

Supporting Information

Visible-light initiated direct oxysulfonylation of alkenes with sulfinic acids leading to β -ketosulfones

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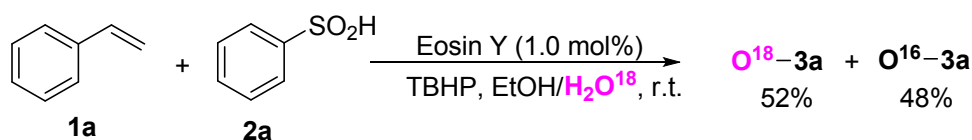
General experimental procedures

All reagents and solvents were obtained from commercial suppliers and used without further purification. TBHP= *tert*-butyl hydroperoxide solution 5.5M in decane. Eosin Y (spirit soluble, 99% dye content) was purchased from Sigma Aldrich. Flash chromatography was performed on silica gel (200 ~ 300 mesh). ¹H and ¹³C NMR data were recorded at 500 and 125 MHz on a BRUKER 500 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm), coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded using tetramethylsilane (TMS) in the solvent of CDCl₃ as the internal standard (¹H NMR: TMS at 0.00 ppm, CDCl₃ at 7.28 ppm; ¹³C NMR: CDCl₃ at 77.0 ppm). Mass analyses and HRMS were obtained by ESI on a TOF mass analyzer.

General procedure for synthesis of substituted β -ketosulfones

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with styrene (0.2 mmol), benzenesulfinic acid (0.3 mmol), Eosin Y (1.3 mg, 1 mol%). The tube was evacuated and backfilled with nitrogen (three times). TBHP (0.6 mmol, 3.0 equiv) in 2 mL of EtOH/H₂O ($v_1/v_2 = 4:1$) were added by syringe under nitrogen. The solution was stirred at room temperature with the irradiation of a 11 W LED lamp for 24 h. Upon completion of the reaction, the mixture was diluted with EtOAc, and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/10 to 1/3) to give the corresponding products **3**.

Experiments of investigations on the mechanism



A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with styrene **1a** (0.2 mmol), benzenesulfinic acid **2a** (0.3 mmol), Eosin Y (1.3 mg, 1 mol%). The tube was evacuated and backfilled with nitrogen (three times). TBHP (0.6 mmol, 3.0 equiv) in 2 mL of EtOH/H₂O¹⁸ ($v_1/v_2 = 4:1$) were added by syringe under nitrogen. The solution was stirred at room temperature with the irradiation of a 11 W

LED lamp for 24 h. Upon completion of the reaction, the mixture was diluted with EtOAc, and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel to give the corresponding products **3a**. The products were measured by HRMS.

The HRMS spectra of products was listed as bellow (Figure 1).

