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Rh(III)-Catalyzed Trifluoromethylthiolation of Indoles via C−H Activation

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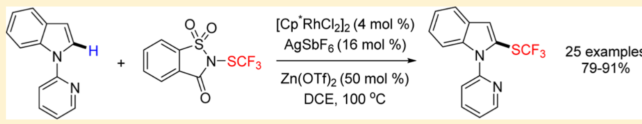
Supporting Information

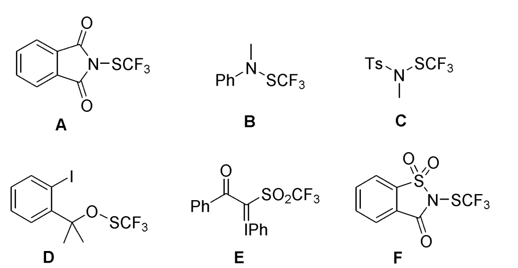
ABSTRACT: Cp*Rh(III) complexes have been applied as efficient catalysts for the C−H activation and trifluoromethylthiolation of indoles functionalized with a heterocycle. With *N*-trifluoromethylthiosaccharin being an electrophilic SCF_3 reagent, this C−S coupling occurred selectively at the 2-position with good functional group tolerance.



It has been well accepted that incorporation of a SCF_3 moiety into organic molecules greatly contributes to enhancement of transmembrane permeation owing to the enhancement of the lipophilicity, solubility, metabolic stability, and bioavailability of the molecule.[1] Thus, the introduction of a trifluoromethylthio group has been of great interest to the pharmaceutical and agrochemical industries for its utilization in isosetere-based drug design.[2] Over the decades, much attention has been devoted to the development of convenient methods for introduction of the trifluoromethylthio group into organic molecules.[3]

Earlier, halogen−fluorine exchange reactions of polyhalogenomethyl thioethers[4] or trifluoromethylthiolation of sulfur-containing compounds such as disulfides, thiocyanates, and thiols via a single-electron transfer mechanism[5] were typically employed to introduce a SCF_3 moiety. However, the harsh reaction conditions limited its utilization. In this context, the trifluoromethylthiolation of compounds such as (hetero)aryl halides have been developed employing nucleophilic trifluoromethylthiolation reagents such as $AgSCF_3$, $CuSCF_3$, and NH_4SCF_3. These reagents are generally not sufficiently stable; making it inconvenient for storage overextended periods.[6] Therefore, the development of important methodologies for $C-SCF_3$ bond formation has received increasing attention. Thus, some shelf-stable and easy-to-handle reagents have been developed for electrophilic trifluoromethylthiolation of arenes. Among them, Munavalli's *N*-trifluoromethylthiophthalimide (**A**, Scheme 1),[7] Billard's trifluoromethanesulfanylamides (**B**),[8] and Lu and Shen's trifluoromethanesulfenate (**D**)[9] have received significant attention. In addition, Shibata described an elegant method of trifluomethylthiolation using a stable hypervalent iodine reagent **E**, which releases a SCF_3 group upon reduction and rearrangement. These reagents showed high reactivity toward terminal alkynes, β-ketoesters, and arylboronic acid. In addition, Shen[10a] and our group[10b] independently reported reagent **F** for the trifluoromethylthiolation of electron-rich arenes. Shen also reported that terminal alkynes, amines, alcohols, and ketoesters are also viable substrates besides arenes.[10a]

Scheme 1. Shelf-Stable Trifluoromethylthiolating Reagents



Chemical transformations through transition-metal-catalyzed C−H bond activation represent one of the most promising strategies in organic synthesis.[11] In this context, C−S coupling has been realized via C−H activation of arenes under palladium-,[12] copper-,[13] and rhodium-catalyzed[14] conditions when functionalized by electrophilic sulfur reagents. However, trifluoromethylthiolation of arenes through direct C−H bond activation is still rare and only a few systems have been reported.[15] Recently, it has been demonstrated that Cp*Rh(III) complexes are highly active in the C−H activation of a broad scope of arenes with high functional group compatibility under relatively mild conditions. While no rhodium(III)-catalyzed C−H trifluoromethylthiolation has been reported, we reasoned that the rather high activity of rhodium(III) complexes and the high polarity and nucleophilicity of the Rh(III)-aryl bond may bode well for trifluoromethylthiolation of arenes via a formal S_N type transformation.[16]

We initiated our studies by optimizing the coupling reaction conditions of 2-pyridyl-5-chloroindole (**1i**) with reagent **F**. When $[Cp{*}RhCl_2]_2/AgSbF_6$ was applied as the catalyst in DCE at 50 °C, the expected trifluoromethylthiolation reaction occurred in low efficiency, and the product **2i** was isolated in only 32% yield (Table 1, entry 1). The use of an electrophilic Ag(I) additive proved necessary since omission of it or switching to other silver salts led to lower yields (Table 1, entries 4, 5).

