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电化学固定 CO_2 构建羧酸衍生物的研究进展

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摘要 CO_2 由于其含量丰富、无毒和低成本等特性可作为有机合成中的重要 C1 源, 因此, 使用 CO_2 作为 C1 源合成高附加值的化合物具有重要的意义. 本综述重点介绍了在电化学条件下使用 CO_2 作为亲电试剂参与有机化合物羧化反应的最新进展. 主要介绍了非活化有机卤化物、不饱和烯烃化合物和一些特殊化合物的电化学羧化, 并就使用和不使用牺牲阳极进行了详细分类, 讨论了这些反应的反应机制, 为今后此类反应在有机合成中的应用提供参考.
关键词 二氧化碳; 羧化; 羧酸衍生物; 电化学合成

Recent Progress in Electrochemical Fixation of CO_2 to Construct Carboxylic Acid Derivatives

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Abstract CO_2 is an important C1 source in organic synthesis due to its abundant, non-toxic and low-cost properties. Therefore, it is of great significance to use CO_2 as a C1 source to synthesize compounds with high added value. This review focuses on the recent progress in the carboxylation of organic compounds using CO_2 as an electrophile under electrochemical conditions. The electrochemical carboxylation of non-activated organic halides, unsaturated alkene compounds and some special compounds are mainly introduced. And the use of sacrificial anodes and non-sacrificial anodes is classified in detail. The reaction mechanisms of these reactions are also discussed. This review provides a reference for the application of such reactions in organic synthesis in the future.
Keywords carbon dioxide; carboxylation; carboxylic acid derivatives; electrochemical synthesis

Carbon dioxide is considered a greenhouse gas, which is the most important contributor to global warming. Despite the low thermodynamic stability and low reactivity of carbon dioxide, the synthesis of high value-added compounds such as carboxylic acid derivatives with carbon dioxide as a source of C1 has become a research hotspot at present, because carbon dioxide has the advantages of abundance, non-toxicity and low cost. The need for "carbon neutrality" continues to drive accelerated research in carbon capture and storage technologies, whether through biological carbon sequestration in plants or soils, or physical carbon sequestration in coal seams or the deep ocean. The conversion of CO_2 into organic chemicals has broad industrial application prospects and significant economic value. Therefore, the research on chemical carbon sequestration from CO_2 conversion into organic chemicals has become an important direction in the field of carbon sequestration technology.[1]

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Carboxylic acid derivatives have good pharmacological activity and are widely present in medicines (Figure 1). Due to the low reactivity of CO_2, the direct reaction with CO_2 to generate carboxylic acid usually requires the use of Grignard reagents or lithium reagents with high nucleophilicity.[2] Significant progress has been made in transition metal-catalyzed carbon dioxide carboxylation in recent decades.[3] However, these methods require the use of a stoichiometric amount of reductants, which make the reaction cost prohibitive and environmentally unfriendly. In the past ten years, chemists have successfully synthesized carboxylic acid compounds using photocatalytic fixation of CO_2, avoiding the use of stoichiometric oxidants.[4]

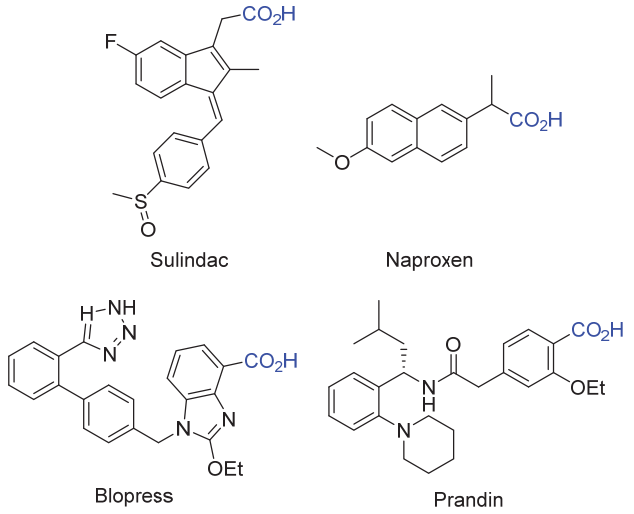

Figure 1 Some representative drug molecules containing carboxylic acids

Electro-organic synthesis is the use of electricity to realize the charge transfer of organic molecules or catalytic mediators at the "electrode/solution" interface, as well as the mutual conversion of electrical and chemical energy, making it possible to break old bonds and form old and new bonds.[5-13] Through electron transfer, the redox reaction is realized, which successfully replaces the use of traditional oxidizing/reducing agents, reduces the reaction cost, suppresses side reactions, and is environmentally friendly. Therefore, electrochemical fixation of CO_2 to generate carboxylic acid compounds is a feasible method.

As a device for realizing electrochemical reactions, electrochemical reactors commonly include batch-type reactors and microreactors. The batch-type reactors also include undivided cell, divided cell and quasi-divided cell (the difference between quasi-divided cell and undivided cell is that the quasi-cell is equipped with a much smaller counter electrode than the working electrode). The traditional batch reactor is characterized by simple device structure, convenient processing, great operation flexibility, and easy control and change of reaction conditions.[14] However, batch reactors have some limitations, such as limited electrode surfaces, the need to add supporting electrolytes, and the difficulty of scaling up. In addition, microreactors have the following advantages: (1) Large surface area, high mass transfer and heat transfer efficiency, which can make scale-up protocols simpler; (2) Precise control of temperature, flow rate, pressure and residence time; (3) Due to the continuous flow reaction, the reaction mixture continuously flows out of the reactor, reducing the possibility of over-oxidation.

Sacrificial anodes are widely used in electrochemical carboxylation reactions. It is worth noting that the use of sacrificial anode has the following effects: (1) The metal ions produced by the anode can stabilize the negative ions produced in the reaction process; (2) Inhibit unnecessary oxidation reaction of substrate at the anode. The factors that determine whether a reaction can use a non-sacrificial anode are: (1) When other substances, *e.g.*, Et_3N, *N*,*N*-dimethylformamide (DMF), triethylenediamine (DABCO), can be used to oxidize at the anode to produce cations instead of metal ions, which can also play the role of stabilizing negative ions; (2) The substrate needs to be oxidized at the anode, and there will be competition between which sacrificial anode is used. In general, the electrochemical carboxylation reaction requires the use of sacrificial anodes as follows: (1) metal-catalyzed electrochemical carboxylation of organic halides or electrochemical carboxylation of alkenes that generally requires the use of sacrificial anodes; (2) electrochemical carboxylation of some specific substrates, *e.g.*, arylsulfones, *N*-Boc-*α*-aminosulfone, cyclopropane, *N*-acylimines, heteroaromatics, *β*-hydroxy acids; (3) electrocarboxylation reactions that require the use of special metal materials as anodes to activate CO_2. In addition to the above three cases, electrochemical carboxylation reactions usually do not use sacrificial anodes, which use CO_2 as the reaction substrate.

This review summarizes the recent advances in electrochemical carboxylation using CO_2 as a reaction substrate over the past few years. Although reviews of electrochemical carboxylation reactions using CO_2 have been published,[15] there are new works that need to be summarized and supplemented recently.

1 Electrochemical carboxylation of organic (pseudo)halides

In contrast, the most commonly used substrates for electrochemical carboxylation of organic halides are aryl bromides, chlorides, while aryl iodides, sulfonates and alkyl halides are less frequently used.

1.1 Electrochemical carboxylation of organic halides without sacrificial anodes

In undivided cell, the anode is often sacrificed to achieve electrochemical carboxylation. However, there are some problems with the use of sacrificial anodes in electroreductive carboxylation, such as cathode passivation caused by the precipitation of insoluble salts of anode metal on the cathode surface. In continuous electrolysis, it is also troublesome to replace exhausted anodes.

In 2015, Senboku and co-workers[16] reported efficient

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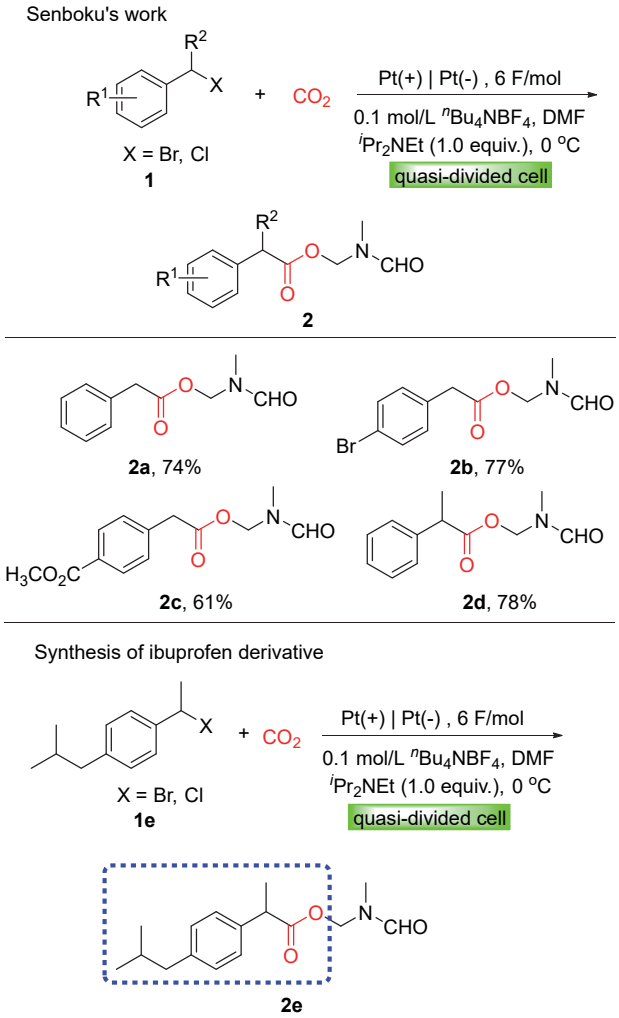
electrochemical carboxylation in quasi-divided cell without the use of a sacrificial anode (Scheme 1). In the presence of CO_2, benzyl halide **1** was electrolyzed in DMF at a constant current of 20 mA/cm^2, which was achieved in an electrolytic quasi-divided cell with a Pt plate cathode and a Pt wire anode. A three-component coupling of benzyl halide, CO_2, and DMF was achieved to yield *N*-methyl-*N*-(phenylacetoxy)methylformamides **2** in good yield. Using this method, benzyl bromides with electron withdrawing groups and benzyl chlorides can be converted to the corresponding carboxylated products. They successfully applied the current carboxylation method to the synthesis of ibuprofen derivatives, which are well-known non-steroidal anti-inflammatory agents. A DMF solution of benzylic bromide **1e** was electrolyzed in the presence of CO_2 under similar conditions until 9 F/mol of electricity was passed. After the usual work-up and purification by column chromatography on silica gel, ibuprofen derivative **2e** was obtained as a three-component coupling product in 66% yield.



Scheme 1 Efficient electrochemical carboxylation of benzyl halides by using sacrificial-free anode

It is well known that microreactors have several advantages such as a large surface-to-volume ratio, precise temperature control and high-speed mixing.[17-19] Based on previous research, Atobe group[20] developed a novel electrochemical carboxylation system for the carboxylation of benzyl halides **3** using a microreactor to fix of CO_2 without the need for a sacrificial anode (Scheme 2). Using this method, benzyl bromide, benzyl chloride with electron-withdrawing groups and electron-donating groups can be converted into the corresponding carboxylated products. The microreactor consists of two regions: In the electrolysis zone: benzyl halide **3** is reduced at the cathode to form nucleophile **5**, nucleophile **5** combines with CO_2 to form carboxylate ion **6**; In the acidification zone: carboxylate ions **6** reacts rapidly with hydrochloric acid to form 2-phenylpropanoic acid **4**.

Most electrocarboxylation reactions are accomplished via sacrificial anodes (*e.g.*, magnesium, zinc, aluminum) or metal catalysis (*e.g.*, palladium, nickel, cobalt).[21] Based on previous research work, Manthiram and co-workers[22] selected benzyl ammonium salts **7** as substrates and **7** successfully reacted with CO_2 to obtain the corresponding carboxylic acid products **8** (Scheme 3). The electrocarboxylation process does not require metal catalysis and the use of sacrificial anodes. The reaction conditions are mild and can be applied to primary and secondary benzyl C—N bonds with a wide range of substrates. By varying the carbon chain length (using phenyltrimethylammonium bromide and phenethyltrimethylammonium bromide as substrates), benzoic acid **10b** and 3-phenylpropionic acid **10a** were obtained under optimized conditions, respectively. This result shows that the method is not limited to benzyl ammonium salts which can possibly be extended to aromatic and aliphatic ammonium salt substrates.

