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银催化三氟甲硫基化-环化-水解: 含 F_3CS 基喹啉酮合成

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摘要 以氰基作为自由基受体, 开发了一种实用的银催化三氟甲硫化/环化/水解策略. 在中等到较高产率的条件下, 获得了各种结构多样的 F_3CS-取代喹啉酮类化合物. 该方法易于放大量制备, 且产物具有进一步衍生化的潜力. 因此, 对制备其他有价值的含氟砌块的氮杂环化合物很有吸引力. 机理研究表明, 该催化体系涉及自由基途径, H_2O 在水解过程中起着不可或缺的作用.

关键词 三氟甲硫基化; 氮杂环; 环化; 自由基; 衍生化

Silver-Mediated Trifluoromethylthiolation-Cyclization-Hydrolysis: Access to F_3CS-Containing Quinolinones

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Abstract Herein, a practical formal silver-mediated trifluoromethylthiolation cyclization hydrolysis protocol was developed with the cyano group as a radical acceptor. Various structurally diverse F_3CS-substituted quinolinones were obtained in moderate to high yields. Easy scale-up operation and the potential for product derivatization make this method attractive for the preparation of other valuable F_3CS-containing *N*-heterocycles. Mechanistic studies suggest that the catalytic system involves a radical pathway and H_2O plays an indispensable role in the hydrolysis process.

Keywords trifluoromethylthiolation; *N*-heterocycles; cyclization; radical; derivatization

1 Introduction

Compounds bearing fluorine-containing groups have been widely used as agrochemicals, pharmaceuticals, and materials because of their unique physical, chemical and biological properties.[1] Among all intriguing fluorinated moieties, the trifluoromethylthio group (SCF_3) has attracted ongoing attention because of its special biological properties, such as absorption rate, enhancement of membrane permeability, and improvement of the stability of parent molecules because of its high electronegativity and lipophilicity.[2] *N*-Heterocycles are privileged scaffolds in synthetic and medicinal chemistry, which not only exist in a wide range of bioactive molecules but also are valuable synthetic building blocks that can be transformed into a series of valuable structures.[3] Moreover, nitrogen-containing heterocycles are present in almost half of the top 200 pharmaceuticals on sale.[4] Therefore, the efficient construction of *N*-heterocycles has been a hot and classical concern in organic synthetic research. To date, the development of effective strategies for the introduction of the SCF_3 group to *N*-heterocycles has attracted much attention from chemists, and various elegant strategies, including nucleophilic,[5] electrophilic,[6] and radical[7] trifluoromethylthiolations, have been established.

In recent decades, the radical cascade reaction has emerged as a versatile tool to prepare a large variety of functional molecules. Such synthetic strategies will open new ways for the rapid buildup of molecular complexity.[8] Early in 2014, Wang's group[9] reported the first $AgSCF_3$-mediated trifluoromethylthiolation cyclization of activated alkenes in a radical process to produce valuable trifluoro-

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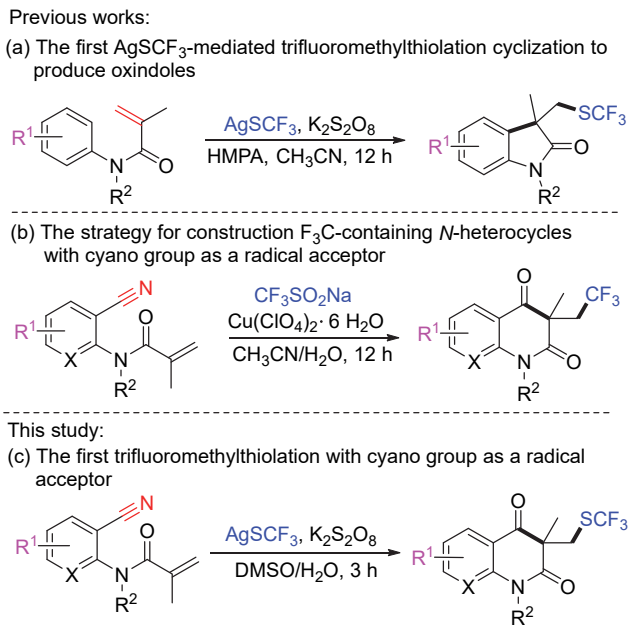
methylthio-oxindoles (Scheme 1a). In 2015, a novel trifluoromethylthiolation oxidative aromatic cyclization strategy involving a 1,4-aryl migration and desulfonylation was disclosed by Nevado's group[10] Later, a radical trifluoromethylthiolation cascade cyclization of *N*-tethered 1,6-enynes to synthesize trifluoromethylthio-substituted piperidines was disclosed by Liang *et al*.[11] In 2018, Zhu *et al*.[12] presented an efficient copper-catalyzed domino cyclization trifluoromethylthiolation of alkenes for the construction of F_3CS-containing pyrrolines. The cyano group is a valuable and readily available functional group for the preparation of various functional groups, and the application of the cyano group as a radical acceptor in cascade reactions provides diverse opportunities for the convenient construction of various important carbocycles and heterocycles.[13] In 2016, Li *et al*.[14] established the strategy for the construction of CF_3-containing *N*-heterocycles with the cyano group as a radical acceptor (Scheme 1b). As part of our ongoing interest in heterocycle modification,[15] herein, we attempted a one-pot formal trifluoromethylthiolation cyclization hydrolysis to construct a series of structurally diverse quinolinones, which are widely found *N*-heterocycles in natural products, pharmaceuticals, and agrochemicals (Scheme 1c). Gram-scale synthesis, with selective diversification via oxidation and reduction, shows the practicability of the reaction and its potential use in industrial applications.



