Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Visible-light-Induced phosgenation of amines by chloroform oxygenation using chlorine dioxide

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1. General Information:

All reactions were performed in dry solvents using oven-dried glassware. Chloroform (ethanol-free, 99+%, stab. with ca 50 ppm amylene) purchased from Alfa Aesar and was directly used without further drying or purification. Unless otherwise noted, materials were purchased from Aldrich Inc., Tokyo Chemical Industry, Wako Chemicals, and other commercial suppliers and were used without purification.

NMR spectra were recorded using JEOL JNM-ECS 400 spectrometer with tetramethylsilane as an internal reference (0.00 ppm for ^{1}H and ^{13}C NMR). ^{1}H NMR spectral data are reported in terms of chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectral data are reported in terms of chemical shift (δ, ppm). The following abbreviations indicate the multiplicities: s, singlet. d, doublet. t, triplet. q, quartet. m, multiplet. br, broad. IR spectra were recorded by Perkin Elmer Spectrum Two FTIR with a diamond window. All spectra were acquired at 4 cm^{-1} resolutions over 100 scans in the scan range of 500-4000 cm^{-1}. High-resolution mass spectra were obtained on an AB SCEIX Triplet TOF 4600 mass spectrometer. Melting points were recorded on a M-560 (Büchi Labortechnik) and were uncorrected.

Theoretical Calculations: Density functional theory (DFT) calculations were performed with Gaussian09 (Revision C.02, Gaussian, Inc.). The calculations were performed on a 16-processor high performance computer (ForScientist XD1, HPC Systems Inc., Japan).

2. General Procedure and Spectral Data:

Sodium chlorite (228 mg, 2.0 mmol: 1.6 mmol as $ClO_2^{\bullet}$) in water (5.7 mL) with 35% HCl (114 µL) was added in chamber A, solution of nucleophiles (0.2 mmol) and *N*,*N*-diisopropylethylamine (102 µL, 0.6 mmol) in $CHCl_3$ (2 mL) was added in chamber B (Fig. S1(a)). After closing the cap, the reaction vessel was irradiated with 405 nm LED lamp (90 mW/cm^2) for 60 minutes at room temperature (Fig. S1(b,c)). The reaction mixture (B chamber) was quenched with a saturated aqueous $NaHCO_3$ solution (3 mL) and extracted with chloroform, and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the mixture was purified by individual procedures according to the respective compounds. Details are given in the respective compound sections.

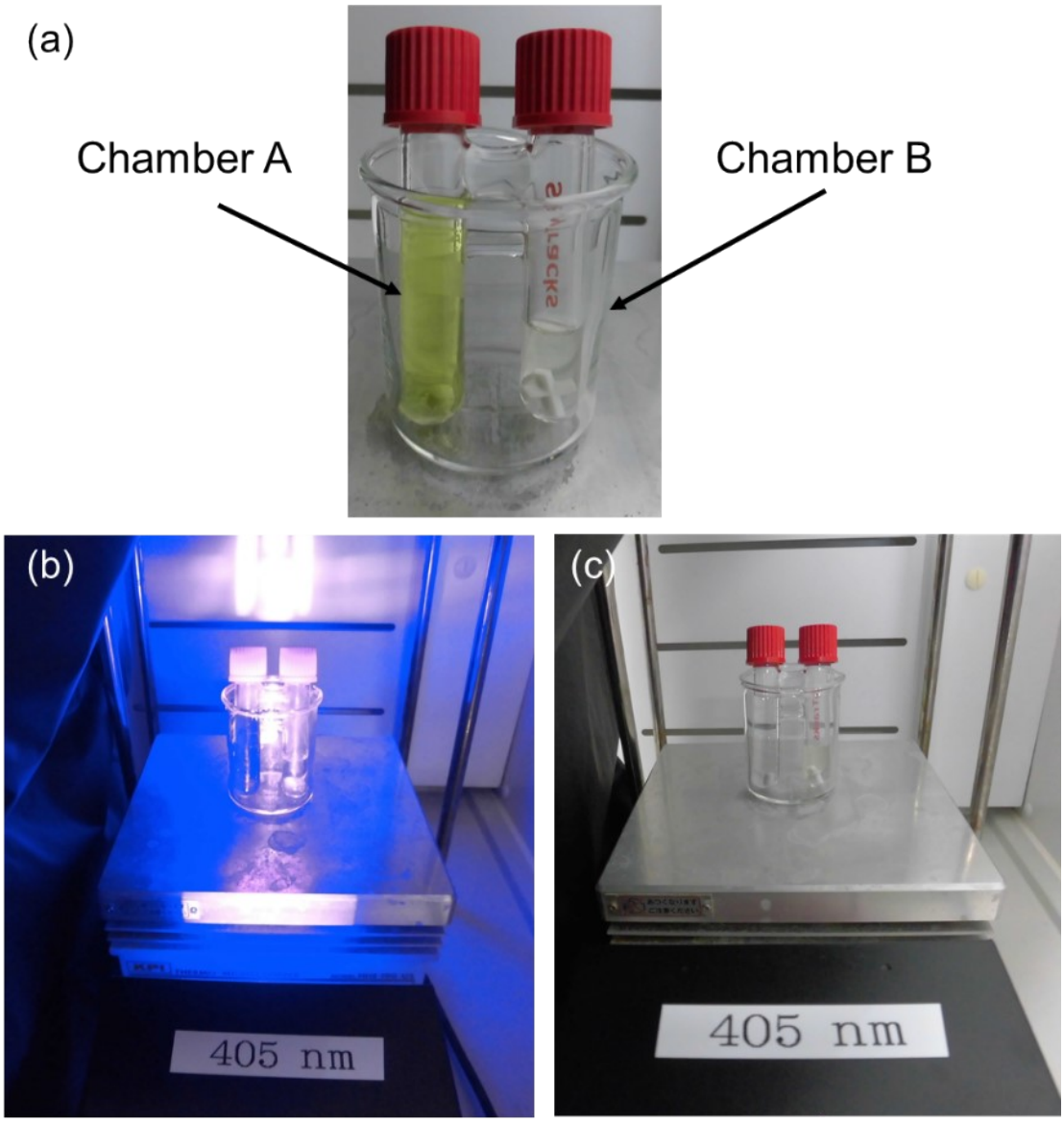
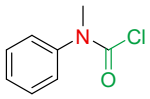


