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Transition-metal-free direct trifluoromethylthiolation of electron-rich aromatics using CF_3SO_2Na in the presence of $PhPCl_2$

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ABSTRACT

A novel transition metal-free route for the direct trifluoromethylthiolation of electron-rich aromatics using CF_3SO_2Na in the presence of $PhPCl_2$ was developed. More specifically, $PhPCl_2$ was used as both a reducing and a chlorinating reagent for the first time in this CF_3SO_2Na-based trifluoromethylthiolation reaction. The absence of transition metals and the use of cheap and readily available reagents render this method an alternative and practical strategy for the trifluoromethylthiolation of electron-rich aromatics.

1. Introduction

The trifluoromethylthio (SCF_3) group is an important pharmacophore that is present in many pharmaceutical and agrochemical products, including cefazaflur, tiflorex, toltrazuril, and vaniliprole.[1] Indeed, the incorporation of an SCF_3 group into pharmaceuticals is known to greatly improve their metabolic stabilities[2] and cell membrane permeabilities.[3] As such, the incorporation of SCF_3 groups into small molecules is an active research area in synthetic chemistry. Indeed, great progress has recently been made in the electrophilic trifluoromethylthiolation of aromatic compounds, and a series of shelf-stable electrophilic SCF_3 reagents have been developed (compounds **1**–**9**, Scheme 1).[4–13]

In this context, sodium trifluoromethanesulfinate (CF_3SO_2Na, **10**), otherwise known as the Langlois reagent, is an essentially odourless, readily accessible solid, which has been employed as a trifluoromethylation reagent.[14] In addition, Yi and Zhang reported a CuCl-mediated trifluoromethylthiolation of C(sp^2)–H bonds using a CF_3SO_2Na/diethyl phosphonate ($(EtO)_2P(O)H$) system (Scheme 2, equation (1)).[15] Furthermore, the Cai group recently reported the trifluoromethylthiolation of indoles using a CF_3SO_2Na/triphenylphosphine (PPh_3)/*N*-chlorophthalimide system, while the Yi and Zhang group reported a similar transformation using a CF_3SO_2Na/$(EtO)_2P(O)H$/chlorotrimethylsilane (TMSCl) system (Scheme 2, equations (2) and (3)).[16] In these two protocols, PPh_3 and $(EtO)_2P(O)H$ were used as reductants, while *N*-chlorophthalimide and TMSCl were employed as the chlorination reagents. However, the above mentioned CF3SO2Na-based trifluoromethylthiolation reaction either need transition metal catalysis or need additional chlorination reagents.

In addition, both our group and the Liu group recently independently reported the CF_3SO_2Na-based trifluoromethylthiolation of electron-rich aromatics in the presence of PCl_3, which was employed both as a reductant and as a chlorination reagent (Scheme 2, equation (4)).[17] In our protocol, the slow addition of PCl_3 was carried out using a syringe pump, as this reagent reacted rapidly with indole. Thus, as we are interested in developing efficient methods to construct C–S bonds,[13c,17b,18] we herein report the development of a CF_3SO_2Na-based transition metal-free trifluoromethylthiolation of electron-rich aromatics in the presence of dichloro(phenyl)phosphane ($PhPCl_2$), as the latter is less electrophilic than PCl_3, and so is expected to react less rapidly with indole (Scheme 2, equation (5)).

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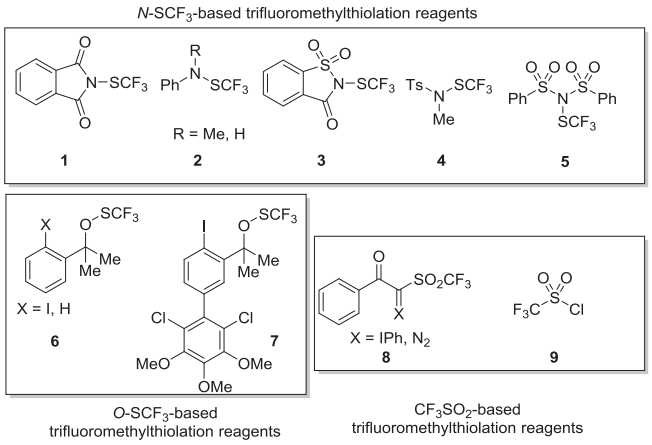
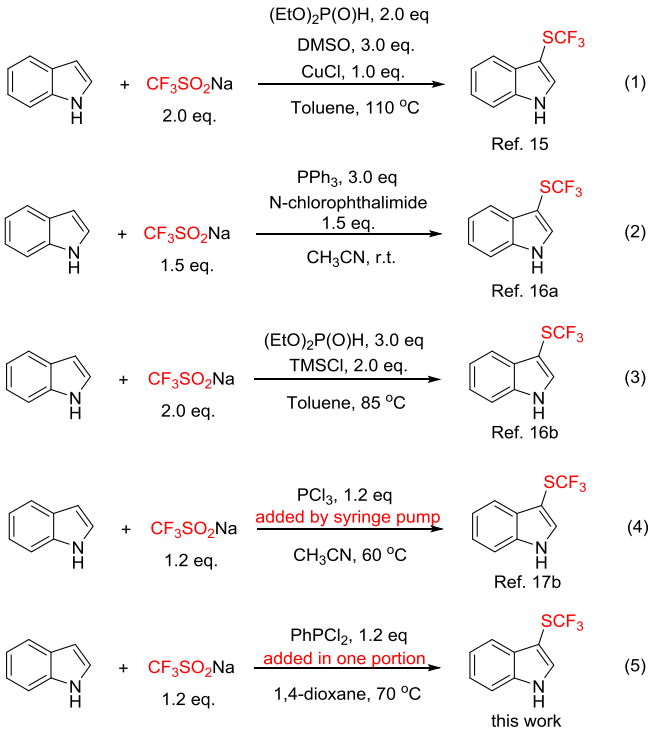


