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Metal- and Solvent-Free Approach to Access 3-Se/S-Chromones from the Cyclization of Enaminones in the Presence of Dichalcogenides Catalyzed by KIO_3

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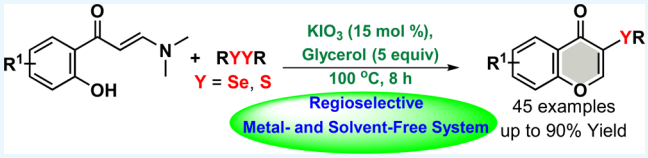
Supporting Information

ABSTRACT: Herein, we describe a greener protocol for the one-pot synthesis of 3-Se/S-4*H*-chromen-4-ones. The desired products were obtained in good to excellent yields using 2-hydroxyphenyl enaminones and half equivalents of various odorless diorganyl dichalcogenides (S/Se) in the presence of glycerol (5 molar equiv) and KIO_3 (15 mol %) as the catalyst under solvent-free conditions.



1. INTRODUCTION

The chromone core is a ubiquitous heterocycle present in many natural bioactive products, and it represents an important "privileged scaffold".[1] Numerous types of biological activities are associated with simple chromones and analogues, including anti-inflammatory, antiplatelet, anticancer, anti-HIV, immune-stimulatory, anti-Alzheimer, and antimicrobial.[1,2] Several commercially available drugs have the chromone moiety in their core structure, for example, khelline (used in folk medicines), Rapitil (for asthma and allergic eye reactions), and Intal (for asthma) (Figure 1).[3] Several promising radioiodinated styrylchromone derivatives have been used as probes for imaging because of the fluorescence of the core structure.[4]Hence, considering their structural diversity, biological properties, and synthetic utility, these structures have received considerable attention.[1,5]

Analogously, the construction of the C−S/Se bond is a very important transformation in organic synthesis, as these compounds exhibit fascinating biological characteristics.[6] In the past few decades, these compounds have gained increasing interest, mainly because of their antioxidant, anti-inflammatory, antitumor, and antiviral activities.[6,7] They also play a fundamental role in modern organic synthesis and are employed as catalysts, ligands, and ionic liquids in certain reactions and as synthetic intermediates in total synthesis.[8,9] In addition, they are applied in asymmetric catalysis and in materials science.[10]

Despite the biological importance of organochalcogen compounds and the wide spectrum of therapeutic properties of chromones, only a few synthetic methods for the construction of these hybrid structures in a single molecule, 3-chalcogenayl-4*H*-chromen-4-ones, have been reported.[11]

Zeni and co-workers have reported the synthesis of selenylated chromones from the reaction of alkynyl aryl ketones and diselenides in the presence of 1.5 equiv of $FeCl_3$ (Scheme 1a).[11a] Recently, Blond and co-workers have demonstrated the AgOTf-mediated synthesis of chromone containing the phenylselenyl moiety through the reaction of 2-hydroxy-phenyl enaminones and phenylselenyl chloride (Scheme 1b).[11e] The common approach to access sulfenylated chromones is through the direct sulfenylation of the C−H bond of chromones using different sources of organosulfur and 2−4 molar equiv of NH_4I (Scheme 1c).[11b−d] During the preparation of this manuscript, a related study using aryl thiols as a sulfenylating agent and 0.3 molar equiv of KIO_3 to produce sulfenylated chromones in ethyl lactate as the solvent appeared in the literature (Scheme 1d).[11f]

Some of the methods described in the literature are associated with limitations that reduce their synthetic utility. These downsides include the use of nongreen solvents, prefunctionalized coupling partners, low atom economy, narrow substrate scope, the use of transition metal salts, malodorous reagents, and elaborate, multistep processes.

In recent years, various types of organic transformations have been carried out with the application of metal- and solvent-free systems.[12]

An alternative greener method with a broad scope for the synthesis of these compounds, involving a solvent- and metal-free system that could provide high efficiency, would be advantageous and highly desirable in view of the significance of chalcogenated chromones. As part of our wider research program aimed at designing and developing sustainable processes and solvent-free systems for the chalcogenation of heteroarenes and organochalcogen chemistry,[13] herein, we

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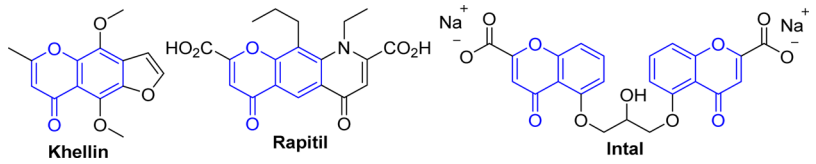
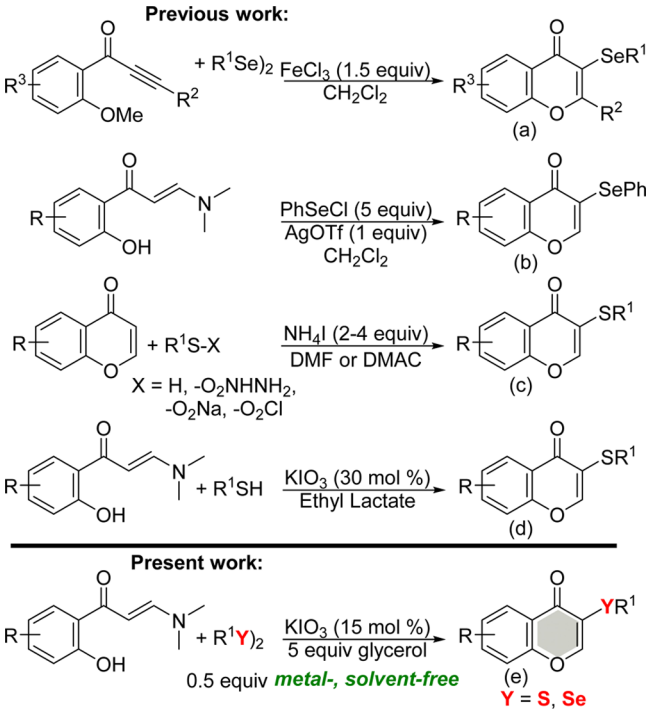


Figure 1. Chromone-based drugs.

Scheme 1. Synthetic Routes for Chalcogenated Chromones



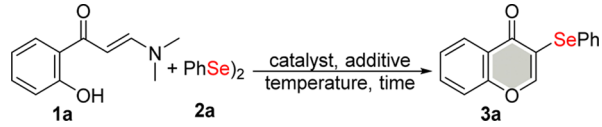
report, for the first time, the KIO_3/glycerol catalytic system for the synthesis of C-3 chalcogenated chromones (Scheme 1e). Our new regioselective, broader, metal-, and solvent-free approach worked effectively using enaminones with a half-molar equivalent of diorganyl diselenides or disulfides as a nonmalodorous source of chalcogens, in the presence of catalytic loading of KIO_3 (15 mol %).

2. RESULTS AND DISCUSSION

To identify the best reaction conditions, enaminone **1a** and diphenyl diselenide **2a** were selected as model substrates. These were then evaluated under various conditions (Table 1).

On the basis of our previous experience of solvent-free systems,[13a−d] preliminary experiments were carried out in the presence of a stoichiometric amount of poly(ethylene glycol) (PEG-400) as an additive at 110 °C with a reaction time of 10 h and without a catalyst. The reaction under open air (entry 1) and under inert atmosphere (entry 2) conditions was unsuccessful. When the reaction was performed in the presence of 20 mol % of CuI as the transition metal catalyst, **3a** was formed in trace amounts (entry 3), whereas the use of ZnI_2 was completely ineffective (entry 4). When the reaction was carried out in the presence of KI as the catalyst, the desired product was obtained in 10% yield (entry 5). On switching from KI to KIO_3, **3a** was isolated with a 61% yield (entry 6) but its sodium analogue gave the selenylated product with a 35% yield (entry 7). Molecular iodine was also not effective and afforded **3a** with a 38% yield (entry 8).

