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Iron(III) Chloride and Diorganyl Diselenides-Mediated 6-*endo-dig* Cyclization of Arylpropiolates and Arylpropiolamides Leading to 3-Organoselenyl-2*H*-coumarins and 3-Organoselenyl-quinolinones

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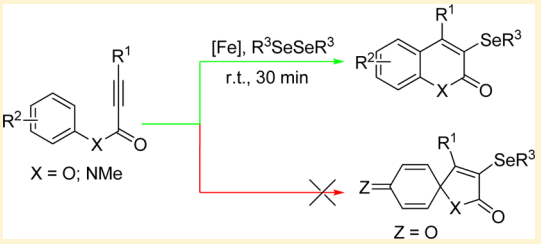
Supporting Information

ABSTRACT: Combination of iron(III) chloride and diorganyl diselenides was used for cyclization of arylpropiolates and arylpropiolamides in formation of 3-organoselenyl-2*H*-coumarins and 3-organoselenyl-quinolinones, respectively. Systematic study to determine the ideal conditions revealed that the two substrates reacted in the same way using identical reaction conditions. The versatility of this method has been demonstrated by extension of the best reaction conditions to substrate having a variety of substituents. Analyses of the optimization reaction also showed that diorganyl diselenides have a dual role by acting as cycling agent and base to restore the aromatic system. Mechanistic investigation studies and analyses of the products obtained have revealed that the cyclization reactions follow an initial 6-*endo-dig* process to give the six-membered heterocycles without involving an intramolecular *ipso*-cyclization route.



INTRODUCTION

Application of organoselenium compounds as synthetic intermediates and discovery of their useful biological activities have attracted much interest in the synthetic community.[1] Thus, extensive studies have been focused on development of new synthetic strategies to introduce a selenium moiety into chemical structures.[2] Incorporation of the selenium atom in a carbon chain modifies the reactivity and physical, pharmacological, and toxicological properties. Regarding the pharmacological properties, the presence of the selenium atom in a potentially bioactive molecule can dramatically increase the native biological activity of the substrate.[3] This is mainly attributed to the fact that the selenium atom can serve as hydrogen-bond acceptor or electron donor, altering the chemical characteristics of enzyme active sites. The methods used for incorporation of an organoselenium moiety into the organic structures are based on the use of electrophile,[4] nucleophile,[5] or radical selenium species.[6] After being introduced in an organic substrate, the organoselenium group confers wide utility due to its peculiar reactivity, mild reaction conditions, and tolerance of many functional groups avoiding protection group chemistry.[7] In this context, organic selenium chemistry has been described as a powerful method to construct new carbon−carbon,[8] carbon−lithium,[9] carbon−halogen,[10] and carbon−hydrogen bonds.[11] We and others have reported another synthetic application of organoselenium and -iron(III) salts as cyclizing agents in electrophilic cyclization reactions.[12] Electrophilic cyclization reactions are known as the most powerful tools for preparation of carbo- and heterocycle compounds.[13] The most commonly used cyclizing agents for these cyclization reactions are $(coll)_2PF_6/BF_3{\cdot}3OEt_2$,[14] IPy_2BF_4,[15] trichloroisocyanuric acid (TCCA),[16] NXS,[17] and halogens.[18] The main advantage for use of halogens as cyclizing agents, in particular, iodine and bromine, is that the final cyclized product becomes an active precursor for use in many other reactions, especially, in palladium-catalyzed cross-coupling reactions. Development of environmentally benign protocols which apply green, mild, and relatively cheaper methods is an important goal for academic researchers and industry. The low price and low toxicity make iron salts a very suitable alternative in organic transformation with a significant impact on advancement of green chemistry concepts. In this regard, various iron salts have been used frequently for activating the cross-coupling reaction of Grignard reagents with organic electrophiles[19] to promote carbon−heteroatom (C−N, C−O, C−S),[20] heteroatom−heteroatom, and carbon−carbon bond formation[21] and for synthesis of heterocycle compounds.[22] We wish to join the green chemistry principles of the iron-based reactions with the peculiar properties of the organoselenium chemistry in the preparation of 3-organoselenyl-2*H*-coumarins **3** and 3-organoselenyl-quinolinones **4** via electrophilic cyclization reaction of arylpropiolates **1** and arylpropiolamides **2**, respectively

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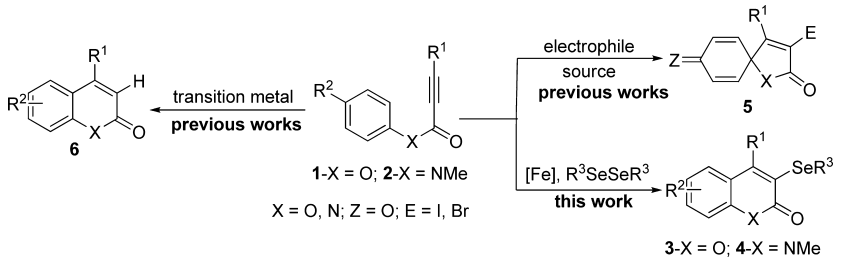
Scheme 1

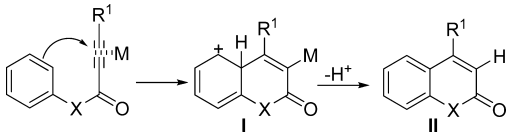


(Scheme 1). There are many excellent methods for cyclization of arylpropiolates and arylpropiolamides via metal-catalyzed intramolecular hydroarylation. In this regard, various transition metals, such as Pt,[23] Au,[24] Pd,[25] In,[26] and Fe,[27] have been used to activate the triple bond and promote cyclization. Elegant and efficient methodologies to cyclization of arylpropiolates **1** and arylpropiolamides **2** have been reported, employing electrophilic cyclization reactions. Most of these protocols represent a powerful route to spiro-type compounds **5** via intramolecular electrophilic *ipso*-halocyclization reaction (Scheme 1).[28] In this study, our challenge is to develop a protocol for cyclization of arylpropiolates **1** and arylpropiolamides **2** that is effective to introduce an organoselenium group in the final structure, avoiding formation of spiro-type compounds **5** (Scheme 1).

RESULTS AND DISCUSSION

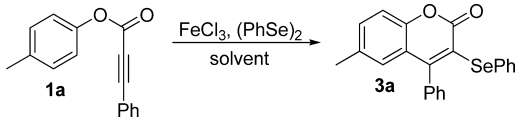
Our study started with optimization of the reaction conditions that provide the best results in the cyclization of arylpropiolates **1**[29] to give the 3-organoselenyl-2*H*-coumarin **3**. In this intramolecular cyclization the key steps involve slow reaction of the aryl carbon−carbon bond with an activated carbon−carbon triple bond to give a resonance-stabilized carbocation **I** and removal of the proton by breaking the C−H to restore the aromatic system **II** (Scheme 2). It is suggested that a proton

Scheme 2



could be delivered into the reaction medium, giving the hydrogenated coumarin **II** instead of forming the 3-organoselenyl-substituted one (Scheme 2).[30] For this reason, in the first attempt we examined the influence of bases in this cyclization process. Thus, reaction of *p*-tolyl-3-phenylpropiolate **1a** (0.25 mmol) with diphenyl diselenide (0.5 equiv) and $FeCl_3$ (1.0 equiv) in the presence of Na_2CO_3 (2.0 equiv) as base and in CH_2Cl_2 (3 mL) as solvent, at room temperature, gave 3-organoselenyl-2*H*-coumarin **3a** in 62% yield (Table 1, entry 1). To determine the influence of variation of bases in formation of coumarin **3a**, some experiments were carried out using common and inexpensive bases, such as K_2CO_3, $NaHCO_3$, K_3PO_4, and KOH. The bases used were rather effective but did not increase the yields of the reactions (Table 1, entries 2−5). We also evaluated the influence of different solvents in the yield of the cyclization reaction of arylpropiolate **1a**. As shown in Table 1, only moderate yields were observed with $MeNO_2$, MeCN, and toluene (Table 1, entries 6−8). On the contrary, dioxane, DMSO, and EtOH gave no product at all (Table 1,

Table 1. Effect of Different Reaction Parameters on Preparation of 3-Organoselenyl-2*H*-coumarin 3a[a]



entry	$FeCl_3$ (equiv)	$(PhSe)_2$ (equiv)	base	solvent	yield (%)[b]
1	1.0	0.5	Na_2CO_3	CH_2Cl_2	62
2	1.0	0.5	K_2CO_3	CH_2Cl_2	54
3	1.0	0.5	$NaHCO_3$	CH_2Cl_2	64
4	1.0	0.5	K_3PO_4	CH_2Cl_2	60
5	1.0	0.5	KOH	CH_2Cl_2	61
6	1.0	0.5	$NaHCO_3$	$MeNO_2$	45
7	1.0	0.5	$NaHCO_3$	MeCN	20
8	1.0	0.5	$NaHCO_3$	toluene	39
9	1.0	0.5	$NaHCO_3$	dioxane	0
10	1.0	0.5	$NaHCO_3$	DMSO	0
11	1.0	0.5	$NaHCO_3$	EtOH	0
12	1.0	0.5		CH_2Cl_2	67
13	2.0	1.0		CH_2Cl_2	86
14	3.0	1.0		CH_2Cl_2	87
15	1.0	1.0		CH_2Cl_2	30
16	0.2	1.0		CH_2Cl_2	46
17	1.0	0.5		CH_2Cl_2	40[c]

[a]The reaction was performed in the presence of *p*-tolyl-3-phenylpropiolate **1a** (0.25 mmol), base (2.0 equiv), diphenyl diselenide, and $FeCl_3$ using solvent (3 mL) under an argon atmosphere at room temperature. [b]Yields were determined by GC analysis. [c]The reaction was carried out under aerobic conditions.

