Supporting Information

Catalytic and Direct Methyl Sulfonylation of Alkenes and Alkynes Using Methyl Sulfonyl Radical Generated from DMSO, Dioxygen and Copper System

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**General methods:**

All reactions were carried out in flame or oven-dried glassware under nitrogen atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel 60 (230 – 400 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining with base solution of potassium permanganate and molybdate. NMR spectra were recorded at RT on 400 MHz Bruker spectrometers. The residual solvent signals were taken as the reference (0.00 ppm for $^1$H NMR spectra and 77.0 ppm for $^{13}$C NMR spectra in CDCl$_3$). Chemical shift ($\delta$) is reported in ppm, coupling constants ($J$) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, q = quartet and br = broad signal. HRMS (ESI) spectra were recorded on a Waters Q-Tof premierTM mass spectrometer.

**Materials:** All solvents were distilled under nitrogen atmosphere from the following drying agents immediately before use: THF was distilled from Na powder, CH$_3$CN was distilled from P$_2$O$_5$. 


Detail Screening Reaction Conditions:

Table-1 Optimization of reaction conditions for β-keto methyl sulfones

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Additive</th>
<th>Temp.</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>FeCl₂ (10%)/H₂O₂ (10. Eq.)</td>
<td>D-1 (20%)</td>
<td>90</td>
<td>15%</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>CuBr (10%)/H₂O₂ (10. Eq.)</td>
<td>D-1 (20%)</td>
<td>90</td>
<td>27%</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-1 (20%)</td>
<td>90</td>
<td>24%</td>
</tr>
<tr>
<td>4</td>
<td>DCE</td>
<td>CuBr (10%)</td>
<td>D-2 (2.0 eq.)</td>
<td>90</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>DMF</td>
<td>CuBr (10%)</td>
<td>D-2 (2.0 eq.)</td>
<td>90</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>ToF</td>
<td>CuBr (10%)</td>
<td>D-2 (2.0 eq.)</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>ACN</td>
<td>CuBr (10%)</td>
<td>D-2 (2.0 eq.)</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-2 (2.0 eq.)</td>
<td>90</td>
<td>52</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>CuBr (5%)</td>
<td>D-2 (2.0 eq.)</td>
<td>90</td>
<td>47</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>-</td>
<td>D-2 (2.0 eq.)</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>Pyridine (2.0 eq.)</td>
<td>90</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>CuBr (20%)</td>
<td>D-2 (2.0 eq.)</td>
<td>90</td>
<td>42</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-2 (2.0 eq.)</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-2 (2.0 eq.)</td>
<td>70</td>
<td>48</td>
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<tr>
<td>15</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-2 (2.0 eq.)</td>
<td>110</td>
<td>45</td>
</tr>
<tr>
<td>16</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-2 (2.0 eq.)</td>
<td>90</td>
<td>86(82%)</td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-2 (2.0 eq.)</td>
<td>90</td>
<td>71</td>
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<tr>
<td>18</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-2 (1.5 eq.)</td>
<td>90</td>
<td>50</td>
</tr>
<tr>
<td>19</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-2 (0.5 eq.)</td>
<td>90</td>
<td>15</td>
</tr>
<tr>
<td>20</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>-</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>21</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-3 (3.0 eq.)</td>
<td>90</td>
<td>75</td>
</tr>
<tr>
<td>22</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-4 (3.0 eq.)</td>
<td>90</td>
<td>80</td>
</tr>
<tr>
<td>23</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-5 (3.0 eq.)</td>
<td>90</td>
<td>64</td>
</tr>
<tr>
<td>24</td>
<td>2</td>
<td>CuBr (10%)</td>
<td>D-6 (3.0 eq.)</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>CuCl (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>25</td>
</tr>
<tr>
<td>26</td>
<td>2</td>
<td>CuI (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>55</td>
</tr>
<tr>
<td>27</td>
<td>2</td>
<td>Cu(OTf₂).Benzene (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>77</td>
</tr>
<tr>
<td>28</td>
<td>2</td>
<td>Cu(OAc) (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>54</td>
</tr>
<tr>
<td>29</td>
<td>2</td>
<td>CuCN (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>47</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
<td>CuTC (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>73</td>
</tr>
<tr>
<td>31</td>
<td>2</td>
<td>Cu(OTf₂) (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>36</td>
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<tr>
<td>32</td>
<td>2</td>
<td>Cu(hfacac) (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>52</td>
</tr>
<tr>
<td>33</td>
<td>2</td>
<td>Cu₃O (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>69</td>
</tr>
<tr>
<td>34</td>
<td>2</td>
<td>Cu(OAc)₂ (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>64</td>
</tr>
</tbody>
</table>
CuBr₂ (10%)  D-2 (3.0 eq.)  90  28
                        
