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Synthesis of 3-Organoselenyl-2*H*-coumarins from Propargylic Aryl Ethers via Oxidative Radical Cyclization

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Abstract. A metal-free oxidative radical cyclization/selenylation of propargylic aryl ethers with diaryl diselenides was developed. This protocol provided an alternative method to synthesize 3-organoselenyl-2*H*-coumarins via the formation of C–Se bond, C–C bond, and C=O bond in one step. Moreover, a broad range of functional groups (such as halogen, aldehyde, ketone, cyano, and nitro group) were tolerated.

Keywords: 3-Organoselenyl-2*H*-coumarins; Oxidative Radical Cyclization; Selenium; Propargylic Aryl Ethers

Heterocyclic compounds, especially those containing oxygen, are ubiquitous and valuable structural skeleton in natural products.[1] Among them, coumarin and its derivatives represent an important class of naturally occurring compounds for its significant biological and pharmacological properties,[2] which have proven to be antimicrobial, antitumor, anti-HIV, anticoagulant, antioxidant, and anti-inflammatory (Figure 1). Additionally, coumarins also could be widely applied in pesticides, cosmetics, fluorescent sensors and dyes.[3] From this point of view, these promising applications would lead to a great demand for the development of versatile and efficient methods to construct diverse coumarins.[4] In 2000, Fujiwara's group firstly discovered a palladium-catalyzed intramolecular hydroarylation of alkynoates via C–H activation as an efficient method for the synthesis of coumarin motifs.[5] Afterward, other transition metals or Lewis acids (Fe, Au, In, Hf, etc.) were also effective for this transformation.[6] Alternatively, radical cyclization with mild conditions has emerged as an increasingly popular approach for the construction of cyclic compounds,[7] especially 3-substituded coumarins[8] (including 3-trifluoromethylation,[8a-b] 3-trifluoromethylthiolation,[8c] 3-acylation,[8d-e] 3-phosphorylation,[8f] 3-sulfonation,[8g-i] 3-difluoroacetylation,[8j] and 3-iodination[8k]) by employing alkynoates.

Synthesis of organoselenium compounds is a long-standing focus for chemists because of their wide applications in organic synthesis and increased biological activities.[9] Consequently, it is of urgent desire to develop new strategies to embed an organoselenium moiety into organic molecules, especially for natural building blocks. Commonly used strategies mainly include transiton-metal-catalyzed or -mediated cross-coupling and radical addition reactions.[10] Although numerous cyclic or acyclic organoselenium compounds were synthesized, reports for constructing 3-selenylated coumarins are still less disclosed and remain both challenging and of great value.[11] In 2014, Zeni's group reported an iron(III) chloride mediated 6-*endo*-dig cyclization of alkynoates with diselenides (Scheme 1a).[11a] Very recently, a direct C(sp^2)–H selenylation of 4-amino substituted coumarins via visible-light-promoted process was presented by Wei and co-workers (Scheme 1b).[11b] Considering our ongoing interests in the synthesis of sulfur- or selenium-containing compounds,[12] herein we report a highly efficient method for the synthesis of 3-organoselenyl-2*H*-coumarins under metal-free reaction conditions (Scheme 1c). To the best of our knowledge, there is no report on the construction of coumarin motifs

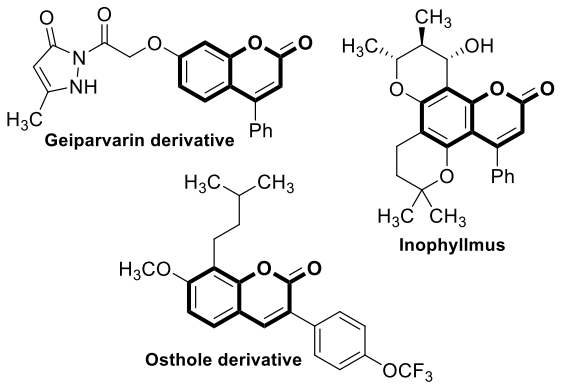

Figure 1. Selected examples of biologically active coumarins.

