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Efficient copper-induced coupling between *NH*-fluoroalkylated sulfoximines and aryl iodides or bromides

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ABSTRACT

A high yielding, simple, and flexible copper-based system for N-arylation of fluorinated sulfoximines is reported. Best results were achieved using copper iodide in combination with DMEDA and Cs_2CO_3 to provide a wide range of *N*-arylated perfluoroalkylated sulfoximines. These conditions tolerate a great number of substituents on either aromatic cycle, including heteroaromatic rings, for the N-functionalization.

1. Introduction

Sulfoximines bear uncommon and intriguing sulfur (VI) functionality. The extensive variety of existing synthetic methods offers an easy access to these molecules, including their preparation in pure enantiomeric form.[1] These broad synthetic opportunities have stimulated widespread applications for sulfoximines as chiral auxiliary,[2] ligand in asymmetric catalysis,[3] and biologically active group in life sciences.[4] Surprisingly, the field of application is more restricted for *S*-perfluoroalkyl sulfoximines presumably because of their so far cumbersome synthesis. Nevertheless, some recent applications made them very attractive tools. They have been indeed described as very powerful electron withdrawing groups,[5] employed for material science purposes[6] and above all, introduced as very efficient electrophilic fluoroalkylating reagents as recently demonstrated by Shibata for trifluoro- and monofluoromethylation,[7] Hu for difluoromethylation,[8] and us for bromodifluoro- and dichloromethylation.[9]

These former challenging discoveries nicely illustrate the need and the importance to develop new, pathway for the synthesis of various *S*-perfluoroalkylated sulfoximines.

In connection with studies devoted to the preparation of fluorinated sulfilimines, we recently unlocked the access to fluoroalkylated aryl sulfoximines by the discovery of a safe method, avoiding the use of solvent and toxic reagents.[10]

Our versatile approach allowed the variation of the aromatic substituent, the nature of the fluorinated chain (from trifluoromethyl to perfluoroalkyl) and moreover, the scalable isolation of free *NH*-sulfoximines, enabling thus further post-functionalization. In this article, we disclose our results concerning the copper promoted N-arylation[11] of fluorinated sulfoximines, as a part of our studies devoted to a better understanding of the peculiar reactivity of this nitrogen atom.

2. Results and discussion

The optimization of reaction conditions was first carried out with trifluoromethyl phenyl sulfoximine **1a** and phenyl iodide **2a**. The influence of reaction parameters was evaluated and is summarized in Table 1.

Preliminary blank experiments revealed the importance of the metal as well as the ligand for the success of the coupling (entries 1 and 6). A set of copper salts, introduced in stoichiometric amount, was then investigated (entries 2–5). Good yields of functionalized sulfoximine **3a** were obtained whatever the nature of the salt. As copper iodide showed the best performance (entry 5), this reagent was chosen as our standard for the next studies. The use of

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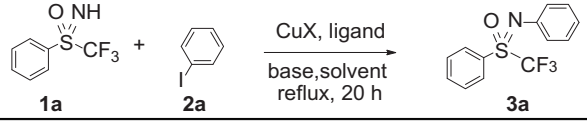
Table 1
Evaluation of the reaction conditions for the coupling of sulfoximine **1a** with phenyl iodide **2a**



1a **2a** **3a**

Entry	Copper salt[a]	Equiv	Ligand	Base	Solvent	Yield[b] %
1	—	—	DMEDA	Cs_2CO_3	Toluene	0[c]
2	$CuSO_4$	1	DMEDA	Cs_2CO_3	Toluene	81
3	CuCl	1	DMEDA	Cs_2CO_3	Toluene	80
4	CuBr	1	DMEDA	Cs_2CO_3	Toluene	86
5	CuI	1	DMEDA	Cs_2CO_3	Toluene	96
6	CuI	1	—	Cs_2CO_3	Toluene	0[c]
7	CuI	1	TMEDA	Cs_2CO_3	Toluene	70
8	CuI	1	*N*,*N*-Dimethylethylenediamine	Cs_2CO_3	Toluene	76
9	CuI	1	Proline	Cs_2CO_3	Toluene	82
10	CuI	1	*cis* 1,2-Diaminocyclohexane	Cs_2CO_3	Toluene	96
11	CuI	1	DMEDA	Na_2CO_3	Toluene	90
12	CuI	1	DMEDA	K_2CO_3	Toluene	90
13	CuI	0.5	DMEDA	Cs_2CO_3	Toluene	94
14	CuI	0.25	DMEDA	Cs_2CO_3	Toluene	3[c]
15	CuI	0.1	DMEDA	Cs_2CO_3	Toluene	Traces[c]
16	CuI	0.1	DMEDA[d]	Cs_2CO_3	Toluene	52
17	CuI	0.5	DMEDA	Cs_2CO_3	DMSO	20
18	CuI	0.5	DMEDA	Cs_2CO_3	Dioxane	91
19	CuI	0.5	DMEDA	Cs_2CO_3	THF	92

[a] Reaction conditions otherwise stated: sulfoximine **1a** (1.0 equiv), phenyl iodide **2a** (2.0 equiv), base (2.5 equiv), copper salt, ligand (twice the quantity of copper salt), solvent (1 M).
[b] Isolated yield.
[c] Starting material **1a** was degraded.
[d] 1.0 equiv related to **1a**.

