Supporting Information

Direct carbonylative difunctional of terminal alkynes with sodium sulfinates to access olefin sulfonyl methyl esters under metal-free conditions

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1 General information

Reagents, solvents and analytical methods:
Unless otherwise noted, all reactions were carried out under a carbon monoxide or nitrogen atmosphere. All reagents were commercially available. All solvents were dried by standard techniques, and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (b. p. 30-60 °C) and ethyl acetate as eluent. $^1$H and $^{13}$C NMR spectra were taken on Bruker AVANCE III 400 MHz spectrometers and CDCl$_3$ ($^1$H NMR $\delta$ 7.26, $^{13}$C NMR $\delta$ 77.0) as solvent. All coupling constants ($J$) are reported in Hz with the following abbreviations: s = singlet, d = doublet, dd = double doublet , t = triplet, dt = double triplet, q = quadruplet, m = multiplet, br = broad. Gas chromatography (GC) analyses were performed on an Agilent HP-7890A instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d. 0.25 μm film thickness) using argon as carrier gas. Gas chromatography mass spectrometer (GC-MS) analyses were performed on an Shimadzu QP2020 NX instrument. High resolution mass spectra (HRMS) were recorded on Agilent 8890-7250 and Agilent Q-TOF 6540.
Because of the high toxicity of carbon monoxide, all of the reactions should be performed in an autoclave. The laboratory should well-equipped with a CO detector and alarm system.

2 Optimization of reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>[I] source</th>
<th>solvent</th>
<th>temperature</th>
<th>CO pressure</th>
<th>Yield %</th>
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<tbody>
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<td>KI (10 mol%)</td>
<td>MeOH (1.6 mL)/H$_2$O (0.4 mL)</td>
<td>110°C</td>
<td>60 bar</td>
<td>trace</td>
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<tr>
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<tr>
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<td>79</td>
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<tr>
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<td>22</td>
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<td>23</td>
<td>KI (1.5 eq.)/[1.5 eq. PhSO₂Na]</td>
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<td>40 bar</td>
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<td>KI (1.1 eq.)</td>
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<td>40 bar</td>
<td>79</td>
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<tr>
<td>26</td>
<td>KI (1.1 eq.)/[K₂S₂O₈ 2.2 eq.]</td>
<td>MeOH (1.6 mL)/H₂O (0.4 mL)</td>
<td>130°C</td>
<td>40 bar</td>
<td>61</td>
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<tr>
<td></td>
<td>Reagents</td>
<td>Solvent</td>
<td>Temperature</td>
<td>Pressure</td>
<td>Yield (%)</td>
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<td>27</td>
<td>KI (1.1 eq.)/[(NH₄)₂S₂O₈ 2.2 eq.]</td>
<td>MeOH (1.6 mL)/H₂O (0.4 mL)</td>
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<td>40 bar</td>
<td>41</td>
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<tr>
<td>28</td>
<td>I₂ (0.5 eq.)</td>
<td>MeOH (1.6 mL)/H₂O (0.4 mL)</td>
<td>130°C</td>
<td>40 bar</td>
<td>72</td>
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<tr>
<td>29</td>
<td>KI (1.1 eq.)/[H₂O₂ 5.0 eq.]</td>
<td>MeOH (1.6 mL)/H₂O (0.4 mL)</td>
<td>130°C</td>
<td>40 bar</td>
<td>ND</td>
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<tr>
<td>30</td>
<td>KI (1.1 eq.)/[Ag₂CO₃ 2.2 eq.]</td>
<td>MeOH (1.6 mL)/H₂O (0.4 mL)</td>
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<td>40 bar</td>
<td>ND</td>
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<td>31</td>
<td>KI (1.1 eq.)/[BQ 2.2 eq.]</td>
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<td>40 bar</td>
<td>ND</td>
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<tr>
<td>32</td>
<td>KI (1.1 eq.)/[Mn(OAc)₃ 2H₂O 2.2 eq.]</td>
<td>MeOH (1.6 mL)/H₂O (0.4 mL)</td>
<td>130°C</td>
<td>40 bar</td>
<td>ND</td>
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<tr>
<td>33</td>
<td>KI (1.1 eq.)/[Oxone 2.2 eq.]</td>
<td>MeOH (1.6 mL)/H₂O (0.4 mL)</td>
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<td>40 bar</td>
<td>20</td>
</tr>
<tr>
<td>34</td>
<td>KI (1.1 eq.)/[PhI(OAc)₂ 2.2 eq.]</td>
<td>MeOH (1.6 mL)/H₂O (0.4 mL)</td>
<td>130°C</td>
<td>40 bar</td>
<td>ND</td>
</tr>
</tbody>
</table>

a) The yields were determined by GC using hexadecane as the internal standard. b) Isolated yield.
3 General procedure

A 4 mL screw-cap vial was charged with alkynes (0.2 mmol), sodium sulfinates (0.4 mmol), Na$_2$S$_2$O$_8$ (0.44 mmol, 105 mg), KI (0.22 mmol, 36 mg) and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After MeOH (1.6 mL) and water (0.4 mL) were added with a syringe under N$_2$ atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N$_2$ atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 40 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 130 °C for 20 h. The reaction mixture was then diluted with EtOAc, filtered through silica gel with copious washings (Et$_2$O or EtOAc), concentrated, and purified by column chromatography.

