A Mild and Efficient Procedure for the N-Functionalization of S-Perfluoroalkylated Aryl Sulfoximines

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Abstract: N-Acylated perfluoroalkylated sulfoximines are synthesized easily from the corresponding free NH-sulfoximines on reaction with acid chlorides. This mild procedure is extended to diacid chlorides for the preparation of dimeric N-bridged sulfoximines and to reactions with chloroformates, carbamoyl chlorides, chlorothionoformates and thiocarbamoyl chlorides as electrophiles.

Key words: fluorinated sulfoximines, acylation, carbamoylation, ureas, N-bridged sulfoximines

Sulfoximines are very fascinating and intriguing compounds in organic chemistry. This sulfur(VI) group is structurally similar to a sulfone moiety, but the replacement of one of the oxygen atoms with a nitrogen has important electronic and structural consequences, and expands significantly the utility of this particular moiety.[1] The presence of the nitrogen atom allows additional functionalization (*vide infra*) and increases the electron-withdrawing ability of the sulfoximine group. Also, the chirality of these groups (centered on the sulfur atom) is a major feature of their applications. Sulfoximines have been widely employed as reagents in asymmetric synthesis,[2] as ligands in enantioselective metal catalysis and in organocatalysis.[3] They have also demonstrated potential in medicinal chemistry[4] and in crop sciences.[5] The state-of-art was, until recently, more limited to *S*-perfluoroalkylated sulfoximines, however, a growing number of applications have since emerged. These compounds have been described as strongly electron-withdrawing substituents,[6] as building blocks in liquid crystals[7] and as efficient reagents for perfluoroalkyl group transfer.[8] Sulfoximine derivatives have been employed successfully for the electrophilic introduction of trifluoro- and monofluoromethyl moieties by Shibata,[9] difluoromethyl groups by Hu,[10] and bromodifluoro- and dichloromethyl by our group.[11] In 2012, Hu expanded the applications of perfluoroalkylated sulfoximines and showed that mono- and difluoromethyl derivatives were efficient reagents for the nucleophilic transfer of perfluorinated units.[12]

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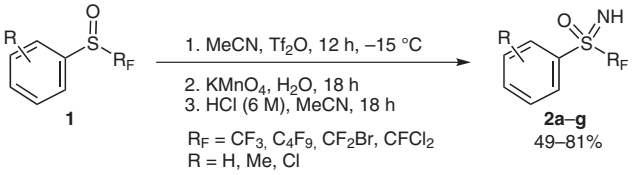
In contrast to non-fluorinated sulfoximines, which have been studied extensively,[1] access to the *S*-perfluoroalkylated analogues was, since 1986, strictly limited to the efficient, but quite cumbersome, synthesis as described by Yagupolskii and co-workers.[13] In 2009, we proposed a more friendly construction of *S*-perfluoroalkyl sulfoximines,[14] whereas Bolm and co-workers have described an access to N-protected *S*-trifluoromethyl substituted sulfoximines.[15] Our general and versatile methodology allows the production of a wide range of free NH-sulfoximines in two steps from the corresponding perfluoroalkyl arylsulfoxides (Scheme 1).

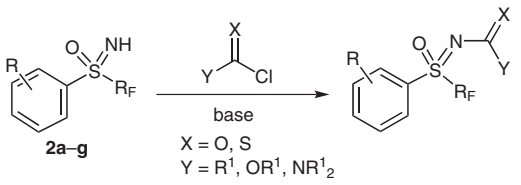


Scheme 1 Previous synthesis of free NH-sulfoximines

Compounds **2** represent a common platform for various applications, which can be finely-tuned by appropriate choice of the group attached to the nitrogen atom. For example, we have shown that in the case of electrophilic perfluoroalkylating reagents, the reactivity was specific to the fluorinated moiety being delivered.[11] Also, an investigation of the coupling reactions between compounds **2** and aryl iodides or bromides, induced by a copper catalyst, revealed an obvious difference with the non-halogenated derivatives.[16] During this study, we noticed that the quantities of catalyst required were greater than those used in the non-fluorinated series. These results clearly showed the need for a comprehensive investigation devoted to the N-functionalization of fluorinated sulfoximines.

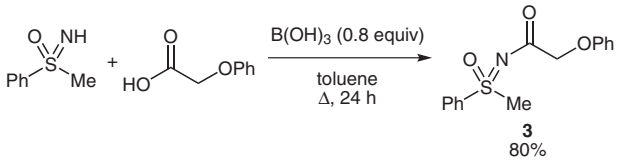
In continuation of our research on the synthesis of complex sulfoximines, we describe herein our studies devoted to the direct introduction of various acyl groups (Scheme 2). The knowledge we have acquired in the field of perfluoroalkylated sulfoximines indicated that these substrates were unstable under basic conditions. The challenge of

this present study was to find conditions that would tolerate the reactivity of our uncommon complex systems.



Scheme 2 A general route for the N-acylation of sulfoximines

Harmata et al. have reported a smooth and convenient method for the direct acylation of free NH-sulfoximines from a carboxylic acid in the presence of a catalytic amount of boric acid.[17] One of the advantages of this methodology was the direct isolation of the coupling product **3** in good yield (up to 80%, Scheme 3). However with our perfluoroalkylated substrates, no reaction occurred, despite changing the reaction conditions (solvent, temperature, classical heating or microwave activation, catalytic or stoichiometric amounts of boric acid). The starting fluorinated sulfoximine was always recovered without any trace of N-acylation.



