

# Photoredox-catalyzed synthesis of sulfones through deaminative insertion of sulfur dioxide

Xuefeng Wang, Yunyan Kuang, Shengqing Ye,\* and Jie Wu\*

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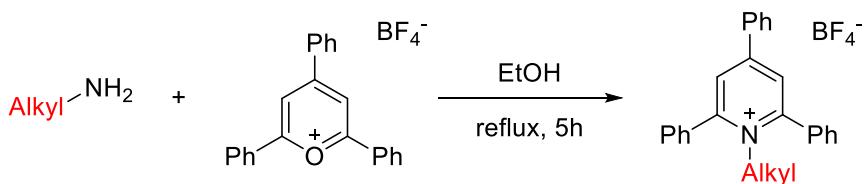
## 1. General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. Dimethyl sulfoxide (DMSO, 99.7%, Extra Dry, with molecular sieves, Water $\leq$ 50 ppm) was purchased from *Energy Chemicals* and used as received. Most alkyl amines and 2,4,6-triphenylpyrylium tetrafluoroborate were purchased from *Bidepharm* and used as received. Flash column chromatography was performed using silica gel (300-400 mesh, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to 254 nm ultraviolet light or iodine stain. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 30–40°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million(ppm) from solvent residual peak on the  $\delta$  scale.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded in Chloroform-*d* on a Bruker DRX-400 spectrometer operating at 400 MHz, 101 MHz and 376 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on Agilent GCQTOF or microTOF Instrument.

## 2. General experimental procedure:

### 2.1 Procedure of synthesis of Katritzky salts

General experimental procedure for the synthesis of 1-alkyl-2,4,6-triphenyl-pyridin-1-i um tetrafluoroborate **1** as reported in *Org. Lett.* **2019**, 218, 2941-2946.

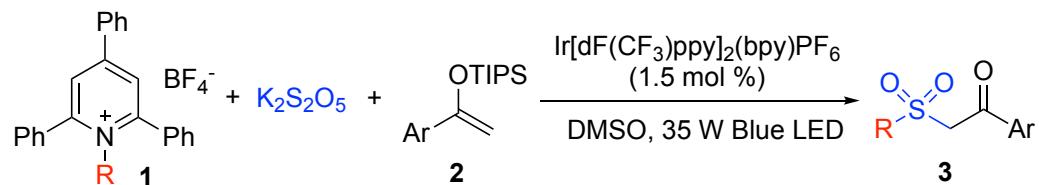


The corresponding alkyl amine (2.4 mmol, 1.2 equiv) was diluted in anhydrous EtOH (2.0 mL) and added to 2,4,6-triphenylpyrylium tetrafluoroborate (2.0 mmol, 792 mg) under N<sub>2</sub>. The mixture was refluxed at 90 °C for 5 hours. After the scheduled time, the mixture was cooled down to 0 °C and diethyl ether (10 mL) was added under vigorous stirring. The precipitates were filtered and washed with diethyl ether to give the Katritzky salts as white to off-white solids. If necessary, the salts could be washed in refluxing EtOAc or recrystallized with EtOH to achieve better purities. When amine

hydrochloride was used, Et<sub>3</sub>N (1.2 equiv.) was added in the reaction and the Katritzky salts were washed with deionized water (5 mL) before purification to remove triethylamine hydrochloride.

## 2.2 Procedure of visible-light induced reaction

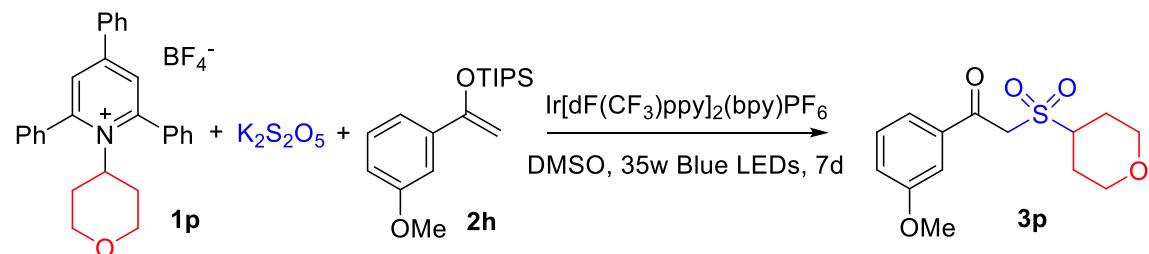
*General experimental procedure for the reaction of 1-alkyl-2,4,6-triphenyl-pyridin-1-ium tetrafluoroborate **1**, K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and triisopropyl((1-arylvinyl)oxy)silane **2**.*



