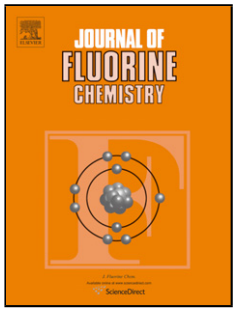

Regioselective deoxygenative C<ce:glyph name="sbnd"/>H trifluoromethylthiolation of heteroaryl *N*-oxides with $AgSCF_3$

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Regioselective deoxygenative C–H trifluoromethylthiolation of heteroaryl *N*-oxides with $AgSCF_3$

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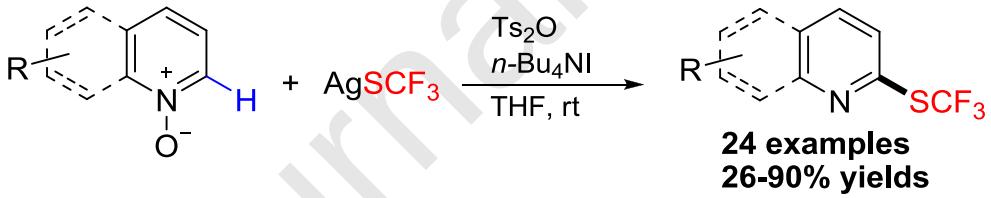
Graphical Abstract



Highlights

- C–H trifluoromethylthiolation of heteroaryl N-oxides.
- Broad functional group compatibility and excellent regioselectivity.

- Facile synthesis of C2-trifluoromethylthiolated heteroaromatic compounds.

Abstract

A mild and efficient method for the regioselective deoxygenative C─H trifluoromethylthiolation of heteroaryl *N*-oxides with $AgSCF_3$ is presented, employing *p*-toluenesulfonic anhydride and tetra-*n*-butylammonium iodide as the activators. This reaction delivers a series of C2-trifluoromethylthiolated heteroaromatic compounds in moderate to excellent yields. It provides a complementary method for C─H trifluoromethylthiolation reactions.

Keywords: Trifluoromethylthiolation; Regioselective; Heteroaromatics; *N*-oxide; Silver trifluoromethanethiolate.

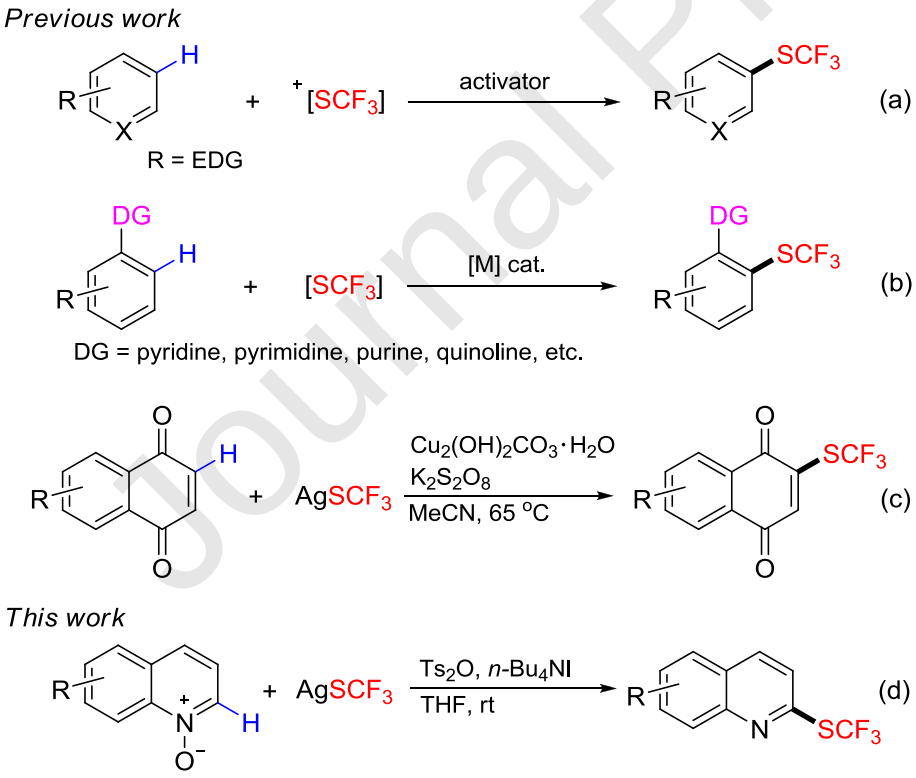
1. Introduction

The trifluoromethylthio (SCF_3) group has received growing interest in pharmaceuticals, agrochemicals, and functional materials due to its unique properties such as extremely high lipophilicity, strong electron-withdrawing power, transmembrane permeability, and metabolic stability [1]. Recently, extensive research efforts have been devoted to the development of methods for the incorporation of SCF_3 group into diverse skeletal structures [2]. In this regard, a series of new trifluoromethylthiolating reagents [3] and various novel trifluoromethylthiolation reactions, such as transition metal-mediated/catalyzed trifluoromethylthiolation of prefunctionalized (hetero)aromatics [4] and radical trifluoromethylthiolation of unsaturated substrates [5], have been reported.

