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Iron-Mediated Cyclization of 1,3-Diynyl Propargyl Aryl Ethers with Dibutyl Diselenide: Synthesis of Selenophene-Fused Chromenes

Guilherme Lutz [a], Davi F. Back [b] and Gilson Zeni [a,*]

[a] Laboratório de Síntese, Reatividade, Avaliação Farmacológica e Toxicológica de Organocalcogênios CCNE, UFSM, Santa Maria, Rio Grande do Sul, Brazil 97105-900.

E-mail: gzeni@ufsm.br; Fax: (+55)55-3220-8978; Tel: (+55)55-3220-9611.

[b] Laboratório de Materiais Inorgânicos, Departamento de Química, UFSM, Santa Maria, Rio Grande do Sul, Brazil 97105-900.

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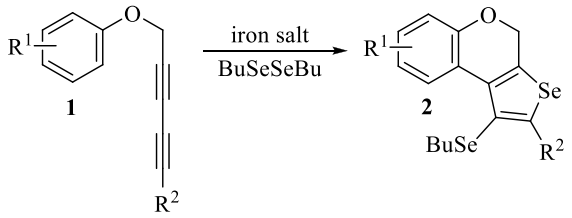
Abstract. The synthesis of selenophene-fused chromene derivatives starting from 1,3-diynyl propargyl aryl ethers is reported herein. The method is based on carbon-carbon, carbon-selenium, selenium-carbon and carbon-selenium bonds formation in a one-pot protocol, using iron(III) chloride and dibutyl diselenide as promoters. The same reaction conditions were applied to propargyl anilines leading to the formation of 1-(butylselanyl)-selenophene quinolines. The results showed that the dilution and temperature of substrate addition had a crucial influence in the products obtained. When the substrates were added at room temperature, in the absence of a solvent, a mixture of products was obtained, whereas the slowly addition (15 min) of starting materials, as a dichloromethane solution, at 0 °C led to the product formation in good yields. The mechanistic study indicates that the cooperative action between iron(III) chloride and dibutyl diselenide was essential to promote the cyclization, whereas separately none of them was effective in promoting the cyclization. We proved the synthetic utility of heterocycles obtained in the Suzuki cross coupling reaction, giving the corresponding cross-coupled products in good yields. In addition, the organoselenium moiety was removed from the structures of products by using *n*-butyllithium.

Keywords: chromenes; selenophenes; diselenides; selenides; heterocycles; iron.

Introduction

Although the development of heterocycle-related field merges with that of chemistry, there are continuous improvements in their synthesis.[1] This is because heterocycle derivatives have displayed broad spectrum applications in medicine, agriculture, industry, and chemistry.[2] In this context, selenium-containing heterocycles,[3] even though not present in natural products, have been widely used in material science, as intermediaries in organic synthesis, and also searched for different biological activities.[4] Among selenium-containing heterocycles, selenophene derivatives are synthetic compounds, which have impressive biological,[5] optical, and electronic properties.[6] Consequently, a number of synthetic methods have been developed for their preparation.[7] Classical methods, such as the addition of selenium nucleophilic[8] or electrophilic[9] species to alkynes, have been frequently used for the synthesis of functionalized selenophenes. Furthermore, the electrophilic cyclization of alkynes is also an efficient alternative to their synthesis.[10] Recently, Koketsu and co-workers successfully combined the green chemistry principles of iron-based reactions with the peculiar properties of the organoselenium chemistry in the preparation of selenophene-fused quinolines via an intramolecular cascade cyclization of 1,3-diyne and 1,3,5-triyne.[11] Based on the results reported in the literature, which demonstrate that the cooperative action between iron(III) salts and diorganyl dichalcogenides is a useful tool to promote the cyclization of unsaturated substrates,[12] we hypothesized that this

system could be an alternative to the cyclization and functionalization of 1,3-diynyl propargyl aryl ethers. Thus, we reported, in the present study, a route to obtain selenophene-fused chromene derivatives **2** through the cascade cyclization of 1,3-diynyl propargyl aryl ethers **1** promoted by iron(III) salt and diorganyl diselenides (Scheme 1). Particularly, the selenophene-fused chromenes have attracted our attention because of their cytotoxic activity against various tumor cell lines, in vitro and in vivo anti-angiogenic, antioxidant, and prooxidant properties.[13] Whereas the synthesis of furan-fused chromenes[14] and thiophene-fused chromenes[15] is widespread in the literature, the preparation of 1-(organoselenyl)-selenophene-fused chromenes is not reported. The advantages of this methodology are the formation of carbon-carbon, carbon-selenium, selenium-carbon, and carbon-selenium bonds sequence in a one-pot protocol and the preparation of fused-heterocycles with simultaneous functionalization. Another feature of our methodology is the introduction of an organoselenium group in the heterocycles, which becomes the final product attractive as a substrate for new organic transformations[16] and for biological studies.[17]



Scheme 1. Cyclization of 1,3-diynyl propargyl aryl ethers **1** promoted by iron(III) salt and diorganyl diselenides.

Results and Discussion

For the preparation of 1,3-diynyl propargyl aryl ethers **1** we chose the reaction of phenol with propargyl bromide in the presence of K_2CO_3 in acetone at reflux for 24 h.[18] After that, we installed the bromine in the alkyne using *N*-bromosuccinimide and silver nitrate.[19] The copper-catalyzed cross-coupling of bromoacetylene with terminal alkynes led to 1,3-diynyl propargyl aryl ethers **1**.[20] The examples prepared, yields, identification data, and NMR spectra are listed in the Supporting Information. After that, we attempted to determine the best reaction conditions to the cyclization of 1,3-diynyl propargyl aryl ether **1a** (Table 1). Because the second step of the reaction mechanism involves the release of the group directly attached to the selenium atom (See mechanism discussion, Scheme 6), we can anticipate that the use of an alkyl diselenide is an indispensable requirement for the reaction to proceed sequentially. Thus, we began our investigation with the addition of **1a** (0.25 mmol), at room temperature, under argon atmosphere, to a solution of $FeCl_3$ (2.5 equiv) and dibutyl diselenide (1.1 equiv) in dichloroethane (4 mL), which was prepared 10 min before. The reaction was stirred for 0.5 h at room temperature. These reaction conditions resulted in the formation of an inseparable 1:1 mixture of **2a** and hydrogenated products **3** in 60% yield (Table 1, entry 1). To avoid the formation of the by-product **3**, we performed the addition of starting material **1a** as a dichloromethane solution; however, no improvement in the selectivity or yield was observed (Table 1, entry 2). The desired **2a** was obtained in good yield (74%), as a sole product, when the reaction was carried out by slowly adding (15 min) the starting material **1a**, as a dichloroethane solution in the mixture of iron salt and dibutyl diselenide at 0 °C (Table 1, entry 3). The screening of promoters revealed that none of them showed higher efficiency than iron(III) chloride, although iron(III) chloride hexahydrate gave the product **2a** in moderate yield (Table 1, entries 4-9). Thus, we chose iron(III) chloride as the promoter to study the other parameters. A screening of the promoter amount indicated that the use of 3 equivalents of iron(III) chloride did not improve the yield of **2a**, whereas 2.0 and 1.5 equivalents resulted in a decrease of yields (Table 1, entries 10-12). We found that increasing the amount of dibutyl diselenide to 1.5 and 2.1 equivalents did not result in an improvement in the yields (Table 1, entries 13 and 14). Next, we screened other solvents, such as dichlormethane, dioxane, toluene, acetonitrile, and nitromethane. These studies showed that all solvents tested led to the product **2a** formation; however, dichloromethane was the solvent that gave the highest yield. Thus, we selected dichloromethane, the best solvent, for the next studies (Table 1, entries 15-19). We also observed that the reaction did not proceed without iron(III) chloride (Table 1, entry 20). After these series of experiments, we established the optimal reaction conditions as the slowly addition (15 min) at 0 °C of starting material **1a** (0.25 mmol), as a dichloromethane solution (2 mL), to a mixture of iron (III) chloride (2.5 equiv) and dibutyl diselenide (1.1 equiv) in dichloromethane (4 mL) which was prepared 10 min before. After that, the reaction was stirred for 0.5 h at room temperature (Table 1, entry 15).

