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Tandem Chemoselective 1,2-/1,4-Migration of the Thio Group in Keto Thioesters: An Efficient Approach to Substituted Butenolides

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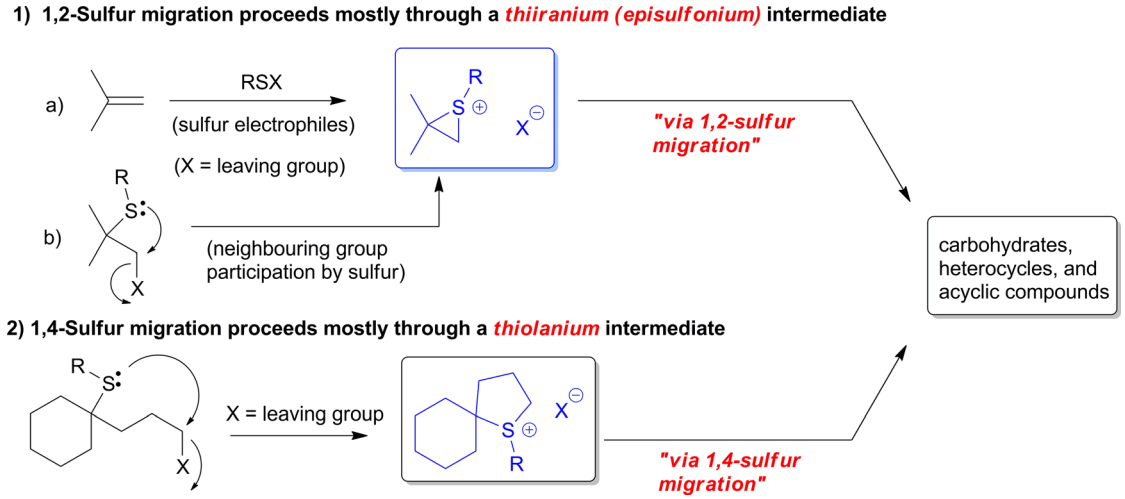
Abstract: We report herein an efficient and mechanistically unique tandem chemoselective 1,2-/1,4-migration of the thio group in keto thioesters that provides substituted butenolides in moderate to excellent yields. Thus, α-keto thioesters in the presence of stabilized phosphonate carbanions undergo tandem 1,2-sulfur migration; whereas 1,4-migration of the thio group has been achieved with the same thioesters after the treatment with Wittig reagents followed by $BF_3{\cdot}OEt_2$-catalyzed tandem reaction. The crossover experiments and the isolation of intermediates reveal a stepwise mechanism for both of these transformations.

Keywords: heterocycles; isomerization; keto thioesters; rearrangement; sulfanyl group migration

Introduction

Sulfanyl group migration is an important chemical transformation and has been extensively studied in the synthesis of modified carbohydrates, heterocycles as well as acyclic compounds.[1,2] Several elegant approaches have been developed for the 1,2-migration of the thio group in the past few years.[1] Among the numerous methods developed, the most common route reported so far proceeds mainly through a key thiiranium intermediate, which undergoes either rearrangement and elimination or substitution reactions [Scheme 1; Eq. (1)]. Unlike 1,2-migration of the thio group, there has been limited success in 1,4-sulfanyl



Scheme 1. Common strategies for the 1,2-/1,4-migration of the thio group.

group migration.[1a,2] The most common route reported so far proceeds through the thiolanium intermediate [Scheme 1; Eq. (2)]. To the best of our knowledge, there are no reports of tandem chemoselective 1,2-/1,4-migration of the thio group from keto thioesters.

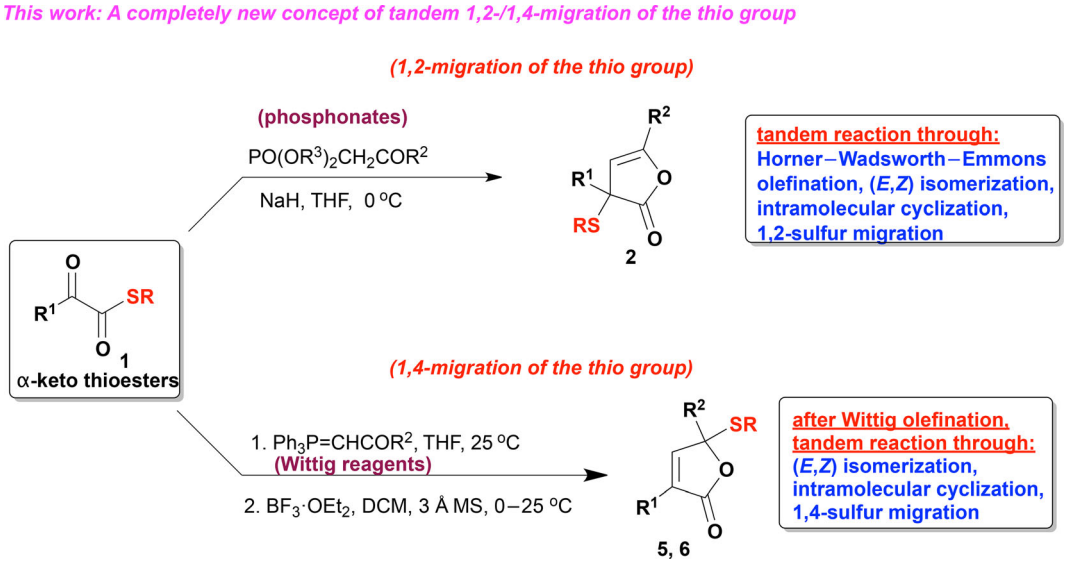
Substituted butenolides with one or more quaternary centres are privileged structural motifs occurring in a plethora of biologically active natural products and pharmaceutically important molecules.[3] However, chemical synthesis of such molecules is very challenging and has remained a dynamic area of research for the past few decades.[4,5] Several elegant approaches have been developed for their synthesis,[4] which are mostly limited to the direct functionalization of pre-existing substituted butenolide scaffolds.[5] Therefore, general approaches for the construction of these essential scaffolds, under metal-free/ligand-free conditions, are still highly desirable.

Herein we describe a novel tandem chemoselective 1,2-/1,4-migration of the thio group in keto thioesters (Scheme 2). This unprecedented cascade allows the development of an efficient and practical method for the synthesis of substituted butenolide skeletons bearing multiple reactive sites for further functionalization. We found that α-keto thioesters in the presence of Horner–Wadsworth–Emmons reaction conditions undergo tandem 1,2-sulfur migration whereas tandem 1,4-migration of the thio group has been observed in the presence of $BF_3{\cdot}OEt_2$ with γ-keto thioesters. More importantly, we have shown for the first time that 1,2-/1,4-migration of the thio group proceeds without any conventional thiiranium/thiolanium ion intermediates, respectively.

Results and Discussion

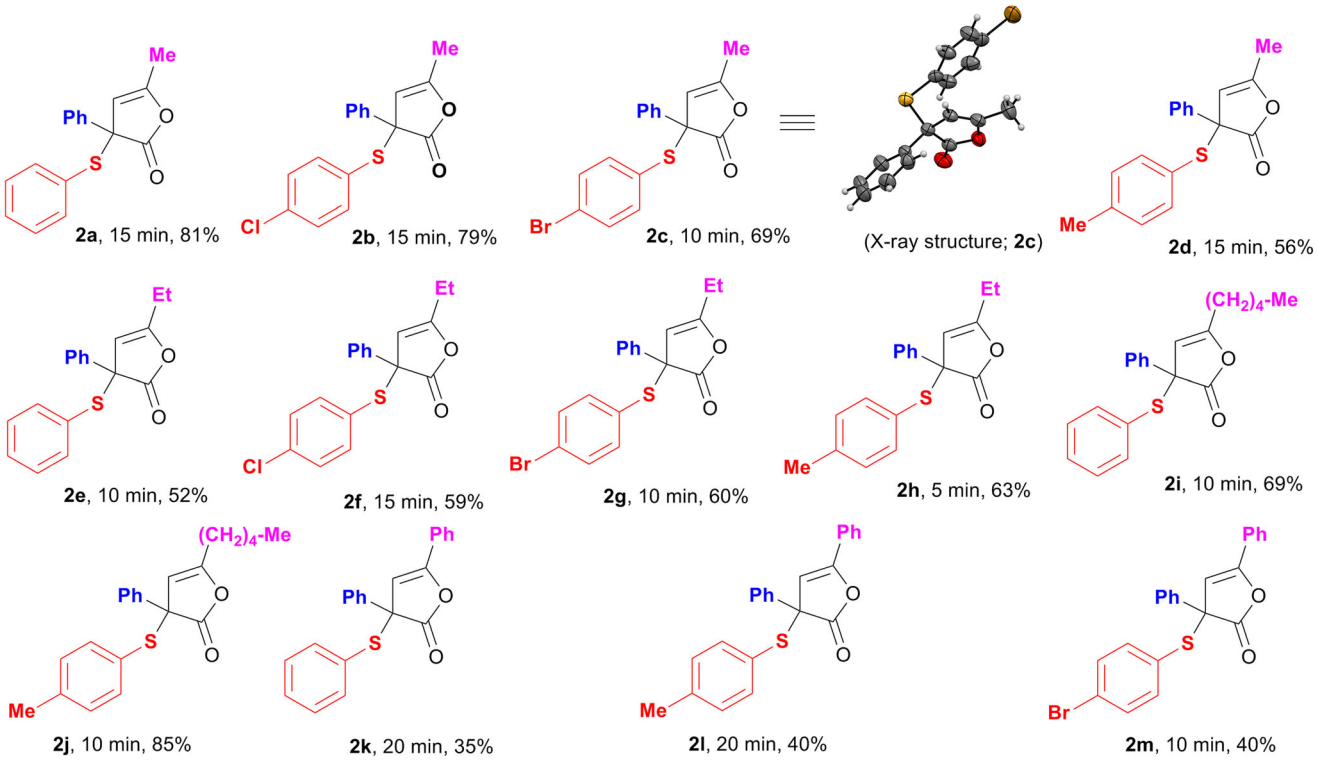
To optimize the reaction conditions for the tandem chemoselective 1,2-migration of the thio group, we began our investigation with α-keto thioester **1a** as the model substrate and commercially available phosphonates/Wittig salts as the source of olefin (see the Supporting Information for optimization studies). To our delight, the conversion could be achieved smoothly and efficiently when one equivalent of dimethyl 2-oxopropylphosphonate (**A**) was used in the presence of NaH (1.5 equiv.) and THF at 0 °C. We isolated **2a** in 81% yield, although minor amount of **3a** resulting from the tandem 1,4-sulfur migration was also observed. However, decrease or increase in base/phosphonate loading led to a reduction in product yield. A brief screening of the phosphonate/Wittig salt indicated that the electronic nature/steric bulk/nucleophilicity of the reagents have an obvious effect on the reaction and phosphonate **A** proved to be the best with respect to both the yields and the reaction time. Different bases such as NaOEt, NaO-*t*-Bu, and DBU failed to deliver the desired product **2a** in good yields.

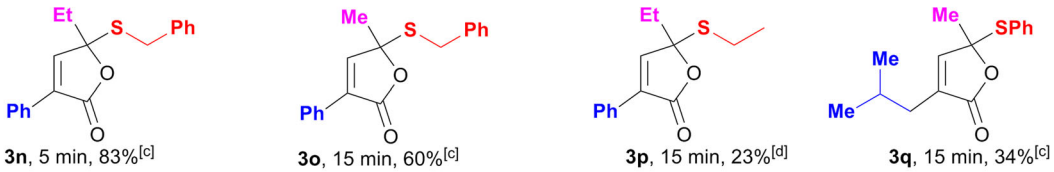
Subsequently, we investigated the substrate scope and generality of this transformation with α-keto thioesters[6] having aromatic thiols under the optimized conditions (Table 1). We observed that all these reactions proceeded smoothly *via* tandem 1,2-migration of the thio group and produced the substituted butenolides in moderate to good yields (**2a–j**, Table 1). However, the presence of a phenyl group in the phosphonate delivered the corresponding butenolides (**2k–m**, Table 1) only in moderate yields, ostensibly owing to the electronic nature/steric bulk of the phosphonate. The structure of **2c** was established by a single crystal X-ray diffraction analysis.[7] Surprisingly, replacement



Scheme 2. Proposed tandem chemoselective1,2-/1,4-migration of the thio group for accessing substituted butenolides.

Table 1. Substrate scope for accessing butenolides *via* the tandem 1,2-migration of the thio group.[a,b]





[a] *Reaction conditions:* NaH (1.5 equiv./mmol), phosphonate (1.0 equiv./mmol), and THF (2.0 mL) were stirred at 0 °C for 1 h; the phosphonate-stabilized carbanion was added dropwise *via* syringe to a stirred solution of **1** (0.05 g, 1.0 equiv.) in THF (1.5 mL) at 0 °C, employing the time as mentioned; yields are of isolated products.

[b] Minor amount of the tandem 1,4-sulfur migration product **3** was observed.

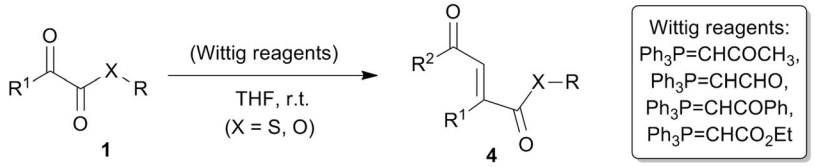
[c] Isolated exclusively as the 1,4-sulfur migration product.

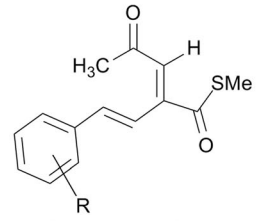
[d] Along with **3p**, inseparable mixtures of the 1,2-sulfur migration product **2p** and the corresponding olefin were isolated in minor amounts.

of an aromatic thiol with an aliphatic thiol in α-keto thioesters led to the formation of butenolides resulting from the tandem 1,4-migration of the thio group (**3n–p**, Table 1), instead of the expected 1,2-sulfur migration (see also Table 4, *vide infra*). Similarly, replacement of the α-phenyl group with either an isobutyl group (**3q**, Table 1) or a styrenyl substrate (**5a**, Table 3, *vide infra*) revealed the same situation. This might be attributed to the higher reactivity of the corresponding α-keto thioesters having aliphatic thiol/α-alkyl group, although the exact reason is not very clear at the moment. The formation of α-styrenyl-substituted butenolide **5a** in low yields might be attributed, after the initial formation of the highly conjugated γ-keto thioester *via* Horner–Wadsworth–Emmons olefination reaction, to the possibility of a competing Michael-type addition which might play an important role.