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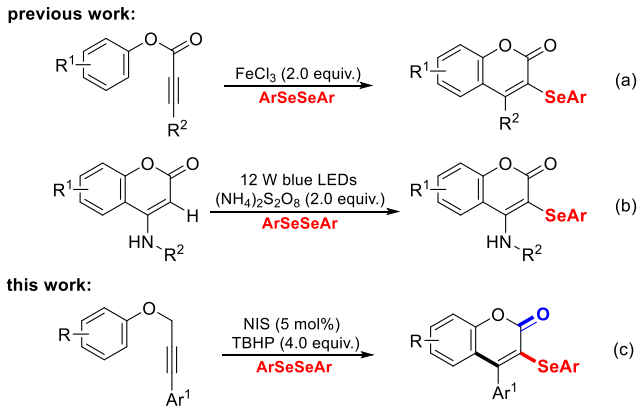


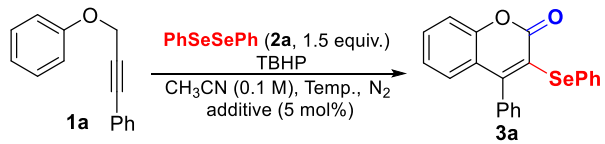
Scheme 1. Strategies for the synthesis of 3-selenylated coumarins.

through radical cyclization of propargylic aryl ethers, which accompanied with the formation of C=O double bonds simultaneously.

We started our investigations by exploring the reaction of (3-phenoxyprop-1-yn-1-yl)benzene (**1a**) with diphenyl diselenide (**2a**) (Table 1, see Table S1-S5 in Supporting Information for more details). The initial experiment revealed that reaction under the condition of *tert*-butyl hydroperoxide (TBHP, 4.0 equiv.) in CH_3CN at 80 °C for 48 h gave 85% yield of the desired product **3a** (Table 1, entry 1). However, lower loading of THBP (2.0 or 3.0 equiv.) decreased the yield to 36% and 72%, respectively (Table 1, entries 2-3). Other oxidants and solvents were inferior for this reaction (see Table S2 and S3). Subsequently, screening of temperature showed that 80 °C is still the notable temperature for this transformation (Table 1, entries 4-7). Inspired by some radical reactions, we further optimized several iodinated compounds with the aim of increasing the reaction yield (Table 1, entries 8-12).[13] A slight better yield (87%) was obtained when a catalytic amount of iodine was added (Table 1, entry 8). To our delight, the use of NIS (5 mol%) gave a much better yield (92%) (Table 1, entry 9).[14] However, the reaction could be significantly inhibited when other iodinated compounds such as NaI, KI, and TBAI were used (Table 1, entries 10-12). Based on the detailed investigations, we confirmed that the optimal reaction conditions were NIS (5 mol%), TBHP (4.0 equiv.) in CH_3CN at 80 °C under N_2 (Table 1, entry 9).

We subsequently focused on examining the generality of this protocol (Table 2). Firstly, a number of propargylic aryl ethers derived from substituted aryl phenols were investigated. The desired