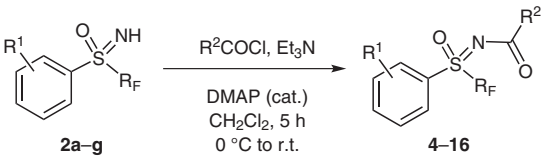
Scheme 3 Direct coupling reaction of a sulfoximine with a carboxylic acid catalyzed by boric acid

Although very simple and easy to run, the previous synthetic method, in our hands, could not be extrapolated to electron-poor systems. The lower reactivity of the nitrogen is one of the most plausible explanations for this disappointing result, which again pointed toward the particular reactivity of these compounds.

Other procedures have also been reported in the literature for the acylation of non-fluorinated sulfoximines.[18] We thus turned our attention toward a milder pathway, without direct deprotonation of the nitrogen atom. Compound **2a** was treated with one equivalent of benzyl chloride along with one equivalent of triethylamine in the presence of a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) to afford N-acylated compound **4** in quantitative yield (Table 1, entry 1). The order of the introduction of each reagent was crucial to the success of this transformation.

To investigate the scope of this procedure, several acyl chlorides and sulfoximines were tested. A large panel of different electrophiles was engaged in the reaction. The product N-acylated sulfoximines were isolated in good yields (74–100%) with benzyl (Table 1, entry 2), alkyl (Table 1, entries 3 and 6), sterically hindered tertiary alkyl

Table 1 N-Acylation of Free NH-Sulfoximines

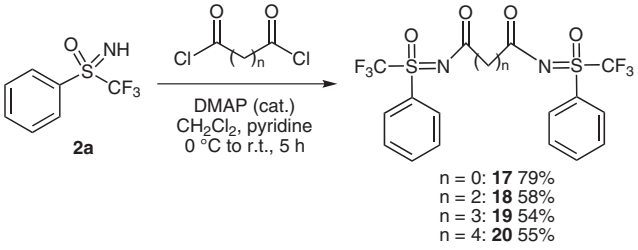


Entry	Substrate	R^1	R_F	R^2	Product	Yield (%)[a]
1	**2a**	H	CF_3	Ph	**4**	100
2	**2a**	H	CF_3	$PhCH_2$	**5**	96
3	**2a**	H	CF_3	Me	**6**	97
4	**2a**	H	CF_3	*t*-Bu	**7**	97
5	**2a**	H	CF_3	$MeOCOCH_2$	**8**	74
6	**2a**	H	CF_3	$Ph(CH_2)_3$	**9**	91
7	**2a**	H	CF_3	C_9H_{19}	**10**	49
8	**2b**	4-Me	CF_3	Ph	**11**	100
9	**2c**	2-Cl	CF_3	Ph	**12**	93
10	**2d**	4-Cl	CF_3	Ph	**13**	97
11	**2e**	H	CF_2Br	Ph	**14**	98
12	**2f**	H	$CFCl_2$	Ph	**15**	95
13	**2g**	H	C_4F_9	Ph	**16**	93

[a] Yield of isolated product.

(Table 1, entry 4) or electron-withdrawing (Table 1, entry 5) groups. A moderate 49% yield was obtained in the case of decanoyl chloride (Table 1, entry 7) due to the difficulties encountered during purification. The presence of substituents on the aromatic ring of the sulfoximines was not detrimental to the yield (Table 1, entries 8–10), nor was the nature of the perfluoroalkyl chain (Table 1, entries 11–13). All the products were stable and have been fully characterized.

Encouraged by these results, we extended our study to the synthesis of N-bridged sulfoximines obtained by the reaction of **2a** with various diacyl chlorides (Scheme 4). A slight modification of our procedure (pyridine was used as the base instead of triethylamine) afforded the desired compounds in moderate to good yields (54–79%).



Scheme 4 Synthesis of N-bridged sulfoximines

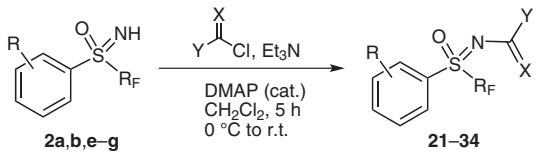
These novel structures appear attractive due to their potential applications as ligands in metal catalysis. Closely related molecules (non-fluorinated bis-sulfoximines linked by an alkyl tether) have been used as ligands in palladium-catalyzed allylic alkylations.[19] The latter were prepared by reduction of the carbonyl group of acetylated sulfoximines with dimethylsulfide borane complex. We next tested this protocol with our substrates, but unfortunately, unreacted starting materials were recovered. This was the case with several other mild reducing agents (borane, silane or boron trifluoride–diethyl etherate complex), whereas more potent reagents (lithium aluminum hydride or diisobutylaluminum hydride) led to the formation of degradation compounds with loss of the fluorinated moiety. We assume that these negative results are the consequence of the deactivation of the acyl function due to the electron-withdrawing properties of the sulfoximine moiety. Further studies on this topic are ongoing in our group, but their details fall beyond the scope of this article.

