

# Visible-Light-Driven, Palladium-Catalyzed Heck Reaction of Internal Vinyl Bromides with Styrenes

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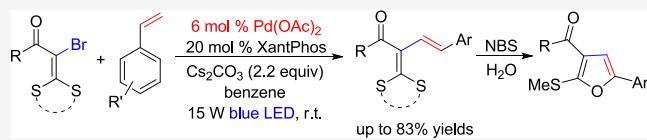
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**ABSTRACT:** Functionalized 1,3-dienes were efficiently accessed from visible-light-driven, palladium-catalyzed Heck reaction of *S,S*-functionalized internal vinyl bromides with styrenes under mild conditions. This Heck reaction showcased tolerance of a wide array of functional groups, afforded the target products in moderate to excellent yields through a radical reaction pathway. The resultant diene products could be further transformed to highly functionalized trisubstituted furan derivatives.



## INTRODUCTION

Transition-metal-catalyzed Heck coupling<sup>1,2</sup> between active olefins and aryl or vinyl halides under basic conditions has become one of the most powerful methods for C–C bond formation.<sup>3</sup> For Heck-type alkenylation, much attention has been paid to the development of coupling partners including alkyl,<sup>4</sup> aryl,<sup>5</sup> and vinyl<sup>6</sup> halides as well as arylboronic acids,<sup>7</sup> and in some cases aryl radical can be generated with the aid of a transition-metal catalyst and oxidant. However, in most of the cases, terminal alkenes were applied in the Heck-type cross-coupling reaction, and internal vinyl halides have seldom been applied as the coupling partners.<sup>8</sup>

Visible-light-driven catalysis has emerged as a powerful tool for the construction and functionalization of structurally diverse compounds in organic synthesis.<sup>9</sup> The combination of photoredox and transition-metal catalysis expands the scope of coupling partners by alternating the reaction pathways.<sup>10</sup> The photocatalytic reaction always starts with excitation of the photocatalyst by visible light, which usually gets one electron from the reagents through a single electron transfer (SET) process to initiate the reaction.<sup>11</sup> C–H bonds can be used as the nucleophile precursors for C–C bond formation through triple catalysis of photocatalysis, hydrogen atom transfer, and transition-metal catalysis. Köhler and co-workers reported first UV- and visible-light-induced Heck reaction of bromobenzene with styrenes catalyzed by Pd(OAc)<sub>2</sub> in 2010, indicating that irradiation with UV and visible light could significantly improve the rate of the Heck reaction (Scheme 1a).<sup>12</sup> Shang and Fu et al. documented the photo-induced palladium-catalyzed Heck reaction of terminal alkenes with alkyl halides at room temperature.<sup>13a,13b</sup> The Gevorgyan group<sup>13c</sup> and Novák lab<sup>13d</sup> reported similar catalytic systems for the Heck reaction of styrenes with tertiary alkyl halides and fluoroalkyl iodides, respectively, in this area. Very recently, Gevorgyan et al. realized light-induced Pd-catalyzed alkyl-Heck reaction of oximes.<sup>13e</sup> Jui et al. developed a mild catalytic process enabling the general hydro-heteroarylation of simple alkenes *via* a

photoredox radical mechanism.<sup>14</sup> Weiss and co-workers recently reported that energy transfer from CdS QDs to a photogenerated palladium complex could increase the rate and selectivity of a Pd-photocatalyzed Heck reaction for the synthesis of 2-cyclohexylstyrenes under mild conditions (Scheme 1b).<sup>15</sup>

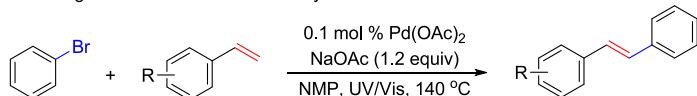
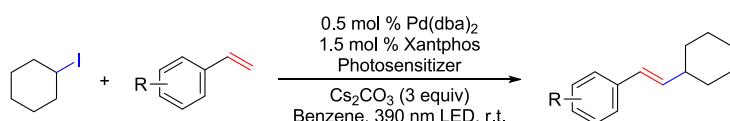
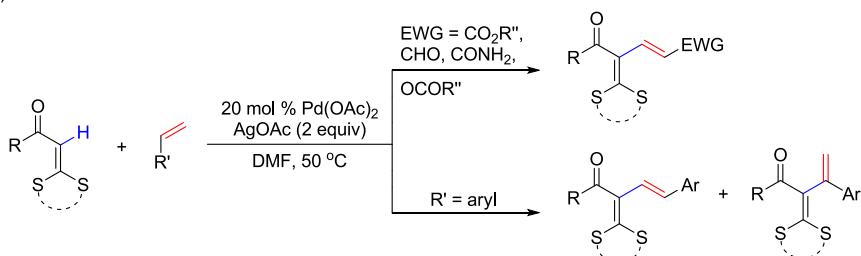
Although photocatalytic Heck reactions have recently been paid much attention,<sup>16</sup> the cross-coupling of internal vinyl halides with terminal alkenes has rarely been reported.<sup>8</sup> To realize such a cross-coupling reaction, the low reactivity of the internal vinylic C–halide bonds should be overcome. We previously introduced a structural element, that is, 1,2-dithiane functionality, at one terminus of an olefinic C=C bond, and an electron-withdrawing group at its other end, to polarize the vinyl C=C backbone by an electronic push-pull effect, activating the internal olefinic C–H bond.<sup>17</sup> Featuring such an activation mode, we found that the olefinic C–H bonds of *S,S*-functionalized internal alkenes could undergo oxidative Heck-type cross-coupling with activated terminal alkenes such as acrylates and styrenes (2.5–3.0 equiv) in the presence of a high loading of a catalyst (20 mol % Pd(OAc)<sub>2</sub>) to afford 1,3-dienes (Scheme 1c).<sup>17b</sup> When the terminal alkenes were styrenes, two isomeric diene products were usually produced. Thus, we envisioned that *S,S*-functionalized internal vinyl halides with reactivity enhanced by the push-pull effect might be applied in transition-metal-catalyzed Heck cross-coupling with alkenes. Herein, we disclose a visible-light-driven, palladium-catalyzed Heck-type cross-coupling of *S,S*-function-

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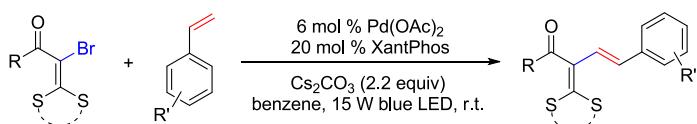
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## Scheme 1. Visible-Light-Driven, Transition-Metal-Catalyzed Heck Cross-Couplings of Alkenes

(a) Visible-light-driven Heck reaction of aryl halides<sup>12</sup>(b) Visible-light-driven Heck reaction of alkyl halides<sup>15</sup>(c) Previous work<sup>17b</sup>

(d) This work

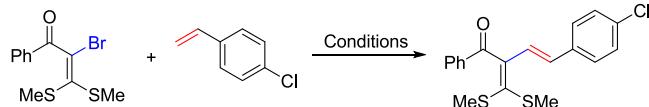


alized internal vinyl bromides with styrenes to access 1,3-dienes (**Scheme 1d**).

## RESULTS AND DISCUSSION

Initially, the reaction of 2-bromo-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (**1a**) with 4-chlorostyrene (**2a**) was conducted to optimize the reaction conditions (**Table 1**). With 10 mol % Pd(OAc)<sub>2</sub> as the catalyst, 20 mol % XantPhos as the ligand, and 2 equiv of Cs<sub>2</sub>CO<sub>3</sub> as the base, the reaction of **1a** and **2a** in a 1.0:1.5 molar ratio underwent in benzene at ambient temperature under visible-light irradiation of a 15 W blue LED bulb. The target product, that is, (*E*)-2-(bis(methylthio)methylene)-4-(4-chlorophenyl)-1-phenylbut-3-en-1-one (**3a**), was obtained in 65% isolated yield after the reaction mixture was stirred under irradiation for 12 h (**Table 1**, entries 1–4). Use of benzene as the solvent is crucial for the success of the reaction. Pd(OAc)<sub>2</sub> acted as the most efficient catalyst among the screened palladium sources Pd(OAc)<sub>2</sub>, Pd(TFA)<sub>2</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, PdCl<sub>2</sub>(MeCN)<sub>2</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, and Pd(PPh<sub>3</sub>)<sub>4</sub> (**Table 1**, entries 4–9). After further screening the catalyst loadings and substrate ratios, the optimal conditions were achieved to give **3a** in 76% isolated yield (**Table 1**, entry 14). It is noteworthy that the reaction did not occur without the light irradiation nor in the absence of either of the palladium catalyst and Cs<sub>2</sub>CO<sub>3</sub> base or under heating at 110 °C (see the *Supporting Information* for details).

