Simple and Efficient Synthesis of Allyl Sulfones through Cs₂CO₃-Mediated Radical Sulfonylation of Morita–Baylis–Hillman Adducts with Thiosulfonates

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Abstract A highly efficient and eco-friendly method has been developed for the synthesis of allyl sulfones using Morita–Baylis–Hillman (MBH) adducts and thiosulfonates under mild conditions. The Cs₂CO₃-promoted radical sulfonylation provided a series of allyl sulfones in good to high yields with high stereoselectivities. A wide variety of MBH bromides/acetates as well as thiosulfonates were tolerated and reliable in scaled-up synthesis. A plausible mechanism is proposed to rationalize the radical sulfonylation.

Key words allyl sulfones, cesium carbonate, MBH adducts, radical sulfonylation, thiosulfonates

Thiosulfonates (R’SO₂-SR²)¹ have emerged as powerful reactants to synthesize many valuable organosulfur compounds.² Also known as sulfonothioates or S-esters of thiosulfonic acid, they generally show low toxicity. Typically, thiosulfonates serve as electrophilic sulfenylating reagents,³ generating a sulfenyl moiety as by-product. Additionally, homolytic cleavage of the S–S(O₂) bond of thiosulfonates generates sulfenyl and sulfenyl radicals under thermal or photochemical conditions.⁴ As a result, thiosulfonates have been utilized to install two distinct C–S bonds (sulfenyl and sulfonyl) through atom transfer thiosulfonylation.⁵ Despite these achievements, thiosulfonates have rarely been explored as sulfonylating agents.⁶

On the other hand, allyl aryl sulfones are attractive intermediates in organic synthesis⁷ and they are widely distributed pharmacophores,⁸ for instance in antican...
At the outset, our optimization investigations began with S-phenyl benzenesulfonylthioate (1a) and (Z)-methyl 2-(bromomethyl)-3-phenylacrylate (2a) as model substrates (Table 1). Initially, the reaction between 1a and 2a in a 1:1.5 ratio in the presence of Cs2CO3 in EtOH provided the allyl sulfone 3aa in 65% yield (entry 1). On reversing the ratios of 1a and 2a (1.5:1) the desired product 3aa was produced in 79% yield (entry 2). Various solvents, such as DMF, CH3CN, 1,4-dioxane, DMSO and toluene were screened (entries 3–7). Among these solvents, CH3CN proved the best choice for the transformation, giving 3aa in 80% yield (entry 4). In CH3CN at 80 °C, the yield of the reaction between 1a, 2a and Cs2CO3 (1:1.5:2 ratio) was improved considerably, giving 3aa in 91% yield (entry 8). To our satisfaction, use of 1 equiv of Cs2CO3 provided the desired allyl sulfone (3aa) in 96% yield (entry 9). Using 1.2 equiv of 2a or 1.5 equiv of Cs2CO3 or performing the reaction at room temperature were not beneficial (entries 10–12).

We then examined other bases (K2CO3, Na2CO3 and DABCO) but all afforded diminished yields (Table 1, entries 13–15). No reaction was observed in the absence of Cs2CO3, indicating that it plays a vital role in the sulfonylation process (entry 16). Only sulfonylated 3aa was obtained in all cases; the other anticipated allyl thioether (3aa') did not form, probably due to the lower stability of the thiyl radical (ArS•).13

With the reaction conditions optimized, we then explored a broad range of thiosulfonates (1a–i) and MBH allyl bromides (2a–n) to furnish a series of allyl sulfones (3aa–i and 3ab–n) in good to excellent yields and stereoselectivities (Scheme 2). Various alkyl and halo-substituted thiosulfonates (1a–f) reacted smoothly with 2a, providing the corresponding allyl sulfones 3aa–fa in 69–95% yields; an exception was 4-bromophenyl thiosulfonate (1f), which afforded moderate yields. In addition, 1/2-naphthyl and

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### Table 1  Optimization for the Sulfonylation of MBH Bromide with Thiosulfonate

