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Graphical Abstract

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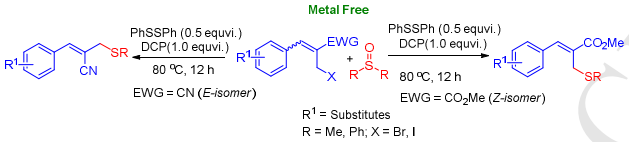

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Metal-free, regio- and stereoselective *S*-methylation/phenylation of allyl halides using sulfoxides as sulfenylating agent

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ABSTRACT

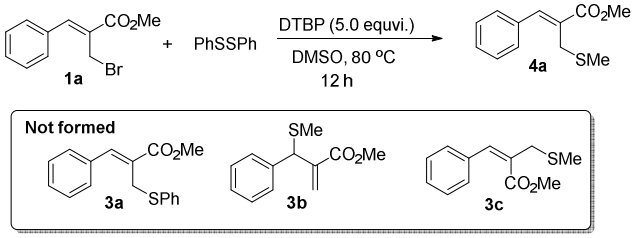
A DCP promoted metal-free, regio and stereoselective *S*-methylation/phenylation of allyl halides using sulfoxides as sulfenylating agent is described. A variety of multifunctional allyl halides underwent *S*-methylation and *S*-phenylation by using dimethyl sulfoxide (DMSO) and diphenyl sulfoxide (DPSO) under the reaction conditions employed to provide the resulting thioethers in good to excellent yields.

1. Introduction

Due to their important multidimensional applications in organic synthesis, pharmaceutical industry and materials science, development of synthetic routes for the synthesis of aryl thioethers have gained much attention in recent years.[1,2] Traditionally, the syntheses of thioethers have been carried out *via* transition-metal-catalyzed C-S bond coupling reaction of thiols with aryl halides and pseudo halides.[1a-c,3] Various transition metals such as Pd,[4a-d] Cu,[4e-g] Ni,[4h,4i] Fe,[4j,4k] In,[4l] Co,[4m] Au,[4n] Mg,[4o] Ag[4p] *etc*. so far shown their catalytic efficiency in the C-S cross coupling reactions. Due to environmental concerns and cost issues, presently beside metal catalysis, metal-free C-S bond-formation processes have received much attention.[5]

Being simple, cheap, and easy-to-handle, recently DMSO emerged as a sustainable methylthiolation reagent.[6] Various transition metal catalytic systems such as $Cu(OAc)_2$,[6a] CuF_2-$K_2S_2O_8$,[6b] AgF-$Cu(OAc)_2$,[6c] CuBr/CuI-ZnF_2[6d] have been so far used for the preparation of aryl methyl thioethers using DMSO as a methylthiolation agent. However, these protocols often required harsh reaction conditions and use of transition metals. Very recently, DMSO has been used as a sulfenylating agent for methylthiolation of alcohol containing indoles,[7a] in the synthesis of 3-methylthiofurans from homopropargylic alcohols[7b] and in methylthiolation of arylamines.[7c]

During our attempts towards the development of metal free C-S bond formations between allyl bromide derivatives **1a** and diphenyl disulfide, we obtained unexpected and unprecedented results. The C-S coupling reaction of **1a** and diphenyl disulfide under the influence of di-*tert*-butyl peroxide (DTBP) using DMSO (**2a**) as a solvent could not yield into the desired allyl phenyl thioether **3a** instead allyl methyl thioether **4a** was obtained in 90% yield as shown in Scheme 1 (Table 1, entry 1). Furthermore, it is important to note that a complete retention in stereochemistry across the double bond was observed in the product. The other possible products **3b** and **3c** were also not obtained. Best of our knowledge,[7d] no example for the preparation of allyl methyl thioethers in this fashion has appeared so far. Intrigued by this interesting observation, we decided to optimize the reaction conditions for methylthiolation of allyl halides and herein report the metal-free, regio- and stereoselective, peroxide promoted synthesis of allyl methyl/phenyl thioethers by using sulfoxides as methyl or phenylthiolation reagent for the first time.



Scheme 1. *S*-Methylation of allyl bromide **1a** showing the possible products.

