Electronic Supplementary Information

A straightforward and convenient synthesis of functionalized allyl thiosulfonates and allyl disulfanes

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General Experimental

All reagents were purchase from Sigma-Aldrich, Alfa Aesar, Acros, SDFine, Spectrochem or AVRA and used without further purification unless otherwise stated. For all reactions carried out under inert atmosphere, solvents were dried over activated 4 Å molecular sieves. Silicon oil baths on stirrer hotplates were employed with temperature control via thermometer. Reaction progress was monitored by Thin Layer Chromatography (TLC) performed using TLC Silica gel 60 F254. TLC plate’s visualisation was achieved by a combination of ultraviolet light (254 nm), potassium permanganate solution, iodine treatment or p-anisaldehyde stains. Flash column chromatography was performed using silica gel (100-200 mesh) as a stationary phase. Melting points were measured in open capillaries using DBK digital melting point apparatus and are uncorrected. 1H NMR and 13C NMR’s were recorded using Bruker AVIII400 (1H = 400 MHz, 13C = 101 MHz) or Bruker AVIII500 (1H = 500 MHz, 13C = 126 MHz) with the spectrometers at 300 K. Chemical shifts (δ) are given in ppm relative to TMS and coupling constants (J) are quoted in Hz to one decimal place. For spectra recorded in chloroform-d (CDCl₃) the 7.26 ppm resonance of residual CHCl₃ for proton spectra and 77.16 ppm resonance of CDCl₃ for carbon spectra were used as internal references. Spectral data for 1H NMR spectroscopy is reported as follows: Chemical shift (multiplicity, coupling constant, number of protons); and for 13C NMR spectroscopy: Chemical shift. The following abbreviations were used for multiplicity in 1H NMR: s (singlet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublets), td (triplet of doublets), quin (quin quintuplet), bs (broad singlet), m (multiplet), app. (apparent). All NMR spectrums are processed using MestReNova version 6.0.2 (v). High resolution mass spectroscopy (HRMS) were recorded using ESI-TOF techniques and was obtained using a lock-mass to adjust the calibrated mass scale.

Synthesis of Starting Materials

Synthesis of Morita-Baylis-Hillman allyl bromides (1a-t)

According to known procedure, a variety of Morita-Baylis-Hillman alcohols¹ have been prepared and were treated with HBr/H₂SO₄ in CH₂Cl₂ for formation of desired Morita-Baylis-Hillman allyl bromides (1a-o,q-t)¹,² and nitrostyrene derived allyl bromide (1p)³ as described in Scheme 1.

\[ \text{MBH alcohol} \xrightarrow{\text{HBr, H}_2\text{SO}_4} \text{CH}_2\text{Cl}_2, 0\, ^\circ\text{C-rt, 15 h} \]

Scheme 1: Synthesis of Morita-Baylis-Hillman bromides (1a-t).

Synthesis of sodium thiosulfonates (2a-d)

The sodium thiosulfonates (2a-d)⁴ were prepared according to known procedure by reaction of corresponding sodium sulfinates with elemental sulfur in the presence of triethyl amine as shown in Scheme 2.
Scheme 2: Synthesis of sodium arylthiosulfonates (2a-d).

**Table 1.** Optimization for Sulfonylation of MBH bromide (1a) with sodium benzenethiosulfonate 2a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction conditions</th>
<th>Time</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2a (2.0 eq.), DMF, RT</td>
<td>4 h</td>
<td>84%</td>
</tr>
<tr>
<td>2</td>
<td>2a (2.0 eq.), DMSO, RT</td>
<td>4 h</td>
<td>80%</td>
</tr>
<tr>
<td>3</td>
<td>2a (2.0 eq.), 1,4-Dioxane, RT</td>
<td>4 h</td>
<td>77%</td>
</tr>
<tr>
<td>4</td>
<td>2a (2.0 eq.), Toluene, RT</td>
<td>6 h</td>
<td>NR</td>
</tr>
<tr>
<td>5</td>
<td>2a (2.0 eq.), EtOH, RT</td>
<td>3 h</td>
<td>82%</td>
</tr>
<tr>
<td>6</td>
<td>2a (2.0 eq.), CH&lt;sub&gt;3&lt;/sub&gt;CN, RT</td>
<td>2 h</td>
<td>92%</td>
</tr>
<tr>
<td>7</td>
<td>2a (2.0 eq.), THF, RT</td>
<td>3 h</td>
<td>90%</td>
</tr>
<tr>
<td>8</td>
<td>2a (1.5 eq.), CH&lt;sub&gt;3&lt;/sub&gt;CN, RT</td>
<td>2 h</td>
<td>96%</td>
</tr>
<tr>
<td>9</td>
<td>2a (1.5 eq.), CH&lt;sub&gt;3&lt;/sub&gt;CN, 60 °C</td>
<td>2 h</td>
<td>92%</td>
</tr>
<tr>
<td>10</td>
<td>2a (1.2 eq.), CH&lt;sub&gt;3&lt;/sub&gt;CN, RT</td>
<td>2 h</td>
<td>84%</td>
</tr>
<tr>
<td>11</td>
<td>2a (1.5 eq.), Et&lt;sub&gt;3&lt;/sub&gt;N (1.5 eq.), CH&lt;sub&gt;3&lt;/sub&gt;CN, RT</td>
<td>4 h</td>
<td>NR</td>
</tr>
<tr>
<td>12</td>
<td>2a (1.5 eq.), K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; (1.5 eq.), CH&lt;sub&gt;3&lt;/sub&gt;CN, RT</td>
<td>4 h</td>
<td>NR</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: a Reactions performed on a 0.4 mmol scale of 1a in solvent (2 mL). <sup>b</sup> Isolated yields after column chromatography. NR: No Reaction.

**General Procedure-1 (GP1) for synthesis of allyl thiosulfonates**

A heat gun-dried Schlenk tube was charged Morita-Baylis-Hillman allyl bromides 1a-t (0.4 mmol, 1.0 equiv.) and sodium thiosulfonates 2a-d (0.6 mmol, 1.5 equiv.) in CH<sub>3</sub>CN (2.0 mL). The reaction mixture was stirred at room temperature for 2 h and monitored by TLC either complete or appeared to be proceeding no further progress. The mixture was quenched by addition of water (10 mL) followed by extraction with EtOAc (3x10 mL). The combined organic layers was washed with brine (2x10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 20–30% ethyl acetate/petether) to afford desired allyl thiosulfonates.