4 failed examples
A 100 mL beaker was charged with ethynylbenzene (2.0 mmol), sodium benzenesulfinate (4 mmol), Na$_2$S$_2$O$_8$ (4.4 mmol, 1050 mg), KI (2.2 mmol, 360 mg) and an oven-dried stirring bar. After MeOH (16 mL) and water (4 mL) were added with a syringe under N$_2$ atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N$_2$ atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 40 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 130 °C for 20 h. The reaction mixture was then diluted with EtOAc, filtered through silica gel with copious washings, concentrated, and purified by column chromatography (EtOAc/PE = 1:4 v/v), obtained **3aa** 248 mg (yield 41%).
6 Spectroscopic data of products

methyl 2-phenyl-3-(phenylsulfonyl)acrylate

\[
\text{COO} \to \begin{array}{c}
\text{COO} \to \\
\text{Ph} \to \\
\text{Ph} \to \\
\text{SO}_2\text{Ph} \to \\
\end{array}
\]

3aa, a mixture of E and Z = 3:1, yellow oil, yield 68%.

\[^1H\text{NMR (700 MHz, Chloroform-}d\text{)}\delta 7.98 \text{ – 7.92 (m, 0.65H), 7.51 (s, 1.00H), 7.48 (dd, } J = 8.4, 1.5 \text{ Hz, 2.31H), 7.46 – 7.44 (m, 1.02H), 7.36 – 7.31 (m, 1.60H), 7.29 (tt, } J = 7.4, 1.6 \text{ Hz, 2.96H), 7.22 (dd, } J = 8.5, 7.0 \text{ Hz, 1.96H), 7.08 – 7.03 (m, 1.95H), 6.55 (s, } 0.34 \text{H).}
\]

\[^{13}C\text{NMR (176 MHz, CDCl}_3\text{)}\delta 166.5, 165.5, 146.1, 143.1, 140.5, 140.2, 139.7, 133.9, 133.7, 132.1, 131.3, 130.8, 129.4, 129.3, 129.2, 128.0, 127.8, 127.0, 126.5, 53.4, 53.2.
\]

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C\text{16}H\text{14}O\text{4}S 303.0686; Found: 303.0685.

methyl 3-(phenylsulfonyl)-2-(p-tolyl)acrylate

\[
\text{COO} \to \begin{array}{c}
\text{COO} \to \\
\text{Ph} \to \\
\text{Ph} \to \\
\text{SO}_2\text{Ph} \to \\
\end{array}
\]

3ba, a mixture of E and Z = 3:1, yellow oil, yield 41%.

\[^1H\text{NMR (400 MHz, Chloroform-}d\text{)}\delta 8.00 \text{ – 7.91 (m, 0.6H), 7.55 – 7.50 (m, 2.30H), 7.49 – 7.44 (m, 2.32H), 7.34 – 7.27 (m, 2.11H), 7.23 (d, } J = 8.3 \text{ Hz, 0.79H), 7.11 (d, } J = 8.2 \text{ Hz, 0.68H), 7.04 (d, } J = 8.0 \text{ Hz, 2.04H), 6.98 (d, } J = 8.2 \text{ Hz, 2.05H), 6.52 (s, } 0.30 \text{H), 3.94 (s, } 0.88 \text{H), 3.69 (s, } 3.00 \text{H), 2.30 (s, } 2.99 \text{H), 2.28 (s, } 0.87 \text{H).}
\]

\[^{13}C\text{NMR (101 MHz, CDCl}_3\text{)}\delta 166.6, 165.7, 143.1, 142.0, 140.4, 139.9, 139.9, 139.5, 133.8, 133.6, 129.9, 129.4, 129.4, 128.9, 128.5, 128.0, 127.0, 127.0, 125.3, 53.4, 53.1, 21.5, 21.4.
\]

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C\text{17}H\text{16}O\text{4}S 317.0842; Found: 317.0840.

methyl 3-(phenylsulfonyl)-2-(m-tolyl)acrylate

\[
\text{COO} \to \begin{array}{c}
\text{COO} \to \\
\text{Ph} \to \\
\text{Ph} \to \\
\text{SO}_2\text{Ph} \to \\
\end{array}
\]

3ca, a mixture of E and Z = 3:1, yellow oil, yield 57%.

\[^1H\text{NMR (400 MHz, Chloroform-}d\text{)}\delta 7.99 – 7.90 (m, 0.70H), 7.52 – 7.41 (m, 4.70H), 7.32 – 7.24 (m, 2.22H), 7.21 – 7.06 (m, 3.83H), 6.87 (dt, } J = 7.3, 1.8 \text{ Hz, 0.99H), 6.74 (d, } J = 2.0 \text{ Hz, 0.99H), 6.53 (s, 3.05H), 3.94 (s, 1.00H), 3.69 (s, 3.00H), 2.26 (s, 1.09H), 2.20 (s, 3.01H).}
\]

\[^{13}C\text{NMR (101 MHz, CDCl}_3\text{)}\delta 166.5, 165.6, 146.3, 143.3, 140.4, 140.3, 139.8, 139.1, 137.4, 133.8, 133.5, 132.1, 132.2, 130.0, 129.7, 129.4, 129.1, 128.8, 128.1, 128.0, 127.7, 127.5, 126.5, 126.3, 124.2, 53.4, 53.2, 21.4, 21.3.
\]

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C\text{17}H\text{16}O\text{4}S 317.0842; Found: 317.0843.
**methyl 2-(4-(tert-butyl)phenyl)-3-(phenylsulfonyl)acrylate**

![Chemical Structure]

**3da**, a mixture of E and Z = 10:3, yellow oil, yield 55%.

**1H NMR (400 MHz, Chloroform-d)** \(\delta\) 7.98 – 7.91 (m, 0.60H), 7.56 – 7.46 (m, 2.05H), 7.45 – 7.38 (m, 3.15H), 7.35 – 7.26 (m, 1.59H), 7.25 – 7.17 (m, 4.30H), 6.53 (s, 0.28H) 7.01 – 6.94 (m, 1.96H), 3.94 (s, 0.9H), 3.70 (s, 3.00H), 1.25 (s, 9.24H), 1.22 (d, \(J = 3.2\) Hz, 2.98H).

