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Regio- and stereoselective syntheses of allylic thioethers under metal free conditions†

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A metal free, regio and stereoselective syntheses of allylic thioethers using allyl iodides and aryl or alkyl disulfides as coupling partners is described. The densely functionalized allyl iodides having different stereochemistry (*E* & *Z*) reacted well with a variety of disulfides in a regio and stereoselective manner providing the resulting allyl aryl thioethers in 62–92% yields.

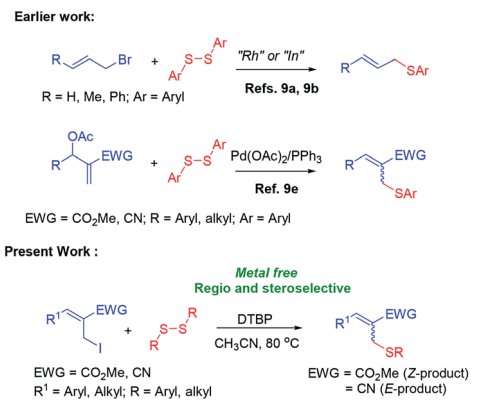
Introduction

Due to environmental concerns and cost issues, the metal-free organic transformations are in great need. Enough progress has been made in this direction by using various catalytic systems in recent years;[1] the peroxide alone or with additives has emerged as the perfect substitute to the traditional transition metal catalysis for several organic transformations.[2] Meanwhile, aryl thioethers have been found to play important roles in organic synthesis, the pharmaceutical industry and materials science.[3,4] Various transition metals such as Pd,[5a–d] Cu,[5e–g] Fe,[5h,i] Ni,[5j,k] In,[5l] Co,[5m] Au,[5n] Ag,[5o] Mg[5p] *etc.* have been used so far for the syntheses of thioethers *via* C–S bond formation between aryl halides or pseudo halides and thiols.[6] Recently, the syntheses of aryl thioethers and thioesters have been reported under metal-free conditions *via* C–H functionalization using a variety of sulphur surrogates.[7,8] Various catalyst or catalytic systems such as DTBP,[7a,c,d,f,g] TBHP,[7h,i] $K_2S_2O_8$,[7j–l] AcOOH,[8c] *etc.* have been used so far for the syntheses of thioethers *via* C–H functionalization. In the case of syntheses of allyl aryl thioethers, various metals such as Rh,[9a] In,[9b] Co,[9c] Ni,[9d] *etc.* were used for the C–S coupling between allyl halides/acetates and disulfides (Scheme 1). A palladium acetate catalyzed synthesis of allyl aryl thioethers *via* cross-coupling reaction between Baylis–Hillman acetates and diphenyl disulfides was reported by Sreedhar and co-workers (Scheme 1).[9e] The syntheses of allyl aryl thioethers *via* the C–S bond formation between allyl halides and sulphur surrogate under metal free conditions is not well studied. Therefore, we have decided to find out suitable methodology for the synthesis of allylic thioethers and herein report the first regio- and stereoselective syntheses of allylic thioethers *via* C–S bond formation between densely functionalized allyl iodides and disulfides under metal free conditions (Scheme 2).

Results and discussion

Accordingly, we have selected the allyl iodide **1a** (2.0 mmol) and diphenyl disulfide **2a** (1.0 mmol) as model substrate and treated them under the influence of DCP (dicumyl peroxide, 10.0 mmol) using CH_3CN as solvent at 80 °C for 48 h. The data collection of isolated product revealed the formation of only allyl phenyl thioether **4a** in 42% yield (Table 1, entry 1). There was no formation of the thioethers **3a** and **3b** which were confirmed by GCMS of crude reaction mixture. It is to note here that complete retention in stereochemistry across the double bond was obtained in this reaction *i.e.* *Z*-selectivity.

Encouraged by these results, we decided to optimize the reaction conditions for this fascinating C–S bond formation strategy. Accordingly, a variety of oxidants were employed to catalyze the reaction between **1a** and **2a** (Table 1). Oxidant such as BPO (benzoyl peroxide), $K_2S_2O_8$ could not provide the encouraging results (entries 2 & 3). H_2O_2, TBHP (*tert*-butyl



Scheme 1 Syntheses of allylic thioethers.

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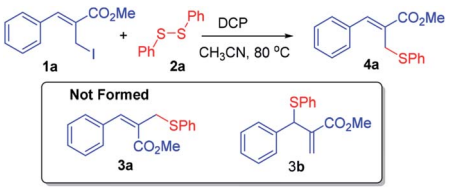
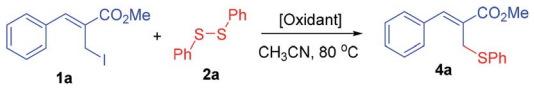


Scheme 2 Synthesis of allyl aryl thioethers **4a**.

Table 1 Optimization of the reaction conditions[a]



Entry	Oxidant (equiv.)	Time (h)	Yield[b] (%)
1	DCP (5.0)	12	42
2	BPO (5.0)	12	36
3	$K_2S_2O_8$ (5.0)	12	30
4	H_2O_2 (5.0)	12	51
5[c]	TBHP (5.0)	12	58
6	TBPB (5.0)	12	55
7	DTBP (5.0)	12	60
8	DTBP (5.0)	48	68
9[d]	**DTBP (5.0)**	**48**	**88**
10[e]	DTBP (5.0)	48	82
11[f]	DTBP (5.0)	48	76
12[g]	DTBP (2.0)	48	48

[a] Reaction conditions: allyl iodide **1a** (2.0 mmol), diphenyl disulfide **2a** (1.0 mmol) and oxidant (10.0 mmol) were reacted in CH_3CN (2.0 mL) at 80 °C for 12 h. [b] Isolated yields are based on **1a**. [c] TBHP solution in water. [d] 2.0 mmol of **2a** was used. [e] 120 °C. [f] 1.0 mL CH_3CN was used. [g] 2.0 equivalent of DTBP was used.