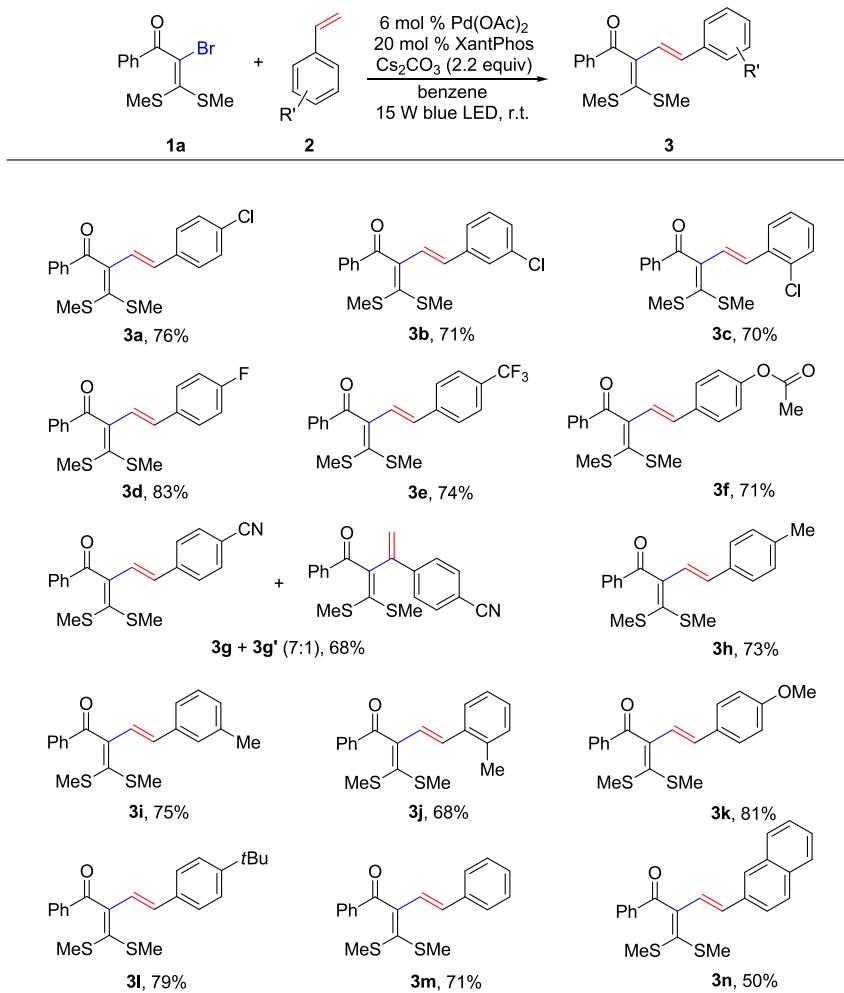
Under the optimal conditions, the scope of styrenes (**2**) was explored (**Scheme 2**). The analogs of **2a**, that is, 3- and 2-chloro-substituted styrenes, exhibited a similar reactivity to form the target 1,3-diene products **3b** (71%) and **3c** (70%), respectively. *p*-F-Styrene efficiently reacted with **1a** to give the corresponding product **3d** in 83% yield. 4-Trifluoromethyl and

**Table 1.** Screening of Conditions<sup>a</sup>

entry	catalyst (mol %)	Cs <sub>2</sub> CO <sub>3</sub> (equiv)	solvent	yield <sup>b</sup> (%)
1	Pd(OAc) <sub>2</sub> (10)	2	DMF	0
2	Pd(OAc) <sub>2</sub> (10)	2	dioxane	0
3	Pd(OAc) <sub>2</sub> (10)	2	toluene	10
4	Pd(OAc) <sub>2</sub> (10)	2	benzene	71 (65) <sup>c</sup>
5	Pd(TFA) <sub>2</sub> (10)	2	benzene	26
6	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (10)	2	benzene	0
7	PdCl <sub>2</sub> (MeCN) <sub>2</sub> (10)	2	benzene	34
8	Pd <sub>2</sub> (dba) <sub>3</sub> (10)	2	benzene	7
9	Pd(PPh <sub>3</sub> ) <sub>4</sub> (10)	2	benzene	56
10	Pd(OAc) <sub>2</sub> (4)	2	benzene	49
11	Pd(OAc) <sub>2</sub> (6)	2	benzene	76
12	Pd(OAc) <sub>2</sub> (8)	2	benzene	74
13	Pd(OAc) <sub>2</sub> (6)	1.8	benzene	68
14	Pd(OAc) <sub>2</sub> (6)	2.2	benzene	80 (76) <sup>c</sup>
15 <sup>d</sup>	Pd(OAc) <sub>2</sub> (6)	2.2	benzene	0
16 <sup>d,e</sup>	Pd(OAc) <sub>2</sub> (6)	2.2	benzene	0
17		2.2	benzene	0
18	Pd(OAc) <sub>2</sub> (6)		benzene	0

<sup>a</sup>Conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), catalyst (4–12 mol %), XantPhos (20 mol %), solvent (3 mL), 15 W blue LED, 25 °C, 0.1 MPa N<sub>2</sub>, 12 h. <sup>b</sup>The yields were determined by <sup>1</sup>H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. <sup>c</sup>Isolated yield given in parentheses. <sup>d</sup>Without LED irradiation. <sup>e</sup>110 °C.

<sup>a</sup>Conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), catalyst (4–12 mol %), XantPhos (20 mol %), solvent (3 mL), 15 W blue LED, 25 °C, 0.1 MPa N<sub>2</sub>, 12 h. <sup>b</sup>The yields were determined by <sup>1</sup>H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. <sup>c</sup>Isolated yield given in parentheses. <sup>d</sup>Without LED irradiation. <sup>e</sup>110 °C.

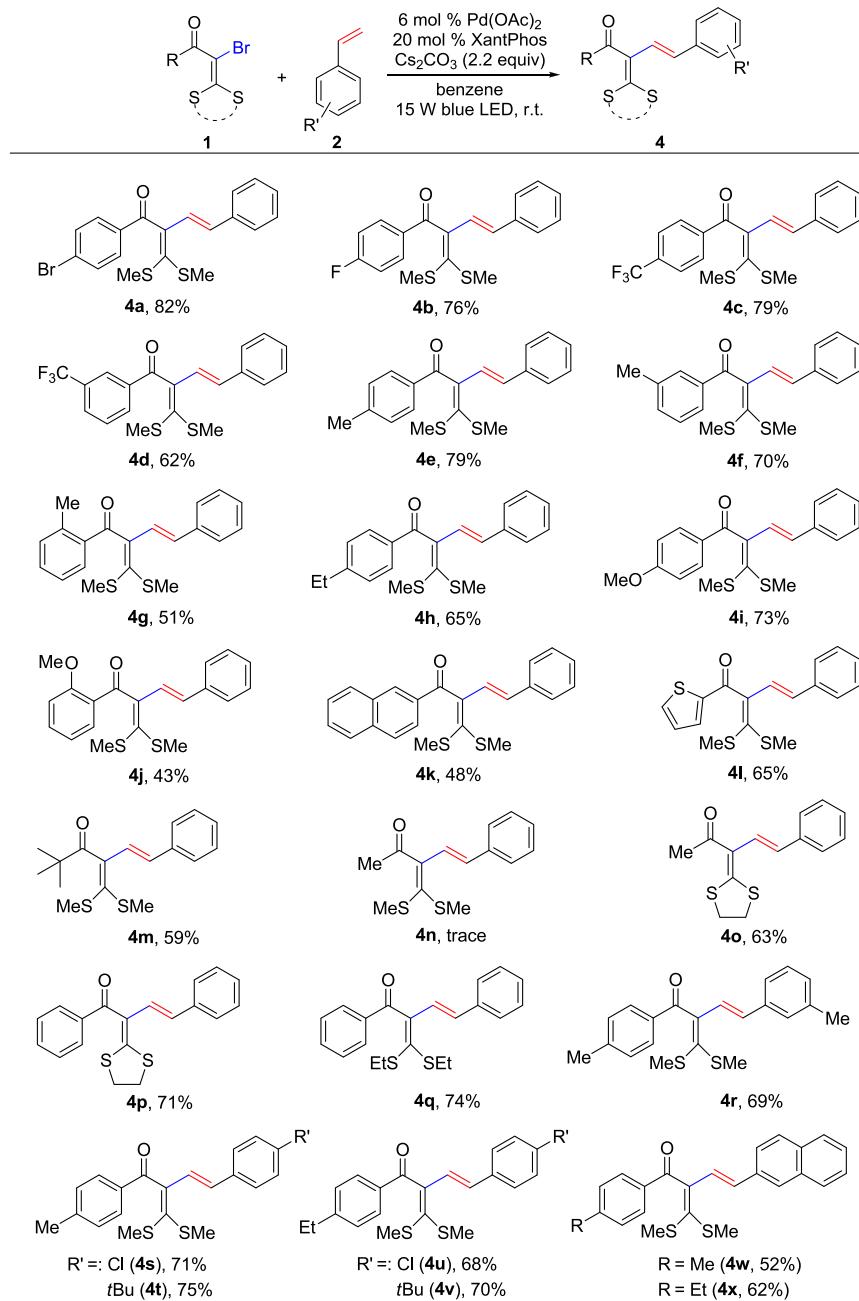
Scheme 2. Scope of Styrenes (2)<sup>a</sup>

<sup>a</sup>Conditions: **1a** (0.3 mmol), **2** (0.45 mmol), Pd(OAc)<sub>2</sub> (0.018 mmol), XantPhos (0.06 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.66 mmol), benzene (3 mL), 25 °C, 15 W blue LED, 0.1 MPa N<sub>2</sub>, 12 h.

4-acetoxy exhibited no obvious negative electronic impact on the yields of **3e** (74%) and **3f** (71%). However, the strong electron-withdrawing group 4-cyano led to formation of both the corresponding product **3g** and its inseparable isomer **3g'** (7:1) in 68% yield, which is similar to the palladium-catalyzed oxidative Heck cross-coupling between styrenes and *S,S*-functionalized internal alkenes<sup>17b</sup> or acrylates.<sup>18</sup> Methyl-substituted styrenes reacted well with **1a** to afford products **3h** and **3i** in 73–75% yields, and in the case of using 2-methylstyrene, a slightly negative steric effect was observed to diminish the yield of **3j** to 68%. Both 4-methoxy and 4-*tert*-butyl facilitated the reaction to form **3k** and **3l** (79–81%), respectively. Unsubstituted styrene (**2m**) also efficiently reacted with **1a** to generate the target product (**3m**, 71%). Notably, a decreased yield (50%) for (*E*)-2-(bis(methylthio)-methylene)-4-(naphthalen-2-yl)-1-phenylbut-3-en-1-one (**3n**) was obtained due to the steric hindrance from the 2-naphthyl group in the terminal alkene substrate.

