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Synthesis of Densely Substituted 1,3-Butadienes through Acid-Catalyzed Alkenylations of α-Oxoketene Dithioacetals with Aldehydes

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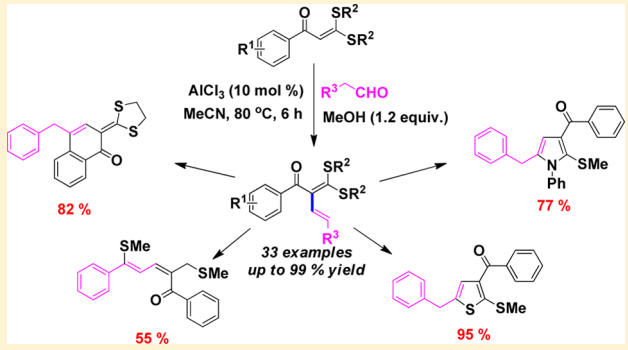
Supporting Information

ABSTRACT: Aldehydes were proved to be viable reagents for implementing alkenylation of α-oxoketene dithioacetals. $AlCl_3$ was found to be the best catalyst. The established reaction opened an avenue to access densely substituted 1,3-butadiene derivatives. The obtained product bears multiple reactive sites that can be converted into various valuable molecules.



INTRODUCTION

The 1,3-diene unit is often found in natural products that have shown potential biological activities.[1] Organic compounds that have a fragment of conjugated diene have often been used as key intermediates in the synthesis of pharmaceutically interesting molecules.[2] Because of the great importance of the 1,3-diene unit, these derivatives are very attractive synthetic targets in the search for efficient and selective synthetic methods. Some conjugated dienes can be prepared by Wittig-type olefination[3] or transition-metal-mediated coupling reactions of the deliberately functionalized precursors.[4] Recently, olefin−olefin dehydrogenative coupling methods for the synthesis of 1,3-butadienes have also been reported.[5] Although there are numerous methods for the preparation of 1,3-butadiene derivatives, most of these methods suffer from the use of expensive reagents or catalysts. In some cases, the reaction was established on the basis of the use of stoichiometric or overstoichiometric amounts of environmentally unfriendly additives (or sacrificial reagents). Furthermore, some reported reactions were performed under less favorable reaction conditions and suffered from the lack of simplicity and also the yields and selectivities reported were far from satisfactory. Therefore, there is a need to develop general and efficient routes to the selective synthesis of conjugated dienes.

Acid-catalyzed alkenylation of a nucleophile with an aldehyde or its congeners that contains at least one proton in an α position has proved recently to be an effective method for introducing a carbon−carbon double bond into the target molecules.[6] The reaction was established on the basis of a mechanism involving reversible carbon−carbon or carbon−heteroatom bond formation, and a good leaving ability of the nucleophile is the key for rendering the alkenylation protocol possible. While this is readily accomplished with activated substrates, such as 2-alkylindole and alkyl carbamates, the use of unactivated compounds is exceedingly rare and, up to now, represents a formidable challenge.

α-Oxoketene dithioacetals have recently emerged as valuable building blocks for organic synthesis.[7] The reactions with α-oxoketene dithioacetals often produced molecules that bear multiple reactive sites, allowing for further functionalizations. Because of the unique reactivity that cannot be attained with other substances, we were attracted to use these molecules in acid-catalyzed organic synthesis.[8] In this paper, some densely substituted 1,3-butadiene derivatives were synthesized through an acid-catalyzed alkenylation of α-oxoketene dithioacetal with some suitable aldehydes. The reaction displayed a fairly good scope with respect to both components. Remarkably, the generated compound was proven to be a unique kind of bifunctional building block that can be used in the synthesis of some valuable molecules.

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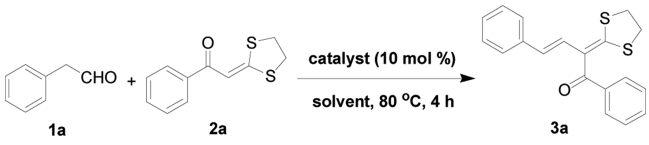
RESULTS AND DISCUSSION

Initially, phenylacetaldehyde **1a** was treated with the α-oxoketene dithioacetal **2a**. The reaction was performed in acetonitrile at 80 °C. No reaction was observed in the absence of catalyst (Table 1, entry 1). When $AlCl_3$ was used as catalyst, the alkenylation product **3a** was obtained in 36% yield after 6 h of reaction (Table 1, entry 2). The ^1H NMR spectrum of **3a** showed that only *trans* isomer was obtained, indicating that this reaction is exclusively stereoselective. This is probably a result of stereo hindrance arising from the existence of bulky groups on the two sides of the C−C double bond. Intriguingly, the yield can be improved to 88% by adding 1.2 equiv of methanol to the reaction system (entry 3). In this case, formation of the dimethyl acetal of **1a** may be responsible for the yield improvement. This can be verified by the fact that 83% yield could be obtained by using **4a** as substrate (Scheme 1). When ethanol was used instead of methanol, the yield decreased to 73% (entry 4).

Table 1. Alkenylation of α-Oxoketene Dithioacetal 2a with 1a[a]



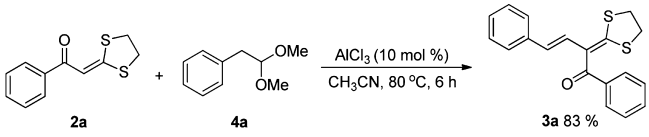
1a 2a 3a

entry	catalyst (10 mol %)	additive	solvent	yield (%)
1		MeOH	CH_3CN	0
2	$AlCl_3$		CH_3CN	36
3	$AlCl_3$	MeOH	CH_3CN	88
4	$AlCl_3$	EtOH	CH_3CN	73
5	$FeCl_3·6H_2O$	MeOH	CH_3CN	18
6	$Fe(OTf)_3$	MeOH	CH_3CN	26
7	$CuBr_2$	MeOH	CH_3CN	50
8	$LiBr·H_2O$	MeOH	CH_3CN	trace
9	H_2SO_4	MeOH	CH_3CN	34
10	PTSA	MeOH	CH_3CN	21
11	$AlCl_3$	MeOH	PhCl	72
12	$AlCl_3$	MeOH	CH_3NO_2	62
13[b]	$AlCl_3$		MeOH	NR
14[b]	$AlCl_3$	MeOH	toluene	35
15[b]	$AlCl_3$	MeOH	DCE	23
16[c]	$AlCl_3$	MeOH	CH_3CN	57
17[d]	$AlCl_3$	MeOH	CH_3CN	64
18[e]	$AlCl_3$	MeOH	CH_3CN	67

[a]Conditions unless specified otherwise: **2a**, 0.2 mmol; additive, 0.24 mmol; catalyst, 0.02 mmol; solvent, 1.0 mL; 80 °C; 6 h. [b]Conditions: 12 h. [c]Conditions: $AlCl_3$: 0.01 mmol, 16 h. [d]Conditions: 60 °C, 24 h. [e]Conditions: 3 h.

Various Lewis acids were then examined in the reaction of **1a** and **2a**. $FeCl_3·6H_2O$ has been reported by Yu[9] to be an efficient catalyst for the alkenylation of indole with aldehyde. However, with this catalyst, **3a** was obtained only in 18% yield (entry 5).

Scheme 1. Reaction of 2a with 4a Catalyzed by $AlCl_3$



2a 4a 3a 83 %

When $Fe(OTf)_3$ was used as catalyst, no significant yield improvement was observed (entry 6). A moderate yield, 50%, was obtained when $CuBr_2$ was used (entry 7). An attempt to use a weak Lewis acid, $LiBr·H_2O$, as catalyst led only to recovery of unreacted starting materials (entry 8). Brønsted acids, such as sulfuric acid and toluenesulfonic acid, were also examined, and the yields obtained were rather poor (entries 9 and 10).

