

Supporting Information

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

Qixue Qin, Daan Ren, Shouyun Yu*

*State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical
Engineering, Nanjing University, Nanjing 210093, China.*

E-mail: yushouyun@nju.edu.cn;

Homepage: <http://hysz.nju.edu.cn/yusy>

Table of Contents

1. General Methods.....	S2
2. General Procedure for Chloramination of Olefins.....	S2
3. Data for All Compounds.....	S3
4. Control Experiments.....	S14
5. NMR Spectra for All Compounds.....	S15

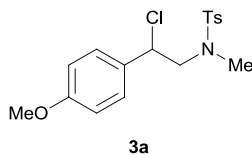
1. General Methods.

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. ^1H 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}).

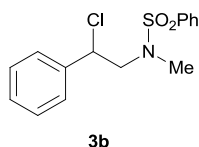
2. General Procedure for Chloramination of Olefins.

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 $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (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_2O and 20 mL of CH_2Cl_2 . The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 \times 20 mL). The combined organic layers were dried with Na_2SO_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**.

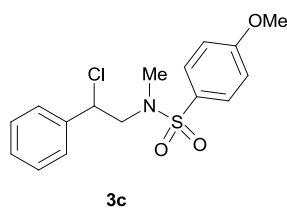
3. Data for Compounds.



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)PF₆ (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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) 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 C₁₇H₂₀ClNNaO₃S: 376.0750; found: 376.0746.

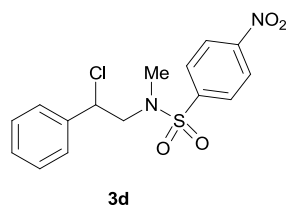


N-(2-chloro-2-phenylethyl)-N-methylbenzenesulfonamide (3b): According to general procedure, **1b** (0.1 mmol, 10.4 mg), **2b** (0.15 mmol, 30.6 mg), Ir(ppy)₂(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3b** (21.6 mg, 70%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm⁻¹) 2973.5, 1446.0, 1340.5, 1163.6, 931.8, 690.3, 554.3. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) 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 C₁₅H₁₇ClNO₂S: 310.0669; found: 310.0662.



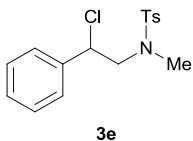
N-(2-chloro-2-phenylethyl)-4-methoxy-N-methylbenzenesulfonamide (3c):

According to general procedure, **1b** (0.1 mmol, 10.4 mg), **2c** (0.15 mmol, 35.4 mg), Ir(ppy)₂(dtbbpy)PF₆ (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. ¹H NMR (400 MHz, CDCl₃) δ 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). ¹³C NMR (100 MHz, CDCl₃) δ 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 C₁₆H₁₉ClNO₃S: 340.0774; found: 340.0771.

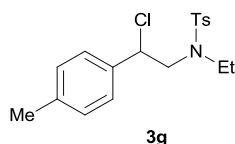


N-(2-chloro-2-phenylethyl)-N-methyl-4-nitrobenzenesulfonamide (3d): According to general procedure, **1b** (0.1 mmol, 10.4 mg), **2d** (0.15 mmol, 37.4 mg), Ir(ppy)₂(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3d** (17.7 mg, 50%) as a yellow oil after purification on silica gel (hexanes: 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. ¹H NMR (400 MHz, CDCl₃) δ 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). ¹³C NMR (100 MHz, CDCl₃) δ 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

C₁₅H₁₅ClN₂NaO₄S: 377.0339; found: 377.0335.

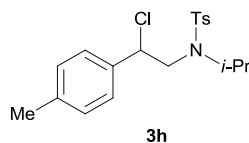


N-(2-chloro-2-phenylethyl)-N,4-dimethylbenzenesulfonamide (3e): According to general procedure, **1b** (0.1 mmol, 10.4 mg), **2a** (0.15 mmol, 32.8 mg), Ir(ppy)₂(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3e** (23.2 mg, 72%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm⁻¹) 2922.7, 1597.6, 13397, 1156.5, 717.7, 526.5. ¹H NMR (400 MHz, CDCl₃) δ 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). ¹³C NMR (100 MHz, CDCl₃) δ 143.6, 138.7, 134.7, 129.8, 128.8, 128.8, 127.5, 127.3, 61.3, 58.0, 36.9, 21.5. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₆H₁₉ClNO₂S: 324.0825; found: 324.0822.