**Allyl Thiosulfonate 3aa:** Prepared according to GP1 using 1a (101.2 mg, 0.4 mmol) with sodium benzenethiosulfonate 2a (117.6 mg, 0.6 mmol) to afford 3aa (130.6 mg, 94%) using 20% ethyl acetate/petether as a colorless solid. mp: 95–97 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87–7.77 (m, 3H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.42–7.32 (m, 5H), 4.17 (s, 2H), 3.75 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.8, 144.6, 144.3, 134.0, 133.7, 129.8, 129.7(2C), 129.4(2C), 129.0(2C), 127.2(2C), 124.4, 52.6, 33.4; HRMS (ESI) calculated for C<sub>17</sub>H<sub>16</sub>Na<sub>2</sub>O<sub>4</sub>S: [M+Na]<sup>+</sup>: m/z 371.0388, found 371.0389.

Prepared according to GP1 using 1a (1.02 g, 4.0 mmol) with sodium benzenethiosulfonate 2a (1.47 g, 6.0 mmol) in CH<sub>3</sub>CN (20 mL) to afford 3aa (1.1 g, 79%) as a colorless solid.
**Allyl Thiosulfonate 3ba:** Prepared according to **GP1** using 1b (133.6 mg, 0.4 mmol) with sodium benzenethiosulfonate 2a (117.6 mg, 0.6 mmol) to afford 3ba (151.8 mg, 89%) using 20% ethyl acetate/petether as a colorless solid. mp: 91-93 °C; 1H NMR (400 MHz, CDCl3) δ 7.81 (dd, J = 8.4, 1.2 Hz, 2H), 7.74 (s, 1H), 7.69–7.63 (tt, J = 7.4, 1.2 Hz, 1H), 7.54 (m, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 4.09 (s, 2H), 3.76 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 166.5, 144.4, 142.9, 133.9, 132.9, 132.2(2C), 131.1(2C), 129.4(2C), 127.2(2C), 125.2, 124.2, 52.7, 33.2; HRMS (ESI) calculated for C17H16O4S2Br [M+H]+: m/z 426.9673, found 426.9672.

Prepared according to **GP1** using 1b (0.67 g, 2.0 mmol) with sodium benzenethiosulfonate 2a (0.59 g, 3.0 mmol) in CH3CN (10 mL) to afford 3ba (0.69 g, 78%) as a colorless solid.

**Allyl Thiosulfonate 3ca:** Prepared according to **GP1** using 1c (115.8 mg, 0.4 mmol) with sodium benzenethiosulfonate 2a (117.6 mg, 0.6 mmol) to afford 3ca (128.4 mg, 84%) using 20% ethyl acetate/petether as a colorless solid. mp: 82-84 °C; 1H NMR (400 MHz, CDCl3) δ 7.82 (d, J = 7.3 Hz, 2H), 7.76 (s, 1H), 7.66 (tt, J = 7.5, 1.8 Hz, 1H), 7.57-7.49 (m, 2H), 7.35–7.27 (m, 4H), 4.10 (s, 2H), 3.76 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 166.6, 144.5, 142.9, 135.9, 133.9, 132.5, 131.0(2C), 129.4(2C), 129.3(2C), 127.2(2C), 125.0, 52.7, 33.2; HRMS (ESI) calculated for C17H16O4S2Cl [M+H]+: m/z 383.0179, found 383.0175.

**Allyl Thiosulfonate 3ab:** Prepared according to **GP1** using 1a (101.2 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3ab (133.0 mg, 92%) using 20% ethyl acetate/petether as a colorless solid. mp: 95-97 °C; 1H NMR (400 MHz, CDCl3) δ 7.82 (s, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.40–7.32 (m, 5H), 7.29 (d, J = 8.0 Hz, 2H), 4.14 (s, 2H), 3.76 (s, 3H), 2.45 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 166.8, 144.8, 144.1, 141.7, 134.0, 129.9(2C), 129.7(3C), 128.9(2C), 127.2(2C), 124.4, 52.5, 33.3, 21.7; HRMS (ESI) calculated for C18H19O4S [M+H]+: m/z 363.0725, found 363.0720.

Prepared according to **GP1** using 1a (1.02 g, 4.0 mmol) with sodium 4-methylphenylthiosulfonate 2b (1.26 g, 6.0 mmol) in CH3CN (20 mL) to afford 3ab (1.16 g, 80%) as a colorless solid.

**Allyl Thiosulfonate 3bb:** Prepared according to **GP1** using 1b (133.6 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3bb (158.6 mg, 90%) using 20% ethyl acetate/petether as a colorless solid. mp: 91-93 °C; 1H NMR (400 MHz, CDCl3) δ 7.74 (s, 1H), 7.72–7.67 (m, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 4.07 (s, 2H), 3.77 (s, 3H), 2.48 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 166.6, 145.1, 142.8, 141.6, 132.9, 132.1(2C), 131.1(2C), 130.0(2C), 127.3(2C), 125.2, 124.1, 52.7, 33.2, 21.8; HRMS (ESI) calculated for C18H18O4S2Br [M+H]+: m/z 440.9830, found 440.9821.

Prepared according to **GP1** using 1b (0.67 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate 2b (0.63 g, 3.0 mmol) in CH3CN (10 mL) to afford 3bb (0.69 g, 78%) as a colorless solid.
**Allyl Thiosulfonate 3cb**: Prepared according to GP1 using 1c (115.6 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3cb (123.6 mg, 78%) using 20% ethyl acetate/petether as a colorless solid. mp: 76–78 °C; 1H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.27 (d, J = 8.1 Hz, 4H), 4.08 (s, 2H), 3.77 (s, 3H), 2.48 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 166.6, 145.0, 142.8, 141.7, 135.8, 132.5, 130.9(2C), 130.0(2C), 129.2(2C), 127.3(2C), 125.1, 52.7, 33.2, 21.8; HRMS (ESI) calculated for C_{18}H_{16}O_{6}S_{2}Cl [M+H]⁺: m/z 397.0335, found 397.0331.

*Prepared according to GP1 using 1c (0.58 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate 2b (0.63 g, 3.0 mmol) in CH₃CN (10 mL) to afford 3cb (0.54 g, 68%) as a colorless solid.*

**Allyl Thiosulfonate 3db**: Prepared according to GP1 using 1d (107.6 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3db (132.2 mg, 88%) using 20% ethyl acetate/petether as a colorless solid. mp: 91-93 °C; 1H NMR (400 MHz, CDCl₃) δ 7.79 (s, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 4.16 (s, 2H), 3.74 (s, 3H), 2.46 (s, 3H), 2.39 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 167.0, 144.8, 144.4, 141.9, 140.3, 131.2, 129.93(2C), 129.92(2C), 129.7(2C), 127.3(2C), 123.2, 52.5, 33.6, 21.8, 21.6; HRMS (ESI) calculated for C_{19}H_{21}O_{6}S_{2} [M+H]⁺: m/z 377.0881, found 377.0876.