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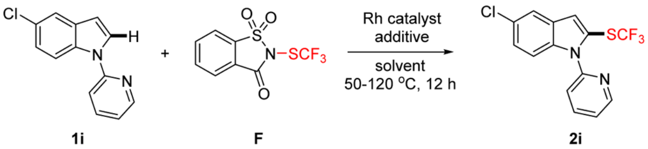
Table 1. Optimization Studies[a]



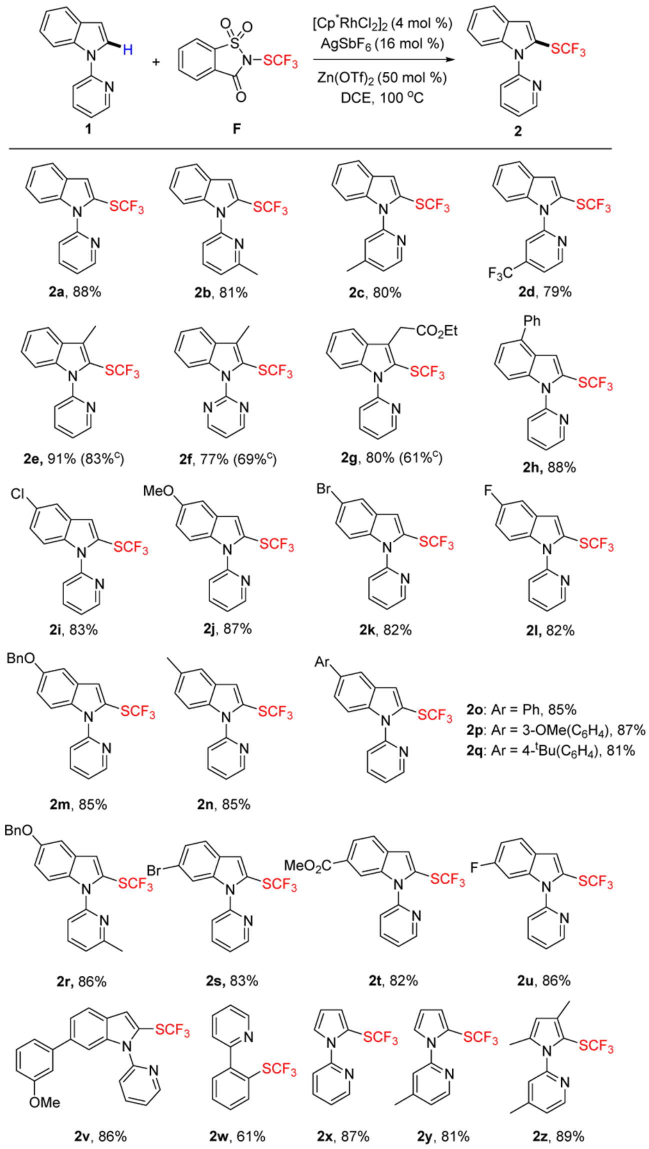
entry	silver salt	additive (mol %)	temp (°C)	solvent	yield[b]
1	$AgSbF_6$	–	50	DCE	32%
2	–	–	50	DCE	N.D.
3	$AgSbF_6$	$Zn(OTf)_2$ (30)	50	DCE	41%
4	AgOAc	$Zn(OTf)_2$ (30)	50	DCE	22%
5	AgOTf	$Zn(OTf)_2$ (30)	50	DCE	20%
6	$AgSbF_6$	$Zn(OTf)_2$ (30)	50	dioxane	N.D.
7[c]	–	$Zn(OTf)_2$ (30)	50	DCE	23%
8[d]	–	$Zn(OTf)_2$ (30)	50	DCE	20%
9	$AgSbF_6$	–	80	DCE	65%
10	$AgSbF_6$	–	100	DCE	77%
11	$AgSbF_6$	$Zn(OTf)_2$ (30)	100	DCE	81%
12	**$AgSbF_6$**	**$Zn(OTf)_2$ (50)**	**100**	**DCE**	**83%**
13	$AgSbF_6$	$Zn(OTf)_2$ (50)	100	THF	57%
14	$AgSbF_6$	$Zn(OTf)_2$ (50)	100	*t*-AmOH	N.D.
15	$AgSbF_6$	$Zn(OTf)_2$ (50)	100	DCM	81%
16	$AgSbF_6$	$Zn(OTf)_2$ (50)	120	DCE	87%
17	$AgSbF_6$	$Cu(OTf)_2$ (50)	100	DCE	53%

[a]Conditions: indole **1i** (0.2 mmol), reagent **F** (0.2 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), additive, solvent (3 mL), sealed tube under a N_2 atmosphere, 12 h. [b]Isolated yield. [c]$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (8 mol %) was used as a catalyst. [d]$[Cp^*Rh(H_2O)_3](OTf)_2$ (8 mol %) was used as a catalyst.

Furthermore, switching to a preformed cationic rhodium complex such as $[Cp^*Rh(MeCN)_3](SbF_6)_2$ and $[Cp^*Rh(H_2O)_3](OTf)_2$ all gave inferior results (entries 7, 8). The reaction efficiency is strongly temperature dependent (entries 9), and an isolated yield of 77% was obtained when the temperature was raised to 100 °C (entry 10). Our previous work indicated that a Lewis acid can effectively activate reagent **F**.[10b] Thus, the product was isolated in 83% yield when $Zn(OTf)_2$ (50 mol %) was further introduced as an additive (entry 11). The role of the Zn(II) is likely a suitable Lewis acid. When we replaced the $Zn(OTf)_2$ with $Cu(OTf)_2$ (Table 1, entry 17), the product yield decreased sharply, which may indicate that the oxidizing property is not related in this reaction system. Screening of solvents revealed that DCE seems optimal (entries 12 to 15).