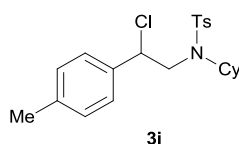
N-(2-chloro-2-(p-tolyl)ethyl)-N-ethyl-4-methylbenzenesulfonamide (3g): According to general procedure, **1c** (0.1 mmol, 11.8 mg), **2e** (0.15 mmol, 35.0 mg), Ir(ppy)₂(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3g** (27.7 mg, 79%) as a yellow oil after purification on silica gel (hexanes: 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. ¹H NMR (400 MHz, CDCl₃) δ 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). ¹³C NMR (100 MHz, CDCl₃) δ 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 C₁₈H₂₃ClNO₂S: 352.1138; found:

352.1135.



N-(2-chloro-2-(p-tolyl)ethyl)-N-isopropyl-4-methylbenzenesulfonamide (3h):

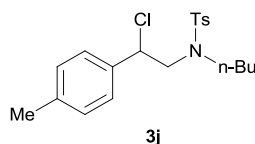
According to general procedure, **1c** (0.1 mmol, 11.8 mg), **2f** (0.15 mmol, 37.1 mg), Ir(ppy)₂(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3h** (19.3 mg, 53%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm⁻¹) 2977.0, 2923.4, 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, 127.7, 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):

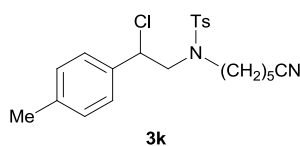
According to general procedure, **1c** (0.1 mmol, 11.8 mg), **2g** (0.15 mmol, 43.1 mg), Ir(ppy)₂(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3i** (19.8 mg, 49%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm⁻¹) 2923.4, 2848.5, 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

NMR (100 MHz, CDCl₃) δ 143.3, 138.5, 137.3, 136.1, 129.6, 129.2, 127.7, 127.3, 61.9, 58.9, 52.2, 31.4, 31.0, 26.1, 26.0, 25.2, 21.5, 21.1. HRMS (ESI) ([M+H]⁺) Calcd. for C₂₂H₂₉ClNO₂S: 406.1608; found: 406.1607.



N-butyl-N-(2-chloro-2-(p-tolyl)ethyl)-4-methylbenzenesulfonamide (3j):

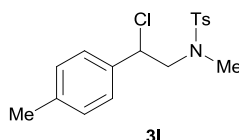
According to general procedure, **1c** (0.1 mmol, 11.8 mg), **2h** (0.15 mmol, 39.1 mg), Ir(ppy)₂(dtbbpy)PF₆ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3j** (28.1 mg, 74%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm⁻¹) 2922.4, 1702.9, 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.



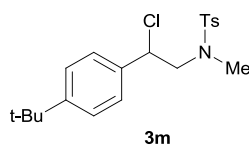
N-(2-chloro-2-(p-tolyl)ethyl)-N-(5-cyanopentyl)-4-methylbenzenesulfonamide

(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) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{22}\text{H}_{28}\text{ClN}_2\text{O}_2\text{S}$: 419.1560; found: 419.1556.

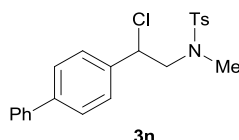


N-(2-chloro-2-(p-tolyl)ethyl)-N,4-dimethylbenzenesulfonamide (3l): According to general procedure, **1c** (0.1 mmol, 11.8 mg), **2a** (0.15 mmol, 32.8 mg), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3l** (28.1 mg, 83%) as a white solid after purification 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. ^1H 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) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{17}\text{H}_{21}\text{ClNO}_2\text{S}$: 338.0982; found: 338.0983.

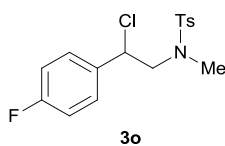


N-(2-(4-(tert-butyl)phenyl)-2-chloroethyl)-N,4-dimethylbenzenesulfonamide (3m): According to general procedure, **1d** (0.1 mmol, 16.0 mg), **2a** (0.15 mmol, 32.8 mg), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3m** (31.4 mg, 83%) as a white solid 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. ^1H NMR (400 MHz, CDCl_3) δ 7.65 (2H, d, $J = 8.3$ Hz), 7.41–7.36 (2H,

m), 7.35–7.28 (4H, m), 5.10 (1H, t, $J = 7.3$ Hz), 3.56 (1H, dd, $J = 14.5, 7.7$ Hz), 3.43 (1H, dd, $J = 14.5, 7.7$ Hz), 2.66 (3H, s), 2.42 (3H, s), 1.32 (9H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 152.0, 143.6, 135.6, 134.7, 129.7, 127.3, 127.1, 125.7, 61.3, 57.8, 36.9, 34.6, 31.2, 21.5. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{20}\text{H}_{27}\text{ClNO}_2\text{S}$: 380.1451; found: 380.1444.