C─H bond functionalization has recently gained prominence as a valuable approach in organic synthesis due to its inherent economic and environmentally benign nature [6]. Over the past several years, various Csp─H [7], Csp^2─H [8-10], and Csp^3─H [11] trifluoromethylthiolation methods have been developed as alternative approaches towards CF_3S-substituted compounds. Among them, Csp^2─H

trifluoromethylthiolation has received more attention because of the widespread biological activities of CF_3S-substituted (hetero)aromatic compounds. However, the reported Csp^2–H trifluoromethylthiolation reactions suffer from limited substrate scope, which mainly focused on two types of substrates, electron-rich (hetero)arenes and (hetero)arenes bearing a directing group. Electron-rich arenes [8] and heteroarenes [9] reacted with electrophilic trifluoromethylthiolating reagents via electrophilic aromatic substitution (S_EAr) to afford the C–H trifluoromethylthiolated products (Scheme 1a), whereas the directing group-assisted, transition-metal-promoted trifluoromethylthiolation of aryl C–H bonds normally furnished *ortho*-trifluoromethylthiolated products (Scheme 1b). Despite these progresses, the development of robust and operationally simple Csp^2–H trifluoromethylthiolation reactions remains largely underexplored.

Scheme 1 Csp^2–H trifluoromethylthiolation



In 2015, our group reported a copper-mediated oxidative C─H trifluoromethylthiolation of quinones with easily prepared and stable $AgSCF_3$ using $K_2S_2O_8$ as the oxidant (Scheme 1c) [12]. As an extension of this work and in continuation of our recent research interest in C─H fluoroalkylation reactions [9b,11a,13], herein we disclose a direct C─H trifluoromethylthiolation of heteroaryl *N*-oxides with $AgSCF_3$ in the presence of Ts_2O and *n*-Bu_4NI (Scheme 1d). Being different from the previously reported electrophilic (Scheme 1a), transition-metal-mediated/catalyzed (Scheme 1a), and radical (Scheme 1c) trifluoromethylthiolation reactions, a nucleophilic process is involved in this reaction. Notably, during the preparation of this manuscript, Kuninobu and co-workers reported a similar 2-position-selective trifluoromethylthiolation of six-membered heteroaromatic *N*-oxides with $AgSCF_3$ using 2,4-dinitrobenzenesulfonyl chloride as the activator [14].

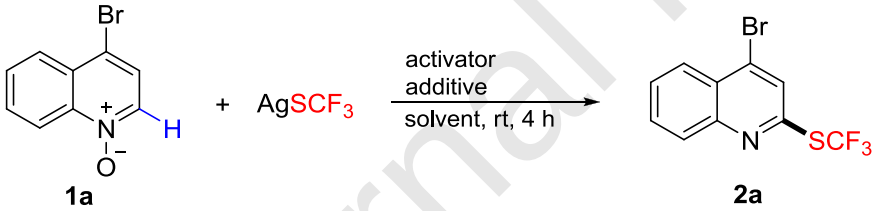
2. Results and Discussion

Heterocyclic *N*-oxides are important and readily available synthetic intermediates, which have emerged as attractive substrates for the preparation of various *N*-heterocycles bearing different substituents in the C2 position [15]. Recently, the C─H fluoroalkylation and fluoroalkenylation of heteroaryl *N*-oxides have been reported for the regioselective incorporation of fluoroalkyl and fluoroalkenyl groups into heteroarenes [16]. Very recently, Hartwig disclosed a novel C─H trifluoromethoxylation of heteroaryl *N*-oxides with CF_3OTf as both of the activator and OCF_3 source [17]. Inspired by these works, we became interested in exploring the C─H trifluoromethylthiolation of heteroaryl *N*-oxides.

We initiated our investigation by choosing 4-bromoquinoline 1-oxide (**1a**) as the model substrate for screening of the reaction parameters (Table 1). The reaction of **1a** and $AgSCF_3$ in MeCN did not occur when Tf_2O was used as an activator (entry 1). Further examination of the activators (entries 2-6) revealed that the reaction worked efficiently in the presence of Ts_2O, giving the desired product **2a** in 46% yield

(entry 4). We envisioned that the addition of another activator for promoting the generation of nucleophilic SCF_3 anion from $AgSCF_3$ might accelerate this reaction. Thus, different additives, including CuI, KI, *n*-Bu_4NI, and *n*-Bu_4NBr were investigated (entries 7-10). Among them, *n*-Bu_4NI was superior to other additives, affording **2a** in 63% yield (entry 9). Further screening of the solvents led to the discovery that THF was the best choice among those tested solvents (entries 9 and 11-16), and the yield of **2a** reached up to 85% (entry 13). When an organic or inorganic base was added to the reaction mixture, slightly lower yields were observed (entries 17 and 18). Finally, the reaction under N_2 atmosphere gave the same yield of **2a** (entry 19 vs 13). Notably, during the optimization process, **2a** was formed as the major product. Other CF_3S-substituted isomer was hardly detected by ^{19}F NMR analysis of the crude reaction mixture (see the Supporting Information).

