

# Transition-metal catalyzed carboxylation of organoboron compounds with CO<sub>2</sub>

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## ABSTRACT

Without slight doubt synthesis of carboxylic acids and their derivatives through the carboxylation reactions of organometallic compounds using CO<sub>2</sub> as the raw material are one of the most attractive and hot research topics in the field of CO<sub>2</sub> utilization. Therefore, broadening the scope of nucleophilic reagents for this appealing page of carboxylic acids synthesis is always interesting. Over the past few decades, organoboron compounds have aroused great interest in the organic chemistry community as promising organometallic reagents owing to their high stability, reactivity, safety, and easy accessibility. Not surprisingly, these compounds have recently found application in the area of CO<sub>2</sub>-fixation reactions. This review describes the achievements that have been reported on this fast-growing research arena.

## 1. Introduction

The utilization of carbon dioxide (CO<sub>2</sub>) as a renewable one-carbon (C1) feedstock for producing fine and bulk chemicals is currently attracting considerable interest [1]. Over the years, several proficient reactions have been developed for CO<sub>2</sub> catalytic conversion into value-added chemicals such as amines, amides, aldehydes, ketones, esters, and many more [2–10]. The synthesis of carboxylic acids through the carboxylation of carbon-based nucleophiles with CO<sub>2</sub> as the electrophilic partner is one of the most representative and promising applications of CO<sub>2</sub> in organic synthesis [11]. However, due to high thermodynamic stability and low reactivity of CO<sub>2</sub> [12], strongly nucleophilic organometallic reagents (e.g., unstable and moisture sensitive organolithium compounds and violent organomagnesiums compounds) are usually required for the success of this synthetic strategy. Recently, organosilicon reagents have emerged as attractive nucleophilic partners for the titled reaction owing to their easy handling, easy accessibility, low toxicity, and good thermal-moisture stability [13]. However, due to the poor polarization of C-Si bonds, these reagents are less reactive toward electrophiles than the other organometallic nucleophiles and fluoride ions are usually required for their activation [14]. Therefore, there is still further need to develop alternative or complementary C-nucleophiles for this page of carboxylic acid synthesis.

Organoboron compounds, compounds containing a boron-carbon bond, are one of the most widely studied and applied reagents in modern organic synthesis [15]. This stems from their ease of preparation, coupled with their high stability, low toxicity, and ability to undergo an extensive variety of chemical transformations [16]. Not surprisingly, these compounds have also found application in the field of CO<sub>2</sub> chemical utilization. Since many great achievements on the carboxylation of organoboron compounds with CO<sub>2</sub> have occurred over the last two decades, a comprehensive review on this interesting research arena seems to be timely. In connection with our preceding works on the chemical conversion of CO<sub>2</sub> [6,9,10,17] and modern organic synthesis [18], we summarize here the most representative and important reports on the preparation of carboxylic acids from the corresponding organoboron compounds and CO<sub>2</sub> via carbon-boron bond cleavage (Fig. 1), which may stimulate researchers for further thinking and research on this domain. It should be mentioned that several interesting reviews were briefly highlighted some of the accomplishments on this chemistry [19], however, a comprehensive review is still lacking.

Transition-metal catalyzed reactions are very important from efficiency point of view [20–30]. Here, we summarized some transition-metal catalyzed including, rhodium, silver, copper, nickel and palladium catalyzed reactions.

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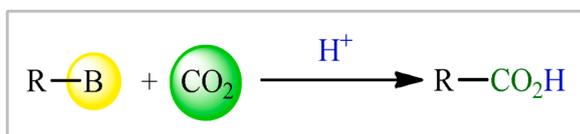
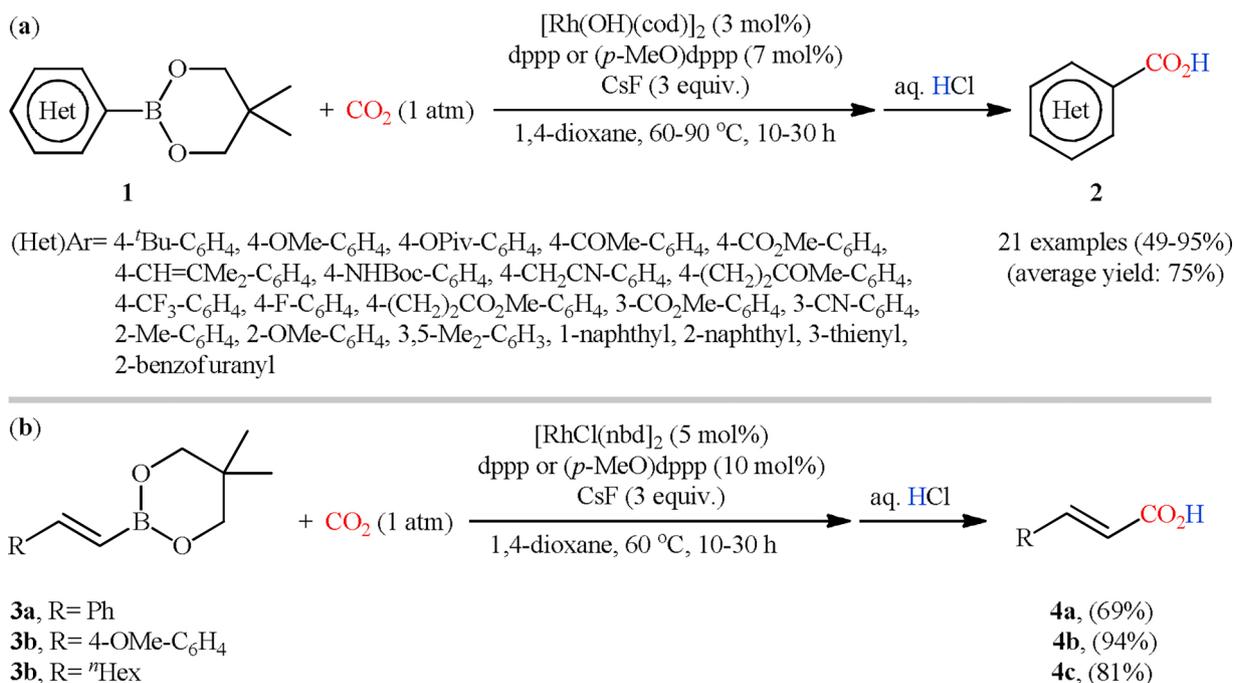


Fig. 1. Preparation of carboxylic acids from organoboron compounds and CO<sub>2</sub>.

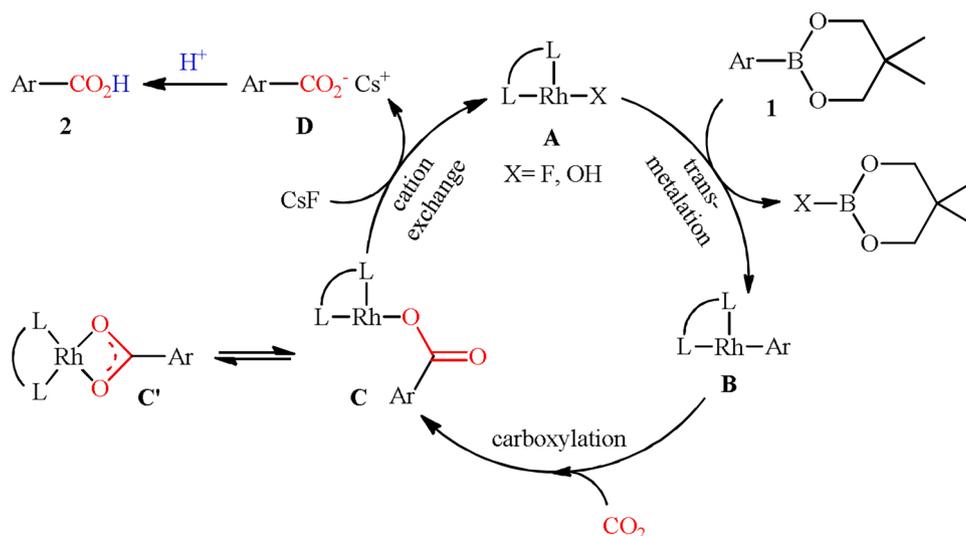
## 2. Rhodium-catalyzed reactions

The first report deals with the preparation of carboxylic acids through the transition metal-catalyzed carboxylation of organoboron compounds with CO<sub>2</sub> can be found in a 2006 paper by Iwasawa et al. [31]. In this report, the authors disclosed that a diverse range of 5, 5-dimethyl-2-(hetero)aryl-1,3,2-dioxaborinanes **1** could effectively undergo carboxylation with atmospheric CO<sub>2</sub> in the presence of [Rh(OH)

