Supporting Information

Visible-light-promoted chloramination of olefins with 
N-chlorosulfonamide as both nitrogen and chlorine 
sources

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1. General Methods.

All reagents were used without further purification. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. $^1$H NMR (400 MHz) and $^{13}$C NMR (100MHz) were measured on a Bruker AVANCE III–400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumber (cm$^{-1}$).

2. General Procedure for Chloramination of Olefins.

A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and charged with N-chlorosulfonamide derivative 2 (0.15 mmol, 1.5 equiv) and Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.01 equiv). The flask was evacuated and backfilled with nitrogen for 3 times. Olefin 1 (0.1 mmol, 1.0 equiv) and DCE (2.0 mL, 0.20 M) were added with syringe under nitrogen. The mixture was then irradiated by white LED strips. After the reaction was complete (as judged by TLC analysis), the mixture was poured into a separatory funnel containing 20 mL of H$_2$O and 20 mL of CH$_2$Cl$_2$. The layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 $\times$ 20 mL). The combined organic layers were dried with Na$_2$SO$_4$ and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product 3.
3. Data for Compounds.

**N-(2-chloro-2-(4-methoxyphenyl)ethyl)-N,4-dimethylbenzenesulfonamide (3a):**
According to general procedure, 1a (0.1 mmol, 13.4 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3a (28.6 mg, 81%) as a yellow oil after purification on silica gel (hexanes: diethyl ether = 1:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2924.3, 2854.1, 1330.9, 1158.2, 709.3, 551.6. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (2H, d, $J$ = 8.3 Hz), 7.33–7.27 (4H, m), 6.91–6.86 (2H, m), 4.87 (1H, dd, $J$ = 8.8, 3.3 Hz), 3.80 (3H, s), 3.27 (1H, dd, $J$ = 14.1, 8.9 Hz), 2.97 (1H, dd, $J$ = 14.1, 3.5 Hz), 2.79 (3H, s), 2.41 (3H, s). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.3, 143.6, 134.2, 133.1, 129.8, 127.4, 127.2, 113.9, 71.7, 58.2, 55.3, 36.7, 21.5. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{17}$H$_{20}$ClNNaO$_3$S: 376.0750; found: 376.0746.

**N-(2-chloro-2-phenylethyl)-N-methylbenzenesulfonamide (3b):** According to general procedure, 1b (0.1 mmol, 10.4 mg), 2b (0.15 mmol, 30.6 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3b (21.6 mg, 70%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2973.5, 1446.0, 1340.5, 1163.6, 931.8, 690.3, 554.3. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.76 (2H, dd, $J$ = 5.3, 3.3 Hz), 7.62–7.56 (1H, m), 7.54–7.48 (2H, m), 7.43–7.31 (5H, m), 5.11 (1H, t, $J$ = 7.3 Hz), 3.61 (1H, dd, $J$ = 14.5, 7.4 Hz), 3.42 (1H, dd, $J$ = 14.5, 7.4 Hz), 2.65 (3H, s). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.6, 137.7, 132.8, 129.2, 128.9, 128.8, 127.5, 127.2, 61.2, 58.0, 36.9. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{15}$H$_{17}$ClNO$_2$S: 310.0669; found: 310.0662.
N-(2-chloro-2-phenylethyl)-4-methoxy-N-methylbenzenesulfonamide (3c): According to general procedure, 1b (0.1 mmol, 10.4 mg), 2c (0.15 mmol, 35.4 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3c (24.8 mg, 73%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2973.4, 1595.4, 1454.9, 1339.2, 1111.9, 931.4, 696.9, 553.1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73–7.64 (2H, m), 7.45–7.31 (5H, m), 7.00–6.93 (2H, m), 5.10 (1H, t, $J$ = 7.3 Hz), 3.86 (3H, s), 3.58 (1H, dd, $J$ = 14.5, 7.4 Hz), 3.40 (1H, dd, $J$ = 14.5, 7.4 Hz), 2.62 (3H, s). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.0, 138.7, 129.4, 129.3, 128.8, 128.8, 127.5, 114.3, 61.3, 58.0, 55.6, 36.9. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{16}$H$_{19}$ClNO$_3$S: 340.0774; found: 340.0771.

