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Synthesis of 5-Aryl-3(2*H*)-furanones Using Intramolecular Cyclization of Sulfonium Salts

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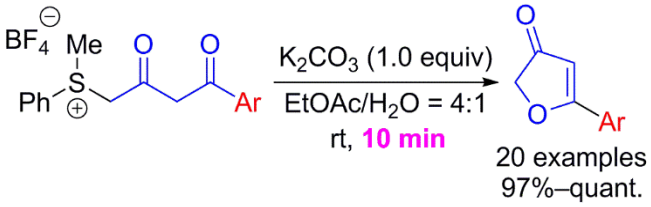


Abstract

Base-induced intramolecular cyclization of novel (4-aryl-2,4-dioxobutyl)methylphenylsulfonium salts prepared from the commercially available 1-arylethanone by a cost-effective process is described in this paper. The reaction was completed within 10 min to produce a family of 2-unsubstituted 5-aryl-3(2*H*)-furanones in excellent yield. This procedure is simple, and can be carried out under mild conditions and an ambient atmosphere.

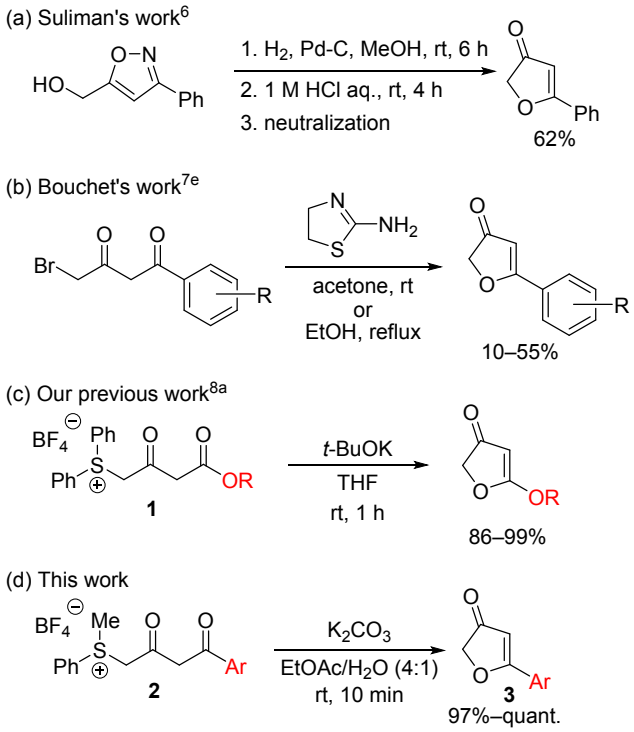
Introduction

The 3(2*H*)-furanone core is a significant subunit present in several natural products and pharmaceuticals.[1] Many techniques have been developed for the synthesis of functionalized 3(2*H*)-furanones.[2] Among 3(2*H*)-furanone derivatives, 5-aryl-3(2*H*)-furanone is an important partial structure present in biologically active compounds such as polmacoxib,[3] hyperolactone C,[4] and bullatenone.[5] In addition, 5-aryl-3(2*H*)-furanones can be used as scaffolds for the synthesis of fluorescent organic dyes.[6] Most of the synthetic methods available for 5-aryl-3(2*H*)-furanones are used to produce 2,2-disubstituted 5-aryl-3(2*H*)-furanones, and there are very few methods for synthesizing 5-aryl-3(2*H*)-furanones that are unsubstituted at the 2-position of the 3(2*H*)-furanone ring. A few synthetic methods of 5-phenyl-3(2*H*)-furanone are reported, for example, the procedure including hydrogenation of isoxazole followed by intramolecular cyclization (Scheme 1a).[6,7a-d] Additionally, to our knowledge, the synthesis of 5-(substituted phenyl)-3(2*H*)-furanones has been only reported by Bouchet and co-workers (Scheme 1b).[7e] Furthermore, these methods have been suffered from some problem to be solved, such as limited substrate scope and unsatisfactory yield of the desired products. Thus, the development of a novel method for the preparation of 5-aryl-3(2*H*)-furanones is an ongoing challenge.

We have previously reported methods for the synthesis of 5-alkoxy-3(2*H*)-furanones via the intramolecular cyclization of sulfonium salts **1** having an ester group at the 3-position (Scheme 1c).[8a] In addition, the reaction between an enolate generated by the treatment of sulfonium salt **1** with a base and various electrophiles furnished various functionalized 3(2*H*)-furanone derivatives.[8a–c] Based on these studies, we expected that using novel sulfonium salts **2** having an aroyl group instead of an ester group at the 3-position, intramolecular cyclization with the elimination of sulfonio group would efficiently proceed to give 5-aryl-3(2*H*)-furanones **3** (Scheme 1d). In this paper, we report an efficient method for the synthesis of 5-aryl-3(2*H*)-furanones via the intramolecular cyclization of sulfonium salts. This reaction is simple to operate and highly productive, and proceeds to completion within 10 min under an ambient

atmosphere.

Scheme 1. Approaches to 5-Aryl-3(2*H*)-furanones

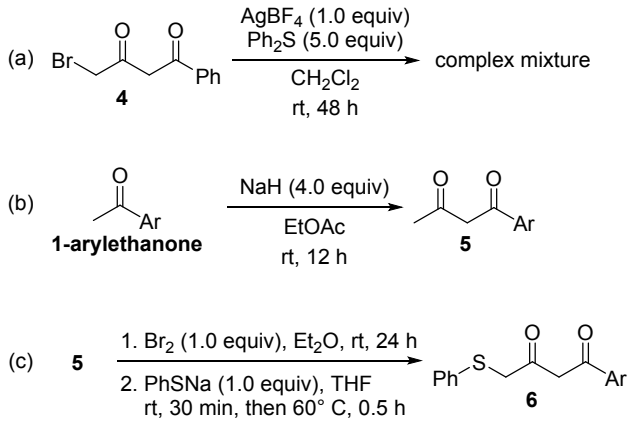


Results & Discussion

In starting our study, methods for accessing these substrates have not been reported to date, although a straightforward preparation of 4-aryl-2,4-dioxobutylsulfonium salt (**2**) was required. A reaction between 4-bromo-1-phenyl-1,3-butadione **4** and diphenylsulfide (Ph_2S) was attempted in the presence of silver (I) tetrafluoroborate ($AgBF_4$) under our previously reported conditions,[8a] but a complex mixture was obtained and it was difficult to isolate the desired sulfonium salt (Scheme 2a). Therefore, we planned a synthetic route to sulfonium salts involving the *S*-methylation of asymmetric sulfide **6** as the key step. 1-Aryl-1,3-butadione **5** was obtained in high yield by Claisen-type condensation between 1-arylethanone and ethyl acetate (EtOAc) in the presence of 4.0 equiv of sodium hydride (NaH) (Scheme 2b).[9] Subsequently, starting sulfides **6** were prepared in good yields by mono-bromination at the 4-position of the

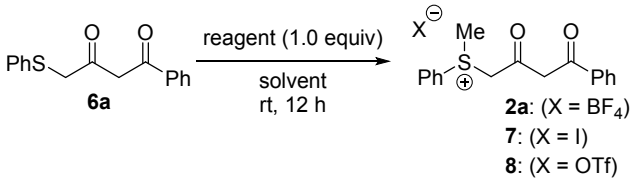
corresponding 1-aryl-1,3-butadiones **5**, followed by nucleophilic substitution using sodium benzenethiolate (PhSNa) (Scheme 2c).[10] However, it was difficult to obtain the target sulfides **6** in some case. 1-Arylethanones, such as 4-nitrophenyl, 4-*t*-butoxycarbonylaminophenyl and 4-trifluoromethanesulfonyloxyphenyl resulted in complex mixture through the Claisen-type reaction (Scheme 2b). Furthermore, 1-aryl-1,3-butadiones, such as 4-methanesulfonylphenyl and nitrogen-containing aromatic rings such as 2-pyrrolyl, 4-pyridinyl and 3-indolyl resulted in complex mixture through bromination/sulfanylation (Scheme 3c).

Scheme 2. Reaction of 4 and Ph_2S and Preparation of Starting Sulfides 6



Next, we examined the *S*-methylation reaction using 1-phenyl-4-(phenylsulfanyl)-1,3-butadione **6a** as the substrate among the resulting sulfides (Table 1). Reaction of sulfide with methyl iodide (MeI) in acetone at room temperature or under reflux did not produce the desired product **7**, and the starting materials were recovered (entries 1 and 2). We then attempted to use more reactive conditions by the addition of 1.0 equiv of $AgBF_4$, but the reaction gave a complex mixture (entries 3 and 4). Fortunately, when more powerful methylating reagents, methyl trifluoromethanesulfonate (MeOTf) and trimethyloxonium tetrafluoroborate (Me_3OBF_4), were used, the reaction proceeded successfully. Among the tested reagents, Me_3OBF_4 afforded the highest yield of 85% (entry 6).

Table 1. Preparation of Sulfonium Salts 2a[a,b]



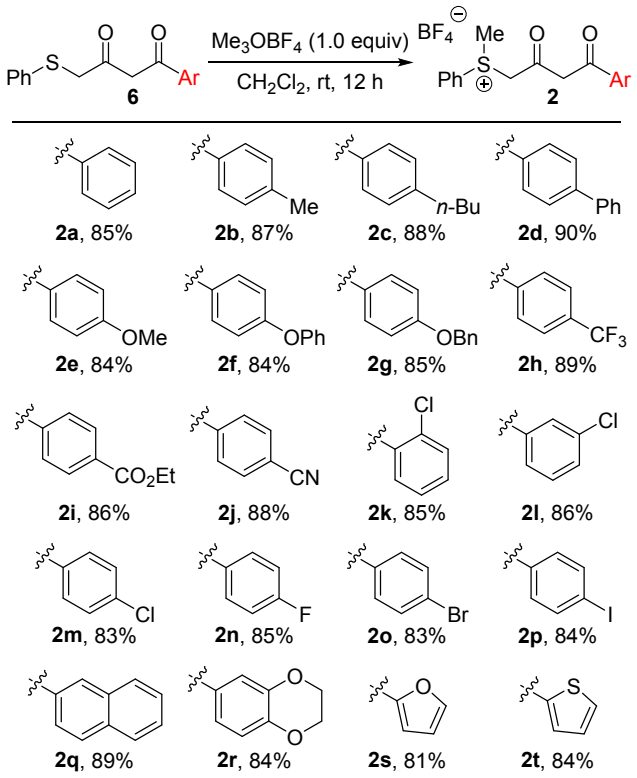
entr	reagent	additi	solve	produ	yield/
1	MeI		aceto	**7**	n.r.[c]
2[d]	MeI		aceto	**7**	n.r.[c]
3	MeI	$AgBF_4$	aceto	**2a**	–[e]
4	MeI	$AgBF_4$	CH_2Cl	**2a**	–[e]
5	MeOTf		CH_2Cl	**8**	75
6	Me_3OBF_4		CH_2Cl	**2a**	85

[a]Reaction conditions: sulfide **6a** (3.0 mmol) and reagent (1.0 equiv), additive (1.0 equiv) in solvent (12 mL). MeI = methyl iodide, MeOTf = methyl trifluoromethanesulfonate, Me_3OBF_4 = trimethyloxonium tetrafluoroborate. [b]The crude product was purified by recrystallization; the isolated yield is based on **6a**. [c]No reaction. [d]The reaction was performed under reflux conditions. [e]Complex mixture.

With the optimized conditions in hand, we attempted to synthesize sulfonium salts bearing a variety of aromatic rings (Table 2). First, we focused on the conversion of sulfides bearing a number of functional groups on phenyl moiety into sulfonium salts. Electron-donating groups (**6b–6g**) as well as electron-withdrawing groups (**6h–6j**) on the phenyl ring were tolerant to the reaction conditions, affording the desired sulfonium salts **(2b–2j)** in high yields. In addition, the reaction proceeded smoothly without being influenced by the substituent pattern (**6k–6m**) and halogen group (**6m–6p**). Sulfonium salts having 2-naphthyl (**2q**), 2,3-dihydro-1,4-benzodioxin-6-yl (**2r**), and heteroaromatic rings such as 2-furyl (**2s**) and 2-thienyl (**2t**) were also obtained in 89%, 84%, 81%, and 84% yield, respectively. It is noteworthy that all the resulting sulfonium salts were in the solid state and hence could be purified by recrystallization from acetonitrile/diethyl ether (**2a–2q**) or methanol/diethyl ether (**2r–2t**). Moreover, the ^{1}H NMR spectrum in acetonitrile-d_3 indicated that the sulfonium salts were present almost entirely in

enol tautomers.

Table 2. Synthesis of Sulfonium Salts 2[a,b]

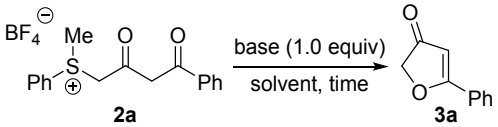


[a]Reaction conditions: sulfide **6** (3.0 mmol), Me_3OBF_4 (1.0 equiv) in CH_2Cl_2 (12 mL). [b]The crude product was purified by recrystallization; the isolated yield is based on **6**.