Dimethyl sulfoxide (2.5 mL) was added to a tube containing 1-alkyl-2,4,6-triphenyl-pyridin-1-ium tetrafluoroborate **1** (0.2 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (0.4 mmol, 2.0 equiv) and Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(bpy)PF<sub>6</sub> (0.003 mmol, 1.5 mol %) under Ar atmosphere via a syringe. Silyl enol ether **2** (0.6 mmol, 3.0 equiv) was then added by another microsyringe. The mixture was then exposed to a 35 W blue LED lamp at room temperature (~ 25°C) for 48 hours (as shown next page in Picture 1 and 2). After the scheduled time, the reaction mixture was diluted with water (60 mL) then extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine before dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (EtOAc/n-hexane 1:3) to afford the corresponding product **3**.

## 2.3 Procedure of the gram-scale synthesis

*Experimental procedure for the gram-scale reaction of 2,4,6-triphenyl-1-(tetrahydro-2H-pyran-4-yl)pyridin-1-ium tetrafluoroborate **1p**, K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and triisopropyl((1-(3-methoxyphenyl)vinyl)oxy)silane **2h**.*

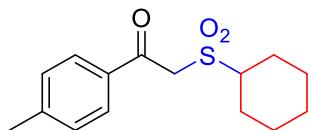


Dimethyl sulfoxide (25.0 mL) was added to a flask (50 mL) containing 2,4,6-triphenyl-1-(tetrahydro-2*H*-pyran-4-yl)pyridin-1-ium tetrafluoroborate **1p** (2.0 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (4.0 mmol, 2.0 equiv) and Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(bpy)PF<sub>6</sub> (0.03 mmol, 1.5 mol %) under Ar atmosphere via a syringe. Triisopropyl((1-(*p*-tolyl)vinyl)oxy)silane **2h** (6.0 mmol, 3.0 equiv.) was then added by another syringe. The mixture was then exposed to a 35 W blue LED lamp at room temperature (20 – 25°C) for 7d. After the scheduled time, the reaction mixture was diluted with water (200 mL) then extracted with EtOAc (100 mL × 4). The organic phases were combined and washed with brine for two times before dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 25% EtOAc/Hexanes) to afford the corresponding product **3p** (362 mg, 61% yield).



**Picture 1 and 2 Photoreactors**

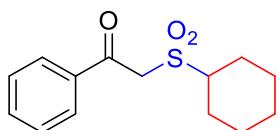
### 3. Characterization data:



2-(Cyclohexylsulfonyl)-1-(*p*-tolyl)ethan-1-one (**3a**)

51.3 mg (92% yield). White Solid. Melting point: 91.2 – 91.8 °C.

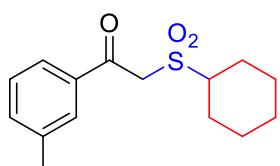
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 4.52 (s, 2H), 3.28 (t, *J* = 12.1 Hz, 1H), 2.42 (s, 3H), 2.21 (d, *J* = 12.0 Hz, 2H), 1.92 (d, *J* = 12.9 Hz, 2H), 1.72 (d, *J* = 12.2 Hz, 1H), 1.59 (q, *J* = 10.8 Hz, 2H), 1.39 – 1.20 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.97, 145.88, 133.58, 129.72, 129.62, 61.34, 56.88, 25.15, 25.03, 24.85, 21.89. HRMS (EI) Calc. for C<sub>15</sub>H<sub>21</sub>O<sub>3</sub>S<sup>+</sup>: 281.1206. Found: 281.1224.



