

## REVIEW

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# Recent advances in electrochemical difunctionalization of alkenes and alkynes for the synthesis of organohalides

Yu Zheng, \* Wenguang Lu, Chunxi Chen, Yanju Lu and Shenlin Huang \*

Organohalides are particularly important and versatile, as they are found not only in bioactive natural products, pharmaceuticals, agrochemicals, and materials but also serve as fundamental reagents in synthetic chemistry. The rapid development of electrosynthesis as an environmentally friendly and efficient technology provides solutions for the synthesis of organohalides that avoid the use of chemical oxidants and minimize the formation of by-products. This review summarizes recent advances in the electrochemical difunctionalization of alkenes and alkynes for the synthesis of organohalides, as well as their underlying mechanisms. We anticipate that this work will stimulate new strategies for the synthesis of organohalides.

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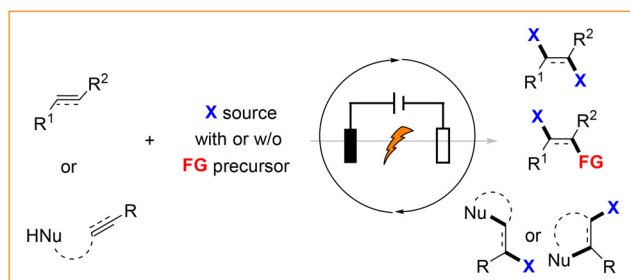
## 1. Introduction

Organohalides are important structural units in natural products, pharmaceuticals, agrochemicals, and materials.<sup>1</sup> They are also fundamental and widely used coupling reagents in synthetic chemistry.<sup>2</sup> As a consequence, great efforts have been devoted to incorporating the halide atom in organic molecules. Among the numerous established methods,<sup>3</sup> the difunctionalization of alkenes and alkynes represents an efficient and straightforward strategy for the synthesis of halide-containing compounds, partially because alkenes and alkynes are readily available substrates. Although the dihalogenation of alkenes is one of the earliest organic reactions,<sup>4</sup> wherein molecular chlorine or bromine is used as the halogenating reagent, which has several severe drawbacks, including the operation of toxic and corrosive reagent, poor chemoselectivity, harsh reaction conditions, and the formation of hazardous HCl or HBr as a by-product. In this context, alternatives including a new generation of halogenation reagents,<sup>5</sup> the combination of electrophilic halogenated reagent and halogen source<sup>6</sup> or halogen anion and external oxidant,<sup>7</sup> halogenation by metal catalysis<sup>8</sup> and photocatalysis<sup>9</sup> among others have been extensively developed to mitigate the toxic and corrosive issues. Furthermore, the halogenium ion intermediate in the electrophilic halogenation reaction would be readily trapped by other nucleo-

philes, resulting in the corresponding halofunctionalized products being endowed with halide and another functional group at the same time.<sup>10</sup> In addition, radical based-halofunctionalization of alkene/alkynes provides another strategy for synthesizing halogenated compounds.<sup>11</sup> However, these strategies present one or more disadvantages, which include: (1) the preparation of some reagents still involves the use of elemental halides or high acquisition costs; (2) the need for stoichiometric amounts of oxidants; (3) the need for expensive transition metals or photocatalysts; (4) the harsh reaction conditions. Therefore, synthetic organic chemists are constantly motivated to search for environmentally friendly and sustainable tactics in this field.

With the renaissance of electrosynthesis as an environmentally friendly and sustainable platform for organic synthesis,<sup>12</sup> it also offers an alternative out of the above-mentioned dilemma. This benefits from the direct use of traceless and green electrons as redox reagents, thereby circumventing the reliance on stoichiometric chemical redox reagents. Despite a few reviews have been comprehensively summarized on the electrochemical difunctionalization of alkenes and alkynes,<sup>13</sup> the relevant synthesis of organohalides was sporadically discussed. Recently, Deagostino and co-workers reviewed the progress in the synthesis of chlorinated compounds *via* electrocatalysis and photoredox catalysis.<sup>14</sup> In this review, we focally showcase the progress in the electrochemical difunctionalization of alkenes and alkynes for the synthesis of organohalides, as well as their proposed mechanisms (Scheme 1). In addition, possible directions for further development in this field are suggested with the hope of stimulating further new strategies for the synthesis of diverse organohalides.

Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, International Innovation Center for Forest Chemicals and Materials, College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China. E-mail: zhengy@njfu.edu.cn, shuang@njfu.edu.cn



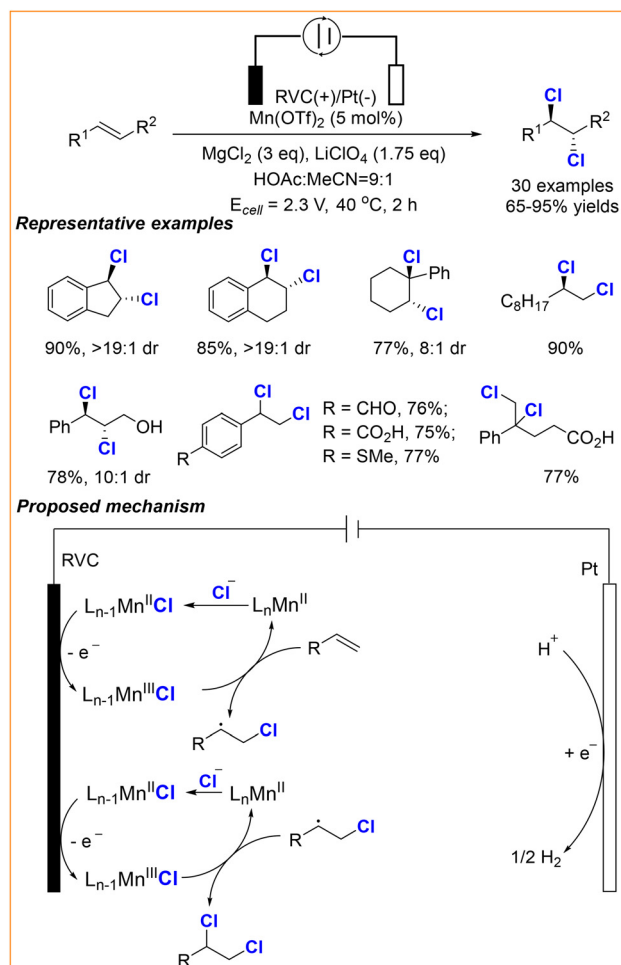
**Scheme 1** Electrochemical difunctionalization of alkenes and alkynes for the synthesis of organohalides.

## 2. Electrochemical dihalogenation of alkenes and alkynes

Dihalogenation of alkenes/alkynes provides an efficient and straightforward strategy to simultaneously incorporate two vicinal carbon-halogen bonds in one molecule. In recent years, some elegant sustainable electrocatalytic dihalogenation approaches using different halogen sources have been developed in this field. Accordingly, the following section discusses recent advances in the electrochemical dihalogenation of alkenes and alkynes.

In 2017, the Lin group reported the first Mn-catalyzed electrochemical dichlorination of alkenes (Scheme 2).<sup>15</sup> This operationally simple and efficient protocol utilizes electricity as an energy input and  $\text{MgCl}_2$  as a safe chlorine source, enabling various vicinal dichlorides in excellent yields with good to excellent diastereomeric ratios. Notably, a series of compounds bearing oxidatively fragile functionalities, including alcohol, aldehyde, sulfide, and carboxylic acid, remain unaffected under the optimized conditions, offering the possibility of further derivatization. Control experiments demonstrated that the mechanism *via* electrochemical generation of  $\text{Cl}_2$  followed by its electrophilic addition to the alkene could be excluded. Combined with the CV studies, the authors proposed the plausible mechanism for dichlorination as outlined at the bottom of Scheme 2. First, the Cl-bound  $\text{Mn}^{\text{II}}$  is formed through ligand exchange, followed by anodic oxidation that generates  $\text{Mn}^{\text{III}}\text{Cl}$  species. The  $\text{Mn}^{\text{III}}\text{Cl}$  species serves as a vital atom-transfer reagent and adds to the alkene to form a carbon-centered radical. After the Mn-assisted second round of radical group transfer, the final dichlorinated product is formed.

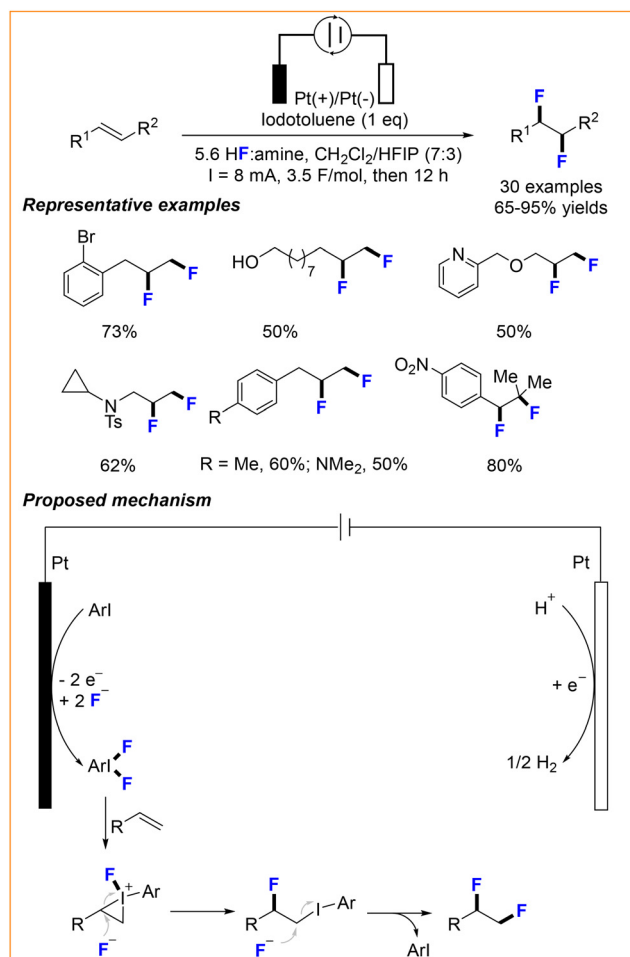
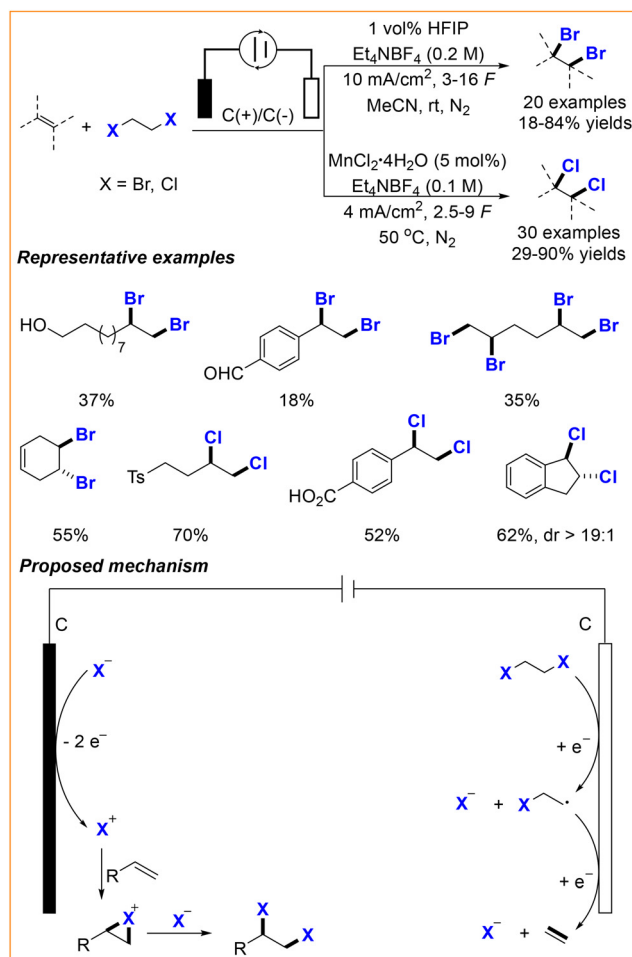
Fluorinating alkyl groups as a class of important structural motifs have received considerable attention since their functions in improving bioactivity and pharmacokinetics. Oxidative difluorination of alkenes provides an expedient strategy for incorporating fluorine atoms in molecules to access vicinal difluorides. However, the traditional strategies suffer from toxicity, high cost, stoichiometric oxidants, and limited substrate scope with restricted to electron-poor ones.<sup>16</sup> To tackle these shortcomings, the Lennox group developed an electrochemical method for the generation of *p*-tolyl difluoro  $\lambda^3$ -iodane (Scheme 3),<sup>17</sup> which was previously reported as an oxidant for



