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Copper-Catalyzed Sulfenylation, Sulfonylation, and Selenylation of 2,3-Allenoic Acids with Disulfides or Diselenides

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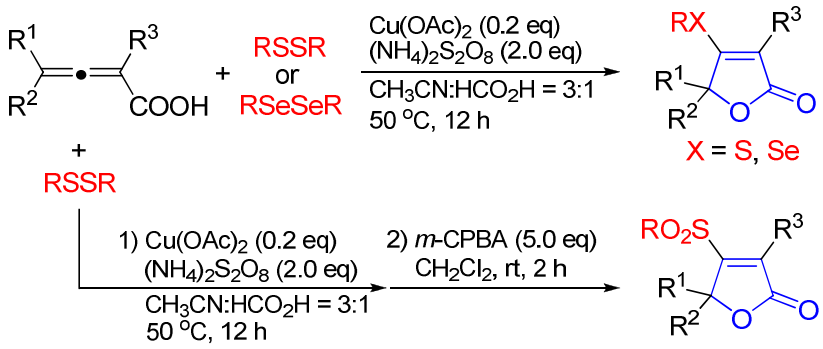


Abstract

The efficient copper-catalyzed sulfenylation and selenylation of 2,3-allenoic acids with disulfides or diselenides were developed, respectively. These reactions proceeded through tandem radical addition/intramolecular cyclization processes, affording a series of 4-sulfenylated and 4-selenylated butenolides in moderate to excellent yields. Moreover, 4-sulfonylated butenolides could also be obtained by sulfenylation of 2,3-allenoic acids and subsequent oxidation. Further transformation of the sulfur- and selenium-containing butenolides afforded the corresponding furan derivatives in good yields.

Introduction

Furan-2(5*H*)-ones (butenolides) are an important class of compounds, which are often found in natural products and biological compounds.[1] Some representative examples of bioactive butenolides are depicted in Figure 1. Butenolides are also important intermediate in organic synthesis,[2] because of the presence of conjugated C=C bond and five-membered lactone ring. Consequently, the development of synthetic strategies of butenolides has attracted enormous attention from chemists.[3] On the other hand, organosulfur compounds are significant structural motifs existing in medicinal chemistry, agrochemistry, and material sciences.[4] Therefore, a great amount of effort has been directed at the preparation of sulfur-containing butenolides, which combine the butenolide moiety with sulfur-containing group.

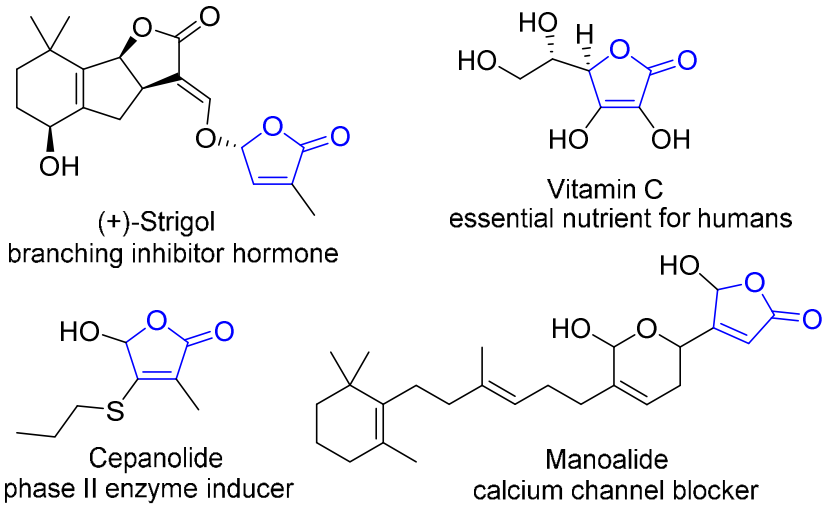


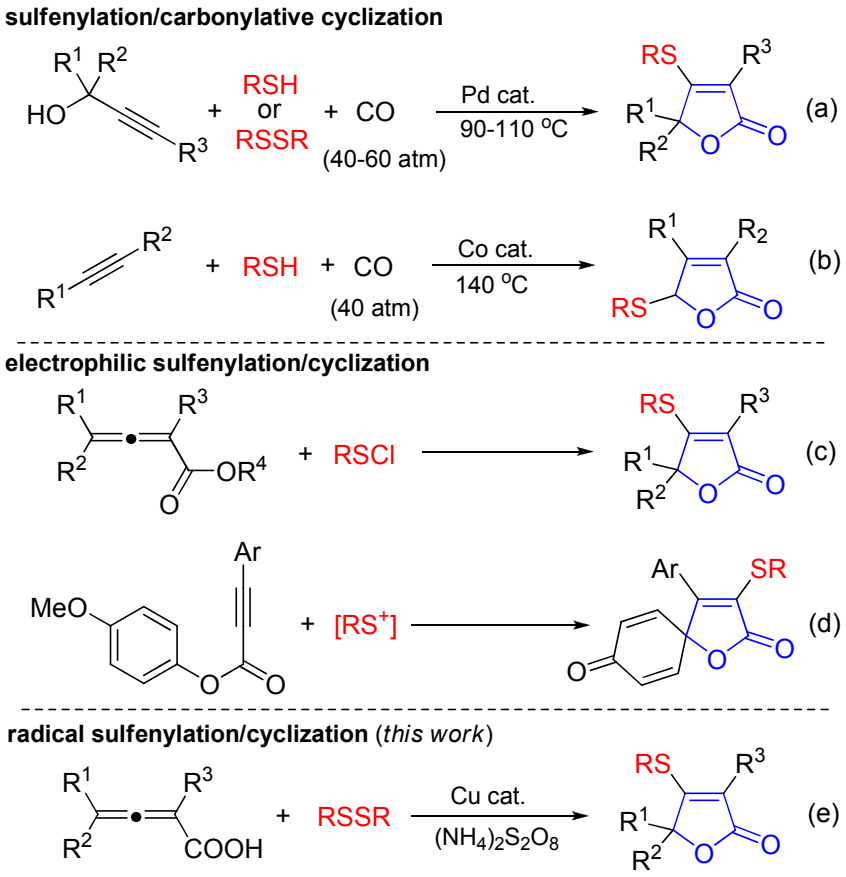
Figure 1. Bioactive butenolides

Traditional approaches to sulfur-containing butenolides mainly include sulfenylation of functionalized butenolides,[5] elimination of sulfur-containing γ-butyrolactones,[6] oxidation of sulfur-containing furans,[7] reduction of sulfur-containing maleic anhydrides,[8] transformation of sulfur-containing 2-silyloxyfurans,[9] and cyclization of sulfur-containing building blocks.[10] However, these methods suffer from the prefunctionalized substrates. From the viewpoint of step-economy, the methods for the simultaneous

introduction of sulfur-containing groups and construction of butenolide moiety are more appealing. In 1997, Alper[11a] and Ogawa[11b] independently reported the Pd-catalyzed carbonylative cyclization of propargylic alcohols with carbon monoxide and disulfides or thiols to provide the corresponding 4-sulfenylated butenolides (Scheme 1a). Afterward, Ogawa's group realized a novel Co-catalyzed thiolative lactonization of alkynes with thiols with incorporation of two molecules of carbon monoxide for the preparation of 5-sulfenylated butenolides (Scheme 1b).[12] In 2004, Ma and co-workers elegantly reported an electrophilic cyclization of 2,3-allenoic acids with PhSCl (Scheme 1c).[13a] Recently, Christov extended this electrophilic cyclization protocol to 2,3-allenoates affording high functionalized butenolides.[13b,c] More recently, the cyclization of 4-methoxyphenyl-3-phenylpropiolate with electrophilic sulfenylating reagents were uncovered to deliver sulfenylated spirocyclic products (Scheme 1d).[14] Despite these impressive achievements, the development of new methods by thiolative cyclization of readily available substrates to access sulfenylated butenolides is highly desirable.

