Recent Advances in Electrochemically Mediated Reactions of Diselenides

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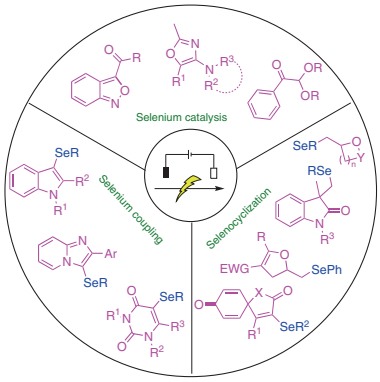

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Abstract Organoselenium compounds are crucial molecules that are utilized extensively in diverse fields such as medicine, agriculture, catalysis, and organic materials. The incorporation of selenium atoms into organic molecules holds significant importance in synthetic chemistry. Organic electrochemical synthesis, a green, mild, and efficient strategy, has displayed remarkable potential for organoselenium chemistry synthesis. Consequently, there has been substantial interest in recent years in researching electrochemically mediated synthesis of organoselenium compounds. This review provides an overview of the progress made in electrochemically mediated organic selenium reactions over the last decade, including electrochemical mediated selenium catalysis, electrochemical oxidation of diselenide coupling, and electrochemical oxidation tandem selenocyclization. The scope, limitations, and mechanisms of those reactions are emphasized.

Key words organic electrochemical synthesis, organoselenium compounds, selenium catalysis, diselenide coupling, tandem selenocyclization

1 Introduction

Organoselenium compounds are pivotal entities within organic synthesis, finding application as intermediates in materials, catalysis, and organic reactions.[1] In addition, organoselenium compounds have various pharmacological activities, such as anticonvulsant, antioxidant, antidepressant, anticancer, antitumor, anti-inflammatory, and antiviral properties, as depicted in Figure 1.[2] The introduction of a selenium atom into a potentially bioactive molecule can dramatically increase the native biological activity of the substrate. Given these distinctive biological and chemical attributes, organoselenium compounds have garnered significant research interest.

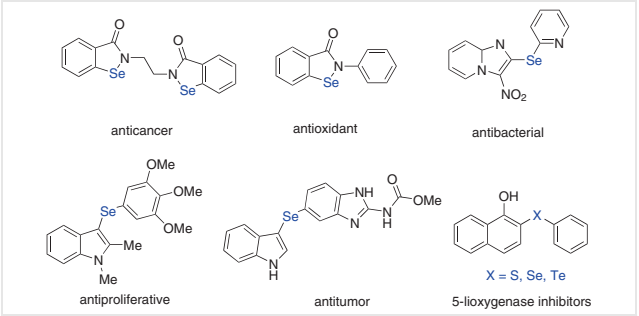


Figure 1 Examples of organoseleniums as pharmaceuticals and drugs

At present, the primary methods for the synthesis of organoselenium compounds involve metal catalysis/cyclization, photocatalysis, and oxidation with a strong oxidant.[3] However, these methods often present challenges such as metal residues, acid corrosion, high costs, and toxicity. Thus, a pressing need exists to develop greener, more efficient synthesis techniques for organic selenium compounds. Electromechanical synthesis utilizes clean electrical energy to drive redox reactions, circumventing the necessity for additional chemical oxidizers or reductants.[4] This technique affords precise control over current potential and demonstrates substantial application potential in synthetic chemistry due to its green, straightforward, and efficient nature. Consequently, electrochemical synthesis of

organic selenium compounds has emerged as an appealing strategy, and it has made noteworthy strides in recent times. Drawing from both domestic and international research groups' recent findings on organic selenium compound synthesis under electrochemical conditions, this article comprehensively summarizes and discusses three main facets: electrochemical mediated selenium catalysis, electrochemical oxidation of diselenide coupling, and electrochemical oxidation tandem selenocyclization. We hope that the review will help promote the future development of methods for constructing organic selenium compounds.

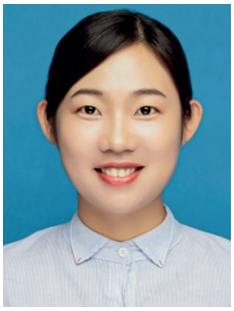
2 Electrochemical Selenium-Catalyzed Reactions

Selenium catalysis has emerged as a viable alternative to transition-metal catalysts due to its excellent functional group compatibility, mild reaction conditions, and remarkable selectivity.[5] Since the pioneering work of Sharpless in 1979 that demonstrated the organoselenium-catalyzed allylic chlorination of olefins with N-chlorosuccinimide, the field of organoselenium catalysis has undergone significant development, yielding diverse and reliable synthetic strategies.[6] Notably, the combination of selenides with oxidants, such as hypervalent iodine reagents and peroxides, has been widely employed to generate catalytically active selenium species.[7] However, the use of external oxidants in these methods often involves irritant reagents, increased costs, and limited substrate scope, prompting researchers to explore more cost-effective and environmentally friendly approaches to initiate selenium-catalyzed processes. Electrochemistry stands as a green synthesis tool, and the integration of electrochemical technology with selenium catalysis presents an avenue that not only eliminates the need for external oxidants but also opens up possibilities for innovative activation methods. As a result, this hybrid approach has garnered attention among synthetic chemists in recent years.

Heterocyclic compounds such as 2,1-benzoisoxazoles are widely used in the fields of surfactants and pharmaceutical intermediates, and methods that can be used for the mild and simple synthesis of such compounds have attracted much attention. In 2021, Pan's research group introduced an electrochemical selenium catalytic system for the intramolecular nucleophilic cyclization of *o*-nitrophenylacetylenes **1** to afford 2,1-benzoxazoles **2** (Scheme 1). Within an undivided cell setup, a platinum plate served as the anode, carbon as the cathode, CH_3CN as the solvent, and Et_4NPF_6 as the electrolyte. A range of benzoxazole compounds were synthesized through the intramolecular cyclization of *o*-nitrophenylacetylenes catalyzed by PhSeSePh. This methodology showcased commendable functional group tolerance and substrate applicability. The reaction employed cost-effective diphenyl diselenide as the catalyst, relying on constant pressure rather than external oxidants. Successful scaling up of the reaction to gram-level highlighted the potential practical utility of this approach.[8]

Biographical Sketches

Ying-Ming Pan is a professor in the Guangxi Normal University. He received his BSc degree from Gannan Normal University and his MSc degree from Guangxi University (China). He obtained his PhD degree at Xianmen University in 2010. He was awarded Mingde Teacher Award in 2018. His present research interests focus on electrochemical synthesis and heterogeneous catalysis.



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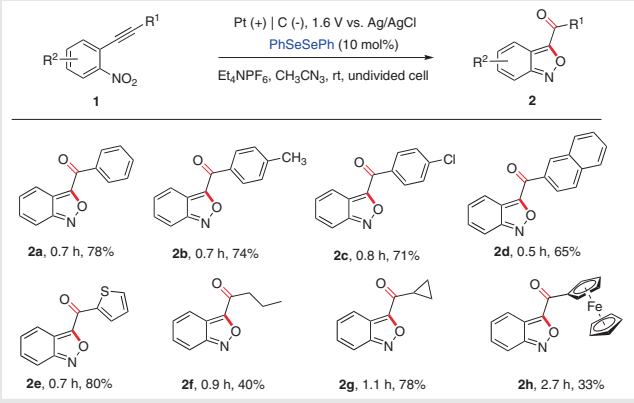
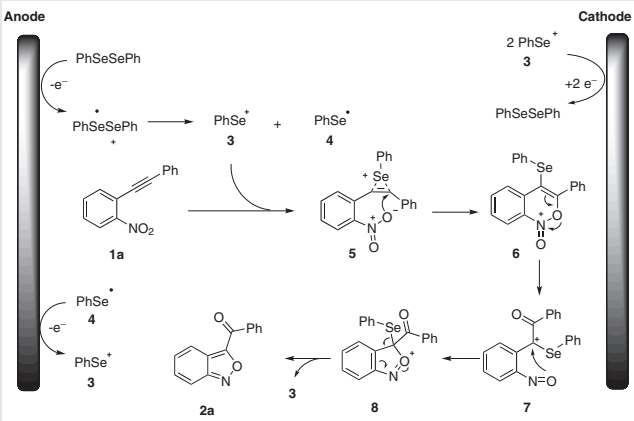


Scheme 1 Electrochemically enabled selenium catalytic synthesis of 2,1-benzoxazoles from *o*-nitrophenylacetylenes

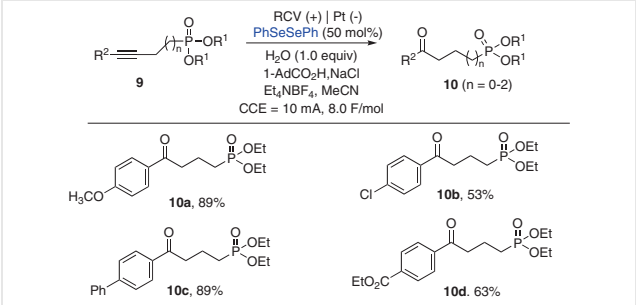
The research group probed the plausible reaction mechanism through control experiments and cyclic voltammetry, and proposed the mechanism depicted in Scheme 2. First, diphenyl diselenide is oxidized to yield selenium cation **3** and phenyl selenium radical **4**. Concurrently, phenyl selenium radical **4** donates electrons to the anode, generating selenium cation **3**. Subsequent interaction of substrate **1a** with selenium cation **3** furnishes intermediate **5**. The oxygen on the nitro group in intermediate **5** undergoes intramolecular nucleophilic cyclization, affording intermediate **6**. Cleavage of the N–O bond in intermediate **6** leads to intermediate **7**, and cyclization-induced release of selenium cations gives the final target product **2a**. At the cathode, the electrons from selenium cation **3** facilitate the reduction of diphenyl diselenide.



