

# Electronic Supplementary Information

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

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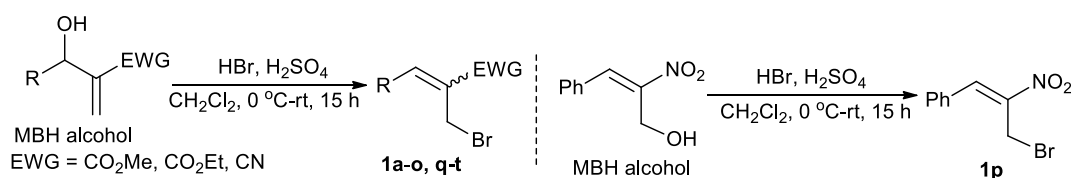
## General Experimental

All reagents were purchased 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.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR's were recorded using Bruker AVIII400 ( $^1\text{H}$  = 400 MHz,  $^{13}\text{C}$  = 101 MHz) or Bruker AVIII500 ( $^1\text{H}$  = 500 MHz,  $^{13}\text{C}$  = 126 MHz) with the spectrometers at 300 K. Chemical shifts ( $\delta$ ) 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* ( $\text{CDCl}_3$ ) the 7.26 ppm resonance of residual  $\text{CHCl}_3$  for proton spectra and 77.16 ppm resonance of  $\text{CDCl}_3$  for carbon spectra were used as internal references. Spectral data for  $^1\text{H}$  NMR spectroscopy is reported as follows: Chemical shift (multiplicity, coupling constant, number of protons); and for  $^{13}\text{C}$  NMR spectroscopy: Chemical shift. The following abbreviations were used for multiplicity in  $^1\text{H}$  NMR: s (singlet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublets), td (triplet of doublets), 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)

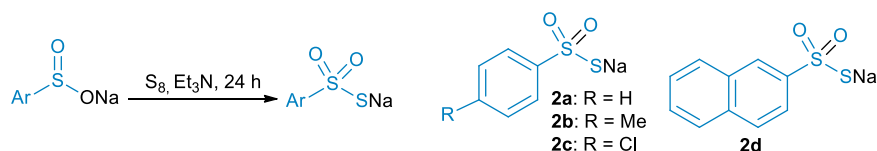
According to known procedure, a variety of Morita-Baylis-Hillman alcohols<sup>1</sup> have been prepared and were treated with HBr/ $\text{H}_2\text{SO}_4$  in  $\text{CH}_2\text{Cl}_2$  for formation of desired Morita-Baylis-Hillman allyl bromides (**1a-o,q-t**)<sup>1,2</sup> and nitrostyrene derived allyl bromide (**1p**)<sup>3</sup> as described in Scheme 1.



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

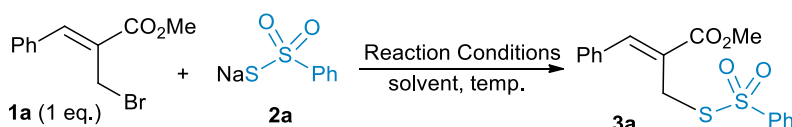
### Synthesis of sodium thiosulfonates (2a-d)

The sodium thiosulfonates (**2a-d**)<sup>4</sup> 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 Sulfenylation of MBH bromide (**1a**) with sodium benzenethiosulfonate **2a**.<sup>a</sup>



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

**Reaction conditions:** <sup>a</sup> 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.

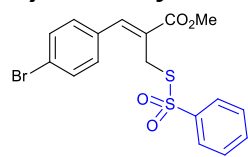
### General Procedure-1 (GP1) for synthesis of allyl thiosulfonates

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>O<sub>4</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *m/z* 371.0388, found 371.0389.

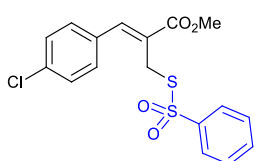
Prepared according to **GP1** using **1a** (1.02 g, 4.0 mmol) with sodium benzenethiosulfonate **2a** (1.47 g, 6.0 mmol) in CH<sub>3</sub>CN (20 mL) to afford **3aa** (1.1 g, 79%) as a colorless solid.