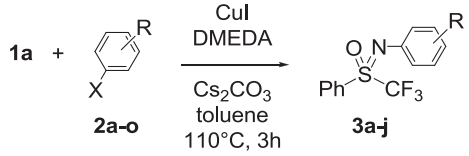
TMEDA,[12] *N*,*N*-dimethylethylenediamine,[13] and proline[14] (entries 7–9) proved efficient. However, 1,2-diaminocyclohexane and DMEDA[15] (entries 5 and 10) gave the best results and the latter was chosen for practical convenience. Concerning the influence of the base cation, cesium proved to be slightly more efficient than sodium or potassium (entry 5 vs entries 11 and 12). Another crucial point that we evaluated was the charge of copper salt. The amount of copper iodide could be reduced to 50 mol % without real impact on yield (entry 13), whereas poor yields were obtained below this amount (entry 14–15). It should be noticed that the quantities needed are greater than those used for the arylation of non fluorinated sulfoximines.[16]

We presume that this effect results from the particular structure of fluorinated substrate **1a** acting as competitive ligand for copper.[17]To test this hypothesis, we performed an experiment with a tenfold excess of ligand relative to the copper salt (entry 16). Under those catalytic conditions, an acceptable yield (52%) was retrieved but not as high as with a sub-stoichiometric amount of copper able to achieve a practically quantitative yield for this transformation. The solvent, toluene gave the best yield (entry 13), closely followed by dioxane and THF (entries 18 and 19), which could be used as well, while DMSO gave the poorest yield (entry 17). Finally, experiments described in Table 1, were all conducted using 20 h reflux for consistency, but the reaction time could be reduced to 3 h (vide infra) without impact on the yield.

These conditions have been retained for the substrate scope investigation using various aryl halides. The results are summarized in Table 2.

A wide variety of *N*-arylated fluoroalkylated aryl sulfoximines was synthesized in excellent yield from corresponding aryl iodides (up to 99%, entries 1–10). Two trends are emerging from these results. The substitution of the aryl iodide has no influence on the yield as demonstrated by the variation of the position of a methyl (entries 2–4) or a methoxy group (entries 8–10) as well as the use

Table 2
Copper-catalyzed N-arylation of trifluoromethyl phenylsulfoximine **1a** with aryl halides **2a**–**o**[a]



2a-o **3a-j**

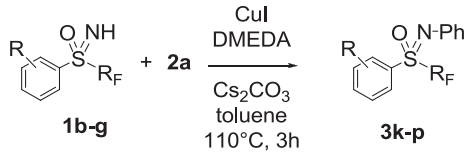
Entry	Aryl halide	X	R	Product	Yield[b] %
1	**2a**	I	H	**3a**	97
2	**2b**	I	2-Me	**3b**	98
3	**2c**	I	3-Me	**3c**	99
4	**2d**	I	4-Me	**3d**	99
5	**2e**	I	3,5-Me	**3e**	97
6	**2f**	I	4-NO_2	**3f**	>99
7	**2g**	I	4-CO_2Et	**3g**	>99
8	**2h**	I	2-OMe	**3h**	98
9	**2i**	I	3-OMe	**3i**	99
10	**2j**	I	4-OMe	**3j**	98
11	**2k**	Br	H	**3a**	92
12	**2l**	Br	2-OMe	**3h**	99
13	**2m**	Br	3-OMe	**3i**	99
14	**2n**	Br	4-OMe	**3j**	98
15	**2o**	Cl	H	**3a**	Traces[c]

[a] Reaction conditions: sulfoximine **1a** (1.0 equiv), aryl halide (2.0 equiv), CuI (50 mol %), DMEDA (1.0 equiv), Cs_2CO_3 (2.5 equiv) in toluene (1 M) at 110 °C.
[b] Isolated yield.
[c] Starting material **1a** was degraded.

of compound **2e** (entry 5). The presence of electron withdrawing substituents, such as nitro or ester (entries 6 and 7) are not deleterious to the yield. Moreover, a direct comparison between aryl iodides **2a**, **2h**–**j** and aryl bromides **2k**–**n** for this coupling reaction showed that both aryl halides reacted equally well and gave quantitative yields (entries 1, 8–10 vs 11–14). Unsurprisingly, no reaction occurred with chlorobenzene**2o** (entry 15).[18]

The reactivity of variously substituted perfluoroalkyl aryl sulfoximines has been also evaluated during the cross coupling process. The results are reported in Table 3.

