SUPPORTING INFORMATION

FOR

Highly Chemoselective Deoxygenation of N-Heterocyclic N-Oxides
Under Transition Metal-Free Conditions

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GENERAL INFORMATION

General Methods
Experiments involving moisture- and/or air-sensitive compounds were performed in oven- or flame-dried glassware with rubber septa under a positive pressure of nitrogen using standard Schlenk techniques. Non-aqueous reagents were transferred by hypodermic syringe. Heating was accomplished by silicon oil bath using a temperature controller. Brine is defined as a saturated aqueous solution of sodium chloride. Organic solutions were concentrated under reduced pressure at 30 °C (water bath temperature) using a Büchi rotary evaporator, unless otherwise noted. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) or GC. Yields refer to chromatographically and spectroscopically (1H NMR) homogeneous (>95%) materials, unless otherwise stated. Melting point were measured using a Stuart SMP50 apparatus and are uncorrected.

Chromatography
TLC was performed on E. Merck 60–F254 precoated plates (0.25 mm), and spots were visualized by UV fluorescence (254 nm) quenching, iodine vapor, and KMnO₄ staining. Flash chromatography was carried out with Merck silica gel 60 (200–400 mesh) according to the procedure of Still et al.¹

NMR & IR Spectroscopy
¹H and ¹³C NMR spectra were recorded with Bruker AVANCE III Ascend 500 (500 MHz and 126 MHz, respectively) and AVANCE III HD (400 MHz and 101 MHz, respectively) spectrometers. ¹⁹F NMR spectra were obtained on a Bruker AVANCE III Ascend 500 spectrometer (471 MHz). Chemical shifts of the ¹H NMR (CDCl₃: 7.26 ppm, DMSO-d₆: 2.50 ppm, CD₃CN: 1.94 ppm) and ¹³C NMR (CDCl₃: 77.00 ppm, DMSO-d₆: 39.50 ppm, CD₃CN: 118.26 ppm) spectra were referenced to residual solvent peaks or tetramethysilane (0.00 ppm) as an internal standard. 2-Phenylquinoline N-oxide (2u) was dissolved in a minimum amount of CDCl₃, and the resulting homogeneous solution was diluted with CD₃CN. ¹H NMR spectra are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quarter, quin = quintet, sext = sextet, sept = septet, m = multiplet, br = broad), coupling constant (J) in Hz and integration. Infrared (IR) spectra were recorded on a Brucker AVATAR 370 DTGS spectrometer using thin film samples on KBr plates and are reported in terms of frequency of absorption (cm⁻¹).
Mass Spectrometry
Low-resolution mass spectra were acquired using a HP 6890 GC system coupled with a HP 5973 mass
selective detector with electron impact (EI) mode or an Agilent 1260 infinity LC-MS system coupled with
an Agilent 6120 quadrupole mass spectrometer with electrospray ionization (ESI) mode. High-
resolution mass spectra (HRMS) were obtained from the Organic Chemistry Research Center (OCRC)
at Sogang University (Seoul, Korea) using a Bruker Compact ESI-TOF mass spectrometer.

Starting Materials
Unless otherwise stated, all reagents and solvents were purchased at the highest commercial quality
from commercial suppliers (Sigma-Aldrich, TCI, Alpha Aesar, Strem, or Acros) and used as received
without further purification.

Visible Light-Mediated Deoxygenation Setup
For all deoxygenation reactions, irradiation of the stirred mixture in a borosilicate test tube or a
borosilicate round-bottomed flask fitted with a rubber setup was accomplished using two MR16 3W
green LED spotlight lamps (12 V, 530–535 nm). For mmol scale reactions, the two green LEDs were
placed 3-cm-away from the reaction tube located in a customized reactor made from acrylic plates. A
fan was employed for maintaining the reaction temperature between 20–30 °C during the irradiation.

Figure S1. Deoxygenation setup (front view).  Figure S2. Deoxygenation setup (top view)
EXPERIMENTAL DATA

Experimental Procedures and Compounds Characterization Data

Preparation of Hantzsch esters (1)
Hantzsch esters were prepared according to the literature procedures, further purified by recrystallization from an appropriate mixture of solvents as indicated and stored in a refrigerator under an N₂ atmosphere.

Preparation of Di-tert-butyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2a)

Prepared according to the literature procedure and further purified by recrystallization from a hot MeOH to afford the title compound as a light green solid.²

³¹H NMR (500 MHz, CDCl₃) δ 5.09 (s, 1H), 3.16 (s, 2H), 2.13 (s, 6H), 1.47 (s, 18H).
³¹C NMR (126 MHz, CDCl₃) δ 167.6, 143.7, 100.9, 79.4, 28.4, 25.4, 19.2.
GC-MS (EI, 70 eV) m/z calculated for [M]⁺ (C₁₇H₂₇NO₄) 309.2, found 309.3.

Preparation of Di-tert-butyl 2,4,6-Trimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2b)

Prepared according to the literature procedure and further purified by recrystallization from a hot MeOH to afford the title compound as a white solid.³

³¹H NMR (500 MHz, CDCl₃) δ 5.39 (s, 1H), 3.74 (q, J = 6.5 Hz, 1H), 2.21 (s, 6H), 1.48 (s, 18H), 0.94 (d, J = 6.5 Hz, 3H).
³¹C NMR (126 MHz, CDCl₃) δ 167.3, 143.1, 106.0, 79.3, 29.2, 28.3, 22.1, 19.4.
GC-MS (EI, 70 eV) m/z calculated for [M]⁺ (C₁₇H₂₇NO₄) 323.2, found 323.3.
Preparation of Diethyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2c)

Prepared according to the literature procedure and further purified by recrystallization from a hot EtOH to afford the title compound as a light green solid.\(^4\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.24 (s, 1H), 4.16 (q, \(J = 7.1\) Hz, 4H), 3.25 (s, 2H), 2.18 (s, 6H), 1.27 (t, \(J = 7.1\) Hz, 6H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 168.0, 144.8, 99.5, 59.6, 24.8, 19.1, 14.4.

GC-MS (EI, 70 eV) \(m/z\) calculated for \([M]^+\) (C\(_{13}\)H\(_{19}\)NO\(_4\)) 253.1, found 253.1.

Preparation of Dimethyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2d)

Prepared according to the literature procedure and further purified by recrystallization from a hot MeOH to afford the title compound as a light green solid.\(^2\)

\(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.32 (s, 1H), 3.58 (s, 6H), 3.13 (s, 2H), 2.11 (s, 6H).

\(^{13}\)C NMR (126 MHz, DMSO) \(\delta\) 167.4, 146.7, 96.9, 50.6, 24.7, 17.8.

GC-MS (EI, 70 eV) \(m/z\) calculated for \([M]^+\) (C\(_{11}\)H\(_{15}\)NO\(_4\)) 225.1, found 225.1.

Preparation of Di-tert-butyl 4-Deuterio-2,6-dimethyl-1,4-dihydro-4-deuteriopyridine-3,5-dicarboxylate (2a-d\(_2\))

Prepared according to the literature procedure and further purified by recrystallization from a hot MeOH to afford the title compound as a light green solid.\(^5\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.12 (s, 1H), 2.13 (s, 6H), 1.47 (s, 18H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 167.6, 143.8, 100.7, 79.4, 28.4, 19.1.
IR (KBr) 3325, 3242, 2967, 2082, 1695, 1642, 1487, 1366, 1349, 1302, 1252, 1153, 1133, 1058, 1021, 831, 742 cm⁻¹.

HRMS (ESI, TOF) m/z calculated for [M + Na]⁺ (C₁₇H₂₆D₂NNaO₄) 334.1958, found 334.1958.

Melting point: 165.5-167.4 °C.

Preparation of N-Heterocyclic N-Oxides (1)

N-Heterocyclic N-oxides were prepared according to the literature procedures, further purified by recrystallization from an appropriate mixture of solvents as indicated and stored in a desiccator.

3-Quinolinecarbonitrile N-Oxide (1a)

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.⁵,⁶

¹H NMR (400 MHz, CDCl₃) δ 8.75 (d, J = 8.8 Hz, 1H), 8.60 (s, 1H), 8.05 (s, 1H), 7.99–7.88 (m, 2H), 7.79 (t, J = 7.6 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 143.3, 134.8, 133.3, 130.5, 129.7, 129.0 (two carbons), 120.0, 114.9, 107.2.

LC-MS (ESI) m/z calculated for [M+1]⁺ (C₁₀H₇N₂O) m/z 171.1, found m/z 171.1.

2-Quinolinecarbonitrile N-Oxide (1b)

Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:1, v/v) to afford the title compound as a white solid.⁶

¹H NMR (500 MHz, CDCl₃) δ 8.66 (d, J = 8.7 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.83 (ddd, J = 8.6, 7.0, 1.3 Hz, 1H), 7.79–7.71 (m, 2H), 7.52 (d, J = 8.8 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 142.0, 131.5, 131.1, 130.9, 128.5, 124.6, 123.4, 121.3, 119.9, 112.9.

LC-MS (ESI) m/z calculated for [M+1]⁺ (C₁₀H₇N₂O) m/z 171.1, found m/z 171.1.
Methyl 3-Quinolinecarboxylate N-Oxide (1c)

\[
\text{Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.}^{5,7}
\]

\[
^1H \text{ NMR (500 MHz, CDCl}_3\text{)} \delta 9.02 (d, J = 1.5 Hz, 1H), 8.75 (dd, J = 8.7, 0.9 Hz, 1H), 8.38 (s, 1H), 7.97 (dd, J = 8.1, 1.6 Hz, 1H), 7.86 (ddd, J = 8.7, 7.0, 1.4 Hz, 1H), 7.71 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 3.99 (s, 3H).
\]

\[
^{13}C \text{ NMR (126 MHz, CDCl}_3\text{)} \delta 163.8, 143.1, 135.0, 132.5, 129.6, 129.5, 129.1, 127.6, 124.4, 120.0, 52.9.
\]

\[
\text{LC-MS (ESI) } m/z \text{ calculated for [M+1]}^+ (C_{11}H_{10}NO_3) 204.1, \text{ found 204.1.}
\]

Methyl 6-Quinolinecarboxylate N-Oxide (1d)

\[
\text{Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.}^{5,7}
\]

\[
^1H \text{ NMR (500 MHz, CDCl}_3\text{)} \delta 8.78 (d, J = 9.1 Hz, 1H), 8.60 (d, J = 1.8 Hz, 1H), 8.57 (dd, J = 6.1, 1.0 Hz, 1H), 8.31 (dd, J = 9.1, 1.8 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.35 (dd, J = 8.5, 6.1 Hz, 1H), 3.99 (s, 3H).
\]

\[
^{13}C \text{ NMR (126 MHz, CDCl}_3\text{)} \delta 165.7, 143.3, 137.0, 130.9, 130.5, 130.0, 129.8, 126.4, 121.9, 120.4, 52.6.
\]

\[
\text{LC-MS (ESI) } m/z \text{ calculated for [M+1]}^+ (C_{11}H_{10}NO_3) 204.1, \text{ found 204.1.}
\]

Ethyl 6-Quinolinecarboxylate N-Oxide (1e)
Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature. 5,8

^1^H NMR (500 MHz, CDCl$_3$) δ 8.77 (d, J = 9.1 Hz, 1H), 8.59 (d, J = 1.8 Hz, 1H), 8.56 (dd, J = 6.0, 1.0 Hz, 1H), 8.31 (dd, J = 9.1, 1.8 Hz, 1H), 7.84–7.78 (m, 1H), 7.35 (dd, J = 8.4, 6.1 Hz, 1H), 4.44 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H).

^13^C NMR (126 MHz, CDCl$_3$) δ 165.2, 143.2, 137.0, 130.8 (two carbons), 129.9, 129.8, 126.4, 121.8, 120.3, 61.7, 14.3.

**LC-MS (ESI)** m/z calculated for [M+1]^+ (C$_{12}$H$_{12}$NO$_3$) 218.1, found 218.1.

**Isopropyl 6-Quinolinecarboxylate N-Oxide (1f)**

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature. 5,9

^1^H NMR (500 MHz, CDCl$_3$) δ 8.77 (d, J = 9.1 Hz, 1H), 8.62–8.55 (m, 2H), 8.31 (dd, J = 9.2, 1.8 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.35 (dd, J = 8.5, 6.0 Hz, 1H), 5.31 (sept, J = 6.3 Hz, 1H), 1.41 (d, J = 6.3 Hz, 6H).

^13^C NMR (126 MHz, CDCl$_3$) δ 164.7, 143.2, 137.0, 131.2, 130.7, 129.9 (two carbons), 126.4, 121.8, 120.3, 69.4, 21.9.

**LC-MS (ESI)** m/z calculated for [M+1]^+ (C$_{13}$H$_{13}$NO$_3$) 232.1, found 232.1.

**tert-Butyl 6-Quinolinecarboxylate N-Oxide (1g)**

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature. 5,7

^1^H NMR (500 MHz, CDCl$_3$) δ 8.76 (d, J = 9.1 Hz, 1H), 8.56 (d, J = 6.1 Hz, 1H), 8.53 (d, J = 1.8 Hz, 1H), 8.26 (dd, J = 9.1, 1.8 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.34 (dd, J = 8.5, 6.0 Hz, 1H), 1.64 (s, 9H).
**Methyl 8-Quinolinecarboxylate N-Oxide (1h)**

A 10 mL round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with 8-quinolinecarboxylic acid (173 mg, 1.0 mmol), MeOH (2.0 mL), and H$_2$SO$_4$ (0.4 mL). The resulting mixture was heated in an oil bath (bath temperature = 80 °C) under reflux overnight. The mixture was allowed to cool to room temperature, diluted with CH$_2$Cl$_2$, and neutralized with an aqueous solution of saturated NaHCO$_3$ (Caution! Evolution of CO$_2$). The mixture was then extracted with CH$_2$Cl$_2$ (5 mL × 3). The combined organic layer was washed successively with water and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 1:1) on silica gel to afford methyl 8-quinolinecarboxylate (3h, 146 mg, 78 %) as a yellow oil. One dram vial equipped with a small magnetic stir bar was charged with 3h (187 mg, 1.76 mmol, 1.0 equiv), MeReO$_3$ (40 mg, 0.18 mmol), and CH$_2$Cl$_2$ (0.9 mL, ca. 2 M). The resulting mixture was cooled to 0 °C and treated with 30% H$_2$O$_2$ (0.36 mL, 2.0 equiv) via syringe. After stirring at the same temperature for 24 h, the mixture was extracted with CH$_2$Cl$_2$ (5 mL × 3). The combined organic layer was washed successively with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc/MeOH = 9:1) on silica gel to afford the title compound (130 mg, 36%) as an off-white solid.

