JOC Article

Condensation of α-Aroylketene Dithioacetals and 2-Hydroxyarylaldehydes Results in Facile Synthesis of a Combinatorial Library of 3-Aroylcoumarins[#]

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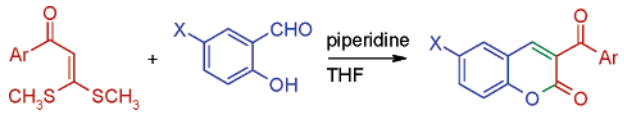

A facile, convenient, efficient, and high yielding synthesis of a combinatorial library of 3-aroylcoumarins has been developed by the condensation of easily available α-aroylketene dithioacetals (AKDTAs) and 2-hydroxybenzaldehydes (salicylaldehydes)/2-hydroxy-1-naphthaldehyde in the presence of catalytic amount of piperidine in THF reflux. The condensation of ferrocene derived α-aroylketene dithioacetal and 2-hydroxybenzaldehyde furnished coumarin installed on a ferrocene platform.

Introduction

The coumarins (2*H*-chromen-2-ones, 2*H*-1-benzopyran-2-ones) are among the best-known oxygen heterocycles, well represented as a structural motif in numerous natural products.[1] Several coumarins have found application in technological[2] and therapeutic[3] fields. Naturally, there has been a continuous effort to develop new, convenient, and versatile syntheses of coumarins with defined structural features. Classical routes to coumarins incorporate Pechmann,[4] Knoevenagel,[5] Perkin,[6] Reformatsky,[7] and Wittig[8] condensation reactions. To make these classical reactions efficacious, several variations in terms of catalyst and reaction conditions have been introduced.[9] In recent years versatile coumarin syntheses could be achieved through organopalladium intermediates.[10] A few combinatorial library syntheses of derivatives of this important scaffold have been developed, principally to test their utility as drug candidates.[11] In continuation of our interest in polarized keteneacetals,[12] we now report a conceptually novel route for the synthesis of 3-aroylcoumarins starting from a readily available α-aroylketene dithioacetals (AKDTAs) **1** and the 2-hydroxybenzaldehydes (salicylalde-

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[#] Ketene Acetal Chemistry: Part 4; see ref 12c.

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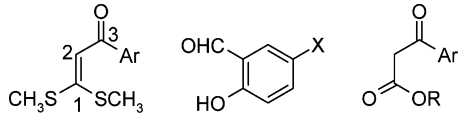
hydes) **2**. Some of the 3-aroylcoumarins-target molecules of the present study-were shown to be efficient triplet sensitizers.[13] Moreover, 3-aroylcoumarins are good Michael acceptors, amenable to further synthetic transformations.[14]

The AKDTAs **1** are three carbon synthons, employed extensively for the synthesis of a wide variety of heterocyclic compounds.[15] They also serve as intermediates for benzo- and heteroaromatic annulations, en route to the synthesis of complex heterocycles.[16] They are essentially masked β-ketoesters **3** with reactivity difference emanating from respective structural features. When required, the ester functionality in **1** can be unmasked through simple hydrolysis.[17] In several reactions the AKDTAs **1** behave as α,β-unsaturated carbonyl compounds, where in, depending on the nucleophile, either 1,2- or 1,4-addition takes place.[16]



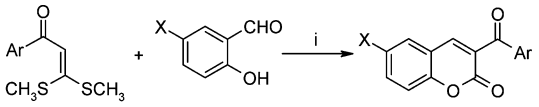
1 **2** **3**

The AKDTAs **1** are polarized alkenes wherein polarization flows from two electron-donating alkylsulfanyl groups on C-1 to the electron-withdrawing carbonyl group on C-2. While C-1 in **1** exhibits electrophilic characteristics, the C-2 shows nucleophilic characteristics. We reasoned that condensation reaction of **1** with the 2-hydroxybenzaldehydes (salicylaldehydes) **2**, molecules having nucleophilic oxygen and electrophilic carbonyl carbon, could result in two-component condensation, and subsequent hydrolysis and dehydration could lead to 3-aroylcoumarins. A wide variety of AKDTAs **1** are easily available and the unknown ones can be prepared readily from substituted acetophenones, carbon disulfide, and an alkylating agent in a single-pot operation.[18] Similarly, a wide variety of 2-hydroxybenzaldehydes **2** can be prepared from corresponding phenols via the Reimer-Tiemann reaction.[19] With leads available in both the aromatic rings, condensation of the AKDTAs **1** with the 2-hydroxybenzaldehydes **2** could lead to the synthesis of a combinatorial library of 3-aroylcoumarins.

Results and Discussion

Indeed, condensation of the AKDTA, 3,3-bis(methylsulfanyl)-1-phenyl-2-propen-1-one **1a** with 2-hydroxybenzaldehyde **2a** took place smoothly in the presence of piperidine in THF reflux to result in the formation of 3-benzoylcoumarin[20] **4a** in 97% yield (Scheme 1; entry 1, Table 1). The condensation of **1a** with **2a** to generate coumarin **4a** was investigated under a variety of conditions (base, solvent, etc.), as a test case, to optimize the yield, and the results are gathered in Table 1. The condensation took place even with a catalytic amount of piperidine (10 mol %; entry 2). Though the condensation reaction with a catalytic amount of piperidine was clean, it took a longer time (48 h) and about 5% of **1a** remained as such. On the other hand, the reaction was relatively fast (8 h) when 1 equiv of piperidine was employed. The reaction did not take place when piperidine in EtOH was used (entry 3). The other secondary amines, pyrrolidine (entry 4) and morpholine (entry 5), gave only poor yield of the desired product **4a**. The reaction

SCHEME 1 [a]



1a-c **2a-e** **4a-l**

1a: Ar = C_6H_5, **1b**: Ar = 4-$CH_3C_6H_4$ **1c**: Ar = 4-ClC_6H_4

2a: X = H **2b**: X = CH_3 **2c**: X = OCH_3 **2d**: X = Cl

4a: X = H, Ar = C_6H_5
4b: X = H, Ar = 4-$CH_3C_6H_4$
4c: X = H, Ar = 4-ClC_6H_4
4d: X = CH_3, Ar = C_6H_5
4e: X = CH_3, Ar = 4-$CH_3C_6H_4$
4f: X = CH_3, Ar = 4-ClC_6H_4
4g: X = OCH_3, Ar = C_6H_5
4h: X = OCH_3, Ar = 4-$CH_3C_6H_4$
4i: X = OCH_3, Ar = 4-ClC_6H_4
4j: X = Cl, Ar = C_6H_5
4k: X = Cl, Ar = 4-$CH_3C_6H_4$
4l: X = Cl, Ar = 4-ClC_6H_4

[a] Reagents and conditions: (i) piperidine 10 mol %, THF reflux, 12−48 h, 74−95%.

TABLE 1. Synthesis of 3-Benzoylcoumarin 4a from 1a (1 mmol) and 2a (1 mmol) Using Different Bases/Conditions

entry	base (equiv)	solvent[a]	yield %
1	piperidine (1.0)	THF	97[b]
2	piperidine (0.1)	THF	94[c]
3	piperidine (1.0)	EtOH	*d*
4	pyrrolidine (1.1)	THF	25[e]
5	morpholine (0.1 or 1.1)	THF	27[e]
6	DBU or Et_3N or DABCO (0.1 or 1.1)	THF	no reaction
7	NaH (1.0)	THF/DMF (10:1)	19[e]
8	K_2CO_3 or NaOH (aq, 1.1), TBAB (0.05)	DCM	no reaction
9	basic alumina or KF/neutral alumina	neat[f]	no reaction[g]

[a] All solution-phase reactions were conducted at reflux temperature of the solvent used. [b] After 8 h reflux. [c] Based on the recovered **1a** (5%) after 48 h reflux. [d] Anticipated coumarin **4a** did not form, instead the reaction furnished the chalcone **16a** (vide infra). [e] After 48 h reflux; yield based on recovered **1a**. [f] The reaction was conducted under microwave irradiation (2.45 GHz; 370 W, 2 min). [g] Extensive decomposition of **1a** took place.