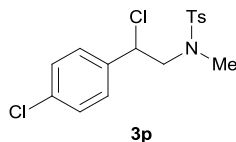


N-(2-((1,1'-biphenyl)-4-yl)-2-chloroethyl)-N,4-dimethylbenzenesulfonamide (3n): According to general procedure, **1e** (0.1 mmol, 18.0 mg), **2a** (0.15 mmol, 32.8 mg), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3n** (27.9 mg, 70%) as a white solid 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, CDCl_3) 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). ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 141.8, 140.2, 137.6, 134.7, 129.8, 128.8, 127.9, 127.6, 127.5, 127.3, 127.1, 61.1, 57.9, 37.0, 21.5. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{22}\text{H}_{23}\text{ClNO}_2\text{S}$: 400.1138; found: 400.1138.



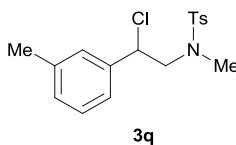
N-(2-chloro-2-(4-fluorophenyl)ethyl)-N,4-dimethylbenzenesulfonamide (3o): According to general procedure, **1f** (0.1 mmol, 12.2 mg), **2a** (0.15 mmol, 32.8 mg), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3o** (20.8 mg, 61%) as a yellow oil after 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, CDCl_3) 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) δ 164.0, 161.5, 143.7, 134.6, 134.5, 134.5, 129.8, 129.4, 129.3, 127.3, 115.8, 115.6, 60.4, 58.0, 37.0, 21.5. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{16}\text{H}_{18}\text{ClFNO}_2\text{S}$: 342.0731; found: 342.0727.



N-(2-chloro-2-(4-chlorophenyl)ethyl)-N,4-dimethylbenzenesulfonamide (3p):

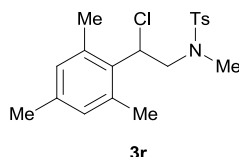
According to general procedure, **1g** (0.1 mmol, 13.9 mg), **2a** (0.15 mmol, 32.8 mg), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3p** (17.8 mg, 50%) as a yellow oil after purification on silica gel (hexanes: EtOAc = 15:1). Reaction time: 6 h. IR (neat, cm^{-1}) 2921.7, 1597.3, 1492.2, 1339.3, 1157.4, 1089.1, 930.4, 648.2, 531.5. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 143.7, 137.2, 134.7, 134.5, 129.8, 129.0, 128.9, 127.3, 60.3, 57.9, 37.0, 21.5. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{NO}_2\text{S}$: 358.0435; found: 358.0431.



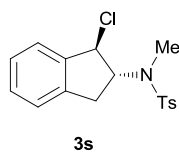
N-(2-chloro-2-(m-tolyl)ethyl)-N,4-dimethylbenzenesulfonamide (3q):

According to general procedure, **1h** (0.1 mmol, 11.8 mg), **2a** (0.15 mmol, 32.8 mg), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (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. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{17}\text{H}_{21}\text{ClNO}_2\text{S}$: 338.0982; found: 338.0988.

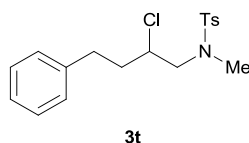


N-(2-chloro-2-mesitylethyl)-N,4-dimethylbenzenesulfonamide (3r): According to general procedure, **1i** (0.1 mmol, 14.6 mg), **2a** (0.15 mmol, 32.8 mg), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3r** (28.5 mg, 78%) as a yellow oil after purification 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. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{19}\text{H}_{24}\text{ClNNaO}_2\text{S}$: 388.1114; found: 388.1111.