entries 9−11). The cyclization reaction gave a satisfactory yield in the absence of base, although the presence of side product, most probably produced by decomposition of the starting material, made the purification process hard (Table 1, entry 12). The acceptable yield delivered in this condition implies that other species could be acting as base. This result and knowledge that diphenyl diselenide has two equal reactivity portions (2 PhSe) suggest that one portion is incorporated in the final product and the other is acting as base. This means that at least 1 equiv of diphenyl diselenide is necessary so the reaction can be completed within the maximum. To confirm this hypothesis, we changed the amount of diphenyl diselenide from 0.5 to 1.0 equiv. In this condition, the reaction was completed in 30 min, giving 3-organoselenyl-2*H*-coumarin **3a** in 86% yield (Table 1, entry 13). This experimental evidence supports the hypothesis that one portion of diphenyl diselenide ($PhSe^-$) is the base necessary to restore the aromatic system (see Scheme 5; mechanism proposal). It was also observed that an increase in $FeCl_3$ loading to 3.0 equiv or a reduction to 1.0 equiv did not result in a significant increase in the product yield

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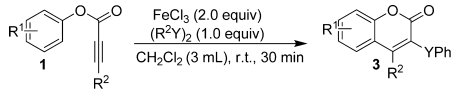
Table 2. Synthesis of 3-Organoselenyl-2*H*-coumarins 3[a]



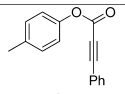
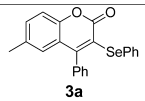
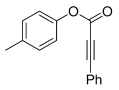
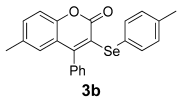
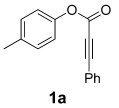
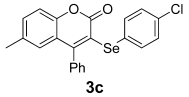
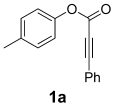
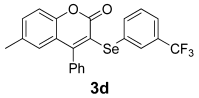
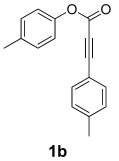
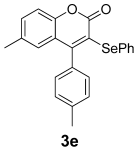
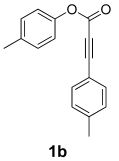
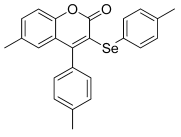
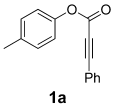
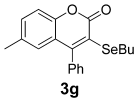
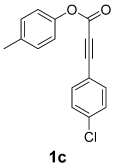
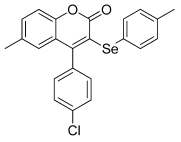
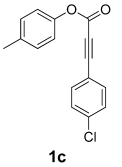
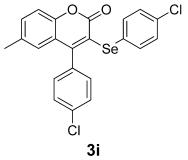
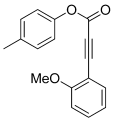
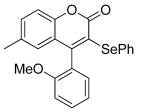
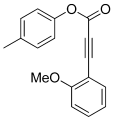
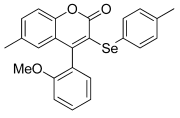
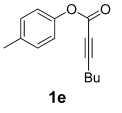
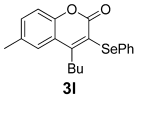
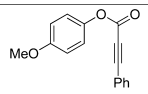
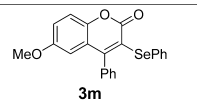
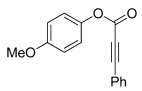
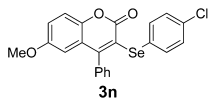
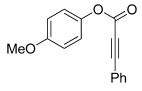
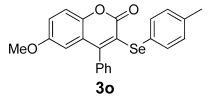
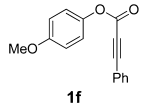
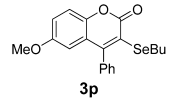
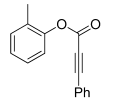
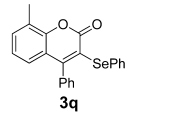
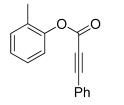
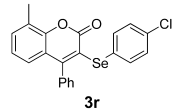
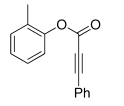
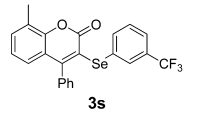
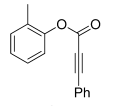
entry	arylpropiolates 1	$(R^2Y)_2$	3-organoselenyl-2*H*-coumarins 3	yield (%)
1	 1a	$(PhSe)_2$	 3a	91
2	 1a	$(p\text{-}MeC_6H_4Se)_2$	 3b	94
3	 1a	$(p\text{-}ClC_6H_4Se)_2$	 3c	73
4	 1a	$(m\text{-}CF_3C_6H_4Se)_2$	 3d	66
5	 1b	$(PhSe)_2$	 3e	41[b]
6	 1b	$(p\text{-}MeC_6H_4Se)_2$	 3f	74
7	 1a	$(n\text{-}BuSe)_2$	 3g	72
8	 1c	$(p\text{-}MeC_6H_4Se)_2$	 3h	67
9	 1c	$(p\text{-}ClC_6H_4Se)_2$	 3i	54
10	 1d	$(PhSe)_2$	 3j	96
11	 1d	$(p\text{-}MeC_6H_4Se)_2$	 3k	73
12	 1e	$(PhSe)_2$	 3l	61
13	 1f	$(PhSe)_2$	 3m	48[b]
14	 1f	$(p\text{-}ClC_6H_4Se)_2$	 3n	61
15	 1f	$(p\text{-}MeC_6H_4Se)_2$	 3o	59
16	 1f	$(n\text{-}BuSe)_2$	 3p	62
17	 1g	$(PhSe)_2$	 3q	81
18	 1g	$(p\text{-}ClC_6H_4Se)_2$	 3r	68
19	 1g	$(m\text{-}CF_3C_6H_4Se)_2$	 3s	72
20	 1g	$(p\text{-}MeC_6H_4Se)_2$	3t	74
21	1g	$(n\text{-}BuSe)_2$	3u	70
22	1h	$(PhSe)_2$	3v	79
23	1i	$(PhSe)_2$	3w	74
24	1i	$(p\text{-}MeC_6H_4Se)_2$	3x	95
25	1i	$(p\text{-}ClC_6H_4Se)_2$	3y	77
26	1a	$(PhTe)_2$	3z	44[b]

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Table 2. continued

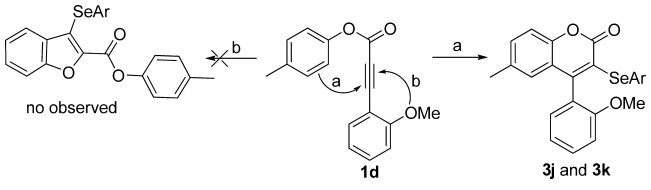
[a]The reaction was performed in the presence of arylpropiolates **1** (0.25 mmol), diorganyl diselenide (or diphenyl ditelluride) (1.0 equiv), and $FeCl_3$ (2.0 equiv) in CH_2Cl_2 (3 mL) under an argon atmosphere at room temperature for 30 min. [b]The reaction carried out for 10 h at room temperature or for 8 h under reflux did not improve the product yield.

(Table 1, entries 14 and 15). Although we carried out many experiments using different amounts of $FeCl_3$ and 0.5 equiv of diorganyl diselenides under aerobic conditions to determine if oxygen could be the mediator for diorganyl diselenide regeneration, an improvement in the efficiency of the reaction was only obtained with 1.0 equiv of diorganyl diselenide under argon atmosphere (Table 1, entries 16 and 17). For determination of the reaction time during the optimization reactions, samples of the reaction mixture were analyzed by TLC, which showed that 30 min was the reaction time necessary for the reaction to go completion.

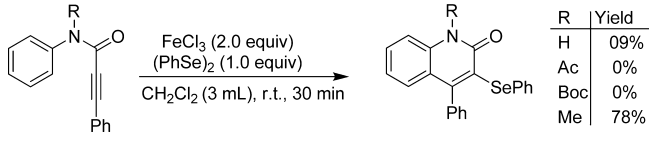
On the basis of the optimized reaction conditions (Table 1, entry 13), reaction between a wide range of arylpropiolates **1** and different diorganyl diselenides was carried out to establish the generality of our method. First, we examined the influence of functional groups in the aromatic ring of diaryl diselenides. Thus, a variety of substituted diaryl diselenides were subjected to optimized conditions with arylpropiolates **1a**,**b** as given in Table 2, entries 1−7. It was found that reactions of diaryl diselenides having electronically neutral, withdrawing, and electron-donating groups were efficient, giving good yields of the cyclized 3-organoselenyl-2*H*-coumarins **3a**−**f** (Table 2, entries 1−6). In more detail, it can be noted that the cyclization reaction was a little more efficient with diaryl diselenides having neutral and electron-donating groups (Table 2, entries 1 and 2) than that of withdrawing groups (Table 2, entries 3 and 4). The reaction was also effective with dialkyl diselenide, giving 3-butylselanyl-2*H*-coumarin **3g** in 72% yield (Table 2, entry 7). This result is significant because in most cases use of dialkyl diselenides is avoided due to the possibility of a selenium alkyl group undergoing *β*-selenoxide elimination during the purification or workup process, giving the final product without the selenium group incorporated in the structure. We next investigated the influence of the substituent directly bonded to alkyne (Table 2, entries 8−12). These examples were demonstrated to be strongly influenced by the electronic effect of the substituent. Alkynes having an electron-deficient aromatic ring gave the corresponding coumarins **3h** and **3i** in moderate yields (Table 2, entries 8 and 9). In contrast, yields were increased considerably when electron-rich aromatic rings, such as *o*-methoxyphenyl, are bonded to the alkyne (Table 2, entries 10 and 11). It should be noted that cyclization of arylpropiolate **1d** (Table 2, entries 10 and 11), which is an *o*-alkynyl anisole derivative, could give a competitive electrophilic cyclization reaction to form the benzofuran derivatives (Scheme 3).[13d] However, under our optimized reaction conditions we found that cyclization afforded exclusively the corresponding coumarins **3j** and **3k** in the complete absence of benzofuran derivatives (Scheme 3). This high selectivity may be attributed to the cationic character of the intermediate and the higher nucleophilicity of the phenyl ring when compared to the methoxy group. Moreover, we examined the reactivity of arylpropiolate **1e**, which has an alkyl chain directly bonded to the carbon−carbon triple bond. Usually the absence of *π* bonds next to the alkyne might hamper coordination with the electrophilic source, resulting in decreased reactivity for nucleophilic attack at the carbon−carbon triple bond. In our case, the rate of the reaction was not sensitive to the presence of the alkyl chain and substrate **1e** reacted under standard conditions giving the desired coumarin **3l** in good yield (Table 2, entry 12). To expand the substrate scope of this reaction, arylpropiolate **1f**, which has a *p*-methoxy substituent, was employed to react under our optimized iron(III) chloride and diorganyl diselenides system. Results revealed that the coumarins **3m**−**p** were obtained in moderate yields (Table 2, entries 13−16). These results are significant because it is known that halocyclization of these substrates produced 3-halospirotrienones as products exclusively.[31] Additional reactions with substituted arylpropiolates bearing *o*-methyl and *o*-*tert*-butyl groups and unsubstituted arylpropiolate with different diorganyl diselenides were also attempted under optimized conditions. It was notable that in all cases the related products were successfully obtained in high yields (Table 2, entries 17−25). Finally, we investigated the reactivity of a diorganyl ditelluride toward our typical cyclization condition. Under standard conditions, diphenyl ditelluride gave the predictable cyclized 3-phenyltellanyl-2*H*-coumarin **3z** in moderate yield (Table 2, entry 26). Compounds containing a Csp^2−Te bond are of particular interest because the tellurium moiety offers high application for further structure elaboration.[32] Concerning the use of disulfides instead of diselenides or ditellurides, we found some limitations in this methodology. For example, there was no reaction with diorganyl disulfides such as diphenyl disulfide under optimized condition.

