# Simple and Efficient Synthesis of Allyl Sulfones through $\mathrm{Cs}_{2} \mathrm{CO}_{3}-$ Mediated Radical Sulfonylation of Morita-Baylis-Hillman Adducts with Thiosulfonates 

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Received: 16.02.2021
Accepted after revision: 08.03.2021
Published online: 10.03.2021
DOI: 10.1055/a-1422-9411; Art ID: so-2021-d0009-psp

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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 $\mathrm{Cs}_{2} \mathrm{CO}_{3}-$ 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 $\left(\mathrm{R}^{1} \mathrm{SO}_{2}-\mathrm{SR}^{2}\right)^{1}$ 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 $\mathrm{S}-\mathrm{S}\left(\mathrm{O}_{2}\right)$ 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 $\mathrm{C}-\mathrm{S}$ 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, ${ }^{8 a}$ cysteine protease inhibitors, ${ }^{8 b, c}$ TSH receptor antagonists, ${ }^{8 \mathrm{~d}}$ and antibacterial agents ${ }^{8 \mathrm{e}}$ (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, ${ }^{10 a}$ arenesulfonylmethyl isocyanide, ${ }^{10 \mathrm{~b}}$ and sulfinyl chlorides, ${ }^{10 \mathrm{c}}$ sulfonyl hydrazines, ${ }^{10 \mathrm{~d}}$ and sulfinic acids ${ }^{10 \mathrm{e}}$ ) 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 ${ }^{1 \mathrm{c}}$ 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, ${ }^{3 c, d, 5 e, 6 c, 12 b, c}$ we report herein a simple and efficient radical sulfonylation of MBH allyl bromides/acetates with thiosulfonates in the presence of $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ to access a range of (hetero)aryl/alkyl allyl sulfones. To our knowledge, radical sulfonylation using thiosulfonates has not been previously explored. ${ }^{6 c-e}$


Anticancer agents \& antiabnormal cell proliferation


Cysteine protease inhibitors


Figure 1 Representative biologically active allyl sulfones

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| SynOpen | A. Shankar et al. | $\begin{aligned} & \text { OPEN } \\ & \text { ACCESS } \end{aligned}$ | PSP |


(b) Present work: Radical sulfonylation of MBH adducts


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 $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ in EtOH provided the allyl sulfone 3aa in $65 \%$ yield (entry 1 ). On reversing the ratios of $\mathbf{1 a}$ and $\mathbf{2 a}$ (1.5:1) the desired product 3aa was produced in $79 \%$ yield (entry 2 ). Various solvents, such as DMF, $\mathrm{CH}_{3} \mathrm{CN}, 1,4$-dioxane, DMSO and toluene were screened (entries 3-7). Among these solvents, $\mathrm{CH}_{3} \mathrm{CN}$ proved the best choice for the transformation, giving 3aa in $80 \%$ yield (entry
4). In $\mathrm{CH}_{3} \mathrm{CN}$ at $80^{\circ} \mathrm{C}$, the yield of the reaction between $\mathbf{1 a}$, 2a and $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (1:1.5:2 ratio) was improved considerably, giving 3aa in $91 \%$ yield (entry 8 ). To our satisfaction, use of 1 equiv of $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ provided the desired allyl sulfone (3aa) in $96 \%$ yield (entry 9 ). Using 1.2 equiv of 2a or 1.5 equiv of $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ or performing the reaction at room temperature were not beneficial (entries 10-12).

We then examined other bases $\left(\mathrm{K}_{2} \mathrm{CO}_{3}, \mathrm{Na}_{2} \mathrm{CO}_{3}\right.$ and DABCO) but all afforded diminished yields (Table 1, entries $13-15)$. No reaction was observed in the absence of $\mathrm{Cs}_{2} \mathrm{CO}_{3}$, 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 ( $\mathrm{ArS}{ }^{*}$ ). ${ }^{13}$

With the reaction conditions optimized, we then explored a broad range of thiosulfonates ( $\mathbf{1 a - i}$ ) and MBH allyl bromides ( $\mathbf{2 a - n}$ ) 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 ( $\mathbf{1 a - f}$ ) 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 ${ }^{\text {a }}$


