PAPER

Check for updates

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

Raju Jannapu Reddy, [ID]* Md. Waheed‡ and Jangam Jagadesh Kumar‡

A practical, highly flexible and eco-friendly method has been developed for the synthesis of allyl thiosulfonates using Morita–Baylis–Hillman (MBH) allyl bromides and sodium arylthiosulfonates, which were readily assembled without any reagent/catalyst. Moreover, the allyl thiosulfonates were successfully transformed into a set of two synthetically viable diallyl disulfanes and unsymmetrical allyl disulfanes in the presence of Cs_2CO_3. The present protocols are operationally simple and convenient to generate a wide range of functionalized allyl thiosulfonates and allyl disulfanes in good to excellent yields.
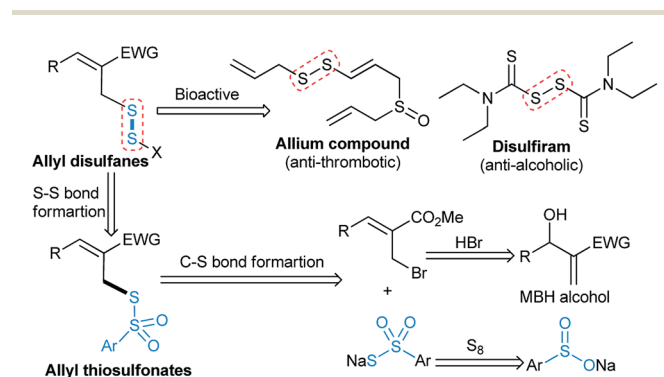
Introduction

Organosulfur compounds have received much attention in recent years.[1] The direct construction of a carbon–sulfur bond is a potent method in modern organic synthesis.[2] Among a variety of organosulfur compounds, the thiosulfonates ($RS–SO_2R^1$)[3] and the disulfanes ($RS–SR^1$)[4] are a privileged class of compounds and they serve as electrophilic sulfenylating agents in organic synthesis. Additionally, the thiosulfonates and the disulfanes have several advantages, which include being an odourless sulfur source, higher reactivity, and better stability than other frequently used sulfenylating agents. In general, the thiosulfonates have shown a broad spectrum of clinical properties like antiviral, antimicrobial and fungicidal activities.[5] A wide range of effective strategies have been established for the synthesis of *S*-aryl arenethiosulfonates.[6–8] Although the reactions of sodium thiosulfonates with alkyl halides have been studied,[9] a general method is still highly desirable. This fact motivated us to develop a new strategy for the synthesis of functionalized allyl thiosulfonates.

In contrast, the disulfanes also have significant importance in pharmaceutical chemistry[10] and chemical biology.[11] The S–S bond plays an indispensable role in allium compounds[10a] and disulfiram,[10b–d] which act as anti-thrombotic and anti-alcoholic drugs (Scheme 1). Numerous synthetic methods have been reported, which rely on the oxidative coupling of thiols to construct the S–S bond.[12] However, these methods have some disadvantages, either they involve the tedious use

of thiols or their equivalents or they are limited by commercial scarcity. Therefore, it is still necessary to develop a facile methodology for the synthesis of allyl disulfides from easily accessible starting materials.

According to retrosynthetic analysis, the proposed strategy has a great advantage of extensively available starting materials (Scheme 1). In fact, the allyl bromides can be derived from Morita–Baylis–Hillman (MBH) adducts[13] and sodium thiosulfonates easily prepared from sulfinate salts.[14] In particular, the sodium thiosulfonate precursors are preferable to use as sulfenylating agents since they are bench stable and generally crystalline solids with low toxicity.[14b] We have also envisaged that the allyl thiosulfonates would be converted into the corresponding unprecedented allyl disulfanes. In a continuation of our interest in organosulfur chemistry,[15] we decided to study MBH bromide with sodium thiosulfonate for direct C–S bond construction, which represents an interesting and challenging endeavour in organic synthesis. In this context, we disclose our findings and report the scope for the

Department of Chemistry, Osmania University, Hyderabad 500 007, India. E-mail: rajuchem77@osmania.ac.in; rajuchem08@yahoo.co.in

† Electronic supplementary information (ESI) available: General experimental procedures, spectroscopic data and NMR spectra for the new compounds. See DOI: 10.1039/c8ra06938g

‡ These authors contributed equally.

Scheme 1 Strategy for synthesis of allyl thiosulfonates and allyl disulfanes.

synthesis of unsymmetrical allyl thiosulfonates and allyl disulfanes with a variety of substitution patterns.

Results and discussion

At the outset, optimization studies were undertaken (see ESI†) for the nucleophilic substitution reaction of (*Z*)-methyl 2-(bromo-methyl)-3-phenylacrylate (**1a**) with sodium thiosulfonate (**2a**) as a model substrate. To our delight, an excellent yield (94%) of the desired allyl thiosulfonate (**3aa**) was achieved with 1.5 equiv. of **2a** in CH_3CN at room temperature within 2 h. Then we explored a broad range of allyl bromides (**1a–t**) with sodium thiosulfonates (**2a–d**) for the synthesis of allyl thiosulfonates **3aa–tb** (Table 1). In addition to **3aa**, the 4-bromo and 4-chloro-substituted allyl bromides (**1b** and **1c**) readily reacted with **2a**, giving the desired thiosulfonates (**3ba–ca**) in 89% and 84% yields, respectively. Various aryl-substituted MBH bromides (**1a–h**) smoothly reacted with sodium 4-methyl-benzenesulfonothioate **2b** to provide the desired products (**3ab–hb**) in 70–92% yield. The 2-naphthyl derived thiosulfonates (**3ia** and **3jb**) were obtained in high yield under optimised reaction conditions. Heteroaryl derived allyl bromide (**1k**) also served as a good substrate, affording **3kb** in 68% yield. Moreover,

Table 1   Substrate scope for synthesis of allyl thiosulfonates[a,b]
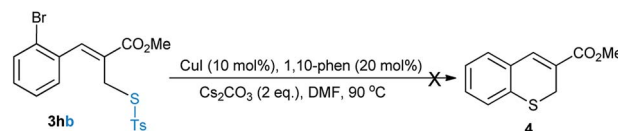
Scheme 2   Synthesis of methyl 2*H*-thiochromene-3-carboxylate (**4**).

