

Chemistry

Special Topic: Chemistry Boosts Carbon Neutrality

Progress and challenges in dicarboxylation with CO₂

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Abstract: Dicarboxylic acids, which are appealing structural motifs in organic synthesis and exist widely in bioactive compounds, have been widely used as important monomers in the polymer industry to construct valuable materials. The dicarboxylation with CO₂ provides a convenient and potent way to furnish value-added dicarboxylic acids via the chemical fixation of two CO₂ molecules. Beyond any doubt, the development of dicarboxylation, especially the dicarboxylation of bulk chemicals, might represent a promising prospect in CO₂ capture and utilization (CCU). In this review, we critically summarized and comprehensively reviewed the advances made in the past decades in dicarboxylation with CO₂ under electro-, photo- and transition metal-mediated/catalytic systems. Moreover, the advantages and limitations of such dicarboxylation reactions are pointed out to unravel further development for future scientific and industrial advances in dicarboxylation with CO₂ to synthesize dicarboxylic acids in high selectivity and efficiency.

Keywords: carbon dioxide, dicarboxylation, electrochemistry, photoredox catalysis, transition-metal catalysis

Introduction

Dicarboxylic acids are important structural motifs in a large quantity of pharmaceuticals and natural products. Moreover, diacids are also attractive monomers to construct functional polymers (Figure 1) [1–3]. Therefore, the development of elegant and efficient catalytic systems for the synthesis of diacids is of much interest and importance. It has long been known that dicarboxylation reactions through the oxidation of hydrocarbons [4,5] or the hydrolysis of cyanogen [6] represent a major method to produce diacid derivatives in industry. With the development of transition-metal catalysis, the feedstock gas carbon monoxide (CO) has been extensively used as a carbonyl source in the synthesis of diacids [7]. However, both the use of stoichiometric acids and the high toxicity of CO limit the development of such dicarboxylation reactions. As a consequence, other safe reagents to be the carbon source have attracted prominent recognition. Among these transformations, dicarboxylation with CO₂ complies well with the criteria of green and sustainable chemistry [8] and has received more attention due to its availability, sustainability, and nontoxicity [9–16]. In

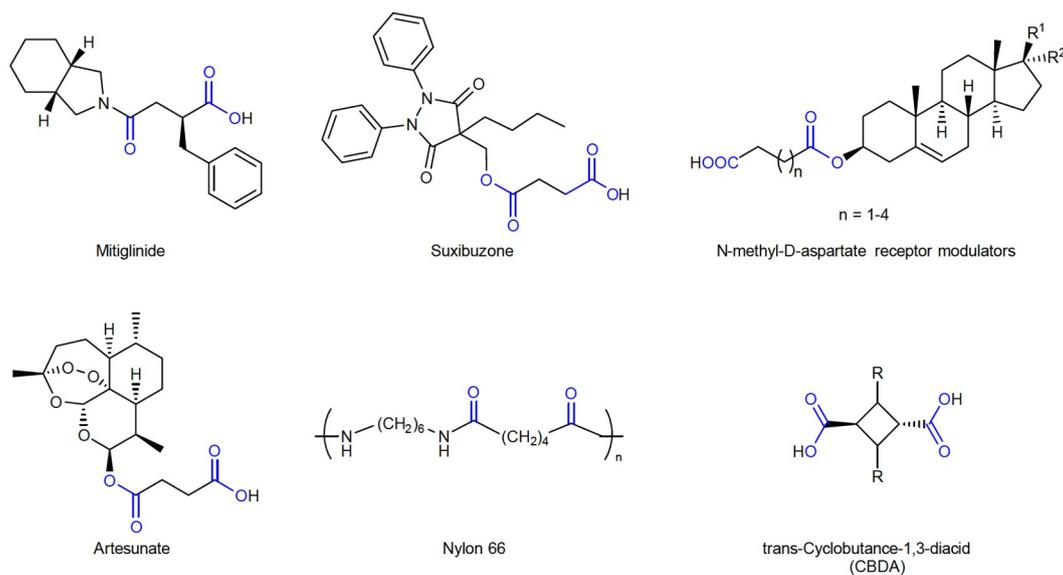


Figure 1 Selected bioactive compounds, monomers and polymers containing diacid motifs.

this respect, the dicarboxylation with CO_2 provides not only an approach for turning CO_2 into fine chemicals but also a new idea for implementing the low carbon policy. The dicarboxylation with CO_2 , especially those of unsaturated substrates, has been well documented in the past 30 years, providing an effective method for the synthesis of various functionalized carboxylic acids and derivatives. Generally, single-electron reduction process was involved in the photocatalytic/electrochemical dicarboxylation of unsaturated substrates with CO_2 , which proposes two possible pathways for the C–C bond formation: (1) reducing the unsaturated substrates to corresponding radical anions, which could attack CO_2 to form carboxylated organic radicals; (2) reducing carbon dioxide to $\text{CO}_2^{\cdot-}$, then reacting with unsaturated substrates to generate the carboxylated organic radicals. Moreover, the dicarboxylation process could be achieved via low-valent transition-metal catalysis, which is facilitated by oxidation metallacyclization to produce corresponding CO_2 incorporated alkyl-metal cycle species and the insertion of another CO_2 into an alkyl-metal bond. In addition to dicarboxylation of unsaturated compounds, the dicarboxylation of C–X (X = C, B, O, and H) single bonds has been systemically investigated to form diverse dicarboxylic acids via electrochemical, base-mediated, and transition-metal-catalyzed strategies. Herein, we discuss the developments and progress toward the dicarboxylation with CO_2 through electrochemical, photochemical, and transition-metal-catalyzed strategies (Figures 2A–C).

Dicarboxylation of unsaturated substrates with CO_2

Electrochemical dicarboxylation of unsaturated substrates with CO_2

Electrochemical dicarboxylation of alkenes with CO_2

Alkenes, which are one kind of bulk chemical in industry, have been widely investigated to react with CO_2 under reductive conditions, affording dicarboxylative products at the early stage of dicarboxylation with

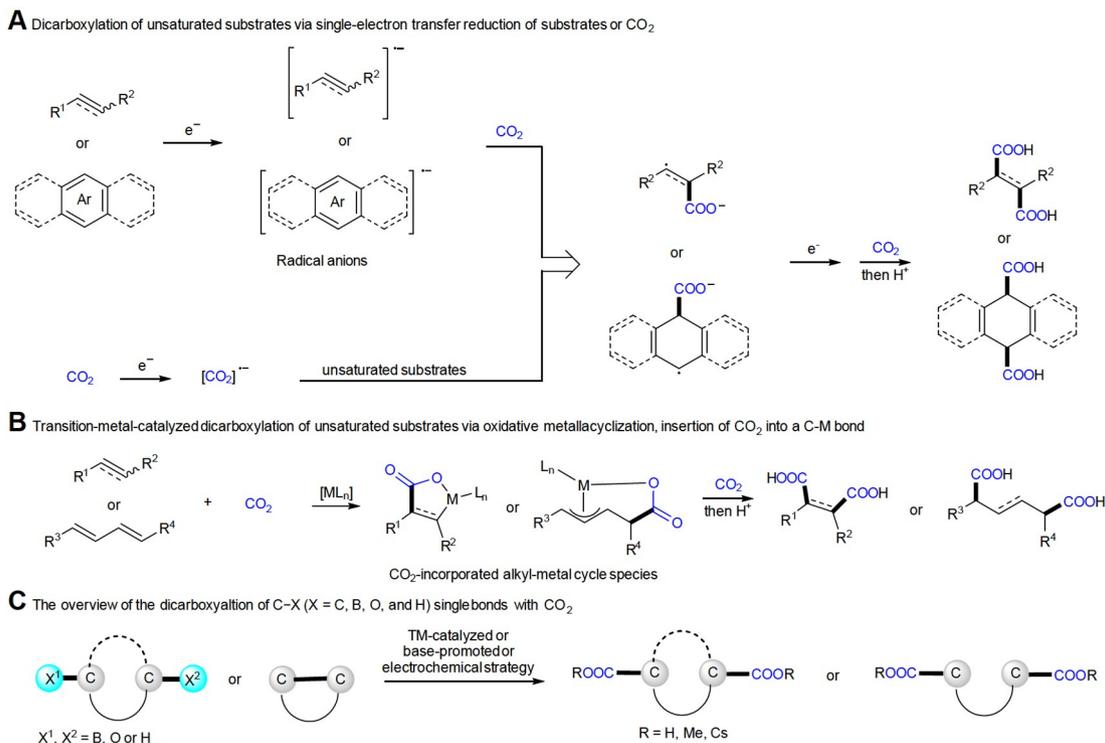


Figure 2 General schemes for dicarboxylation with CO₂. (A) Dicarboxylation of unsaturated substrates via single-electron transfer reduction of substrates or CO₂; (B) transition-metal-catalyzed dicarboxylation of unsaturated substrates via oxidative metallacyclization, insertion of CO₂ into C-M bond; (C) the overview of the dicarboxylation of C-X (X = C, B, O and H) single bonds with CO₂.

CO₂. Since 1970s, many efforts have been devoted to this field [17–19], probing two potent possible pathways involving olefin radical anions and CO₂ radical anion, respectively. However, these preliminary investigations provided diacids without accurate yields and left substrate scope limited.

In 1974, Tyssee and Baizer [20] reported the electrochemical dicarboxylation of activated alkenes with CO₂ using tetraethylammonium trifluoromethanesulfonates (TEAOTs) and 1-octene as electrolyte and reductant via successive single-electron transfer (SET) reduction (Figure 3). Several acrylates were investigated to give diacids in moderate yields, which were settled by current efficiency. In this case, chlorine anion and 1-octene acted as the sacrificial reagents. Activated olefins in the presence or absence of dissolved CO₂ are compared in the polarographic analysis experiments, which can be used as one criterion of reactivity provided that there is not interference from the reduction wave of CO₂. Furthermore, the oxalic acid derivatives could also be detected in this system, which might support the SET reduction of CO₂.

In 1992, Duñach and co-workers [21] reported electrochemical carboxylation of styrenes, which featured negative reductive potential than acrylates (Figure 4). Electrochemical study showed that Ni(0) catalyst was employed to coordinate with alkenes and CO₂, producing key intermediate oxonickelacycle to decrease both reductive potentials with anode Mg as the electron donor. Finally, in the presence of Lewis acid Mg²⁺, the oxonickelacycle species would release the stable magnesium carboxylates and regenerate Ni(0) catalyst. Besides, the dicarboxylation of norbornene with CO₂ to produce dicarboxylation products could be obtained in lower yield after adjusting the reaction conditions. Although the dicarboxylation of styrenes and derivatives with CO₂ has been realized, the low conversion and unsatisfactory yields still need to get improved.

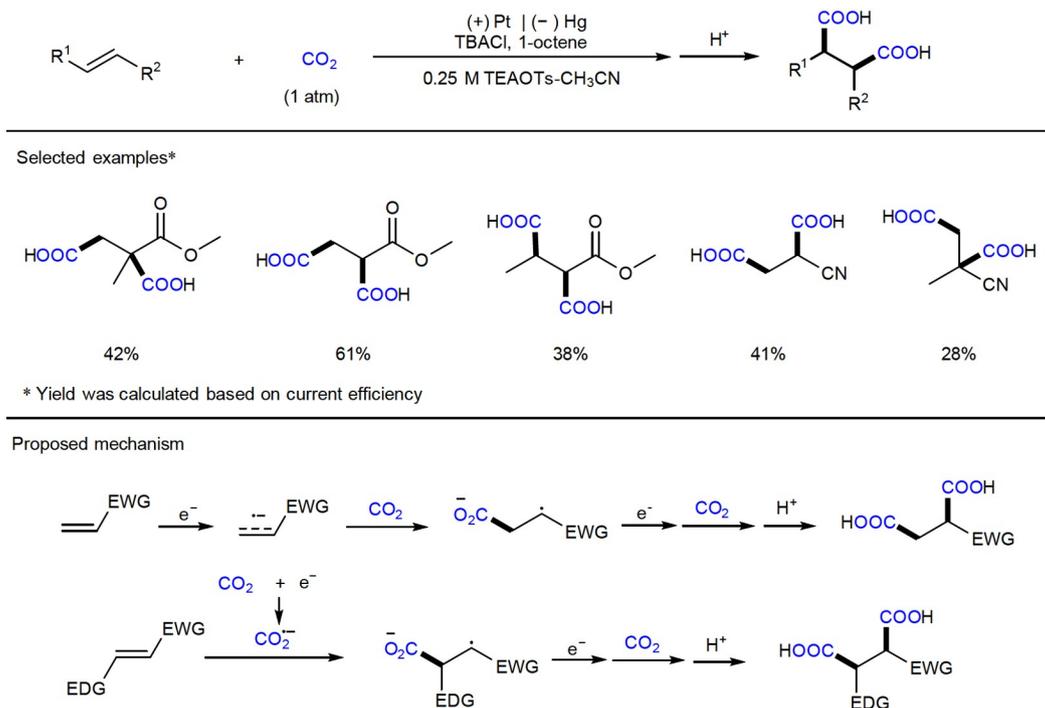
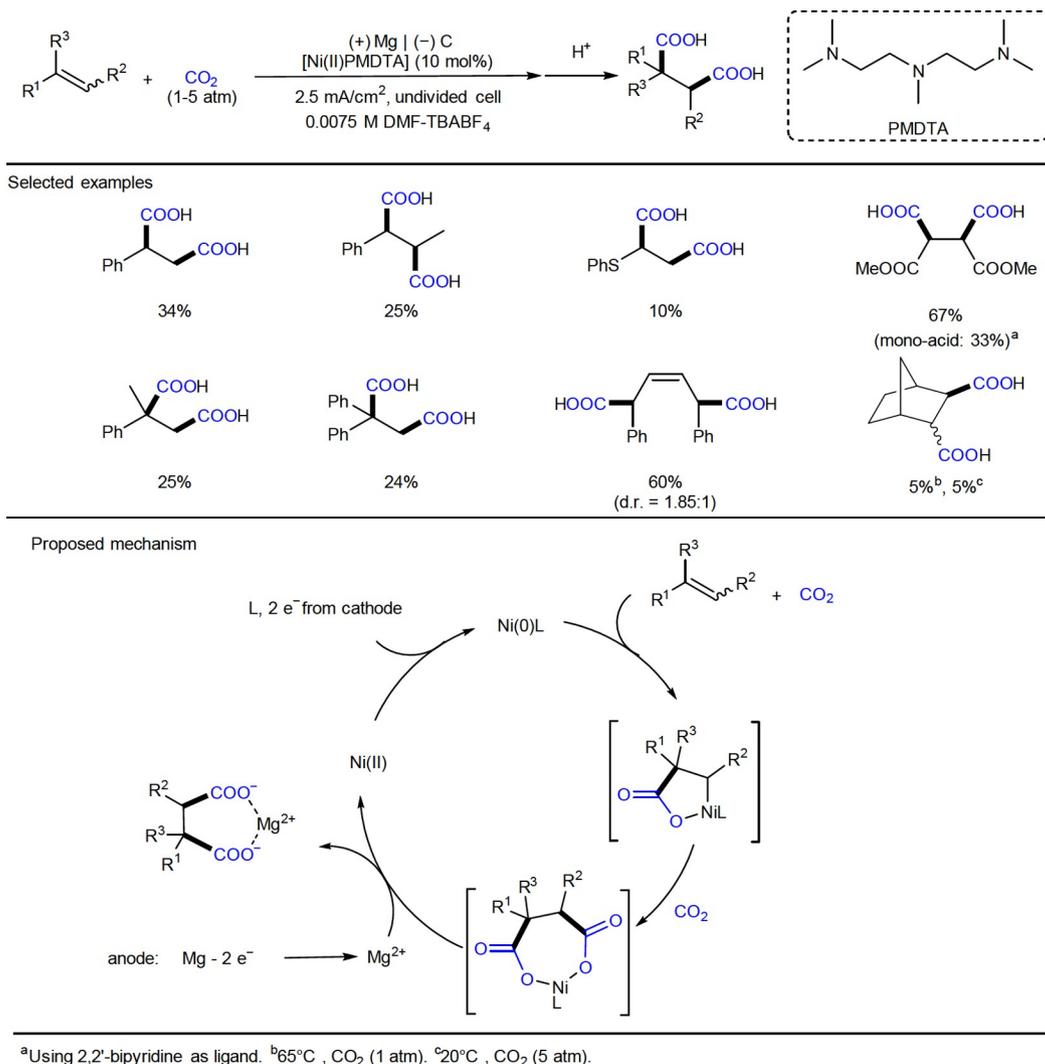


Figure 3 Electrochemical dicarboxylation of activated alkenes.