After establishing a novel procedure for the preparation of sulfonium salts, we focused on intramolecular cyclization using sulfonium salt **2a** as the model substrate (Table 3). Although the reaction was completed within 1 h using 1.0 equiv of potassium *t*-butoxide (*t*-BuOK) under our previously reported conditions,[8a] the cyclized product **3a** was obtained in only 33% yield, and longer reaction time was found to be less effective (entries 1 and 2). The use of other bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), DMAP, trimethylamine (Et_3N), *N,N*-diisopropylethylamine (DIPEA), and potassium bicarbonate (K_2CO_3) also gave the desired products in low yields (entries 3–7). Next, solvent effects on the

intramolecular cyclization were examined. *N,N*-dimethylformamide (DMF), which is a polar aprotic solvent, afforded **3a** in 90% yield (entry 11). Further investigation revealed that polar protic solvents dramatically accelerated the reaction. When methanol was used, the reaction was completed within 10 min, but the yield of **3a** decreased slightly in comparison with that obtained by using DMF (entry 12). Furthermore, the reaction proceeded more efficiently in the presence of water than in the presence of methanol and gave **3a** in 90% yield, similar to the case of DMF (entry 13). Considering these results, we carefully examined solvent systems containing water. After optimization, we found that the reaction in EtOAc/H_2O = 4:1 (v/v), which is a heterogeneous solvent system, furnished **3a** in an excellent yield of 99% (entry 16). Incidentally, the use of sodium hydroxide (NaOH) or potassium hydroxide (KOH) instead of K_2CO_3, or the reaction in homogeneous solvent systems such as THF/H_2O = 4:1 (v/v) resulted in somewhat lower yields (entries 17–19).

Table 3. Optimization of Intramolecular Cyclization[a,b]



2a **3a**

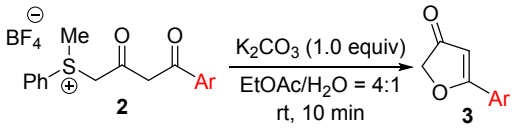
entry	base	solvent	time	yield/
1	*t*-BuOK	THF	1 h	33
2	*t*-BuOK	THF	12 h	32
3	DBU	THF	1 h	25
4	DMAP	THF	1 h	39
5	Et_3N	THF	1 h	40
6	DIPEA	THF	1 h	38
7	K_2CO_3	THF	1 h	40
8	K_2CO_3	CH_2Cl_2	1 h	16
9	K_2CO_3	$CHCl_3$	1 h	4
10	K_2CO_3	MeCN	1 h	20
11	K_2CO_3	DMF	1 h	90
12	K_2CO_3	MeOH	10 min	82

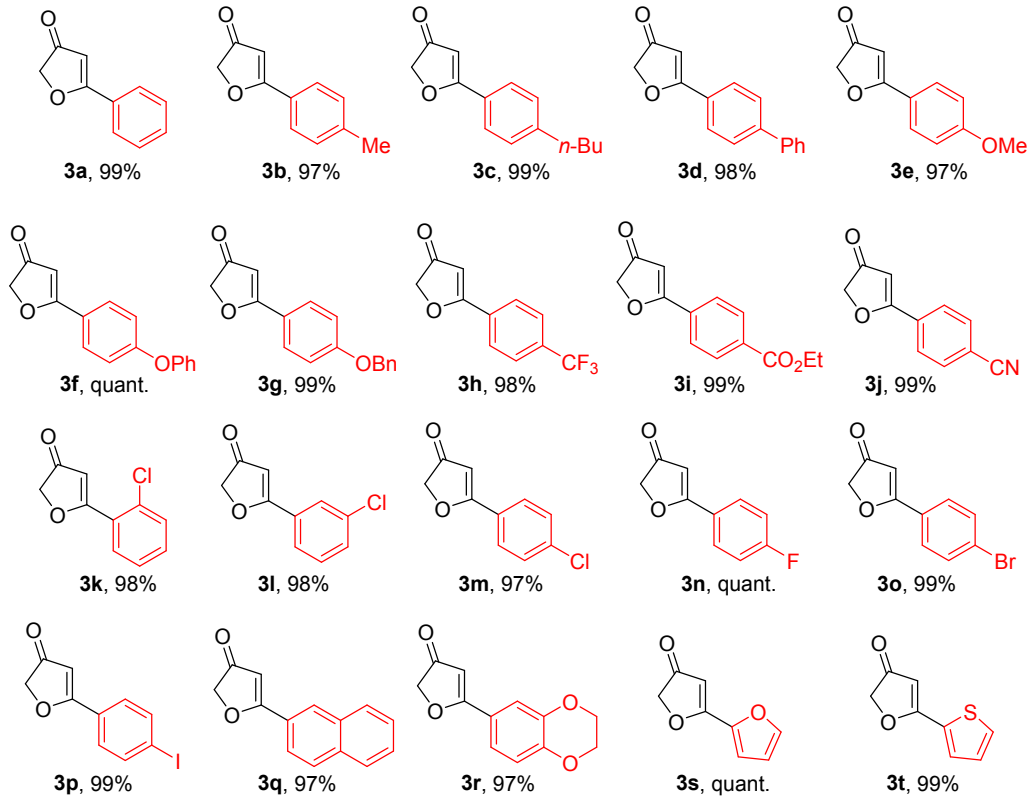
13	K_2CO_3	H_2O	10 min	90
14	K_2CO_3	EtOAc/ H_2O (1:4)	10 min	90
15	K_2CO_3	EtOAc/ H_2O (1:1)	10 min	92
16	K_2CO_3	EtOAc/H_2O (4:1)	10 min	99
17	NaOH	EtOAc/H_2O (4:1)	10 min	92
18	KOH	EtOAc/H_2O (4:1)	10 min	94
19	K_2CO_3	THF/H_2O (4:1)	10 min	95

[a]Reaction conditions: sulfonium salt **2a** (0.2 mmol) and base (1.0 equiv) in solvent (2 mL). DBU = 1.8-diazabicyclo[5.4.0]undec-7-ene, DMAP = 4-(dimethylamino)pyridine, DIPEA = *N,N*-diisopropylethylamine, THF = tetrahydrofuran, MeCN = acetonitrile, DMF = *N,N*-dimethylformamide. [b]The residue was purified by silica gel column chromatography; the isolated yield is based on **2a**.

Next, we investigated the scope of the intramolecular cyclization (Table 4). Sulfonium salts bearing electron-donating groups and electron-withdrawing groups on the phenyl ring successfully underwent intramolecular cyclization to give the corresponding 5-aryl-3(2*H*)-furanones (**3b–3j**) in excellent yields. Moreover, the reaction was successful for various types of halogen-substituted phenyl rings (Table 4, **3k–3p**). Furthermore, 3(2*H*)-furanone derivatives having 2-napthyl (**3q**), 2,3-dihydro-1,4-benzodioxin-6-yl (**3r**), 2-furyl (**3s**), and 2-thienyl (**3t**) were obtained in excellent yields. Notably, all the reactions were completed within 10 min under an ambient atmosphere, resulting in an almost quantitative yield of the products.

Table 4. Intramolecular Cyclization of Sulfonium Salts 2[a,b]





[a]Reaction conditions: sulfonium salt **2** (0.2 mmol) and 0.5 M K_2CO_3 aq. (0.4 mL, 1.0 equiv) in EtOAc (1.6 mL). [b]The residue was purified by silica gel column chromatography; the isolated yield is based on **2**.

Further investigations were conducted to elucidate the reaction mechanism; the results are shown in Table 3. Thus, we believe that the reactivity of intramolecular cyclization depends on the nature of the solvent rather than the nature of the base. In order to investigate the effects of solvents on the reaction, ^{1}H NMR spectra of sulfonium salt **2a** in CD_3CN and CD_3CN containing 20% water were measured (Figure 1). The ^{1}H NMR spectrum of **2a** recorded in CD_3CN showed the characteristic four peaks for the enol tautomer at δ6.47 (C3-H), 4.86 (J = 15.8 Hz, C3-H), 4.76 (J = 15.8 Hz, C3-H), and 3.27 (-CH_3) ppm in a 1:1:1:3 ratio, indicating that most of **2a** existed as the enol tautomer in the polar aprotic solvent CD_3CN

(Figure 1a). On the other hand, in the spectrum of **2a** recorded in CD_3CN containing 20% water, three new signals derived from the keto tautomer were observed at δ5.07, 4.38, and 3.20 ppm in addition to the signals of the enol tautomer (Figure 1b). These results indicated that the keto tautomer was more stabilized in CD_3CN containing water, which is a protic polar solvent having a high dielectric constant, than in CD_3CN.[10] In addition, the spectrum in the aqueous solvent revealed that the keto and enol tautomers of **2a** existed in 1:3 ratio nearly. In order to obtain further mechanistic information, in the presence of a half equivalent of K_2CO_3, ^1H NMR of **2a** in CD_3CN was measured. The spectrum after 10 min treatment showed small peaks of keto tautomer in addition to the peaks of enol tautomer, but cyclized product was not observed (Figure S1). On the other hand, in the spectrum after 1 h, the ratio of keto tautomer increased and cyclized product **3a** was detected slightly (Figure S2). However, in the spectrum after longer time, the ratio among enol tautomer, keto tautomer and **3a** was observed not to be almost changed (Figure S3–S5). In contrast, in the presence of a half equivalent of K_2CO_3 in CD_3CN containing 20% water, the spectrum after 10 min revealed that the added base was consumed for intramolecular cyclization and the ratio of enol tautomer, keto tautomer, and **3a** was 4:1:9 (Figure S6). From the above results, it is suggested that the generation of keto tautomer of **2** is essential for the intramolecular cyclization and the water dramatically promotes both the generation of keto tautomer of **2** and the intramolecular cyclization. Besides, the role of the base in cyclization is presumed to be also important, but in generation of keto tautomer is supposed to be rather weak.

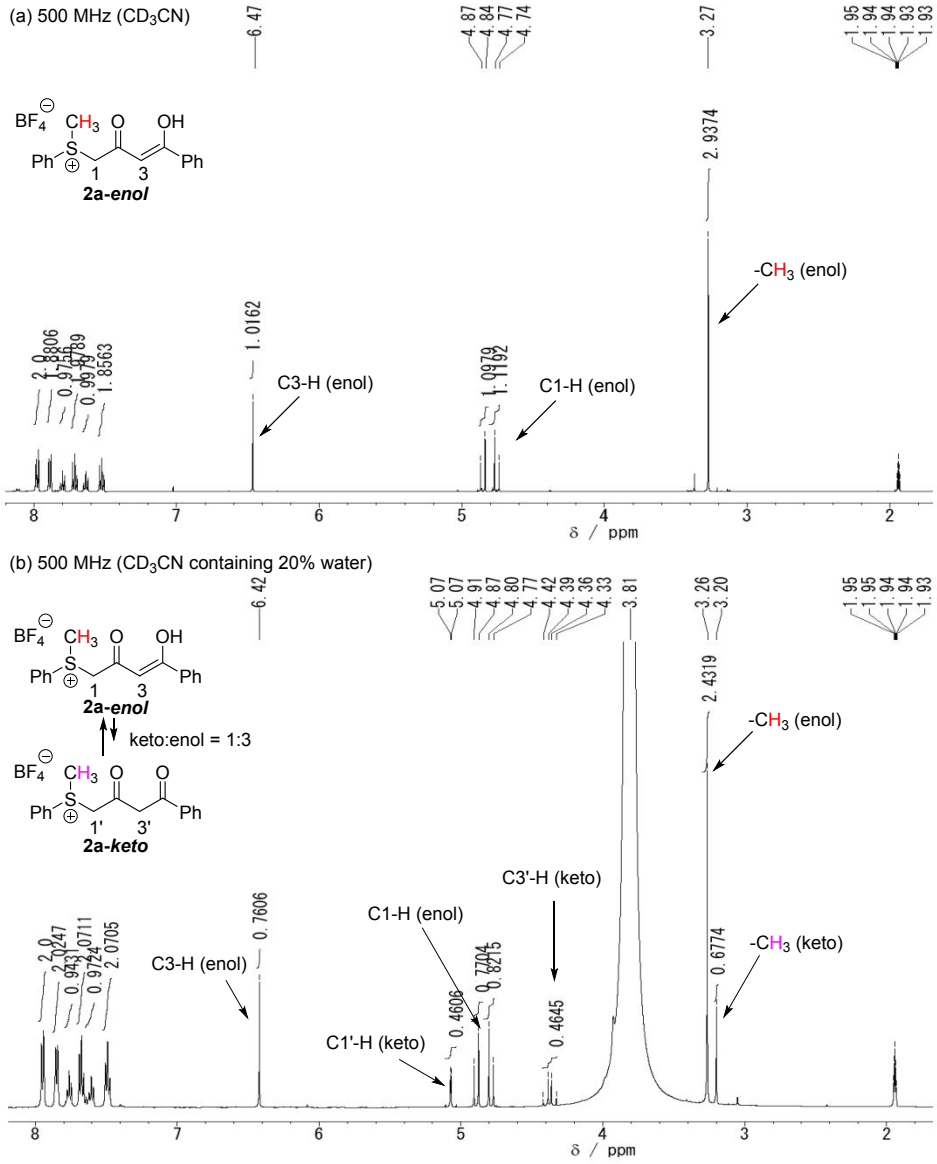
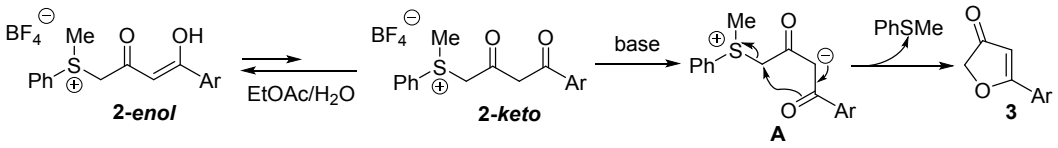


Figure 1. ^{1}H NMR spectra of sulfonium salt **2a** (a) in CD_3CN and (b) in CD_3CN containing 20% water.

