



Recent investigations in synthesis of α -hydroxycarboxylic acids by reductive carboxylation of aldehydes with CO₂ (microreview)

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ABSTRACT

Carbon dioxide (CO₂) is a plentiful, nontoxic, nonflammable, renewable C1 feedstock and the major component of greenhouse gases, thereby the research for sustainable and efficient conversion of this waste gas into valuable chemicals has received great attention in recent years. The catalytic reaction between aldehydes and CO₂ is a novel and attractive pathway for CO₂-utilization as it can lead to the formation of highly important α -hydroxycarboxylic acids with ideal atom economy. This review discusses the advancements made within this research topic with the hope of promoting future research in the field of CO₂-utilization.

1. Introduction

Carbon dioxide (CO₂) is the main component of greenhouse gases in the atmosphere, accounting for approximately 64% of the warming effect on the climate, mainly because of fossil fuel combustion and cement production [1]. From the perspectives of synthetic chemistry, CO₂ is an ideal C1 synthon owing to its readily available, cheap, non-toxic, and nonflammable [2-5]. In recent years, the chemical conversion of CO₂ into value-added compounds has gained a great deal of attention [6-10]. Among them, the conversions of CO₂ into carboxylic acid derivatives has particularly garnered considerable attention [11-13], which are common moieties in many medicines and natural products [14]. In this family of reactions,

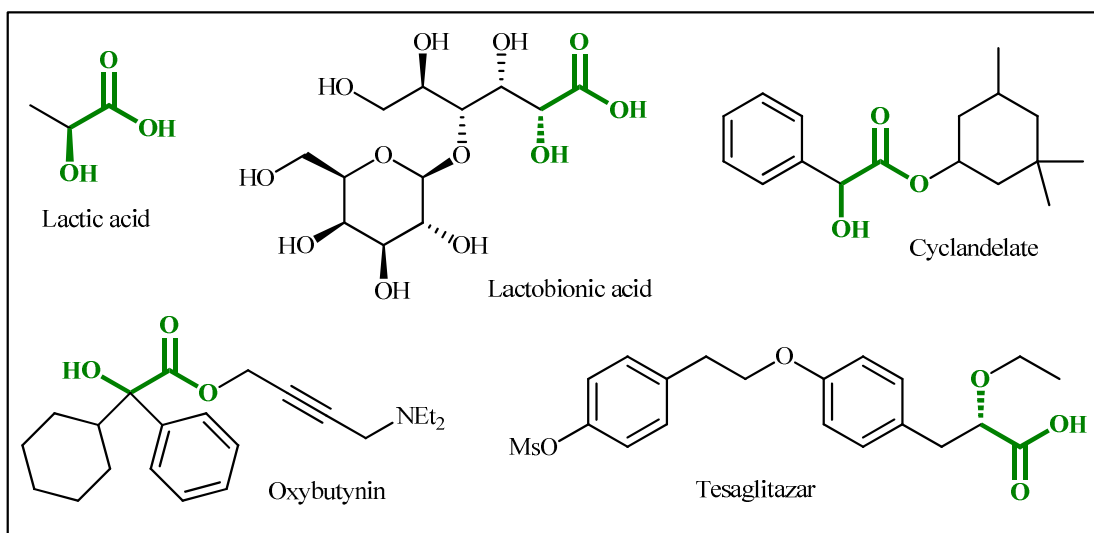
reductive carboxylation of aldehydes with CO₂ offers a promising strategy for the selective synthesis of synthetically [15] and biologically important α -hydroxycarboxylic acids (Scheme 1) [16].

To the best of our awareness, a comprehensive review on this rapidly growing research arena has not yet been appeared in literature. In order to fill this gap, herein, we will highlight the most important investigations on the preparation of α -hydroxycarboxylic acids through the reductive carboxylation of corresponding aldehydes with CO₂ (Figure 1) which insightful mechanistic discussions. The review is divided into three sections depending on the type of catalysts.

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Scheme 1. Selected examples of bioactive compounds possessing an α -hydroxycarboxylic acid unit.

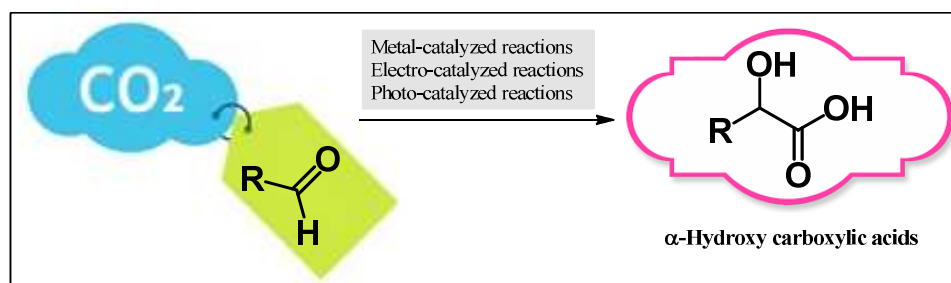
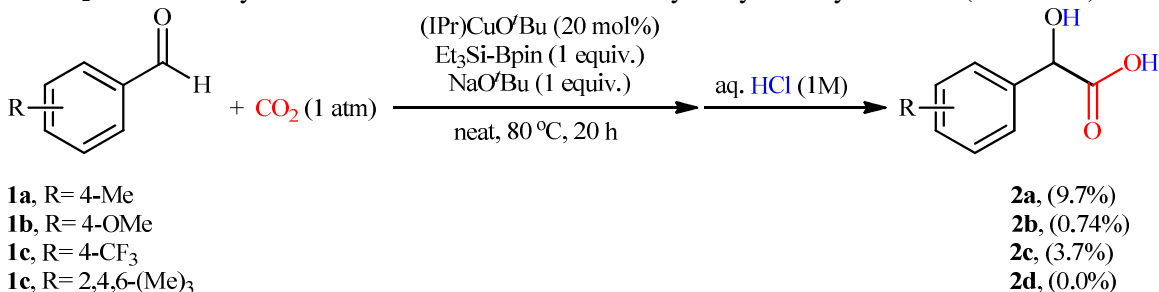