2-(Cyclohexylsulfonyl)-1-phenylethan-1-one (**3b**)

47.2 mg (89% yield). White Solid. Melting point: 87.4 – 88.5 °C.

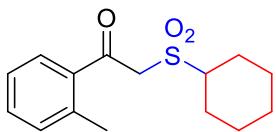
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 4.56 (s, 2H), 3.30 (t, *J* = 12.1 Hz, 1H), 2.23 (d, *J* = 12.2 Hz, 2H), 1.94 (d, *J* = 13.2 Hz, 2H), 1.74 (d, *J* = 12.5 Hz, 1H), 1.66 – 1.56 (m, 2H), 1.40 – 1.21 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.52, 136.04, 134.68, 129.52, 129.09, 61.46, 56.99, 25.19, 25.10, 24.93. HRMS (EI) Calc. for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>S: 266.0977. Found: 266.0974.



2-(Cyclohexylsulfonyl)-1-(*m*-tolyl)ethan-1-one (**3c**)

50.2 mg (90% yield). White Solid. Melting point: 87.8 – 90.2 °C.

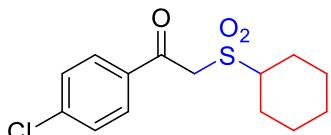
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 4.54 (s, 2H), 3.29 (d, *J* = 12.4 Hz, 1H), 2.41 (s, 3H), 2.20 (d, *J* = 12.1 Hz, 2H), 1.92 (d, *J* = 13.0 Hz, 2H), 1.73 (d, *J* = 12.4 Hz, 1H), 1.64 – 1.54 (m, 2H), 1.38 – 1.21 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.63, 138.92, 136.02, 135.42, 129.81, 128.88, 126.75, 61.33, 56.88, 25.13, 25.02, 24.83, 21.41. HRMS (EI) Calc. for C<sub>15</sub>H<sub>21</sub>O<sub>3</sub>S<sup>+</sup>: 281.1206. Found: 281.1213.



**2-(Cyclohexylsulfonyl)-1-(*o*-tolyl)ethan-1-one (**3d**)**

17.7 mg (32% yield). Colorless oil.

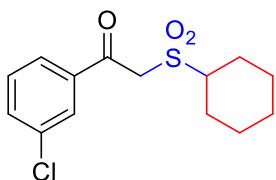
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 4.51 (s, 2H), 3.34 (t, *J* = 12.1 Hz, 1H), 2.55 (s, 3H), 2.23 (d, *J* = 11.8 Hz, 2H), 1.95 (d, *J* = 13.1 Hz, 2H), 1.75 (d, *J* = 12.7 Hz, 1H), 1.67 – 1.60 (m, 2H), 1.43 – 1.27 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.12, 167.20, 133.13, 132.54, 130.60, 126.24, 61.48, 59.02, 25.23, 25.14, 24.91, 21.83. HRMS (EI) Calc. for C<sub>15</sub>H<sub>21</sub>O<sub>3</sub>S<sup>+</sup>: 281.1206. Found: 281.1220.



**2-(Cyclohexylsulfonyl)-1-(4-chlorophenyl)ethan-1-one (**3e**)**

52.8 mg (89% yield). Off-white Solid. Melting point: 106.9 – 109.2 °C.

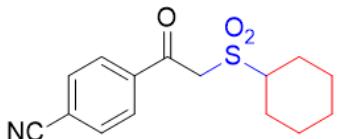
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 4.52 (s, 2H), 3.23 (tt, *J* = 12.2, 3.7 Hz, 1H), 2.20 (d, *J* = 12.0 Hz, 2H), 1.93 (d, *J* = 13.0 Hz, 2H), 1.73 (d, *J* = 12.4 Hz, 1H), 1.59 (q, *J* = 12.3, 11.6 Hz, 2H), 1.32 (dt, *J* = 19.0, 9.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.33, 141.38, 134.33, 130.94, 129.37, 61.57, 57.05, 25.11, 25.03, 24.89. HRMS (EI) Calc. for C<sub>14</sub>H<sub>18</sub>ClO<sub>3</sub>S<sup>+</sup>: 301.0660. Found: 301.0663.