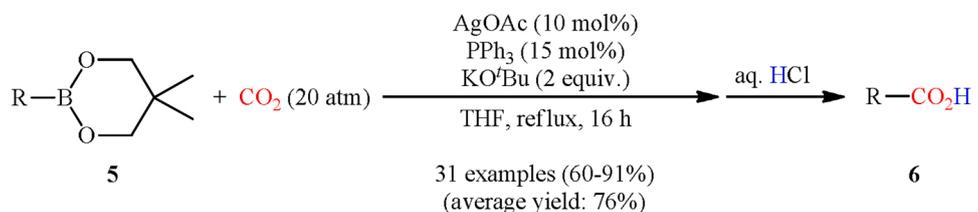
(cod)<sub>2</sub>/dppp/CsF combination as a catalytic system, to afford the corresponding (hetero)aromatic carboxylic acids **2** in moderate to excellent yields after hydrolysis (Scheme 1a). Interestingly, the reaction tolerated the presence of various sensitive functional groups such as fluoro, cyano, protected amine, ester, ether, and ketone functionalities, and promised its potential applications for further modifications of the end products. However, due to loss of product in the workup process, 5,5-dimethyl-2-(1-methylindolyl)-1,3,2-dioxaborinane failed to give the expected 1-methyl-1*H*-indole-2-carboxylic acid under this reaction condition. The authors nicely solved this limitation by synthesizing its methyl ester derivative. It is worthy of note that carboxylation reactions of alkenylboronic esters **3** also proceeded under similar conditions in good yields (Scheme 1b), except that [RhCl(nbd)]<sub>2</sub> was employed instead of [Rh(OH)(cod)]<sub>2</sub>. The authors proposed a plausible mechanistic pathway for this transformation, such as that shown in Scheme 2. Initially, transmetalation between the Rh-catalyst A and the boronic



Scheme 1. Rh-catalyzed carboxylation of (a) arylboronic esters **1**; (b) alkenylboronic esters **2** with CO<sub>2</sub>.



Scheme 2. Postulated mechanism for the reaction in Scheme 1.



R = -CH=CHPh, Ph, 4-Me-C<sub>6</sub>H<sub>4</sub>, 4-<sup>t</sup>Bu-C<sub>6</sub>H<sub>4</sub>, 4-Ph-C<sub>6</sub>H<sub>4</sub>, 4-OMe-C<sub>6</sub>H<sub>4</sub>, 4-OPh-C<sub>6</sub>H<sub>4</sub>, 4-CN-C<sub>6</sub>H<sub>4</sub>, 4-CHO-C<sub>6</sub>H<sub>4</sub>, 4-COMe-C<sub>6</sub>H<sub>4</sub>, 4-CO<sub>2</sub>Me-C<sub>6</sub>H<sub>4</sub>, 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>, 4-F-C<sub>6</sub>H<sub>4</sub>, 4-Cl-C<sub>6</sub>H<sub>4</sub>, 4-Br-C<sub>6</sub>H<sub>4</sub>, 4-I-C<sub>6</sub>H<sub>4</sub>, 4-(CH<sub>2</sub>=CH)-C<sub>6</sub>H<sub>4</sub>, 4-phenylacetylenyl-C<sub>6</sub>H<sub>4</sub>, 3-OMe-C<sub>6</sub>H<sub>4</sub>, 3-Cl-C<sub>6</sub>H<sub>4</sub>, 3-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>, 3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 2-Cl-C<sub>6</sub>H<sub>4</sub>, 2-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>, 2,4-OCH<sub>2</sub>O-C<sub>6</sub>H<sub>3</sub>, 1-naphthyl, 2-naphthyl, 2-benzofuryl, 2-thienyl, 3-thienyl

**Scheme 3.** Ag-catalyzed carboxylation of boronic esters **5** with CO<sub>2</sub>.

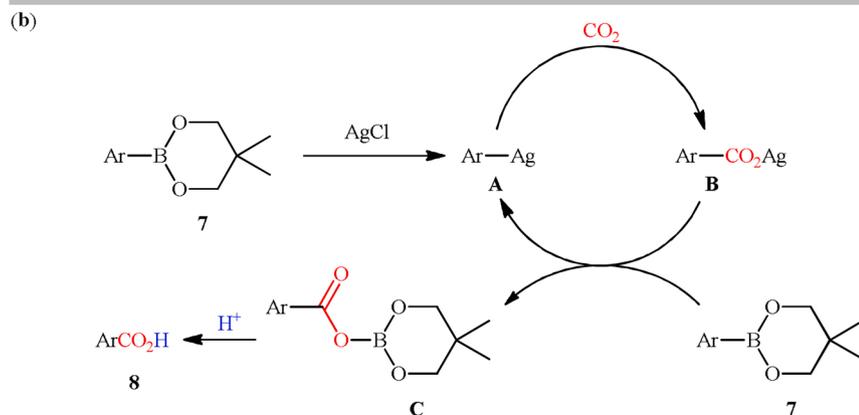
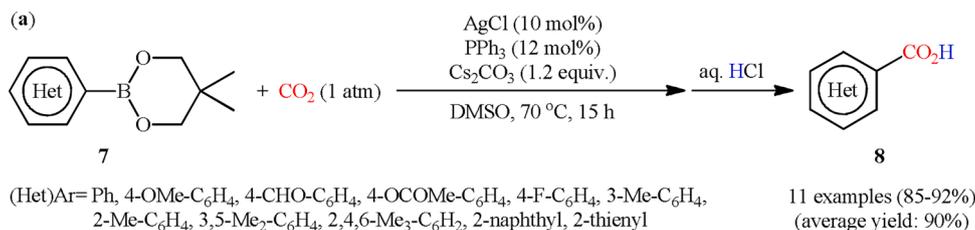
ester **1** leads to the formation of [(dppp)Rh-Ar] intermediate **B** that, after carboxylation with CO<sub>2</sub> provides the monodentate complex **C** which is in equilibrium with the bidentate complex **C'**. Next, the cation exchange between complex **C** and CsF affords cesium benzoate **D** and regenerates the putative active catalyst **A**. Finally, hydrolysis of cesium benzoate **D** produces the expected carboxylic acid **2**. Later, this mechanism was corroborated by density functional theory (DFT) calculations [32]. Drawing inspiration from these works, very recently, Li and co-workers disclosed the first regioselective arylcarboxylation of electron-deficient acrylamides with arylboronic acids under atmospheric pressure of CO<sub>2</sub> employing [Rh(cod)Cl]<sub>2</sub>/AgOTf/Cs<sub>2</sub>CO<sub>3</sub>/N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA) combination as a catalytic system [33].