Fig. S1 (a) Reaction setup of two chamber reaction vessel using this study. (b) During and (c) after photo irradiation with 405 nm LED lamp.

Under sunlight: Sodium chlorite (228 mg, 2.0 mmol: 1.6 mmol as $ClO_2^{\bullet}$) in water (5.7 mL) with 35% HCl (114 µL) was added in chamber A, solution of nucleophiles (0.2 mmol) and *N*,*N*-diisopropylethylamine (102 µL, 0.6 mmol) in $CHCl_3$ (2 mL) was added in chamber B. After closing the cap, the reaction vessel was kept under sunlight irradiation (a sunny day, 11:20–13:20) for 2 h at room temperature (Fig. S2). The reaction mixture (B chamber) was quenched with a saturated aqueous $NaHCO_3$ solution (3 mL) and extracted with chloroform, and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and ^1H NMR yield obtained based on the internal standard of 1,1,2,2-tetrachloroethane.

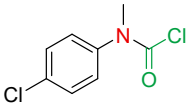
Fig. S2 Reaction setup of two chamber reaction vessel under sunlight. (a) before and (b) after irradiation.

Methyl(phenyl)carbamic chloride (**2a**):[1]



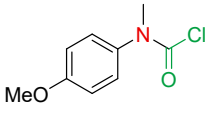
The title compound was prepared according to the general procedure. The mixture was purified by washing with methanol. Yield: 95%, colorless crystal. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.39 (m, 3H), 7.25 (d, *J* = 7.5 Hz, 2H), 3.38 (br, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 143.2, 129.6, 128.5, 127.4, 40.4.

N-(4-Chlorophenyl)-*N*-methylcarbamic chloride (**2b**):[2]



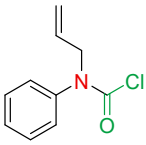
The title compound was prepared according to the general procedure. The mixture was purified by silica gel column chromatography. Yield: 86%, colorless crystal. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 11.2 Hz, 2H), 7.20 (d, *J* = 11.2 Hz, 2H), 3.36 (br, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 141.7, 134.5, 129.9, 128.8, 40.3.

N-(4-Methoxyphenyl)-*N*-methylcarbamic chloride (**2c**):[2]



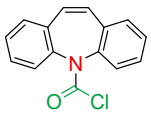
The title compound was prepared according to the general procedure. The mixture was purified by silica gel column chromatography. Two *N*-Me signals were observed as diastereomeric mixtures. Yield: 81%, colorless crystal. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.14 (m, 2H), 6.94–6.91 (m, 2H), 3.84 (s, 3H), 3.49 (minor), 3.34 (Major) (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 149.6, 136.2, 128.5, 114.7, 55.5, 40.5.

N-(4-Methoxyphenyl)-*N*-methylcarbamic chloride (**2d**):[3]



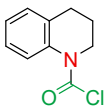
The title compound was prepared according to the general procedure. The mixture was purified by silica gel column chromatography. Yield: 77%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.40 (m, 3H), 7.22 (d, *J* = 11.6 Hz, 2H), 5.92–5.84 (m, 1H), 5.24–5.10 (m, 2H), 4.32–4.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 141.8, 131.1, 129.5, 128.6, 128.3, 119.6, 55.6.

5*H*-Dibenz[*b*,*f*]azepine-5-carbonyl chloride (**2e**):[4]



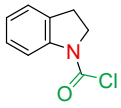
The title compound was prepared according to the general procedure. The mixture was purified by silica gel column chromatography. Yield: 66%, pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.45 (m, 4H), 7.42–7.39 (m, 4H), 7.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 138.5, 138.4, 133.2, 132.3, 129.5, 128.8, 128.6, 128.6, 128.3, 128.1, 127.6, 127.5, 127.4, 126.3.