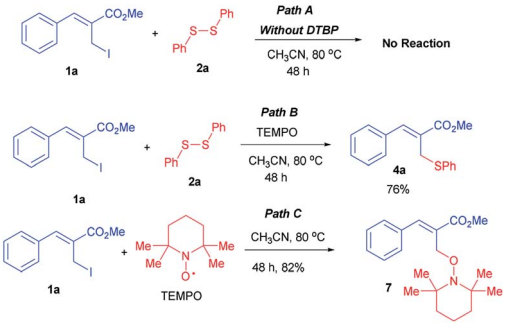
hydroperoxide) and TBPB (*tert*-butyl peroxybenzoate) provided slightly better results (entries 4–6). The DTBP (di-*tert*-butyl peroxide) provided the desired product in 60% yield after 12 h (entry 7). When the same reaction was carried out for 48 h under the influence of DTBP, provided the thioether **4a** in 68% yield (entry 8). Interestingly, when the amount of disulfide was doubled, thioether **4a** was obtained in 88% yield (entry 9). Enhancement in the reaction temperature could not increase the yield significantly (entry 10). Diminishing the CH_3CN and DTBP amounts were not found favourable for this coupling between **1a** and **2a** (entry 11 & 12).

Once we have optimized reaction conditions in hand (Table 1, entry 9), we then studied the substrate scope for this interesting C–S bond formation. Accordingly, a variety of allyl iodides **1** and **5** were synthesized from the Baylis–Hillman alcohols following the literature procedures.[10a,b] It is worth mentioning here that Baylis–Hillman adducts or their derivatives possessing ester functionality (obtained from alkyl acrylates) and nitrile functionality (obtained from acrylonitrile) be evidence for remarkable opposite stereochemical directions in various organic transformations.[10a,b,11] This effect of reversibility might be attributed to the steric difference between the nitrile (smaller) and ester (larger) functionalities. The alcohols possessing ester functionality provided the allyl iodides as *Z*-isomer[12] only whereas the alcohols possessing nitrile functionality provided allyl iodides as *E*-isomer. Therefore, *Z*-isomer of allyl iodides **1** and *E*-isomer of allyl iodide **5** was used as coupling partner for C–S bond formation with disulfides.

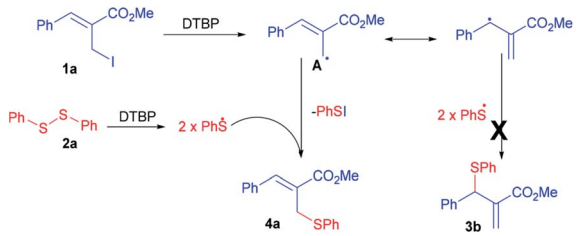
Firstly, the various allyl iodides possessing ester functionality with *Z* stereochemistry were treated with different disulfides **2** under the influence of DTBP following the optimized reaction conditions, provided the resulting allylic thioethers **4** in 62–85% isolated yields. The structures of these allylic thioethers **4** were determined from their spectral (^{1}H NMR, ^{13}C NMR and MS) data which suggested complete retention in stereochemistry across the double bond in the products *i.e. Z*-stereochemistry were observed (in ^{1}H NMR the olefinic proton appeared at δ 7.64–7.81 range confirm *Z*-stereochemistry).[10a,b,11] Allyl iodides possessing substitutes at *o*/*m*/*p*-position underwent regio- and stereo selective C–S coupling reaction with both aryl and alkyl disulfides to provide the desired allyl aryl thioethers (**4a–d** & **4f–r**) and allyl alkyl thioethers (**4e** & **4s–v**) in good to excellent yields. We have also employed the allyl iodides **1** (*E*-isomer) possessing alkyl group instead that of aryl group for the C–S bond formation with disulfides under the optimized reaction conditions, provided the desired allyl aryl thioethers **4w** and **4x** in 72% and 70% yields respectively. In these case also complete retention in stereochemistry across the double bond in the products *i.e. E*-stereochemistry were observed.[12]

Subsequently, we have employed the densely functionalized *E*-allyl iodides **5** possessing nitrile functionality for the C–S coupling with variety of disulfides **2** under the influence of DTBP following the optimized reaction conditions. Both the aryl and alkyl disulfide coupled well with allyl iodides **5** to provide the resulting allylic thioethers **6** in 72–92% yield. Substrates possessing substituent at *o*, *m*, *p* position of phenyl ring coupled well under the reaction conditions employed. The structures of these allylic thioethers **6** were determined from their spectral (^{1}H NMR, ^{13}C NMR and MS) data which suggest that a complete retention in stereochemistry across the double bond in the products *i.e. E*-stereochemistry were observed (in ^{1}H NMR the olefinic proton appeared at δ 6.47–6.76 range confirm *E*-stereochemistry).[10a,b,11]

To establish a possible reaction pathway for this methodology, we have performed few control experiments as shown in Scheme 3. Initially, we have performed the C–S coupling reaction between allyl iodide **1a** and disulfide **2a** in absence of DTBP



Scheme 3 Control experiments.



Scheme 4 Plausible mechanism for the synthesis of thioether **4a**.

under optimized reaction conditions and observed that no reaction took place (Path A, Scheme 3). Next, the same reaction was carried out in presence of TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) using optimized reaction conditions which provided the allylic thioether **4a** in 76% isolated yield (Path B, Scheme 3). It was found that the TEMPO coupled well with allyl iodide **1a** under same reaction conditions to provide coupled product **7** in 82% isolated yield (Path C, Scheme 3). On the basis of these control experiments we proposed plausible mechanism which follows the radical pathway (Scheme 4).

A plausible mechanism for the syntheses of allylic thioethers is presented in the Scheme 4 by taking **4a** as model case. In the presence of DTBP, the allyl iodide **1a** generated allyl radical **A**. At the same time disulfide converted into phenyl sulphide radical. The coupling of allyl radical **A** with phenyl sulphide radical yielded into the resulting thioether **4a**.

Conclusions

In conclusions, we have developed a methodology for the synthesis of allylic thioethers *via* C–S bond formation between allyl iodides and disulfides under metal free conditions for the first time. A variety of densely functionalized allyl iodides and disulfides coupled well under the influence of DTBP provided the thioethers in 62–92% yield. A complete stereo- and regioselectivity were observed in these transformations.

Experimental

General information

All chemicals were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on a Jeol resonance-400 instrument using $CDCl_3$ 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.

General procedure for Table 1

To a stirred solution of allyl iodide **1a** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol) and diphenyl disulfide (2.0 mmol, 0.436 g) in CH_3CN (2.0 mL) was added oxidant (10.0 mmol) and then the reaction mixture was stirred for 80 °C under nitrogen atmosphere for 48 h. The solvent was then removed under reduced pressure and the crude product thus obtained was purified by column chromatography (silica gel, 1% EtOAc in hexanes) to provide the allyl thioether **4a** as pale yellow colour liquid.