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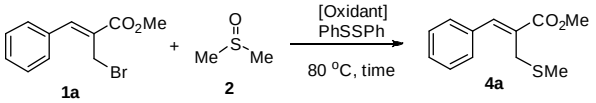
2. Results and Discussion

For optimization, we have selected the allyl bromide **1a** as model substrate and treated it with diphenyl disulfide under the influence of various oxidants using DMSO (**2a**) as solvent at 80 ^{o}C for 12 h (Table 1). As mentioned earlier, the DTBP provided the allylmethyl thioether **4a** in 90% yield (Table 1, entry 1). Other oxidants such as H_2O_2, TBHP, BPO couldn't provide encouraging results (Table 1, entries 2-4) whereas $K_2S_2O_8$ and TBPB provided **4a** in 86% and 30% yield respectively (Table 1, entries 5 & 6). 5.0 equivalent of DCP provided the thioether **4a** in 80% yield (Table 1, entry 7). Interestingly, deduction in the amount of DCP from 5.0 to 1.0 equivalent provided the best result with 96% yield of thioether **4a** (Table 1, entry 8). When the reaction was carried out at room temperature no product formation was observed, although DMSO got converted into dimethyl disulfide which was confirmed by GCMS (Table 1, entry 9). Similarly, no desired product **4a** was formed in absence of diphenyl disulfide (Table 1, entry 10). It was found that higher reaction temperature (Table 1, entry 11) and lower amount of DMSO (Table 1, entry 12) diminished the yield of the product.

Table 1. Optimization of the reaction conditions[a]



Entry	Oxidant (equiv.)	Time (h)	Yield (%)[b]
1	DTBP (5.0)	12	90
2	H_2O_2 (5.0)	24	N.R.
3[c]	TBHP (5.0)	24	N.R.
4	BPO (5.0)	24	N. R.
5	$K_2S_2O_8$ (5.0)	24	86
6	TBPB (5.0)	24	30
7	DCP (5.0)	12	80
8	**DCP (1.0)**	**12**	**96**
9[d]	DCP (1.0)	12	N.R.
10[e]	DCP (1.0)	12	N.R.
11[f]	DCP (1.0)	12	90
12[g]	DCP (1.0)	12	94

[a] Reaction conditions: Allyl bromide **1a** (2.0 mmol), diphenyl disulfide (1.0 mmol) and oxidant were reacted in DMSO (2.0 mL) at 80 ^{o}C.

[b] Isolated yields are based on **1a**.

[c] TBHP solution in water.

[d] Room temperature.

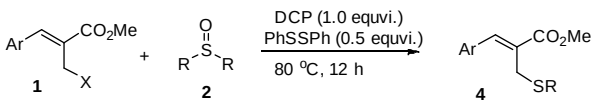
[e] Without phenyl disulfide.

[f] 120 ^{o}C.

[g] 1.0 mL DMSO was used. (DTBP = di-*tert*-butyl peroxide, TBHP = *tert*-butyl hydroperoxide, TBPB = *tert*-Butyl peroxybenzoate, BPO = benzoyl peroxide, DCP = dicumyl peroxide).

Once, we have optimized conditions in hand, we then turned our attention towards the study of substrate scope for this fascinating methodology. For this, various allyl bromides/allyl iodides derivatives (**1** & **5**) were synthesized from the Baylis-Hillman alcohols following the literature procedures.[8a,8b] Firstly, the allyl bromides (**1b**-**1e**) possessing ester functionality with *Z*-stereochemistry were employed for *S*-methylation using phenyl disulfide and DMSO (**2a**) reagent system under the influence of DCP following the optimized reaction conditions which provided the desired product **4b**-**e** in 82-91% yields (Table 2, entries 1-4). Similarly, allyl bromide **1a**-**b**,**e** reacted with phenyl disulfide and DPSO (**2b**) reagent system in presence of DCP to provide allyl phenyl thioethers **4f**-**h** in 85-88% yield (Table 2, entries 5-7). In all these reactions complete retention in stero-chemistry *i.e. Z*-stereochemistry was found. However, the allyl bromide **1f** could not provide the desired product (Table 2, entries 8 & 9). Furthermore, it was observed that the allyl bromides provided the superior results than that of allyl iodides (Table 2, entries 10-14).