Table 3
Copper-catalyzed N-arylation of substituted fluoroalkyl sulfoximine **1b**–**g** with phenyl iodide **2a**[a]



1b-g **3k-p**

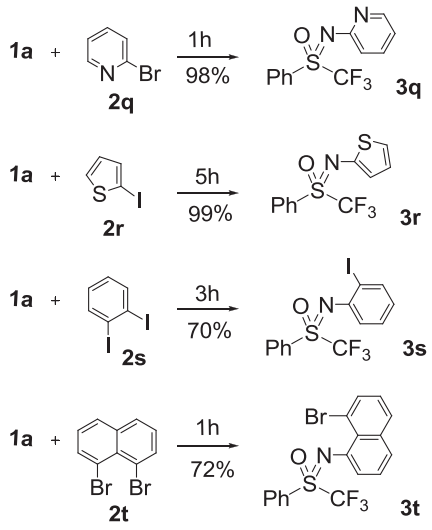
Entry	Aryl halide	R	R_F	Product	Yield[b] (%)
1	**1b**	*o*-Cl	CF_3	**3k**	0[c]
2	**1c**	*m*-Cl	CF_3	**3l**	68
3	**1d**	*p*-Cl	CF_3	**3m**	99
4	**1e**	*o*-Me	CF_3	**3n**	99
5	**1f**	*p*-Me	CF_3	**3o**	99
6	**1g**	H	C_4F_9	**3p**	98

[a] Reaction conditions: sulfoximine (1.0 equiv), phenyl iodide **2a** (2.0 equiv), CuI (50 mol %), DMEDA (1.0 equiv), Cs_2CO_3 (2.5 equiv) in toluene (1 M) at 110 °C for 3 h.
[b] Isolated yield.
[c] Starting material **1b** was degraded.

Whereas the methyl group had no influence and allowed a quantitative transformation (entries 4 and 5), the presence of a chlorine atom resulted in more contrasted results (entries 1–3). Its presence was not detrimental to the yield in *para* position and to a lesser degree in *meta* position. However, the reaction was totally inhibited when this halogen was linked *ortho* to the sulfoximine functionality. In this particular case, starting material **1b** was fully

degraded. We presume that in this case, a new species is formed by copper insertion into the aryl–chlorine bond of **1b** induced by the strong stabilizing *ortho* effect of the sulfoximine.[19] The complex formed may then evolved through decomposition species. Finally the length of the perfluorinated chain can be increased without loss of efficiency (entry 6).

Our methodology was further extended to the synthesis of more elaborated *N*-aryl sulfoximines in order to demonstrate the functional tolerance of this process (Scheme 1).



Scheme 1. Copper-catalyzed coupling with functionalized aryl iodides. Reaction conditions: sulfoximine **1a** (1.0 equiv), aryl halide (2.0 equiv, 1.1 equiv for **2s** and **2t**), CuI (50 mol %), DMEDA (1.0 equiv), Cs_2CO_3 (2.5 equiv) in toluene (1 M) at 110 °C.

We were very pleased to isolate in quantitative yield the sulfoximines **3q** and **3r** obtained from the coupling reaction with, respectively, 2-bromopyridine **2q** and 2-iodothiophene **2r**. The presence of a heteroatom in this second aromatic ring is of importance for future developments of fluorinated sulfoximines. In the same context, with the judicious choice of conditions (1.1 equiv of aryl halide for 1 equiv of sulfoximine), both bis-iodobenzene **2s** and dibromonaphthalene **2t** reacted equally well, to give around 70% yield of halogenated product **3s** and **3t**. The structure of molecule **3s** has been secured by X-ray analysis (Fig. 1).

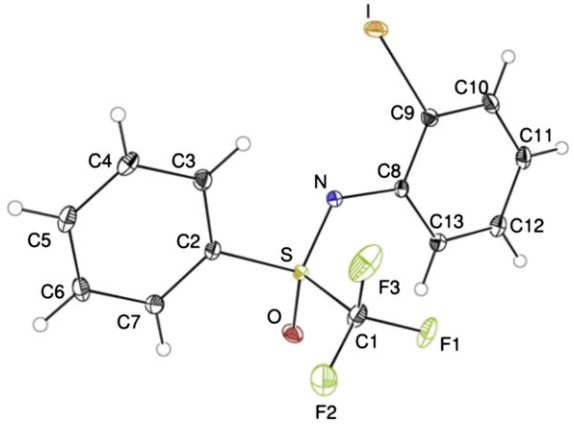


Fig. 1. ORTEP drawing of compound **3s** with the atom labeling scheme. Ellipsoids are drawn at the 30% probability level.

3. Conclusion

In summary, we have developed a simple and versatile copper-catalyzed system for the N-arylation of fluorinated sulfoximines in excellent yield. This innovative process allows a new and low cost access to a large panel of *N*-arylated fluoroalkylated sulfoximines. Some examples bearing additional functionalities would enable further transformations.