Based on the results of cyclic voltammetry and differential electrochemical mass spectrometry (DEMS) methods, the mechanism of the above reaction is proposed (Scheme 4). First, benzyl radical **11** is generated through reduction of benzylammonium **7** at the cathode. Meanwhile, trimethylamine **12** is produced during reduction through C—N bond breaking, which can then diffuse to the anode to be oxidized to the trimethylamine radical cation **13**. However, due to similar oxidation potentials of bromide anion and trimethylamine, the possibility of Br^- mediated trimethylamine oxidation cannot be excluded. Then it infers that both processes exist in the reaction based on the fact that they have similar oxidation potentials, and observation of brominated byproducts, since the carboxylated products still form when bromide is entirely excluded through use of a different anion (BF_4^-) for the substrate. The trimethylamine radical cation **13** tends to release one proton with the formation of the *α*-amino radical **14**. The benzyl radical **11** can gain one more electron to form a benzyl anion **15** at the cathode, which can be trapped by CO_2 generating the 2-phenylacetate anion **16**. Finally, **16** gets proton to form carboxylation product **8**. Meanwhile, at the anode, the *α*-amino radical **14** loses one electron to form the iminium cation **17** that can form dimethyl(phenylacetoxymethyl)-amine with **16**.

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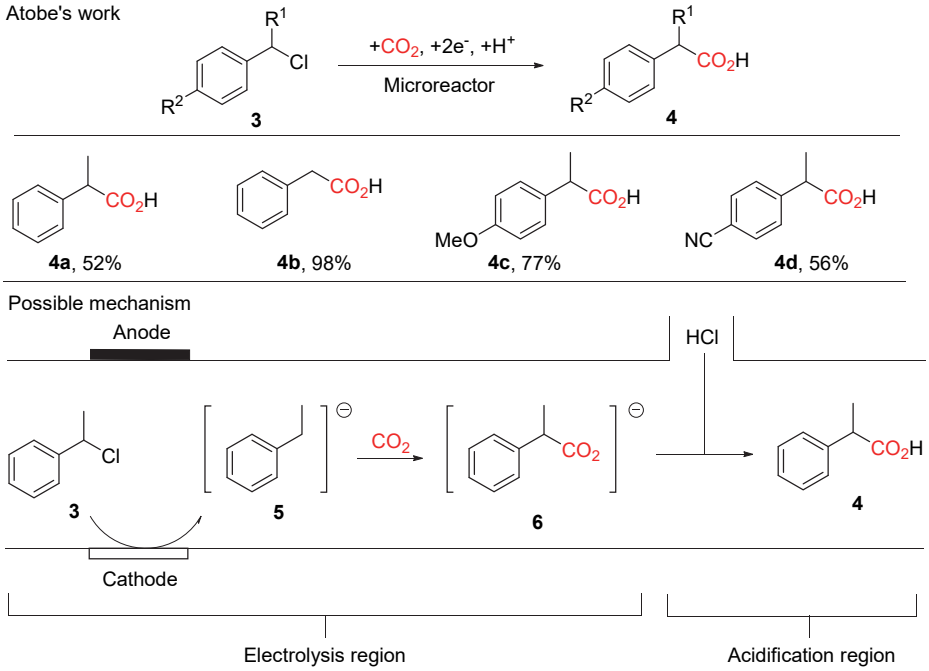
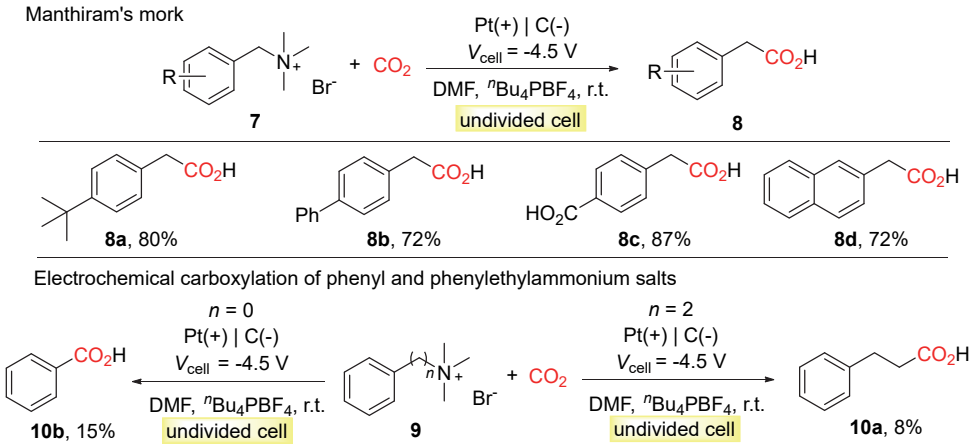
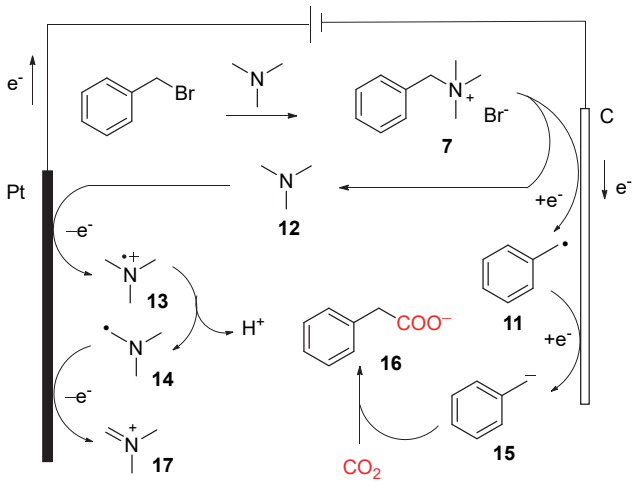


Scheme 2 CO_2 immobilization on phenyl halides using a microreactor without sacrificial anode



Scheme 3 Direct electrochemical carboxylation of benzylic C—N bonds with CO_2 by using sacrificial-free anode



Scheme 4 Mechanism of electrochemical carboxylation of phenyl and phenethylammonium salts

In 2022, Qiu and co-workers[23] reported the electroreduction carboxylation of organic halides **18** using organic mediator (Scheme 5). Using graphite felt as anode and platinum sheet as cathode, electrolysis was carried out at a constant current of 20 mA in an undivided cell. The use of naphthalene as the reducing mediator does not require the use of expensive transition metals. The reaction conditions are mild and suitable for the conversion of various aryl halides and alkyl halides to the corresponding carboxylated products. Drug molecular derivatives including menthol, isoborneol, carveol, phytol, citronellol and perillyl alcohol (**19c**～**19h**) were all amenable to the electroreductive carboxylation transformation. At the same time, the method can be carried out in a lower concentration CO_2 atmosphere (30%). A plausible reaction mechanism for the catalytic cycle was proposed as follows. First, naphthalene **20** is reduced to the radical anion **21** at the cathode. Then,

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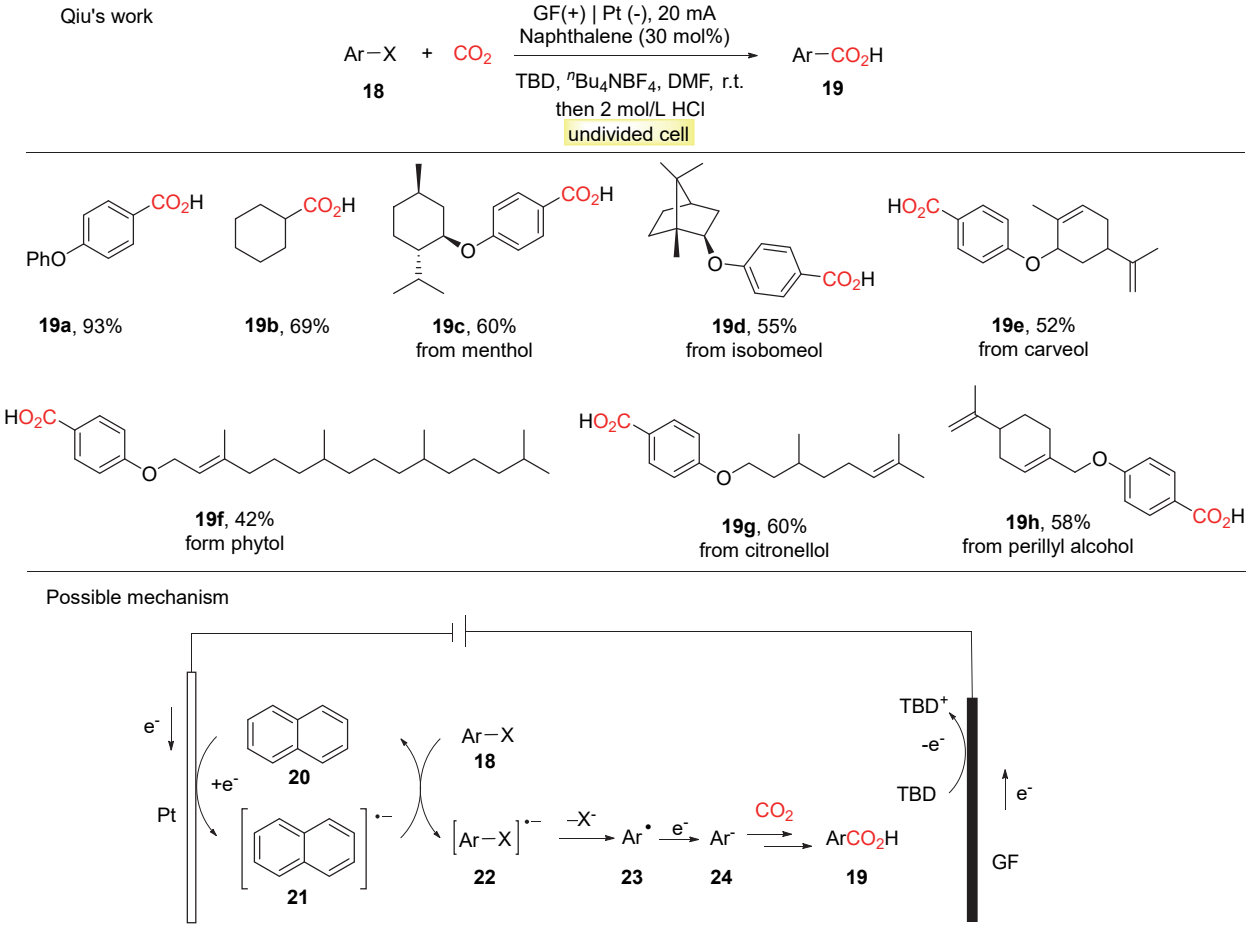

Scheme 5 Electroreductive carboxylation of organic halides by organic mediators

radical anion **21** with the aryl halide **18** through a one-electron transfer reaction to generate the radical anion **22**. The radical anion **22** dissociates to give the aryl radical **23**. Subsequently, the aryl radical is reduced to the aryl anion **24** via another one-electron reduction process (gathering electrons from the cathode or radical anion **21**), nucleophilic attack on CO_2, and acidification to give the corresponding carboxylated product. At the same time, 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD) is oxidized at the anode.

1.2 Electrochemical carboxylation of organic halides with sacrificial anodes

1.2.1 Electrochemical carboxylation of aryl halides

It is green and feasible to replace toxic and harmful reducing agents by electrochemical methods, which are due to electrons as reducing agents. Some results have been achieved in the electrocarboxylation of aromatic halides, but these methods generally use metal complexes as catalysts and are limited to a CO_2 insertion route.

In 2019, Mellah and co-workers[24] reported the reductive carboxylation of aryl halides **25** to produce the corresponding benzoic acids **26** using samarium electrode as sacrificial anode, providing a smooth strategy for CO_2 activation (Scheme 6). Using this method, various aryl bromides and aryl chlorides with electron withdrawing and electron donating groups can be converted into the corresponding carboxylation products. The carboxylation reaction occurs after the efficient reduction of carbon dioxide, which reduces via the electrogenerated Sm(II) complex as a strong one-electron reducing agent. CO_2 was bubbled in an undivided cell equipped with a cylindrical rod of samarium as the anode and a stainless-steel grid as the cathode, and the substrate bromobenzene **25** was electrolyzed in DMF at a constant current of 100 mA. Using $^nBu_4NBF_4$ as the supporting electrolyte, the reaction was carried out at room temperature for 4 h to obtain phenylacetic acid **26**.