cinnamyl and isovaleraldehyde derived allyl bromides (**1l–m**) were also suitable substrates to produce the desired allyl thiosulfonates (**3lb** and **3mb**) in high yields. The ethyl ester derived MBH bromides (**1n** and **1o**) provided the corresponding products **3nb** and **3ob** in 78% and 72% yields, respectively. Disappointingly, the nitrostyrene derived bromide (**1p**) was sluggish to react with **2a**. The substrate scope was further extended to acrylonitrile derived MBH bromides (**1q–t**). This successfully achieved the corresponding thiosulfonates (**3qa/b**, **3(r–t)b**) in moderate to good yields with inseparable regioisomers (ESI†).[16] Overall, these reactions were scalable to provide the desired allyl thiosulfonates with a little deviation in the outcome (ESI†).

Next, we explored the synthetic utility of readily accessible allyl thiosulfonates in organic synthesis. We desired to synthesise methyl 2*H*-thiochromene-3-carboxylate (**4**)[17] *via* the cyclization of 2-bromo derived thiosulfonate **3hb** (Scheme 2). Unfortunately, we did not attain the anticipated cyclic product **4**; however, other interesting allyl disulfanes were obtained under these conditions (Table 2). Hence, we directed our attention toward the synthesis of allyl disulfanes using allyl thiosulfonates.

Encouraged by this result, we commenced the optimization of reaction conditions using thiosulfonates **3ab** (Table 2). The use of CuI (10 mol%) and CuBr (10 mol%) with 1,10-phen (20 mol%) in the presence of Cs_2CO_3 (2 eq.) in DMF afforded the desired disulfanes (**5a** and **6a**) in low yield (entries 1 and 2). There was no reaction in the presence of K_2CO_3 in DMF; however, substantial progress was seen in toluene and THF (entries 3–5). In the absence of a ligand (1,10-phen), the reaction proceeded with 5 mol% of CuBr, but there was no reaction with only CuBr and without Cs_2CO_3 (entries 6–8). To our surprise, Cs_2CO_3 alone afforded the desired disulfanes with improved yields (entries 9–11). A satisfactory yield of diallyl disulfane **5a** (49%) and unsymmetrical disulfane **6a** (44%) were obtained when the reaction was carried out using 1.0 eq. of Cs_2CO_3 in THF at 60 °C (entry 10). Low yields were obtained with DBU, DABCO, and K_2CO_3 (entries 12–14) and no reaction was found without a base (entry 15). It is worth noting that our attempts to produce as a single product either **5a** or **6a** were unsuccessful.
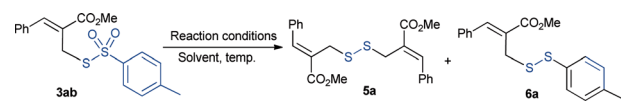
With the optimized conditions in hand, the scope of the reaction was further verified and the results are summarized in Table 3. Pleasingly, the allyl thiosulfonate substrates (**3a, d, e, g, h, o/b** and **3aa/b**) bearing different groups at the *para*, *meta* or *ortho* position of the aromatic rings proceeded efficiently to afford the corresponding allyl disulfanes (**5a–g** and **6a–h**) in good to high yields. The bulky 2-naphthalene derived thiosulfonates (**3jb/3ad**) were also well tolerated to provide the diallyl disulfanes (**5h/a**) and unsymmetrical disulfanes (**6i/j**) in good yields. The ethyl ester derived thiosulfonate (**3nb**) was also a good substrate to furnish allyl disulfane **5i** and **6k** in 40% and
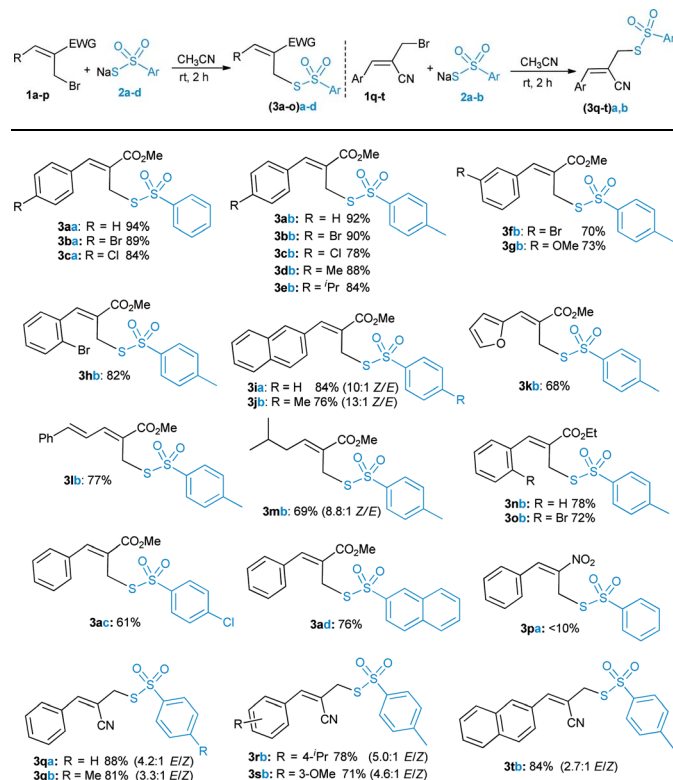
[a] All reactions performed on 0.4 mmol of **1a–t** (1 eq.), sodium thiosulfonates **2a–d** (1.5 eq.) in CH_3CN (2 mL) at room temperature. [b] Isolated yields. Reactions performed on a 4 mmol scale for synthesis of **3aa/b** and 2 mmol scale for synthesis of **3ba**, (**3b–e, g–i, k, n, o, q**)**b** and **3ad** (see ESI).