Scheme 1. Thiolation of indolizines and *N*-methylindoles using sulfonyl chlorides as sulfenylation reagents.

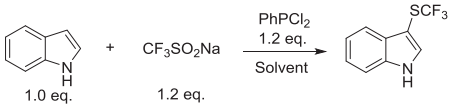


Scheme 2. Trifluoromethylthiolation of indole using CF_3SO_2Na as an SCF_3 source.

2. Results and discussion

To probe the trifluoromethylthiolation of electron-rich aromatics using our $CF_3SO_2Na/PhPCl_2$ system, we treated indole **11a** with CF_3SO_2Na (**10**) in the presence of $PhPCl_2$ in acetonitrile (CH_3CN) at 60 °C over 0.5 h to yield the desired product **12a** in 39% yield. Optimisation of the reaction conditions was then carried out to enhance this yield. Initially, the effect of the reaction solvent was investigated using toluene, 1,4-dioxane, and 1,2-dichloroethane (DCE) (Table 1, entries 2–4), with 1,4-dioxane giving the optimal yield (i.e., 65%, entry 3). The effect of the reaction temperature was then examined between 50 and 80 °C. Upon decreasing the reaction temperature to 50 °C, the yield of **12a** decreased to 60% (entry 5), while increasing the temperature to 70 °C increased the yield to 70% (entry 6). However, further increasing the reaction

Table 1
Optimisation of the trifluoromethylthiolation of **11a** with **10** in the presence of $PhPCl_2$.[a]



Entry	Solvent	Volume (mL)	Temperature (°C)	Yield (%)
1	CH_3CN	3.0	60	39
2	Toluene	3.0	60	59
3	1,4-Dioxane	3.0	60	65
4	DCE	3.0	60	50
5	1,4-Dioxane	3.0	50	60
6	1,4-Dioxane	3.0	70	70
7	1,4-Dioxane	3.0	80	58
8	1,4-Dioxane	3.0	70	70
9	1,4-Dioxane	2.0	70	75
10	1,4-Dioxane	1.0	70	80
11	1,4-Dioxane	0.5	70	66
12	1,4-Dioxane	1.0	70	84[b]
13	1,4-Dioxane	1.0	70	89[c]
14	1,4-Dioxane	1.0	70	90[d]

[a] Reaction conditions: **11a** (0.5 mmol), **10** (0.6 mmol), $PhPCl_2$ (0.6 mmol), 0.5 h.
[b] **10** (0.65 mmol) and $PhPCl_2$ (0.65 mmol) were used.
[c] **10** (0.7 mmol) and $PhPCl_2$ (0.7 mmol) were used.
[d] **10** (0.75 mmol) and $PhPCl_2$ (0.75 mmol) were used.

temperature to 80 °C led to a diminished yield (i.e., 58%, entry 7). Finally, the reaction concentration and stoichiometry were investigated (entries 8–14). More specifically, upon increasing the concentration of **11a** from 0.167 to 0.5 M, the yield of **12a** increased from 70 to 80% (entries 8–10), while a further increase in the concentration of **11a** had a detrimental effect (i.e., 66%, entry 11). In addition, upon increasing the loading of **10** and $PhPCl_2$ from 1.2 to 1.4 equiv., the yield increased from 80 to 89% (entries 10, 12, and 13), although a further increase to 1.5 equiv. had little effect on the obtained yield (i.e., 90%, entry 14). The optimised reaction conditions for this transformation were therefore confirmed to be as follows: **11a** (0.5 mmol), **10** (0.7 mmol), $PhPCl_2$ (0.7 mmol), and 1,4-dioxane (1 mL) at 70 °C over 0.5 h.

