Simple and Efficient Synthesis of Allyl Sulfones through Cs_2CO_3-Mediated Radical Sulfonylation of Morita–Baylis–Hillman Adducts with Thiosulfonates

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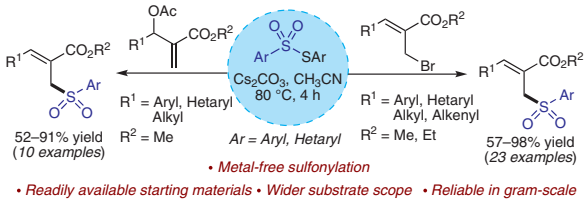

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Abstract A highly efficient and eco-friendly method has been developed for the synthesis of allyl sulfones using Morita–Baylis–Hillman (MBH) adducts and thiosulfonates under mild conditions. The Cs_2CO_3-promoted radical sulfonylation provided a series 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^1SO_2-SR^2)[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 sulfonyl moiety as by-product. Additionally, homolytic cleavage of the S–S(O_2) bond of thiosulfonates generates sulfonyl 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 synthesis[7] and they are widely distributed pharmacophores,[8] for instance in anticancer agents,[8a] cysteine protease inhibitors,[8b,c] TSH receptor antagonists,[8d] and antibacterial agents[8e] (Figure 1). Therefore, the development of efficient and straightforward methods for the synthesis of allyl sulfones continues to attract considerable attention. In this context, various sulfonyl reagents[9,10] (sulfinates,[9] arylsulfonyl cyanides,[10a] arenesulfonylmethyl isocyanide,[10b] and sulfinyl chlorides,[10c] sulfonyl hydrazines,[10d] and sulfinic acids[10e]) have been used for the sulfonylation of Morita–Baylis–Hillman (MBH) adducts for the synthesis of allyl sulfone derivatives (Scheme 1a). Compared to these sulfonyl reactants, aryl thiosulfonates[1c] are usually stable crystalline solids, easy to handle and widely accessible starting precursors. Accordingly, we envisaged that thiosulfonates could be alternative starting materials to offer an opportunity for the synthesis of allyl sulfones. This fact motivated us to develop a possible new strategy for radical sulfonylation of Morita–Baylis–Hillman (MBH) adducts under mild conditions (Scheme 1b). Of note, the multifunctional MBH allyl bromides and MBH acetates can be easily prepared and have been widely studied.[11] As part of our ongoing research programme on organosulfur chemistry[12] and the utilization of thiosulfonates,[3c,d,5e,6c,12b,c] we report herein a simple and efficient radical sulfonylation of MBH allyl bromides/acetates with thiosulfonates in the presence of Cs_2CO_3 to access a range of (hetero)aryl/alkyl allyl sulfones. To our knowledge, radical sulfonylation using thiosulfonates has not been previously explored.[6c–e]

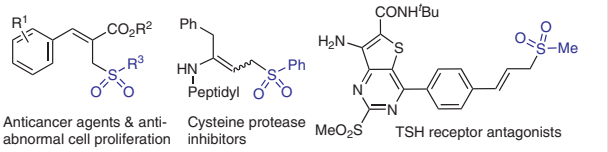
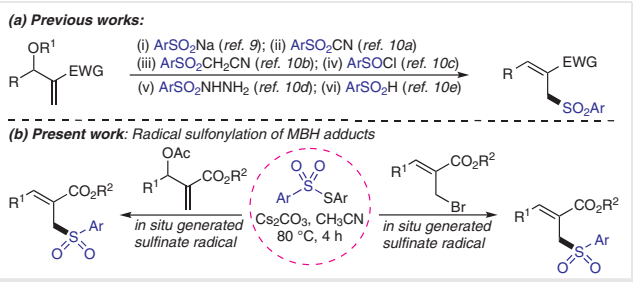


Figure 1 Representative biologically active allyl sulfones



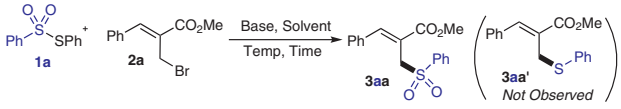
Scheme 1 Allyl sulfonylation of MBH adducts using various sulfonyl reagents

At the outset, our optimization investigations began with *S*-phenyl benzenesulfonothioate (**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 Cs_2CO_3 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, CH_3CN, 1,4-dioxane, DMSO and toluene were screened (entries 3–7). Among these solvents, CH_3CN proved the best choice for the transformation, giving **3aa** in 80% yield (entry 4). In CH_3CN at 80 °C, the yield of the reaction between **1a**, **2a** and Cs_2CO_3 (1:1.5:2 ratio) was improved considerably, giving **3aa** in 91% yield (entry 8). To our satisfaction, use of 1 equiv of Cs_2CO_3 provided the desired allyl sulfone (**3aa**) in 96% yield (entry 9). Using 1.2 equiv of **2a** or 1.5 equiv of Cs_2CO_3 or performing the reaction at room temperature were not beneficial (entries 10–12).