Scheme 1 Metal-catalyzed trifluoromethylation/trifluoromethylthiolation cyclization strategy

2 Results and discussion

Our initial attempt was started by employing compound **1a** (0.3 mmol) as the model substrate with $AgSCF_3$ (1.2 equiv) and $K_2S_2O_8$ (2.0 equiv.) in dimethyl sulfoxide (DMSO) at 80 ℃ under an air atmosphere for 3 h. To our delight, our anticipated product **2a** was isolated in a 35% yield (Table 1, Entry 1). The ratio of DMSO/H_2O was then studied, which revealed that the best volume ratio of DMSO/H_2O was 4∶1 (Entries 2～4). A further survey of other solvents showed that CH_3CN/ H_2O and acetone/H_2O gave similar yields of product **2a** (Entries 5～9). To improve the yield further, the temperature was next investigated. No better result was obtained when the temperature was decreased to 60 ℃; whereas increasing the temperature to 100 ℃ and 120 ℃ improved the reaction efficiency, giving the desired **2a** in 68% and 85% yields, respectively (Entries 10～12). A wide range of oxidants, including $Na_2S_2O_8$, $(NH_4)_2S_2O_8$, $PhI(OAc)_2$, *t*-butylhydroperoxide (TBHP), selectfluor, and oxone were investigated to trigger the F_3CS• radical, which proved to be less efficient than $K_2S_2O_8$ (Entries 13～18).

Table 1 Screening of reaction conditions[a,b]

Entry	Solvent	Oxidant	*T*/℃	Yield[b]/%
1	DMSO	$K_2S_2O_8$	80	35
2	*V*(DMSO)∶*V*(H_2O)=4∶1	$K_2S_2O_8$	80	59
3	*V*(DMSO)∶*V*(H_2O)=2∶1	$K_2S_2O_8$	80	33
4	*V*(DMSO)∶*V*(H_2O)=1∶1	$K_2S_2O_8$	80	33
5	*V*(CH_3CN)∶*V*(H_2O)=4∶1	$K_2S_2O_8$	80	55
6	*V*(DMF)∶*V*(H_2O)=4∶1	$K_2S_2O_8$	80	46
7	*V*(acetone)∶*V*(H_2O)=4∶1	$K_2S_2O_8$	80	57
8	*V*(dioxane)∶*V*(H_2O)=4∶1	$K_2S_2O_8$	80	36
9	*V*(EtOAc)∶*V*(H_2O)=4∶1	$K_2S_2O_8$	80	0
10	*V*(DMSO)∶*V*(H_2O)=4∶1	$K_2S_2O_8$	60	25
11	*V*(DMSO)∶*V*(H_2O)=4∶1	$K_2S_2O_8$	100	68
12	*V*(DMSO)∶*V*(H_2O)=4∶1	$K_2S_2O_8$	120	85
13	*V*(DMSO)∶*V*(H_2O)=4∶1	$Na_2S_2O_8$	120	71
14	*V*(DMSO)∶*V*(H_2O)=4∶1	$(NH_4)_2S_2O_8$	120	40
15	*V*(DMSO)∶*V*(H_2O)=4∶1	$PhI(OAc)_2$	120	Trace
16	*V*(DMSO)∶*V*(H_2O)=4∶1	TBHP	120	0
17	*V*(DMSO)∶*V*(H_2O)=4∶1	Selectfluor	120	0
18	*V*(DMSO)∶*V*(H_2O)=4∶1	Oxone	120	0

[a] Reaction conditions: **1a** (0.3 mmol), $AgSCF_3$ (1.2 equiv.), oxidant (2.0 equiv.), solvent (2.5 mL) with heating for 3 h; [b] Yields of isolated product.

With the optimized conditions in hand, *N*-(2-cyanophenyl)-*N*-methylmethacrylamides **1** bearing different substituents were investigated to evaluate the scope of this transformation. As shown in Table 2, substrates **1** with electron-donating groups, such as Me, OMe, cyclopropyl, and Ar, and electron-withdrawing groups, such as F, Cl, and Br on the aryl rings, were trifluoromethylthiolated smoothly to give the corresponding quinolinones in moderate to good yields (**2b**～**2p**). The presence of halogen atoms (F, Cl, Br) in the quinolinones offers the potential for further synthetic elaboration by transition-metal-catalyzed cross-coupling reactions. It is worth noting that when the substrates bearing methyl and methoxy at 3 or 6 positions, probably due to the electronic effect, no desired products could be obtained. Multisubstituted substrates were further tested and reacted smoothly with $AgSCF_3$ to provide **2q** and **2r** in 32% and 64% yields,

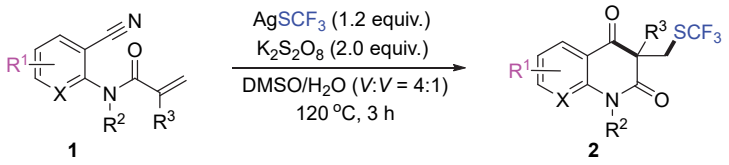
respectively. Note that the yield was affected by the electron density of the benzene ring. When 6-Cl-substituted substrates were used, the yields decreased to 35% and 32% for **2p** and **2q**, respectively. In addition, we were pleased to find that pyridineacrylamide **1s**, a heterocyclic substrate, can react well with $AgSCF_3$, and the expected product **2s** was obtained in a 75% yield. Unsurprisingly, Bn- and Et-protecting substrates afforded the quinolinones **2t** (R^2=Bn) and **2u** (R^2=Et) in 81% and 83% yields, respectively. Finally, the monosubstituted olefin (R^3=H) was also tested, which was found not to be a suitable substrate in this reaction.