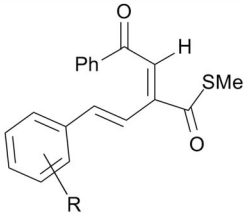
To expand the domain for the 1,4-sulfur migration and to achieve higher yields with α-styrenyl substrates, conjugated γ-keto thioesters or γ-keto oxoesters **4** were synthesized from α-keto thioesters or α-keto oxoesters **1** *via* the standard Wittig olefination reaction (Table 2).[8,9] All the reactions proceeded in

Table 2. Synthesis of γ-keto thioesters or γ-keto oxoesters **4** from substituted α-keto thioesters or α-keto oxoesters **1** *via* Wittig olefination.[a]

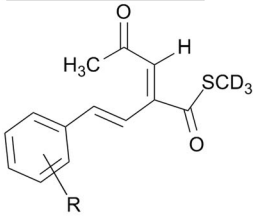




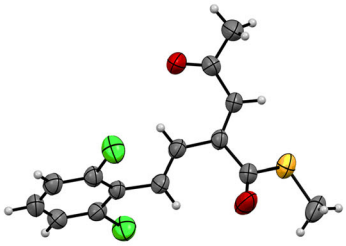
4aa: C_6H_5; 1 h, 84%
4ab: 4-OMe-C_6H_4; 7 h, 66%
4ac: 3,4-$(OMe)_2$-C_6H_3; 14 h, 61%
4ad: 4-Me-C_6H_4; 4 h, 71%
4ae: 2,6-$(Cl)_2$-C_6H_3; 2 h, 64%
4af: 4-Cl-C_6H_4; 1 h, 81%
4ag: 4-F-C_6H_4; 1 h, 80%
4ah: 2-Br-C_6H_4; 2 h, 58%
4ai: 3-CN-C_6H_4; 1.5 h, 85%
4aj: 3-NO_2-C_6H_4; 2 h, 0 °C, 51%
4ak: 2-naphthyl; 3 h, 89%
4al: 1-naphthyl; 2 h, 83%
4am: 2-thienyl; 3 h, 82%



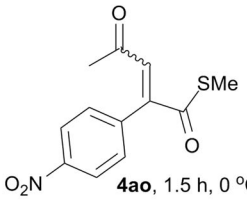
4av: C_6H_5[b]
4aw: 4-Me-C_6H_4[b]
4ax: 2,4-$(Cl)_2$-C_6H_3[b]



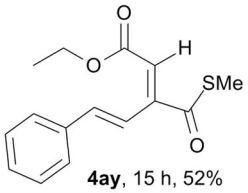
4bd: 3,4-$(OMe)_2$-C_6H_3; 14 h, 57%
4be: C_6H_5; 1 h, 74%



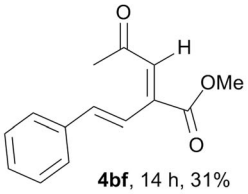
(X-ray structure; **4ae**)



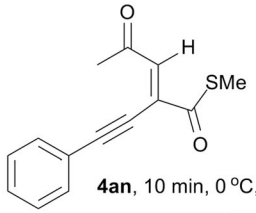
4ao, 1.5 h, 0 °C, 71%
trans:*cis* = ~1:1



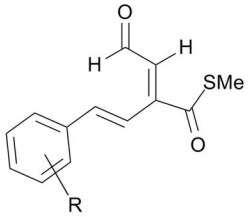
4ay, 15 h, 52%



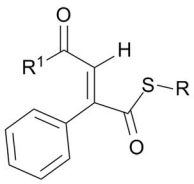
4bf, 14 h, 31%



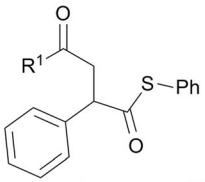
4an, 10 min, 0 °C, 42%



4ap: C_6H_5; 4 h, 36%
4aq: 4-Me-C_6H_4; 14 h, 44%
4ar: 4-Cl-C_6H_4; 5 h, 56%
4as: 4-CN-C_6H_4; 2 h, 36%
4at: 2-naphthyl; 16 h, 31%
trans:*cis* = 7:1
4au: 3-thienyl; 14 h, 27%



4az: R = Ph; R^1 = Me; 1 h, 43%
4ba: R = 2-naphthyl; R^1 = Me; 1.5 h, 35%
4bb: R = benzyl; R^1 = Me; 3 h, 70%
4bc: R = benzyl; R^1 = Ph; 10 h, 40%



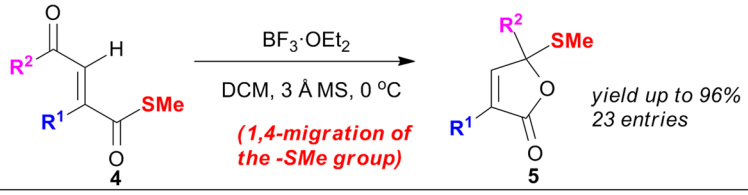
4bg: R^1 = Ph; 86%[c]
4bh: R^1 = Me; 54%[c]

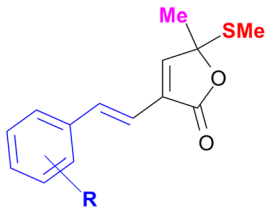
[a] *Reaction conditions:* **1** (0.1 g, 1.0 equiv.), corresponding Wittig reagent (2.0 equiv./mmol), dry THF (4.0 mL), argon atmosphere, ambient temperature or at 0 °C, employing the time as mentioned; yields are of isolated products.
[b] Used directly in the next step after passage through a short column.
[c] See the Supporting Information for their syntheses.

full conversion and only the corresponding *trans*-isomer was isolated, except in a few cases where both *cis*- and *trans*-isomers were formed (**4ao** and **4at**, Table 2). The structure of **4ae** was established by a single-crystal X-ray diffraction analysis.[7]

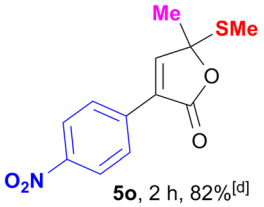
After successfully synthesizing conjugated γ-keto thioesters, we began our optimization studies with **4aa** as the model substrate for the chemoselective 1,4-migration of the thio group (see the Supporting Information for optimization studies). To our delight, the conversion could be achieved smoothly and in excellent yield when one equivalent of $BF_3{\cdot}OEt_2$ was used as a catalyst in the presence of 3 Å MS and DCM as a solvent. However, decrease or increase in catalyst loading led to a reduction in product yield. Among the solvents tested, DCM proved to be the best with respect to both the yields and the reaction time. The reaction did not proceed well when conducted with

Table 3. Substrate scope of γ-ketomethyl, γ-aldehyde, and γ-ketophenyl derivatives for accessing butenolides *via* the tandem 1,4-sulfur migration.[a,b]

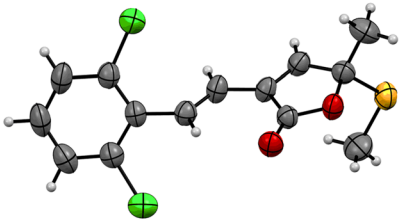




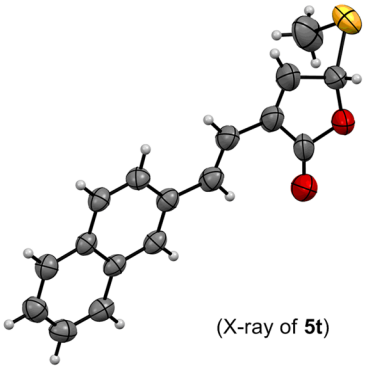
5a: C_6H_5; 1 h, 96%
5a: C_6H_5; 10 min, 8%[b]
5a: C_6H_5; 1 h, 92%[c]
5b: 4-OMe-C_6H_4; 0.5 h, 82%
5c: 3,4-$(OMe)_2$-C_6H_3; 20 min, 80%
5d: 4-Me-C_6H_4; 1 h, 70%
5e: 2,6-$(Cl)_2$-C_6H_3; 2 h, 88%
5f: 4-Cl-C_6H_4; 0.5 h, 80%
5g: 4-F-C_6H_4; 40 min, 74%
5h: 2-Br-C_6H_4; 45 min, 76%
5i: 3-CN-C_6H_4; 1.5 h, 80%
5j: 3-NO_2-C_6H_4; 0.5 h, 78%
5k: 2-naphthyl; 45 min, 76%
5l: 1-naphthyl; 1 h, 82%
5m: 2-thienyl; 0.5 h, 90%



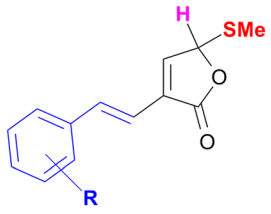
5o, 2 h, 82%[d]



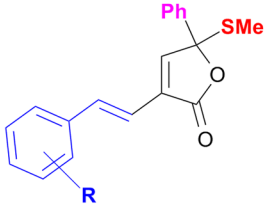
(X-ray of **5e**)



(X-ray of **5t**)



5p: C_6H_5; 20 min, 50%
5q: 4-Me-C_6H_4; 20 min, 40%
5r: 4-Cl-C_6H_4; 10 min, 46%
5s: 4-CN-C_6H_4; 30 min, 50%
5t: 2-naphthyl; 10 min, 56%
5u: 3-thienyl; 20 min, 40%



5v: C_6H_5; 10 min, 56%[e]
5w: 4-Me-C_6H_4; 20 min, 44%[e]
5x: 2,4-$(Cl)_2$-C_6H_3; 15 min, 60%[e]

[a] *Reaction conditions:* **4** (0.05 g, 1.0 equiv.), $BF_3{\cdot}OEt_2$ (1.0 equiv.), 3 Å MS (0.05 g), DCM (2.0 mL), 0 °C, argon atmosphere, employing the time as mentioned; yields are of isolated products.
[b] Reaction conditions same as in Table 1.
[c] Batch size: 2.03 mmol of **4aa**, DCM (20 mL), and $BF_3{\cdot}OEt_2$ (50 mol%).
[d] The reaction was carried out at 0 °C for 30 min followed by stirring at room temperature.
[e] The reaction was carried out at −10 °C.

a Brønsted acid such as trifluoromethanesulfonic acid (CF_3SO_3H) or with different Lewis acids such as $Sc(OTf)_3$, $In(OTf)_3$, $TiCl_4$, $SnCl_4$, or TMSOTf.

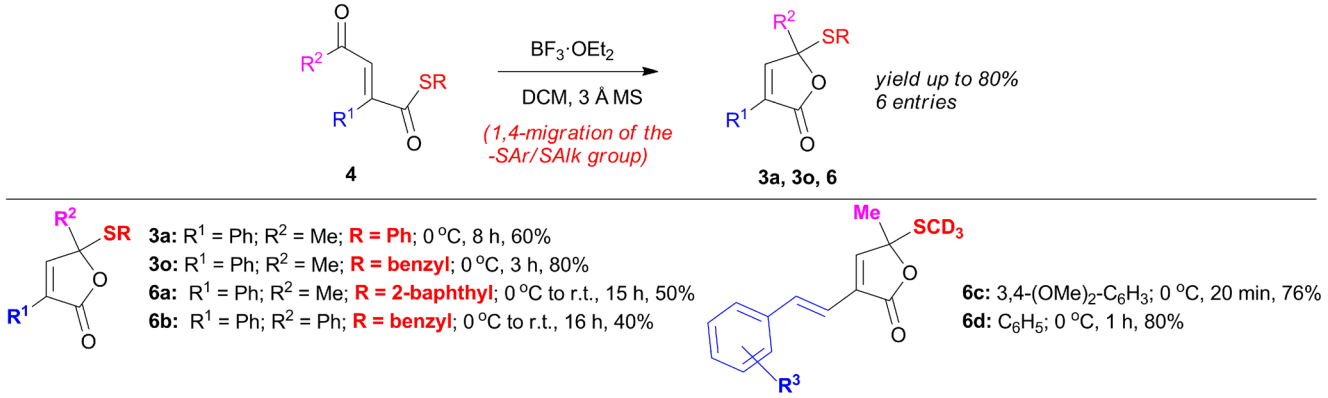
Under the optimized conditions, we investigated the substrate scope and generality for this transformation with α-substituted conjugated γ-ketomethyl thioesters (Table 3). We observed that various α-substituted styrenyl substrates and vinyl substituted polynuclear aromatic hydrocarbons or heteroaryl substituents, and substituted aromatic substrates underwent smooth conversion *via* tandem 1,4-sulfanyl group migration and produced the substituted butenolides in good to excellent yields (**5a–m**, **5o**, Table 3). To show the efficacy of the developed cascade, we conducted the reaction with 2.0 mmol of **4aa**, and isolated **5a** without any significant diminution in the yield (Table 3). However, the presence of an alkynyl group on the α-position of γ-ketomethyl thioester **4an** did not result in any expected product, may be due to the high reactivity of the alkynyl group.

Subsequently, various γ-aldehyde/γ-ketophenyl thioesters were tested and found to be compatible under the standard reaction conditions (**5p–x**, Table 3). The moderate yields obtained (**5p–x**, Table 3) were due either to the lack of stability of the *in situ* generated secondary carbocation for γ-aldehyde substituents or to the inherent reactivity of γ-ketophenyl derivatives. However, in case of γ-ketophenyl derivatives (**5v–x**, Table 3) the involvement of steric factors during 1,4-migration of the thio group cannot be ruled out. On the other hand, the presence of an ester group on the γ-position in **4ay** resulted in no conversion, ostensibly due to the lack of poor nucleophilic character of the ester carbonyl group. The structures of **5e** and **5t** was established by a single crystal X-ray diffraction analysis.[7]

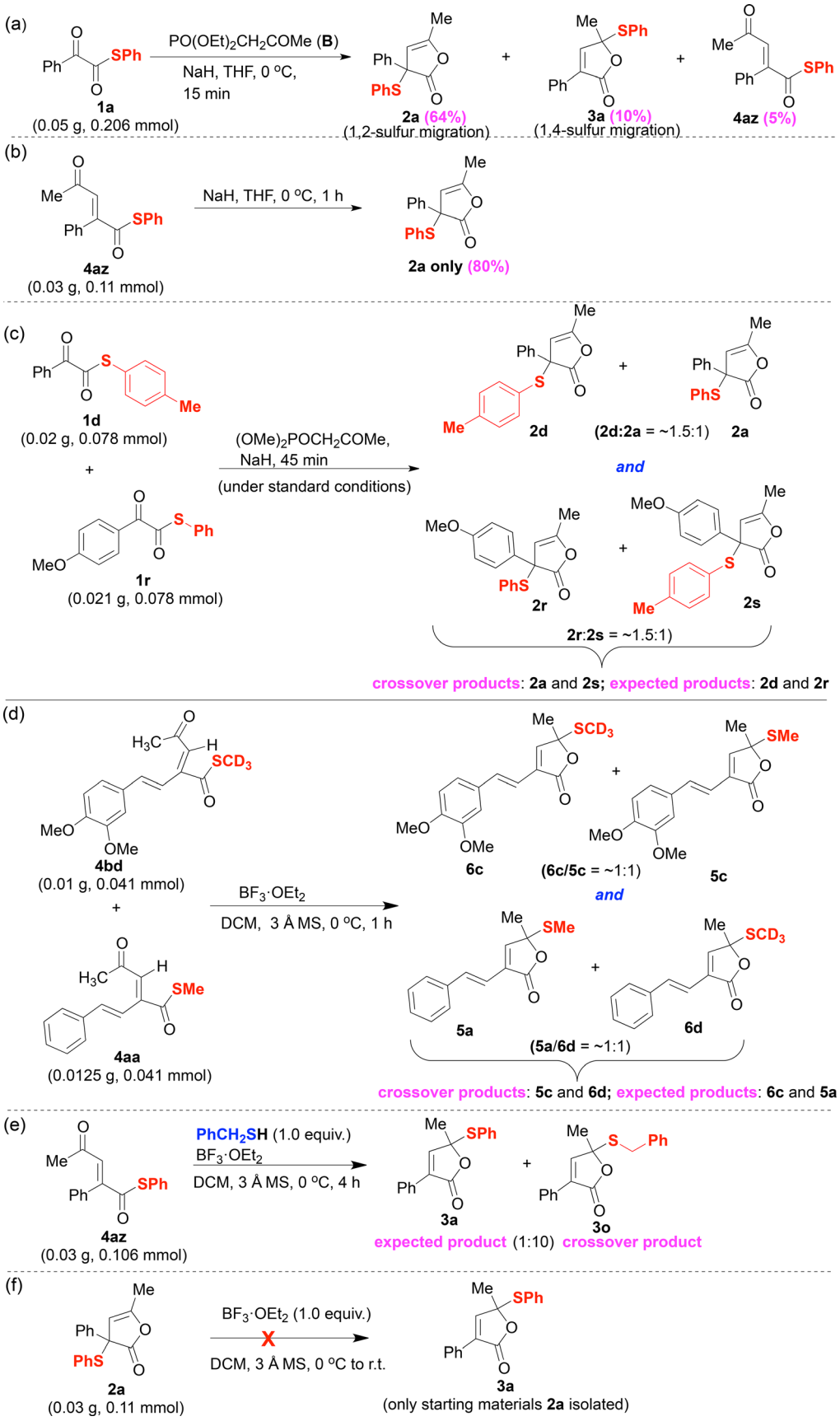
Turning our attention to a broad range of thiols containing γ-keto thioesters (Table 4), we observed that all these reactions proceeded smoothly *via* tandem 1,4-sulfur migration, providing the desired butenolides in moderate to good yields (**3a**, **3o**, **6a–d**, Table 4). However, no expected product was ever observed when unconjugated γ-carbonyl thioesters **4bg–h** or γ-keto oxoesters **4bf** were tested under the same reaction conditions. This is not unexpected for **4bf** as the C–O bond in oxoesters is stronger and hence less reactive compared to the C–S bond in thioesters. In addition, the poor nucleophilicity of the oxygen atom impedes the oxygen migration.