Radical-triggered cascade reactions serve as ideal strategies in the synthesis of heterocyclic scaffolds. However, the radical cascade cyclization to access sulfenylated butenolides remains underexplored. Recently, our group disclosed a tandem radical trifluoromethylthiolation/intramolecular cyclization of 2,3-allenoic acids with $AgSCF_3$ to afford 4-trifluoromethylthiolated butenolides.[15] In continuation of our recent research interest in organosulfur compounds[15,16] and to extend the scope of radical cascade cyclization of 2,3-allenoic acids, herein we disclose a copper-catalyzed sulfenylation of 2,3-allenoic acids with disulfides in the presence of $(NH_4)_2S_2O_8$ (Scheme 1e). It should be noted that this protocol could be applied in the preparation of 4-selenylated butenolides with diselenides as the selenylating reagent. Furthermore, 4-sulfonylated butenolides could be also obtained by sulfenylation of 2,3-allenoic acids and subsequent oxidation.

Scheme 1. Synthesis of Sulfur-Containing Butenolides by Tandem Sulfenylation/Cyclization Reactions

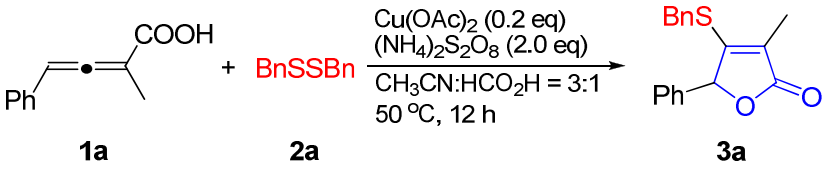


Results and Discussion

Initially, the radical thiolative cyclization of 2-methyl-4-phenyl-2,3-allenoic acid (**1a**) was chosen as a model reaction with 1,2-dibenzyldisulfide (**2a**) as the sulfenylating reagent. The reaction was performed in the presence of catalytic $Cu(OAc)_2$ with $(NH_4)_2S_2O_8$ as the oxidant in CH_3CN/HCO_2H, which were similar to those previously employed in the copper-catalyzed trifluoromethylthiolation/intramolecular cyclization of 2,3-allenoic acids.[15] To our delight, under these conditions the reaction afforded the desired 4-benzylsulfenyl butenolide **3a** in 94% yield (Table 1, entry 1). The catalytic copper salt was crucial to this reaction. Only trace of **3a** was detected without the cooper salt (entry 2), and switching $Cu(OAc)_2$ to CuCN or CuI led to lower yields (entries 3 and 4). The

oxidant was also necessary for this reaction, as **3a** was formed in only 8% yield in the absence of $(NH_4)_2S_2O_8$ (entry 5). When $K_2S_2O_8$ was used instead of $(NH_4)_2S_2O_8$, the reaction proceeded smoothly to give **3a** in slightly lower yield (entry 6). Being similar to the trifluoromethylthiolation of 2,3-allenoic acids,[15] the use of acid as the co-solvent was critical to achieve this reaction (entry 7). Using HOAc instead of HCO_2H or changing the ratio of CH_3CN/HCO_2H did not improve the efficiency of this reaction (entries 8-10). Finally, decreasing the reaction temperature or shortening the reaction time led to lower yields (entries 11 and 12).

Table 1. Optimization of Reaction Conditions[a]

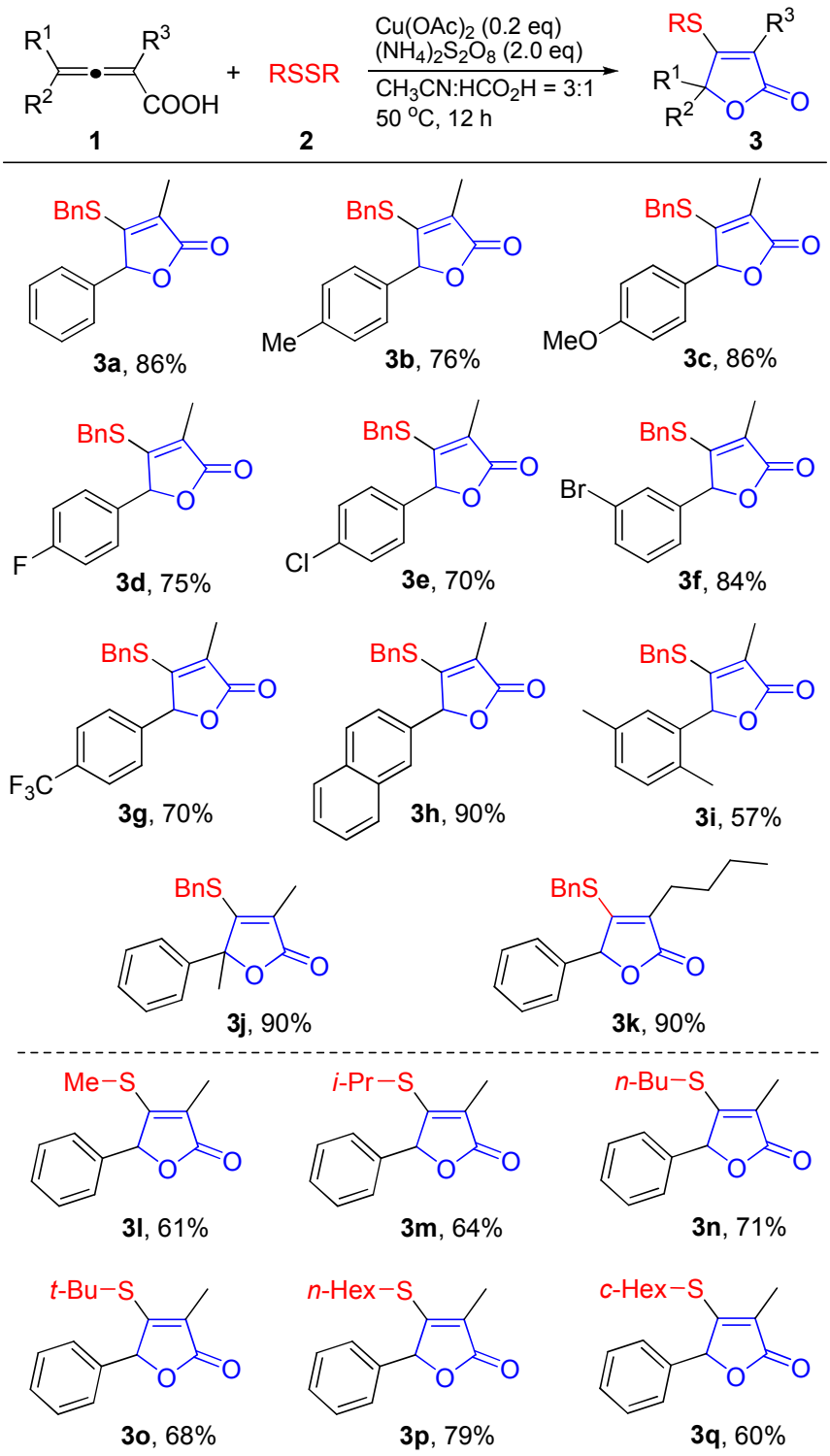


1a **2a** **3a**

entry	variant conditions	yield (%)[b]
1	standard conditions	94
2	without $Cu(OAc)_2$	trace
3	CuCN instead of $Cu(OAc)_2$	80
4	CuI instead of $Cu(OAc)_2$	84
5	without $(NH_4)_2S_2O_8$	8
6	$K_2S_2O_8$ instead of $(NH_4)_2S_2O_8$	89
7	without HCO_2H	trace
8	HOAc instead of HCO_2H	62
9	$CH_3CN:HCO_2H$ = 1:1	59
10	$CH_3CN:HCO_2H$ = 5:1	80
11	room temperature	67
12	3 h	83

[a]Reaction conditions: **1a** (0.1 mmol), BnSSBn (0.2 mmol), $Cu(OAc)_2$ (0.02 mmol), $(NH_4)_2S_2O_8$ (0.2 mmol), CH_3CN/HCO_2H (1.5 mL/0.5 mL), under N_2, 50 °C, 12 h. [b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethylphenol as an internal standard.