The effect of the $FeCl_3$ and diorganyl diselenides system applied to arylpropiolates **1** (Table 2) was further extended to arylpropiolamides **2**.[33] The strong influence of N substitution in the electrophilic cyclization reaction of the aniline analog has been described. It has been shown that the presence of electron-donating groups on the nitrogen had a positive influence on the reaction yields.[31b] Taking this into account four different N-substitued arylpropiolamides were examined under our optimized reaction conditions to determine the efficiency on formation of 3-organoselenyl-quinolinones **4** (Scheme 4). In the course of these test experiments we could observe that in arylpropiolamides having the hydrogen atom directly bonded to the nitrogen the product yield was no more

Scheme 3



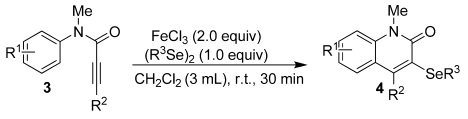
Scheme 4

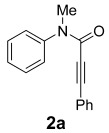
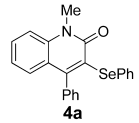
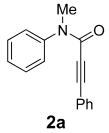
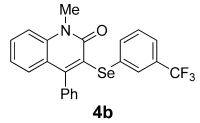
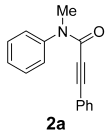
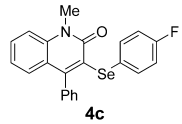
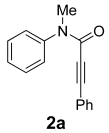
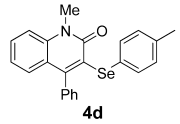
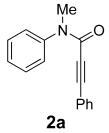
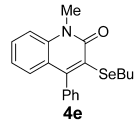
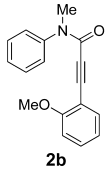
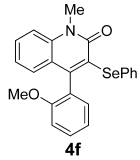
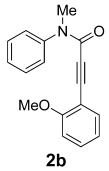
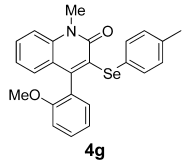
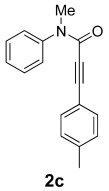
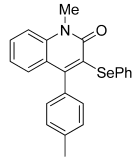
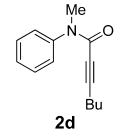
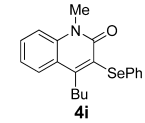
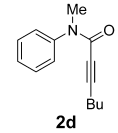
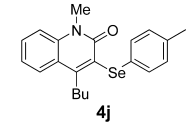
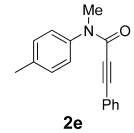
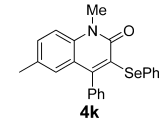
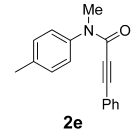
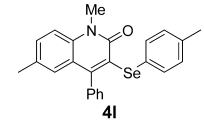
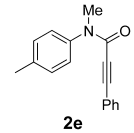
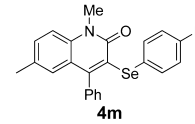
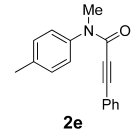
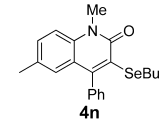
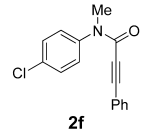
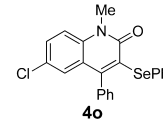
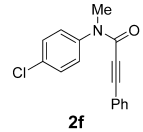
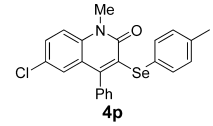
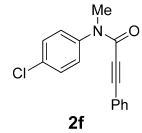
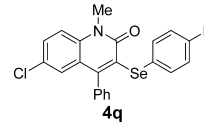
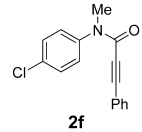
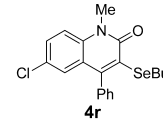


R	Yield
H	09%
Ac	0%
Boc	0%
Me	78%

dx.doi.org/10.1021/jo502199q | J. Org. Chem. 2014, 79, 10526−10536

Table 3. Synthesis of 3-Organoselenyl-quinolinones 4[a]



entry	N-methyl arylpropiolamides 3	$(R^3Se)_2$	3-organoselenyl-quinolinones 4	yield (%)
1	 **2a**	$(PhSe)_2$	 **4a**	78
2	 **2a**	$(m\text{-}CF_3C_6H_4Se)_2$	 **4b**	73
3	 **2a**	$(p\text{-}FC_6H_4Se)_2$	 **4c**	84
4	 **2a**	$(p\text{-}MeC_6H_4Se)_2$	 **4d**	85
5	 **2a**	$(n\text{-}BuSe)_2$	 **4e**	79
6	 **2b**	$(PhSe)_2$	 **4f**	72
7	 **2b**	$(p\text{-}MeC_6H_4Se)_2$	 **4g**	99
8	 **2c**	$(PhSe)_2$	 **4h**	56
9	 **2d**	$(PhSe)_2$	 **4i**	58
10	 **2d**	$(p\text{-}MeC_6H_4Se)_2$	 **4j**	61
11	 **2e**	$(PhSe)_2$	 **4k**	76
12	 **2e**	$(p\text{-}MeC_6H_4Se)_2$	 **4l**	92
13	 **2e**	$(p\text{-}FC_6H_4Se)_2$	 **4m**	73
14	 **2e**	$(n\text{-}BuSe)_2$	 **4n**	81
15	 **2f**	$(PhSe)_2$	 **4o**	68
16	 **2f**	$(p\text{-}MeC_6H_4Se)_2$	 **4p**	80
17	 **2f**	$(p\text{-}FC_6H_4Se)_2$	 **4q**	63
18	 **2f**	$(n\text{-}BuSe)_2$	 **4r**	53

[a]The reaction was performed in the presence of *N*-methyl arylpropiolamides **3** (0.25 mmol), diorganyl diselenides (1.0 equiv), and $FeCl_3$ (2.0 equiv) in CH_2Cl_2 (3 mL) under an argon atmosphere at room temperature for 30 min.

than 9%. Additionally, no reactions occurred when *N*-Ac and *N*-Boc groups were tested. In contrast, *N*-methyl arylpropiolamide afforded the corresponding *N*-methyl quinolinone in 78% yield (Scheme 4). After these initial experiments the effect of the optimized condition was tested in the cyclization of other *N*-methyl arylpropiolamides **2** (Table 3). In the initial trials *N*-methyl arylpropiolamide **2a** was chosen as a model to investigate the influence of different diorganyl diselenides in the cyclization. Neutral, electron-rich, and electron-deficient diorganyl diselenides were effective to generate the corresponding *N*-quinolines **4a**–**d** in good to excellent yields (Table 3, entries 1–4). Dialkyl diselenides, such as dibutyl diselenide,

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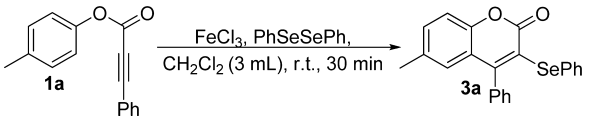
gave a result similar to those with diaryl diselenides, providing the cyclized product **4e** in 79% yield (Table 3, entry 5). Again, decomposition by selenoxide via syn elimination of the alkyl selenide moiety was not observed. To further explore the effect of other substituents on the alkyne we replaced phenyl by *o*-methoxyphenyl, *p*-methylphenyl, and butyl groups. The electron-donating *o*-methoxyphenyl afforded *N*-quinolines **4f** and **4g** in 72% and 99% yields (Table 3, entries 6 and 7). Anti attack of the oxygen atom at the activated triple bond to give the benzofuran derivative via an *endo-dig* cyclization is expected in the cyclization of this substrate. However, no such cyclized product was obtained. When the reaction was carried out with *p*-methylphenyl the yield of *N*-quinoline **4h** did not exceed 56% (Table 3, entry 8). Moreover, the alkyl group bonded to alkynes is assumed to exert a negative effect on the electrophilic cyclization reactions. This effect was not observed for the *N*-methyl arylpropiolamide **2d**, which was subjected to the reaction conditions giving the *N*-methyl quinolines **4i** and **4j** in 58% and 61% yields, respectively (Table 3, entries 9 and 10). Finally, we compared the reactivity of the substituent on the aryl bonded to the nitrogen atom under the same conditions. This evaluation showed that both electron-donating and electron-withdrawing groups gave the corresponding *N*-methyl quinolines in good yields (Table 3, entries 11−18), although the presence of an electron-withdrawing chlorine group in the para position of the aromatic ring had a small negative effect on the yields of desired products (Table 3, entries 15−18).