Scheme 2 Mechanism of electrochemical selenium-catalyzed synthesis of 2,1-benzoxazoles from *o*-nitrophenylacetylenes

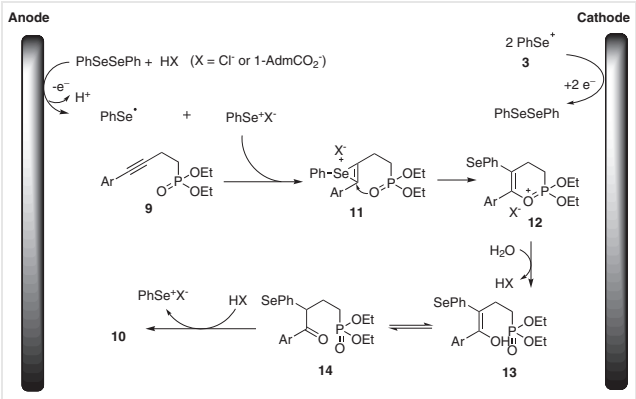
In the realm of selenium-π-acid catalysis, catalytically active selenium cation species can be generated through anodic oxidation. In 2022, Mei's group developed an efficient phosphonate-assisted hydration of internal alkynes **9** *via* electro-catalysis with a PhSeSePh mediator (Scheme 3).[9]

Employing room temperature conditions, utilizing RVC as the anode, platinum plate as the cathode, CH_3CN as the solvent, Et_4NBF_4 as the electrolyte, and a constant current of 10 mA, the reaction, catalyzed by 0.5 equivalent of PhSeSePh, proceeded between acetylenes and phosphonic acid groups to furnish a series of (heterogeneous) aryl and alkyl ketone compounds **10**. This protocol showcases remarkable chemo-/regioselectivity and scalability with internal alkynes harboring diverse functional groups, enabling facile access to a broad spectrum of (hetero) aryl and alkyl ketones with high efficiency.

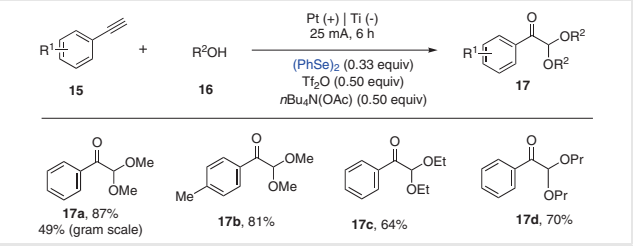


Scheme 3 Electrochemical selenium-π-acid promoted hydration of alkynyl phosphonates

The mechanism underlying this reaction unfolds as shown in Scheme 4: at the anode, the electrophilic phenyl selenium cation is generated via the electrodeless oxidation of diphenyl diselenide. Subsequent interaction between the phenyl selenium cation and alkyne phosphate **9** engenders the formation of selenium ion intermediate **11**. An intramolecular attack by the phosphonate group yields intermediate **12**, which then undergoes nucleophilic attack by H_2O to yield alcohol **13**. Tautomerization of alcohol **13** leads to compound **14**, which undergoes protonation, giving rise to the phenyl selenium cation and the desired product **10**.



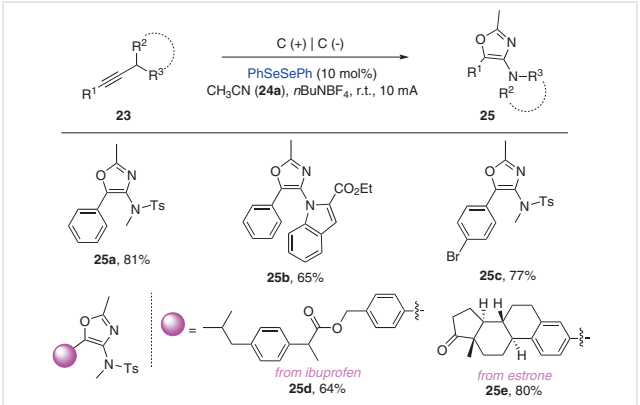
Scheme 4 Mechanism of electrochemical selenium-π-acid promoted hydration of alkynyl phosphonates



Scheme 5 Electrochemical selenium-catalyzed synthesis of α-keto acetals from terminal alkynes and alcohols

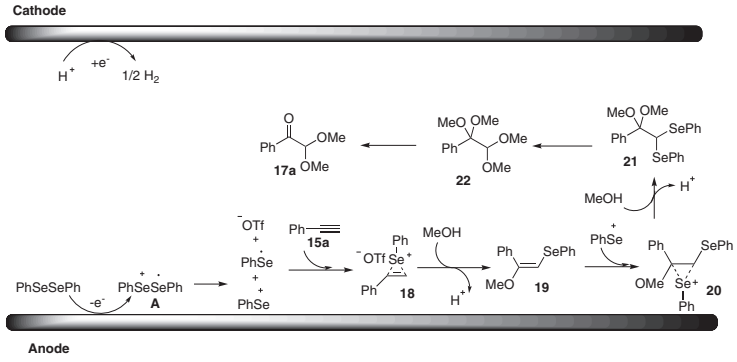
α-Keto acetals represent pivotal intermediates in organic synthesis. In 2022, Wei's research group introduced a novel strategy for synthesizing α-keto acetals **17** from terminal alkynes **15** and alcohols **16** (Scheme 5).[10] This approach synergistically combines electrochemical and organic selenium catalytic processes. Operating within an undivided cell setup, utilizing a platinum sheet as the anode, titanium as the cathode, methanol as the solvent, triflic anhydride (Tf_2O) as the additive, $nBu_4N(OAc)$ as the electrolyte, and 0.33 equivalent of PhSeSePh as the catalyst, terminal alkynes and alcohols engage in a reaction to furnish a series of α-keto acetal compounds. When ethanol and *n*-propanol were used instead of methanol, the corresponding α-ketone acetals were obtained with isolated yields of 64% (**17c**) and 70% (**17d**), respectively. When the electrochemical selenization of **15a** was carried out as a gram-scale synthesis (2 mmol), the product **17a** was obtained in 49% yield. A distinct feature of this system is the cooperative effect of organic selenium catalysis and electrochemical oxidation, obviating the need for external chemical oxidants.

On the basis of control experiments and previous reports, a plausible mechanism is proposed in Scheme 6. First, anodization of PhSeSePh takes place to produce selenium cation and selenium radical. The selenium cation then reacts with π-acid and terminal alkyne **15a**, leading to the formation of intermediate **18**. Subsequently, methanol **16a** undergoes nucleophilic attack on the activated alkyne **18**, yielding intermediate **19**. A subsequent sequence of activation and nucleophilic attack involving intermediate **19** results in the formation of **21**. This intermediate **21** is dissolved and hydrolyzed, ultimately yielding the target product **17a**. On the cathode, protons undergo electron reduction to form hydrogen.



