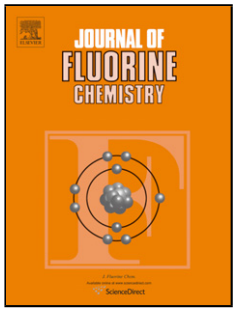

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Interrupted Reduction of CF_3SO_2Cl Using Tricyclohexylphosphine Allows for Electrophilic Trifluoromethylsulfinylation

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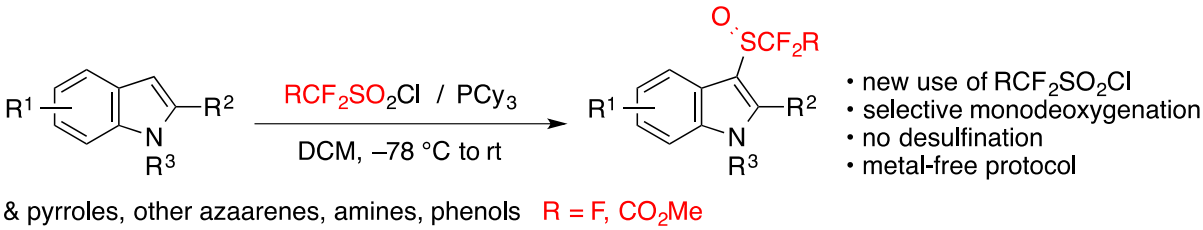
Graphical abstract



Highlights

• A new use of trifluoromethanesulfonyl chloride CF_3SO_2Cl is described for the transfer of $CF_3S(O)^+$ cation.
• A new method is presented for direct electrophilic trifluoromethylsulfinylation.
• We performed the trifluoromethylsulfinylation of indoles, pyrroles, other azaarenes, amines, and phenols.
• The reaction mechanism involves a reductive monodeoxygenation of CF_3SO_2Cl by means of tricyclohexylphosphine initiated by halogen bonding.

Abstract: The monoreduction of trifluoromethanesulfonyl chloride by an appropriate phosphine, preferentially tricyclohexylphosphine, generates the reactive trifluoromethanesulfinyl chloride CF_3SOCl as donor of $CF_3S(O)^+$ cation. The direct trifluoromethylsulfinylation of indoles, pyrroles, other azaarenes, amines, and phenols was successfully achieved in moderate to high yields.
Keywords: Sulfur; Fluorine; Phosphine; Indole; Halogen bond

1. Introduction

A substantial number of molecules bearing the $CF_3S(O)$ group have been synthesized for applications in the pharmaceutical and agrochemical fields. The introduction of the $CF_3S(O)$ motif into organic molecules modifies and often enhances their biological properties. For example, the broadly used insecticide Fipronil and several analogues feature a trifluoromethanesulfinyl moiety that is responsible for increased lipid solubility favouring the transport of the molecule across lipid membranes [1,2]. The $CF_3S(O)$ group stands between its lower and higher oxidation state congeners CF_3S and CF_3SO_2, respectively, in terms of Hammett substituent constants [3] and Taft's σ^* parameters [4]. The synthesis of trifluoromethanesulfoxides was achieved mainly by two approaches: (i) the monooxidation of the corresponding trifluoromethyl sulfides by means of a wide variety of oxidants (ii) the nucleophilic trifluoromethylation of sulfinyl halides or sulfinic esters with $TMSCF_3$ [5]. The direct introduction of the $CF_3S(O)$ group using trifluoromethanesulfinyl halides $CF_3S(O)F$ or $CF_3S(O)Cl$ has seldom been reported because of the toxicity, the volatility and the poor stability of these reagents [6]. Alternatively, few direct trifluoromethylsulfinylation methods were described on (het)arenes with the aid of sodium or potassium triflinates CF_3SO_2M (M = Na, K) in the presence of triflic acid [7] or phosphoryl chloride [8], or with *N*-$SOCF_3$

succinimide as $CF_3S(O)^+$ donor source [9, 10]. The electrophilic *O*-trifluoromethylthiolation of allylic alcohols followed by a [2,3]-sigmatropic rearrangement is also a route to prepare allylic trifluoromethyl sulfoxides [11]. As part of our ongoing research on the synthesis of SCF_3 compounds, we recently reported a novel use of trifluoromethanesulfonyl chloride, CF_3SO_2Cl, as a new source of electrophilic SCF_3 in the presence of a phosphine as the reducing agent. The complete reduction of CF_3SO_2Cl generates the highly reactive CF_3SCl that reacts in situ with various nucleophiles [12]. We now report that tuning the nature of the phosphine and the ratio substrate / CF_3SO_2Cl / phosphine allows for the controlled monoreduction of CF_3SO_2Cl into $CF_3S(O)Cl$ for the direct *C*-trifluoromethylsulfinylation of indoles, pyrroles, other azaarenes and phenols as well as the *N*-trifluoromethylsulfinylation of amines.

2. Results and discussion

As mentioned earlier in the text, we recently developed an innovative methodology allowing the *C*-trifluoromethylthiolation of a variety of nucleophiles by reacting them with the in situ generated CF_3SCl from a combination of CF_3SO_2Cl / trimethylphosphine in a ratio 1:2 in THF at –78°C to room temperature [12]. During the experiments carried out as part of this work with indole as substrate, an interesting side product was invariably observed: the trifluoromethylsulfinylated derivative featuring the $CF_3S(O)$ group, which resulted from the reaction between said substrate and monodeoxygenated sulfonyl chloride. The formation of this a priori undesired side product was however greatly disfavoured compared to the trifluoromethylthiolated analogue, and it was consequently isolated in very poor yields (Table 1, entries 1, 2). Yet, interestingly enough, it was obtained in particularly higher proportions (62% NMR yield) when using tricyclohexylphosphine as the reducing agent, instead of trimethylphosphine or triphenylphosphine (Table 1, entry 3). This phenomenon can be explained by a subtle variation of the nucleophilicity of phosphines, making the sulfinyl chloride reduction process slower than its reaction with indole [13]. Steric hindrance appeared to be less influential, considering the important difference between the yields reached using PPh_3 and PCy_3. Trimethyl phosphite, $P(OMe)_3$, failed to generate $CF_3S(O)Cl$ under our reaction conditions [14].