Representative example of Table 1: methyl-(*Z*)-3-phenyl-2-((phenylthio)methyl)acrylate (entry 9, 4a)[10c]

The title compound was prepared following the general procedure for Table 1, using allyl iodide **1a** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol, 0.604 g), diphenyl disulfide (2.0 mmol, 0.436 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4a** as pale yellow liquid. Yield: 0.499 g, 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H), 4.05 (s, 2H), 7.20–7.32 (m, 3H), 7.38–7.42 (m, 7H), 7.79 (s, 1H); ^{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, 167.6.

General procedure for Table 2

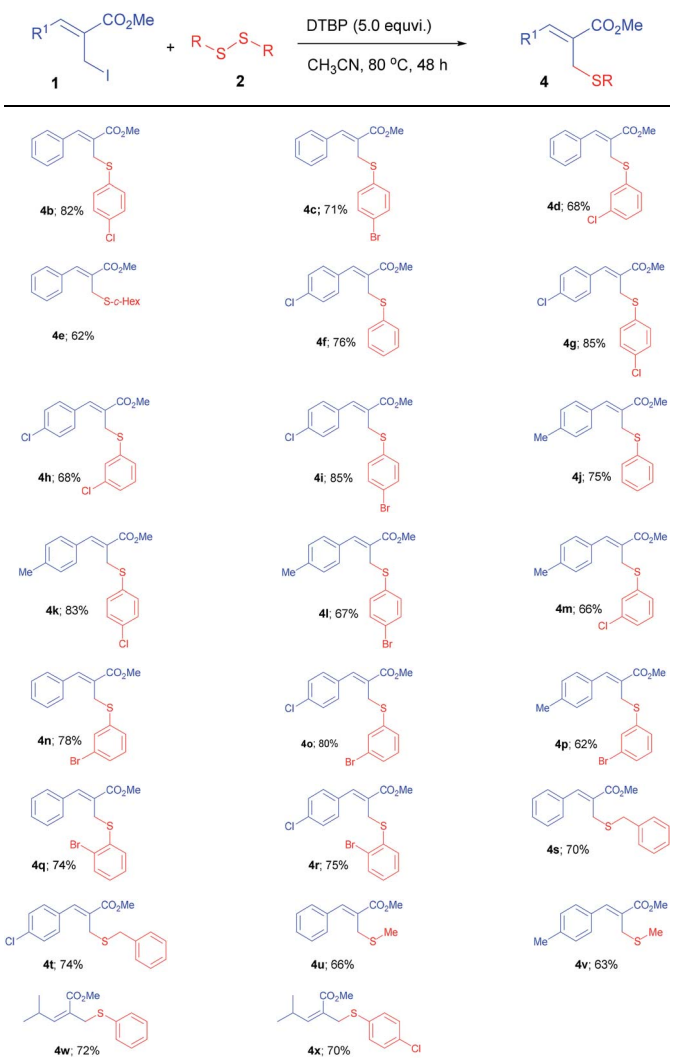
To a stirred solution of allyl iodide **1** (2.0 mmol) and disulfide (2.0 mmol) in CH_3CN (2.0 mL) was added DTBP (10.0 mmol), then the reaction mixture was stirred for 48 h at 80 °C under nitrogen atmosphere. The solvent was then removed under reduced pressure and the crude product thus obtained was purified by column chromatography (silica gel, 1% EtOAc in hexanes) to provide the allyl thioether **4**.

Methyl-(*Z*)-2-(((4-chlorophenyl)thio)methyl)-3-phenylacrylate (4b). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1a** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol, 0.604 g), bis(4-chlorophenyl)disulfide (2.0 mmol, 0.574 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4b** as pale yellow liquid. Yield: 0.522 g, 82%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H), 3.98 (s, 2H), 7.11 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 7.30–7.32 (m, 5H), 7.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.5, 52.3, 128.0, 128.7, 129.0, 129.1, 129.4, 132.4, 132.9, 134.3, 134.7, 141.6, 167.4; HRMS (ESI) exact mass calcd for $C_{17}H_{15}ClO_2S$ + K (M + K), 357.0118; found: 357.0127.

Methyl-(*Z*)-2-(((4-bromophenyl)thio)methyl)-3-phenylacrylate (4c). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1a** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol, 0.604 g), bis(4-bromophenyl)disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4c** as pale yellow liquid. Yield: 0.515 g, 71%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 3H), 4.00 (s, 2H), 7.16 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.31–7.33 (m, 5H), 7.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.3, 52.4, 120.9, 127.9, 128.7, 129.1, 129.4, 131.9, 132.5, 141.7, 167.5; HRMS (ESI) exact mass calcd for $C_{17}H_{15}BrO_2S$ + Na (M + Na), 384.9874; found: 384.9881.

Methyl-(*Z*)-2-(((3-chlorophenyl)thio)methyl)-3-phenylacrylate (4d). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1a** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol, 0.604 g), bis(3-

Table 2 DTBP-promoted C–S bond formation between allyl iodides **1** and disulfides **2**[a,b]



[a] Reaction conditions: allyl iodide **1** (2.0 mmol), disulfide **2** (2.0 mmol) and DTBP (10.0 mmol) were reacted in CH_3CN (2.0 mL) at 80 °C for 48 h. [b] Isolated yields are based on allyl iodide **1**.

chlorophenyl)disulfide (2.0 mmol, 0.574 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4d** as pale yellow liquid. Yield: 0.433 g, 68%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), 4.05 (s, 2H), 7.08–7.24 (m, 3H), 7.26–7.42 (m, 6H), 7.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.9, 52.4, 126.7, 127.7, 128.3, 128.8, 129.2, 129.4, 129.8, 129.9, 134.61, 134.65, 138.2, 142.0, 167.5; HRMS (ESI) exact mass calcd for $C_{17}H_{15}ClO_2S$ + Na (M + Na), 341.0379; found: 341.0367.

Methyl-(*Z*)-2-((cyclohexylthio)methyl)-3-phenylacrylate (4e). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1a** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol, 0.604 g), dicyclohexyl disulfide (2.0 mmol, 0.44 mL), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4e** as pale yellow liquid. Yield: 0.359 g, 62%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06–1.38 (m, 6H), 1.62–1.75 (m, 2H), 1.78–1.93 (m, 2H), 2.61–2.66 (m, 1H), 3.61 (s, 2H), 3.79 (s, 3H), 7.25–7.40 (m, 3H), 7.41–7.52 (m, 2H), 7.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.9, 26.1, 26.9, 33.5, 44.5, 52.2, 128.6, 128.9, 129.5, 129.7, 135.1, 140.3, 167.9; HRMS (ESI) exact mass calcd for $C_{17}H_{22}O_2S$ + Na (M + Na), 313.1238; found: 313.1059.