**$^1$H NMR** (500 MHz, CDCl$_3$) δ 7.89 (dd, $J$ = 7.9, 1.5 Hz, 1H), 7.73 (d, $J$ = 8.4 Hz, 1H), 7.67–7.56 (m, 2H), 7.31 (dd, $J$ = 8.4, 6.1 Hz, 1H), 4.01 (s, 2H).

**$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 169.1, 137.8, 135.7, 130.8, 129.5, 129.4, 128.0, 127.6, 125.6, 121.7, 52.9.

**HRMS (ESI, TOF) m/z** calculated for [M + Na]$^+$ (C$_{11}$H$_9$NNaO$_3$) 226.0475, found 226.0475
**IR** (KBr) 3463, 3275, 1726, 1695, 1672, 1610, 1575, 1489, 1468, 1437, 1328, 1287, 1271, 1253, 1200, 1154, 1128, 1069 cm\(^{-1}\).

**Melting point**: 170-185 °C.

**3-Acetylquinoline N-Oxide (1i)**

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.\(^5,6\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.98 (d, \(J = 1.5\) Hz, 1H), 8.77–8.71 (m, 1H), 8.24 (s, 1H), 8.00 (dd, \(J = 8.2, 1.4\) Hz, 1H), 7.86 (ddd, \(J = 8.5, 7.0, 1.4\) Hz, 1H), 7.72 (ddd, \(J = 8.0, 6.9, 1.1\) Hz, 1H), 2.69 (s, 3H).

\(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 194.1, 143.0, 134.0, 132.6, 130.6, 129.8, 129.6, 129.2, 126.2, 120.0, 26.6.

**LC-MS** (ESI) \(m/z\) calculated for [M+1]\(^+\) (C\(_{11}\)H\(_{10}\)NO\(_2\)) 188.1, found 188.1.

**N,N-Diphenyl-6-quinolinecarboxamide N-Oxide (1j)**

A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 6-quinolinecarboxylic acid (693 mg, 4.00 mmol, 1.0 equiv), 1,1'carbodiimidazole (685 mg, 4.00 mmol, 1.0 equiv), and dry DMF (5.8 mL, 0.69 M). After stirring in an oil bath (bath temperature = 40 °C) for 2 h, the mixture was treated with diphenylamine (2.03 g, 12.0 mmol, 3.0 equiv) followed by DBU (609 mg, 4.00 mmol, 1.0 equiv). After stirring at 80 °C for 16 h, the mixture was allowed to cool to room temperature and extracted with CH\(_2\)Cl\(_2\) (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na\(_2\)SO\(_4\), filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 1:2) on silica gel to afford N,N-diphenyl-6-quinolinecarboxamide (3j, 177 mg, 21 %) as a white solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 3j (277 mg, 0.850 mmol, 1.0 equiv) and CH\(_2\)Cl\(_2\) (1.5 mL). The
resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with \textit{m}-CPBA (77%, 287 mg, 1.28 mmol, 1.5 equiv) in CH$_2$Cl$_2$ (1.3 mL), and the resulting \textit{m}-CPBA solution was added dropwise to the flask containing 3\textit{j} at 0 °C via syringe. The pear-shaped flask was rinsed with CH$_2$Cl$_2$ (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 4 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (10 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated NaHCO$_3$, water, and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc/MeOH = 9:1) on silica gel to afford as an off-white solid, which was further purified by recrystallization from a hot mixture of EtOAc and hexanes (2:1, v/v) to yield the title compound (192 mg, 66%) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.53–8.47 (m, 1H), 8.11 (d, \(J = 1.6\) Hz, 1H), 7.66 (dd, \(J = 9.1, 1.8\) Hz, 1H), 7.35–7.27 (m, 4H), 7.20 (t, \(J = 7.0\) Hz, 4H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 168.8, 143.1, 141.6, 136.8, 136.4, 129.9, 129.8, 129.7, 129.3, 127.4, 126.8, 126.0, 121.6, 119.5.

HRMS (ESI, TOF) \(m/z\) calculated for [M + Na]$^+$ (C$_{22}$H$_{16}$N$_2$NaO$_2$) 363.1104, found 363.1104

IR (KBr) 3059, 3035, 1653, 1621, 1590, 1494, 1457, 1422, 1366, 1300, 1271, 1236, 1211, 1173 cm$^{-1}$.

Melting point: 241.5-246.7 °C.

\textit{N,N-Dibenzyl-6-quinolinecarboxamide N-Oxide (1k)}

![Chemical structure](attachment:structure.png)

A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 6-quinolinecarboxylic acid (693 mg, 4.00 mmol, 1.0 equiv), 1,1’-carbodiimidazole (685 mg, 4.00 mmol, 1.0 equiv), and dry DMF (5.8 mL, 0.69 M). After stirring in an oil bath (bath temperature = 40 °C) for 2 h, the mixture was treated with dibenzylamine (2.37 g, 12.0 mmol, 3.0 equiv) followed by DBU (609 mg, 4.00 mmol, 1.0 equiv). After stirring at 80 °C for 15 h, the mixture was allowed to cool to room temperature and extracted with CH$_2$Cl$_2$ (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous
Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 1:2) on silica gel to afford \(N,N\)-dibenzyl-6-quinolinecarboxamide (3k, 253 mg, 21\%) as an off-white solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 3k (352 mg, 0.500 mmol, 1.0 equiv) and CH$_2$Cl$_2$ (1.7 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with \textit{m}-CPBA (77\%, 168 mg, 0.750 mmol, 1.5 equiv) in CH$_2$Cl$_2$ (1.7 mL), and the resulting \textit{m}-CPBA solution was added dropwise to the flask containing 3k at 0 °C via syringe. The pear-shaped flask was rinsed with CH$_2$Cl$_2$ (1.0 mL \(\times\) 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 12 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (10 mL \(\times\) 3). The combined organic layer was washed successively with an aqueous solution of saturated NaHCO$_3$, water, and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc as a sole eluent) on silica gel to afford an off-white solid, which was further purified by recrystallization from a hot mixture of EtOAc and hexanes (3:1, v/v) to yield the title compound as a white solid (135 mg, 73\%).

**$^1$H NMR** (500 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 9.0$ Hz, 1H), 8.48 (d, $J = 6.0$ Hz, 1H), 7.96 (s, 1H), 7.79 (d, J = 8.9 Hz, 1H), 7.64 (d, $J = 8.5$ Hz, 1H), 7.43–7.27 (m, 13H), 7.10 (s, 2H), 4.75 (s, 2H), 4.38 (s, 2H).

**$^{13}$C NMR** (126 MHz, CDCl$_3$) $\delta$ 170.4, 141.5, 136.6, 136.4, 136.1, 135.8, 130.1, 128.8, 128.7, 128.4, 128.2, 127.7, 126.7, 126.5, 125.5, 121.8, 120.4, 51.5, 47.3.

**HRMS** (ESI, TOF) \(m/z\) calculated for [M + Na]$^+$ (C$_{24}$H$_{20}$N$_2$NaO$_3$) 391.1417, found 391.1417

**IR** (KBr) 3075, 3056, 3019, 2997, 1636, 1620, 1578, 1492, 1474, 1450, 1426, 1362, 1271, 1177 cm$^{-1}$.

**Melting point**: 159-163 °C.

### $N,N$-Diphenyl-3-quinolinecarboxamide N-Oxide (1l)

A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 3-quinolinecarboxylic acid (520 mg, 3.00 mmol, 1.0 equiv), 1,1’-carbodiimidazole (535 mg, 3.30 mmol, 1.1 equiv), and dry
DMF (4.4 mL, 0.69 M). After stirring in an oil bath (bath temperature = 40 °C) for 24 h, the mixture was treated with diphenylamine (1.02 g, 6.00 mmol, 2.0 equiv) followed by DBU (457 mg, 3.00 mmol, 1.0 equiv). After stirring at 80 °C for 11 h, the mixture was allowed to cool to room temperature and extracted with CH$_2$Cl$_2$ (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 3:2) on silica gel to afford N,N-diphenyl-3-quinolinecarboxamide (3l, 407 mg, 42 %) as an off-white solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 3l (407 mg, 1.26 mmol, 1.0 equiv) and CH$_2$Cl$_2$ (2.1 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with m-CPBA (77%, 422 mg, 1.88 mmol, 1.5 equiv) in CH$_2$Cl$_2$ (2.1 mL), and the resulting m-CPBA solution was added dropwise to the flask containing 3l at 0 °C via syringe. The pear-shaped flask was rinsed with CH$_2$Cl$_2$ (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 12 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (10 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated NaHCO$_3$, water, and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc as a sole eluent) on silica gel to afford an off-white solid, which was further purified by recrystallization from a hot mixture of EtOAc and hexanes (5:1, v/v) to yield the title compound as a white solid (305 mg, 71%).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.64 (d, $J$ = 8.7 Hz, 1H), 8.57 (s, 1H), 7.78–7.70 (m, 4H), 7.60 (t, $J$ = 7.5 Hz, 1H), 7.33 (t, $J$ = 7.5 Hz, 5H), 7.25–7.16 (m, 8H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.9, 142.8, 141.6, 135.2, 131.6, 130.2, 129.5, 129.2, 129.0, 128.9, 127.2, 126.5, 119.7.

HRMS (ESI, TOF) m/z calculated for [M + Na]$^+$ (C$_{22}$H$_{16}$N$_2$NaO$_2$) 363.1104, found 363.1104.

IR (KBr) 3106, 3051, 1651, 1585, 1495, 1460, 1384, 1219, 1195, 1138, 1084 cm$^{-1}$.

Melting point: 257.1-263.5 °C.
**N,N-Diethyl-3-quinolinecarboxamide N-Oxide (1m)**

![Chemical Structure](image)

A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with N,N-diethyl-3-quinolinecarboxamide\(^9\) (3m, 114 mg, 0.500 mmol, 1.00 equiv) and CH\(_2\)Cl\(_2\) (1.7 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with \(m\)-CPBA (77\%, 168 mg, 0.750 mmol, 0.75 equiv) in CH\(_2\)Cl\(_2\) (1.5 mL), and the resulting \(m\)-CPBA solution was added dropwise to the flask containing 3m at 0 °C via syringe. The pear-shaped flask was rinsed with CH\(_2\)Cl\(_2\) (0.5 mL × 2), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 30 min at that temperature, the reaction mixture was poured into water (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (10 mL × 3). The combined organic layer was washed successively with aqueous solution of saturated NaHCO\(_3\), water, and brine, dried over anhydrous Na\(_2\)SO\(_4\), filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc/MeOH = 9:1) on silica gel to afford the title compound (64 mg, 53%) as a yellow dense oil. Spectroscopic data matched with those reported in the literature.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.71 (d, \(J = 8.7\) Hz, 1H), 8.51 (d, \(J = 1.4\) Hz, 1H), 7.87 (dd, \(J = 8.1, 1.4\) Hz, 1H), 7.78 (ddd, \(J = 8.6, 6.9, 1.4\) Hz, 1H), 7.71 (s, 1H), 7.66 (ddd, \(J = 8.1, 6.8, 1.2\) Hz, 1H), 3.56 (br s, 2H), 3.33 (br s, 2H), 1.25 (br s, 3H), 1.17 (br s, 3H).

\(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 166.2, 141.5, 133.5, 131.1, 130.9, 129.6, 129.4, 128.5, 123.0, 119.7, 43.5, 39.7, 14.3, 12.8.

LC-MS (ESI) \(m/z\) calculated for [M+1]\(^+\) (C\(_{14}\)H\(_{16}\)N\(_2\)O\(_2\)) 245.1, found 245.1.

**3-[Bis(tert-butoxycarbonyl)amino]quinoline N-Oxide (1n)**

![Chemical Structure](image)

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.\(^5,\)\(^10\)
$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.70 (d, $J = 8.8$ Hz, 1H), 8.38 (d, $J = 1.8$ Hz, 1H), 7.84 (dd, $J = 8.2$, 1.6 Hz, 1H), 7.75 (ddd, $J = 8.7$, 6.9, 1.4 Hz, 1H), 7.64 (ddd, $J = 8.2$, 7.0, 1.4 Hz, 1H), 7.55 (s, 1H), 1.41 (s, 18H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 150.6, 140.5, 136.2, 133.1, 130.5, 129.2 (two carbons), 128.3, 124.6, 119.7, 84.1, 27.8.

LC-MS (ESI) $m/z$ calculated for [M+1]$^+$ (C$_{19}$H$_{25}$N$_2$O$_5$) 361.2, found 361.2.

4,7-Dichloroquinoline N-Oxide (1o)

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.$^{5,11}$

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.77 (d, $J = 2.1$ Hz, 1H), 8.41 (d, $J = 6.6$ Hz, 1H), 8.14 (d, $J = 8.9$ Hz, 1H), 7.68 (dd, $J = 9.0$, 2.1 Hz, 1H), 7.36 (d, $J = 6.6$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 142.4, 138.1, 135.8, 130.8, 129.5, 126.7, 126.5, 121.2, 120.0.

LC-MS (ESI) $m/z$ calculated for [M+1]$^+$ (C$_9$H$_6$Cl$_2$NO) 214.0, found 214.0.