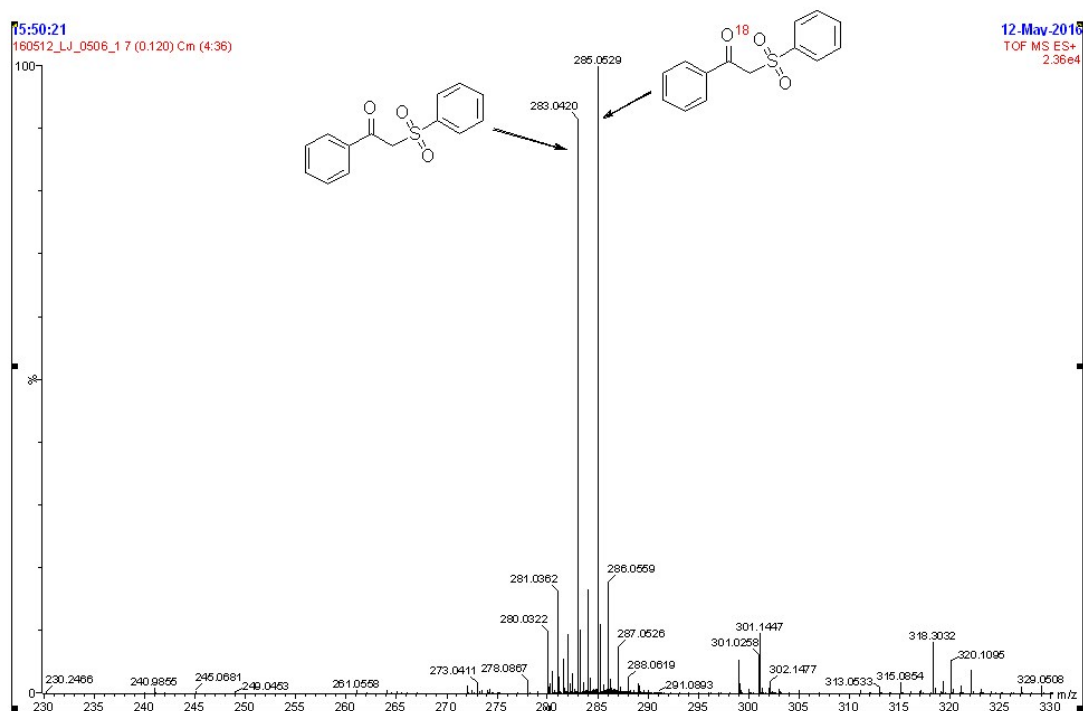


Figure S1. HRMS spectra of **3a**

The UV–vis spectra and Fluorescence spectra of the reaction solution

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. The sample was prepared by mixing Eosin Y, styrene, TBHP and benzene sulfinic acid with solvent ($V_{\text{ethanol}} : V_{\text{H}_2\text{O}} = 4:1$) ($M_{\text{[Eosin Y]}} = 1.0 \times 10^{-5} \text{ mol/L}$, $M_{\text{[styrene]}} = 1.0 \times 10^{-3} \text{ mol/L}$, $M_{\text{[TBHP]}} = 3.0 \times 10^{-3} \text{ mol/L}$, $M_{\text{[benzene sulfinic acid]}} = 1.5 \times 10^{-3} \text{ mol/L}$) in a light path quartz UV cuvette. The UV-visible spectroscopy indicated that the maximum absorption wavelength of reaction solution was found to be 531 nm. The absorption was collected and the result was listed in Figure S1.

The fluorescence emission intensity of reaction solution was recorded on a Fluoromax-4 spectrofluorimeter. The excitation wavelength was fixed at 500nm, and the emission wavelength was measured at 547nm. The sample was prepared by mixing Eosin Y, styrene, TBHP and benzene sulfinic acid with solvent ($V_{\text{ethanol}} : V_{\text{H}_2\text{O}} = 4:1$) ($M_{\text{[Eosin Y]}} = 2.0 \times 10^{-7} \text{ mol/L}$, $M_{\text{[styrene]}} = 2.0 \times 10^{-5} \text{ mol/L}$, $M_{\text{[TBHP]}} = 6.0 \times 10^{-5} \text{ mol/L}$, $M_{\text{[benzene sulfinic acid]}} = 3.0 \times 10^{-5} \text{ mol/L}$) in a light path quartz fluorescence cuvette. The emission intensity was collected and the result was listed in Figure S2.

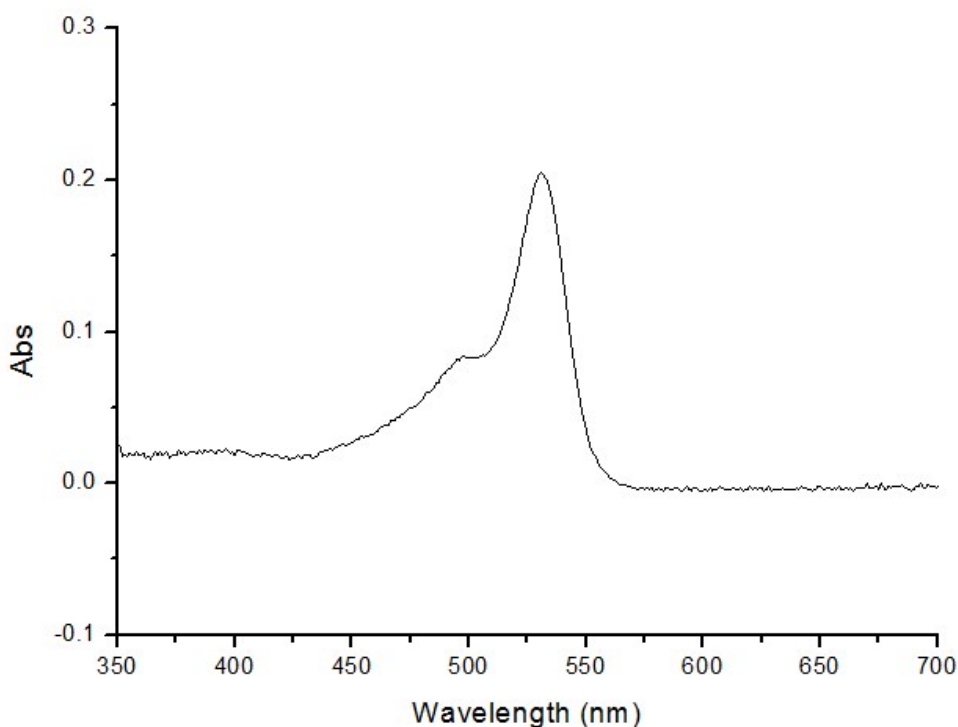


Figure S2. UV-vis spectra of the photooxysulfonylation reaction mixture.

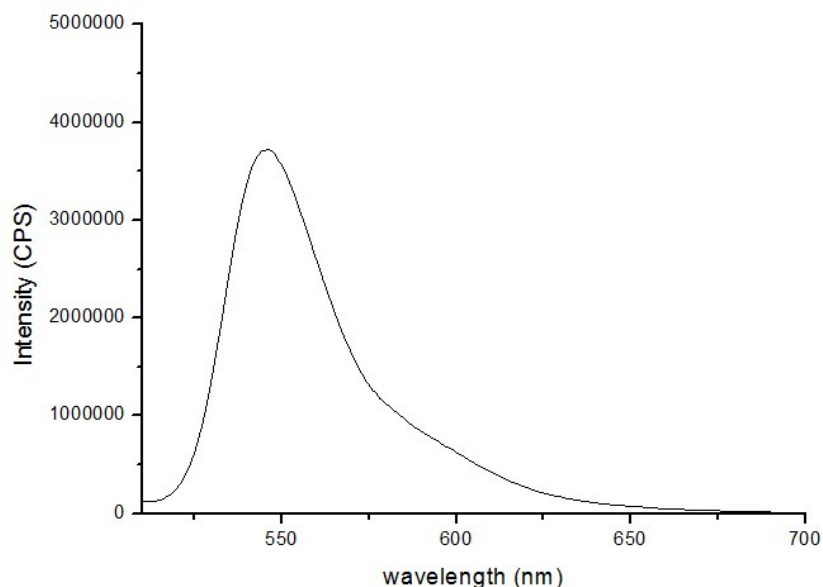


Figure S3. Fluorescence spectra of the photooxysulfonylation reaction mixture

Determination of Quantum Yield (Φ_H).