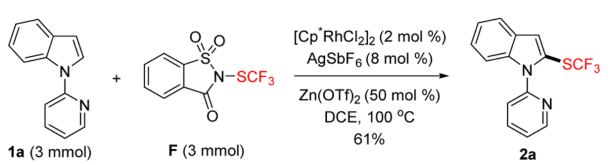
With the established optimal conditions, we next explored the scope of the indole substrate (Scheme 2). It turned out that indoles bearing various electron-donating and -withdrawing groups at different positions all coupled smoothly. In addition, a bromide substituent was also compatible (**2k**, **2s**), which should offer opportunity for further functionalization. A slight decrease of the yield was observed when pyrimidine was used as a directing group (**2f**). We noted that, in the absence of the rhodium and the silver additive, the reaction of indoles with blocked 3-positions (**2e**–**g**) could also proceed albeit in lower yields. This observation indicates that this transformation can be catalyzed by Lewis acids, which is consistent with our latest report.[10b] The arene is not limited to indoles; the coupling of 2-(1*H*-pyrrol-1-yl)pyridine occurred in high yield (**2x**–**z**). In addition, trifluoromethylthiolation of 2-phenylpyridine[15b] could also be realized under the standard conditions, albeit with a somewhat lower yield (**2w**).

Scheme 2. Substrate Scope for Trifluoromethylthiolation[a,b]



[a]Reaction conditions: arene (0.2 mmol), **F** (0.2 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), and $Zn(OTf)_2$ (50 mol %), DCE (3 mL), 100 °C, sealed tube under N_2 for 12 h. [b]Isolated yield. [c]Standard conditions except that the Rh(III) catalyst and $AgSbF_6$ were omitted.

Furthermore, when the reaction was performed in a 3 mmol scale with a decreased catalyst loading of 2 mol %, the corresponding product could be isolated in moderate yield under air (eq 1), which demonstrates the potential synthetic utilization of this transformation.



(1)

In contrast, when 1-phenyl-1*H*-indole was used as a substrate under the standard conditions, the functionalization occurred exclusively at the 3-position (eq 2). Thus, the selectivity is correlated to the *N*-substituent. In the presence of an *N*-directing group, the reaction occurred via a C–H activation pathway, while

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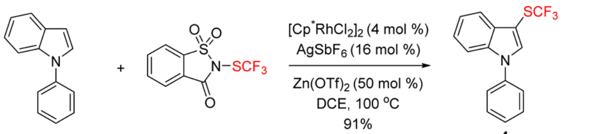
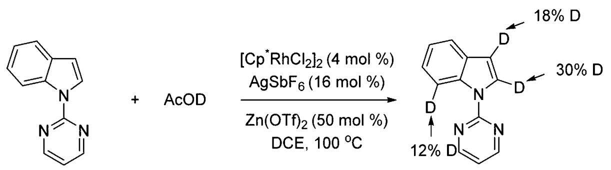


(2)

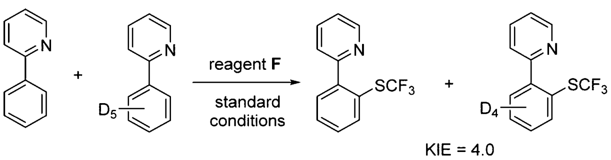
in the absence of such a group the reaction is Lewis acid catalyzed.[10b]

Preliminary mechanistic studies have been performed. When the reaction of 1-(pyrimidin-2-yl)-1*H*-indole was conducted under conditions with CD_3CO_2D in the absence of reagent **F**, H/D exchange at the 2-, 3-, and 7-positions was observed, indicating that the initial C−H activation at the 2-position is reversible (eq 3). A significant primary kinetic isotope effect ($k_H/k_D = 4.0$) was



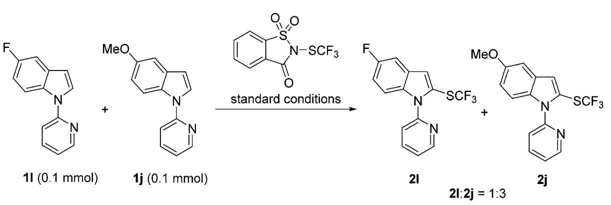
(3)

observed from an intermolecular competitive coupling using an equimolar mixture of 2-phenyl- and 2-phenylpyridine-d_5 (eq 4). This relatively large value suggests that C−H activation is probably involved in the catalytic cycle.[17]



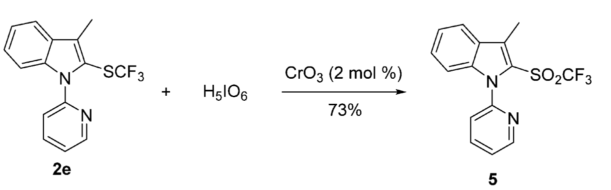
(4)

We further performed an intermolecular competition experiment using an equimolar mixture of two indoles (**1l** and **1j**) that differ in electronic effect (eq 5). ^{1}H NMR analysis of the product mixture revealed that products **2l** and **2j** were generated in a nearly 1:3 ratio, indicating that an electron-rich indole is kinetically favored.



(5)

Oxidation of **2e** using H_5IO_6 catalyzed by CrO_3 afforded the corresponding sulfone **5** in 73% yield (eq 6), which is another class of useful fluorine-containing products.