3,4-Dihydroquinolin-1(2*H*)-carbonyl chloride (**2g**):[2b]



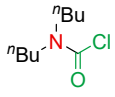
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$. The mixture was purified by silica gel column chromatography. Yield: 94%, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.63 (m, 1H), 7.26–7.13 (m, 3H), 3.94 (t, *J* = 8.8 Hz, 2H), 2.81 (t, *J* = 9.2 Hz, 2H), 2.04 (tt, *J* = 8.8, 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 137.6, 131.6, 128.7, 126.3, 125.9, 124.8, 48.8, 26.7, 23.8.

2,3-dihydro-1*H*-Indole-1-carbonyl chloride (**2h**):[5]



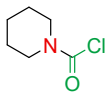
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$. The mixture was purified by silica gel column chromatography. Yield: 89%, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 10.4 Hz, 1H), 7.26–7.19 (m, 2H), 7.12 (d, *J* = 11.2 Hz, 1H), 4.25 (t, *J* = 11.2 Hz, 1H), 3.20 (t, *J* = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 141.3, 132.2, 127.9, 125.2, 116.4, 51.7, 27.2.

N,*N*-Dibutylcarbamic chloride (**2i**):[5]



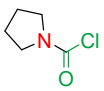
The title compound was prepared according to the general procedure. The mixture was purified by silica gel column chromatography. Yield: 99%, colorless oil. The two butyl groups were observed to be non-equivalent in the NMR measurement. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39 (t, *J* = 10.4 Hz, 2H), 3.34 (t, *J* = 10.4 Hz, 2H), 1.65–1.51 (m, 4H), 1.40–1.25 (m, 4H), 0.96 (t, *J* = 10.4 Hz, 3H), 0.94 (t, *J* = 10.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 51.0, 49.7, 30.5, 29.6, 19.9, 19.9, 13.8, 13.7.

1-Piperidinecarbonyl chloride (**2j**):[5]



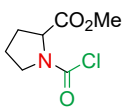
The title compound was prepared according to the general procedure with low amine concentration (0.02 M). Due to its low boiling point, the reaction was conducted in $CDCl_3$ and NMR was measured as is after washing water. NMR Yield: 58%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.68–3.66 (m, 2H), 3.60–3.58 (m, 2H), 1.67–1.60 (m, 6H).

1-Pyrrolidinecarbonyl chloride (**2k**):[2b]



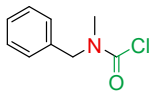
The title compound was prepared according to the general procedure with low amine concentration (0.02 M). Due to its low boiling point, the reaction was conducted in $CDCl_3$ and NMR was measured as is after washing water. NMR Yield: 65%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.59 (t, *J* = 6.4 Hz, 2H), 3.51 (t, *J* = 6.4 Hz, 2H), 1.97 (t, *J* = 6.4 Hz, 2H), 1.97 (t, *J* = 6.4 Hz, 2H).

1-(Chlorocarbonyl)proline methyl ester (**2l**):[6]



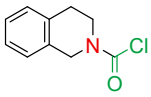
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$ and DIPEA (5 equiv.). The mixture was purified by silica gel column chromatography. Yield: 99%, colorless oil. (diastereomer mixture; Major/minor = 60/40). Major; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.48 (dd, *J* = 4.0, 8.8 Hz, 1H), 3.84–3.80 (m, 1H), 3.76 (s, 3H), 3.75–3.65 (m, 1H), 2.40–2.25 (m, 1H), 2.18–2.08 (m, 1H), 2.04–1.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 147.6, 60.7, 52.7, 50.6, 30.3, 23.6. minor; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.59 (dd, *J* = 4.0, 8.8 Hz, 1H), 3.80 (s, 3H), 3.71–3.64 (m, 1H), 3.60–3.56 (m, 1H), 2.35–2.25 (m, 2H), 2.18–2.09 (m, 1H), 2.05–1.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 146.7, 62.4, 52.8, 49.2, 30.3, 23.6.

N-Methyl-*N*-(phenylmethyl)carbamic chloride (**2m**):[5]



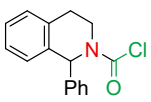
The title compound was prepared according to the general procedure. The mixture was purified by silica gel column chromatography. Yield: 95%, brown oil. (diastereomer mixture; Major/minor = 57/43). Major; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.32 (m, 3H), 7.29–7.26 (m, 2H), 4.59 (s, 2H), 3,07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 135.3, 128.9, 128.1, 128.1, 54.4, 37.9. minor; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.32 (m, 3H), 7.29–7.26 (m, 2H), 4.72 (s, 2H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 135.1, 128.9, 128.1, 127.1, 56.3, 36.4.

