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Selective Trifluoromethylthiolation and Trifluoromethylsulfinylation of Indoles with Sodium Trifluoromethanesulfinate promoted by Phosphorus Reagents

Dong-Wei Sun,[a] Xu Jiang,[b] Min Jiang,[a] Yun Lin,*[b] and Jin-Tao Liu*[a]

Dedication ((optional))

Abstract: Direct trifluoromethylthiolation and trifluoromethylsulfinylation with sodium trifluoromethanesulfinate promoted by different phosphorus reagent were achieved selectively under transition metal-free and mild conditions. In the presence of phosphorus trichloride, sodium trifluoromethanesulfinate reacted readily with indole and its derivatives in DMF at room temperature to give 3-trifluoromethylthiolated products in good yields. While trifluoromethylsulfinylation reaction occured at C-3 position when phosphorus oxychloride was used, and the corresponding sulfoxides were obtained in high yields. The protocol could also be expanded to other sodium perfluoroalkanesulfinates.

Introduction

In recent years, fluorined compounds have attracted more and more attention due to their significant application in medicinal and life sciences.[1] It is well known that the introduction of fluorine atom or fluorine-containing groups into organic molecules can improve their physical, chemical and biological properties.[2] Among various fluorine-containing groups, trifluoromethylthiol (CF_3S) plays an important role in organofluorine chemistry because of its electron-withdrawing effect and high lipophilicity.[3] In addition, enhancement of biological activity has also been found in some trifluoromethylsulfinyl-containing compounds such as insecticide Fipronil and its analogues.[4]

So far, great progress has been made to introduce trifluoromethylthiol group into aromatic compounds, and a series of electrophilic trifluoromethylthiolating reagents were developed.[5] Initially, highly reactive trifluoromethanesulfenyl chloride (CF_3SCl) was used for direct trifluoromethylthiolation,[6] but its toxicity and hard-to-handle gaseous nature limited its utilization. Although a series of highly efficient and CF_3S-based reagents (such as Me_4NSCF_3,[7] $AgSCF_3$ and $CuSCF_3$[8] was discovered in the last decades,[9] these reagents also have some shortcomings which is that multiple steps are required before its application, and expensive chemicals could be used. In the past decade, several mild and efficient CF_3S-N or CF_3S-O based electrophilic trifluoromethylthiolating reagents were developed and achieved great success in a range of trifluoromethylthiolation reactions.[9] Recently, a new trifluoromethylthiolation strategy emerged involving the conbination of trifluoromethanesulfonyl chloride (CF_3SO_2Cl) and a reducing reagent, such as PMe_3,[10] $(EtO)_2P(O)H$,[11] and CF_3SO_2Cl/PPh_3.[12]

Sodium trifluoromethanesulfinate (CF_3SO_2Na), also known as Langlois reagent, and other sodium perfluoroalkanesulfinates are cheap and easily available commercial chemicals. In 2009, Magnier and co-workers reported that a small quantity of trifluoromethylthiolation product was formed in the reaction of CF_3SO_2K and biphenyl for the preparation of Umemoto reagent.[13] In 2015, Zhang et al reported a CuCl catalyzed trifluoromethylthiolation reaction of indoles with $CF_3SO_2Na/(EtO)_2P(O)H$ system.[14] And metal-free electrophilic fluoroalkylthiolation with the similar reagent system was achieved very recently.[15] Meanwhile, Cai and co-workers reported a transition metal-free trifluoromethylthiolation reaction of indole and its derivatives with CF_3SO_2Na/PPh_3 system, and it was found that an additional X^+ source such as *N*-chlorophthalimide and *N*-Bromophthalimide was essential for the reaction.[16]

On the other hand, trifluoromethylsulfides can be oxidized to the corresponding trifluoromethyl sulfoxides.[17] Another method to make trifluoromethylated sulfoxides is nucleophilic trifluoromethylation of sulfinyl halides or sulfinic esters with $TMSCF_3$.[18] Direct trifluoromethylsulfinylation of aromatic compounds with $CF_3S(O)F$ and $CF_3S(O)Cl$ is rarely reported due to the instability and toxicity of these reagents.[19] In 2016, Cahard and co-workers reported the synthesis of hereroaryl trifluoromethyl sulfoxides by direct trifluoromethylsulfinylation of hereroarenes with CF_3SO_2Cl/PCy_3 system, but low temperature (-78℃) was required.[20] http://www.njnu.edu.cn/

Previously, our group had focus on the chemistry of perfluoroalkanesulfinates and their derivatives.[21] During the study on the synthesis and properties of perfluoroalkanesulfenyl chlorides (R_fSCl), it was found that R_fSCl was good perfluoroalkylthiolating reagent for some aromatic compounds, especially indole.[22] Considering that CF_3SCl may be formed in situ by the reduction of CF_3SO_2Na with a chlorine-containing phosphorus (III) reagent and the importance of inexpensive and

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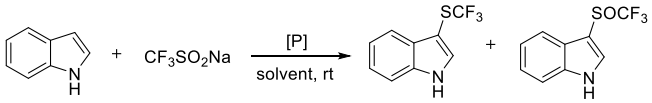
effective trifluoromethylthiolation method, we further studied the reactions of indole and its derivatives with CF_3SO_2Na in the presence of different phosphorus reagents. The results are reported in this paper.