**13C NMR (101 MHz, CDCl3)** \(\delta\) 166.6, 165.7, 155.1, 152.5, 146.0, 143.3, 140.4, 139.7, 133.8, 133.4, 129.4, 129.3, 128.7, 128.0, 127.9, 126.8, 126.2, 125.4, 124.7, 53.3, 53.1, 34.9, 34.7, 31.3, 31.0.

**HRMS (ESI-TOF) m/z**: [M + H]+ Calcd for C\(_{20}\)H\(_{22}\)O\(_{4}\)S 359.1312; Found: 359.1314.

**methyl 2-(4-fluorophenyl)-3-(phenylsulfonyl)acrylate**

![Chemical Structure]

**3ea**, a mixture of E and Z = 15:1, yellow oil, yield 50%.

**1H NMR (400 MHz, Chloroform-d)** \(\delta\) 7.55 – 7.46 (m, 4H), 7.37 – 7.31 (m, 2H), 7.11 – 7.05 (m, 2H), 6.92 (t, \(J = 8.7\) Hz, 2H), 3.71 (s, 3H).

**13C NMR (101 MHz, CDCl3)** \(\delta\) 165.3, 164.3 (d, \(J = 251.48\) Hz), 141.9, 140.8, 139.7, 133.9, 131.6 (d, \(J = 8.39\) Hz), 129.1, 128.0, 126.7 (d, \(J = 3.9\) Hz), 115.0 (d, \(J = 22.32\) Hz), 53.5.

**19F NMR (376 MHz, CDCl3)** \(\delta\) -111.15.

**HRMS (ESI-TOF) m/z**: [M + H]+ Calcd for C\(_{16}\)H\(_{13}\)FO\(_{4}\)S 321.0591; Found: 321.0596.

**methyl 2-(2-fluorophenyl)-3-(phenylsulfonyl)acrylate**

![Chemical Structure]

**3fa**, a mixture of E and Z = 4:1, yellow oil, yield 42%.

**1H NMR (400 MHz, Chloroform-d)** \(\delta\) 8.00 – 7.92 (m, 0.61H), 7.62 – 7.47 (m, 4.97H), 7.38 – 7.27 (m, 3.97H), 7.23 (td, \(J = 7.4\), 1.8 Hz, 1.19H), 7.11 (td, \(J = 7.5\), 1.1 Hz, 1.40H), 6.86 (ddd, \(J = 9.5\), 8.3, 1.1 Hz, 1.16H), 6.78 (s, 0.30H), 3.93 (s, 0.85H), 3.70 (s, 3.00H).

**13C NMR (101 MHz, CDCl3)** \(\delta\) 168.1, 164.5, 159.4 (d, \(J = 247.49\) Hz), 142.0, 139.3, 137.6, 133.9, 131.8 (d, \(J = 2.58\) Hz), 131.6 (d, \(J = 8.27\) Hz), 129.4, 129.1, 128.1, 128.0, 124.9 (d, \(J = 3.68\) Hz), 123.7 (d, \(J = 3.68\) Hz), 119.1 (d, \(J = 16.11\) Hz), 116.7 (d, \(J = 22.55\) Hz), 115.1 (d, \(J = 21.34\) Hz), 53.5, 53.3.

**19F NMR (376 MHz, CDCl3)** \(\delta\) -111.1, -111.8.

**HRMS (ESI-TOF) m/z**: [M + H]+ Calcd for C\(_{16}\)H\(_{13}\)FO\(_{4}\)S 321.0591; Found: 321.0599.
methyl 2-(4-chlorophenyl)-3-(phenylsulfonyl)acrylate

\[
\begin{align*}
&\text{Cl} \\
&\text{SO}_2\text{Ph} \\
&\text{COOMe}
\end{align*}
\]

3ga, a mixture of \(E\) and \(Z\) > 20:1, yellow oil, yield 31%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.55 – 7.51 (m, 3H), 7.35 (t, \(J = 7.8\) Hz, 2H), 7.23 – 7.19 (m, 2H), 7.02 (d, \(J = 8.5\) Hz, 2H), 3.71 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 165.1, 141.7, 140.9, 139.6, 135.6, 133.9, 130.9, 129.1, 128.1, 128.0, 53.5.

HRMS (ESI-TOF) \(m/z\): [M + H] + Calcd for C\(_{16}\)H\(_{13}\)ClO\(_4\)S 337.0296; Found: 337.0299.

3ha, a mixture of \(E\) and \(Z\) > 20:1, yellow oil, yield 49%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.57 – 7.48 (m, 4H), 7.40 – 7.33 (m, 4H), 6.98 – 6.90 (m, 2H), 3.70 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 165.0, 141.7, 140.9, 139.6, 133.9, 129.7, 129.1, 128.0, 123.9, 53.5.

