Supporting Information

Visible-light promoted C2 trifluoromethylation of quinoline N-oxides
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1. Preparation and characterization of substrates

1.1. Preparation of Togni’s reagent

Togni’s reagent (1-trifluoromethyl-1,2-benziodoxol-3(1H)-one) were prepared as reported in literature. And all characterization data are in accordance with the previous literature.

1.2. Preparation of substituted quinoline N-oxide

To a 100 mL round flask, 1.0 equiv. substituted quinoline, 0.25 M DCM (dichloromethane), magnetic stir bar and 1.2 equiv. m-CPBA (m-chlorobenzoperoxoic acid) were added in sequence. The reaction mixture was allowed to stir at room temperature overnight to finish the reaction. After the reaction finished (monitored by TLC), the reaction mixture was concentrated in vacuo, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate or methanol/DCM) to give the substituted quinoline N-oxide.

1.3. Characterization of substrates

4-methylquinoline N-oxide (1a). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.81 (d, $J = 8.7$ Hz, 1H), 8.43 (d, $J = 6.1$ Hz, 1H), 7.97 (d, $J = 8.3$ Hz, 1H), 7.77 (t, $J = 7.4$ Hz, 1H), 7.67 (t, $J = 7.2$ Hz, 1H), 7.12 (d, $J = 6.1$ Hz, 1H), 2.66 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 140.81, 134.85, 134.54, 129.95, 129.71, 128.36, 124.63, 121.32, 120.19, 18.24.

4-chloroquinoline N-oxide (1b). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.76 (d, $J = 8.7$ Hz, 1H), 8.44 (d, $J = 6.5$ Hz, 1H), 8.20 (d, $J = 8.3$ Hz, 1H), 7.83 (t, $J = 7.8$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 6.5$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 141.98, 135.05, 131.08, 129.88, 129.55, 127.88, 125.06, 120.93, 120.24.

4-bromoquinoline N-oxide (1c). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.76 (d, $J = 8.5$ Hz, 1H), 8.40 (d, $J = 6.5$ Hz, 1H), 8.17 (dd, $J = 8.5$, 1.3 Hz, 1H), 7.83 (ddd, $J = 8.5$, 6.9, 1.4 Hz, 1H), 7.76 (ddd, $J = 8.3$, 6.9, 1.3 Hz, 1H), 7.59 (d, $J = 6.5$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 142.06, 135.30, 131.23, 129.88, 129.25, 127.75, 124.51, 120.25 (2C).

4-nitroquinoline N-oxide (1d). Commercial reagents from Macklin, China.

4-methoxyquinoline N-oxide (1e). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.62 (d, $J = 8.7$ Hz, 1H), 8.38 (d, $J = 6.7$ Hz, 1H), 8.07 (d, $J = 8.3$ Hz, 1H), 7.69 (t, $J = 7.8$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 6.53 (d, $J = 6.8$ Hz, 1H), 3.93 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 154.27, 140.30, 135.90, 130.47, 127.40, 122.10, 121.94, 119.12, 99.11, 55.82.

4-cyclopropylquinoline N-oxide (1f). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.61 (d, $J = 8.6$ Hz, 1H), 8.31 (d, $J = 5.7$ Hz, 1H), 8.14 (d, $J = 8.0$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.49 (t, $J = 7.1$ Hz, 1H), 6.78 (d, $J = 5.8$ Hz, 1H), 2.11 (s, 1H), 0.98 (d, $J = 7.8$ Hz, 2H), 0.62 (d, $J = 4.7$ Hz, 2H). $^{13}$C NMR
(151 MHz, CDCl$_3$)  δ 139.55, 139.45, 134.39, 129.45, 129.19, 127.54, 123.93, 119.06, 116.85, 77.21, 77.00, 76.79, 11.17, 6.86.

4-phenylquinoline N-oxide (1g). $^1$H NMR (600 MHz, CDCl$_3$)  δ 8.74 (dd, $J = 13.7, 8.7$ Hz, 1H), 8.46 (dd, $J = 14.4, 6.4$ Hz, 1H), 7.84 (dd, $J = 15.2, 8.3$ Hz, 1H), 7.66 (dt, $J = 16.9, 8.5$ Hz, 1H), 7.51 – 7.46 (m, 1H), 7.45 – 7.35 (m, 5H), 7.14 (dd, $J = 15.8, 6.2$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$)  δ 141.35, 138.54, 136.80, 134.79, 130.06, 129.41 (2C), 128.62 (2C), 128.56 (d, $J = 4.8$ Hz), 128.52, 128.47, 126.55, 121.19, 119.90.

4-(4-fluorophenyl)quinoline N-oxide (1h). $^1$H NMR (400 MHz, CDCl$_3$)  δ 8.85 (d, $J = 8.7$ Hz, 1H), 8.58 (d, $J = 6.2$ Hz, 1H), 7.90 (d, $J = 8.4$ Hz, 1H), 7.82 – 7.77 (m, 1H), 7.65 – 7.61 (m, 1H), 7.49 – 7.46 (m, 2H), 7.26 – 7.22 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$)  δ 162.85 (d, $J = 248.9$ Hz), 141.46, 137.55, 134.89, 132.86 (d, $J = 3.4$ Hz), 131.28, 131.20, 130.27, 128.78, 126.67, 126.38, 121.33, 120.09, 115.94, 115.72. $^{19}$F NMR (376 MHz, CDCl$_3$)  δ -112.57 (tt, $J = 8.5, 5.2$ Hz).