In order to gain mechanistic insights, we conducted control and crossover experiments, as described in Scheme 3. When the reaction of **1a** and phosphonate (**B**) was conducted under standard conditions, along with **2a** (64%) and **3a** (10%), olefin **4az** was also isolated in 5% yield [Eq. (a), Scheme 3]. In a parallel experiment, **4az** was treated with NaH under standard conditions and **2a** was isolated in 80% yield [Eq. (b), Scheme 3)]; thus suggesting that the tandem 1,2-sulfur migration might proceed through the corresponding olefin intermediate. To determine whether tandem 1,2-sulfur migration is a stepwise process, when an equimolar mixture of keto thioesters **1d** and **1r** was treated under the standard conditions, the crossover products **2a** and **2s** were isolated in addition to the expected products **2d** and **2r** [Eq. (c), Scheme 3]; thus suggesting that the 1,2-migration of the thio group proceeds in an intermolecular manner, and also indicates a stepwise mechanism for this reaction. The crossover experiments either with **4bd** and **4aa** [Eq. (d), Scheme 3] or with **4az** and benzyl mercaptan [Eq. (e), Scheme 3] under standard conditions also confirmed that 1,4-migration of the thio group proceeds in a stepwise mechanism. Furthermore, to confirm whether 1,4-sulfur migration product **3a** was generated *via* 1,2-sulfur migration product **2a** followed by rearrangement,[10] **2a** was treated with $BF_3{\cdot}OEt_2$ under optimized reaction conditions [Eq. (f), Scheme 3]. However, we have not isolated any **3a** even upon stir-

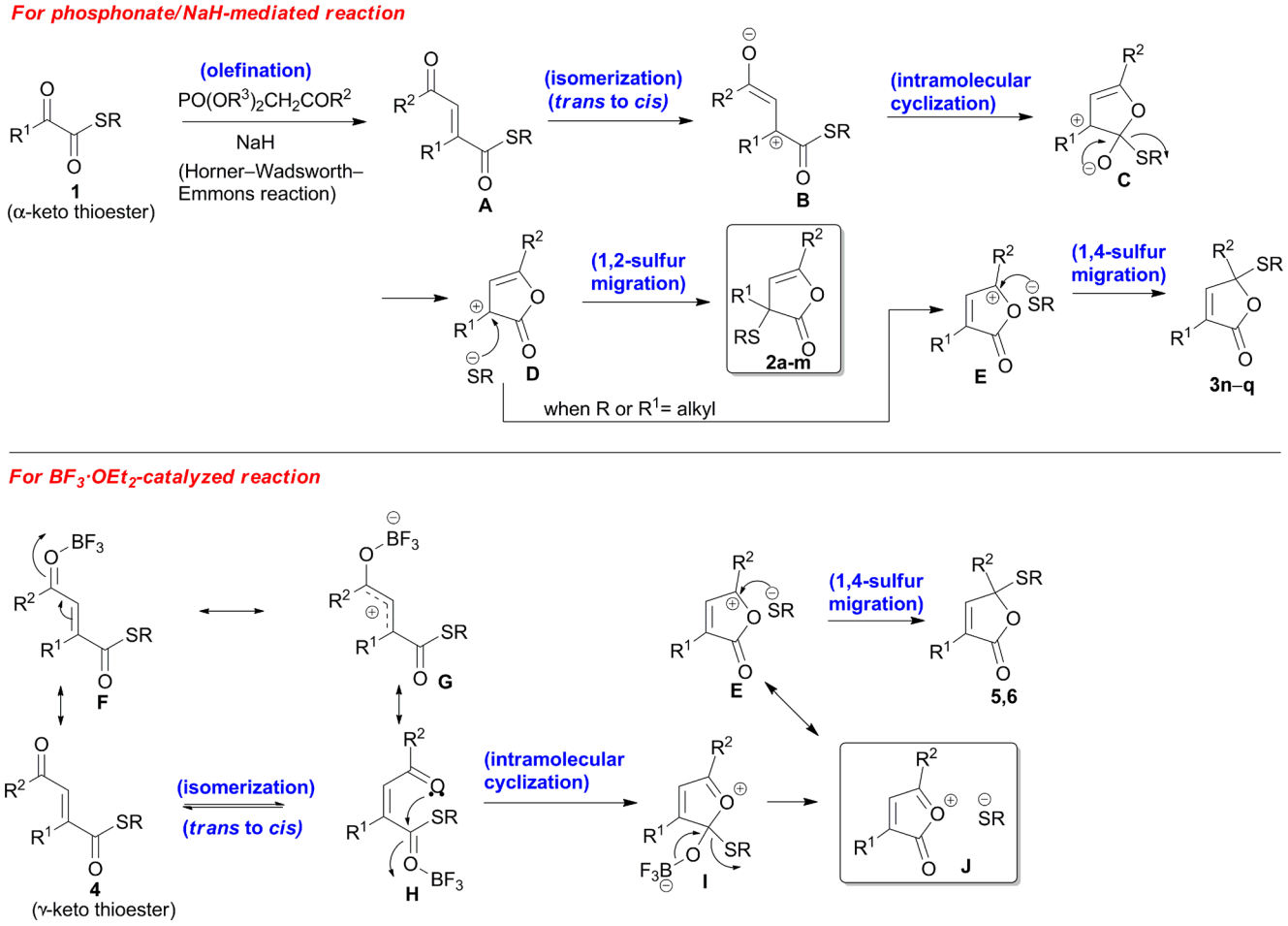
Table 4. Substrate scope of S-Ar/S-Alk derivatives for 1,4-sulfur migration.[a]



[a] Unless otherwise noted, reactions were carried out under the reaction conditions in Table 3, yields are of isolated products.



Scheme 3. Crossover and control experiments. Eqs. (a), (b), and (c) for 1,2-migration of the thio group. Eqs. (d), (e), and (f) for 1,4-migration of the thio group.

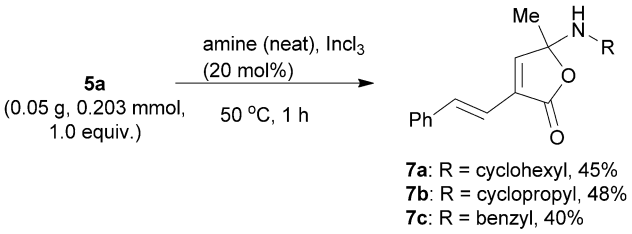


Scheme 4. A plausible reaction mechanism.

ring the reaction mixtures for several hours, thus suggesting **3a** was formed directly from γ-keto thioester **4az** *via* (*E*,*Z*) isomerization, intramolecular lactonization, and 1,4-sulfur migration without the intermediacy of any **2a**.

Based on the above results and the crossover experiments, we propose a plausible mechanism for these two tandem reactions as outlined in Scheme 4. For the phosphonate/base-mediated tandem reaction, we presume that initial Horner–Wadsworth–Emmons reaction of **1** with the stabilized phosphonate carbanions could lead to the olefin **A**, which undergoes rapid *trans* to *cis* (**B**) isomerization under basic conditions. Subsequent tandem lactonization (**C**) followed by thiolate capture would furnish butenolides (**2a–m**) *via* intermediate **D**, resulting in 1,2-sulfur migration. On the other hand, the formation of the 1,4-sulfur migration product **2n–q** could be explained by the thiolate capture to the intermediate **E**. For the BF_3·OEt_2-catalyzed pathway, the reaction is believed to proceed through the initial *trans* (**4**) to *cis* (**H**) isomerization *via* intermediates **F** and **G**, probably as a result of the stabilization of the allylic carbocationic intermediate **G**.[2a] Subsequent tandem lactonization and nucleophilic attack by the thiolate would furnish substituted butenolides (**5**, **6**), resulting in 1,4-migration of the thio group (Scheme 4). Research is currently in progress to further confirm the proposed mechanistic pathway.

To demonstrate the potential utility of the synthesized butenolides, we have carried out the synthesis of γ-aminobutenolides under mild reaction conditions (Scheme 5). Thus, direct displacement of the thiomethyl group with neat amines (cyclohexylamine, cyclopropylamine, and benzylamine) in the presence of



Scheme 5. Synthetic applications to γ-aminobutenolides.

20 mol% $InCl_3$ at 50 °C produced the amine derivatives in moderate yields (**7a–c**, 40–48%, Scheme 5).

Conclusions

In conclusion, we have demonstrated an unprecedented tandem chemoselective 1,2-/1,4-migration of the thio group in keto thioesters that provides substituted butenolides in moderate to excellent yields. α-Keto thioesters in the presence of Horner–Wadsworth–Emmons reaction conditions undergo tandem 1,2-sulfur migration whereas tandem 1,4-migration of the thio group has been observed in the presence of $BF_3{\cdot}OEt_2$ with γ-keto thioesters. The potential of these derivatives has been extended by synthesizing γ-aminobutenolides under mild reaction conditions. Research is currently in progress to develop the asymmetric version of this tandem reaction and to reiterate the superior reactivity of the keto thioesters towards the synthesis of biologically active heterocycles.

Experimental Section

General Information

Melting points were determined in open-end capillary tubes and are uncorrected. TLC was performed on silica gel plates (Merck silica gel 60, f_{254}), and the spots were visualized with UV light (254 and 365 nm) or by charring the plate dipped in 5% H_2SO_4-MeOH or vanillin charring solution. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent using TMS as the internal standard. HR-MS (*m/z*) were measured using EI (magnetic sector, positive ion) and ESI (Q-TOF, positive ion) techniques. Infrared (IR) spectra were recorded on a Fourier transform infrared spectrometer, only intense peaks are reported.

General Procedure for the Synthesis of 2

To a well-stirred solution of NaH (1.5 equiv./mmol) in dry THF (2.0 mL) at 0 °C, the corresponding phosphonate (1.0 equiv./mmol) was added. The resulting reaction mixture was stirred at the same temperature for 1 h. The *in situ* generated phosphonate-stabilized carbanions were added dropwise *via* syringe to a stirred solution of **1** (0.05 g, 1.0 equiv.) in THF (1.5 mL) at 0 °C, employing the time as mentioned. After completion of the reaction (TLC), saturated ammonium chloride solution was added, and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was passed through a short pad of silica gel column [230–400; eluent: ethyl acetate/*n*-hexane] to obtain **2**.

General Procedure for the Synthesis of 4

α-Keto thioesters/α-keto oxoesters **1** (0.1 g, 1.0 equiv.), the corresponding Wittig reagent (2.0 equiv./mmol), and dry THF (4.0 mL) were added successively to a round-bottom flask under an argon atmosphere, and the resulting mixture was stirred either at ambient temperature or at 0 °C employing the time as mentioned. After completion of the reaction (TLC), saturated ammonium chloride solution was added, and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was passed through a short pad of silica gel column [230–400; eluent: ethyl acetate/*n*-hexane] to obtain **4**.

General Procedure for the Synthesis of 5 and 6

To a well-stirred solution of **4** (0.05 g, 1 equiv.) in dry DCM (2.0 mL) and 3 Å MS (0.05 g), $BF_3{\cdot}OEt_2$ (1 equiv/mmol) was added dropwise at 0 °C. The resulting reaction mixture was stirred at the same temperature or at ambient temperature employing time as mentioned. After completion of the reaction (TLC), the reaction mixture was extracted with DCM (10 mL), and washed with saturated NH_4Cl solution. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was purified by silica gel column chromatography [230–400; eluent: ethyl acetate/*n*-hexane] to obtain **5** and **6**.

General Procedure for the Synthesis of 7a–c

To a stirred solution of **5a** (0.05 g, 0.203 mmol, 1 equiv.) in neat amine [cyclohexylamine, cyclopropylamine, and benzylamine; 1.5 mL], $InCl_3$ (20 mol%) was added, and the resulting mixture was heated at 50 °C for 1 h. After completion of the reaction (TLC), saturated ammonium chloride solution was added, and the product was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was purified through silica gel column chromatography [230–400; eluent: ethyl acetate/*n*-hexane] to obtain **7a–c**.

5-Methyl-3-phenyl-3-(phenylthio)furan-2(3*H*)-one (2a): Prepared according to the general procedure discussed above: $R_f = 0.3$; eluent, EtOAc/*n*-hexane (2%); isolated yield: 0.047 g (81%); white solid; mp 69–71 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.69$ (d, $J = 6.6$ Hz, 2H), 7.30–7.48 (m, 8H), 5.55 (d, $J = 1.2$ Hz, 1H), 1.81 (d, $J = 0.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 175.4$, 151.9, 137.0 (2 CH), 135.0, 130.0, 130.0, 128.7 (2 CH), 128.6 (2 CH), 128.5, 127.3 (2 CH), 106.0, 62.1, 13.6; IR (KBr): $\nu_{max} = 3061$, 1794, 1680, 1492, 1441, 1383, 1291, 1234, 1144, 1081, 950, 750, 694 cm^{-1}; HR-MS (ESI): $m/z = 305.0612$, calcd. for $C_{17}H_{14}O_2SNa$ $[M+Na]^+$: 305.0613.

3-[(4-Chlorophenyl)thio]-5-methyl-3-phenylfuran-2(3*H*)-one (2b): Prepared according to the general procedure discussed above: $R_f = 0.3$; eluent, EtOAc/*n*-hexane (1.5%); isolated yield: 0.045 g (79%); white solid; mp 79–81 °C. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.62$–7.64 (m, 2H), 7.32–7.39 (m, 5H), 7.26–7.29 (m, 2H), 5.55 (d, $J = 1.2$ Hz, 1H), 1.86 (d, $J = 1.2$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 175.0, 152.4, 138.3 (2 CH), 136.7, 134.7, 128.9 (2 CH), 128.8 (2 CH), 128.6, 128.4, 127.4 (2 CH), 105.8, 62.0, 13.8; IR (KBr): $\nu_{max} = 2921$, 1795, 1680, 1572, 1475, 1446, 1386, 1290, 1144, 1084, 1013, 949, 824, 747, 695, 505 cm^{-1}; HR-MS

(ESI): m/z = 339.0228, calcd. for $C_{17}H_{13}ClO_2SNa$ $[M+Na]^+$: 339.0223.

3-[(4-Bromophenyl)thio]-5-methyl-3-phenylfuran-2(3*H*)-one (2c): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (1%); isolated yield: 0.039 g (69%); white solid; mp 83–85 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (dd, J = 1.8, 8.4 Hz, 2H), 7.37–7.44 (m, 4H), 7.28–7.35 (m, 3H), 5.55 (d, J = 1.5 Hz, 1H), 1.86 (d, J = 1.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.0, 152.4, 138.4 (2 CH), 134.7, 131.9 (2 CH), 129.0, 128.7 (2 CH), 128.6, 127.3 (2 CH), 125.1, 105.8, 61.9, 13.8; IR (KBr): ν_{max} = 1783, 1679, 1443, 1380, 1290, 1172, 1143, 1080, 1008, 951, 809, 749, 691, 598 cm^{-1}; HR-MS (ESI): m/z = 382.9718, calcd. for $C_{17}H_{13}BrO_2SNa$ $[M+Na]^+$: 382.9718.

5-Methyl-3-phenyl-3-(*p*-tolylthio)furan-2(3*H*)-one (2d): Prepared according to the general procedure discussed above: R_f = 0.35; eluent, EtOAc/*n*-hexane (1.5%); isolated yield: 0.032 g (56%); white solid; mp 74–76 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.67 (m, 2H), 7.31–7.39 (m, 5H), 7.11 (d, J = 7.8 Hz, 2H), 5.53 (s, 1H), 2.35 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.4, 151.9, 140.4, 137.0 (2 CH), 135.1, 129.4 (2 CH), 128.6 (2 CH), 128.5, 127.4 (2 CH), 126.5, 106.1, 62.1, 21.3, 13.7; IR (KBr): ν_{max} = 2922, 1794, 1681, 1595, 1492, 1444, 1383, 1292, 1234, 1144, 1083, 950, 810, 749, 696, 599, 505 cm^{-1}; HR-MS (ESI): m/z = 319.0761, calcd. for $C_{18}H_{16}O_2SNa$ $[M+Na]^+$: 319.0769.

5-Ethyl-3-phenyl-3-(phenylthio)furan-2(3*H*)-one (2e): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (1.5%); isolated yield: 0.032 g (52%); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, J = 6.9 Hz, 2H), 7.46–7.49 (m, 2H), 7.29–7.42 (m, 6H), 5.52 (s, 1H), 1.97–2.19 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.7, 157.1, 137.1 (2 CH), 135.1, 130.1 (CH, C^0), 128.7 (4 CH), 128.6, 127.4 (2 CH), 104.5, 61.9, 21.2 (CH_2), 9.6; IR (KBr): ν_{max} = 2978, 1794, 1674, 1492, 1443, 1309, 1145, 1083, 945, 750, 694, 495 cm^{-1}; HR-MS (ESI): m/z = 319.0764, calcd. for $C_{18}H_{16}O_2SNa$ $[M+Na]^+$: 319.0769.

3-[(4-Chlorophenyl)thio]-5-ethyl-3-phenylfuran-2(3*H*)-one (2f): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (1%); isolated yield: 0.035 g (59%); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64–7.66 (m, 2H), 7.32–7.40 (m, 5H), 7.27–7.29 (m, 2H), 5.53 (t, J = 1.8 Hz, 1H), 2.09–2.22 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.3, 157.5, 138.3 (2 CH), 136.7, 134.8, 128.9 (2 CH), 128.8 (2 CH), 128.7, 128.5, 127.3 (2 CH), 104.2, 61.8, 21.3 (CH_2), 9.7; IR (KBr): ν_{max} = 2968, 1789, 1671, 1570, 1473, 1389, 1358, 1152, 1083, 992, 946, 827, 748, 694, 507 cm^{-1}; HR-MS (ESI): m/z = 353.0378, calcd. for $C_{18}H_{15}ClO_2SNa$ $[M+Na]^+$: 353.0379.