*Prepared according to GP1 using 1d (0.54 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate 2b (0.63 g, 3.0 mmol) in CH₃CN (10 mL) to afford 3db (0.55 g, 73%) as a colorless solid.*

**Allyl Thiosulfonate 3eb**: Prepared according to GP1 using 1e (118.8 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3eb (135.6 mg, 84%) using 20% ethyl acetate/petether as a colorless solid. mp: 83-85 °C; 1H NMR (400 MHz, CDCl₃) δ 7.79 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.37–7.28 (m, 4H), 7.20 (d, J = 8.2 Hz, 2H), 4.18 (s, 2H), 3.74 (s, 3H), 2.93 (sept, J = 6.9 Hz, 1H), 2.47 (s, 3H), 1.27 (d, J = 6.9 Hz, 6H); 13C NMR (101 MHz, CDCl₃) δ 167.0, 151.1, 144.8, 144.4, 141.9, 131.6, 130.1(2C), 129.9(2C), 127.3(2C), 127.1(2C), 123.0, 52.5, 34.2, 33.6, 23.9(2C), 21.8; HRMS (ESI) calculated for C_{21}H_{25}O_{6}S_{2} [M+H]⁺: m/z 405.1176, found 405.1194.

*Prepared according to GP1 using 1e (0.59 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate 2b (0.63 g, 3.0 mmol) in CH₃CN (10 mL) to afford 3eb (0.62 g, 77%) as a colorless solid.*

**Allyl Thiosulfonate 3fb**: Prepared according to GP1 using 1f (133.6 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3fb (123.5 mg, 70%) using 20% ethyl acetate/petether as a colorless solid. mp: 71-73 °C; 1H NMR (400 MHz, CDCl₃) δ 7.74 (s, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.56–7.52 (m, 1H), 7.48 (s, 1H), 7.34–7.27 (m, 4H), 4.09 (s, 2H), 3.78 (s, 3H), 2.46 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 166.4, 144.9, 142.0, 141.5, 136.1, 132.5, 132.4, 130.4, 129.9(2C), 127.9, 127.1(2C), 126.4, 123.0, 52.7, 32.9, 21.8; HRMS (ESI) calculated for C_{18}H_{16}O_{6}S_{2}Br [M+H]⁺: m/z 440.9830, found 440.9822.
**Allyl Thiosulfonate 3gb:** Prepared according to GP1 using 1g (114.0 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3gb (114.6 mg, 73%) using 30% ethyl acetate/petether as a colorless solid. mp: 86–88 °C; 1H NMR (400 MHz, CDCl3) δ 7.81 (s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.35–7.27 (m, 3H), 7.00–6.92 (m, 3H), 4.17 (s, 2H), 3.84 (s, 3H), 3.76 (s, 3H), 2.46 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 166.8, 160.0, 144.8, 144.2, 141.7, 135.3, 130.0, 129.9(2C), 127.2(2C), 124.6, 122.1, 116.1, 114.4, 55.5, 52.6, 33.4, 21.8; HRMS (ESI) calculated for C13H21O5S2 [M+H]+: m/z 393.0830, found 393.0810.

Prepared according to GP1 using 1g (0.57 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate 2b (0.63 g, 3.0 mmol) in CH3CN (10 mL) to afford 3gb (0.56 g, 71%) as a colorless solid.

**Allyl Thiosulfonate 3hb:** Prepared according to GP1 using 1h (133.6 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3hb (144.4 mg, 82%) using 20% ethyl acetate/petether as a colorless solid. mp: 87–89 °C; 1H NMR (400 MHz, CDCl3) δ 7.86 (s, 1H), 7.67–7.61 (m, 3H), 7.29–7.23 (m, 2H), 7.27 (m, 3H), 3.99 (s, 2H), 3.78 (s, 3H), 2.44 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 166.4, 144.8, 143.0, 141.7, 134.6, 133.2, 130.8, 130.3, 129.9(2C), 127.7, 127.2(2C), 126.9, 124.4, 52.7, 33.0, 21.8; HRMS (ESI) calculated for C18H18O4S3Br [M+H]+: m/z 440.9830, found 440.9826.

Prepared according to GP1 using 1h (0.67 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate 2b (0.63 g, 3.0 mmol) in CH3CN (10 mL) to afford 3hb (0.65 g, 74%) as a colorless solid.

**Allyl Thiosulfonate 3ia:** Prepared according to GP1 using 1i (122.0 mg, 0.4 mmol) with sodium benzenethiosulfonate 2a (117.6 mg, 0.6 mmol) to afford 3ia (133.4 mg, 84%) using 20% ethyl acetate/petether as a colorless solid. mp: 99-101 °C; 1H NMR (400 MHz, CDCl3) this compound exists in a 10:1 Z/E isomeric mixture δ 7.99 (s, 1H), 7.94 (s, 1H), 7.89–7.81 (m, 3H), 7.75 (dd, J = 8.5, 1.1 Hz, 2H), 7.60–7.52 (m, 3H), 7.45 (dd, J = 8.4, 1.7 Hz, 1H), 7.37 (t, J = 7.9 Hz, 2H), 4.25 (s, 2H), 3.79 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 166.9, 144.5, 144.3, 133.7, 133.6, 133.2, 131.5, 130.1, 129.3(2C), 128.9, 128.7(2C), 127.8, 127.6, 127.1, 126.9, 126.5, 124.6, 52.6, 33.5; HRMS (ESI) calculated for C21H19O4S2 [M+H]+: m/z 399.0725, found 399.0722.

**Allyl Thiosulfonate 3jb:** Prepared according to GP1 using 1j (122.0 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3jb (125.4 mg, 76%) using 20% ethyl acetate/petether as a colorless solid. mp: 87–88 °C; 1H NMR (400 MHz, CDCl3) this compound exists in a 13:1 Z/E isomeric mixture δ 7.99 (s, 1H), 7.94 (s, 1H), 7.89–7.81 (m, 3H), 7.75 (dd, J = 8.5, 1.1 Hz, 2H), 7.60–7.52 (m, 2H), 7.45 (dd, J = 8.4, 1.7 Hz, 1H), 7.37 (t, J = 7.9 Hz, 2H), 4.25 (s, 2H), 3.79 (s, 3H), 2.38 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 167.0, 144.8, 144.2, 141.7, 133.6, 133.2, 131.6, 130.1, 129.8(2C), 128.9, 128.7, 127.8, 127.6, 127.2(2C), 126.9, 126.6, 124.7, 52.6, 33.5, 21.7; HRMS (ESI) calculated for C22H21O4S2 [M+H]+: m/z 413.0881, found 413.0877.
Prepared according to GP1 using 1j (0.61 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate 2b (0.63 g, 3.0 mmol) in CH₃CN (10 mL) to afford 3jb (0.55 g, 67%) as a colorless solid.