Table 2 Optimization for synthesis of allyl disulfanes from thiosulfonate **3ab**[a]

Entry	Reaction conditions	Time	**5a**[b]	**6a**[b]
1	CuI (10 mol%), 1,10-phen (20 mol%), Cs$_2$CO$_3$ (2 eq.), DMF, 90 °C	6 h	20%	14%
2	CuBr (10 mol%), 1,10-phen (20 mol%), Cs$_2$CO$_3$ (2 eq.), DMF, 90 °C	6 h	29%	20%
3	CuBr (10 mol%), 1,10-phen (20 mol%), K$_2$CO$_3$ (2 eq.), DMF, 90 °C	6 h	NR	NR
4	CuBr (10 mol%), 1,10-phen (20 mol%), Cs$_2$CO$_3$ (2 eq.), toluene, 90 °C	6 h	34%	11%
5	CuBr (10 mol%), 1,10-phen (20 mol%), Cs$_2$CO$_3$ (2 eq.), THF, 60 °C	4 h	30%	20%
6	CuBr (10 mol%), Cs$_2$CO$_3$ (2 eq.), THF, 60 °C	4 h	35%	22%
7	CuBr (5 mol%), Cs$_2$CO$_3$ (2 eq.), THF, 60 °C	4 h	38%	24%
8	CuBr (10 mol%), THF, 60 °C	6 h	NR	NR
9	Cs$_2$CO$_3$ (2 eq.), THF, 60 °C	2 h	45%	36%
10	**Cs$_2$CO$_3$ (1 eq.), THF, 60 °C**	**2 h**	**49%**	**44%**
11	Cs$_2$CO$_3$ (0.5 eq.), THF, 60 °C	4 h	38%	29%
12	DBU (2 eq.), THF, 60 °C	6 h	20%	20%
13	DABCO (2 eq.), THF, 60 °C	6 h	NR	NR
14	K$_2$CO$_3$ (2 eq.), THF, 60 °C	6 h	NR	NR
15	Without base, THF, 60 °C	6 h	NR	NR

[a] All reactions performed on a 0.4 mmol scale of **3ab** in solvent (2 mL). [b] Isolated yields. NR: no reaction.

35% yields, respectively. But an extension to other thiosulfonates **3kb** and **3qb** failed to provide the desired allyl disulfides.

Recently, Jiang and co-workers[18] demonstrated the potential application of *S*-acetyl disulfanes in oxidative coupling with arylboronic acids. In this direction, the allyl thiosulfonates **3(a/h)b** were treated with potassium thioacetate in DMF and the anticipated products (**7a/b**) were achieved in 88% and 85% yields, respectively (Scheme 3). Sequential one-pot nucleophilic substitution reactions were performed using MBH bromide **1a** with sodium thiosulfonate (**2b**) followed by potassium thioacetate (Scheme 3). The desired product **7a** was obtained in 78% yield and this procedure has notable advantages, such as straightforwardness, step-economy and scalability in a one-pot operation (see ESI†).

To gain more insight, the *S*-aryl arenethiosulfonates (**8a** and **8b**) were treated with Cs$_2$CO$_3$ under the same reaction conditions. Thus, it was found that no reaction representing the allyl moiety played a vital role in the formation of disulfanes. A radical-trapping experiment was also performed with **3ab** using TEMPO (2 equiv.) as a radical scavenger under standard conditions. The disulfanes **5a** and **6a** were isolated in low yields, alongside the TEMPO derived product (**9**),[4d] as detected by HRMS (Scheme 4b). These experimental results indicate that the reaction may proceed *via* a radical pathway leading to the formation of allyl disulfanes **5** and **6**.

Experimental

General procedure-1 (GP1) for synthesis of allyl thiosulfonates

A heat gun-dried Schlenk tube was charged with Morita–Baylis–Hillman allyl bromides **1a–t** (0.4 mmol, 1.0 equiv.) and sodium thiosulfonates **2a–d** (0.6 mmol, 1.5 equiv.) in CH$_3$CN (2.0 mL). The reaction mixture was stirred at room temperature for 2 h
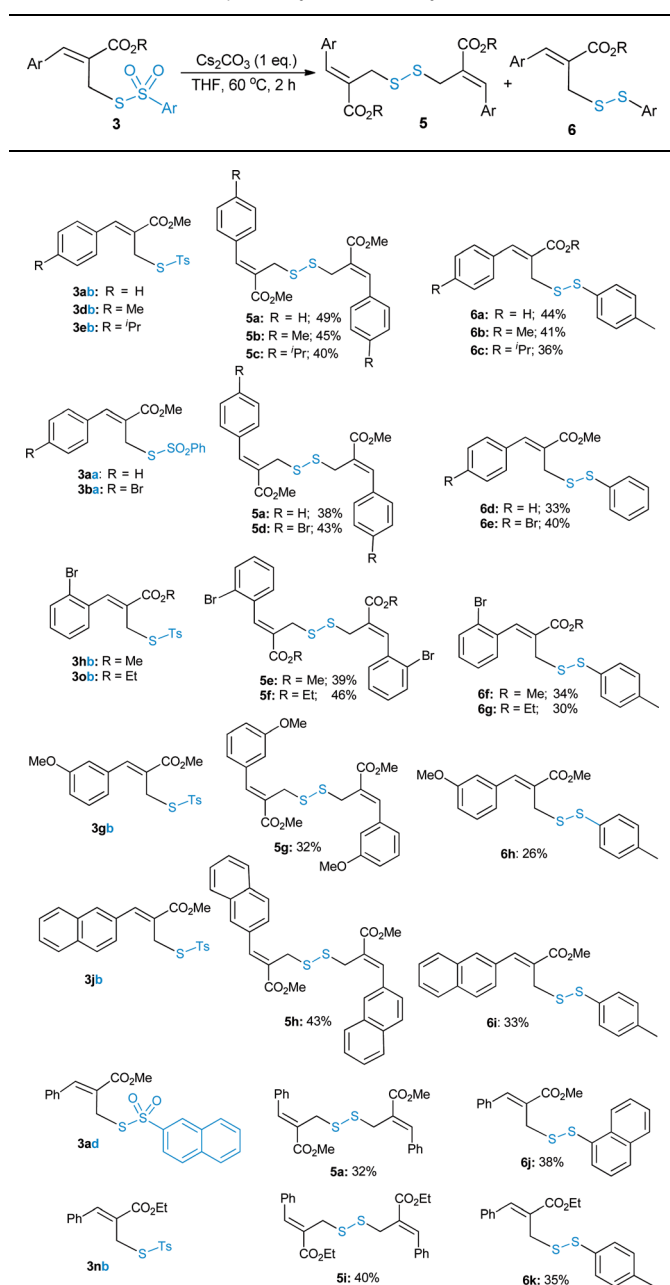
and monitored by TLC until it was either complete or appeared to be making no further progress. The mixture was quenched by the addition of water (10 mL) followed by extraction with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (2 × 10 mL), dried over anhydrous Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 20–30% ethyl acetate/petether) to afford the desired allyl thiosulfonates.