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>17</sub>H<sub>16</sub>O<sub>4</sub>S<sub>2</sub>Br [M+H]<sup>+</sup>: *m/z* 426.9673, found 426.9672.

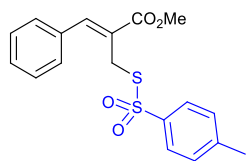


Prepared according to **GP1** using **1b** (0.67 g, 2.0 mmol) with sodium benzenethiosulfonate **2a** (0.59 g, 3.0 mmol) in CH<sub>3</sub>CN (10 mL) to afford **3ba** (0.69 g, 78%) as a colorless solid.

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>17</sub>H<sub>16</sub>O<sub>4</sub>S<sub>2</sub>Cl [M+H]<sup>+</sup>: *m/z* 383.0179, found 383.0175.

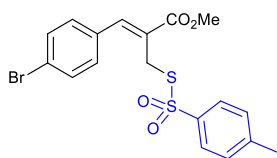


**Allyl Thiosulfonate 3ab:** Prepared according to **GP1** using **1a** (101.2 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate **2b** (126.0 mg, 0.6 mmol) to afford **3ab** (133.0 mg, 92%) using 20% ethyl acetate/petether as a colorless solid. mp: 95-97 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>18</sub>H<sub>19</sub>O<sub>4</sub>S [M+H]<sup>+</sup>: *m/z* 363.0725, found 363.0720.



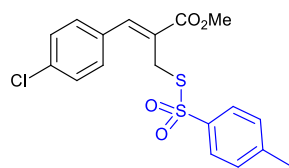
Prepared according to **GP1** using **1a** (1.02 g, 4.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (1.26 g, 6.0 mmol) in CH<sub>3</sub>CN (20 mL) to afford **3ab** (1.16 g, 80%) as a colorless solid.

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>Br [M+H]<sup>+</sup>: *m/z* 440.9830, found 440.9821.



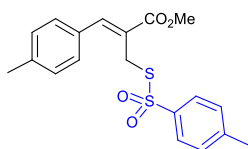
Prepared according to **GP1** using **1b** (0.67 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in CH<sub>3</sub>CN (10 mL) to afford **3bb** (0.69 g, 78%) as a colorless solid.

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sub>18</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>Cl [M+H]<sup>+</sup>: *m/z* 397.0335, found 397.0331.



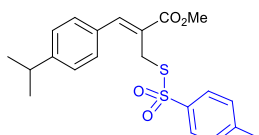
Prepared according to **GP1** using **1c** (0.58 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in CH<sub>3</sub>CN (10 mL) to afford **3cb** (0.54 g, 68%) as a colorless solid.

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sub>19</sub>H<sub>21</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup>: *m/z* 377.0881, found 377.0876.



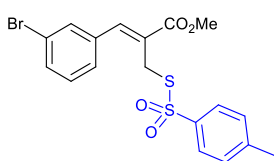
Prepared according to **GP1** using **1d** (0.54 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in CH<sub>3</sub>CN (10 mL) to afford **3db** (0.55 g, 73%) as a colorless solid.

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sub>21</sub>H<sub>25</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup>: *m/z* 405.1176, found 405.1194.

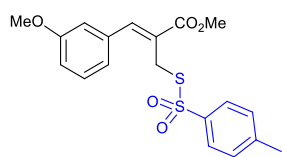


Prepared according to **GP1** using **1e** (0.59 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in CH<sub>3</sub>CN (10 mL) to afford **3eb** (0.62 g, 77%) as a colorless solid.

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sub>18</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>Br [M+H]<sup>+</sup>: *m/z* 440.9830, found 440.9822.