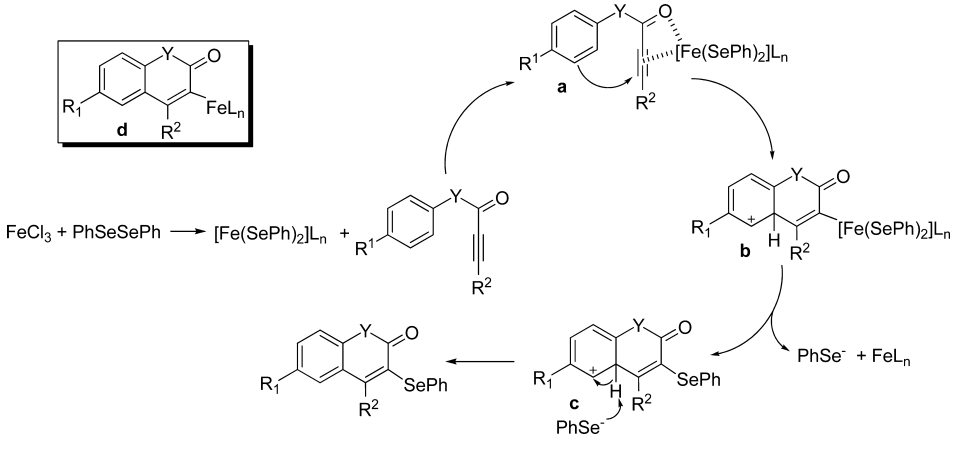
To best understand the mechanism of this cyclization reaction, further investigations were carried out with control experiments, and the results are summarized in Table 4. It has been previously reported in the literature that Brønsted acids promote cyclizations similar to those described in Tables 2 and 3.[34] Thus, when *p*-tolyl-3-phenylpropiolate **1a** (0.25 mmol) was reacted under optimized reaction conditions, in the presence of gaseous HCl and in the absence of iron(III) chloride the corresponding product **2a** was not observed but rather led to recovering unreacted starting material **1a** (Table 4, entry 1). This result suggests that gaseous HCl, which could be generated in situ from iron(III) chloride, was not the cyclization promoter. We next treated *p*-tolyl-3-phenylpropiolate **1a** (0.25 mmol) with $FeCl_3$ (2 equiv) in CH_2Cl_2 (3 mL), and after 1 h at room temperature diphenyl diselenide (1.0 equiv) was added (Table 4, entry 2). Using this condition no trace amount of cyclized product **3a** was observed. From this result we concluded that reaction of a cyclized intermediated **d** (Scheme 5), which has a Csp^2−Fe bond, with diphenyl diselenide to give the product is not supported. In order to determine whether product **3a** was formed via a direct electrophilic cyclization pathway, promoted by PhSeCl, without the participation of iron(III) chloride, we performed a reaction test adding PhSeCl[35] to a solution of substrate **1a** in CH_2Cl_2 (3 mL) in the absence of iron(III) chloride (Table 4, entry 3). Product **3a** was not observed, and the starting material was recovered unchanged. This observation shows that the presence of a cooperative reaction of iron(III) chloride and diphenyl diselenide is crucial for the reaction outcome. Bolm and co-workers demonstrated that in the reactions promoted by transition metals occasionally trace metal impurities were the active catalytic species.[36] When $FeCl_3$ is used to promote the reactions the presence of trace amounts of Cu_2O as contaminant could be the catalyst. We carried out the reaction of *p*-tolyl-3-phenylpropiolate **1a** under optimized reaction conditions in the absence of $FeCl_3$ and presence of CuO_2 to exclude the effect of Cu_2O in this cyclization. There was no product formed when CuO_2 1%, 3%, 5%, and 2.0 equiv were employed (Table 4, entries 4−7). These results indicate that $FeCl_3$ is the active species in these cyclizations. On the basis of these experimental results and the knowledge that the iron selenolate complexes $[Fe(SeR)_2]Ln$ can be prepared by reaction of the iron species with organoselenolates,[37] it is reasonable to assume that the reaction proceeds through initial activation of the carbon−carbon triple bond of substrate by the complex $[Fe(SeR)_2]Ln$ to form the intermediate **a**. Attack of the electron cloud from the aromatic ring at the activated intermediate **a** produces the cyclized species **b**. Reductive

Table 4. Control Experiments and Mechanism Investigation



entry	$FeCl_3$ (equiv)	$(PhSe)_2$ (equiv)	additive	yield (%)
1		1.0	$HCl_{(g)}$	0
2	2.0	1.0		0
3			PhSeCl	0
4		1.0	Cu_2O 1%	0
5		1.0	Cu_2O 3%	0
6		1.0	Cu_2O 5%	0
7		1.0	Cu_2O 2 equiv	0

Scheme 5



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elimination from **b** gives the stabilized carbocation **c**. Removal of the hydrogen by breaking the C−H bond, promoted by the selenolate anion, restores the aromatic system, giving the cyclized product. The structure of coumarins **3** and quinolinones **4** agree with HRMS and ^{1}H and ^{13}C NMR spectra as listed in the Experimental Section. In addition, the crystal structure of **3a**, shown in Figure 1 (Supporting Information), provided proof of the exact position of the cyclization as a 6-*endo-dig* cyclization process.

CONCLUSION

In summary, the iron(III) chloride and diorganyl diselenides system has been used to synthesize 3-organoselenyl-2*H*-coumarins and 3-organoselenyl-quinolinones from readily available arylpropiolates and arylpropiolamides, respectively. The results obtained demonstrated that the advantages of using this methodology are (1) the reactions were carried out under mild conditions (at room temperature in a short reaction time), (2) the same reaction conditions were effective to cyclize two different substrates, (3) one new carbon−carbon bond and one new carbon−selenium bond were formed in a one-pot procedure, (4) cyclization was regioselective, giving exclusively the six-membered heterocycles following an initial 6-*endo-dig* mechanism instead of spirocycle products, and (5) association of iron(III) chloride with diorganyl diselenides was useful not only as a cyclizing agent but also to introduce an organoselenium functionality into the quinolone and coumarin rings. The chemoselectivity of the reaction with *o*-alkynyl anisole derivatives has been briefly examined through the competitive oxygen versus selenium cyclization. We found that cyclization afforded exclusively the product corresponding to selenium cyclization in the complete absence of benzofuran derivatives. The advantage to introducing the organoselenium moiety to quinolones and coumarins is that the products formed are suitable substrates for numerous synthetically useful procedures.

EXPERIMENTAL SECTION

General Procedure for Synthesis of 3-Organoselenyl-2*H*-coumarins 3 and 3-Organoselenyl-quinolinones 4. In a Schlenk tube, under air, containing dichloromethane (3 mL) was added $FeCl_3$ (0.082 g, 0.5 mmol) and diorganyl dichalcogenides (0.25 mmol). The resulting solution was stirred at room temperature for 20 min. After this time, arylpropiolates or arylpropiolamides (0.25 mmol) was added and the reaction was stirred for 30 min at room temperature. The mixture was cooled to room temperature, dissolved in ethyl acetate, washed with a saturated solution of NH_4Cl, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography over silica gel to provide the 3-organoselenyl-2*H*-coumarins **3** or 3-organoselenyl-quinolinones **4**. Column chromatography was carried out using hexane/ethyl acetate (95/5) as eluent for 3-organoselenyl-2*H*-coumarins **3** and hexane/ethyl acetate (85/55) for 3-organoselenyl-quinolinones **4**.

6-Methyl-4-phenyl-3-(phenylselanyl)-2*H*-chromen-2-one (3a). Obtained as a yellow solid. Yield: 0.084 g (86%); mp 123−125 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.45−7.42 (m, 3H), 7.32−7.29 (m, 3H), 7.25−7.23 (m, 1H), 7.18−7.10 (m, 5H), 6.79 (s, 1H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.5, 158.9, 151.7, 136.4, 133.9, 132.9, 132.8, 130.5, 128.9, 128.7, 128.4, 128.2, 127.7, 127.3, 120.7, 120.2, 116.5, 20.8. MS (EI, 70 eV; *m*/*z* (relative intensity)): 375 (89), 348 (58), 295 (74), 252 (67), 189 (100), 165 (40), 126 (20), 77 (22). HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{17}O_2Se$ (M + H$^+$) 393.0394; found 393.0398 (M + H)$^+$.

6-Methyl-4-phenyl-3-(*p*-tolylselanyl)-2*H*-chromen-2-one (3b). Obtained as a yellow solid. Yield: 0.095 g (94%); mp 120−122 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.46−7.45 (m, 3H), 7.30−7.28 (m, 1H), 7.25−7.21 (m, 3H), 7.17−7.15 (m, 2H), 6.96 (d, *J* = 7.7 Hz, 2H), 6.79 (s, 1H), 2.26 (s, 3H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.6, 158.5, 151.5, 137.4, 136.4, 133.8, 133.2, 132.8, 129.7, 128.7, 128.3, 128.2, 127.4, 126.5, 120.9, 120.2, 116.4, 21.0, 20.8. MS (EI, 70 eV; *m*/*z* (relative intensity)): 406 (70), 325 (100), 298 (48), 255 (11), 178 (52), 91 (34). HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{18}O_2Se$ (M + H$^+$) 407.0550; found 407.0556 (M + H)$^+$.

3-((4-Chlorophenyl)selanyl)-6-methyl-4-phenyl-2*H*-chromen-2-one (3c). Obtained as a yellow solid. Yield: 0.077 g (73%); mp 121−123 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.47−7.44 (m, 3H), 7.33−7.30 (m, 1H), 7.26−7.22 (m, 3H), 7.16−7.14 (m, 2H), 7.09 (d, *J* = 0.5 Hz, 2H), 6.80 (s, 1H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.4, 158.8, 151.5, 136.1, 134.2, 134.0, 133.6, 133.1, 129.0, 128.5, 128.4, 128.1, 127.4, 120.3, 120.0, 116.4, 20.7. MS (EI, 70 eV; *m*/*z* (relative intensity)): 425 (37), 345 (39), 318 (29), 281 (39), 178 (45), 152 (19). HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{15}ClO_2Se$ (M + H$^+$) 427.0004; found 427.0010 (M + H)$^+$.