The effect of solvent was also investigated. Among different solvents tested in the reaction between **1a** and **2a**, acetonitrile clearly stood out, producing the desired product **3a** with the highest yield (88%), with chlorobenzene and nitromethane in a distant second place (62−72%). Methanol, toluene, and 1,2-dichloroethane resulted in significantly lower efficiency of the reaction (entries 11−15). A decrease in the catalyst loading from 10 to 5 mol % resulted in a significant decrease in the reaction yield. Only 57% yield was obtained, although the reaction time was increased to 16 h (entry 16). Further investigation revealed that the reaction was also affected by temperature and reaction time, and the optimal conditions are 80 °C and 6 h (entries 17 and 18).

With the optimized conditions in hand, we probed the scope of the reaction with respect to both the α-oxoketene dithioacetal and the aldehyde components. As evidenced by the results in Figure 1, ketene dithioacetals with different substituents smoothly reacted with phenylacetaldehyde, producing the expected 1,3-butadienes in generally good yield. Both electron rich and moderately electron poor α-oxoketene dithioacetals readily participated in the reaction. The moderate yield obtained with 2-(1,3-dithiolan-2-ylidene)-1-(4-iodophenyl)ethanone can be ascribed partially to its poor solubility in the reaction system (**3f**). Only 58% yield was obtained with a ketene dithioacetal that contains a strongly electron-withdrawing group, 2-(1,3-dithiolan-2-ylidene)-1-(4-nitrophenyl)ethanone (**3g**). This may result from its low reactivity.[10] A ketene dithioacetal containing a sterically demanding substituent, such as 3,3-bis(methylthio)-1-phenyl-2-propen-1-one (**3h**), can also be used in this type of reaction, but the yield obtained is inferior as compared with that of **2a**.

The scope of the reaction with respect to aldehydes was next investigated and found to be excellent. We selected a set of aldehydes spanning a convenient spectrum of reactivity. In all cases, **2a** was used as a benchmark substrate in order to compare the reactivities of different aldehydes. Results with β-arylacetaldehydes largely paralleled, in most cases, the yield of phenylacetaldehyde (**3i−t**). Remarkably, 3-phenylpropanal and butyraldehyde can also be used as alkenylation reagents, and the corresponding products, **3u,x**, were obtained in 87% and 90% yields, respectively. Cyclohexanecarbaldehyde and 3-cyclohexene-1-carboxaldehyde participated readily in the alkenylation reaction as well (**3aa,ab**). Only moderate yields were obtained when methyl 3,3-dimethoxypropanoate and ethyl 3,3-diethoxypropanoate were used (**3ac,ad**). In these cases, the 3,3-dimethoxypropanoate was completely consumed, whereas nearly half of the **2a** can be recovered at the end of the reaction. We therefore suspected that the susceptibility of 3,3-dialkoxypropanoate toward the strong acid, $AlCl_3$ catalyst, might be partially responsible for the embarrassing yields.

It is significant to note that the reaction can also be effectively scaled up with the similar efficiency (Scheme 2). For example, the reaction of **2a** (20 mmol) with 2,2-diphenylacetaldehyde (**1b**; 20 mmol) gave the corresponding product **3j** in 92% yield (7.4 g). Significantly, **3j** was obtained by filtration as

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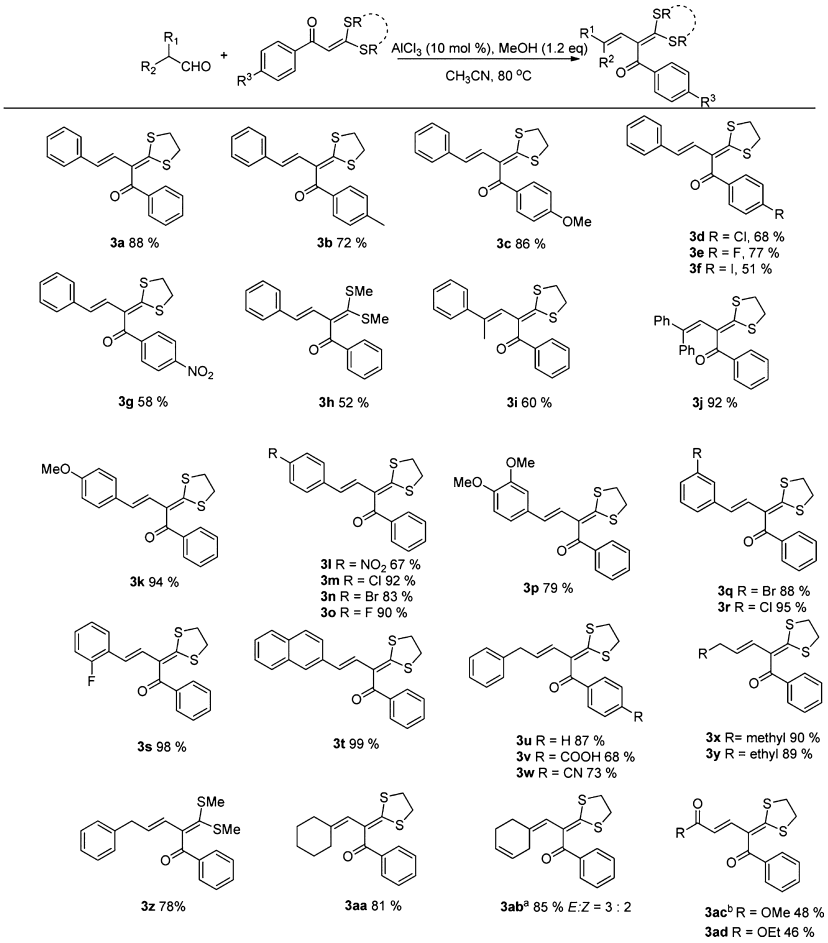
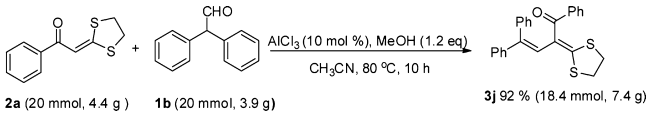


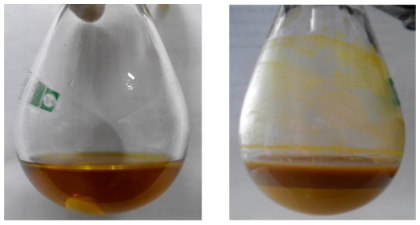
Figure 1. Alkenylation of α-oxoketene dithioacetals with aldehydes or their congeners. Legend to superscripts: (a) the configuration was determined by ^{1}H NMR; (b) **3ac** and **3ad** were synthesized with methyl 3,3-dimethoxypropanoate and ethyl 3,3-diethoxypropanoate in the absence of methanol.

Scheme 2. Large-Scale Synthesis of 3j



it precipitated out from the reaction mixture at the end of the reaction (parts a and b of Figure 2). The structures of **3j** have been unambiguously confirmed by X-ray structural analysis (see Figure S1 in the Supporting Information).[11]

It should be noted that the previous methods to access the similar vinylated α-oxoketene dithioacetal derivatives not only involved the use of noble-metal-based catalysts but also suffered from some drawbacks, such as insufficient reactions, long reaction times, and harsh conditions.[12] The present reaction thus opens an efficient route to synthesize these kinds of functionalized α-oxoketene dithioacetals. The mechanism of the alkenylation reaction most likely involves an acid-assisted carbon cation based nucleophilic substitution. That is, activation of phenylacetalaldehyde **1a** is achieved via the formation of an acetal or a hemiacetal. A carbon cation (**I**) was formed by elimination of either methanol or water. This is followed by nucleophilic attack of α-oxoketene dithioacetal **2a**, which leads to generation of an intermediate (**II**) that can be then converted into **3a** (Figure 3).



(a) **(b)**

Figure 2. Large-scale synthesis of **3j**: (a) before reaction; (b) after reaction.

When aldehyde is used as an alkenylation reagent, the existence of an α-proton is the key for rendering the reaction possible. However, we found that, in this reaction, this is not always the case. An exception was found with cocal (**1c**) and 4-methyl-2-phenyl-2-pentenal (**1d**). These two aldehydes have no α-proton but were also applicable in this type of alkenylation. Different from the case for **1a**-induced alkenylation, the present reactions are associated with an elimination of a γ-proton, which unexpectedly generated **5a**,**b** in 45% and 40% yields, respectively (Scheme 3). These structures contain a skeleton of 1,3,5-triene which has often occurred in natural products.[13] Previous methods to access this scaffold involved the use of either hazardous reaction conditions[14] or metallic reagents.[15] This reaction thus provided a convenient way to synthesize this type of structure.