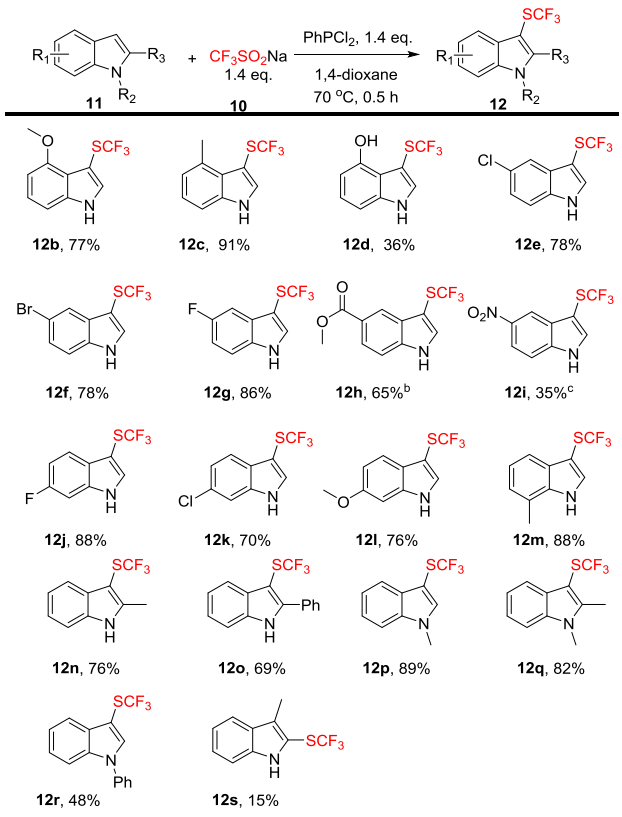
With the optimised conditions in hand, the substrate scope of the trifluoromethylthiolation reaction was examined using a series of indole derivatives (Table 2).

As indicated, both electron-donating and electron-withdrawing substituents were well tolerated in the 2, 4, 5, 6, and 7 positions (**11b, 11c, 11e**–**11o**), as were *N*-substituted indoles (**11p**–**11r**), with the desired products being obtained in moderate to good yields. However, when 4-hydroxylindole (**11d**) and 3-methylindole (**11s**) were employed as substrates, relatively low yields of the desired products were obtained (i.e., 36 and 15%, respectively). Notably, when indoles bearing electron-withdrawing substituents (**11h** and **11i**) were employed, it was necessary to increase the number of equivalents of **10** and $PhPCl_2$ to obtain acceptable yields (i.e., 65 and 35%, respectively).

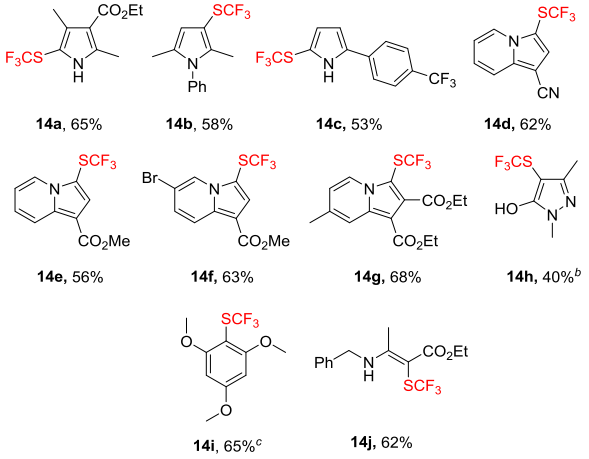
Encouraged by these results, the use of other electron-rich aromatics and alkene, such as pyrrole (**13a**–**13c**), indolizine (**13d**–**13g**), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**13h**), 1,3,5-trimethoxybenzene (**13i**) and methyl (E)-3-(benzylamino)but-2-enoate (**13j**) was examined under the optimised conditions. Indeed, we found that these substrates could be smoothly transformed into the desired products (**14a**–**14j**) in moderate yields (i.e., 40–68%, Scheme 3).

Based on previous literature,[17b] a plausible reaction mechanism

Table 2
Scope of trifluoromethylthiolation of indole derivatives.[a]



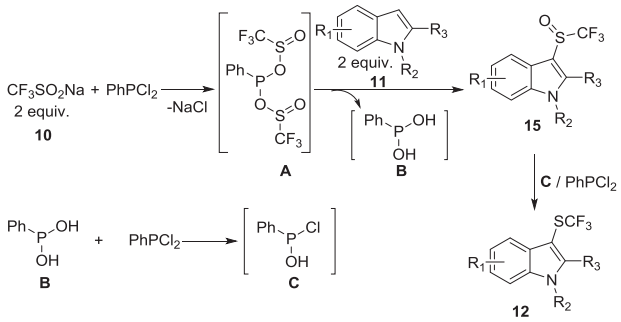
[a] Reaction conditions: **11** (0.5 mmol), **10** (0.7 mmol), $PhPCl_2$ (0.7 mmol), 1,4-dioxane (1.0 mL) at 70 °C. [b] **10** (1.0 mmol) and $PhPCl_2$ (1.0 mmol) were used. [c] **10** (0.9 mmol) and $PhPCl_2$ (0.9 mmol) were used for 12 h.



[a] Reaction conditions: **13** (0.5 mmol), **10** (0.7 mmol), $PhPCl_2$ (0.7 mmol), 1,4-dioxane (1.0 mL) at 70 °C for 0.5 h. [b] the reaction was allowed to proceed for 3 h. [c] CH_3CN (1.0 mL) was used.