HRMS (ESI-TOF) \(m/z\): [M + H] + Calcd for C\(_{16}\)H\(_{13}\)BrO\(_4\)S 380.9791; Found: 380.9787.

methyl 2-(4-methoxyphenyl)-3-(phenylsulfonyl)acrylate

\[
\begin{align*}
&\text{MeO} \\
&\text{SO}_2\text{Ph} \\
&\text{COOMe}
\end{align*}
\]

3ia, a mixture of \(E\) and \(Z\) = 9:4, yellow oil, yield 18%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.97 – 7.91 (m, 0.87H), 7.56 – 7.50 (m, 2.68H), 7.49 – 7.43 (m, 2.63H), 7.36 – 7.26 (m, 2.95H), 7.10 – 7.03 (m, 2.03H), 6.84 – 6.79 (m, 0.95H), 6.78 – 6.73 (m, 2.04H), 6.46 (s, 0.44H), 3.95 (s, 1.25H), 3.76 (s, 3.04H), 3.75 (s, 1.33H), 3.71 (s, 3.00H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 165.8, 160.6, 142.8, 140.0, 139.5, 133.7, 133.6, 131.2, 129.3, 128.9, 128.8, 128.0, 127.9, 123.7, 123.0, 114.7, 113.3, 55.5, 55.3, 53.3, 53.1.

HRMS (ESI-TOF) \(m/z\): [M + H] + Calcd for C\(_{17}\)H\(_{16}\)O\(_5\)S 333.0791; Found: 333.0790.

methyl 2-(4-cyanomethyl)phenyl)-3-(phenylsulfonyl)acrylate

\[
\begin{align*}
&\text{CN} \\
&\text{SO}_2\text{Ph} \\
&\text{COOMe}
\end{align*}
\]

3ja, a mixture of \(E\) and \(Z\) = 3:2, yellow oil, yield 26%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.98 – 7.92 (m, 1.47H), 7.58 – 7.49 (m, 6.36H), 7.36 (td, \(J = 6.8, 5.7, 1.7\) Hz, 4.54H), 7.30 (d, \(J = 8.3\) Hz, 2.00H), 7.22 (d, \(J = 8.0\) Hz, 2.46H), 7.15 – 7.09 (m, 2.13H), 6.56 (s, 0.64H), 3.95 (s, 1.91H), 3.71 (s, 5.00H), 3.70 (s, 1.36H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.2, 165.2, 145.1, 141.9, 140.8, 140.0, 139.6, 134.0, 134.0, 133.2, 132.1, 131.1, 130.9, 130.2, 129.5, 129.1, 128.8, 128.1, 128.0, 127.8, 127.5, 127.3, 117.4, 117.0, 53.5, 53.3, 23.6, 23.5.

HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{18}$H$_{15}$NO$_4$S 342.0795; Found: 342.0796.

**methyl 2-(4-acetylphenyl)-3-(phenylsulfonyl)acrylate**

![Chemical Structure](image)

3ka, a mixture of E and Z = 5:2, yellow oil, yield 44%.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.95 (dd, $J$ = 8.7, 1.6 Hz, 1.01H), 7.90 – 7.83 (m, 3.24H), 7.59 – 7.48 (m, 5.62H), 7.44 (d, $J$ = 8.5 Hz, 0.99H), 7.39 – 7.33 (m, 2.39H), 7.21 (dt, $J$ = 9.0, 2.1 Hz, 2.19H), 6.63 (s, 0.46H), 3.96 (s, 1.21H), 3.70 (s, 3.00H), 2.56 (s, 3.01H), 2.52 (s, 1.21H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.5, 197.0, 166.0, 164.9, 144.8, 141.7, 140.8, 139.8, 139.6, 138.7, 137.3, 136.3, 135.7, 134.1, 134.1, 129.7, 129.5, 129.2, 129.0, 128.6, 128.1, 128.0, 127.7, 127.3, 53.6, 53.4, 26.7, 26.7.

HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{18}$H$_{16}$O$_5$S 345.0791; Found: 345.0794.

**methyl 3-(phenylsulfonyl)-2-(thiophen-3-yl)acrylate**

![Chemical Structure](image)

3la, a mixture of E and Z = 10:3, yellow oil, yield 55%.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.98 – 7.89 (m, 0.62H), 7.59 – 7.53 (m, 2.31H), 7.52 – 7.44 (m, 3.58H), 7.43 – 7.39 (m, 0.34H), 7.37 – 7.26 (m, 2.43H), 7.13 (dd, $J$ = 5.1, 3.0 Hz, 0.99H), 7.08 – 7.04 (m, 0.35H) 6.83 (dd, $J$ = 5.0, 1.3 Hz, 0.97H), 6.05 (s, 0.30H), 3.96 (s, 0.91H), 3.72 (s, 3.00H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.4, 165.2, 140.3, 139.7, 138.2, 133.8, 133.7, 130.2, 129.4, 129.2, 128.9, 128.8, 128.2, 127.9, 127.8, 127.7, 125.0, 125.0, 124.7, 53.4, 53.2.

HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{14}$H$_{12}$O$_5$S 309.0250; Found: 309.0250.

**methyl 2-((phenylsulfonyl)methylene)octanoate**

![Chemical Structure](image)

3ma, a mixture of E and Z = 20:3, yellow oil, yield 60%.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.87 (dq, $J$ = 7.1, 2.0 Hz, 2.32H), 7.63 – 7.57 (m, 1.04H), 7.53 – 7.48 (m, 2.24H), 7.08 (s, 0.90H), 6.09 (s, 0.16H), 3.84 (s, 0.46H), 3.70 (s, 3.00H), 2.76 (dd, $J$ = 8.8, 6.4 Hz, 2.05H), 1.40 – 1.12 (m, 11.00H), 0.81 (t, $J$ = 6.7 Hz, 4.17H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.0, 145.8, 140.8, 136.7, 134.0, 129.5, 127.7, 52.9, 31.4, 29.4, 29.1, 27.3, 22.5, 14.0.

HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{16}$H$_{22}$O$_5$S 311.1312; Found: 311.1316.
methyl 2-cyclopropyl-3-(phenylsulfonyl)acrylate

\[
\begin{align*}
\text{COO}\text{Me} & \quad \text{SO}_2\text{Ph} \\
\end{align*}
\]

3na, a mixture of E and Z = 15:1, colorless oil, yield 12%.

\[^1\text{H NMR (}400 \text{ MHz, Chloroform-}d)\ \delta \ 7.96 – 7.92 \text{ (m, } 0.41\text{H}), 7.91 – 7.86 \text{ (m, } 2.17\text{H}), 7.62 – 7.57 \text{ (m, } 1.17\text{H}), 7.53 – 7.48 \text{ (m, } 2.57\text{H}), 6.83 \text{ (s, } 0.95\text{H}), 3.83 \text{ (s, } 0.21\text{H}), 3.63 \text{ (s, } 3.00\text{H}), 2.69 \text{ (tt, } J = 8.6, 5.2 \text{ Hz, } 1.11\text{H}), 1.11 – 1.05 \text{ (m, } 1.99\text{H}), 0.91 \text{ (dt, } J = 8.6, 3.2 \text{ Hz, } 2.10\text{H}).\]

\[^{13}\text{C NMR (}176 \text{ MHz, CDCl}_3) \delta 164.6, 152.2, 148.3, 141.1, 134.7, 133.8, 133.5, 133.2, 129.4, 129.2, 129.0, 128.2, 127.5, 127.1, 52.5, 25.8, 10.9, 10.7, 9.5, 9.3.\]

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C_{13}H_{13}O_4S 267.0686; Found: 267.0691.

methyl (E)-3-(phenylsulfonyl)acrylate

\[
\begin{align*}
\text{MeOOC} & \quad \text{SO}_2\text{Ph} \\
\end{align*}
\]

3oa, the product was obtained from ethynyltrimethylsilane, colorless oil, yield 13%.

\[^1\text{H NMR (}400 \text{ MHz, Chloroform-}d)\ \delta \ 7.93 – 7.80 \text{ (m, } 2\text{H}), 7.68 – 7.57 \text{ (m, } 1\text{H}), 7.58 – 7.49 \text{ (m, } 2\text{H}), 7.28 \text{ (d, } J = 15.2 \text{ Hz, } 1\text{H}), 6.78 \text{ (d, } J = 15.1 \text{ Hz, } 1\text{H}), 3.74 \text{ (s, } 3\text{H)}.\]

\[^{13}\text{C NMR (}176 \text{ MHz, CDCl}_3) \delta 163.9, 143.5, 138.4, 134.4, 130.5, 129.7, 128.4, 52.8.\]

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C_{10}H_{10}O_4S 227.0373; Found: 223.0375.

methyl 6-methoxy-2-((phenylsulfonyl)methylene)hexanoate

\[
\begin{align*}
\text{MeO} & \quad \text{COO}\text{Me} \\
\text{SO}_2\text{Ph} \\
\end{align*}
\]

3pa, the product was obtained from 6-iodohex-1-yne, A mixture of E and Z > 20:1, colorless oil, yield 27%.

\[^1\text{H NMR (}400 \text{ MHz, Chloroform-}d)\ \delta \ 7.90 – 7.85 \text{ (m, } 2\text{H}), 7.64 – 7.57 \text{ (m, } 1\text{H}), 7.55 – 7.47 \text{ (m, } 2\text{H}), 7.09 \text{ (s, } 1\text{H}), 3.70 \text{ (s, } 3\text{H}), 3.33 \text{ (t, } J = 6.4 \text{ Hz, } 2\text{H}), 3.26 \text{ (s, } 3\text{H}), 2.87 – 2.76 \text{ (m, } 2\text{H}), 1.59 \text{ (ddt, } J = 7.2, 5.9, 1.6 \text{ Hz, } 2\text{H}), 1.49 – 1.43 \text{ (m, } 2\text{H)}.\]

\[^{13}\text{C NMR (}101 \text{ MHz, CDCl}_3) \delta 165.9, 145.3, 140.6, 137.0, 134.0, 129.5, 127.7, 72.2, 58.5, 53.0, 29.5, 26.9, 25.8.\]

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C_{13}H_{22}O_5S 313.1104; Found: 313.1113.
methyl 3-oxo-2-(tosylmethylene)octanoate

\[
\begin{align*}
\text{COOMe} & \\
\text{n-Hex} & \\
\text{O} & \\
\text{S} & \text{O}
\end{align*}
\]

3mb, a mixture of \(E\) and \(Z\) = 10:1, colorless oil, yield 67%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.84 – 7.64 (m, 2.53H), 7.29 (d, \(J = 8.1\) Hz, 2.57H), 7.07 (s, 0.95H), 6.08 (s, 0.11H), 3.83 (s, 0.30H), 3.69 (s, 3.00H), 2.74 (dd, \(J = 8.8, 6.4\) Hz, 2.02H), 2.38 (s, 3.97H), 1.39 – 1.10 (m, 10.89H), 0.89 – 0.73 (m, 4.20H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.1, 145.3, 145.1, 137.8, 137.1, 130.1, 127.8, 52.9, 31.5, 29.4, 29.1, 27.3, 22.5, 21.7, 14.1.

HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) Calcd for C\(_{17}\)H\(_{23}\)O\(_4\)S 325.1468; Found: 325.1477.

methyl 2-(((4-fluorophenyl)sulfonyl)methylene)-3-oxooctanoate

\[
\begin{align*}
\text{COOMe} & \\
\text{n-Hex} & \\
\text{O} & \\
\text{S} & \text{O}
\end{align*}
\]

3mc, a mixture of \(E\) and \(Z\) = 5:1, colorless oil, yield 81%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.94 – 7.84 (m, 2.37H), 7.27 – 7.11 (m, 2.60H), 7.05 (s, 0.95H), 6.08 (s, 0.18H), 3.84 (s, 0.56H), 3.71 (s, 3.00H), 2.80 – 2.70 (m, 2.02H), 2.32 – 2.26 (m, 0.38H), 1.42 – 1.10 (m, 10.50H), 0.92 – 0.71 (m, 3.93H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 167.6, 166.0 (d, \(J = 258.34\) Hz), 165.9, 149.7, 145.9, 136.8 (d, \(J = 3.03\) Hz), 136.5, 130.9 (d, \(J = 9.75\) Hz), 130.7 (d, \(J = 9.48\) Hz), 127.4, 116.8 (d, \(J = 23.11\) Hz), 116.6 (d, \(J = 22.54\) Hz), 53.0, 52.8, 34.8, 31.4, 31.3, 29.4, 29.2, 28.4, 27.3, 26.5, 22.5, 22.4, 14.0, 13.9.

HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) Calcd for C\(_{16}\)H\(_{21}\)FO\(_3\)S 329.1217; Found: 329.1222.
methyl 2-(((4-chlorophenyl)sulfonyl)methylene)-3-oxooctanoate

\[
\begin{align*}
\text{COOMe} & \\
\text{n-Hex} & \\
\text{SO} & \\
\text{O} & \\
\text{Cl} & \\
\end{align*}
\]

3md, a mixture of E and Z = 5:1, colorless oil, yield 58%.

\( ^1H \) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.83 – 7.77 (m, 2.22H), 7.51 – 7.43 (m, 2.38H), 7.05 (s, 0.89H), 6.07 (s, 0.18H), 3.84 (s, 0.57H), 3.71 (s, 3.00H), 2.82 – 2.69 (m, 2.03H), 2.33 – 2.25 (m, 0.40H), 1.44 – 1.11 (m, 11.14H), 0.80 (dt, \( J = 17.0, 6.7 \) Hz, 4.16H).

\( ^{13}C \) NMR (101 MHz, CDCl\( _3 \)) \( \delta \) 167.5, 165.9, 150.1, 146.3, 140.8, 139.2, 136.2, 129.8, 129.6, 129.4, 129.2, 127.2, 53.0, 52.8, 34.8, 31.4, 31.3, 29.4, 29.2, 28.4, 27.4, 26.5, 22.5, 22.4, 14.0, 13.9.

HRMS (ESI-TOF) \( m/z \): \( [M + H]^+ \) Calcd for C\( _{16} \)H\( _{20} \)ClO\( _4 \)S 345.0922; Found: 345.0926.

methyl 3-(((4-chlorophenyl)sulfonyl)-2-phenylacrylate

\[
\begin{align*}
\text{COOMe} & \\
\text{O} & \\
\text{SO} & \\
\text{Cl} & \\
\end{align*}
\]

3ad, a mixture of E and Z = 20:3, yellow oil, yield 16%.

\( ^1H \) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.91 – 7.86 (m, 0.34H), 7.51 (s, 0.99H), 7.50 – 7.45 (m, 0.38H), 7.41 – 7.35 (m, 2.28H), 7.35 – 7.29 (m, 1.61H), 7.27 – 7.21 (m, 3.96H), 7.05 – 7.01 (m, 1.88H), 6.53 (s, 0.15H), 3.95 (s, 0.44), 3.71 (s, 3.00H).

\( ^{13}C \) NMR (101 MHz, CDCl\( _3 \)) \( \delta \) 165.3, 143.4, 140.5, 140.3, 138.1, 130.7, 129.7, 129.5, 129.4, 129.3, 129.2, 127.9, 127.0, 53.5.

HRMS (ESI-TOF) \( m/z \): \( [M + H]^+ \) Calcd for C\( _{16} \)H\( _{13} \)ClO\( _4 \)S 337.0296; Found: 337.0298.

methyl 3-(ethylsulfonyl)-2-phenylacrylate

\[
\begin{align*}
\text{COOMe} & \\
\text{S} & \\
\text{O} & \\
\text{Et} & \\
\end{align*}
\]

3ae, a mixture of E and Z = 4:1, yellow oil, yield 45%.

\( ^1H \) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.42 – 7.31 (m, 7.31H), 6.57 (s, 0.26H) 3.86 (s, 0.77H), 3.76 (s, 3.00H), 3.12 (q, \( J = 7.5 \) Hz, 0.58H), 2.66 (q, \( J = 7.4 \) Hz, 2.12H), 1.35 (t, \( J = 7.5 \) Hz, 0.96H), 1.17 (t, \( J = 7.4 \) Hz, 3.28H).