Further, Mellah group[25] used benzyl halide instead of aryl halide, and realized the direct carboxylation of alkyl halide. In undivided cells equipped with samarium anode and stainless-steel grid as cathode, and solution of tetrabutylammonium iodide (TBAI) in MeCN, electrolysis was performed at I=100 mA for 386 s. Then the polarity of the electrodes was switched and dry ice, benzyl halide **27** and chlorotrimethylsilane (TMSCl) (TMSCl) were added (Scheme 7). Using this method, benzyl bromide, benzyl chloride with electron-withdrawing groups and electron-donating groups can be converted into the corresponding carboxylated products. Based on controlled experiments and cyclic voltammetry studies, the following reasonable mechanism was proposed. First, CO_2 was inserted into Sm(II) to produce complex **29**, and benzyl chloride reacted

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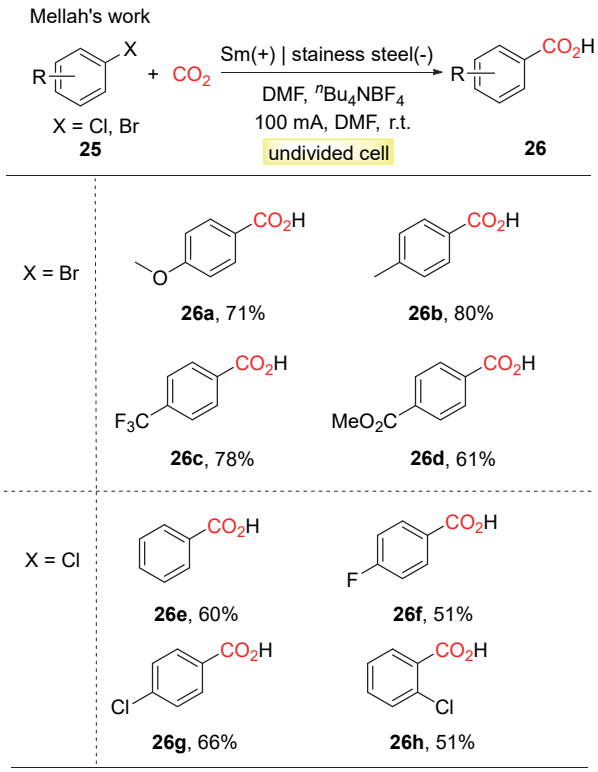


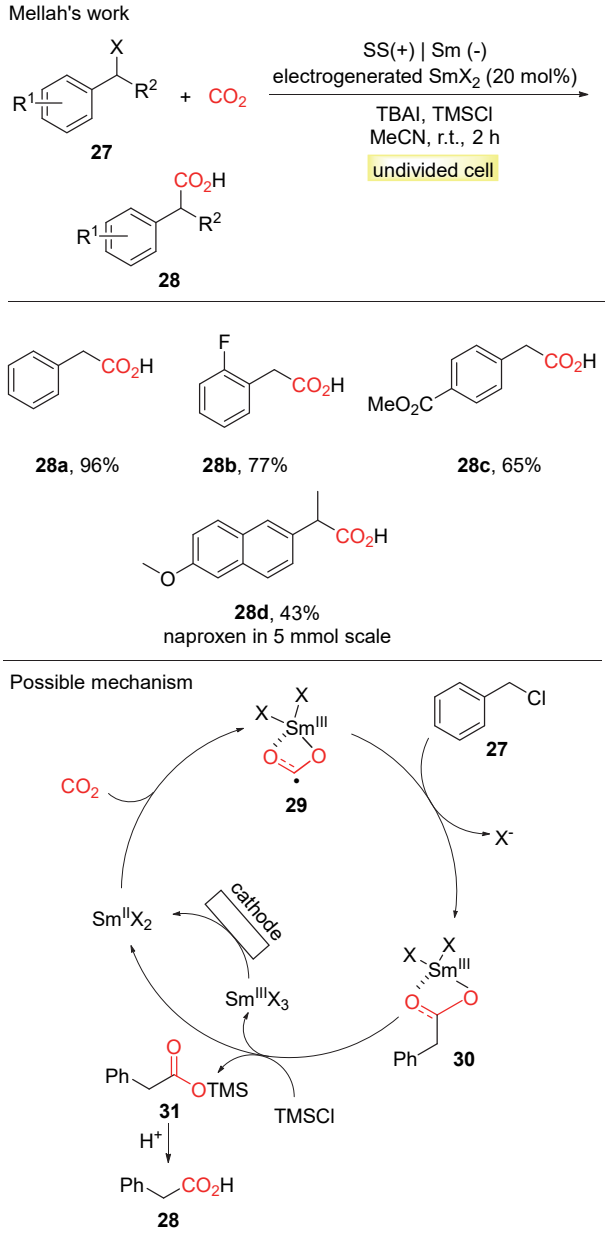
Scheme 6 CO_2 activation by electrogenerated divalent samarium for aryl halide carboxylation

with **29** to produce intermediate **30**, TMSCl replaced Sm(III) to produce the samarium carboxylate intermediate **31**, and then **31** generated carboxylic acid **28** under acidic conditions. Finally Sm(III) was reduced to Sm(II) at the cathode to start the next catalytic cycle.

In 2021, Yu *et al.*[26] reported the carboxylation of aryl halides **32** with CO_2 under electrochemical conditions using nickel as a catalyst (Scheme 8). This transformation can be performed with either aryl chlorides, bromides, iodides and sulfonates. Alkyl bromides can also afford the corresponding carboxylated products in moderate yields. This reaction conditions are mild, with a wide range of substrates and good functional group tolerance. A plausible reaction mechanism for the catalytic cycle was proposed as follows. First, in the presence of bipyridine ligands and 4-dimethylaminopyridine (DMAP), $Ni(acac)_2$ produces L"Ni(0) species **34** at the cathode, then **34** is oxidatively added to the substrate aryl halide **32** to obtain intermediate **35**, **35** in the cathode is further reduced to obtain intermediate **36**, then **36** reacts with CO_2 to obtain nickel carboxylate intermediate **37**. Finally, **37** is reduced at the cathode to obtain carboxylate anion **38**, and further protons are obtained to generate carboxylic acid **33**. Simultaneously releasing L"Ni(0) to start the next catalytic cycle.

2 Electrochemical carboxylation of alkenes

The electrocarboxylation of alkenes mainly concentrated in the terminal alkene, but with the continuous development, dienes, α,α- or α,β *or* β,β-disubstituted alkenes, α-CF_3 alkenes, α-fluoroacrylic acid, homostryrenyl acetates *etc.* can also occur electrocarboxylation reaction.



Scheme 7 Electrogenerated Sm(II)-catalyzed CO_2 activation for carboxylation of benzyl halides

2.1 Electrochemical carboxylation of alkenes without sacrificial anodes

To date the majority of diene carboxylation processes afford the α,δ-dicarboxylated product, and the selective monocarboxylation of dienes is a significant challenge.[27-30] Buckley group[31] reported the electrochemical realization of selective δ-carboxylation of dienes **39** without the use of metal catalysts and sacrificial anodes. The reaction was carried out at room temperature in an undivided electrolytic cell with carbon as anode and stainless steel as cathode. The reaction conditions are mild and have a broad range of functional groups for a variety of aryl and

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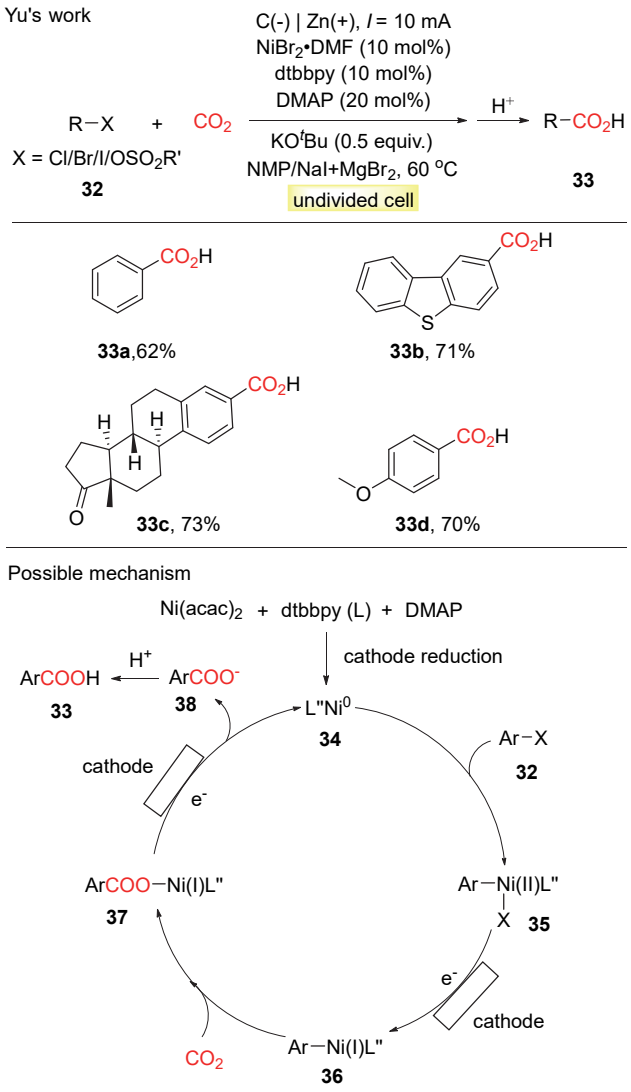
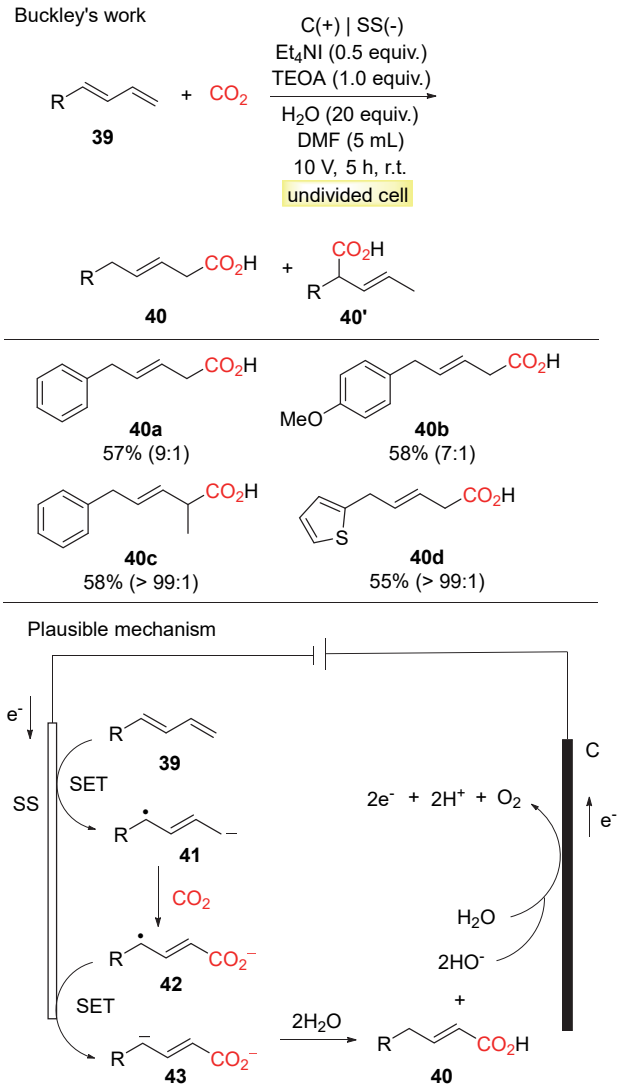


Scheme 8 Nickel-catalyzed electrochemical carboxylation of unactivated aryl and alkyl halides with CO_2



Scheme 9 Selective α,δ-hydrocarboxylation of conjugated dienes utilizing CO_2 and electrosynthesis. Regioselectivity **40**/**40'** given in parentheses, only major products are shown

aliphatic dienes (Scheme 9). Based on deuterium labeling studies, they proposed the following reasonable mechanism. First, the dienes **39** undergoes electron transfer on the surface of the cathode to form the adsorbed radical anion of the diene **41**, which combines with CO_2 to form carboxylation product **42**. **42** further electron transfer and protonation from water affords the final α,δ-monocarboxylated product **40**.

The carboxylation of alkenes mainly focuses on terminal alkenes, and although there are few examples of carboxylation of α,α- or α,β-disubstituted alkenes, the selective monocarboxylation of β,β-substituted alkenes remains a major challenge.[32] In 2020, Buckley and co-workers[33] reported a new electrocarboxylation of alkenes with CO_2 (Scheme 10). The reported method allows direct access to carboxylic acids derived from β,β-trisubstituted alkenes in a highly regioselective manner. The reaction was carried out at room temperature with styrene **44** as substrate, carbon as cathode and anode, DMF as solvent, and electrolysis at a constant current of 60 mA. Based on deuterium labeling studies and cyclic voltammetry studies, the following reasonable mechanism was proposed. The alkene **44** undergoes electron transfer at the cathode surface to give the alkene radical anion **46**; subsequent carboxylation and further electron transfer and protonation from water provide the final monocarboxylated product **45**.

