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Recent progress in electrochemical rearrangement reactions

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Rearrangement reactions are among the most critical transformations in synthetic chemistry, enabling the construction of complex molecules from simple starting materials through the cleavage and reformation of chemical bonds. Synthetic electrochemistry, as a sustainable synthesis method, eliminates the need for stoichiometric redox reagents, significantly advancing green chemistry. Over the past decade, numerous electrochemically promoted rearrangement reactions have been developed, demonstrating the broad applicability of electrochemistry in facilitating rearrangement processes. This review highlights the application of electrochemistry in rearrangements, focusing on functional group migrations, ring expansion reactions, and selective migratory cyclization reactions.

1. Introduction

A reaction in which the molecular skeleton undergoes cleavage and reorganization through chemical bonds to generate structural isomers is typically known as a rearrangement. This process normally involves the migration of functional groups within the molecule to form isomers of the original compound or the release of simple molecules (such as H_2O or SO_2) to produce other compounds. Rearrangement reactions enable the synthesis of complex target compounds from simple starting materials by adjusting the position of atoms or groups within or between molecules.[1] Therefore, these reactions can effectively build carbon skeletons that are difficult to synthesize by traditional methods, greatly aiding the synthesis of natural products and drugs. Traditional rearrangement reactions are typically categorized as ionic nucleophilic rearrangements and electrophilic rearrangements.[2] These reactions have been extensively developed, and many named reactions fall into this category,[3] such as Hofmann,[4] Smiles–Truce,[5] and Beckmann.[6] Although this type of rearrangement has been well developed, the process involves the use of stoichiometric oxidants and toxic, harmful reagents, which limits practical application development.

In recent years, due to the promotion of the green chemistry concept, the electrochemical synthesis technology has experienced a revival.[7] Electrochemical organic synthesis is considered a green and efficient method for carrying out oxidative or reductive reactions through electron transfer, eliminating the need for stoichiometric oxidants and reductants.[8] Compared to traditional organic synthesis, electrochemical organic synthesis offers advantages of mild conditions, shorter reaction times, and simpler operation. Furthermore, most reactions do not require special conditions such as high temperature or pressure, making them more beneficial for industrial applications. Recently, there has been significant progress in electrochemical-mediated cyclizations,[9] C–H functionalization reactions,[10] and difunctionalization of alkenes and alkynes,[11] among others.[12] With the rapid growth of electrochemical chemistry, electrochemical-mediated rearrangement reactions have emerged as an important research area in organic chemistry, garnering widespread attention from the chemical community.[13] Thus, in this review, we summarize the latest progress in the field of electrochemical rearrangements over the past decade, focusing on functional group migrations, ring expansions and migratory cyclization reactions, to provide new perspectives and references for researchers in this field (Scheme 1).

2. Electrochemical functional group migrations

Functional group migration is one of the most effective synthetic strategies for rapidly constructing high-value-added compounds from simple molecules. Among these reactions, the selective migration of groups remains one of the most challenging issues. Traditionally, such transformations often rely on stoichiometric oxidants or expensive photocatalysts, which has limited their further development. With the rapid advancement of electrochemical technologies, several sustain-

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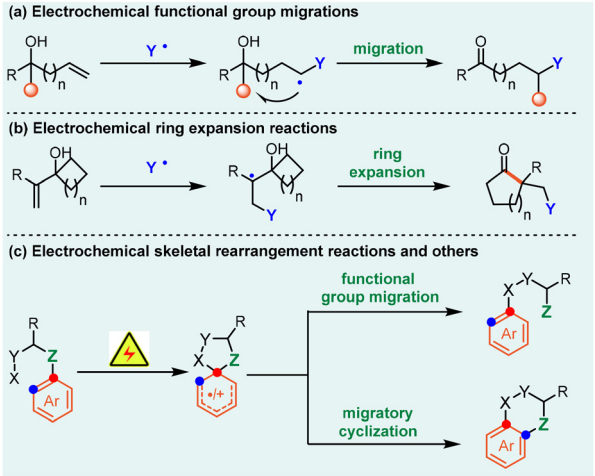
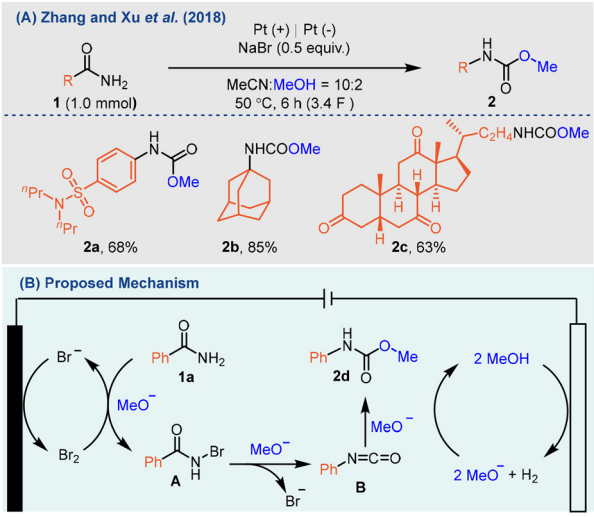


Scheme 1 Electrochemical rearrangement reactions.



Scheme 2 Electrochemical Hofmann rearrangements.

able electrochemically driven functional group migration reactions have been developed.

2.1 1,2-Functional group migrations

The traditional Hofmann rearrangement requires stoichiometric halogen and sodium hydroxide, and the use of these toxic and harmful reagents limits its practical application. To address this, Zhang *et al.* reported an electrochemical Hofmann rearrangement using NaBr as a mediator in an undivided cell under constant current conditions (Scheme 2A).[14] The synthetic strategy is well compatible with various commercially available medicine derivatives (**2a** and **2c**) and amantadine derivatives (**2b**) demonstrating its practicality in synthesis. The proposed mechanism begins with the cathodic reduction of MeOH, which generates H_2 and the base MeO^-. Meanwhile, the bromine produced at the anode reacts with amide (**1a**) to form an intermediate (**A**). Intermediate (**A**) then undergoes Hofmann rearrangement, followed by nucleophilic attack by the methoxy group to form the target product (**2d**, Scheme 2B). In 2023, Cantillo and co-workers realized the electrochemical Hofmann rearrangement of primary amines to synthesize methyl carbamates using a spinning cylinder electrode cell.[15]

Recently, the bifunctionalization of alkenes mediated by free radicals has emerged as a powerful tool for the synthesis of various bioactive molecules.[16] In 2019, the Lei group reported the electrochemical oxidation of allyl alcohols (**3**) to synthesize β-trifluoromethyl ketones (**5**) *via* a 1,2-migration process (Scheme 3A).[17] This reaction features mild conditions and simple operation, and eliminates the need for metal catalysis or chemical oxidants. Notably, this protocol enables not only the migration of various aryl groups (**5a–c**) but also the formation of alkyl-migration product (**5d**). Subsequently, Ackermann *et al.* extended this approach, achieving electrochemical 1,2- and 1,4-aryl migration of allyl alcohols (**3**, Scheme 3B).[18]

In 2023, the Xiong group developed an efficient electrochemical 1,2-migration reaction of allyl alcohol derivatives (**7**) to synthesize γ-keto sulfones (**10**) containing a β-quaternary carbon center (Scheme 4A).[19] A possible mechanism was proposed (Scheme 4B). Firstly, *p*-toluenesulfohydrazide (**9**) loses electrons and deprotonates at the anode forming an unstable

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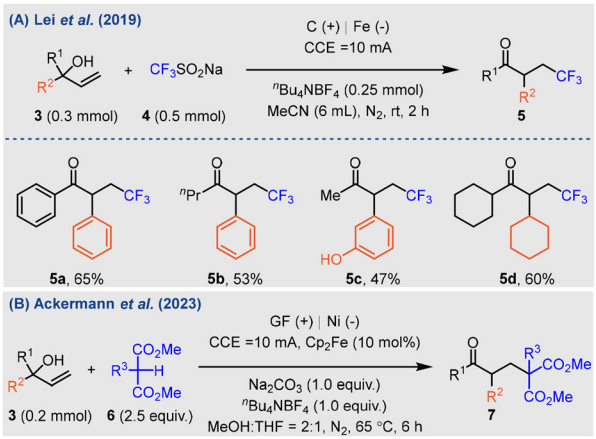
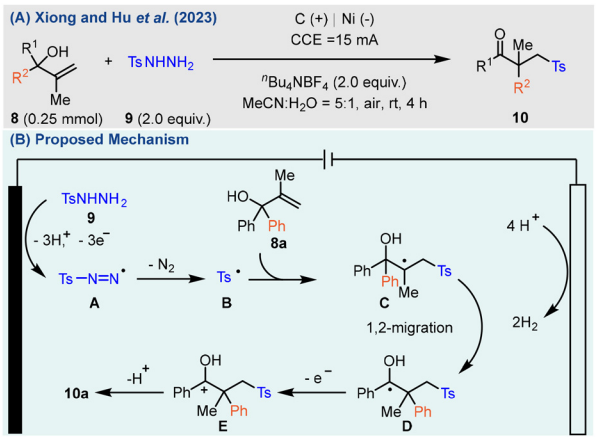
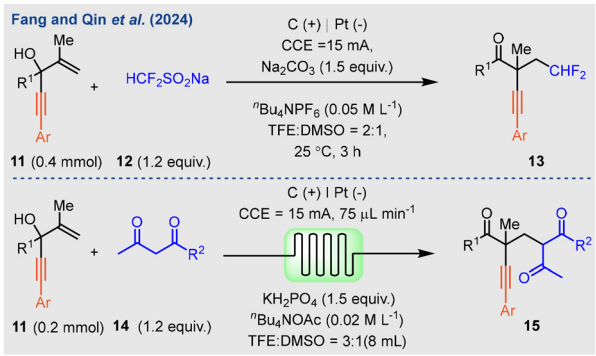


Scheme 3 Electrochemical 1,2-migration of allyl alcohols.



Scheme 4 Electrochemical synthesis of α-keto sulfones.

intermediate (**A**), which then releases N_2 and transforms into the sulfonyl radical intermediate (**B**). Next, intermediate (**B**) reacts with substrate (**8a**) *via* radical addition to generate intermediate (**C**). Subsequently, intermediate (**C**) undergoes a 1,2-phenyl migration producing intermediate (**D**), which is further oxidized at the anode to form the cation (**E**). Finally, intermediate (**E**) undergoes deprotonation to yield the target product (**10a**).



Scheme 5 Electrochemical 1,2-alkynyl migration of allyl alcohols.

Although the electrochemical 1,2-migration of allyl alcohols has been well developed, there are few reports on the corresponding flow chemical syntheses. Recently, Fang and coworkers revealed a continuous-flow electrochemical synthesis of α-alkynyl ketones (**13** and **15**) *via* radical 1,2-alkynyl migration (Scheme 5).[20] This strategy eliminates the need for metal catalysts or chemical oxidants, operates under mild conditions, exhibits high reaction efficiency, and accommodates a broad substrate range. As a result, this continuous-flow electrochemical synthesis strategy has broad potential applications.

1,2-Diaryl compounds are widely found in various pharmaceutical molecules.[21] These compounds can be efficiently synthesized *via* the 1,2-aryl migration strategy, in which the 1,1-diaryl ethyl radical is the key intermediate to realize 1,2-aryl migration.[22] Traditional synthesis strategies often require the additional introduction of free radicals or chemical oxidants, which limits the substrate scope.[23] Recently, electrochemical decarboxylation has emerged as a promising alternative

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without transition-metal catalysts, photocatalysts, external oxidants, or high temperatures.[24] Therefore, electrochemical decarboxylation is an ideal method to obtain radical species from carboxylic acids. In 2020, the Lei group reported an electrochemical oxidative decarboxylation and 1,2-aryl migration strategy for the synthesis of 1,2-diaryl ethers (**18**, Scheme 6A).[25] The synthetic strategy exhibits good substrate compatibility, and methanol (**18a**) as well as cyclohexanol (**18b**) can be effectively applied in the reaction. It is worth noting that the reaction can still be realized when one of the two aryl groups is replaced by methoxy (**18c**) or benzyl (**18d**).

Through cyclic voltammetry studies, it is determined that the oxidation peak appears at 1.68 V (*vs.* Ag/AgCl in MeOH/DCE) when **16a** and 1.0 equivalent of $^{n}Bu_4NOAc$ are mixed. Mechanistic investigations suggested that 3,3-diphenylpropionic acid (**16a**) undergoes deprotonation in the presence of acetate to produce carboxylate (**A**), which is oxidized at the anode to generate a carboxyl radical (**B**). The next decarboxylation reaction can obtain the primary carbon radical (**C**). A subsequent 1,2-aryl migration and anodic oxidation step generate a benzyl carbocation (**E**). Finally, the reaction between the benzyl carbocation (**E**) and methanol can yield the desired product (**18a**) with the help of acetate (Scheme 6B).

The Beckmann rearrangement has been widely applied in the synthesis of pharmaceuticals, pesticides, and natural products.[26] It remains one of the most important methods for synthesizing amide compounds. Recently, several improved Beckmann rearrangement reactions have been reported, including metal-complex-catalyzed,[27] boronic acid-mediated,[28] and photocatalytic[29] rearrangement reactions. Although these methods have shown good results, the development of more efficient and environmentally friendly synthesis strategies remains essential. The Guan group developed an electrochemical Beckmann rearrangement (Scheme 7A).[30] This strategy efficiently synthesizes amide derivatives (**20**) by direct electrolysis of ketoximes at room temperature under constant current conditions. The reaction exhibits a broad substrate scope and functional group compatibility, accommodating substrates such as aniline (**20a**), indole (**20b**), styrene (**20c**), and methyl (**20d**).