Allyl thiosulfonate 3aa

Prepared according to **GP1** using **1a** (101.2 mg, 0.4 mmol) with sodium benzenethiosulfonate **2a** (117.6 mg, 0.6 mmol) to afford **3aa** (130.6 mg, 94%) using 20% ethyl acetate/petether as a colorless solid. Mp: 95–97 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87–7.77 (m, 3H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.42–7.32 (m, 5H), 4.17 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.8, 144.6, 144.3, 134.0, 133.7, 129.8, 129.7 (2C), 129.4 (2C), 129.0 (2C), 127.2 (2C), 124.4, 52.6, 33.4; HRMS (ESI) calculated for C$_{17}$H$_{16}$O$_4$S$_2$Na [M + Na]$^+$: *m/z* 371.0388, found 371.0389. Prepared according to **GP1** using **1a** (1.02 g, 4.0 mmol) with sodium benzenethiosulfonate **2a** (1.47 g, 6.0 mmol) in CH$_3$CN (20 mL) to afford **3aa** (1.1 g, 79%) as a colorless solid.

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

A heat gun-dried Schlenk tube was charged with allyl thiosulfonates **3** (0.8 mmol, 1.0 equiv.) and cesium carbonate (260.6 mg, 0.8 mmol, 1.0 equiv.) in dry THF (4.0 mL). The reaction mixture was stirred at 60 °C for 2 h and monitored by TLC either until it was complete or appeared to be making no further progress. The mixture was allowed to cool to room temperature and quenched by the addition of water (20 mL)

Table 3 Substrate scope for synthesis of allyl disulfanes[a,b]

3ab: R = H
3db: R = Me
3eb: R = ^{i}Pr

5a: R = H; 49%
5b: R = Me; 45%
5c: R = ^{i}Pr; 40%

6a: R = H; 44%
6b: R = Me; 41%
6c: R = ^{i}Pr; 36%

3aa: R = H
3ba: R = Br

5a: R = H; 38%
5d: R = Br; 43%

6d: R = H; 33%
6e: R = Br; 40%

3hb: R = Me
3ob: R = Et

5e: R = Me; 39%
5f: R = Et; 46%

6f: R = Me; 34%
6g: R = Et; 30%

3gb

5g: 32%

6h: 26%

3jb

5h: 43%

6i: 33%

3ad

5a: 32%

6j: 38%

3nb

5i: 40%

6k: 35%

[a] All reactions performed on 0.8 mmol of allyl thiosulfonates (1 eq.) and Cs$_2$CO$_3$ (1.0 eq.) in dry THF (4 mL) at 60 °C for 2 h. [b] Isolated yields.
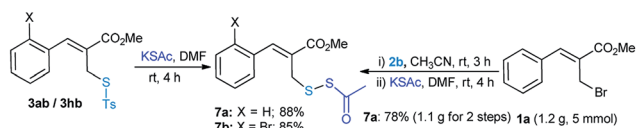
Scheme 3 Reactions performed on 0.8 mmol of **3ab/3hb** with KSAc (1.5 eq.). A gram scale reaction of allyl bromide **1a** with **2b**/KSAc for the synthesis of **7a**.
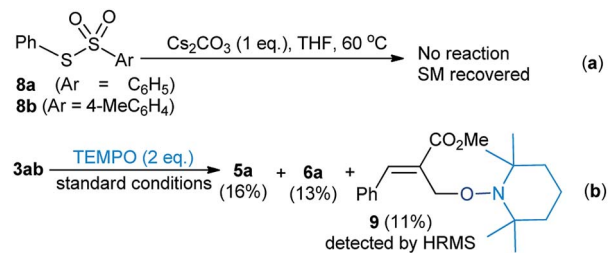
Scheme 4 Control experiments.

followed by extraction with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (2 × 20 mL), dried over anhydrous Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 20–30% ethyl acetate/petether) to afford desired allyl disulfanes **5** and **6**.

Diallyl disulfane 5a

Prepared according to **GP2** using **3ab** (289.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5a** (81.2 mg, 24.5% × 2 = 49%) using 20% ethyl acetate/petether as a colorless solid. Mp: 110–112 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.82 (s, 1H), 7.51 (dd, J = 7.3, 1.0 Hz, 2H), 7.41–7.34 (m, 3H), 3.88 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.6, 142.4, 134.9, 129.7 (2C), 129.2, 128.8 (2C), 128.0, 52.4, 36.7; HRMS (ESI) calculated for C$_{22}$H$_{22}$O$_4$S$_2$Na [M + Na]$^+$: m/z 437.0857, found 437.0857.

Allyl disulfane 6a

Prepared according to **GP2** using **3ab** (289.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6a** (116.2 mg, 44%) using 30% ethyl acetate/petether as a colorless solid. Mp: 163–165 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 (s, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.50–7.43 (m, 2H), 7.40–7.33 (m, 3H), 7.27 (d, J = 8.0 Hz, 2H), 4.47 (s, 2H), 3.61 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.1, 146.3, 145.5, 144.9, 136.5, 133.8, 129.8 (2C), 129.3 (2C), 128.8 (2C), 128.7 (2C), 121.2, 55.3, 52.5, 21.7; HRMS (ESI) calculated for C$_{18}$H$_{18}$O$_4$S$_2$Na [M + Na]$^+$: m/z 353.0823, found 353.0829.

