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Electrochemical C–H Functionalization for the Construction of C–O Bonds: A Comprehensive Review

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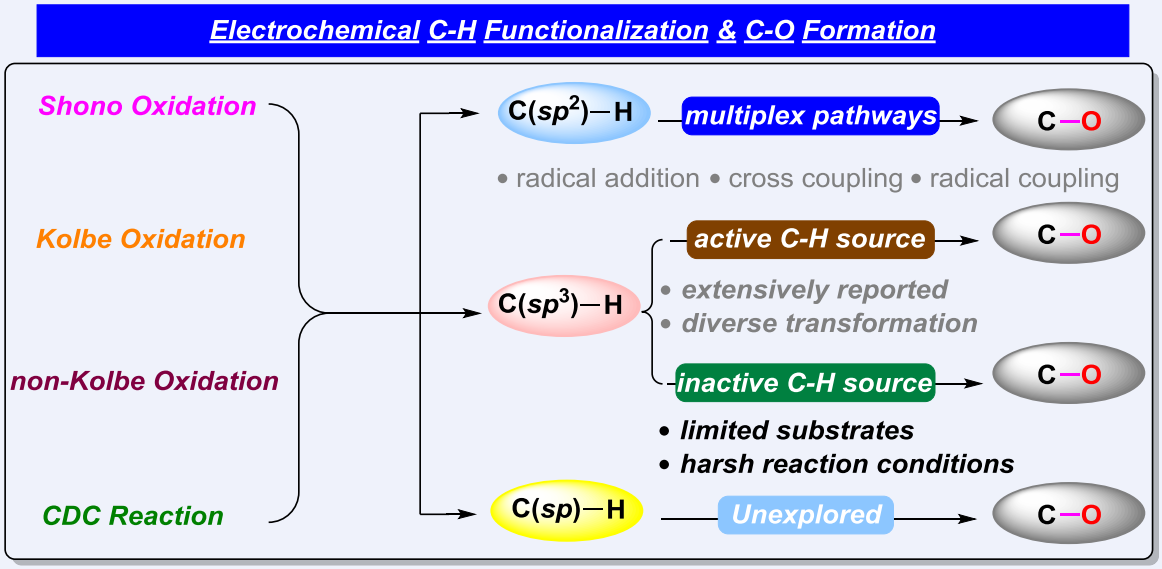
Keywords

Electrochemical synthesis | C–H functionalization | C–O formation | Radicals | Sustainable chemistry | Green chemistry

Comprehensive Summary



The topic of C–H functionalization and C–O formation is the most important area in organic synthesis. Traditional methods are very limited due to the necessary external oxidants, whereas the rapidly developing electrochemical synthesis uses electrons as internal redox reagents. Consequently, electrochemical C–H functionalization for the construction of C–O bonds has emerged as an active area of research. This review categorizes recent reports on the electrochemical formation of C–O bonds with various C–H sources based on the hybridization (sp^3, sp^2) of the carbon atoms involved. Potential readers will gain a more comprehensive understanding of advances in the field through this review.

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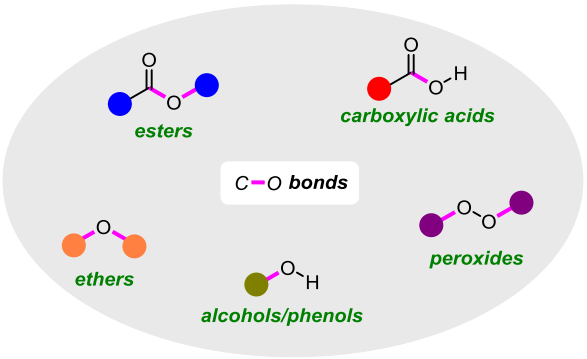
Key Scientists

Contents

1. Introduction

Compounds containing C–O bonds, such as esters, ethers, alcohols, *etc*., comprise the majority of the family of organic compounds (Scheme 1). As an essential component of most organic compounds, the C–O bond is one of the most frequently formed and transformed chemical bonds in organic reactions.[1-5] Given the broad application of the C–O bond in natural products,[6-7] synthetic pharmaceuticals,[8-9] photoelectric materials,[10-11] agricultural chemicals[12-13] and other fields, the efficient construction of the C–O bond has become a focal topic in organic synthetic chemistry. To date, numerous methods have been developed using different reagents and catalysts under diverse conditions to access C–O bonds.[14-18]

Scheme 1 Organic compounds containing C–O bonds

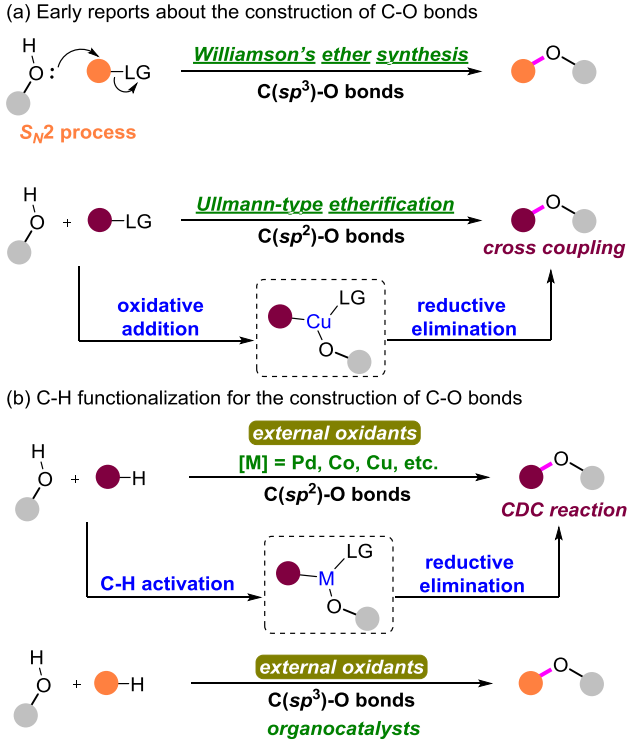


In early reports, the well-known Williamson ether synthesis exemplifies a series of methods that use C(sp^3)-LG (leaving groups) and oxygen nucleophiles to construct C–O bonds *via* the classic S_N2 mechanism.[19-22] However, the requirement for basic conditions and substrates free of other incompatible nucleophilic groups limits the further application of this approach for C(sp^3)-O bond formation (top of Scheme 2a). Meanwhile, Ullmann-type etherification reaction employes substrates with C(sp^2)-LG to construct C(sp^2)-O bonds through copper-catalyzed cross-coupling.[23-27] Although significant progress has been made, the reliance on high reaction temperatures and rare ligands makes these methods challenging to access in some cases (bottom of Scheme 2a). Additionally, the C-LG substrates involved are often not readily available without a prior C–H functionalization process, which results in low step- and atom-economy for these strategies when forming C–O bonds. Moreover, achieving selective C–H pre-functionalization to prepare desired materials for complex molecules can be very difficult. Therefore, there is an urgent need for methods that use readily available substrates to form C–O bonds.

In comparison, C–H sources are inexpensive and common starting materials for various transformations. Generally, C–H bond with high dissociation energy and redox potential is one of the most stable covalent bonds. C–H bonds at different sites usually own diverse reactivity. Compound with multiple C–H bonds can be very difficult to proceed reactions chem-selectively and efficiently. For inactive C–H source, the transformation can't occur in the absence of powerful catalyst and harsh conditions. Thus, C–H functionalization is full of challenges and fascination.

Direct C–H functionalization has been successfully utilized to construct diverse covalent bonds.[28-42] Among these, transition metal catalysts such as Pd,[43-47] Co[48-51] and Cu[52-55] have been applied to access C(sp^2)-O bonds *via* C–H activation process, as reported in the previous literatures (top of Scheme 2b). Additionally, organocatalytic pathways have also contributed to the formation of C(sp^3)-O bonds using C–H sources through polarity reversed process[56-59] (bottom of Scheme 2b). Notably, these oxidative methods for obtaining C–O bonds from C–H bonds rely on

Scheme 2 The construction of C–O bonds involving oxygen nucleophiles

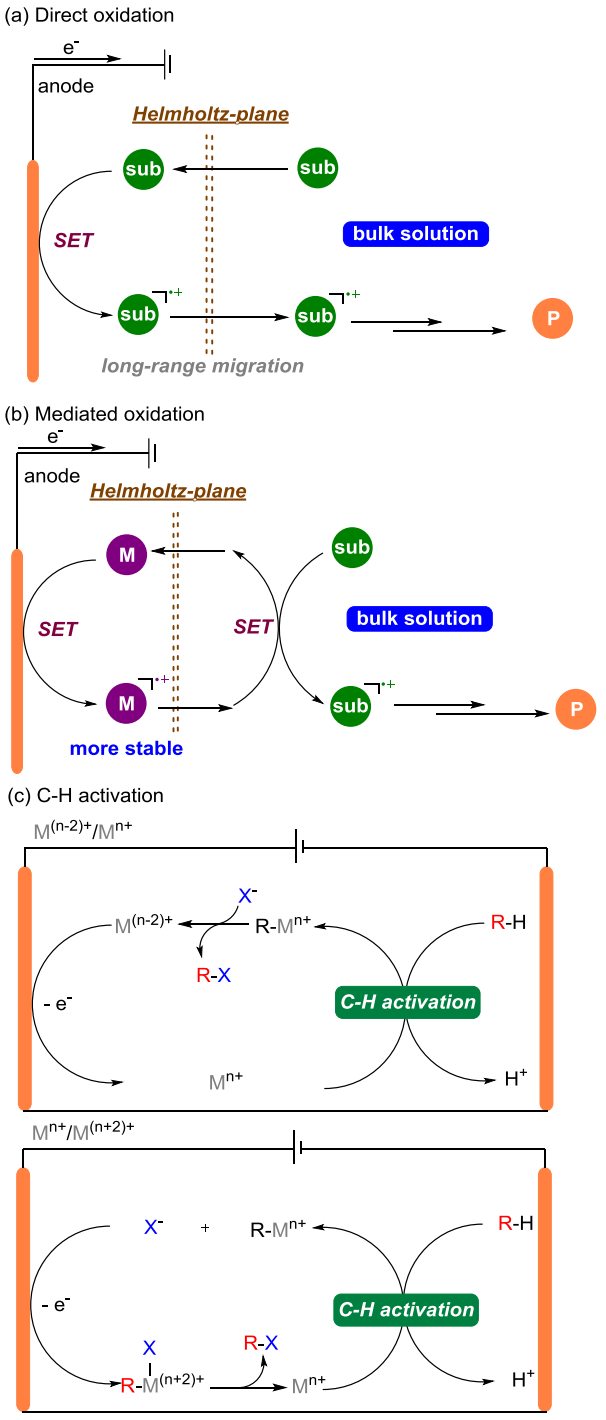


external oxidants, which theoretically produce stoichiometric wastes. The use of some expensive or hazardous oxidants is also detrimental to the application of these methods. Given the advantages of direct C–H functionalization, introducing a green oxidative pathway instead of traditional oxidants may offer an alternative approach to accessing C–O bonds.

Electrochemical organic synthesis has been rapidly developed in recent years. This clean strategy can meet the requirements of green chemistry and sustainable synthesis.[60-61] With increasing interests from organic chemists, electrochemical synthesis has made significant progress in various fields, such as asymmetric catalysis,[62-63] total synthesis,[64-65] industrial production,[66] and so on. Electrons are used as internal redox reagents, eliminating the need for additional oxidants in electrochemical reactions, thereby reducing waste production and improving atom-economy of transformations. Electrochemical oxidation typically proceeds *via* two pathways: 1) When single electron transfer (SET) occurs between the substrate and the anode, the direct oxidation of the substrate is achieved to obtain the corresponding cation radical (Scheme 3a); 2) When a redox mediator is employed, the initial oxidation of the mediator provides a relatively stable intermediate that accesses the bulk solution, which then oxidizes the substrate to drive the reaction (Scheme 3b). With the assist of transition metal catalysts, C–H activation could be enabled by different electrochemical ways (Scheme 3c). On the one hand, lower valent metal obtained from reductive elimination would be oxidized to complete the catalytic cycle; on the other hand, intermediate with higher valent metal gained at anode might proceed reductive elimination to deliver the product and regenerate catalyst.

Overall, electrochemical C–H functionalization is a powerful strategy with unique advantages for efficiently and sustainably constructing C–O bonds. Comparing with classic pathways, electrochemical synthesis can avoid any utilization of external oxidants to improve atom-economy. The electrochemical pathway is environmentally friendly and sustainable for the production of diverse compounds. But in some cases, substrates with sensitive groups can't survive well from electrochemical conditions because of the unmanageable over-oxidation, while many traditional oxidants with excellent selectivity may be available in the classic

Scheme 3 Pathways in electrochemical oxidation



pathway.

As a result, the electrochemical C–O formation using C–H sources has become a burgeoning field of research. It is evident that some relevant reviews have been published previously. In 2020, Mo and co-workers focused on electrochemical C–X bond formations, but they often included only a cursory discussion of formal addition reactions rather than a detailed description of C–H functionalization.[67] There is also a notable absence of coverage on methods involving metal catalysts. In the same year, reviews by Ackermann[68] and Mei[36] presented examples involving transition-metal catalyzed C–H activation, while cases based on organic catalysis and direct oxidation were not included. Consequently, there is an urgent need for a comprehensive review that highlights the recent advances in electrochemical C–O formation, encompassing both metal-catalyzed and metal-free pathways. This review will systematically categorize the latest advancements in electrochemical C–H alkoxylation, hydroxylation, acyloxylation, and so on, focusing on the hybridization states (sp^3 or sp^2) of the C–H bonds targeted. By meticulously organizing these recent developments, this review aims to provide readers with a more holistic understanding of the progress made in the domain of electrochemical C–O formation.

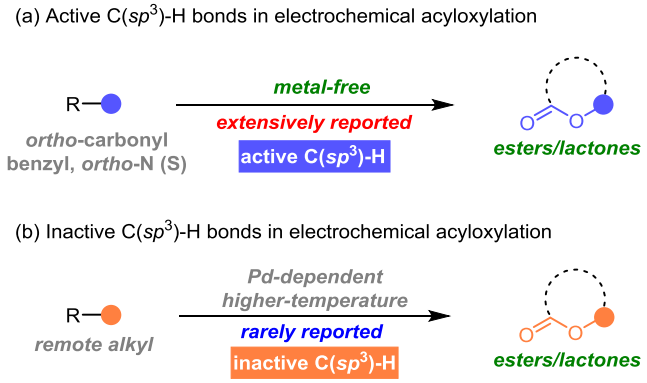
2. Electrochemical C–H Acyloxylation

2.1. Electrochemical C(sp^3)-H acyloxylation

2.1.1. Acyloxylation of active C–H bonds. The electrochemical acyloxylation of C–H bonds with carboxylic acids as oxygen sources is a crucial pathway for constructing C–O bonds. In fact, a series of esters and lactones have been obtained through electrochemical oxidation. Various C–H sources can be converted to C–O bonds *via* direct or indirect oxidation, metal catalysis or other electrochemical processes. Due to the difference of C(sp^2)-H and C(sp^3)-H bonds, the corresponding electrochemical C–H acyloxylation pathways are usually not similar. Thus, the involved information is presented separately based on the reactivity of C–H bonds.

Commonly, C(sp^3)-H bonds, known for their higher stability, exhibit lower activity in various chemical reactions. For electrochemical C(sp^3)-H acyloxylation, the reaction sites are relatively limited to active C–H bonds, such as benzyl, *α*-carbonyl and *α*-heteroatom C–H bonds (Scheme 4a). With higher reactivity of substrates, which can be converted to reactive intermediates by direct or indirect oxidation, a series of products can be obtained under different conditions. But for inactive C(sp^3)-H bonds, like remote alkyl, the transformation can be very difficult to access. Even with participation of metal catalysts, harsh conditions are critical in electrochemical acyloxylation according to several examples (Scheme 4b).

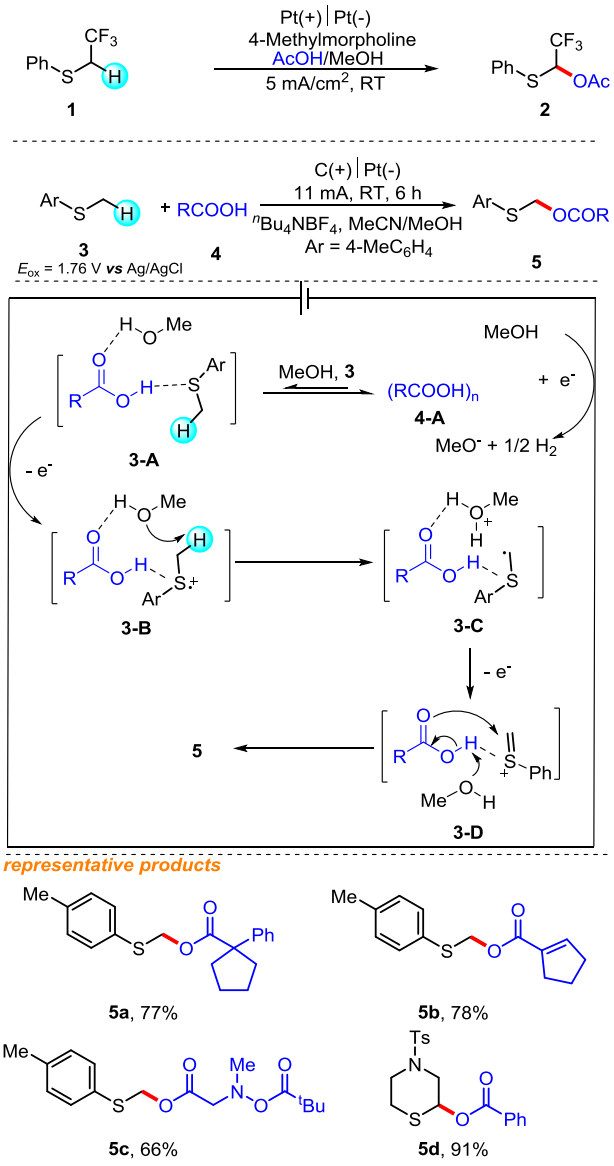
Scheme 4 Electrochemical acyloxylation of C(sp^3)-H



For example, *ortho*-heteroatom C–H bonds usually serve as C–H sources for acyloxylation cases. Due to their greater electronegativity, heteroatoms would be electron-enriched to affect the activity of *ortho*-C–H bonds and stabilize intermediates. In 2009, Nakajima and co-workers reported the C(sp^3)-H acyloxylation of thioether **1**,[69] which contained a critical trifluoromethyl moiety to make the C–H bond more active. With the specific porous polystyrene-supported 4-methylmorpholine as a base, the desired product **2** could be obtained effectively (top of Scheme 5). Furthermore, in 2021, Lei's group used ordinary aryl thioether **3** as a substrate to realize the C–H acyloxylation with carboxylic acid **4** as nucleophile.[70] Corresponding product *α*-acyloxy thioether **5** could be synthesized *via* electrochemical C–H/O-H cross-coupling. In the proposed mechanism, the cluster **4-A** could form complex

3-A with methanol and substrate **3**. The anodic oxidation of **3-A** was promoted by intermolecular hydrogen bonding to form radical cation **3-B**. Then the internal deprotonation occurred to obtain radical **3-C**, which was oxidized to thionium ion **3-D**. The product **5** was obtained from the nucleophilic addition while the hydrogen was released at the cathode (bottom of Scheme 5).