We then examined other bases (K_2CO_3, Na_2CO_3 and DABCO) but all afforded diminished yields (Table 1, entries 13–15). No reaction was observed in the absence of Cs_2CO_3, 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 ($ArS^{\bullet}$).[13]

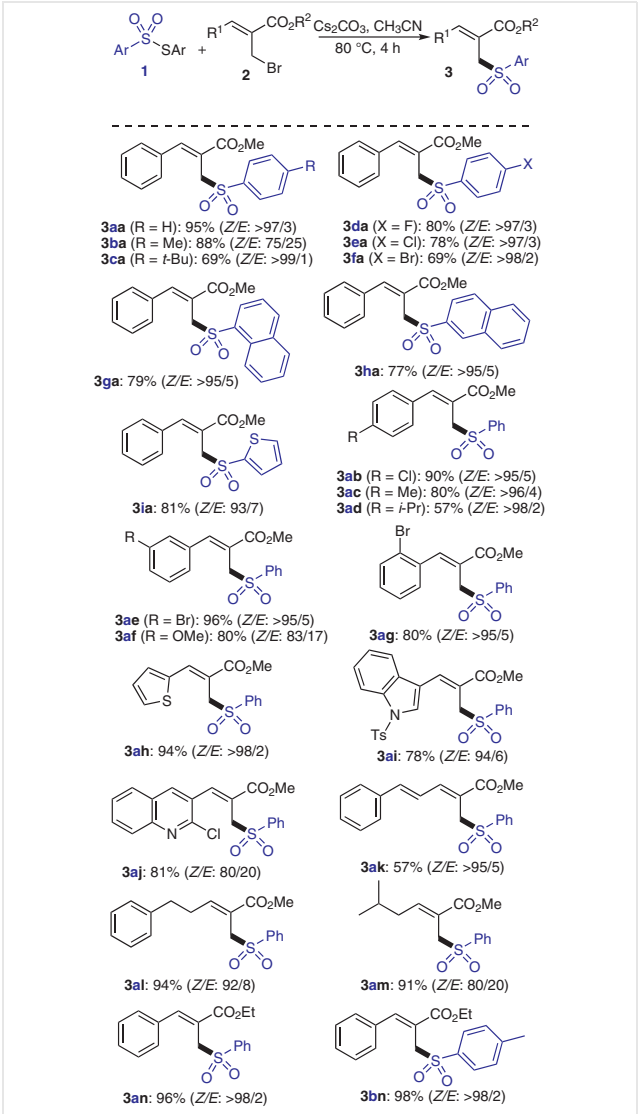
With the reaction conditions optimized, we then explored a broad range of thiosulfonates (**1a–i**) and MBH allyl bromides (**2a–n**) to furnish a series of allyl sulfones (**3aa–i** and **3ab–n**) in good to excellent yields and stereoselectivities (Scheme 2). Various alkyl and halo-substituted thiosulfonates (**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

Table 1 Optimization for the Sulfonylation of MBH Bromide with Thiosulfonate[a]



Entry	**1a** (equiv)	**2a** (equiv)	Base (equiv)	Solvent	Temp (°C)	Time (h)	Yield of **3aa** (%)[b]
1	1.0	1.5	Cs_2CO_3 (2.0)	EtOH	90	6	65
2	1.5	1.0	Cs_2CO_3 (2.0)	EtOH	90	6	79
3	1.5	1.0	Cs_2CO_3 (2.0)	DMF	90	6	47
4	1.5	1.0	Cs_2CO_3 (2.0)	CH_3CN	80	5	80
5	1.5	1.0	Cs_2CO_3 (2.0)	dioxane	80	5	32
6	1.5	1.0	Cs_2CO_3 (2.0)	DMSO	90	6	47
7	1.5	1.0	Cs_2CO_3 (2.0)	toluene	90	6	25
8	1.0	1.5	Cs_2CO_3 (2.0)	CH_3CN	80	4	91
9	**1.0**	**1.5**	**Cs_2CO_3 (1.0)**	**CH_3CN**	**80**	**4**	**96**
10	1.0	1.2	Cs_2CO_3 (1.0)	CH_3CN	80	5	79
11	1.0	1.5	Cs_2CO_3 (1.5)	CH_3CN	80	4	91
12	1.0	1.5	Cs_2CO_3 (1.0)	CH_3CN	rt	8	33
13	1.0	1.5	K_2CO_3 (1.0)	CH_3CN	80	5	60
14	1.0	1.5	Na_2CO_3 (1.0)	CH_3CN	80	8	trace
15	1.0	1.5	DABCO (1.0)	CH_3CN	80	8	NR
16	1.0	1.5	–[c]	CH_3CN	80	8	NR