Results and Discussion

In our preliminary experiments, indole (**1a**) was chosen as the model substrate and ordinary phosphine reagents were used. The reaction was carried out with 1.2 equiv of CF_3SO_2Na and 1.0 equiv of trimethylphosphine (PMe_3) in *N, N*-dimethyl formide (DMF) at room temperature. However, ^{19}F NMR monitoring showed that the reaction was complicated and no desired product was isolated after 30min (Table 1, entry 1). Triphenylphosphine (PPh_3) also failed to promote the desired reaction (entry 2). Gratefully, when phosphorus trichloride (PCl_3) was used as reducing reagent, trifluoromethylthiolation and trifluoromethylsulfinylation products (**2a** and **3a**) were obtained in 58% and 39% yields, respectively (entry 2). Further investigation showed that increasing the amount of CF_3SO_2Na or PCl_3 was in favour of the selectivity of trifluoromethylthiolation product. Screening the ratio of reactants indicated that 85% yield of **2a** could be achieved with a ratio of indole/CF_3SO_2Na/PCl_3 = 1:1.2:3, and only trace of **3a** was observed (entries 4-10). Various solvents were next examined. It was found that acetonitrile, tetrahydrofuran (THF), 1,4-dioxane, toluene and dimethylamide (DMA) could not give better result although they also afforded **2a** as major product, and DMF was the most suitable solvent for this reaction (entries 11-16). To our surprise, when phosphorus oxychloride ($P(O)Cl_3$) was used instead of PCl_3, **3a** was obtained as major product (entries 17-19). After condition screening, the optimal conditions for the formation of **3a** were set to 1.0 equiv of **1a**, 1.2 equiv of CF_3SO_2Na and 1.0 equiv of $P(O)Cl_3$ in DMF at room temperature (entry 19).

Table 1: Condition optimization for the trifluoromethylthiolation and trifluoromethylsulfinylation of **1a** with CF_3SO_2Na

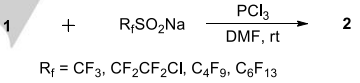


1a **2a** **3a**

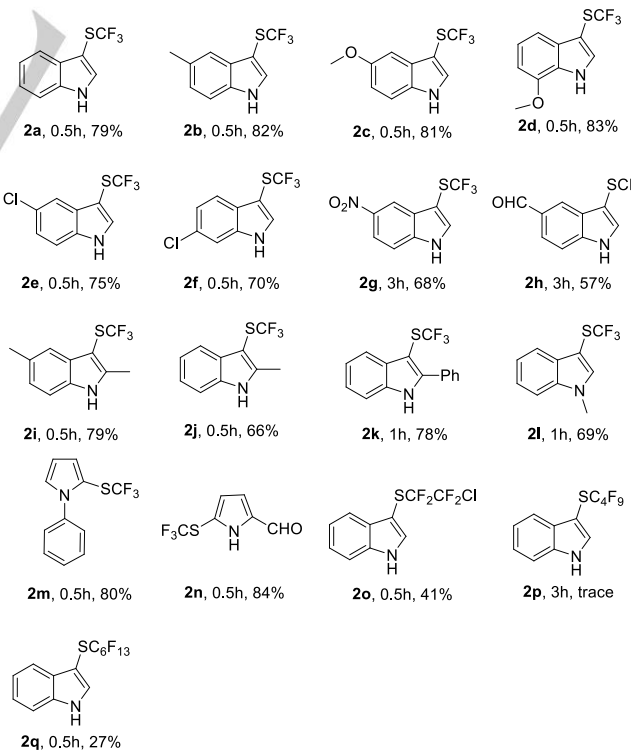
entry[a]	[P]	**1a**:CF_3SO_2Na:[P]	solvent	**2a**/%[b]	**3a**/%[b]
1	PMe_3	1:1.2:1	DMF	0	0
2	PPh_3	1:1.2:1	DMF	0	0
3	PCl_3[c]	1:1.2:1	DMF	58	39
4	PCl_3[c]	1:1.2:2	DMF	69	trace
5	PCl_3[c]	1:1.5:1.5	DMF	69	4.8
6	PCl_3[c]	1:1.5:2	DMF	77	trace
7	PCl_3[c]	1:1.5:3	DMF	71	trace
8	PCl_3[c]	1:1.2:2	DMF	75	21
9	PCl_3[c]	1:1.2:3	DMF	85	trace
10	PCl_3[c]	1:1.2:4	DMF	73	trace
11	PCl_3[c]	1:1.2:3	CH_3CN	76	trace
12	PCl_3[c]	1:1.2:3	THF	80	trace
13	PCl_3[c]	1:1.2:3	1.4-Dioxane	67	Trace
14	PCl_3[c]	1:1.2:3	Toluene	60	20
15	PCl_3[c]	1:1.2:3	DMSO	NR	NR
16	PCl_3[c]	1:1.2:3	DMA	79	20
17	$P(O)Cl_3$	1:1.2:1.5	DMF	16	66
18	$P(O)Cl_3$	1:1.5:1	DMF	18	62
19	$P(O)Cl_3$	1:1.2:1	DMF	trace	89