<table>
<thead>
<tr>
<th>Entry</th>
<th>1a (equiv)</th>
<th>2a (equiv)</th>
<th>Base (equiv)</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield of 3aa (%)b</th>
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<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>1.5</td>
<td>Cs2CO3 (2.0)</td>
<td>EtOH</td>
<td>90</td>
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<td>65</td>
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<tr>
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<td>1.0</td>
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<td>EtOH</td>
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<td>79</td>
</tr>
<tr>
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<td>1.0</td>
<td>Cs2CO3 (2.0)</td>
<td>DMF</td>
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<tr>
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<td>1.0</td>
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<td>1.0</td>
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<td>5</td>
<td>32</td>
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<tr>
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<td>1.0</td>
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<td>–c</td>
<td>CH3CN</td>
<td>80</td>
<td>8</td>
<td>NR</td>
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</table>

a All reactions were carried out on a 0.2 mmol scale.
b Isolated yields.
c Without Cs2CO3.
throughphenyl derived thiosulfonates 1g–i also served as suitable substrates to furnish the expected allyl sulfones in high yields. A variety of para-, meta- and ortho-substituted allyl bromides 2b–g were readily sulfonylated with 1a to give the anticipated allyl sulfones in 57–96% yields. The position and electronic nature of substituents on the phenyl ring of MBH bromides had a limited effect on this sulfonylation process. Additionally, different heteroaryl allylic (hetero)aryl sulfones, show activity against cancer and abnormal cell proliferation activity. The E/Z stereochemistry of the allylic sulfones was assigned based on 1H NMR chemical shift values of the olefinic protons as compared with the reported values.

Furthermore, the scope of the sulfonylation reaction could be extended to other representative classes of allyl bromides, such as acrylonitrile derived MBH allylic bromide (2o) or cinnamyl bromide (2p), as presented in Scheme 4. Disappointingly, they did not provide the desired allylic sulfones 3ao and 3ap under the same conditions.

Scheme 2 Substrate scope for the synthesis of allyl sulfones via radical sulfonylation of MBH bromides with thiosulfonates. Reagents and conditions (performed on a 0.5 mmol scale of thiosulfonate): 1 (1.0 equiv), MBH bromide 2 (1.5 equiv), Cs₂CO₃ (1.0 equiv) in MeCN (2.5 mL) at 80 °C. Isolated yields are given. Z/E ratio based on 1H NMR analysis.

Scheme 3 Substrate scope for the synthesis of allyl sulfones via radical sulfonylation of MBH acetates with thiosulfonates. Reagents and conditions (performed on a 0.5 mmol scale of thiosulfonate): 1 (1.0 equiv), MBH acetate 4 (1.5 equiv), Cs₂CO₃ (1.0 equiv) in MeCN (2.5 mL) at 80 °C. Isolated yields are given. Z/E ratio based on 1H NMR analysis.
The efficacy of radical sulfonation was demonstrated at gram-scale under the optimal conditions (see the Supporting Information). Thus, a 5 mmol scale reaction of S-phenyl benzenesulfonothioate (1a) (1.25 g) and (Z)-methyl 2-(bromomethyl)-3-phenylacrylate (2a) (1.90 g) gave 3aa in 72% yield (1.14 g). Similarly, allyl sulfone 3aj was obtained in 78% yield (1.25 g) from acetate 4j. Thus, the protocol is scalable with little deviation of the outcome (Scheme 4).

Several control experiments were performed to gain insight into the reaction mechanism (Scheme 5). The standard reaction was performed with radical scavengers (BHT or TEMPO), in an attempt to define whether the reaction involved an ionic or radical pathway. With BHT, the product 3aa formed in <10% yield; whereas the reaction was totally inhibited with TEMPO (Scheme 5i). These experiments suggest the process involves a radical sulfonation pathway and this is in keeping with the known homolytic cleavage of thiosulfonate 1a to generate sulfonyl radical (I) and thiyl radical (II) species (Scheme 5ii). Based on the above results and on literature precedent,4,6,13 a plausible mechanism is proposed for this transformation (Scheme 5). The radical initiation of PhSSO2Ph (1a)6d,e may lead to sulfonyl radical (I) and thiyl radical (II) in the presence of Cs2CO3. Subsequent propagation of 2a will form allyl radical (A) and termination product sulfonyl bromide (PhSO2Br).6 Finally, the termination product triggers the sulfonation of A with PhSO2Br to give the expected allyl sulfone 3aa. Similarly, sulfonyl radical can add onto MBH acetate to form radical B and eliminate an acetyl radical to afford the desired allyl sulfone 3aa. Overall, in this process, the Cs2CO3 might be playing a dual role as a radical initiator and as a base to trap the bromine radical.