3-[(4-Bromophenyl)thio]-5-ethyl-3-phenylfuran-2(3*H*)-one (2g): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (1%); isolated yield: 0.035 g (60%); white solid; mp 119–121 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64–7.66 (m, 2H), 7.42–7.45 (m, 2H), 7.37–7.39 (m, 2H), 7.32–7.35 (m, 1H), 7.29–7.31 (m, 2H), 5.52 (t, J = 1.2 Hz, 1H), 2.09–2.22 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.3, 157.5, 138.5 (2 CH), 134.8, 131.9 (2 CH), 129.1, 128.8 (2 CH), 128.7, 127.3 (2 CH), 125.1, 104.2, 61.7, 21.3 (CH_2), 9.7; IR (KBr): ν_{max} = 2971, 1776, 1671, 1563, 1466, 1357, 1261, 1156, 1091, 1063, 1012, 941, 807, 698 cm^{-1}; HR-MS (ESI): m/z = 396.9877, calcd. for $C_{18}H_{15}BrO_2SNa$ $[M+Na]^+$: 396.9874.

5-Ethyl-3-phenyl-3-(*p*-tolylthio)furan-2(3*H*)-one (2h): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (1.5%); isolated yield: 0.038 g (63%); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, J = 7.2 Hz, 2H), 7.30–7.40 (m, 5H), 7.11 (d, J = 7.8 Hz, 2H), 5.51 (s, 1H), 2.34 (s, 3H), 1.99–2.18 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.7, 157.0, 140.4, 137.1 (2 CH), 135.2, 129.5 (2 CH), 128.7 (2 CH), 128.5, 127.4 (2 CH), 126.6, 104.5, 61.9, 21.3, 21.2 (CH_2), 9.6; IR (KBr): ν_{max} = 2978, 1795, 1674, 1596, 1492, 1452, 1307, 1145, 1084, 945, 807, 750, 696, 505 cm^{-1}; HR-MS (ESI): m/z = 333.0925, calcd. for $C_{19}H_{18}O_2SNa$ $[M+Na]^+$: 333.0926.

5-Pentyl-3-phenyl-3-(phenylthio)furan-2(3*H*)-one (2i): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (1%); isolated yield: 0.048 g (69%); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67–7.70 (m, 2H), 7.46–7.48 (m, 2H), 7.37–7.41 (m, 2H), 7.28–7.37 (m, 4H), 5.51 (t, J = 1.2 Hz, 1H), 2.04–2.09 (m, 2H), 1.14–1.32 (m, 6H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.7, 156.0, 137.1 (2 CH), 135.2, 130.1, 130.0, 128.7 (2 CH), 128.7 (2 CH), 128.5, 127.3 (2 CH), 105.1, 61.9, 31.0 (CH_2), 27.8 (CH_2), 25.0 (CH_2), 22.2 (CH_2), 13.8; IR (KBr): ν_{max} = 2949, 2861, 1789, 1675, 1440, 1313, 1168, 1140, 1081, 950, 752, 694 cm^{-1}; HR-MS (ESI): m/z = 361.1230, calcd. for $C_{21}H_{22}O_2SNa$ $[M+Na]^+$: 361.1239.

5-Pentyl-3-phenyl-3-(*p*-tolylthio)furan-2(3*H*)-one (2j): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (0.75%); isolated yield = 0.058 g (85%); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (dd, J = 1.8, 8.4 Hz, 2H), 7.32–7.41 (m, 5H), 7.11 (d, J = 8.1 Hz, 2H), 5.51 (t, J = 0.9 Hz, 1H), 2.34 (s, 3H), 2.05–2.10 (m, 2H), 1.14–1.34 (m, 6H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.8, 155.9, 140.4, 137.0 (2 CH), 135.3, 129.5 (2 CH), 128.7 (2 CH), 128.5, 127.4 (2 CH), 126.6, 105.2, 62.0, 31.1 (CH_2), 27.9 (CH_2), 25.1 (CH_2), 22.3 (CH_2), 21.3, 13.8; IR (KBr): ν_{max} = 2928, 2862, 1794, 1673, 1596, 1492, 1451, 1145, 1083, 949, 696 cm^{-1}; HR-MS (ESI): m/z = 375.1392, calcd. for $C_{22}H_{24}O_2SNa$ $[M+Na]^+$: 375.1395.

3,5-Diphenyl-3-(phenylthio)furan-2(3*H*)-one (2k): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (1%); isolated yield: 0.025 g (35%); white solid; mp 169–171 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (dd, J = 1.8, 8.4 Hz, 2H), 7.35–7.48 (m, 10H), 7.18–7.29 (m, 3H), 6.16 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7, 152.2, 137.0 (2 CH), 135.0, 130.1 (2 CH), 129.7, 128.8 (2 CH), 128.7 (2 CH), 128.7, 128.6 (2 CH), 127.5 (2 CH), 125.1 (2 CH), 104.2, 62.7; IR (KBr): ν_{max} = 1760, 1492, 1444, 1272, 1158, 1099, 1013, 959, 743, 691 cm^{-1}; HR-MS (ESI): m/z = 367.0780, calcd. for $C_{22}H_{16}O_2SNa$ $[M+Na]^+$: 367.0769.

3,5-Diphenyl-3-(*p*-tolylthio)furan-2(3*H*)-one (2l): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (1%); isolated yield: 0.029 g (40%); white solid; mp 189–191 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, J = 7.8 Hz, 2H), 7.46–7.47 (m, 2H), 7.33–7.41 (m, 8H), 7.01 (d, J = 7.8 Hz, 2H), 6.15 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.7,

152.1, 140.5, 137.0 (2 CH), 135.1, 130.0, 129.5 (2 CH), 128.8 (2 CH), 128.6, 128.6 (2 CH), 127.6, 127.5 (2 CH), 126.2, 125.1 (2 CH), 104.4, 62.7, 21.2; IR (KBr): ν_{max} = 1790, 1758, 1490, 1447, 1269, 1153, 1090, 1016, 946, 809, 761, 692 cm^{-1}; HR-MS (ESI): m/z = 381.0927, calcd. for $C_{23}H_{18}O_2SNa$ $[M+Na]^+$: 381.0926.

3-[(4-Bromophenyl)thio]-3,5-diphenylfuran-2(3*H*)-one (2m): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (0.5%); isolated yield: 0.026 g (40%); white solid; mp 139–141 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70–7.71 (m, 2H), 7.48–7.50 (m, 2H), 7.38–7.42 (m, 5H), 7.33–7.37 (m, 3H), 7.28–7.29 (m, 2H), 6.16 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.3, 152.5, 138.4 (2 CH), 134.6, 132.0 (2 CH), 130.4, 128.9 (2 CH), 128.8, 128.7 (2 CH), 127.4 (2 CH), 125.1 (2 CH), 103.8, 62.5; IR (KBr): ν_{max} = 1776, 1446, 1265, 1159, 1090, 1012, 942, 814, 754, 690 cm^{-1}; HR-MS (ESI): m/z = 444.9875, calcd. for $C_{22}H_{15}BrO_2SNa$ $[M+Na]^+$: 444.9874.

5-(Benzylthio)-5-ethyl-3-phenylfuran-2(5*H*)-one (3n): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (2.5%); isolated yield: 0.05 g (83%); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (dd, J = 3.0, 6.9 Hz, 2H), 7.39–7.41 (m, 3H), 7.22–7.28 (m, 6H), 3.70 (d, J = 13.2 Hz, 1H), 3.62 (d, J = 13.2 Hz, 1H), 2.06–2.22 (m, 2H), 1.02 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.1, 148.8, 136.8, 131.3, 129.7, 128.8 (2 CH), 128.7 (2 CH), 128.6 (2 CH), 127.2, 127.2 (2 CH), 93.9, 33.1 (CH_2), 31.6 (CH_2), 8.5; IR (KBr): ν_{max} = 2929, 1761, 1452, 1191, 1104, 959, 904, 789, 697 cm^{-1}; HR-MS (ESI): m/z = 333.0926, calcd. for $C_{19}H_{18}O_2SNa$ $[M+Na]^+$: 333.0926.

5-(Benzylthio)-5-methyl-3-phenylfuran-2(5*H*)-one (3o): Prepared according to the general procedure discussed above under phosphonate/NaH-mediated reaction: R_f = 0.3; eluent, EtOAc/*n*-hexane (4%); isolated yield: 0.035 g (60%); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.76 (m, 2H), 7.39–7.41 (m, 3H), 7.31 (s, 1H), 7.22 (m, 5H), 3.71 (d, J = 13.2 Hz, 1H), 3.63 (d, J = 13.5 Hz, 1H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.9, 149.9, 136.7, 130.6, 129.7, 128.8 (3 CH), 128.6 (3 CH), 127.2, 127.2 (3 CH), 90.3, 33.7 (CH_2), 25.4; IR (KBr): ν_{max} = 3064, 1762, 1493, 1448, 1212, 1090, 959, 879, 790, 698 cm^{-1}; HR-MS (EI): m/z = 296.0876, calcd. for $C_{18}H_{16}O_2S$ $[M]^+$: 296.0871.

5-Ethyl-5-(ethylthio)-3-phenylfuran-2(5*H*)-one (3p): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (3%); isolated yield: 0.015 g (23%); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.90 (m, 2H), 7.41–7.44 (m, 4H), 2.44 (q, J = 7.5, 14.7 Hz, 2H), 2.04–2.28 (m, 2H), 1.21 (t, J = 7.2 Hz, 3H), 1.03 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 148.7, 131.3 (2 C^0), 129.7, 128.7 (2 CH), 127.1 (2 CH), 93.9, 31.5 (CH_2), 22.5 (CH_2), 14.6, 8.5; IR (KBr): ν_{max} = 2974, 1760, 1492, 1451, 1192, 1106, 960, 905, 791, 748, 694 cm^{-1}; HR-MS (ESI): m/z = 271.0760, calcd. for $C_{14}H_{16}O_2SNa$ $[M+Na]^+$: 271.0769.

3-Isobutyl-5-methyl-5-(phenylthio)furan-2(5*H*)-one (3q): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (4%); isolated yield: 0.02 g (34%); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.49 (m, 2H), 7.29–7.35 (m, 3H), 6.81 (s, 1H), 1.90 (d, J = 6.9 Hz, 2H), 1.78 (s, 3H), 0.88–0.99 (m, 1H), 0.70 (d, J = 6.6 Hz, 3H), 0.67 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0, 150.6, 136.6 (2 CH), 133.1, 129.7, 129.0 (2 CH), 128.9, 92.2, 33.6 (CH_2), 26.8, 24.9, 22.1, 22.1; IR (KBr): ν_{max} = 2959, 2927, 1767, 1468, 1441, 1374, 1255, 1087, 1038, 958, 882, 751, 696 cm^{-1}; HR-MS (ESI): m/z = 285.0926, calcd. for $C_{15}H_{18}O_2SNa$ $[M+Na]^+$: 285.0926.

***S*-Methyl (*E*)-4-oxo-2-[(*E*)-styryl]pent-2-enethioate (4aa):** Prepared according to the general procedure discussed above: R_f = 0.4; eluent, EtOAc/*n*-hexane (7%); isolated yield: 0.1 g (84%); yellow gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, J = 16.5 Hz, 1H), 7.52 (d, J = 6.6 Hz, 2H), 7.31–7.38 (m, 3H), 7.08 (d, J = 16.5 Hz, 1H), 6.41 (s, 1H), 2.47 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.4, 194.8, 149.1, 140.7, 136.0, 129.5, 128.7 (2 CH), 127.8 (2 CH), 124.0, 120.3, 32.4, 12.4; IR (KBr): ν_{max} = 3027, 2928, 1672, 1609, 1565, 1494, 1447, 1422, 1356, 1192, 977, 750, 696, 614 cm^{-1}; HR-MS (ESI): m/z = 269.0599, calcd. for $C_{14}H_{14}O_2SNa$ $[M+Na]^+$: 269.0613.

***S*-Methyl (*E*)-2-[(*E*)-4-methoxystyryl]-4-oxopent-2-enethioate (4ab):** Prepared according to the general procedure discussed above: R_f = 0.35; eluent, EtOAc/*n*-hexane (10%); isolated yield: 0.077 g, (66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, J = 16.5 Hz, 1H), 7.47 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 16.5 Hz, 1H), 6.88 (d, J = 8.7 Hz, 2H), 6.34 (s, 1H), 3.83 (s, 3H), 2.46 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.3, 195.0, 160.8, 149.6, 140.5, 129.3 (2 CH), 128.9, 122.7, 118.3, 114.2 (2 CH), 55.3, 32.3, 12.3; IR (KBr): ν_{max} = 2929, 1671, 1601, 1557, 1511, 1421, 1251, 1174, 1030, 977, 825 cm^{-1}; HR-MS (EI): m/z = 276.0823, calcd. for $C_{15}H_{18}O_3S$ $[M]^+$: 276.0820.

***S*-Methyl (*E*)-2-[(*E*)-3,4-dimethoxystyryl]-4-oxopent-2-enethioate (4ac):** Prepared according to the general procedure discussed above: R_f = 0.4; eluent, EtOAc/*n*-hexane (20%); isolated yield: 0.07 g (61%); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.95 (dd, J = 0.6, 16.2 Hz, 1H), 7.09 (dd, J = 1.8, 8.4 Hz, 1H), 7.05 (d, J = 2.4 Hz, 1H), 7.03 (d, J = 16.8 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.35 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 2.46 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.4, 195.0, 150.5, 149.6, 149.1, 140.8, 129.2, 122.7, 122.0, 118.5, 111.0, 109.5, 55.9, 55.9, 32.4, 12.4; IR (KBr): ν_{max} = 2929, 1671, 1588, 1514, 1461, 1266, 1141, 1026, 978, 808, 758 cm^{-1}; HR-MS (ESI): m/z = 329.0851, calcd. for $C_{16}H_{18}O_4SNa$ $[M+Na]^+$: 329.0824.

***S*-Methyl (*E*)-2-[(*E*)-4-methylstyryl]-4-oxopent-2-enethioate (4ad):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); isolated yield: 0.084 g (71%); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99 (d, J = 16.2 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 7.06 (d, J = 16.8 Hz, 1H), 6.37 (s, 1H), 2.46 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.3, 194.9, 149.4, 140.8, 139.8, 133.3, 129.5 (2 CH), 127.8 (2 CH), 123.4, 119.4, 32.4, 21.4, 12.4; IR (KBr): ν_{max} = 2925, 1671, 1606, 1562, 1191, 977, 810 cm^{-1}; HR-MS (ESI): m/z = 283.0779, calcd. for $C_{15}H_{16}O_2SNa$ $[M+Na]^+$: 283.0769.

***S*-Methyl (*E*)-2-[(*E*)-2,6-dichlorostyryl]-4-oxopent-2-enethioate (4ae):** Prepared according to the general procedure discussed above: R_f = 0.35; eluent, EtOAc/*n*-hexane (7%); isolated yield: 0.073 g (64%); yellow crystalline soild; mp 115–117 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90 (d, J = 16.8 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 16.8 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 6.54 (s, 1H), 2.47 (s, 3H), 2.35

(s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.2, 194.2, 147.3, 134.8, 134.1, 133.4, 129.2, 128.7 (2 CH), 128.3, 126.6, 32.2, 12.4; IR (KBr): ν_{max} = 1665, 1615, 1563, 1426, 1353, 1181, 978, 946 cm^{-1}; HR-MS (ESI): m/z = 336.9841, calcd. for $C_{14}H_{12}Cl_2O_2SNa$ $[M+Na]^+$: 336.9833.

***S*-Methyl (*E*)-2-[(*E*)-4-chlorostyryl]-4-oxopent-2-enethioate (4af):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (7%); isolated yield: 0.094 g (81%); yellow solid; mp 119–121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, J = 16.5 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 16.2 Hz, 1H), 6.44 (s, 1H), 2.47 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.3, 194.6, 148.6, 139.1, 135.1, 134.5, 128.9 (2 CH), 128.8 (2 CH), 124.4, 120.8, 32.4, 12.3; IR (KBr): ν_{max} = 2928, 1672, 1609, 1564, 1490, 1410, 1356, 1266, 1192, 1092, 977, 818, 749, 691, 613 cm^{-1}; HR-MS (ESI): m/z = 303.0212, calcd. for $C_{14}H_{13}ClO_2SNa$ $[M+Na]^+$: 303.0223.