FeBr₂ (10%)  D-2 (3.0 eq.)  90  -
                        
NiCl₂ (10%)  D-2 (3.0 eq.)  90  -
                        
CoBr₂ (10%)  D-2 (3.0 eq.)  90  -
                        
CuBr (10%)  D-2 (3.0 eq.)  90  73
                        
CuBr₂ (2.5 %)/FeBr₃ (5 %)  -  55  -

**Conditions:** 1 (0.25 mmol, 28.6 μL), catalyst and additive were stirred in 1 mL DMSO under 1 atm. O₂ balloon for about 12h. GC yields. 5 mmol DMSO in 1 mL referred solvent. Lei’s condition. Isolated yield. D-1:1,10-phenanthroline D-2: HPO(OEt)₂; D-3: HPO(OMe)₂; D-4: HP(O₂Bu)₂; D-5: HPO(₂Bu)₂; D-6: HPO(₂Ph). 1 atm. air balloon. Ji’s condition

**Table-2 Optimization reaction conditions for (E)-vinyl methyl sulfones**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additives</th>
<th>Temp.</th>
<th>GC Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuBr(10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>64</td>
</tr>
<tr>
<td>2</td>
<td>CuBr(10%)</td>
<td>-</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>CuBr (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>CuBr (10%)</td>
<td>D-2 (4.0 eq.)</td>
<td>90</td>
<td>53</td>
</tr>
<tr>
<td>5</td>
<td>Cu(OTf)(10%), Benzene</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>Cu(OAc)(10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>CuCN(10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>54</td>
</tr>
<tr>
<td>8</td>
<td>CuTC(10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>27</td>
</tr>
<tr>
<td>9</td>
<td>CuCl</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>28</td>
</tr>
<tr>
<td>10</td>
<td>CuI (10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>43</td>
</tr>
<tr>
<td>11</td>
<td>Cu(OTf)₂(10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>39</td>
</tr>
<tr>
<td>12</td>
<td>Cu(OAc)₂(10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>90</td>
<td>51</td>
</tr>
<tr>
<td>13</td>
<td>CuBr(10%)</td>
<td>D-4 (3.0 eq.)</td>
<td>90</td>
<td>60</td>
</tr>
<tr>
<td>14</td>
<td>CuBr(10%)</td>
<td>D-6 (3.0 eq.)</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>CuBr(10%)</td>
<td>D-2 (3.0 eq.)</td>
<td>120</td>
<td>75</td>
</tr>
<tr>
<td>16</td>
<td>CuBr(10%)</td>
<td>D-2 (3.0 eq.)+TEA</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>CuBr(10%)</td>
<td>D-2 (3.0 eq.)+HOAc</td>
<td>120</td>
<td>45</td>
</tr>
<tr>
<td>18</td>
<td>CuBr(10%)</td>
<td>D-2 (3.0 eq.)+Ag(OTf)</td>
<td>120</td>
<td>54</td>
</tr>
<tr>
<td>19</td>
<td>CuBr(10%)</td>
<td>D-2 (3.0 eq.)+NiCl₂</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>CuBr(10%)</td>
<td>D-2 (3.0 eq.)+ZnBr₂</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>21</td>
<td>CuBr(10%)</td>
<td>D-2 (3.0 eq.)+FeBr₃</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>CuBr(10%)</td>
<td>D-2 (3.0 eq.)+H₂O (10 eq.)</td>
<td>120</td>
<td>88 (85°)</td>
</tr>
<tr>
<td>23</td>
<td>CuBr(10%)</td>
<td>D-2 (3.0 eq.)+H₂O (20 eq.)</td>
<td>120</td>
<td>83</td>
</tr>
</tbody>
</table>

**Conditions:** 1 (0.25 mmol, 27.5 μL), catalyst and additive were stirred in 1 mL DMSO under 1 atm. O₂ balloon for about 24h. GC yields. 3.0 eq. *20 mol%. Isolated yield. D-2: HPO(OEt)₂; D-3: HPO(OMe)₂; D-4: HP(O₂Bu)₂; D-5: HPO(₂Bu)₂; D-6: HPO(₂Ph).
Mechanism study:

1. Styrene reacted with dimethyl sulfone:

\[
\text{Ph} + \text{Me-S-O-Me} \xrightarrow{\text{CuBr/O}_2} \text{Ph-S-O-Me}
\]

A mixture of alkene 1a (0.25 mmol, 28.6 μL), dimethyl sulfone 4 (5 mmol, 470.5 mg), HPO(OEt)\(_2\) (0.75 mmol, 96.6 μL) and CuBr (0.025 mmol, 3.6 mg) in 0.1 mL DCE in an oven-dried tube, which was stirred at 90 °C under 1 atm O\(_2\) atmosphere for 24h. After cooling down, the reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with Na\(_2\)SO\(_4\), the mixture was concentrated under reduced pressure to give the crude material, there is no product was detected by GC analysis.