### 3. Silver-catalyzed reactions

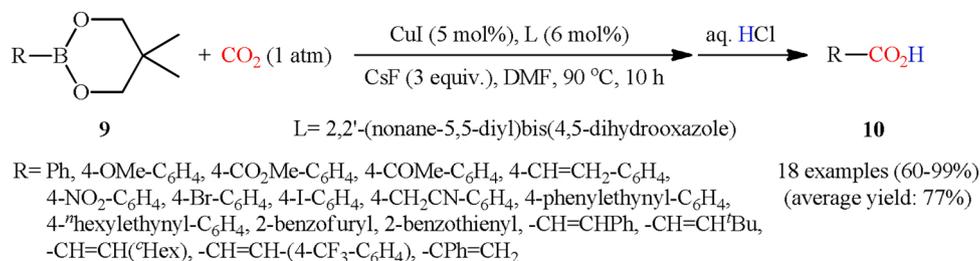
In 2012, Zhang and Lu along with their co-workers revealed for the first time the usefulness of silver catalysts for the carboxylation of organoboron compounds with CO<sub>2</sub> [34]. In order to identify the best catalytic system, they investigated the activities of various silver salts (e.g., AgF, AgBF<sub>4</sub>, AgPF<sub>6</sub>, AgOAc, AgNO<sub>3</sub>), ligands (e.g., PPh<sub>3</sub>, PCy<sub>3</sub>, IPr, SIPr, IMes, SIMes, dppe), and bases (e.g., CsF, K<sub>2</sub>CO<sub>3</sub>, KO<sup>t</sup>Bu) in the carboxylation of 2,2-dimethyl-1,3-propanediol ester with compressed

CO<sub>2</sub> (20 atm) as a model reaction. The combination of low-cost and commercially available AgOAc with PPh<sub>3</sub> and KO<sup>t</sup>Bu was proved to be most efficient system, which gave a better yield of the desired carboxylic acid product in refluxing THF. Using the optimized conditions, a library of vinyl, aryl, and heteroaryl substituted organoboronic esters **5** gave the corresponding carboxylic acids **6** in very good to excellent yields, ranging from 60 % to 91 % (Scheme 3). Although the reaction displayed a remarkable level of functional group tolerance, the need for high pressure of CO<sub>2</sub> may limit its range of application.

Five years later, L. He's research group found that cheaper AgCl catalyst could be employed for similar conversion when combined with PPh<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub>, resulting in a protocol that allowed for significantly lowering down the CO<sub>2</sub> pressure [35]. Under the catalytic conditions, eleven (hetero)arylboronic esters **7** were effectively carboxylated with atmospheric CO<sub>2</sub> and afforded the desired products **8** in high to excellent yields (Scheme 4a). Interestingly, the results indicated that the electronic and steric characters of the substituents on the aryl ring periphery of substrates had no influence on the facility of this reaction. According to the authors, the mechanism for this transformation is likely to follow the pathway outlined in Scheme 4b. Initially, silver catalyst interacts with the arylboronic ester **7** to give the arylsilver species **A** via the transmetalation from the boron to the silver. Next, CO<sub>2</sub> inserts into the Ar-Ag bond of **A** to form carboxylate complex **B** that, after



**Scheme 4.** (a) He's synthesis of (hetero)aromatic carboxylic acids **8**; (b) Suggested mechanism for the formation of carboxylic acids **8**.



**Scheme 5.** Cu-catalyzed carboxylation of boronic esters **9** with CO<sub>2</sub> developed by Iwasawa.

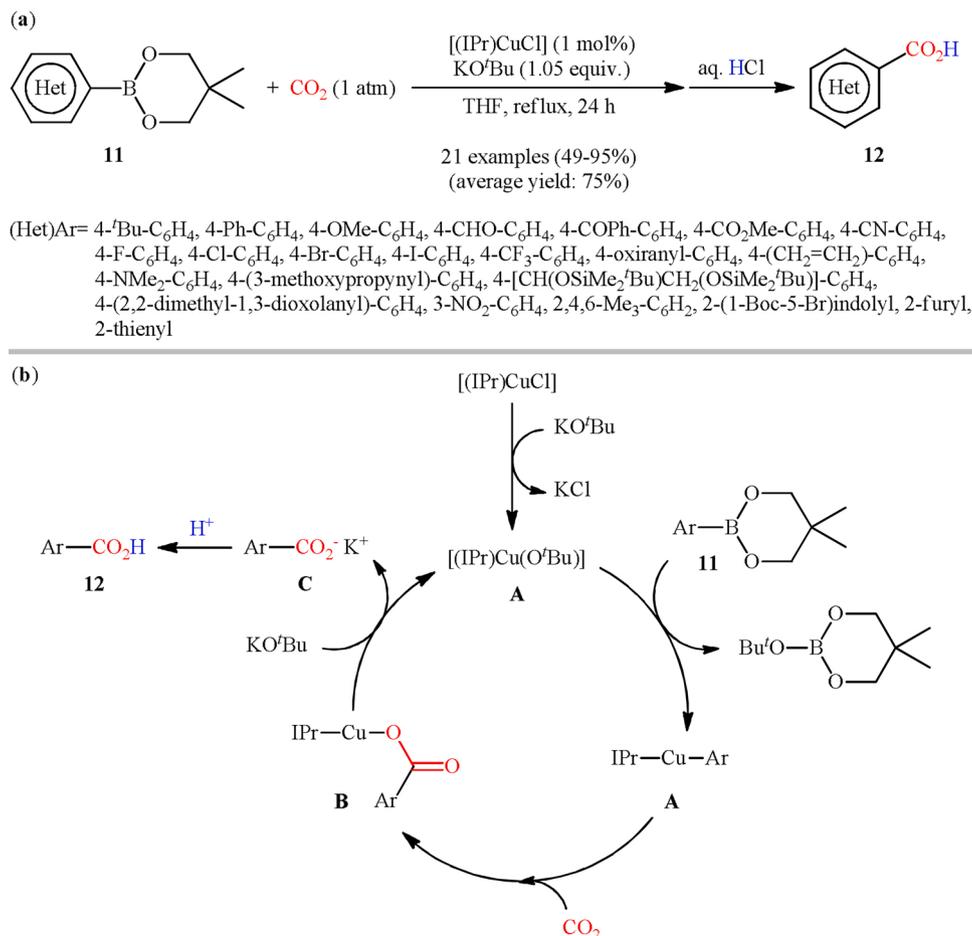
transmetalation to the arylboronic ester **7** affords the carboxylate intermediate **C** and regenerates arylsilver species **A**. Finally, hydrolysis of intermediate **C** yields the target product **8**.

#### 4. Copper-catalyzed reactions

Compared with rhodium and silver, copper is a cheap and abundant metal. Utilization of this earth-abundant metal in catalysis is very attractive from the point of view of economy and environmental sustainability [36]. One of the fundamental utilities of copper catalysis is in the C–C bond formation by using nucleophiles and CO<sub>2</sub> [12,37]. Of the large amount of published papers, without question, copper is the most widely used catalyst on the deborylative carboxylation of organoboron compounds with CO<sub>2</sub>. In 2008, Iwasawa and co-workers rendered the first example of Cu-catalyzed carboxylation of organoboron reagents by using CO<sub>2</sub> [38]. They showed that a combination of copper catalyst (CuI), nitrogen ligand (bisoxazoline), and base (CsF) enables

carboxylation of aryl- and alkenyl-boronic esters **9** with atmospheric CO<sub>2</sub> giving the corresponding aryl- and alkenyl-carboxylic acids **10** in good to quantitative yields (Scheme 5). The results clearly indicated the wider applicability and generality of this protocol compared to the Rh-catalyzed reaction. While vinyl-, ethynyl-, bromo-, iodo-, and nitro-substituted boronic esters were inappropriate substrates in the Rh-catalyzed reaction, afford the desired products in high yields (70–86 %) by using this Cu-catalyzed protocol.

Concurrently, Hou's research group demonstrated that a variety of (hetero)aryl-boronic esters **11** underwent carboxylation with atmospheric CO<sub>2</sub> using only 1 mol% of [(IPr)CuCl] as catalyst in combination with 1.05 equiv. of KO<sup>t</sup>Bu [39]. The expected (hetero)aromatic carboxylic acids **12** were formed in high to quantitative yields after hydrolysis (Scheme 6a). Interestingly, electron-donating and electron-withdrawing groups as well as *ortho*-, *meta*- and *para*-positions showed no significant effects over the reaction yields. Furthermore, three  $\alpha,\beta$ -unsaturated carboxylic acids were obtained in high yields from the corresponding



**Scheme 6.** (a) Hou's synthesis of (hetero)aromatic carboxylic acids **12**; (b) A plausible reaction mechanism for the formation of carboxylic acids **12**.