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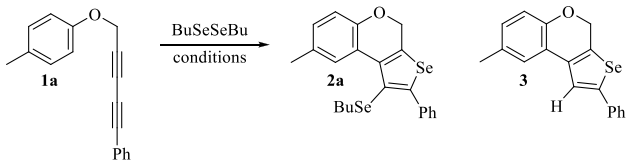
Table 1. Effects of different reaction parameters on the preparation of 1-(butylselanyl)-selenophene chromene **2a**.[a]



entry	promoter (equiv)	solvent	yield[b] (%)
1	$FeCl_3$ (2.5)	DCE	**2a**:**3** (1:1)
2	$FeCl_3$ (2.5)	DCE	**2a**:**3** (1:1)[c]
3	$FeCl_3$ (2.5)	DCE	74[d]
4	$FeSO_4 \cdot 7H_2O$ (2.5)	DCE	-
5	Fe^0 (2.5)	DCE	-
6	$Fe(acac)_3$ (2.5)	DCE	-
7	$FeCl_3 \cdot 6H_2O$ (2.5)	DCE	54
8	$BF_3 \cdot OEt_2$ (2.5)	DCE	trace
9	CuI (2.5)	DCE	-
10	$FeCl_3$ (2)	DCE	67
11	$FeCl_3$ (1.5)	DCE	64
12	$FeCl_3$ (3)	DCE	73
13	$FeCl_3$ (2.5)	DCE	56[e]
14	$FeCl_3$ (2.5)	DCE	53[f]
15	$FeCl_3$ (2.5)	CH_2Cl_2	78
16	$FeCl_3$ (2.5)	dioxane	37
17	$FeCl_3$ (2.5)	toluene	49
18	$FeCl_3$ (2.5)	CH_3CN	30
19	$FeCl_3$ (2.5)	CH_3NO_2	37
20	-	CH_2Cl_2	-

[a] The reaction was performed by the addition of **1a** (0.25 mmol), at room temperature, under argon atmosphere, to a solution of $FeCl_3$ (2.5 equiv) and dibutyl diselenide (1.1 equiv) in dichloroethane (4 mL), which was prepared 10 min before. The reaction was stirred for 0.5 h at room temperature.
[b] Isolated yield after column chromatography.
[c] **1a** was added as a dichloroethane solution (2 mL).
[d] **1a** was added at 0 °C as a dichloroethane solution (2 mL).
[e] Dibutyl diselenide (1.5 equiv) was added.
[f] Dibutyl diselenide (2.1 equiv) was added.

After the optimum conditions for the cyclization being determined, we applied them to other 1,3-diynyl propargyl aryl ethers **1**, to investigate the effects of different substituents on the structure of starting material. The results of the cyclization reactions are summarized in Table 2. We started these studies investigating the influence of substituents directly bonded to the alkyne. Generally, electron rich aryl groups led to the formation of 1-(butylselanyl)-selenophene chromene products in better yields than electron poor aryl groups (Table 2, **2b**-**g**). It was observed that hindered 2-naphthyl substituents in the alkynes had no steric influence in the reaction (Table 2, **2h**). Furthermore, 1,3-diynyl propargyl aryl ethers having the aromatic ring with *para*-fluoro, *meta*-methoxy, *ortho*-amino, and 3-pyridyl afforded the desired products; however, they decomposed during the purification process. When the substituents were alkyl, propargyl alcohol, and hydrogen no reaction took place and the starting materials decomposed. Next, we evaluated the influence of substituents in the aromatic ring directly bonded to the oxygen atom. We supposed that increasing the electron density of the aromatic ring would increase the nucleophilicity of the aromatic, consequently, electron donating groups should lead to products in higher yields than electron withdrawing groups.[21] Contrary to our expectations, the results obtained did not indicate any relationship between the yields and electronic effects of substituents on the aromatic ring (Table 2, **2i**-**2r**). We also studied the regioselectivity of the nucleophilic attack of the aromatic ring on the alkynes by adding a chlorine substituent at the *meta*-position of the aryl group directly bonded to the oxygen atom. In this case, as *ortho*-carbons behave as nucleophiles, they may lead to a mixture of products. We observed that the reaction was moderately regioselective giving a 3:1 mixture (determined by GCMS) of **2p** and **2p'** in 70% yields (Table 2, **2p** and **2p'**). The regioselectivity in favor of **2p** may be influenced by the steric hindrance caused by the chlorine atom in the **2p'** regioisomer. The results demonstrated that the yields of cyclized products were influenced by the chalcogen atom, because 1,3-diynyl propargyl aryl thioether gave low yields of thiochromene derivative **2s**, whereas the corresponding selenoether and telluroether did not give the products (Table 2, **2s**). Finally, for products **2f**, **2g**, **2j** and **2s**, which were obtained in moderate yields, we observed the total consumption of the starting material and the presence of unidentified by-products.

The generality of optimized conditions utilizing propargyl anilines rather than propargyl aryl ethers as the substrate was further studied (Table 3). In general, all examples prepared were obtained in moderate to good yields. We concluded that there was no relationship between substituents present in the substrate and achieved yields, thus an extensive discussion on the yields obtained would make it speculative. However, simple observation can be made conserning the aromatic ring directly bonded to the oxygen atom, which once again showed that the electron withdrawing groups gave the products in good yields. These results, similar to those found with propargyl aryl ethers, contradict our expectation that the product should be obtained; however, in lower yields than electron rich aromatic groups. Thus, we can conclude that in addition to aromatic nucleophilicity, steric effects, the characteristics of the electrophile, and the