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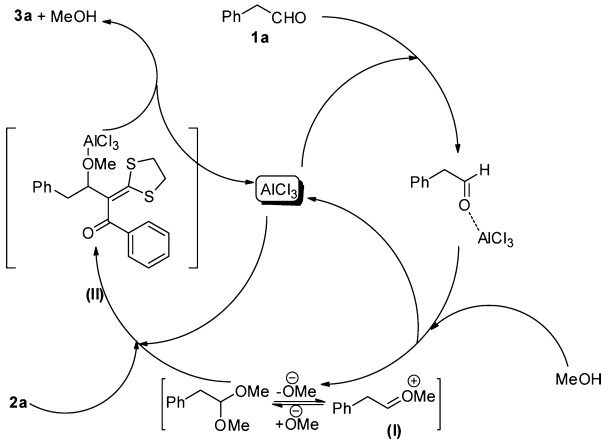
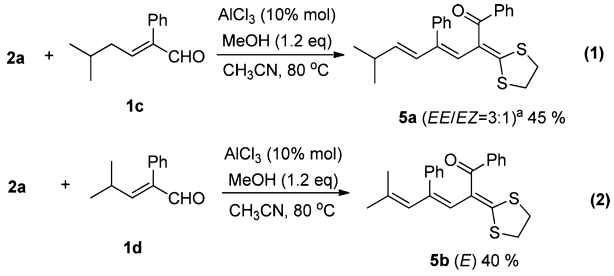


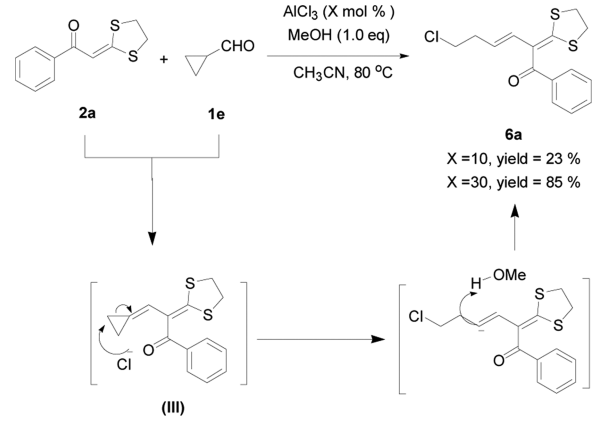
Figure 3. Proposed mechanism.

Scheme 3. Alkenylation of 2a with cocal (1c) and 4-Methyl-2-phenyl-2-pentenal (1d)



Alkylidenecyclopropane derivatives have been widely used as intermediates in organic synthesis over the past few decades.[16] On the basis of the aforementioned results, we envisioned that it is possible to synthesize an alkylidenecyclopropane derivative by using cyclopropanecarboxaldehyde (**1e**) as an alkenylation reagent. Indeed, a product was obtained when **2a** was treated with **1e** in the presence of $AlCl_3$ (Scheme 4). However,

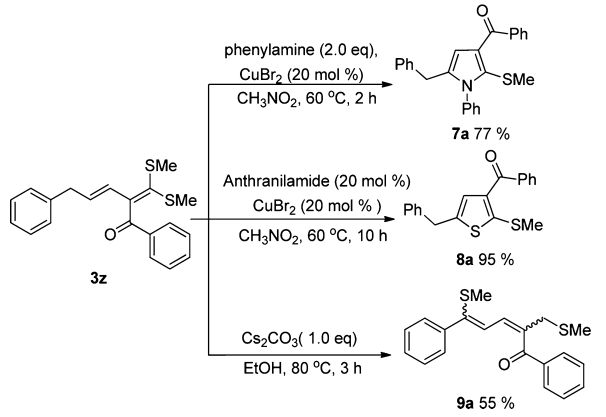
Scheme 4. Alkenylation of 2a with 1e



spectroscopic analysis of the product revealed that the structure of this product is **6a**. Considering the fact that, in this reaction, $AlCl_3$ acts as a dual catalyst and reagent, we then increased its loading to 30 mol %. To our delight, **6a** was obtained in 85% yield. The mechanism of the reaction may involve the following two steps: (i) the alkenylation reaction occurred with the aid of $AlCl_3$ catalyst, generating alkylidenecyclopropane intermediate **III**, and then (ii) the intermediate **III** underwent a ring-opening reaction triggered by an attack of chloride anion in the presence of a proton donor (presumably methanol), producing **6a**.

After establishing the synthetic method, we then investigated the transformations of the obtained products. The study commenced from the use of the compound **3z** in the synthesis of some important heterocycles. First, the densely substituted pyrrole derivative **7a** was obtained in 77% yield when **3z** was treated with aniline in the presence of $CuBr_2$ catalyst (Scheme 5). The initial event of the reaction might be the formation of a

Scheme 5. Catalytic Reactions Developed with 3z as Starting Material



Michael adduct, which then underwent intramolecular nucleophilic substitution[17] and an aromatization reaction to generate **7a**. Interestingly, when aniline was replaced by anthranilamide, the substituted thiophene derivative **8a** was obtained. Further investigation revealed that a catalytic amount of anthranilamide (20 mol %) is sufficient to ensure an excellent yield for this reaction (Scheme 5). In the absence of anthranilamide, only a trace amount of **8a** was detected. No reaction occurred when $CuBr_2$ was omitted from this catalytic system. Although the detailed mechanism of the cooperative catalysis remains to be delineated, the established reaction is valuable for organic synthesis because many thiophene derivatives with a methylthio group in a C2 position have exhibited good bioactivities for antibacterial use.[18] Compound **3z** was also proved to be susceptible toward basic reagents. For example, an unexpected product, **9a**, was obtained in 55% yield when it was treated with Cs_2CO_3 in refluxing ethanol for 3 h (Scheme 5). The mechanism of this reaction might be associated with the formation of a carbon anion, which then triggered an intramolecular migration of both a proton and a methylthio group.

In addition, in the presence of 1.2 equiv of $CuBr_2$, **3u** could be smoothly converted into **10a** in nitromethane (Scheme 6). Compound **10a** contains a scaffold of naphthalenone, which is an important medicinal intermediate.[19] The reaction might proceed according to the following pathways: (i) an intramolecular Friedel–Crafts reaction, generating the intermediate **IV** and (ii) dehydrogenation of the intermediate **IV**, which led to the formation of **10a**. $CuBr_2$ acted as a dual Lewis acid catalyst and an oxidant, thus allowing the reaction to proceed smoothly. All of these examples demonstrated that the title reactions of α-oxoketene dithioacetals using aldehyde as an alkenylation reagent are indeed valuable for organic synthesis.

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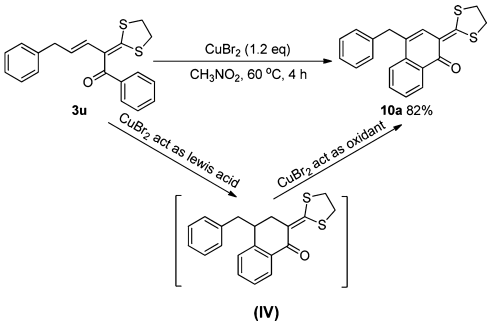
Scheme 6. Synthesis of 10a from 3u



CONCLUSIONS

In summary, the alkenylation reaction of α-oxoketene dithioacetal with aldehyde has been established by using $AlCl_3$ as catalyst. With this reaction, various densely substituted 1,3-butadiene derivatives were synthesized in moderate to excellent yields. The generated conjugated dienes not only bear a reactive C−C double bond but also contain a few active sites from α-oxoketene dithioacetal, which can be used as bifunctional building blocks for the synthesis of some valuable molecules. Given the large number of commercially available aldehydes and the easy access to α-oxoketene dithioacetals, the present method should be able to synthesize a wide range of conjugated dienes. Considering the unique reactivity of the products, we believe that this method has a great potential to be applied extensively in the field of synthetic chemistry.

