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Electrifying green synthesis: recent advances in electrochemical annulation reactions

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Electricity originating from renewable resources can be used for highly sustainable and economically attractive applications. With electrons as the mass-free reagent, the use of a stoichiometric amount of oxidants in annulation reactions can be avoided, thereby eliminating the production of waste. Considered as a modern reaction configuration, the availability of electrochemical methods is expanding synthetic applications in the field of organic chemistry. Electrochemical transformations possess many benefits over traditional reagent-based methodologies, such as high functional group tolerance, mild conditions, easy scale up setup, high yields and selective transformations. In this review, we targeted electrochemical annulation reactions involving mediators and mediator-free conditions with generation of new C–C, C–heteroatom and heteroatom–heteroatom bonds, their mechanistic insights, as well as the reactivity of substrates. We also explain the recent use of sacrificial electrodes in annulation reactions.

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1. Introduction

Annulation is broadly defined as the construction of a new ring to organic molecules by introducing new bonds between the same or different atoms. In annulation reactions, the new bond-formation *via* conventional procedures commonly employs stoichiometric chemical oxidants, the use of which reduces the sustainability of the synthesis and carries safety and environmental concerns.[1–3] Conventional synthetic methods are generally performed at high temperatures or

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pressures; however, electrochemical reactions are generally carried out under mild conditions without the addition of external oxidants, and in short reaction times, saving energy. In addition, by changing the operating current, the reaction time can be controlled. By varying the current or voltage, the oxidation or reduction capacity of the electrochemical system can be manipulated, which is another advantage compared to conventional methodologies.[4,5] An intriguing discussion on the advantages of electrosynthesis compared to traditional methods was presented by Lei and Yuan, where the authors addressed the difficulties and limitations found in electrochemical reactions. Ways to solve these possible limitations in electrosynthesis, making it cleaner, are discussed.[6] Very recently, Gerhard Hilt published an enlightening review addressing the basic strategies and types of applications in organic electrochemistry, containing an overview of the requirements and possibilities in electrosynthesis.[7]

Recent developments in various cyclic reactions have been reported through a range of electrochemical annulations for the development of pharma-, agro- and fine chemicals as well as the synthesis of complex molecules derived from natural products.[8–10] Due to the abundance in nature and the respective reactivity of aromatic heterocycles, the direct C–H or C–heteroatom functionalization calls the attention of several scientists, being extensively applied to obtain target compounds. In general, annulation reactions can occur through the intramolecular coupling when the electrogenerated center and another reactive center are in appropriate energies and positions in the molecule, favoring the reaction, or by intermolecular coupling. In the latter case, the annulation reaction involves the formation of two separate or simultaneous bonds.[11] Electrochemical conversions include the cleavage of a covalent bond as the main reaction pathway. This way, both indirect electrolysis, which requires electron transfer mediators, and direct electrolysis, which involves the heterogeneous transfer of electrons directly between the electrode and the substrate, play an important role.[12] Regarding the radical, it is possible to observe changes in the geometry structure after electron gain or loss, and cleavage or formation of new bonds may occur. With the removal of an electron from the highest occupied molecular orbital (HOMO), a radical cation is formed. On the other hand, if an electron is introduced externally, it will occupy the smallest unoccupied molecular orbital (LUMO), providing an anionic radical. Ionic radicals present a double character, have a charge and therefore are close to the ions, and present an unpaired electron that can react as radicals.[13]

1.1. Scope of this review

Herein, we present the recent advances in annulation reactions under electrochemical conditions. Over the past few years, researchers in this area have made significant progress, proving that electrolysis is a powerful tool for the hetero- and carboannulations. To aid the reading, this review is divided into five sections: (1) Introduction, (2) Mediator-promoted electrochemical annulation reactions, (3) Mediator-free electrochemical annulation reactions, (4) Sacrificial electrodes for electrochemical annulation reactions and (5) Conclusions and outlook. Electrochemical methodologies related to obtaining new C–C, C–heteroatom and Het–Het bonds are discussed, evaluating the mechanistic pathway, as well as the reactivity of substrates.

2. Mediator-promoted electrochemical annulation reactions

Indirect reactions are those in which the exchange of electrons occurs between a mediator and the organic substrate. The mediators allow the transformation of organic compounds at lower oxidation potentials than the standard potentials. They also increase the selectivity and efficiency of the reaction, redu-

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cing energy consumption.[14] Mediators can be organic derivatives (*e.g.* triarylamines, TEMPO, and hypervalent compounds), or inorganic derivatives (*e.g.* transition metal complexes, multivalent metal ions, and halide ions), which can originate from the electrolyte or can be added externally to the system.[15] In addition, the use of catalysts is necessary when an organic substrate is not reactive enough or when the reaction leads to parallel reactions, superoxidation, dimerization, or electrode passivation.[16] Next, we will discuss the reactivity and the need for the use of mediators in electrochemical annulation reactions.

2.1. C–Heteroatom and C–C bond formation

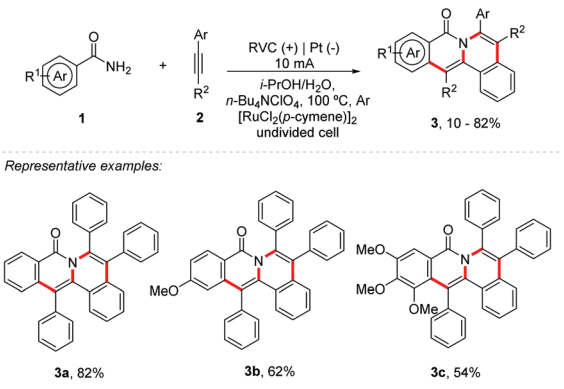
Carbon–heteroatom and carbon–carbon bond forming reactions are constantly applied in the synthesis of medically significant molecules and agrochemicals, and they are of great value to materials science.[17] Electrosynthesis catalyzed by metals activates the organic substrate by the active electrogenerated species of the transition metal catalyst, providing an organometallic intermediate that can be reduced or oxidized more easily. The metallic species can be regenerated electrochemically without the addition of external oxidants. Considering this, electrosynthesis catalysed by metals has been explored with several metals, such as Co, Mn, Cu, Ru, Rh, Ir, and Fe, among others.[15] Lei and Ackermann group's recently described a C–H/N–H bond functionalization using cobalt as a mediator in electrochemistry.[18,19] Similarly, Sundararaju and co-workers reported a cobalt and photoredox catalysis.[20] Additionally, Borggraeve and co-workers described an interesting review comparing photoredox catalysis and electrochemistry in organic synthesis.[21] Likewise, Ahmed and co-workers summarized some of the latest research efforts in using photoelectrochemical cells.[22]

Protected amides commonly react with alkynes, providing simple isoquinolones, being catalyzed by Ni, Ru, Rh, and Co, among others.[23–27] Likewise, Tang and co-workers proposed the first double-electrocatalytic organometallic C–H activation with amides **1** and alkynes **2** for the synthesis of polycyclic isoquinolinones **3** (Scheme 1).[28] No external oxidants were applied and after 14 h, using $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), NaOPiv (1.0 equiv.), and n-Bu_4NClO_4 (1.0 equiv.) under a 10 mA current, the products were obtained in yields up to 82%. Substrates with electron-rich and electron-deficient substituents in both alkynes and benzoylamides were well tolerated; however, the increase in the number of methoxy substituents in benzoylamides resulted in decreased reaction efficiency (Scheme 1 – **3b** and **3c**). The role of the electric current is to anodically oxidize Ru(0) to Ru(II) to regenerate the catalyst in the cycle. Compared to the literature using a strong oxidizer,[29] the most notable feature is the effective improvement of product regioselectivity under mild electrical conditions and no use of protective groups.

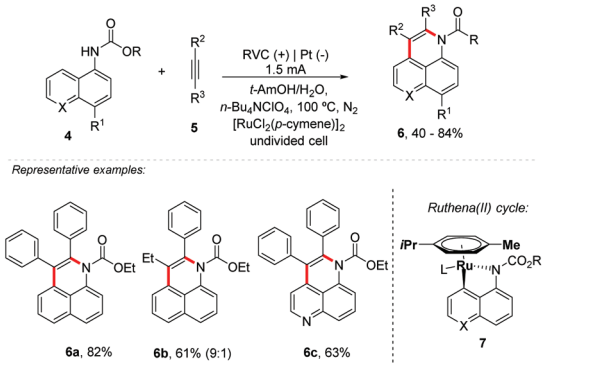
Electro-oxidative activation of C–H/N–H carbamate and C–H/O–H 1-naphthols **4** with internal alkynes **5** catalyzed by Ru has been described by Ackermann's group (Scheme 2).[30] Good tolerance of functional groups, such as ester, fluorine, chlorine or bromine substituents, was achieved; however, it presented the need to protect the amine group for N–H activation. Asymmetric alkynes provided the desired product **6b** with high levels of regio-control (9 : 1), favouring the aromatic portion on the nitrogen heteroatom side. The mechanism was proposed through ruthena(II) cycle **7**, followed by alkyne insertion.

Considering the remarkable interest of Ackermann's group in the reactions of C–H/heteroatom–H activation with alkynes,[31,32] the group also proposed the synthesis of isochromen-1-one derivatives from alkynes and benzoic acid,[33] and good yields (up to 93%) were obtained for both electron-rich and electron-deficient arenes, providing products from symmetric and non-symmetric, aromatic and aliphatic alkynes. Recently, the same group developed a modular electrochemical route for aza-PAHs **10** through a rhodium-catalyzed cascade C–H activation for alkyne annulation (Scheme 3).[34] Aryl amidoximes **8** bearing electron-donating and electron-withdrawing groups were well tolerated. Asymmetric substrates were isolated with high levels of regioselectivity and good yields. The authors also isolated two main rodacyclic intermediates (**11** and **12**, Scheme 3), making it possible to identify the exact order of activation of the C–H bond.

In addition, Ackermann's group reported the use of a cobalt catalyst for the activation of C–H/N–H bonds with carbon monoxide and isocyanate derivatives (Scheme 4).[35]



Scheme 1 Synthesis of polycyclic isoquinolinones.



Scheme 2 Ruthenium-catalyzed alkyne annulations by C–H/Het–H activation.

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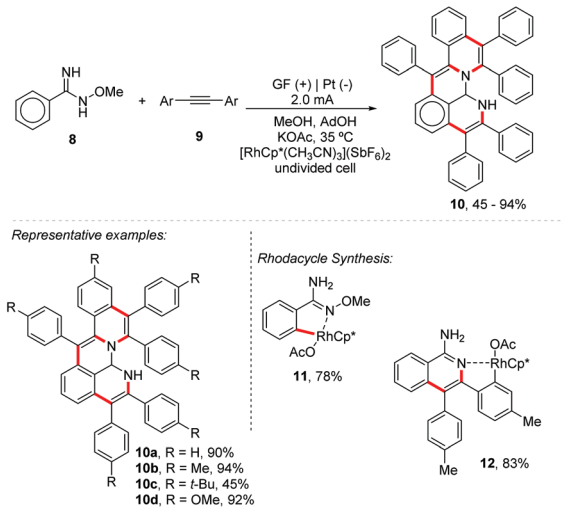
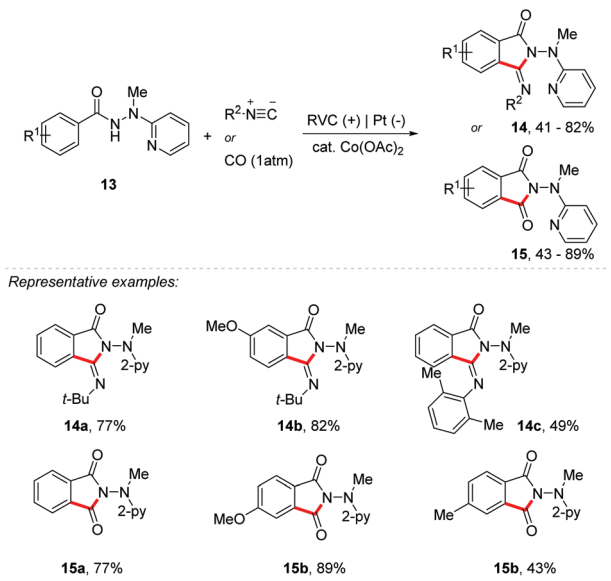


Scheme 3 Rhoda-electrocatalyzed C–H/N–H activation.