4. Experimental section

4.1. General

Each reaction was carried out under an argon atmosphere in a freshly distilled solvent, unless otherwise noted. All chemicals were purchased from commercial sources (Sigma–Aldrich, ABCR or Alfa Aesar) and were used without further purification. Organic solvents were purchased from Merck and Carlo Erba. Reactions were monitored by thin-layer chromatography on silica gel 60 F_{254}, or by ^{19}F NMR spectroscopy. Unless otherwise noted, yields refer to materials purified by column chromatography. NMR spectra were recorded on a Bruker AC-200 spectrometer. Reported coupling constants and chemicals shifts were based on a first order analysis. Internal reference was the residual peak of $CHCl_3$ (7.27 ppm) for ^1H (200 MHz), central peak of $CDCl_3$ (77 ppm) for ^{13}C (50 MHz) spectra, and internal $CFCl_3$ (0 ppm) for ^{19}F (282 MHz) NMR spectra. High-resolution electrospray mass spectra in the positive ion mode were obtained on a Xevo Q-Tof WATERS. Melting points were determined on a Büchi melting point apparatus. X-ray diffraction data were collected by using a Kappa X8 APPEX II Bruker diffractometer.

4.2. General procedure for preparation of sulfoximines as exemplified by the preparation of *S*-(phenyl)-*S*-(trifluoromethyl)-sulfoximine (1a)

Trifluoromethanesulfonate anhydride (6.5 mL, 38.7 mmol, 1.5 equiv) was added under argon to a precooled (−15 °C) mixture of phenyl trifluoromethyl sulfoxide (5 g, 25.8 mmol, 1 equiv) and acetonitrile (2 mL, 38.7 mmol, 1.5 equiv). The reaction mixture was stirred for 12 h at −15 °C, and then carefully hydrolyzed with water (5 mL), sodium hydroxide (2 g, 51.5 mmol, 2 equiv) and potassium permanganate (4 g, 25.8 mmol, 1 equiv) were added, the reaction was heated at 110 °C for 4 h. The mixture was cooled, cleared with $Na_2S_2O_4$, then diluted with water (15 mL), and extracted with CH_2Cl_2 (3×20 mL). The organic layers were dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, ether/pentane 3/7) to give 4.37 g (81%) of **1a** as a white solid. Mp: 89.9±0.2 °C; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −79.3 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.16 (2H, d, J=7.3 Hz), 7.83–7.75 (1H, m), 7.69–7.61 (2H, m), 3.62 (1H, br s for NH); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ: 35.5, 131.6, 130.6, 129.5, 120.9 (q, J=332 Hz, CF_3); MS (pos. ESI): m/z=210 (MH^+), 232 (MNa^+), 441 ($2MNa^+$).

*4.2.1. S-((o-Chloro)phenyl)-S-(trifluoromethyl)-sulfoximine (**1b**).* Pale yellow oil, yield 49%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −76.9 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.34 (1H, dd, J=8.1, 1.5 Hz), 7.69–7.58 (2H, m), 7.55–7.48 (1H, m), 3.89 (1H, br s for NH); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 136.2, 135.1, 134.4, 133.0, 130.3, 127.6, 120.8 (q, J=333 Hz, CF_3); MS (pos. ESI, for ^{35}Cl): m/z=173 ($[MH-CF_3]^+$), 244 (MH^+); HRMS: calculated for $C_7H_6^{35}ClF_3NOS$ 243.9805 found 243.9810 (δ=−2.1 ppm).

*4.2.2. S-((m-Chloro)phenyl)-S-(trifluoromethyl)-sulfoximine (**1c**).* White powder, mp: 37–39 °C, yield 73%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −78.9 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.14–8.09 (1H, m), 8.01 (1H, d, J=8.1 Hz) 7.74–7.67 (1H, m), 7.55 (1H, t, J=8.1 Hz), 3.94 (1H, br s for NH); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 135.7, 135.5, 133.3, 130.6, 130.3, 128.6, 120.6 (q, J=332 Hz, CF_3); MS (pos. ESI, for ^{35}Cl): m/z=173 ($[MH-CF_3]^+$), 244 (MH^+);

HRMS: calculated for $C_7H_6^{35}ClF_3NOS$ 243.9805 found 243.9806 (δ=−0.2 ppm).

*4.2.3. S-((p-Chloro)phenyl)-S-(trifluoromethyl)-sulfoximine (**1d**).* Pale yellow powder, mp: 58–60 °C, yield 78%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −79.1 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.07 (2H, d, J=8.7 Hz), 7.60 (2H, d, J=8.9 Hz), 3.80 (1H, br s for NH); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 142.6, 131.9, 130.0, 129.8, 120.7 (q, J=332 Hz, CF_3); MS (pos. ESI, for ^{35}Cl): m/z=173 ($[MH-CF_3]^+$), 244 (MH^+); HRMS: calculated for $C_7H_6^{35}ClF_3NOS$ 243.9805 found 243.9803 (δ=1.0 ppm).

