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Stereoselective one-pot synthesis of β-alkylsulfide enol esters. Base-triggered rearrangement under mild conditions†

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A stereoselective one-pot procedure was developed to prepare *S*-substituted (*Z*)-enol esters through a base-triggered rearrangement. This transition metal-free multicomponent approach can be performed under an air atmosphere at room temperature, tolerates a wide set of chemical functionalities and generally affords high isolated yields. The (*Z*)-selectivity arises from the [1,4]-*S*- to *O*-acyl migration.

Introduction

Recently, multicomponent reactions have attracted a great deal of attention allowing the chemists to prepare molecules in a more efficient manner, avoiding cost- and time-consuming procedures, thus enabling molecular complexity, versatility, and robustness.[1] It is well known that enol esters are useful in aldol-, Mannich-, and Povarov-type reactions.[2] Besides, enol esters are employed in polymerizations,[3] as acylating agents under mild conditions,[4] as substrates in asymmetric protonation,[5] and recently in Ni-catalyzed Heck couplings,[6] among other valuable chemical reactions.[7] Moreover, substituted enol esters are of great interest in asymmetric synthesis since they can be stereoselectively hydrogenated.[8] On the other hand, vinyl sulfides (or enol thioethers) are useful reagents[9] and building blocks in organic synthesis[10] and several bioactive molecules bear this motif in their structure.[11] Also, they offer a unique pattern of reactivity,[12] behaving as a regiochemical modulator in Diels–Alder cycloadditions[13] and a stereochemical controlling element in certain Al- and Tf_2O-promoted cyclizations,[14] as well as Paternò–Büchi photoreactions.[15]

A common strategy to obtain enol esters is the addition of carboxylic acids to alkynes by means of metal-catalysis[16] or promoted by halogen-donors,[17] although alkyne dimerization and stereo- and regioisomer formation occur in some cases.[18] Also, the alkyne Cu- or Zr-catalyzed carbometalation–oxidation sequence has been achieved[19] with little diene formation as side-reaction. Furthermore, the addition of alkoxides or enolates to ketenes rendering enol esters displays high versatility *en route* to enantioenriched chiral products.[20] Recently, an esterification-Pd-catalyzed olefin isomerization sequence was elegantly realized furnishing enol esters, albeit with moderate stereoselectivity.[21] However, transition metal-free approaches to synthesize stereodefined olefins are rather scarce but possible, as very recently demonstrated by the reaction of ketenes with isocyanides and carboxylic acid,[22a] or aryl acetic acid and isocyanides to prepare captodative alkenes.[22b] In another approach, the Baeyer–Villiger oxidation of α,β-unsaturated carbonyl compounds by means of Oxone® can be successfully applied in the synthesis of enolesters.[23a]

Regarding alkylthio-substituted enolesters, just a couple of reports can be found. In these procedures starting from propargyl esters and allyl sulfides, the intermediacy of Au-catalysis is always needed, featuring a rearrangement/Au-carbenoid formation/isomerization sequence,[24] and leading to high yields of the target compounds.

Here we present our results on the (*Z*)-selective multicomponent preparation of β-thioalkyl enol esters at room temperature in non-dried solvents under an air atmosphere without using transition metal catalysts. Also, mechanistic features of the intramolecular rearrangement are discussed.

Results and discussion

In contrast to readily available α-haloketones, sulfur-containing substituents may easily be introduced.[25] Likewise, we envisaged the use of a reagent enabling sulfur donation and facile further S-deprotection, such as the versatile and commercially available potassium thioacetate (KSAc, **1**).[26] Hence, phenacyl

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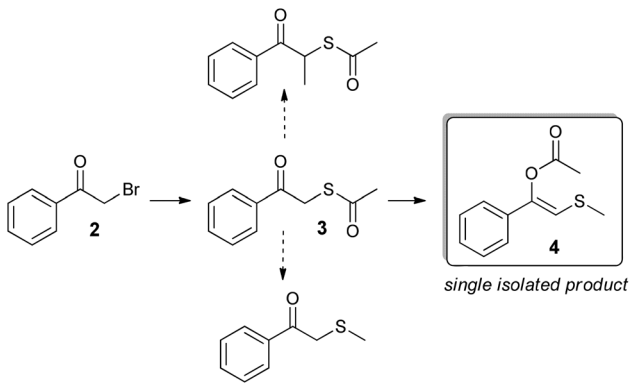
bromide (**2**) was reacted with **1** and the thioester **3** was readily formed. When *t*-BuOK and an electrophile such as MeI were added, the expected α-methylated acetophenone was not detected. Surprisingly, a rearranged product (**4**) was instead obtained as the sole isolated product (Scheme 1).[27] Albeit similar basic conditions, no Eschenmoser's sulfur extrusion products were noticed, likely due to the absence of thiophilic reagents.[28] After a careful NMR and MS analysis, the structure of the enol acetate **4** (Scheme 1) was proposed. The SMe group was evident in the NMR spectra (δ = 2.36 ppm) displaying the nuclear Overhauser effect (nOe) with the olefinic H (δ = 6.36 ppm) and, interestingly, no nOe was noticed between this methyl and *ortho*-hydrogens (Fig. 1). Indeed, vinylic hydrogen did show nOe with *ortho*-hydrogens, thus supporting the assigned (*Z*)-configuration at the double bond.

For the sake of comparison, preparation of (*E*)-configured enol acetate was attempted by C–C double bond photoisomerization.[29] Departing from the (*Z*)-**4**, a photostationary state with *ca.* 1 : 1 (*Z*,*E*) mixture was obtained. Unfortunately, isomers were inseparable by standard chromatography methods; however, MS and NMR analyses of the mixture allowed (*E*)-**4** characterization (Fig. 1).



Scheme 1 Formation of β-alkylsulfide enol ester (**4**) and possible competitive reactions. *Conditions*: KSAc (**1**, 0.44 mmol), phenacyl bromide (**2**, 1 equiv.) stirred in DMF (1 mL) at r.t. then MeI (2 equiv.) and *t*-BuOK (1 equiv.) were added and continued stirring for 5 h.

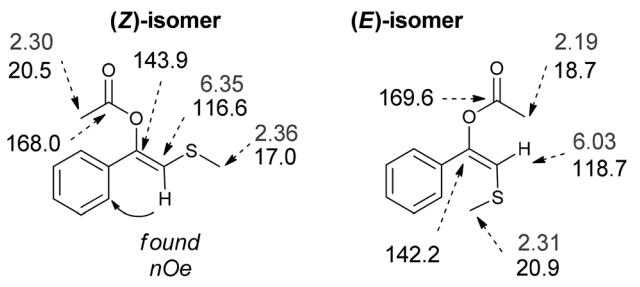


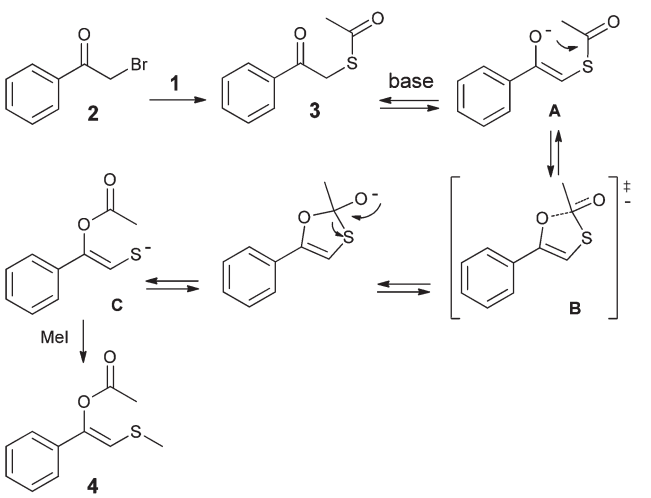
Fig. 1 Representative ^{1}H- and ^{13}C-NMR chemical shifts (in grey and black, respectively, in ppm) of (*Z*)- and (*E*)-4. Curved arrows show found nOe, thus indicating (*Z*)-configuration for the multicomponent-obtained enol ester **4**.