3,4-Dihydro-2(1*H*)-isoquinolinecarbonyl chloride (**2n**):[5]



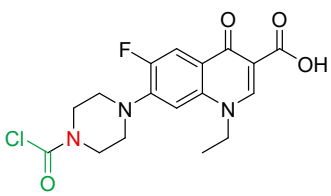
The title compound was prepared according to the general procedure with low amine concentration (0.02 M). The mixture was purified by silica gel column chromatography. Yield: 89%, pale yellow crystal. (diastereomer mixture; Major/minor = 56/44). Major; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.12 (m, 4H), 4.76 (s, 2H), 3.92 (t, *J* = 6.0 Hz, 2H), 2.96 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 134.0, 132.0, 128.5, 127.2, 126.8, 126.3, 48.0, 46.5, 28.9. minor; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.12 (m, 4H), 4.84 (s, 2H), 3.85 (t, *J* = 6.0 Hz, 2H), 2.94 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 133.9, 131.7, 128.7, 127.2, 126.8, 126.2, 50.0, 44.3, 28.5.

1-phenyl-1,2,3,4-tetrahydroisoquinolinecarbonylchloride (**2o**):[7]



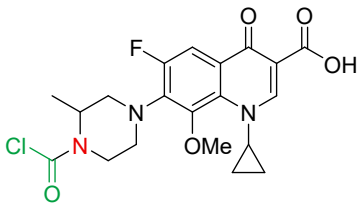
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$. The mixture was purified by silica gel column chromatography. Yield: 98%, colorless crystal. (diastereomer mixture; Major/minor = 73/27). Major; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.25 (m, 3H), 7.24–7.18 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.60 (s, 1H), 4.24–4.18 (m, 1H), 3.51–3.45 (m, 1H), 3.11–3.01 (m, 1H), 2.89–2.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 140.7, 134.1, 133.9, 128.9, 128.6, 128.5, 128.5, 128.1, 127.6, 126.6, 60.0, 43.0, 28.5. minor; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.25 (m, 3H), 7.24–7.18 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.57 (s, 1H), 4.24–4.18 (m, 1H), 3.40–3.31 (m, 1H), 3.11–3.01 (m, 1H), 2.90–2.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 140.3, 134.3, 134.0, 129.0, 128.5, 128.5, 128.3, 127.9, 127.8, 126.5, 62.4, 41.3, 27.8; MS (GC–EI): $C_{16}H_{14}ClNO$ $[M+Na]^+$: 294.07.

N-chlorocarbonyl norfloxacin (**2p**):



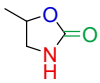
The title compound was prepared according to the general procedure with low amine concentration (0.05 M) and 4 equivalents of $ClO_2^{\bullet}$. Due to its low solubility, the reaction was conducted in $CDCl_3$ and NMR was measured as is after washing water and only ^{1}H NMR and IR data were obtained. Yield: 88%, white solid. Mp: 182.7 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.13 (d, *J* = 12.8 Hz, 1H), 6.87 (d, *J* = 6.8 Hz, 1H), 4.33 (q, *J* = 7.3 Hz, 4H), 4.01-3.98 (m, 2H), 3.91-3.89 (m, 2H), 3.38-3.35 (m, 4H), 1.60 (t, *J* = 7.4 Hz, 3H); IR (ATR/cm^{-1}) 1726 (NCOCl).

N-chlorocarbonyl gatifloxacin (**2q**):



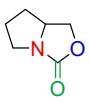
The title compound was prepared according to the general procedure with low amine concentration (0.05 M) and 4 equivalents of $ClO_2^{\bullet}$. The mixture was purified by washing with water. Yield: 77%, white solid. Mp: 179.1 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 7.87 (d, *J* = 16.0 Hz, 1H), 4.63 (m, 1H), 4.25 (d, *J* = 18.4 Hz, 1H), 4.05 (ddq, *J* = 9.2, 10.4, 14.8 Hz, 1H), 3.78 (s, 3H), 3.75–3.50 (m, 1H), 3.56 (d, *J* = 16.4 Hz, 2H), 3.39 (d, *J* = 16.4 Hz, 2H), 1.48 (d, *J* = 9.2 Hz, 3H), 1.29–1.20 (m, 2H), 1.08–0.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9 (d, $J_{C\text{-}F}$ = 2.8 Hz), 166.5, 156.0 (d, $J_{C\text{-}F}$ = 249.8 Hz), 150.2, 148.7, 145.8 (d, $J_{C\text{-}F}$ = 3.8 Hz), 139.4 (d, $J_{C\text{-}F}$ = 11.5 Hz), 134.0, 122.6 (d, $J_{C\text{-}F}$ = 9.5 Hz), 108.3 (d, $J_{C\text{-}F}$ = 22.9), 107.9, 63.6, 55.0, 52.9, 50.6, 44.4, 40.4, 16.0, 9.7, 9.6. IR (ATR/cm^{-1}) 1730 (NCOCl). MS (ESI-TOF): Calculated for $C_{20}H_{21}ClFN_3O_5Na$ $[M+Na]^+$: 460.10460, found: 460.10283.

5-Methyl-2-oxazolidinone (**4a**):[8]



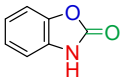
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$. The mixture was purified by silica gel column chromatography. Yield: 80%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40 (br, 1H), 4.51 (dd, *J* = 6.4, 6.4 Hz, 1H), 4.02 (ddq, *J* = 4.8, 5.2, 6.4 Hz, 2H), 3.95 (dd, *J* = 4.8, 6.4 Hz, 2H), 1.30 (d, *J* = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 71.7, 48.3, 20.8.