EXPERIMENTAL SECTION

General Information. Chemical shifts are expressed in ppm relative to Me_4Si in solvent. All chemicals used were of reagent grade and were used as received without further purification. α-Oxoketene dithioacetals were prepared according to previously reported methods.[20] All reactions were conducted in a 10 mL V-type flask equipped with triangle magnetic stirring.

General Procedure for the Reactions of α-Oxoketene Dithioacetal and Aldehyde. In a typical reaction, ketene dithioacetal (0.20 mmol) was mixed with the aldehyde (0.20 mmol), MeOH (0.24 mmol), and $AlCl_3$ (10 mol %) in acetonitrile (1.0 mL). The mixture was then stirred at 80 °C for 6 h. After the reaction, the mixture was cooled to room temperature, and the product was obtained by isolation with preparative TLC (elutent: petroleum ether/ethyl acetate 10/1 (v/v)). Tests for substrate scope were all performed with an analogous procedure.

*Large-Scale Synthesis of **3j**.* A solution of **2a** (20 mmol, 4.4 g) in nitromethane (25 mL) was mixed with **1b** (20 mmol, 3.9 g), MeOH (24 mmol, 768 mg), and $AlCl_3$ (10 mol %, 2.0 mmol, 266 mg). The mixture was stirred at 80 °C for 10 h. After the reaction, the product was obtained in 92% yield (18.4 mmol, 7.4 g) by filtration.

*Procedure for the Synthesis of **6a**.* A solution of **2a** (0.2 mmol, 44.0 mg) in nitromethane (1 mL) was mixed with **1e** (0.2 mmol, 14.0 mg), MeOH (0.24 mmol, 7.7 mg), and $AlCl_3$ (30 mol %, 0.06 mmol, 8.0 mg). The mixture was stirred at 80 °C for 10 h. Then, the product was obtained in 85% yield (0.17 mmol, 52.7 mg) by isolation with preparative TLC (eluent: petroleum ether/ethyl acetate 10/1 (v/v)).

*Procedure for the Synthesis of **7a**.* A solution of **3z** (0.4 mmol, 136.0 mg) in nitromethane (2 mL) was mixed with aniline (2.0 eq, 0.8 mmol, 74.4 mg) and $CuBr_2$ (20 mol %, 0.08 mmol, 17.6 mg). The mixture was stirred at 60 °C for 2 h. Then, the product was obtained in 77% yield (0.31 mmol, 118.7 mg) by isolation with preparative TLC (eluent: petroleum ether/ethyl acetate 10/1 (v/v)).

*Procedure for the Synthesis of **8a**.* A solution of **3z** (0.4 mmol, 136.0 mg) in nitromethane (2 mL) was mixed with $CuBr_2$ (20 mol %, 0.08 mmol, 17.6 mg) and 2-aminobenzamide (20 mol %, 0.08 mmol, 10.9 mmg) as catalysts. The mixture was stirred at 60 °C for 10 h. Then, the product was obtained in 95% yield (0.38 mmol, 123.1 mg) by isolation with preparative TLC (eluent: petroleum ether/ethyl acetate 10/1 (v/v)).

*Procedure for the Synthesis of **9a**.* A solution of **3z** (0.4 mmol, 136.0 mg) in ethanol (2 mL) was mixed with Cs_2CO_3 (1.0 equiv, 0.4 mmol, 130.0 mg). The mixture was stirred at 80 °C for 3 h. Then, the product was obtained in 55% yield (0.22 mmol, 74.8 mg) by isolation with preparative TLC (eluent: petroleum ether/ethyl acetate 10/1 (v/v)).

*Procedure for the Synthesis of **10a**.* A solution of **3u** (0.4 mmol, 135.2 mg) in nitromethane (2 mL) was mixed with $CuBr_2$ (1.2 equiv, 0.48 mmol, 105.6 mg) The mixture was stirred at 60 °C for 4 h. Then, the product was obtained in 82% yield (0.33 mmol, 110.2 mg) by isolation with preparative TLC (eluent: petroleum ether/ethyl acetate 10/1 (v/v)).

Characterization Data of New Compounds. *(E)-2-(1,3-Dithiolan-2-ylidene)-1,4-diphenylbut-3-en-1-one (**3a**).* Yield: 88%, 0.18 mmol, 57.0 mg; yellowish oil. ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 7.88−7.80 (m, 2H), 7.50 (dd, *J* = 11.7, 4.4 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.31−7.15 (m, 5H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 3.51−3.38 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C): δ 194.0, 137.9, 137.2, 132.4, 131.2, 129.7, 128.6, 128.3, 127.5, 126.6, 126.2, 38.6, 36.9 ppm. IR (KBr): ν 2961, 2924, 2853, 1724, 1659, 1450, 1262, 1074, 912, 801, 745, 691 cm^{-1}. HRMS (TOF, ESI): *m*/*z* calcd for $C_{19}H_{16}NaOS_2$, $[M + Na]^+$ 347.0540, found 347.0547.

*(E)-2-(1,3-Dithiolan-2-ylidene)-4-phenyl-1-(p-tolyl)but-3-en-1-one (**3b**).* Yield: 72%, 0.14 mmol, 48.7 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.34−7.24 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 16.2 Hz, 1H), 6.25 (d, *J* = 16.2 Hz, 1H), 3.49−3.44 (m, 2H), 3.40 (dd, *J* = 6.9, 4.7 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 194.1, 151.9, 143.4, 137.3, 134.9, 130.6, 130.0, 129.1, 128.6, 127.5, 126.6, 126.2, 125.6, 38.5, 37.0, 21.7 ppm. IR (KBr): ν2955, 2925, 2855, 1745, 1659, 1603, 1456, 1284, 1217, 1173, 952, 751, 694 cm^{-1}. HRMS (TOF, ESI): *m*/*z* calcd for $C_{20}H_{18}NaOS_2$, $[M + Na]^+$ 361.0697, found 361.0701.

*(E)-2-(1,3-Dithiolan-2-ylidene)-1-(4-methoxyphenyl)-4-phenylbut-3-en-1-one (**3c**).* Yield: 86%, 0.17 mmol, 60.9 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.88 (d, *J* = 8.9 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 16.1 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.24 (d, *J* = 16.2 Hz, 1H), 3.84 (s, 3H), 3.46 (t, *J* = 6.1 Hz, 2H), 3.39 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.6, 163.5, 149.5, 137.3, 132.3, 130.1, 129.9, 128.6, 127.5, 126.6, 126.2, 126.0, 113.7, 55.5, 38.5, 37.2 ppm. IR (KBr): ν 2957, 2927, 2842, 1725, 1652, 1595, 1459, 1303, 1256, 1164, 1027, 952, 841, 752 cm^{-1}. HRMS (TOF, ESI): *m*/*z* calcd for $C_{20}H_{18}NaO_2S_2$, $[M + Na]^+$ 377.0646, found 377.0654.

*(E)-1-(4-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-4-phenylbut-3-en-1-one (**3d**).* Yield: 68%, 0.14 mmol, 48.7 mg; yellowish oil. ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 3.6 Hz, 4H), 7.24−7.19 (m, 1H), 7.00 (d, *J* = 16.2 Hz, 1H), 6.25 (d, *J* = 16.2 Hz, 1H), 3.53−3.35 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 192.4, 156.2, 138.6, 137.0, 136.3, 131.6, 131.1, 128.7, 128.6, 127.7, 126.4, 126.2, 124.5, 38.6, 36.9 ppm. IR (KBr): ν 3024, 2923, 2852, 1725, 1660, 1586, 1282, 1167, 1088, 1007, 952, 838, 747, 693 cm^{-1}. HRMS (TOF, ESI): *m*/*z* calcd for $C_{19}H_{15}ClNaOS_2$, $[M + Na]^+$ 381.0151, found 381.0130.

*(E)-2-(1,3-Dithiolan-2-ylidene)-1-(4-fluorophenyl)-4-phenylbut-3-en-1-one (**3e**).* Yield: 77%, 0.15 mmol, 52.7 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.87 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.33−7.25 (m, 5H), 7.23−7.18 (m, 1H), 7.07 (t, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.24 (d, *J* = 16.2 Hz, 1H), 3.48−3.44 (m, 2H), 3.43−3.39 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 192.5, 166.1, 164.4, 154.5, 137.1, 134.0, 134.0, 132.4, 132.3, 131.2, 128.6, 127.7, 126.4, 126.2, 124.8, 115.5, 115.4, 38.6, 37.0 ppm. ^{19}F NMR (377 MHz, $CDCl_3$, TMS, 25 °C): δ −105.9 ppm. IR (KBr): ν

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3024, 2926, 2854, 1724, 1662, 1595, 1499, 1455, 1284, 1229, 1153, 954, 845, 753, 694, 565 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{19}H_{16}FOS_2$, $[M + H]^+$ 343.0627, found 343.0621.