**Scheme 2** Electrochemical vicinal dichlorination of alkenes.<sup>15</sup>

the difluorination of alkenes.<sup>16e,f</sup> Under their “undivided cell” optimized conditions, a range of alkenes harboring electron-poor moiety could be difluorinated in good to excellent yields. However, the electron-rich substrates failed since they are more easily oxidized before iodotoluene, thereby hampering the key formation of *p*-tolyl difluoro  $\lambda^3$ -iodane. By redeveloping the reaction carried out in a divided cell, a wide range of electron-rich substrates was tolerated and afforded the desired products in moderate to very good yields. Mechanistically, the key to success is the *in situ* electrochemical generation of the hypervalent iodine, which serves as an oxidant and enables the subsequent difluorination of alkenes (Scheme 3). Meanwhile, the generation of  $\text{H}_2$  as the sole byproduct at the cathode makes this method attractive and eco-friendly.

In contrast to the above-mentioned oxidative dichlorination and difluorination of alkenes, in which the generation of  $\text{H}_2$  is a sacrificial half-reaction, Waldvogel and Morandi reported a consecutive paired electrolysis merged with a halogen shuttle reaction for the vicinal dibromination and dichlorination of alkenes (Scheme 4).<sup>18</sup> This strategy employs 1,2-dihaloethane such as 1,2-dibromoethane or 1,1,1,2-tetrachloroethane, as a simple, easily available, and noncorrosive halide source

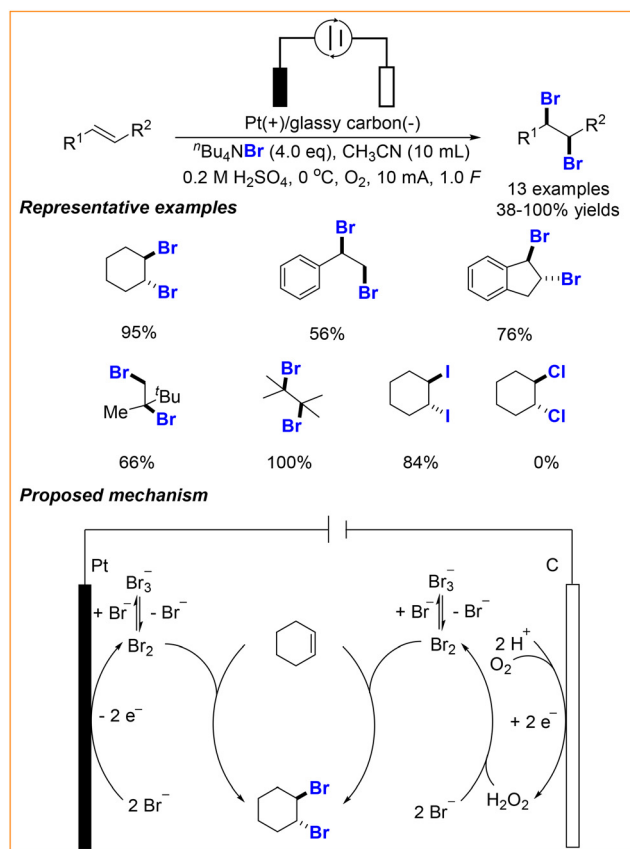
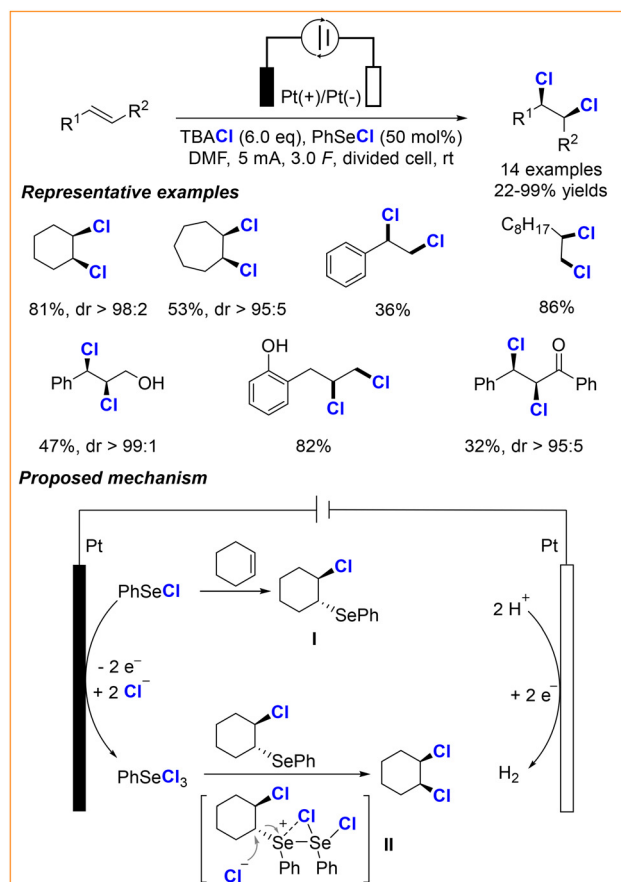
Scheme 3 Electrochemical vicinal difluorination of alkenes.<sup>17</sup>Scheme 4 Electrochemical vicinal dibromination and dichlorination of alkenes.<sup>18</sup>

thereby eluding the use of volatile and corrosive  $\text{Br}_2$  and  $\text{Cl}_2$ . It is worth mentioning that the addition of small amounts of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) facilitates the reduction of the halide donor and suppresses the undesirable side reaction, and the supporting electrolyte can be recycled by simple crystallization. Under their optimal conditions, various dibrominated and dichlorinated products were obtained in moderate to good yields. This scalable reaction, equipped with two inexpensive graphite electrodes, tolerates a range of functional groups including amide, free alcohol, aldehyde, ester, and imide. Remarkably, the previously worldwide used insecticide, lindane as a persistent pollutant could be fully dechlorinated by interconversion with simple alkenes. The authors designed this reaction with the following possible mechanism. Initially, the single-electron reduction of the dihalide at the cathode produces the  $\text{X}^-$  and releases the alkene with simultaneous reduction of the carbon-centered radical and subsequent loss of  $\text{X}^-$ . Subsequently, oxidation of  $\text{X}^-$  at the anode generates  $\text{X}^+$ , which then undergoes electrophilic addition to the alkene to form the desired vicinal products.

Apart from the consecutive paired electrolysis, Hilt and co-workers developed a linear paired electrolysis for the dibromi-

nation of alkenes during the same period (Scheme 5).<sup>19</sup> The protocol shows a good substrate scope and affords the desired dibromination products in good to excellent yields with perfect current efficiency (up to 200%). Moreover, the functional group compatibility test indicates that several sensitive groups such as alkyne, ester, halides, and ethers are tolerated under the electrochemical conditions. Furthermore, the diiodination of cyclohexene is compatible with the linear paired electrolysis. However, the analogous dichlorination of cyclohexene failed due to the higher oxidation potential of the chloride anion. The plausible mechanism for the dibromination of alkenes outlined in Scheme 5 was proposed by the authors. At the cathode, the reduction of oxygen in the presence of a proton generates hydrogen peroxide, which then oxidizes the  $\text{Br}^-$  to bromine. Bromination of the alkene then yields the final dibrominated product. Meanwhile, the  $\text{Br}^-$  is oxidized at the anode to also afford bromine, making this reaction perform with perfect current efficiency.