6-Methyl-4-phenyl-3-((3-(trifluoromethyl)phenyl)selanyl)-2*H*-chromen-2-one (3d). Obtained as a yellow oil. Yield: 0.075 g (66%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.53−7.38 (m, 6H), 7.33−7.21 (m, 3H), 7.16−7.11 (m, 2H), 6.83 (s, 1H), 2.26 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.5, 159.2, 151.6, 136.1, 135.8, 134.1, 133.3, 131.1 (*J* = 32.2 Hz), 129.3 (*J* = 3.6 Hz), 129.2, 128.9, 128.4, 128.0, 127.4, 124.1 (*J* = 3.6 Hz), 123.4 (*J* = 272 Hz), 119.9, 116.5, 20.7. MS (EI, 70 eV; *m*/*z* (relative intensity)): 460 (76), 379 (36), 352 (81), 235 (15), 178 (100), 152 (45), 126 (14), 77 (14). HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{15}F_3O_2Se$ (M + H$^+$): 461.0268; found 461.0270 (M + H)$^+$.

6-Methyl-3-(phenylselanyl)-4-(*p*-tolyl)-2*H*-chromen-2-one (3e). Obtained as a yellow solid. Yield: 0.084 g (41%); mp 140−142 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 7.34−7.23 (m, 6H), 7.19−7.13 (m, 3H), 7.08−7.04 (m, 2H), 6.86 (s, 1H), 2.44 (s, 3H), 2.26 (3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.6, 159.1, 151.6, 138.7, 133.8, 133.4, 132.9, 132.6, 130.5, 129.0, 128.8, 128.1, 127.6, 127.2, 120.4, 120.2, 116.4, 21.3, 20.8. MS (EI, 70 eV; *m*/*z* (relative intensity)): 406 (15), 298 (14), 178 (33), 152 (14), 115 (11), 77 (100). HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{18}O_2Se$ (M + H$^+$) 407.0550; found 407.0553 (M + H)$^+$.

6-Methyl-4-*p*-tolyl-3-(*p*-tolylselanyl)-2*H*-chromen-2-one (3f). Obtained as a yellow solid. Yield: 0.077 g (74%); mp 136−138 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.28−7.21 (m, 6H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.84 (s, 1H), 2.45 (s, 3H), 2.26 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.5, 158.6, 151.5, 138.6, 137.3, 135.6, 133.7, 133.4, 133.1, 132.7, 129.6, 129.0, 128.5, 127.5, 126.5, 120.8, 120.2, 116.3, 21.3, 21.0, 20.7. MS (EI, 70 eV; *m*/*z* (relative intensity)): 420 (15), 339 (23), 312 (14), 178 (35), 91 (100), 65 (31). HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{20}O_2Se$ (M + H$^+$) 421.0707; found 421.0709 (M + H)$^+$.

3-(Butylselanyl)-6-methyl-4-phenyl-2*H*-chromen-2-one (3g). Obtained as a yellow solid. Yield: 0.066 g (72%); mp 61−63 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.55−7.48 (m, 3H), 7.30−7.22 (m, 4H), 6.77 (s, 1H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.25 (s, 3H), 1.51 (quint, *J* = 7.3 Hz, 2H), 1.28 (sex, *J* = 7.5 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.6, 156.8, 151.2, 136.7, 133.7, 132.2, 128.7, 128.5, 126.9, 120.2, 119.4, 116.3, 33.4, 27.3, 22.6, 20.8,13.4. MS (EI, 70 eV; *m*/*z* (relative intensity)): 372 (41), 314 (100), 178 (34), 165 (15), 152 (12). HRMS (ESI-TOF) *m*/*z* cald for $C_{20}H_{20}O_2Se$ (M + H$^+$) 373.0707; found 373.0712 (M + H)$^+$.

4-(4-Chlorophenyl)-6-methyl-3-(*p*-tolylselanyl)-2*H*-chromen-2-one (3h). Obtained as a yellow oil. Yield: 0.073 g (67%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.38 (d, *J* = 8.3 Hz, 2H), 7.31−7.29 (m, 1H), 7.25−7.23 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.75 (s, 1H), 2.27 (s, 3H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.5, 156.7, 151.3, 137.6, 134.7, 134.4, 133.9, 133.4, 132.9, 129.7, 128.6, 126.8, 126.1, 121.5, 119.8, 116.4, 21.0, 20.7. MS (EI, 70 eV; *m*/*z* (relative intensity)): 440 (37), 359 (40), 332 (24), 281 (43), 178 (20), 91 (35). HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{17}ClO_2Se$ (M + H$^+$) 441.0161; found 441.0167 (M + H)$^+$.

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4-(4-Chlorophenyl)-3-((4-chlorophenyl)selanyl)-6-methyl-2*H*-chromen-2-one (3i). Obtained as a yellow oil. Yield: 0.06 g (54%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.44−7.41 (m, 2H), 7.35−7.32 (m, 1H), 7.27−7.21 (m, 3H), 7.13−7.07 (m, 4H), 7.76 (s, 1H), 2.27 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.3, 157.4, 151.5, 135.0, 134.5, 134.2, 133.9, 133.3, 129.6, 129.1, 128.8, 128.1, 127.0, 120.9, 119.8, 116.6, 20.8. MS (EI, 70 eV; *m*/*z* (relative intensity)): 459 (38), 352 (26), 281 (41), 178 (30), 152 (15), 73 (40). HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{14}Cl_2O_2Se$ (M + H^+) 460.9614; found 460.9616 (M + H)$^+$.

4-(2-Methoxyphenyl)-6-methyl-3-(phenylselanyl)-2*H*-chromen-2-one (3j). Obtained as a yellow solid. Yield: 0.101 g (96%); mp 132−134 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.45−7.41 (m, 1H), 7.34−7.32 (m, 2H), 7.27−7.22 (m, 2H), 7.15−7.12 (m, 3H), 7.06−7.05 (m, 2H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.77 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.5, 156.8, 155.9, 151.7, 133.7, 132.7, 132.5, 130.4, 130.3, 129.3, 128.7, 127.1, 127.0, 125.3, 121.2, 120.4, 120.0, 116.3, 110.9, 55.2, 20.7. MS (EI, 70 eV; *m*/*z* (relative intensity)): 421 (56), 264 (79), 249 (100), 178 (20), 165 (51), 77 (28). HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{18}O_3Se$ (M + H^+) 423.0499; found 423.0502 (M + H)$^+$.

4-(2-Methoxyphenyl)-6-methyl-3-(*p*-tolylselanyl)-2*H*-chromen-2-one (3k). Obtained as a yellow solid. Yield: 0.079 g (73%); mp 172−174 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.46−7.42 (m, 1H), 7.25−7.21 (m, 4H), 7.07−7.06 (m, 2H), 6.96−6.93 (m, 3H), 6.75 (s, 1H), 3.67 (s, 3H), 2.25 (s, 3H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.5, 156.2, 156.0, 151.6, 137.1, 133.6, 133.1, 132.5, 130.4, 129.5, 127.1, 126.4, 125.4, 121.7, 120.5, 120.1, 116.3, 110.9, 55.2, 21.0, 20.8. MS (EI, 70 eV; *m*/*z* (relative intensity)): 436 (31), 281 (41), 265 (42), 165 (39), 133 (18), 73 (36). HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{20}O_3Se$ (M + H^+) 437.0655; found 437.0659 (M + H)$^+$.

4-Butyl-6-methyl-3-(phenylselanyl)-2*H*-chromen-2-one (3l). Obtained as a yellow solid. Yield: 0.056 g (61%); mp 70−72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.46−7.43 (m, 3H), 7.32(dd, *J* = 0.5 Hz, *J* = 1.9 Hz, 1H), 7.24−7.19 (m, 4H), 3.23 (m,2H), 2.43 (s, 3H), 1.60−1.45 (m, 4H), 0.97 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.2, 159.4, 151.6, 133.9, 133.0, 131.4, 130.7, 129.1, 127.0, 125.2, 119.0, 118.6, 116.8, 33.4, 31.8, 22.9, 21.0, 17.3. MS (EI, 70 eV; *m*/*z* (relative intensity)): 372 (100), 330 (21), 281 (29), 221 (32), 178 (27), 145 (84), 115 (90), 91 (39), 77 (56), 51 (23). HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{20}O_2Se$ (M + H^+) 373.0707; found 373.0709 (M + H)$^+$.

6-Methoxy-4-phenyl-3-(phenylselanyl)-2*H*-chromen-2-one (3m). Obtained as a yellow solid. Yield: 0.048 g (48%); mp 153−157 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.43−7.42 (m, 3H), 7.31−7.25 (m, 3H), 7.18−7.10 (m, 6H), 7.07 (dd, *J* = 2.9 Hz, *J* = 9.0 Hz, 1H), 6.47 (d, *J* = 2.9 Hz, 1H), 3.63 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.5, 158.4, 155.7, 147.8, 136.1, 132.8, 130.2, 128.9, 128.7, 128.4, 128.0, 127.2, 121.2, 120.8, 119.0, 117.5, 110.7, 55.6. MS (EI, 70 eV; *m*/*z* (relative intensity)): 407 (100), 327 (53), 300 (83), 257 (14), 152 (54), 126 (20), 105 (27), 77 (11). HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{16}O_3Se$ (M + H^+) 409.0343; found 409.0346 (M + H)$^+$.

3-(4-Chlorophenylselanyl)-6-methoxy-4-phenyl-2*H*-chromen-2-one (3n). Obtained as a yellow oil. Yield: 0.067 g (61%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.49−7.46 (m, 3H), 7.32−7.25 (m, 3H), 7.20−7.17 (m, 2H), 7.13−7.09 (m, 3H), 6.50 (d, *J* = 2.9 Hz, 1H), 3.66 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.4, 158.3, 155.8, 147.8, 135.9, 134.3, 133.6, 129.0, 128.9, 128.5, 128.2, 128.0, 120.9, 120.7, 119.1, 117.6, 110.6, 55.6. MS (EI, 70 eV; *m*/*z* (relative intensity)): 425 (59), 347 (24), 345 (63), 281 (40), 178 (73), 152 (31), 138 (14). HRMS (ESI) calcd for $C_{22}H_{15}ClO_3Se$ (M + H^+) 442.9953; found 442.9956 (M + H)$^+$.