Finally, we focused our efforts on the extension of the scope of our protocol through the reaction of perfluoroalkylated sulfoximines with other acyl electrophiles (Table 2). The conditions previously used with acid chlorides were also suitable for the coupling reactions with various aliphatic, allylic and aromatic chloroformates (Table 2, entries 1–7). Each transformation delivered novel, stable sulfoximines in good to excellent yields. Varying the nature of the fluorinated moiety (Table 2, entries 8–10) did not affect the yield adversely, and allowed the construction of functionalized sulfoximines bearing mono-, di- and nonafluoroalkyl moieties. We also increased the structural diversity of our targets with various electrophiles. Carbamoyl chloride (Table 2, entries 11 and 12) chlorothionoformate (Table 2, entry 13) and thiocarbamoyl chloride (Table 2, entry 14) reacted successfully with *S*-trifluoromethyl sulfoximines to afford new sulfur(VI) skeletons in good yields. The lower reactivity of the carbamoyl chlorides was accompanied by an increase in the reaction time. Heating by classical or non-conventional (microwaves) methods did not improve the yield and led to degradation compounds.

Thus, we have obtained novel ureas and thioureas in satisfactory yields. These products may have applications as ligands, organocatalysts and as new key structures for chemical or agrochemical targets.

In summary, we have described an efficient and mild procedure for the N-functionalization of *S*-perfluoroalkylated sulfoximines, despite the presence of the fluorinated group, which deactivates the imino sulfanyl group and makes the compound highly sensitive to a base. The method has been extended to the synthesis of ureas, thioureas

Table 2 N-Functionalization of Sulfoximines with Heteroelectrophiles



2a,**b**,**e**–**g** **21**–**34**

Entry	Substrate	R	R_F	X	Y	Product	Yield (%)[a]
1	**2a**	H	CF_3	O	*i*-BuO	**21**	100
2	**2a**	H	CF_3	O	EtO	**22**	100
3	**2a**	H	CF_3	O	MeO	**23**	93
4	**2a**	H	CF_3	O	BnO	**24**	77
5	**2a**	H	CF_3	O	$Cl(CH_2)_2O$	**25**	64
6	**2a**	H	CF_3	O	allyl-O	**26**	85
7	**2a**	H	CF_3	O	Cl_3CCH_2O	**27**	91
8	**2e**	H	CF_2Br	O	Cl_3CCH_2O	**28**	79
9	**2f**	H	$CFCl_2$	O	Cl_3CCH_2O	**29**	94
10	**2g**	H	C_4F_9	O	Cl_3CCH_2O	**30**	64
11	**2a**	H	CF_3	O	Me_2N	**31**	82[b]
12	**2b**	4-Me	CF_3	O	Me_2N	**32**	64[b]
13	**2a**	H	CF_3	S	C_6F_5O	**33**	60
14	**2a**	H	CF_3	S	Me_2N	**34**	62[b]

[a] Yield of isolated product.
[b] Reaction over 5 d instead of 5 h.

and C_2-symmetric bis-sulfoximines. Further investigations are currently underway in our laboratory toward the use of these latter substrates as ligands in metal catalysis.

All reactions were conducted under an argon atmosphere in a freshly distilled solvent, unless otherwise stated. CH_2Cl_2 was distilled over calcium hydride. Reactions were monitored by ^{19}F NMR spectroscopy, or by thin-layer chromatography (TLC) on Merck silica gel 60 F_{254}, with the components being visualized under UV light (254 nm). Column chromatography was performed using Merck silica gel 60 mesh (40–63 μm). Melting points were determined using a Büchi Tottoli apparatus. NMR spectra were recorded on Bruker AC 200 or AC 300 spectrometers in $CDCl_3$. The internal reference was the residual peak of $CHCl_3$ (7.27 ppm) for ^1H NMR (200 or 300 MHz), the central peak of $CDCl_3$ (77 ppm) for ^{13}C NMR (75 or 50 MHz) and internal $CFCl_3$ (0 ppm) for ^{19}F NMR (188 MHz) spectra. Chemical shifts (δ) are given in ppm and standard abbreviations are used to describe the signal multiplicities. Low-resolution mass spectrometry and high-resolution mass spectrometry (HRMS) were performed using a Xevo Qtof Waters spectrometer at ILV, Versailles. Elemental analyses were performed in Gif sur Yvette (ICSN) using a Perkin Elmer CHN 2400 analyzer.

N-Acylated Sulfoximines; General Procedure

The sulfoximine (1 equiv, 0.5 mmol) and acid chloride (1.1 equiv, 0.55 mmol) were dissolved in anhyd CH_2Cl_2 (10 mL) under Ar at 0 °C. A catalytic amount of DMAP (0.1 equiv, 0.05 mmol) and Et_3N (1.2 equiv, 0.6 mmol) were added, and the mixture was stirred for 5 h at r.t. H_2O (10 mL) was added and the resulting mixture extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (pentane–Et_2O, 7:3) to give the N-acylated sulfoximine.