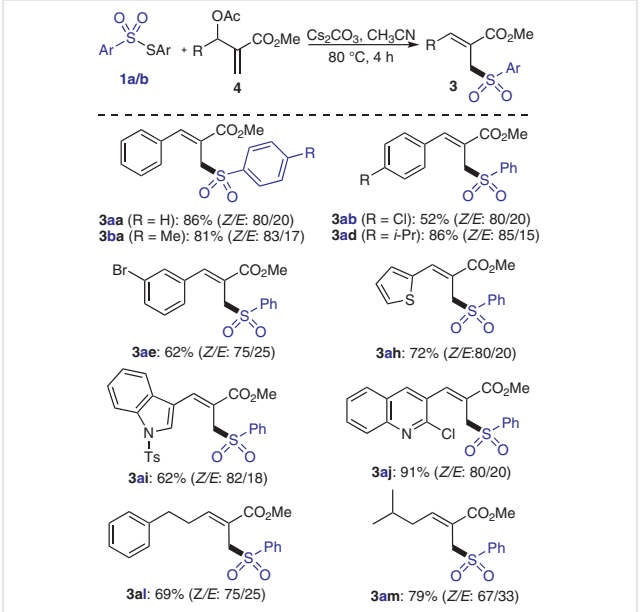
[a] All reactions were carried out on a 0.2 mmol scale.
[b] Isolated yields.
[c] Without Cs_2CO_3.



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), Cs_2CO_3 (1.0 equiv) in MeCN (2.5 mL) at 80 °C. Isolated yields are given. *Z*/*E* ratio based on ^{1}H NMR analysis.

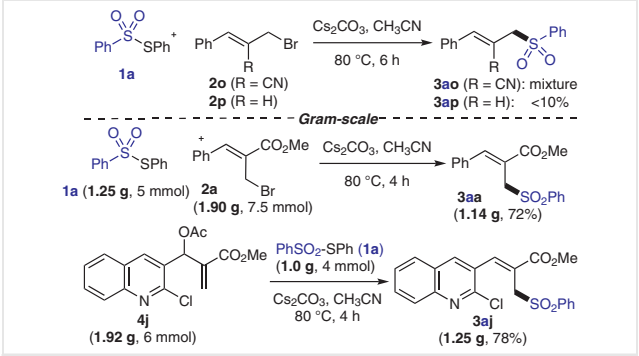
thiophenyl derived thiosulfonates **1g–i** also served as suitable substrates to furnish the expected allyl sulfones in high yields. A variety of *para*-, *meta*- and *ortho*-substituted allyl bromides **2b–g** were readily sulfonylated with **1a** to give the anticipated allyl sulfones in 57–96% yields. 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 allyl sulfones **3ah–aj** were produced in satisfactory yields from the corresponding allyl bromides. Interestingly, the alkenyl and alkyl-substituted MBH bromides **2k–m** reacted well with **1a**, giving the synthetically useful alkyl allyl sulfones in acceptable yields. The substrate scope was further extended to ethyl acrylate derived MBH bromide **2n**, and the corresponding products **3an** and **3bn** were obtained in 96% and 98% yield, respectively.