Figure 1. Reductive carboxylation of aldehydes with CO_2 .

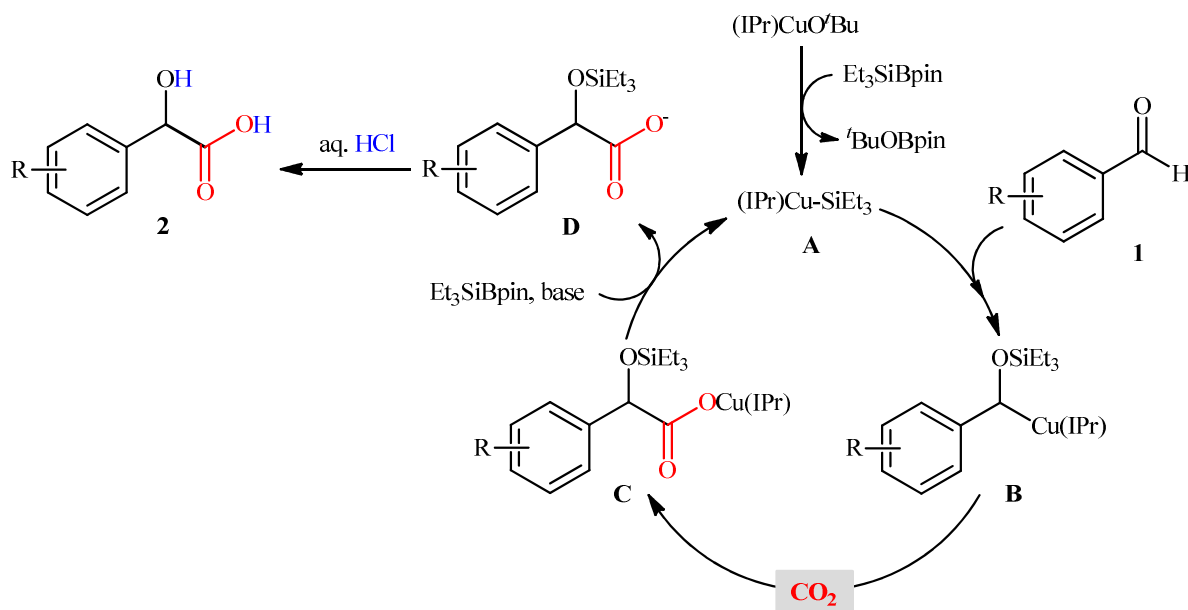
2. Metal-catalyzed reactions

One of the earliest reports on the synthesis of α -hydroxycarboxylic acid derivatives from aldehydes and CO_2 appeared in 2020, when aromatic aldehydes **1** underwent reductive carboxylation with atmospheric CO_2 in the presence of a catalytic amount of the copper alcoholato complex $[(\text{IPr})\text{CuO}^t\text{Bu}]$ and stoichiometric amounts of NaO^tBu and silylborane Et_3SiBpin as the base and reductant, respectively, under neat conditions [17]. Although only four examples were disclosed and the desired α -hydroxycarboxylic acids **2** were generally obtained in poor yields (Scheme 2), this paper represents the first example of metal-catalyzed reductive coupling of CO_2 and aldehyde and could be an

inspiration for further researchers. The mechanistic cycle proposed by the authors for this CO_2 -fixation reaction starts with the formation of silylcopper complex **A** through the reaction of $(\text{IPr})\text{CuO}^t\text{Bu}$ and Et_3SiBpin , which undergoes reaction with aldehyde **1** to produce silyloxycarbonyl copper species **B** via aldehyde insertion followed by 1,2-Brook rearrangement. Next, CO_2 insertion into the copper-carbon bond of the newly generated intermediate **B** leads to the copper carboxylate **C** that subsequently transforms to carboxylate **D** by liberation of silylcopper complex **A** via reaction with a base and Et_3SiBpin . Finally, hydrolysis of the carboxylate intermediate **D** leads to the formation of the final α -hydroxycarboxylic acid **2** (Scheme 3)