***S*-Methyl (*E*)-2-[(*E*)-4-fluorostyryl]-4-oxopent-2-enethioate (4ag):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); isolated yield: 0.094 g (80%); yellow solid; mp 109–111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, J = 16.8 Hz, 1H), 7.50 (dd, J = 6.0, 8.7 Hz, 2H), 7.07 (s, 1H), 7.03 (d, J = 8.4 Hz, 2H), 6.41 (s, 1H), 2.46 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.3, 194.7, 163.4 (d, J = 249.0 Hz, 1 C), 148.8, 139.3, 132.3 (d, J = 3.7 Hz, 1 C), 129.5, 129.4, 124.0, 120.0 (d, J = 2.2 Hz, 1 C), 116.0, 115.7, 32.4, 12.3; IR (KBr): ν_{max} = 2928, 1672, 1597, 1563, 1508, 1418, 1357, 1231, 1191, 977, 827, 743 cm^{-1}; HR-MS (ESI): m/z = 287.0510, calcd. for $C_{14}H_{13}FO_2SNa$ $[M+Na]^+$: 287.0518.

***S*-Methyl (*E*)-2-[(*E*)-2-bromostyryl]-4-oxopent-2-enethioate (4ah):** Prepared according to the general procedure discussed above: R_f = 0.35; eluent, EtOAc/*n*-hexane (6%); isolated yield: 0.067 g (58%); yellow gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, J = 16.5 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 16.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.15–7.21 (m, 1H), 6.51 (s, 1H), 2.50 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.6, 194.6, 148.5, 139.2, 136.1, 133.3, 130.5, 127.8, 127.7, 125.3, 125.3, 123.0, 32.6, 12.6; IR (KBr): ν_{max} = 1670, 1565, 1434, 1356, 1193, 1023, 976, 752 cm^{-1}; HR-MS (ESI): m/z = 346.9710, calcd. for $C_{14}H_{13}BrO_2SNa$ $[M+Na]^+$: 346.9718.

***S*-Methyl (*E*)-2-[(*E*)-3-cyanostyryl]-4-oxopent-2-enethioate (4ai):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (15%); isolated yield: 0.1 g (85%); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99 (dd, J = 0.6, 16.2 Hz, 1H), 7.73–7.75 (m, 2H), 7.58 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 16.2 Hz, 1H), 6.52 (s, 1H), 2.47 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.3, 194.3, 147.7, 137.5, 137.4, 132.3, 131.3, 131.1, 129.6, 125.8, 122.6, 118.4, 113.1, 32.4, 12.4; IR (KBr): ν_{max} = 2929, 1792, 1718, 1673, 1556, 1514, 1266, 1141, 1025 cm^{-1}; HR-MS (ESI): m/z = 294.0552, calcd. for $C_{15}H_{13}NO_2SNa$ $[M+Na]^+$: 294.0565.

***S*-Methyl (*E*)-2-[(*E*)-3-nitrostyryl]-4-oxopent-2-enethioate (4aj):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (15%); isolated yield: 0.059 g (51%); yellow soild; mp 117–119 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.30 (m, 1H), 8.16 (dd, J = 1.8, 8.4 Hz, 1H), 8.04 (d, J = 16.2 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 8.4 Hz, 1H), 7.13 (d, J = 16.2 Hz, 1H), 6.54 (s, 1H), 2.48 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.3, 194.3, 148.6, 147.6, 137.9, 137.5, 132.7, 129.7, 126.0, 123.6, 123.1, 122.6, 32.4, 12.4; IR (KBr): ν_{max} = 2926, 1671, 1568, 1530, 1425, 1351, 1194, 976, 736, 697 cm^{-1}; HR-MS (ESI): m/z = 314.0486, calcd. for $C_{14}H_{13}NO_4SNa$ $[M+Na]^+$: 314.0463.

***S*-Methyl (*E*)-2-[(*E*)-2-(naphthalen-2-yl)vinyl]-4-oxopent-2-enethioate (4ak):** Prepared according to the general procedure discussed above: R_f = 0.35; eluent, EtOAc/*n*-hexane (6%); isolated yield: 0.103 g (89%); yellow gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, J = 16.5 Hz, 1H), 7.90 (s, 1H), 7.82–7.85 (m, 3H), 7.75 (d, J = 8.7 Hz, 1H), 7.48–7.52 (m, 2H), 7.27 (d, J = 16.5 Hz, 1H), 6.45 (s, 1H), 2.51 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.4, 194.8, 149.1, 140.8, 133.8, 133.6, 133.3, 129.1, 128.4, 128.4, 127.7, 126.8, 126.5, 123.8, 123.6, 120.6, 32.4, 12.4; IR (KBr): ν_{max} = 2926, 1672, 1601, 1561, 1356, 1187, 976, 814, 747 cm^{-1}; HR-MS (ESI): m/z = 319.0773, calcd. for $C_{18}H_{16}O_2SNa$ $[M+Na]^+$: 319.0769.

***S*-Methyl (*E*)-2-[(*E*)-2-(naphthalen-1-yl)vinyl]-4-oxopent-2-enethioate (4al):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (7%); isolated yield: 0.096 g (83%); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 16.2 Hz, 1H), 7.95 (d, J = 16.2 Hz, 1H), 7.83–7.86 (m, 3H), 7.53–7.56 (m, 1H), 7.48–7.52 (m, 2H), 6.51 (s, 1H), 2.52 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.4, 194.9, 148.8, 137.6, 133.6, 133.5, 131.4, 129.7, 128.7, 126.5, 126.0, 125.6, 124.8, 124.7, 123.4, 122.8, 32.4, 12.5; IR (KBr): ν_{max} = 1667, 1561, 1354, 1195, 975, 797, 776, cm^{-1}; HR-MS (ESI): m/z = 319.0776, calcd. for $C_{18}H_{16}O_2SNa$ $[M+Na]^+$: 319.0769.

***S*-Methyl (*E*)-4-oxo-2-[(*E*)-2-(thiophen-2-yl)vinyl]pent-2-enethioate (4am):** Prepared according to the general procedure discussed above: R_f = 0.35; eluent, EtOAc/*n*-hexane (6%); isolated yield: 0.097 g (82%); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, J = 16.2 Hz, 1H), 7.33 (d, J = 4.8 Hz, 1H), 7.23 (d, J = 16.2 Hz, 1H), 7.17 (d, J = 3.0 Hz, 1H), 7.02 (dd, J = 3.6, 4.8 Hz, 1H), 6.38 (s, 1H), 2.46 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.2, 194.7, 148.7, 141.9, 133.5, 129.5, 128.0, 127.8, 123.5, 119.6, 32.4, 12.4; IR (KBr): ν_{max} = 2927, 1715, 1662, 1423, 1357, 1180, 966, 756, 706 cm^{-1}; HR-MS (ESI): m/z = 275.0166, calcd. for $C_{12}H_{12}O_2S_2Na$ $[M+Na]^+$: 275.0177.

***S*-Methyl (*E*)-4-oxo-2-(phenylethynyl)pent-2-enethioate (4an):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (4%); isolated yield: 0.05 g (42%); brown gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.61–7.62 (m, 2H), 7.39–7.44 (m, 3H), 7.12 (s, 1H), 2.56 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.6, 190.3, 134.6, 131.9 (2 CH), 130.1, 128.6 (2 CH), 121.5, 103.7, 84.4, 30.9, 12.9; IR (KBr): ν_{max} = 2928, 2199, 1666, 1573, 1361, 1248, 1180, 1110, 1010, 760, 690 cm^{-1}; HR-MS (ESI): m/z = 267.0463, calcd. for $C_{14}H_{12}O_2SNa$ $[M+Na]^+$: 267.0456.

***S*-Methyl 2-(4-nitrophenyl)-4-oxopent-2-enethioate (4ao):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (15%); isolated yield: 0.083 g (71%); yellow solid; mp 119–121 °C; *trans*:-*cis* = ~1:1; NMR of mixture, major peaks: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.13 (s, 1H), 2.39 (s, 3H), 2.15 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.2, 192.3, 148.3, 144.7, 140.3, 132.3, 130.8 (2 CH), 123.4 (2 CH), 31.5, 12.9; IR (KBr): ν_{max} = 2926, 1656, 1595, 1519, 1421, 1345, 1174, 1071, 1020, 857, 803, 731, 703 cm^{-1}; HR-MS (ESI): m/z = 288.0288, calcd. for $C_{12}H_{11}NO_4SNa$ $[M+Na]^+$: 288.0307.

***S*-Methyl (*E*)-4-oxo-2-[(*E*)-styryl]but-2-enethioate (4ap):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (4%); isolated yield: 0.04 g (36%); yellow gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.20 (d, J = 7.2 Hz, 1H), 7.47–7.56 (m, 3H), 7.40–7.42 (m, 3H), 7.06 (d, J = 15.9 Hz, 1H), 6.48 (d, J = 6.6 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.0, 190.8, 152.2, 142.1, 135.4, 130.0, 129.0 (2 CH), 127.7 (2 CH), 127.6, 117.9, 12.3; IR (KBr): ν_{max} = 2927, 1721, 1666, 1159, 1080, 971, 754, 699 cm^{-1}; HR-MS (ESI): m/z = 255.0454, calcd. for $C_{13}H_{12}O_2SNa$ $[M+Na]^+$: 255.0456.

***S*-Methyl (*E*)-2-[(*E*)-4-methylstyryl]-4-oxobut-2-enethioate (4aq):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (6%); isolated yield: 0.05 g (44%); yellow gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.18 (d, J = 6.9 Hz, 1H), 7.37–7.44 (m, 3H), 7.21 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 15.9 Hz, 1H), 6.44 (d, J = 6.9 Hz, 1H), 2.48 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.1, 190.8, 152.5, 142.1, 140.4, 132.7, 129.7 (2 CH), 127.6 (2 CH), 127.0, 116.8, 21.4, 12.3; IR (KBr): ν_{max} = 2925, 1719, 1669, 1606, 1179, 1082, 972, 810 cm^{-1}; HR-MS (EI): m/z = 246.0722, calcd. for $C_{14}H_{14}O_2S$ $[M]^+$: 246.0715.

***S*-Methyl (*E*)-2-[(*E*)-4-chlorostyryl]-4-oxobut-2-enethioate (4ar):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (7%); isolated yield: 0.062 g (56%); yellow solid; mp 109–111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.18 (d, J = 6.6 Hz, 1H), 7.46–7.49 (m, 2H), 7.37–7.41 (m, 3H), 7.02 (d, J = 15.9 Hz, 1H), 6.49 (d, J = 6.6 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.9, 190.6, 151.7, 140.5, 135.8, 133.8, 129.2 (2 CH), 128.8 (2 CH), 127.6, 118.4, 12.3; IR (KBr): ν_{max} = 1669, 1609, 1565, 1080, 972, 946 cm^{-1}; HR-MS (EI): m/z = 266.0159, calcd. for $C_{13}H_{11}ClO_2S$ $[M]^+$: 266.0168.

***S*-Methyl (*E*)-2-[(*E*)-4-cyanostyryl]-4-oxobut-2-enethioate (4as):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (15%); isolated yield: 0.04 g (36%); yellowish white solid; mp 95–97 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.17 (d, J = 6.0 Hz, 1H), 7.67–7.70 (m, 2H), 7.53–7.62 (m, 3H), 7.07 (d, J = 15.9 Hz, 1H), 6.56 (d, J = 6.3 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.2, 192.7, 143.6, 143.2, 140.4, 136.9, 136.2, 132.6, 131.5, 127.6, 122.1, 118.6, 112.3, 12.3; IR (KBr): ν_{max} = 2925, 2224, 1674, 1602, 1130, 970 cm^{-1}; HR-MS (ESI): m/z = 280.0407, calcd. for $C_{14}H_{11}NO_2SNa$ $[M+Na]^+$: 280.0408.

***S*-Methyl 2-[(*E*)-2-(naphthalen-2-yl)vinyl]-4-oxobut-2-enethioate and *S*-methyl (*Z*)-2-[(*E*)-2-(naphthalen-2-yl)vinyl]-4-oxobut-2-enethioate (4at):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (6%); isolated yield: 0.034 g (31%); yellow solid; mp 114–116 °C; *trans*:*cis* = 7:1. NMR of mixtures (major peaks): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.23 (d, J = 7.2 Hz, 1H), 7.90 (s, 1H), 7.83–7.86 (m, 3H), 7.70 (dd, J = 1.8, 9.0 Hz, 1H), 7.57 (d, J = 15.6 Hz, 1H), 7.51–7.52 (m, 2H), 7.22 (d, J = 15.6 Hz, 1H), 6.48 (d, J = 6.6 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.1, 190.7, 152.3, 142.1, 134.0, 133.3, 132.9, 129.4, 128.8, 128.5, 127.8, 127.3, 127.2, 126.8, 123.2, 118.1, 12.3; IR (KBr): ν_{max} = 2926, 1716, 1665, 1507, 1176, 968, 816, 753 cm^{-1}; HR-MS (ESI): m/z = 305.0633, calcd. for $C_{17}H_{14}O_2SNa$ $[M+Na]^+$: 305.0613.

***S*-Methyl (*E*)-4-oxo-2-[(*E*)-2-(thiophen-3-yl)vinyl]but-2-enethioate (4au):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); isolated yield: 0.031 g (27%); yellow gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.18 (d, J = 6.9 Hz, 1H), 7.46 (s, 1H), 7.33–7.38 (m, 3H), 7.08 (d, J = 15.9 Hz, 1H), 6.43 (d, J = 6.9 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.1, 190.6, 152.3, 138.6, 135.6, 127.3, 127.0, 126.8, 124.7, 117.6, 12.3; IR (KBr): ν_{max} = 2925, 1717, 1668, 1604, 1082, 967, 779 cm^{-1}; HR-MS (ESI): m/z = 261.0043, calcd. for $C_{11}H_{10}O_2S_2Na$ $[M+Na]^+$: 261.0020.

Ethyl (2*E*,4*E*)-3-[(methylthio)carbonyl]-5-phenylpenta-2,4-dienoate (4ay): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (2%); isolated yield: 0.07 g (52%); yellow gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, J = 16.5 Hz, 1H), 7.53 (d, J = 6.6 Hz, 2H), 7.31–7.38 (m, 3H), 7.06 (d, J = 16.2 Hz, 1H), 6.14 (s, 1H), 4.26 (q, J = 7.2, 14.1 Hz, 2H), 2.47 (s, 3H), 1.34 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.5, 165.4, 151.5, 139.3, 136.1, 129.3, 128.7 (2 CH), 127.6 (2 CH), 119.9, 118.8, 60.7 (CH_2), 14.2, 12.3; IR (KBr): ν_{max} = 2982, 1711, 1673, 1613, 1587, 1201, 1166, 1034, 980, 755, 694 cm^{-1}; HR-MS (ESI): m/z = 299.0726, calcd. for $C_{15}H_{16}O_3SNa$ $[M+Na]^+$: 299.0718.

***S*-Phenyl (*E*)-4-oxo-2-phenylpent-2-enethioate (4az):** Prepared according to the general procedure discussed above: R_f = 0.4; eluent, EtOAc/*n*-hexane (4%); isolated yield: 0.05 g (43%); yellow solid; mp 111–113 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.50 (m, 10H), 7.03 (s, 1H), 1.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.1, 191.6, 146.1, 134.4 (2 CH), 133.1, 132.9, 129.8 (2 CH), 129.7 (2 CH), 129.3 (2 CH), 128.4 (2 CH), 127.4, 30.6; IR (KBr): ν_{max} = 2925, 1678, 1478, 1440, 1356, 1175, 1066, 1020, 748, 697 cm^{-1}; HR-MS (ESI): m/z = 305.0616, calcd. for $C_{17}H_{14}O_2SNa$ $[M+Na]^+$: 305.0613.

***S*-(Naphthalen-2-yl) (*E*)-4-oxo-2-phenylpent-2-enethioate (4ba):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); isolated yield: 0.04 g (35%); yellow solid; mp 84–86 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 (s, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.46–7.56 (m, 5H), 7.43 (dd, J = 1.2, 8.4 Hz, 1H), 7.41 (dd, J = 1.2, 7.8 Hz, 2H), 7.04 (s, 1H), 1.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 200.2, 191.9, 146.1, 134.5, 133.5, 133.4, 133.1, 133.0, 130.6, 129.9 (2 CH), 129.7, 128.9, 128.5 (2 CH), 128.0, 127.8, 127.3, 126.6, 124.8, 30.7; IR (KBr): ν_{max} = 1672, 1493, 1349, 1067, 1014, 813, 748, 702 cm^{-1}; HR-MS (EI): m/z = 332.0874, calcd. for $C_{21}H_{16}O_2S$ $[M]^+$: 332.0871.