Table 2. Syntheses of thioethers **4** containing ester functionality[a]



X = Br (**1a**-**f**); I (**1g**-**i**)

Entry	Ar	R	Product	Yield (%)[b]
1	4-MePh (**1b**)	Me	**4b**	88
2	4-OMePh (**1c**)	Me	**4c**	82
3	3-ClPh (**1d**)	Me	**4d**	91
4	4-ClPh (**1e**)	Me	**4e**	90
5	Ph (**1a**)	Ph	**4f**	88
6	4-MePh (**1b**)	Ph	**4g**	86
7	4-ClPh (**1e**)	Ph	**4h**	85
8	2-NO_2Ph (**1f**)	Me	-	N.R.
9	2-NO_2Ph (**1f**)	Ph	-	N.R.
10[c]	4-ClPh (**1g**)	Me	**4e**	55
11[c]	4-ClPh (**1g**)	Ph	**4h**	51
12[c]	Ph (**1h**)	Me	**4a**	68
13[c]	Ph (**1h**)	Ph	**4f**	62
14[c]	4-MePh (**1i**)	Ph	**4g**	65

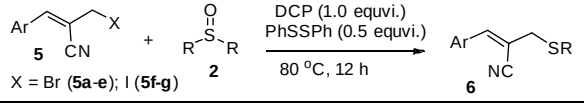
[a] Reaction conditions: Allyl bromides/iodides **1** (2.0 mmol), diphenyl disulfide (1.0 mmol) and DCP (2.0 mmol) were reacted in DMSO (2.0 mL) or DPSO (1.0 g) at 80 ^{o}C for 12 h.

[b] Isolated yields of **4** are based on allyl bromides/iodides **1**.

[c] Instead of allyl bromide, iodide was used.

Next, we have employed the allyl bromides/ iodides **5a-g** possessing nitrile functionality with *E*-stereochemistry for *S*-methylation using phenyl disulfide and DMSO (**2a**) under the influence of DCP following the optimized conditions which provided resulting thioethers **6a-e** in 48-91% yields with complete retention in stereochemistry across the double bond *i.e. E*-stereochemistry (Table 3, entries 1-5 & 8-10). Notably, replacement of DMSO (**2a**) with DPSO (**2b**) in these reactions provided the allyl phenyl thioethers **6f-g** in 79-82% yield with retention in stereochemistry around the double bond (Table 3, entries 6-7, 10). In this case also bromides provided the superior results than that of iodides (Table 3, entries 8-10).

Table 3 Syntheses of thioethers **6** containing nitrile functionality[a]



X = Br (**5a**-**e**); I (**5f**-**g**)

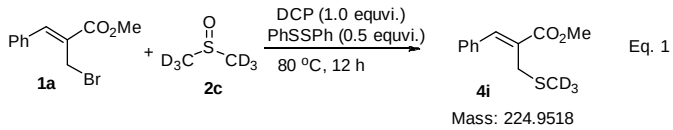
Entry	Ar	R	Product	Yield (%)[b]
1	Ph (**5a**)	Me	**6a**	88
2	4-MePh (**5b**)	Me	**6b**	88
3	2-BrPh (**5c**)	Me	**6c**	82
4	3-ClPh (**5d**)	Me	**6d**	91
5	4-ClPh (**5e**)	Me	**6e**	88
6	Ph (**5a**)	Ph	**6f**	82
7	4-MePh (**5b**)	Ph	**6g**	79
8[c]	Ph (**5f**)	Me	**6a**	52
9[c]	4-MePh (**5g**)	Me	**6b**	48
10[c]	4-MePh (**5g**)	Ph	**6g**	41

[a] Reaction conditions: Allyl bromides/iodides **5** (2.0 mmol), diphenyl disulfide (1.0 mmol) and DCP (2.0 mmol) were reacted in DMSO (2.0 mL) or DPSO (1.0 g) at 80 ^{o}C for 12 h.

[b] Isolated yields of **6** are based on allyl bromides/iodides **5**.

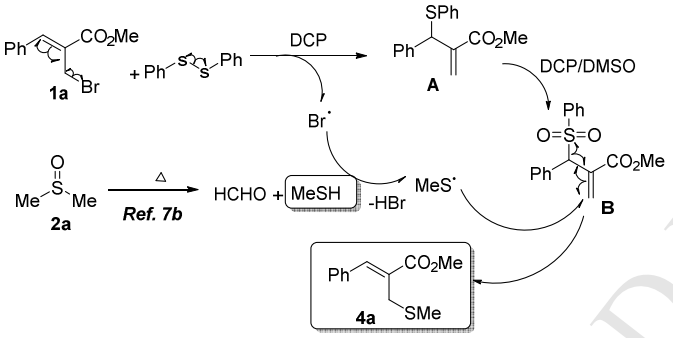
[c] Instead of allyl bromide, iodide was used.