4-(4-chlorophenyl)quinoline N-oxide (1i). $^1$H NMR (600 MHz, CDCl$_3$)  δ 8.84 (d, $J = 8.7$ Hz, 1H), 8.57 (d, $J = 5.9$ Hz, 1H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.79 (t, $J = 7.6$ Hz, 1H), 7.63 (t, $J = 7.5$ Hz, 1H), 7.52 (d, $J = 7.7$ Hz, 2H), 7.44 (d, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 5.9$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$)  δ 141.46, 137.14, 135.27, 134.84, 134.74, 130.76 (2C), 130.27, 128.95 (2C), 128.81, 128.45, 126.24, 121.23, 120.07.

4-(4-(trifluoromethyl)phenyl)quinoline N-oxide (1j). $^1$H NMR (400 MHz, CDCl$_3$)  δ 8.86 (d, $J = 8.7$ Hz, 1H), 8.60 (d, $J = 6.2$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.83 – 7.79 (m, 3H), 7.67 – 7.63 (m, 3H), 7.28 (d, $J = 6.2$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$)  δ 141.57, 140.57, 136.72, 134.86, 130.68 (q, $J = 33.3$ Hz), 130.43, 129.94 (2C), 129.06, 128.38, 126.12, 125.71 (q, $J = 3.7$ Hz, 2C), 123.87 (q, $J = 273.7$ Hz), 121.41. $^{19}$F NMR (376 MHz, CDCl$_3$)  δ -62.55.

6-bromo-4-chloroquinoline N-oxide (1k). $^1$H NMR (400 MHz, CDCl$_3$)  δ 8.62 (d, $J = 9.3$ Hz, 1H), 8.43 (d, $J = 6.6$ Hz, 1H), 8.35 (d, $J = 2.0$ Hz, 1H), 7.88 (dd, $J = 9.3, 2.1$ Hz, 1H), 7.40 (d, $J = 6.6$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$)  δ 140.86, 135.28, 134.52, 129.07, 128.43, 127.41, 124.63, 122.24, 122.10.

4-chloro-6-methoxyquinoline N-oxide (1l). $^1$H NMR (400 MHz, CDCl$_3$)  δ 8.65 (d, $J = 9.5$ Hz, 1H), 8.30 (d, $J = 6.5$ Hz, 1H), 7.41 (dd, $J = 9.5, 2.6$ Hz, 1H), 7.37-7.30 (m, 2H), 3.99 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$)  δ 160.17, 137.59, 133.18, 129.38, 128.49, 123.39, 122.06, 121.42, 102.94, 55.79.

4-chloro-6-phenylquinoline N-oxide (1m). $^1$H NMR (600 MHz, CDCl$_3$)  δ 8.79 (d, $J = 8.5$ Hz, 1H), 8.43 (d, $J = 5.7$ Hz, 1H), 8.30 (s, 1H), 8.03 (d, $J = 9.0$ Hz, 1H), 7.70 (d, $J = 6.0$ Hz, 2H), 7.51 (t, $J = 7.6$ Hz, 2H), 7.45 (d, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 5.2$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$)  δ 142.49, 141.17, 138.82, 134.95, 130.68, 130.05, 129.06 (2C), 128.55, 128.15, 127.48 (2C), 122.54, 121.29, 120.92.

4,7-dichloroquinoline N-oxide (1n). $^1$H NMR (600 MHz, CDCl$_3$)  δ 8.77 (d, $J = 2.0$ Hz, 1H), 8.43
(d, J = 6.6 Hz, 1H), 8.14 (d, J = 8.9 Hz, 1H), 7.69 (dd, J = 8.9, 2.0 Hz, 1H), 7.38 (d, J = 6.6 Hz, 1H).
$^{13}$C NMR (151 MHz, CDCl$_3$) δ 142.22, 138.06, 135.81, 130.68, 129.60, 126.65, 126.41, 121.16, 119.81.

7-bromo-4-chloroquinoline N-oxide (1o). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.95 (s, 1H), 8.44 (d, J = 6.2 Hz, 1H), 8.05 (d, J = 8.7 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 7.39 (d, J = 6.3 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 142.27, 135.87, 133.28, 129.86, 126.69, 126.56, 126.27, 123.06, 121.29.

4-chloro-7-methoxyquinoline N-oxide (1p). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 (d, J = 6.6 Hz, 1H), 8.10 – 8.08 (m, 2H), 7.37 (dd, J = 9.3, 2.5 Hz, 1H), 7.25 (d, J = 6.6 Hz, 1H), 4.07 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.53, 143.40, 135.82, 130.63, 126.52, 122.94, 122.69, 118.53, 98.72, 56.18.