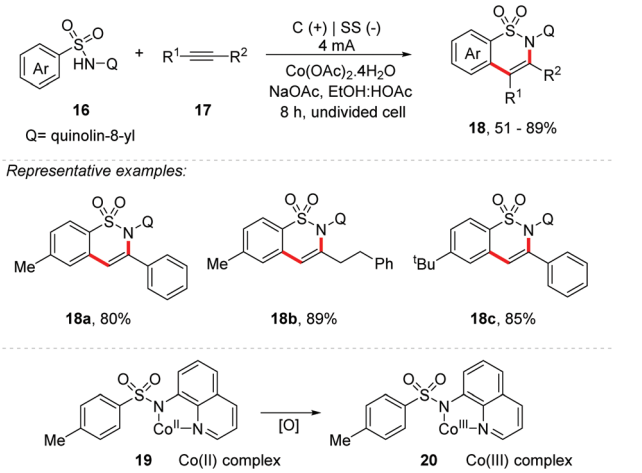


Scheme 4 Cobalt catalyst for the activation of C–H/N–H bonds with carbon monoxide and isocyanate derivatives.

Both reactions were successful using an RVC anode and a platinum cathode as electrodes with $Co(OAc)_2$ (20 mol%) and NaOPiv (1 equiv.) as additives and benzhydrazide **13** as the starting material common to both methodologies. However, for the reactions with isocyanate the best electrolyte was *n*-Bu_4NBF_4 (2 equiv.), DMSO as solvent, and a constant current electrolysis of 4 mA at 120 °C, giving products **14** in up to 82% yield. On the other hand, for the reaction with carbon monoxide, the best electrolyte was *n*-Bu_4NClO_4 (0.6 equiv.), with TFE : HFIP (2 : 1) as a solvent mixture under a constant current electrolysis of 3 mA at room temperature, giving products **15** in up to 89% yield. Competition studies have shown that electron-rich benzhydrazides achieved higher speeds than the electron-poor derivative. According to these results, the authors concluded that the mechanism follows the base-assisted internal electrophilic-type substitution (BIES) C–H metalation.[36] In order to understand the role of the cobalt catalyst, the authors performed cyclic voltammetry, concluding that through anodic oxidation a cobalt(III) species was formed.

Lei and co-workers described a transition metal cobalt catalyzed electrochemical [4 + 2] annulation of sulfonamides **16** with alkynes **17** to obtain sultam derivatives **18** (Scheme 5).[37] The reaction was carried out under a constant current electrolysis of 4.0 mA in an undivided cell, with a carbon cloth anode and a stainless steel plate cathode, in the presence of $Co(OAc)_2{\cdot}4H_2O$ (20 mol%) and NaOAc (2 equiv.) additives, using a mixture of ethanol and acetic acid as the co-solvent, at 75 °C for 8 h (3.4 $Fmol^{-1}$). Both electron-deficient and electron-rich acetylene derivatives were efficient in the annulation reaction, affording products in up to 85% yield. Alkyl alkynes were also evaluated, providing products in yields of up to 89%. Following the same *modus-operandi*, sulfonamides were explored with a wide scope of substituents. Considering a study using cyclic voltammetry, the authors suggest that the mechanism follows *via* a Co(II) species that initially coordinates with the sulfonamide, providing an intermediate complex **19**; through a single electron oxidation, access to the Co(III) complex **20** is achieved. This protocol proved to be practical and scalable, and by scaling up to 5.0 mmol, 86% yield was obtained.

It is appropriate here to highlight the advances made in reactions mediated by vitamin B_{12} derivatives. Through controlled-potential electrolysis, the catalytic cycle is based on a change in the valence of cobalt naturally derived from vitamin B_{12}.[38,39] Researchers have already applied cyano-cobalamin and its derivatives as catalysts in organic synthesis, such as double bond addition reactions, dehalogenation, halide coupling, oxidation, ring expansion, and functionalization of C–H bonds, among others.[40–43] Important discoveries with a new point of view on the chemistry of a B_{12} derivative in an organic



Scheme 5 Substrate scope for the synthesis of sultams *via* cobalt catalyzed electrochemical [4 + 2] annulation.

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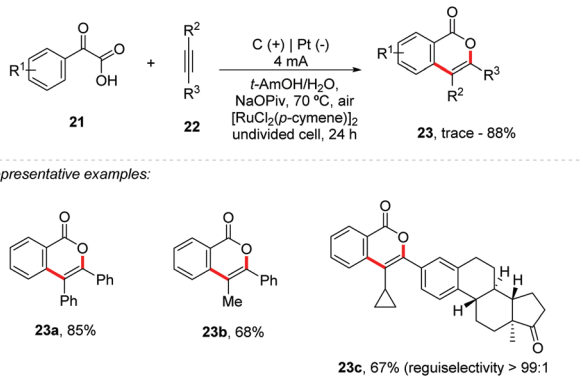
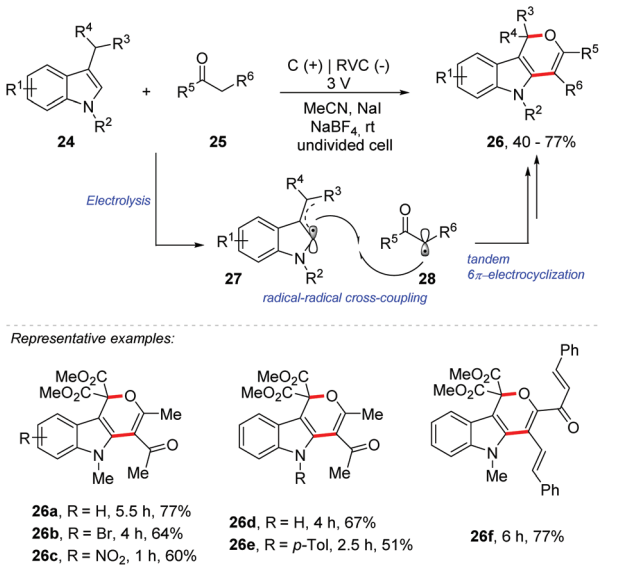
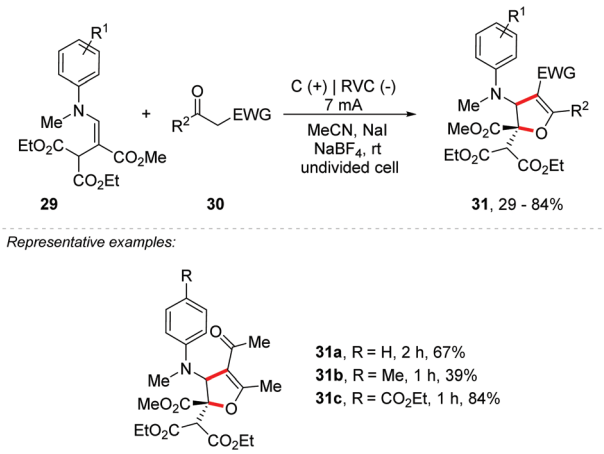


Scheme 6 Ruthenium-catalyzed decarboxylative [4 + 2] annulation of arylglyoxylic acids with internal alkynes.



Scheme 7 Electrochemical double oxidative [3 + 3] cycloaddition for the synthesis of substituted dihydropyrano[4,3-*b*]indoles.



Scheme 8 Electrochemical double oxidative [3 + 3] cycloaddition for the synthesis of substituted 2,3-dihydrofuran derivatives.

and aprotic environment were made by Hisaeda and co-workers,[44] and these should be considered by the new generation of researchers.

He and co-workers developed a new strategy for [4 + 2] annulation of arylglyoxylic acids **21** with internal alkynes **22** using ruthenium catalysis, providing the respective 1*H*-isochromen-1-one **23** in yields of up to 88% (Scheme 6).[45] Symmetric and unsymmetric internal alkynes were suitable, but it was not feasible for terminal alkynes and 1,2-di-*o*-tolylethyne. Control experiments showed that the reaction under an inert atmosphere was identical to that under air; however with an O_2 atmosphere the **23a** yield decreased to 43%. The results suggest that the newly formed carboxyl oxygen atoms are not from O_2, which was also supported by the ^{18}O-labeled isotope experiment. Interestingly, both oxygen atoms were replaced by ^{18}O isotopes when $H_2{}^{18}O$ was used. The authors emphasize that the reaction *via* electrochemistry occurs through a different pathway from Ru-catalyzed decarboxylative annulations previously reported by Wang and co-workers.[46] The Hammett graph analysis for competition experiments is in accordance with the reactivity order of the aryl glyoxylic acids: electron-rich aryl glyoxylic acids > 2-oxo-2-phenylacetic acid > electron-deficient aryl glyoxylic acids.

Very recently, Park and co-workers reported an electrochemical double oxidative [3 + 3] cycloaddition for the synthesis of substituted dihydropyrano[4,3-*b*]indoles **26** (Scheme 7).[47] The methodology was extended to the synthesis of 2,3-dihydrofuran derivatives **31** (Scheme 8). Electrolysis was carried out in an undivided cell, equipped with graphite electrodes as the anode and reticulated vitreous carbon (RVC) as the cathode, in acetonitrile as a solvent in the presence of NaI as a mediator and $NaBF_4$ as an electrolyte, under a constant voltage of 3 V. Given the scope of indole **24**, the method was efficient with halide, nitro, nitrile, methoxy and *N*-Boc substituents. *N*-Alkyl and *N*-aryl indoles, as well as 7-azaindole, were also compatible in the transformation. Regarding the variation of the active methylene compound (AMC) **25**, unsymmetric diketones reacted with complete regioselectivity and several electron donating and withdrawing substituents were efficient in this transformation. According to the authors, the reaction proceeds by radical–radical cross-coupling of the indole/enamine radicals **27** with the radical species derived from the AMCs **28**, followed by tandem 6π-electrocyclization.

2.2. C–Heteroatom bond formation

The discovery that catalysts could mediate similar transformations replacing organometallic derivatives was a huge scientific advance for the formation of carbon–heteroatom bonds, being useful for the construction of several heterocycles.[48] In addition, mediated reactions are widely used for the formation of C–N bonds, being able to assemble a wide range of heterocycles of interest containing nitrogen, for example, pyrroles, indoles, benzimidazoles, quinolines, among others. Recently, Huang and co-workers developed an efficient approach for the

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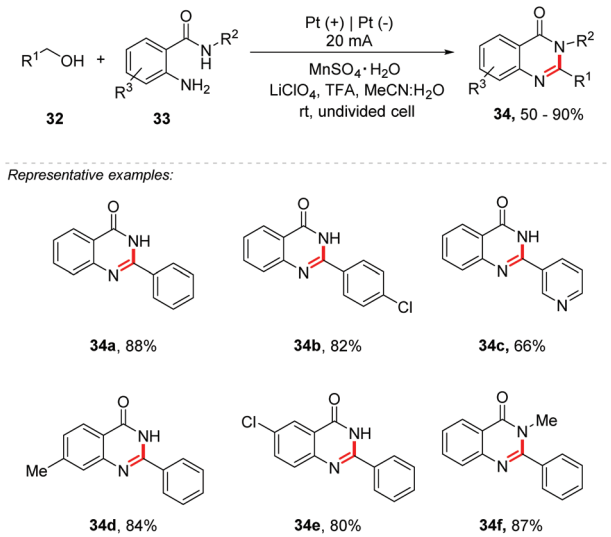
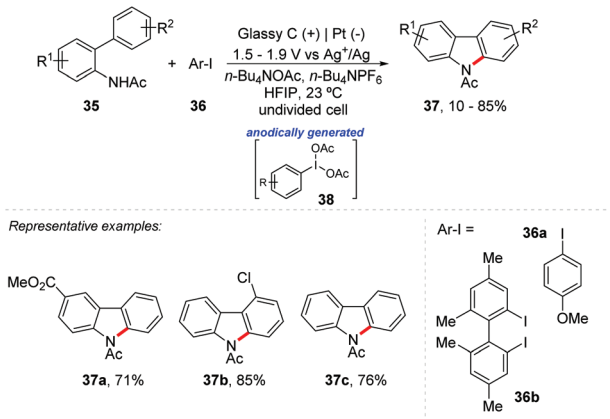


Scheme 9 Mn-Catalyzed electrochemical synthesis of quinazolinones from primary alcohols and *o*-aminobenzamides.

synthesis of quinazolinones **34** from *o*-aminobenzamides **33** and alcohols **32** by the combination of electrochemistry and a redox-metal catalyst (Scheme 9).[49] The authors describe the first Mn catalysed cascade cyclization reaction to afford quinazolinones. Primary benzylic alcohols bearing electron-donating or electron-withdrawing groups were evaluated, and also, sterically hindered substrates. Additionally, *o*-aminobenzamides bearing electron-donating or electron-withdrawing groups were tested as well. The reaction was performed under a constant current electrolysis of 20 mA in an undivided cell, with Pt foil as electrodes, $LiClO_4$ as the electrolyte, MeCN : H_2O (48 : 2) as the solvent, TFA as an additive, and $MnSO_4{\cdot}H_2O$ (10 mol%) as a redox catalyst, under air at room temperature. The authors stated that water had a significant influence on this reaction. The compounds **34** were obtained in good yields, up to 90%. Interestingly, heteroaromatic alcohols with pyridinyl (**34c**), furanyl and thienyl groups were also suitable coupling partners, with good yields (up to 72%). Halide substituents were well tolerated under the electrochemical conditions. Benzyl methyl ethers were tested affording quinazolinone derivatives in good yields, up to 83%. The reaction mechanism was proposed, and considering the oxidation peak for Mn(II) at 1.87 V (*vs.* SCE) in the presence of TFA observed by cyclic voltammetry, the authors suggest that the reaction is mediated by Mn (III).