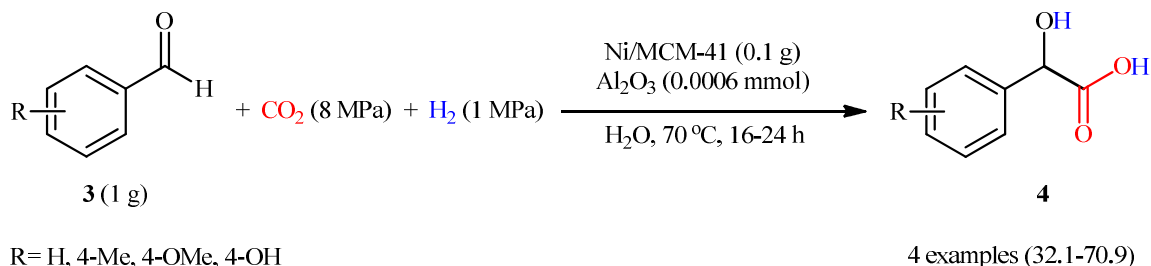
Scheme 2. Cu(I)-catalyzed reductive coupling of carbon dioxide and aldehydes **1** developed by Nozaki.



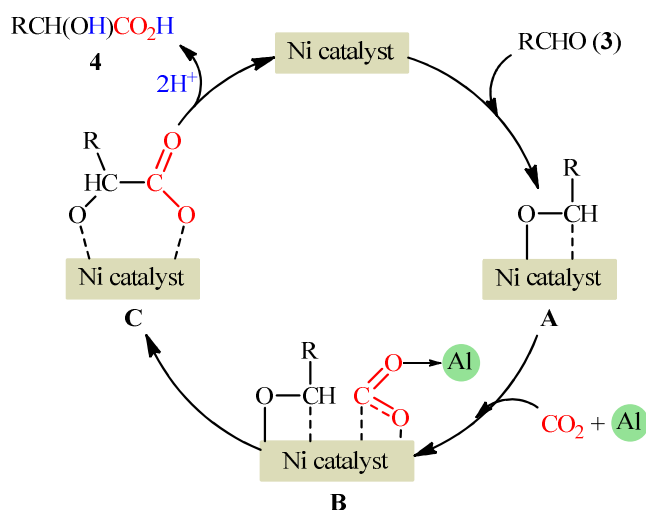
Scheme 3. Plausible mechanism for the reaction in Scheme 2.

Very recently, the combination of heterogeneous Ni catalyst (Ni/MCM-41) and Lewis acid promoter (Al_2O_3) was found by Chatterjee, Kawanami and co-workers as an efficient and selective catalytic system for reductive carboxylation of aldehydes under the condition of a CO_2/H_2 atmosphere in water [18]. In this reaction, a small library of aromatic aldehydes **3** proceeded well to afford the desired α -hydroxycarboxylic acids **4** in satisfactory yields (Scheme 4), even acetaldehyde (simple aliphatic aldehyde) also converted into lactic acid in an 80.2% yield. However, furfural (a heteroaromatic aldehyde)

failed to participate in this transformation. Based on the experimental results and density functional theory (DFT) studies, a possible mechanism was proposed (Scheme 5), whereby the reaction is initiated with coordination of the $-\text{CHO}$ group of acetaldehyde **3** with the Ni(II) center in a preferential $\eta^2(\text{CO})$ configuration to give complex **A**. Subsequently, the activated CO_2 coordinates with the Ni(II) center to form the adduct **B**, which undergoes carbon-carbon bond formation affording intermediate **C**. Finally, intermediate **C** abstracts two hydrogen atoms to furnish the desired product **4** and regenerate the active catalyst.



Scheme 4. Synthesis of α -hydroxy carboxylic acids **4** by carboxylation of aldehydes **3** with CO_2 on Ni(II) catalyst.

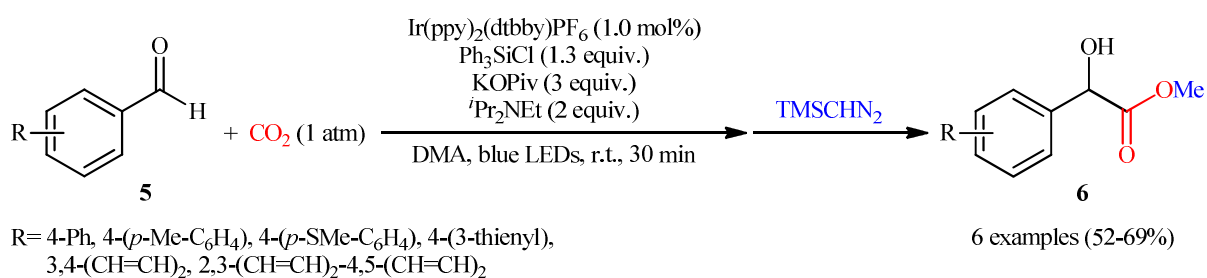


Scheme 5. Plausible mechanism of Ni-catalyzed carboxylation of aldehydes **3** with CO₂.

