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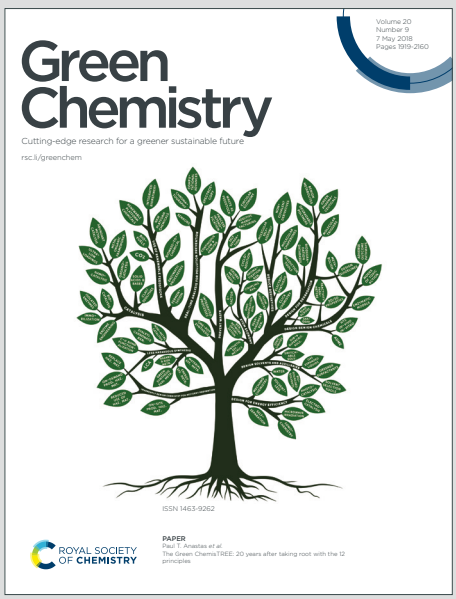

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ARTICLE

Electrochemical oxidative cyclization of activated alkynes with diselenides or disulfides: access to functionalized coumarins or quinolinones†

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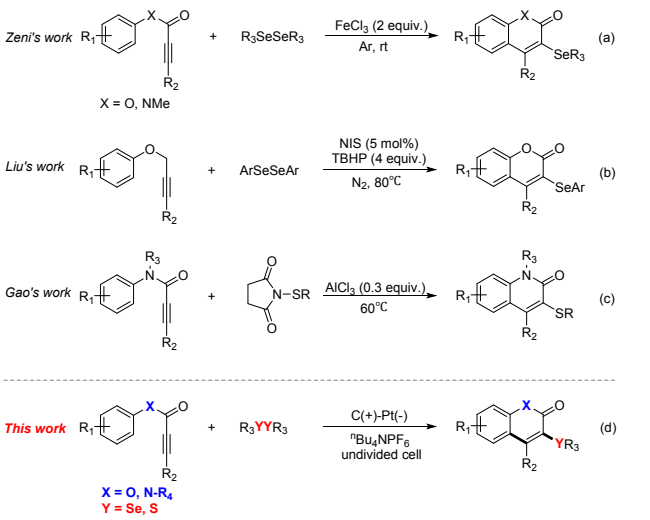
A direct electrochemical oxidative cyclization of alkynoates and alkynamides with diselenide or disulfide for the synthesis of the coumarins and quinolinones bearing a chalcogen functional group has been developed. This green and efficiency approach was realized through the constant current electrolysis in an undivided cell under metal-free and oxidant-free conditions. Moreover, a series of selenium/sulfur-substituted coumarins and quinolinones products were obtained in moderate to good yields with broad scope and functional group tolerance.

Introduction

Organoselenides and sulfides are impressive compounds with high pharmacological activities, that serve as the key building blocks in organic synthesis.[1] In addition, extensive applications of organic chalcogenide compounds have been found in functional materials.[2] Consequently, much attempts have been made to investigate and develop novel methods for preparing more valuable organic chalcogenide compounds.[3] In particularly, the addition of selenium or sulfur group to unsaturated compounds (alkenes, alkynes or allenes) *via* radical cascade reaction is a common strategy.[4]

As the reliable coupling partners, activated alkynes (alkynoates or alkynamides) have been successfully transformed to the substituted heterocycles[5] (coumarins or quinolinones) by means of radical mediated cyclization to accomplish the difunctionalization of alkynes. Coumarins and quinolinones represent privileged structural scaffolds, which are ubiquitous in diverse bioactive natural products and clinical pharmaceuticals.[6] Furthermore, coumarins and quinolinones have been recognized as the important skeletons of biologically active molecules for anti-cancer, anti-HIV, anti-psoriasis, anti-protozoal, anti-inflammatory, anti-depressant and anti-diabetic treatment.[7] Undoubtedly, it is highly desirable to develop novel and efficient strategies to provide chalcogen-substituted coumarins and quinolinones. In 2014, Zeni and co-workers discovered an iron (III) chloride mediated 6-*endo*-dig cyclization of arylpropiolates and arylpropiolamides with diorganyl diselenides (Scheme 1a).[8] Recently, Liu's group reported a metal-free method for the preparation of selenium-containing coumarins from propargylic aryl ethers (Scheme 1b).[9] In 2017, Gao and co-workers developed an intramolecular cyclization of N-arylpropynamides with N-sulfanylsuccinimides for the synthesis of 3-sulfenyl quinolin-2-ones by using $AlCl_3$ as the catalyst (Scheme 1c).[10] However, there are still some drawbacks exited, including the usage of excessive metal, the demand of oxidant and heating conditions, and the unavoidable toxic byproducts.