6-Methoxy-4-phenyl-3-(*p*-tolylselanyl)-2*H*-chromen-2-one (3o). Obtained as a yellow solid. Yield: 0.062 g (59%); mp 99−101 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.45−7.43 (m, 3H), 7.29−7.25 (m, 1H), 7.23−7.21 (m, 2H), 7.18−7.15 (m, 2H), 7.08−7.05 (m, 1H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.46 (dd, *J* = 8.9 Hz, *J* = 2.9 Hz, 1H),3.63 (s, 3H), 2.26 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.6, 158.0, 155.8, 147.8, 137.5, 136.3, 133.3, 129.7, 128.8, 128.4, 128.2, 126.4, 121.6, 120.9, 118.9, 117.6, 110.7, 55.6, 21.0. MS (EI, 70 eV; *m*/*z* (relative intensity)): 418 (23), 341 (63), 314 (73), 152 (59), 119 (48), 96 (36). HRMS (ESI) calcd for $C_{23}H_{18}O_3Se$ (M + H^+) 423.0499; found 423.0503 (M + H)$^+$.

3-(Butylselanyl)-6-methoxy-4-phenyl-2*H*-chromen-2-one (3p). Obtained as a yellow oil. Yield: 0.059 g (62%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.55−7.47 (m, 3H), 7.30−7.23 (m, 3H), 7.06 (dd, *J* = 9.0 Hz, *J* = 2.9 Hz, 1H), 6.45 (d, *J* = 2.9 Hz, 1H), 3.65 (s, 3H), 2.94 (t, *J* = 7.6 Hz,2H), 1.51 (quint, *J* = 7.6 Hz, 2H), 1.33−1.23 (m, 2H), 0.83 (t, *J* = 7.3 Hz,3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.6, 156.3, 155.8, 147.5, 136.6, 128.9, 128.6, 128.2, 121.0, 120.1, 118.2, 117.4, 110.3, 55.6, 32.4, 27.4, 22.6, 13.4.MS (EI, 70 eV; *m*/*z* (relative intensity)): 388 (46), 330 (100), 224 (27), 206 (31), 165 (15), 152 (44). HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{20}O_3Se$ (M + H^+) 389.0656; found 389.0657 (M + H)$^+$.

8-Methyl-4-phenyl-3-(phenylselanyl)-2*H*-chromen-2-one (3q). Obtained as a yellow solid. Yield: 0.079 g (81%); mp 116−118 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.43−7.41 (m, 3H), 7.35−7.31 (m, 3H), 7.15−7.12 (m, 5H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 2.47 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.4, 159.2, 136.5, 133.2, 132.7, 130.3, 128.8, 128.6, 128.3, 128.1, 127.2, 126.0, 125.6, 123.6, 120.2, 15.4. MS (EI, 70 eV; *m*/*z* (relative intensity)): 392 (68), 311 (91), 284 (83), 269 (21), 178 (100), 152 (41). HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{16}O_2Se$ (M + H^+) 393.0394; found 393.0398 (M + H)$^+$.

3-(4-Chlorophenylselanyl)-8-methyl-4-phenyl-2*H*-chromen-2-one (3r). Obtained as a yellow oil. Yield: 0.072 g (68%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.45−7.44 (m, 3H), 7.36 (d, *J* = 7.33 Hz, 1H), 7.25 (d, *J* = 8.55 Hz, 2H), 7.16−7.09 (m, 4H), 7.03 (t, 1H), 6.87 (d, *J* = 8.07 Hz, 1H), 2.48 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.2, 151.7, 136.4, 134.3, 133.7, 133.4, 129.0, 128.8, 128.4, 128.3, 128.1, 126.2, 125.6, 123.7, 120.1, 120.0, 15.5.MS (EI, 70 eV; *m*/*z* (relative intensity)): 426 (100), 345 (91), 318 (71), 282 (24), 178 (75), 152 (31). HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{15}ClO_2Se$ (M + H^+) 427.0004; found 427.0010 (M + H)$^+$.

Methyl-4-phenyl-3-(3-(trifluoromethyl)phenylselanyl)-2*H*-chromen-2-one (3s). Obtained as a yellow oil. Yield: 0.082 g (72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.54−7.37 (m, 7H), 7.29−7.21 (m, 1H), 7.15−7.01 (m, 3H), 6.89 (d, *J* = 7.94 Hz, 1H), 2.49 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.5, 151.7, 136.3, 136.1, 133.5, 129.9 (q, *J* = 32.2 Hz), 129.6 (q, *J* = 3.6 Hz), 129.1, 128.9, 128.4, 128.1, 126.2, 125.6, 124.2 (q, *J* = 3.6 Hz), 123.8, 123.4 (q, *J* = 272 Hz), 120.0, 119.6, 15.4. MS (EI, 70 eV; *m*/*z* (relative intensity)): 456 (29), 379 (39), 352 (100), 235 (17), 178 (63), 151 (25). HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{15}F_3O_2Se$ (M + H^+) 461.0268; found 461.0271 (M + H)$^+$.

8-Methyl-4-phenyl-3-(*p*-tolylselanyl)-2*H*-chromen-2-one (3t). Obtained as a yellow oil. Yield: 0.074 (74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.46−7.42 (m, 3H), 7.34 (dq, *J* = 7.5 Hz, *J* = 0.8 Hz, 1H), 7.25−7.22 (m, 2H), 7.18−7.13 (m, 2H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 6.87−6.85 (m, 1H), 2.46 (s, 3H), 2.26 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.4, 158.8, 151.6, 137.4, 136.6, 133.2, 133.0, 129.7, 128.6, 128.3, 128.2, 126.4, 126.0, 125.5, 123.5, 120.6, 120.2, 21.0, 14.4. MS (EI, 70 eV; *m*/*z* (relative intensity)): 405 (53), 325 (100), 298 (39), 178 (81), 152 (33), 91 (34). HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{18}O_2Se$ (M + H^+) 407.0550; found 407.0555 (M + H)$^+$.

3-(Butylselanyl)-8-methyl-4-phenyl-2*H*-chromen-2-one (3u). Obtained as a yellow solid. Yield: 0.064 g (70%); mp 48−50 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.53−7.48 (m, 3H), 7.33 (d, *J* = 6.3 Hz, 1H), 7.25−7.21 (m, 2H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.50 (s, 3H), 1.52 (quint, *J* = 7.3 Hz, 2H), 1.28 (sex, *J* = 7.3 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.5, 157.2, 151.4, 136.9, 132.5, 128.7, 128.4, 128.2, 125.9, 125.1, 123.5, 120.3, 119.1, 32.4, 27.3, 22.6, 15.4, 13.4. MS (EI, 70 eV; *m*/*z* (relative intensity)): 372 (16), 315 (36), 253 (17), 191 (26), 178 (14), 133 (12), 96 (12). HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{20}O_2Se$ (M + H^+) 373.0707; found 373.0714 (M + H)$^+$.

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8-(*tert*-Butyl)-4-phenyl-3-(phenylselanyl)-2*H*-chromen-2-one (3v). Obtained as a yellow oil. Yield: 0.085 g (79%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.50 (dd, J = 7.8 Hz, J = 1.3 Hz, 1H), 7.44−7.42 (m, 3H), 7.38−7.36 (m, 2H), 7.19−7.13 (m, 5H), 7.05 (t, J = 7.8 Hz, 1H), 6.8 (dd, J = 7.9 Hz, J = 1.3 Hz, 1H), 1.53 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.3, 158.8, 152.2, 137.8, 136.9, 133.2, 130.1, 129.4, 128.9, 128.6, 128.6, 128.3, 128.2, 127.4, 126.3, 123.5, 120.9, 119.9, 35.0, 29.9. MS (EI, 70 eV; m/z (relative intensity)): 434 (100), 377 (23), 311 (23), 234 (20), 194 (17), 165 (26), 105 (32), 77 (10). HRMS (ESI-TOF) m/z calcd for $C_{25}H_{22}O_2Se$ (M + H$^+$) 435.0863; found 435.0870 (M + H)$^+$.

4-Phenyl-3-(phenylselanyl)-2*H*-chromen-2-one (3w). Obtained as a yellow solid. Yield: 0.0697 g (74%); mp 143−145 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.52−7.43 (m, 4H), 7.36−7.30 (m, 3H), 7.17−7.11 (m, 6H), 7.05−7.03 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.3, 158.8, 153.4, 136.1, 132.8, 131.8, 130.2, 128.9, 128.7, 128.4, 128.2, 127.8, 127.3, 124.1, 120.7, 120.4, 116.6. MS (EI, 70 eV; m/z (relative intensity)): 378 (9), 165 (86), 164 (27), 139 (18), 77 (100), 51 (31). HRMS (ESI-TOF) m/z calcd for $C_{21}H_{14}O_2Se$ (M + H$^+$) 379.0237; found 379.0241 (M + H)$^+$.

4-Phenyl-3-(*p*-tolylselanyl)-2*H*-chromen-2-one (3x). Obtained as a yellow solid. Yield: 0.092 g (95%); mp 92−94 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 7.53−7.41 (m, 4H), 7.36−7.31 (m, 1H), 7.25−6.93 (m, 8H), 2.26 (s, 3H). $CDCl_3$, 400 MHz, δ (ppm): 7.45−7.31 (m, 6H), 7.35−6.92 (m, 7H), 2.26 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm): 159.4, 158.4, 153.4, 137.5, 136.2, 133.3, 131.7, 129.7, 128.7, 128.4, 128.2, 127.8, 126.3, 124.1, 121.1, 120.5, 116.7, 21.0.MS (EI, 70 eV; m/z (relative intensity)): 392 (15), 311 (29), 165 (81), 139 (14), 91 (82), 73 (100). HRMS (ESI-TOF) m/z calcd for $C_{22}H_{16}O_2Se$ (M + H$^+$) 393.0394; found 393.0395 (M + H)$^+$.