**Allyl Thiosulfonate 3kb**: Prepared according to GP1 using 1k (98.0 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3kb (95.8 mg, 68%) using 20% ethyl acetate/petether as a colorless solid. mp: 81-83 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.3 Hz, 2H), 7.47 (s, 1H), 7.42 (s, 1H), 7.31 (d, J = 8.3 Hz, 2H), 6.69 (d, J = 3.5 Hz, 1H), 6.50 (dd, J = 3.4, 1.8 Hz, 1H), 4.42 (s, 2H), 3.73 (s, 3H), 2.45 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 150.3, 145.9, 144.6, 142.2, 129.8(2C), 128.9, 127.3(2C), 120.4, 118.4, 112.7, 52.5, 33.2, 21.8; HRMS (ESI) calculated for C₁₆H₁₇O₅S₂ [M+H]⁺: m/z 353.0517, found 353.0518.

Prepared according to GP1 using 1k (0.49 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate 2b (0.63 g, 3.0 mmol) in CH₃CN (10 mL) to afford 3kb (0.52 g, 61%) as a colorless solid.

**Allyl Thiosulfonate 3lb**: Prepared according to GP1 using 1l (112.4 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3lb (119.2 mg, 77%) using 20% ethyl acetate/petether as a colorless viscous liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 8.4 Hz, 2H), 7.50 (dd, J = 8.0, 1.2 Hz, 2H), 7.43–7.36 (m, 4H), 7.28 (d, J = 8.1 Hz, 2H), 7.08 (dd, J = 15.3, 11.6 Hz, 1H), 6.92 (d, J = 15.3 Hz, 1H), 4.17 (s, 2H), 3.72 (s, 3H), 2.40 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 144.8, 142.9, 142.8, 142.3, 135.9, 129.9(2C), 129.8, 129.0(2C), 127.8(2C), 127.1(2C), 123.3, 122.7, 52.3, 32.4, 21.7; HRMS (ESI) calculated for C₂₀H₂₁O₄S₂ [M+H]⁺: m/z 389.0881, found 389.0992.

**Allyl Thiosulfonate 3mb**: Prepared according to GP1 using 1m (94.0 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3mb (94.0 mg, 69%) using 20% ethyl acetate/petether as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) this compound exists in a 8.8:1 Z/E isomeric mixture δ 7.83 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 6.94 (t, J = 7.7 Hz, 1H), 3.93 (s, 2H), 3.67 (s, 3H), 2.45 (s, 3H), 2.04 (t, J = 7.3 Hz, 2H), 1.72 (sept, J = 6.7 Hz, 1H), 0.89 (d, J = 6.7 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 166.3, 147.9, 144.8, 142.0, 129.9(2C), 127.2(2C), 125.8, 52.2, 37.9, 31.7, 28.2, 22.5(2C), 21.7; HRMS (ESI) calculated for C₁₆H₂₃O₄S₂ [M+H]⁺: m/z 343.1038, found 343.1041.

**Allyl Thiosulfonate 3nb**: Prepared according to GP1 using 1n (107.6 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3nb (117.0 mg, 78%) using 20% ethyl acetate/petether as a colorless solid. mp: 89-91 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.82 (s, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.43–7.33 (m, 5H), 7.28 (d, J = 8.0 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 4.15 (s, 2H), 2.45 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.3, 144.8, 143.8, 141.8, 134.1, 129.9(2C), 129.7(2C), 129.6, 128.9(2C), 127.2(2C), 124.8, 61.6, 33.4, 21.7, 14.2; HRMS (ESI) calculated for C₁₅H₁₉O₄S₂Na [M+Na]⁺: m/z 399.0701, found 399.0704.
Prepared according to **GP1** using **1n** (0.54 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in CH$_3$CN (10 mL) to afford **3nb** (0.54 g, 72%) as a colorless solid.

**Allyl Thiosulfonate 3ob:** Prepared according to **GP1** using **1o** (139.2 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate **2b** (126.0 mg, 0.6 mmol) to afford **3ob** (131.0 mg, 72%) using 30% ethyl acetate/petether as a colorless solid. mp: 73-75 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 (s, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.38-7.30 (m, 2H), 7.29-7.22 (m, 4H), 4.25 (q, J = 7.1 Hz, 2H), 4.00 (s, 2H), 2.44 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.8, 144.7, 142.6, 141.6, 134.6, 133.1, 130.6, 130.2, 129.9(2C), 127.6, 127.1, 127.0(2C), 124.3, 61.7, 33.0, 21.7, 14.2; HRMS (ESI) calculated for C$_{14}$H$_{20}$O$_2$S$_2$Br [M+H]$^+$: m/z 454.9986, found 454.9986.

Prepared according to **GP1** using **1o** (0.70 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in CH$_3$CN (10 mL) to afford **3ob** (0.59 g, 65%) as a colorless solid.

**Allyl Thiosulfonate 3ac:** Prepared according to **GP1** using **1a** (102.0 mg, 0.4 mmol) with sodium 4-chlorophenylthiosulfonate **2c** (137.4 mg, 0.6 mmol) to afford **3ac** (93.5 mg, 61%) using 30% ethyl acetate/petether as a colorless solid. mp: 71-73 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (s, 1H), 7.70 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 7.42-7.36 (m, 3H), 7.35-7.31 (m, 2H), 4.15 (s, 2H), 3.78 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 166.8, 144.3, 143.0, 140.4, 134.1, 129.9, 129.64(2C), 129.61(2C), 129.0(2C), 128.6(2C), 124.5, 52.7, 33.4; HRMS (ESI) calculated for C$_{15}$H$_{16}$O$_2$S$_2$Cl [M+H]$^+$: m/z 383.0179, found 383.0179.

**Allyl Thiosulfonate 3ad:** Prepared according to **GP1** using **1a** (102.0 mg, 0.4 mmol) with sodium 2-naphthalenethiosulfonate **2d** (147.6 mg, 0.6 mmol) to afford **3ad** (120.6 mg, 76%) using 30% ethyl acetate/petether as a colorless solid. mp: 95-97 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.33 (d, J = 1.4 Hz, 1H), 7.98 (d, J = 8.7 Hz, 1H), 7.93 (t, J = 7.6 Hz, 2H), 7.86 (dd, J = 8.7, 1.9 Hz, 1H), 7.79 (s, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.31-7.25 (m, 3H), 7.21 (dd, J = 9.3, 5.6 Hz, 2H), 4.18 (s, 2H), 3.67 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 166.8, 144.2, 141.3, 135.3, 134.0, 131.9, 129.9, 129.8, 129.7, 129.63(2C), 129.8(2C), 128.7, 128.1, 127.9, 124.5, 122.2, 52.5, 33.5; HRMS (ESI) calculated for C$_{23}$H$_{18}$O$_2$S$_2$Na [M+Na]$^+$: m/z 421.0544, found 421.0546.

Prepared according to **GP1** using **1a** (0.51 g, 2.0 mmol) with sodium 2-naphthalene thiosulfonate **2d** (0.74 g, 3.0 mmol) to afford **3ad** (0.50 g, 63%) as a colorless solid.