**2-(Cyclohexylsulfonyl)-1-(3-chlorophenyl)ethan-1-one (**3f**)**

54.7 mg (90% yield). Off-white Solid. Melting point: 96.1 – 97.8 °C.

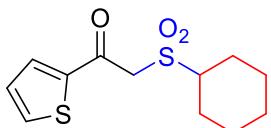
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 4.53 (s, 2H), 3.24 (t, *J* = 12.1 Hz, 1H), 2.20 (d, *J* = 11.9 Hz, 2H), 1.93 (d, *J* = 13.0 Hz, 2H), 1.73 (d, *J* = 12.5 Hz, 1H), 1.64 – 1.53 (m, 2H), 1.39 – 1.20 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.40, 137.45, 135.42, 134.49, 130.34, 129.28, 127.76, 61.59, 57.01, 25.10, 25.02, 24.87. HRMS (EI) Calc. for C<sub>14</sub>H<sub>18</sub>ClO<sub>3</sub>S<sup>+</sup>: 301.0660. Found: 301.0665.



**4-(2-(Cyclohexylsulfonyl)acetyl)benzonitrile (3g)**

Get 39.6 mg (68% yield). White solid. Melting point: 114.4 – 114.8 °C.

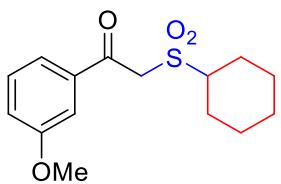
<sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.13 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 4.57 (s, 2H), 3.20 (t, *J* = 12.0 Hz, 1H), 2.21 (d, *J* = 12.1 Hz, 2H), 1.95 (d, *J* = 13.0 Hz, 2H), 1.75 (d, *J* = 12.4 Hz, 1H), 1.64 – 1.55 (m, 2H), 1.38 – 1.24 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-d) δ 188.46, 138.79, 132.79, 129.95, 117.71, 117.69, 61.87, 57.28, 25.08, 25.03, 24.94. HRMS(ESI) Calc. for C<sub>15</sub>H<sub>21</sub>O<sub>4</sub>S<sup>+</sup>: 292.1002. Found: 292.0998.



**2-(Cyclohexylsulfonyl)-1-(thiophen-2-yl)ethan-1-one (3h)**

49.6 mg (91% yield). Off-white Solid. Melting point: 95.0 – 96.1 °C.

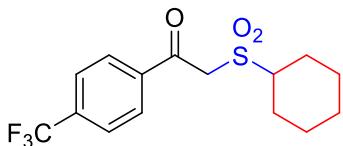
<sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.87 (d, *J* = 3.0 Hz, 1H), 7.79 (d, *J* = 4.7 Hz, 1H), 7.20 (t, *J* = 3.6 Hz, 1H), 4.46 (s, 2H), 3.28 (t, *J* = 12.1 Hz, 1H), 2.22 (d, *J* = 12.2 Hz, 2H), 1.93 (d, *J* = 12.9 Hz, 2H), 1.73 (d, *J* = 12.2 Hz, 1H), 1.60 (q, *J* = 12.2 Hz, 2H), 1.39 – 1.21 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-d) δ 181.59, 143.46, 136.90, 135.66, 128.99, 61.37, 58.07, 25.16, 25.05, 24.91. HRMS (ESI) Calc. for C<sub>12</sub>H<sub>16</sub>NaO<sub>3</sub>S<sub>2</sub>: 295.0433. Found: 295.0445.



**2-(Cyclohexylsulfonyl)-1-(3-methoxyphenyl)ethan-1-one (3i)**

55.1 mg (93% yield). Colorless oil.