Next, the protocol generality was investigated by performing the reaction of various vinyl halides **1** with styrene (**2m**) and its analogs (Scheme 3). The substituents on the  $\alpha$ -aroyl moieties of compounds **1** exhibited obvious impacts on the yields of the target products **4**. Under the standard conditions,  $\alpha$ -(4-bromobenzoyl) *S,S*-functionalized vinyl bromide (**1b**)

efficiently reacted with styrene to yield the corresponding product **4a** (82%). Substituents 4-F, 4-CF<sub>3</sub>, 4-Me, and 3-Me facilitated the reaction to form the target products **4b**, **4c**, **4e**, and **4f** in 70–79% yields, while 3-CF<sub>3</sub> and 2-Me exhibited a negative electronic/steric effect on the formation of **4d** (62%) and **4g** (51%), respectively.  $\alpha$ -(4-Ethylbenzoyl)-functionalized vinyl bromide (**1i**) showed a lower reactivity than its  $\alpha$ -toloyl analog (**1f**) to form **4h** (65%), whereas **4e** was accessed in 79% yield. 4-Methoxy facilitated the reaction to give **4i** (73%), but 2-MeO diminished the reaction efficiency to form **4j** (43%). Sterically hindered 2-naphthyl had an obvious negative steric effect on the reaction.  $\alpha$ -Thienoyl-based vinyl bromide also reacted with styrene to afford the corresponding product **4l** (65%). It should be noted that  $\alpha$ -pivaloyl-based vinyl bromide (**1n**) effectively reacted with styrene to give **4m** (59%) and its  $\alpha$ -acetyl analog (**1o**) exhibited no reactivity under the same conditions. However, its cyclic  $\alpha$ -acetyl analog (**1p**) reacted well with styrene to produce **4o** (63%), demonstrating a remarkable steric/electronic effect from the  $\alpha$ -oxo moiety in substrates **1**. In a similar fashion, the cyclic and diethylthio analogs of **1a**, that is, **1q** and **1r**, efficiently reacted with styrene to give **4p** (71%) and **4q** (74%), respectively.  $\alpha$ -Aroyl vinyl bromides could also react with various substituted styrenes to form the target 1,3-diene products **4r–4x** (52–75%). In the

Scheme 3. Scope of Internal Vinyl Bromides (1)<sup>a</sup>

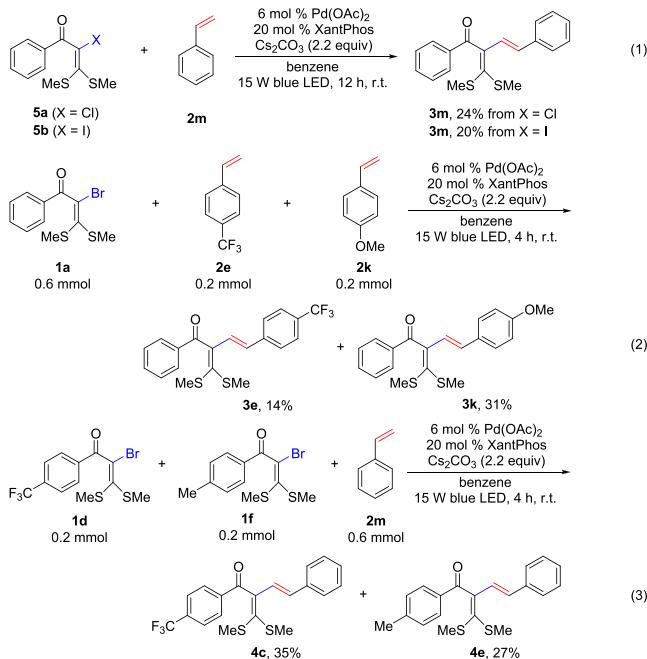
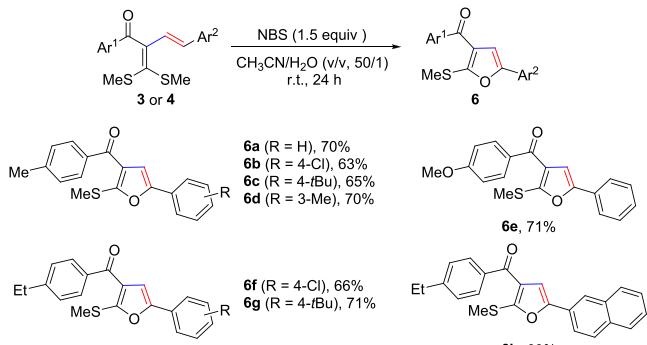
<sup>a</sup>Conditions: **1** (0.3 mmol), **2** (0.45 mmol), Pd(OAc)<sub>2</sub> (0.018 mmol), XantPhos (0.06 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.66 mmol), benzene (3 mL), 25 °C, 15 W blue LED, 0.1 MPa N<sub>2</sub>, 12 h.

cases of using di- and trisubstituted styrenes, the reaction efficiency was very poor or no reaction occurred. Notably, the present reaction regioselectively formed the conjugate dienes of type **4** without generation of isomeric dienes of type **3g'** as the coalesced side products, which were generally produced in the thermal palladium-catalyzed reactions developed by Loh<sup>18</sup> and Yu et al.<sup>17b</sup>

It should be noted that the corresponding internal vinyl chloride and iodide of type **1**, that is, **5a** and **5b**, were subjected to the standard reaction conditions to react with styrene (**2m**), affording the target product **3m** in 20–24% yields (eq 1), revealing that the chloride and iodide of type **1** are not the suitable coupling partners under the stated conditions. The control experiments of vinyl bromide **1a** with styrenes **2e**/**2k**

and vinyl bromides **1d**/**1f** with styrene **2m** by shortening the reaction time to 4 h differentiate the substrate reactivity as demonstrated in eqs 2 and 3, respectively. Electron-donating 4-OMe-substituted styrene (**2k**) exhibited a higher reactivity than electron-withdrawing 4-CF<sub>3</sub>-substituted styrene (**2e**) (eq 2), and 4-CF<sub>3</sub>-substituted vinyl bromide (**1d**) reacted more efficiently than electron-donating 4-Me-substituted vinyl bromide (**1f**) (eq 3).

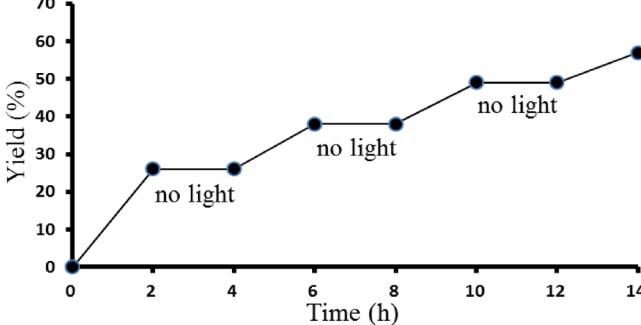
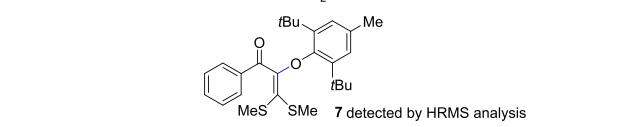
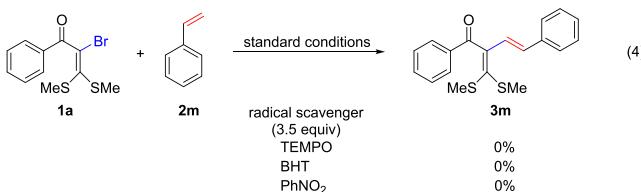
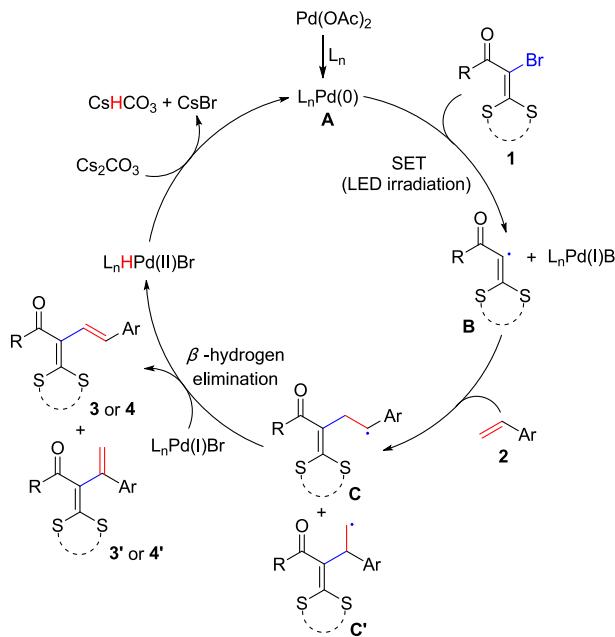
Furan is a key structural unit in many natural products, pharmaceuticals, and biologically relevant synthetic molecules.<sup>19</sup> In our case, the Heck-type 1,3-diene products of **3** and **4** could be efficiently transformed to the corresponding 2,3,5-trisubstituted furans **6** (Scheme 4). In the presence of NBS as the promoter/reactant in the mixed solvent CH<sub>3</sub>CN/

**Scheme 4. Derivatization of 1,3-Dienes (3 and 4)**

$\text{H}_2\text{O}$  (50:1, v/v), the target furan derivatives **6a–6h** were obtained in 63–71% yields under mild conditions, which has demonstrated a potential application of the present synthetic methods.

To gain insight into the reaction mechanism, radical scavengers 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO) and 2,6-di-*t*-butyl-4-methylphenol (BHT) and radical inhibitor  $\text{PhNO}_2$  were introduced to the reaction system of internal vinyl bromide **1a** and styrene (**2m**) under the standard conditions, respectively. All the three reagents completely inhibited the Heck-type alkenylation reaction, and species **7** was detected in the reaction mixture by HRMS determination (see the Supporting Information for details), but it was not successfully isolated (eq 4), which suggests that a radical pathway might be involved in the coupling reaction.<sup>20</sup> The formation of **3m** from the reaction of **1a** and **2m** was also monitored with light on/off over time<sup>21</sup> (Figure 1). Smooth transformation occurred under blue LED irradiation, and no product increase was observed in the dark, revealing a photoredox catalytic mechanism (see the Supporting Information for details).

A plausible mechanism is proposed in Scheme 5. Initially, the active  $\text{Pd}(0)$  species **A** is generated by the *in situ* reduction of  $\text{Pd}(\text{OAc})_2$  with the ligand and absorbs light to promote the reaction.<sup>22</sup> It is noted that, in the absence of the palladium

**Figure 1.** Profile for the formation of **3m** from the reaction of **1a** and **2m** with light on/off over time.**Scheme 5. Proposed Mechanism**

catalyst, the reaction did not occur (Table 1, entry 17). Species **A** undergoes an SET process with internal vinyl bromide **1** to form the putative  $\text{L}_n\text{Pd}(\text{I})\text{Br}$  species and vinyl radical **B** under LED irradiation. Interaction of **B** with styrene **2** produces radicals **C/C'**. Subsequent  $\beta$ -H-elimination delivers the target product 1,3-diene **3/4** and/or the side product **3'** with release of the  $\text{Pd}(\text{II})$  species  $\text{L}_n\text{HPd}(\text{II})\text{Br}$ . Reductive elimination regenerates species **A** by removal of  $\text{HBr}$  from species  $\text{L}_n\text{HPd}(\text{II})\text{Br}$  by the base, completing the catalytic cycle.