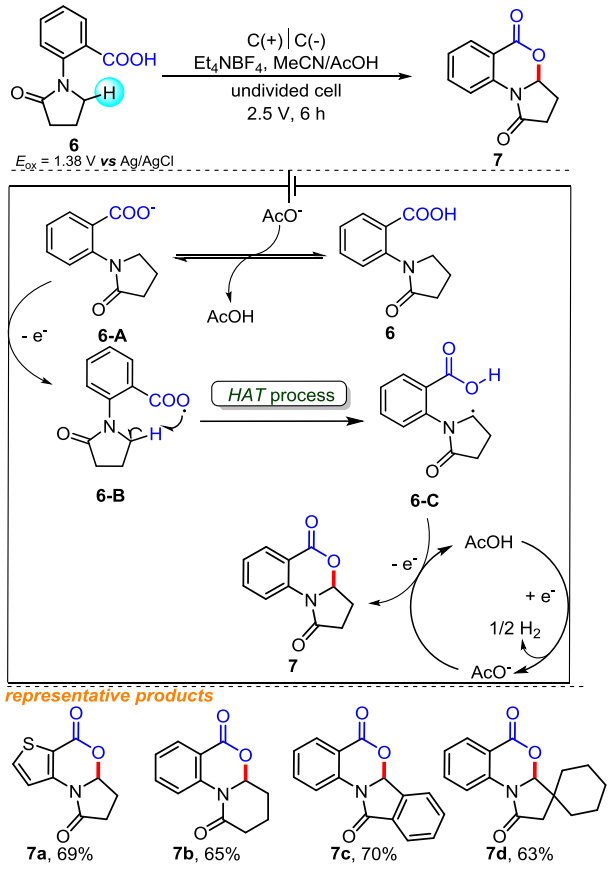
Scheme 5 C–H acyloxylation of thioethers



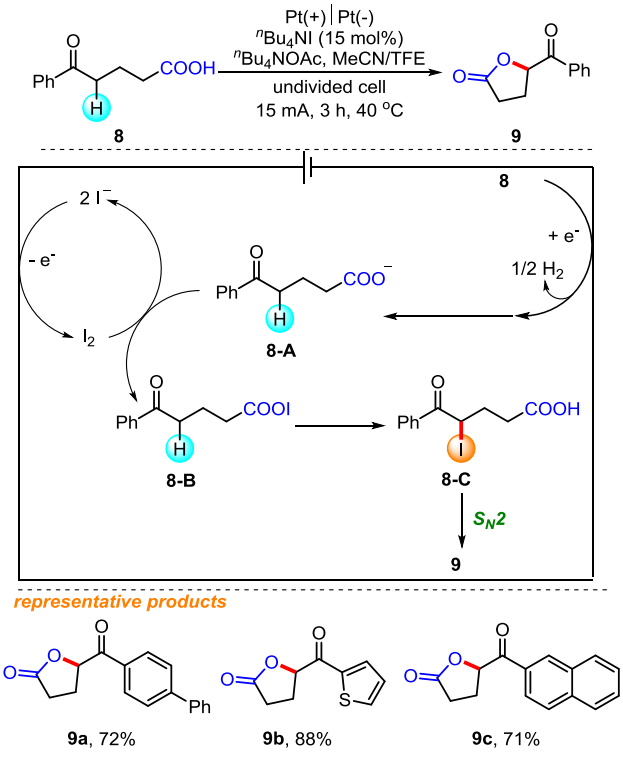
Azaheterocycles were also viable C–H sources for the electrochemical acyloxylation. For example, in 2024, Zhang and co-workers found that the C(sp^3)-H lactonization of a pyrrolidone moiety could be achieved *via* C–H/O-H cross coupling.[71] In their mechanism, functionalized benzoic acid **6** could be reversibly deprotonated to form carboxylate **6-A**. Then the oxidation of **6-A** provided carboxyl radical **6-B**, which may undergo intramolecular HAT (hydrogen atom transfer) to form *α-N* radical **6-C**. The subsequent oxidative cyclization proceeded to generate the final product **7**, accompanied with the release of a proton (Scheme 6).

ortho-Carbonyl C–H bonds with definite acidity seemed to be suitable materials for the C(sp^3)-H acyloxylation *via* organocatalytic pathway according to previous reports. In 2017, Xu's group discovered the C–H lactonization of substrate **8** using ^{n}Bu$_4$NI as a catalyst (Scheme 7).[72] As described, the reduction of carboxylic acid **8** generated anion **8-A**, while iodine was produced *in situ* by the oxidation of ^{n}Bu$_4$NI. Reaction of **8-A** and iodine would create the acyl hypoiodite **8-B** and iodine ion together. Accompanying the intramolecular iodination process, **8-B** was converted to intermediate **8-C** with an active C–I bond. Finally, nucleophilic substitution proceeded to give the product **9**.

Scheme 6 C–H lactonization of azaheterocycle

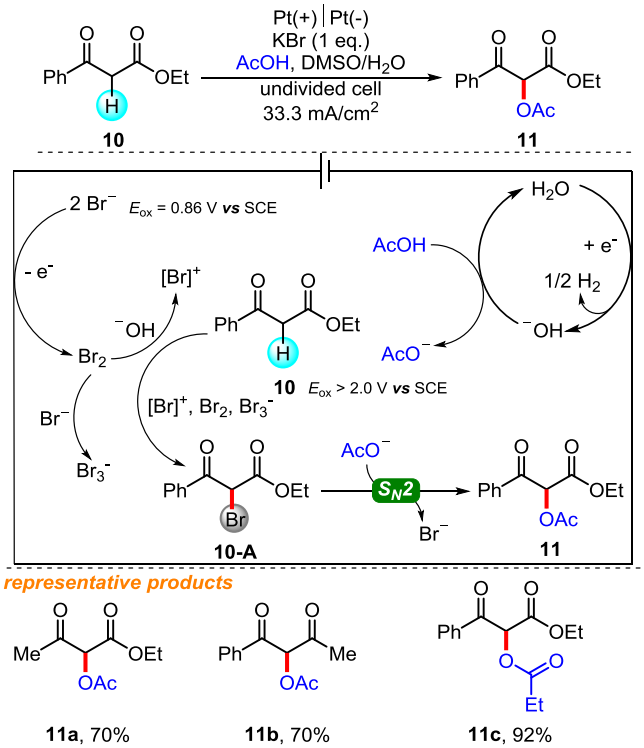


Scheme 7 *ortho*-Carbonyl C–H acyloxylation



In 2019, Terent'ev realized α-carbonyl C–H acyloxylation using β-ketoesters or β-diketones as C–H reagents, which are converted to bromides as intermediates *in situ via* electrochemical oxidation (Scheme 8).[73] In this transformation, bromide anion was initially oxidized to form molecular bromine, while the hydroxide ion was released at cathode. With the assistance of hydroxide ion and bromide anion, various bromides could be prepared such as Br_3^- and $[Br]^+$. The bromides convert substrate **10** to the more active **10-A** with a C–Br bond. Subsequent nucleophilic substitution proceeded between **10-A** and acetate ion to generate product **11**. Meanwhile, based on Wirth's report in the same year,[74] chiral iodoarene was also effective catalyst for the electrochemical enantioselective acyloxylation of α-carbonyl C–H bond (Scheme 9). The chiral intermediate **12-A** with a C–I bond could be provided by the reaction with substate **12** and catalyst **14**. The intramolecular nucleophilic substitution afforded final product **13** and regenerated catalyst **14** under anodic oxidation. When alcohol or H_2O was used as nucleophile instead of carboxylic acid, the enantioselective C–H alkoxylation and hydroxylation were also realized.

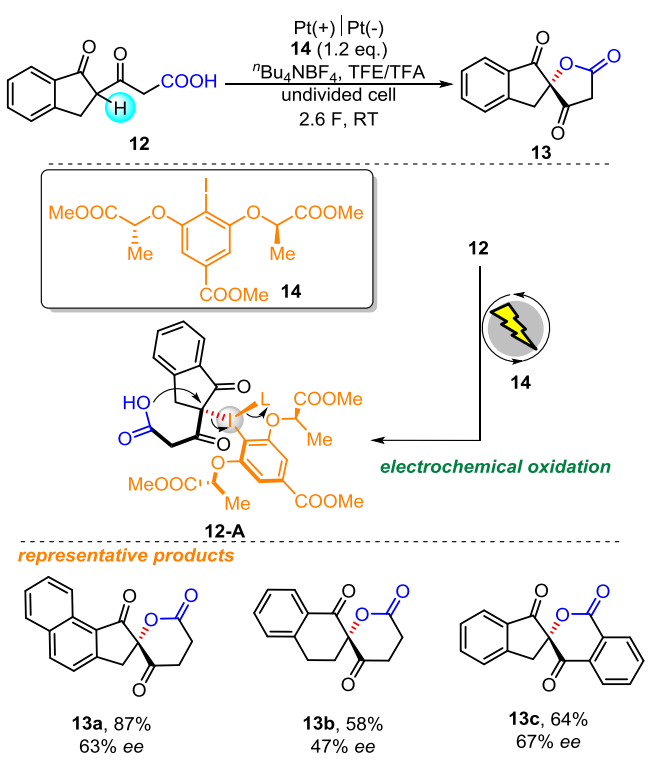
Scheme 8 C–H acyloxylation of methylene



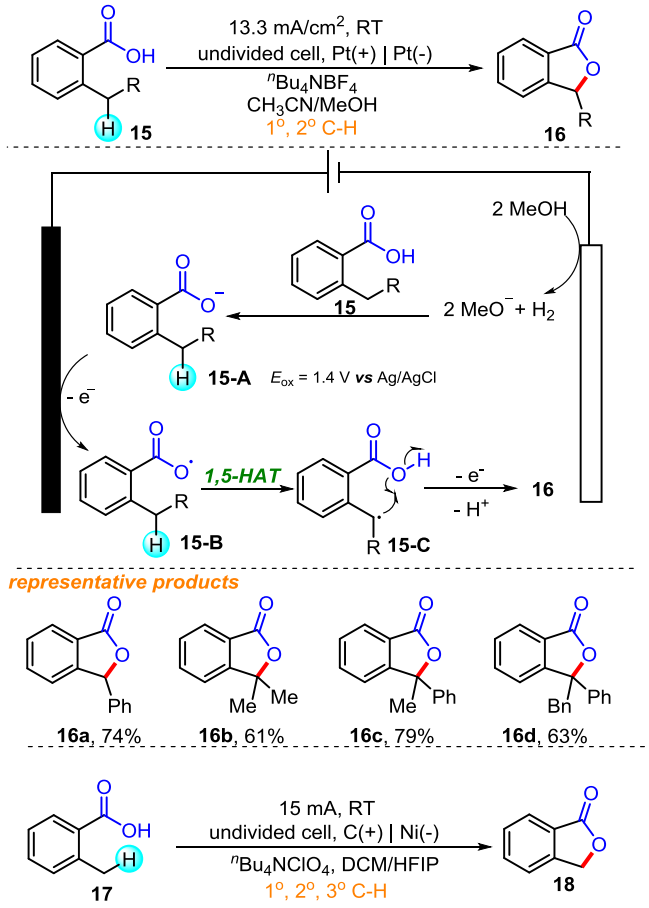
Benzyl C–H bonds were more applicable partners for the electrochemical C–H acyloxylation with relevant reports. The benzyl radical and cation which might be involved should be stable *via* p-π conjugation to make the benzyl C–H acyloxylation achievable. For example, in 2018, Zeng's group reported the benzyl C–H lactonization of 2-alkylbenzoic acid **15** by electrochemical oxidation in the absence of any catalysts and mediators (top of Scheme 10).[75] During the transformation, the carboxylic acid **15** was deprotonated by MeO^- obtained from methanol at cathode. The oxidation of carboxylate **15-A** occurred at anode to form the carboxyl radical **15-B**. Then the intramolecular 1,5-HAT process would provide a stable benzyl radical **15-C**, which underwent oxidation and deprotonation to gain the desired lactone **16**. Additionally, this transformation could be realized by Park in 2023 with 1°, 2° and 3° benzyl C–H sources **17** driven by direct oxidation at the anode (bottom of Scheme 10).[76]

Besides, the intermolecular C–H acyloxylation could also be accessed with various benzyl C–H sources. In 2022, Lennox and

Scheme 9 C(sp^3)-H enantioselective acyloxylation



Scheme 10 Benzyl C(sp^3)-H lactonization

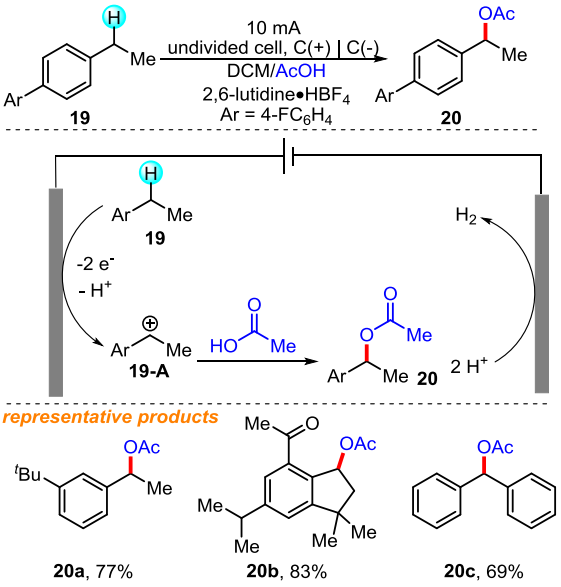


co-workers developed a method to realize the benzyl C–H acyloxylation with external carboxylic acids as nucleophiles (Scheme 11).[77] For the direct oxidation of substrate **19**, the continuous SET

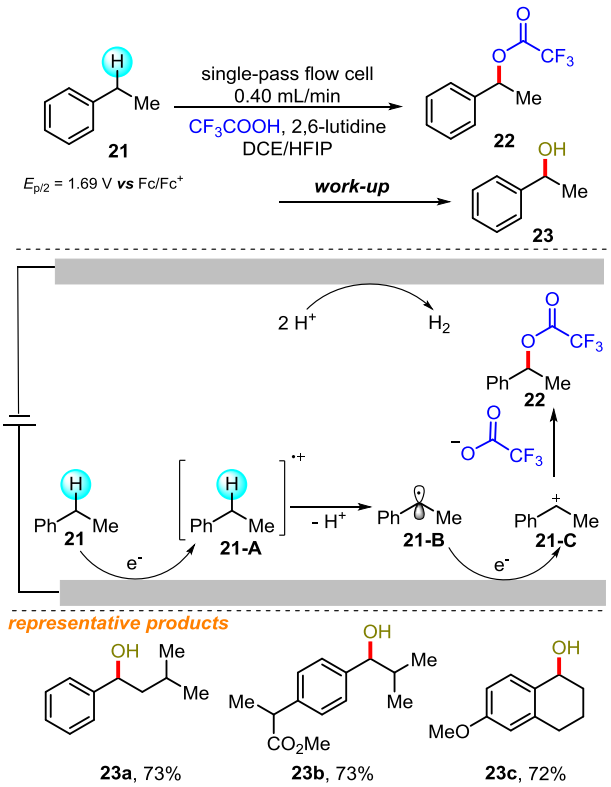
and deprotonation processes would generate the benzyl cation **19-A**. The nucleophilic addition of AcOH to the electrophilic intermediate **19-A** brought final ester **20** and a leaving proton. The free protons were reduced to release hydrogen at the cathode. In addition, Xu's group utilized the strategy of continuous flow electrochemistry to actualize the benzyl C–H acyloxylation practically and site-selectively in 2023 (Scheme 12).[78] Various trifluoroacetates were obtained as active intermediates to be converted to corresponding alcohols in the work-up process. In their proposed mechanism, which was similar to Lennox's, the substrate **21** was initially oxidized to radical cation **21-A**. The radical cation **21-A** was prone to lose a proton to give the benzyl radical **21-B**. Along with another electron loss, **21-B** became benzyl cation **21-C** with the reactivity as an electrophile. With the participation of trifluoroacetate anion, the intermediate **21-C** was converted to intermediate **22** and the C–H acyloxylation was accomplished. The final benzyl alcohol **23** was obtained by aqueous workup of **22**.

What's more, the electro-photocatalytic method was also applied by Lambert to realize the C–H acyloxylation in 2022 (Scheme 13).[79] The involved mechanism contained the key SET process between the substrate **24** and photoexcited catalyst **TAC**$^{\bullet 2+*}$ to realize the benzyl C–H oxygenation. Based on their report, the primordial catalyst **TAC**$^{+}$ would be oxidized to generate **TAC**$^{\bullet 2+}$, which had a deep red color to be photoexcited to deliver **TAC**$^{\bullet 2+*}$ with excellent oxidation capacity. The intermolecular SET proceeded to convert the substrate **24** to its radical cation. The subsequent electrochemical or chemical transformations supported the target product **25**. Such benzyl C–H acyloxylation was also completed for the electrochemical *tri*-oxygenation of allyl arene **26** to deliver product **27** according to Shen in 2024 (Scheme 14).[80]

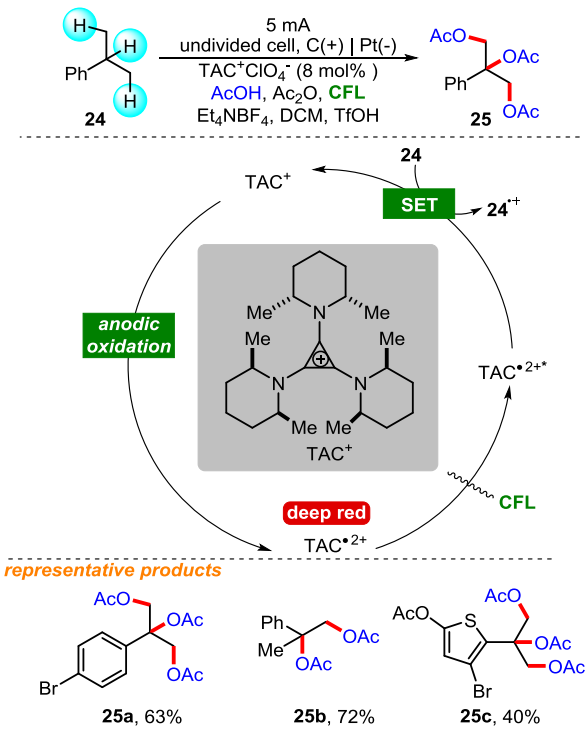
Scheme 11 Benzyl C(sp^3)-H acyloxylation



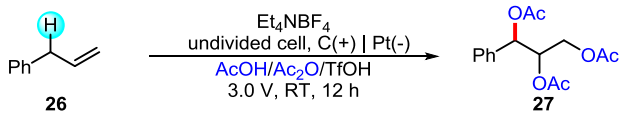
Scheme 12 Benzyl C–H acyloxylation for hydroxylation