Next, a multicomponent version of the above discussed reaction sequence was successfully accomplished furnishing comparable yields and clean reactions, thus, all the following reactions were likewise conducted. In order to rationalize the formation of the enol esters in this approach, we propose a stepwise mechanism (Scheme 2). First, S_N2 reaction of **1** onto the α-carbon of haloketone **2** gives thioester **3**, followed by base-promoted formation of enolate **A**. This anion may undergo intramolecular nucleophilic addition to the thioester carbonyl moiety[30] through a 5-membered transition state **B** (instead of the three-membered one from Eschenmoser's sulfur extrusion),[31] and further elimination gives rise to the *O*-acyl derivative **C** bearing a free thiolate moiety. The latter suffers alkylation, rendering the rearranged product **4** and preventing reversion into the *S*-acyl precursor.

Further, a variety of commonly employed solvents were screened (polar, non-polar, protic, aprotic, basic, aqueous, *etc.*; see Table 1, entries 1–10); from which DMF and DMSO rendered smooth conversion at r.t. employing 1 equiv. of K_2CO_3 as the base (74% and 65%, entries 1 and 3, respectively), meanwhile, MeCN did it to a lesser extent (55%, entry 2).

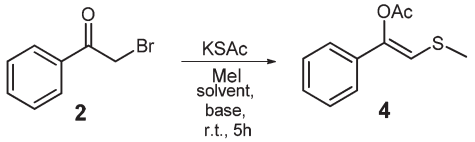
In parallel, a set of bases was surveyed (see Table 1; entries 1 and 11–17). Unexpectedly, K_2CO_3 and K_3PO_4, which are barely soluble in DMF, displayed the best performance (entries 1 and 13, respectively), whereas soluble nitrogen bases (TEA, pyridine, DABCO; entries 15, 16 and 17, respectively) yielded unsatisfactory results. When two equivalents of K_2CO_3 were added, isolated yield improved (87%, entry 18).

It is noteworthy that the use of inexpensive inorganic bases represents a great benefit since conjugated acids can be removed by liquid–liquid partition and, after passing through silica plug and solvent evaporation, a practically pure product could be obtained (around 80% isolated yield) without the need for further purification.



Scheme 2 Proposed reaction pathway for the multicomponent reaction.[32]

Table 1 Solvent and base screening for the synthesis of (*Z*)-enol esters

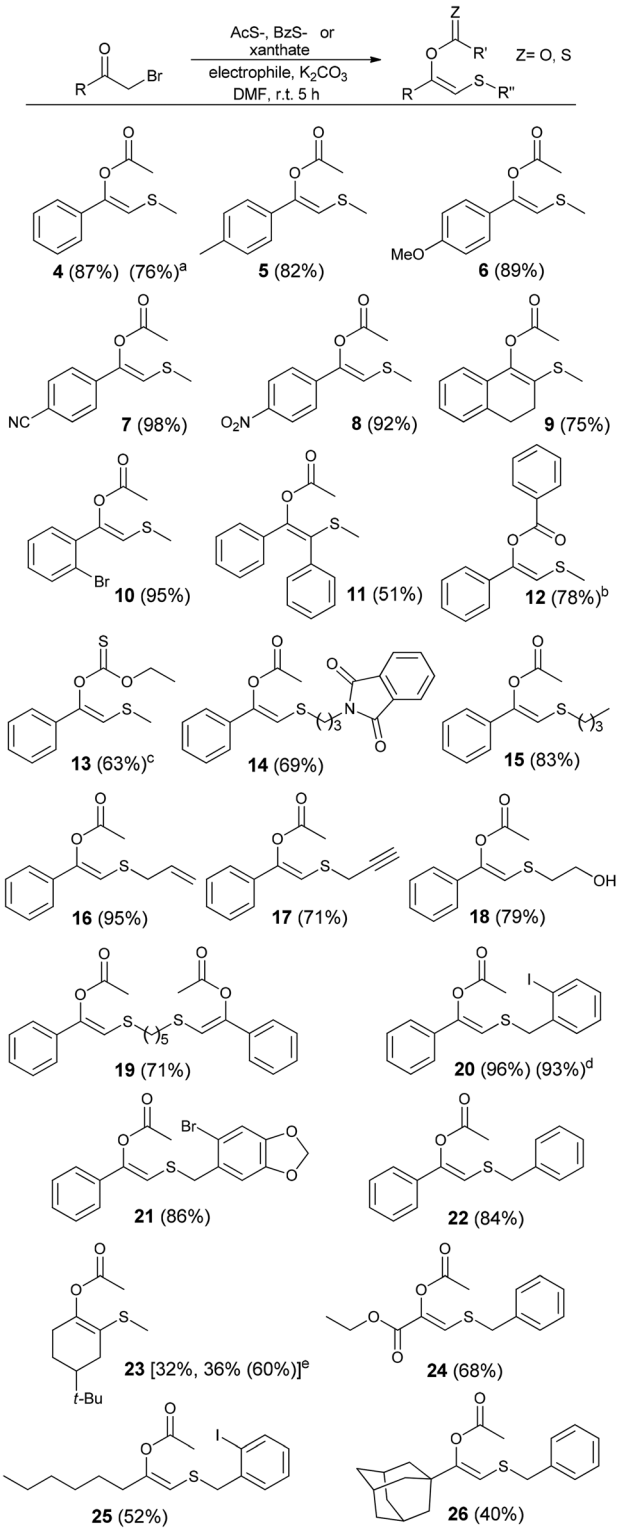


Entry[a]	Solvent	Base	Yield %[b]
1	DMF	K_2CO_3	74
2	MeCN	K_2CO_3	55
3	DMSO	K_2CO_3	65
4	EtOH	K_2CO_3	35
5	Water	K_2CO_3	<1
6	DCM	K_2CO_3	<1
7	Toluene	K_2CO_3	<1
8	THF	K_2CO_3	<1
9	1,4-Dioxane	K_2CO_3	<1
10	DME	K_2CO_3	26
11	DMF	Na_2CO_3	53
12	DMF	$NaHCO_3$	30
13	DMF	K_3PO_4	79
14	DMF	*t*-BuOK	72
15	DMF	TEA	15
16	DMF	Pyridine	<1
17	DMF	DABCO	<1
18[c]	DMF	K_2CO_3	**87**

[a] Reactions performed with KSAc (0.44 mmol), phenacyl bromide (1 equiv.), MeI (2 equiv.) and base (1 equiv.) unless otherwise stated in 1 mL of solvent at r.t. and air atmosphere for 5 h. [b] Quantified by GC using the internal standard method. [c] 2 equiv. of the base were employed.