In conclusion, we have described the Cs2CO3-promoted radical sulfonation of Morita–Baylis–Hillman (MBH) bromides with thiosulfonates under mild conditions. A series of allyl sulfones was readily generated in good to high yields with high stereoselectivities. Various aryl, heteroaryl, alkenyl and alkyl MBH bromides/acetates and aryl/heteroaryl thiosulfonates with diverse substitution patterns and broad functional group compatibility were elaborated. Furthermore, the MBH acetates efficiently furnished the corresponding allyl sulfones in high yields. The protocol was proven to be applicable to gram-scale synthesis, which can be challenging with other approaches. A plausible mechanism is presented to rationalize the experimental outcome.

Synthesis of Allyl Sulfones; General Procedure 1 (GP1)
A heat gun-dried Schleck tube was charged with thiosulfonate (0.5 mmol, 1.0 equiv), Morita–Baylis–Hillman allyl bromide (0.75 mmol, 1.5 equiv) or Morita–Baylis–Hillman acetate (0.75 mmol, 1.0 equiv) and Cs2CO3 (0.5 mmol, 1.0 equiv) in CH3CN (2.5 mL). The reaction mixture was stirred at 80 °C for 4 h and monitored by TLC until the reaction was judged to be either complete or to be proceeding no further. The reaction was quenched by addition of water (10 mL) followed by extraction with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (2 × 10 mL), dried over anhydrous Na2SO4, filtered and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluting with 10–20% EtOAc/petroleum ether) to afford the desired allyl sulfones.

Methyl (Z)-3-Phenyl-2-([(phenylsulfonyl)methyl]acrylate (3aa)
Obtained by following GP1 using S-phenyl benzenesulfonothioate 1a (125.0 mg, 0.5 mmol), methyl (Z)-2-(bromomethyl)-3-phenylacrylate 2a (191.3 mg, 0.75 mmol), and Cs2CO3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded the title compound 3aa.
Yield: 150.3 mg (95%); colorless solid; mp 63–65 °C (Lit.6 64–66 °C); Rf = 0.38 (20% EtOAc in petroleum ether); mixture of Z/E isomers (>97:3) based on 1H NMR analysis.

1H NMR (400 MHz, CDCl3): δ = 7.95 (s, 1 H), 7.85 (dd, J = 8.4, 1.2 Hz, 2 H), 7.60 (tt, J = 7.4, 1.2 Hz, 1 H), 7.52–7.46 (m, 4 H), 7.39–7.35 (m, 3 H), 4.49 (s, 2 H), 3.59 (s, 3 H).
13C NMR (101 MHz, CDCl3): δ = 166.9, 146.5, 139.3, 133.8, 133.7, 129.8, 129.2 (2C), 129.1 (2C), 128.8 (2C), 128.6 (2C), 120.9, 55.2, 52.5.

The title compound is known in the literature and the data are consistent with reported values.10e

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**Scheme 4** Study of other allyl bromides 2o/p and gram-scale synthesis

**Scheme 5** Control experiments and a plausible mechanism
Methyl (Z)-3-Phenyl-2-[(tosylmethyl)acrylate (3ba)

Obtained by following GP1 using 5-(p-toly1) 4-methylbenzenesulfonylithioate 1b (139.1 mg, 0.5 mmol), methyl (Z)-2-[(bromomethyl)-3-phenylacrylate 2a (191.3 mg, 0.75 mmol), and Cs₂CO₃ (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded the title compound 3ba.

Yield: 136.3 mg (69%); yellow solid; mp 99–101 °C; mixture of Z/E isomers (>99:1) based on 1H NMR analysis.

1H NMR (400 MHz, CDCl₃): δ = 7.93 (s, 1 H), 7.64 (dt, J = 8.8, 2.0 Hz, 2 H), 7.50 (dt, J = 8.8, 1.7 Hz, 2 H), 7.48–7.45 (m, 2 H), 7.39–7.34 (m, 3 H), 4.48 (s, 2 H), 3.57 (s, 3 H), 1.34 (s, 9 H).

13C NMR (101 MHz, CDCl₃): δ = 166.9, 146.6, 138.0, 133.6, 132.4 (2C), 129.9, 129.3, 129.1 (2C), 128.9 (2C), 126.1 (2C), 121.2, 55.2, 52.4, 35.4, 31.2 (3C).

LCMS (ESI): m/z 373.00 [M + H]+.