6-Fluoroquinoline N-Oxide (1p)

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.$^{5,12}$

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.76 (dd, $J = 9.0$, 5.2 Hz, 1H), 8.47 (d, $J = 6.0$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.53–7.45 (m, 2H), 7.31 (dd, $J = 8.5$, 6.0 Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.8 (d, $^{1}J_{C-F}$ = 251.8 Hz), 138.7, 135.0, 131.7 (d, $^{3}J_{C-F}$ = 10.0 Hz), 124.9 (d, $^{4}J_{C-F}$ = 5.8 Hz), 122.9 (d, $^{3}J_{C-F}$ = 9.3 Hz), 122.2, 120.3 (d, $^{2}J_{C-F}$ = 25.5 Hz), 111.5 (d, $^{2}J_{C-F}$ = 22.7 Hz).

$^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ −109.4.
LC-MS (ESI) m/z calculated for [M+1]^+ (C_{9}H_{7}FNO) 164.1, found 164.1.

6-Chloroquinoline N-Oxide (1q)

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.\(^7\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.69 (d, \(J_{\text{HH}} = 9.3\) Hz, 1H), 8.49 (d, \(J_{\text{HH}} = 6.0\) Hz, 1H), 7.85 (d, \(J_{\text{HH}} = 2.1\) Hz, 1H), 7.68 (dd, \(J_{\text{HH}} = 9.3\), 2.1 Hz, 1H), 7.63 (d, \(J_{\text{HH}} = 8.5\) Hz, 1H), 7.32 (dd, \(J_{\text{HH}} = 8.5\), 6.1 Hz, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.2, 135.7, 135.1, 131.2, 131.2, 126.8, 124.6, 122.2, 121.8.

LC-MS (ESI) m/z calculated for [M+1]^+ (C_{9}H_{7}ClNO) 180.0, found 180.0.

6-Bromoquinoline N-Oxide (1r)

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.\(^5,13\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.62 (d, \(J = 9.2\) Hz, 1H), 8.51 (d, \(J = 6.0\) Hz, 1H), 8.04 (d, \(J = 2.0\) Hz, 1H), 7.82 (dd, \(J = 9.2\), 2.1 Hz, 1H), 7.63 (d, \(J = 8.5\) Hz, 1H), 7.32 (dd, \(J = 8.5\), 6.0 Hz, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.4, 135.8, 133.8, 131.6, 130.1, 124.6, 123.3, 122.2, 121.8.

LC-MS (ESI) m/z calculated for [M+1]^+ (C_{9}H_{7}BrNO) 224.0, found 224.0.

2-(Trifluoromethyl)quinoline N-Oxide (1s)

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.\(^5,14\)
1\textsuperscript{H} NMR (500 MHz, CDCl\textsubscript{3}) δ 8.76 (d, J = 8.8 Hz, 1H), 7.91 (dd, J = 8.1, 1.4 Hz, 1H), 7.81 (ddd, J = 8.7, 6.9, 1.4 Hz, 1H), 7.78–7.70 (m, 2H), 7.63 (d, J = 8.9 Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl\textsubscript{3}) δ 142.8, 134.9 (q, $^2$J\textsubscript{C–F} = 34.2 Hz), 131.2, 131.1, 130.4, 128.3, 124.4, 120.5 (q, $^1$J\textsubscript{C–F} = 272.5 Hz), 119.9, 118.6 (q, $^3$J\textsubscript{C–F} = 4.1 Hz). 

$^{19}$F NMR (471 MHz, CDCl\textsubscript{3}) δ –67.7.

**LC-MS (ESI)** $m/z$ calculated for [M+1]\textsuperscript{+} (C\textsubscript{10}H\textsubscript{7}F\textsubscript{3}NO) 214.0, found 214.1.

**6-Methylquinoline N-Oxide (1t)**

\[
\text{Me} \quad \text{N} \quad \text{C}^- 
\]

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.\textsuperscript{5,13,15}

1\textsuperscript{H} NMR (400 MHz, CDCl\textsubscript{3}) δ 8.63 (d, J = 8.9 Hz, 1H), 8.47 (d, J = 5.9 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.62 (s, 1H), 7.59 (dd, J = 8.9, 1.7 Hz, 1H), 7.27–7.23 (m, 1H), 2.54 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl\textsubscript{3}) δ 140.1, 139.0, 135.0, 132.6, 130.7, 127.0, 125.5, 120.9, 119.6, 21.4.

**LC-MS (ESI)** calculated for [M+1]\textsuperscript{+} (C\textsubscript{10}H\textsubscript{10}NO) $m/z$ 160.1, found $m/z$ 160.1.

**2-Phenylquinoline N-Oxide (1u)**

\[
\text{Ph} \quad \text{N} \quad \text{C}^- 
\]

Prepared according to the literature procedure and spectroscopic data matched with those reported in the literature.\textsuperscript{5,15,16}

1\textsuperscript{H} NMR (500 MHz, CD\textsubscript{3}CN) δ 8.69 (d, J = 8.8 Hz, 1H), 7.98–7.90 (m, 3H), 7.82 (dd, J = 8.7 Hz, 1H), 7.79 (ddd, J = 8.6, 6.9, 1.4 Hz, 1H), 7.67 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.57–7.43 (m, 4H).

$^{13}$C NMR (126 MHz, CD\textsubscript{3}CN) δ 145.6, 143.2, 134.9, 131.5, 130.9, 130.6, 130.4, 129.5, 129.4, 129.2, 126.1, 124.6, 120.6.

**LC-MS (ESI)** $m/z$ calculated for [M+1]\textsuperscript{+} (C\textsubscript{15}H\textsubscript{12}NO) 222.1, found 222.1.
6-Benzoyloxyquinoline N-Oxide (1v)

A 100 ml round-bottomed flask equipped with a magnetic stir bar was charged with 6-hydroxyquinoline (155 mg, 1.07 mmol, 1.0 equiv), 4-(dimethylamino)pyridine (DMAP, 6.6 mg, 0.054 mmol, 5 mol%), triethylamine (Et₃N, 5 mL), and CH₂Cl₂ (25 mL). To this mixture was added dropwise benzoyl chloride (156 mg, 1.07 mmol, 1.0 equiv) via syringe at room temperature, and the resulting mixture was stirred for 1 h. The reaction was quenched by H₂O (1 mL), and the mixture was extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried with Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 2:1) on silica gel to afford 6-benzoyloxyquinoline (3v, 188 mg, 71 %) as an off-white solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 3v (188 mg, 0.760 mmol, 1.0 equiv) and CH₂Cl₂ (1.2 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with m-CPBA (77%, 254 mg, 1.13 mmol, 1.5 equiv) in CH₂Cl₂ (1.3 mL), and the resulting m-CPBA solution was added dropwise to the flask containing 3v at 0 °C via syringe. The pear-shaped flask was rinsed with CH₂Cl₂ (1 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 1 hour at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (10 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated NaHCO₃, water, and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc/MeOH = 9:1) on silica gel to afford the title compound as an off-white solid, which was further purified by recrystallization from a hot mixture of EtOAc and hexanes (5:1, v/v) to yield the title compound as a white solid (102 mg, 51 %).

¹H NMR (500 MHz, CDCl₃) δ 8.80 (d, J = 9.4 Hz, 1H), 8.49 (d, J = 6.0 Hz, 1H), 8.21 (d, J = 7.3 Hz, 2H), 7.76 (d, J = 2.3 Hz, 1H), 7.71–7.57 (m, 4H), 7.52 (t, J = 7.8 Hz, 2H), 7.29 (dd, J = 8.4, 6.1 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 164.6, 150.6, 139.5, 135.3, 134.0, 131.2, 130.2, 128.8, 128.7, 125.5, 125.3, 121.8, 121.7, 119.1.
HRMS (ESI, TOF) \( m/z \) calculated for \( [M + Na]^+ \) \( (C_{16}H_{11}NNaO_3) \) 288.0631, found 288.0631.

IR (KBr) 3304, 3278, 3097, 3060, 1674, 1599, 1581, 1488, 1469, 1384, 1366, 1265, 1144, 906 cm\(^{-1}\).

Melting point: 195-200.9 °C.

**1-Isoquinolinecarbonitrile N-Oxide (1w)**

A 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with 1-Isoquinolinecarbonitrile (3w) (308 mg, 2.00 mmol, 1.00 equiv) and CH\(_2\)Cl\(_2\) (3.0 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with \( m \)-CPBA (77%, 672 mg, 3.00 mmol, 1.5 equiv) in CH\(_2\)Cl\(_2\) (4 mL), and the resulting \( m \)-CPBA solution was added dropwise to the flask containing 3w at 0 °C via syringe. The pear-shaped flask was rinsed with CH\(_2\)Cl\(_2\) (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 12 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (15 mL × 3). The combined organic layer was washed successively with aqueous solution of saturated NaHCO\(_3\), water, and brine, dried over anhydrous Na\(_2\)SO\(_4\), filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAC/MeOH =12:1) on silica gel to afford the title compound as a white solid, which was further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:1, v/v) to yield the title compound as a white solid (186 mg, 55%). Spectroscopic data matched with those reported in the literature.\(^{17}\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.16 (d, \( J = 7.2 \) Hz, 1H), 8.02–7.96 (m, 2H), 7.87 (d, \( J = 8.2 \) Hz, 1H), 7.84 (d, \( J = 7.2 \) Hz, 1H), 7.82–7.77 (m, 2H), 7.71–7.64 (m, 1H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 137.0, 131.8, 130.1, 129.6, 127.5, 127.4, 127.0, 123.0, 121.7, 111.2.

LC-MS (ESI) \( m/z \) calculated for \([M+1]^+\) \( (C_{10}H_{11}N_2O) \) \( m/z \) 171.1, found \( m/z \) 171.1.
1-Benzoylisoquinoline \( N \)-Oxide (1x)

\[
\text{\begin{center}
\includegraphics[width=0.1\textwidth]{benzoylisoquinoline.png}
\end{center}
}
\]

Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:1, \( v/v \)) to afford the title compound as a white solid. Spectroscopic data matched with those reported in the literature.\(^{18}\)

\(^1\text{H NMR} (500 \text{ MHz}, \text{CDCl}_3) \delta 8.13 (d, J = 7.1 \text{ Hz}, 1 \text{H}), 7.88–7.82 (m, 6 \text{H}), 7.77 (d, J = 7.1 \text{ Hz}, 1 \text{H}), 7.65–7.57 (m, 4 \text{H}), 7.54 (td, J = 7.6, 6.9, 1.2 \text{ Hz}, 1 \text{H}), 7.52–7.41 (m, 4 \text{H}).

\(^{13}\text{C NMR} (126 \text{ MHz, CDCl}_3) \delta 189.6, 142.3, 136.6, 135.2, 134.4, 130.0, 129.2, 129.0, 129.0, 128.7, 127.4, 127.2, 124.8, 123.1.

\textbf{LC-MS (ESI)} \textit{m/z} calculated for [M+1]\(^+\) (C\(_{16}\)H\(_{11}\)NO\(_2\)) 250.1, found 250.1.

1-Acetylisoquinoline \( N \)-Oxide (1y)

A 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with isoquinoline (517 mg, 4.00 mmol, 1.0 equiv), acetaldehyde (705 mg, 16.0 mmol, 4.0 equiv), tetra-\(n\)-butylammonium bromide (387 mg, 1.20 mmol, 0.3 equiv), K\(_2\)S\(_2\)O\(_8\) (2.16 g, 8.00 mmol, 2.0 equiv), and 1,2-dichloroethane (33 mL). The resulting mixture was heated in an oil bath (bath temperature = 100 °C) under reflux for 3 h. The mixture was allowed to cool to room temperature, and the solvent was removed under vacuum. The crude mixture was diluted with CH\(_2\)Cl\(_2\), washed successively with an aqueous solution of saturated NaHCO\(_3\), water, and brine, dried over anhydrous Na\(_2\)SO\(_4\), filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography on silica gel (CH\(_2\)Cl\(_2\) as a sole eluent) to afford 1-acetylisoquinoline (3y, 437 mg, 64 %) as a white solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 3y (437 mg, 2.55 mmol, 1.0 equiv) and CH\(_2\)Cl\(_2\) (4.0 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with \(m\)-CPBA (77%, 1.14 g, 5.11 mmol, 2.0 equiv) in CH\(_2\)Cl\(_2\) (4.5 mL), and the resulting \(m\)-CPBA solution was added dropwise to the flask containing 3y at 0 °C via syringe. The
A 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with quinoxaline (1.50 g, 11.9 mmol, 1.0 equiv) and CH₂Cl₂ (7.5 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with m-CPBA (77%, 2.60 g, 11.6 mmol, 1.0 equiv) in CH₂Cl₂ (7.5 mL), and the resulting m-CPBA solution was added dropwise to the flask containing the heterocycle at 0 °C via syringe. The pear-shaped flask was rinsed with CH₂Cl₂ (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 4 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (15 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated NaHCO₃, water, and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc as a sole eluent) on silica gel to afford an off-white solid, which was further purified by recrystallization from a hot mixture of hexanes and EtOAc (3:1, v/v) to yield the title compound as a white solid (209 mg, 44%). Spectroscopic data matched with those reported in the literature.¹⁹

¹H NMR (500 MHz, CDCl₃) δ 8.05 (d, J = 7.1 Hz, 1H), 7.82–7.74 (m, 1H), 7.67 (dd, J = 17.3, 7.6 Hz, 2H), 7.58 (pd, J = 6.9, 1.3 Hz, 4H), 2.73 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 197.0, 143.2, 136.4, 130.2, 128.9, 127.1, 126.0, 124.9, 123.0, 29.7.

LC-MS (ESI) m/z calculated for [M+1]⁺ (C₁₁H₉NO₃) 188.1, found 188.1.