In summary, visible-light-driven, palladium-catalyzed Heck cross-coupling of *S,S*-functionalized internal vinyl bromides with styrenes has been efficiently realized under mild

conditions, providing an alternative route to highly functionalized 1,3-dienes and exhibiting a potential to access 2,3,5-trisubstituted furans. The present results have demonstrated a strategy for internal vinyl C-halide bonds to undergo regioselective radical Heck reactions.

## EXPERIMENTAL SECTION

**General Considerations.** The solvents were dried and distilled prior to use by the literature methods.  $^1\text{H}$  and  $^{13}\text{C}\{\text{H}\}$  NMR spectra were recorded on a 400 MHz spectrometer, and all chemical shift values refer to  $\text{CDCl}_3$  ( $\delta$  ( $^1\text{H}$ ), 7.26 ppm;  $\delta$  ( $^{13}\text{C}$ ), 77.16 ppm). High-resolution mass spectra were measured on a GC-TOF mass spectrometer. All the melting points were measured and uncorrected. Analytical TLC plates were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. The starting chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Compounds internal vinyl bromides (**1**),<sup>23</sup> internal vinyl chloride (**5a**),<sup>23</sup> and iodide (**5b**)<sup>24</sup> were prepared by the reported procedures. Compounds **1a**,<sup>23</sup> **1f**,<sup>23</sup> **1j**,<sup>23</sup> **1l**,<sup>23</sup> **1n**,<sup>23</sup> **1p**,<sup>23</sup> **1q**,<sup>23</sup> **1r**,<sup>23</sup> **3m**,<sup>19a</sup> **4a**,<sup>19a</sup> **4e**,<sup>19a</sup> **4i**,<sup>19a</sup> **4o**,<sup>23</sup> **4p**,<sup>23</sup> **6a**,<sup>19a</sup> and **6e**,<sup>19a</sup> are known, and their NMR spectroscopic features are consistent with those reported previously.

**2-Bromo-1-(4-bromophenyl)-3,3-bis(methylthio)prop-2-en-1-one (1b).** 336 mg (eluent: petroleum ether (60–90 °C)/ethyl acetate, 10:1, v/v), 88% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (m, 2 H), 7.63 (m, 2 H), 2.48 and 2.15 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  188.3, 139.2, 133.7, 132.3, 131.2, 129.3, 117.1, 19.1, and 16.4. HRMS (EI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{11}\text{OS}_2\text{Br}_2$  [M + H]<sup>+</sup>: 380.8618; Found: 380.8618.

**2-Bromo-1-(4-fluorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (1c).** 289 mg, 90% yield (eluent: petroleum ether (60–90 °C)/ethyl acetate, 10:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (m, 2 H), 7.14 (m, 2 H), 2.45 and 2.13 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  187.7, 166.2 (d,  $J$  = 254.9 Hz), 138.7, 132.4 (d,  $J$  = 9.5 Hz), 131.0 (d,  $J$  = 2.8 Hz), 117.2, 116.1 (d,  $J$  = 21.9 Hz), 18.9, and 16.3.  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  -103.4. HRMS (EI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{11}\text{OS}_2\text{FBr}$  [M + H]<sup>+</sup>: 320.9418; Found: 320.9419.

**2-Bromo-3,3-bis(methylthio)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (1d).** 316 mg, 85% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J$  = 8.1 Hz, 2 H), 7.73 (d,  $J$  = 8.2 Hz, 2 H), 2.46 and 2.11 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  188.0, 140.2, 137.9, 134.8 (q,  $J$  = 32.6 Hz), 129.9, 125.8 (q,  $J$  = 3.7 Hz), 123.5 (q,  $J$  = 271.3 Hz), 116.5, 18.9, and 16.3.  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.1. HRMS (EI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{11}\text{OS}_2\text{F}_3\text{Br}$  [M + H]<sup>+</sup>: 370.9386; Found: 370.9383.

**2-Bromo-3,3-bis(methylthio)-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one (1e).** 290 mg, 78% yield (eluent: petroleum ether (60–90 °C)/ethyl acetate, 10:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (s, 1 H), 8.04 (d,  $J$  = 7.8 Hz, 1 H), 7.83 (d,  $J$  = 7.7 Hz, 1 H), 7.62 (t,  $J$  = 7.8 Hz, 1 H), 2.47 and 2.12 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  187.8, 140.4, 135.6, 132.8, 131.5 (q,  $J$  = 32.8 Hz), 130.1 (q,  $J$  = 3.5 Hz), 129.5, 126.2 (q,  $J$  = 3.8 Hz), 123.6 (q,  $J$  = 271.1 Hz), 116.4, 18.8, and 16.4.  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{11}\text{OS}_2\text{F}_3\text{Br}$  [M + H]<sup>+</sup>: 370.9386; Found: 370.9387.

**2-Bromo-3,3-bis(methylthio)-1-(m-tolyl)prop-2-en-1-one (1g).** 206 mg, 65% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (s, 1 H), 7.66 (d,  $J$  = 7.4 Hz, 1 H), 7.36 (m, 2 H), 2.45, 2.39 and 2.11 (s each, 3:3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  189.3, 138.7, 138.1, 134.7, 134.6, 129.9, 128.6, 127.1, 117.9, 21.3, 18.8, and 16.3. HRMS (EI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{14}\text{OS}_2\text{Br}$  [M + H]<sup>+</sup>: 316.9669; Found: 316.9670.

**2-Bromo-3,3-bis(methylthio)-1-(o-tolyl)prop-2-en-1-one (1h).** 301 mg, 95% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J$  = 7.7 Hz, 1 H), 7.44 (t,  $J$  = 7.4 Hz, 1 H), 7.29 (m, 2 H), 2.64,

2.50 and 2.02 (s each, 3:3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.0, 140.4, 140.0, 135.5, 132.2, 132.0, 130.5, 125.4, 120.3, 21.4, 18.3, and 16.5. HRMS (EI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{14}\text{OS}_2\text{Br}$  [M + H]<sup>+</sup>: 316.9669; Found: 316.9669.

**2-Bromo-1-(4-ethylphenyl)-3,3-bis(methylthio)prop-2-en-1-one (1i).** 265 mg, 80% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 2:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J$  = 8.2 Hz, 2 H), 7.30 (d,  $J$  = 8.2 Hz, 2 H), 2.71 (q, 2 H), 2.46 and 2.15 (s each, 3:3 H), 1.26 (t,  $J$  = 7.6 Hz, 3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  189.0, 151.2, 137.8, 132.2, 130.1, 128.4, 118.2, 29.1, 19.0, 16.3, and 15.2. HRMS (EI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{16}\text{OS}_2\text{Br}$  [M + H]<sup>+</sup>: 330.9825; Found: 330.9826.

**2-Bromo-1-(2-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (1k).** 240 mg, 72% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (m, 1 H), 7.47 (m, 1 H), 6.99 (t,  $J$  = 7.5 Hz, 1 H), 6.94 (d,  $J$  = 8.4 Hz, 1 H), 3.84, 2.42 and 2.04 (s each, 3:3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  188.3, 159.1, 137.5, 134.6, 131.9, 125.7, 121.9, 120.6, 112.0, 55.9, 18.4, and 16.5. HRMS (EI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{S}_2\text{Br}$  [M + H]<sup>+</sup>: 332.9618; Found: 332.9619.

**2-Bromo-3,3-bis(methylthio)-1-(thiophen-2-yl)prop-2-en-1-one (1m).** 220 mg, 71% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (m, 1 H), 7.62 (m, 1 H), 7.12 (m, 1 H), 2.44 and 2.17 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  181.8, 141.6, 139.0, 135.6, 134.7, 128.4, 116.8, 19.2, and 16.4. HRMS (EI)  $m/z$  calcd for  $\text{C}_9\text{H}_{10}\text{OS}_2\text{Br}$  [M + H]<sup>+</sup>: 308.9077; Found: 308.9077.

**3-Bromo-4,4-bis(methylthio)but-3-en-2-one (1o).** 176 mg, 73% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.46, 2.44 and 2.33 (s each, 3:3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.0, 142.4, 120.4, 29.4, 19.7, and 17.1. HRMS (EI)  $m/z$  calcd for  $\text{C}_6\text{H}_{10}\text{OS}_2\text{Br}$  [M + H]<sup>+</sup>: 240.9356; Found: 240.9356.

**General Procedure for the Synthesis of 1,3-Dienes 3 and 4.** A Typical Procedure for the Synthesis of (E)-2-(Bis(methylthio)methylene)-4-(4-chlorophenyl)-1-phenylbut-3-en-1-one (3a). A mixture of 2-bromo-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (**1a**) (91 mg, 0.3 mmol), 4-chlorostyrene (**2a**) (62 mg, 0.45 mmol),  $\text{Pd}(\text{OAc})_2$  (4 mg, 0.018 mmol), XantPhos (35 mg, 0.06 mmol), and  $\text{Cs}_2\text{CO}_3$  (215 mg, 0.66 mmol) in 3 mL of benzene was stirred at ambient temperature under visible-light irradiation of a 15 W blue LED bulb (450–460 nm) for 12 h. After complete consumption of **1a** by TLC monitoring,  $\text{EtOAc}$  (10 mL) and saturated aqueous  $\text{NaCl}$  (10 mL) were successively added. The organic phase was separated, and the aqueous phase was extracted with  $\text{EtOAc}$  (3 × 10 mL). The combined organic phase was washed with water (3 × 10 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The resultant mixture was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/dichloromethane = 20:1, v/v) to afford **3a** as a yellow liquid (82 mg, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (m, 2 H), 7.58 (m, 2 H), 7.48 (t,  $J$  = 7.6 Hz, 2 H), 7.30 (m, 2 H), 7.25 (m each, 1:1 H), 6.29 (d,  $J$  = 16.5 Hz, 1 H), 2.43 and 2.14 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.2, 145.1, 136.8, 136.6, 135.4, 133.9, 133.7, 132.0, 129.4, 128.9, 128.0, 125.3, 17.5, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{18}\text{OS}_2\text{Cl}$  [M + H]<sup>+</sup>: 361.0487; Found: 361.0487.