| Entry | 1a (equiv) | 2a (equiv) | Base (equiv) | Solvent | Temp ( ${ }^{\circ} \mathrm{C}$ ) | Time (h) | Yield of 3aa (\%) ${ }^{\text {b }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 1.0 | 1.5 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (2.0) | EtOH | 90 | 6 | 65 |
| 2 | 1.5 | 1.0 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}(2.0)$ | EtOH | 90 | 6 | 79 |
| 3 | 1.5 | 1.0 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}(2.0)$ | DMF | 90 | 6 | 47 |
| 4 | 1.5 | 1.0 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (2.0) | $\mathrm{CH}_{3} \mathrm{CN}$ | 80 | 5 | 80 |
| 5 | 1.5 | 1.0 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (2.0) | dioxane | 80 | 5 | 32 |
| 6 | 1.5 | 1.0 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}(2.0)$ | DMSO | 90 | 6 | 47 |
| 7 | 1.5 | 1.0 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}(2.0)$ | toluene | 90 | 6 | 25 |
| 8 | 1.0 | 1.5 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}(2.0)$ | $\mathrm{CH}_{3} \mathrm{CN}$ | 80 | 4 | 91 |
| 9 | 1.0 | 1.5 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (1.0) | $\mathrm{CH}_{3} \mathrm{CN}$ | 80 | 4 | 96 |
| 10 | 1.0 | 1.2 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}(1.0)$ | $\mathrm{CH}_{3} \mathrm{CN}$ | 80 | 5 | 79 |
| 11 | 1.0 | 1.5 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}(1.5)$ | $\mathrm{CH}_{3} \mathrm{CN}$ | 80 | 4 | 91 |
| 12 | 1.0 | 1.5 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}(1.0)$ | $\mathrm{CH}_{3} \mathrm{CN}$ | rt | 8 | 33 |
| 13 | 1.0 | 1.5 | $\mathrm{K}_{2} \mathrm{CO}_{3}(1.0)$ | $\mathrm{CH}_{3} \mathrm{CN}$ | 80 | 5 | 60 |
| 14 | 1.0 | 1.5 | $\mathrm{Na}_{2} \mathrm{CO}_{3}(1.0)$ | $\mathrm{CH}_{3} \mathrm{CN}$ | 80 | 8 | trace |
| 15 | 1.0 | 1.5 | DABCO (1.0) | $\mathrm{CH}_{3} \mathrm{CN}$ | 80 | 8 | NR |
| 16 | 1.0 | 1.5 | - ${ }^{\text {c }}$ | $\mathrm{CH}_{3} \mathrm{CN}$ | 80 | 8 | NR |

[^0]

3aa ( $\mathrm{R}=\mathrm{H}$ ): $95 \%$ (Z/E: >97/3) 3ba ( $\mathrm{R}=\mathrm{Me}$ ): $88 \%$ (Z/E: 75/25

3e (X $=$ F): $80 \%$ (Z/E: >97/3) 3ea ( $\mathrm{X}=\mathrm{Cl}$ ): 78\% (Z/E: >97/3) 3fa (X = Br): 69\% (Z/E: >98/2)

$3 \mathrm{ab}(\mathrm{R}=\mathrm{Cl})$ : $90 \%$ (Z/E: >95/5) 3ac ( $\mathrm{R}=\mathrm{Me}$ ): $80 \%$ (Z/E: $>96 / 4$ )
3ia: 81\% (Z/E: 93/7) 3ad ( $\mathrm{R}=i-\mathrm{Pr}$ ): $57 \%$ ( $Z / \mathrm{E}: ~>98 / 2$ )

3ae ( $\mathrm{R}=\mathrm{Br}$ ): 96\% (Z/E: >95/5) 3af ( $\mathrm{R}=\mathrm{OMe}$ ): $80 \%$ (Z/E: 83/17)

3ah: 94\% (Z/E: >98/2)

3aj: $81 \%$ (Z/E: 80/20)

3al: $94 \%$ (Z/E: 92/8)

3an: 96\% (Z/E: >98/2)

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): $\mathbf{1}$ ( 1.0 equiv), MBH bromide 2 ( 1.5 equiv), $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( 1.0 equiv) in $\mathrm{MeCN}(2.5 \mathrm{~mL}$ ) at $80^{\circ} \mathrm{C}$. Isolated yields are given. Z|E ratio based on ${ }^{1} \mathrm{H}$ NMR analysis.
thiophenyl derived thiosulfonates $\mathbf{1 g - i}$ also served as suitable substrates to furnish the expected allyl sulfones in high yields. A variety of para-, meta- and ortho-substituted allyl bromides $\mathbf{2 b}-\mathbf{g}$ 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 al-kyl-substituted MBH bromides $\mathbf{2 k}-\mathbf{m}$ reacted well with $\mathbf{1 a}$, 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 ( $\mathbf{1 a / b}$ ). Under the same conditions, acetate $\mathbf{4 a}$ was smoothly sulfonated with $S$-aryl arylsulfonothioate ( $\mathbf{1 a} / \mathbf{b}$ ), 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 ( $\mathbf{4 b}, \mathbf{d}, \mathbf{e}, \mathbf{h} \mathbf{- j}$ ) reacted well with 1a to form expected products ( $\mathbf{3 a b}, \mathbf{d}, \mathbf{e}, \mathbf{h}-\mathbf{j}$ ) in reasonable yields. Similarly, the alkyl sulfones 3al and 3am were obtained in $69 \%$ and $79 \%$ yield, respectively, from the corresponding MBH acetates $41 / \mathbf{m}$ 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. ${ }^{8 a}$ The $E / Z$ stereochemistry of the allyl sulfones was assigned based on the ${ }^{1} \mathrm{H}$ NMR chemical shift values of the olefinic protons as compared with the reported values. ${ }^{15}$


3aa (R $=H$ ): $86 \%(Z / E: 80 / 20)$
3ba ( $\mathrm{R}=\mathrm{Me}$ ): 81\% (Z/E: 83/17)


3ae: 62\% (Z/E: 75/25)