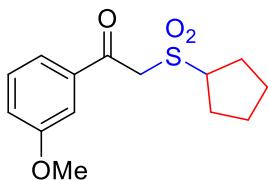
<sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.51 (s, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 4.54 (s, 2H), 3.85 (s, 3H), 3.29 (t, *J* = 12.1 Hz, 1H), 2.21 (d, *J* = 12.2 Hz, 2H), 1.93 (d, *J* = 13.1 Hz, 2H), 1.73 (d, *J* = 12.4 Hz, 1H), 1.59 (q, *J* = 12.5 Hz, 2H), 1.38 – 1.22 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-d) δ 189.31, 160.06, 137.28, 130.03, 122.33, 121.43, 113.08, 61.45, 57.03, 55.61, 25.14, 25.04, 24.86. HRMS (EI) Calc. for C<sub>15</sub>H<sub>20</sub>O<sub>4</sub>S: 296.1082. Found: 296.1082.



**2-(Cyclohexylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**3j**)**

55.4 mg (83% yield). Off-white Solid. Melting point: 110.2 – 113.9 °C.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.9 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 4.58 (s, 2H), 3.23 (t, *J* = 12.0 Hz, 1H), 2.22 (d, *J* = 12.0 Hz, 2H), 1.95 (d, *J* = 12.9 Hz, 2H), 1.75 (d, *J* = 12.4 Hz, 1H), 1.60 (q, *J* = 12.1 Hz, 2H), 1.40 – 1.22 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.78, 138.57, 135.66 (d, *JF* = 33.1 Hz), 129.92, 126.08 (q, *JF* = 3.6 Hz), 123.46 (q, *JF* = 274.0 Hz), 61.78, 57.28, 25.11, 25.05, 24.94. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -63.34. HRMS (ESI) Calc. for C<sub>15</sub>H<sub>17</sub>F<sub>3</sub>NaO<sub>4</sub>S: 357.0743. Found: 357.0755.

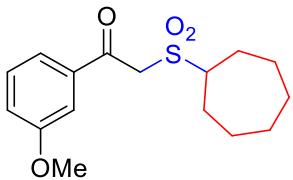


**2-(Cyclopentylsulfonyl)-1-(3-methoxyphenyl)ethan-1-one (**3k**)**

55.2 mg (96% yield). Colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.52 (s, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 4.54 (s, 2H), 3.85 (s, 3H), 3.77 (p, *J* = 8.0 Hz, 1H), 2.09 (dh, *J* = 13.4, 6.7 Hz, 4H), 1.87 – 1.78 (m, 2H), 1.72 – 1.62 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.12, 160.08, 137.24, 130.04, 122.39, 121.42, 113.17, 61.97, 59.24, 55.62, 26.95, 26.17. HRMS (EI) Calc. for C<sub>14</sub>H<sub>18</sub>O<sub>4</sub>S: 282.0926. Found: 282.0926.

Found: 282.0926.

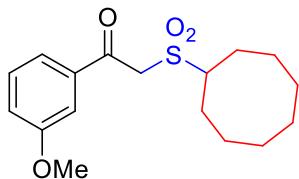


**2-(Cycloheptylsulfonyl)-1-(3-methoxyphenyl)ethan-1-one (**3l**)**

57.9 mg (94% yield). Colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.51 (s, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 4.56 (s, 2H), 3.84 (s, 3H), 3.38 (hept, *J* = 4.4 Hz, 1H), 2.30 – 2.21 (m, 2H), 1.91 – 1.78 (m, 4H), 1.63 – 1.49 (m, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.27, 160.05, 137.27, 130.02, 122.35, 121.43, 113.06, 63.24,

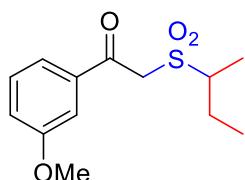
57.37, 55.60, 28.21, 26.55, 25.87. HRMS (EI) Calc. for C<sub>16</sub>H<sub>22</sub>O<sub>4</sub>S: 310.1239. Found: 310.1238.



**2-(Cyclooctylsulfonyl)-1-(3-methoxyphenyl)ethan-1-one (**3m**)**

51.2 mg (80% yield). Off-white Solid. Melting point: 61.9 – 63.4 °C.

