

RESEARCH ARTICLE

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11, 5813Electrochemical synthesis of selenyl imidazo
[2,1-*b*]thiazinones via three-component reactions†Yuancheng Yue,^{‡a} Ziren Chen,^{‡a} Fei Xue,^a Bin Wang,^{‡a} Yonghong Zhang,^{‡a}
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An efficient, green and one-pot strategy for the concise synthesis of diverse selenyl imidazo[2,1-*b*]thiazinones from diselenides, acryloyl chlorides and 2-mercaptobenzimidazoles/2-mercaptoimidazoles via electrochemical oxidative three-component tandem reactions in the absence of transition metals and oxidants has been developed. The electrochemical method has the advantages of good functional group tolerance, readily available raw materials, high step economy, and mild reaction conditions. Mechanistic studies indicated that selenium cations formed via direct electrochemical oxidation of diselenides may be involved as important intermediates in this process.

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Introduction

Nitrogen- and sulfur-containing heterocycles are prevalent in a diverse array of natural products and small-molecule pharmaceuticals.¹ Among them, compounds featuring the imidazo[2,1-*b*]thiazinone skeleton occupy a prominent position in the realm of medicine due to their superior biological activities such as tuberculostatic activity,^{2,4} antiviral activity,³ antitumor activity⁵ and more⁶ (Scheme 1). Therefore, imidazo[2,1-*b*]thiazinone derivatives have attracted significant attention from organic chemists, and some excellent approaches have been discovered in recent years for the preparation of such compounds.⁷ Traditionally, the synthesis of imidazo[2,1-*b*]thiazinone skeletons was achieved by the cyclization reaction of 2-mercaptobenzimidazoles with 2-halobenzoyl chlorides,⁸ *o*-iodobenzoic acids,⁹ or benzamides with a directing group¹⁰ under heating and transition-metal-catalyzed conditions (Scheme 2a-c). Alternatively, such compounds could also be synthesized at room temperature using an expensive NHC catalyst from 2-mercaptobenzimidazoles and alkynyl acids (Scheme 2d). Although these known methods are generally

efficient, there are still some limitations, such as the requirement of transition metals, high temperature, pre-functionalized raw materials, or expensive NHC, which confine their applications. Therefore, the development of gentle and facile methods for synthesizing imidazo[2,1-*b*]thiazinones from simple starting materials under transition metal- and oxidant-free conditions is highly desirable.

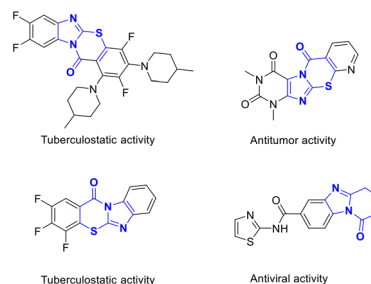
Organoselenium compounds are widely present in the fields of natural products, pharmaceuticals, agrochemicals, and functional materials and have received widespread attention from synthetic organic chemists and medicinal chemists.¹¹ Therefore, the synthesis of organoselenium compounds,¹² especially the construction of C–Se bonds,¹³ has become a research hotspot in recent years. In this context, various selenium reagents are used to introduce selenium atoms into organic molecules, such as diselenides, PhSeBr, PhSeCl, PhthSe and selenium powder. Among them, diselenides have become one of the most popular selenium reagents for constructing C–Se bonds owing to their stability, easy availability, and con-

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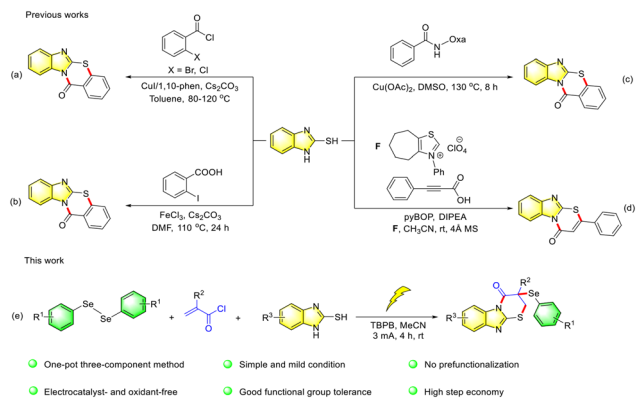
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Scheme 1 Bioactive molecules containing an imidazo[2,1-*b*]thiazinone skeleton.