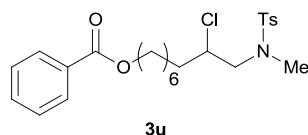


N-((1R,2R)-1-chloro-2,3-dihydro-1H-inden-2-yl)-N,4-dimethylbenzenesulfonamide (3s): According to general procedure, **1j** (0.1 mmol, 11.6 mg), **2a** (0.15 mmol, 32.8 mg), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3s** (26.8 mg, 80%) as a yellow 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. ^1H NMR (400 MHz, CDCl_3) δ 7.79 (2H, d, $J = 8.3$ Hz), 7.34 (3H,

d, $J = 8.2$ Hz), 7.29–7.23 (2H, m), 7.20–7.15 (1H, m), 5.09 (1H, d, $J = 5.6$ Hz), 4.94 (1H, dt, $J = 8.2, 6.2$ Hz), 3.19 (1H, dd, $J = 16.4, 8.2$ Hz), 2.83 (1H, dd, $J = 16.4, 8.2$ Hz), 2.68 (3H, s), 2.46 (3H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 140.0, 139.5, 136.2, 129.7, 129.3, 127.7, 127.5, 125.0, 124.6, 66.8, 62.6, 33.2, 29.7, 21.6. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{17}\text{H}_{19}\text{ClNO}_2\text{S}$: 336.0825; found: 336.0823.

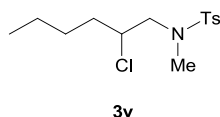


N-(2-chloro-4-phenylbutyl)-N,4-dimethylbenzenesulfonamide (3t): According to general procedure, **1k** (0.1 mmol, 13.2 mg), **2a** (0.15 mmol, 32.8 mg), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3t** (18.6 mg, 53%) as a yellow oil after purification 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, CDCl_3) 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). ^{13}C NMR (100 MHz, CDCl_3) 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) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{18}\text{H}_{23}\text{ClNO}_2\text{S}$: 352.1138; found: 352.1135.

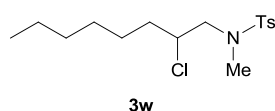


8-chloro-9-(N,4-dimethylphenylsulfonamido)nonyl benzoate (3u): According to general procedure, **1l** (0.1 mmol, 24.6 mg), **2a** (0.15 mmol, 32.8 mg), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (0.001 mmol, 0.9 mg) in DCE (2.0 mL) afforded **3u** (24.6 mg,

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, CDCl_3) 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), 3.37 (1H, dd, $J = 14.2, 6.8$ Hz), 3.08 (1H, dd, $J = 14.2, 6.8$ Hz), 2.83 (3H, s), 2.43 (3H, s), 1.98–1.86 (1H, m), 1.82–1.73 (2H, m), 1.70–1.55 (2H, m), 1.52–1.29 (7H, m). ^{13}C NMR (100 MHz, CDCl_3) 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) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{24}\text{H}_{33}\text{ClNO}_4\text{S}$: 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), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (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, CDCl_3) 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). ^{13}C NMR (100 MHz, CDCl_3) 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) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{14}\text{H}_{23}\text{ClNO}_2\text{S}$: 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), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (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. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{16}\text{H}_{27}\text{ClNO}_2\text{S}$: 332.1451; found: 332.1448.

4. Control experiments

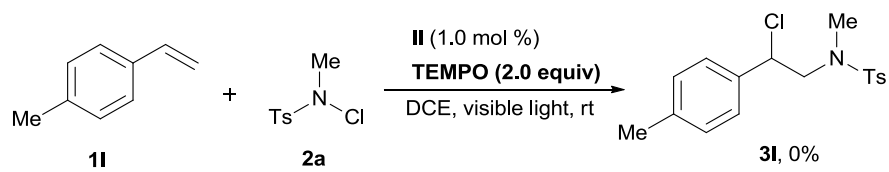


Figure S1. TEMPO experiment

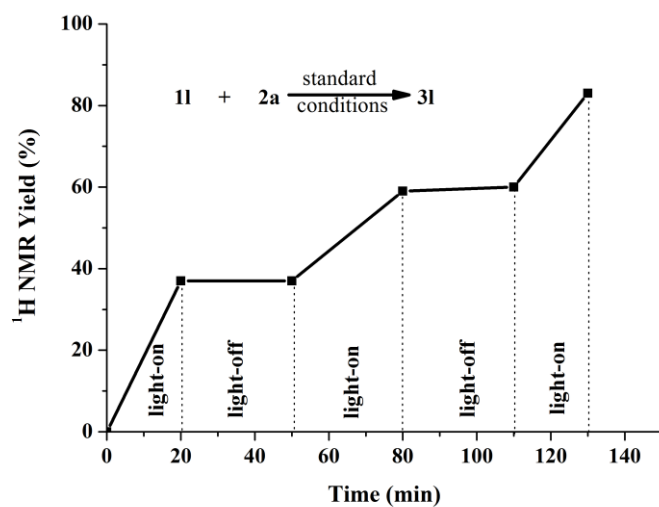


Figure S2. light off/on and time profile experiment.

5. NMR Spectra for All Compounds