Methyl (Z)-2-[(4-Fluorophenyl)sulfonyl]methyl)-3-phenylacrylate (3fa)

Obtained by following GP1 using S-(4-fluorophenyl)-4-fluorobenzene-sulfonothioate 1f (204.0 mg, 0.5 mmol), methyl (Z)-2-(bromomethyl)-3-phenylacrylate 2a (191.3 mg, 0.75 mmol), and Cs₂CO₃ (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded the title compound 3fa.

Yield: 136.3 mg (69%); yellow solid; mp 99–101 °C; Rf = 0.33 (20% EtOAc in petroleum ether); mixture of Z/E isomers (>98:2) based on 1H NMR analysis.

1H NMR (400 MHz, CDCl₃): δ = 7.93 (s, 1 H), 7.64 (dt, J = 8.8, 2.0 Hz, 2 H), 7.57 (dt, J = 8.7, 2.0 Hz, 2 H), 7.40–7.36 (m, 5 H), 4.51 (s, 2 H), 3.67 (s, 3 H).

13C NMR (101 MHz, CDCl₃): δ = 166.9, 146.6, 138.0, 133.6, 132.4 (2C), 130.2 (2C), 129.9, 129.3, 129.1 (2C), 128.9 (2C), 128.0, 54.9, 52.7.

The title compound has been reported in the literature and the data are consistent with reported values.

Methyl (Z)-2-[(4-Chlorophenyl)sulfonyl]methyl)-3-phenylacrylate (3ea)

Obtained by following GP1 using S-(4-chlorophenyl)-4-chlorobenzene-sulfonothioate 1e (175.4 mg, 0.5 mmol), methyl (Z)-2-(bromomethyl)-3-phenylacrylate 2a (191.3 mg, 0.75 mmol), and Cs₂CO₃ (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded the title compound 3ea.

Yield: 136.3 mg (69%); yellow solid; mp 99–101 °C; Rf = 0.33 (20% EtOAc in petroleum ether); mixture of Z/E isomers (>98:2) based on 1H NMR analysis.

1H NMR (400 MHz, CDCl₃): δ = 7.93 (s, 1 H), 7.64 (dt, J = 8.7, 2.0 Hz, 2 H), 7.57 (dt, J = 8.7, 2.0 Hz, 2 H), 7.40–7.36 (m, 5 H), 4.51 (s, 2 H), 3.67 (s, 3 H).

13C NMR (101 MHz, CDCl₃): δ = 166.9, 146.6, 138.0, 133.6, 132.4 (2C), 130.2 (2C), 129.9, 129.3, 129.1 (2C), 128.9 (2C), 128.0, 54.9, 52.7.

The title compound has been reported in the literature and the data are consistent with reported values.

Methyl (Z)-2-[(Naphthalen-1-yl)sulfonyl]methyl)-3-phenylacrylate (3ga)

Obtained by following GP1 using S-(naphthalen-1-yl)naphthalene-1-sulfonothioate 1g (175.2 mg, 0.5 mmol), methyl (Z)-2-(bromomethyl)-3-phenylacrylate 2a (191.3 mg, 0.75 mmol), and Cs₂CO₃ (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded the title compound 3ga.

Yield: 144.6 mg (79%); colorless solid; mp 119–121 °C; Rf = 0.35 (20% EtOAc in petroleum ether); mixture of Z/E isomers (>95:5) based on 1H NMR analysis.

1H NMR (400 MHz, CDCl₃): δ = 8.28 (s, 1 H), 7.84–7.77 (m, 4 H), 7.69 (dd, J = 8.7, 1.7 Hz, 1 H), 7.56 (t, J = 7.5 Hz, 1 H), 7.50 (t, J = 7.5 Hz, 1 H), 7.27 (d, J = 7.8 Hz, 2 H), 7.17–7.11 (m, 3 H), 4.47 (s, 2 H), 3.36 (s, 3 H).

13C NMR (101 MHz, CDCl₃): δ = 166.9, 146.3, 136.2, 135.4, 133.6, 132.1, 130.5, 129.6, 129.5, 129.3, 129.0 (2C), 128.7 (2C), 128.0, 127.6, 123.2, 121.1, 55.1, 52.4.