Scheme 3. Trifluoromethylthiolation of other aromatics with **10** in the presence of $PhPCl_2$.

for this reaction was then proposed (Scheme 4). More specifically, CF_3SO_2Na (**10**) can initially react with $PhPCl_2$ to form intermediate **A**, which reacts twice with indole-based substrates to afford **15** in addition to intermediate (**B**). Intermediate (**B**) then reacts with



Scheme 4. Proposed reaction mechanism.

$PhPCl_2$ to generate PhP(OH)Cl (**C**), and subsequent reduction of **15** by $PhPCl_2$ and (**C**) affords the corresponding indole trifluoromethylthioethers **12**.

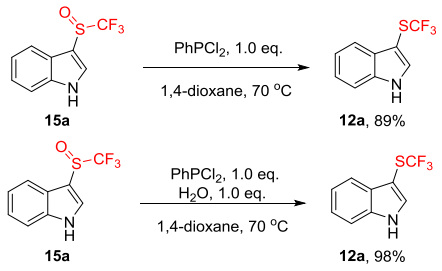
To confirm this mechanism, 3-((trifluoromethyl)sulfinyl)-1*H*-indole (**13a**) was treated with either $PhPCl_2$ (1.0 equiv.) or chloro(hydroxy)(phenyl)phosphane (PhP(OH)Cl) (1.0 equiv.), generated *in situ* from $PhPCl_2$ (1.0 equiv.) and H_2O (1.0 equiv.), in 1,4-dioxane at 70 °C. As expected based on our proposed mechanism, the desired product **12a** was obtained in 89% and 98% yields, respectively (Scheme 5).

Finally, to demonstrate the practical application of this method, the gram-scale trifluoromethylthiolation of indole was carried out to give the desired product **12a** in 84% yield (Scheme 6).

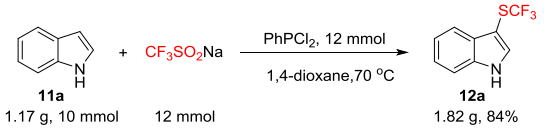
3. Experimental section

3.1. General methods and material

All solvents were distilled prior to use. Unless otherwise noted, chemicals were used as received without further purification. For chromatography, 200–300 mesh silica gel was employed. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. HRMS was performed on an FTMS mass instrument. Melting points are reported as uncorrected.



Scheme 5. Reduction of **13a** to **12a** by $PhPCl_2$ or PhP(OH)Cl.



Scheme 6. Large scale synthesis of **13a**.

3.2. General procedure for trifluoromethylthiolation of electron-rich aromatic by CF_3SO_2Na in the presence of $PhPCl_2$

To a flame-dried Schlenk tube was added electron-rich aromatic (0.5 mmol), CF_3SO_2Na (118 mg, 0.7 mmol) dry 1,4-dioxane or CH_3CN (1 mL). The mixture was heated to 60 °C by a preheated oil bath. $PhPCl_2$ (125 mg, 0.7 mmoL) was added. The reaction mixture was stirred at 70 °C for the indicated time. Then the reaction mixture was cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography to afford the pure product.

3-((trifluoromethyl)thio)-1H-indole (12a):[13c] After purification by silica gel column chromatography (PE: EA = 10: 1), compound **12a** was isolated as a pale yellow solid (97 mg, 89%); R_f (PE: EA = 10: 1) = 0.21; mp (melting point) = 52–53 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.82–7.79 (m, 1H), 7.52 (d, J = 2.7 Hz, 1H), 7.40–7.44 (m, 1H), 7.32–7.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 132.8, 129.5 (q, J = 308.2 Hz, 1C), 129.4, 123.4, 121.6, 119.3, 111.7, 95.5 (q, J = 2.4 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.59 (s, 3F).

4-methoxy-3-((trifluoromethyl)thio)-1H-indole (12b):[13c] After purification by silica gel column chromatography (PE: EA = 10: 1), compound **12b** was isolated as a yellow solid (95 mg, 77%); R_f (PE: EA = 10: 1) = 0.20; mp (melting point) = 61–63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.40 (d, J = 2.4 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.01 (dd, J = 8.0 Hz, 0.6 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 137.9, 132.3, 129.4 (q, J = 307.5 Hz, 1C), 124.3, 118.6, 104.8, 102.1, 94.5 (q, J = 2.6 Hz, 1C), 55.5 (q, J = 2.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −45.48 (s, 3F).

4-methyl-3-((trifluoromethyl)thio)-1H-indole (12c):[13c] After purification by silica gel column chromatography (PE: EA = 10: 1), compound **12c** was isolated as a pink solid (105 mg, 91%); R_f (PE: EA = 10: 1) = 0.24; mp (melting point) = 63–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 7.51 (d, J = 2.8 Hz, 1H), 7.26 (d, J = 8.8 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 6.99 (d, J = 6.8 Hz, 1H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 134.0, 131.6, 129.2 (q, J = 307.5 Hz, 1C), 126.7, 123.4, 123.4, 109.7, 95.1 (q, J = 2.6 Hz, 1C), 19.31; ^{19}F NMR (376 MHz, $CDCl_3$): δ −45.88 (s, 3F).