Scheme 7 Electrochemical selenium-catalyzed N,O-difunctionalization of amides to synthesize polysubstituted oxazoles

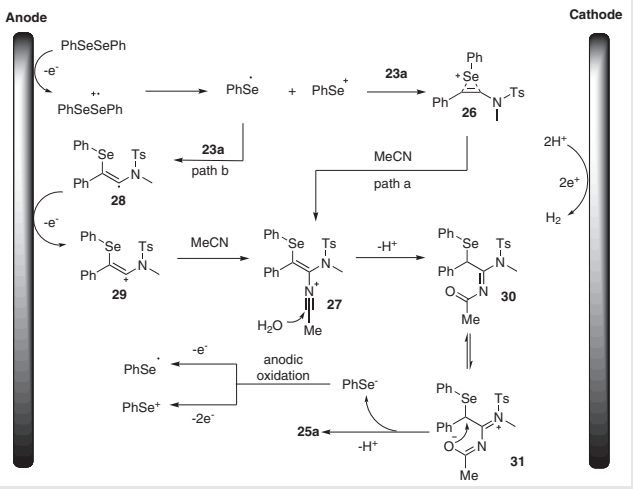
Heterocycles containing nitrogen and oxygen are vital structural motifs in pharmaceuticals and agricultural chemicals. In 2022, Ren's group reported a strategy that synergistically combines electrochemical and organic selenium catalytic processes to achieve the bifunctionalization of amides, resulting in the synthesis of multisubstituted oxazole compounds (Scheme 7).[11] The reaction between acrylamides **23** and nitriles **24** yields a series of benzoxazoles **25** using carbon rods as electrodes, CH_3CN as the solvent, nBu_4NBF_4 as the electrolyte, and PhSeSePh as the catalyst. This method demonstrates broad substrate applicability. When the substrate contains multiple substituents on the nitrogen atom, the reaction proceeds smoothly, leading to the formation of the corresponding polysubstituted oxazoles. Furthermore, compounds derived from ibuprofen and estrone also react effectively under these conditions to afford the desired products **25d** and **25e**. Overall, this strat-



Scheme 6 Mechanism of electrochemical selenium-catalyzed synthesis of α-keto acetals from terminal alkynes and alcohols

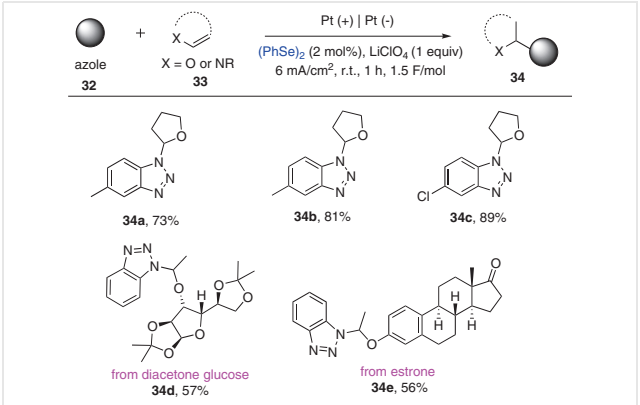
egy boasts mild reaction conditions, wide functional group tolerance, high atom-economy, and obviates the need for external chemical oxidants, presenting a sustainable alternative for the synthesis of polysubstituted oxazoles.

Two plausible mechanisms for this arylacetonitrile synthesis are proposed based on cyclic voltammetry and control experiments (Scheme 8). In path A: PhSeSePh generates selenium cations and selenium radicals upon anodic oxidation. Simultaneously, selenium radicals can also undergo electron loss on the anode, generating selenium cations. Subsequently, substrate **23a** reacts with selenium cation, leading to the formation of intermediate **26**. Intermediate **26** undergoes a nucleophilic reaction with acetonitrile to yield intermediate **27**. Deprotonation of intermediate **27**, *via* hydrolysis, yields intermediate **30**, which is isomerized into intermediate **31**. This is followed by C–Se bond cleavage, deprotonation, and, ultimately, the formation of product **25a**. The phenyl selenium anion generated undergoes anodic oxidation, regenerating the electrophilic phenyl selenium cation. On the cathode, selenium cations are reduced to PhSeSePh. In path B, selenium radicals add to **23a**, forming free radical intermediate **28**, which is subsequently oxidized to form cationic intermediate **29**. A Ritter-type reaction follows, yielding intermediate **27**, which undergoes analogous processes to afford cyclization product **25a**.



Scheme 8 Mechanism of electrochemical selenium-catalyzed N,O-difunctionalization of amides to synthesize polysubstituted oxazoles

Organic selenium-catalyzed olefin amination reactions are promising avenues for constructing functionalized amines. However, the use of chemical oxidants and the inevitable formation of allylamines are the main limitations of these methods. In 2022, Zeng's group reported an electro-selenocatalytic approach for the hydroazolylation of alkenes **33** with azoles **32** under external oxidant-free conditions (Scheme 9).[12] The protocol's merits include low catalyst loading, absence of external oxidants, high current efficiency and regioselectivity, and excellent functional group

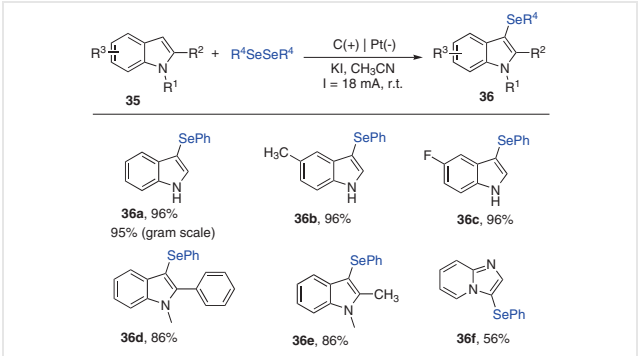


Scheme 9 Electrochemical selenium-catalyzed amination of alkenes

tolerance, as demonstrated by the azolation of olefins derived from natural products. Olefins derived from natural products can also be used to obtain the corresponding products (**34d** and **34e**) under these reaction conditions.

3 Electrochemically Mediated Coupling of Aromatic/Heterocyclic Rings with Diselenides

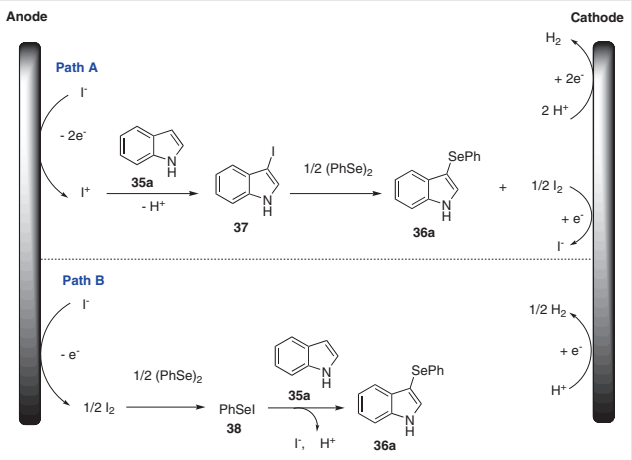
From the point of view of drug design, the combination of (hetero)arene and organoselenium groups has been successfully applied in various drug candidates. Therefore, the building of C–Se bonds on (hetero)arenes has become a research hotspot in the last decade. In 2018, Sun's group introduced an efficient electrochemical strategy for the direct C–H selenation of various indole derivatives and imidazo[1,2-*a*]pyridines (Scheme 10).[13] This reaction demonstrates impressive functional group tolerance. Notably, when the nitrogen atom on indole 35 is substituted with a methyl group or when the benzene ring contains substituents such as methyl, halogen, or ester groups, the reaction proceeds smoothly, yielding the corresponding products 36. Moreover, by extending the electrolysis time, gram-scale



Scheme 10 Electrochemical oxidative C–H bond selenization of indole compounds

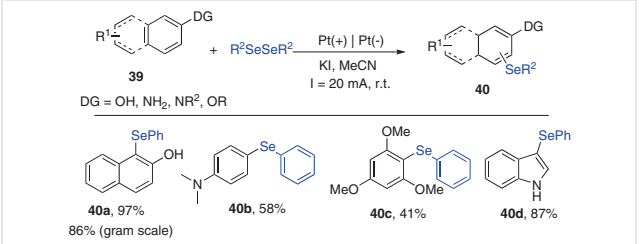
selenation approached the same efficiency as the reaction conducted on a 0.3 mmol scale, highlighting the significant potential of this method for large-scale synthesis.

The cyclic voltammograms of potassium iodide show double oxidation peaks at 0.07 and 0.46 V (vs. Ag/Ag^+), which are much lower than the oxidation potential of 1*H*-indole and diselenide diphenyl. Therefore, iodine anions are preferentially oxidized under constant current. Based on the results of cyclic voltammetry and control experiments, the research group proposed two reaction paths, as shown in Scheme 11. In path A, the iodide anion undergoes anodic oxidation to generate the iodide cation, which subsequently engages in electrophilic substitution with indole **35a**, leading to the formation of intermediate **37**. This intermediate then undergoes selenization *via* reaction with PhSeSePh in the solution, yielding the selenized product **36a**. On the cathode, elemental iodine and protons participate in a reduction reaction. In path B, the iodine anion undergoes anodic oxidation, producing iodine that, in turn, oxidizes PhSeSePh to generate iodinated selenide **38**. This species then engages in a substitution reaction with indole **35a**, resulting in the formation of the target compound **36a** (Scheme 11).