N-Bis-acylated Sulfoximines; General Procedure

The sulfoximine (1 equiv, 0.5 mmol) and diacyl chloride (0.5 equiv, 0.25 mmol) were dissolved in anhyd CH_2Cl_2 (10 mL) under Ar at 0 °C. Py (1.2 equiv, 0.6 mmol) and a catalytic amount of DMAP (0.1 equiv, 0.05 mmol) were added, and the mixture was stirred for 5 h at r.t. H_2O (10 mL) was added and the resulting mixture extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (pentane–Et_2O, 7:3) to give the N-bis-acylated sulfoximine.

***N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]benzamide (4)**

Yield: 150 mg (100%); colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.5 (t, *J* = 7.3 Hz, 2 H), 7.6 (t, *J* = 7.5 Hz, 1 H), 7.7 (t, *J* = 7.3 Hz, 2 H), 7.85 (t, *J* = 7.7 Hz, 1 H), 8.1 (d, *J* = 7.7 Hz, 2 H), 8.2 (d, *J* = 7.9 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.3 (q, $^1J_{C–F}$ = 328 Hz), 128.2, 129.8, 130.1, 130.3, 133.1, 133.9, 136.1, 172.9.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.9 (s, 3 F).

HRMS (EI): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{11}F_3NO_2S$: 314.0457; found: 314.0452 (δ = 1.7 ppm).

***N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]-2-phenylacetamide (5)**

Yield: 157 mg (96%); brown oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.7 and 3.75 (AB system, *J* = 14.5 Hz, 2 H), 7.1–7.3 (m, 5 H), 7.5 (t, *J* = 7.3 Hz, 2 H), 7.7 (q, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.8, 120.2 (q, $^1J_{C–F}$ = 328 Hz), 127.0, 128.5, 129.6, 130.0, 130.1, 130.2, 134.8, 136.1, 178.9.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –75.1 (s, 3 F).

HRMS (EI): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{12}F_3NO_2SNa$: 350.0433; found: 350.0423 (δ = 3 ppm).

Anal. Calcd for $C_{15}H_{12}F_3NO_2S$: C, 55.04; H, 3.67; N, 4.28. Found: C, 54.92; H, 3.78; N, 4.28.

***N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]acetamide (6)**

Yield: 116 mg (97%); yellow oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.2 (s, 3 H), 7.6 (t, *J* = 8.0 Hz, 2 H), 7.7 (t, *J* = 7.5 Hz, 1 H), 8.0 (d, *J* = 7.7 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.8, 124.0 (q, $^1J_{C–F}$ = 328 Hz), 130.0, 130.1, 130.2, 136.5, 178.6.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.9 (s, 3 F).

HRMS (EI): *m*/*z* $[M + Na]^+$ calcd for $C_9H_8F_3NO_2SNa$: 274.0120; found: 274.0121 (δ = –1.3 ppm).

Anal. Calcd for $C_9H_8F_3NO_2S$: C, 43.03; H, 3.21; N 5.58. Found: C, 43.19; H, 3.35; N, 5.61.

2,2-Dimethyl-*N*-[oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]propanamide (7)

Yield: 136 mg (97%); yellow oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.0 (s, 9 H), 7.4 (t, *J* = 8.5 Hz, 2 H), 7.6 (t, *J* = 7.5 Hz, 1 H), 7.8 (d, *J* = 7.7 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.3, 42.0, 124.0 (q, $^1J_{C–F}$ = 328 Hz), 130.0, 130.8, 136.0, 186.9.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.5 (s, 3 F).

HRMS (EI): *m*/*z* $[M + Na]^+$ calcd for $C_{12}H_{14}F_3NO_2SNa$: 316.0590; found: 316.0584 (δ = 1.9 ppm).

Methyl 3-Oxo-3-{[oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]amino}propanoate (8)

Yield: 123 mg (74%); colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.5 and 3.6 (AB system, *J* = 16 Hz, 2 H), 3.7 (s, 3 H), 7.6 (t, *J* = 8.2 Hz, 2 H), 7.7 (t, *J* = 7.7 Hz, 1 H), 8.0 (d, *J* = 7.9 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.9, 52.7, 120.0 (q, $^1J_{C–F}$ = 328 Hz), 129.5, 130.1, 130.2, 136.4, 167.3, 173.5.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –75.5 (s, 3 F).

HRMS (EI): *m*/*z* $[M + Na]^+$ calcd for $C_{11}H_{10}F_3NO_4SNa$: 332.0175; found: 332.0168 (δ = 1.9 ppm).

***N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]-4-phenylbutanamide (9)**

Yield: 162 mg (91%); colorless oil.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.0 (quin, *J* = 7.4 Hz, 2 H), 5.5 (t, *J* = 7.2 Hz, 2 H), 2.7 (t, *J* = 7.2 Hz, 2 H), 7.0–7.4 (m, 5 H), 7.7 (t, *J* = 7.9 Hz, 2 H), 7.8 (t, *J* = 7.4 Hz, 1 H), 8.0 (d, *J* = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.8, 35.0, 38.9, 120.3 (q, $^1J_{C–F}$ = 327 Hz), 125.9, 128.3, 128.5, 130.0, 130.1, 136.0, 141.6, 181.0.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.6 (s, 3 F).