3ai: 62\% (Z/E: 82/18)


3al: 69\% (Z/E: 75/25)

3ab ( $\mathrm{R}=\mathrm{CI}$ ): $52 \%$ (Z/E: 80/20)
3ad ( $\mathrm{R}=i$-Pr): 86\% (Z/E: 85/15)


3ah: 72\% (Z/E:80/20)


3aj: 91\% (Z/E: 80/20)


3am: 79\% (Z/E: 67/33)

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), $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( 1.0 equiv) in $\mathrm{MeCN}(2.5 \mathrm{~mL}$ ) at $80^{\circ} \mathrm{C}$. Isolated yield are given. $Z / E$ ratio based on ${ }^{1} \mathrm{H}$ 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 (20) 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 20/p and gram-scale synthesis

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 ( $\mathbf{1 a}$ ) ( 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 $(1.25 \mathrm{~g})$ from acetate $\mathbf{4} \mathbf{j}$. 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 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 5ii). ${ }^{4}$ 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 $\mathrm{PhSSO}_{2} \mathrm{Ph}(\mathbf{1 a})^{6 d, e}$ may lead to sulfonyl radical (I) and thiyl radical (II) in the presence of $\mathrm{Cs}_{2} \mathrm{CO}_{3}$. Subsequent propagation of $\mathbf{2 a}$ will form allyl $\operatorname{radical}(\mathbf{A})$ and termination product sulfonyl bromide $\left(\mathrm{PhSO}_{2} \mathrm{Br}\right) .{ }^{16}$ Finally, the termination product triggers the sulfonylation of A with $\mathrm{PhSO}_{2} \mathrm{Br}$ 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 $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ 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 $\mathrm{Cs}_{2} \mathrm{CO}_{3}$-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


Scheme 5 Control experiments and a plausible mechanism
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 ( $0.75 \mathrm{mmol}, 1.5$ equiv) and $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( $0.5 \mathrm{mmol}, 1.0$ equiv) in $\mathrm{CH}_{3} \mathrm{CN}(2.5 \mathrm{~mL}$ ). The reaction mixture was stirred at $80{ }^{\circ} \mathrm{C}$ 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 $(3 \times 20 \mathrm{~mL})$. The combined organic layers were washed with brine $(2 \times 10 \mathrm{~mL})$, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, 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 ( $125.0 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl ( $Z$ )-2-(bromomethyl)-3-phenylacrylate 2a ( $191.3 \mathrm{mg}, 0.75 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5 \mathrm{mmol})$ 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 ${ }^{\circ} \mathrm{C}$ (Lit. ${ }^{6} 64-66{ }^{\circ} \mathrm{C}$ ); $R_{f}$ $=0.38$ (20\% EtOAc in petroleum ether); mixture of $Z / E$ isomers ( $>97: 3$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.95(\mathrm{~s}, 1 \mathrm{H}), 7.85(\mathrm{dd}, J=8.4,1.2 \mathrm{~Hz}, 2$ H), $7.60(\mathrm{tt}, \mathrm{J}=7.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.52-7.46(\mathrm{~m}, 4 \mathrm{H}), 7.39-7.35(\mathrm{~m}, 3 \mathrm{H})$, $4.49(\mathrm{~s}, 2 \mathrm{H}), 3.59(\mathrm{~s}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.9,146.5,139.3,133.8,133.7$, $129.8,129.2$ (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. ${ }^{10 e}$

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

Obtained by following GP1 using $S$-(p-tolyl) 4-methylbenzenesulfonothioate $\mathbf{1 b}$ ( $139.1 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl ( $Z$ )-2-(bromomethyl)-3phenylacrylate 2a $(191.3 \mathrm{mg}, 0.75 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5$ 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 $Z \mid E$ isomers ( $75: 25$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.83(\mathrm{~s}, 1 \mathrm{H}), 7.61(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 2 \mathrm{H})$, $7.38-7.35$ (m, 2 H ), 7.29-7.26 (m, 3 H ), 7.17 (d, J = $8.0 \mathrm{~Hz}, 2 \mathrm{H}), 4.38$ (s, $2 \mathrm{H}), 3.52(\mathrm{~s}, 3 \mathrm{H}), 2.32(\mathrm{~s}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=167.1,146.5,146.2,144.8,136.4$, 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. ${ }^{9 a, 10 d}$

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

Obtained by following GP1 using S-(4-(tert-butyl)phenyl) 4-(tertbutylbenzenesulfonothioate $\mathbf{1 c}(128.5 \mathrm{mg}, 0.5 \mathrm{mmol})$, methyl $(Z)-2-$ (bromomethyl)-3-phenylacrylate 2a (191.3 mg, 0.75 mmol ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( $162.5 \mathrm{mg}, 0.5 \mathrm{mmol}$ ) 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 $100-102{ }^{\circ} \mathrm{C} ; R_{f}=0.42(20 \%$ EtOAc in petroleum ether); mixture of $Z / E$ isomers ( $>99: 1$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.93(\mathrm{~s}, 1 \mathrm{H}), 7.76(\mathrm{dt}, J=8.6,2.0 \mathrm{~Hz}, 2$ H), 7.50 (dt, $J=8.8,2.1 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.48-7.45 (m, 2 H$), 7.39-7.34(\mathrm{~m}, 3 \mathrm{H})$, 4.48 (s, 2 H ), 3.57 ( $\mathrm{s}, 3 \mathrm{H}$ ), 1.34 ( $\mathrm{s}, 9 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=167.1,157.8,146.3,136.3,133.8$, $129.8,129.3$ (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 $373.00[\mathrm{M}+\mathrm{H}]^{+}$.

