# **Supporting Information**

# Biomimetic Photocatalytic Sulfonation of Alkenes to Access β-ketosulfones with Single-Atom-Site Iron

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#### 1. General information

The glassware was oven dried at 100 °C for hours and cooled down under vacuum. Sulfinic acids were prepared according to reported procedures.<sup>1</sup> All of the reaction solvents of CH<sub>3</sub>CN (99.9%, Extra Dry with molecular sieves, Water≤50 ppm) and others were purchased from Innochem. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. X-ray diffraction (XRD) patterns were recorded on a Rigaku smartlab system at 45 kV and 200 mA with Cu-Ka radiation. Fourier transform infrared (FT-IR) were measured using Bruker VERTEX 70 spectrophotometers. The spherical aberration corrected Transmission Electron Microscope (ACTEM) was carried out on a FEI Themis G2 microscope at 100 kV. The scanning electron microscope (SEM) was carried out on a ZEISS Merlin. The elemental composition was characterized with an energy dispersive X-ray spectroscope (EDX, EMAX-5770, HORIBA). UV-vis absorbance spectra were obtained on a Scan UV-vis spectrophotometer (PerkinElmer, Lambda 750S) at the range of 200 - 800 nm. N<sub>2</sub> adsorption-desorption isotherms were conducted with a Micromeritics Model ASAP 2020 instrument at 77 K for surface area analysis. Inductively coupled plasma mass spectrometry (ICP-MS) result was obtained on a GSE200plus. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60 - 90 °C). <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts ( $\delta$ ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively.

# 2. Preparation of photocatalysts

**Synthesis of carbon nitride (CN)** An aliquot of 10.0 g urea was placed in an alumina crucible with a cover followed by thermally decomposing at 550°C for 2 h in static air with a ramp rate of 5°C/min. After cooling down, the prepared yellow product was ground and collected for further use.

**Synthesis of hemin-coupled carbon nitride (CNH)** An aliquot of 10mL of CN dispersion (10.0 mg/mL) was added into 10 mL of 2-(Nmorpholino) ethane sulfonic acid (MES), buffer (3.9 mg/mL) in a 50-mL round-bottom flask at 60 °C. Then, 95.0 mg of 1- (3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and 37.5 mg of N-hydroxysuccinimide (NHS) were added to the mixture. After stirring for 15 min, 10 mg of hemin was introduced, and the final mixture was stirred at 60 °C for 6 h. Meanwhile, the amino groups of CN and the carboxylic groups of hemin were activated to form the hemin-coupled carbon nitride (CNH), which were collected by centrifugation at 7,000 rpm for 6 min and washed with deionized water three times.

# 3. Characterization of the photocatalysts



**Figure S 1**. (a) FT-IR results of CN and CNH. (b) BET results of CN and CNH. (c) Pore diameter results of CN and CNH.

Entry	Sampling Quality/g	Constant Volume/mL	Constant Volume	Element	Swot mg/mL	Content mg/kg
Sample-1	0.0015	50	1	Fe	1.087	36221.3

				-	
Table 9	S 1	ICP-MS	results	of	CNH

4. General procedure for visible light-promoted sulfonation of alkenes with sulfinic acids access to β-ketosulfones.

$$R^{1} + Na/HO^{H}S^{R^{2}} + R^{2} +$$

A schlenk tube equipped with a stir bar was loaded with 1.25 mg (0.625 mg/mL) of CNH, alkenes **1** (0.5 mmol), Sulfonic acid/sodium **2** (1.0 mmol) and hydrochloric acid (1.5 equiv) in 2.0 mL CH<sub>3</sub>CN under air atmosphere. The solution was then stirred at room temperature under the irradiation of blue LED lamp (460 nm) for 12 h. After the completion of reaction, the reaction mixture was washed with saturated potassium carbonate solution and extracted with  $CH_2Cl_2$  (10 mL × 3). The organic layers were combined, dried over  $Na_2SO_4$ , and concentrated. Then, the pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl ether = 5:1 - 10:1) to afford corresponding naphthalene products **3**.