In 2001, Senboku, Tokuda, and co-workers [22] demonstrated an efficient electrochemical dicarboxylation of phenyl-substituted alkenes, providing various substituted succinic acids (Figure 5). In comparison with Duñach's work [21], they employed a direct electrolysis system equipped with platinum (Pt) cathode and sacrificial magnesium (Mg) anode at -10°C , obtaining much more optimizing conversion and yields because of the removal of Ni-catalyst and resulting in fewer monocarboxylic acids. It is noteworthy that tri-substituted styrenes derivatives could also be tolerated in this system, obtaining the desired products in moderate to good yields. However, the type of substituents on the alkenes is rarely investigated. The cyclic voltammetry (CV) test of styrene showed a reduction peak at $-2.58 \text{ V vs. Ag/Ag}^+$, whose potential was slightly more negative than that of CO_2 ($-2.53 \text{ V vs. Ag/Ag}^+$) [23]. Therefore, they proposed two possible mechanisms involving the generation of CO_2 radical anion or olefin radical anion. In path a, CO_2 radical anion would add to styrenes bearing electron-donating groups (EDGs) and electron-neutral groups. While for styrenes with EWGs, it was preferentially reduced at the cathode to give olefin radical anion, which then attacked CO_2 to generate a carboxylated benzyl radical (path b). Further SET reduction delivered carbanion species, which would attack another CO_2 to afford dicarboxylates and followed by acidification to give the final diacids.

Different from Senboku and Tokuda's work using expensive Pt cathode, in 2008, Jiang and co-workers [24] reported another electrochemical dicarboxylation to provide aryl succinic acids at room temperature by using non-noble metal Ni as cathode and aluminum (Al) as sacrificial anode (Figure 6A). Concerning the electronic influence of substituents on arene-, styrenes with EDGs or EWGs were all reactive under such mild conditions. Meanwhile, it is not surprising that styrenes bearing aryl C-Cl bond and alkenyl C-Br bond could undergo direct carboxylation as well as reductive cleavage and following dicarboxylation under such strong reductive conditions. As for the mechanism, it was analogous to the above. In 2007, Lu and co-workers [25]



^aUsing 2,2'-bipyridine as ligand. ^b65°C, CO₂ (1 atm). ^c20°C, CO₂ (5 atm).

Figure 4 Ni-catalyzed electrochemical dicarboxylation of activated alkenes.

employed titanium (Ti) as cathode and Mg as a sacrificial anode to synthesize aryl succinic acids in good yields with styrenes and CO₂ as the starting materials (Figure 6B).

Compared with the electrochemical dicarboxylation of multi-substituted alkenes with CO₂, only a few reports have reported on the electrochemical dicarboxylation of ethylene with CO₂. In 1973, Silvestri and co-workers [26] reported the dicarboxylation of ethylene with CO₂ to produce succinic acid (Figure 7). In this work, no succinic acid was produced when CO₂ was at one atmospheric pressure and ethylene was at 2.5 atm. When the pressure of CO₂ was increased to 14 atm and the pressure of ethylene was adjusted to 0.5 atm, the yield of oxalic acid could increase but slightly improved the yield of succinic acid. Increasing the pressure of CO₂ to 4.8 atm and ethylene to 24.2 atm effectively promoted the formation of succinic acid. Although the reaction was still limited to the millimole level, it has guided significance for us to realize its large-scale application.

Besides electrochemical dicarboxylation of activated acrylates and styrenes, other bulk chemicals, such as

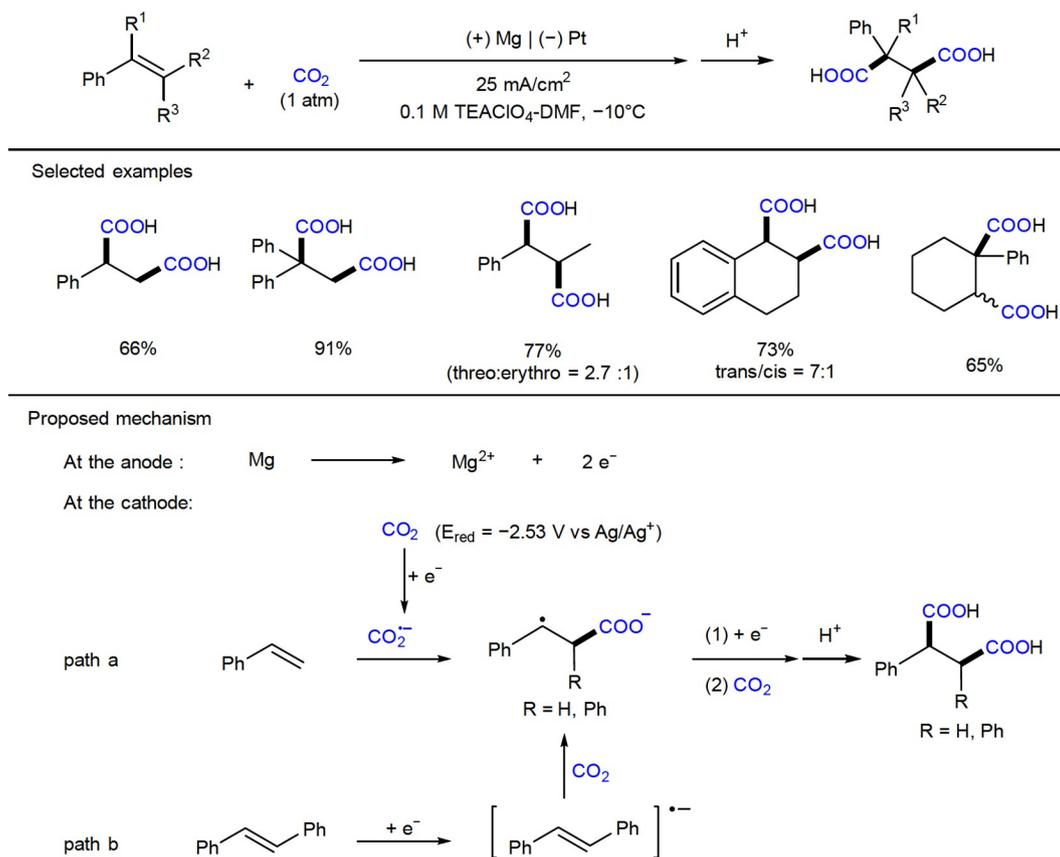


Figure 5 Electrochemical dicarboxylation of phenyl-substituted alkene.

1,3-butadiene, propene, and 1-propene, have also attracted much attention to the field of dicarboxylation with CO_2 . In 2000, Ballivet-Tkatchenko and co-workers [27] established an electrocatalytic dicarboxylation method of styrenes and isoprene with employed mercury (Hg) as cathode and Al as a sacrificial anode. In this reaction, $[\text{CpFe}(\text{CO})_2]_2$ was reduced to bind CO_2 due to its electron-abundance, generating CO_2 radical anion to provide dicarboxylic acid products at a less negative reductive potential (Figure 8A). Besides styrenes, the unactivated isoprene was also reactive, albeit with tough-to-control selectivity of tautomerization, which might be caused by β -H elimination of the adduct of transition-metal complex and radical intermediate. In 2001, Dinjus and co-workers [28] realized electrochemical dicarboxylation of 1,3-butadiene with CO_2 , equipped with Ta as cathode and Mg as a sacrificial anode (Figure 8B). With the addition of NiN3 (2,4,4-trimethyl-1,5,9-triazacyclododecene nickel(II) tetrafluoroborate) mediator, which might cause oxidative cycloaddition to decrease required reductive potential, the coupling products of 1,3-butadiene could be suppressed and high yields of dicarboxylic acids were obtained. Moreover, in 2017 the Schindler group [29] also employed another Ni complex as an electron mediator to furnish the 1,4-dicarboxylic acids under the same electrochemical conditions (Figure 8C).

Although the above-mentioned work has resolved the reactivity of dicarboxylation with CO_2 , limitations still existed, including the low chemo- or regio-selectivity. In 2011, Jiang and co-workers [30] developed an electrochemical dicarboxylation of 1,3-diene and derivatives to synthesize unsaturated dicarboxylic acids in

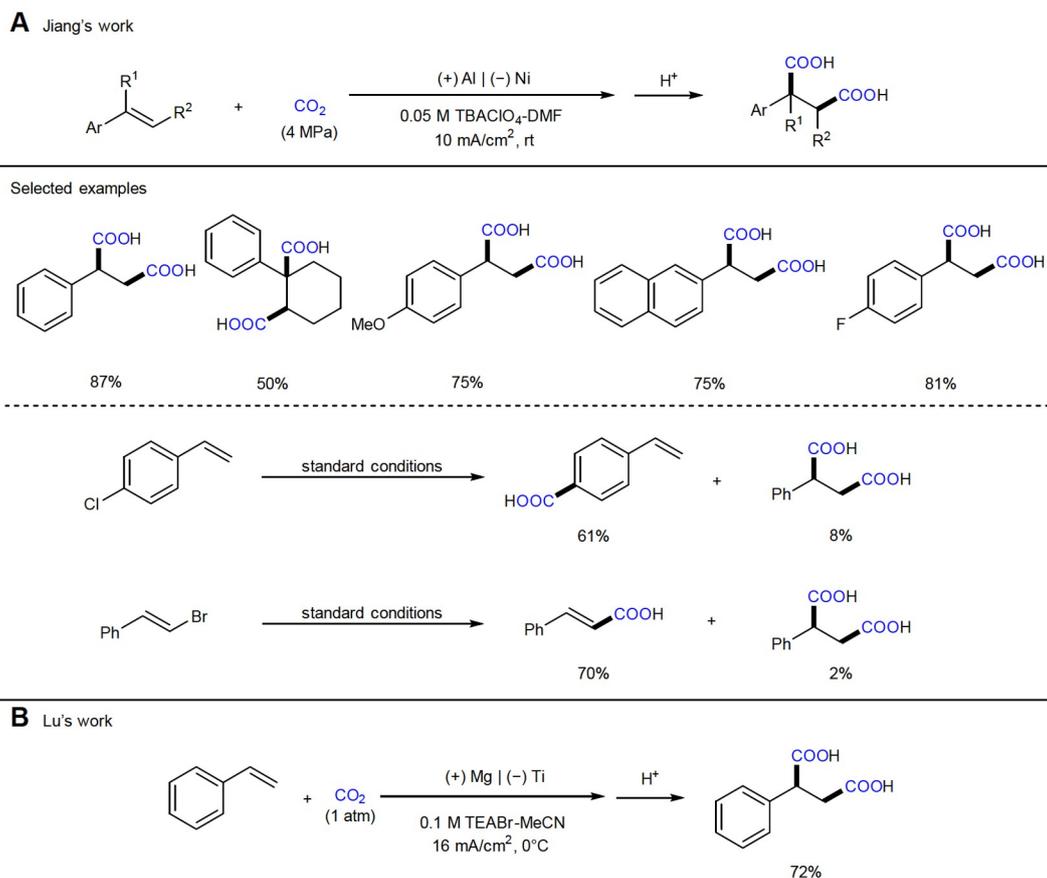


Figure 6 Electrochemical dicarboxylation of styrenes with different cathodes. (A) Jiang group's work; (B) Lu group's work.

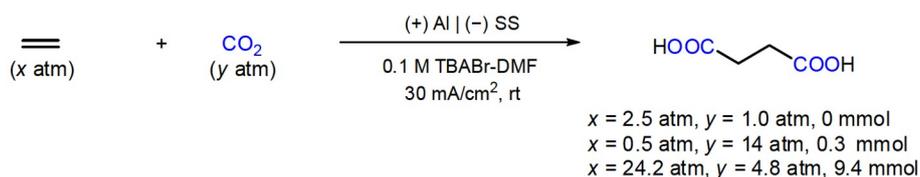


Figure 7 Electrochemical dicarboxylation of ethylene with CO₂.

high yield with high regioselectivity and *Z/E* selectivity (Figure 9). Sacrificial Al anode and easily available Ni cathode were utilized in tetrabutylammonium bromide-*N,N*-dimethylformamide (TBAB-DMF) electrolyte solution under 3 MPa of CO₂. However, 1,3-butadiene showed no *Z/E* selectivity, perhaps due to no steric hindrance on the alkene. It is noteworthy that the unsaturated dicarboxylic acids, such as 3-hexene-1,6-dioic acid, could undergo easy SET reduction, equipped with Ni cathode and Pt anode at 60°C in 3 F/mol electricity, to adipic acids, which is a key monomer of polymer Nylon 66.

Later, in 2013, De Vos and co-workers [31] also reported electrochemical dicarboxylation of a series of internal 1,3-dienes with CO₂, obtaining desired diacids in moderate to high yields by employing sacrificial Mg anode and Ni cathode under 5 bar of CO₂ atmosphere (Figure 10A). Due to the gradual consumption of sacrificial anode, it hindered a continuous process and lowered atom efficiency usually. De Vos and co-

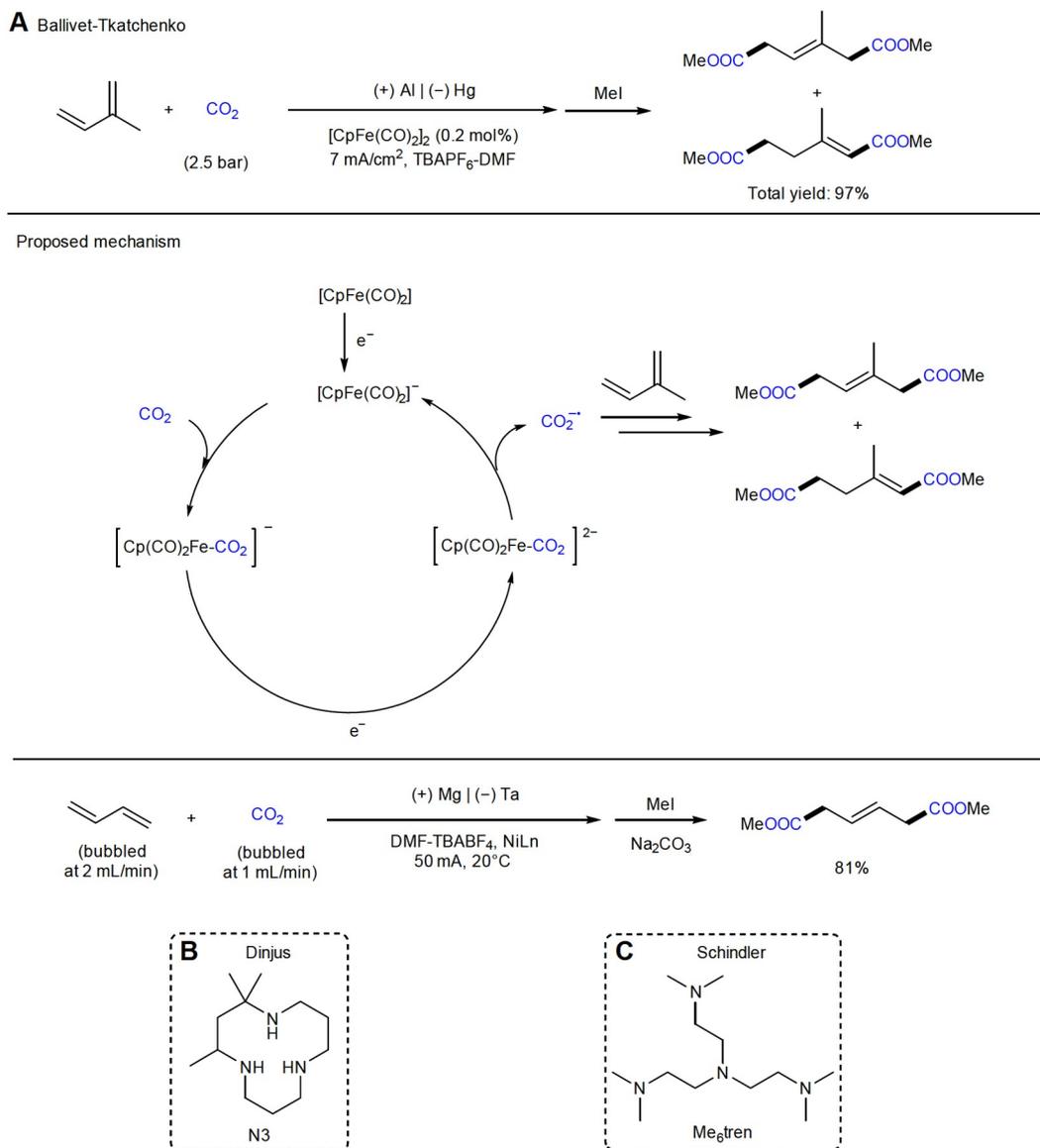


Figure 8 Electrochemical dicarboxylation of 1,3-dienes with TM-complex mediator. (A) Ballivet-Tkatchenko group's work; (B) Dinjus group's work; (C) Schindler group's work.