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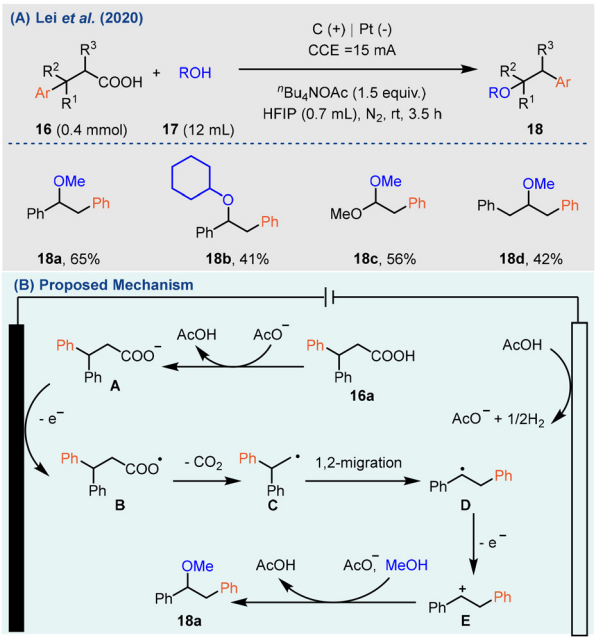
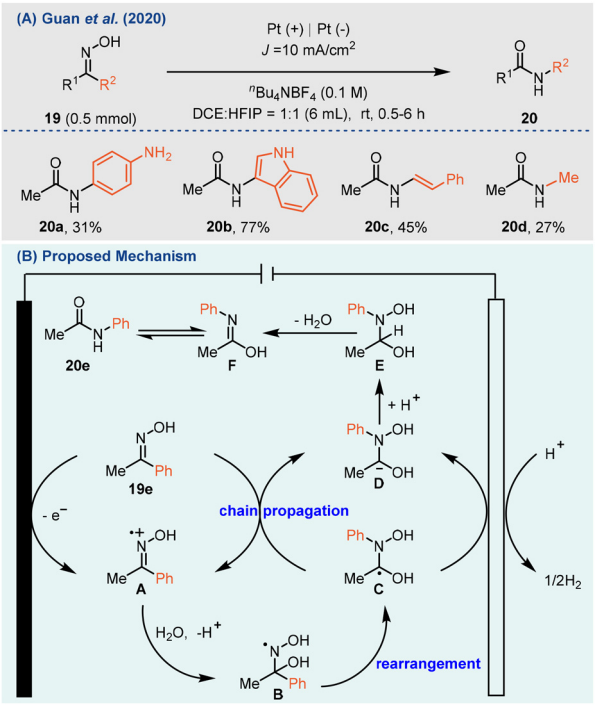


Scheme 6 Electrochemical oxidative decarboxylations and 1,2-aryl migrations.

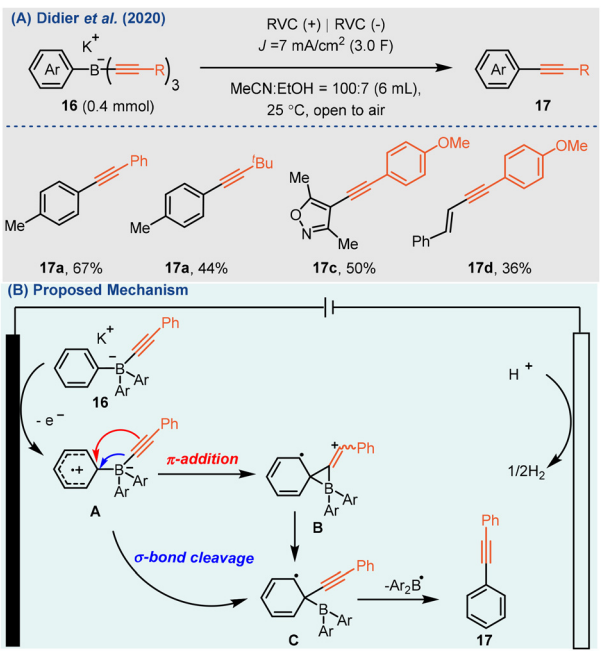


Scheme 7 Electrochemical Beckmann rearrangements.

Mechanistic studies proposed the following pathway that ketoxime (**20e**, E_{ox} = 1.42 V *vs.* Ag/AgCl in DCE/HFIP) undergoes a single-electron transfer to form a radical cation (**A**). Then intermediate (**A**) is attacked by nucleophilic water in the system to form intermediate (**B**), which undergoes a 1,2-rearrangement to generate a radical intermediate (**C**). Subsequently, the intermediate (**C**) is reduced at the cathode or reacts with another ketoxime (**19**) *via* chain propagation, closing the catalytic cycle to obtain the intermediate (**D**), which is protonated to form the intermediate (**E**). Finally, intermediate (**E**) loses one molecule of water to produce (**F**), which tautomerizes to form the product amide (**20e**, Scheme 7B).

Alkynes are one of the most significant organic functional groups, commonly found in many natural products as well as bioactive compounds.[31] Meanwhile, alkynes are often used as key intermediates in synthesis. Therefore, it is crucial to develop efficient and convenient synthetic methods for creating unsymmetrical alkynes. In 2021, Didier and co-workers developed an electrochemical intramolecular rearrangement of trialkynylorganoborates to synthesize unsymmetrical alkyne compounds (**17**, Scheme 8A).[32] All kinds of alkynes (**17a** and **17b**), heterocycles (**17c**), and natural products (**17d**) can be successfully produced using this simple and mild reaction.

The authors proposed a potential mechanism (Scheme 8B). First, the aryl group of the trialkynylarylborate (**16a**, E_{ox} = 1.14 V *vs.* SCE) undergoes oxidation at the anode, resulting in the formation of intermediate (**A**). Subsequently, a C–C bond can be created through either π bond addition or σ bond cleavage, leading to intermediates (**B**) and (**C**), respectively. Finally, intermediate (**C**) undergoes further oxidation to eliminate boron, facilitating the re-aromatization of the desired product (**17**).

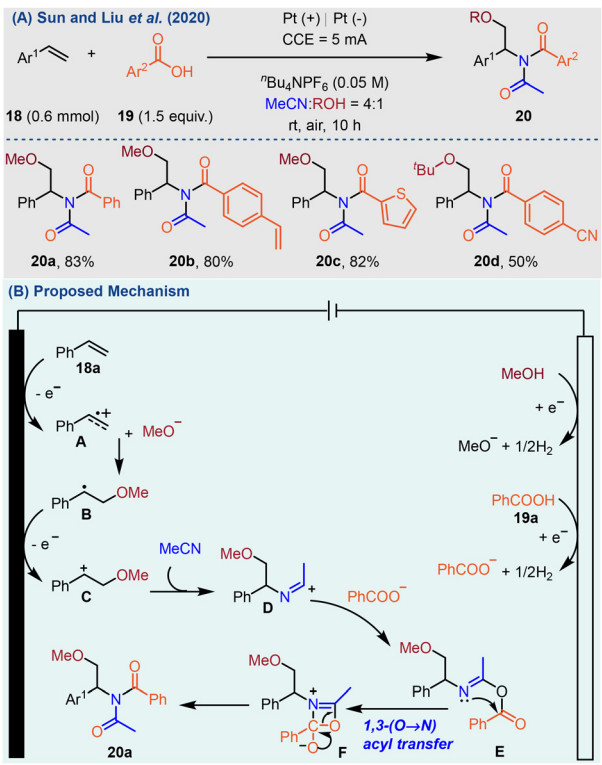


Scheme 8 Electrochemical intramolecular rearrangement of trialkynylorganoborates.

2.2 1,3-Functional group migrations

In early investigations, imine derivatives were synthesized by the 1,3 (O → N) acyl migration strategy (Mumm rearrangement) of *O*-acyl isoamides. However, this approach requires the preparation of unstable precursor imidoyl chlorides,[33] which restricts its applicability. The synthesis of imides using *O*-acyl isoamides generated *in situ* from readily available substrates under mild conditions is environmentally desirable. To address this, the Sun group developed an electrochemical functionalization of alkenes by a four-component cascade reaction cascade to synthesize imides (**20**, Scheme 9A).[34] This reaction uses simple and readily accessible starting materials, the conditions are mild, and the substrate range is wide. Different types of benzoic acids (**20a–c**) and alcohol (**20d**) can be effectively utilized. Additionally, the electrochemical four-component reaction can be successfully scaled up to gram quantities, highlighting the practical utility of this synthesis method.

Based on mechanistic studies (Scheme 9B), it is proposed that styrene (**18a**, E_{ox} = 1.6 V *vs.* SCE in MeCN) is oxidized at the anode to form a free radical cation intermediate (**A**). This intermediate is then reacted with the nucleophilic reagent MeO^- to create radical intermediate (**B**), which is subsequently anodized to produce cation (**C**). The intermolecular trapping of cation (**C**) with acetonitrile leads to the formation of carbocation (**D**), which can combine with $PhCOO^-$ to generate intermediate (**E**). Finally, due to its structural instability, intermedi-



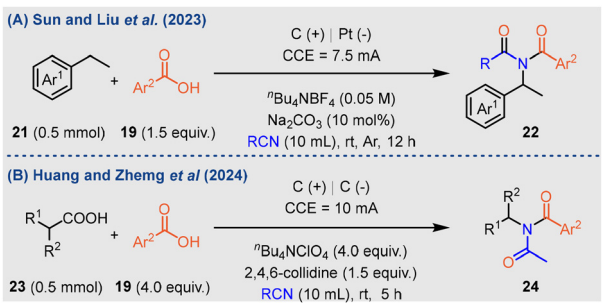
Scheme 9 Electrochemical Mumm rearrangements.

ate (**E**) quickly undergoes a Mumm rearrangement to furnish the desired product (**20a**).

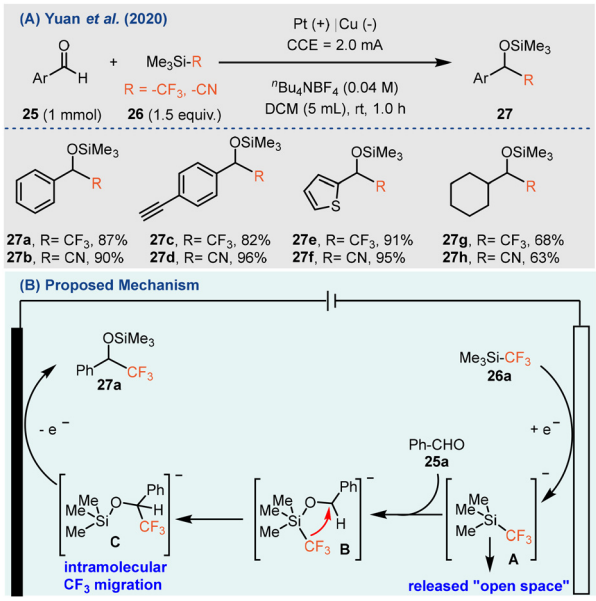
Recently, the Sun group reported an electrochemical three-component reaction cascade Mumm rearrangement which was developed for the synthesis of imides (**22**, Scheme 10A).[35] This method utilizes commercially available aryl acids (**19**), nitriles, and alkylbenzenes (**21**) as substrates, allowing for the creation of various imine derivatives through electrolysis at a constant current (7 mA) without using metal catalysts or chemical oxidants. Following this, the Huang group introduced an electrochemically promoted decarboxylation of carboxylic acid (**23**) followed by a Mumm rearrangement to produce imide derivatives (**24**, Scheme 10B).[36] The reaction conditions are mild, exhibit good tolerance for different functional groups, and yield a range of imides in moderate to high amounts.

Incorporating $-CF_3$ and $-CN$ functional groups into carbonyl structural units can alter the inherent properties of drug molecules.[37] Among these, trimethylsilyl nucleophilic reagents, such as Me_3SiCF_3 and Me_3SiCN, are easily available,[38] and they are non-toxic trifluoromethyl and cyanide sources that react with carbonyl electrophilic reagents, in which the slow release of CF_3^- or CN^- anions in aprotic solvents requires necessary initiators.[39] To address this, Yuan *et al.* developed an initiator-free electrochemical trifluoromethylsilylation and cyanosilylation of aldehydes (Scheme 11A).[40] The reaction has a wide range of substrates, and accommodates aromatic aldehydes (**27a–d**), heterocyclic aldehydes (**27e** and **27f**), and alkyl aldehydes (**27g** and **27h**). Mechanistic studies indicated that Me_3SiCF_3 (**26a**) is initially reduced at the cathode to form an anionic intermediate (**A**), which then reacts with benzaldehyde (**25a**) to form another intermediate (**B**). This intermediate (**B**) subsequently undergoes intramolecular CF_3 migration and loses electrons at the anode, resulting in the desired product (**27a**, Scheme 11B).