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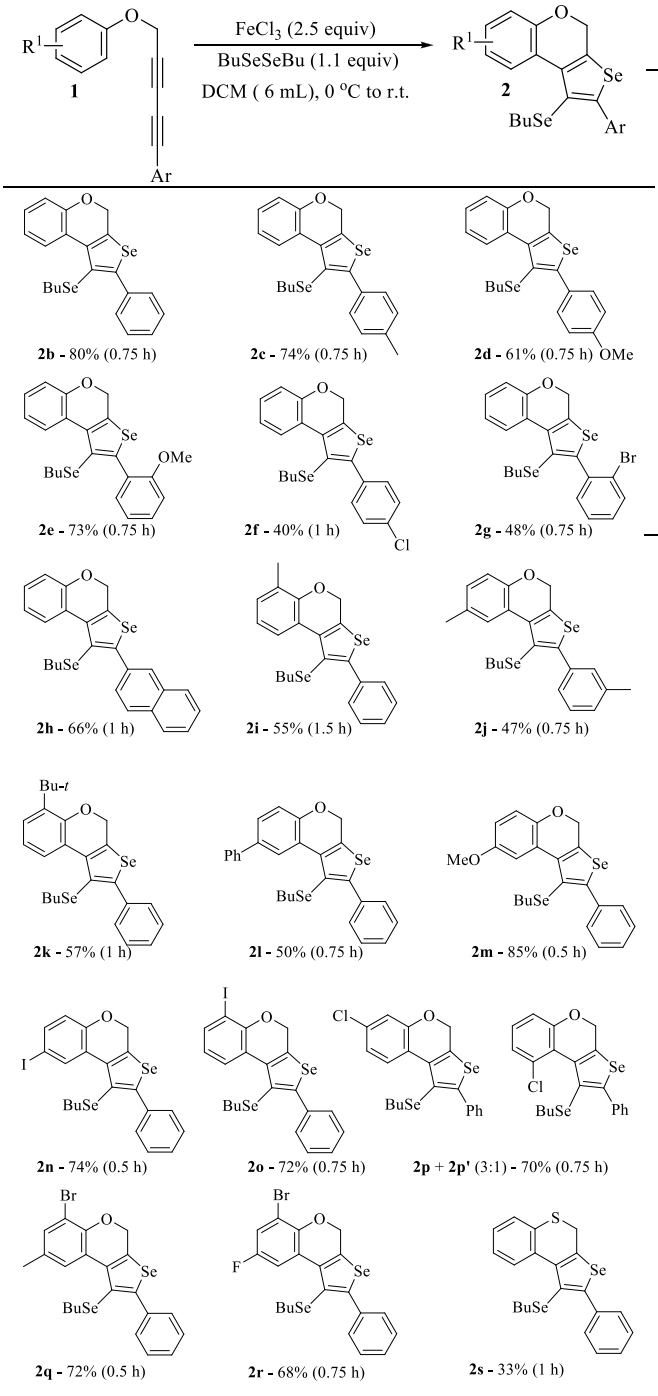
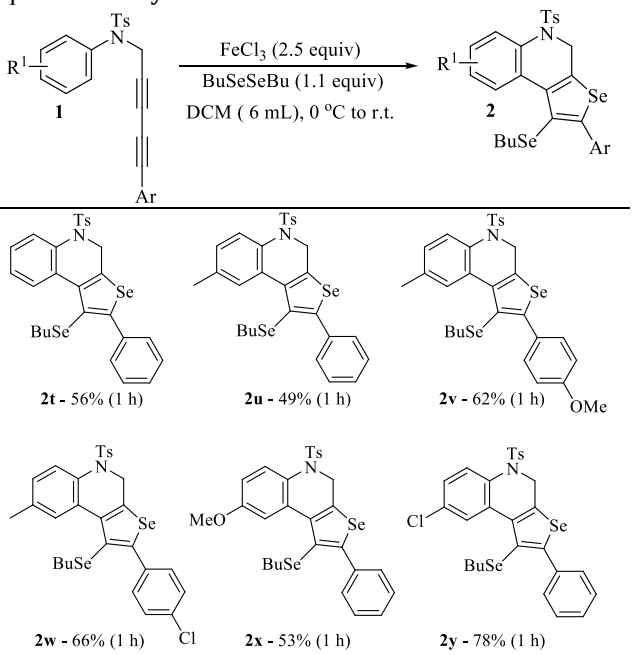
reactivity of carbon-carbon triple bond, among others, can influence the yields of this cyclization reaction.

Table 2. Synthesis of 1-(butylselanyl)-selenophene chromenes **2a-s**.[a], [b]



[a] The reaction was performed by slowly addition (15 min) at 0 °C of 1,3-diynyl propargyl aryl ethers **1** (0.25 mmol), as a dichloromethane solution (2 mL), to a mixture of iron (III) chloride (2.5 equiv) and dibutyl diselenide (1.1 equiv), in dichloromethane (4 mL), which was prepared 10 min before. After that, the reaction was stirred at room temperature for the time indicated in Table 2.
[b] Isolated yield after column chromatography.

Table 3. Synthesis of 1-(butylselanyl)-selenophene quinolines **2t-y**.[a], [b]



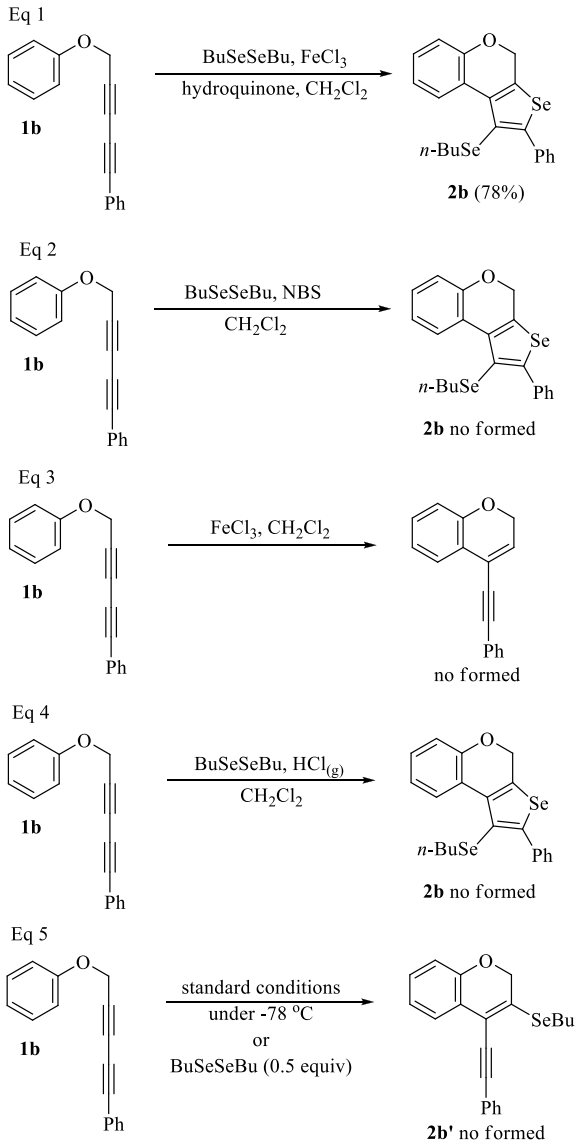
[a] The reaction was performed by slowly addition (15 min) at 0 °C of 1,3-diynyl propargyl anilines **1** (0.25 mmol), as a dichloromethane solution (2 mL), to a mixture of iron (III) chloride (2.5 equiv) and dibutyl diselenide (1.1 equiv) in dichloromethane (4 mL), which was prepared 10 min before. After that, the reaction was stirred at room temperature for the time indicated in Table 3.
[b] Isolated yield after column chromatography.

Mechanistic Considerations

Next, a series of control experiments were conducted to gain insights into the mechanism for this cyclization. In the first experiment, hydroquinone was used as a radical scavenger. Thus, the reaction of 1,3-diynyl propargyl aryl ethers, under the optimized conditions, in the presence of hydroquinone led to the formation of 1-(butylselanyl)-selenophene chromene **2a** in 78% yield. This result weakens the hypothesis that the reaction occurs via selenium radical species prepared in situ by the reaction of dibutyl diselenide with iron(III) chloride (Scheme 2, eq 1). In the next set of experiments, we carried out the cyclization by using a selenium electrophilic species, prepared via the reaction of dibutyl diselenide with NBS (Scheme 2, eq 2) and with iron(III) chloride in the absence of dibutyl diselenide (Scheme 2, eq 3). The purpose of this experiment was to determine if the products were formed via an electrophilic cyclization reaction with an electrophilic selenium species acting as a promoter without the participation of iron(III) chloride. In either case, the product **2a** was not formed under these conditions. Thus, we