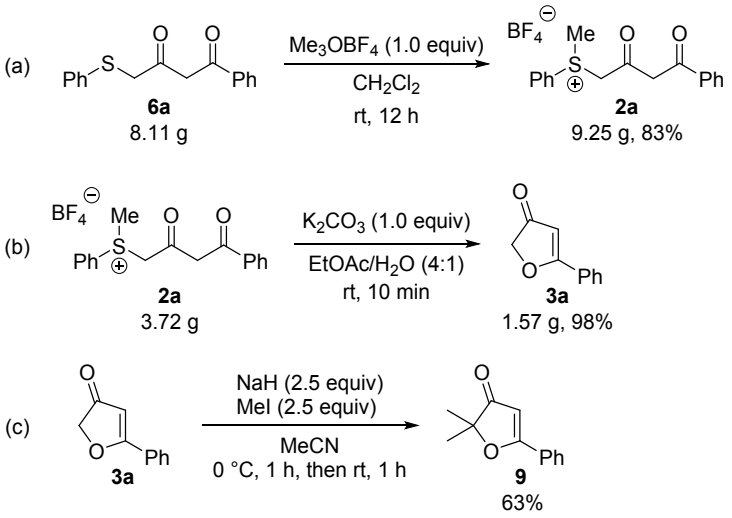
Based on the above results, a plausible mechanism is described in Scheme 3.[8a] Initially, generation of the keto tautomer of **2** was promoted by the presence of water. The resulting **2-*keto*** was treated with a base to give enolate anion **A**. Finally, intramolecular nucleophilic attack of the oxygen anion onto the C1 carbon atom of **A** led to the formation of 5-aryl-3(2*H*)-furanone **3** and methylphenylsulfide.

Scheme 3. Proposed Mechanism



To substantiate the potential utility of our method, we performed the reaction on gram scale. The treatment of sulfide **6a** (8.11 g, 30 mmol) with 1.0 equiv of Me_3OBF_4 furnished 9.25 g of **2a** in 83% yield (Scheme 4a). Subsequently, intramolecular cyclization of **2a** on a 20 mmol scale proceeded smoothly to give the cyclized product 5-phenyl-3(2*H*)-furanone **3a** in 98% yield (Scheme 4b). Further, **3a** could be converted into various useful compounds. For instance, 2,2-dimethylation of **3a** using 2.5 equiv of MeI and 2.5 equiv of NaH in MeCN led to the formation of 2,2,-dimethyl-5-phenyl-3(2*H*)-furanone **9**, bullatenone, in 63% yield (Scheme 4c).

Scheme 4. Gram-Scale Synthesis and Conversion of 3a into Bullatenone 9



Conclusion

In summary, we have developed an efficient protocol for the synthesis of 5-aryl-3(2*H*)-furanones via the intramolecular cyclization of 4-aryl-2,4-dioxobutylsulfonium salts. In this reaction, the sulfonio group

effectively worked as a leaving group, which gave the corresponding 5-aryl-3(2*H*)-furanone in excellent yields. The examination on reaction mechanism showed that water as a protic solvent dramatically promoted the conversion of enol tautomer of sulfonium salt into keto tautomer followed by intramolecular cyclization. Furthermore, our procedure did not require anhydrous conditions and was completed within 10 min. Moreover, 20 novel sulfonium salts could be easily prepared with good yields from the readily accessible 1-arylethanones and ethyl acetate through the series reactions, Claisen-type reaction, bromination, sulfanylation, and *S*-methylation. Our method is practically applicable for the synthesis of various related heterocyclic compounds.

Experimental Section

The reagents and solvents were used as received from commercial suppliers without further purification, unless otherwise indicated. Silica gel (40–50 mesh) was used for flash column chromatography. Components separated by thin-layer chromatography (TLC) were detected under UV light at 254 nm or by staining with ethanoic *p*-anisaldehyde. IR spectra were recorded on an FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra recorded in $CDCl_3$ were referenced to TMS (0.00 ppm) and the solvent peak (77.0 ppm). ^{1}H and ^{13}C NMR spectra recorded in CD_3CN were referenced to the solvent peaks (1.94 ppm and 1.32 ppm, respectively). High-resolution mass spectra (HRMS) were obtained using ESI-TOF, ESI-Orbitrap and APCI Orbitrap mass spectrometers.

General Procedure for Synthesis of 1-Aryl-1,3-butadione (5).[9a] To a suspension of NaH (1.60 g of dispersion in oil, 40 mmol) in EtOAc (20 mL) was added a solution of 1-arylethanone (10 mmol) in EtOAc (20 mL) slowly at 0 °C, and then, the mixture was stirred at room temperature for 12 h. The mixture was carefully treated with 10% aqueous NH_4Cl (30 mL) and adjusted to pH 5 with hydrochloric acid. The aqueous phase was separated and extracted with EtOAc. The combined organic extracts were dried over

anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (*n*-hexane/EtOAc = 7:1) gave the desired 1-aryl-1,3-butadione **5** (keto–enol mixture).

*1-Phenyl-1,3-butadione (**5a**).*[11] 1.48 g, 91% yield; pale yellow solid; mp 47.5–48.2 °C; R_f = 0.60 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1600, 1570, 1484, 766, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.90–7.87 (m, 2 H), 7.55–7.51 (m, 1 H), 7.47–7.44 (m, 2 H), 6.19 (s, 1 H), 2.21 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 193.8, 183.3, 134.8, 132.3, 128.6 (2C), 127.0 (2C), 96.7, 25.8; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{10}H_9O_2$, 161.0608; found, 161.0614.

*1-(4-Methylphenyl)-1,3-butadione (**5b**).*[11] 1.61 g, 91% yield; pale yellow oil; R_f = 0.66 (*n*-hexane/EtOAc = 2:1); IR (neat): 1611, 1504, 777 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.77 (d, J = 8.3 Hz, 2 H), 7.24 (d, J = 8.3 Hz, 2 H), 6.15 (s, 1 H), 2.40 (s, 3 H), 2.18 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 193.0, 183.7, 143.0, 132.1, 129.3 (2C), 127.0 (2C), 96.2, 25.6, 21.5; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{11}H_{11}O_2$, 175.0765; found, 175.0763.

*1-(4-n-Butylphenyl)-1,3-butadione (**5c**).* 2.03 g, 93% yield; yellow solid; mp 30.8–31.2 °C; R_f = 0.66 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1609, 1502, 848, 780 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.80–7.79 (m, 2 H), 7.26–7.24 (m, 2 H), 6.15 (s, 1 H), 2.66 (t, J = 7.7 Hz, 2 H), 2.19 (s, 3 H), 1.64–1.58 (m, 2 H), 1.40–1.32 (m, 2 H), 0.93 (t, J = 7.3 Hz, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 193.1, 183.7, 148.0, 132.4, 128.7 (2C), 127.1 (2C), 96.3, 35.6, 33.3, 25.7, 22.3, 13.9; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{14}H_{17}O_2$, 217.1234; found, 217.1228.

*1-(4-Biphenyl)-1,3-butadione (**5d**).*[12] 2.27 g, 95% yield; pale yellow solid; mp 159.8–160.1 °C; R_f = 0.64 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1604, 1576, 1483, 849, 766, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.95 (d, J = 8.6 Hz, 2 H), 7.68 (d, J = 8.6 Hz, 2 H), 7.64–7.62 (m, 2 H), 7.48–7.45 (m, 2 H), 7.41–7.38 (m, 1 H), 6.22 (s, 1 H), 2.22 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 193.7, 182.9, 145.0, 139.9, 133.6, 128.9 (2C), 128.1, 127.5 (2C), 127.24 (2C), 127.18 (2C), 96.7 (2C),

25.9; HRMS (ESI-TOF): *m*/*z* [M − H]$^-$ calcd for $C_{16}H_{13}O_2$, 237.0921; found, 237.0920.

*1-(4-Methoxyphenyl)-1,3-butadione (**5e**).*[11] 1.80 g, 94% yield; white solid; mp 54.5–55.2 °C; R_f = 0.52 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1606, 1503, 1259, 1180, 1025, 841, 780 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.86 (d, *J* = 8.9 Hz, 2 H), 6.94 (d, *J* = 8.9 Hz, 2 H), 6.12 (s, 1 H), 3.87 (s, 3 H), 2.17 (s, 3 H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (enol form): δ 191.6, 184.1, 163.1, 129.1 (2C), 127.5 (2C), 113.9, 95.8, 55.4, 25.3; HRMS (ESI-TOF): *m*/*z* [M − H]$^-$ calcd for $C_{11}H_{11}O_3$, 191.0714; found, 191.0714.

*1-(4-Phenoxyphenyl)-1,3-butadione (**5f**).* 2.34 g, 92% yield; white solid; mp 84.4–84.6 °C; R_f = 0.62 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1604, 1587, 1486, 1258, 853, 777, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.86 (d, *J* = 8.9 Hz, 2 H), 7.41–7.37 (m, 2 H), 7.21–7.18 (m, 1 H), 7.08–7.06 (m, 2 H), 7.01 (d, *J* = 8.9 Hz, 2 H), 6.12 (s, 1 H), 2.18 (s, 3 H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (enol form): δ 192.3, 183.5, 161.4, 155.7, 130.0 (2C), 129.4, 129.1 (2C), 124.5, 120.0 (2C), 117.6 (2C), 96.1, 25.5; HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}O_3$, 255.1016; found, 255.1013.

*1-(4-Benzyloxyphenyl)-1,3-butadione (**5g**).*[11] 2.50 g, 93% yield; white solid; mp 115.1–115.5 °C; R_f = 0.56 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1604, 1503, 1256, 1174, 1008, 836, 783, 747, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.86 (d, *J* = 9.0 Hz, 2 H), 7.44–7.38 (m, 4 H), 7.36–7.33 (m, 1 H), 7.01 (d, *J* = 9.0 Hz, 2 H), 6.11 (s, 1 H), 5.12 (s, 2 H), 2.16 (s, 3 H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (enol form): δ 191.7, 184.0, 162.2, 136.2, 129.1 (2C), 128.7 (2C), 128.2, 127.7, 127.5 (2C), 114.7 (2C), 95.8, 70.1, 25.3; HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}O_3$, 269.1172; found, 269.1174.

*1-(4-Trifluoromethylphenyl)-1,3-butadione (**5h**).*[13] 2.10 g, 91% yield; pale yellow solid; mp 45.0–45.4 °C; R_f = 0.58 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1613, 1572, 1328, 1130, 860, 787 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.98 (d, *J* = 8.3 Hz, 2 H), 7.71 (d, *J* = 8.3 Hz, 2 H), 6.20 (s, 1 H), 2.24 (s, 3 H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (enol form): δ 195.2, 180.9, 138.09–138.06 (m), 133.6 (q, *J* = 32.7 Hz), 127.3 (2C), 125.6 (q, *J* = 3.8 Hz, 2C), 123.7 (q, *J* = 272.5 Hz), 97.4, 26.2; HRMS (ESI-Orbitrap): *m*/*z* [M − H]$^-$ calcd for $C_{11}H_8F_3O_2$, 229.0482; found, 229.0482.

*Ethyl 4-(1,3-Dioxobutyl)benzoate (**5i**)*. 2.23 g, 95% yield; pale yellow solid; mp 81.3–81.8 °C; R_f = 0.54 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1714, 1604, 1281, 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 8.11 (d, J = 8.7 Hz, 2 H), 7.92 (d, J = 8.7 Hz, 2 H), 6.21 (s, 1 H), 4.41 (q, J = 7.2 Hz, 2 H), 2.24 (s, 3 H), 1.42 (t, J = 7.2 Hz, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 195.3, 181.1, 165.8, 138.5, 133.5, 129.7 (2C), 126.8 (2C), 97.5, 61.4, 26.3, 14.3; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{13}H_{13}O_4$, 233.0819; found, 233.0817.

*1-(4-Cyanophenyl)-1,3-butadione (**5j**)*.[12] 1.76 g, 94% yield; white solid; mp 93.5–94.1 °C; R_f = 0.46 (*n*-hexane/EtOAc = 2:1); IR (KBr): 2226, 1588, 848, 782 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.96 (d, J = 8.7 Hz, 2 H), 7.74 (d, J = 8.7 Hz, 2 H), 6.20 (s, 1 H), 2.21 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 195.8, 179.8, 138.7, 132.4 (2C), 127.4 (2C), 118.1, 115.4, 97.6, 26.3; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{11}H_8NO_2$, 186.0561; found, 186.0554.

*1-(2-Chlorophenyl)-1,3-butadione (**5k**)*.[12] 1.93 g, 98% yield; yellow oil; R_f = 0.60 (*n*-hexane/EtOAc = 2:1); IR (neat): 1605, 1557, 1540, 767 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.57 (dd, J = 7.6, 1.8 Hz, 1 H), 7.43 (dd, J = 7.9, 1.2 Hz, 1 H), 7.38–7.31 (m, 2 H), 6.04 (s, 1 H), 2.18 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 192.7, 184.6, 135.5, 131.6, 131.5, 130.6, 129.9, 126.8, 101.8, 25.4; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{10}H_8{}^{35}ClO_2$, 195.0218; found, 195.0218.