As one of the earliest organic reactions reported in 1877, dichlorination of alkenes typically delivers *trans*-dichlorinated products. Until 2015, the Denmark group disclosed the first

Scheme 5 Electrochemical vicinal dibromination of alkenes.<sup>19</sup>Scheme 6 Electrochemical vicinal *cis*-dichlorination of alkenes.<sup>21</sup>

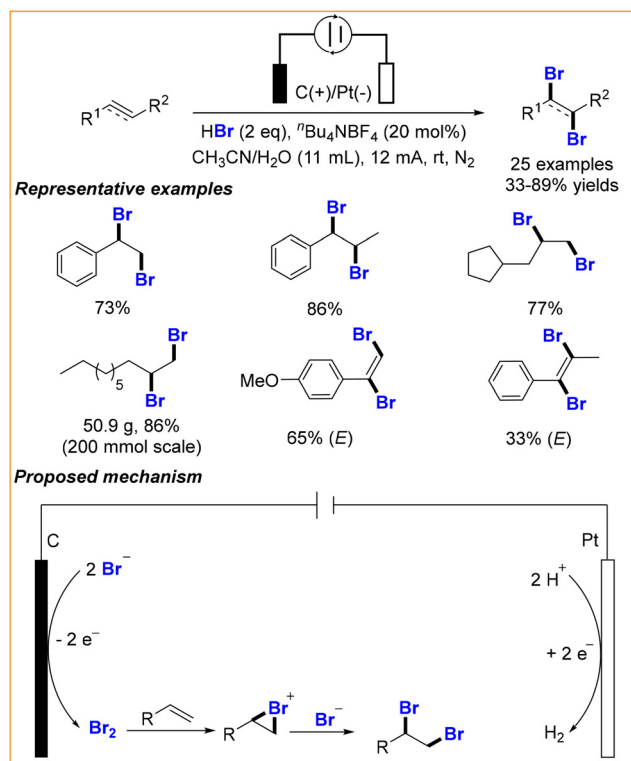
elegant example of *cis*-dichlorination of alkenes, in which diselenide was employed as a precatalyst, benzyltriethylammonium chloride ( $\text{BnEt}_3\text{NCl}$ ) as a chlorine source, and the *N*-fluoropyridinium salt as an oxidant.<sup>20</sup> Inspired by this work and to obviate the use of stoichiometric amounts of oxidant, the Hilt group described an electrochemical version for the *cis*-dichlorination of alkenes (Scheme 6).<sup>21</sup> This strategy is carried out with 50 mol% phenylselenenyl chloride ( $\text{PhSeCl}$ ) as a substoichiometric mediator and  $\text{TBACl}$  as the electrolyte and partially source of chloride in DMF. Under their optimized conditions, a variety of cyclic and acyclic produced *cis*-dichlorides with high diastereoselectivities. Typically, aliphatic alkene substrates worked well, while styrene derivatives afforded only moderate yields. In combination with control experiments and cyclic voltammetric (CV) studies, the authors proposed a possible mechanism for this *cis*-dichlorination of alkenes. First, phenylselenenyl chloride serves two roles. On the one hand, it reacts with alkene to generate the phenylselenenyl chloride-alkene adduct **I**. On the other hand, it is oxidized at the anode and combines with the  $\text{Cl}^-$  to give  $\text{PhSeCl}_3$ , which then reacts with phenylselenenyl chloride-alkene adduct **I** to produce intermediate **II**. Finally, nucleophilic substitution by the  $\text{Cl}^-$  leads to the *cis*-dichlorinated product.

In 2019, the Lei group used  $\text{HBr}$  as a bromide source to realize the dibromination of alkenes and alkynes under

electrochemical oxidation conditions (Scheme 7).<sup>22</sup> The reaction tolerated a wide variety of aromatic alkenes and aliphatic alkenes and provided the dibrominated products in moderate to high yields. Moreover, this method was not limited to terminal alkenes, internal alkenes were also compatible and produced exclusive *trans*-dibromides. Notably, the reaction was easily scaled up to 200 mmol and afforded the pure product in 86% yield (50.9 g), which is inaccessible using the orthodox method. It is worth noting that this protocol can be applied to the dibromination of alkynes and furnished *E*-isomers as sole isomerism. Control experiments of the reaction of alkene with molecular  $\text{Br}_2$  also afforded the same dibromination product, indicating that the  $\text{Br}_2$  intermediate is involved.

### 3. Electrochemical intermolecular halofunctionalization of alkenes and alkynes

The heterodifunctionalization of alkenes and alkynes, leading to the concurrent formation of compounds with two useful functionalities, is a step-economy and sustainable strategy.<sup>23</sup> Among them, halofunctionalization of alkenes and alkynes for the synthesis of compounds with halide and another func-

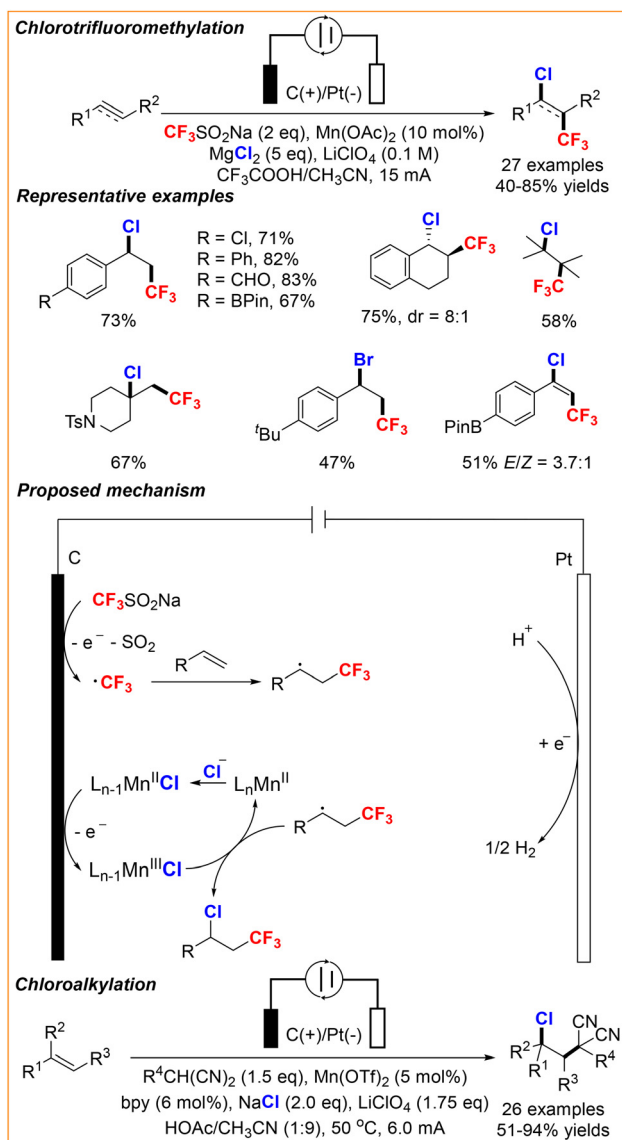


**Scheme 7** Electrochemical vicinal dibromination of alkenes and alkynes.<sup>22</sup>

tional group in a vicinal position is synthetically attractive since the C–X bond could easily participate in the array of transformations. This section focuses on summarizing the electrochemical halofunctionalization of alkenes and alkynes.

### 3.1 The simultaneous formation of C–X and C–C bonds

After accomplishing the Mn-catalyzed electrochemical dichlorination of alkenes,<sup>15</sup> the Lin group achieved an anodically coupled electrolysis for the chlorotrifluoromethylation of alkenes (Scheme 8).<sup>24</sup> The success of this proof-of-principle reaction is due to the redox potentials of  $\text{CF}_3\text{SO}_2\cdot/\text{CF}_3\text{SO}_2^-$  ( $E_{\text{p}/2} = 800$  mV) and  $[\text{Mn}^{\text{II}}-\text{Cl}]/[\text{Mn}^{\text{III}}-\text{Cl}]$  ( $E = 780$  mV) are matched well, thereby fulfilling these two open-shell species generated simultaneously at the anode under mild conditions. Compared to the previously described photochemical method,<sup>25</sup> this protocol showcases a wide substrate scope. For example, styrene derivatives bearing oxidatively sensitive functional groups and tetrasubstituted alkenes could be well tolerated. However, electron-rich styrenes failed due to the competing arene trifluoromethylation. By simply using KBr instead of  $\text{MgCl}_2$  as a bromide source, the reaction could be applied for bromotrifluoromethylation. Moreover, alkynes could also be chlorotrifluoromethylated using this electrocatalytic method. After a year, the same group accomplished the chloroalkylation of alkenes using malononitriles or cyanoacetates and NaCl as a chloride donor *via* the similar Mn-catalyzed anodically coupled electrolysis.<sup>26</sup>