HRMS (EI): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{17}F_3NO_2S$: 356.0932; found: 356.0934 (δ = 0.6 ppm).

***N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]decanamide (10)**

Yield: 90 mg (49%); yellow oil.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.9 (t, *J* = 6.5 Hz, 3 H), 1.2–1.5 (m, 12 H), 1.7 (quin, *J* = 6.8 Hz, 2 H), 2.5 (t, *J* = 7.0 Hz, 2 H), 7.7 (t, *J* = 7.2 Hz, 2 H), 7.9 (t, *J* = 7.3 Hz, 1 H), 8.0 (d, *J* = 7.8 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 25.2, 29.2, 29.1, 29.4, 31.8, 39.7, 120.3 (q, $^1J_{C–F}$ = 329 Hz), 129.9, 130.0, 130.6, 135.9, 181.5.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.7 (s, 3 F).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{25}F_3NO_2S$: 364.1558; found: 364.1554 (δ = –1.1 ppm).

_N_-[Oxo-(_p_-tolyl)(trifluoromethyl)-λ6-sulfanylidene]benzamide (11)
Yield: 164 mg (100%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.5 (s, 3 H), 7.5 (t, *J* = 8.0 Hz, 4 H), 7.6 (t, *J* = 7.3 Hz, 1 H), 8.0 (d, *J* = 8.7 Hz, 2 H), 8.3 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.9, 120.4 (q, $^1J_{C–F}$ = 326 Hz), 128.3, 129.9, 130.2, 130.9, 133.2, 134.2, 148.1, 173.1.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –75.3 (s, 3 F).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}F_3NO_2S$: 328.0614; found: 328.0618 (δ = –1.2 ppm).

_N_-[(2-Chlorophenyl)-oxo-(trifluoromethyl)-λ6-sulfanylidene]benzamide (12)
Yield: 161 mg (93%); pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5 (t, *J* = 7.3 Hz, 2 H), 7.5–7.6 (m, 3 H), 7.7 (t, *J* = 7.3 Hz, 1 H), 8.2 (d, *J* = 8.4 Hz, 2 H), 8.3 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.3 (q, $^1J_{C–F}$ = 328 Hz), 128.2, 129.9, 133.2, 133.5, 134.3, 134.4, 136.7, 172.9.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –72.8 (s, 3 F).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{10}ClF_3NO_2S$: 348.0067; found: 348.0059 (δ = 2.4 ppm).

_N_-[(4-Chlorophenyl)-oxo-(trifluoromethyl)-λ6-sulfanylidene]benzamide (13)
Yield: 168 mg (97%); yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.3–7.7 (m, 5 H), 8.1 (d, *J* = 8.0 Hz, 2 H), 8.2 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.1 (q, $^1J_{C–F}$ = 328 Hz), 128.3, 128.8, 129.8, 130.3, 130.5, 131.5, 133.3, 134.5, 143.5, 172.7.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.9 (s, 3 F).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{10}ClF_3NO_2S$: 348.0067; found: 348.0064 (δ = –0.4 ppm).

_N_-{[Bromo(difluoro)methyl]-oxo-(phenyl)-λ6-sulfanylidene}benzamide (14)
Yield: 184 mg (98%); yellow crystalline solid; mp 97 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5 (t, *J* = 7.7 Hz, 2 H), 7.6 (t, *J* = 7.5 Hz, 1 H), 7.7 (t, *J* = 7.5 Hz, 2 H), 7.8 (t, *J* = 7.5 Hz, 1 H), 8.1 (d, *J* = 7.9 Hz, 2 H), 8.2 (d, *J* = 7.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.1 (dd, *J* = 342, 346 Hz), 128.2, 129.6, 129.9, 130.6, 132.9, 134.2, 135.9, 172.5 (d, $^4J_{C–F}$ = 2 Hz).

^{19}F NMR (188 MHz, $CDCl_3$): δ = –54.8 and –57.4 (AB system, *J* = 212 Hz, 2 × 1 F).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{11}BrF_2NO_2S$: 373.9656; found: 373.9652 (δ = 1.1 ppm).

_N_-{[Dichloro(fluoro)methyl]-oxo-(phenyl)-λ6-sulfanylidene}benzamide (15)
Yield: 97.4 mg (95%); yellow crystalline solid; mp 83 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5 (t, *J* = 7.7 Hz, 2 H), 7.6 (t, *J* = 7.5 Hz, 1 H), 7.7 (t, *J* = 7.5 Hz, 2 H), 7.8 (t, *J* = 7.5 Hz, 1 H), 8.1 (d, *J* = 8.3 Hz, 2 H), 8.2 (d, *J* = 7.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.5 (d, $^1J_{C–F}$ = 339 Hz), 128.2, 129.7, 129.8, 130.0, 131.2, 132.9, 134.4, 135.9, 172.5.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –60.8 (s, 1 F).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{11}Cl_2FNO_2S$: 345.9866; found: 345.9852 (δ = –3.6 ppm).