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst (mol %)	additive (equiv)	temp (°C)	time (h)	yield[b] (%)
1		PEG-400 (5)	110	10	NR
2[c]		PEG-400 (5)	110	10	NR
3	CuI (20)	PEG-400 (5)	110	10	traces
4	ZnI_2 (20)	PEG-400 (5)	110	10	NR
5	KI (20)	PEG-400 (5)	110	10	10
6	KIO_3 (20)	PEG-400 (5)	110	10	61
7	$NaIO_3$ (20)	PEG-400 (5)	110	10	35
8	I_2 (20)	PEG-400 (5)	110	10	38
9	KIO_3 (20)	Et. lactate (5)	110	10	67
10	KIO_3 (20)	glycerol (5)	110	10	86
11	KIO_3 (20)	DMSO (5)	110	10	52
12	KIO_3 (20)	toluene (5)	110	10	traces
13	KIO_3 (15)	glycerol (5)	110	10	85
14	KIO_3 (10)	glycerol (5)	110	10	65
15	KIO_3 (15)	glycerol (5)	100	10	86
16	KIO_3 (15)	glycerol (5)	90	10	72
17	**KIO_3 (15)**	**glycerol (5)**	**100**	**8**	**86**
18	KIO_3 (15)	glycerol (5)	100	6	70
19	KIO_3 (15)	glycerol (3)	100	10	71
20[d]	KIO_3 (15)	glycerol	100	10	85

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.125 mmol), catalyst (mol %), and additive (equivalent). [b]Isolated yields. [c]Reaction under argon atmosphere. [d]2 mL glycerol.

After determining the appropriate catalyst, in the next step, the type of additive was screened for this transformation (entries 9−12). Ethyl lactate promoted some improvement in the reaction (entry 9), and this motivated us to test other greener additives. With the use of glycerol, **3a** was isolated with an 86% yield (entry 10). An adverse effect on the yield was noted when dimethylsulfoxide (DMSO) was used (entry 11), whereas toluene afforded **3a** in traces (entry 12).

Subsequently, the catalyst loading, reaction time, and temperature were screened for this transformation (entries 13−18). Lowering the catalyst loading to 15 mol % did not affect the yield of **3a** (entry 13 vs 10). Further decreasing the catalyst quantity to 10 mol % resulted in a lower yield of **3a** (entry 14). The reaction temperature and time were screened for this transformation (entries 15−17), and ideal values of 100 °C and 8 h were obtained.

The use of glycerol (2 mL) as the solvent did not provide any further positive influence on the yield of **3a** (entry 20 vs 17). Decreasing the quantity of glycerol to 3 molar equiv afforded **3a** with a lower yield (entry 19).

With the optimized conditions in hand (Table 1, entry 17), the applicability of other enaminones **1** and various diorganyl dichalcogenides was investigated (Schemes 2−4). We first

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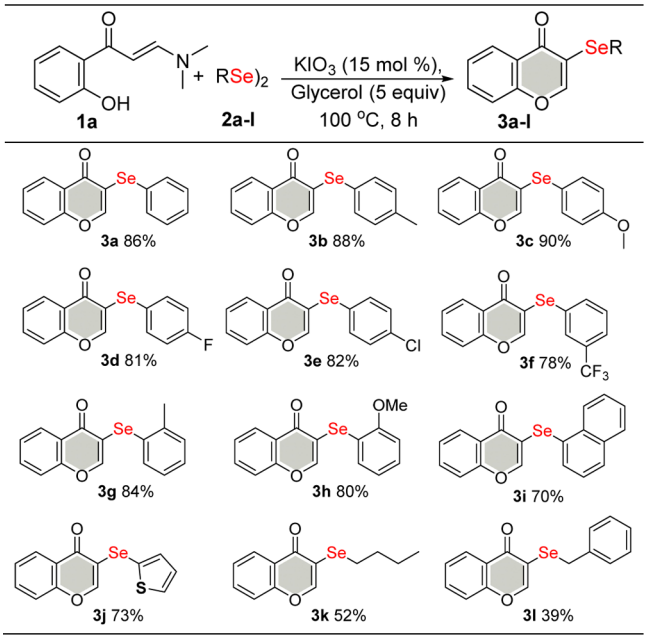
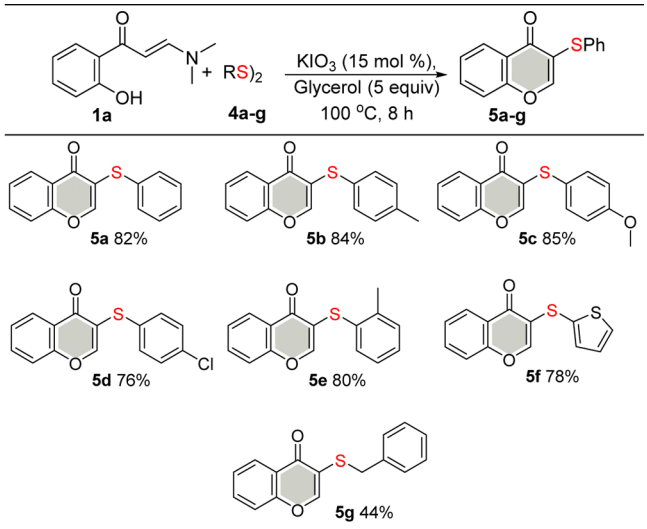
evaluated the efficiency and generality of this method with respect to different diorganyl diselenides **2** while keeping enaminone **1a** constant (Scheme 2).

Scheme 2. Scope of Diorganyl Diselenide 2[a]



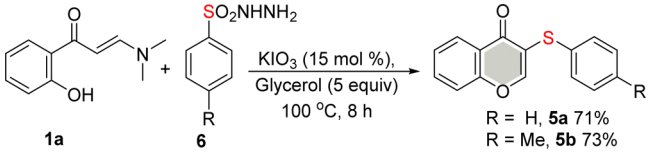
[a]Isolated yield.

Scheme 3. Scope of Diorganyl Disulfides 4[a]



[a]Isolated yield.

Scheme 4. Thiolation Using Arylsulfonyl Hydrazides 6



The reaction worked effectively for structurally diverse diselenides **2**. Substituents on the aryl moiety, that is, electron-donating (R = F, Cl, and CF_3) and electron-withdrawing (R = Me and OMe) groups and a bulky group (naphthyl) successfully afforded the corresponding products **3a−i** in good to excellent yields (70−90%; **3a−i**). The course of the reaction appears to be influenced by electronic effects. It can be noted that diaryl diselenides with electron-donating groups usually gave the selenylated products (**3b−c**) in better yields than those achieved with electron-withdrawing groups (**3d−f**). Furthermore, steric hindrance of the ortho-substituted aryl substrates showed a weaker influence on the yields in relation to the corresponding para-derivatives (**3b−c** vs **3g−h**). However, product **3i** was obtained in 70% yield when a fused aromatic substrate (R = naphthyl) was used.

C-2 heteroaryl diselenide **2j** afforded the desired product **3j** with a 73% yield. Aliphatic diorganyl diselenides **2k** and **2l** furnished the respective selenylated chromones **3k** and **3l** in 52 and 39% yields, respectively. **3l** was observed when benzylic diselenide was used as the substrate.

The success observed for the KIO_3-catalyzed synthesis of selenylated chromones **3** prompted us to expand the scope of this method to access sulfenylated chromones **5** using diorganyl disulfides **4** as the coupling partner (Scheme 3). The desired products **5a−g** were obtained in 44−85% yields. Using diphenyl disulfide **4a** as the substrate, the sulfenylated product **5a** was obtained in 82% yield. It was noted that the method used to prepare the sulfenylated product **5** from disulfides **4** presented electronic and steric effects similar to that used for diorganyl diselenides **2**. There was a small decrease in the product yields of sulfenylated compound **5** compared with selenylated analogue **3**, which can probably be attributed to the stronger S−S bond of the diaryl disulfides in relation to the respective diselendies **2**.