concluded that a cooperative action between dibutyl diselenide and iron(III) chloride is essential for the outcome of the cyclization. When 1,3-diynyl propargyl aryl ether **1a** was reacted under the standard reaction in the presence of gaseous HCl and the absence of iron(III) chloride, the product **2a** was not formed (Scheme 2, eq 4). This result shows that the gaseous HCl, formed in situ by decomposition of iron(III) chloride, was not the cyclization promoter. In order to isolate and identify the intermediate **2b'** (Scheme 2, eq 5), we carried out the reactions under low temperature (-78 ^{o}C) and reduced amounts of dibutyl diselenide (0.5 equiv); however, in none of these experiments this intermediate was obtained. In these cases, the product **2b** was always obtained, although in low yields. Thus, it seems that the reaction mechanism for the cyclization of 1,3-diynyl propargyl aryl ethers **1** promoted by iron(III) salt and diorganyl diselenide involves an initial formation of seleniranium ion **I** through activation of the carbon-carbon triple bond promoted by an organoselenium iron complex. The attack of the electron cloud from the aromatic ring at the activated intermediate **I** gives the cyclized species **II**. The removal of a hydrogen from intermediate **III** restores the aromatic ring, giving the 3-(butylselanyl)-2*H*-chromene **IV**. The organoselenium iron complex promoted the activation of the second alkynes for the selenium nucleophilic attack, generating the selenophene cation **VI**. The removal of the butyl group bonded to the selenium atom via S_N2 displacement by the chloride ion, present in the reaction mixture, affords the selenophene chromene derivatives **2** and butyl chloride, which was detected by CGMS. Because of the last step of the reaction mechanism involves a S_N2 type reaction, the substrates must have a group with a Csp^3 directly bonded to the selenium atom. Therefore, the reactions with diaryl diselenide derivatives would not lead to the product formation.

The formation of a carbon-carbon bond by using palladium catalysts is one of the most important discovery of organic chemistry. The aryl or vinyl halides are frequently used as substrates, although triflate, tosylate, phosphonate, and sulfonate can be a good alternative. Recently, the use of organochalcogens as an electrophile in the palladium cross-coupling has emerged as a powerful substitutes to these substrates.[22] The simple and easy preparation of organochalcogenides associated with their chemo-, regio- and stereoselective reactions and the fact that the oxidative addition of organoselenides on palladium is faster than organohalides, because the carbon-selenium bond is more labile than the carbon-halogen bond, became these compounds an impressive choice for the carbon-carbon bond construction.[23] In a last set of experiments, we



Scheme 2. Control experiments for the mechanistic study.

explored the potential of these selenophene chromene derivatives **2** towards Suzuki cross-coupling reactions catalyzed by palladium salts. Thus, the reaction of selenophene chromene **2b** with different boronic acids under Suzuki conditions[24] gave the corresponding products **4a** and **4b** in 82% and 72% yields, respectively (Scheme 4, eq 1). When the same conditions were applied to the reaction of selenophene quinoline **2u** with 4-methoxyphenylboronic acid, the cross-coupled product **4c** was obtained in 43% yield (Scheme 4, eq 2).

The structures containing selenium atoms may contain important biological activities as previously

justified; however, in some cases, the selenium chemistry can be used as a tool for the construction of new structures. For this reason and to expand the synthetic application of the compounds prepared, we carried out the reaction of selenophene chromene **2b** with *n*-buthyllithium to promote the opening of selenophene ring and, consequently, eliminate the butyl selenolate anion. Thus, the addition of *n*-buthyllithium (1.0 equiv) to a solution of **2b** in THF (3 mL) at 78 ^{0}C, followed by 24 h at room temperature, gave the 4-alkynyl coumarin **5** in 80% yield (Scheme 5). 4-Alkynyl coumarin is an important class of compounds because some of them have found applications in medicinal, pharmaceutical[25] and advanced optical materials.[26]

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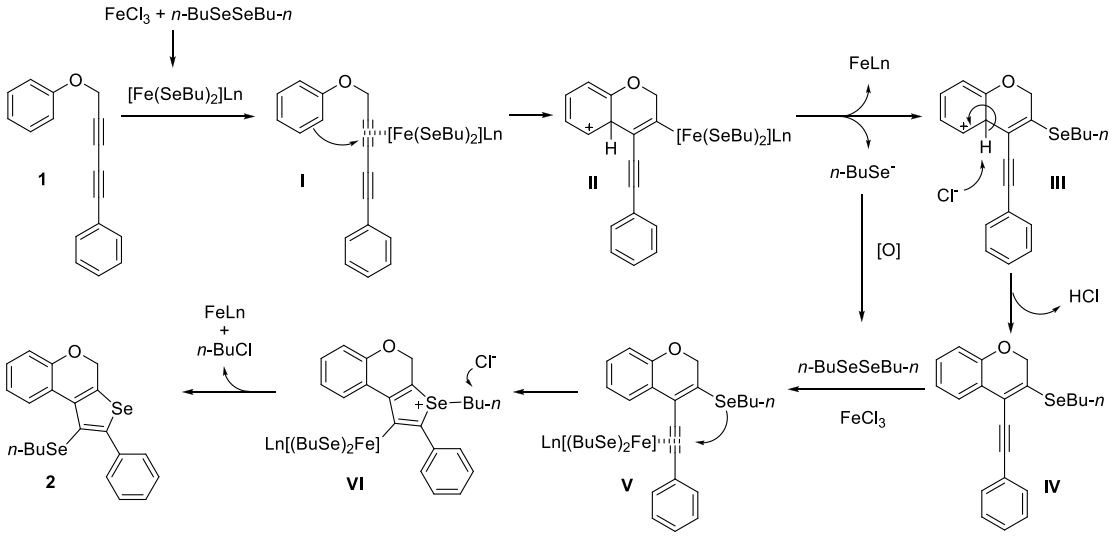
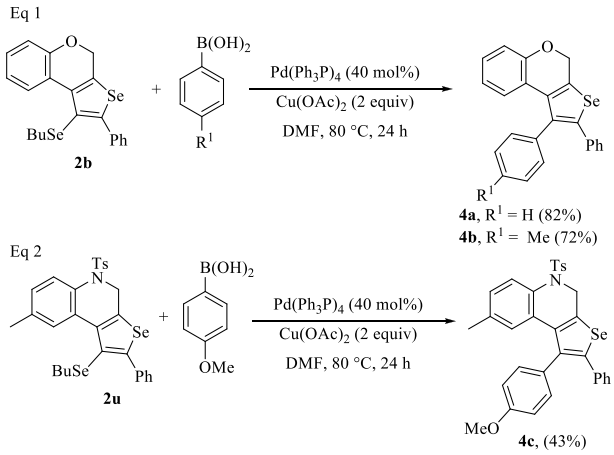
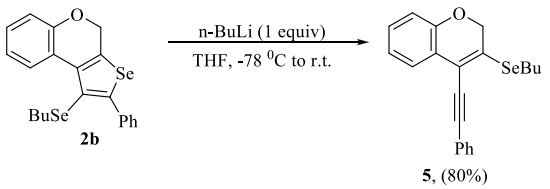


Scheme 3. Proposed reaction mechanism.



Scheme 4. Reactivity of **2b** and **2u** towards palladium-catalyzed Suzuki cross-coupling reactions.



Scheme 5. Reactivity of **2b** towards *n*-buthyllithium reaction.