In 2020, Zhou and co-workers[34] first reported γ-carboxylation of α-CF_3 alkenes **50** with CO_2 (Scheme 11). In an undivided cell equipped with a platinum plate as the working electrolysis, α-CF_3 alkenes **50** reacted in DMF with ^{n}Bu$_4$NClO$_4$ as the supporting electrolyte at a constant current of 8 mA to obtain fluorinated carboxylic acids **51** in good yields. α-CF_3 alkenes with α-alkyl substituents and various aryl substituents are viable substrates. To better expand the applicability of substrates and the application of target products, a series of natural product or drug molecular groups (such as β-*D*-glucose, fructose, and estrone)

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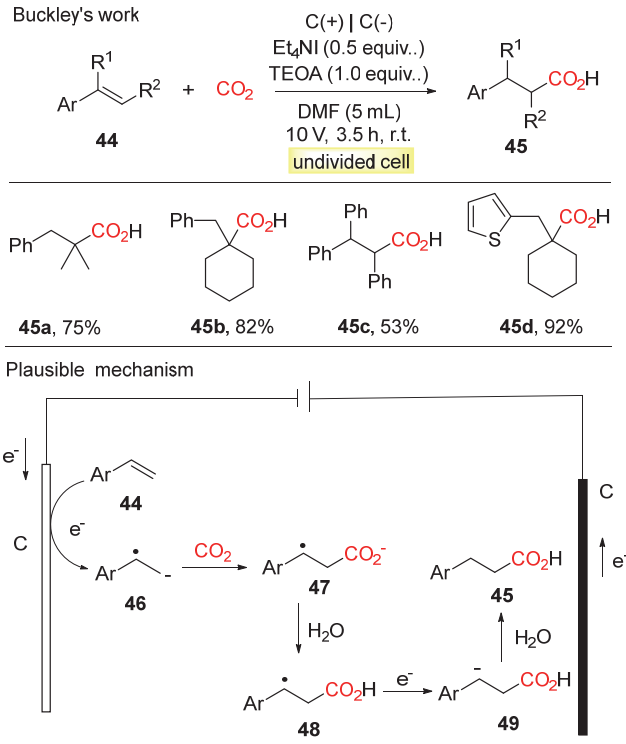
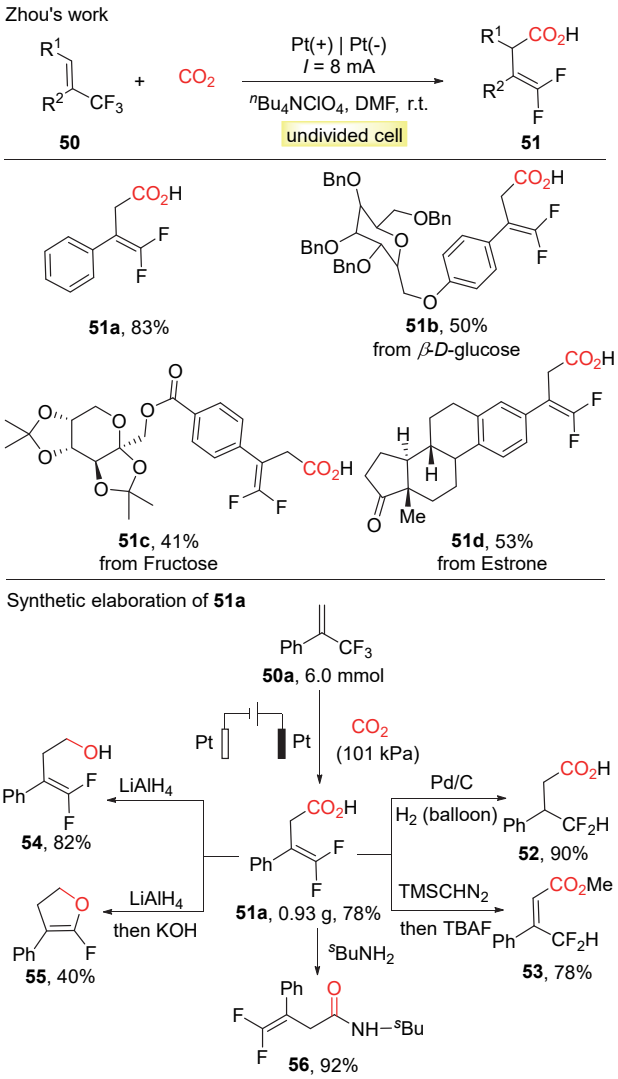


Scheme 10 Selective *β*-hydrocarboxylation of substituted alkenes

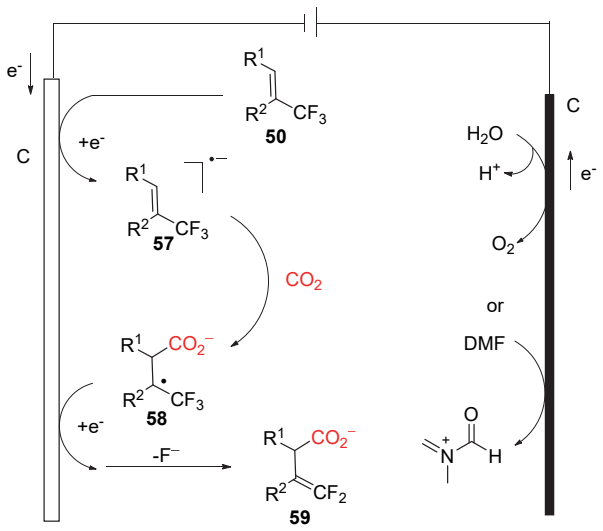
were introduced to obtain the desired products (**51b**~**51d**) in good yields. To further demonstrate the utility of the developed electrochemical carboxylation, the gram-scale reaction of **51a** was performed on a 6.0 mmol scale and the product **51a** was isolated in 0.93 g in comparable yield (78%). **51a** was hydrogenated in 90% yield under Pd/C catalysis to afford *β*-fluoromethylcarboxylic acid **52**. Methylation and subsequent tetrabutylammonium fluoride (TBAF) promoted olefin isomerization to provide **53** in 78% yield. Condensation of **51a** with an amine afforded amide **56** in excellent yield. Reduction of **51a** with $LiAlH_4$ gave alcohol **54** in 82% yield. Furthermore, *α*-fluorodihydrofuran **55** was obtained in 40% yield by $LiAlH_4$ reduction followed by defluorinated cyclization under KOH (Scheme 11).

Based on controlled experiments and cyclic voltammetry studies, the following reasonable mechanism was proposed (Scheme 12). First, *α*-CF_3 alkene **50** is reduced at the cathode to generate radical anion **57**, which reacts immediately with CO_2 to obtain radical intermediate **58**. Subsequently, radical intermediate **58** is reductively defluorinated at the cathode to form carboxylate anion **59**. Meanwhile, DMF or H_2O is anodized to release imine cation or hydrogen ion, both of which can interact with carboxylate anion **59** to generate protected carboxylate or directly generate carboxylic acid.

In 2021, Buckley and co-workers[35] successfully combined with CO_2 under electrochemical conditions to provide all-carbon *α*-quaternary centered carboxylic acids **61** in good yields by using *α*,*β*-unsaturated alkenes **60** as substrates (Scheme 13). This method uses carbon anode and



Scheme 11 Direct electrochemical defluorinative carboxylation of *α*-CF_3 alkenes with CO_2



Scheme 12 Reaction mechanism of direct electrochemical defluorocarboxylation dioxide of *α*-CF_3 alkene with CO_2

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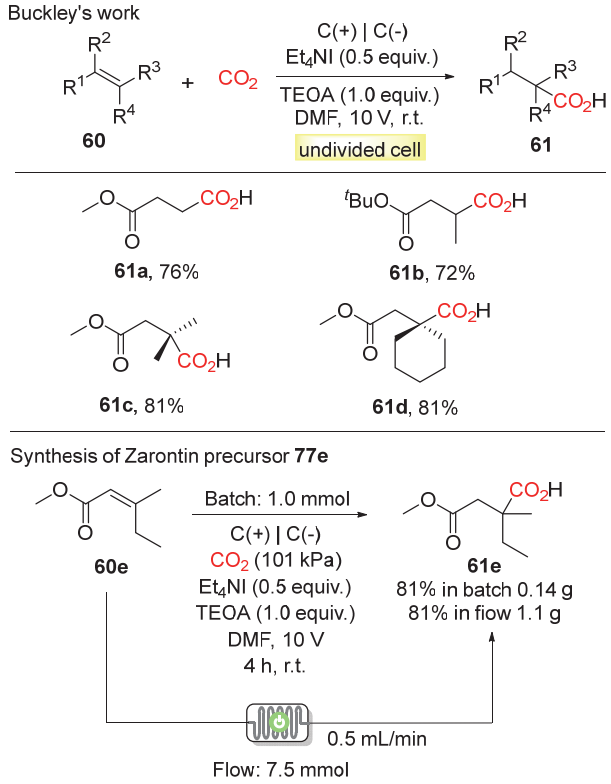
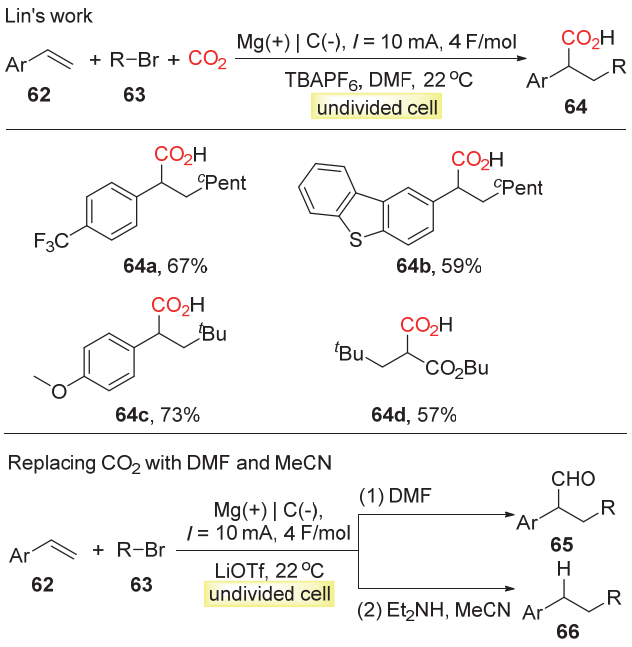
cathode for electrolysis in an undivided cell. They used Glorius' reaction robustness to study the scope and limitation of this electrochemical method for alkene functionalization, and observed overall good levels of tolerance to a range of basic, nucleophilic, and electrophilic additives. They found that the electrochemical method, whether using commercial batch reactors or commercial flow reactors, can synthesize compound **61e** in 81% yield. **61e** is the precursor of the antiepileptic and absence seizure drug Zarontin. The synthesis of **61e** by traditional methods requires three steps and the use of toxic hydrogen cyanide. The electrochemical method can be used to synthesize **61e** in one step.



Scheme 13 Electrosynthesis all-carbon α-quaternary centered carboxylic acids from α,β-unsaturated esters

2.2 Electrochemical carboxylation of alkenes with sacrificial anodes

In 2020, Lin and co-workers[36] adopted an electrolytic strategy using alkyl bromides **63** to provide radicals and CO_2 as the electrophile to achieve bifunctionalization of alkenes **62** (Scheme 14). The reaction was carried out in an undivided cell with Mg as the anode, carbon as the cathode, constant current of 10 mA, and DMF as the solvent. The reaction tolerates electron-rich and electron-poor styrenes, including aryl chlorides and bromides. The experimental results show that this method can successfully synthesize formylated product **65** and hydroalkylated product **66** when DMF and MeCN are used instead of CO_2, which have a broad substrate range and good functional group compatibility.



Scheme 14 Electroreductive carbofunctionalization of alkenes with alkyl bromides via a radical-polar crossover mechanism

Subsequently Zhou's gruop[37] reported the electrocarboxylation of the geminal difluoroalkene **67** with CO_2, which successfully gave α-fluoroacrylic acid **68** in good yield (Scheme 15). The reaction was carried out at room temperature with a constant current of 8 mA in an undivided cell equipped with a platinum plate as the cathode and a nickel plate as the sacrificial anode. Geminal difluoroalkenes substituted with a variety of functional groups β-aryl groups (such as phenyl, ester, amide, sulfonyl, cyano, fluorine, CF_3, *etc.*), and substrates with β-alkenyl or alkynyl groups all perform well good responsiveness. The method does not require transition metal catalysis and a broad range of functional groups. A possible mechanism is proposed. First, the gem-fluoroalkene **68** is reduced on the cathode to generate the radical anion **69**, which is then reacted with CO_2 to give the intermediate **70**. Then the intermediate **70** is reduced at the cathode, followed by defluorination to yield the carboxylate anion **71**, which is finally acidified to give the target α-fluoroacrylic acid.