3-((trifluoromethyl)thio)-1H-indol-4-ol (12d):[13c] After purification by silica gel column chromatography (PE: EA = 5: 1), compound **12d** was isolated as a white solid (42 mg, 36%); R_f (PE: EA = 5: 1) = 0.30; mp (melting point) = 120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 7.45 (d, J = 2.8 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 6.72 (s, 1H), 6.71 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 137.7, 132.7, 128.3 (q, J = 310 Hz, 1C), 125.1, 116.5, 107.1, 104.4, 91.6 (q, J = 2.3 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −45.75 (s, 3F).

5-chloro-3-((trifluoromethyl)thio)-1H-indole (12e):[13c] After purification by silica gel column chromatography (PE: EA = 7: 1), compound **12e** was isolated as a brown solid (98 mg, 78%); R_f (PE: EA = 5: 1) = 0.27; mp (melting point) = 57–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 7.66 (d, J = 1.6 Hz, 1H), 7.55 (d, J = 2.8 Hz, 1H), 7.34 (dd, J = 8.4 Hz, 0.3 Hz, 1H), 7.24 (dd, J = 8.4 Hz, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.4, 133.9, 130.7, 129.3 (q, J = 308.1 Hz, 1C), 127.7, 124.0, 118.9, 112.8, 95.5 (q, J = 2.6 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.53 (s, 3F).

5-bromo-3-((trifluoromethyl)thio)-1H-indole (12f):[13c] After purification by silica gel column chromatography (PE: EA = 5: 1), compound **12f** was isolated as a pink solid (115 mg, 78%); R_f (PE: EA = 5: 1) = 0.21; mp (melting point) = 53–55 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.93 (d, J = 1.3 Hz, 1H), 7.54 (d, J = 2.8 Hz, 1H), 7.38 (dd, J = 8.8 Hz, 1.6 Hz, 1H), 7.31 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 133.8 (d, J = 10 Hz, 1C), 131.2, 129.2 (q, J = 308.3 Hz, 1C), 126.6, 122.0, 115.2, 113.1, 95.5 (q, J = 2.4 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.50 (s, 3F).

5-fluoro-3-((trifluoromethyl)thio)-1H-indole (12g):[13c] After purification by silica gel column chromatography (PE: EA = 7: 1), compound **12g** was isolated as a brown solid (101 mg, 86%); R_f (PE: EA = 5: 1) = 0.30; mp (melting point) = 52–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.57 (d, J = 2.8 Hz, 1H), 7.44 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 7.36 (dd, J = 8.8 Hz, 4.0 Hz, 1H), 7.04 (td, J = 9.2 Hz, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1 (d, J = 236.4 Hz, 1C), 134.3, 132.5, 130.4 (d, J = 9.0 Hz, 1C), 129.3 (q, J = 308.0 Hz, 1C), 112.6 (d, J = 9.0 Hz, 1C), 112.2 (d, J = 26.4 Hz, 1C), 104.6 (d, J = 24.5 Hz, 1C), 95.8 (q, J = 2.2 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.62 (s, 3F), −121.59 (s, 1F).

Methyl 3-((trifluoromethyl)thio)-1H-indole-5-carboxylate (12h):[13c] After purification by silica gel column chromatography (PE: EA = 3: 1), compound **12h** was isolated as a white solid (89 mg, 65%); mp (melting point) = 177–179 °C; R_f (PE: EA = 2: 1) = 0.40; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.4 (s, 1H), 8.30 (s, 1H), 8.12 (d, J = 2.8 Hz, 1H), 7.87 (dd, J = 8.6 Hz, 1.6 Hz, 1H), 7.62 (dd, J = 8.6 Hz, 0.4 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 166.7, 139.0, 137.0, 129.3 (q, J = 308.2 Hz, 1C), 128.6, 123.4, 122.6, 120.2, 112.8, 92.8 (q, J = 2.2 Hz, 1C), 51.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.11 (s, 3F).

5-nitro-3-((trifluoromethyl)thio)-1H-indole (12i):[13c] After purification by silica gel column chromatography (PE: EA = 3: 1), compound **12i** was isolated as a yellow solid (46 mg, 35%); R_f (PE: EA = 2: 1) = 0.35; mp (melting point) = 170–172 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.7 (s, 1H), 8.48 (d, J = 2.0 Hz, 1H), 8.25 (d, J = 2.4 Hz, 1H), 8.12 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 7.71 (d, J = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 142.3, 139.6, 139.0, 129.2 (q, J = 308.1 Hz, 1C), 128.5, 117.9, 114.6, 113.6, 94.3 (q, J = 2.4 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −43.97 (s, 3F).