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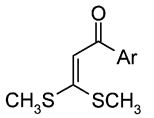
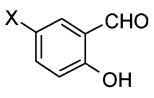
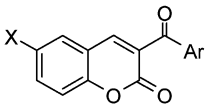
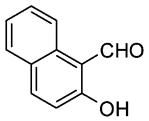
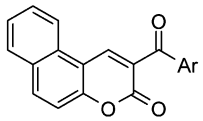
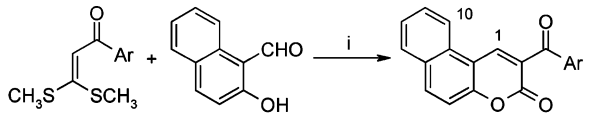
TABLE 2. Synthesis of 3-Aroylcoumarins from AKDTAs and 2-Hydroxyarylaldehydes in Piperidine (Catalytic) and THF Reflux

Entry	α-Aroylketene dithioacetal	2-Hydroxy arylaldehyde	3-Aroyl coumarin	Yield %
				
1	**1a**: Ar = C_6H_5	**2a**: X = H	**4a**: Ar = C_6H_5, X = H	94
2	**1b**: Ar = 4-$CH_3C_6H_4$	**2a**: X = H	**4b**: Ar = 4-$CH_3C_6H_4$, X = H	90
3	**1c**: Ar = 4-ClC_6H_4	**2a**: X = H	**4c**: Ar = 4-ClC_6H_4, X = H	95
4	**1a**: Ar = C_6H_5	**2b**: X = CH_3	**4d**: Ar = C_6H_5, X = CH_3	80
5	**1b**: Ar = 4-$CH_3C_6H_4$	**2b**: X = CH_3	**4e**: Ar = 4-$CH_3C_6H_4$, X = CH_3	80
6	**1c**: Ar = 4-ClC_6H_4	**2b**: X = CH_3	**4f**: Ar = 4-ClC_6H_4, X = CH_3	92
7	**1a**: Ar = C_6H_5	**2c**: X = OCH_3	**4g**: Ar = C_6H_5, X = OCH_3	94
8	**1b**: Ar = 4-$CH_3C_6H_4$	**2c**: X = OCH_3	**4h**: Ar = 4-$CH_3C_6H_4$, X = OCH_3	74
9	**1c**: Ar = 4-ClC_6H_4	**2c**: X = OCH_3	**4i**: Ar = 4-ClC_6H_4, X = OCH_3	93
10	**1a**: Ar = C_6H_5	**2d**: X = Cl	**4j**: Ar = C_6H_5, X = Cl	88
11	**1b**: Ar = 4-$CH_3C_6H_4$	**2d**: X = Cl	**4k**: Ar = 4-$CH_3C_6H_4$, X = Cl	92
12	**1c**: Ar = 4-ClC_6H_4	**2d**: X = Cl	**4l**: Ar = 4-ClC_6H_4, X = Cl	85
				
13	**1a**: Ar = C_6H_5	**5**	**6a**: Ar = C_6H_5	89
14	**1b**: Ar = 4-$CH_3C_6H_4$		**6b**: Ar = 4-$CH_3C_6H_4$	80
15	**1c**: Ar = 4-ClC_6H_4		**6c**: Ar = 4-ClC_6H_4	85

did not take place when non-nuclophilic *tert*-amine bases such as 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), 1,4-diazabicyclo-[2,2,2]octane (DABCO) or triethylamine (TEA) was employed either in catalytic or in stoichiometric quantities (entry 6). Yield of the desired product was poor when the strong base NaH was employed (entry 7). There was no condensation when the two-phase reaction was conducted with a mild base (aq K_2CO_3) or a strong base (aq NaOH) under the biphasic conditions (DCM, H_2O) in the presence of a catalytic amount of tetrabutylammonium bromide (TBAB; entry 8). The microwave mediated heating under neat conditions by adsorbing the two reactants on basic alumina or 5% KF on neutral alumina led to extensive decomposition of the reaction mixture (entry 9). Thus, it is clear from the aforementioned experiments that the best yield of coumarin **4a** could be obtained by employing piperidine as base and THF as solvent.

To test generality of the condensation and to realize synthesis of a small combinatorial library of 3-aroylcoumarins, three AKDTAs **1a**−**c** were reacted with four 2-hydroxybenzaldehydes **2a**−**d** to furnish twelve coumarins **4a**−**l** in good yields (Scheme 1 and Table 2) by using piperidine (10 mol %) as base in THF reflux. All the coumarins **4a**−**l** were characterized by analytical and spectral data.[21] The ^{1}H NMR spectra of the coumarins **4a**−**l** displayed a characteristic singlet for the olefinic hydrogen at about δ 8.0. Condensation of three AKDTAs **1a**−**c** with

SCHEME 2 [a]



1a-c **5** **6a-c**

1a: Ar = C_6H_5 **6a**: Ar = C_6H_5
1b: Ar = 4-$CH_3C_6H_4$ **6b**: Ar = 4-$CH_3C_6H_4$
1c: Ar = 4-ClC_6H_4 **6c**: Ar = 4-ClC_6H_4

[a] Reagents and conditions. (i) piperidine 10 mol %, THF reflux, 12−36 h, 80−89%.

2-hydroxy-1-naphthaldehyde **5** furnished 2-aroyl-3*H*-benzo[*f*]-chromen-3-ones **6a**−**c** in good yields (Scheme 2).[14c,20] The ^{1}H NMR spectra of the coumarins **6a**−**c** displayed a singlet for the C-1 olefinic hydrogen at about δ 8.8 and doublet for the C-10 peri-hydrogen in the bay region at δ 8.2.

Since the 3-aroylcoumarin derivatives exhibit characteristics of triplet sensitizers, particularly when there is extended conjugation to aromatic rings, we next planned the synthesis of the 3-aroylcoumarins incorporating naphthalene ring or biphenyl group in the aroyl portion of the target coumarins. Following the procedure described above, we have conducted the condensation of the AKDTAs **7**, **9**,[22] and **11** with 2-hydroxybenzaldehyde **2a** to furnish the 3-aroylcoumarins **8**, **10**, and **12** in good yields (Scheme 3). The coumarins **8**, **10**, and **12** were characterized on the basis of spectral data which matched well with the parent molecules **4**. The AKDTAs **7** and **11** were prepared from the corresponding aryl methyl ketones, carbon disulfide, and dimethyl sulfate. The ^{1}H NMR spectrum

(21) Some of the 3-aroylcoumarins prepared in this study are known compounds. See refs 13, 14c, and 20; however, see Experimental Section for complete spectral data for all the products prepared in this study.