Methyl-(*Z*)-3-(4-chlorophenyl)-2-((phenylthio)methyl)acrylate (4f).[10c] The title compound was prepared following the general procedure for Table 2, using allyl iodide **1b** *i.e.* methyl-(*Z*)-3-(4-chlorophenyl)-2-(iodomethyl)acrylate (2.0 mmol, 0.673 g), diphenyl disulfide (2.0 mmol, 0.436 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4f** as pale yellow liquid. Yield: 0.484 g, 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 3H), 3.98 (s, 2H), 7.20–7.282 (m, 3H), 7.34 (s, 4H), 7.36 (d, J = 8.4 Hz, 2H), 7.67 (s, 1H); ^{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.

Methyl-(*Z*)-3-(4-chlorophenyl)-2-(((4-chlorophenyl)thio)methyl) acrylate (4g). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1b** *i.e.* methyl-(*Z*)-3-(4-chlorophenyl)-2-(iodomethyl)acrylate (2.0 mmol, 0.673 g), bis(4-chlorophenyl)disulfide (2.0 mmol, 0.574 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4g** as pale yellow liquid. Yield: 0.600 g, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H), 3.93 (s, 2H), 7.14 (d, J = 8.8 Hz, 2H), 7.222 (d, J = 8.8 Hz, 2H), 7.228 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 7.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.5, 52.4, 128.5, 128.9, 129.0, 130.6, 132.6, 133.0, 133.2, 133.9, 135.1, 140.2, 167.2; HRMS (ESI) exact mass calcd for $C_{17}H_{14}Cl_2O_2S$ + Na (M + Na), 374.9989; found: 374.9922.

Methyl-(*Z*)-3-(4-chlorophenyl)-2-(((3-chlorophenyl)thio)methyl) acrylate (4h). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1b** *i.e.* methyl-(*Z*)-3-(4-chlorophenyl)-2-(iodomethyl)acrylate (2.0 mmol, 0.673 g), bis(3-chlorophenyl)disulfide (2.0 mmol, 0.574 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4h** as pale yellow liquid. Yield: 0.480 g, 68%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H), 3.96 (s, 2H), 7.05–7.20 (m, 3H), 7.22–7.36 (m, 5H), 7.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.8, 52.5, 126.9, 128.2, 128.5, 129.0, 129.9, 130.0, 130.7, 133.0, 134.6, 135.2, 137.8, 140.5, 167.1; HRMS (ESI) exact mass calcd for $C_{17}H_{14}Cl_2O_2S$ + Na (M + Na), 374.9989; found: 374.9978.

Methyl-(*Z*)-2-(((4-bromophenyl)thio)methyl)-3-(4-chlorophenyl) acrylate (4i). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1b** *i.e.* methyl-(*Z*)-3-(4-chlorophenyl)-2-(iodomethyl)acrylate (2.0 mmol, 0.673 g), bis(4-bromophenyl)disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4i** as yellow solid. Mp: 63 °C; yield: 0.675 g, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H), 3.93 (s, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.27–7.29 (m, 4H), 7.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.3, 52.5, 121.2, 128.4, 128.9, 130.6, 131.9, 132.7, 133.0, 134.6, 135.1, 140.2, 167.2; HRMS (ESI) exact mass calcd for $C_{17}H_{14}BrClO_2S$ + K (M + K), 434.9223; found: 434.9227.

Methyl-(*Z*)-2-((phenylthio)methyl)-3-(*p*-tolyl)acrylate (4j). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1c** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-

(*p*-tolyl)acrylate (2.0 mmol, 0.632 g), diphenyl disulfide (2.0 mmol, 0.436 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4j** as pale yellow liquid. Yield: 0.447 g, 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 3.81 (s, 3H), 4.09 (s, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.21–7.29 (m, 3H), 7.38 (d, J = 8.4 Hz, 2H), 7.40–7.42 (m, 2H), 7.80 (s, 1H); ^{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: 337.0652.

Methyl-(*Z*)-2-(((4-chlorophenyl)thio)methyl)-3-(*p*-tolyl)acrylate (4k). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1c** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-(*p*-tolyl)acrylate (2.0 mmol, 0.632 g), bis(4-chlorophenyl)disulfide (2.0 mmol, 0.574 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4k** as pale yellow liquid. Yield: 0.551 g, 83%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.79 (s, 3H), 4.03 (s, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 32.5, 52.2, 127.0, 128.9, 129.4, 129.6, 131.8, 132.2, 132.9, 134.5, 139.4, 141.9, 167.5; HRMS (ESI) exact mass calcd for $C_{18}H_{17}ClO_2S$ + K (M + K), 371.0275; found: 371.0271.

Methyl-(*Z*)-2-(((4-bromophenyl)thio)methyl)-3-(*p*-tolyl)acrylate (4l). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1c** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-(*p*-tolyl)acrylate (2.0 mmol, 0.632 g), bis(4-bromophenyl)disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4l** as yellow solid. Mp: 61 °C; yield: 0.505 g, 67%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.79 (s, 3H), 4.02 (s, 2H), 7.14–7.19 (m, 4H), 7.27–7.31 (m, 4H), 7.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 32.3, 52.3, 120.8, 126.9, 129.5, 129.6, 131.8, 131.9, 132.3, 135.2, 139.5, 142.0, 167.7; HRMS (ESI) exact mass calcd for $C_{18}H_{17}BrO_2S$ + Na (M + Na), 399.0030; found: 398.9935.

Methyl-(*Z*)-2-(((3-chlorophenyl)thio)methyl)-3-(*p*-tolyl)acrylate (4m). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1c** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-(*p*-tolyl)acrylate (2.0 mmol, 0.632 g), bis(3-chlorophenyl)disulfide (2.0 mmol, 0.574 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4m** as pale yellow liquid. Yield: 0.438 g, 66%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.81 (s, 3H), 4.07 (s, 2H), 7.05–7.24 (m, 5H), 7.25–7.40 (m, 3H), 7.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 31.9, 52.3, 126.6, 128.1, 129.60, 129.65, 129.67, 129.9, 131.8, 134.6, 138.4, 139.6, 142.2, 167.5; HRMS (ESI) exact mass calcd for $C_{18}H_{17}ClO_2S$ + Na (M + Na), 355.0535; found: 355.0531.