To further exploit this unique property of tricyclohexylphosphine, we conducted a series of experiments on indole aimed at maximizing the yield of the trifluoromethylsulfinylation reaction. To this end, we first screened different solvents (Table 1, entries 3–6). However, it was soon found out that their influence on the yield of the reaction was quite negligible. Indeed, the use of DCM only allowed to slightly increase the yield from 62 to 67%. On the other hand, the ratio CF_3SO_2Cl / PCy_3 proved to be a much more significant parameter: quite intuitively, decreasing it to 1:1 lead to the formation of fewer SCF_3 by-product, and consequently to an improved yield of 79% (Table 1, entries 7, 8). The yield was ultimately increased to 89% when reducing the equivalents of CF_3SO_2Cl and PCy_3 from 1.8 to 1.5 (Table 1, entries 9, 10), which was an appreciable result in a perspective of reagent economy. Any attempt to perform the reaction at higher temperatures resulted in lower yields, especially above –20°C (Table 1, entries 11–14). Similarly, diluting or concentrating any further the reaction medium appeared to be detrimental to the formation of the desired product (Table 1, entries 15, 16). It is noteworthy to report that when raising the concentration to 0.9 M, tricyclohexylphosphine was no more properly soluble in DCM at –78°C, which caused the freezing of the reaction mixture, making its stirring impossible until the temperature had increased enough to reverse the phenomenon.

A variety of indole derivatives were then submitted to the optimized trifluoromethylsulfinylation reaction conditions. The reaction proceeded smoothly with most of them, regardless of the carried functional groups or their positions. Indeed, electron-withdrawing and electron-donating substituents in positions 2, 4, 5, 6 and 7 were equally well tolerated, even though it was necessary to increase the quantities of CF_3SO_2Cl and PCy_3 to 1.8 equivalents for the less reactive brominated indoles in order to achieve full conversion of the starting material (Table 2, entries 2, 3). *N*-Methylated indoles appeared to be compatible as well with the selected reaction conditions (Table 1, entries 8, 9). 7-Azaindole showed the least satisfying results (Table 1, entry 10), which was however predictable considering the deactivating effect of its electron-deficient pyridine moiety.

Considering the encouraging results obtained with indole derivatives, we decided to submit other azaarenes to our reaction conditions. We first examined pyrrole derivatives, which afforded their trifluoromethylsulfinylated analogues in moderate to good yields (Table 3, entries 1–5). Pyrrole itself provided product **3a** in 52% yield, as the starting material was involved in side polymerisation reactions (Table 3, entry 1). Despite their very similar structures, 2,4-dimethylpyrrole gave access to a lower yield than 2,5-dimethylpyrrole (Table 3, entries 2, 3). This is due to partial consumption of product **3b** by bis-functionalisation, whereas product **3c** remained untouched, its available C3 position being more hindered. As for *N*-methylpyrrole, formation of product **3e** was observed in good yield by ^{19}F NMR, but it however appeared to be unstable and could not be isolated in a pure form. The $CF_3S(O)$ group was also successfully introduced in moderate yields on methyl indolizine-1-carboxylate and pyrazolone after slight adjustment of the reaction conditions (Table 3, entries 6, 7); on the other hand the $CF_3S(O)$-substituted imidazo[1,2-a]pyridine **6** could only be obtained with a disappointing 9% yield, mostly due to steric hindrance issues (Table 3, entry 8).

Moreover, azaarenes were not the only substrates worth considering: a variety of aryl and aliphatic amines were also readily converted to the corresponding sulfinamides using our CF_3SO_2Cl / PCy_3 system via regioselective *N*-trifluoromethylsulfinylation. Aniline derivatives in particular showed a great reactivity toward our reagent; however, degradation of the obtained products occurred invariably in the reaction medium, which lead to moderate yields despite the full consumption of the starting materials and the absence of trifluoromethylthiolated side product (Table 4, entries 1–5). It is noteworthy to specify that the isolated products were stable yet, except for the *N*-methylsulfonamide **7d** that could not be isolated in a pure form. Benzylamine and isopropyl amine were more difficultly consumed, and consequently afforded products **7f** and **7g** in lower yields. Sulfinamide **7g** was also unstable and underwent degradation during its purification.

The reaction was finally performed on two phenol derivatives, 1-naphthol and resorcinol, which gave access to the corresponding *C*-trifluoromethylsulfinylated products albeit in poor yields (Table 5). An interesting phenomenon was nonetheless observed during the reaction realised on 1-naphthol: formation of a species with a ^{19}F NMR chemical shift of –79.5 ppm, which could corresponds to the *O*-trifluoromethylsulfinylated product. This product was then consumed, as the quantity of the *C*-trifluoromethylsulfinylated product (δ = –74.1 ppm) increased. This could suggest that the reaction mechanism involves a Thia-Fries rearrangement. Even if this kind of process usually requires a Lewis acid [15] or a strong base

[16, 17] to proceed, which doesn't match our conditions, some examples of similar photocatalyzed reactions were also reported [18, 19], making our hypothesis conceivable.

Additionnally, the direct transfer of the difluoromethylsulfinyl motif $S(O)CF_2R$ in which R is a functional group would be of great interest allowing rapid generation of molecular complexity. In this context, we performed the reductive selective monodeoxygenation of methyl 2-(chlorosulfonyl)-2,2-difluoroacetate $MeO_2CCF_2SO_2Cl$ [20]. The reaction proceeded smoothly and the reaction with indole provided the expected product **9**, which was isolated in a good yield of 65% (Scheme 1).

The mechanism of the reductive monodeoxygenation consists in the heterolytic cleavage of the covalent S−Cl bond triggered by the halogen bond that forms between the positive electrostatic potential on the outer side of the chlorine atom in RCF_2SO_2Cl and the lone pair of phosphorus atom in PCy_3. The chlorophosphonium sulfinate is then converted into the *O*-sulfinatophosphonium chloride, which undergo Arbuzov collapse to sulfinyl chloride $RCF_2S(O)Cl$ and tricyclohexylphosphine oxide, as confirmed by ^{31}P NMR spectroscopy. Then, the electrophilic $RCF_2S(O)Cl$ reacts with indole or other nucleophiles with release of HCl (Scheme 2). The addition of an inorganic or an organic base to the reaction mixture lowered the reaction yield and favored the trifluoromethanesulfonylation at the nitrogen atom of indole.