# 5. Preliminary mechanistic studies

# (1) Active species trapping experiments



A schlenk tube equipped with a stir bar was loaded with 1.25 mg of CNH, styrenes **1a** (0.50 mmol), 4-methylbenzenesulfinic acid **2b** (1.0 mmol), hydrochloric acid (1.5 equiv) and two equivalent of ammonium oxalate (AO: hole scavenger), or benzoquinone (BQ: superoxide scavenger) or sodium azide (NaN<sub>3</sub>: singlet oxygen scavenger) in 2.0 mL CH<sub>3</sub>CN under air atmosphere. The mixture was then stirred at room temperature under the irradiation of blue LED lamp (460 nm) for 12 h. After the completion of reaction, it was washed with saturated potassium carbonate solution and then extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 3). The organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. Subsequently, the pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl ether = 5:1) to afford products **3ab** in 31%, 15% and 35% yield,

respectively.

(2) The reaction of 1a and 2b with TEMPO or BHT under the standard conditions.



In an oven-dried schlenk tube equipped with a stir bar, CNH (0.625 mg/mL), styrenes **1a** (0.5 mmol), 4-methylbenzenesulfinic acid **2b** (1.0 mmol), hydrochloric acid (1.5 equiv), TEMPO or BHT (1.0 mmol) and CH<sub>3</sub>CN (2.0 mL) were separately added. The mixture was then stirred at room temperature under the irradiation of blue LED lamp (460 nm) for 12 h. When the reaction was completed, only a trace amount of the product **3ab** was observed by thin layer chromatography (TLC).

# (3) The radical trapping experiments.



In an oven-dried schlenk tube equipped with a stir bar, CNH (0.625 mg/mL), 1,1diphenytlethylene **1u** (0.5 mmol), 4-methylbenzenesulfinic acid **2b** (1.0 mmol), hydrochloric acid (1.5 equiv), and CH<sub>3</sub>CN (2.0 mL) were added. The mixture was then stirred at room temperature under the irradiation of blue LED lamp (460 nm) for 12 h. When the reaction was finished, the mixture was washed with saturated potassium carbonate solution and then extracted with  $CH_2Cl_2$  (10 mL × 3). The organic layers were combined, dried over  $Na_2SO_4$ , and concentrated. Finally, the pure product of **3ub** was obtained in 52% yield by flash column chromatography on silica gel (petroleum: ethyl ether = 7:1).



Figure S2. The <sup>1</sup>HNMR results of 3ub.

# (4) The intermediate experiments



In an oven-dried schlenk tube equipped with a stir bar, CNH (0.625 mg/mL), prop-1-en-2ylbenzene **1r**(0.5 mmol), 4-methylbenzenesulfinic acid **2b** (1.0 mmol), hydrochloric acid (1.5 equiv), and CH<sub>3</sub>CN (2.0 mL) were introduced. The mixture was then stirred at room temperature under the irradiation of blue LED lamp (460 nm) for 12 h. When the reaction was finished, the mixture was washed with saturated potassium carbonate solution and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 3). The organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The resulting pure product of **3rb** was finally obtained in 95% yield by flash column chromatography on silica gel (petroleum: ethyl ether = 5:1).

## (5) Procedure for cyclic voltammetry (CV).

Cyclic voltammetry measurements were performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a glass carbon electrode, and the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, which was separated from reaction by a salt bridge. 10 mL anhydrous degassed  $CH_3CN$  containing 0.5 mmol  $nBu_4NBF_4$  were poured into the electrochemical cell in all experiments. The scan rate is 0.050 V/s, ranging from 0 V to 2.0 V.



Figure S3. Cyclic voltammetry results of CNH, 1a, 2a, and 3aa in CH<sub>3</sub>CN.

# 6. References

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# 7. Detail descriptions for products.



**1-phenyl-2-(phenylsulfonyl)ethan-1-one (3aa):**<sup>2</sup> white solid was obtained with 90% isolated yield (117.0 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.02 – 7.88 (m, 4H), 7.73 – 7.63 (m, 2H), 7.59 (t, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 4.77 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 187.97, 138.68, 135.71, 134.43, 134.28, 129.32, 129.24, 128.90, 128.62, 63.47.



**phenyl-2-tosylethan-1-one (3ab):**<sup>2</sup> white solid was obtained with 94% isolated yield (130.1mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, *J* = 7.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.64 (s, 2H), 2.37 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  188.16, 145.40, 135.79, 135.77 134.35, 129.86, 129.36, 128.86, 128.64, 63.62, 21.73.