(6)

In conclusion, we have developed the first example of a Rh(III)-catalyzed electrophilic trifluoromethylthiolation of arenes via a C−H activaton pathway. The reaction occurred selectively at the 2-position. Moreover, this coupling system gives high efficiency and tolerates a broad range of substrates bearing different functional groups. This coupling system expanded the scope of Rh(III)-catalyzed C−H activation. Future work will be directed to other electrophilic functionalizations of arenes via C−H activation.

■ EXPERIMENTAL SECTION

All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox. All reagents were obtained from commercial sources and were used without further purification. NMR spectra were recorded on a spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), and 376 MHz (^{19}F NMR). All coupling constants were reported in Hz. HRMS data were obtained via ESI mode with a TOF mass analyzer.

Preparation of *N*-(Trifluoromethylthio)saccharin (F).[10b] To a solution of *N*-bromosaccharin (5 mmol, 1.31 g) in CH_3CN (10 mL) was added a solution of $AgSCF_3$ (5 mmol, 1.05 g) with CH_3CN (10 mL). After the reaction was stirred at room temperature for 3 h, the solvent was removed under reduced pressure, and then the crude product was purified by flash column chromatography (CH_2Cl_2) to yield *N*-(trifluoromethylthio)saccharin (**F**, 1.07 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 7.6 Hz, 1H), 8.03 (t, J = 6.8 Hz, 2H), 7.94 (t, J = 6.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 137.9, 136.3, 134.9, 127.2 (q, J = 315 Hz), 126.5, 126.1, 120.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −47.33. HRMS (M + H) calcd for $C_8H_4F_3NO_3S_2$: m/z 283.9663; found: 283.9660.

Procedures for the Trifluoromethylthiolation of Indoles. *N*-(Trifluoromethylthio)saccharin (**F**, 0.2 mmol, 59.5 mg) and a substituted indole (0.2 mmol) were added to a pressure tube equipped with a magnetic stir bar, to which were added $(Cp^*RhCl_2)_2$ (0.008 mmol, 2.5 mg, 4 mol %), $AgSbF_6$ (0.032 mmol, 5.5 mg), and DCE (3 mL). The reaction tube was placed into a preheated oil bath at 100 °C and was heated for 12 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel (300−400 mesh) column chromatography to provide the final product **2**.

*1-(Pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2a**).* By following the general procedure, **2a** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (52 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, J = 4.8, 1.4 Hz, 1H), 7.94 (td, J = 7.8, 1.9 Hz, 1H), 7.70 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.3 Hz, 1H), 7.39 (dd, J = 7.4, 4.9 Hz, 1H), 7.34−7.28 (m, 1H), 7.26−7.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 149.5, 139.2, 138.2, 128.3 (q, J = 309 Hz), 127.4, 125.0, 122.8, 122.1, 121.6, 121.3, 118.9, 117.6, 111.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.70. HRMS m/z (M + H) calcd for $C_{14}H_9F_3N_2S$: 295.0517; found: 295.0524. Mp 61−62 °C.

*1-(6-Methylpyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2b**).* By following the general procedure, **2b** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 60/1) as a solid (50 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, J = 7.7 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.24 (ddt, J = 19.1, 12.7, 3.3 Hz, 5H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 149.2, 139.0, 138.4, 128.3 (q, J = 309 Hz), 127.4, 124.8, 122.38, 121.5, 121.3, 119.1, 118.8, 117.0, 111.4, 24.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.60. HRMS m/z (M + H) calcd for $C_{15}H_{11}F_3N_2S$: 309.0673; found: 309.0686. Mp 60−61 °C.

*1-(4-Methylpyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2c**).* By following the general procedure, **2c** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2/diethyl ether: 50/2/1) as an oil (50 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.79−7.63 (m, 2H), 7.37 (t, J = 9.0 Hz, 2H), 7.30 (t, J = 7.7 Hz, 1H), 7.25−7.18 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 147.7, 139.3, 138.7, 132.8, 128.2 (q, J = 309 Hz), 127.3, 124.8, 121.6, 121.4, 121.3, 118.9, 117.2, 111.3, 18.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.69. HRMS m/z (M + H) calcd for $C_{15}H_{11}F_3N_2S$: 309.0673; found: 309.0675.

*1-(4-(Trifluoromethyl)pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2d**).* By following the general procedure, **2d** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (57 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95−8.90 (m,

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1H), 8.13 (dd, J = 8.4, 2.3 Hz, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.36−7.29 (m, 1H), 7.30−7.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 146.6 (q, J = 4 Hz), 138.8, 135.6 (q, J = 4 Hz), 128.1 (q, J = 309 Hz) 127.7, 125.6, 125.3 (q, J = 34 Hz), 122.3, 121.6, 121.2, 119.1, 118.8 (q, J = 2 Hz), 113.8, 111.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.72, −62.11. HRMS m/z (M + H) calcd for $C_{15}H_8F_6N_2S$: 363.0391; found: 363.0403. Mp 70−71 °C.

3-Methyl-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2e**). By following the general procedure, **2e** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (55 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60−8.54 (m, 1H), 7.79 (td, J = 7.7, 1.9 Hz, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.35−7.28 (m, 2H), 7.27−7.17 (m, 2H), 7.17−7.09 (m, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 149.5, 139.0, 138.09, 128.6 (q, J = 310 Hz), 127.7, 127.1, 125.5, 122.6, 122.5, 121.0, 120.0, 115.8 (q, J = 2 Hz), 111.4, 10.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.25. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.25. HRMS m/z (M + H) calcd for $C_{15}H_{11}F_3N_2S$: 309.0673; found: 309.0682. Mp 65−66 °C.