Inspired by these results, we sought to evaluate the scope of MBH acetates **4** with *S*-aryl arylsulfonothioate (**1a/b**). Under the same conditions, acetate **4a** was smoothly sulfonated with *S*-aryl arylsulfonothioate (**1a/b**), to give the desired products **3aa** and **3ba** in 86% and 81% yields, respectively, with slightly inferior stereoselectivities as compared to the allyl bromides (Scheme 3).[14] Several aryl and heteroaryl derived substrates (**4b**,**d**,**e**,**h–j**) reacted well with **1a** to form expected products (**3ab**,**d**,**e**,**h–j**) in reasonable yields. Similarly, the alkyl sulfones **3al** and **3am** were obtained in 69% and 79% yield, respectively, from the corresponding MBH acetates **4l/m** under the standard conditions. It is worth noting that these allyl sulfones, particularly allyl (hetero)aryl sulfones, show activity against cancer and abnormal cell proliferation activity.[8a] The *E*/*Z* stereochemistry of the allyl sulfones was assigned based on the ^{1}H NMR chemical shift values of the olefinic protons as compared with the reported values.[15]

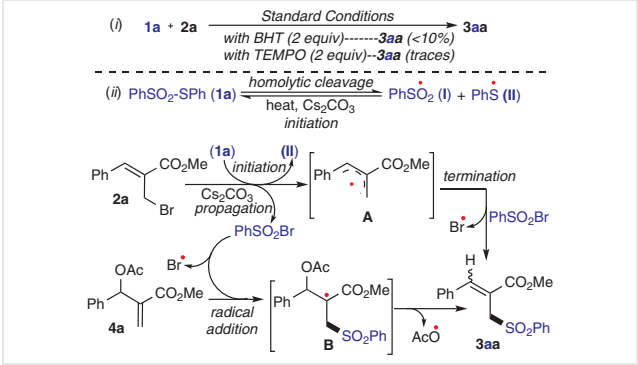


Scheme 3 Substrate scope for the synthesis of allyl sulfones via radical sulfonylation of MBH acetates with thiosulfonates. *Reagents and conditions* (performed on a 0.5 mmol scale of thiosulfonates): **1** (1.0 equiv), MBH acetate **4** (1.5 equiv), Cs_2CO_3 (1.0 equiv) in MeCN (2.5 mL) at 80 °C. Isolated yield are given. *Z*/*E* ratio based on ^{1}H NMR analysis.

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



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



Scheme 5 Control experiments and a plausible mechanism

The efficacy of radical sulfonylation 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 5*i*). These experiments suggest the process involves a radical sulfonylation pathway and this is in keeping with the known homolytic cleavage of thiosulfonate **1a** to generate sulfonyl radical (**I**) and thiyl radical (**II**)[13] species (Scheme 5*ii*).[4] 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 $PhSSO_2Ph$ (**1a**)[6d,e] may lead to sulfonyl radical (**I**) and thiyl radical (**II**) in the presence of Cs_2CO_3. Subsequent propagation of **2a** will form allyl radical (**A**) and termination product sulfonyl bromide ($PhSO_2Br$).[16] Finally, the termination product triggers the sulfonylation of **A** with $PhSO_2Br$ 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 Cs_2CO_3 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 Cs_2CO_3-promoted radical sulfonylation 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/hetereoaryl 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, 1.5 equiv) and Cs_2CO_3 (0.5 mmol, 1.0 equiv) in CH_3CN (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 Na_2SO_4, 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 Cs_2CO_3 (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); R_f = 0.38 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>97:3) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (101 MHz, $CDCl_3$): 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]

Methyl (*Z*)-3-Phenyl-2-(tosylmethyl)acrylate (3ba)

Obtained by following **GP1** using *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate **1b** (139.1 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-phenylacrylate **2a** (191.3 mg, 0.75 mmol), and Cs_2CO_3 (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: 145.4 mg (88%); colorless liquid R_f = 0.50 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (75:25) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (s, 1 H), 7.61 (d, *J* = 8.3 Hz, 2 H), 7.38–7.35 (m, 2 H), 7.29–7.26 (m, 3 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 4.38 (s, 2 H), 3.52 (s, 3 H), 2.32 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1, 146.5, 146.2, 144.8, 136.4, 133.8, 129.8, 129.7 (2C), 129.3, 129.1, 128.9, 128.8, 128.6, 121.2, 55.2, 52.5, 21.7.

The title compound is known in the literature and the data are consistent with reported values.[9a,10d]

Methyl (*Z*)-2-{[(4-(*tert*-Butyl)phenyl)sulfonyl]methyl}-3-phenylacrylate (3ca)

Obtained by following **GP1** using *S*-(4-(*tert*-butyl)phenyl) 4-(*tert*-butylbenzenesulfonothioate **1c** (128.5 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-phenylacrylate **2a** (191.3 mg, 0.75 mmol), and Cs_2CO_3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded title compound **3ca**.

