

Recent Advances on Defluorinative Carboxylation of C-F Bonds with CO₂

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ABSTRACT

Compared with most studies in the field of CO₂ utilization, which focused on the carboxylation of C-I, C-Br, C-Cl, C-B, C-Si, C-O bonds, the direct defluorinative carboxylation of C-F bonds is more challenging due to the much higher bond dissociation energy and less reactivity of C-F bonds, for which it is difficult to initiate the oxidative addition process under mild conditions. Recently, various catalytic systems have been developed that allow the direct carboxylation of inert C-F bonds with atmospheric CO₂ and provide versatile methodologies for green synthesis of carboxylic acid derivatives. This review focuses on recent advances in this challenging and hot research topic with special emphasis on the mechanistic details of the reaction pathways.

1. Introduction

The utilization of carbon dioxide (CO₂) as a ubiquitous, cheap, abundant, non-toxic, non-flammable and renewable one-carbon (C1) feedstock for the synthesis of chemicals and fuels is currently attracting great interest [1]. In the last few decades, many proficient reactions have been developed for CO₂ catalytic conversion into high-value chemicals such as amines, amides, carbonates, carbamates, ureas, alcohols, aldehydes, ketones, esters, among others [2-10]. In this context, the synthesis of carboxylic acids through the reductive carboxylation of C-X bond (X=halide or pseudohalide) has been extensively investigated, in terms of economy and versatility of this transformation [11]. However, owing to their high energy and low activity, C-F bonds are difficult to activate [12] and their carboxylation is still an extremely challenging research topic. In this regard, the development of catalytic systems that enable the direct carboxylation of inert and unreactive C-F bonds with inert CO₂ has gained widespread attention and considerable progress has been

made in the past few years. This review summarizes the most representative and important reports on the preparation of carboxylic acids from the corresponding organofluorine compounds and CO₂ via carbon-fluorine bonds cleavage (Fig 1), which may stimulate researchers for further thinking and research on CO₂ utilization with other inert substrates.

2. Defluorinative carboxylation of C_(alkyl)-F bonds

One of the earliest reports on the defluorinative carboxylation of fluoroalkanes with CO₂ was published by Yu and colleagues in 2019 [13], who showed that the treatment of trifluoromethyl alkene derivatives 1 with atmospheric CO₂ in the presence of the combination of CuCl/Xantphos/KOME/bis(hexylene glycolato)diboron as the catalytic system in NMP at 80 °C, resulted in the formation of the corresponding α,α -difluorocarboxylates 2 in moderate to good yields (Scheme 1). Beside good yields, broad substrate scope, and high mono-, chemo-, and stereoselectivities, were the advantages, mentioned for this C-F bond functionalization reaction.

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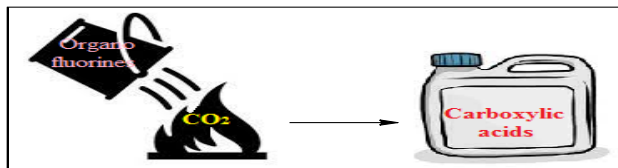
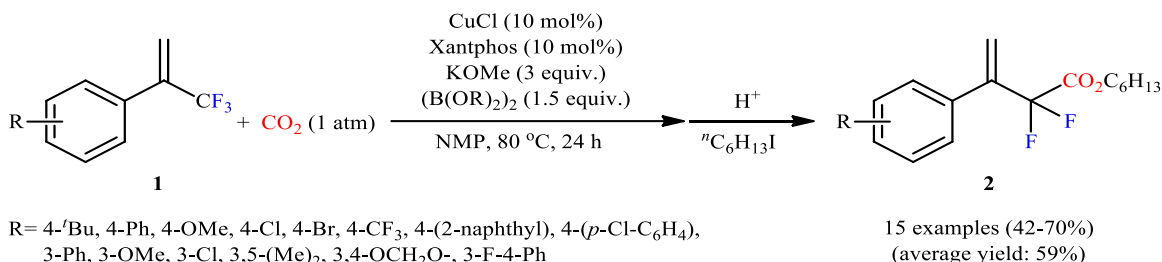


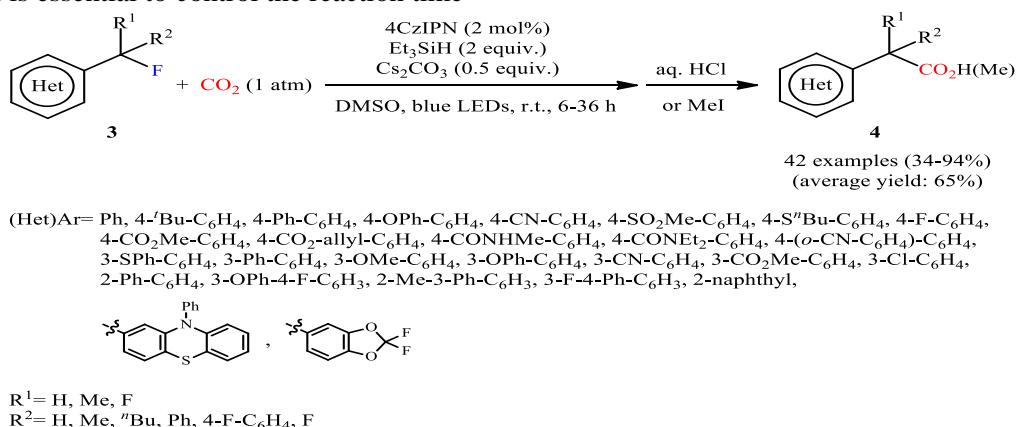
Fig 1. Direct defluorinative carboxylation of C-F bonds with CO₂.