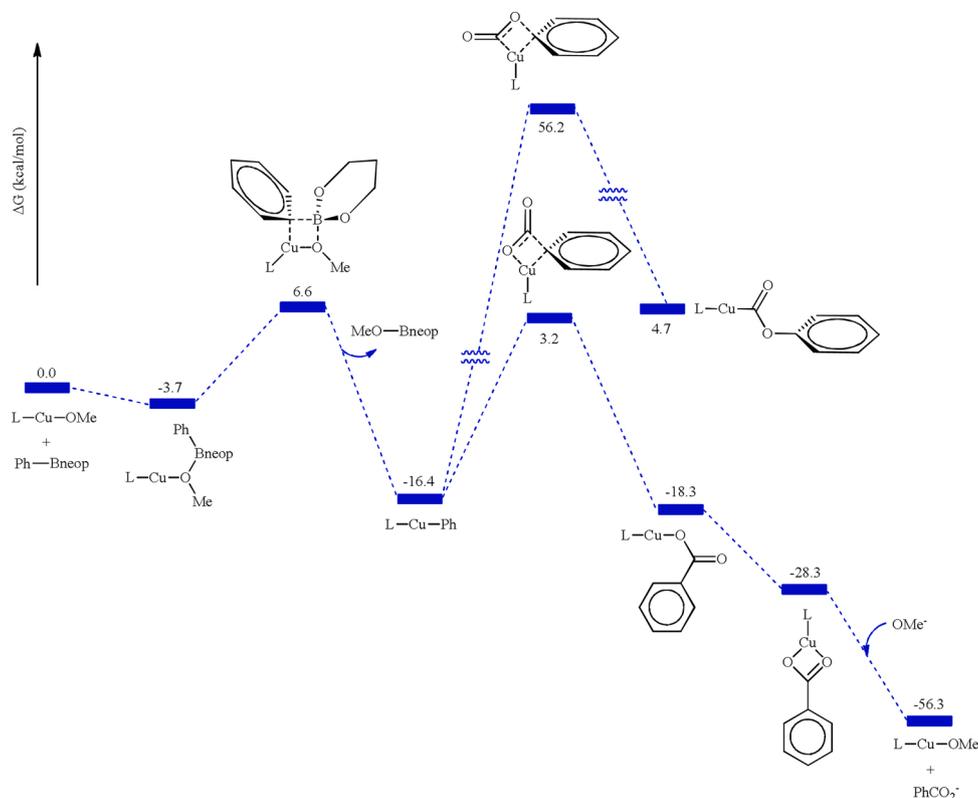
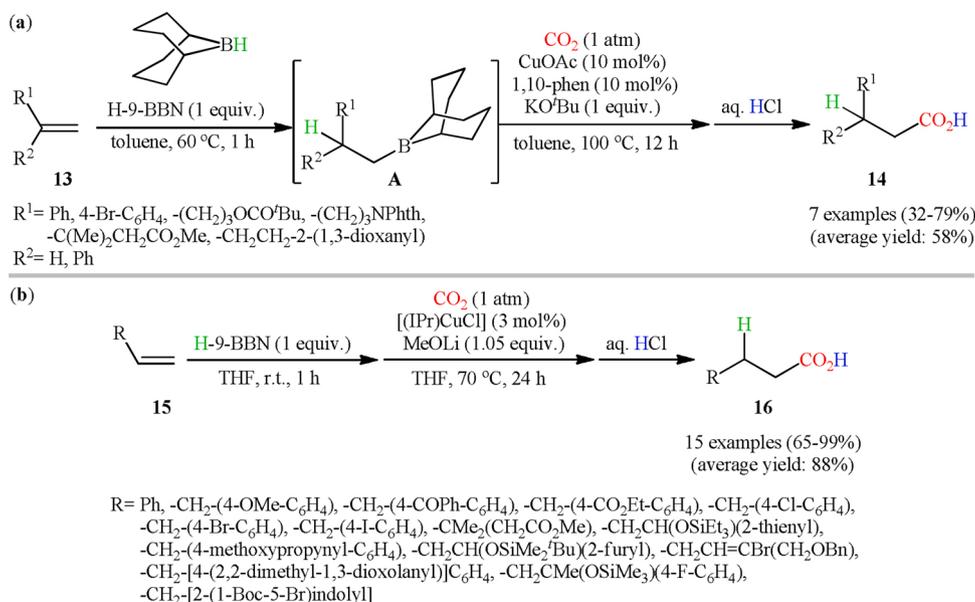


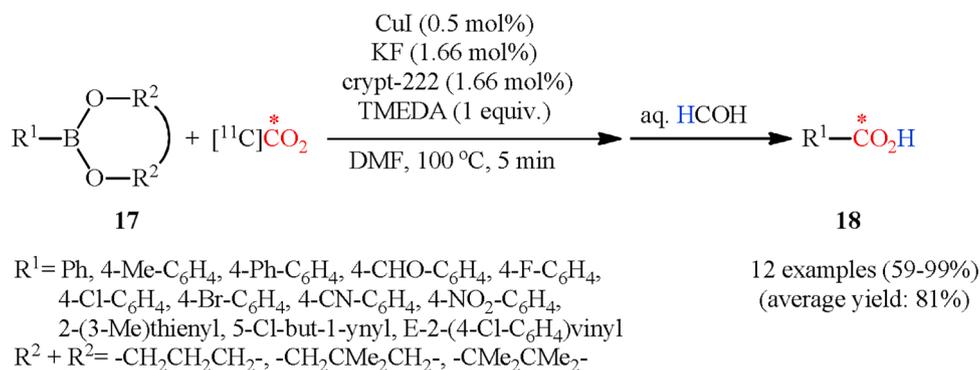
Fig. 2. Reaction profile for the (Me<sub>2</sub>IM)Cu(OMe)-catalyzed carboxylation of phenylboronic ester with CO<sub>2</sub>.

alkenylboronic esters under the identical conditions. Based on a series of control experiments, the authors proposed that the reaction proceeded through the similar mechanistic pathway to the one described for Rh-catalyzed reaction (Scheme 6b). This procedure was later elegantly applied by Lail's group for the double carboxylation of bisboronate ester arenes [40]. In 2010, DFT calculations were carried out by Dang and Lin to explore the detailed mechanistic pathway of the titled reaction, using PhBneop as the model substrate and (Me<sub>2</sub>IM)Cu(OMe) (Me<sub>2</sub>IM = 1, 3-dimethylimidazol-2-ylidene) as the model complex (Fig. 2) [41]. The

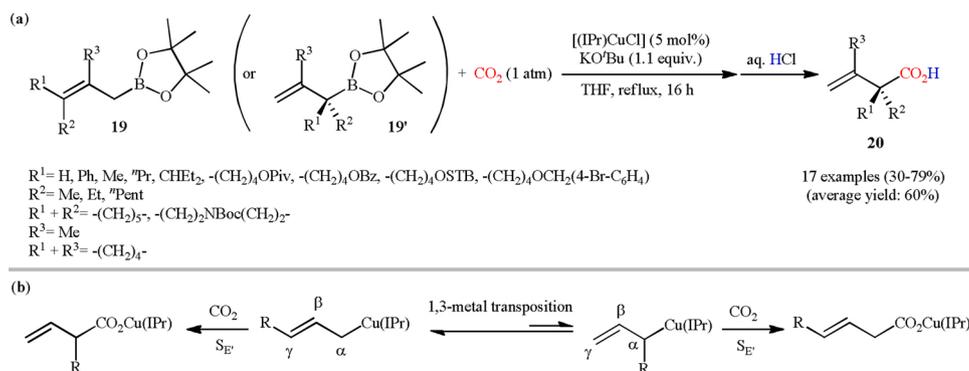
results have affirmed the proposed mechanism by Hou. The results also indicated that the insertion of CO<sub>2</sub> into the Cu-Ph bond is the rate-determining step for this reaction. Moreover, it was found that transmetalations of PhBneop and PhBpin to Cu have similar barriers, and therefore, ArBpin esters should also be reasonable substrates for the carboxylation reaction. These innovative authors also examined the insertions of CO<sub>2</sub> into Cu-C(vinyl, ethyl, ethynyl) bonds. In accord with the experimental observations, insertion of CO<sub>2</sub> into the Cu-C(vinyl) bond has approximately the same barrier as that into the



Scheme 7. (a) Synthesis of aliphatic carboxylic acids **14** by hydroboration of terminal alkenes **13** with 9-BBN and subsequent carboxylation with CO<sub>2</sub>; (b) Reductive carboxylation of terminal alkenes **15** with CO<sub>2</sub> reported by Hou.