Scheme 13 Electro-photocatalytic C–H acyloxylation



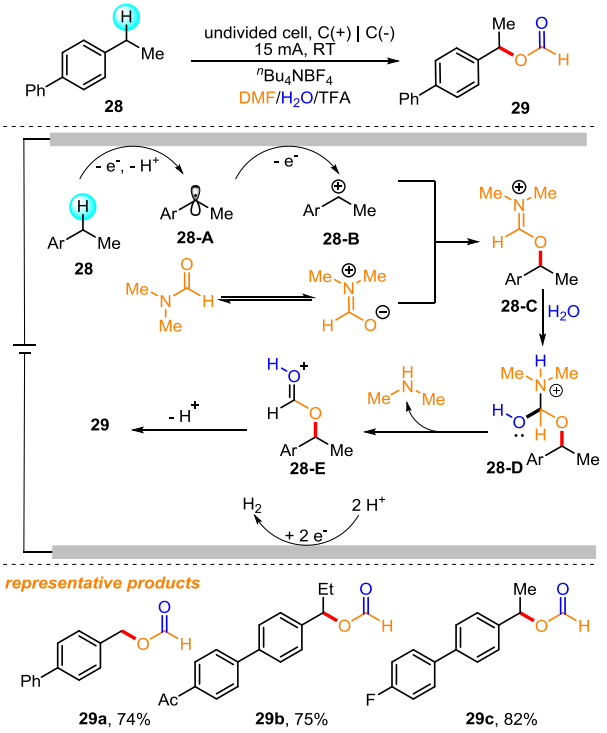
Scheme 14 *Tri*-acyloxylation of allylarene



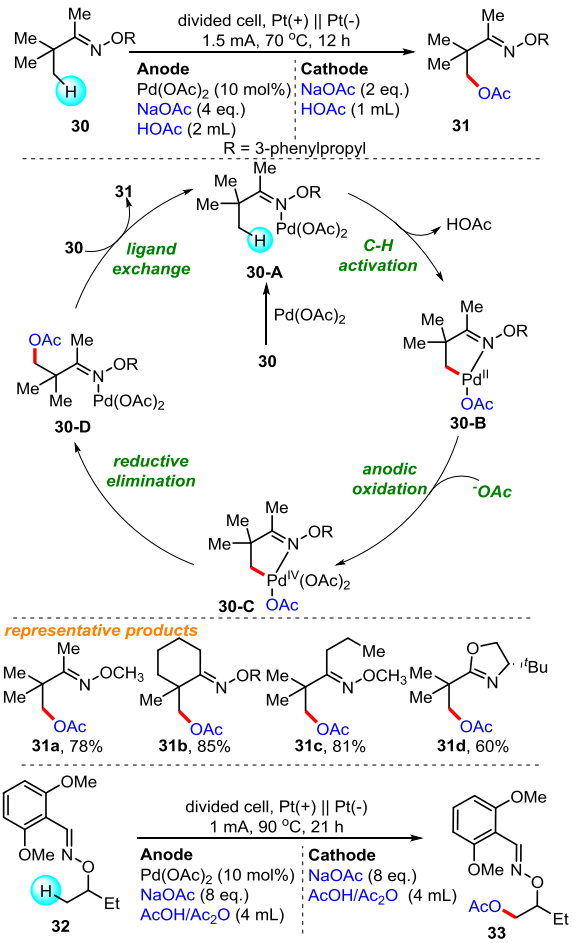
Not only the carboxylic acids, but DMF and H_2O could also serve as co-acyloxylation reagent for benzyl C–H bonds. In 2023, He's group reported an interesting case of C–H acyloxylation without any nucleophilic carboxylic acids (Scheme 15).[81] According to their report, the substrate **28** with a benzyl C–H bond would be converted to benzyl radical **28-A** *via* oxidation and deprotonation. Another SET process provided benzyl cation **28-B**. Meanwhile, the tautomeric isomer of DMF reacted with **28-B** to obtain iminium **28-C** as intermediate. The hydrolysis of **28-C** yielded ammonium **28-D**, which formed product **29** accompanied by the release of proton and dimethylamine.

2.1.2. Acyloxylation of inactive C–H bonds. Contrast to the diverse oxidation of reactive C–H bonds, once inactivated C–H

Scheme 15 Benzyl acyloxylation with DMF and H_2O



Scheme 16 Pd-catalyzed inactivated C–H acyloxylation



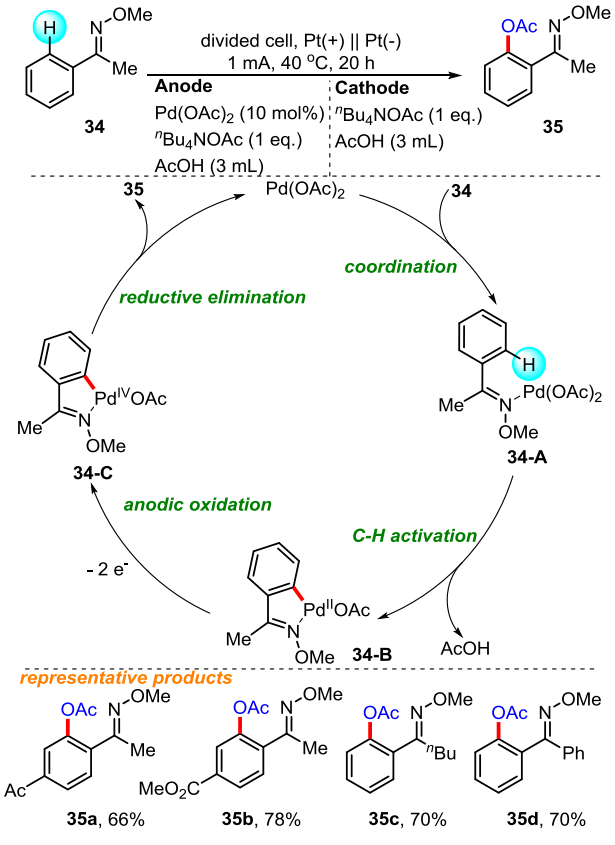
sources were used for the electrochemical acyloxylation, transition-metal catalyzed C–H activation may be the only efficient pathway so far. For instance, in 2017, Mei introduced an oxime ether moiety as the directing group into substrate **30** with a terminal tertiary butyl as inert C–H source (top of Scheme 16).[82] In the catalytic cycle, Pd catalyst would coordinate with oxime ether **30** to form complex **30-A**. The β-C–H activation proceeded to obtain the intermediate **30-B**. Anodic oxidation of central Pd(II) to Pd(IV) could deliver complex **30-C**. The high-valent Pd center was inclined to undergo reductive elimination to generate Pd(II) complex **30-D**, which exchanged ligands with another molecule **30** to give the final product **31** and regenerate **30-A** to complete the catalytic cycle. There was another case for the remote C–H acetoxylation of oxime ether **32** *via* Pd-catalyzed C–H activation reported by Kakiuchi in 2024 (bottom of Scheme 16).[83] The proximate catalytic cycle proceeded to obtain product **33**. In comparison, the same oxime ether moiety in their substrates seemed to be crucial in the C–H activation for the electrochemical acyloxylation. The higher temperature instead of room temperature and the utilization of divided cell also indicated the difficulty of this transformation.

2.2. Electrochemical C(sp^2)-H acyloxylation

2.2.1. C(sp^2)-H acyloxylation *via* CDC reaction. Similar to inactive C(sp^3)-H, C(sp^2)-H bonds were metal-dependent partly in the electrochemical C(sp^2)-H acyloxylation of arenes. Transition-metal catalyzed cross dehydrogenative coupling (CDC) reactions *via* C–H activation have been developed gradually to realize the desired transformation. Various catalysts contributed to the reaction in different ways. In the common process involving Pd, Co, Ru and Rh, the anodic oxidation contributed to the formation of high valent intermediate, which would undergo reductive elimination, the final product was then obtained. But in some examples about Co and Ru, the anodic oxidation occurred after the reductive elimination to regenerate the high valent metal as catalyst.

To access the site-selective C–H functionalization in arenes, directing groups are commonly pre-introduced to complex the metal catalysts. For example, in 2017, Mei and Zhang described a Pd-catalyzed acetoxylation of aryl C–H bond using oxime ether moiety as the directing group (Scheme 17).[84] The substrate **34**

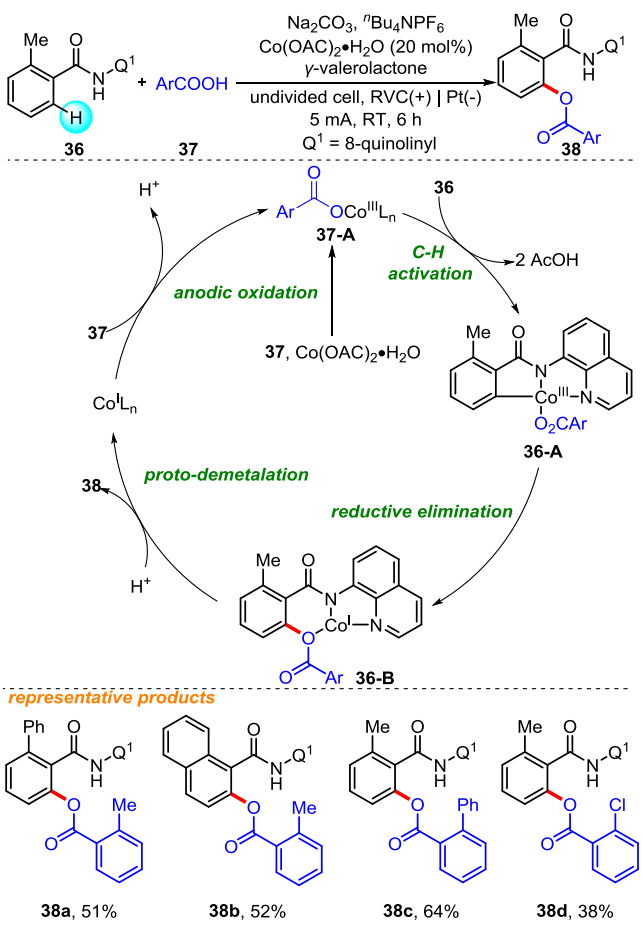
Scheme 17 Pd-catalyzed aryl C–H acyloxylation



was used to produce corresponding ether **35** in an H-type divided cell under 40 °C with AcOH as solvent. During the reaction, the coordination between oxime ether **1** and $Pd(OAc)_2$ delivered the complex **34-A**, followed by *ortho*-C–H activation to generate the intermediate **34-B**. The central metal Pd(II) of **34-B** would be oxidized at the anode to produce Pd(IV) complex **34-C**, which could then be converted to product **35** through a reductive elimination process. Meanwhile, the catalyst was released to complete the Pd(II/IV) catalytic cycle.

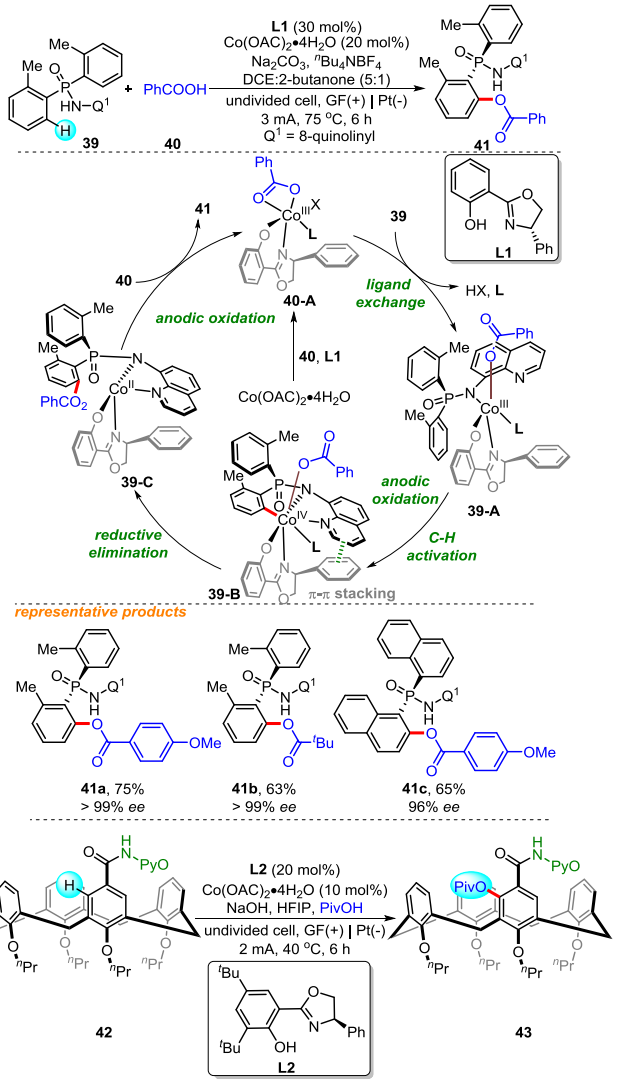
Cobalt-based catalysts have also proven effects for C(sp^2)-H acyloxylation in certain cases. In 2019, Ackermann's group reported an electrochemical C–H acyloxylation process using Co-catalysis (Scheme 18).[85] In the initial stage of the reaction, catalytical Co(III) species **37-A** was obtained from carboxylic acid **37** at anode. After the coordination of **37-A** with benzamide **36**, C–H activation proceeded with the assistance of carboxylates to provide complex **36-A**, which was then converted to Co(I) complex **36-B** *via* reductive elimination. The final product **38** was delivered through protonation, while the anodic oxidation of Co(I) species regenerated **37-A**.

Scheme 18 Co-catalyzed aryl C–H acyloxylation



In 2024, Ling and co-workers used phosphamide **39** as aryl C–H source, along with chiral Salox ligand **L1**, to achieve the desired product **41** *via* enantioselective C–H acyloxylation (top of Scheme 19).[86] According to the report, the additive $Co(OAc)_2$ was oxidized to provide Co(III) species **40-A** with the participation of **40** and **L1**. The complex **40-A** was allowed to exchange ligands with substrate **39** to form intermediate **39-A**, which could then undergo tandem anodic oxidation and enantioselective C–H activation to form the Co(IV) species **39-B**. Subsequent reductive elimination and ligand exchange occurred to generate product **41** and regenerate **40-A** through another anodic oxidation. In the same year, Niu's group accessed the enantioselective synthesis of chiral calix[4]arene **43** *via* an electrochemical Co-catalyzed aryl C–H acyloxylation.[87] With the chiral oxazoline ligand **L2**, various substrates **42** could be converted to form the corresponding calix[4]arenes **43** with excellent yields and enantioselectivity (bottom of Scheme 19). The proposed mechanism included proposed C–H activation and reductive elimination processes.

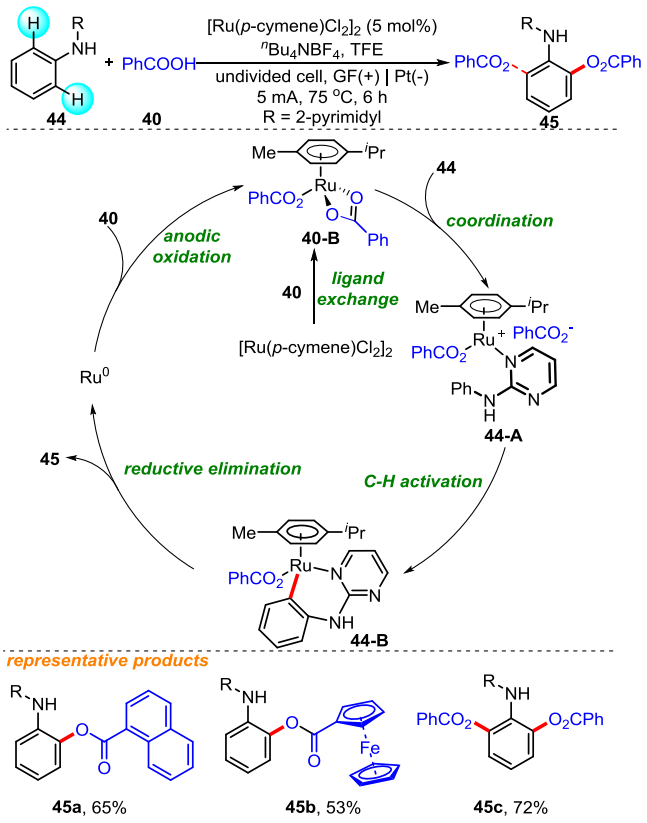
Scheme 19 Co-catalyzed enantioselective C–H acyloxylation



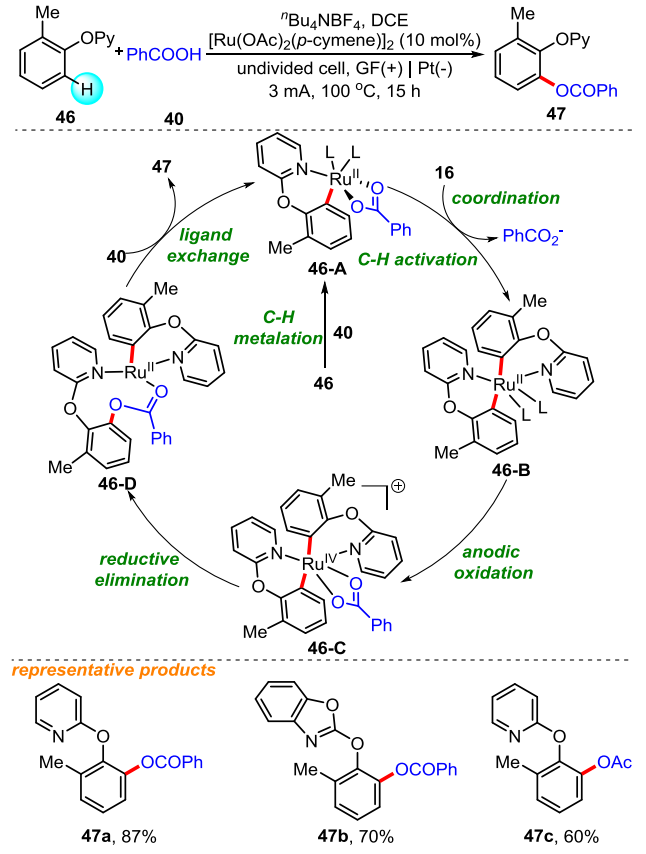
Besides, Ru, Rh-catalyzed C–H activations were efficient alternative for realizing C–H electrochemical acyloxylation. In 2020, Zhong and colleagues developed a method for the mono- and di-acyloxylation of aryl C–H bonds driven by electrochemical Ru catalysis (Scheme 20).[88] This transformation could be applied in the late-stage diversification of various carboxylic acids derived from pharmaceuticals, natural products, and so on. For the mechanism, complex **40-B** was firstly formed from the ligand exchange between Ru catalyst and **40**. The coordination of substrate **44** with **40-B** and the C–H activation proceeded continuously to form intermediate **44-B**. The product **45** was acquired after the reductive elimination of **44-B**. The released Ru(0) species with low valence was oxidized to regenerate catalytical Ru(II) complex.