Yield: 128.3 mg (69%); colorless solid; mp 100–102 °C; R_f = 0.42 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>99:1) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1 H), 7.76 (dt, *J* = 8.6, 2.0 Hz, 2 H), 7.50 (dt, *J*= 8.8, 2.1 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).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1, 157.8, 146.3, 136.3, 133.8, 129.8, 129.3 (2C), 128.9 (2C), 128.6 (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 (3da)

Obtained by following **GP1** using *S*-(4-fluorophenyl)4-fluorobenzenesulfonothioate **1d** (143.1 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-phenylacrylate **2a** (191.3 mg, 0.75 mmol), and Cs_2CO_3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded title compound **3da**.

Yield: 133.8 mg (80%); colorless solid; mp 72–74 °C; R_f = 0.37 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>97:1) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1 H), 7.85–7.78 (m, 2 H), 7.45–7.41 (m, 2 H), 7.39–7.35 (m, 3 H), 7.12 (t, *J* = 8.5 Hz, 2 H), 4.50 (s, 2 H), 3.66 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.0 (d, *J* = 256.4 Hz), 166.9, 146.5, 135.3 (d, *J* = 3.1 Hz), 133.7, 131.5 (d, *J* = 9.7 Hz), 129.9, 129.2 (3C), 128.9 (3C), 120.9, 116.4 (d, *J* = 22.6 Hz), 55.1, 52.6.

LCMS (ESI): *m*/*z* 334.90 $[M]^+$.

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

Obtained by following **GP1** using *S*-(4-chlorophenyl)-4-chlorobenzenesulfonothioate **1e** (175.4 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-phenylacrylate **2a** (191.3 mg, 0.75 mmol), and Cs_2CO_3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded title compound **3ea**.

Yield: 136.8 mg (78%); colorless solid; mp 86–88 °C; R_f = 0.35 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>97:3) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 1 H), 7.71 (dt, *J* = 8.6, 1.9 Hz, 2 H), 7.41–7.35 (m, 7 H), 4.51 (s, 2 H), 3.66 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 146.5, 140.7, 137.6, 133.6, 130.1 (2C), 129.8, 129.4 (2C), 129.1 (2C), 128.9 (2C), 120.9, 55.0, 52.6.

LCMS (ESI): *m*/*z* 351.90 $[M + H]^+$.

Methyl (*Z*)-2-{[(4-Bromophenyl)sulfonyl]methyl}-3-phenylacrylate (3fa)

Obtained by following **GP1** using *S*-(4-bromophenyl)-4-bromobenzenesulfonothioate **1f** (204.0 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-phenylacrylate **2a** (191.3 mg, 0.75 mmol), and Cs_2CO_3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded title compound **3fa**.

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

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (101 MHz, $CDCl_3$): 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), 120.8, 54.9, 52.7.

The title compound has been reported in the literature and the data are consistent with reported values.[10d]

Methyl (*Z*)-2-[(Naphthalen-1-ylsulfonyl)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 Cs_2CO_3 (162.5 mg, 0.5 mmol), for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded title compound **3ga**.

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

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (101 MHz, $CDCl_3$): 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, 127.6, 123.2, 121.1, 55.1, 52.4.

LCMS (ESI): *m*/*z* 366.95 $[M]^+$.

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 Cs_2CO_3 (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; R_f = 0.37 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>95:5) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 1 H), 7.84–7.77 (m, 4 H), 7.69 (d, *J* = 8.5 Hz, 1 H), 7.56 (t, *J* = 7.5 Hz, 1 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.29–7.25 (m, 2 H), 7.14 (d, *J* = 7.4 Hz, 3 H), 4.47 (s, 2 H), 3.34 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): 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), 128.3 (2C), 127.6, 127.3, 122.8, 120.7, 54.7, 52.0.

LCMS (ESI): *m*/*z* 366.95 $[M]^+$.

Methyl (*Z*)-3-Phenyl-2-[(thiophen-2-ylsulfonyl)methyl]acrylate (3ia)

Obtained by following **GP1** using S-(thiophen-2-yl) thiophene-2-sulfonothioate **1i** (115.1 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-phenylacrylate **2a** (191.3 mg, 0.75 mmol), and Cs_2CO_3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded title compound **3ia**.