3-(4-Chlorophenylselanyl)-4-phenyl-2*H*-chromen-2-one (3y). Obtained as a yellow solid. Yield: 0.079 g (77%); mp 101−103 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.53−7.45 (m, 4H), 7.35 (d, J = 9.4 Hz, 1H), 7.25 (d, J = 8.5 Hz, 2H), 7.17−7.03 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.2, 158.8, 153,4, 136.0, 134.4, 133.7, 132.0, 129.0, 128.9, 128.4, 128.1, 127.8, 124.2, 120.4, 120.3, 116.7. MS (EI, 70 eV; m/z (relative intensity)): 412 (18), 331 (23), 165 (100), 155 (9), 139 (32), 75 (29). HRMS (ESI-TOF) m/z calcd for $C_{21}H_{13}ClO_2Se$ (M + H$^+$) 412.9848; found 412.9851 (M + H)$^+$.

6-Methyl-4-phenyl-3-(phenyltellanyl)-2*H*-chromen-2-one (3z). Obtained as a brown oil. Yield: 0.035 (36%). ^{1}H NMR: $CDCl_3$, 400 MHz, δ (ppm): 7.54 (d, J = 7.6 Hz, 2H), 7.40−7.17 (m, 6H), 7.80−7.03 (m, 4H), 6.74 (s, 1H), 2.22 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.2,160.9, 151.9, 139.4, 138.2, 133.8, 132.7, 128.9, 128.7, 128.5, 128.1, 127.9, 127.0, 120.2, 116.4, 114.5, 110.6, 20.8. MS (EI, 70 eV;m/z (relativeintensity)): 441 (90), 311 (74), 284 (49), 191 (24), 178 (100), 105 (63), 77 (79), 51 (29). HRMS (ESI-TOF) m/z calcd for $C_{22}H_{16}O_2Te$ (M + H$^+$) 443.0291; found 443.02.95 (M + H)$^+$.

1-Methyl-4-phenyl-3-(phenylselanyl)quinolin-2(1*H*)-one (4a). Obtained as a yellow solid. Yield: 0.076 (78%); mp 72−74 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.59−7.50 (m, 1H), 7.41−7.36 (m, 4H), 7.29−7.24 (m, 2H), 7.18−7.03 (m, 7H), 3.80 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.4, 154.9, 139.7, 137.9, 132.0, 131.6, 130.7, 128.7, 128.6, 128.1, 127.9, 126.5, 126.1, 121.9, 121.4, 114.0, 30.7. MS (EI, 70 eV; m/z (relative intensity)): 391 (53), 310 (100), 190 (14), 165 (23), 77 (15), 51 (8). HRMS (ESI-TOF) m/z calcd for $C_{22}H_{17}NOSe$ (M + H$^+$) 392.0554; found 392.0556 (M + H)$^+$.

1-Methyl-4-phenyl-3-((3-(trifluoromethyl)phenyl)selanyl)-quinolin-2(1*H*)-one (4b). Obtained as a yellow oil. Yield: 0.083 g (73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.62−7.53 (m, 1H), 7.46−7.35 (m, 7H), 7.25−7.05 (m, 5H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.4, 154.8, 139.8, 137.4, 135.7, 132.6, 130.7 3 (J = 32.2 Hz),128.9, 128.6, 128.5, 128.2, 123.6 (J = 272 Hz), 123.4 (J = 3.6 Hz), 122.1, 121.4, 114.2, 30.7. MS (EI, 70 eV; m/z (relative intensity)): 459 (85), 378 (100), 314 (15), 189 (27), 164 (38), 144 (27), 77 (10). HRMS (ESI-TOF) m/z calcd for $C_{23}H_{16}F_3NOSe$ (M + H$^+$) 460.0427; found 460.0430 (M + H)$^+$.

3-(4-Fluorophenylselanyl)-1-methyl-4-phenylquinolin-2(1*H*)-one (4c). Obtained as a yellow solid. Yield: 0.085 g (84%); mp 127−129 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.55−7.51 (m, 1H), 7.40−7.37 (m, 4H), 7.28−7.24 (m, 2H), 7.14−7.07 (m, 4H), 6.78 (t, J = 8.8 Hz, 2H), 3.80 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.0 (d, J = 246 Hz), 160.4, 154.2, 139.6, 137.7, 134.9 (d, J = 8 Hz), 130.7, 128.7, 128.5, 128.3, 128.1, 126.4, 125.9 d, J = 3.6 Hz), 121.9, 121.4, 115.7 (d, J = 22 Hz), 114.0, 30.6. MS (EI, 70 eV; m/z (relative intensity)): 409 (72), 407 (37), 328 (100), 312 (10), 204 (15), 189 (12), 164 (14). HRMS (ESI-TOF) m/z calcd for $C_{22}H_{16}FNOSe$ (M + H$^+$) 410.0459; found 410.0462 (M + H)$^+$.

1-Methyl-4-phenyl-3-(*p*-tolylselanyl)quinolin-2(1*H*)-one (4d). Obtained as a yellow solid. Yield: 0.082 g (85%), mp 82−84 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.55−7.51 (m, 1H), 7.40−7.37 (m, 4H), 7.19−7.12 (m, 5H), 7.08−7.04 (m, 1H), 6.91 (d, J = 8 Hz, 2H), 3.79 (s, 3H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.4, 154.4, 139.7, 138.0, 136.5, 132.5, 130.6, 129.5, 128.6, 128.5, 128.1, 127.9, 127.7, 126.4, 121.8, 121.4, 114.0, 30.7, 21.0.MS (EI, 70 eV; m/z (relative intensity)): 405 (43), 324 (100), 281 (10), 190 (11), 165 (17), 91 (15). HRMS (ESI-TOF) m/z calcd for $C_{23}H_{19}NOSe$ (M + H$^+$) 406.0710; found 406.0713 (M + H)$^+$.

3-(Butylselanyl)-1-methyl-4-phenylquinolin-2(1*H*)-one (4e). Obtained as a yellow solid. Yield: 0.082 g (85%), mp 82−84 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.56−7.48 (m, 4H), 7.41 (d, J = 8.4 Hz, 1H), 7.26−7.23 (m, 2H), 7.15−7.07 (m, 2H), 3.85 (s, 3H), 2.93 (t, J = 7.4 Hz, 3H), 1.51 (quint, J = 7.4 Hz, 2H), 7.29 (sex, J = 7.4 Hz, 2H), 0.84 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.8, 152.9, 139.3, 138.4, 130.0, 128.8, 128.3, 128.1, 128.0, 124.9, 121.8, 121.5, 113.9, 32.5, 30.5, 27.1, 22.7, 13.4. MS (EI, 70 eV; m/z (relative intensity)): 371 (19), 369 (9), 315 (88), 281 (33), 234 (32), 164 (28), 132 (19), 96 (19), 73 (42). HRMS (ESI-TOF) m/z calcd for $C_{20}H_{21}NOSe$ (M + H$^+$) 372.0867; found 372.0871 (M + H)$^+$.

4-(2-Methoxyphenyl)-1-methyl-3-(phenylselanyl)quinolin-2(1*H*)-one (4f). Obtained as a yellow solid. Yield: 0.075 g (72%); mp 144−146 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.57−7.53 (m, 1H), 7.43−7.39 (m, 2H), 7.36−7.34 (m, 2H), 7.17−7.03 (m, 7H), 6.92 (d, J = 8.24 Hz, 1H), 3.82 (s, 3H), 3.63 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.4, 156.1, 152.3, 139.8, 132.1, 131.5, 130.5, 129.9, 129.8, 128.5, 128.2, 127.0, 126.8, 126.4, 121.8, 121.2, 120.4, 114.0, 110.7, 55.1, 30.6. MS (EI, 70 eV; m/z (relative intensity)): 421 (26), 419 (13), 281 (39), 264 (41), 177 (15), 133 (22), 77 (15). HRMS (ESI-TOF) m/z calcd for $C_{23}H_{19}NO_2Se$ (M + H$^+$) 422.0659; found 422.0663 (M + H)$^+$.

4-(2-Methoxyphenyl)-1-methyl-3-(*p*-tolylselanyl)quinolin-2(1*H*)-one (4g). Obtained as a yellow solid. Yield: 0.107 g (99%); mp 187−189 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.56−7.51 (m, 1H), 7.44−7.38 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.17−7.14 (m, 1H), 7.12−7.03 (m, 3H), 6.96−6.92 (m, 3H), 3.80 (s, 3H), 3.65 (s, 3H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.5, 156.2, 151.8, 139.8, 136.3, 132.7, 130.3, 130.1, 129.7, 129.3, 128.2, 127.6, 127.2, 121.7, 121.3, 120.4, 113.9, 110.8, 55.1, 30.6. MS (EI, 70 eV; m/z (relative intensity)): 435 (10), 327 (11), 253 (21), 191 (22), 133 (22), 96 (13), 73 (49). HRMS (ESI-TOF) m/z calcd for $C_{24}H_{21}NO_2Se$ (M + H$^+$) 436.0816; found 436.0820 (M + H)$^+$.

1-Methyl-3-(phenylselanyl)-4-*p*-tolylquinolin-2(1*H*)-one (4h). Obtained as a yellow solid. Yield: 0.056 g (56%); mp 119−121 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.55−7.50 (m, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.29−7.26 (m, 2H), 7.19−7.17 (m, 3H), 7.10−7.01 (m, 6H), 3.78 (s, 3H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.4, 155.0, 139.8, 137.7, 135.0, 132.1, 131.7, 130.6, 128.8, 128.7, 128.6, 128.5, 126.5, 126.1, 121.8, 121.5, 114.0, 30.7, 21.2. MS (EI, 70 eV; m/z (relative intensity)): 405 (72), 403 (34), 325 (26), 324 (100), 281 (29), 77 (45). HRMS (ESI-TOF) m/z calcd for $C_{23}H_{19}NOSe$ (M + H$^+$) 406.0710; found 406.0714 (M + H)$^+$.