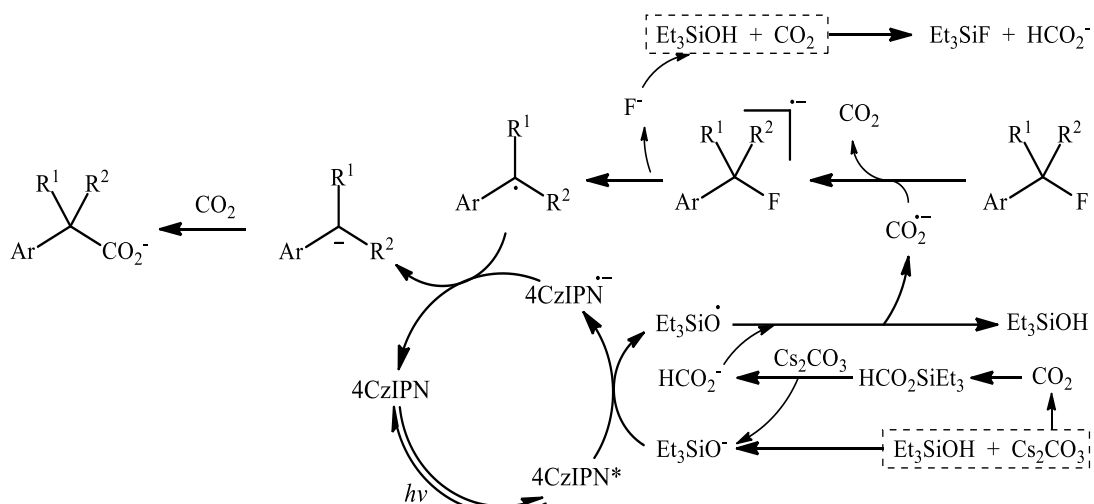
Scheme 1. Cu-catalyzed defluorinative carboxylation trifluoromethyl alkenes 1 with CO₂.

Recently, this innovative research group disclosed the possibility of visible-light photoredox-catalyzed defluorinative carboxylation of inert C(sp³)-F bonds with CO₂ [14]. In order to identify the best catalytic system, they investigated the activities of various photocatalyst, reductants, and bases in the carboxylation of methyl 4-(1,1-difluoroethyl)benzoate with atmospheric CO₂ as a model reaction. The combination of inexpensive and commercially available 2,4,5,6-tetra(carbazol-9-yl)isophthalonitrile (4CzIPN) with Et₃SiH and Cs₂CO₃ was proved to be most efficient system, which gave a better yield of the desired carboxylic acid product in DMSO under visible-light irradiation at room temperature. Using the optimized conditions, a variety of mono-, di-, and tri-fluoromethylarenes 3 underwent selective monofunctionalization to afford the corresponding aryl acetic acids, α-fluorocarboxylic acids, and α,α-difluorocarboxylic acids 4, respectively, in moderate to very good, ranging from 34% to 94% (Scheme 2). Particularly important for this transformation, it is essential to control the reaction time

in order to avoid further hydrodefluorination and decarboxylation of the desired products. Noteworthy, a wide panel of sensitive functional groups (e.g., CN, OR, SR, CO₂R, CONR₂) were tolerated under these conditions. Moreover, access to α-fluoromalonic acid derivatives were also possible from the corresponding α,α-difluorocarboxylic esters and amides. Interestingly, a substrate bearing an aryl C-Cl bond underwent selective C-F bond carboxylation, affording the desired product in good yield with high chemoselectivity. Therefore, this principle can be applied for the diversification of alkyl halides with multiple competing sites by doubly and triply selective sequential functionalization. Notably, control experiments and DFT calculations demonstrate the dual role of CO₂ as an electron carrier and electrophile during this transformation. The fluorinated substrates would undergo single-electron reduction by electron-rich CO₂ radical anions, which are generated *in situ* from CO₂ *via* sequential hydride-transfer reduction and hydrogen-atom-transfer processes (Scheme 3).



Scheme 2. Carboxylation of C(alkyl)-F bonds with CO₂ *via* visible-light photoredox catalysis.

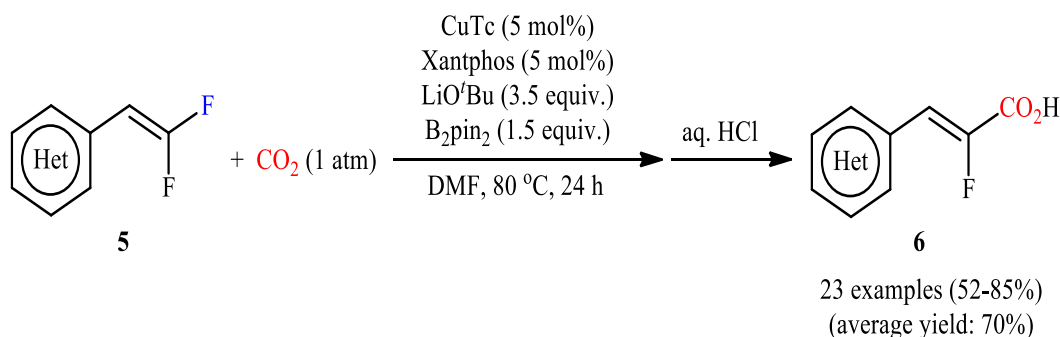


Scheme 3. Mechanistic proposal for the reaction in Scheme 2.