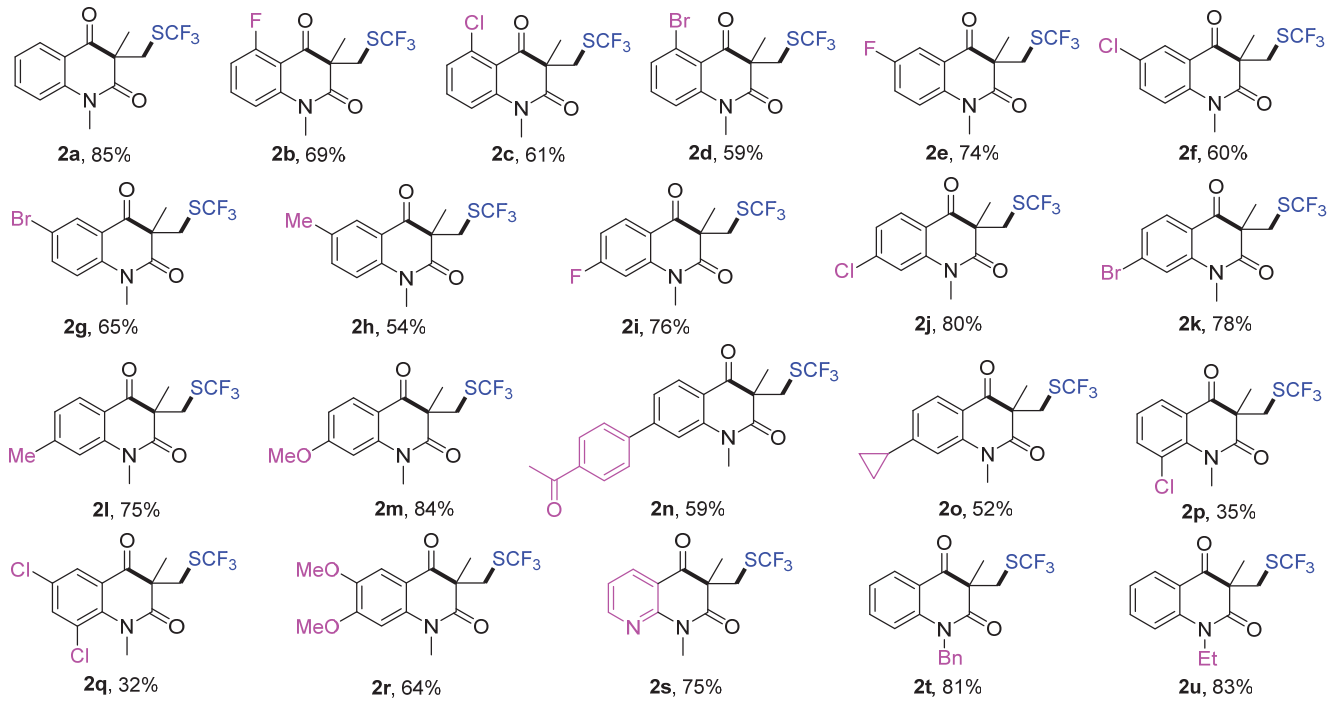
To demonstrate the synthetic utility of this protocol, the Ag-mediated trifluoromethylthiolation cyclization of **1a** on a larger 10 mmol scale was performed, affording the desired product **2a** in 78% yield (Scheme 2a). Moreover, compound **2a** could be selectively reduced to give **3** in excellent yield, which enabled further synthetic manipulations (Scheme 2b). Furthermore, the oxidation of **2a** gave the corresponding **4** in excellent yield, which is a useful building block for further derivatization to afford a new F_3CSO_2-containing moiety (Scheme 2c). As free NH is very useful for further derivatization, the possibility of dealkylation of N-Me from product **2a** was attempted. With coper salt and *N*-fluorobenzenesulfonimide (NFSI) combination, the desired dealkylation product **5** was obtained in 57% yield (Scheme 2d).

To probe the reaction mechanism, several control experiments were carried out (Scheme 3). Initially, when the radical inhibitor 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 2.0 equiv. and 4.0 equiv.) was added to the standard reaction conditions, the trifluoromethylthiolation cyclization process was remarkably suppressed (Scheme 3a). Moreover, when 2,6-di-*tert*-butyl-4-methylphenol (BHT, 2.0 equiv.) and 1,1-diphenylethene (2.0 equiv.) were added, the reaction was suppressed, and adducts **6** and **7** were detected using HRMS (Schemes 3b and 3c). These results indicate that the reaction should proceed through a radical pathway. Furthermore, an ^{18}O-labeling experiment was performed with corresponding product **2a'** obtained in 83% yield after 3 h (**2a'** was confirmed using HRMS, Scheme 3d).

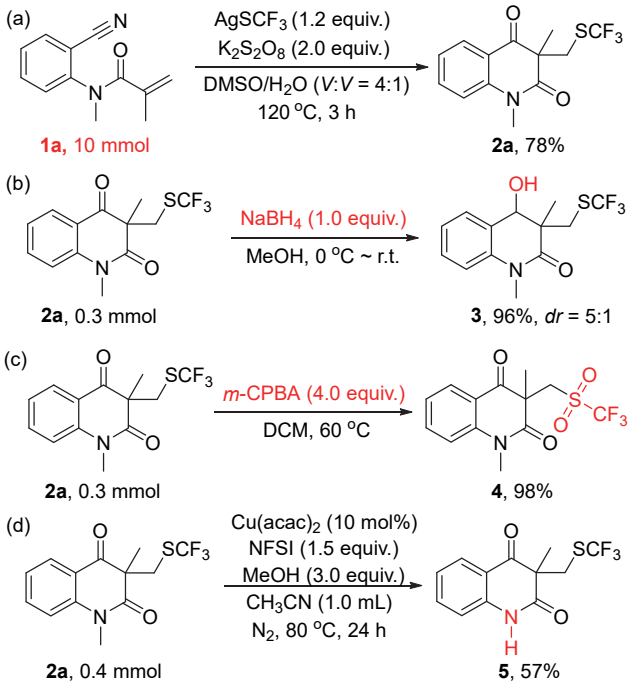
Based on the above results and the literature,[16] a plausible mechanism for this reaction is proposed in Scheme 4. Initially, $AgSCF_3$ is oxidized by $K_2S_2O_8$ and generated the SCF_3• radical.[9,11] The intermolecular regioselective addition of the SCF_3• radical to the double bond of substrate **1** affords radical intermediate **A**, which undergoes a subsequent 6-*exo*-*dig* process to give imine radical **B**. Subsequently, radical intermediate **B** undergoes hydrogen abstra-