When the quantum yield of a photochemical reaction was determined, the reaction mixture was irradiated using a green high-power LED ($P = 5\text{ W}$, $\text{max} = 520\text{ nm}$) for 12h. The photon flux was estimated to $1.47 \times 10^{-8}\text{ E s}^{-1}$ by using potassium Reineckate as an actinometer.⁸ The initial rate of formation of **3a** was obtained by crude NMR using acetonitrile as internal standard. It was found to be $2.12 \times 10^{-9}\text{ mol s}^{-1}$ (46% conversion) which was converted into quantum yield ($\Phi_H = 0.144$).

Fluorescence quenching experiments

The fluorescence emission intensities were recorded on a Fluoromax-4spectrofluorimeter. The excitation wavelength was fixed at 510 nm, and the emission wavelength was measured at 540 nm (emission maximum). The samples were prepared by mixing Eosin Y ($3 \times 10^{-8}\text{ mol/L}$) and different amount of TBHP in ethanol (total volume = 0.2 mL) in a light path quartz fluorescence cuvette. The concentration of TBHP stock solution is $2.0 \times 10^{-7}\text{ mol/L}$ in ethanol. For each quenching experiment, 0.1 mL of TBHP stock solution was titrated to a mixed solution of Eosin Y (0.1 mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure 4.

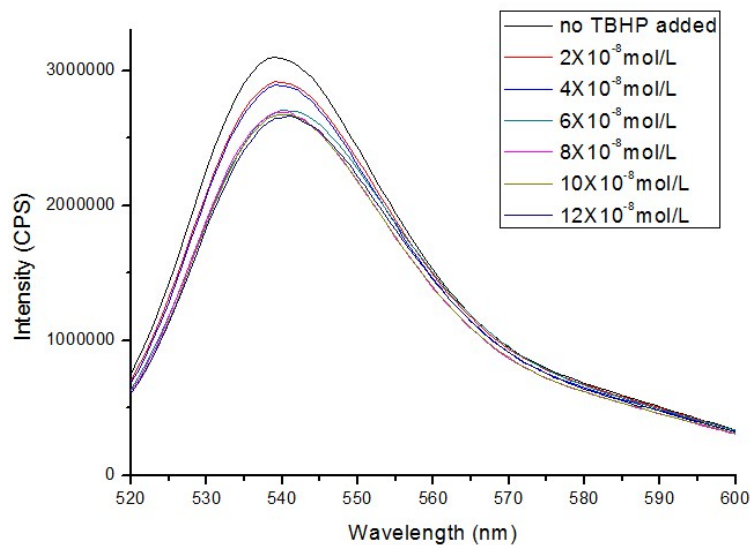


Figure S4. Quenching of Eosin Y fluorescence emission in the presence of TBHP

An indeed fluorescence quenching phenomenon of Eosin Y under various concentrations of TBHP was demonstrated in a curve of $[I_0/I]$ vs $C_{[TBHP]}$, as shown in Figure 5 (Stern-Volmer plots). For example, when $C_{[TBHP]}$ is $4 \times 10^{-8} \text{ mol/L}$, the non-linear Stern-Volmer plots indicated energy transfer event operating between Eosin Y's excited state and TBHP.

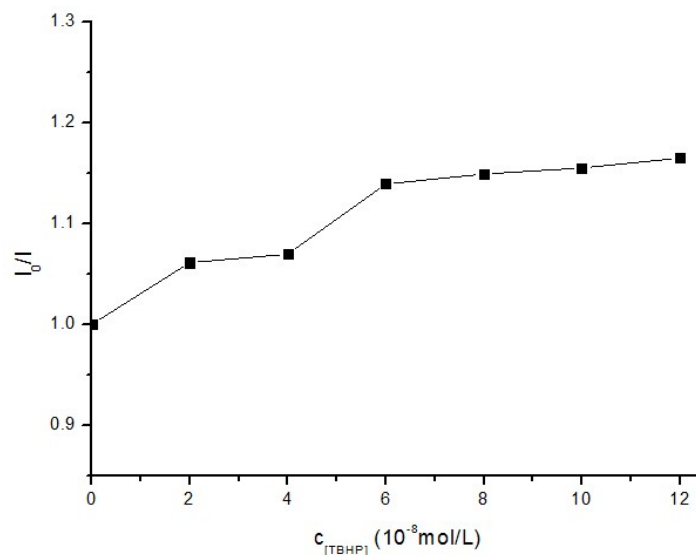


Figure S5. Stern-Volmer plots

We also investigate fluorescence quenching experiments with respect to benzenesulfinic acid. The samples were prepared by mixing Eosin Y ($3 \times 10^{-7} \text{ mol/L}$)

and different amount of benzenesulfonic acid in ethanol (total volume = 0.2 mL) in a light path quartz fluorescence cuvette. The concentration of benzenesulfonic acid stock solution is 2×10^{-6} mol/L in ethanol. For each quenching experiment, 0.1 mL of benzenesulfonic acid stock solution was titrated to a mixed solution of Eosin Y (0.1 mL, in a total volume = 1.0 mL). The emission intensity was collected and the results were presented in Figure 6. An fluorescence quenching phenomenon of Eosin Y under various concentrations of benzenesulfonic acid was shown in Figure 7 (Stern-Volmer plots).