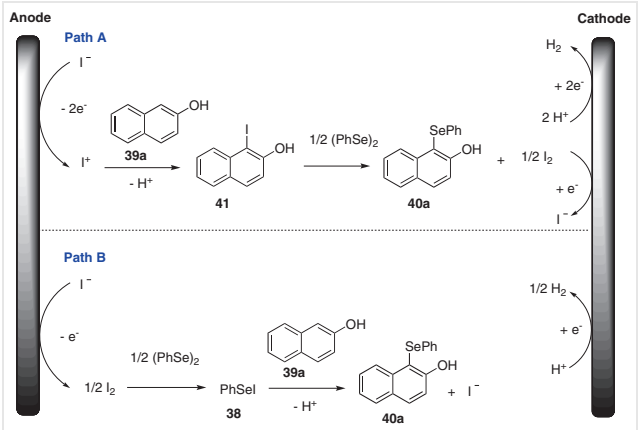
Scheme 11 Mechanism of electrochemical oxidative C–H bond selenization of indole compounds

Subsequently in 2019, Mendes' group reported an electrochemical oxidative C(sp^2)–H selenylation of activated arenes **39**, leading to the synthesis of selenylated arenes **40** (Scheme 12).[14] This strategy yielded the desired products in good to excellent yields using Pt as electrode, KI as electrolyte, and CH_3CN as a solvent. Throughout the reaction process, the aromatic substrate's benzene ring can be substituted with oxygen- or nitrogen-containing groups. The electrochemical selenization of 2-naphthol was carried out on a gram-scale (5 mmol) and, after 8.5 hours, product **40a** was obtained in 86% yield. This indicates that the reaction has the potential for industrial application. This method exhibits notable regioselectivity, mild reaction conditions, favorable yields, wide applicability, and the potential to synthesize biologically active aromatic selenium compounds.



Scheme 12 Electrochemical oxidative C (sp^2)–H bond selenylation of activated arenes

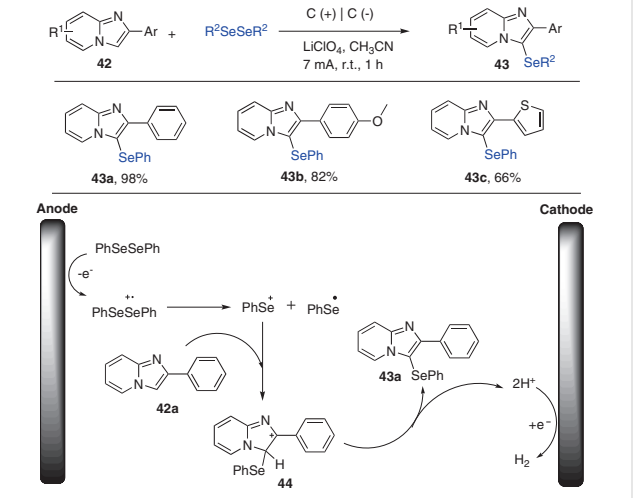
Based on control experiments, two plausible mechanisms for the electrochemical selenylation of 2-naphthol with diphenyl diselenide are proposed (Scheme 13). In pathway A, iodine cations generated through anodic oxidation of iodine anions undergo electrophilic substitution with the 2-naphthol compound **39a**, yielding intermediate **41**. This intermediate then rapidly reacts with PhSeSePh, resulting in the formation of product **40a**, concurrently with cathode iodine reduction and hydrogen liberation. In pathway B, iodine anions react with PhSeSePh, generating intermediate **38**, which then undergoes substitution with 2-naphthol **39a**, yielding product **40a**.



Scheme 13 Mechanism of electrochemical oxidative C (sp^2)–H bond selenylation of activated arenes

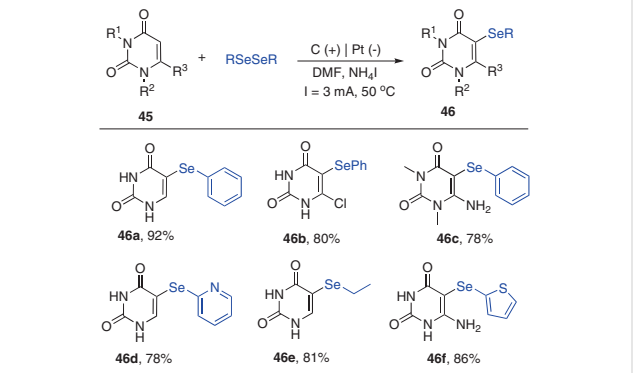
Imidazo[1,2-*a*]pyridines serve as privileged scaffolds with crucial applications as drug candidates. In 2019, Kim's group developed an efficient strategy for synthesizing 3-selenylated imidazopyridine derivatives through electrochemically oxidative selenylation of imidazo[1,2-*a*]pyridine derivatives **42** using diselenides (Scheme 14).[15] The reaction took place in an undivided cell with carbon as electrodes, CH_3CN as the solvent, and $LiClO_4$ as the electrolyte. This method employs stable diselenides as selenium sources and utilizes electrons as oxidizing agents, providing a

straightforward route for synthesizing 3-selenide imidazopyridine derivatives **43**. A reaction mechanism was proposed based on control experiments and cyclic voltammetry. Initially, diphenyl diselenide undergoes oxidation, generating the phenylselenium cation. This cation then reacts with imidazo[1,2-*a*]pyridine **42a**, forming intermediate **44**, which subsequently undergoes deprotonation to yield product **43a**.



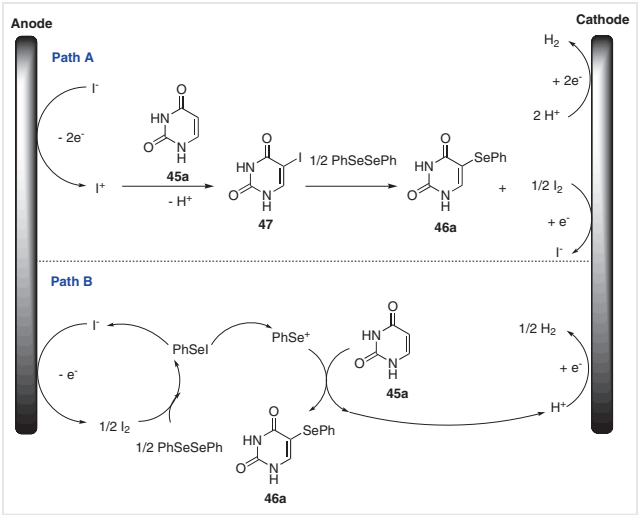
Scheme 14 Electrochemical oxidative selenylation of imidazo[1,2–*a*]pyridines with diselenides

C-5 selenium-substituted uracil is prevalent in drug molecules and active compounds. Consequently, 5-selenouracil compounds have garnered the attention of chemists. In 2020, Xu's group reported an efficient electrochemical selenylation of uracil derivatives **45** for the synthesis of 5-selenouracil derivatives **46** (Scheme 15).[16] The reaction demonstrated good substrate applicability and functional group tolerance. Compounds with substituents on the phenyl ring of selenide, such as electron-donating groups like methyl or methoxy, or electron-accepting groups like halogens, yielded the target compounds in good yield. Moreover, alkyl selenides and heterocyclic selenides were compatible with this reaction.



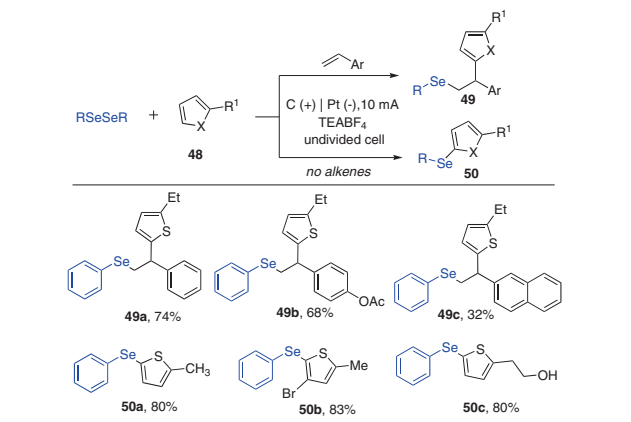
Scheme 15 Electrochemical synthesis of 5-selenouracil derivatives by selenylation of uracils

The research group proposed two potential reaction mechanisms based on control experiments (Scheme 16). In pathway A, anodic oxidation of I^- generates I^+, which undergoes electrophilic substitution with uracil **45a** and loses protons, resulting in the formation of 5-iodine uracil **47**. Subsequently, **47** undergoes selenidation reaction with PhSeSePh to yield the target product **46a**. In pathway B, anodic oxidation of I^- generates I_2, and then elemental iodine oxidizes PhSeSePh to produce iodized selenide. This iodized selenide undergoes hetero-splitting and reacts with uracil **45a**, leading to the desired product **46a**.