In 2022, Ackermann and co-workers employed phenol derivative as aryl C–H source to access the electrochemical C–H acyloxylation *via* Ru catalysis (Scheme 21).[89] The reaction had been successfully applied for the late-stage diversification of tyrosine and oligopeptide. According to their report, complex **46-A** was formed by C–H metalation of substrate **46**. Then the coordination

Scheme 20 Ru-catalyzed C–H acyloxylation of aniline

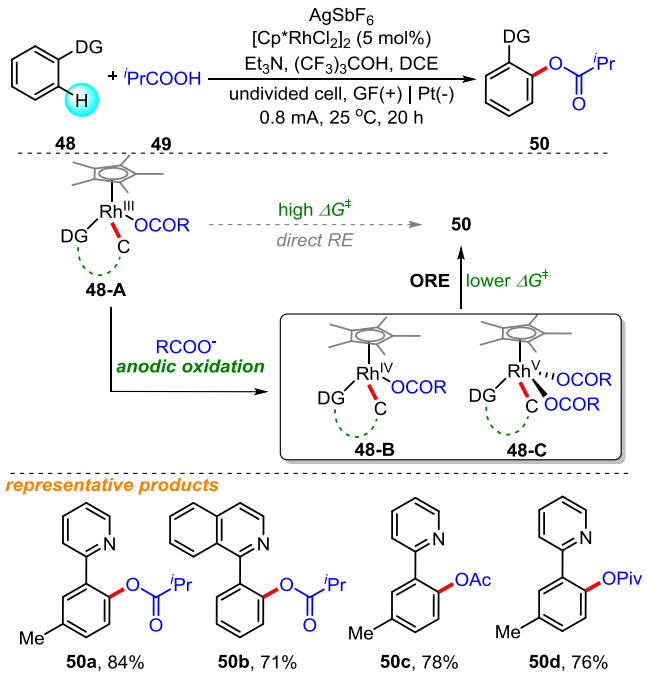


Scheme 21 Ru-catalyzed C–H acyloxylation of phenol derivative



between another molecule of **46** and **46-A** occurred, followed by C–H activation to give intermediate **46-B**. The Ru(IV) species **46-C** was obtained *via* anodic oxidation. The formation of desired ester **47** and the regeneration of **46-A** would be realized by tandem reductive elimination and ligand exchange. In 2021, according to Chang's report (Scheme 22), the Ru-catalyzed aryl C–H activation could also be approached *via* an ORE (oxidatively induced reductive elimination) with Rh(IV/V) complexes as high valent intermediates.[90] Rather than the direct reductive elimination of Rh(III) intermediate **48-A**, it was oxidized to corresponding high valent intermediates **48-B** and **48-C** to undergo the ORE process with lower Gibbs free energy.

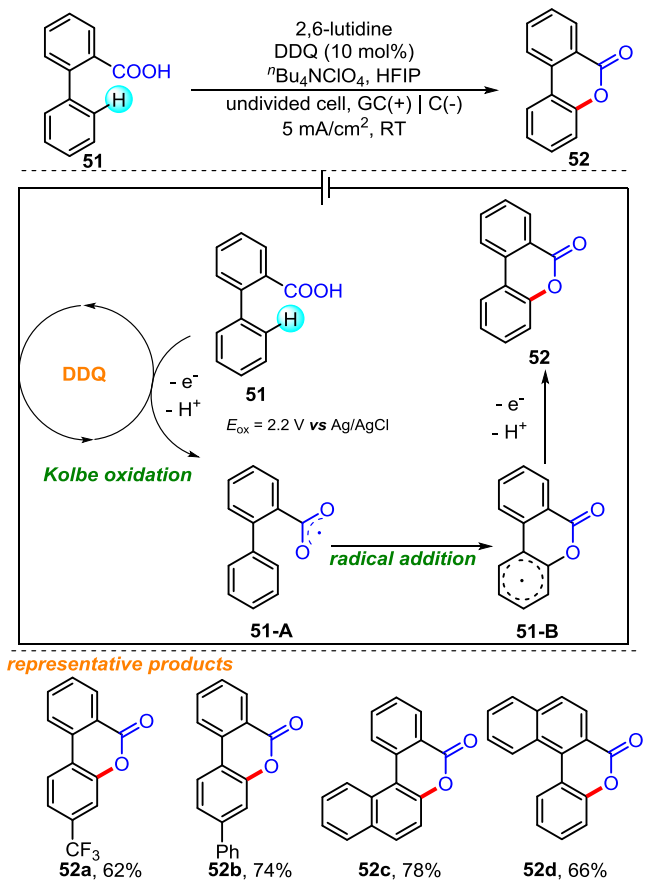
Scheme 22 Rh-catalyzed C–H acyloxylation of phenol derivative



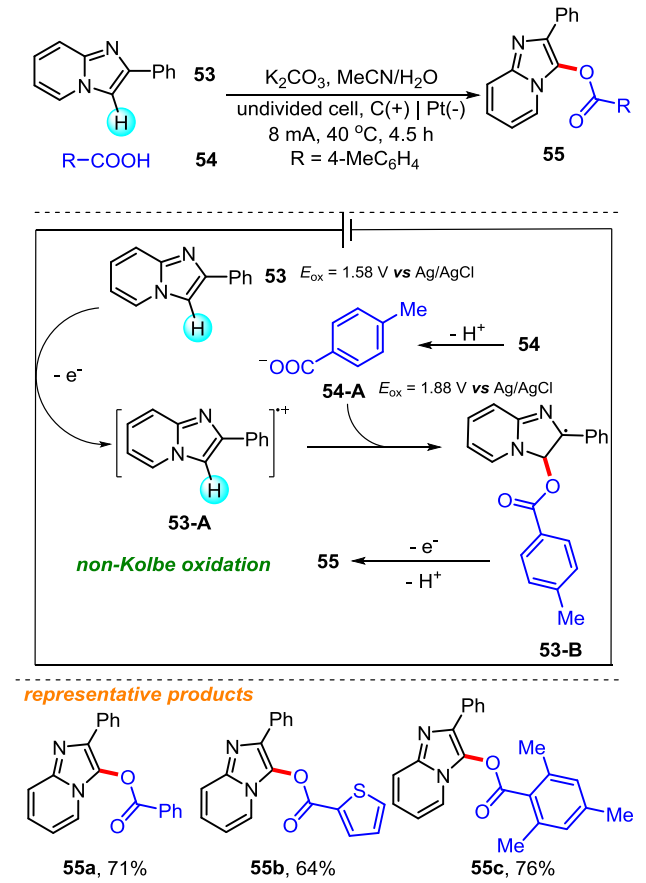
2.2.2. Kolbe/non-Kolbe oxidation enabled acyloxylation. Although the C–H activation process is remarkably effective, given the potential risk and high costs of transition-metal catalysts, some metal-free electrochemical transformations had been developed. Due to the lower oxidation potential of carboxylic acid, the transformation usually initiated with the Kolbe oxidation of carboxylic acid to form carboxyl radical. The product would be delivered after subsequent electrochemical and chemical processes. For instance, C(sp^2)-H bonds in 2-arylbenzoic acids could be favorable sources for the C–H acyloxylation by electrochemical oxidative methods. In 2018, Luo's group discovered the DDQ-mediated C–H lactonization driven by electrochemical oxidation (Scheme 23).[91] In their report, substrate **51** would be oxidized to corresponding carboxyl radical **51-A** with the mediation of DDQ in a Kolbe-type pathway. Then the radical addition between carboxyl radical **51-A** and *ortho*-arene provided an intermediate **51-B**, which could form final lactone **52** after the tandem oxidation and deprotonation. Notably, Lei,[92] Xu,[93] Mo[94] and Zeng[75] also accessed this transformation *via* direct anodic oxidation without any mediators. Additionally, some C–H bonds of alkenes were also suitable in their description.

It could be seen that, for C(sp^2)-H sources with lower electron density, the C–H acyloxylation was initiated by oxidation of carboxylic acid to undergo a Kolbe-type pathway. However, when substrates with high electron density were used instead, the process was entirely different *via* non-Kolbe process. In 2021, Lei's group realized the C–H acyloxylation using imidazo[1,2-*a*]pyridine **53** as heteroaryl C–H source (Scheme 24).[95] With this method, site-selective acyloxylation product **55** could be obtained. During the reaction, the heteroaromatic **53** with lower oxidation potential was firstly oxidized at the anode to form the radical cation

Scheme 23 C–H acyloxylation of 2-arylbenzoic acids



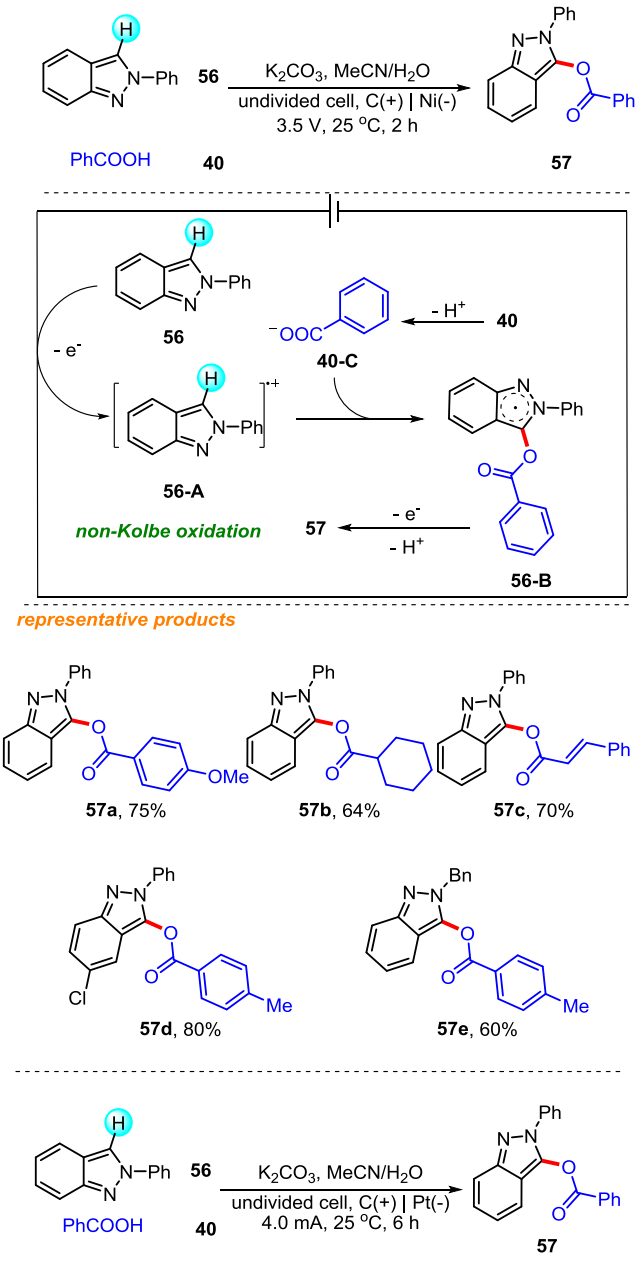
Scheme 24 C–H acyloxylation of imidazo[1,2-*a*]pyridine



53-A. Meanwhile, benzoic acid **54** was deprotonated under basic condition to obtain carboxylate **54-A**. The nucleophilic addition between **53-A** and **54-A** afforded a benzyl radical **53-B**, which could be converted to product **55** after the tandem oxidation and deprotonation.

Similarly, in 2023, Sharma and co-workers used *2H*-indazole **56** as C–H source to accomplish the C–H acyloxylation *via* direct oxidation (top of Scheme 25).[96] In their proposed mechanism, benzoic acid **40** was converted to carboxylate **40-C** by deprotonation with K_2CO_3. The intermediate **56-A** was obtained from the oxidation of substrate **56** at the anode. The nucleophilic addition of **40-C** to **56-A** would provide the radical **56-B**. After the oxidation and deprotonation of **56-B**, the C–H acyloxylation was completed to give product **57**. Shen's group also completed this transformation through a similar non-Kolbe pathway in the same year (bottom of Scheme 25).[97]

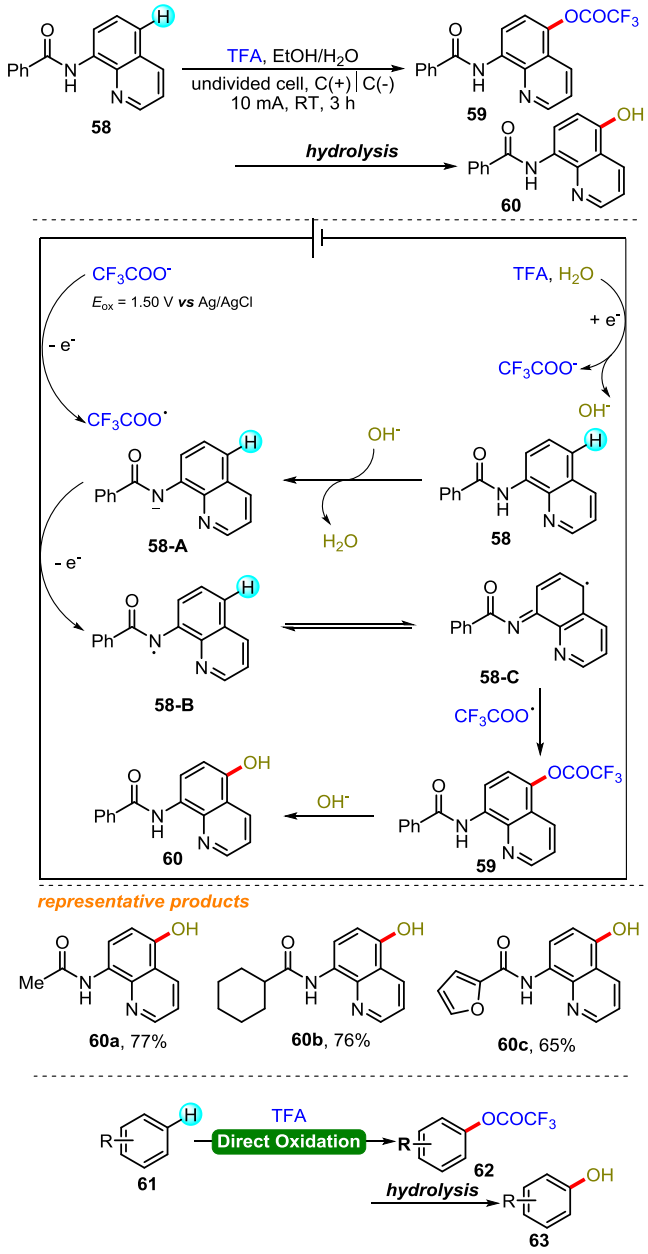
Scheme 25 C–H acyloxylation of *2H*-indazole



The anodic oxidation driven C(sp^2)-H acyloxylation would also offer key intermediates for further transformations. In 2020, Guo reported the *para*-selective trifluoroacetoxylation of *N*-aryl amide

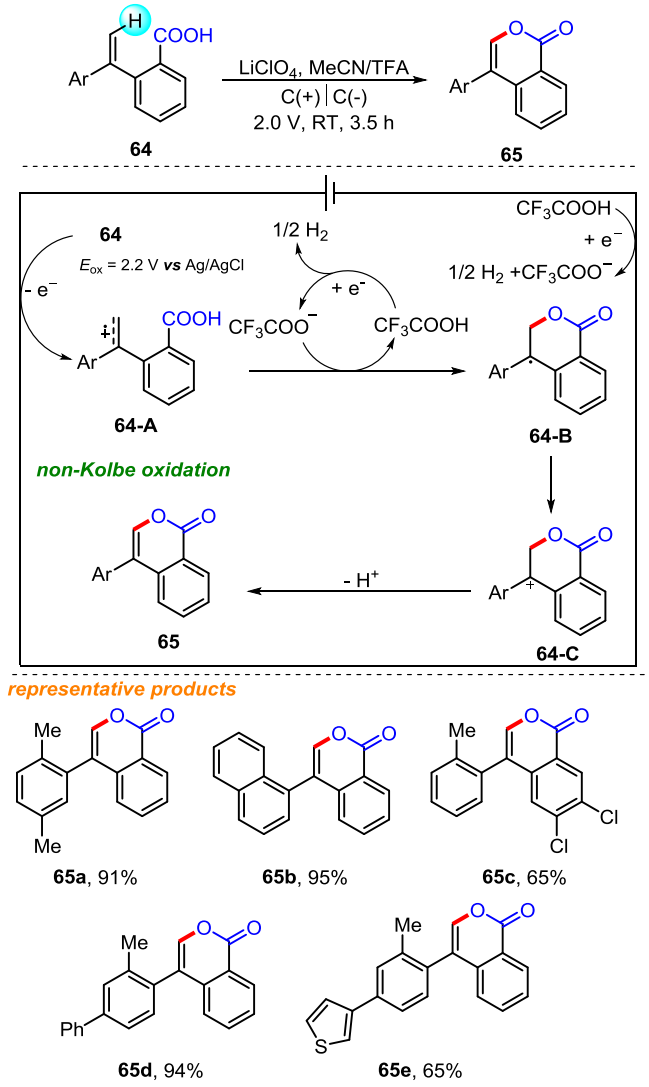
for the final C–H hydroxylation *via* electrochemical oxidation (top of Scheme 26).[98] The reaction could be proceeded both in batch and continuous flow. In their proposed mechanism, the substrate **58** was deprotonated to form *N*-anion **58-A** with lower oxidation potential, while trifluoroacetate anion was released by the reduction of trifluoroacetic acid. The oxidation of *N*-anion **58-A** and trifluoroacetate anion formed corresponding radicals. The *N*-radical **58-B** resonated to generate a stable radical **58-C**, which underwent radical-radical coupling with trifluoroacetoxyl radical to form the intermediate **59**. Further hydrolysis of the intermediate **59** yielded the final product **60**. In 2022, Xu used electron-rich arene **61** as C–H source for the electrochemical hydroxylation in continuous flow with the same trifluoro acetoxyl intermediate **62**.[99] Complex molecules from pharmaceuticals and natural products were also suitable in their report. A similar transformation was realized by Ošeka in the same year (bottom of Scheme 26).[100]

Scheme 26 Aryl C–H acyloxylation for hydroxylation



Furthermore, there was a special case about the non-Kolbe oxidation of alkene to realize the C–H acyloxylation. According to Zhang's repot in 2024,[101] the substrate **64** with a styrene moiety could be used instead of electron-rich arenes and heteroaromatics. During the reaction, the styrene moiety of **64** was initially oxidized to drive the transformation. The formed intermediate **64-A** was converted to **64-B** *via* the intramolecular nucleophilic cyclization, assisted by trifluoroacetate released from the cathode. The cation **64-C** was provided by the oxidation of **64-B**. The desired isocoumarin **65** was generated after the deprotonation of **64-C** (Scheme 27).

Scheme 27 C–H acyloxylation of styrene



3. Electrochemical C–H Alkoxylation

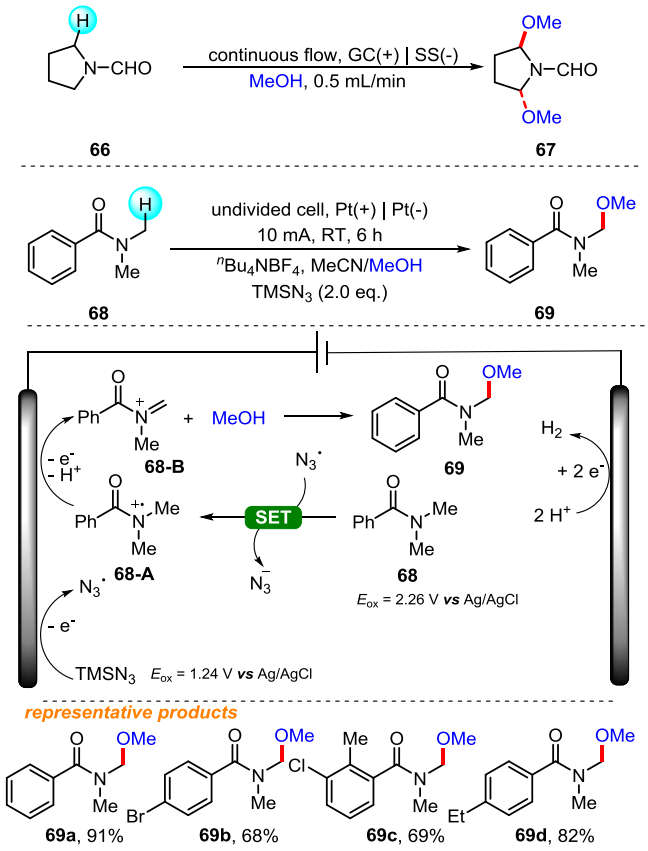
3.1. Electrochemical C(sp^3)-H alkoxylation

Ethers, which have a wide range of applications in various fields, can be prepared directly from alcoholic oxygen sources *via* C–H alkoxylation with active C(sp^3)-H sources. For the topic of C(sp^3)-H alkoxylation, Shono oxidation was a widely applied method for multiple electrochemical transformation of amines. *ortho*-Nitrogen C–H bond was activated by the large electronegativity of nitrogen atom. With the high electron density, the initial oxidation of nitrogen usually drove the electrochemical transformation and provided the active iminium intermediates. The *α-N* C–H alkoxylation could be completed with amides or sulfonamides as C–H sources.