6-fluoro-3-((trifluoromethyl)thio)-1H-indole (12j):[13c] After purification by silica gel column chromatography (PE: EA = 10: 1), compound **12j** was isolated as a brown solid (103 mg, 88%); R_f (PE: EA = 10: 1) = 0.21; mp (melting point) = 60–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 7.71 (dd, J = 8.8 Hz, 5.2 Hz, 1H), 7.51 (d, J = 2.8 Hz, 1H), 7.10 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 7.04 (td, J = 9.2 Hz, 2.2 Hz, 0.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6 (d, J = 238.8 Hz, 1C), 136.0 (d, J = 12.5 Hz, 1C), 133.1, 129.4 (q, J = 308.1 Hz, 1C), 127.8, 120.4 (d, J = 10.1 Hz, 1C), 110.6 (d, J = 24.4 Hz, 1C), 98.1 (d, J = 27.0 Hz, 1C), 96.1 (q, J = 3.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.54 (s, 3F), −119.06 (s, 1F).

6-chloro-3-((trifluoromethyl)thio)-1H-indole (12k):[13c] After purification by silica gel column chromatography (PE: EA = 10: 1), compound **12k** was isolated as a brown solid (88 mg, 70%); R_f (PE: EA = 10: 1) = 0.21; mp (melting point) = 55–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.53 (d, J = 2.8 Hz, 1H), 7.42 (d, J = 1.6 Hz, 1H), 7.24 (dd, J = 8.5 Hz, J = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 133.3, 129.6, 129.3 (q, J = 308.0 Hz, 1C), 128.0, 122.5, 120.4, 111.6, 96.2 (q, J = 2.3 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.46 (s, 3F).

6-methoxy-3-((trifluoromethyl)thio)-1H-indole (12l):[13c] After purification by silica gel column chromatography (PE: EA = 5: 1), compound **12l** was isolated as a pale yellow solid (94 mg, 76%); R_f (PE: EA = 5: 1) = 0.20; mp (melting point) = 161–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.42 (d, J = 2.7 Hz, 1H), 6.95 (dd, J = 8.7 Hz, 2.2 Hz, 1H), 6.89 (d, J = 2.1 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 136.9, 131.6, 129.4 (q, J = 308.1 Hz, 1C), 123.7, 120.0, 111.7, 95.7 (q, J = 2.3 Hz, 1C), 95.0, 55.7 (q, J = 1.8 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.63 (s, 3F).

7-methyl-3-((trifluoromethyl)thio)-1H-indole (12 m):[13c] After purification by silica gel column chromatography (PE: EA = 10: 1), compound **12m** was isolated as a pale yellow solid (102 mg, 88%); R_f (PE: EA = 10: 1) = 0.24; mp (melting point) = 76-77 °C; ^{1}H NMR

(400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 2.8 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.1 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 132.4, 129.4 (q, J = 308.2 Hz, 1C), 129.1, 124.0, 121.8, 120.8, 117.0, 96.2 (q, J = 2.5 Hz, 1C), 16.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.57 (s, 3F).

2-methyl-3-((trifluoromethyl)thio)-1H-indole (12n):[13c] After purification by silica gel column chromatography (PE: EA = 10: 1), compound **12n** was isolated as a pink solid (88 mg, 76%); R_f (PE: EA = 10: 1) = 0.24; mp (melting point) = 58–60 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.71–7.69 (m, 1H), 7.31–7.28 (m, 1H), 7.24–7.19 (m, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 135.0, 130.6, 129.8 (q, J = 309.0 Hz, 1C), 122.6, 121.3, 118.6, 110.8, 92.4 (q, J = 2.2 Hz, 1C), 11.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.46 (s, 3F).

2-phenyl-3-((trifluoromethyl)thio)-1H-indole (12o):[13c] After purification by silica gel column chromatography (PE: EA = 10: 1), compound **12o** was isolated as a brown solid (101 mg, 69%); R_f (PE: EA = 10: 1) = 0.27; mp (melting point) = 83–85 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 7.86–7.84 (m, 1H), 7.78–7.76 (m, 2H), 7.54–7.47 (m, 3H), 7.45–7.41 (m, 1H), 7.33–7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 135.3, 131.4, 130.6, 129.7 (q, J = 309.4 Hz, 1C), 129.2, 128.8, 128.7, 123.7, 121.8, 119.8, 111.2, 92.6 (q, J = 2.3 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −43.43 (s, 3F).

1-methyl-3-((trifluoromethyl)thio)-1H-indole (12p):[13c] After purification by silica gel column chromatography (PE: EA = 20: 1), compound **12p** was isolated as a pale yellow solid (103 mg, 89%); R_f (PE: EA = 10: 1) = 0.50; mp (melting point) = 58–59 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.6 Hz, 1H), 7.38–7.35 (m, 2H), 7.31 (td, J = 6.8 Hz, 1.2 Hz, 1H), 7.27 (td, J = 7.3 Hz, 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 136.9, 130.2, 129.4 (q, J = 308.2 Hz, 1C), 122.9, 121.3, 119.4, 109.8, 93.1 (q, J = 2.3 Hz, 1C), 33.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.95 (s, 3F).

1,2-dimethyl-3-((trifluoromethyl)thio)-1H-indole (12q):[13c] After purification by silica gel column chromatography (PE: EA = 10: 1), compound **12q** was isolated as a pale yellow solid (100 mg, 82%); R_f (PE: EA = 10: 1) = 0.50; mp (melting point) = 114–116 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73–7.71 (m, 1H), 7.33–7.31 (m, 1H), 7.28–7.21 (m, 2H), 3.74 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 136.9, 130.1, 129.8 (q, J = 309.1 Hz, 1C), 122.2, 121.1, 118.7, 109.2, 91.2 (q, J = 2.2 Hz, 1C), 30.3, 10.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.92 (s, 3F).