N-(2-chloro-2-phenylethyl)-N-methyl-4-nitrobenzenesulfonamide (3d): According to general procedure, 1b (0.1 mmol, 10.4 mg), 2d (0.15 mmol, 37.4 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3d (17.7 mg, 50%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2973.4, 1526.8, 1346.7, 1161.6, 933.5, 696.5, 530.4. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.38–8.31 (2H, m), 7.96–7.88 (2H, m), 7.44–7.33 (5H, m), 5.10 (1H, t, $J$ = 7.3 Hz), 3.66 (1H, dd, $J$ = 14.5, 7.6 Hz), 3.51 (1H, dd, $J$ = 14.5, 7.6 Hz), 2.73 (3H, s). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.1, 143.8, 138.1, 129.1, 128.9, 128.4, 127.4, 124.4, 60.9, 57.9, 36.7. HRMS (ESI) ([M+Na]$^+$) Calcd. for
N-(2-chloro-2-phenylethyl)-N,4-dimethylbenzenesulfonamide (3e): According to general procedure, 1b (0.1 mmol, 10.4 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3e (23.2 mg, 72%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2922.7, 1597.6, 13397, 1156.5, 717.7, 526.5. $^1$H NMR (400 MHz, CDCl$_3$) \(\delta\) 7.64 (2H, d, \(J = 8.3\) Hz), 7.38 (5H, m), 7.30 (2H, d, \(J = 8.1\) Hz), 5.11 (1H, t, \(J = 7.3\) Hz), 3.59 (1H, dd, \(J = 14.5, 7.3\) Hz), 3.40 (1H, dd, \(J = 14.5, 7.3\) Hz), 2.62 (3H, s), 2.42 (3H, s). $^{13}$C NMR (100 MHz, CDCl$_3$) \(\delta\) 143.6, 138.7, 134.7, 129.8, 128.8, 128.5, 127.5, 127.3, 61.3, 58.0, 36.9, 21.5. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{16}$H$_{19}$ClNO$_2$S: 324.0825; found: 324.0822.

N-(2-chloro-2-(p-tolyl)ethyl)-N-ethyl-4-methylbenzenesulfonamide (3g): According to general procedure, 1c (0.1 mmol, 11.8 mg), 2e (0.15 mmol, 35.0 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3g (27.7 mg, 79%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2923.7, 1597.7, 1514.2, 1335.4, 1154.4, 903.1, 716.5, 531.2. $^1$H NMR (400 MHz, CDCl$_3$) \(\delta\) 7.69–7.65 (2H, m), 7.31–7.26 (4H, m), 7.16 (2H, d, \(J = 7.9\) Hz), 5.14 (1H, t, \(J = 7.3\) Hz), 3.65 (1H, dd, \(J = 14.9, 7.3\) Hz), 3.51 (1H, dd, \(J = 14.9, 7.3\) Hz), 3.20 (1H, dq, \(J = 14.9, 7.3\) Hz), 2.95 (1H, dq, \(J = 14.4, 7.2\) Hz), 2.42 (3H, s), 2.35 (3H, s), 0.89 (3H, dd, \(J = 9.5, 4.8\) Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) \(\delta\) 143.4, 138.7, 136.7, 135.9, 129.7, 129.4, 127.4, 127.2, 61.3, 55.1, 44.3, 21.5, 21.2, 13.1. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{18}$H$_{23}$ClNO$_2$S: 352.1138; found:
N-(2-chloro-2-(p-tolyl)ethyl)-N-isopropyl-4-methylbenzenesulfonamide (3h): According to general procedure, 1c (0.1 mmol, 11.8 mg), 2f (0.15 mmol, 37.1 mg), Ir(ppy)₂(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3h (19.3 mg, 53%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm⁻¹) 2977.0, 2923.4, 1514.5, 1338.7, 1151.1, 851.1, 531.1. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (2H, d, J = 8.3 Hz), 7.35 (2H, d, J = 8.1 Hz), 7.29 (2H, d, J = 8.1 Hz), 7.17 (2H, d, J = 7.9 Hz), 5.43 (1H, t, J = 7.1 Hz), 3.90–3.82 (1H, m), 3.50 (1H, dd, J = 15.1, 7.2 Hz), 3.41 (1H, dd, J = 15.1, 7.2 Hz), 2.42 (3H, s), 2.35 (3H, s), 0.93 (3H, d, J = 6.8 Hz), 0.64 (3H, d, J = 6.8 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 138.5, 136.7, 136.2, 129.7, 129.2, 129.7, 127.4, 61.8, 51.3, 50.2, 21.5, 21.1, 20.5, 20.5. HRMS (ESI) ([M+H]+) Calcd. for C₁₉H₂₅ClNO₂S: 366.1295; found: 366.1289.