The selective functionalization of the allylic C (sp^3)–H bond enables the construction of a diversified molecular skeleton which can be further transformed into high-value-added products.[41] Currently, allylic C–H bond functionalization is primarily restricted to terminal alkenes or substrates with a single allylic site,[42] which limits its broader application. Additionally, isothiocyanates are commonly found in natural products and functional materials.[43] Conventional methods

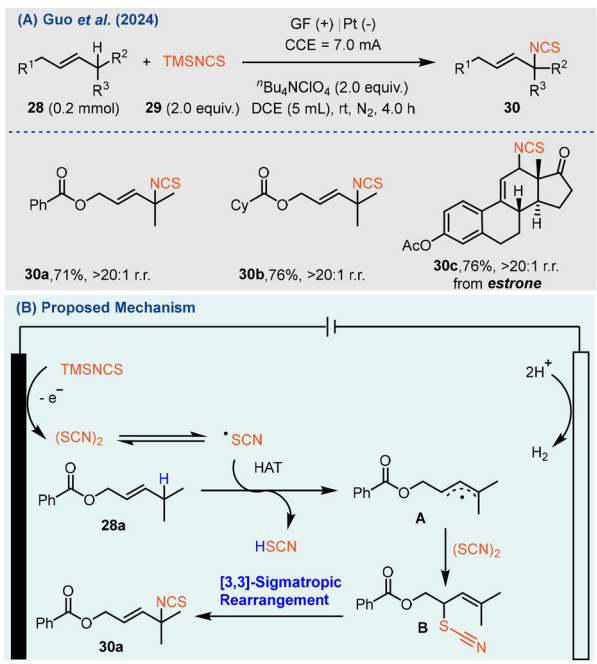


Scheme 10 Electrochemical Mumm rearrangement of imides.



Scheme 11 Electrochemical trifluoromethylsilylation and cyanosilylation of aldehydes.

for synthesizing isothiocyanates are not only harsh but also involve toxic thio-reagents.[44] Therefore, it is crucial to develop greener and more efficient direct C(sp^3)–H isothiocyanation techniques. Recently, the Guo group reported an electrochemically promoted allylic C(sp^3)–H isothiocyanation of internal alkenes (Scheme 12A).[45] The method not only has high chemical selectivity and position selectivity but also has wide functional group tolerance and excellent selectivity (**30a** and **30b**).



Scheme 12 Electrochemical allylic C(sp^3)–H isothiocyanation *via* [3,3]-sigmatropic rearrangements.

Additionally, it can be applied for the late-stage isothiocyanation of bioactive molecules (**30c**).

The control experiments and DFT calculations showed that TMSNCS plays a dual role of HAT reagent and coupling partner (Scheme 12B). Initially, the SCN anion is oxidized at the anode to produce thiocyanogen, which exists in equilibrium with the SCN radical. Subsequently, SCN radicals can selectively capture the hydrogen atom of the substrate (**28a**) and generate allylic radical species (**A**). Then, intermediate (**A**) is captured by $(SCN)_2$ to produce intermediate (**B**). Finally, the thermodynamically favored isothiocyanate (**30a**) is obtained *via* a [3,3]-sigmatropic rearrangement.

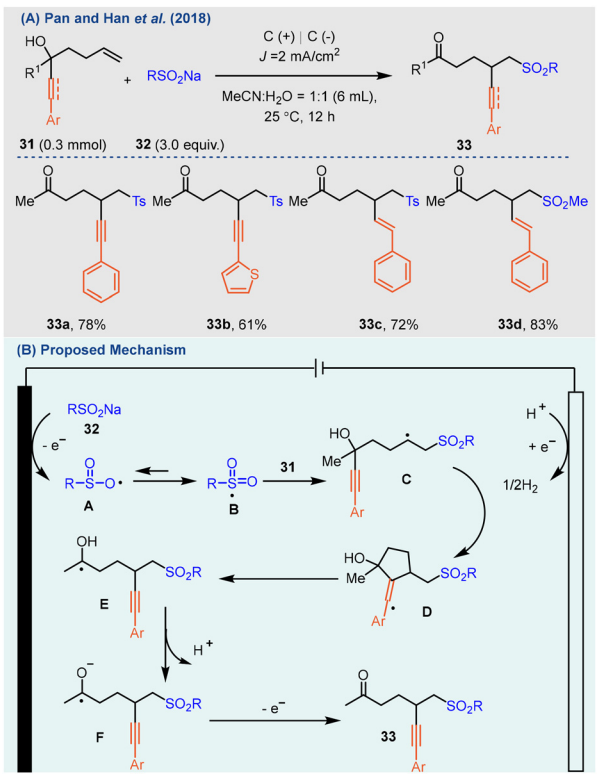
2.3 1,4-Functional group migrations

The remote functional group transfer strategy is a special type of organic transformation in the field of organic synthesis because it can synthesize some high-value-added compounds that are difficult to obtain by traditional methods.[46] Among them, remote functional group migration by forming intramolecular cyclic intermediates or transition states has been developed.[47] These reactions mainly focus on photocatalysis and metal catalysis.[1,48] In 2018, the Pan group reported the electrochemical enhancement of 1,4-alkynyl migration in tertiary alcohol derivatives, achieving 1,2-sulfonylation/alkynylation of alkenes (Scheme 13A).[49] The reaction affords various products of alkynyl migration (**33a** and **33b**) or alkenyl migration (**33a** and **33b**) with moderate to excellent yields under constant current electrolysis.

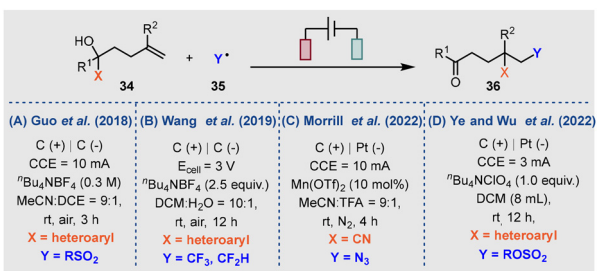
Mechanistic investigations suggested that sodium sulfinate (**32**) is oxidized at the anode to produce oxygen-centered radical (**A**). This radical intermediate (**A**) can resonate to form a more stable sulfonyl radical (**B**). Subsequently, the radical (**B**) and substrate (**31**) form an intermediate (**C**) through radical addition. Following this, intermediate (**C**) undergoes intramolecular radical cyclization to produce a vinyl radical (**D**), which then experiences selective C–C bond cleavage to yield a free radical (**E**). Finally, the intermediate (**E**) is dehydrogenated and oxidized at the anode to generate the target product (**33**, Scheme 13B).

Meanwhile, the Guo group reported a method for the direct electrooxidation sulfonylation/heteroarylation of alkenes using sulfinic acid, which operates under mild conditions and is effective for various heteroaromatic hydrocarbons (Scheme 14A).[50] Shortly after, the Wang group developed the electrochemical bifunctionalization of olefins through the remote migration of radical groups (Scheme 14B).[51] In 2022, Morrill *et al.* developed an electrochemical azidocyanation reaction of olefins through a 1,4-nitrile strategy. This method has high substrate tolerance and is suitable for various alkene-containing cyanohydrins, providing a good way to synthesize 1,2-azidonitriles (Scheme 14C).[52] In the same year, Ye *et al.* developed the electrochemical oxidation of inorganic sulfites with alcohols to generate alkoxysulfonyl radicals, which are used in the subsequent difunctionalization of allylic alcohols to provide various sulfonate esters (Scheme 14D).[53]

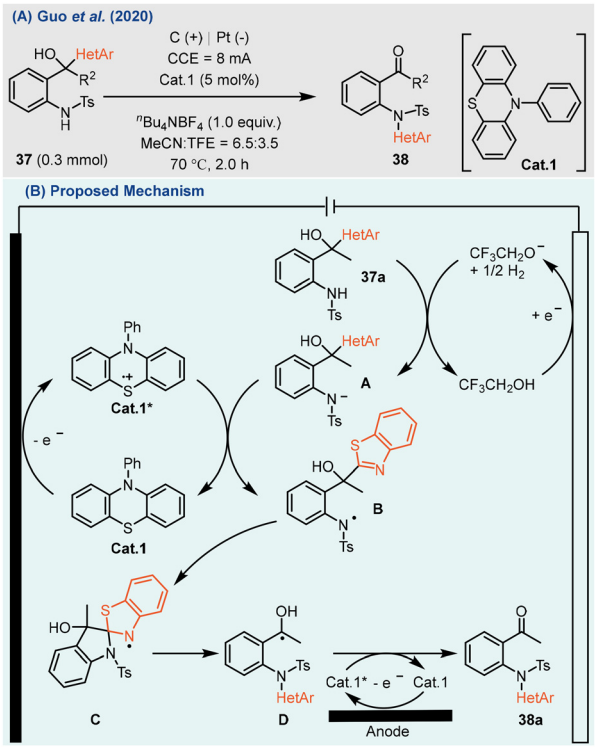
In 2020, the Guo group reported that the electrochemically triggered process by the N radical promotes remote heteroaryl migration (Scheme 15A).[54] This approach is environmentally friendly and efficient, exhibiting strong compatibility with various functional groups and high atomic efficiency. Mechanistic studies revealed that intermediate (**A**) is formed from the substrate (**37a**) through TFE anion exchange. Concurrently, the organic catalyst (**Cat. 1**, E_{ox} = 0.84 V and 1.65 V *vs.* SCE in MeCN) is oxidized at the anode to form a stable radical cation intermediate (**Cat. 1**$^{\bullet+}$), and then the intermediate (**A**) is oxidized to form a radical intermediate (**B**). Then, the intermediate (**B**) undergoes intramolecular radical cyclization to obtain spiro radical intermediate (**C**). Finally, the intermediate (**D**) is produced through C–C bond cleavage, which was oxidized by the (**cat. 1**$^{\bullet+}$) to form the desired product (**38a**, Scheme 15B).



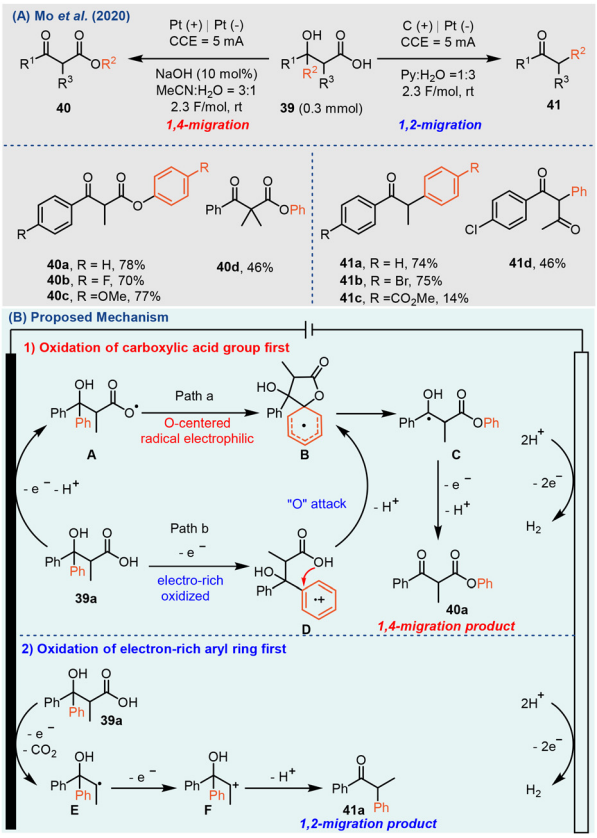
Scheme 13 Electrochemical migration of 1,4-alkynyls/alkenyls.



Scheme 14 Electrochemical 1,4-functional group migrations.



Scheme 15 Electrochemical heteroaryl migration initiated by N-centered radicals.

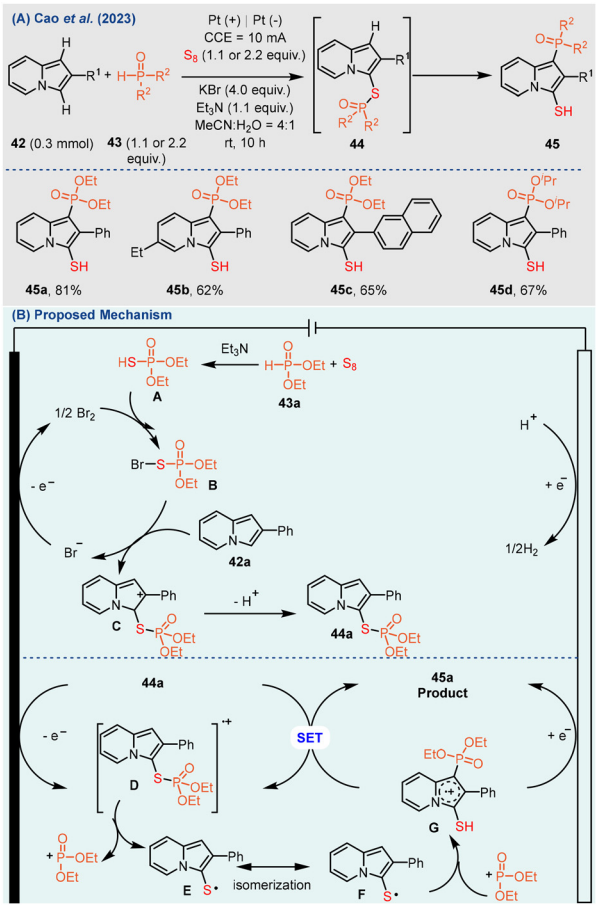


Scheme 16 Electrochemically promoted migration of 1,2- and 1,4-functional groups of β-hydroxycarboxylic acids.