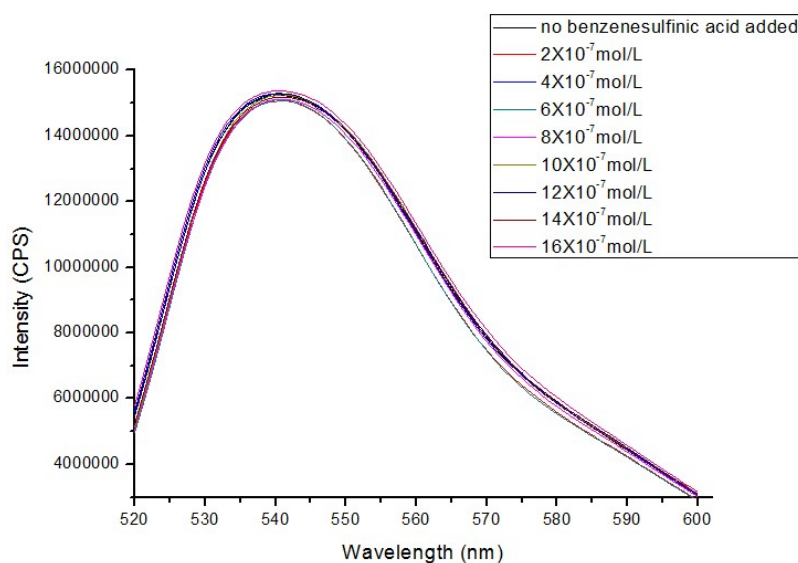


Figure S6. Quenching of Eosin Y fluorescence emission in the presence of benzenesulfonic acid

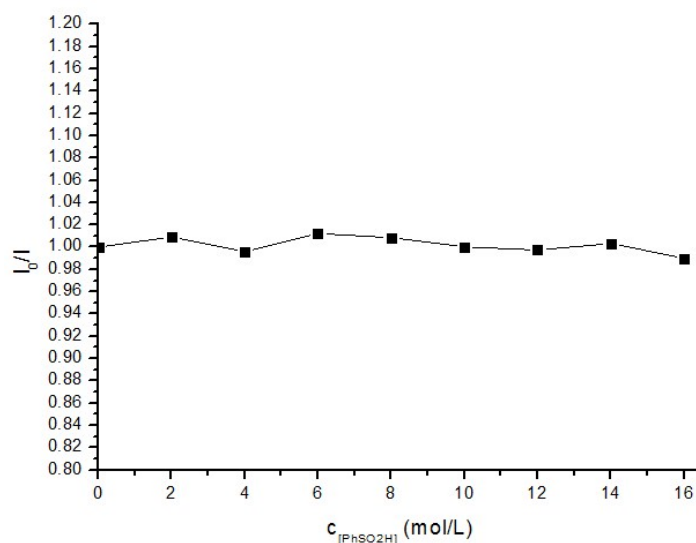
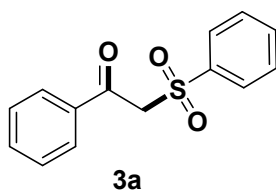
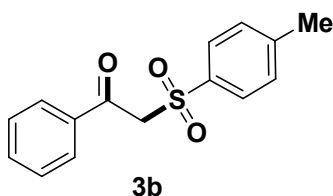


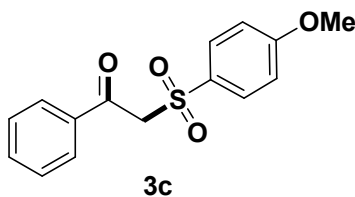
Figure S7. Stern-Volmer plots



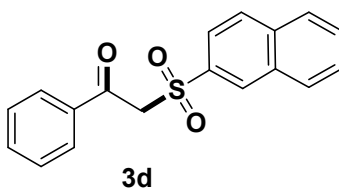
1-Phenyl-2-(phenylsulfonyl)ethanone (3a).¹ Eluent petroleum ether/ethyl acetate (3:1). 39 mg, 75% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.96 (d, 2H, J = 10.0 Hz), 7.92 (d, 2H, J = 10.0 Hz), 7.69 (t, 1H, J = 10.0 Hz), 7.64 (t, 1H, J = 10.0 Hz), 7.59-7.56 (m, 2H), 7.52-7.49 (m, 2H), 4.76 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 188.0, 138.8, 135.8, 134.4, 134.2, 129.3, 129.2, 128.9, 128.6, 63.5. HRMS calc. for C₁₄H₁₂NaO₃S (M+Na)⁺, 283.0399; found, 2283.0420.



