Review

Electrochemical-induced hydrofunctionalizations of alkenes and alkynes

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Abstract

The hydrofunctionalizations of readily available alkenes and alkynes are one of the most effective and useful routes to afford diverse value-added compounds. Although traditional hydrofunctionalization strategies catalyzed by metal catalysts present convenient approaches, they are also accompanied by resource consumption and environmental crisis. Electrosynthesis, as a renewable and sustainable technology, has become a cost- and atom-efficient and useful synthetic route. In this review, the electrochemical-induced hydrofunctionalizations of alkenes and alkynes are summarized and presented. In each section, the electrochemical synthetic strategy to access hydrogenation and other hydrofunctionalization (hydroboration, hydrosilylation, hydroalkylation, hydroalkoxylation, hydrocyanation, hydrocarboxylation, *etc.*) products are elaborated in detail separately. Finally, the current challenges and prospects for electrochemical hydrofunctionalizations of unsaturated carbon–carbon (C–C) bonds are also discussed briefly.

Keywords: Electrochemical, alkene, alkyne, hydrofunctionalization, synthesis

INTRODUCTION

Alkenes and alkynes, as ubiquitous building blocks, are widely employed in organic synthesis, agricultural chemicals, and biological organic materials[1-3]. Although they can be directly applied, one of the most atomically economical and straightforward routes is hydrofunctionalization addition reactions across multiple bonds[4]. Given the easy accessibility and rich reactivity of alkenes and alkynes, diverse functional groups (FG) have been successfully introduced to construct valuable molecular scaffolds. For the hydrogenation of alkenes and alkynes, plentiful homogeneous[5-7] and heterogeneous[8-10] metal catalytic systems have been explored, involving various earth-abundant metals such as Co[5], Fe[6,7], and Ni[9], along with noble metals such as Pd[8-10], Rh[6,9], and Ru[6]. Moreover, some metal-free systems, such as frustrated Lewis pairs (FLPs)[11], have also made significant progress in catalyzing the hydrogenation of alkenes and alkynes. Similarly, numerous metal catalysts and metal-free systems have also been developed to achieve the other types of hydrofunctionalizations of alkenes and alkynes, such as hydroamination, hydroboration, hydroalkylation, hydrophosphorylation, hydrosilylation, *etc.* Metals involved in the former include Ag[12], Mn[13], Cu[14,15], Fe[16], Co[17,18], Pd[19], and others[20], while ionic liquids involved in the latter have also been proved to be promising complementary catalysts for the synthesis of hydrogenated products[21-23]. Nevertheless, in this modern era of resource exhaustion and environmental pollution[24], although these catalytic systems have made great progress in the hydrofunctionalizations of alkenes and alkynes, their harsh reaction conditions and hazardous wastes should not be ignored.

Over the past decades, the development of renewable energy sources, such as wind, solar, and biomass, has increased dramatically and tripled the global power generation capacity[25]. This deployment in power generation has driven the transition from the thermochemical to the electrochemical era[26,27]. The conversion of electricity directly to chemical energy offers advantages over the more classic synthetic routes[28-31], which promotes the exciting and ongoing renaissance of electrochemistry since its beginning in the 19th century[32]. As an environmentally friendly and atomically efficient methodology[33], electrochemical synthesis has been involved in the sustainable production of over 35% of value-added compounds[34], including electrochemical manufacturing in the chemical industry[35,36], such as the electrochemical hydrodimerization of acrylonitrile into adiponitrile[37]. The success of electrochemical synthesis depends on its intrinsic properties, in which the chemoselectivity and reactivity of electrochemical reaction can be achieved by adjusting current or potential, avoiding the utilization of hazardous, toxic, and polluting reagents[38,39].

So far, electrochemical transformation has made significant advances through manipulating redox potential[40-43]. In addition to the significant progress made in anodic oxidation reactions[44-46], reductive electrolysis reactions have also received extensive attention in recent years[47]. Compared to traditional approaches, reductive electrolysis provides a promising benign alternative for the hydrofunctionalizations of alkenes and alkynes under mild conditions[48]. The utilization of current allows the addition of H–FG to multiple carbon–carbon (C–C) bonds with low toxicity and high efficiency. Although several impressive reviews regarding the advances of electrochemical reduction have been reported, these reviews mainly summarize the hydrogenation of unsaturated compounds[49,50]. This review [Scheme 1] focuses on the electrochemical hydrofunctionalizations of alkenes and alkynes, highlighting not only the recent advances in their hydrogenation to generate the corresponding alkanes or alkenes.

HYDROFUNCTIONALIZATION REACTIONS

Hydrogenation

Hydrogenation of alkenes and alkynes, which is the introduction of H atoms to π bonds, is widely used from basic research to industrial application. So far, various hydrogenation platforms have been explored and
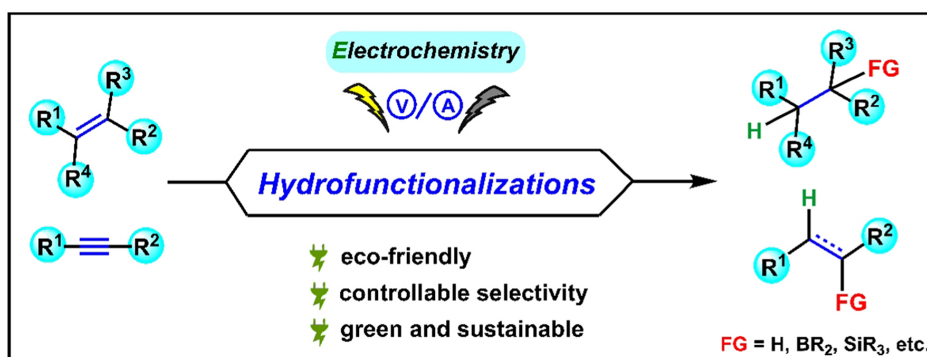
Scheme 1. Electrochemical hydrofunctionalizations of alkenes and alkynes. FG: Functional groups.
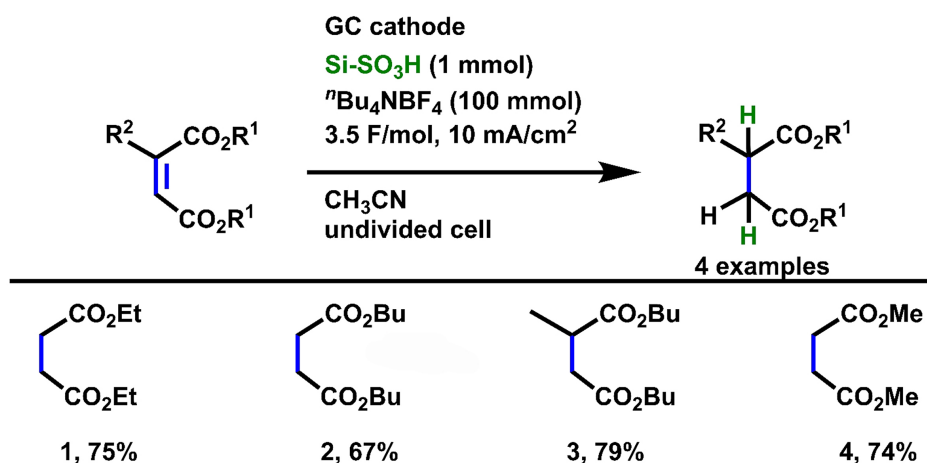
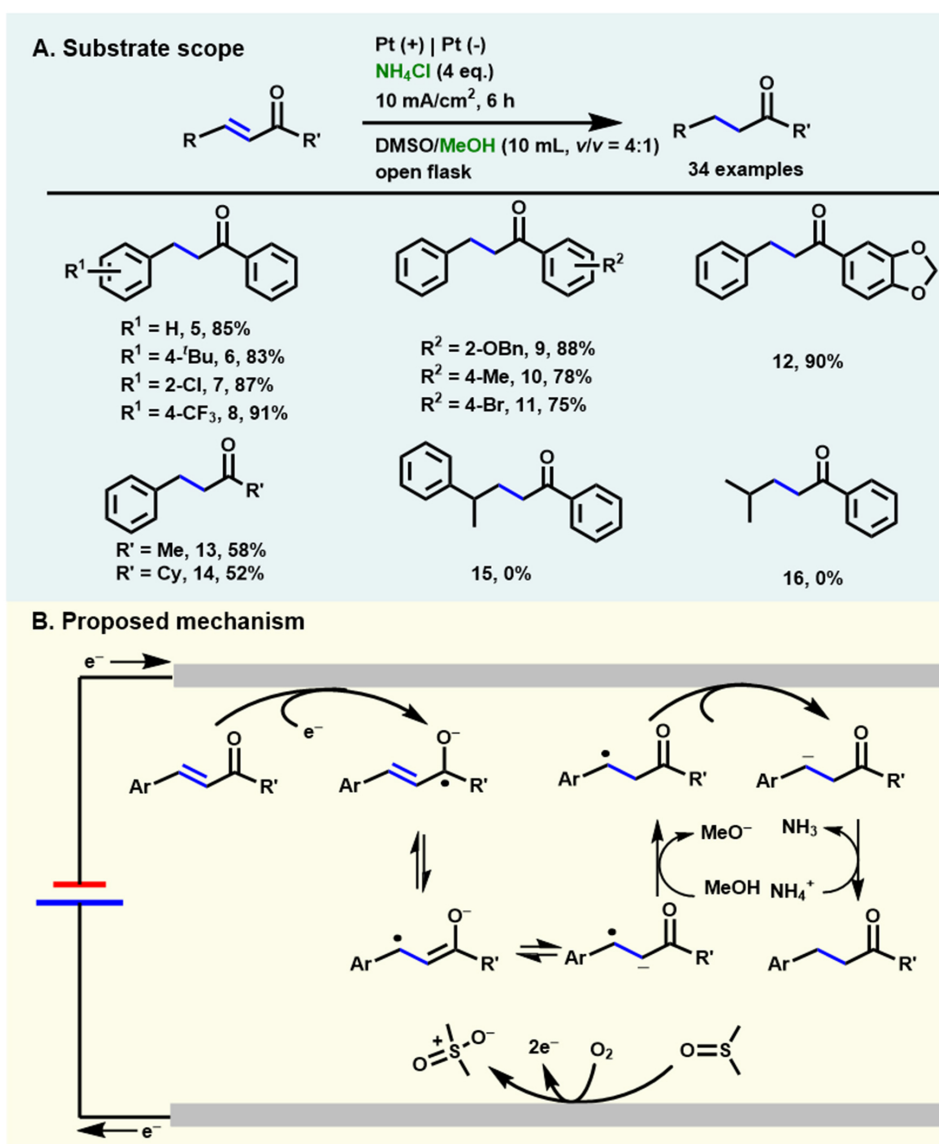**Scheme 2.** Reduction of activated alkenes using the concept of site isolation. Copyright 2016, Elsevier[58].

play an irreplaceable role in synthesizing fine chemicals and pharmaceuticals[13,51,52]. Moreover, two employed strategies are summarized. Thereinto, transfer hydrogenation with a non-hydrogen gas (H_2) reagent as a hydrogen source represents a more convenient, safer, and more powerful method in preparing hydrogenated products than direct hydrogenation with H_2[53]. The electrochemical process, using electrons as redox regents, provides an attractive protocol for the selective transfer hydrogenation of unsaturated hydrocarbons with non-H_2 reagents as hydrogen sources[49,50,54,55].

Hydrogenation of alkenes

Hydrogenation of alkenes to afford corresponding alkanes is a fundamental and powerful reaction[56]. So far, some innovative examples induced by electrochemistry have been developed in the presence of various hydrogen transfer reagents, including alcohol, CH_3CN, dimethyl sulfoxide (DMSO), H_2O, ammonia (NH_3), sulfonic acid, and other hydrogen sources.

Hydrogenation of activated alkenes

Generally, unactivated alkenes possess a high reduction potential and are difficult to reduce. Nevertheless, the electron-withdrawing groups (EWGs) based on the unsaturated C–C bonds of alkenes[57] can make the cathodic reduction more practical in the presence of a hydrogen source. Tomida *et al.* developed an electrochemical hydrogenation method of activated alkenes substituted by different electron-withdrawing ester groups [Scheme 2], using silica gel-supported sulfonic acid (Si–SO_3H, size: 40-63 μm, loading:

A. Substrate scope

Pt (+) | Pt (-)
NH$_4$Cl (4 eq.)
10 mA/cm^2, 6 h

DMSO/MeOH (10 mL, v/v = 4:1)
open flask

34 examples

R^1 = H, 5, 85%
R^1 = 4-^{t}Bu, 6, 83%
R^1 = 2-Cl, 7, 87%
R^1 = 4-CF$_3$, 8, 91%

R^2 = 2-OBn, 9, 88%
R^2 = 4-Me, 10, 78%
R^2 = 4-Br, 11, 75%

12, 90%

R' = Me, 13, 58%
R' = Cy, 14, 52%

15, 0%

16, 0%

B. Proposed mechanism

Scheme 3. Electroreduction of *α,β*-unsaturated ketones. (A) The scope of substrates; (B) A possible mechanism is proposed. Copyright 2019, Royal Society of Chemistry[59].