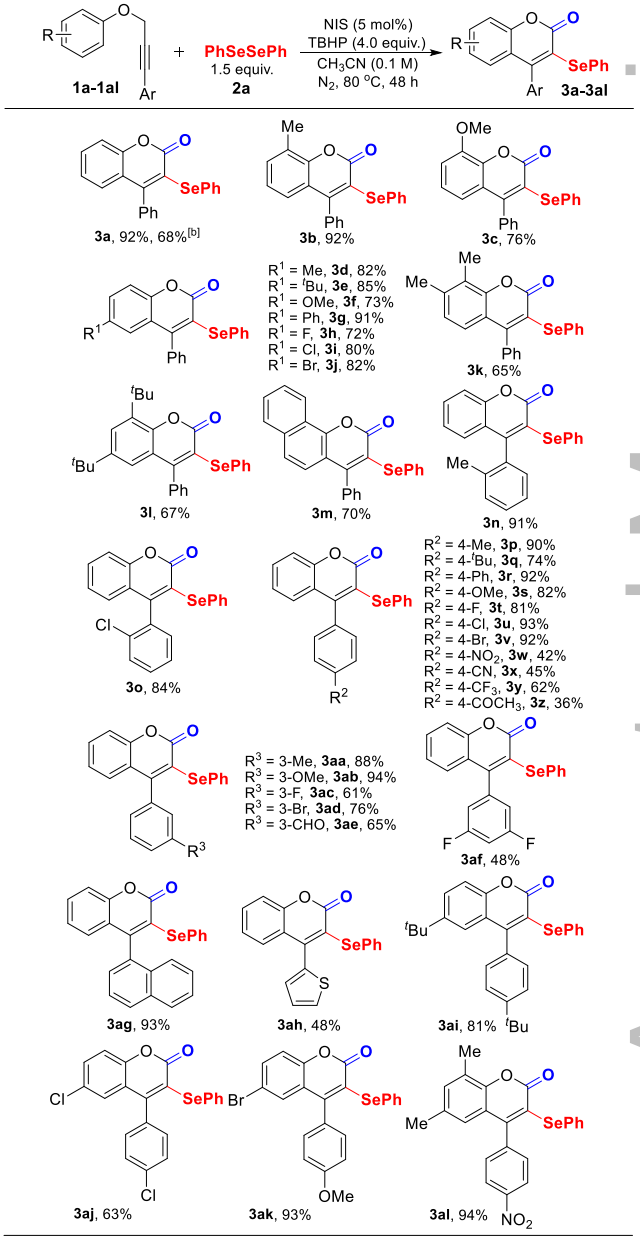
Table 1. Optimization of reaction conditions.[a]



entry	TBHP (equiv.)	additive	Temp. (°C)	yield (%)[b]
1	4.0	-	80	85
2	2.0	-	80	36
3	3.0	-	80	72
4	4.0	-	50	46
5	4.0	-	70	70
6	4.0	-	90	85
7	4.0	-	100	83
8	4.0	I_2	80	87
9	**4.0**	**NIS**	**80**	**92**
10	4.0	NaI	80	trace
11	4.0	KI	80	0
12	4.0	TBAI	80	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv.) and THBP (4.0 equiv., 5.0-6.0 M in decane) in CH_3CN (2.0 mL) were stirred at 80 °C for 48 h under N_2. [b] Isolated yields.

Table 2. Substrate scope of propargylic aryl ethers.[a]



[a] Reaction conditions: **1a-1al** (0.2 mmol), **2a** (1.5 equiv.), NIS (5 mol%), and THBP (4.0 equiv., 5.0-6.0 M in decane) in CH_3CN (2.0 mL) were stirred at 80 °C for 48 h under N_2. Isolated yields. [b] 4.0 mmol scale. Reaction time was extended to 72 h and **1a** (15%) was recovered.

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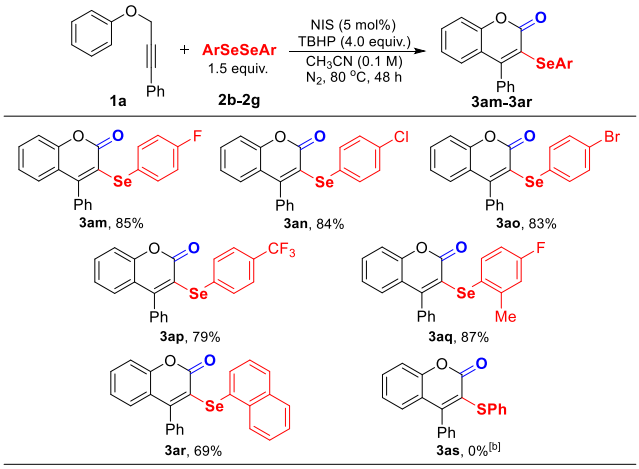
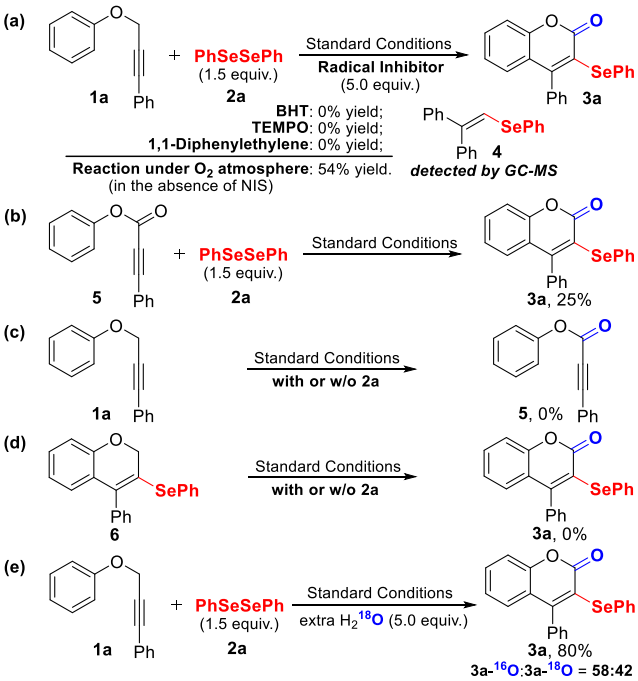
Table 3. Substrate scope of diaryl diselenides.[a]