3-Quinoxalinecarbonitrile N-Oxide (1z)

A 100 mL round-bottomed flask was rinsed with CH₂Cl₂ (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 17 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (15 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated NaHCO₃, water, and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc/MeOH =
8:1) on silica gel to afford quinoxaline N-oxide as an off-white solid (1.56 g, 92%). A 250 mL round-bottomed flask equipped with a magnetic stir bar was charged with quinoxaline N-oxide (1.70 g, 11.6 mmol, 1.0 equiv) dissolved in MeCN (51 mL) and KCN (1.51 g, 23.2 mmol, 2.0 equiv) dissolved in MeOH (39 mL). To this mixture was added dropwise benzyol chloride (3.3 g, 23.2 mmol, 2.0 equiv) at room temperature and the reaction mixture was stirred at that temperature for 9 h. After the completion of the reaction as judged by TLC, the solvent was evaporated under reduced pressure. The resulting residue was diluted with CH$_2$Cl$_2$, washed successively with water and brine, dried over anhydrous Na$_2$SO$_4$, filtered and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexenes/EtOAc = 6:1) on silica gel to afford a yellow solid, which was further purified by recrystallization from a hot mixture of EtOAc and hexanes (9:1, v/v) to yield 2-quinoxalinecarbonitrile (3z) as a white solid (352 mg, 20%). A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 3z (135 mg, 0.870 mmol, 1.0 equiv) and CH$_2$Cl$_2$ (1.5 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with m-CPBA (77%, 291 mg, 1.30 mmol, 1.5 equiv) in CH$_2$Cl$_2$ (1.5 mL), and the resulting m-CPBA solution was added dropwise to the flask containing 3z at 0 °C via syringe. The pear-shaped flask was rinsed with CH$_2$Cl$_2$ (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 48 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (15 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated NaHCO$_3$, water, and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (EtOAc as a sole eluent) on silica gel to afford the title compound as an off-white solid (62 mg, 39%). Spectroscopic data matched with those reported in the literature.20

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.56 (d, $J$ = 7.2 Hz, 1H), 8.23–8.17 (m, 1H), 8.00–7.86 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 145.2, 138.4, 133.3, 133.0, 131.3, 131.0, 130.9, 118.9, 114.4.

LC-MS (ESI) m/z calculated for [M+1]$^+$ (C$_9$H$_5$N$_3$O) 172.0, found 172.0.
Methyl 3-Quinoxalinecarboxylate N-Oxide (1aa)

A 100 mL round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with 3-quinoxalinecarboxylic acid (522 mg, 3.00 mmol), MeOH (10 mL) and H$_2$SO$_4$ (0.3 mL). The resulting mixture was heated in an oil bath (bath temperature = 100 °C) under reflux for 3 h. The mixture was allowed to cool to room temperature, diluted with CH$_2$Cl$_2$, and neutralized with an aqueous solution of saturated NaHCO$_3$ (Caution! Evolution of CO$_2$). The mixture was then extracted with CH$_2$Cl$_2$ (5 mL × 3). The combined organic layer was washed successively with water and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexenes/EtOAc = 3:1) on silica gel to afford methyl 3-quinoxalinecarboxylate (3aa, 217 mg, 38 %) as an yellow solid. A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 3aa (188 mg, 1.00 mmol, 1.0 equiv) and CH$_2$Cl$_2$ (1.5 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with m-CPBA (77%, 896 mg, 4.00 mmol, 4.0 equiv) in CH$_2$Cl$_2$ (1.5 mL), and the resulting m-CPBA solution was added dropwise to the flask containing 3aa at 0 °C via syringe. The pear-shaped flask was rinsed with CH$_2$Cl$_2$ (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 13 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (15 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated NaHCO$_3$, water, and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography on silica gel (EtOAc/MeOH = 9:1) to afford the title compound as an off-white solid (108 mg, 53%). Spectroscopic data matched with those reported in the literature.$^{21}$

$^1$H NMR (500 MHz, CDCl$_3$) δ 9.01 (s, 1H), 8.59 (dd, $J = 8.5, 1.3$ Hz, 1H), 8.31 (dd, $J = 8.3, 1.1$ Hz, 2H), 7.87 (dddd, $J = 23.8, 8.4, 7.0, 1.4$ Hz, 3H), 4.10 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 163.4, 145.0, 144.7, 138.1, 132.5, 132.2, 131.3, 130.0, 118.9, 53.7.

LC-MS (ESI) m/z calculated for [M+1]$^+$ (C$_{10}$H$_8$N$_2$O$_3$) 205.1, found 205.1.
3-Acetylquinoxaline N-Oxide (1ab)

A 150 mL round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with quinoxaline (651 mg, 5.00 mmol, 1.0 equiv), acetaldehyde (1.10 g, 20.0 mmol, 4.0 equiv), tetra-n-butylammonium bromide (484 mg, 1.50 mmol, 0.3 equiv), K$_2$S$_2$O$_8$ (2.70 g, 10.0 mmol, 2.0 equiv), and 1,2-dichloroethane (42 mL). The resulting mixture was heated in an oil bath (bath temperature = 100 °C) under reflux for 2 h. The mixture was allowed to cool to room temperature, and the solvent was removed under vacuum. The crude mixture was diluted with CH$_2$Cl$_2$, washed successively with an aqueous solution of saturated NaHCO$_3$, water, and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography on silica gel (hexanes/EtOAc = 7:1) to afford 2-acetylquinoxaline (3aa) as a white solid (437 mg, 64 %). A 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with 3aa (528 mg, 3.08 mmol, 1.00 equiv) and CH$_2$Cl$_2$ (5.0 mL). The resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with m-CPBA (77%, 1.38 g, 6.16 mmol, 2.0 equiv) in CH$_2$Cl$_2$ (5.3 mL), and the resulting m-CPBA solution was added dropwise to the flask containing 3aa at 0 °C via syringe. The pear-shaped flask was rinsed with CH$_2$Cl$_2$ (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 10 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (15 mL × 3). The combined organic layer was washed successively with aqueous solution of saturated NaHCO$_3$, water, and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (hexene/EtOAc = 4:1) on silica gel to afford a yellow solid, which was further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:1, v/v) to yield the title compound as a white solid (209 mg, 44%). Spectroscopic data matched with those reported in the literature.$^{22}$

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.86 (s, 1H), 8.58–8.52 (m, 2H), 8.22–8.16 (m, 2H), 7.92–7.78 (m, 4H), 2.79 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 197.7, 149.6, 144.3, 137.9, 132.2, 132.0, 131.1, 127.2, 119.0, 25.2.
LC-MS (ESI) m/z calculated for [M+1]⁺ (C₁₀H₈N₂O₂) 189.1, found 189.1.

3-Benzoylquinoxaline N-Oxide (1ac) and 2-Benzoylquinoxaline N,N-Oxide (1ac')

A 150 mL round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with quinoxaline (651 mg, 5.00 mmol, 1.0 equiv), benzaldehyde (2.12 g, 20.0 mmol, 4.0 equiv), tetra-n-butylammonium bromide (484 mg, 1.50 mmol, 0.30 equiv), K₂S₂O₈ (2.70 g, 10.0 mmol, 2.0 equiv), and 1,2-dichloroethane (42 mL). The resulting mixture was heated in an oil bath (bath temperature = 110 °C) under reflux for 2 h. The mixture was then cooled to room temperature, and the solvent was removed under vacuum. The crude mixture was diluted with CH₂Cl₂, washed successively with water and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue thus obtained was purified by flash column chromatography (CH₂Cl₂ as a sole eluent) on silica gel to afford 2-benzoylquinoxaline (3ac) as a brown solid (615 mg, 53 %). A 50 mL round-bottomed flask was charged with 3ac (234 mg, 1.00 mol, 1.0 equiv) and CH₂Cl₂ (1.5 mL), and the resulting mixture was cooled in an ice-water bath. A separate pear-shaped flask was charged with m-CPBA (77%, 448 mg, 2.00 mmol, 2.0 equiv) in CH₂Cl₂ (1.8 mL), and the resulting m-CPBA solution was added dropwise to the flask containing the heterocycle at 0 °C via syringe. The pear-shaped flask was rinsed with CH₂Cl₂ (1.0 mL × 3), and the resulting solution was added via syringe. After stirring for 10 min, the cold reaction mixture was allowed to slowly warm to room temperature. After stirring for 12 h at that temperature, the reaction mixture was poured into water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (15 mL × 3). The combined organic layer was washed successively with an aqueous solution of saturated NaHCO₃, water, and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue thus obtained was loaded onto a column packed with silica gel. The column was eluted with a 25:1 mixture of CH₂Cl₂ and EtOAc to yield 3-benzoylquinoxaline N-oxide (1ac) along with 2-benzoylquinoxaline N,N-oxide (1ac') as separable mixtures. 3-Benzoylquinoxaline N-oxide (1ac) was isolated as an off-white solid (52 mg, 21%).
1H NMR (500 MHz, CDCl₃) δ 9.48 (s, 1H), 8.27–8.16 (m, 7H), 7.92–7.81 (m, 3H), 7.65 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 3H).

13C NMR (126 MHz, CDCl₃) δ 192.2, 148.6, 145.2, 143.1, 140.4, 135.5, 133.6, 131.9, 131.2, 130.7, 130.4, 129.4, 128.3.

HRMS (ESI, TOF) m/z calculated for [M + Na]⁺ (C₁₅H₁₀N₂NaO₂) 273.0634, found 273.0634.

IR (KBr) 3076, 3055, 1703, 1607, 1577, 1498, 1415, 1369, 1350, 1249, 1218, 1133, 922 cm⁻¹.

Melting point: 137.7-144.4 °C.

2-Benzoylquinoxaline N,N-Oxide (1ac') was isolated as an off-white solid (68 mg, 27%) and spectroscopic data matched with those reported in the literature.²³

1H NMR (500 MHz, CDCl₃) δ 9.15 (s, 1H), 8.67–8.61 (m, 2H), 8.38 (d, J = 8.2 Hz, 1H), 7.98–7.87 (m, 3H), 7.48 (t, J = 7.9 Hz, 2H), 7.38–7.27 (m, 4H).

13C NMR (126 MHz, CDCl₃) δ 161.6, 150.4, 144.8, 144.7, 138.3, 132.7, 132.5, 131.5, 130.3, 129.7, 126.7, 121.4, 119.0.

LC-MS (ESI) m/z calculated for [M+1]⁺ (C₁₅H₁₀N₂O₃) 267.1, found 267.1.

3-Pyrazinecarbonitrile N-Oxide (1ad)

Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of hexanes and EtOAc (4:1, v/v) to afford the title compound as an off-white solid. Spectroscopic data matched with those reported in the literature.²⁴

1H NMR (500 MHz, DMSO) δ 9.11–9.09 (m, 1H), 8.66 (d, J = 4.1 Hz, 1H), 8.60 (dd, J = 4.2, 1.6 Hz, 1H).

13C NMR (126 MHz, DMSO) δ 148.91, 139.05, 137.20, 132.70, 132.00, 114.59.

LC-MS (ESI) m/z calculated for [M+1]⁺ (C₅H₃N₃O) 122.0, found 122.0.

Methyl Pyrazine-3-carboxylate N-Oxide (1ae)
Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of EtOAc to afford the title compound as an off-white solid. Spectroscopic data matched with those reported in the literature.\textsuperscript{25}

\textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.74 (dd, \(J = 1.6, 0.7\) Hz, 1H), 8.58–8.52 (m, 1H), 8.20 (dd, \(J = 4.0, 1.6\) Hz, 1H), 4.03 (s, 2H).

\textbf{\textsuperscript{13}C NMR} (126 MHz, CDCl\textsubscript{3}) \(\delta\) 162.6, 147.6, 147.3, 135.9, 135.9, 53.6.

\textbf{LC-MS (ESI)} \(m/z\) calculated for [M+1]\textsuperscript{+} (C\textsubscript{6}H\textsubscript{6}N\textsubscript{2}O\textsubscript{3}) 155.0, found 155.0.

3-Acetylpyrazine N-Oxide (1af)

\begin{center}
\includegraphics[width=0.1\textwidth]{3-Acetylpyrazine_N-Oxide.png}
\end{center}

Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:3, \(v/v\)) to afford the title compound as a white solid. Spectroscopic data matched with those reported in the literature.\textsuperscript{26}

\textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.63 (dd, \(J = 1.6, 0.7\) Hz, 1H), 8.50 (d, \(J = 3.9\) Hz, 1H), 8.18 (dd, \(J = 4.0, 1.7\) Hz, 1H), 2.70 (s, 2H).

\textbf{\textsuperscript{13}C NMR} (126 MHz, CDCl\textsubscript{3}) \(\delta\) 196.9, 152.3, 146.6, 135.9, 132.7, 25.8.

\textbf{LC-MS (ESI)} \(m/z\) calculated for [M+1]\textsuperscript{+} (C\textsubscript{6}H\textsubscript{6}N\textsubscript{2}O\textsubscript{2}) 139.0, found 139.0.

Methyl Nicotinate N-Oxide (1ag)

\begin{center}
\includegraphics[width=0.1\textwidth]{Methyl_Nicotinate_N-Oxide.png}
\end{center}

Prepared according to the literature procedure and further purified by recrystallization from a hot mixture of hexanes and EtOAc (1:1, \(v/v\)) to afford the title compound as a white solid. Spectroscopic data matched with those reported in the literature.\textsuperscript{27}

\textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.71 (t, \(J = 1.5\) Hz, 1H), 8.28 (ddd, \(J = 6.5, 1.5, 1.0\) Hz, 1H), 7.79 (dt, \(J = 7.9, 1.1\) Hz, 1H), 7.33 (dd, \(J = 7.7, 6.7\) Hz, 1H), 3.91 (s, 3H).

\textbf{\textsuperscript{13}C NMR} (126 MHz, CDCl\textsubscript{3}) \(\delta\) 163.1, 142.3, 140.1, 129.8, 126.0, 125.7, 52.9.

\textbf{LC-MS (ESI)} \(m/z\) calculated for [M+1]\textsuperscript{+} (C\textsubscript{7}H\textsubscript{8}NO\textsubscript{3}) 154.0, found 154.1.
General Procedure for the Initial Optimization Studies (Table 1)

A 10 mL test tube equipped with a small magnetic stir bar was charged with 3-quinolinecarbonitrile N-oxide (1a, 34.0 mg, 0.200 mmol, 1.00 equiv), HEH (1, 0.300 mmol, 1.50 equiv), and a photocatalyst (2.0 µmol, 1.0 mol%). The tube was fitted with a rubber septum and CH₃CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N₂ bubbling at room temperature for 5–10 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs for the indicated time (see Table 1). Upon the completion of the reaction as determined by TLC, the reaction mixture was concentrated on a rotary evaporator. The resulting residue was directly purified by flash column chromatography on silica gel (hexanes/EtOAc = 3:1) to afford 3-quinolinecarbonitrile (3a) as a white solid.