_N_-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)-oxo-(phenyl)-λ6-sulfanylidene]benzamide (16)
Yield: 215 mg (93%); white crystalline solid; mp 86 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5 (t, *J* = 7.0 Hz, 2 H), 7.6 (t, *J* = 7.3 Hz, 1 H), 7.7 (t, *J* = 8.0 Hz, 2 H), 7.8 (t, *J* = 7.0 Hz, 1 H), 8.1 (d, *J* = 8.0 Hz, 2 H), 8.2 (d, *J* = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.3, 128.4, 129.8, 130.0, 130.1, 130.6, 131.1, 133.2, 133.7, 133.9, 136.3, 172.5 (d, $^4J_{C–F}$ = 2 Hz).

^{19}F NMR (188 MHz, $CDCl_3$): δ = –81.0 (s, 3 F), –105.6 and –111.8 (AB system, *J* = 362 Hz, 2 F), –118.8 and –121.5 (AB system, *J* = 450 Hz, 2 F), –125.2 and –127.2 (AB system, *J* = 434 Hz, 2 F).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{11}F_9NO_2S$: 464.0361; found: 464.0352 (δ = 2 ppm).

***N*,*N*′-Bis[oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]oxamide (17)**
Yield: 93 mg (79%); white crystalline solid; mp 100 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.6–7.8 (m, 4 H), 7.8 (t, *J* = 7.3 Hz, 2 H), 8.1 (t, *J* = 7.9 Hz, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.1 (q, $^1J_{C–F}$ = 328 Hz), 120.2 (q, $^1J_{C–F}$ = 328 Hz), 129.7, 130.3, 136.6, 166.0, 166.1.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –75.1 (s, 3 F), –75.2 (s, 3 F).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{11}F_6N_2O_4S_2$: 473.0064; found: 473.0064 (δ = 0 ppm).

***N*,*N*′-Bis[oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]butanediamide (18)**
Yield: 72 mg (58%); white crystalline solid; mp 122 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.8–3.0 (m, 4 H), 7.5–7.8 (m, 6 H), 8.1 (t, *J* = 7.7 Hz, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 34.4, 34.5, 120.1 (q, $^1J_{C–F}$ = 329 Hz), 120.2 (q, $^1J_{C–F}$ = 328 Hz), 129.4, 129.9, 130.0, 130.1, 130.3, 130.4, 135.9, 136.0.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –75.0 (s, 3 F), –75.8 (s, 3 F).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}F_6N_2O_4S_2$: 501.0377; found: 501.0374 (δ = –0.6 ppm).

***N*,*N*′-Bis[oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]pentanediamide (19)**
Yield: mg (54%); white crystalline solid; mp 81 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.1 (quin, *J* = 7.2 Hz, 2 H), 2.6 (t, *J* = 7.3 Hz, 4 H), 7.7 (t, *J* = 7.4 Hz, 4 H), 7.8 (t, *J* = 7.4 Hz, 2 H), 7.9 (d, *J* = 7.2 Hz, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 38.5, 120.3 (q, $^1J_{C–F}$ = 327 Hz), 124.1 (q, $^1J_{C–F}$ = 329 Hz), 129.4, 130.0, 130.1, 130.3, 136.1, 180.6.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.6 (s, 3 F), –74.7 (s, 3 F).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{17}F_6N_2O_4S_2$: 515.0534; found: 515.0535 (δ = 0.2 ppm).

***N*,*N*′-Bis[oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]hexanediamide (20)**
Yield: 73 mg (55%); colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.6–1.9 (m, 4 H), 2.6 (t, *J* = 6.8 Hz, 4 H), 7.7 (t, *J* = 7.5 Hz, 4 H), 7.8 (t, *J* = 7.4 Hz, 2 H), 8.1 (d, *J* = 7.7 Hz, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.6, 39.2, 120.3 (q, $^1J_{C–F}$ = 329 Hz), 126.5 (q, $^1J_{C–F}$ = 329 Hz), 130.0, 130.1, 130.5, 135.9, 180.9.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.6 (s, 6 F).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{19}F_6N_2O_4S_2$: 529.0690; found: 529.0684 (δ = –1.1 ppm).

***O*-*iso*-Butyl *N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]carbamoate (21)**
Yield: 146 mg (100%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.8 (dd, *J* = 2.7 Hz, *J* = 6.7 Hz, 6 H), 1.9 (hept, *J* = 6.7 Hz, 1 H), 3.9 (d, *J* = 6.7 Hz, 2 H), 7.6 (t, *J* = 8.3 Hz, 2 H), 7.7 (t, *J* = 7.5 Hz, 1 H), 8.0 (d, *J* = 7.7 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9, 27.7, 73.4, 120.3 (q, $^1J_{C-F}$ = 329 Hz), 130.1, 130.3, 136.3, 156.2.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.4 (s, 3 F).

HRMS (EI): *m*/*z* $[M + Na]^+$ calcd for $C_{12}H_{14}F_3NO_3SNa$: 332.0539; found: 332.0523 (δ = 4.6 ppm).

***O*-Ethyl *N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]carbamoate (22)**
Yield: 119 mg (100%); yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.2 (t, *J* = 7.2 Hz, 3 H), 4.1 (q, *J* = 7.2 Hz, 2 H), 7.6 (t, *J* = 7.5 Hz, 2 H), 7.7 (t, *J* = 7.0 Hz, 1 H), 8.0 (t, *J* = 8 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 63.2, 120.3 (q, $^1J_{C-F}$ = 329 Hz), 130.2, 130.3, 130.5, 136.4, 156.3.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.1 (s, 3 F).