1-phenyl-3-((trifluoromethyl)thio)-1H-indole (12r):[13c] After purification by silica gel column chromatography (PE), compound **12r** was isolated as a white solid (70 mg, 48%); R_f (PE) = 0.67; mp (melting point) = 53–55 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.87–7.85 (m, 1H), 7.65 (s, 1H), 7.56–7.48 (m, 5H), 7.45–7.41 (m, 1H), 7.34–7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 136.7, 135.9, 130.6, 129.8, 129.4 (q, J = 308.3 Hz, 1C), 127.7, 124.7, 123.7, 122.1, 119.7, 111.1, 96.3 (q, J = 2.3 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.31 (s, 3F).

3-methyl-2-((trifluoromethyl)thio)-1H-indole (12s):[13c] After purification by silica gel column chromatography (PE: EA = 20: 1), compound **12s** was isolated as a pale yellow solid (17 mg, 15%); R_f (PE: EA = 10: 1) = 0.33; mp (melting point) = 92–94 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.54 (dd, J = 8.0 Hz, 0.6 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.25–7.21 (m, 1H), 7.11–7.07 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 128.7 (q, J = 309.8 Hz, 1C), 127.9, 124.8, 123.7, 120.1, 120.0, 113.0 (q, J = 2.2 Hz, 1C), 111.1, 9.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ −43.08 (s, 3F).

Ethyl 2,4-dimethyl-5-((trifluoromethyl)thio)-1H-pyrrole-3-carboxylate (14a):[13c] After purification by silica gel column chromatography (PE: EA = 10: 1), compound **13a** was isolated as a brown solid (87 mg, 65%); R_f (PE: EA = 10: 1) = 0.37; mp (melting point) = 142–145 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 12.04 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.41 (s, 3H), 2.26 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 140.2, 132.1, 128.5 (q, J = 310.3 Hz, 1C), 112.0, 102.9 (q, J = 2.3 Hz, 1C), 58.8, 14.2, 13.5 (q, J = 1.2 Hz, 1C), 11.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.48 (s, 3F).

2,5-dimethyl-1-phenyl-3-((trifluoromethyl)thio)-1H-pyrrole (14b)[13c] After purification by silica gel column chromatography (PE), compound **13b** was isolated as a brown solid (79 mg, 58%); Rf (PE) = 0.47; mp (melting point) = 62–64 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51–7.42 (m, 3H), 7.21–7.18 (m, 2H), 6.12 (s, 1H), 2.10 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.31, 136.57, 129.78 (q, J = 307.5 Hz, 1C), 129.47, 129.36, 128.46, 128.04, 112.62, 97.61 (q, J = 2.2 Hz, 1C), 12.70, 11.10; ^{19}F NMR (376 MHz, $CDCl_3$): δ −45.31 (s, 3F).

2-(4-(trifluoromethyl)phenyl)-5-((trifluoromethyl)thio)-1H-pyrrole (14c)[4f] After purification by silica gel column chromatography (PE: EA = 20: 1), compound **13c** was isolated as a white solid (82 mg, 53%); Rf (PE: EA = 20: 1) = 0.47; mp (melting point) = 40–45 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 6.74 (t, J = 3.2 Hz, 1H), 6.66 (t, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 134.5, 129.4 (q, J = 32 Hz, 1C), 128.3 (q, J = 309 Hz, 1C), 126.1 (q, J = 4 Hz, 1C), 124.4, 124.0 (q, J = 271 Hz, 1C), 123.2, 110.0 (q, J = 2 Hz, 1C), 109.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.77 (s, 3F), - 62.57 (s, 3F).

3-((trifluoromethyl)thio)indolizine-1-carbonitrile (14d): After purification by silica gel column chromatography (PE: EA = 10: 1), compound **13d** was isolated as a yellow solid (75 mg, 62%); R_f (PE: EA = 10: 1) = 0.36; mp (melting point) = 109–110 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 7.0 Hz, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.51 (s, 1H), 7.33 (ddd, J = 8.8 Hz, 6.8 Hz, 0.8 Hz, 1H), 7.03 (td, J = 7.0 Hz, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 129.5, 128.1 (q, J = 311.9 Hz, 1C), 125.3, 124.9, 118.1, 115.0, 114.5, 103.5 (q, J = 2.9 Hz, 1C), 84.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.06 (s); HRMS (ESI) *m/e* calcd for $C_{10}H_6F_3N_2S^+$ $(M+H)^+$ 243.0198, found 243.0198.