*1-(3-Chlorophenyl)-1,3-butadione (**5l**)*. 1.96 g, quant.; pale yellow solid; mp 42.2–43.1 °C; R_f = 0.62 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1610, 1565, 784, 678 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.86–7.85 (m, 1 H), 7.76–7.74 (m, 1 H), 7.49 (ddd, J = 7.9, 2.1, 1.1 Hz, 1 H), 7.41–7.38 (m, 1 H), 6.15 (s, 1 H), 2.22 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 194.1, 181.8, 136.7, 134.8, 132.1, 129.9, 127.1, 125.0, 96.9, 25.9; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{10}H_8{}^{35}ClO_2$, 195.0218; found, 195.0217.

*1-(4-Chlorophenyl)-1,3-butadione (**5m**)*.[11] 1.96 g, quant.; pale yellow solid; mp 71.2–71.9 °C; R_f = 0.64 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1612, 1594, 1484, 840, 779 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol

form): δ 7.82 (d, J = 8.7 Hz, 2 H), 7.42 (d, J = 8.7 Hz, 2 H), 6.14 (s, 1 H), 2.21 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 193.7, 182.3, 138.5, 133.3, 128.9 (2C), 128.3 (2C), 96.6, 25.8; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{10}H_8{}^{35}ClO_2$, 195.0218; found, 195.0218.

*1-(4-Fluorophenyl)-1,3-butadione (**5n**).*[11] 1.78 g, 99% yield; pale yellow solid; mp 37.0–37.8 °C; R_f = 0.62 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1604, 1505, 849, 785 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.91–7.89 (m, 2 H), 7.15–7.11 (m, 2 H), 6.13 (s, 1 H), 2.20 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 192.9, 182.9, 165.3 (d, J = 253.4 Hz), 131.2 (d, J = 3.0 Hz), 129.4 (d, J = 9.0 Hz) (2C), 115.7 (d, J = 21.9 Hz) (2C), 96.3, 25.5; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{10}H_8FO_2$, 179.0514; found, 179.0510.

*1-(4-Bromophenyl)-1,3-butadione (**5o**).*[14] 2.30 g, 95% yield; pale yellow solid; mp 84.4–84.9 °C; R_f = 0.64 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1613, 1587, 1479, 842, 782 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.75 (d, J = 8.7 Hz, 2 H), 7.59 (d, J = 8.7 Hz, 2 H), 6.15 (s, 1 H), 2.21 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 193.9, 182.3, 133.8, 131.9 (2C), 128.5 (2C), 127.1, 96.6, 25.8; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{10}H_8{}^{79}BrO_2$, 238.9713; found, 238.9711.

*1-(4-Iodophenyl)-1,3-butadione (**5p**).*[15] 2.77 g, 96% yield; pale yellow solid; mp 119.5–120.0 °C (sealed tube); R_f = 0.64 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1612, 1584, 1480, 837, 784 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.81–7.79 (m, 2 H), 7.60–7.58 (m, 2 H), 6.14 (s, 1 H), 2.20 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 194.0, 182.3, 137.9 (2C), 134.3, 128.4 (2C), 99.6, 96.6, 25.9; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{10}H_8IO_2$, 286.9575; found, 286.9573.

*1-(2-Naphthyl)-1,3-butadione (**5q**).*[11] 2.04 g, 96% yield; pale yellow solid; mp 78.0–78.5 °C; R_f = 0.60 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1604, 1588, 1564, 870, 830, 788 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 8.44 (s, 1 H), 7.96–7.86 (m, 4 H), 7.59–7.53 (m, 2 H), 6.33 (s, 1 H), 2.25 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 193.8, 183.1, 135.2, 132.7, 132.1, 129.3, 128.4, 128.2, 128.0, 127.7, 126.7, 123.1, 97.0, 25.9; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{14}H_{11}O_2$, 211.0765; found,

211.0766.

*1-(2,3-Dihydro-1,4-benzodioxin-6-yl)-1,3-butadione (**5r**).*[11] 2.08 g, 94% yield; pale yellow solid; mp 89.6–89.8 °C; R_f = 0.56 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1611, 1544, 1493, 1284, 862, 770 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.44 (d, J = 2.1 Hz, 1 H), 7.41 (dd, J = 8.4, 2.1 Hz, 1 H), 6.90 (d, J = 8.4 Hz, 1 H), 6.08 (s, 1 H), 4.33–4.31 (m, 2 H), 4.29–4.27 (m, 2 H), 2.16 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 191.7, 183.8, 147.4, 143.4, 128.5, 120.9, 117.3, 116.5, 95.9, 64.6, 64.1, 25.3; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{12}H_{11}O_4$, 219.0663; found, 219.0661.

*1-(2-Furyl)-1,3-butadione (**5s**).*[16] 1.41 g, 93% yield; orange oil; R_f = 0.56 (*n*-hexane/EtOAc = 2:1); IR (neat): 1614, 1469, 760 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.57 (dd, J = 1.6, 0.8 Hz, 1 H), 7.15 (dd, J = 3.5, 0.8 Hz, 1 H), 6.55 (dd, J = 3.5, 1.6 Hz, 1 H), 6.55 (s, 1 H), 2.15 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 189.5, 176.2, 150.5, 145.9, 115.5, 112.4, 96.1, 25.4; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_8H_7O_3$, 151.0401; found, 151.0404.

*1-(2-Thienyl)-1,3-butadione (**5t**).*[11] 1.58 g, 94% yield; pale orange solid; mp 35.5–36.0 °C; R_f = 0.54 (*n*-hexane/EtOAc = 2:1); IR (KBr): 1613, 1519, 1410, 778, 722 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.69 (dd, J = 3.8, 1.1 Hz, 1 H), 7.60 (dd, J = 4.9, 1.1 Hz, 1 H), 7.13 (dd, J = 4.9, 3.8 Hz, 1 H), 6.03 (s, 1 H), 2.14 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 187.2, 181.8, 141.7, 132.3, 130.1, 128.2, 96.4, 23.8; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_8H_7O_2S$, 167.0172; found, 167.0169.

General Procedure for Synthesis of Sulfide (6).[9b] Bromine (0.26 mL, 5.1 mmol) was added dropwise to a solution of 1-aryl-1,3-butadione **5** (5.0 mmol) in dry diethyl ether (8 mL) at 0 °C under an argon atmosphere. The mixture was stirred at 0 °C for 2 h and at room temperature for further 24 h. The mixture was treated with ice water and extracted with diethyl ether. The combined organic extracts were washed with a saturated aqueous solution of $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give crude 1-aryl-4-bromo-1,3-butadione. Benzenethiol (0.51 mL, 5.0 mmol) was added slowly to a suspension of NaH (0.20 g of a dispersion in oil, 5.0 mmol) in dry

THF (5.0 mL) at 0 °C under an argon atmosphere, and the mixture was stirred at room temperature for 30 min. To a suspension of sodium benzenethiolate in THF was added a solution of the crude 1-aryl-4-bromo-1,3-butadione in THF (5 mL) via a cannula. The mixture was stirred at room temperature for 30 min and then at 60 °C for 1 h. The mixture was concentrated under reduced pressure, and purification by flash column chromatography on silica gel (*n*-hexane/EtOAc = 7:1) gave sulfide **6** (keto-enol mixture).

*1-Phenyl-4-(phenylsulfanyl)-1,3-butadione (**6a**)*.[17] 1.19 g, 88% yield; pale orange solid; mp 49.8–50.2 °C; R_f = 0.50 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1599, 1573, 1480, 758, 740, 687 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.83–7.81 (m, 2 H), 7.54–7.50 (m, 1 H), 7.45–7.40 (m, 4 H), 7.31–7.28 (m, 2 H), 7.24–7.21 (m, 1 H), 6.38 (s, 1 H), 3.74 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 193.1, 182.1, 134.9, 134.2, 132.5, 130.0 (2C), 129.1 (2C), 128.6 (2C), 127.0 (3C), 95.6, 41.3; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{16}H_{13}O_2S$, 269.0642; found, 269.0646.

*1-(4-Methylphenyl)-4-(phenylsulfanyl)-1,3-butadione (**6b**)*. 1.23 g, 87% yield; yellow oil; R_f = 0.52 (*n*-hexane/EtOAc = 3:1); IR (neat): 1609, 1571, 1507, 794, 740, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.73–7.72 (m, 2 H), 7.42–7.40 (m, 2 H), 7.32–7.28 (m, 2 H), 7.24–7.22 (m, 3 H), 6.34 (s, 1 H), 3.73 (s, 2 H), 2.40 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 192.4, 182.6, 143.4, 135.0, 131.5, 130.0 (2C), 129.4 (2C), 129.1 (2C), 127.1 (2C), 127.0, 95.2, 41.2, 21.6; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{17}H_{15}O_2S$, 283.0798; found, 283.0798.

*1-(4-n-Butylphenyl)-4-(phenylsulfanyl)-1,3-butadione (**6c**)*. 1.48 g, 91% yield; red oil; R_f = 0.58 (*n*-hexane/EtOAc = 3:1); IR (neat): 1608, 1566, 1506, 794, 739, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.74 (d, *J* = 8.2 Hz, 2 H), 7.41–7.40 (m, 2 H), 7.31–7.28 (m, 2 H), 7.25–7.22 (m, 3 H), 6.35 (s, 1 H), 3.73 (s, 2 H), 2.65 (t, *J* = 7.7 Hz, 2 H), 1.63–1.57 (m, 2 H), 1.39–1.31 (m, 2 H), 0.93 (t, *J* = 7.4 Hz, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 192.4, 182.5, 148.3, 134.9, 131.6, 130.0 (2C), 129.1 (2C), 128.7 (2C), 127.1 (2C), 126.9, 95.2, 41.1, 35.6, 33.2, 22.3, 13.9; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{20}H_{21}O_2S$, 325.1268; found, 325.1266.

*1-(4-Biphenyl)-4-(phenylsulfanyl)-1,3-butadione (**6d**)*. 1.56 g, 90% yield; white solid; mp 87.0–87.5 °C; R_f = 0.52 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1606, 1579, 1556, 847, 768, 749, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.90 (d, J = 8.6 Hz, 2 H), 7.67 (d, J = 8.6 Hz, 2 H), 7.63–7.61 (m, 2 H), 7.48–7.45 (m, 2 H), 7.43–7.38 (m, 3 H), 7.33–7.29 (m, 2 H), 7.25–7.22 (m, 1 H), 6.41 (s, 1 H), 3.76 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 193.1, 181.7, 145.3, 139.8, 134.9, 132.9, 130.1 (2C), 129.1 (2C), 129.0 (2C), 128.2, 127.6 (2C), 127.3 (2C), 127.2 (2C), 127.0, 95.5, 41.3; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{22}H_{17}O_2S$, 345.0955; found, 345.0952.

*1-(4-Methoxyphenyl)-4-(phenylsulfanyl)-1,3-butadione (**6e**)*. 1.26 g, 84% yield; pale orange solid; mp 71.9–72.0 °C; R_f = 0.54 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1603, 1567, 1508, 1263, 1178, 841, 796, 740, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.79 (d, J = 9.0 Hz, 2 H), 7.41–7.39 (m, 2 H), 7.30–7.25 (m, 2 H), 7.23–7.19 (m, 1 H), 6.90 (d, J = 9.0 Hz, 2 H), 6.29 (s, 1 H), 3.84 (s, 3 H), 3.71 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 190.9, 182.9, 163.2, 135.0, 129.9 (2C), 129.1 (2C), 129.0 (2C), 126.9, 126.7, 113.9 (2C), 94.7, 55.4, 40.8; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{17}H_{15}O_3S$, 299.0747; found, 299.0744.

*1-(4-Phenoxyphenyl)-4-(phenylsulfanyl)-1,3-butadione (**6f**)*. 1.58 g, 87% yield; pale orange solid; mp 60.0–60.4 °C; R_f = 0.50 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1604, 1584, 1487, 1245, 844, 780, 746, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.80 (d, J = 8.9 Hz, 2 H), 7.41–7.38 (m, 4 H), 7.31–7.28 (m, 2 H), 7.24–7.18 (m, 2 H), 7.08–7.05 (m, 2 H), 6.99 (d, J = 8.9 Hz, 2 H), 6.30 (s, 1 H), 3.73 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 191.7, 182.3, 161.7, 155.5, 134.9, 130.03 (2C), 129.99 (2C), 129.2 (2C), 129.1 (2C), 128.6, 127.0, 124.6, 120.1 (2C), 117.6 (2C), 95.0, 41.0; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{22}H_{17}O_3S$, 361.0904; found, 361.0902.

*1-(4-Benzyloxyphenyl)-4-(phenylsulfanyl)-1,3-butadione (**6g**)*. 1.60 g, 85% yield; white solid; mp 61.2–61.5 °C; R_f = 0.46 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1604, 1509, 1263, 1174, 842, 789, 753, 744, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.80 (d, J = 9.0 Hz, 2 H), 7.43–7.38 (m, 6 H), 7.36–

7.33 (m, 1 H), 7.32–7.27 (m, 2 H), 7.23–7.20 (m, 1 H), 7.00 (d, J = 9.0 Hz, 2 H), 6.30 (s, 1 H), 5.12 (s, 2 H), 3.72 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 191.1, 182.8, 162.4, 136.1, 135.0, 129.9 (2C), 129.2 (2C), 129.1 (2C), 128.7 (2C), 128.2, 127.5 (2C), 127.0, 126.9, 114.8 (2C), 94.7, 70.1, 40.9; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{23}H_{19}O_3S$, 375.1060; found, 375.1060.

