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Perfluoroalkylated Bis(sulfilimine)s and Bis(sulfoximine)s by a Ritter-Type Reaction

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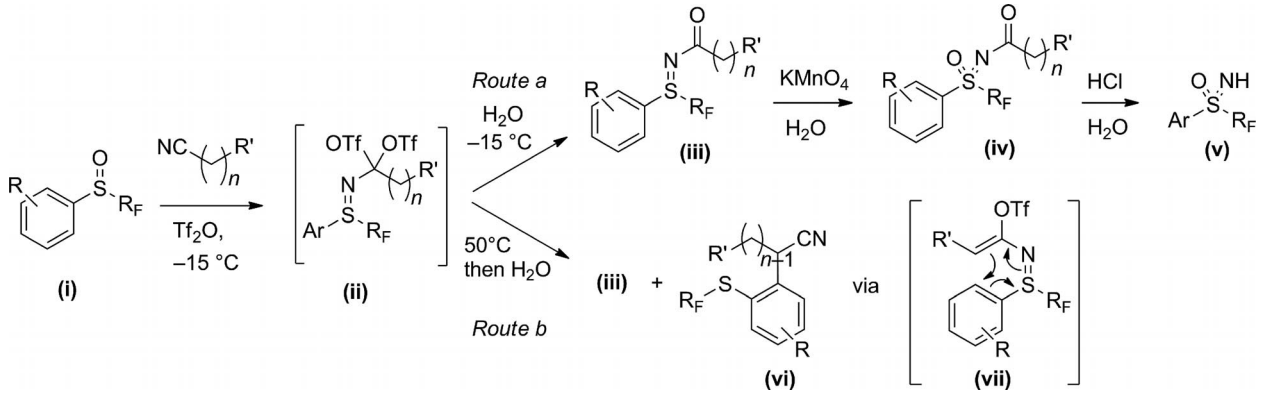
Our synthetic methodology, which was previously developed for the preparation of perfluoroalkyl sulfilimines by a reaction between fluorinated sulfoxides and nitriles, has been successfully extended to dinitriles. According to the reaction conditions, we can preferentially produce a cyano monosulfilimine or a bis(sulfilimine). New cyano thioethers have been synthesized through a rearrangement process. Mono- and bis(sulfilimine)s were also oxidized to afford the corresponding sulfoximines, which provide a direct route to potential new ligands for catalysis and new electrophilic perfluoroalkylating reagents.

Introduction

A sulfilimine contains a sulfur(IV) atom and belongs to the family of sulfur–nitrogen ylides. Their fascinating and original skeleton makes them attractive compounds in organic chemistry. Increasing research has been devoted to both their preparation and the study of their properties.[1] This functionality is indeed an emergent group in chemistry because of its increasing applications to the life sciences,[2] organic synthesis,[3] and catalysis as a coordination ligand.[4] Sulfilimines are usually obtained by the imination of a thioether or sulfoxide with various elaborate reagents and either assisted or not by a transition-metal catalyst.[5] Beyond their inherent properties, sulfilimines are also of great interest as they are precursors to another highly important class of sulfur(VI) compounds. They are easily oxidized to give sulfoximines,[6] which are also a key functional group for various applications such as ligands for catalysis,[7] reagents,[8] or biologically active molecules.[9,10] Until recently, the synthesis of the perfluoroalkylated derivatives (i.e., the introduction of a halogenated group that is directly attached to the sulfur) was relatively unknown for sulfilimines and quite cumbersome for sulfoximines. Our research group has described a flexible and versatile methodology for the straightforward preparation of a wide range of perfluoroalkyl sulfur(IV) and (VI) compounds. The main



Scheme 1. General synthesis of sulfilimines, sulfoximines, and *ortho*-substituted thioethers.

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results are summarized in the Scheme 1. Our divergent synthetic pathway started with simple perfluoroalkyl sulfoxides **i**. A Ritter-like reaction with nitriles as nucleophiles afforded bis(trifluoromethanesulfonate) ketal **ii**.[11] Structure **ii** rapidly appeared as a common platform and key intermediate to routes that provide molecular diversity. Its hydroly-

sis afforded acylsulfilimines **iii**, which were either isolated or smoothly oxidized by potassium permanganate to give the corresponding sulfoximines **iv** (see Scheme 1, route a). The acyl function could then be easily removed by treatment with acid.[12] These resulting NH-sulfoximines provide a direct path to both existing and new electrophilic perfluoroalkylating reagents,[13] but also to new electron-withdrawing groups.[14] Heating intermediate **ii** before hydrolysis led to the divergent synthetic pathway that allowed for the isolation of perfluoroalkyl thioethers **vi** as the major product (see Scheme 1, route b).[15] The formation of these sulfur(II) compounds (i.e., **vi**) can been explained by a transposition process. We assume that the pathway started with the elimination of trifluoromethanesulfonic acid to form intermediate **vii**, which could undergo a pericyclic reaction. As a result, this transformation only occurred with nitriles that contained hydrogen atoms at the α position.

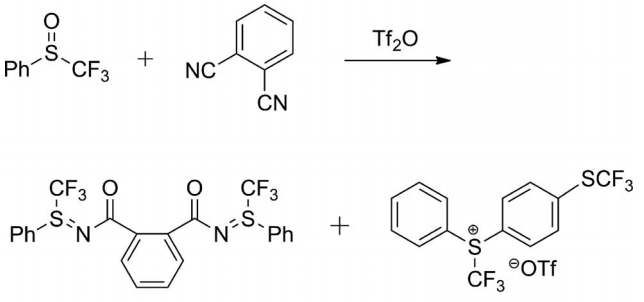
Our methodology is ecofriendly as it does not require a metal or a solvent, it uses a nontoxic oxidizing agent and, furthermore, provides great structural flexibility. Variations of the aromatic substituents (electron-donating and electron-withdrawing groups), the nitrile (aromatic and aliphatic), and of the fluorinated chain (monofluoro- to perfluoroalkyl chains) are feasible and have been described previously.