Scheme 2. Copper-Catalyzed Sulfenylation of 2,3-Allenoic Acids with Disulfides[a]

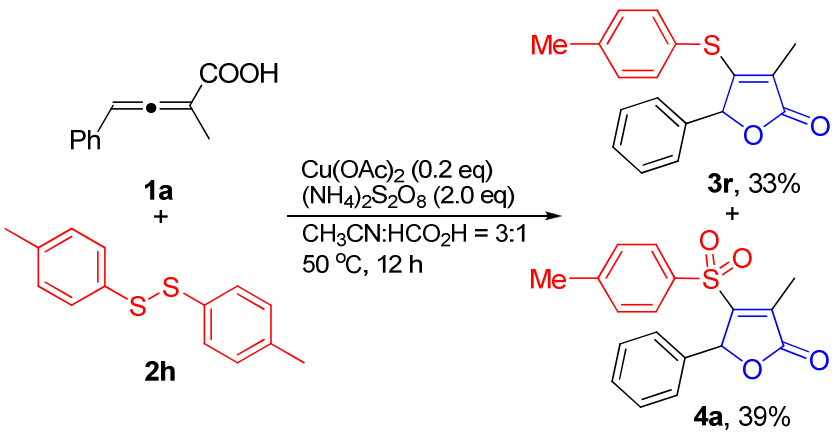


[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $Cu(OAc)_2$ (0.04 mmol), $(NH_4)_2S_2O_8$ (0.4 mmol), CH_3CN/HCO_2H (3.0 mL/1.0 mL), under N_2, 50 °C, 12 h. Yields are those of the isolated products.

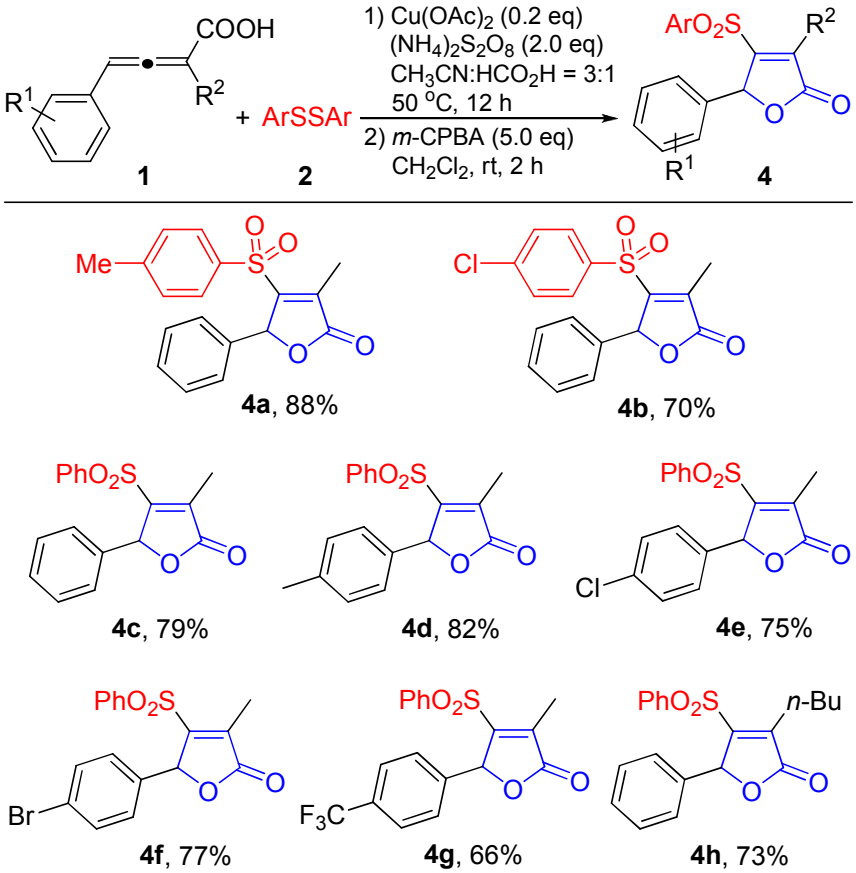
With optimized conditions in hand, the substrate scope of 2,3-allenoic acids and disulfides were investigated. As shown in Scheme 2, a range of 2,3-allenoic acids **1a-k** reacted with disulfide **2a** to afford the corresponding butenolides **3a-k** in good to excellent yields. A series of functional groups including alkyl, alkoxy, fluoride, chloride, bromide, and trifluoromethyl were well tolerated under the mild conditions. Satisfactorily, the 2,3-allenoic acid bearing naphthyl group (**1h**) was also suitable for this reaction. In the case of substrate with *ortho*-substitution on the benzene (**1i**), lower yield was obtained. Interestingly, 2,4,4-trisubstituted 2,3-allenoic acid (**1j**) reacted smoothly to give polysubstituted product (**2j**) in 90% yield.

Next, we examined the scope and limitation of disulfides. The reaction of 2-methyl-4-phenyl-2,3-allenoic acid (**1a**) and different dialkyldisulfides **2** cloud also give the desired products **3l-q** in moderate yields (Scheme 2). In general, the yields are lower than that of these obtained with 1,2-dibenzyldisulfide (**2a**) as the sulfenylating reagent, probably due to the lower stability and/or reactivity of alkylthio radical. To our surprise, when diaryldisulfide **2h** was subjected to the reaction conditions, the sulfenylated product **3r** was obtained in 33% yield along with an unexpected sulfonylated product **4a** in 39% yield (Scheme 3). The amount of sulfonylated product **4a** did not change much by varying the reaction conditions, such as the amount of $(NH_4)_2S_2O_8$, temperature, and reaction time.

Scheme 3. Reaction of 1a with Diaryldisulfide



Scheme 4. Sulfonylation of 2,3-Allenoic Acids[a]



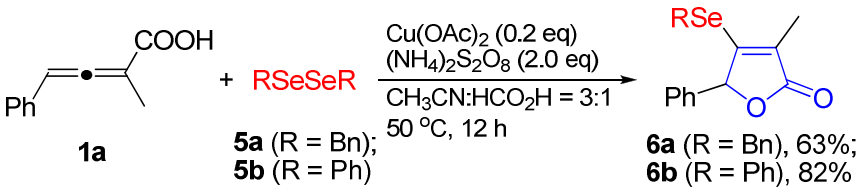
[a]Reaction conditions: 1) **1** (0.2 mmol), **2** (0.4 mmol), $Cu(OAc)_2$ (0.04 mmol), $(NH_4)_2S_2O_8$ (0.4 mmol), CH_3CN/HCO_2H (3.0 mL/1.0 mL), under N_2, 50 °C, 12 h; 2) *m*-CPBA (1.0 mmol), DCM (10.0 mL), rt, 2 h. Yields are those of the isolated products.

Considering the importance of sulfonylated compounds in organic synthesis and medicinal chemistry,[17] we then turned our attention to prepare sulfonylated butenolides. After optimization of the reaction conditions (see the Supporting Information), we were pleased to find that reaction of 2,3-allenoic acids **1** and diaryldisulfides **2** under the standard conditions followed by the oxidation with *m*-CPBA (*m*-chloroperbenzoic acid) could deliver the corresponding sulfonylated butenolides **4** in high yields (Scheme 4). Both of the electron-donating and electron-withdrawing groups on the aromatic ring of 2,3-allenoic acids **1** or diaryldisulfides **2** were well tolerated. Unfortunately, dialkyldisulfides were not suitable substrates for this transformation, as a complex mixture was obtained. This procedure

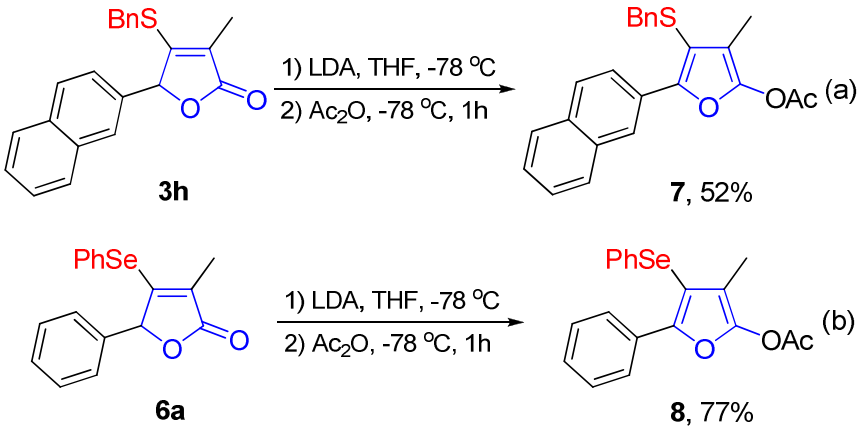
provided a convenient and efficient approach to sulfonylated butenolides without purification of the sulfide intermediates. Notably, no sulfinylated product was isolated in this reaction.