To find out the source of SMe group for these reactions, we have carried out the reaction between allyl bromide **1a** with phenyl disulfide and DMSO-d_6 under the influence of DCP following the optimized conditions which provided the deuterated thioether **4i** confirmed by HRMS data analysis hence, proved the DMSO as a source of *S*-methylation (Eq. 1).



Eq. 1

A plausible mechanism for obtaining allyl methyl thioethers is presented in Scheme 2 taking **4a** as a model case. Initially, in presence of oxidant, the phenyl disulfide generated phenyl sulfide radical which then coupled with allyl radical (generated from allyl bromide **1a**) to provide the thioether **A**. The thioether **A** then instantly may get oxidized by DCP and DMSO into sulfone **B**. Meanwhile, on heating, the DMSO generated MeSH and HCHO.[7b] The bromide radical can generate methyl sulfide radical. Since, the sulfones are reasonably good leaving group[9] the methyl sulfide radical may substitute it to provide the desired allyl methyl thioether **4a.**



Scheme 2. Plausible mechanism for synthesis of thioethers **4a**

3. Conclusions

In conclusions, we have developed the metal free unexpected and unprecedented regio- and stereoselective synthesis of allyl methyl and allyl phenyl thioethers from allyl halides *via* the C-S coupling reaction using sulfoxides as a sulfenylating agent for the first time. In presence of phenyl disulfide and DCP, the DMSO and DPSO resulted into *in-situ* formation of SMe and SPh group respectively which underwent the C-S bond formation with allyl halides to provide the thioethers in good to excellent yields. During the reactions the stereochemistry around the double bond found unchanged. Both the allyl bromides and iodides were employed for this fascinating reactions and allyl bromides provided the superior results over iodides.

4. Experimental section

4.1. General remarks

All chemicals were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on a JEOL Ressonanc-400 instrument using $CDCl_3$/DMSO-d_6 as solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constant (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet. HRMS data were collected on Waters - Xevo G2S QTof with UPLC H-Class Ultra Performance Liquid chromatography - mass spectrometry (LC-MS) facility. GCMS data were collected on Thermo Scientific "TSQ 8000" Triple quadrupole GC-MS-MS System with Pyrolyzer facility.

4.2. General procedure for Table 1:

Synthesis of methyl (Z)-2-((methylthio)methyl)-3-phenylacrylate (entry 8, **4a**)*.*[10] To a stirred solution of allyl bromide **1a** *i.e.* methyl (2*Z*)-2-bromomethyl-3-phenylprop-2-enoate (2.0 mmol, 0.510 g) and diphenyl disulfide (1.0 mmol, 0.218 g) in DMSO (2.0 mL) was added oxidant and then the reaction mixture was stirred for 80 °C under nitrogen atmosphere. The reaction mixture was then diluted with EtOAc (10 mL) and water (5.0 mL). After usual workup, the organic layer was dried over anhydrous Na_2SO_4, solvent was evaporated and the crude product thus obtained was purified by column chromatography (silica gel, 2% EtOAc in Hexanes) to provide the thioether **4a** as pale yellow color oil. Yield: 0.426 g, 96%; Rf (6% EtOAc/hexanes) 0.31; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 3 H), 3.62 (s, 2 H), 3.83 (s, 3 H), 7.32-7.41 (m, 3 H), 7.47 (d, *J* = 7.6 Hz, 2 H), 7.75 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.3, 30.6, 52.3, 128.7, 128.9, 129.4, 129.6, 135.0, 140.7, 168.0.

4.3. General procedure for Table 2:

To a stirred solution of allyl bromide **1** (2.0 mmol) and diphenyl disulfide (1.0 mmol, 0.218 g) in DMSO (2.0 mL) or DPSO (1.0 g) was added DCP (2.0 mmol, 0.540 g) and then the reaction mixture was stirred for 12 h at 80 °C under nitrogen atmosphere. The reaction mixture was then diluted with ethyl acetate (10 mL) and water (5.0 mL). After usual workup the organic layer was dried over anhydrous Na_2SO_4, solvent was evaporated and the crude product thus obtained was purified by column chromatography (silica gel, 1 or 2% EtOAc in hexanes) to provide the thioether **4**.