Tetrahydro-1H,3H-pyrrolo[1,2-c]oxazol-3-one (**4b**):[9]



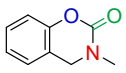
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$. The mixture was purified by silica gel column chromatography. Yield: 72%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.51 (dd, *J* = 7.6, 8.8 Hz, 1H), 4.17 (dd, *J* = 3.6, 8.8 Hz, 1H), 3.93–3.86 (m, 1H), 3.65 (ddd, *J* = 7.6, 7.6, 11.6 Hz, 1H), 3.18 (ddd, *J* = 4.8, 10.0, 11.6 Hz, 1H), 2.12–2.04 (m, 2H), 2.00–1.88 (m, 1H), 1.51–1.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 67.8, 59.5, 45.8, 30.7, 25.7.

2(3*H*)-Benzoxazolone (**5**):[10]



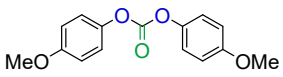
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$. The mixture was purified by silica gel column chromatography. Yield: 90%, colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (br, 1H), 7.26–7.17 (m, 1H), 7.16–7.10 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 143.9, 129.3, 124.2, 122.8, 110.2, 110.0.

3,4-Dihydro-3-methyl-2*H*-1,3-benzoxazin-2-one (**6**):[5]



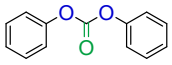
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$. The mixture was purified by washing with water. Yield: 90%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.24 (m, 1H), 7.11–7.09 (m, 2H), 7.03 (d, *J* = 4.8 Hz, 1H), 4.48 (s, 2H), 3.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 149.8, 129.0, 125.3, 124.2, 117.0, 116.3, 49.5, 36.4.

Bis(4-methoxyphenyl) carbonate (**8a**):[11]



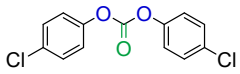
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$ and DIPEA (5 equiv.). The mixture was purified by washing with methanol. Yield: 99%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 9.2 Hz, 4H), 6.91 (d, *J* = 9.2 Hz, 4H), 3.81 (s, 6H).

Diphenyl carbonate (**8b**):[11]



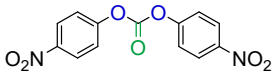
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$ and DIPEA (5 equiv.). The mixture was purified by washing with methanol. Yield: 98%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.40 (m, 4H), 7.30–7.26 (m, 6H).

Bis(4-chlorophenyl) carbonate (**8c**):[11]



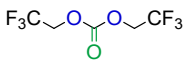
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$ and DIPEA (5 equiv.). The mixture was purified by washing with methanol. Yield: 99%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.37 (m, 2H), 7.26–7.20 (m, 2H).

Bis(4-nitrophenyl) carbonate (**8d**):[11]



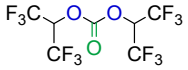
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$ and DIPEA (5 equiv.). The mixture was purified by washing with methanol. Yield: 97%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 9.2 Hz, 4H), 7.51 (d, *J* = 9.2 Hz, 4H).

Bis(2,2,2-trifluoroethyl) carbonate (**8e**):[11]



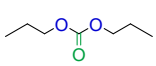
Due to its low boiling point, the reaction was conducted in $CDCl_3$ and NMR was measured just after the reaction. NMR Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60 (q, $J_{H\text{-}F}$ = 7.6 Hz).

Bis(1,1,1,3,3,3-hexafluoropropan-2-yl) carbonate (**8f**):[11]



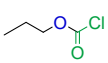
Due to its low boiling point, the reaction was conducted in $CDCl_3$ and NMR was measured just after the reaction. NMR Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.60 (sep, $J_{H\text{-}F}$ = 5.2 Hz, 2H).

Dipropyl carbonate (**8g**):[5]



The title compound was prepared according to the general procedure with high alcohol concentration (0.4 M) and 2 equivalents of $ClO_2^{\bullet}$. Pyridine was used as base. Due to its low boiling point, the reaction was conducted in $CDCl_3$ and NMR was measured as is after washing water. NMR Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.10 (t, *J* = 8.8 Hz, 2H), 1.70 (tq, *J* = 8.8, 9.6 Hz, 2H), 0.97 (t, *J* = 9.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 64.4, 31.0, 10.2.

Propyl chloroformate (**8g'**):[11]

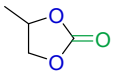


The title compound was prepared according to the general procedure with low alcohol concentration (0.02 M) and 8 equivalents of $ClO_2^{\bullet}$. 2,6-Lutidine was used as base. Due to its low boiling point, the reaction was conducted in $CDCl_3$ and NMR was measured just after the reaction. NMR Yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.29 (t, *J* = 9.2 Hz, 2H), 1.77 (tq, *J* = 9.2, 9.6 Hz, 2H), 1.00 (t, *J* = 9.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 73.8, 21.3, 10.0.