[a] Reaction conditions: **1a** (0.2 mmol), **2b-2g** (1.5 equiv.), NIS (5 mol%), and THBP (4.0 equiv., 5.0-6.0 M in decane) in CH_3CN (2.0 mL) were stirred at 80 °C for 48 h under N_2. Isolated yields. [b] Diphenyl disulfide (1.5 equiv.) was used instead of substrate **2**.

coumarins (**3b-3c**) were obtained in good yields when the *ortho* position were substituted with methyl and methoxyl groups. Notably, substrates containing electron-donating substituents (Me, ^{t}Bu, OMe, Ph) and electron-withdrawing substituents (F, Cl, Br) on the *para* position also showed good compatibility (**3d-3j**). The structure of **3g** was confirmed by X-ray crystallography (see the Supporting Information).[15] In addition, substrates derived from disubstituted aryl phenols and 1-naphthol afforded the coumarins (**3k-3m**) in good yields. The reaction could be scaled up to gram-scale and produced **3a** with 68% yield.

Furthermore, the influences of substituents on the aryl groups attached to the alkyne were also tested. The steric hindrance didn't affect the efficiency of this transformation. *Ortho*-substituted substrates reacted smoothly and gave the desired coumarins (**3n-3o**) in 91% and 84% yield, respectively. Moreover, a gamut of functionalities such as alkyl or aryl units (**3p-3r**, **3aa**), methoxyl (**3s**, **3ab**), halogen (**3t-3v**, **3y**, **3ac-3ad**, **3af**), ketone (**3z**), aldehyde (**3ae**) were accommodated. It is noteworthy that the substrates bearing strong electron-withdrawing groups (NO_2 and CN) could also be tolerated in this reaction (**3w-3x**). Substrates with naphthalene and thiophene attached to the triple bond were also compatible with the reaction conditions, affording the desired coumarins (**3ag-3ah**) in 93% and 48% yield, respectively. Additionally, other multi-substituted substrates could also smoothly transform into the coumarins (**3ai-3al**) in moderate to excellent yields.

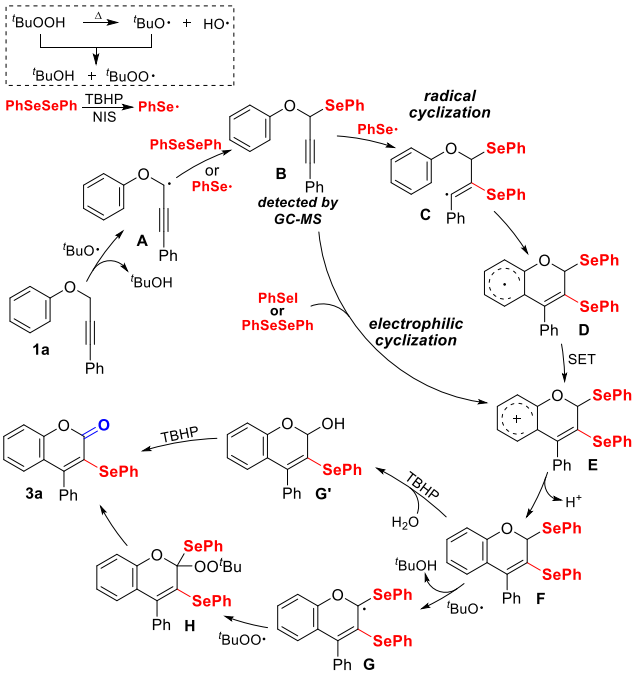


Scheme 2. Control experiments.