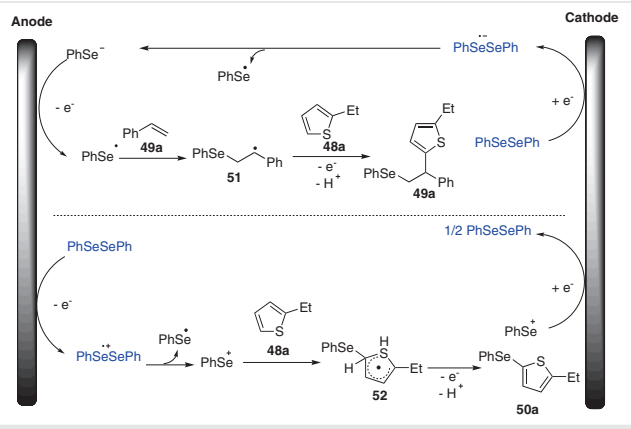
Scheme 16 Mechanism of electrochemical synthesis of 5-selenouracil derivatives by selenylation of uracils

Lei and colleagues have achieved significant advancements in the realm of electrochemical-mediated C–Se bond construction. In 2021, they reported a novel electrochemical radical selenylation of olefins **48** and activated aromatics **45** without the use of external oxidants (Scheme 17).[17] This approach yielded an array of aryl–aryl, aryl–alkyl, and alkyl–alkyl selenoethers (**49** and **50**) when using a platinum sheet as the cathode, carbon as the anode, tetraethylammonium tetrafluoroborate ($TEABF_4$) as the electrolyte, $Y(CF_3CO_2)_3$, HOAc, and dichloromethane (DCM)/1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as cosolvents in an undivided cell. This method also demonstrated efficiency when applied to gram-scale reactions. Notably, direct radical coupling of selenium radical and activated arenes was achieved in the absence of alkene. However, the yields of reactions involving thiophenes substituted at different positions displayed significant variation, likely attributed to their distinct electrical oxidation potentials.



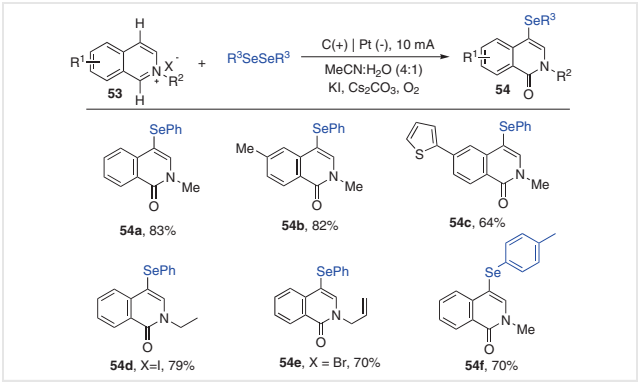
Scheme 17 Electrochemical radical selenylation of alkenes and arenes

Based on control experiments and radical quenching experiments, a possible reaction mechanism was proposed (Scheme 18). At the cathode, PhSeSePh undergoes reduction to form selenium radical and selenium anion. The selenium radical then reacts with styrene, generating intermediate **51** with good regioselectivity. Subsequently, intermediate **51** is oxidized to a carbocation, which combines with thiophene **48a**, leading to deprotonation and the formation of product **49a**. Additionally, the interaction of selenium radical with **48a** produces radical **52**, which subsequently loses an electron and a proton, resulting in the formation of unsymmetrical organoselenide **50a**.



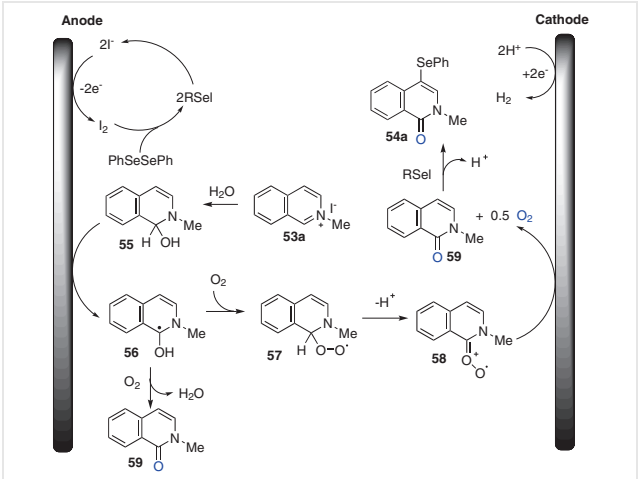
Scheme 18 Mechanism of electrochemical radical selenylation of alkenes and arenes

Cao and co-workers achieved significant advancements in the electrochemically mediated regioselective C(sp^2)–H bond selenidation of *N*-alkylisoquinolinium salts. In 2021, they reported a novel electrochemical regioselective 1,4-difunctionalization of isoquinolinium salts **53** using diselenides (Scheme 19).[18] The reaction was conducted with a constant current of 10 mA, using a platinum plate as the cathode, carbon rod as the anode, CH_3CN/H_2O as the mixed solvent, KI as the electrolyte, and Cs_2CO_3 as the base. This protocol provided access to various selenide isoquinolones **54** under undivided electrolytic conditions. Furthermore, the electrocatalytic system was successfully extended to synthesize selenide quinolones and 1,3-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-ones. Notably, antiviral bioassays indicated that compound **54c** exhibited excellent antiviral activity against tobacco mosaic virus (TMV), with an inhibition rate of up to 90%.



Scheme 19 Electrochemical regioselective selenylation/oxidation of *N*-alkylisoquinolinium salts

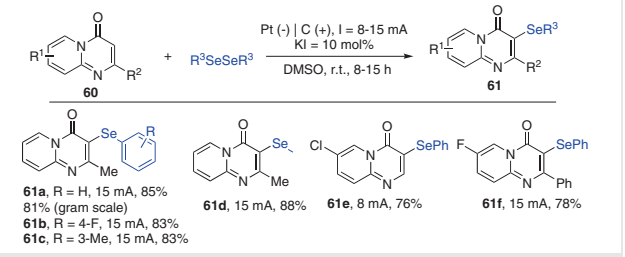
A plausible reaction mechanism for the electrochemical 1,4-difunctionalization of isoquinolinium salts has been proposed (Scheme 20). At the anode, H_2O undergoes nucleophilic addition with **53a** to form intermediate **55**, which is subsequently oxidized to intermediate **56**. The transformation of intermediate **56** into compound **59** could follow two pathways. In pathway A, oxygen reacts with intermediate **56** to generate peroxide **57**, which loses a proton to form oxygen-centered radical **58**. The intermediate **59** is then obtained by cleaving the O–O bond in **58** at the cathode. In pathway B, intermediate **56** is directly oxidized to produce



Scheme 20 Mechanism of electrochemical regioselective selenylation/oxidation of *N*-alkylisoquinolinium salts

intermediate **59**. Simultaneously, direct anodic oxidation of I^- generates I_2, which reacts with diselenide to form RSeI. Finally, RSeI is captured by **59**, yielding product **54a**.

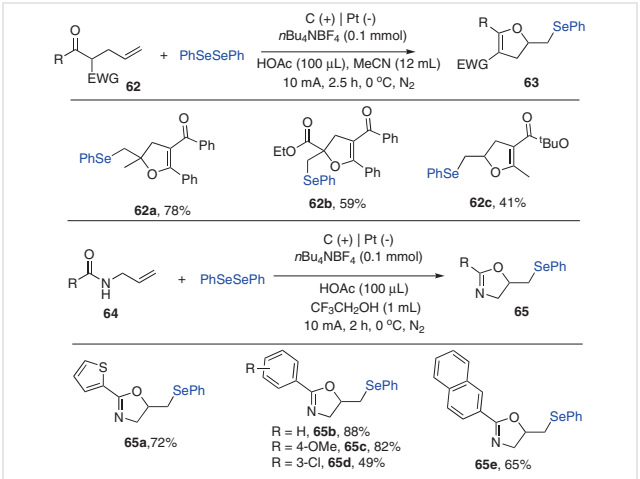
4*H*-Pyrido[1,2-*a*]pyrimidin-4-one is a fundamental scaffold in the realm of natural products and biologically relevant compounds. Given its valuable biological activity, it is an attractive target within organic chemistry. In 2023, Ouyang's group developed an efficient protocol for synthesizing C3-selenylated 4*H*-pyrido[1,2-*a*]pyrimidin-4-ones **61** *via* the iodide-catalyzed electrochemical selenation of 4*H*-pyrido[1,2-*a*]pyrimidin-4-ones **60** with diaryl (alkyl) diselenides (Scheme 21).[19] This approach has a wide range of substrate applicability and functional group tolerance. Employing a carbon rod as the anode, a platinum plate as the cathode, DMSO as the solvent, and KI as the electrolyte, the reaction of 4*H*-pyridyl[1,2-*a*]pyrimidin-4-ones **60** with diselenides gave the corresponding products **61** in yields ranging from good to excellent. This electrochemical selenization reaction can also be carried out on a larger scale. When 5 mmol of 2-methyl-4*H*-pyrido[1,2-*a*]pyrimidin-4-one **60a** reacted with diphenyldiselenide (2.5 mmol) in DMSO (16 mL) under optimal conditions by increasing the constant current to 30 mA, the target product **61a** was obtained in a yield of 81%. Due to the mild reaction conditions and excellent yields, this work provides a convenient method for the synthesis of selenylated 4*H*-pyrido[1,2-*a*]pyrimidin-4-one derivatives.