2. Keto phosphonate reacted with DMSO:

\[
\text{Ph-PO(OEt)}_2 + \text{Me-S-O-Me} \xrightarrow{\text{CuBr/O}_2} \text{Ph-S-O-Me}
\]

A mixture of phosphonate 5 (0.25 mmol, 64 mg), HPO(OEt)\(_2\) (0.75 mmol, 96.6 μL) and CuBr (0.025 mmol, 3.6 mg) in 1 mL DMSO in an oven-dried tube, which was stirred at 90 °C under 1 atm O\(_2\) atmosphere for 24h. After cooling down, the reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with Na\(_2\)SO\(_4\), the mixture was concentrated under reduced pressure to give the crude material, there is no product was detected by GC analysis.

3. Styrene reacted with DMSO with D-labeling of dibutyl phosphite:

\[
\text{Ph} + \text{Me-S-O-Me} \xrightarrow{\text{CuBr/O}_2} \text{Ph-S-O-Me} + \text{Ph-S-O-Me} \text{D(D)}
\]

A mixture of alkene 1a (0.25 mmol, 28.6 μL), DPO(O\(^{13}\)Bu)\(_2\) (0.75 mmol, 146.4 mg) and CuBr (0.025 mmol, 3.6 mg) in 1 mL DMSO in an oven-dried tube, which was stirred at 90 °C
under O\textsubscript{2} atmosphere for 24h. After cooling down, the reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with Na\textsubscript{2}SO\textsubscript{4}, the mixture was concentrated under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (1:1) to give 3a in 80% isolated yield, there is no D-labeling product 6 was detected.

### 4. Styrene reacted with DMSO within D\textsubscript{2}O

A mixture of alkene 1a (0.25 mmol, 28.6 \( \mu \)L), D\textsubscript{2}O (5 mmol, 100 \( \mu \)L), HPO(OEt\textsubscript{2})\textsubscript{2} (0.75 mmol, 96.6 \( \mu \)L) and CuBr (0.025 mmol, 3.6 mg) in 1 mL DMSO in an oven-dried tube, which was stirred at 90 °C under 1atm. O\textsubscript{2} atmosphere for 24h. After cooling down, the reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with Na\textsubscript{2}SO\textsubscript{4}, the mixture was concentrated under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (1:1) to give 3a in 83% isolated yield, there is no D-labeling product 6 was detected.
General procedure for β-keto methyl sulfones:

A mixture of alkene (0.25 mmol), DMSO 2 (1 mL), HPO(OEt)₂ (0.75 mmol, 96.6 μL) and CuBr (0.025 mmol, 3.6 mg) in an oven-dried tube, which was stirred at 90 °C under 1 atm. O₂ atmosphere until the starting material was fully consumed (12 - 24 h). The reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with Na₂SO₄, the mixture was concentrated under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (1:1) to give desired product.

2-(Methylsulfonyl)-1-phenylethanone (3a):

The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp.104 - 105 °C. Yield: 82%. ¹H NMR (400 MHz, CDCl₃) δ 8.01 - 7.99 (m, 2H), 7.68 - 7.64 (m, 1H), 7.55 - 7.51 (m, 2H), 4.61 (s, 2H), 3.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 189.2, 135.6, 134.6, 129.2, 129.0, 61.2, 41.8; HRMS (ESI) m/z [M+H]⁺: Calcd for C₉H₁₁O₃S: 199.0429. Found: 199.0424.

2-(Methylsulfonyl)-1-phenylethanone (3a’):

The title compound was prepared according to the general procedure with using 1 atm. O₁₈₂ instead of O₂. The product was obtained as white solid, Mp.109 - 110 °C. Yield: 64%. ¹H NMR (400 MHz, CDCl₃) δ 8.01 - 7.99 (m, 2H), 7.68 - 7.64 (m, 1H), 7.55 - 7.51 (m, 2H), 4.61 (s, 2H), 3.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 189.2, 189.2, 135.6, 134.7, 129.2,
129.0, 61.3, 41.8; HRMS (ESI) m/z [M+H]^+: Calcd for C₉H₁₁O₃S: 203.0514. Found: 203.0516.

2-(Methylsulfonyl)-1-phenylethanone (3a”):

The title compound was prepared according to the general procedure with using d-DMSO instead. The product was obtained as white solid, Mp.114 - 115 °C. Yield: 76%. ¹H NMR (400 MHz, CDCl₃) δ 8.02 - 7.99 (m, 2H), 7.68 - 7.64 (m, 1H), 7.55 - 7.51 (m, 2H), 4.61 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 189.2, 135.6, 134.7, 129.2, 129.0, 61.2; HRMS (ESI) m/z [M+H]^+: Calcd for C₉H₈D₃O₃S: 202.0617. Found: 202.0617.