Table 1. Optimization of reaction conditions.[a]



Entry	Activator	Additive	Solvent	Yield (%)[b]
1	Tf_2O	—	MeCN	0
2	BzCl	—	MeCN	5
3	TsCl	—	MeCN	33
4	Ts_2O	—	MeCN	46
5	Ms_2O	—	MeCN	34
6	TMSCl	—	MeCN	11
7	Ts_2O	CuI	MeCN	58
8	Ts_2O	KI	MeCN	44
9	Ts_2O	*n*-Bu_4NI	MeCN	63
10	Ts_2O	*n*-Bu_4NBr	MeCN	60
11	Ts_2O	*n*-Bu_4NI	$MeNO_2$	73

12	Ts_2O	*n*-Bu_4NI	DCM	62
13	Ts_2O	*n*-Bu_4NI	THF	85
14	Ts_2O	*n*-Bu_4NI	Toluene	50
15	Ts_2O	*n*-Bu_4NI	DMF	59
16	Ts_2O	*n*-Bu_4NI	DMSO	0
17	Ts_2O	*n*-Bu_4NI/NEt_3	THF	78
18	Ts_2O	*n*-Bu_4NI/Na_2CO_3	THF	73
19[c]	Ts_2O	*n*-Bu_4NI	THF	85

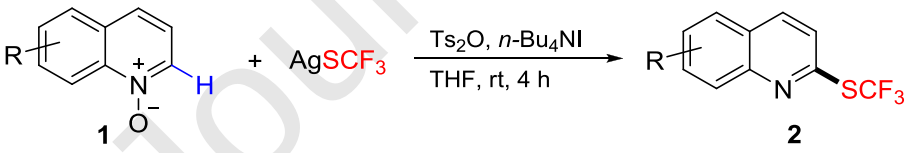
[a]Reaction conditions: **1a** (0.1 mmol), $AgSCF_3$ (0.2 mmol), activator (0.15 mmol), additive (0.2 mmol), solvent (1.0 mL), rt, under air, 4 h.

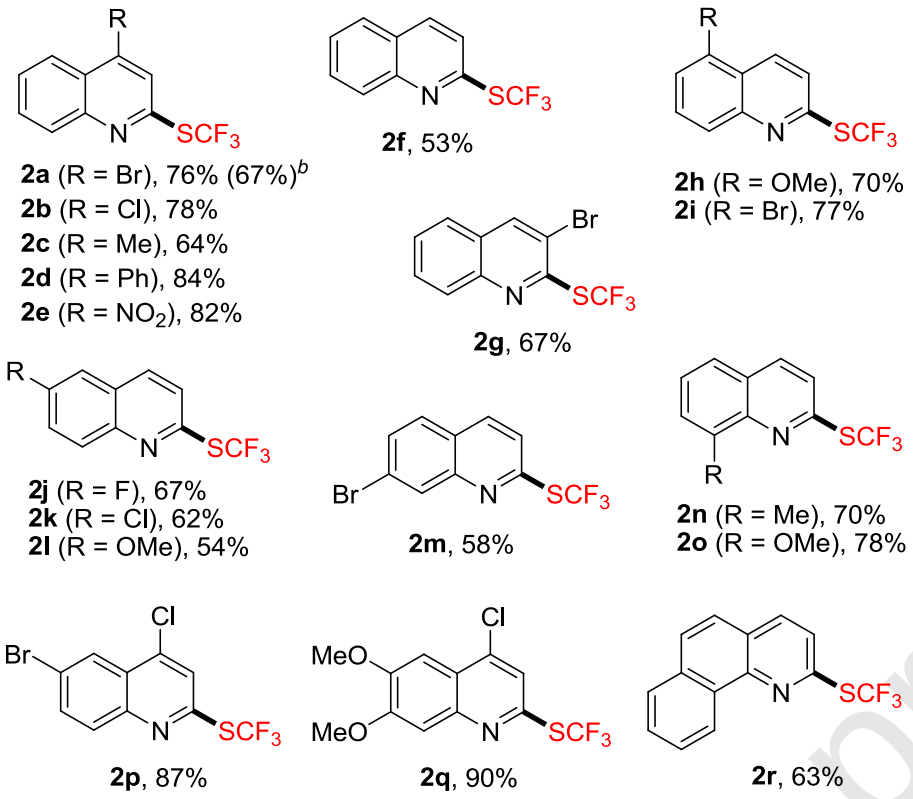
[b]Yields were determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as an internal standard.

[c]Under N_2.

With the optimized reaction conditions in hand (Table 1, entry 13), the substrate scope of this transformation was investigated (Table 2). A wide range of quinoline *N*-oxides (**1a-r**) were firstly evaluated. Quinoline *N*-oxides bearing electron-donating groups (Me, OMe, Ph) or electron-withdrawing groups (Cl, Br, NO_2) reacted smoothly, affording the corresponding products in moderate to excellent yields. Notably, the effect of the substituents on the phenyl ring of the quinoline *N*-oxides was not apparent. Mono-substituted (**1h-o**), di-substituted (**1p**), and tri-substituted (**1q**) quinoline *N*-oxides as well as benzo[*h*]quinoline *N*-oxide (**1r**) were all compatible with the reaction conditions. In addition, the reaction of **1a** could be scaled up to 5.0 mmol, affording **2a** in 67% yield.

Table 2. Scope of quinoline *N*-oxides.[a]