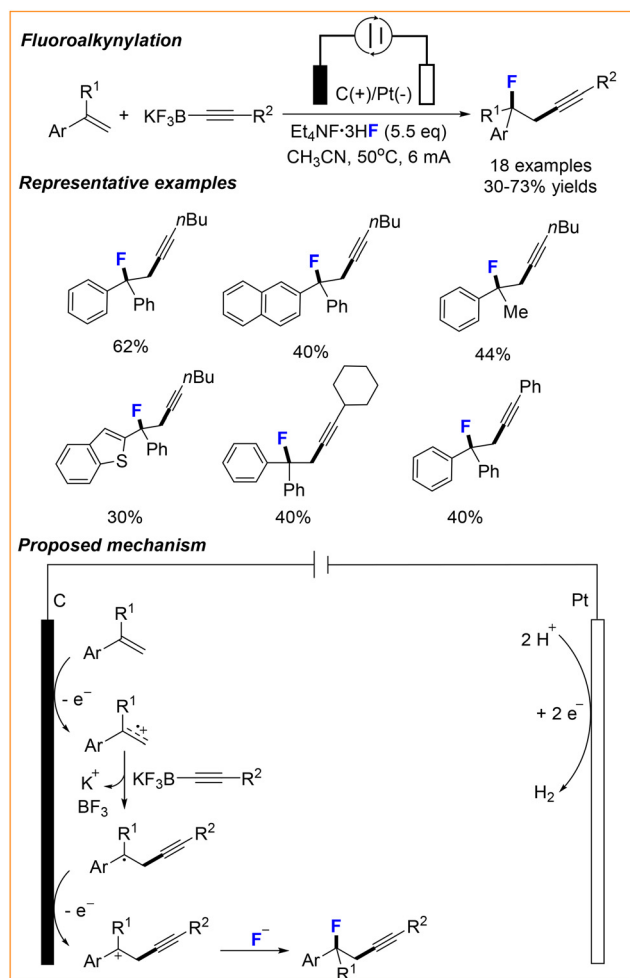


**Scheme 8** Electrochemical chlorotrifluoromethylation/chloroalkylation of alkenes and alkynes.<sup>24,26</sup>

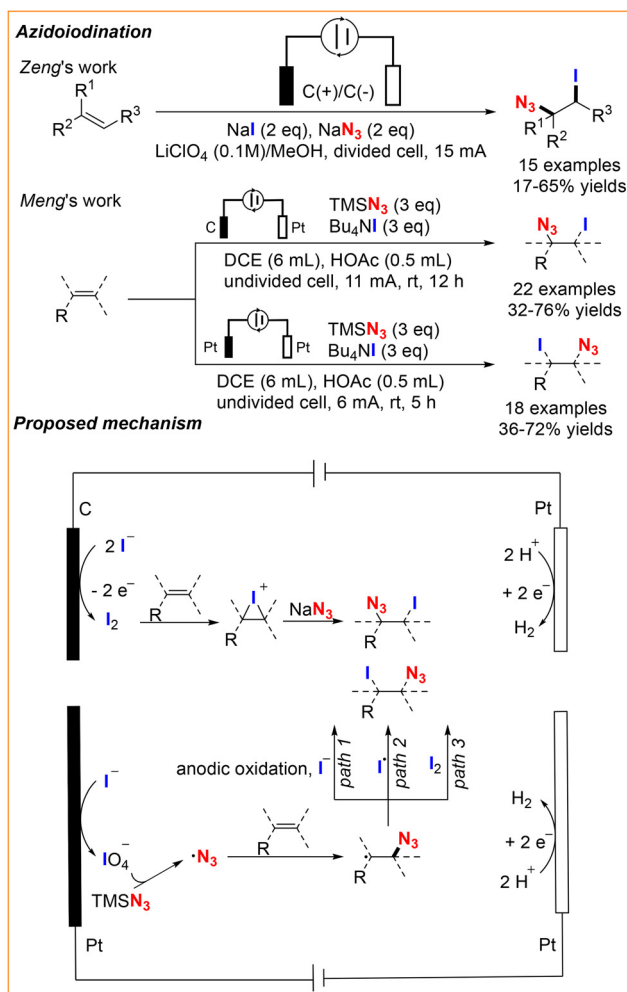
In the same year, the Xu group disclosed an electrochemical method for the fluoroalkynylation of alkenes using  $\text{Et}_4\text{NF}\cdot 3\text{HF}$  as a fluoride source and alkynyltrifluoroborate salts as the alkynylation source (Scheme 9).<sup>27</sup> The alkene is firstly oxidized to the corresponding radical cation, which is then trapped by the alkynyltrifluoroborate to generate a carbon-centered radical intermediate. This intermediate further undergoes single-electron oxidation to give rise to the cation species, which is attacked by nucleophile  $\text{F}^-$  to afford the final difunctionalized product.

### 3.2 The simultaneous formation of C–X and C–N<sub>3</sub> bonds

The electrochemical azidoiodination of alkenes was first reported by the Zeng group in 2016 (Scheme 10).<sup>28</sup> In this method,  $\text{IN}_3$ , an explosive reagent that is conventionally used

Scheme 9 Electrochemical fluoroalkynylation of alkenes.<sup>27</sup>

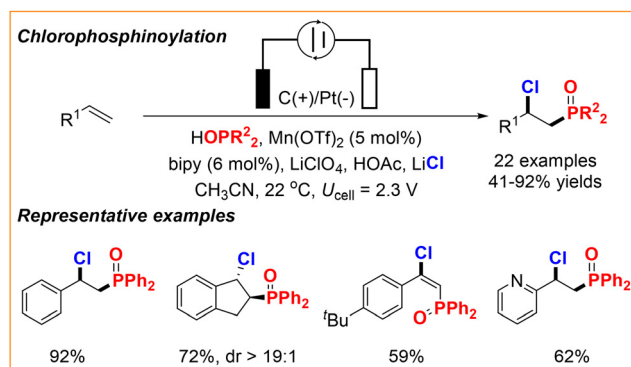
to react with alkenes to access vicinal iodoazides, could be generated by indirect electrolysis using NaI as an iodide source followed by reacting with NaN<sub>3</sub>. Driven by constant current electrolysis, the Markovnikov addition products were exclusively obtained. In the proposed mechanism, the *in situ* generated IN<sub>3</sub> predominantly acts as an I<sup>+</sup> source for the reaction with alkene to form an iodonium intermediate, which was trapped by azide to complete the reaction. Very recently, Ren, Meng, and co-workers reported an interesting electrode-switchable regiodivergent azidoiodination of alkenes (Scheme 10).<sup>29</sup> When the reaction was conducted in an undivided cell with a graphite plate as the anode and a Pt plate as the cathode, Markovnikov α-azidoiodination products were obtained. Interestingly, when a Pt plate was used as the anode, the reaction afforded anti-Markovnikov β-azidoiodination products under otherwise identical conditions. Density functional theory (DFT) calculations revealed that the adsorption energy of I<sup>-</sup> on graphite and Pt plates is about -0.56 and -2.81 eV, respectively. Control experiments and cyclic voltammogram (CV) studies showed that I<sup>-</sup> underwent successive anodic oxidation processes to produce I<sub>2</sub> at the graphite plate anode. In

Scheme 10 Electrochemical azidoiodination of alkenes.<sup>28,29</sup>

contrast, intermediate IO<sub>4</sub><sup>-</sup> was generated at the Pt plate surface. Based on these findings, the authors proposed the following mechanism for this regiodivergent azidoiodination of alkenes (Scheme 10). When a graphite plate was used as the anode, the reaction proceeded *via* an iodonium ion mechanism to deliver Markovnikov addition products. When the Pt anode was employed, I<sup>-</sup> was oxidized to produce hypervalent IO<sub>4</sub><sup>-</sup> due to the higher adsorption energy of I<sup>-</sup> on the Pt surface. IO<sub>4</sub><sup>-</sup> was able to oxidize TMSN<sub>3</sub> to produce an azide radical, which underwent addition to the alkene, providing the corresponding α-carbon-centered radical. The resulting radical may undergo three processes. It could be further oxidized to the carbocation intermediate, which was attacked by N<sub>3</sub><sup>-</sup> to yield an anti-Markovnikov product. Alternatively, it could also react with I<sup>-</sup> or I<sub>2</sub> to deliver the final product, and the latter is more favorable.

### 3.3 The simultaneous formation of C-X and C-P bonds

To further expand their strategy of Mn-catalyzed anodically coupled electrolysis, Lin and co-workers successfully developed the chlorophosphinoylation of alkenes in 2019 (Scheme 11).<sup>30</sup>

Scheme 11 Electrochemical chlorophosphinoylation of alkenes.<sup>30</sup>

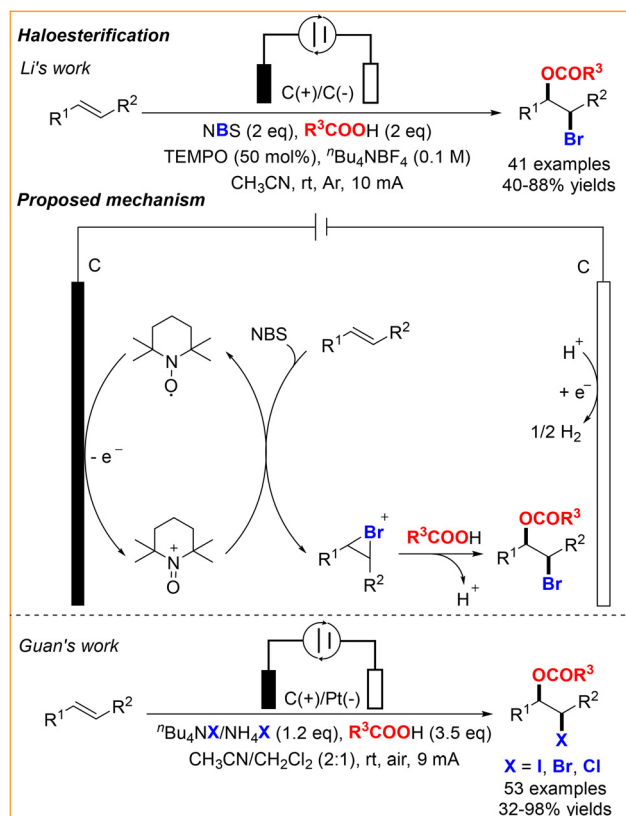
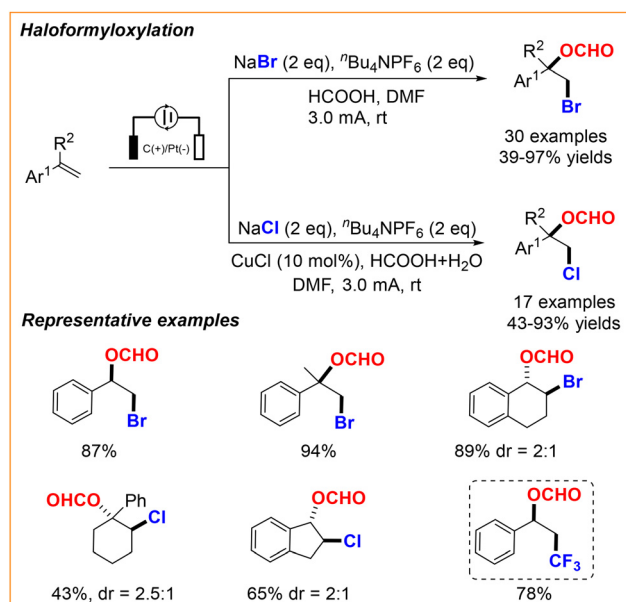
This electrocatalytic chlorophosphinoylation reaction tolerates a wide range of alkene derivatives with high efficiency and regioselectivity. In addition, alkynes were also compatible with this reaction and afforded the corresponding *E*-isomer as a single product. However, the attempt for bromophosphinoylation failed since only the dibromination product was detected.