**Allyl Thiosulfonate 3qa:** Prepared according to **GP1** using **1q** (88.8 mg, 0.4 mmol) with sodium benzenethiosulfonate **2a** (117.6 mg, 0.6 mmol) to afford **3qa** (111.0 mg, 88%) using 20% ethyl acetate/petether as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) this compound exists in a 4:2:1 E/Z isomeric mixture δ 7.87 (dd, J = 8.5, 1.2 Hz, 2H), 7.58 (dd, J = 7.7, 1.5 Hz, 2H), 7.52-7.48 (m, 1H), 7.47-7.35 (m, 5H), 7.06 (s, 1H), 4.06 (d, J = 1.0 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.9, 145.1, 134.0, 131.3, 129.5(2C), 129.1(2C), 129.0(2C), 127.2, 127.1(2C), 116.9, 104.5, 41.3; HRMS (ESI) calculated for C$_{16}$H$_{16}$NO$_2$S$_2$ [M+H]$^+$: m/z 316.0466, found 316.0468.
**Allyl Thiosulfonate 3qb**: Prepared according to **GP1** using 1q (88.8 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3qb (106.6 mg, 81%) using 20% ethyl acetate/petether as a pale-yellow liquid; ¹H NMR (400 MHz, CDCl₃) this compound exists in a 3:3:1 E/Z isomeric mixture δ 7.75 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.43–7.38 (m, 3H), 7.17 (d, J = 8.0 Hz, 2H), 6.99 (s, 1H), 4.04 (s, 2H), 2.28 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 146.6, 145.3, 142.3, 131.2, 130.0(2C), 129.1(2C), 129.0(2C), 127.8(2C), 117.0, 104.5, 41.2, 21.6; HRMS (ESI) calculated for C₁₇H₁₉N₂O₂S₂ [M+Na]⁺: m/z 347.0888, found 347.0889.

Prepared according to **GP1** using 1q (0.44 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate 2b (0.63 g, 3.0 mmol) in CH₃CN (10 mL) to afford 3qb (0.43 g, 65%) as a colorless solid.

**Allyl Thiosulfonate 3rb**: Prepared according to **GP1** using 1r (105.6 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3rb (115.2 mg, 78%) using 20% ethyl acetate/petether as a colorless liquid; ¹H NMR (400 MHz, CDCl₃) this compound exists in 4:2:1 E/Z isomeric mixture δ 7.74 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.94 (s, 1H), 4.03 (d, J = 0.9 Hz, 2H), 2.94 (septet, J = 6.9 Hz, 1H), 2.27 (s, 3H), 1.26 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 152.7, 146.7, 145.2, 142.3, 130.2, 130.0(2C), 129.1(2C), 129.0(2C), 127.4, 127.2(2C), 127.1(2C), 41.3, 34.3, 23.8(2C), 21.6; HRMS (ESI) calculated for C₂₀H₂₁NO₂S₂Na [M+Na]⁺: m/z 394.0911, found 394.0908.

**Allyl Thiosulfonate 3sb**: Prepared according to **GP1** using 1s (100.8 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3sb (102.4 mg, 71%) using 30% ethyl acetate/petether as a pale-yellow liquid; ¹H NMR (400 MHz, CDCl₃) this compound exists in 4:6:1 E/Z isomeric mixture δ 7.79–7.72 (m, 2H), 7.35–7.27 (m, 2H), 7.18 (d, J = 8.0 Hz, 3H), 6.96 (s, 2H), 4.03 (d, J = 1.0 Hz, 2H), 3.82 (s, 3H), 2.30 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.8, 146.6, 145.3, 142.3, 133.7, 130.1(2C), 130.0, 127.3, 127.2(2C), 122.0, 117.5, 113.4, 104.6, 55.5 41.2, 21.6; HRMS (ESI) calculated for C₁₈H₁₈NO₂S₂ [M+H]⁺: m/z 360.0728, found 360.0735.

**Allyl Thiosulfonate 3tb**: Prepared according to **GP1** using 1t (108.8 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate 2b (126.0 mg, 0.6 mmol) to afford 3tb (127.2 mg, 84%) using 20% ethyl acetate/petether as a pale-yellow liquid; ¹H NMR (400 MHz, CDCl₃) this compound exists in 2:7:1 E/Z isomeric mixture δ 7.97–7.85 (m, 4H), 7.80 (d, J = 8.4 Hz, 2H), 7.63–7.54 (m, 2H), 7.51–7.44 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 4.16 (d, J = 1.0 Hz, 2H), 2.30 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 146.7, 145.4, 144.9, 142.1, 133.5, 131.3, 130.8, 130.1(2C), 129.6, 129.0, 127.3, 127.2(2C), 126.6, 125.3, 123.2, 117.0, 108.4, 40.5, 21.6; HRMS (ESI) calculated for C₂₁H₁₈NO₂S₂ [M+H]⁺: m/z 380.0779, found 380.0771.

**General Procedure-2 (GP2) for synthesis of allyl disulfanes**

A heat gun-dried Schlenk tube was charged allyl thiosulfonates 3 (0.8 mmol, 1.0 equiv.) and cesium carbonate (260.6 mg, 0.8 mmol, 1.0 equiv.) in dry THF (4.0 mL). The reaction mixture was stirred at 60 °C for 2 h and monitored by TLC either complete or appeared to be
proceeding no further progress. The mixture was allowed to room temperature and quenched by addition of water (20 mL) followed by extraction with EtOAc (3x30 mL). The combined organic layers was washed with brine (2x20 mL), dried over anhydrous Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 20-30% ethyl acetate/petether) to afford desired allyl disulfanes 5 and 6.

**Diallyl disulfane 5a:** Prepared according to GP2 using 3ab (289.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford 5a$^5$ (81.2 mg, 24.5%×2 = 49%) using 20% ethyl acetate/petether as a colorless solid. mp: 110-112 $^\circ$C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (s, 1H), 7.51 (dd, $J$ = 7.3, 1.0 Hz, 2H), 7.41–7.34 (m, 3H), 3.88 (s, 2H), 3.81 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.6, 142.4, 134.9, 129.7(2C), 129.2, 128.8(2C), 128.0, 52.4, 36.7; HRMS (ESI) calculated for C$_{22}$H$_{22}$O$_5$S$_2$Na [M+Na]$^+$: m/z 437.0857, found 437.0857.