In the past few years, electrochemistry has gradually become a hot topic in the field of organic synthesis because of its environmentally benign and economy.[11] The emerging electrosynthesis is a green alternative for chemical redox



Scheme 1. Electrochemical oxidative cyclization of activated alkynes with diselenides or disulfides

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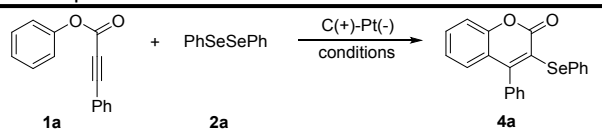
Table 1. Optimization of reaction conditions[a]



1a 2a 4a

Entry	Solvent	Electrolyte (equiv.)	I (mA)	Yield[b] (%)
1	CH_3CN	$^nBu_4NBF_4$ (2)	15	53
2	DMF	$^nBu_4NBF_4$ (2)	15	21
3	DCE	$^nBu_4NBF_4$ (2)	15	19
4	HFIP	$^nBu_4NBF_4$ (2)	15	60
5	CH_3CN/HFIP (4/1)	$^nBu_4NBF_4$ (2)	15	68
6	CH_3CN/HFIP (4/1)	$^nBu_4NPF_6$ (2)	15	**83**
7	CH_3CN/HFIP (4/1)	$^nBu_4NI$ (2)	15	0
8	CH_3CN/HFIP (4/1)	$^nBu_4NBr$ (2)	15	0
9	CH_3CN/HFIP (4/1)	Et_4NClO_4 (2)	15	46
10	CH_3CN/HFIP (4/1)	$^nBu_4NPF_6$ (0.5)	15	51
11	CH_3CN/HFIP (4/1)	$^nBu_4NPF_6$ (1)	15	69
12	CH_3CN/HFIP (4/1)	$^nBu_4NPF_6$ (3)	15	80
13	CH_3CN/HFIP (4/1)	$^nBu_4NPF_6$ (2)	0	0
14	CH_3CN/HFIP (4/1)	$^nBu_4NPF_6$ (2)	5	51
15	CH_3CN/HFIP (4/1)	$^nBu_4NPF_6$ (2)	10	63
16	CH_3CN/HFIP (4/1)	$^nBu_4NPF_6$ (2)	20	81
17	CH_3CN/HFIP (4/1)	$^nBu_4NPF_6$ (2)	15	59[c]
18	CH_3CN/HFIP (4/1)	$^nBu_4NPF_6$ (2)	15	79[d]

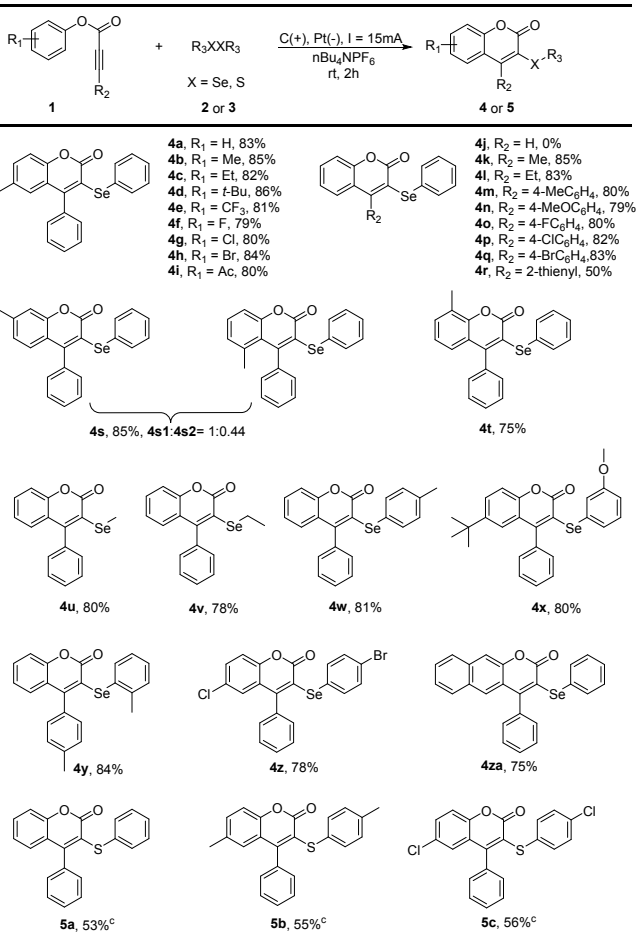
[a]Reaction conditions: Pt plate cathode (15 mm × 15 mm × 0.1 mm) cathode, graphite rod anode (Φ 6 mm), **1a** (0.5 mmol), **2a** (0.5 mmol), solvent (10 mL), electrolyte, constant current, room temperature, 2h, undivided cell. [b]Isolated yield. [c]0.5 equiv. of **2a**. [d]1.5 equiv. of **2a**.