(E)-2-(Bis(methylthio)methylene)-4-(3-chlorophenyl)-1-phenylbut-3-en-1-one (**3b**). 77 mg, 71% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (m, 2 H), 7.60 (m, 2 H), 7.48 (t,  $J$  = 7.6 Hz, 2 H), 7.38 (s, 1 H), 7.20 (m each, 2:1 H), 6.27 (d,  $J$  = 16.5 Hz, 1 H), 2.44 and 2.15 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.1, 144.9, 138.8, 137.4, 136.8, 134.7, 133.7, 131.8, 129.9, 129.4, 128.9, 128.2, 126.5, 126.1, 125.2, 17.6, and 16.9. HRMS (EI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{18}\text{OS}_2\text{Cl}$  [M + H]<sup>+</sup>: 361.0487; Found: 361.0489.

(E)-2-(Bis(methylthio)methylene)-4-(2-chlorophenyl)-1-henylbut-3-en-1-one (**3c**). 76 mg, 70% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J$  = 7.4 Hz, 2 H), 7.64 (d,  $J$  = 7.0 Hz, 1 H),

7.58 (m, 2 H), 7.49 (t,  $J = 7.6$  Hz, 2 H), 7.28 (d,  $J = 8.3$  Hz, 1 H), 7.22 (d,  $J = 7.6$  Hz, 1 H), 7.15 (m, 1 H), 6.74 (d,  $J = 16.5$  Hz, 1 H), 2.43 and 2.16 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.2, 145.3, 137.5, 136.9, 135.1, 133.8, 133.6, 129.9, 129.5, 129.4, 129.1, 128.9, 127.2, 126.9, 126.7, 17.6, and 16.9. HRMS (EI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{18}\text{OS}_2\text{Cl} [\text{M} + \text{H}]^+$ : 361.0487; Found: 361.0488.

(E)-2-(Bis(methylthio)methylene)-4-(4-fluorophenyl)-1-phenylbut-3-en-1-one (**3d**). 86 mg, 83% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (m, 2 H), 7.52 (m, 4 H), 7.35 (m, 2 H), 6.97 (m each, 1:1 H), 6.31 (d,  $J = 16.5$  Hz, 1 H), 2.43 and 2.13 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.2, 162.7 (d,  $J = 247.0$  Hz), 145.3, 136.8, 135.8, 133.6, 133.1 (d,  $J = 3.4$  Hz), 132.2, 129.3, 128.8, 128.4 (d,  $J = 8.0$  Hz), 124.6 (d,  $J = 2.4$  Hz), 115.7 (d,  $J = 21.7$  Hz), 17.5, and 16.7.  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.0. HRMS (EI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{18}\text{OS}_2\text{F} [\text{M} + \text{H}]^+$ : 345.0783; Found: 345.0785.

(E)-2-(Bis(methylthio)methylene)-1-phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en-1-one (**3e**). 88 mg, 74% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 7.5$  Hz, 2 H), 7.69 (d,  $J = 16.5$  Hz, 1 H), 7.59 (m, 1 H), 7.52 (m, 3 H), 7.47 (m each, 2:1 H), 6.35 (d,  $J = 16.5$  Hz, 1 H), 2.45, and 2.16 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 144.6, 140.4, 138.4, 136.8, 133.8, 131.6, 129.4, 129.0, 127.0, 126.9, 125.7 (q,  $J = 3.8$  Hz), 17.6, and 16.9.  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.6. HRMS (EI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{18}\text{OS}_2\text{F}_3 [\text{M} + \text{H}]^+$ : 395.0751; Found: 395.0751.

(E)-4-(3-Benzoyl-4,4-bis(methylthio)buta-1,3-dien-1-yl)phenyl acetate (**3f**). 82 mg, 71% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.7$  Hz, 2 H), 7.57 (m, 2 H), 7.48 (t,  $J = 7.5$  Hz, 2 H), 7.38 (d,  $J = 8.4$  Hz, 2 H), 7.02 (m each, 1:1 H), 6.32 (d,  $J = 16.5$  Hz, 1 H), 2.42 and 2.13 (s each, 3:3 H), 2.27 (s, 3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.2, 169.3, 150.5, 145.2, 136.7, 136.0, 134.6, 133.6, 132.3, 129.3, 128.8, 127.7, 125.0, 121.8, 21.2, 17.4, and 16.7. HRMS (EI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{21}\text{O}_3\text{S}_2 [\text{M} + \text{H}]^+$ : 385.0932; Found: 385.0930.

(E)-4-(3-Benzoyl-4,4-bis(methylthio)buta-1,3-dien-1-yl)-benzonitrile (**3g**) and 4-(3-Benzoyl-4,4-bis(methylthio)buta-1,3-dien-2-yl)benzonitrile (**3g'**). 72 mg, 68% ( $3\text{g}:3\text{g}' = 7:1$ ) yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (m, 2 H), 7.90 (m, 0.2 H), 7.71 and 6.30 (d,  $J = 16.5$  Hz, 2 H), 7.57 (m, 3 H), 7.46 (m, 4.6 H), 7.26 and 6.77 (s each, 0.1:0.1 H), 2.46, 2.52, 2.44 and 2.15 (s each, 0.4:0.4:3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 144.1, 141.4, 139.8, 136.7, 133.8, 132.4, 131.8, 130.8, 129.3, 128.9, 128.5, 128.0, 127.8, 127.1, 119.0, 111.1, 109.6, 17.6, 17.4, 16.9, and 15.2. HRMS (EI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{18}\text{ONS}_2 [\text{M} + \text{H}]^+$ : 352.0829; Found: 352.0831.

(E)-2-(Bis(methylthio)methylene)-1-phenyl-4-(*p*-tolyl)but-3-en-1-one (**3h**). 75 mg, 73% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (m, 2 H), 7.57 (m, 2 H), 7.47 (m, 2 H), 7.28 (d,  $J = 8.1$  Hz, 2 H), 7.09 (m each, 1:1 H), 6.32 (d,  $J = 16.5$  Hz, 1 H), 2.43 and 2.13 (s each, 3:3 H), 2.31 (s, 3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 145.9, 138.5, 136.9, 134.8, 134.1, 133.7, 133.6, 129.5, 129.4, 128.8, 126.8, 123.9, 21.4, 17.5, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{21}\text{OS}_2 [\text{M} + \text{H}]^+$ : 341.1033; Found: 341.1034.

(E)-2-(Bis(methylthio)methylene)-1-phenyl-4-(*m*-tolyl)but-3-en-1-one (**3i**). 77 mg, 75% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (m, 2 H), 7.59 (m, 2 H), 7.48 (t,  $J = 7.6$  Hz, 2 H), 7.19 (m, 3 H), 7.05 (d,  $J = 6.7$  Hz, 1 H), 6.34 (d,  $J = 16.5$  Hz, 1 H), 2.44 and 2.15 (s each, 3:3 H), 2.32 (s, 3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 145.7, 138.3, 136.9, 136.8, 135.4, 133.8, 133.5, 129.4, 129.2, 128.8, 128.6, 127.6, 124.6, 124.0, 21.4, 17.5, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{21}\text{OS}_2 [\text{M} + \text{H}]^+$ : 341.1033; Found: 341.1034.

(E)-2-(Bis(methylthio)methylene)-1-phenyl-4-(*o*-tolyl)but-3-en-1-one (**3j**). 69 mg, 68% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,

$\text{CDCl}_3$ )  $\delta$  7.97 (m, 2 H), 7.57 (m, 2 H), 7.49 (m, 3 H), 7.15 (m, 2 H), 7.07 (d,  $J = 7.1$  Hz, 1 H), 6.58 (d,  $J = 16.4$  Hz, 1 H), 2.43 and 2.11 (s each, 3:3 H), 2.16 (s, 3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 145.9, 136.9, 136.3, 135.9, 135.7, 133.6, 131.5, 130.5, 129.4, 128.8, 128.2, 126.2, 126.0, 125.4, 19.7, 17.5, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{21}\text{OS}_2 [\text{M} + \text{H}]^+$ : 341.1033; Found: 341.1034.

(E)-2-(Bis(methylthio)methylene)-4-(4-methoxyphenyl)-1-phenylbut-3-en-1-one (**3k**). 87 mg, 81% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 7.5$  Hz, 2 H), 7.57 (t,  $J = 7.3$  Hz, 1 H), 7.48 (m, 3 H), 7.32 (d,  $J = 8.7$  Hz, 2 H), 6.82 (m each, 1:1 H), 6.30 (d,  $J = 16.5$  Hz, 1 H), 3.79 (s, 3 H), 2.42 and 2.12 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 160.0, 146.1, 137.0, 133.9, 133.5, 133.3, 129.7, 129.4, 128.8, 128.3, 122.9, 114.2, 55.4, 17.5, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{21}\text{O}_2\text{S}_2 [\text{M} + \text{H}]^+$ : 357.0983; Found: 357.0983.

(E)-2-(Bis(methylthio)methylene)-4-(4-(tert-butyl)phenyl)-1-phenylbut-3-en-1-one (**3l**). 91 mg, 79% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (m, 2 H), 7.57 (m, 2 H), 7.47 (t,  $J = 7.6$  Hz, 2 H), 7.32 (m each, 2:1 H), 6.33 (d,  $J = 16.5$  Hz, 1 H), 2.43 and 2.13 (s each, 3:3 H), 1.29 (s each, 3:3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.4, 151.7, 145.9, 136.9, 134.9, 134.1, 133.6, 133.5, 129.4, 128.8, 126.7, 125.7, 124.2, 34.8, 31.3, 17.5, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{27}\text{OS}_2 [\text{M} + \text{H}]^+$ : 383.1503; Found: 383.1504.

(E)-2-(Bis(methylthio)methylene)-4-(4-(tert-butyl)phenyl)-1-phenylbut-3-en-1-one (**3m**). <sup>19a</sup> 70 mg, 71% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (m, 2 H), 7.64 (m, 2 H), 7.54 (m, 2 H), 7.45 (m, 2 H), 7.32 (m each, 2:1 H), 6.41 (d,  $J = 16.5$  Hz, 1 H), 2.49 and 2.20 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 145.6, 136.9, 135.7, 133.6, 129.4, 128.9, 128.7, 128.4, 126.9, 124.8, 17.5, and 16.8.