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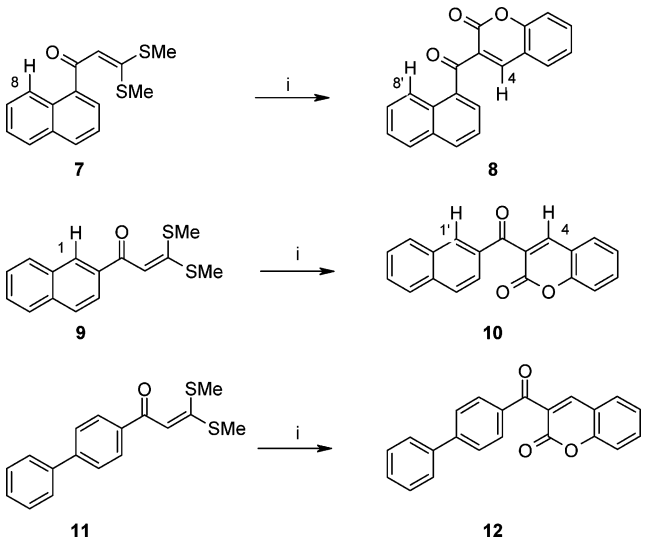
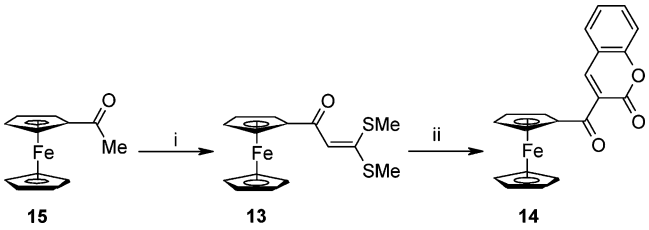
SCHEME 3 [a]



[a] Reagents and conditions: (i) piperidine 10 mol %, 2-hydroxybenzaldehyde 1 equiv, THF reflux, 10−24 h, 69−92%.

SCHEME 4 [a]



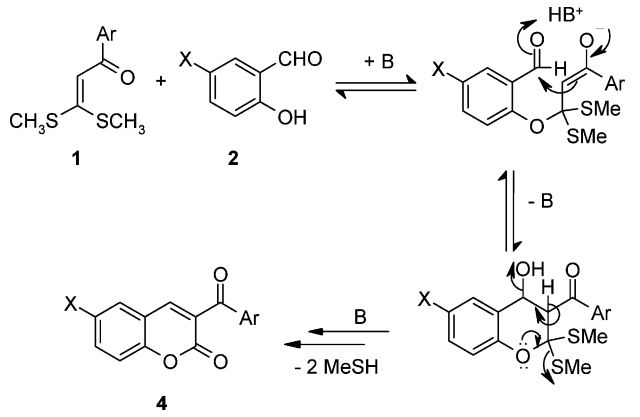
[a] Reagents and conditions: (i) (a) CS_2, *t*-BuONa, THF, 0 °C, 90 min; (b) Me_2SO_4, 0 °C, 90 min, 67%; (ii) piperidine 10 mol %, 2-hydroxybenzaldehyde, THF reflux, 9 h, 85%.

of the coumarin, 3-(1-naphthylcarbonyl)-2*H*-2-chromenone **8** displayed a singlet for the C-4 olefinic hydrogen at δ 8.2 in tandem with other coumarins, whereas the C-8′ peri-hydrogen in the naphthalene ring shifted to downfield and it appeared at δ 8.52 (cf. δ 8.44 for C-8-H in **7**) indicating that the C-8′ peri-hydrogen is having CH−O type hydrogen bonding interactions with the oxygen of the carbonyl group. Similarly, the ^{1}H NMR spectrum of 3-(2-naphthylcarbonyl)-2*H*-2-chromenone **10** displayed a singlet for the C-1′ peri-hydrogen at δ 8.56 (cf. δ 8.40 for C-1-H in **9**).

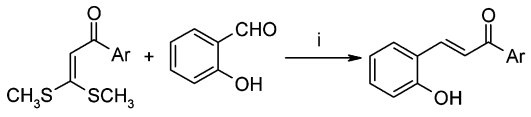
As a next attempt, we have installed coumarin motif on the ferrocene platform following the method presently developed. The ferrocene based AKDTA **13** was smoothly transformed into coumarin 3-η^5-ferrocenoyl-2*H*-2-chromenone **14** by condensation with 2-hydroxybenzaldehyde **2a** in the presence of a catalytic amount of piperidine (Scheme 4). The ^{1}H NMR and ^{13}C NMR spectral data of the coumarin portion of **14** matched well with the parent coumarins **4.** The AKDTA **13** was prepared from acetyl ferrocene **15** by reaction with carbon disulfide and sodium *tert*-butoxide followed by alkylation with dimethyl sulfate.

A possible mechanism for the formation of coumarins **4** from the AKDTAs **1** and the 2-hydroxybenzaldehydes **2** is given in Scheme 5. Conjugate addition (Michael reaction) of the anion generated from **2** to **1** would result in enolate anion, which participates in subsequent intramolecular aldol condensation. Dehydration followed by hydrolysis of the thioacetal assisted

SCHEME 5



SCHEME 6 [a]



1a: Ar = C_6H_5, **16a**: Ar = C_6H_5
1b: Ar = 4-$CH_3C_6H_4$ **16b**: Ar = 4-$CH_3C_6H_4$

[a]Reagents and conditions: (i) piperidine, EtOH reflux, 10 h, 82−90%.

by neighboring group effect of oxygen would furnish coumarins **4** in a multistep process. Even though product formation can be explained by concerted cycloaddition involving **1** and enolate form of **2**, in view of the polar nature of **1** and the requirement to dearomatize **2** before cycloaddition, the concerted process is unlikely.

When the reaction of the AKDTA **1a** with 2-hydroxybenzaldehyde **2a** was conducted in ethanol reflux instead of in THF reflux, the reaction furnished known chalcone[23] **16a** in 90% yield, instead of coumarin **4a** (entry 3, Table 1 and Scheme 6). Similarly, the reaction of **1b** with **2a** furnished chalcone[24] **16b** instead of coumarin **4b**. Evidently, in ethanol reflux **1a** was reverting to acetophenone before aldol condensation with 2-hydroxybenzaldehyde **2a**.[25]

Conclusions

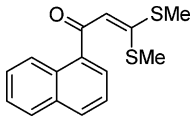
From this investigation we have shown that facile synthesis of 3-aroylcoumarins can be achieved under mild conditions from easily available AKDTAs and 2-hydroxybenzaldehydes. The condensation reaction works well with a catalytic amount of piperidine in THF reflux. This scheme offers a good scope for the synthesis of a wide variety of 3-aroylcoumarins. Considering that the aroylacetic esters, which are traditional reacting partners for 2-hydroxybenzaldehydes in the 3-aroylcoumarin syntheses are difficult to prepare,[26] present procedure is a significant

(23) William, E. T.; Cheng-I, M. L. *J. Am. Chem. Soc.* **1973**, *95*, 4426−4428.
(24) Le Fevre, C. G; Le Fevre, R. J. W.; Pearson, J. *J. Chem. Soc.* **1934**, 37−43.
(25) (a) Ireland, R. E.; Marshall, J. A. *J. Am. Chem. Soc.* **1959**, *81*, 6336−6337. (b) Apparao, S.; Rahman, A.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1982**, *23*, 971−974.
(26) (a) Hauser, C. R.; Hudson, B. E., Jr. *Org. React.* **1942**, *1*, 266−289. (b) Schaefer, J. P.; Bloomfield, J. J. *Org. React.* **1967**, *15*, 1.(c) Shiosaki, K.; Fels, G.; Rapoport, H. *J. Org. Chem.* **1981**, *46*, 3230−3234. (d) Katritzky, A. R.; Wang, Z.; Wang, M.; Wilkerson, C. R.; Hall, C. D.; Akhmedov, N. G. *J. Org. Chem.* **2004**, *69*, 6617−6622.

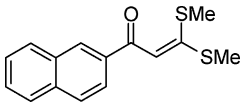
improvement over existing methods. We are now concentrating on the synthesis of some 3-aroylcoumarins with tailored properties.