## Methyl (Z)-2-\{[(4-Fluorophenyl)sulfonyl]methyl\}-3-phenylacrylate (3da)

Obtained by following GP1 using S-(4-fluorophenyl)4-fluorobenzenesulfonothioate $1 \mathbf{d}(143.1 \mathrm{mg}, 0.5 \mathrm{mmol})$, methyl $(Z)$-2-(bromometh-yl)-3-phenylacrylate 2a ( $191.3 \mathrm{mg}, 0.75 \mathrm{mmol}$ ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (162.5 $\mathrm{mg}, 0.5 \mathrm{mmol}$ ) 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; $\mathrm{mp} 72-74{ }^{\circ} \mathrm{C} ; R_{f}=0.37(20 \%$ EtOAc in petroleum ether); mixture of $Z / E$ isomers ( $>97: 1$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.93(\mathrm{~s}, 1 \mathrm{H}), 7.85-7.78(\mathrm{~m}, 2 \mathrm{H}), 7.45-$ 7.41 (m, 2 H$), 7.39-7.35(\mathrm{~m}, 3 \mathrm{H}), 7.12(\mathrm{t}, \mathrm{J}=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.50(\mathrm{~s}, 2 \mathrm{H})$, 3.66 (s, 3 H).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.0(\mathrm{~d}, J=256.4 \mathrm{~Hz}), 166.9,146.5$, $135.3(\mathrm{~d}, J=3.1 \mathrm{~Hz}), 133.7,131.5(\mathrm{~d}, J=9.7 \mathrm{~Hz}), 129.9,129.2$ (3C), 128.9 (3C), 120.9, 116.4 (d, $J=22.6 \mathrm{~Hz}), 55.1,52.6$.

LCMS (ESI): m/z $334.90[\mathrm{M}]^{+}$.

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

Obtained by following GP1 using S-(4-chlorophenyl)-4-chlorobenzenesulfonothioate $\mathbf{1 e}(175.4 \mathrm{mg}, 0.5 \mathrm{mmol})$, methyl $(Z)$-2-(bro-momethyl)-3-phenylacrylate 2a ( $191.3 \mathrm{mg}, 0.75 \mathrm{mmol}$ ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ $(162.5 \mathrm{mg}, 0.5 \mathrm{mmol})$ 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; $\mathrm{mp} 86-88{ }^{\circ} \mathrm{C}$; $R_{f}=0.35(20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $>97: 3$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.92(\mathrm{~s}, 1 \mathrm{H}), 7.71(\mathrm{dt}, J=8.6,1.9 \mathrm{~Hz}, 2$ H), 7.41-7.35 (m, 7 H ), 4.51 ( $\mathrm{s}, 2 \mathrm{H}$ ), 3.66 ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.9,146.5,140.7,137.6,133.6,130.1$ (2C), 129.8, 129.4 (2C), 129.1 (2C), 128.9 (2C), 120.9, 55.0, 52.6.

LCMS (ESI): m/z $351.90[\mathrm{M}+\mathrm{H}]^{+}$.

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

Obtained by following GP1 using $S$-(4-bromophenyl)-4-bromobenzenesulfonothioate 1 f $(204.0 \mathrm{mg}, 0.5 \mathrm{mmol})$, methyl ( $Z$ )-2-(bro-momethyl)-3-phenylacrylate 2a ( $191.3 \mathrm{mg}, 0.75 \mathrm{mmol}$ ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( $162.5 \mathrm{mg}, 0.5 \mathrm{mmol}$ ) 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 ${ }^{\circ} \mathrm{C}$; $R_{f}=0.33(20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $>98: 2$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.93(\mathrm{~s}, 1 \mathrm{H}), 7.64(\mathrm{dt}, \mathrm{J}=8.7,2.0 \mathrm{~Hz}, 2$ H), 7.57 (dt, J = 8.7, $2.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.40-7.36 (m, 5 H ), 4.51 (s, 2 H ), 3.67 (s, 3 H ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.9,146.6,138.0,133.6,132.4$ (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. ${ }^{10 \mathrm{~d}}$