3. Defluorinative carboxylation of C_(alkenyl)-F bonds

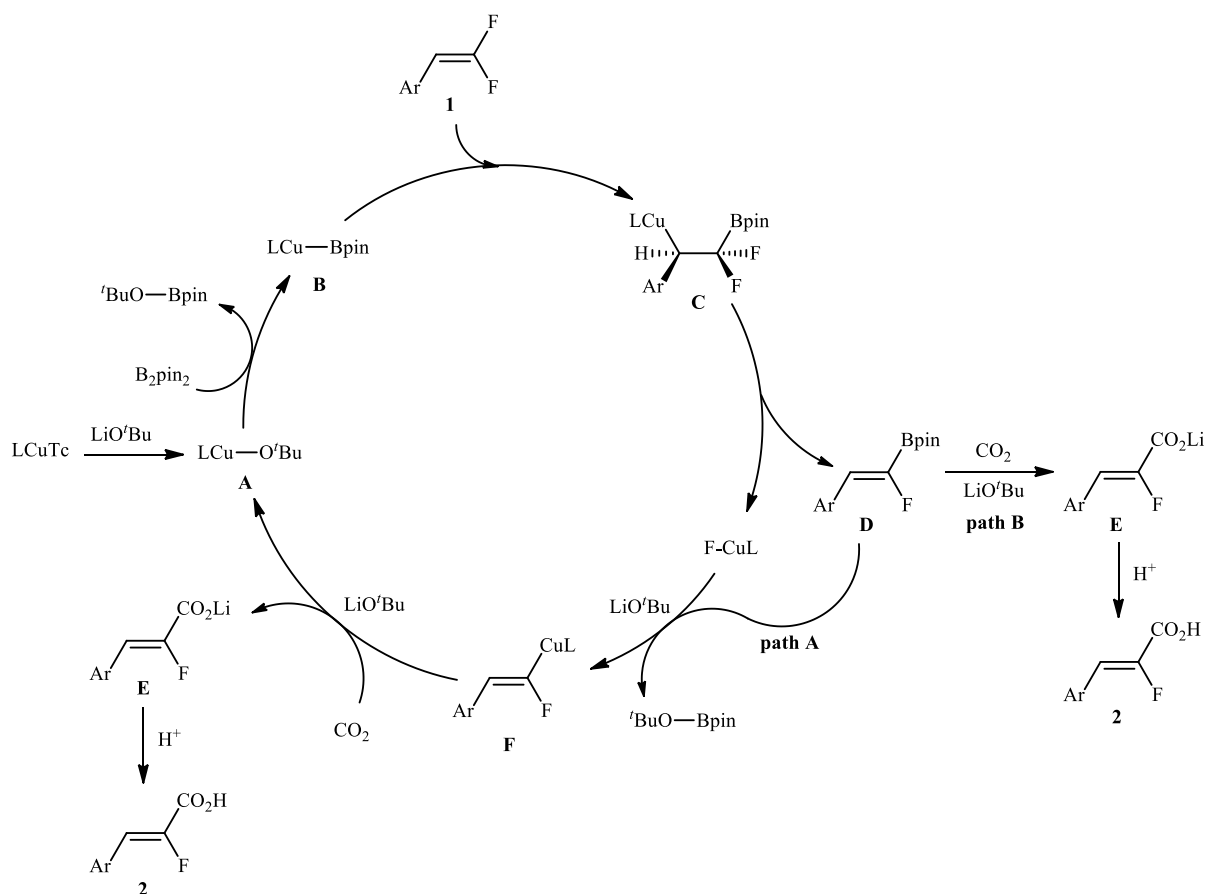
In 2019, in the same paper describing the defluorinative carboxylation of fluoroalkanes to aliphatic carboxylic acids in the presence of catalytic amounts of copper, Yu and co-workers reported the successful copper/diboron catalyzed preparation of acrylic acid derivatives from respective fluoroalkenes [13]. Thus, in the presence of a combination of CuTc, Xantphos, LiO^tBu, and B₂pin₂ in DMF at 80 °C, the reaction of various gem-difluoroalkenes **5** with atmospheric CO₂ furnished the corresponding α-fluoroacrylic acids **6** in moderate to high yields, ranging from 52% to 85% (Scheme 4). Notably, this *ipso* mono-carboxylation of the C-F bond occurred with outstanding (*Z*)-selectivity and can be performed on gram scale with no significant decrease in yield. Beside *gem*-difluoroalkenes, *gem*-difluorodienes were also found to be suitable substrates

for this CO₂-fixation reaction. A plausible mechanism proposed by the authors was started with transmetalation of *in situ* generated copper(I) alkoxide A with the diboron reagent to form boryl-copper(I) species B. Subsequently, difluoroalkene **5** inserted into the Cu-B bond of B to achieve intermediate C which was then underwent syn β-F elimination to generate (*Z*)-fluorinated pinacol alkenylboronate D and a Cu(I)-F species. Finally, intermediate D afforded the desired product **6** by a Cu(I)-catalyzed transmetalation/carboxylation sequential process (Scheme 5, path a). In another possibility, the direct carboxylation of D with CO₂ in the presence of LiO^tBu resulted in the formation of the corresponding carboxylate (Scheme 5, path b), even though this is less efficient than path A and less favored in the reaction mixture.



(Het)Ar= Ph, 4-Me-C₆H₄, 4-ⁱPr-C₆H₄, 4-^tBu-C₆H₄, 4-Ph-C₆H₄, 4-OMe-C₆H₄, 4-OPh-C₆H₄, 4-OCF₃-C₆H₄, 4-F-C₆H₄, 4-Cl-C₆H₄, 4-Br-C₆H₄, 4-NPh₂-C₆H₄, 4-(CH₂CH₂CH=CF₂)-C₆H₄, 3-OMe-C₆H₄, 3-Me-C₆H₄, 3-Cl-C₆H₄, 2-Me-C₆H₄, 2-OMe-C₆H₄, 2-F-C₆H₄, 3-OMe-4-F-C₆H₃, 3-benzothienyl, 1-naphthyl, 2-naphthyl