HRMS (EI): *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_{10}F_3NO_3SNa$: 304.0226; found: 304.0221 (δ = 1.4 ppm).

***O*-Methyl *N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]carbamoate (23)**
Yield: 124 mg (93%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.8 (s, 3 H), 7.6–7.9 (m, 3 H), 8.1 (d, *J* = 11.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.0, 120.3 (q, $^1J_{C-F}$ = 327 Hz), 130.0, 130.4, 136.4, 156.8.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –73.7 (s, 3 F).

MS (ES): *m*/*z* (%) = 290 $[M + Na]^+$, 268 $[M + H]^+$, 236 $[M - OCH_3]^+$, 151.

HRMS (EI): *m*/*z* $[M + H]^+$ calcd for $C_9H_9F_3NO_3S$: 268.0255; found: 268.0266 (δ = 4.1 ppm).

***O*-Benzyl *N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]carbamoate (24)**
Yield: 131 mg (77%); colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.1 and 5.2 (AB system, *J* = 12.1 Hz, 2 H), 7.3 (s, 5 H), 7.6 (t, *J* = 7.2 Hz, 2 H), 7.8 (t, *J* = 7.5 Hz, 1 H), 8.0 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 68.6, 120.0 (q, $^1J_{C-F}$ = 327 Hz), 127.2, 128.1, 128.3, 129.6, 129.9, 135.2, 136.3, 155.9.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.5 (s, 3 F).

HRMS (EI): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{13}F_3NO_3S$: 344.0568; found: 344.0566 (δ = –0.6 ppm).

***O*-(1-Chloroethyl) *N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]carbamoate (25)**
Yield: 101 mg (64%) as a mixture of two diastereomers; colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.8 (dd, *J* = 5.8 Hz, *J* = 3.1 Hz, 3 H), 6.5 (q, *J* = 5.9 Hz, 1 H), 7.7 (t, *J* = 7.4 Hz, 2 H), 7.9 (t, *J* = 7.3 Hz, 1 H), 8.1 (d, *J* = 7.7 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9, 83.7, 120.0 (q, $^1J_{C-F}$ = 326 Hz), 129.2, 130.3, 136.7, 154.2.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.0 (s, 3 F), –74.8 (s, 3 F).

HRMS (EI): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{10}F_3NO_3SCl$: 316.0022; found: 316.0031 (δ = 2.8 ppm).

***O*-Allyl *N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]carbamoate (26)**
Yield: 127 mg (85%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.6 (d, *J* = 5.8 Hz, 2 H), 5.2 (2 dd, J_{AX} = 10.4 Hz, J_{BX} = 17.1 Hz, J_{AB} <1.0 Hz, 2 H), 5.9 (ddt, *J* = 5.8 Hz, J_{AX} = 10.4 Hz, J_{BX} = 17.1 Hz, 1 H), 7.7 (t, *J* = 7.7 Hz, 2 H), 7.9 (t, *J* = 7.5 Hz, 1 H), 8.1 (t, *J* = 7.6 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 67.8, 118.8, 120.3 (q, $^1J_{C-F}$ = 327 Hz), 130.0, 130.4, 131.6, 136.4, 156.0.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.2 (s, 3 F).

MS (ES): *m*/*z* (%) = 294 $[M + H]^+$, 189, 126 $[PhSOH]^+$.

HRMS (EI): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{11}F_3NO_3S$: 294.0412; found: 294.0406 (δ = –2.0 ppm).

***O*-(2,2,2-Trichloroethyl) *N*-[Oxo-phenyl(trifluoromethyl)-λ6-sulfanylidene]carbamoate (27)**
Yield: 174 mg (91%); waxy solid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.7 and 4.8 (AB system, *J* = 12.0 Hz, 2 H), 7.7 (t, *J* = 7.2 Hz, 2 H), 7.9 (t, *J* = 7.5 Hz, 1 H), 8.1 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 75.8, 94.5, 120.0 (q, $^1J_{C-F}$ = 326 Hz), 130.2, 130.4, 136.7, 154.6.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.7 (s, 3 F).

HRMS (EI): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_8F_3Cl_3NO_3S$: 383.9243; found: 383.9252 (δ = 2.6 ppm).

***O*-(2,2,2-Trichloroethyl) *N*-{[Bromo(difluoro)methyl]oxo-phenyl-λ6-sulfanylidene}carbamoate (28)**
Yield: 176 mg (79%); waxy solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.7 and 4.8 (AB system, *J* = 12.0 Hz, 2 H), 7.7 (t, *J* = 7.3 Hz, 2 H), 7.9 (t, *J* = 7.5 Hz, 1 H), 8.1 (d, *J* = 7.3 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 75.6, 94.6, 120.8 (dd, *J* = 345, 346 Hz), 129.0, 130.0, 130.8, 136.4, 154.5.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –54.6 and –56.6 (AB system, *J* = 210 Hz, 2 F).