[a] Reaction conditions: **1a** (0.4 mmol), CH_3SO_2Na (1.2-1.5 equiv), [P] (1.0-4.0 equiv), solvent (1.0 mL), under N_2 at room temperature for 0.5 h. [b] Determined by ^{19}F NMR using $PhCF_3$ as internal standard. [C] A solution of phosphorus chloride in dichloromethane (2 M).

Table 2. Perfluoroalkylthiolation of **1** in the presence of PCl_3



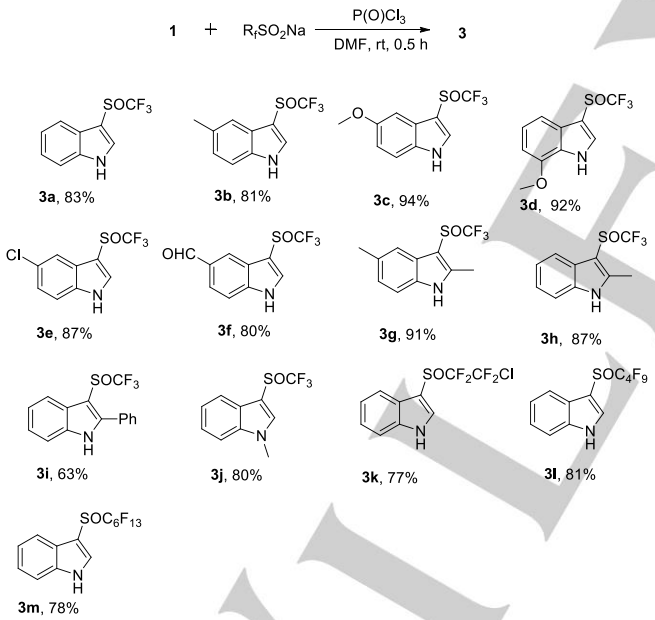
R_f = CF_3, CF_2CF_2Cl, C_4F_9, C_6F_{13}



[a] Reaction conditions: **1** (0.4 mmol), R_fSO_2Na (0.48 mmol), PCl_3 (1.2 mmol), DMF (1 mL) under N_2 at room temperature, isolated yields.

Under the optimized conditions, the scope of substrates was investigated for the PCl_3-promoted reaction. As shown in Table 2, a series of indoles with both electron-withdrawing and electron-donating groups at 5, 6 and 7-position (**1a**-**1h**) were good substrate for this trifluoromethylthiolation reaction, affording the corresponding trifluoromethylthiolated products (**2a**-**2h**) in moderate to good yields (57 to 83%). Usually, the substrate with an electron-donating substituent gave higher yields. Under similar conditions, 2-methyl, 2-phenyl and *N*-methyl indoles could also react with CF_3SO_2Na to give the desired products in good yields and excellent selectivities (**2i**-**2l**). Moreover, the reaction of *N*-phenyl pyrrole worked well and gave the corresponding 2-trifluoromethylthiolated product **2m** in 80% yield. When unprotected pyrrole was used as substrate, unexpected product **2n** containing an aldehyde group was obtained in 84% yield. Except CF_3SO_2Na, we also tried other sodium perfluoroalkanesulfinates. It was found that $ClCF_2CF_2SO_2Na$ and *n*-$C_6F_{13}SO_2Na$ could react smoothly with indole in a similar way to give the corresponding perfluoroalkylthiolation products, but the yield was lower. Unfortunately, perfluorobutylthiolation was unsuccessful under similar conditions and 3-perfluorobutylsulfinylindole was formed as the major product.