\( ^{13}C \) NMR (101 MHz, CDCl\( _3 \)) \( \delta \) 165.4, 143.8, 137.2, 131.4, 131.0, 129.8, 129.4, 129.3, 128.1, 127.0, 124.7, 53.5, 53.1, 50.2, 49.0, 6.8, 6.7.
methyl 3-(methylsulfonyl)-2-phenylacrylate

\[
\text{COO} \quad \text{SO}_2\text{Me}
\]

3af, a mixture of E and Z = 5:1, yellow oil, yield 67%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.46 – 7.30 (m, 7.17H), 6.66 (s, 0.21), 3.87 (s, 0.61H), 3.76 (s, 3.00H), 3.04 (s, 0.60H), 2.58 (s, 0.30H).

\(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.1, 165.4, 148.5, 142.9, 139.3, 131.9, 131.5, 130.9, 130.0, 129.5, 129.3, 128.3, 127.1, 126.7, 53.5, 53.2, 43.9, 42.9.

HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) Calcd for C\(_{11}\)H\(_{14}\)O\(_4\)S 255.0686; Found: 255.0691.

methyl 2-[[1,1'-biphenyl]-4-yl]-3-(methylsulfonyl)acrylate

\[
\text{COO} \quad \text{SO}_2\text{Me}
\]

3qf, a mixture of E and Z = 15:4, yellow oil, yield 44%.

\(^1\)H NMR (700 MHz, Chloroform-\(d\)) \(\delta\) 7.62 – 7.57 (m, 3.11H), 7.56 – 7.51 (m, 3.57H), 7.46 – 7.40 (m, 4.06H), 7.38 (t, \(J = 7.8\) Hz, 3.58H), 7.32 – 7.28 (m, 2.12H), 6.70 (s, 0.30), 3.89 (s, 0.80H), 3.79 (s, 3.00H), 3.06 (s, 0.77H), 2.65 (s, 3.06H).

\(^1^3\)C NMR (176 MHz, CDCl\(_3\)) \(\delta\) 166.2, 165.5, 148.2, 144.4, 142.8, 142.7, 140.0, 139.1, 130.1, 129.9, 129.7, 129.1, 129.0, 128.9, 128.8, 128.3, 128.0, 127.9, 127.7, 127.6, 127.4, 127.2, 127.1, 126.9, 126.2, 53.6, 53.3, 43.9, 43.0.

HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) Calcd for C\(_{17}\)H\(_{16}\)O\(_5\)S 317.0842; Found: 317.0850.

methyl 3-(methylsulfonyl)-2-(4-(trifluoromethoxy)phenyl)acrylate

\[
\text{COO} \quad \text{SO}_2\text{Me}
\]

3rf, a mixture of E and Z > 20:1, colorless oil, yield 43%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.37 (d, \(J = 8.8\) Hz, 2H), 7.26 – 7.17 (m, 2H), 3.78 (s, 3H), 2.71 (s, 3H).

\(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 165.0, 150.2, 141.8, 139.3, 131.3, 129.2, 120.3 (t, \(J = 137.69\) Hz), 53.6, 43.1.

\(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -57.7.

HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) Calcd for C\(_{12}\)H\(_{11}\)F\(_3\)O\(_5\)S 325.0352; Found: 325.0355.
methyl 4-(3-methoxy-1-(methylsulfonyl)-3-oxoprop-1-en-2-yl)benzoate

\[
\text{MeOOC} \quad \text{COO}\text{Me} \quad \text{Me} \quad \text{SO}_2\text{Me}
\]

3sf, a mixture of E and Z > 20:1, colorless oil, yield 50%.

\( ^1H \text{ NMR (700 MHz, Chloroform-d)} \delta 8.03 (d, J = 8.3 \text{ Hz}, 2H), 7.48 (s, 1H), 7.39 (d, J = 8.4 \text{ Hz}, 2H), 3.86 (s, 3H), 3.77 (s, 3H), 2.70 (s, 3H). \)

\( ^{13}C \text{ NMR (176 MHz, CDCl}_3) \delta 165.3, 163.8, 141.2, 138.5, 134.4, 130.3, 128.5, 128.3, 52.7, 51.3, 42.2. \)

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C_{13}H_{14}O_6S 299.0584; Found: 299.0589.

methyl 2-(4-cyanophenyl)-3-(methylsulfonyl)acrylate

\[
\text{NC} \quad \text{COO}\text{Me} \quad \text{Me} \quad \text{SO}_2\text{Me}
\]

3tf, a mixture of E and Z > 20:1, yellow oil, yield 23%.

\( ^1H \text{ NMR (400 MHz, Chloroform-d)} \delta 7.68 – 7.63 (m, 2H), 7.51 (s, 1H), 7.41 (d, J = 8.5 \text{ Hz}, 2H), 3.78 (s, 3H). \)

\( ^{13}C \text{ NMR (101 MHz, CDCl}_3) \delta 164.4, 141.5, 139.5, 135.5, 131.7, 130.2, 118.2, 113.6, 53.8, 43.4. \)

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C_{12}H_{11}NO_4S 266.0482; Found: 266.0483.

methyl 2-(2-fluorophenyl)-3-(methylsulfonyl)acrylate

\[
\text{F} \quad \text{COO}\text{Me} \quad \text{Me} \quad \text{SO}_2\text{Me}
\]

3uf, a mixture of E and Z = 5:1, yellow oil, yield 64%.

