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FULL PAPER

Cuprous halide catalysed carboxylation of alkenyl boronic acids and alkenyl boronic acid pinacol esters with CO_2

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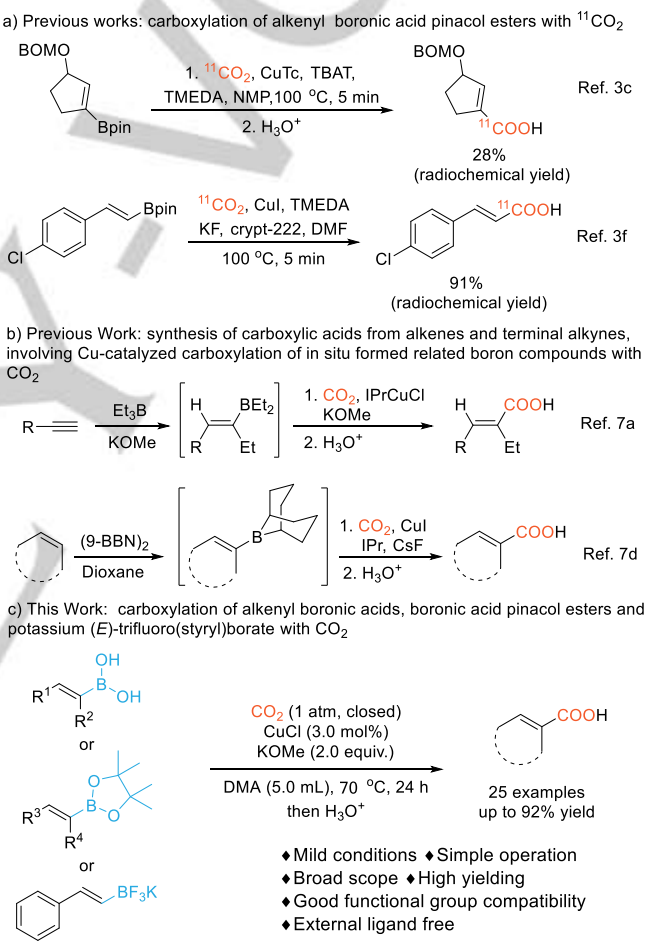
Abstract: A cuprous halide catalysed carboxylation of alkenyl boronic acids and alkenyl boronic acid pinacol esters under CO_2, affording the corresponding α, β-unsaturated carboxylic acids in good yield, has been developed. The potassium (*E*)-trifluoro(styryl)borate is also compatible with this reaction. This simple and efficient copper(I) catalytic system showed good functional group tolerance.

Introduction

Carbon dioxide (CO_2) is an ideal carboxylative reagent, and it can be fixed into organic substrates to provide carboxylic acids and derivatives.[1] However, CO_2 is a less-reactive electrophile, so this transformation usually required a suitable transition-metal catalyst and a carbon nucleophile.[1f] Recently, organoboronic acids and their derivatives have attracted much attention as the carbon nucleophiles in carboxylation with CO_2. The earliest work was the rhodium-catalysed carboxylation of aryl- and alkenyl boronic esters with CO_2 reported by Iwasawa in 2006.[2] Since then, many similar transition metal catalysed carboxylation of organoboronates with CO_2 have been reported using Cu,[3] Ag,[4] Ni[5] catalysts. In almost all of these cases, the C(sp^2)-B bond was carboxylated with CO_2, except in one case where the alkyl C(sp^3)-B bond was carboxylated with CO_2.[3e] In 2010, Lin and Marder[6] disclosed the DFT studies of the carboxylation reactions of arylboronate esters with CO_2 catalysed by (NHC)Cu(I) complexes, affirming the basic mechanistic proposal in Hou's work[3h].

In the carboxylation of C(sp^2)-B bond with CO_2, alkenyl boronic acid esters are used as substrates, especially alkenyl 5,5-dimethyl-1,3,2-dioxaborinane (-Bneop),[2, 3g, 3h, 4b, 5] and only two cases used alkenyl boronic acid pinacol esters (-Bpin) [3c, 3f] with only one example each (Scheme 1a). These two reactions aim to afford [^{11}C]-labeled carboxylic acids with direct application of [^{11}C]CO_2. And they both proceeded under a micromolar scale, with copper catalysts, and finished within several minutes. However, such catalytic systems have the limits of complex operating conditions, using ligands and additives, trapping [^{11}C]CO_2 below -10 °C, etc. Furthermore, several works[7] on the synthesis of carboxylic acids from alkenes and terminal alkynes, involves Cu-catalysed carboxylation of in situ formed related boron compounds with CO_2 (Scheme 1b). However, the carboxylation of alkenyl boric acid and alkenyl potassium trifluoroborate with CO_2 have not been developed yet.