Table 3. Perfluoroalkylsulfinylation of **1** in the presence of $P(O)Cl_3$



Reaction conditions: **1** (0.4 mmol), R_fSO_2Na (0.48 mmol), $P(O)Cl_3$ (0.4 mmol), DMF (1 mL) under N_2 at room temperature, isolated yields.

Indoles **1** were also examined in the $P(O)Cl_3$-promoted trifluoromethylsulfinylation reaction and the results are summarized in Table 3. As expected, the reaction showed a wide scope for the structural variation of **1** and excellent selectivity was achieved with compound **3** as major product in each reaction. High yields were obtained not only with electron-donating substituted products, but also with electron-withdrawing substituted compounds. Good results were also obtained when 2-methyl, 2-phenyl and *N*-methyl indoles were used. Furthermore, similar transformation was achieved with other sodium perfluoroalkanesulfinates, such as $ClCF_2CF_2SO_2Na$, *n*-$C_4F_9SO_2Na$ and *n*-$C_6F_{13}SO_2Na$, and the corresponding 3-perfluoroalkylsulfinylated products **3k-3m** were obtained in good yields.

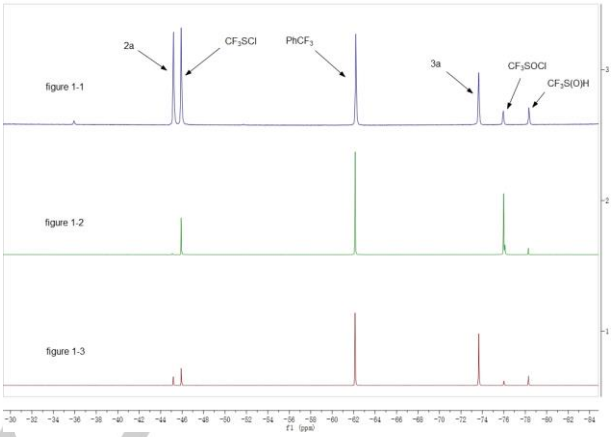


Figure 1. ^{19}F NMR spectra for the mechanistic.

In order to gain insight to the reaction mechanism, we carried out the following reaction: A mixture of CF_3SO_2Na (1.5 equiv) and PCl_3 (1.0 equiv) in DMF was stirred at room temperature. After 10 min, 1.0 equiv of **1a** was added. As shown in Figure 1, ^{19}F NMR analysis showed both CF_3SCl (δ = -45.92 ppm) and CF_3SOCl (δ = -75.98 ppm) existed in the reaction system (Figure 1-1). Similarly, the signals of CF_3SCl and CF_3SOCl were also observed in the mixture of CF_3SO_2Na and $P(O)Cl_3$ with a ratio of 1.2:1 in DMF (Figure 1-2). After addition of **1a** to the $P(O)Cl_3$-promoted reaction system, **2a** and **3a** were rapidly produced (Figure 1-3).

Further investigation found that **2a** and **3a** could not transfer each other under the two standard conditions. It can be inferred that the formation of **2a** and **3a** was a competitive process. Based on the above experimental results and previous reports,[11-15, 22] it could be deduced that CF_3SCl and CF_3SOCl were formed as key intermediates in the reaction system and underwent the subsequent trifluoromethylthiolation and trifluoromethylsulfinylation reaction with **1**, respectively. In the PCl_3-promoted reaction, increasing the amount of CF_3SO_2Na or PCl_3 was favor for the formation of CF_3SCl and thus resulted in better selectivity for product **2**. On the contrary, in the $P(O)Cl_3$-promoted reaction, decreasing the equivalent of CF_3SO_2Na and $P(O)Cl_3$ easily afforded **3** with high yield and good selectivity.

Conclusions

In summary, we have developed an efficient protocol for the direct trifluoromethylthiolation and trifluoromethylsulfinylation of indole and its derivatives with sodium trifluoromethanesulfinate. By using different phosphorus reagent, trifluoromethylthiolation and trifluoromethylsulfinylation products could be obtained

selectively in good yields, respectivity. The reaction tolerates a wide range of functional groups, providing a practical method for the synthesis of various trifluoromethylthiol- and trifluoromethylsulfinyl-containing compounds. The key advantage of this method includes: cheap and easily available reagents, easy-to-handle, transition-metal-free and mild reaction conditions. Moreover, the protocol could also be expanded to perfluoromethylthiolation and perfluoromethylsulfinylation reaction with sodium perfluoroalkanesulfinates.