For example, in 2019, Wirth and co-workers reported the flow

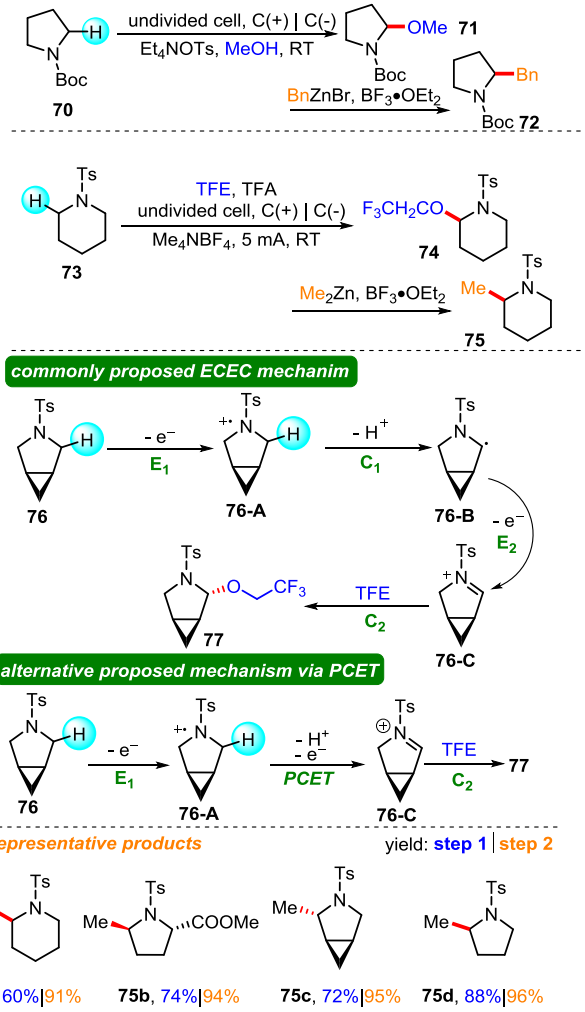
electrochemical C–H alkoxylation with pyrrolidine-1-carbaldehyde **66** as a substrate (top of Scheme 28).[102] Under different electrolytic conditions, the C–H mono- or di-alkoxylation could be accessed selectively *via* Shono oxidation, products **67** with various substituents were obtained efficiently. In 2023, according to Cai's report,[103] the mediated oxidation of amides could also be accomplished for the *α-N* C–H alkoxylation by Shono-type pathway (bottom of Scheme 28). Based on their results, the process started from the oxidation of $TMSN_3$ to provide $N_3^{\bullet}$ radical. The intermolecular SET occurred between the $N_3^{\bullet}$ radical and amide **68** to form the radical cation **68-A** *via* mediated oxidation. The key iminium **68-B** was prepared at anode from the further oxidation and deprotonation of radical cation **68-A**. The nucleophilic addition from methanol to iminium **68-B** obtained the target product **69**.

Scheme 28 Shono oxidation of amides



The Shono-type oxidation supported electrochemical C–H alkoxylation could also provide crucial intermediates for diverse C–H functionalization. In 2021, Alcázar's team generated *α-N* ether **71** *via* the electrochemical C–H methoxylation of *N*-Boc piperidine **70** (top of Scheme 29).[104] As an intermediate, the *α-N* ether **71** could be converted to corresponding alkylation product **72** with the organozinc compound and Lewis acid under flow conditions. This method completed the formal construction of $C(sp^3)$-$C(sp^3)$ bond. In 2022, Lin's group reported the C–H trifluoroethoxylation of cyclic sulfonamide **73** *via* the Shono oxidation (bottom of Scheme 29).[105] The products, as key intermediates would react with dimethylzinc with the assistance of Lewis acid to complete the *in-situ* introduction of methyl group. The tandem method was also suitable for the late-stage methylation of complex pharmaceutical and natural product molecules. In the description of mechanism, they detailed the transformation involving two different pathways: 1) for the commonly **ECEC** (electrochemical-chemical-electrochemical-chemical) mechanism, the initial anodic oxidation of substrate **76** delivered corresponding *N*-central radical cation **76-A**, which was deprotonated to form the *α-N* radical **76-B**. The further oxidation of *α-N* radical **76-B** obtained iminium cation **76-C**. The nucleophilic addition between the iminium cation **76-C** and TFE resulted in the final product **77** with the release of a proton; 2) for the alternative **PCET** (proton-coupled electron transfer) mechanism, after the formation of *N*-central radical cation **76-A** from the oxidation of substrate, the leaving of an electron and a proton occurred concurrently to prepare iminium cation **76-C** *via* **PCET** process. The subsequent steps were consisted with **ECEC** mechanism.

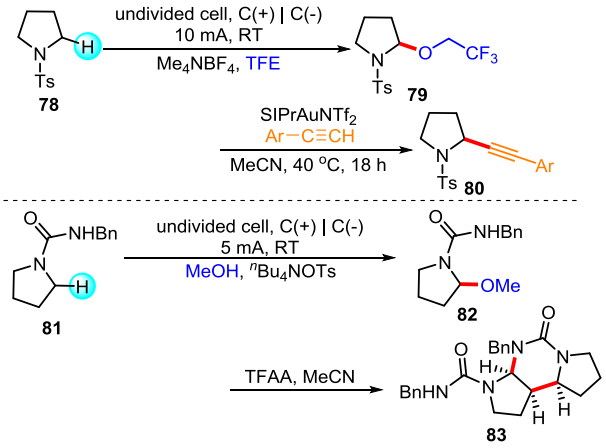
Scheme 29 Shono-oxidation for C–H alkylation



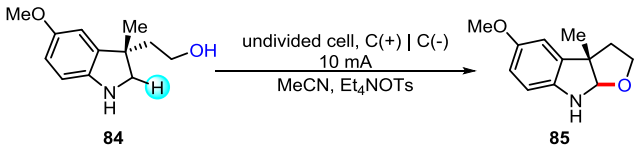
After that, more kinds of C–H functionalization had been accessed with the same electrochemical acquired intermediate. In 2023, Michelet used *N*-heterocycle **78** as C–H source to realize the Shono-type *α-N* C–H trifluoroethoxylation (top of Scheme 30).[106] The desired trifluoroethoxyl product **79** could proceed crossing coupling with terminal alkyne *via* Au(I)-catalyzed alkynylation to gain the final product **80**. What's more, urea **81** could be applied as substrate to complete C–H methoxylation by Shono oxidation according to Masson in 2024 (bottom of Scheme 30).[107] In their report, fissoldhimine alkaloid analogue **83** could be prepared after the heterodimerization process of methoxyl product **82** with the assistance of trifluoroacetic anhydride. Diverse functional groups were practical for this tandem transformation.

In addition, the intramolecular Shono-type processes could be included in some electrochemical reactions. In 2022, the *N*-heterocycle substate **84** with a remote hydroxyl was utilized by Frankowski to accomplish the electrochemical construction of C–O bond (Scheme 31).[108] After the anodic oxidation of substrate,

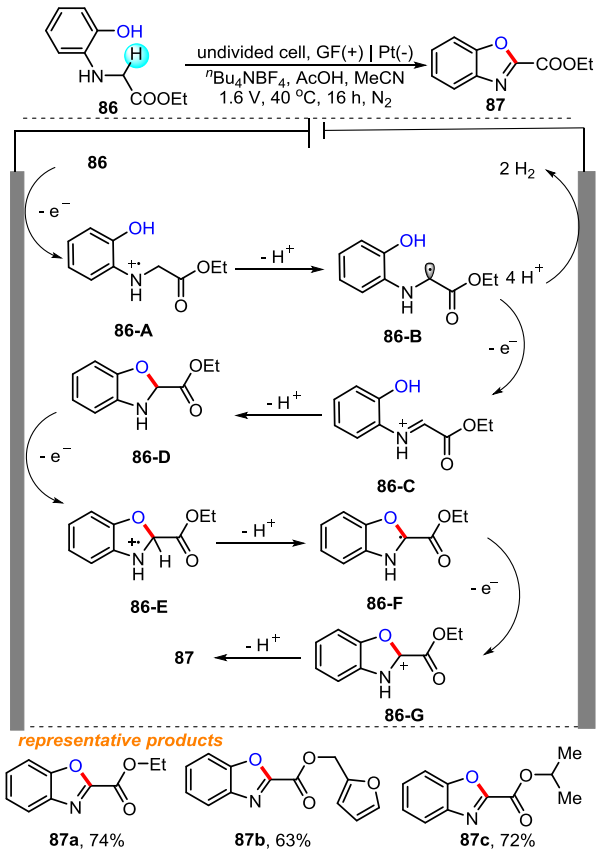
Scheme 30 Shono-oxidation for other functionalization



Scheme 31 Shono-oxidation for synthesis of physovenine



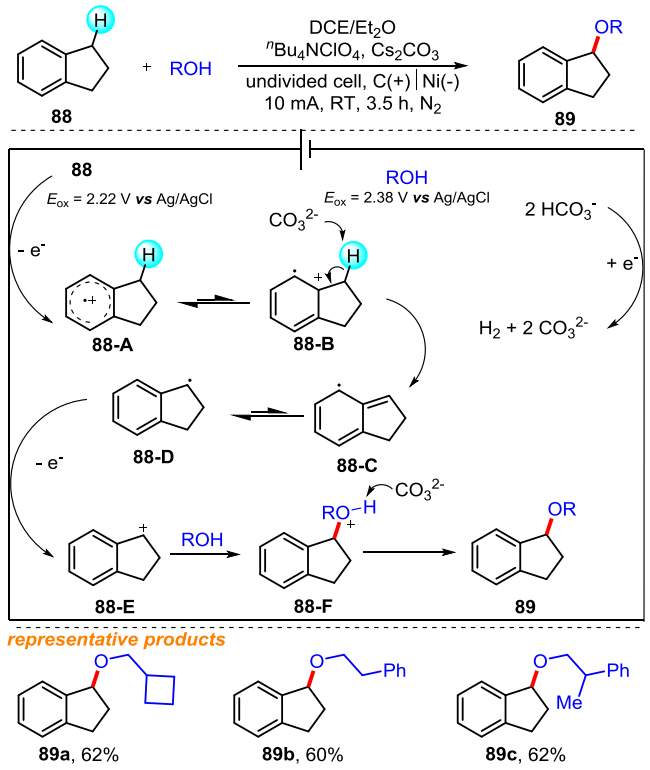
Scheme 32 Shono-oxidation for synthesis of oxazole



iminium with nucleophilic hydroxyl was formed. The intramolecular addition proceeded subsequently to generate the desired natural product (±)-physovenine **85**. In the same year, Zhong utilized ethyl glycinate derivative **86** as C–H source with an internal hydroxyl to synthesize benzoxazole **87** by electrochemical oxidation (Scheme 32).[109] The transformation was driven by Shono oxidation to offer radical cation **86-A**, which was deprotonated to form *α-N* radical **86-B**. The further oxidation generated the key iminium cation **86-C**. Then the nucleophilic cyclization took place intramolecularly to construct the C–O bond to deliver oxazoline **86-D**. Another course of Shono oxidation proceeded to form cation **86-G**, which obtained the final benzoxazole **87** *via* deprotonation.

More broadly, electrochemical C–H alkoxylation could be carried out using substrates containing benzyl, allyl, *α*-carbonyl C–H bonds with alcohols. In 2020, Lei's group reported that the benzyl and allyl C(sp^3)-H bonds could be activated by electrochemical oxidation (Scheme 33).[110] Based on their results, the more easily oxidized substrate **88** firstly proceeded SET process to generate the radical cation **88-A**, which formed resonance structure **88-B**. The base-assisted deprotonation would deliver the radical **88-C**, which resonated to obtain the benzyl radical **88-D** with greater stability to be oxidized to corresponding benzyl cation **88-E**. The nucleophilic reaction of alcohol and the intermediate **88-E** afforded final product **89** accompanied by the transfer of proton. In 2021, Patureau and co-workers realized the electrochemical esterification of methylarene *via* the continuous benzyl C–H alkoxylation. The *di-* and *tri*-alkoxyl products served as key intermediates in this transformation (Scheme 34).[111] In the initial period of the reaction, the substrate **90** with EDG (electron-donating group) was oxidized to obtain radical cation **90-A**, which was converted to quinone methide derivative **90-B** after another SET and deprotonation. Attacked by alcohol or alkoxide prepared *in-situ*, the intermediate **90-B** could deliver mono-alkoxyl product **90-C** to access the C–H alkoxylation. Benzyl C–H bond of the mono-alkoxyl product **90-C** was more active for C–H alkoxylation theoretically. Thus, acetal **90-D** or orthoester **90-E** as intermediates would be generated *via* further oxidation at anode. The hydrolysis of above intermediates in the reaction or during work-up provided final ester product **91**.

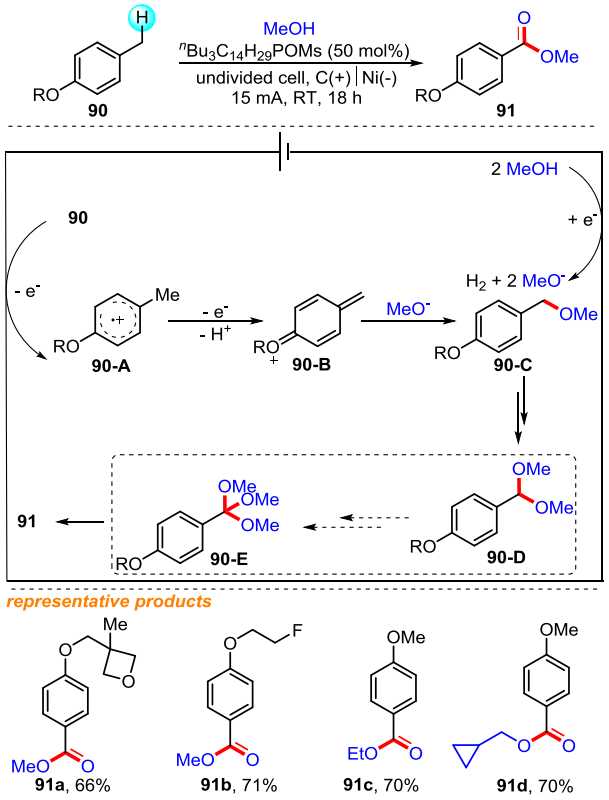
Scheme 33 Benzyl C–H alkoxylation



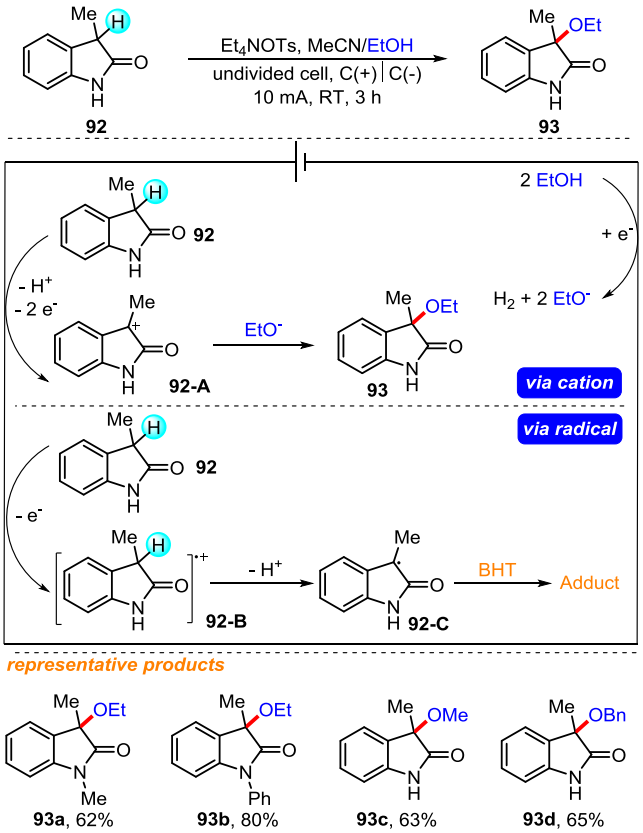
Amides were also applicable substrates for electrochemical *α*-carbonyl C–H alkoxylation. In 2022, Maulide's team completed the electrochemical umpolung transformation of oxindole **92** (Scheme 35).[112] Diverse alkoxyl products were prepared in the reaction. The plausible mechanism *via* carbocation was described as the two-electron oxidation of the substrate **92** to form carbo-

cation **92-A** with the release of proton. The carbocation would be trapped by ethanol to give the final product **93**. The alternative mechanism was driven by initial SET of the substrate **92** to acquire radical cation **92-B**, which lost a proton to obtain radical intermediate **92-C** that could be indicated with the addition of BHT. In 2024, Zhang's report presented C–H alkoxylation of thiophene-containing amide **94** *via* electrochemical oxidation (Scheme 36).[113] For the initial mechanism, ethanol was reduced to release H_2 and EtO^- at cathode. In path **A**, the anodic oxidation of substrate **94** took place to deliver radical cation **94-A**, which would lose a proton with the assist of base to form *α*-carbonyl radical **94-B** that was oxidated to carbocation **94-C**. The final nucleophilic addition of EtO^- to the *α*-carbonyl carbocation **94-C** provided product **95**. In path **B**, the EtO^- deprotonated the substrate **94** to obtain *α*-carbonyl anion **94-A$_2$**, which resonated to form enolate **94-B$_2$**. The further oxidation of enolate **94-B$_2$** would gain the *α*-carbonyl radical **94-B** to proceed similar steps in path **A**.