**Scheme 8.** [<sup>11</sup>C]-carboxylation of boronic esters **17** with [<sup>11</sup>C]CO<sub>2</sub> developed by Riss.



**Scheme 9.** (a) Synthesis of  $\beta,\gamma$ -unsaturated carboxylic acids **20** via Cu-catalyzed carboxylation of allyl pinacol boronic esters **19** with CO<sub>2</sub>; (b) possible explanation for the observed regioselectivity.

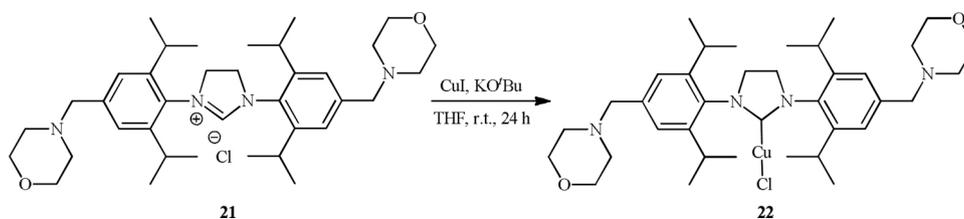
Cu-C-(phenyl) bond. The calculated barriers for CO<sub>2</sub> insertion into Cu-C(sp<sup>3</sup>) and Cu-C(sp) bonds are greater by 4 and 10 kcal/mol, respectively, compared with insertion into a Cu-C(sp<sup>2</sup>) bond. These results point to the possibility of carboxylation of alkylboronate esters with CO<sub>2</sub> under somewhat harsher reaction conditions, whereas the related carboxylation using alkynylboronate esters seems less likely to occur.

Drawing inspiration from these works, the group of Sawamura developed a unique protocol for the preparation of aliphatic carboxylic acids **14** through a sequential hydroboration reaction of terminal alkenes **13** with 9-borabicyclo[3.3.1]nonane (9-BBN), followed by Cu-catalyzed carboxylation of *in situ* generated alkylboron compounds **A** with atmospheric CO<sub>2</sub> (Scheme 7a) [42]. The reaction is noteworthy in that various mono-substituted aliphatic and aromatic terminal alkenes as well as 1,1-disubstituted alkenes were well tolerated. However, internal alkenes were unsuitable substrates under such conditions. Moderate to good yields, good functional group tolerance, using readily available starting materials and inexpensive Cu(phen) catalyst were the merits, mentioned for this synthetic procedure. At the same time, Hou and co-workers provided a further example of alkanolic acids **16** synthesis from the corresponding terminal alkenes **15** and atmospheric CO<sub>2</sub> assisted by [(IPr)CuCl] as a catalyst and MeOLi as a base (Scheme 7b) [43]. Although, just like Sawamura's work, this reaction limited to

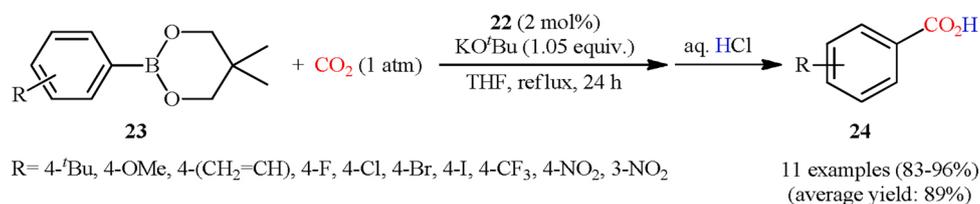
terminal alkenes; the product yields were considerably better than those reported by Sawamura. Recently, Nielsen and Skrydstrup along with their colleagues extended the substrate scope of this chemistry to internal alkenes by using CuCl/IPr/CsF combination as the catalytic system and dioxane as the solvent [44].

In 2012, Riss and co-workers reported the first radiosynthesis of <sup>11</sup>C-labeled carboxylic acids via cyclotron-produced [<sup>11</sup>C]CO<sub>2</sub> carboxylation of the corresponding boronic esters using the combination of CuI, KF, crypt-222, and TMEDA as the catalytic system and DMF as the solvent [45]. Various commercially available aryl, heteroaryl, alkenyl, and alkynyl boronic esters **17** were reacted well under the optimal reaction conditions to produce the desired [<sup>11</sup>C] labeled carboxylic acids **18** in fair to outstanding radiochemical yields within 5 min (Scheme 8). However, alkyl, N-heteroaryl, and aryl boronic esters bearing free amino and hydroxy groups did not work well under otherwise identical reaction conditions. Five years later, the Frølund laboratory demonstrated similar Cu-catalyzed radiosynthesis of [<sup>11</sup>C]3-hydroxycyclopent-1-enecarboxylic acid from cyclopent-2-enol-3-boronic acid pinacol ester [46]. Importantly, the prepared <sup>11</sup>C-labeled carboxylic acid found to be a suitable PET-radioligand for *in vivo* imaging of the high-affinity  $\gamma$ -hydroxybutyric acid (GHB) sites in the live pig.

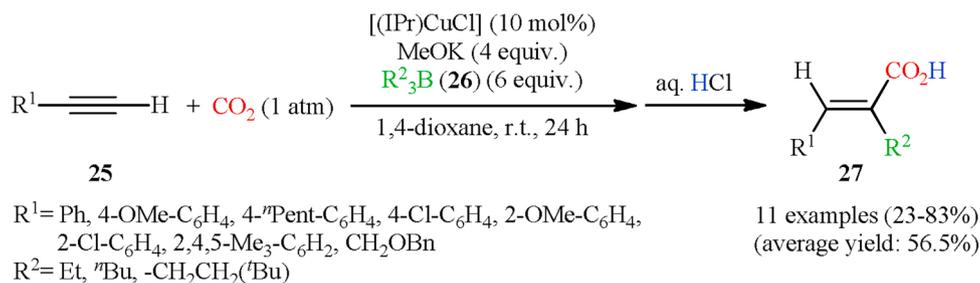
In 2013, Duong described a method for synthesis of  $\beta,\gamma$ -unsaturated



**Scheme 10.** Synthesis of morpholine-functionalized copper complex **22**.



**Scheme 11.** Carboxylation of arylboronic acid esters **23** with atmospheric CO<sub>2</sub> catalyzed by copper complex **22**.

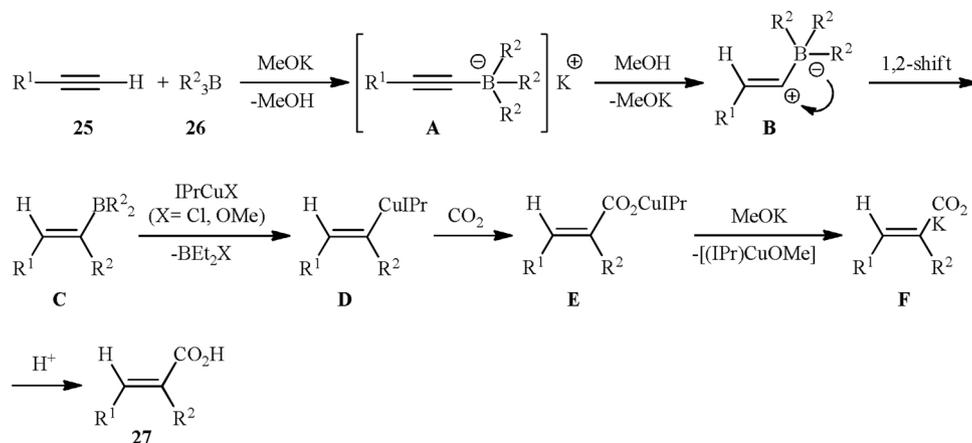


**Scheme 12.** Cu-catalyzed three-component reaction between aromatic terminal alkynes **25**, trialkylboranes **26**, and CO<sub>2</sub>.