General Procedure for the Visible Light-Mediated Photoredox-Catalyzed Deoxygenation of N-Heterocyclic N-Oxides Using Na₂-eosin Y (4) as the Photocatalyst (Scheme 2)

A 10 mL test tube equipped with a small magnetic stir bar was charged with N-heterocyclic N-oxide (1, 0.200 mmol, 1.0 equiv), tert-Bu-HEH (1c, 92.8 mg, 0.300 mmol, 1.5 equiv), and Na₂-eosin Y (4, 1.4 mg, 2.0 µmol, 1.0 mol%). The tube was fitted with a rubber septum and CH₃CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N₂ bubbling at room temperature for 5–10 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs for the indicated time (see Scheme 2). Upon the completion of the reaction as determined by TLC, the reaction mixture was concentrated on a rotary evaporator. The resulting residue was directly purified by flash column chromatography on silica gel (hexanes and EtOAc) to afford the corresponding deoxygenated N-heterocycle (3).

3-Quinolinecarbonitrile (3a)

Prepared using 3-quinolinecarbonitrile N-oxide (1a, 34.0 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 µmol, 1.0 mol%), and CH₃CN (4.0 mL, 0.05 M). 3-Quinolinecarbonitrile (3a, 29.3 mg, 95%) was isolated (hexanes/EtOAc = 3:1) as a white solid. Spectroscopic data matched with those reported in the literature.²⁸
$^1$H NMR (500 MHz, CDCl$_3$) δ 8.98 (d, $J = 2.1$ Hz, 1H), 8.49 (d, $J = 2.0$ Hz, 1H), 8.12 (d, $J = 9.0$ Hz, 1H), 7.89–7.82 (m, 2H), 7.69–7.62 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 149.6, 148.6, 141.3, 132.6, 129.7, 128.3, 128.1, 126.0, 117.0, 106.4.

GC-MS (EI, 70 eV) m/z calculated for [M]$^+$ (C$_{10}$H$_6$N$_2$) 154.1, found 154.1.

2-Quinolinecarbonitrile (3b)

Prepared using 2-quinolinecarbonitrile N-oxide (1b, 34.0 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). 2-Quinolinecarbonitrile (3b, 27.5 mg, 89%) was isolated (hexanes/EtOAc = 6:1) as a white solid. Spectroscopic data matched with those reported in the literature.$^{28}$

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.31 (d, $J = 8.4$ Hz, 1H), 8.16 (d, $J = 8.5$ Hz, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.84 (ddd, $J = 8.4$, 6.9, 1.3 Hz, 1H), 7.75–7.67 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 148.2, 137.4, 133.6, 131.2, 130.0, 129.4, 128.6, 127.8, 123.3, 117.5.

GC-MS (EI, 70 eV) m/z calculated for [M]$^+$ (C$_{10}$H$_6$N$_2$) 154.1, found 154.1.

Methyl 3-Quinolinecarboxylate (3c)

Prepared using methyl 3-quinolinecarboxylate N-oxide (1c, 40.6 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). Methyl 3-quinolinecarboxylate (3c, 36.5 mg, 98%) was isolated (hexanes/EtOAc = 3:2) as a white solid. Spectroscopic data matched with those reported in the literature.$^7$

$^1$H NMR (500 MHz, CDCl$_3$) δ 9.35 (d, $J = 2.2$ Hz, 1H), 8.71 (dd, $J = 2.3$, 0.9 Hz, 1H), 8.06 (dd, $J = 8.5$, 1.0 Hz, 1H), 7.81 (dd, $J = 8.2$, 1.4 Hz, 1H), 7.73 (ddd, $J = 8.5$, 6.9, 1.5 Hz, 1H), 7.51 (ddd, $J = 8.1$, 6.9, 1.2 Hz, 1H), 3.93 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.6, 149.8, 149.6, 138.5, 131.6, 129.3, 128.9, 127.2, 126.6, 122.7, 52.2.

GC-MS (EI, 70 eV) m/z calculated for [M]$^+$ (C$_{11}$H$_9$NO$_2$) 187.1, found 187.1.
Methyl 6-Quinolinecarboxylate (3d)

Prepared using methyl 6-quinolinecarboxylate N-oxide (1d, 40.6 mg, 0.200 mmol, 1.00 equiv), 2a (92.8 mg, 0.300 mmol, 1.50 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH₃CN (4.00 mL, 0.05 M). Methyl quinoline-6-carboxylate (3d, 36.5 mg, 98%) was isolated (hexanes/EtOAc = 3:2) as a white solid. Spectroscopic data matched with those reported in the literature.¹⁶

¹H NMR (500 MHz, CDCl₃) δ 8.86 (dd, J = 4.2, 1.8 Hz, 1H), 8.40 (d, J = 2.0 Hz, 1H), 8.15 (dd, J = 8.8, 2.0 Hz, 1H), 8.08 (dd, J = 8.4, 1.8 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.30 (dd, J = 8.3, 4.2 Hz, 1H), 3.86 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 166.2, 152.2, 149.7, 137.0, 130.7, 129.5, 128.6, 127.8, 127.1, 121.5, 52.1.

GC-MS (EI, 70 eV) m/z calculated for [M]+ (C₁₁H₉NO₂) 187.1, found 187.1.

Ethyl 6-Quinilinecarboxylate (3e)

Prepared using ethyl 6-quinolinecarboxylate N-oxide (1e, 43.4 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH₃CN (4.0 mL, 0.05 M). Ethyl 6-quinolinecarboxylate (3e, 37.8 mg, 94%) was isolated (hexanes/EtOAc = 2:1) as a white solid. Spectroscopic data matched with those reported in the literature.²⁹

¹H NMR (500 MHz, CDCl₃) δ 8.98 (dd, J = 4.2, 1.8 Hz, 1H), 8.57 (d, J = 2.0 Hz, 1H), 8.29 (dd, J = 8.8, 1.9 Hz, 1H), 8.24 (dd, J = 8.3, 2.0 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.44 (dd, J = 8.3, 4.2 Hz, 1H), 4.43 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 166.0, 152.4, 150.0, 137.2, 130.8, 129.7, 128.9, 128.4, 127.3, 121.7, 61.3, 14.3.

GC-MS (EI, 70 eV) m/z calculated for [M]+ (C₁₂H₁₁NO₂) 201.1, found 201.1.
Isopropyl 6-Quinolinecarboxylate (3f)

Prepared using isopropyl 6-quinolinecarboxylate N-oxide (1f, 46.3 mg, 0.200 mmol, 1.00 equiv), 2a (92.8 mg, 0.300 mmol, 1.50 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH$_3$CN (4.00 mL, 0.05 M). Isopropyl 6-quinolinecarboxylate (3f, 42.3 mg, 98%) was isolated (hexanes/EtOAc = 3:1) as a white solid. Spectroscopic data matched with those reported in the literature.$^{30}$

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.95 (dd, $J = 4.2$, 1.8 Hz, 1H), 8.53 (d, $J = 2.0$ Hz, 1H), 8.27 (dd, $J = 8.8$, 1.9 Hz, 1H), 8.22 (dd, $J = 8.2$, 2.0 Hz, 1H), 8.10 (d, $J = 8.7$ Hz, 1H), 7.41 (dd, $J = 8.3$, 4.2 Hz, 1H), 5.29 (hept, $J = 6.3$ Hz, 1H), 1.39 (d, $J = 6.3$ Hz, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.5, 152.3, 149.9, 137.2, 130.7, 129.6, 128.9, 128.8, 127.3, 121.7, 68.8, 21.9.

GC-MS (EI, 70 eV) m/z calculated for [M]$^+$ (C$_{13}$H$_{13}$NO$_2$) 215.1, found 215.2.

 tert-Butyl 6-Quinolinecarboxylate (3g)

Prepared using tert-butyl 6-quinolinecarboxylate N-oxide (1g, 49.0 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). tert-Butyl 6-quinolinecarboxylate (3g, 42.2 mg, 98%) was isolated (hexanes/EtOAc = 3:1) as a white solid. Spectroscopic data matched with those reported in the literature.$^{31}$

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.97 (dd, $J = 4.2$, 1.8 Hz, 1H), 8.50 (d, $J = 2.0$ Hz, 1H), 8.27–8.19 (m, 2H), 8.10 (d, $J = 8.8$ Hz, 1H), 7.43 (dd, $J = 8.3$, 4.2 Hz, 1H), 1.63 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.2, 152.2, 149.9, 137.2, 130.5, 129.9, 129.5, 129.0, 127.3, 121.6, 81.5, 28.2.

GC-MS (EI, 70 eV) m/z calculated for [M]$^+$ (C$_{14}$H$_{15}$NO$_2$) 229.1, found 229.1.
Methyl 8-Quinolinecarboxylate (3h)

Prepared using methyl 8-quinolinecarboxylate N-oxide (1h, 40.6 mg, 0.200 mmol, 1.0 equiv), 2a (123.8 mg, 0.400 mmol, 2.0 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH₃CN (4.0 mL, 0.05 M). Methyl 8-quinolinecarboxylate (3h, 26.6 mg, 98%) was isolated (hexanes/EtOAc = 3:2) as a white solid. Spectroscopic data matched with those reported in the literature.³²

¹H NMR (500 MHz, CDCl₃) δ 9.04 (dd, J = 4.2, 1.7 Hz, 1H), 8.17 (dd, J = 8.3, 1.7 Hz, 1H), 8.02 (dd, J = 7.1, 1.3 Hz, 1H), 7.93 (dd, J = 8.2, 1.2 Hz, 1H), 7.58–7.51 (m, 1H), 7.44 (dd, J = 8.3, 4.2 Hz, 1H), 4.04 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 168.2, 151.4, 145.4, 136.2, 131.5, 131.3, 130.4, 128.4, 125.5, 121.5, 52.6.

GC-MS (EI, 70 eV) m/z calculated for [M]+ (C₁₁H₉NO₂) 187.1, found 187.1.

3-Acetylquinoline (3i)

Prepared using 3-acetylquinoline N-oxide (1i, 37.4 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH₃CN (4.0 mL, 0.05 M). 3-Acetylquinoline (3i, 33.0 mg, 97%) was isolated (hexanes/EtOAc = 1:1) as a white solid. Spectroscopic data matched with those reported in the literature.⁶

¹H NMR (500 MHz, CDCl₃) δ 9.41 (d, J = 2.3 Hz, 1H), 8.68 (dd, J = 2.3, 0.9 Hz, 1H), 8.13 (dd, J = 8.5, 1.0 Hz, 1H), 7.92 (dd, J = 8.1, 1.4 Hz, 1H), 7.82 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.61 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 2.72 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 196.6, 149.8, 149.1, 137.2, 131.9, 129.4, 129.3, 129.2, 127.5, 126.8, 26.7.

GC-MS (EI, 70 eV) m/z calculated for [M]+ (C₁₁H₉NO) 171.1, found 171.1.
**N,N-Diphenyl-6-quinolinecarboxamide (3j)**

Prepared using N,N-diphenyl-6-quinolinecarboxamide N-oxide (1j, 68.1 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH₃CN (4.0 mL, 0.05 M). N,N-Diphenyl-6-quinolinecarboxamide (3j, 59.0 mg, 91%) was isolated (hexanes/EtOAc = 1:3) as a white solid.

**¹H NMR (500 MHz, CDCl₃)** δ 8.88 (dd, J = 4.1, 1.4 Hz, 1H), 8.07–8.01 (m, 2H), 7.69 (dd, J = 8.8, 1.9 Hz, 1H), 7.34 (dd, J = 8.3, 4.2 Hz, 1H), 7.29–7.14 (m, 9H).

**¹³C NMR (126 MHz, CDCl₃)** δ 169.6, 151.6, 148.3, 143.5, 136.6, 134.2, 129.7, 129.1, 128.9, 127.3, 127.2, 126.4, 121.5.

**GC-MS (EI, 70 eV) m/z** calculated for [M⁺]⁺ (C₂₂H₁₆N₂O) 324.1, found 324.1.

**HRMS (ESI, TOF) m/z** calculated for [M + H⁺]⁺ (C₂₂H₁₇N₂O) 325.1335, found 325.1335.

**IR (KBr)** 3062, 3037, 1657, 1623, 1589, 1490, 1461, 1450, 1355, 1335, 1304, 1291, 1122 cm⁻¹

**Melting point:** 175.4-179.7 °C.

**N,N-Dibenzyl-6-quinolinecarboxamide (3k)**

Prepared using N,N-dibenzyl-6-quinolinecarboxamide N-oxide (1k, 73.7 mg, 0.200 mmol, 1.0 equiv), 2a (123.8 mg, 0.400 mmol, 2.0 equiv), 4 (6.9 mg, 10.0 μmol, 5.0 mol%), and CH₃CN (4.0 mL, 0.05 M). N,N-Dibenzyl-6-quinolinecarboxamide (3k, 61.0 mg, 87%) was isolated (hexanes/EtOAc = 1:3) as a white solid.

**¹H NMR (500 MHz, CDCl₃)** δ 8.92 (dd, J = 4.2, 1.7 Hz, 1H), 8.11 (td, J = 6.4, 5.8, 3.1 Hz, 2H), 7.97 (d, J = 1.7 Hz, 1H), 7.82 (dd, J = 8.7, 1.9 Hz, 1H), 7.50–7.28 (m, 11H), 7.15 (s, 2H), 4.77 (s, 2H), 4.45 (s, 2H).

**¹³C NMR (126 MHz, CDCl₃)** δ 171.4, 151.4, 148.2, 136.7, 136.3, 136.1, 134.2, 129.9, 128.7, 128.4, 127.6, 127.5, 126.8, 126.4, 121.7, 51.5, 47.1.