**Allyl disulfane 6a:** Prepared according to GP2 using 3ab (289.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford 6a (116.2 mg, 44%) using 30% ethyl acetate/petether as a colorless solid. mp: 163-165 $^\circ$C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 (s, 1H), 7.71 (d, $J$ = 8.3 Hz, 2H), 7.50–7.43 (m, 2H), 7.40–7.33 (m, 3H), 7.27 (d, $J$ = 8.0 Hz, 2H), 4.47 (s, 2H), 3.61 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.1, 146.3, 145.5, 144.9, 136.5, 133.8, 129.8(2C), 129.3(2C), 128.8(2C), 128.7(2C), 121.2, 55.3, 52.5, 21.7; HRMS (ESI) calculated for C$_{18}$H$_{18}$O$_5$S$_2$Na [M+Na]$^+$: m/z 353.0823, found 353.0829.

**Diallyl disulfane 5b:** Prepared according to GP2 using 3db (300.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford 5b (80.3 mg, 22.7%×2 = 45%) using 20% ethyl acetate/petether as a pale-yellow solid. mp: 197-199 $^\circ$C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.87–7.74 (m, 1H), 7.45 (d, $J$ = 8.1 Hz, 2H), 7.19 (d, $J$ = 8.0 Hz, 2H), 3.97 (s, 2H), 3.81 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.7, 142.5, 139.6, 131.9, 129.9(2C), 129.5(2C), 126.9, 52.3, 37.1, 21.5; HRMS (ESI) calculated for C$_{24}$H$_{26}$O$_5$S$_2$Na [M+Na]$^+$: m/z 465.1170, found 465.1172.

**Allyl disulfane 6b:** Prepared according to GP2 using 3db (300.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford 6b (112.7 mg, 41%) using 30% ethyl acetate/petether as a pale-yellow solid. mp: 212-214 $^\circ$C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 (s, 1H), 7.72 (d, $J$ = 8.2 Hz, 2H), 7.41 (d, $J$ = 8.0 Hz, 2H), 7.27 (d, $J$ = 8.0 Hz, 2H), 7.18 (d, $J$ = 8.0 Hz, 2H), 4.48 (s, 2H), 3.58 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.2, 146.4, 144.8, 140.2, 136.5, 130.9, 129.6(2C), 129.50(2C), 129.48(2C), 128.6(2C), 120.0, 55.3, 52.3, 21.7, 21.5; HRMS (ESI) calculated for C$_{19}$H$_{20}$O$_5$S$_2$Na [M+Na]$^+$: m/z 367.06980; found 367.06980.
**Diallyl disulfane 5c:** Prepared according to **GP2** using 3eb (323.2 mg, 0.8 mmol) with Cs₂CO₃ (260.6 mg, 0.8 mmol) to afford 5c (79.7 mg, 20%×2 = 40%) using 20% ethyl acetate/petether as a pale-yellow solid. mp: 178-180 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.50 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 3.96 (s, 2H), 3.81 (s, 3H), 2.91 (sept, J = 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 167.8, 150.5, 142.6, 132.3, 130.1(2C), 126.9(2C), 126.87, 52.4, 37.1, 34.1, 23.9(2C); HRMS (ESI) calculated for C₂₈H₃₃O₄S₂ [M+H]⁺: m/z 499.1957, found 499.1939.

**Allyl disulfane 6c:** Prepared according to **GP2** using 3eb (323.2 mg, 0.8 mmol) with Cs₂CO₃ (260.6 mg, 0.8 mmol) to afford 6c (107.0 mg, 36%) using 30% ethyl acetate/petether as a colorless solid. mp: 216-218 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.29 (dd, J = 8.7, 2.3 Hz, 4H), 4.54 (s, 2H), 3.63 (s, 3H), 3.04–2.88 (m, 1H), 2.46 (s, 3H), 1.30 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 151.1, 146.4, 144.7, 136.5, 131.3, 129.67(2C), 129.66(2C), 128.7(2C), 126.9(2C), 120.1, 55.4, 52.4, 34.1, 23.9(2C), 21.7; HRMS (ESI) calculated for C₂₁H₂₆O₂SNa [M+Na]⁺: m/z 395.1293, found 395.1293.

**Diallyl disulfane 5a:** Prepared according to **GP2** using 3aa (278.4 mg, 0.8 mmol) with Cs₂CO₃ (260.6 mg, 0.8 mmol) to afford 5a (63.2 mg, 19%×2 = 38%) using 20% ethyl acetate/petether as a colorless solid.

**Allyl disulfane 6d:** Prepared according to **GP2** using 3aa (278.4 mg, 0.8 mmol) with Cs₂CO₃ (260.6 mg, 0.8 mmol) to afford 6d (83.5 mg, 33%) using 30% ethyl acetate/petether as a pale-yellow viscous liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.84 (dd, J = 8.3, 1.2 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.51–7.45 (m, 4H), 7.40–7.34 (m, 3H), 4.49 (s, 2H), 3.58 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 146.4, 139.4, 133.8, 133.7, 129.8, 129.2(2C), 129.1(2C), 128.8(2C), 128.5(2C), 121.0, 55.2, 52.4; HRMS (ESI) calculated for C₁₃H₁₆O₂S₂Na [M+Na]⁺: m/z 339.0667, found 339.0665.

**Diallyl disulfane 5d:** Prepared according to **GP2** using 3ba (341.6 mg, 0.8 mmol) with Cs₂CO₃ (260.6 mg, 0.8 mmol) to afford 5d (98.6 mg, 21.5%×2 = 43%) using 20% ethyl acetate/petether as a pale-yellow gummy. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (s, 1H), 7.52 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 3.84 (s, 2H), 3.81 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.3, 141.0, 133.7, 132.0(2C), 131.2(2C), 128.6, 123.7, 52.5, 36.6; HRMS (ESI) calculated for C₂₂H₂₁O₂S₂Br₂ [M+H]⁺: m/z 570.9248, found 570.9259.

**Allyl disulfane 6e:** Prepared according to **GP2** using 3ba (341.6 mg, 0.8 mmol) with Cs₂CO₃ (260.6 mg, 0.8 mmol) to afford 6e (126.3 mg, 40%) using 30% ethyl acetate/petether as a pale-yellow gummy. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.85 (dd, J = 8.4, 1.2 Hz, 2H), 7.66–7.60 (m, 1H), 7.54–7.48 (m, 4H), 7.39 (d, J = 8.3 Hz, 2H), 4.43 (s, 2H), 3.57 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 145.2, 139.4, 134.0, 132.6, 132.2(2C),...
130.8(2C), 129.2(2C), 128.6(2C), 124.4, 121.6, 55.2, 52.6; HRMS (ESI) calculated for C$_{17}$H$_{15}$O$_{4}$S$_{2}$BrNa [M+Na]$^+\); m/z 416.9772, found 416.9776.