*4-(phenylsulfanyl)-1-(4-trifluoromethylphenyl)-1,3-butadione (**6h**)*. 1.41 g, 83% yield; pale yellow solid; mp 48.5–49.1 °C; R_f = 0.54 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1624, 1605, 1330, 1122, 856, 799, 748, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.91 (d, J = 8.3 Hz, 2 H), 7.69 (d, J = 8.3 Hz, 2 H), 7.42–7.40 (m, 2 H), 7.32–7.29 (m, 2 H), 7.26–7.23 (m, 1 H), 6.38 (s, 1 H), 3.75 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 194.5, 179.5, 137.4 (q, J = 1.2 Hz), 134.5, 133.7 (q, J = 32.7 Hz), 130.2 (2C), 129.2 (2C), 127.3 (2C), 127.2, 125.6 (q, J = 3.6 Hz, 2C), 123.6 (q, J = 272.5 Hz), 96.3, 41.5; HRMS (ESI-Orbitrap): m/z $[M - H]^-$ calcd for $C_{17}H_{12}F_3O_2S$, 337.0516; found, 337.0516.

*Ethyl 4-[1,3-Dioxo-4-(phenylsulfanyl)butyl]benzoate (**6i**)*. 1.37 g, 80% yield; yellow solid; mp 88.5–88.9 °C; R_f = 0.42 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1712, 1604, 1569, 1281, 1105, 763, 728, 687 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 8.09 (d, J = 8.7 Hz, 2 H), 7.86 (d, J = 8.7 Hz, 2 H), 7.42–7.40 (m, 2 H), 7.32–7.29 (m, 2 H), 7.26–7.22 (m, 1 H), 6.39 (s, 1 H), 4.40 (q, J = 7.1 Hz, 2 H), 3.75 (s, 2 H), 1.41 (t, J = 7.1 Hz, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 194.5, 179.8, 165.7, 137.8, 134.6, 133.6, 130.1 (2C), 129.7 (2C), 129.2 (2C), 127.1, 126.8 (2C), 96.4, 61.4, 41.6, 14.3; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{19}H_{17}O_4S$, 341.0853; found, 341.0853.

*1-(4-Cyanophenyl)-4-(phenylsulfanyl)-1,3-butadione (**6j**)*. 1.24 g, 83% yield; pale orange solid; mp 76.3–76.6 °C; R_f = 0.36 (*n*-hexane/EtOAc = 3:1); IR (KBr): 2230, 1614, 1583, 1559, 852, 795, 743, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.89 (d, J = 8.7 Hz, 2 H), 7.72 (d, J = 8.7 Hz, 2 H), 7.41–7.39 (m, 2 H), 7.33–7.29 (m, 2 H), 7.26–7.23 (m, 1 H), 6.39 (s, 1 H), 3.75 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 195.2, 178.2, 138.0, 134.4, 132.4 (2C), 130.1 (2C), 129.2 (2C), 127.3 (2C), 127.2, 118.0, 115.5, 96.6, 41.6; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{17}H_{12}NO_2S$, 294.0594;

found, 294.0594.

*1-(2-Chlorophenyl)-4-(phenylsulfanyl)-1,3-butadione (**6k**)*. 1.24 g, 81% yield; yellow oil; R_f = 0.48 (*n*-hexane/EtOAc = 3:1); IR (neat): 1603, 1583, 1479, 766, 740, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.54 (dd, J = 7.7, 1.8 Hz, 1 H), 7.42–7.40 (m, 3 H), 7.38–7.34 (m, 1 H), 7.32–7.28 (m, 3 H), 7.25–7.21 (m, 1 H), 6.27 (s, 1 H), 3.72 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 192.0, 183.0, 134.7, 134.5, 131.9, 131.8, 130.7, 130.2, 130.1, 129.1, 127.1, 126.9, 101.1, 41.0; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{16}H_{12}{}^{35}ClO_2S$, 303.0252; found, 303.0253.

*1-(3-Chlorophenyl)-4-(phenylsulfanyl)-1,3-butadione (**6l**)*. 1.35 g, 88% yield; yellow oil; R_f = 0.52 (*n*-hexane/EtOAc = 3:1); IR (neat): 1604, 1566, 787, 746, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.77–7.76 (m, 1 H), 7.69–7.66 (m, 1 H), 7.49–7.46 (m, 1 H), 7.42–7.39 (m, 2 H), 7.38–7.35 (m, 1 H), 7.32–7.29 (m, 2 H), 7.26–7.22 (m, 1 H), 6.30 (s, 1 H), 3.73 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 193.5, 180.3, 136.0, 134.9, 134.6, 132.3, 130.2, 129.9, 129.2, 127.2, 127.1, 125.0, 95.9, 41.3; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{16}H_{12}{}^{35}ClO_2S$, 303.0252; found, 303.0251.

*1-(4-Chlorophenyl)-4-(phenylsulfanyl)-1,3-butadione (**6m**)*. 1.27 g, 83% yield; pale orange solid; mp 49.9–50.1 °C; R_f = 0.56 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1634, 1588, 1479, 845, 794, 739, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.75 (d, J = 8.7 Hz, 2 H), 7.42–7.40 (m, 4 H), 7.32–7.29 (m, 2 H), 7.25–7.23 (m, 1 H), 6.32 (s, 1 H), 3.74 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 193.1, 180.9, 138.8, 134.7, 132.6, 130.1 (2C), 129.1 (2C), 129.0 (2C), 128.3 (2C), 127.1, 95.5, 41.2; HRMS (ESI-TOF): m/z $[M - H]^-$ calcd for $C_{16}H_{12}{}^{35}ClO_2S$, 303.0252; found, 303.0255.

*1-(4-Fluorophenyl)-4-(phenylsulfanyl)-1,3-butadione (**6n**)*. 1.20 g, 83% yield; pale yellow solid; mp 55.6–56.1 °C; R_f = 0.54 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1637, 1598, 1508, 1232, 848, 795, 736, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.85–7.82 (m, 2 H), 7.41–7.40 (m, 2 H), 7.31–7.28 (m, 2 H), 7.24–7.22 (m, 1 H), 7.13–7.09 (m, 2 H), 6.31 (m, 1 H), 3.73 (m, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 192.3, 181.6, 165.4 (d, J = 254.1 Hz), 134.8, 130.5 (d, J = 3.0 Hz), 130.0 (2C),

129.5 (d, J = 9.1 Hz) (2C), 129.1 (2C), 127.1, 115.8 (d, J = 22.0 Hz) (2C), 95.3, 41.0; HRMS (ESI-TOF): m/z [M − H]$^-$ calcd for $C_{16}H_{12}FO_2S$, 287.0548; found, 287.0548.

*1-(4-Bromophenyl)-4-(phenylsulfanyl)-1,3-butadione (**6o**)*. 1.61 g, 92% yield; pale orange solid; mp 58.0–58.2 °C; R_f = 0.56 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1604, 1585, 1479, 841, 787, 740, 690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.67 (d, J = 8.7 Hz, 2 H), 7.56 (d, J = 8.7 Hz, 2 H), 7.41–7.39 (m, 2 H), 7.31–7.28 (m, 2 H), 7.25–7.21 (m, 1 H), 6.32 (s, 1 H), 3.73 (s, 2 H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (enol form): δ 193.3, 180.9, 134.7, 133.1, 131.9 (2C), 130.1 (2C), 129.1 (2C), 128.5 (2C), 127.3, 127.1, 95.5, 41.3; HRMS (ESI-TOF): m/z [M − H]$^-$ calcd for $C_{16}H_{12}{}^{79}BrO_2S$, 346.9747; found, 346.9748.

*1-(4-Iodophenyl)-4-(phenylsulfanyl)-1,3-butadione (**6p**)*. 1.61 g, 81% yield; pale yellow solid; mp 70.1–70.6 °C; R_f = 0.56 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1586, 1553, 1481, 840, 793, 740, 689 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.79–7.77 (m, 2 H), 7.52–7.51 (m, 2 H), 7.41–7.38 (m, 2 H), 7.31–7.28 (m, 2 H), 7.23 (tt, J = 7.3, 1.2 Hz, 1 H), 6.32 (s, 1 H), 3.73 (s, 2 H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (enol form): δ 193.4, 181.0, 137.9 (2C), 134.7, 133.6, 130.1 (2C), 129.1 (2C), 128.4 (2C), 127.1, 99.9, 95.5, 41.3; HRMS (ESI-TOF): m/z [M − H]$^-$ calcd for $C_{16}H_{12}IO_2S$, 394.9608; found, 394.9608.

*1-(2-Naphthyl)-4-(phenylsulfanyl)-1,3-butadione (**6q**)*. 1.36 g, 85% yield; white solid; mp 95.2–95.7 °C; R_f = 0.50 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1627, 1577, 1560, 1477, 867, 795, 755, 737, 689 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (enol form): δ 8.37 (s, 1 H), 7.92 (d, J = 8.0 Hz, 1 H), 7.87–7.81 (m, 3 H), 7.59–7.52 (m, 2 H), 7.45–7.43 (m, 2 H), 7.32–7.29 (m, 2 H), 7.25–7.22 (m, 1 H), 6.49 (s, 1 H), 3.77 (s, 2 H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (enol form): δ 193.0, 182.0, 135.3, 134.9, 132.6, 131.4, 130.1 (2C), 129.3, 129.1 (2C), 128.4, 128.3, 128.2, 127.7, 127.1, 126.8, 123.0, 95.9, 41.4; HRMS (ESI-TOF): m/z [M − H]$^-$ calcd for $C_{20}H_{15}O_2S$, 319.0798; found, 319.0796.

*1-(2,3-Dihydro-1,4-benzodioxin-6-yl)-4-(phenylsulfanyl)-1,3-butadione (**6r**)*. 1.50 g, 91% yield; pale yellow solid; mp 70.6–71.0 °C; R_f = 0.28 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1605, 1575, 1507, 1284, 1066, 887, 771, 734, 686 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.41–7.38 (m, 3 H), 7.35 (dd,

J = 8.5, 2.1 Hz, 1 H), 7.31–7.28 (m, 2 H), 7.22 (tt, *J* = 7.3, 1.5 Hz, 1 H), 6.89 (d, *J* = 8.5 Hz, 1 H), 6.26 (s, 1 H), 4.32–4.30 (m, 2 H), 4.28–4.27 (m, 2 H), 3.72 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 191.1, 182.6, 147.7, 143.5, 135.0, 130.0 (2C), 129.1 (2C), 127.7, 126.9, 121.0, 117.4, 116.5, 94.9, 64.7, 64.1, 40.9; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{18}H_{15}O_4S$, 327.0697; found, 327.0698.

1-(2-Furyl)-4-(phenylsulfanyl)-1,3-butadione (***6s***). 1.05 g, 81% yield; yellow oil; R_f = 0.40 (*n*-hexane/EtOAc = 3:1); IR (neat): 1611, 1585, 1546, 759, 741, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.56 (dd, *J* = 1.7, 0.7 Hz, 1 H), 7.41–7.39 (m, 2 H), 7.31–7.27 (m, 2 H), 7.24–7.20 (m, 1 H), 7.13 (dd, *J* = 3.5, 0.7 Hz, 1 H), 6.54 (dd, *J* = 3.5, 1.7 Hz, 1 H), 6.26 (s, 1 H), 3.70 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 189.2, 174.6, 149.8, 146.3, 134.8, 130.1 (2C), 129.1 (2C), 127.0, 116.0, 112.6, 95.2, 40.4; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{14}H_{11}O_3S$, 259.0434; found, 259.0433.

4-(Phenylsulfanyl)-1-(2-thienyl)-1,3-butadione (***6t***). 1.16 g, 84% yield; pale yellow solid; mp 37.6–37.8 °C; R_f = 0.42 (*n*-hexane/EtOAc = 3:1); IR (KBr): 1602, 1579, 1481, 734, 724, 687 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.62 (dd, *J* = 3.8, 1.1 Hz, 1 H), 7.59 (dd, *J* = 4.9, 1.1 Hz, 1 H), 7.42–7.41 (m, 2 H), 7.31–7.28 (m, 2 H), 7.25–7.21 (m, 1 H), 7.11–7.10 (m, 1 H), 6.16 (s, 1 H), 3.69 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (enol form): δ 186.6, 180.6, 140.7, 134.8, 132.7, 130.5, 130.3 (2C), 129.1 (2C), 128.3, 127.1, 95.8, 39.9; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{14}H_{11}O_2S_2$, 275.0206; found, 275.0204.

General Procedure for Synthesis of Sulfonium salts (2). To a suspension of trimethyloxonium tetrafluoroborate (0.45 g, 3.0 mmol) in dry CH_2Cl_2 (10 mL) was added sulfide **6** (3.0 mmol) in dry CH_2Cl_2 (2 mL) via a cannula under an argon atmosphere. After stirring at room temperature for 12 h, the reaction mixture was concentrated under reduced pressure. *t*-Butyl methyl ether was added to the precipitated crude product, the mixture was stirred vigorously, and the *t*-butyl methyl ether phase was decanted. The solid was washed with *t*-butyl methyl ether several times, and the residue was collected and recrystallized to give sulfonium salt **2** (keto–enol mixture).