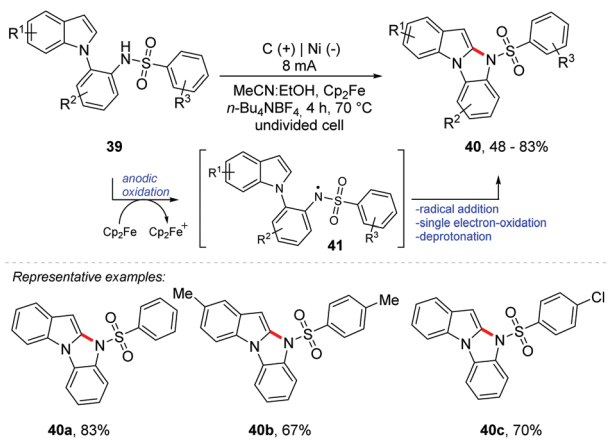
Hypervalent iodine reagents are classified as organic oxidants and have already been explored in various chemical transformations. Due to their great importance, there have already been several revisions and books reporting the recent advances in hypervalent iodine(III)-catalyzed functionalization, and it is still a topic of interest.[50–53] Recently, Wirth *et al.* reported an interesting review on the electrochemical generation of hypervalent iodine reagents through anodic oxidation of iodoarenes, reporting their application as mediators for



Scheme 10 Electrocatalytic C–N coupling *via* anodically generated hypervalent iodine oxidants.

different chemical transformations.[54] Additionally, Powers and co-workers reported electrocatalytic C–N coupling *via* anodically generated hypervalent iodine oxidants **38** (Scheme 10).[55] A series of *N*-acetylcarbazole **37** were obtained with yields of up to 85% in an undivided cell with glassy carbon anode and platinum cathode electrodes, under a potential of 1.5 V (CPE) to 1.9 V *vs.* Ag^+/Ag reference electrode at room temperature using HFIP as solvent.

Lei and co-workers described an intramolecular oxidative electrochemical C–H/N–H cross-coupling methodology to achieve 10*H*-benzo[4,5]imidazo[1,2-*a*]-indole derivatives **40** mediated by Cp_2Fe, obtaining products with up to 83% yield (Scheme 11).[56] An undivided cell was equipped with a graphite electrode at the anode and a nickel electrode at the cathode using a solvent mixture of MeCN : EtOH (1 : 1) and *n*-Bu_4NBF_4 as the electrolyte under a constant current of 8 mA at 70 °C for 4 h (4 $Fmol^{-1}$). From the anodic oxidation of Cp_2Fe to Cp_2Fe^+, the reaction proceeds to the oxidation of the conjugated base of **39** delivering the radical nitrogen species **41**. Intramolecular



Scheme 11 Intramolecular oxidative electrochemical C–H/N–H cross-coupling.

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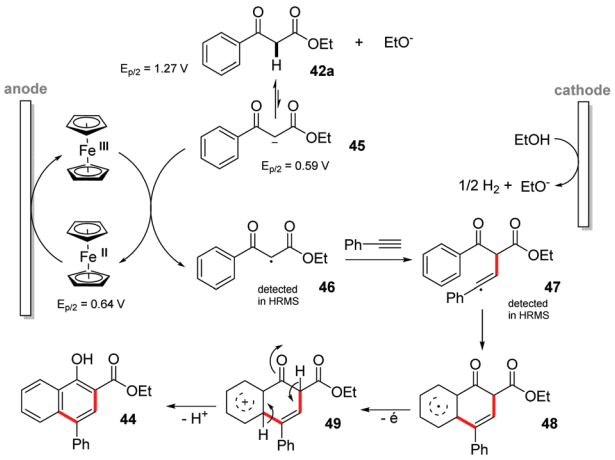
radical addition, single electron oxidation and deprotonation provide the product **40**.

2.3. C–C bond formation

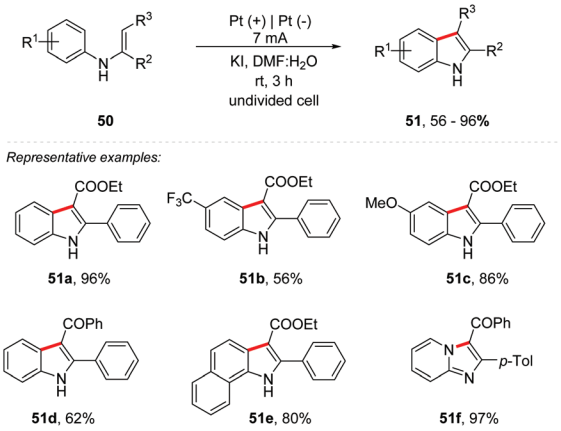
In the last few years, new procedures for obtaining naphthol derivatives by C–H bond activation have been developed by Wang,[57] Narender,[58] Yu,[59] Yamamoto,[60] and Larock.[61] In the same way, Pan and co-workers proposed a synthesis of 1-naphthols **44** by C-centered radical cyclization of highly functionalized 1,3-dicarbonyl compounds **42** with alkynes **43** by [4 + 2] intermolecular annulation (Scheme 12).[62] The reaction was conducted in an undivided cell in the presence of Cp_2Fe as a catalyst in a THF : EtOH (1 : 1) mixed solvent at a constant potential of 1.15 V *vs.* Ag/AgCl with NaOEt (30 mol%) as the base. Both the electron donating and electron withdrawing substituents were evaluated and all groups showed good yields (up to 84%). However, the electron donating substituents showed better yields than the electron withdrawing groups. From the cyclic voltammetry (Ag/AgCl) experiments, the oxidation potentials of **42a** (1.27 V), the conjugate base **45** (0.59 V) and Cp_2Fe (0.64 V) were obtained. In addition, the **42a** curve together with Cp_2Fe had practically no change in the potential compared to the Cp_2Fe curve. However, the mixture of **42a**, EtO^- and Cp_2Fe showed a significant increase, indicating that the electron transfer had occurred. In summary, it was observed that the reaction between Cp_2Fe and **42a** did not occur; however the reaction between the conjugated base **45** and Cp_2Fe promotes the transformation efficiently. Based on the control experiments, the reaction mechanism was proposed. It was also possible to detect by HRMS the adducts of intermediate radicals **46** and **47** with TEMPO, proving the presence of these species in the medium (Scheme 13).

In recent years, there has been an increasing number of reactions involving iodine as a mediator, often with equivalent or even better efficiency compared to those catalyzed by transition metals. Recently, Lei and co-workers published an overview of the recent development of iodine-mediated electrochemical coupling reactions.[63] Zhang and co-workers developed an interesting study of I^-, I_2, and ICl *via* cyclic voltammetry.[64] Likewise, Lei and co-workers proposed an iodine-promoted intramolecular dehydrogenative annulation of *N*-aryl enamine **50** for the synthesis of indole derivatives **51** (Scheme 14).[65] A constant current of 7 mA in an undivided cell, with a Pt plate as an electrode, KI (0.15 M) as the electrolyte, and DMF : H_2O (10 : 1) as a mixture of solvents at room temperature promoted the formation of products in yields of up to 96%. The use of 10% water showed a reaction improvement. It is noteworthy that KI not only works as an electrolyte, but also plays the role of a redox mediator. Electron-deficient and electron-rich *N*-phenyl enamines showed excellent yields; however the replacement of the carboxylic ester core by ketone was less efficient (**51d**). *N*-Naphthyl and *N*-pyridyl enamine derivatives were also fruitful, providing the respective products in good yields (**51e–51f**).

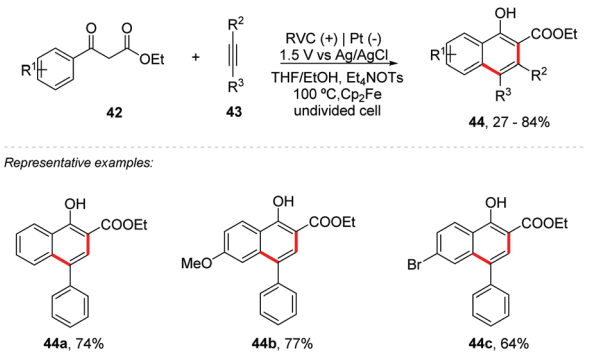
Considering the importance of fluorinated molecules, several protocols for fluoroalkylation have been described,



Scheme 13 Proposed mechanism for electrochemical synthesis of 1-naphthols.



Scheme 14 Intramolecular dehydrogenative C–H/C–H cross-coupling for the synthesis of indoles.



Scheme 12 C-Centered radical cyclization of highly functionalized 1,3-dicarbonyl compounds with alkynes.

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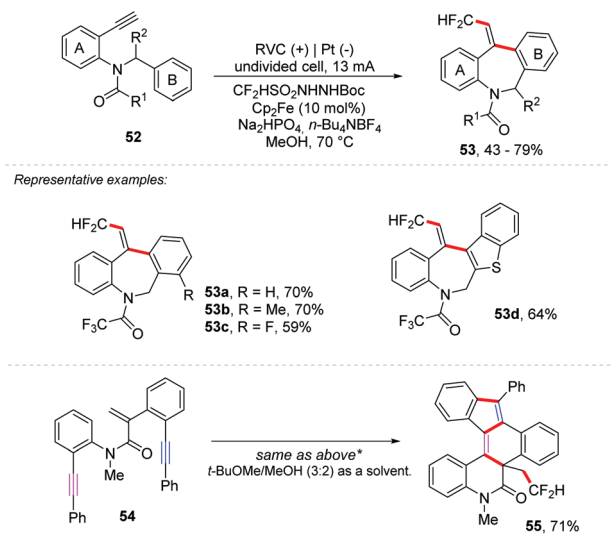
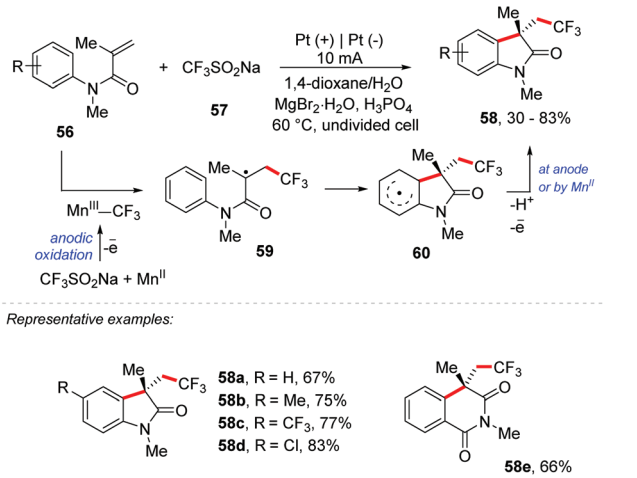
such as metallic catalysis[66,67] or photoredox catalysis,[68,69] and an interesting overview of fluorine in medicinal chemistry has been described by Gouverneur and co-workers.[70] Recently, Tian and co-workers reported a tandem trifluoromethylation/cyclization of *N*-arylacrylamides with TfNHNHBoc to give 3-(β,β,β-trifluoroethyl)-oxindole derivatives.[71] Additionally, Xu and co-workers have developed an unexplored ferrocene-mediated electrochemical alkyne difluoromethylarylation, using $CF_2HSO_2NHNHBoc$ as a CF_2H radical source, to provide derivatives of fluorinated dibenzazepines **53** in yields of up to 79% (Scheme 15).[72] The reaction was set up in an undivided cell containing an RVC anode and platinum cathode electrodes (7.4 $Fmol^{-1}$) with Cp_2Fe (10 mol%) as a mediator, Na_2HPO_4 (2 equiv.) as the base, and *n*-Et_4NBF_4 (1 equiv.) as the electrolyte in MeOH as the solvent at 70 °C. Enyne **54** was subjected to functionalization and four new C–C bonds and three new rings were obtained, providing the hexacyclic product **55** in 71% yield.