4-Butyl-1-methyl-3-(phenylselanyl)quinolin-2(1*H*)-one (4i). Obtained as a yellow solid. Yield: 0.055 g (60%); mp 86−89 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.81 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 8.5 Hz, 1H), 7.42−7.40 (m, 2H), 7.35 (d, J = 8.6 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 7.18−7.14 (m, 3H), 3.71 (s, 3H), 3.33 (t, J = 7.8 Hz,

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2H), 1.57 (q, 2H), 1.49 (q, 2H), 0.95 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.3, 156.2, 140.0, 132.0, 130.8, 130.6, 128.9, 126.3, 126.1, 125.0, 122.0, 119.8, 114.5, 33.8, 32.3, 30.7, 23.0, 13.7. MS (EI, 70 eV; m/z (relative intensity)): 371 (100), 369 (51), 329 (20), 248 (71), 184 (29), 144 (54). HRMS (ESI-TOF) m/z calcd for $C_{20}H_{21}NOSe$ (M + H^+) 372.0867; found 372.0871 (M + H)$^+$.

4-Butyl-1-methyl-3-(*p*-tolylselanyl)quinolin-2(1*H*)-one (4j). Obtained as a yellow oil. Yield: 0.055 g (58%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.81 (d, J = 8.0 Hz, 1H), 7.58−7.54 (m, 1H), 7.37−7.33 (m, 3H), 7.28−7.23 (m, 1H), 7.0 (d, J = 8.5 Hz, 1H), 3.72 (s, 3H), 3.34 (t, J = 8.4 Hz, 2H), 2.26 (s, 3H), 1.60−1.44 (m, 4H), 0.96 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.4, 155.7, 140.1, 136.4, 131.3, 130.7, 129.8, 128.2, 126.1, 125.6, 122.0, 120.0, 114.5, 33.8, 32.3, 30.7, 23.0, 21.0, 13.8.MS (EI, 70 eV; m/z (relative intensity)): 385 (97), 328 (20), 281 (45), 262 (82), 144 (39), 115 (38), 91 (65). HRMS (ESI-TOF) m/z calcd for $C_{21}H_{23}NOSe$ (M + H^+) 386.1023; found 386.1031 (M + H)$^+$.

1,6-Dimethyl-4-phenyl-3-(phenylselanyl)quinolin-2(1*H*)-one (4k). Obtained as a yellow solid. Yield: 0.076 g (76%); mp 126−129 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.39−7.34 (m, 4H), 7.29−7.24 (m, 3H), 7.12−7.04 (s, 5H), 6.91 (s, 1H), 3.78 (s, 3H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm): 160.3, 154.7, 138.0, 137.7, 132.2, 131.9, 131.4, 128.6, 128.5, 128.2, 128.0, 127.8, 126.6, 126.4, 126.0, 121.2, 114.0, 30.7, 20.5. MS (EI, 70 eV; m/z (relative intensity)): 405 (65), 324 (100), 281 (22), 178 (10), 165 (9), 77 (24). HRMS (ESI-TOF) m/z calcd for $C_{23}H_{19}NOSe$ (M + H^+) 406.0710; found 406.0713 (M + H)$^+$.

1,6-Dimethyl-4-phenyl-3-(*p*-tolylselanyl)quinolin-2(1*H*)-one (4l). Obtained as a yellow solid. Yield: 0.096 g (92%); mp 118−120 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.41−7.33 (m, 4H), 7.28−7.24 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.13−7.11 (m, 2H), 6.9 (d, J = 7.6 Hz, 3H), 3.77 (s, 3H), 2.24 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.3, 154.3, 138.1, 137.8, 136.4, 132.4, 131.8, 131.4, 129.4, 128.6, 128.0, 127.8, 126.3, 121.3, 113.9, 30.7, 20.9, 20.6. MS (EI, 70 eV; m/z (relative intensity)): 419 (54), 338 (100), 281 (10), 91 (16), 65 (8). HRMS (ESI-TOF) m/z calcd for $C_{24}H_{21}NOSe$ (M + H^+) 420.0867; found 420.0869 (M + H)$^+$.

3-((4-Fluorophenyl)selanyl)-1,6-dimethyl-4-phenylquinolin-2(1*H*)-one (4m). Obtained as a yellow solid. Yield: 0.079 g (75%); mp 110−112 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.41−7.34 (m, 4H), 7.28−7.23 (m, 3H), 7.11−7.09 (m, 2H), 6.90 (s, 1H), 6.78 (t, J = 8.8 Hz, 2H), 3.78 (s, 3H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.2 (d, J = 246 Hz), 160.3, 154.0, 137.8 (d, J = 13 Hz), 134.7 (d, J = 8 Hz), 131.9, 131.5, 128.6, 128.1, 128.0 (d, J = 13 Hz), 126.4, 125.9, 121.2, 115.7 (d, J = 22 Hz), 114.0, 30.6, 20.5. MS (EI, 70 eV; m/z (relative intensity)): 423 (61), 342 (100), 327 (10), 281 (10), 178 (9), 96 (14). HRMS (ESI-TOF) m/z calcd for $C_{23}H_{18}FNOSe$ (M + H^+) 424.0616; found 424.0618 (M + H)$^+$.

3-(Butylselanyl)-1,6-dimethyl-4-phenylquinolin-2(1*H*)-one (4n). Obtained as a brown oil. Yield: 0.077 g (81%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.52−7.46 (m, 3H), 7.35−7.20 (m, 4H), 6.88 (s, 1H), 3.81 (s, 3H), 2.89 (t, J = 7.4 Hz, 2H), 2.25 (s, 3H), 1.48 (quint, J = 7.6 Hz, 2H), 1.26 (sex, J = 7.5 Hz, 2H), 0.81 (sex, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.6, 152.7, 138.5, 137.3, 131.3, 131.2, 128.7, 128.2, 127.9, 127.7, 124.8, 121.3, 113.8, 32.4, 30.4, 27.0, 22.6, 20.5, 13.4. MS (EI, 70 eV; m/z (relative intensity)): 383 (11), 329 (100), 313 (15), 304 (27), 281 (30), 248 (22), 73 (28). HRMS (ESI-TOF) m/z calcd for $C_{21}H_{23}NOSe$ (M + H^+) 386.1023; found 386.1025 (M + H)$^+$.

6-Chloro-1-methyl-4-phenyl-3-(phenylselanyl)quinolin-2(1*H*)-one (4o). Obtained as a yellow oil. Yield: 0.072 g (68%). ^1H ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.48 (dd, J = 8.9 Hz, J = 2.3 Hz, 1H), 7.41−7.38 (m, 3H), 7.32 (d, J = 8.9 Hz, 1H), 7.29−7.25 (m, 2H), 3.78 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.1, 153.1, 138.2, 137.1, 132.6, 131.1, 130.5, 128.7, 128.5, 128.3, 128.2, 128.1, 127.5, 127.4, 126.8, 122.5, 115.5, 30.8. MS (EI, 70 eV; m/z (relative intensity)): 424 (58), 344 (100), 281 (29), 252 (12), 189 (18), 162 (26), 77 (36), 51 (18). HRMS (ESI-TOF) m/z calcd for $C_{22}H_{16}ClNOSe$ (M + H^+) 426.0164; found 426.0169 (M + H)$^+$.

6-Chloro-1-methyl-4-phenyl-3-(*p*-tolylselanyl)quinolin-2(1*H*)-one (4p). Obtained as a yellow solid. Yield: 0.087 g (80%); mp 124−126 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 7.49−7.25 (m, 5H), 7.19−7.07 (m, 5H), 6.91 (d, J = 7.93 Hz, 2H), 3.76 (s, 3H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.0, 152.7, 138.1, 137.1, 136.8, 132.9, 130.3, 129.5, 128.5, 128.3, 128.1, 127.4, 127.3, 127.2, 122.5, 115.4, 30.8, 20.9. MS (EI, 70 eV; m/z (relative intensity)): 439 (6), 358 (16), 281 (35), 191 (22), 133 (24), 73 (50). HRMS (ESI-TOF) m/z calcd for $C_{23}H_{18}ClNOSe$ (M + H^+) 440.0320; found 440.0325 (M + H)$^+$.

6-Chloro-3-(4-fluorophenylselanyl)-1-methyl-4-phenylquinolin-2(1*H*)-one (4q). Obtained as a yellow solid. Yield: 0.069 g (63%); mp 135−137 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.49−7.47 (m, 1H), 7.42−7.40 (m, 3H), 7.32 (d, J = 9.0 Hz, 1H), 7.27−7.23 (m, 2H), 7.10−7.07 (m, 3H), 6.79 (t, J = 8.6 Hz, 2H), 3.78 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.2 (d, J = 246 Hz), 152.6, 138.1, 137.0, 135.4 (d, J = 8 Hz), 130.6, 128.5 (d, J = 13 Hz), 128.4, 127.6, 127.3, 122.5, 115.9 (d, J = 21 Hz), 115.6, 30.9. MS (EI, 70 eV; m/z (relative intensity)): 443 (13), 362 (25), 281 (35), 253 (20), 191 (22), 133 (24). HRMS (ESI-TOF) m/z calcd for $C_{22}H_{15}ClFNOSe$ (M + H^+) 444.0070; found 444.0074 (M + H)$^+$.

3-(Butylselanyl)-6-chloro-1-methyl-4-phenylquinolin-2(1*H*)-one (4r). Obtained as a yellow oil. Yield: 0.053 g (53%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.54−7.48 (m, 3H), 7.45 (dd, J = 8.9 Hz, J = 2.4 Hz, 1H), 7.32 (d, J = 8.9 Hz, 1H), 7.22−7.19 (m, 2H), 3.80 (s, 3H), 2.90 (t, J = 7.3 Hz, 2H), 1.49 (quint, J = 7.3 Hz, 2H), 1.27 (sex, J = 7.2 Hz, 2H), 0.82 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.4, 151.3, 137.7, 129.8, 128.7, 128.5, 128.4, 127.4, 127.0, 126.9, 122.5, 115.4, 32.4, 30.6, 27.2, 22.6, 13.4. MS (EI, 70 eV; m/z (relative intensity)): 405 (23), 348 (100), 324 (32), 268 (29), 190 (14), 162 (15). HRMS (ESI-TOF) m/z calcd for $C_{20}H_{20}ClNOSe$ (M + H^+) 406.0477; found 406.0479 (M + H)$^+$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and CIF files giving spectroscopic data for all new compounds; X-ray results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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