Conclusions

In summary, we demonstrate the synthesis of several 1,3-diynyl propargyl aryl ethers and 1,3-diynyl propargyl anilines, which were used as the starting materials in the cyclization reactions promoted by iron(III) chloride and dibutyl diselenide, establishing an efficient route to obtain selenophene-fused chromenes and 1-(butylselanyl)-selenophene quinolines. The results showed that both dilution and temperature of substrate addition had a fundamental influence on the reaction outcome. When the substrates were added at room temperature, in the absence of a solvent, a mixture of products was obtained, whereas the slow addition (15 min) of the starting materials, as a dichloromethane solution, at 0 °C led to the desired products in good yields. The reaction mechanism indicates that the cooperative action between iron(III) chloride and dibutyl diselenide was essential to promote cyclization. We also found that electronic and steric effects of substituents did not directly affect the yields, indicating that besides the nucleophilicity of aromatic ring other factors, such as the nature of the electrophilic source and polarization of the carbon-carbon triple bond can also significantly influence the yields. All the compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy. Furthermore, the 6-*endo*-dig

followed by a 5-*endo*-dig cyclization was confirmed by X-ray analyses of the crystalline sample (Supporting Information, Figure S1 and S2, CCDC 1961007, and 1961008 for compounds **2o** and **2u**, respectively).[27]

Experimental Section

General procedure for 1-(butylselanyl)-selenophene chromenes/quinolines 2a-2y: The reaction was performed by the dropwise addition of dichloroethane (2 mL) solution containing 1,3-diynyl propargyl aryl ethers/propargyl anilines **1** (0.25 mmol), at 0 ^{0}C, under argon atmosphere, to a solution of $FeCl_3$ (0.625 mmol, 2.5 equiv) and diorganoyl dichalcogenide (0.275 mmol, 1.1 equiv) in dichloroethane (4 mL), which was prepared 10 min before. The reaction mixture was stirred under room temperature for the time indicated in Tables 2 and 3. The organic phase was separated, dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography. **1-(Butylselanyl)-8-methyl-2-phenyl-4*H*-selenopheno[2,3-c]chromene (2a):** The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.09 g (78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.65 (d, *J* = 2.1 Hz, 1H), 7.54-7.35 (m, 5H), 7.01 (dd, *J* = 8.2 Hz, *J* = 2.1 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 5.17 (s, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 2.36 (s, 3H), 1.32 (quint, *J* = 7.4 Hz, 2H), 1.11 (sex, *J* = 7.4 Hz, 2H), 0.68 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 151.4, 150.5, 136.7, 136.2, 134.9, 130.9, 130.3, 128.6, 128.0, 124.5, 123.2, 118.9, 116.5, 66.6, 31.4, 29.5, 22.4, 21.0, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 462 (22), 325 (73), 246 (22), 245 (100), 207 (23). HRMS: calcd for $C_{22}H_{23}OSe_2$ (ESI-TOF, [M + H]$^+$): 463.0079, found: 463.0085.

1-(Butylselanyl)-2-phenyl-4*H*-selenopheno[2,3-c]chromene (2b): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.086 g (80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.83 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, 1H), 7.52-7.36 (m, 5H), 7.21 (td, *J* = 7.9 Hz, *J* = 1.6 Hz, 1H), 7.07 (td, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H), 7.03 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 5.20 (s, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 1.28 (quint, *J* = 7.4 Hz, 2H), 1.07 (sex, *J* = 7.4 Hz, 2H), 0.66 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.5, 150.6, 136.5, 136.0, 134.8, 130.3, 128.2, 128.0, 126.1, 124.0, 123.4, 121.7, 118.7, 116.8, 66.6, 31.3, 29.4, 22.4, 13.3. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as internal reference): δ (ppm) 644.3, 192.6. MS (EI, 70 eV. *m/z* (relative intensity)): 446 (15), 311 (53), 231 (100), 202 (62). HRMS: calcd for $C_{21}H_{21}OSe_2$ (ESI-TOF, [M + H]$^+$): 448.9923, found: 448.9939.

1-(Butylselanyl)-2-(p-tolyl)-4*H*-selenopheno[2,3-c]chromene (2c): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.086 g (74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.83 (dd, *J* = 7.9 Hz, *J* = 1.6 Hz, 1H), 7.42-7.13 (m, 5H), 7.05 (td, *J* = 7.6 Hz, *J* = 1.3 Hz, 1H), 7.01 (dd, *J* = 8.0 Hz, *J* =1.3 Hz, 1H), 5.19 (s, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 2.39 (s, 3H), 1.30 (quint, *J* = 7.4 Hz, 2H), 1.10 (sex, *J* = 7.4 Hz, 2H), 0.67 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 153.6, 151.0, 138.0, 135.8, 134.9, 133.8, 130.2, 128.8, 128.2, 126.1, 124.1, 123.6, 121.7, 116.8, 66.7, 31.5, 29.5, 22.4, 21.2, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 462 (16), 405 (3), 325 (61), 245 (100), 202 (19). HRMS: calcd for $C_{22}H_{23}OSe_2$ (ESI-TOF, [M + H]$^+$): 463.079, found: 463.0086.

1-(Butylselanyl)-2-(4-methoxyphenyl)-4*H*-selenopheno[2,3-c]chromene (2d): The product was isolated by column chromatography (hexane/ethyl acetate 99:1 as eluent) as a yellow oil. Yield: 0.073 g (61%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.82 (dd, *J* = 7.8, *J* = 1.6 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.19 (td, *J* = 7.7, *J* = 1.7 Hz, 1H), 7.06 (td, *J* = 7.6, *J* = 1.4 Hz, 1H), 7.01 (dd, *J* = 8.0, *J* = 1.3 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 5.19 (s, 2H), 3.85 (s, 3H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.30 (quint, *J* = 7.4 Hz, 2H), 1.10 (sex, *J* = 7.4 Hz, 2H), 0.68 (t, *J* = 7.4 Hz. 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 159.5, 153.6, 150.7, 135.5, 134.8, 131.5, 129.0, 128.1, 124.1, 123.6, 121.7, 118.4, 116.8, 113.5, 66.7, 55.3, 31.4, 29.4, 22.4, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 478 (36), 418 (7), 341 (100), 261 (72), 218 (28). HRMS: calcd for $C_{22}H_{23}O_2Se_2$ (ESI-TOF, [M + H]$^+$): 479.028, found: 479.0037.

1-(Butylselanyl)-2-(2-methoxyphenyl)-4*H*-selenopheno[2,3-c]chromene (2e): The product was isolated by column chromatography (hexane/ethyl acetate 99:1 as eluent) as a yellow oil. Yield: 0.087 g (73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.90 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H), 7.37 (td, *J* = 7.4 Hz, *J* = 1.8 Hz, 1H), 7.31 (dd, *J* = 7.5 Hz, *J* = 1.7 Hz, 1H), 7.18 (td, *J* = 7.4 Hz, *J* = 1.7 Hz, 1H), 7.07-6.98 (m, 3H), 6.96 (dd, *J* = 8.3 Hz, *J* = 1.0 Hz, 1H), 5.21 (s, 2H), 3.82 (s, 3H), 2.43 (t, *J* = 7.4 Hz. 2H), 1.31 (quint, *J* = 7.4 Hz. 2H), 1.10 (sex, *J* = 7.4 Hz, 2H), 0.68 (t. *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 156.9, 153.4, 146.3, 136.59, 133.9, 132.3, 129.8, 128.0, 125.6, 123.9, 123.5. 121.6, 121.1, 120.1, 116.8, 110.8, 66.7, 55.4, 31.5, 28.7, 22.5, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 478 (46), 241 (13), 341 (100), 325 (44), 261 (60), 207 (45). HRMS: calcd for $C_{22}H_{23}O_2Se_2$ (ESI-TOF, [M + H]$^+$): 479.0028, found: 479.0036.