In addition, Mo and co-workers proposed an Mn-mediated electrochemical strategy for the trifluoromethylation/C(sp^2)–H functionalization using sodium trifluoromethanesulfinate (Langlois' reagent) as the CF_3 source (Scheme 16).[73] Several oxindoles and related heterocycles containing a trifluoromethyl group, including a series of novel compounds, were obtained with yields of up to 83%. The authors adopted $MnBr_2$ as a mediator and Pt as the electrode with a constant electric current of 10 mA for 6 h. H_3PO_4 (2 equiv.) was necessary as a sacrificial oxidizer; however the use of AcOH instead of H_3PO_4 showed practically identical results, and no electrolyte was needed. The Mn(III)–CF_3 species is generated by anodic oxidation of Mn(II) in the presence of Langlois' reagent. The CF_3 radical species is added to an olefin and a transitory radical centered **59** is formed, which can be oxidized by the Mn(II) species or at the anode; the elimination of a proton re-aromatizes the ring **60** providing the product **58**.



Scheme 15 Electrochemical difluoromethylarylation of alkynes.



Scheme 16 Mn-Mediated electrochemical strategy for the trifluoromethylation/C(sp^2)–H functionalization.

3. Mediator-free electrochemical annulation reactions

In the direct reactions, electron transfer occurs directly between the surface of the electrode and the organic substrate; in this context, all the essential properties of electrochemistry are completely applied, without any mediators. The main reaction region is the electrode surface itself, which can also occur close to the surface; however, the surface must have a large electric field, which is the differential of the common redox reactions in heterogeneous catalysts. The reactions on the electrodes occur in specifically exclusive fields, and the adsorption of the reagent/intermediate/product is a very important variable. Another very important factor is the choice of the electrode material, as the material is not only the interface for electron transfer, but also acts as an electrocatalyst.[74] The electrode acts as a collector or source of electrons, and the choice of the electrode material is usually dictated by the heterogeneous electron transfer rate, redox potential and propensity to adsorb molecules from the solution. The choice of the electrode material has an influence on the selectivity and reactivity of electrosynthetic reactions, depending also on other experimental parameters, improving the reaction performance.[75] In the following section, we will discuss some recent methodologies under conditions free of external mediators for electrochemical annulation reactions.

3.1 C–Heteroatom and C–C bond formation

Recently, Li and co-workers proposed a synthesis of isoxazolidine-fused isoquinolin-1(2*H*)-one derivatives **62** by electrochemical-oxidation-induced intramolecular annulation *via* amidyl radicals under metal-additive- and external oxidant free conditions (Scheme 17).[76] Ethanol as solvent in an undivided cell equipped with carbon felt electrodes afforded products in yields of up to 99%. As the electric current increased, the yield decreased due to the decomposition of the starting material

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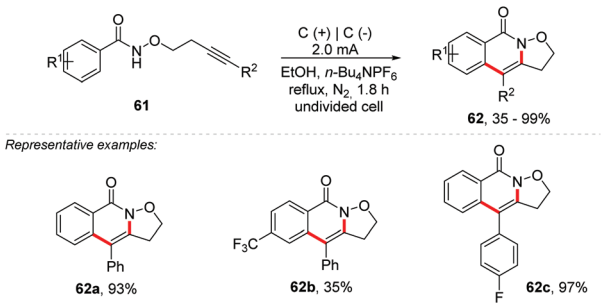
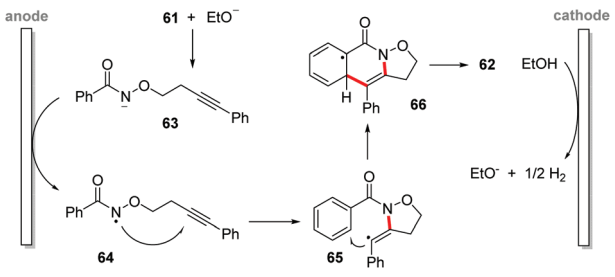


Scheme 17 C–H/N–H functionalization.

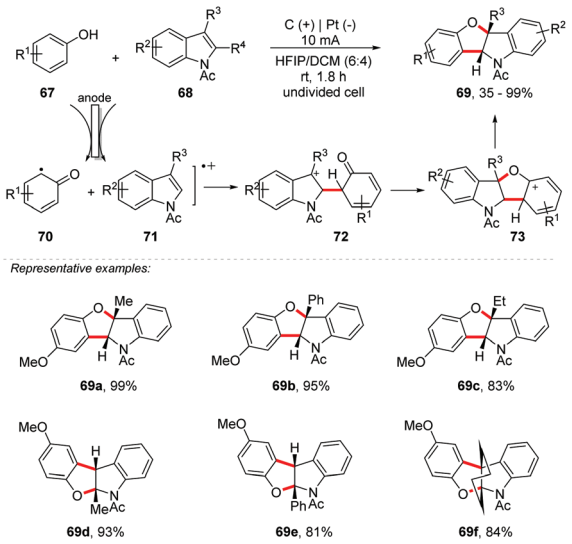
and the final product, with the best-established condition being 2 mA (3 $Fmol^{-1}$) at reflux temperature under an inert atmosphere. A wide reaction scope was achieved, being efficient for both electron-withdrawing and electron-donating groups; however, *meta*-substituted benzamides gave product mixtures, being selective for the less hindered position of the aromatic ring. For *ortho*-substituted benzamides there was no inhibitory effect, and the products were obtained with excellent yields. In the cyclic voltammetry experiments, a 1.5 V *vs.* SCE oxidation potential for ethanol was observed, as well as a 0.8 V oxidation potential for benzamide **62a**.

Based on the control experiments, the authors suggest that the mechanism begins with a cathodic formation of EtO^- (Scheme 18); deprotonation of amide **61** provides anion **63**, undergoing single-electron-transfer (SET) anodic oxidation to afford the *N*-centered radical **64**. 5-*exo*-*dig* annulation delivers radical **65**, which proceeds for a second annulation **66**. In the end, a re-aromatization affords the product **62**.

Compared to C–N bond formation, it is observed that obtaining new C–O bonds has been less explored. However, C–H/O–H functionalization has been efficiently applied in the construction of O-heterocycles, such as benzofurans, benzoxazoles, benzofuranones, oxazolines and others, being of great interest in the medicinal field due to the several biological functions present.[77] Recently, Lei and co-workers described an annulation reaction for the preparation of indolines[78] and polysubstituted pyrroles.[79] Likewise, the author proposed an electrooxidative [3 + 2] annulation using activated phenols **67** with *N*-acetylindoles **68** under undivided electrolytic conditions with no external oxidant and catalyst, providing the



Scheme 18 Proposed mechanism for C–H/N–H functionalization.



Scheme 19 Synthesis of benzofuro[3,2]indolines.

respective benzofuro[3,2]indolines **69** in up to 99% yield (Scheme 19).[80] Both 3-substituted *N*-acetylindoles and 2-substituted *N*-acetylindoles were suitable for this transformation. 2,3-Disubstituted *N*-acetylindoles are also efficient in providing excellent yields (**69f**). With a 6 : 4 solvent mixture of HFIP : DCM, the product **69a** was obtained in 99% yield. Interestingly, using only HFIP as a solvent, the yield decreased from 99 to 78%. Note the importance of HFIP as a co-solvent, probably due to its ability to stabilize aromatic radical cations, as reported by Eberson and co-workers.[81–83] Cyclic voltammetry was performed, and the oxidation potential of *p*-methoxyphenol was close to that of 3-methyl-*N*-acetylindole; in this way, oxidation of both was possible. A trapping experiment with triethyl phosphite was conducted and no desired products could be observed.

Masson and co-workers developed an electrochemical intramolecular oxytrifluoromethylation of *N*-tethered alkenyl alcohols to access morpholine derivatives **76** (Scheme 20).[84] The authors applied mild reaction conditions with direct anodic oxidation of Langlois' reagent (CF_3SO_2Na) **75** as a cheap and easy method to handle the trifluoromethylation reagent. The reaction was performed from alken-6-ol **74** with **75** in an undivided cell, using a graphite carbon anode and a nickel cathode plate as electrodes under a constant current electrolysis of 15 mA, with $LiClO_4$ (0.2 M) as the electrolyte and MeCN as the solvent, 3.2 $Fmol^{-1}$ at room temperature. Additional experiments have shown that a change of the electrolyte or current intensity (from 15 to 30 mA) leads to a significant decrease in yields. A set of representative *N*-tethered alken-6-ols with various aryl groups on the alkene proved to be suitable substrates, and morpholine derivatives were obtained in good yields, up to 88%. The *N*-2-nitrophenylsulfonyl substrates underwent the oxytrifluoromethylation reaction with equal efficiency (**76b**). Pleasingly, secondary alcohol was well tolerated furnishing the morpholine **76c** in good yield as a mixture

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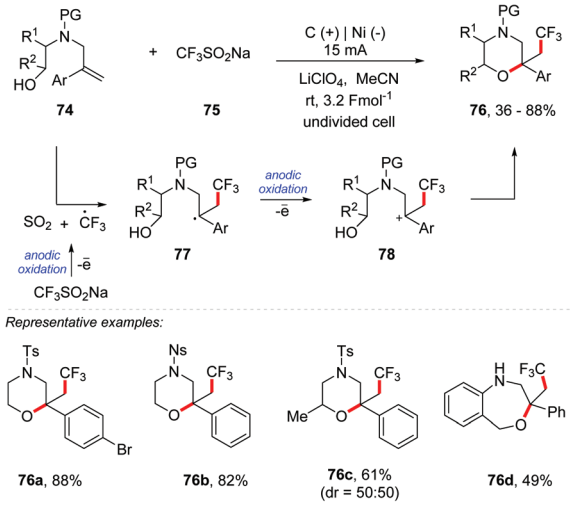
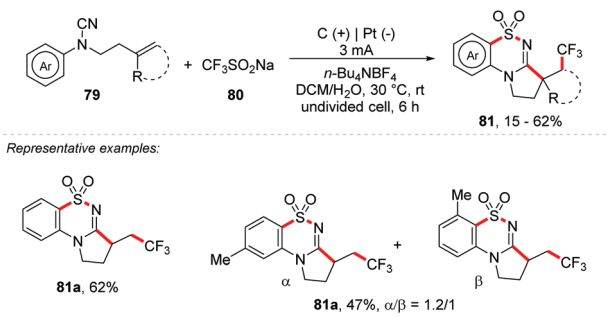


Scheme 20 Intramolecular trifluoromethylation of N-tethered alken-6-ols and alken-7-ols.

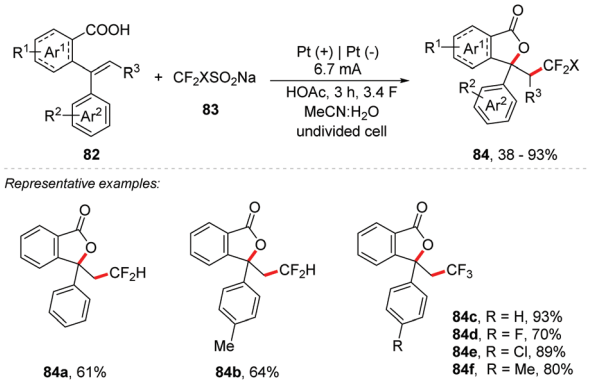
of diastereoisomers. This condition was found to be efficient in the formation of a seven-membered oxacycle by intramolecular oxytrifluoromethylation of *N*-tethered alken-7-ol (**76d**).

Liao and co-workers developed an electrochemical strategy for a trifluoromethylation/SO_2 insertion/cyclization process with Langlois' reagent as a source of CF_3 and SO_2, promoting the synthesis of trifluoromethylated cyclic *N*-sulfonylimines **81** (Scheme 21). Two new bonds (C–S/S–N), two new C–C bonds and two new rings were formed in a single step. Cyanamides substituted in *ortho* and *para* positions were well tolerated (yields of up to 62%); however the *meta*-substituted analogue **81b** provided a mixture of regioisomers (1.2 : 1) with yields of up to 47%. Heterocyclic scaffolds such as indoles and naphthyls were fruitful with high regioselectivity and yields of up to 47%. *N*-Aryl-cyanamides with disubstituted alkenes were also evaluated, providing products with moderate yields (32–40%).