On the basis of our previous work,[3b] we further examined the carboxylation of alkenyl boric acids and alkenyl boronic acid pinacol esters to expand the organoboron substrates on the incorporation of CO_2. Herein, we report a simple and efficient cuprous halide catalysed system for the carboxylation of three kinds of alkenyl boron compounds (Scheme 1c), with the advantage of mild conditions, simple operation, good functional group compatibility, high yields and external ligand free.



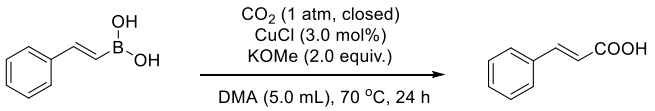
Scheme 1. a) Previous works: carboxylation of alkenyl boronic acid pinacol esters with $^{11}CO_2$; b) Previous Work: synthesis of carboxylic acids from alkenes and terminal alkynes, involving Cu-catalysed carboxylation of in situ formed related boron compounds with CO_2; c) This Work: carboxylation of alkenyl boronic acids, boronic acid pinacol esters and potassium (*E*)-trifluoro(styryl)borate with CO_2.

Results and Discussion

In the optimization study (table 1), we chose (*E*)-styrylboronic acid **1a** as model substrate to react with CO_2 at ambient pressure. After an extensive survey of reaction parameters, we obtained 95%

yield of the desired product by using 3.0 mol% CuCl and 2.0 equiv. KOMe in DMA at 70 °C for 24 h (entry 1). Other cuprous halides such as CuI, CuBr were relatively less effective (entries 2-3). Further study showed that a smaller amount of CuCl was not conducive to the reaction, and 3 mol% was sufficient (entries 1, 4-5). In addition, the use of other alkoxide bases such as KO^{t}Bu, LiOMe showed less effective (entries 6-7). And 2.0 equiv. is the optimal stoichiometry of KOMe (entries 1, 8-9). Other solvents such as DMF, DMSO, MeCN and THF provided low yields of the desired product (entries 10-13). Furthermore, the reaction temperature proved to be crucial. Low temperature would seriously reduce the yield, but it should not either be too high (entries 1, 14-16). Finally, control experiments show that both the catalyst and the base are crucial to the reaction (entries 17-18).

Table 1. Optimization of the reaction conditions[a].



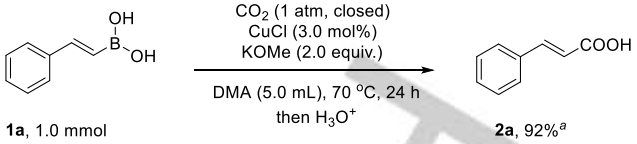
1a, 1.0 mmol **2a**

Entry	Variation from standard conditions	Yield (%) [b]
1	None	95
2	CuI instead of CuCl	80
3	CuBr instead of CuCl	86
4	With 2.0 mol% CuCl	79
5	With 4.0 mol% CuCl	95
6	KO^{t}Bu instead of KOMe	60
7	LiOMe instead of KOMe	80
8	With 1.5 equiv. KOMe	83
9	With 2.5 equiv. KOMe	92
10	DMF instead of DMA	41
11	DMSO instead of DMA	34
12	MeCN instead of DMA	21
13	THF instead of DMA	20
14	Reaction at room temperature	trace
15	Reaction at 50 °C	48
16	Reaction at 100 °C	75
17	Without copper catalyst	NR
18	Without base	NR

[a] Reaction performed on 1.0 mmol scales. [b] Yields were determined by ^{1}H NMR with 1,1,2,2-Tetrachloroethane as an internal standard.