Experimental Section

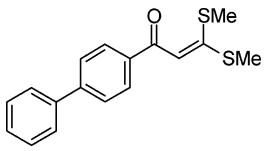
General Procedure for the Preparation of 1-Aryl-3,3-bis-(methylsulfanyl)-2-propen-1-ones. To a stirred suspension of freshly prepared sodium *tert*-butoxide (3.0 g, 31 mmol) in dry THF (7 mL) at 0 °C a solution of aryl ketones (9.0 mmol) and carbon disulfide (84 mg, 0.66 mL, 11 mmol) in dry THF (10 mL) was added through a pressure equalizer funnel, and the mixture was vigorously stirred at 0 °C for 90 min. Appearance of reddish solid in the reaction medium indicated the formation of disodium salt of 1-aryl-3,3-bissulfanyl-2-propen-1-ones. To this suspension, a solution of dimethyl sulfate (1.2 mL, 10.8 mmol) in dry THF (5 mL) was carefully added dropwise during 10 min at 0 °C, and the reaction mixture was allowed to stir at 0 °C for 90 min. After completion of the reaction (TLC; hexanes/EtOAc = 8:2), the mixture was transferred into a 100 mL beaker containing 50 g of crushed ice, and the contents of the beaker were stirred well. A light yellow colored solid formed, was filtered, and was washed with water (20 mL × 3). The crude solid was recrystallized from 5% DCM in hexanes or EtOH. Physical, spectral, and analytical data of the hitherto unknown AKDTAs are subsequently given.



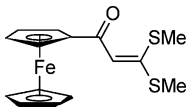
3,3-Bis(methylsulfanyl)-1-(1-naphthyl)-2-propen-1-one 7. Following the general procedure described above, the reaction of 1-acetylnaphthalene (1.53 g, 9.0 mmol) with carbon disulfide (0.64 mL, 10.8 mmol), sodium *tert*-butoxide (3.1 g, 31.2 mmol) and freshly distilled dimethyl sulfate (1.0 mL, 10.8 mmol) furnished 1.47 g of 3,3-bis(methylsulfanyl)-1-(1-naphthyl)-2-propen-1-one **7** in 60% yield as light yellow colored crystals after recrystallization: mp 98−102 °C (ethanol). UV λ_{max} (MeOH): 350 nm (log ϵ = 4.6), 281 nm (log ϵ = 4.33). IR (KBr) 3053, 1608, 1505, 1478, 1236, 1187, 783 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, J = 9.0 Hz, 1H), 7.42−7.95 (m, 6H), 6.54 (s, 1H,), 2.55 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.4, 166.1, 139.9, 133.7, 130.8, 130.1, 128.2, 126.9, 126.1, 125.9, 125.8, 124.6, 113.5, 17.2, 14.9. Anal. Calcd for $C_{15}H_{14}OS_2$: C, 65.66; H, 5.14. Found: C, 65.23; H, 5.14.



3,3-Bis(methylsulfanyl)-1-(2-naphthyl)-2-propen-1-one 9. Following the general procedure described above, the reaction of 2-acetylnaphthalene (1.5 g, 9.0 mmol), carbon disulfide (0.65 mL, 11 mmol), sodium *tert*-butoxide (3.0 g, 31.0 mmol), and freshly distilled dimethyl sulfate (1.0 mL, 10.8 mmol) furnished 1.74 g of 3,3-bis(methylsulfanyl)-1-(2-naphthyl)-2-propen-1-one **9** in 70% yield as light yellow colored crystals after recrystallization: mp 79−81 °C (5% DCM in hexanes). UV λ_{max} (MeOH): 356 nm (log ϵ = 4.19), 258 nm (log ϵ = 4.01). IR (KBr): 2915, 1609, 1480, 1426, 1256, 1183, 790, 567 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.51−8.03 (m, 6H), 6.91 (s, 1H), 2.60 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.5, 166.4, 136.7, 134.9, 132.6, 129.3, 128.4, 128.3, 127.8, 127.7, 126.5, 124.3, 109.6, 17.4, 15.1. Anal. Calcd for $C_{15}H_{14}OS_2$: C, 65.66; H, 5.14. Found: C, 65.64; H, 5.07.

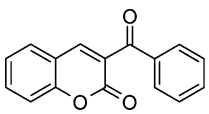


1-Biphenyl-4-yl-3,3-bismethylsulfanyl-2-propen-1-one 11. Following the general procedure described above, the reaction of 4-phenylacetophenone (1.75 g, 9.0 mmol), carbon disulfide (0.66 mL, 11 mmol), sodium *tert*-butoxide (3.0 g, 31 mmol), and freshly distilled dimethyl sulfate (1.0 mL, 10.8 mmol) furnished 1.75 g of 1-biphenyl-4-yl-3,3-bismethylsulfanyl-2-propen-1-one **11** in 65% yield as light yellow colored crystals after recrystallization: mp 112−114 °C (ethanol) (lit.[18a] 122 °C. UV λ_{max} (MeOH): 356 nm (log ϵ = 3.75), 287 nm (log ϵ = 3.6). IR (KBr) 2971, 1612, 1474, 1237, 755 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, J = 8.7 Hz, 2H), 7.35−7.70 (m, 7H), 6.81 (s, 1H), 2.58 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.1, 166.4, 144.4, 140.1, 138.0, 128.8, 128.3, 127.9, 127.2, 127.1, 109.4, 17.4, 15.0. Anal. Calcd for $C_{17}H_{16}OS_2$: C, 67.96; H, 5.37. Found: C, 67.96; H, 5.35.

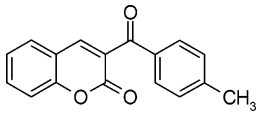


3,3-Bis(methylsulfanyl)-1-η^5-ferrocenyl-2-propen-1-one 13. Following the general procedure described above, the reaction of acetylferrocene (2 g, 9.0 mmol), carbon disulfide (0.64 mL, 10.8 mmol), sodium *tert*-butoxide (3.05 g, 31.05 mmol), and freshly distilled dimethyl sulfate (1.0 mL, 10.8 mmol) furnished 1.84 g of 3,3-bis(methylsulfanyl)-1-η^5-ferrocenyl-2-propen-1-one **13** in 67% yield as brown powder after recrystallization: mp 112−115 °C (ethanol). UV λ_{max} (MeOH): 483 nm (log ϵ = 3.01), 392 nm (log ϵ = 3.03), 295 nm (log ϵ = 2.91), 240 nm (log ϵ = 3.02). IR (KBr): 2984, 1600, 1482, 1375, 1243, 1093, 761, 624 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.35 (s, 1H), 4.78 (br s, 2H), 4.45 (br s, 2H), 4.13 (br s, 5H), 2.52 (br s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.8, 161.4, 111.8, 82.0, 72.1, 70.3, 69.5, 17.2, 15.4. Anal. Calcd for $C_{15}H_{16}OS_2Fe$: C, 54.22; H, 4.85. Found: C, 54.19; H, 4.91.

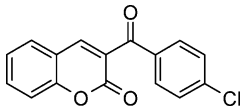
General Procedure for the Preparation of 3-Aroyl Coumarins: To a stirred solution of 2-hydroxyarylaldehydes (**2a**−**e**, 2.2 mmol) and 1-aryl-3,3-bis(methylsulfanyl)-2-propen-1-ones (**1a**−**c**, 2.2 mmol) in dry THF (15 mL), piperidine (19 mg, 22 μL, 0.22 mmol) in dry THF (5 mL) was added dropwise over 5 min at room temperature under a blanket of dry nitrogen. The reaction mixture was heated at reflux in a preheated oil bath (80 °C) for 12−15 h for completion of the reaction (TLC; hexanes/EtOAc = 8:2). The reaction mixture was then diluted with dichloromethane (25 mL), and the organic solution was washed sequentially with water (3 × 25 mL) and brine (2 × 10 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure resulted in crude 3-aroylcoumarins as gummy liquid. The crude product was subjected to column chromatography on SiO_2 (25 g; 15 cm × 1 cm) using increasing amounts of ethyl acetate in hexanes as eluent. Evaporation of the pooled fractions having the required 3-aroylcoumarins resulted in free flowing solids. Analytical samples were obtained by crystallization from EtOH or DCM/hexanes. In some reactions, a small amount (≤5%) of AKDTAs were recovered from the reaction mixture. In cases where AKDTAs were recovered, yields of the coumarins have been computed on the basis of recovered starting material.