N-(2-chloro-2-(p-tolyl)ethyl)-N-cyclohexyl-4-methylbenzenesulfonamide (3i): According to general procedure, 1c (0.1 mmol, 11.8 mg), 2g (0.15 mmol, 43.1 mg), Ir(ppy)₂(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3i (19.8 mg, 49%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm⁻¹) 2923.4, 2848.5, 1516.3, 1333.3, 1152.0, 817.3, 706.2, 530.2. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (2H, d, J = 8.3 Hz), 7.34 (2H, d, J = 8.1 Hz), 7.28 (2H, d, J = 8.2 Hz), 7.17 (2H, d, J = 7.9 Hz), 5.39 (1H, t, J = 7.1 Hz), 3.59–3.46 (2H, m), 3.39 (1H, tt, J = 12.0, 3.5 Hz), 2.42 (3H, s), 2.35 (3H, s), 1.68 (1H, m), 1.57–1.43 (2H, m), 1.31 (2H, m), 1.20–1.06 (3H, m), 1.00–0.86 (2H, m). ¹³C

N-butyl-N-(2-chloro-2-(p-tolyl)ethyl)-4-methylbenzenesulfonamide (3j):
According to general procedure, 1c (0.1 mmol, 11.8 mg), 2h (0.15 mmol, 39.1 mg), Ir(ppy)₂(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3j (28.1 mg, 74%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm⁻¹) 2922.4, 1702.9, 1450.5, 1339.1, 1156.2, 879.3, 712.1, 550.7. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (2H, d, J = 8.3 Hz), 7.28 (4H, dd, J = 8.2, 2.0 Hz), 7.16 (2H, d, J = 7.9 Hz), 5.15 (1H, t, J = 7.3 Hz), 3.65 (1H, dd, J = 14.9, 7.4 Hz), 3.49 (1H, dd, J = 14.9, 7.4 Hz), 3.04 (1H, ddd, J = 15.1, 9.5, 5.9 Hz), 2.92–2.81 (1H, m), 2.42 (3H, s), 2.35 (3H, s), 1.34–1.16 (2H, m), 1.15–1.02 (2H, m), 0.77 (3H, t, J = 7.3 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 143.4, 138.7, 136.4, 136.0, 129.6, 129.3, 127.5, 127.3, 61.2, 55.9, 49.7, 29.9, 21.5, 21.1, 19.8, 13.5. HRMS (ESI) ([M+Na]+) Calcd. for C₂₀H₂₇ClNO₂S: 402.1270; found: 402.1266.