0.68 mmol·g^{-1}) with the concept of site isolation[58]. The sulfonic acid conjunct on the solid support not only promotes the selectivity and efficiency of this electrolysis reaction but also minimizes and even eliminates the polymerization of radical intermediates. However, this electrochemical method is limited by the tolerance of the alkene species (only four examples).

In 2019, Huang *et al.* disclosed a chemoselective 1,4-reduction of *α,β*-unsaturated ketones under constant current using ammonium chloride (NH$_4$Cl) and MeOH as hydrogen donors [Scheme 3A], realizing the selective hydrogenation of alkenes[59]. The scope and limitation of this electrochemical method are also investigated; the substrates of chalcones derivatives with diverse electronic effects (**5-11**) and *α,β*-unsaturated ketones containing heterocycles (**12**) or alkyl substituents (**13, 14**) are all smoothly reduced to corresponding alkanes in moderate (52%) to excellent (91%) yields. Unfortunately, this electroreduce method is not suitable for substrates (**15, 16**) where R' is substituted by an alkyl group. Furthermore, a series
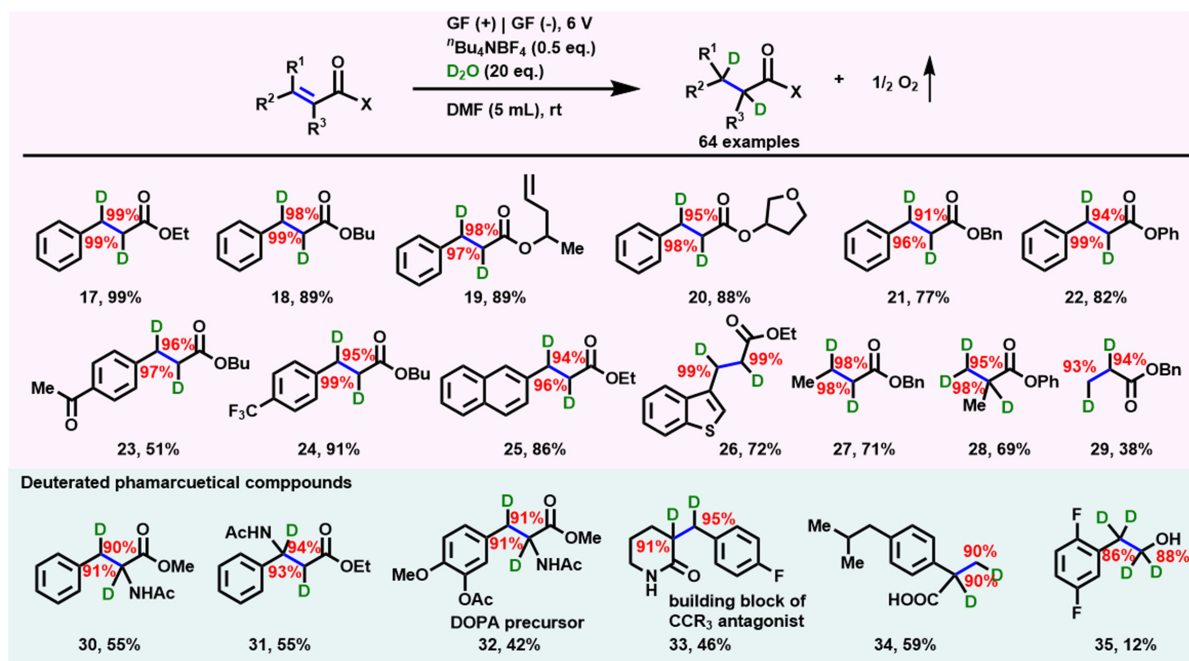
Scheme 4. Electrochemical deuteration reaction using D_2O. Copyright 2020, Wiley-VCH[61]. Red numbers: Content of 100% indicates one D atom on one carbon of products.

of control experiments are performed, including radical trapping and deuterium labeling. A possible reaction mechanism is proposed in the section below of Scheme 3B, in which solvent DMSO is constantly oxidized at the anode surface and continuously provides electrons for the reduction of all substrates. Meanwhile, α,β-unsaturated ketones are reduced and isomerized to obtain stable benzyl radicals, followed by a multi-step protonation and reduction to obtain the target products.

Deuterium-labeled pharmaceutical compounds are key diagnostic tools for drug and biomarker discovery studies in terms of action and toxicity information, and they also provide significant information for the biological transport and metabolites of drugs[60]. Therefore, the introduction of isotopic labels with cheaper and more accessible routes is urgently needed. Liu *et al.* realized the electrochemical deuteration reaction of α,β-unsaturated hydrocarbons using D_2O as a deuteration source and a sacrificial reducing reagent under neutral electrolysis conditions[61] [Scheme 4]. The utility of graphite felt electrodes on cathode and anode is critical to ensuring the deuterium rates (as high as 99%), chemoselectivity (yield up to 91% in 2 h), and broad substrate applicability (64 examples). Additionally, gram-scale experiments up to 15 g can also be performed, and the deuterium rate (60% yield) is almost the same as the 0.2 mmol (68% yield). Notably, this protocol can also be applied to synthesize some deuterated pharmaceutical compounds (30-35). The detailed mechanistic studies confirm oxygen precipitated on the anode surface promotes this electroreduction process by adjusting the solution pH.

The same group first disclosed the electrochemical hydrogenation of alkenes with gaseous NH_3 as the proton source directly[62] [Scheme 5A]. The undivided electrolysis device is equipped with two carbon electrodes and connects to a balloon filled with NH_3 at room temperature. Compound **36** gives a 73% yield under standard conditions with a Faraday efficiency (FE) of 54%. This electrochemical hydrogenation protocol is tolerant to various substrates (40 examples) substituted by valuable groups, including pyridine nitrogen, sulfide, esters, amides, hydroxyl, and nitrile. A fast stepwise electrochemical reduction mechanism
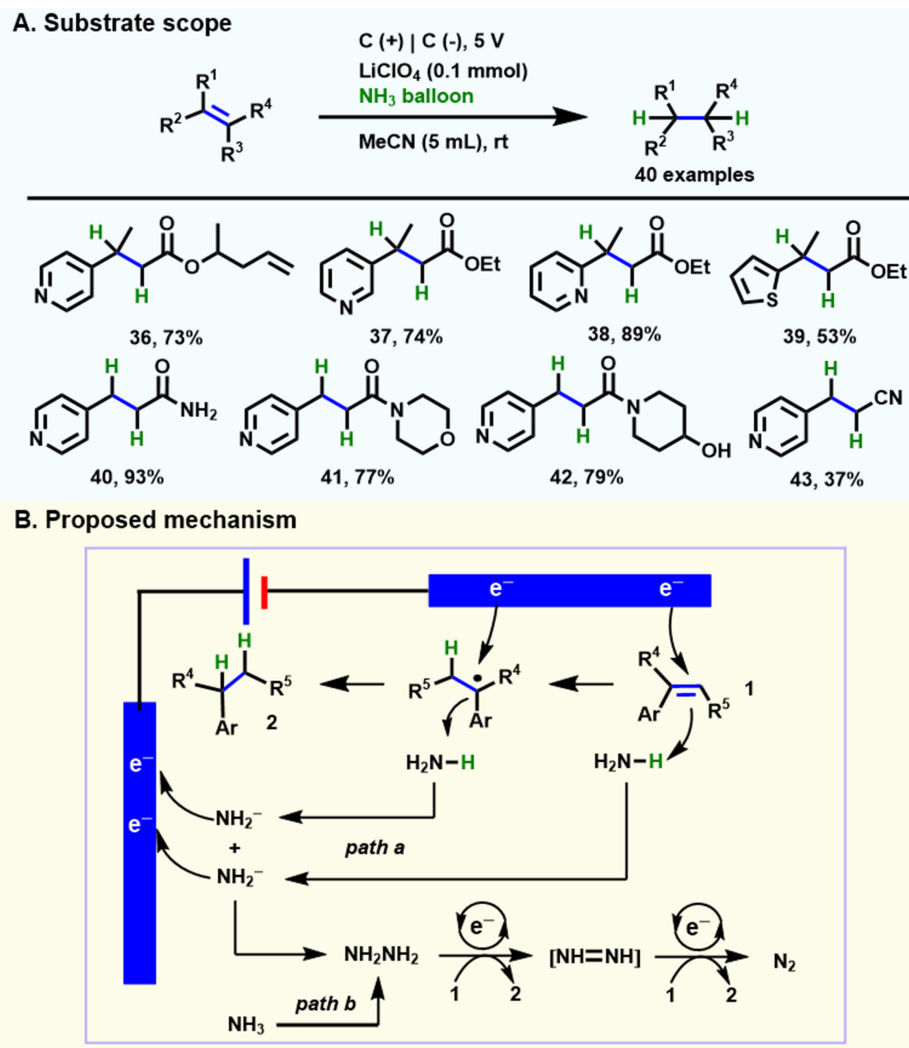
Scheme 5. Electrochemical hydrogenation of alkenes with NH_3. (A) The scope of substrates; (B) A possible mechanism is proposed. Copyright 2019, Wiley-VCH[62].

of NH_3 is proposed [Scheme 5B]. First, alkenes undergo two rounds of cathode reduction and abstract protons on ammonia, while ammonia experiences anion oxidation to form hydrazine. The intermediate hydrazine has been shown to provide protons under standard conditions by a variety of control experiments, thereby, in turn, reducing alkenes to generate the target products and releasing nitrogen gas (N_2).

Subsequently, inspired by the work of Cheng and Xia, a simple method for chemoselective electrochemical hydrogenation of unsaturated C–C bonds with DMSO and H_2O as hydrogen donors was developed by Qin *et al.*[63], generating a series of carbonyl compounds and chain alkanes. This reaction is performed in the absence of metal catalysts and external reducing agents. The substrate scope involves acid, esters, amides, and unactivated alkenes. Moreover, gram-scale experiments were also performed smoothly with desired yields, confirming the potential of this protocol in practical production.
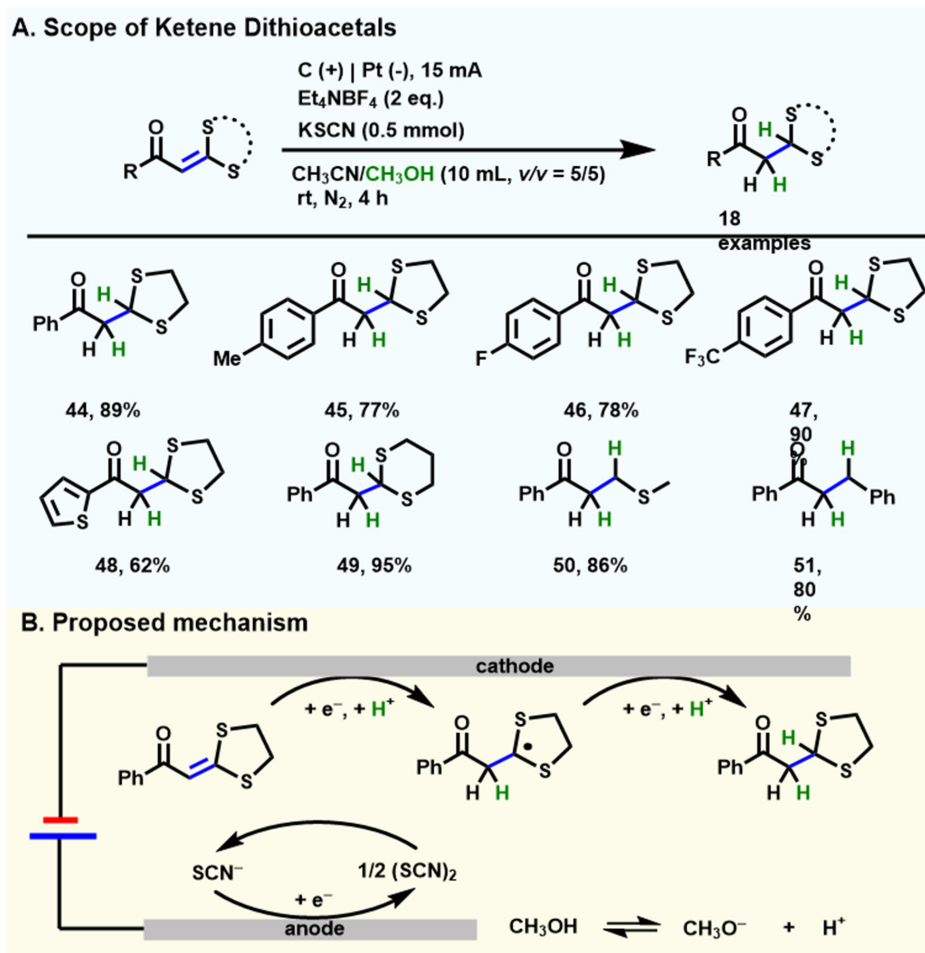
Scheme 6. Electrochemical-induced hydrogenation of electron-deficient internal alkenes. (A) The scope of substrates; (B) A plausible reaction mechanism is proposed. Copyright 2021, Wiley-VCH[64].