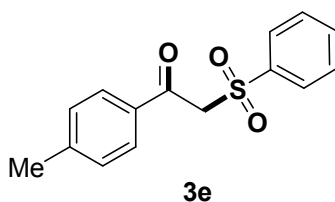
1-Phenyl-2-tosylethanone (3b).¹ Eluent petroleum ether/ethyl acetate (3:1). 38 mg, 69% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.96 (d, 2H, J = 10.0 Hz), 7.78 (d, 2H, J = 10.0 Hz), 7.63 (t, J = 10.0 Hz, 1H), 7.49 (t, 2H, J = 10.0 Hz), 7.35 (d, 2H, J = 10.0 Hz), 4.74 (s, 2H), 2.46 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 188.1, 145.2, 135.8, 135.7, 134.2, 129.7, 129.3, 128.7, 128.6, 63.5, 21.6. HRMS calc. for C₁₅H₁₄NaO₃S (M+Na)⁺, 297.0556; found, 297.0542.



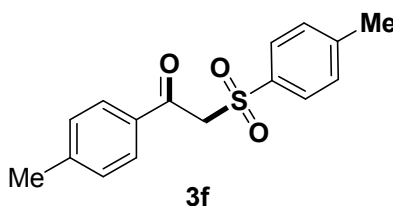
2-(4-Methoxyphenylsulfonyl)-1-phenylethanone (3c).¹ Eluent petroleum ether/ethyl acetate (3:1). 37 mg, 64% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.97 (d, 2H, J = 10.0 Hz), 7.83 (d, 2H, J = 10.0 Hz), 7.64 (t, 1H, J = 10.0 Hz), 7.50 (t, 2H, J = 10.0 Hz), 7.01 (d, 2H, J = 10.0 Hz), 4.73 (s, 2H), 3.90 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 188.3, 164.1, 135.8, 134.3, 130.9, 130.2, 129.3, 128.9, 114.4, 63.8, 55.7. HRMS calc. for C₁₅H₁₄NaO₄S (M+Na)⁺, 313.0505; found, 313.0512.



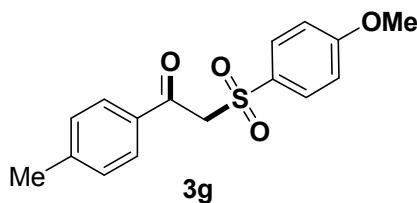
2-(Naphthalen-2-ylsulfonyl)-1-phenylethanone (3d).¹ Eluent petroleum ether/ethyl acetate (4:1). 36 mg, 58% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 8.49 (s, 1H), 8.03-7.89 (m, 6H), 7.71 (t, 1H, J = 10.0 Hz), 7.67-7.60 (m, 2H), 7.48 (t, 2H, J = 10.0 Hz), 4.87 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 188.0, 135.8, 135.6, 135.5, 134.4, 132.0, 130.7, 129.6, 129.5, 129.4, 129.4, 128.9, 128.0, 127.7, 123.0, 63.6. HRMS calc. for C₁₈H₁₄NaO₃S (M+Na)⁺, 333.0556; found, 333.0551.



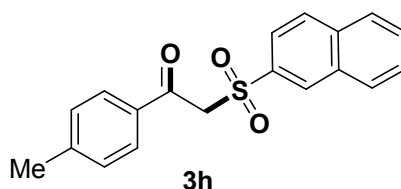
2-(Phenylsulfonyl)-1-p-tolyleanone (3e).¹ Eluent petroleum ether/ethyl acetate (3:1). 36 mg, 66% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.91 (d, 1H, J = 10.0 Hz), 7.86 (d, 1H, J = 10.0 Hz), 7.68 (t, 1H, J = 10.0 Hz), 7.56 (t, 1H, J = 10.0 Hz), 7.48 (t, 2H, J = 10.0 Hz), 7.30 (t, 2H, J = 10.0 Hz), 4.83 (s, 2H), 2.45 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 187.5, 145.6, 138.8, 134.2, 133.3, 129.6, 129.5, 129.2, 128.6, 63.5, 21.8. HRMS calc. for C₁₅H₁₄NaO₃S (M+Na)⁺, 297.0556; found, 297.0542.



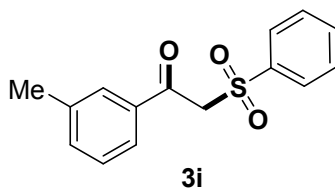
1-p-Tolyl-2-tosylethanone (3f).² Eluent petroleum ether/ethyl acetate (4:1). 43 mg, 74% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.87 (d, 2H, J = 10.0 Hz), 7.78 (d, 2H, J = 10.0 Hz), 7.37 (d, 2H, J = 10.0 Hz), 7.30 (d, 2H, J = 10.0 Hz), 4.71 (s, 2H), 2.46 (s, 3H), 2.45 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 187.7, 145.6, 145.3, 135.8, 133.4, 129.8, 129.6, 129.5, 128.6, 63.6, 21.8, 21.7. HRMS calc. for C₁₆H₁₆NaO₃S (M+Na)⁺, 311.0712; found, 311.0728.



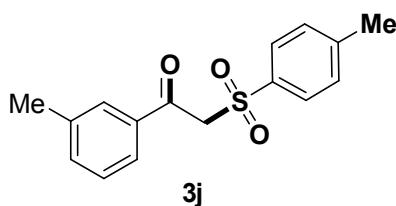
2-(4-Methoxyphenylsulfonyl)-1-*p*-tolylethanone (3g). Eluent petroleum ether/ethyl acetate (4:1). 60 mg, 52% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.87 (d, 2H, $J = 10.0$ Hz), 7.82 (d, 2H, $J = 10.0$ Hz), 7.29 (d, 2H, $J = 10.0$ Hz), 7.00 (d, 2H, $J = 10.0$ Hz), 4.70 (s, 2H), 3.89 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 187.8, 164.1, 145.5, 133.4, 130.9, 130.2, 129.6, 129.5, 114.3, 63.8, 55.7, 21.8. HRMS calc. for $\text{C}_{16}\text{H}_{16}\text{NaO}_4\text{S}$ ($\text{M}+\text{Na}$) $^+$, 327.0662; found, 327.0671.