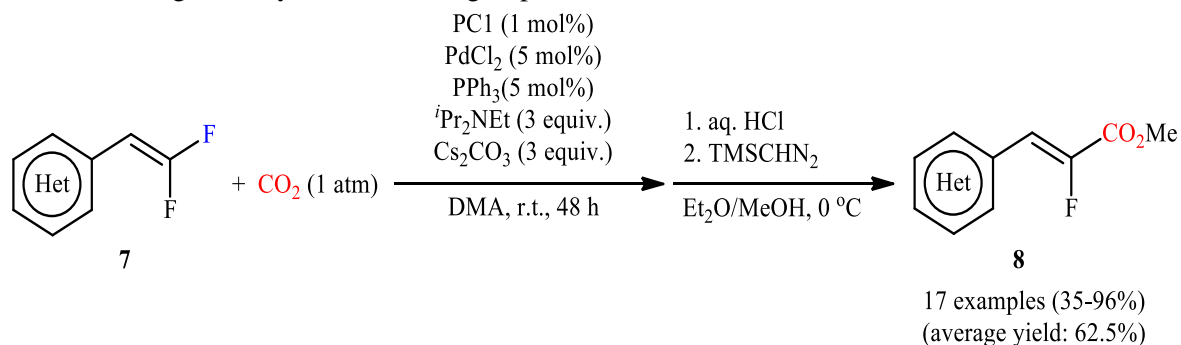
Scheme 4. Yu's synthesis of α-fluoroacrylic acids **6**.



Scheme 5. Possible pathway of α -fluoroacrylic acids **6** formation.

Another independent C(alkenyl)-F bond carboxylation method was published by Feng and co-workers using a photoredox/palladium dual catalysis [15]. They showed that a number of gem-difluoroalkenes **7** were effectively converted in the corresponding α -fluoroacrylic acids **8** using the combination of PdCl₂/PPh₃/PCl/Pr₂NEt/Cs₂CO₃ combination as the catalytic system, employing CO₂ as the carboxylating agent (Scheme 6). A large variety of functional groups

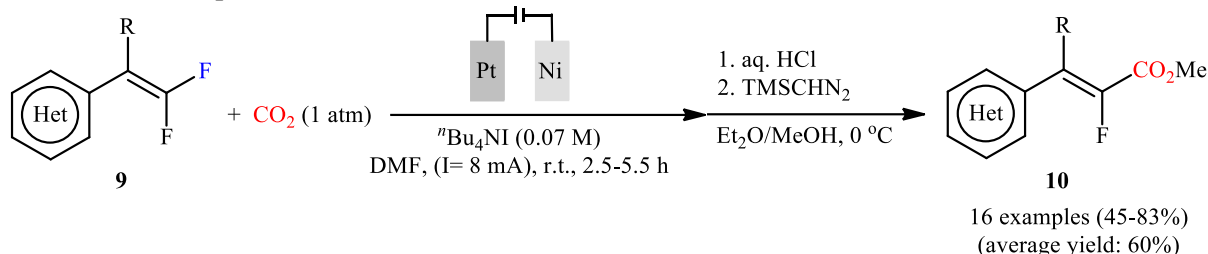
(e.g., CF₃, OCF₃, CN, SO₂Me, CO₂^tBu, CONEt₂) is compatible with the reaction conditions. Thus, the protocol offers scope for further elaboration of products. Noteworthy, gem-difluoroalkenes containing two substituents were also amenable in the current transformation, albeit requiring a prolonged reaction time. However, alkyldifluoroalkenes failed to participated in this CO₂-fixation reaction.



(Het)Ar = 4-CF₃-C₆H₄, 4-CONEt₂-C₆H₄, 4-SO₂Me-C₆H₄, 3-CF₃-C₆H₄, 3-CN-C₆H₄, 3-CO₂^tBu-C₆H₄, 2-CF₃-C₆H₄, 3,5-F₂-C₆H₃, 4-(*p*-OMe-C₆H₄)-C₆H₄, 4-(*p*-OCF₃-C₆H₄)-C₆H₄, 4-(2-naphthyl)-C₆H₄, 4-(1-pyrazolyl)-C₆H₄, 1-naphthyl, 2-naphthyl, 3-dibenzofuryl, 2-benzothieryl, 6-(1-Boc)-indolyl

Scheme 6. Direct defluorinative carboxylation of gem-difluoroalkenes **7** with CO₂ through photoredox/palladium dual catalysis.

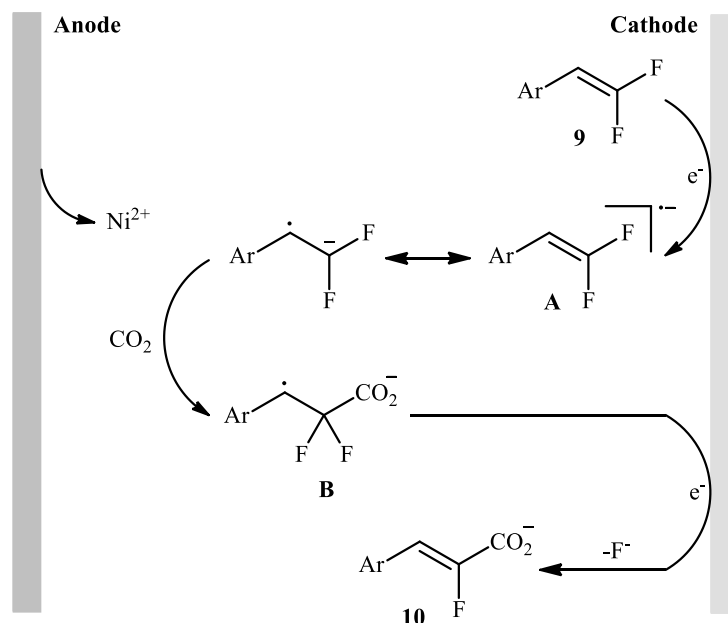
Inspired by these works, Wu-Zhou group has developed an electrochemical protocol for direct defluorinative carboxylation of gem-difluoroalkenes with CO₂ [16]. By using a platinum plate as the cathode and a cheap nickel plate as the anode in an undivided cell under constant current conditions (8 mA), the reaction of various aryldifluoroalkenes **9** with CO₂ (1 atm) proceed smoothly under room temperature, without the use of