Then, Qin *et al.* realized the electrochemical-induced hydrogenation of electron-deficient internal alkenes to generate saturated ketones[64], using CH_3OH as a single hydrogen donor and KSCN as the anode parallel paired electrolysis reagents [Scheme 6A]. Except for alkyl dithioacetals, enamides, and styrene, a series of electron-deficient internal alkenes (**44-51**) are compatible with this method in good to excellent yield. The addition of KSCN plays an important role in the efficient and smooth generation of these hydrogenated products. A possible reaction mechanism was outlined in Scheme 6B. The target products can be smoothly obtained by the two successive steps of cathode reduction and protonation of ketene dithioacetals. At the anode surface, KSCN is oxidized to $(SCN)_2$ acting as a parallel paired electrolysis agent, while CH_3OH is oxidized to methoxide anion and releases hydrogen atoms.

In the same year, using fumarate esters as model objects, Derosa *et al.* [Scheme 7A] described a net reduction ($2e^-/2H^+$) of the C–C π bond at -1.30 V *vs.* $Fc^{+/0}$, using a concerted proton-electron transfer (CPET) mediator comprising of cobaltocene ($[CpCo^{II}(Cp^{NH})]^+$) catalyst with a tethered Bronsted base (*N,N*-dimethylaniline)[65]. This electrochemical approach exhibits high selectivity only in the presence of a synthetically integrated CPET mediator, and two different kinetic mechanistic analyses based on the substrate concentration are revealed: namely rate-limiting CPET followed by an electron-transfer/proton-transfer (ET/PT) step at low concentration and CPET followed by a rate-limiting ET/PT step at high concentration.
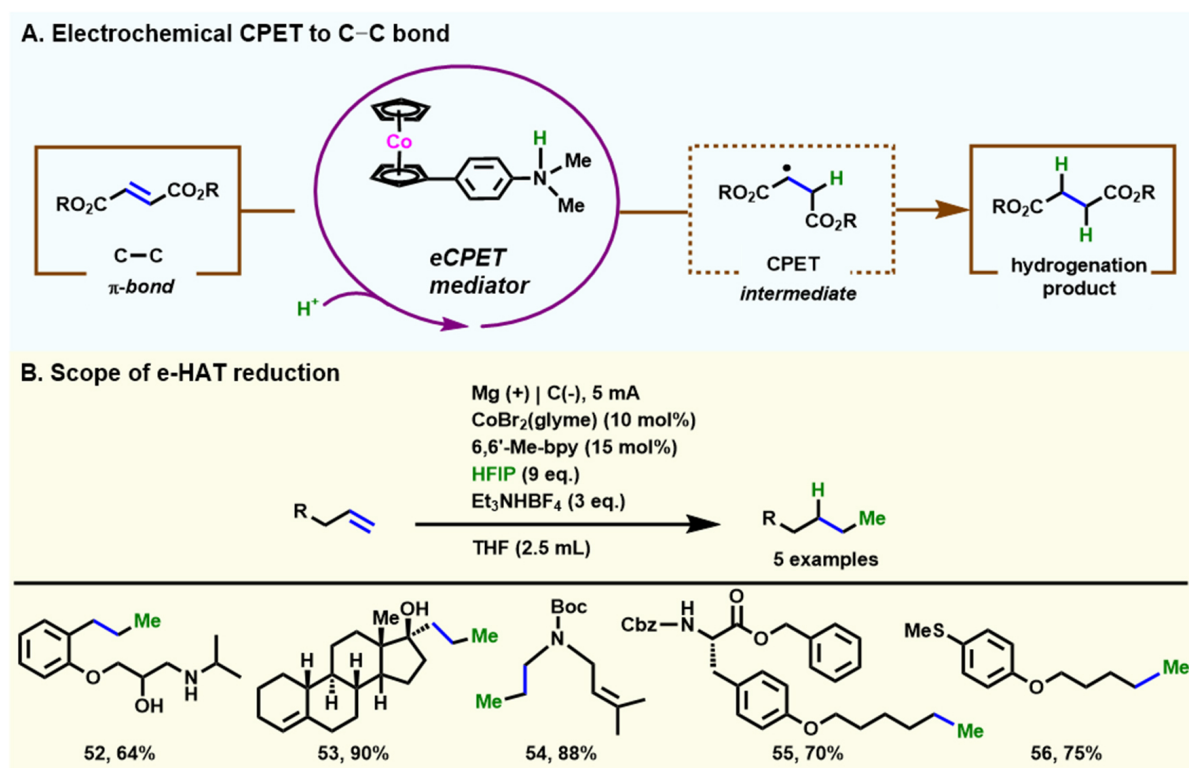
Scheme 7. Electrochemical reduction of unsaturated C–C bonds. (A) Electrochemical CPET to C–C bond using a catalytic molecular mediator. Copyright 2021, American Chemical Society[65]; (B) Cobalt-electrocatalytic HAT for hydrogenation of alkenes. Copyright 2022, Springer Nature[66]. CPET: Concerted proton-electron transfer; HAT: hydrogen atom transfer.

In 2022, Gnaim *et al.* developed a variety of electrochemical [Co–H]-involved hydrogen atom transfer (HAT) protocols using hexafluoroisopropanol (HFIP) as a proton source[66] [Scheme 7B]. This scalable electrochemical sequence enables the selective functionalization of alkenes by adjusting the electrode material, where the metal Mg electrode is more favorable for the reductive hydrogenation of alkenes, and a series of alkenes was then successfully reduced to alkanes in the absence of stoichiometric oxidants. Moreover, large-scale experiments can also be smoothly implemented without strict avoidance of water and oxygen. This electrochemical protocol provides a new perspective on how decades of energy storage research can be utilized to open up electrocatalytic approaches with versatile applications.

Recently, our group presented a new approach for the hydrogenation of aryl alkenes with the three-component system of CH$_3$CN/tetrahydrofuran (THF)/*N,N*-diisopropylethylamine (DIEA) at a constant current of 25 mA[67] [Scheme 8A]. This strategy is also tolerant to those substrates (**69, 70, 71**) containing heteroatom substituents. The detailed mechanism demonstrated the key role of the dual solvent system CH$_3$CN/THF, in which the proportion (*v*/*v* = 4:1) of these two solvents is decisive for the alkenes hydrogenation. The DIEA itself is one of the hydrogen sources and also promotes the electrolysis of CH$_3$CN to release hydrogen ions. Afterward, Kolb and Werz developed an operationally simple protocol to realize general site-selective hydrogenation of benzylic alkenes with H$_2$O/D$_2$O as the hydrogen/deuterium source[68] [Scheme 8B]. This method overcomes many limitations (such as the necessity of conjugated EWGs) that possibly appear in classic metal-catalyzed hydrogenation and shows broader substrate applicability (> 50 examples).
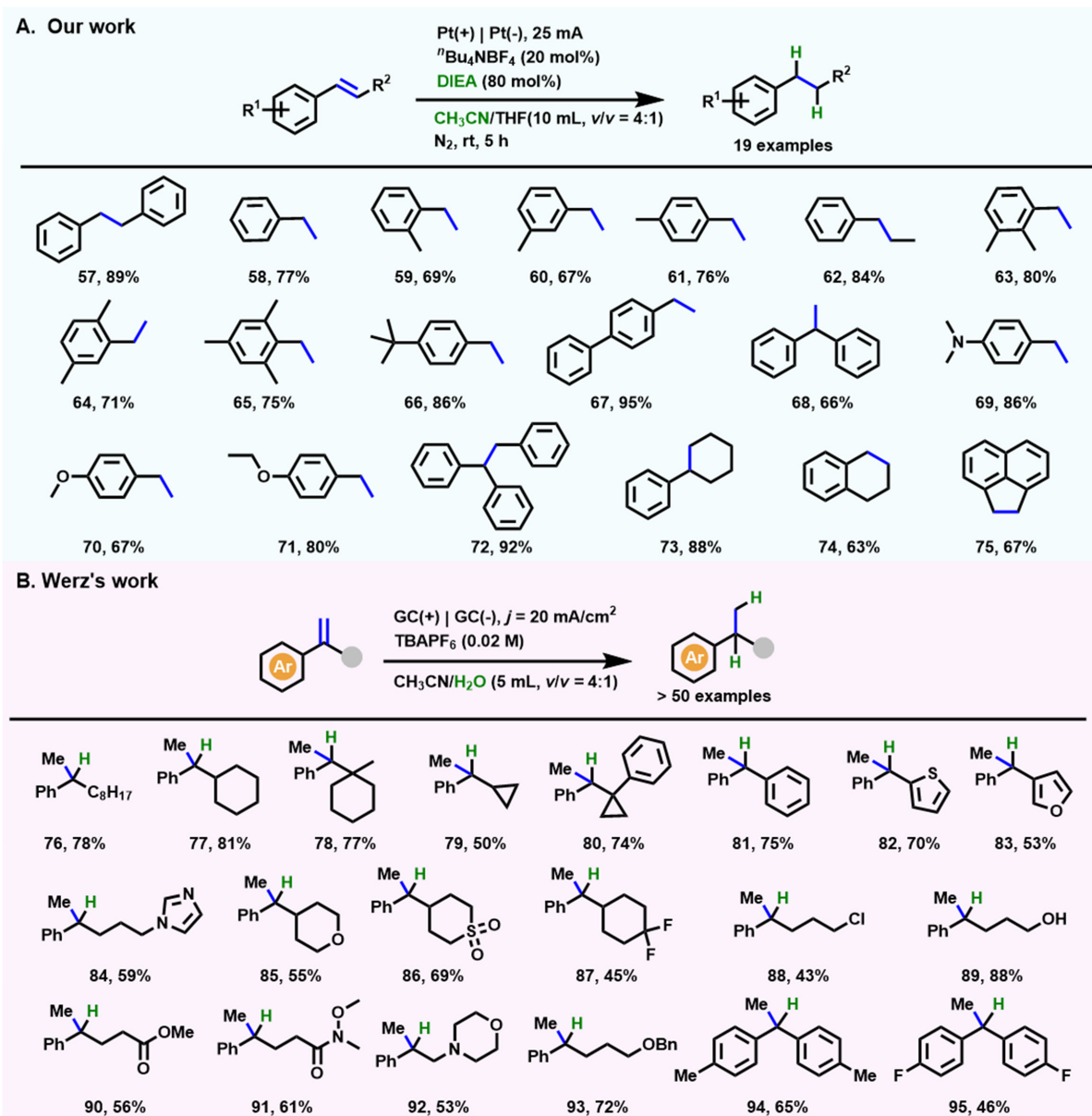
Scheme 8. Electrochemical reduction of aryl alkenes. (A) CH_3CN/DIEA hydrogen sources. Copyright 2023, Wiley-VCH[67]; (B) Site-selective hydrogenation of benzylic olefins with water. Copyright 2023, Wiley-VCH[68]. DIEA: *N,N*-diisopropylethylamine.