3-Benzoyl-2*H*-2-chromenone 4a. Following the general procedure described previously, the reaction of 2-hydroxybezaldehyde (salicyladehyde) **2a** (268 mg, 2.2 mmol), 3,3-bis(methylsulfanyl)-1-phenyl-2-propen-1-one **1a** (500 mg, 2.2 mmol), and peperidine (19 mg, 0.22 mmol) furnished 533 mg of 3-benzoyl-2*H*-2-chromenone **4a** in 94% yield as colorless crystals after column purification and recrystallization: mp 134−136 °C (ethanol) (lit.[13] 137−139 °C). UV λ_{max} (MeOH): 290 nm (log ϵ = 3.98), 253 nm (log ϵ = 3.82). IR (KBr): 3063, 1719, 1607, 1243, 755 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.88 (d, J = 8.1 Hz, 2H), 7.51−7.69 (m, 3H), 7.49 (d, J = 8.1 Hz, 2H), 7.32−7.49 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.6 158.4, 154.7, 145.4, 136.2, 133.8, 133.6, 129.5, 129.2, 128.6, 126.9, 124.9, 118.1, 116.0.

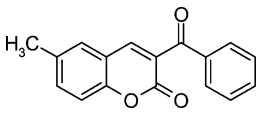


3-(4-Methylbenzoyl)-2*H*-2-chromenone 4b. Following the general procedure described above, the reaction of 2-hydroxybenzaldehyde **2a** (256 mg, 2.1 mmol), 1-(4-methylphenyl)-3,3-bis(methylsulfanyl)-2-propen-1-one **1b** (500 mg, 2.1 mmol), and peperidine (18 mg, 0.2 mmol) furnished 498 mg of 3-(4-methylbenzoyl)-2*H*-2-chromenone **4b** in 90% yield as colorless crystals after column purification and recrystallization: mp 132−134 °C (5% DCM in hexanes) (lit.[20c] 133−134 °C). UV (MeOH): λ_{max} 288 nm (log ϵ = 4.08). IR (KBr): 3075, 1713, 1606, 1241, 762 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.55−7.68 (m, 2H), 7.31−7.43 (m, 2H), 7.27 (d, J = 8.4 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.2, 158.3, 155.1, 145.0, 144.9, 133.6, 133.5, 129.8, 129.3, 129.1, 126.9, 124.9, 118.2, 116.9. 21.9.

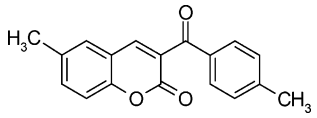


3-(4-Chlorobenzoyl)-2*H*-2-chromenone 4c. Following the general procedure described above, the reaction of 2-hydroxybenzaldehyde **2a** (232 mg, 1.9 mmol), 1-(4-chlorophenyl)-3,3-bis(methylsulfanyl)-2-propen-1-one **1c** (500 mg, 1.9 mmol), and peperidine (18 mg, 0.2 mmol) furnished 512 mg of 3-(4-chlorobenzoyl)-2*H*-2-chromenone **4c** in 95% yield as colorless crystals after column purification and recrystallization: mp above 200 °C (5% DCM in hexanes). UV (MeOH): λ_{max} 289 nm(log ϵ = 4.10). IR (KBr): 3059, 1713, 1656, 1608, 1237, 754 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 7.3 Hz, 1H), 7.68 (t, J = 7.3 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.35−7.43 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.8, 157.5, 154.1, 145.5, 138.9, 134.4, 133.2, 130.7, 129.5, 128.4, 125.8, 124.5, 117.9, 116.0. Anal. Calcd for $C_{16}H_9O_3Cl$: C, 67.50; H, 3.19. Found: C, 67.52; H, 3.16.

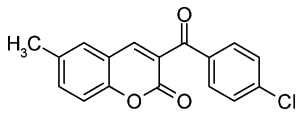
3-Benzoyl-6-methyl-2*H*-2-chromenone 4d. Following the general



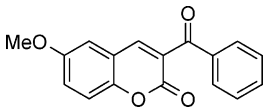
procedure described above, the reaction of 2-hydroxy-5-methylbenzaldehyde **2b** (299 mg, 2.2 mmol), 3,3-bis(methylsulfanyl)-1-phenyl-2-propen-1-one **1a** (500 mg, 2.2 mmol), and peperidine (19 mg, 0.22 mmol) furnished 464 mg of 3-benzoyl-6-methyl-2*H*-2-chromenone **4d** in 80% yield after column purification as colorless crystals: mp 174 °C (5% DCM in hexanes) (lit.[20a] 174 °C). UV (MeOH): λ_{max} 341 nm (log ϵ = 3.65), 292 nm (log ϵ = 4.03). IR (KBr): 3090, 2993, 1721, 1656, 1605, 1248, 686 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.88 (d, J = 7.8 Hz, 2H), 7.28−7.64 (m, 6H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.8, 152.9, 145.5, 136.3, 134.8, 134.7, 133.7, 129.6, 128.8, 128.6, 126.9, 117.9, 116.6, 115.4, 20.7. Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.35; H, 4.55.



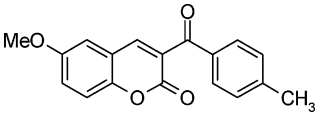
6-Methyl-3-(4-methylbenzoyl)-2*H*-2-chromenone 4e. Following the general procedure described above, the reaction of 2-hydroxy-5-methylbenzaldehyde **2b** (285 mg, 2.1 mmol), 1-(4-methylphenyl)-3,3-bis(methylsulfanyl)-2-propen-1-one **1b** (500 mg, 2.1 mmol), and peperidine (18 mg, 0.2 mmol) furnished 467 mg of 6-methyl-3-(4-methylbenzoyl)-2*H*-2-chromenone **4e** in 80% yield as colorless crystals after column purification: mp 158−160 °C (5% DCM in hexanes). UV (MeOH): λ_{max} 334 nm (log ϵ = 3.59), 290 nm (log ϵ = 4.00). IR (KBr): 3061, 2917, 1715, 1651, 1605, 1252, 781 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.78 (d, J = 7.8 Hz, 2H), 7.25−7.46 (m, 5H), 2.43 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.4, 158.9, 152.9, 145.1, 144.8, 134.7, 134.6, 133.72, 129.8, 129.3, 128.8, 127.2, 117.9, 116.6, 21.8, 20.7. Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.62; H, 5.13.