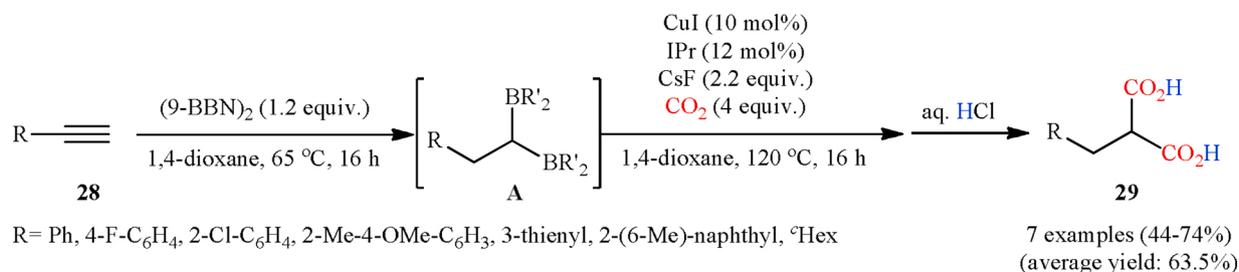
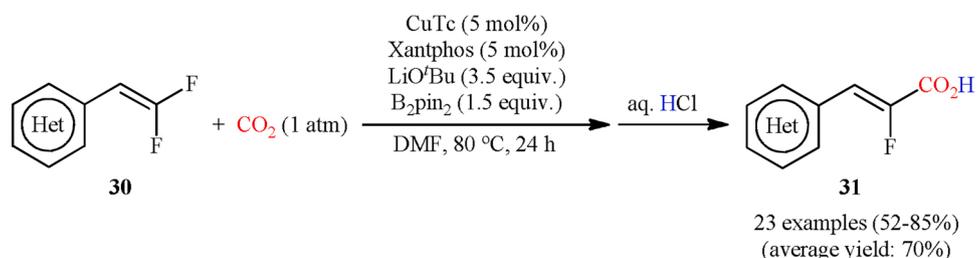
carboxylic acids **20** based on carboxylation of allyl pinacol boronic esters **19** with atmospheric CO<sub>2</sub> by using Hou's conditions (Scheme 9a) [47]. It is worth mentioning that in this reaction, both  $\alpha,\alpha$ -disubstituted and  $\gamma,\gamma$ -disubstituted allylboronates afforded  $\beta,\gamma$ -unsaturated carboxylic acid products, suggesting that the carboxylations of these two kinds of substrates likely proceed *via* the same intermediate. The authors explained the observed regioconvergence in this carboxylation reaction by a reaction of CO<sub>2</sub> with an allylcopper, which exists in a metalotropic equilibrium between two  $\sigma$ -complexes (Scheme 9b).

At the same year, Li and co-workers designed and synthesized a novel pH responsive tertiary amine-functionalized copper complex **22** by reaction of as-prepared morpholine-functionalized [SIPr]·HCl **21** with CuI under a basic condition (Scheme 10) [48]. The resulted Cu complex demonstrated considerably high catalytic activity for the synthesis of benzoic acid derivatives **24** through the carboxylation of corresponding arylboronic acid esters **23** with atmospheric CO<sub>2</sub> in the presence of a stoichiometric amount of KO<sup>t</sup>Bu in refluxing THF (Scheme 11). Interestingly, the presence of a morpholine group in the structure of this catalyst permits to switch the catalytic system from monophasic to biphasic conditions, by protonation, to form a polar ammonium salt. The insoluble Cu catalyst can then be removed by simple centrifugation from the reaction mixture and reused four consecutive cycles with negligible loss in its catalytic performance (from 96 % in the first run to 90 % in the fourth run).

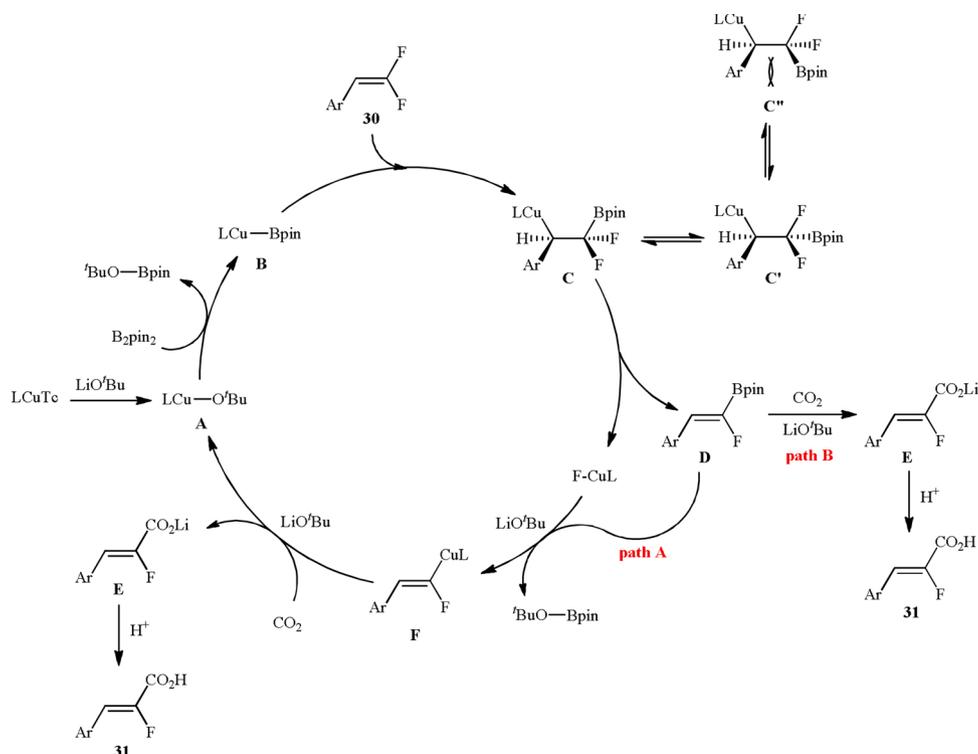
Afterwards, Kimura and colleagues described an interesting one-pot access to synthetically and biologically important  $\alpha,\beta$ -unsaturated carboxylic acids **27** by Cu-catalyzed three-component reaction between aromatic terminal alkynes **25**, trialkylboranes **26**, and CO<sub>2</sub> at atmospheric pressure using [(IPr)CuCl] as the catalyst and MeOK as the base [49]. The reactions were carried out at room temperature, tolerated both electron-rich and electron-poor (hetero)aryl alkynes, and provided the target polysubstituted acrylic acids in good yields with excellent (*E*)-stereoselectivity (Scheme 12). However, aliphatic terminal alkynes did not furnish the desired products under these conditions. The authors evoke a reaction mechanism initiated by reaction of terminal alkyne **25** with trialkylborane **26** in the presence of a base to yield alkynyl-triethylborate **A** that further undergoes protonation at the  $\beta$ -carbon position to afford vinylic cation intermediate **B**. Next, this intermediate undergoes a stereoselective [1,2]-alkyl migration to form the vinyl-diethylborane intermediate **C** that, after transmetalation with a carbene-copper species affords a vinylcopper intermediate **D**. Subsequently, nucleophilic addition of this intermediate to CO<sub>2</sub> leads to the formation of a carboxylate salt **E**, which after reaction with MeOK yields the potassium carboxylate **F** and regenerates the carbene-copper species. Finally, hydrolysis of carboxylate **F** gives the expected product **27** (Scheme 13). It is worthy of note that the mechanism of this CO<sub>2</sub>-fixation reaction was proposed based on the deuterium-labeling experiments, determining that the hydrogen atom at the vinylic



**Scheme 13.** Proposed reaction mechanism for the formation of  $\alpha,\beta$ -unsaturated carboxylic acids **27**.

Scheme 14. Skrydstруп's synthesis of dicarboxylic acids **29**.