R= H, Ph

(Het)Ar= 4-Ph-C₆H₄, 4-CO₂Me-C₆H₄, 4-CF₃-C₆H₄, 4-CONEt₂-C₆H₄, 4-SO₂Me-C₆H₄, 3-CF₃-C₆H₄, 3-OCF₃-C₆H₄, 3-CN-C₆H₄, 3-CO₂Me-C₆H₄, 2-CF₃-C₆H₄, 3,5-F₂-C₆H₃, 3-CN-4-F-C₆H₃, 1-naphthyl, 2-naphthyl, 2-benzothienyl, 3-benzothienyl

Scheme 7. Electrochemical approach to α -fluoroacrylic acids **10**.



Scheme 8. Mechanism that accounts for the formation of α -fluoroacrylic acids **10**.

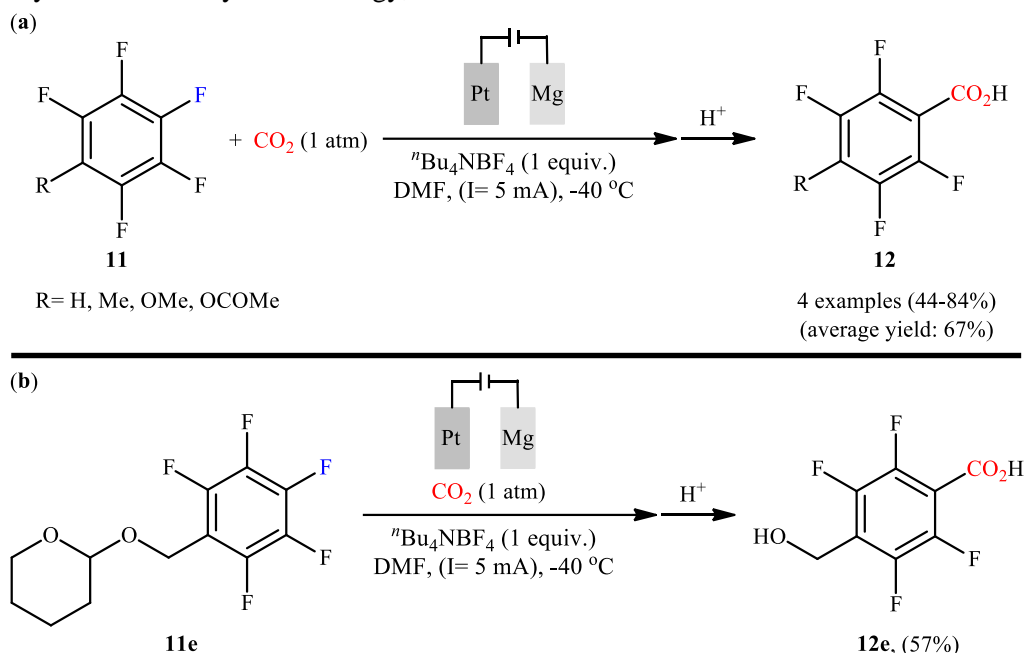
4. Defluorinative carboxylation of C_(aryl)-F bonds

One of the earliest reports deals with the synthesis of benzoic acid derivatives through the defluorinative carboxylation of fluoroarenes with CO₂ can be found in a 2013 paper by Senboku and co-workers [18]. In this report, the authors disclosed that a small series of polyfluoroarenes **11** could effectively undergo defluorinative carboxylation with atmospheric CO₂ in an undivided cell assembled with a magnesium rod anode and a platinum plate cathode employing ^tBu₄NBF₄ as the

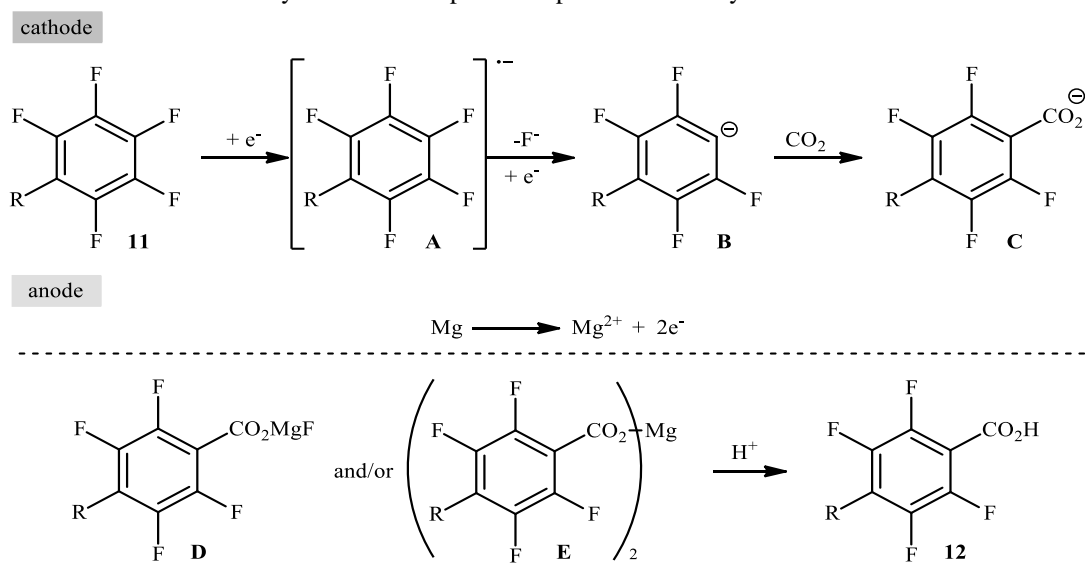
supporting electrolyte under 5 mA in DMF at -40 °C, to afford the corresponding polyfluorobenzoic acids **12** in moderate to good yields after hydrolysis (Scheme 9a). Interestingly, this transformation exhibited a high degree of regio- and chemoselectivity, in which the corresponding mono-carboxylated polyfluorobenzoic acids were obtained as the main products, while the yield of dicarboxylation products was less than 10%. Unfortunately, the reason for the regio- and