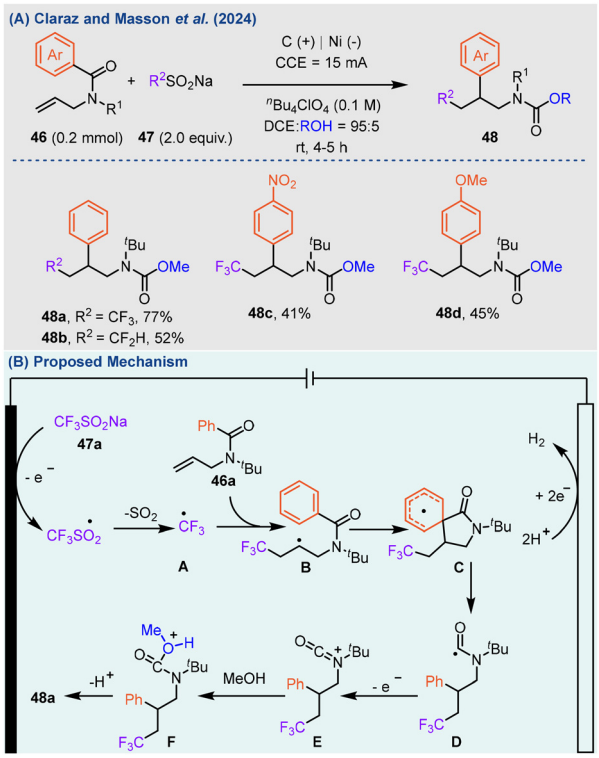
Meanwhile, the Mo group developed an electrochemical reaction to regulate the migration of 1,2-and 1,4-functional groups in β-hydroxycarboxylic acid (Scheme 16A).[55] The synthetic strategy controls the anodic oxidation of carboxylic acid by electrochemistry through a one-electron or two-electron pathway, resulting in 1,4-aryl transfer or semipinacol-type 1,2-group transfer products with excellent chemical selectivity. At the same time, this synthetic strategy can synthesize a series of β-keto acid esters (**40a–d**) and ketones (**41a–d**) with excellent yields. A potential mechanism is proposed for 1,4-migration (Scheme 16B-1). The deprotonated substrate (*i.e.*, the carboxylate, E_{ox} = 0.77 V *vs.* $Fc^{+/0}$ in MeCN/H_2O) undergoes single-electron oxidation to form O-center radical species (**A**). This is followed by intramolecular radical cyclization, resulting in radical species (**B**). At the same time, there is an alternative pathway (path b) where an electron-rich arene is first oxidized, and then an intramolecular nucleophilic carboxylate attacks it to create an intermediate (**B**). Finally, the intermediate (**B**) is further oxidized and deprotonated to obtain the target product (**40a**). The study of the 1,2-migration mechanism shows that the substrate (**39a**) is oxidized at the anode to remove a molecule of CO_2 to obtain the intermediate (**E**). Subsequently, the intermediate (**E**) was further oxidized and loses hydrogen ions to produce the target product (**41a**, Scheme 16B-2).

Phosphorothioates containing C–S–P (O) bonds are widely found in agrochemicals and active biomolecules.[56] In recent years, reagents containing phosphorus sulfide have been developed and effectively utilized in phosphorothiolation reactions.[57] Additionally, elemental sulfur (S_8) is a cost-effective, readily available, and abundant resource, making it an appealing option for creating C–S–P (O) bonds.[58] In 2023, the Cao group realized the electrochemical regioselective C–H phosphorothioation reaction of indolizines by using elemental sulfur (S8) as the sulfur source, leading to the synthesis of various mercapto-phosphono-substituted indolizine derivatives through intramolecular S- to C-[1,4] phosphoryl migration (Scheme 17A).[59] The migration products (**45**) can be synthesized efficiently and conveniently *via* electrolysis at a constant current of 10 mA, accommodating a wide range of substrates, with moderate to good yields for various substituted indolizines (**45a–45c**) and H-phosphonates (**45d**).

A potential mechanism was proposed for the formation of phosphorothiolation products (**44**). Initially, Br_2 is produced by anodic oxidation. Then, Br_2 reacts with *O*,*O*-diethyl *S*-hydrogen phosphorothioate (**A**) to form intermediate (**B**). Next, indolizine (**42a**) reacts with intermediate (**B**) to obtain intermediate (**C**) which then deprotonates to form the phosphorothioate product (**44a**). For the formation of the rearrangement product (**45a**), the compound (**44a**) undergoes single-electron oxidation to provide a radical cation (**D**), which breaks the S–P bond to produce $(EtO)_2P(O)^+$ and a sulfur-centered radical (**E**). Subsequently, the free radical (**E**) is isomerized to form a free radical intermediate (**F**). Following this, the



Scheme 17 Electrochemical 1,4-S → C phospho-Fries rearrangements.



Scheme 18 Electrochemically driven 1,4-aryl migration of *N*-allylbenzamides.

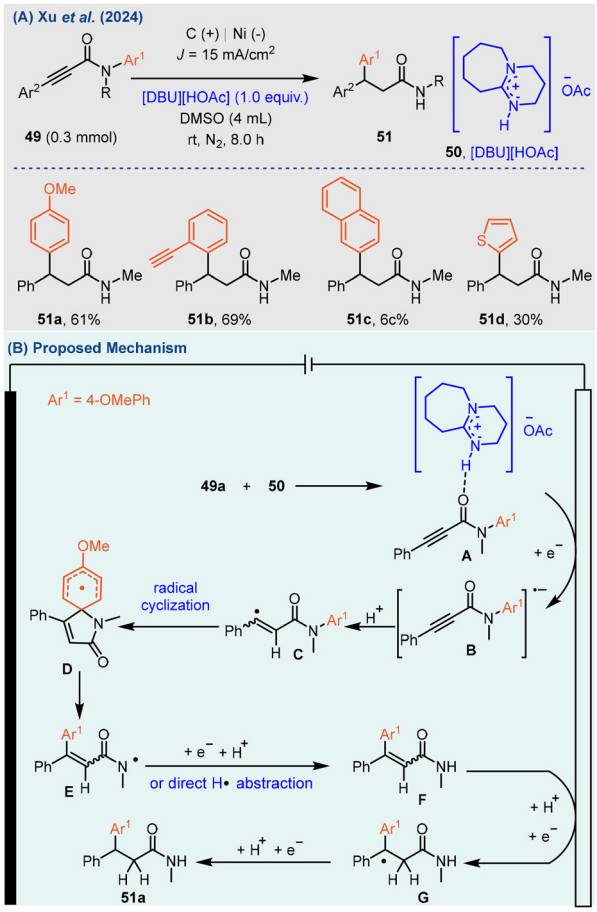
intermediate (**F**) captures $(EtO)_2P(O)^+$ to generate free radical cation (**G**). Finally, the radical cation (**G**) is spontaneously reduced by another molecule (**44a**), or the charge may be passed from the cation radical back to the electrode (backward electron transfer). Finally, the rearrangement product (**45a**) is formed (Scheme 17B).

The β-arylethylamine structure is widely found in some endogenous neurotransmitters and several drugs used for treating central nervous system diseases.[60] Among them, the structure can be prepared by radical desulfonylative rearrangement of arylsulfonamides, with the generation of a β-amino radical being crucial for these reactions.[61] In recent years, numerous methods for producing β-amino radicals under mild conditions have been developed.[62] Although these synthetic strategies have made great achievements, there is still a great need for simpler, milder, atomic-economical, and wider methods. Recently, Claraz *et al.* reported an electrochemically promoted radical fluoromethylation of *N*-allylbenzamides (**46**), leading to the synthesis of various functionalized β-arylethylamine derivatives (**48**) through 1,4-aryl migration (Scheme 18A).[63] This reaction can access valuable tri- and difluorocontaining arylethylamine derivatives (**48a** and **48b**) and realize 1,4-migration for substrates containing strong electron-withdrawing groups (**48c**) or electron-rich groups (**48d**).

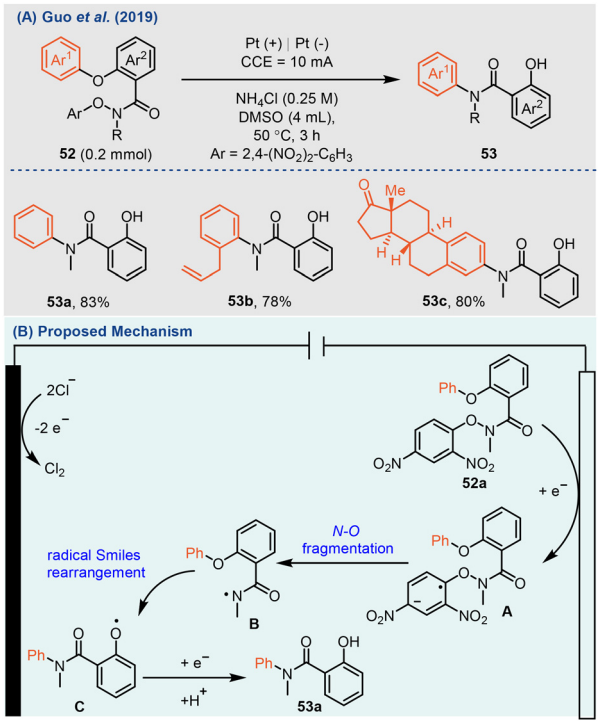
A potential reaction mechanism was proposed by density functional theory (DFT) calculations (Scheme 18B). Initially, the substrate (**47a**, E_{ox} = 0.73 V *vs.* $Fc^{+/0}$ in DCE/MeOH) is oxidized at the anode and SO_2 is removed to obtain $CF_3^{\bullet}$ radical (**A**). Then, the substrate (**46a**) and the radical (**A**) undergo radical addition to obtain an intermediate (**B**) which undergoes intramolecular radical cyclization to produce a spiro radical intermediate (**C**). Next, selective C–C bond cleavage occurs to obtain carbamoyl radical (**D**). Subsequently, the intermediate (**D**) is oxidized at the anode to produce the corresponding carbamoyl cation (**E**), which undergoes nucleophilic addition of methanol to produce carbamoyl cation (**F**). Finally, the target product (**48a**) is obtained by deprotonation.

Very recently, the Xu group used [DBU][HOAc] as a hydrogen bonding donor to achieve 1,4-aryl migration of *N*-arylpropiolamides by an electrochemical reduction strategy, resulting in the synthesis of various diarylpropanamide compounds (Scheme 19A).[64] The reductive activation of chemical bonds at lower negative potentials allows for high tolerance and selectivity towards different functional groups. Various substituted aromatic hydrocarbons (**51a–c**) and thiophene (**51d**) can also realize 1,4-migration. It is worth noting that [DBU][HOAc] is used as both a hydrogen bond donor and a supporting electrolyte for the first time.

The mechanism investigations revealed that the substrate (**49a**) interacts with [DBU][HOAc] (**50**) to form a complex (**A**, E_{red} = −2.3 V *vs.* $Ag/AgNO_3$ in MeCN) *via* hydrogen bonding.



Scheme 19 Electrochemical reductive 1,4-aryl migration of *N*-arylpropiolamides.



Scheme 20 Electrochemically driven 1,5-aryl migrations.

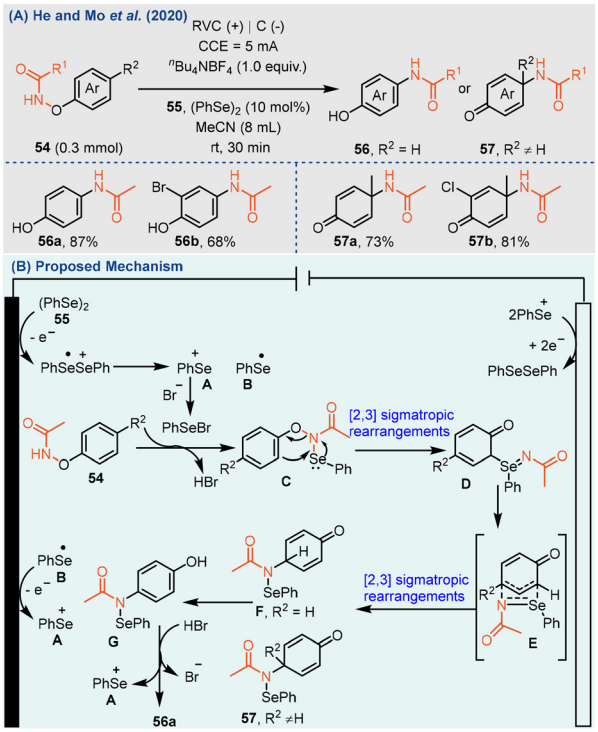
This complex is then reduced at the cathode to yield an intermediate (**B**). Following this, intermediate (**B**) undergoes protonation to generate vinyl radical (**C**), which subsequently undergoes intramolecular radical cyclization to form a spiro intermediate (**D**). Then, the (**D**) is selectively cleaved by the C–N bond to produce amide radical intermediate (**E**). The (**E**) is abstracted by a hydrogen atom or reduced by SET and then protonated to produce intermediate (**F**). Next, intermediate (**F**) is reduced at the cathode and deprotonated to obtain (**G**). Finally, (**G**) obtained the target product (**51a**) through a radical-polar crossover (RPC) (Scheme 19B).