In 2018, Mei and co-workers[38] reported the first Pd-catalyzed selective electrocarboxylation of homostryrenyl acetates **72** with CO_2 to obtain α-arylcarboxylic acids **73** (Scheme 16). Using $Pd(OAc)_2$ as catalyst and 1,2-bis(diphenylphosphino)benzene (DPPPh) as ligand, the reaction was carried out in undivided cell equipped with platinum electrodes and magnesium rods as sacrificial anodes, and Et_4NOTs as the supporting electrolyte at 30 ℃. The reaction of styryl groups with CO_2 in DMF was carried out at constant current of 8.0 mA. Substrates with different electron withdrawing and electron donating properties are suitable for this reaction. The enantioselective carboxylation of allyl acetate is main challenge. They found that chi-

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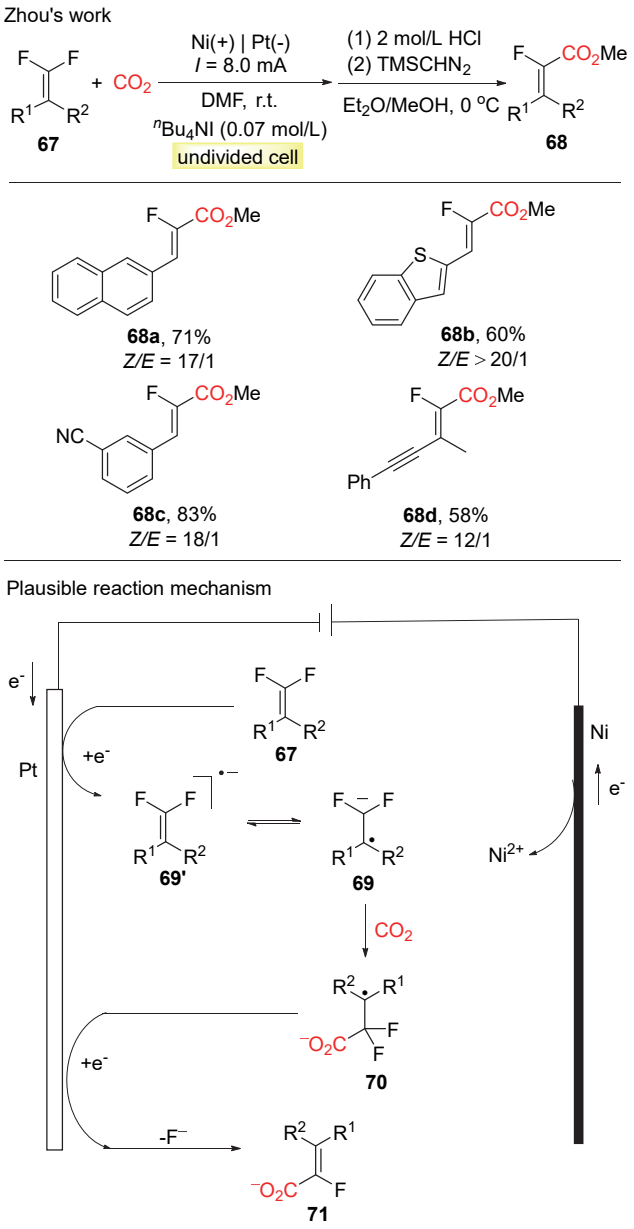
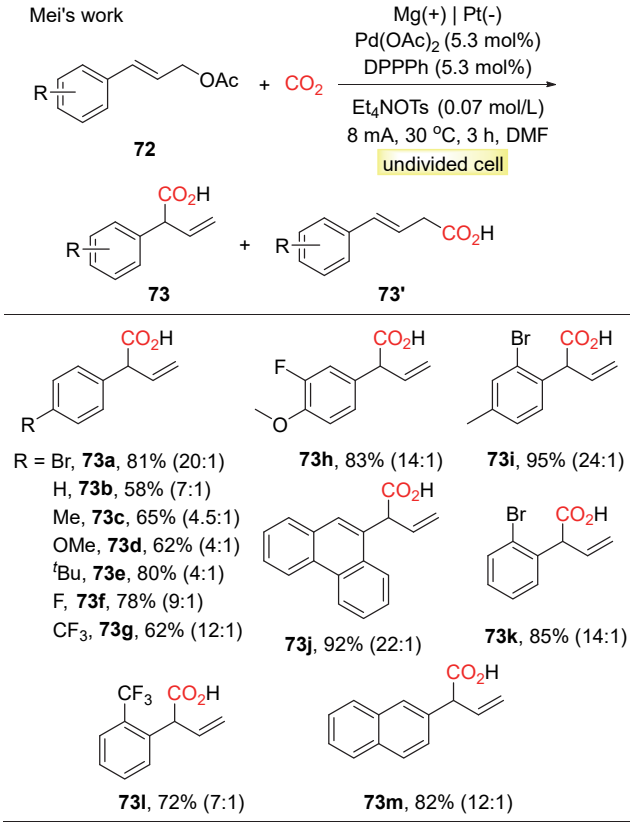


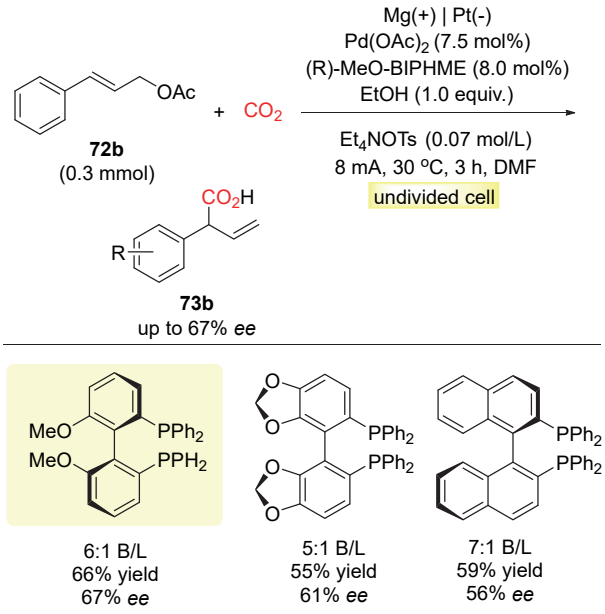
Scheme 15 Direct electrochemical defluorinative carboxylation of gem-difluoroalkenes with CO_2

ral bidentate triarylphosphine ligands were efficient for this catalytic asymmetric carboxylation reaction and achieved moderate enantioselectivity (67% *ee*) (Scheme 17). Interestingly, chiral bidentate phosphine ligands are known to be inactive in Pd-catalyzed allylation of aldehydes.[44]

According to the research results of cyclic voltammetry experiments, the following mechanism was proposed (Scheme 18). First, the oxidative addition of Pd(0) to substrate **72** yields π-allylpalladium(II) complex **74**, and the rearrangement of π-allylpalladium(II) complex **74** can form intermediates **75** and **76**. Intermediate **75** is difficult to form due to the large steric hindrance between the palladium and the aryl group. Intermediate **76** is then reduced at the cathode to give anion **77**, and finally **77** reacts with CO_2 at the γ-position to give product **78**.



Scheme 16 Palladium-catalyzed reductive electrocarboxylation of allyl esters with carbon dioxide (regioselectivity **73**/**73'** given in parentheses, only major products are shown)



Scheme 17 Electrochemically mediated enantioselective carboxylation of allyl acetate with CO_2

The combination of halides with CO_2 catalyzed by metal complexes (Co, Ni, Pd) is an effective way to synthesize carboxylic acids.[39-41] Lu *et al.*[42] synthesized the active catalytic [Cu]@Ag composite for the first time, and used it as the cathode to realize the electrocarboxylation of cinna-

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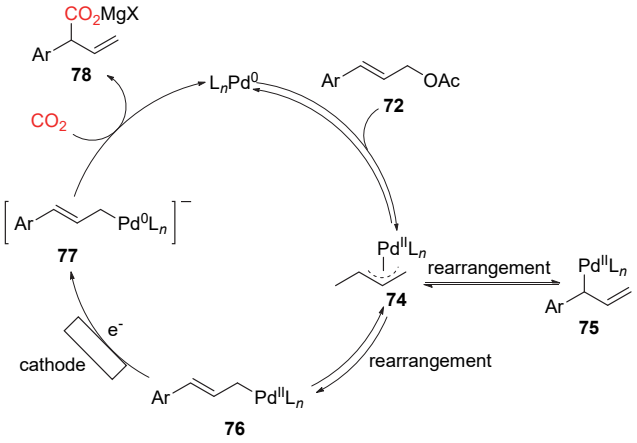
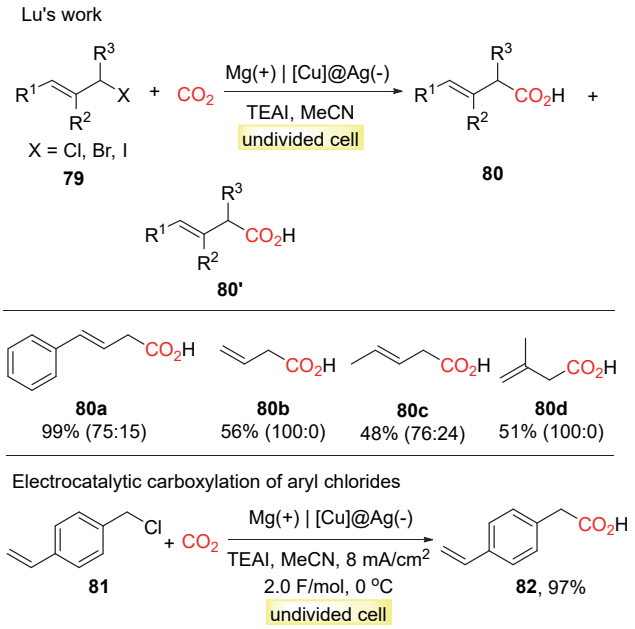


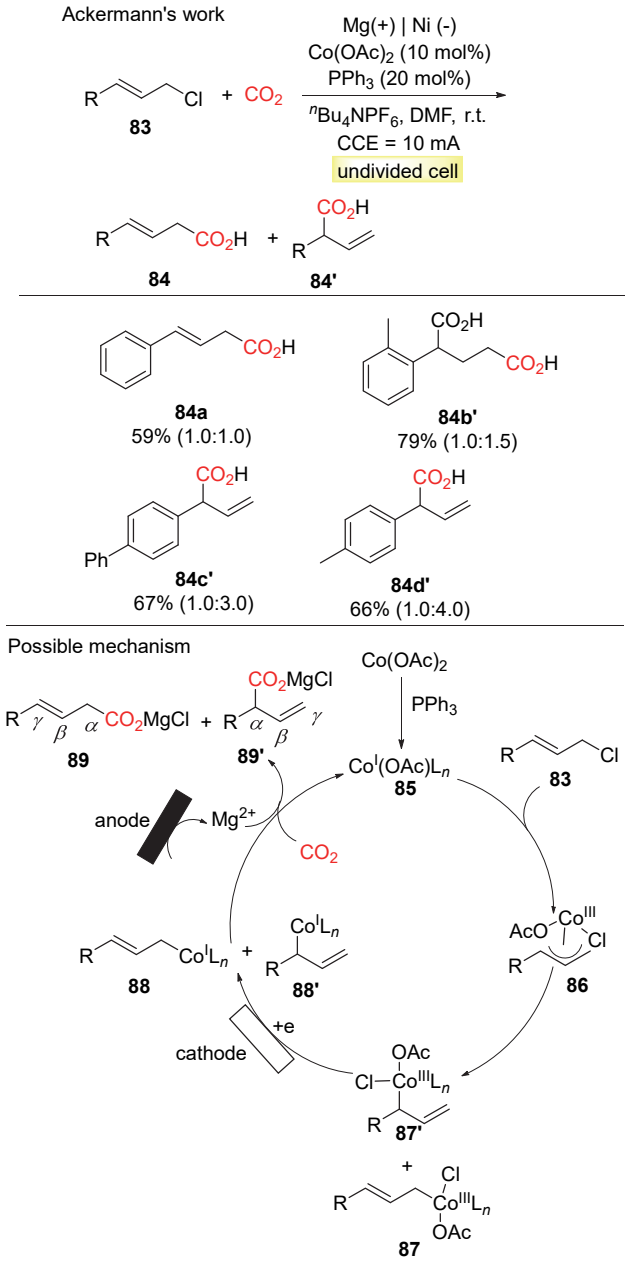
Scheme 18 Reaction mechanism of palladium-catalyzed reductive electrocarboxylation of allyl esters with CO_2

myl chloride **79** with CO_2 to obtain β,γ-unsaturated carboxylic acid **80** (Scheme 19). At the same time, they found that cinnamoyl bromide and allyl halides are also suitable for this method. Furthermore, they also perform electrocarboxylation on the [Cu]@Ag electrode using 4-vinylbenzyl chloride **81** as a substrate, and the corresponding carboxylic acid product **82** could be obtained in an excellent yield of 97%.