Hydrogenation of unactivated alkenes

Compared to the hydrogenation of activated alkenes, the selective electroreduction of unactivated alkenes is more challenging. Unlike the preparation of metal–H by hydride transfer[69], Wu *et al.* [Scheme 9] reported a unique electroreduction approach to generate [Co^{III}–H] that allowed a canonical hydrogen evolution reaction while achieving the selective deuteration of alkenes with CD_3CO_2D as a deuterium source[70]. In addition, the formation process and activity of [Co^{III}–H] are monitored and studied in detail by systematic electroanalytical [including cyclic voltammetry (CV) and rotating disk electrode (RDE) voltammetry techniques] and spectroscopic investigations [including electron paramagnetic resonance (EPR) and differential electrochemical mass spectrometry (DEMS) experiments]. This work provides a strategy for transition-metal hydrides (M–Hs) as a general platform to participate in a variety of useful electrochemical reactions.
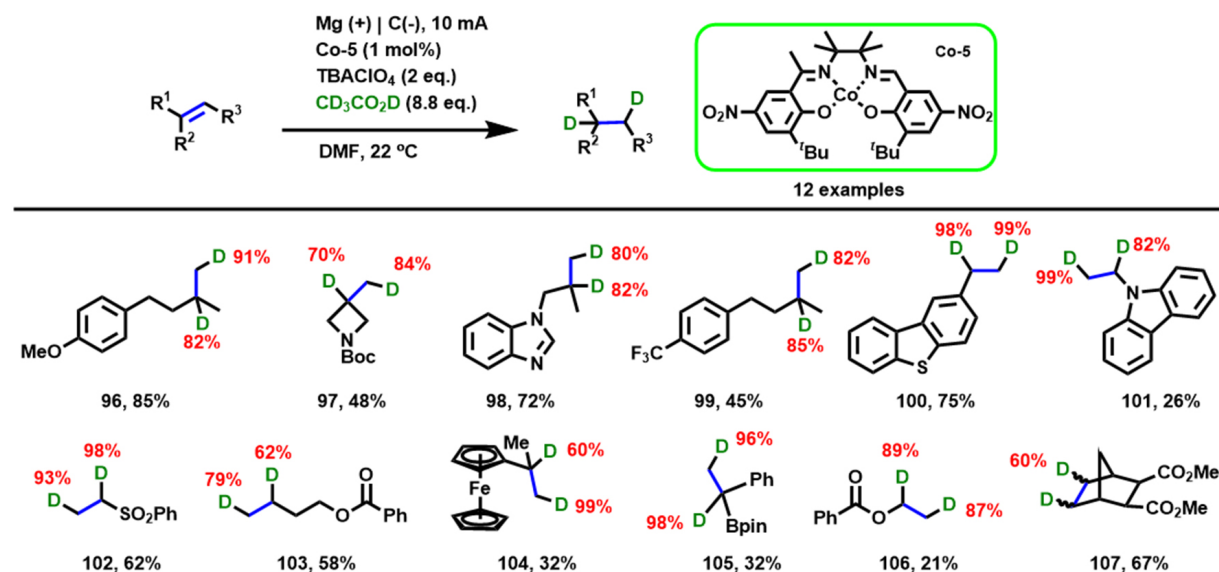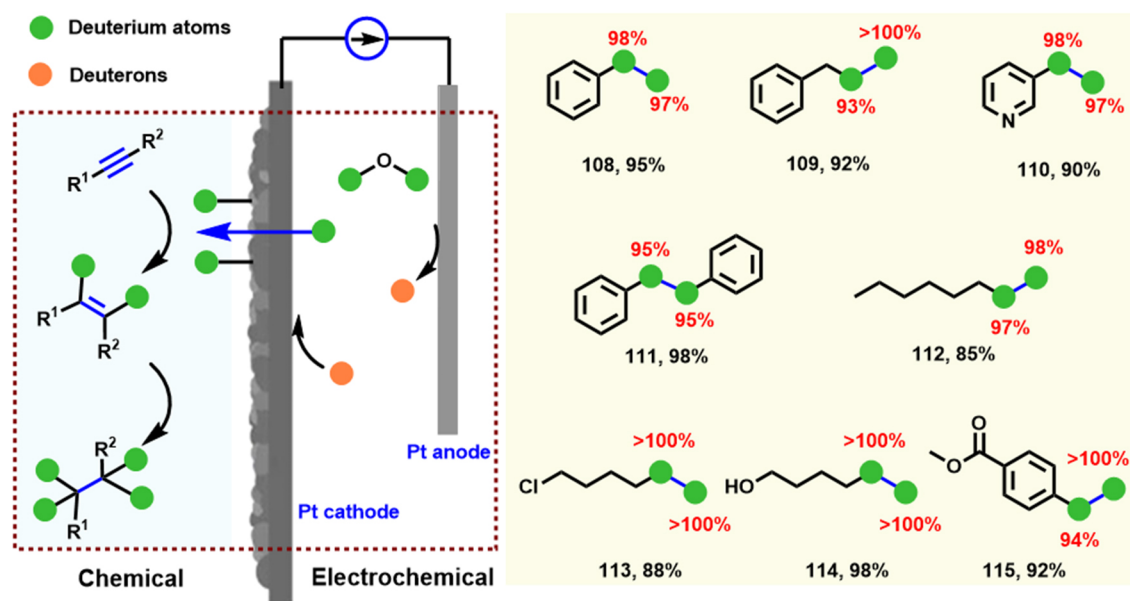
Scheme 9. Electron-initiated hydrogenation of alkenes. Copyright 2022, American Chemical Society[70]. Red numbers: Content of 100% indicates one D atom on one carbon of products.

Hydrogenation of alkynes

The catalytic hydrogenation[71,72] or semihydrogenation[73-75] of alkynes to the corresponding alkenes or alkanes is an extremely important process in the bulk and fine chemical industries. The electroreduction method provides a promising alternative for these metal-facilitated transformations under ambient conditions[76].

Alkynes can also be reduced in some of the alkenes hydrogenation systems described above[61,62,64,66], which will not be repeated here. In 2018, Sherbo *et al.* disclosed a paired electrolysis of alkynes using a dense palladium membrane, and a reductive deuteration of alkynes was successfully realized with D_2O as a deuterium source[77]. The palladium membrane used in this paired electrolysis reaction is impervious to solvent and electrolyte, and two reactions (hydrogenation and electrochemical oxidation reaction) with distinct reaction conditions can be achieved independently in the anode and cathode of a three-compartment cell, respectively. Additionally, this palladium membrane reactor can also be applied to introducing deuterium atoms to afford drug molecules[78] [Scheme 10]. Moreover, no palladium is detected in the reaction mixture determined by inductively coupled plasma-optical emission spectrometry (ICP-OES), even in the amplification experiment, highlighting the great potential of this protocol in drug synthesis.

In 2019, Li and Ge reported the first example of $PdCl_2$-catalytic semihydrogenation of alkynes to produce a series of *Z*-alkenes under electrochemical conditions[79]. Moreover, this electroeduction method also enables the hydrogenation of alkynes to produce alkanes when the constant current is increased to 300 mA and the solvent MeOH is replaced by CH_3CN. The palladium (0) nanoparticles on the cathode surface and electrochemical reaction solvent are all characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) tests and have been demonstrated as the chemisorbed hydrogen carrier.

Scheme 10. Deuterium incorporation and yield by palladium membrane deuteration of alkynes. Copyright 2018, Springer Nature[78]. Red numbers: Content of 100% indicates one D atom on one carbon of products.
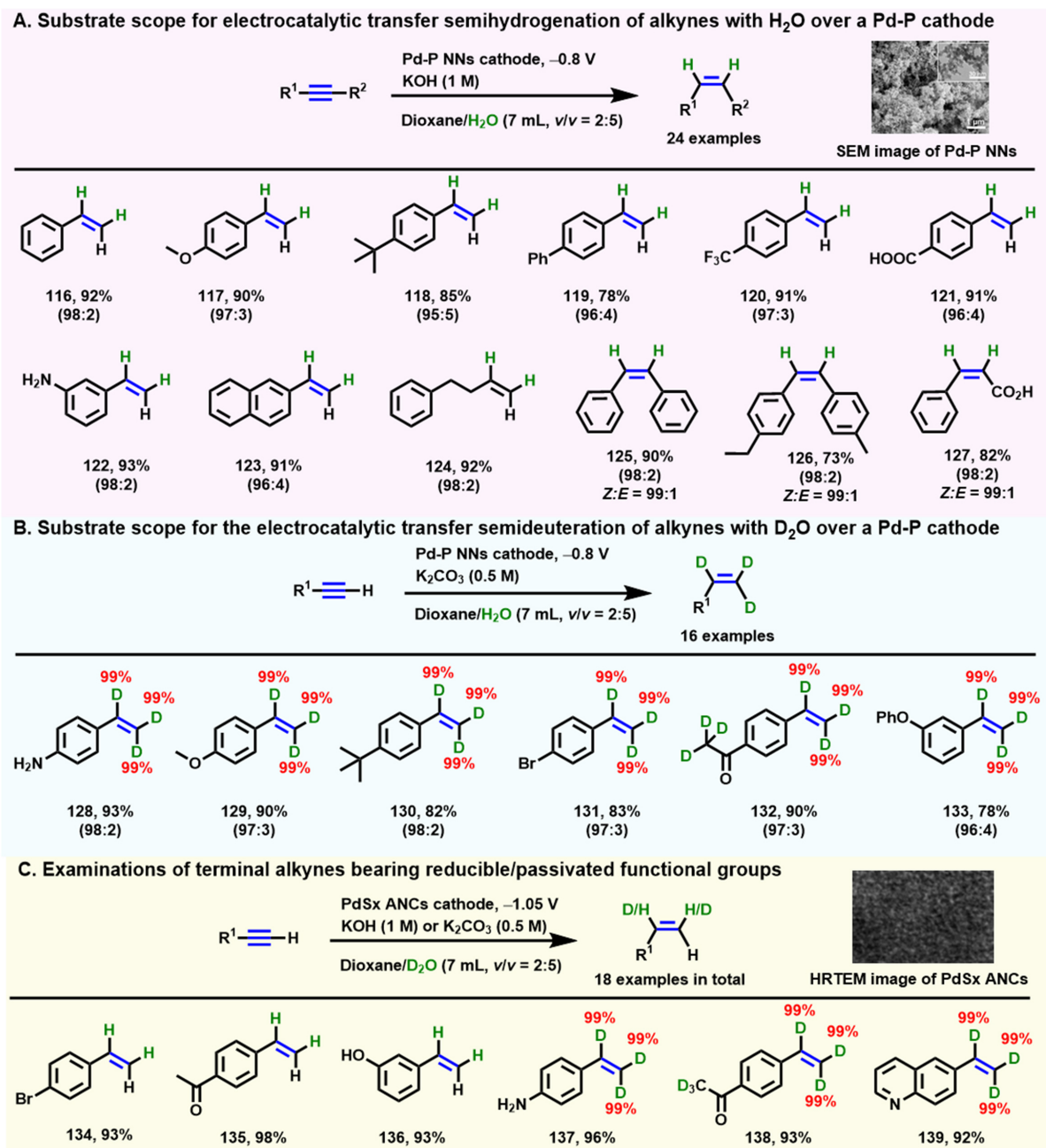
Interestingly, Wu *et al.* developed a series of selective electrochemical semihydrogenation (deuteration) systems [Scheme 11] of alkynes (terminal and internal) employing H_2O (D_2O) as the H (D) source over various Pd-containing alloy cathodes, including Pd-P alloy nanoparticle networks (Pd-P NNs)[80] [Scheme 11A], palladium sulfide nanocapsules (PdSx ANCs)[81] [Scheme 11B and C], and thiolate-modified Pd nanotips (ArS-Pd$_4$S NTs)[82]. The SEM image of Pd-P NNs and high-resolution transmission electron microscopy (HRTEM) image of PdSx ANCs are inserted in Scheme 11. These homemade electrodes have a major advantage over the commercially available ones that have appeared in the reported literature on the efficient selective electroreduction of alkynes, in which the doping of the P or S elements in the Pd nanoparticle enhances the specific adsorption of alkynes on the cathode surface and the inherent activity of generating adsorbed atom hydrogen.

Similarly, Lee *et al.* realized the semihydrogenation of alkynes with a simple catalyst of earth-abundant nickel [Ni(bpy)$_3$]$^{2+}$ with excellent *Z* isomer stereoselectivity under mild conditions[83] [Scheme 12A]. Furthermore, these facile and controllable electrochemical semihydrogenation methods all exhibit strong substrate tolerance, and gram-scale experiments can be performed smoothly, establishing a paradigm for highly efficient electrocatalytic alkynes semihydrogenation in homogeneous or heterogeneous systems. A series of experiments were carried out to study the mechanism, in which (spectro)-electrochemical results indicated that this electrochemical process was promoted by a nickelacyclopropene complex, which was further protonated to give the Ni(II)-vinyl intermediate [Scheme 12B].

Other hydrofunctionalization reactions
Hydroboration
As one of the most versatile building blocks, organoboron compounds are widely used in synthetic chemistry[84]. They usually have broad applications, good stability, and rich functional transformations, and thus have won the Nobel Prize in Chemistry twice in 1979 and 2010[85]. Hydroboration of alkenes and alkynes provides a straightforward strategy for synthesizing organoboron compounds[86], and electrochemical hydroboration has attracted increasing attention in recent years[87,88].

A. Substrate scope for electrocatalytic transfer semihydrogenation of alkynes with H₂O over a Pd-P cathode

B. Substrate scope for the electrocatalytic transfer semideuteration of alkynes with D₂O over a Pd-P cathode

C. Examinations of terminal alkynes bearing reducible/passivated functional groups

Scheme 11. Electrochemical semihydrogenation (deuteration) of various alkynes. (A) Pd-P alloy and H₂O are used as the cathode and a hydrogen source. Copyright 2020, Wiley-VCH[80]; (B) Pd-P alloy and D₂O are used as the cathode and a hydrogen source. The data in brackets refer to the ratio of yields of the semihydrogenated and full-hydrogenated products; (C) PdSx ANCs and H₂O or D₂O are used as the cathode and hydrogen sources. Copyright 2022, American Chemical Society[81].