2.3 1,5-Functional group migrations

In 2019, the Guo group discovered that amidyl radicals could be produced through the electrochemical reduction of N–O bonds. Following this, they synthesized a variety of amide derivatives (**53**) *via* intramolecular 1,5-aryl migration (Scheme 20A).[65] This synthetic strategy is suitable for the post-modification of hydroxylamine derivatives (**53a** and **53b**) with different substituents and bioactive molecules (**53c**). A potential mechanism was proposed (Scheme 20B). Initially, the substrate (**52a**, E_{red} = −1.52 V *vs.* SCE in DMSO) is reduced at the cathode to produce an intermediate (**A**). Then, the N–O bond is cleaved to generate amidyl radical (**B**). Next, intramolecular free radical Smiles rearrangement occurs to form radical intermediate (**C**). Finally, the cathodic reduction and protonation of (**C**) generates the target product (**53a**).

Aminophenol exists widely in the molecular structures of many compounds.[66] Nowadays, the synthetic methods for polysubstituted aminophenol are mainly realized by metal catalysis and ligands.[67] Thus, it is crucial to develop more environmentally friendly and cost-effective synthesis methods. In 2023, the He group developed an electrochemical organoselenium-catalyzed 1,5-amide migration of *N*-aryloxyamides to synthesize a series of aminophenol derivatives (**56a** and **56b**) (Scheme 21A).[68] Meanwhile, when the *para*-substituent on the benzene ring of the substrate (**54**) is not hydrogen, the obtained product is an aminoketone derivative (**57a** and **57b**).

The mechanism studies showed that the catalyst (**55**, E_{ox} = 1.54 V and 1.91 V *vs.* Ag/AgCl in MeCN) is oxidized and activated at the anode to form selenium cation (**A**) and phenyl selenium radical (**A**). Meanwhile, radical (**B**) can also produce selenium cation (**A**) through single-electron transfer at the anode. Following this, intermediate (**A**) combines with the bromine anion to form PhSeBr and reacts with the substrate (**54**) to form Se–N intermediate (**C**). Intermediate (**C**) undergoes two [2,3] sigmatropic rearrangements to obtain *para*-aminated intermediate (**F**, R^2 = H) or product (**57**) ($R^2 \neq$ H). Finally, the intermediate (**F**) removes cation (**A**) under the action of HBr to complete the cycle and afford the final target product (**56a**, Scheme 21B).

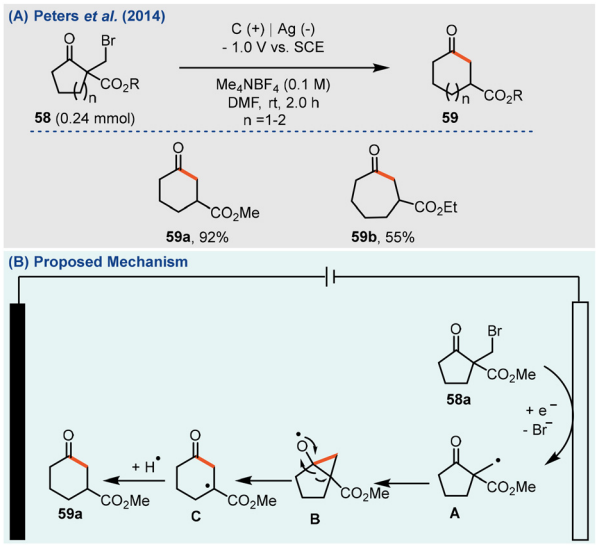


Scheme 21 Electrochemical selenium-catalyzed *para*-amination of *N*-aryloxyamides.

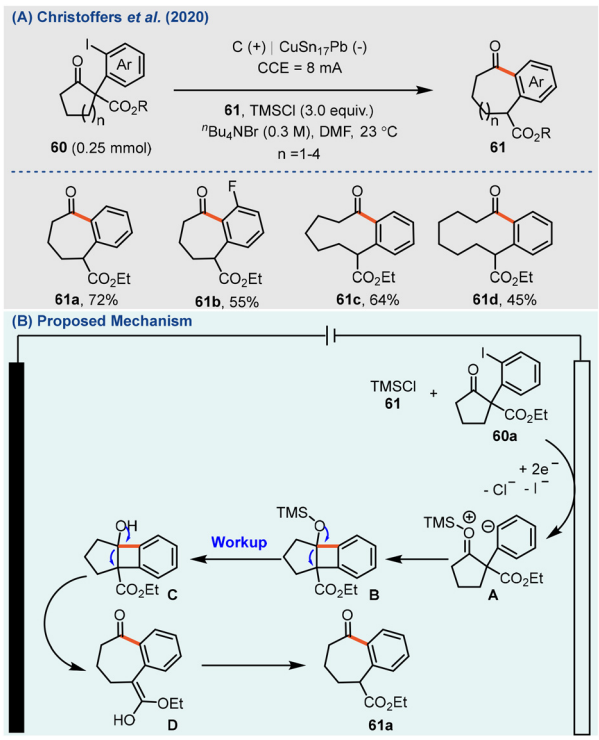
3. Electrochemical ring expansion reactions

The synthesis of medium-sized rings is difficult due to the unfavorable enthalpy and entropy barriers present in their transition states.[69] The common strategy to achieve this synthetic goal is ring expansion from more easily available five-membered or six-membered ring compounds.[70] In 2014, Peters and colleagues demonstrated an electrochemical direct reduction ring extension reaction using a silver cathode, successfully synthesizing six- to seven-membered ring compounds (**59**, Scheme 22A).[71] First, the substrate (**58a**, E_{red} = −0.6 V and −1.51 V *vs.* SCE in DMF) is reduced at the cathode to generate a radical intermediate (**A**), which then quickly generates a cyclopropyl alkoxy radical (**B**). This radical (**B**) subsequently undergoes a ring-expansion reaction to form an intermediate (**C**), which ultimately abstracts a hydrogen atom from the solvent DMF to yield the desired product (**59a**, Scheme 22B).

Later, Christoffers *et al.* reported the electrochemical reduction and ring extension reaction of cyclic α-(*ortho*-iodophenyl)-β-oxoesters to synthesize a series of benzannulated cycloalkanone carboxylic esters (**61**, Scheme 23A).[72] The reaction exhibits good substrate tolerance, allowing for the synthesis of benzocycloheptanone (**61a** and **61b**), nonanone (**61c**), and decanone (**61d**) in moderate to good yields. The mechanism studies showed that the substrate (**60a**) is reduced at the cathode to obtain phenyl anion derivative (**A**). Subsequently, the anion center attacks the carbonyl group (activated by



Scheme 22 Electrochemical reduction ring expansion reactions.



Scheme 23 Electrochemical ring expansion of α-(*ortho*-iodophenyl)-β-oxoesters.

TMSCl) to produce a tricyclic intermediate (**B**) with a *cis*-configuration. Finally, the target product (**61a**) is obtained by hydrolysis (Scheme 23B).

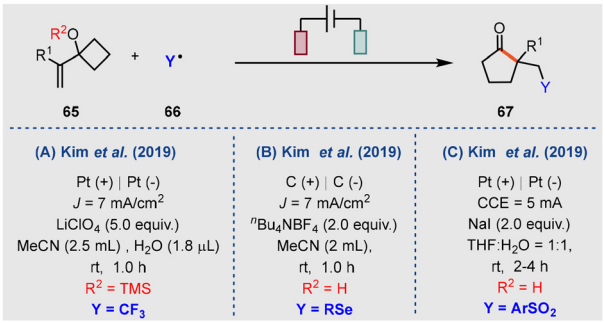
A structure containing an all-carbon quaternary stereocenter is widely found in many bioactive natural products and pharmaceuticals.[73] Among these, the semipinacol rearrangement of allylic alcohols has emerged as a popular method for

creating carbonyl compounds with α-quaternary carbon centers.[74] Traditional synthesis methods often rely on chemical oxidants or metal reagents, which significantly restrict their broader application.[75] Therefore, developing a more greener and efficient synthesis strategy is necessary. In 2019, the Zhang group used cheap and stable RSO_2Na (R = CF_3, Ph) as a free radical precursor to realize electrochemical phenol rearrangement of allyl alcohol (Scheme 24A).[76] This strategy does not need oxidants and metal reagents, and the conditions are mild. It can synthesize various β-trifluoromethyl (**64a** and **64b**) and sulfonated ketones (**64c** and **64d**) with moderate to excellent yields.

A potential mechanism was proposed (Scheme 24B). Initially, CF_3SO_2Na undergoes oxidation *via* SET at the anode, resulting in the formation of a sulfonyl radical. This is followed by a rapid release of SO_2, leading to the creation of a CF_3 radical (**B**). Next, radical addition occurs with the substrate (**62a**) to obtain radical (**C**), which is further oxidized to cation (**D**). Finally, the target product (**64a**) is obtained through the deprotonation process of ring expansion.

Around the same period, Kim *et al.* also reported the electrochemical trifluoromethylation/ring extension reaction of alkenyl alcohols to synthesize a series of β-CF_3 substituted ketones (Scheme 25A).[77] Then, Kim and co-workers continued to report the electrochemical oxidation of alkenylcyclobutanols, radical selenylation/ring expansion reactions (Scheme 25B),[78] along with radical arylsulfonylation and ring expansion reactions (Scheme 25C).[79]

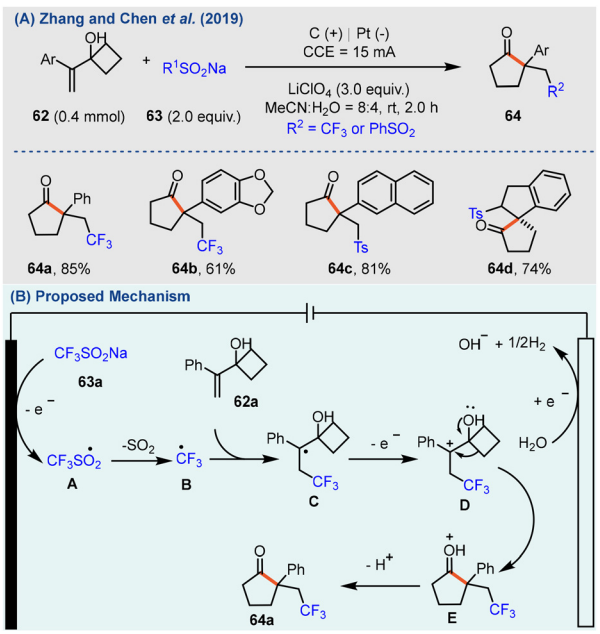
In 2019, the Zhang group used inorganic halide salts as sources of halogen to synthesize a series of β-halocarbonyl compounds (**70**) with an all-carbon α-quaternary center



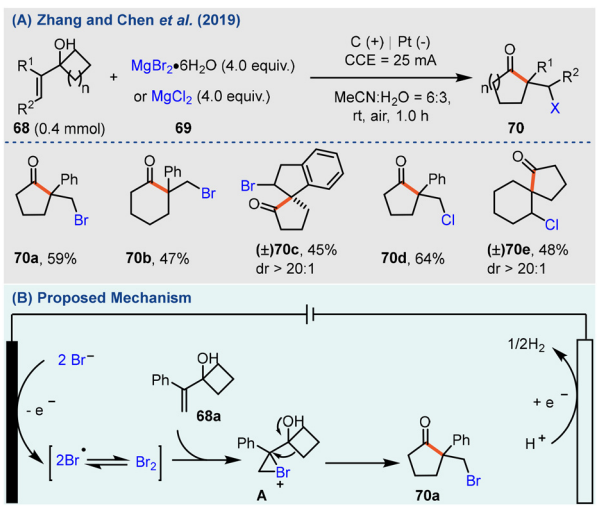
Scheme 25 Electrochemical ring expansion of alkenyl alcohols.

through the electrochemical halogenation/ring expansion reaction of allyl alcohol (Scheme 26A).[80] This reaction features mild conditions and a wide range of substrates, which can not only synthesize five-membered (**70a** and **70d**) and six-membered (**70b**) β-halocarbonyl compounds but also realize the construction of spirocyclic skeletons (**70c** and **70e**). The mechanism study shows that halide anions are first oxidized to halogen molecules at the anode. Subsequently, halogen molecules react with the double bond of the substrate (**68a**) to generate an intermediate (**A**), which then undergoes a semipinacol rearrangement to yield the desired product (**70a**, Scheme 26B).

Medium-sized nitrogen-containing heterocycles, specifically those with 8 to 11-membered rings, are commonly found in bioactive compounds and natural products.[81] However, this kind of molecular skeleton is mainly synthesized by intramolecular carbonylation,[82] closed-ring metathesis (RCM)[83], Claisen rearrangement,[84] *etc.*[85] Therefore, these synthetic strategies require the use of metal catalysts or stoichiometric oxidants, which greatly limits their application scope. In 2020, the Ruan group designed an electrochemical strategy to syn-



Scheme 24 Electrochemical semipinacol rearrangement of allylic alcohols.