Diallyl disulfane 5b

Prepared according to **GP2** using **3db** (300.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5b** (80.3 mg, 22.7% × 2 = 45%) using 20% ethyl acetate/petether as a pale-yellow solid. Mp: 197–199 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87–7.74 (m, 1H), 7.45 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 3.97 (s, 2H), 3.81 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.7, 142.5, 139.6, 131.9, 129.9 (2C), 129.5 (2C), 126.9, 52.3, 37.1, 21.5; HRMS (ESI) calculated for C$_{24}$H$_{26}$O$_4$S$_2$Na [M + Na]$^+$: m/z 465.1170, found 465.1172.

Allyl disulfane 6b

Prepared according to **GP2** using **3db** (300.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6b** (112.7 mg, 41%) using 30% ethyl acetate/petether as a pale-yellow solid. Mp: 212–

214 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (s, 1H), 7.72 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 4.48 (s, 2H), 3.58 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.2, 146.4, 144.8, 140.2, 136.5, 130.9, 129.6 (2C), 129.50 (2C), 129.48 (2C), 128.6 (2C), 120.0, 55.3, 52.3, 21.7, 21.5; HRMS (ESI) calculated for C$_{19}$H$_{20}$O$_2$S$_2$Na [M + Na]$^+$: m/z 367.06980; found 367.06980.

Diallyl disulfane 5c

Prepared according to **GP2** using **3eb** (323.2 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5c** (79.7 mg, 20% × 2 = 40%) using 20% ethyl acetate/petether as a pale-yellow solid. Mp: 178–180 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80 (s, 1H), 7.50 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 3.96 (s, 2H), 3.81 (s, 3H), 2.91 (sept, J = 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.8, 150.5, 142.6, 132.3, 130.1 (2C), 126.9 (2C), 126.87, 52.4, 37.1, 34.1, 23.9 (2C); HRMS (ESI) calculated for C$_{28}$H$_{35}$O$_4$S$_2$ [M + H]$^+$: m/z 499.1957, found 499.1939.

Allyl disulfane 6c

Prepared according to **GP2** using **3eb** (323.2 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6c** (107.0 mg, 36%) using 30% ethyl acetate/petether as a colorless solid. Mp: 216–218 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (s, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.29 (dd, J = 8.7, 2.3 Hz, 4H), 4.54 (s, 2H), 3.63 (s, 3H), 3.04–2.88 (m, 1H), 2.46 (s, 3H), 1.30 (d, J = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.2, 151.1, 146.4, 144.7, 136.5, 131.3, 129.67 (2C), 129.66 (2C), 128.7 (2C), 126.9 (2C), 120.1, 55.4, 52.4, 34.1, 23.9 (2C), 21.7; HRMS (ESI) calculated for C$_{21}$H$_{24}$O$_2$SNa [M + Na]$^+$: m/z 395.1293, found 395.1293.

Diallyl disulfane 5a

Prepared according to **GP2** using **3aa** (278.4 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5a** (63.2 mg, 19% × 2 = 38%) using 20% ethyl acetate/petether as a colorless solid.

Allyl disulfane 6d

Prepared according to **GP2** using **3aa** (278.4 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6d** (83.5 mg, 33%) using 30% ethyl acetate/petether as a pale-yellow viscous liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (s, 1H), 7.84 (dd, J = 8.3, 1.2 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.51–7.45 (m, 4H), 7.40–7.34 (m, 3H), 4.49 (s, 2H), 3.58 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.9, 146.4, 139.4, 133.8, 133.7, 129.8, 129.2 (2C), 129.1 (2C), 128.8 (2C), 128.5 (2C), 121.0, 55.2, 52.4; HRMS (ESI) calculated for C$_{17}$H$_{16}$O$_2$S$_2$Na [M + Na]$^+$: m/z 339.0667, found 339.0665.

Diallyl disulfane 5d

Prepared according to **GP2** using **3ba** (341.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5d** (98.6 mg, 21.5% × 2 = 43%) using 20% ethyl acetate/petether as a pale-yellow gum. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (s, 1H), 7.52 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 3.84 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.3, 141.0, 133.7, 132.0 (2C), 131.2 (2C), 128.6,

123.7, 52.5, 36.6; HRMS (ESI) calculated for C$_{22}$H$_{21}$O$_4$S$_2$Br$_2$ [M + H]$^+$: m/z 570.9248, found 570.9259.

Allyl disulfane 6e

Prepared according to **GP2** using **3ba** (341.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6e** (126.3 mg, 40%) using 30% ethyl acetate/petether as a pale-yellow gum. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (s, 1H), 7.85 (dd, J = 8.4, 1.2 Hz, 2H), 7.66–7.60 (m, 1H), 7.54–7.48 (m, 4H), 7.39 (d, J = 8.3 Hz, 2H), 4.43 (s, 2H), 3.57 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.7, 145.2, 139.4, 134.0, 132.6, 132.2 (2C), 130.8 (2C), 129.2 (2C), 128.6 (2C), 124.4, 121.6, 55.2, 52.6; HRMS (ESI) calculated for C$_{17}$H$_{15}$O$_4$S$_2$BrNa [M + Na]$^+$: m/z 416.9772, found 416.9776.

Diallyl disulfane 5e

Prepared according to **GP2** using **3hb** (341.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5e** (89.2 mg, 19.5% × 2 = 39%) using 20% ethyl acetate/petether as a pale-yellow viscous liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 (s, 1H), 7.59 (dd, J = 8.0, 1.1 Hz, 1H), 7.45 (dd, J = 7.6, 1.3 Hz, 1H), 7.32 (td, J = 7.5, 0.8 Hz, 1H), 7.20 (td, J = 7.5, 1.3 Hz, 1H), 3.82 (s, 3H), 3.57 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.0, 141.2, 135.4, 133.0, 130.6, 130.2, 129.8, 127.5, 124.5, 52.5, 35.9; HRMS (ESI) calculated for C$_{22}$H$_{20}$O$_4$S$_2$Br$_2$Na [M + Na]$^+$: m/z 592.9063, found 592.9055.