*(2,4-Dioxo-4-phenylbutyl)methylphenylsulfonium Tetrafuoroborate (**2a**)*. 0.98 g, 85% yield; yellow solid (MeCN/Et_2O); mp 129.4–130.2 °C; R_f = 0.54 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1626, 1589, 1576, 1073, 1045, 1034, 748, 681 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 7.99–7.97 (m, 2 H), 7.90–7.88 (m, 2 H), 7.82–7.78 (m, 1 H), 7.73–7.70 (m, 2 H), 7.65–7.62 (m, 1 H), 7.54–7.51 (m, 2 H), 6.47 (s, 1 H), 4.85 (d, *J* = 15.8 Hz, 1 H), 4.76 (d, *J* = 15.8 Hz, 1 H), 3.27 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 188.0, 181.7, 135.9, 134.7, 133.4, 132.0 (2C), 131.7 (2C), 130.1 (2C), 128.2 (2C), 124.1, 97.6, 54.2, 27.2; HRMS (ESI-TOF): *m*/*z* $[M - BF_4]^+$ calcd for $C_{17}H_{17}O_2S$, 285.0944; found, 285.0942.

*(4-Methylphenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2b**)*. 1.01 g, 87% yield; pale yellow solid (MeCN/Et_2O); mp 143.0–143.7 °C; R_f = 0.54 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1621, 1581, 1570, 1509, 1073, 1047, 1034, 835, 792, 749, 681 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 7.98–7.96 (m, 2 H), 7.81–7.78 (m, 3 H), 7.73–7.69 (m, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 6.43 (s, 1 H), 4.83 (d, *J* = 15.7 Hz, 1 H), 4.83 (d, *J* = 15.7 Hz, 1 H), 3.27 (s, 3 H), 2.40 (s, 1 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 187.2, 182.2, 146.1, 135.9, 132.0 (2C), 131.7 (2C), 130.8 (2C), 130.7, 128.3 (2C), 124.1, 97.2, 54.0, 27.2, 21.7; HRMS (ESI-TOF): *m*/*z* $[M - BF_4]^+$ calcd for $C_{18}H_{19}O_2S$, 299.1100; found, 299.1098.

*(4-n-Butylphenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2c**)*. 1.13 g, 88% yield; white solid (MeCN/Et_2O); mp 120.5–120.9 °C; R_f = 0.56 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1620, 1581, 1509, 1074, 1049, 1037, 845, 787, 747, 680 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 7.98–7.96 (m, 2 H), 7.81–7.78 (m, 3 H), 7.73–7.70 (m, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 6.42 (s, 1 H), 4.82 (d, *J* = 15.7 Hz, 1 H), 4.72 (d, *J* = 15.7 Hz, 1 H), 3.27 (s, 3 H), 2.68 (t, *J* = 7.7 Hz, 2 H), 1.63–1.57 (m, 2 H), 1.38–1.30 (m, 2 H), 0.92 (t, *J* = 7.4 Hz, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 187.2, 182.2, 150.9, 135.9, 132.0 (2C), 131.7 (2C), 130.9, 130.2 (2C), 128.3 (2C), 124.1, 97.2, 54.1, 36.2, 34.0, 27.2, 23.0, 14.1; HRMS (ESI-TOF): *m*/*z* $[M - BF_4]^+$ calcd for $C_{21}H_{25}O_2S$, 341.1570; found, 341.1570.

*(4-Biphenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2d**).* 1.21 g, 90% yield; light yellow solid (MeCN/Et_2O); mp 134.1–134.8 °C; R_f = 0.58 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1608, 1580, 1574, 1555, 1078, 1053, 845, 761, 746, 686 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 7.98–7.96 (m, 4 H), 7.83–7.79 (m, 3 H), 7.74–7.71 (m, 4 H), 7.52–7.49 (m, 2 H), 7.46–7.42 (m, 1 H), 6.50 (s, 1 H), 4.84 (d, J = 15.8 Hz, 1 H), 4.75 (d, J = 15.8 Hz, 1 H), 3.27 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 187.8, 181.3, 146.9, 140.2, 135.9, 132.0 (3C), 131.7 (2C), 130.1 (2C), 129.6, 128.8 (2C), 128.5 (2C), 128.1 (2C), 124.1, 97.5, 54.2, 27.2; HRMS (ESI-TOF): m/z $[M - BF_4]^+$ calcd for $C_{23}H_{21}O_2S$, 361.1257; found, 361.1257.

*(4-Methoxyphenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2e**).* 1.01 g, 84% yield; amber solid (MeCN/Et_2O); mp 123.8–124.2 °C; R_f = 0.52 (CH_2Cl_2/MeOH = 9:1); IR (neat): 1628, 1602, 1568, 1509, 1244, 1175, 1073, 1045, 1032, 843, 793, 748, 681 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 7.97–7.95 (m, 2 H), 7.87 (d, J = 9.0 Hz, 2 H), 7.82–7.78 (m, 1 H), 7.72–7.69 (m, 2 H), 7.03 (d, J = 9.0 Hz, 2 H), 6.37 (s, 1 H), 4.79 (d, J = 15.5 Hz, 1 H), 4.69 (d, J = 15.5 Hz, 1 H), 3.86 (s, 3 H), 3.26 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 185.7, 182.5, 165.4, 135.9, 132.0 (2C), 131.6 (2C), 130.6 (2C), 125.6, 124.1, 115.5 (2C), 96.7, 56.5, 53.8, 27.1; HRMS (ESI-TOF): m/z $[M - BF_4]^+$ calcd for $C_{18}H_{19}O_3S$, 315.1049; found, 315.1043.

*(2,4-Dioxo-4-Phenyloxyphenylbutyl)methylphenylsulfonium Tetrafluoroborate (**2f**).* 1.17 g, 84% yield; pale yellow solid (MeCN/Et_2O); mp 138.0–138.4 °C (dec.); R_f = 0.52 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1627, 1604, 1585, 1504, 1238, 1072, 1044, 1033, 848, 794, 751, 692 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 7.97–7.95 (m, 2 H), 7.89–7.87 (m, 2 H), 7.81–7.78 (m, 1 H), 7.73–7.70 (m, 2 H), 7.47–7.43 (m, 2 H), 7.28–7.25 (m, 1 H), 7.12–7.10 (m, 2 H), 7.05–7.02 (m, 2 H), 6.39 (s, 1 H), 4.80 (d, J = 15.6 Hz, 1 H), 4.71 (d, J = 15.6 Hz, 1 H), 3.27 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 186.6, 181.7, 163.6, 156.2, 135.9, 132.0 (2C), 131.7 (2C), 131.3 (2C), 130.7 (2C), 127.6, 126.0, 124.1, 121.3 (2C), 118.6 (2C), 97.1, 53.9, 27.2; HRMS (ESI-TOF): m/z $[M - BF_4]^+$ calcd for $C_{23}H_{21}O_3S$, 377.1206;

found, 377.1206.

*(4-Benzyloxyphenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2g**).* 1.22 g, 85% yield; orange solid (MeCN/Et_2O); mp 137.0–137.5 °C; R_f = 0.52 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1603, 1547, 1509, 1245, 1177, 1053, 1038, 845, 789, 754, 682 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (enol form): δ 7.97–7.95 (m, 2 H), 7.87 (d, J = 9.0 Hz, 2 H), 7.81–7.78 (m, 1 H), 7.72–7.69 (m, 2 H), 7.46–7.45 (m, 2 H), 7.42–7.39 (m, 2 H), 7.36–7.34 (m, 1 H), 7.10 (d, J = 9.0 Hz, 2 H), 6.37 (s, 1 H), 5.18 (s, 2 H), 4.78 (d, J = 15.5 Hz, 1 H), 4.68 (d, J = 15.5 Hz, 1 H), 3.26 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 185.8, 182.4, 164.4, 137.5, 135.9, 132.0 (2C), 131.6 (2C), 130.6 (2C), 129.6 (2C), 129.2, 128.8 (2C), 125.9, 124.1, 116.3 (2C), 96.8, 71.1, 53.8, 27.1; HRMS (ESI-TOF): m/z $[M - BF_4]^+$ calcd for $C_{24}H_{23}O_3S$, 391.1362; found, 391.1362.

*(4-Trifluoromethylphenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2h**).* 1.09 g, 83% yield; pale yellow solid (MeCN/Et_2O); mp 132.0–132.8 °C (dec.); R_f = 0.52 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1628, 1575, 1326, 1128, 1065, 1047, 1036, 859, 778, 770, 681 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 8.04–8.02 (m, 2 H), 7.99–7.97 (m, 2 H), 7.84–7.79 (m, 3 H), 7.74–7.71 (m, 2 H), 6.52 (s, 1 H), 4.88 (d, J = 16.1 Hz, 1 H), 4.79 (d, J = 16.1 Hz, 1 H), 3.28 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 189.5, 178.9, 137.1, 135.9, 134.6 (q, J = 32.5 Hz), 132.0 (2C), 131.7 (2C), 130.1, 128.8 (2C), 127.0 (q, J = 3.8 Hz, 2C), 124.8 (q, J = 271.8 Hz), 98.5, 54.5, 27.2; HRMS (ESI-Orbitrap): m/z $[M - BF_4]^+$ calcd for $C_{18}H_{16}F_3O_2S$, 353.0818; found, 353.0814.

*(4-Ethoxycarbonylphenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2i**).* 1.15 g, 86% yield; white solid (MeCN/Et_2O); mp 133.5–133.9 °C; R_f = 0.52 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1736, 1633, 1584, 1567, 1275, 1107, 1070, 1047, 1037, 774, 748, 682 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 8.11–8.09 (m, 2 H), 7.98–7.95 (m, 4 H), 7.83–7.79 (m, 1 H), 7.74–7.71 (m, 2 H), 6.50 (s, 1 H), 4.87 (d, J = 16.1 Hz, 1 H), 4.78 (d, J = 16.1 Hz, 1 H), 4.36 (q, J =7.1 Hz, 2 H), 3.27 (s, 3 H), 1.37 (t, J = 7.1 Hz, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 189.4, 179.4, 166.3, 137.2, 135.9, 135.6,

132.0 (2C), 131.7 (2C), 130.7 (2C), 128.2 (2C), 124.1, 98.3, 62.4, 54.5, 27.2, 14.5; HRMS (ESI-TOF): *m*/*z* $[M - BF_4]^+$ calcd for $C_{20}H_{21}O_4S$, 357.1155; found, 357.1156.

*(4-Cyanophenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2j**)*. 1.05 g, 88% yield; cream yellow solid (MeCN/Et_2O); mp 141.3–142.1 °C (dec.); R_f = 0.52 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 2234, 1639, 1577, 1560, 1066, 1050, 1035, 860, 783, 750, 682 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 8.00–7.97 (m, 4 H), 7.87–7.85 (m, 2 H), 7.82–7.79 (m, 1 H), 7.74–7.70 (m, 2 H), 6.51 (s, 1 H), 4.89 (d, *J* = 16.1 Hz, 1 H), 4.80 (d, *J* = 16.1 Hz, 1 H), 3.27 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 189.8, 178.2, 137.4, 135.9, 133.9 (2C), 132.0 (2C), 131.7 (2C), 128.6 (2C), 124.0, 118.9, 117.0, 98.7, 54.6, 27.2; HRMS (ESI-TOF): *m*/*z* $[M - BF_4]^+$ calcd for $C_{18}H_{16}NO_2S$, 310.0896; found, 310.0896.

*(2-Chlorophenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2k**)*. 1.04 g, 85% yield; shell pink solid (MeCN/Et_2O); mp 107.9–108.5 °C; R_f = 0.56 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1620, 1597, 1579, 1043, 766, 747, 681 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 7.98–7.96 (m, 2 H), 7.83–7.80 (m, 1 H), 7.74–7.71 (m, 2 H), 7.59–7.57 (m, 1 H), 7.54–7.52 (m, 2 H), 7.46–7.42 (m, 1 H), 6.21 (s, 1 H), 4.73 (d, *J* = 15.9 Hz, 1 H), 4.73 (d, *J* = 15.9 Hz, 1 H), 3.27 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 187.5, 182.0, 136.0, 134.0, 133.9, 132.6, 132.0 (2C), 131.9, 131.7 (2C), 131.4, 128.6, 123.9, 102.9, 54.1, 27.2; HRMS (ESI-TOF): *m*/*z* $[M - BF_4]^+$ calcd for $C_{17}H_{16}{}^{35}ClO_2S$, 319.0554; found, 319.0548.

*(3-Chlorophenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2l**)*. 1.05 g, 86% yield; pink solid (MeCN/Et_2O); mp 133.5–133.9 °C; R_f = 0.56 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1624, 1579, 1564, 1072, 1045, 1036, 789, 747, 681 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 7.98–7.96 (m, 2 H), 7.87–7.86 (m, 1 H), 7.82–7.79 (m, 2 H), 7.74–7.70 (m, 2 H), 7.64–7.62 (m, 1 H), 7.52–7.49 (m, 1 H), 6.46 (s, 1 H), 4.85 (d, *J* = 15.9 Hz, 1 H), 4.75 (d, *J* = 15.9 Hz, 1 H), 3.27 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 188.4, 179.7, 135.9, 135.6, 135.5, 134.2, 132.0 (2C), 131.8, 131.7 (2C),

127.9, 126.6, 124.0, 98.1, 54.2, 27.2; HRMS (ESI-TOF): *m*/*z* [M − BF_4]$^+$ calcd for $C_{17}H_{16}{}^{35}ClO_2S$, 319.0554; found, 319.0546.