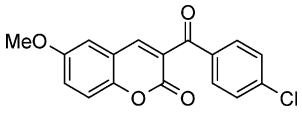
3-(4-Chlorobenzoyl)-6-methyl-2*H*-2-chromenone 4f. Following the general procedure described above, the reaction of 2-hydroxy-5-methylbenzaldehyde **2b** (258 mg, 1.9 mmol), 1-(4-chlorophenyl)-3,3-bis(methylsulfanyl)-2-propen-1-one **1c** (500 mg, 1.9 mmol), and peperidine (17 mg, 0.2 mmol) furnished 520 mg of 3-(4-chlorobenzoyl)-6-methyl-2*H*-2-chromenone **4f** in 92% yield as colorless crystals after column purification: mp above 200 °C (ethanol). UV (MeOH): λ_{max} 336 nm (log ϵ = 3.69), 291 nm (log ϵ = 4.08). IR (KBr): 3062, 2917, 1713, 1675, 1605, 1243, 765 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.48−7.31 (m, 5H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.2, 158.2, 152.4, 145.5, 139.6, 134.5, 134.4, 134.2, 130.4, 128.5, 128.4, 125.7, 117.3, 116.1, 20.2. Anal. Calcd for $C_{17}H_{11}O_3Cl$: C, 68.35; H, 3.71. Found: C, 68.41; H, 3.81.



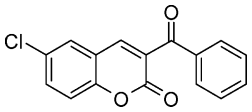
3-Benzoyl-6-methoxy-2*H*-2-chromenone 4g. Following the general procedure described above, the reaction of 2-hydroxy-5-methoxybenzaldehyde **2c** (335 mg, 2.2 mmol), 3,3-bis(methylsulfanyl)-1-phenyl-2-propen-1-one **1a** (500 mg, 2.2 mmol) and peperidine (19 mg, 0. 22 mmol) furnished 579 mg of 3-benzoyl-6-methoxy-2*H*-2-chromenone **4** g in 94% yield as colorless crystals after column purification: mp 160−162 °C (5% DCM in hexanes). UV (MeOH): λ_{max} 362 nm (log ϵ = 3.77), 289 nm (log ϵ = 4.21), 248 nm (log ϵ = 4.2). IR (KBr): 3082, 2934, 1710, 1650, 1603, 1249, 686 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.15−7.65 (m, 6H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.7, 158.7, 156.3, 149.2, 145.2, 136.2, 133.7, 129.7, 128.5, 127.7, 121.7, 118.4, 117.9, 110.6, 55.9.



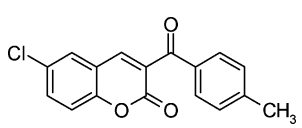
6-Methoxy-3-(4-methylbenzoyl)-2*H*-2-chromenone 4h. Following the general procedure described above, the reaction of 2-hydroxy-5-methoxybenzaldehyde **2c** (320 mg, 2.1 mmol), 1-(4-methylphenyl)-3,3-bis(methylsulfanyl)-2-propen-1-one **1b** (500 mg, 2.1mmol), and peperidine (18 mg, 0.21 mmol) furnished 456 mg of 6-methoxy-3-(4-methylbenzoyl)-2*H*-2-chromenone **4h** in 74% yield as colorless crystals after column purification and recrystallization: mp 174−176 °C (ethanol). UV (MeOH): λ_{max} 361 nm (log ϵ = 3.64), 287 nm (log ϵ = 4.20). IR (KBr): 3079, 2963, 1710, 1650, 1569, 1256, 748 cm^{-1}.; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.21−7.37 (m, 5H), 3.86 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.3, 158.7, 156.3, 149.2, 144.9, 144.8, 133.6, 129.8, 129.3, 127.5, 121.5, 118.5, 117.9, 110.5, 55.9, 21.8. Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.41; H, 4.76.



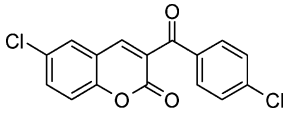
3-(4-Chlorobenzoyl)-6-methoxy-2*H*-2-chromenone 4i. Following the general procedure described above, the reaction of 2-hydroxy-5-methoxybenzaldehyde **2c** (289 mg, 1.9 mmol), 1-(4-chlorophenyl)-3,3-bis(methylsulfanyl)-2-propen-1-one **1c** (500 mg, 1.9 mmol) and peperidine (17 mg, 0.2 mmol) furnished 554 mg of 3-(4-chlorobenzoyl)-6-methoxy-2*H*-2-chromenone **4i** in 93% yield as colorless crystals after column purification and recrystallization: mp above 200 °C (ethanol). UV (MeOH): λ_{max} 350 nm (log ϵ = 3.68), 287 nm (log ϵ = 4.17), 256 nm (log ϵ = 4.22). IR (KBr): 3123, 2940, 1706, 1625, 1581, 1262, 780 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.22−7.49 (m, 5H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.1, 157.8, 155.9, 148.7, 145.4, 134.1, 130.4, 128.4, 128.5, 125.7, 121.6, 117.9, 117.4, 110.3, 55.4. Anal. Calcd for $C_{17}H_{11}O_4Cl$: C, 64.88; H, 3.52. Found: C, 64.38; H, 3.75.



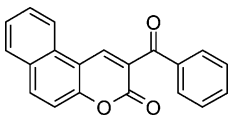
3-Benzoyl-6-chloro-2*H*-2-chromenone 4j. Following the general procedure described above, the reaction of 5-chloro-2-hydroxybenzaldehyde **2d** (344 mg, 2.2 mmol), 3,3-bis(methylsulfanyl)-1-phenyl-2-propen-1-one **1a** (500 mg, 2.2 mmol), and peperidine (19 mg, 0.22 mmol) furnished 549 mg of 3-benzoyl-6-chloro-2*H*-2-chromenone **4j** in 88% yield as colorless crystals after column purification and recrystallization: mp 162−164 °C (ethanol) (lit.[20b] 163 °C). UV (MeOH): λ_{max} 336 nm (log ϵ = 3.96), 284 nm (log ϵ = 4.33). IR (KBr): 3050, 1725, 1635, 1237, 683 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.53−7.62 (m, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.43 (br s, 1H), 7.33 (t, J = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.6, 157.3, 153.2, 143.5, 136.0, 133.9, 133.2, 130.2, 129.6, 128.6, 126.7, 128.2, 119.3, 118.4. Anal. Calcd for $C_{16}H_9O_3Cl$: C, 67.50; H, 3.36. Found: C, 67.45; H, 3.36.



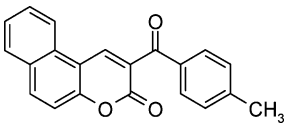
6-Chloro-3-(4-methylbenzoyl)-2*H*-2-chromenone 4k. Following the general procedure described above, the reaction of 5-chloro-2-hydroxybenzaldehyde **2d** (329 mg, 2.1 mmol), 1-(4-methylphenyl)-3,3-bis(methylsulfanyl)-2-propen-1-one **1b** (500 mg, 2.1 mmol), and peperidine (18 mg, 0.2 mmol) furnished 575 mg of 6-chloro-3-(4-methylbenzoyl)-2*H*-2-chromenone **4k** in 92% yield as colorless crystals after column purification and recrystallization: mp above 200 °C (ethanol). UV (MeOH): λ_{max} 334 nm (log ϵ = 3.51), 383 nm (log ϵ = 3.97). IR (KBr): 3104, 2993, 1725, 1650, 1606, 1287, 775 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.54−7.58 (m, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.4 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.4, 157.5, 153.2, 144.9, 143.2, 133.5, 133.2, 130.2, 129.8, 129.4, 128.9, 128.1, 119.4, 118.4, 21.9. Anal. Calcd for $C_{17}H_{11}O_3Cl$: C, 68.35; H, 3.71. Found: C, 68.47; H, 3.76.