Scheme 2 Strategies related to the construction of imidazo[2,1-*b*]thiazinones.

venient operation. Recently, electrochemical synthesis¹⁴ has been widely used in organic transformations as a green and powerful synthesis method, due to its ability to efficiently generate active intermediates under environmentally friendly and sustainable conditions. This strategy to prepare organoselenium compounds has become a highly favored choice for synthesizers, and a series of excellent achievements have been made.¹⁵ Given the importance of organoselenium compounds and imidazo[2,1-*b*]thiazinones, as well as our sustained focus on 2-mercaptobenzimidazoles¹⁶ and electrochemical synthesis,¹⁷ herein we report a new three-component cascade reaction for the synthesis of selenyl imidazo[2,1-*b*]thiazinones from diselenides, acryloyl chlorides and 2-mercaptobenzimidazoles/2-mercaptoimidazoles under electrochemical conditions, avoiding the use of transition metals and oxidants (Scheme 2e).

Results and discussion

At the outset, we selected diphenyl diselenide (**1a**), methacryloyl chloride (**2a**), and 2-mercaptobenzimidazole (**3a**) as the model substrates to investigate the ideal reaction conditions for the electrochemical preparation of 3-methyl-3-(phenylselenyl)-2,3-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*][1,3]thiazin-4-one (**4a**). To our delight, the target compound **4a** was obtained in 90% isolated yield when the model reaction was performed in an undivided electrolytic cell with Cs₂CO₃ (0.1 mmol) as the base, tetrabutylphosphonium bromide (TBPB, 0.2 mmol) as the electrolyte, MeCN (4 mL) as the solvent and carbon plates as electrodes under a constant current of 3 mA at room temperature for 4 h (Table 1, entry 1). The subsequent control experiments clearly demonstrated that the reaction was an electrochemical synthesis reaction, and the electrolyte and base were crucial for the reaction (Table 1, entries 2–4). Next, other solvents were also examined, including MeOH, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidone (NMP), but the yields were very poor (Table 1, entries 5–8). Screening of electrolytes showed that tetrabutylammonium iodide (TBAI), tetrabutylammonium hexa-

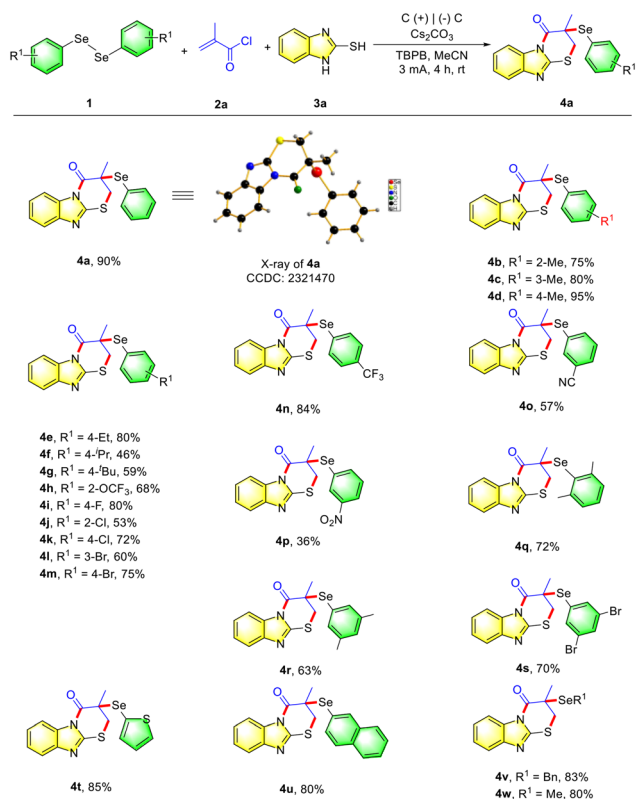
Table 1 Optimization of reaction conditions^a