Methyl-(*Z*)-2-(((3-bromophenyl)thio)methyl)-3-phenylacrylate (4n). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1a** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol, 0.604 g), bis(3-bromophenyl)disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4n** as pale yellow liquid. Yield: 0.566, 78%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 4.04 (s, 2H), 7.07 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.33–7.44 (m, 5H), 7.46 (s, 1H), 7.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.0, 52.4, 122.7, 127.7, 128.8, 128.9, 129.2, 129.4, 129.7, 130.2, 132.7, 134.6, 138.4, 142.0, 167.5; HRMS (ESI) exact mass calcd for $C_{17}H_{15}BrO_2S$ + Na (M + Na), 384.9874; found: 384.9698.

Methyl-(*Z*)-2-(((3-bromophenyl)thio)methyl)-3-(4-chlorophenyl) acrylate (4o). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1b** *i.e.* methyl-(*Z*)-3-(4-chlorophenyl)-2-(iodomethyl)acrylate (2.0 mmol, 0.673 g), bis(3-bromophenyl)disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4o** as pale yellow liquid. Yield: 0.635 g, 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 3H), 3.98 (s, 2H), 7.07 (t, J = 8.0 Hz, 1H), 7.21–7.23 (m, 1H), 7.26–7.32 (m, 5H), 7.43 (t, J = 1.6 Hz, 1H), 7.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.0, 52.5, 122.7, 128.3, 129.0, 129.2, 129.9, 130.2, 130.7, 133.0, 135.2, 138.0, 140.5, 167.2; HRMS (ESI) exact mass calcd for $C_{17}H_{14}BrClO_2S$ + K (M + K), 434.9223; found: 434.9226.

Methyl-(*Z*)-2-(((3-bromophenyl)thio)methyl)-3-(*p*-tolyl)acrylate (4p). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1c** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-(*p*-tolyl)acrylate (2.0 mmol, 0.632 g), bis(3-bromophenyl)disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4p** as pale yellow liquid. Yield: 0.467 g, 62%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 3.81 (s, 3H), 4.06 (s, 2H), 7.08 (t, J = 8.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.24–7.32 (m, 4H), 7.46 (t, J = 1.6 Hz, 1H), 7.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 32.0, 52.4, 122.7, 126.6, 128.7, 129.5, 129.6, 130.1, 131.7, 132.5, 138.6, 139.6, 142.2, 167.6; HRMS (ESI) exact mass calcd for $C_{18}H_{17}BrO_2S$ + Na (M + Na), 399.0030; found: 399.6734.

Methyl-(*Z*)-2-(((2-bromophenyl)thio)methyl)-3-phenylacrylate (4q). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1a** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol, 0.604 g), bis(2-bromophenyl)disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4q** as pale yellow liquid. Yield: 0.537 g, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 4.04 (s, 2H), 7.02 (td, J = 8.0 Hz & 1.6 Hz, 1H), 7.19 (td, J = 8.4 Hz & 1.2 Hz, 1H), 7.27 (dd, J = 6.4 Hz & 1.6 Hz, 1H), 7.32–7.38 (m, 3H), 7.41–7.45 (m, 2H), 7.50 (dd, J = 6.4 Hz & 1.6 Hz, 1H), 7.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.4, 52.4, 125.1, 127.2, 127.6, 127.8, 128.8, 129.2, 129.5, 130.6, 133.0, 134.6, 137.3, 142.4, 167.5; HRMS (ESI) exact mass calcd for $C_{17}H_{15}BrO_2S$ + K (M + K), 400.9613; found: 400.9681.

Methyl-(*Z*)-2-(((2-bromophenyl)thio)methyl)-3-(4-chlorophenyl) acrylate (4r). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1b** *i.e.* methyl-(*Z*)-3-(4-chlorophenyl)-2-(iodomethyl)acrylate (2.0 mmol, 0.673 g), bis(2-bromophenyl)disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4p** as yellow solid. Mp: 74 °C; yield: 0.595 g, 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 3H), 3.99 (s, 2H), 7.03 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.26–7.38 (m, 5H), 7.50 (d, J = 8.0 Hz, 1H), 7.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.4, 52.5, 125.4, 127.7, 127.922, 127.928, 129.03, 130.9, 131.0, 133.0, 133.1, 135.2, 136.9, 141.0, 167.2; HRMS (ESI) exact mass calcd for $C_{17}H_{14}$-$BrClO_2S$ + K (M + K), 434.9223; found: 434.9214.

Methyl-(*Z*)-2-((benzylthio)methyl)-3-phenylacrylate (4s). The title compound was prepared following the general procedure

for Table 2, using allyl iodide **1a** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol, 0.604 g), dibenzyl disulfide (2.0 mmol, 0.492 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4s** as pale yellow liquid. Yield: 0.417 g, 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.46 (s, 2H), 3.64 (s, 2H), 3.72 (s, 3H), 7.10–7.16 (m, 5H), 7.21–7.22 (m, 3H), 7.28–7.30 (m, 2H), 7.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.5, 37.4, 52.3, 127.0, 128.5, 128.7, 129.0, 129.1, 129.8, 134.9, 138.3, 140.8, 168.0; HRMS (ESI) exact mass calcd for $C_{18}H_{18}O_2S$ + Na (M + Na), 321.0925; found: 321.0920.

Methyl-(*Z*)-2-((benzylthio)methyl)-3-(4-chlorophenyl)acrylate (4t). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1b** *i.e.* methyl-(*Z*)-3-(4-chlorophenyl)-2-(iodomethyl)acrylate (2.0 mmol, 0.673 g), dibenzyl disulfide (2.0 mmol, 0.492 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4t** as pale yellow liquid. Yield: 0.493 g, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.52 (s, 2H), 3.74 (s, 2H), 3.82 (s, 3H), 7.22–7.32 (m, 9H), 7.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.3, 37.4, 52.4, 127.1, 128.5, 128.94, 128.99, 129.0, 129.5, 131.0, 133.2, 135.0, 138.1, 139.5, 167.7; HRMS (ESI) exact mass calcd for $C_{18}H_{17}ClO_2S$ + Na (M + Na), 355.0535; found: 355.0529.