Our group developed the first example of aryl alkenes electrochemical hydroboration with pinacolborane (HBpin) with moderate (57%) to excellent (84%) yields[89], in which DIEA-assisted CH₃CN for electrolysis and the selection of solvents were the key to the whole hydroboration process [Scheme 13A]. The smooth implementation of the gram-scale experiments and the multi-functional conversions of organoboron compounds further confirm the great potential of this electrochemical method for industrial applications. The detailed deuterium-labeling tests and H₂ detection experiments indicate that CH₃CN and HBpin are
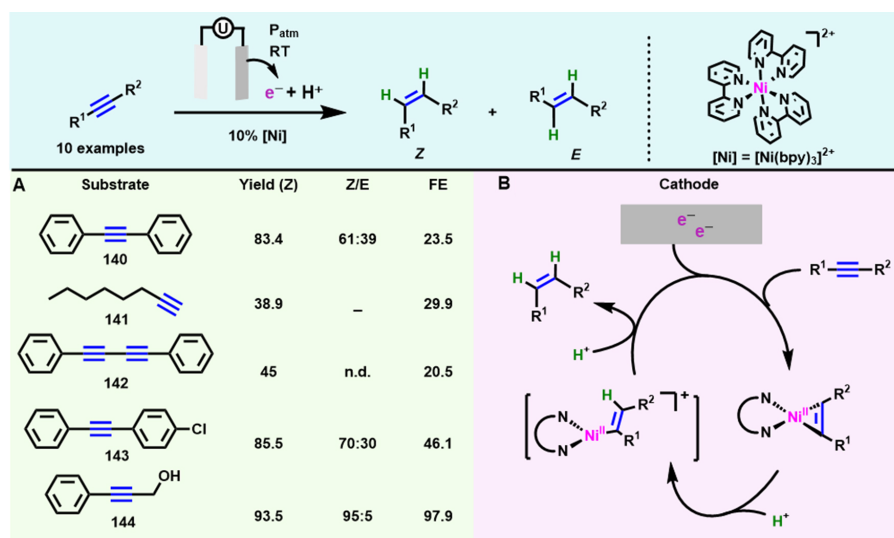
Scheme 12. Electrocatalytic semihydrogenation of alkynes with [Ni(bpy)₃]²⁺.(A) Substrate scope; (B) The formation of a nickelacyclopropene complex and Ni(II)-vinyl intermediate. Copyright 2022, American Chemical Society[83].
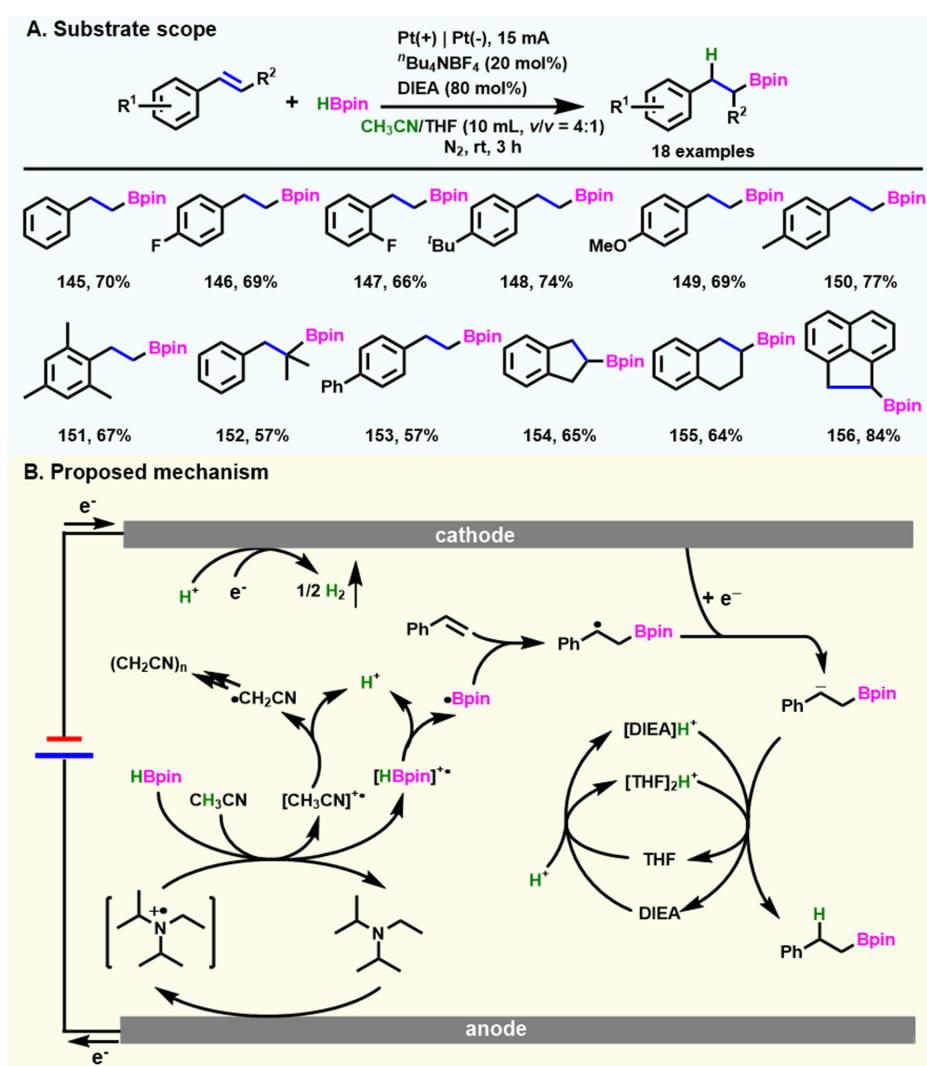
Scheme 13. Electrochemical hydroboration of aryl alkenes. (A) The scope of substrates; (B) A possible mechanism is proposed. Copyright 2021, Royal Society of Chemistry[89].

hydrogen sources and the former is the main hydrogen source, which provides a unique strategy for producing hydrogen ions in electrochemical systems. Some key intermediates are captured by a series of radical trapping experiments using 2,2',6,6'-tetramethyl-1-piperidinyloxy (TEMPO) or the galvinoxyl free radical as the radical scavengers, respectively. Combined with cyclic voltammetric (CV) tests, a possible mechanism of this electrochemical hydroboration is proposed in Scheme 13B. DIEA is first oxidized on the anode surface and then grabs electrons from HBpin and CH_3CN, which, in turn, promotes the formation of boron radicals and the release of hydrogen atoms. Subsequently, the boron radical is added to styrene to form a carbon-centered radical intermediate, which again undergoes cathodic reduction and protonation to give the target product.

Recently, Aelterman *et al.*[90], Yuan *et al.*[91], Guo *et al.*[92] successively reported the electrochemical hydroboration of alkenes with B_2Pin_2 as a boron source and CH_3OH and CH_3CN as hydrogen sources, respectively. Unlike HBpin, this diboron reagent exhibits better stability to oxygen and water, which provides more convenience in experimental operation. Under mild conditions or even in the air, versatile borylated building blocks are obtained in good to excellent yields with multiple electrode pairs of different materials, including stainless steel electrodes (SST) cathode and anode, Fe(+)|Al(-), and Fe(+)|Pt(-). However, the electrochemical system using SST as the electrodes is only suitable for activated electron-deficient alkenes. When iron is used as the anode and aluminum or platinum as the cathode, although hydroboration of unactivated alkene can be achieved, two equivalents of KO^{t}Bu or one equivalent of CsF is necessary.

For electrochemical boration of alkynes, the products of the only two examples reported so far remain in vinyl boronates, either HBpin or B_2pin_2 as a hydrogen source. The first electrochemical hydroboration of alkynes was achieved by Aelterman *et al.* in 2021 using B_2Pin_2 as the boron source[93] [Scheme 14A]. This cost-effective and catalyst-free method is performed in an undivided cell open to the air. A total of 44 substrates are investigated, showing broad substrate compatibility with excellent yields (yield up to 92%). A putative methoxy-bound boryl radical formed in situ oxidized on the anode surface is involved in the reaction mechanism [Scheme 14B]. Similarly, Qiu *et al.* also realized the direct hydroboration of alkynes with HBpin as a boron source, carbon as the anode, and platinum as the cathode[94]. The corresponding vinyl boronates can be obtained in good to excellent yields in only 30 min at room temperature.

Hydrosilylation
Organosilicon compounds are one of the most valuable precursors and are widely used in modern chemistry, including chemical synthesis, drug development, and polymer production[95,96]. Thus, efficient methods for synthesizing organosilicons are highly desired. The addition of silicon compounds to alkenes and alkynes provides a very profitable process to afford organosilicon[97]. Among them, as a green technology, electrochemistry has also made some progress in the hydrosilylation reaction of unsaturated hydrocarbons[98-100].

In 2020, Lu *et al.* disclosed the electrochemical synthesis of organosilicon compounds[101], in which the disilylation, silacycle synthesis, hydrosilylation, allylic silylation, and carbonsilylation of alkenes were successfully achieved in the presence of three equivalents of chlorosilane. During the preparation of hydrosilylated products [Scheme 15A], the substrate scope involves conjugated alkenes, alkynes, and chlorosilanes (**172-182**). The Mg is used as a sacrificial anode to assist the generation of silicon radical intermediates, while CH_3CN provides hydrogen protons to complete the alkene hydrosilylation process and the deuterosilylation product could be obtained in the presence of CD_3CN. As shown in Scheme 15B, the entire process of incorporating hydrogen atoms and silicon groups into unsaturated C–C bonds is carried
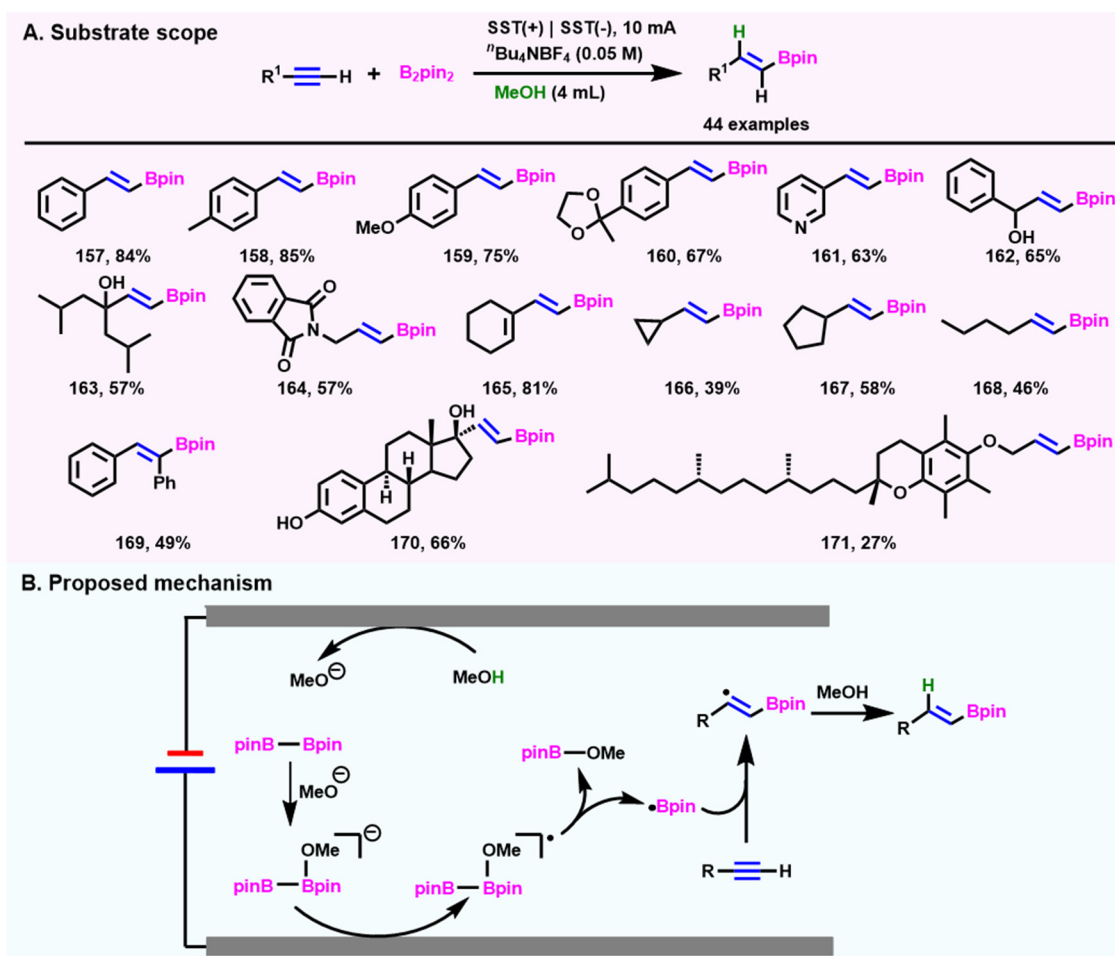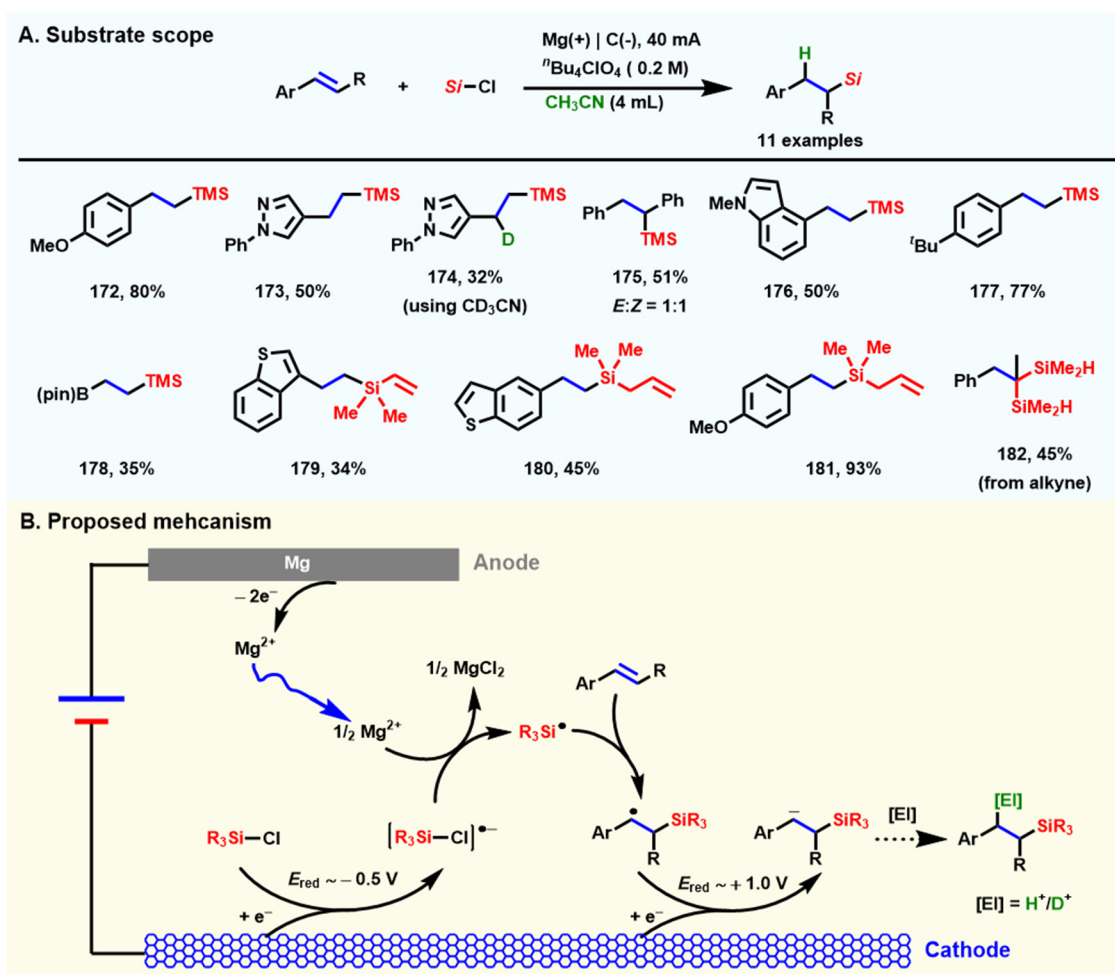
Scheme 14. Electrochemical hydroboration of alkynes. (A)The scope of substrates; (B) A plausible mechanism is proposed. Copyright 2021, Wiley-VCH[93].