3. Conclusion

During our investigation of the reductive deoxygenation–trifluoromethylthiolation reaction, we discovered that tuning the nature of the phosphine and the ratio substrate / CF_3SO_2Cl / phosphine allows for the controlled monoreduction of CF_3SO_2Cl into $CF_3S(O)Cl$ as donor of $CF_3S(O)^+$ cation. A number of reactions were carried out that include the direct *C*-trifluoromethylsulfinylation of indoles, pyrroles, other azaarenes and phenols as well as the *N*-trifluoromethylsulfinylation of aryl- and alkylamines. Moreover, methyl 2-(chlorosulfonyl)-2,2-difluoroacetate was also selectively monodeoxygenated allowing the direct transfer of the electrophilic difluoromethylsulfinyl motif $MeO_2CCF_2S(O)$.

4. Experimental

4.1. General remarks

The reactions were monitored by thin-layer chromatography (TLC) performed with 0.20 mm silica gel 60 with fluorescent indicator UV_{254}. The TLC plates were visualized with UV light (254 nm). Column chromatography was performed on a column packed with silica gel 60M spherical neutral size 40-63 μm. ^1H (300 MHz), ^{13}C (75.5 MHz) and ^{19}F (282 MHz) NMR spectra for solution in $CDCl_3$ or DMSO-d_6 were recorded on Bruker Avance 300. Chemical shifts (δ) for ^1H and ^{13}C NMRs are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard ($CDCl_3$, ^1H 7.26 ppm and ^{13}C 77.16 ppm; DMSO-d_6 ^1H 2.50 ppm and ^{13}C 39.52 ppm) or, for ^{19}F NMR, upfield from $CFCl_3$ as the internal standard (^{19}F 0.00 ppm). The following abbreviations were used to show the multiplicities: s: singlet, d: doublet, t: triplet, q: quadruplet, dd: doublet of doublets, td: triplet of doublets, dt: doublet of triplets, m: multiplet, b: broad. High resolution mass spectrometry (HRMS) was carried out on an electrospray ionization mass spectrometer with a micro-TOF analyzer. Unless otherwise noted, all reagents were purchased from commercial sources and

were used without further purification. 2-Phenylpyrrole [21], 2-phenylimidazo[1,2-a]pyridine [22], methyl indolizine-1-carboxylate [23] and methyl 2-(chlorosulfonyl)-2,2-difluoroacetate [20] were prepared referring to previously reported procedures.

4.2. Representative procedure for the trifluoromethylsulfinylation

To a solution of substrate (0.85 mmol) and tricyclohexylphosphine (Procedure A: 1.5 equiv or Procedure B: 1.8 equiv) in DCM (5 mL) was added trifluoromethanesulfonyl chloride (Procedure A: 1.5 equiv or Procedure B: 1.8 equiv) at –78 °C. The reaction mixture was stirred until the full consumption of the starting material (TLC monitored), as the temperature was let to increase to room temperature. The reaction mixture was quenched with water. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over magnesium sulfate, and concentrated under vacuum. The crude product was purified by flash chromatography (cyclohexane/ethyl acetate).

3-((Trifluoromethyl)sulfinyl)-1H-indole (**2a**) [12]. CAS [1909315-34-9]. Procedure A. White solid. 176 mg, 88% yield. ^{1}H NMR ($CDCl_3$): δ 9.64 (s, 1H), 7.99 (d, *J* = 7.4 Hz, 1H), 7.84 (d, *J* = 2.6 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.35 (qt, *J* = 7.7 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 136.8, 130.79, 125.6 (q, *J* = 334.5 Hz), 124.5, 124.1, 122.8, 120.2 (q, *J* = 1.7 Hz), 112.5, 108.4 (q, *J* = 2.2 Hz) ppm; ^{19}F NMR ($CDCl_3$): δ –73.6 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3103, 1502, 1415, 1176, 1127, 1038, 748. HRMS (ESI): Calculated for $C_9H_{10}N_2OF_3S$ $[M+NH_4]^+$: 251.0461; Found: 251.0466.

4-Bromo-3-((trifluoromethyl)sulfinyl)-1H-indole (**2b**). Procedure B. White solid. 212 mg, 80%. ^{1}H NMR ($CDCl_3$): δ 9.58 (s, 1H), 8.07 (s, 1H), 7.48 (t, *J* = 8.5 Hz, 2H), 7.21 (t, *J* = 7.9 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6): δ 137.9, 132.3, 125.5, 125.1 (q, *J* = 337.8 Hz), 124.7, 124.3, 112.8, 111.0, 107.8 (q, *J* = 2.2 Hz) ppm; ^{19}F NMR ($CDCl_3$): δ –75.6 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3132, 1735, 1631, 1171, 1123, 1038, 775, 732, 607. HRMS (ESI): Calculated for $C_9H_6NOF_3SBr$ $[M+H]^+$: 311.9304; Found: 311.9306.

5-Bromo-3-((trifluoromethyl)sulfinyl)-1H-indole (**2c**). Procedure B. White solid. 241 mg, 91%. ^{1}H NMR ($CDCl_3$): δ 9.69 (s, 1H), 8.11 (s, 1H), 7.78 (d, *J* = 2.1 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 135.4, 131.3, 127.8, 125.7, 125.5 (q, *J* = 334.5 Hz), 122.9 (q, *J* = 2.2 Hz), 116.2, 113.9, 108.4 (q, *J* = 2.2 Hz) ppm; ^{19}F NMR ($CDCl_3$): δ –73.8 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3208, 2931, 1450, 1411, 1295, 1178, 1128, 1039, 802, 611. HRMS (ESI): Calculated for $C_9H_9N_2OF_3SBr$ $[M+NH_4]^+$: 328.9565; Found: 328.9571.

5-Methoxy-3-((trifluoromethyl)sulfinyl)-1*H*-indole (**2d**). Procedure B. White solid. 192 mg, 85% yield. ^{1}H NMR ($CDCl_3$): δ 8.92 (s, 1H), 7.75 (d, *J* = 2.6 Hz, 1H), 7.38 (d, *J* = 9.1 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 1H), 3.87 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 156.1, 131.5, 130.7, 125.7 (q, *J* = 334.5 Hz), 125.0, 115. 3, 113.3, 107.9, 101.5 (q, *J* = 1.7 Hz), 55.7 ppm; ^{19}F NMR ($CDCl_3$): δ –73.6 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3117, 3000, 2958, 1588, 1488, 1293, 1213, 1178, 1030, 811. HRMS (ESI): Calculated for $C_{10}H_{12}N_2O_2F_3S$ $[M+NH_4]^+$: 281.0569; Found: 281.0572.