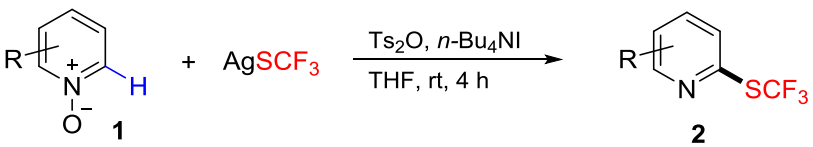


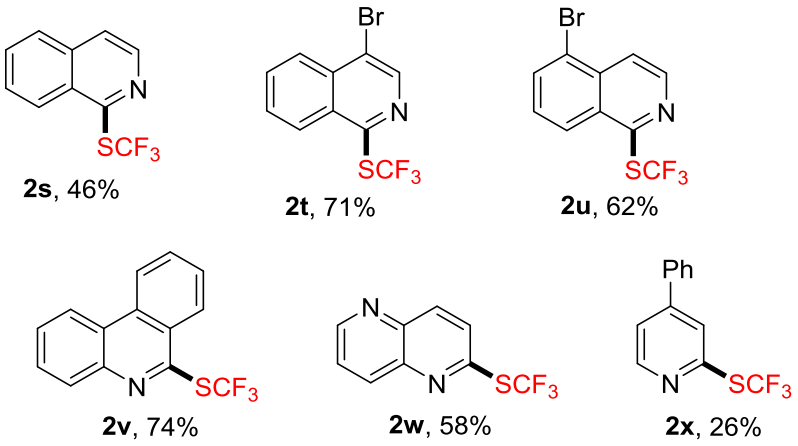


[a]Reaction conditions: **1** (0.4 mmol), $AgSCF_3$ (0.8 mmol), Ts_2O (0.6 mmol), *n*-Bu_4NI (0.8 mmol), THF (4.0 mL), rt,, 4 h, isolated yields.
[b]Reaction was performed on a 5.0 mmol scale.

This reaction system was easily extended to other heteroaryl *N*-oxides including isoquinoline *N*-oxides (**1s-u**), phenanthridine *N*-oxide (**1v**), and 1,5-naphthyridine *N*-oxide (**1w**) (Table 3). Finally, several pyridine *N*-oxides including 4-methylpyridine *N*-oxide, 4-cyanopyridine *N*-oxide, and 4-phenylpyridine *N*-oxide were subjected to the standard reaction conditions. Consistent with the previous studies [15-17], pyridine *N*-oxides were generally less reactive than bi- and tricyclic heterocyclic *N*-oxides. Among them, 4-phenylpyridine *N*-oxide (**1x**) delivered the trifluoromethylthiolated product **2x** in highest yield (26%). Switching the activator from Ts_2O to $4\text{-}NO_2C_6H_4SO_2Cl$ led to a lower yield of **2x** (20%).

Table 3. Scope of other heteroaryl *N*-oxides.[a]

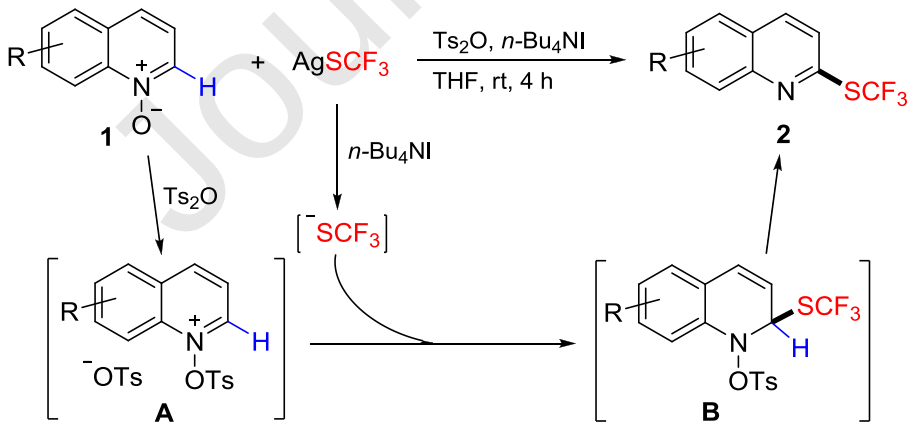




[a]Reaction conditions: **1** (0.4 mmol), $AgSCF_3$ (0.8 mmol), Ts_2O (0.6 mmol), *n*-Bu_4NI (0.8 mmol), THF (4.0 mL), rt, 4 h, isolated yields.

On the basis of the previous reports [15-17], a plausible mechanism for this C─H trifluoromethylthiolation reaction is depicted in Scheme 2. Initially, the reaction of quinoline *N*-oxides **1** and Ts_2O gives intermediate **A**. On the other hand, the activation of $AgSCF_3$ with *n*-Bu_4NI generates a nucleophilic source of SCF_3 anion [18]. Subsequently, the regioselective nucleophilic attack of SCF_3 anion at α-carbon of quinolines affords the dearomatized intermediate **B**. Finally, the resulting intermediate **B** undergoes deprotonation/aromatization to furnish the C2-trifluoromethylthiolated products **2**.

Scheme 2 Proposed reaction mechanism.



3. Conclusion

In conclusion, we have presented a practical C─H trifluoromethylthiolation of heteroaryl *N*-oxides with $AgSCF_3$ as the trifluoromethylthio source using Ts_2O and *n*-Bu_4NI as the activators. This method proves applicable to a variety of heterocycles, such as quinolines, benzo[*h*]quinolines, isoquinolines, phenanthridines, and 1,5-naphthyridines, possessing a variety of substitution patterns. Efforts are in progress towards further exploration of other C─H fluoroalkylation and fluoroalkylthiolation reactions.

4. Experimental Section

4.1. General information

^1H NMR (TMS as the internal standard), ^{13}C NMR and ^{19}F NMR spectra ($CFCl_3$ as the outside standard and low field is positive) were recorded on a 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HRMS data using ESI were obtained on a Thermo Fisher Scientific LTQ FTICR-MS. All reagents were used as received from commercial sources without further purification or prepared as described in references. Substrates **1e**, **1f**, **1l**, and **1s** were purchased and used directly from commercial sources. Substrates **1a-d**, **1g-k**, **1m-r**, and **1t-x** were prepared in accordance with methods described in the references [15a,16a].