(E)-2-(Bis(methylthio)methylene)-4-(naphthalen-2-yl)-1-phenylbut-3-en-1-one (**3n**). 56 mg, 50% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (m, 2 H), 7.71 (m, 4 H), 7.62 (d,  $J = 6.9$  Hz, 2 H), 7.53 (d,  $J = 7.4$  Hz, 1 H), 7.45 (t,  $J = 7.5$  Hz, 2 H), 7.38 (m each, 1:1 H), 6.50 (d,  $J = 16.5$  Hz, 1 H), 2.41, and 2.11 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 145.5, 134.3, 133.6, 133.3, 129.4, 128.8, 128.3, 128.2, 127.7, 127.5, 126.4, 126.3, 125.1, 123.3, 17.5, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{OS}_2 [\text{M} + \text{H}]^+$ : 377.1034; Found: 377.1033.

(E)-2-(Bis(methylthio)methylene)-1-(4-bromophenyl)-4-phenylbut-3-en-1-one (**4a**). <sup>19a</sup> 99 mg, 82% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.3$  Hz, 2 H), 7.64 (m, 3 H), 7.41 (d,  $J = 7.3$  Hz, 2 H), 7.31 (m, 3 H), 6.35 (d,  $J = 16.5$  Hz, 1 H), 2.46 and 2.18 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.2, 144.8, 136.7, 136.2, 135.7, 133.6, 132.2, 130.8, 128.8, 128.5, 126.9, 124.6, 17.6, and 16.8.

(E)-2-(Bis(methylthio)methylene)-1-(4-fluorophenyl)-4-phenylbut-3-en-1-one (**4b**). 79 mg, 76% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (m, 2 H), 7.64 (d,  $J = 16.5$  Hz, 1 H), 7.41 (d,  $J = 7.3$  Hz, 2 H), 7.31 (m, 3 H), 7.18 (m, 2 H), 6.35 (d,  $J = 16.6$  Hz, 1 H), 2.46 and 2.19 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.8, 166.1 (d,  $J = 254.1$  Hz), 145.1, 136.8, 135.9, 133.6, 133.3 (d,  $J = 2.7$  Hz), 132.0 (d,  $J = 9.4$  Hz), 128.8, 128.5, 126.9, 124.7, 116.1 (d,  $J = 21.8$  Hz), 17.6, and 16.8.  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.2. HRMS (EI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{18}\text{OS}_2\text{F} [\text{M} + \text{H}]^+$ : 345.0783; Found: 345.0783.

(E)-2-(Bis(methylthio)methylene)-4-phenyl-1-(4-(trifluoromethyl)phenyl)but-3-en-1-one (**4c**). 93 mg, 79% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J = 8.0$  Hz, 2 H), 7.77 (d,  $J = 8.1$  Hz, 2 H), 7.63 and 6.34 (d,  $J = 16.5$  Hz, 2 H), 7.41 (d,  $J = 7.3$  Hz, 2 H), 7.31 (m, 3 H), 2.46 and 2.16 (s each, 3:3 H).

H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.1, 144.6, 139.7, 136.6 (d,  $J = 4.3$  Hz), 134.7 (d,  $J = 32.2$  Hz), 133.7, 129.6, 128.8, 128.6, 126.9, 126.0 (q,  $J = 3.3$  Hz), 124.5, 17.6, and 16.8.  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.1. HRMS (EI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{18}\text{OS}_2\text{F}_3$  [M + H] $^+$ : 395.0751; Found: 395.0752.

(E)-2-(Bis(methylthio)methylene)-4-phenyl-1-(3-(trifluoromethyl)phenyl)but-3-en-1-one (**4d**). 73 mg, 62% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (s, 1 H), 8.13 (d,  $J = 7.8$  Hz, 1 H), 7.85 (d,  $J = 7.6$  Hz, 1 H), 7.64 (m 2 H), 7.42 (d,  $J = 7.3$  Hz, 2 H), 7.31 (m, 3 H), 6.35 (d,  $J = 16.5$  Hz, 1 H), 2.46 and 2.15 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.8, 144.4, 137.1 (d,  $J = 88.9$  Hz), 136.8, 133.7, 132.5, 131.6 (d,  $J = 32.8$  Hz), 129.9 (q,  $J = 3.6$  Hz), 129.6, 128.8, 128.7, 128.6, 127.9, 126.9, 125.9 (q,  $J = 4.0$  Hz), 124.5, 17.5, and 16.8.  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.7. HRMS (EI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{18}\text{OS}_2\text{F}_3$  [M + H] $^+$ : 395.0751; Found: 395.0751.

(E)-2-(Bis(methylthio)methylene)-4-phenyl-1-(*p*-tolyl)but-3-en-1-one (**4e**). 81 mg, 79% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.0$  Hz, 2 H), 7.69 and 6.41 (d,  $J = 16.5$  Hz, 2 H), 7.44 (d,  $J = 7.4$  Hz, 2 H), 7.34 (m, 4 H), 7.29 (d,  $J = 7.1$  Hz, 1 H), 2.49 (s each, 3:3 H), and 2.22 (s, 3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 145.7, 144.6, 136.9, 135.4, 134.3, 133.4, 129.6, 128.7, 128.3, 126.8, 124.9, 21.9, 17.5, and 16.8.

(E)-2-(Bis(methylthio)methylene)-4-phenyl-1-(*m*-tolyl)but-3-en-1-one (**4f**). 72 mg, 70% yield, yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (s, 1 H), 7.78 (d,  $J = 7.2$  Hz, 1 H), 7.68 and 6.41 (d,  $J = 16.5$  Hz, 2 H), 7.45 (d,  $J = 7.2$  Hz, 3 H), 7.31 (m, 4 H), 2.49 (s each, 3:3 H), and 2.20 (s, 3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 145.7, 138.7, 136.9, 136.8, 135.5, 134.5, 133.5, 129.6, 128.7, 128.3, 126.9, 124.8, 21.5, 17.5, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{21}\text{OS}_2$  [M + H] $^+$ : 341.1033; Found: 341.1034.

(E)-2-(Bis(methylthio)methylene)-4-phenyl-1-(*o*-tolyl)but-3-en-1-one (**4g**). 52 mg, 51% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (m, 2 H), 7.47 (m, 3 H), 7.38 (m, 3 H), 7.30 (m each, 1:1 H), 6.57 (d,  $J = 16.5$  Hz, 1 H), 2.80 (s, 3 H), 2.47 and 2.03 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.0, 147.6, 140.6, 137.1, 137.0, 136.2, 133.6, 132.1, 131.1, 128.7, 128.3, 126.9, 125.6, 125.4, 21.9, 17.1, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{21}\text{OS}_2$  [M + H] $^+$ : 341.1033; Found: 341.1034.

(E)-2-(Bis(methylthio)methylene)-1-(4-ethylphenyl)-4-phenylbut-3-en-1-one (**4h**). 69 mg, 65% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.9$  Hz, 2 H), 7.68 and 6.40 (d,  $J = 16.5$  Hz, 2 H), 7.44 (d,  $J = 7.3$  Hz, 2 H), 7.35 (m, 4 H), 7.29 (d,  $J = 7.1$  Hz, 1 H), 2.78 (m, 2 H), 2.49 and 2.23 (s each, 3:3 H), 1.33 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 150.6, 145.7, 136.8, 135.3, 134.5, 133.4, 129.6, 128.6, 128.4, 128.2, 126.8, 124.8, 29.1, 17.5, 16.8, and 15.1. HRMS (EI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{23}\text{OS}_2$  [M + H] $^+$ : 355.1190; Found: 355.1190.

(E)-2-(Bis(methylthio)methylene)-1-(4-methoxyphenyl)-4-phenylbut-3-en-1-one (**4i**). 78 mg, 73% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.4$  Hz, 2 H), 7.69 and 6.41 (d,  $J = 16.5$  Hz, 2 H), 7.45 (d,  $J = 7.6$  Hz, 2 H), 7.32 (m, 3 H), 7.02 (d,  $J = 8.4$  Hz, 2 H), 3.93 (s, 3 H), 2.49 and 2.25 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.1, 164.0, 145.7, 136.9, 135.2, 133.4, 131.8, 129.8, 128.7, 128.3, 126.8, 124.9, 114.1, 55.6, 17.6, and 16.8.

(E)-2-(Bis(methylthio)methylene)-1-(2-methoxyphenyl)-4-phenylbut-3-en-1-one (**4j**). 46 mg, 43% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.6$  Hz, 1 H), 7.63 and 6.49 (d,  $J = 16.5$  Hz, 2 H), 7.56 (m, 1 H), 7.47 (d,  $J = 7.4$  Hz, 2 H), 7.35 (m, 2 H), 7.28 (m, 1 H), 7.07 (m, 2 H), 3.92 (s, 3 H), 2.46 and 2.14 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.8, 159.8, 148.5, 137.2, 134.6, 134.0, 132.7, 132.3, 128.6, 128.1, 126.8, 125.0, 120.5, 112.3, 55.9, 17.2, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{21}\text{O}_2\text{S}_2$  [M + H] $^+$ : 357.0983; Found: 357.0983.

(*E*)-2-(Bis(methylthio)methylene)-1-(naphthalen-2-yl)-4-phenylbut-3-en-1-one (**4k**). 54 mg, 48% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.52 (s, 1 H), 8.19 (dd,  $J = 8.6, 1.5$  Hz, 1 H), 8.02 (t,  $J = 6.9$  Hz, 2 H), 7.95 (d,  $J = 8.1$  Hz, 1 H), 7.79 and 6.49 (d,  $J = 16.5$  Hz, 2 H), 7.66 (m, 1 H), 7.60 (m, 1 H), 7.46 (d,  $J = 7.4$  Hz, 2 H), 7.32 (m, 3 H), 2.53 and 2.19 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 145.6, 136.8, 136.0, 135.9, 134.3, 133.6, 132.7, 131.4, 129.8, 128.8, 128.7, 128.3, 127.9, 126.9, 126.8, 124.9, 124.6, 17.5, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{OS}_2$  [M + H] $^+$ : 377.1033; Found: 377.1034.