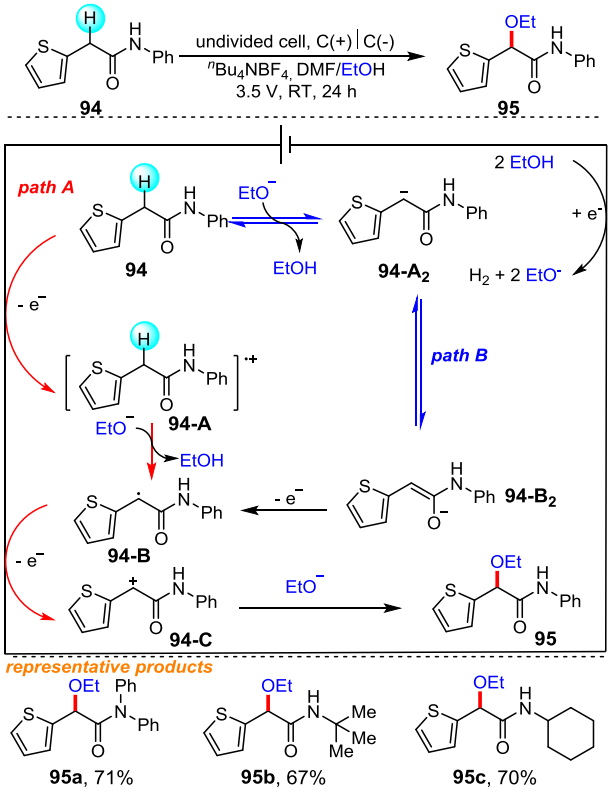
Scheme 34 Benzyl C–H multiple-alkoxylation



Scheme 35 Benzyl C–H alkoxylation of oxindole



Scheme 36 Benzyl alkoxylation of thiophenol acetamide

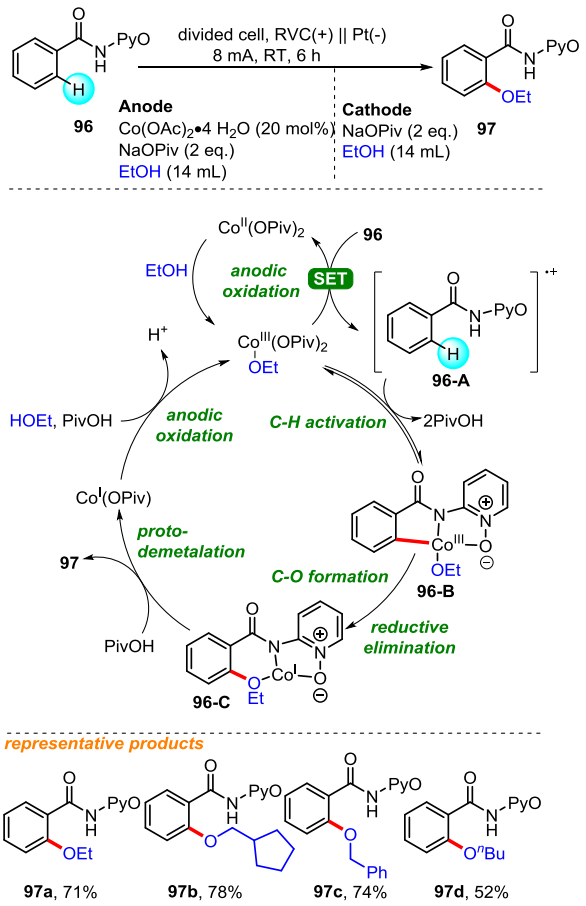


3.2. Electrochemical C(sp^2)-H alkoxylation

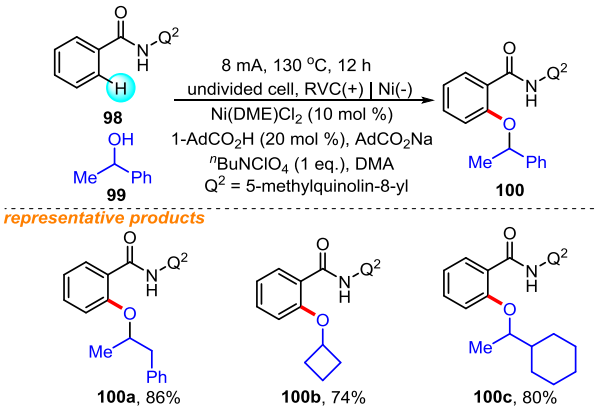
3.2.1. C(sp^2)-H alkoxylation *via* CDC reaction. Like the C–H acyloxylation, Co, Ni-catalyzed C–H activation remained effective strategy. For instance, in 2017, Ackermann found that benzamide **96** with a *N*-pyridine oxide moiety as the directing group could be oxidized to desired aryl ether **97** *via* Co-catalysis (Scheme 37).[114] In their proposed catalytic cycle, a Co(III) complex was obtained by anodic oxidation, and the subsequent SET process converted the substrate **96** to corresponding radical cation **96-A**. Then C–H activation proceeded to deliver intermediate **96-B**. Along with reductive elimination of central Co(III) to Co(I), the complex **96-C** with the formative C–O bond was gained. The protonation and demetalation with PivOH provided the final product **97** and Co(I). The regeneration of Co(III) could be completed at the anode by the oxidation of Co(I). Additionally, decisive mechanistic insights were studied by their group in 2020.[115]

In 2020, Ackermann's group used secondary alcohol **99** as oxygen source for the alkoxylation of *ortho*-C–H bond of benzamide **98** through Ni-electrocatalyzed C–H activation (Scheme 38).[116] Besides, in 2023, Ackermann[117] and Shi[118] applied the electrochemical Co-catalyzed method to realize C–H enantioselective

Scheme 37 Co-catalyzed C–H alkoxylation



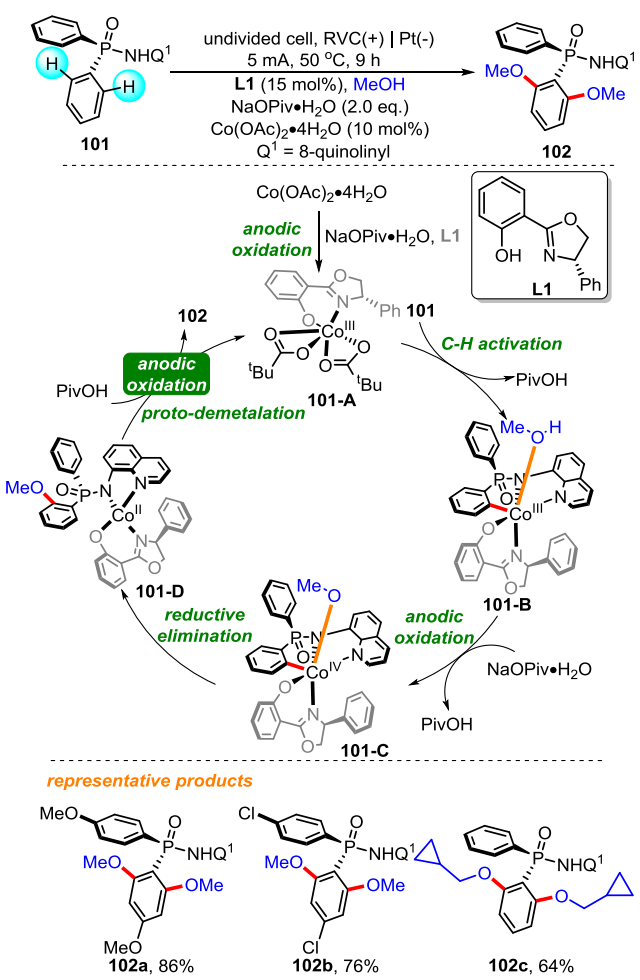
Scheme 38 Ni-catalyzed C–H alkoxylation



alkoxylation with the chiral Salox ligand (Scheme 39). According to the result, $Co(OAc)_2$ underwent initial anodic oxidation to form Co(III) complex **101-A** with the assistance of base and ligand **L1**. Then the C–H enantioselective activation occurred to give intermediate **101-B**. After the anodic oxidation of Co(III) complex **101-B**, a complex **101-C** with high-valent Co(IV) was obtained. The following ORE process would provide the Co(II)-product complex **101-D**, which was converted to product **102** *via* proto-demetalation with PivOH. The released Co(II) species was oxidized to catalytically active Co(III) complex **101-A**.

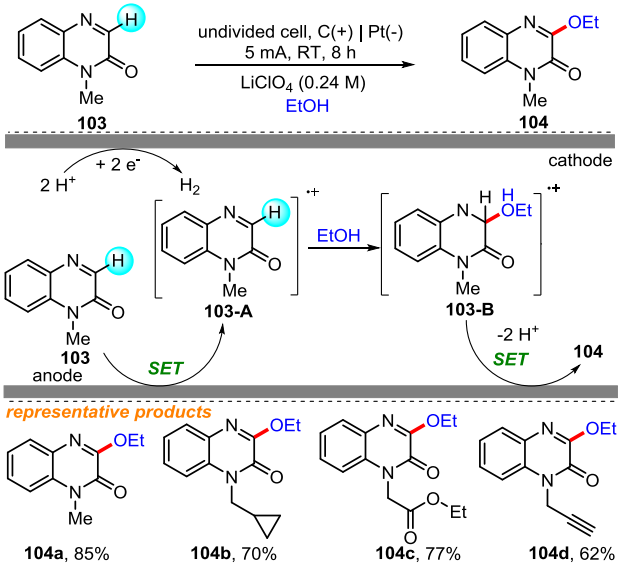
3.2.2. Direct/indirect oxidation enabled alkoxylation. Additionally, the direct or mediated oxidation of C(sp^2)-H sources to electrophilic intermediates was a metal-free pathway with wide application. In 2020, Yu and co-workers described the electrochemical synthesis of quinoxalin-2(*1H*)-one **104** with alkoxy (Scheme 40).[119] In the transformation, the substrate **103** with

Scheme 39 Co-catalyzed C–H *di*-alkoxylation

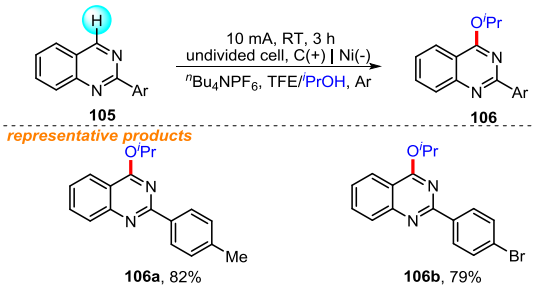


high electron density was facilely oxidized *via* SET process to form radical cation **103-A**, which was electrophilic to react with ethanol to afford the adduct **103-B**. Another SET process took place accompanied with the release of protons to obtain the final product **104**, while free protons in the bulk solution reduced at cathode to sustain the whole electrolysis. There was a similar transformation in Das's work (Scheme 41).[120]

Scheme 40 C–H alkoxylation of heteroaromatic by Yu

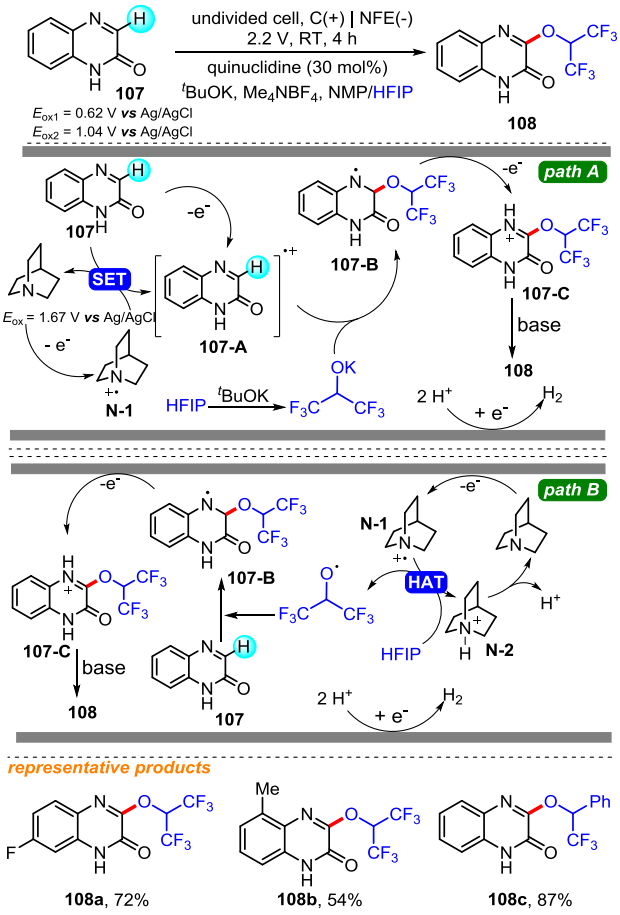


Scheme 41 C–H alkoxylation of heteroaromatic by Das



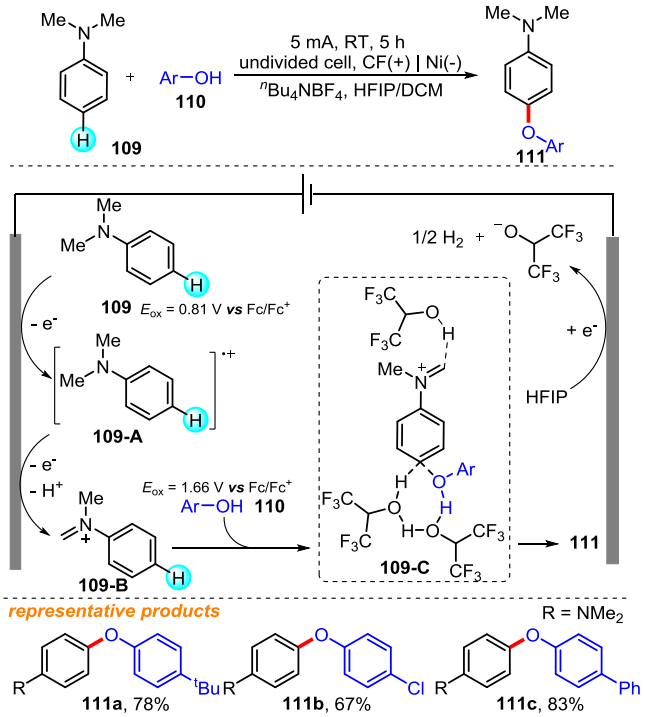
Furtherly, Zhang reported the indirect oxidation of quinoxalin-2(*1H*)-one **107** with quinuclidine as a mediator for the C–H fluoroalkoxylation in 2024 (Scheme 42).[121] In the initial stage of this reaction, quinuclidine with lower oxidation potential was oxidized firstly to form the active radical cation **N-1**. There were two possible pathways: path a) the SET process between radical cation **N-1** and substrate **107** provided intermediate **107-A**, which would be attacked by alkoxyl potassium prepared *in-situ* from HFIP and ^{t}BuOK. The resulting *N*-center radical **107-B** was converted to iminium **107-C**, which formed the final product **108** *via* deprotonation; path b) the HAT process between HFIP and the radical cation **N-1** generated the alkoxyl radical, which could undergo radical addition with substrate **107** to afford *N*-center radical **107-B**. The consistent oxidation and deprotonation also delivered the product **108**.

Scheme 42 C–H alkoxylation of heteroaromatic by Zhang

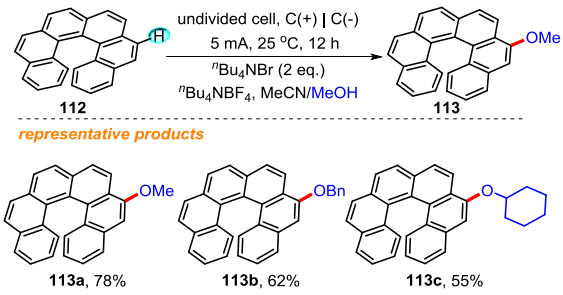


Aniline **109**, as electron-rich arene, could also be utilized as a source for the oxidative C–H alkoxylation according to Vercammen in 2021 (Scheme 43).[122] The tertiary aniline moiety of the substrate **109** was anodically oxidized to deliver a radical cation **109-A**, which could be converted to iminium **109-B** as an intermediate *via* oxidation and deprotonation. Due to the high dielectric constant and low nucleophilicity of HFIP as solvent, the nucleophilic addition of phenol **110** to the iminium **109-B** formed the stable complex **109-C**. The product **111** was generated while protons were reduced concomitantly at the anode. In 2023, Qiu and co-workers used helicene **112** to realize the remote C–H alkoxylation by electrochemical oxidation to deliver product **113** (Scheme 44).[123]

Scheme 43 C–H alkoxylation of aniline

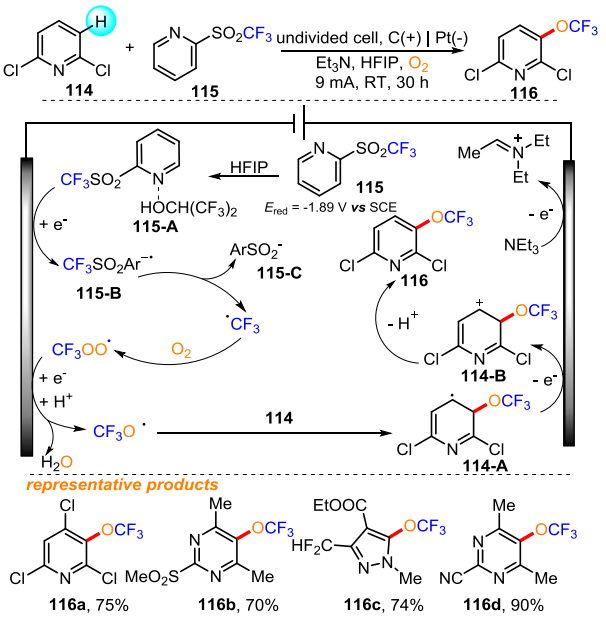


Scheme 44 C–H alkoxylation of helicene



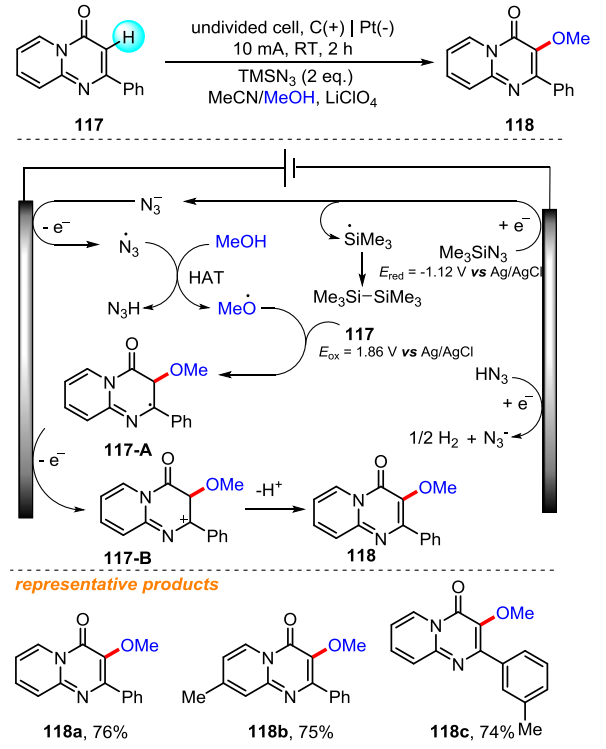
The pre-activation of oxygen sources instead of the oxidation of C–H sources was an alternative approach for the C(sp^2)-H alkoxylation. In 2022, Qing's group employed a trifluoromethyl source **115** and oxygen as co-alkoxylation reagents to realize the trifluoromethoxylation of aryl C–H bond *via* electrochemical oxidation (Scheme 45).[124] During the reaction, the combination of trifluoromethyl 2-pyridyl sulfone **115** and HFIP through hydrogen bonding afforded intermediate **115-A**, which was reduced to radical anion **115-B**. Sulfinate ion **115-C** and $CF_3^\bullet$ radical would be obtained *via* the decomposition of radical anion **115-B**. The reaction of oxygen and $CF_3^\bullet$ radical obtained $CF_3OO^\bullet$ radical, which was inclined to be reduced at the cathode to release $CF_3O^\bullet$ radical with the assistance of protons. The crucial $CF_3O^\bullet$ radical underwent radical addition to the substrate **114** to form the intermediate **114-A**, which was converted to desired product **116** after the subsequent oxidation and deprotonation. In the meantime, the additive Et_3N was oxidized as sacrificial reagent to sustain the electrolysis.