**1-(p-tolyl)-2-tosylethan-1-one (3bb):** <sup>2e</sup> yellow solid was obtained with 88% isolated yield (127.2 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 1H), 4.71 (s, 2H), 2.46 (s, 3H), 2.45 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 187.66, 145.57, 145.31, 135.81, 133.39, 129.82, 129.56, 129.53, 128.62, 63.60, 21.80, 21.72.



**1-(4-methoxyphenyl)-2-tosylethan-1-one (3cb):** <sup>2e</sup> white solid was obtained with 82% isolated yield (125.0 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 8.9 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.59 (s, 2H), 3.81 (s, 3H), 2.37 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 186.35, 164.57, 145.28, 135.80, 131.95, 129.82, 128.93, 128.60, 114.08, 63.61, 55.64, 21.73.



1-(4-fluorophenyl)-2-tosylethan-1-one (3db): <sup>2e</sup> yellow oil was obtained with 80% isolated

yield (117.2 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 – 7.88 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 4.61 (s, 2H), 2.38 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  186.57, 166.50 (d, *J* = 257.7 Hz), 145.54, 135.61, 132.29 (d, *J* = 9.6 Hz), 129.91, 128.58, 116.13 (d, *J* = 22.1 Hz), 63.78, 21.74. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -102.42.



**2-(1,3-dithiolan-2-ylidene)-1-(4-fluorophenyl)-2-thiocyanatoethan-1-one** (**3ea**): <sup>2e</sup> white solid was obtained with 84% isolated yield (129.8 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 4.61 (s, 2H), 2.38 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  187.03 (s), 145.59 (s), 141.13 (s), 135.57 (s), 134.11 (s), 130.81 (s), 129.93 (s), 129.23 (s), 128.58 (s), 63.77 (s), 21.74 (s).



**1-(4-bromophenyl)-2-tosylethan-1-one (3fb):** <sup>2e</sup> white solid was obtained with 86% isolated yield (151.8 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.60 (s, 2H), 2.38 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 187.27, 145.60, 135.56, 134.50, 132.24, 130.86, 129.94, 128.59, 63.80, 21.75.



**2-tosyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one** (**3gb**): <sup>2e</sup> yellow solid was obtained with 73% isolated yield (125.1 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.74 (dd, *J* = 8.4, 2.0 Hz, 4H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.74 (s, 2H), 2.45 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 187.48, 145.73, 138.32, 135.36 (q, *J* = 25.4 Hz), 129.98, 129.74, 128.57, 127.96, 126.04 (q, *J* = 273.6 Hz), 125.90 (q, *J* = 3.7 Hz), 63.92, 21.71.



**1-(3-chlorophenyl)-2-tosylethan-1-one (3hb):** <sup>2e</sup> white solid was obtained with 83% isolated yield (128.2 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.55 – 7.46 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 4.61 (s, 2H), 2.38 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 187.08, 145.63, 137.24, 135.56, 135.26, 134.22, 130.18, 129.94, 129.16, 128.60, 127.60, 63.72, 21.74.



**1-(2-chlorophenyl)-2-tosylethan-1-one (3ib):** <sup>2e</sup> yellow oil was obtained with 78% isolated yield (120.5 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d, *J* = 8.2 Hz, 2H), 7.48 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.32 – 7.23 (m, 4H), 4.74 (s, 2H), 2.37 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  190.33, 145.39, 137.35, 135.93, 133.13, 131.58, 130.69, 130.63, 129.87, 128.57, 127.23, 66.46, 21.72.



(S)-1,2-diphenyl-2-tosylethan-1-one (3jb): yellow oil was obtained with 66% isolated yield (115.5 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.4 Hz, 2H), 7.16 – 7.12 (m, 4H), 6.05 (s, 1H), 2.33 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  190.83, 145.05, 133.94 130.45, 130.19, 129.61, 129.04, 128.88, 128.84, 128.79, 128.50, 128.17, 127.30, 76.15, 21.71. HRMS (EI) calcd for C<sub>21</sub>H<sub>19</sub>O<sub>3</sub>SNa [M+Na]<sup>+</sup>: 373.0869; found: 373.0865.