Table 2 Substrate scope of Ag-mediated trifluoromethylthiolation[a,b]

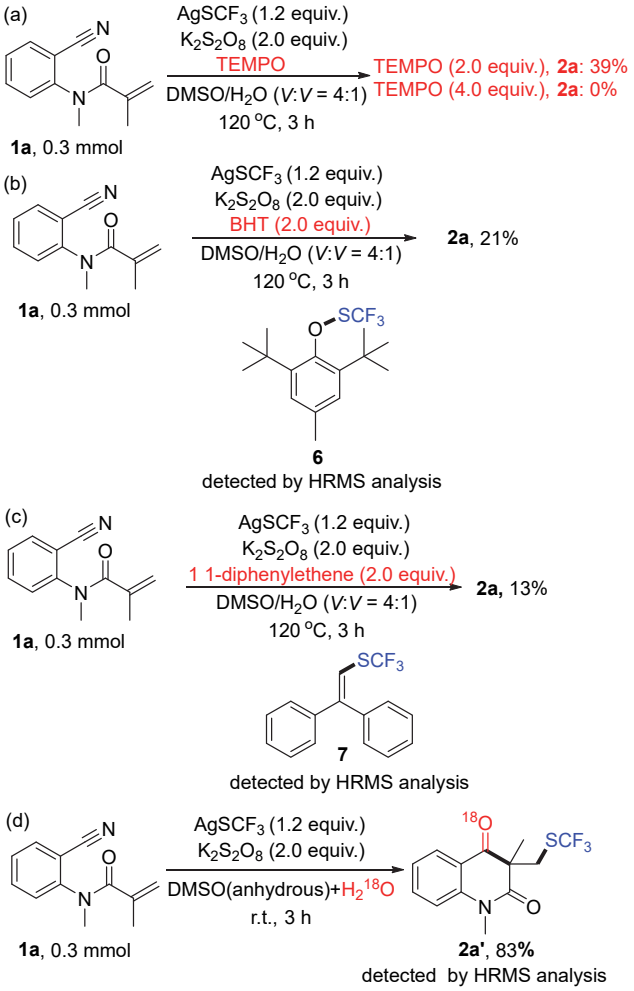




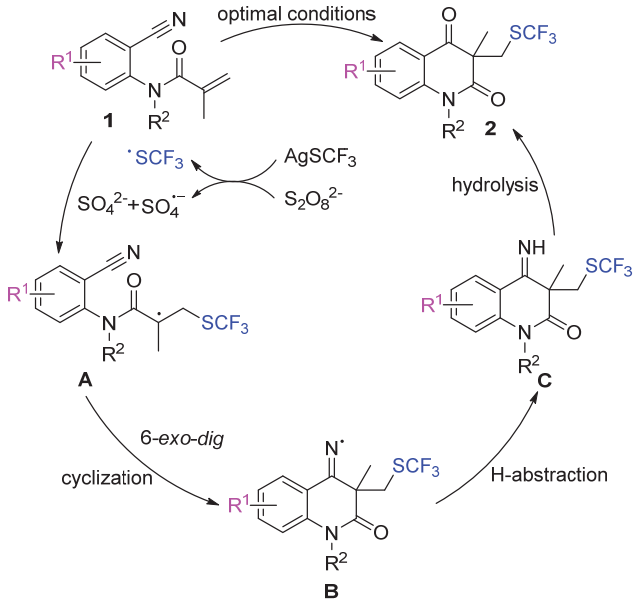
[a] Reaction conditions: **1a** (0.3 mmol), $AgSCF_3$ (1.2 equiv.), $K_2S_2O_8$ (2.0 equiv.), DMSO/H_2O (V∶V=4∶1, 2.5 mL) at 120 ℃ for 3 h; [b] Yields of isolated product.



Scheme 2 Application investigation



Scheme 3 Control experiments



Scheme 4 Proposed reaction mechanism

ction to give imine **C**. Finally, imine **C** is hydrolyzed by H_2O to give product **2**.

3 Conclusions

In summary, the first example of silver-mediated sequential trifluoromethylthiolation cyclization hydrolysis to produce valuable trifluoromethylthio-containing quinolinones has been developed, which is widely found N-heterocycles in natural products, pharmaceuticals, and agrochemicals. Ease of scale-up operation and product derivatization, such as selectively oxidation, reduction and dealkylation make this strategy attractive for the preparation of other valuable molecules. A possible radical mechanism is proposed based on the results of control experiments. Further research on the use of this protocol in the synthesis of bioactive molecules is currently in progress.

4 Experimental section

4.1 General information

All reagents were purchased from commercial sources and used without further purification. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on a Bruker Ascend™ 400 or Bruker Ascend™ 500 or a Bruker Ascend™ 600 spectrometer in deuterated solvents containing TMS as an internal reference standard. All high-resolution mass spectra (HRMS) were measured on a mass spectrometer by using electrospray ionization orthogonal acceleration time-of-flight (ESI-OA-TOF), and the purity of all samples used for HRMS (>95%) was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopic analysis. Melting points were measured on a melting point apparatus equipped with a thermometer and were uncorrected. All the reactions were monitored by thin-layer chromatography (TLC) using GF254 silica gel-coated TLC plates. Purification by flash column chromatography was performed over SiO_2 (silica

gel 200～300 mesh).