Scheme 19 Electroallylation of CO_2 with chlorides at [Cu]@Ag cathode (regioselectivity **80**/**80'** given in parentheses, only major products are shown)

In 2020, Ackermann and co-workers[43] reported a cobalt-catalyzed carboxylation of cinnamoyl chlorides **83** with CO_2 (Scheme 20). The reaction was carried out at room temperature with magnesium as anode, nickel foam as cathode, cobalt acetate as catalyst, triphenylphosphine as ligand, ^{n}Bu$_4$NPF$_6$ as electrolyte, DMF as solvent, and a constant current of 10 mA. Styrylacetic acid derivatives **84**



Scheme 20 Electroreductive cobalt-catalyzed carboxylation of CO_2 and allylic chlorides (regioselectivity **84**/**84'** given in parentheses, only major products are shown)

were obtained with moderate to good yields and good functional group tolerance. Various cinnamoyl chlorides with different aromatic groups containing electron-withdrawing (halogen, trifluoromethyl, *etc*.) and electron-donating (Me, OMe, *etc*.) can be converted to the corresponding carboxylated products. A plausible reaction mechanism for the catalytic cycle was proposed as follows. First, the alkene **83** undergoes a coordination reaction with an active cobalt(I) catalyst **85**, which promotes the cleavage of the adjacent allylic C—H bond, leading to the oxidative addition of the substrate **83** to form an η^3-allyl-cobalt(III) intermediate **86**. According to different ligand effects, intermediate **86** can rearrange to form η^1-allyl-cobalt(III) in-

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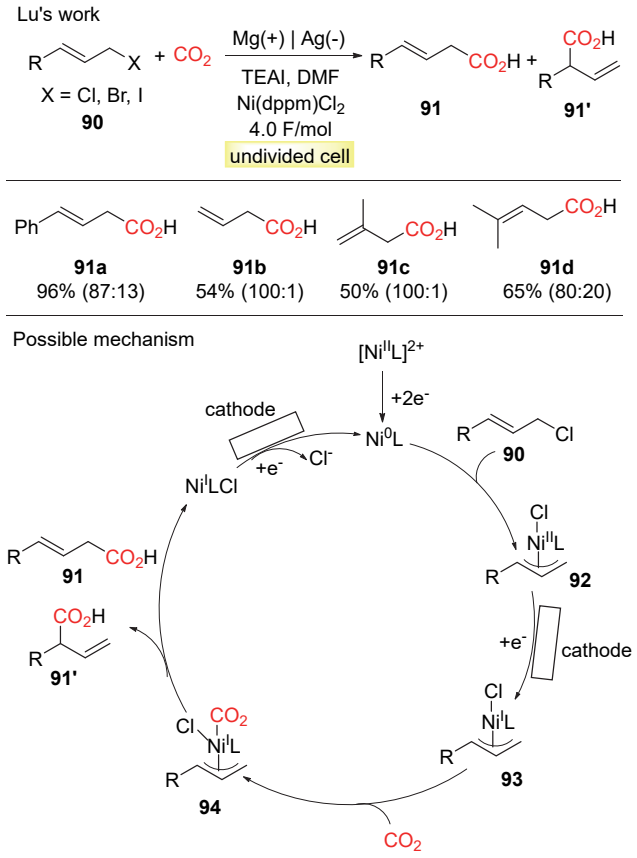
termediates **87** and **87'**. For instance, heteroatoms such as *O*-atom containing ligands are known to promote tautomerization of η^3- to η^1-allyl intermediates in related cobalt complexes.[44] Intermediates **87** or **87'** can be reduced at the cathode to form the corresponding low valent η^1-allyl cobalt(I) species **88** or **88'**, which is highly dependent on the ligand being employed. η^1-Allyl cobalt(I) species **88** or **88'** gave the carboxylated product **89** by nucleophilic addition with CO_2 at the γ-position, simultaneously releasing Co(I) species to start the next catalytic cycle.

In 2021, Lu's team[45] described a Ni-catalyzed CO_2 fixation of cinnamoyl chloride **90** to generate β,γ-unsaturated carboxylic acids **91** in good yield and regioselectivity under electrochemical conditions (Scheme 21). At the same time, they found that cinnamoyl bromide and allyl halides are also suitable for this method. They proposed a reasonable reaction mechanism through the study of cyclic voltammetry. A plausible reaction mechanism for the catalytic cycle was proposed as follows. First, the nickel catalyst [Ni(II)Cl_2(dppm)] is reduced to [Ni(0)(dppm)] at the cathode. Then, the cinnamyl chloride **90** undergoes a coordination reaction with nickel catalyst [Ni(0)(dppm)] and leads to the oxidative addition of substrate **90** to form π-allyl Ni(II) intermediate complex **92**. Intermediate **92** is reduced at the cathode to form the corresponding intermediate **93**. Then CO_2 insertion to **93** forms an intermediate adduct **94**, which can evolve to the carboxylated products **91** and **91'**, simultaneously releasing Ni(I)-complex species to start the next catalytic cycle.



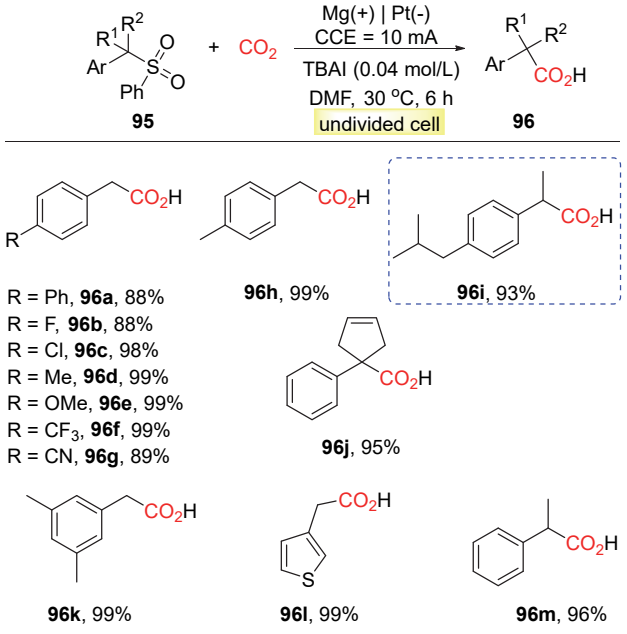
Scheme 21 Nickel-catalyzed electrocarboxylation of allylic halides with CO_2 (regioselectivity **91**/**91'** given in parentheses, only major products are shown)

3 Electrochemical carboxylation of other compounds

In addition to the common organic halides and alkenes, chemists have also developed some special substrates to realize the electrocarboxylation of CO_2, such as arylsulfones, *N*-Boc-*α*-aminosulfone, cyclopropane, *N*-acylimines, heteroaromatics, and *β*-hydroxy acids.

Organic arylsulfones have the following properties: (1) The high stability of organic arylsulfones makes them easy to prepare and manipulate;[46-49] (2) the acidic *α*-C—H bonds of sulfones provide plenty of room for functional elaboration prior to electrocarboxylation;[50] (3) desulfonylative electrocarboxylation makes the sulfone moieties, most frequently is used as protecting groups in organic synthesis, and valuable synthetical precursors, thus providing a novel connection means for organic synthesis.[51-52] Therefore, using organic arylsulfones as electrocarboxylation substrates to fixation CO_2 to generate carboxylic acid derivatives is a feasible strategy.

In 2021, Ye group[53] developed an efficient electrochemical desulfonylative carboxylation to fix CO_2 using arylsulfones **95** as substrates (Scheme 22). This reaction served as a very facile approach to a variety of 2-phenylacetic acid substrates **95** under mild reaction conditions. Using Mg as the anode, Pt as the cathode, TBAI as the electrolyte, DMF as the solvent, the reaction was carried at a reaction temperature of 30 ℃ and constant current electrolysis (10 mA) for 6 h. Substrates with different aromatic groups containing electron-withdrawing or electron-dona-



Scheme 22 Desulfonylative electrocarboxylation with CO_2

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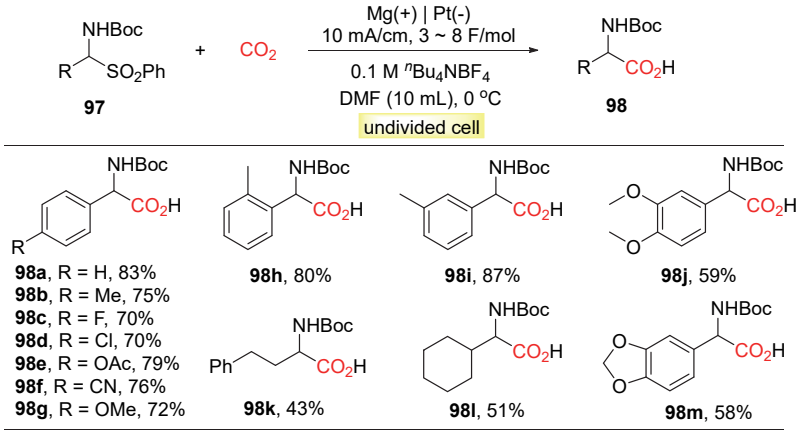
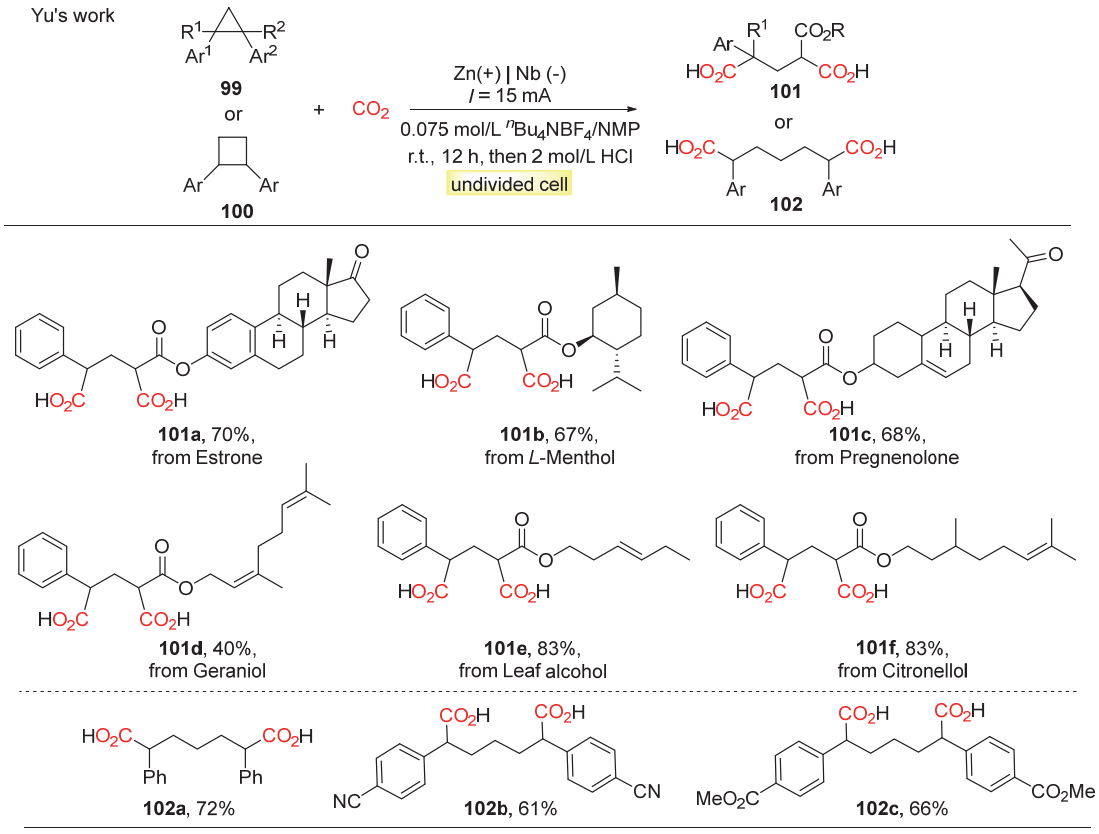
ting substituents groups can obtain good yields. The non-steroidal anti-inflammatory drug ibuprofen **96i** was successfully synthesized by this method with a yield of 93%.