2-(Methylsulfonyl)-1-(p-tolyl)ethanone (3b):

The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 116 - 117 °C. Yield: 84%. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 4.57 (s, 2H), 3.14 (s, 3H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 188.7, 146.0, 135.6, 134.7, 129.2, 129.0, 61.2; HRMS (ESI) m/z [M+H]^+: Calcd for C₁₀H₁₃O₃S: 213.0585. Found: 213.0591.

Ethyl 2-isopropyl-6-phenylnicotinate (3c):

The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 65 - 66 °C. Yield: 77%. ¹H NMR (400 MHz, CDCl₃) δ 7.81 - 7.89 (m, 2H), 7.48 - 7.39 (m, 2H), 4.59 (m, 2H), 3.15 (s, 3H), 2.44 (s, 3H); ¹³C NMR (100
MHz, CDCl$_3$) $\delta$ 189.4, 139.0, 135.7, 135.5, 129.6, 128.9, 126.5, 61.3, 41.8, 21.3; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{10}$H$_{13}$O$_3$S: 213.0585. Found: 213.0578.

2-(Methylsulfonyl)-1-(o-tolyl)ethanone (3d):

![Structure](image)

The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 80%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J$ = 8.0 Hz, 1H), 7.49 - 7.45 (m, 1H), 7.36 - 7.29 (m, 2H), 4.56 (m, 2H), 3.17 (s, 3H), 2.56 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.6, 140.1, 135.7, 133.1, 132.5, 130.2, 126.1, 63.4, 42.0, 21.6; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{10}$H$_{13}$O$_3$S: 213.0585. Found: 213.0578.

1-Mesityl-2-(methylsulfonyl)ethanone (3e):

![Structure](image)

The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 136 - 137 ºC. Yield: 43%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.88 (s, 2H), 4.34 (d, $J$ = 0.8 Hz, 2H), 3.23 (s, 3H), 2.29 (s, 3H), 2.28 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.9, 140.5, 137.1, 133.9, 129.2, 65.6, 42.6, 21.1, 19.6; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{12}$H$_{17}$O$_3$S: 241.0898. Found: 241.0899.

1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethanone (3f):

![Structure](image)

The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 74%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J$ = 8.8 Hz, 2H), 7.53 (d, $J$ = 8.8 Hz, 2H), 4.58 (s, 2H), 3.14 (s, 3H), 1.35 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 188.7, 158.9, 133.1, 129.3, 126.0, 61.2, 41.7, 35.3, 30.9; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{13}$H$_{19}$O$_3$S: 255.1055. Found: 255.1055.
2-(Methylsulfonyl)-1-(naphthalen-2-yl)ethanone (3g):

The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 99 - 100 °C. Yield: 78%. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.52 (s, 1H), 8.04 - 7.93 (m, 2H), 7.91 - 7.87 (m, 2H), 7.67 - 7.57 (m, 2H), 4.73 (s, 2H), 3.19 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 189.1, 136.1, 133.0, 132.3, 132.1, 130.0, 129.5, 129.0, 127.8, 127.3, 123.7, 61.3, 41.8; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{13}$H$_{13}$O$_3$S: 249.0585. Found: 249.0579.

2-(methylsulfonyl)-1-(thiophen-2-yl)ethanone (3h):

The title compound was prepared according to the general procedure. The product was obtained as brown solid, Mp. 121 - 122 °C. Yield: 75%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 - 7.84 (m, 1H), 7.82 - 7.81 (m, 1H), 7.23 - 7.20 (m, 1H), 4.51 (s, 2H), 3.15 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 181.2, 143.0, 137.0, 135.4, 128.9, 62.3, 41.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_7$H$_9$O$_3$S$_2$: 204.9993. Found: 204.9993.

1-(4-fluorophenyl)-2-(methylsulfonyl)ethanone (3i):

The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 89 - 90 °C. Yield: 74%. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 - 8.04 (m, 2H), 7.22 - 7.18 (m, 2H), 4.58 (s, 2H), 3.15 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 187.6, 168.0, 165.4, 132.2 ($J = 9.8$ Hz), 116.3 ($J_1 = 22.2$ Hz, $J_2 = 1.3$ Hz), 61.4 ($J = 2.8$ Hz), 41.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_9$H$_{10}$O$_3$SF: 217.0335. Found: 217.0337.

1-(4-Chlorophenyl)-2-(methylsulfonyl)ethanone (3j):
The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 149 - 150 °C. Yield: 65%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 - 7.94 (m, 2H), 7.52 - 7.50 (m, 2H), 4.57 (s, 2H), 3.14 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 188.1, 141.5, 133.9, 130.7, 129.4, 61.3, 41.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_9$H$_{10}$O$_3$SCl: 233.0039. Found: 233.0033.

1-(4-Bromophenyl)-2-(methylsulfonyl)ethanone (3k):

The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 160 - 161 °C. Yield: 77%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 - 7.86 (m, 2H), 7.69 - 7.67 (m, 2H), 4.56 (s, 2H), 3.14 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 188.3, 134.3, 132.4, 130.7, 130.4, 61.3, 41.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_9$H$_{10}$O$_3$SBr: 276.9534. Found: 276.9535.