out by an electron transfer, chemical protonation, electron transfer, chemical protonation (ECEC) mechanism.

Using alkynes and Suginome reagent (PhMe$_2$Si–Bpin) as substrates, Biremond *et al.* realized the electrochemical hydrosilylation of alkynes to prepare vinyl silicates with stainless steel as the anode and cathode[102] [Scheme 16]. This electrochemical method exhibited excellent substrate compatibility and massive unactivated terminal and internal alkynes are smoothly transferred to the corresponding hydrosilylation products. Only the reactivity of internal alkynes was significantly lower than that of terminal alkynes and the yields of the hydrosilylated products of the inner alkynes are only about 50% compared to the high yields (yield up to 91%) of the hydrosilylation reaction of the terminal alkynes. Subsequently, Zhou *et al.* described an electrochemical hydrosilylation with PhMe$_2$Si–Bpin as a substrate[103], also using the SST material. However, this protocol is limited to the electron-withdrawing alkenes.

Hydroalkylation
Hydroalkylation of alkenes is a new way to build the C–C bond skeleton, allowing the synthesis of molecules with higher molecular complexity, ranging from active molecules to functional polymers[104,105]. Electrochemical synthesis provides a green complementary method to achieve the C–C coupling for the
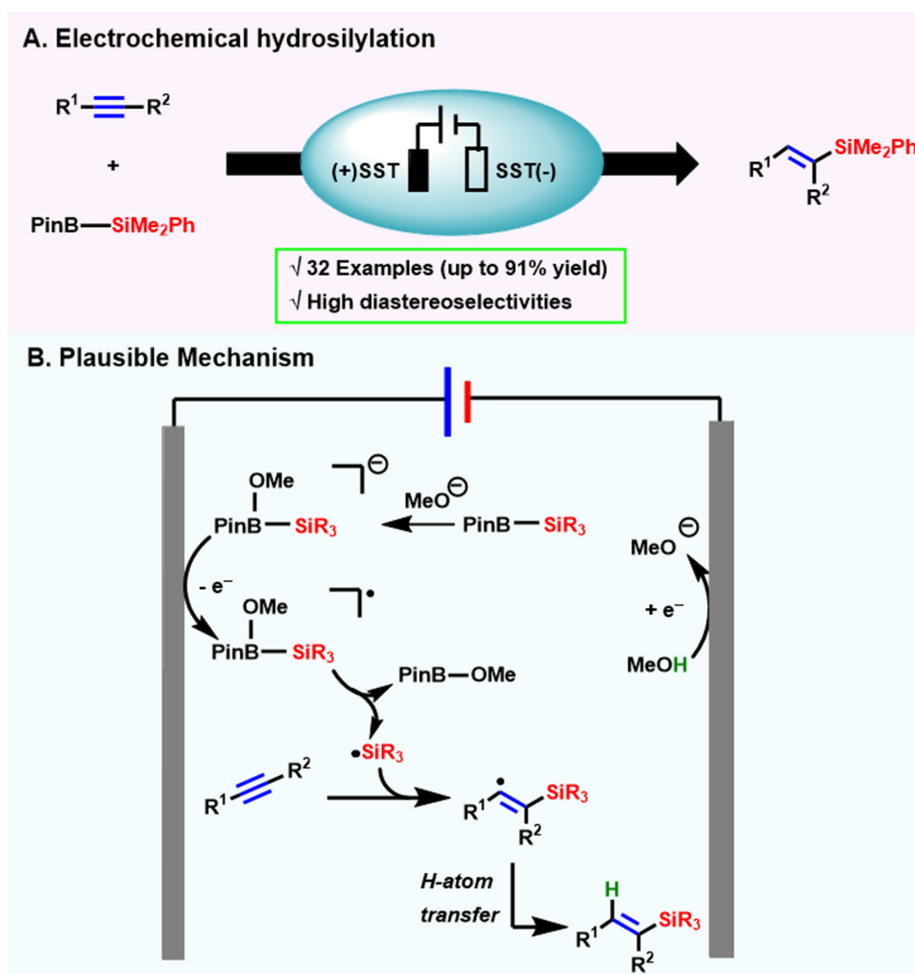
Scheme 15. Electrochemical hydrosilylation of alkenes and alkynes. (A) The scope of substrates; (B) A possible reaction mechanism is proposed. Copyright 2020, American Chemical Society[101].

hydroalkylation of alkenes, and significant advances have been received[100].

In 2018, Wu *et al.* described a Ti[III]-catalyzed radical alkylation method between electron-deficient alkenes and 2° and 3° alkyl chlorides, in which Lewis acid plays a key role in generating active catalysts[106]. Based on this research result, they used Mg as an anode sacrificial electrode to achieve *anti*-Markovnikov hydroalkylation reaction of alkenes in the presence of alkyl halide[107] [Scheme 17A]. Such a direct coupling of the Csp³–Csp³ bond with unactivated alkyl halides as substrate is very challenging and rare. The broad substrate range (activated aryl alkenes or 2° and 3° alkyl bromides) confirms the strong compatibility of this electrochemical method for diverse FGs. Similarly, a one-carbon elongation of a terminal alkenes approach with CDCl₃ as the substrate was developed by Zhang and Cheng in 2022[108] [Scheme 17B]. Different proton sources give rise to the generation of various alkene hydroalkylation products in moderate to excellent yields.

In 2020, Hu *et al.* presented a scalable electroreductive alkene-ketone coupling to afford *anti*-Markovnikov addition product tertiary alcohols with Zn as the anode under environmental conditions[109] [Scheme 18A], in which ketones were added to the unsaturated C–C bond of alkenes as nucleophile reagents. More than 40
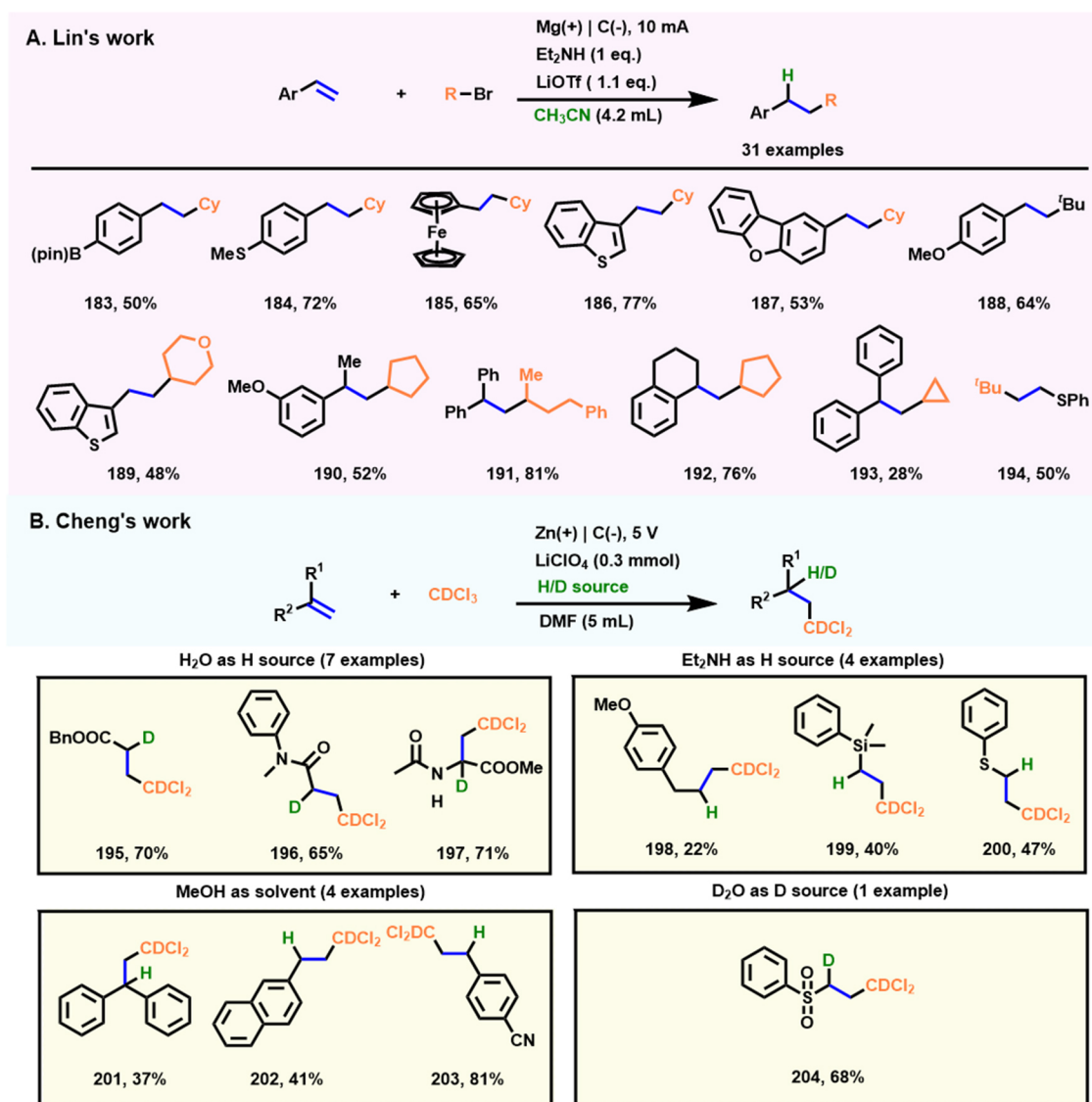
Scheme 16. Electrochemical hydrosilylation of alkynes. (A) State of the present work; (B) A possible mechanism is proposed. Copyright 2022, American Chemical Society[102].

examples (alkenes or ketones bearing different substituents) are smoothly investigated and moderated to excellent (yield up to 98%) yields are obtained. Besides, the synthesis of several medicinally relevant structures is also tolerated in this protocol. Interestingly, in a similar type of alkene hydroalkylation addition reaction, Wu *et al.* realized a substrate-dependent coupling between ketones and alkenes[110] [Scheme 18B]. A series of *anti*-Markovnikov (linear) and Markovnikov (branched) addition products are successfully obtained in good to excellent yields by adjusting the alkene species and the scale-up experiments at a ten mmol scale under a constant current also confirm the practicability of this method. Additionally, owing to the unique chemical property of benzonitrile derivatives, a range of hydroalkylation products of electron-deficient alkenes are also prepared[111-113].