***S*-Benzyl (*E*)-4-oxo-2-phenylpent-2-enethioate (4bb):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (3%); isolated yield: 0.081 g (70%); yellow solid; mp 124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.46 (m, 4H), 7.27–7.30 (m, 6H), 6.99 (s, 1H), 4.19 (s, 2H), 1.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.3, 192.7, 146.1, 136.6, 133.1, 132.8, 129.8 (2 CH), 129.6, 129.0 (2 CH), 128.7 (2 CH), 128.4 (2 CH), 127.5, 34.6 (CH_2), 30.7; IR (KBr): ν_{max} = 3060, 3029,

2925, 2853, 1660, 1614, 1494, 1449, 1417, 1358, 1198, 1176, 1072, 1022, 766, 703 cm^{-1}; HR-MS (EI): m/z = 296.0869, calcd. for $C_{18}H_{16}O_2S$ $[M]^+$: 296.0871.

***S*-Benzyl (*E*)-4-oxo-2,4-diphenylbut-2-enethioate (4bc):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (3%); isolated yield: 0.056 g (40%); yellow gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.83–7.85 (m, 2H), 7.60 (s, 1H), 7.50–7.53 (m, 1H), 7.37–7.40 (m, 2H), 7.27–7.32 (m, 6H), 7.24–7.26 (m, 4H), 4.23 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.8, 192.6, 146.5, 136.7, 136.5, 133.7, 133.0, 131.4, 129.9 (2 CH), 129.1, 129.0 (2 CH), 128.9 (2 CH), 128.7 (2 CH), 128.6 (2 CH), 128.0 (2 CH), 127.5, 34.6 (CH_2); IR (KBr): ν_{max} = 1663, 1599, 1493, 1449, 1236, 1178, 1073, 1023, 920, 867, 764, 696 cm^{-1}; HR-MS (ESI): m/z = 381.0928, calcd. for $C_{23}H_{18}O_2SNa$ $[M+Na]^+$: 381.0926.

***S*-(Methyl-d_3) (*E*)-2-[(*E*)-3,4-dimethoxystyryl]-4-oxopent-2-enethioate (4bd):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (22%); isolated yield: 0.065 g (57%); yellow gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.95 (dd, J = 0.6, 16.2 Hz, 1H), 7.08 (dd, J = 1.8, 8.4 Hz, 1H), 7.05 (d, J = 1.8 Hz, 1H), 7.03 (d, J = 16.2 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.35 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.4, 195.0, 150.5, 149.6, 149.1, 140.8, 129.2, 122.7, 122.0, 118.4, 111.0, 109.5, 55.9, 55.9, 32.4; IR (KBr): ν_{max} = 2927, 1669, 1555, 1513, 1461, 1267, 1140, 1025, 975 cm^{-1}; HR-MS (ESI): m/z = 332.1021, calcd. for $C_{16}H_{15}D_3O_4SNa$ $[M+Na]^+$: 332.1012.

***S*-(Methyl-d_3) (*E*)-4-oxo-2-[(*E*)-styryl]pent-2-enethioate (4be):** Prepared according to the general procedure discussed above: R_f = 0.4; eluent, EtOAc/*n*-hexane (8%); isolated yield: 0.088 g (74%); yellow gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.00 (dd, J = 0.6, 16.2 Hz, 1H), 7.51–7.53 (m, 2H), 7.31–7.36 (m, 3H), 7.08 (d, J = 16.8 Hz, 1H), 6.41 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.3, 194.8, 149.0, 140.7, 136.0, 129.5, 128.7 (2 CH), 127.8 (2 CH), 124.1, 120.3, 32.4; IR (KBr): ν_{max} = 3028, 2931, 2133, 1661, 1566, 1494, 1449, 1357, 1190, 1110, 1032, 977, 756, 699 cm^{-1}; HR-MS (ESI): m/z = 272.0772, calcd. for $C_{14}H_{11}D_3O_2SNa$ $[M+Na]^+$: 272.0801.

Methyl (*E*)-4-oxo-2-[(*E*)-styryl]pent-2-enoate (4bf): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (8%); isolated yield: 0.038 g (31%); yellow solid; mp 127–129 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, J = 16.5 Hz, 1H), 7.53 (d, J = 6.3 Hz, 2H), 7.31–7.38 (m, 4H), 6.62 (s, 1H), 3.90 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.0, 167.6, 141.4, 140.6, 136.5, 129.4, 128.9 (2 CH), 127.8 (2 CH), 127.7, 121.1, 52.8, 32.5; IR (KBr): ν_{max} = 1726, 1608, 1573, 1437, 1250, 751, 696 cm^{-1}; HR-MS (ESI): m/z = 253.0849, calcd. for $C_{14}H_{14}O_3Na$ $[M+Na]^+$: 253.0841.

***S*-Phenyl 4-oxo-2,4-diphenylbutanethioate (4bg):** Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (4%); isolated yield: 0.043 g (86%); colorless gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.96 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.32–7.39 (m, 10H), 4.66 (dd, J = 4.2, 9.0 Hz, 1H), 4.03 (dd, J = 9.6, 18.0 Hz, 1H), 3.32 (dd, J = 4.8, 18.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.1, 197.1, 137.7, 136.3, 134.5 (2 CH), 133.3, 129.3, 129.1 (4 CH), 128.6 (2 CH), 128.3 (2 CH), 128.1 (2 CH), 127.9, 127.8, 54.5, 42.8 (CH_2); IR (KBr): ν_{max} = 2921, 1687, 1591, 1447, 995, 938, 749, 693 cm^{-1}; HR-MS (ESI): m/z = 369.0934, calcd. for $C_{22}H_{18}O_2SNa$ $[M+Na]^+$: 369.0926.

***S*-Phenyl 4-oxo-2-phenylpentanethioate (4bh):** Prepared according to the general procedure discussed above: R_f = 0.35; eluent, EtOAc/*n*-hexane (8%); isolated yield: 0.027 g (54%); colorless gum. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.38 (m, 10H), 4.45 (dd, J = 4.5, 9.3 Hz, 1H), 3.45 (dd, J = 9.6, 18.0 Hz, 1H), 2.76 (dd, J = 4.5, 18.0 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.5, 198.0, 137.3, 134.4 (2 CH), 129.2, 129.0 (2 CH), 128.9 (2 CH), 128.2 (2 CH), 127.8, 127.5, 54.2, 46.9 (CH_2), 29.9; IR (KBr): ν_{max} = 2922, 1702, 1441, 1398, 1361, 1232, 1162, 1075, 1029, 746, 696 cm^{-1}; HR-MS (EI): m/z = 284.0877, calcd. for $C_{17}H_{16}O_2S$ $[M]^+$: 284.0871.

(*E*)-5-Methyl-5-(methylthio)-3-styrylfuran-2(5*H*)-one (5a): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); isolated yield: 0.048 g (96%); white solid; mp 71–73 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.72 (d, J = 16.2 Hz, 1H), 7.50 (d, J = 7.8 Hz, 2H), 7.35–7.38 (m, 2H), 7.30–7.32 (m, 1H), 7.09 (s, 1H), 6.81 (d, J = 16.2 Hz, 1H), 1.96 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.0, 148.8, 136.1, 136.0, 129.1, 128.9, 128.8 (2 CH), 127.0 (2 CH), 115.8, 90.2, 25.1, 11.5; IR (KBr): ν_{max} = 1754, 1054, 985, 960, 889, 747, 693 cm^{-1}; HR-MS (ESI): m/z = 269.0605, calcd. for $C_{14}H_{14}O_2SNa$ $[M+Na]^+$: 269.0613.

(*E*)-3-(4-Methoxystyryl)-5-methyl-5-(methylthio)furan-2(5*H*)-one (5b): Prepared according to the general procedure discussed above: R_f = 0.4; eluent, EtOAc/*n*-hexane (10%); isolated yield: 0.041 g (82%); colorless gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.66 (d, J = 16.2 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.02 (s, 1H), 6.89 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 16.2 Hz, 1H), 3.83 (s, 3H), 1.95 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.2, 160.3, 147.6, 135.5, 129.3, 128.9, 128.4 (2 CH), 114.2 (2 CH), 113.6, 90.2, 55.3, 25.1, 11.5; IR (KBr): ν_{max} = 2926, 1756, 1601, 1509, 1445, 1255, 1176, 1108, 1053, 972, 889, 849, 817, 770 cm^{-1}; HR-MS (ESI): m/z = 299.0717, calcd. for $C_{15}H_{16}O_3SNa$ $[M+Na]^+$: 299.0718.

(*E*)-3-(3,4-Dimethoxystyryl)-5-methyl-5-(methylthio)furan-2(5*H*)-one (5c): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); isolated yield: 0.04 g (80%); colorless gum. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, J = 16.2 Hz, 1H), 7.04–7.08 (m, 3H), 6.86 (d, J = 8.1 Hz, 1H), 6.68 (d, J = 16.2 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 1.96 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 149.9, 149.1, 147.7, 135.7, 129.2, 129.2, 120.7, 113.7, 111.1, 109.0, 90.3, 55.9, 55.8, 25.1, 11.5; IR (KBr): ν_{max} = 2929, 1762, 1638, 1596, 1514, 1461, 1265, 1141, 1052, 1026, 966 cm^{-1}; HR-MS (ESI): m/z = 329.0820, calcd. for $C_{16}H_{18}O_4SNa$ $[M+Na]^+$: 329.0824.

(*E*)-5-Methyl-3-(4-methylstyryl)-5-(methylthio)furan-2(5*H*)-one (5d): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); isolated yield: 0.035 g (70%); yellow gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.68 (d, J = 16.2 Hz, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 7.06 (s, 1H), 6.76 (d, J = 16.2 Hz, 1H), 2.36 (s, 3H), 1.95 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.1, 148.2, 139.0, 135.9, 133.4, 129.5 (2 CH), 129.3, 126.9 (2 CH), 114.8, 90.2, 25.1, 21.3, 11.5; IR (KBr): ν_{max} = 2925, 1763, 1099, 1052, 967 cm^{-1};

HR-MS (ESI): m/z = 283.0779, calcd. for $C_{15}H_{16}O_2SNa$ $[M+Na]^+$: 283.0769.

(*E*)-3-(2,6-Dichlorostyryl)-5-methyl-5-(methylthio)furan-2(5*H*)-one (5e): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (4%); isolated yield: 0.044 g (88%); yellow crystalline solid; mp 79–81 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, J = 16.8 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.12–7.17 (m, 2H), 6.90 (d, J = 16.5 Hz, 1H), 1.99 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.5, 150.7, 134.5 (2 C^0), 133.4, 130.1, 128.9, 128.6 (2 CH), 128.5, 124.2, 90.0, 24.9, 11.5; IR (KBr): ν_{max} = 2926, 1764, 1431, 1095, 1052, 966, 890, 844, 777 cm^{-1}; HR-MS (ESI): m/z = 336.9860, calcd. for $C_{14}H_{12}Cl_2O_2SNa$ $[M+Na]^+$: 336.9833.

(*E*)-3-(4-Chlorostyryl)-5-methyl-5-(methylthio)furan-2(5*H*)-one (5f): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); isolated yield: 0.04 g (80%); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69 (d, J = 16.2 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.10 (s, 1H), 6.77 (d, J = 16.2 Hz, 1H), 1.95 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.9, 149.3, 134.7, 134.6, 129.0 (2 CH), 128.8, 128.1 (2 CH), 116.3, 90.2, 25.0, 11.5; IR (KBr): ν_{max} = 2926, 1762, 1489, 1091, 1051, 996, 890, 854, 769 cm^{-1}; HR-MS (ESI): m/z = 303.0246, calcd. for $C_{14}H_{13}ClO_2SNa$ $[M+Na]^+$: 303.0223.

(*E*)-3-(4-Fluorostyryl)-5-methyl-5-(methylthio)furan-2(5*H*)-one (5g): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); isolated yield: 0.037 g (74%); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, J = 16.8 Hz, 1H), 7.45–7.48 (m, 2H), 7.08 (s, 1H), 7.05 (t, J = 9.0 Hz, 2H), 6.72 (d, J = 16.8 Hz, 1H), 1.95 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.0, 163.0 (d, J = 247.5 Hz, 1 C), 148.9, 134.8, 132.4 (d, J = 3.0 Hz, 1 C), 128.9, 128.7, 128.6, 115.9, 115.8, 115.5 (d, J = 1.5 Hz, 1 C), 90.2, 25.0, 11.5; IR (KBr): ν_{max} = 2926, 1763, 1598, 1508, 1436, 1236, 1098, 1052, 967, 855, 767 cm^{-1}; HR-MS (ESI): m/z = 287.0516, calcd. for $C_{14}H_{13}FO_2SNa$ $[M+Na]^+$: 287.0518.

(*E*)-3-(2-Bromostyryl)-5-methyl-5-(methylthio)furan-2(5*H*)-one (5h): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); isolated yield: 0.038 g (76%); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (d, J = 16.2 Hz, 1H), 7.58–7.60 (m, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.19 (s, 1H), 7.15–7.18 (m, 1H), 6.74 (d, J = 16.2 Hz, 1H), 1.97 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.9, 149.4, 136.1, 134.7, 133.3, 130.0, 129.1, 127.6, 126.8, 124.6, 118.2, 90.2, 25.0, 11.5; IR (KBr): ν_{max} = 2984, 1763, 1434, 1096, 1053, 965, 890, 751, 574 cm^{-1}; HR-MS (ESI): m/z = 346.9709, calcd. for $C_{14}H_{13}BrO_2SNa$ $[M+Na]^+$: 346.9718.

(*E*)-3-{2-[5-Methyl-5-(methylthio)-2-oxo-2,5-dihydrofuran-3-yl]vinyl}benzonitrile (5i): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (15%); isolated yield: 0.04 g (80%); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.78 (m, 3H), 7.59 (d, J = 7.5 Hz, 1H), 7.48 (t, J = 8.1 Hz, 1H), 7.17 (s, 1H), 6.86 (d, J = 16.2 Hz, 1H), 1.97 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.6, 150.8, 137.5, 133.5, 131.8, 131.2, 130.0, 129.6, 128.3, 118.4, 118.4, 113.1, 90.2, 24.9, 11.5; IR (KBr): ν_{max} = 2985, 2230, 1762, 1247, 1094, 1053, 890, 770, 684 cm^{-1}; HR-MS (ESI): m/z = 294.0560, calcd. for $C_{15}H_{13}NO_2SNa$ $[M+Na]^+$: 294.0565.

(*E*)-5-Methyl-5-(methylthio)-3-(3-nitrostyryl)furan-2(5*H*)-one (5j): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (15%); isolated yield: 0.039 g (78%); yellowish white solid; mp 124–126 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.36–8.37 (m, 1H), 8.15 (dd, J = 1.2, 7.8 Hz, 1H), 7.83 (d, J = 16.8 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.19 (s, 1H), 6.94 (d, J = 16.2 Hz, 1H), 1.97 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.6, 151.0, 148.7, 138.0, 133.4, 133.1, 129.8, 128.2, 123.2, 121.0, 118.8, 90.3, 24.9, 11.5; IR (KBr): ν_{max} = 1763, 1523, 1437, 1351, 1090, 1049, 968, 888, 733, 699 cm^{-1}; HR-MS (ESI): m/z = 314.0444, calcd. for $C_{14}H_{13}NO_4SNa$ $[M+Na]^+$: 314.0463.

(*E*)-5-Methyl-5-(methylthio)-3-[2-(naphthalen-2-yl)vinyl]-furan-2(5*H*)-one (5k): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (6%); isolated yield: 0.038 g (76%); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.87–7.90 (m, 2H), 7.80–7.84 (m, 3H), 7.67 (dd, J = 1.2, 9.0 Hz, 1H), 7.46–7.50 (m, 2H), 7.12 (s, 1H), 6.92 (d, J = 16.2 Hz, 1H), 1.97 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.1, 148.8, 136.0, 133.6, 133.5, 133.5, 129.1, 128.5, 128.3, 128.1, 127.7, 126.6, 126.5, 123.0, 116.0, 90.2, 25.1, 11.5; IR (KBr): ν_{max} = 2925, 1761, 1096, 1052, 964, 891, 861, 816, 775 cm^{-1}; HR-MS (ESI): m/z = 319.0767, calcd. for $C_{18}H_{16}O_2SNa$ $[M+Na]^+$: 319.0769.