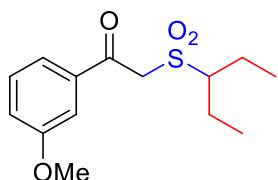
<sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.52 (s, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 4.55 (s, 2H), 3.85 (s, 3H), 3.49 (t, *J* = 9.3 Hz, 1H), 2.24 – 2.19 (m, 2H), 1.86 – 1.79 (m, 4H), 1.64 – 1.51 (m, 8H). <sup>13</sup>C NMR (101 MHz, Chloroform-d) δ 189.30, 160.10, 137.37, 130.06, 122.41, 121.50, 113.07, 62.29, 57.20, 55.65, 26.40, 26.13, 25.60, 25.16. HRMS (EI) Calc. for C<sub>17</sub>H<sub>24</sub>O<sub>4</sub>S: 324.1395. Found: 324.1396.



**2-(sec-Butylsulfonyl)-1-(3-methoxyphenyl)ethan-1-one (**3n**)**

38.0 mg (71% yield). Colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.51 (s, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 4.56 (dd, *J* = 24.0, 14.4 Hz, 2H), 3.85 (s, 3H), 3.30 (broad, 1H), 2.14 – 2.07 (m, 1H), 1.62 (dp, *J* = 15.5, 7.7 Hz, 1H), 1.43 (d, *J* = 6.8 Hz, 3H), 1.06 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-d) δ 189.23, 160.04, 137.23, 130.03, 122.32, 121.40, 113.09, 59.62, 57.43, 55.59, 21.91, 12.21, 11.06. HRMS (EI) Calc. for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub>S: 270.0926. Found: 270.0921.

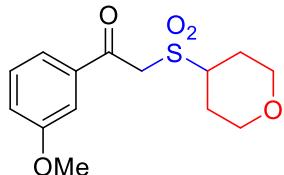


**1-(3-Methoxyphenyl)-2-(pentan-3-ylsulfonyl)ethan-1-one (**3o**)**

35.7 mg (63% yield). Colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.52 (s, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 4.56 (s, 2H), 3.86 (s, 3H), 3.24 – 3.18 (m, 1H),

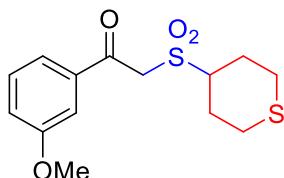
2.01 (dp,  $J = 13.2, 7.3$  Hz, 2H), 1.86 (dp,  $J = 14.7, 7.3$  Hz, 2H), 1.10 (t,  $J = 7.5$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  189.32, 160.11, 137.36, 130.07, 122.39, 121.49, 113.11, 64.87, 58.50, 55.65, 20.02, 11.07. HRMS (EI) Calc. for  $\text{C}_{13}\text{H}_{18}\text{O}_4\text{S}$ : 284.1082. Found: 284.1077.



**1-(3-Methoxyphenyl)-2-((tetrahydro-2H-pyran-4-yl)sulfonyl)ethan-1-one (**3p**)**

58.2 mg (97% yield). White Solid. Melting point: 123.4 – 124.2 °C.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.59 (d,  $J = 7.6$  Hz, 1H), 7.51 (s, 1H), 7.44 (t,  $J = 7.9$  Hz, 1H), 7.20 (d,  $J = 8.2$  Hz, 1H), 4.55 (s, 2H), 4.13 (d,  $J = 10.5$  Hz, 2H), 3.86 (s, 3H), 3.59 (tt,  $J = 10.4, 4.1$  Hz, 1H), 3.45 (t,  $J = 11.4$  Hz, 2H), 2.11 – 1.95 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  189.29, 160.18, 137.13, 130.17, 122.38, 121.65, 113.18, 66.45, 58.39, 56.98, 55.67, 24.89. HRMS (EI) Calc. for  $\text{C}_{14}\text{H}_{18}\text{O}_5\text{S}$ : 298.0875. Found: 298.0871.