*4.2.4. S-((o-Methyl)phenyl)-S-(trifluoromethyl)-sulfoximine (**1e**).* Pale yellow oil, yield 69%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −78.9 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.22 (1H, d, J=8.1 Hz), 7.63–7.53 (1H, m), 7.45–7.33 (2H, m), 3.70 (1H, br s for NH), 2.78 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 141.7, 135.2, 133.5, 132.9, 129.7, 126.8, 121.2 (q, J=333 Hz, CF_3), 21.1; MS (pos. ESI): m/z=224 (MH^+); HRMS: calculated for $C_8H_9F_3NOS$ 224.0357 found 224.0355 (δ=1.1 ppm).

*4.2.5. S-((p-Methyl)phenyl)-S-(trifluoromethyl)-sulfoximine (**1f**).* White powder, mp: 69.3±0.2 °C, yield 72%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −79.5 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.03 (2H, d, J=8.3 Hz), 7.43 (2H, d, J=8.1 Hz), 3.47 (1H, br s for NH), 2.50 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 146.9, 130.6, 130.2, 128.6, 121.0 (q, J=332 Hz, CF_3), 21.7; MS (pos. ESI): m/z=224 (MH^+), 246 (MNa^+); HRMS: calculated for $C_8H_9F_3NOS$ 224.0351 found 224.0361 (δ=−4.2 ppm).

*4.2.6. S-(Phenyl)-S-(nonafluorobutyl)-sulfoximine (**1g**).* Colorless oil, yield 75%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −81.3 (3F, m), −111.6 (2F, m), −121.0 (2F, m), −126.5 (2F, m); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.14 (2H, d, J=7.9 Hz), 7.77–7.70 (1H, m), 7.64–7.55 (2H, m), 4.03 (1H, br s for NH); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 135.4, 132.3, 130.8, 129.2; MS (pos. ESI): m/z=360 (MH^+); HRMS: calculated for $C_{10}H_7F_9NOS$ 360.0099 found 360.0100 (δ=−0.1 ppm).

4.3. General procedure for N-arylations of sulfoximines as exemplified by the preparation of *N*-(phenyl) phenyl trifluoromethyl sulfoximine (3a)

Under argon atmosphere a dry Schlenk tube was charged with sulfoximine **1a** (0.10 g, 1.0 equiv, 0.5 mmol), aryl halide (0.19 g, 2.0 equiv, 1 mmol), CuI (46 mg, 0.5 equiv, 0.25 mmol), DMEDA (21 mg, 1 equiv, 0.5 mmol), Cs_2CO_3 (0.39 g, 2.5 equiv, 1.25 mmol), and degassed (or freshly distilled) toluene (2 mL). After heating to 110 °C for 3 h, the mixture was cooled to room temperature and neutralized with aqueous HCl (10 mL at 1 M). The aqueous layer was extracted with dichloromethane (3×20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by preparative chromatography (SiO_2, pentane/diethyl ether, 9/1) to give 0.14 g (97%) of **3a** as a yellow liquid. ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −72.6 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.19 (2H, d, J=7.32 Hz), 7.78–7.70 (1H, m), 7.65–7.57 (2H, m), 7.31–7.20 (4H, m), 7.10–7.03 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 141.1, 135.4, 131.7, 130.5, 129.5, 129.2, 124.0, 123.9, 121.4 (q, J=339 Hz, CF_3); MS (pos. ESI): m/z=308 (MNa^+); HRMS: calculated for $C_{13}H_{10}F_3NNaOS$ 308.0327 found 308.0331 (δ=−1.2 ppm).

*4.3.1. N-((o-Methyl)phenyl) phenyl trifluoromethyl sulfoximine (**3b**).* White powder, mp: 41–43 °C, yield 98%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −73.3 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.13 (2H, d, J=7.3 Hz), 7.70–7.62 (1H, m), 7.58–7.49 (2H, m), 7.23 (1H, dd, J=7.9 Hz, J=1.2 Hz), 7.13–7.08 (1H, m), 7.02 (1H, td, J=7.5, 1.7 Hz), 6.90 (1H, td, J=7.3, 1.4 Hz) 2.32 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 139.8, 135.3, 132.6, 132.2, 130.6, 130.4, 129.5, 126.5, 123.8, 123.1, 121.5 (q, J=339 Hz, CF_3), 18.5; MS (pos. ESI): m/z=322 (MNa^+); HRMS: calculated for $C_{14}H_{12}F_3NNaOS$ 322.0489 found 322.0481 (δ=2.5 ppm).