4.2. General procedure for the synthesis of quinoline N-oxides

To a solution of quinolone (5.0 mmol) in CH_2Cl_2 (10.0 mL) was added *m*-CPBA (1.73 g, 10 mmol) at 0 °C. The reaction mixture was then stirred at room temperature overnight. The reaction mixture was diluted with CH_2Cl_2 and washed with aq. KOH. The organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The resulting residue was purified by silica gel flash column chromatography (EA/MeOH = 20: 1) to give the product.

*4.2.1. 6-Bromo-4-chloroquinoline 1-oxide (**1p**)*. Compound **1p** was obtained as a white solid (770.8 mg, 60%), mp 220-222 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 9.2 Hz, 1H), 8.34 (d, *J* = 6.6 Hz, 1H), 8.26 (s, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 7.31 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 135.2, 134.4, 129.0, 128.2, 127.3, 124.6, 122.2, 122.1. IR (thin film) ν 3059, 1548, 1491, 1337, 1288, 1216, 868, 814 cm^{-1}; MS (ESI): m/z 258 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_9H_5BrClNO^+$: 257.9316; Found: 257.9315.

*4.2.2. 4-Chloro-6,7-dimethoxyquinoline 1-oxide (**1q**)*. Compound **1q** was obtained as a white solid (780.1 mg, 65%), mp 182-184 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 6.5 Hz, 1H), 8.00 (s, 1H), 7.26 (s, 1H), 7.17 (d, *J* = 6.6 Hz, 1H), 4.03 (s, 3H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 151.9, 138.1, 133.9, 128.4, 123.4, 119.2, 102.7, 99.5, 56.7, 56.4. IR (thin film) ν 1618, 1506, 1749, 1418, 1340, 1267, 1246, 850 cm^{-1}; MS (ESI): m/z 240 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{11}H_{10}ClNO_3^+$: 240.0422; Found: 240.0442.

4.3. General procedure for C─H trifluoromethylthiolation of heteroaryl N-oxides

A mixture of heteroaryl *N*-oxide (0.4 mmol), $AgSCF_3$ (166.3 mg, 0.8 mmol), Ts_2O (195.8 mg, 0.6 mmol), and *n*-Bu_4NI (295.5 mg, 0.8 mmol) was added in a 25 mL Schlenk tube, and then THF (4.0 mL) was added. The mixture was stirred at room temperature for 4 h. After the reaction was complete, saturated NH_4Cl solution was added. The resulting mixture was extracted with EtOAc for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA= 100:1) to give the desired product **(2a-2w)**.

*4.3.1. 4-Bromo-2-(trifluoromethylthio)quinoline (**2a**)*. Compound **2a** was obtained as a colorless oil (93.3 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4, 1H), 8.11 (d, *J* = 8.4, 1H), 7.90 (s, 1H), 7.86-8.82 (m, 1H), 7.75-7.69 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.17 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6 (q, *J* = 2.7 Hz), 148.6, 135.2, 131.5, 129.7, 129.1 (q, *J* = 310.1 Hz), 128.9, 126.8, 126.6

(q, *J* = 2.2 Hz). IR (thin film) ν 1566, 1485, 1394, 1107, 1077, 814, 756, 687 cm^{-1}; MS (ESI): m/z 308 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_6BrF_3NS^+$: 307.9351; Found: 307.9350.

*4.3.2. 4-Chloro-2-(trifluoromethylthio)quinoline (**2b**)*. Compound **2b** was obtained as a colorless oil (82.1 mg, 78%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4, 1H), 8.11 (d, *J* = 8.5, 1H), 7.86-7.82 (m, 1H), 7.74-7.63 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.19 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ149.6 (q, *J* = 2.7 Hz), 148.8, 143.9, 131.5, 129.6, 129.1 (q, *J* = 310.1 Hz), 128.6, 125.4, 124.1, 122.9 (d, *J* = 2.3 Hz). IR (thin film) ν 1627, 1551, 1494, 1376, 1291, 1222, 1083, 916, 874 cm^{-1}; MS (ESI): m/z 264 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_6ClF_3NS^+$: 263.9856; Found: 263.9856.

*4.3.3. 4-Methyl-2-(trifluoromethylthio)quinoline (**2c**)*. Compound **2c** was obtained as a white solid (62.2 mg, 64%), mp 74-75 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 1H), 8.00 (dd, *J* = 8.4 Hz, 1H), 7.78-7.74 (m, 1H), 7.64-7.60 (m, 1H), 7.45 (s, 1H), 2.73 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.33 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 147.1, 145.4, 129.2, 128.9, 128.4 (q, *J* = 310.1 Hz), 126.4, 126.2, 122.9 (d, *J* = 2.1 Hz), 122.7, 17.7. IR (thin film) ν 1593, 1557, 1382, 1294, 1090, 904, 844, 560 cm^{-1}; MS (ESI): m/z 244 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{11}H_9F_3NS^+$: 244.0402; Found: 244.0402.

*4.3.4. 4-Phenyl-2-(trifluoromethylthio)quinoline (**2d**)*. Compound **2d** was obtained as a white solid (102.5 mg, 84%), mp 94-95 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.5, 1H), 7.79-7.75 (m, 1H), 7.59-7.45 (m, 7H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.17 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 149.5 (q, *J* = 2.6 Hz), 148.9, 136.9, 130.4, 129.7, 129.4 (q, *J* = 310.1 Hz), 129.4, 128.9, 128.7, 127.7, 125.92, 125.85, 123.4 (q, *J* = 2.1 Hz). IR (thin film) ν 1599, 1536, 1488, 1409, 1161, 1086, 768 cm^{-1}; MS (ESI): m/z 306 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{16}H_{11}F_3NS^+$: 306.0559; Found: 306.0559.