Results and Discussion

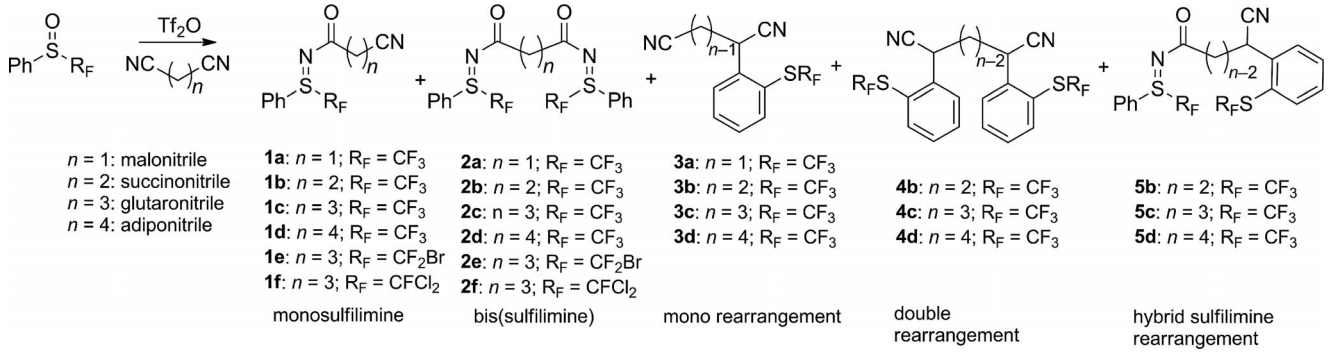
As part of our program devoted to the development of new sulfur derivatives for the aforementioned purposes, we were intrigued by the extension of our methodology to employ dinitriles as nucleophiles. The presence of two reactive sites would greatly enhance the achieved structural diversity, providing that we could control the selectivity of our transformations. The number of compounds formed would be dependent not only on the reaction conditions but also on the length of the tether between the two nitriles moieties. Scheme 2 summarizes the great structural opportunities offered by employing a dinitrile. Even the simplest member, malonitrile, can lead to the formation of three molecules, that is, monosulfilimine **1a**, bis(sulfilimine) **2a**, and the rearranged dinitrile **3a**, which is derived from sulfur(IV) compound **1a**. The addition of one carbon atom to the linking chain may increase the molecular diversity of the products with the possible formation of rearranged bis(thioether) skeleton **4b** and also hybrid substrate **5b**, which results from a single transposition process from product **2b**. Glutaronitrile and adiponitrile have also been considered to complete our study.

To decrease the number of compounds potentially formed and consequently simplify the reaction profile, we ran the first assay with phthalonitrile. The absence of a labile hydrogen atom would prevent any rearrangement process. According to our previously described conditions, phthalonitrile and phenyl trifluoromethyl sulfoxide were first treated with trifluoromethanesulfonic anhydride at –15 °C over two days (see Table 1). Even with 1 equiv. of sulfoxide, no trace amount of the monosulfilimine was detected. The only fluorinated product formed was the original bis(sulfilimine) **2g**, albeit in low yield (see Table 1, Entry 1). Increasing the amount of sulfoxide to 2 and 4 equiv. led to the isolation of compound **2g** along with sulfonium **6** (see Table 1, Entries 2 and 3). This salt is formed by an autocondensation procedure of the trifluoromethyl sulfoxide as previously described by both our group and Shreeve and co-workers.[16] Finally, the yield for **2g** was slightly im-

Table 1. Synthesis of sulfilimines with phthalonitrile.



Entry	Time [h]	Temperature [°C]	$PhSOCF_3$ [equiv.]	% Yield **2g**	% Yield **6**
1	48	–15	1	11	–
2	48	–15	2	34	13
3	48	–15	4	45	13
4	24	r.t.	2	53	12



Scheme 2. Overview of thioethers, sulfilimines, and sulfoximines potentially obtained with dinitriles (Tf = trifluoromethanesulfonyl).

proved to 53% through a change of the reaction temperature and a concomitant reduction of the equivalents of sulfoxide.

These encouraging first results prompted us to study the reactivity of aliphatic dinitriles. The first member of the family, malonitrile, was tested unsuccessfully, despite a few examples of Ritter-type reactions in literature.[17] Sulfonium **6** was the only product obtained. Fortunately, this lack of reactivity disappeared with a spacer of two carbon atoms. This supplementary methylene dramatically changed the structural conformation of the molecule and increased the distance between the two nitrile functions. This steric decompression may account for this clear-cut difference of reactivity. The results for the synthesis of sulfilimines with succinonitrile are reported in Table 2. Unlike the phthalonitrile series, we were able to prepare the pure monosulfilimine. With 1 equiv. of sulfoxide, a separable mixture of monosulfilimine **1b** and bis(sulfilimine) **2b** was obtained (see Table 2, Entry 1). The isolated yield of each new derivative **1b** and **2b** significantly increased by using 2 equiv. of sulfoxide, but the ratio was still in favor of compound **1b** (see Table 2, Entry 2). The scale-up of the reaction resulted in a slightly better overall yield along with a change of the ratio to favor sulfilimine **2b** (see Table 2, Entry 3). This modification could be explained by the use of a vessel system that allowed for better stirring and provided the traditional solidification of the reaction medium. This particular iterative sequence could be a barrier to the second transformation. The employment of 4 equiv. of sulfoxide provided for the isolation of bis(sulfilimine) **2b** with some amount of sulfonium **6** (see Table 2, Entry 4). Warming the reaction mixture to room temperature was not deleterious to the yield of sulfur(IV) compound **2b** and also afforded thioether **3b**, which was formed by the rearrangement process of compound **1b** (see Table 2, Entry 5). Using only 1 equiv. of the starting sulfoxide was detrimental to the yield of molecule **2b** (see Table 2, Entry 6). Although isolated in a very modest yield, the formation of this original sulfur compound **3b** is remarkable in the stimulating modern context of the renewal of the chemistry of this perfluoroalkyl thioether function.[18] We assume that we could improve the yield of formation of trifluoromethyl thioether **3b** with an adaptation of the reaction conditions (e.g., temperature, time, etc.), but this study is beyond the scope of this article.

Table 2. Synthesis of sulfilimines with succinonitrile.

Entry	Time [h]	Temperature [°C]	$PhSOCF_3$ [equiv.]	% Yield **1b**	**2b**	**3b**	**6**
1	48	–15	1	15	8	–	–
2	48	–15	2	38	17	–	–
3[a]	48	–15	2	29	30	–	–
4	48	–15	4	–	57	–	12
5	24	r.t.	2	–	50	17	–
6	24	r.t.	1	3	19	19	–

[a] Scaleup conditions: Reaction conducted with 5.1 mmol of sulfoxide (instead of 0.51 mmol for other entries).

Neither the formation of bis(thioether) **4b** nor sulfilimine **5b** was detected during this study. Steric hindrance seemed be the most plausible explanation. To test this hypothesis, we then turned out our attention to the reactivity of glutaronitrile, which has one more carbon atom in the spacer between the two nitrile groups (n = 3). The results are reported in Table 3.

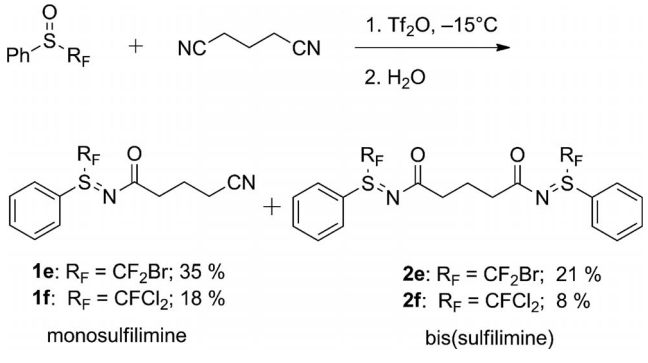
Table 3. Synthesis of sulfilimines with glutaronitrile.