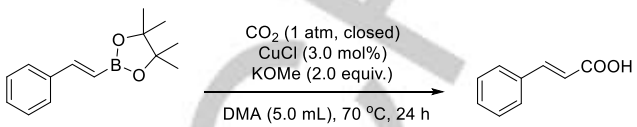
While investigating the boron-containing structure in alkenyl boron compounds, we found that in addition to (*E*)-styrylboronic acid **1a**, (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane **3a** and potassium (*E*)-trifluoro(styryl)borate **4** also reacted well under identical conditions (Scheme 2). These three boron compounds gave the carboxylated product **2a** in 92%, 88%, 83% isolated yields, respectively. We are encouraged that the current method could be adopted to a broad scope of alkenyl boron compounds, especially alkenyl boronic acids and alkenyl boronic acid pinacol esters, since both are commercially available.

a) The reaction of (*E*)-styrylboronic acid **1a** with CO_2 in the optimal conditions



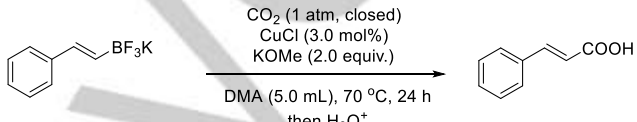
1a, 1.0 mmol **2a**, 92%[a]

b) The reaction of (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane **3a** with CO_2 in the optimal conditions



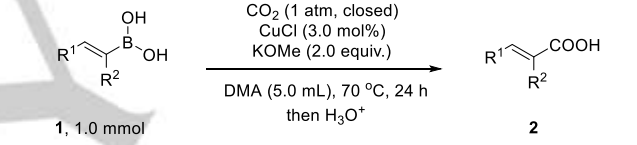
3a, 1.0 mmol **2a**, 88%[a]

c) The reaction of potassium (*E*)-trifluoro(styryl)borate **4** with CO_2 in the optimal conditions

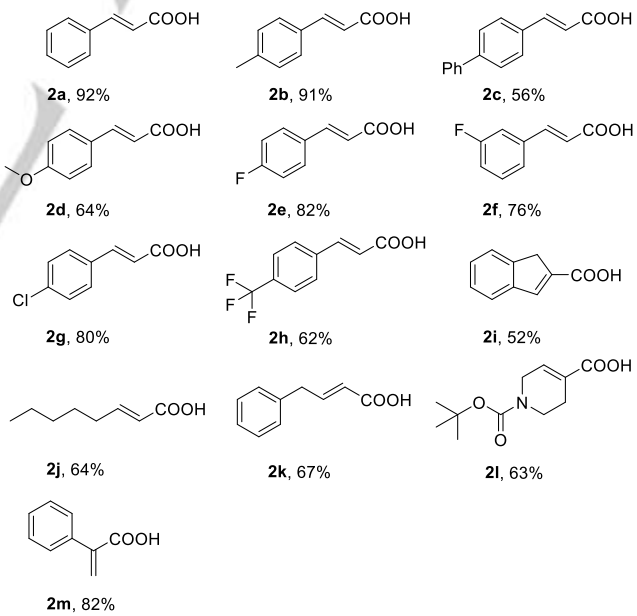


4, 1.0 mmol **2a**, 83%[a]

Scheme 2. The reaction of (*E*)-styrylboronic acid **1a**, (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane **3a**, (*E*)-trifluoro(styryl)borate **4** with CO_2 in the optimal conditions. [a] Isolated yield.



1, 1.0 mmol **2**

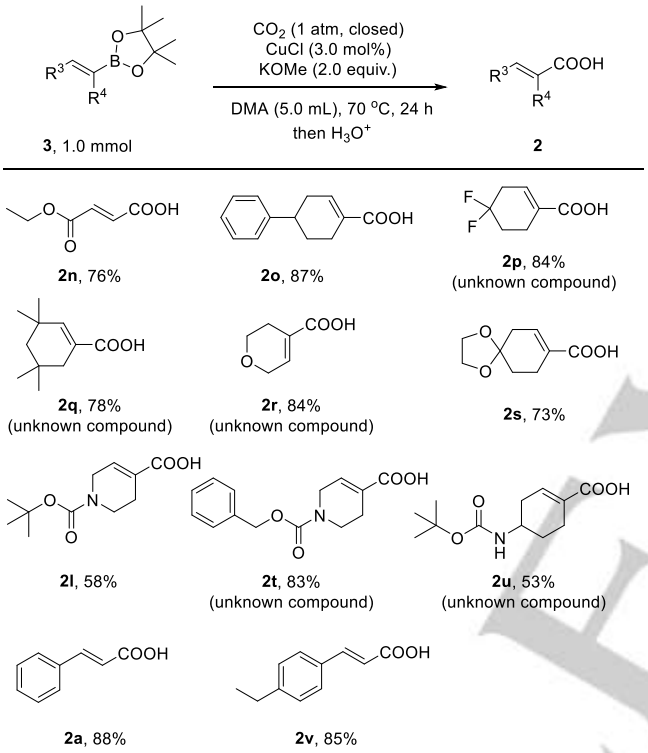


2a, 92% **2b**, 91% **2c**, 56%
2d, 64% **2e**, 82% **2f**, 76%
2g, 80% **2h**, 62% **2i**, 52%
2j, 64% **2k**, 67% **2l**, 63%
2m, 82%