Xu and co-workers developed an electrochemical fluoromethylation triggered lactonization of alkenes **82** using CF_2HSO_2Na and CF_3SO_2Na as the reagents (Scheme 22).[85] The



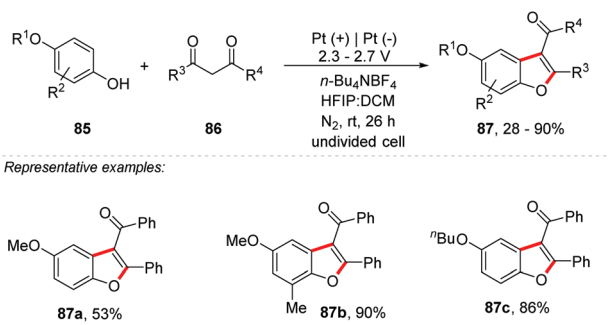
Scheme 21 Trifluoromethylation/SO_2 insertion/cyclization process with Langlois' reagent as a source of CF_3 and SO_2.



Scheme 22 Electrochemical carboxydifluoromethylation.

reaction was performed under a constant current electrolysis of 6.7 mA in an undivided cell with a Pt plate as an electrode, MeCN : H_2O (7 : 1) as a mixture of solvents, and HOAC (3 equiv.) as an additive at room temperature for 3 h. Both CF_2H- and CF_3-containing lactone products (**84**) were obtained in yields up to 93%. The mechanism was studied by cyclic voltammetry experiments. CF_2HSO_2Na and CF_3SO_2Na showed oxidation potentials of 0.72 V and 1.06 V (*vs.* Ag/AgCl), respectively. The oxidation potential of alkenes was 1.58 V (*vs.* Ag/AgCl). These results indicated that CF_2HSO_2Na and CF_3SO_2Na are much easier to be electrochemically oxidized to generate fluoromethyl radicals than the alkene moiety.

Shi and co-workers proposed a synthesis of benzofuran derivatives **87** *via* electrochemical cross-dehydrogenative coupling between phenols **85** and β-dicarbonyl compounds **86** (Scheme 23).[86] The reaction proved to be chemoselective, without by-products from homocoupling reactions. Interestingly, HFIP played a crucial role in the reaction, and according to the authors it has a fundamental importance in the coupling stage, also facilitating the anodic current, which helps in the oxidation of phenol. A crucial step is the anodic oxidation of phenol, which provides the phenoxonium cation, being isomerized to the oxonium ion, a reactive Michael acceptor, which reacts with the nucleophilic species β-dicarbonyl compounds **86**. Intermolecular condensation delivers benzofurans **87**. It is worth mentioning that according to the cyclic



Scheme 23 Synthesis of benzofuran derivatives *via* electrochemical cross-dehydrogenative coupling.

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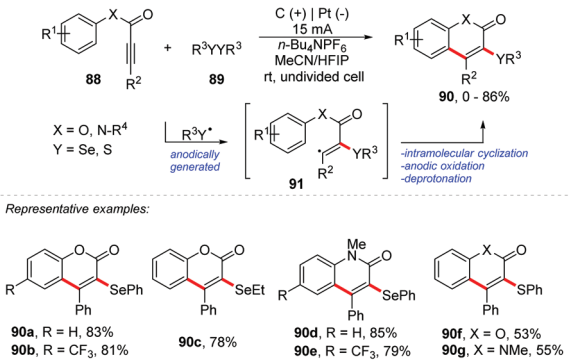
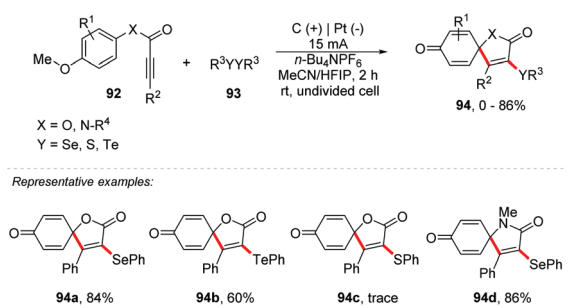


Scheme 24 Cyclization of activated alkynes with diselenides or disulfides.

voltammetry results, the authors determined that the phenol must be more easily oxidized than the enol from diketone.

An interesting approach proposed by Guo and co-workers describes an electrochemical oxidative cyclization of activated alkynes to access functionalized coumarins and quinolinones with selenium or sulphur, reaching products **90** in yields of up to 86% (Scheme 24).[87] The reaction was completely inhibited with the addition of TEMPO, verifying that the mechanistic route follows a radical pathway. The oxidation peak of diphenyl diselenide and diphenyl disulfide was determined by cyclic voltammetry with values of 1.47 V and 1.76 V, respectively (*vs.* Ag/AgCl). The phenyl-3-phenylpropiolate **88a** showed a peak of oxidation at 2.43 V (*vs.* Ag/AgCl). It should be noted that the reactions with disulfides must be carried out under an inert atmosphere, to minimize oxidation. As part of the group's interest, the same authors developed an intriguing electrochemical route for the synthesis of spiro[4.5]trienone derivatives through radical-initiated dearomative spirocyclization of alkynes with diselenides (Scheme 25).[88] The products were obtained in an undivided cell equipped with graphite at the anode and platinum at the cathode, with a solvent mixture of MeCN : HFIP (3 : 1) using *n*-Bu_4NPF_6 as the electrolyte under a constant current of 15 mA at room temperature. The scope was evaluated by varying the electron donating and withdrawing substituents, as well as different alkyl diselenides, with diphenyl ditellurides also being efficient, delivering the products **94** in yields of up to 86%. It is important to use the derivative of **92** with a methoxy group at position 4, which will be responsible for oxidizing the ring and forming the product with a cyclohexa-2,5-dien-1-one scaffold. Additionally, in 2013, Wang and co-workers proposed a route to obtain a tricyclic spiro dihydrofuran scaffold *via* multi-component electrochemical reaction of dimedone with aryl aldehyde.[89]

Very recently, Martins and co-workers published an overview with recent advances in electrochemical chalcogen (S/Se)-functionalization of organic molecules, and more information about reactions involving chalcogens in electrochemistry can be found.[90]

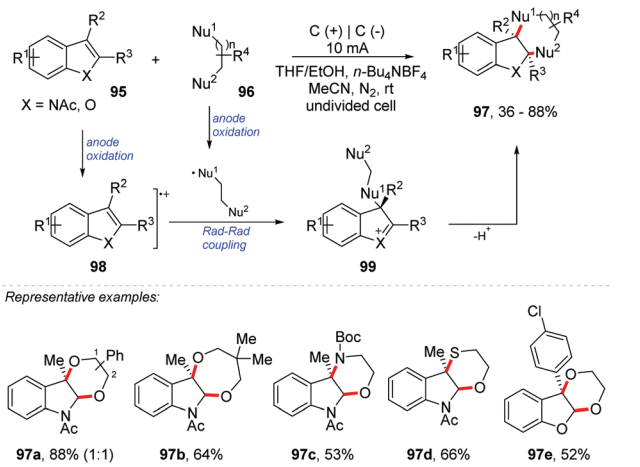


Scheme 25 Electrochemical synthesis of spiro[4.5]trienones.

3.2 C–Heteroatom bond formation

The oxidative functionalization of C–heteroatom represents one of the most powerful strategies to achieve organic compounds and access target molecular structures.[91] Lei and Stahl groups proposed an Hofmann–Löffler–Freytag procedure for C(sp^3)–H amination.[92,93] Harran and co-workers developed an electrochemical and a hypervalent iodine(III) route for the direct synthesis of benzofuro[2,3-*b*]indoline through the oxidative coupling of indoles and phenols.[94,95] In addition, Vincent and co-workers performed the synthesis of benzofuro [2,3-*b*]indoline derivatives by [3 + 2] oxidative coupling between nucleophilic phenols and indoles with NIS as an oxidant.[96] There are many reports on cross-coupling and difunctionalization of alkenes by electrochemical methods, and good reviews have recently been published.[97,98]

Lei and co-workers proposed an exciting method for a dearomative annulation of indoles and benzofurans under electrochemical conditions, providing several highly functionalized five to eight-membered heterocycle-2,3-fused indolines and dihydrobenzofurans **97** (Scheme 26).[99] Desired [3 + 2], [4 + 2], [5 + 2] and [6 + 2] annulation occurred regioselectively with nucleophilic species of N, O, and S in yields up to 88%. The mechanism was evaluated through cyclic voltammetry, electron paramagnetic resonance (EPR), radical capture experiments and kinetic studies. Considering these results, the



Scheme 26 Dearomative annulation of indoles and benzofurans.

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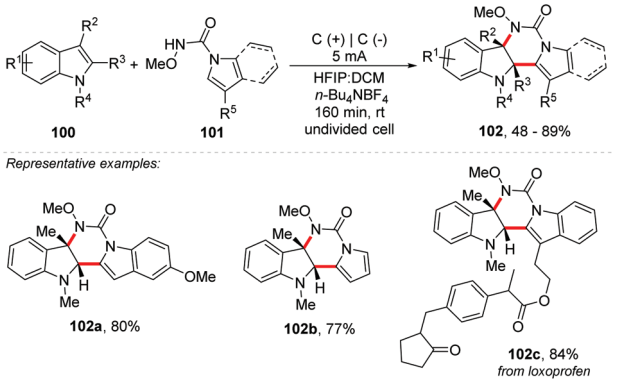
authors proposed that the reaction proceeds through the cross-coupling between the radical of the nucleophilic species and the indole radical cation **98** at the C-3 position, considering that the radical species is stabilized by the aromatic ring. The second nucleophilic attack would take place in the imine C-2 formed in the five-membered indole ring **99**, delivering the final product **97**.

Based on their experience, the same authors also developed an electrochemical intermolecular dearomative [4 + 2] annulation between 1-alkylindole **100** and indole-1*H*-carboxamide **101** to obtain pyrimido[5,4-*b*]indole derivatives **102**, with many biological and pharmaceutical applications (Scheme 27).[100]

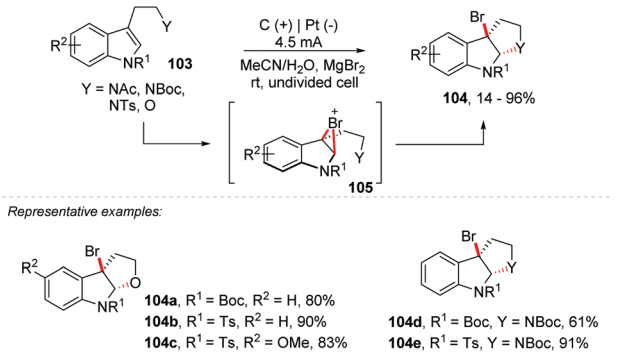
An important protocol was developed by Tong and co-workers, using KX/oxone for halo-oxidative cyclization (Br/Cl) of tryptamine/tryptophan derivatives (78–95% yield), also proposing a concise total synthesis of cyclo-tryptamine alkaloid protubonines A and B, which was efficiently completed in 7 steps with 29% overall yield.[101] Likewise, Vincent and co-workers reported a clean and simple approach *via* electrosynthesis, being environmentally friendly and efficient for bromination of tryptophan, tryptamine and tryptophol derivatives **103** (Scheme 28).[102] The electrochemical reactions were performed in the ElectraSyn 2.0 package (IKA) with a platinum electrode at the cathode and a graphite electrode at the anode. The electrophilic bromine reagent was generated *in situ* by the electrochemical oxidation of $MgBr_2$, and no toxic by-products were obtained, avoiding an additional electrolyte. Replacing $MgBr_2$ with $MgCl_2$ delivered the equivalent of **104b** in just 37% yield. It is worth mentioning that the same authors developed an electrochemical approach to perform a general oxidative and dearomative difunctionalization of indoles with two C–O or two C–N new bonds.[103]

Recently, Ruan and co-workers proposed an elegant electrolytic route for the synthesis of medium-sized lactams **107** (8–11-membered rings) (Scheme 29).[104] The reaction followed a rare migration of amidyl radicals by C–C bond cleavage, delivering products in up to 98% yield. The reaction was carried out in an undivided cell equipped with a graphite electrode at the anode and a platinum electrode at the cathode, in a mixture of $MeCN:H_2O$ (9 : 1) as the solvent and *n*-Bu_4NBF_4 (1 equiv.) as the electrolyte, under a current of 8 mA at room temperature in an open system. The reaction scope was evaluated and the electron donating and withdrawing groups proved to be efficient for the transformation; however some substrates containing azacycles showed less efficiency (**107d**). The mechanism was suggested to be anodic oxidation of **106**, leading to the radical amidyl **108**, in which intramolecular cyclization could proceed with the ring to form N–C bonds. The selective cleavage of the C–C bond followed by single-electron oxidation would deliver products **107**. From the cyclic voltammetry experiments, the authors observed that the potential of **106** (2.2 V *vs.* Ag/AgCl) was below that of **107** (2.5 V *vs.* Ag/Cl), protecting the possible degradation.