*4.3.1. Synthesis of methyl (Z)-2-((methylthio)methyl)-3-(p-tolyl)*acrylate (*entry 1,* ***4b***). The title compound was prepared following the general procedure for Table 2, using allyl bromide **1b** *i.e.* methyl (2*Z*)-2-bromomethyl-3-(4-methylphenyl)prop-2-enoate (2.0 mmol, 0.538 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **4b** as pale yellow oil. Yield: 0.415 g, 88%; Rf (6% EtOAc/hexanes) 0.28; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10 (s, 3 H), 2.35 (s, 3 H), 3.64 (s, 2 H), 3.82 (s, 3 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.39 (d, *J* = 8.0 Hz, 2 H), 7.73 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.2, 21.4, 30.6, 52.2, 128.4, 129.4, 129.8, 132.2, 139.2, 140.8, 168.1; HRMS (ESI) exact mass calcd for $C_{13}H_{16}O_2S$ + K (M + K), 275.0508; Found: 275.0501.

4.3.2. Synthesis of methyl (Z)-3-(4-methoxyphenyl)-2-((methylthio)methyl)acrylate (entry 2, ***4c****).* The title compound was prepared following the general procedure for Table 2, using allyl bromide **1c** *i.e.* methyl (*Z*)-2-(bromomethyl)-3-(4-methoxyphenyl)acrylate (2.0 mmol, 0.570 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **4c** as pale yellow oil. Yield: 0.413 g, 82%; Rf (6% EtOAc/hexanes) 0.19; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3 H), 3.60 (s, 2 H), 3.75 (s, 3 H), 3.76 (s, 3 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 8.8 Hz, 2 H), 7.65 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.2, 30.7, 52.2, 114.1, 126.8, 127.4, 131.7, 140.7, 160.3, 168.2; HRMS (ESI) exact mass calcd for $C_{13}H_{16}O_3S$ + K (M + K), 291.0457; Found: 291.0462.

4.3.3. Synthesis of methyl (Z)-3-(3-chlorophenyl)-2-((methylthio)methyl)acrylate (entry 3, ***4d****).* The title compound was prepared following the general procedure for Table 2, using

allyl bromide **1d** *i.e.* methyl (*Z*)-2-(bromomethyl)-3-(3-chlorophenyl)acrylate (2.0 mmol, 0.579 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **4d** as pale yellow oil. Yield: 0.467 g, 91%; Rf (6% EtOAc/hexanes) 0.25; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3 H), 3.55 (s, 2 H), 3.81 (s, 3 H), 7.28-7.32 (m, 3 H), 7.44 (s, 1 H), 7.63 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.3, 29.7, 52.4, 127.6, 128.9, 129.5, 129.9, 130.7, 134.6, 136.8, 138.9, 167.1; HRMS (ESI) exact mass calcd for $C_{12}H_{13}ClO_2S$ + K (M + K), 294.9962; Found: 294.9952.

*4.3.4. Synthesis of methyl (Z)-3-(4-chlorophenyl)-2-((methylthio)methyl)acrylate (entry 4, **4e**).* The title compound was prepared following the general procedure for Table 2, using allyl bromide **1e** *i.e.* methyl (*Z*)-2-(bromomethyl)-3-(4-chlorophenyl)acrylate (2.0 mmol, 0.579 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **4e** as pale yellow oil. Yield: 0.462 g, 90%; Rf (6% EtOAc/hexanes) 0.26; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.98 (s, 3 H), 3.51 (s, 2 H), 3.73 (s, 3 H), 7.43 (d, J = 8.8 Hz, 2 H), 7.51 (d, J = 8.8 Hz, 2 H), 7.59 (s, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 16.0, 30.4, 52.6, 129.2, 130.1, 131.8, 133.7, 134.4, 138.8, 167.4; HRMS (ESI) exact mass calcd for $C_{12}H_{13}ClO_2S$ + K (M + K), 294.9962; Found: 294.9956.

*4.3.5. Synthesis of methyl (Z)-3-phenyl-2-((phenylthio)methyl)acrylate (entry 5 , **4f**).* The title compound was prepared following the general procedure for Table 3, using allyl bromide **1a** *i.e.* methyl (*Z*)-2-(bromomethyl)-3-phenylacrylate (2.0 mmol, 0.510 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DPSO (1.0 g), providing **4f** as pale yellow oil. Yield: 0.500 g, 88%; Rf (6% EtOAc/hexanes) 0.26; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3 H), 4.05 (s, 2 H) 7.20-7.38 (m, 3 H), 7.40-7.42 (m, 7 H), 7.79 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.3, 52.3, 126.8, 128.2, 128.7, 129.0, 129.1, 129.6, 130.7, 134.8, 136.0, 141.6, 167.5; HRMS (ESI) exact mass calcd for $C_{17}H_{16}O_2S$ + K (M + K), 323.0508; Found: 323.0502.