chemoselectivity in the present electrochemical carboxylation is not clear at the present stage. Notably, lower yields were obtained using either higher reaction temperature or higher current density. It should be mentioned that electrochemical carboxylation of a THP-protected pentafluorobenzyl alcohol 11e was also proceeded under similar conditions, affording 2,3,5,6-tetrafluoro-4-hydroxymethylbenzoic acid 12e through one-pot carboxylation and deprotection of tetrahydropyran-2-yl group under acidic condition (Scheme 9b). The authors proposed a plausible mechanistic pathway for this carboxylation strategy, such

as that shown in Scheme 10. At the beginning, one-electron reduction of polyfluoroarene 11 at the cathode produces the anion radical of A that, after elimination of a fluoride ion followed by further one-electron reduction affords aryl radical B. Subsequently, fixation of carbon dioxide to newly formed anion B leads to the formation of carboxylate ion C. On the other hand, at the anode, dissolution of a magnesium metal takes place to give magnesium ion. Carboxylate ion C would readily capture magnesium ion to afford salts D and/ or E, which upon an acid treatment give polyfluorinated benzoic acid 12.



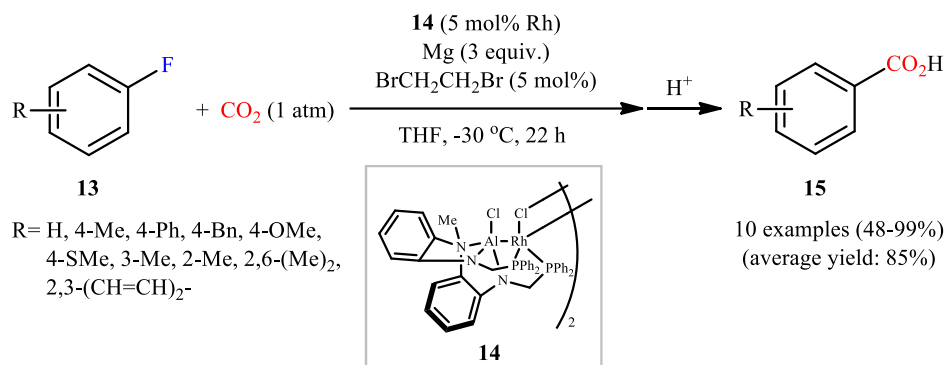
Scheme 9. (a) Catalyst-free electrochemical defluorinative carboxylation of fluoroarenes 11 with CO₂; (b) electrochemical carboxylation of THP-protected pentafluorobenzyl alcohol 11e.



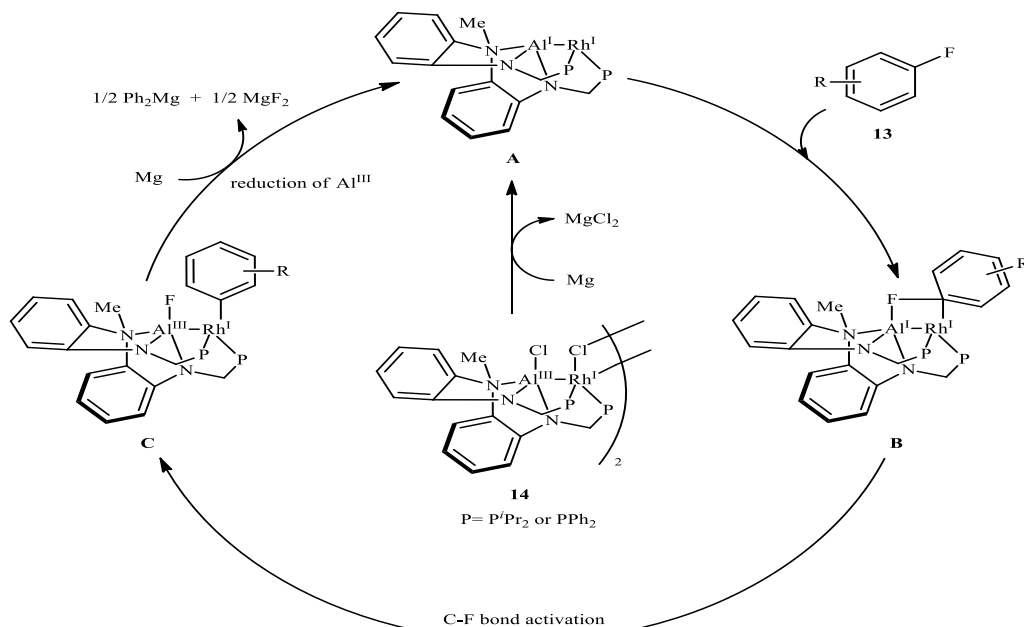
Scheme 10. Probable reaction mechanism of the electrochemical synthesis of polyfluorinated benzoic acids 12.