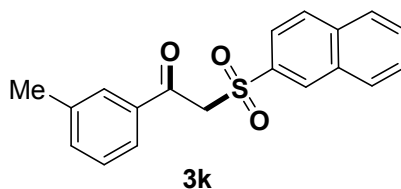
2-(Naphthalen-2-ylsulfonyl)-1-*p*-tolylethanone (3g). Eluent petroleum ether/ethyl acetate (4:1). 44 mg, 68% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 8.47 (s, 1H), 8.02-7.94 (m, 3H), 7.89 (d, 1H, $J = 10.0$ Hz), 7.87 (d, 1H, $J = 10.0$ Hz), 7.70 (t, 1H, $J = 5.0$ Hz), 7.64 (t, 1H, $J = 5.0$ Hz), 7.26 (d, 1H, $J = 5.0$ Hz), 4.81 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 187.5, 135.7, 135.5, 133.4, 132.0, 130.6, 129.6, 129.55, 129.50, 129.48, 129.47, 128.0, 127.7, 123.0, 63.6, 21.8. HRMS calc. for $\text{C}_{19}\text{H}_{16}\text{NaO}_3\text{S}$ ($\text{M}+\text{Na}$) $^+$, 347.0712; found, 347.0724.



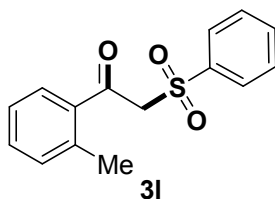
2-(Phenylsulfonyl)-1-*m*-tolylethanone (3i).³ Eluent petroleum ether/ethyl acetate (3:1). 40 mg, 76% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.92 (d, 2H, $J = 10.0$ Hz), 7.75 (d, 2H, $J = 10.0$ Hz), 7.69 (t, 1H, $J = 10.0$ Hz), 7.57 (t, 2H, $J = 10.0$ Hz), 7.45 (d, 1H, $J = 10.0$ Hz), 7.39 (t, 1H, $J = 10.0$ Hz), 4.75 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 188.1, 135.8, 135.2, 134.2, 129.7, 129.2, 128.8, 128.6, 126.6, 63.5, 21.3. HRMS calc. for $\text{C}_{15}\text{H}_{14}\text{NaO}_3\text{S}$ ($\text{M}+\text{Na}$) $^+$, 297.0556; found, 297.0542.



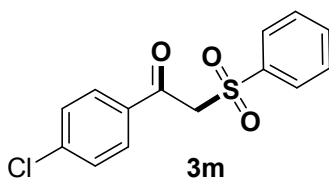
1-*m*-Tolyl-2-tosylethanone (3j).⁴ Eluent petroleum ether/ethyl acetate (4:1). 41 mg, 72% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.79-7.74 (m, 4H), 7.75 (d, 1H, J = 5.0 Hz), 7.39 (d, 1H, J = 10.0 Hz), 7.35 (d, 2H, J = 10.0 Hz), 4.72 (s, 2H), 2.46 (s, 3H), 2.42 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 188.3, 145.3, 138.7, 135.8, 135.1, 129.8, 129.7, 128.7, 128.6, 126.7, 63.6, 21.7, 21.3. HRMS calc. for C₁₆H₁₆NaO₃S (M+Na)⁺, 311.0712; found, 311.0728.



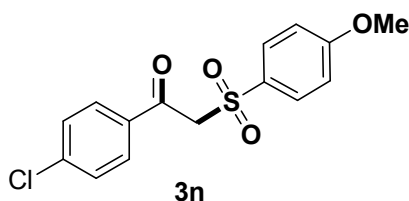
2-(Naphthalen-2-ylsulfonyl)-1-*m*-tolylethanone (3k). Eluent petroleum ether/ethyl acetate (3:1). 40 mg, 62% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 8.48 (s, 1H), 8.02-7.94 (m, 3H), 7.89 (d, 1H, J = 10.0 Hz), 7.76 (d, 1H, J = 10.0 Hz), 7.71 (t, 2H, J = 10.0 Hz), 7.65 (t, 1H, J = 10.0 Hz), 7.41 (d, 1H, J = 10.0 Hz), 7.36 (t, 1H, J = 10.0 Hz), 4.82 (s, 2H), 2.37 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 188.1, 138.7, 135.8, 135.7, 135.5, 135.1, 132.0, 130.7, 129.7, 129.6, 129.5, 129.4, 128.7, 128.0, 127.7, 126.6, 123.0, 63.6, 21.2. HRMS calc. for C₁₉H₁₆NaO₃S (M+Na)⁺, 347.0712; found, 347.0724.