1-(Butylselanyl)-2-(4-chlorophenyl)-4*H*-selenopheno[2,3-c]chromene (2f): The product was isolated by column chromatography (hexane as eluent) as a orange oil. Yield: 0.049 g (40%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.82 (dd, *J* = 7.8 Hz, *J* =1.6 Hz, 1H), 7.46-7.34 (m, 4H), 7.20 (td, *J* = 7.2 Hz, *J* = 1.6 Hz, 1H), 7.06 (td, *J* = 7.6 Hz, *J* = 1.3 Hz, 1H), 7.02 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1H), 5.19 (s, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.29 (quint, *J* = 7.4 Hz, 2H), 1.09 (sex, *J* = 7.4 Hz, 2H), 0.68 (t. *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 153.5, 149.2, 136.3, 135.1, 135.0, 134.1, 131.5, 129.1, 128.3, 128.3, 124.0, 123.3, 121.7, 116.9, 66.5, 31.4, 29.6, 22.4, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 482 (56), 425 (16), 344 (100), 265 (95), 202 (39). HRMS: calcd for $C_{21}H_{20}ClOSe_2$ (ESI-TOF, [M + H]$^+$): 482.9533, found 482.9539.

2-(2-Bromophenyl)-1-(butylselanyl)-4*H*-selenopheno[2,3-c]chromene (2g): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.063 g (48%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.91 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, 1H), 7.70-7.65 (m, 1H), 7.39-7.31 (m, 2H), 7.28-7.22 (m, 1H), 7.20 (td, *J* = 7.4 Hz, *J* = 1.6 Hz, 1H), 7.06 (td. *J* = 7.4 Hz, *J* = 1.4 Hz, 1H), 7.02 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1H), 5.23 (s, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 1.37 (quint, *J* = 7.4 Hz, 2H), 1.14 (sex, *J* = 7.4 Hz, 2H), 0.72 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 153.4, 149.0, 137.6, 137.0, 133.7, 132.7, 132.6, 129.7, 128.3, 126.8, 125.2, 123.7, 123.3, 121.8, 121.7, 116.8, 66.5, 31.7, 29.1, 22.5, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 525 (2), 447 (39), 389 (100), 309 (52), 281 (21), 202 (63). HRMS: calcd for $C_{21}H_{20}BrOSe_2$ (ESI-TOF, $[M + H]^+$): 526.9028, found: 526.9036.

1-(Butylselanyl)-2-(naphthalen-2-yl)-4*H*-selenopheno[2,3-c]chromene (2h): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.082 g (66%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.91 (dd, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 7.90-7.85 (m, 2H), 7.82 (dd, *J* = 8.5 Hz, *J* = 1.3 Hz, 1H), 7.50 - 7.40 (m, 4H), 7.19 (td, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.08 - 7.01 (m, 2H), 5.24 (s, 2H), 2.39 (q, *J* = 6.9 Hz, 2H), 1.25 (quint, *J* = 7.4 Hz, 2H), 1.00 (sex, *J* = 7.4 Hz, 2H), 0.61 (t, *J* = 7.3 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 153.6, 148.4, 136.9, 134.2, 134.1, 133.5, 132.6, 128.9, 128.8, 128.3, 128.1, 126.3, 126.1, 126.0, 124.8, 123.9, 123.5, 122.0, 121.7, 116.9, 66.6, 31.6, 29.4, 22.4, 13.2. MS (EI, 70 eV. *m/z* (relative intensity)): 498 (29), 441 (36), 361 (39), 281 (100), 252 (46), 207 (76). HRMS: calcd for $C_{25}H_{20}OSe_2$ (ESI-TOF, $[M + H]^+$): 499.0079, found: 499.0085.

1-(Butylselanyl)-6-methyl-2-phenyl-4*H*-selenopheno[2,3-c]chromene (2i): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.064 g (55%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.65 (dd, *J* = 7.9 Hz, *J* = 1.7 Hz, 1H), 7.54-7.34 (m, 5H), 7.07 (dq, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 5.19 (s, 2H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.29 (s, 3H), 1.28 (quint, *J* = 7.4 Hz, 2H), 1.07 (sex, *J* = 7.4 Hz, 2H), 0.66 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 151.6, 150.4, 136.7, 135.8, 135.3, 130.3, 129.9, 128.0, 128.0, 126.1, 123.0, 121.8, 120.9, 119.0, 66.4, 31.4, 29.4, 22.4, 16.3, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 462 (23), 325 (81), 323 (41), 245 (100), 207 (64), 202 (23). HRMS: cald for $C_{22}H_{23}OSe_2$ (ESI-TOF, $[M + H]^+$): 463.0079, found: 463.0083.

1-(Butylselanyl)-8-methyl-2-(m-tolyl)-4*H*-selenopheno[2,3-c]chromene (2j): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.056 g (47%), ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.65 (d, *J* = 2.1 Hz, 1H), 7.29 (d, *J* = 4.8 Hz, 3H), 7.18 (td, *J* = 4.3 Hz, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 8.2 Hz, *J* = 2.1 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 5.15 (s, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 1.32 (quint, *J* = 7.4 Hz, 2H), 1.12 (sex, *J* = 7.4 Hz, 2H), 0.69 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 151.4, 150.7, 137.6, 136.6, 136.0, 134.9, 130.9, 130.8, 128.8, 128.6, 127.9, 127.4, 124.5, 123.3, 118.7, 116.5, 66.6, 31.4, 29.4, 22.4, 21.3, 21.0, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 476 (36), 417 (9), 339 (87), 259 (100), 215 (25), 207 (29). HRMS: cald for $C_{23}H_{25}OSe_2$ (ESI-TOF, $[M + H]^+$): 477.0236, found: 477.0230.

6-(Tert-butyl)-1-(butylselanyl)-2-phenyl-4*H*-selenopheno[2,3-c]chromene (2k): The product was isolated by column chromatography (hexane as eluent) as a yellow solid. Yield: 0.072 g (57%); mp 97-98 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 8.60 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, 1H), 7.59-7.34 (m, 5H), 7.24 (dd, *J* = 7.8 Hz, *J* = 1.4 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 5.13 (s, 2H), 2.41 (t, *J* = 7.4 Hz, 2H), 1.42 (s, 9H), 1.28 (quint, *J* = 7.4 Hz, 2H). 1.07 (sex. *J* = 7.4 Hz, 2H), 0.65 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 152.2, 150.1, 138.6, 136.8, 135.8, 135.8, 130.3, 128.0, 128.0, 125.7, 124.5, 122.5, 121.0, 119.2, 65.7, 34.7, 31.4, 29.9, 29.4, 22.4, 13.3. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as internal reference): δ (ppm) 617.0, 203.7. MS (EI, 70 eV. *m/z* (relative intensity)): 504 (17), 367 (100), 365 (48), 287 (27), 231 (12) 57 (26). HRMS: cald for $C_{25}H_{29}OSe_2$ (ESI-TOF, $[M + H]^+$): 505.0549, found: 505.0555.

1-(Butylselanyl)-2,8-diphenyl-4*H*-selenopheno[2,3-c]chromene (2l): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.065 g (50%). H^1 NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.17 (d, *J* = 2.3 Hz, 1H), 7.64 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.53-7.26 (m, 10H), 7.08 (d, *J* = 8.4 Hz, 1H), 5.23 (s, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.28 (quint, *J* = 7.4 Hz, 2H), 1.05 (sex, *J* = 7.4 Hz, 2H), 0.61 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 153.2, 151.1, 141.0, 136.6, 136.3, 134.9, 134.6, 130.4, 128.8, 128.1, 128.1, 126.8, 126.8, 126.7, 123.7, 122.9, 118.9, 117.2, 66.8, 31.5, 29.7, 22.5, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 524 (26), 388 (61), 307 (100), 230 (50), 215 (33) HRMS: calcd for $C_{27}H_{25}OSe_2$ (ESI-TOF, $[M + H]^+$): 525.0236, found: 525.0230.