Allyl disulfane 6f

Prepared according to **GP2** using **3hb** (341.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6f** (112.1 mg, 34%) using 30% ethyl acetate/petether as a pale-yellow viscous liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (s, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.62 (dd, J = 7.7, 1.1 Hz, 1H), 7.56 (dd, J = 8.0, 1.1 Hz, 1H), 7.35 (td, J = 7.6, 1.6 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.22 (td, J = 7.6, 1.2 Hz, 1H), 4.35 (s, 2H), 3.64 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.5, 145.1, 144.8, 136.4, 134.2, 133.0, 130.7, 130.2, 129.8 (2C), 128.5 (2C), 127.7, 124.2, 123.0, 55.0, 52.6, 21.7; HRMS (ESI) calculated for C$_{18}$H$_{17}$O$_2$S$_2$BrNa [M + Na]$^+$: m/z 430.9751, found 430.9926.

Diallyl disulfane 5f

Prepared according to **GP2** using **3ob** (353.0 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5f** (108.4 mg, 23.0% × 2 = 46%) using 20% ethyl acetate/petether as a pale-yellow viscous liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.77 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.19 (t, J = 7.7 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.59 (s, 2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.5, 140.9, 135.4, 132.9, 130.6, 130.2, 130.1, 127.4, 124.5, 61.5, 36.1, 14.4; HRMS (ESI) calculated for C$_{24}$H$_{24}$O$_4$S$_2$Br$_2$Na [M + Na]$^+$: m/z 620.9380, found 620.9373.

Allyl disulfane 6g

Prepared according to **GP2** using **3ob** (353.0 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6g** (101.3 mg, 30%) using 30% ethyl acetate/petether as a pale-yellow viscous liquid. [1]H

NMR (400 MHz, CDCl$_3$) δ 7.94 (s, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.62 (dd, J = 7.7, 1.1 Hz, 1H), 7.56 (dd, J = 8.0, 1.1 Hz, 1H), 7.35 (td, J = 7.5, 0.9 Hz, 1H), 7.28 (d, J = 8.3 Hz, 2H), 7.22 (td, J = 7.6, 1.3 Hz, 1H), 4.35 (s, 2H), 4.10 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.0, 144.78, 144.76, 136.5, 134.3, 132.9, 130.7, 130.2, 129.8 (2C), 128.5 (2C), 127.7, 124.2, 123.3, 61.8, 55.0, 21.7, 14.1; HRMS (ESI) calculated for C$_{19}$H$_{19}$O$_2$S$_2$BrNa [M + Na]$^+$: m/z 445.0088, found 445.0082.

Diallyl disulfane 5g

Prepared according to **GP2** using **3gb** (313.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5g** (60.6 mg, 16% × 2 = 32%) as a pale-yellow solid. Mp: 192–194 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 (s, 1H), 7.25–7.19 (m, 1H), 7.03 (d, J = 2.2 Hz, 2H), 6.85 (dd, J = 8.1, 1.9 Hz, 1H), 3.87 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.6, 159.8, 142.5, 136.1, 129.8, 128.1, 122.1, 115.4, 114.6, 55.5, 52.4, 37.0; HRMS (ESI) calculated for C$_{24}$H$_{26}$O$_6$S$_2$Na [M + Na]$^+$: m/z 497.1068, found 497.1069.

Allyl disulfane 6h

Prepared according to **GP2** using **3gb** (313.6 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6h** (74.8 mg, 26%) using 30% ethyl acetate/petether as a pale-yellow gum. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (s, 1H), 7.72 (d, J = 8.2 Hz, 2H), 7.32–7.24 (m, 3H), 7.11 (s, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 4.48 (s, 2H), 3.85 (s, 3H), 3.61 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.0, 159.9, 146.3, 144.9, 136.5, 135.1, 129.84, 129.76 (2C), 128.7 (2C), 121.7, 121.4, 116.0, 114.1, 55.6, 55.4, 52.5, 21.7; HRMS (ESI) calculated for C$_{19}$H$_{20}$O$_5$SNa [M + Na]$^+$: m/z 383.0929, found 383.0937.

Diallyl disulfane 5h

Prepared according to **GP2** using **3jb** (330.0 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5h** (89.3 mg, 21.7% × 2 = 43%) using 20% ethyl acetate/petether as a yellow solid. Mp: 187–198 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (s, 1H), 7.95 (s, 1H), 7.79 (dd, J = 8.7, 5.3 Hz, 3H), 7.57 (dd, J = 8.5, 1.5 Hz, 1H), 7.49 (ddd, J = 8.0, 6.7, 1.4 Hz, 2H), 4.03 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.6, 142.4, 133.4, 133.2, 132.3, 129.8, 128.7, 128.4, 128.1, 127.8, 127.2, 126.8, 126.7, 52.4, 37.2; HRMS (ESI) calculated for C$_{30}$H$_{26}$O$_4$S$_2$Na [M + Na]$^+$: m/z 537.1165, found 537.1170.

Allyl disulfane 6i

Prepared according to **GP2** using **3jb** (330.0 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6i** (99.6 mg, 33%) using 30% ethyl acetate/petether as yellow solid. Mp: 195–197 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.07 (s, 1H), 7.97 (s, 1H), 7.88–7.78 (m, 3H), 7.70 (d, J = 8.3 Hz, 2H), 7.55–7.47 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 4.57 (s, 2H), 3.67 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.2, 146.2, 144.9, 136.5, 133.6, 133.2, 131.3, 129.7 (2C), 129.6, 128.8, 128.7 (2C), 128.5, 127.8, 127.5, 126.8,

126.1, 121.4, 55.4, 52.6, 21.7; HRMS (ESI) calculated for C$_{22}$H$_{20}$O$_2$S$_2$Na [M + Na]$^+$: m/z 403.0980, found 403.0983.

Diallyl disulfane 5a

Prepared according to **GP2** using **3ad** (318.8 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5a** (52.6 mg, 15.8% × 2 = 32%) using 20% ethyl acetate/petether as a colorless solid.