## Methyl (Z)-2-[(Naphthalen-1-ylsulfonyl)methyl]-3-phenylacrylate (3ga)

Obtained by following GP1 using $S$-(naphthalen-1-yl) naphthalene-1sulfonothioate $\mathbf{1 g}(175.2 \mathrm{mg}, 0.5 \mathrm{mmol})$, methyl $(Z)$-2-(bromometh-yl)-3-phenylacrylate 2a ( $191.3 \mathrm{mg}, 0.75 \mathrm{mmol}$ ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( 162.5 $\mathrm{mg}, 0.5 \mathrm{mmol}$ ), for 4 h . Purification by flash column chromatography (silica gel, $15 \%$ EtOAc in petroleum ether) yielded title compound 3ga.
Yield: $144.6 \mathrm{mg}(79 \%)$; colorless solid; mp $119-121^{\circ} \mathrm{C} ; R_{f}=0.35(20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $>95: 5$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.28(\mathrm{~s}, 1 \mathrm{H}), 7.84-7.77(\mathrm{~m}, 4 \mathrm{H}), 7.69$ (dd, $J=8.7,1.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.56(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.50(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$, 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 ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.9,146.3,136.2,135.4,133.6$, $132.1,130.5,129.6,129.5,129.4,129.3,129.0$ (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-2sulfonothioate $\mathbf{1 h}(175.2 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl ( Z )-2-(bromometh-yl)-3-phenylacrylate $\mathbf{2 a}(191.3 \mathrm{mg}, 0.75 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5$ $\mathrm{mg}, 0.5 \mathrm{mmol}$ ) 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 $116-118^{\circ} \mathrm{C}$; $R_{f}=0.37(20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $>95: 5$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.27$ (s, 1 H ), 7.84-7.77 (m, 4 H ), 7.69 (d, $J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.56(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.50(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$, 7.29-7.25 (m, 2 H), 7.14 (d, $J=7.4 \mathrm{~Hz}, 3 \mathrm{H}$ ), 4.47 ( s, 2 H ), 3.34 (s, 3 H ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.6,146.0,135.7,135.0,133.2$, $131.7,130.1,129.3,129.1,129.04,128.96,128.7$ (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 $\mathbf{1 i}$ ( $115.1 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl ( $Z$ )-2-(bromomethyl)-3phenylacrylate $\mathbf{2 a}(191.3 \mathrm{mg}, 0.75 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5$ mmol ) for 4 h . Purification by flash column chromatography (silica gel, $15 \%$ EtOAc in petroleum ether) yielded title compound 3ia.
Yield: $130.6 \mathrm{mg}(81 \%)$; colorless liquid; $R_{f}=0.37$ ( $20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $>93: 7$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.99(\mathrm{~s}, 1 \mathrm{H}), 7.67(\mathrm{dd}, J=5.0,1.3 \mathrm{~Hz}, 1$ H), $7.60(\mathrm{dd}, J=3.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.47(\mathrm{dd}, J=6.4,3.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.39-$ 7.36 (m, 3 H ), 7.08 (dd, J = 5.0, $3.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 4.59 ( s, 2 H ), 3.67 ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.9,146.7,140.0,134.9,134.7$, 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 ( $125.0 \mathrm{mg}, 0.5 \mathrm{mmol}$ ) methyl ( $Z$ )-2-(bromomethyl)-3-(4-chlorophenyl) acrylate $\mathbf{2 b}(217.1 \mathrm{mg}, 0.75 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5$ mmol ), for 4 h . Purification by flash column chromatography (silica gel, $15 \%$ EtOAc in petroleum ether) yielded the title compound 3ab.
Yield: $157.8 \mathrm{mg}(90 \%)$; liquid; $R_{f}=0.20$ ( $30 \%$ EtOAc in petroleum ether); mixture of $Z / E$ isomers ( $>95: 5$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.88(\mathrm{~s}, 1 \mathrm{H}), 7.84(\mathrm{dd}, J=8.3,1.0 \mathrm{~Hz}, 2$ H), $7.62(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.50(\mathrm{t}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.45(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2$ H), $7.34(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.43(\mathrm{~s}, 2 \mathrm{H}), 3.57(\mathrm{~s}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.7,145.1,139.4,136.0,134.0$, $132.2,130.7$ (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. ${ }^{9 f}$

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

Obtained by following GP1 using $S$-phenyl benzenesulfonothioate 1a ( $125.0 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl ( $Z$ )-2-(bromomethyl)-3-( $p$-tolyl)acrylate $\mathbf{2 c}(201.8 \mathrm{mg}, 0.75 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5 \mathrm{mmol})$ for 4 h. Purification by flash column chromatography (silica gel, $15 \%$ EtOAc in petroleum ether) yielded the title compound.
Yield: $132.1 \mathrm{mg}(80 \%)$; colorless liquid; $R_{f}=0.29$ ( $20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $>96: 4$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.92(\mathrm{~s}, 1 \mathrm{H}), 7.86(\mathrm{dd}, J=8.3,1.1 \mathrm{~Hz}, 2$ H), $7.60(\mathrm{tt}, J=7.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.49(\mathrm{t}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.43(\mathrm{~d}, J=8.1$ $\mathrm{Hz}, 2 \mathrm{H}$ ), 7.18 (d, J = $8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), $4.50(\mathrm{~s}, 2 \mathrm{H}), 3.54(\mathrm{~s}, 3 \mathrm{H}), 2.36(\mathrm{~s}, 3$ H).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=167.1,146.6,140.3,139.4,133.8$, $130.9,129.6$ (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. ${ }^{10 e}$