Entry	Time [h]	Temperature [°C]	$PhSOCF_3$ [equiv.]	% Yield **1c**	**2c**	**3c**	**4c**	**5c**	**6**
1	48	–15	1	29	4	–	–	–	–
2	48	–15	2	60	13	–	–	–	–
3[a]	48	–15	2	36	25	–	–	–	–
4	48	–15	4	–	41	–	–	–	16
5	24	r.t.	2	5	33	12	9	9	1

[a] Scaleup conditions: Reaction conducted with 5.1 mmol of sulfoxide (instead of 0.51 mmol for other entries).

The first benefit of this additional carbon atom is the greater overall yield of the reaction, in general, and the yield of isolated monosulfilimine **1c**, in particular, which reached 60% (see Table 3, Entry 2). As previously described, the scale-up of the reaction as well as a greater number of equivalents of sulfoxide favored the synthesis of **2c** (see Table 3, Entries 3 and 4). The second advantage was the ability to prepare other new molecules as pure compounds. At room temperature, not only monosulfilimine **1c** and bis(sulfilimine) **2c** were formed but also thioethers **3c** and **4c**, which resulted from the transposition process of the mono- and bis[sulfur(IV)] molecules, respectively (see Table 3, Entry 5). A fifth compound **5c** with an uncommon structure that contains both a sulfilimine moiety and a thioether function is formed during the same process. This skeleton is the result of either the reaction of the primary nitrile of **3c** with sulfoxide or a single rearrangement process starting from **2c**. This last hypothesis appears the most plausible explanation to us.

Our best reaction conditions with glutaronitrile (see Table 3, Entry 2) were then tested using other fluoroalkylated sulfoxides (see Scheme 3). Bromodifluoromethyl sulfoxide was then transformed with acceptable yield into a



Scheme 3. Synthesis of dichlorofluoro- and bromodifluoromethyl sulfilimines.

separable mixture of monosulfilimine **1e** as the major product along with bis(sulfilimine) **2e**. An equal distribution of compounds **1f** and **2f** were produced by using the dichlorofluoro sulfoxide substrate, albeit in lower and moderate yield. The reduced reactivity of this sulfoxide is not so surprising and has already been noted in our previous studies.[12]

The previous results were very similar to those obtained with adiponitrile and allowed us to extrapolate upon our methodology (see Table 4). Monosulfilimine **1d** was obtained as the major product with an acceptable yield by using 2 equiv. of the substrate (see Table 4, Entry 2), whereas bis(sulfilimine) **2d** was the unique sulfur(IV) derivative isolated when an excess amount of the substrate was used (see Table 4, Entry 4). Once again, increasing the reaction temperature afforded the new thioethers **3d** and **4d** as well as the hybrid molecule **5d** (see Table 4, Entry 5).

Table 4. Synthesis of sulfilimines with adiponitrile.

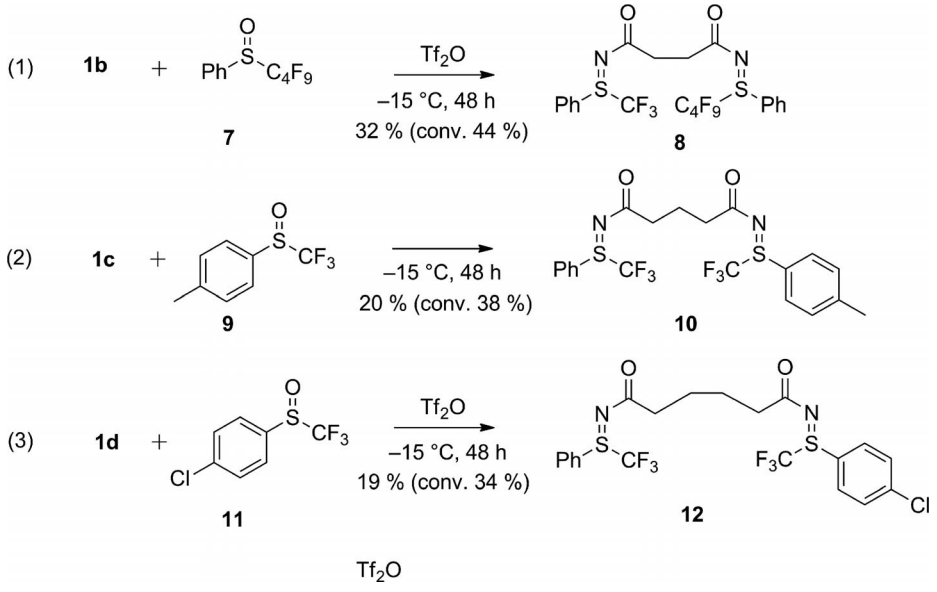
Entry	Time [h]	Temperature [°C]	$PhSOCF_3$ [equiv.]	% Yield 1d	2d	3d	4d	5d	6
1	48	–15	1	34	4	–	–	–	–
2	48	–15	2	50	14	–	–	–	–
3[a]	48	–15	2	38	25	–	–	–	–
4	48	–15	4	–	34	–	–	–	14
5	24	r.t.	2	15	12	15	10	6	1

[a] Scaleup conditions: reaction conducted with 5.1 mmol of sulfoxide (instead of 0.51 mmol for other entries).

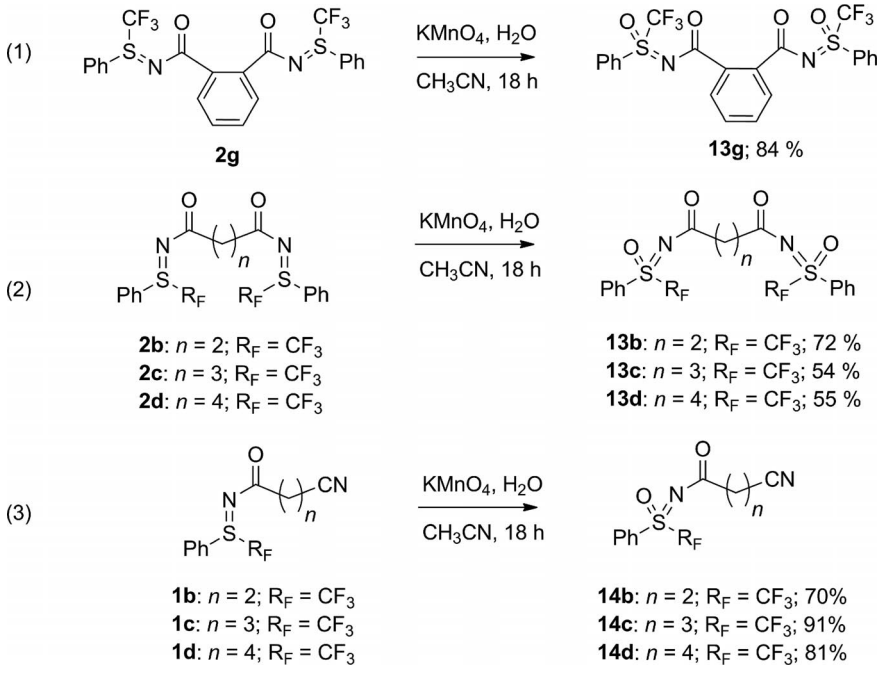
The chemical potential of our original perfluoroalkylated sulfilimines was then explored according to two synthetic directions. Monosulfilimines **1b**–**1d** were first transformed into unsymmetrical bis(sulfilimine)s by engaging in a reaction with 2 equiv. of sulfoxide to afford the corresponding nonsymmetrical bis[sulfur(IV)] molecules (see Scheme 4). The variation of the perfluoroalkylated chain was firstly realized with **1b** to afford compound **8** [see Scheme 4, Equation (1)]. The variation of the aromatic moieties then delivered sulfilimines **10** and **12** [see Scheme 4, Equations (2) and (3)]. Despite using a slight excess amount of the sulfur reagent and an increased reaction time, the conversions of the three transformations were rather low and, consequently, the isolated yields were quite poor. We did not carry out these reactions for a longer amount of time to avoid unwanted side reactions. We preferred to give priority to the recovery of starting materials **1b**–**1d**.