4.2 Synthesis procedure for compounds **2**

To a reaction tube, acrylamides **1** (0.3 mmol), $AgSCF_3$ (1.2 equiv., 0.36 mmol) and $K_2S_2O_8$ (2.0 equiv., 0.6 mmol) were mixed in DMSO/H_2O (V∶V=4∶1, 2.5 mL). The mixture was stirred in an oil bath at 120 ℃ until complete consumption of starting material as monitored by TLC analysis. After the completion of the reaction, the mixture was quenched by $NaHCO_3$ (sat. aq. 15 mL) and extracted with CH_2Cl_2 (5 mL×3). Then the organic solvent was concentrated *in vacuo*. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluent to products **2**.

1,3-Dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2a**): The product was purified by column chromatography on silica gel [V(petroleum ether∶V(ethyl acetate)=10∶1, R_f=0.21], colourless liquid (77 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01～8.00 (m, 1H), 7.68～7.64 (m, 1H), 7.22～7.18 (m, 2H), 3.54 (s, 2H), 3.48 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.13, 171.81, 142.97, 136.65, 130.56 (q, J=306.6 Hz), 128.37, 123.56, 119.69, 115.08, 57.52, 33.32 (q, J=2.1 Hz), 29.97, 25.98; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.69; HRMS (ESI) calcd for $C_{13}H_{13}F_3NO_2S$ $[M+H]^+$ 304.0614, found 304.0607.

5-Fluoro-1,3-dimethyl-3-(((trifluoromethyl)thio)-methyl)quinoline-2,4(1*H*,3*H*)-dione (**2b**): The product was purified by column chromatography on silica gel [V(petroleum ether∶V(ethyl acetate)=10∶1, R_f=0.15], colourless liquid (66 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62～7.57 (m, 1H), 7.00 (d, J=8.5 Hz, 1H), 6.93～7.89 (m, 1H), 3.50 (d, J=2.7 Hz, 2H), 3.48 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 192.48, 171.17, 162.13 (d, J=266.7 Hz), 143.89 (d, J=3.3 Hz), 136.70 (d, J=11.6 Hz), 130.59 (q, J=306.6 Hz), 111.74 (d, J=21.3 Hz), 110.87 (d, J=3.6 Hz), 109.63 (d, J=10.1 Hz), 58.47, 32.58 (q, J=2.0 Hz), 30.79, 25.00; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.96, −109.91; HRMS (ESI) calcd for $C_{13}H_{12}F_4NO_2S$ $[M+H]^+$ 322.0519, found 322.0512.

5-Chloro-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2c**): The product was purified by column chromatography on silica gel [V(petroleum ether∶V(ethyl acetate)=10∶1, R_f=0.12], white soild (62 mg, 61%), m.p. 72～73 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43 (t, J=8.2 Hz, 1H), 7.20～7.16 (m, 1H), 7.05 (d, J=8.4 Hz, 1H), 3.41 (s, 2H), 3.40 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.60, 170.62, 144.15, 135.48, 134.72, 130.69 (q, J=306.3 Hz), 126.76, 118.33, 113.86, 58.60, 32.18 (q, J=2.5 Hz), 30.87, 23.59; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −42.30; HRMS (ESI) calcd for $C_{13}H_{12}ClF_3NO_2S$ $[M+H]^+$ 338.0224, found 338.0217.

5-Bromo-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2d**): The product was purified by column chromatography on silica gel [V(petroleum ether∶V(ethyl acetate)=10∶1, R_f=0.12], yellow soild (67 mg, 59%), m.p. 78～79 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47～7.44 (m, 1H), 7.40 (t, J=8.1 Hz, 1H), 7.16 (d, J=8.3 Hz, 1H), 3.47 (s, 2H), 3.46 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.02, 170.51, 144.23, 134.86, 130.69 (q, J=306.8 Hz), 130.32, 123.05, 119.64, 114.55, 58.37, 32.18 (q, J=2.4 Hz), 30.82, 23.36; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −42.32; HRMS (ESI) calcd for $C_{13}H_{12}BrF_3NO_2S$ $[M+H]^+$ 381.9716, found 381.9713.

6-Fluoro-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2e**): The product was purified by column chromatography on silica gel [V(petroleum ether∶V(ethyl acetate)=10∶1, R_f=0.24], yellow liquid (71 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.70～7.68 (m, 1H), 7.40～7.36 (m, 1H), 7.20～7.17 (m, 1H), 3.55 (s, 2H), 3.48 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.35, 171.38, 158.66 (d, J=246.3 Hz), 139.41 (d, J=2.4 Hz), 130.45 (q, J=306.5 Hz), 123.63 (d, J=23.2 Hz), 120.83 (d, J=6.4 Hz), 116.96 (d, J=7.2 Hz), 114.14 (d, J=23.4 Hz), 57.48, 33.42 (q, J=1.9 Hz), 30.25, 25.93; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.58, −118.71; HRMS (ESI) calcd for $C_{13}H_{12}F_4NO_2S$ $[M+H]^+$ 322.0519, found 322.0514.

6-Chloro-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2f**): The product was purified by column chromatography on silica gel [V(petroleum ether∶V(ethyl acetate)=10∶1, R_f=0.26], yellow liquid (61 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (d, J=2.6 Hz, 1H), 7.62～7.60 (m, 1H), 7.15 (d, J=8.9 Hz, 1H), 3.54 (s, 2H), 3.48 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.10, 171.48, 141.49, 136.24, 130.43 (q, J=306.4 Hz), 129.45, 127.84, 120.65, 116.70, 57.68, 33.36 (q, J=2.0 Hz), 30.16, 25.92; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.55; HRMS (ESI) calcd for $C_{13}H_{12}ClF_3NO_2S$ $[M+H]^+$ 338.0224, found 338.0218.