N-(2-chloro-2-(p-tolyl)ethyl)-N-(5-cyanopentyl)-4-methylbenzenesulfonamide (3k):
According to general procedure, 1c (0.1 mmol, 11.8 mg), 2i (0.15 mmol, 45.1 mg), Ir(ppy)₂(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3k (28.8 mg, 69%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm⁻¹) 2918.8, 1514.6, 1454.5, 1339.2, 1155.3, 815.3, 717.5, 551.4. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (2H, d, J = 8.3 Hz), 7.30 (4H, dd, J = 9.9, 8.2 Hz), 7.17 (2H, d, J = 7.9 Hz), 5.17 (1H, t, J = 7.2 Hz), 3.63 (1H, dd, J =
14.9, 7.1 Hz), 3.44 (1H, dd, J = 14.9, 7.1 Hz), 3.04–2.85 (2H, m), 2.43 (3H, s), 2.36 (3H, s), 2.23 (2H, t, J = 7.1 Hz), 1.55–1.42 (2H, m), 1.37–1.13 (4H, m). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.7, 138.8, 135.9, 135.8, 129.8, 129.4, 127.5, 127.3, 119.5, 61.2, 56.7, 50.0, 27.4, 25.5, 24.9, 21.5, 21.2, 16.9. HRMS (ESI) ([M+H$^+$]) Calcd. for C$_{22}$H$_{28}$ClN$_2$O$_2$S: 419.1560; found: 419.1556.

N-(2-chloro-2-(p-tolyl)ethyl)-N,4-dimethylbenzenesulfonamide (3l): According to general procedure, 1c (0.1 mmol, 11.8 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3l (28.1 mg, 83%) as a white solid after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2919.9, 1597.2, 1513.9, 1343.8, 1156.2, 702.6, 530.4. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (2H, d, J = 8.3 Hz), 7.29 (4H, dd, J = 8.3, 2.3 Hz), 7.17 (2H, d, J = 8.0 Hz), 5.07 (1H, t, J = 7.3 Hz), 3.57 (1H, dd, J = 14.4, 7.4 Hz), 3.40 (1H, dd, J = 14.4, 7.4 Hz), 2.63 (3H, s), 2.42 (3H, s), 2.35 (3H, s). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.6, 138.8, 135.7, 134.7, 129.7, 129.4, 127.4, 127.3, 61.2, 57.9, 36.9, 21.5, 21.2. HRMS (ESI) ([M+H$^+$]) Calcd. for C$_{17}$H$_{21}$ClNO$_2$: 338.0982; found: 338.0983.

N-(2-(4-(tert-butyl)phenyl)-2-chloroethyl)-N,4-dimethylbenzenesulfonamide (3m): According to general procedure, 1d (0.1 mmol, 16.0 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3m (31.4 mg, 83%) as a white solid after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2963.1, 1597.8, 1457.7, 1340.9, 1267.1, 1109.0, 689.9, 551.1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 (2H, d, J = 8.3 Hz), 7.41–7.36 (2H,
N-(2-([1,1′-biphenyl]-4-yl)-2-chloroethyl)-N,4-dimethylbenzenesulfonamide (3n):
According to general procedure, 1e (0.1 mmol, 18.0 mg), 2a (0.15 mmol, 32.8 mg),
Ir(ppy)_2(dtbbpy)PF_6 (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3n (27.9 mg, 70%) as a white solid after purification on silica gel (hexanes: EtOAc = 15:1).
Reaction time: 6 h. IR (neat, cm⁻¹) 2919.8, 1488.7, 1341.8, 1155.9, 836.2, 766.8, 541.4. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (2H, d, J = 8.3 Hz), 7.62–7.56 (4H, m), 7.50–7.42 (4H, m), 7.39–7.34 (1H, m), 7.30 (2H, d, J = 8.0 Hz), 5.16 (1H, t, J = 7.3 Hz), 3.61 (1H, dd, J = 14.5, 7.4 Hz), 3.46 (1H, dd, J = 14.5, 7.4 Hz), 2.67 (3H, s), 2.41 (3H, s). ¹³C NMR (100 MHz, CDCl₃) δ 143.6, 141.8, 140.2, 137.6, 134.7, 129.8, 128.8, 127.9, 127.6, 127.5, 127.1, 61.1, 57.9, 37.0, 21.5. HRMS (ESI) ([M+H]⁺) Calcd. for C_{22}H_{23}ClNO_2S: 400.1138; found: 400.1138.