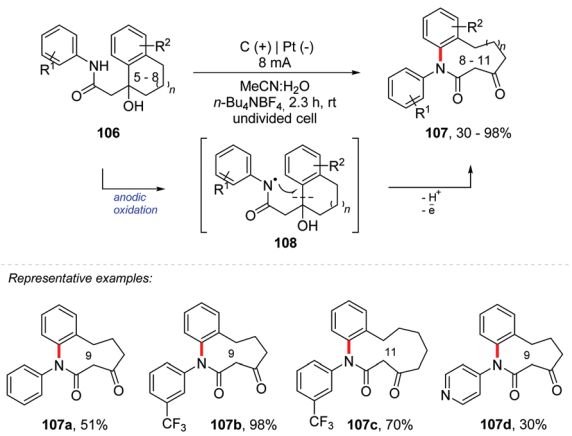
Zhang and co-workers reported a dehydrogenative C–N cross-coupling reaction under electrochemical conditions for the synthesis of 1,2,4-triazole-fused heterocycles **111** (Scheme 30).[105] The method proved to be efficient for a wide variety of substrates with yields of up to 94%, tolerating groups such as halide, CF_3, CO_2Me, nitrile, amine, and alkyl groups, and is also efficient for heterocyclic portions such as furans, indoles, pyridines and thiazoles. The undivided cell was equipped with a graphite electrode at the anode and a plati-



Scheme 27 Intermolecular dearomative [4 + 2] annulation between indole-1*H*-carboxamide and 1-alkylindole.



Scheme 28 Dearomative annulation of indoles.



Scheme 29 Synthesis of medium-sized lactams (5–11-membered rings).

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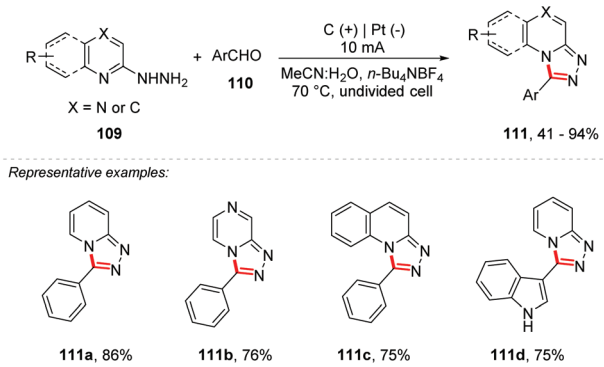
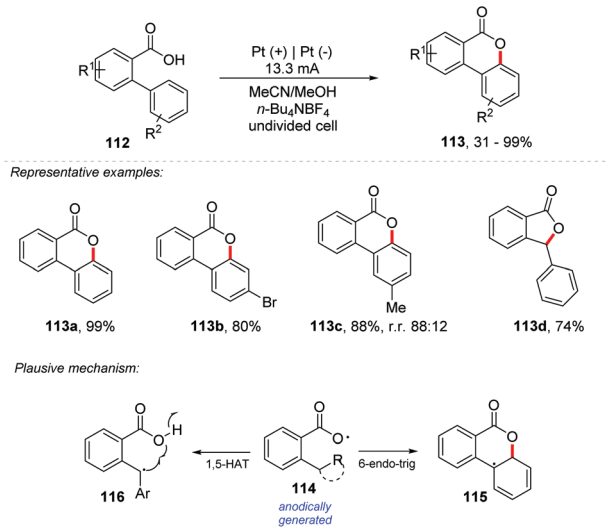
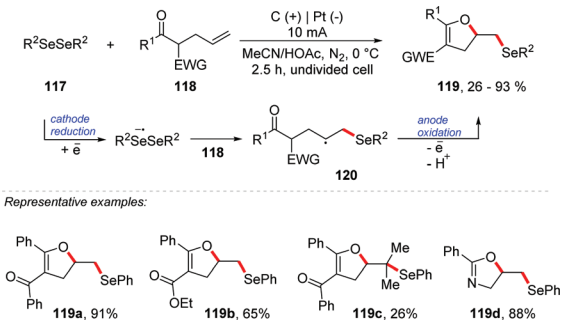


Scheme 30 Cyclization of activated alkynes with diselenides or disulfides.



Scheme 31 Lactonization of C(sp^2/sp^3)–H bonds.



Scheme 32 Cyclization of olefinic carbonyls with diselenides.

num electrode at the cathode with a mixture of MeCN : H_2O (9 : 1) as the solvent and n-Bu_4NBF_4 as the electrolyte, under a constant current of 10 mA.

Among different approaches, the direct C–H/O–H oxidative coupling reaction gained special attention due to its high atom economy. Recently, Prabhu and co-workers reported a cascade reaction involving the activation of C–H/O–H bonds for regioselective oxidative ringing [4 + 2] and concomitant lactonization with carboxylic acids.[106] Similarly, Yatham and co-workers developed the first photocatalyzed dehydrogenative lactonization of 2-arylbenzoic acids by $CeCl_3$.[107] Palladium and copper catalysts have also been developed for C–H/O–H activation.[108,109] However, these methods make industrial use unfeasible due to their high cost. Additionally, the treatment of carboxylic acids with a base generates carboxylate anions, which can undergo anodic oxidation to provide carboxylate radicals, which could be added to alkenes to produce lactones. This suggests that lactonization may occur if the C–O coupling is fast enough to overcome Kolbe's decarboxylation.[110,111] If 1,5-hydrogen-atom-transfer (HAT) makes remote C–H homolytic cleavage possible, the lactonization would be achieved. Considering this, Xu and co-workers described an electrochemical dehydrogenative lactonization of carboxylic acids **112** with C(sp^2/sp^3)–H bonds (Scheme 31).[112] The procedure required n-Bu_4NOAc as the electrolyte in a mixture of MeCN : MeOH (9 : 1) with platinum electrodes under a current of 13.3 mA cm^{-2}. It exhibited a broad substrate scope, and high regioselectivity under conditions free of external oxidants. Scalability was assessed with 40 g of **112a**, demonstrating its potential in industrial applications (**113a** – 84% yield). From cyclic voltammetry experiments, it was observed that the carboxylate moiety has an oxidation potential of 1.4 V *vs.* Ag/AgCl, while the aromatic moiety has an oxidation potential above 2.0 V *vs.* Ag/AgCl, indicating that the carboxylate moiety is oxidized preferentially, being consistent with radical trapping experiments.

Lei and co-workers reported an electrochemical oxidative cascade cyclization of olefinic carbonyls with diselenides for C–O and C–Se bond formation (Scheme 32).[113] A series of functionalized dihydrofurans and oxazolines **119** were synthesized. Several diaryl diselenides were employed, providing products in good yields (up to 93%). It is important to mention that the reaction was well tolerated with dimethyl and dibenzyl diselenides. Olefinic carbonyls containing γ,δ-substituted groups were also efficient. The steric effect had a great influence on the reaction (Scheme 32 – **119c**). To explore the mechanism, control experiments were conducted under different conditions, and only traces of **119a** were detected when 2 equivalents of TEMPO were added. According to cyclic voltammetry analysis, oxidation and reduction peaks of diphenyl diselenide were observed at 1.8 V and −1.5 V *vs.* Ag/AgCl, respectively. Thus, considering the control reactions and the results reported in the literature,[114,115] the authors suggest a mechanism route *via* a radical intermediate. Diphenyl diselenide is reduced at the cathode to give an anion radical as an intermediate, which is further decomposed to give the phenyl-selenium radical and phenyl-selenium anion.

In addition, an electrochemical synthesis of selenyl-dihydrofurans *via* anodic selenofunctionalization of allyl-naphthol/phenol derivatives was proposed by Braga and co-workers.[116] Siewert and co-workers developed an anodic amination and esterification reaction of non-activated alkenes catalyzed by

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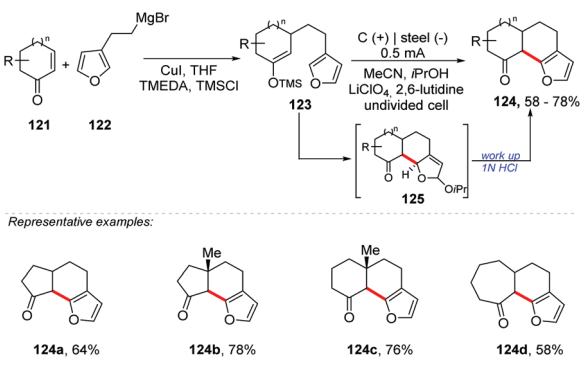
diselenides.[117] Torii and co-workers described the first procedure involving selenium-based catalysts in electrosynthesis.[118] Wirth and co-workers re-studied Torri's reaction, applying the electrochemical sequence of selenenylation/elimination reactions using catalytic amounts of diphenyl diselenide.[119] It is worth mentioning that in the review paper by Breder and co-workers, the authors describe the recent oxidative alkene functionalization *via* selenium-π-acid catalysis.[120]

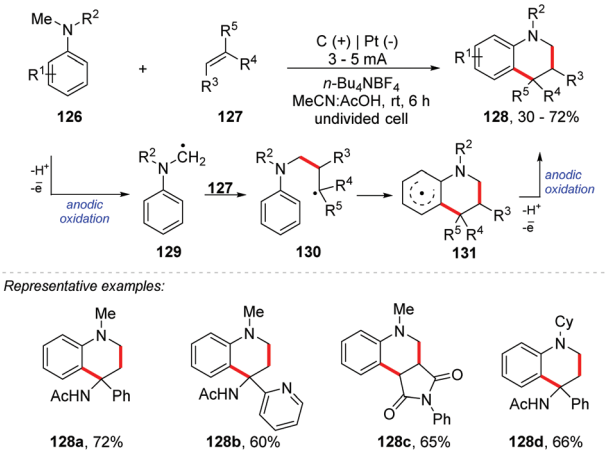
3.3 C–C bond formation

In the last century, we have seen huge advances in the construction of new C–C bonds by radical reactions. Due to its high reactivity and practical tolerance, it provided motivation for the development of new synthetic methodologies.[121] Currently, several methods for obtaining radical carbons are known, *e.g.* using halides, carboxylic acids, borates, alcohols, and silicates, metal catalysis, photoredox catalysis, ultrasound, microwaves, and electrochemistry, among others.[21,122–130] In the same way, the construction of functionalized ring systems through an oxidative annulation process is possible. An example of this was proposed by Wright and co-workers, who developed a two-stage electrochemical annulation for fused furan products **124** (Scheme 33).[131] After the conjugated addition of a furyethyl cuprate and the capture of the enolate as the corresponding silyl enol ether, the annulation step involves the anodic coupling of furan and silyl enol ether (**123**), providing the six-membered ring. High current densities may promote the formation of oligomers by providing other electroactive species.[132] With relatively low current densities (0.5–1 mA cm^{-2}) the amount of charge required for complete consumption of the enol ether was almost the same as the theoretical amount (2 $Fmol^{-1}$). However, with a high current density (>1 mA cm^{-2}), the amount of charge consumed was greater than the theoretical amount.

Lei and co-workers proposed an electrochemical oxidative [4 + 2] annulation between alkenes and tertiary anilines for the synthesis of tetrahydroquinoline derivatives **128** (yields of up to 72%) (Scheme 34).[133] The undivided cell was equipped with platinum electrodes, n-Bu_4NBF_4 as the electrolyte, and MeCN : AcOH (4 : 1) as a solvent mixture under a constant current (3–5 mA) at room temperature. The methodology presented a wide reaction scope, both for electron donating groups and for electron withdrawing groups. Additionally, heterocyclic enamines were well tolerated (naphthyl, thiophene, tetrahydrofuran, pyridine, and pyrrolidinone). The authors propose that the mechanism involves anodic oxidation of **126** to generate the radical cation stabilized by acetic acid, which after deprotonation would deliver the tertiary α-amino carbon radical **129**. This radical would react with **127** *via* radical addition providing **130**, followed by intramolecular cyclization. Anodic oxidation of **131** delivers product **128**.



Scheme 33 Preparation of fused furans.



Scheme 34 Electrochemical oxidative [4 + 2] annulation between alkenes and tertiary anilines.