### 3.4 The simultaneous formation of C–X and C–O bonds

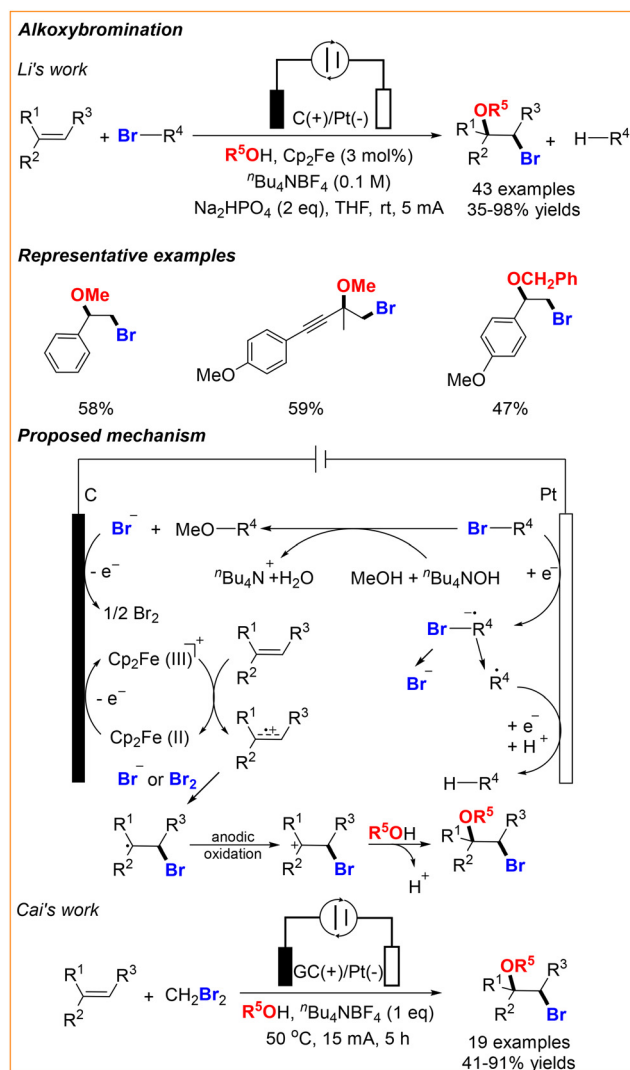
In 2019, the Li group reported a three-component electrochemical oxidative bromoesterification of alkenes,<sup>31</sup> in which *N*-bromosuccinimide (NBS) as the Br source, TEMPO as the promoter with a constant current of 10 mA (Scheme 12, top). During the reaction, TEMPO<sup>+</sup> could be generated by a single oxidation of TEMPO at the anode. Subsequent addition of NBS to the alkene yielded the bromonium ion intermediate with the assistance of TEMPO<sup>+</sup>. The bromoesterification product was ultimately formed through nucleophilic addition and deprotonation. Four years later, He and Guan used tetrabutylammonium iodide as both an electrolyte and an iodine source to realize iodoesterification under chemical oxidant-free conditions (Scheme 12, below).<sup>32</sup> Furthermore, this method is also applicable to the chloroesterification and bromoesterification of alkenes using the appropriate halide source instead.

In 2019, Hu, Fang, and co-workers developed an electrochemical oxidative method for the haloformyloxylation of alkenes using readily available NaCl or NaBr as the halide source and DMF as the formyloxylation reagent (Scheme 13).<sup>33</sup> During the reaction, Cl<sup>−</sup> or Br<sup>−</sup> underwent a single-electron oxidation and formed the Cl<sup>•</sup> or Br<sup>•</sup>. Then the resultant radical was added to the alkene and generated the corresponding benzyl radical, which was further oxidized to the benzyl carbocation. After nucleophilic attack and hydrolysis *via* an imine intermediate, the corresponding product was formed along with a hydrogen ion. In addition, the synthetic method could be used to synthesize trifluoromethylation-formyloxylation products by employing Langlois reagent (CF<sub>3</sub>SO<sub>2</sub>Na) as a trifluoromethyl radical source.

The halide sources could also be acquired from organohalides. In 2020, the Li group reported a convergent electrochemical method for the alkoxybromination of alkenes

Scheme 12 Electrochemical haloesterification of alkenes and alkynes.<sup>31,32</sup>Scheme 13 Electrochemical haloformyloxylation of alkenes.<sup>33</sup>

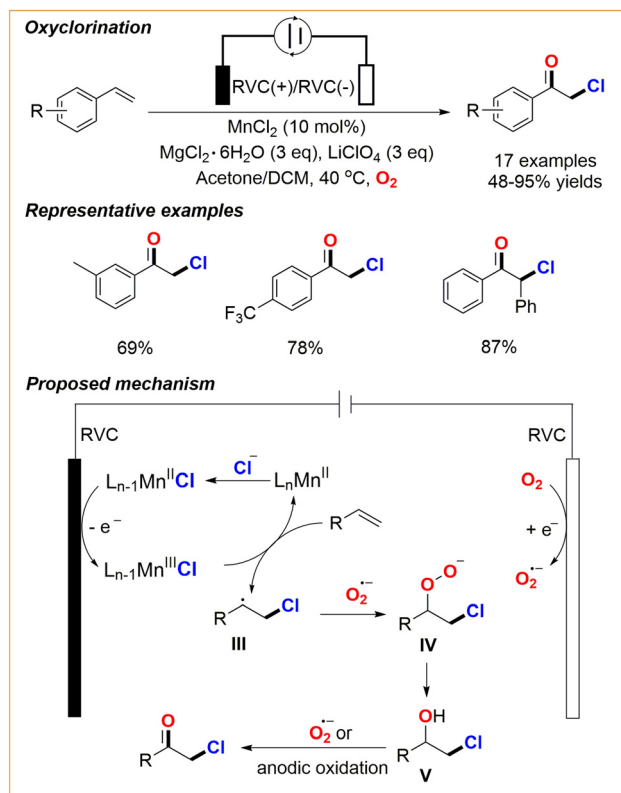
(Scheme 14).<sup>34</sup> Alkyl halides or aryl bromides could offer the halide anion either in the presence of MeOH and tetrabutylammonium hydroxide or through reduction at the cathode. Meanwhile, the alkene was



**Scheme 14** Electrochemical alkoxybromination of alkenes.<sup>34,35</sup>

oxidized to the radical cation with the assistance of  $\text{Cp}_2\text{Fe}$ . The combination of halide anion and radical cation delivered the alkyl radical, which was subsequently oxidized to the alkyl cation. Subsequent nucleophilic addition by alcohol generated the product. Besides, the halide anion could also be oxidized and provided the product *via* a halonium ion mechanism. A couple of years later, the Cai group also achieved the alkoxybromination of alkenes by employing dibromomethane ( $\text{CH}_2\text{Br}_2$ ) as a bromide source under electrochemical oxidation conditions.<sup>35</sup> Initially, single-electron oxidation of  $\text{CH}_2\text{Br}_2$  at the anode generates bromine radical, which would undergo addition to an alkene, resulting in a carbon-centered radical. This radical would further undergo another SET and afford the corresponding carbocation intermediate. The addition of alcohol as a nucleophilic reagent and subsequent deprotonation leads to the formation of the product.

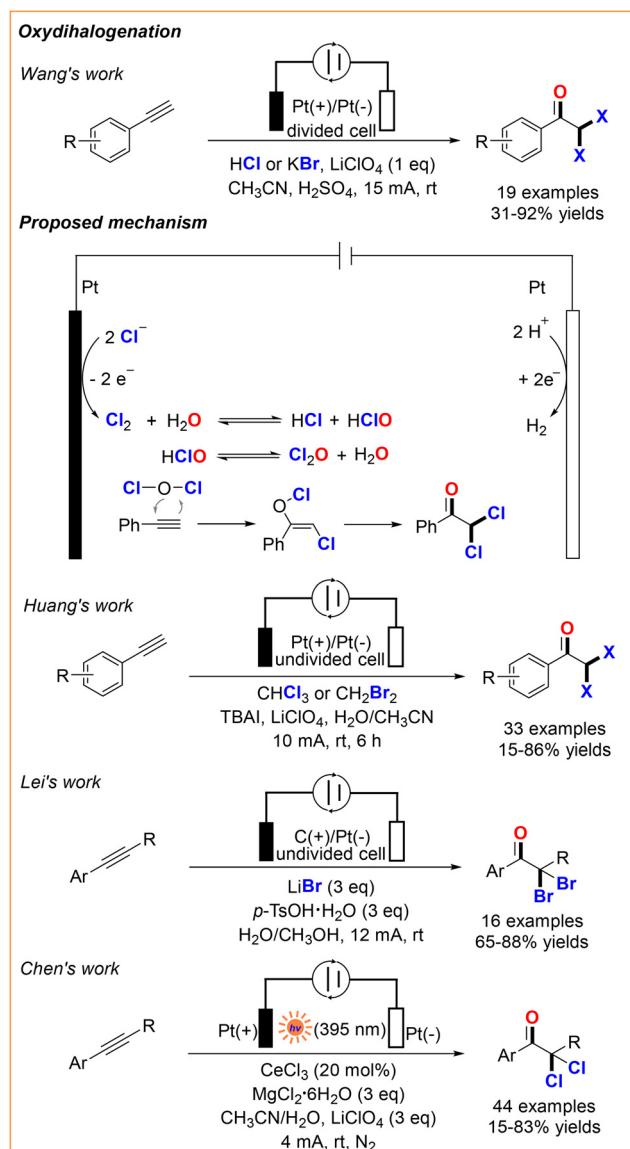
Inspired by previous Mn-catalyzed paired electro-synthesis,<sup>15,24</sup> the Chen group reported a system for oxychlorination of styrenes (Scheme 15).<sup>36</sup> Anodic oxidation of



**Scheme 15** Electrochemical oxychlorination of alkenes.<sup>36</sup>

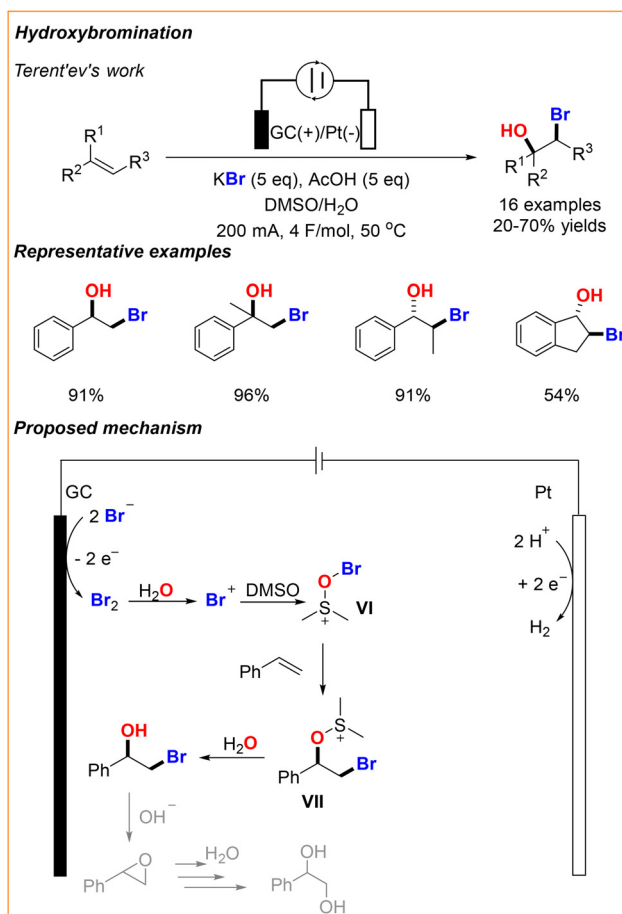
$\text{L}_{n-1}\text{Mn}^{\text{II}}\text{Cl}_2$  to  $\text{L}_{n-1}\text{Mn}^{\text{III}}\text{Cl}_2$  which could transfer chlorine radical to the alkene, affording the transient alkyl radical **III**. Single-electron reduction of oxygen produces the persistent superoxide ion  $\text{O}_2^{\cdot-}$ . The combination of these two species results in intermediate **IV**, which then decomposes to form compound **V**. Further oxidation by superoxide or electricity affords the chloroacetophenone product.