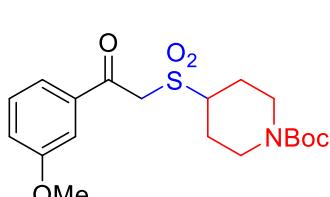


**1-(3-Methoxyphenyl)-2-((tetrahydro-2H-thiopyran-4-yl)sulfonyl)ethan-1-one (**3q**)**

28.7 mg (46% yield). Light yellow oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.58 (d,  $J = 7.6$  Hz, 1H), 7.50 (s, 1H), 7.43 (t,  $J = 7.9$  Hz, 1H), 7.19 (d,  $J = 8.1$  Hz, 1H), 4.56 (s, 2H), 3.86 (s, 3H), 3.35 (t,  $J = 11.8$  Hz, 1H), 2.81 – 2.70 (m, 4H), 2.53 (d,  $J = 12.8$  Hz, 2H), 2.00 (qd,  $J = 12.4, 4.0$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  189.21, 160.15, 137.12, 130.14, 122.33, 121.60, 113.15, 61.01, 56.86, 55.66, 27.51, 26.28. HRMS (EI) Calc. for  $\text{C}_{14}\text{H}_{18}\text{O}_4\text{S}_2$ : 314.0647.

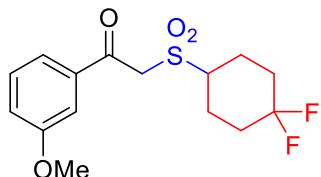
Found: 314.0644.



**tert-Butyl 4-((2-(3-methoxyphenyl)-2-oxoethyl)sulfonyl)piperidine-1-carboxylate (**3r**)**

60.8 mg (78% yield). Off-white crystalline solid. Melting point: 118.8 – 119.9 °C.

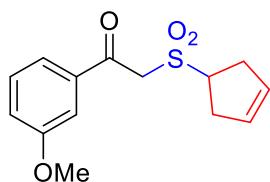
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.50 (s, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 4.56 (s, 2H), 4.29 (broad, 2H), 3.85 (s, 3H), 3.49 (t, *J* = 12.0 Hz, 1H), 2.78 (broad, 2H), 2.12 (d, *J* = 12.3 Hz, 2H), 1.80 (qd, *J* = 12.4, 4.2 Hz, 2H), 1.45 (s, 9H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.26, 160.15, 154.40, 137.09, 130.15, 122.33, 121.63, 113.14, 80.31, 59.46, 57.17, 55.65, 28.49, 24.34. HRMS (ESI) Calc. for C<sub>19</sub>H<sub>27</sub>NNaO<sub>6</sub>S: 420.1451. Found: 420.1458.



**2-((4,4-Difluorocyclohexyl)sulfonyl)-1-(3-methoxyphenyl)ethan-1-one (3s)**

53.5 mg (81% yield). White powder. Melting point: 130.5 – 134.9 °C.

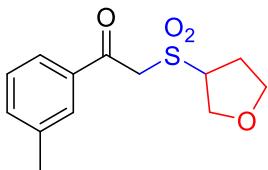
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.51 (s, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 4.59 (s, 2H), 3.87 (s, 3H), 3.42 (t, *J* = 11.5 Hz, 1H), 2.39 – 2.24 (m, 4H), 2.05 (q, *J* = 12.8, 11.8 Hz, 2H), 1.93 – 1.77 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.27, 160.20, 137.05, 130.21, 122.34, 121.68, 113.21, 58.40, 57.65, 55.68, 32.19 (*t*, *J*<sub>F</sub> = 25.2 Hz), 21.81, 21.71. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -94.34 (d, *J* = 239.4 Hz), -101.80 (dt, *J* = 240.3, 31.6 Hz). HRMS (EI) Calc. for C<sub>15</sub>H<sub>18</sub>F<sub>2</sub>O<sub>4</sub>S: 332.0894. Found: 332.0889.



**2-(Cyclopent-3-en-1-ylsulfonyl)-1-(3-methoxyphenyl)ethan-1-one (3t)**

32.9 mg (59% yield). Light yellow oil.