(E)-2-(1,3-Dithiolan-2-ylidene)-1-(4-iodophenyl)-4-phenylbut-3-en-1-one ***(3f)***. Yield: 51%, 0.10 mmol, 45.8 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.75 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.32−7.27 (m, 4H), 7.21 (ddd, J = 8.6, 5.7, 2.9 Hz, 1H), 6.99 (d, J = 16.2 Hz, 1H), 6.26 (d, J = 16.2 Hz, 1H), 3.47−3.41 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 192.6, 156.6, 137. 6, 137.3, 137.0, 131.7, 131.2, 128.7, 127.7, 126.4, 126.3, 124.3, 100.0, 38.7, 36.9 ppm. IR (KBr): ν 2957, 2925, 2854, 1725, 1662, 1611, 1578, 1452, 1389, 1309, 1285, 1252, 1173, 1057, 1001, 953, 835, 746, 694, 507 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{19}H_{16}IOS_2$, $[M + H]^+$ 450.9687, found 450.9667.

(E)-2-(1,3-Dithiolan-2-ylidene)-1-(4-nitrophenyl)-4-phenylbut-3-en-1-one ***(3g)***. Yield: 58%, 0.12 mmol, 42.8 mg; red solid, mp 110−112 °C. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 8.22 (d, J = 8.7 Hz, 2H), 7.88 (d, J = 8.7 Hz, 2H), 7.29−7.22 (m, 5H), 6.95 (d, J = 16.2 Hz, 1H), 6.26 (d, J = 16.2 Hz, 1H), 3.48 (s, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 190.3, 163.3, 149.2, 144.3, 136.6, 133.4, 130.9, 130.6, 130.3, 129.5, 128.8, 128.7, 128.0, 126.3, 125.9, 124.1, 124.0, 123.8, 123.4, 123.1, 38.9, 36.7 ppm. IR (KBr): ν2957, 2926, 2855, 1725, 1672, 1596, 1522, 1452, 1346, 1284, 956, 854, 754, 728, 695 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{19}H_{16}NO_3S_2$, $[M + H^+]$ 370.0572, found 370.0553.

(E)-2-(Bis(methylthio)methylene)-1,4-diphenylbut-3-en-1-one ***(3h)***.[21] Yield: 52%, 0.10 mmol, 33.9 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.96 (d, J = 7.2 Hz, 2H), 7.61 (d, J = 16.5 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.37 (d, J = 7.5 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 6.34 (d, J = 16.5 Hz, 1H), 2.42 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 196.2, 145.4, 136.8, 136.8, 135.7, 133.5, 133.5, 129.3, 128.8, 128.8, 128.8, 128.6, 128.6, 128.3, 126.8, 124.7, 17.4, 16.7 ppm. IR (KBr): ν 3028, 2921, 2852, 1737, 1669, 1596, 1577, 1517, 1492, 1447, 1421, 1314, 1288, 1213, 1170, 1054, 961, 908, 751, 724 cm^{-1}.

(E)-2-(1,3-Dithiolan-2-ylidene)-1,4-diphenylpent-3-en-1-one ***(3i)***. Yield: 60%, 0.12 mmol, 40.6 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.50−7.22 (m, 10H), 6.61 (s, 1H), 3.47 (t, J = 6.4 Hz, 2H), 3.40−3.36 (m, 2H), 1.71 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 190.9, 165.1, 142.6, 139.5, 139.4, 131.0, 130.3, 128.8, 128.3, 128.3, 127.9, 127.6, 127.4, 127.0, 126.9, 125.9, 125.7, 124.7, 122.5, 39.1, 36.1, 17.9 ppm. IR (KBr): ν 2959, 2925, 2852, 1726, 1616, 1462, 1279, 1021, 914, 727, 695, 635 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{20}H_{18}NaOS_2$, $[M + Na]^+$ 361.0697, found 361.0703.

2-(1,3-Dithiolan-2-ylidene)-1,4,4-triphenylbut-3-en-1-one ***(3j)***. Yield: 92%, 0.18 mmol, 73.6 mg; light yellow solid, mp 210−212 °C. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.28 (dt, J = 3.9, 2.1 Hz, 3H), 7.24−7.21 (m, 3H), 7.21−7.17 (m, 2H), 7.15−7.08 (m, 3H), 7.03 (t, J = 7.7 Hz, 2H), 6.77 (s, 1H), 6.58 (dd, J = 8.0, 0.9 Hz, 2H), 3.47−3.41 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 191.6, 163.2, 144.2, 142.8, 139.6, 138.4, 130.7, 130.3, 128.3, 128.3, 128.1, 127.9, 127.7, 127.3, 127.1, 125.8, 124.2, 38.5, 36.6 ppm. IR (KBr): ν 3055, 2924, 2853, 1622, 1598, 1458, 1316, 1279, 1247, 1075, 1009, 910, 772, 729, 696 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{25}H_{20}NaOS_2$, $[M + Na]^+$ 423.0853, found 423.0840.

(E)-2-(1,3-Dithiolan-2-ylidene)-4-(4-methoxyphenyl)-1-phenylbut-3-en-1-one ***(3k)***. Yield: 94%, 0.19 mmol, 66.6 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.87−7.79 (m, 2H), 7.48 (dd, J = 10.5, 4.3 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 16.2 Hz, 1H), 6.80 (d, J = 8.7 Hz, 2H), 6.21 (d, J = 16.2 Hz, 1H), 3.77 (s, 3H), 3.45−3.42 (m, 2H), 3.41−3.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 194.0, 159.3, 137.9, 132.3, 130.8, 130.0, 129.7, 128.3, 127.8, 127.5, 125.3, 124.7, 114.1, 55.3, 38.6, 36.9 ppm. IR (KBr): ν2999, 2926, 2834, 1739, 1659, 1603, 1507, 1449, 1248, 1174, 1029, 814, 715 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{20}H_{18}NaO_2S_2$, $[M + Na]^+$ 377.0646, found 377.0636.

(E)-2-(1,3-Dithiolan-2-ylidene)-4-(4-nitrophenyl)-1-phenylbut-3-en-1-one ***(3l)***. Yield: 67%, 0.13 mmol, 49.4 mg; red solid, mp 155−157 °C. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 8.11 (d, J = 8.7 Hz, 2H), 7.83 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 16.1 Hz, 1H), 6.27 (d, J = 16.1 Hz, 1H), 3.54−3.49 (m, 2H), 3.45 (dd, J = 11.9, 5.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.9, 157.1, 146.5, 143.9, 137.4, 132.9, 130.5, 129.7, 128.5, 127.7, 126.5, 124.1, 38.8, 37.2 ppm. IR (KBr): ν 3070, 2926, 2852, 1660, 1589, 1514, 1450, 1339, 1248, 1179, 1109, 949, 910, 866, 728, 693, 637 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{19}H_{16}NO_3S_2$, $[M + H]^+$ 370.0572, found 370.0572.

(E)-4-(4-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-1-phenylbut-3-en-1-one ***(3m)***. Yield: 92%, 0.18 mmol, 65.9 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.85−7.77 (m, 2H), 7.50 (t, J = 6.8 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.21 (q, J = 8.7 Hz, 4H), 6.99 (d, J = 16.2 Hz, 1H), 6.19 (d, J = 16.2 Hz, 1H), 3.46−3.43 (m, 2H), 3.42−3.39 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 186.0, 155.0, 137.7, 135.7, 133.1, 132.5, 132.1, 129.7, 129.6, 128.8, 128.8, 128.5, 128.4, 128.3, 127.9, 127.8, 127.4, 127.1, 124.8, 108.3, 38.6, 37.0 ppm. IR (KBr): ν 3026, 2926, 2854, 1725, 1660, 1614, 1486, 1450, 1279, 1250, 1224, 957, 809, 695, 637 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{19}H_{15}ClOS_2$, $[M + H]^+$ 359.0331, found 359.0324.

