### **Supporting Information**

# Selective remote C–H trifluoromethylation of aminoquinolines with CF<sub>3</sub>SO<sub>2</sub>Na under visible light irradiation in the absence of external photocatalyst

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#### **1. General considerations**

All <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). All chemical shifts are given as  $\delta$  value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

#### 2. Representative procedure for the model reaction



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 4-methyl-*N*-(quinolin-8-yl)benzamide (**1a**, 0.20 mmol), sodium trifluoromethanesulfinate (**2a**, 0.40 mmol) and 1,2-dichloroethane (3.0 mL). The reaction vessel was exposed to blue LED (410–415 nm, 1.5 W) irradiation at room temperature in air with stirring for 20 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1 to 50:1) to give the desired product **3a**.

#### 3. Mechanism investigation

#### **3.1 Free radical-trapping experiment (I)**



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 4-methyl-*N*-(quinolin-8-yl) benzamide (**1a**, 24.9 mg, 0.10 mmol), sodium trifluoromethanesulfinate (**2a**, 31.2 mg, 0.20 mmol), TEMPO (62.5 mg, 0.20 mmol) and 1,2-dichloroethane (3.0 mL). The reaction vessel was exposed to blue LED (410–415 nm, 1.5 W) irradiation in air at room temperature with stirring for 20 h. The reaction was completely inhibited, indicating a radical pathway involved in the reaction.

#### 3.2 Free radical-trapping experiment (II)



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with sodium trifluoromethanesulfinate (**2a**, 31.2 mg, 0.20 mmol), 1,1-diphenylethylene (**4**, 0.40 mmol) and 1,2-dichloroethane (3.0 mL). The reaction vessel was exposed to blue LED (410–415 nm, 1.5 W) irradiation in air at room temperature with stirring for 20 h. The adduct **5** was detected by the HRMS analysis of reaction mixture (Figure S1).



Figure S1. HRMS analysis of reaction mixture

#### **3.3** Determination of electron paramagnetic resonance (EPR)

#### **3.3.1 Determination of singlet oxygen species**

For further explore the active species of singlet oxygen involved during the reaction, 2,2,6,6-tetramethylpiperidine (TEMP) were used to trap  ${}^{1}O_{2}$ . Irradiation of air-saturated 1,2-dichloroethane solution of TEMP and *N*-(quinolin-8-yl)benzamide (**1b**) in air under blue LED (410–415 nm) irradiation resulted in the formation of a strong characteristic signal  ${}^{1}O_{2}$  (g = 2.0070, a<sub>O</sub> = 15. 79 G) adduct with TEMP (Figure S2). A series of stronger characteristic signal of  ${}^{1}O_{2}$  were collected with prolonged irradiation time (Figure S2b and S2c), implying that  ${}^{1}O_{2}$  was present in the reaction.





(b) A solution of *N*-(quinolin-8-yl)benzamide (1b) with TEMP (0.20 mol/L) in air-saturated DCE under LED (410–415 nm) irradiation for 30 s.

(c) A solution of *N*-(quinolin-8-yl)benzamide (1b) with TEMP (0.20 mol/L) in air-saturated DCE under LED (410-415 nm) irradiation for 60 s.

#### **3.3.2 Determination of superoxide radicals**

In order to determine the active species of oxygen involved in the present reaction, 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) were employed to capture  $O_2^{-}$ . There was no signal when DMPO was added into air-saturated 1,2-dichloroethane (DCE) solution of 4-methyl-*N*-(quinolin-8-yl)benzamide (**1a**) in the absence of light irradiation (Figure S3a). Irradiation of air-saturated DCE solution of DMPO with **1a** in air with blue LED (410–415 nm) resulted in the formation of a strong characteristic signal of  $O_2^{-}$  (g = 2.0050,  $a_0 = 12.71$  G) adduct with DMPO (Figure S3b). When the reaction time was prolonged, a series of stronger characteristic signal of  $O_2^{-}$  were observed (Figure S3c and S3d), indicating the formation of  $O_2^{-}$  in the reaction.



**Figure S3**. Electron spin resonance (ESR) spectra of  $O_2^-$  adduct with DMPO (a) A solution of DMPO (0.20 mol/L) with 4-methyl-*N*-(quinolin-8-

yl)benzamide (1a) in air-saturated DCE without light irradiation.

(**b**) A solution of DMPO (0.2 mol/L) with 4-methyl-*N*-(quinolin-8-yl)benzamide (**1a**) in air-saturated DCE under blue LED (410–415 nm) irradiation for 30 s.

(c) A solution of DMPO (0.2 mol/L) with 4-methyl-N-(quinolin-8-yl)benzamide

(1a) in air-saturated DCE under blue LED (410–415 nm) irradiation for 60 s.

(d) A solution of DMPO (0.2 mol/L) with 4-methyl-N-(quinolin-8-yl)benzamide

(1a) in air-saturated DCE under blue LED (410-415 nm) irradiation for 180 s.

### 3.4 Absorption spectra of selected substrates and products



**Figure S4.** Absorption spectra of 4-methyl-*N*-(quinolin-8-yl) benzamide (**1a**) and 4-methyl-*N*-(5-(trifluoromethyl)quinolin-8-yl) benzamide (**3a**) in ClCH<sub>2</sub>CH<sub>2</sub>Cl (3.0 mL)  $[\Delta \lambda \max = 18.32 \text{ nm}].$ 



Figure S5. Absorption spectra of *N*-(quinolin-8-yl)benzamide (1b) and *N*-(5-(trifluoromethyl) quinolin-8-yl)benzamide (3b) in ClCH<sub>2</sub>CH<sub>2</sub>Cl (3.0 mL) [ $\Delta \lambda$  max = 17.22 nm].





in ClCH<sub>2</sub>CH<sub>2</sub>Cl (3.0 mL) [ $\Delta \lambda$  max = 8.94 nm].



Figure S7. Absorption spectra of *N*-(4-methylquinolin-8-yl)benzamide (1z) and *N*-(4-methyl-5-(trifluoromethyl)quinolin-8-yl)benzamide (3z) in ClCH<sub>2</sub>CH<sub>2</sub>Cl (3.0

mL) [ $\Delta \lambda \max = 6.91 \text{ nm}$ ].



Figure S8. Absorption spectra of sodium trifluoromethanesulfinate (2a) in water (3.0 mL).

## 3.4 Light/Dark experiments



Figure S9. Light/dark experiments.





















































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