We then turned out our attention to the oxidation of the sulfilimines. The reappraisal of our former protocol was necessary to prevent the formation of a complex mixture of the mono- and bis(sulfoximine)s along with the starting material. The use of 10 equiv. of potassium permanganate over 18 h provided for the isolation of the desired products in good yields and as the sole fluorinated compounds. The results are presented in Scheme 5. Four original bis(trifluoromethyl sulfoximine)s **13b**–**13d** and **13g** were synthesized with acceptable [for a long carbon spacer, see Scheme 5, Equation (2)] to good yields [for a short carbon spacer and an aromatic spacer, see Scheme 5, Equations (1) and (2)]. Cyano sulfoximines **14b**–**14d** were also prepared with good to excellent yields [see Scheme 5, Equation (3)].

Bis(sulfilimine)s and bis(sulfoximine)s are already known in the literature,[19] but the preparation of the perfluoroalkylated versions of these sulfur(IV) and sulfur(VI) compounds through traditional methods was not previously possible. Our contribution now allows the complete syntheses of the whole series. We have provided access to the straightforward formation of new perfluoroalkylating reagents as well as bidentate ligands for catalysis. An investigation into these topics is currently under development in our laboratory.



Scheme 4. Synthesis of dissymmetric sulfilimine.



Scheme 5. Synthesis of mono- and bis(sulfoximine)s.

Conclusions

We have demonstrated that we can access either mono- or bis(sulfilimine)s through a modification of the experimental conditions of a reaction between fluorinated sulfoxides and various dinitriles. Original thioethers that contain a cyano group have been also prepared. We also proved that structural diversity was possible by varying the perfluoroalkyl chain, the substituents of the aromatic ring, and of the alkyl chain that links the two cyano functional groups. Unsymmetrical bis(sulfilimine)s have been also synthesized. Finally, various sulfoximines have been prepared using mild oxidizing conditions. The full potential of these new compounds will be evaluated and reported in due course.

Experimental Section

General Methods: The ^{1}H (200 or 300 MHz) and ^{13}C NMR (50 or 75 MHz) spectroscopic data were recorded with 200 or 300 MHz spectrometers, and the samples were dissolved in deuterated chloroform with the residual solvent peak as an internal standard. The solvent peak of $CFCl_3$ was the internal standard for the ^{19}F NMR (188 MHz) spectroscopic data. Chemical shifts (δ) are given in parts per million, and coupling constants are given as absolute values expressed in Hertz. Reported coupling constants and chemicals shifts were recorded on the basis of first-order analysis. Electrospray ionization mass spectra were collected with a Q-TOF instrument. Thin-layer chromatography was carried out with aluminum sheets precoated with silica gel 60 F254. Column chromatography separations were performed with silica gel (0.040–0.060 mm).

General Procedure for the Preparation of Monosulfilimine Through the Preparation of *N*-(3-Cyanopropionyl) Phenyl Trifluoromethyl Sulfilimine (1b): Trifluoromethanesulfonic anhydride (160 μL, 0.78 mmol, 3 equiv.) was added under argon to a precooled (–15 °C) mixture of phenyl trifluoromethyl sulfoxide (97 mg, 0.5 mmol, 2 equiv.) and succinonitrile (21 mg, 0.26 mmol, 1 equiv.). The reaction mixture was stirred at –15 °C for 48 h. After the addition of CH_2Cl_2 (2 mL), the solution was then hydrolyzed with water (2 mL). The resulting mixture was extracted with CH_2Cl_2 (3 × 5 mL), and the combined extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (diethyl ether) to give **1b** (27 mg, 38% yield) as a yellow viscous oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.65–2.73 (m, 2 H), 2.80–2.88 (m, 2 H), 7.59–7.75 (m, 3 H), 7.90 (d, J = 7.4 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.8 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 32.8, 119.3, 123.9 (q, J = 322 Hz, CF_3), 126.5, 128.8, 130.3, 134.7, 181.4 ppm. MS (ESI+): m/z = 275 $[M + H]^+$, 297 $[M + Na]^+$, 571 $[2M + Na]^+$. HRMS (ESI): calcd. for $C_{11}H_9F_3N_2OSNa$ $[M + Na]^+$ 297.0285; found 297.0271 (δ = –4.7 ppm).

***N*-(4-Cyanobutyryl) Phenyl Trifluoromethyl Sulfilimine (1c):** Viscous yellow oil (45 mg, 60% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.04 (quintuplet, J = 7.1 Hz, 2 H), 2.47 (t, J = 7.2 Hz, 2 H), 2.66 (t, J = 7.3 Hz, 2 H), 7.59–7.74 (m, 3 H), 7.89 (d, J = 7.3 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.8 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.7, 22.1, 35.5, 119.5, 124.0 (q, J = 324 Hz, CF_3), 126.9, 128.7, 130.2, 134.5, 183.9 ppm. MS (ESI+): m/z = 311 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{12}H_{11}F_3N_2OSNa$ $[M + Na]^+$ 311.0442; found 311.0435 (δ = –2.3 ppm).

***N*-(5-Cyanovaleryl) Phenyl Trifluoromethyl Sulfilimine (1d):** Viscous yellow oil (39 mg, 50% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.65–1.91 (m, 4 H), 2.36 (t, J = 6.8 Hz, 2 H), 2.53 (t, J = 6.8 Hz, 2 H), 7.57–7.76 (m, 3 H), 7.87 (d, J = 7.3 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.7 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.7, 24.8, 25.0, 36.0, 119.4, 124.0 (q, J = 324 Hz, CF_3), 126.8, 128.4, 130.0 134.2, 184.8 ppm. MS (ESI+): m/z = 303 $[M + H]^+$, 325 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{13}H_{14}F_3N_2OS$ $[M + H]^+$ 303.0779; found 303.0780 (δ = 0.3 ppm).