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

Obtained by following GP1 using S-phenyl benzenesulfonothioate 1a ( $125.0 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl ( $Z$ )-2-(bromomethyl)-3-(4-isopropylphenyl)acrylate $\mathbf{2 d}(222.8 \mathrm{mg}, 0.75 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5$ mmol ), for 4 h . Purification by flash column chromatography (silica gel, $15 \%$ EtOAc in petroleum ether) yielded title compound 3ad.
Yield: $102.1 \mathrm{mg}(57 \%)$; colorless liquid; $R_{f}=0.39$ ( $20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $>98: 2$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.93(\mathrm{~s}, 1 \mathrm{H}), 7.86(\mathrm{dd}, J=8.4,1.2 \mathrm{~Hz}, 2$ $\mathrm{H}), 7.60(\mathrm{tt}, J=7.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.51-7.45(\mathrm{~m}, 4 \mathrm{H}), 7.24(\mathrm{~d}, J=8.2 \mathrm{~Hz}$, $2 \mathrm{H}), 4.52(\mathrm{~s}, 2 \mathrm{H}), 3.56(\mathrm{~s}, 3 \mathrm{H}), 2.91$ (sept, $J=6.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.25(\mathrm{~d}, J=$ $6.9 \mathrm{~Hz}, 6 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=167.2,151.2,146.7,139.5,133.8$, 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) $\mathrm{m} / \mathrm{z} 359.00[\mathrm{M}+\mathrm{H}]^{+}$.

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

Obtained by following GP1 using $S$-phenyl benzenesulfonothioate 1a ( $125.0 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl ( $Z$ )-2-(bromomethyl)-3-(3-bromophenyl)acrylate 2 e ( $239.9 \mathrm{mg}, 0.75 \mathrm{mmol}$ ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5$ 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 ${ }^{\circ} \mathrm{C}$; $R_{f}=0.29$ ( $20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $>95: 5$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.96(\mathrm{~s}, 1 \mathrm{H}), 7.84(\mathrm{dd}, J=8.3,1.1 \mathrm{~Hz}, 2$ H), $7.64-7.60(\mathrm{~m}, 2 \mathrm{H}), 7.57$ (dd, $J=8.0,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.50(\mathrm{t}, J=7.7 \mathrm{~Hz}$, $2 \mathrm{H}), 7.35(\mathrm{td}, J=7.5,0.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.22(\mathrm{td}, J=7.6,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.36(\mathrm{~s}$, 2 H), 3.62 ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.3,145.3,139.4,134.1,133.9$, 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. ${ }^{9 f}$

## Methyl (Z)-3-(3-Methoxyphenyl)-2-[(phenylsulfonyl)methyl]-

 acrylate (3af)Obtained by following GP1 using $S$-phenyl benzenesulfonothioate 1a ( $125.0 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl ( $Z$ )-2-(bromomethyl)-3-(3-methoxyphenyl) acrylate $\mathbf{2 f}(213.8 \mathrm{mg}, 0.75 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5$ 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 $Z \mid E$ isomers ( $83: 17$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.88(\mathrm{~s}, 1 \mathrm{H}), 7.80(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H})$, 7.56 (t, J = 7.9 Hz, 1 H), 7.44 (t, J = 7.0 Hz, 2 H ), 7.23 (t, J = $8.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.09(\mathrm{~s}, 1 \mathrm{H}), 6.98(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.87(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.46(\mathrm{~s}, 2$ H), 3.78 (s, 3 H ), 3.54 ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.7,159.7,146.2,139.3,134.8$, $133.7,129.7,129.0$ (2C), 128.4 (2C), 121.5, 121.0, 115.9, 113.9, 55.4, 55.2, 52.3.

LCMS (ESI): m/z $346.95[\mathrm{M}]^{+}$.

## Methyl (Z)-3-(2-Bromophenyl)-2-[(phenylsulfonyl)methyl]acrylate (3ag)

Obtained by following GP1 using S-phenyl benzenesulfonothioate 1a $(125.0 \mathrm{mg}, 0.5 \mathrm{mmol})$, methyl ( $Z$ )-2-(bromomethyl)-3-(2-bromophenyl)acrylate $\mathbf{2 g}(239.9 \mathrm{mg}, 0.75 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5$ 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; $\mathrm{mp} 110-112{ }^{\circ} \mathrm{C} ; R_{f}=0.27(20 \%$ EtOAc in petroleum ether); mixture of $Z / E$ isomers ( $>95: 5$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.85-7.79(\mathrm{~m}, 3 \mathrm{H}), 7.63(\mathrm{tt}, J=7.4,1.2$ Hz, 1 H ), $7.51-7.45(\mathrm{~m}, 3 \mathrm{H}), 7.44(\mathrm{~s}, 1 \mathrm{H}), 7.41(\mathrm{dd}, J=7.7,0.7 \mathrm{~Hz}, 1 \mathrm{H})$, $7.24(\mathrm{t}, \mathrm{J}=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.44(\mathrm{~s}, 2 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.5,144.4,138.9,135.7,134.0$, $132.5,131.9,130.8,129.2$ (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. ${ }^{10 a}$