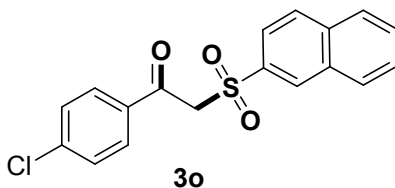
2-(Phenylsulfonyl)-1-*o*-tolylethanone.⁵ Eluent petroleum ether/ethyl acetate (5:1). 28 mg, 51% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.91-7.89 (m, 2H), 7.33 (d, 1H, J = 5.0 Hz), 7.68 (t, 1H, J = 10.0 Hz), 7.44 (t, 1H, J = 10.0 Hz), 7.31-7.27 (m, 2H), 4.73 (s, 2H), 2.46 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 190.3, 140.1, 139.0, 135.7, 134.1, 132.8, 132.3, 130.3, 129.2, 128.5, 125.9, 65.5, 21.5. HRMS calc. for C₁₅H₁₄NaO₃S (M+Na)⁺, 297.0556; found, 297.0542.



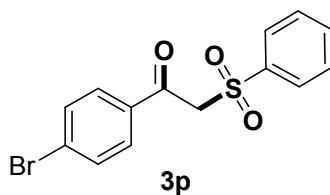
1-(4-Chlorophenyl)-2-(phenylsulfonyl)ethanone (3m).¹ Eluent petroleum ether/ethyl acetate (3:1). 49 mg, 84% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.91 (t, 4H, J = 10.0 Hz), 7.71 (t, 1H, J = 10.0 Hz), 7.58 (t, 2H, J = 10.0 Hz), 7.47 (d, 2H, J = 10.0 Hz), 4.73 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 186.9, 138.6, 134.4, 134.1, 130.8, 129.3, 129.2, 128.6, 63.6. HRMS calc. for C₁₄H₁₁ClNaO₃S (M+Na)⁺, 317.0010; found, 317.0023.



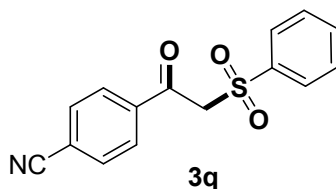
1-(4-Chlorophenyl)-2-(4-methoxyphenylsulfonyl)ethanone (3n). Eluent petroleum ether/ethyl acetate (5:1). 33 mg, 52% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.93 (d, 2H, J = 10.0 Hz), 7.80 (d, 2H, J = 10.0 Hz), 7.49 (d, 2H, J = 5.0 Hz), 7.02 (d, 2H, J = 5.0 Hz), 4.70 (s, 2H), 3.91 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 187.2, 164.3, 141.1, 134.1, 130.8, 130.7, 129.9, 129.2, 114.5, 63.9, 55.7. HRMS calc. for C₁₅H₁₃ClNaO₄S (M+Na)⁺, 347.0115; found, 347.0119.



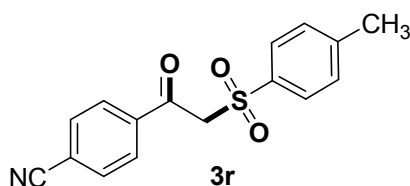
1-(4-Chlorophenyl)-2-(naphthalen-2-ylsulfonyl)ethanone (3o). Eluent petroleum ether/ethyl acetate (3:1). 33 mg, 48% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 8.46 (s, 1H), 8.03-7.93 (m, 3H), 7.91 (d, 2H, J = 5.0 Hz), 7.87 (d, 1H, J = 10.0 Hz), 7.72 (t, 1H, J = 10.0 Hz), 7.67 (t, 1H, J = 10.0 Hz), 7.46 (d, 2H, J = 10.0 Hz), 4.80 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 186.9, 141.2, 135.6, 135.4, 134.1, 132.0, 130.8, 130.7, 129.63, 129.60, 129.2, 128.1, 127.9, 122.8, 63.7, 29.7. HRMS calc. for C₁₈H₁₃ClNaO₃S (M+Na)⁺, 367.0166; found, 367.0164.



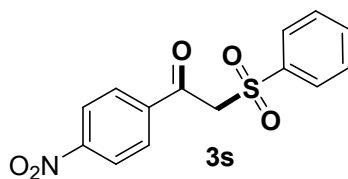
1-(4-Bromophenyl)-2-(phenylsulfonyl)ethanone (3p).¹ Eluent petroleum ether/ethyl acetate (5:1). 54 mg, 80% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.89 (t, 4H, J = 10.0 Hz), 7.83 (d, 2H, J = 10.0 Hz), 7.70 (t, 1H, J = 10.0 Hz), 7.65 (d, 2H, J = 10.0 Hz), 7.58 (t, 1H, J = 10.0 Hz), 4.72 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 187.1, 134.4, 134.44, 134.40, 132.3, 130.8, 130.0, 129.3, 128.5, 63.6. HRMS calc. for C₁₄H₁₁BrNaO₃S (M+Na)⁺, 360.9504; found, 360.9500, 362.9486.



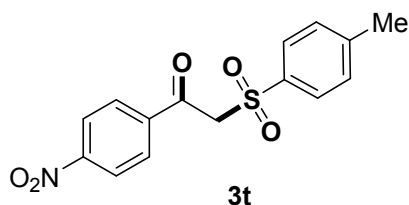
4-(2-(Phenylsulfonyl)acetyl)benzonitrile (3q).⁵ Eluent petroleum ether/ethyl acetate (3:1). 34 mg, 61% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 8.09 (d, 2H, J = 5.0 Hz), 7.88 (d, 2H, J = 10.0 Hz), 7.81 (d, 2H, J = 5.0 Hz), 7.72 (t, 1H, J = 10.0 Hz), 7.59 (t, 2H, J = 10.0 Hz), 4.76 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 187.0, 138.5, 138.4, 134.6, 132.6, 129.7, 129.4, 128.5, 117.6, 117.5, 63.7. HRMS calc. for C₁₅H₁₁NNaO₃S (M+Na)⁺, 308.0352; found, 308.0361.