Experimental Section

General information

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. Solvents were freshly distilled by standard procedure prior to use. Melting points were measured on a RY-I apparatus and uncorrected. ^{1}H NMR and ^{19}F NMR were recorded on ^{1}H at 400 Hz and ^{19}F at 376 MHz, respectively. ^{13}C NMR spectra were recorded on ^{13}C at 100 MHz. High Resolution Mass Spectra (HRMS) were recorded on an IonSpec FT-ICR mass spectrometer with ESI resource.

Typical procedure for the trifluoromethylthiolation

To a solution of indole **1a** (0.4 mmol) and CF_3SO_2Na (0.48 mmol) in DMF (1.0 mL) was added a solution of phosphorus chloride (1.2 mmol in dichloromethane, 2 M) dropwise over a period of 3 min. The mixture was stirred at room temperature for 0.5h. After the reaction was completed (monitored by ^{19}F NMR), the mixture was quenched with water. The aqueous layer was extracted with EtOAc three times. The organic layers were combined, dried over Na_2SO_4 and concentrated. The resulting crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=10/1 v/v) to give the corresponding product **2a**.

Typical procedure for the trifluoromethylsulfinylation

To a solution of indole **1a** (0.4 mmol) and CF_3SO_2Na (0.48 mmol) in DMF (1.0 mL) was added $P(O)Cl_3$ (0.4 mmol). The mixture was stirred at room temperature for 0.5h. After the reaction was completed (monitored by ^{19}F NMR), the mixture was quenched with water. The aqueous layer was extracted with EtOAc three times and the organic layers were combined, dried over Na_2SO_4 and concentrated. The resulting crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=5/1 v/v) to give the corresponding product **3a**.

3-((Trifluoromethyl)thio)-1*H*-indole (2a): Yellow solid, 68.6 mg, yield: 79%. This is a known compound.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (br, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.44 – 7.42 (m, 1H), 7.32 – 7.28 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.63 (s).

5-Methyl-3-((trifluoromethyl)thio)-1*H*-indole (2b): Brown solid, 75.8 mg, yield: 82%. This is a known compound.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (br, 1H), 7.55 (s, 1H), 7.46 (d, *J* = 2.5 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 2.46 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.69 (s).

3-((Trifluoromethyl)thio)-5-methoxy-1*H*-indole (2c): Yellow solid, 80.1 mg, yield: 81%. This is a known compound.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (br, 1H), 7.51 (s, 1H), 7.32 (d, *J* = 8.9 Hz, 1H), 7.22 (s, 1H), 6.95 (q, *J* = 8.9 Hz, 1H), 3.90 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.71 (s).

7-Methoxy-3-(trifluorooctyl)thio)-1*H*-indole (2d): Yellow solid, 82.1 mg, yield: 83%. m.p. 85-87 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (br, 1H), 7.49 (d, *J* = 2.7 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.25 (s), 132.20 (s), 130.84 (s), 129.44 (q, *J* = 317.0 Hz), 126.70 (s), 122.10 (s), 111.76 (s), 103.03 (s), 95.82 (s), 55.47 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.72 (s). ESI-MS (m/z, %): 248.0 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{10}H_9F_3NOS$ $[M+H]^+$ requires 248.0351, found 248.0349.

5-Chloro-3-((trifluoromethyl)thio)-1*H*-indole (2e): Yellow solid, 39.2 mg, yield: 75%. This is a known compound.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (br, 1H), 7.75 (d, *J* = 1.2 Hz, 1H), 7.55 (d, *J* = 2.8 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.25 – 7.21 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.56 (s).

6-Chloro-3-((trifluoromethyl)thio)-1*H*-indole (2f): Yellow solid, 70.5 mg, yield: 70%. This is a known compound.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (br, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 2.7 Hz, 1H), 7.43 (d, *J* = 1.7 Hz, 1H), 7.25 (q, *J* = 4.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.54 (s).

5-Nitro-3-((trifluoromethyl)thio)-1*H*-indole (2g): Yellow solid, 71.3 mg, yield: 68%. This is a known compound.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (br, 1H), 8.74 (s, 1H), 8.21 (d, *J* = 8.9 Hz, 1H), 7.73 (s, 1H), 7.51 (d, *J* = 9.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.22 (s).

3-((Trifluoromethyl)thio)-1*H*-indole-5-carbaldehyde (2h): Yellow solid, 55.9 mg, yield: 57%. m.p. 148-150 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.96 (br, 1H), 8.32 (s, 1H), 7.88 (q, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.35 (s), 139.55 (s), 134.57 (s), 131.22 (s), 129.90 (s), 128.98 (q, *J* = 308.2 Hz), 124.76 (s), 123.33 (s), 112.61 (s), 97.92 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.30 (s). ESI-MS (m/z, %): 246.0 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{10}H_7F_3NOS$ $[M+H]^+$ requires 246.0195, found 246.0192.