To further probe the applicability of this method, the tandem selenylation/cyclization was also tested. As shown in Scheme 5, treatment of 2-methyl-4-phenyl-2,3-allenoic acid (**1a**) with dibenzyldiselenide (**5a**) or diphenyldiselenide (**5b**) under the standard conditions provided selenylated butenolides **6a** and **6b** in good yields, respectively. To the best of our knowledge, these results represent the first example of preparation of selenylated butenolides through radical processes.[18]

Scheme 5. Selenylation of 2,3-Allenoic Acids



Scheme 6. Transformation of the Sulfenylated and Selenylated Butenolides

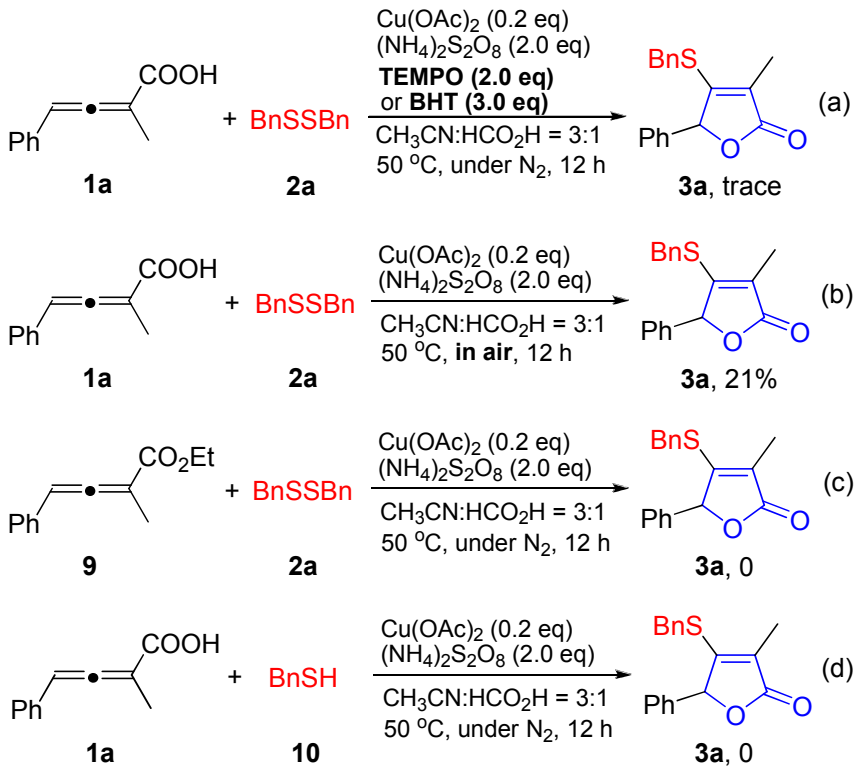


The synthetic value of this protocol was demonstrated by transformation of the sulfenylated and selenylated butenolides. For example, deprotonation of sulfenylated butenolide **3h** with LDA followed by acetylation with Ac_2O delivered sulfenylated furan **7** in 52% yield (Scheme 6a). Similarly,

selenylated butenolide **6b** was transformed to selenylated furan **8** in 77% yield by deprotonation/acetylation (Scheme 6b).

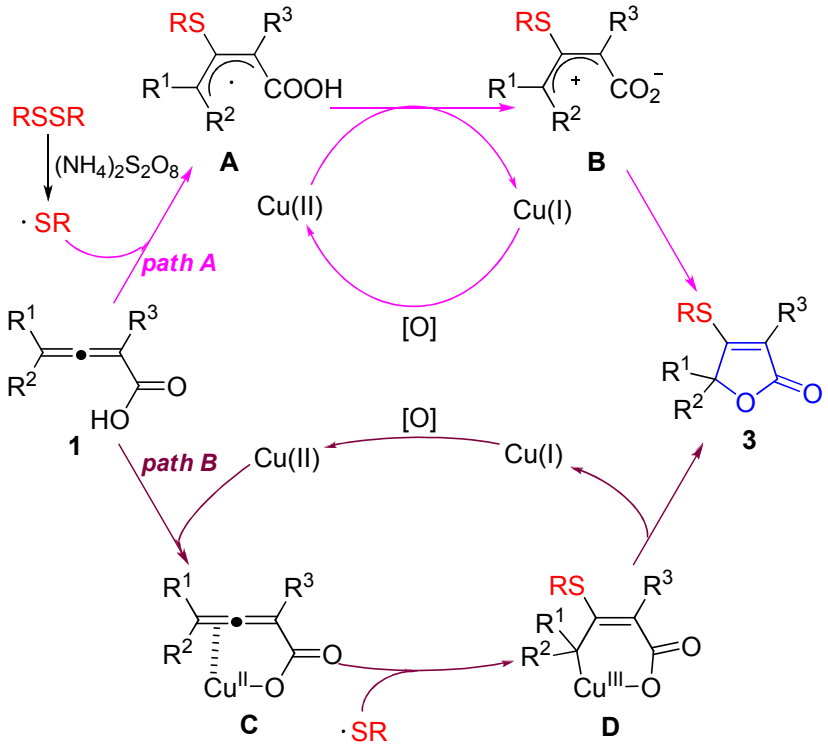
To gain insight into the reaction mechanism, several mechanistic studies were carried out. When the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added to the standard reaction conditions, most of the starting material (**1a**) was recovered and only a trace amount of the desired product **3a** was detected (Scheme 7a). These observations demonstrated that a radical pathway was probably involved in this reaction. Furthermore, this reaction could be conducted in air, but affording product **3a** in a much lower yield along with the recovery of some of the starting material (Scheme 7b), which was consistent with the fact that O_2 may inhibit the radical reaction. Finally, the control experiments with 2,3-allenoate **9** or thiol **10** in place of 2,3-allenoic acid **1a** or disulfide **2a** could not yield any of the desired product **3a** (Scheme 7c and 7d). These results indicated that both 2,3-allenoic acid and disulfide were crucial for this reaction.

Scheme 7. Mechanistic Experiments



Based on the above results and literature precedents,[15,19] a plausible mechanism for the reaction is proposed in Scheme 8. First, disulfides were oxidized to the sulfenyl radical by $(NH_4)_2S_2O_8$. Then, the addition of sulfenyl radical to 2,3-allenoic acids **1** generated the radical intermediate **A**, which could be further oxidized by Cu(II) for the formation of intermediate **B**. Finally, the intramolecular attack of intermediate **B** furnished the cyclized products **3** (*path A*). Alternatively, another pathway is also possible. The coordination of Cu(II) with 2,3-allenoic acids **1** formed complex **C**. Subsequently, the reaction of complex **C** and sulfenyl radical provided Cu(III) intermediate **D**, which would undergo reductive elimination to release the desired product **3** (*path B*). In both pathways, the regenerated Cu(I) species could be oxidized to Cu(II) species for the next catalytic cycle. However, the exact mechanism of this transformation remains unclear at the present stage.

Scheme 8. Proposed Reaction Mechanism



Conclusion

We have developed a copper-catalyzed sulfenylation and selenylation of 2,3-allenoic acids with disulfides or diselenides, to afford a series of 4-sulfenylated and 4-selenylated butenolides in moderate to excellent yields. This protocol also allows a convenient access to 4-sulfonylated butenolides by tandem sulfenylation/cyclization and subsequent oxidation. Furthermore, the sulfenylated and selenylated butenolides could be transformed to the corresponding furan derivatives. Most of these sulfenylated, sulfonylated, and selenylated butenolides are previous unknown and might have potential utility in medical chemistry. Further exploration of the reaction mechanism and the application of this method are underway in our laboratory.