6-Chloro-3-(4-chlorobenzoyl)-2*H*-2-chromenone 4l. Following the general procedure described above, the reaction of 5-chloro-2-hydroxybenzaldehyde **2d** (297 mg, 1.9 mmol), 1-(4-chlorophenyl)-3,3-bis(methylsulfanyl)-2-propen-1-one **1c** (500 mg, 1.9 mmol), and peperidine (18 mg, 0.2 mmol) furnished 513 mg of 6-chloro-3-(4-chlorobenzoyl)-2*H*-2-chromenone **4l** in 85% yield as colorless crystals after column purification and recrystallization: mp above 200 °C (ethanol). UV (MeOH): λ_{max} 286 nm (log ϵ = 4.22), 238 nm (log ϵ = 4.15). IR (KBr): 3050, 2993, 1725, 1635, 1243, 765 cm^{-1}. ^{1}H NMR (300 MHz, DMSO): δ 8.37 (s, 1H), 7.95 (dd, J = 8.1, 2.1 Hz, 2H), 7.94 (br s, 1H), 7.74 (dd, J = 8.7, 1.8 Hz, 1H), 7.58 (br d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.7 Hz, 1H). ^{13}C NMR (75 MHz, DMSO): δ 190.2, 157.5, 152.8, 144.4, 138.9, 134.6, 133.0, 131.3, 128.7, 128.6, 128.5, 126.9, 119.6, 118.2. Anal. Calcd for $C_{16}H_8O_3Cl_2$: C, 60.22; H, 2.52. Found: C, 59.98; H, 2.50.

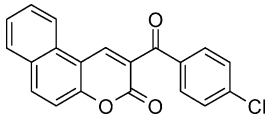


2-Benzoyl-3*H*-benzo[*f*]chromen-3-one 6a. Following the general procedure described above, the reaction of 2-hydroxy-1-naphthaldehyde **5** (343 mg, 2.2 mmol), 3,3-bis(methylsulfanyl)-1-phenyl-2-propen-1-one **1a** (500 mg, 2.2 mmol), and peperidine (19 mg, 0.22 mmol) furnished 587 mg of 2-benzoyl-3*H*-benzo[*f*]chromen-3-one **6a** in 89% yield as colorless crystals after column purification and recrystallization: mp above 200 °C (ethanol) (lit.[20c] 216−217 °C). UV (MeOH): λ_{max} 372 nm (log ϵ = 4.03), 256 nm (log ϵ = 4.22), 230 nm (log ϵ = 4.60). IR (KBr): 3102, 2959, 1700, 1654, 12 1262, 752 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.89 (s, H), 8.24 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 9.3 Hz, 1H), 7.89−7.94 (m, 3H), 7.7 (t, J = 7.3 Hz, 1H), 7.57−7.65 (m, 2H), 7.45−7.51 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.9, 158.4, 155.4, 141.7, 136.5, 135.3, 133.6, 130.3, 129.6, 129.4, 129.2, 128.9, 128.5, 126.5, 125.4, 121.5, 116.7, 112.6.

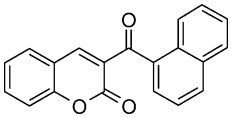


2-(4-Methylbenzoyl)-3*H*-benzo[*f*]chromen-3-one 6b. Following the general procedure described above, the reaction of 2-hydroxy-1-naphthaldehyde **5** (327 mg, 2.1 1 mmol), 1-(4-methylphenyl)-3,3-bis(methylsulfanyl)-2-propen-1-one **1b** (500 mg, 2.1 mmol), and peperidine (18 mg, 0.21 mmol) furnished 527 mg of 2-(4-methylbenzoyl)-3*H*-benzo[*f*]chromen-3-one **6b** in 80% yield as colorless crystals after column purification and recrystallization: mp 190−192 °C (ethanol) (lit.[20c] 190−191 °C) (toluene). UV (MeOH): λ_{max} 370 nm (log ϵ = 3.86), 258 nm (log ϵ = 4.08). IR (KBr): 3065, 2950, 1706, 1656, 1562, 1256, 780 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.25 (d, J = 8.8 Hz, 1H), 8.11

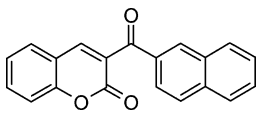
(d, J = 9.3 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.71 (br t, J = 7.3 Hz, 1H), 7.61 (br t, J = 7.8 Hz, 1H), 7.51 (d, J = 9.3 Hz, 1H), 7.29 (d, J = 8.3 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 158.6, 155.27, 144.8, 141.4, 135.2, 133.8, 130.3, 129.8, 129.4, 129.3, 129.2, 128.9, 126.5, 125.6, 121.5, 116.7, 112.7, 21.8.



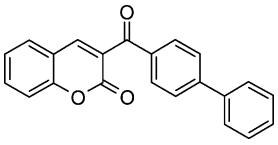
2-(4-Chlorobenzoyl)-3*H*-benzo[*f*]chromen-3-one 6c. Following the general procedure described above, the reaction of 2-hydroxy-1-naphthaldehyde **5** (296 mg, 1.9 mmol), 1-(4-chlorophenyl)-3,3-bis(methylsulfanyl)-2-propen-1-one **1c** (500 mg, 1.9 mmol), and peperidine (18 mg, 0.2 mmol) furnished 539 mg of 2-(4-chlorobenzoyl)-3*H*-benzo[*f*]chromen-3-one **6c** in 85% yield as colorless crystals after column purification and recrystallization: mp above 200 °C, (ethanol) (lit.[20c] 232−233 °C) (toluene). UV (MeOH): λ_{max} 374 nm (log ϵ = 3.90), 260 nm (log ϵ = 4.12). IR (KBr): 3020, 1706, 1656, 1562, 1256, 780 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.28 (d, J = 8.3 Hz, 1H), 8.13 (d, J = 8.8 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 8.8 Hz, 2H), 7.75 (t, J = 7.3 Hz, 1H), 7.63 (t, J = 7.9 Hz, 1H), 7.52 (d, J = 9.3 Hz, 1H), 7.47 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 158.7, 155.6, 142.5, 140.2, 135.7, 134.9, 130.9, 130.3, 129.4, 129.3, 129.1, 128.9, 126.6, 124.8, 121.5, 116.7, 112.7.



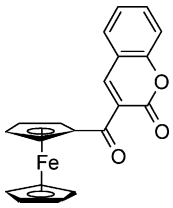
3-(1-Naphthylcarbonyl)-2*H*-2-chromenone 8. Following the general procedure described above, the reaction of 2-hydroxybenzaldehyde **2a** (267 mg, 2.1mmol), 3,3-bis(methylsulfanyl)-1-(1-naphthyl)-2-propen-1-one **7** (500 mg, 1.8 mmol), and peperidine (18 mg, 0.2 mmol) furnished (437 mg) of 3-(1-naphthylcarbonyl)-2*H*-2-chromenone **8** in 80% yield as colorless crystals after column purification and recrystallization: mp above 200 °C (5% DCM in hexanes). UV (MeOH): λ_{max} 383 nm (log ϵ = 2.98), 302 nm (log ϵ = 2.87), 245 nm (log ϵ = 2.95). IR (KBr): 1719, 1652, 1564, 1233, 1195, 911, 786, 755 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-D_6/$CDCl_3$; 1:9): δ 8.55 (d, J = 8.8 Hz, 1H), 8.20 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.73, (d, J = 6.8 Hz, 1H), 7.50−7.65 (m, 4H), 7.49 (t, J = 7.4 Hz, 1H), 7.38 (d, J = 8.3 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-D_6/$CDCl_3$; 9:1): δ 193.1, 158.0, 154.9, 146.7, 134.5, 133.9, 133.8, 133.3, 130.6, 129.6, 129.5, 128.5, 128.1, 127.5, 126.7, 125.4, 124.9, 124.3, 118.2, 116.9. HRMS (ESI$^+$): calcd for $C_{20}H_{12}O_3$ (MH$^+$), 301.0786; found, 301.0774.