Scheme 3. The substrates scope of alkenyl boron acids. Reactions were carried out by using alkenyl boronic acid **1** (1.0 mmol), cat. CuCl (3.0 mol%), base KOMe (2.0 equiv.) in DMA at 70 °C for 24 h under 1 atm CO_2. Isolated yields were reported.

We first evaluated the scope of alkenyl boronic acids under the optimal conditions (Scheme 3). When the substituent R^1 was aryl and R^2 was hydrogen, substrates (*E*)-Styrylboronic acids were successfully converted to the corresponding cinnamic acids (**2a**-

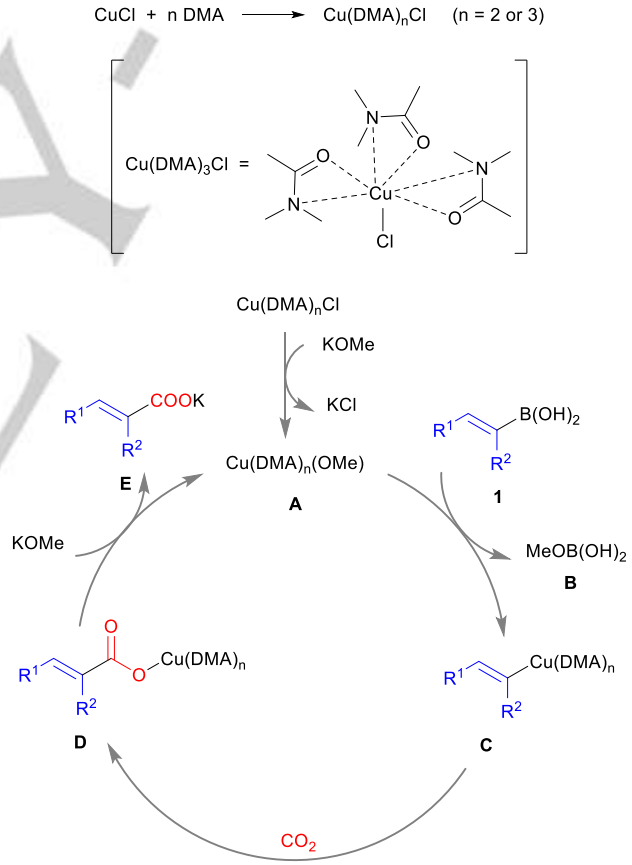
h). The *p*-methyl-substituted styrylboronic acid gave a high yield (91%, **2b**), while *p*-phenyl-substituted styrylboronic acid and *p*-methoxy -substituted styrylboronic acid provided obviously lower yields (56%, **2c** and 64%, **2d**), probably because electronic effect promoted the generation of protodeboronation by-products. Halogen-substituted styrylboronic acids were compatible and gave the corresponding products (**2e**-**h**) in moderate to good yields. With the substituent R^1 as hydrogen and R^2 as aryl, the substrate (1-phenylvinyl)boronic acid can also gave the desired product **2m** in 82% yield. In addition, cyclic alkenyl substrates provided the corresponding products (**2i** and **2l**) in good yields. Also, Boc-protected amines was compatible under the reaction conditions (**2l**). Moreover, when R^1 was linear alkyl or benzyl, both the substrates underwent the reaction smoothly (**2j** and **2k**).



Scheme 4. The substrates scope of alkenyl boronic acid pinacol esters. Reactions were carried out by using alkenyl boronic acid pinacol ester **3** (1.0 mmol), cat. CuCl (3.0 mol%), base KOMe (2.0 equiv.) in DMA at 70 °C for 24 h under 1 atm CO_2. Isolated yields were reported.