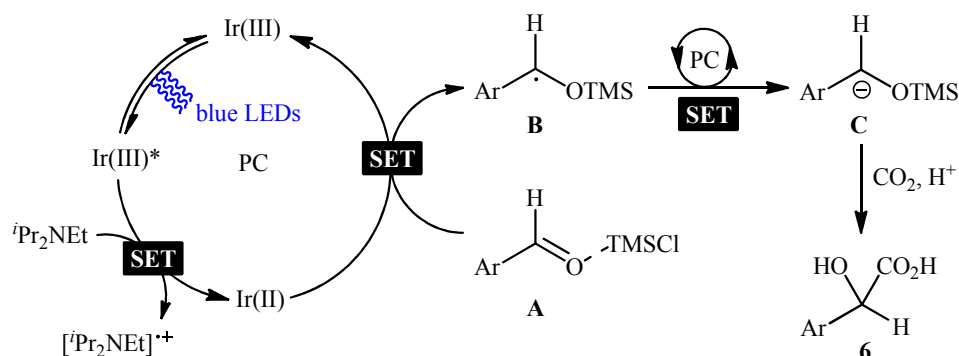
3. Photo-catalyzed reactions

In 2017, Yu and co-workers realized an elegant strategy for visible-light photoredox-catalyzed carboxylation of aldehydes with CO₂ using Lewis acidic chlorosilanes as activating reagents [19]. In this study, six secondary α -hydroxycarboxylic acids **6** were selectively synthesized through the treatment of the respective benzaldehydes **5** with atmospheric CO₂ and Ph₃SiCl, in the presence of Ir(ppy)₂(dtbby)PF₆/KOPiv/ⁱPr₂NEt combination as the catalytic system in DMA under irradiation of blue LEDs at room temperature (Scheme 6). Besides aldehydes, this transformation proved applicable to a wide range of ketones, including alkyl aryl ketones, diaryl ketones, α -ketoamides, and α -ketoesters. In order to further value the applicability of their methodology, the authors investigated its utility by the synthesis of various valuable intermediates and bioactive compounds such as

oxyphenonium, mepenzolate bromide, benactyzine, and tiotropium. On the basis of several control experiments such as radical scavenging and isotope labeling experiments and Stern-Volmer experiment, the author proposed the catalytic mechanism as shown in Scheme 7. In the beginning, the ground state Ir(III) photoredox catalyst undergoes excitation under irradiation of visible light to produce the excited state *Ir(III), which reductively quenches by the ⁱPr₂NEt to produce reduced Ir(II). Subsequently, reduction of the TMSCl-activated aldehyde **A** by Ir(II) produces the α -siloxybenzyl radical **B** and regenerates Ir(III) catalyst. Finally, α -siloxybenzyl radical **B** undergoes a further single electron transfer (SET) reduction by another photocatalytic cycle to afford a benzylic carbanion **C** which captures the CO₂ to synthesize the expected carboxylated product **6**.



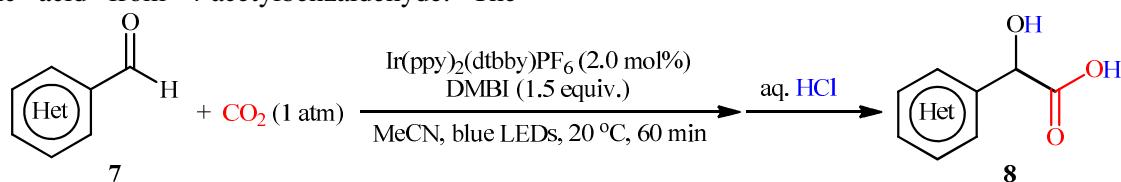
Scheme 6. Visible-light photoredox-catalyzed carboxylation of aldehydes **5** with CO₂.



Scheme 7. Tentative mechanism for the formation of α -hydroxycarboxylic acids **6**.

Concurrently, in a related investigation, Okumura and Uozumi reported the use of $\text{Ir}(\text{ppy})_2(\text{dtbby})\text{PF}_6$ in combination with 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzimidazole (DMBI) for direct carboxylation of (hetero)aromatic aldehydes **7** with atmospheric CO_2 under the irradiation of blue LEDs [20]. The reactions were implemented in MeCN at 20 °C, tolerated a wide range of important functional groups (e.g., chloro, cyano, ester, ketone, sulfone, trifluoromethyl) and afforded the target α -hydroxycarboxylic acids **8** in moderate to high yields (Scheme 8). Notably, the protocol was also compatible for carboxylation of ketones. Interestingly, this carboxylation reaction was selective for aldehydes over ketones, as judged from selective formation of 2-(4-acetylphenyl)-2-hydroxyacetic acid from 4-acetylbenzaldehyde. The