Once established standard conditions as 1 equiv. of haloketone, 1 equiv. of thiocarboxylate nucleophile, 2 equiv. of K_2CO_3, 1 equiv. of electrophile (2 equiv. in case of MeI), DMF as solvent, room temperature and air atmosphere, the scope of this multicomponent reaction was studied (Scheme 3). Different haloketones, thiocarboxylates and electrophiles were explored. When aromatic haloketones were employed, after 5 h, products were smoothly obtained at room temperature.[33]

Remarkably, after aqueous work-up and passing through a short silica pad, the products were obtained with high purity. Isolated yields were good to excellent (69–98%), except for compounds coming from aliphatic α-haloketones that rendered somewhat lower yields (32–68%) probably due to instability of the enol ester functionality during the work-up;[23a] however, the stereochemistry of the obtained enol esters was not impaired at all. Although less likely, another reason for lower yields starting from aliphatic haloketones as compared to aromatic ones is the lower rate of enolate formation.[23b] We have performed experiments with K_2CO_3 (mild and small) and *t*-BuOK (stronger and bulkier) affording similar results (32% and 36%, respectively, see Scheme 3, compound **23**). However, when 4 equiv. of K_2CO_3 were used, a two-fold yield increase was achieved. Since these bases are barely soluble in DMF, its availability in solution may be the issue. As can be noticed, no detrimental effects were exerted by the electron-donating (82–89% yield for *p*-methyl and *p*-methoxy substituents, respectively) or electron-withdrawing (92–98% yield for *p*-nitro



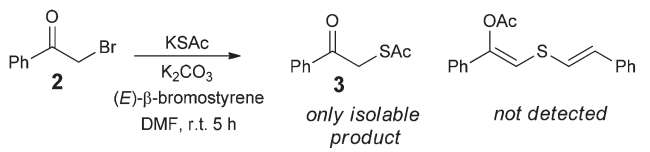
Scheme 3 One-pot synthesis of (*Z*)-enol esters. *Conditions*: haloketone (0.44 mmol), **1** (1 equiv.), K_2CO_3 (2 equiv.) and electrophile (1 equiv.); except for SMe compounds (2 equiv. of MeI were applied). Isolated yield in parentheses. [a]Phenacyl chloride as the substrate and 1 equiv. of the base. [b]HSBz and an extra equiv. of the base were used. [c]Haloketone (0.44 mmol, 1 equiv.), potassium ethyl xanthate (1 equiv.), K_2CO_3 (2 equiv.) and electrophile (1 equiv.) were employed. [d]Gram-scale reaction (1.55 g, 3.81 mmol of isolated product). [e]K_2CO_3 (2 equiv. standard cond.), *t*-BuOK (1 equiv.), K_2CO_3 (4 equiv.) respectively.

and *p*-cyano substituents, respectively) substituents in the aromatic ring in any of the substrates. Steric hindrance was not an issue since *ortho*-substitution does not affect the reaction yield, as shown for compounds **9** (75% yield) and **10** (95% yield). Besides, functional groups such as nitro, cyano, methoxy, methylen dioxo, alkyl, alkenyl, alkynyl, hydroxy, phthalimido, ester, haloaryl, *etc*. are well tolerated. Regarding the late S-alkylation, several electrophiles were tested bearing different leaving groups (I, Br, Cl, OTs) with similar good reactivity and selectivity (see the Experimental section). Moreover, when thiobenzoic acid or potassium ethyl xanthate was employed, acyl migration was not impaired. It must be emphasized that the protocol was very efficient when performed on the gram scale (compound **20**, 93% isolated yield, 1.55 g). All these features account for the versatility and operational simplicity of the here described methodology to prepare stereodefined compounds. To gain some insight into the reaction mechanism, we tested the effect of the phenacyl halide, the electrophile and the base concentration on the formation of **4**.

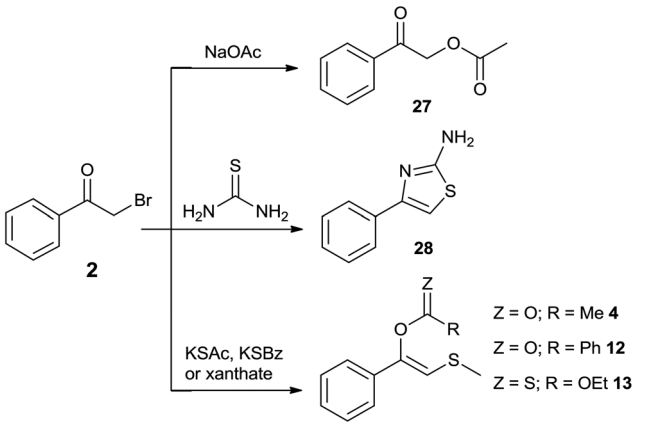
Thus, at low conversion, there was no significant difference by using phenacyl bromide or chloride. Assuming that with a poorer leaving group the overall process will slow down, the experimental results would suggest that the first S_N2[34] is not rate-determining (Scheme 2). The addition of 2 or 3 equiv. of MeI did not affect the reaction rate as well, indicating that the final S-alkylation step was not crucial. A different scenario took place when 2 equiv. of K_2CO_3 were employed instead of 1 equiv. In 1 h, almost 67% of the final product was already formed and 78% and 87% at 2 h and 5 h, respectively. Meanwhile, when 1 equiv. of the base was used, in 2 h, only 53% of the product was obtained. These data suggest that the proton abstraction would be the critical pathway in the reaction mechanism. However, deeper studies must be conducted in order to unambiguously establish the rate-determining step.

In line with the proposed mechanism (Scheme 2), when the S-alkylation is not efficient, *e.g.* with (*E*)-β-bromostyrene as an electrophile, the obtained product is the corresponding thioester **3**, supporting the reversibility of the reaction until such a stage (Scheme 4).

The equilibrium between the charged species **A** and **C** through a cyclic transition state accounts for the perfect (*Z*)-selectivity of this methodology (Scheme 2). Since the alkyl (pseudo)halide is present as soon as the charged species are formed, the S-alkylation takes place readily. To rule out (*Z*→*E*) conversion when the final S-alkylation is delayed, an experiment adding MeI 5 h after the addition of the base was conducted and analysed by GC and ^{1}H-NMR, indicating that the enol ester is exclusively formed in (*Z*)-form.



Scheme 4 The use of a poorer electrophile prevents acyl migration rendering the corresponding thioester.



Scheme 5 Dependency on the nucleophile in the reaction outcome. *Conditions*: nucleophile (0.44 mmol), phenacyl bromide (**2**, 1 equiv.), MeI (2 equiv.), K_2CO_3 (2 equiv.), in DMF (1 mL), stirring at R.T. for 5 h under an air atmosphere.

In contrast to the observed thiocarboxylate anions, with nucleophiles such as thiourea and sodium acetate, different reaction outcomes were noticed (Scheme 5). These findings suggest unique reactivity pattern for the thioacid analogues[35] under the selected conditions.