agents, which employs sustainable and renewable electric current as the driving force of chemical reactions.[12] In electrochemical environment, the reactivity of specific redox events could be precisely controlled by slightly adjusting the applied electromotive force. With the rising attention to electrochemistry, combining electrocatalysis with dehydrogenation cross coupling reactions and radical cascade reactions for constructing C-C, C-N, C-O and C-S bonds have been reported by Lin,[13] Lei,[14] Xu[15] and other groups. Inspired by these elegant works on synthetic electrochemistry, herein, we develop a direct selenation or sulfuration of activated alkynes to achieve intramolecular cyclization through electrochemical oxidation (Scheme 1d). To the best of our knowledge, electrochemical-catalyzed oxidative cyclization of alkynes for the synthesis of chalcogen-substituted coumarins or quinolinones under metal-free and oxidant-free conditions has not been reported to date.

Results and discussion

Initially, the electrochemical oxidative cyclization of phenyl 3-phenylpropiolate **1a** to prepare 3-organoselenyl-2H-coumarin **4a** with diphenyl diselenide **2a** by using graphite anode and platinum cathode was chosen as the model reaction. First, different kinds of solvents were examined with $^nBu_4NBF_4$ as the

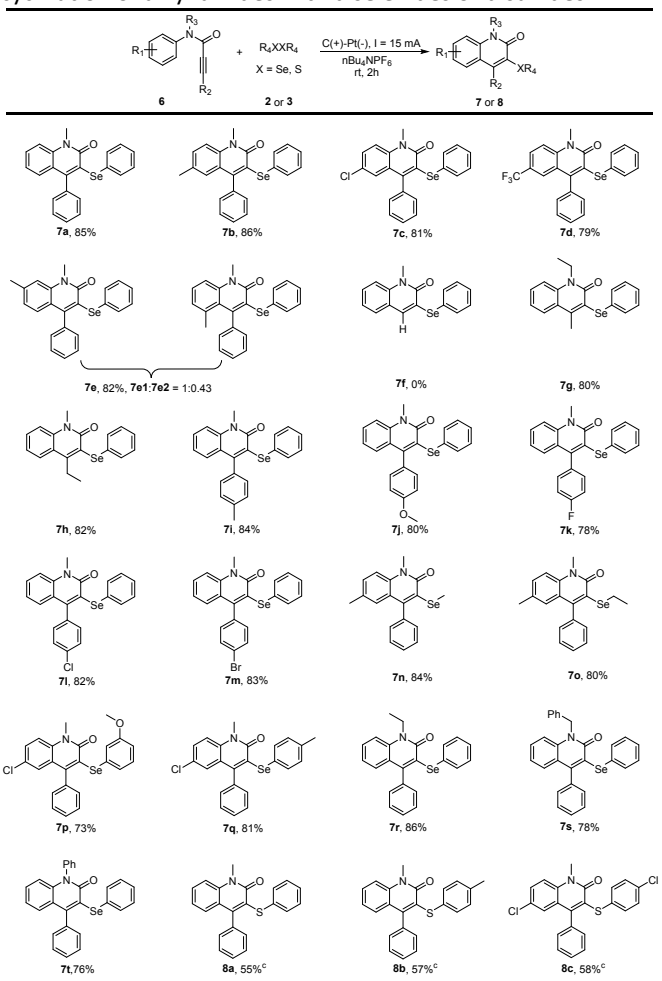
Table 2. Substrate scope of electrochemical oxidative cyclization of alkynoates with diselenides or disulfides