The compatibility of diaryl diselenides in this transformation was also evaluated (Table 3). Not surprisingly, the reaction of substrate **1a** and a series of diaryl diselenides furnished the corresponding coumarins (**3am-3ar**) in moderate to good yields. In addition, the halogenated coumarins (**3am-3ao**, **3aq**) may provide a significant opportunity for further modifications through orthogonal cross-couplings, especially in pharmacological demand. Unfortunately, 3-sulfenylated coumarin (**3as**) could not be detected when diphenyl disulfide was used.

To gain further understanding of the reaction mechanism, some necessary control experiments were performed (Scheme 2). The reaction of **1a** and **2a** was significantly inhibited in the presence of a radical inhibitor such as BHT, TEMPO, and 1,1-diphenylethylene (Scheme 2a). The radical trapping product **4** was detected by GC-MS. Moreover, this reaction could be inhibited by O_2 in the absence of NIS (*vs.* Table 1, entry 1). These results implied that the oxidative cyclization might proceed through a radical pathway. Additionally, two possible intermediates (**5** and **6**) were prepared and applied to verify the potential mechanism. The desired product **3a** was obtained in 25% isolated yield when alkynoate **5** coupled with **2a** under standard conditions (Scheme 2b). However, substrate **1a** and selenium-containing cyclic compound **6** could not be directly oxidized to construct the C=O double bonds (Scheme 2c-2d). Therefore, the reaction might not likely proceed through compound **5** and **6**. Besides, when the reaction was performed in the presence of $H_2{}^{18}O$, the ^{18}O-labeled product was obtained (**3a**-^{16}O:**3a**-^{18}O = 58:42) (Scheme 2e). The ^{18}O-labeling experiment shown that the oxygen atom of newly formed carbonyl group comes from TBHP or H_2O in the solvent (CH_3CN).[16]

Based on the above results and previous reports,[10l-m,14c,17] the plausible mechanism has been proposed (Scheme 3). Notably, the selenium-containing compound **B** (detected by GC-MS) might be the key intermediate.[18] The regioselective radical cyclization of the PhSe· radical onto the triple bond of intermediate **B** affords intermediate **F**. Otherwise, the electrophilic cyclization of PhSeI (coming from NIS) with intermediate **B** is also possible. Subsequently, an oxidative way to form **3a** from intermediate **F**, can be given by a Pummerer-type reaction, where H_2O in the



Scheme 3. Proposed mechanism.

solvent is the nucleophile giving an alcohol which it is further oxidized to construct the carbonyl group by high concentration of TBHP. Besides this route, there is another possible pathway towards the desired product (**3a**). The intermediate **F** passes through allylic hydrogen abstraction by *tert*-butoxy radical and generates the radical intermediate **G**, which can be easily trapped by the *tert*-butylperoxy radical to generate intermediate **H**.[12c,17,19] Then the desired product is obtained through simultaneous C–Se and O–O bonds cleavage of intermediate **H**.

In summary, we have demonstrated an oxidative radical cyclization of propargylic aryl ethers with diaryl diselenides for the synthesis of 3-organoselenyl-2*H*-coumarins in a simple and efficient way. The reaction performed smoothly with C–Se bond, C–C bond, and C=O bond constructed concurrently in moderate to excellent yields. The excellent functional group compatibility and broad substrate scope suggest that the potential application of this transformation in pharmaceuticals and biologically active compounds is expected.