We then extended our study to sulfonyl hydrazides **6** (Scheme 4), applying the optimal reaction conditions (Table 1, entry 17), to explore the scope of this new methodology. The protocol described herein is versatile, being applicable to different types of organochalcogen sources. For instance, the reaction of different arylsulfonyl hydrazides **6** with enaminone **1a** afforded the corresponding coupled products **5a** and **5b** in isolated yields of 71 and 73%, respectively (Scheme 4).

To broaden the scope of the optimized reaction in relation to the substrate, the influence of the enaminone **1** moiety was evaluated with **2a** and **4a** (Scheme 5). Enaminone **1** with different functional groups attached at the aryl moiety, for example, alkyl, alkoxy, halogen, and naphthyl groups, were tested. The system tolerated the electronic effects of the substituents on the phenyl group, and both electron-withdrawing and electron-donating groups are suitable substrates, affording the corresponding products **7a−l** and **7aa−al** in 70−88% yields. In this case, the electron-donating groups (−Me, −MeO, and −EtO) showed superiority over electron-withdrawing groups (−F, Cl, and Br). Furthermore, the reaction tolerated disubstituted substrates, furnishing the respective product in good to excellent yields. Similarly, a fused aromatic substrate (naphthyl) resulted in the desired products **7m** and **7am** in 80 and 76% yields, respectively.

In general, we observed that diselenides **2a** furnished the targeted selenylated products **7a−m** in slightly better yields compared with disulfides **4a**.

On the basis of reports in the literature[11] and the chemical shifts observed from the nuclear magnetic resonance (NMR) (^1H and ^{13}C) spectra of each of the chalcogenated chromone derivatives (**3**, **8**), all products have an organochalcogen moiety

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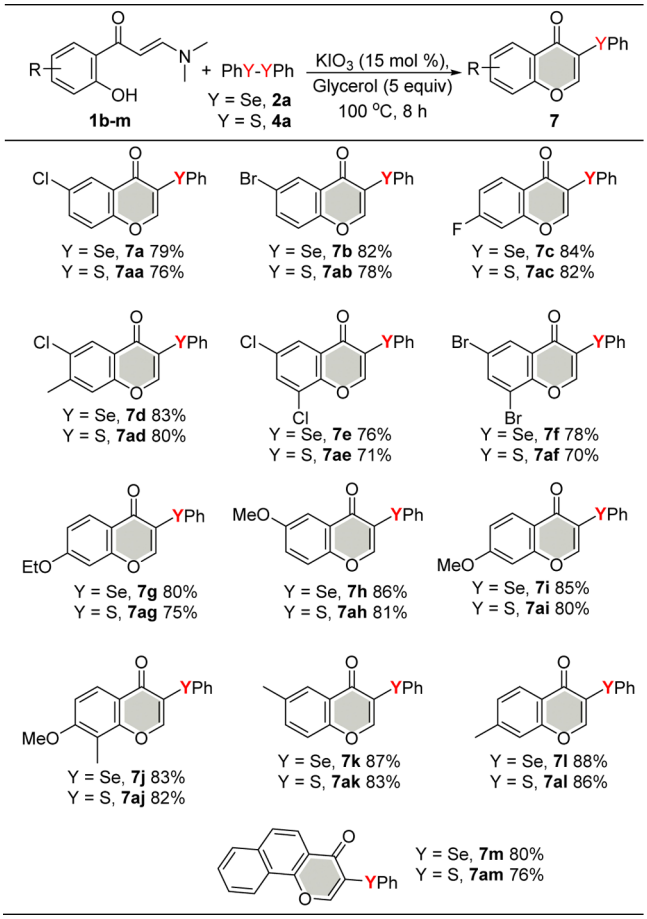
Scheme 5. Scope of Enaminones 1[a]



[a]Isolated yield.

bonded at the α-positions of the ketone functions of the chromones.

In view of the unique features of the KIO_3-catalyzed one-pot cyclization of enaminones and chalcogenation in the presence of dichalcogenide, we decided to investigate the mode of action. Some control experiments were therefore conducted (Scheme 6). The addition of a stoichiometric amount of TEMPO, as a radical inhibitor, did not hamper the reaction, and the selenylated product **3a** was obtained in 81% yield (Scheme 6a), which excluded the possibility of a radical pathway. While under an inert atmosphere, the standard reaction shows a decrease in the efficacy (Scheme 6b), indicating that the presence of oxygen is important for this transformation. In agreement with that, the reaction under oxygen atmosphere exhibited some improvement in the isolated yield of **3a** (Scheme 6c), indicating the importance of oxygen in the reaction medium. When (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **8** was used instead of enaminone **1a** under standard conditions for **2a** and **4a**, the expected chalcogenated enaminone **9** was not observed (Scheme 6d). Thus, apparently, the hydroxy group of enaminones plays a key role in the reaction. Subsequently, the reaction in the absence of dichalcogenides furnished the chromone in a low yield (Scheme 6e), signifying that most likely it is not the intermediate in our reaction. Additionally, chromone **10** itself, under optimized conditions, provided the desired products in low yields (Scheme 6f). The presence of DABCO (as base) did not hamper the reaction, and product **3a** was obtained in 82% yield (Scheme 6g). This result indicates that most likely the reaction did not involve any active iodine acid species (such as HI) during the catalytic pathway, as previously observed.[13a−c]

On the basis of these results and of previous reports,[13,14a] a mechanism for this transformation can be proposed (Scheme 7). Initially, the reaction between diorganyl dichalcogenide and enaminone **1** would form species (A) and organochalcogenyl anion, which would suffer oxidation by air and regenerate the dichalcogenide. The species (A) would afford the cyclic intermediate (C) through the intramolecular cyclization from the tautomeric intermediate (B). Subsequently, the elimination of dimethylamine from the intermediate (C) would furnish the desired chalcogenated chromone.

3. CONCLUSIONS

We developed a KIO_3-catalyzed, simple, greener, metal-, and solvent-free approach for the preparation of 3-selenyl- and 3-sulfenyl-chromones, a class of compounds of interest for therapeutic applications. Under optimized reaction conditions, the reaction worked well in the presence of KIO_3/glycerol, as a nontoxic catalytic system, with 2-hydroxy-phenylenaminones and a half molar equivalent of diorganyl dichalcogenides as an odorless source of chalcogens. This afforded a wide range of chalcogenated (S, Se) chromones at the C3 position in good to excellent yields. The optimized reaction conditions were appropriate for various substituents with different electronic and steric effects. Furthermore, sulfonyl hydrazides were also successfully applied as alternative sulfenylating agents.

The important features of this robust and benign protocol are as follows: (1) it is metal-free and solvent-free; (2) it is performed open air; (3) it is atom-economic, (4) regioselective, and (5) inexpensive; (6) it is a nontoxic catalytic system with (7) a low catalytic loading; and (8) it is applicable to different sources of organochalcogenides and a wide range of enaminones.