3-Methyl-1-(pyrimidin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2f**). By following the general procedure, **2f** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (49 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, J = 4.8, 1.2 Hz, 2H), 8.00 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.16 (dd, J = 14.7, 7.4 Hz, 1H), 7.08 (dd, J = 8.7, 4.0 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 157.1, 138.4, 130.1, 128.9 (q, J = 310 Hz), 128.5, 126.2, 122.0, 119.9, 117.9, 116.2, 116.1, 113.2, 10.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.05. HRMS m/z (M + H) calcd for $C_{14}H_{10}F_3N_3S$: 309.0673; found: 309.0679. Mp 58−59 °C.

Ethyl-2-(1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indol-3-yl)-acetate (**2g**). By following the general procedure, **2g** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 30/1) as a solid (61 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 4.8, 1.2 Hz, 1H), 7.92 (td, J = 7.8, 1.9 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.39 (dt, J = 6.2, 3.1 Hz, 2H), 7.35−7.28 (m, 1H), 7.23 (dd, J = 11.4, 4.4 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 4.06 (s, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 150.2, 149.6, 139.1, 138.2, 128.1 (q, J = 311 Hz), 126.9, 125.7, 123.3, 122.9, 122.7, 121.5, 120.5, 117.3, 111.5, 61.0, 31.6, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.01. HRMS m/z (M + H) calcd for $C_{18}H_{15}F_3N_2O_2S$: 381.0885; found: 381.0885. Mp 89−90 °C.

4-Phenyl-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2h**). By following the general procedure, **2h** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (70 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, J = 4.9, 1.2 Hz, 1H), 7.96 (td, J = 7.7, 1.9 Hz, 1H), 7.72 (d, J = 7.4 Hz, 2H), 7.54 (dd, J = 16.1, 8.0 Hz, 3H), 7.48−7.36 (m, 5H), 7.31 (dd, J = 6.2, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 149.6, 140.2, 139.8, 138.3, 135.4, 128.8, 128.7, 128.2 (q, J = 309 Hz), 127.5, 125.8, 125.3, 123.0, 122.3, 121.4, 119.2 (q, J = 2 Hz), 117.2, 110.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.57. HRMS m/z (M + H) calcd for $C_{20}H_{13}F_3N_2S$: 371.0830; found: 371.0837. Mp 135−136 °C.

5-Chloro-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2i**). By following the general procedure, **2i** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (54 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66−8.54 (m, 1H), 7.86 (td, J = 7.8, 1.8 Hz, 1H), 7.57 (d, J = 1.9 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.32 (dd, J = 7.3, 5.1 Hz, 1H), 7.27 (d, J = 8.9 Hz, 1H), 7.16 (dd, J = 8.9, 1.9 Hz, 1H), 7.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 149.6, 138.4, 137.4, 128.2, 128.1 (q, J = 309 Hz), 127.3, 123.4, 123.1, 121.9, 120.6, 120.5 (q, J = 2 Hz), 116.6, 112.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.44. HRMS m/z (M + H) calcd for $C_{14}H_8ClF_3N_2S$: 329.0127; found: 329.0130. Mp 75−77 °C.

5-Methoxy-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2j**). By following the general procedure, **2j** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 20/1) as a solid (56 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, J = 4.8, 1.2 Hz, 1H), 7.91 (td, J = 7.7, 1.7 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 6.8 Hz, 2H), 7.15 (s, 1H), 7.09 (d, J = 2.4 Hz, 1H), 6.96 (dd, J = 9.1, 2.5 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.27, 150.12, 149.47, 138.28, 134.50, 128.2 (q, J = 309 Hz), 127.83, 122.72, 121.88, 118.77, 117.22, 115.92, 112.47, 102.00, 55.75. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.79. HRMS m/z (M + H) calcd for $C_{15}H_{11}F_3N_2OS$: 325.0622; found: 325.0627. Mp 66−67 °C.

5-Bromo-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2k**). By following the general procedure, **2k** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (61 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 4.8, 1.0 Hz, 1H), 7.94 (td, J = 7.8, 1.8 Hz, 1H), 7.82 (d, J = 1.5 Hz, 1H), 7.47−7.36 (m, 3H), 7.30 (d, J = 8.9 Hz, 1H), 7.16 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.64, 149.61, 138.5, 137.7, 128.8, 128.1 (q, J = 309 Hz), 127.9, 123.7, 123.2, 122.0, 120.3, 116.5, 114.8, 113.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.43. HRMS m/z (M + H) calcd for $C_{14}H_8BrF_3N_2S$: 372.9622; found: 372.9627. Mp 76−77 °C.