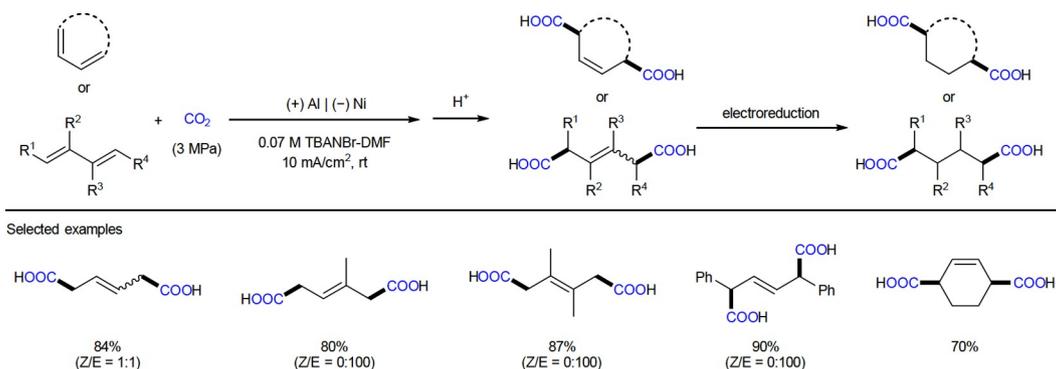


Figure 9 Electrochemical dicarboxylation of 1,3-dienes with non-noble cathode Ni.

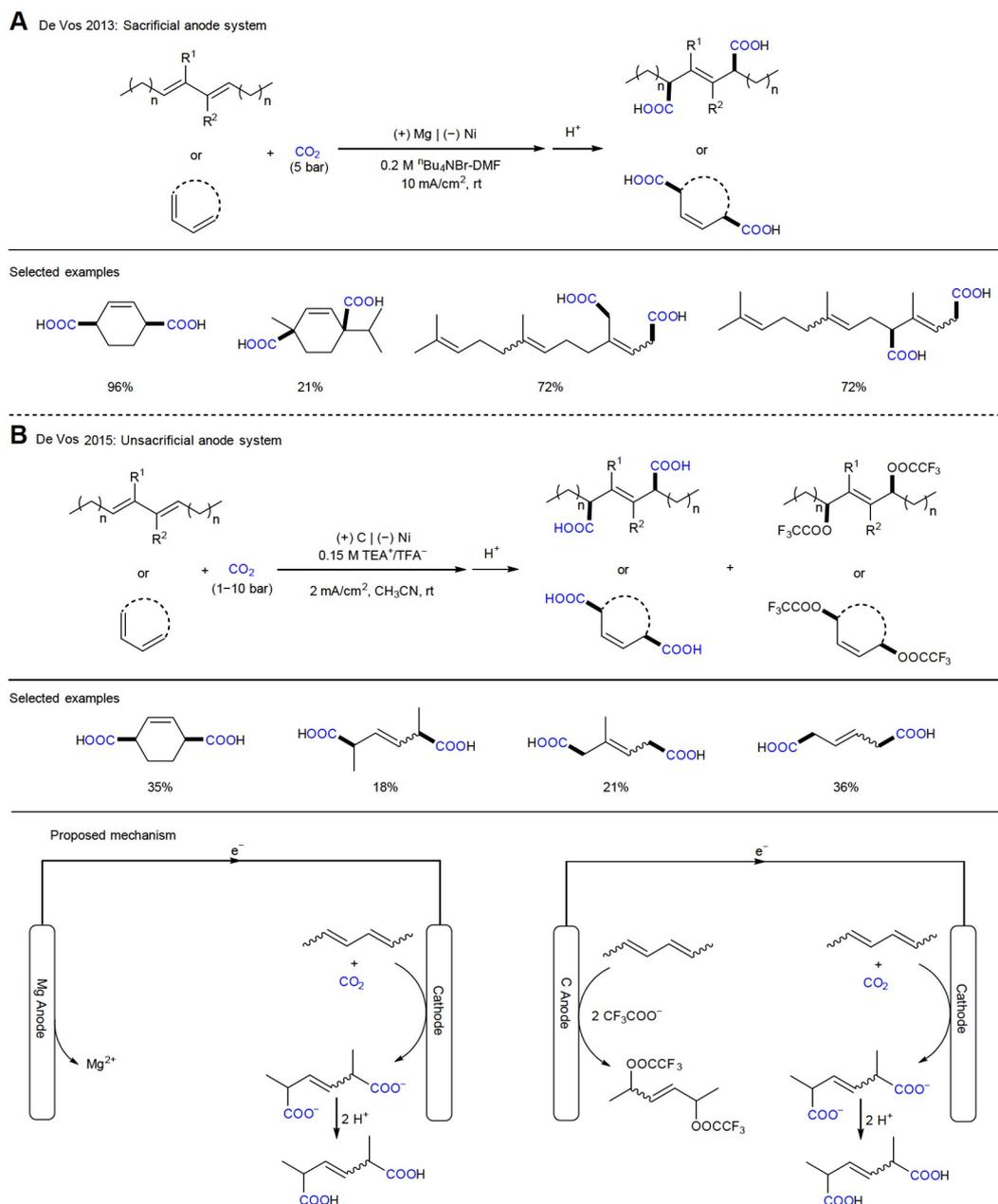


Figure 10 Electrochemical dicarboxylation of 1,3-dienes with CO₂ in sacrificial system and unsacrificial system. (A) De Vos group's work: Sacrificial anode system; (B) De Vos group's work: Unsacrificial anode system.

workers [32] further developed a paired electrosynthesis of dicarboxylation with CO₂ employing non-sacrificial graphite anode and Ni as the cathode (Figure 10B). Notably, the sequential cathodic carboxylation is paired with simultaneous anodic acetylation of conjugated alkenes with trifluoroacetate (TFA) salt in the undivided cell, resulting in the formation of dicarboxylate salts and diacetate esters, respectively. These elegant studies demonstrated a new avenue for further application in industrial continuous use of electrochemical synthesis of dicarboxylic acids with CO₂.

Generally, the electrochemical dicarboxylation of alkenes always confronts undesired processes, such as

direct reduction of alkene, monocarboxylation, and dicarboxylation with desired regioselectivity. Despite early progress on dicarboxylation of alkenes with CO₂ has overcome some of the above difficulties, unsacrificial system still needs further exploration with the requirement for enhancement of efficiency and selectivity. In the last few years, challenging unordinary selectivity control has also gradually attracted chemists. Nam group [33] had realized the hydrocarboxylation using a sacrificial anode system in the presence of water as a proton source. Very recently, this limitation with the use of sacrificial anode was overcome by Buckley and co-workers [34], who developed the non-sacrificial electrochemical system, realizing hydrocarboxylation reaction of activated alkenes. Yu and co-workers [35] also realized the electrochemical Ni-catalyzed carboxylation of unactivated aryl halides with the non-sacrificial system. Though the dicarboxylation products were detected as side products in Buckley's work, it provided a direction to achieve the dicarboxylation of alkenes in increased chemo-selectivity under this non-sacrificial electrochemical system, which might also represent a further application in industrial production.

Electrochemical dicarboxylation of alkynes with CO₂

In 1989, Duñach and co-workers [36] reported the dicarboxylation of internal alkynes with CO₂ via Ni catalysis (Figure 11). This reaction used Ni(bipy)₃(BF₄)₂ as a catalyst, metal Mg as a sacrificial anode, and carbon fiber as a cathode. The alkynes bearing strong EWGs could be suitable for this dicarboxylation to give desired products in good yields. However, those alkynes, which are not electron-deficient enough, usually generated monocarboxylic products with poor selectivity, including *Z/E* selectivity and regioselectivity. It might be the polarization of the triple bond influencing the second carboxylation with CO₂.

After the exploration of dicarboxylation of internal alkynes, Duñach and co-workers [37] continued endeavoring dicarboxylation of enynes and terminal alkynes with CO₂. Specifically, they found that the utilization of Ni(bpy)₃(BF₄)₂ as the catalyst under electrochemically reductive conditions allowed for the generation of Ni(0), which triggered a regioselective metalation followed by subsequent two CO₂ insertions to afford the diacids in a low yield with employing sacrificial Mg anode and Ni cathode. It was until 2008 that

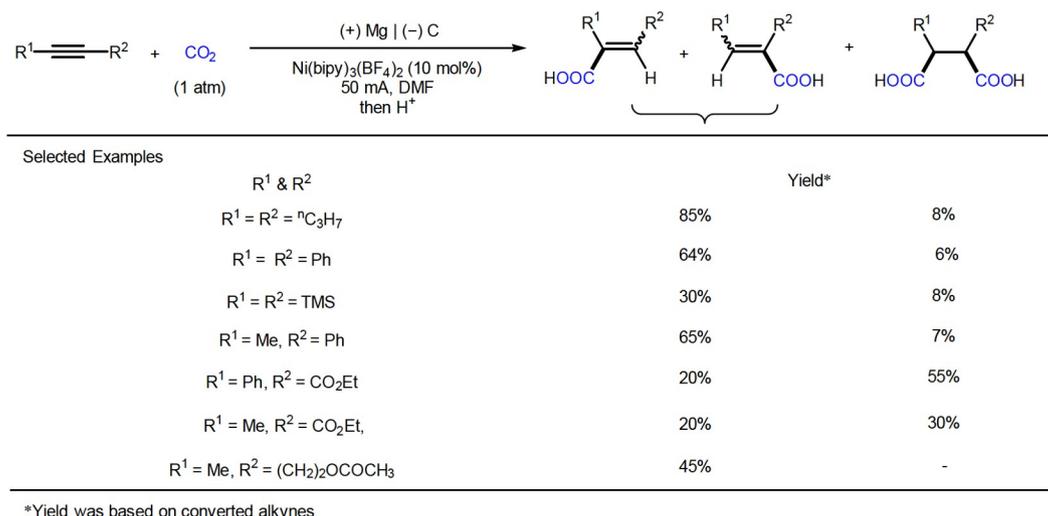


Figure 11 Electrochemical Ni-catalyzed dicarboxylation of alkynes with CO₂.

the successful electrochemical dicarboxylation of arylacetylenes was reported by Jiang and co-workers [38], which was equipped with Ni cathode and sacrificial Al anode in TBAB-DMF solution at constant current under 3 MPa of CO₂ atmosphere at room temperature, affording aryl-maleic anhydride as major product under milder conditions (Figure 12). Interestingly, water seems significant for the control of chemoselectivity, which would promote the generation of aryl succinic acids in the system. Mechanistically, the aryl acetylenes could be transformed into monocarboxylate radical intermediate via either addition of CO₂ radical anion to alkynes or nucleophilic attack on CO₂ by an alkyne radical anion in the absence of water. Further SET reduction process and dehydration cyclization delivered the aryl-maleic anhydride. While in the presence of water, due to the introduction of proton source, the arylacetylenes would undergo reduction and protonation process to form arylethene via either of the above pathways.

Continuing their research on electrochemical carboxylation of arylacetylenes with CO₂, in 2010 Jiang and co-workers [39] further demonstrated tricarboxylation of arylacetylenes in the presence of CuI catalyst employing sacrificial Al anode and Ni cathode. Initiated by the reduction of CO₂ or alkynes, it would

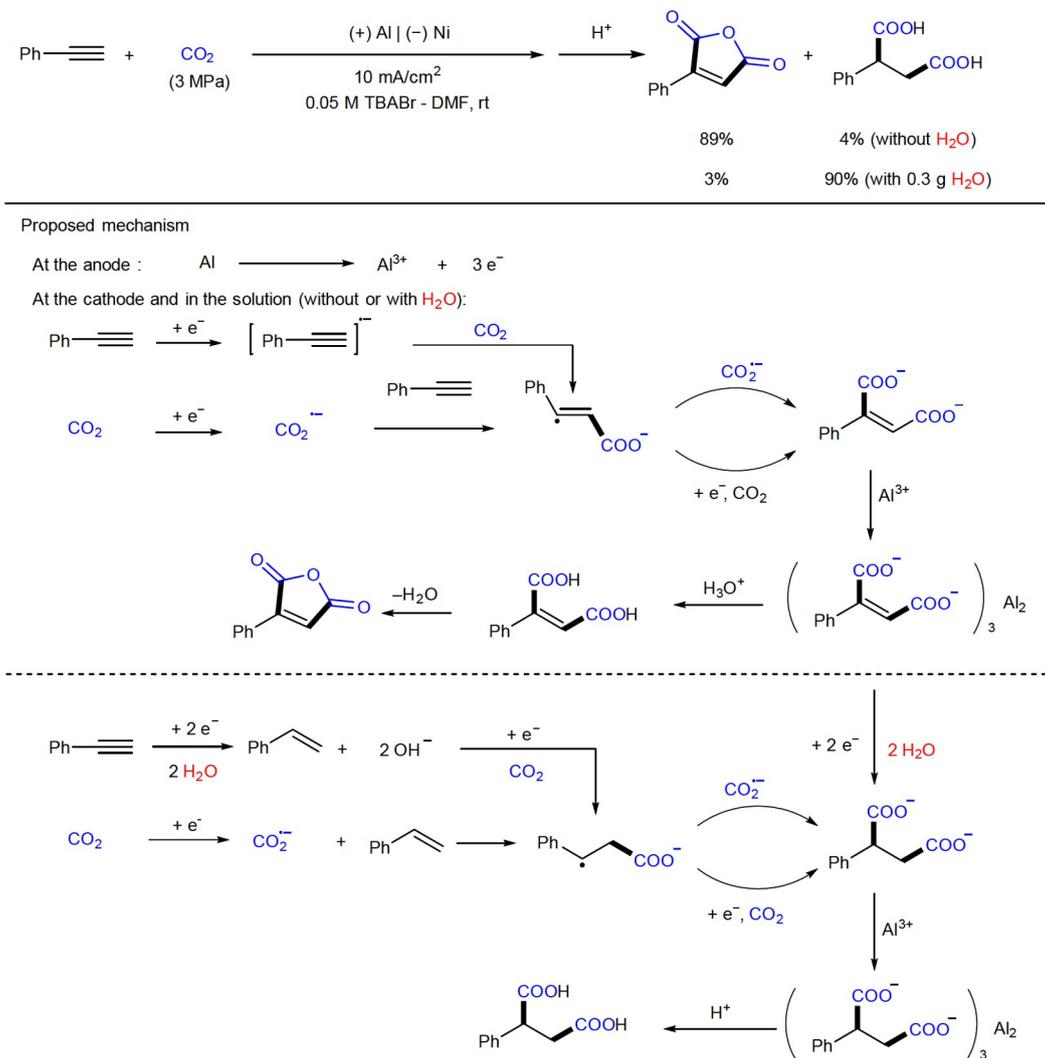


Figure 12 Electrochemical dicarboxylation of arylacrylates with CO₂.

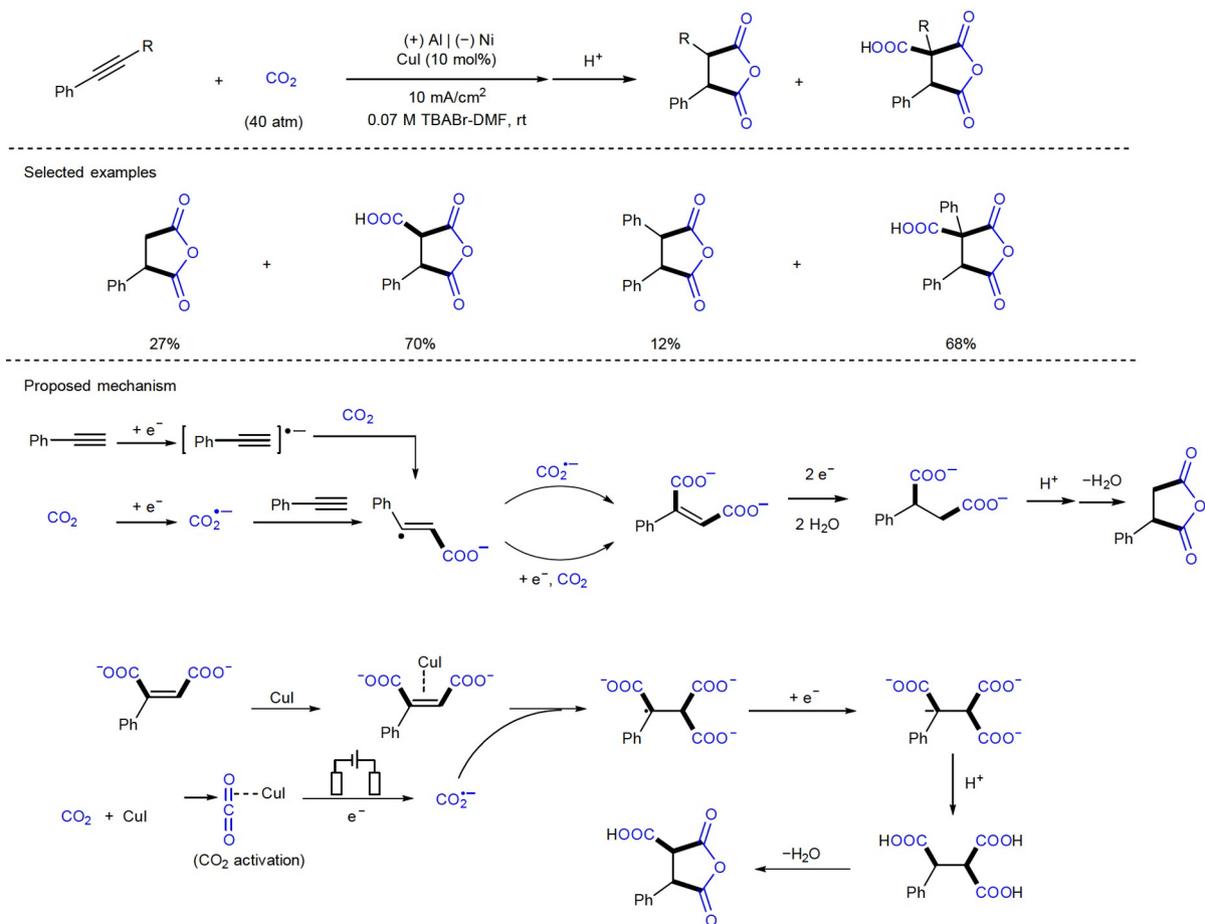


Figure 13 Electrochemical Cu-promoted dicarboxylation and tricarboxylation of arylacetynes with CO₂.

generate dicarboxylic alkene as the key intermediate (Figure 13). As the coordination of CuI with dicarboxylated alkene might lower electron-density on the alkenyl group and CO₂, the final CO₂ radical anion addition on dicarboxylic alkene intermediate could be more polar-matched and facile to generate tricarboxylation products in comparison with the above work. Besides, the coordination of CuI might also result in an easier reduction and being captured by water, to avoid the generation of the undesired aryl succinic anhydrides.