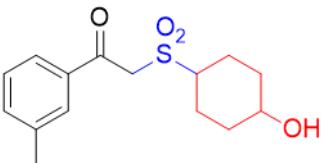
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.42 (s, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 5.61 (s, 2H), 4.45 (s, 2H), 4.01 (p, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 2.85 (dd, *J* = 15.8, 6.4 Hz, 2H), 2.72 (dd, *J* = 15.6, 9.7 Hz, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.93, 160.12, 137.22, 130.08, 128.39, 122.42, 121.51, 113.20, 59.97, 58.87, 55.64, 33.66. HRMS (EI) Calc. for C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>S: 280.0769. Found: 280.0769.



**1-(*m*-Tolyl)-2-((tetrahydrofuran-3-yl)sulfonyl)ethan-1-one (**3u**)**

36.3 mg (68% yield). White powder. Melting point: 132.3 – 132.5 °C.

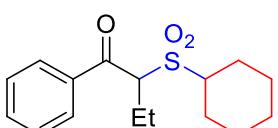
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 6.6 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 4.58 (s, 2H), 4.26 – 4.21 (m, 1H), 4.15 – 4.07 (m, 2H), 4.00 (q, *J* = 7.3 Hz, 1H), 3.86 (q, *J* = 7.3 Hz, 1H), , 2.48 – 2.41 (m, 1H), 2.44 (s, 3H), 2.38 – 2.32 (m, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.11, 139.18, 135.80, 129.93, 129.07, 126.89, 68.57, 67.31, 61.72, 59.68, 27.53, 21.49. HRMS (EI) Calc. for C<sub>13</sub>H<sub>17</sub>O<sub>4</sub>S<sup>+</sup>: 269.0842. Found: 269.0844.



**2-((4-Hydroxycyclohexyl)sulfonyl)-1-(*m*-tolyl)ethan-1-one (**3v**)**

Get 44.3 mg (75% yield). Colorless oil. 1:1 mixture of two isomers.

<sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>) δ 7.92 – 7.89 (m, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 4.84 (s, 1H), 4.82 (s, 1H), 4.02 (s, 0.5H), 3.86 (d, *J* = 3.2 Hz, 0.5H), 3.67 (s, 0.5H), 3.59 – 3.54 (m, 0.5H), 3.37 – 3.26 (m, 1H), 2.42 (s, 3H), 2.24 (d, *J* = 12.7 Hz, 1H), 2.12 – 2.04 (m, 2H), 1.98 – 1.91 (m, 2H), 1.61 (t, *J* = 12.9 Hz, 2H), 1.36 – 1.28 (m, 1H). <sup>13</sup>C NMR (101 MHz, Acetone-*d*<sub>6</sub>) δ 190.57, 190.50, 139.46, 139.44, 137.53, 137.48, 135.63, 135.59, 130.51, 129.51, 127.45, 69.30, 64.29, 61.82, 61.32, 57.93, 57.60, 34.63, 32.14, 24.10, 21.26, 19.59. HRMS(ESI) Calc. for C<sub>15</sub>H<sub>21</sub>O<sub>4</sub>S<sup>+</sup>: 297.1155. Found: 297.1149.



**2-(Cyclohexylsulfonyl)-1-phenylbutan-1-one (**3w**)**

21.7 mg (37% yield). Colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 3.98 – 3.88 (m, 1H), 3.72 (dd, *J* = 17.7, 2.7 Hz, 1H), 3.21 (dd, *J* = 18.0, 9.3 Hz, 1H), 3.02 (t, *J* = 12.1 Hz, 1H), 2.22 (d, *J* = 13.8 Hz, 1H), 2.12 (d, *J* = 12.4 Hz, 1H), 1.95 (t, *J* = 11.6 Hz, 2H), 1.74 (d, *J* = 9.3 Hz, 1H), 1.68 – 1.59 (m, 2H),

1.43 (d,  $J = 6.7$  Hz, 3H), 1.35 – 1.27 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  196.27, 133.90, 128.95, 128.32, 58.35, 49.68, 37.40, 25.78, 25.28, 25.24, 25.23, 24.03, 14.67. HRMS (ESI) Calc. for  $\text{C}_{16}\text{H}_{22}\text{NaO}_3\text{S}$ : 317.1182. Found: 317.1189.

**4.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra of compounds 3.**