5-Fluoro-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2l**). By following the general procedure, **2l** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 60/1) as a solid (51 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 4.8, 1.2 Hz, 1H), 7.94 (td, J = 7.8, 1.8 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.39 (ddd, J = 13.6, 8.2, 4.6 Hz, 2H), 7.33 (dd, J = 8.9, 2.4 Hz, 1H), 7.19 (s, 1H), 7.05 (td, J = 9.1, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 (d, J = 237 Hz), 149.8, 149.6, 138.4, 135.7, 128.1 (q, J = 309 Hz), 127.6 (d, J = 10 Hz), 123.1, 122.0, 120.5, 117.1, 117.0, 113.7 (d, J = 26 Hz), 112.6 (d, J = 10 Hz), 105,9 (d, J = 24 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.50, −121.81. HRMS m/z (M + H) calcd for $C_{14}H_8F_4N_2S$: 313.0423; found: 313.0437. Mp 59−60 °C.

5-(Benzyloxy)-1-(pyridin-2-yl)-2-(trifluoro-methylthio)-1H-indole (**2m**). By following the general procedure, **2m** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 20/1) as a solid (67 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71−8.64 (m, 1H), 7.91 (td, J = 7.7, 1.1 Hz, 1H), 7.51 (d, J = 7.2 Hz, 2H), 7.40 (ddd, J = 12.5, 10.7, 6.6 Hz, 6H), 7.19 (td, J = 8.2, 2.5 Hz, 1H), 7.01 (dd, J = 8.3, 3.1 Hz, 1H), 6.65 (dd, J = 7.8, 2.1 Hz, 1H), 5.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 150.1, 149.5, 140.7, 138.2, 137.0, 128.2 (q, J = 310 Hz), 128.6, 128.0, 127.4, 126.1, 122.9, 122.2, 118.9, 117.1, 115.5, 104.7, 102.4, 70.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.85. HRMS m/z (M + H) calcd for $C_{21}H_{15}F_3N_2OS$: 401.0935; found: 401.0943. Mp 120−121 °C.

5-Methyl-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2n**). By following the general procedure, **2n** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (52 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, J = 4.8, 1.1 Hz, 1H), 7.89 (td, J = 7.8, 1.8 Hz, 1H), 7.48−7.40 (m, 2H), 7.38−7.28 (m, 2H), 7.18−7.03 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 149.4, 138.2, 137.6, 131.0, 128.3 (q, J = 309 Hz), 127.6, 126.7, 122.6, 121.8, 120.7, 118.6, 117.2, 111.1, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.79. HRMS m/z (M + H) calcd for $C_{15}H_{11}F_3N_2S$: 309.0673; found: 309.0675. Mp 57−58 °C.

5-Phenyl-1-(pyridin-2-yl)-2-(trifluoromethyl thio)-1H-indole (**2o**). By following the general procedure, **2o** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (63 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 4.9, 1.2 Hz, 1H), 7.91 (td, J = 7.8, 1.9 Hz, 1H), 7.87 (d, J = 1.2 Hz, 1H), 7.64−7.60 (m, 2H), 7.55 (dd, J = 8.7, 1.7 Hz, 1H), 7.50−7.40 (m, 4H), 7.39−7.32 (m, 2H), 7.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 149.5, 141.7, 138.6, 138.3, 135.2, 128.8, 128.3 (q, J = 309 Hz), 127.9, 127.3, 126.8, 124.9, 122.9, 121.9, 119.7, 119.5 (q, J = 2 Hz), 117.8, 111.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.58. HRMS m/z (M + H) calcd for $C_{20}H_{13}F_3N_2S$: 371.0830; found: 371.0836. Mp 91−92 °C.

5-(3-Methoxyphenyl)-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2p**). By following the general procedure, **2p** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 60/1) as a solid (69 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, J = 4.8, 1.0 Hz, 1H), 7.93 (t, J = 7.7 Hz, 1H), 7.89 (s, 1H), 7.55 (dd, J = 8.7, 1.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.38 (dd, J = 14.8, 7.5 Hz, 2H), 7.29 (s, 1H), 7.26−7.20 (m, 1H), 7.17 (s, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 150.0, 149.6, 143.2, 138.6, 138.3, 135.0, 129.7, 128.3 (q, J = 309 Hz), 127.8, 126.6, 124.9, 122.9, 121.9, 119.8, 119.7, 119.5, 117.8, 113.1, 112.2, 111.7, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.59. HRMS m/z (M + H) calcd for $C_{21}H_{15}F_3N_2OS$: 401.0935; found: 401.0936. Mp 127−128 °C.

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*5-(4-tert-Butylphenyl)-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2q**).* By following the general procedure, **2q** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (73 mg, 81%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, J = 4.8, 1.2 Hz, 1H), 7.93 (td, J = 7.8, 1.9 Hz, 1H), 7.88 (d, J = 1.0 Hz, 1H), 7.56 (dd, J = 13.8, 5.0 Hz, 3H), 7.51−7.46 (m, 4H), 7.39 (dd, J = 7.4, 4.9 Hz, 1H), 7.28 (s, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 149.8, 149.5, 138.7, 138.52 138.3, 135.1, 128.3 (q, J = 310 Hz), 127.8, 127.0, 125.7, 124.9, 119.5, 119.3, 117.9, 111.6, 34.5, 31.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.63. HRMS m/z (M + H) calcd for $C_{24}H_{21}F_3N_2S$: 427.1456; found: 427.1453. Mp 90−91 °C.