Subsequently, in 2013, Yuan, Jiang, and co-workers [40] further reported dicarboxylation of 1,3-diyne in the presence of CuI catalyst employing sacrificial Al anode and Ni cathode (Figure 14). Initiated by the direct reduction of the alkynyl group or CO₂ to give corresponding radical anions, the *in situ* generated alkenyl-diradical intermediate would coordinate with Cu(I) catalyst to produce π -allylic copper species, which then underwent intramolecular cyclization to afford final products after protonation.

In addition to the above-mentioned direct dicarboxylation of alkynyl group, Senboku and co-workers [41] also reported the cascade dicarboxylation of alkynyl group (Figure 15). Based on their previous cascade reaction about carboxylation with CO₂, they employed Pt as cathode and Mg as sacrificial anode with 4-*tert*-butylbenzoate as an electron-transfer mediator in TBABF₄-DMF solution at -10°C. These reactions provided a variety of 5-membered and 6-membered (het)rings, albeit in moderate yields and diastereoselectivity ratio.

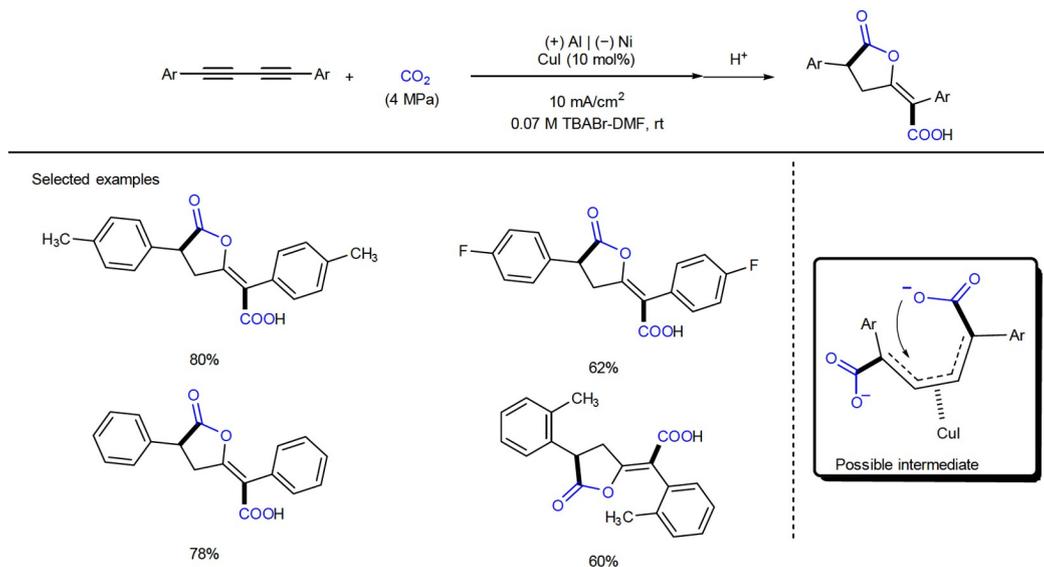


Figure 14 Electrochemical Cu-promoted dicarboxylation of 1,3-diynes.

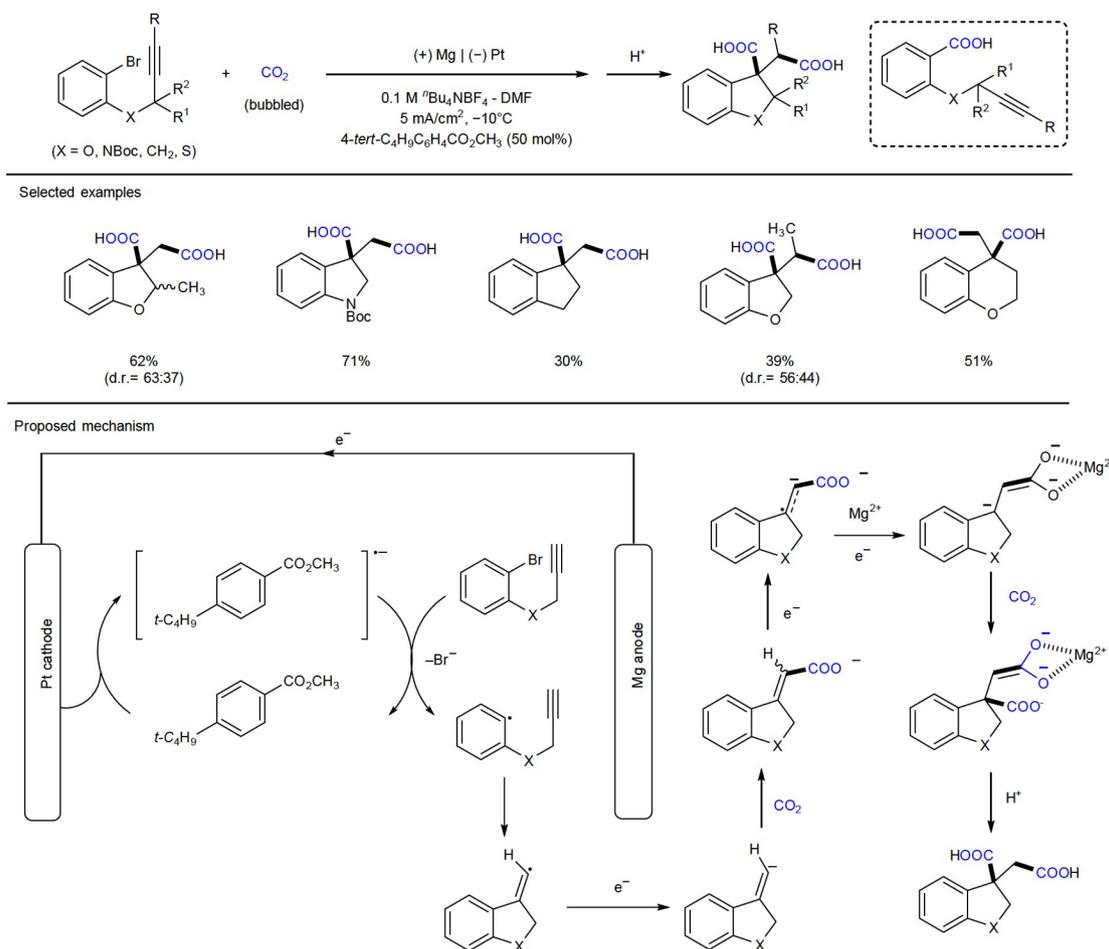


Figure 15 Electrochemical tandem dicarboxylation.

Initiated by the generation of aryl radicals, which are generated through a reduction step by the electron-transfer mediator and the release of bromide anions, the radical addition process would smoothly occur to form alkenyl radical species. After further SET reduction to generate alkenyl anion, which could cause nucleophilic attack on CO₂, the alkenyl carboxylates would be generated and undergo a SET reduction to dianion, which could be stabilized by Mg²⁺. The following attack on another CO₂ and a protonation process would finally deliver diacids. Based on their previous work, the electron-transfer mediator might decrease the reductive potential of the electric cell, avoiding over-reduction on the aryl bromide group generating benzoic acid, enhancing the selectivity of aryl radical cyclization to furnish the cascade product.

So far, the present electrochemical systems have indeed made contributions to the dicarboxylation of alkynes whether final dicarboxylic acids are saturated or not. However, internal alkynes, terminal alkynes, and 1,3-diynes in the above-mentioned work all required sacrificial anode systems to furnish target products. Solving the non-economic electrochemical system with high efficiency to produce target products would be a challenge and hit an issue.

Electrochemical dicarboxylation of arenes with CO₂

In 2010, Yuan and co-workers [42] further reported electrochemical dicarboxylation of fused arenes with CO₂ to give dicarboxylic acids in good yields with *trans*-selectivity (Figure 16). The configuration of final diacids might be contributed to the steric hindrance of the conjugated system and the repelling force between two carboxylates.

Carboxyl-substituted heteroaromatics are extremely used in medicine. Recently, Maeda, Mita and co-workers [43] have provided a highly reductive electrochemical condition, realizing dearomative dicarboxylation of heterocycles to get the carboxyl-substituted heteroaromatics, which can be potentially transformed into high value-added bioactive compounds (Figure 17). This reaction is compatible with indole, (benzo)-furan, (benzo)thiophene, and pyrazole derivatives. Notably, this strategy could be applied for octahydroindole-2-carboxylic acid (Oic) derivative synthesis. This work also uses magnesium as a sacrificial anode. Mechanistic studies indicate that SET reduction of CO₂ or substrate is the key step in the reaction.

Following significant efforts by several groups, many activated unsaturated compounds can undergo electrochemical reductive dicarboxylation with CO₂ to generate highly valuable diacids and derivatives. Yet, the substrate scope remains limited: the successful dicarboxylation of unactivated unsaturated compounds, including alkyl alkenes, alkyl alkynes, and benzene, is highly anticipated. In general, the dicarboxylation with CO₂ is realized by using sacrificial anodes, which calls for exploring electrochemical systems with unsacrificial anodes in the field. In our view, the primary task of electrochemical dicarboxylation with CO₂ is to develop a suitable non-sacrificial anodic reaction, matching high-value added oxidized products with the reduced carboxylation even dicarboxylation acids. In an ideal world, the dicarboxylation with CO₂ would only use water oxidation as the anodic reaction or other more valuable anodic reaction.

Photocatalytic dicarboxylation of unsaturated substrates with CO₂

Photocatalysis is an important part of sustainable chemistry, which has gradually become a powerful tool in synthetic organic chemistry due to its availability, safety, and environmental friendliness. With great efforts

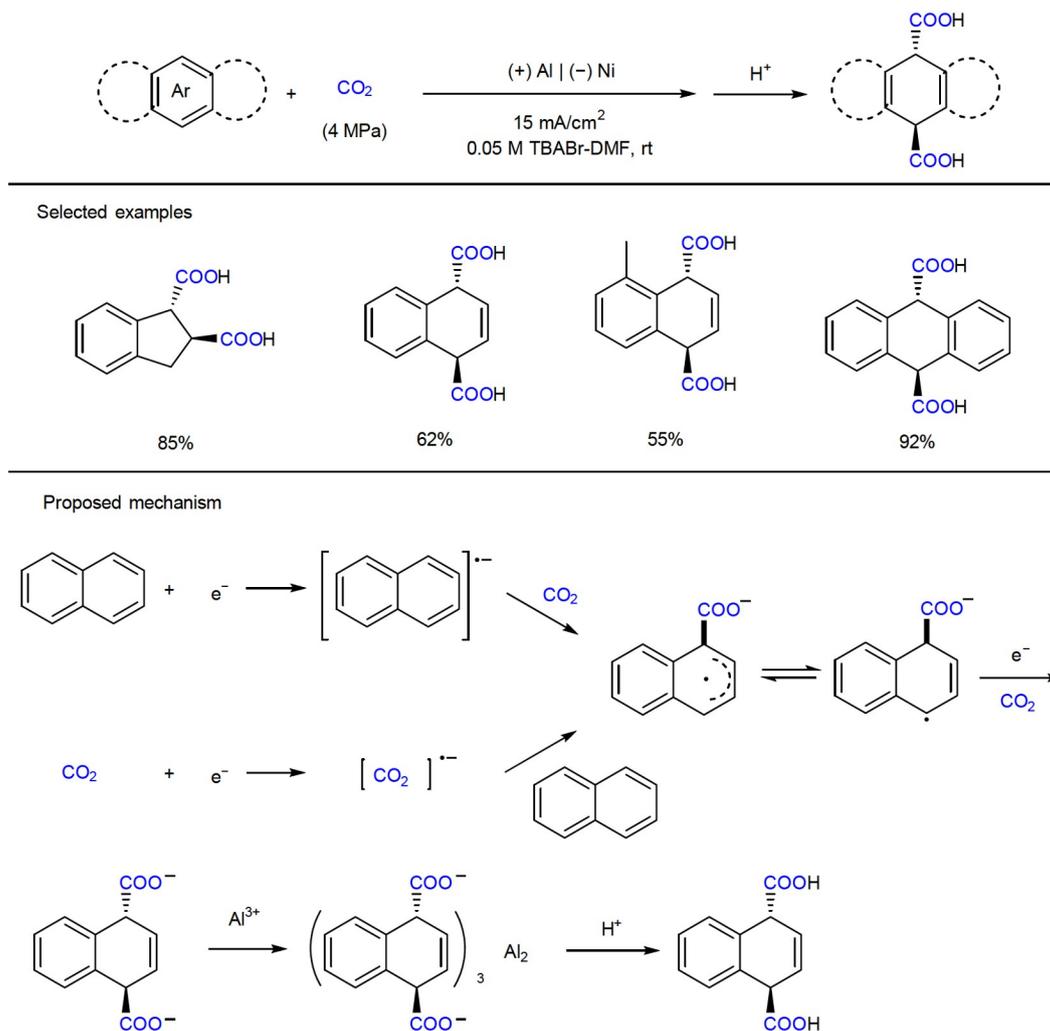


Figure 16 Electrochemical dicarboxylation of fused arenes with CO₂.

from many groups, much progress has been made in the development of carboxylation with CO₂ via photocatalysis to form diverse carboxylic acids [44–50]. However, there are still significant challenges to the development of photocatalytic dicarboxylation of unsaturated substrates with CO₂, which arise from the low reactivity of CO₂ and other competing side reactions. In this section, we cover the examples of dicarboxylation of unsaturated substrates with CO₂ through photocatalysis.

In 1993, Kubiak and co-workers [51] reported the photocatalytic dicarboxylation of cyclohexene with CO₂ to generate succinic acid derivatives (Figure 18A). In this original report, they used tetrahydrofuran (THF) as solvent and [Ni₃(μ₃-I)₂(dppm)₃] as the photocatalyst, the latter of which could directly reduce CO₂ to CO₂^{•-} under the irradiation of ultraviolet light ($\lambda > 290$ nm). Moreover, they found carboxylate $\nu(\text{CO})$ bonds in the infrared (IR), which could indirectly indicate that the CO₂^{•-} was an important intermediate in these reactions. Although there was only one example of such dicarboxylation reaction, it delivered a new direction for further development of CO₂ activation. With great efforts, Jamison and co-workers reported the unique β -selective hydrocarboxylation of styrene with CO₂ under ultraviolet (UV) light in continuous flow in 2017

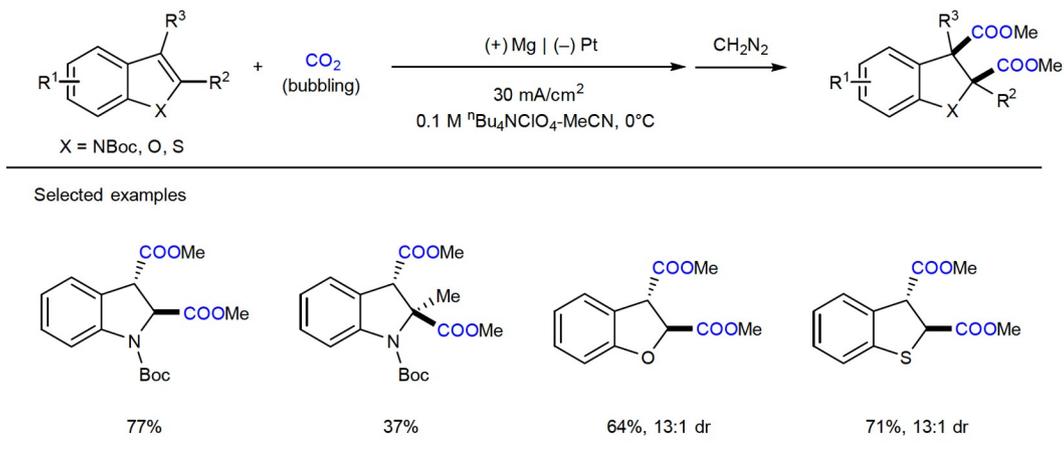


Figure 17 Electrochemical dicarboxylation of heteroarenes with CO₂.