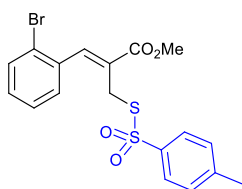


**Allyl Thiosulfonate 3gb:** Prepared according to **GP1** using **1g** (114.0 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate **2b** (126.0 mg, 0.6 mmol) to afford **3gb** (114.6 mg, 73%) using 30% ethyl acetate/petether as a colorless solid. mp: 86-88 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>19</sub>H<sub>21</sub>O<sub>5</sub>S<sub>2</sub> [M+H]<sup>+</sup>: *m/z* 393.0830, found 393.0810.



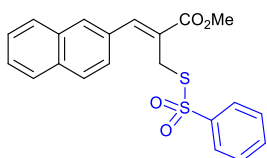
Prepared according to **GP1** using **1g** (0.57 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in CH<sub>3</sub>CN (10 mL) to afford **3gb** (0.56 g, 71%) as a colorless solid.

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>Br [M+H]<sup>+</sup>: *m/z* 440.9830, found 440.9826.

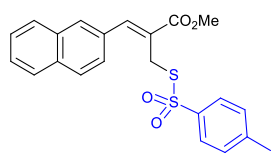


Prepared according to **GP1** using **1h** (0.67 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in CH<sub>3</sub>CN (10 mL) to afford **3hb** (0.65 g, 74%) as a colorless solid.

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup>: *m/z* 399.0725, found 399.0722.

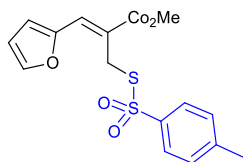


**Allyl Thiosulfonate 3jb:** Prepared according to **GP1** using **1j** (122.0 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate **2b** (126.0 mg, 0.6 mmol) to afford **3jb** (125.4 mg, 76%) using 20% ethyl acetate/petether as a colorless solid. mp: 87-88 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup>: *m/z* 413.0881, found 413.0877.



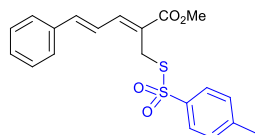
Prepared according to **GP1** using **1j** (0.61 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) to afford **3jb** (0.55 g, 67%) as a colorless solid.

**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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{16}\text{H}_{17}\text{O}_5\text{S}_2$   $[\text{M}+\text{H}]^+$ :  $m/z$  353.0517, found 353.0518.

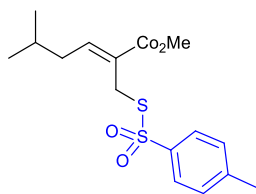


Prepared according to **GP1** using **1k** (0.49 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) to afford **3kb** (0.52 g, 61%) as a colorless solid.

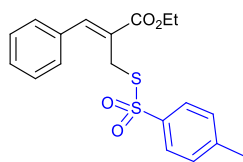
**Allyl Thiosulfonate 3lb:** Prepared according to **GP1** using **1l** (112.4 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate **2b** (126.0 mg, 0.6 mmol) to afford **3lb** (119.2 mg, 77%) using 20% ethyl acetate/petether as a colorless viscous liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{20}\text{H}_{21}\text{O}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ :  $m/z$  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.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) *this compound exists in a 8.8:1 Z/E isomeric mixture*  $\delta$  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);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{16}\text{H}_{23}\text{O}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ :  $m/z$  343.1038, found 343.1041.

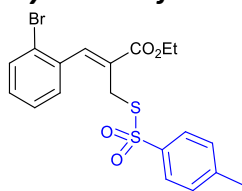


**Allyl Thiosulfonate 3nb:** Prepared according to **GP1** using **1n** (107.6 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate **2b** (126.0 mg, 0.6 mmol) to afford **3nb** (117.0 mg, 78%) using 20% ethyl acetate/petether as a colorless solid. mp: 89-91 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{19}\text{H}_{20}\text{O}_4\text{S}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ :  $m/z$  399.0701, found 399.0704.



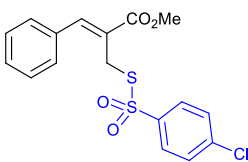
Prepared according to **GP1** using **1n** (0.54 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in CH<sub>3</sub>CN (10 mL) to afford **3nb** (0.54 g, 72%) as a colorless solid.