6-Fluoro-3-((trifluoromethyl)sulfinyl)-1*H*-indole (**2e**). Procedure A. White solid. 184 mg, 86% yield. ^{1}H NMR ($CDCl_3$): δ 9.76 (s, 1H), 7.89 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.76 (d, *J* = 2.8 Hz, 1H), 7.14 (dd, *J* = 8.9, 1.7 Hz, 1H), 7.06 (td, *J* = 9.1, 1.9 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 160.8 (d, *J* = 242.6 Hz), 137.1 (d, *J* = 12.7 Hz), 131.2, 125.5 (q, *J* = 334.5 Hz), 121.4 (dq, *J* = 10.5, 2.2 Hz), 120.4, 111.8 (d, *J* = 24.8 Hz), 108.7 (q, *J* = 2.2 Hz), 99.0 (d, *J* =

26.4 Hz) ppm; ^{19}F NMR ($CDCl_3$): δ –73.4 (s, 3F), –117.1 (s, 1F) ppm. ATR-FTIR (cm^{-1}): 3125, 3002, 2920, 1616, 1511, 1419, 1242, 1187, 1132, 1040, 809. HRMS (ESI): Calculated for $C_9H_9N_2OF_4S$ $[M+NH_4]^+$: 269.0372; Found: 269.0370.

7-Methyl-3-((trifluoromethyl)sulfinyl)-1*H*-indole (**2f**). Procedure B. Beige solid. 128 mg, 61% yield. ^{1}H NMR ($CDCl_3$): δ 9.36 (s, 1H), 7.85–7.71 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.0 Hz, 1H), 2.53 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 136.3, 130.0, 125.5 (q, *J* = 334.5 Hz), 125.0, 123.9, 122.9, 121.7, 117.9, 109.3 (q, *J* = 1.9 Hz), 16.5 ppm; ^{19}F NMR ($CDCl_3$): δ –73.7 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3207, 2929, 1435, 1167, 1134, 1042, 784, 736. HRMS (ESI): Calculated for $C_{10}H_{12}N_2OF_3S$ $[M+NH_4]^+$: 265.0622; Found: 265.0619.

2-Methyl-3-((trifluoromethyl)sulfinyl)-1*H*-indole (**2g**). Procedure A. White solid. 183 mg, 87% yield. ^{1}H NMR ($CDCl_3$): δ 8.88 (s, 1H), 7.97 (d, *J* = 7.0 Hz, 1H), 7.41–7.34 (m, 1H), 7.32–7.20 (m, 2H), 2.60 (s, 3H) ppm; ^{13}C NMR (DMSO-d_6): δ 144.8, 135.8, 126.2 (q, *J* = 337.3 Hz), 124.9, 122.9, 121.6, 119.2 (q, *J* = 2.2 Hz), 112.1, 102.2 (q, *J* = 2.2 Hz), 11.8 ppm; ^{19}F NMR ($CDCl_3$): δ –72.8 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3096, 1519, 1457, 1171, 1129, 1050, 741. HRMS (ESI): Calculated for $C_{10}H_9NOF_3S$ $[M+H]^+$: 248.0357; Found: 248.0359.

1-Methyl-3-((trifluoromethyl)sulfinyl)-1*H*-indole (**2h**). Procedure A. Pale yellow solid. 167 mg, 79% yield. ^{1}H NMR ($CDCl_3$): δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.69 (s, 1H), 7.48–7.29 (m, 3H), 3.90 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 137.7, 133.8, 125.6 (q, *J* = 335.0 Hz), 125.1, 124.1, 122.5, 120.5, 110.5, 107.2 (q, *J* = 2.2 Hz), 33.8 ppm; ^{19}F NMR ($CDCl_3$): δ –74.1 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3097, 2922, 1519, 1457, 1174, 1128, 1061, 740. HRMS (ESI): Calculated for $C_{10}H_9NOF_3S$ $[M+H]^+$: 248.0357; Found: 248.0357.

1,2-Dimethyl-3-((trifluoromethyl)sulfinyl)-1*H*-indole (**2i**). Procedure A. Pink solid. 163 mg, 73% yield. ^{1}H NMR ($CDCl_3$): δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.41–7.22 (m, 3H), 3.74 (s, 3H), 2.61 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 143.8, 137.3, 126.1 (q, *J* = 335.6 Hz), 124.9, 123.2, 122.4, 120.2, 109.7, 103.6 (q, *J* = 2.8 Hz), 30.0, 11.1 ppm; ^{19}F NMR ($CDCl_3$): δ –73.0 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 1477, 1404, 1315, 1165, 1129, 1064, 749. HRMS (ESI): Calculated for $C_{11}H_{11}NOF_3S$ $[M+H]^+$: 262.0513; Found: 262.0517.

3-((Trifluoromethyl)sulfinyl)-1*H*-pyrrolo[2,3-*b*]pyridine (**2j**). Procedure A. White solid. 70 mg, 35% yield. ^{1}H NMR ($CDCl_3$): δ 8.52 (d, *J* = 4.2 Hz, 1H), 8.40 (d, *J* = 7.9 Hz, 1H), 8.03 (s, 1H), 7.35 (dd, *J* = 7.9, 4.7 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6): δ 137.9, 132.3, 125.0 (q, *J* = 337.3 Hz), 124.7, 124.4, 112.8, 111.0, 107.8 (q, *J* = 2.2 Hz) ppm; ^{19}F NMR ($CDCl_3$): δ –73.9 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3123, 2928, 2855, 1581, 1410, 1281, 1159, 1131, 1067, 769. HRMS (ESI): Calculated for $C_8H_6N_2OF_3S$ $[M+H]^+$: 235.0153; Found: 235.0145.

2-((Trifluoromethyl)sulfinyl)-1*H*-pyrrole (**3a**) [24]. CAS [62665-45-6]. Procedure A. Colourless oil. 81 mg, 52% yield. ^{1}H NMR ($CDCl_3$): δ 10.88 (s, 1H), 7.23–7.17 (m, 1H), 6.95–6.89 (m, 1H), 6.39–6.32 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 127.3, 124.5 (q, *J* = 334.5 Hz), 119.0 (d, *J* = 1.7 Hz), 118.7 (d, *J* = 1.1 Hz), 110.4 ppm; ^{19}F NMR ($CDCl_3$): δ –74.2 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3242, 2960, 1176, 1126, 1029, 743. HRMS (ESI): Calculated for $C_5H_3NOF_3S$ $[M-H]^-$: 181.9887; Found: 181.9889.