3.4 Heteroatom–heteroatom bond formation

There are several methods for reactions for the formation of new C–C and C–Het bonds; however the formation of new Het–Het bonds remains statistically less explored. This topic was recently discussed by Antonchick and co-workers in the book *Patai's Chemistry of Functional Groups*, highlighting reactions mediated by hypervalent iodine.[134] Compounds containing Het–Het bonds (Het = N, S, O, P) have already been found and isolated from a variety of natural products, and their biological activities and reactivities have attracted the attention of chemists and chemical biologists.[135]

Xu and co-workers report an oxidizing reagent- and transition metal-free synthesis of [1,2,3]triazolo[1,5-*a*] pyridines **133** through electrochemical dehydrogenative cyclization of pyridyl hydrazones **134** (Scheme 35).[136] The reaction was carried out in two stages: first the hydrazine **132** was obtained by refluxing the respective ketone with hydrazine in MeOH in the presence of AcOH (0.1 equiv.). After complete conversion, the n-Et_4NPF_6 electrolyte, water, and K_2CO_3 (1.0 equiv.) were added, equipping the undivided cell with an RVC electrode at the anode and Pt at the cathode.

Another important heterocycle is the phthalazin-1,4-dione derivatives. This skeleton is part of a range of drugs with antibacterial, anti-inflammatory, anti-convulsant and analgesic properties, and has been applied as an anesthetic in the past.[137–141] So far, methods for the synthesis of these deriva-

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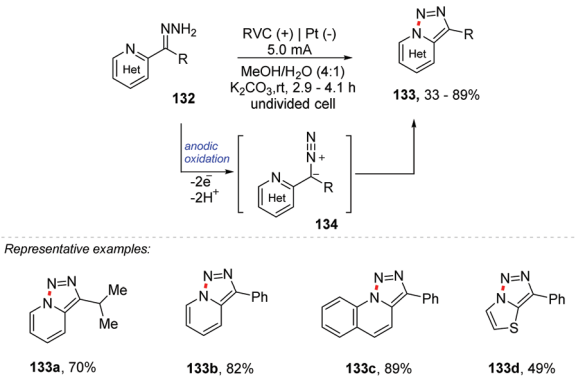
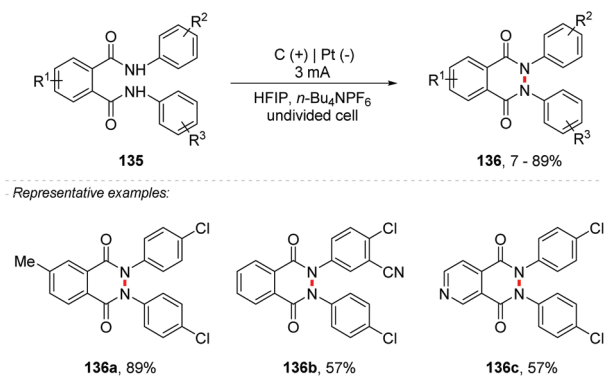


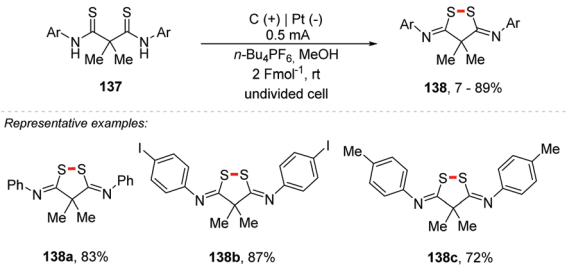
Scheme 35 Cyclization of pyridyl hydrazones.

tives involved the use of metals, such as Ni, Rh, Pd, Cu, and others.[142–145] Electrosynthetic methods for the formation of N–N bonds have recently been explored by the Waldvogel and Baran group.[146–151] Considering this, Waldvogel and co-workers proposed the synthesis of phthalazin-1,4-diones **136** from phthaldianilides **135** *via* dehydrogenative N–N bond formation (Scheme 36).[152] The undivided cell was equipped with graphite electrodes at the anode and platinum at the cathode with HFIP as the solvent and only 0.01 M *n*-Bu_4NPF_6, under a constant current of 3 mA. The method proved to be efficient for a wide variety of substrates with yields of up to 89%, tolerating substituent groups such as halide, triflate, nitrile, and alkyl groups, and being also efficient for heterocyclic portions such as pyridine **136c**. The authors consider the formation of amidyl radicals as intermediates, which would be stabilized by the HFIP solvent.

Waldvogel and co-workers also reported an electrochemical approach for S–S coupling of dithioanilines **137**, providing the cyclic 3,5-diimido-1,2-dithiolane derivatives **138** with yields of up to 89%, tolerating various groups of substituents (Scheme 37).[153] In 2016, the same authors proposed a method for access to pyrazolidin-3,5-diones through anodic N–N bond formation.[150] Additionally, in 2018, the group developed an



Scheme 36 Synthesis of phthalazin-1,4-diones from phthaldianilides *via* dehydrogenative N–N bond formation.

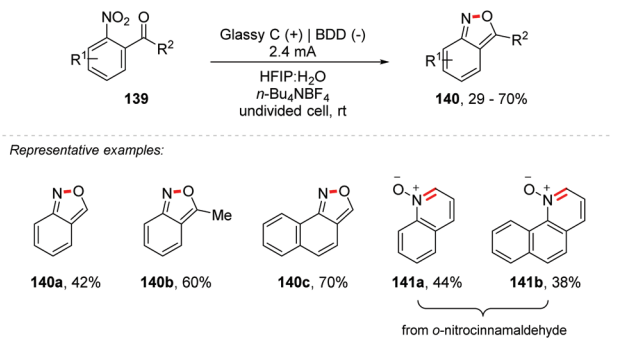


Scheme 37 S–S coupling of dithioanilines.

electrochemical conversion of phthaldianilides to phthalazin-1,4-diones by dehydrogenative N–N bond formation.[152]

Additionally, Waldvogel and co-workers considering their experience, as well as recent publications proposing the electrochemical reduction of aryl-nitro derivatives,[154] nitrones[155] and the synthesis of heterocycles containing nitrogen,[148,152,156] proposed the synthesis of 2,1-benzisoxazoles (**140a–c**) and quinoline *N*-oxides (**141a–b**) through cathodic reduction of the nitro portion of *o*-nitrobenzaldehyde and *o*-nitrocinnamaldehyde, with subsequent intramolecular cyclization (Scheme 38).[157] Using glassy carbon at the anode and Boron Doped Diamond (BDD) at the cathode as electrodes in a mixture of HFIP : H_2O (1 : 1) under a current of 2.4 mA it was possible to obtain the products in good yields (29–70%). The use of HFIP is crucial for the total conversion, avoiding the need for additives, and can be recovered at the end. It highlights that the addition of 4% (v/v) acetone facilitated the dissolution of the substrate. Using the theoretical amount of charge (4 $Fmol^{-1}$) the yield was low, requiring up to 7 $Fmol^{-1}$. The authors explain this restriction due to the less favored condensation between the hydroxylamine and the carbonyl moiety of the enal, because of the alkene conjugation, and if the condensation is not fast enough, there may be a re-oxidation of the hydroxylamine to nitrous species. Other electrosynthetic methodologies for obtaining 2,1-benzisoxazoles have been reported.[158–160]

Recently, oxidative N–S bond formation has been established with catalysis by copper,[161] I_2,[162,163] hypervalent iodine,[164] and DCC in the presence of KF/Al_2O_3 with thiourea,



Scheme 38 Synthesis of 2,1-benzisoxazoles and quinoline *N*-oxides.

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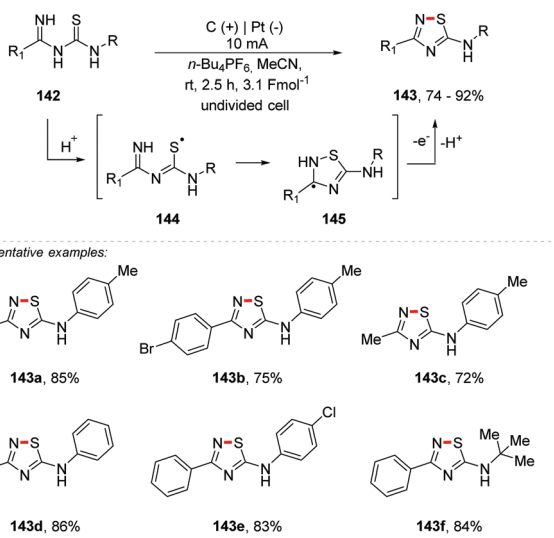
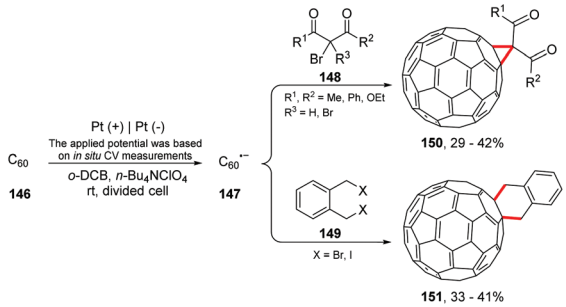
etc.[165] It is free of catalysts *via* the use of elemental sulfur with amidines[166] and hydrazones,[167] and dimerization of thioamides[168] or thiobenzamides with methyl bromocyanoacetate.[169] Yang and co-workers describe a facile and efficient protocol for the synthesis of 3-substituted 5-amino-1,2,4-thiadiazoles **143** that avoids the use of metal catalysts and stoichiometric oxidants (Scheme 39).[170] The thiadiazoles were obtained *via* electrochemical oxidative intramolecular dehydrogenative N–S bond formation with imidoyl thioureas **142**, in yields of up to 92%. The reaction was carried out using various imidoyl thioureas in the presence of MeCN at room temperature, and an undivided cell was equipped with a carbon rod anode and a Pt plate cathode under a 10 mA constant current using 0.03 M n-Bu_4NBF_4 as the electrolyte. Importantly, alkyls of imidoyl thioureas were tolerated in this reaction and the corresponding products were obtained in good yields (**143c** and **143f**). The plausible mechanism was proposed and the formation of the radical cation **144** was supported by cyclic voltammetry (*vs*. SCE) results. To evaluate the scalability, a gram-scale reaction was performed, delivering **143a** in 74% yield.

3.5 Carboannulations involving fullerenes

Electrolysis has been shown to be an important ally in fullerene chemistry. The reversion of electrophilic-to-nucleophilic reactivity of fullerenes has great potential, being a new field for chemists.[171,172] Electrochemical generation of C_{60}^{n-} anions was first employed by Kadish and co-workers in 1993 for the controlled functionalization of fullerenes.[173] Currently, researchers are improving these studies; Suzuki and co-workers conducted the reaction of $C_{60}^{\bullet-}$ with alkyl dihalides and alkyl halides. Cycloaddition and 1,4-dialkylation products were obtained (Scheme 40).[174] The authors suggest that the reaction proceeds *via* electron transfer from $C_{60}^{\bullet-}$ to the alkyl halide (**148** or **149**), and the alkyl radical attacks C_{60}. Then, the addition of the alkyl radical to the alkylated C_{60} radical intermediates provides the cyclization products. Thus, the high recovery of C_{60} (39–63%) at the end of the reaction would be justified.



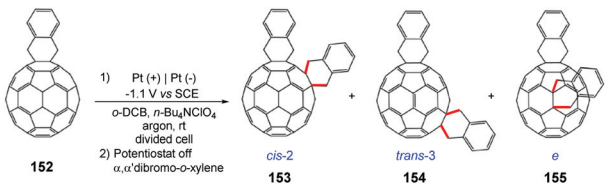
Scheme 39 N–S bond formation of thiadiazoles.



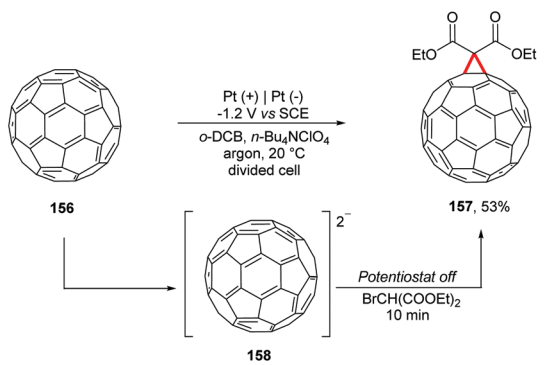
Scheme 40 Reaction of $C_{60}^{\bullet-}$ with alkyl dihalides and alkyl halides.

Gao and co-workers proposed an electrosynthetic approach for the preparation of C_{60} *o*-quinodimethane bisadducts [$C_{60}(QM)_2$] (Scheme 41).[175] The authors emphasized the importance of these products in the study of organic solar cells (OSC);[176] however, the synthetic methodologies previously described resulted in up to 8 regioisomers.[177] Electrolysis showed high regiocontrol, providing *cis*-2, *trans*-3 and $C_{60}(QM)_2$ products.