(*E*)-2-(Bis(methylthio)methylene)-4-phenyl-1-(thiophen-2-yl)but-3-en-1-one (**4l**). 65 mg, 65% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (dd,  $J = 4.9, 1.2$  Hz, 1 H), 7.62 (dd,  $J = 3.8, 1.1$  Hz, 1 H), 7.57 and 6.45 (d,  $J = 16.5$  Hz, 2 H), 7.40 (m, 2 H), 7.29 (m, 2 H), 7.23 (m, 1 H), 7.12 (m, 1 H), 2.43 and 2.22 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  188.6, 145.2, 144.4, 136.8, 136.7, 134.7, 134.1, 133.5, 128.7, 128.4, 126.9, 124.5, 17.8, and 16.9. HRMS (EI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{17}\text{OS}_3$  [M + H] $^+$ : 333.0441; Found: 333.0442.

(*E*)-4-(Bis(methylthio)methylene)-2,2-dimethyl-6-phenylhex-5-en-3-one (**4m**). 54 mg, 59% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (m each, 2:1 H), 7.33 (m, 2 H), 7.26 (m, 1 H), 6.33 (d,  $J = 16.6$  Hz, 1 H), 2.36 and 2.32 (s each, 3:3 H), and 1.29 (s each, 3:3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  213.9, 147.8, 136.8, 133.4, 133.0, 128.8, 128.4, 126.9, 124.1, 44.3, 28.5, 17.6, and 16.9. HRMS (EI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{23}\text{OS}_2$  [M + H] $^+$ : 307.1190; Found: 307.1190.

(*E*)-3-(1,3-Dithiolan-2-ylidene)-5-phenylpent-4-en-2-one (**4o**).<sup>17b</sup> 50 mg, 63% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 6.99 (d,  $J = 16.2$  Hz, 1 H), 6.69 (d,  $J = 16.2$  Hz, 1 H), 3.43 and 3.29 (m each, 2:2 H), and 2.33 (s, 3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.0, 162.9, 137.0, 134.3, 128.8, 128.1, 126.5, 124.2, 39.4, 35.6, and 28.6.

(*E*)-2-(1,3-Dithiolan-2-ylidene)-1,4-diphenylbut-3-en-1-one (**4p**).<sup>25</sup> 69 mg, 71% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (m, 2 H), 7.48 (m, 1 H), 7.39 (m, 2 H), 7.26 (m, 4 H), 7.18 (m, 1 H), 7.03 and 6.26 (d,  $J = 16.2$  Hz, 2 H), and 3.41 (m each, 2:2 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.0, 154.8, 137.9, 137.3, 132.4, 131.2, 129.8, 128.7, 128.4, 127.6, 126.7, 126.3, 125.1, 38.7, and 37.0.

(*E*)-2-(Bis(ethylthio)methylene)-1,4-diphenylbut-3-en-1-one (**4q**). 79 mg, 74% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 3:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (m, 2 H), 7.71 and 6.35 (d,  $J = 16.5$  Hz, 2 H), 7.56 (m, 1 H), 7.45 (m, 2 H), 7.38 (m, 2 H), 7.29 (m, 2 H), 7.22 (m, 1 H), 2.90 and 2.69 (m each, 2:2 H), 1.35 and 1.02 (s each, 3:3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.7, 148.0, 136.9, 133.5, 133.4, 133.1, 129.5, 128.8, 128.7, 128.3, 126.9, 125.1, 28.5, 28.0, 15.4, and 14.6. HRMS (EI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{23}\text{OS}_2$  [M + H] $^+$ : 355.1190; Found: 355.1190.

(*E*)-2-(Bis(methylthio)methylene)-4-(*m*-tolyl)-1-(*p*-tolyl)but-3-en-1-one (**4r**). 73 mg, 69% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.0$  Hz, 2 H), 7.71 and 6.42 (d,  $J = 16.5$  Hz, 2 H), 7.38 (d,  $J = 7.9$  Hz, 2 H), 7.28 (m, 3 H), 7.15 (d,  $J = 6.2$  Hz, 1 H), 2.53 (s each, 3:3 H), 2.42 (s, 3 H), and 2.27 (s, 3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.1, 145.9, 144.5, 138.2, 136.8, 135.0, 134.4, 133.7, 129.6, 129.2, 128.6, 127.6, 124.7, 124.0, 21.9, 21.4, 17.6, and 16.8. HRMS (EI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{23}\text{OS}_2$  [M + H] $^+$ : 355.1190; Found: 355.1190.

(*E*)-2-(Bis(methylthio)methylene)-4-(4-chlorophenyl)-1-(*p*-tolyl)-but-3-en-1-one (**4s**). 80 mg, 71% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 7.7$  Hz, 2 H), 7.60 and 6.30 (d,  $J = 16.5$  Hz, 2 H), 7.27 (m, 6 H), 2.44 (s each, 3:3 H), and 2.17 (s, 3 H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 145.2, 144.7, 136.3, 135.4, 134.2, 133.8, 131.9, 129.6, 129.5, 128.8, 128.0, 125.4, 21.9,

17.5, and 16.8. HRMS (EI)  $m/z$  calcd for  $C_{20}H_{20}OS_2Cl$  [M + H]<sup>+</sup>: 375.0644; Found: 375.0644.

(E)-2-(Bis(methylthio)methylene)-4-(4-(tert-butyl)phenyl)-1-(*p*-tolyl)but-3-en-1-one (**4t**). 89 mg, 75% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (d,  $J$  = 7.8 Hz, 2 H), 7.64 and 6.39 (d,  $J$  = 16.5 Hz, 2 H), 7.33 (m, 6 H), 2.46 (s each, 3:3 H), 2.20 (s, 3 H), and 1.34 (s each, 3:3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 196.0, 151.5, 146.0, 144.4, 134.5, 134.3, 134.1, 133.4, 129.5, 126.6, 125.6, 124.1, 34.7, 31.3, 21.8, 17.5, and 16.7. HRMS (EI)  $m/z$  calcd for C<sub>24</sub>H<sub>29</sub>OS<sub>2</sub> [M + H]<sup>+</sup>: 397.1659; Found: 397.1660.

(E)-2-(Bis(methylthio)methylene)-4-(4-chlorophenyl)-1-(4-ethylphenyl)but-3-en-1-one (**4u**). 79 mg, 68% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (d,  $J$  = 8.0 Hz, 2 H), 7.61 and 6.30 (d,  $J$  = 16.5 Hz, 2 H), 7.31 (m, 4 H), 7.25 (d,  $J$  = 8.4 Hz, 2 H), 2.73 (m, 2 H), 2.44 and 2.17 (s each, 3:3 H), and 1.28 (t,  $J$  = 7.6 Hz, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 195.9, 150.7, 145.2, 136.2, 135.4, 134.4, 133.8, 131.9, 129.6, 128.8, 128.4, 128.0, 125.3, 29.1, 17.5, 16.8, and 15.1. HRMS (EI)  $m/z$  calcd for C<sub>21</sub>H<sub>22</sub>OS<sub>2</sub>Cl [M + H]<sup>+</sup>: 389.0800; Found: 389.0801.

(E)-2-(Bis(methylthio)methylene)-4-(4-(tert-butyl)phenyl)-1-(4-ethylphenyl)but-3-en-1-one (**4v**). 86 mg, 70% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d,  $J$  = 8.2 Hz, 2 H), 7.58 and 6.33 (d,  $J$  = 16.5 Hz, 2 H), 7.30 (m, 6 H), 2.72 (m, 2 H), 2.43 and 2.16 (s each, 3:3 H), 1.29 (s each, 3:3 H), 1.27 (t,  $J$  = 7.6 Hz, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 196.0, 151.5, 150.5, 146.0, 134.5, 134.1, 133.4, 129.6, 129.5, 128.3, 126.6, 125.6, 124.1, 34.7, 31.3, 29.1, 17.5, 16.8, and 15.1. HRMS (EI)  $m/z$  calcd for C<sub>25</sub>H<sub>31</sub>OS<sub>2</sub> [M + H]<sup>+</sup>: 411.1816; Found: 411.1816.

(E)-2-(Bis(methylthio)methylene)-4-(naphthalen-2-yl)-1-(*p*-tolyl)-but-3-en-1-one (**4w**). 61 mg, 52% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d,  $J$  = 8.0 Hz, 2 H), 7.76 (m each, 3:1 H), 7.67 (m, 2 H), 7.43 (m, 2 H), 7.30 (d,  $J$  = 7.9 Hz, 2 H), 6.53 (d,  $J$  = 16.5 Hz, 1 H), 2.45 (s each, 3:3 H), and 2.19 (s, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 196.1, 145.8, 144.6, 135.5, 134.4, 134.3, 133.6, 133.5, 133.3, 129.6, 128.3, 128.2, 127.7, 127.5, 126.4, 126.3, 125.1, 123.3, 21.9, 17.6, and 16.8. HRMS (EI)  $m/z$  calcd for C<sub>24</sub>H<sub>23</sub>OS<sub>2</sub> [M + H]<sup>+</sup>: 391.1190; Found: 391.1190.

(E)-2-(Bis(methylthio)methylene)-1-(4-ethylphenyl)-4-(naphthalen-2-yl)but-3-en-1-one (**4x**). 75 mg, 62% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d,  $J$  = 8.1 Hz, 2 H), 7.76 (m each, 3:1 H), 7.67 (m, 2 H), 7.42 (m, 2 H), 7.33 (d,  $J$  = 8.1 Hz, 2 H), 6.53 (d,  $J$  = 16.5 Hz, 1 H), 2.73 (m, 2 H), 2.46 and 2.19 (s each, 3:3 H), and 1.28 (t,  $J$  = 7.6 Hz, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 196.1, 150.7, 145.7, 135.4, 134.5, 134.4, 133.5, 133.3, 129.6, 128.4, 128.3, 128.1, 127.7, 127.5, 126.4, 126.2, 125.1, 123.3, 29.1, 17.6, 16.8, and 15.1. HRMS (EI)  $m/z$  calcd for C<sub>25</sub>H<sub>25</sub>OS<sub>2</sub> [M + H]<sup>+</sup>: 405.1346; Found: 405.1347.