1-(2-(allyloxy)phenyl)-2-(methylsulfonyl)ethanone (3l):

The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 75%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 - 7.81 (m, 1H), 7.55 - 7.51 (m, 1H), 7.07 - 7.03 (m, 1H), 6.99 (d, $J = 8.4$ Hz, 1H), 6.16 - 6.06 (m, 1H), 5.47 - 5.37 (m, 2H), 4.78 (s, 2H), 4.71 - 4.69 (m, 2H), 3.15 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.2, 158.3, 135.5, 131.9, 131.3, 126.4, 121.3, 119.4, 113.1, 69.9, 65.4, 42.4; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{12}$H$_{15}$O$_4$S: 255.0691. Found: 255.0702.

2-(Methylsulfonyl)-1-(4-phenoxyphenyl)ethanone (3m):
The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 124 - 125 °C. Yield: 75%. ^1H NMR (400 MHz, CDCl₃) δ 7.99 - 7.97 (m, 2H), 7.44 - 7.40 (m, 2H), 7.26 - 7.22 (m, 1H), 7.10 - 7.07 (m, 2H), 7.04 - 7.02 (m, 2H), 4.55 (s, 2H), 3.14 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ 187.5, 163.6, 154.8, 131.8, 130.2, 125.1, 120.5, 117.3, 61.2, 41.7; HRMS (ESI) m/z [M+H]^+: Calcd for C₁₅H₁₅O₄S: 291.0691. Found: 291.0686.

1-(4-Methoxyphenyl)-2-(methylsulfonyl)ethanone (3n):

The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 139 - 140 °C. Yield: 68%. ^1H NMR (400 MHz, CDCl₃) δ 7.99 (dd, J₁ = 6.8 Hz, J₂ = 2.4 Hz, 2H), 6.98 (dd, J₁ = 7.2 Hz, J₂ = 2.4 Hz, 2H), 4.55 (s, 2H), 3.89 (s, 3H), 3.13 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ 187.3, 164.8, 131.8, 128.7, 114.2, 61.2, 55.6, 41.7; HRMS (ESI) m/z [M+H]^+: Calcd for C₁₀H₁₃O₄S: 229.0535. Found: 229.0529.

2-(Methylsulfonyl)-1-(3-nitrophenyl)ethanone (3o):

The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 104 - 105 °C. Yield: 66%. ^1H NMR (400 MHz, CDCl₃) δ 8.85 - 8.84 (m, 1H), 8.53 - 8.50 (m, 1H), 8.37 - 8.34 (m, 1H), 7.79 - 7.75 (m, 1H), 4.67 (s, 2H), 3.17 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ 187.5, 148.7, 136.9, 134.7, 130.4, 128.7, 124.1, 61.5, 41.8; HRMS (ESI) m/z [M+H]^+: Calcd for C₁₀H₁₀NO₅S: 244.0280. Found: 244.0285.
Methyl 4-(2-(methylsulfonyl)acetyl)benzoate (3p):

The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 129 - 130 °C. Yield: 52%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 - 8.17 (m, 2H), 8.08 - 8.06 (m, 2H), 4.63 (s, 2H), 3.97 (s, 3H), 3.16 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 188.9, 165.8, 138.6, 135.2, 130.1, 129.2, 61.6, 52.6, 41.8; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{11}$H$_{13}$O$_5$S: 257.0484. Found: 257.0489.

2-(Methylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethanone (3q):

The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 100 - 101 °C. Yield: 81%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J$ = 8.4 Hz, 2H), 7.80 (d, $J$ = 8.0 Hz, 2H), 4.64 (s, 2H), 3.16 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 188.5, 138.2, 135.8 ($J$ = 32.8 Hz), 129.6, 126.1 ($J$ = 3.5 Hz), 123.3 ($J$ = 271.3 Hz), 61.5, 41.8; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{10}$H$_{10}$O$_3$SF$_3$: 267.0303. Found: 267.0311.

2-(Methylsulfonyl)-1-phenylpropan-1-one (3r):

The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 71%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 - 8.02 (m, 2H), 7.68 - 7.64 (m, 1H), 7.55 - 7.51 (m, 2H), 4.96 (q, $J$ = 7.2 Hz, 1H), 2.98 (s, 3H), 1.75 (d, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 194.0, 135.7, 134.5, 129.2, 129.0, 64.0, 36.9, 13.9; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{10}$H$_{13}$O$_3$S: 213.0585. Found: 213.0591.