7-chloro-4-methoxyquinoline N-oxide (1q). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.76 (s, 1H), 8.47 (d, J = 6.8 Hz, 1H), 8.15 (d, J = 8.9 Hz, 1H), 7.58 (d, J = 8.9 Hz, 1H), 6.65 (d, J = 6.8 Hz, 1H), 4.07 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 154.35, 141.40, 137.82, 137.01, 128.99, 124.25, 120.92, 119.44, 99.82, 77.21, 77.00, 76.79, 56.33.

4-chloro-6,7-dimethoxyquinoline N-oxide (1r). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.33 (d, J = 6.6 Hz, 1H), 8.06 (s, 1H), 7.31 (s, 1H), 7.24 (d, J = 6.6 Hz, 1H), 4.11 (s, 3H), 4.07 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.85, 151.84, 138.10, 133.84, 128.42, 123.41, 119.13, 102.65, 99.43, 56.69, 56.29.

quinoline N-oxide (1s). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.76 (d, J = 8.8 Hz, 1H), 8.55 (d, J = 5.9 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.78 -7.74 (m, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 141.40, 135.53, 130.39, 130.34, 128.66, 128.03, 125.96, 120.86, 119.63.

quinolxaline N-oxide (1t). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.70 (d, J = 3.5 Hz, 1H), 8.59 (d, J = 8.6 Hz, 1H), 8.39 (d, J = 3.5 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.84 (t, J = 7.6 Hz, 1H), 7.76 (t, J = 7.7 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 145.85, 145.82, 137.36, 131.67, 130.16, 130.00, 129.16, 118.80.
2. NMR Spectra of substrates

$^1$H and $^{13}$C spectra of 1a
$^1$H and $^{13}$C spectra of 1b
$^1$H and $^{13}$C spectra of 1c
$^1$H and $^{13}$C spectra of 1d
$^1$H and $^{13}$C spectra of 1f
$^1$H and $^{13}$C spectra of $1g$
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 1h
$^1$H and $^{13}$C spectra of 1i
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 1j
$^1$H and $^{13}$C spectra of 1k
$^1$H and $^{13}$C spectra of 11
$^1$H and $^{13}$C spectra of 1m
\(^1\)H and \(^{13}\)C spectra of 1n
$^1$H and $^{13}$C spectra of 1o
$^1$H and $^{13}$C spectra of 1p
$^1$H and $^{13}$C spectra of 1q
$^1$H and $^{13}$C spectra of 1r
$^1$H and $^{13}$C spectra of 1s
$^1$H and $^{13}$C spectra of 1t
3. NMR Spectra of products

${}^1\text{H}, {}^{13}\text{C}$ and $^{19}\text{F}$ NMR spectra of 2a
$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of 2b
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2c
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2d
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2e
$^{1}\text{H}$, $^{13}\text{C}$ and $^{19}\text{F}$ NMR spectra of 2f
$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of 2g
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2h
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2i
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2j
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2k
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2l
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2m
$^{1}H,^{13}C$ and $^{19}F$ NMR spectra of 2n
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2o
$^{1}\text{H}$, $^{13}\text{C}$ and $^{19}\text{F}$ NMR spectra of 2p
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2q
$^{1}\text{H}, ^{13}\text{C}$ and $^{19}\text{F}$ NMR spectra of 2r
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2s
$^1$H, $^{13}$C and $^{19}$F NMR spectra of 2t
4. X-ray data of 2a

4-methyl-2-(trifluoromethyl)quinoline N-oxide (2a), CCDC No. 1945114.

Figure 1 Crystal structure refinement for 2a.

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<th>Table 1 Crystal data and structure refinement for 2a.</th>
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5. Stern-Volmer experiments

The fluorescent quenching experiments were conducted at 340 nm and the emission intensity from 450 to 650 nm was recorded. To a 3 mL solution of \( \text{fac-Ir(ppy)}_3 \) (0.0001 mmol/ mL) in MeCN, Togni’s reagent (0 mM, 0.2 mM, 0.4 mM, 0.6 mM, 0.8 mM, 1.0 mM in turn) or 1a (0 mM, 0.2 mM, 0.4 mM, 0.6 mM, 0.8 mM, 1.0 mM in turn) was added.

![Fluorescence spectra](image-url)

Figure 2 Fluorescence spectra of a solution of photocatalyst \( \text{fac-Ir(ppy)}_3 \) in MeCN containing 0 mM, 0.2 mM, 0.4 mM, 0.6 mM, 0.8 mM or 1.0 mM of 1a.
Figure 3 Fluorescence spectra of a solution of photocatalyst fac-Ir(ppy)$_3$ in MeCN containing 0 mM, 0.2 mM, 0.4 mM, 0.6 mM, 0.8 mM or 1.0 mM of Togni’s reagent.

Figure 4 a) Stern–Volmer Quenching experiments. b) Electron transfer from Togni’s reagent to *Ir$^{III}$. c) Energy transfer from *Ir$^{III}$ to 1a.

Reference