Experimental Section

General Experimental Methods. ^{1}H NMR (TMS as the internal standard) and ^{19}F NMR spectra ($CFCl_3$ as the outside standard and low field is positive) were recorded on a 400 MHz spectrometer. ^{13}C NMR was recorded on 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HRMS data were obtained on a GC-TOF mass spectrometer. Unless otherwise noted, all reagents were obtained commercially and used without further purification. Substrates were purchased from commercial sources or were prepared according to literature procedures.

General procedure for sulfenylation of 2,3-allenoic acids

A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 2,3-allenoic acid (0.2 mmol, 1.0 equiv), $Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 0.2 equiv), disulfides (0.4 mmol, 2.0 equiv), and $(NH_4)_2S_2O_8$ (91.3 mg, 0.4 mmol, 2.0 equiv). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Then CH_3CN (3.0 mL) and HCO_2H (1.0 mL) were added by a syringe. The mixture was stirred at 50 ^{o}C for 12 h. After the reaction was complete, a saturated ammonium chloride aqueous solution was added. The resulting mixture was filtered by Celite, eluted with DCM. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified with silica gel column chromatography to provide the pure product.

4-(Benzylthio)-3-methyl-5-phenylfuran-2(5H)-one (3a). Compound **3a** was obtained as a yellow oil (51.0 mg, 86%), hexane/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.32 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.22-7.14 (m, 5H), 7.05-7.01 (m, 2H), 5.61 (s, 1H), 3.76 (d, *J* = 13.1 Hz, 1H), 3.59 (d, *J* = 13.1 Hz, 1H), 1.85 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.2, 158.1, 135.5, 134.5, 130.0, 129.2, 128.9, 128.6, 128.0, 127.9, 123.8, 83.5, 35.4, 9.6; IR (thin film) ν 1737, 1630, 1494, 1456, 1313, 1290, 1087, 988, 907 cm^{-1}; MS (ESI): *m/z* 297 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{18}H_{17}O_2S$: 297.0944; Found: 297.0941.

4-(Benzylthio)-3-methyl-5-p-tolylfuran-2(5H)-one (3b). Compound **3b** was obtained as a yellow oil (47.2 mg, 76%), hexane/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.19-7.15 (m, 3H), 7.14 (d, *J* = 6.1 Hz, 2H), 7.10 (d, *J* = 5.7 Hz, 2H), 7.08-7.03 (m, 2H), 5.58 (d, *J* = 1.5 Hz, 1H), 3.75 (d, *J* = 13.1 Hz, 1H), 3.60 (d, *J* = 13.1 Hz, 1H), 2.27 (s, 3H), 1.84 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.2, 157.1, 138.9, 134.5, 130.4, 128.8, 127.8, 127.5, 126.9, 126.8, 122.4, 82.3, 34.2, 20.3, 8.5; IR (thin film) ν 1740, 1616, 1505, 1397, 1288, 1078, 821, 704 cm^{-1}; MS (ESI): *m/z* 311 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{19}H_{19}O_2S$: 311.1100; Found: 311.1098.

4-(Benzylthio)-5-(4-methoxyphenyl)-3-methylfuran-2(5H)-one (3c). Compound **3c** was obtained as a yellow oil (56.3 mg, 86%), hexane/EA = 3:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.19 (t, *J* = 7.3 Hz, 3H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.59 (d, *J* = 1.5 Hz, 1H), 3.77 (d, *J* = 13.1 Hz, 1H), 3.73 (s, 3H), 3.62 (d, *J* = 13.1 Hz, 1H), 1.85 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.1, 159.8, 157.0, 134.5, 128.3, 127.8, 127.5, 126.9, 125.3, 122.3, 113.5, 82.1, 54.3, 34.1, 8.5; IR (thin film) ν 1725, 1616, 1488, 1405, 1288, 1203, 1087, 907, 880 cm^{-1}; MS (ESI): *m/z* 349 $[M+Na]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{19}H_{19}O_3S$: 327.1049; Found: 327.1048.

4-(Benzylthio)-5-(4-fluorophenyl)-3-methylfuran-2(5H)-one (3d). Compound **3d** was obtained as a yellow oil (47.3 mg, 75%), hexane/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.23-7.12 (m, 5H), 7.06-6.95 (m, 4H), 5.59 (s, 1H), 3.77 (d, *J* = 13.1 Hz, 1H), 3.62 (d, *J* = 13.1 Hz, 1H), 1.85 (d, *J* = 1.5 Hz, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.61 to -110.68 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.9, 162.4 (d, *J* = 250.5 Hz), 156.8, 134.3, 129.4 (d, *J* = 3.0 Hz), 128.8 (d, *J* = 9.1 Hz), 127.9, 127.5, 127.0, 123.0, 115.3, 81.6, 34.4, 8.6; IR (thin film) ν 1744, 1606, 1509, 1289, 1229, 1079, 987, 908, 839 cm^{-1}; MS (ESI): *m/z* 315 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{18}H_{16}FO_2S$: 315.0850; Found: 315.0847.

4-(Benzylthio)-5-(4-chlorophenyl)-3-methylfuran-2(5H)-one (3e). Compound **3e** was obtained as a yellow oil (46.1 mg, 70%), hexane/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.30-7.25 (m, 2H), 7.20-7.15 (m, 3H), 7.14-7.09 (m, 2H), 7.04 (dd, *J* = 7.4, 1.8 Hz,

2H), 5.57 (d, *J* = 1.5 Hz, 1H), 3.77 (d, *J* = 13.2 Hz, 1H), 3.63 (d, *J* = 13.2 Hz, 1H), 1.85 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.9, 156.6, 134.8, 134.3, 132.0, 128.3, 128.2, 127.9, 127.5, 127.0, 123.3, 81.6, 34.5, 8.6; IR (thin film) ν 1742, 1616, 1492, 1289, 1076, 987, 908 cm^{-1}; MS (ESI): *m/z* 331 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{18}H_{16}ClO_2S$: 331.0554; Found: 331.0552.

4-(Benzylthio)-5-(3-bromophenyl)-3-methylfuran-2(5H)-one (3f). Compound **3f** was obtained as a yellow oil (63.1 mg, 84%), hexane/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46-7.41 (m, 2H), 7.20-7.17 (m, 3H), 7.07-7.03 (m, 4H), 5.55 (d, *J* = 1.6 Hz, 1H), 3.77 (d, *J* = 13.2 Hz, 1H), 3.64 (d, *J* = 13.2 Hz, 1H), 1.85 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.9, 157.6, 135.4, 133.6, 132.4, 129.5, 129.0, 128.5, 128.1, 124.4, 124.1, 82.7, 35.5, 9.7; IR (thin film) ν 1744, 1616, 1489, 1390, 1289, 1068, 988, 908 cm^{-1}; MS (ESI): *m/z* 375 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{18}H_{16}BrO_2S$: 375.0049; Found: 375.0045.

4-(Benzylthio)-3-methyl-5-(4-(trifluoromethyl)phenyl)furan-2(5H)-one (3g). Compound **3g** was obtained as a yellow oil (50.8 mg, 70%), hexane/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.33-7.30 (m, 3H), 7.19-7.14 (m, 2H), 5.74 (s, 1H), 3.91 (d, *J* = 13.3 Hz, 1H), 3.79 (d, *J* = 13.3 Hz, 1H), 2.01 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.77 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.9, 157.4, 138.5, 135.3, 131.9 (q, *J* = 32.8 Hz), 129.0, 128.5, 128.2, 128.1, 126.1 (q, *J* = 3.7 Hz), 125.1, 123.7 (q, *J* = 272.4 Hz), 82.6, 35.7, 9.8; IR (thin film) ν 1766, 1623, 1501, 1408, 1289, 1088, 992, 880 cm^{-1}; MS (ESI): *m/z* 365 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{19}H_{16}F_3O_2S$: 365.0818; Found: 365.0818.