*(4-Chlorophenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2m**).* 1.01 g, 83% yield; pale pink solid (MeCN/Et_2O); mp 151.9–152.4 °C; R_f = 0.56 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1626, 1593, 1561, 1071, 1046, 1035, 841, 789, 749, 681 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) (enol form): δ 7.97–7.95 (m, 2 H), 7.86 (d, *J* = 8.8 Hz, 2 H), 7.82–7.79 (m, 1 H), 7.74–7.70 (m, 2 H), 7.54 (d, *J* = 8.8 Hz, 2 H), 6.43 (s, 1 H), 4.83 (d, *J* = 15.9 Hz, 1 H), 4.73 (d, *J* = 15.9 Hz, 1 H), 3.26 (s, 3 H); ^{13}C{^{1}H} NMR (126 MHz, CD_3CN) (enol form): δ 188.2, 180.3, 140.2, 135.9, 132.2, 132.0 (2C), 131.7 (2C), 130.3 (2C), 129.8 (2C), 124.0, 97.7, 54.2, 27.2; HRMS (ESI-TOF): *m*/*z* [M − BF_4]$^+$ calcd for $C_{17}H_{16}{}^{35}ClO_2S$, 319.0554; found, 319.0546.

*(4-Fluorophenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2n**).* 1.00 g, 85% yield; pale orange solid (MeCN/Et_2O); mp 142.5–143.0 °C; R_f = 0.56 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1627, 1600, 1577, 1507, 1230, 1072, 1045, 1035, 850, 795, 748, 681 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) (enol form): δ 7.98–7.93 (m, 4 H), 7.82–7.78 (m, 1 H), 7.73–7.70 (m, 2 H), 7.27–7.24 (m, 1 H), 6.43 (s, 1 H), 4.83 (d, *J* = 15.8 Hz, 1 H), 4.73 (d, *J* = 15.8 Hz, 1 H), 3.27 (s, 3 H); ^{13}C{^{1}H} NMR (126 MHz, CD_3CN) (enol form): δ 187.3, 181.0, 166.9 (d, *J* = 253.2 Hz), 135.9, 132.0 (2C), 131.7 (2C), 131.1 (d, *J* = 9.7 Hz) (2C), 130.0 (d, *J* = 3.0 Hz), 124.0, 117.2 (d, *J* = 22.6 Hz) (2C), 97.5, 54.0, 27.2; HRMS (ESI-TOF): *m*/*z* [M − BF_4]$^+$ calcd for $C_{17}H_{16}FO_2S$, 303.0850; found, 303.0847.

*(4-Bromophenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2o**).* 1.12 g, 83% yield; pale pink solid (MeCN/Et_2O); mp 141.3–142.2 °C; R_f = 0.60 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1625, 1590, 1560, 1067, 1046, 1036, 838, 787, 749, 681 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) (enol form): δ 7.97–7.95 (m, 2 H), 7.82–7.76 (m, 3 H), 7.73–7.67 (m, 4 H), 6.44 (s, 1 H), 4.84 (d, *J* = 15.9 Hz, 1 H), 4.74 (d, *J* = 15.9 Hz, 1 H), 3.26 (s, 3 H); ^{13}C{^{1}H} NMR (126 MHz, CD_3CN) (enol form): δ 188.3, 180.3, 135.9, 133.3 (2C), 132.6, 132.0 (2C), 131.7 (2C), 129.9 (2C), 128.9, 124.0, 97.7, 54.2, 27.2; HRMS (ESI-TOF): *m*/*z*

$[M - BF_4]^+$ calcd for $C_{17}H_{16}{}^{79}BrO_2S$, 363.0049; found, 363.0041.

*(4-Iodophenyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2p**).* 1.26 g, 84% yield; pale yellow solid (MeCN/Et_2O); mp 149.2–149.9 °C (dec.); R_f = 0.60 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1622, 1586, 1554, 1071, 1058, 1035, 835, 786, 750, 682 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 7.98–7.95 (m, 2 H), 7.90 (d, J = 8.6 Hz, 2 H), 7.82–7.78 (m, 1 H), 7.73–7.70 (m, 2 H), 7.61 (d, J = 8.6 Hz, 2 H), 6.44 (s, 1 H), 4.83 (d, J = 15.9 Hz, 1 H), 4.74 (d, J = 15.9 Hz, 1 H), 3.26 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 188.3, 180.5, 139.4 (2C), 135.9, 133.0 132.0 (2C), 131.7 (2C), 129.6 (2C), 124.0, 101.6, 97.6, 54.3, 27.2; HRMS (ESI-TOF): m/z $[M - BF_4]^+$ calcd for $C_{17}H_{16}IO_2S$, 410.9910; found, 410.9910.

*(4-Naphthyl-2,4-dioxobutyl)methylphenylsulfonium Tetrafluoroborate (**2q**).* 1.13 g, 89% yield; yellowish green solid (MeCN/Et_2O); mp 112.3–112.8 °C; R_f = 0.54 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1618, 1582, 1571, 1067, 1046, 1035, 878, 822, 792, 749, 681 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 8.51 (s, 1 H), 8.04–7.96 (m, 5 H), 7.87 (dd, J = 8.7, 1.8 Hz, 1 H), 7.82–7.79 (m, 1 H), 7.74–7.71 (m, 2 H), 7.67–7.64 (m, 1 H), 7.63–7.59 (m, 1 H), 6.60 (s, 1 H), 4.88 (d, J = 15.8 Hz, 1 H), 4.78 (d, J = 15.8 Hz, 1 H), 3.29 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 187.7, 181.6, 136.6, 135.9, 133.6, 132.0 (2C), 131.7 (2C), 130.7, 130.5, 130.0, 129.9, 129.8, 128.8, 128.3, 124.1, 123.6, 97.9, 54.2, 27.2; HRMS (ESI-TOF): m/z $[M - BF_4]^+$ calcd for $C_{21}H_{19}O_2S$, 335.1100; found, 335.1092.

*[4-(2,3-Dihydro-1,4-benzodioxin-6-yl)-1,4-dioxobutyl]mehylphenylsulfonium Tetrafluoroborate (**2r**).* 1.09 g, 84% yield; pink solid (MeOH/Et_2O); mp 127.6–128.2 °C; R_f = 0.44 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1608, 1575, 1510, 1289, 1065, 1035, 886, 789, 749, 682 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) (enol form): δ 7.97–7.95 (m, 2 H), 7.80 (tt, J = 7.5, 1.4 Hz, 1 H), 7.72–7.69 (m, 2 H), 7.42–7.39 (m, 2 H), 6.95 (d, J = 8.4 Hz, 1 H), 6.35 (s, 1 H), 4.77 (d, J = 15.5 Hz, 1 H), 4.67 (d, J = 15.5 Hz, 1 H), 4.33–4.31 (m, 2 H), 4.28–4.26 (m, 2 H), 3.26 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 185.7, 182.3, 150.0, 145.0, 135.9, 132.0 (2C), 131.6 (2C), 126.6, 124.1, 122.3, 118.7, 117.3, 97.1, 65.9, 65.2, 53.8, 27.1;

HRMS (ESI-TOF): *m*/*z* $[M - BF_4]^+$ calcd for $C_{19}H_{19}O_4S$, 343.0999; found, 343.0999.

*[4-(2-Furyl)-2,4-dioxobutyl]methylphenylsulfonium Tetrafluoroborate (**2s**)* (keto–enol = 0.14:0.86). 0.88 g, 81% yield; dark brown solid (MeOH/Et_2O); mp 108.6–109.4 °C; R_f = 0.44 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1633, 1590, 1546, 1093, 1015, 768, 749, 684 cm^{-1}; ^1H NMR (500 MHz, CD_3CN): δ 7.97–7.95 (m, 2 H), 7.82–7.78 (m, 1.86 H), 7.76–7.75 (m, 0.14 H), 7.73–7.69 (m, 2 H), 7.34 (dd, *J* = 3.7, 0.7 Hz, 0.14 H), 7.30 (dd, *J* = 3.7, 0.6 Hz, 0.86 H), 6.68 (dd, *J* = 3.7, 1.7 Hz, 0.86 H), 6.65 (dd, *J* = 3.7, 1.7 Hz, 0.14 H), 6.23 (s, 1 H), 5.03 (d, *J* = 17.6 Hz, 0.14 H), 4.99 (d, *J* = 17.6 Hz, 0.14 H), 4.76 (d, *J* = 15.4 Hz, 0.86 H), 4.67 (d, *J* = 15.4 Hz, 0.86 H), 4.17 (s, 0.28 H), 3.27 (s, 2.58 H), 3.20 (s, 0.42 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 184.0, 173.1, 149.5, 149.0, 135.9, 132.0 (2C), 131.7 (2C), 123.9, 119.2, 114.3, 97.3, 53.4, 27.1; (keto form): δ 196.2, 181.7, 152.5, 149.5, 135.8, 131.9 (2C), 131.7 (2C), 124.1, 120.8, 113.9, 58.1, 52.1. 27.0; HRMS (ESI-TOF): *m*/*z* $[M - BF_4]^+$ calcd for $C_{15}H_{15}O_3S$, 275.0736; found, 275.0736.

*[2,4-Dioxo-4-(2-thienyl)butyl]methylphenylsulfonium Tetrafluoroborate (**2t**)* (keto-enol = 0.16:0.84). 0.95 g, 84% yield; orange solid (MeOH/Et_2O); mp 106.5–107.0 °C; R_f = 0.44 (CH_2Cl_2/MeOH = 9:1); IR (KBr): 1593, 1078, 1065, 1036, 747, 683 cm^{-1}; ^1H NMR (500 MHz, CD_3CN): δ 7.96–7.94 (m, 2 H), 7.89–7.86 (m, 1 H), 7.82–7.78 (m, 2 H), 7.73–7.70 (m, 2 H), 7.23–7.20 (m, 1 H), 6.32 (s, 0.84 H), 5.03 (d, *J* = 17.5 Hz, 0.16 H), 4.99 (d, *J* = 17.5 Hz, 0.16 H), 4.70 (d, *J* = 15.0 Hz, 0.84 H), 4.59 (d, *J* = 15.0 Hz, 0.84 H), 4.30 (s, 0.32 H), 3.28 (s, 2.52 H), 3.20 (s, 0.48 H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) (enol form): δ 180.7, 180.0, 139.4, 136.2, 136.0, 133.6, 132.0 (2C), 131.7 (2C), 130.2, 123.8, 98.5, 52.7, 26.9; (keto form): δ 196.3, 186.9, 143.9, 137.1, 135.8, 135.7, 132.0 (2C), 131.7 (2C), 129.9, 124.1, 58.1, 52.7, 27.0; HRMS (ESI-TOF): *m*/*z* $[M - BF_4]^+$ calcd for $C_{15}H_{15}O_2S_2$, 291.0508; found, 291.0508.

General Procedure for the Synthesis of 5-Aryl-3(2*H*)-furanones 3. An aqueous solution of 0.5 M K_2CO_3 (0.4 mL, 0.2 mmol) was added to a suspension of the sulfonium salt (0.2 mmol) in EtOAc (1.6 mL) at room temperature, and the reaction mixture was stirred for 10 min. The aqueous phase was

separated and extracted with EtOAc. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (*n*-hexane/EtOAc = 2:1) gave 5-aryl-3(2*H*)-furanone **3**.

*5-Phenyl-3(2H)-furanone (**3a**).*[6] 31.9 mg, 99% yield; white solid; mp 88.7–89.4 °C; R_f = 0.46 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1686, 1604, 1590, 1562, 1491, 772, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.83–7.81 (m, 2 H), 7.57 (tt, J = 7.4, 1.6 Hz, 1 H), 7.51–7.48 (m, 2 H), 6.08 (s, 1 H), 4.71 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.2, 186.9, 132.7, 128.9 (2C), 128.7, 127.0 (2C), 101.5, 75.3; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_9O_2$, 161.0597; found, 161.0596.

*5-(4-Methylphenyl)-3(2H)-furanone (**3b**).*[7e] 33.8 mg, 97% yield; white solid; mp 94.3–95.2 °C; R_f = 0.48 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1679, 1606, 1593, 1563, 1505, 794 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8.1 Hz, 2 H), 7.29 (d, J = 8.1 Hz, 2 H), 6.03 (s, 1 H), 4.69 (s, 2 H), 2.43 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.2, 187.1, 143.6, 129.6 (2C), 127.0 (2C), 126.0, 100.8, 75.3, 21.7; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{11}O_2$, 175.0754; found, 175.0750.

*5-(4-n-Butylphenyl)-3(2H)-furanone (**3c**).* 42.8 mg, 99% yield; white solid; mp 88.1–88.9 °C; R_f = 0.56 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1698, 1615, 1599, 1561, 1507, 806 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J = 8.3 Hz, 2 H), 7.30 (d, J = 8.3 Hz, 2 H), 6.04 (s, 1 H), 4.70 (s, 2 H), 2.68 (t, J = 7.8 Hz, 2 H), 1.66–1.60 (m, 2 H), 1.40–1.33 (m, 2 H), 0.94 (t, J = 7.4 Hz, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.2, 187.1, 148.6, 128.9 (2C), 127.1 (2C), 126.1, 100.8, 75.3, 35.7, 33.2, 22.2, 13.8; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{17}O_2$, 217.1223; found, 217.1216.