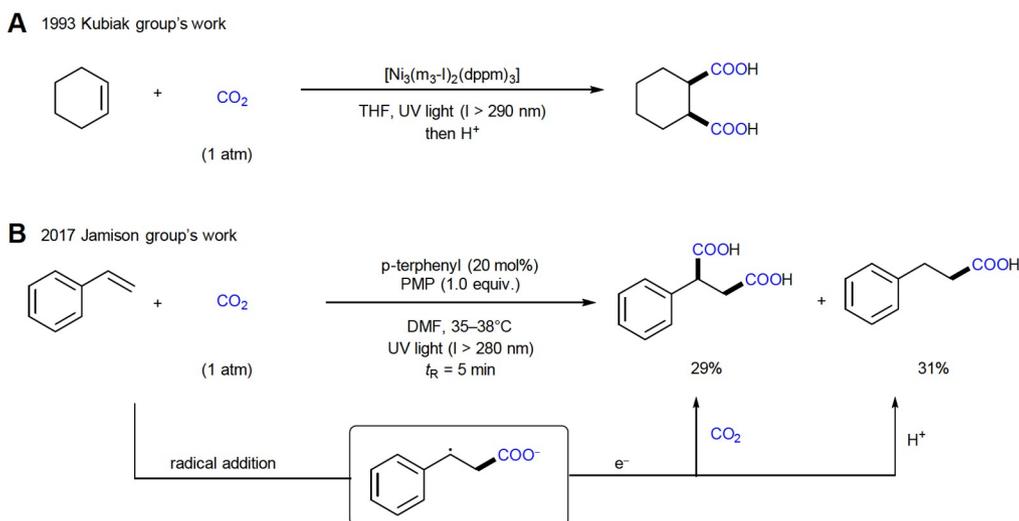


Figure 18 UV light-driven dicarboxylation of olefins with CO₂. (A) Kubiak group's work; (B) Jamison group's work.

(Figure 18B) [52]. In this case, the dicarboxylate products appeared as by-products, which could be obtained with a maximum yield of 29%, in which the amount of CO₂ or proton source determined the predominant selectivity of final products. Mechanistically, CO₂ was reduced to its radical anions, which would react with olefins to generate the corresponding products.

In addition to dicarboxylation of alkenes with CO₂, UV light-driven dicarboxylation of arenes with CO₂ has also been developed. In 1996, Neckers and co-workers [53] reported that a UV light-driven dicarboxylation of phenanthrene (PHN) with CO₂ produced *trans*-9,10-dihydrophenanthrene-9,10-dicarboxylic acid in 11% yield, along with hydrocarboxylation product as the major product (Figure 19). In this case, the yield of dicarboxylic acid decreased with the introduction of a proton source. Moreover, the reaction pathway changed according to the concentration of CO₂. When it increased to 50 atm, only a trace amount of the monoacid and diacid products were detected and the byproducts phenanthrene-9-carboxylic acid and 10-(4-(dimethylamino)phenyl)-9,10-dihydrophenanthrene-9-carboxylic acid became dominant. Based on the mechanistic investigation, the authors proposed that the key intermediate PHN^{•-} was generated from the SET reduction of photoirradiated PHN (PHN^{*}) with *N,N*-dimethylaniline (DMA). Moreover, the PHN^{•-} could also act as a reductant.

In contrast to previous work using UV light, Yu and co-workers [54] have recently reported the visible light photoredox-catalyzed dicarboxylation of activated alkenes and allenes with CO₂ via successive single electron transfer (SSET) reduction (Figure 20). Moreover, an impressive variety of (hetero)arenes also productively underwent the desired process to generate the dearomatization dicarboxylation products with

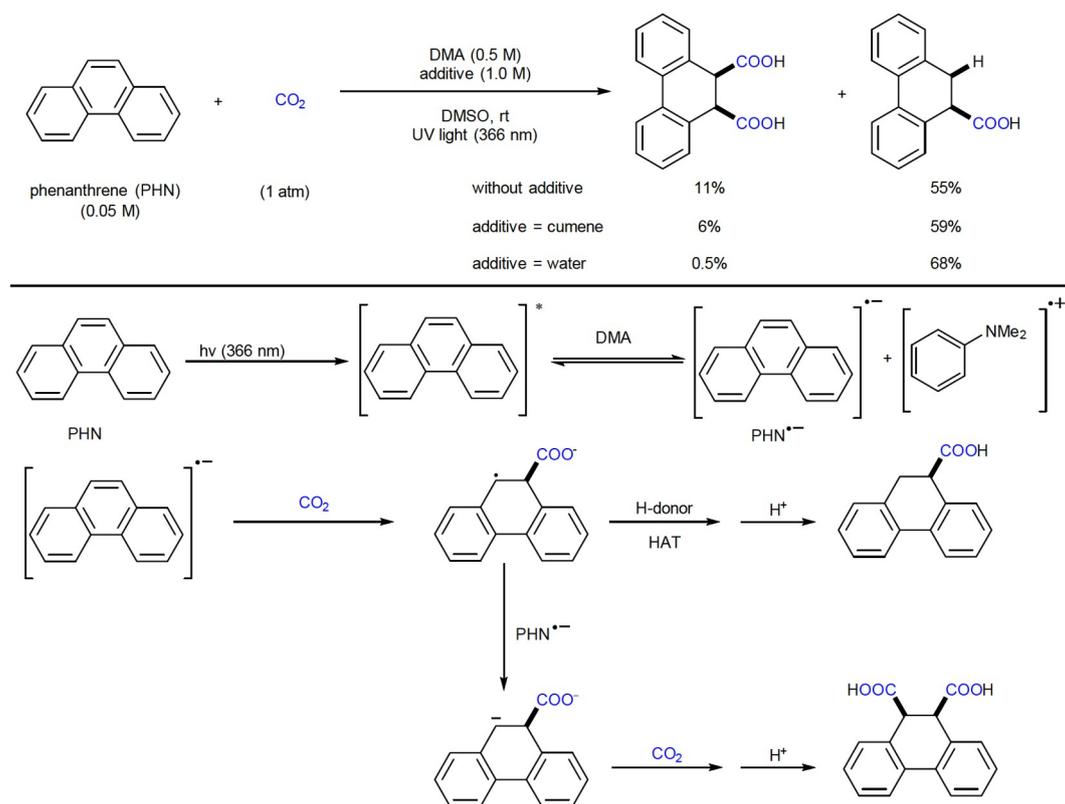
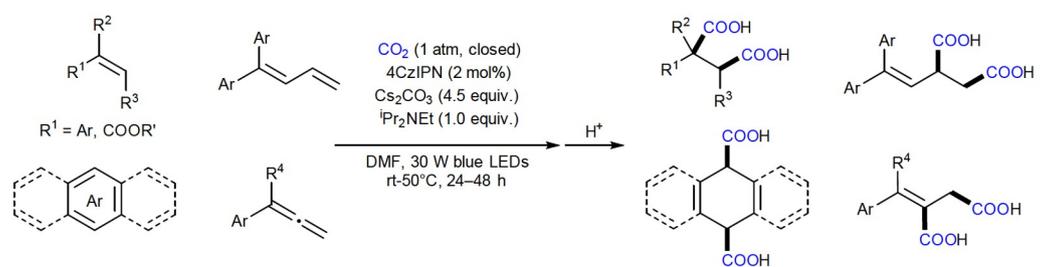
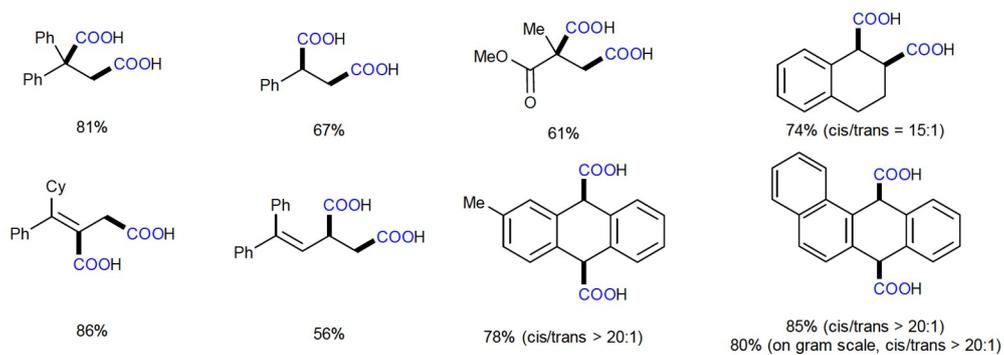


Figure 19 UV light-driven dicarboxylation of phenanthrene with CO₂.



Selected examples



Control experiments

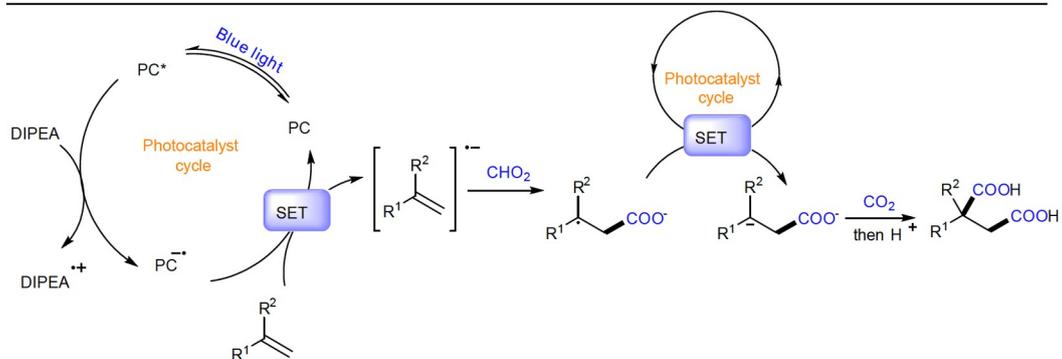
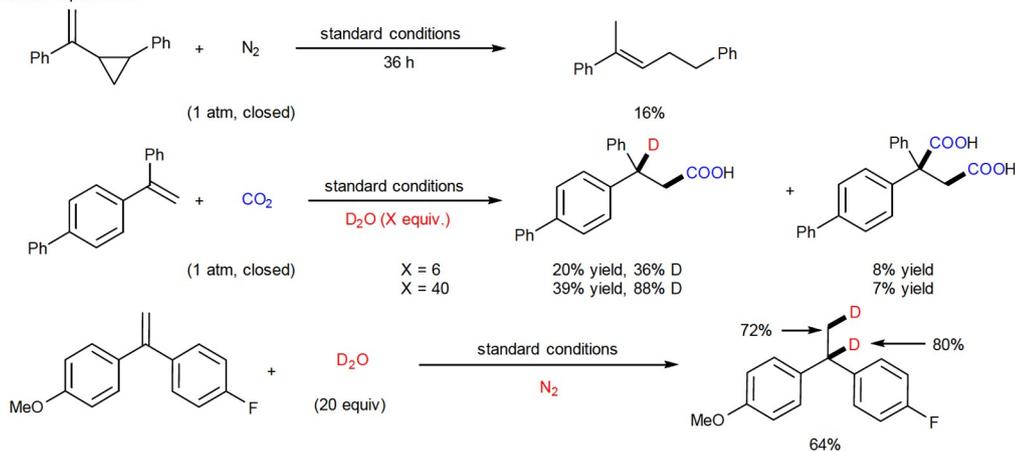


Figure 20 Visible-light photoredox-catalyzed dicarboxylation with CO₂.

high regio- and diastereoselectivity. Interestingly, the observed *cis*-diastereoselectivity of (hetero)arenes was opposite to the *trans*-selectivity under electrochemical conditions reported by Yuan *et al.* [42]. The radical clock experiment indicated that benzyl radical was involved and the deuterium-labeling control experiments suggested the benzylic carbanion was a reactive intermediate in this reaction. Furthermore, Stern-Volmer quenching studies and other control experiments indicated that alkene radical anion might be generated via the reduction of alkene. A possible mechanism for dicarboxylation of alkenes was shown as follows: the reaction might begin from the photoexcitation of the organic PC to produce the excited state species PC*, which underwent SET process with DIPEA to provide the reductant PC^{•-}. PC^{•-} would reduce the alkenes to generate alkene radical anions as the key intermediates, which then reacted with CO₂ to provide the carboxylated benzyl radical. The benzyl radical could undergo a similar SET process and following reaction with CO₂ to provide the target dicarboxylates. At the same time, the way to generate benzyl radical through the formation of CO₂^{•-} cannot be ruled out. This example strongly illustrated that visible light photoredox catalysis could be employed to construct functional diacids via either reducing CO₂ or substrates process.

Generally, it is of great significance to use CO₂ as the source of carboxyl to construct important diacids via photocatalysis. In reference to previous work, monocarboxylation, dimerization, or even polymerization under ultraviolet light or visible light would hinder the dicarboxylation. With great effort, a few examples have been reported. However, new methodologies and higher efficiency are still demanding, while the strategies for dicarboxylation of unactivated substrates in excellent reactivity and selectivity, such as industry alkenes and benzenes, still remain to be solved.

Metal-mediated/catalytic dicarboxylation of unsaturated substrates with CO₂

Metal-mediated/catalytic dicarboxylation of alkenes with CO₂

In the early research, Wright [55] used a stoichiometric amount of alkali metals, such as Na or K, to promote dicarboxylation of diphenylethene with CO₂ (Figure 21). As a strong reductant, the alkali metal would reduce the alkenes to their anion state, being stabilized by counter metal cation, which would attack CO₂ to generate dicarboxylates. The employment of stoichiometric alkali metal demonstrated the high reductive potential of alkene, which set an exploration barrier in this field.

Due to the high reductive potential of CO₂ and alkene, further investigation was not conducted until 1984. Hoberg and co-workers [56] discovered the Ni(TMEDA) (TMEDA = *N,N'*-tetramethyldiamine)-mediated dicarboxylation of 1,3-diene at -15°C to produce 1,6-dicarboxylic acid selectively (Figure 22A). Although a stoichiometric nickel complex was used, this work laid a solid foundation in this field. In this reaction, the

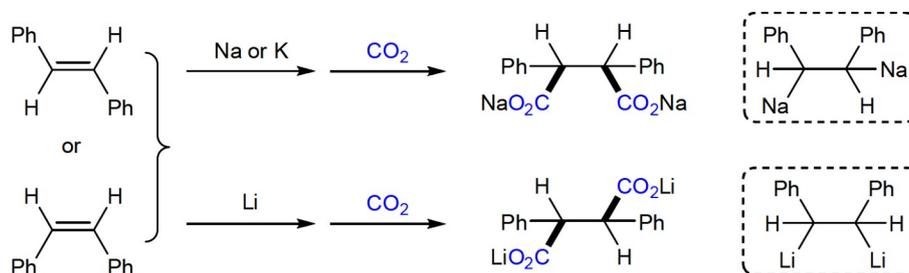


Figure 21 Alkali metal-mediated dicarboxylation of diphenylethene with CO₂.