4-(Benzylthio)-3-methyl-5-(naphthalen-2-yl)furan-2(5H)-one (3h). Compound **3h** was obtained as a yellow oil (62.5 mg, 90%), hexane/EA = 10:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.01 (d, *J* = 8.3 Hz, 1H), 7.90-7.84 (m, 2H), 7.56-7.47 (m, 2H), 7.43 (d, *J* = 4.6 Hz, 2H), 7.18-7.12 (m, 3H), 6.92 (dd, *J* = 6.3, 2.7 Hz, 2H), 6.42-6.39 (m, 1H), 3.64 (d, *J* = 13.3 Hz, 1H), 3.54 (d, *J* = 13.3 Hz, 1H), 1.94 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.9, 157.0, 134.3, 133.0, 130.8, 129.7, 129.0, 128.0, 127.8, 127.5, 126.9, 126.2, 125.3, 124.5, 124.4, 122.8, 121.7, 78.1, 34.3, 8.7; IR (thin film) ν 1744, 1616, 1540, 1478, 1409, 1291, 1090, 976, 789 cm^{-1}; MS (ESI): *m/z* 347 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{22}H_{19}O_2S$: 347.1100; Found: 347.1097.

4-(Benzylthio)-5-(2,5-dimethylphenyl)-3-methylfuran-2(5H)-one (3i). Compound **3i** was obtained as a yellow oil (37.1 mg, 57%), hexane/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.21-7.15 (m, 3H), 7.04-6.99 (m, 4H), 6.86 (s, 1H), 5.82 (d, *J* = 1.6 Hz, 1H), 3.72 (d, *J* = 13.2 Hz, 1H), 3.59 (d, *J* = 13.2 Hz, 1H), 2.26 (s, 3H), 2.22 (s, 3H), 1.88 (d, *J* = 1.6 Hz, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ ppm 171.2, 157.1, 135.3, 134.4, 133.4, 131.0, 130.0, 129.5, 127.8, 127.4, 126.9, 126.6, 122.6, 79.4, 34.1, 20.0, 17.5, 8.6; IR (thin film) ν 1742, 1616, 1495, 1454, 1289, 1080, 980, 906 cm^{-1}; MS (ESI): *m/z* 325 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{20}H_{21}O_2S$: 325.1257; Found: 325.1256.

4-(Benzylthio)-3,5-dimethyl-5-phenylfuran-2(5H)-one (3j). Compound **3j** was obtained as a yellow oil (56.0 mg, 90%), hexane/EA = 5:1 as eluent for the column chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.29–7.27 (m, 5H), 7.17–7.15 (m, 3H), 6.98 (dd, *J* = 6.5, 2.8 Hz, 2H), 3.78 (d, *J* = 12.6 Hz, 1H), 3.66 (d, *J* = 12.6 Hz, 1H), 1.84 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.5, 162.6, 138.3, 136.0, 128.81, 128.77, 128.74, 128.69, 127.9, 126.2, 125.6, 88.6, 37.2, 24.2, 10.3; IR (thin film) ν 1740, 1616, 1454, 1329, 1088, 1045, 880, 698 cm^{-1}; MS (ESI): *m/z* 311 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{19}H_{19}O_2S$: 311.1100; Found: 311.1097.

4-(Benzylthio)-3-butyl-5-phenylfuran-2(5H)-one (3k). Compound **3k** was obtained as a yellow oil (60.6 mg, 90%), hexane/EA = 10:1 as eluent for the column chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.38-7.32 (m, 3H), 7.25-7.14 (m, 5H), 7.08-7.02 (m, 2H), 5.64 (s, 1H), 3.74 (d, *J* = 13.1 Hz, 1H), 3.58 (d, *J* = 13.1 Hz, 1H), 2.39-2.22 (m, 2H), 1.55-1.42 (m, 2H), 1.37-1.23 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.8, 158.0, 135.5, 134.6, 130.0, 129.3, 128.9, 128.6, 128.1, 128.02, 127.98, 83.2, 35.3, 29.6, 24.3, 22.7, 13.9; IR (thin film) ν 2973, 1736, 1616, 1455, 1380, 1274, 1087, 880 cm^{-1}; MS (ESI): *m/z* 339 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{21}H_{23}O_2S$: 339.1413; Found: 339.1411.

3-Methyl-4-(methylthio)-5-phenylfuran-2(5H)-one (3l). Compound **3l** was obtained as a yellow oil (26.9 mg, 61%), hexane/EA = 3:1 as eluent for the column chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.36-7.32 (m, 3H), 7.26-7.21 (m, 2H), 5.75 (d, *J* = 1.6 Hz, 1H), 2.07 (s, 3H), 1.90 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.2, 158.2, 133.6, 128.9, 128.2, 126.8, 121.0, 82.1, 12.6, 8.3; IR (thin film) ν 1741, 1618, 1457, 1290, 1083, 992, 906 cm^{-1}; MS (ESI): *m/z* 221 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{12}H_{13}O_2S$: 221.0631; Found: 221.0629.

4-(Isopropylthio)-3-methyl-5-phenylfuran-2(5H)-one (3m). Compound **3m** was obtained as a yellow oil (32.0 mg, 64%), hexane/EA = 4:1 as eluent for the column chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.39-7.29 (m, 3H), 7.21 (dd, *J* = 6.4, 3.0 Hz, 2H), 5.77-5.68 (m, 1H), 1.91 (d, *J* = 1.3 Hz, 1H), 1.29-1.24 (m, 3H), 1.18 (s, 3H), 1.02 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.6, 158.6, 134.8, 129.8, 129.0, 127.6, 124.4, 83.9, 36.2, 24.8, 23.1, 9.8; IR (thin film) ν 2921, 1750, 1616, 1496, 1380, 1290, 1083, 987 cm^{-1}; MS (ESI): *m/z* 271 $[M+Na]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{14}H_{17}O_2S$: 249.0944; Found: 249.0944.

4-(Butylthio)-3-methyl-5-phenylfuran-2(5H)-one (3n). Compound **3n** was obtained as a yellow oil (37.4 mg, 71%), hexane/EA = 5:1 as eluent for the column chromatography. ^1H NMR (400 MHz,

$CDCl_3$) δ ppm 7.37-7.27 (m, 3H), 7.21 (dd, *J* = 5.7, 2.3 Hz, 2H), 5.74 (s, 1H), 2.69-2.55 (m, 1H), 2.45-2.34 (m, 1H), 1.88 (s, 3H), 1.42-1.27 (m, 2H), 1.26-1.12 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.4, 158.2, 133.7, 128.8, 128.1, 126.8, 121.4, 82.4, 30.6, 29.4, 20.5, 12.3, 8.5; IR (thin film) ν 2973, 1736, 1615, 1498, 1378, 1252, 1046, 880 cm^{-1}; MS (ESI): *m/z* 263 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{15}H_{19}O_2S$: 263.1100; Found: 263.1098.

4-(Tert-butylthio)-3-methyl-5-phenylfuran-2(5H)-one (3o). Compound **3o** was obtained as a yellow oil (35.6 mg, 68%), hexane/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.33-7.28 (m, 3H), 7.21 (dd, *J* = 6.8, 2.9 Hz, 2H), 6.01 (d, *J* = 1.5 Hz, 1H), 1.99 (d, *J* = 1.6 Hz, 3H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.2, 159.9, 133.6, 128.4, 127.8, 126.6, 124.6, 82.5, 48.8, 28.6, 8.8; IR (thin film) ν 1755, 1616, 1457, 1297, 1162, 1089, 903 cm^{-1}; MS (ESI): *m/z* 263 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{15}H_{19}O_2S$: 263.1100; Found: 263.1098.