6-Bromo-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2g**): The product was purified by column chromatography on silica gel [V(petroleum ether∶V(ethyl acetate)=10∶1, R_f=0.24], yellow soild (74 mg, 65%), m.p. 60～61 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.11 (d, J=2.4 Hz, 1H), 7.76～7.74 (m, 1H), 7.09 (d, J=8.8 Hz, 1H), 3.54 (s, 2H), 3.47 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.99, 171.49, 141.95, 139.11, 130.86, 130.43 (q, J=306.8 Hz), 120.93, 116.98, 116.65, 57.71, 33.34 (q, J=2.0 Hz), 30.13, 25.93; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.54; HRMS (ESI) calcd for $C_{13}H_{12}BrF_3NO_2S$ $[M+H]^+$ 381.9716, found 381.9713.

1,3,6-Trimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2h**): The product was purified by column chromatography on silica gel [V(petroleum ether∶V(ethyl acetate)=10∶1, R_f=0.24], white soild (51 mg, 54%), m.p. 47～48 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (d, J=1.6 Hz, 1H), 7.48～7.46 (m, 1H), 7.09 (d, J=8.4 Hz, 1H), 3.55 (s, 2H), 3.47 (s, 3H), 2.37 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.34, 171.69, 140.81, 137.42, 133.40, 130.57 (q, J=306.3 Hz), 128.30, 119.48, 115.05, 57.41, 33.41 (q, J=2.4 Hz), 29.94, 25.93,

20.33; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.66; HRMS (ESI) calcd for $C_{14}H_{15}F_3NO_2S$ $[M+H]^+$ 318.0770, found 318.0765.

7-Fluoro-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2i**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=10∶1, R_f=0.29], yellow liquid (73 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.07～8.04 (m, 1H), 6.93～6.86 (m, 2H), 3.54 (s, 2H), 3.46 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.55, 171.96, 167.87 (d, *J*=257.2 Hz), 145.36 (d, *J*=11.6 Hz), 131.44 (d, *J*=11.2 Hz), 130.44 (q, *J*=306.4 Hz), 116.24 (d, *J*=2.1 Hz), 111.01 (d, *J*=22.2 Hz), 102.78 (d, *J*=27.7 Hz), 57.43, 33.52 (q, *J*=1.9 Hz), 30.13, 26.05; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.55, −97.82; HRMS (ESI) calcd for $C_{13}H_{12}F_4NO_2S$ $[M+H]^+$ 322.0519, found 322.0515.

7-Chloro-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2j**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=10∶1, R_f=0.32], yellow liquid (81 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96 (d, *J*=8.2 Hz, 1H), 7.19～7.17 (m, 2H), 3.54 (s, 2H), 3.47 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.98, 171.83, 143.95, 143.09, 130.43 (q, *J*=306.8 Hz), 129.79, 123.85, 117.99, 115.43, 33.46 (q, *J*=1.9 Hz), 30.10, 25.98; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.54; HRMS (ESI) calcd for $C_{13}H_{12}ClF_3NO_2S$ $[M+H]^+$ 338.0224, found 338.0218.

7-Bromo-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2k**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=10∶1, R_f=0.35], yellow liquid (89 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87 (d, *J*=8.2 Hz, 1H), 7.37～7.34 (m, 2H), 3.54 (s, 2H), 3.47 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ: 194.20, 171.79, 143.81, 130.43 (q, *J*=306.4 Hz), 131.85, 129.70, 126.82, 118.36, 57.65, 33.45 (q, *J*=2.0 Hz), 30.11, 25.96; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.53; HRMS (ESI) calcd for $C_{13}H_{12}BrF_3NO_2S$ $[M+H]^+$ 381.9716, found 381.9713.

1,3,7-Trimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2l**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=10∶1, R_f=0.26], yellow liquid (71 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91 (d, *J*=7.9 Hz, 1H), 7.02 (d, *J*=7.9 Hz, 1H), 6.98 (s, 1H), 3.54 (s, 2H), 3.47 (s, 3H), 2.46 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.66, 172.12, 148.26, 143.06, 130.56 (q, *J*=306.7 Hz), 128.45, 124.59, 117.49, 115.53, 57.24, 33.55 (q, *J*=1.9 Hz), 29.91, 26.00, 22.48; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.66; HRMS (ESI) calcd for $C_{14}H_{15}F_3NO_2S$ $[M+H]^+$ 318.0770, found 318.0764.

7-Methoxy-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2m**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=8∶1, R_f=0.08], yellow liquid (84 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99 (d, *J*=8.7 Hz, 1H), 6.73～7.71 (m, 1H), 6.62 (d, *J*=2.2 Hz, 1H), 3.91 (s, 3H), 3.53 (d, *J*=1.9 Hz, 2H), 3.45 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.40, 172.38, 166.42, 145.02, 130.97, 130.55 (q, *J*=306.6 Hz), 113.48, 108.65, 101.16, 56.85, 55.87, 33.83 (q, *J*=1.8 Hz), 29.92, 26.18; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.61; HRMS (ESI) calcd for $C_{14}H_{15}F_3NO_3S$ $[M+H]^+$ 334.0719, found 334.0710.

7-(4-Acetylphenyl)-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2n**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=10∶3, R_f=0.16], white soild (75 mg, 59%), m.p. 143～144 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.13～8.08 (m, 3H), 7.73 (d, *J*=8.4 Hz, 2H), 7.46～7.44 (m, 1H), 7.37 (d, *J*=1.2 Hz, 1H), 3.58 (s, 2H), 3.58 (s, 3H), 2.66 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 197.44, 194.67, 171.97, 148.31, 143.92, 143.50, 137.19, 130.51 (q, *J*=306.8 Hz), 129.18, 129.14, 127.64, 122.59, 118.96, 113.89, 57.60, 33.54 (q, *J*=2.2 Hz), 30.11, 26.76, 26.05; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.54; HRMS (ESI) calcd for $C_{21}H_{19}F_3NO_3S$ $[M+H]^+$ 422.1032, found 422.1025.