(S)-2-tosyl-2,3-dihydro-1H-inden-1-onee (3kb): yellow oil was obtained with 79% isolated yield (113.4 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.30 (dd, *J* = 15.1, 7.8 Hz, 3H), 4.19 (dd, *J* = 8.4, 3.3 Hz, 1H), 3.74 (dd, *J* = 18.2, 3.0 Hz, 1H), 3.46 (dd, *J* = 18.2, 8.4 Hz, 1H), 2.37 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  194.66, 151.93, 145.38, 135.93, 134.59, 129.77, 129.33, 128.21, 126.44, 124.88, 68.76, 28.17, 21.76. HRMS (EI) calcd for C<sub>16</sub>H<sub>15</sub>O<sub>3</sub>SNa [M+Na]<sup>+</sup>: 309.0556; found: 309.0554.



(S)-2-tosyl-3,4-dihydronaphthalen-1(2H)-one/(1R,2S)-2-tosyl-1,2,3,4-

tetrahydronaphthalen-1-ol (3lb/3lb'): yellow solid was obtained with 78% isolated yield (117.3 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.18 (dd, *J* = 7.9, 6.2 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 5.13 (d, *J* = 9.2 Hz, 1H), 4.01 (t, *J* = 5.6 Hz, 1H), 3.48 – 3.38 (m, 1H), 3.30 (ddd, *J* = 12.4, 9.3, 3.5 Hz, 1H), 2.90 (dt, *J* = 16.9, 5.3 Hz, 1H), 2.80 – 2.68 (m, 3H), 2.60 – 2.51 (m, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 2.11 – 2.05 (m, 1H), 1.71 – 1.62 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 188.78, 145.52, 145.09, 143.62, 135.99, 135.86, 134.84, 134.49, 133.46, 131.79, 130.05, 129.69, 129.23, 129.14, 128.97, 128.05, 127.96, 127.71, 127.67, 127.04, 126.90, 69.71, 67.57, 67.02, 27.97, 26.58, 23.72, 22.99, 21.71. HRMS (EI) calcd for  $C_{17}H_{17}O_3SNa$  [M+Na]\*: 323.0712; found: 323.0712,  $C_{17}H_{19}O_3SNa$  [M+Na]\*: 325.0869; found: 325.0848.



(1S,2R)-2-tosylcyclohexan-1-ol (3mb): yellow solid was obtained with 75% isolated yield
(95.6 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.75 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H),
4.22 (ddd, J = 11.2, 8.6, 4.8 Hz, 1H), 3.56 – 3.44 (m, 1H), 2.38 (s, 3H), 1.99 – 1.89 (m, 2H),

1.60 (dd, J = 6.0, 2.3 Hz, 2H), 1.37 (ddd, J = 24.0, 12.7, 3.5 Hz, 1H), 1.25 – 1.11 (m, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  144.89, 133.97, 129.90, 127.77, 86.70, 72.03, 32.37, 30.83, 23.90, 23.28, 21.69. HRMS (EI) calcd for C<sub>13</sub>H<sub>19</sub>O<sub>3</sub>SK [M + K]<sup>+</sup>: 293.0608; found: 293.0844



**1-(thiophen-2-yl)-2-tosylethan-1-one (3nb):** yellow oil was obtained with 46% isolated yield (64.4 mg) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 – 7.80 (m, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.13 (m, 1H), 4.61 (s, 2H), 2.44 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  180.40, 145.57, 143.30, 136.48, 135.36, 130.27, 129.97, 128.71, 128.13, 64.81, 21.80. HRMS (EI) calcd for C<sub>13</sub>H<sub>13</sub>O<sub>3</sub>S<sub>2</sub> [M + H]<sup>+</sup>: 281.0301; found: 281.0300.



**2-(2-tosylethyl)pyridine (3ob)**: yellow oil was obtained with 72% isolated yield (93.9 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.44 (d, *J* = 4.1 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.58 (td, *J* = 7.6, 1.4 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.18 – 7.07 (m, 2H), 3.65 – 3.53 (m, 2H), 3.28 – 3.13 (m, 2H), 2.43 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  157.19, 149.34, 144.67, 136.68, 136.11, 129.89, 128.12, 123.23, 121.86, 55.26, 30.90, 21.60. HRMS (EI) calcd for C<sub>14</sub>H<sub>16</sub>NO<sub>2</sub>S [M + H]\*: 262.0896; found: 262.0890.