**GC-MS (EI, 70 eV) m/z** calculated for [M⁺]⁺ (C₂₄H₂₀N₂O) 352.2, found 352.2
**HRMS** (ESI, TOF) \( m/z \) calculated for [M + H]\(^{+}\) (C\(_{24}\)H\(_{21}\)N\(_{2}\)O) 353.1648, found 353.1648.

**IR** (KBr) 3069, 3027, 3003, 2922, 2855, 1631, 1592, 1495, 1464, 1352, 1324, 1266, 1114 cm\(^{-1}\)

**Melting point:** 121.2-123.9 °C.

**N,N-Diphenyl-3-quinolinecarboxamide (3l)**

![Structure of N,N-Diphenyl-3-quinolinecarboxamide (3l)]

Prepared using N,N-diphenyl-3-quinolinecarboxamide N-oxide (1l, 68.1 mg, 0.200 mmol, 1.0 equiv), 2a (123.8 mg, 0.400 mmol, 2.0 equiv), 4 (6.9 mg, 10.0 μmol, 5.0 mol%), and CH\(_3\)CN (4.0 mL, 0.05 M).

**N,N-Diphenyl-3-quinolinecarboxamide (3l)**, 64.7 mg, 99% was isolated (hexanes/EtOAc = 3:2) as a white solid.

**\(^1\)H NMR** (500 MHz, CDCl\(_3\)) \( \delta \) 8.87 (d, \( J = 2.2 \) Hz, 1H), 8.34 (d, \( J = 1.8 \) Hz, 1H), 8.02 (d, \( J = 8.4 \) Hz, 1H), 7.76–7.68 (m, 3H), 7.55–7.49 (m, 1H), 7.30 (t, \( J = 7.6 \) Hz, 5H), 7.21 (dd, \( J = 14.3, 7.2 \) Hz, 8H).

**\(^{13}\)C NMR** (126 MHz, CDCl\(_3\)) \( \delta \) 168.0, 149.5, 148.0, 143.2, 137.6, 130.9, 129.3, 129.2, 129.1, 128.4, 127.4, 127.1, 126.8, 126.7.

**GC-MS** (EI, 70 eV) \( m/z \) calculated for [M]\(^{+}\) (C\(_{22}\)H\(_{17}\)N\(_{2}\)O) 324.1, found 324.1

**HRMS** (ESI, TOF) \( m/z \) calculated for [M + H]\(^{+}\) (C\(_{22}\)H\(_{17}\)N\(_{2}\)O) 325.1335, found 325.1335.

**IR** (KBr) 3102, 3062, 3050, 1657, 1623, 1589, 1490, 1461, 1450, 1425, 1356, 1334, 1304, 1291, 1256, 1219 cm\(^{-1}\)

**Melting point:** 173.2-182.2 °C.

**N,N-Diethyl-3-quinolinecarboxamide (3m)**

![Structure of N,N-Diethyl-3-quinolinecarboxamide (3m)]

Prepared using N,N-diethyl-3-quinolinecarboxamide N-oxide (1m, 48.9 mg, 0.200 mmol, 1.0 equiv), 2a (123.8 mg, 0.400 mmol, 2.0 equiv), 4 (6.9 mg, 10.0 μmol, 5.0 mol%), and CH\(_3\)CN (4.0 mL, 0.05 M).

**N,N-Diethyl-3-quinolinecarboxamide (3m)**, 41.0 mg, 85% was isolated (hexenes/EtOAc = 1:3) as a yellow oil. Spectroscopic data matched with those reported in the literature.\(^{33}\)
Supporting Information

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.93 (d, $J = 2.2$ Hz, 1H), 8.19 (d, $J = 2.1$ Hz, 1H), 8.12 (d, $J = 8.4$ Hz, 1H), 7.84 (dd, $J = 8.2, 1.4$ Hz, 1H), 7.76 (ddd, $J = 8.4, 6.8, 1.5$ Hz, 1H), 7.59 (ddd, $J = 8.1, 6.7, 1.2$ Hz, 1H), 3.61 (br s, 2H), 3.32 (br s, 2H), 1.29 (br s, 3H), 1.16 (br s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 168.7, 148.1, 148.0, 134.0, 130.4, 130.1, 129.4, 128.1, 127.3, 127.1, 43.5, 39.6, 14.3, 12.9.

GC-MS (EI, 70 eV) m/z calculated for [M]$^+$ (C$_{14}$H$_{16}$N$_2$O) 228.1, found 228.1.

3-[Bis(tert-butoxycarbonyl)amino]quinoline (3n)

Prepared using 3-[bis(tert-butoxycarbonyl)amino]quinoline N-oxide (1n, 72.1 mg, 0.200 mmol, 1.0 equiv), 2a (123.8 mg, 0.400 mmol, 2.0 equiv), 4 (6.9 mg, 10.0 μmol, 5.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). 3-[Bis(tert-butoxycarbonyl)amino]quinoline (3n, 66.0 mg, 96%) was isolated (hexanes/EtOAc = 4:1) as a yellow solid. Spectroscopic data matched with those reported in the literature.$^{10}$

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.69 (d, $J = 2.5$ Hz, 1H), 8.10 (d, $J = 8.5$ Hz, 1H), 7.92 (d, $J = 2.5$ Hz, 1H), 7.80 (dd, $J = 8.2, 1.4$ Hz, 1H), 7.71 (ddd, $J = 8.5, 6.9, 1.5$ Hz, 1H), 7.55 (ddd, $J = 8.1, 6.8, 1.1$ Hz, 1H), 1.39 (s, 18H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 151.2, 150.4, 146.6, 133.4, 132.7, 129.7, 129.2, 127.8, 127.6, 127.0, 83.5, 27.8.

GC-MS (EI, 70 eV) m/z calculated for [M]$^+$ (C$_{19}$H$_{24}$N$_2$O$_4$) 344.2, found 344.1.

4,7-Dichloroquinoline (3o)

Prepared using 4,7-dichloroquinoline N-oxide (1o, 42.8 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (2.8 mg, 4.0 μmol, 2.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). 4,7-Dichloroquinoline (3o, 30.8 mg, 78%) was isolated (hexanes/EtOAc = 1:1) as a white solid. Spectroscopic data matched with those reported in the literature.$^{34}$
**6-Fluoroquinoline (3p)**

![6-Fluoroquinoline](image)

Prepared using 6-fluoroquinoline N-oxide (1p, 32.6 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (2.8 mg, 4.0 μmol, 2.0 mol%), and CH₃CN (4.0 mL, 0.05 M). 6-Fluoroquinoline (3p, 22.8 mg, 78%) was isolated (hexanes/EtOAc = 2:1) as a yellow oil. Spectroscopic data matched with those reported in the literature.¹⁵

**¹H NMR** (500 MHz, CDCl₃) δ 8.82 (dd, J = 4.3, 1.7 Hz, 1H), 8.05 (dd, J = 9.3, 5.3 Hz, 1H), 8.01 (dd, J = 8.4, 1.8 Hz, 1H), 7.46–7.38 (m, 1H), 7.37–7.30 (m, 2H).

**¹³C NMR** (126 MHz, CDCl₃) δ 160.2 (d, ¹J_{C-F} = 248.3 Hz), 149.5 (d, ⁴J_{C-F} = 2.9 Hz), 145.3, 135.2 (d, ⁴J_{C-F} = 5.4 Hz), 131.9 (d, ³J_{C-F} = 9.2 Hz), 128.7 (d, ³J_{C-F} = 10.0 Hz), 121.6, 119.6 (d, ²J_{C-F} = 25.8 Hz), 110.5 (d, ²J_{C-F} = 21.8 Hz).

**¹⁹F NMR** (471 MHz, CDCl₃) δ –112.3.

**GC-MS** (EI, 70 eV) m/z calculated for [M]⁺ (C₉H₆FN) 147.0, found 147.1.

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**6-Chloroquinoline (3q)**

![6-Chloroquinoline](image)

Prepared using 6-chloroquinoline N-oxide (1q, 35.9 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (2.8 mg, 4.0 μmol, 2.0 mol%), and CH₃CN (4.0 mL, 0.05 M). 6-Chloroquinoline (3q, 28 mg, 86%) was isolated (hexanes/EtOAc = 3:1) as a yellow oil. Spectroscopic data matched with those reported in the literature.¹⁵

**¹H NMR** (500 MHz, CDCl₃) δ 8.90 (dd, J = 4.1, 1.3 Hz, 1H), 8.05 (t, J = 9.7 Hz, 2H), 7.79 (d, J = 2.3 Hz, 1H), 7.64 (dd, J = 8.9, 2.3 Hz, 1H), 7.41 (dd, J = 8.3, 4.2 Hz, 1H).
$^{13}\text{C} \text{NMR}$ (126 MHz, CDCl$_3$) $\delta$ 150.51, 146.55, 135.14, 132.31, 131.03, 130.42, 128.81, 126.38, 121.87.

$\text{GC-MS}$ (EI, 70 eV) $m/z$ calculated for [M]$^+$ (C$_9$H$_6$CN) 163.0, found 163.0.

6-Bromoquinoline (3r)

Prepared using 6-bromoquinoline N-oxide (1r, 44.8 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (2.8 mg, 4.0 μmol, 2.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). 6-Bromoquinoline (3r, 40.4 mg, 97%) was isolated (hexanes/EtOAc = 3:1) as a yellow oil. Spectroscopic data matched with those reported in the literature.$^{15}$

$^1\text{H} \text{NMR}$ (500 MHz, CDCl$_3$) $\delta$ 8.90 (dd, $J$ = 4.3, 1.8 Hz, 1H), 8.03 (dd, $J$ = 8.3, 1.7 Hz, 1H), 7.98–7.93 (m, 2H), 7.75 (dd, $J$ = 9.0, 2.2 Hz, 1H), 7.39 (dd, $J$ = 8.3, 4.2 Hz, 1H).

$^{13}\text{C} \text{NMR}$ (126 MHz, CDCl$_3$) $\delta$ 150.7, 146.8, 134.9, 132.9, 131.2, 129.7, 129.3, 121.8, 120.4.

$\text{GC-MS}$ (EI, 70 eV) $m/z$ calculated for [M]$^+$ (C$_9$H$_6$BrN) 207.0, found 207.1.

2-(Trifluoromethyl)quinoline (3s)

Prepared using 2-(trifluoromethyl)quinoline N-oxide (1s, 42.6 mg, 0.200 mmol, 1.0 equiv), 2a (123.8 mg, 0.400 mmol, 2.0 equiv), 4 (6.9 mg, 10.0 μmol, 5.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). 2-(Trifluoromethyl)quinoline (3s, 34.8 mg, 88%) was isolated (hexanes/Et$_2$O = 15:1) as a white solid. Spectroscopic data matched with those reported in the literature.$^{15}$

$^1\text{H} \text{NMR}$ (500 MHz, CDCl$_3$) $\delta$ 8.33 (d, $J$ = 8.5 Hz, 1H), 8.22 (d, $J$ = 8.3 Hz, 1H), 7.89 (dd, $J$ = 8.2, 1.4 Hz, 1H), 7.81 (ddd, $J$ = 8.5, 6.9, 1.5 Hz, 1H), 7.72 (d, $J$ = 8.5 Hz, 1H), 7.66 (ddd, $J$ = 8.1, 6.8, 1.2 Hz, 1H).

$^{13}\text{C} \text{NMR}$ (126 MHz, CDCl$_3$) $\delta$ 147.9 (q, $^2\text{J}_{\text{C}-\text{F}}$ = 34.5 Hz), 147.1, 138.1, 130.8, 130.1, 128.8, 128.6, 127.6, 121.6 (q, $^1\text{J}_{\text{C}-\text{F}}$ = 275.2 Hz), 116.7 (q, $^3\text{J}_{\text{C}-\text{F}}$ = 2.3 Hz).

$^{19}\text{F} \text{NMR}$ (471 MHz, CDCl$_3$) $\delta$ –66.5.

$\text{GC-MS}$ (EI, 70 eV) $m/z$ calculated for [M]$^+$ (C$_{10}$H$_6$F$_3$N) 197.0, found 197.1.
6-Methylquinoline (3t)

![6-Methylquinoline](image)

Prepared using 6-methylquinoline N-oxide (1t, 31.8 mg, 0.200 mmol, 1.0 equiv), 2a (123.8 mg, 0.400 mmol, 2.0 equiv), 4 (6.9 mg, 10.0 μmol, 5.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). 6-Methylquinoline (3t, 22.5 mg, 79%) was isolated (hexanes/EtOAc = 2:1) as a white solid. Spectroscopic data matched with those reported in the literature.$^{15}$

$^1$H NMR (400 MHz, CDCl$_3$) 6 8.63 (d, $J = 8.9$ Hz, 1H), 8.47 (d, $J = 5.9$ Hz, 1H), 7.65 (d, $J = 8.5$ Hz, 1H), 7.62 (s, 1H), 7.59 (dd, $J = 8.9$, 1.7 Hz, 1H), 7.27–7.23 (m, 1H), 2.54 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) 6 140.1, 139.0, 135.0, 132.6, 130.7, 127.0, 125.5, 120.9, 119.6, 21.4.

LC-MS (ESI) calculated for [M+1]$^+$ (C$_{10}$H$_{10}$NO) m/z 144.1, found m/z 144.1.

2-Phenylquinoline (3u)

![2-Phenylquinoline](image)

Prepared using 2-phenylquinoline N-oxide (2u, 44.3 mg, 0.200 mmol, 1.0 equiv), 2a (123.8 mg, 0.400 mmol, 2.0 equiv), 4 (6.9 mg, 10.0 μmol, 5.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). 2-Phenylquinoline (3u, 21.3 mg, 52%) was isolated (hexanes/EtOAc = 2:1) as a pale yellow oil. Spectroscopic data matched with those reported in the literature.$^{15}$

$^1$H NMR (500 MHz, CDCl$_3$) 6 8.25 (d, $J = 8.6$ Hz, 1H), 8.23–8.17 (m, 3H), 7.91 (d, $J = 8.6$ Hz, 1H), 7.86 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.76 (ddd, $J = 8.4$, 6.8, 1.5 Hz, 1H), 7.61–7.53 (m, 3H), 7.53–7.46 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) 6 157.3, 148.3, 139.7, 136.7, 129.8, 129.6, 129.3, 128.8, 127.6, 127.4, 127.2, 126.2, 119.0.