Subsequently Senboku and co-workers[54] successfully performed electrochemical carboxylation of *N*-Boc-*α*-aminosulfones (Scheme 23). Electrolysis of *N*-Boc-*α*-aminosulfone **97** in DMF at a constant current of 20 mA in an undivided cell equipped with a Pt cathode and a Mg anode resulted in cleavage of the C—S bond of substrate, resulting in the corresponding anion nucleophilic with CO_2, and the corresponding *N*-Boc-*α*-amino acids **98** was given in moderate to good yields. Under standard conditions, when the benzene ring has substituents such as methyl, methoxy, halogen, cyano, acetoxy and trimethylsilyl, the corresponding *N*-Boc-phenylglycine was obtained. Notably, alkyl-substituted *N*-Boc-*α*-aminosulfones (**98k**, **98l**) also gave *N*-Boc-*α*-aminoacids through this electrochemical carboxylation.

Diacids are important monomers in the polymer industry to construct valuable materials.[55] Yu and his co-workers[56] first realized the formation of glutaric acid **101** and adipic acid **102** derivatives by combining CO_2 simultaneously under electrochemical conditions using cyclopropane **99** and cyclobutene **100** as substrates (Scheme 24). Reactions were carried out with a constant current of 15 mA in an undivided cell. The reaction conditions are mild with



Scheme 23 Synthesis of *N*-Boc-*α*-amino acids via electrochemical carboxylation of *N*-Boc-*α*-aminosulfones and CO_2



Scheme 24 Synthesis of diacids via electrochemical ring-opening

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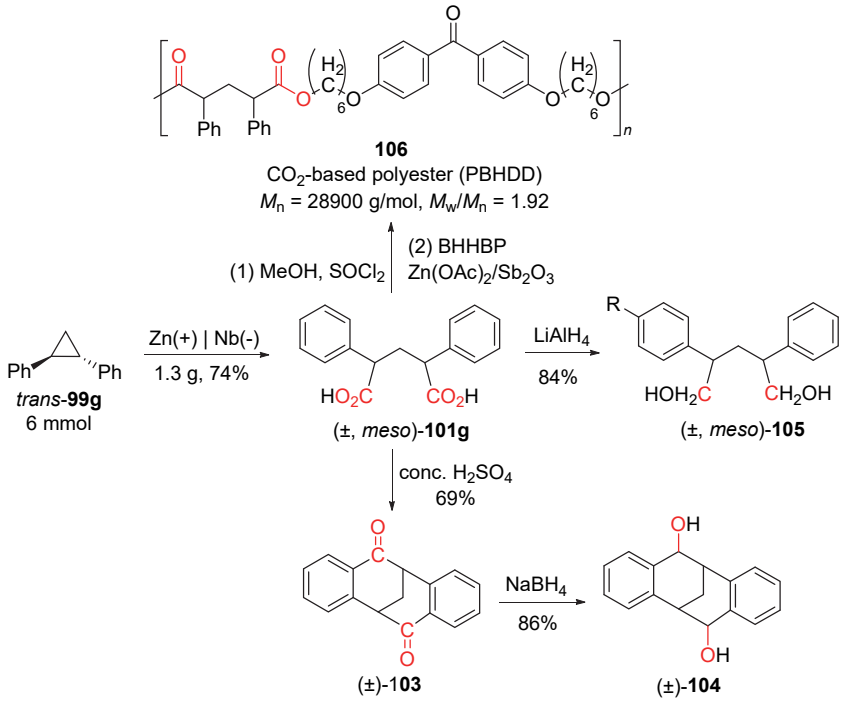
good functional group tolerance, and the product can be further derivatized. To better expand the applicability of substrates and the application of target products, a series of natural products or drug molecular groups (such as estrone, *L*-menthol, pregnenolone, geraniol, leaf alcohol, and citronellol) were introduced to obtain the desired products (**101a**～**101f**) in good yields.

To further demonstrate the utility of the developed electrochemical carboxylation, a gram-scale reaction of **99g** was performed on a 6.0 mmol scale to afford **101g** in 74% yield (Scheme 25). The diacid **101g** can be converted into the diketone **102** in excellent yield, which can then be reduced to give the carbocyclic diol cleft molecule **104**. **101g** can also be reduced to diol **105** in a one-step reduction with $LiAlH_4$ in excellent yield. Furthermore, they used **101g**-Me (the dimethyl ester of **100g**) to polymerize with the diol 4,4'-bis(6-hydroxyhexyloxy)biphenyl (BHHBP), which yielded a molecular weight of 28900 (M_w/M_n=1.92) of polyester poly[4,4'-bis(6-hydroxyhexyloxy)biphenyl 9, 10-dihydro-10-[2,3-di(hydroxycarbonyl)propyl]phosphaphenanthrene-10-oxide] (PBHDD, **106**).

α-Amino acids are found in many natural products and biologically active compounds that are widely used as biochemistry, pharmaceutical science, materials science, and synthetic organic chemistry.[57] Zhang and co-workers[58] reported that using *N*-acylimines **107** as the substrate combined with CO_2 in an undivided electrolytic cell with platinum as the cathode, magnesium as the sacrificial anode, and TBAI as the electrolyte in DMF, electrolysis was performed at a constant current of 10 mA to generate *α*-amino acids **108** (Scheme 26). Using this method, various ketone amines with different aromatic groups containing electron-donating or electron-withdrawing groups, and acetyldiamines with various functional groups can obtain the corresponding carboxylation products. They found that using triethanolamine (TEOA) as an external reductant and has the same reaction effect as using platinum as a non-sacrificial anode. Based on cyclic voltammetry studies, the following mechanism is proposed. *N*-Acylimines **107** undergoes single-electron transfer at the cathode to generate *N*-radical carbanion **109**. **109** combines with CO_2 to generate *N*-radical carboxylate **110**, and then generates N anion **111** through single-electron transfer. The target product **108** is obtained under acidic conditions. Meanwhile, Mg is oxidized to Mg^{2+} under condition A, or amine is oxidized to amine cation in anodization under condition B.

In 2022, Mita's team[59] reported a method for the reaction of heteroaromatics **112** with CO_2 to generate dicarboxylic acids **113** under electrochemical conditions (Scheme 27). Radical anions are generated by CO_2 ($E_{1/2}$= −2.2 V in DMF and −2.3 V in MeCN vs. SCE) reduction at the cathode, which then combine with heteroaromatics to generate the desired diacids. By calculating the reduction potential of the substrate, *N*-Ac- (−2.5 V), Boc- (−2.76 V), and Ph-protected indoles (−2.94 V), even indoles whose reduction potential reaches −3 V are the corresponding diacids which can be smoothly generated. In addition, they also expanded the substrates to benzofuran, benzothiophene, electron-deficient furans, thiophenes, 1,3-diphenylisobenzofuran, and *N*-Boc-pyrazole, which can also successfully carry out the required decarboxylation.

To demonstrate the utility of this approach, they achieved gram-scale preparation of **112a** to obtain product **113a** (Scheme 28). After multiple transformations of **113a**, compounds **114** and **115** can be obtained, respectively. Compound **114** is an inhibitor of the adenosine 3',5'-cyclic



Scheme 25 Derivatization and polymerization of **101g**

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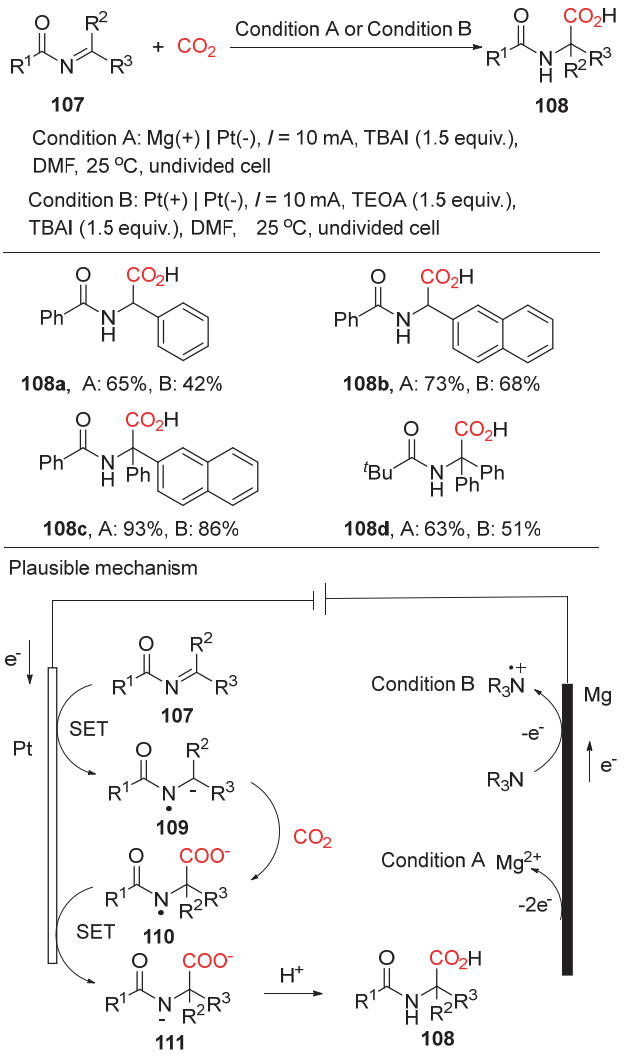
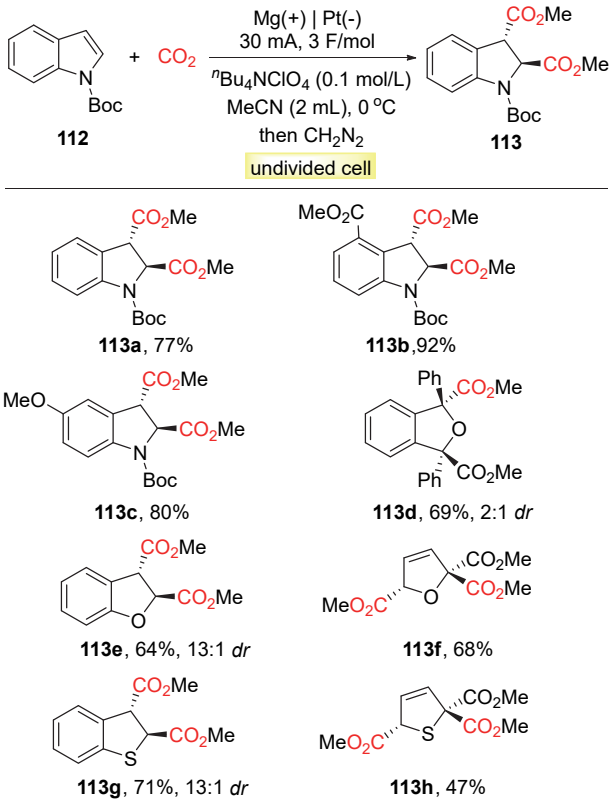
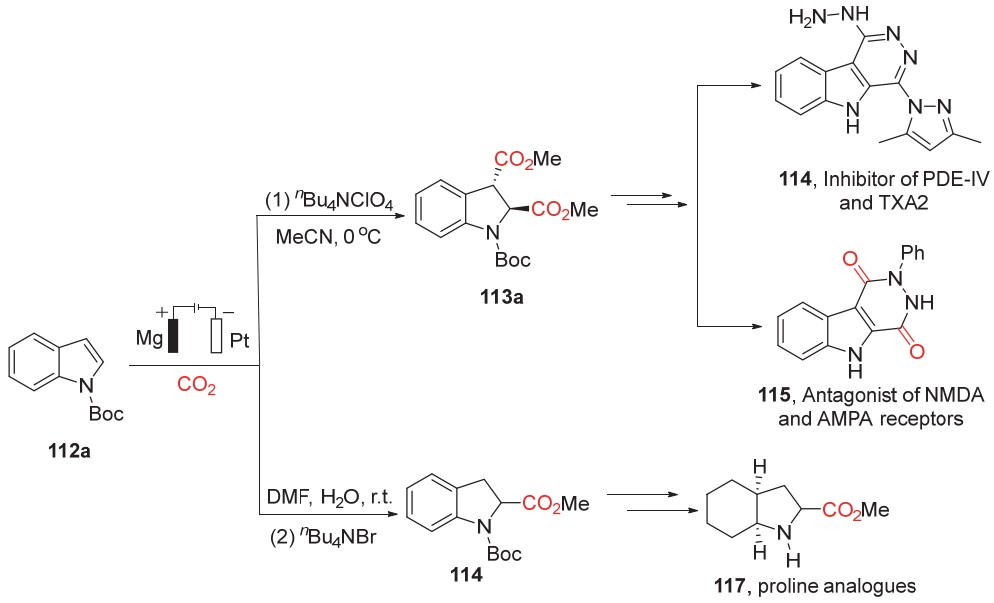