2,5-Dimethyl-3-((trifluoromethyl)thio)-1*H*-indole (2i): Yellow solid, 77.5 mg, yield: 79%. This is a known compound.[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (br, 1H), 7.47 (s, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 2.54 (s, 3H), 2.46 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.54 (s).

3-((Trifluoromethyl)thio)-2-methyl-1*H*-indole (2j): Brown solid, 61.0 mg, yield: 66%. This is a known compound.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (br, 1H), 7.76 – 7.61 (m, 1H), 7.35 – 7.26 (m, 1H), 7.24 – 7.16 (m, 2H), 2.57 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.49 (s).

2-Phenyl-3-((trifluoromethyl)thio)-1*H*-indole (2k): Yellow solid, 91.5 mg, yield: 78%. This is a known compound.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (br, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.45 (m, 3H), 7.45 – 7.39 (m, 1H), 7.28-7.30 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.49 (s).

3-((Trifluoromethyl)thio)-1-methyl-1*H*-indole (2l): Yellow solid, 63.8 mg, yield: 69%. This is a known compound.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.33 – 7.28 (m,

1H), 7.28 – 7.27 (m, 1H), 3.85 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -45.00 (s).

1-phenyl-2-((trifluoromethyl)thio)-1H-pyrrole (2m): Yellow oil, 77.84 mg, yield: 80%. This is a known compound. [23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.36 (m, 2H), 7.33 – 7.29 (m, 2H), 7.08 (t, *J* = 2.4 Hz, 1H), 6.50 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -45.19 (s).

5-((Trifluoromethyl)thio)-1H-pyrrole-2-carbaldehyde (2n): Yellow solid, 66.6 mg, yield: 84%. m.p. 49-50 °C. ^{1}H NMR (400 MHz, DMSO) δ 13.15 (br, 1H), 9.56 (s, 1H), 7.07-7.06 (m, 1H), 6.75-6.73 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ 180.95, 137.31, 128.76 (q, *J* = 308.04 Hz), 122.06, 120.32, 116.19. ^{19}F NMR (376 MHz, DMSO) δ -43.02 (s). HRMS (ESI) Calcd. for $C_6H_5F_3NOS$ $[M+H]^+$ requires 196.0038, found 196.0037.

3-((2-Chloro-1,1,2,2-tetrafluoroethyl)thio)-1*H*-indole (2o): Yellow solid, 46.5 mg, yield: 41%. m.p. 46-47 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (br, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 2.6 Hz, 1H), 7.42 – 7.40 (m, 1H), 7.31 – 7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.03 (s), 133.46 (s), 129.92 (s), 123.41 (s), 121.66 (s), 119.47 (s), 111.73 (s), 94.23 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.62 (t, *J* = 6.3 Hz, 2F), -88.47 (t, *J* = 6.3 Hz, 2F). ESI-MS (m/z, %): 282.0 (100) [M]. HRMS (ESI) Calcd. For $C_{10}H_6ClF_4NS$ $[M]^+$ requires 282.9840, found 282.9837.

3-((Perfluorohexyl)thio)-1*H*-indole (2q): White solid, 50.5 mg, yield: 27%. This is a known compound.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (br, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 2.3 Hz, 1H), 7.42 (d, *J* = 6.6 Hz, 1H), 7.31 – 7.27 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.82 (t, *J* = 10.0 Hz, 3F), -88.17 (tt, *J* = 11.28, 1.13 Hz, 2F), -119.44 (t, *J* = 3.78 Hz, 2F), -121.46 – -121.47 (m, 2F), -122.83 – -122.84 (m, 2F), -126.60 – -133.04 (m, 2F).

3-((Trifluoromethyl)sulfinyl)-1*H*-indole (3a): Yellow solid, 77.4 mg, yield: 83%. This is a known compound.[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (br, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 2.8 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27 – 7.25 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.16 (s).

5-Methyl-3-((trifluoromethyl)sulfinyl)-1*H*-indole (3b): Yellow solid, 81.1 mg, yield: 81%. m.p. 126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (br, 1H), 7.73 (s, 1H), 7.69 (d, *J* = 2.9 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.13 (s), 132.49 (s), 130.99 (s), 126.20 (s), 125.62 (q, *J* = 335.5 Hz), 124.16 (s), 119.75 (s), 112.22 (s), 107.42 (s), 21.48 (s).^{19}F NMR (376 MHz, $CDCl_3$) δ -73.07 (s). ESI-MS (m/z, %): 248.0 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{10}H_9F_3NOS$ $[M+H]^+$ requires 248.0351, found 248.0350.