N-(2-chloro-2-(4-fluorophenyl)ethyl)-N,4-dimethylbenzenesulfonamide (3o):
According to general procedure, 1f (0.1 mmol, 12.2 mg), 2a (0.15 mmol, 32.8 mg),
Ir(ppy)_2(dtbbpy)PF_6 (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3o (20.8 mg, 61%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1).
Reaction time: 6 h. IR (neat, cm⁻¹) 2923.3, 1604.5, 1510.2, 1454.8, 1339.0, 1157.0, 929.9, 704.6. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (2H, d, J = 8.3 Hz), 7.43–7.37 (2H,
m), 7.31 (2H, d, $J = 8.0$ Hz), 7.09–7.03 (2H, m), 5.10 (1H, t, $J = 7.4$ Hz), 3.55 (1H, dd, $J = 14.5, 7.1$ Hz), 3.38 (1H, dd, $J = 14.5, 7.1$ Hz), 2.63 (3H, s), 2.43 (3H, s). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.0, 161.5, 143.7, 134.6, 134.5, 129.8, 129.4, 129.3, 127.3, 115.8, 115.6, 60.4, 58.0, 37.0, 21.5. HRMS (ESI) ($[M+H]^+$) Calcd. for C$_{16}$H$_{18}$ClFNO$_2$S: 342.0731; found: 342.0727.

N-(2-chloro-2-(4-chlorophenyl)ethyl)-N,4-dimethylbenzenesulfonamide (3p): According to general procedure, 1g (0.1 mmol, 13.9 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3p (17.8 mg, 50%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2921.7, 1597.3, 1492.2, 1339.3, 1157.4, 1089.1, 930.4, 648.2, 531.5. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (2H, d, $J = 8.3$ Hz), 7.38–7.33 (4H, m), 7.31 (2H, d, $J = 8.1$ Hz), 5.08 (1H, t, $J = 7.4$ Hz), 3.54 (1H, dd, $J = 14.5, 7.1$ Hz), 3.38 (1H, dd, $J = 14.5, 7.1$ Hz), 2.63 (3H, s), 2.43 (3H, s). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.7, 137.2, 134.7, 134.5, 129.8, 129.4, 129.3, 127.3, 115.8, 115.6, 60.3, 57.9, 37.0, 21.5. HRMS (ESI) ($[M+H]^+$) Calcd. for C$_{16}$H$_{18}$Cl$_2$NO$_2$S: 358.0435; found: 358.0431.

N-(2-chloro-2-(m-tolyl)ethyl)-N,4-dimethylbenzenesulfonamide (3q): According to general procedure, 1h (0.1 mmol, 11.8 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3q (23.2 mg, 69%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2921.7, 1597.5, 1461.3, 1344.1, 1156.7, 1087.2, 701.9, 653.5. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (2H, d, $J = 8.3$ Hz), 7.30 (2H, d, $J = 8.0$ Hz), 7.26 (1H, t, $J = 4.0$ Hz), 7.20 (2H, d, $J = 3.3$ Hz), 7.14 (1H, d, $J = 7.2$ Hz),
5.06 (1H, t, J = 7.3 Hz), 3.58 (1H, dd, J = 14.5, 7.0 Hz), 3.41 (1H, dd, J = 14.5, 7.0 Hz), 2.65 (3H, s), 2.42 (3H, s), 2.35 (3H, s). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.6, 138.6, 138.5, 134.8, 129.7, 129.6, 128.7, 128.1, 127.3, 124.5, 61.4, 57.9, 36.9, 21.5, 21.3. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{17}$H$_{21}$ClNO$_2$S: 338.0982; found: 338.0988.