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.8, 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<sub>19</sub>H<sub>20</sub>O<sub>4</sub>S<sub>2</sub>Br [M+H]<sup>+</sup>: *m/z* 454.9986, found 454.9986.

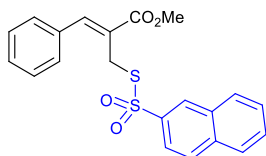


Prepared according to **GP1** using **1o** (0.70 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in CH<sub>3</sub>CN (10 mL) to afford **3ob** (0.59 g, 65%) as a colorless solid.

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) 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<sub>17</sub>H<sub>16</sub>O<sub>4</sub>S<sub>2</sub>Cl [M+H]<sup>+</sup>: *m/z* 383.0179, found 383.0179.

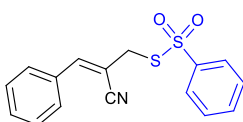


**Allyl Thiosulfonate 3ad:** Prepared according to **GP1** using **1a** (102.0 mg, 0.4 mmol) with sodium 2-naphthalenethiosulfonate **2d** (147.6 mg, 0.6 mmol) to afford **3ad** (120.6 mg, 76%) using 30% ethyl acetate/petether as a colorless solid. mp: 95-97 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 166.8, 144.2, 141.3, 135.3, 134.0, 131.9, 129.9, 129.8, 129.7, 129.6(3C), 128.9(2C), 128.7, 128.1, 127.9, 124.5, 122.2, 52.5, 33.5; HRMS (ESI) calculated for C<sub>21</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *m/z* 421.0544, found 421.0546.



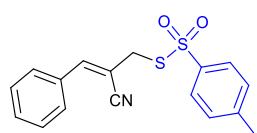
Prepared according to **GP1** using **1a** (0.51 g, 2.0 mmol) with sodium 2-naphthalene thiosulfonate **2d** (0.74 g, 3.0 mmol) to afford **3ad** (0.50 g, 63%) as a colorless solid.

**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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sub>16</sub>H<sub>14</sub>NO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: *m/z* 316.0466, found 316.0468.



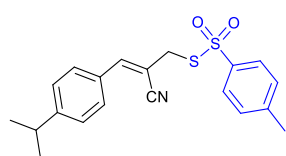


**Allyl Thiosulfonate 3qb:** Prepared according to **GP1** using **1q** (88.8 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate **2b** (126.0 mg, 0.6 mmol) to afford **3qb** (106.6 mg, 81%) using 20% ethyl acetate/petether as a pale-yellow liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) *this compound exists in a 3.3:1 E/Z isomeric mixture*  $\delta$  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);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.6, 145.3, 142.3, 132.5, 131.2, 130.0(2C), 129.1(2C), 129.0(2C), 127.2(2C), 117.0, 104.5, 41.2, 21.6; HRMS (ESI) calculated for  $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2\text{S}_2$   $[\text{M}+\text{NH}_4]^+$ :  $m/z$  347.0888, found 347.0889.

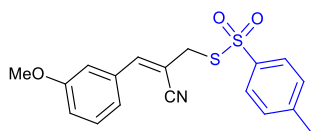


Prepared according to **GP1** using **1q** (0.44 g, 2.0 mmol) with sodium 4-methylphenylthiosulfonate **2b** (0.63 g, 3.0 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) to afford **3qb** (0.43 g, 65%) as a colorless solid.