*5-(Benzyloxy)-1-(6-methylpyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2r**).* By following the general procedure, **2r** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 30/1) as a solid (69 mg, 86%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (t, J = 7.7 Hz, 1H), 7.49 (d, J = 7.3 Hz, 2H), 7.39 (t, J = 7.3 Hz, 3H), 7.32 (t, J = 7.2 Hz, 1H), 7.24−7.12 (m, 3H), 7.00 (d, J = 8.4 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 5.22 (s, 2H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 152.4, 149.3, 140.6, 138.3, 137.1, 128.5, 128.3 (q, J = 309 Hz),127.9, 127.3, 126.7, 125.8, 122.4, 118.9, 117.2, 115.0, 104.7, 102.3, 70.0, 24.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.73. HRMS m/z (M + H) calcd for $C_{22}H_{17}F_3N_2OS$: 415.1092; found: 415.1092. Mp 99−100 °C.

*6-Bromo-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2s**).* By following the general procedure, **2s** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (62 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 3.8 Hz, 1H), 7.94 (td, J = 7.8, 1.7 Hz, 1H), 7.59 (s, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.46−7.37 (m, 2H), 7.32 (dd, J = 8.5, 1.3 Hz, 1H), 7.19 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 149.5, 139.7, 138.4, 128.0 (q, J = 309 Hz), 126.1, 125.1, 123.2, 122.5, 122.0, 119.7, 119.7 (q, J = 2 Hz), 117.5, 114.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.54. HRMS m/z (M + H) calcd for $C_{14}H_8BrF_3N_2S$: 372.9622; found: 372.9625. Mp 80−81 °C.

*Methyl-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole-6-carboxylate (**2t**).* By following the general procedure, **2t** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 20/1) as a solid (57 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.72−8.69 (m, 1H), 8.13 (s, 1H), 7.99 (td, J = 7.8, 1.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.49−7.41 (m, 1H), 7.25 (s, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 149.7, 149.4, 138.7, 138.3, 130.7, 128.2 (q, J = 309 Hz), 126.5, 123.3, 122.8, 122.4, 122.0, 121.1, 116.5, 113.5, 52.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.11. HRMS m/z (M + H) calcd for $C_{16}H_{11}F_3N_2O_2S$: 353.0572; found: 353.0568. Mp 88−89 °C.

*6-Fluoro-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2u**).* By following the general procedure, **2u** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (53 mg, 86%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.73−8.60 (m, 1H), 7.94 (td, J = 7.8, 1.9 Hz, 1H), 7.62 (dd, J = 8.7, 5.4 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.42−7.38 (m, 1H), 7.23 (s, 1H), 7.15 (dd, J = 9.8, 2.2 Hz, 1H), 7.00 (td, J = 9.1, 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, J = 241 Hz), 149.7, 149.6, 139.4 (d, J = 12 Hz), 138.4, 128.1 (q, J = 309 Hz), 123.8, 123.1, 122.5 (d, J = 10 Hz), 121.9, 119.0, 117.9, 110.1 (d, J = 24 Hz), 98.1(d, J = 27 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.85, −115.72. HRMS m/z (M + H) calcd for $C_{14}H_8F_4N_2S$: 313.0423; found: 313.0429. Mp 60−61 °C.

*6-(3-Methoxyphenyl)-1-(pyridin-2-yl)-2-(trifluoromethylthio)-1H-indole (**2v**).* By following the general procedure, **2v** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as a solid (69 mg, 86%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.62−8.54 (m, 1H), 7.83 (td, J = 7.8, 1.8 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.49 (s, 1H), 7.37 (dd, J = 11.2, 4.4 Hz, 2H), 7.28 (dd, J = 7.3, 5.0 Hz, 1H), 7.23 (t, J = 7.9 Hz, 1H), 7.16 (s, 1H), 7.07 (d, J = 7.7 Hz, 1H), 7.03 (d, J = 1.9 Hz, 1H), 6.77 (dd, J = 8.1, 2.3 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 150.0, 149.6, 143.3, 139.6, 138.5, 138.4, 129.7, 128.3 (q, J = 310 Hz), 126.8, 123.0, 122.2, 121.7, 121.6, 120.1, 119.4 (q, J = 2 Hz), 117.5, 113.5, 112.3, 109.9, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.63. HRMS m/z (M + H) calcd for $C_{21}H_{15}F_3N_2OS$: 401.0935; found: 401.0937. Mp 110−112 °C.

*2-(2-(Trifluoromethylthio)phenyl)pyridine (**2w**).*[10a] By following the general procedure, **2w** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 60/1) as an oil (31 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 4.8 Hz, 1H), 7.80 (dd, J = 8.5, 4.3 Hz, 2H), 7.60 (d, J = 7.6 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.35−7.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 148.9, 145.2, 136.2, 135.8, 130.7, 130.1, 129.6 (q, J = 307 Hz), 129.1, 124.2, 124.1, 122.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.76. HRMS m/z (M + H) calcd for $C_{12}H_8F_3NS$: 256.0408; found: 256.0405.

*2-(2-(Trifluoromethylthio)-1H-pyrrol-1-yl)pyridine (**2x**).* By following the general procedure, **2x** was isolated by column chromatography on silica gel (Petroleum ether/CH_2Cl_2: 50/1) as a solid (43 mg, 87%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, J = 4.8, 1.1 Hz, 1H), 7.85 (td, J = 7.8, 1.9 Hz, 1H), 7.53−7.44 (m, 2H), 7.35−7.28 (m, 1H), 6.87 (dd, J = 3.6, 1.8 Hz, 1H), 6.41 (t, J = 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 150.9, 149.0, 138.0, 128.2 (q, J = 311 Hz), 127.8, 125.5, 122.5, 119.4, 110.6. HRMS m/z (M + H) calcd for $C_{10}H_7F_3N_2S$: 245.0360; found: 245.0365. Mp 55−56 °C.