Methyl (Z)-2-[(Naphthalen-2-ylsulfonyl)methyl]-3-phenylacrylate (3ha)

Obtained by following GP1 using S-(naphthalen-2-yl) naphthalene-2-sulfonothioate 1h (175.2 mg, 0.5 mmol), methyl (Z)-2-(bromomethyl)-3-phenylacrylate 2a (191.3 mg, 0.75 mmol), and Cs₂CO₃ (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded title compound 3ha.

Yield: 141.2 mg (77%); colorless solid; mp 116–118 °C.

Obtained by following GP1 using S-(naphthalen-2-yl) naphthalene-2-sulfonothioate 1h (217.1 mg, 0.75 mmol), methyl (Z)-2-(bromomethyl)-3-phenylacrylate 2c (201.8 mg, 0.75 mmol), and Cs₂CO₃ (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded title compound 3ha.

Yield: 132.1 mg (80%); colorless liquid; Rᵣ = 0.29 (20% EtOAc in petroleum ether); mixture of Z/E isomers (>96:4) based on 1³H NMR analysis.

1³H NMR (400 MHz, CDCl₃): δ = 7.92 (s, 1 H), 7.86 (dd, J = 8.3, 1.1 Hz, 2 H), 7.60 (tt, J = 7.4, 1.2 Hz, 1 H), 7.49 (t, J = 7.7 Hz, 2 H), 7.43 (d, J = 8.1 Hz, 2 H), 7.18 (d, J = 8.0 Hz, 2 H), 4.50 (s, 2 H), 3.54 (s, 3 H), 2.36 (s, 3 H).

1³C NMR (101 MHz, CDCl₃): δ = 166.6, 146.0, 135.7, 135.0, 133.2, 131.7, 130.1, 129.3, 129.1, 129.04, 128.96, 128.7 (2C), 128.4 (2C), 127.1, 127.3, 122.8, 120.7, 54.7, 52.0.

LCMS (ESI): m/z 366.95 [M⁺].
Methyl (Z)-3-(3-Methoxyphenyl)-2-[(phenylsulfonyl)methyl]-acrylate (3af)
Obtained by following GP1 using S-phenyl benzenesulfonothioate 1a (125.0 mg, 0.5 mmol), methyl (Z)-2-(bromomethyl)-3-(3-methoxyphenyl)acrylate 2f (213.8 mg, 0.75 mmol), and Cs₂CO₃ (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) yielded title compound 3af.
Yield: 141.0 mg (80%); liquid; Rₛ = 0.42 (30% EtOAc in petroleum ether); mixture of Z/E isomers (83:17) based on 1H NMR analysis.
1H NMR (400 MHz, CDCl₃): δ = 7.88 (s, 1 H), 7.80 (d, J = 8.0 Hz, 2 H), 7.56 (t, J = 7.9 Hz, 1 H), 7.44 (t, J = 7.0 Hz, 2 H), 7.23 (s, J = 8.0 Hz, 1 H), 7.09 (s, 1 H), 6.98 (d, J = 7.5 Hz, 1 H), 6.87 (d, J = 8.0 Hz, 1 H), 4.46 (s, 2 H), 3.78 (s, 3 H), 3.54 (s, 3 H).
13C NMR (101 MHz, CDCl₃): δ = 166.7, 159.7, 146.2, 139.3, 134.8, 133.7, 129.7, 129.0 (2C), 128.4 (2C), 121.5, 121.0, 115.9, 113.9, 55.4, 55.2, 52.3.
LCMS (ESI): m/z 346.95 [M]+.

Methyl (Z)-3-(2-Bromophenyl)-2-[(phenylsulfonyl)methyl]-acrylate (3ag)
Obtained by following GP1 using S-phenyl benzenesulfonothioate 1a (125.0 mg, 0.5 mmol), methyl (Z)-2-(bromomethyl)-3-(2-bromophenyl)acrylate 2g (239.9 mg, 0.75 mmol), and Cs₂CO₃ (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded title compound 3ag.
Yield: 158.1 mg (80%); colorless solid; mp 110–112 °C; Rₛ = 0.27 (20% EtOAc in petroleum ether); mixture of Z/E isomers (>95:5) based on 1H NMR analysis.
1H NMR (400 MHz, CDCl₃): δ = 7.85–7.79 (m, 3 H), 7.63 (tt, J = 7.4, 1.2 Hz, 1 H), 7.51–7.45 (m, 3 H), 7.44 (s, 1 H), 7.41 (dd, J = 7.7, 0.7 Hz, 1 H), 7.24 (t, J = 7.8 Hz, 1 H), 4.44 (s, 2 H), 3.65 (s, 3 H).
13C NMR (101 MHz, CDCl₃): δ = 166.5, 144.4, 138.9, 135.7, 134.0, 132.5, 131.9, 130.8, 129.2 (2C), 128.5 (2C), 127.4, 122.9, 122.5, 54.8, 52.7.
The title compound is reported in the literature and the data are consistent with reported values.
Methyl (Z)-5-Phenyl-2-[(phenylsulfonyl)methyl]pent-2-enoate (3al)
Obtained by following G1 using S-phenyl benzenesulphonothioate 1a (125.0 mg, 0.5 mmol), methyl (Z)-2-[(bromomethyl)-5-methylhex-2-enoate 2m (165.8 mg, 0.75 mmol), and Cs2CO3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded the title compound 3al.
Yield: 161.7 mg (94%); colorless liquid; mixture of Z/E isomers (>98:2) based on 1H NMR analysis.