Allyl disulfane 6j

Prepared according to **GP2** using **3ad** (318.8 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6j** (110.6 mg, 38%) using 30% ethyl acetate/petether as a pale-yellow solid. Mp: 227–229 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.38 (s, 1H), 7.97–7.87 (m, 4H), 7.79 (dd, J = 8.7, 1.8 Hz, 1H), 7.69–7.57 (m, 2H), 7.37 (dd, J = 7.4, 1.6 Hz, 2H), 7.27–7.22 (m, 3H), 4.57 (s, 2H), 3.45 (s, 3H); ^{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, 127.7, 123.2, 121.1, 55.1, 52.4; HRMS (ESI) calculated for C$_{21}$H$_{19}$O$_4$S$_2$ [M + H]$^+$: m/z 367.1004, found 367.1005.

Diallyl disulfane 5i

Prepared according to **GP2** using **3nb** (300.8 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **5i** (70.7 mg, 20% × 2 = 40%) using 20% ethyl acetate/petether as a pale-yellow liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (s, 1H), 7.50 (d, J = 6.9 Hz, 2H), 7.40–7.33 (m, 3H), 4.27 (q, J = 7.1 Hz, 2H), 3.89 (s, 2H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.1, 142.1, 134.9, 129.7, 129.1 (2C), 128.8, 128.3 (2C), 61.4, 36.8, 14.4; HRMS (ESI) calculated for C$_{24}$H$_{27}$O$_4$S$_2$ [M + H]$^+$: m/z 443.1334, found 443.1351.

Allyl disulfane 6k

Prepared according to **GP2** using **3nb** (300.8 mg, 0.8 mmol) with Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) to afford **6k** (96.5 mg, 35%) using 30% ethyl acetate/petether as a pale-yellow liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (s, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.50–7.43 (m, 2H), 7.39–7.33 (m, 3H), 7.26 (d, J = 8.0 Hz, 2H), 4.48 (s, 2H), 4.07 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.7, 146.0, 144.8, 136.5, 133.9, 129.7 (2C), 129.6, 129.3 (2C), 128.8 (2C), 128.7 (2C), 121.6, 61.7, 55.2, 21.7, 14.2; HRMS (ESI) calculated for C$_{19}$H$_{20}$O$_2$S$_2$Na [M + Na]$^+$: m/z 367.0980, found 367.0981.

Conclusions

We have successfully developed a convenient protocol for the synthesis of allyl thiosulfonates. A range of aryl/heteroaryl/aliphatic allyl bromides and sodium arylthiosulfonates were readily assembled to furnish allyl thiosulfonates. Cs$_2$CO$_3$ serves as an efficient reagent for the synthesis of diallyl disulfanes and allyl disulfanes in moderate to high yields under mild reaction conditions. The present methodologies are operationally simple, tolerate a broad range of functional groups and are also reliable in a gram scale reaction for the synthesis of thiosulfonates.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 Leading reviews: (a) C. Ni, M. Hu and J. Hu, *Chem. Rev.*, 2015, **115**, 765; (b) J. E. M. D. McReynolds, J. M. Dougherty and P. R. Hanson, *Chem. Rev.*, 2004, **104**, 2239; (c) *Organosulfur Chemistry I & II*, ed. P. C. B. Page, Springer, Berlin, 1999.

2 Review articles: (a) C.-F. Lee, R. S. Basha and S. S. Badsara, *Top. Curr. Chem.*, 2018, **376**, 25; (b) K. L. Dunbar, D. H. Scharf, A. Litomska and C. Hertweck, *Chem. Rev.*, 2017, **117**, 5521; (c) X.-H. Xu, K. Matsuzaki and N. Shibata, *Chem. Rev.*, 2015, **115**, 731; (d) C.-F. Lee, Y.-C. Liu and S. S. Badsara, *Chem.–Asian J.*, 2014, **9**, 706; (e) H. Liu and X. Jiang, *Chem.–Asian J.*, 2013, **8**, 2546.

3 (a) P. K. Shyam and H.-Y. Jang, *J. Org. Chem.*, 2017, **82**, 1761; (b) K. Kanemoto, Y. Sugimura, S. Shimizu, S. Yoshida and T. Hosoya, *Chem. Commun.*, 2017, **53**, 10640; (c) W. Wang, X. Peng, F. Wei, C.-H. Tung and Z. Xu, *Angew. Chem., Int. Ed.*, 2016, **55**, 649; (d) S. Yoshida, Y. Sugimura, Y. Hazama, Y. Nishiyama, T. Yano, S. Shimizu and T. Hosoya, *Chem. Commun.*, 2015, **51**, 16613; (e) P. Mampuys, Y. Zhu, T. Vlaar, E. Ruijter, R. V. A. Orru and B. U. W. Maes, *Angew. Chem., Int. Ed.*, 2014, **53**, 12849.

4 Recent examples: (a) Y. Yu, Y. Zhou, Z. Song and G. Liang, *Org. Biomol. Chem.*, 2018, **16**, 4958; (b) F. Xiao, D. Wang, S. Yuan, H. Huang and G.-J. Deng, *RSC Adv.*, 2018, **8**, 23319; (c) Y. Siddaraju and K. R. Prabhu, *Org. Biomol. Chem.*, 2017, **15**, 5191; (d) P. Singh, R. Bai, R. Choudhary, M. C. Sharma and S. S. Badsara, *RSC Adv.*, 2017, **7**, 30594; (e) J. Sun, D. Zhang-Negrerie and Y. Du, *Adv. Synth. Catal.*, 2016, **358**, 2035; (f) S.-r. Guo, Y.-q. Yuan and J.-n. Xiang, *Org. Lett.*, 2013, **15**, 4654.

5 (a) N. S. Zefirof, N. V. Zyk, E. K. Beloglazkina and A. G. Kutateladze, *Sulfur Rep.*, 1993, **14**, 223; (b) J. P. Weidner and S. S. Block, *J. Med. Chem.*, 1964, **7**, 671.

6 Synthesis of thiosulfonates from disulfides and thiols oxidation, see: (a) P. K. Shyam, Y. K. Kim, C. Lee and H.-Y. Jang, *Adv. Synth. Catal.*, 2016, **358**, 56; (b) P. Natarajan, *Tetrahedron Lett.*, 2015, **56**, 4131; (c) T. X. T. Luu, T.-T. T. Nguyen, T. N. Le, J. Spanget-Larsen and F. Duus, *J. Sulfur Chem.*, 2015, **36**, 340; (d) M. Kirihara, S. Naito, Y. Nishimura, Y. Ishizuka, T. Iwai, H. Takeuchi, T. Ogata, H. Hanai, Y. Kinoshita, M. Kishida, K. Yamazaki, T. Noguchi and S. Yamashoji, *Tetrahedron*, 2014, **70**, 2464.