3,5-Dimethyl-2-((trifluoromethyl)sulfinyl)-1*H*-pyrrole (**3b**). Procedure A. Beige solid. 111 mg, 61% yield. ^{1}H NMR ($CDCl_3$): δ 9.52 (s, 1H), 5.89 (s, 1H), 2.30 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 137.9, 132.2, 124.9 (q, *J* = 335.1 Hz), 114.0 (q, *J* = 1.7 Hz), 111.0, 13.2, 10.9 ppm; ^{19}F NMR ($CDCl_3$): δ –74.2 (s, 3F). ATR-FTIR (cm^{-1}): 3219, 3170, 1390, 1169,

1123, 1036, 801. HRMS (ESI): Calculated for $C_7H_9NOF_3S$ $[M+H]^+$: 212.0357; Found: 212.0354.

2,5-Dimethyl-3-((trifluoromethyl)sulfinyl)-1*H*-pyrrole (**3c**). Procedure A. Beige solid. 149 mg, 83% yield. ^{1}H NMR ($CDCl_3$): δ 8.68 (s, 1H), 6.23 (s, 1H), 2.38 (s, 3H), 2.23 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 134.8, 129.6, 125.3 (q, *J* = 332.9 Hz), 112.1 (q, *J* = 2.2 Hz), 104.4, 12.7, 11.3 ppm; ^{19}F NMR ($CDCl_3$): δ –74.6 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3253, 1404, 1167, 1132, 1046, 807. HRMS (ESI): Calculated for $C_7H_9NOF_3S$ $[M+H]^+$: 212.0357; Found: 212.0360.

2-Phenyl-5-((trifluoromethyl)sulfinyl)-1*H*-pyrrole (**3d**). Procedure A. Purple solid. 136 mg, 62% yield. ^{1}H NMR ($CDCl_3$): δ 10.58 (s, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 6.96 (dd, *J* = 4.0, 2.7 Hz, 1H), 6.63 (dd, *J* = 3.8, 2.6 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 141.2, 130.6, 129.0, 128.4, 125.3, 125.6 (q, *J* = 335.6 Hz), 120.0 (d, *J* = 1.1 Hz), 119.9 (q, *J* = 2.2 Hz), 107.9 ppm; ^{19}F NMR ($CDCl_3$): δ –73.8 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3240, 1459, 1179, 1132, 1034, 800, 763. HRMS (ESI): Calculated for $C_{11}H_9NOF_3S$ $[M+H]^+$: 260.0357; Found: 260.0358.

Methyl 3-((trifluoromethyl)sulfinyl)indolizine-1-carboxylate (**4**). Procedure B. Yellow solid. 134 mg, 54% yield. ^{1}H NMR ($CDCl_3$): δ 8.93 (d, *J* = 7.0 Hz, 1H), 8.38 (d, *J* = 9.1 Hz, 1H), 7.83 (s, 1H), 7.40 (t, *J* = 8.7 Hz, 1H), 7.00 (t, *J* = 6.8 Hz, 1H), 3.92 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 163.6, 140.8, 127.6 (q, *J* = 2.7 Hz), 127.0, 125.7 (q, *J* = 338.4 Hz), 125.5, 120.3, 114.8, 111.4 (q, *J* = 2.2 Hz), 106.3, 51.4 ppm; ^{19}F NMR ($CDCl_3$): δ –70.7 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3118, 1696, 1510, 1185, 1163, 1125, 1048, 775, 753. HRMS (ESI): Calculated for $C_{11}H_9NO_3F_3S$ $[M+H]^+$: 292.0255; Found: 292.0260.

3-Methyl-1-phenyl-4-((trifluoromethyl)sulfinyl)-1*H*-pyrazol-5-ol (**5**). Procedure B. Yellow solid. 115 mg, 46% yield. ^{1}H NMR ($CDCl_3$): δ 7.70 (d, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.0 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 2.12 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 162.6, 147.4, 139.1, 128.4, 125.4 (q, *J* = 335.6 Hz), 124.6, 120.6, 120.4, 13.0 ppm; ^{19}F NMR ($CDCl_3$): δ –74.3 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 2927, 2856, 1603, 1574, 1358, 1170, 1126, 1008, 757, 728. HRMS (ESI): Calculated for $C_{11}H_{10}N_2O_2F_3S$ $[M+H]^+$: 291.0415; Found: 291.0419.

2-Phenyl-3-((trifluoromethyl)sulfinyl)imidazo[1,2-a]pyridine (**6**). Procedure B. Dark brown oil. 24 mg, 9% yield. ^{1}H NMR ($CDCl_3$): δ 8.98 (d, *J* = 6.8 Hz, 1H), 7.83 (d, *J* = 9.1 Hz, 1H), 7.79–7.71 (m, 2H), 7.59–7.43 (m, 4H), 7.07 (t, *J* = 7.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 155.5, 149.1, 131.2, 130.2, 130.0 (q, *J* = 337.8 Hz), 129.6, 129.3, 128.9, 128.5 (q, *J* = 3.3 Hz), 118.2, 114.6, 108.6 (q, *J* = 2.8 Hz) ppm; ^{19}F NMR ($CDCl_3$): δ –68.7 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3041, 2921, 2851, 1461, 1440, 1350, 1172, 1122, 1066, 765, 689. HRMS (ESI): Calculated for $C_{14}H_{10}N_2OF_3S$ $[M+H]^+$: 311.0466; Found: 311.0461.

1,1,1-Trifluoro-*N*-phenylmethanesulfinamide (**7a**) [8]. CAS [108530-14-9]. Procedure B. Yellow solid. 124 mg, 70% yield. ^{1}H NMR ($CDCl_3$): δ 7.37 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.48 (bs, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 138.0, 129.9, 125.5, 123.6 (q, *J* = 333.4 Hz), 120.4 ppm; ^{19}F NMR ($CDCl_3$): δ –78.4 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3167, 1482, 1186, 1083, 906, 753. HRMS (ESI): Calculated for $C_7H_5NOF_3S$ $[M-H]^-$: 208.0040; Found: 208.0044.