Conclusions

In summary, we have developed a practical one-pot stereoselective methodology to synthesize β-sulfur-substituted enol esters in a multicomponent fashion with high atom economy.[36] The described transition metal-free protocol tolerates air atmosphere and can be conducted at room temperature in non-dried polar aprotic solvents. Moreover, several functional groups are perfectly compatible with this methodology, including electron-donating and -withdrawing substituents. Most of the obtained compounds are bench stable (for months). The availability of several α-haloketones and alkyl halides makes the system a powerful tool to create chemical diversity in a straightforward manner.[37]

Experimental section

General methods

^{1}H and ^{13}C NMR spectra were recorded at 400.16 and 100.62 MHz respectively on a Bruker 400 spectrometer, and chemical shifts were reported in δ (ppm) relative to TMS with $CDCl_3$ as the solvent. GC-FID measurements were performed on an Agilent 6890 apparatus equipped with a 30 m capillary column of a 0.32 mm × 0.25 μm film thickness, with a 5% phenylpolysiloxane phase. GC-MS analyses were performed on a Shimadzu apparatus by electronic impact (70 eV) positive mode employing a 30 m × 0.25 mm × 0.25 μm with a 5%

phenylpolysiloxane phase column. HRMS were recorded on a MicroTOF Q II equipment, operated with an ESI source and positive mode, using nitrogen as the nebulizing and drying gas and sodium formate 10 mM as the internal calibrant. IR spectra were obtained on an FT-IR Avatar 360 spectrometer. Melting points were recorded on capillary tubes in regular Electrothermal IA9100 apparatus.

General experimental methods

All reactions were performed under an air atmosphere in a 10 mL round-bottom flask. DMF, MeCN and DMSO were used without further purification and stored over molecular sieves (4 Å). Toluene, dioxane, THF, DME, and DCM were distilled by standard procedures and stored over molecular sieves (4 Å). Ultrapure water and ethanol were used without further purification. Commercially available reagents were used without further purification. α-Haloketones were prepared from the corresponding ketones following standard procedures.[38] The identity of all products was confirmed by ^{1}H and ^{13}C NMR, MS and IR.

General procedure for the multicomponent synthesis of β-alkylsulfide enol esters

The reactions were carried out in a 10 mL round-bottom flask, equipped with a magnetic bar. The flask was charged keeping the following addition order to ensure best yields: DMF (1.0 mL), thiocarboxylate (0.44 mmol), α-haloketone (0.44 mmol), alkyl or benzyl halide (generally 0.44 mmol, except for MeI, 0.88 mmol) and the base (0.88 mmol) were added and the mixture was stirred at room temperature for 5 h. Then, ethyl acetate (2 mL) and water (2 mL) were added and the mixture was stirred. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 2 mL). The combined organic extract was dried over anhydrous Na_2SO_4 and the products were isolated by filtration through a silica gel pad from the crude reaction mixture.

Procedure for the photoisomerization experiment

A 50 mL Schlenk tube equipped with a nitrogen gas inlet and a magnetic stirrer was dried under vacuum, filled with N_2, and then loaded with 40 mL of dried acetone. To the degassed solvent, 76.5 mg of **4** (0.368 mmol, 9.2 mM) were added and, while stirring, the reaction was irradiated at 300 nm. During the irradiation (12 h), the reaction progress was analyzed by GC-MS. Finally, the solvent was evaporated and the residue dissolved in $CDCl_3$ for both ^{1}H and ^{13}C NMR analysis.

Synthesis of *S*-phenacyl thioacetate (3)[39]

The reaction was carried out in a 10 mL round-bottom flask, equipped with a magnetic bar. The flask was charged with DMF (1.0 mL), potassium thioacetate (**1**, 50.2 mg, 0.44 mmol) and phenacyl bromide (**2**, 87.3 mg, 0.44 mmol). The mixture was stirred at room temperature for 10 minutes. Ethyl acetate (2 mL) and water (2 mL) were added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 2 mL). The organic layers were pooled together, dried over anhydrous Na_2SO_4. Solvent was evaporated to afford pure **3** as a brownish oil (83.2 mg, quant. yield). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 8.00 (d, J = 7.5 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 4.41 (s, 2H), 2.41 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 194.2, 193.2, 135.5, 133.7, 128.7, 128.5, 36.6, 30.2 ppm. MS (EI): m/z (%) = 152 (8) $[M - CH_2CO]^+$, 105 (100), 77 (33), 43 (19).

(*Z*)-2-(Methylthio)-1-phenylvinyl acetate (4)[40]

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), phenacyl bromide (**2**, 87.6 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether–diethyl ether = 70 : 30) to afford pure **4** as a yellow solid (88.4 mg, 87%); mp 56–58 °C. ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.38–7.27 (m, 4H), 7.27–7.21 (m, 1H), 6.35 (s, 1H), 2.36 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.0, 143.9, 134.0, 128.6, 128.0, 123.7, 116.6, 20.5, 17.0 ppm. IR (neat, cm^{-1}) 2960, 2920, 2850, 1759, 1198, 1180, 1041, 1024, 752. MS (EI): m/z (%) = 208 (12) $[M]^+$, 166 (100), 151 (41), 123 (12), 105 (20), 88 (17), 77 (29), 45 (14), 43 (19). HRMS (ESI^+) calcd for $C_{11}H_{12}NaO_2S$ $[M + Na]^+$ 231.0450; found 231.0465.

Procedure for gram-scale synthesis of (*Z*)-2-((2-iodobenzyl)-thio)-1-phenylvinyl acetate (20)

In a 50 mL round-bottom flask, equipped with a magnetic stirrer, DMF (10 mL), potassium thioacetate (**1**, 0.468 g, 4.1 mmol), 2-chloroacetophenone (0.631 g, 4.1 mmol), 2-iodobenzyl bromide (1.242 g, 4.6 mmol) and K_2CO_3 (1.215 g, 8.2 mmol) were added and the mixture was stirred at room temperature for 5 h. Ethyl acetate (15 mL) and water (15 mL) were added and the mixture was stirred. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 15 mL). The combined organic extract was dried over anhydrous Na_2SO_4 and the crude residue was purified by flash column chromatography on silica gel (eluting with petroleum ether–dichloromethane = 50 : 50) to afford pure **20** as a yellow solid (1.55 g, 3.81 mmol, 93%).

(*Z*)-2-(Methylthio)-1-(*p*-tolyl)vinyl acetate (5)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), 2-bromo-1-(4-tolyl)ethanone (93.4 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether–diethyl ether = 70 : 30) to afford pure **5** as a yellow oil (77.6 mg, 82%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.24 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 6.28 (s, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.1, 144.2, 138.0, 131.3, 129.3, 123.7, 115.3, 21.2, 20.5, 17.0 ppm. IR (neat, cm^{-1}) 2966, 2926, 2837, 1757, 1196, 1174, 1039, 1024, 796, 825. MS (EI): m/z (%) = 222 (12) $[M]^+$, 181 (11), 180 (100), 165 (50), 137 (13), 119 (50), 91 (44), 88 (22), 65 (21), 45 (14), 43 (23).

HRMS (ESI$^+$) calcd for $C_{12}H_{15}O_2S$ $[M + H]^+$ 223.0787, found 223.0809.