Yield: 130.6 mg (81%); colorless liquid; R_f = 0.37 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>93:7) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1 H), 7.67 (dd, *J* = 5.0, 1.3 Hz, 1 H), 7.60 (dd, *J* = 3.8, 1.3 Hz, 1 H), 7.47 (dd, *J* = 6.4, 3.1 Hz, 2 H), 7.39–7.36 (m, 3 H), 7.08 (dd, *J* = 5.0, 3.8 Hz, 1 H), 4.59 (s, 2 H), 3.67 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 146.7, 140.0, 134.9, 134.7, 133.6, 129.8, 129.2 (2C), 128.8 (2C), 127.9, 120.8, 56.2, 52.6.

LCMS (ESI): *m*/*z* 322.90 $[M]^+$.

Methyl (*Z*)-3-(4-Chlorophenyl)-2-[(phenylsulfonyl)methyl]acrylate (3ab)

Obtained by following **GP1** using *S*-phenyl benzenesulfonothioate **1a** (125.0 mg, 0.5 mmol) methyl (*Z*)-2-(bromomethyl)-3-(4-chlorophenyl) acrylate **2b** (217.1 mg, 0.75 mmol), and Cs_2CO_3 (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 **3ab**.

Yield: 157.8 mg (90%); liquid; R_f = 0.20 (30% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>95:5) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1 H), 7.84 (dd, *J* = 8.3, 1.0 Hz, 2 H), 7.62 (t, *J* = 7.5 Hz, 1 H), 7.50 (t, *J* = 7.8 Hz, 2 H), 7.45 (d, *J* = 8.5 Hz, 2 H), 7.34 (d, *J* = 8.5 Hz, 2 H), 4.43 (s, 2 H), 3.57 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7, 145.1, 139.4, 136.0, 134.0, 132.2, 130.7 (2C), 129.20 (2C), 129.17 (2C), 128.6 (2C), 121.5, 55.2, 52.6.

The title compound is known in the literature and the data are consistent with reported values.[9f]

Methyl (*Z*)-2-[(Phenylsulfonyl)methyl]-3-(*p*-tolyl)acrylate (3ac)

Obtained by following **GP1** using *S*-phenyl benzenesulfonothioate **1a** (125.0 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-(*p*-tolyl)acrylate **2c** (201.8 mg, 0.75 mmol), and Cs_2CO_3 (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.

Yield: 132.1 mg (80%); colorless liquid; R_f = 0.29 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>96:4) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1, 146.6, 140.3, 139.4, 133.8, 130.9, 129.6 (2C), 129.5 (2C), 129.1 (2C), 128.6 (2C), 119.7, 55.3, 52.4, 21.5.

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

Methyl (*Z*)-3-(4-Isopropylphenyl)-2-[(phenylsulfonyl)methyl]acrylate (3ad)

Obtained by following **GP1** using *S*-phenyl benzenesulfonothioate **1a** (125.0 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-(4-isopropylphenyl)acrylate **2d** (222.8 mg, 0.75 mmol), and Cs_2CO_3 (162.5 mg, 0.5 mmol), for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded title compound **3ad**.

Yield: 102.1 mg (57%); colorless liquid; R_f = 0.39 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>98:2) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1 H), 7.86 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.60 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.51–7.45 (m, 4 H), 7.24 (d, *J* = 8.2 Hz, 2 H), 4.52 (s, 2 H), 3.56 (s, 3 H), 2.91 (sept, *J* = 6.9 Hz, 1 H), 1.25 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.2, 151.2, 146.7, 139.5, 133.8, 131.3, 129.7 (2C), 129.1 (2C), 128.7 (2C), 127.1 (2C), 119.8, 55.4, 52.4, 34.1, 23.9 (2C).

LCMS (ESI) *m*/*z* 359.00 $[M + H]^+$.

Methyl (*Z*)-3-(3-Bromophenyl)-2-[(phenylsulfonyl)methyl]acrylate (3ae)

Obtained by following **GP1** using *S*-phenyl benzenesulfonothioate **1a** (125.0 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-(3-bromophenyl)acrylate **2e** (239.9 mg, 0.75 mmol), and Cs_2CO_3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 15% EtOAc in petroleum ether) yielded title compound **3ae**.

Yield: 189.7 mg (96%); pale-yellow solid; mp 64–66 °C; R_f = 0.29 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>95:5) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 1 H), 7.84 (dd, *J* = 8.3, 1.1 Hz, 2 H), 7.64–7.60 (m, 2 H), 7.57 (dd, *J* = 8.0, 1.1 Hz, 1 H), 7.50 (t, *J* = 7.7 Hz, 2 H), 7.35 (td, *J* = 7.5, 0.9 Hz, 1 H), 7.22 (td, *J* = 7.6, 1.4 Hz, 1 H), 4.36 (s, 2 H), 3.62 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.3, 145.3, 139.4, 134.1, 133.9, 133.0, 130.8, 130.1, 129.2 (2C), 128.5 (2C), 127.7, 124.1, 122.8, 55.0, 52.6.