(*E*)-5-Methyl-5-(methylthio)-3-[2-(naphthalen-1-yl)vinyl]-furan-2(5*H*)-one (5l): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (7%); isolated yield: 0.041 g (82%); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.61 (d, J = 16.2 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.84–7.87 (m, 2H), 7.72 (d, J = 7.2 Hz, 1H), 7.55–7.58 (m, 1H), 7.51–7.53 (m, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.14 (s, 1H), 6.88 (d, J = 16.2 Hz, 1H), 2.00 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.0, 149.3, 133.8, 133.7, 133.2, 131.3, 129.3, 129.2, 128.6, 126.5, 126.1, 125.5, 123.7, 123.6, 118.5, 90.2, 25.1, 11.6; IR (KBr): ν_{max} = 1762, 1091, 1056, 963, 779 cm^{-1}; HR-MS (ESI): m/z = 319.0748, calcd. for $C_{18}H_{16}O_2SNa$ $[M+Na]^+$: 319.0769.

(*E*)-5-Methyl-5-(methylthio)-3-[2-(thiophen-2-yl)vinyl]furan-2(5*H*)-one (5m): Prepared according to the general procedure discussed above: R_f = 0.35; eluent, EtOAc/*n*-hexane (5%); isolated yield: 0.045 g (90%); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (d, J = 16.2 Hz, 1H), 7.26–7.27 (m, 1H), 7.14 (d, J = 3.6 Hz, 1H), 7.01–7.03 (m, 2H), 6.60 (d, J = 15.6 Hz, 1H), 1.94 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.9, 148.5, 141.7, 129.1, 128.7, 128.5, 127.9, 126.2, 115.2, 90.3, 25.1, 11.5; IR (KBr): ν_{max} = 2984, 1761, 1632, 1428, 1251, 1183, 1093, 1052, 960, 890, 705 cm^{-1}; HR-MS (ESI): m/z = 275.0164, calcd. for $C_{12}H_{12}O_2S_2Na$ $[M+Na]^+$: 275.0177.

5-Methyl-5-(methylthio)-3-(4-nitrophenyl)furan-2(5*H*)-one (5o): Prepared according to the general procedure discussed above: R_f = 0.35; eluent, EtOAc/*n*-hexane (15%); isolated yield: 0.041 g (82%); white solid; mp 111–113 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.29 (d, J = 9.0 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 7.62 (s, 1H), 1.99 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.0, 152.5, 148.3, 134.6, 129.1, 128.1 (2 CH), 124.0 (2 CH), 89.7, 24.7, 11.5; IR (KBr): ν_{max} = 1760, 1596, 1519, 1348, 1213, 1093, 958,

855 cm^{-1}; HR-MS (ESI): m/z = 288.0309, calcd. for $C_{12}H_{11}NO_4SNa$ $[M+Na]^+$: 288.0307.

(*E*)-5-(Methylthio)-3-styrylfuran-2(5*H*)-one (5p): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); isolated yield = 0.025 g, 50%; yellow gum. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, J = 16.2 Hz, 1H), 7.51 (d, J = 6.9 Hz, 2H), 7.31–7.40 (m, 3H), 7.15 (d, J = 2.1 Hz, 1H), 6.83 (d, J = 16.2 Hz, 1H), 6.05 (d, J = 1.8 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.6, 143.5, 136.2, 136.0, 130.9, 129.0, 128.8 (2 CH), 127.1 (2 CH), 115.9, 83.9, 12.0; IR (KBr): ν_{max} = 2925, 1762, 1641, 1429, 1078, 1047, 972, 939, 751, 696 cm^{-1}; HR-MS (ESI): m/z = 255.0461, calcd. for $C_{13}H_{12}O_2SNa$ $[M+Na]^+$: 255.0456.

(*E*)-3-(4-Methylstyryl)-5-(methylthio)furan-2(5*H*)-one (5q): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); isolated yield: 0.02 g (40%); yellow gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, J = 16.2 Hz, 1H), 7.40 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 2.4 Hz, 1H), 6.78 (d, J = 16.2 Hz, 1H), 6.03 (d, J = 1.8 Hz, 1H), 2.36 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.6, 142.8, 139.1, 136.2, 133.3, 131.1, 129.5 (2 CH), 127.0 (2 CH), 114.9, 83.9, 21.3, 12.0; IR (KBr): ν_{max} = 2924, 1763, 1670, 1607, 1568, 1077, 1047, 974, 935, 846, 777 cm^{-1}; HR-MS (ESI): m/z = 269.0598, calcd. for $C_{14}H_{14}O_2SNa$ $[M+Na]^+$: 269.0613.

(*E*)-3-(4-Chlorostyryl)-5-(methylthio)furan-2(5*H*)-one (5r): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); isolated yield: 0.023 g (46%); yellowish white solid; mp 114–116 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.71 (d, J = 16.8 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.33–7.34 (m, 2H), 7.15 (d, J = 1.8 Hz, 1H), 6.79 (d, J = 16.8 Hz, 1H), 6.04 (d, J = 1.8 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.4, 144.0, 134.9, 134.7, 134.6, 130.7, 129.0 (2 CH), 128.2 (2 CH), 116.5, 83.9, 12.1; IR (KBr): ν_{max} = 1755, 1081, 1048, 975, 935, 857, 817 cm^{-1}; HR-MS (ESI): m/z = 289.0062, calcd. for $C_{13}H_{11}ClO_2SNa$ $[M+Na]^+$: 289.0066.

(*E*)-4-{2-[5-(Methylthio)-2-oxo-2,5-dihydrofuran-3-yl]vinyl}benzonitrile (5s): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (25%); isolated yield: 0.025 g (50%); yellow gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.79 (d, J = 16.2 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 1.8 Hz, 1H), 6.92 (d, J = 16.2 Hz, 1H), 6.07 (d, J = 1.2 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.1, 145.8, 140.5, 134.2, 132.6 (2 CH), 130.2, 127.4 (2 CH), 119.3, 118.6, 112.0, 84.0, 12.2; IR (KBr): ν_{max} = 2923, 2225, 1762, 1082, 1048, 975, 939 cm^{-1}; HR-MS (EI): m/z = 257.0507, calcd. for $C_{14}H_{11}NO_2S$ $[M]^+$: 257.0510.

(*E*)-5-(Methylthio)-3-[2-(naphthalen-2-yl)vinyl]furan-2(5*H*)-one (5t): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); isolated yield: 0.028 g (56%); yellowish white solid; mp 120–122 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.90–7.92 (m, 2H), 7.81–7.85 (m, 3H), 7.68 (dd, J = 1.2, 8.4 Hz, 1H), 7.48–7.50 (m, 2H), 7.18 (d, J = 1.8 Hz, 1H), 6.95 (d, J = 16.8 Hz, 1H), 6.06 (d, J = 1.8 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.6, 143.4, 136.3, 133.6, 133.5, 133.5, 131.0, 128.5, 128.3, 128.3, 127.7, 126.6, 126.5, 123.1, 116.1, 84.0, 12.0; IR (KBr): ν_{max} = 1754, 1088, 1046, 971, 938 cm^{-1}; HR-MS (ESI): m/z = 305.0583, calcd. for $C_{17}H_{14}O_2SNa$ $[M+Na]^+$: 305.0613.

(*E*)-5-(Methylthio)-3-[2-(thiophen-3-yl)vinyl]furan-2(5*H*)-one (5u): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (12%); isolated yield: 0.02 g (40%); yellow gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.75 (d, J = 16.2 Hz, 1H), 7.38 (d, J = 1.8 Hz, 1H), 7.32–7.33 (m, 1H), 7.30 (dd, J = 1.2, 4.8 Hz, 1H), 7.09 (d, J = 2.4 Hz, 1H), 6.66 (d, J = 16.2 Hz, 1H), 6.03 (d, J = 1.8 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.5, 142.9, 139.1, 131.0, 130.3, 126.6, 125.3, 124.5, 115.8, 83.9, 12.0; IR (KBr): ν_{max} = 2924, 1761, 1639, 1424, 1080, 1047, 970, 938, 769 cm^{-1}; HR-MS (ESI): m/z = 261.0024, calcd. for $C_{11}H_{10}O_2S_2Na$ $[M+Na]^+$: 261.0020.

(*E*)-5-(Methylthio)-5-phenyl-3-styrylfuran-2(5*H*)-one (5v): Prepared according to the general procedure discussed above: R_f = 0.4; eluent, EtOAc/*n*-hexane (8%); isolated yield: 0.028 g (56%); yellow gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, J = 16.2 Hz, 1H), 7.57–7.59 (m, 2H), 7.49 (d, J = 7.2 Hz, 2H), 7.40–7.42 (m, 3H), 7.35–7.37 (m, 3H), 7.31 (t, J = 7.2 Hz, 1H), 6.82 (d, J = 16.8 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.8, 147.3, 136.9, 136.4, 136.1, 129.0, 128.9, 128.8 (2 CH), 128.8 (2 CH), 128.5, 127.0 (2 CH), 125.6 (2 CH), 115.8, 93.6, 12.7; IR (KBr): ν_{max} = 2924, 1767, 1147, 1056, 975, 746, 694 cm^{-1}; HR-MS (EI): m/z = 308.0879, calcd. for $C_{19}H_{16}O_2S$ $[M]^+$: 308.0871.

(*E*)-3-(4-Methylstyryl)-5-(methylthio)-5-phenylfuran-2(5*H*)-one (5w): Prepared according to the general procedure discussed above: R_f = 0.4; eluent, EtOAc/*n*-hexane (4%); isolated yield: 0.022 g (44%); yellow gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.71 (d, J = 16.8 Hz, 1H), 7.57–7.59 (m, 2H), 7.39–7.42 (m, 3H), 7.38 (s, 1H), 7.34–7.37 (m, 2H), 7.17 (d, J = 7.8 Hz, 2H), 6.77 (d, J = 16.2 Hz, 1H), 2.36 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.9, 146.7, 139.1, 137.0, 136.3, 133.3, 129.5 (2 CH), 128.9, 128.8 (2 CH), 128.7, 127.0 (2 CH), 125.6 (2 CH), 114.8, 93.6, 21.3, 12.7; IR (KBr): ν_{max} = 2923, 1767, 1146, 1056, 976, 749, 695 cm^{-1}; HR-MS (ESI): m/z = 345.0914, calcd. for $C_{20}H_{18}O_2SNa$ $[M+Na]^+$: 345.0926.

(*E*)-3-(2,4-Dichlorostyryl)-5-(methylthio)-5-phenylfuran-2(5*H*)-one (5x): Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (2%); isolated yield: 0.03 g (60%); colorless gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.00 (d, J = 16.2 Hz, 1H), 7.58–7.59 (m, 1H), 7.56–7.57 (m, 1H), 7.53 (d, J = 9.0 Hz, 1H), 7.48 (s, 1H), 7.40–7.43 (m, 3H), 7.35–7.38 (m, 1H), 7.25 (dd, J = 1.8, 8.4 Hz, 1H), 6.78 (d, J = 16.2 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.5, 148.4, 136.7, 134.9, 134.6, 132.9, 131.3, 129.8, 129.1, 128.9 (2 CH), 128.2, 127.4, 127.3, 125.6 (2 CH), 118.6, 93.7, 12.7; IR (KBr): ν_{max} = 2924, 1768, 1582, 1469, 1102, 1055, 976, 749 cm^{-1}; HR-MS (ESI): m/z = 398.9972, calcd. for $C_{19}H_{14}Cl_2O_2SNa$ $[M+Na]^+$: 398.9990.

5-Methyl-3-phenyl-5-(phenylthio)furan-2(5*H*)-one (3a): Prepared according to the general procedure discussed above under $BF_3{\cdot}OEt_2$-catalyzed conditions: R_f = 0.35; eluent, EtOAc/*n*-hexane (3%); isolated yield: 0.03 g (60%); white solid; mp 99–101 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.48–7.51 (m, 4H), 7.30–7.33 (m, 3H), 7.26–7.29 (m, 4H), 1.89 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.7, 149.3, 137.1 (2 CH), 131.2, 129.9, 129.4, 128.9 (2 CH), 128.7, 128.5 (2 CH), 128.5, 127.1 (2 CH), 91.6, 24.5; IR (KBr): ν_{max} =

1753, 1442, 1301, 1216, 1115, 1085, 958, 789, 750, 691 cm^{-1}; HR-MS (ESI): $m/z = 305.0606$, calcd. for $C_{17}H_{14}O_2SNa$ $[M+Na]^+$: 305.0613.

5-(Benzylthio)-5-methyl-3-phenylfuran-2(5*H*)-one (3o): Prepared according to the general procedure discussed above under $BF_3{\cdot}OEt_2$-catalyzed conditions: $R_f = 0.3$; eluent, EtOAc/*n*-hexane (4%); isolated yield: 0.04 g (80%); colorless gum. Analytical data were exactly matched with the previously discussed data.

5-Methyl-5-(naphthalen-2-ylthio)-3-phenylfuran-2(5*H*)-one (6a): Prepared according to the general procedure discussed above: $R_f = 0.3$; eluent, EtOAc/*n*-hexane (3%); isolated yield: 0.025 g (50%); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.05$ (s, 1H), 7.78–7.80 (m, 1H), 7.75–7.77 (m, 1H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.54 (dd, $J = 1.8$, 8.4 Hz, 1H), 7.47–7.49 (m, 2H), 7.41 (dd, $J = 1.2$, 7.8 Hz, 2H), 7.36 (s, 1H), 7.23–7.27 (m, 3H), 1.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 169.7$, 149.2, 137.1, 133.4, 133.2, 132.8, 131.4, 129.3, 128.6, 128.6, 128.4 (2 CH), 128.0, 127.6, 127.3, 127.0 (2 CH), 126.6, 125.9, 91.9, 24.7; IR (KBr): $\nu_{max} = 2924$, 1764, 1495, 1215, 1088, 959, 871, 788, 748, 693 cm^{-1}; HR-MS (EI): $m/z = 332.0877$, calcd. for $C_{21}H_{16}O_2S$ $[M]^+$: 332.0871.

5-(Benzylthio)-3,5-diphenylfuran-2(5*H*)-one (6b): Prepared according to the general procedure discussed above: $R_f = 0.3$; eluent, EtOAc/*n*-hexane (3%); isolated yield = 0.02 g (40%); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.77$–7.79 (m, 2H), 7.63–7.64 (m, 3H), 7.35–7.43 (m, 6H), 7.21–7.25 (m, 5H), 3.80 (d, $J = 12.6$ Hz, 1H), 3.68 (d, $J = 12.6$ Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 169.7$, 148.3, 136.9, 136.3, 130.3, 129.8, 129.1, 129.0 (2 CH), 128.9 (2 CH), 128.7 (2 CH), 128.6 (2 CH), 128.5, 127.3 (3 CH), 125.7 (2 CH), 93.6, 34.9 (CH_2); IR (KBr): $\nu_{max} = 2925$, 1764, 1492, 1450, 1157, 1086, 959, 899, 747, 696 cm^{-1}; HR-MS (ESI): $m/z = 381.0935$, calcd. for $C_{23}H_{18}O_2SNa$ $[M+Na]^+$: 381.0926.

(*E*)-3-(3,4-Dimethoxystyryl)-5-methyl-5-[(methyl-d_3)thio]-furan-2(5*H*)-one (6c): Prepared according to the general procedure discussed above: $R_f = 0.3$; eluent, EtOAc/*n*-hexane (20%); isolated yield: 0.038 g (76%); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.65$ (d, $J = 16.2$ Hz, 1H), 7.06 (dd, $J = 1.8$, 8.4 Hz, 1H), 7.03–7.04 (m, 2H), 6.86 (d, $J = 8.4$ Hz, 1H), 6.68 (d, $J = 16.8$ Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.3$, 149.9, 149.1, 147.7, 135.8, 129.2, 129.2, 120.7, 113.8, 111.1, 109.0, 90.2, 55.9, 55.9, 25.1; IR (KBr): $\nu_{max} = 2925$, 1761, 1595, 1513, 1461, 1265, 1140, 1050, 1026 cm^{-1}; HR-MS (ESI): $m/z = 332.1036$, calcd. for $C_{16}H_{15}D_3O_4SNa$ $[M+Na]^+$: 332.1012.

(*E*)-5-Methyl-5-[(methyl-d_3)thio]-3-styrylfuran-2(5*H*)-one (6d): Prepared according to the general procedure discussed above: $R_f = 0.4$; eluent, EtOAc/*n*-hexane (8%); isolated yield: 0.04 g (80%); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.72$ (d, $J = 16.2$ Hz, 1H), 7.50 (d, $J = 7.8$ Hz, 2H), 7.37 (t, $J = 7.2$ Hz, 2H), 7.30–7.32 (m, 1H), 7.09 (s, 1H), 6.81 (d, $J = 16.2$ Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.0$, 148.8, 136.1, 136.0, 129.1, 128.9, 128.8 (2 CH), 127.0 (2 CH), 115.8, 90.1, 25.1; IR (KBr): $\nu_{max} = 2926$, 1755, 1443, 1277, 1051, 964, 889, 742, 691 cm^{-1}; HR-MS (ESI): $m/z = 272.0815$, calcd. for $C_{14}H_{11}D_3O_2SNa$ $[M+Na]^+$: 272.0801.