*4.3.5. 4-Nitro-2-(trifluoromethylthio)quinoline (**2e**)*. Compound **2e** was obtained as a yellow solid (89.8 mg, 82%), mp 52-53 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.7, 1H), 8.23 (d, *J* = 8.5, 1H), 8.06

(s, 1H), 7.95-7.91 (m, 1H), 7.84-7.80 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.09 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 150.4, 150.3 (d, *J* = 2.8 Hz), 132.1, 130.6, 129.9, 128.7 (q, *J* = 310.1 Hz), 122.8, 117.6, 117.0 (q, *J* = 2.4 Hz). IR (thin film) ν 1603, 1518, 1494, 1346, 1152, 1080, 853, 693 cm^{-1}; MS (ESI): m/z 275 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_6F_3N_2O_2S^+$: 275.0097; Found: 275.0097.

*4.3.6. 2-(Trifluoromethylthio)quinoline (**2f**)*. Compound **2f** was obtained as a colorless oil (48.6 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 8.5, 1H), 7.77 (d, *J* = 8.2, 1H), 7.70-7.68 (m, 1H), 7.56-7.49 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.34 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9 (d, *J* = 2.8 Hz), 147.4, 136.6, 129.5, 128.4 (q, *J* = 309.1 Hz), 128.3, 126.7, 126.6, 126.0, 122.3 (d, *J* = 2.2 Hz). IR (thin film) ν 1618, 1497, 1234, 1131, 1080, 919, 868, 835 cm^{-1}; MS (ESI): m/z 230 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_7F_3NS^+$: 230.0246; Found: 230.0245.

*4.3.7. 3-Bromo-2-(trifluoromethylthio)quinoline (**2g**)*. Compound **2g** was obtained as a white solid (82.3 mg, 67%), mp 80-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.02 (d, *J* = 8.6, 1H), 7.77-7.67 (m, 2H), 7.57-7.53 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.33 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 146.6, 138.8, 130.6, 129.1, 128.7 (q, *J* = 310.1 Hz), 127.6, 127.5, 126.6, 115.1 (q, *J* = 2.9 Hz). IR (thin film) ν 1548, 1488, 1324, 1086, 956,904, 874, 771 cm^{-1}; MS (ESI): m/z 308 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_6BrF_3NS^+$: 307.9351; Found: 307.9351.

*4.3.8. 5-Methoxy-2-(trifluoromethylthio)quinoline (**2h**)*. Compound **2h** was obtained as a white solid (72.5 mg, 70%), mp 70-71°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.7 Hz, 1H), 7.67-7.63 (m, 2H), 7.55 (d, *J* = 8.7 Hz, 1H), 6.89 (d, *J* = 5.9, 1H), 4.00 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.34 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 155.0, 149.1, 139.9, 131.8, 129.2 (q, *J* = 310.1 Hz), 121.3, 120.4, 117.2 (d, *J* = 2.1 Hz), 105.4, 56.0. IR (thin film) ν 1615, 1569, 1470, 1355, 1267, 1088, 753, 629 cm^{-1}; MS (ESI): m/z 260 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{11}H_9F_3NOS^+$: 260.0351; Found: 260.0352.

*4.3.9. 5-Bromo-2-(trifluoromethylthio)quinoline (**2i**)*. Compound **2i** was obtained as a white solid (94.5 mg, 77%), mp 48-49 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.8, 1H), 8.05 (d, *J* = 8.5, 1H), 7.85 (d, *J* = 7.5, 1H), 7.70-7.56 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.17 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 148.8, 137.2, 131.2, 130.7 (d, *J* = 12.7 Hz), 129.2 (q, *J* = 310.1 Hz), 129.1, 126.5, 123.8 (q, *J* = 2.3 Hz), 121.8. IR (thin film) ν 1578, 1548, 1285, 1116, 1080, 944, 805, 744 cm^{-1}; MS (ESI): m/z 308 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_6BrF_3NS^+$: 307.9351; Found: 307.9351.

*4.3.10. 6-Fluoro-2-(trifluoromethylthio)quinoline (**2j**)*. Compound **2j** was obtained as a white solid (62.2 mg, 67%), mp 58-59 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.07 (m, 2H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.38 (s, 3F), -110.83 to -110.89 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1 (d, *J* = 251.5 Hz), 149.4, 145.4, 137.0 (d, *J* = 5.5 Hz), 131.9 (d, *J* = 9.2 Hz), 129.3 (q, *J* = 310.1 Hz), 127.9 (d, *J* = 10.3 Hz), 124.3 (d, *J* = 2.5 Hz), 121.0 (d, *J* = 25.9 Hz), 110.8 (d, *J* = 22.0 Hz). IR (thin film) ν 1627, 1494, 1291, 1222, 1083, 916, 874, 823 cm^{-1}; MS (ESI): m/z 248 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_6F_4NS^+$: 248.0152; Found: 248.0151.

*4.3.11. 6-Chloro-2-(trifluoromethylthio)quinoline (**2k**)*. Compound **2k** was obtained as a white solid (65.5 mg, 62%), mp 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 2.3 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.27 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5 (d, *J* = 2.6 Hz), 146.7, 136.7, 133.7 (d, *J* = 28.1 Hz), 131.6, 130.8 (d, *J* = 5.4 Hz), 129.3 (q, *J* = 310.1 Hz), 127.6, 126.3, 123.9 (d, *J* = 2.2 Hz). IR (thin film) ν 1581, 1551, 1479, 1288, 1137, 895, 826, 756 cm^{-1}; MS (ESI): m/z 264 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_6ClF_3NS^+$: 263.9856; Found: 263.9856.