**A Procedure for Gram-Scale Preparation of 3a.** A mixture of 2-bromo-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (**1a**) (1.52 g, 5 mmol), 4-chlorostyrene (**2a**) (1.04 g, 7.5 mmol), Pd(OAc)<sub>2</sub> (67 mg, 0.3 mmol), XantPhos (579 mg, 1 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (3.6 g, 11 mmol) in 50 mL of benzene was stirred at ambient temperature under visible-light irradiation of a 15 W blue LED bulb (450–460 nm) for 24 h. After complete consumption of **1a** by TLC monitoring on silica gel, EtOAc (50 mL) and brine (50 mL) were successively added. The organic phase was separated, and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic phase was washed with water (3 × 15 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/dichloromethane = 20:1, v/v) to afford **3a** as a yellow liquid (1.17 g, 65%).

**Control Experiments.** Under an N<sub>2</sub> atmosphere, a mixture of 2-bromo-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (**1a**) (182 mg, 0.6 mmol), 1-(trifluoromethyl)-4-vinylbenzene (**2e**) (34 mg, 0.2

mmol), 1-methoxy-4-vinylbenzene (**2k**) (27 mg, 0.2 mmol), Pd(OAc)<sub>2</sub> (5 mg, 0.024 mmol), XantPhos (46 mg, 0.08 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (287 mg, 0.88 mmol) in 4 mL of benzene was stirred at ambient temperature under visible-light irradiation of a 15 W blue LED bulb for 4 h. The corresponding products of **3e** (11 mg, 14%) and **3k** (22 mg, 31%) were isolated by column chromatography on silica gel (60–120 mesh) using petroleum ether (60–90 °C)/dichloromethane (1:1, v/v) as the eluent. In a similar fashion, products of **4c** (28 mg, 35%) and **4e** (18 mg, 27%) were generated from the competition reaction of **1d**, **1f**, and **2m** in a molar ratio of 1:1:3 under visible-light irradiation of a 15 W blue LED bulb for 4 h.

**Derivatization of 1,3-Dienes 3 and 4. A Typical Procedure for the Derivatization of 3 or 4 to Furans: Synthesis of (2-Methylthio)-5-phenylfuran-3-yl)(*p*-tolyl)methanone (**6a**).<sup>19a</sup>**

A mixture of **4e** (68 mg, 0.2 mmol) and NBS (53 mg, 0.3 mmol) in 1 mL of CH<sub>3</sub>CN/H<sub>2</sub>O (50:1, v/v) was stirred at 25 °C for 24 h. The reaction mixture was poured into ice-cold water (100 g) and extracted with dichloromethane (20 mL). The organic layer was separated and dried over anhydrous sodium sulfate. All the volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (60–120 mesh) using petroleum ether (60–90 °C)/dichloromethane (1:1, v/v) as the eluent to give **6a** as a white solid (43 mg, 70%), mp: 64–65 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d,  $J$  = 8.0 Hz, 2 H), 7.52 (d,  $J$  = 7.3 Hz, 2 H), 7.45 (s, 1 H), 7.37 (t,  $J$  = 7.5 Hz, 2 H), 7.29 (m each, 2:1 H), 2.65 (s, 3 H), and 2.44 (s, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 190.0, 152.0, 142.8, 140.4, 136.6, 135.9, 133.5, 129.5, 129.2, 127.9, 125.9, 125.5, 21.8, and 19.2.

(5-(4-Chlorophenyl)-2-(methylthio)furan-3-yl)(*p*-tolyl)methanone (**6b**). 43 mg, 63% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), white solid, mp: 89–90 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 (d,  $J$  = 7.5 Hz, 2 H), 7.41 (d,  $J$  = 8.2 Hz, 3 H), 7.29 (m each, 3:1 H), 2.62 (s, 3 H), and 2.42 (s, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 189.8, 152.5, 142.9, 138.9, 136.5, 135.8, 133.6, 132.0, 129.4, 129.3, 129.2, 126.6, 126.2, 21.8, and 19.2. HRMS (EI)  $m/z$  calcd for C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>SCl [M + H]<sup>+</sup>: 343.0560; Found: 343.0559.

(5-(4-(tert-Butyl)phenyl)-2-(methylthio)furan-3-yl)(*p*-tolyl)methanone (**6c**). 47 mg, 65% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), white solid, mp: 75–76 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (d,  $J$  = 7.9 Hz, 2 H), 7.57 (d,  $J$  = 8.3 Hz, 2 H), 7.43 (d,  $J$  = 8.4 Hz, 2 H), 7.30 (d,  $J$  = 7.8 Hz, 2 H), 6.90 (s, 1 H), 2.68 (s, 3 H), 2.44 (s, 3 H), and 1.34 (s each, 3:3:3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 189.2, 157.2, 154.4, 151.3, 142.9, 136.4, 129.2, 129.1, 127.2, 125.9, 123.5, 123.3, 106.7, 34.8, 31.4, 21.8, and 14.3. HRMS (EI)  $m/z$  calcd for C<sub>23</sub>H<sub>25</sub>O<sub>2</sub>S [M + H]<sup>+</sup>: 365.1575; Found: 365.1575.

(2-(Methylthio)-5-(*m*-tolyl)furan-3-yl)(*p*-tolyl)methanone (**6d**). 45 mg, 70% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), white solid, mp: 68–69 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (d,  $J$  = 8.0 Hz, 2 H), 7.43 (s, 2 H), 7.29 (m, 3 H), 7.11 (d,  $J$  = 7.5 Hz, 1 H), 6.93 (s, 1 H), 2.69 (s, 3 H), 2.44 (s, 3 H), and 2.40 (s, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 189.1, 157.5, 154.3, 142.9, 138.7, 136.3, 129.8, 129.2, 129.1, 128.9, 124.2, 123.2, 120.8, 107.3, 21.8, 21.6, and 14.3. HRMS (EI)  $m/z$  calcd for C<sub>20</sub>H<sub>19</sub>O<sub>2</sub>S [M + H]<sup>+</sup>: 323.1105; Found: 323.1106.

(4-Methoxyphenyl)(2-(methylthio)-5-phenylfuran-3-yl)(*p*-tolyl)methanone (**6e**).<sup>19a</sup> 46 mg, 71% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), white solid, mp: 109–110 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d,  $J$  = 8.8 Hz, 2 H), 7.53 (d,  $J$  = 7.4 Hz, 2 H), 7.45 (s, 1 H), 7.38 (t,  $J$  = 7.5 Hz, 2 H), 7.30 (t,  $J$  = 7.4 Hz, 1 H), 6.98 (m each, 1:1 H), 3.89 (s, 3 H), and 2.64 (s, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 189.1, 163.0, 150.7, 140.8, 136.5, 133.5, 131.8, 131.7, 129.2, 128.0, 125.7, 125.5, 113.8, 55.6, and 19.4.

(5-(4-Chlorophenyl)-2-(methylthio)furan-3-yl)(4-ethylphenyl)methanone (**6f**). 47 mg, 66% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), white solid, mp: 83–84 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (d,  $J$  = 8.1 Hz, 2 H), 7.44 (m each, 2:1 H), 7.32 (m, 4 H), 2.74 (m, 2 H), 2.64 (s, 3 H), and 1.30 (t,  $J$  = 7.6 Hz, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 189.8, 152.6,

149.1, 138.9, 136.7, 135.8, 133.7, 132.0, 129.5, 129.3, 128.0, 126.7, 126.3, 29.1, 19.2, and 15.4. HRMS (EI)  $m/z$  calcd for  $C_{20}H_{18}O_2S\text{Cl}$  [M + H]<sup>+</sup>: 357.0716; Found: 357.0716.

(5-(4-(*tert*-Butyl)phenyl)-2-(methylthio)furan-3-yl)(4-ethylphenyl)methanone (**6g**). 54 mg, 71% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), white solid, mp: 78–79 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 (d,  $J$  = 8.2 Hz, 2 H), 7.43 (m each, 4:1 H), 7.30 (d,  $J$  = 8.0 Hz, 2 H), 2.74 (m, 2 H), 2.65 (s, 3 H), 1.33 (s, 9 H), and 1.30 (t,  $J$  = 7.6 Hz, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  190.0, 151.5, 151.2, 149.0, 140.5, 136.9, 135.8, 130.7, 129.6, 128.0, 126.1, 125.6, 125.3, 34.8, 31.4, 29.1, 19.2, and 15.4. HRMS (EI)  $m/z$  calcd for  $C_{24}H_{27}O_2S$  [M + H]<sup>+</sup>: 379.1731; Found: 379.1732.

(4-Ethylphenyl)(2-(methylthio)-5-(naphthalen-2-yl)furan-3-yl)methanone (**6h**). 51 mg, 69% yield (eluent: petroleum ether (60–90 °C)/dichloromethane, 1:1, v/v), white solid, mp: 74–75 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (s, 1 H), 7.80 (m, 5 H), 7.64 (m, 1 H), 7.59 (s, 1 H), 7.54 (m, 1 H), 7.48 (m, 1 H), 7.32 (m, 2 H), 2.75 (m, 2 H), 2.68 (s, 3 H), and 1.31 (t,  $J$  = 7.6 Hz, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  189.9, 152.5, 149.0, 140.4, 136.8, 133.7, 132.9, 131.6, 129.6, 129.5, 128.9, 128.0, 127.9, 126.9, 126.3, 123.9, 123.6, 29.1, 19.2, and 15.4. HRMS (EI)  $m/z$  calcd for  $C_{24}H_{21}O_2S$  [M + H]<sup>+</sup>: 373.1262; Found: 373.1262.

**Radical-Trapping Experiments.** Under an N<sub>2</sub> atmosphere, a mixture of 2-bromo-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (**1a**) (91 mg, 0.3 mmol), styrene (**2m**) (47 mg, 0.45 mmol), Pd(OAc)<sub>2</sub> (4 mg, 0.018 mmol), XantPhos (35 mg, 0.06 mmol), Cs<sub>2</sub>CO<sub>3</sub> (215 mg, 0.66 mmol), and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (164 mg, 1.05 mmol) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) (231 mg, 1.05 mmol) or PhNO<sub>2</sub> (129 mg, 1.05 mmol) in 3 mL of benzene was stirred at ambient temperature under visible-light irradiation of a 15 W blue LED bulb for 12 h. No target product **3m** was detected by GC and proton NMR analyses of the resultant reaction mixture. However, species **7** was detected in the reaction mixture by HRMS determinations.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.1c00838>.

Experimental materials and procedures, analytical data, and NMR spectra of compounds ([PDF](#))

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### Notes

The authors declare no competing financial interest.

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## DEDICATION

Dedicated to Professor Christian Bruneau.

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