Entry	Variation from the standard conditions	Yield (%)
1	None	90
2	No electricity	N.D.
3	No TBPB	42
4	No Cs ₂ CO ₃	38
5	MeOH instead of MeCN	Trace
6	DMF instead of MeCN	30
7	DMSO instead of MeCN	Trace
8	NMP instead of MeCN	N.D.
9	TBAI instead of TBPB	67
10	TBAPF ₆ instead of TBPB	81
11	TBAOAc instead of TBPB	73
12	DBU instead of Cs ₂ CO ₃	57
13	<i>t</i> -BuOK instead of Cs ₂ CO ₃	68
14	Pyridine instead of Cs ₂ CO ₃	44
15	0.15 mmol or 0.08 mmol of Cs ₂ CO ₃ instead of 0.1 mmol of Cs ₂ CO ₃	85/73
16	3 or 5 h instead of 4 h	70/83
17	2 or 4 mA instead of 3 mA	80/88
18	C (+) Ni (-) instead of C (+) C (-)	69
19	Pt (+) Pt (-) instead of C (+) C (-)	82
20	Ni (+) Pt (-) instead of C (+) C (-)	Trace

^a Reaction conditions: **1a** (0.05 mmol), **2a** (0.4 mmol), **3a** (0.2 mmol), TBPB (0.2 mmol), Cs₂CO₃ (0.1 mmol), MeCN (4 mL), C plate (15 mm × 10 mm × 1 mm) cathode, C plate (15 mm × 10 mm × 1 mm) anode, undivided cell, current = 3 mA, room temperature, air and 4 h. Isolated yields. N.D. = not detected.

fluorophosphate (TBAPF₆), or tetrabutylammonium acetate (TBAOAc) led to decreased yields (Table 1, entries 9–11). Other bases, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), *t*-BuOK, and pyridine, led to lower yields or inhibited the reaction (Table 1, entries 12–14). When the amount of Cs₂CO₃ was increased or decreased, only compound **4a** could be obtained in 85% and 73% yields, respectively (Table 1, entry 15). Thereafter, we explored the effects of current and time on the reaction results and found that increasing or decreasing the current and prolonging or shortening the time did not further improve the reaction efficiency (Table 1, entries 16 and 17). Finally, we investigated the effect of electrode materials on the reaction and found that the carbon anode and carbon cathode were the best choice (Table 1, entries 18–20).

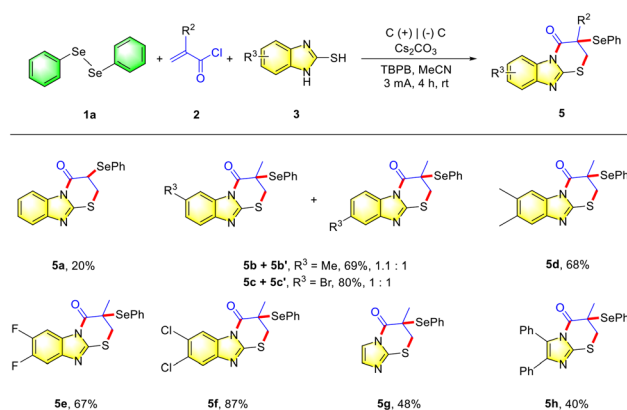
After determining the optimal reaction conditions, we further explored the substrate range of diselenides (**1**) with **2a** and **3a** to verify the practicality and universality of the electrochemical strategy, as shown in Scheme 3. Generally, diphenyl diselenides with either an electron donating group or an electron withdrawing group on the benzene ring could be converted into the target products **4b–4m** in 46–95% yields. It was evident that this reaction was almost unaffected by the electronic effect; however, steric hindrance played an important role in the process. It is worth mentioning that strong electron withdrawing groups such as trifluoromethyl, cyano, and nitro could be tolerated, and the corresponding products **4n**, **4o**,



and **4p** could be obtained with yields of 84%, 57%, and 36%, respectively. Diphenyl diselenides with two substituents attached to the benzene ring could also be efficiently transformed into selenyl imidazo[2,1-*b*]thiazinones (**4q–4s**, 63–72%). The reaction was also compatible with diheteroaryl diselenides such as di(thiophen-2-yl)diselane, providing the corresponding product **4t** in 85% yield. In order to further prove the generality of the method, we also investigated the reactivity of 1,2-di(naphthalen-2-yl)diselane, 1,2-dibenzyl-diselane, and 1,2-dimethyldiselane and found that the appropriate products **4u–4w** could still be obtained in 80–83% yields.