(8R,9S,10R,13S,14S)-4-hydroxy-10,13-dimethyl-3-tosyl-1,8,9,10,11,12,13,14,15,16-

**decahydro-7H-cyclopenta[a]phenanthrene-7,17(2H)-dione (3qb):** yellow oil was obtained with 45% isolated yield (102.3 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.65 (s, 1H), 3.01 – 2.87 (m, 1H), 2.75 – 2.58 (m, 2H), 2.41 (s, 3H), 2.11 – 1.91 (m, 4H), 1.82 – 1.76 (m, 2H), 1.70 – 1.54 (m, 7H), 1.12 (s, 3H), 0.81 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 206.71, 200.83, 200.40, 145.23, 133.73, 131.29, 130.04, 128.90, 126.58, 70.64, 51.13, 49.92, 47.79, 44.37, 37.08, 35.59, 31.14, 30.62, 22.92, 21.71, 21.10, 20.45, 19.84, 13.73. HRMS (EI) calcd for  $C_{26}H_{31}O_5S$  [M+H] <sup>+</sup>: 455.1887; found: 455.1889.



**2-phenyl-1-tosylpropan-2-ol (3rb):** <sup>2</sup> yellow oil was obtained with 95% isolated yield (138.0 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.21 (m, 5H), 4.00 (d, *J* = 14.3 Hz, 1H), 3.81 (d, *J* = 14.3 Hz, 1H), 2.46 (s, 3H), 1.75 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  145.21, 143.41, 136.99, 129.99, 128.51, 128.11, 127.59, 124.47, 84.39, 61.90, 26.90, 21.67. HRMS (EI) calcd for C<sub>16</sub>H<sub>18</sub>KO<sub>3</sub>S [M+K]<sup>+</sup>: 329.0608; found: 329.0644.



**2-((4-fluorophenyl)sulfonyl)-1-phenylethan-1-one (3ac):** <sup>2</sup> yellow oil was obtained with 88% isolated yield (122.3 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 – 7.80 (m, 4H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 8.5 Hz, 2H), 4.67 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  188.02, 166.16 (d, *J* = 257.4 Hz), 135.62, 134.55, 131.69 (d, *J* = 9.8 Hz), 129.27, 128.96, 126.19, 116.57 (d, *J* = 22.7 Hz), 63.45. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -102.35.



**2-((4-chlorophenyl)sulfonyl)-1-phenylethan-1-one (3ad):** <sup>2</sup> white oil was obtained with 86% isolated yield (126.4 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 16.5, 8.2 Hz, 4H), 4.78 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 188.01, 141.06, 137.17, 135.59, 134.55, 130.20, 129.54, 129.25, 128.96, 63.27.



**2-((4-bromophenyl)sulfonyl)-1-phenylethan-1-one (3ae):**<sup>2</sup> yellow oil was obtained with 81% isolated yield (136.8 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.67 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 187.90, 137.61, 135.58, 134.59, 132.55, 130.23, 129.82, 129.27, 128.98, 63.33.



**1-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethan-1-one (3af)**:<sup>2</sup> yellow oil was obtained with 75% isolated yield (123 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 4.71 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 187.73, 142.09, 139.30, 135.87 (q, *J* = 33.5 Hz), 134.69, 129.42, 129.22, 129.02, 126.35 (q, *J* = 3.7 Hz), 122.9 (q, *J* =273.7 Hz), 63.10, 29.71.



**2-((5-chloro-2,4-difluorophenyl)sulfonyl)-1-phenylethan-1-one** (**3ag**):<sup>2f</sup> yellow oil was obtained with 78% isolated yield (128.7 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 – 7.85 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.24 (dt, *J* = 13.5, 6.6 Hz, 1H), 7.04 (t, *J* = 8.7 Hz, 1H), 4.83 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  187.60, 162.08 (dd, *J* = 261.7, 11.9 Hz), 158.53 (dd, *J* = 258.6, 11.4 Hz), 135.42, 134.81, 132.53, 129.17, 129.07, 128.90, 125.72, 124.00 (dd, *J* = 15.8, 4.2 Hz), 118.20 (dd, *J* = 18.4, 4.1 Hz), 106.90 (t, *J* = 26.1 Hz). 62.01. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -98.73 (d, *J* = 12.9 Hz), -105.85 (d, *J* = 12.9 Hz).