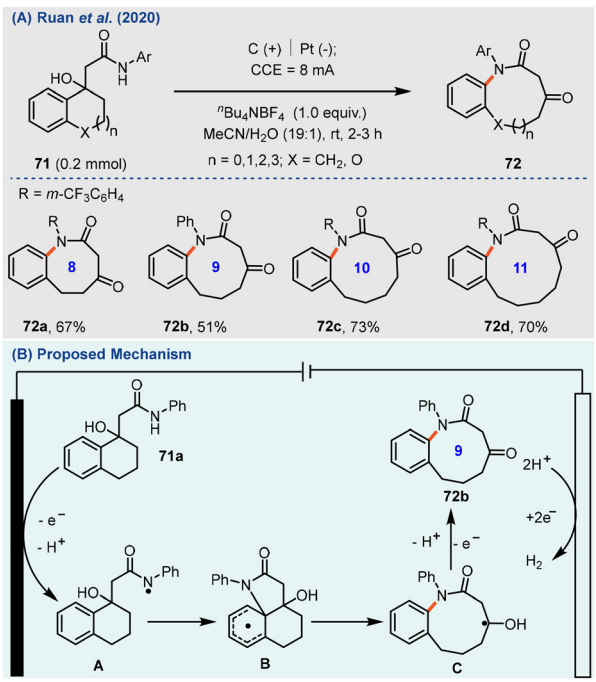


Scheme 26 Approaches for synthesising β-halocarbonyls *via* electrochemical rearrangement of allylic alcohols.

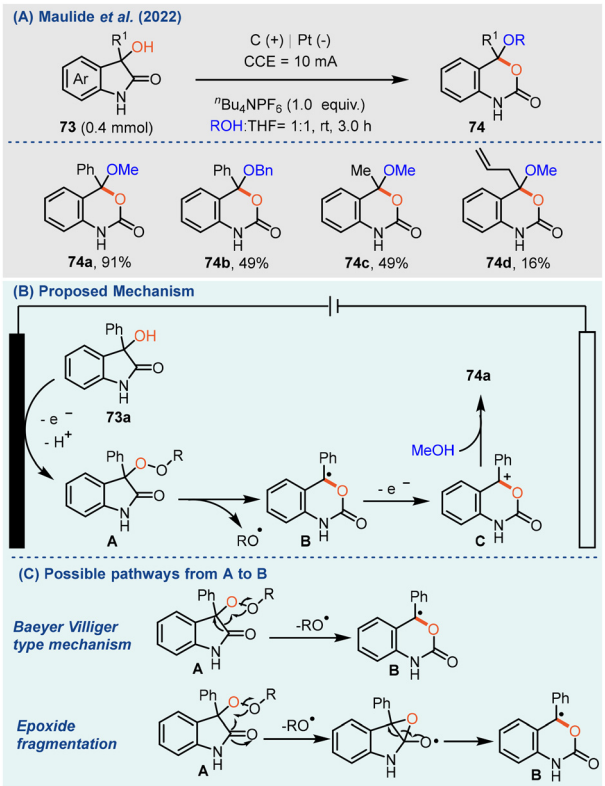
thesize annulated medium-sized lactams (**72**) by promoting the cleavage of C–C bonds through N radicals (Scheme 27A).[86] The synthetic strategy features mild conditions, and 8–11 annulated lactams (**70a–d**) can be synthesized with moderate to good yields without metal reagents and chemical oxidants.

A potential mechanism was proposed by DFT calculations (Scheme 27B). Initially, the N–H bond in the substrate (**71a**, E_{ox} = 2.2 V *vs.* Ag/AgCl in MeCN) is oxidized at the anode to produce an amido radical intermediate (**A**), which undergoes intramolecular cyclization to form a radical intermediate (**B**). Next, the selective C–C bond of intermediate (**B**) is cleaved to generate a neutral radical (**C**). Finally, (**C**) undergoes single electron oxidation and deprotonation to produce the target product (**72b**). Additionally, the Lei group realized the electrochemical ring-expanding reaction between molecules by using benzocyclic ketone and aniline.[87]

The benzoxazinone skeleton exists widely in some drug molecules and bioactive compounds.[88] Currently, most of these compounds' synthesis methods require the use of strong alkali or stoichiometric organometallic reagents, and the steps are cumbersome and the atom economy is poor.[89] Therefore, developing more greener, efficient, and sustainable synthetic methods under mild conditions is particularly important. In 2022, Maulide *et al.* reported the electrochemical rearrangement of 3-hydroxyoxindoles to synthesize benzoxazinone derivatives (Scheme 28A).[90] This reaction demonstrates broad tolerance for different functional groups, allowing various nucleophiles (**74a** and **74b**) and alkyl (**74c** and **74d**) substitutions to participate.



Scheme 27 Electrochemical synthesis of annulated medium-sized lactams.



Scheme 28 Electrochemical ring expansion of 3-hydroxyoxindoles.

The mechanism studies showed that the substrate (**73a**) is oxidized at the anode to form the peroxide intermediate (**A**), which can be rearranged to form the intermediate (**B**) (Scheme 28C) in two possible ways. The ring-expanding reaction is carried out by a Baeyer–Villiger type rearrangement or an intermediate (**B**) which can be produced by an oxa-Dowd–Beckwith-type rearrangement formed in the molecule on the epoxide. Subsequently, the intermediate (**B**) was further oxidized to obtain a cationic intermediate (**C**), which was further captured by methanol to obtain the target product (**74a**, Scheme 28B).

4. Electrochemical migratory cyclization reactions

Electrochemically promoted radical cyclization has been developed rapidly in recent decades and provided a powerful tool for the synthesis of nitrogen-containing heterocyclic compounds.[9c,10a,91] Among them, the migratory cyclization reaction can quickly realize the recombination of the molecular skeleton to obtain a brand-new cyclic compound. However, there are few studies on electrochemically promoted migratory cyclization reactions, because the occurrence of *ortho*-cyclization reactions often accompanies the occurrence of migratory cyclization reactions, so it is difficult to control its selectivity.

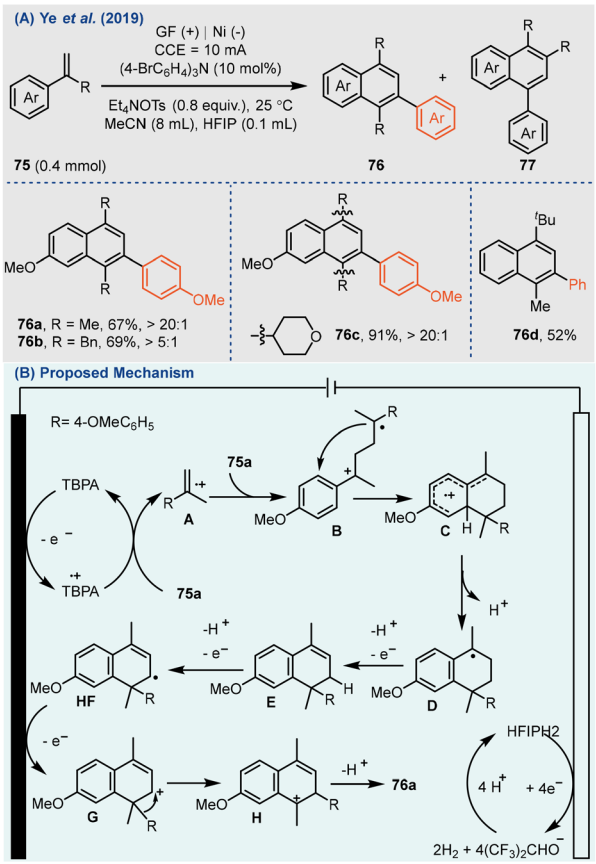
In 2019, the Ye group reported for the first time that the [4 + 2] annulation-rearrangement-aromatization of styrene was electrochemically promoted to synthesize functional naphthalene derivatives (Scheme 29A).[92] This reaction is notable for not requiring a metal catalyst or oxidant, demonstrating excellent atom economy. Additionally, it shows strong substrate tolerance, allowing various substituted styrenes (**76a–d**) to afford the desired product with moderate to good yields and chemical selectivity.

The proposed mechanism is that TBPA (E_{ox} = 1.15 V *vs.* SCE in MeCN) is first oxidized at the anode to form the radical cation TBPA (TBPAC$^{\bullet+}$). Following this, the electron-rich styrene (**75a**) is oxidized by SET to obtain free radical cation (**A**) and TBPA. Substrate (**75a**) attacks cation (**A**) to form intermediate (**B**), which undergoes intramolecular radical cyclization and deprotonation to obtain (**D**). Subsequently, (**D**) loses electrons and protons to obtain intermediate (**E**), which is further oxidized and protonated to obtain carbon radical (**F**). Intermediate (**F**) is oxidized to (**G**). Finally, the secondary carbon cation is rearranged into a more stable tertiary carbon cation (**H**) and deprotonated to obtain the migratory cyclization product (**76a**, Scheme 29B).

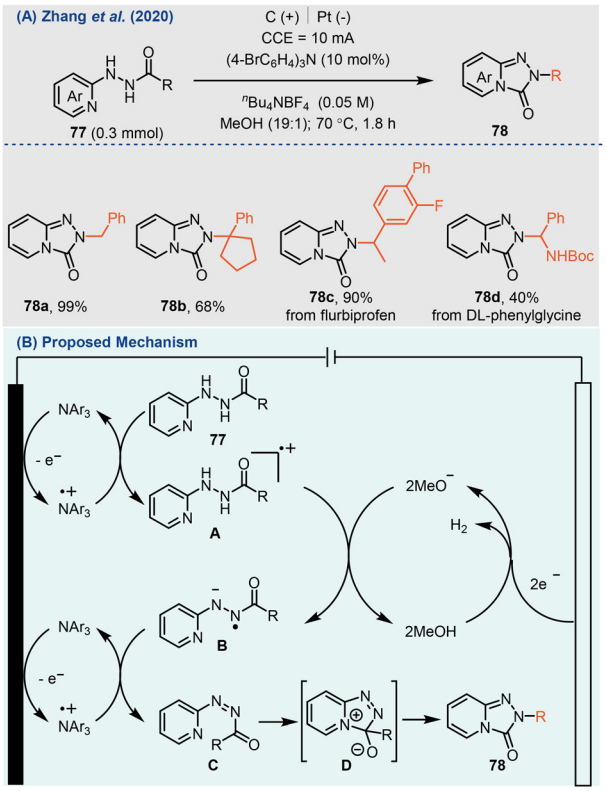
Triazolopyridinone derivatives are widely used in medicine, materials, and agricultural chemicals.[93] However, there are no reports on sterically hindered substituted triazolopyridine derivatives. In 2020, the Zhang group reported an electrochemical rearrangement for effective synthesis of triazolopyridine from various alkyl carboxylic acids, which are difficult to obtain by traditional methods (Scheme 30A).[94] This synthetic strategy features simple and mild conditions and a wide range of substrates. It can not only synthesize various conventional functionalized triazolopyridines (**78a** and **78b**) but also proves the potential application value of this synthetic strategy for the late-stage modification of bioactive molecules (**78c**) and amino acid derivatives (**78d**).

The proposed mechanism is that triarylamine (NAr_3) is first oxidized at the anode to form the radical cation NAr_3 ($NAr_3^{\bullet+}$). Next, the substrate (**77**) undergoes SET oxidation to generate the radical cation (**A**) and NAr_3. Following this, the intermediate (**A**) is deprotonated to produce a trans-diazo compound, which can be easily converted into a *cis*-diazo compound (**C**). Finally, an intramolecular nucleophilic attack of the carbonyl group by the pyridine nitrogen followed by a concerted 1,2-alkyl migration from carbon to nitrogen affords the rearranged product (**78**) *via* intermediate (**D**) (Scheme 30B).

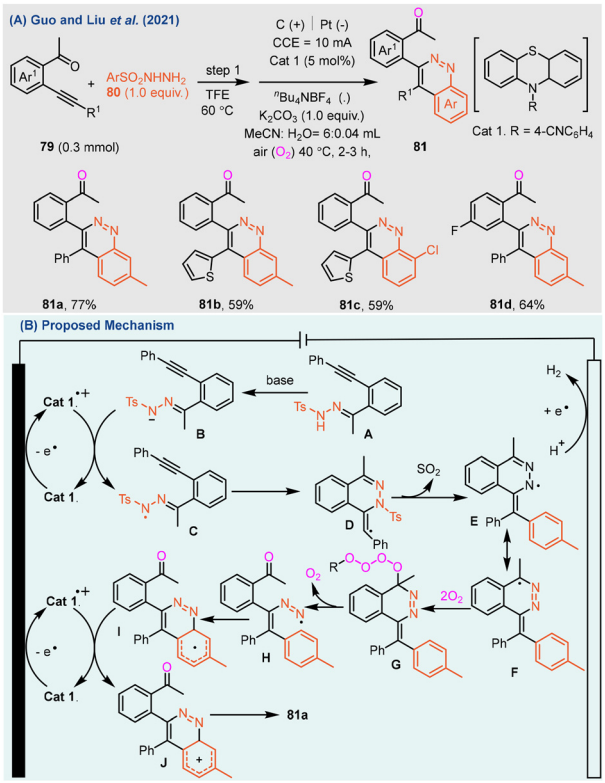
In 2021, the Guo group developed the electrochemical synthesis of cinnoline derivatives (**81**) by using *ortho*-alkynyl acetophenones and sulfonyl hydrazides as starting materials through organic catalytic radical cyclization and migration (Scheme 31A).[95] The method features mild conditions, excel-



Scheme 29 Electrochemical rearrangement and cyclization of styrenes.



Scheme 30 Synthesis of triazolopyridinone derivatives by electrochemical rearrangement.



Scheme 31 Organocatalytic electrosynthesis of cinnolines through migratory cyclization.