Wang and co-workers proposed a reaction with electrochemically generated dianions of [60]fullerene **158** with bulky secondary alkyl bromides (Scheme 42).[178] In a divided cell equipped with platinum electrodes under an argon atmo-



Scheme 41 Regiocontrolled electrosynthesis of [60]fullerene bisadducts [$C_{60}(QM)_2$].



Scheme 42 Reactions with electrochemically generated dianions of [60]fullerene.

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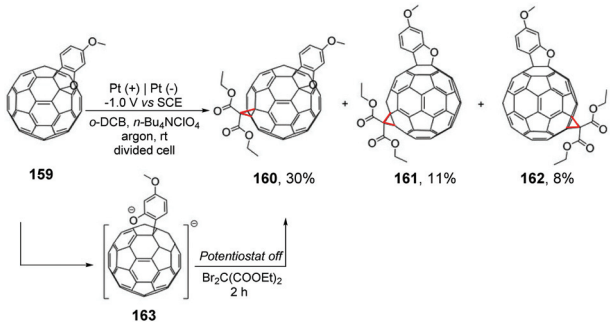
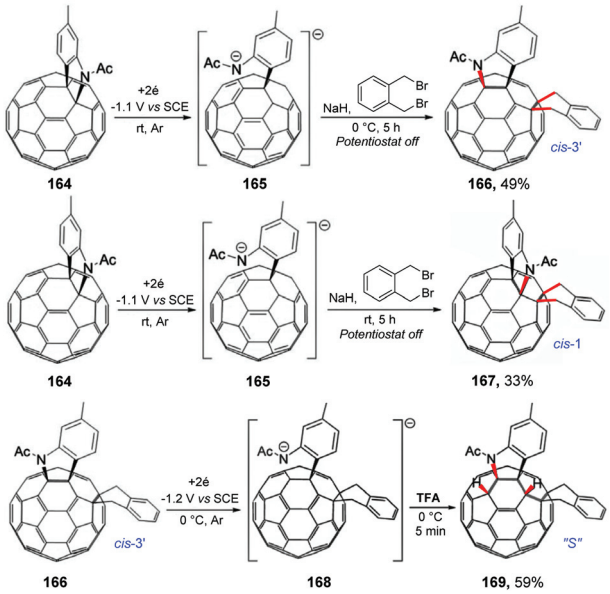


Scheme 43 Reactions of electrochemically generated dianions of [60] fullerene with diethyl dibromomalonate.

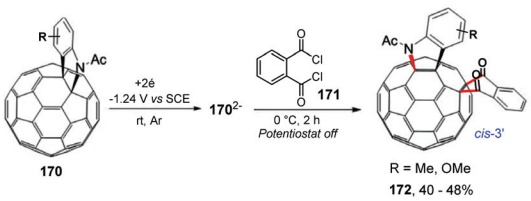
sphere, the reaction was controlled until it reached the theoretical number of coulombs necessary for the complete conversion of C_{60} to C_{60}^{2-} (−1.2 V *vs.* SCE); the potentiostat was turned off and then the respective alkyl bromide was added. Using $BrCH(CO_2Et)_2$ it was possible to obtain the carboannulation product **157**. The authors emphasize that the reaction of C_{60}^{2-} with of $BrCHPh_2$ and TFA led to the monoalkylation product. In the absence of TFA the reaction proceeded to form the di-alkylation products.

The same group described a cyclopropanation reaction of electrochemically generated dianionic [60]fullerobenzofurans **163** with diethyl dibromomalonate (Scheme 43). The sterically favored bisadducts *e* **160** were obtained as the major product, and *trans*-3 bisadducts **161** and **162** were obtained as minor products.[179] Considering the previous work, the group emphasized that the fused benzofuran heterocycle derivatives did not reorganize from [6,6]-bonds to [5,6]-bonds.[180–184] For the electrophilic reactions of fullerene dianionic derivatives, these results provided information about the control factors, such as electronic and steric factors.

Wang and co-workers also reported an interesting reaction between the electrochemically generated dianionic [60]fulleroindoline and 1,2-bis(bromomethyl)benzene for the regioselective synthesis of the tetra-functionalized 1,2,4,17-adduct (*cis*-3′) and 1,2,3,4,9,10-adduct (*cis*-1) of C_{60} (Scheme 44).[185] The experimental procedure followed the same *modus operandi* previously discussed by the authors; however when the reaction was carried out at 0 °C, product **166** (*cis*-3′) was obtained in 49% yield. By carrying out the reaction at a temperature of 25 °C, product **167** (*cis*-1) was obtained in 33% yield. The authors observed that at room temperature isomer **166** (*cis*-3′) has a tendency to decompose to isomer **167** (*cis*-1). Considering that the potential energy surface (PES) scan enabled a reasonable prediction of the ring-closure position, theoretical calculations were performed, showing that *cis*-3′ isomer **166** was less stable than *cis*-1 isomer **167** by 14.2 kcal mol^{-1} at the B3LYP/6-31G(d) level. The authors also observed that protonation of dianionic **168** with 2 equivalents of TFA at 0 °C for 5 min provides 1,2,3,4,9,10-adduct **169** ("S") in 59% yield.



Scheme 44 Regiocontrolled electrochemical reaction between the electrochemically generated dianionic [60]fulleroindoline and 1,2-bis (bromomethyl)benzene.



Scheme 45 Carboannulation of the electrochemically generated dianionic [60]fulleroindoline with phthaloyl chloride.

In the same year, Wang and co-workers performed the carboannulation of the electrochemically generated dianionic [60] fulleroindoline **170** with phthaloyl chloride **171**, providing the products 1,2,4,17-functionalized [60]fullerene derivatives **172** (*cis*-3′) (Scheme 45).[172] The method presented a unique addition pattern, with a hererocyclic rearrangement to a [5,6]-junction and the carbocycle was fused to an adjacent [6,6]-junction, being in agreement with the biscycloadducts discussed previously. It is worth mentioning that the 1,2,4,17-adducts **172** can also be protonated with TFA to provide hexafunctionalized fullerene products with an "S"-shaped addition pattern with yields of up to 40%.

4. Sacrificial electrodes for electrochemical annulation reactions

A wide literature search has shown that in the last 20 years there have been few methodologies for organic electrosynthesis using sacrificial electrodes. The application of sacrificial

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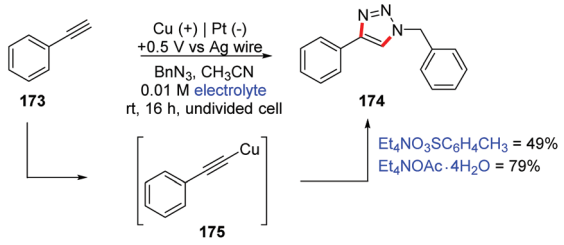
metals has been studied in the past for carboxylation reactions, functionalization of organic halides, formation of metal complexes, *etc.*[186,187] In 1986, Le Guillanton and co-workers used an efficient sulfur/carbon mix cathode for the synthesis of thiophenes and related compounds from acetylenes.[188] The same authors reported an overview of the synthesis of thioorganic compounds derived from the electrogenerated species S_x^{2-} and S_y^{2+}.[189] The direct synthesis of diaryl diselenides and ditellurides using Se and Te electrodes has also been explored.[190]

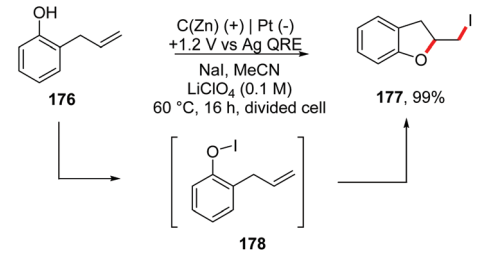
Over 30 years ago, Pahil and Banait proposed the synthesis of copper(II) alkoxides (*e.g.* Cu(OR): R = methyl, ethyl, propyl, butyl, amyl, phenyl and quinoline groups), by direct electrolysis of alcohols in DMF using a copper sacrificial anode and *n*-Bu_4NCl as a supporting electrolyte.[191] Recently, Wilden and co-workers proposed an electrochemical synthesis of copper(I) acetylides **175** (Scheme 46) using simultaneous oxidation of copper foil and Hofmann elimination of quaternary ammonium salts.[192,193] The authors evaluated its importance through a click reaction (CuAAC reaction), successfully obtaining two conditions in a one-pot electrochemical process, which is a promising approach for these reactions. According to control reactions, they propose that the active Cu species is $Cu(MeCN)_4X$ (X = PF_6 or $CH_3C_6H_4SO_3$).

In addition, the same group reported an electrochemical method to generate Zn(II) *in situ* from a zinc-coated graphite electrode, achieving iodocyclization of 2-allylphenols **176** to obtain dihydrobenzofuran derivatives **177** (Scheme 47).[194] Considering that the standard reduction potential of Zn(II) is lower than that of I_2 (−0.76 V/+0.54 V *vs.* SHE), and the first oxidation of I^- to form the reactive oxidative species I^{3-} occurs at +1.0 V (*vs.* Ag quasi-reference electrode, QRE), the authors set the potential at +1.2 V to a zinc-coated graphite electrode (40 mol% Zn^0) in a divided 'H cell'.

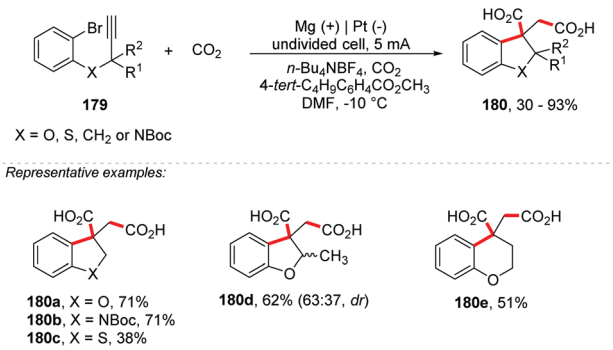
Hara and co-workers described the synthesis of succinic acid derivatives **180** through a cyclization reaction of 2-(2-propynyloxy)bromobenzenes **179**, followed by CO_2 carboxylation mediated by methyl 4-*tert*-butylbenzoate using Mg electrodes at the anode and Pt at the cathode under a current of 5 mA cm^{-2} (Scheme 48).[195] Derivatives of indoline, indane, dihydrobenzothiophene, dihydrobenzofuran and tetrahydropyran were obtained with yields of up to 93%. According to the authors, the role of Mg(II) in the solution is to form a stable enolate and



Scheme 46 One-pot electrochemical CuAAC reaction by electrochemically mediated cyclization of 2-allylphenols using the Cu sacrificial electrode.



Scheme 47 Electrochemically mediated cyclization of 2-allylphenols.



Scheme 48 Cyclization of 2-(2-propynyloxy)bromobenzenes followed by tandem carboxylation.

also to prevent the oxidized species at the anode. The same group also reported an electrochemical carboxylation of flavones in the presence of carbon dioxide by using an undivided cell equipped with a Pt cathode and Mg anode at 0 °C.[196] Further clarification on reactions involving carbon dioxide and sacrificial electrodes can be obtained in the review paper by Filardo and co-workers.[197]

5. Conclusions and outlook

Recent advances in electrochemical annulation reactions considering methodologies for obtaining new C–C, C–heteroatom and heteroatom–heteroatom bonds were discussed, evaluating the mechanistic pathway, as well as the reactivity of substrates. Additionally, it has been shown that this approach provides new synthetic routes, yielding products with excellent atom economy, following green chemistry principles. However, there is a lot to be done in the development of this technology, mainly with regard to hetero- and carboannulations. The substrate scope is still narrow, limiting control in synthesis, especially when compared to the various natural heterocycles present in nature. That is why the continuous study and applications of new electrosynthetic routes are so important, as it allows us to better understand this technology and to have control of these reaction conditions. Despite advances in the application of electrochemistry for the functionalization of organic compounds, most synthetic protocols require a complicated catalytic system or adverse conditions, which need to

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be improved. The use of new electrode materials must be implemented, such as sacrificial electrodes, which have been explored in the past in simpler molecules. We believe that the ongoing efforts to develop efficient reaction methods in this field, as well as scientific advancement, should provide more access to diverse heterocycles, which may facilitate synthetic control of new molecules. Despite all the benefits offered by electrosynthesis, this is still not a common method in research laboratories. Considering this, our objective is to motivate and demystify electrochemistry in organic synthesis, disseminating this technology so that, in the future, we will have more research groups performing research in this field.

Conflicts of interest

The authors declare no conflict of interest.

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