7-Cyclopropyl-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2o**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=10∶1, R_f=0.26], colourless liquid (54 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (d, *J*=8.1 Hz, 1H), 6.89 (d, *J*=1.1 Hz, 1H), 6.88～6.80 (m, 1H), 3.54 (s, 2H), 3.48 (s, 3H), 2.02～1.96 (m, 1H), 1.53 (s, 3H), 1.16～1.12 (m, 2H), 0.87～0.83 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.42, 172.20, 154.95, 143.10, 130.57 (q, *J*=306.2 Hz), 128.58, 119.99, 117.31, 112.46, 57.14, 33.60 (q, *J*=1.9 Hz), 29.88, 26.06, 16.64, 10.87; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.64; HRMS (ESI) calcd for $C_{16}H_{17}F_3NO_2S$ $[M+H]^+$ 344.0927, found 344.0919.

8-Chloro-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2p**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=15∶1, R_f=0.25], white soild (35 mg, 35%), m.p. 70～71 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.79～7.77 (m, 1H), 7.66～7.65 (m, 1H), 7.20 (t, *J*=7.8 Hz, 1H), 3.59 (s, 3H), 3.47～3.40 (m, 2H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.46, 172.10, 141.52, 138.54, 130.70 (q, *J*=306.8 Hz), 126.46, 125.56, 124.80, 123.03, 57.97, 37.19, 32.24 (q, *J*=2.3 Hz), 23.83; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −42.47; HRMS (ESI) calcd for $C_{13}H_{12}ClF_3NO_2S$ $[M+H]^+$ 338.0224, found 338.0219.

6,8-Dichloro-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2q**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=15∶1, R_f=0.31], yellow soild (36 mg, 32%), m.p. 75～76 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.75 (d, *J*=2.5 Hz, 1H), 7.65 (d, *J*=2.5 Hz, 1H), 3.57 (s, 3H), 3.46～3.40 (m, 2H), 1.54 (s, 3H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ: 194.39, 171.79, 140.21, 137.61, 130.72, 130.60 (q, J=306.8 Hz), 126.24, 125.24, 123.84, 58.06, 37.14, 32.18 (q, J=2.2 Hz), 23.86; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −42.37; HRMS (ESI) calcd for $C_{13}H_{11}Cl_2F_3NO_2S$ $[M+H]^+$ 371.9834, found 371.9830.

6,7-Dimethoxy-1,3-dimethyl-3-(((trifluoromethyl)thio)-methyl)quinoline-2,4(1*H*,3*H*)-dione (**2r**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=2∶1, R_f=0.14], yellow soild (70 mg, 64%), m.p. 106～107 ℃; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.44 (s, 1H), 6.61 (s, 1H), 4.00 (s, 3H), 3.90 (s, 3H), 3.53 (d, J=2.5 Hz, 2H), 3.47 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.58, 172.31, 156.18, 145.58, 139.38, 130.53 (q, J=306.8 Hz), 112.25, 108.93, 98.25, 56.73, 56.41, 56.28, 34.06 (q, J=1.8 Hz), 29.97, 26.49; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.50; HRMS (ESI) calcd for $C_{15}H_{17}F_3NO_4S$ $[M+H]^+$ 364.0825, found 364.0817.

1,3-Dimethyl-3-(((trifluoromethyl)thio)methyl)-1,8-naphthyridine-2,4(1*H*,3*H*)-dione (**2s**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=8∶1, R_f=0.23], yellow liquid (68 mg, 75%); ^1H NMR (500 MHz, $CDCl_3$) δ: 8.63～8.63 (m, 1H), 8.28～8.26 (m, 1H), 7.17～7.15 (m, 1H), 3.60 (s, 3H), 3.55 (d, J=0.9 Hz, 2H), 1.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.61, 172.40, 154.79, 154.06, 136.87, 130.39 (q, J=306.8 Hz), 119.23, 114.87, 57.81, 33.49 (q, J=2.4 Hz), 28.85, 26.05; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.47; HRMS (ESI) calcd for $C_{12}H_{12}F_3N_2O_2S$ $[M+H]^+$ 305.0566, found 305.0558.

1-Benzyl-3-methyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**2t**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=8∶1, R_f=0.23], white soild (92 mg, 81%), m.p. 78～79 ℃; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.96～7.94 (m, 1H), 7.45～7.41 (m, 1H), 7.26 (t, J=7.4 Hz, 2H), 7.22～7.15 (m, 3H), 7.11～7.06 (m, 1H), 7.00 (d, J=8.4 Hz, 1H), 5.34 (d, J=16.3 Hz, 1H), 5.11 (d, J=16.3 Hz, 1H), 3.56 (q, J=13.1 Hz, 2H), 1.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.97, 172.23, 142.22, 136.54, 135.57, 130.57 (q, J=306.7 Hz), 128.49, 127.63, 126.30, 123.68, 119.87, 116.03, 57.86, 46.42, 33.10 (q, J=1.8 Hz), 26.22; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.56; HRMS (ESI) calcd for $C_{19}H_{17}F_3NO_2S$ $[M+H]^+$ 380.0927, found 380.0921.

1-Ethyl-3-methyl-3-(((trifluoromethyl)thio)methyl)-quinoline-2,4(1*H*,3*H*)-dione (**2u**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=8∶1, R_f=0.25], yellow liquid (79 mg, 83%). ^1H NMR (500 MHz, $CDCl_3$) δ: 8.03～8.01 (m, 1H), 7.69～7.63 (m, 1H), 7.21～7.16 (m, 2H), 4.13～4.08 (m, 2H), 3.54 (s, 2H), 1.54 (s, 3H), 1.29 (t, J=7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.28, 171.42, 153.04, 141.87, 136.63, 130.58 (q, J=306.7 Hz), 128.70, 123.36, 119.91, 114.92, 57.38, 37.72, 33.21 (q, J=1.9 Hz), 25.79, 12.29; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.71; HRMS (ESI) calcd for $C_{14}H_{15}F_3NO_2S$ $[M+H]^+$ 318.0770, found 318.0766.