4-(Hexylthio)-3-methyl-5-phenylfuran-2(5H)-one (3p). Compound **3p** was obtained as a yellow oil (46.0 mg, 79%), hexane/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.36-7.30 (m, 3H), 7.24-7.20 (m, 2H), 5.73 (d, *J* = 1.5 Hz, 1H), 2.67-2.59 (m, 1H), 2.45-2.36 (m, 1H), 1.89 (d, *J* = 1.5 Hz, 3H), 1.44-1.28 (m, 2H), 1.21-1.04 (m, 6H), 0.78 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.3, 158.1, 133.8, 128.8, 128.1, 126.8, 121.6, 82.4, 30.0, 29.8, 28.6, 27.0, 21.4, 12.9, 8.5; IR (thin film) ν 2972, 1744, 1616, 1456, 1288, 1081, 986 cm^{-1}; MS (ESI): *m/z* 291 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{17}H_{23}O_2S$: 291.1413; Found: 291.1413.

4-(Cyclohexylthio)-3-methyl-5-phenylfuran-2(5H)-one (3q). Compound **3q** was obtained as a yellow oil (34.7 mg, 60%), hexane/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34-7.30 (m, 3H), 7.23-7.18 (m, 2H), 5.73 (s, 1H), 2.92-2.82 (m, 1H), 1.89 (s, 3H), 1.83 (d, *J* = 13.0 Hz, 1H), 1.71-1.62 (m, 1H), 1.57-1.49 (m, 1H), 1.49-1.39 (m, 2H), 1.29-1.10 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.6, 157.6, 133.9, 128.7, 128.0, 126.6, 122.7, 82.9, 43.0, 33.8, 32.2, 24.7, 24.1, 8.7; IR (thin film) ν 2919, 1746, 1616, 1497, 1409, 1289, 1088, 985 cm^{-1}; MS (ESI): *m/z* 289 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{17}H_{21}O_2S$: 289.1257; Found: 289.1261.

3-Methyl-5-phenyl-4-(phenylthio)furan-2(5H)-one (3r). Compound **3r** was obtained as a yellow oil (19.5mg, 33%), hexane/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34-7.23 (m, 3H), 7.09-7.02 (m, 4H), 6.88 (d, *J* = 7.4 Hz, 2H), 5.57 (s, 1H), 2.37 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.5, 159.6, 140.0, 134.7, 134.4, 130.1, 129.3, 128.5, 127.5, 123.8, 122.4, 83.4, 21.3, 9.5; IR (thin film) ν 2934, 2840, 1602, 1503, 1380, 1262, 1080, 998, 805 cm^{-1}; MS (ESI): *m/z* 297 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{18}H_{17}O_2S$: 297.0944; Found: 297.0943.

General procedure for sulfonylation of 2,3-allenoic acids

A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 2,3-allenoic acid (0.2 mmol, 1.0 equiv), $Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 0.2 equiv), disulfides (0.4 mmol, 2.0 equiv), and $(NH_4)_2S_2O_8$ (91.3 mg, 0.4 mmol, 2.0 equiv). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Then CH_3CN (3.0 mL) and HCO_2H (1.0 mL) was added by a syringe. The mixture was stirred at 50 ^oC for 12 h. After the reaction was complete, a saturated ammonium chloride aqueous solution was added. The resulting mixture was filtered by Celite, eluted with DCM (10.0 mL). Then, *m*-CPBA (172.6 mg, 1.0 mmol, 5 equiv) was added and the mixture was stirred at room temperature for 2 hours. After that, the organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified with silica gel column chromatography to provide the pure product.

3-Methyl-5-phenyl-4-tosylfuran-2(5H)-one (4a). Compound **4a** was obtained as a white solid (57.8 mg, 88%), hexane/EA = 3:1 as eluent for the column chromatography. MP: 112-114 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.26 (d, J = 7.5 Hz, 1H), 7.15 (t, J = 7.6 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 7.01-6.95 (m, 4H), 5.98 (d, J = 2.0 Hz, 1H), 2.30 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.0, 155.8, 144.6, 135.2, 134.7, 131.3, 128.7, 127.7, 126.9, 126.8, 81.5, 20.6, 9.3; IR (thin film) ν 2919, 1772, 1659, 1470, 1378, 1153, 700 cm^{-1}; MS (ESI): *m/z* 329 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{18}H_{17}O_4S$: 329.0842; Found: 329.0846. These data matched with the reported results.[20]

4-((4-Chlorophenyl)sulfonyl)-3-methyl-5-phenylfuran-2(5H)-one (4b). Compound **4b** was obtained as a white solid (48.6 mg, 70%), hexane/EA = 3:1 as eluent for the column chromatography. MP: 140-142 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.28 (t, J = 7.4 Hz, 1H), 7.20-7.06 (m, 6H), 6.94 (d, J = 7.5 Hz, 2H), 5.98 (d, J = 2.0 Hz, 1H), 2.31 (d, J = 2.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.7, 155.0, 140.2, 136.2, 136.1, 131.1, 128.9, 128.4, 128.1, 127.8, 126.9, 81.3, 9.4; IR (thin film) ν2920, 1773, 1652, 1598, 1466, 1330, 1154, 1000, 702 cm^{-1}; MS (ESI): *m/z* 349 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{17}H_{14}ClO_4S$: 349.0296; Found: 349.0295.

3-Methyl-5-phenyl-4-(phenylsulfonyl)furan-2(5H)-one (4c). Compound **4c** was obtained as a white solid (49.7 mg, 79%), hexane/EA = 3:1 as eluent for the column chromatography. MP: 115-117 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.44 (dt, J = 8.5, 3.9 Hz, 1H), 7.20 (d, J = 5.2 Hz, 5H), 7.13 (t, J = 7.6 Hz, 2H), 6.95 (d, J = 7.7 Hz, 2H), 6.00 (d, J = 2.0 Hz, 1H), 2.33 (d, J = 2.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.9, 155.4, 137.7, 135.8, 133.2, 131.1, 128.8, 128.1, 127.7, 126.9, 126.7, 81.5, 9.4; IR (thin film) ν 1754, 1552, 1473, 1264, 896, 731 cm^{-1}; MS (ESI): *m/z* 337 $[M+Na]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{17}H_{15}O_4S$: 315.0686; Found: 315.0685.

3-Methyl-4-(phenylsulfonyl)-5-(p-tolyl)furan-2(5H)-one (4d). Compound **4d** was obtained as a white solid (54.2 mg, 82%), hexane/EA = 3:1 as eluent for the column chromatography. MP: 118-120 ^oC. ^1H

NMR (400 MHz, $CDCl_3$) δ ppm 7.51 (t, *J* = 6.9 Hz, 1H), 7.32-7.23 (m, 4H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.02 (d, *J* = 2.0 Hz, 1H), 2.39 (d, *J* = 2.1 Hz, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.0, 156.5, 140.0, 138.8, 136.6, 134.1, 129.4, 129.02, 128.99, 127.8, 82.4, 77.4, 21.3, 10.4; IR (thin film) ν 2919, 1772, 1646, 1575, 1448, 1329, 1155, 1087, 998 cm^{-1}; MS (ESI): *m/z* 351 $[M+Na]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{18}H_{17}O_4S$: 329.0842; Found: 329.0841.

5-(4-Chlorophenyl)-3-methyl-4-(phenylsulfonyl)furan-2(5H)-one (4e). Compound **4e** was obtained as a white solid (52.3 mg, 75%), hexane/EA = 3:1 as eluent for the column chromatography. MP: 139-141 ^oC. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.52-7.48 (m, 1H), 7.26 (d, *J* = 4.1 Hz, 4H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.96 (d, *J* = 2.0 Hz, 1H), 2.33 (d, *J* = 2.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.6, 155.2, 137.7, 136.0, 135.0, 133.4, 129.7, 128.21, 128.16, 128.0, 126.6, 80.5, 9.4; IR (thin film) ν 2919, 1773, 1647, 1494, 1378, 1155, 1088, 998 cm^{-1}; MS (ESI): *m/z* 349 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{17}H_{14}ClO_4S$: 349.0296; Found: 349.0298.