**2-(naphthalen-2-ylsulfonyl)-1-phenylethan-1-one (3ah):** <sup>2</sup> white solid was obtained with 84% isolated yield (130.2 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.39 (s, 1H), 7.98 – 7.89 (m, 2H), 7.86 (t, *J* = 8.3 Hz, 3H), 7.80 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 4.74 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 188.01, 135.78, 135.56, 134.38, 132.04, 130.70, 129.63, 129.56, 129.53, 129.33, 128.87, 128.04, 127.76, 122.98, 63.59.



**2-(methylsulfonyl)-1-phenylethan-1-one (3ai):** <sup>2e</sup> yellow oil was obtained with 85% isolated yield (84.1 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 – 7.79 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 4.53 (s, 2H), 3.09 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  189.23 135.63, 134.76, 129.27, 129.07, 61.31, 41.83. HRMS (EI) calcd for C<sub>9</sub>H<sub>10</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 221.0243; found: 221.0244.



**2-(ethylsulfonyl)-1-phenylethan-1-one (3aj):** <sup>2e</sup> white solid was obtained with 87% isolated yield (92.2 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 4.50 (s, 2H), 3.22 (dd, *J* = 14.5, 7.2 Hz, 2H), 1.39 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  189.29, 135.76, 134.66, 129.34, 129.02, 58.76, 48.22, 6.68. HRMS (EI) calcd for C<sub>10</sub>H<sub>12</sub>NaO<sub>3</sub>S [M+Na] <sup>+</sup>: 235.0399; found: 235.0400.

8. Copy NMR Spectra of products

(a)



Figure S4. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3ab.



Figure S5. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3bb.



Figure S6. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3cb.





Figure S7. The <sup>1</sup>HNMR (a), <sup>13</sup>CNMR (b) and <sup>19</sup>FNMR (c) spectra of 3db.



Figure S8. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3eb.



Figure S9. The  $^{1}$ HNMR (a) and  $^{13}$ CNMR (b) spectra of 3fb.



(a)



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)

Figure S10. The <sup>1</sup>HNMR (a), <sup>13</sup>CNMR (b) and <sup>19</sup>FNMR (c) spectra of 3gb.



Figure S11. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3hb.



Figure S12. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3ib.



Figure S13. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3jb.



Figure S14. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3kb.





Figure S15. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3lb/3lb'.



Figure S16. The  $^{1}$ HNMR (a) and  $^{13}$ CNMR (b) spectra of 3mb.



Figure S17. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3nb.



Figure S18. The  $^{1}$ HNMR (a) and  $^{13}$ CNMR (b) spectra of 3ob.



Figure S19. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3qb.



Figure S20. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3rb.



<sup>210</sup> 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 **Figure S21**. The <sup>1</sup>HNMR (**a**) and <sup>13</sup>CNMR (**b**) spectra of **3aa**.





Figure S22. The <sup>1</sup>HNMR (a), <sup>13</sup>CNMR (b) and 19FNMR (c) spectra of 3ac.



Figure S23. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3ad.



Figure S24. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3ae.



![](_page_40_Figure_0.jpeg)

) -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 f1 (ppm)

Figure S25. The <sup>1</sup>HNMR (a), <sup>13</sup>CNMR (b) and <sup>19</sup> FNMR spectra of 3af.

![](_page_41_Figure_0.jpeg)

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1 f1 (ppm)

![](_page_42_Figure_0.jpeg)

Figure S26. The <sup>1</sup>HNMR (a), <sup>13</sup>CNMR (b) and <sup>19</sup> FNMR (c) spectra of 3ag.

![](_page_43_Figure_0.jpeg)

Figure S27. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3ah.

![](_page_44_Figure_0.jpeg)

Figure S28. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3ai.

![](_page_45_Figure_0.jpeg)

Figure S29. The <sup>1</sup>HNMR (a) and <sup>13</sup>CNMR (b) spectra of 3aj.