(Het)Ar= Ph, 4-Me-C<sub>6</sub>H<sub>4</sub>, 4-<sup>i</sup>Pr-C<sub>6</sub>H<sub>4</sub>, 4-<sup>t</sup>Bu-C<sub>6</sub>H<sub>4</sub>, 4-Ph-C<sub>6</sub>H<sub>4</sub>, 4-OMe-C<sub>6</sub>H<sub>4</sub>, 4-OPh-C<sub>6</sub>H<sub>4</sub>, 4-OCF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>, 4-F-C<sub>6</sub>H<sub>4</sub>, 4-Cl-C<sub>6</sub>H<sub>4</sub>, 4-Br-C<sub>6</sub>H<sub>4</sub>, 4-NPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 4-(CH<sub>2</sub>CH<sub>2</sub>CH=CF<sub>2</sub>)-C<sub>6</sub>H<sub>4</sub>, 3-OMe-C<sub>6</sub>H<sub>4</sub>, 3-Me-C<sub>6</sub>H<sub>4</sub>, 3-Cl-C<sub>6</sub>H<sub>4</sub>, 2-Me-C<sub>6</sub>H<sub>4</sub>, 2-OMe-C<sub>6</sub>H<sub>4</sub>, 2-F-C<sub>6</sub>H<sub>4</sub>, 3-OMe-4-F-C<sub>6</sub>H<sub>3</sub>, 3-benzothieryl, 1-naphthyl, 2-naphthyl

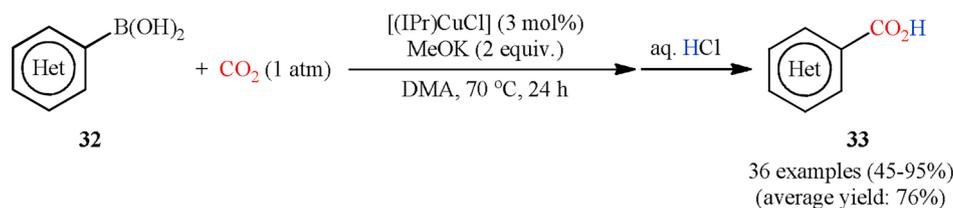
Scheme 15. Cu-catalyzed carboxylation of C–F bonds with CO<sub>2</sub>.Scheme 16. Proposed mechanism for the formation of  $\alpha$ -fluoroacrylic acids **31**.

position originated from the terminal acetylene proton.

At one time, in the same paper describing preparation of secondary carboxylic acids through a hydroboration-carboxylation sequence of disubstituted alkenes [44], Nielsen-Skrydstруп's research team described the synthesis of a small library of dicarboxylic acids **29** in moderate to good yields *via* the double hydroboration of terminal

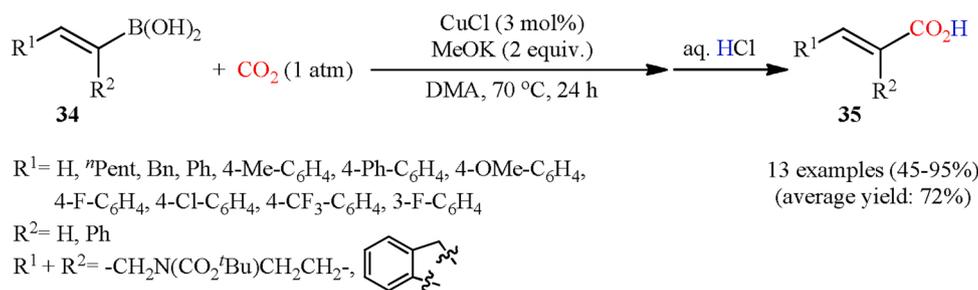
alkynes **28** using 9-BBN followed by Cu-catalyzed carboxylation of the generated 1,1-gem-diboryl intermediates with CO<sub>2</sub> in the presence of a fluoride source (Scheme 14).

Yu and co-workers have recently accomplished a robust Cu-catalyzed selective carboxylation of C–F bonds with CO<sub>2</sub> employing a diboron reagent as the C–F bond activator [50]. They carefully investigated the



(Het)Ar= Ph, 4-Me-C<sub>6</sub>H<sub>4</sub>, 4-Et-C<sub>6</sub>H<sub>4</sub>, 4-<sup>n</sup>Pr-C<sub>6</sub>H<sub>4</sub>, 4-<sup>t</sup>Bu-C<sub>6</sub>H<sub>4</sub>, 4-<sup>n</sup>Pent-C<sub>6</sub>H<sub>4</sub>, 4-Ph-C<sub>6</sub>H<sub>4</sub>, 4-OMe-C<sub>6</sub>H<sub>4</sub>, 4-CN-C<sub>6</sub>H<sub>4</sub>, 4-COMe-C<sub>6</sub>H<sub>4</sub>, 4-CO<sub>2</sub>Me-C<sub>6</sub>H<sub>4</sub>, 4-CO<sub>2</sub>H-C<sub>6</sub>H<sub>4</sub>, 4-F-C<sub>6</sub>H<sub>4</sub>, 4-Cl-C<sub>6</sub>H<sub>4</sub>, 4-Br-C<sub>6</sub>H<sub>4</sub>, 4-I-C<sub>6</sub>H<sub>4</sub>, 4-SMe-C<sub>6</sub>H<sub>4</sub>, 4-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 4-NPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 4-OH-C<sub>6</sub>H<sub>4</sub>, 4-CH<sub>2</sub>O(4-OMe-C<sub>6</sub>H<sub>4</sub>)C<sub>6</sub>H<sub>4</sub>, 4-CH<sub>2</sub>OH-C<sub>6</sub>H<sub>4</sub>, 3-Me-C<sub>6</sub>H<sub>4</sub>, 3-OMe-C<sub>6</sub>H<sub>4</sub>, 3-Br-C<sub>6</sub>H<sub>4</sub>, 3-I-C<sub>6</sub>H<sub>4</sub>, 2-Me-C<sub>6</sub>H<sub>4</sub>, 2-Br-C<sub>6</sub>H<sub>4</sub>, 2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 3,4-(OMe)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>, 3,4-OCH<sub>2</sub>O-C<sub>6</sub>H<sub>4</sub>, 2-naphthyl, 6-quinolinyl, 9-anthracenyl, 5-indolyl

**Scheme 17.** Cu-catalyzed carboxylation of aryl boronic acids **32** with CO<sub>2</sub>.



**Scheme 18.** Cu-catalyzed carboxylation of alkenyl boronic acids **34** with CO<sub>2</sub>.

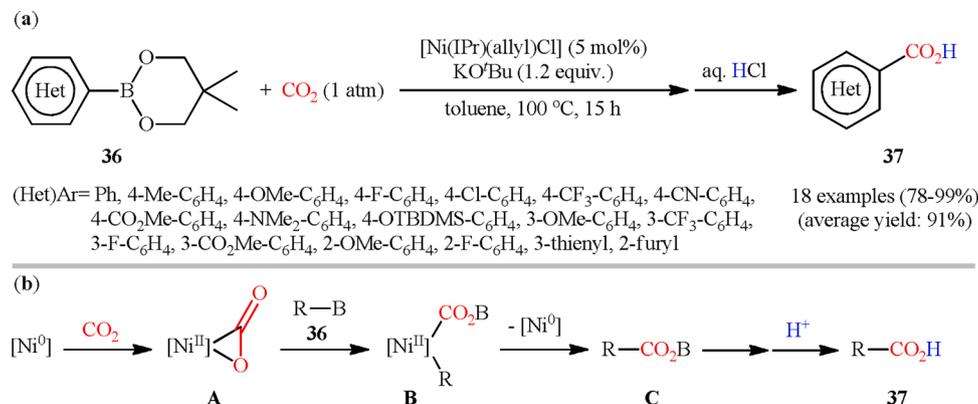
effects of reaction variables (i.e., catalyst, ligand, base, and solvent) in the carboxylation of 4-(2,2-difluorovinyl)-1,1'-biphenyl with an atmospheric pressure of CO<sub>2</sub>. The highest conversion efficiency was achieved for the reaction containing CuTc (5 mol%), Xantphos (5 mol%), and LiO<sup>t</sup>Bu (3.5 equiv.) in DMF at 80 °C. Among the various diboron reagents like B<sub>2</sub>nep<sub>2</sub>, B<sub>2</sub>pin<sub>2</sub>, B<sub>2</sub>neop<sub>2</sub>, B<sub>2</sub>cate<sub>2</sub>, B<sub>2</sub>hex<sub>2</sub>; B<sub>2</sub>pin<sub>2</sub> was the most efficient for this transformation. A diverse range of *gem*-difluoroalkenes **30** reacted under the optimized reaction conditions to produce the corresponding  $\alpha$ -fluoroacrylic acids **31** in moderate to high yields (Scheme 15). Importantly, 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 and  $\alpha$ -trifluoromethyl alkenes were also found to be suitable substrates for this CO<sub>2</sub>-fixation reaction. Based on the experimental results and literature, the authors proposed a catalytic cycle such as that depicted in Scheme 16.