1,3-Dioxolan-2-one (**9a**):[5]

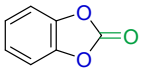
The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$ and DIPEA (5 equiv.). The mixture was purified by washing with hexane. Yield: 99%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.54 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 64.6.

4-Methyl-1,3-dioxolan-2-one (**9b**):[5]



The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$ and DIPEA (5 equiv.). The mixture was purified by washing with hexane. Yield: 99%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.86 (ddq, *J* = 6.4, 7.2, 8.4 Hz, 1H), 4.56 (dd, *J* = 8.4, 8.4 Hz, 1H), 4.03 (dd, *J* = 7.2, 8.4 Hz, 1H), 1.50 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 73.6, 70.7, 19.5.

Benzo[d][1,3]dioxol-2-one (**10**):[11]



The title compound was prepared according to the general procedure with 4 equivalents of $ClO_2^{\bullet}$ and DIPEA (5 equiv.). The mixture was purified by washing with methanol. Yield: 90%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 143.2, 124.9, 110.5.

3. Detection of in situ generated phosgene

Sodium chlorite (114 mg, 1.0 mmol: 0.8 mmol as $ClO_2^{\bullet}$) in water (5.7 mL) with 35% HCl (57 µL) was added in A chamber, $CDCl_3$ (2 mL) was added in B chamber. After closing the cap, the reaction vessel was irradiated with 405 nm LED lamp (90 mW/cm^2) at room temperature. After 20 min, 600 µL of $CDCl_3$ solution was taken out and ^{13}C NMR measurement was conducted directly. As shown in Figure S3, a signal of 143 ppm derived from phosgene was observed, suggesting *in situ* generation of phosgene by the oxygenation of chloroform-*d*.

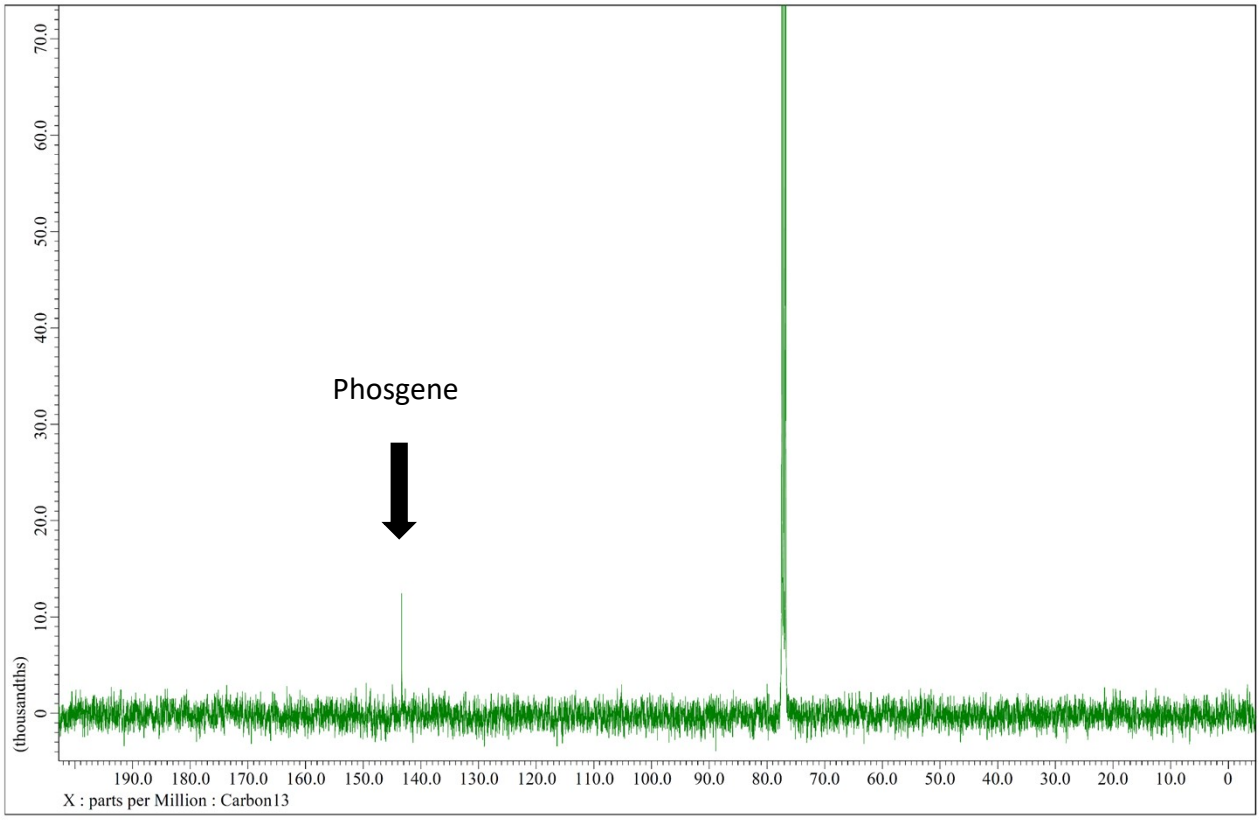
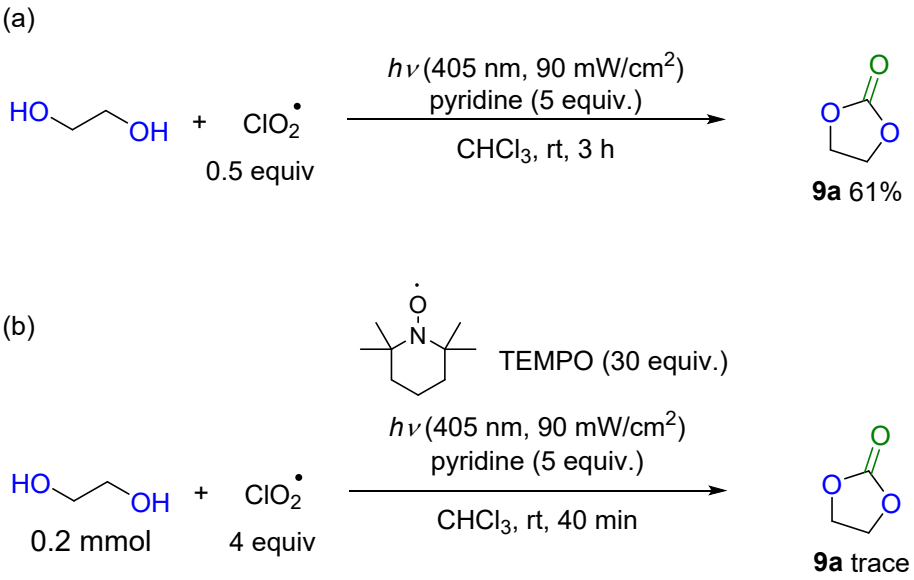