***N*-(4-Cyanobutyryl) Bromodifluoromethyl Phenyl Sulfilimine (1e):** Viscous yellow oil (32 mg, 35% yield). ^{1}H NMR (200 MHz,

$CDCl_3$): δ = 2.07 (quintuplet, J = 7.2 Hz, 2 H), 2.50 (t, J = 7.2 Hz, 2 H), 2.67 (td, J = 7.2 Hz, J = 3.5 Hz, 2 H), 7.63 (t, J = 7.7 Hz, 2 H), 7.74 (t, J = 7.7 Hz, 1 H), 7.93 (d, J = 7.7 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –45.7 and –46.9 (AB system, $J_{A,B}$ = 135 Hz, 2 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.7, 22.1, 36.2, 119.57, 123.8 (CF_2Br), 127.9, 129.4, 129.7, 134.5, 183.7 ppm. MS (ESI+): m/z = 348.98 $[M + H]^+$. HRMS (ESI): calcd. for $C_{12}H_{12}F_2BrN_2OS$ $[M + H]^+$ 348.9822; found 348.9823 (δ = 0.3 ppm).

***N*-(4-Cyanobutyryl) Dichlorofluoromethyl Phenyl Sulfilimine (1f):** Viscous yellow oil (15 mg, 18% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.04 (quintuplet, J = 7.2 Hz, 2 H), 2.47 (t, J = 7.2 Hz, 2 H), 2.66 (dt, J = 1.5 Hz, J = 7.2 Hz, 2 H), 7.63 (t, J = 7.7 Hz, 2 H), 7.70–7.76 (m, 1 H), 7.88 (d, J = 7.7 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.7 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.7, 22.1, 35.5, 119.5, 124.1 (d, J = 324 Hz, $CFCl_2$), 126.9, 128.7, 130.3, 134.6, 184.0 ppm. MS (ESI+): m/z = 321 $[M + H]^+$. HRMS (ESI): calcd. for $C_{12}H_{12}FCl_2N_2OS$ $[M + H]^+$ 321.0029; found 321.0029 (δ = –0.6 ppm).

General Procedure for the Preparation of Bis(sulfilimine) Through the Preparation of *N*,*N*′-Bis[trifluoromethyl(phenyl)-λ^4-sulfanylidene]butanediamide (2b): Trifluoromethanesulfonic anhydride (160 μL, 0.78 mmol, 3 equiv.) was added under argon to a precooled (–15 °C) mixture of phenyl trifluoromethyl sulfoxide (194 mg, 1 mmol, 4 equiv.) and succinonitrile (21 mg, 0.26 mmol, 1 equiv.). The reaction mixture was stirred at –15 °C for 48 h. After the addition of CH_2Cl_2 (2 mL), the solution was then hydrolyzed with water (2 mL). The resulting mixture was extracted with CH_2Cl_2 (3× 5 mL), and the combined extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (diethyl ether) to give **2b** (69 mg, 57% yield; mixture of two diastereomers, 1:1) as a yellow waxy solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.9 (s, 4 H), 7.53–7.68 (m, 6 H), 7.87 (d, J = 7.3 Hz, 4 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.9 (s, 6 F), –64.8 (s, 6 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.5, 33.6, 124.1 (q, J = 332 Hz, CF_3), 127.2, 127.3, 128.6, 129.9, 130.0, 134.1, 134.2, 185.0 ppm. MS (ESI+): m/z = 469 $[M + H]^+$, 491 $[M + Na]^+$, 959 $[2M + Na]^+$. HRMS (ESI): calcd. for $C_{18}H_{15}F_6N_2O_2S_2$ $[M + H]^+$ 469.0479; found 469.0465 (δ = –3.0 ppm).

***N*,*N*′-Bis[trifluoromethyl(phenyl)-λ^4-sulfanylidene]pentanediamide (2c):** Yellow waxy solid (51 mg, 41% yield; mixture of two diastereomers, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.05–2.16 (m, 2 H), 2.52–2.61 (m, 4 H), 7.56–7.87 (m, 6 H), 7.93 (t, J = 4.6 Hz, 4 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.7 (s, 6 F), –64.6 (s, 6 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.0, 23.2, 36.4, 36.6, 124.0 (q, J = 322 Hz, CF_3), 124.1 (q, J = 322 Hz, CF_3), 127.3, 127.4, 128.6, 128.7, 130.6, 130.7, 134.2, 185.8 ppm. MS (ESI+): m/z = 483 $[M + H]^+$, 505 $[M + Na]^+$, 987 $[2M + Na]^+$. HRMS (ESI): calcd. for $C_{19}H_{16}F_6N_2O_2S_2Na$ $[M + Na]^+$ 505.0455; found 505.0450 (δ = –1.0 ppm).

***N*,*N*′-Bis[trifluoromethyl(phenyl)-λ^4-sulfanylidene]hexanediamide (2d):** Yellow solid (44 mg, 34% yield; mixture of two diastereomers, 1:1); m.p. 107–108 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.73–1.80 (m,4 H), 2.50–2.56 (m, 4 H), 7.56–7.73 (m, 6 H), 7.87 (d, J = 7.2 Hz, 4 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.7 (s, 6 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1, 37.0, 124.2 (q, J = 322 Hz, CF_3), 127.3, 128.5, 130.0, 134.2, 186.1 ppm. MS (ESI+): m/z = 497 $[M + H]^+$, 519 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{20}H_{18}F_6N_2O_2S_2Na$ $[M + Na]^+$ 519.0612; found 519.0597 (δ = –2.9 ppm).

***N*,*N*′-Bis[bromodifluoromethyl(phenyl)-λ^4-sulfanylidene]pentanediamide (2e):** Yellow waxy solid (33 mg, 21% yield; mixture of two diastereomers, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.16 (d quintuplet, J = 7.2 Hz, J = 2.1 Hz, 2 H), 2.61 (dt, J = 7.2 Hz, J = 2.1 Hz, 4 H), 7.60 (t, J = 7.7 Hz, 4 H), 7.71 (t, J = 7.7 Hz, 2 H), 7.93–7.97 (m, 4 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –45.1 and –46.4 (AB system, $J_{A,B}$ = 136 Hz, 4 F), –45.2 and –46.5 (AB system, $J_{A,B}$ = 136 Hz, 4 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.2, 23.3, 37.5, 37.6, 125.5 (CF_2Br), 128.5, 129.4, 129.8, 134.2, 185.6 ppm. MS (ESI+): m/z = 603 $[M + H]^+$. HRMS (ESI): calcd. for $C_{19}H_{17}F_4Br_2N_2O_2S_2$ $[M + H]^+$ 602.9034; found 602.9030 (δ = –0.7 ppm).