2-(Methylsulfonyl)-1-phenylpentan-1-one (3r'):
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 50%. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 - 8.02 (m, 2H), 7.67 - 7.63 (m, 1H), 7.55 - 7.51 (m, 2H), 4.87 (dd, $J_1$ = 11.6 Hz, $J_2$ = 3.2 Hz, 1H), 2.96 (s, 3H), 2.32 - 2.15 (m, 2H), 1.38 - 1.32 (m, 2H), 0.93 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 194.2, 136.9, 134.4, 129.1, 129.0, 68.8, 37.2, 31.2, 20.7, 13.8; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{12}$H$_7$O$_3$S: 241.0898. Found: 241.0902.

2-(methylsulfonyl)-2,3-dihydro-$^1$H-inden-1-one (3s):

The title compound was prepared according to the general procedure. The product was obtained as yellow solid. Mp: 157 - 158 °C. Yield: 70%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J$ = 7.6 Hz, 1H), 7.70 - 7.66 (m, 1H), 7.56 - 7.54 (m, 1H), 7.46 - 7.42 (m, 1H), 4.15 (dd, $J_1$ = 8.4 Hz, $J_2$ = 3.6 Hz, 1H), 3.80 (dd, $J_1$ = 18.0 Hz, $J_2$ = 3.6 Hz, 1H), 3.51 (dd, $J_1$ = 18.0 Hz, $J_2$ = 8.4 Hz, 1H), 3.27 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 195.7, 152.5, 136.3, 135.4, 128.4, 126.6, 125.1, 67.0, 40.2, 26.1; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{10}$H$_{11}$O$_3$S: 211.0429. Found: 211.0428.
General procedure for (E)-vinyl methyl sulfones:

A mixture of alkyne compound (0.25 mmol), DMSO 2 (1 mL), HPO(OEt)$_2$ (0.75 mmol, 96.6 μL), H$_2$O (2.5 mmol, 45 μL) and CuBr (0.025 mmol, 3.6 mg) in an oven-dried tube, which was stirred at 120 °C under 1 atm. O$_2$ atmosphere until the starting material was fully consumed. The reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with Na$_2$SO$_4$, the mixture was concentrated under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (1:1) to give desired product.

(E)-(2-(methylsulfonyl)vinyl)benzene (5a):

The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 85%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, $J = 15.2$ Hz, 1H), 7.54 - 7.51 (m, 2H), 7.46 - 7.43 (m, 3H), 6.92 (d, $J = 15.2$ Hz, 1H), 3.04 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.0, 132.0, 131.3, 129.1, 128.5, 126.2, 43.2; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_9$H$_{11}$O$_2$S: 183.0480. Found: 183.0476.

(E)-1-fluoro-4-(2-(methylsulfonyl)vinyl)benzene (5b):

The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 126 - 127 °C. Yield: 82%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, $J = 15.2$ Hz, 1H), 7.54 - 7.51 (m, 2H), 7.15 - 7.10 (m, 2H), 6.86 (d, $J = 15.6$ Hz, 1H), 3.04 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.5 ($J = 251.9$ Hz), 142.7, 130.6 ($J = 34.5$ Hz),
128.3, 125.9, 116.4 ($J = 22.1$ Hz), 43.3; HRMS (ESI) m/z [M+H]$: Calcd for C$_9$H$_{10}$O$_2$SF: 201.0386. Found: 201.0382.

$(E)$-1-(tert-butyl)-4-(2-(methylsulfonyl)vinyl)benzene (5c):

![Chemical structure of 5c](image)

The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 87 - 88 °C. Yield: 79%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 15.2$ Hz, 1H), 7.48 - 7.43 (m, 4H), 6.88 (d, $J = 15.6$ Hz, 1H), 3.03 (s, 3H), 1.33 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.2, 144.0, 129.3, 128.4, 126.1, 125.1, 43.4, 35.0, 31.1; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{13}$H$_{19}$O$_2$S: 239.1106. Found: 239.1104.

$(E)$-1-methyl-2-(2-(methylsulfonyl)vinyl)benzene (5d):

![Chemical structure of 5d](image)

The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 85 -86 °C. Yield: 75%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (d, $J = 15.2$ Hz, 1H), 7.52 - 7.50 (m, 1H), 7.36 - 7.32 (m, 1H), 7.26 - 7.23 (m, 2H), 6.84 (d, $J = 15.2$ Hz, 1H), 3.04 (m, 3H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.7, 138.3, 131.1, 131.0, 127.1, 126.8, 126.6, 43.3, 19.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{10}$H$_{13}$O$_2$S: 197.0636. Found: 197.0639.

$(E)$-1,2,4-trimethyl-5-(2-(methylsulfonyl)vinyl)benzene (5e):

![Chemical structure of 5e](image)

The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 97 - 98 °C. Yield: 54%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 15.2$ Hz, 1H), 7.29 (s, 1H), 7.01 (s, 1H), 6.80 (d, $J = 15.2$ Hz, 1H), 3.03 (s, 3H), 2.38 (s,
3H), 2.25 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.6, 140.5, 135.8, 134.7, 132.4, 128.3, 127.9, 125.5, 43.4, 19.7, 19.2, 19.0; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{12}$H$_7$O$_2$S: 225.0949. Found: 225.0953.