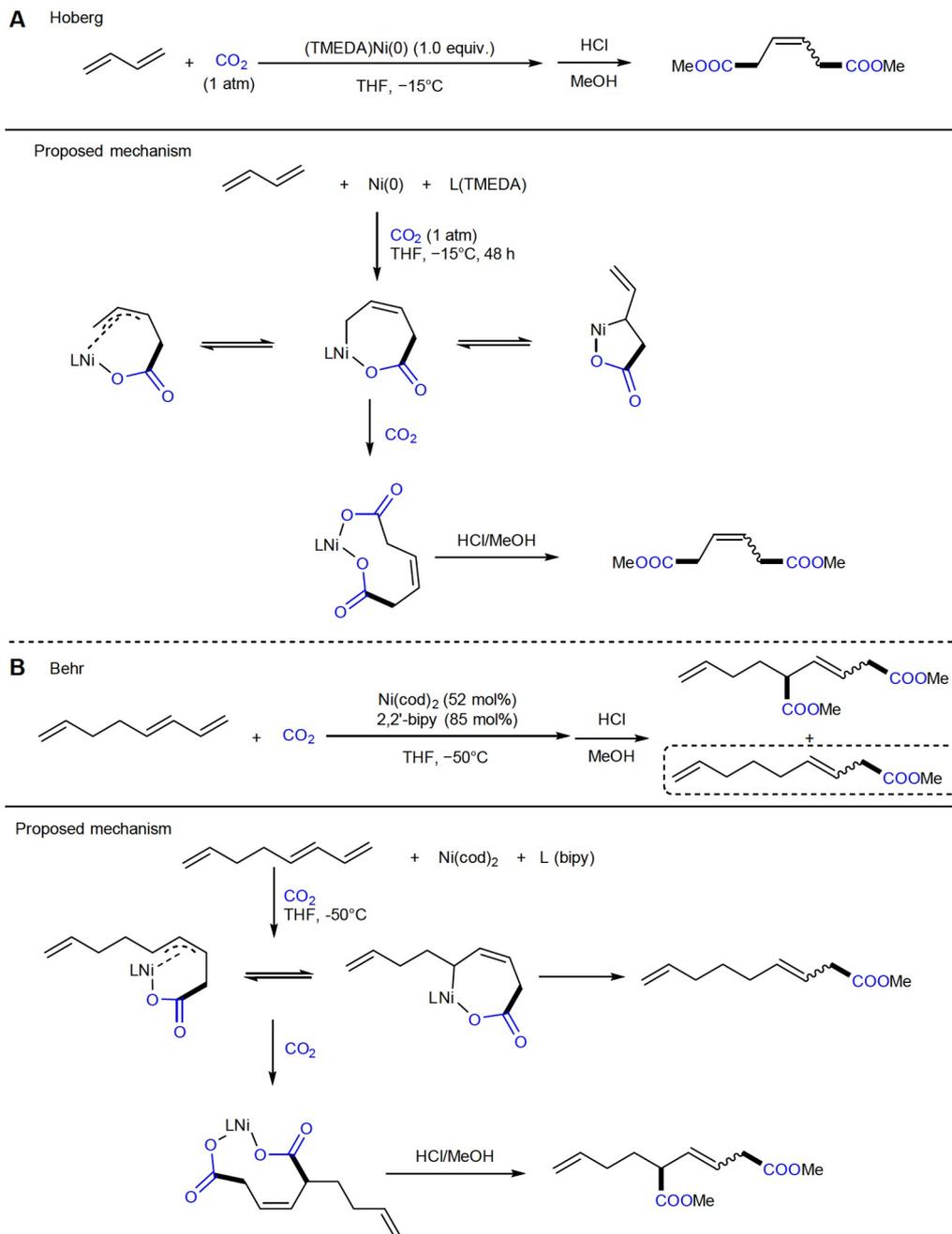


Figure 22 Ni complex-mediated dicarboxylation of 1,3-diene with CO₂. (A) Hoberg group's work; (B) Behr group's work.

oxidative metallacyclization of Ni complex with CO₂ and 1,3-diene would form a η -3 nickel cycle species, which undergoes insertion of another molecule CO₂ to form the desired dicarboxylate.

In 1986, Behr and co-workers [57] also reported that Ni(0) complex would prefer coordinating with 1,3-diene rather than the single alkenyl group, which is followed by oxidative metallacyclization to produce corresponding η -3 Ni complex (Figure 22B). The 1:2 ratio of mono/di-carboxylic ester generated in this protocol indicated that the nickel cycle species preferred the formation of dicarboxylate via a 9-membered

metalacycle pathway. Nonetheless, the *Z/E*-selective generation of 1,4-dicarboxylates from 1,3-diene had not been figured out until 2001. Mori and co-workers [58] employed $\text{Ni}(\text{cod})_2$ with Me_2Zn to realize the dicarboxylation of 1,3-dienes in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), affording (*Z*)-1,4-dicarboxylation products in moderate to high yields (Figure 23). It could be inferred from the *trans*-selective dicarboxylation of cyclohexadiene that the nickel cycle, which is generated via migrative insertion and transmetalation, may undergo a backside attack process instead of a 9-membered bulk cycle or reductive elimination, thus determining the specific figuration of the final product. However, when the Me_2Zn was replaced by Ph_2Zn , arylation carboxylation could be the major pathway. It indicated that steric hindrance determined whether backside attack or reductive elimination would occur first, in which bulky hindrances tended to experience reductive elimination (*vice versa*).

Although much progress has been developed in this area, the use of a (sub)stoichiometric metal complex was always necessary but unsatisfactory. It was not changed until 2018 that Martin and co-workers [59] reported the breakthrough of Ni-catalyzed dicarboxylation of 1,3-dienes with excellent regioselectivity and broad substrate scope. It was conducted with $\text{NiBr}_4(\text{TBA})_2$ catalyst, phenanthroline derivative as ligand, and Mn as reductant at 50°C (Figure 24). In addition, a catalytic hydrogenation strategy was applied to overcome *Z/E* selectivity issue to furnish aliphatic dicarboxylic acids. Though only an ambiguous mechanism was proposed in their protocol, the process may be initiated by the reduction of Ni(II) to Ni(0). Then the Ni(0) species would undergo oxo-metalacyclization to produce η -3 allylic Ni(II) species, which were reduced by

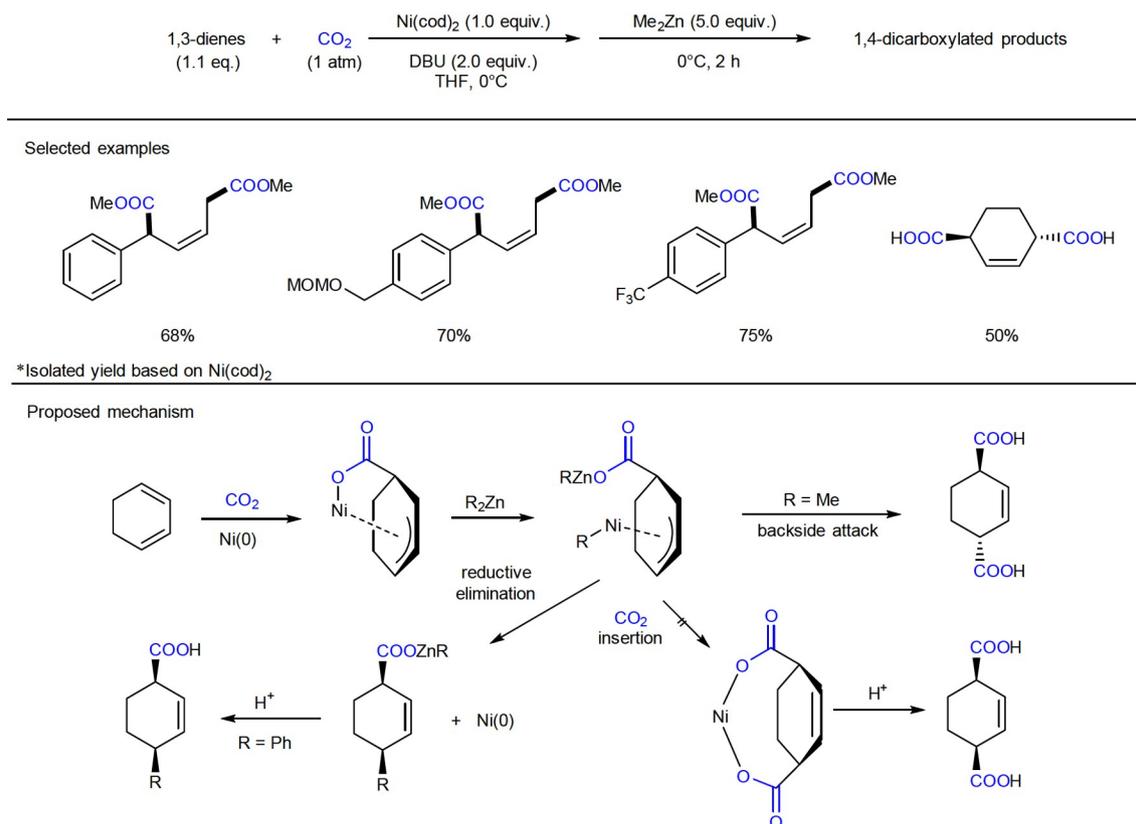


Figure 23 Ni(0) complex-mediated *Z*-selectivity dicarboxylation of 1,3-dienes with Me_2Zn and CO_2 .

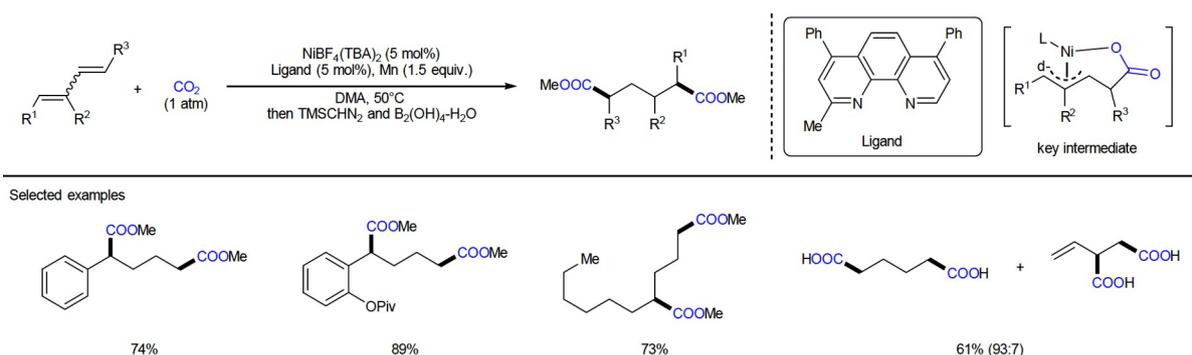


Figure 24 Ni-catalyzed dicarboxylation of 1,3-dienes with CO₂.

Mn to Ni(I). Due to the electron-abundance of Ni(I) species, the terminal site of η -3 allylic Ni(I) species was featured with smaller steric hindrance and latent nucleophilicity to attack another molecule CO₂ affording the dicarboxylated products. With the continuous reduction, Ni(I) was reduced to Ni(0) ending the whole catalytic cycle. Recently, the most favourable mechanism has also been calculated by Ahlquist, Yu, Fu, and co-workers [60].

Besides concentrating on 1,3-dienes, a few examples of dicarboxylation of ethylene with CO₂ have also been reported. Up to 1991, Hoberg and co-workers [61] reported that the methylmalonate could be formed from metallalactone via second CO₂ insertion under CO₂ atmosphere, albeit the use of stoichiometric metal complexes was necessary (Figure 25A). As described in the above photochemistry part, it could be a powerful tool for providing electron transfer pathway. Hence, recently, the elegant catalytic synthesis method for methylmalonic acid via dicarboxylation process of ethylene with CO₂ under metallaphotoredox system has been reported by Iwasawa and co-workers [62] (Figure 25B). The combination of [Ir]/DIPEA as the photocatalysis part not only provides electrons for Ni catalyst but also promotes isomerizing the five-membered nickelalactone ring into four-membered ring, in which the Ni–O bond length of five-membered ring would be elongated to dissociation. In addition, the photoirradiation would activate the latter ring to triplet excited state, which would be more advantageous for next insertion of CO₂ than ground state Ni catalyst referring to density functional theory (DFT) calculations.

Transition metal-catalyzed dicarboxylation of allenes with CO₂

During the period of 2001–2004, Mori and co-workers [63] contributed greatly to Ni-catalysed carboxylation of unsaturated substrates. Different from their previous work, in which β -H elimination or reductive elimination usually occurred, they reported a catalytic dicarboxylation of 1-trimethylsilylallenes with good *Z*-selectivity and regioselectivity (Figure 26). Followed by oxidative cycloaddition and transmetalation, the η -3 allylic nickel intermediate, characterized by the latent nucleophile, would attack another molecule of CO₂. After further transmetalation and reductive elimination, the Ni(0) can be regenerated to close the catalytic cycle. This reaction furnished a Ni-catalysed dicarboxylation of silylallene with good yield, chemoselectivity, and regioselectivity, albeit with trimethylsilyl substituent on the allene as a bulky group to control the reactive site, narrowing its synthetic application.

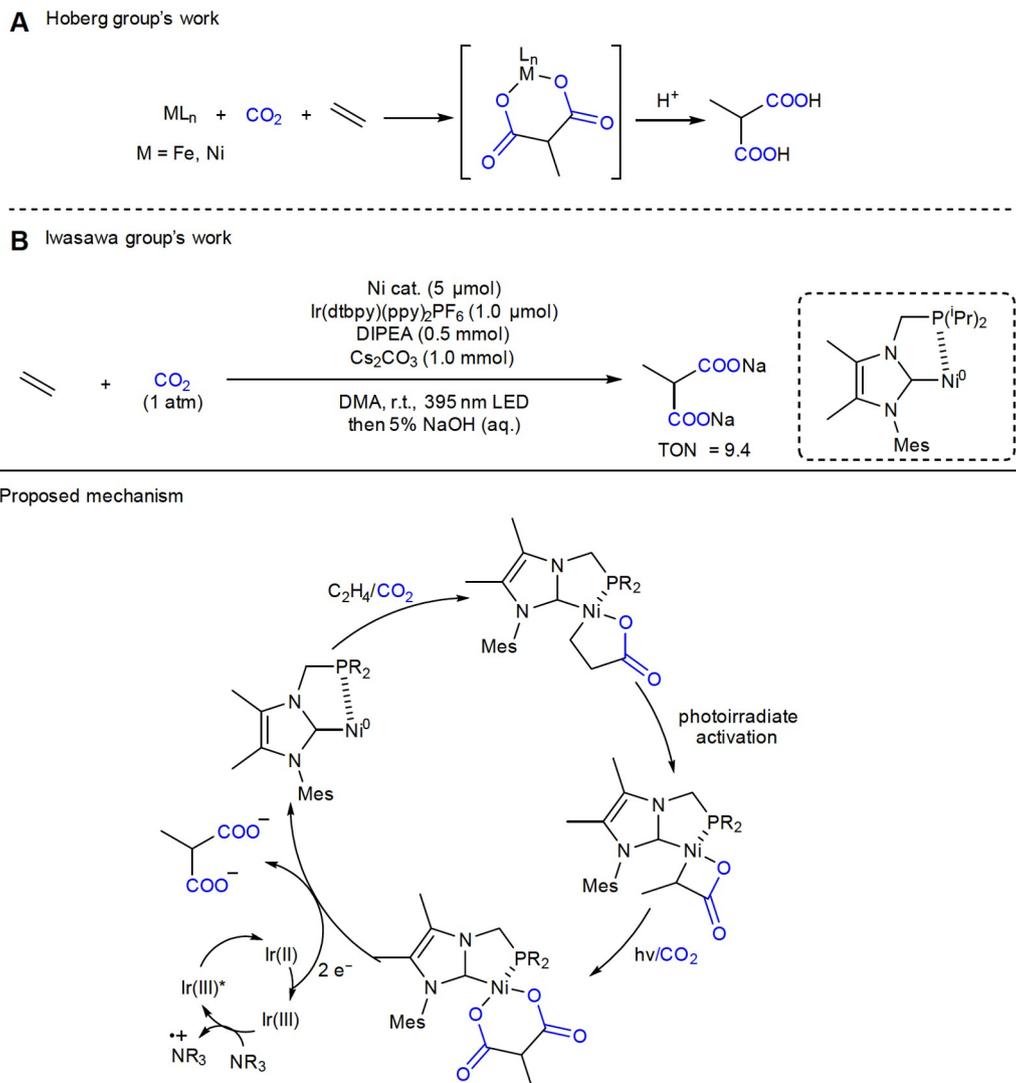


Figure 25 Dicarboxylation of ethylene with CO_2 . (A) Stoichiometric metal-induced dicarboxylation of ethylene with CO_2 ; (B) Ni-catalysed dicarboxylation of ethylene with CO_2 .