Methyl-(*Z*)-2-((methylthio)methyl)-3-phenylacrylate (4u).[13] The title compound was prepared following the general procedure for Table 2, using allyl iodide **1a** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol, 0.604 g), dimethyl disulfide (2.0 mmol, 0.188 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4u** as colourless oil. Yield: 0.293 g, 66%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3H), 3.55 (s, 2H), 3.76 (s, 3H), 7.25–7.34 (m, 3H), 7.40 (d, J = 7.6 Hz, 2H), 7.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.1, 30.4, 52.2, 128.6, 128.8, 129.3, 129.5, 134.9, 140.6, 167.9.

Methyl-(*Z*)-2-((methylthio)methyl)-3-(*p*-tolyl)acrylate (4v). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1c** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-(*p*-tolyl)acrylate (2.0 mmol, 0.632 g), dimethyl disulfide (2.0 mmol, 0.188 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4v** as colourless oil. Yield: 0.297 g, 63%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.09 (s, 3H), 2.35 (s, 3H), 3.63 (s, 2H), 3.82 (s, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.1, 21.3, 30.5, 52.1, 128.3, 129.3, 129.6, 132.0, 139.0, 140.7, 168.0; HRMS (ESI) exact mass calcd for $C_{13}H_{16}O_2S$ + K (M + K), 275.0508; found: 275.0501.

Methyl-(*E*)-4-methyl-2-((phenylthio)methyl)pent-2-enoate (4w). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1d** *i.e.* methyl-(*E*)-2-(iodomethyl)-4-methylpent-2-enoate (2.0 mmol, 0.536 g), diphenyl disulfide (2.0 mmol, 0.436 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4w** as pale yellow liquid. Yield: 0.360 g, 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (s, 3H), 0.85 (s, 3H), 2.39–2.45 (m, 1H), 3.71 (s, 3H), 3.79 (s, 2H), 6.60 (d, J = 10.4 Hz, 1H), 7.18–7.26 (m, 3H), 739–7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 22.1, 28.4, 31.4, 52.0, 125.9, 127.1, 128.8, 128.9, 131.9, 135.9, 152.0, 167.4; HRMS (ESI) exact mass calcd for $C_{14}H_{18}O_2S$ + Na (M + Na), 273.0925; found: 273.0920.

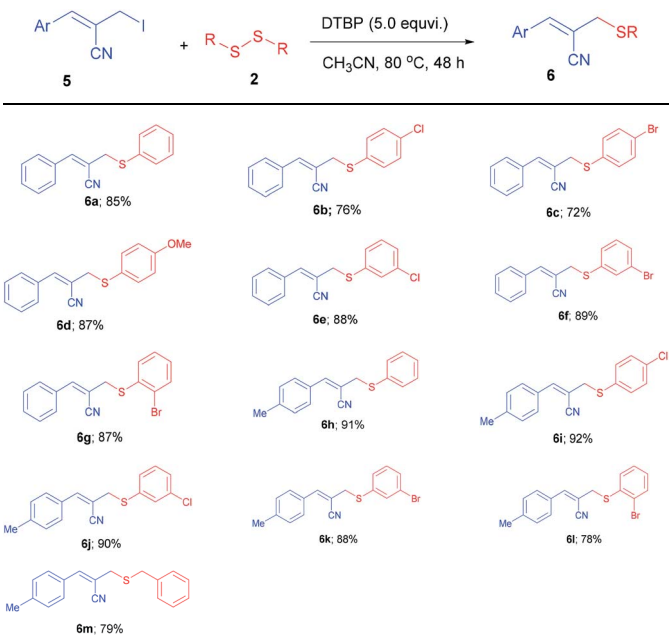
Methyl-(*E*)-2-(((4-chlorophenyl)thio)methyl)-4-methylpent-2-enoate (4x). The title compound was prepared following the general procedure for Table 2, using allyl iodide **1d** *i.e.* methyl-(*E*)-2-(iodomethyl)-4-methylpent-2-enoate (2.0 mmol, 0.536 g), bis(3-chlorophenyl)disulfide (2.0 mmol, 0.574 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **4x** as pale yellow liquid. Yield: 0.398 g, 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (s, 3H), 0.88 (s, 3H), 2.39–2.45 (m, 1H), 3.72 (s, 3H), 3.76 (s, 2H), 6.62 (d, J = 10.4 Hz, 1H), 7.22 (dd, J = 8.4 Hz & 2.0 Hz, 2H), 7.32 (dd, J = 8.4 Hz & 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.1, 28.4, 31.6, 52.0, 125.6, 128.9, 133.2, 134.4, 152.3, 167.2; HRMS (ESI) exact mass calcd for $C_{14}H_{17}ClO_2S$ + Na (M + Na), 307.0535; found: 307.0539.

General procedure for Table 3

To a stirred solution of allyl bromide **5** (2.0 mmol) and disulfide (2.0 mmol) in CH_3CN (2.0 mL) was added DTBP (10.0 mmol), then the reaction mixture was stirred for 48 h at 80 °C under nitrogen atmosphere. The solvent was then removed under reduced pressure and the crude product thus obtained was purified by column chromatography (silica gel, 1% EtOAc in hexanes) to provide the allyl thioether **6**.

(*E*)-3-Phenyl-2-((phenylthio)methyl)acrylonitrile (6a).[10c] The title compound was prepared following the general procedure for Table 3, using allyl iodide **5a** *i.e.* (*E*)-2-(iodomethyl)-3-phenylacrylonitrile (2.0 mmol, 0.538 g), diphenyl disulfide (2.0 mmol, 0.436 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6a** as pale yellow liquid. Yield: 0.426 g, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 2H), 6.65 (s, 1H), 7.27–7.35

Table 3 DTBP-promoted C–S bond formation between allyl iodides **5** and disulfides **2**[a,b]



[a] Reaction conditions: allyl iodide **5** (2.0 mmol), disulfide **2** (2.0 mmol) and DTBP (10.0 mmol) were reacted in CH_3CN (2.0 mL) at 80 °C for 48 h. [b] Isolated yields are based on allyl iodide **5**.

(m, 6H), 7.44–7.46 (m, 2H), 7.58–7.59 (m, 2H); ^{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.