4.3 Scale-up reaction with **1a**

To a reaction tube, acrylamide **1a** (10 mmol), $AgSCF_3$ (1.2 equiv., 12 mmol) and $K_2S_2O_8$ (2.0 equiv., 20 mmol) were mixed in DMSO/H_2O (*V*∶*V*=4∶1, 25 mL). The mixture was stirred in an oil bath at 120 ℃ until complete consumption of starting material as monitored by TLC analysis. After the completion of the reaction, the mixture was quenched by $NaHCO_3$ (sat. aq. 150 mL) and extracted with CH_2Cl_2 (50 mL×3). Then the organic solvent was concentrated *in vacuo*. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluent to product **2a** in 78% yield.

4.4 Synthesis procedure for compound **3**

To a reaction tube, quinolinone **2a** (0.3 mmol) was dissolved in methanol (3 mL). It was cooled to 0 ℃ and then sodium borohydride (1.0 equiv., 0.3 mmol) was added slowly in portions in the period of 0.25 h. The reaction mixture was stirred at room temperature until complete consumption of starting material as monitored by TLC analysis. After completion of the reaction, methanol was removed *in vacuo*. The slurry was cooled to 0 ℃ and quenched with saturated sodium chlorid and extracted with ethyl acetate (10 mL×3). The combined organic layer was washed with water (10 mL), brine (10 mL) and then concentrated *in vacuo*, then purified by flash column chromatography on silica gel with ethyl acetate and petroleum ether as the eluent to afford the corresponding product **3** in 96% yield.

4-Hydroxy-1,3-dimethyl-3-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1*H*)-one (**3**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=10∶1, R_f=0.21], colourless liquid (88 mg, 96%). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.54 (d, J=7.5 Hz, 1H), 7.35 (t, J=7.5 Hz, 1H), 7.18 (t, J=7.5 Hz, 1H), 7.01 (d, J=8.1 Hz, 1H), 5.17 (s, 1H), 3.45 (d, J=13.5 Hz, 1H), 3.35 (s, 3H), 3.13 (d, J=13.5 Hz, 1H), 2.44 (s, 1H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.73, 137.18, 131.38 (q, J=305.9 Hz), 128.77, 127.53, 125.61, 123.91, 114.35, 68.21, 48.51, 33.61 (q, J=1.6 Hz), 30.08, 15.83; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.86; HRMS (ESI) calcd for $C_{13}H_{15}F_3NO_2S$ $[M+H]^+$ 306.0770, found 306.0762.

4.5 Synthesis procedure for compound **4**

To a reaction tube, quinolinone **2a** (0.3 mmol) in dichloromethane (DCM) (2.0 mL), *m*-cholorperoxybenzoic acid (*m*-CPBA, 4.0 equiv., 1.2 mmol) was added. The reaction mixture was stirred at 60 ℃ until complete consumption of starting material as monitored by TLC analysis. After the reaction finished, the reaction mixture was cooled to room temperature and quenched by water. The mixture was extracted with EtOAc (5 mL×3), the combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The residue

was purified by column chromatography to give the corresponding product **4** in 98% yield.

1,3-Dimethyl-3-(((trifluoromethyl)sulfonyl)methyl)quinoline-2,4(1*H*,3*H*)-dione (**4**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=5∶1, R_f=0.11], white soild (99 mg, 98%), m.p. 104～105 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01～7.99 (m, 1H), 7.63 (t, *J*=8.6 Hz, 1H), 7.19～7.16 (m, 2H), 4.27～4.19 (m, 2H), 3.46 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.39, 170.92, 142.83, 136.90, 128.79, 123.73, 119.14 (q, *J*=327.8 Hz), 118.81, 115.30, 55.53, 54.87, 30.28, 25.92; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −78.83; HRMS (ESI) calcd for $C_{13}H_{13}F_3NO_4S$ $[M+H]^+$ 336.0512, found 336.0505.

4.6 Synthesis procedure for compound **5**

To a 10 mL Schlenk tube, quinolinone **2a** (0.4 mmol), NFSI (1.5 equiv., 0.6 mmol), $Cu(acac)_2$ (10 mol%) and MeOH (3.0 equiv., 1.2 mmol) were mixed in CH_3CN (1 mL) under atmosphere of nitrogen. The mixture was stirred in a pre-heated oil bath at 80 ℃ for 24 h under nitrogen atmosphere. The mixture was extracted with EtOAc (5 mL×3), the combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The residue was purified by column chromatography to give the corresponding product **5** in 57% yield.

3-Methyl-3-(((trifluoromethyl)thio)methyl)quinoline-2,4(1*H*,3*H*)-dione (**5**): The product was purified by column chromatography on silica gel [*V*(petroleum ether∶*V*(ethyl acetate)=5∶1, R_f=0.24], white soild (66 mg, 57%), m.p. 92～93 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 7.98～7.96 (m, 1H), 7.64～7.59 (m, 1H), 7.21～7.18 (m, 1H), 7.04 (d, *J*=8.0 Hz, 1H), 3.59 (d, *J*=3.0 Hz, 2H), 1.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.99, 173.79, 140.51, 136.76, 130.49 (q, *J*=306.2 Hz), 128.14, 124.13, 118.35, 116.55, 57.42, 32.80 (q, *J*=2.2 Hz), 25.84; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −41.41; HRMS (ESI) calcd for $C_{12}H_{11}F_3NO_2S$ $[M+H]^+$ 290.0457, found 290.0450.

Supporting Information ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for compounds **2**～**5**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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