1,1,1-Trifluoro-N-(4-methoxyphenyl)methanesulfinamide (**7b**) [25]. CAS [868395-06-6]. Procedure A. Brown solid. 95 mg, 47%. ^{1}H NMR ($CDCl_3$): δ 7.11 (dt, *J* = 8.9, 2.1 Hz, 2H),

6.89 (dt, *J* = 8.9, 2.1 Hz, 2H), 6.25 (s, 1H), 3.81 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 158.2, 130.2, 124.5, 123.6 (q, *J* = 333.9 Hz), 115.0, 55.5 ppm; ^{19}F NMR ($CDCl_3$): δ –78.4 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3172, 2846, 1509, 1303, 1180, 1076, 1029, 903, 826. HRMS (ESI): Calculated for $C_8H_7NO_2F_3S$ $[M-H]^-$: 238.0150; Found: 238.0147.

1,1,1-Trifluoro-*N*-(*m*-tolyl)methanesulfinamide (**7c**). Procedure A. Brown solid. 65 mg, 34% yield. ^{1}H NMR ($CDCl_3$): δ 7.23 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.63 (s, 1H), 2.35 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 140.0, 138.0, 129.6, 126.2, 123.6 (q, *J* = 333.4 Hz), 120.9, 117.3, 21.3 ppm; ^{19}F NMR ($CDCl_3$): δ –78.4 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3218, 2926, 1609, 1472, 1149, 1170, 1091, 773. HRMS (ESI): Calculated for $C_8H_7NOF_3S$ $[M-H]^-$: 222.0200; Found: 222.0204.

1,1,1-Trifluoro-*N*-(naphthalen-1-yl)methanesulfinamide (**7e**). Procedure A. Beige solid. 138 mg, 62% yield. . ^{1}H NMR ($CDCl_3$): δ 8.04 (d, *J* = 7.4 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 6.2 Hz, 1H), 7.59 (qt, *J* = 3.8 Hz, 2H), 7.53–7.41 (m, 2H), 6.55 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 134.4, 133.1, 128.9, 128.6, 128.2 (q, *J* = 334.0 Hz), 127.8, 127.2, 126.9, 125.5, 121.8, 121.5 ppm; ^{19}F NMR ($CDCl_3$): δ –78.3 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3236, 1403, 1162, 1148, 1086, 784, 765. HRMS (ESI): Calculated for $C_{10}H_{12}N_2O_2F_3S$ $[M-H]^-$: 258.0194; Found: 258.0200.

N-Benzyl-1,1,1-trifluoromethanesulfinamide (**7f**) [26]. CAS [868395-10-2]. Procedure A. Colourless oil. 61 mg, 32% yield. ^{1}H NMR ($CDCl_3$): δ 7.45–7.29 (m, 5H), 4.77 (s, 1H), 4.48 (dd, *J* = 14.0, 6.2 Hz, 1H), 4.32 (dd, *J* = 14.0, 5.3 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 136.5, 128.9, 128.3, 128.1, 123.7 (q, *J* = 334.5 Hz), 46.4 ppm; ^{19}F NMR ($CDCl_3$): δ –77.3 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3208, 1456, 1169, 1148, 1079, 1027, 741, 696. HRMS (ESI): Calculated for $C_8H_7NOF_3S$ $[M-H]^-$: 222.0200; Found: 222.0192.

Naphthalen-1-yl trifluoromethanesulfinate (**8a**) [15]. CAS [655226-96-3]. Procedure B. Brown solid. 37 mg, 16% yield. ^{1}H NMR (DMSO-d_6): δ 8.30 (d, *J* = 7.9 Hz, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.69 (td, *J* = 8.3, 1.1 Hz, 1H), 7.61 (td, *J* = 8.1, 0.9 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6): δ 159.2, 131.7, 128.7, 126.1, 125.5 (q, *J* = 337.8 Hz), 124.6, 123.2, 121.8, 118.7, 108.2 ppm; ^{19}F NMR ($CDCl_3$): δ –74.1 (s, 3F) ppm. ATR-FTIR (cm^{-1}): 3240, 2924, 1571, 1346, 1172, 1123, 1042, 826, 757. HRMS (ESI): Calculated for $C_{11}H_6O_2F_3S$ $[M-H]^-$: 259.0041; Found: 259.0038.

4-((Trifluoromethyl)sulfinyl)benzene-1,3-diol (**8b**). Procedure A. Colourless oil. 46 mg, 24% yield. . ^{1}H NMR (DMSO-d_6): δ 7.49 (d, *J* = 8.9 Hz, 1H), 6.54 (dd, *J* = 8.7, 2.1, 1H), 6.44 (d, *J* = 2.1 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6): δ 163.9, 158.6, 127.6, 125.3 (q, *J* = 337.8 Hz), 109.9 (q, *J* = 1.7 Hz), 108.9, 102.7 ppm; ^{19}F NMR (DMSO-d_6): δ –75.1 (s, 3F) ppm. HRMS (ESI): Calculated for $C_7H_4O_3F_3S$ $[M-H]^-$: 224.9833; Found: 224.9830.

Methyl 2-((1*H*-indol-3-yl)sulfinyl)-2,2-difluoroacetate (**9**). Procedure A. Beige solid. 153 mg, 65% yield. ^{1}H NMR ($CDCl_3$): δ 9.72 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 3.0 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.36–7.21 (m, 2H), 3.72 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 160.1 (t, *J* = 29.2 Hz), 136.5, 129.9, 124.7, 124.2, 122.4, 120.0, 118.6 (t, *J* = 301.5 Hz), 112.5, 108.3 (t, *J* = 3.8 Hz), 54.1 ppm; ^{19}F NMR ($CDCl_3$): δ –109.9 (d, *J* = 225.8 Hz, 1F), –110.9 (d, *J* = 225.8 Hz, 1F) ppm. ATR-FTIR (cm^{-1}): 3204, 2930, 1753, 1419, 1318, 1164, 1124, 1048, 742, 701. HRMS (ESI): Calculated for $C_{10}H_{12}N_2O_2F_3S$ $[M+H]^+$: 274.0349; Found: 274.0349.