(*E*)-2-(((4-Chlorophenyl)thio)methyl)-3-phenylacrylonitrile (6b). The title compound was prepared following the general procedure for Table 3, using allyl iodide **5a** *i.e.* (*E*)-2-(iodomethyl)-3-phenylacrylonitrile (2.0 mmol, 0.538 g), bis(4-chlorophenyl) disulfide (2.0 mmol, 0.574 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6b** as pale yellow liquid. Yield: 0.433 g, 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.71 (s, 2H), 6.68 (s, 1H), 7.24 (dd, J = 8.8 Hz & 2.0 Hz, 2H), 7.35–7.37 (m, 5H; multiplet conations one doublet at δ 7.36, J = 8.4 Hz, 2H and multiplet for 3H), 7.58–7.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.2, 107.5, 118.0, 128.8, 128.9, 129.4, 130.7, 132.0, 132.9, 134.2, 134.3, 145.1, HRMS (ESI) exact mass calcd for $C_{16}H_{12}ClNS$ + Na (M + Na), 308.0277; found: 308.0092.

(*E*)-2-(((4-Bromophenyl)thio)methyl)-3-phenylacrylonitrile (6c). The title compound was prepared following the general procedure for Table 3, using allyl iodide **5a** *i.e.* (*E*)-2-(iodomethyl)-3-phenylacrylonitrile (2.0 mmol, 0.538 g), bis(4-bromophenyl) disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6c** as yellow solid. Mp: 83 °C; yield: 0.475 g, 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 2H), 6.70 (s, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.36–7.40 (m, 5H, multiplet contains one doublet at δ 7.37, J = 8.4 Hz, 2H and one multiplet for 3H), 7.59–7.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.0, 107.4, 118.0, 122.3, 128.8, 129.0, 130.7, 132.3, 132.7, 132.9, 134.3, 145.1; HRMS (ESI) exact mass calcd for $C_{16}H_{12}BrNS$ + Na (M + Na), 351.9772; found: 351.9749.

(*E*)-2-(((4-Methoxyphenyl)thio)methyl)-3-phenylacrylonitrile (6d). The title compound was prepared following the general procedure for Table 3, using allyl iodide **5a** *i.e.* (*E*)-2-(iodomethyl)-3-phenylacrylonitrile (2.0 mmol, 0.538 g), bis(4-methoxyphenyl)disulfide (2.0 mmol, 0.556 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6d** as pale yellow liquid. Yield: 0.488 g, 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.60 (s, 2H), 3.71 (s, 3H), 6.47 (s, 1H), 6.79 (d, J = 8.8 Hz, 2H), 7.32–7.34 (m, 3H), 7.38 (d, J = 8.8 Hz, 2H), 7.53–7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.7, 55.4, 108.0, 114.8, 118.2, 123.5, 128.7, 128.9, 130.4, 133.1, 136.3, 144.7, 160.1; HRMS (ESI) exact mass calcd for $C_{17}H_{15}NOS$ + K (M + K), 320.0511; found: 320.0517.

(*E*)-2-(((3-Chlorophenyl)thio)methyl)-3-phenylacrylonitrile (6e). The title compound was prepared following the general procedure for Table 3, using allyl iodide **5a** *i.e.* (*E*)-2-(iodomethyl)-3-phenylacrylonitrile (2.0 mmol, 0.538 g), bis(3-chlorophenyl) disulfide (2.0 mmol, 0.574 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6e** as pale yellow liquid. Yield: 0.502 g, 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.75 (s, 2H), 6.76 (s, 1H), 7.07–7.22 (m, 2H), 7.24–7.44 (m, 5H), 7.55–7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.5, 107.2, 118.0, 128.0, 128.9, 129.0, 130.2, 130.3, 130.7, 131.7, 132.9, 134.8, 135.7, 145.3; HRMS (ESI) exact mass calcd for $C_{16}H_{12}ClNS$ + Na (M + Na), 308.0277; found: 308.0091.

(*E*)-2-(((3-Bromophenyl)thio)methyl)-3-phenylacrylonitrile (6f). The title compound was prepared following the general procedure for Table 3, using allyl iodide **5a** *i.e.* (*E*)-2-(iodomethyl)-3-phenylacrylonitrile (2.0 mmol, 0.538 g), bis(3-bromophenyl) disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6f** as pale yellow liquid. Yield: 0.587 g, 89%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 2H), 6.76 (s, 1H), 7.11 (t, J = 8.0 Hz, 1H), 7.21–7.41 (m, 5H), 7.56 (s, 1H), 7.61–7.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.6, 107.2, 118.0, 122.9, 128.9, 129.05, 129.06, 130.7, 130.8, 130.9, 132.9, 134.5, 136.1, 145.4; HRMS (ESI) exact mass calcd for $C_{16}H_{12}BrNS$ + Na (M + Na), 351.9772; found: 351.9625.

(*E*)-2-(((2-Bromophenyl)thio)methyl)-3-phenylacrylonitrile (6g). The title compound was prepared following the general procedure for Table 3, using allyl iodide **5a** *i.e.* (*E*)-2-(iodomethyl)-3-phenylacrylonitrile (2.0 mmol, 0.538 g), bis(2-bromophenyl) disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6g** as yellow solid. Mp: 79 °C; yield: 0.574 g, 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 2H), 6.74 (s, 1H), 7.10 (td, J = 7.6 Hz & 1.6 Hz, 1H), 7.21 (td, J = 7.6 Hz & 1.2 Hz, 1H), 7.31–7.37 (m, 3H), 7.45 (dd, J = 8.0 Hz & 1.6 Hz, 2H), 7.53–7.62 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.5, 106.8, 118.1, 127.3, 128.2, 128.8, 128.9, 129.3, 130.7, 133.0, 133.5, 133.6, 134.5, 145.4; HRMS (ESI) exact mass calcd for $C_{16}H_{12}BrNS$ + Na (M + Na), 351.9772; found: 351.9713.

(*E*)-2-((Phenylthio)methyl)-3-(*p*-tolyl)acrylonitrile (6h).[10c] The title compound was prepared following the general procedure for Table 3, using allyl iodide **5b** *i.e.* (*E*)-2-(iodomethyl)-3-(*p*-tolyl) acrylonitrile (2.0 mmol, 0.566 g), diphenyl disulfide (2.0 mmol, 0436 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6h** as pale yellow liquid. Yield: 0.482 g, 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 3.71 (s, 2H), 6.63 (s, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.26–7.29 (m, 3H), 7.44 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 41.1, 106.3, 118.4, 128.0, 128.9, 129.3, 129.6, 130.4, 132.8, 133.7, 141.0, 144.9.