MS (ES): *m*/*z* (%) = 467 $[M + Na]^+$, 444 $[M + H]^+$, 296 $[M - OCH_2CCl_3]^+$, 151.

HRMS (EI): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_8F_2NO_3SCl_3Br$: 443.8442; found: 443.8436 (δ = –1.4 ppm).

***O*-(2,2,2-Trichloroethyl) *N*-{[Dichloro(fluoro)methyl]oxo-phenyl-λ6-sulfanylidene}carbamoate (29)**
Yield: 157 mg (94%); waxy solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.7 and 4.8 (AB system, *J* = 12.0 Hz, 2 H), 7.7 (m, 3 H), 8.1 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 75.5, 94.7, 123.3 (d, $^1J_{C-F}$ = 338 Hz), 129.4, 129.8, 131.5, 136.3, 154.5.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –60.2 (s, 1 F).

MS (ES): *m*/*z* (%) = 439 $[M + Na]^+$, 415 $[M + H]^+$, 268 $[M - OCH_2CCl_3]^+$, 125 $[PhSO]^+$.

HRMS (EI): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_8FNO_3SCl_5$: 415.8652; found: 415.8650 (δ = –0.5 ppm).

***O*-(2,2,2-Trichloroethyl) *N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)-oxo-phenyl-λ6-sulfanylidene]carbamoate (30)**
Yield: 154 mg (64%); waxy solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.7 and 4.8 (AB system, *J* = 11.9 Hz, 2 H), 7.7 (t, *J* = 6.0 Hz, 2 H), 7.9 (t, *J* = 6.0 Hz 1 H), 8.2 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 75.9, 94.5, 130.1, 130.9, 136.8, 154.1.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –81.1 (s, 3 F), –106.3 and –109.6 (AB system, J = 362 Hz, 2 F), –118.8 and –121.5 (AB system, J = 444 Hz, 2 F), –125.5 and –127.1 (AB system, J = 434 Hz, 2 F).

HRMS (EI): m/z $[M + H]^+$ calcd for $C_{13}H_8F_9NO_3SCl_3$: 533.9147; found: 533.9148 (δ = –0.2 ppm).

1,1-Dimethyl-3-[oxo-phenyl-(trifluoromethyl)-λ6-sulfanylidene]urea (31)
Yield: 115 mg (82%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.9 (s, 3 H), 3.1 (s, 3 H), 7.7 (t, J = 7.1 Hz, 2 H), 7.8 (t, J = 7.4 Hz, 1 H), 8.0 (d, J = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.5, 37.8, 120.4 (q, $^1J_{C–F}$ = 327 Hz), 129.7, 130.1, 131.5, 135.5, 157.5.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.0 (s, 3 F).

HRMS (EI): m/z $[M + Na]^+$ calcd for $C_{10}H_{11}F_3N_2O_2SNa$: 303.0391; found: 303.0393 (δ = 0.7 ppm).

1,1-Dimethyl-3-[oxo-(*p*-tolyl)(trifluoromethyl)-λ6-sulfanylidene]urea (32)
Yield: 94 mg (64%); colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.5 (s, 3 H), 2.9 (s, 3 H), 3.1 (s, 3 H), 7.6 (d, J = 8.0 Hz, 2 H), 7.9 (d, J = 8.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 35.5, 37.8, 120.4 (q, $^1J_{C–F}$ = 327 Hz), 128.2, 130.2, 130.5, 147.2, 157.6.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.5 (s, 3 F).

HRMS (EI): m/z $[M + H]^+$ calcd for $C_{11}H_{14}F_3N_2O_2S$: 295.0728; found: 295.0726 (δ = –0.7 ppm).

***O*-(2,3,4,5,6-Pentafluorophenyl) *N*-[Oxo-phenyl-(trifluoromethyl)-λ6-sulfanylidene]carbamothioate (33)**
Yield: 125.8 mg (60%); white crystalline solid; mp 80 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.7 (t, J = 7.7 Hz, 2 H), 7.9 (t, J = 8.0 Hz, 1 H), 8.0 (t, J = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 119.7 (q, $^1J_{C–F}$ = 325 Hz), 127.3, 130.6, 137.1, 142.7 (m), 192.5.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –76.3 (s, 3 F), –152.4 (m, 2 F), –157.6 (s, 1 F), –162.9 (m, 2 F).

HRMS (EI): m/z $[M + Na]^+$ calcd for $C_{14}H_5F_8NO_2S_2Na$: 457.9526; found: 457.9520 (δ = 1.4 ppm).

1,1-Dimethyl-3-[oxo-phenyl-(trifluoromethyl)-λ6-sulfanylidene]thiourea (34)
Yield: 92 mg (62%); colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.3–3.4 (m, 6 H), 7.6–7.8 (m, 3 H), 8.0 (d, J = 8.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.4, 42.2, 119.8 (q, $^1J_{C–F}$ = 319 Hz), 129.9, 130.2, 131.5, 135.2, 182.9.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –77.7 (s, 3 F).

HRMS (EI): m/z $[M + H]^+$ calcd for $C_{10}H_{12}F_3N_2OS_2$: 297.0343; found: 297.0351 (δ = 2.7 ppm).

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