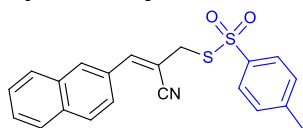
**Allyl Thiosulfonate 3rb:** Prepared according to **GP1** using **1r** (105.6 mg, 0.4 mmol) with sodium 4-methylphenylthiosulfonate **2b** (126.0 mg, 0.6 mmol) to afford **3rb** (115.2 mg, 78%) using 20% ethyl acetate/petether as a colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) *this compound exists in 5.0:1 E/Z isomeric mixture*  $\delta$  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);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.7, 146.7, 145.2, 142.3, 130.2, 130.0(2C), 129.8, 129.3(2C), 127.4, 127.2(2C), 127.1(2C), 41.3, 34.3, 23.8(2C), 21.6; HRMS (ESI) calculated for  $\text{C}_{20}\text{H}_{21}\text{NO}_2\text{S}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ :  $m/z$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) *this compound exists in 4.6:1 E/Z isomeric mixture*  $\delta$  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);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{18}\text{H}_{18}\text{NO}_3\text{S}_2$   $[\text{M}+\text{H}]^+$ :  $m/z$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) *this compound exists in 2.7:1 E/Z isomeric mixture*  $\delta$  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);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{21}\text{H}_{18}\text{NO}_2\text{S}_2$   $[\text{M}+\text{H}]^+$ :  $m/z$  380.0779, found 380.0771.

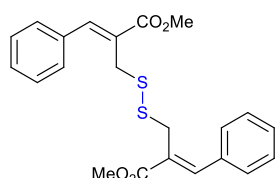


## General Procedure-2 (GP2) for synthesis of allyl disulfanes

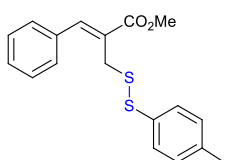
A heat gun-dried Schlenk tube was charged allyl thiosulfonates **3** (0.8 mmol, 1.0 equiv.) and cesium carbonate (260.6 mg, 0.8 mmol, 1.0 equiv.) in dry THF (4.0 mL). The reaction mixture was stirred at 60 °C for 2 h and monitored by TLC either complete or appeared to be

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<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 disulfanes **5** and **6**.

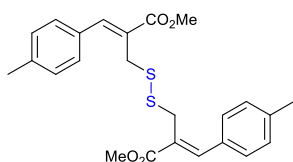
**Diallyl disulfane 5a:** Prepared according to **GP2** using **3ab** (289.6 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **5a**<sup>5</sup> (81.2 mg, 24.5%x2 = 49%) using 20% ethyl acetate/petether as a colorless solid. mp: 110-112 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sub>22</sub>H<sub>22</sub>O<sub>4</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *m/z* 437.0857, found 437.0857.



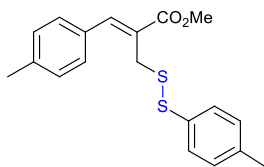
**Allyl disulfane 6a:** Prepared according to **GP2** using **3ab** (289.6 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **6a** (116.2 mg, 44%) using 30% ethyl acetate/petether as a colorless solid. mp: 163-165 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sub>18</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *m/z* 353.0823, found 353.0829.



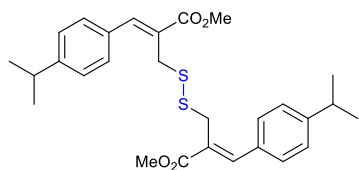
**Diallyl disulfane 5b:** Prepared according to **GP2** using **3db** (300.6 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **5b** (80.3 mg, 22.7%x2 = 45%) using 20% ethyl acetate/petether as a pale-yellow solid. mp: 197-199 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sub>24</sub>H<sub>26</sub>O<sub>4</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *m/z* 465.1170, found 465.1172.



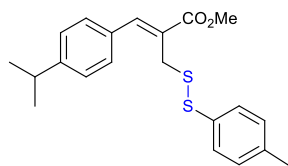
**Allyl disulfane 6b:** Prepared according to **GP2** using **3db** (300.6 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **6b** (112.7 mg, 41%) using 30% ethyl acetate/petether as a pale-yellow solid. mp: 212-214 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sub>19</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *m/z* 367.06980; found 367.06980.



**Diallyl disulfane 5c:** Prepared according to **GP2** using **3eb** (323.2 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **5c** (79.7 mg, 20% $\times$ 2 = 40%) using 20% ethyl acetate/petether as a pale-yellow solid. mp: 178-180 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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 C<sub>28</sub>H<sub>35</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup>:  $m/z$  499.1957, found 499.1939.