4. EXPERIMENTAL SECTION

4.1. General. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained at 200 MHz on a Bruker AC-200 NMR spectrometer. The spectra were recorded in $CDCl_3$ solutions. The chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in hertz, and integrated intensity. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were obtained at 50 MHz on a Bruker AC-200 NMR spectrometer. The spectra were recorded in $CDCl_3$ solutions. The chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), and m (multiplet). Selenium-77 nuclear magnetic resonance (^{77}Se NMR) spectra were recorded at 38.14 MHz on a Bruker AC-200 NMR spectrometer. The spectra were recorded in $CDCl_3$ solutions. The chemical shifts are reported in ppm, referenced to diphenyl diselenide as the external reference (463.15 ppm). High-resolution mass spectra were recorded on a Bruker micrOTOF-Q II ESI mass spectrometer equipped with an automatic syringe pump for sample injection. The melting points were determined using a Microquimica MQRPF-301 digital model equipment with a heating plate. Column

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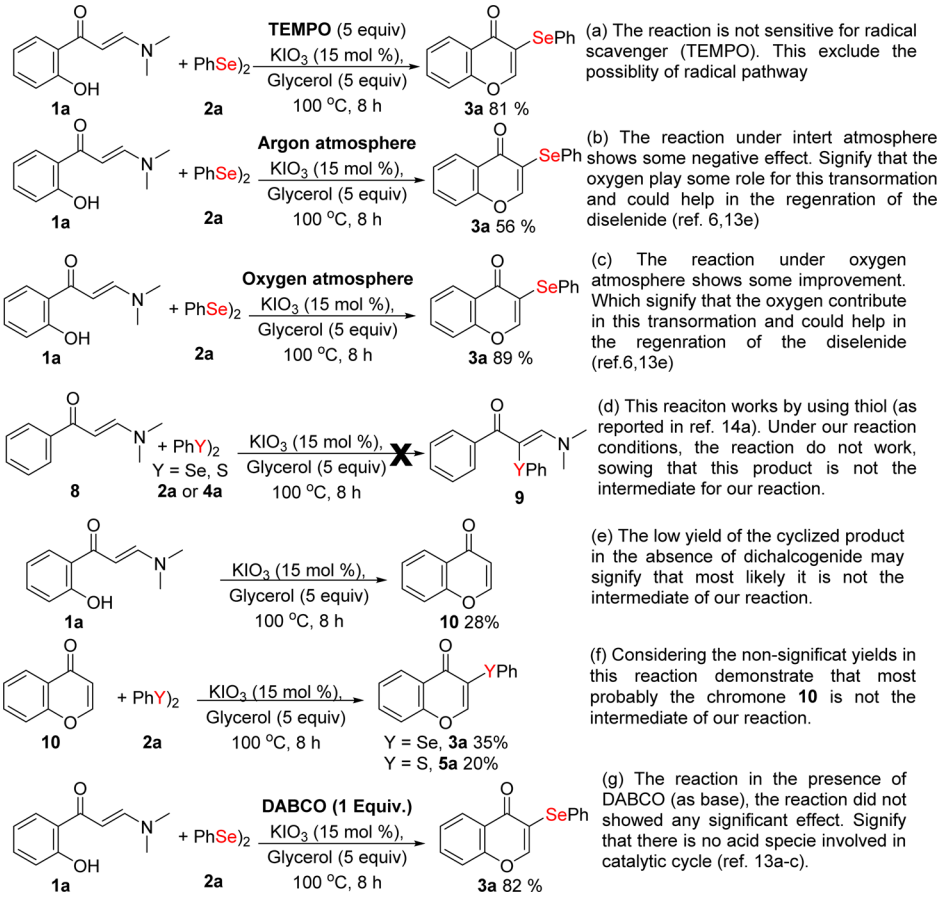
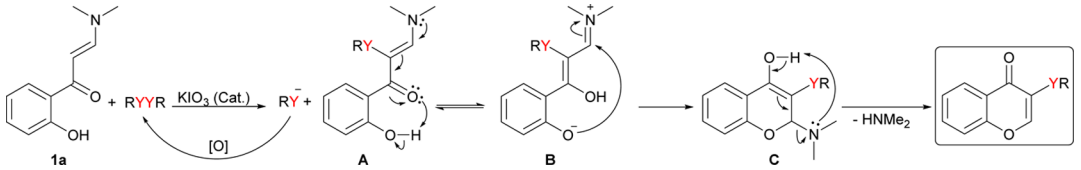
Scheme 6. Control Experiments



Scheme 7. Proposed Mechanism for the Reaction



chromatography was performed using silica gel (230−400 mesh). Thin-layer chromatography (TLC) was performed using Merck silica gel GF_{254} of 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light or stained with iodine vapor and acidic vanillin.

Unless otherwise stated, all reactions were carried out in a Schlenk tube; all reagents and solvents were obtained from commercial sources and used without any further purification. Enaminones **1a−m** were synthetized following the procedure reported.[14]

4.2. General Procedure for the KIO_3-Catalyzed Synthesis of 3-Se/S-Chromones from the Cyclization of Enaminones 1a−m Using Diorganyl Chalcogenides. A mixture of appropriate enaminone **1** (0.25 mmol), diorganyl dichalcogenide **2** or **4** (0.125 mmol), KIO_3 (15 mol %, 8 mg), and 3 equiv of glycerol (1.25 mmol, 115 mg) was charged in a Schlenck tube. The mixture was heated to 100 °C in an oil bath for 8 h. After this, the reaction mixture was dissolved in ethyl acetate (10 mL) and washed with 2 × 5 mL of an aqueous solution of 10% $Na_2S_2O_3$. The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified using flash chromatography on silica gel using hexane or a mixture of hexane/ethyl acetate (9:1) as the eluent.

4.3. General Procedure for the KIO_3-Catalyzed Reactions of Arylsulfonyl Hydrazides 6 with Enaminones 1a. A mixture of enaminone **1a** (0.25 mmol, 48 mg) and appropriate arylsulfonyl hydrazide **6** (0.25 mmol) was used under standard conditions. Yield: **5a**, 71% (45 mg) and **5b**, 73% (49 mg).

4.4. Control Experiments for the Study of Mechanism. *4.4.1. Radical Trapping Study.* A mixture of enaminone **1a** (0.25 mmol, 48 mg), diphenyl diselenide **2a** (0.125 mmol, 39 mg), and TEMPO (1.25 mmol, 195 mg) was used under standard conditions. Yield: 81% (61 mg).

4.4.2. Standard Reaction under Interatmosphere. A mixture of enaminone **1a** (0.25 mmol, 48 mg) and diphenyl diselenide **2a** (0.125 mmol, 39 mg) was used under standard conditions in the argon atmosphere. Yield: 56% (42 mg).

4.4.3. Standard Reaction under Oxygen Atmosphere. A mixture of enaminone **1a** (0.25 mmol, 48 mg) and diphenyl

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diselenide **2a** (0.125 mmol, 39 mg) was used under standard conditions in the oxygen atmosphere. Yield: 89% (67 mg).

*4.4.4. Reaction between **8** and **2a** or **4a**.* A mixture of enaminone **8** (0.25 mmol, 44 mg) and diphenyl diselenide **2a** (0.125 mmol, 39 mg) or diphengyl disulfide **4a** (0.125 mmol, 28 mg) was used under standard conditions.

*4.4.5. Cyclization of Enaminone **1a** Catalyzed by KIO_3.* A mixture of enaminone **1a** (0.25 mmol, 48 mg), KIO_3 (15 mol %, 8 mg), and 3 equiv of glycerol (1.25 mmol, 115 mg) was charged in a Schlenck tube under standard conditions. Yield: **10**, 28% (37 mg).

*4.4.6. Reaction between **10** and **2a** Catalyzed by KIO_3.* A mixture of **10** (0.25 mmol, 37 mg) and diphenyl diselenide **2a** (0.125 mmol, 39 mg) or diphenyl disulfide **4a** (0.125 mmol, 28 mg) was used under standard conditions. Yield: **3a**, 35% (26 mg) and **5a**, 20% (13 mg).

4.4.7. Standard Reaction in the Presence of DABCO (as Base). A mixture of enaminone **1a** (0.25 mmol, 48 mg), diphenyl diselenide **2a** (0.125 mmol, 39 mg), and DABCO (0.25 mmol, 28 mg) was used under standard conditions. Yield: 82% (62 mg).