5-(4-Bromophenyl)-3-methyl-4-(phenylsulfonyl)furan-2(5H)-one (4f). Compound **4f** was obtained as a white solid (60.1 mg, 77%), hexane/EA = 3:1 as eluent for the column chromatography. MP: 142-144 ^oC. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51-7.46 (m, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.26 (s, 4H), 7.08-6.99 (m, 2H), 6.89 (s, 1H), 5.94-5.91 (m, 1H), 2.35 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.5, 154.8, 137.5, 136.2, 133.6, 133.4, 132.0, 129.4, 129.3, 128.2, 126.6, 125.9, 121.8, 80.4, 9.5; IR (thin film) ν 2973, 1788, 1656, 1499, 1274, 1088, 880 cm^{-1}; MS (ESI): *m/z* 393 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{17}H_{14}BrO_4S$: 392.9791; Found: 392.9796.

3-Methyl-4-(phenylsulfonyl)-5-(4-(trifluoromethyl)phenyl)furan-2(5H)-one (4g). Compound **4g** was obtained as a white solid (50.6 mg, 66%), hexane/EA = 3:1 as eluent for the column chromatography. MP: 125-127 ^oC. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48-7.42 (m, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 5.0 Hz, 4H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.04 (d, *J* = 2.0 Hz, 1H), 2.36 (d, *J* = 2.0 Hz, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.89 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.5, 155.0, 137.6, 136.3, 135.3, 133.5, 131.0 (q, *J* = 32.8 Hz), 128.2, 127.3, 126.5, 124.7 (q, *J* = 3.8 Hz), 122.5 (q, *J* = 273.7 Hz), 80.4, 9.5; IR (thin film) ν 2920, 1776, 1647, 1448, 1378, 1154, 1088, 1000, 872 cm^{-1}; MS (ESI): *m/z* 400 $[M+NH_4]^+$; HRMS (ESI-TOF): *m/z* $[M+NH_4]^+$ Calculated for $C_{18}H_{17}F_3NO_4S$: 400.0825; Found: 400.0822.

3-Butyl-5-phenyl-4-(phenylsulfonyl)furan-2(5H)-one (4h). Compound **4h** was obtained as a white solid (51.9 mg, 73%), hexane/EA = 3:1 as eluent for the column chromatography. MP: 118-120 ^oC. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.45-7.41 (m, 1H), 7.27-7.18 (m, 5H), 7.14 (t, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 2H), 5.97 (s, 1H), 2.79-2.66 (m, 2H), 1.66-1.45 (m, 2H), 1.46-1.34 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.6, 155.0, 140.0, 137.8, 133.1, 131.3, 128.8, 128.0, 127.8, 126.9, 126.8, 81.3, 29.3, 23.8, 22.0, 12.8; IR (thin film) ν 2920, 2841, 1800, 1652, 1522, 1380,

1132, 1012, 752 cm^{-1}; MS (ESI): *m/z* 357 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{20}H_{21}O_4S$: 357.1155; Found: 357.1156.

General procedure for selenylation of 2,3-allenoic acids

A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 2,3-allenoic acid (0.2 mmol, 1.0 equiv), $Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 0.2 equiv), diselenides (0.4 mmol, 2.0 equiv), and $(NH_4)_2S_2O_8$ (91.3 mg, 0.4 mmol, 2.0 equiv). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Then CH_3CN (3.0 mL) and HCO_2H (1.0 mL) was added by a syringe. The mixture was stirred at 50 ^oC for 12 h. After the reaction was complete, a saturated ammonium chloride aqueous solution was added. The resulting mixture was filtered by Celite, eluted with DCM. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified with silica gel column chromatography to provide the pure product.

4-(Benzylselanyl)-3-methyl-5-phenylfuran-2(5H)-one (6a). Compound **6a** was obtained as a yellow oil (43.5 mg, 63%), hexane/EA = 5:1 as eluent for the column chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.36-7.32 (m, 3H), 7.24-7.19 (m, 3H), 7.18-7.16 (m, 2H), 7.04-7.01 (m, 2H), 5.64 (d, *J* = 1.6 Hz, 1H), 3.78 (d, *J* = 11.3 Hz, 1H), 3.59 (d, *J* = 11.3 Hz, 1H), 1.85 (d, *J* = 1.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.0, 154.6, 136.4, 134.5, 129.8, 129.1, 128.9, 128.8, 128.7, 127.80, 127.75, 85.2, 29.7, 10.8; IR (thin film) ν 2920, 1798, 1494, 1281, 1083, 1000, 763 cm^{-1}; MS (ESI): *m/z* 367 $[M+Na]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{18}H_{17}O_2Se$: 345.0390; Found: 345.0388.

3-Methyl-5-phenyl-4-(phenylselanyl)furan-2(5H)-one (6b). Compound **6b** was obtained as a yellow oil (54.1 mg, 82%), hexane/EA = 5:1 as eluent for the column chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.30-7.07 (m, 8H), 6.78 (d, *J* = 7.4 Hz, 2H), 5.47 (s, 1H), 1.84 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.0, 156.5, 136.0, 134.4, 129.5, 129.4, 129.3, 128.6, 127.6, 126.8, 123.9, 84.8, 10.6; IR (thin film) ν 1742, 1499, 1379, 1275, 1088, 880 cm^{-1}; MS (ESI): *m/z* 331 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{17}H_{15}O_2Se$: 331.0229; Found: 331.0232. These data matched with the reported results.[18c]

Transformation of the sulfenylated and selenylated butenolides

4-(Benzylthio)-3-methyl-5-(naphthalen-2-yl)furan-2-yl acetate (7). A solution of LDA (2M in THF, 0.15 mL) was slowly added a solution of **3h** (69.3 mg, 0.2 mmol) in dry THF (3.0 mL) at -78 ^oC. After the reaction mixture was stirred for 0.5 h at -78 ^oC, Ac_2O (40.9 mg, 0.4 mmol) was added slowly. The mixture was stirred at -78 ^oC for 1 h. Then, saturated ammonium chloride aqueous solution was added. Then resulting mixture was eluted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified with silica gel

column chromatography (hexane/EA = 20:1) to give product **7** as a yellow oil (40.4 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.78 (t, *J* = 7.7 Hz, 3H), 7.37-7.42 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.25 (s, 1H), 7.01 (s, 3H), 6.93-6.86 (m, 2H), 3.54 (s, 2H), 2.24 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.8, 148.9, 145.4, 136.5, 132.6, 130.8, 128.4, 128.1, 127.8, 127.2, 127.1, 125.9, 125.6, 125.4, 125.0, 124.8, 123.8, 114.5, 106.3, 39.0, 19.3, 6.3; IR (thin film) ν 2923, 2852, 1790, 1650, 1494, 1337, 1260, 1170, 1059, 877 cm^{-1}; MS (ESI): *m/z* 389 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{24}H_{21}O_3S$: 389.1206; Found: 389.1208.

3-Methyl-5-phenyl-4-(phenylselanyl)furan-2-yl acetate (8). A solution of LDA (2M in THF, 0.15 mL) was slowly added a solution of **6a** (68.7 mg, 0.2 mmol) in dry THF (3.0 mL) at -78 ^{o}C. After the reaction mixture was stirred for 0.5 h at -78 ^{o}C, Ac_2O (40.9 mg, 0.4 mmol) was added slowly. The mixture was stirred at -78 ^{o}C for 1 h. Then, saturated ammonium chloride aqueous solution was added. Then resulting mixture was eluted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified with silica gel column chromatography (hexane/EA = 20:1) to give product **8** as a yellow oil (59.3 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.85 (d, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 3H), 7.10 (t, *J* = 7.3 Hz, 2H), 7.05 (d, *J* = 7.1 Hz, 1H), 2.23 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.6, 148.5, 145.5, 130.8, 129.0, 128.3, 127.5, 127.2, 127.0, 125.4, 125.0, 107.7, 105.5, 19.2, 7.3; IR (thin film) ν2961, 2856, 1791, 1646, 1578, 1477, 1355, 1261, 1166, 1009, 872 cm^{-1}; MS (ESI): *m/z* 373 $[M+H]^+$; HRMS (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{19}H_{17}O_3Se$: 373.0337; Found: 373.0373.

Supporting Information Available: Optimization of reaction conditions for sulfonylation of 2,3-allenoic acid **1a**, as well as copies of ^{1}H and ^{13}C NMR spectra. These material are available free of charge via the Internet at http://pubs.acs.org.

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