*4.3.12. 6-Methoxy-2-(trifluoromethylthio)quinoline (**2l**)*. Compound **2l** was obtained as a white solid (56.0 mg, 54%), mp 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 9.2 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 9.2, 1H), 7.07 (d, *J* = 2.8 Hz, 1H), 3.94 (s, 3H). ^{19}F NMR (376 MHz,

$CDCl_3$) δ -39.69 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 144.9 (q, *J* = 2.6 Hz), 143.6, 135.3, 129.8, 128.5 (q, *J* = 310.1 Hz), 127.6, 123.9 (d, *J* = 2.0 Hz), 122.5, 103.8, 54.6. IR (thin film) ν 1618, 1497, 1376, 1234, 1131, 1080, 1019, 835 cm^{-1}; MS (ESI): m/z 260 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{11}H_9F_3NOS^+$: 260.0351; Found: 260.0351.

*4.3.13. 7-Bromo-2-(trifluoromethylthio)quinoline (**2m**)*. Compound **2m** was obtained as a white solid (71.2 mg, 58%), mp 64-65 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 4.5 Hz, 1H), 8.28 (s, 1H), 8.17 (d, *J* = 9.0 Hz, 1H), 7.78-7.59 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.93 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 148.3, 132.2 (d, *J* = 2.2 Hz), 131.4, 130.6, 128.0, 127.8 (q, *J* = 311.1 Hz), 126.9, 125.5, 123.8. IR (thin film) ν 1600, 1545, 1485, 1340, 1152, 1092, 820, 774 cm^{-1}; MS (ESI): m/z 308 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_6BrF_3NS^+$: 307.9351; Found: 307.9348.

*4.3.14. 8-Methyl-2-(trifluoromethylthio)quinoline (**2n**)*. Compound **2n** was obtained as a colorless oil (68.0 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 1H), 7.48-7.39 (m, 2H), 7.32-7.27 (m, 2H), 2.64 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.45 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1 (d, *J* = 2.3 Hz), 147.5, 137.6, 137.3, 130.5, 129.4 (q, *J* = 308.0 Hz), 127.2, 126.8, 125.4, 121.9 (d, *J* = 2.4 Hz), 17.6. IR (thin film) ν 1569, 1494, 1418, 1373, 1297, 1092, 874, 826 cm^{-1}; MS (ESI): m/z 244 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{11}H_9F_3NS^+$: 244.0402; Found: 244.0403.

*4.3.15. 8-Methoxy-2-(trifluoromethylthio)quinoline (**2o**)*. Compound **2o** was obtained as a white solid (81.1 mg, 78%), mp 66-67 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 4.09 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.41 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 148.9 (q, *J* = 2.9 Hz), 140.2, 137.7, 129.6 (q, *J* = 309.1 Hz), 128.3, 128.1, 124.2 (q, *J* = 2.2 Hz), 119.2, 109.0, 56.2. IR (thin film) ν 1612, 1551, 1463, 1373, 1086, 986, 829, 753 cm^{-1}; MS (ESI): m/z 260 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{11}H_9F_3NOS^+$: 260.0351; Found: 260.0351.

*4.3.16. 6-Bromo-4-chloro-2-(trifluoromethylthio)quinoline (**2p**)*. Compound **2p** was obtained as a white solid (118.6 mg, 87%), mp 66-68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.66 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.10 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4 (d, *J* = 2.7 Hz), 147.4, 142.6, 135.1, 131.2, 128.9 (q, *J* = 310.1 Hz), 126.5, 126.4, 123.3 (q, *J* = 2.3 Hz), 123.1. IR (thin film) ν 1557, 1536, 1470, 1370, 1258, 1113, 871, 838 cm^{-1}; MS (ESI): m/z 342 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_5BrClF_3NS^+$: 341.8961; Found: 341.8963.

*4.3.17. 4-Chloro-6,7-dimethoxy-2-(trifluoromethylthio)quinoline (**2q**)*. Compound **2q** was obtained as a white solid (116.3 mg, 90%), mp 112-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.50 (s, 1H), 7.39 (s, 1H), 4.08 (s, 3H), 4.06 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.61 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 151.8, 146.2, 145.6 (d, *J* = 2.9 Hz), 141.4, 129.3 (q, *J* = 310.1 Hz), 122.8 (d, *J* = 2.0 Hz), 121.6, 108.1, 101.4, 56.4, 56.3. IR (thin film) ν 1621, 1566, 1427, 1249, 1080, 998, 844, 756 cm^{-1}; MS (ESI): m/z 308 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{12}H_{10}ClF_3NO_2S^+$: 324.0067; Found: 324.0067.

*4.3.18. 2-(Trifluoromethylthio)benzo[h]quinoline (**2r**)*. Compound **2r** was obtained as a white solid (70.3 mg, 63%), mp 33-34 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.4 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.67-7.58 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.51 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7 (d, *J* = 3.1 Hz), 147.0, 137.1, 133.8, 130.8, 129.7 (q, *J* = 309.1 Hz), 128.9, 128.8, 127.7, 127.5, 125.3, 124.7, 124.5, 123.5 (d, *J* = 2.2 Hz). IR (thin film) ν 1624, 1584, 1491, 1400, 838, 756, 644 cm^{-1}; MS (ESI): m/z 280 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{14}H_9F_3NS^+$: 280.0402; Found: 280.0402.