Recently, the carboxylation of boronic acids with CO<sub>2</sub> was explored

by Mo et al. [51]. They showed that treatment of aryl boronic acids **32** with atmospheric CO<sub>2</sub> in the presence of a catalytic amount of [(IPr)CuCl] and 2 equiv. of MeOK at 70 °C, resulted in the formation of the corresponding carboxylic acids **33** in moderate to excellent yields, ranging from 45 % to 95 % (Scheme 17). Noteworthy, a wide panel of sensitive functional groups (e.g., OH, CO<sub>2</sub>H, CN, F, Cl, Br, I, OMe, SMe, COMe, CO<sub>2</sub>Me) were tolerated under these conditions. Moreover, access to dicarboxylic acids were also possible from the corresponding bis-boronic acids. However, the system was not tolerant toward aliphatic boronic acids. Very recently, the same authors successfully extended their methodology to alkenyl boronic acids **34** for the preparation of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids **35** (Scheme 18) [52].

## 5. Nickel-catalyzed reactions

One of the latest metals to join the story of transition metal-catalyzed deborylative carboxylation of organoboron compounds with CO<sub>2</sub> is



**Scheme 19.** (a) Ni-catalyzed carboxylation of boronic esters **36** with CO<sub>2</sub>; (b) Authors proposed mechanistic pathway for the formation of (hetero)carboxylic acids **37**.

**Table 1**Pd-catalyzed carboxylation of allylboranes **38** with atmospheric CO<sub>2</sub> developed by Wu and Hazari.

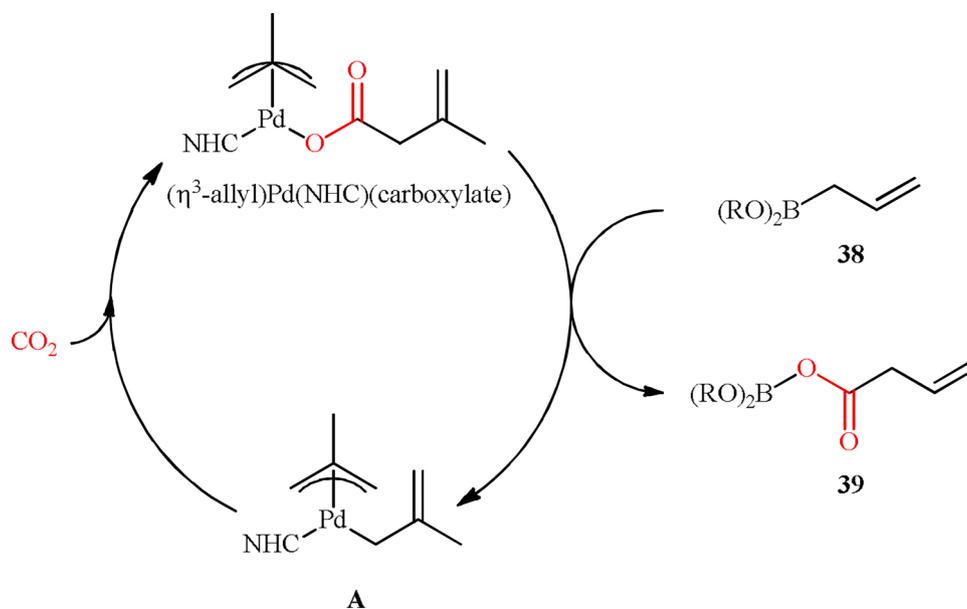
Entry	Substrate	Time (h)	Yield (%)
1	(Pinacol)B(2-methylallyl)	52	81
2	(Pinacol)B(allyl)	24	78
3	( <sup>t</sup> PrO) <sub>2</sub> B(allyl)	23	44
4	(OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O)B(allyl)	46	36
5	(Catechol)B(allyl)	2	0
6	(OCH <sub>2</sub> CH <sub>2</sub> O)B(allyl)	2	0
7	(OCH(Me)CH(Me)O)B(allyl)	2	0

nickel. In 2014, Nolan and colleagues disclosed that sterically hindered IPr\* ligand-supported allyl-nickel complex [Ni(IPr\*)(allyl)Cl] (IPr\* = 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene) could effectively catalyze the carboxylation of various aromatic and heteroaromatic boronates **36** with atmospheric CO<sub>2</sub> in the presence of an alkoxide base in toluene (100 °C) to provide the corresponding (hetero)carboxylic acids **37** in high to almost quantitative yields after quenching of the reaction mixture with aq. HCl (Scheme 19a) [53]. In the same report, the authors also successfully demonstrated deborylative carboxylation of a small series of alkenylboronates, employing the same reaction conditions. Noteworthy, no side-reactions (e.g., homocoupling, protodeborylation) was observed under these conditions and the starting boronate was the only recovered material when reactions did not proceed efficiently to product. It should be mentioned that the outcome of this reaction was strongly depend on the choice of the solvent, since the reaction was completely failed using polar (e.g., DMA) or chlorinated (e.g., DCM) solvents. Based on the literature, the authors suggested that this transformation proceeds through an oxidative cyclization/transmetalation/reductive elimination sequential process (Scheme 19b). Recently, Das and Kapur investigated the possible mechanistic pathways of this transformation on the basis of DFT calculations [54]. The results indicated that the direct CO<sub>2</sub> addition to the catalyst is kinetically disfavored and formation of the Aresta-type intermediate **A** as suggested by Nolan's group is unlikely to occur. Therefore, they proposed another complementary mechanism which was postulated to proceed via addition of the borate species to the

catalyst, followed by transmetalation, CO<sub>2</sub> cycloaddition and carboxylation.

## 6. Palladium-catalyzed reactions

The reported examples on palladium catalyzed carboxylation of organoboron compounds with CO<sub>2</sub> via C–B bond cleavage are scarce and to the best of our knowledge there are only two examples on such reactions. In 2011, Wu and Hazari disclosed a beautiful approach for the synthesis of boron allylcarboxylates **39** through the coupling of allylboranes **38** with atmospheric CO<sub>2</sub> using (η<sup>3</sup>-allyl)Pd(NHC)(carboxylate) complex, [NHC = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene)], as catalyst in the absence of any base or additive at room temperature [55]. As shown in Table 1, the choice of the ancillary substituent on boron is crucial for the success of this reaction. Noteworthy, treatment of allylcarboxylates with HCl rapidly generated the corresponding free carboxylic acid in almost quantitative yields. The optimized condition was also allowed the carboxylation of allylstannanes. The results indicated that reactions with allylstannanes were faster than with allylboranes. The mechanism of this transformation was proposed to involve two steps: transmetalation and CO<sub>2</sub> insertion (Scheme 20). Concurrently, the same research group demonstrated that a Pd<sup>I</sup>-bridging allyl dimer [(η<sup>1</sup>-allyl)(η<sup>3</sup>-allyl)Pd(NHC)] could also promoted this reaction [56]. However, in this study only two examples were reported, without any substrate scope exploration.

**Scheme 20.** Plausible mechanistic pathway for the formation of allylcarboxylates **39**.

## 7. Conclusion

We summarized here the most representative and important reports on the preparation of carboxylic acids from the corresponding organoboron compounds and CO<sub>2</sub> via carbon-boron bond cleavage. Interestingly, almost all of the reactions covered in this Mini-Review were performed under atmospheric pressure of CO<sub>2</sub>. This is very attractive from the point of view of sustainable chemistry. As illustrated, various types of C–B bonds [i.e., C(alkyl)-B, C(allyl)-B, C(vinyl)-B, C(aryl)-B, and C(heteroaryl)-B bonds] were applicable to this reaction. However, no reports were found in the literature on the carboxylation of C(alkynyl)-B bonds with CO<sub>2</sub>. Moreover, this chemistry widely relies on the use of copper catalysts. Therefore, development of related processes employing other inexpensive first row transition metal catalysts (e.g., iron and zinc) will be attractive. We conclude this Mini-Review by hoping that it will serve as an inspiration for future studies and research on the field.

## Declaration of Competing Interest

The authors report no declarations of interest.

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