The electrochemical oxydihalogenation of alkynes was soon reported by several groups (Scheme 16).<sup>37-40</sup> In 2020, Wang, Zha, and co-workers disclosed the electrochemistry for the oxyhalogenation of alkynes using HCl or KBr as a halide source in a divided cell.<sup>37</sup> The authors proposed that anodic oxidation of  $\text{Cl}^-$  generates  $\text{Cl}_2$ , which reacts with  $\text{H}_2\text{O}$  to afford HClO. HClO then transforms into  $\text{Cl}_2\text{O}$  which would add across the alkyne to finally provide the product. During the same period, the Huang group reported another electrochemical method to access the same  $\alpha,\alpha$ -dihaloketones using readily available organohalides such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{ClCH}_2\text{CH}_2\text{Cl}$ , and  $\text{CH}_2\text{Br}_2$  as halogen sources in an undivided cell.<sup>38</sup> Subsequently, the Lei group developed the electrochemical oxydibromination of arylalkynes using LiBr as both the halogen source and supporting electrolyte.<sup>39</sup> Recently, the Chen group developed an efficient photoelectrochemical cerium-catalyzed method to synthesize  $\alpha,\alpha$ -dichloroketones *via* electricity enabling the ligand to metal charge transfer (LMCT) of  $\text{Ce}(\text{IV})$  to provide the key  $\text{Cl}^\cdot$  intermediate.<sup>40</sup>



**Scheme 16** Electrochemical oxydihalogenation of alkynes.<sup>37–40</sup>

The electrochemical hydroxybromination of alkenes was achieved by Terent'ev group in 2021 (Scheme 17).<sup>41</sup> The choice of DMSO as a solvent to stabilize the anodically generated bromide cation to generate **VI** is crucial for the success of this method. This species then reacts with the alkene to produce the sulfonimsalt **VII**, which is attacked by water to furnish the desired product. The reaction proceeds *via* a cyclic bromonium cation mechanism, which is also a possible pathway, and the radical pathway cannot be ruled out completely. However, the observation that bromine drips from the electrodes during the reaction suggests that the radical route seems unlikely. The addition of AcOH as an additive is also very important as it could lower the concentration of hydroxide ions, thereby diminishing the by-production of epoxide and diol. Besides, by replacing the solvent with the mixture of CH<sub>3</sub>CN/ROH, the reaction could also provide the corresponding alkoxybromina-

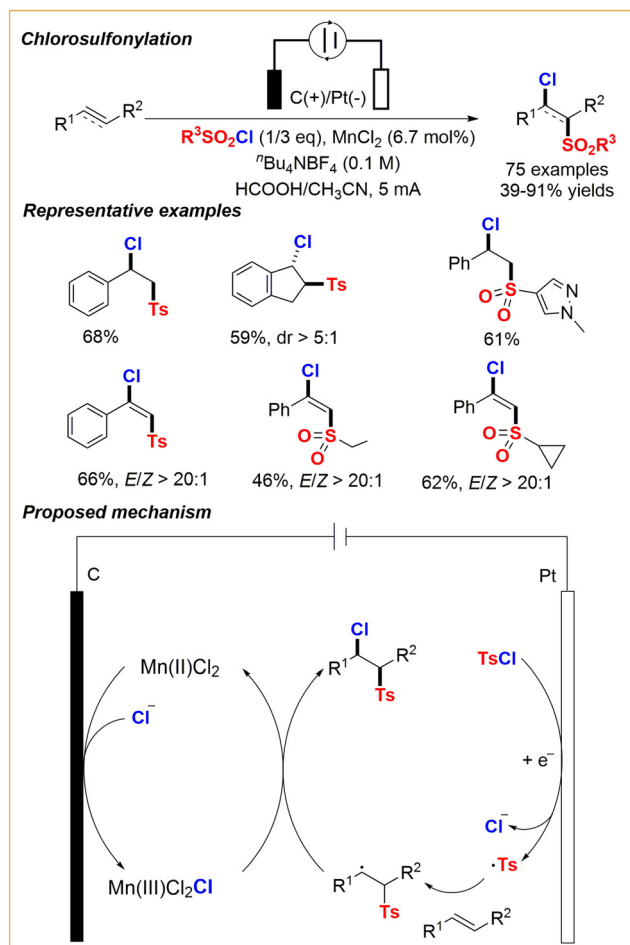


**Scheme 17** Electrochemical hydroxybromination of alkenes.<sup>41</sup>

tion product. The generation of bromide from HBr in an electrochemical flow reactor was demonstrated by Wirth in the same year.<sup>42</sup> This methodology converts various alkenes into their corresponding dibromination and hydroxybromination products. In addition, the use of alcohols as nucleophiles and internal nucleophiles would also provide the desired alkoxybromination and cyclization products.

### 3.5 The simultaneous formation of C–X and C–S/Se bonds

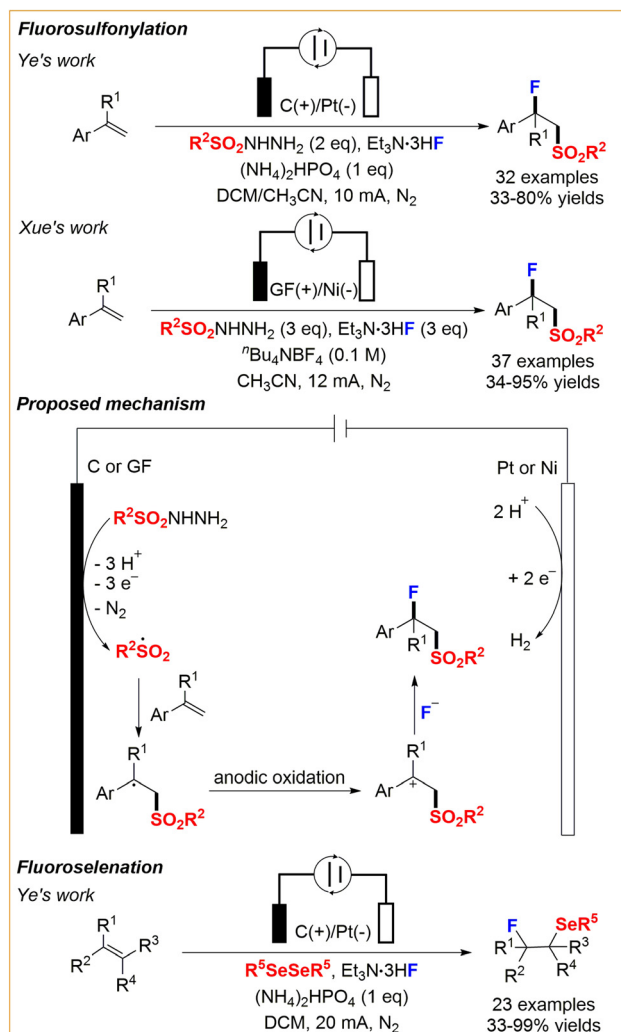
The construction of the C–S bond is of great interest in organic synthesis because the resulting organosulfur compounds occur in many natural products and pharmaceuticals as well as versatile building blocks.<sup>43</sup> Mechanistically different from Mn-catalyzed anodically coupled electrolysis for three-component difunctionalization of alkenes,<sup>15,24,26,32</sup> the Lei group reported a Mn-catalyzed two-component chlorosulfonylation of alkenes/alkynes *via* convergent paired electrolysis (Scheme 18).<sup>44</sup> As described, sulfonyl chloride, as a bifunctional reagent, is reduced to a sulfonyl radical and a chloride ion. Subsequently, the radical reacts with the alkene to furnish the alkyl radical intermediate. The resulting chloride anion is oxidized to the chlorine radical at the anode and subsequently combines with Mn(III)Cl<sub>2</sub> to form Mn(III)Cl<sub>3</sub>, which acts as the

Scheme 18 Electrochemical chlorosulfonylation of alkenes/alkynes.<sup>44</sup>

atom-transfer reagent to pass the chlorine atom to the alkyl radical intermediate, and finally delivers the target product.

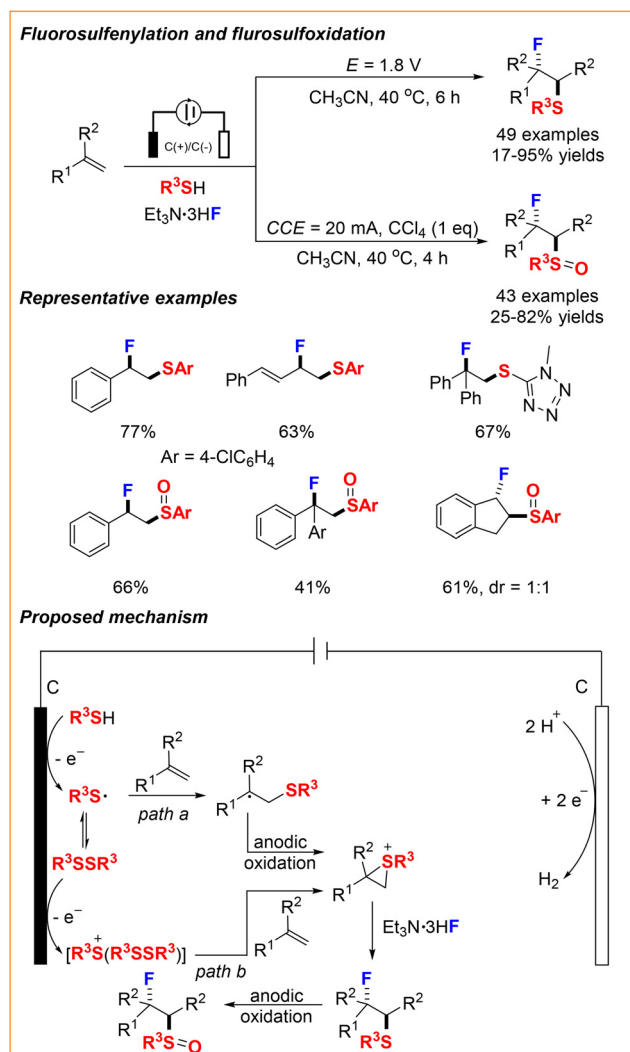
Shortly thereafter, the groups of Ye<sup>45</sup> and Xue<sup>46</sup> independently developed an anodically oxidative electrolysis for fluorosulfonylation, starting from alkenes, sulfonylhydrazides, and triethylamine trihydrofluoride as the fluorination reagent (Scheme 19). They proposed the mechanism as follows: the anodically generated sulfonyl radical adds to the alkene to form a benzyl radical, which subsequently undergoes anodic oxidation to give the carbocation intermediate. Subsequent nucleophilic fluorination with NEt<sub>3</sub>·HF affords the final product. Given the important applications of fluorine- and sulfone-containing molecules and their continued interest in electrochemistry, the Ye group reported a similar fluoroselenation reaction of olefins to access diverse β-fluoroselenides.<sup>47</sup>