\( ^1H \text{ NMR (400 MHz, Chloroform-d)} \delta 7.52 (s, 1.02H), 7.37 (ddt, J = 12.9, 5.3, 2.6 \text{ Hz}, 1.32H), 7.30 (qd, J = 7.5, 7.0, 1.8 \text{ Hz}, 1.19H), 7.15 (td, J = 7.6, 1.1 \text{ Hz}, 1.27H), 7.07 (tdd, J = 9.5, 8.0, 1.1 \text{ Hz}, 1.38H), 6.83 (s, 0.23H), 3.85 (s, 0.64H), 3.76 (s, 3.00H), 3.10 (s, 0.64H), 2.78 (s, 3.08H). \)

\( ^{13}C \text{ NMR (101 MHz, CDCl}_3) \delta 165.5, 164.5, 159.4 (d, J = 246.95 \text{ Hz}), 143.0, 140.2, 138.2, 133.1 (d, J = 8.57 \text{ Hz}), 131.9 (d, J = 8.57 \text{ Hz}), 131.6 (d, J = 2.34 \text{ Hz}), 129.9 (d, J = 2.61 \text{ Hz}), 125.0 (d, J = 3.75 \text{ Hz}), 124.0 (d, J = 3.75 \text{ Hz}), 119.1 (d, J = 16.03 \text{ Hz}), 116.7 (d, J = 21.58 \text{ Hz}), 115.4 (d, J = 20.98 \text{ Hz}), 53.7, 53.3, 43.9, 42.9. \)

\( ^{19}F \text{ NMR (376 MHz, CDCl}_3) \delta -111.40, -112.28. \)

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C_{11}H_{11}FO_4S 259.0435; Found: 259.0441.
methyl 2-(3-chlorophenyl)-3-(methylsulfonyl)acrylate

\[ \text{Cl} - \text{C} = \text{C} - \text{SO}_2\text{Me} \]

3vf, a mixture of E and Z = 10:1, yellow oil, yield 46%.

\(^1\)H NMR (700 MHz, Chloroform-\(d\)) \(\delta 7.45 (s, 0.90H), 7.36 (ddd, J = 8.1, 2.1, 1.1 \text{ Hz}, 0.93H), 7.32 - 7.27 (m, 1.98H), 7.22 (dt, J = 7.7, 1.4 \text{ Hz}, 0.92H), 6.66 (s, 0.10H), 3.88 (s, 0.28H), 3.78 (s, 3.00H), 3.05 (s, 0.23H) 2.72 (s, 3.00H).

\(^1^3\)C NMR (176 MHz, CDCl\(_3\)) \(\delta 164.9, 141.6, 139.5, 134.2, 132.5, 130.0, 129.5, 129.3, 127.8, 53.7, 43.2.

HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{11}\)H\(_{11}\)ClO\(_4\)S 275.0139; Found: 275.0138.

methyl 3-(methylsulfonyl)-2-(naphthalen-2-yl)acrylate

\[ \text{COOMe} - \text{C} = \text{C} - \text{SO}_2\text{Me} \]

3wf, a mixture of E and Z = 5:1, yellow oil, yield 47%.

\(^1\)H NMR (700 MHz, Chloroform-\(d\)) \(\delta 7.89 - 7.86 (m, 0.97H), 7.84 - 7.77 (m, 3.80H), 7.52 - 7.44 (m, 3.63H), 7.37 (dd, J = 8.4, 1.8 \text{ Hz}, 0.99H), 6.78 (s, 0.23H), 3.92 (s, 0.61H), 3.77 (s, 3.00H), 3.08 (s, 0.60H), 2.57 (s, 3.14H).

\(^1^3\)C NMR (176 MHz, CDCl\(_3\)) \(\delta 165.2, 164.4, 147.5, 141.9, 139.4, 138.4, 133.4, 132.5, 131.9, 131.4, 128.7, 128.3, 128.0, 127.9, 127.6, 127.3, 127.2, 127.1, 127.0, 126.8, 126.8, 126.8, 126.8, 126.4, 126.2, 125.8, 125.6, 125.1, 121.8, 52.5, 52.3, 42.9, 41.9.

HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{15}\)H\(_{14}\)O\(_4\)S 291.0686; Found: 291.0681.

methyl (E)-3-(methylsulfonyl)acrylate

\[ \text{MeOOC} - \text{C} = \text{C} - \text{SO}_2\text{Me} \]

3xf, the product was obtained from ethynyltrimethylsilane, colorless oil, yield 46%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta 7.34 (d, J = 15.2 \text{ Hz}, 1H), 6.82 (d, J = 15.2 \text{ Hz}, 1H), 3.79 (s, 3H), 2.96 (s, 3H).

\(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 163.7, 142.1, 132.5, 52.9, 42.4.

HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{6}\)H\(_{6}\)O\(_2\)S 165.0216; Found: 165.0218.
methyl 6-methoxy-2-((methylsulfonyl)methylene)hexanoate

3yf, the product was obtained from 6-iodohex-1-yne, A mixture of E and Z > 20:1, colorless oil, yield 28%.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.11 (s, 1H), 3.77 (s, 3H), 3.33 (t, $J$ = 6.2 Hz, 2H), 3.25 (s, 3H), 2.97 (s, 3H), 2.81 – 2.75 (m, 2H), 1.60 – 1.51 (m, 4H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.8, 146.7, 135.7, 72.1, 58.5, 53.1, 43.8, 29.4, 27.0, 25.9.

HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{10}$H$_{18}$O$_5$S 251.0948; Found: 251.0953.
7 Copies of NMR spectra for compounds

3aa
3mc