Scheme 21 Electrochemical oxidative selenation of 4*H*-pyrido[1,2-*a*]pyrimidin-4-ones with diorganyldiselenides

4 Electrochemically Mediated Tandem Selenocyclization

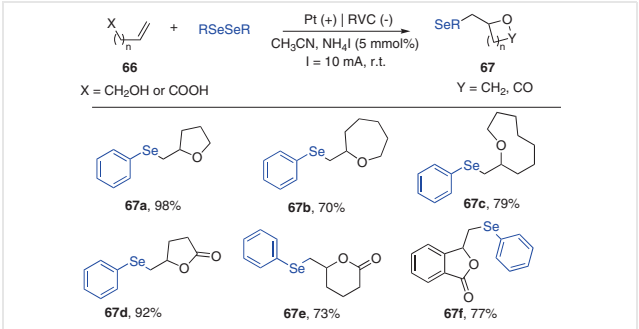
Dihydrofurans serve as significant structural frameworks in a wide array of natural products, as well as key motifs in organic synthesis. In 2019, Lei and colleagues demonstrated an electrochemical oxidative cyclization of olefinic carbonyls with diselenides, leading to seleno dihydrofurans and seleno oxazolines (Scheme 22).[20] Employing nBu$_4$NBF$_4$ as the supporting electrolyte, HOAc as an additive, and acetonitrile as the solvent, a series of seleno dihydrofurans **63** could be isolated in moderate to excellent yields using a graphite rod anode and a platinum sheet cathode. This method exhibits good functional group tolerance, facilitating the smooth reaction of symmetric olefinic carbonyls bearing electron-withdrawing or electron-donating groups on the *para*/*meta* position of the phenyl ring with diphenyl diselenide to afford the corresponding dihydrofuran compounds. Furthermore, the use of slightly modified conditions allowed the successful production of a range of oxazolines. *N*-Allylamides **64**, with electron-rich aryl groups (Ph, 4-OMePh, 2-MePh, Naph), could be used to readily construct C–Se and C–O bonds with 1,2-diphenyldiselane, yielding seleno oxazolines **65** in moderate to excellent yields.



Scheme 22 Electrochemical oxidative cyclization of unsaturated amides with diselenides

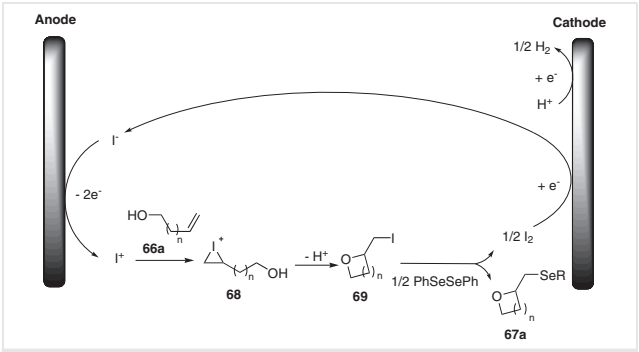
Inspired by this work, in 2020, Pan's group introduced a metal- and oxidant-free electrolysis method for synthesizing selenomethyl-substituted cyclic ethers and lactones. This method utilized a catalytic amount of ammonium iodide at room temperature from selenides and unsaturated alcohols or acids **66**, respectively (Scheme 23).[21] Electrolysis took place in an undivided cell equipped with a reticulated vitreous carbon (RVC) cathode and a platinum anode, resulting in a series of selenomethyl-substituted cyclic ethers **67** with constant current of 10 mA and 5 mol% NH_4I used as the electrolyte and electrocatalyst. This technique exhibited excellent chemical selectivity and functional group compatibility, providing various cyclic ether or lactone compounds with moderate to excellent yields. Manipulating the chain length of enol compounds or the substituents of selenide compounds allowed for the production of the corresponding cyclic ether compounds with favorable yields. Additionally, replacing enol with enoic acid enabled successful and smooth formation of cyclic lactone compounds.

The addition of TEMPO or BHT to the system resulted in the production of the target product **67a** with isolated yields of 75 and 74%, respectively. These outcomes might exclude the possibility of a radical mechanism. The authors proposed a mechanism depicted in Scheme 24. Initially, iodine negative ions undergo anodic oxidation to generate io-



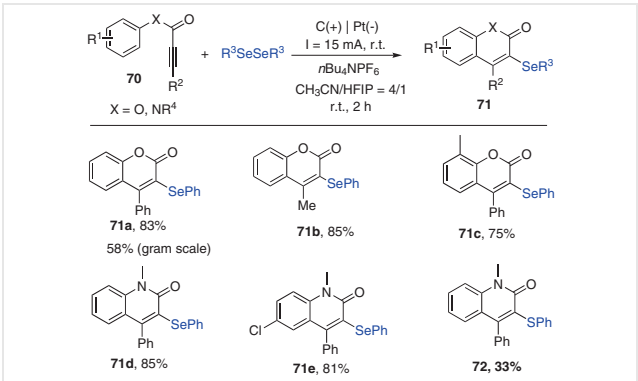
Scheme 23 Electrochemical oxidative cyclization of olefins with diselenides

dine positive ions. Subsequently, iodine positive ions react with terminal alkene **66a** to form intermediate **68**, which then undergoes intramolecular cyclization to form intermediate **69**. Intermediate **69** rapidly undergoes selenization with PhSeSePh to produce product **67a**, with a reduction reaction occurring at the cathode to release hydrogen, thus completing the electrochemical cycle process.



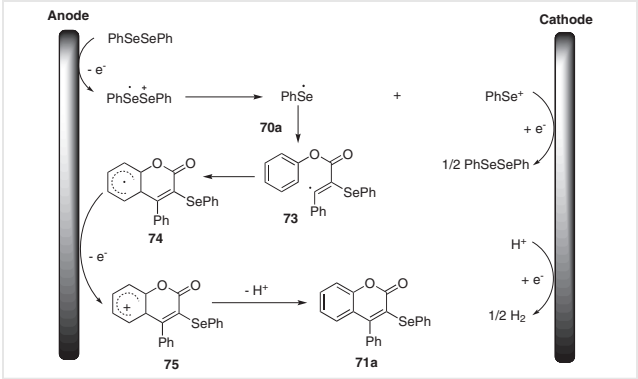
Scheme 24 Mechanism of electrochemical oxidative cyclization of olefins with diselenides

Activated alkynes, such as alkyne salts or alkyne amides, offer a means to synthesize substituted heterocyclic compounds. Coumarin or quinolinone, characterized by unique structural frameworks, are widely present in natural products and drug molecules, and they exhibit various biological activities including anticancer, anti-inflammatory, and antidepressant properties.[22] In 2019, Guo and colleagues developed an electrochemical oxidative cyclization of alkynoates and alkynamides **70** with diselenides or disulfides for the synthesis of coumarins and quinolinones (**71** and **72**) (Scheme 25).[23] This approach utilized graphite as an anode, platinum as a cathode, nBu$_4$NBF$_4$ as an electrolyte, and CH$_3$CN/HFIP (v/v 4:1) as a solvent. The strategy displayed a broad scope and compatibility with functional groups, and resulted in a series of chalcogen-substituted coumarins and quinolinones with moderate to good yields. The electrochemical reaction was completely inhibited by the addition of 3 equivalents of the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), confirming that the process proceeds through a radical pathway. Furthermore, this reaction demonstrated industrial feasibility, yielding gram-scale reaction product **71a** with a yield of 58%.