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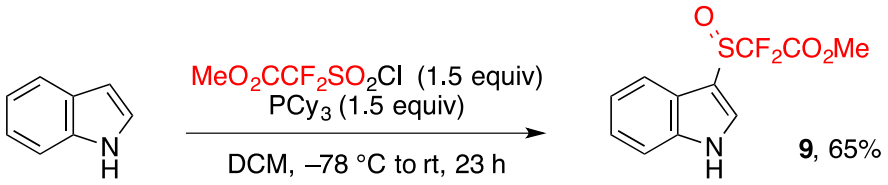
Scheme 1
Synthesis of methyl 2-((1*H*-indol-3-yl)sulfinyl)-2,2-difluoroacetate.



Scheme 2
Proposed monodeoxygenative sulfinylation mechanism.

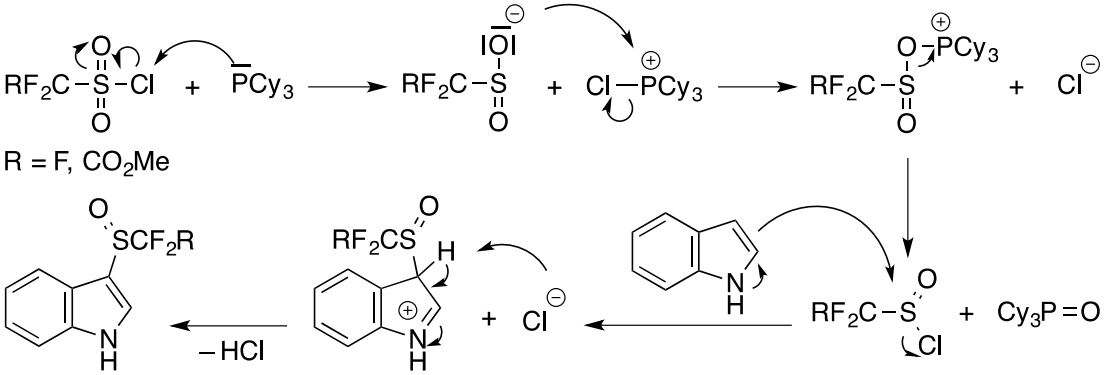
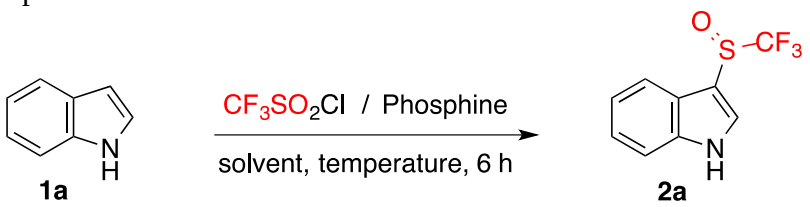


Table 1
Optimization of reaction conditions

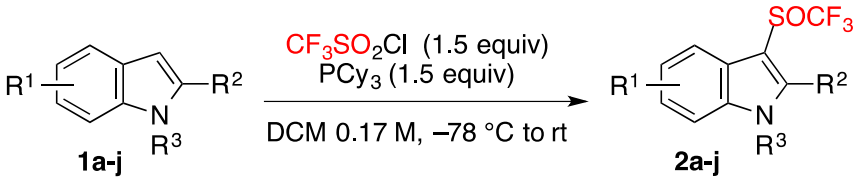


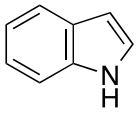
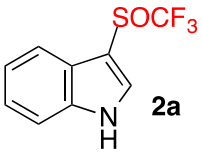
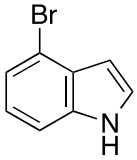
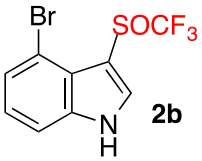
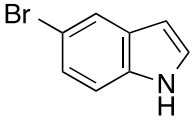
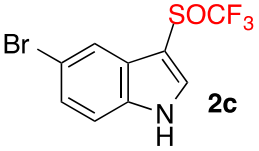
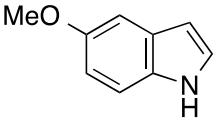
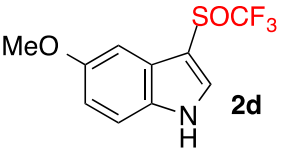
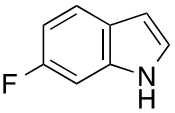
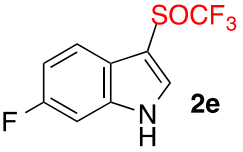
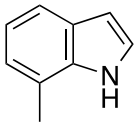
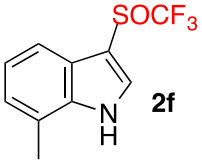
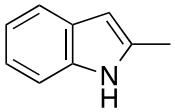
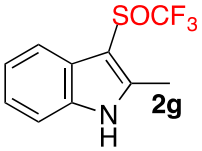
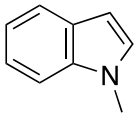
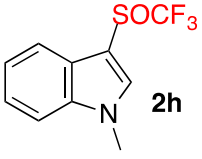
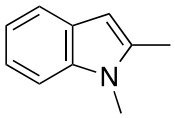
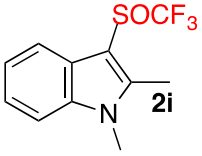
Entry	Phosphine	Ratio **1a**/CF_3SO_2Cl/phosphine	Solvent[a]	Temp. (°C)	Yield (%)[b]
1	PMe_3	1:1.8:3.6	THF	–78 to rt	11
2	PPh_3	1:1.8:3.6	THF	–78 to rt	5
3	PCy_3	1:1.8:3.6	THF	–78 to rt	62
4	PCy_3	1:1.8:3.6	toluene	–78 to rt	66
5	PCy_3	1:1.8:3.6	DCM	–78 to rt	67

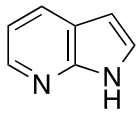
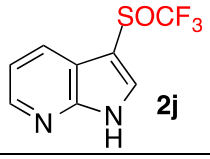
6	PCy_3	1:1.8:3.6	MeCN	–78 to rt	65
7	PCy_3	1:1.8:2.7	DCM	–78 to rt	73
8	PCy_3	1:1.8:1.8	DCM	–78 to rt	79
9	PCy_3	1:1.5:1.5	DCM	–78 to rt	89
10	PCy_3	1:1.1:1.1	DCM	–78 to rt	85
11	PCy_3	1:1.5:1.5	DCM	–40 to rt	85
12	PCy_3	1:1.5:1.5	DCM	–20 to rt	84
13	PCy_3	1:1.5:1.5	DCM	0 to rt	61
14	PCy_3	1:1.5:1.5	DCM	rt	59
15	PCy_3	1:1.5:1.5	DCM[c]	–78 to rt	77
16	PCy_3	1:1.5:1.5	DCM[d]	–78 to rt	53

[a] Concentration: 0.17 M. [b] Yields were determined by ^{19}F NMR using trifluorotoluene as an internal standard. [c] Concentration: 0.09 M. [d] Concentration: 0.9 M.