GC-MS (El, 70 eV) m/z calculated for [M]$^+$ (C$_{15}$H$_{11}$N) 205.1, found 205.1.

6-Benzoyloxyquinoline (3v)

![6-Benzoyloxyquinoline](image)

Prepared using 6-benzoyloxyquinoline N-oxide (1v, 53.0 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). 6-
Benzoyloxyquinoline (3v, 32.4 mg, 65%) was isolated (hexanes/EtOAc = 3:2) as a white solid. Spectroscopic data matched with those reported in the literature.  

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.91 (dd, \(J = 4.2, 1.5\) Hz, 1H), 8.27–8.21 (m, 2H), 8.17 (d, \(J = 9.1\) Hz, 1H), 8.12 (d, \(J = 7.9\) Hz, 1H), 7.69 (d, \(J = 2.5\) Hz, 1H), 7.59 (dd, \(J = 9.1, 2.5\) Hz, 1H), 7.52 (t, \(J = 7.8\) Hz, 2H), 7.40 (dd, \(J = 8.3, 4.2\) Hz, 1H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 165.0, 150.2, 148.7, 146.3, 135.7, 133.8, 131.0, 130.2, 129.2, 128.6, 128.5, 124.8, 121.5, 118.5.

GC-MS (EI, 70 eV) m/z calculated for [M]\(^+\) (C\(_{16}\)H\(_{11}\)NO\(_2\)) 249.1, found 249.1

\(1\)-Isoquinolinecarbonitrile (3w)

\[\text{Prepared using 1-i} \text{-isoquinolinecarbonitrile N-oxide (1w, 34.3 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 \mu\text{mol, 1.0 mol\%}, and CH}_3\text{CN (4.0 mL, 0.05 M). 1-i} \text{-isoquinolinecarbonitrile (3w, 30.3 mg, 97\%) was isolated (hexanes/EtOAc = 1:1) as a white solid. Spectroscopic data matched with those reported in the literature.}^{36}\]

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.64 (d, \(J = 5.6\) Hz, 1H), 8.32 (d, \(J = 8.2\) Hz, 1H), 7.94 (d, \(J = 7.7\) Hz, 1H), 7.90 (d, \(J = 5.6\) Hz, 1H), 7.86–7.76 (m, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 143.2, 135.8, 134.8, 131.7, 129.8, 129.3, 127.3, 125.2 (two carbons), 124.4, 115.8.

GC-MS (EI, 70 eV) m/z calculated for [M]\(^+\) (C\(_{10}\)H\(_{6}\)N\(_2\)) 154.1, found 154.1.

\(1\)-Benzoylisoquinoline (3x)

\[\text{Prepared using 1-benzo} \text{-yli} \text{soquinoline N-oxide (1x, 49.9 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 \mu\text{mol, 1.0 mol\%}, and CH}_3\text{CN (4.0 mL, 0.05 M). 1-benzo} \text{-yli} \text{soquinoline (3x, 40.1 mg, 86\%) was isolated (hexanes/EtOAc = 6:1) as a white solid. Spectroscopic data matched with those reported in the literature.}^{37}\]
1H NMR (500 MHz, CDCl3) δ 8.60 (d, J = 5.6 Hz, 1H), 8.22 (d, J = 8.5 Hz, 1H), 8.02–7.93 (m, 3H), 7.91 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 5.6 Hz, 1H), 7.78–7.70 (m, 2H), 7.65–7.57 (m, 4H), 7.47 (t, J = 7.8 Hz, 2H).

13C NMR (126 MHz, CDCl3) δ 194.7, 156.4, 141.1, 136.6, 136.6, 133.6, 130.7, 130.6, 128.4, 128.3, 127.0, 126.4, 126.1, 122.5.

GC-MS (El, 70 eV) m/z calculated for [M]+ (C16H11NO) 233.1, found 233.1.

1-Acetylisoquinoline (3y)

Prepared using 1-acetylisoquinoline N-oxide (1y, 37.4 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH3CN (4.0 mL, 0.05 M). 1-Acetylisoquinoline (3y, 23.1 mg, 68%) was isolated (CH2Cl2 as a sole eluent) as a white solid. Spectroscopic data matched with those reported in the literature.38

1H NMR (500 MHz, CDCl3) δ 8.96 (d, J = 8.4 Hz, 1H), 8.58 (d, J = 5.5 Hz, 1H), 7.86 (d, J = 7.5 Hz, 1H), 7.82 (d, J = 5.5 Hz, 1H), 7.75–7.65 (m, 2H), 2.86 (s, 2H).

13C NMR (126 MHz, CDCl3) δ 202.7, 152.8, 141.0, 137.0, 130.3, 129.1, 126.9, 126.9, 125.7, 124.6, 28.5.

GC-MS (El, 70 eV) m/z calculated for [M]+ (C11H9NO2) 187.1, found 187.1.

2-Quinoxalinecarbonitrile (3z)

Prepared using 3-quinoxalinecarbonitrile N-oxide (1z, 34.2 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH3CN (4.0 mL, 0.05 M). 2-Quinoxalinecarbonitrile (3z, 27.9 mg, 90%) was isolated (hexanes/EtOAc = 9:1) as a white solid. Spectroscopic data matched with those reported in the literature.39

1H NMR (500 MHz, CDCl3) δ 9.07 (s, 1H), 8.21–8.14 (m, 3H), 7.94 (dtt, J = 13.5, 6.8, 3.5 Hz, 4H).

13C NMR (126 MHz, CDCl3) δ 145.6, 142.9, 142.0, 133.3, 131.9, 129.9, 129.8, 129.6, 115.9.
**Methyl 2-Quinoxalinecarboxylate (3aa)**

Prepared using methyl 3-quinoxalinecarboxylate \( N \)-oxide (1aa, 40.8 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH\(_3\)CN (4.0 mL, 0.05 M). Methyl 2-quinoxalinecarboxylate (3aa, 37.3 mg, 99%) was isolated (hexanes/EtOAc = 3:1) as a white solid. Spectroscopic data matched with those reported in the literature.\(^{40}\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 9.52 (s, 1H), 8.27 (dd, \( J = 8.3, 1.2 \) Hz, 2H), 8.15 (dd, \( J = 8.3, 1.2 \) Hz, 2H), 7.92–7.80 (m, 4H), 4.09 (s, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 164.6, 145.0, 143.7, 142.3, 141.4, 132.3, 131., 130.5, 129.3, 53.3.

**GC-MS (El, 70 eV) m/z calculated for [M]\(^+\) (C\(_9\)H\(_5\)N\(_3\)) 155.0, found 155.0.

\**2-Acetylquinoxaline (3ab)**

Prepared using 3-acetylquinoxaline \( N \)-oxide (1ab, 37.6 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH\(_3\)CN (4.0 mL, 0.05 M). 2-Acetylquinoxaline (3ab, 34.1 mg, 94%) was isolated (hexanes/EtOAc = 7:1) as a white solid. Spectroscopic data matched with those reported in the literature.\(^{41}\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 9.47 (s, 1H), 8.20–8.11 (m, 3H), 2.83 (s, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 199.7, 146.5, 143.8, 143.0, 141.0, 132.1, 130.6, 130.4, 129.4, 25.4.

**GC-MS (El, 70 eV) m/z calculated for [M]\(^+\) (C\(_{10}\)H\(_8\)N\(_2\)O) 188.1, found 188.1.

\**2-Benzoylquinoxaline (3ac)**

Prepared using 3-benzoylquinoxaline \( N \)-oxide (1ab, 37.6 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH\(_3\)CN (4.0 mL, 0.05 M). 2-Benzoylquinoxaline (3ac, 34.1 mg, 94%) was isolated (hexanes/EtOAc = 7:1) as a white solid. Spectroscopic data matched with those reported in the literature.\(^{42}\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 9.47 (s, 1H), 8.20–8.11 (m, 3H), 2.83 (s, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 199.7, 146.5, 143.8, 143.0, 141.0, 132.1, 130.6, 130.4, 129.4, 25.4.

**GC-MS (El, 70 eV) m/z calculated for [M]\(^+\) (C\(_{10}\)H\(_8\)N\(_2\)O) 172.1, found 172.1.
Prepared using 3-benzoylquinoxaline \( N \)-oxide (1ac, 48.9 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 \( \mu \)mol, 1.0 mol%), and CH\(_3\)CN (4.00 mL, 0.05 M). 2-Benzoylquinoxaline (3ac, 44.0 mg, 94%) was isolated (hexenes/EtOAc = 4:1) as a white solid. Spectroscopic data matched with those reported in the literature.\(^{42}\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 9.48 (s, 1H), 8.27–8.12 (m, 7H), 7.98–7.78 (m, 3H), 7.66 (s, 0H), 7.64 (d, \( J = 7.4 \) Hz, 1H), 7.53 (t, \( J = 7.8 \) Hz, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 192.2, 148.6, 145.2, 143.1, 140.4, 135.5, 133.6, 131.9, 131.2, 130.7, 130.4, 129.4, 128.3.

GC-MS (El, 70 eV) \( m/z \) calculated for [M]+ (C\(_{15}\)H\(_{10}\)N\(_2\)O) 234.1, found 234.1.

2-Benzoylquinoxaline (3ac)

Prepared using 3-benzoylquinoxaline \( N,N \)-dioxide (1ac', 53.3 mg, 0.200 mmol, 1.0 equiv), 2a (185.6 mg, 0.600 mmol, 3.0 equiv), 4 (1.4 mg, 2.0 \( \mu \)mol, 1.0 mol%), and CH\(_3\)CN (4.0 mL, 0.05 M). 2-Benzoylquinoxaline (3ac, 43.2 mg, 94%) was isolated (CH\(_2\)Cl\(_2\)/EtOAc = 30:1) as a white solid. Spectroscopic data matched with those reported in the literature.\(^{42}\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 9.48 (s, 1H), 8.27–8.14 (m, 7H), 7.91–7.81 (m, 3H), 7.66 (s, 0H), 7.64 (d, \( J = 7.4 \) Hz, 1H), 7.53 (t, \( J = 7.8 \) Hz, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 192.2, 148.6, 145.2, 143.1, 140.4, 135.5, 133.6, 131.9, 131.2, 130.7, 130.4, 129.4, 128.3.

GC-MS (El, 70 eV) \( m/z \) calculated for [M]+ (C\(_{15}\)H\(_{10}\)N\(_2\)O) 234.1, found 234.1.

3-Pyrazinecarbonitrile (3ad)

Prepared using 3-pyrazinecarbonitrile \( N \)-oxide (1ad, 24.2 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 \( \mu \)mol, 1.0 mol%), and CH\(_3\)CN (4.0 mL, 0.05 M). The truth is that the deoxygenated product 2-pyrazinecarbonitrile (3ad) is volatile. Hence, an NMR yield (98%) was
estimated using 1,3,5-trimethoxybenzene as an internal standard. An analytical sample was obtained by flash column chromatography of the crude mixture (hexanes/EtOAc = 4:1) on silica gel. Spectroscopic data matched with those reported in the literature.\textsuperscript{43}

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.92 (d, $J = 1.4$ Hz, 1H), 8.79 (d, $J = 2.4$ Hz, 1H), 8.75–8.69 (m, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 148.5, 138.2, 136.5, 134.0, 113.5.

GC-MS (EI, 70 eV) $m/z$ calculated for [M]$^+$ (C$_5$H$_3$N$_3$) 105.0, found 105.0.

**Methyl 3-Pyrazinecarboxylate (3ae)**

![Structural formula of Methyl 3-Pyrazinecarboxylate (3ae)](image)

Prepared using methyl 3-pyrazinecarboxylate N-oxide (1ae, 30.8 mg, 0.200 mmol, 1.0 equiv), 2a (92.8 mg, 0.300 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). Methyl 3-pyrazinecarboxylate (3ae, 24.3, 88%) was isolated (hexenes/EtOAc = 1:1) as a pale yellow oil. Spectroscopic data matched with those reported in the literature.\textsuperscript{44}

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.32 (s, 1H), 8.77 (d, $J = 2.2$ Hz, 1H), 8.72 (s, 1H), 4.04 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 164.4, 147.7, 146.3, 144.4, 143.3, 53.1.

LC-MS (ESI) $m/z$ calculated for [M+1]$^+$ (C$_6$H$_7$N$_2$O$_2$) 139.0, found 139.0.

**3-Acetylpyrazine (3af)**

![Structural formula of 3-Acetylpyrazine (3af)](image)

Prepared using 3-acetylpyrazine N-oxide (1af, 27.6 mg, 0.200 mmol, 1.0 equiv), 2a (123.8 mg, 0.400 mmol, 2.0 equiv), 4 (1.4 mg, 2.0 μmol, 1.0 mol%), and CH$_3$CN (4.0 mL, 0.05 M). The truth is that the deoxygenated product 3-acetylpyrazine (3af) is volatile. Hence, an NMR yield (90%) was estimated using 1,3,5-trimethoxybenzene as an internal standard. An analytical sample was obtained by flash column chromatography of the crude mixture (hexanes/EtOAc = 1:1) on silica gel. Spectroscopic data matched with those reported in the literature.\textsuperscript{45}

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.74 (d, $J = 2.4$ Hz, 1H), 8.67–8.61 (m, 1H), 2.71 (s, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 199.3, 147.7, 143.5, 28.2, 25.7.
**LC-MS (ESI) m/z** calculated for [M+1]+ (C₆H₆N₂O) 123.0, found 123.0.

