, s); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.71$ (2H, t, $J = 5.1$ Hz), 7.82 (1H, t, $J = 4.9$ Hz), 7.97 (2H, d, $J =$ 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 117.8$, 123.6 (CF_3, q, $J = 334$ Hz), 126.6, 128.0, 130.6, 135.5; anal. calcd. for $C_8H_5F_3N_2S$: C 44.04, H 2.31, N 12.84; found: C 44.38, H 2.27, N 12.58.

***N*-*tert*-Butoxycarbonyl phenyl trifluoromethyl sulfilimine (12h):** To a solution of trifluoromethyl phenyl sulfilimine **7g** (30 mg, 0.16 mmol, 1.0 equiv.) and triethylamine (0.13 mL, 0.93 mmol, 6.0 equiv.) in CH_2Cl_2 (1 mL) was added di-*tert*-butyl dicarbonate (0.11 mL, 0.47 mmol, 3.0 equiv.). The mixture was stirred overnight at room temperature. CH_2Cl_2 (20 mL) and 1 M hydrochloric acid solution (20 mL) were then added. The phases were separated and the aqueous layer extracted with CH_2Cl_2 (2×20 mL). The combined organic phases were dried over magnesium sulfate and evaporated under vacuum. Purification on a silica gel preparative plate (SiO_2, pentane/Et_2O, 7/3) afforded **12h** as a white solid; yield: 32 mg (70%); mp 66–68 °C; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -67.2$ (3F, s); ^1H NMR (200 MHz,

$CDCl_3$): $\delta = 1.51$ (9H, s), 7.56–7.77 (3H, m), 7.95–7.99 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 28.2$, 80.8, 123.8 (CF_3, q, $J = 329$ Hz), 127.4, 128.8, 130.0, 134.3, 164.0; anal. calcd. for $C_{12}H_{14}F_3NO_2S$: C 49.14, H 4.81, N 4.78; found: C 49.37, H 4.91, N 4.58.

Phenyl *N*-2-[(tridecafluorohexyl)sulfonyl]ethyl trifluoromethyl sulfilimine (12i): To a solution of trifluoromethyl phenyl sulfilimine **7g** (30 mg, 0.16 mmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added vinyl tridecafluorohexyl sulfone (64 mg, 0.16 mmol, 1.0 equiv.). The mixture was stirred for 30 min at room temperature. CH_2Cl_2 (20 mL) and water (20 mL) were then added. The phases were separated and the aqueous layer extracted with CH_2Cl_2 (2×20 mL). The combined organic phases were dried over magnesium sulfate and evaporated under vacuum. Purification on asilica gel preparative plate (SiO_2, pentane/Et_2O, 7/3) afforded **12i**; yield: 77 mg, (83%); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -126.6$ (2F, m), -123.2 (2F, m), -122.2 (2F, m), -120.8 (2F, m), -113.9 (2F, br t, $J = 14.8$ Hz), -81.2 (3F, tt, $J = 10.0$ Hz, $J = 2.5$ Hz), -67.5 (3F, s); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 3.41$–3.69 (2H, m), 3.74–3.98 (2H, m), 7.53–7.72 (3H, m), 7.82–7.86 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 44.4$, 54.1, 125.3 (CF_3, q, $J = 346$ Hz), 127.7, 129.9, 131.8, 133.0; anal. calcd. for $C_{15}H_9F_{16}NO_2S_2$: C 29.86, H 1.50, N 2.32; found: C 30.01, H 1.48, N 2.34.

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