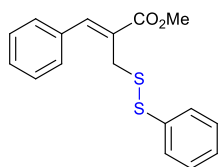


**Allyl disulfane 6c:** Prepared according to **GP2** using **3eb** (323.2 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **6c** (107.0 mg, 36%) using 30% ethyl acetate/petether as a colorless solid. mp: 216-218 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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 C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>SNa [M+Na]<sup>+</sup>:  $m/z$  395.1293, found 395.1293.

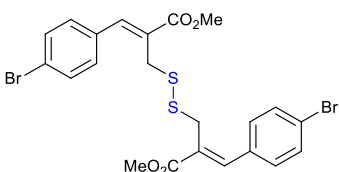


**Diallyl disulfane 5a:** Prepared according to **GP2** using **3aa** (278.4 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **5a** (63 .2 mg, 19% $\times$ 2 = 38%) using 20% ethyl acetate/petether as a colorless solid.

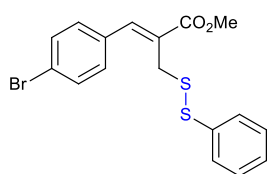
**Allyl disulfane 6d:** Prepared according to **GP2** using **3aa** (278.4 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **6d** (83.5 mg, 33%) using 30% ethyl acetate/petether as a pale-yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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 C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>:  $m/z$  339.0667, found 339.0665.



**Diallyl disulfane 5d:** Prepared according to **GP2** using **3ba** (341.6 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **5d** (98.6 mg, 21.5% $\times$ 2 = 43%) using 20% ethyl acetate/petether as a pale-yellow gummy. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.3, 141.0, 133.7, 132.0(2C), 131.2(2C), 128.6, 123.7, 52.5, 36.6; HRMS (ESI) calculated for C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>S<sub>2</sub>Br<sub>2</sub> [M+H]<sup>+</sup>:  $m/z$  570.9248, found 570.9259.

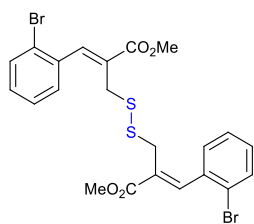


**Allyl disulfane 6e:** Prepared according to **GP2** using **3ba** (341.6 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **6e** (126.3 mg, 40%) using 30% ethyl acetate/petether as a pale-yellow gummy. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (s, 1H), 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.7, 145.2, 139.4, 134.0, 132.6, 132.2(2C),

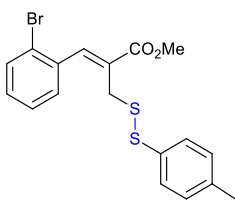


130.8(2C), 129.2(2C), 128.6(2C), 124.4, 121.6, 55.2, 52.6; HRMS (ESI) calculated for  $C_{17}H_{15}O_4S_2BrNa$   $[M+Na]^+$ :  $m/z$  416.9772, found 416.9776.

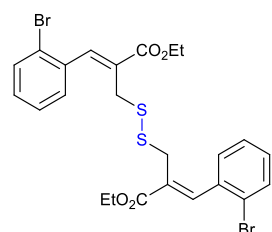
**Diallyl disulfane 5e:** Prepared according to **GP2** using **3hb** (341.6 mg, 0.8 mmol) with  $Cs_2CO_3$  (260.6 mg, 0.8 mmol) to afford **5e**<sup>5</sup> (89.2 mg, 19.5% $\times$ 2 = 39%) using 20% ethyl acetate/petether as a pale-yellow viscous liquid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  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  $C_{22}H_{20}O_4S_2Br_2Na$   $[M+Na]^+$ :  $m/z$  592.9063, found 592.9055.



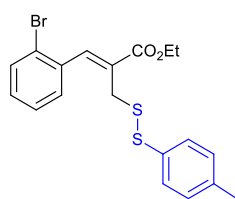
**Allyl disulfane 6f:** Prepared according to **GP2** using **3hb** (341.6 mg, 0.8 mmol) with  $Cs_2CO_3$  (260.6 mg, 0.8 mmol) to afford **6f** (112.1 mg, 34%) using 30% ethyl acetate/petether as a pale-yellow viscous liquid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.94 (s, 1H), 7.70 (d,  $J$  = 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  $C_{18}H_{17}O_2S_2BrNa$   $[M+Na]^+$ :  $m/z$  430.9751, found 430.9926.