7 Recent reports for thiosulfonates from sulfinate salts, see: (a) N. Taniguchi, *J. Org. Chem.*, 2015, **80**, 1764; (b) N. Taniguchi, *Eur. J. Org. Chem.*, 2014, 5691; (c) G. Liang, M. Liu, J. Chen, J. Ding, W. Gao and H. Wu, *Chin. J. Chem.*, 2012, **30**, 1611; (d) G. Liang, J. Chen, J. Chen, W. Li, J. Chen and H. Wu, *Tetrahedron Lett.*, 2012, **53**, 6768.

8 Recent examples using sulfonyl chlorides and hydrazines, see: (a) Z. Peng, X. Zheng, Y. Zhang, D. An and W. Dong, *Green Chem.*, 2018, **20**, 1760; (b) Q. Chen, Y. Huang, X. Wang, J. Wu and G. Yu, *Org. Biomol. Chem.*, 2018, **16**, 1713; (c) G.-Y. Zhang, S.-S. Lv, A. Shoberu and J.-P. Zou, *J. Org. Chem.*, 2017, **82**, 9801; (d) X. Zhao, T.-X. Liu and G. Zhang, *Asian J. Org. Chem.*, 2017, **6**, 677; (e) Y. Zheng, F.-L. Qing, Y. Huang and X.-H. Xu, *Adv. Synth. Catal.*, 2016, **358**, 3377.

9 (a) M. Musiejuk, J. Doroszuk and D. Witt, *RSC Adv.*, 2018, **8**, 9718; (b) M. Salvadl, B. Amgarten, S. Castillln, G. J. L. Bernardes and O. Boutureira, *Org. Lett.*, 2015, **17**, 2836; (c) D. P. Gamblin, P. Garnier, S. J. Ward, N. J. Oldham, A. J. Fairbanks and B. G. Davis, *Org. Biomol. Chem.*, 2003, **1**, 3642; (d) S. Takano, K. Hiroya and K. Ogasawara, *Chem. Lett.*, 1983, 255; (e) A. P. Kozikowskif, A. Ames and H. Wetter, *J. Organomet. Chem.*, 1979, **164**, C33 and also see ref. 3b.

10 (a) E. Block, *Angew. Chem., Int. Ed.*, 1992, **31**, 1135; (b) S. Wang and H. Kohn, *J. Med. Chem.*, 1999, **42**, 788; (c) T. T. Conway, E. G. DeMaster, D. J. W. Goon, F. N. Shirota and H. T. Nagasawa, *J. Med. Chem.*, 1999, **42**, 4016; (d) C. Wright and R. D. Moore, *Am. J. Med.*, 1990, **88**, 647; (e) S. A. Caldarelli, M. Hamel, J.-F. Duckert, M. Ouattara, M. Calas, M. Maynadier, S. Wein, C. Périgaud, A. Pellet, H. J. Vial and S. Peyrottes, *J. Med. Chem.*, 2012, **55**, 4619.

11 (a) M. Song, J.-S. Kim, L. Liu, M. Husain and A. Vázquez-Torres, *Cell Rep.*, 2016, **14**, 2901; (b) T. Ilani, A. Alon, I. Grossman, B. Horowitz, E. Kartvelishvily, S. R. Cohen and D. Fass, *Science*, 2013, **341**, 74; (c) J. Alegre-Cebollada, P. Kosuri, J. A. Rivas-Pardo and J. M. Fernández, *Nat. Chem.*, 2011, **3**, 882; (d) M. Góngora-Benítez, J. Tulla-Puche and F. Albericio, *Chem. Rev.*, 2014, **114**, 901.

12 (a) B. Mandal and B. Basu, *RSC Adv.*, 2014, **4**, 13854 and references herein; (b) T. M. Postma and F. Albericio, *Eur. J. Org. Chem.*, 2014, 3519.

13 Selected reviews on MBH reaction, see: (a) K. Kaur and I. N. N. Namboothiri, *Chimia*, 2012, **66**, 913; (b) D. Basavaiah, B. S. Reddy and B. S. Badsara, *Chem. Rev.*, 2010, **110**, 5447; (c) V. Declerck, J. Martinez and F. Lamaty, *Chem. Rev.*, 2009, **109**, 1; (d) V. Singh and S. Batra, *Tetrahedron*, 2008, **64**, 4511; (e) D. Basavaiah, K. V. Rao and R. J. Reddy, *Chem. Soc. Rev.*, 2007, **36**, 1581.

14 Synthesis of sodium thiosulfonates, (a) R. Sato, T. Goto, Y. Takikawa and S. Takizawa, *Synthesis*, 1980, 615; (b) A. J Fischmanna and L. Spiccia, *Dalton Trans.*, 2011, **40**, 12310.

15 (a) R. J. Reddy, Md. Waheed, T. Karthik and A. Shankar, *New J. Chem.*, 2018, **42**, 980; (b) R. J. Reddy, A. Shankar, M. Waheed and J. B. Nanubolu, *Tetrahedron Lett.*, 2018, **59**, 2014.

16 The regioselectivities of thiosulfonates based on the corresponding MBH allyl bromides (as a mixture of *E* and *Z* isomers), see: D. Basavaiah, K. R. Reddy and N. Kumaragurubaran, *Nat. Protoc.*, 2007, **2**, 2665.

17 (*a*) M. J. Cha, Y. S. Song, E.-G. Han and K.-J. Lee, *J. Heterocycl. Chem.*, 2008, **45**, 235; (*b*) M. J. Cha, Y. S. Song and K.-J. Lee, *Bull. Korean Chem. Soc.*, 2006, **27**, 1900.

18 X. Xiao, M. Feng and X. Jiang, *Angew. Chem., Int. Ed.*, 2016, **55**, 14121.