Transition metal-mediated/catalytic dicarboxylation of alkynes with CO_2

Up to 2012, Jang, Lee, and co-workers [64] presented the organic base-mediated dicarboxylation of acetylene, in which TBD- CO_2 complex played a key role as nucleophile in the transformation; meanwhile, the catalytic dicarboxylation of alkyne was realized by Sakaki, Tsuji, and co-workers in 2014 (Figure 27) [65]. This reaction employed Ni(II) as pre-catalyst with Zn as reductant, $MgBr_2$ as an additive in the presence of 3 Å molecular sieves in DMF solution under 1 atm of CO_2 . Followed by the reduction of Ni(II) to Ni(0), oxidative cycloaddition with CO_2 and alkyne to generate nickel cycle would occur. Later, it would be reduced by Zn with the help of $MgBr_2$ to generate Ni(I) species, which could attack another molecule of CO_2 due to its high nucleophilicity and potential coordination of CO_2 to Lewis acid $MgBr_2$. After further reduction, Ni(0) species was regenerated in company with target products. In this transformation, the $MgBr_2$, as a necessary

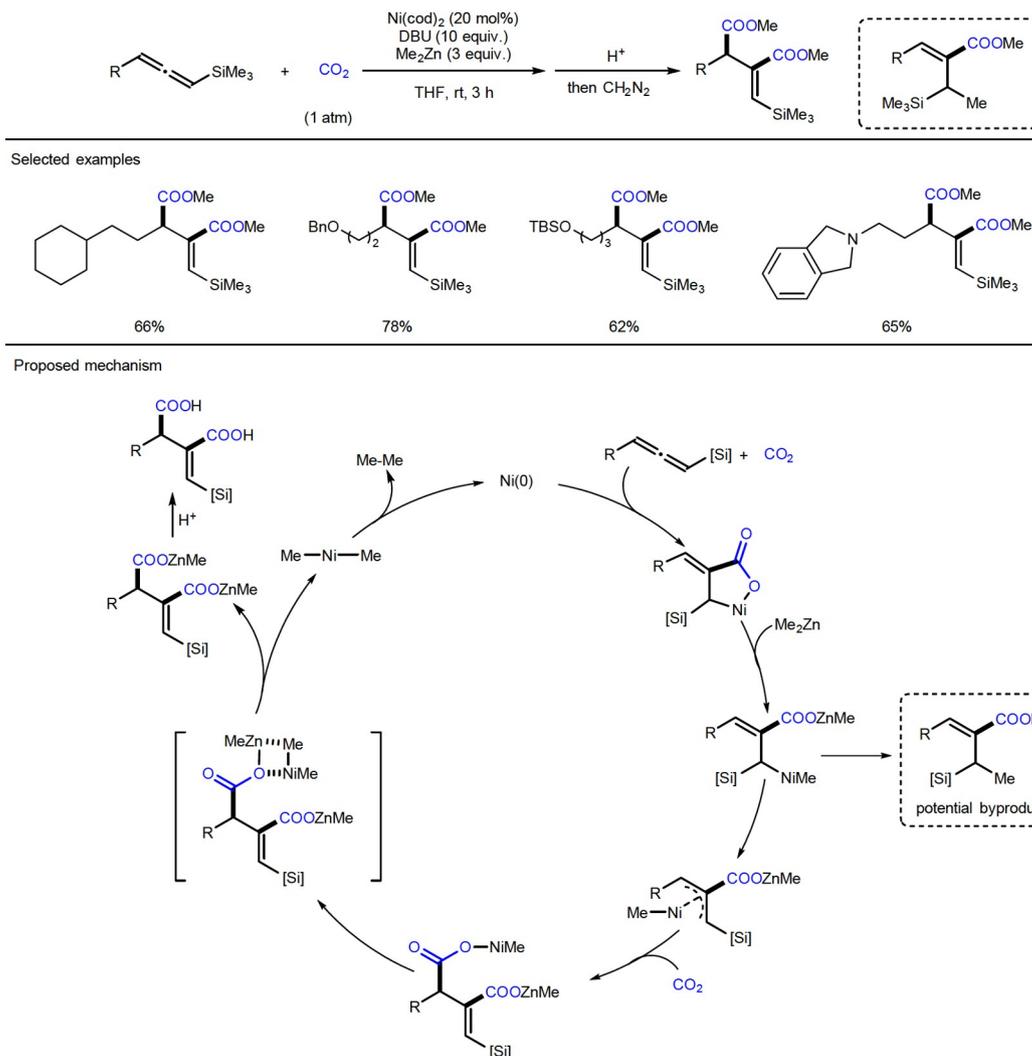


Figure 26 Ni-catalyzed dicarboxylation of silyllallenes with CO_2 .

additive, may act as an electron mediator between Zn reductant and Ni(II) catalyst and also as Lewis acid to facilitate the second CO_2 insertion. Despite its contribution to the catalytic process, the scope limitation in internal alkyne calls for further investigations.

In 2016, Zhang and co-workers [66] have reported a cascade dicarboxylation on the alkynyl group and α -carbonyl site, which is not typical direct-dicarboxylation on the alkynyl group. Sequentially, in 2017, Nielsen, Skrydstrup, and co-workers [67] have realized catalytic continuous hydrocarboxylation on terminal alkynyl group, providing dicarboxylic acid (Figure 28). This reaction employed (9-BBN)₂ to produce diboron reagent *in situ*, which would undergo transmetalation in the presence of CsF and Cu(I) catalyst and following attacking on CO_2 , due to the strong nucleophilicity of organic Cu(I) intermediate endowed by an electron-rich NHC ligand. After the succession process and hydrolysis, the final dicarboxylic acid could be produced. It is noteworthy that the key step is the anti-Markovnikov hydroboration of alkyne to provide the key intermediate 1,1-diboron reagent.

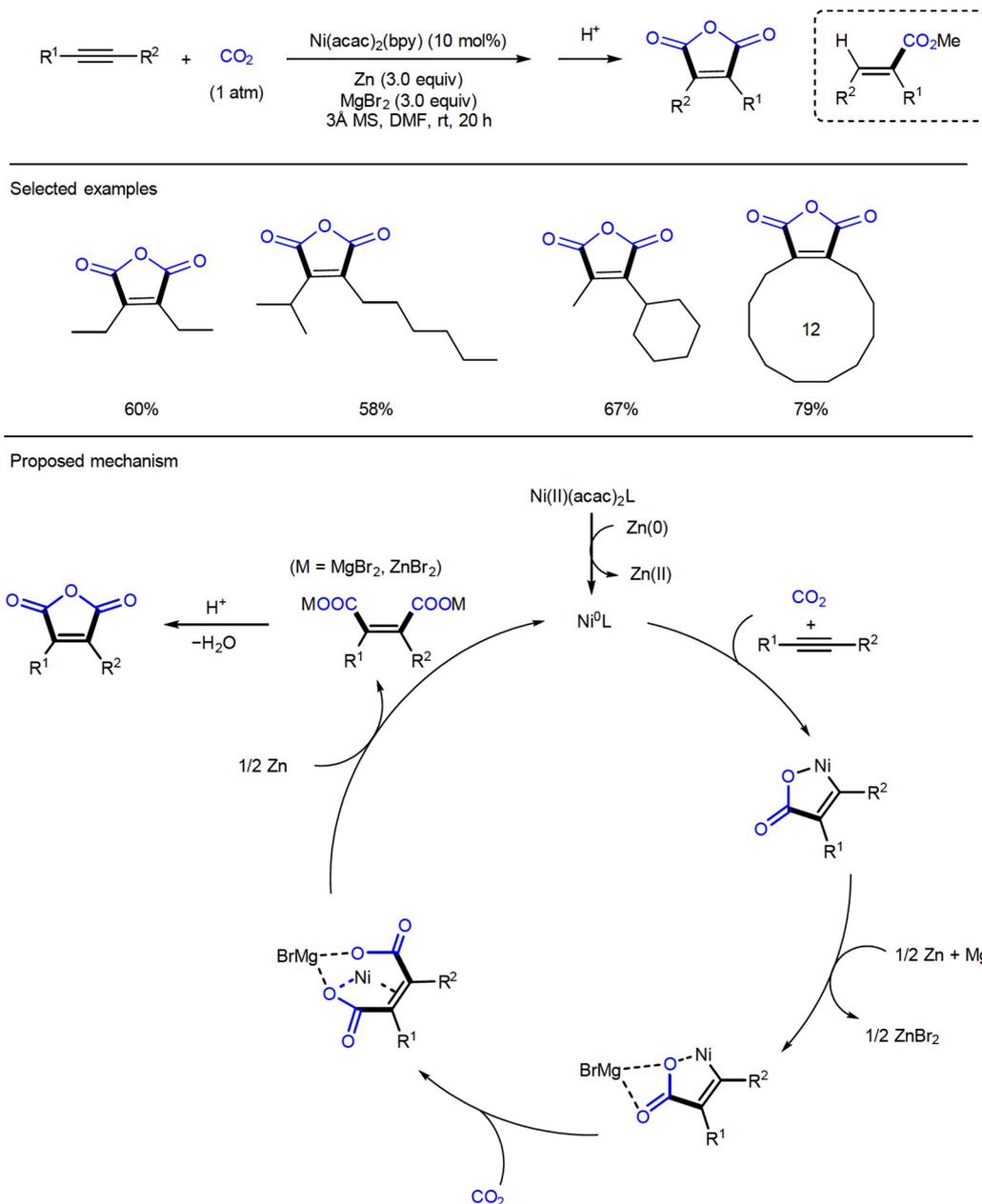


Figure 27 Ni-catalyzed dicarboxylation of internal alkyne with CO₂.

Drawing a brief conclusion from the above work in this field, though it did make progress in recent years, the direct metal-catalyzed dicarboxylation on terminal alkynes and ethyne has not been reported so far. It is probably because of the high acidity of C(sp)–H bond, which commonly leads to deprotonation and the following direct nucleophilic attack to CO₂ in such a general basic environment required for carboxylation. It would be challenging and excellent work for solving such an issue, transforming easily available feedstock into high-valued dicarboxylic products [68]. Similar with the electrochemical and photocatalytic dicarboxylation with CO₂, the transition metal-catalyzed dicarboxylation is also affected by protonation and monocarboxylation. In addition, β-H elimination also limits the selectivity of dicarboxylation with CO₂.

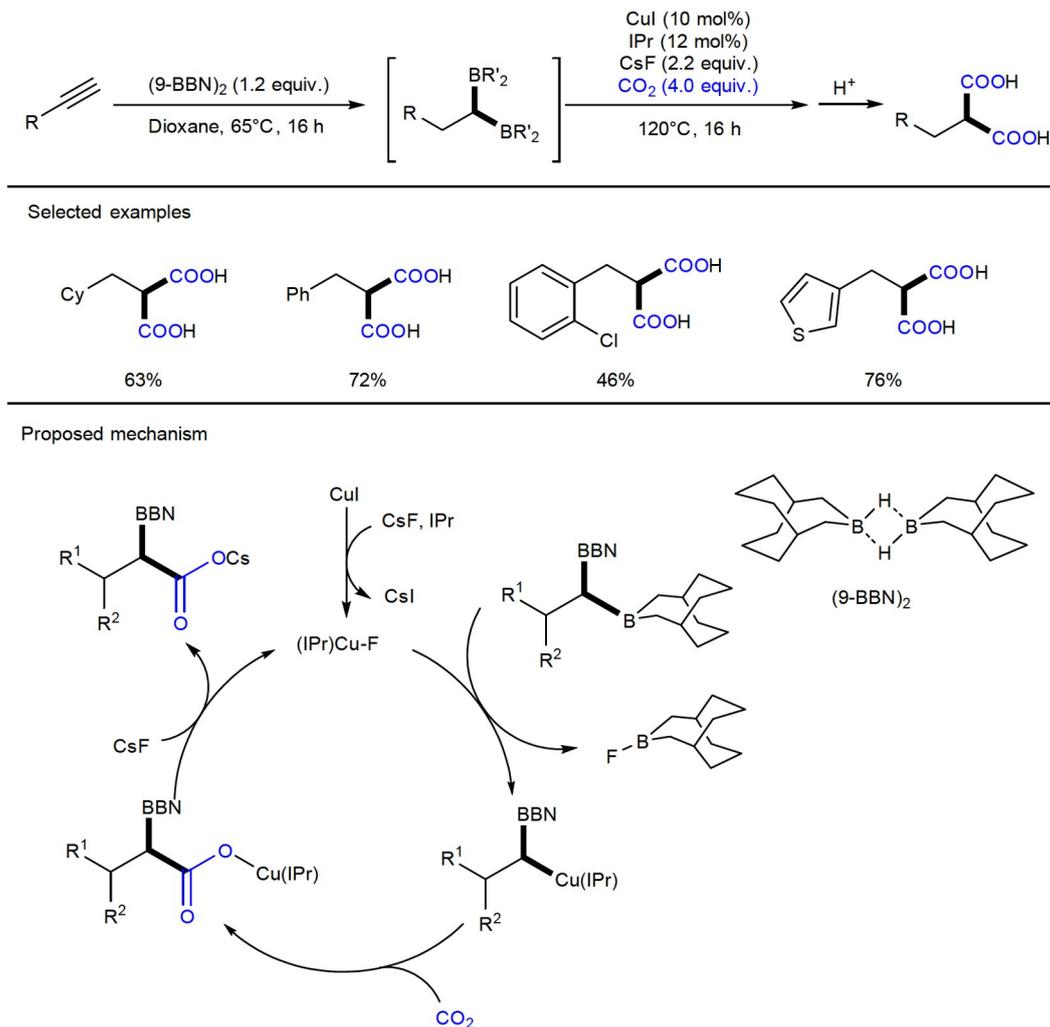


Figure 28 Copper-catalyzed dicarboxylation of terminal alkynes with CO_2 .

Dicarboxylation of single bonds with CO_2

Electrochemical dicarboxylation of C–C single bonds with CO_2

Dicarboxylation of unsaturated carbon–carbon bonds with CO_2 , either alkenes and alkynes, has been demonstrated as a promising synthetic method. However, dicarboxylation of C–C single bonds with CO_2 has been rarely investigated. Very recently, Yu and co-workers [69] have reported a novel method, which is electrochemical ring-opening dicarboxylation of C–C single bonds in strained rings with CO_2 (Figure 29). It can be derived from substituted cyclopropanes and cyclobutanes to structurally diverse glutaric acid and adipic acid derivatives, resulting in moderate-to-good yields. Control experiments indicated that ring-opening radical anions and carbanions might be the key intermediates in this reaction. Significantly, the authors further conducted the polymerization of the corresponding diesters with diols. Diverse materials can be obtained, including a potential UV-shielding material featured with self-healing function and a fluorine-containing polyester, whose performance tests show a promising application.

bisBpin esters acted as the substrate in Lail's work. The authors speculated that the steric of Bpin and the oncoming bulky isopropyl groups of the NHC ligand potentially inhibit the formation of C–Cu bond.

Dicarboxylation of two C–H bonds with CO₂

C–H bonds, which widely exist in organic compounds, have attracted much attention to their carboxylation with CO₂. Despite the progress in monocarboxylation of C–H bonds with CO₂, the dicarboxylation of two C–H bonds is still in exploration. In the past few decades, several examples, requiring specific substrates, have been demonstrated by employing strong Brønsted bases [64,72–74], which suffered from limited functional group tolerance and systematic substrate scopes (Figure 31).

Besides the base-mediated dicarboxylation of two C–H bonds with CO₂, the transition metal-catalyzed dicarboxylation of two C–H bonds with CO₂ is another efficient strategy to synthesize dicarboxylic acids. In 2010, Nolan and co-workers [75] reported the NHC gold(I)-catalyzed dicarboxylation of two C–H bonds on the arenes to produce terephthalic acids with CO₂ (Figure 32A). Almost at the same time, the same group reported the NHC-Cu(I)-catalyzed dicarboxylation of two C–H bonds on the arenes (Figure 32B) [76]. In these cases, the amount of base plays a key role in the control of selectivity. Monocarboxylation acid was obtained when 1.05 equiv. of base was used and dicarboxylation acid was obtained when 2.0 equiv. of base was used.

With great efforts, Iwasawa and co-workers [77] reported the Rh(I)-catalyzed direct carboxylation of arenes with CO₂ via chelation-assisted C–H bond activation in 2010. It is interesting that the dicarboxylation products could be realized by tuning the directing group property enhancing the C–H carboxylation effi-

Examples of strong Brønsted base promoted dicarboxylation of C–H bonds

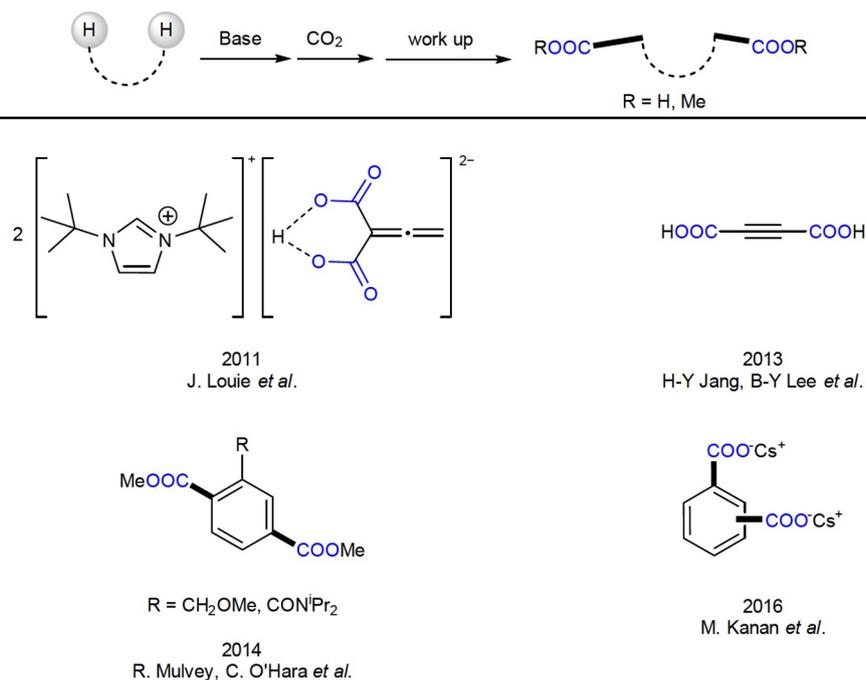


Figure 31 Base-promoted dicarboxylation C–H bond with CO₂.