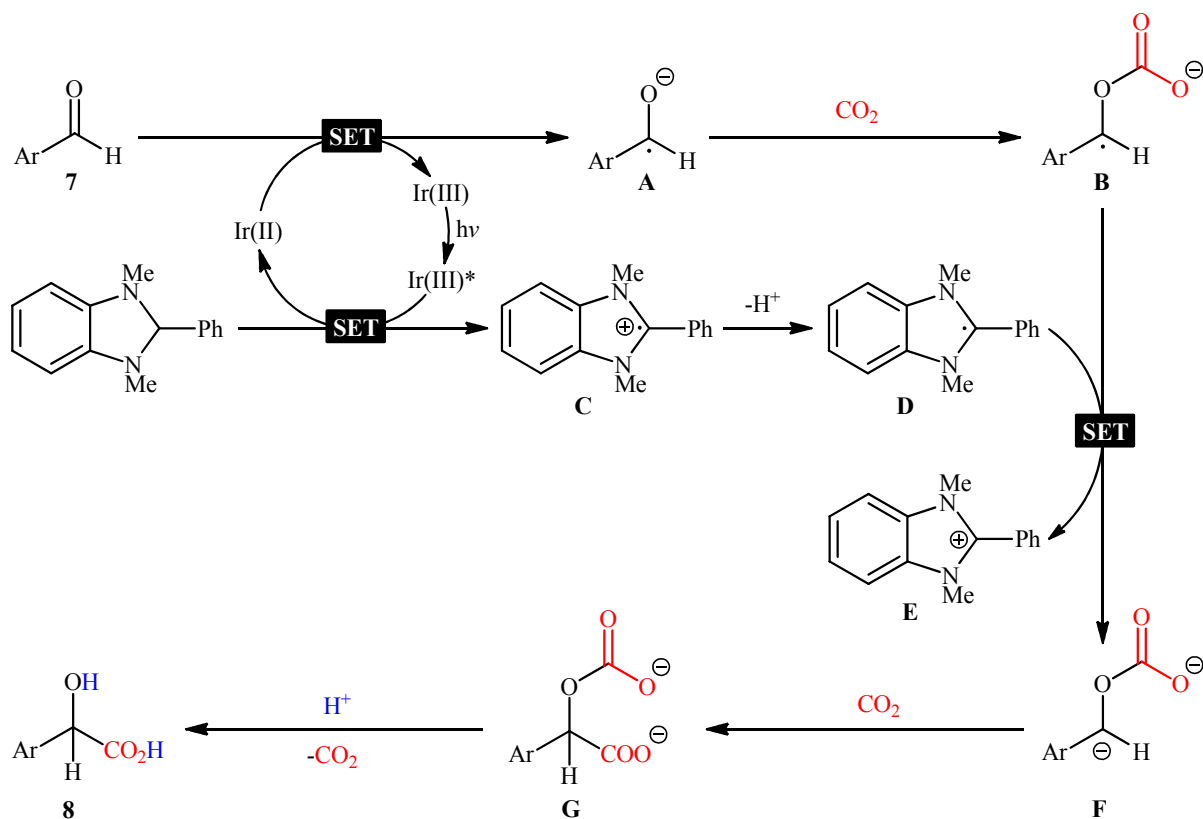
mechanism was proposed to explain this reaction that involves the following sequence of steps (Scheme 9): (i) excitation of Ir(III) photocatalyst by visible light; (ii) reduction of excited Ir(III) photocatalyst by DMBI to give an Ir(II) species and the DMBI radical cation **C**; (iii) reduction of aldehyde **7** by Ir(II) species to generate radical **A**, with reproduction of the Ir(III) photocatalyst; (iv) reaction of the oxygen anion of **A** with CO_2 to form carbonate anion **B**; (v) one electron reduction of **B** by DMBI radical **D** (produced by deprotonation of the DMBI radical cation **C**) to give the carbinol anion species **F**; (vi) reaction of the carbon anion of **F** with another molecule of CO_2 to generate the dianion intermediate **G**; and (vii) protonation and decarboxylation of **G** to afford the final product **H**.



(Het)Ar= 4-Ph-C₆H₄, 4-COMe-C₆H₄, 4-CO₂Me-C₆H₄, 4-CF₃-C₆H₄,
4-CN-C₆H₄, 4-SO₂Me-C₆H₄, 4-CH=CHPh-C₆H₄, 2-Cl-C₆H₄,
2-naphthyl, 9-phenanthrenyl, 2-benzofuryl

11 examples (40-86%)

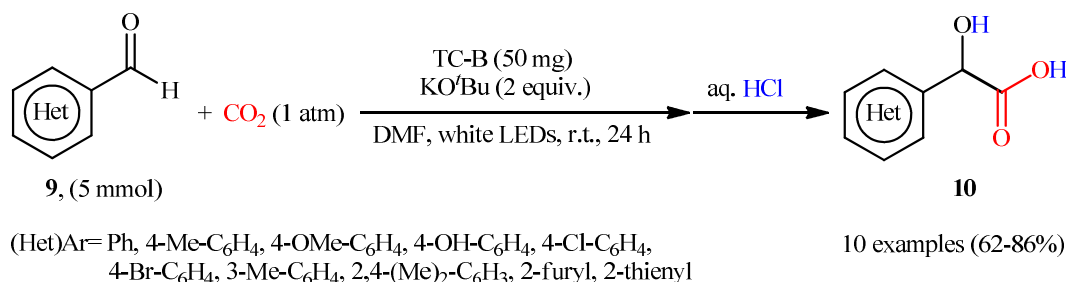
Scheme 8. Okumura-Uozumi's synthesis of α -hydroxycarboxylic acids **8**.



Scheme 9. Possible mechanism of the reaction in Scheme 8.

Drawing inspiration from these works, very recently, Jain and co-workers developed a heterostructured photocatalyst made up of titanium-based MOF (MIL-125-NH₂(Ti)) coupled with g-C₃N₄ (TC-B) for the light-induced synthesis of α -hydroxycarboxylic acids **10** from aromatic aldehydes **9** and atmospheric CO₂ [21]. The reaction was conducted

in DMF at room temperature and yields of up to 86% were obtained (Scheme 10). However, it appears to be limited to electron-rich aromatic aldehydes. Accordingly, Benzaldehydes having strong withdrawing groups like -CN, -COOH and -NO₂ failed to produce any corresponding acid under the optimized conditions.