N-(2-chloro-2-mesitylethyl)-N,4-dimethylbenzenesulfonyamide (3r): According to general procedure, 1i (0.1 mmol, 14.6 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3r (28.5 mg, 78%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2919.9, 1453.1, 1339.8, 1157.8, 1088.7, 915.4, 726.7, 616.2. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (2H, d, J = 8.3 Hz), 7.29 (2H, d, J = 8.0 Hz), 6.85 (2H, s), 5.70–5.65 (1H, m), 3.71 (1H, dd, J = 14.7, 8.0 Hz), 3.62–3.56 (1H, m), 2.74 (3H, s), 2.45 (9H, d, J = 26.8 Hz), 2.26 (3H, s). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.5, 138.3, 134.8, 131.3, 129.7, 127.3, 58.2, 55.2, 37.0, 21.5, 20.9, 20.8. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{19}$H$_{24}$CINaO$_2$S: 388.1114; found: 388.1111.

N-((1R,2R)-1-chloro-2,3-dihydro-1H-inden-2-yl)-N,4-dimethylbenzenesulfonyamide (3s): According to general procedure, 1j (0.1 mmol, 11.6 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3s (26.8 mg, 80%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm$^{-1}$) 2922.2, 1597.3, 1462.3, 1339.0, 1156.1, 1088.1, 966.1, 744.5, 661.4. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (2H, d, J = 8.3 Hz), 7.34 (3H,
N-(2-chloro-4-phenylbutyl)-N,4-dimethylbenzenesulfonamide (3t): According to general procedure, 1k (0.1 mmol, 13.2 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)₄(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3t (18.6 mg, 53%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm⁻¹) 2921.6, 1598.0, 1454.3, 1339.9, 1159.3, 1088.8, 909.7, 736.2, 676.0. ^1H NMR (400 MHz, CDCl₃) δ 7.65 (2H, d, J = 8.3 Hz), 7.34–7.27 (4H, m), 7.24–7.18 (3H, m), 4.06–3.96 (1H, m), 3.40 (1H, dd, J = 14.1, 7.1 Hz), 3.10 (1H, dd, J = 14.1, 7.1 Hz), 2.96 (1H, ddd, J = 14.0, 9.3, 4.8 Hz), 2.76 (3H, s), 2.75 (1H, m), 2.43 (3H, s), 2.31–2.21 (1H, m), 1.96 (1H, m). ^13C NMR (100 MHz, CDCl₃) δ 143.6, 140.6, 134.3, 129.8, 128.5, 128.5, 127.4, 126.1, 59.4, 56.6, 36.8, 36.7, 32.1, 21.5. HRMS (ESI) ([M+H]^+) Calcd. for C₁₈H₂₃ClNO₂S: 352.1138; found: 352.1135.

8-chloro-9-(N,4-dimethylphenylsulfonamido)nonyl benzoate (3u): According to general procedure, 1l (0.1 mmol, 24.6 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)₄(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3u (24.6 mg,
53%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h.

IR (neat, cm⁻¹) 2923.5, 2859.0, 1703.7, 1597.7, 1450.5, 1339.4, 1156.4, 967.5, 712.1. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (2H, dd, J = 5.2, 3.3 Hz), 7.68 (2H, d, J = 8.3 Hz), 7.59–7.52 (1H, m), 7.44 (2H, dd, J = 10.6, 4.7 Hz), 7.33 (2H, d, J = 8.1 Hz), 4.32 (2H, t, J = 6.6 Hz), 4.06 (1H, m), 3.57 (1H, dd, J = 14.2, 6.8 Hz), 3.08 (1H, dd, J = 14.2, 6.8 Hz), 2.83 (3H, s), 2.44 (3H, s), 1.92 (1H, m), 1.71–1.52 (2H, m), 1.48–1.28 (3H, m), 0.93 (3H, t, J = 7.2 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 166.7, 143.6, 134.4, 132.8, 130.5, 129.8, 129.5, 128.3, 127.4, 65.0, 60.7, 56.8, 36.9, 35.2, 29.1, 28.9, 28.6, 26.0, 25.9, 21.5. HRMS (ESI) ([M+H]⁺) Calcd. for C_{24}H_{33}ClNO_4S: 466.1819; found: 466.1818.