5-Methoxy-3-((trifluoromethyl)sulfinyl)-1*H*-indole (3c): Yellow solid, 99.0 mg, yield: 94%. This is a known compound.[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (br, 1H), 7.71 (s, 1H), 7.35 (d, *J* = 9.2 Hz, 2H), 6.97 (dd, *J* = 8.9 Hz, 1H), 3.83 (s, 3H).^{19}F NMR (376 MHz, $CDCl_3$) δ -73.02 (s).

7-Methoxy-3-((trifluoromethyl)sulfinyl)-1*H*-indole (3d): Yellow solid, 94.8 mg, yield: 92%. m.p. 160-162 °C. ^{1}H NMR (400 MHz, DMSO) δ 12.64 (br, 1H), 8.22 (d, *J* = 3.2 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 147.17 (s), 133.60 (s), 127.74 (s), 126.12 (q, *J* = 341.5 Hz), 125.81 (s), 123.31 (s), 112.59 (s), 107.37 (s), 104.54 (s), 55.93 (s). ^{19}F NMR (376 MHz, DMSO) δ -72.69 (s). ESI-MS (m/z, %): 264.0 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{10}H_9F_3NO_2S$ $[M+H]^+$ requires 264.0301, found 264.0297.

5-Chloro-3-((trifluoromethyl)sulfinyl)-1*H*-indole (3e): Yellow solid, 93.1 mg, yield: 87%. m.p. 133-135 °C. ^{1}H NMR (400 MHz, DMSO) δ 12.61 (br, 1H), 8.40 (s, 1H), 7.76 (s, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 136.06 (s), 135.52 (s), 126.95 (s), 126.21 (q, *J* = 337.8 Hz), 125.41 (s), 124.31 (s), 119.24 (s), 115.37 (s), 106.43 (s). ^{19}F NMR (376 MHz, DMSO) δ -73.02 (s). ESI-MS (m/z, %): 268.0 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_9H_6ClF_3NOS$ $[M+H]^+$ requires 267.9805 , found 267.9803.

3-((trifluoromethyl)sulfinyl)-1*H*-indole-5-carbaldehyde (3f): Yellow solid, 83.6 mg, yield: 80%. m.p. 155-156 °C. ^{1}H NMR (400 MHz, DMSO) δ 12.84 (br, 1H), 10.04 (s, 1H), 8.51 (s, 1H), 8.40 (s, 1H), 7.83 – 7.81 (m, 1H), 7.73 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 193.22 (s), 140.93 (s), 136.33 (s), 131.41 (s), 125.49 (q, *J* = 334.8 Hz), 124.51 (s), 124.24 (s), 124.04 (s), 114.46 (s), 108.63 (s). ^{19}F NMR (376 MHz, DMSO) δ -72.87 (s). ESI-MS (m/z, %): 262.0 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{10}H_7F_{13}NOS$ $[M+H]^+$ requires 262.0144, found 262.0142.

2,5-Dimethyl-3-((trifluoromethyl)sulfinyl)-1*H*-indole (3g): Yellow solid, 95.0 mg, yield: 91%. m.p. 198-199°C. ^{1}H NMR (400 MHz, DMSO) δ 12.19 (br, 1H), 7.51 (s, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 2.51 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 145.11 (s), 134.48 (s), 130.91 (s), 126.67 (q, *J* = 338.4 Hz), 125.68 (s), 124.79 (s), 119.32 (s), 112.21 (s), 102.02 (s), 21.65 (s), 12.27 (s). ^{19}F NMR (376 MHz, DMSO) δ -72.34 (s). ESI-MS (m/z, %): 262.0 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{11}H_{11}F_3NOS$ $[M+H]^+$ requires 262.0508, found 262.0505.

2-Methyl-3-((trifluoromethyl)sulfinyl)-1*H*-indole (3h): Yellow solid, 86.0 mg, yield: 87%. This is a known compound.[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (br, 1H), 7.94 (d, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.26 (s, 1H), 7.24 – 7.16 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.32 (s).

2-Phenyl-3-((trifluoromethyl)sulfinyl)-1*H*-indole (3i): Yellow solid, 77.9 mg, yield: 63%. m.p. 126-127 °C. ^{1}H NMR (400 MHz, DMSO) δ 12.79 (br, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.57-7.55 (m, 6H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 146.41 (s), 136.89 (s), 130.72 (s), 129.84 (s), 129.57 (s), 129.21 (s), 126.90 (q, *J* = 340.2 Hz), 125.60 (s), 124.46 (s), 122.56 (s), 120.89 (s), 113.25 (s), 103.57 (s). ^{19}F NMR (376 MHz, DMSO) δ -70.77 (s). ESI-MS (m/z, %): 310.0 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{15}H_{11}F_3NOS$ $[M+H]^+$ requires 310.0508, found 310.0505.