Experimental Section

General Procedure for the Synthesis of 3-Organoselenyl-2*H*-coumarins. To an oven-dried reaction tube equipped with a stir bar was sequentially added propargylic aryl ethers **1** (0.2 mmol), diaryl diselenides **2** (0.3 mmol, 1.5 equiv.) and NIS (2.3 mg, 5 mol%). The reaction tube was vacuumed and refilled with nitrogen for three times. After that, a solution of TBHP (150 μL, 4.0 equiv., 5.0-6.0 M in decane) in CH_3CN (2.0 mL) was added to the reaction tube. Then the reaction mixture was stirred at 80 °C for 48 h. After completion, the reaction mixture was evaporated to dryness. The crude residue was purified by silica gel column to give the desired product.

Acknowledgements

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[14] In this reaction, NIS might have the following two roles. One hand, NIS might promote or accelerate the formation of arylselenide radical. On the other hand, diaryl diselenide decomposes to produce ArSeI in the presence of NIS. Several related references, see: a) H.-A. Du, R.-Y. Tang, C.-L. Deng, Y. Liu, J.-H. Li, X.-G. Zhang. *Adv. Synth. Catal.* **2011**, *353*, 2739; b) M. Xu, X.-H. Zhang, P. Zhong. *Tetrahedron Lett.* **2011**, *52*, 6800; c) Z.-J. Yang, B.-L. Hu, C.-L. Deng, X.-G. Zhang. *Adv. Synth. Catal.* **2014**, *356*, 1962; d) W. Wu, Y. An, J. Li, S. Yang, Z. Zhu, H. Jiang. *Org. Chem. Front.* **2017**, *4*, 1751. Also see: ref. 13d and ref. 13e.

[15] CCDC 1877472 contain the supplementary crystallographic data for compound **3g**.

[16] The results in Table S3 were carefully reviewed, and we found that only TBHP was effective for this reaction. In light of the results, we hypothesized that the oxygen atom of newly formed carbonyl group might come from TBHP. Several related references, see: a) H. Jiang, H. Huang, H. Cao, C. Qi. *Org. Lett.* **2010**, *12*, 5561; b) W.-T. Wei, R.-J. Song, X.-H. Ouyang, Y. Li, H.-B. Li, J.-H. Li. *Org. Chem. Front.* **2014**, *1*, 484; c) X.-H. Ouyang, R.-J. Song, Y. Li, B. Liu, J.-H. Li. *J. Org. Chem.* **2014**, *79*, 4582.

[17] a) A. Bravo, H.-R. Bjørsvik, F. Fontana, L. Liguori, F. Minisci. *J. Org. Chem.* **1997**, *62*, 3849; b) R. Shchepin, M. N. Möller, H.-y. H. Kim, D. M. Hatch, S. Bartesaghi, B. Kalyanaraman, R. Radi, N. A. Porter. *J. Am. Chem. Soc.* **2010**, *132*, 17490; c) H.-L. Hua, Y.-T. He, Y.-F. Qiu, Y.-X. Li, B. Song, P. Gao, X.-R. Song, D.-H. Guo, X.-Y. Liu, Y.-M. Liang. *Chem. Eur. J.* **2015**, *21*, 1468; d) L. M. Smith, H. M. Aitken, M. L. Coote. *Acc. Chem. Res.* **2018**, *51*, 2006.

[18] The GC-MS result for the detection of possible intermediate **B** was attached in Supporting Information. Due to the unstability of intermediate **B**, we failed to prepare and isolate it.

[19] Selected references: a) A. Studer. *Chem. Eur. J.* **2001**, *7*, 1159; b) A. Studer. *Chem. Soc. Rev.* **2004**, *33*, 267; c) D. Li, Y. Li, W. Yu. *Synthesis* **2017**, *49*, 4283.

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COMMUNICATION

Synthesis of 3-Organoselenyl-2*H*-coumarins from Propargylic Aryl Ethers via Oxidative Radical Cyclization

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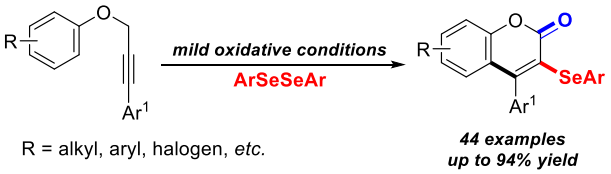

R = alkyl, aryl, halogen, *etc.*

44 examples
up to 94% yield