1-(Butylselanyl)-8-methoxy-2-phenyl-4*H*-selenopheno[2,3-c]chromene (2m): The product was isolated by column chromatography (hexane/ethyl acetate 99:1 as eluent) as a yellow oil. Yield: 0.102 g (85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.55 (d, *J* = 3.0 Hz, 1H), 7.53-7.36 (m, 5H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.77 (dd, *J* = 8.8 Hz, *J* = 3.0 Hz, 1H), 5.16 (s, 2H), 3.83 (s, 3H), 2.46 (t, *J* = 7.4 Hz. 2H), 1.30 (quint, *J* = 7.4 Hz, 2H), 1.10 (sex, *J* = 7.4 Hz, 2H), 0.68 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.3, 150.9, 147.5, 137.0, 136.6, 134.7, 130.3, 128.1, 128.0, 124.1, 118.8, 117.3, 113.9, 109.1, 66.7, 55.8, 31.5, 29.6, 22.4, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 479 (23), 341 (54), 261 (100), 207 (79). HRMS: calcd for $C_{22}H_{23}O_2Se_2$ (ESI-TOF, $[M + H]^+$): 479.0028, found: 479.0033.

1-(Butylselanyl)-8-iodo-2-phenyl-4*H*-selenopheno[2,3-c]chromene (2n): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.106 g (74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.22 (d, *J* = 2.2 Hz, 1H), 7.51-7.38 (m, 6H), 6.77 (d, *J* = 8.5 Hz, 1H), 5.21 (s, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.35 (quint, *J* = 7.4 Hz, 2H), 1.15 (sex, *J* = 7.4 Hz, 2H), 0.71 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$,100

MHz): δ (ppm) 153.3, 151.4, 136.8, 136.7, 136.3, 132.5, 130.3, 129.0, 128.2, 128.1, 126.1, 125.6, 119.0, 84.4, 66.6, 31.4, 29.7, 22.5, 13.4. MS (EI, 70 eV. *m/z* (relative intensity)): 574 (100), 515 (25), 437 (96), 389 (28), 357 (97), 202 (51). HRMS: calcd for $C_{21}H_{20}IOSe_2$ (ESI-TOF, $[M + H]^+$): 574.8889, found: 574.8894.

1-(Butylselanyl)-6-iodo-2-phenyl-4*H*-selenopheno[2,3-c]chromene (2o): The product was isolated by column chromatography (hexane as eluent) as a white solid. Yield: 0.103 g (72%); mp 102-103 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.82 (dd, *J* = 7.6 Hz, *J* =1.2 Hz, 1H), 7.64 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H), 7.51-7.37 (m, 5H), 6.83 (t, *J* = 7.9 Hz, 1H), 5.28 (s, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 1.26 (quint, *J* = 7.4 Hz, 2H), 1.06 (sex, *J* = 7.4 Hz, 2H), 0.66 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 152.7, 151.2, 137.8, 136.4, 136.3, 134.4, 130.2, 128.1, 128.0, 124.1, 124.0, 123.3, 118.5, 84.9, 67.2, 31.3, 29.5, 22.3, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 572 (5), 437 (73), 435 (19), 357 (70), 202 (100). HRMS: cald for $C_{21}H_{20}IOSe_2$ (ESI-TOF, $[M + H]^+$): 574.8889, found: 574.8893.

6-Bromo-1-(butylselanyl)-8-methyl-2-phenyl-4*H*-selenopheno[2,3-c]chromene (2q): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.097 g (72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.62 (dd, *J* = 2.0 Hz, *J* = 0.9 Hz, 1H), 7.51-7.36 (m, 5H), 7.27-7.25 (m, 1H), 5.25 (s, 2H), 2.41 (t, *J* = 7.4 Hz. 2H), 2.34 (s, 3H), 1.28 (quint, *J* = 7.4 Hz, 2H), 1.09 (sex, *J* = 7.4 Hz, 2H), 0.68 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 151.0, 148.1, 136.6, 136.4, 134.4, 132.0, 132.0, 130.2, 128.1, 128.1, 124.4, 123.7, 118.6, 110.5, 67.1, 31.3, 29.5, 22.4, 20.7, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 541 (16), 405 (75), 403 (100), 401 (50), 325 (79), 323 (84), 215 (93). HRMS: calcd for $C_{22}H_{22}BrOSe_2$ (ESI-TOF, $[M + H]^+$): 540.9184, found: 540.9189.

6-Bromo-1-(butylselanyl)-8-fluoro-2-phenyl-4*H*-selenopheno[2,3-c]chromene (2r): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.093 g (68%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.73 (dd, *J* = 10.3 Hz, *J* = 2.9 Hz, 1H), 7.51-7.35 (m, 5H), 7.18 (dd, *J* = 7.5 Hz, *J* = 2.9 Hz, 1H), 5.28 (s, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 1.28 (quint, *J* = 7.4 Hz, 2H), 1.10 (sex, *J* = 7.4 Hz, 2H), 0.69 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 156.9 (d, *J* = 242.0 Hz), 151.8, 146.8 (d, *J* = 3.0 Hz),137.7, 136.2, 133.5, 130.3, 128.3, 128.1, 125.3, 125.2, 118.7, 118.4 (d, *J* = 26.3 Hz), 110.7 (d, *J* = 11.0 Hz), 110.1 (d, *J* = 26.4 Hz) 67.2, 31.4, 29.8, 22.4, 13.3. MS (EI, 70 eV. *m/z* (relative intensity)): 546 (30), 544 (45), 542 (36), 488 (19), 409 (71), 407 (98), 329 (88), 327 (100), 220 (67). HRMS: calcd for $C_{21}H_{19}BrFOSe_2$ (ESI-TOF, $[M + H]^+$): 544.8934, found: 544,8940.

1-(Butylselanyl)-2-phenyl-4*H*-selenopheno[2.3-c]thiochromene (2s): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.039 g (33%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.44 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H), 7.54 (dd, *J* = 8.1 Hz, *J* = 1.5 Hz, 2H), 7.48 (dd, *J* = 7.7 Hz, *J* = 1.5 Hz, 1H), 7.44 -7.34 (m, 3H), 7.27 (td, *J* = 7.4 Hz, *J* = 1.5 Hz, 1H), 7.18 (td, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 3.93 (s. 2H), 2.23 (t, *J* = 7.4 Hz. 2H), 1.17 (quint, *J* = 7.4 Hz, 2H), 0.99 (sex, *J* = 7.4 Hz. 2H), 0.62 (t, *J* = 7.4 Hz. 3H). ^{13}C {^{1}H} NMR (100 MHz. $CDCl_3$): δ (ppm) 148.1, 140.0, 138.3, 136.9, 133.3, 132.8, 130.2, 128.4, 128.1, 127.9, 126.8, 126.8, 125.6, 120.5, 31.2, 29.3, 29.1, 22.3, 13.3. MS (EI. 70 eV. *m/z* (relative intensity)): 464 (24), 405 (13), 325 (47), 247 (100), 215 (34), 207 (49). HRMS: cald for $C_{21}H_{21}SSe_2$ (ESI-TOF, $[M + H]^+$): 464.9694, found 464.9694.

1-(Butylselanyl)-2-phenyl-5-tosyl-4,5-dihydroselenopheno[2,3-c]quinolone (2t): The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.084 g (56%), ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.64-8.59 (m, 1H), 7.86-7.81 (m, 1H), 7.43-7.32 (m, 7H), 7.24-7.19 (m, 2H), 6.93 (dd, *J* = 8.5 Hz, *J* = 0.8 Hz, 2H), 4.96 (s, 2H), 2.27 (s, 3H), 2.13 (t, *J* = 7.4 Hz, 2H), 1.29 (quint, *J* = 7.4 Hz, 2H), 1.13 (sex, *J* = 7.4 Hz, 2H), 0.73 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 150.0, 142.8, 137.3, 136.6, 135.9, 135.5, 134.8, 130.1, 130.0, 128.7, 128.1, 128.1, 128.0, 127.4, 127.1, 126.6, 124.6, 119.0, 47.6, 31.3, 29.4, 22.6, 21.5, 13.4. HRMS: cald for $C_{28}H_{28}NO_2SSe_2$ (ESI-TOF, $[M + H]^+$): 602.0171, found: 602.0177.