Table 2
Scope of trifluoromethylsulfinylation of indole derivatives.

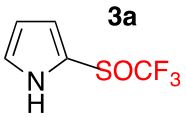
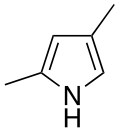
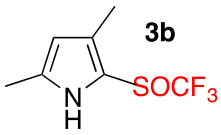
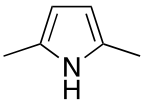
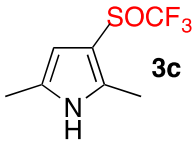
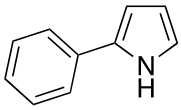
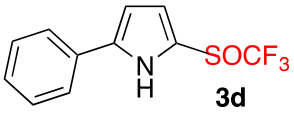
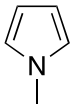
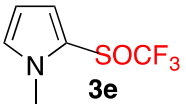
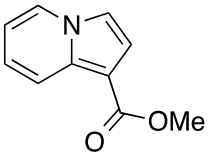
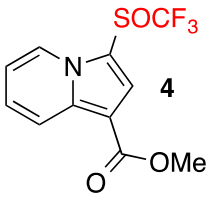
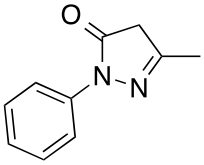
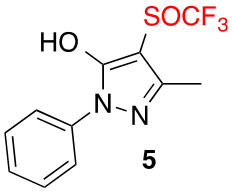
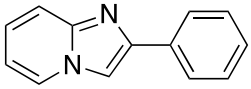
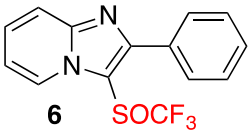


Entry	Substrate **1**	Time (h)	Product **2**	Yield (%)[a]
1		6	 **2a**	88
2[b]		18	 **2b**	80
3[b]		18	 **2c**	91
4		6	 **2d**	85
5		5	 **2e**	86
6[b]		7	 **2f**	61
7		6	 **2g**	87
8		6	 **2h**	79
9		6	 **2i**	73

10		24	 **2j**	35	

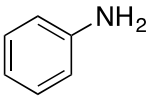
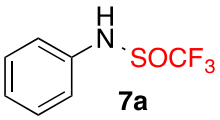
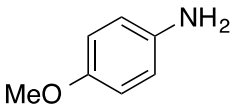
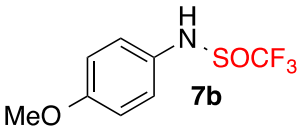
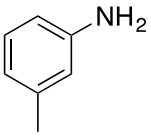
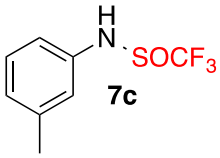
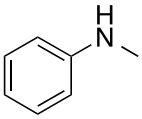
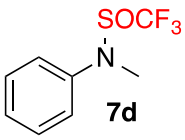
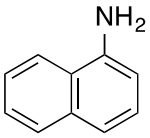
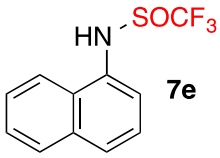
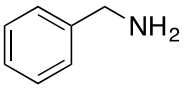
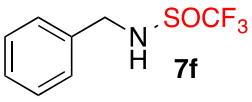
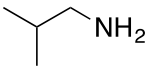
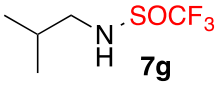
[a] Isolated yields. [b] 1.8 equivalents of trifluoromethanesulfonyl chloride and tricyclohexyl phosphine were used.

Table 3
Scope of trifluoromethylsulfinylation of pyrrole derivatives and other azaarenes.

Entry	Substrate	Time (h)	Product	Yield (%)[a]
1		2	 **3a**	52
2		2	 **3b**	61
3		2	 **3c**	83
4		8	 **3d**	62
5[b]		24	 **3e**	73[c]
6[b]		8	 **4**	54
7[b]		6	 **5**	46
8[b]		24	 **6**	9

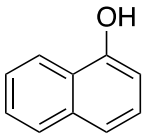
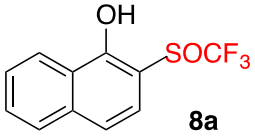
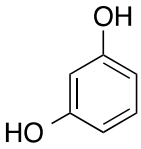
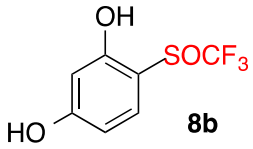
[a] Isolated yields. [b] 1.8 equivalents of trifluoromethanesulfonyl chloride and tricyclohexyl phosphine were used. [c] Yield was determined by ^{19}F NMR using trifluorotoluene as an internal standard.

Table 4
Scope of *N*-trifluoromethylsulfinylation of aryl- and alkylamines.

Entry	Substrate	Time (h)	Product	Yield (%)[a]
1		6	 **7a**	70
2		4	 **7b**	47
3		7	 **7c**	34
4[b]		4	 **7d**	42[c]
5		6	 **7e**	62
6		6	 **7f**	32
7		7	 **7g**	28[c]

[a] Isolated yields. [b] 1.8 equivalents of trifluoromethanesulfonyl chloride and tricyclohexyl phosphine were used. [c] Yields were determined by ^{19}F NMR using trifluorotoluene as an internal standard.

Table 5
C-Trifluoromethylsulfinylation of phenol derivatives.

Entry	Substrate	Time (h)	Product	Yield (%)[a]
1[b]		24	 **8a**	16[c,d]
2		24	 **8b**	24[c]

[a] Isolated yields. [b] 1.8 equivalents of trifluoromethanesulfonyl chloride and tricyclohexyl phosphine were used [c] The starting material was partly recovered. [d] The corresponding trifluoromethylthiolated side-product was formed.