**Diallyl disulfane 5e:** Prepared according to **GP2** using **3hb** (341.6 mg, 0.8 mmol) with Cs$_{2}$CO$_{3}$ (260.6 mg, 0.8 mmol) to afford **5e** (89.2 mg, 19.5%×2 = 39%) using 20% ethyl acetate/petether as a pale-yellow viscous liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (s, 1H), 7.59 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.45 (dd, $J = 7.6, 1.3$ Hz, 1H), 7.32 (td, $J = 7.5, 0.8$ Hz, 1H), 7.20 (td, $J = 7.5, 1.3$ Hz, 1H), 3.82 (s, 3H), 3.57 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.0, 141.2, 135.4, 133.0, 130.6, 130.2, 129.8, 127.5, 124.5, 52.5, 35.9; HRMS (ESI) calculated for C$_{22}$H$_{20}$O$_{4}$S$_{2}$BrNa [M+Na]$^+\); m/z 592.9063, found 592.9055.

**Allyl disulfane 6f:** Prepared according to **GP2** using **3hb** (341.6 mg, 0.8 mmol) with Cs$_{2}$CO$_{3}$ (260.6 mg, 0.8 mmol) to afford **6f** (112.1 mg, 34%) using 30% ethyl acetate/petether as a pale-yellow viscous liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (s, 1H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.62 (dd, $J = 7.7, 1.1$ Hz, 1H), 7.56 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.35 (td, $J = 7.6, 1.6$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.22 (td, $J = 7.6, 1.2$ Hz, 1H), 4.35 (s, 2H), 3.64 (s, 3H), 2.43 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.5, 145.1, 144.8, 136.4, 134.2, 133.0, 130.7, 130.2, 129.8(2C), 128.5(2C), 127.7, 124.2, 123.0, 55.0, 52.6, 21.7; HRMS (ESI) calculated for C$_{18}$H$_{17}$O$_{3}$S$_{2}$BrNa [M+Na]$^+\); m/z 430.9751, found 430.9926.

**Diallyl disulfane 5f:** Prepared according to **GP2** using **3ob** (353.0 mg, 0.8 mmol) with Cs$_{2}$CO$_{3}$ (260.6 mg, 0.8 mmol) to afford **5f** (108.4 mg, 23.0%×2 = 46%) using 20% ethyl acetate/petether as a pale-yellow viscous liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (s, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.46 (d, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.19 (t, $J = 7.7$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 3.59 (s, 2H), 1.33 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.5, 140.9, 135.4, 132.9, 130.6, 130.2, 130.1, 127.4, 124.5, 61.5, 36.1, 14.4; HRMS (ESI) calculated for C$_{24}$H$_{24}$O$_{4}$S$_{2}$Br$_{2}$Na [M+Na]$^+\); m/z 620.9380, found 620.9373.

**Allyl disulfane 6g:** Prepared according to **GP2** using **3ob** (353.0 mg, 0.8 mmol) with Cs$_{2}$CO$_{3}$ (260.6 mg, 0.8 mmol) to afford **6g** (101.3 mg, 30%) using 30% ethyl acetate/petether as a pale-yellow viscous liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (s, 1H), 7.71 (d, $J = 8.3$ Hz, 2H), 7.62 (dd, $J = 7.7, 1.1$ Hz, 1H), 7.56 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.35 (td, $J = 7.5, 0.9$ Hz, 1H), 7.28 (d, $J = 8.3$ Hz, 2H), 7.22 (td, $J = 7.6, 1.3$ Hz, 1H), 4.35 (s, 2H), 4.10 (q, $J = 7.1$ Hz, 2H), 2.43 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.0, 144.78, 144.76, 136.5, 134.3, 132.9, 130.7, 130.2, 129.8(2C), 128.5(2C), 127.7, 124.2, 123.3, 61.8, 55.0, 21.7, 14.1; HRMS (ESI) calculated for C$_{19}$H$_{19}$O$_{3}$S$_{2}$BrNa [M+Na]$^+\); m/z 445.0088, found 445.0082.
**Diallyl disulfane 5g:** Prepared according to **GP2** using **3gb** (313.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5g** (60.6 mg, 16%$\times2$ = 32%) using 30% ethyl acetate/petether as a pale-yellow solid. mp: 192-194 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (s, 1H), 7.25-7.19 (m, 1H), 7.03 (d, $J$ = 2.2 Hz, 2H), 6.85 (dd, $J$ = 8.1, 1.9 Hz, 1H), 3.87 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.6, 159.8, 142.5, 136.1, 129.8, 128.1, 122.1, 115.4, 114.6, 55.5, 52.4, 37.0; HRMS (ESI) calculated for C$_{24}$H$_{26}$O$_6$S$_2$Na [M+Na]$^+$: $m/z$ 497.1068, found 497.1069.

**Allyl disulfane 6h:** Prepared according to **GP2** using **3gb** (313.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6h** (74.8 mg, 26%) using 30% ethyl acetate/petether as a pale-yellow gummy. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (s, 1H), 7.72 (d, $J$ = 8.2 Hz, 2H), 7.32–7.24 (m, 3H), 7.11 (s, 1H), 7.01 (d, $J$ = 7.6 Hz, 1H), 6.92 (d, $J$ = 8.0 Hz, 1H), 4.48 (s, 2H), 3.85 (s, 3H), 3.61 (s, 3H), 2.43 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.0, 159.9, 146.3, 144.9, 136.5, 135.1, 129.8, 129.7(2C), 128.7(2C), 121.7, 121.4, 116.0, 114.1, 55.6, 55.4, 52.5, 21.7; HRMS (ESI) calculated for C$_{30}$H$_{26}$O$_5$S$_2$Na [M+Na]$^+$: $m/z$ 383.0929, found 383.0937.

**Diallyl disulfane 5h:** Prepared according to **GP2** using **3jb** (330.0 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5h** (89.3 mg, 21.7%$\times2$ = 43%) using 20% ethyl acetate/petether as a yellow solid. mp: 187-198 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (s, 1H), 7.74 (m, 3H), 7.30 (ddd, $J$ = 8.5, 1.5 Hz, 1H), 7.49 (ddd, $J$ = 8.0, 6.7, 1.4 Hz, 2H), 4.03 (s, 2H), 3.81 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.6, 142.4, 133.4, 133.2, 132.3, 129.8, 128.7, 128.4, 128.1, 127.8, 127.2, 126.8, 126.7, 52.4, 37.2; HRMS (ESI) calculated for C$_{30}$H$_{26}$O$_5$S$_2$Na [M+Na]$^+$: $m/z$ 537.1165, found 537.1170.

**Allyl disulfane 6i:** Prepared according to **GP2** using **3jb** (330.0 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6i** (99.6 mg, 33%) using 20% ethyl acetate/petether as yellow solid. mp: 195-197 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (s, 1H), 7.97 (s, 1H), 7.88–7.78 (m, 3H), 7.70 (d, $J$ = 8.3 Hz, 2H), 7.55–7.47 (m, 3H), 7.18 (d, $J$ = 8.0 Hz, 2H), 4.57 (s, 2H), 3.67 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.2, 146.2, 144.9, 136.5, 133.6, 133.2, 131.3, 129.7(2C), 129.6, 128.8, 128.7(2C), 128.5, 127.8, 127.5, 126.8, 126.1, 121.4, 55.4, 52.6, 21.7; HRMS (ESI) calculated for C$_{22}$H$_{20}$O$_5$S$_2$Na [M+Na]$^+$: $m/z$ 403.0980, found 403.0983.