***N*,*N*′-Bis[dichlorofluoromethyl(phenyl)-λ^4-sulfanylidene]pentanediamide (2f):** Yellow waxy solid (12 mg, 8% yield; mixture of two diastereomers, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.16 (q, J = 7.2 Hz, 2 H), 2.61 (t, J = 7.2 Hz, 4 H), 7.59 (t, J = 7.7 Hz, 4 H), 7.71 (t, J = 7.2 Hz, 2 H), 7.92 (dd, J = 8.2 Hz, J = 3.0 Hz, 4 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.7 (s, 2 F), –64.6 (s, 2 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.1, 23.2, 36.5, 36.7, 124.2 (d, J = 323 Hz, $CFCl_2$), 124.3 (d, J = 322 Hz, $CFCl_2$), 127.3, 127.4, 128.7, 130.1, 134.3, 185.7 ppm. MS (ESI+): m/z = 547 $[M + H]^+$. HRMS (ESI): calcd. for $C_{19}H_{17}F_2Cl_4N_2O_2S_2$ $[M + H]^+$ 546.9454; found 546.9450 (δ = –0.7 ppm).

***N*,*N*′-Bis[trifluoromethyl(phenyl)-λ^4-sulfanylidene]phthalamide (2g):** Trifluoromethanesulfonic anhydride (160 μL, 0.78 mmol, 3 equiv.) was added under argon to a mixture of phenyl trifluoromethyl sulfoxide (100 mg, 0.5 mmol, 2 equiv.) and phthalonitrile (32 mg, 0.25 mmol, 1 equiv.). The reaction mixture was stirred at room temperature for 24 h. After the addition of CH_2Cl_2 (2 mL), the solution was then hydrolyzed with water (2 mL). The resulting mixture was extracted with CH_2Cl_2 (3× 5 mL), and the combined extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (diethyl ether) to give **2g** (68 mg, 53% yield; mixture of two diastereomers, 1:1) as a yellow solid; m.p. 128 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40–7.62 (m, 8 H), 7.79–7.92 (m, 6 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.8 (s, 6 F), –64.6 (s, 6 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 124.1 (q, J = 324 Hz, CF_3), 124.2 (q, J = 324 Hz, CF_3), 126.9, 127.1, 128.6, 128.7, 128.8, 129.5, 129.8, 133.9, 134.0, 136.3, 136.4, 180.0 ppm. MS (ESI+): m/z = 517 $[M + H]^+$, 539 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{22}H_{15}F_6N_2O_2S_2$ $[M + H]^+$ 517.0479; found 517.0477 (δ = –0.4 ppm).

General Procedure for the Preparation of Unsymmetrical Bis(sulfilimine) Through the Preparation of *N*-[Trifluoromethyl(phenyl)-λ^4-sulfanylidene]-*N*′-[nonafluorobutyl(phenyl)-λ^4-sulfanylidene]butanediamide (8): Trifluoromethanesulfonic anhydride (55 μL, 0.4 mmol, 2 equiv.) was added under argon to a precooled (–15 °C) mixture of phenyl nonafluorobutyl sulfoxide (137 mg, 0.4 mmol, 2 equiv.) and **1b** (55 mg, 0.2 mmol, 1 equiv.). The reaction mixture was stirred at –15 °C for 48 h. After the addition of CH_2Cl_2 (2 mL), the solution was then hydrolyzed with water (2 mL). The resulting mixture was extracted with CH_2Cl_2 (3× 5 mL), and the combined extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (diethyl ether) to give **8** (39 mg, 32% yield; mixture of two diastereomers, 1:1) as a yellow waxy solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.89 (s, 4 H), 7.55–7.69 (m, 6 H), 7.89 (t, J = 6.5 Hz, 4 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.8 (s, 3 F), –64.9 (s, 3 F), –81.1 (m, 3 F), –104.4 and –109.4 (AB system, $J_{A,B}$ = 234 Hz, 2 F), –119.8 (m, 2 H), –125.2 and –127.1 (AB system, $J_{A,B}$ = 291 Hz, 2 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.7, 30.3, 34.6, 34.7, 34.0, 34.1, 124.2 (q, J = 324 Hz, CF_3), 124.1 (q, J = 324 Hz, CF_3),

126.4, 126.5, 127.3, 127.4, 128.6, 129.7, 129.9, 130.0, 134.1, 134.4, 184.7, 185.1 ppm. MS (ESI+): *m/z* = 619 [M + H]$^+$, 641 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{21}H_{15}F_{12}N_2O_2S_2$ [M + H]$^+$ 619.0383; found 619.0386 (δ = 0.5 ppm).

***N*-[Trifluoromethyl(phenyl)-λ^4-sulfanylidene]-*N*′-[trifluoromethyl(*p*-tolyl)-λ^4-sulfanylidene]pentanediamide (10):** Yellow waxy solid (20 mg, 20% yield; mixture of two diastereomers, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.03–2.15 (m, 2 H), 2.27 (s, 3 H), 2.56 (q, *J* = 6.8 Hz, 4 H), 7.41 (d, *J* = 8.2 Hz, 2 H), 7.59–7.96 (m, 7 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.1 (s, 3 F), –64.2 (s, 3 F), –64.5 (s, 3 F), –64.6 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 23.1, 23.2, 36.5, 36.8, 124.3 (q, *J* = 324 Hz, CF_3), 124.4 (q, *J* = 322 Hz, CF_3), 124.0, 124.1, 128.7, 130.1, 130.8, 134.2, 145.5, 185.8, 185.9 ppm. MS (ESI+): *m/z* = 497 [M + H]$^+$. HRMS (ESI): calcd. for $C_{20}H_{19}F_6N_2O_2S_2$ [M + H]$^+$ 497.0792; found 497.0792 (δ = 0 ppm).

***N*-[Trifluoromethyl(phenyl)-λ^4-sulfanylidene]-*N*′-[trifluoromethyl-(*p*-chlorophenyl)-λ^4-sulfanylidene]hexanediamide (12):** Yellow waxy solid (20 mg, 19% yield; mixture of two diastereomers, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.71–1.80 (m, 4 H), 2.49–2.54 (m, 4 H), 7.56–7.71 (m, 5 H), 7.80–7.90 (m, 4 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.7 (s, 6 F), –64.6 (s, 6 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1, 29.7, 30.3, 36.9, 37.0, 124.1 (q, *J* = 324 Hz, CF_3), 124.2 (q, *J* = 322 Hz, CF_3), 127.3, 127.4, 128.6, 129.8, 130.1, 130.5, 134.2, 141.1 186.1, 186.2 ppm. MS (ESI+): *m/z* = 531 [M + H]$^+$, 553 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{20}H_{18}F_6N_2O_2S_2Cl$ [M + H]$^+$ 531.0402 found; 531.0406 (δ = 0.8 ppm).