Encouraged by the above results, the scopes of acryloyl chlorides (**2**) and 2-mercaptobenzimidazoles/2-mercaptoimidazoles (**3**) were explored subsequently (Scheme 4). When acryloyl chloride reacted with diphenyl diselenide (**1a**) and 2-mercaptobenzimidazole (**3a**) under the optimal conditions, product **5a** was obtained in 20% yield. Thereafter, the nature of 2-mercaptobenzimidazoles was investigated to further demonstrate the versatility of the system. 2-Mercaptobenzimidazoles with an electron-donating (Me) or electron-withdrawing (Br) group at the 5 position reacted successfully, and the corresponding products **5b + 5b'** and **5c + 5c'** could be obtained with yields of 69% and 80%, respectively. To our delight, 2-mercaptobenzimidazoles with electron-rich

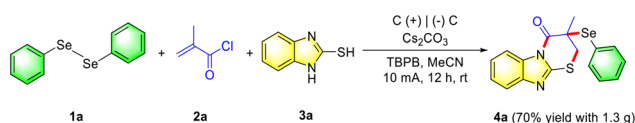
(Me) or electron-deficient (F and Cl) groups at the 5 and 6 positions could successfully afford the desired products with moderate to good yields (**5d–5f**, 67–87%). Furthermore, 2-mercaptoimidazole and 4,5-diphenyl-1*H*-imidazole-2-thiol were also converted into selenium containing products **5g** and **5h** with yields of 48% and 40%, respectively.



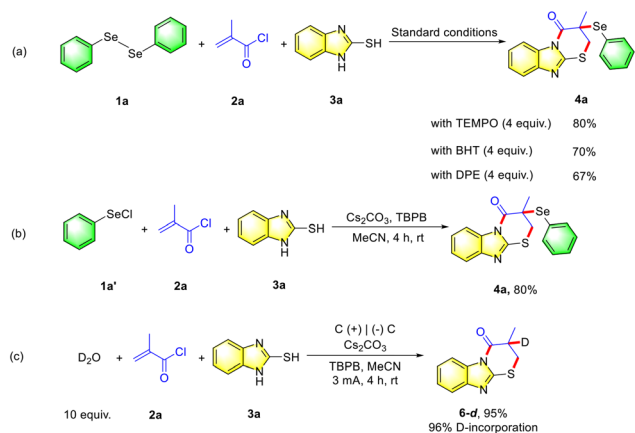
Additional, this three-component tandem reaction could be readily scaled up to the gram scale. Under slightly adjusted conditions, **1a** (0.78 g, 2.5 mmol) reacted with **2a** (2.1 mL, 20 mmol) and **3a** (1.5 g, 10 mmol), affording the desired product **4a** in 70% yield after 12 hours (Scheme 5). This outcome to some extent indicated the potential applicability of the method.

To investigate the possible reaction mechanism of this reaction, a series of control experiments were systematically conducted (Scheme 6). First, the radical nature of this reaction was studied through radical trapping experiments. Clearly, under standard conditions, when a radical scavenger such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT), or 1,1-diphenylethene (DPE) was added to the reaction mixture, the reaction could proceed smoothly, with only a slight decrease in the yield. Therefore, we speculated that the main reaction pathway of this reaction was not the radical pathway, but an ionic reaction process. Based on previous reports,^{17a} selenium cations may be formed *via* direct

Gram-scale reaction. Reaction conditions: **1a** (2.5 mmol), **2a** (20.0 mmol), **3a** (10.0 mmol), TBPB (10.0 mmol), Cs₂CO₃ (5.0 mmol), MeCN (50 mL), C plate (30 mm × 20 mm × 1 mm) cathode, C plate (30 mm × 20 mm × 1 mm) anode, undivided cell, current = 10 mA, room temperature, air and 12 h. Isolated yields.