Hydroalkoxylation
Oxygen-bearing modules are found in a wide range of natural or synthetic bioactive scaffolds[114]. Hydroalkoxylation, namely the addition of alcohols across C–C multiple bonds, is one of the straightforward and efficient routes for synthesizing these building blocks[115-117]. However, compared to other hydrofunctionalization of unsaturated hydrocarbons, the development of electrochemical hydroalkoxylation is relatively slow.

Scheme 17. Electrochemical hydroalkylation of alkenes. (A) Substrate Scope of Hydroalkylation. Copyright 2020, American Chemical Society[107]; (B) Electrochemical cyclopropanation with CDCl₃ as a one-carbon D/Cl building block. Copyright 2022, American Chemical Society[108].

In 2022, Yang *et al.* developed a cost-effective electrochemical oxidative hydroalkoxylation protocol of alkenes *via* a Co(II/III/IV) cycle[118] [Scheme 19A]. A large number of hydroalkoxylation products (33 examples including oxygen-hetero or chain) with diverse FGs are obtained in good yields in the absence of stoichiometric chemical oxidants. Mechanical and stereochemical studies demonstrate that an ECEC process is involved in generating Co^{IV} intermediates. Meanwhile, Park *et al.* described an analogous Co-electrocatalytic hydroalkoxylation approach of alkenes for synthesizing alkyl aryl ethers using phenol as a substrate[119] [Scheme 19B]. The precise control of electrochemical potential and the key role of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the co-solvent are highlighted in this paper; their combined action promotes the consecutive oxidations of the Co(II) salen catalyst and drives the alkenes to produce carbocationic species. Therefore, the optimal and exclusive chemoselectivity and broad substrate compatibility are smoothly obtained.
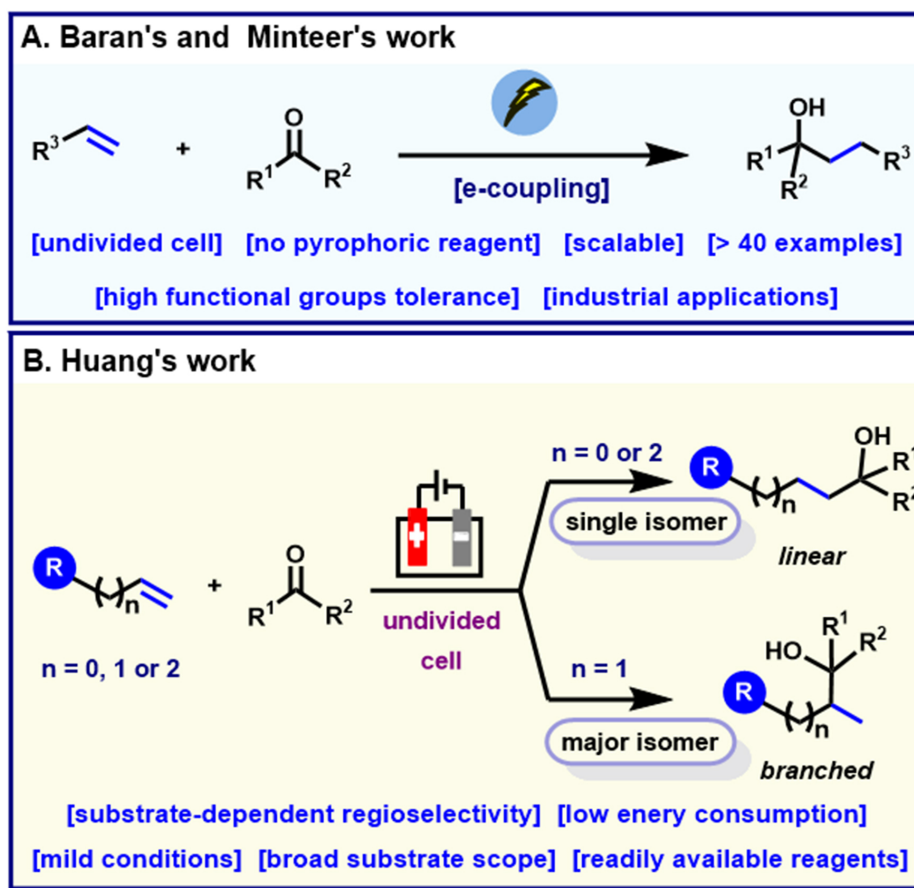
Scheme 18. Electroreductive alkene-ketone coupling. (A) Electrochemical protocol of olefin-ketone coupling. Copyright 2020, American Chemical Society[109]; (B) Electrochemical protocol for accessing linear or branched products. Copyright 2022, American Chemical Society[110].

Hydrocyanation

Nitriles are key intermediates and precursors in synthesizing valuable compounds, including useful pharmaceuticals and functional materials[120-122]. Alkene hydrocyanation, where H and CN groups are added to the two carbon atoms of the C=C π bond in alkenes, respectively, is an attractive functional transformation to form nitriles. Usually, the selection of toxic hydrocyanation (HCN) as a substrate greatly limits its use in non-industrial laboratories[123]. Song *et al.* realized a highly efficient Co/Cu dual electrocatalytic enantioselective hydrocyanation of alkenes using trimethylsilyl cyanide (TMSCN) as a nitrile source in 2020[124] [Scheme 20A]. The combination of serine-derived bisoxazolines (sBOXs), Co(salen) complex, and Cu(OTf)$_2$ provides a complementary approach for the synthesis of chiral nitriles [Scheme 20B]. Moreover, sBOXs have been demonstrated to be effective chiral ligands in improving the reaction enantioselectivity and promoting the generation of target chiral nitriles. Under the precise control of the electrochemical voltage, two typical radical reactions (cobalt-mediated hydrogen-atom transfer and copper-promoted radical cyanation) are combined seamlessly at the anode surface, further accomplishing the high enantioselective generation of nitriles with a wide substrate scope. This system opens up a new era for electrochemistry and provides a paradigm for its application in synthesizing high-value fine chemicals.

Hydrocarboxylation

Direct selective hydrocarboxylation of alkenes and alkynes using carbon dioxide (CO_2) as a renewable and
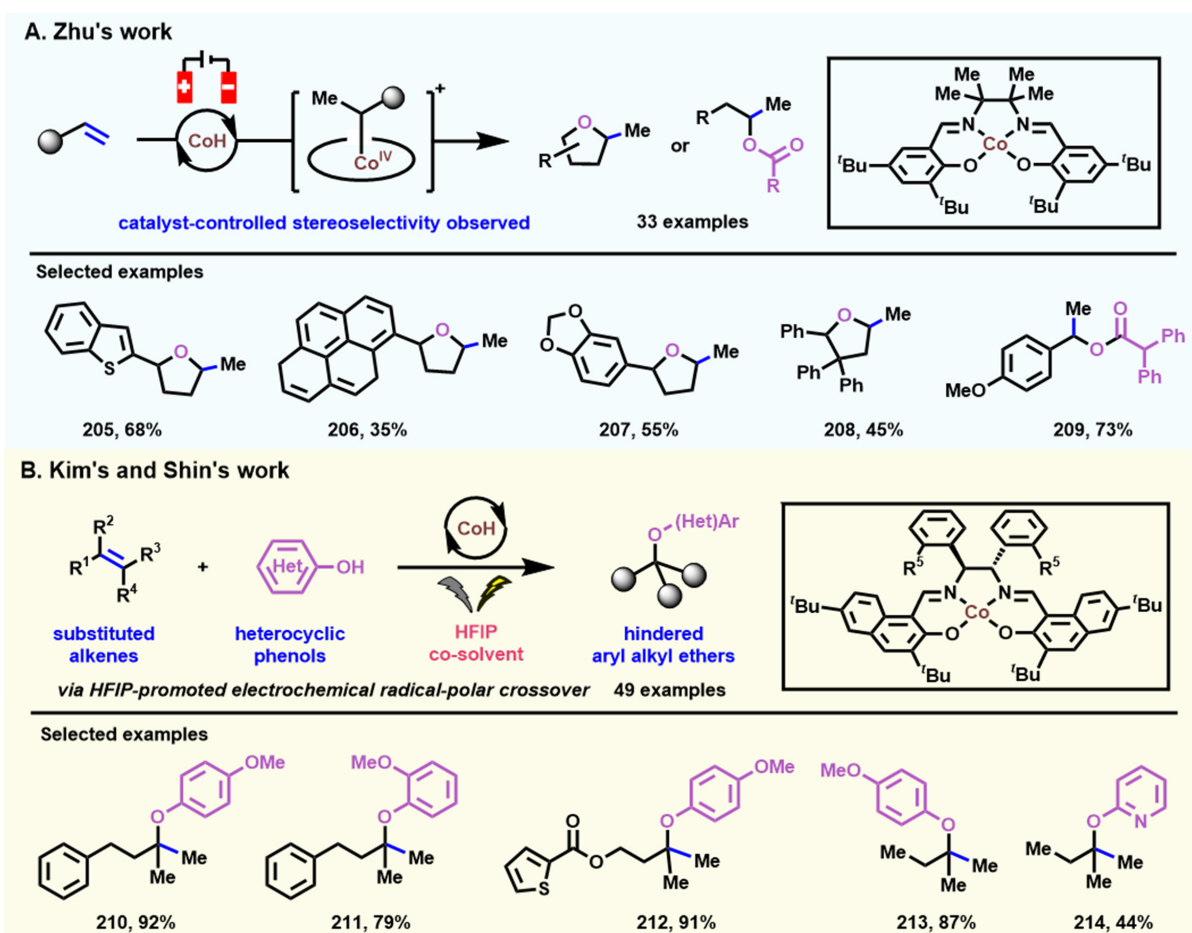
Scheme 19. Electrocatalytic oxidative hydroalkoxylation of alkenes. (A) Substrate scope for electrocatalytic hydroalkoxylation of alkenes *via* Co(II/III/IV) cycle. Copyright 2022, American Chemical Society[118]; (B) Substrate scope for electrocatalytic radical-polar crossover hydroalkoxylation of alkenes with phenols. Copyright 2022, American Chemical Society[119].

non-toxic carbon source is a feasible strategy for synthesizing various high-value-added carboxylic acids[125-127]. So far, transition metal-[128] and photo-catalyzed[129] α- or β-hydrocarboxylation of alkenes has been recognized as an attractive synthetic method for producing carboxylic acids and their derivatives. As a complementary approach, the electrochemical fixation of CO_2 across C–C multiple bonds to yield hydrocarboxylation products has gained increasing attention[130-132].

In 2020, Kim *et al.* realized electrochemical β-selective hydrocarboxylation of styrene using H_2O as a clean proton source in the CO_2 atmosphere, in which Mg and Ni were used as an anode and cathode in an undivided cell, respectively[133]. In this platform, the addition of H_2O significantly improved the β-site selectivity of hydrocarboxylation and inhibited the formation of dicarboxylate products [Scheme 21A]. In terms of selectivity, the ratio of product **227** to **226** increased gradually from 3% to 96% as the H_2O concentration increased from 0 to 1 M. However, regarding product yield, the FE of **227** was highest (65%) at 0.1 M H_2O and decreased by 47% with 1 M water. The electrochemical β-hydrocarboxylation of other styrene derivatives (0.1 M) was performed in the mixture of CO_2-saturated *N,N*-dimethylformamide (DMF), H_2O (0.1 M), and electrolyte $^nBu_4NBF_4$ (0.1 M) at a 10 mA·cm^{-2} current density [Scheme 21B].

A. Substrate scope

B. Proposed mechanism
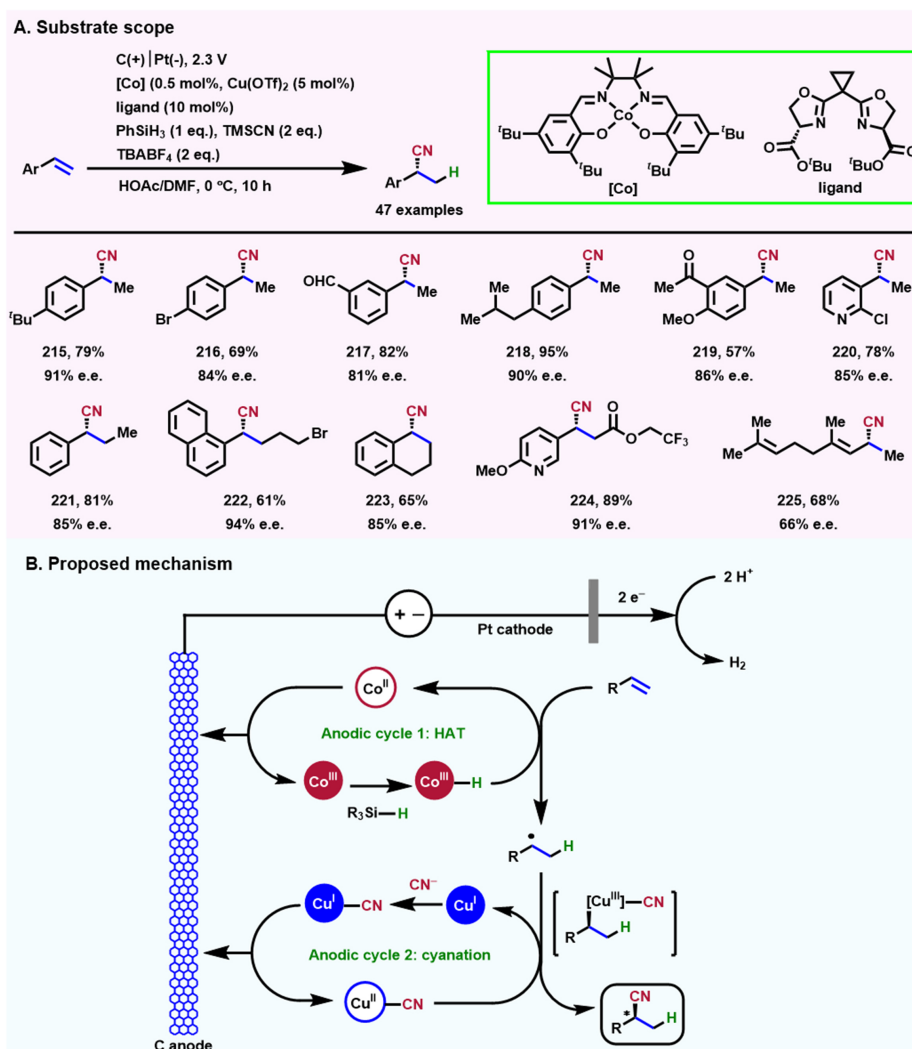
Scheme 20. Electrochemical enantioselective hydrocyanation of conjugated alkenes. (A) The scope of substrates; (B) A possible mechanism is proposed. Copyright 2020, Springer Nature[124].