2-{2-[(Trifluoromethyl)thio]phenyl}butanedinitrile (3b): Viscous yellow oil (13 mg, 19% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.94 (dd, *J* = 6.4 Hz, *J* = 13.5 Hz, 1 H), 3.06 (dd, *J* = 6.4 Hz, *J* = 13.5 Hz, 1 H), 5.04 (t, *J* = 6.4 Hz, 1 H), 7.55 (td, *J* = 7.4 Hz, *J* = 1.5 Hz, 1 H), 7.70 (td, *J* = 7.8 Hz, *J* = 1.3 Hz, 1 H), 7.84 (dd, *J* = 7.8 Hz, *J* = 1.3 Hz, 1 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –42.7 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9, 31.5, 114.6, 117.4, 122.9, 128.8 (q, *J* = 309 Hz, CF_3), 129.3, 130.8, 133.1, 137.7, 139.5 ppm. MS (ESI–): *m/z* = 255 [M – H]$^-$. HRMS (ESI): calcd. for $C_{11}H_6F_3N_2S$ [M – H]$^-$ 255.0204; found 255.0211 (δ = 2.7 ppm).

2-{[2-(Trifluoromethyl)thio]phenyl}pentanedinitrile (3c): Viscous yellow oil (9 mg, 12% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.22–2.30 (m, 2 H), 2.59–2.64 (m, 2 H), 4.78 (t, *J* = 8.0 Hz, 1 H), 7.49 (td, *J* = 7.7 Hz, *J* = 1.5 Hz, 1 H), 7.62–7.70 (m, 2 H), 7.81 (d, *J* = 7.7 Hz, 1 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –42.1 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3, 31.0, 34.2, 117.3, 118.7, 123.0, 128.8 (q, *J* = 309 Hz, CF_3), 129.0, 130.8, 132.9, 139.4 ppm. MS (ESI+): *m/z* = 271 [M + H]$^+$. HRMS (ESI): calcd. for $C_{12}H_{10}F_3N_2S$ [M + H]$^+$ 271.0517; found 271.0522 (δ = 1.8 ppm).

2-{[2-(Trifluoromethyl)thio]phenyl}hexanedinitrile (3d): Viscous yellow oil (9 mg, 12% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75–2.11 (m, 4 H), 2.43–2.49 (m, 2 H), 4.62–4.70 (m, 1 H), 7.45 (td, *J* = 7.4 Hz, *J* = 1.6 Hz, 1 H), 7.58–7.80 (m, 3 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –42.7 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.7, 23.0, 34.2, 34.5, 118.4, 119.6, 124.6 (q, *J* = 315 Hz, CF_3), 128.9, 129.7, 130.9, 132.7,139.2, 140.6 ppm. MS (ESI+): *m/z* = 285 [M + H]$^+$. HRMS (ESI): calcd. for $C_{13}H_{12}F_3N_2S$ [M + H]$^+$ 285.0673; found 285.0681 (δ = 2.8 ppm).

2,4-Bis[2-(trifluoromethylsulfanyl)phenyl]pentanedinitrile (4c): Viscous yellow oil (10 mg, 9% yield; mixture of two diastereomers, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.39–2.49 (m, 1 H), 2.69–2.79 (m, 1 H), 4.64 (t, *J* = 7.7 Hz, 2 H), 7.27 (td, *J* = 7.7 Hz, *J* = 1.5 Hz, 2 H), 7.63–7.74 (m, 4 H), 7.80 (d, *J* = 7.7 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –42.2 (s, 6 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.3, 39.1, 117.7, 122.5, 127.7 (q, *J* = 308 Hz, CF_3), 128.3, 129.3, 131.9, 138.1, 138.3 ppm. MS (ESI+): *m/z* = 447 [M + H]$^+$. HRMS (ESI): calcd. for $C_{19}H_{13}F_6N_2S_2$ [M + H]$^+$ 447.0424; found 447.0435 (δ = 2.5 ppm).

2,5-Bis[2-(trifluoromethylsulfanyl)phenyl]hexanedinitrile (4d): Viscous yellow oil (11 mg, 9% yield; mixture of two diastereomers, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.00–2.26 (m, 4 H), 4.63–4.70 (m, 2 H), 7.46 (td, *J* = 7.8 Hz, *J* = 1.8 Hz, 2 H), 7.63 (m, 4 H), 7.78 (d, *J* = 7.7 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –42.8 (s, 6 F), –42.7 (s, 6 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.9, 33.0, 34.5, 34.6, 119.5, 124.8 (q, *J* = 310 Hz, CF_3), 128.9, 129.8, 130.9, 132.7, 132.8, 139.3, 140.5, 140.5 ppm. MS (ESI+): *m/z* = 483 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{20}H_{15}F_6N_2S_2$ [M + H]$^+$ 461.0581; found 461.0599 (δ = 3.9 ppm).

4-Cyano-*N*-[phenyl(trifluoromethyl)-λ^4-sulfanylidene]-4-{[2-(trifluoromethyl)thio]phenyl}butanamide (5c): Viscous yellow oil (11 mg, 9% yield; mixture of two diastereomers, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.18–2.33 (m, 2 H), 2.67–2.75 (m, 2 H), 4.75–4.87 (m, 1 H), 7.41 (td, *J* = 7.5 Hz, *J* = 1.7 Hz, 1 H), 7.55–7.77 (m, 6 H), 7.89 (d, *J* = 7.5 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.2 (s, 3 F), –42.4 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.7, 34.3, 34.5, 120.4, 124.2 (q, *J* = 315 Hz, CF_3), 124.9 (q, *J* = 310 Hz, CF_3), 127.0, 128.7, 129.0, 129.3, 130.2, 131.0, 132.5, 134.5, 138.9, 141.6, 184.9 ppm. MS (ESI+): *m/z* = 465 [M + H]$^+$. HRMS (ESI): calcd. for $C_{19}H_{15}F_6ON_2S_2$ [M + H]$^+$ 465.0530; found 465.0531 (δ = 0.2 ppm).

5-Cyano-*N*-[phenyl(trifluoromethyl)-λ^4-sulfanylidene]-4-[2-(trifluoromethylsulfanyl)phenyl]pentanamide (5d): Viscous yellow oil (8 mg, 6% yield; mixture of two diastereomers, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86–2.00 (m, 4 H), 2.52–2.60 (m, 2 H), 4.60–4.66 (m, 1 H), 7.40 (td, *J* = 7.5 Hz, *J* = 1.8 Hz, 1 H), 7.53–7.77 (m, 6 H), 7.87 (d, *J* = 7.3 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –64.7 (s, 3 F), –64.6 (s, 3 F), –42.8 (s, 3 F), –42.9 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9, 35.0, 35.2, 36.4, 123.0, 123.5 (q, *J* = 335 Hz, CF_3), 124.0 (q, *J* = 324 Hz, CF_3), 126.8, 127.3, 128.7, 129.2, 129.3, 130.2, 132.5, 134.5, 138.9, 141.3, 183.5 ppm. MS (ESI+): *m/z* = 479 [M + H]$^+$. HRMS (ESI): calcd. for $C_{20}H_{17}F_6N_2OS_2$ [M + H]$^+$ 479.0687; found 479.0690 (δ = 0.6 ppm).