1H NMR (400 MHz, CDCl3): δ = 7.95 (dd, J = 8.3, 1.2 Hz, 2 H), 7.73 (tt, J = 7.4, 1.2 Hz, 1 H), 7.63 (t, J = 7.7 Hz, 2 H), 7.43–7.38 (m, 2 H), 7.32 (d, J = 7.4 Hz, 1 H), 7.30–7.27 (m, 3 H), 4.27 (s, 2 H), 3.57 (s, 3 H), 2.87 (t, J = 7.6 Hz, 2 H), 2.66 (q, J = 7.6 Hz, 2 H).

13C NMR (101 MHz, CDCl3): δ = 134.9 mg (91%); colorless liquid; Rf = 0.30 (20% EtOAc in petroleum ether); mixture of Z/E isomers (80:20) based on 1H NMR analysis.

Yield: 134.9 mg (91%); colorless liquid; Rf = 0.30 (20% EtOAc in petroleum ether); mixture of Z/E isomers (80:20) based on 1H NMR analysis.

1H NMR (400 MHz, CDCl3): δ = 7.83 (dd, J = 8.4, 1.2 Hz, 2 H), 7.62 (tt, J = 7.4, 1.2 Hz, 1 H), 7.51 (t, J = 7.7 Hz, 2 H), 7.14 (t, J = 7.5 Hz, 1 H), 4.22 (s, 2 H), 3.46 (s, 3 H), 2.08 (t, J = 7.2 Hz, 2 H), 1.77–1.67 (m, 1 H), 0.89 (d, J = 6.7 Hz, 6 H).

13C NMR (101 MHz, CDCl3): δ = 166.2, 151.1, 133.9, 129.6, 129.1 (2C), 128.9 (2C), 126.4, 121.2, 54.1, 52.2, 34.3, 31.5.

LCMS (ESI): m/z 296.95 [M]+.

Ethyl (Z)-3-Phenyl-2-(tosylmethyl)acrylate (3bn)
Obtained by following GP1 using S-phenyl benzenesulphonothioate 1a (125.0 mg, 0.5 mmol), ethyl (Z)-2-[(bromomethyl)-5-methylpent-2-enoate 2n (201.8 mg, 0.75 mmol), and Cs2CO3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded the title compound 3bn.
Yield: 168.7 mg (98%); colorless liquid; Rf = 0.42 (20% EtOAc in petroleum ether); mixture of Z/E isomers (>98:2) based on 1H NMR analysis.

1H NMR (400 MHz, CDCl3): δ = 8.01 (s, 1 H), 7.80 (d, J = 8.2 Hz, 2 H), 7.56 (dd, J = 6.5, 2.7 Hz, 2 H), 7.47–7.44 (m, 3 H), 7.35 (d, J = 8.2 Hz, 2 H), 4.58 (s, 2 H), 4.16 (q, J = 7.1 Hz, 2 H), 2.51 (s, 3 H), 1.34 (t, J = 7.1 Hz, 3 H).

13C NMR (101 MHz, CDCl3): δ = 166.6, 146.0, 144.8, 136.5, 133.9, 129.7 (2C), 129.68, 129.3 (2C), 128.8 (2C), 128.7 (2C), 121.5, 61.7, 55.2, 21.7, 14.2.
The title compound is known in the literature and the data are consistent with reported values.9d

Conflict of Interest
The authors declare no conflict of interest.

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References