Scheme 45 C–H aerobic alkoxylation of azaheterocycle



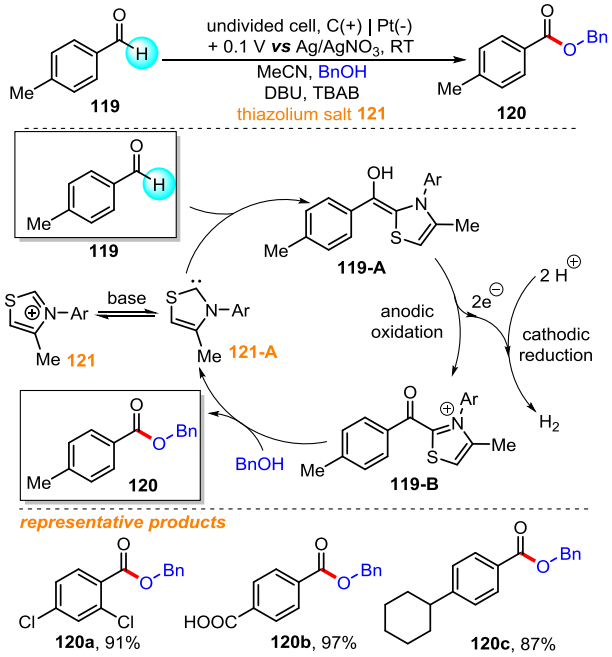
Analogously, Das and co-workers reported the C(sp^2)-H alkoxylation *via* mediated process with aliphatic alcohol as oxygen source in 2024 (Scheme 46).[125] According to their description, $TMSN_3$ was firstly reduced to trimethylsilyl radical and N_3^-. The anodic oxidation of N_3^- would provide $N_3^{\bullet}$ radical as the key mediator. The intermolecular HAT process between $N_3^{\bullet}$ radical and methanol occurred to give the methoxyl radical, which was active to undergo radical addition with the substrate **117** to deliver the radical **117-A**. The subsequent anodic oxidation and deprotonation offered the final product **118**.

Scheme 46 Mediated C–H alkoxylation of azaheterocycle

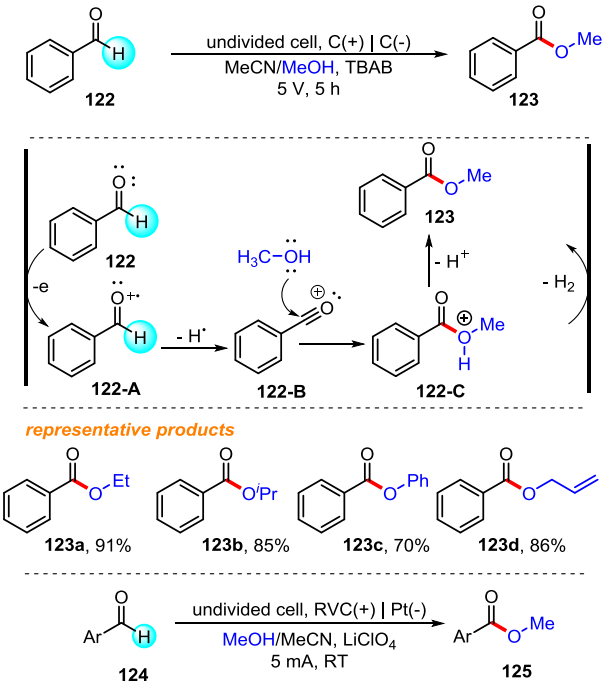


Surprisingly, there were interesting examples utilizing aldehydes as C(sp^2)-H sources for the C–H alkoxylation, where esters would be obtained when alcoholic nucleophiles were used. In 2012, Boydston realized the NHC (*N*-heterocyclic carbene) catalyzed C–H alkoxylation of aldehyde **119** *via* electrochemical oxidation (Scheme 47).[126] Various esters could be prepared directly with medium to excellent yields. In the transformation, the NHC precursor **121** was deprotonated to generate NHC **121-A** *in-situ* to initiate the catalytic cycle. The reaction of NHC and aldehyde **119** provided the adduct **119-A**, which would undergo oxidation at anode to form 2-acylazolium specie **119-B** with electrophilicity. The nucleophilic attack from alcohol obtained the product **120** and regenerated the NHC catalyst **121-A** for another transformation. In addition, the direct anodic oxidation of aldehyde was completed by Shaikh[127] and Meng[128] in 2021 (Scheme 48). With the formation of acylium cation **122-B** as electrophilic intermediate, the succedent nucleophilic addition might obtain desired ester **123**.

Scheme 47 NHC-catalyzed C–H alkoxylation of aldehyde



Scheme 48 Alkoxylation of aldehyde *via* direct oxidation

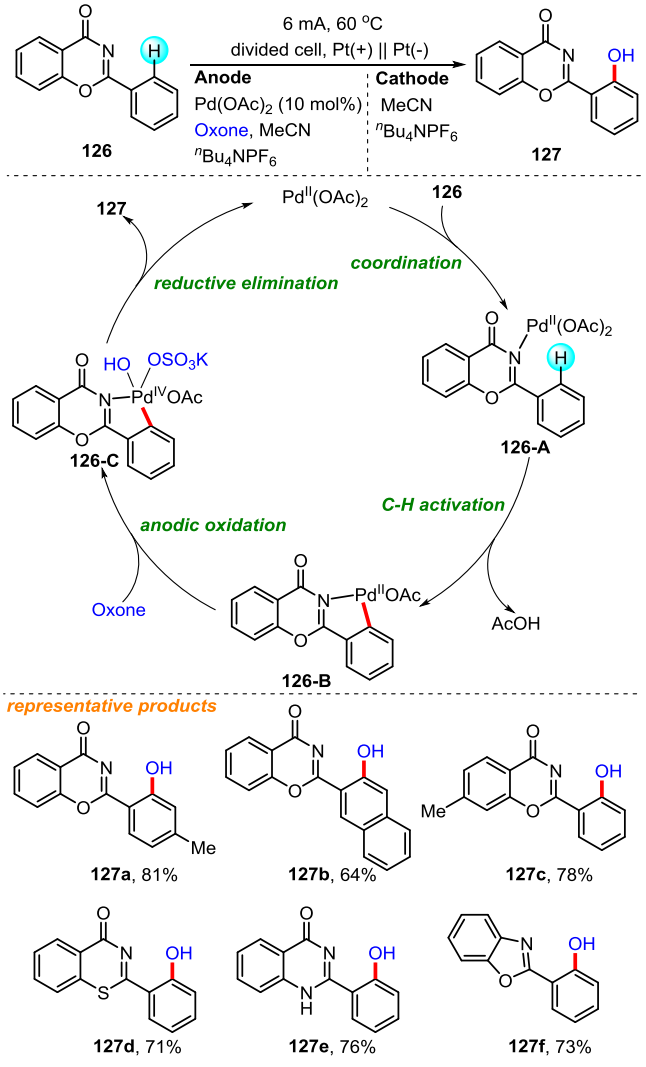


4. Other Electrochemical C–O Formation

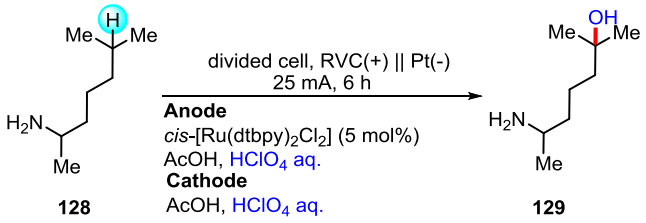
4.1. C–H hydroxylation

Electrochemical C–H hydroxylation was an efficient method for the direct preparation of alcohols and phenols from available sources containing C–H bonds. In 2020, Sun's team reported the Pd-catalyzed C(sp^2)-H hydroxylation under electrochemical oxidation (Scheme 49).[129] With the substrate **126** containing aryl C–H bond, the *ortho*-oxazine directing C–H hydroxylation could proceed site-selectively with the addition of Oxone as hydroxyl source. In the Pd-catalyzed mechanism, coordination of $Pd(OAc)_2$ and the substrate **126** afforded the complex **126-A**, which was converted to intermediate **126-B** *via ortho*-C–H activation. The subsequent oxidation of intermediate **126-B** occurred to deliver Pd(IV) species **126-C** at anode with the participation of Oxone. The reductive elimination would provide hydroxyl product **127** and regenerate Pd(II) to complete the catalyzed cycle. Additionally, Sigman and co-workers completed the remote C–H hydroxylation of amine derivative **128** by electrochemical Ru-catalysis in 2020 (Scheme 50).[130] The crucial step in the transformation was enabled by the oxidation of Ru(II) complex to form Ru(IV) species and the desired alcohol **129** could be efficiently produced.

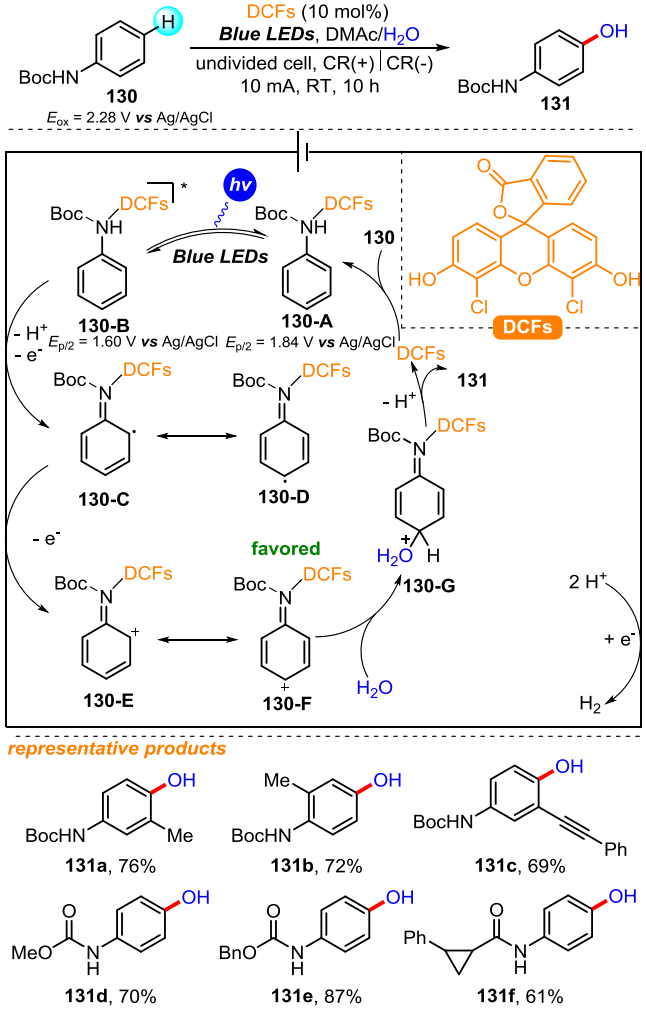
Scheme 49 Pd-catalyzed hydroxylation of arene



Scheme 50 Ru-catalyzed C–H hydroxylation



Scheme 51 Photo-electrochemical hydroxylation of arene

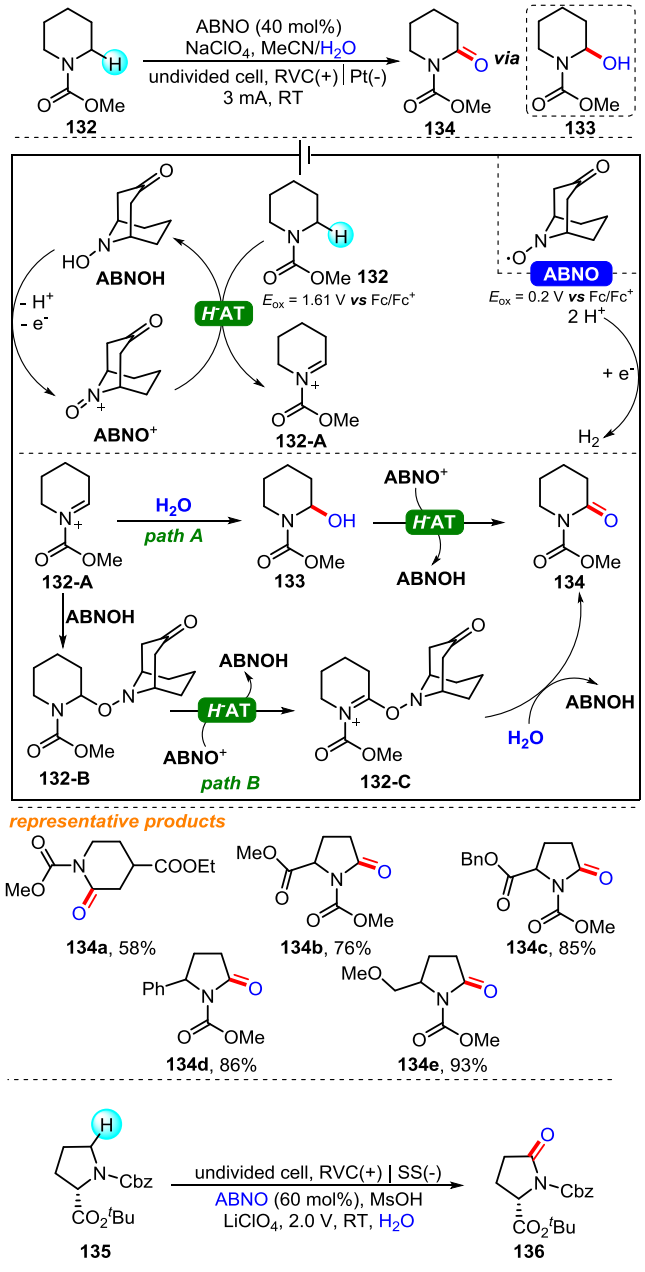


The photo-electrochemical pathway was also practical for the transformation according to Lei in 2024 (Scheme 51).[131] The aniline derivate **130** was used as a *para*-selective C–H donor with the aid of the specific photocatalyst DCFS to deliver the more easily oxidized product **131**. According to their description, the electrochemical regioselectivity could be improved by the reduced oxidation potential of substrate **130**. In the detailed mechanism, the coordination of substrate **130** and DCFS would generate intermediate **130-A**, which was excited to activated state **130-B** by the irradiation of bule LEDs. The activated state **130-B** lose an electron and a proton, resulting in the radical intermediates **130-C** and **130-D**. Further oxidation produced cations **130-E** and **130-F**. Due to the steric effect of DCFS, the *para*-cation **130-F** was favored to be caught by H_2O to form intermediate **130-G**, which was deprotonated to regenerate DCFS and deliver the final product **131**.

As for C(sp^3)-H bonds, the Shono-type oxidation involving iminium as intermediate was also applied for the C–H hydroxylation. In 2018, Stahl reported the aminoxyl mediator enabled electrochemical C–H hydroxylation for the carbonylation of methylene in cyclic carbamate (top of Scheme 52).[132] The mediated oxidation of the substrate **132** with the aid of ABNO provided iminium

132-A, as the indispensable intermediate. In path **A**, the nucleophilic addition of H_2O to the iminium **132-A** accessed the C–H hydroxylation to hydroxyl intermediate **133**, which was further oxidized to the carbonyl product **134**. The iminium **132-A** could also be trapped by ABNOH to form *N*,*O*-acetal **132-B**, which offered the final product **134** by the subsequent oxidation and hydrolysis *via* path **B**. These results were consistent with Deprez's report using pyrrolidine **135** as C–H source in 2021 (bottom of Scheme 52).[133] The intermediates containing the formed C–O bonds were essential for further oxidation to deliver the final product **136**.

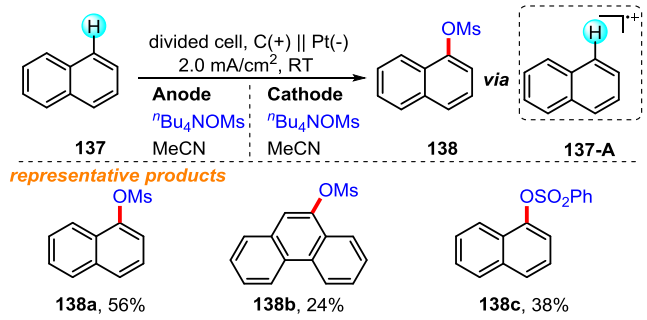
Scheme 52 Mediated hydroxylation of C(sp^3)-H bonds



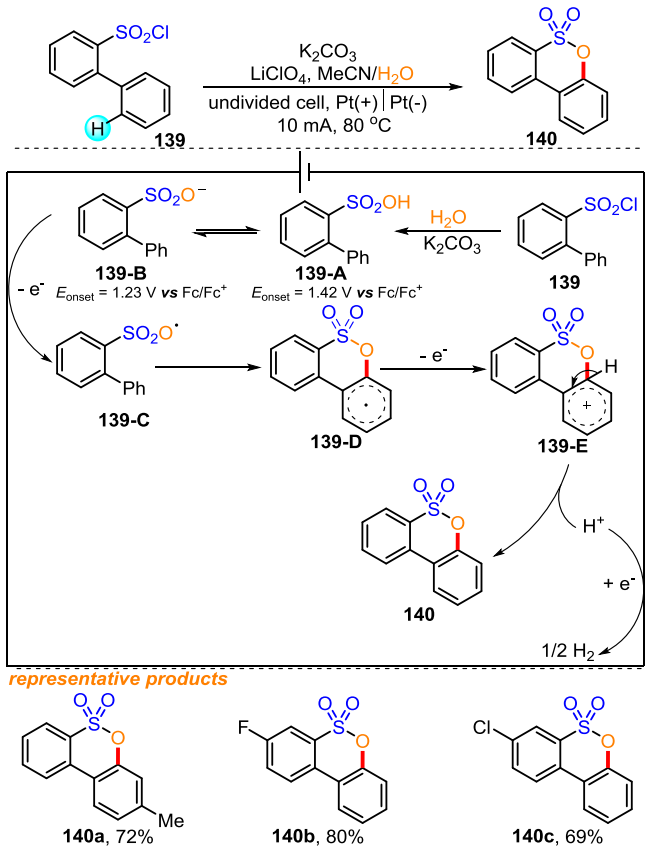
4.2. C–H phosphinoyloxylation & sulfonyloxylation

Sulfonates and phosphates could be prepared by electrochemical C–H functionalization with various C–H sources. In 2019, the electrochemical synthesis of aryl mesylate **138** was accomplished by Waldvogel with arene **137** as C–H source *via* non-Kolbe oxidation (Scheme 53).[134] In other words, the substate **137** was first oxidized to form unstable radical cation **137-A**, which would be captured by the concentrated mesylate anion to give the desired product **138**. In addition, the aryl C–H sulfonyloxylation could be accessed intramolecularly *via* the Kolbe-type pathway according to Suga's report in 2023 (Scheme 54).[135] Sulfonyl chloride **139** was used as the initial substrate to prepare sulfonic acid **139-A** *in-situ* by hydrolysis. The sulfonate anion **139-B**, which was generated from the deprotonation of sulfonic acid **139-A**, formed the radical **139-C** *via* anodic oxidation. The radical **139-C** was allowed to proceed intramolecular cyclization to deliver carbon radical **139-D**. The oxidation and deprotonation for re-aromatization would afford the final sulfonate **140**. For C(sp^3)-H sulfonyloxylation, organocatalytic electrochemical transformation was an efficient pathway. In 2023, Moran realized the *α*-carbonyl C–H tosyloxylation of ketone **141** catalyzed by the electrochemically generated hypervalent iodine species to yield **142** (Scheme 55).[136] Similarly, based on Mo's report in 2018 (Scheme 56),[137] the phosphonic Kolbe oxidation of **143** could occur intramolecularly to obtain **143-A** as intermediate to realize the C–H phosphinoyloxylation to deliver **144**.