Seven years later, Sakaki and Nakao along with their co-workers demonstrated that a variety of mono-fluorinated arenes **13** undergo defluorinative carboxylation with atmospheric CO₂ in the presence of a catalytic amount of rhodium–aluminum complex **14** in combination with 3 equiv. of Mg powder and 5 mol% of 1,2-dibromoethane [19]. The expected benzoic acids **15** were formed in moderate to quantitative yields after hydrolysis (Scheme 11). The reaction scope appears to be relatively broad as alkyl, aryl, benzyl, and alkoxy groups were tolerated at various substitution sites of fluorobenzenes. The reaction could also be conducted

successfully on a gram scale (1.4 g, 82% yield). In addition, D₂O, B(OⁱPr)₃, and *N*-methoxy-*N*-methylbenzamide can also serve as quenching electrophiles to generate the corresponding deuterated, borylated, and acylated products. The authors undertook in-depth computational studies to elucidate the mechanism of this CO₂ fixation reaction through density functional theory (DFT). Thus, they indicated that the C–F bond activation would afford Z-type Al^{III}–Rh^I complex **C**, which could potentially be reduced with Mg to realize a catalytic magnesiation of Ar–F bonds (Scheme 12).



Scheme 11. Sakaki-Nakao's synthesis of benzoic acids **15**.



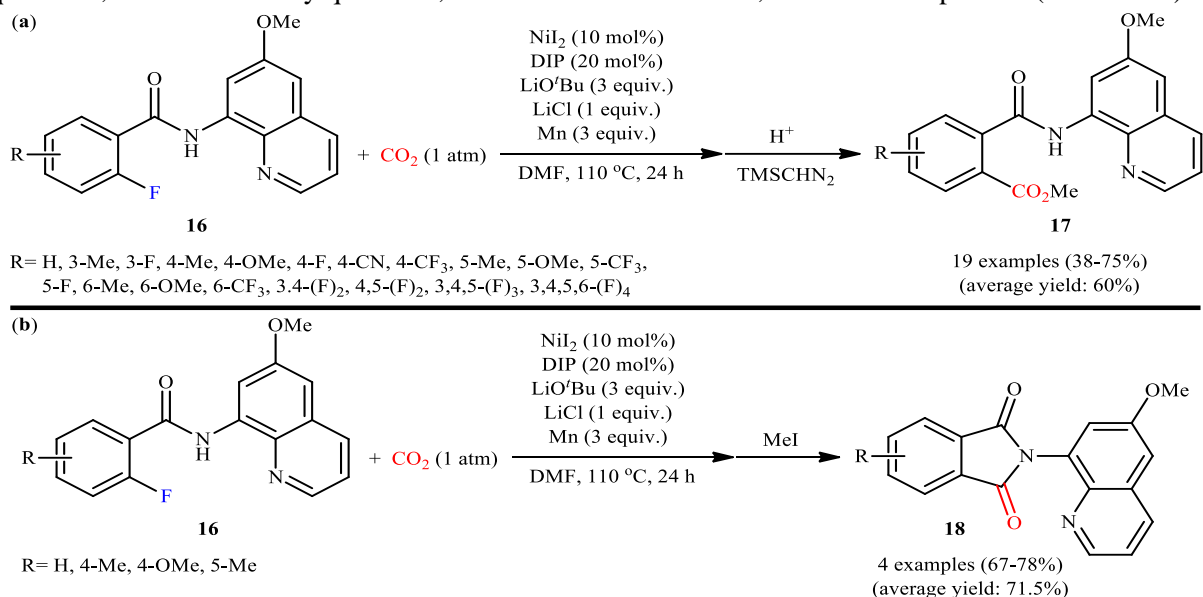
Scheme 12. A plausible reaction mechanism for the formation of benzoic acids **15**.

Shortly afterwards, Pei and Wang unraveled the first nickel-catalyzed selective defluorinative carboxylation of aryl C–F bonds with CO₂ [20]. They showed that treatment of various decorated 2-fluorobenzoic acids **16** masked by 8-amino-6-methoxyquinoline directing group with atmospheric CO₂

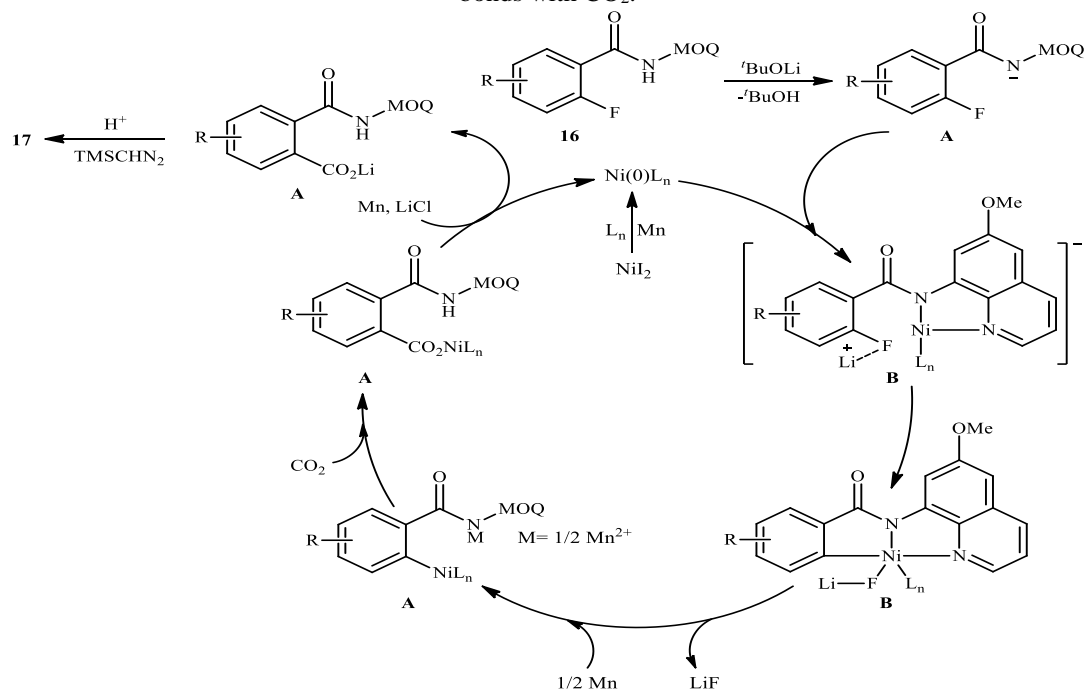
in the presence of NiI₂/4,7-diphenyl-1,10-phenanthroline (DIP)/LiO^tBu/LiCl/Mn combination as a catalytic system in DMF provided the corresponding carboxylic acid methyl esters **17** in moderate to good yields after esterification of *in situ* formed acids with TMSCHN₂ (Scheme 13a). Interestingly, the electronic nature of the