4.5. 3-(Phenylselanyl)-4*H*-chromen-4-one (3a).[11] Yield: 86% (65 mg); beige crystalline solid; mp: 59−60 °C (59 °C);[2] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.24 (d, J = 8.4 Hz, 1H), 7.89 (s, 1H), 7.72−7.57 (m, 3H), 7.43 (d, J = 7.4 Hz, 2H), 7.34−7.25 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.2, 156.4, 155.8, 133.9, 129.6, 128.2, 128.2, 126.4, 125.6, 123.2, 118.1, 117.9; ^{77}Se NMR (38 MHz, $CDCl_3$): δ = 303.06; HRMS m/z calcd for $C_{15}H_{11}O_2Se$ $[M + H]^+$ 302.9919; found, 302.9920.

4.6. 3-(*p*-Tolylselanyl)-4*H*-chromen-4-one (3b, New Compound). Yield: 88% (69 mg); beige solid; mp: 88−89 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.22 (dd, J = 8.2, 1.4 Hz, 1H), 7.76 (s, 1H), 7.70−7.60 (m, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.46−7.34 (m, 2H), 7.12 (d, J = 7.8 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.2, 156.3, 154.8, 138.5, 134.6, 133.7, 130.4, 126.2, 125.4, 123.9, 123.0, 118.6, 118.0, 21.2; HRMS m/z calcd for $C_{16}H_{13}O_2Se$ $[M + H]^+$ 317.0076; found, 317.0079.

4.7. 3-((4-Methoxyphenyl)selanyl)-4*H*-chromen-4-one (3c, New Compound). Yield: 90% (74 mg); white crystalline solid; mp: 92−94 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.19 (dd, J = 8.2, 1.6 Hz, 1H), 7.71−7.53 (m, 4H), 7.43−7.31 (m, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.1, 16.1, 156.2, 153.7, 137.0, 133.6, 126.0, 125.3, 122.8, 119.2, 117.9, 116.9, 115.3, 55.2; HRMS m/z calcd for $C_{16}H_{13}O_3Se$ $[M + H]^+$ 333.0025; found, 333.0023.

4.8. 3-((4-Fluorophenyl)selanyl)-4*H*-chromen-4-one (3d, New Compound). Yield: 81% (65 mg); yellow crystalline solid; mp: 84−85 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.21 (dd, J = 8.3, 1.5 Hz, 1H), 7.89 (s, 1H), 7.71−7.57 (m, 3H), 7.46−7.36 (m, 2H), 7.05−6.91 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.1, 163.0 (d, J_{C-F} = 248.6 Hz), 156.3, 155.6, 136.4 (d, J_{C-F} = 8.1 Hz), 133.9, 126.3, 125.6, 123.1, 122.6 (d, J_{C-F} = 3.6 Hz), 118.1, 118.0, 116.8 (d, J_{C-F} = 21.6 Hz); HRMS m/z calcd for $C_{15}H_{10}O_2SeF$ $[M + H]^+$ 320.9825; found, 320.9827.

4.9. 3-((4-Chlorophenyl)selanyl)-4*H*-chromen-4-one (3e, New Compound). Yield: 82% (69 mg); beige crystalline solid; mp: 118−119 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.26−8.18 (m, 1H), 8.00 (s, 1H), 7.72−7.62 (m, 1H), 7.54−7.38 (m, 4H), 7.23 (d, J = 8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.0, 156.5, 156.3, 134.8, 134.3, 134.0, 129.6, 126.7, 126.4, 125.7, 123.2, 118.1, 117.2; HRMS m/z calcd for $C_{15}H_{10}O_2SeCl$ $[M + H]^+$ 336.9532; found, 336.9535.

4.10. 3-((3-(Trifluoromethyl)phenyl)selanyl)-4*H*-chromen-4-one (3f, New Compound). Yield: 78% (72 mg); beige crystalline sold; mp: 110−111 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8 8.21 (d, J = 7.9 Hz, 1H), 8.14 (s, 1H), 7.83−7.79 (m, 1H), 7.75−7.63 (m, 2H), 7.53−7.32 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.9, 157.5, 156.4, 136.1, 134.1, 131.63 (q, J_{C-F} = 32.5 Hz), 130.2, 129.7, 129.30 (q, J_{C-F} = 3.3 Hz), 126.4, 125.8, 124.58 (q, J_{C-F} = 3.5 Hz), 126.3 (q, J_{C-F} = 271 Hz), 123.4, 118.2, 116.3; HRMS m/z calcd for $C_{16}H_{10}O_2SeF_3$ $[M + H]^+$ 370.9793; found, 370.9795.

4.11. 3-(*o*-Tolylselanyl)-4*H*-chromen-4-one (3g, New Compound). Yield: 84% (66 mg); red crystalline solid; mp: 118 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.22 (dd, J = 8.3, 1.5 Hz, 1H), 7.75−7.58 (m, 2H), 7.51−7.34 (m, 3H), 7.27−7.03 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.2, 156.3, 154.6, 140.5, 134.5, 133.7, 130.4, 128.5, 128.4, 127.0, 126.2, 125.4, 122.9, 118.0, 117.3, 22.3; HRMS m/z calcd for $C_{16}H_{13}O_2Se$ $[M + H]^+$ 317.0076; found, 317.0072.

4.12. 3-((2-Methoxyphenyl)selanyl)-4*H*-chromen-4-one (3h, New Compound). Yield: 80% (67 mg); white solid; mp: 110−111 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.27 (dd, J = 7.9, 1.8 Hz, 1H), 8.08 (s, 1H), 7.75−7.63 (m, 1H), 7.50−7.39 (m, 2H), 7.28−7.16 (m, 2H), 6.91−6.79 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.5, 157.8, 157.5, 156.5, 133.9, 131.8, 128.7, 126.6, 125.7, 123.4, 121.8, 118.5, 118.2, 114.9, 110.8, 56.0; HRMS m/z calcd for $C_{16}H_{13}O_3Se$ $[M + H]^+$ 333.0025; found, 333.0024.

4.13. 3-(Naphthalen-1-ylselanyl)-4*H*-chromen-4-one (3i, New Compound). Yield: 70% (61 mg); yellow solid; mp: 67−68 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.22 (dd, J = 8.2, 1.6 Hz, 1H), 8.13−8.05 (m, 1H), 7.86 (s, 1H), 7.79−7.58 (m, 5H), 7.50−7.34 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.2, 156.3, 155.7, 134.0, 133.8, 133.3, 132.7, 130.8, 129.1, 127.8, 127.5, 126.6, 126.6, 126.3, 125.5, 125.4, 123.1, 118.1, 118.0; HRMS m/z calcd for $C_{19}H_{13}O_2Se$ $[M + H]^+$ 353.0076; found, 353.0074.

4.14. 3-(Thiophen-2-ylselanyl)-4*H*-chromen-4-one (3j, New Compound). Yield: 73% (56 mg); yellow solid; mp: 114−116 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.20 (dd, J = 8.2, 1.6 Hz, 1H), 7.64 (ddd, J = 8.8, 7.1, 1.7 Hz, 1H), 7.56 (s, 1H), 7.51−7.47 (m, 1H), 7.44−7.35 (m, 3H), 7.09−7.03 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.0, 156.3, 153.3, 137.9, 133.8, 132.8, 128.6, 126.0, 125.5, 122.7, 120.0, 119.9, 118.1; HRMS m/z calcd for $C_{13}H_9O_2SeS$ $[M + H]^+$ 308.9483; found, 308.9485.

4.15. 3-(Butylselanyl)-4*H*-chromen-4-one (3k, New Compound). Yield: 52% (37 mg); yellow solid; mp: 54−55 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.38−8.13 (m, 2H), 7.68 (ddd, J = 8.5, 7.0, 1.7 Hz, 1H), 7.56−7.38 (m, 2H), 2.89 (t, J = 6.7 Hz, 2H), 1.66 (dt, J = 15.0, 7.1 Hz, 2H), 1.43 (dq, J = 14.8, 6.9 Hz, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.9, 156.4, 156.3, 133.8, 126.4, 125.5, 123.3, 118.1, 114.8, 32.2, 26.1, 22.9, 13.6; HRMS m/z calcd for $C_{13}H_{15}O_2Se$ $[M + H]^+$ 283.0232; found, 283.0228.