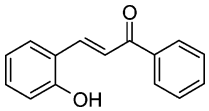
3-(2-Naphthylcarbonyl)-2*H*-2-chromenone 10. Following the general procedure described previously, the reaction of 2-hydroxybenzaldehyde **2a** (267 mg, 2.1mmol), 3,3-bis(methylsulfanyl)-1-(2-naphthyl)-2-propen-1-one **9** (500 mg, 1.8 mmol), and peperidine (18 mg, 0.2 mmol) furnished (503 mg) of 3-(2-naphthylcarbonyl)-2*H*-2-chromenone **10** in 92% yield as colorless crystals after column purification and recrystallization: mp above 200 °C (ethanol). UV (MeOH): λ_{max} 407 nm (log ϵ = 3.04), 311 nm (log ϵ = 2.87), 242 nm (log ϵ = 2.95). IR (KBr): 1643, 1588, 1458, 1336, 1186, 748, cm^{-1}. ^{1}H NMR (60 MHz, CCl_4 + $CDCl_3$; 5:1): δ 8.56 (s, 1H) 6.85−8.17 (m, 11H). ^{13}C NMR (100 MHz, DMSO/$CDCl_3$; 1:5): δ 188.9, 156.3, 139.4, 134.5, 133.9, 131.2, 130.5, 128.5, 128.2, 127.9 (×2), 127.1, 127.0, 126.5, 125.5, 123.1, 120.6, 120.3, 118.3, 115.3. HRMS (ESI$^+$): calcd for $C_{20}H_{12}O_3$ (MH$^+$), 301.0786; found, 301.0784.



3-(Biphenyl-4-yl-carbonyl)-2*H*-2-chromenone 12. Following the general procedure described above, the reaction of 2-hydroxybenzaldehyde **2a** (244 mg, 2.0 mmol), 1-biphenyl-4-yl-3,3-*bis*-methylsulfanyl-2-propen-1-one **11** (500 mg, 1.66 mmol), and peperidine (18 mg, 0.2 mmol) furnished 374 mg of 3-(biphenyl-4-yl-carbonyl)-2*H*-2-chromenone **12** in 69% yield as light yellow powder after column purification and recrystallization: mp above 200 °C (ethanol). UV (MeOH): λ_{max} 353 nm (log ϵ = 2.91), 302 nm (log ϵ = 2.89), 244 nm (log ϵ = 2.98). IR (KBr): 1713, 1659, 1603, 1450, 1264, 1241, 918, 749, 692 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.89 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.22−7.64 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 154.7, 146.6, 145.4, 134.7, 134.8, 133.6, 130.2, 129.2, 128.9 (× 2), 128.3, 127.3, 127.2, 127.2, 124.9, 118.2, 116.9. HRMS (ESI$^+$): calcd for $C_{22}H_{14}O_3$ (MH$^+$), 327.0643; found, 327.0652.

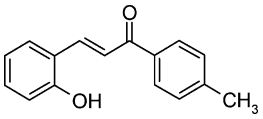


3-η^5-Ferrocenoyl-2*H*-2-chromenone 14. Following the general procedure described previously, the reaction of 2-hydroxybenzaldehyde **2a** (219 mg, 1.8 mmol), 3,3-bis(methylsulfanyl)-1-η^5-ferrocenyl-2-propen-1-one **13** (500 mg, 1.5 mmol), and peperidine (16 mg, 0.19 mmol) furnished 484 mg of 3-η^5-ferrocenoyl-2*H*-2-chromenone **14** in 85% yield of a brownish red powder after column purification: mp above 200 °C (ethanol). UV ($CHCl_3$): λ_{max} 498 nm (log ϵ = 2.77), 359 nm (log ϵ = 2.96), 304 nm (log ϵ = 2.96), 262 nm (log ϵ = 2.93). IR (KBr): 1643, 1588, 1458, 1336, 1186, 748 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.63 (t, J = 8.3 Hz, 1H), 7.60 (d, J = 8.34 Hz, 1H), 7.40 (d, J = 8.3 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 4.86 (br s, 2H), 4.64 (br s, 2H), 4.29 (s, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 158.0, 154.4, 141.8, 133.1, 128.8, 128.0, 124.8, 118.0, 116.9, 82.04, 73.4, 70.9, 70.5. HRMS (ESI$^+$): calcd for $C_{20}H_{14}O_3Fe$ (MH$^+$), 359.0292; found, 359.0272.



(*E*)-3-(2-Hydroxyphenyl)-1-phenyl-2-propen-1-one 16a. Following the general procedure described above, the reaction of 2-hydroxybenzaldehyde **2a** (268 mg, 2.2 mmol), 3,3-bis(methylsulfanyl)-1-phenyl-2-propen-1-one **1a** (500 mg, 2.20 mmol), and peperidine (18 mg, 0.2 mmol) in ethanol reflux furnished 443 mg of 3-benzoyl-2*H*-2-chromenone 1**6a** in 90% yield as a light yellow solid: mp 151−153 °C (ethanol) (lit.[24] 153 °C). UV (MeOH): λ_{max} 353 nm (log ϵ = 3.70), 299 nm (log ϵ = 3.8), 267 nm (log ϵ = 3.64). IR (KBr): 3203, 3063, 2994, 1638, 1594, 1556, 1243, 755 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.54 (br s, 1H), 8.11 (d, J = 15.6 Hz, 1H), 8.01 (br d, J = 6.9 Hz, 2H), 7.71 (d, J = 15.6 Hz, 1H), 7.30−7.60 (m, 4H), 7.23 (br t, J = 8.4 Hz, 1H), 6.96 (d, J = 7.2 Hz,

1H), 6.87 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$/DMSO, 7:2): δ 190.8, 157.0, 140.9, 138.1, 132.0, 131.1, 129,1, 128.1, 128.0, 121.7, 121.5, 119.2, 116.1.



(*E*)-3-(2-Hydroxyphenyl)-1-(4-methylphenyl)-2-propen-1-one 16b. Following the procedure described above, the reaction of 2-hydroxybenzaldehyde **2a** (256 mg, 2.1 mmol), 3,3-bis(methylsulfanyl)-1-(4-methylphenyl)-2-propen-1-one **1b** (500 mg, 2.1 mmol), and peperidine (18 mg, 0.2 mmol) in ethanol reflux furnished 409 mg of (*E*)-3-(2-hydroxyphenyl)-1-(4-methylphenyl)-2-propen-1-one **16b** in 82% yield as light yellow colored powder after column purification: mp 157−158 °C (ethanol) (lit.[25] 158−159 °C). UV (MeOH): λ_{max} 353 nm (log $\epsilon = 3.70$), 299 nm (log $\epsilon = 3.8$), 267 (log $\epsilon = 3.64$) nm. IR (KBr): 3203, 3063, 2994, 1638, 1594, 1556, 1243, 755 cm^{-1}. ^{1}H NMR (400 MHz, acetone-D_6): δ 9.47 (br s, 1H), 8.14 (d, $J = 15.6$ Hz, 1H), 8.05 (br d, $J = 9.3$ Hz, 2H), 7.85 (br d, $J = 15.6$ Hz, 1H), 7.67 (br d, $J = 7.8$ Hz, 1H), 7.34 (d, $J = 8.3$ Hz, 2H), 7.24 (t, $J = 7.8$ Hz, 1H), 6.84−6.99 (m, 2H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, acetone-D_6): δ 189.9, 157.9, 144.1, 140.1, 136.9, 132.4, 130.1, 129.7, 129.3, 122.9, 122.4, 120.7, 116.9, 21.5.

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Supporting Information Available: General experimental details, ^{1}H and ^{13}C NMR spectra for compounds **4a**−**l**, **6a**−**c**, and **7**−**14** are given in this section. This material is available free of charge via the Internet at http://pubs.acs.org.

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