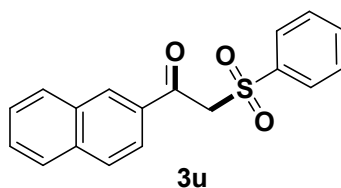
4-(2-(Tosylacetyl)benzonitrile (3r). Eluent petroleum ether/ethyl acetate (4:1). 38 mg, 64% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 8.10 (d, 2H, J = 10.0 Hz), 7.82 (d, 2H, J = 10.0 Hz), 7.76 (d, 2H, J = 10.0 Hz), 7.38 (d, 2H, J = 10.0 Hz), 4.74 (s, 2H), 2.48 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 187.2, 145.9, 138.5, 135.4, 132.6, 130.0, 129.8, 128.5, 117.6, 117.5, 63.9, 21.8. HRMS calc. for C₁₆H₁₃NNaO₃S (M+Na)⁺, 322.0508; found, 322.0517.



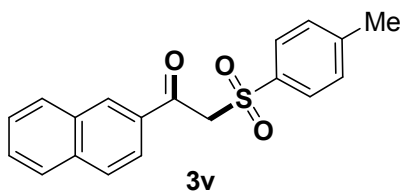
1-(4-Nitrophenyl)-2-(phenylsulfonyl)ethanone (3s).⁶ Eluent petroleum ether/ethyl acetate (10:1). 38 mg, 62% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 8.36 (d, 2H, J = 10.0 Hz), 8.18 (d, 2H, J = 10.0 Hz), 7.91 (d, 2H, J = 10.0 Hz), 7.73 (t, 1H, J = 10.0 Hz), 7.61 (t, 2H, J = 10.0 Hz), 4.79 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 186.8, 171.2, 139.9, 134.7, 130.5, 129.5, 128.5, 124.0, 64.0. HRMS calc. for C₁₄H₁₁NNaO₅S (M+Na)⁺, 328.0250; found, 328.0257.



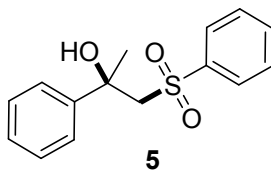
1-(4-Nitrophenyl)-2-(tosylethanone (3t).⁴ Eluent petroleum ether/ethyl acetate (10:1). 43 mg, 67% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 8.36 (d, 2H, J = 10.0 Hz), 8.16 (d, 2H, J = 10.0 Hz), 7.77 (d, 2H, J = 10.0 Hz), 7.39 (d, 2H, J = 10.0 Hz), 4.77 (s, 2H), 2.49 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 187.0, 135.4, 130.5, 130.1, 129.3, 128.5, 128.1, 124.1, 124.0, 64.2, 21.8. HRMS calc. for C₁₅H₁₃NNaO₅S (M+Na)⁺, 342.0407; found, 342.0416.



4-(2-Tosylacetyl)benzonitrile (3u).³ Eluent petroleum ether/ethyl acetate (6:1). 40 mg, 64% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 8.50 (s, 1H), 7.99 (t, 2H, J = 10.0 Hz), 7.95-7.90 (m, 4H), 7.68 (t, 1H, J = 10.0 Hz), 7.62-7.55 (m, 3H), 4.89 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 187.9, 138.7, 136.1, 134.3, 133.1, 132.3, 132.2, 130.0, 129.4, 129.2, 128.9, 128.6, 127.8, 127.2, 123.9, 63.7. HRMS calc. for C₁₈H₁₄NaO₃S (M+Na)⁺, 333.0556; found, 333.0547.



1-(Naphthalen-2-yl)-2-tosylethanone (3v).^[1] Eluent petroleum ether/ethyl acetate (6:1). 27 mg, 42% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 8.48 (s, 1H), 7.99 (d, 2H, J = 10.0 Hz), 7.92-7.89 (m, 2H), 7.80 (d, 2H, J = 10.0 Hz), 7.66 (t, 1H, J = 10.0 Hz), 7.61 (t, 1H, J = 10.0 Hz), 7.34 (d, 2H, J = 10.0 Hz), 4.87 (s, 2H), 2.43 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 188.0, 145.4, 136.0, 135.7, 133.1, 132.3, 132.2, 130.0, 129.9, 129.4, 128.8, 128.7, 127.8, 127.1, 124.0, 63.8, 21.7. HRMS calc. for C₁₈H₁₄NaO₃S (M+Na)⁺, 347.0712; found, 347.0710.



2-Phenyl-1-tosylpropan-2-ol (5).⁷ Eluent petroleum ether/ethyl acetate (30:1). White solid, 40 mg, 72% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.51 (d, 2H, J = 10.0 Hz), 7.31 (d, 2H, J = 10.0 Hz), 7.22-7.19 (m, 5H), 3.72 (d, 1H, J = 15.0 Hz), 3.62 (d, 1H, J = 15.0 Hz), 2.41 (s, 3H), 1.73 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 144.5, 137.4, 129.7, 128.3, 127.6, 127.1, 124.6, 73.2, 66.7, 30.7, 21.6. HRMS calc. for C₁₅H₁₆NaO₃S (M+Na)⁺, 299.0712; found, 299.0723.

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