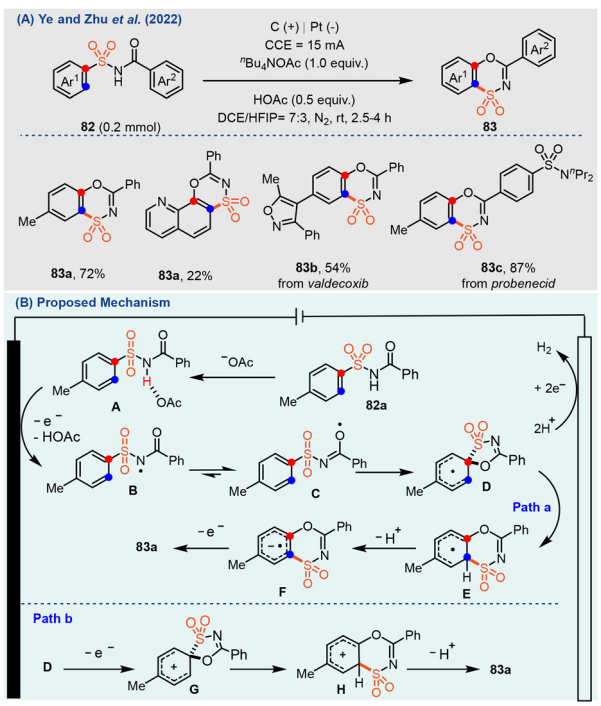
lent regioselectivity, and wide functional group tolerance, and can obtain various substituted cinnoline derivatives (**81a–d**) with moderate to excellent yields.

The mechanism studies showed that (**Cat 1** E_{ox} = 2.32 V *vs.* Ag/AgCl in MeCN/TFE/H_2O) is first oxidized to free radical cation intermediate (**Cat 1**$^{\bullet+}$) at the anode. Meanwhile, the intermediate (**A**) generates anion (**B**) under the action of a base, which is converted into radical (**C**) by the intermediate (**Cat 1**$^{\bullet+}$). This is followed by (**C**) intramolecular radical cyclization and Smiles rearrangement to obtain intermediate (**E**). The alkyl radical intermediates (**F**) and (**E**) are formed by resonance. Subsequently, the radical coupling of (**F**) and O_2 generates the corresponding tetraoxide intermediate (**G**), and the continuous O–O and C–N bond homolysis furnishes diazo radical (**H**). Then (**H**) generates aryl radical (**I**) by intramolecular cyclization, which is oxidized by (**Cat 1**$^{\bullet+}$) to form cationic intermediate (**J**). Finally, the target product (**81a**) is obtained by deprotonation (Scheme 31B).

The core skeleton of diazoxide compounds is nitrogen-containing six-membered heterocyclic compounds containing sulfanilamide groups. These compounds are widely found in nature and used in clinical research because of their good biological activities.[96] As a bioisostere, benzoxathiazine dioxide has potential hypoglycemic and fungicidal effects.[97] However, currently, only a few synthetic methods generally have some disadvantages, such as the need for the preparation of starting materials in advance, complex synthetic routes, limited substrate range, low yield, and many by-products, which do not conform to the concept of green chemistry.[98] Therefore, developing an efficient, novel, green synthesis method to construct these compounds conveniently is crucial.

In 2022, Ye and co-workers used simple and easily available *N*-acylsulfonamides to efficiently synthesize various benzoxathiazine dioxides (**83**) through an electrochemical oxidation migratory cyclization strategy (Scheme 32A).[99] The reaction avoids SO_2 removal under mild electrochemical conditions, reduces environmental pollution, and improves atom economy. This method has a wide range of substrates, good functional group tolerance, and good compatibility with heterocyclic quinoline (**83b**). It is worth noting that this strategy allows for the late modification of pharmaceutically active molecules (**83c** and **83d**). The preliminary activity test results indicate that benzoxathiazine dioxide shows potential antitumor activity.

The possible mechanism was proposed based on experimental results and DFT calculations (Scheme 32B). The N–H bond in the substrate (**82a**, E_{ox} = 2.40 V *vs.* $Fc^{+/0}$ in MeCN) first forms intramolecular hydrogen bonds with acetate. Then, the radical (**B**) is generated at the anode through proton-coupled electron transfer (PCET), which can be rapidly isomerized to form O radical species (**C**). Subsequently, spirocyclic cyclohexadienyl radical intermediate (**D**) was generated by intramolecular radical cyclization. The reaction then proceeds through two possible reaction pathways. Path a involves radical migration (**D** to **E**) and subsequent removal of a proton to form (**F**), which is further oxidized to obtain the target product



Scheme 32 Electrochemical migratory cyclization of *N*-acylsulfonamides.

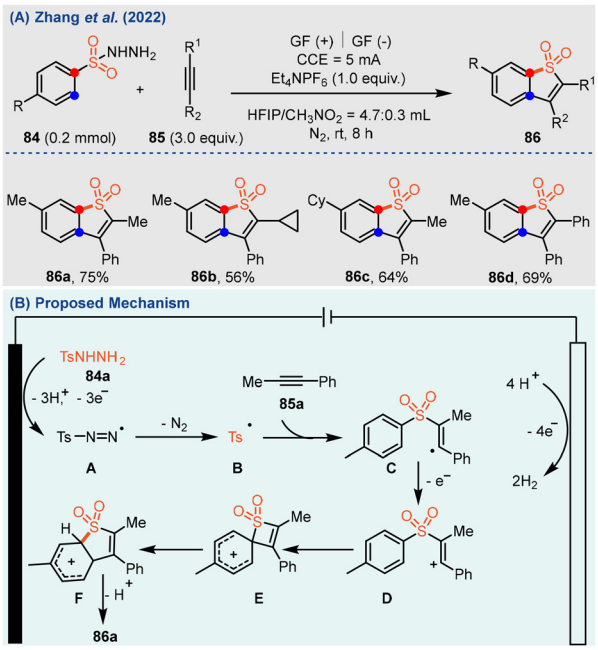
(**83a**). Radical (**D**) may generate the corresponding carbocation (**G**) through single electron oxidation in path b. After cationic migration (**G** to **H**) and deprotonation, the migratory cyclization product (**83a**) is obtained.

In the same year, the Zhang group reported the synthesis of benzothiophene derivatives (**86**) *via* a migratory cyclization reaction between sulfonyl hydrazides and alkynes under electrochemical conditions (Scheme 33A).[100] The experimental results indicate that the reaction proceeds through an intermediate quaternary spirocyclisation, ultimately leading to the migratory cyclization process. Computational research has revealed the selectivity and compatibility of drug molecules and demonstrates the potential applications of the protocols. The reaction has good substrate tolerance, and the target product can be obtained in moderate yields for various sulfonyl hydrazides (**86a** and **86c**) and alkynes (**86b** and **86d**).

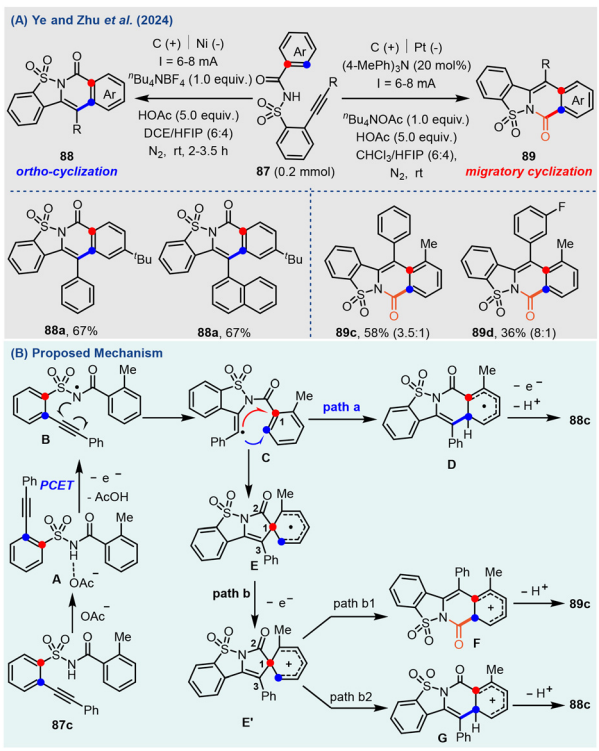
The potential mechanism was proposed (Scheme 33B). Initially, sulfonyl hydrazides (**84a**, E_{ox} = 1.80 V and 2.48 V *vs.* Ag/AgCl in MeCN) are deprotonated, oxidized at the anode, and released with nitrogen to generate sulfonyl radical (**B**). Then (**B**) reacts with (**85a**, E_{ox} = 2.67 V *vs.* Ag/AgCl in MeCN) to generate alkenyl radical (**C**), which is further oxidized by the anode to generate alkenyl cation intermediate (**D**). (**D**) undergoes intramolecular cyclization to form a quaternary spirocyclization species (**E**). Then, ring extension generation involving 1,2-S-migration occurs rapidly to form (**F**). Finally, further oxidation and deprotonation lead to the formation of the product (**86a**).

The free radical is a typical highly active species, but it can still form different products through selective transformation.[101] The key to achieving high selectivity in free radical reactions lies in effectively controlling the competitive reaction. Recently, Ye and co-workers reported the synthesis of a series of sultam-fused pyridinone derivatives (**88** and **89**) *via* electrochemical selective migratory cyclization and *ortho*-cascade cyclization of 2-alkynylbenzenesulfonamides (Scheme 34A).[102] It is found that the incorporation of an extra 2-methyl substituent leads to the selective migration of the acyl group of the key spirocyclic cation intermediate, thus promoting a cascade migration cyclization process.

The potential mechanism was proposed based on DFT calculations (Scheme 34B). Firstly, the N–H bond in the substrate (**87c**) preferentially combines with acetate to form intramolecular hydrogen bonds, and then the nitrogen radical (**B**) is generated at the anode by PCET. Subsequently, intramolecular cyclization occurs rapidly to obtain carbon radical (**C**). Then, there are two possible reaction pathways. In the first reaction pathway (path a), the intermediate (**C**) attacks the *ortho*-position of the benzene ring to undergo radical cyclization, which is further oxidized at the anode and then dehydrogenates to obtain the cyclization product (**88c**). Another reaction pathway (path b) is that the intermediate (**C**) attacks the carbon atom (C1) to obtain the spiro radical intermediate (**E**), which is further oxidized into a cationic species (**E′**). Subsequently, the cationic species (**E′**) undergoes C1–C2 bond cleavage and recombination to obtain the intermediate (**F**) which then dehydrogenates to obtain the product of acyl migration (**89c**). If the C1–C3 bond of the cationic species (**E′**)



Scheme 33 Electrochemically promoted synthesis of benzo[*b*]thiophene-1,1-dioxides.



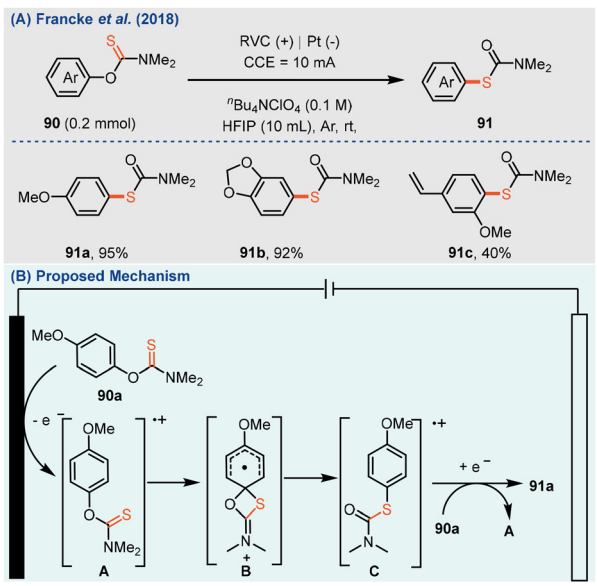
Scheme 34 Electrochemical migration *versus ortho*-cyclization of 2-alkynylbenzenesulfonamides.

cleaves, the intermediate (**G**) is obtained. Finally, the cyclization product is obtained by a deprotonation process (**88c**).

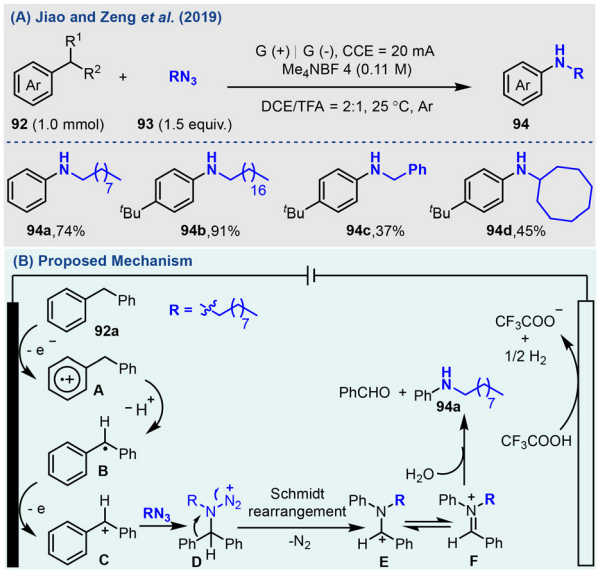
5. Miscellaneous rearrangements

The rearrangement of *O*-aryl thiocarbamate to *S*-aryl thiocarbamate at high temperatures is commonly called the Newman–Kwart rearrangement (NKR).[103] The conventional approach necessitates the utilization of elevated temperatures (>200 °C). In 2018, Francke *et al.* reported that electrolytic *O*-aryl thiocarbamate can be rearranged to obtain *S*-aryl thiocarbamate under constant current conditions (Scheme 35A).[104] A variety of *S*-aryl thiocarbamate derivatives (**91a–c**) can be obtained at room temperature with moderate to excellent yields. Meanwhile, continuous-flow electrochemical synthesis can achieve almost quantitative yields without using electrolytes, which proves the potential application value of this synthesis strategy. The mechanism study shows that the substrate (**90a**) is oxidized to radical cation (**A**) at the anode. Then (**A**) undergoes intramolecular cyclization and selective cleavage of the C–O bond occurs to form intermediate (**C**). Ultimately, the desired product (**91a**) is achieved through a reduction process, which may occur *via* reverse electron transfer (BET) or a radical chain mechanism (**91a**, Scheme 35B).