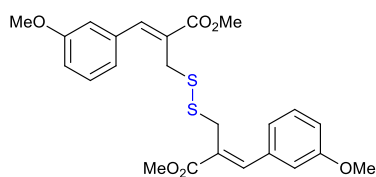
**Diallyl disulfane 5f:** Prepared according to **GP2** using **3ob** (353.0 mg, 0.8 mmol) with  $Cs_2CO_3$  (260.6 mg, 0.8 mmol) to afford **5f** (108.4 mg, 23.0% $\times$ 2 = 46%) using 20% ethyl acetate/petether as a pale-yellow viscous liquid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.77 (s, 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  $C_{24}H_{24}O_4S_2Br_2Na$   $[M+Na]^+$ :  $m/z$  620.9380, found 620.9373.



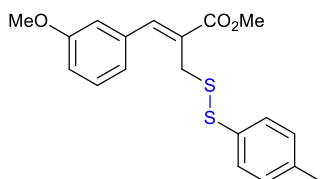
**Allyl disulfane 6g:** Prepared according to **GP2** using **3ob** (353.0 mg, 0.8 mmol) with  $Cs_2CO_3$  (260.6 mg, 0.8 mmol) to afford **6g** (101.3 mg, 30%) using 30% ethyl acetate/petether as a pale-yellow viscous liquid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.94 (s, 1H), 7.71 (d,  $J$  = 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  $C_{19}H_{19}O_2S_2BrNa$   $[M+Na]^+$ :  $m/z$  445.0088, found 445.0082.



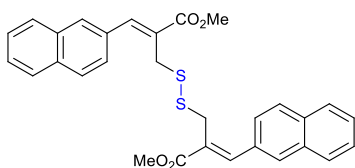
**Diallyl disulfane 5g:** Prepared according to **GP2** using **3gb** (313.6 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **5g** (60.6 mg, 16% $\times$ 2 = 32%) using 30% ethyl acetate/petether as a pale-yellow solid. mp: 192-194 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>24</sub>H<sub>26</sub>O<sub>6</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *m/z* 497.1068, found 497.1069.



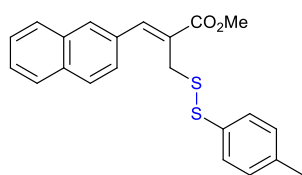
**Allyl disulfane 6h:** Prepared according to **GP2** using **3gb** (313.6 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **6h** (74.8 mg, 26%) using 30% ethyl acetate/petether as a pale-yellow gummy. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (s, 1H), 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.0, 159.9, 146.3, 144.9, 136.5, 135.1, 129.84, 129.76(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<sub>19</sub>H<sub>20</sub>O<sub>5</sub>SNa [M+Na]<sup>+</sup>: *m/z* 383.0929, found 383.0937.



**Diallyl disulfane 5h:** Prepared according to **GP2** using **3jb** (330.0 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **5h** (89.3 mg, 21.7% $\times$ 2 = 43%) using 20% ethyl acetate/petether as a yellow solid. mp: 187-198 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (s, 1H), 7.95 (s, 1H), 7.79 (dd, *J* = 8.7, 5.3 Hz, 3H), 7.57 (dd, *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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>30</sub>H<sub>26</sub>O<sub>4</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *m/z* 537.1165, found 537.1170.

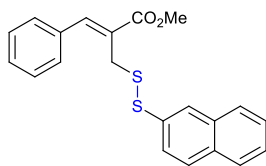


**Allyl disulfane 6i:** Prepared according to **GP2** using **3jb** (330.0 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **6i** (99.6 mg, 33%) using 20% ethyl acetate/petether as yellow solid. mp: 195-197 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>22</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *m/z* 403.0980, found 403.0983.