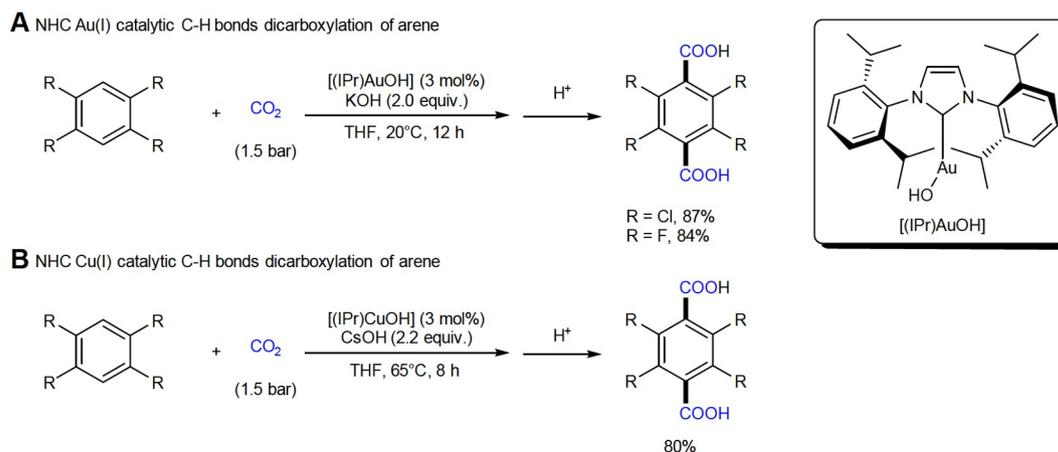


Figure 32 NHC-metal-catalyzed dicarboxylation of arene with CO₂. (A) NHC-Au(I)-catalyzed dicarboxylation of aryl C–H bonds; (B) NHC-Cu(I) catalyzed dicarboxylation of aryl C–H bonds.

ciency, in which pyrazolyl group helps double C–H carboxylation to occur while pyridine group only helps mono-carboxylation to occur. It might be attributed to the change of C–H activity due to the variety of electron density on the directing group (Figure 33).

Up to 2019, the LiO^tBu and CsF-mediated direct dicarboxylation of two C–H bonds with CO₂ has been systematically studied by Kondo and co-workers [78] (Figure 34). Under such conditions, the combined base might undergo cationic exchange to generate CsO^tBu with a stronger basicity, which could deprotonate the acidic C(sp³)–H bond to produce a carbanion. After attacking CO₂, sequential deprotonation occurred at this position, followed by tautomerization to deliver a benzyl carbanion, which could undergo nucleophilic attack to CO₂ to afford the final dicarboxylate. Different from path a, it was initiated by carboxylation on β-position in path b. Though it also underwent base-mediated deprotonation of acidic C–H bonds, it did provide a method for double carboxylation of two C–H bonds with wide substrate scope.

Exploring novel methods for dicarboxylation of two C–H bonds is of much significance and challenging. It

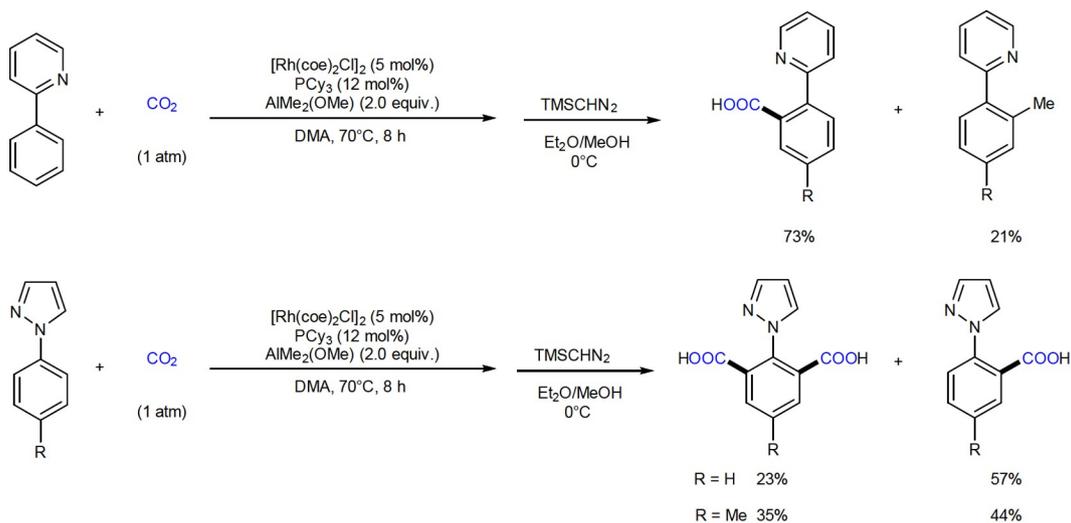


Figure 33 Rh(I)-catalyzed C–H bond dicarboxylation of arene with CO₂.

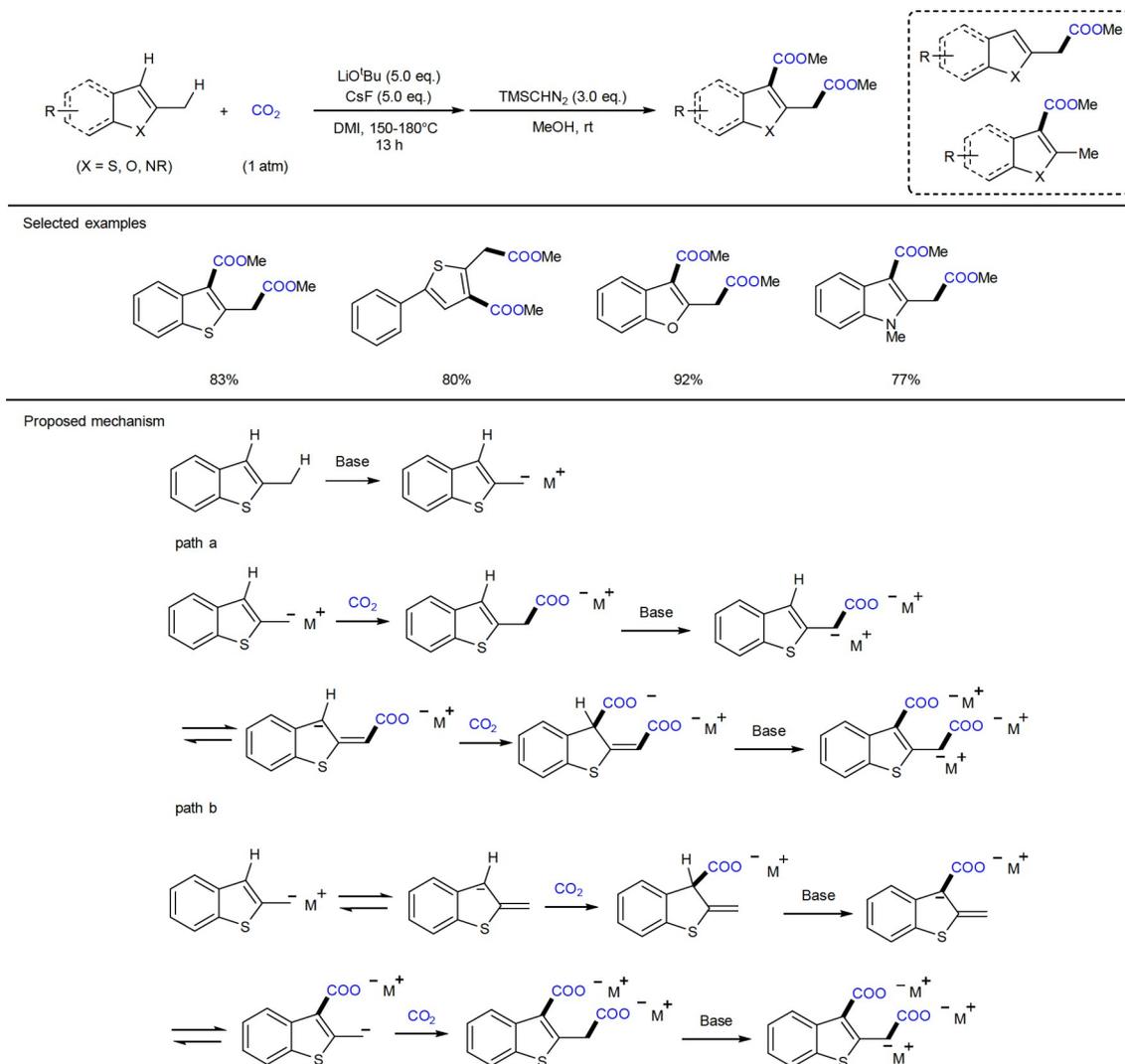


Figure 34 Base-mediated dicarboxylation of two C–H bonds with CO_2 .

would be a challenging but meaningful issue in this field to realize the dicarboxylation of two C–H bonds under mild conditions with generality.

Transition metal-catalyzed dicarboxylation of C–O/C–H bonds with CO_2

(Hetero)aryl dicarboxylic acids are important synthetic precursors for pharmaceuticals, agrochemicals, and biologically active molecules. In 2018, Sato and co-workers [79] reported the Pd-catalyzed dicarboxylation of 2-indolylmethyl acetates with CO_2 (Figure 35A). The dicarboxylation product was obtained in moderate yields due to the competing β -hydride elimination and monocarboxylation. Mechanistically, the η^3 -allylpalladium was generated *in situ* through oxidative addition of C–O bond in substrate to Pd(0) complex. The transmetalation between allylpalladium and ZnEt_2 could afford the nucleophilic η^1 -allylpalladium, which reacted with CO_2 to give the palladium carboxylate. Further transmetalation with ZnEt_2 and reduction

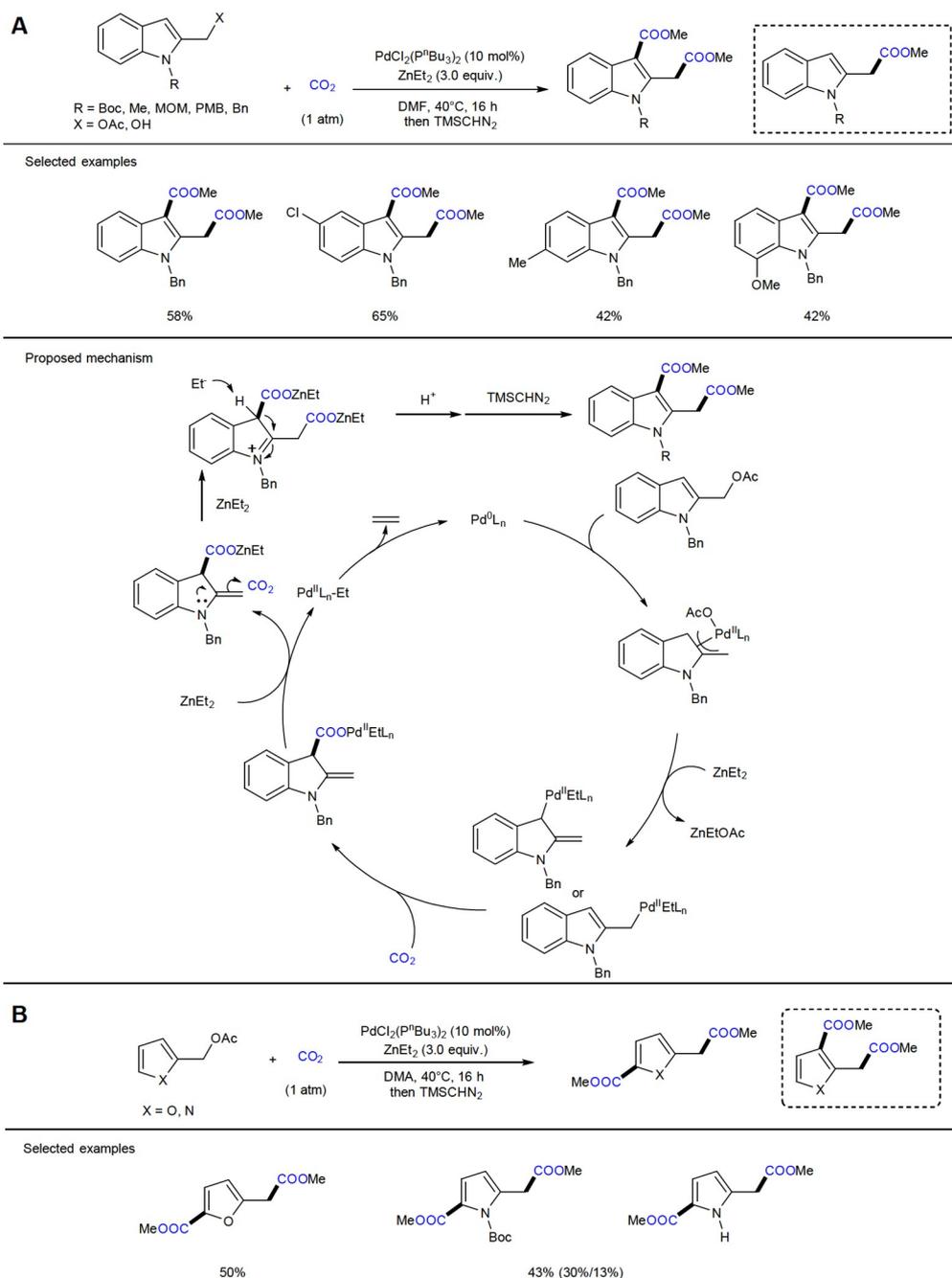


Figure 35 Palladium-catalyzed dicarboxylation of C–O/C–H bonds with CO₂. (A) Pd-catalyzed dicarboxylation of 2-indolylmethyl acetates with CO₂; (B) Pd-catalyzed dicarboxylation of furans and pyrroles with CO₂.

regenerates Pd(0) and enamine intermediate. The enamine would undergo a second carboxylation with CO₂ to give the iminium intermediate. The following rearomatization and hydrolysis would give the dicarboxylic acids. In 2019, the same group [80] achieved a dicarboxylation of furans and pyrroles with CO₂ by employing a similar Pd/ZnEt₂ system (Figure 35B). In these cases, the EWGs help increase the yield of dicarboxylation of pyrrole. However, the protecting group was partially eliminated in the purification process.

Conclusions

By using electrochemistry, photocatalysis, and transition-metal catalysis, significant progress toward dicarboxylation with CO₂ has been made over the past decades. In contrast to the base-promoted dicarboxylation [64,72–74], the examples in this review allow the performance of such dicarboxylation under mild reactions, with broad substrate scope and good functional group tolerance. The key step in the dicarboxylation of unsaturated substrates with CO₂ is the generation of free radical anion of substrates and stepwise reaction with CO₂ or reducing CO₂ to CO₂^{•-}, which would selectively add to substrates. Most of the efforts have been devoted to the formation of key intermediate (the free radical anion of substrates, CO₂^{•-} and carbon-metal species).

Although many kinds of dicarboxylation reactions with CO₂ have been developed to construct important diacids, such methods still suffer from several limitations. First of all, most electrochemical dicarboxylation reactions required a sacrificial anode strategy, which greatly limited the maximum energy utilization. Second, there are rare examples of photocatalytic dicarboxylation and the dicarboxylation of unactivated substrates, which need to be developed vigorously. Third, the mechanistic studies and the evidence of key intermediates are still lacking. In these cases, while the dicarboxylation methods are of advantage in the synthesis of the fine chemicals, the ability to produce the bulk chemicals is worthy of great attention in the field of CO₂ capture and utilization (CCU). Thus, the community should focus more on the dicarboxylation of bulk chemicals with CO₂, such as ethylene, butadiene, and benzene. In such a way, it will not only be of great contribution to CCU but also meet the huge demand for dicarboxylic acids in academia and industry probably by addressing the following unsolved challenges.

Firstly, it would be ideal that CO₂ in low concentration and/or low purity could be applied as the carboxyl source in dicarboxylation reaction. Almost all of the dicarboxylation reactions have been reported by using pure CO₂ and many cases used high pressure of CO₂, which is energy-intensive and expensive for industrial applications. However, low concentrations of CO₂ as carboxyl source should be feasible. For example, Yu and co-workers [81] have demonstrated recently that the decarboxylation of α -amino acids or peptides could provide stoichiometric amount of CO₂ for the carbocarboxylation of activated alkenes. On the other hand, formate, a downstream product of CO₂, would be a promising carboxyl source in dicarboxylation, as highlighted by recent reports on photocatalytic carboxylation by Li, Jui, Wickens and co-workers [82–84].

Secondly, the reaction systems and mechanism for dicarboxylations with CO₂ should be comprehensively investigated. For example, most of dicarboxylations with CO₂ required toxic amide solvents, which violates the principle of green and low toxicity in industry. Greener solvents, such as ionic liquids and deep-eutectic solvents, should be tested in dicarboxylation. In order to facilitate the dicarboxylation with CO₂ to be prosperous, it is also vitally important to lay a solid foundation for detailed mechanism. One could have the reason to believe that computer-assisted study, including DFT calculation and machine learning for prediction could be elegant tools to promote diversified transformations of CO₂ [85].

Finally, the pace of dicarboxylation with CO₂ from laboratory research to industrial application still needs to be accelerated. The communication between research chemists and process engineers should be strengthened for interdisciplinary research, which might help the design of inexpensive catalysts or more economical reaction conditions that are suitable for industrial production.

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Conflict of interest

The authors declare no competing financial interest.

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