Fig. S3 ^{13}C NMR spectrum (100 MHz) of $CDCl_3$ upon photoirradiation with a 405 nm LED lamp for 20 min under $ClO_2^{\bullet}$ atmosphere at room temperature.

4. Mechanistic Study



Scheme S1 Mechanistic experiment.

(a) Sodium chlorite (28.5 mg, 0.25 mmol: 0.2 mmol as $ClO_2^{\bullet}$) in water (5.7 mL) with 35% HCl (14 µL) was added in chamber A, solution of ethylene glycol (0.4 mmol) and pyridine (161 µL, 2.0 mmol) in $CHCl_3$ (4 mL) was added in chamber B (Scheme S2). After closing the cap, the reaction vessel was irradiated with 405 nm LED lamp (90 mW/cm^2) for 3 h at room temperature. The reaction mixture (B chamber) was quenched with a saturated aqueous $NaHCO_3$ solution (3 mL) and extracted with chloroform, and the organic layer was dried over anhydrous Na_2SO_4. After the solvent was evaporated, the residue was dissolved in chloroform-*d* and the yield was determined by ^{1}H NMR measurement using 1,1,2,2-tetrachloroethane as an internal standard.

(b) Sodium chlorite (114 mg, 1.0 mmol: 0.8 mmol as $ClO_2^{\bullet}$) in water (5.7 mL) with 35% HCl (57 µL) was added in chamber A, solution of ethylene glycol (0.2 mmol), pyridine (81 µL, 1.0 mmol), and TEMPO (938 mg, 6 mmol) in $CHCl_3$ (2 mL) was added in chamber B (Scheme S2). After closing the cap, the reaction vessel was irradiated with 405 nm LED lamp (90 mW/cm^2) for 40 min at room temperature. The reaction mixture (B chamber) was quenched with a saturated aqueous $NaHCO_3$ solution (3 mL) and extracted with chloroform, and the organic layer was dried over anhydrous Na_2SO_4. After the solvent was evaporated, the residue was dissolved in chloroform-*d* and the yield was determined by ^{1}H NMR measurement using 1,1,2,2-tetrachloroethane as an internal standard.

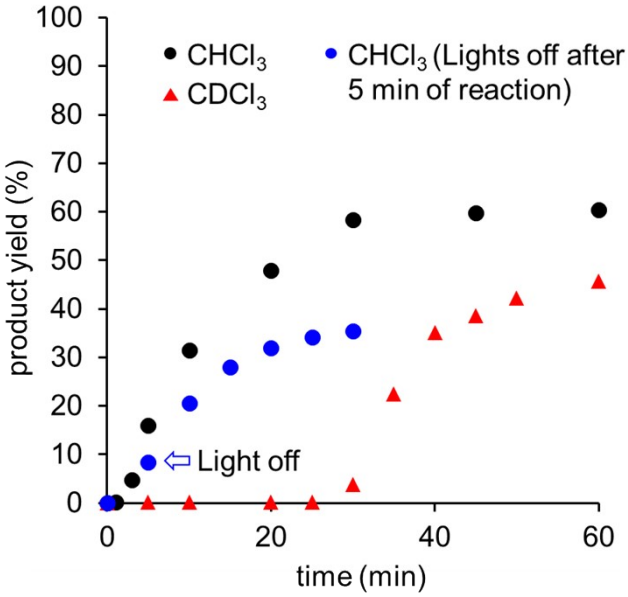


Fig. S4 Time course of product yield against reaction time for samples in $CHCl_3$ (black circle) and $CDCl_3$ (red triangle). Time course of product yield against reaction time for samples when light irradiation was turned off 5 min after the start of the reaction in $CHCl_3$ (blue circle). The reaction conditions: ethylene glycol 0.4 mmol (0.1 M), $ClO_2^{\bullet}$ (0.5 equiv.), and pyridine (5 equiv.) at room temperature. The product yields were determined using ^{1}H NMR.