The title compound is known in the literature and the data are consistent with reported values.[9f]

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 Cs_2CO_3 (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; R_f = 0.42 (30% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (83:17) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): 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 (t, *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).

^{13}C NMR (101 MHz, $CDCl_3$): 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 Cs_2CO_3 (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; R_f = 0.27 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>95:5) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (101 MHz, $CDCl_3$): 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.[10a]

Methyl (*Z*)-2-((Phenylsulfonyl)methyl)-3-(thiophen-2-yl)acrylate (3ah)

Obtained by following **GP1** using *S*-phenyl benzenesulfonothioate **1a** (125.0 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-(thiophen-2-yl)acrylate **2h** (185.0 mg, 0.75 mmol), and Cs_2CO_3 (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 **3ah**.

Yield: 151.5 mg (94%); colorless liquid; R_f = 0.39 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>98:2) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1 H), 7.89 (d, *J* = 8.2 Hz, 2 H), 7.59 (t, *J* = 7.4 Hz, 1 H), 7.53–7.47 (m, 4 H), 7.08 (t, *J* = 3.9 Hz, 1 H), 4.62 (s, 2 H), 3.51 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.8, 139.5, 138.3, 136.8, 134.3, 133.9, 131.0, 129.0 (2C), 128.7 (2C), 127.9, 116.2, 56.0, 52.4.

The title compound is reported in the literature and the data are consistent with reported values.[10a]

Methyl (*Z*)-2-((Phenylsulfonyl)methyl)-3-(1-tosyl-1*H*-indol-2-yl)-acrylate (3ai)

Obtained by following **GP1** using *S*-phenyl benzenesulfonothioate **1a** (125.0 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-(1-tosyl-1*H*-indol-2-yl)acrylate **2i** (336.2 mg, 0.75 mmol), and Cs_2CO_3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) yielded the title compound **3ai**.

Yield: 198.7 mg (78%); colorless solid; mp 137–139 °C; R_f = 0.31 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>94:6) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1 H), 8.09 (s, 1 H), 8.03 (d, *J* = 8.3 Hz, 1 H), 7.98 (d, *J* = 7.2 Hz, 2 H), 7.89 (d, *J* = 8.4 Hz, 2 H), 7.62 (tt, *J* = 7.4, 2.1 Hz, 1 H), 7.58–7.52 (m, 3 H), 7.41–7.36 (m, 1 H), 7.32–7.26 (m, 3 H), 4.51 (s, 2 H), 3.63 (s, 3 H), 2.35 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.6, 145.7, 139.6, 136.0, 134.9, 134.7, 134.0, 130.3 (2C), 130.0, 129.3 (2C), 128.6 (2C), 127.5, 127.3 (2C), 125.7, 124.0, 119.9, 119.3, 115.9, 113.9, 56.8, 52.6, 21.7.

LCMS (ESI): *m*/*z* 509.90 $[M]^+$.

Methyl (*Z*)-3-(2-Chloroquinolin-3-yl)-2-[(phenylsulfonyl)methyl]-acrylate (3aj)

Obtained by following **GP1** using *S*-phenyl benzenesulfonothioate **1a** (125.0 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-3-(2-chloroquinolin-3-yl)acrylate **2j** (254.1 mg, 0.75 mmol), and Cs_2CO_3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) yielded the title compound **3aj**.

Yield: 162.6 mg (81%); colorless solid; mp 129–13 °C; R_f = 0.21 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (80:20) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (s, 1 H), 8.09 (s, 1 H), 8.04 (d, *J* = 8.5 Hz, 1 H), 7.95 (d, *J* = 7.7 Hz, 1 H), 7.90 (d, *J* = 7.3 Hz, 2 H), 7.80 (t, *J* = 7.7 Hz, 1 H), 7.65 (t, *J* = 6.9 Hz, 2 H), 7.53 (t, *J* = 7.7 Hz, 2 H), 4.36 (s, 2 H), 3.63 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 148.3, 143.3, 139.5, 139.3, 138.7, 134.2, 131.8, 129.4 (2C), 128.7, 128.6 (2C), 128.5, 128.4, 128.0, 126.9, 124.0, 55.6, 52.9.