N-(2-chlorohexyl)-N,4-dimethylbenzenesulfonamide (3v): According to general procedure, 1m (0.1 mmol, 8.4 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)_2(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3v (22.4 mg, 74%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h.

IR (neat, cm⁻¹) 2964.8, 2925.3, 2863.6, 1596.3, 1452.5, 1336.4, 1160.2, 942.8, 734.2. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (2H, d, J = 8.3 Hz), 7.33 (2H, d, J = 8.0 Hz), 4.10–4.02 (1H, m), 3.37 (1H, dd, J = 14.2, 6.7 Hz), 3.08 (1H, dd, J = 14.2, 6.7 Hz), 2.83 (3H, s), 2.44 (3H, s), 1.92 (1H, m), 1.71–1.52 (2H, m), 1.48–1.28 (3H, m), 0.93 (3H, t, J = 7.2 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 143.6, 134.4, 129.8, 127.4, 60.8, 56.8, 36.9, 35.0, 28.2, 22.1, 21.5, 13.9. HRMS (ESI) ([M+H]⁺) Calcd. for C_{14}H_{23}ClNO_2S: 304.1138; found: 304.1135.

N-(2-chlorooctyl)-N,4-dimethylbenzenesulfonamide (3w): According to general procedure, 1n (0.1 mmol, 11.2 mg), 2a (0.15 mmol, 32.8 mg), Ir(ppy)_2(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded 3w (21.3 mg, 64%) as a yellow oil...
after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm\(^{-1}\)) 2925.5, 2858.2, 1457.8, 1330.9, 1160.9, 1089.9, 918.8, 747.2, 530.7. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.68 (2H, d, \(J = 8.3\) Hz), 7.33 (2H, d, \(J = 8.0\) Hz), 4.10–4.01 (1H, m), 3.37 (1H, dd, \(J = 14.2, 6.7\) Hz), 3.08 (1H, dd, \(J = 14.2, 6.7\) Hz), 2.83 (3H, s), 2.44 (3H, s), 1.91 (1H, m), 1.70–1.52 (3H, m), 1.46–1.23 (6H, m), 0.89 (3H, t, \(J = 6.8\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.6, 134.4, 129.7, 127.4, 60.8, 56.8, 36.9, 35.3, 31.6, 28.7, 26.0, 22.5, 21.5, 14.0. HRMS (ESI) ([M+H]\(^+\)) Calcd. for C\(_{16}\)H\(_{27}\)ClNO\(_2\)S: 332.1451; found: 332.1448.
4. Control experiments

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
11 & \quad + \\
\text{Ts} & \quad \text{Cl} \\
2a & \quad \text{Cl} \\
\text{II} (1.0 \text{ mol } \%) & \quad \text{TEMPO (2.0 equiv)} \\
\text{DCE, visible light, rt} & \quad \text{Me} \\
\rightarrow & \quad \text{Me} \\
3l, 0\% & \quad \text{N} \\
\end{align*}
\]

**Figure S1.** TEMPO experiment

\[
\begin{align*}
\text{1H NMR Yield (\%)} & \quad 0 \quad 20 \quad 40 \quad 60 \quad 80 \quad 100 \quad 120 \quad 140 \\
\text{Time (min)} & \quad \text{light-off} \quad \text{light-off} \quad \text{light-off} \quad \text{light-off} \quad \text{light-on} \\
\end{align*}
\]

**Figure S2.** light off/on and time profile experiment.
5. NMR Spectra for All Compounds

![NMR Spectra for Compound 3a](image-url)
$^{1}\text{H NMR}$

$\text{CDCl}_3$, 400 MHz

$^{13}\text{C NMR}$

$\text{CDCl}_3$, 100 MHz
$^{1}H$ NMR
CDCl$_3$, 400 MHz

$^{13}C$ NMR
CDCl$_3$, 100 MHz
\[ ^1\text{H NMR} \]
\[ \text{CDCl}_3, 400 \text{ MHz} \]

\[ ^{13}\text{C NMR} \]
\[ \text{CDCl}_3, 100 \text{ MHz} \]