Sodium chlorite (28.5 mg, 0.25 mmol: 0.2 mmol as $ClO_2^{\bullet}$) in water (5.7 mL) with 35% HCl (14 µL) was added in chamber A, solution of ethylene glycol (0.4 mmol) and pyridine (161 µL, 2.0 mmol) in $CHCl_3$ or $CDCl_3$ (4 mL) was added in chamber B. After closing the cap, the reaction vessel was irradiated with 405 nm LED lamp (90 mW/cm^2) at room temperature. The 100 µL of reaction mixture (B chamber) was taken with a syringe at every specified time. The reaction mixture was evaporated and the residue was dissolved in chloroform-*d* and the yield was determined from the ratio of starting material to product by ^{1}H NMR measurement.

Light off experiment: Sodium chlorite (28.5 mg, 0.25 mmol: 0.2 mmol as $ClO_2^{\bullet}$) in water (5.7 mL) with 35% HCl (14 µL) was added in chamber A, solution of ethylene glycol (0.4 mmol) and pyridine (161 µL, 2.0 mmol) in $CHCl_3$ (4 mL) was added in chamber B. After closing the cap, the reaction vessel was irradiated with 405 nm LED lamp (90 mW/cm^2) at room temperature. Light irradiation was turned off after 5 min and the chamber was wrapped in aluminum foil to shade the light. The 100 µL of reaction mixture (B chamber) was taken with a syringe at every specified time. The reaction mixture was evaporated and the residue was dissolved in chloroform-*d* and the yield was determined from the ratio of starting material to product by ^{1}H NMR measurement.

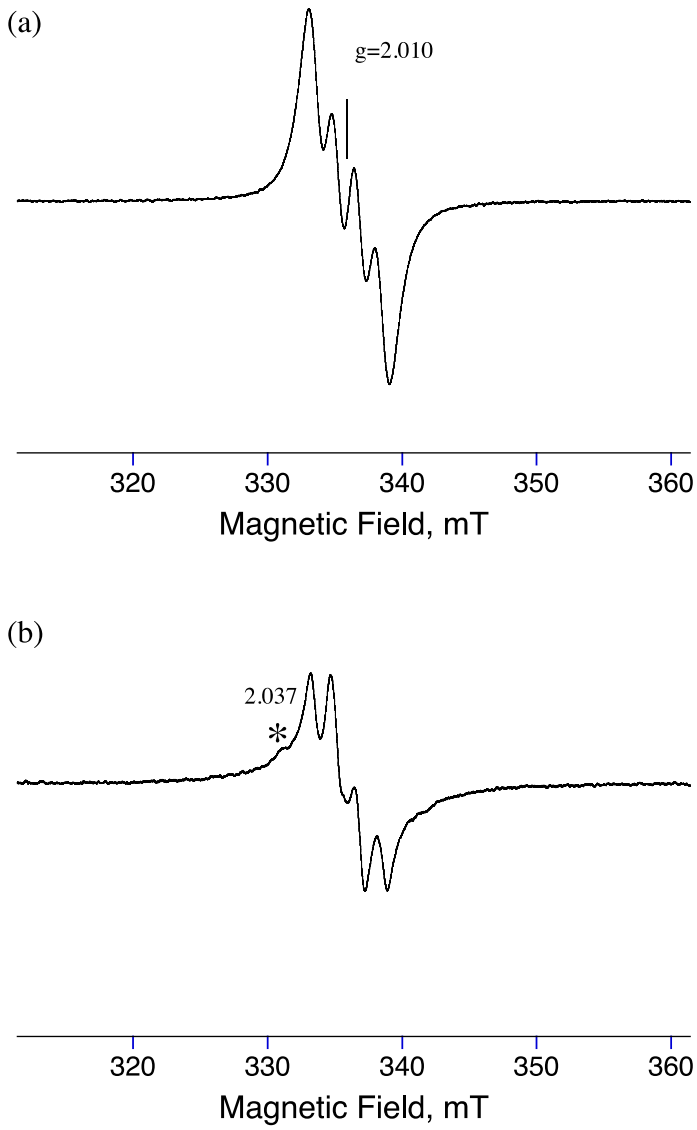


Fig. S5 ESR spectra of chloroform solutions containing $ClO_2^{\bullet}$ observed (a) in the dark and (b) under LED light irradiation (λ = 365 nm). Asterisk denotes signal due to $Cl_3COO^{\bullet}$ radical as a radical intermediate in photochemical reaction.

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