(*Z*)-1-(*p*-Methoxyphenyl)-2-(methylthio)vinyl acetate (6)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), 2-bromo-1-(4-methoxyphenyl)ethanone (100.5 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether–diethyl ether = 70 : 30) to afford pure **6** as a white solid (90.0 mg, 89%); mp. 71–73 °C. ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.28 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 6.18 (s, 1H), 3.79 (s, 3H), 2.36 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.1, 159.6, 144.2, 126.9, 125.3, 114.0, 114.0, 55.3, 20.5, 17.0 ppm. IR (neat, cm^{-1}) 2980, 2926, 2850, 1755, 1200, 1178, 1039, 1257, 741, 796, 825. MS (EI): m/z (%) = 238 (18) $[M]^+$, 196 (100), 181 (68), 135 (22), 107 (16), 92 (12), 77 (21), 43 (20). HRMS (ESI$^+$) calcd for $C_{12}H_{15}O_3S$ $[M + H]^+$ 239.0736, found 239.0738.

(*Z*)-1-(*p*-Cyanophenyl)-2-(methylthio)vinyl acetate (7)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), 2-bromo-1-(4-cyanophenyl)ethanone (98.2 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with diethyl ether) to afford pure **7** as a yellow solid (98.3 mg, 98%); mp 79–81 °C. ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.58 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 6.61 (s, 1H), 2.42 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 167.8, 141.5, 138.0, 132.4, 123.8, 121.8, 118.7, 110.9, 20.4, 17.0 ppm. IR (neat, cm^{-1}) 2958, 2920, 2850, 2224, 1757, 1180, 1035, 1020, 741, 795, 833. MS (EI): m/z (%) = 233 (7) $[M]^+$, 191 (100), 176 (30), 148 (11), 130 (15), 102 (21), 45 (13), 43 (43). HRMS (ESI$^+$) calcd for $C_{12}H_{12}NO_2S$ $[M + H]^+$ 234.0583, found 234.0583.

(*Z*)-2-(Methylthio)-1-(*p*-nitrophenyl)vinyl acetate (8)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), 2-bromo-1-(4-nitrophenyl)ethanone (105.4 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with diethyl ether) to afford pure **8** as an orange solid (98.6 mg, 92%); mp 95–97 °C. ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 8.14 (d, J = 9.0 Hz, 2H), 7.44 (d, J = 9.0 Hz, 2H), 6.70 (s, 1H), 2.44 (s, 3H), 2.34 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 167.8, 146.7, 141.2, 139.8, 124.1, 123.8, 123.0, 20.4, 17.0 ppm. IR (neat, cm^{-1}) 2926, 2850, 1757, 1107, 1585, 1508, 1196, 1180, 1036, 1020, 854, 833, 800, 748. MS (EI): m/z (%) = 253 (7) $[M]^+$, 212 (17), 211 (100), 150 (35), 121 (16), 104 (13), 76 (15), 43 (68). HRMS (ESI$^+$) calcd for $C_{11}H_{12}NO_4S$ $[M + H]^+$ 254.0482, found 254.0497.

2-(Methylthio)-3,4-dihydronaphthalen-1-yl acetate (9)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), 2-chloro-3,4-dihydronaphthalen-1(2*H*)-one (79.5 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether–diethyl ether = 90 : 10) to afford pure **9** as a yellow solid (77.2 mg, 75%); mp 63.5–65.1 °C. ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.19–7.10 (m, 3H), 7.04–7.02 (m, 1H), 2.97–2.92 (m, 2H), 2.67–2.63 (m, 2H), 2.35 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.3, 141.7, 134.6, 130.7, 127.4, 127.3, 126.6, 123.9, 120.4, 28.0, 26.4, 20.5, 14.2 ppm. IR (neat, cm^{-1}) 3024, 2931, 2854, 1758, 1187, 1049, 894, 740. MS (EI): m/z (%) = 234 (15) $[M]^+$, 192 (100), 177 (51), 149 (19), 116 (13), 115 (63), 43 (17). HRMS (ESI$^+$) calcd for $C_{13}H_{14}NaO_2S$ $[M + Na]^+$ 257.0607, found 257.0624.

(*Z*)-1-(2-Bromophenyl)-2-(methylthio)vinyl acetate (10)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), 2-bromo-1-(2-bromophenyl)ethanone (121.4 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether–diethyl ether = 80 : 20) to afford pure **10** as a brownish oil (119.5 mg, 95%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.55 (dd, J = 8.0, 1.0 Hz, 1H), 7.40 (dd, J = 7.7, 1.7 Hz, 1H), 7.27 (td, J = 7.6, 1.1 Hz, 1H), 7.13 (td, J = 7.7, 1.7 Hz, 1H), 6.14 (s, 1H), 2.36 (s, 3H), 2.20 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 167.9, 142.7, 135.9, 133.5, 130.7, 129.6, 127.3, 121.4, 121.3, 20.5, 16.9 ppm. IR (neat, cm^{-1}) 3455, 2915, 2854, 1758, 1187, 1018, 756. MS (EI): m/z (%) = 288 (4) $[M]^+$, 246 (39), 244 (39), 165 (100), 150 (61), 43 (43). HRMS (ESI$^+$) calcd for $C_{11}H_{11}BrNaO_2S$ $[M + H]^+$ 286.9736, found 286.9735.

(*Z*)-2-(Methylthio)-1,2-diphenylvinyl acetate (11)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), 2-bromo-1,2-diphenylethanone (121 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with diethyl ether) to afford pure **11** as a light yellow solid (63.7 mg, 51%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.30–7.23 (m, 5H), 7.11–7.06 (m, 5H), 2.29 (s, 3H), 1.86 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.8, 143.2, 135.3, 135.2, 130.6, 128.8, 128.5, 128.3, 127.9, 127.8, 127.7, 20.8, 14.8 ppm. IR (neat, cm^{-1}) 3054, 2915, 2854, 1758, 1434, 1187, 1064, 756, 694. MS (EI): m/z (%) = 284 (10) $[M]^+$, 243 (17), 242 (100), 194 (14), 165 (21), 149 (60), 121 (46), 105 (22), 77 (38), 43 (17). HRMS (ESI$^+$) calcd for $C_{17}H_{16}NaO_4S$ $[M + Na]^+$ 307.0763, found 307.0783.

(*Z*)-2-(Methylthio)-1-phenylvinyl benzoate (12)[41]

The typical above described procedure was followed using first thiobenzoic acid (51.4 μL, 0.44 mmol) with K_2CO_3 (60.7 mg,

0.44 mmol) in order to *in situ* deprotonate it, then phenacyl bromide (2, 87.3 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol) were added. After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether–dichloromethane = 50 : 50) to afford pure **12** as a brownish oil (62.4 mg, 78%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 8.23 (d, J = 7.4 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.41 (d, J = 7.2 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 6.47 (s, 1H), 2.39 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 163.7, 143.9, 134.0, 133.7, 130.3, 129.1, 128.6 (2C), 128.0, 123.8, 116.8, 17.1 ppm. IR (neat, cm^{-1}) 2956, 2918, 2850, 1757, 1194, 1178, 1041, 1024, 750. MS (EI): m/z (%) = 270 (8) $[M]^+$, 106 (8), 105 (100), 77 (33), 51 (7). HRMS (ESI^+) calcd for $C_{16}H_{15}O_2S$ $[M + H]^+$ 271.0787, found 271.0799.