4.3.6. Synthesis of methyl (*Z*)-2-((phenylthio)methyl)-3-(*p*-tolyl)acrylate (entry 6, ***4g**).* The title compound was prepared following the general procedure for Table 3, using allyl bromide **1b** *i.e.* methyl (*Z*)-2-(bromomethyl)-3-(*p*-tolyl)acrylate (2.0 mmol, 0.538 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DPSO (1.0 g), providing **4g** as pale yellow oil. Yield: 0.513 g, 86%; Rf (6% EtOAc/hexanes) 0.25; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3 H), 3.81 (s, 3 H), 4.09 (s, 2 H), 7.17-7.22 (m, 3 H), 7.25-7.29 (m, 2 H), 7.37-7.42 (m, 4 H), 7.80 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 32.3, 52.3, 126.7, 127.2, 129.0, 129.5, 129.8, 130.6, 132.0, 136.3, 139.4, 141.9, 167.8; HRMS (ESI) exact mass calcd for $C_{18}H_{18}O_2S$ + K (M + K), 337.0665; Found: 337.0661.

*4.3.7. Synthesis of methyl (Z)-3-(4-chlorophenyl)-2-((phenylthio)methyl)acrylate (entry 7, **4h**).* The title compound was prepared following the general procedure for Table 3, using allyl bromide **1e** *i.e.* methyl (*Z*)-2-(bromomethyl)-3-(4-chlorophenyl)acrylate (2.0 mmol, 0.579 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DPSO (1.0 g), providing **4h** as pale yellow oil. Yield: 0.527 g, 85%; Rf (6% EtOAc/hexanes) 0.23; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 3 H), 3.98 (s, 2 H), 7.20-7.28 (m, 3 H), 7.34 (m, 4 H), 7.34-7.36 (m, 2 H), 7.67 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.3, 52.4, 127.0, 128.8, 128.9, 129.0, 130.8, 131.1, 133.2, 135.0, 135.6, 140.1, 167.4; HRMS (ESI) exact mass calcd for $C_{17}H_{15}ClO_2S$ + K (M + K), 357.0118; Found: 357.0112.

*4.3.8. Synthesis of methyl (Z)-3-(4-chlorophenyl)-2-((methylthio)methyl)acrylate (entry 10, **4e**).* The title compound was prepared following the general procedure for Table 2, using allyl iodide **1g** *i.e.* methyl (*Z*)-3-(4-chlorophenyl)-2-(iodomethyl)acrylate (2.0 mmol, 0.673 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **4e** as pale yellow oil. Yield: 0.282 g, 55%. Spectral data were found same as entry 4.

*4.3.9. Synthesis of methyl (Z)-3-(4-chlorophenyl)-2-((phenylthio)methyl)acrylate (entry 11, **4h**).* The title compound was prepared following the general procedure for Table 3, using allyl iodide **1g** *i.e.* methyl (*Z*)-2-(iodomethyl)-3-(4-chlorophenyl)acrylate (2.0 mmol, 0.673 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DPSO (1.0 g), providing **4h** as pale yellow oil. Yield: 0.325 g, 51%; Spectral data were found same as entry 7.

*4.3.10. Synthesis of methyl (Z)-2-((methylthio)methyl)-3-phenylacrylate (entry 12, **4a**).*[10] The title compound was prepared following the general procedure for Table 3, using allyl iodide **1h** *i.e.* methyl (2*Z*)-2-bromomethyl-3-phenylprop-2-enoate (2.0 mmol, 0.604 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **4a** as pale yellow oil. Yield: 0.302 g, 68%. Spectral data were found same as Table 1.

*4.3.11. Synthesis of methyl (Z)-3-phenyl-2-((phenylthio)methyl)acrylate (entry 13 , **4f**).* The title compound was prepared following the general procedure for Table 3, using allyl iodide **1h** *i.e.* methyl (*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol, 0.604 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DPSO (1.0 g), providing **4f** as pale yellow oil. Yield: 0.352 g, 62%; Spectral data were found same as entry 5.

*4.3.12. Synthesis of methyl (Z)-2-((phenylthio)methyl)-3-(p-tolyl)acrylate (entry 14, **4g**).* The title compound was prepared following the general procedure for Table 3, using allyl iodide **1i** *i.e.* methyl (*Z*)-2-(iodomethyl)-3-(*p*-tolyl)acrylate (2.0 mmol, 0.632 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DPSO (1.0 g), providing **4g** as pale yellow oil. Yield: 0.382 g, 65%; Spectral data were found same as entry 6.