1-(Butylselanyl)-8-methyl-2-phenyl-5-tosyl-4,5-dihydroselenopheno[2,3-c]quinolone (2u): The product was isolated by column chromatography (hexane/ethyl acetate 98:2 as eluent) as a yellow solid. Yield: 0.075 g (49%); mp 96-97 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.44 (dd, *J* = 1.5 Hz, *J* = 0.6 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.43-7.31 (m, 5H), 7.24-7.20 (m, 2H), 7.17 (ddd, *J* = 8.1 Hz, *J* = 2.0 Hz, *J* = 0.8 Hz, 1H), 6.93 (dd, *J* = 8.6 Hz, *J* = 0.7 Hz, 2H), 4.94 (s, 2H), 2.41 (s, 3H), 2.27 (s, 3H), 2.12 (t, *J* = 7.4 Hz, 2H), 1.31 (quint, *J* = 7.4 Hz, 2H), 1.16 (sex. *J* = 7.4 Hz, 2H), 0.75 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz. $CDCl_3$): δ (ppm) 149.9, 142.7, 137.2, 136.7, 136.4, 136.0, 135.6, 132.3, 130.0, 129.8, 128.7, 128.2, 128.0, 127.9, 127.1, 125.1, 119.1, 77.3, 77.0, 76.6, 47.7, 31.3, 29.4, 22.6, 21.5, 21.4, 13.4. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as internal reference): δ (ppm) 649.8, 194.7. HRMS: cald for $C_{29}H_{30}NO_2SSe_2$ (ESI-TOF, $[M + H]^+$): 616.0328, found: 616.0335.

1-(Butylselanyl)-2-(4-methoxyphenyl)-8-methyl-5-tosyl-4,5-dihydroselenopheno[2,3-c]quinoline (2v): The product was isolated by column chromatography (hexane/ethyl acetate 95:5 as eluent) as a yellow solid. Yield: 0.100 g (62%); mp 105-106 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.48 (dd, *J* = 1.5 Hz, *J* = 0.6 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.35-7.27 (m, 2H), 7.30-7.21 (m, 2H), 7.19 (ddd, *J* = 8.1 Hz, *J* = 2.1 Hz, *J* = 0.7 Hz, 1H), 7.00-6.91 (m. 4H), 4.95 (s, 2H), 3.89 (s, 3H), 2.43 (s, 3H), 2.29 (s, 3H), 2.15 (t, *J* = 7.4 Hz. 2H), 1.35 (quint, *J* = 7.4 Hz, 2H), 1.20 (sex, *J* = 7.4 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 159.5, 149.9, 142.6, 136.7, 136.3, 135.9, 135.6, 132.2, 131.1, 129.8, 129.0, 128.7, 128.1, 127.8, 127.1, 125.1, 118.7, 113.5, 55.3, 47.6, 31.3, 29.3, 22.6, 21.4, 21.4, 13.4. HRMS: cald for $C_{30}H_{32}NO_3SSe_2$ (ESI-TOF, $[M + H]^+$): 646.0433, found 646.0440.

1-(Butylselanyl)-2-(4-chlorophenyl)-8-methyl-5-tosyl-4.5-dihydroselenopheno[2,3-c]quinoline (2w): The product was isolated by column chromatography

(hexane/ethyl acetate 98:2 as eluent) as a orange solid. Yield: 0.108 g (66%); mp 117-118 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.44 (dd, *J* = 1.5 Hz *J* = 0.5 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.40 - 7.25 (m, 4H), 7.24-7.20 (m, 2H), 7.17 (ddd, *J* = 8.1 Hz, *J* = 2.1 Hz, *J* = 0.7 Hz, 1H), 6.92 (dd, *J* = 8.6 Hz, *J* = 0.7 Hz, 2H), 4.93 (s, 2H), 2.40 (s, 3H), 2.26 (s, 3H), 2.13 (t, *J* = 7.4 Hz, 2H), 1.32 (quint, *J* = 7.4 Hz, 2H), 1.18 (sex, *J* = 7.4 Hz, 2H), 0.77 (t, *J* = 7.4 Hz. 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 148.4, 142.7, 137.6, 136.4, 136.1, 135.7, 135.1, 134.2, 132.3, 131.2, 129.6, 128.7, 128.3, 127.8, 127.2, 125.1, 119.7, 47.6, 31.3, 29.5, 22.6, 21.4, 21.4, 13.4. HRMS: cald for $C_{29}H_{29}ClNO_2SSe_2$ (ESI-TOF, [M + H]$^+$): 649.9938, found: 649.9944.

1-(Butylselanyl)-8-methoxy-2-phenyl-5-tosyl-4,5-dihydroselenopheno[2,3-c]quinoline (2x): The product was isolated by column chromatography (hexane/ethyl acetate 95:5 as eluent) as a yellow solid. Yield: 0.084g (53%); mp 137-138 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.30 (d, *J* = 2.9 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.41-7.31 (m, 5H), 7.23-7.19 (m, 2H), 6.97-6.86 (m, 3H), 4.94 (s, 2H), 3.85 (s, 3H), 2.28 (s, 3H), 2.13 (t, *J* = 7.4 Hz, 2H), 1.29 (quint,*J* = 7.4 Hz, 2H), 1.13 (sex, *J* = 7.4 Hz, 2H), 0.73 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz. $CDCl_3$): δ (ppm) 158.0, 150.1, 142.7, 137.8, 136.5, 135.6, 135.3, 131.0, 130.0, 129.2, 128.7, 128.1, 128.0, 127.6, 127.1, 118.9, 113.1, 109.6, 55.5, 47.7, 31.3, 29.4, 22.6, 21.5, 13.4. HRMS: cald for $C_{29}H_{30}NO_3SSe_2$ (ESI-TOF, [M + H]$^+$): 632.0277, found: 632.0281.

1-(Butylselanyl)-8-chloro-2-phenyl-5-tosyl-4,5-dihydroselenopheno[2,3-c]quinoline (2y): The product was isolated by column chromatography (hexane/ethyl acetate 98:2 as eluent) as a orange solid. Yield: 0.124g (78%); mp 143-144 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.73 (d, *J* = 2.4 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.45-7.30 (m, 6H), 7.23 -7.19 (m, 2H), 7.04-6.85 (m, 2H), 4.96 (s, 2H), 2.28 (s, 3H), 2.12 (t, *J* = 7.4 Hz, 2H), 1.33 (quint, *J* = 7.4 Hz, 2H), 1.17 (sex, *J* = 7.4 Hz, 2H), 0.76 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 150.6, 143.1, 138.3, 136.2, 134.9, 134.5, 133.0, 132.5, 131.3, 130.0, 129.3, 128.8, 128.2, 128.1, 127.3, 127.0, 124.4, 118.7, 47.5, 31.2, 29.5, 22.6, 21.5, 13.4. HRMS: cald for $C_{28}H_{27}ClNO_2SSe_2$ (ESI-TOF, [M + H]$^+$): 635.9781, found: 635.9785.

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FULL PAPER

Iron-Mediated Cyclization of 1,3-Diynyl Propargyl Aryl Ethers with Dibutyl Diselenide: Synthesis of Selenophene-Fused Chromenes

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Guilherme Lutz[a], Davi F. Back[b] and Gilson Zeni [a,] *