*4.3.2. N-((m-Methyl)phenyl) phenyl trifluoromethyl sulfoximine (**3c**).* Yellow oil, yield 99%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −72.5 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.25 (2H, d, J=7.5 Hz), 7.83–7.75 (1H, m), 7.71–7.63 (2H, m), 7.21 (1H, t, J=7.9 Hz), 7.15–7.08 (2H, m), 6.95 (1H, d, J=7.5 Hz), 2.36 (3H,s); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 141.0, 139.0, 135.3, 131.8, 129.5, 128.9, 124.7, 124.6, 121.4 (q, J=339 Hz, CF_3), 120.9, 21.3; MS (pos. ESI): m/z=322 (MNa^+); HRMS: calculated for $C_{14}H_{12}F_3NNaOS$ 322.0489 found 322.0478 (δ=3.4 ppm).

*4.3.3. N-((p-Methyl)phenyl) phenyl trifluoromethyl sulfoximine (**3d**).* Brown powder, mp: 59–61 °C, yield 99%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −72.4 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.25 (2H, d, J=7.9 Hz), 7.83–7.75 (1H, m), 7.70–7.62 (2H, m), 7.20 (2H, d, J=8.3 Hz), 7.13 (2H, d, J=8.1 Hz), 2.34 (3H,s); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 138.4, 135.3, 133.3, 131.8, 130.5, 129.8, 129.5, 123.7, 121.4 (q, J=340 Hz, CF_3), 20.8; MS (pos. ESI): m/z=253 ($[MNa-CF_3]^+$), 322 (MNa^+); HRMS: calculated for $C_{14}H_{12}F_3NNaOS$ 322.0484 found 322.0481 (δ=0.8 ppm).

*4.3.4. N-((3,5-Dimethyl)phenyl) phenyl trifluoromethyl sulfoximine (**3e**).* Brown oil, yield 97%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −72.5 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.25 (2H, d, J=7.3 Hz), 7.83–7.75 (1H, m), 7.70–7.62 (2H, m), 6.95 (2H, s), 6.78 (1H, s) 2.33 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 140.8, 138.7, 135.2, 131.9, 130.5, 129.4, 125.7, 121.6, 121.4 (q, J=339 Hz, CF_3), 21.2; MS (pos. ESI): m/z=267 ($[MNa-CF_3]^+$), 336 (MNa^+); HRMS: calculated for $C_{15}H_{14}F_3NNaOS$ 336.0640 found 336.0634 (δ=1.9 ppm).

*4.3.5. N-((p-Nitro)phenyl) phenyl trifluoromethyl sulfoximine (**3f**).* Yellow powder, mp: 62–64 °C, yield 100%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −73.2 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.20 (2H, d, J=7.5 Hz), 8.15 (2H, d, J=9.3 Hz), 7.95–7.80 (1H, m), 7.74–7.65 (2H, m), 7.34 (2H, d, J=9.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 148.4, 143.6, 138.6, 136.1, 130.4, 129.8, 125.0, 124.7, 123.9, 121.1 (q, J=337 Hz, CF_3); MS (pos. ESI): m/z=331 (MH^+), 353 (MNa^+); HRMS: calculated for $C_{13}H_{10}F_3N_2O_3S$ 331.0359 found 331.0357 (δ=0.5 ppm).

*4.3.6. N-((p-Ethyloxycarbonyl)phenyl) phenyl trifluoromethyl sulfoximine (**3g**).* Brown powder, mp: 63–65 °C, yield 100%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −73.0 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.20 (2H, d, J=7.3 Hz), 7.97 (2H, d, J=8.9 Hz), 7.83–7.75 (1H, m), 7.70–7.60 (2H, m), 7.30 (2H, d, J=8.9 Hz), 4.35 (2H, q, J=7.1 Hz), 1.37 (3H, t, J=7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 166.2, 146.0, 135.6, 131.1, 130.8, 130.5, 129.6, 125.7, 132.5, 121.2 (q, J=338 Hz, CF_3), 60.7, 14.2; MS (pos. ESI): m/z=380 (MNa^+); HRMS: calculated for $C_{16}H_{14}F_3NNaO_3S$ 380.0539 found 380.0533 (δ=−2.8 ppm).

*4.3.7. N-((o-Methoxy)phenyl) phenyl trifluoromethyl sulfoximine (**3h**).* Yellow oil, yield 99%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −74.6 (3F, s); ^1H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.19 (2H, d, J=7.5 Hz), 7.79–7.70 (1H, m), 7.67–7.58 (2H, m), 7.30 (1H, dd, J=7.7, 1.7 Hz), 7.07 (1H, td, J=7.7, 1.7 Hz), 6.95–6.87 (2H, m), 3.74 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 152.4, 134.9, 133.1, 130.2, 130.0, 129.4, 125.1, 124.5, 121.0 (q, J=335 Hz, CF_3), 120.9, 111.7, 55.5; MS (pos. ESI): m/z=269 ($[MNa-CF_3]^+$), 338 (MNa^+); HRMS: calculated for $C_{14}H_{12}F_3NNaO_2S$ 338.0433 found 338.0428 (δ=1.6 ppm).