Scheme 26 Synthesis of *α*-amino acids via electrochemical carboxylation of *N*-acylimines and CO_2

phosphate phosphodiesterase (PDE-IV) and thromboxane A2 synthetase (TXA2).[60] And compound **115** is an antagonist of *N*-methyl-*D*-aspartic acid receptor (NMDA) and *α*-amino-3-hydroxy-5-methyl-4-isoxazole-propionicaci (AMPA) receptors. Subsequently, they slightly changed the reaction conditions, using $^{n}Bu_4NBr$ as the electrolyte, DMF



Scheme 27 Synthesis of diacids via electrochemical carboxylation of heterocycles with highly negative reduction potentials



Scheme 28 Application of an electrochemical method for the carboxylation of heteroaromatics

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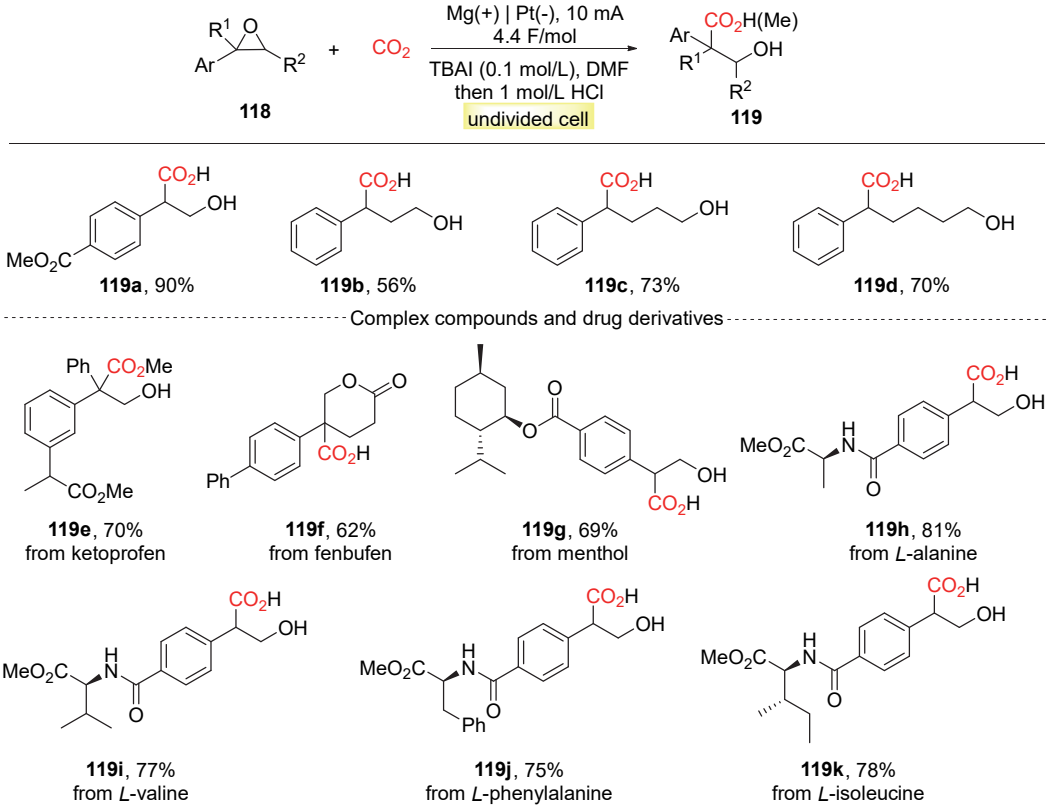
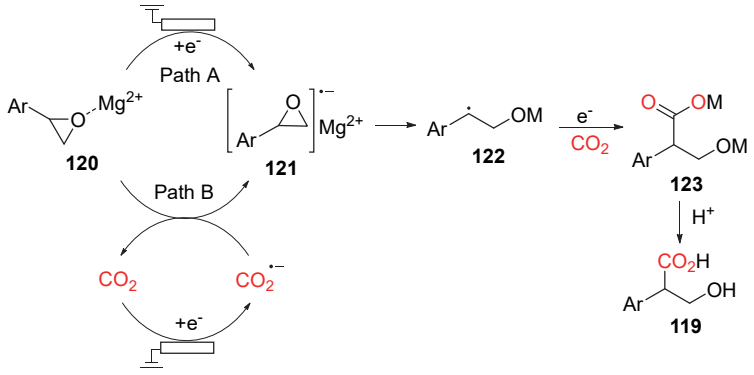
as the solvent, and adding 4 equiv. of H_2O to obtain compound **116**. After multiple transformations of **116**, octahydroindole-2-carboxylic acid (Oic) derivatives **117** were obtained in the yield of 74%. Compound **117** is a useful proline analog and is widely available in many biologically active molecules.[61] Therefore, the dearomatization monocarboxylation hydrogenation strategy is proved to be practical.

β-Hydroxy acid is an important structural motif.[62] Qiu and co-workers[63] reported that electrocarboxylation of aryl epoxides **118** with CO_2 provided valuable *β*-hydroxy acids **119** (Scheme 29). This method uses Mg as the sacrificial anode and Pt as the cathode. It is electrolyzed at a constant current of 10 mA in an undivided cell under mild conditions. The method has good functional group compatibility, drug molecules derivatives including ketoprofen, fenbufen, menthol, and *α*-amino acid derivatives, including *L*-alanine, *L*-valine, *L*-phenylalanine and *L*-isoleucine (**119e**～**119k**) were all amenable to the electroreductive carboxylation transformation. In addition to aryl epoxides, four to six-membered aryl ethers can also be used to synthesize the corresponding hydroxyl acids (**119b**～**119d**). At the same time, the electrochemical strategy can be carried out at lower concentrations of CO_2, and the yield of the product was linearly related to the CO_2 concentration.

Based on controlled experiments and cyclic voltammetry studies, they proposed the following reasonable mechanism (Scheme 30). Mg is anodized to produce Mg^{2+}, which combines with epoxide to form intermediate **120**. Two possible approaches are proposed in the initial steps. The substrate with more positive reduction potential is reduced at the cathode to form intermediate **121** (Path A).



Scheme 29 Synthesis of *β*-hydroxy acid via electrochemical carboxylation of aryl epoxides and CO_2



Scheme 30 Reaction mechanism of electrocarboxylation of aryl epoxides and CO_2

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On the other hand, the cathodic reduction of CO_2 produces CO_2 radical anions. As an alternative pathway, the CO_2 radical anion provides an electron to the epoxide to give intermediate **121** (path B). Intermediate **121** is then ring-opened to give intermediate **122**. Subsequently, another one-electron reduction of CO_2 and a nucleophilic *C*-nucleophilic attack lead to intermediate **123**. Intermediate **123** was protonated in HCl to form *β*-hydroxy acid **119**.

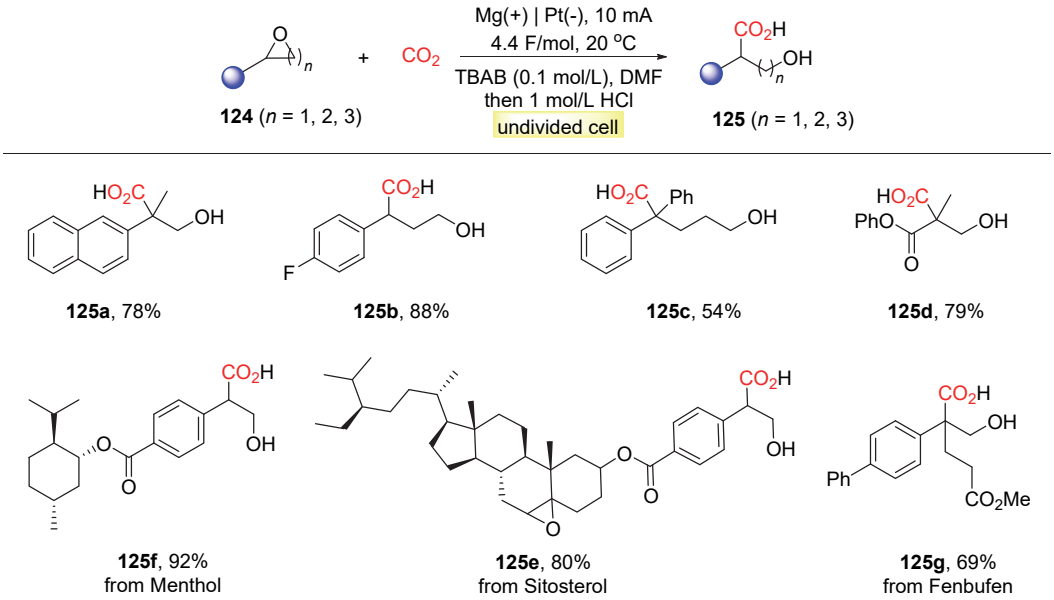
At the same time, Zhang's group[64] also reported the method of electrocarboxylation of styrene epoxide and CO_2 to obtain *β*-hydroxy acid **125** (Scheme 31). This method uses Mg as sacrificial anode and Pt as cathode. Under mild conditions, DMF was used as a solvent for electrolysis at a constant current of 10 mA in an undivided cell. The method has good functional group compatibility, and the drug molecular derivatives including sitosterol, menthol and fenbufen (**125e**～**125g**) are suitable for reductive carboxylation conversion. The reaction was also used for carboxylate-substituted epoxides (**125d**). In addition, quaternary and hexaaryl ethers could also be used to synthesize the corresponding hydroxy acids (**125b**, **125c**).

4 Conclusions

This review mainly summarizes the synthesis of carboxylic acid derivatives using CO_2 under electrochemical conditions. The main route is to reduce halides or compounds containing unsaturated bonds through the cathode to generate carbanions, and then CO_2 acts as an electrophile to attack carbanions to form the carboxylic acid derivatives. Furthermore, studies have shown that carboxylic acid derivatives obtained through electrochemically mediated CO_2 participation reactions possess important pharmacological activities, which illustrates the importance and application value of such reactions.

Electrochemical fixation of CO_2 has the following advantages: (1) relatively single products can be obtained by controlling cathode reduction potentials, so that the selectivity of the obtained products is higher; (2) The reaction can be carried out under mild experimental conditions, which have relatively low requirements on the experimental device, and the system is relatively simple and low-cost.

Although significant progress has been made in electrochemical fixation of CO_2, several challenges remain. (1) Under electrochemical conditions, the bifunctionalization with unactivated alkenes or alkynes as substrates combined with CO_2 still needs to be further developed. The traditional difunctionalization reaction of unactivated alkene or alkynes with CO_2 generally has three reaction pathways: (a) CO_2 is reduced to a radical anion and combined with alkenes or alkynes to form a carbon radical, which is coupled with other radicals; (b) The oxidation substrate produces radicals to combine with alkenes or alkynes to form carbon radicals, which are reduced to carbon anion and then combined with CO_2; (c) Alkenes or alkynes are reduced to radical anions combined with CO_2. However, it is difficult to realize the important step of these reaction pathways under electrochemical conditions. For example, the reduction potential of alkene is −2.6 V, and the reduction potential of CO_2 is −2.3 V. Under electrochemical conditions, CO_2 should be preferentially reduced. Therefore, more favorable reaction pathways need to be developed to enable such reactions under electrolytic conditions. (2) The application in enantioselective carboxylation still needs further research. The reason may be that many ligands are incompatible under electrochemical conditions, or the existing ligands have poor enantioselectivity in electrocarboxylation applications, and there is a need to develop more compounds that are compatible under electrochemical conditions and yield good enantioselectivity



Scheme 31 Synthesis of *β*-hydroxy acid via electrochemical carboxylation of epoxides and CO_2

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ligand. (3) The construction of pharmacologically active heterocyclic compounds (*e.g.*, 2-oxazolidinones) using CO_2 under electrochemical conditions has less applications. At present, there are few researchers on the electrochemical carboxylation of CO_2, and the developed substrates for the electrochemical carboxylation of CO_2 are relatively simple. It is difficult to realize the electrochemical carboxylation cyclization. More complex substrates need to be developed to react with CO_2. (4) The type of bond formation is single, and the application of this method at this stage focuses on the construction of C—C, and the construction of C—X bonds needs to be strengthened. The reason may be that heteroatom substrate are more likely to undergo self-oxidation or self-reduction reactions under electrochemical conditions, which leads to the difficulty of reacting with CO_2 according to the envisaged pathway. The problem of heteroatom substrate can be avoided by using redox catalyst, changing electrode and other electrolytic reaction conditions.

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