[5-Methyl-3-phenyl-3-(*p*-tolylthio)furan-2(3*H*)-one (2d) plus 5-methyl-3-phenyl-3-(phenylthio)furan-2(3*H*)-one (2a)] and [3-(4-methoxyphenyl)-5-methyl-3-(*p*henylthio)furan-2(3*H*)-one (2r) plus 3-(4-methoxyphenyl)-5-methyl-3-(*p*-tolylthio)furan-2(3*H*)-one (2s)]: NMR of mixtures **2d** plus **2a**; major peaks: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.64$–7.69 (m, 2H), 7.45 (dd, $J = 8.2$, 1.2 Hz, 1H), 7.35–7.41 (m, 2H), 7.29–7.35 (m, 3H), 7.11 (d, $J = 7.8$ Hz, 1H), 5.51–5.55 (m, 1H), 2.35 (s, 2H), 1.81 (d, $J = 1.4$ Hz, 2H), 1.79 (d, $J = 1.4$ Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 175.4$, 152.0, 151.9, 140.4, 137.1, 137.0, 135.1, 135.0, 130.0, 129.4, 128.7, 128.7, 128.5, 128.5, 127.4, 126.5, 106.1, 106.0, 62.1, 21.3, 13.7, 13.7. NMR of mixtures **2r** plus **2s**; major peaks: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.56$–7.61 (m, 2H), 7.43–7.47 (m, 1H), 7.29–7.34 (m, 2H), 7.11 (d, $J = 7.8$ Hz, 1H), 6.87–6.91 (m, 2H), 5.48–5.53 (m, 1H), 3.81 (s, 3H), 2.35 (s, 2H), 1.80 (d, $J = 1.3$ Hz, 2H), 1.78 (d, $J = 1.4$ Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 175.6$, 159.6, 151.8, 151.7, 140.3, 137.0, 137.0, 130.2, 129.9, 129.4, 128.7, 128.6, 127.0, 126.7, 114.0, 114.0, 106.2, 106.1, 61.8, 55.3, 21.3, 13.7, 13.6.

{(*E*)-5-Methyl-5-(methylthio)-3-styrylfuran-2(5*H*)-one (5a) plus (*E*)-5-methyl-5-[(methyl-d_3)thio]-3-styrylfuran-2(5*H*)-one (6d)} and {(*E*)-3-(3,4-dimethoxystyryl)-5-methyl-5-(methylthio)furan-2(5*H*)-one (5c) plus (*E*)-3-(3,4-dimethoxystyryl)-5-methyl-5-[(methyl-d_3)thio]furan-2(5*H*)-one (6c)}: NMR of mixtures **5a/6d**; major peaks: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.72$ (d, $J = 16.8$ Hz, 1H), 7.50 (d, $J = 7.2$ Hz, 2H), 7.37 (t, $J = 7.2$ Hz, 2H), 7.30–7.32 (m, 1H), 7.09 (s, 1H), 6.81 (d, $J = 16.2$ Hz, 1H), 1.96 (s, 2H), 1.81 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.0$, 148.8, 148.8, 136.1, 136.0, 129.1, 128.9, 128.8 (2 CH), 127.0 (2 CH), 115.8, 90.2, 90.1, 25.1, 25.1, 11.5. NMR of mixtures **5c/6c**; major peaks: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.66$ (d, $J = 16.2$ Hz, 1H), 7.08 (dd, $J = 1.8$, 8.4 Hz, 1H), 7.06 (s, 1H), 7.04 (d, $J = 1.8$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 1H), 6.69 (d, $J = 16.2$ Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 1.97 (s, 2H), 1.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.3$, 149.9, 149.2, 147.7, 135.8, 129.2, 120.7, 113.8, 111.1, 109.0, 90.3, 90.3, 55.9, 55.9, 25.2, 25.1, 11.5. NMR data of **5a/6d/5c/6c** were exactly matched with our previous data discussed in the Experimental Section.

[5-(Benzylthio)-5-methyl-3-phenylfuran-2(5*H*)-one (3o) and 5-methyl-3-phenyl-5-(phenylthio)furan-2(5*H*)-one (3a)]: NMR of mixtures **3o/3a**; major peaks: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.73$–7.75 (m, 2H), 7.40–7.41 (m, 3H), 7.31 (s, 1H), 7.20–7.24 (m, 5H), 3.71 (d, $J = 13.2$ Hz, 1H), 3.64 (d, $J = 13.2$ Hz, 1H), 1.89 (s, CH_3, minor compound peak), 1.84 (s, 3H, CH_3, major compound peak); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 169.9$, 149.9, 136.7, 129.7, 128.8, 128.7, 128.6, 127.3, 127.2, 90.3, 33.7, 25.4. NMR data of **3o** and **3a** were exactly matched with our previous data discussed in the Experimental Section.

(*E*)-5-(Cyclohexylamino)-5-methyl-3-styrylfuran-2(5*H*)-one (7a): Prepared according to the general procedure discussed above: $R_f = 0.3$; eluent, EtOAc/*n*-hexane (15%); isolated yield: 0.027 g (45%); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.76$ (d, $J = 15.9$ Hz, 1H), 7.47 (d, $J = 7.2$ Hz, 2H), 7.29–7.36 (m, 3H), 6.78 (d, $J = 16.5$ Hz, 1H), 6.67 (s, 1H), 3.33–3.44 (m, 1H), 2.23–2.42 (m, 2H), 1.84–1.85 (m, 2H), 1.66–1.69 (m, 4H), 1.58 (s, 3H), 1.25–1.28 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 167.6$, 140.9, 136.8, 134.9, 133.9, 128.7 (2 CH), 128.3, 126.8 (2 CH), 118.0, 88.4, 52.0, 30.6 (CH_2), 30.2 (CH_2), 26.4 (2 CH_2), 25.3 (CH_2), 23.0; IR (KBr): $\nu_{max} = 2930$, 2855, 1758, 1674, 1446, 1426, 1373,

1126, 967, 752, 695 cm^{-1}; HR-MS (ESI): $m/z = 320.1599$, calcd. for $C_{19}H_{23}NO_2Na$ $[M+Na]^+$: 320.1627.

(*E*)-5-(Cyclopropylamino)-5-methyl-3-styrylfuran-2(5*H*)-one (7b): Prepared according to the general procedure discussed above: $R_f = 0.3$; eluent, EtOAc/*n*-hexane (25%); isolated yield: 0.025 g (48%); white solid; mp 129–131 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.69$ (d, $J = 16.2$ Hz, 1H), 7.46 (d, $J = 7.5$ Hz, 2H), 7.27–7.36 (m, 3H), 6.76 (d, $J = 16.2$ Hz, 1H), 6.70 (s, 1H), 2.41–2.48 (m, 1H), 2.25 (br. s., 1H), 1.67 (s, 3H), 1.23–1.29 (m, 1H), 0.90–0.97 (m, 1H), 0.72–0.80 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 169.8$, 141.7, 136.7, 135.0, 133.3, 128.7 (2 CH), 128.4, 126.8 (2 CH), 117.7, 88.9, 22.9, 21.2, 5.7 (CH_2), 3.0 (CH_2); IR (KBr): $\nu_{max} =$ 2990, 1684, 1636, 1411, 1128, 975, 746, 694 cm^{-1}; HR-MS (ESI): $m/z = 278.1173$, calcd. for $C_{16}H_{17}NO_2Na$ $[M+Na]^+$: 278.1157.

(*E*)-5-(Benzylamino)-5-methyl-3-styrylfuran-2(5*H*)-one (7c): Prepared according to the general procedure discussed above: $R_f = 0.3$; eluent, EtOAc/*n*-hexane (20%); isolated yield: 0.025 g (40%); colorless gum. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.74$ (d, $J = 16.5$ Hz, 1H), 7.50 (d, $J = 6.9$ Hz, 2H), 7.28–7.40 (m, 8H), 6.82 (d, $J = 16.5$ Hz, 1H), 6.75 (s, 1H), 4.75 (d, $J = 15.3$ Hz, 1H), 4.51 (d, $J = 15.3$ Hz, 1H), 2.65 (br. s., 1H), 1.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 168.8$, 142.1, 138.3, 136.7, 135.1, 133.0, 128.7 (2 CH), 128.5 (3 CH), 127.9 (2 CH), 127.2, 126.9 (2 CH), 117.8, 88.2, 41.8 (CH_2), 23.5; IR (KBr): $\nu_{max} = 2926$, 1670, 1493, 1415, 1127, 750, 698 cm^{-1}; HR-MS (ESI): $m/z = 328.1311$, calcd. for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 328.1314.

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References

[1] For 1,2-sulfur migration, see reviews: a) D. J. Fox, D. House, S. Warren, *Angew. Chem.* **2002**, *114*, 2572; *Angew. Chem. Int. Ed.* **2002**, *41*, 2462; b) A. W. Sromek, V. Gevorgyan, *Top. Curr. Chem.* **2007**, *274*, 77; c) I. P. Smoliakova, *Curr. Org. Chem.* **2000**, *4*, 589; for selected references, see: d) J. T. Kim, A. V. Kel'in, V. Gevorgyan, *Angew. Chem.* **2003**, *115*, 102; *Angew. Chem. Int. Ed.* **2003**, *42*, 98; *Angew. Chem.* **2003**, *115*, 102; e) L. Peng, X. Zhang, J. Ma, Z. Zhong, J. Wang, *Org. Lett.* **2007**, *9*, 1445; f) Y. Jiang, X.-Y. Tang, M. Shi, *Chem. Commun.* **2015**, *51*, 2122; g) A. S. Dudnik, A. W. Sromek, M. Rubina, J. T. Kim, A. V. Kel'in, V. Gevorgyan, *J. Am. Chem. Soc.* **2008**, *130*, 1440; h) S. E. Denmark, T. Vogler, *Chem. Eur. J.* **2009**, *15*, 11737; i) D. Yadagiri, P. Anbarasan, *Chem. Sci.* **2015**, *6*, 5847; For 1,3-sulfur migration, see review: j) S. K. Bur, *Top. Curr. Chem.* **2007**, *274*, 125.

[2] For 1,4-sulfur migration, see review in ref.[1] and for references, see: a) L. Peng, X. Zhang, M. Ma, J. Wang, *Angew. Chem.* **2007**, *119*, 1937; *Angew. Chem. Int. Ed.* **2007**, *46*, 1905; *Angew. Chem.* **2007**, *119*, 1937; b) Z. Fang, J. Liu, Q. Liu, X. Bi, *Angew. Chem.* **2014**, *126*, 7337; *Angew. Chem. Int. Ed.* **2014**, *53*, 7209; *Angew. Chem.* **2014**, *126*, 7337.

[3] For selected reviews of natural products containing butenolides, see: a) Y. S. Rao, *Chem. Rev.* **1976**, *76*, 625; b) F. Q. Alali, X-X. Liu, J. L. McLaughlin, *J. Nat. Prod.* **1999**, *62*, 504; c) P. A. Roethlem, D. Trauner, *Nat. Prod. Rep.* **2008**, *25*, 298; d) A. Bermejo, B. Figadere, M.-C. Zafra-Polo, I. Barrachina, E. Estornellc, D. Cortes, *Nat. Prod. Rep.* **2005**, *22*, 269.

[4] For selected reviews on the synthesis of butenolides, see: a) G. Casiraghi, F. Zanardi, G. Appendino, G. Rassu, *Chem. Rev.* **2000**, *100*, 1929; b) S. E. Denmark, J. R. Heemstra Jr, G. L. Beutner, *Angew. Chem.* **2005**, *117*, 4760; *Angew. Chem. Int. Ed.* **2005**, *44*, 4682; *Angew. Chem.* **2005**, *117*, 4760; c) T. Montagnon, M. Tofi, G. Vassilikogiannakis, *Acc. Chem. Res.* **2008**, *41*, 1001; d) R. R. A. Kitson, A. Millemaggi, R. J. K. Taylor, *Angew. Chem.* **2009**, *121*, 9590; *Angew. Chem. Int. Ed.* **2009**, *48*, 9426; *Angew. Chem.* **2009**, *121*, 9590; e) S. V. Pansare, E. K. Paul, *Chem. Eur. J.* **2011**, *17*, 8770; f) S. Ma, *Acc. Chem. Res.* **2003**, *36*, 701; g) E. Negishi, M. Kotora, *Tetrahedron* **1997**, *53*, 6707.

[5] For selected references on the synthesis of butenolides having one or more quaternary centres, see: a) Y. Liu, F. Song, S. Guo, *J. Am. Chem. Soc.* **2006**, *128*, 11332; b) Q. Zhang, M. Cheng, X. Hu, B.-G. Li, J.-X. Ji, *J. Am. Chem. Soc.* **2010**, *132*, 7256; c) H. Miura, K. Takeuchi, T. Shishido, *Angew. Chem.* **2016**, *128*, 286; *Angew. Chem.* **2016**, *128*, 286; *Angew. Chem. Int. Ed.* **2016**, *55*, 278; d) W. Zhang, D. Tan, R. Lee, G. Tong, W. Chen, B. Qi, K.-W. Huang, C.-H. Tan, Z. Jiang, *Angew. Chem.* **2012**, *124*, 10216; *Angew. Chem. Int. Ed.* **2012**, *51*, 10069; e) K. Endo, S. Yakeishi, R. Takayama, T. Shibata, *Chem. Eur. J.* **2014**, *20*, 8893; f) H.-L. Cui, J.-R. Huang, J. Lei, Z.-F. Wang, S. Chen, L. Wu, Y.-C. Chen, *Org. Lett.* **2010**, *12*, 720; g) H. Xiao, H.-y. Duan, J. Ye, R.-s. Yao, J. Ma, Z.-z. Yuan, G. Zhao, *Org. Lett.* **2014**, *16*, 5462; h) C. Zheng, W. Yao, Y. Zhang, C. Ma, *Org. Lett.* **2014**, *16*, 5028; i) A. Quintard, A. Lefranc, A. Alexakis, *Org. Lett.* **2011**, *13*, 1540; j) W. Mao, C. Zhu, *Org. Lett.* **2015**, *17*, 5710; k) S. Li, B. Miao, W. Yuan, S. Ma, *Org. Lett.* **2013**, *15*, 977; l) A. M. Hyde, S. L. Buchwald, *Org. Lett.* **2009**, *11*, 2663.

[6] For other applications of α-keto thioesters, see: a) M. Arisawa, S. Tanii, T. Yamada, M. Yamaguchi, *Tetrahedron* **2015**, *71*, 6449; b) S. Kukolja, S. E. Draheim, J. L. Pfeil, R. D. G. Cooper, B. J. Graves, R. E. Holmes, D. A. Neel, G. W. Huffman, J. A. Webber, *J. Med. Chem.* **1985**, *28*, 1886; c) A. Wilsily, E. Fillion, *Org. Lett.* **2008**, *10*, 2801.

[7] CCDC 1484008 (**2c**), CCDC 1480818 (**4ae**), CCDC 1480819 (**5e**), and CCDC 1480820 (**5t**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. See also the Supporting Information.

[8] For the preparation of β,γ-unsaturated α-keto thioesters, see: a) K. Mal, A. Sharma, P. R. Maulik, I. Das, *Chem. Eur. J.* **2014**, *20*, 662; b) K. Mal, S. Das, N. C. Maiti, R. Natarajan, I. Das, *J. Org. Chem.* **2015**, *80*, 2972; c) K. Mal, A. Kaur, F. Haque, I. Das, *J. Org. Chem.* **2015**, *80*, 6400.

[9] For other applications of γ-keto thioesters, see: a) M. Takahashi, N. Sekine, T. Fujita, S. Watanabe, K. Yamaguchi, M. Sakamoto, *J. Am. Chem. Soc.* **1998**, *120*, 12770; b) M. Sakamoto, M. Takahashi, S. Moriizumi, K. Yamaguchi, T. Fujita, S. Watanabe, *J. Am. Chem. Soc.* **1996**, *118*, 8138; c) K. Ogura, N. Yahata, M. Minoguchi, K. Ohtsuki, K. Takahashi, H. Iida, *J. Org. Chem.* **1986**, *51*, 508; d) J.-P. Bouillon, V. Kikelj, B. Tinant, D. Harakat, C. Portella, *Synthesis* **2006**, 1050.

[10] A similar pathway has been proposed for the formation of γ-hydroxybutenolides *via* hydroxy transposition after the annulation. For details, see: W. Mao, C. Zhu, *Chem. Commun.* **2016**, *52*, 5269.

20 Tandem Chemoselective 1,2-/1,4-Migration of the Thio Group in Keto Thioesters: An Efficient Approach to Substituted Butenolides

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