[a]Reaction conditions： Pt plate cathode (15 mm × 15 mm × 0.1 mm) cathode, graphite rod anode (Φ 6 mm), constant current = 15 mA, **1** (0.5 mmol), **2** (0.5 mmol), $^nBu_4NPF_6$ (1 mmol), CH_3CN/ HFIP (10 mL, v/v = 4/1), room temperature, 2h (2.2 F/mol), undivided cell. [b]Isolated yield. [c]**3** (0.5 mmol), under N_2.

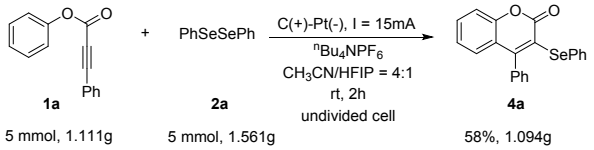
electrolyte under 15mA constant current, and the results indicated that the cosolvent of CH_3CN/HFIP (v/v = 4/1) might be the suitable choice (Table 1, entry 5). Due to its low-nucleophilic and protic nature, HFIP could enhance the stability of radical intermediates.[16] Then a series of supporting electrolytes such as $^nBu_4NBF_4$, $^nBu_4NPF_6$, $^nBu_4NI$, $^nBu_4NBr$, and Et_4NClO_4 were screened (Table 1, entries 5-9). $^nBu_4NPF_6$ was proven to be the most efficient electrolyte to give the product **4a** in 83% yield (Table 1, entry 6). Either decreasing or increasing the amount of $^nBu_4NPF_6$ failed to improve the yield of **4a** (Table 1, entries 10-12). With the further investigation of electrochemical parameters, no desired products were detected without constant current (Table 1, entry 13). Compared to the condition of 15mA constant current, lower yields of **4a** were obtained when decreasing the operating current to 5 mA or 10mA (Table 1, entries 14-15). While increasing the operating current to 20 mA merely resulted in a relative close transformation (Table 1, entry 16). Finally, adjustment of the amount of diphenyl diselenide **2a** led to less reaction efficiency as well (Table 1, entries 17-18).

Table 3. Substrate scope of electrochemical oxidative cyclization of alkynamides with diselenides or disulfides[a,b]



[a]Reaction conditions： Pt plate cathode (15 mm × 15 mm × 0.1 mm) cathode, graphite rod anode (Φ 6 mm), constant current = 15 mA, **6** (0.5 mmol), **2** (0.5 mmol), $^{n}Bu_4NPF_6$ (1 mmol), CH_3CN/ HFIP (10 mL, v/v = 4/1), room temperature, 2h (2.2 F/mol), undivided cell. [b]Isolated yield. [c]**3** (0.5 mmol), under N_2

With the optimized reaction conditions in hand, substrate scope of electrochemical oxidative cyclization of alkynoates **1** with diselenides **2** or disulfides **3** was next explored. As shown in Table 2, a variety of alkynoates derived from *para*-substituted phenols, that bear both electron-donating groups (Me, Et, t-Bu) and electron-withdrawing groups (CF_3, F, Cl, Br, Ac), showed great compatibility to give the corresponding products (Table 2, **4b**-**4i**). And the molecular structure of **4i** was identified by singlecrystal X-ray diffraction (CCDC 1935858, Figure S1). On the other hand, the substrates that substituents were attached to the alkyne were also investigated under the optimal conditions. To our delight, the reactions proceeded smoothly to achieve the desired products in moderate to good yields ranging from 50% to 85% (Table 2, **4k**-**4r**). However, the reaction of phenyl propiolate **1j** with diphenyl diselenide **2a** failed to generate the desired product **4j**.These two isomers **4s1** and **4s2** were generated when 3-methyl substituted substrate **1s** reacted with **2a**, which might be caused by regioselectivity of the cyclization (Table 2, **4s**). Moreover, substrate **1t** with the methyl group on the *ortho* position of phenyl ring tolerated well (Table 2, **4t**). It is noteworthy that a range of diselenides including aliphatic diselenides and aryl diselenides were successfully suitable for the strategy to furnish the cyclization products in 78%-84% yields (Table 2, **4u**-**4z**). Similarly, 2-naphthyl alkynoates **1za** performed well under the standard conditions (Table 2, **4za**). Gratifyingly, disulfides **3** exhibited good tolerance through electrochemical oxidative cyclization to give the predicable products in 53%-56% yields (Table 2, **5a**-**5c**).