Scheme 25 Electrochemical oxidative cyclization of alkynoates and alkynamides with diselenides or disulfides for the synthesis of coumarins and quinolinones

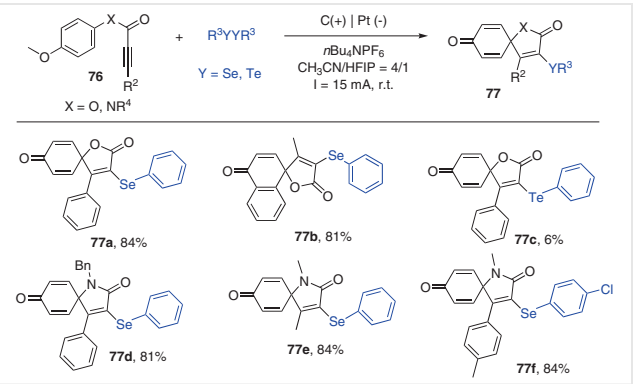
Regarding the mechanism, control experiments and radical quenching experiments confirmed that this process proceeds via a radical pathway. The authors proposed a plausible reaction mechanism as shown in Scheme 26. Initially, diphenyl diselenide generates phenylselenium radical and phenyl selenium cation through anodic oxidation. The addition of phenylselenium radical to the C–C triple bond of **70a** generates vinyl radical **73**, which subsequently undergoes intramolecular cyclization, anodic oxidation, and proton loss to form compound **71a**. At the cathode, the phenylselenium cation is reduced to generate diphenyldiselenide.



Scheme 26 Mechanism of electrochemical oxidative cyclization of alkynoates with diselenides for the synthesis of coumarins

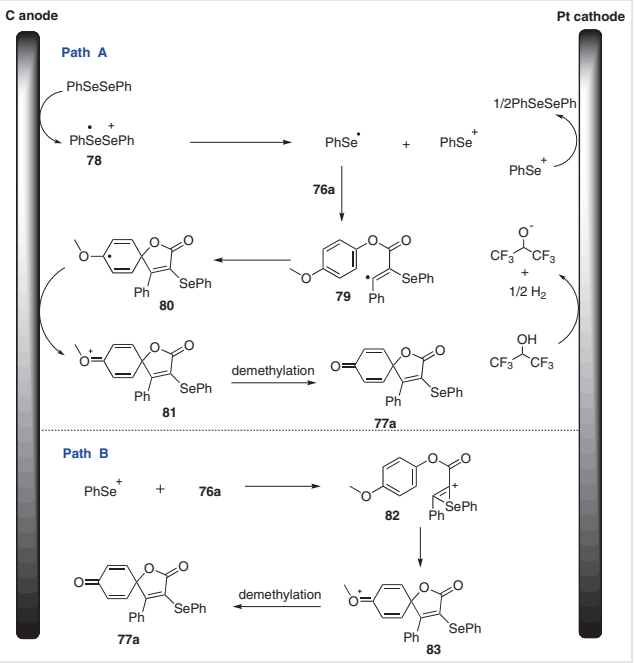
Building on this protocol, Guo's group further developed an electrochemical oxidative radical dearomative spirocyclization for the synthesis of selenation spiro[4.5]trienones **77** from alkynes **76** with diselenides (Scheme 27).[24] Utilizing a graphite carbon anode, platinum plate cathode,

CH_3CN/HFIP (v/v 3:1) mixed solvent, and nBu_4NPF_6 electrolyte, alkynoates reacted with diselenide to yield a series of spirocyclization products. This reaction circumvents the need for metals and oxidants, displaying broad substrate adaptability. Furthermore, diphenyl ditelluride could be employed to yield tellurium-substituted products.



Scheme 27 Electrochemical synthesis of spiro[4.5]trienones through radical-initiated dearomative spirocyclization

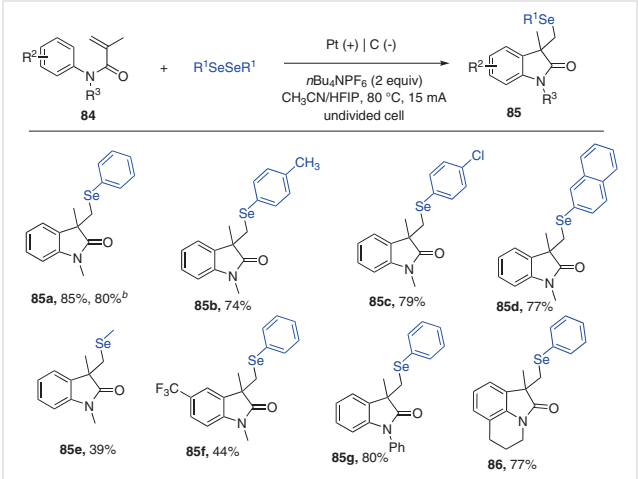
Mechanistic studies, cyclic voltammetry experiments, and literature analysis led to the authors to propose two potential reaction pathways (Scheme 28). In path A, diphenyl diselenide undergoes anodization to form intermediate **78**, which dissociates into phenylselenium radical and phenyl selenium cation. The phenylselenium radical then adds



Scheme 28 Mechanism of electrochemical synthesis of spiro[4.5]trienones through radical-initiated dearomative spirocyclization

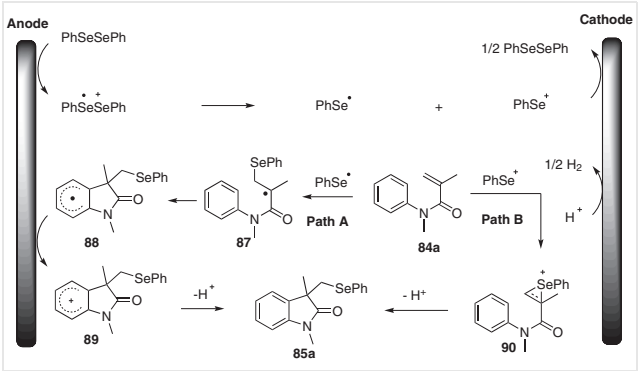
to alkyne **76a** to form vinyl radicals **79**, which subsequently undergo intramolecular spirocyclization to furnish intermediate **80**. This is followed by electron loss and dehydrogenation to yield intermediate **81**, which undergoes dearomatization to yield product **77a**. In path B, phenyl selenium cation reacts with **76a** to generate intermediate **82**. This intermediate rapidly converts into intermediate **83**, which undergoes demethylation to produce product **77a**. Simultaneously, electron reduction of benzene selenium-based cations occurs.

In 2021, Pan's group reported an electrochemical oxidative cyclization of *N*-arylacrylamides **84** with diorganyl diselenides to synthesize seleno oxindoles **85** (Scheme 29).[25] A series of seleno oxindoles were obtained in moderate to excellent yields under a constant current (15 mA) for 2 hours, using nBu_4NPF_6 and CH_3CN/HFIP in an 8:2 ratio as a cosolvent. This method exhibited good functional group tolerance; both electron-donating and electron-withdrawing groups on the *para*-position of the two different aromatic rings of *N*-arylacrylamide worked well with diselenides, yielding the corresponding selenium-containing oxindole products in significant yields. The antitumor activities of all compounds were assessed using the MTT method. The results revealed that the seleno oxindole products exhibited superior antitumor activity compared to other oxindole skeletons.

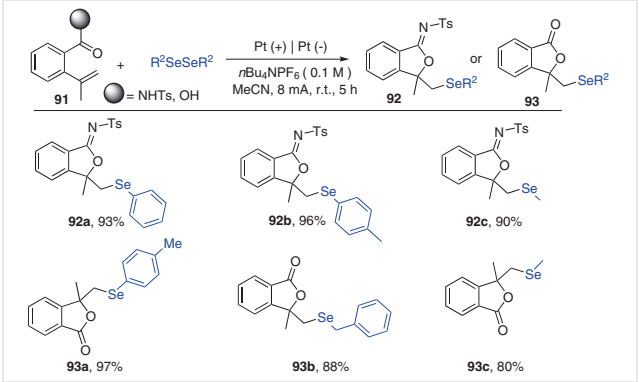


Scheme 29 Electrochemical oxidative cyclization of *N*-arylacrylamides with diorganyl diselenides

Control experiments indicated that the reaction primarily proceeded through a radical mechanism, with a possible selenium cation pathway. Therefore, the research group proposed potential reaction mechanisms as shown in Scheme 30. In path A, diphenyl diselenide forms seleno radical and selenium cation through anodic oxidation. Subsequently, the seleno radical adds to **84a** to form radical intermediate **87**, followed by intramolecular cyclization of intermediate **87** to yield radical intermediate **88**. Further anodic



Scheme 30 Mechanism of electrochemical oxidative cyclization of *N*-arylacrylamides with diorganyl diselenides



Scheme 31 Electrochemical selenylation/cyclization of alkenes for the synthesis of selenide benzheterocycles

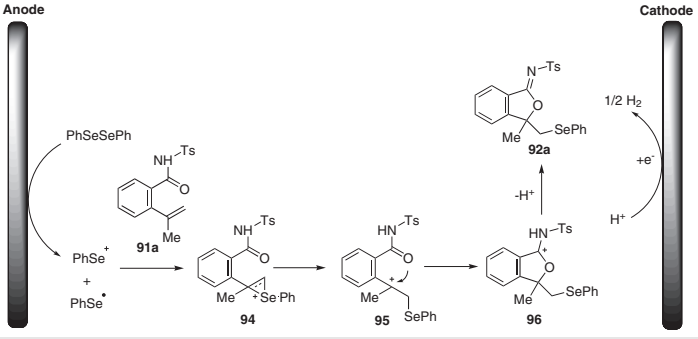
oxidation and deprotonation results in the formation of product **85a**. In path B, the selenium cation adds to the double bond of **84a**, producing intermediate **90**. Intermediate **90** undergoes further oxidative cyclization and deprotonation, leading to the formation of product **85a**.