The formation of oxidized C–N bonds by C–H/C–C bond cleavage has aroused great interest from scientists, and this synthetic strategy has been widely used in the synthesis of pharmaceutical intermediates and materials.[105] In 2019, Jiao and co-workers reported the synthesis of aniline derivatives (**94a–d**) by electrochemical oxidative cleavage of C–C bonds of alkylarenes (Scheme 36A).[106] This strategy uses a cheap and durable graphite plate as the electrode and can be carried out



Scheme 35 Electrochemical Newman–Kwart rearrangements.



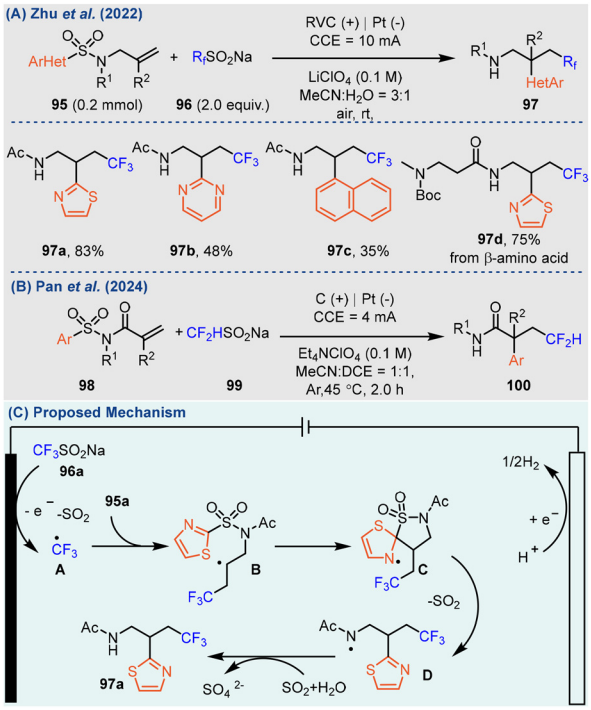
Scheme 36 Electrochemical oxidative C–C bond amination of alkylarenes.

without using any external catalyst or oxidant. The protocol is green, sustainable, efficient, and easy to operate.

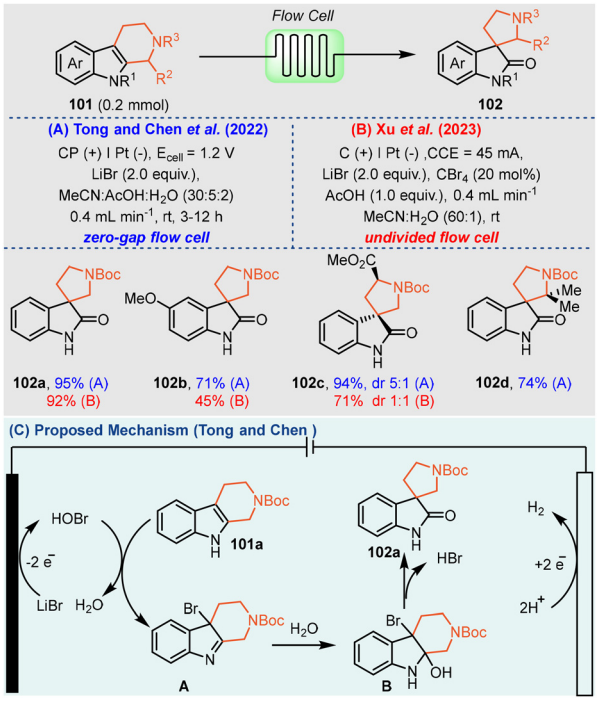
The mechanism studies showed that the substrate (**92a**, E_{ox} = 2.05 V and 2.39 V *vs.* $Ag/AgNO_3$ in MeCN) is oxidized at the anode, thus generating free radical cation (**A**). Subsequently, benzyl radical (**B**) is generated by deprotonation, which is further oxidized to form intermediate cation (**C**). Then, nucleophilic organic azides (**93**) attack cation (**C**) to produce (**D**). Next, intermediate (**E**) is formed by a Schmidt-type rearrangement of intermediate (**D**), and dinitrogen gas is released as the driving force. Finally, isomerization and hydrolysis produce alkylanilines (**94a**) and benzaldehydes (Scheme 36B).

Heteroarylethylamine compounds exhibit good biological activity and have been widely used in medicine and agricultural chemicals.[107] In 2022, Zhu and co-workers reported the synthesis of various β-heteroaryl-γ-trifluoromethylamine derivatives by electrochemically promoting the heteroaryltrifluoromethylation reaction of allylamine (**97**, Scheme 37A).[108] The synthetic strategy demonstrates good substrate tolerance and enables the migration of various heteroaryl groups (**97a–c**) as well as the late-stage modification of bioactive compounds (**97d**).

The mechanism studies showed that CF_3SO_2Na (E_{ox} = 1.37 V *vs.* Ag/AgCl in MeCN) is initially oxidized at the anode, releasing SO_2 to obtain CF_3 radical (**A**). Subsequently, the radical (**A**) is added to the double bond of the substrate (**95a**) to form the radical (**B**). Through intramolecular radical cyclization, the spirocyclic intermediate (**C**) is obtained. Next, the intermediate (**C**) releases SO_2 through a Smiles rearrangement to generate nitrogen-free radical (**D**). Finally, the radical intermediate (**D**) is reduced by SO_2 in the aqueous solution to obtain the product (**97a**, Scheme 36C). Recently, the Pan group reported the electrochemical synthesis of



Scheme 37 Electrochemical Smiles rearrangements.

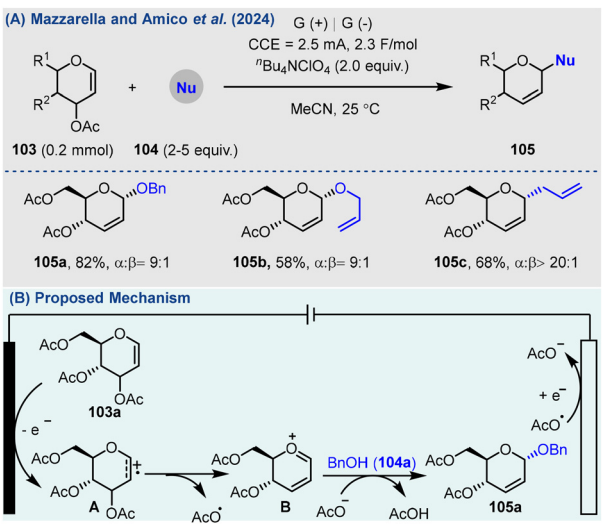


Scheme 38 Synthesis of spirooxindoles by electrochemical rearrangements.

β-difluoromethylamide compounds (**100**) from *N*-benzenesulfonylacrylamide and difluorine reagents (Scheme 37B).[109]

The spirooxindole skeleton exists widely in many natural products and biologically active molecules.[110] Most of the traditional syntheses of this molecular skeleton require the oxidative rearrangement of indole using chemical oxidants.[111] However, these chemical oxidants are dangerous and toxic and will produce stoichiometric harmful chemical waste. In 2022, Tong *et al.* reported an electrochemical oxidation rearrangement of tetrahydro-β-carbolines in a zero-gap flow cell to synthesize spirooxindole derivatives (Scheme 38A).[112] Almost simultaneously, the Xu group also reported the synthesis of spirooxindoles by electrochemical rearrangement in an undivided flow cell (Scheme 38B).[113] These synthetic strategies feature a good substrate scope, and various spirooxindole derivatives (**902a–d**) were obtained with moderate to excellent yields. The mechanistic investigations revealed that LiBr is oxidized to HOBr at the anode. Then, HOBr oxidizes the substrate (**101a**) to bromo-indoline intermediate (**A**). After the addition of water, spirobenzindole (**102a**) is produced through a semi-pinacol rearrangement (Scheme 38C).

The Ferrier rearrangement (FR) is a nucleophilic substitution with an allylic rearrangement, resulting in the conversion of glycal into a 2,3-unsaturated glycosyl derivative.[114] This strategy has been widely used in the synthesis of many natural products.[115] Recently, Mazzarella *et al.* reported an electrochemically promoted Ferrier rearrangement to synthesize a variety of unsaturated glycosyl derivatives (Scheme 39A).[116] This synthetic strategy exhibits wide substrate compatibility, and



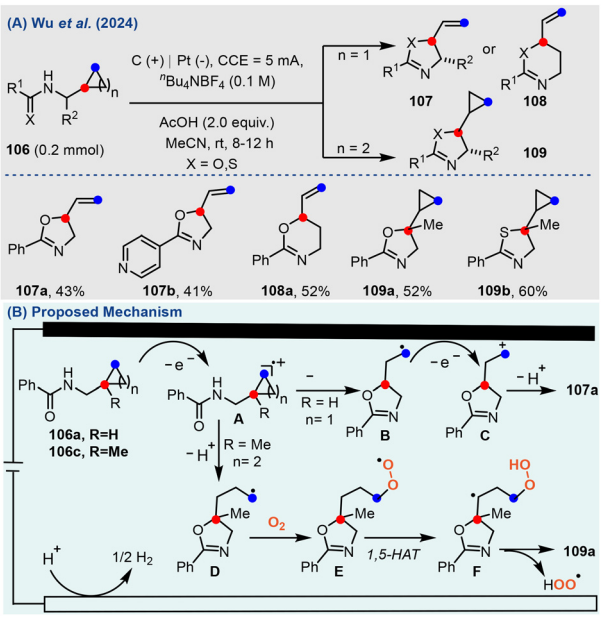
Scheme 39 Electrochemical Ferrier rearrangement of glycals.

various nucleophiles can provide 2,3-unsaturated glycosyl derivatives (**105a–c**) with high yields and excellent diastereoselectivities. This sustainable method is expected to expand the electrochemical application in sugar chemistry. The mechanism study shows that glucose (**103a**) generates radical cation (**A**) through single electron oxidation at the anode. Subsequently, the acetoxy group is lost, and it evolves into an oxonium species (**B**). The substrate (**104a**) reacts with the inter-

mediate (**B**) by deprotonation to form the product (**105a**, Scheme 39B).

Small cycloalkanes have moderate ring strain and usually require dense functionalization to induce the bias or distal activation of (hetero) aromatic rings *via* single-electron oxidation for relieving the tension.[117] Very recently, Wu and coworkers reported that a variety of oxazoline and oxazine derivatives (**107a–108a**) were synthesized by electrochemical oxidation directly activating alkyl cyclopropanes/butanes (Scheme 40A).[118] This strategy applies to a wide range of substrates. Notably, products derived from cyclobutanes undergo formal ring contraction to cyclopropanes (**109a** and **109b**). This electrochemical synthesis strategy marks significant progress in the skeleton rearrangement reactions driven by the strain release of moderately strained rings and provides a sustainable and efficient synthetic route for the construction of complex heterocyclic compounds.

The mechanism studies showed that cyclopropane and cyclobutane in substrates (**106a**, E_{ox} = 2.16 V and 2.30 V *vs.* Ag/AgCl in MeCN) and (**106c**) are oxidized at the anode to produce radical cation (**A**). Subsequently, the radicals (**B**) and (**D**) are formed by an intramolecular cyclization reaction. The radical (**B**) is further oxidized at the anode to generate cation (**C**) and then deprotonated to generate oxazoline (**107a**). On the other hand, the radical (**D**) captures oxygen to form peroxy radical (**E**), forming carbon radical (**F**) through 1,5-hydrogen atom transfer (HAT). Subsequently, free radical (**F**) participates in the substitution to form a cyclopropyl ring (**109a**), and at the same time releases hydrogen peroxide free radical (Scheme 40B).



Scheme 40 Electrochemical rearrangement of alkyl cyclopropanes/butanes.

6. Conclusions

As a green synthesis method, electrochemical synthesis provides powerful support for exploring new reactions. In the past decade, there has been a growing number of reports on electrochemical rearrangements. This review mainly introduces electrochemically promoted functional group migrations, ring expansions, and migratory cyclization reactions. It is worth noting that electrochemical rearrangements can synthesize numerous molecular structures that are challenging to create using traditional methods. In particular, electrochemically promoted migratory cyclization reactions can often get unexpected results.

Although this field is still in the stage of vigorous development after a decade of progress, many reactions remain undeveloped, such as the discovery of new functional group migrations, enantioselective electrochemical rearrangements, and rearrangement reactions involving the retention of small molecules. However, we believe that with the rapid development of electrochemistry, this field will be gradually explored. More importantly, it highlights the unique charm of electrochemistry in exploring new reactions and will stimulate the further application of electrochemical synthesis strategies in the pharmaceutical and chemical fields.

Data availability

This is a review article with no new data. All the compounds have been reported before.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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