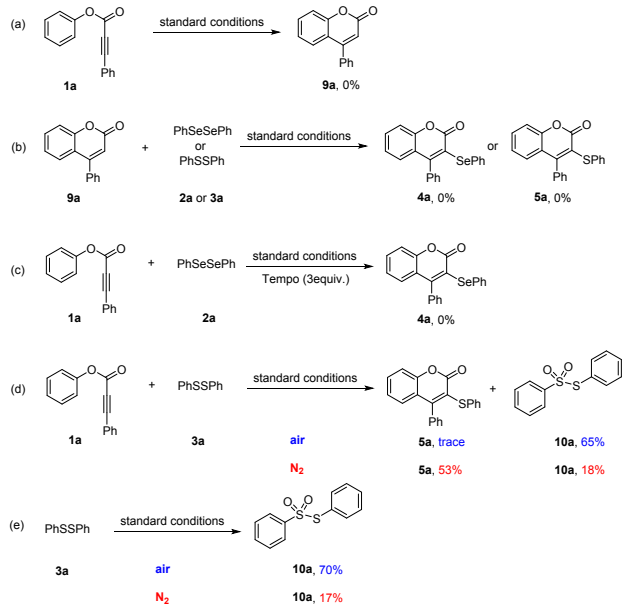
Scheme 2. Gram-scale synthesis

The electrochemical oxidative cyclization was further extended to substrate scope of alkynamides under the analogous reaction conditions. Generally, electron-donating groups and electron-withdrawing groups on the *para*-position of these two different aromatic rings of alkynamides all worked well with diselenides, affording the corresponding quinolinones products in reasonable yields (Table 3, **7b**-**7d**, **7i**-**7m**). The reaction of *meta*-methyl substituted substrate was also tested, offering two isomers **7e1** and **7e2** in a ratio of 1:0.43 (Table 3, **7e**). While no desired product **7f** was observed by using the substrate without phenyl on the alkyne (Table 3, **7f**). The substrates that alkyl substituents (Me and Et) were attached to the alkyne showed excellent tolerance under the optimized conditions (Table 3, **7g**-**7h**). Moreover, both dialkyl diselenides and diaryl diselenides efficiently transformed to the products **7n**-**7q** in 73%-84% yields (Table 3, **7n**-**7q**). N-ethyl, N-benzyl and N-phenyl alkynamides were all subjected to the optimal reaction conditions, which prepare the expected products in excellent yields (Table 3, **7r**-**7t**). Subsequently, we turned our attention to treat disulfides derivatives. It is delightful to discover that these disulfides could proceed well under the electrochemical oxidative conditions (Table 3, **8a**-**8c**).

In order to verify the practical application of the electrochemical oxidative cyclization, a 5mmol scale-up reaction was conducted (Scheme 2). The reaction of phenyl 3-phenylpropiolate **1a** and diphenyl diselenide **2a** performed well through the constant current electrolysis in an undivided cell, affording the product **3a** in 58% yield, which might demonstrate the great potential of this green electrochemical protocol in future industrial application.

To gain further insights into the mechanism of this method, several control experiments were carried out as shown in Scheme 3. When **1a** was treated without **2a** under standard conditions, the coumarin product **9a** was not obtained (Scheme 3a). No desired products **4a or 5a** were detected when **2a or 3a** reacted with prepared **9a** through electrochemical oxidative procedure (Scheme 3b). These results suggested that coumarin **9a** might not be the crucial