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

Obtained by following GP1 using S-phenyl benzenesulfonothioate 1a $(125.0 \mathrm{mg}, 0.5 \mathrm{mmol})$, methyl $(Z)$-2-(bromomethyl)-3-(thiophen-2yl)acrylate 2h ( $185.0 \mathrm{mg}, 0.75 \mathrm{mmol}$ ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5$ 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 ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=8.04(\mathrm{~s}, 1 \mathrm{H}), 7.89(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H})$, $7.59(\mathrm{t}, \mathrm{J}=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.53-7.47(\mathrm{~m}, 4 \mathrm{H}), 7.08(\mathrm{t}, \mathrm{J}=3.9 \mathrm{~Hz}, 1 \mathrm{H}), 4.62$ (s, 2 H ), 3.51 ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.8,139.5,138.3,136.8,134.3$, $133.9,131.0,129.0$ (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. ${ }^{10 \mathrm{a}}$

Methyl (Z)-2-((Phenylsulfonyl)methyl)-3-(1-tosyl-1H-indol-2-yl)acrylate (3ai)
Obtained by following GP1 using S-phenyl benzenesulfonothioate 1a ( $125.0 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl ( $Z$ )-2-(bromomethyl)-3-(1-tosyl-1H-in-dol-2-yl)acrylate $\mathbf{2 i}$ ( $336.2 \mathrm{mg}, 0.75 \mathrm{mmol}$ ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5$ mmol ) for 4 h . Purification by flash column chromatography (silica gel, $20 \%$ EtOAc in petroleum ether) yielded the title compound 3ai.
Yield: $198.7 \mathrm{mg}(78 \%)$; colorless solid; mp $137-139{ }^{\circ} \mathrm{C}$; $R_{f}=0.31(20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $>94: 6$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.57$ (s, 1 H ), 8.09 (s, 1 H ), 8.03 (d, $J=$ $8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.98(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.89(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.62(\mathrm{tt}$, $J=7.4,2.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.58-7.52(\mathrm{~m}, 3 \mathrm{H}), 7.41-7.36(\mathrm{~m}, 1 \mathrm{H}), 7.32-7.26$ (m, 3 H ), 4.51 ( $\mathrm{s}, 2 \mathrm{H}$ ), 3.63 ( $\mathrm{s}, 3 \mathrm{H}$ ), 2.35 ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.6,145.7,139.6,136.0,134.9$, 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 $509.90[\mathrm{M}]^{+}$.

Methyl (Z)-3-(2-Chloroquinolin-3-yl)-2-[(phenylsulfonyl)methyl]acrylate (3aj)
Obtained by following GP1 using S-phenyl benzenesulfonothioate 1a ( $125.0 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl ( $Z$ )-2-(bromomethyl)-3-(2-chloroquin-olin-3-yl)acrylate $\mathbf{2 j}$ ( $254.1 \mathrm{mg}, 0.75 \mathrm{mmol}$ ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( 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; $\mathrm{mp} 129-13^{\circ} \mathrm{C} ; R_{f}=0.21$ ( $20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $80: 20$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=8.74(\mathrm{~s}, 1 \mathrm{H}), 8.09(\mathrm{~s}, 1 \mathrm{H}), 8.04(\mathrm{~d}, \mathrm{~J}=$ $8.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.95(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.90(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.80(\mathrm{t}, J=$ $7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.65(\mathrm{t}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.53(\mathrm{t}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 4.36(\mathrm{~s}, 2$ H), 3.63 ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.2,148.3,143.3,139.5,139.3$, 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 (2Z,4E)-5-Phenyl-2-[(phenylsulfonyl)methyl]penta-2,4-dienoate (3ak)
Obtained by following GP1 using S-phenyl benzenesulfonothioate 1a $(125.0 \mathrm{mg}, 0.5 \mathrm{mmol})$, methyl (2Z,4E)-2-(bromomethyl)-5-phenyl-penta-2,4-dienoate 2k ( $222.8 \mathrm{mg}, 0.75 \mathrm{mmol}$ ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( 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: $97.8 \mathrm{mg}(57 \%)$; colorless solid; mp $143-145^{\circ} \mathrm{C} ; R_{f}=0.35$ (20\% EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $>95: 5$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.89-7.86(\mathrm{~m}, 2 \mathrm{H}), 7.62(\mathrm{dd}, J=7.3,3.5$ $\mathrm{Hz}, 1 \mathrm{H}$ ), 7.56-7.47 (m, 3 H ), 7.44 (dd, $J=8.0,1.6 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.36 (m, 3 H), 6.96-6.93 (m, 2 H ), 4.43 ( s, 2 H ), 3.53 ( s, 3 H ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.5,145.8,143.8,138.7,135.8$, 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. ${ }^{10 \mathrm{a}, \mathrm{d}}$