One of the advantages of electrochemistry in organic chemistry is its promising capability to control reactivity by properly adjusting the applied potential. A good example of this was reported by Ye's group, in which the controllable fluorosulfonylation and fluorosulfoxidation of alkenes was realized by applying an appropriate potential (Scheme 20).<sup>48</sup> CV studies and sampling experiments support that a judicious choice of

Scheme 19 Electrochemical fluorosulfonylation and fluoroselenation of alkenes.<sup>45,46,47</sup>

the applied potential is pivotal to controlling selectivity. By combining these results with other mechanistic experiments, the authors proposed the mechanism shown in Scheme 20. The thiyl radical would be obtained by a single-electron oxidation of thiophenol. Then the radical-radical combination affords disulfide, which could undergo either secondary oxidation or cathode reduction to release the thiyl radical. This radical then adds to the alkene, followed by anodic oxidation, delivering an episulfonium ion. Subsequent nucleophilic fluorination by NEt<sub>3</sub>·HF gives the desired fluorosulfonylation product. Alternatively, the disulfide loses an electron at the anode to generate a bis(arylthio)sulfonium ion which then reacts with the alkene and could also afford the episulfonium ion. When a higher cell potential was applied, fluorosulfides would be smoothly oxidized to fluorosulfoxides in the presence of CCl<sub>4</sub>.

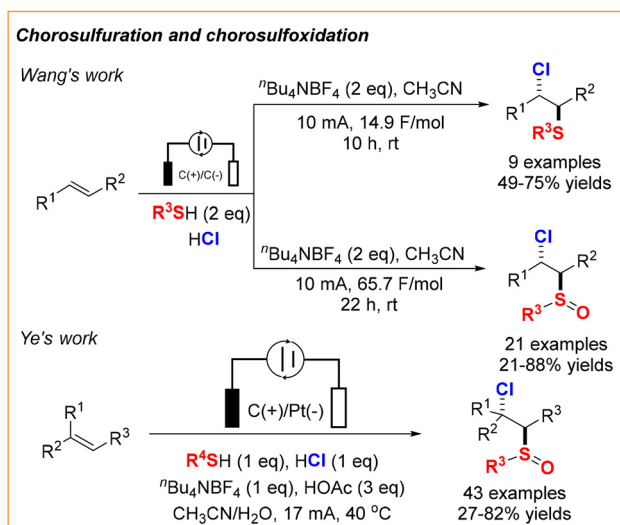
The analogous chlorosulfonylation and chlorosulfoxidation of alkenes using thiols and hydrochloride as a chloride source was soon reported by the Wang group (Scheme 21, top).<sup>49</sup> The



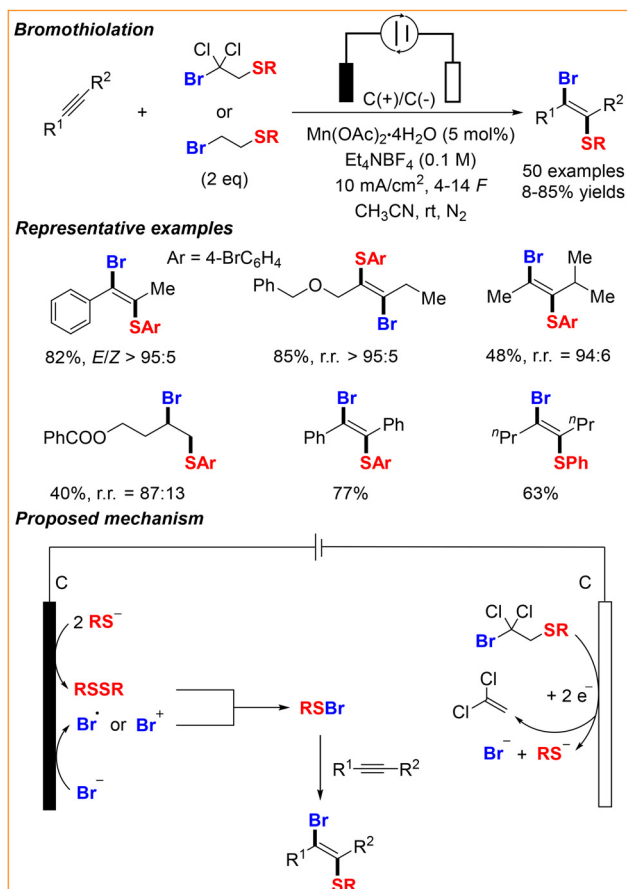
**Scheme 20** Electrochemical fluorosulfonylation and fluoro-sulfoxidation of alkenes.<sup>48</sup>

reaction generally produced the chorosulfenylated product within 10 hours under the optimized conditions. By simply prolonging the reaction time to 22 hours, the desired sulfoxide products were obtained. During the same period, Ye *et al.* extended their previous work and reported the same reaction with the same starting materials and similar reaction conditions (Scheme 21, below).<sup>50</sup> Importantly, diverse post-derivatizations of chlorosulfoxides by taking advantage of chlorine substituent as a practical handle highlight the synthetic potential.

Very recently, Waldvogel and Morandi documented another electrochemically enabled shuttle reaction for the bromothiolation of alkynes *via* a consecutive paired mechanism (Scheme 22).<sup>51</sup> This protocol employed  $\beta$ -bromosulfides as a bifunctional reagent, enabling the construction of diverse bromothiolated products in high chemo-, regio-, and stereo-selectivity. Furthermore, terminal alkenes were also applicable to this method and the anticipated chlorothiolated products could also be obtained using the corresponding  $\beta$ -chlorosulfide



**Scheme 21** Electrochemical chorosulfuration and chorosulfoxidation of alkenes.<sup>49,50</sup>



**Scheme 22** Electrochemical bromothiolation of alkynes.<sup>51</sup>

in place of  $\beta$ -bromosulfide. The diverse transformations of sulfide and bromide moieties in the product highlight its versatile synthetic values. CV analysis reveals that the aryl thiolate

anion (*ca.*  $-0.2$  V) is preferentially oxidized over the bromide anion (*ca.*  $0.6$  V), which is crucial for controlling the chemoselectivity. Therefore, the reduction of  $\beta$ -bromosulfides generates the aryl thiolate anion and the bromide anion along with 1,1-dichloroethene as a byproduct. The thiolate anion is then oxidized prior to the bromide anion and transformed to disulfide. Subsequently, the bromide anion is oxidized to the bromide radical or cation, which would react with disulfide to generate the reactive RSB $\cdot$ . The subsequent addition of alkyne provides the final products.

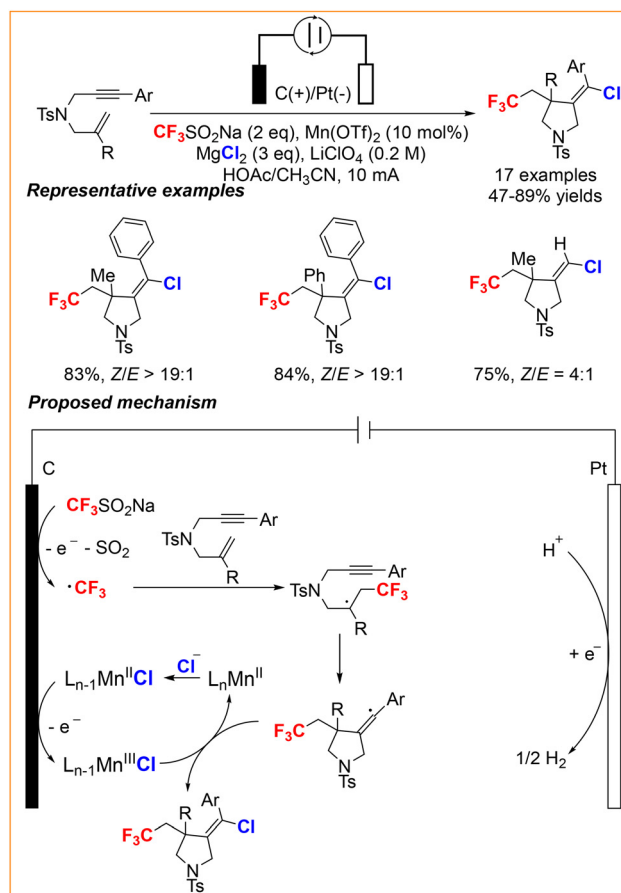
## 4. Electrochemical intramolecular halocyclization

Electrochemically promoted difunctionalization of the unsaturated C–C bond *via* cascade intramolecular cyclization provides an efficient strategy for constructing functionalized cyclic and heterocyclic compounds. In this section, we summarize representative examples of the synthesis of halogenated cycles by intramolecular cyclization of enynes, alkenes, and alkynes under electrochemical conditions.

### 4.1 Intramolecular halocyclization of enynes

In 2018, the Lin group reported an electrochemical intramolecular cyclization of 1,6-enynes, leading to the synthesis of chlorotrifluoromethylated pyrrolidine derivatives (Scheme 23).<sup>52</sup> Similar to their previous work, the reaction involves the parallel generation of two key intermediates,  $\cdot\text{CF}_3$  and  $[\text{Mn}^{\text{III}}]\text{-Cl}$ , at the anode, followed by addition to the 1,6-enyne substrate *via* trifluoromethylation, radical cyclization, and chlorination to afford the final product. Importantly, the introduction of 2,2'-bipyridine as a chelating ligand was key to guaranteeing the reaction with high stereoselectivity.