We then focused on the scope of alkenyl boronic acid pinacol esters (Scheme 4). When the substituent R^3 was aryl and R^4 was hydrogen, substrates (*E*)-Styrylboronic acid pinacol esters provided the desired products (**2a** and **2v**) in good yields. In addition, when the substituent R^3 was ethoxy carbonyl and R^4 was hydrogen, the substrate gave product **2n** in 76% yield. And product **2n** is an important chemical intermediate, monoethyl fumarate, which can be used to produce preservatives. Again, cyclic alkenyl substrates gave the corresponding products (**2o**-**u**) in moderate to good yields. Cyclohexenyl boronic acid pinacol esters afforded products (**2o**-**q**, **2s**) in high yields, except products **2u**, possibly because of the effect of secondary amine and steric hindrance. Besides, heterocyclehexenyl boronic acid pinacol esters also provided the desired products (**2r**, **2l**, **2t**) in good yields, implying that both oxygen-containing heterocycle and nitrogen-containing heterocycle were compatible under the reaction conditions. Notably, this method is suitable for the synthesis of many unknown acrylic acids (**2p**-**r**, **2t**-**u**).

Based on the previous literatures[3g, 3h, 6, 8] and our own study[3b], a plausible mechanism was proposed (Scheme 5). On one hand, previous reports[8] showed very solid evidence that DMA can work actively as an acido ligand coordinating with copper. On the other hand, due to stability issue and the empty d orbital of copper, organocopper species has to be saturated by being coordinated with substrates, ligands or solvents. As such, the proposed mechanism circle starts with the complex $Cu(DMA)_nCl$ (n = 2 or 3) formed from the coordination between CuCl and DMA. Initially, the complex $Cu(DMA)_nCl$ exchanges the ligand with KOMe to generate the copper alkoxide $Cu(DMA)_n(OMe)$ **A**, which undergoes transmetalation with alkenyl boron acid **1** to form the intermediate **B** and **C**. Nucleophilic addition of copper complex **C** to CO_2 provides copper carboxylate **D**. σ-Metathesis with KOMe generates carboxylic acid potassium salt **E** and regenerate $Cu(DMA)_n(OMe)$ **A**, thereby completing the catalytic cycle.



Scheme 5. Proposed mechanism.

Conclusion

In summary, we have succeeded in developing the cuprous halide catalysed carboxylation of alkenyl boronic acids and alkenyl boronic acid pinacol esters with CO_2. The potassium (*E*)-trifluoro(styryl)borate can also be carboxylated using this method.

A wide range of alkenyl boron compounds were effetively transformed into the corresponding α, β-unsaturated carboxylic acids in moderate to high yield. Good functional group tolerance improve the generality of the reaction. And the use of inexpensive cuprous halides, mild conditions and simple operation expand the utility of the reaction.

Experimental Section

General information: Solvents were purchased from TONGGUANG CHEMICAL, Beijing or BEIJING CHEMICAL, in GR (or CCER). Purification of products was conducted by column chromatography on silica gel (200-300 mesh, for some cases 300-400 mesh were used, from Qingdao, China). NMR spectra were measured on a Bruker ARX400 (^{1}H at 400 MHz, ^{13}C at 101 MHz, ^{19}F at 471 MHz) magnetic resonance spectrometer. Chemical shifts (δ) are reported in ppm using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), and coupling constants (*J*) were reported in Hertz (Hz). The substrates were purchased from commercial sources.

General experimental procedure for the synthesis of *(E)*-3-phenylacrylic acid (**2a)**: Phenylvinylboronic acid **1a** (148.0 mg, 1.0 mmol), KOMe (140.3 mg, 2.0 mmol), CuCl (3.0 mg, 0.03 mmol) was charged in a 50 mL Schlenk tube under N_2, followed by 5 mL anhydrous DMA. After that the Schlenk tube was filled with carbon dioxide by applying four-five cycles of evacuation and filling with CO_2. The Schlenk tube was tightly sealed and stirred at 70 °C for 24 hours after which it was quenched by careful addition of 1.0 M aq. HCl sol. The reaction mixture was diluted with water and extracted three times with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and filtered. Then the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (0−25 % EtOAc in pet-ether) to obtain the desired product **2a** 136.2 mg, in 92% yield.