(E)-4-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-1-phenylbut-3-en-1-one ***(3n)***. Yield: 83%, 0.17 mmol, 66.6 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.53−7.47 (m, 2H), 7.42 (dd, J = 15.5, 7.6 Hz, 3H), 7.36 (d, J = 5.0 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 16.2 Hz, 1H), 6.17 (d, J = 16.2 Hz, 1H), 3.47 (dd, J = 7.4, 5.5 Hz, 2H), 3.38 (dt, J = 12.6, 3.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.9, 155.1, 137.7, 136.2, 132.5, 132.1, 131.7, 129.7, 128.5, 128.4, 127.9, 127.7, 127.2, 124.8, 121.2, 108.3, 38.6, 37.0 ppm. IR (KBr): ν 2959, 2925, 2853, 1742, 1660, 1615, 1575, 1483, 1450, 1280, 1250, 1225, 1175, 1049, 960, 806, 695 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{19}H_{16}BrOS_2$, $[M + H]^+$ 402.9826, found 402.9804.

(E)-2-(1,3-Dithiolan-2-ylidene)-4-(4-fluorophenyl)-1-phenylbut-3-en-1-one ***(3o)***. Yield: 90%, 0.18 mmol, 61.6 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.79 (d, J = 7.2 Hz, 2H), 7.51−7.37 (m, 7H), 6.93 (d, J = 16.1 Hz, 1H), 6.66 (d, J = 16.1 Hz, 1H), 3.43 (d, J = 4.6 Hz, 2H), 3.42−3.39 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, TMS, 25 °C): δ 193.6, 158.3, 138.3, 137.2, 133.0, 132.2, 132.1, 130.2, 129.6, 129.2, 128.7, 128.5, 128.3, 127.9, 127.5, 126.4, 124.4, 123.9, 108.3, 38.6, 37.0 ppm. ^{19}F NMR (377 MHz, $CDCl_3$, TMS, 25 °C): δ −102.9, −102.9, −102.9 ppm. IR (KBr): ν 3057, 2925, 2853, 1659, 1615, 1499, 1451, 1279, 1250, 1224, 1022, 954, 803, 753, 694 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{19}H_{16}FOS_2$, $[M + H]^+$ 343.0627, found 343.0629.

(E)-4-(3,4-Dimethoxyphenyl)-2-(1,3-dithiolan-2-ylidene)-1-phenylbut-3-en-1-one ***(3p)***. Yield: 79%, 0.16 mmol, 60.7 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.84 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 6.88 (d, J = 16.1 Hz, 1H), 6.86−6.81 (m, 2H), 6.77 (d, J = 8.3 Hz, 1H), 6.21 (d, J = 16.2 Hz, 1H), 3.86 (d, J = 2.8 Hz, 6H), 3.45 (dd, J = 6.7, 4.7 Hz, 2H), 3.42−3.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 194.1, 153.0, 149.0, 148.9, 137.8, 132.4, 130.9, 130.4, 129.7, 128.3, 125.2, 125.0, 119.4, 111.2, 108.9, 56.0, 55.9, 38.6, 36.9 ppm. IR (KBr): ν 2957, 2928, 2837, 1744, 1660, 1598, 1512, 1461, 1261, 1139, 1025, 728 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{21}H_{21}O_3S_2$, $[M + H]^+$ 385.0932, found 385.0930.

(E)-4-(3-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-1-phenylbut-3-en-1-one ***(3q)***. Yield: 88%, 0.18 mmol, 70.6 mg; yellowish oil. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.85−7.79 (m, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.20 (s, 1H), 7.21−7.09 (m, 3H), 7.03 (d, J = 16.2 Hz, 1H), 6.17 (d, J = 16.2 Hz, 1H), 3.46 (t, J = 5.6 Hz, 2H), 3.44−3.40 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.8, 155.7, 139.1, 137.7, 134.5, 132.5, 129.8, 129.7, 129.5, 128.4, 127.8, 127.4, 126.0, 124.6, 124.5, 38.6, 37.0 ppm. IR (KBr): ν 3060, 2926, 1661, 1615, 1503, 1281, 1250, 1230, 1156, 1049, 961, 815, 700 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{19}H_{16}BrOS_2$, $[M + H]^+$ 402.9826, found 402.9853.

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*(E)-4-(3-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-1-phenylbut-3-en-1-one (**3r**).* Yield: 95%, 0.19 mmol, 68.0 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.74 (d, J = 7.1 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.7 Hz, 2H), 7.19 (s, 1H), 7.14−7.03 (m, 3H), 6.95 (d, J = 16.2 Hz, 1H), 6.10 (d, J = 16.2 Hz, 1H), 3.36 (ddd, J = 11.1, 7.2, 5.1 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.8, 155.6, 139.1, 137.7, 134.4, 132.2, 129.8, 129.7, 129.4, 128.3, 127.9, 127.3, 126.0, 124.6, 124.5, 38.6, 37.0 ppm. IR (KBr): ν 3059, 2926, 2854, 1662, 1612, 1592, 1451, 1317, 1280, 1248, 1172, 952, 781, 731, 689, 638 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{19}H_{15}ClNaOS_2$, $[M + Na]^+$ 381.0151, found 381.0130.

*(E)-2-(1,3-Dithiolan-2-ylidene)-4-(2-fluorophenyl)-1-phenylbut-3-en-1-one (**3s**).* Yield: 98%, 0.20 mmol, 67.0 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.82 (d, J = 7.3 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.38−7.35 (m, 1H), 7.15 (dd, J = 13.8, 6.7 Hz, 1H), 7.10 (d, J = 16.4 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 7.01−6.94 (m, 1H), 6.42 (d, J = 16.4 Hz, 1H), 3.43 (td, J = 11.2, 5.1 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.8, 161.0, 159.3, 156.2, 137.9, 132.3, 129.7, 128.9, 128.9, 128.7, 128.6, 128.3, 127.0, 126.9, 125.2, 125.1, 125.0, 124.1, 124.1, 123.6, 123.6, 115.8, 115.7, 38.6, 36.9 ppm. ^{19}F NMR (377 MHz, $CDCl_3$, TMS, 25 °C): δ −117.6, −117.6 ppm. IR (KBr): ν 3059, 2926, 2854, 1661, 1613, 1486, 1315, 1275, 1229, 1174, 957, 756, 691, 637 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{19}H_{16}FOS_2$, $[M + H]^+$ 343.0627, found 343.0629.

*(E)-2-(1,3-Dithiolan-2-ylidene)-4-(naphthalen-2-yl)-1-phenylbut-3-en-1-one (**3t**).* Yield: 99%, 0.20 mmol, 74.1 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.93 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.55 (dd, J = 11.9, 7.9 Hz, 2H), 7.49 (dd, J = 8.4, 6.3 Hz, 1H), 7.46−7.38 (m, 4H), 7.34 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 10.1 Hz, 1H), 3.47−3.37 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.6, 157.7, 138.6, 135.0, 133.6, 132.1, 132.0, 131.2, 129.7, 129.5, 128.6, 128.5, 128.4, 121.0, 127.9, 126.0, 125.9, 125.7, 124.9, 123.7, 123.2, 108.3, 38.6, 36.9 ppm. IR (KBr): ν 3056, 2925, 2854, 1657, 1617, 1482, 1280, 1226, 1174, 1152, 953, 776, 695 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{23}H_{18}NaOS_2$, $[M + Na]^+$ 397.0697, found 397.0684.

*(E)-2-(1,3-Dithiolan-2-ylidene)-1,5-diphenylpent-3-en-1-one (**3u**).* Yield: 87%, 0.17 mmol, 58.8 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.70 (dd, J = 8.1, 1.0 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.35 (t, J = 7.7 Hz, 2H), 7.21 (t, J = 7.4 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 7.1 Hz, 2H), 6.33 (d, J = 15.7 Hz, 1H), 5.56 (dt, J = 15.7, 7.0 Hz, 1H), 3.38 (dt, J = 5.3, 2.6 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.17, 156.78, 139.67, 138.50, 133.27, 131.60, 129.55, 129.34, 128.49, 128.35, 128.27, 128.02, 126.05, 124.33, 39.40, 38.56, 36.59 ppm. IR (KBr): ν 3058, 3025, 2925, 1723, 1661, 1601, 1452, 1280, 1174, 962, 697 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{20}H_{18}NaOS_2$, $[M + Na]^+$ 361.0697, found 361.0700.