4.16. 3-(Benzylselanyl)-4*H*-chromen-4-one (3l, New Compound). Yield: 39% (31 mg); white solid; mp: 95−96 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.28−8.24 (m, 1H), 7.87 (s, 1H), 7.87−7.62 (m, 1H), 7.47−7.38 (m, 2H), 7.27−7.14 (m, 5H), 4.10 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.0, 157.4, 156.4, 137.8, 133.9, 129.1, 128.5, 127.2, 126.3, 125.7,

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123.6, 118.5, 118.2, 37.2; HRMS m/z calcd for $C_{16}H_{13}O_2Se$ $[M + H]^+$ 317.0076; found, 317.0077.

4.17. 3-(Phenylthio)-4*H*-chromen-4-one (5a).[11] Yield: 82% (52 mg); white crystalline solid; mp: 99−101 °C (98−101 °C);[2] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.24 (dd, J = 7.8, 1.4 Hz, 1H), 8.14 (s, 1H), 7.75−7.63 (m, 1H), 7.49−7.37 (m, 4H), 7.32−7.19 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.09, 157.43, 156.35, 134.05, 129.86, 129.22, 127.14, 126.42, 125.78, 123.66, 119.92, 118.20; HRMS m/z calcd for $C_{15}H_{11}O_2S$ $[M + H]^+$ 255.0474; found, 255.0474.

4.18. 3-(*p*-Tolylthio)-4*H*-chromen-4-one (5b).[11] Yield: 84% (56 mg); white crystalline solid; mp: 107−108 °C (108−110 °C);[2] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.28−8.17 (m, 1H), 8.03 (s, 1H), 7.76−7.60 (m, 1H), 7.48−7.32 (m, 4H), 7.14−7.04 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.1, 156.3, 137.6, 133.9, 131.0, 130.1, 129.8, 126.4, 125.6, 123.6, 121.1, 118.1, 21.1; HRMS m/z calcd for $C_{16}H_{13}O_2S$ $[M + H]^+$ 269.0631; found, 269.0631.

4.19. 3-((4-Methoxyphenyl)thio)-4*H*-chromen-4-one (5c).[11] Yield: 85% (60 mg); white solid; mp: 116−118 °C (117−119 °C);[2] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.23 (dd, J = 7.8, 1.8 Hz, 1H), 7.90 (s, 1H), 7.73−7.60 (m, 1H), 7.52−7.36 (m, 4H), 6.86 (d, J = 8.9 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.2, 159.9, 156.3, 155.0, 134.3, 133.9, 126.3, 125.5, 123.4, 123.1, 122.6, 118.1, 115.0, 55.4; HRMS m/z calcd for $C_{16}H_{13}O_3S$ $[M + H]^+$ 285.0580; found, 285.0578.

4.20. 3-((4-Chlorophenyl)thio)-4*H*-chromen-4-one (5d).[11] Yield: 76% (55 mg); beige solid; mp: 49−50 °C (169−170 °C);[2] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.23 (s, 2H), 7.80−7.08 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.9, 157.9, 156.4, 134.2, 133.1, 132.9, 131.0, 129.3, 126.4, 125.9, 123.8, 119.3, 118.2; HRMS m/z calcd for $C_{15}H_{10}O_2SCl$ $[M + H]^+$ 289.0085; found, 289.0086.

4.21. 3-(*o*-Tolylthio)-4*H*-chromen-4-one (5e, New Compound). Yield: 80% (54 mg); beige crystalline solid; mp: 154−156 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.34−8.20 (m, 1H), 7.86 (s, 1H), 7.76−7.62 (m, 1H), 7.51−7.38 (m, 2H), 7.28−7.09 (m, 4H), 2.49 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.1, 156.4, 155.6, 138.9, 134.0, 132.2, 130.9, 130.7, 127.7, 126.9, 126.4, 125.7, 123.4, 120.4, 118.2, 20.4; HRMS m/z calcd for $C_{15}H_{13}O_2S$ $[M + H]^+$ 269.0631; found, 269.0630.

4.22. 3-(Thiophen-2-ylthio)-4*H*-chromen-4-one (5f, New Compound). Yield: 78% (51 mg); beige solid; mp: 99−102 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.22 (d, J = 7.6 Hz, 1H), 7.86 (s, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.46−7.35 (m, 4H), 7.07−6.98 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.7, 156.2, 154.5, 135.8, 133.9, 131.1, 130.0, 127.9, 126.2, 125.6, 123.3, 123.1, 118.1; HRMS m/z calcd for $C_{13}H_9O_2S_2$ $[M + H]^+$ 261.00375; found, 261.00386.

4.23. 3-(Benzylthio)-4*H*-chromen-4-one (5g, New Compound). Yield: 44% (30 mg); white solid; mp: 112−114 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.28 (dd, J = 7.9, 1.7 Hz, 1H), 7.82 (s, 1H), 7.67 (ddd, J = 8.7, 7.7, 1.6 Hz, 1H), 7.46−7.17 (m, 7H), 4.06 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.0, 157.3, 156.3, 137.8, 133.9, 129.5, 129.1, 128.5, 127.2, 126.3, 125.7, 123.6, 37.2; HRMS m/z calcd for $C_{16}H_{13}O_2S$ $[M + H]^+$ 269.0631; found, 269.0628.

4.24. 6-Chloro-3-(phenylselanyl)-4*H*-chromen-4-one (7a).[11] Yield: 79% (66 mg); yellow crystalline solid; mp: 105−106 °C (105 °C);[2] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.15 (d, J = 2.6 Hz, 1H), 7.82 (s, 1H), 7.67−7.53 (m, 3H), 7.40−7.27 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.0, 155.4, 154.6, 134.1, 134.0, 131.4, 129.6, 128.4, 127.6, 125.6, 123.9, 119.9, 118.2; HRMS m/z calcd for $C_{15}H_{10}O_2SeCl$ $[M + H]^+$ 336.9527; found, 336.9529.

4.25. 6-Chloro-3-(phenylthio)-4*H*-chromen-4-one (7aa).[11] Yield: 76% (55 mg); white crystalline solid; mp: 124−126 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.16 (d, J = 2.5 Hz, 1H), 8.08 (s, 1H), 7.59 (dd, J = 8.9, 2.6 Hz, 1H), 7.43−7.22 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 151.5, 148.0, 137.5, 173.9, 156.9, 154.6, 134.2, 133.4, 131.6, 130.3, 129.3, 127.4, 125.6, 124.4, 120.54, 120.01; HRMS m/z calcd for $C_{15}H_{10}O_2SCl$ $[M + H]^+$ 289.0085; found, 289.0086.

4.26. 6-Bromo-3-(phenylselanyl)-4*H*-chromen-4-one (7b, New Compound). Yield: 82% (78 mg); beige crystalline solid; mp: 104−105 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 7.86−7.48 (m, 4H), 7.37−7.14 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.9, 155.4, 155.1, 136.8, 134.2, 129.6, 128.8, 128.4, 127.6, 124.3, 120.1, 118.9, 118.3; HRMS m/z calcd for $C_{15}H_{10}O_2SeBr$ $[M + H]^+$ 380.9021; found, 380.9023.

4.27. 6-Bromo-3-(phenylthio)-4*H*-chromen-4-one (7ab).[11] Yield: 78% (65 mg); white crystalline solid; mp: 119−120 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.33 (d, J = 2.1 Hz, 1H), 8.08 (s, 1H), 7.74 (dd, J = 8.9, 2.2 Hz, 1H), 7.43−7.24 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.8, 156.9, 155.1, 137.0, 133.4, 130.4, 129.3, 128.9, 127.5, 124.8, 120.7, 120.2, 119.2; HRMS m/z calcd for $C_{15}H_{10}O_2SBr$ $[M + H]^+$ 332.9579; found, 332.9578.