intermediate in this transformation. The electrochemical reaction was completely inhibited by adding 3 equiv. radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to this system, which verified that this process proceeds *via* a radical pathway. The reaction of **1a** with **3a** was conducted under air or N_2 conditions, respectively. The results indicated that the product **5a** failed to generate and the byproduct **10a** was obtained in 65% yield under air conditions. While, 18% yield of byproduct **10a** was still observed under N_2 conditions, which might be explained that **3a** was oxidized by O_2 released from the electrolysis of residual water in the solvent (Scheme 3d). Meanwhile, without the addition of **1a**, the byproduct **10a** was detected in 70% or 17% yield under air or N_2 conditions, respectively (Scheme 3e). Based on the results of Scheme 3d and 3e, the reaction with disulfides should be carried out under N_2 conditions to minimize the oxidation of disulfides. Furthermore, cyclic voltammetry (CV) experiments were performed to investigate the redox potential of the substrates (Figure 1). The oxidation peaks of diphenyl diselenide **2a** and diphenyl disulfide **3a** were observed at 1.47 V and 1.76 V, respectively, while the oxidation peak of **1a** was observed at 2.43 V. And this phenomenon illustrated that **2a** and **3a** are oxidized preferentially at the anode.



Scheme 3. Control experiments

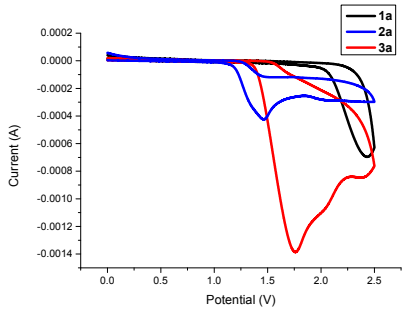
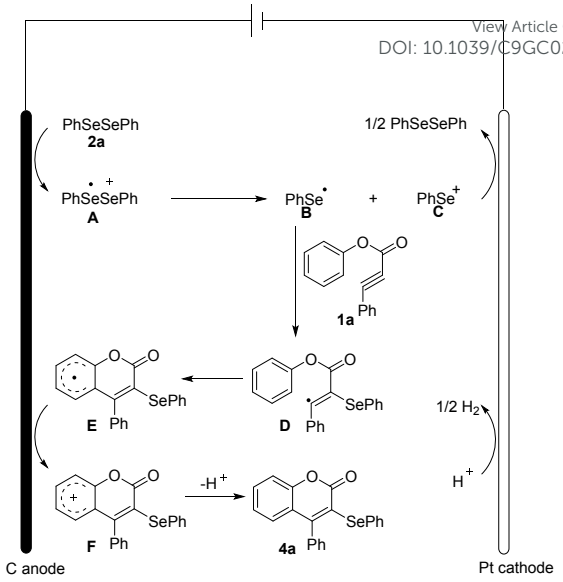


Figure 1. Cyclic voltammograms of **1a**, **2a** and **3a**



Scheme 4. Proposed reaction mechanism

On the basis of the above results and reported literatures,[17] a possible mechanism for the electrochemical oxidative cyclization is proposed in Scheme 4. Initially, cationic radical intermediate **A** is generated from the oxidation of diphenyl diselenide **2a** at the anode, thereby divided into phenylselenium radical **B** and phenyl selenium cation **C**. The addition of radical **B** to the C-C triple bond of **1a** provides vinyl radical **D** in high regioselectivity. Subsequently, vinyl radical **D** proceeds through an intramolecular cyclization to give **E**, which undergoes further anodic oxidation to give intermediate **F**. Finally, the 3-selenated coumarin product **4a** is produced *via* deprotonation of intermediate **F** and regeneration of the aromatic system. At the same time, phenyl selenium cation **C** is reduced to diphenyl diselenide **2a** at the cathode for the next cycle.

Conclusions

In summary, we have developed an efficient intramolecular cyclization of activated alkynes with diselenides or disulfides through the constant current electrolysis under metal-free and oxidant-free conditions. This green and environmental-friendly strategy shows broad scope and great compatibility of functional group, affording a series of chalcogen-substituted coumarins and quinolinones in moderate to good yields. Moreover, the gram-scale experiment has been successfully conducted, which might demonstrate the potential value of this electrochemical protocol. Further research on the mechanism and applications of electrochemical oxidative cyclization are keeping going in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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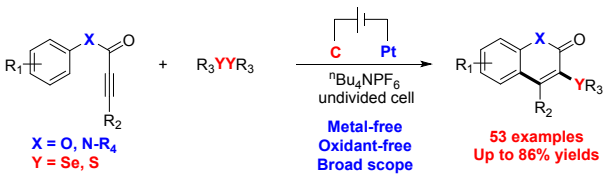

A direct electrochemical oxidative cyclization of activated alkynes with diselenide or disulfide toward functionalized coumarins and quinolinones has been developed.