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

Obtained by following $\mathbf{G 1}$ using $S$-phenyl benzenesulfonothioate 1a $(125.0 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl ( $Z$ )-2-(bromomethyl)-5-phenylpent-2enoate $\mathbf{2 1}(212.3 \mathrm{mg}, 0.75 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5 \mathrm{mmol})$ 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 $Z \mid E$ isomers ( $>92: 8$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.95(\mathrm{dd}, J=8.3,1.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.73(\mathrm{tt}$, $J=7.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.63(\mathrm{t}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.43-7.38(\mathrm{~m}, 2 \mathrm{H}), 7.32(\mathrm{~d}$, $J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.30-7.27(\mathrm{~m}, 3 \mathrm{H}), 4.27(\mathrm{~s}, 2 \mathrm{H}), 3.57(\mathrm{~s}, 3 \mathrm{H}), 2.87(\mathrm{t}$, $J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 2.66(\mathrm{q}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.0,150.5,140.5,138.9,133.9,129.1$ (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 ( $125.0 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), methyl (Z)-2-(bromomethyl)-5-methylhex-2enoate $\mathbf{2 m}$ ( $165.8 \mathrm{mg}, 0.75 \mathrm{mmol}$ ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5 \mathrm{mmol})$ for 4 h . Purification by flash column chromatography (silica gel, $10 \%$ EtOAc in petroleum ether) yielded the title compound 3am.
Yield: $134.9 \mathrm{mg}(91 \%)$; colorless liquid; $R_{f}=0.30$ ( $20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $80: 20$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.83(\mathrm{dd}, J=8.4,1.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.62(\mathrm{tt}$, $J=7.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.51(\mathrm{t}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.14(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.22$
(s, 2 H ), $3.46(\mathrm{~s}, 3 \mathrm{H}), 2.08(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 1.77-1.67(\mathrm{~m}, 1 \mathrm{H}), 0.89$ (d, $J=6.7 \mathrm{~Hz}, 6 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.2,151.1,133.9,129.6,129.1$ (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 ( $125 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), ethyl ( $Z$ )-2-(bromomethyl)-3-phenylacrylate $\mathbf{2 n}$ ( $201.8 \mathrm{mg}, 0.75 \mathrm{mmol}$ ), and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5 \mathrm{mmol})$ 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 ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.93(\mathrm{~s}, 1 \mathrm{H}), 7.84(\mathrm{dd}, J=8.4,1.2 \mathrm{~Hz}, 2$ $\mathrm{H}), 7.58(\mathrm{tt}, J=7.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.49-7.44(\mathrm{~m}, 4 \mathrm{H}), 7.37-7.33(\mathrm{~m}, 3 \mathrm{H})$, 4.49 (s, 2 H ), 4.03 ( $\mathrm{q}, \mathrm{J}=7.1 \mathrm{~Hz}, 2 \mathrm{H}$ ), $1.22(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.6,146.2,139.5,133.85,133.81$, $129.7,129.3$ (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. ${ }^{9 d}$

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

Obtained by following GP1 using $S$-( $p$-tolyl) 4-methylbenzenesulfonothioate $\mathbf{1 b}$ ( $139.1 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), ethyl ( $Z$ )-2-(bromomethyl)-3phenylacrylate $\mathbf{2 n}(191.3 \mathrm{mg}, 0.75 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(162.5 \mathrm{mg}, 0.5$ mmol ) for 4 h . Purification by flash column chromatography (silica gel, $15 \%$ EtOAc in petroleum ether) yielded the title compound 3bn.
Yield: $168.7 \mathrm{mg}(98 \%)$; colorless liquid; $R_{f}=0.42$ ( $20 \%$ EtOAc in petroleum ether); mixture of $Z \mid E$ isomers ( $>98: 2$ ) based on ${ }^{1} \mathrm{H}$ NMR analysis.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=8.01(\mathrm{~s}, 1 \mathrm{H}), 7.80(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H})$, 7.56 (dd, $J=6.5,2.7 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.47-7.44$ (m, 3 H ), 7.35 (d, $J=8.2 \mathrm{~Hz}, 2$ H), $4.58(\mathrm{~s}, 2 \mathrm{H}), 4.16(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 2.51(\mathrm{~s}, 3 \mathrm{H}), 1.34(\mathrm{t}, J=7.1 \mathrm{~Hz}$, 3 H ).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.6,146.0,144.8,136.5,133.9$, 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. ${ }^{10 d}$

## Conflict of Interest

The authors declare no conflict of interest.

## Funding Information

We thank the Department of Science \& Technology - Promotion of University Research and Scientific Excellence (DST-PURSE; SR/PURSE Phase $2 / 32 / G$ ) and the Council of Scientific and Industrial Research (CSIR-EMR-II; 02(0340)/18/EMR-II) for funding support. A.S. and M.W. thank CSIR-SRF and UGC-SRF, respectively, for their Research Fellowships.

## Acknowledgment

R.J.R. thanks UGC for a faculty position under the Faculty Recharge Programme. The authors are highly thankful to Dr Ch. Raji Reddy, Associate Editor of SynOpen, for his generous invitation to publish some of their work in this journal.

## Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1422-9411.

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[^0]:    ${ }^{\text {a }}$ All reactions were carried out on a 0.2 mmol scale.
    ${ }^{\mathrm{b}}$ Isolated yields.
    ${ }^{c}$ Without $\mathrm{Cs}_{2} \mathrm{CO}_{3}$.