*4-Methyl-2-(2-(trifluoromethylthio)-1H-pyrrol-1-yl)pyridine (**2y**).* By following the general procedure, **2y** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 60/1) as an oil (41 mg, 81%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 5.0 Hz, 1H), 7.42 (s, 1H), 7.27 (s, 1H), 7.13 (d, J = 4.8 Hz, 1H), 6.86 (d, J = 1.8 Hz, 1H), 6.39 (t, J = 3.3 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 149.6, 148.6, 128.2 (q, J = 310 Hz), 127.8, 125.2, 123.7, 120.3, 110.5, 109.5, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ −45.26. HRMS m/z (M + H) calcd for $C_{11}H_9F_3N_2S$: 259.0517; found: 259.0511.

*2-(3,5-Dimethyl-2-(trifluoromethylthio)-1H-pyrrol-1-yl)-4-methylpyridine (**2z**).* By following the general procedure, **2z** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 70/1) as an oil (51 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 5.0 Hz, 1H), 7.18 (d, J = 5.0 Hz, 1H), 7.07 (s, 1H), 6.02 (s, 1H), 2.45 (s, 3H), 2.24 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 149.4, 148.8, 136.0, 132.9, 128.5 (q, J = 312 Hz), 124.3, 124.2, 110.8, 106.7, 21.0, 13.4, 12.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −45.29. HRMS m/z (M + H) calcd for $C_{13}H_{13}F_3N_2S$: 287.0830; found: 287.0819.

*1-Phenyl-3-(trifluoromethylthio)-1H-indole (**4**).*[10b] By following the general procedure, **4** was isolated by column chromatography on silica gel (petroleum ether/CH_2Cl_2: 50/1) as an oil (31 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (m, 1H), 7.64 (s, 1H), 7.56−7.47 (m, 5H), 7.43 (m, 1H), 7.35−7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 136.9, 136.2, 130.8, 130.1, 129.5(q, J = 268 Hz), 127.9, 124.9, 123.9, 122.3, 119.9, 111.3, 96.5 (d, J = 2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −44.30. HRMS m/z (M + H) calcd for $C_{15}H_{10}F_3NS$: 294.0564; found: 294.0567.

KIE Experiment. By following the standard procedure for the trifluoromethylthiolation reaction, to a mixture of 2-phenylpyridine (0.1 mmol) and 2-phenylpyridine-d_5 (0.1 mmol) were added *N*-(trifluoromethylthio)saccharin (F, 0.2 mmol), $(Cp^*RhCl_2)_2$ (0.008 mmol, 2.5 mg, 4 mol %), $AgSbF_6$ (0.032 mmol, 5.5 mg), and DCE (3 mL). The reaction mixture was placed into a preheated oil bath at 100 °C and was heated for 12 h. The product was purified by silica gel column chromatography, and the KIE value was determined by NMR spectroscopy.

Oxidation of a Sulfide to a Sulfone. By following a reported procedure,[18] H_5IO_6 (136.7 mg, 0.6 mmol) was dissolved in acetonitrile (10 mL) by vigorous stirring at room temperature for 30 min, and then CrO_3 (0.3 mg, 0.003 mmol, 2 mol %) was added to the solution. To this solution was then added a solution of **2e** (46.2 mg, 0.15 mmol) in CH_3CN (10 mL) at room temperature. The reaction mixture was stirred at room temperature until the oxidation was completed (monitored by TLC). The mixture was then filtered, and the filter cake was washed with CH_3CN (10 mL). The filtrate was concentrated under reduced pressure, and the residue was extracted with ethyl acetate. The combined extracts were washed with a saturated aqueous Na_2SO_3 solution and brine and were then dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by flash silica gel column chromatography (petroleum ether/EtOAc: 10/1) to provide the *1-methyl-4-nitro-3-(trifluoromethylsulfonyl)-1H-indole* (**5**, 36.8 mg, 96%) as a white solid. NMR spectra, ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, J = 4.9, 1.2 Hz, 1H), 7.92−7.84 (m, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.47 (dd, J = 7.5, 0.9 Hz, 1H), 7.34 (td, J = 7.9, 1.3 Hz,

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1H), 7.29 (ddd, J = 7.4, 4.9, 0.9 Hz, 1H), 7.20 (td, J = 7.6, 0.9 Hz, 1H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) ^{13}C NMR (100 MHz, CDCl3) δ 163.3, 160.7, 152.5, 149.3, 134.0, 133.9, 132.8 (q, J = 8 Hz), 132.6, 130.4 (q, J = 312 Hz), 125.8, 124.4, 123.1(d, J = 6 Hz), 119.5, 118.9 (q, J = 22 Hz), 103.3, 20.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.48. HRMS m/z (M + H) calcd for $C_{15}H_{11}F_3N_2O_2S$: 341.0572, found: 341.0575. Mp 151−152 °C.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00940.

^{1}H NMR and ^{13}C NMR spectra for products **2a−z**, **4**, and **5** (PDF)

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Notes

The authors declare no competing financial interest.

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