*4.3.8. N-((m-Methoxy)phenyl) phenyl trifluoromethyl sulfoximine (**3i**).* Pale yellow oil, yield 99%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm)

δ −72.6 (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.23 (2H, d, *J*=7.3 Hz), 7.83–7.74 (1H, m), 7.71–7.61 (2H, m), 7.21 (1H, t, *J*=8.1 Hz), 6.90 (1H, ddd, *J*=7.7, 1.9, 1.0 Hz), 6.85 (1H, t, *J*=2.1 Hz), 6.69 (1H, ddd, *J*=8.3, 2.5, 0.8 Hz), 3.81 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 160.2, 142.3, 135.4, 131.6, 130.5, 129.7, 129.5, 121.3 (q, *J*=339 Hz, CF_3), 116.3, 109.8, 109.7, 55.1; MS (pos. ESI): *m*/*z*=269 ($[MNa-CF_3]^+$), 316 (MH^+), 338 (MNa^+); HRMS: calculated for $C_{14}H_{12}F_3NNaO_2S$ 338.0433 found 338.0433 (δ=0.1 ppm).

*4.3.9. N-((p-Methoxy)phenyl) phenyl trifluoromethyl sulfoximine (**3j**).* Yellow oil, yield 98%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −72.2 (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.23 (2H, d, *J*=7.5 Hz), 7.81–7.73 (1H, m), 7.69–7.60 (2H, m), 7.22 (2H, d, *J*=9.1 Hz), 6.86 (2H, d, *J*=9.1 Hz), 3.79 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 156.2, 135.3, 133.9, 131.6, 130.5, 129.5, 124.8, 121.4 (q, *J*=340 Hz, CF_3), 114.4, 55.3; MS (pos. ESI): *m*/*z*=269 ($[MNa-CF_3]^+$), 338 (MNa^+); HRMS: calculated for $C_{14}H_{12}F_3NNaO_2S$ 338.0433 found 338.0430 (δ=0.8 ppm).

*4.3.10. N-(Phenyl) (m-chloro)phenyl trifluoromethyl sulfoximine (**3l**).* Brown oil, yield 68%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −72.3 (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.22 (1H, s), 8.09 (1H, d, *J*=7.9 Hz), 7.79–7.72 (1H, m), 7.60 (1H, t, *J*=8.1 Hz), 7.37–7.22 (4H, m), 7.16–7.08 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 140.7, 135.9, 135.6, 133.5, 130.7, 130.4, 129.2, 128.6, 124.1, 123.9, 121.3 (q, *J*=339 Hz, CF_3); MS (pos. ESI, for ^{35}Cl): *m*/*z*=342 (MNa^+); HRMS: calculated for $C_{13}H_9^{35}ClF_3NNaOS$ 341.9938 found 341.9939 (δ=−0.3 ppm).

*4.3.11. N-(Phenyl) (p-chloro)phenyl trifluoromethyl sulfoximine (**3m**).* Brown powder, mp: 81–83 °C, yield 99%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −72.5 (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.16 (2H, d, *J*=8.9 Hz), 7.63 (2H, d, *J*=8.7 Hz), 7.35–7.22 (4H, m), 7.15–7.08 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 142.7, 140.8, 132.0, 130.1, 129.9, 129.2, 124.0, 123.9, 121.3 (q, *J*=339 Hz, CF_3); MS (pos. ESI, for ^{35}Cl): *m*/*z*=342 (MNa^+); HRMS: calculated for $C_{13}H_9^{35}ClF_3NNaOS$ 341.9938 found 341.9943 (δ=−1.5 ppm).

*4.3.12. N-(Phenyl) (o-methyl)phenyl trifluoromethyl sulfoximine (**3n**).* Yellow oil, yield 99%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −72.3 (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.29 (1H, d, *J*=8.1 Hz), 7.63–7.55 (1H, m), 7.47–7.36 (2H, m), 7.32–7.20 (4H, m), 7.12–7.04 (1H, m), 2.84 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 141.5, 141.4, 135.2, 133.8, 132.8, 131.1, 129.2, 127.0, 123.8, 123.7, 121.5 (q, *J*=320 Hz, CF_3), 21.3; MS (pos. ESI): *m*/*z*=322 (MNa^+); HRMS: calculated for $C_{14}H_{12}F_3NNaOS$ 322.0489 found 322.0489 (δ=0.2 ppm).

*4.3.13. N-(Phenyl) (p-methyl)phenyl trifluoromethyl sulfoximine (**3o**).* Yellow powder, mp: 63–65 °C, yield 99%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −72.8 (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.07 (2H, d, *J*=7.3 Hz), 7.40 (2H, d, *J*=8.1 Hz), 7.32–7.20 (4H, m), 7.10–7.03 (1H, m), 2.45 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 146.9, 141.3, 130.5, 130.2, 129.1, 128.5, 124.0, 123.7, 121.4 (q, *J*=339 Hz, CF_3), 21.7; MS (pos. ESI): *m*/*z*=322 (MNa^+); HRMS: calculated for $C_{14}H_{12}F_3NNaOS$ 322.0484 found 322.0482 (δ=0.6 ppm).