4.4. General procedure for Table 3:

To a stirred solution of allyl bromide **5** (2.0 mmol) and diphenyl disulfide (1.0 mmol, 0.218 g) in DMSO (2.0 mL) or DPSO (1.0 g) was added DCP (2.0 mmol, 0.540 g) and then the reaction mixture was stirred for 12 h at 80 ^{o}C under nitrogen atmosphere. The reaction mixture was then diluted with ethyl acetate (10 mL) and water (5.0 mL). After usual workup, the organic layer was dried over anhydrous Na_2SO_4, solvent was evaporated . The crude products thus obtained was purified by column chromatography (silica gel, 2% EtOAc in Hexanes) to provide the thioether **6**.

*4.4.1. Synthesis of (E)-2-((methylthio)methyl)-3-phenylacrylonitrile (entry 1, **6a**).* The title compound was prepared following the general procedure for Table 3, using allyl bromide **5a** *i.e.* (*E*)-2-(bromomethyl)-3-phenylacrylonitrile (2.0 mmol, 0.444 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **6a** as pale yellow oil. Yield: 0.332 g, 88%; Rf (6% EtOAc/hexanes) 0.14; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.09 (s, 3 H), 3.40 (s, 2 H), 6.97 (s, 1 H), 7.39-7.41 (m, 3 H), 7.73-7.76 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 29.8, 108.0, 118.2, 128.9, 129.0, 130.6,

133.0, 144.2; HRMS (ESI) exact mass calcd for $C_{11}H_{11}NS$ + K (M + K), 228.0249; Found: 228.0241.

*4.4.2. Synthesis of (E)-2-((methylthio)methyl)-3-(p-tolyl)acrylonitrile (entry 2, **6b**).* The title compound was prepared following the general procedure for Table 3, using allyl bromide **5b** *i.e.* (*E*)-2-(bromomethyl)-3-(*p*-tolyl)acrylonitrile (2.0 mmol, 0.472 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **6b** as pale yellow oil. Yield: 0.357 g, 88%; Rf (6% EtOAc/hexanes) 0.25; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3 H), 2.34 (s, 3 H), 3.36 (s, 2 H), 6.92 (s, 1 H), 7.19 (d, J = 8.4 Hz, 2 H), 7.65 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.8, 21.6, 29.8, 106.7, 118.4, 128.9, 129.7, 130.3, 141.0, 144.3, HRMS (ESI) exact mass calcd for $C_{12}H_{13}NS$ + K (M + K), 242.0406; Found: 242.0412.

*4.4.3. Synthesis of (E)-3-(2-bromophenyl)-2-((methylthio)methyl)acrylonitrile (entry 3, **6c**).* The title compound was prepared following the general procedure for Table 3, using allyl bromide **5c** *i.e.* (*E*)-2-(bromomethyl)-3-(2-bromophenyl)acrylonitrile (2.0 mmol, 0.601 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **6c** as pale yellow oil. Yield: 0.439 g, 82%; Rf (6% EtOAc/hexanes) 0.22; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10 (s, 3 H), 3.40 (s, 2 H), 7.20-7.22 (m, 2 H), 7.23-7.37 (m, 1 H), 7.58 (d, J = 7.2 Hz, 1 H), 7.87 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 38.7, 111.6, 117.3, 124.2, 127.9, 129.6, 131.5, 133.0, 133.5, 143.2; HRMS (ESI) exact mass calcd for $C_{11}H_{10}BrNS$ + K (M + K), 305.9354; Found: 305.9367.

*4.4.4. Synthesis of (E)-3-(3-chlorophenyl)-2-((methylthio)methyl)acrylonitrile (entry 4, **6d**).* The title compound was prepared following the general procedure for Table 3, using allyl bromide **5d** *i.e.* (E)-2-(bromomethyl)-3-(3-chlorophenyl)acrylonitrile (2.0 mmol, 0.513 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **6d** as pale yellow oil. Yield: 0.405 g, 91%; Rf (6% EtOAc/hexanes) 0.21; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10 (s, 3 H), 3.40 (s, 2 H), 6.92 (s, 1H), 7.35-7.36 (m, 2 H), 7.65 (s, 1 H),7.68-7.70 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 39.2, 110.0, 117.6, 126.6, 128.5, 129.0, 130.5, 134.7, 134.9, 142.4; HRMS (ESI) exact mass calcd for $C_{11}H_{10}ClNS$ + K (M + K), 261.9860; Found: 261.9859.