substituents in the phenyl ring periphery of fluoroarenes had a little impact on the facility of the coupling. Thus, this methodology tolerated a variety of electron donor (e.g., Me, OMe) and electron withdrawing (e.g., F, CF₃, CN) functional groups. Notably, the 8-aminoquinoline group can be easily removed by treatment with TsOH and MeOH, affording phthalic acid ester derivatives. It should be mentioned that, replacing 8-amino-6-methoxyquinoline with some other directing groups (e.g., 8-aminoquinoline, 8-amino-5-methylquinoline, 8-amino-

6-methylquinoline, 8-amino-5-methoxyquinoline, 4-anisole) led to much lower yields or even no desired product at all. Interestingly, it was shown that when MeI was used as a post-dealing reagent, the present reaction was applicable to C-F/N-H annulation of *ortho*-fluoro-substituted aromatic amides with CO₂, leading to the formation of phthalimide derivatives 18 (Scheme 13b). According to the proposed mechanism, the reaction proceeds *via* C-F bond oxidative addition, reduction, CO₂ insertion, and reduction process (Scheme 14).



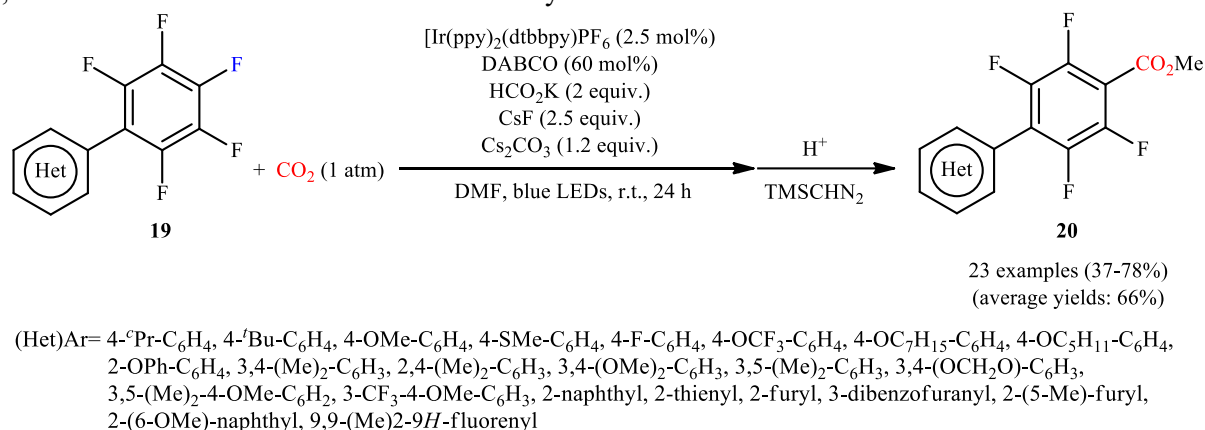
Scheme 13. (a) Ni-catalyzed defluorinative carboxylation of fluoroarenes 16 with CO₂; (b) Ni-catalyzed lactamization of aryl C-F bonds with CO₂.



Scheme 14. Plausible mechanism explaining the Ni-catalyzed synthesis of carboxylic acid methyl esters 17 from fluoroarenes 16 and CO₂.

An improved version of this transformation was recently reported by Zhang, Yu *et al.*, who developed a versatile visible-light photoredox-catalyzed synthesis of poly-fluorobenzoic acid derivatives under ambient conditions [21]. A number of penta-fluoroarenes **19** were converted to the corresponding tetra-fluorobenzoic acid derivatives **20** using only 2.5 mol% of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$, employing DABCO as electron donor, HCO_2K as an additive, and mixed base of $\text{CsF}/\text{Cs}_2\text{CO}_3$ (Scheme 15). Likewise, tetra- and tri-fluoroarenes also effectively

reacted under the standard conditions to generate the corresponding tri-, and di-fluorobenzoic acid products, respectively. A variety of functional groups such as cyano, ether, thioether, sulfonamide, ester, and amine functionalities were compatible with the reaction conditions. Thus, the protocol offers scope for further elaboration of products. Notably, in all cases, the C-F bond cleavage occurred selectively at the para position of the substituents.



Scheme 15. Visible-light photoredox-catalyzed selective carboxylation of C(sp²)-F bonds in polyfluoroarenes **19** with CO₂.

5. Conclusion

The reductive carboxylation of carbon-based nucleophiles with CO₂ as a C1 source is a promising methodology for green and straightforward synthesis of carboxylic acids, which are well-established versatile building-blocks for the construction of various chemical bonds, including C-H, C-O, C-N, C-S, and C-F bonds. In this context, the direct defluorinative carboxylation of C-F bonds has recently devoted a great deal of attention. As illustrated, various C_(alkyl)-F, C_(alkenyl)-F, and C_(aryl)-F bonds were applicable to this reaction. Interestingly, all of the carboxylation reactions covered in this review were performed under atmospheric pressure. This indicates the potential application of this novel page of carboxylic acid synthesis in industry. We hope that this review will attract the synthetic community that focuses on carboxylation of inert substrates and will be observed as an anchor to help and develop focused research in CO₂ utilization field.

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