4.28. 7-Fluoro-3-(phenylselanyl)-4*H*-chromen-4-one (7c, New Compound). Yield: 84% (65 mg); white crystalline solid; mp: 105−107 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.23 (dd, J = 8.7, 6.2 Hz, 1H), 7.79 (s, 1H), 7.60 (dd, J = 6.5, 3.0 Hz, 2H), 7.36−7.27 (m, 3H), 7.19−7.05 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.2, 165.65 (d, J_{C-F} = 255.7 Hz), 157.36 (d, J = 13.2 Hz), 155.35, 134.21, 129.67, 128.98 (d, J_{C-F} = 10.7 Hz), 128.39, 127.73, 119.99, 118.52, 114.46 (d, J_{C-F} = 23.0 Hz), 104.73 (d, J_{C-F} = 25.3 Hz); HRMS m/z calcd for $C_{15}H_{10}O_2SeF$ $[M + H]^+$ 320.9825; found, 320.9828.

4.29. 7-Fluoro-3-(phenylthio)-4*H*-chromen-4-one (7ac, New Compound). Yield: 82% (56 mg); white crystalline solid; mp: 114−117 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.27 (dd, J = 9.6, 6.2 Hz, 1H), 8.06 (s, 1H), 7.43−7.10 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.13, 165.78 (d, J_{C-F} = 256.0 Hz), 157.39 (d, J_{C-F} = 13.3 Hz), 156.93, 133.59, 130.38, 129.34, 29.10 (d, J_{C-F} = 10.7 Hz), 127.47, 120.82, 120.57 (d, J_{C-F} = 2.4 Hz), 114.62 (d, J_{C-F} = 22.8 Hz), 104.90 (d, J_{C-F} = 25.4 Hz); HRMS m/z calcd for $C_{15}H_{10}O_2SF$ $[M + H]^+$ 273.0380; found, 273.0383.

4.30. 6-Chloro-7-methyl-3-(phenylselanyl)-4*H*-chromen-4-one (7d, New Compound). Yield: 83% (72 mg); white crystalline solid; mp: 138−140 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.85−7.75 (m, 1H), 7.63−7.52 (m, 2H), 7.33−7.24 (m, 4H), 2.46 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.0, 155.4, 154.6, 143.2, 134.0, 132.2, 129.6, 128.3, 127.9, 125.8, 122.1, 119.9, 117.9, 20.8; HRMS m/z calcd for $C_{16}H_{12}O_2SeCl$ $[M + H]^+$ 350.9684; found, 350.9681.

4.31. 6-Chloro-7-methyl-3-(phenylthio)-4*H*-chromen-4-one (7ad, New Compound). Yield: 80% (60 mg); white crystalline solid; mp: 140−142 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.15 (s, 1H), 8.06 (s, 1H), 7.45−7.19 (m, 6H), 2.48 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.9, 157.0, 154.6, 143.4, 133.8, 132.4, 130.1, 129.3, 127.3, 126.0, 122.7, 120.2, 120.0, 20.8; HRMS m/z calcd for $C_{16}H_{12}O_2SCl$ $[M + H]^+$ 303.0241; found, 303.0242.

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4.32. 6,8-Dichloro-3-(phenylselanyl)-4*H*-chromen-4-one (7e, New Compound). Yield: 76% (70 mg); white crystalline solid; mp: 113−115 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.08 (d, J = 2.5 Hz, 1H), 7.77 (s, 1H), 7.69 (d, J = 2.5 Hz, 1H), 7.66−7.57 (m, 2H), 7.38−7.30 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.5, 154.3, 150.7, 134.9, 134.0, 131.2, 129.9, 128.8, 126.8, 124.5, 124.4, 119.4; HRMS m/z calcd for $C_{15}H_9O_2SeCl_2$ $[M + H]^+$ 370.9135; found, 370.9133.

4.33. 6,8-Dichloro-3-(phenylthio)-4*H*-chromen-4-one (7ae, New Compound). Yield: 71% (57 mg); white crystalline solid; mp: 129−130 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.08 (d, J = 2.5 Hz, 1H), 8.04 (s, 1H), 7.70 (d, J = 2.5 Hz, 1H), 7.48−7.28 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.2, 155.7, 150.7, 134.1, 132.4, 131.4, 131.2, 129.5, 128.0, 125.1, 124.5, 122.0; HRMS m/z calcd for $C_{15}H_9O_2SCl_2$ $[M + H]^+$ 322.9695; found, 322.9683.

4.34. 6,8-Dibromo-3-(phenylselanyl)-4*H*-chromen-4-one (7f, New Compound). Yield: 78% (89 mg); beige crystalline solid; mp: 116−118 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.28 (d, J = 2.3 Hz, 1H), 7.98 (d, J = 2.3 Hz, 1H), 7.76 (s, 1H), 7.67−7.58 (m, 2H), 7.40−7.30 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.4, 154.3, 152.0, 139.5, 134.9, 129.9, 129.8, 128.8, 128.3, 126.8, 124.8, 119.4, 118.8, 112.9; HRMS m/z calcd for $C_{15}H_9O_2SeBr_2$ $[M + H]^+$ 458.8128; found, 458.8125.

4.35. 6,8-Dibromo-3-(phenylthio)-4*H*-chromen-4-one (7af, New Compound). Yield: 70% (72 mg); brown sold, solid; mp: 126−127 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.30 (d, J = 2.3 Hz, 1H), 8.04 (s, 1H), 8.02 (d, J = 2.3 Hz, 1H), 7.47−7.40 (m, 2H), 7.36−7.27 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.2, 155.8, 152.1, 139.7, 132.4, 131.3, 129.5, 128.4, 128.1, 125.4, 122.1, 119.0, 113.0; HRMS m/z calcd for $C_{15}H_9O_2SBr_2$ $[M + H]^+$ 410.8664; found, 412.86678.

4.36. 7-Ethoxy-3-(phenylselanyl)-4*H*-chromen-4-one (7g, New Compound). Yield: 80% (69 mg); beige crystalline solid; mp: 119−120 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.9 Hz, 1H), 7.79 (s, 1H), 7.63−7.52 (m, 2H), 7.32−7.22 (m, 3H), 6.94 (dd, J = 8.9, 2.3 Hz, 1H), 6.76 (d, J = 2.2 Hz, 1H), 4.08 (q, J = 7.0 Hz, 2H), 1.45 (t, J = 7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.5, 163.5, 158.1, 155.3, 133.7, 129.5, 128.4, 128.0, 127.6, 117.7, 116.9, 115.2, 100.6, 64.3, 14.5; HRMS m/z calcd for $C_{17}H_{15}O_3Se$ $[M + H]^+$ 347.0182; found, 347.0178.

4.37. 7-Ethoxy-3-(phenylthio)-4*H*-chromen-4-one (7ag, New Compound). Yield: 75% (56 mg); white crystalline solid; mp: 119−120 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.9 Hz, 1H), 8.06 (s, 1H), 7.46−7.14 (m, 5H), 6.96 (dd, J = 8.9, 2.0 Hz, 1H), 6.81 (d, J = 2.0 Hz, 1H), 4.11 (q, J = 6.9 Hz, 2H), 1.46 (t, J = 7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.4, 163.7, 158.2, 157.0, 134.4, 129.7, 129.2, 127.8, 127.0, 119.8, 117.5, 115.3, 100.9, 64.4, 14.6; HRMS m/z calcd for $C_{17}H_{15}O_3S$ $[M + H]^+$ 299.0736; found, 299.0738.