**Diallyl disulfane 5a:** Prepared according to **GP2** using **3ad** (318.8 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5a** (52.6 mg, 15.8%$\times2$ = 32%) using 20% ethyl acetate/petether as a colorless solid.
**Allyl disulfane 6j:** Prepared according to **GP2** using 3ad (318.8 mg, 0.8 mmol) with Cs₂CO₃ (260.6 mg, 0.8 mmol) to afford 6j (110.6 mg, 38%) using 30% ethyl acetate/petether as a pale-yellow solid. mp: 227-229 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.38 (s, 1H), 7.97-7.87 (m, 4H), 7.79 (dd, J = 8.7, 1.8 Hz, 1H), 7.69–7.57 (m, 2H), 7.37 (dd, J = 7.4, 1.6 Hz, 2H), 7.27–7.22 (m, 3H), 4.57 (s, 2H), 3.45 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 146.3, 136.2, 135.4, 133.6, 132.1, 130.5, 129.6, 129.5, 129.4, 129.3, 129.0(2C), 128.7(2C), 128.0, 127.7, 123.2, 121.1, 55.1, 52.4; HRMS (ESI) calculated for C₂₁H₁₉O₄S₂ [M+H]+: m/z 367.1004, found 367.1005.

**Diallyl disulfane 5i:** Prepared according to **GP2** using 3nb (300.8 mg, 0.8 mmol) with Cs₂CO₃ (260.6 mg, 0.8 mmol) to afford 5i (70.7 mg, 20%×2 = 40%) using 20% ethyl acetate/petether as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 1H), 7.50 (d, J = 6.9 Hz, 2H), 7.40–7.33 (m, 3H), 4.27 (q, J = 7.1 Hz, 2H), 3.89 (s, 2H), 1.32 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 142.1, 134.9, 129.7, 129.1(2C), 128.8, 128.3(2C), 61.4, 36.8, 14.4; HRMS (ESI) calculated for C₂₄H₂₄O₂S₂ [M+Na]+: m/z 443.1334, found 443.1351.

**Allyl disulfane 6k:** Prepared according to **GP2** using 3nb (300.8 mg, 0.8 mmol) with Cs₂CO₃ (260.6 mg, 0.8 mmol) to afford 6k (96.5 mg, 35%) using 30% ethyl acetate/petether as a pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.50–7.43 (m, 2H), 7.39–7.33 (m, 3H), 7.26 (d, J = 8.0 Hz, 2H), 4.48 (s, 2H), 4.07 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 146.0, 144.8, 136.5, 133.9, 129.7(2C), 129.6, 129.3(2C), 128.8(2C), 128.7(2C), 121.6, 61.7, 55.2, 21.7, 14.2; HRMS (ESI) calculated for C₁₉H₂₀O₂S₂Na [M+Na]+: m/z 307.0980, found 307.0981.

**General Procedure-3 (GP3) for synthesis of S-acetyl allyl disulfanes**
A heat gun-dried Schlenk tube was charged allyl thiosulfonates 3ab and 3hb (0.8 mmol, 1.0 equiv.) and potassium thioacetate (KSAc, 117.6 mg, 1.2 mmol, 1.5 equiv.) in DMF (4.0 mL). The reaction mixture was stirred at room temperature for 4 h and monitored by TLC either complete or appeared to be proceeding no further progress. The mixture quenched by addition of water (20 mL) followed by extraction with EtOAc (3x30 mL). The combined organic layers was washed with brine (2x20 mL), dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 20% ethyl acetate/petether) to afford desired S-acetyl allyl disulfanes 7a and 7b.

**S-Acetyl allyl disulfane 7a:** Prepared according to **GP3** using 3ab (289.6 mg, 0.8 mmol) with KSAc (117.6 mg, 1.2 mmol) to afford 7a (198.2 mg, 88%) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (s, 1H), 7.44–7.35 (m, 5H), 4.07 (s, 2H), 3.84 (s, 3H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 195.0, 167.5, 142.7, 134.6, 129.6(2C), 129.4, 128.8(2C), 126.9, 52.5, 30.4, 27.0; HRMS (ESI) calculated for C₁₃H₁₄O₅S₂Na [M+Na]+: m/z 304.0282, found 305.0287.
**S-Acetyl allyl disulfane 7b:** Prepared according to **GP3** using **3hb** (341.6 mg, 0.8 mmol) with KSAc (117.6 mg, 1.2 mmol) to afford 7b (244.8 mg, 85%) as a pale-yellow solid. mp: 53-55 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (s, 1H), 7.62 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.48 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.38 (td, $J = 7.6, 1.1$ Hz, 1H), 7.22 (td, $J = 7.8, 1.6$ Hz, 1H), 3.89 (s, 3H), 3.79 (s, 2H), 2.27 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.2, 166.7, 141.8, 135.2, 132.9, 130.3, 128.8, 127.6, 124.6, 52.6, 34.7, 28.9; HRMS (ESI) calculated for C$_{13}$H$_{13}$O$_2$S$_2$Na $[M+Na]^+$: m/z 382.9387, found 382.9392.

**Sequential one-pot synthesis of S-acetyl allyl disulfane (7a)**

A heat gun-dried 50 mL RB flask was charged MBH allyl bromide 1a (1.2 g, 5 mmol, 1.0 equiv.) and sodium 4-methylbenzenethiosulfonate 2b (1.6 g, 7.5 mmol, 1.5 equiv.) in CH$_3$CN (20 mL). The reaction mixture was stirred at room temperature for 4 h (monitored by TLC). The solvent was removed under reduced pressure, the resulting residue was dissolved with DMF (20 mL). Then, the potassium thiaoacetate (KSAc, 735 mg, 7.5 mmol, 1.5 equiv.) was added and the reaction mixture was stirred at room temperature for 4 h (monitored by TLC). The mixture was quenched by addition of water (30 mL) followed by extraction with EtOAc (3x50 mL). The combined organic layers was washed with brine (2x50 mL), dried over anhydrous Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 20% ethyl acetate/petether) to afford desired S-acetyl allyl disulfane (7a) in 78% (1.1 g) yield.

**References**

**1H NMR and 13C NMR Spectra of New Compounds**

*(Note: Common laboratory solvents as trace impurities, peaks at δ 1.25 and δ 1.58 refers to grease and moisture respectively in a 1H NMR recorded in CDCl₃. In a 13C NMR recorded in CDCl₃, a peak at δ 29.7 represents to grease; Ref. H. E. Gottlie, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, 62, 7512).*