*4.4.5. Synthesis of (E)-3-(4-chlorophenyl)-2-((methylthio)methyl)acrylonitrile (entry 5, **6e**).* The title compound was prepared following the general procedure for Table 3, using allyl bromide **5e** *i.e.* ((*E*)-2-(bromomethyl)-3-(4-chlorophenyl)acrylonitrile (2.0 mmol, 0.513 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **6e** as pale yellow oil. Yield: 0.402 g, 88%; Rf (6% EtOAc/hexanes) 0.20; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3 H), 3.35 (s, 2 H), 6.88 (s, 1 H), 7.30 (d, J = 8.8 Hz, 2 H), 7.63 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 29.7, 108.8, 117.9, 129.1, 130.1, 131.5, 136.3, 142.6; HRMS (ESI) exact mass calcd for $C_{11}H_{10}ClNS$ + K (M + K), 261.9860; Found: 261.9851.

*4.4.6. Synthesis of (E)-3-phenyl-2-((phenylthio)methyl)acrylonitrile (entry 6, **6f**).* The title compound was prepared following the general procedure for Table 3, using allyl bromide **5a** *i.e.* (*E*)-2-(bromomethyl)-3-phenylacrylonitrile (2.0 mmol, 0.444 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DPSO (1.0 g), providing **6f** as pale yellow oil. Yield: 0.414 g, 82%; Rf (6% EtOAc/hexanes) 0.19; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 2 H), 6.65 (s, 1 H), 7.27-7.35 (m, 6 H), 7.44-7.46 (m, 2 H), 7.58-7.59 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.1, 107.7, 118.2, 128.1, 128.8, 128.9, 129.3, 130.5, 132.9, 133.1, 133.5, 144.9; HRMS (ESI) exact mass calcd for $C_{16}H_{13}NS$ + K (M + K), 290.0406; Found: 290.0409.

*4.4.7. Synthesis of (E)-2-((phenylthio)methyl)-3-(p-tolyl)acrylonitrile (entry 7, **6g**).* The title compound was prepared following the general procedure for Table 3, using allyl bromide **5b** *i.e.* (*E*)-2-(bromomethyl)-3-(*p*-tolyl)acrylonitrile (2.0 mmol, 0.472 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DPSO (1.0 g), providing **6g** as pale yellow oil. Yield: 0.420 g, 79%; Rf (6% EtOAc/hexanes) 0.21; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3 H), 4.19 (s, 2 H), 7.15 (s, 1 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.26-7.46 (m, 5 H), 7.68 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 33.4, 106.6, 117.5, 125.7, 126.9, 128.0, 129.4, 129.8, 142.2, 146.7; HRMS (ESI) exact mass calcd for $C_{17}H_{15}NS$ + K (M + K), 304.0562; Found: 304.0556.

*4.4.8. Synthesis of (E)-2-((methylthio)methyl)-3-phenylacrylonitrile (entry 8, **6a**).* The title compound was prepared following the general procedure for Table 3, using allyl iodide **5f** *i.e.* (*E*)-2-(iodomethyl)-3-phenylacrylonitrile (2.0 mmol, 0.538 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **6a** as pale yellow oil. Yield: 0.196 g, 52%; Spectral data were found same as entry 1.

*4.4.9. Synthesis of (E)-2-((methylthio)methyl)-3-(p-tolyl)acrylonitrile (entry 9, **6b**).* The title compound was prepared following the general procedure for Table 3, using allyl iodide **5g** *i.e.* (*E*)-2-(iodomethyl)-3-(*p*-tolyl)acrylonitrile (2.0 mmol, 0.566 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol, 0.540 g) and DMSO (2.0 mL), providing **6b** as pale yellow oil. Yield: 0.194 g, 48%; Spectral data were found same as entry 2.

*4.4.10. Synthesis of (E)-2-((phenylthio)methyl)-3-(p-tolyl)acrylonitrile (entry 10, **6g**).* The title compound was prepared following the general procedure for Table 3, using allyl iodide **5g** *i.e.* (*E*)-2-(iodomethyl)-3-(*p*-tolyl)acrylonitrile (2.0 mmol, 0.566 g), diphenyl disulfide (1.0 mmol, 0.218 g), DCP (2.0 mmol) and DPSO (1.0 g), providing **6g** as pale yellow oil. Yield: 0.217g, 41%; Spectral data were found same as entry 7.

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