**Methyl Nicotinate (3ag)**

Prepared using methyl nicotinate N-oxide (1ag, 30.6 mg, 0.2 mmol, 1.0 equiv), 2a (92.8 mg, 0.3 mmol, 1.5 equiv), 4 (1.4 mg, 2.0 μmol, 10 mol%), and CH₃CN (4.0 mL, 0.05 M). Methyl nicotinate (3ag, 5.7 mg, 21%) was isolated (hexanes/EtOAc = 2:1) as a yellow oil. Spectroscopic data matched with those reported in the literature.⁴⁶

**¹H NMR** (500 MHz, CDCl₃) δ 9.12 (d, J = 2.4 Hz, 1H), 8.68 (dd, J = 4.9, 1.8 Hz, 1H), 8.19 (dt, J = 8.0, 2.0 Hz, 1H), 7.30 (dd, J = 8.0, 4.9 Hz, 1H), 3.86 (s, 3H).

**¹³C NMR** (126 MHz, CDCl₃) δ 165.5, 153.2, 150.7, 136.8, 125.8, 123.1, 52.2.

**GC-MS (EI, 70 eV) m/z** calculated for [M]+ (C₇H₇NO₂) 137.0, found 137.2.

**Experimental Procedure for Scheme 3a (In the Absence of Visible Light Irradiation)**

A 10 mL test tube equipped with a small magnetic stir bar was charged with 3-quinolinecarbonitrile N-oxide (1a, 34.0 mg, 0.200 mmol, 1.0 equiv) and tert-Bu-HEH (1c, 92.8 mg, 0.300 mmol, 1.5 equiv). The tube was fitted with a rubber septum and wrapped with aluminum foil, and CH₃CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N₂ bubbling at room temperature for 10 min, the reaction mixture was stirred in the dark for 12 h. TLC analysis indicated that no conversion of 1a into the deoxygenated product 3a occurred.

**Experimental Procedure for Scheme 3b (In the Absence of a Photocatalyst)**

A 10 mL test tube equipped with a small magnetic stir bar was charged with 3-quinolinecarbonitrile N-oxide (1a, 34.0 mg, 0.200 mmol, 1.0 equiv) and tert-Bu-HEH (1c, 92.8 mg, 0.300 mmol, 1.5 equiv). The tube was fitted with a rubber septum and CH₃CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N₂ bubbling at room temperature for 10 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs for 24 h. The reaction mixture was concentrated on a rotary evaporator. The resulting residue was directly purified by flash column
chromatography on silica gel (hexanes/EtOAc = 3:1) to afford 3-quinolinecarbonitrile (3a, 16.7 mg, 45%) as a white solid.

**Experimental Procedure for Scheme 3c (Kinetic Deuterium Isotope Effect)**

A 10 mL test tube equipped with a small magnetic stir bar was charged with methyl 3-quinolinecarboxylate N-oxide (1a, 40.6 mg, 0.200 mmol, 1.0 equiv), tert-Bu-HEH (1c, 46.4 mg, 0.150 mmol, 0.75 equiv), t-Bu-HEH-d₃ (1c-d₃, 46.7 mg, 0.150 mmol, 0.75 equiv), and Na₂-eosin Y (4, 1.4 mg, 2.0 μmol, 1.0 mol%). The tube was fitted with a rubber septum and CH₃CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N₂ bubbling at room temperature for 1 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs for 1 h. Upon the completion of the reaction as determined by TLC, the reaction mixture was concentrated on a rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 7:1 → 1.2:1) to afford 3-quinolinecarbonitrile (3a, 36.7 mg, 97%) along with, as determined by 1H NMR analysis, a 1:1.3 mixture of di-tert-butyl 2,6-dimethylpyridine-3,5-dicarboxylate and di-tert-butyl 4-deuterio-2,6-dimethylpyridine-3,5-dicarboxylate.

**Experimental Procedure for Scheme 3d (Using a Radical Inhibitor)**

A 10 mL test tube equipped with a small magnetic stir bar was charged with isopropyl 6-quinolinecarboxylate N-oxide (1a, 48.3 mg, 0.200 mmol, 1.0 equiv), tert-Bu-HEH (2a, 92.8 mg, 0.300 mmol, 1.5 equiv), (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO, 187 mg, 1.20 mmol, 6.0 equiv), and Na₂-eosin Y (4, 1.4 mg, 2.0 μmol, 1.0 mol%). The tube was fitted with a rubber septum and CH₃CN (4.0 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N₂ bubbling at room temperature for 10 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs. After irradiation of the reaction mixture for 6 h, the reaction mixture was concentrated on a rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 3:1) to afford 6-quinolinecarboxylate (3a, 2.8 mg, 7%) as a white solid.
Stern-Volmer Fluorescence Quenching Experiments

Emission Quenching of Na$_2$-eosin Y (4)

A 50 mL volumetric flask containing the photocatalyst Na$_2$-eosin Y (4, 4.3 mg, 6.25 μmol) was fitted with a rubber septum and charged with CH$_3$CN (slightly more than 100 mL) via syringe. The resulting solution was then degassed by sparging with nitrogen until its volume reached to 100 mL. Stern-Volmer luminescence quenching experiments were performed using a Varian Cary eclipse fluorescence spectrophotometer. In each experimentation, the solution of 4 and varying concentrations of quencher (1e, 1q, 1t, or 2a) were combined in degassed CH$_3$CN in 1 cm screw-top quartz cuvettes. For the emission quenching of 4, the photocatalyst concentration was 0.2 μM, the solution was excited at 530 nm, and the emission intensity was observed at 555 nm. Plots were constructed according to the Stern-Volmer equation $I_0/I = 1 + k_q [Q]$. $I_0$ and I represent the intensities of the emission in the absence and presence of a quencher at 555 nm, respectively.

![Figure S3. Emission Quenching of Na$_2$-eosin Y (4)](image-url)
Experimental Procedure for Multigram-Scale Reaction (Scheme 4)

A 500 mL round-bottomed flask equipped with a magnetic stir bar was charged with methyl 6-quinolinecarboxylate N-oxide (1c, 3.00 g, 14.8 mmol, 1.0 equiv), tert-Bu-HEH (2a, 6.85 g, 22.2 mmol, 1.5 equiv), and Na2-eosin Y (4, 103.8 mg, 0.148 mmol, 1.0 mol%). The flask was fitted with a rubber septum and CH3CN (296 mL, 0.05 M) was added via syringe under an atmosphere of nitrogen. After degassing by N2 bubbling at room temperature for 20 min, the reaction mixture was then irradiated at room temperature with two 3 W green LEDs for 6 h. Upon the completion of the reaction as determined by TLC, the reaction mixture was concentrated on a rotary evaporator. The resulting residue was directly purified by flash column chromatography on silica gel (hexanes/EtOAc = 3:1) to afford 6-quinolinecarboxylate (3a, 2.66 g, 96%) as a white solid.
Di-tert-butyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2a)

^1^H NMR (500 MHz, CDCl\textsubscript{3})

\begin{center}
\includegraphics[width=0.8\textwidth]{hnmr}
\end{center}

^1^C NMR (126 MHz, CDCl\textsubscript{3})

\begin{center}
\includegraphics[width=0.8\textwidth]{cmr}
\end{center}
Di-tert-butyl 2,4,6-Trimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2b)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Diethyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2c)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Dimethyl 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2d)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Di-tert-butyl 4-Deuterio-2,6-dimethyl-1,4-dihydro-4-deuteriopyridine-3,5-dicarboxylate (2a-d$_2$)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Quinolinecarbonitrile N-Oxide (1a)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
3-Quinolinecarbonitrile N-Oxide (1b)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Methyl 3-Quinolinecarboxylate N-Oxide (1c)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Methyl 6-Quinolinecarboxylate N-Oxide (1d)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Ethyl 6-Quinolinecarboxylate N-Oxide (1e)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Isopropyl 6-Quinolinecarboxylate N-Oxide (1f)

$^1$H NMR (500 MHz, CDCl₃)

$^{13}$C NMR (126 MHz, CDCl₃)
**tert-Butyl 6-Quinolinecarboxylate N-Oxide (1g)**

**$^1$H NMR (500 MHz, CDCl$_3$)**

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![1H NMR spectrum]
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**$^{13}$C NMR (126 MHz, CDCl$_3$)**

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![$^{13}$C NMR spectrum]
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Methyl 8-Quinolinecarboxylate N-Oxide (1h)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Acetylquinoline N-Oxide (1i)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
N,N-Diphenyl-6-quinolinecarboxamide N-Oxide (1j)

^1H NMR (500 MHz, CDCl₃)

^13C NMR (126 MHz, CDCl₃)
**N,N-Dibenzyl-6-quinolinecarboxamide N-Oxide (1k)**

**$^{1}$H NMR** (500 MHz, CDCl₃)

**$^{13}$C NMR** (126 MHz, CDCl₃)
$N,N$-Diphenyl-3-quinolinecarboxamide $N$-Oxide (1I)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
N,N-Diethyl-3-quinolinecarboxamide N-Oxide (1m)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-[Bis(tert-butoxycarbonyl)amino]quinoline N-Oxide (1n)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
4,7-Dichloroquinoline N-Oxide (1o)

\(^1\)H NMR (500 MHz, CDCl\(_3\))

\(^{13}\)C NMR (126 MHz, CDCl\(_3\))
6-Fluoroquinoline $N$-Oxide (1p)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (471 MHz, CDCl$_3$)
6-Chloroquinoline N-Oxide (1q)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
6-Bromoquinoline N-Oxide (1r)

\(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR (101 MHz, CDCl\(_3\))
2-(Trifluoromethyl)quinoline N-Oxide (1s)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}\text{F NMR}$ (471 MHz, CDCl$_3$)
6-Methylquinoline \(N\)-Oxide (1t)

\(^1H\) NMR (400 MHz, CDCl\(3\))

\(\text{13C NMR (101 MHz, CDCl}_3\))
2-Phenylquinoline N-Oxide (1u)

$^1$H NMR (500 MHz, CD$_3$CN)

$^{13}$C NMR (126 MHz, CD$_3$CN)
6-Benzoyloxyquinoline N-Oxide (1v)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
1-Isoquinolinecarbonitrile N-Oxide (1w)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
1-Benzoylisoquinoline N-Oxide (1x)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
1-Acetylisouquinoline N-Oxide (1y)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Quinoxalinecarbonitrile N-Oxide (1z)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Methyl 3-Quinoxalinecarboxylate N-Oxide (1aa)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Acetylquinoxaline N-Oxide (1ab)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Benzoylquinoxaline N-Oxide (1ac)

$^1\text{H NMR}$ (500 MHz, CDCl$_3$)

$^{13}\text{C NMR}$ (126 MHz, CDCl$_3$)
2-Benzoylquinoxaline N,N-Dioxide (1ad)

\( ^1\text{H NMR} \ (500 \text{ MHz, CDCl}_3) \)

\( ^{13}\text{C NMR} \ (126 \text{ MHz, CDCl}_3) \)
3-Pyrazinecarbonitrile N-Oxide (1ae)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Methyl 3-Pyrazinecarboxylate N-Oxide (1af)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Acetylpyrazine N-Oxide (1ag)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Methyl Nicotinate N-Oxide (1ah)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Quinolinecarbonitrile (3a)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
2-Quinolinecarbonitrile (3b)

\[^1\text{H NMR}\] (500 MHz, CDCl\textsubscript{3})

\[^{13}\text{C NMR}\] (126 MHz, CDCl\textsubscript{3})
Methyl Quinoline-3-carboxylate (3c)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Methyl 6-Quinolinecarboxylate (3d)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Ethyl 6-Quinolinecarboxylate (3e)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Isopropyl 6-Quinolinecarboxylate (3f)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
tert-Butyl 6-Quinolinecarboxylate (3g)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Methyl 8-Quinolinecarboxylate (3h)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Acetylquinoline (3i)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
SUPPORTING INFORMATION

*N,N*-Dimethyl-6-quinolinecarboxamide (3j)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
**N,N-Dibenzyl-6-quinolinecarboxamide (3k)**

**\(^1\)H NMR (500 MHz, CDCl\(_3\))**

**\(^{13}\)C NMR (126 MHz, CDCl\(_3\))**
N,N-Diphenyl-3-quinolinecarboxamide (3I)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
**N,N-Diethyl-3-quinolinecarboxamide (3m)**

**$^1$H NMR (500 MHz, CDCl$_3$)**

![$^1$H NMR spectrum](image)

**$^{13}$C NMR (126 MHz, CDCl$_3$)**

![$^{13}$C NMR spectrum](image)
3-[Bis(tert-butoxycarbonyl)amino]quinoline (3n)

$^1$H NMR (500 MHz, CDCl₃)

$^{13}$C NMR (126 MHz, CDCl₃)
4,7-Dichloroquinoline (3o)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
6-Fluoroquinoiline (3p)

$^1$H NMR (500 MHz, CDCl₃)

$^{13}$C NMR (126 MHz, CDCl₃)
$^{19}$F NMR (471 MHz, CDCl$_3$)
6-Chloroquinoline (3q)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
6-Bromoquinoline (3r)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
2-(Trifluoromethyl)quinoline(3s)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (471 MHz, CDCl$_3$)
6-Methylquinoline (3t)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
2-Phenylquinoline (3u)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
6-Benzoyloxyquinoline (3v)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
1-Isoquinolinecarbonitrile (3w)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
1-Benzoylisoquinoline (3x)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
1-Acetylisouquinoline (3y)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Quinoxalinecarbonitrile (3z)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Methyl 3-Quinoxalinecarboxylate (3aa)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Acetylquinoxaline (3ab)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
2-Benzoylquinoxaline (3ac)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
2-Benzoylquinoxaline (3ac)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Pyrazinecarbonitrile (3ad)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Methyl 3-Pyrazinecarboxylate (3ae)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-Acetylpyrazine (3af)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Methyl Nicotinate (3ag)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Pyridine-2a (Scheme 3c)

$^1$H NMR (500 MHz, CDCl$_3$)

Pyridine-2a-d (Scheme 3c)

$^1$H NMR (500 MHz, CDCl$_3$)
1.3:1 Mixture of Pyridine-2a and Pyridine-2a-d (Scheme 3c)

$^1$H NMR (500 MHz, CDCl$_3$)
Multigram Scale Reaction (Scheme 4)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

References