*4.3.19. 1-(Trifluoromethylthio)isoquinoline (**2s**)*. Compound **2s** was obtained as a colorless oil (42.1 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.6 Hz, 1H), 8.32 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.78-7.75 (m, 1H), 7.72-7.67 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.93 (s, 3F). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 149.9 (d, *J* = 2.3 Hz), 142.6, 136.8, 131.1, 129.8 (d, *J* = 1.7 Hz), 129.1 (q, *J* = 310.1 Hz), 128.5, 127.3, 125.8, 121.9. IR (thin film) ν 1581, 1551, 1488, 1318, 1092, 974, 823, 744 cm^{-1}; MS (ESI): m/z 230 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_7F_3NS^+$: 230.0246; Found: 230.0245.

*4.3.20. 4-Bromo-1-(trifluoromethylthio)isoquinoline (**2t**)*. Compound **2t** was obtained as a white solid (87.2 mg, 71%), mp 52-53 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 8.23 (d, *J* = 8.6 Hz, 1H), 7.90-7.86 (m, 1H), 7.78-7.84 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.17 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4 (d, *J* = 2.3 Hz), 144.3, 135.5, 132.3, 130.6, 129.4, 128.8 (q, *J* = 310.1 Hz), 126.9, 126.2, 121.2. IR (thin film) ν 1615, 1560, 1545, 1191, 1122, 1089, 980 cm^{-1}; MS (ESI): m/z 308 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_6BrF_3NS^+$: 307.9351; Found: 307.9353.

*4.3.21. 5-Bromo-1-(trifluoromethylthio)isoquinoline (**2u**)*. Compound **2u** was obtained as a white solid (76.1 mg, 62%), mp 49-50 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 5.8 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.7-8.03 (m, 2H), 7.56-7.52 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.97 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7 (d, *J* = 4.7 Hz), 143.8, 135.9, 134.8, 130.4 (d, *J* = 1.6 Hz), 128.6, 128.9 (q, *J* = 310.1 Hz), 125.4, 122.3, 120.7. IR (thin film) ν 1569, 1476, 1394, 1318, 1095, 829, 802 cm^{-1}; MS (ESI): m/z 308 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_6BrF_3NS^+$: 307.9351; Found: 307.9350.

*4.3.22. 6-(Trifluoromethylthio)phenanthridine (**2v**)*. Compound **2v** was obtained as a white solid (82.6 mg, 74%), mp 89-90 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 9.5 Hz, 1H), 8.34 (d, *J* = 7.6 Hz, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 7.93-7.88 (m, 1H), 7.79-7.69 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.56 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0 (d, *J* = 2.4 Hz), 143.8, 133.3, 131.5, 130.2, 129.2, 129.1 (q, *J* = 310.1 Hz), 128.0, 127.9, 126.4, 126.3 (q, *J* = 2.0 Hz), 123.8, 122.5, 122.0. IR (thin film) ν 1612, 1563, 1451, 1340, 1107, 1083, 950, 753 cm^{-1}; MS (ESI): m/z 280 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{14}H_9F_3NS^+$: 280.0402; Found: 280.0401.

*4.3.23. 2-(Trifluoromethylthio)-1,5-naphthyridine (**2w**)*. Compound **2w** was obtained as a white solid (68.1 mg, 74%), mp 61-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.2 Hz, 1H), 8.81 (d, *J* = 4.7 Hz, 1H), 8.34 (d, *J* = 6.9 Hz, 1H), 7.72-7.70 (m, 1H), 7.67-7.64 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.55 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 149.1, 142.1, 140.4 (d, *J* = 2.1 Hz), 139.4, 136.8, 128.3 (q, *J* = 310.1 Hz), 124.5, 120.0 (q, *J* = 2.4 Hz). IR (thin film) ν 1575, 1488, 1470, 1288, 1107, 1025, 838, 783 cm^{-1}; MS (ESI): m/z 231 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_9H_6F_3N_2S^+$: 231.0198; Found: 231.0196.

*4.3.24. 4-Phenyl-2-(trifluoromethylthio)pyridine (**2x**)*. Compound **2x** was obtained as a colorless oil (26.5 mg, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 5.2 Hz, 1H), 7.72 (s, 1H), 7.58-7.51 (m, 2H), 7.48-7.36 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.97 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.4, 148.8 (q, *J* = 2.6 Hz), 135.8, 128.7, 128.4 (q, *J* = 310.1 Hz), 128.3, 126.0, 125.0 (q, *J* = 1.9 Hz), 120.8. IR (thin film) ν 1587, 1536, 1457, 1376, 1131, 1104, 1077, 690 cm^{-1}; MS (ESI): m/z 256 $(M+H)^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{12}H_9F_3NS^+$: 256.0402; Found: 256.0401.

4.4. Procedure for gram-scale reaction

A mixture of 4-bromoquinoline 1-oxide **1a** (1.11 g, 5.0 mmol), $AgSCF_3$ (2.08 g, 10.0 mmol), Ts_2O (2.45 g, 7.5 mmol), and *n*-Bu_4NI (3.69 g, 10.0 mmol) was added in a 100 mL Schlenk tube, and then THF (50.0 mL) was added. The mixture was stirred at room temperature for 4 h. After the reaction was complete, saturated NH_4Cl solution was added. The resulting mixture was extracted with EtOAc for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA= 100:1) to afford **2a** in 67% yield (1.03 g).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. jfluchem.xxxx.xx.xxx.

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