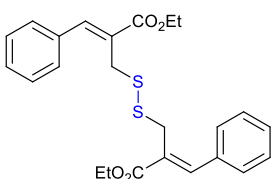


**Diallyl disulfane 5a:** Prepared according to **GP2** using **3ad** (318.8 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **5a** (52.6 mg, 15.8% $\times$ 2 = 32%) using 20% ethyl acetate/petether as a colorless solid.

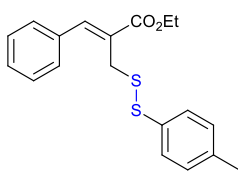
**Allyl disulfane 6j:** Prepared according to **GP2** using **3ad** (318.8 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **6j** (110.6 mg, 38%) using 30% ethyl acetate/petether as a pale-yellow solid. mp: 227-229 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.38 (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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup>: *m/z* 367.1004, found 367.1005.



**Diallyl disulfane 5i:** Prepared according to **GP2** using **3nb** (300.8 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **5i** (70.7 mg, 20% $\times$ 2 = 40%) using 20% ethyl acetate/petether as a pale-yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>24</sub>H<sub>27</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup>: *m/z* 443.1334, found 443.1351.



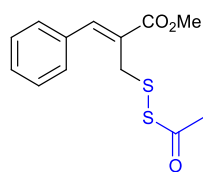
**Allyl disulfane 6k:** Prepared according to **GP2** using **3nb** (300.8 mg, 0.8 mmol) with Cs<sub>2</sub>CO<sub>3</sub> (260.6 mg, 0.8 mmol) to afford **6k** (96.5 mg, 35%) using 30% ethyl acetate/petether as a pale-yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (s, 1H), 7.71 (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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>19</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *m/z* 367.0980, found 367.0981.



### General Procedure-3 (GP3) for synthesis of *S*-acetyl allyl disulfanes

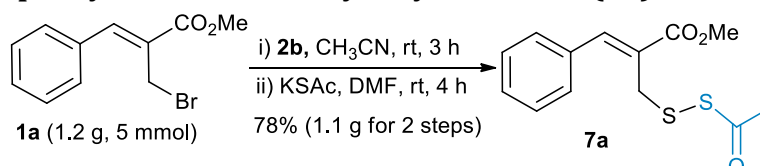
A heat gun-dried Schlenk tube was charged allyl thiosulfonates **3ab** and **3hb** (0.8 mmol, 1.0 equiv.) and potassium thioacetate (KSAc, 117.6 mg, 1.2 mmol, 1.5 equiv.) in DMF (4.0 mL). The reaction mixture was stirred at room temperature for 4 h and monitored by TLC either complete or appeared to be proceeding no further progress. The mixture quenched by addition of water (20 mL) followed by extraction with EtOAc (3 $\times$ 30 mL). The combined organic layers was washed with brine (2 $\times$ 20 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% 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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (s, 1H), 7.44-7.35 (m, 5H), 4.07 (s, 2H), 3.84 (s, 3H), 2.36 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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 C<sub>13</sub>H<sub>14</sub>O<sub>5</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 194.2, 166.7, 141.8, 135.2, 132.9, 130.8, 130.3, 128.8, 127.6, 124.6, 52.6, 34.7, 28.9; HRMS (ESI) calculated for C<sub>13</sub>H<sub>13</sub>O<sub>2</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: *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<sub>3</sub>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 thioacetate (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<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% ethyl acetate/petether) to afford desired S-acetyl allyl disulfane (**7a**) in 78% (1.1 g) yield.

### References

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## $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra of New Compounds

(Note: Common laboratory solvents as trace impurities, peaks at  $\delta$  1.25 and  $\delta$  1.58 refers to grease and moisture respectively in a  $^1\text{H}$  NMR recorded in  $\text{CDCl}_3$ . In a  $^{13}\text{C}$  NMR recorded in  $\text{CDCl}_3$ , a peak at  $\delta$  29.7 represents to grease; Ref. H. E. Gottlie, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512).