*4.3.14. N-(Phenyl) phenyl nonafluorobutyl sulfoximine (**3p**).* Brown oil, yield 98%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −81.3 (3F, m), −107.1 (2F, m), −120.9 (2F, m), −126.5 (2F, m); ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.18 (2H, d, *J*=7.7 Hz), 7.75–7.67 (1H, m), 7.63–7.55 (2H, m), 7.35–7.18 (4H, m), 7.11–7.02 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 141.2, 135.2, 130.5, 129.3, 129.1, 123.9, 120.9, 117.8; MS (pos. ESI): *m*/*z*=239 ($[MNa-C_4F_9]^+$), 458 (MNa^+); HRMS: calculated for $C_{16}H_{10}F_9NNaOS$ 458.0232 found 458.0232 (δ=0.0 ppm).

*4.3.15. N-(2-Pyridinyl) phenyl trifluoromethyl sulfoximine (**3q**).* White powder, mp: 107–109 °C, yield 98%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −73.8 (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.20–8.10 (3H, m), 7.78–7.70 (1H, m), 7.65–7.54 (3H, m), 7.06 (1H, d, *J*=8.1 Hz), 6.93–6.85 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 156.1, 148.1, 138.1, 135.2, 132.0, 130.4, 129.6, 120.6 (q, *J*=332 Hz, CF_3) 118.1, 117.2; MS (pos. ESI): *m*/*z*=218 ($[MH-CF_3]^+$), 287 (MH^+), 309 (MNa^+); HRMS: calculated for $C_{12}H_{10}F_3N_2OS$ 287.0460 found 287.0458 (δ=0.8 ppm).

*4.3.16. N-(2-Thiophenyl) phenyl trifluoromethyl sulfoximine (**3r**).* Brown oil, yield 99%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −71.7 (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.25–8.18 (2H, m), 7.85–7.77 (1H, m), 7.72–7.64 (2H, m), 6.88–6.81 (2H, m), 6.75–6.71 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 143.3, 135.7, 130.5, 129.6, 125.7121.3 (q, *J*=340 Hz, CF_3), 118.4, 117.3; MS (pos. ESI): *m*/*z*=245 ($[MNa-CF_3]^+$), 292 (MH^+), 314 (MNa^+); HRMS: calculated for $C_{11}H_9F_3NOS_2$ 292.0072 found 292.0070 (δ=0.7 ppm).

*4.3.17. N-((o-Iodo)phenyl) phenyl trifluoromethyl sulfoximine (**3s**).* White powder, mp: 72–74 °C, yield 70%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −72.7 (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.38 (2H, d, *J*=7.7 Hz), 7.84 (1H, dd, *J*=7.9, 1.3 Hz), 7.81–7.74 (1H, m) 7.70–7.62 (2H, m), 7.47 (1H, dd, *J*=8.1, 1.4 Hz), 7.30–7.20 (1H, m), 6.82 (1H, dt, *J*=7.7, 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 143.1, 139.3, 135.6, 131.4, 130.9, 129.6, 129.0, 125.2, 124.0, 122.8121.3 (q, *J*=339 Hz, CF_3), 95.4; MS (pos. ESI): *m*/*z*=434 (MNa^+); HRMS: calculated for $C_{13}H_9F_3INNaOS$ 433.9294 found 433.9293 (δ=0.2 ppm).

*4.3.18. N-8-Bromonaphthyl phenyl trifluoromethyl sulfoximine (**3t**).* Brown oil, yield 72%; ^{19}F NMR (188 MHz, $CDCl_3$) (ppm) δ −73.4 (3F, s); ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) δ 8.40 (2H, d, *J*=7.7 Hz), 7.89 (1H, d, *J*=7.3 Hz), 7.82–7.70 (2H, m), 7.70–7.55 (4H, m), 7.41–7.31 (1H, m), 7.30–7.21 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) δ 142.0, 137.4, 137.0, 135.3, 133.6, 131.8, 130.8, 129.6, 128.8, 126.7, 126.2, 126.0, 125.0, 121.6, 121.1 (q, *J*=337 Hz, CF_3), 117.5; MS (pos. ESI, for ^{79}Br): *m*/*z*=367 ($[MNa-CF_3]^+$), 436 (MNa^+); HRMS: calculated for $C_{17}H_{11}^{79}BrF_3NNaOS$ 435.9589 found 435.9583 (δ=1.5 ppm).

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Supplementary data

Copies of ^{1}H, ^{13}C, and ^{19}F NMR for all new compounds. CCDC 816760 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.07.060.

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