4.38. 6-Methoxy-3-(phenylselanyl)-4*H*-chromen-4-one (7h, New Compound). Yield: 86% (71 mg); white crystalline solid; mp: 99−101 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.90 (s, 1H), 7.59 (dd, J = 6.6, 2.9 Hz, 3H), 7.38−7.20 (m, 5H), 3.87 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.0, 157.2, 155.8, 151.2, 133.7, 129.5, 128.4, 128.0, 124.0, 123.8, 116.8, 56.0; HRMS m/z calcd for $C_{16}H_{13}O_3Se$ $[M + H]^+$ 333.0025; found, 333.0022.

4.39. 6-Methoxy-3-(phenylthio)-4*H*-chromen-4-one (7ah, New Compound). Yield: 81% (58 mg); white crystalline solid: 108−109 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.87 (s, 1H), 7.30 (d, J = 3.0 Hz, 1H), 7.14−7.07 (m, 3H), 7.03−6.91 (m, 4H), 3.59 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.0, 157.4, 151.3, 134.4, 129.8, 129.2, 127.1, 124.5, 124.1, 119.6, 119.0, 105.5, 56.0; HRMS m/z calcd for $C_{16}H_{13}O_3S$ $[M + H]^+$ 285.0580; found, 285.0584.

4.40. 7-Methoxy-3-(phenylselanyl)-4*H*-chromen-4-one (7i, New Compound). Yield: 85% (70 mg); yellow solid; mp: 90−92 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.11 (d, J = 8.9 Hz, 1H), 7.80 (s, 1H), 7.61−7.54 (m, 2H), 7.31−7.25 (m, 3H), 6.96 (dd, J = 8.9, 2.3 Hz, 1H), 6.78 (d, J = 2.2 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.5, 164.2, 158.1, 155.3, 133.7, 129.5, 128.4, 128.0, 127.7, 117.8, 117.1, 114.9, 100.2, 55.9; HRMS m/z calcd for $C_{16}H_{13}O_3Se$ $[M + H]^+$ 333.0125; found, 333.0029.

4.41. 7-Methoxy-3-(phenylthio)-4*H*-chromen-4-one (7ai, New Compound). Yield: 80% (57 mg); yellow crystalline solid; mp: 98−100 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.9 Hz, 1H), 8.05 (s, 1H), 7.43−7.17 (m, 5H), 6.97 (dd, J = 8.9, 2.3 Hz, 1H), 6.82 (d, J = 2.2 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.3, 164.3, 158.1, 157.0, 134.3, 129.7, 129.2, 127.8, 127.0, 119.8, 117.6, 115.0, 100.4, 55.9; HRMS m/z calcd for $C_{16}H_{13}O_3S$ $[M + H]^+$ 285.0579; found, 285.0579.

4.42. 7-Methoxy-8-methyl-3-(phenylselanyl)-4*H*-chromen-4-one (7j, New Compound). Yield: 83% (72 mg); yellow crystalline solid; mp: 128−130 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.7 Hz, 1H), 7.87 (s, 1H), 7.58 (s, 2H), 7.27 (s, 3H), 6.95 (d, J = 8.6 Hz, 1H), 3.91 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.0, 161.3, 155.7, 155.4, 133.5, 129.4, 128.5, 127.8, 124.8, 117.0, 116.8, 113.9, 108.9, 56.1, 8.0; HRMS m/z calcd for $C_{17}H_{15}O_3Se$ $[M + H]^+$ 347.0182; found, 347.0180.

4.43. 7-Methoxy-8-methyl-3-(phenylthio)-4*H*-chromen-4-one (7aj, New Compound). Yield: 82% (61 mg); yellow crystalline solid; mp: 134−136 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.28−7.94 (m, 2H), 7.60−7.13 (m, 5H), 7.10−6.85 (m, 1H), 3.92 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.9, 161.5, 157.4, 155.4, 134.5, 129.5, 129.0, 126.8, 124.8, 118.7, 117.5, 114.1, 109.0, 56.1, 8.0; HRMS m/z calcd for $C_{17}H_{15}O_3S$ $[M + H]^+$ 299.0736; found, 299.0738.

4.44. 6-Methyl-3-(phenylselanyl)-4*H*-chromen-4-one (7k, New Compound). Yield: 87% (69 mg); beige crystalline solid; mp: 100−101 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.98 (s, 1H), 7.87 (s, 1H), 7.63−7.53 (m, 2H), 7.44 (dd, J = 8.6, 2.0 Hz, 1H), 7.33−7.22 (m, 4H), 2.42 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.1, 155.8, 154.5, 135.5, 135.0, 133.6, 129.4, 128.4, 127.9, 125.5, 122.8, 117.8, 117.4, 20.9; HRMS m/z calcd for $C_{16}H_{13}O_2Se$ $[M + H]^+$ 317.0076; found, 317.0078.

4.45. 6-Methyl-3-(phenylthio)-4*H*-chromen-4-one (7ak).[11] Yield: 83% (57 mg); white crystalline solid; mp: 119−120 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.11 (s, 1H), 8.07−7.96 (m, 1H), 7.48−7.14 (m, 7H), 2.42 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.0, 157.4, 154.5, 135.7, 135.2, 134.30, 129.6, 129.1, 126.9, 125.6, 123.3, 119.4, 117.9, 20.9; HRMS m/z calcd for $C_{16}H_{13}O_2S$ $[M + H]^+$ 269.0631; found, 269.0629.

4.46. 7-Methyl-3-(phenylselanyl)-4*H*-chromen-4-one (7l, New Compound). Yield: 88% (69 mg); white solid; mp: 110−112 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.6 Hz, 1H), 7.82 (s, 1H), 7.64−7.51 (m, 2H), 7.31−7.15 (m, 5H), 2.44 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.9, 156.4, 155.5, 145.2, 133.6, 129.4, 128.3, 127.9, 127.0, 125.9,

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120.9, 117.7, 117.6, 21.8; HRMS m/z calcd for $C_{16}H_{13}O_2Se$ $[M + H]^+$ 317.0076; found, 317.0073.

4.47. 7-Methyl-3-(phenylthio)-4*H*-chromen-4-one (7al, New Compound). Yield: 86% (58 mg); white solid; mp: 115−116 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 8.18−8.03 (m, 2H), 7.42−7.17 (m, 7H), 2.46 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.8, 157.2, 156.4, 145.4, 134.3, 129.7, 129.1, 127.2, 127.0, 126.1, 121.4, 119.6, 117.8, 21.8; HRMS m/z calcd for $C_{16}H_{13}O_2S$ $[M + H]^+$ 269.0631; found, 269.0633.

4.48. 3-(Phenylselanyl)-4*H*-benzo[*h*]chromen-4-one (7m, New Compound). Yield: 80% (70 mg); brown solid; mp: 111−113 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 8.41 (d, J = 7.0 Hz, 1H), 8.28−8.06 (m, 2H), 7.98−7.86 (m, 1H), 7.81−7.61 (m, 3H), 7.51−7.22 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.8, 155.5, 153.8, 135.9, 133.5, 130.6, 129.6, 129.3, 128.1, 127.5, 127.4, 125.8, 123.8, 122.3, 122.2, 121.1, 119.8; HRMS m/z calcd for $C_{19}H_{13}O_2Se$ $[M + H]^+$ 379.0709; found, 379.0707.

4.49. 3-(Phenylthio)-4*H*-benzo[*h*]chromen-4-one (7am, New Compound). Yield: 76% (58 mg); brown solid; mp: 117−119 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 8.45 (d, J = 8.7 Hz, 1H), 8.27−8.12 (m, 2H), 7.99−7.89 (m, 1H), 7.81−7.64 (m, 3H), 7.53−7.43 (m, 2H), 7.36−7.25 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.9, 153.8, 135.8, 132.2, 129.5, 128.4, 128.1, 127.6, 127.3, 125.7, 123.8, 122.2, 121.1, 120.2, 119.2; HRMS m/z calcd for $C_{19}H_{13}O_2S$ $[M + H]^+$ 305.0631; found, 305.0633.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00445.

Spectra data for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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