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Scheme 6 Control experiments.

electrochemical oxidation of diselenides in the transformation. To substantiate this conjecture, the reaction was replicated without electricity using phenyl selenium chloride in lieu of diphenyl diselenide (Scheme 6b), resulting in product **4a** with 80% yield. This reaction result supports the formation of anionic intermediates during the reaction process. The cyclic voltammetry (CV) experimental results revealed that upon addition of **1a**, a distinct oxidation peak was observed at 1.327 V, indicating the facile oxidation of **1a** under these conditions (Fig. 1). Next, a deuterium labeling experiment was conducted (Scheme 6c) using D_2O as the electrophilic reagent in place of diphenyldiselenide, under standard conditions, yielding the corresponding deuterated product (**6-d**).

Based on our mechanistic probe experiments and literature reports,^{17a} a plausible mechanism for this electrochemical oxidative three-component tandem reaction is proposed. As shown in Scheme 7, diselenide **1a** is first oxidized at the anode to form the cationic radical intermediate **A**, which dissociates into selenium cation **B** and selenium radical **C**. Subsequently,

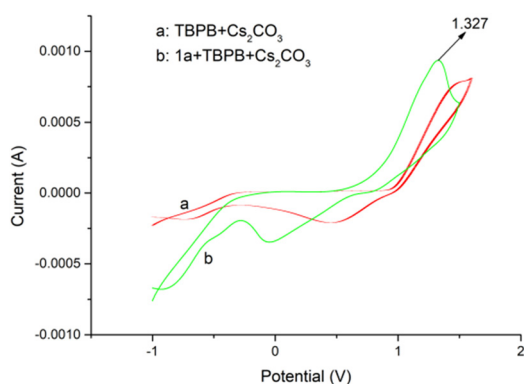
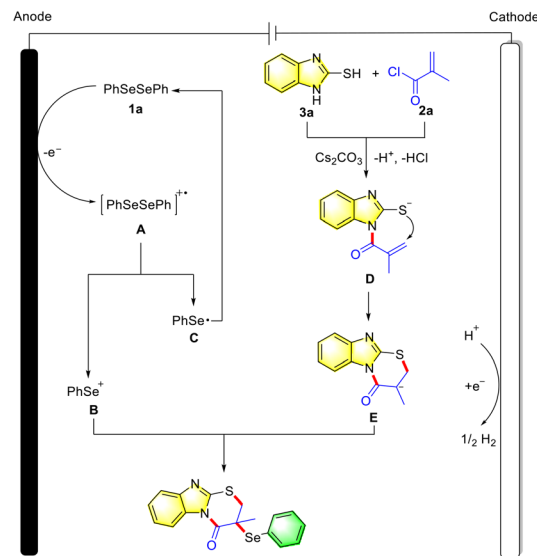


Fig. 1 Cyclic voltammometry experiments. Cyclic voltammograms were recorded using a CHI660E electrochemical workstation at room temperature. A glassy carbon-disk ($R = 5.5$ mm, $h = 10$ mm) was used as the working electrode. A Pt disk ($R = 5.5$ mm, $h = 10$ mm) and Ag/AgCl ($R = 5.0$ mm, $h = 10$ mm) were used as the counter and reference electrodes, respectively. The scan rate was 100 mV s^{-1} .



Scheme 7 Plausible mechanism.

1a is regenerated by auto-coupling of radical **C**. In the presence of a base, the reaction of compound **2a** and **3a** leads to the formation of intermediate **D**. Thereafter, the intramolecular cyclization reaction of intermediate **D** produces intermediate **E**. Finally, intermediate **E** is captured by the cationic species **C** to form the target product **4a**.

Conclusions

In summary, we have developed an environmentally friendly synthesis approach for selenyl imidazo[2,1-*b*]thiazinones using readily available diselenides, acryloyl chlorides, and 2-mercaptobenzimidazoles. This method does not require the addition of oxidants or transition metal catalysts. It has the advantages of good functional group tolerance, simple reaction conditions, and high step economy. Mechanistic studies indicate that the carbanion and selenium cation are significant intermediates in the reaction process.

Author contributions

C. Liu conceived and oversaw the project. Y. Yue and Z. Chen performed the experimental work. B. Wang performed the NMR studies. Y. Yue and Z. Chen jointly wrote the manuscript. F. Xue, S. Wu, Y. Xia, Z. Chen and Y. Zhang provided useful advice. All authors discussed the results and reviewed the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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