(*Z*)-*O*-Ethyl-*O*-(2-(methylthio)-1-phenylvinyl) carbonothioate (13)

The typical above described procedure was followed using potassium ethyl xanthate (70.4 mg, 0.44 mmol), phenacyl bromide (**2**, 87.3 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was purified by column chromatography on silica gel (eluting with ethyl acetate–pentane = 20 : 80) to afford pure **13** as a yellow oil (70.4 mg, 63%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.39–7.31 (m, 4H), 7.29–7.25 (m, 1H), 6.41 (s, 1H), 4.57 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 192.3, 145.9, 133.6, 128.7, 128.1, 123.9, 117.6, 70.5, 17.1, 13.7 ppm. IR (neat, cm^{-1}) 3039, 2977, 2931, 2852, 174.3, 1604, 1280, 1187, 1002, 817, 756, 694. MS (EI): m/z (%) = 254 (39) $[M]^+$, 207 (46), 166 (51), 151 (81), 137 (96), 134 (100), 105 (96), 103 (28), 88 (42), 77 (97), 51 (29), 45 (33). HRMS (ESI^+) calcd for $C_{12}H_{14}NaO_2S_2$ $[M + Na]^+$ 277.0327, found 277.0323.

(*Z*)-2-((3-(1,3-Dioxoisoindolin-2-yl)propyl)thio)-1-phenylvinyl acetate (14)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), phenacyl bromide (**2**, 87.3 mg, 0.44 mmol), 2-(3-bromopropyl)isoindoline-1,3-dione (235.9 mg, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether–diethyl ether = 50 : 50) to afford pure **14** as a white solid (112.5 mg, 69%); mp 113–115 °C. ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.85 (dd, J = 5.4, 3.1 Hz, 2H), 7.72 (dd, J = 5.4, 3.1 Hz, 2H), 7.38–7.22 (m, 5H), 6.39 (s, 1H), 3.82 (t, J = 7.1 Hz, 2H), 2.81 (t, J = 7.1 Hz, 2H), 2.29 (s, 3H), 2.07 (q, J = 7.1 Hz, 2H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.3, 168.0, 145.1, 134.0, 134.0, 132.1, 128.6, 128.1, 123.9, 123.3, 114.1, 36.8, 31.2, 29.4, 20.5 ppm. IR (neat, cm^{-1}) 2955, 2931, 2852, 1768, 1755, 1705, 1200, 1180, 1039, 1024, 752. HRMS (ESI^+) calcd for $C_{21}H_{20}NO_4S$ $[M + H]^+$ 382.1108, found 382.1129.

(*Z*)-2-(Butylthio)-1-phenylvinyl acetate (15)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), phenacyl bromide (**2**, 87.3 mg, 0.44 mmol), *n*-butyl bromide (95 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether–diethyl ether = 70 : 30) to afford pure **15** as a yellow oil (87.7 mg, 83%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.36–7.20 (m, 5H), 6.39 (s, 1H), 2.76 (t, J = 7.4 Hz, 2H), 2.29 (s, 3H), 1.65 (q, J = 7.4 Hz, 2H), 1.43 (sex, J = 7.4 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.0, 144.1, 134.1, 128.6, 127.9, 123.7, 115.3, 33.6, 32.4, 21.7, 20.5, 13.6 ppm. IR (neat, cm^{-1}) 2958, 2929, 2866, 1761, 1196, 1180, 1041, 1024, 752. MS (EI): m/z (%) = 250 (10) $[M]^+$, 208 (54), 152 (12), 134 (12), 120 (52), 105 (100), 77 (30), 45 (16), 43 (29), 41 (14). HRMS (ESI^+) calcd for $C_{14}H_{19}O_2S$ $[M + H]^+$ 251.1100, found 251.1121.

(*Z*)-2-(Allylthio)-1-phenylvinyl acetate (16)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), phenacyl bromide (**2**, 87.3 mg, 0.44 mmol), allyl bromide (74.0 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether–dichloromethane = 50 : 50) to afford pure **16** as an orange oil (96.9 mg, 94%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.36–7.21 (m, 5H), 6.37 (s, 1H), 5.88 (ddt, J = 16.9, 10.0, 7.2 Hz, 1H), 5.25 (ddt, J = 16.9, 1.3, 0.8 Hz, 1H), 5.19 (dd, J = 10.0, 1.3 Hz, 1H), 3.38 (dt, J = 7.2, 0.8 Hz, 2H), 2.31 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.0, 144.6, 134.1, 133.82, 128.6, 128.0, 123.8, 118.2, 113.4, 36.3, 20.5 ppm. IR (neat, cm^{-1}) 2918, 2850, 1759, 1194, 1186, 1039, 1032, 750. MS (EI): m/z (%) = 234 (13) $[M]^+$, 192 (50), 151 (100), 123 (26), 105 (71), 87 (19), 77 (51), 51 (17), 45 (32), 43 (56), 41 (20). HRMS (ESI^+) calcd for $C_{13}H_{15}O_2S$ $[M + H]^+$ 235.0787, found 235.0807.

(*Z*)-1-Phenyl-2-(prop-2-yn-1-ylthio)vinyl acetate (17)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), phenacyl bromide (**2**, 87.3 mg, 0.44 mmol), prop-2-yn-1-yl-*p*-methylbenzenesulfonate (179 mg, 0.85 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether–dichloromethane = 50 : 50) to afford pure **17** as a brownish oil (72 mg, 71%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.46–7.17 (m, 5H), 6.58 (s, 1H), 3.46 (d, J = 2.6 Hz, 2H), 2.32 (t, J = 2.6 Hz, 1H), 2.30 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 167.9, 145.7, 133.9, 128.7, 128.4, 124.1, 112.3, 79.0, 72.3, 21.2, 20.5 ppm. IR (neat, cm^{-1}) 3292, 2960, 2920, 2860, 1761, 1198, 1180, 1041, 1026, 752. MS (EI): m/z (%) = 232 (66) $[M]^+$, 190 (100), 173 (83), 172 (28), 171 (85), 128 (38), 115 (27), 77 (10), 45 (28), 43 (40). HRMS (ESI^+) calcd for $C_{13}H_{12}NaO_2S$ $[M + Na]^+$ 255.0450, found 255.0470.

(*Z*)-2-((2-Hydroxyethyl)thio)-1-phenylvinyl acetate (18)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), phenacyl bromide (**2**, 87.3 mg, 0.44 mmol), 2-hydroxyethyl iodide (69 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether–dichloromethane = 50 : 50) to afford pure **18** as a yellow oil (67.0 mg, 79%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.35–7.22 (m, 5H), 6.43 (s, 1H), 3.79 (t, J = 5.8 Hz, 2H), 2.90 (t_b, J = 5.8 Hz, 2H), 2.90 (1H, OH, overlapped), 2.31 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.4, 145.4, 128.7, 128.6, 128.3, 123.9, 114.3, 62.1, 36.8, 20.6 ppm. IR (neat, cm^{-1}) 3464, 2960, 2929, 2875, 1755, 1201, 1184, 1041, 1026, 754. MS (EI): m/z (%) = 238 (41) $[M]^+$, 178 (26), 105 (100), 87 (57), 77 (29), 43 (70). HRMS (ESI^+) calcd for $C_{12}H_{15}O_3S$ $[M + H]^+$ 239.0736, found 239.0736.