*5-(4-Biphenyl)-3(2H)-furanone (**3d**).* 46.1 mg, 98% yield; pale yellow solid; mp 153.1–154.0 °C; R_f = 0.50 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1694, 1608, 1590, 1557, 1486, 844, 766, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 8.5 Hz, 2 H), 7.72 (d, J = 8.5 Hz, 2 H), 7.65–7.63 (m, 2 H), 7.50–7.43 (m, 2 H), 7.43–7.40 (m, 1 H), 6.11 (s, 1 H), 4.73 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.1, 186.6, 145.5, 139.6, 129.0 (2C), 128.3, 127.6 (2C), 127.5 (3C), 127.2 (2C), 101.4, 75.4; HRMS (ESI-

TOF): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{13}O_2$, 237.0910; found, 237.0902.

*5-(4-Methoxyphenyl)-3(2H)-furanone (**3e**).*[7e] 37.1 mg, 97% yield; white solid; mp 117.7–118.3 °C; R_f = 0.34 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1691, 1608, 1571, 1505, 1258, 841, 779 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 9.0 Hz, 2 H), 6.99 (d, J = 9.0 Hz, 2 H), 5.97 (s, 1 H), 4.69 (s, 2 H), 3.89 (s, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 201.9, 186.8, 163.3, 129.0 (2C), 121.2, 114.3 (2C), 99.9, 75.3, 55.5; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{11}O_3$, 191.0703; found, 191.0699.

*5-(4-Phenyloxyphenyl)-3(2H)-furanone (**3f**).* 50.4 mg, quant.; pale yellow solid; mp 95.3–96.2 °C; R_f = 0.48 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1693, 1608, 1598, 1569, 1498, 1250, 854, 776, 693 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 8.9 Hz, 2 H), 7.42–7.38 (m, 2 H), 7.23–7.19 (m, 1 H), 7.09–7.07 (m, 2 H), 7.04 (d, J = 8.9 Hz, 2 H), 5.99 (s, 1 H), 4.68 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 201.9, 186.3, 161.7, 155.2, 130.0 (2C), 129.0 (2C), 124.7, 122.9, 120.1 (2C), 117.7 (2C), 100.5, 75.3; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{13}O_3$, 253.0859; found, 253.0858.

*5-(4-Benzyloxyphenyl)-3(2H)-furanone (**3g**).* 52.4 mg, 99% yield; white solid; mp 154.8–155.2 °C; R_f = 0.44 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1693, 1605, 1567, 1502, 1254, 840, 752, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.9 Hz, 2 H), 7.74–7.39 (m, 4 H), 7.37–7.33 (m, 1 H), 7.06 (d, J = 8.9 Hz, 2 H), 5.96 (s, 1 H), 5.14 (s, 2 H), 4.68 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 201.9, 186.7, 162.4, 136.0, 129.1 (2C), 128.7 (2C), 128.3, 127.5 (2C), 121.4, 115.2 (2C), 100.0, 75.3, 70.2; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{15}O_3$, 267.1016; found, 267.1016.

*5-(4-Trifluoromethylphenyl)-3(2H)-furanone (**3h**).* 44.9 mg, 98% yield; white solid; mp 146.7–167.4 °C (dec.); R_f = 0.44 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1692, 1602, 1573, 1325, 1175, 812 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, J = 8.2 Hz, 2 H), 7.76 (d, J = 8.2 Hz, 2 H), 6.17 (s, 1 H), 4.75 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.0, 184.9, 134.1 (q, J = 32.9 Hz), 132.0, 127.3 (2C), 126.3 (q, J = 3.8 Hz, 2C), 123.5 (q, J = 272.6 Hz), 103.0, 75.5; HRMS (APCI-Orbitrap): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_8F_3O_2$, 229.0476; found, 229.0468.

*5-(4-Ethoxycarbonylphenyl)-3(2H)-furanone (**3i**).* 46.4 mg, 99% yield; white solid; mp 133.8–134.3 °C; R_f = 0.50 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1709, 1691, 1614, 1595, 1566, 1272, 1104, 779 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, J = 8.6 Hz, 2 H), 7.88 (d, J = 8.6 Hz, 2 H), 6.16 (s, 1 H), 4.74 (s, 2 H), 4.42 (q, J = 7.1 Hz, 2 H), 1.42 (t, J = 7.1 Hz, 3 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.1, 185.5, 165.5, 133.9, 132.4, 129.9 (2C), 126.9 (2C), 102.9, 75.4, 61.5, 14.2; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{13}O_4$, 233.0808; found, 233.0801.

*5-(4-Cyanophenyl)-3(2H)-furanone (**3j**).* 36.7 mg, 99% yield; white solid; mp 137.2–138.0 °C; R_f = 0.40 (*n*-hexane/EtOAc = 1:1); IR (KBr): 2230, 1692, 1614, 1592, 850 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, J = 8.7 Hz, 2 H), 7.80 (d, J = 8.7 Hz, 2 H), 6.19 (s, 1 H), 4.75 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 201.8, 184.1, 132.6 (3C), 127.4 (2C), 117.8, 115.8, 103.6, 75.5; HRMS (ESI-TOF): *m*/*z* $[M - H]^-$ calcd for $C_{11}H_6NO_2$, 184.0404; found, 184.0400.

*5-(2-Chlorophenyl)-3(2H)-furanone (**3k**).* 38.4 mg, 98% yield; pale yellow solid; mp 86.2–86.9 °C; R_f = 0.56 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1686, 1594, 1574, 1561, 772 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.89 (dd, J = 7.8, 1.8 Hz, 1 H), 7.53 (dd, J = 8.0, 1.3 Hz, 1 H), 7.48–7.45 (m, 1 H), 7.42–7.39 (m, 1 H), 6.47 (s, 1 H), 4.65 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.9, 183.3, 133.8, 132.8, 131.2, 129.4, 127.9, 127.1, 107.3, 74.0; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_8{}^{35}ClO_2$, 195.0207; found, 195.0205.

*5-(3-Chlorophenyl)-3(2H)-furanone (**3l**).* 38.4 mg, 98% yield; white solid; mp 106.1–106.9 °C; R_f = 0.54 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1698, 1610, 1590, 1566, 789, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.81–7.80 (m, 1 H), 7.70–7.68 (m, 1 H), 7.55–7.52 (m, 1 H), 7.46–7.43 (m, 1 H), 6.09 (s, 1 H), 4.71 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.0, 185.2, 135.1, 132.6, 130.5, 130.2, 126.9, 125.2, 102.3, 75.4; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_8{}^{35}ClO_2$, 195.0207; found, 195.0205.

*5-(4-Chlorophenyl)-3(2H)-furanone (**3m**).*[7e] 38.3 mg, 97% yield; white solid; mp 110.4–111.2 °C; R_f = 0.52 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1699, 1607, 1561, 1487, 808 cm^{-1}; ^1H NMR (500 MHz,

$CDCl_3$): δ 7.75 (d, J = 8.7 Hz, 2 H), 7.48 (d, J = 8.7 Hz, 2 H), 6.06 (s, 1 H), 4.71 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 201.9, 185.5, 139.0, 129.3 (2C), 128.3 (2C), 127.2, 101.7, 75.4; HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{10}H_8ClO_2$, 195.0207; found, 195.0209.

*5-(4-Fluorophenyl)-3(2H)-furanone (**3n**).*[7e] 35.5 mg, quant; white solid; mp 103.9–104.6 °C; R_f = 0.48 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1691, 1611, 1577, 1506, 1173, 814 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.85–7.81 (m, 2 H), 7.21–7.17 (m, 2 H), 6.03 (s, 1 H), 4.71 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.0, 185.7, 165.4 (d, J = 255.0 Hz), 129.4 (d, J = 9.1 Hz) (2C), 125.0 (d, J = 3.3 Hz), 116.2 (d, J = 22.0 Hz) (2C), 101.2 (d, J = 1.2 Hz), 75.4; HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{10}H_8FO_2$, 179.0503; found, 179.0498.

*5-(4-Bromophenyl)-3(2H)-furanone (**3o**).*[7e] 47.2 mg, 99% yield; white solid; mp 123.6–124.2 °C; R_f = 0.52 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1698, 1605, 1484, 807 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, J = 8.6 Hz, 2 H), 7.64 (d, J = 8.6 Hz, 2 H), 6.07 (s, 1 H), 4.70 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.2, 185.6, 132.3 (2C), 128.4 (2C), 127.64, 127.56, 101.8, 75.4; HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{10}H_8{}^{79}BrO_2$, 238.9702; found, 238.9709.

*5-(4-Iodophenyl)-3(2H)-furanone (**3p**).* 56.8 mg, 99% yield; white solid; mp 141.5–142.3 °C; R_f = 0.56 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1680, 1597, 1551, 1479, 803 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J = 8.6 Hz, 2 H), 7.52 (d, J = 8.6 Hz, 2 H), 6.08 (s, 1 H), 4.69 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.0, 185.8, 138.2 (3C), 128.3 (2C), 101.8, 100.0, 75.4; HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{10}H_8IO_2$, 286.9564; found, 286.9565.

*5-(2-Naphthyl)-3(2H)-furanone (**3q**).* 40.8 mg, 97% yield; white solid; mp 122.4–130.2 °C; R_f = 0.52 (*n*-hexane/EtOAc = 1:2); IR (KBr): 1686, 1608, 1581, 1559, 862, 799, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.38 (s, 1 H), 7.96–7.88 (m, 3 H), 7.78 (dd, J = 8.6, 1.7 Hz, 1 H), 7.63–7.56 (m, 2 H), 6.19 (s, 1 H), 4.76 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.2, 186.8, 135.2, 132.6, 129.2, 128.8, 128.4, 127.9, 127.7, 127.1, 125.9, 123.2, 101.9, 75.4; HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{14}H_{11}O_2$,

211.0754; found, 211.0752.

*5-(2,3-Dihydro-1,4-benzodioxin-6-yl)-3(2H)-furanone (**3r**).* 42.2 mg, 97% yield; white solid; mp 145.6–146.3 °C; R_f = 0.36 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1678, 1593, 1498, 1290, 881, 793 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.34–7.32 (m, 2 H), 6.96–6.94 (m, 1 H), 5.94 (s, 1 H), 4.67 (s, 2 H), 4.35–4.33 (m, 2 H), 4.31–4.29 (m, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 201.9, 186.5, 147.7, 143.7, 122.0, 121.1, 117.8, 116.2, 100.3, 75.4, 64.6, 64.1; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{11}O_4$, 219.0652; found, 219.0652.

*5-(2-Furyl)-3(2H)-furanone (**3s**).* 30.0 mg, quant; white solid; mp 93.2–94.1 °C; R_f = 0.46 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1685, 1627, 1533, 1462, 782 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 1.7, 0.7 Hz, 1 H), 7.09 (dd, *J* = 3.6, 0.7 Hz, 1 H), 6.60 (dd, *J* = 3.6, 1.7 Hz, 1 H), 5.95 (s, 1 H), 4.64 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 201.3, 176.9, 146.9, 144.8, 115.0, 112.5, 100.5, 74.9; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_8H_7O_3$, 151.0390; found, 151.0390.

*5-(2-Thienyl)-3(2H)-furanone (**3t**).* 33.0 mg, 99% yield; pale yellow solid; mp 89.8–90.4 °C; R_f = 0.46 (*n*-hexane/EtOAc = 1:1); IR (KBr): 1673, 1578, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 3.8, 1.1 Hz, 1 H), 7.65 (dd, *J* = 5.0, 1.1 Hz, 1 H), 7.20 (dd, *J* = 5.0, 3.8 Hz, 1 H), 5.92 (s, 1 H), 4.68 (s, 2 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 201.2, 181.1, 131.9, 131.6, 130.7, 128.5, 100.4, 75.3; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_8H_7O_2S$, 167.0161; found, 167.0159.

Synthesis of Bullatenone 9.[5a] To a solution of 5-phenyl-3(2*H*)-furanone **3a** (0.160 g, 1.0 mmol) in dry MeCN (5 mL) was added methyl iodide (0.16 mL, 2.5 equiv) at 0 °C under an argon atmosphere. Next, NaH (0.10 g of a 60% dispersion in oil, 2.5 equiv) was added in one portion at 0 °C. The resulting mixture was stirred at 0 °C for 1 h and at room temperature for another 1 h. The mixture was treated with water and extracted with EtOAc. The combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1) gave bullatenone **9** as a yellow solid (0.118 g, 63%); mp 61.0–61.5 °C; R_f = 0.48 (*n*-

hexane/EtOAc = 2:1); IR (KBr): 1700, 1606, 1592, 1567, 1173, 779, 693 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.84–7.83 (m, 2 H), 7.58–7.54 (m, 1 H), 7.51–7.48 (m, 2 H), 5.97 (s, 1 H), 1.50 (s, 6 H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 207.0, 183.4, 132.6, 129.2, 128.8 (2C), 127.1 (2C), 98.6, 88.9, 23.1; HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{13}O_2$, 189.0910; found, 189.0909.

Supporting Information. ^1H NMR spectral data for sulfonium salt **2a** in the presence of a half equivalent of K_2CO_3 after varying time (10 min–24 h) and ^1H and ^{13}C NMR spectral data for **2**, **3**, **5, 6** and **9** are shown.

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