LCMS (ESI): *m*/*z* 401.80 $[M]^+$.

Methyl (2*Z*,4*E*)-5-Phenyl-2-[(phenylsulfonyl)methyl]penta-2,4-dienoate (3ak)

Obtained by following **GP1** using *S*-phenyl benzenesulfonothioate **1a** (125.0 mg, 0.5 mmol), methyl (2*Z*,4*E*)-2-(bromomethyl)-5-phenylpenta-2,4-dienoate **2k** (222.8 mg, 0.75 mmol), and Cs_2CO_3 (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 **3ak**.

Yield: 97.8 mg (57%); colorless solid; mp 143–145 °C; R_f = 0.35 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>95:5) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.86 (m, 2 H), 7.62 (dd, *J* = 7.3, 3.5 Hz, 1 H), 7.56–7.47 (m, 3 H), 7.44 (dd, *J* = 8.0, 1.6 Hz, 2 H), 7.36 (m, 3 H), 6.96–6.93 (m, 2 H), 4.43 (s, 2 H), 3.53 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.5, 145.8, 143.8, 138.7, 135.8, 134.0, 129.8, 129.1 (2C), 129.0 (2C), 128.9 (2C), 127.9 (2C), 123.0, 118.1, 54.7, 52.3.

The title compound is known in the literature and the data are consistent with reported values.[10a,d]

Methyl (*Z*)-5-Phenyl-2-[(phenylsulfonyl)methyl]pent-2-enoate (3al)

Obtained by following **G1** using *S*-phenyl benzenesulfonothioate **1a** (125.0 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-5-phenylpent-2-enoate **2l** (212.3 mg, 0.75 mmol), and Cs_2CO_3 (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; R_f = 0.41 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>92:8) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.0, 150.5, 140.5, 138.9, 133.9, 129.1 (2C), 128.8 (2C), 128.6 (2C), 128.5 (2C), 126.4, 121.2, 54.1, 52.2, 34.3, 31.5.

LCMS (ESI): *m*/*z* 344.95 [M]$^+$.

Methyl (*Z*)-5-Methyl-2-[(phenylsulfonyl)methyl]hex-2-enoate (3am)

Obtained by following **GP1** using *S*-phenyl benzenesulfonothioate **1a** (125.0 mg, 0.5 mmol), methyl (*Z*)-2-(bromomethyl)-5-methylhex-2-enoate **2m** (165.8 mg, 0.75 mmol), and Cs_2CO_3 (162.5 mg, 0.5 mmol) for 4 h. Purification by flash column chromatography (silica gel, 10% EtOAc in petroleum ether) yielded the title compound **3am**.

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

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 151.1, 133.9, 129.6, 129.1 (2C), 128.9 (2C), 121.2, 54.3, 52.2, 38.4, 28.2, 22.5 (2C).

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

Ethyl (*Z*)-3-Phenyl-2-[(phenylsulfonyl)methyl]acrylate (3an)

Obtained by following **GP1** using *S*-phenyl benzenesulfonothioate **1a** (125 mg, 0.5 mmol), ethyl (*Z*)-2-(bromomethyl)-3-phenylacrylate **2n** (201.8 mg, 0.75 mmol), and Cs_2CO_3 (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 **3an**.

Yield: 158.7 mg (96%); colorless liquid; R_f = 0.40 (20% EtOAc/hexanes); mixture of *Z*/*E* isomers (>98:2) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1 H), 7.84 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.58 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.49–7.44 (m, 4 H), 7.37–7.33 (m, 3 H), 4.49 (s, 2 H), 4.03 (q, *J* = 7.1 Hz, 2 H), 1.22 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.6, 146.2, 139.5, 133.85, 133.81, 129.7, 129.3 (2C), 129.1 (2C), 128.9 (2C), 128.6 (2C), 121.3, 61.7, 55.2, 14.2.

The title compound is known in the literature and the data are consistent with reported values.[9d]

Ethyl (*Z*)-3-Phenyl-2-(tosylmethyl)acrylate (3bn)

Obtained by following **GP1** using *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate **1b** (139.1 mg, 0.5 mmol), ethyl (*Z*)-2-(bromomethyl)-3-phenylacrylate **2n** (191.3 mg, 0.75 mmol), and Cs_2CO_3 (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; R_f = 0.42 (20% EtOAc in petroleum ether); mixture of *Z*/*E* isomers (>98:2) based on ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.6, 146.0, 144.8, 136.5, 133.9, 129.74 (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.[10d]

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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