General Procedure for the Oxidation of Sulfilimine Compounds Through the Preparation of *N*,*N*′-Bis[oxo-phenyl-(trifluoromethyl)-λ^6-sulfanylidene]butanediamide (13b): A mixture of *N*,*N*′-bis(trifluoromethylphenyl-λ^4-sulfanylidene) butanediamide (**2b**, 100 mg, 0.21 mmol) and potassium permanganate (332 mg, 2.1 mmol, 10 equiv.) in water (1 mL) was stirred at room temperature overnight. The mixture became colorless by the addition of a solution of 10% $Na_2S_2O_4$, and the product was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative TLC (diethyl ether) to give **13b** (76 mg, 72% yield; mixture of two diastereomers, 1:1) as a white solid; m.p. 122 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.74–3.01 (m, 4 H), 7.52–7.82 (m, 6 H), 8.05 (t, *J* = 7.3 Hz, 4 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –75.8 (s, 6 F), –75.0 (s, 6 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 34.3, 34.4, 120.0 (q, *J* = 325 Hz, CF_3), 120.1 (q, *J* = 326 Hz, CF_3), 129.9, 130.0, 130.1, 130.2, 130.3, 136.0, 136.1, 179.8, 179.9 ppm. MS (ESI+): *m/z* = 501 [M + H]$^+$, 523 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{18}H_{15}F_6N_2O_4S_2$ [M + H]$^+$ 501.0377; found 501.0381, (δ = 0.8 ppm).

***N*,*N*′-Bis[oxo-phenyl-(trifluoromethyl)-λ⁶-sulfanylidene]pentanediamide (13c):** White solid (58 mg, 54% yield; mixture of two diastereomers, 1:1); m.p. 81 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.97 (quintuplet, J = 7.3 Hz, 2 H), 2.54 (t, J = 7.3 Hz, 4 H), 7.59 (t, J = 7.3 Hz, 4 H), 7.81 (td, J = 7.3 Hz, J = 1.2 Hz, 2 H), 7.97 (d, J = 7.7 Hz, 4 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.2 (s, 6 F), –74.3 (s, 6 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 20.7, 38.4, 38.5, 120.1 (q, J = 327 Hz, CF_3), 129.4, 130.0, 130.1, 130.2, 136.1, 180.5 ppm. MS (ESI+): m/z = 515 $[M + H]^+$, 537 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{19}H_{17}F_6N_2O_4S_2$ $[M + H]^+$ 515.0534; found 515.0530 (δ = –0.8 ppm).

***N*,*N*′-Bis[oxo-phenyl-(trifluoromethyl)-λ⁶-sulfanylidene]hexanediamide (13d):** Slight yellow viscous oil (61 mg, 55% yield; mixture of two diastereomers, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.66–1.71 (m, 4 H), 2.41–2.52 (m, 4 H), 7.60 (td, J = 7.7 Hz, J = 1.9 Hz, 4 H), 7.74 (td, J = 7.7 Hz, J = 1.9 Hz, 2 H), 8.05 (d, J = 7.7 Hz, 4 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.2 (s, 6 F), –74.1 (s, 6 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.6, 39.3, 120.2 (q, J = 328 Hz, CF_3), 130.0, 130.1, 130.4, 136.0, 180.9 ppm. MS (ESI+): m/z = 529 $[M + H]^+$, 551 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{20}H_{19}F_6N_2O_4S_2$ $[M + H]^+$ 529.0690; found 529.0691 (δ = 0.2 ppm).

***N*,*N*′-Bis[oxo-phenyl-(trifluoromethyl)-λ⁶-sulfanylidene]phthalimide (13g):** White gum solid (92 mg, 84% yield; mixture of two diastereomers, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.51–7.87 (m, 10 H), 8.16 (d, J = 7.6 Hz, 4 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –75.3 (s, 6 F), –74.4 (s, 6 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.3, 115.7, 120.1 (q, J = 326 Hz, CF_3), 120.2 (q, J = 327 Hz, CF_3), 129.1, 129.2, 129.8, 129.9, 130.0, 130.3, 130.4, 130.7, 130.8, 133.2, 133.5, 136.0, 136.1, 136.2, 136.3, 174.2, 174.3 ppm. MS (ESI+): m/z = 549 $[M + H]^+$. HRMS (ESI): calcd. for $C_{22}H_{15}F_6N_2O_4S_2$ $[M + H]^+$ 549.0377; found 549.0385 (δ = 1.5 ppm).

3-Cyano-*N*-[oxo-phenyl-(trifluoromethyl)-λ⁶-sulfanylidene]propaneamide (14b): Slight yellow viscous oil (43 mg, 70% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.60 (t, J = 7.2 Hz, 2 H), 2.81 (t, J = 6.7 Hz, 2 H), 7.64 (t, J = 7.2 Hz, 2 H), 7.79 (t, J = 7.7 Hz, 1 H), 8.01 (d, J = 7.7 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.9 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.2, 34.8, 118.8, 120.2 (q, J = 328 Hz, CF_3), 129.8, 130.1, 130.2, 136.5, 176.9 ppm. MS (ESI+): m/z = 291 $[M + H]^+$, 313 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{11}H_{10}F_3N_2O_2S$ $[M + H]^+$ 291.0415; found 291.0416 (δ = 0.3 ppm).

4-Cyano-*N*-[oxo-phenyl-(trifluoromethyl)-λ⁶-sulfanylidene]butaneamide (14c): Yellow viscous oil (58 mg, 91% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.93 (q, J = 7.2 Hz, 2 H), 2.41 (t, J = 7.2 Hz, 2 H), 2.66 (t, J = 6.7 Hz, 2 H), 7.63 (t, J = 7.2 Hz, 2 H), 7.78 (t, J = 7.7 Hz, 1 H), 7.98 (d, J = 7.7 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.6 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.4, 20.8, 37.4, 113.8, 119.3, 120.3 (q, J = 328 Hz, CF_3), 130.1, 130.2, 136.3, 179.4 ppm. MS (ESI+): m/z = 305 $[M + H]^+$, 327 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{12}H_{12}F_3N_2O_2S$ $[M + H]^+$ 305.0572; found 305.0570 (δ = –0.7 ppm).

5-Cyano-*N*-[oxo-phenyl-(trifluoromethyl)-λ⁶-sulfanylidene]pentaneamide (14d): Yellow viscous oil (55 mg, 81% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.66–1.91 (m, 4 H), 2.38 (t, J = 6.8 Hz, 2 H), 2.58 (t, J = 6.8 Hz, 2 H), 7.67 (t, J = 7.8 Hz, 2 H), 7.78 (t, J = 7.8 Hz, 1 H), 8.05 (d, J = 7.5 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.5 (s, 3 F) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.0, 24.1, 24.8, 38.5, 119.4, 120.3 (q, J = 324 Hz, CF_3),130.0, 130.1, 130.3, 136.2, 180.2 ppm. MS (ESI+): m/z = 319 $[M + H]^+$, 341 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{13}H_{14}F_3N_2O_2S$ $[M + H]^+$ 319.0728; found 319.0724 (δ = –1.3 ppm).

Supporting Information (see footnote on the first page of this article): Copies of the NMR spectra of all the compounds.

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