In the same year, the Ruan research group also reported similar work.[26] They developed an electrochemical selenylation/cyclization of alkenes for the synthesis of functionalized benzheterocycles (Scheme 31). *N*-Arylacrylamides or 2-isopropenylbenzoic acids **91** reacted with diphenyl diselenide to yield a series of selenide benzheterocycles **92** or **93**. This selenylation transformation proceeded smoothly and tolerated a wide range of synthetically useful groups, yielding diverse functionalized benzheterocycles, including iminoisobenzofuran, lactones, oxindoles, and quinolinones. Moreover, the synthetic route could be easily scaled up to gram quantities with convenient operation in an undivided cell.

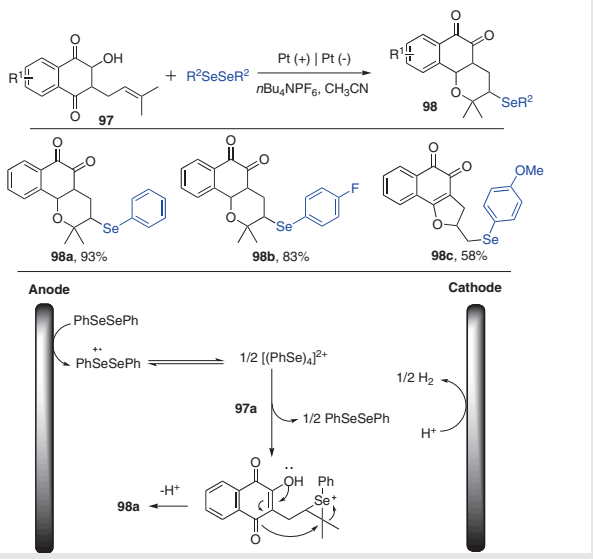
A mechanism of electrochemical selenylation/cyclization of *N*-arylacrylamides was proposed, as shown in Scheme 32. Initially, diphenyl diselenide is oxidized to phenylselenium cation and phenylselenium radical at the anode. Then, the addition of phenylselenium cation to the double bond of **91a** generates intermediate **94**. Intramolecular nucleophilic attack by the ketone forms intermediate **96**, which undergoes deprotonation to yield the desired product **92a**.

In 2020, Silva Júnior and co-workers reported an efficient electrochemical method for synthesizing a wide range of selenium-containing multifunctional redox quinoidal compounds **98** *via* an anodic oxidative selenation/cyclization reaction (Scheme 33).[27] Diphenyl diselenides react with dienoquinones to generate a series of selenium-containing naphthoquinones in an undivided cell, with a platinum plate electrode, CH_3CN as a solvent, and nBu$_4$NPF$_6$ as an electrolyte. Some of the quinone-hybrid molecules exhibit considerable biological activity. For instance, compound **98b** is active against *T. cruzi* with an IC_{50} of 38.3 μM, and against HCT-116 and B16F10 cancer cells with IC_{50} values of 0.95 and 0.98 μM, respectively. Cyclic voltammetry experiments suggest that selenium ions undergo rapid carbophilic reactions with lapanol, forming a cationic intermediate that further undergoes rapid nucleophilic cyclization to produce product **98a**.

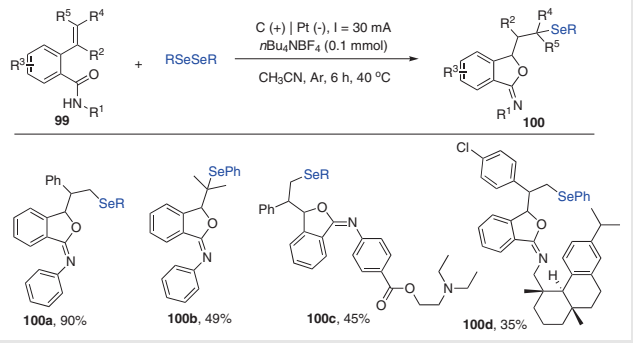
In 2022, Lei's group introduced an electrochemical oxidative radical cascade cyclization of olefinic amides and diselenides without transition-metal catalysts or external oxidants (Scheme 34).[28] A series of iminoisobenzofurans **100** were obtained using nBu$_4$NBF$_4$ as the electrolyte and



Scheme 32 Mechanism of electrochemical selenylation/cyclization of alkenes for synthesis of selenide benzheterocycles



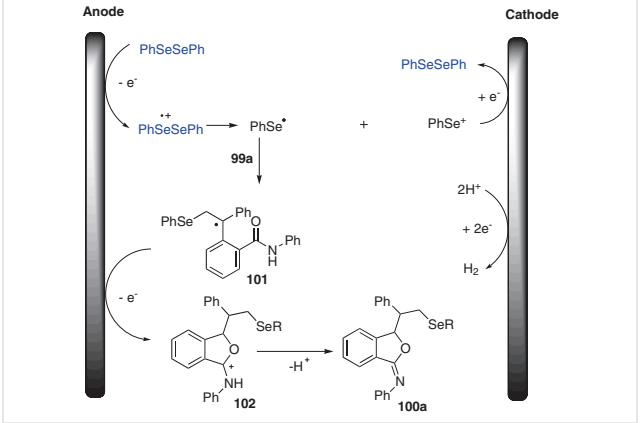
Scheme 33 Electrochemical selenation/cyclization of quinones



Scheme 34 Electrochemical oxidative selenocyclization of olefinic amides towards the synthesis of iminoisobenzofurans

MeCN as the solvent, under a constant current of 30 mA at 40 °C for 6 hours in an undivided cell. This strategy exhibited good substrate applicability and functional group tolerance; various olefinic amides and diselenides were compatible, yielding the desired products—more than 40 examples—in yields of up to 94%.

The authors proposed the following plausible mechanism (Scheme 35). First, diphenyl selenide is oxidized at the anode to form a radical cation intermediate, which further divides into phenylselenium radical and phenylselenium cation. The phenylselenium cation is reduced to diphenyl selenide at the cathode for the next cycle. Thereafter, the phenylselenium radical adds to the double bond of olefin **99a** to generate the alkyl radical **101**. Radical **101** undergoes a radical cyclization and subsequent oxidation to the corresponding carbocation **102**. Finally, carbocation **102** gives the desired products **100a** through deprotonation. At the cathode, proton reduction generates hydrogen gas during the reaction.



Scheme 35 Mechanism of electrochemical oxidative selenocyclization of olefinic amides towards the synthesis of iminoisobenzofurans

5 Conclusion

Through this review, we have summarized recent advances in electrochemical-mediated selenium catalysis, coupling of diselenides with unsaturated hydrocarbons, and tandem cyclization of diselenides with olefins or alkynes. Under electrochemical conditions, various important selenium-containing compounds can be effectively obtained with high regioselectivity and high atomic economy. Additionally, the mechanism characteristics of these transformations were discussed. The numerous successful examples introduced in this review demonstrate the enormous potential of electrochemical methods in drug discovery; certain organoselenium compounds exhibit good inhibitory activity on cancer cells. It can be clearly seen from the literature that rapid progress has been made in electrochemical synthesis of organoselenium compounds. Given their importance in organic and pharmaceutical chemistry, there are still many areas that need to be explored. For instance, electrochemical-mediated selenium-catalyzed reactions are still very limited, and more effective electrochemical selenium-catalyzed reactions should be developed in the future. In addition, many of the tandem selenium-cyclization reactions discussed in this article are based on two different reaction components, and reactions involving three or more components still need to be developed. Furthermore, asymmetric control remains a key challenge. We trust that this review will contribute to the further advancement of the emerging research field of selenocyclization reactions.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

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