*(E)-4-(2-(1,3-Dithiolan-2-ylidene)-5-phenylpent-3-enoyl)benzoic acid (**3v**).* Yield: 68%, 0.14 mmol, 52.0 mg; yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 8.02 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 7.21 (t, J = 7.2 Hz, 2H), 7.16 (d, J = 7.0 Hz, 1H), 6.98 (d, J = 7.2 Hz, 2H), 6.28 (d, J = 15.8 Hz, 1H), 5.53 (dt, J = 15.6, 7.0 Hz, 1H), 3.42 (s, 4H), 3.35 (d, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C): δ 191.5, 143.6, 139.3, 134.7, 129.7, 129.2, 128.7, 128.4, 128.4, 126.2, 123.4, 39.4, 38.8, 36.4 ppm. IR (KBr): ν 3025, 2925, 2627, 1703, 1610, 1449, 1279, 1248, 1108, 1010, 965, 911, 870, 738, 700 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{21}H_{18}NaO_3S_2$, $[M + Na]^+$ 405.0595, found 405.0606.

*(E)-4-(2-(1,3-Dithiolan-2-ylidene)-5-phenylpent-3-enoyl)-benzonitrile (**3w**).* Yield: 73%, 0.15 mmol, 53.0 mg; yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 7.63 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.22 (t, J = 7.9 Hz, 3H), 6.96 (d, J = 6.6 Hz, 2H), 6.26 (d, J = 15.8 Hz, 1H), 5.46 (dt, J = 15.5, 7.1 Hz, 1H), 3.43 (s, 4H), 3.34 (d, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C): δ 190.1, 143.0, 139.1, 135.4, 131.7, 129.7, 128.5, 128.4, 128.3, 126.3, 122.8, 118.3, 114.1, 77.4, 77.1, 76.8, 39.5, 38.9, 36.5 ppm. IR (KBr): ν 3024, 2924, 2852, 2228, 1612, 1451, 1312, 1279, 1251, 1175, 1010, 853, 749, 700 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{21}H_{18}NOS_2$, $[M + H]^+$ 364.0830, found 364.0829.

*(E)-2-(1,3-Dithiolan-2-ylidene)-1-phenylhex-3-en-1-one (**3x**).* Yield: 90%, 0.18 mmol, 49.7 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.74 (d, J = 7.5 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 6.25 (d, J = 15.8 Hz, 1H), 5.43 (dt, J = 15.7, 6.7 Hz, 1H), 3.41−3.36 (m, 4H), 2.09−2.01 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.4, 138.4, 136.8, 131.7, 129.7, 127.9, 127.1, 124.8, 38.5, 36.6, 26.3, 13.3 ppm. IR (KBr): ν 2962, 2927, 2871, 1662, 1616, 1454, 1277, 1173, 962, 804, 720, 692, 633 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{15}H_{16}NaOS_2$, $[M + Na]^+$ 299.0540, found 299.0551.

*(E)-2-(1,3-Dithiolan-2-ylidene)-1-phenylhept-3-en-1-one (**3y**).* Yield: 89%, 0.18 mmol, 51.6 mg; yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$,TMS, 25 °C): δ 7.73 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 6.25 (d, J = 15.8 Hz, 1H), 5.39 (dt, J = 15.6, 7.0 Hz, 1H), 3.37 (s, 4H), 2.07−1.95 (m, 2H), 1.29 (dd, J = 14.6, 7.3 Hz, 2H), 0.88 (t, J = 7.2 Hz, 1H), 0.80 (t, J = 7.4 Hz, 3H), 0.69 (td, J = 7.3, 2.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C): δ 193.4, 138.4, 135.3, 131.7, 129.6, 128.2, 128.0, 38.5, 36.6, 35.3, 22.2, 13.6 ppm. IR (KBr): ν 2958, 2926, 2867, 1659, 1615, 1455, 1314, 1278, 1248, 1175, 964, 693, 633 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{16}H_{18}NaOS_2$, $[M + Na]^+$ 313.0697, found 313.0703.

*(E)-2-(Bis(methylthio)methylene)-1,5-diphenylpent-3-en-1-one (**3z**).* Yield: 78%, 0.16 mmol, 53.0 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.90 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.24−7.18 (m, 4H), 6.93 (d, J = 16.0 Hz, 1H), 5.67 (dt, J = 15.9, 7.0 Hz, 1H), 3.43 (d, J = 7.0 Hz, 2H), 2.37 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 196.2, 154.8, 145.4, 139.2, 136.7, 135.2, 133.4, 129.4, 128.7, 128.6, 128.4, 127.9, 126.2, 39.6, 17.3, 16.5 ppm. IR (KBr): ν 3026, 2923, 2855, 1726, 1670, 1598, 1494, 1450, 1283, 1171, 1073, 964, 698 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}NaOS_2$, $[M + Na]^+$ 363.0853, found 363.0837.

*3-Cyclohexylidene-2-(1,3-dithiolan-2-ylidene)-1-phenylpropan-1-one (**3aa**).* Yield: 81%, 0.16 mmol, 51.2 mg; yellowish solid, mp 122−124 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.68 (d, J = 7.3 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 5.96 (s, 1H), 3.43 (t, J = 6.4 Hz, 2H), 3.35 (t, J = 6.4 Hz, 2H), 2.13−2.06 (m, 2H), 1.80−1.74 (m, 2H), 1.42 (dt, J = 11.9, 5.8 Hz, 2H), 1.35 (dt, J = 11.4, 5.7 Hz, 2H), 1.01 (dt, J = 11.9, 6.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 191.2, 163.8, 144.9, 139.3, 130.8, 129.3, 127.4, 122.4, 120.3, 39.1, 36.4, 35.9, 30.6, 27.7, 26.2, 26.2 ppm. IR (KBr): ν 2927, 2852, 1614, 1574, 1452, 1278, 1014, 839, 727, 634 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{18}H_{20}NaOS_2$, $[M + Na]^+$ 339.0853, found 339.0854.

*3-(Cyclohex-3-en-1-ylidene)-2-(1,3-dithiolan-2-ylidene)-1-phenylpropan-1-one (E/Z = 3/2) (**3ab**).* Yield: 85%, 0.17 mmol, 53.4 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.67 (dd, J = 15.6, 7.5 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.31 (q, J = 7.4 Hz, 2H), 6.08 (d, J = 54.4 Hz, 1H), 5.58 (d, J = 9.6 Hz, 0.5H), 5.55 (s, 1H), 5.40 (d, J = 9.7 Hz, 0.5H), 3.44 (t, J = 6.3 Hz, 2H), 3.38−3.32 (m, 2H), 2.73 (s, 1H), 2.41 (s, 1H), 2.25 (t, J = 6.3 Hz, 1H), 2.10 (s, 1H), 1.93 (t, J = 6.4 Hz, 1H), 1.69 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 191.1, 191.0, 164.3, 164.2, 141.6, 141.1, 139.5, 139.2, 130.9, 130.8, 129.1, 128.9, 127.5, 127.5, 126.7, 126.7, 125.5, 125.2, 122.1, 122.0, 121.6, 121.1, 39.1, 39.1, 36.0, 35.9, 34.2, 32.4, 30.0, 27.2, 27.0, 25.6 ppm. IR (KBr): ν 3024, 2924, 2847, 1721, 1613, 1454, 1277, 1176, 1011, 843, 726, 634 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{18}H_{18}NaOS_2$, $[M + Na]^+$ 337.0697, found 337.0698.