(1*Z*,1′*Z*)-(Pentane-1,5-diylbis(sulfanediyl))bis(1-phenylethene-2,1-diyl) diacetate (19)

The typical above described procedure was followed using 3 mL of DMF with potassium thioacetate (**1**, 100.4 mg, 0.88 mmol), phenacyl bromide (**2**, 175 mg, 0.88 mmol), 1,5-dibromopentane (59 μL, 0.44 mmol) and K_2CO_3 (242.9 mg, 1.76 mmol). After extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether–diethyl ether = 70 : 30) to afford pure **19** as a brownish oil (135.4 mg, 71%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.37–7.21 (m, 10H), 6.37 (s, 2H), 2.77 (t, J = 7.3 Hz, 4H), 2.30 (s, 6H), 1.70 (q, J = 7.3 Hz, 4H), 1.59–1.49 (m, 2H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.0, 144.5, 134.1, 128.6, 128.0, 123.7, 114.9, 33.7, 29.9, 27.3, 20.6 ppm. IR (neat, cm^{-1}) 2927, 2850, 1757, 1195, 1178, 1039, 1024, 750. HRMS (ESI^+) calcd for $C_{25}H_{29}O_4S_2$ $[M + H]^+$ 457.1502, found 457.1485.

(*Z*)-2-((2-Iodobenzyl)thio)-1-phenylvinyl acetate (20)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), phenacyl bromide (**2**, 87.3 mg, 0.44 mmol), 2-iodobenzyl bromide (130.6 mg, 0.44 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether–dichloromethane = 50 : 50) to afford pure **20** as a yellow solid (168 mg, 96%); mp 103–105 °C. ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.85 (dd, J = 7.7, 1.1 Hz, 1H), 7.40 (dd, J = 7.7, 1.6 Hz, 1H), 7.35–7.31 (m, 1H), 7.31–7.21 (m, 5H), 6.95 (td, J = 7.7, 1.6 Hz, 1H), 6.42 (s, 1H), 4.07 (s, 2H), 2.29 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.0, 145.1, 139.9, 139.9, 134.0, 130.2, 129.3, 128.6, 128.6, 128.2, 123.9, 113.2, 100.6, 42.9, 20.6 ppm. IR (neat, cm^{-1}) 3057, 2926, 2850, 1759, 1198, 1180, 1041, 1024, 750. MS (EI): m/z (%) = 410 (9) $[M]^+$, 369 (15), 368 (85), 217 (100), 151 (43), 135 (17), 107 (20), 105 (42), 90 (44), 89 (22), 77 (33), 43 (56). HRMS (ESI^+) calcd for $C_{17}H_{16}IO_2S$ $[M + H]^+$ 410.9910, found 410.9908.

(*Z*)-2-(((6-Bromobenzo[*d*][1,3]dioxol-5-yl)methyl)thio)-1-phenylvinyl acetate (21)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), phenacyl bromide (**2**, 87.3 mg, 0.44 mmol), 5-bromo-6-(bromomethyl)benzo[*d*]-[1,3]dioxole (139.3 mg, 0.44 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether–dichloromethane = 50 : 50) to afford pure **21** as a yellow solid (154 mg, 86%); mp 91–94 °C. ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.34–7.20 (m, 5H), 6.99 (s, 1H), 6.90 (s, 1H), 6.44 (s, 1H), 5.94 (s, 2H), 4.01 (s, 2H), 2.29 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.0, 147.9, 147.7, 144.9, 133.9, 130.0, 128.6, 128.2, 123.9, 114.9, 113.2, 112.8, 110.3, 102.0, 37.9, 20.6 ppm. IR (neat, cm^{-1}) 2958, 2924, 2861, 1761, 1198, 1180, 1039, 1204, 933, 966, 752. MS (EI): m/z (%) = 408 (5), 406 (5) $[M]^+$, 366 (10), 364 (10), 215 (100), 213 (97), 78 (13), 77 (16), 43 (23). HRMS (ESI^+) calcd for $C_{18}H_{16}BrO_4S$ $[M + H]^+$ 406.9947, found 406.9958.

(*Z*)-2-(Benzylthio)-1-phenylvinyl acetate (22)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), phenacyl bromide (**2**, 87.3 mg, 0.44 mmol), benzyl bromide (52.2 μL, 0.44 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether–diethyl ether = 70 : 30) to afford pure **22** as a yellow solid (101.4 mg, 84%); mp 80–82 °C. ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.35–7.27 (m, 10H), 6.34 (s, 1H), 3.97 (s, 2H), 2.29 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.0, 144.6, 137.1, 134.0, 129.0, 128.8, 128.6, 128.1, 127.5, 123.8, 113.6, 37.8, 20.6 ppm. IR (neat, cm^{-1}) 2960, 2918, 2850, 1751, 1198, 1178, 1037, 1024, 752. MS (EI): m/z (%) = 242 (32) $[M]^+$, 151 (12), 105 (20), 91 (100), 77 (15), 65 (10), 43 (23). HRMS (ESI^+) calcd for $C_{17}H_{17}O_2S$ $[M + H]^+$ 285.0944, found 285.0965.

4-(*tert*-Butyl)-2-(methylthio)cyclohex-1-en-1-yl acetate (23)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), 2-bromo-4-(*tert*-butyl)cyclohexanone (102.5 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (242.8 mg, 1.76 mmol). After extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether–diethyl ether = 95 : 5) to afford pure **23** as a colorless oil (64 mg, 60%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 2.37–2.31 (m, 1H), 2.31–2.23 (m, 1H), 2.19 (s, 3H), 2.17 (s, 3H), 2.13–2.37 (m, 1H), 2.13–2.04 (m, 1H), 1.91–1.83 (m, 1H), 1.49–1.41 (m, 1H), 1.40–1.30 (m, 1H), 0.91 (s, 9H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.7, 145.4, 119.6, 44.5, 32.3, 29.8, 29.2, 27.3, 23.8, 20.8, 14.0 ppm. ^{1}H–^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 2.38–2.31/2.13–2.04, 2.38–2.31/1.49–1.41, 2.31–2.23/2.13–2.37, 2.31–2.23/1.91–1.83, 2.31–2.23/1.40–1.30, 2.13–2.37/1.91–1.83, 2.13–2.37/1.40–1.30, 2.13–2.04/1.49–1.41, 1.91–1.83/1.49–1.41, 1.91–1.83/1.40–1.30, 1.49–1.41/1.40–1.30. ^{1}H–^{13}C HSQC NMR