(*E*)-2-(((4-Chlorophenyl)thio)methyl)-3-(*p*-tolyl)acrylonitrile (6i). The title compound was prepared following the general procedure for Table 3, using allyl iodide **5b** *i.e.* (*E*)-2-(iodomethyl)-3-(*p*-tolyl)acrylonitrile (2.0 mmol, 0.566 g), bis(4-chlorophenyl) disulfide (2.0 mmol, 0.574 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6i** as yellow solid. Mp: 73 °C; yield: 0.551 g, 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.71 (s, 2H), 6.65 (s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.7, 41.3, 106.1, 118.1, 128.8, 129.3, 129.6, 130.2, 132.1, 134.20, 134.29, 141.2, 145.0; HRMS (ESI) exact mass calcd for $C_{17}H_{14}ClNS$ + K (M + K), 338.0173; found: 338.0179.

(*E*)-2-(((3-Chlorophenyl)thio)methyl)-3-(*p*-tolyl)acrylonitrile (6j). The title compound was prepared following the general procedure for Table 3, using allyl iodide **5b** *i.e.* (*E*)-2-(iodomethyl)-3-(*p*-tolyl)acrylonitrile (2.0 mmol, 0.566 g), bis(3-chlorophenyl) disulfide (2.0 mmol, 0.574 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6j** as yellow solid. Mp: 70 °C; yield: 0.539 g, 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 3.74 (s, 2H), 6.75 (s, 1H), 7.13 (d, J = 7.6 Hz, 2H), 7.16–7.17 (m, 2H), 7.22–7.31 (m, 1H), 7.39 (s, 1H), 7.46–7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 40.5, 105.8, 118.3, 127.8, 128.9, 129.7, 130.0, 130.2, 130.3, 131.4, 134.7, 136.0, 141.2, 145.4; HRMS (ESI)

exact mass calcd for $C_{17}H_{14}ClNS$ + Na (M + Na), 322.0433; found: 322.0439.

(*E*)-2-(((3-Bromophenyl)thio)methyl)-3-(*p*-tolyl)acrylonitrile (6k). The title compound was prepared following the general procedure for Table 3, using allyl iodide **5b** *i.e.* (*E*)-2-(iodomethyl)-3-(*p*-tolyl)acrylonitrile (2.0 mmol, 0.566 g), bis(3-bromophenyl)disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6k** as yellow solid. Mp: 79 °C; yield: 0.605 g, 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.75 (s, 2H), 6.73 (s, 1H), 7.10–7.20 (m, 3H), 7.30–7.39 (m, 2H), 7.52–7.58 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 40.7, 105.8, 118.2, 122.8, 128.9, 129.7, 130.1, 130.5, 130.7, 130.8, 134.5, 136.1, 141.3, 145.4; HRMS (ESI) exact mass calcd for $C_{17}H_{14}BrNS$ + K (M + K), 381.9667; found: 381.9666.

(*E*)-2-(((2-Bromophenyl)thio)methyl)-3-(*p*-tolyl)acrylonitrile (6l). The title compound was prepared following the general procedure for Table 3, using allyl iodide **5b** *i.e.* (*E*)-2-(iodomethyl)-3-(*p*-tolyl)acrylonitrile (2.0 mmol, 0.566 g), bis(2-bromophenyl)disulfide (2.0 mmol, 0.752 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6l** as yellow solid. Mp: 69 °C; yield: 0.537 g, 78%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 3.80 (s, 2H), 6.71 (s, 1H), 7.10 (td, J = 7.6 Hz & 1.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.21 (td, J = 7.6 Hz, & 1.2 Hz, 1H), 7.43 (dd, J = 8.0 Hz & 1.6 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.58 (dd, J = 8.0 Hz & 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 39.5, 105.5, 118.3, 127.5, 128.1, 128.8, 129.3, 129.6, 130.2, 133.4, 133.9, 141.2, 145.4; HRMS (ESI) exact mass calcd for $C_{17}H_{14}BrNS$ + K (M + K), 381.9667; found: 381.9673.

(*E*)-2-((benzylthio)methyl)-3-(*p*-tolyl)acrylonitrile (6m). The title compound was prepared following the general procedure for Table 3, using allyl iodide **5b** *i.e.* (*E*)-2-(iodomethyl)-3-(*p*-tolyl) acrylonitrile (2.0 mmol, 0.566 g), dibenzyl disulfide (2.0 mmol, 0.492 g), DTBP (10 mmol, 1.46 g, 1.8 mL) and CH_3CN (2.0 mL), providing **6m** as yellow liquid; yield: 0.441 g, 79%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H), 3.31 (s, 2H), 3.76 (s, 2H), 6.83 (s, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.31–7.35 (m, 5H), 7.67 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 35.4, 36.2, 106.7, 118.5, 127.4, 128.8, 129.0, 129.1, 129.7, 130.3, 137.2, 141.2, 144.6; HRMS (ESI) exact mass calcd for $C_{18}H_{17}NS$ + K (M + K), 318.0719; found: 318.0726.

Methyl (*E*)-3-phenyl-2-(((2,2,6,6-tetramethylpiperidin-1-yl) oxy)methyl)acrylate (7). To a stirred solution of allyl iodide **1a** *i.e.* methyl-(*Z*)-2-(iodomethyl)-3-phenylacrylate (2.0 mmol, 0.604 g) in CH_3CN (2.0 mL) was added TEMPO (2.0 mmol, 0.312 g) and then the reaction mixture was stirred for 80 °C under nitrogen atmosphere for 48 h. The solvent was then removed under reduced pressure and the crude product thus obtained was purified by column chromatography (silica gel, 1% EtOAc in hexanes) to provide the allyl thioether 7 as pale yellow colour liquid. Yield: 0.543 g, 82%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (s, 6H), 1.09 (s, 6H), 1.40–1.42 (m, 6H), 3.82 (s, 3H), 4.67 (s, 2H), 7.34–7.68 (m, 3H), 7.47–7.49 (m, 2H), 7.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1, 20.2, 32.9, 40.0, 52.0, 59.9, 70.8, 128.3, 128.9, 129.5, 135.1, 143.6, 168.5; HRMS (ESI) exact mass calcd for $C_{20}H_{29}NO_3$ + K (M + K), 370.1785; found: 370.1778.

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