Scheme 10. Ti-MOF/g-C₃N₄ driven light assisted reductive carboxylation of (hetero)aryl aldehydes **9** with atmospheric CO₂.

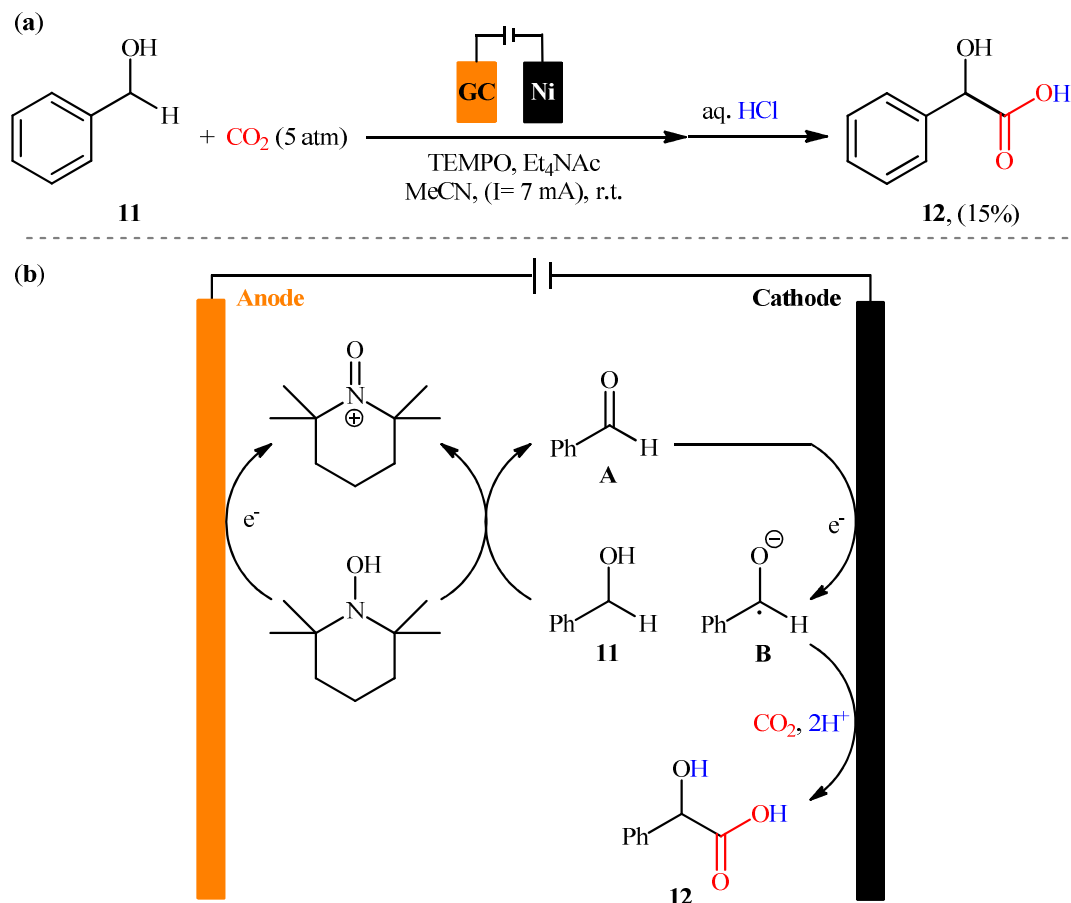
4. Electrocatalytic reactions

Organic electrochemistry as an efficient and emerging environmentally benign alternative to conventional synthetic methods has achieved considerable progress in recent years because it utilizes electric current as a traceless redox agent instead of chemical oxidants or reductants [22]. In this regard, as a

promising and sustainable strategy for the synthesis of carboxylic acids, electrochemical carboxylations using CO₂ has been widely studied recent years [23]. The first mention of synthesizing α -hydroxy acids through electrocarboxylation of aldehydes with CO₂ can be found in a 2019 paper by Muchez, Vos, and Kim [24]. They unraveled that the treatment of benzyl alcohol **11**

as a source of benzaldehyde with pressurized CO₂ (5 bar) in the presence of a catalytic amount of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in a simple undivided cell with a glassy carbon (GC) plate anode and a Ni foil cathode in a MeCN solution containing 0.1 M Et₄Nac under a constant current of 7 mA produced 2-hydroxy-2-phenylacetic acid **12** in a yield of 15%, along with various side products (Scheme 11a). Notably, apart from benzyl alcohol, aliphatic secondary aromatic alcohols were also compatible with this scenario. Mechanistically, at the anode, TEMPO-

mediated alcohol oxidation converted benzyl alcohol **11** into benzaldehyde **A**. Subsequently, aldehyde was diffused to the cathode, and the reduction and carboxylation with CO₂ to generated 2-hydroxy-2-phenylacetic acid **12** (Scheme 11b). At the same year, Baranton's research team successfully synthesized 2-furyl(hydroxy)acetic acid with a yield of 82% through reductive electrocarboxylation of furfural at a Pt/C electrode using γ -valerolactone as a bio-sourced aprotic solvent [25].