3-((trifluoromethyl)thio)indolizine-1-carbonitrile (14e) After purification by silica gel column chromatography (PE: EA = 15: 1), compound **13e** was isolated as a white solid (77 mg, 56%); Rf (PE: EA = 10: 1) = 0.41; mp (melting point) = 85–87 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 7.2 Hz, 1H), 7.08 (s, 1H), 6.97–7.01 (m, 1H), 6.83–6.86 (m, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 136.4, 128.3 (q, J = 311 Hz, 1C), 127.4, 124.1, 121.7, 120.3, 113.9, 104.7, 102.1, 51.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ −43.56 (s, 3F); HRMS (ESI) m/e calcd for $C_{11}H_8F_3NO_2S^+$ $(M+H)^+$ 276.0301, found 276.0300.

6-bromo-3-((trifluoromethyl)thio)indolizine-1-carboxylate (14f) After purification by silica gel column chromatography (PE: EA = 30: 1), compound **13f** was isolated as a white solid (112 mg, 63%); Rf (PE: EA = 30: 1) = 0.26; mp (melting point) = 129–131 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.20 (d, J = 9.6 Hz, 1H), 7.69 (s, 1H), 7.32 (d, J = 9.6 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 137.6, 129.4, 128.5, 128.3 (q, J = 312 Hz, 1C), 124.8, 120.7, 109.3, 106.8, 103.4, 51.5 (q, J = 2.3 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −44.10 (s, 3F); HRMS (ESI) m/e calcd for $C_{11}H_7BrF_3NO_2S^+$ $(M+H)^+$ 352.9328, found 352.9329.

Dimethyl 7-methyl-3-((trifluoromethyl)thio)indolizine-1,2-dicarboxylate (14g) After purification by silica gel column chromatography (PE: EA = 10: 1), compound **13g** was isolated as a white solid (128 mg, 68%); Rf (PE: EA = 10: 1) = 0.27; mp (melting point) = 66–68 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 7.2 Hz, 1H), 8.11 (s, 1H), 6.86 (dd, J = 7.2 Hz, 1.6 Hz, 1H), 4.47 (q, J = 7.2 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 162.8, 139.9, 137.6, 134.7, 128.2 (q, J = 313 Hz, 1C), 123.8, 118.8, 117.4, 102.5, 100.6, 61.9, 60.2, 21.4, 14.3, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ −43.30 (s, 3F); HRMS (ESI) m/e calcd for $C_{16}H_{16}F_3NO_4S^+$ $(M+H)^+$, 376.0825, found 376.0828.

1,3-dimethyl-4-((trifluoromethyl)thio)-1H-pyrazol-5-ol (14h)

After purification by silica gel column chromatography (DCM: MeOH = 10: 1), compound **13h** was isolated as a white solid (42 mg, 40%); R_f (DCM: MeOH = 10: 1) = 0.48; mp (melting point) = 190–192 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.0 (s, 1H), 3.46 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.2, 150.7, 129.5 (q, J = 309 Hz, 1C), 77.8, 33.1, 11.9; ^{19}F NMR (376 MHz, DMSO-d_6): δ −45.50 (s, 3F); HRMS (ESI) m/e calcd for $C_6H_8F_3N_2OS^+$ $(M+H)^+$ 213.0304, found 213.0304.

(trifluoromethyl)(2,4,6-trimethoxyphenyl)sulfane (14i)[13c] After purification by silica gel column chromatography (PE: EA = 30: 1), compound **13i** was isolated as a white solid (87 mg, 65%); R_f (PE: EA = 10: 1) = 0.38; mp (melting point) = 76–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.16 (s, 2H), 3.88 (s, 6H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 163.5, 129.5 (q, J = 308.7 Hz, 1C), 91.9 (q, J = 1.4 Hz, 1C), 91.1, 56.2 (q, J = 2.2 Hz, 1C), 55.4 (q, J = 1.9 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ −43.50 (s, 3F).

Ethyl (E)-3-(benzylamino)-2-((trifluoromethyl)thio)but-2-enoate (14j) After purification by silica gel column chromatography (PE: EA = 20: 1), compound **13j** was isolated as a yellow oil (99 mg, 62%); R_f (PE: EA = 20: 1) = 0.34; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.78 (s, 1H), 7.38–7.24 (m, 5H), 4.51 (d, J = 5.6 Hz, 2H), 4.18 (q, J = 7.2 Hz, 2H), 2.39 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.8, 136.8, 130.0 (q, J = 310 Hz, 1C), 129.0, 127.8, 126.8, 76.6 (q, J = 2.1 Hz, 1C), 60.1, 48.3, 17.7, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ −47.31 (s, 3F). HRMS (ESI) m/e calcd for $C_{14}H_{17}F_3NO_2S^+$ $(M+H)^+$ 320.0927, found 320.0926.

4. Conclusion

In conclusion, we successfully developed a novel transition metal-free method for the direct trifluoromethylthiolation of electron-rich aromatics using CF_3SO_2Na in the presence of $PhPCl_2$. In this protocol, $PhPCl_2$ was employed as both a reducing and a chlorinating reagent of CF_3SO_2Na. Thus, the absence of transition metal-containing reagents from this procedure, in addition to the use of cheap and readily available reagents, render it an alternative strategy for the trifluoromethylthiolation of electron-rich aromatics.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2017.11.019.

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