($CDCl_3$) δ_H/δ_C 2.38–2.31/29.8, 2.31–2.23/29.2, 2.19/14.0, 2.17/20.8, 2.13–2.37/29.2, 2.13–2.04/29.8, 1.91–1.83/23.8, 1.49–1.41/44.5, 1.40–1.30/23.8, 0.91/27.3. ^{1}H–^{13}C HMBC NMR ($CDCl_3$) δ_H/δ_C 2.38–2.31/145.4, 2.38–2.31/119.6, 2.38–2.31/44.5, 2.38–2.31/23.8, 2.31–2.23/145.4, 2.31–2.23/119.6, 2.31–2.23/44.5, 2.31–2.23/23.8, 2.19/119.6, 2.17/168.7, 2.13–2.37/145.4, 2.13–2.37/44.5, 2.13–2.37/29.8, 2.13–2.37/23.8, 2.13–2.04/145.4, 2.13–2.04/119.6, 2.13–2.04/44.5, 2.13–2.04/32.3, 2.13–2.04/23.8, 1.91–1.83/145.4, 1.91–1.83/32.3, 1.91–1.83/29.2, 1.49–1.41/32.3, 1.49–1.41/27.3, 1.49–1.41/23.8, 1.40–1.30/154.4, 1.40–1.30/44.5, 1.40–1.30/29.8, 1.40–1.30/29.2, 0.91/44.5, 0.91/32.3. IR (neat, cm^{-1}) 2960, 2920, 2868, 1755, 1217, 1174, 1039. MS (EI): *m*/*z* (%) = 242 (5) $[M]^+$, 200 (100), 143 (11), 116 (31), 95 (14), 73 (15), 57 (20), 55 (13), 43 (31), 41 (19). HRMS (ESI^+) calcd for $C_{13}H_{23}O_2S$ $[M + H]^+$ 243.1413, found 243.1417.

(*Z*)-Ethyl 2-acetoxy-3-(benzylthio)acrylate (24)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), ethyl 3-bromo-2-oxopropanoate (85.4 mg, 0.44 mmol), benzyl bromide (52.2 μL, 0.44 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane) to afford pure **24** as a yellow oil (83.6 mg, 68%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.37–7.27 (m, 5H), 7.28 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 2H), 2.22 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.0, 160.2, 136.2, 134.2, 131.6, 128.9, 128.9, 127.9, 61.3, 37.9, 20.2, 14.1 ppm. IR (neat, cm^{-1}) 3054, 2977, 2931, 2854, 1758, 1712, 1234, 1187, 1095, 1018, 740, 694. MS (EI): *m*/*z* (%) = 264 (34), 173 (20), 91 (100), 87 (16), 85 (33), 65 (11), 57 (17), 43 (40). HRMS (ESI^+) calcd for $C_{14}H_{16}NaO_4S$ $[M + Na]^+$ 303.0662, found 303.0671.

(*Z*)-1-((2-Iodobenzyl)thio)oct-1-en-2-yl acetate (25)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), 1-bromooctan-2-one (91.0 mg, 0.44 mmol), 2-iodobenzyl bromide (130.6 mg, 0.44 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether) to afford pure **25** as a colorless oil (93.2 mg, 52%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.83 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.37–7.28 (m, 2H), 6.94 (td, *J* = 7.7, 1.8 Hz, 1H), 5.56 (s, 1H), 3.92 (s, 2H), 2.22–2.18 (m, 2H), 2.14 (s, 3H), 1.4 (m, 2H), 1.30–1.25 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 168.1, 150.1, 140.2, 139.8, 130.1, 128.9, 128.4, 109.6, 100.5, 42.9, 33.8, 31.5, 28.6, 26.3, 22.5, 20.7, 14.1 ppm. IR (neat, cm^{-1}) 3054, 2977, 2931, 2854, 1758, 1712, 1234, 1187, 1095, 740, 709. MS (EI): *m*/*z* (%) = 418 (2) $[M]^+$, 376 (46), 217 (100), 135 (15), 90 (36), 43 (57). HRMS (ESI^+) calcd for $C_{17}H_{23}INaO_2S$ $[M + Na]^+$ 441.0356, found 441.0375.

(*Z*)-1-((3r,5r,7r)-Adamantan-1-yl)-2-(benzylthio)vinyl acetate (26)

The typical above described procedure was followed using potassium thioacetate (**1**, 50.2 mg, 0.44 mmol), 1-((3r,5r,7r)-adamantan-1-yl)-2-bromoethanone (113.1 mg, 0.44 mmol), benzyl bromide (52.2 μL, 0.44 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether) to afford pure **26** as a yellow solid (60.2 mg, 40%); mp 93.1–93.9 °C. ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.31 (d, *J* = 4.2 Hz, 4H), 7.28–7.22 (m, 1H), 5.55 (s, 1H), 3.83 (s, 2H), 2.19 (s, 3H), 1.98 (s, 3H), 1.71–1.61 (m, 12H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 167.8, 155.9, 137.5, 129.0, 128.5, 127.2, 108.4, 39.7, 38.6, 37.9, 36.6, 28.1, 20.5 ppm. IR (neat, cm^{-1}) 3471, 3070, 2915, 2854, 2669, 1743, 1187, 1033. MS (EI): *m*/*z* (%) = 342 (3) $[M]^+$, 300 (51), 207 (24), 135 (55), 91 (100), 79 (11), 43 (21). HRMS (ESI^+) calcd for $C_{21}H_{26}O_2S$ $[M + H]^+$ 343.1726, found 343.1728.

2-Oxo-2-phenylethyl acetate (27)[42]

The typical above described procedure was followed using sodium acetate (36.1 mg, 0.44 mmol), phenacyl bromide (**2**, 87.3 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with petroleum ether) to afford pure **27** as a yellow solid (33.7 mg, 43%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.92–7.89 (m, 2H), 7.62–7.58 (m, 1H), 7.50–7.46 (m, 2H), 5.33 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 192.2, 170.4, 134.2, 133.9, 128.9, 127.8, 66.0, 20.6 ppm. IR (neat, cm^{-1}) 3054, 2931, 2854, 1743, 1697, 1218, 1080, 971, 755, 694. MS (EI): *m*/*z* (%) = 118 (4) $[(M - AcOH)]^+$, 105 (100), 77 (33), 51 (10), 43 (16).

4-Phenylthiazol-2-amine (28)[43]

The typical above described procedure was followed using thiourea (33.4 mg, 0.44 mmol), phenacyl bromide (**2**, 87.3 mg, 0.44 mmol), methyl iodide (50.4 μL, 0.88 mmol) and K_2CO_3 (121.4 mg, 0.88 mmol). After extraction, the crude residue was passed through a silica gel pad (eluting with dichloromethane) to afford pure **28** as a light yellow solid (47.2 mg, 61%). ^{1}H NMR (400.16 MHz, $CDCl_3$, 30 °C): δ = 7.78–7.75 (m, 2H), 7.40–7.35 (m, 2H), 7.31–7.26 (m, 1H), 6.71 (s, 1H), 5.24 (s, 2H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 30 °C): δ = 167.4, 151.4, 134.7, 128.6, 127.7, 126.0, 102.8 ppm. IR (neat, cm^{-1}) 3440, 3255, 3116, 3070, 2915, 2854, 1743, 1697, 694. MS (EI): *m*/*z* (%) = 176 (100) $[M]^+$, 134 (65), 104 (11), 90 (15), 89 (18). HRMS (ESI^+) calcd for $C_9H_8N_2S$ $[M + H]^+$ 177.0481, found 177.0498.

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