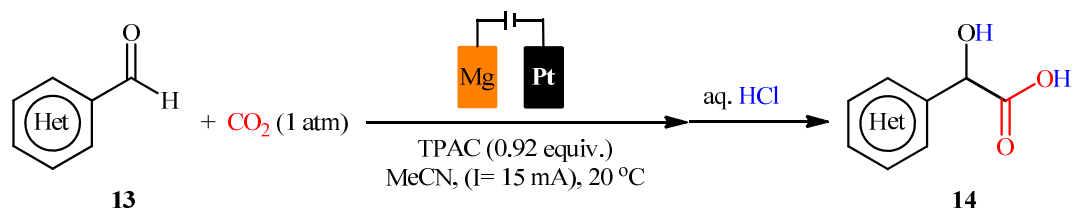
Scheme 11. TEMPO-catalyzed electrocarboxylation of *in situ* generated benzaldehyde **A** with CO₂ Sacrificial anode free conditions.

In 2021, Singh's research group have made an important contribution to the field by developing a practical and efficient electrochemical carboxylation of carbonyl compounds with atmospheric CO₂ in an undivided cell under mild and catalyst-free conditions [26]. They showed that the treatment of various (hetero)aromatic aldehydes **13** with atmospheric CO₂ in an undivided cell assembled with sacrificial Mg anode and Pt cathode, using TPAC as electrolyte under constant current conditions provided the corresponding α -hydroxycarboxylic acids **14** in high yields (Scheme

12); in addition, a tolerance for cinnamaldehydes was also demonstrated. It is worthwhile to note that tertiary α -hydroxycarboxylic acid derivatives can also be achieved in high to excellent yields when aldehydes were replaced with ketones. Intriguingly, no side products were observed in any of examples and products were purified by simple recrystallization. Based on the literature, the authors suggested a possible mechanism for this electrocarboxylation as illustrated in Scheme 13. The reaction may start with the formation of anion radical **A** by one electron cathodic reduction of

starting aldehyde **13**. Subsequently, this intermediate captures one molecule of CO₂ to form carbonate anion **B**, which after another cathodic reduction affords

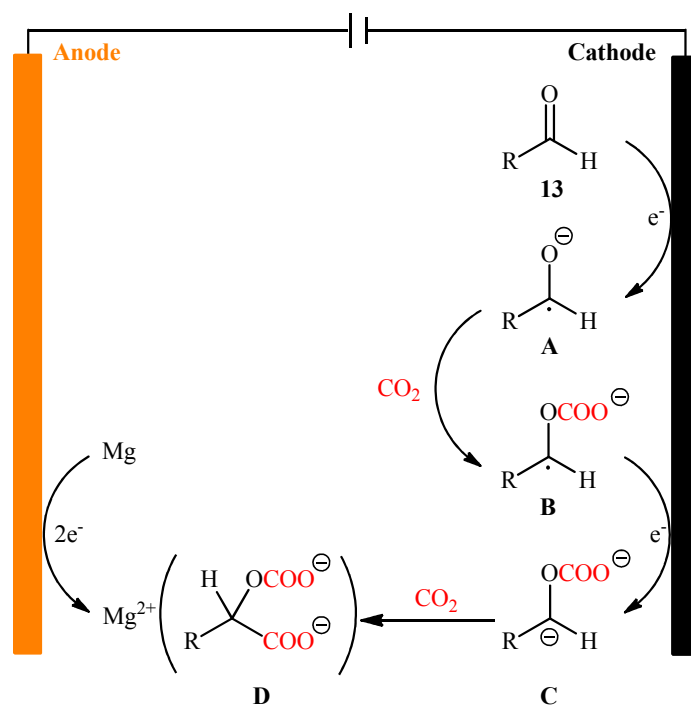
carbon anion **C**. Finally, intermediate **C** captures another molecule of CO₂ to afford the desired α -hydroxycarboxylic acid **14** upon hydrolysis.



(Het)Ar= Ph, 4-Cl-C₆H₄, 4-Br-C₆H₄, 2-pyridyl, 2-furyl, 2-thienyl

6 examples (80-90%)

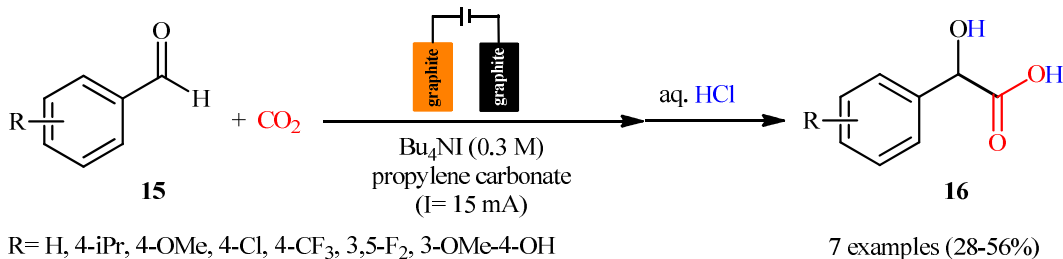
Scheme 12. Singh's synthesis of α -hydroxycarboxylic acids **14**.