1-Methyl-3-((trifluoromethyl)sulfinyl)-1*H*-indole (3j): Yellow solid, 79.1 mg, yield: 80%. This is a known compound.[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.45 – 7.34 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 3.88 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.64 (s).

3-((2-Chloro-1,1,2,2-tetrafluoroethyl)sulfinyl)-1*H*-indole (3k): Yellow solid, 92.3 mg, yield: 77%. m.p. 125-127 °C. ^{1}H NMR (400 MHz, DMSO) δ 12.45 (br, 1H), 8.33 (d, *J* = 2.4 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H).^{13}C NMR (101 MHz, DMSO) δ 137.56 (s), 134.30 (s), 124.77 (s), 124.13 (s), 122.41 (s), 120.37 (s), 113.59 (s), 106.66 (s). ^{19}F NMR (376 MHz, DMSO) δ -67.01 – -67.02 (m, 2F), -109.77 (dt, *J* = 233.12, 3.76Hz, 1F), -118.41(d, *J* = 233.14Hz, 1F). ESI-MS (m/z, %): 300.0 (100) $[M+H]^+$.

HRMS (ESI) Calcd. for $C_{10}H_7ClF_4NOS$ $[M+H]^+$ requires 299.9868, found 299.9864.

3-((Perfluorobutyl)sulfinyl)-1*H*-indole (3l): Yellow solid, 124.2 mg, yield: 81%. m.p. 127-129 ℃. ^{1}H NMR (400 MHz, DMSO) δ 12.50 (br, 1H), 8.36 (d, *J* = 2.6 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 137.60 (s), 134.59 (s), 124.81 (s), 124.18 (s), 122.50 (s), 120.31 (s), 113.62 (s), 106.12 (s). ^{19}F NMR (376 MHz, DMSO) δ -80.44 (t, *J* = 9.3 Hz, 3F), -110.73 – -111.39 (m, 1F), -120.07 – -122.54 (m, 3F), -125.88 – -125.96 (m, 2F). ESI-MS (m/z, %): 384.0 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{12}H_7F_9NOS$ $[M+H]^+$ requires 384.0099, found 384.0096.

3-((Perfluorohexyl)sulfinyl)-1*H*-indole (3m): White solid, 150.8 mg, yield: 78%. m.p. 130-131 ℃. ^{1}H NMR (400 MHz, DMSO) δ 12.49 (br, 1H), 8.36 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 137.61 (s), 134.36 (s), 124.82 (s), 124.07 (s), 122.31 (s), 120.26 (s), 113.54 (s), 106.28 (s). ^{19}F NMR (376 MHz, DMSO) δ -80.78 (t, *J* = 9.9 Hz, 3F), -110.45 – 111.09 (m, 1F), -119.04 – -121.54 (m, 3F), -121.93 – -121.98 (m, 2F), -122.78 – -122.85 (m, 2F), -125.75 – -126.51 (m, 2F). ESI-MS (m/z, %): 484.0 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{14}H_7F_{13}NOS$ $[M+H]^+$ requires 484.0035, , found 484.0028.

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Keywords: trifluoromethylthiolation, trifluoromethylsulfinylation, indole, phosphorus trichloride, phosphorus oxychloride

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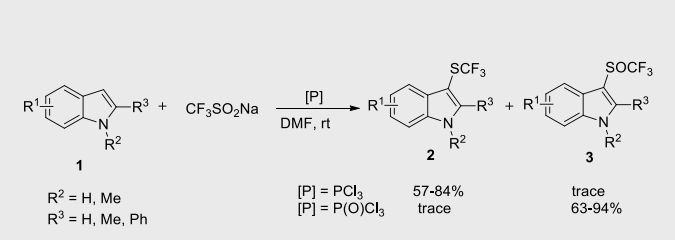

A Facile method for the selective trifluoromethylthiolation and trifluoromethylsulfinylation of indoles with CF_3SO_2Na was developed. A series of trifluoromethylthiol and trifluoromethylsulfinyl-containing compounds were synthesized in good yields under mild and transition-metal-free conditions.

Trifluoromethylthiolation, Trifluoromethylsulfinylation

Key Topic*

Dong-Wei Sun, Xu Jiang, Min Jiang, Yun Lin and Jin-Tao Liu**

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Selective Trifluoromethylthiolation and Trifluoromethylsulfinylation of Indoles with Sodium Trifluoromethanesulfinate promoted by Phosphorus Reagents