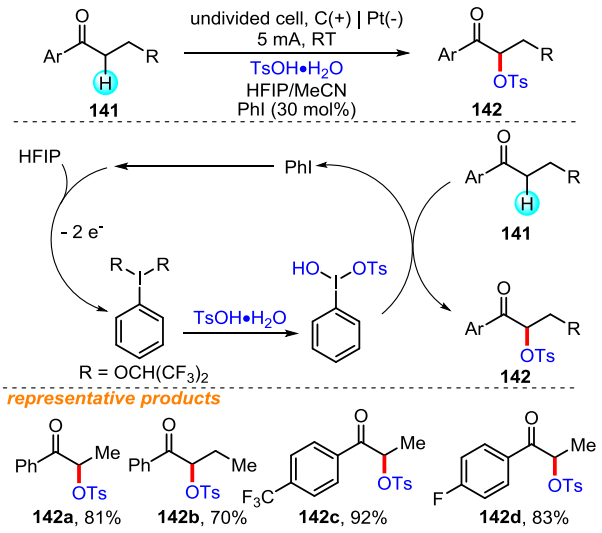
Scheme 53 Non-Kolbe C–H sulfonyloxylation



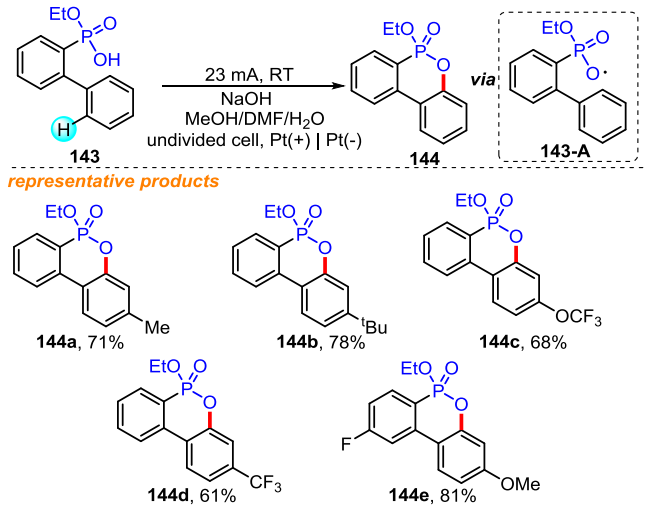
Scheme 54 Kolbe-type C–H sulfonyloxylation



Scheme 55 C(sp^3)-H sulfonyloxylation



Scheme 56 Kolbe-type C–H phosphinoyloxylation

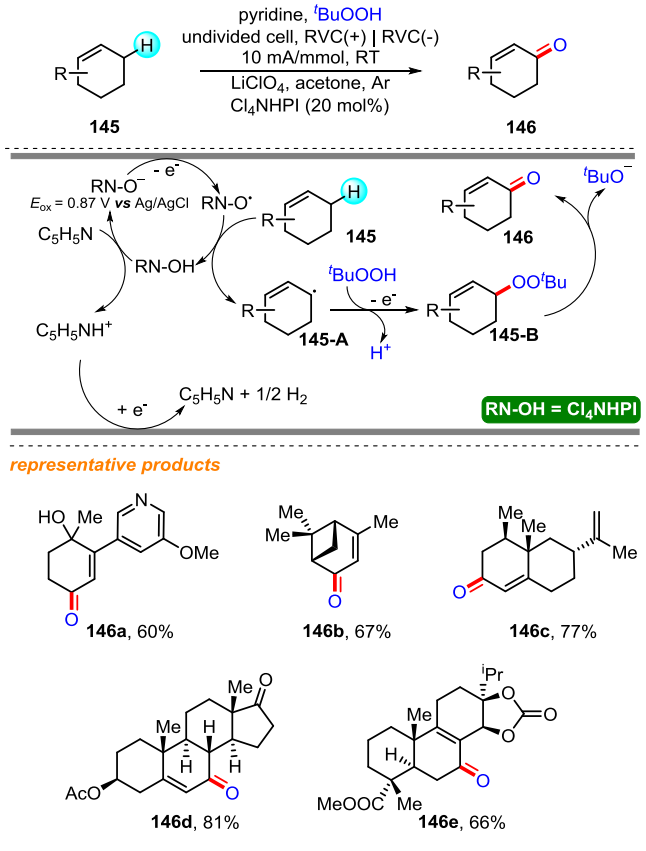


4.3. C–H carbonylation of methylene

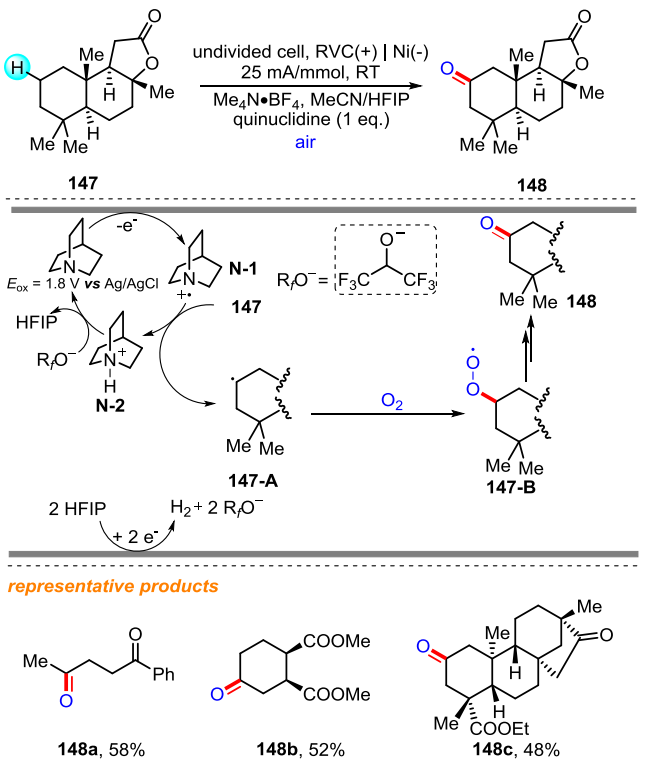
As the topic was particularly focused, electrochemical C–H peroxidation with oxygen or peroxide was a powerful channel to deliver peroxide radical for further carbonylation of methylene. In early 2016, Baran's group started the relevant electrochemical exploration of allylic C–H bonds with the mediation of Cl_4-NHPI (Scheme 57).[138] Various allylic C–H bonds were included in their report. Gram-scale experiments and the application to the synthesis of complex compounds demonstrated the excellent practicality of the electrochemical method. In the mechanism, Cl_4-NHPI was deprotonated by basic pyridine to form the anion, which was oxidized to *N*-oxyl radical. The HAT process between *N*-oxyl radical and the substrate **145** would yield the relatively stable allylic radical species **145-A** and regenerate Cl_4-NHPI for another catalytic event. The ^{t}BuOO$^\bullet$ generated electrochemically from the added ^{t}BuOOH reacted with the allylic radical **145-A** to give the allylic peroxide **145-B**, which afforded enon **146** as product with the elimination of ^{t}BuOH.

What's more, unactivated C–H bonds also caught their attention in 2017 (Scheme 58).[139] Secondary and tertiary C–H bonds in simple or complex molecules were tested with their method. The quinuclidine was used as a mediator to undergo anodic oxidation initially to form radical cation **N-1**. The HAT process of radical cation **N-1** and the C–H source **147** would deliver carbon radical **147-A** and release ammonium **N-2**, which was deprotonated to

Scheme 57 Cl_4NHPI-mediated allyl carbonylation



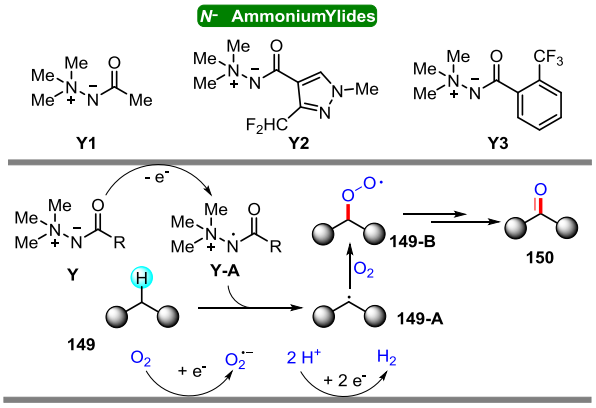
Scheme 58 Quinuclidine-mediated carbonylation



regenerate quinuclidine. The carbon radical **147-A** was quenched by molecular oxygen to give peroxide radical **147-B** for ensuing chemical preparation of final product **148**. In 2021, the discovery and introduction of *N*-ammonium ylides **Y1–Y3** as the mediators

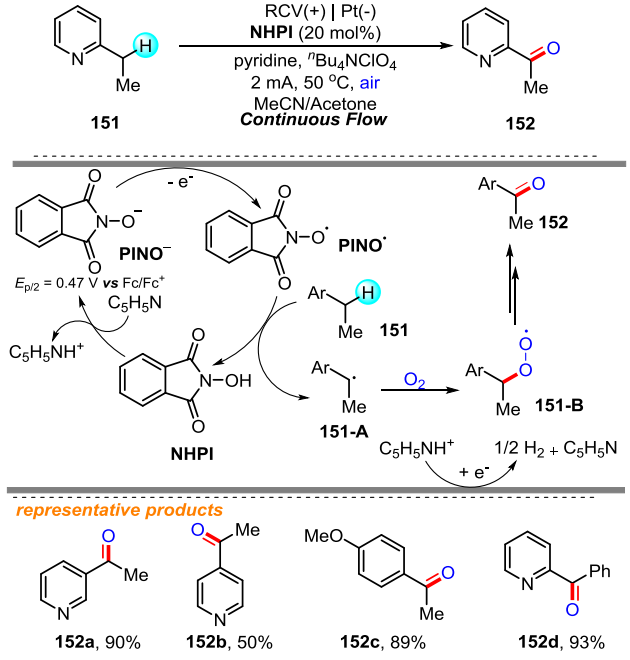
for electrochemical C–H peroxidation was also reported by them (Scheme 59).[140] In the mechanism, the added precursor was deprotonated to form *N*-ammonium ylide **Y**, which was oxidized to deliver *N*-ammonium amidyl radical **Y-A** with an excellent ability for the following C–H abstraction with substrate **149**. The acquired carbon radical **149-A** could be converted to final product **150** with the participation of O_2.

Scheme 59 *N*-Ammonium ylide-mediated carbonylation



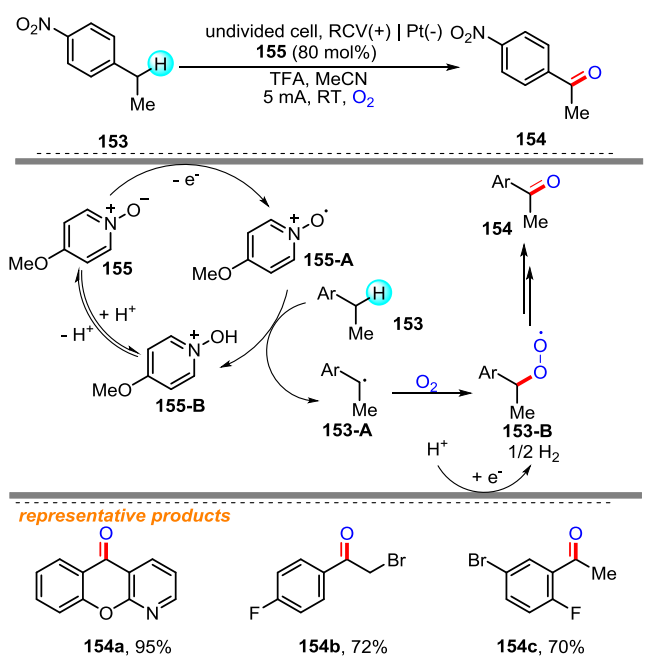
Benzyl C–H bonds with higher reactivity could also be applied in the electrochemical C–H peroxidation incontrovertibly. In 2018, Jensen realized the NHPI-mediated electrochemical carbonylation of benzyl methylene under continuous flow (Scheme 60).[141] Using pyridine as the base, NHPI was deprotonated to form *N*-oxyl anion $PINO^-$, which would be oxidized to the $PINO^•$ radical. The abstraction of benzylic hydrogen atom in **151** was completed by $PINO^•$ radical to deliver benzyl radical **151-A**. The desired carbonylation proceed finally to give the product **152** under O_2 atmosphere. *N*-Oxide **155** was also used as mediator for an analogical transformation by Mo in 2024 (Scheme 61).[142]

Scheme 60 NHPI-mediated carbonylation

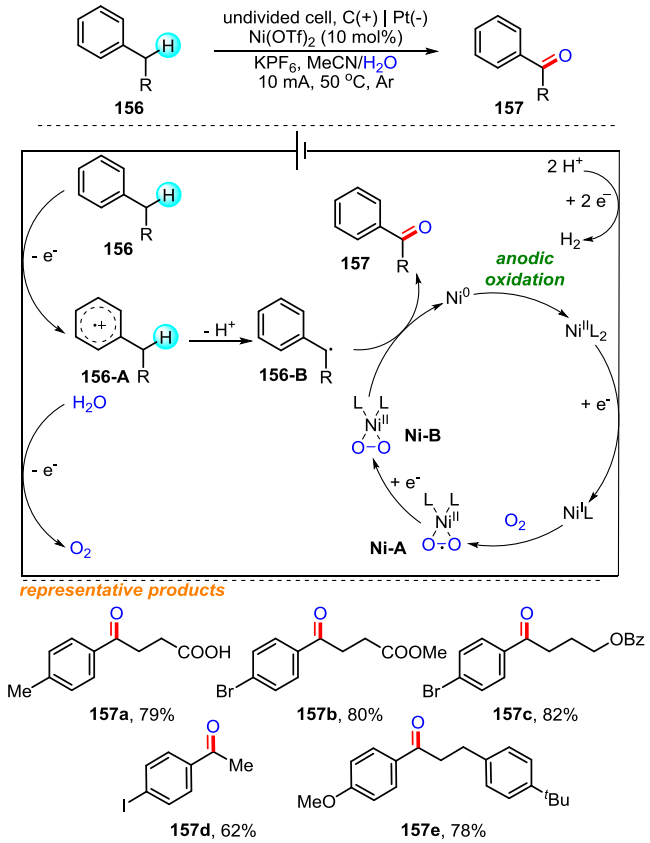


In the same year, according to Qiu's report, Ni-catalyzed electrochemical pathway could be introduced into the transformation of C–H oxygenation with diverse benzyl C–H sources (Scheme 62).[143] The reaction was enabled by the proposed paired electrolysis. At the anode, the oxidation of arene **156** provided corresponding radical cation **156-A**, which formed the benzyl radical

Scheme 61 Pyridine-*N*-oxide-mediated carbonylation



Scheme 62 Ni-catalyzed carbonylation



156-B *via* deprotonation. Meanwhile, O_2 was released from the oxidation of H_2O. At cathode, Ni(II) species was reduced to afford Ni(I) intermediate, which could active O_2 to deliver Ni(II)-superoxo species **Ni-A**. The further reduction occurred to obtain Ni(II)-peroxo species **Ni-B**. The reaction between **Ni-B** and the benzyl radical **156-B** gave the final product **157** and Ni(0) species. The subsequent oxidation of Ni(0) species could regenerate Ni(II) salt to complete the catalytic cycle.

5. Conclusions

As shown in this review, electrochemical formation of C–O bonds using available C–H sources has been widely used for the synthesis of esters, ethers, alcohols, phenols, *etc*. Various C(sp^2)-H and C(sp^3)-H sources can be converted *via* direct or indirect oxidation with the assistance of metals and organic catalysts. The electrochemical formation of C–O bonds can also be a crucial step in the total synthesis and late modification of some complex synthetic drugs or natural products. The construction of C–O bonds can be driven intramolecularly and intermolecularly by electrochemical methods with high step- and atom-economy.

In general, C(sp^2)-H bonds exhibited better reactivities to proceed the electrochemical functionalization with abundant reports. Diverse aryl and heteroaryl substrates can serve as C(sp^2)-H donors while cases involving alkenes were comparatively poor. It should be noted that, due to the widespread existence of alkenes bearing multiplex substituents, more electrochemical modes are urgently needed to accomplish the C(sp^2)-H functionalization for the formation of C–O bonds from alkenes. As for C(sp^3)-H bonds, the electrochemical formation of C–O bonds commonly occurs on active sites such as benzyl, allyl, *α*-*N*(*S*) and *α*-carbonyl C–H bonds. There are very limited reports on the reaction of inactivated C(sp^3)-H bonds. The catalysts with better effects are worth to be developed to treat the situation. The enantioselective formation of C–O bonds is also narrow and ready to be extensively explored. Furthermore, it is the overconcentration of electrons in the C(sp)-H bond that leads to the high activity of oxidation, which is in preferred to the C(sp)-H functionalization. The introduction of other mild pathways may be the chosen one for the survival of alkyne in electrochemical reaction.

Overall, this review is supposed to provide a helpful reference for further research in electrochemical C–H functionalization and C–O formation.

Acknowledgement

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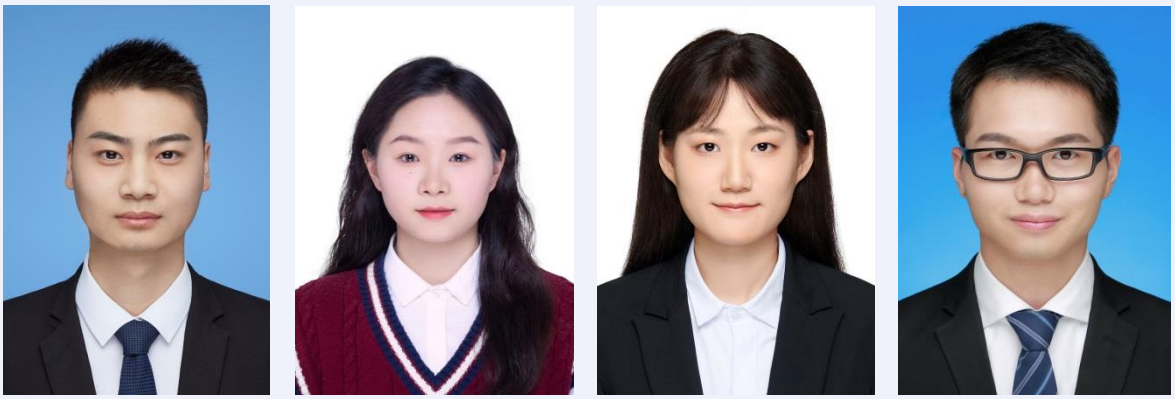

Left to Right: Chen Liu, Renxiu Zhang, Yunge Liu, Yunfei Zhang

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