In 2020, Jiang, Tu, Hao, and co-workers developed an electrochemical method for the halosulfonylation of 1,6-enynes (Scheme 24).<sup>53</sup> This radical-triggered three-component cascade cyclization enables to access halosulfonated 1-indanones in good yields with good stereoselectivities. Mechanistic studies showed that the reaction begins with the anodic oxidation of the iodide ion to its corresponding cation, which reacts with arylsulfonyl hydrazide to produce the arylsulfonyl iodide. This resulting intermediate then undergoes homolysis to generate an arylsulfonyl radical and an iodine radical. The former attacks the double bond of 1,6-enyne, followed by a 5-*exo-dig* cyclization to afford a vinyl radical. Due to the strong steric hindrance between the aryl and arylsulfonyl groups, the vinyl radical (*Z*)-**VIII** is the major stereoisomer, which is the reason for the good stereoselectivity. This vinyl radical can undergo two pathways to generate the final product either reacting with arylsulfonyl iodide or oxidizing to a vinyl cation and further reacting with iodide ion. Following the similar radical addition and cyclization mechanism, the same group reported an example of electrochemical iodosulfonylation of 1,5-enynes to access spiroindenes.<sup>54</sup>

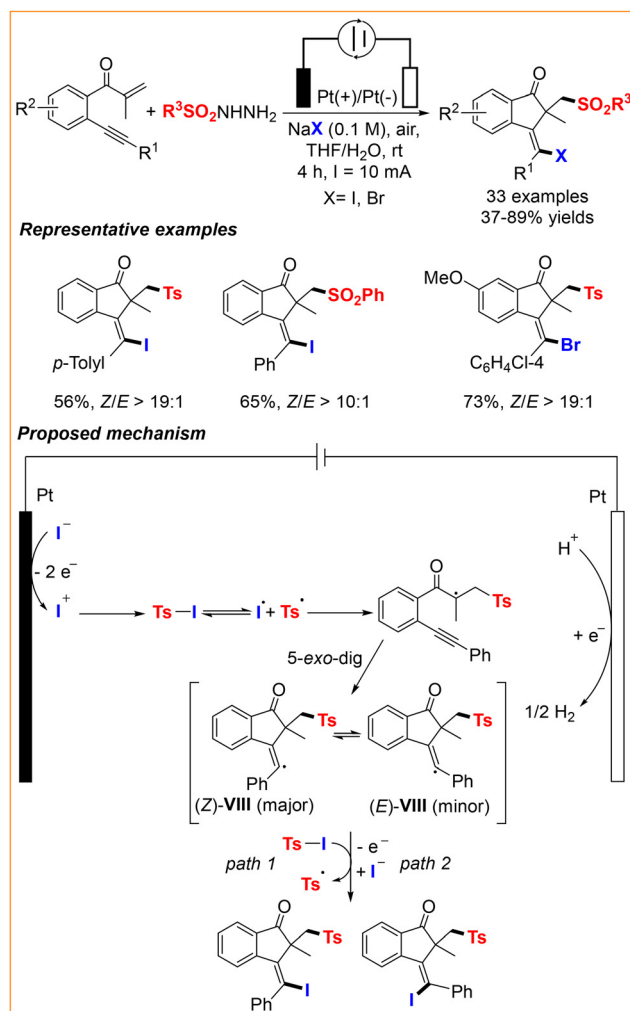


**Scheme 23** Electrochemical cyclization of 1,6-enynes toward pyrrolidines.<sup>52</sup>

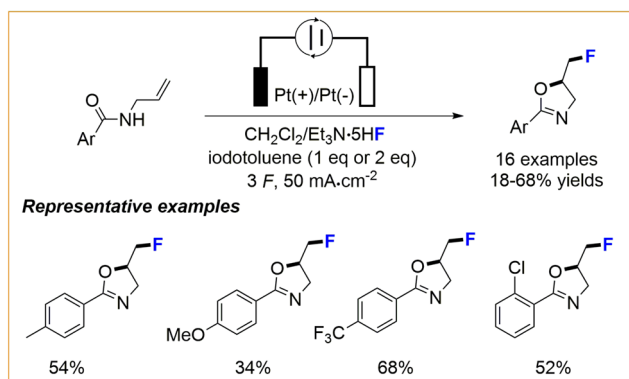
### 4.2 Intramolecular halocyclization of alkenes

Using the *in situ* electrochemical generation of hypervalent iodine as a key mediator in lieu of chemical oxidants, the Waldvogel group reported the synthesis of 5-fluoromethyl-2-oxazoline by fluorocyclization of *N*-allylcarboxamides under electrochemical conditions (Scheme 25).<sup>55</sup> Soon after, the same group applied this strategy to the electrochemical fluorocyclization of *N*-propargylamides, providing the corresponding 5-fluoromethyl-2-oxazoles.<sup>56</sup> To avoid exposure risk and solve scalability issues, the Wirth group developed the same fluorocyclization reaction in flow,<sup>57</sup> which shows high efficiency compared to the batch reaction. Afterward, the Lennox group described a method for the preparation of 3-fluorinated chromanes from allylic phenol esters also using the electrochemical generation of hypervalent iodine species.<sup>58</sup>

In 2019, Zhang, Chen, and colleagues developed an efficient electrochemical generation of molecular bromine that could be further used to trigger the semi-pinacol rearrangement of allylic alcohols for the synthesis of  $\beta$ -halocarbonyls (Scheme 26).<sup>59</sup> It is worth noting that the simulated seawaters can be used as a halogen source in this system for the synthesis of two key intermediates of natural products. In the last several years, electrooxidation of halide salts to their radical or

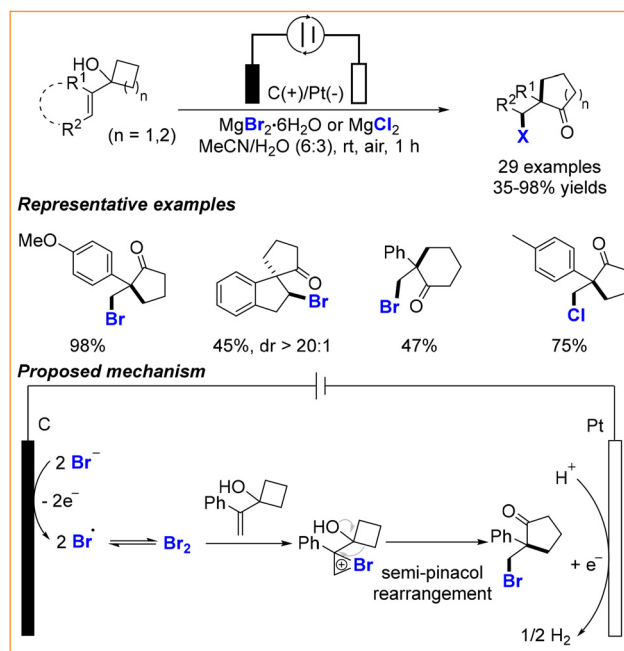


**Scheme 24** Electrochemical cyclization of 1,6-enynes toward 1-indanones.<sup>53</sup>



**Scheme 25** Electrochemical fluorocyclization of alkenes toward oxazolines.<sup>55</sup>

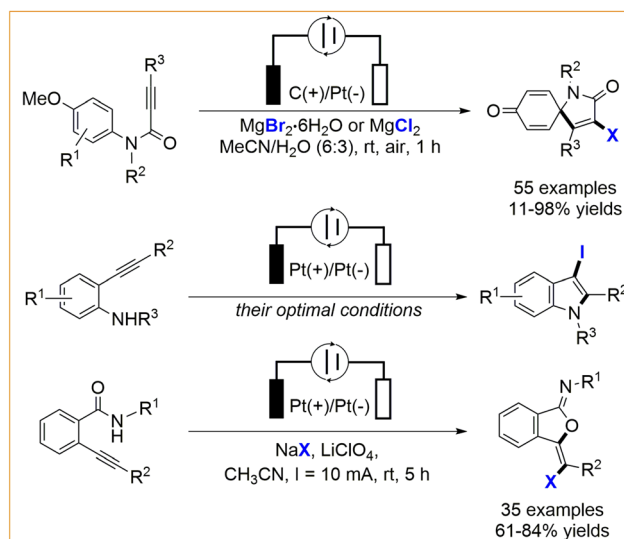
cation intermediates followed by reaction with alkene and subsequent cyclization has been successfully adopted to construct various cyclic and heterocyclic compounds.<sup>60</sup>



**Scheme 26** Electrochemical halogenation/semi-pinacol rearrangement of allylic alcohols.<sup>59</sup>

### 4.3 Intramolecular halocyclization of alkynes

Similar to alkenes, halocyclization of functionalized alkynes under electrochemical conditions has emerged as an efficient strategy to construct various heterocyclic and carbocyclic compounds. For example, the Chen and Xu group reported an electrochemical method for the synthesis of spiro[4,5]troenones from *N*-aryl alkynamides (Scheme 27).<sup>61</sup> Several groups including us reported electrochemical annulation of *o*-alkynylanilines to construct C3-halogenated indoles, respectively



**Scheme 27** Selected examples of electrochemical intramolecular halocyclization of alkynes.<sup>61-63</sup>

(Scheme 27).<sup>62</sup> The electrochemical oxidative halocyclization of *o*-alkynylbenzamides to access isobenzofuran-1-imines was demonstrated by the Anandhan group (Scheme 27).<sup>63</sup> These transformations generally proceed through the electrochemical oxidation of halide salt to halide radical or halide cation, which reacts with alkyne and subsequent cyclization to simultaneously forge C–X and C–C/N/O bonds.

## 5. Conclusions

This review summarizes recent representative examples of electrosynthesis of organohalides by difunctionalization of alkenes and alkynes. These reactions generally enabled the synthesis of organohalides without the need for exogenous chemical oxidants under mild conditions. Reaction types include electrochemical dihalogenation, electrochemical intermolecular halofunctionalization, and electrochemical intramolecular halocyclization of alkenes and alkynes. The electrochemical dihalogenation reaction mainly relies on the generation of halonium ion as a key intermediate, resulting in vicinal dihalide products with *anti*-selectivity. Although an example of *cis*-dichlorination of alkenes has been developed,<sup>21</sup> the strategy for *cis*-difluorination, *cis*-dibromination, and *cis*-diiodination is still highly desirable as they are more valuable and reactive compared with their chloride analogue. The electrochemical intermolecular halofunctionalization of alkenes and alkynes has succeeded in forging C–X and C–C/N/O/P/S/Se bonds simultaneously. However, there is no electrochemical method for introducing C–X and C–B/Si bonds. Despite asymmetric dihalogenation and halofunctionalization of alkenes have been well-established,<sup>64</sup> the enantioselective variants of such reactions using electrocatalysis remain unexploited. This direction can be fulfilled by combining with transition metal catalysis or enzyme catalysis. Furthermore, the application of these approaches in the synthesis of natural products and bioactive compounds would be another promising direction given the synthetic value of the resulting organohalides.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

## Conflicts of interest

There are no conflicts to declare.

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