Scheme 13. Mechanistic proposal for the formation of α -hydroxycarboxylic acids **14**.

Recently, Waldvogel and co-workers described another efficient electrochemical method for carboxylation of aldehydes with CO₂ under catalyst-free conditions [27]. Their cell consisted of two cost-efficient and stable graphite electrodes (acting as anode and cathode) separated by a ceramic filter disk and a 0.3 M solution of *tetra-n*-butylammonium iodide (Bu₄NI) in propylene carbonate as a “green” electrolyte. The transformation was performed under constant current of 8 mA and several aromatic aldehydes **15** were

evaluated, providing the corresponding α -hydroxycarboxylic acids **16** in moderate yields (Scheme 14). 2-Phenylpropanal and 3-phenylpropanal did not effectively take part in the reaction and therefore no other aliphatic aldehydes were examined in the protocol. Apart from aromatic aldehydes, acetophenone derivatives were also compatible with this scenario, providing respective tertiary α -hydroxycarboxylic acids in good yields (up to 63%).

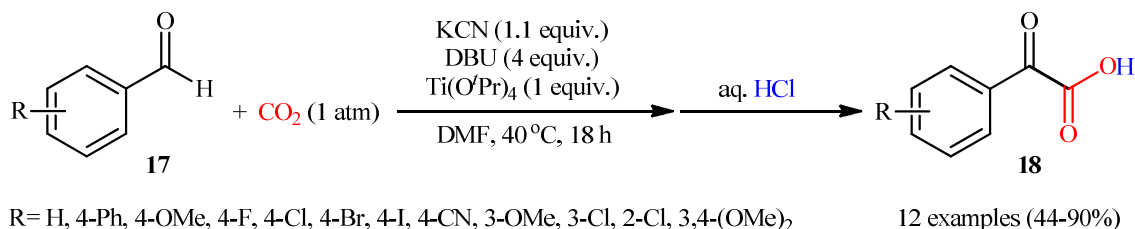


Scheme 14. Waldvogel's synthesis of α -hydroxycarboxylic acids **16**.

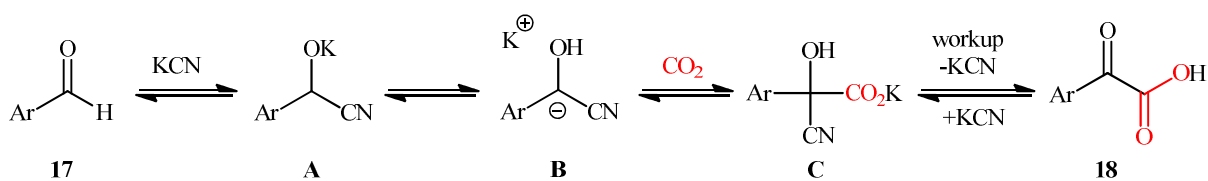
5. Miscellaneous reactions

In 2018, Lee and Juhl disclosed an elegant umpolung reactivity of aldehydes with CO₂ [28]. Thus, by employing KCN/Ti(OⁱPr)₄/DBU combination as a catalytic system in DMF, they achieved direct carboxylation of benzaldehyde derivatives **17** with atmospheric CO₂ to afford added-value α -keto acid products **18**, after hydrolysis (Scheme 15). The reactions showed good tolerance to a series of sensitive functional groups such as the fluoro, chloro, bromo, cyano, and methoxy groups, indicating its general applicability. However, no carboxylation occurred when aliphatic aldehydes were used as the substrates. In this study, the authors nicely expanded their methodology to the

synthesis of α -amino acids derivatives under reductive amination reaction conditions; mimicking the biosynthesis of various amino acids. The mechanism suggested by the authors for this carboxylation reaction is summarized in Scheme 16, and involves the nucleophilic addition of KCN to the aldehyde **17** to give potassium cyanoalkoxide **A** that is in equilibrium with the tetrahedral intermediate **B**. Next, this intermediate **B** undergoes nucleophilic attack on CO₂ to form the cyanated ketoacid **C**, followed by hydrolysis to afford the desired α -keto acid **18**. Notably, this mechanistic proposal indicates catalytic involvement of KCN. However, over-stoichiometric amounts of KCN was necessary to achieve a high yield of the product.



Scheme 15. KCN-mediated carboxylation of benzaldehyde derivatives **17** with atmospheric CO₂.



Scheme 16. Proposed mechanistic pathways for the formation of α -keto acid **18**.

6. Conclusion

α -Hydroxycarboxylic acids, as important scaffolds that are present in many natural products and biologically active compounds, so the development of efficient strategies for their preparation always stand out as an important field. Among the modern methods in this area, reductive carboxylation of aldehydes with CO₂ is one of the highly promising approaches not only

because it beneficial from the use ubiquitous and cheap CO₂ as a sustainable carbonyl source but also from ideal atom economy. Although, considerable successes have been achieved in this field during the past few years, some limitations such as production of unwanted byproducts and restricted scope of aldehydes have remained as the main drawbacks of this page of α -hydroxycarboxylic acids synthesis.

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