*(E)-Methyl 4-(1,3-Dithiolan-2-ylidene)-5-oxo-5-phenylpent-2-enoate (**3ac**).* Yield: 48%, 0.10 mmol, 29.4 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.74 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 15.8 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 5.57 (d, J = 15.8 Hz, 1H), 3.69 (s, 3H), 3.52 (t, J = 6.2 Hz, 2H), 3.47−3.44 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.6, 167.5, 140.8, 137.2, 132.9, 129.5, 128.5, 122.8, 117.8, 51.6, 38.6, 37.4 ppm. IR (KBr): ν 2953, 2927, 2854, 1710, 1663, 1601, 1434, 1281, 1168, 975, 705, 642 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{15}H_{14}NaO_3S_2$, $[M + Na]^+$ 329.0282, found 329.0265.

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*(E)-Ethyl 4-(1,3-Dithiolan-2-ylidene)-5-oxo-5-phenylpent-2-enoate (**3ad**).*[12a] Yield: 46%, 0.09 mmol, 29.4 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.75 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 15.8 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 5.58 (d, J = 15.8 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.54−3.49 (m, 2H), 3.47−3.42 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.7, 167.1, 140.6, 137.2, 132.9, 129.6, 128.5, 122.9, 118.3, 60.4, 38.6, 37.4, 14.3 ppm. IR (KBr): ν 2957, 2927, 2855, 1706, 1662, 1600, 1448, 1368, 1280, 1169, 1037, 974, 704, 642 cm^{-1}.

*(5E)-2-(1,3-Dithiolan-2-ylidene)-7-methyl-1,4-diphenylocta-3,5-dien-1-one (E,E/E,Z = 3/1) (**5a**).* Yield: 45%, 0.09 mmol, 35.3 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.72 (d, J = 7.4 Hz, 2H), 7.39−7.35 (m, 1H), 7.35−7.28 (m, 5H), 7.20 (d, J = 6.9 Hz, 2H), 6.23 (s, 1H), 5.98 (d, J = 15.7 Hz, 1H), 5.27 (dd, J = 15.7, 6.9 Hz, 1H), 3.49−3.44 (m, 2H), 3.43−3.39 (m, 2H), 2.01 (dd, J = 11.5, 6.2 Hz, 1H), 0.83 (d, J = 6.7 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 190.72, 144.01, 142.22, 141.33, 139.26, 130.95, 129.81, 129.07, 128.66, 127.95, 127.43, 127.27, 126.14, 124.83, 122.59, 108.31, 102.30, 96.80, 38.86, 36.40, 31.64, 30.94, 21.95 ppm. IR (KBr): ν 2958, 2925, 2854, 1733, 1619, 1500, 1279, 1225, 1049, 969, 911, 808, 733, 696, 619 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{24}H_{24}NaOS_2$, $[M + Na]^+$ 415.1166, found 415.1169.

*2-(1,3-Dithiolan-2-ylidene)-6-methyl-1,4-diphenylhepta-3,5-dien-1-one (**5b**).* Yield: 40%, 0.08 mmol, 30.2 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.69 (d, J = 7.2 Hz, 2H), 7.36−7.27 (m, 7H), 7.26−7.22 (m, 1H), 6.67 (s, 1H), 5.02 (s, 1H), 3.47−3.39 (m, 4H), 1.66 (s, 3H), 1.16 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 187.5, 160.1, 141.2, 140.1, 140.0, 139.1, 131.1, 128.6, 128.2, 127.4, 127.3, 126.8, 125.9, 125.0, 124.1, 38.3, 36.9, 25.4, 19.4 ppm. IR (KBr): ν 2957, 2924, 2852, 1732, 1633, 1464, 1277, 1016, 912, 799, 695 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{23}H_{22}NaOS_2$, $[M + Na]^+$ 401.1010, found 401.1015.

*(E)-6-Chloro-2-(1,3-dithiolan-2-ylidene)-1-phenylhex-3-en-1-one (**6a**).* Yield: 85%, 0.17 mmol, 49.0 mg; yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 7.73 (d, J = 7.0 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.4 Hz, 2H), 6.38 (d, J = 15.8 Hz, 1H), 5.38 (dt, J = 15.8, 7.1 Hz, 1H), 3.45−3.36 (m, 6H), 2.50 (qd, J = 7.0, 1.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 193.0, 157.3, 138.3, 131.8, 130.9, 129.8, 129.6, 128.0, 124.0, 43.6, 38.6, 36.6, 36.4 ppm. IR (KBr): ν 2956, 2924, 2853, 1735, 1659, 1627, 1452, 1277, 1173, 1009, 960, 804, 691 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{15}H_{16}ClOS_2$, $[M + H]^+$ 311.0331, found 311.0322.

*(5-Benzyl-2-(methylthio)-1-phenyl-1H-pyrrol-3-yl)(phenyl)-methanone (**7a**).* Yield: 77%, 0.31 mmol, 118.7 mg; brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 7.91 (d, J = 7.1 Hz, 2H), 7.57−7.51 (m, 1H), 7.45 (dd, J = 14.7, 7.6 Hz, 5H), 7.21−7.09 (m, 5H), 6.90 (d, J = 6.4 Hz, 2H), 6.34 (s, 1H), 3.73 (s, 2H), 2.17 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 191.6, 139.8, 138.3, 137.4, 135.0, 132.1, 131.7, 130.4, 129.6, 128.9, 128.8, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 126.1, 112.1, 33.7, 20.4 ppm. IR (KBr): ν 2956, 2923, 2853, 1710, 1641, 1597, 1493, 1458, 1242, 1071, 907, 763, 698 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{25}H_{21}NNaOS$, $[M + Na]^+$ 406.1242, found 406.1245.

*(5-Benzyl-2-(methylthio)thiophen-3-yl)(phenyl)methanone (**8a**).* Yield: 95%, 0.38 mmol, 123.1 mg; deep yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.75 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.24 (dd, J = 13.3, 6.6 Hz, 3H), 7.01 (s, 1H), 4.08 (s, 2H), 2.53 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 189.9, 152.3, 140.5, 139.4, 139.4, 134.1, 131.7, 129.3, 129.0, 128.7, 128.5, 128.3, 128.2, 126.9, 36.3, 18.9 cm^{-1}. IR (KBr): ν 2956, 2923, 2852, 1632, 1596, 1492, 1451, 1414, 1259, 1016, 910, 811, 727, 697 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{19}H_{16}NaOS_2$, $[M + Na]^+$ 347.0540, found 347.0546.

*5-(Methylthio)-2-((methylthio)methyl)-1,5-diphenylpenta-2,4-dien-1-one (**9a**).* Yield: 55%, 0.22 mmol, 74.8 mg; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.49 (d, J = 7.9 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.27 (s, 7H), 6.83 (d, J = 11.6 Hz, 1H), 6.51 (d, J = 11.6 Hz, 1H), 3.76 (s, 2H), 2.41 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS, 25 °C): δ 197.4, 153.2, 140.5, 138.4, 136.6, 132.9, 131.1, 129.2, 129.1, 129.0, 128.3, 127.8, 117.0, 28.8, 16.1, 15.9 ppm. IR (KBr): ν 2956, 2923, 2852, 1734, 1636, 1589, 1443, 1263, 1092, 913, 697, 639 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}NaOS_2$, $[M + Na]^+$ 363.0853, found 363.0852.

*4-Benzyl-2-(1,3-dithiolan-2-ylidene)naphthalen-1(2H)-one (**10a**).* Yield: 82%, 0.33 mmol, 110.2 g; yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C): δ 7.61 (d, J = 7.1 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.7 Hz, 2H), 7.23 (dd, J = 4.9, 2.1 Hz, 2H), 6.99 (dd, J = 7.1, 2.0 Hz, 2H), 6.70 (s, 1H), 3.73 (s, 2H), 3.48−3.44 (m, 2H), 3.42−3.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C): δ 181.6, 139.6, 137.2, 132.2, 130.8, 128.9, 128.6, 128.5, 127.6, 126.9, 121.9, 116.7, 47.4, 39.0, 36.3 ppm. IR (KBr): ν 2957, 2924, 2853, 1730, 1623, 1598, 1490, 1454, 1277, 1013, 910, 729, 697, 639 cm^{-1}. HRMS (TOF, ESI): m/z calcd for $C_{20}H_{17}OS_2$, $[M + H]^+$ 337.0721, found 337.0719.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and a CIF file giving details of the synthesis of starting materials, ^{1}H and ^{13}C NMR spectra of the products, and X-ray crystallographic data for compound **3j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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