In the same year, Alkayal *et al.* reported a new and practical electrosynthetic approach for the selective *β*-hydrocarboxylation [Scheme 22A] of terminal, di- and trisubstituted alkenes[134]. Generally, the electrocarboxylation of styrene with CO_2 usually requires a sacrificial anode[133,135], but this electrochemical transformation was conducted on two inert carbon electrodes, with triethanolamine (TEOA) acting as a proton source and sacrificial reducing agent to avoid sacrificing anode. Moreover, a wide variety of styrene derivatives were investigated based on optimized conditions, and good to excellent yields were obtained. In 2022, the same group also achieved electrochemical hydrocarboxylation of *α,β*-unsaturated esters [Scheme 22B] with high regioselectivity using CO_2 as the one-carbon building block[136]. This electrosynthetic platform not only allowed the direct mono-carboxylation of non-aryl *α,β*-unsaturated esters but also could obtain all-quaternary centered carboxylic acids in good to excellent yields. Notably, the generated products can be purified by simple crystallization without further chromatographic separation. Then, Sheta *et al.* applied the optimized electrochemical conditions directly to a commercial flow reactor [Scheme 22C], and the target product was obtained at a desired yield (81%)[136], which confirmed the possibility of this method in industrial production.
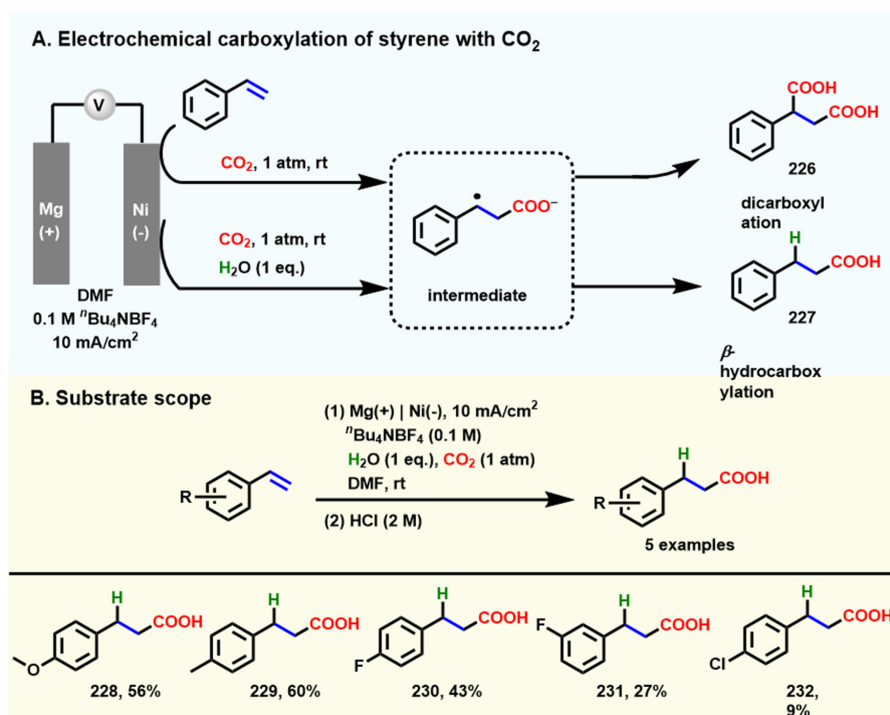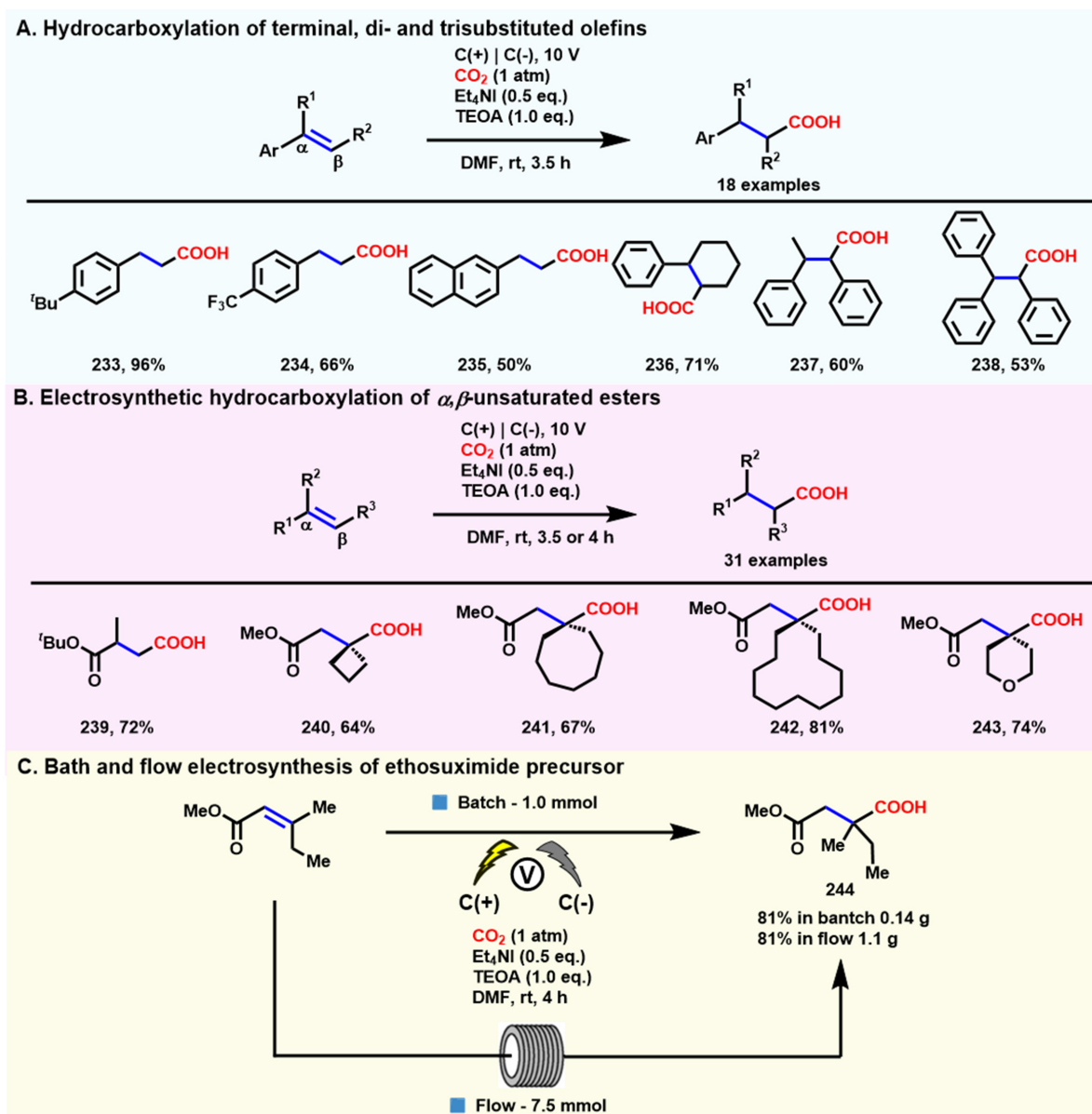
Scheme 21. Electrochemical β-selective hydrocarboxylation of styrene using CO_2 and water. (A) Electrochemical carboxylation of styrene with CO_2; (B) The scope of substrates. Copyright 2020, Wiley-VCH[133].

CONCLUSION AND OUTLOOK

With the development and use of clean and cost-efficient electricity, electrochemical synthesis has been demonstrated as an eco-friendly and energy-renewable tool to achieve various innovative chemical transformations[137-140]. In this review, seven types of viable and economic electrochemical alkene hydrofunctionalization reactions are briefly discussed and summarized. These electrochemical platforms exhibit a particularly broad substrate scope and expansive FG compatibility and avoid the incorporation of stoichiometric redox reagents. To a certain degree, electrosynthesis is recognized as a powerful tool for organic chemistry, and massive functionally valuable chemical reactions with low-cost, high chemo-, regio-, and even stereoselectivities are constructed with high yields smoothly.

However, despite the many advantages of electrochemical reactions, some drawbacks and limitations exist[141]. For example, the involvement of toxic solvents, the necessity of electrolytes, the addition of additives, and the construction of electrochemical devices, to some extent, account for their unfriendliness to industrialization cost and sustainable development. Therefore, based on previous significant advances, further efforts are required to develop more powerful, effective, and harmless electrochemical strategies.

Several promising and potential issues are described in terms of the following: (1) compared to hydrogenation, the development of other hydrofunctionalization strategies from facile alkenes and alkynes has been relatively slower, and more broadly applicable hydrofunctionalization platforms could be explored; (2) enantioselective electrocatalysis for asymmetric synthesis is a new trend, and the development of efficient electrochemical reactions is necessary, which requires the design and preparation of efficient electrochemical chiral catalysts; (3) new electrode materials, reaction mediators, and supporting electrolytes are the key factors to be developed; (4) photoelectrocatalysis provides better group tolerance and

Scheme 22. Electrochemical hydrocarboxylation of styrene derivatives. (A) Selective β-hydrocarboxylation of substituted olefins. Copyright 2020, American Chemical Society[134]; (B) Selective hydrocarboxylation of α,β-unsaturated esters; (C) Application of the hydrocarboxylation process to the flow synthesis of anti-epilepsy and absence seizure drug ethosuximide precursor **244**. Copyright 2021, Wiley-VCH[136].

controllable redox activity, which will be another boon for the field of synthesis; (5) the design and manufacture of high-throughput electrochemical devices[142] [Scheme 23] will provide the possibility of gram-scale and even industrial preparation of electrochemical products. Beyond these challenges, we believe that various outstanding and innovative results will be achieved in the near future.
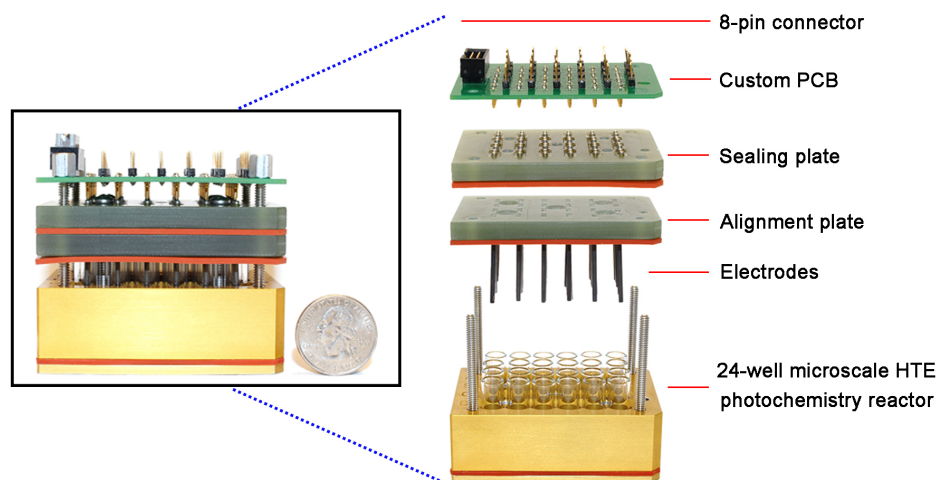
Scheme 23. Design strategy of high-throughput electrosynthesis reactor. Copyright 2021, American Chemical Society[142].

DECLARATIONS

Authors' contributions
Prepared the manuscript: Zhang Y, Zhao X
Performed manuscript correcting: Qing G

Availability of data and materials
Not applicable.

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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