(E)-9-(2-(methylsulfonyl)vinyl)phenanthrene (5f):

![Structure of 5f](image)

The title compound was prepared according to the general procedure. The product was obtained as dark solid, Mp: 122 - 123 °C. Yield: 77%. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.75 (d, J = 8.0 Hz, 1H), 8.68 (d, J = 8.4 Hz, 1H), 8.48 (d, J = 15.2 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.98 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.76 - 7.72 (m, 4H), 7.11 (d, J = 15.2 Hz, 1H), 3.13 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.0, 131.5, 130.8, 130.5, 129.6, 129.4, 129.3, 128.6, 128.3, 127.4, 127.3, 127.3, 124.1, 123.4, 122.7, 43.3; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{17}$H$_{15}$O$_2$S: 283.0793. Found: 283.0799.

(E)-4-(2-(methylsulfonyl)vinyl)benzaldehyde (5g):

![Structure of 5g](image)

The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp: 140 - 141 °C. Yield: 71%. $^1$H NMR (400 MHz, CDCl$_3$) δ 10.06 (s, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 15.2 Hz, 1H), 7.05 (d, J = 15.6 Hz, 1H), 3.07 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 191.2, 142.3, 137.9, 137.6, 130.3, 129.3, 129.1, 43.1; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{10}$H$_{11}$O$_3$S: 211.0429. Found: 211.0425.

(E)-1-(2-(methylsulfonyl)vinyl)-4-(trifluoromethyl)benzene (5h):

![Structure of 5h](image)
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 142 - 143 °C. Yield: 83%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 - 7.63 (m, 5H), 7.02 (d, $J$ = 15.6 Hz, 1H), 3.07 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.2, 135.5, 132.9 ($J$ = 32.5 Hz), 128.9, 128.7, 126.2 ($J$ = 3.7 Hz), 123.6 ($J$ = 270.8 Hz), 43.1; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{10}$H$_{10}$O$_2$SF$_3$: 251.0354. Found: 251.0352.

(E)-1-(2-(methylsulfonyl)vinyl)-4-nitrobenzene (5i):

The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 189 - 190 °C. Yield: 63%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.32 - 8.28 (m, 2H), 7.71 - 7.67 (m, 3H), 7.08 (d, $J$ = 15.6 Hz, 1H), 3.08 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.2, 141.1, 138.1, 130.5, 129.3, 124.4, 43.1; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_9$H$_{10}$NO$_3$: 228.0331. Found: 228.0333.

(E)-1-methoxy-4-(2-(methylsulfonyl)vinyl)benzene (5j):

The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 119 - 120 °C. Yield: 80%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J$ = 15.6 Hz, 1H), 7.47 (dd, $J$_1 = 6.8 Hz, $J$_2 = 2.0 Hz, 2H), 6.94 (dd, $J$_1 = 6.8 Hz, $J$_2 = 2.0 Hz, 2H), 6.76 (d, $J$ = 15.6 Hz, 1H), 3.86 (s, 3H), 3.02 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.2, 143.7, 130.4, 124.7, 123.4, 114.6, 55.5, 43.5; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{10}$H$_{13}$O$_3$S: 213.0585. Found: 213.0583.

(E)-(2-(methylsulfonyl)prop-1-en-1-yl)benzene (5k):
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 75%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (s, 1H), 7.46 - 7.39 (m, 5H), 2.98 (s, 3H), 2.34 (d, $J$ = 1.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.1, 136.8, 133.6, 129.6, 129.5, 128.8, 40.4, 13.4; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{10}$H$_{13}$O$_2$S: 197.0636. Found: 197.0639.

(E)-2-(2-(methylsulfonyl)vinyl)thiophene (5l):

The title compound was prepared according to the general procedure. The product was obtained as brown oil. Yield: 68%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J$ = 15.2 Hz, 1H), 7.48 (d, $J$ = 5.2 Hz, 1H), 7.33 (d, $J$ = 3.6 Hz, 1H), 7.11 - 7.09 (m, 1H), 6.70 (d, $J$ = 15.2 Hz, 1H), 3.03 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.6, 136.5, 132.7, 130.1, 128.4, 124.2, 43.4; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_7$H$_9$O$_2$S$_2$: 189.0044. Found: 189.0047.
Applications of β-keto methyl sulfones:

**(E)-2-(methylsulfonyl)-1,5-diphenylpent-4-en-1-one**

The title compound was prepared according to the following procedure: To a solution of NaH (0.24 mmol, 9.6 mg) in 5 mL THF, 3a (0.20 mmol, 39.6 mg) in 1mL THF solution was added dropwise, the resulted mixture was stirred for 0.5h, then (E)-(3-bromoprop-1-en-1-yl)benzene (0.24 mmol, 47.3 mg) in 1mL THF solution was added at 0 °C. The reaction mixture was allowed at 50 °C for around 6h until the 3a was consumed completely. It quenched with 5mL NH₄Cl, and extracted with ethyl acetate for 3 times. The combined organic lay was concentrated under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (2:1) to give desired product as yellow solid, Mp. 133-135 °C. Yield: 92%. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.6 Hz, 2H), 7.26 - 7.20 (m, 5H), 6.50 (d, J = 15.6 Hz, 1H), 6.03 - 5.95 (m, 1H), 5.00 (dd, J₁ = 10.0 Hz, J₂ = 4.4 Hz, 1H), 3.22 - 3.13 (m, 2H), 3.00 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 193.6, 136.7, 136.3, 134.5, 134.5, 129.2, 129.0, 128.5, 127.8, 126.3, 122.6, 68.7, 37.7, 32.5; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₈H₁₉O₃S: 315.1055. Found: 315.1059.

2-Diazo-2-(methylsulfonyl)-1-phenylethanone:

The title compound was prepared according to the following procedure: 3a (0.20 mmol, 39.6 mg) and tosyl azide (0.24 mmol, 47.3 mg) was added to 5 mL dry CH₃CN, the resulting mixture was cooled at 0 °C. DBU (0.24 mmol, 36.5 mg) was then added dropwisely and the mixture was stirred for around 2h until the 3a was consumed completely based on TLC. The reaction mixture was concentrated directly under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (2:1) to give desired product as yellow oil. Yield: 88%. ¹H NMR (400 MHz, CDCl₃) δ 7.68 - 7.66 (m, 2H), 7.64 - 7.60 (m, 1H), 7.53 - 7.49 (m, 2H), 3.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 183.3, 135.5,
133.4, 129.1, 127.4, 45.0; HRMS (ESI) m/z [M+H]+: Calcd for C₉H₁₀N₂O₃S: 225.0334. Found: 225.0338.

2-Bromo-2-(methylsulfonyl)-1-phenylethanone

\[
\begin{align*}
\text{O} & \quad \text{O} & \quad \text{Br} \\
\text{Me} & \quad \text{KBr} & \quad \text{H}_2\text{O}_2/\text{HOAc} & \quad \text{rt.} \\
\text{O} & \quad \text{O} & \quad \text{Me}
\end{align*}
\]

The title compound was prepared according to the reported procedure. 3a (0.20 mmol, 39.6 mg) and KBr (0.24 mmol, 28.6 mg) was added to 2 mL acetic acid, the resulting mixture was cooled at 0°C. H₂O₂ (1.6 mmol, 48.0 μL) was then added slowly and the mixture was stirred for overnight at room temperature until the 3a was consumed completely based on TLC. The reaction mixture was concentrated directly under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (4:1) to give desired product as white solid, mp. 80-82 °C. Yield: 86%. ¹H NMR (400 MHz, CDCl₃) δ 8.01- 7.98 (m, 2H), 7.72 - 7.68 (m, 1H), 7.57 - 7.53 (m, 2H), 6.00 (s, 1H), 3.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 187.8, 135.1, 133.8, 129.3, 129.2, 55.9, 37.7; HRMS (ESI) m/z [M+H]^+: Calcd for C₉H₁₀BrO₃S: 276.9534. Found: 276.9536.

(2-(Methylsulfonyl)ethyl)benzene

\[
\begin{align*}
\text{O} & \quad \text{O} & \quad \text{Me} \\
\text{Me} & \quad \text{Pd/C, H₂} & \quad \text{EtOH, rt} \\
\text{O} & \quad \text{O} & \quad \text{Me}
\end{align*}
\]

The title compound was prepared according to the following procedure. 3a (0.20 mmol, 36.4 mg) and Pd/C (10%, 4 mg) was added to 2 mL anhydrous ethanol, the resulting mixture was stirred under 1 atm. H₂ balloon for overnight at room temperature until the 3a was consumed completely based on TLC (the product is positive to KMnO₄ solution on TLC). The reaction mixture was concentrated directly under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (2:1) to give desired product as white solid, mp. 88-89 °C. Yield: 95%. ¹H NMR (400 MHz, CDCl₃) δ 7.36 - 7.28 (m, 2H), 7.26 - 7.23 (m, 3H), 3.32 - 3.28 (m, 2H), 3.19 - 3.15 (m, 2H), 2.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 137.4, 129.0, 128.4, 127.1, 56.2, 41.0, 28.6; HRMS (ESI) m/z [M+H]^+: Calcd for C₉H₁₃O₂S: 185.0636. Found: 185.0637.
NMR Spectra for β-keto methyl sulfones

3a

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NMR Spectra for (E)-vinyl methyl sulfones

5a

[Chemical structure image]

5a

[Chemical structure image]
NMR Spectra for transformations of methyl sulfones

![NMR Spectra Diagram](image-url)