***(E)*-3-phenylacrylic acid** (**2a**): White solid, 136.2 mg obtained, yield 92% from **1a**; 130.3 mg obtained, yield 88% from **3a**; 122.9 mg obtained, yield 83% from **4**. R_f: 0.7 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.44 (s, 1H), 7.73 – 7.65 (m, 2H), 7.61 (d, *J* = 16.0 Hz, 1H), 7.41 (p, *J* = 3.5 Hz, 3H), 6.55 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.07, 144.41, 134.69, 130.68, 129.36, 128.67, 119.68.[9]

***(E)*-p-methylcinnamic acid** (**2b**): White solid, 147.5 mg obtained, yield 91%. R_f: 0.4 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.37 (s, 1H), 7.62 – 7.51 (m, 3H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.18, 144.38, 140.56, 131.94, 129.94, 128.61, 118.52, 21.43.[9]

***(E)*-3-([1,1'-biphenyl]-4-yl)acrylic acid** (**2c**): White solid, 125.5 mg obtained, yield 56%. R_f: 0.4 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.43 (s, 1H), 7.82 – 7.61 (m, 7H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.07, 143.91, 142.17, 139.70, 133.83, 129.49, 129.33, 128.40, 127.53, 127.15, 119.62.[9]

***(E)*-3-(4-methoxyphenyl)acrylic acid** (**2d**): White solid, 114.0 mg obtained, yield 64%. R_f: 0.5 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.24 (s, 1H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 16.0 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.31, 161.38, 144.22, 130.42, 127.27, 116.94, 114.80, 55.77.[9]

***(E)*-4-fluorocinnamic acid** (**2e**): White solid, 136.2 mg obtained, yield 82%. R_f: 0.6 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.42 (s, 1H), 7.80 – 7.70 (m, 2H), 7.60 (d, *J* = 16.0 Hz, 1H), 7.23 (t, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.99, 164.82, 162.36, 143.15, 131.16 (d, *J* = 38.4 Hz), 119.55, 116.30 (d, *J* = 22.2 Hz).[9]

***(E)*-3-fluorocinnamic acid** (**2f**): White solid, 126.2 mg obtained, yield 76%. R_f: 0.5 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.53 (s, 1H), 7.63 – 7.52 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.42 (td, *J* = 7.9, 6.0 Hz, 1H), 7.20 (td, *J* = 8.5, 2.5 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.85, 162.87 (d, *J* = 244.4 Hz), 142.98 (d, *J* = 3.0 Hz), 137.24 (d, *J* = 8.1 Hz), 131.18 (d, *J* = 8.1 Hz), 124.99 (d, *J* = 3.0 Hz), 121.28, 117.26 (d, *J* = 22.2 Hz), 114.79 (d, *J* = 22.2 Hz).[10]

***(E)*-4-chlorocinnamic acid** (**2g**): White solid, 145.6 mg obtained, yield 80%. R_f: 0.6 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.52 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 16.1 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 6.58 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.91, 142.97, 135.18, 133.66, 130.37, 129.36, 120.52.[9]

***(E)*-4-(trifluoromethyl)cinnamic acid** (**2h**): White solid, 134.0 mg obtained, yield 62%. R_f: 0.3 (PE/EA=3:1). 5^{1}H NMR (400 MHz, DMSO-d_6) δ 12.63 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 16.0 Hz, 1H), 6.67 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.68, 142.50, 138.69, 130.3 (q, *J* = 32.3 Hz), 129.20, 126.05 (q, *J* = 4.0 Hz), 124.4 (d, *J* = 272.7 Hz), 122.57.[9]

Indene-2-carboxylic acid (**2i**): White solid, 83.2 mg obtained, yield 52%. R_f: 0.5 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.51 (s, 1H), 7.69 (s, 1H), 7.62 – 7.52 (m, 2H), 7.38 – 7.32 (m, 2H), 3.63 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.16, 145.09, 143.04, 140.61, 138.88, 127.75, 127.22, 124.79, 123.78, 38.56.[9]

***(E)*-oct-2-enoic acid** (**2j**): Yellow oil, 90.9 mg obtained, yield 64%. R_f: 0.6 (PE/EA=20:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.13 (s, 1H), 6.87 – 6.75 (m, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 2.16 (q, *J* = 7.0 Hz, 2H), 1.41 (q, *J* = 7.2 Hz, 2H), 1.27 (tt, *J* = 11.9, 5.4 Hz, 4H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.56, 149.22, 122.37, 31.79, 31.26, 27.68, 22.35, 14.28.[11]

***(E)*-4-phenylbut-2-enoic acid** (**2k**): White solid, 108.6 mg obtained, yield 67%. R_f: 0.3 (PE/EA=5:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.35 (s, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.31 (dt, *J* = 16.0, 7.1 Hz, 1H), 3.20 (dd, *J* = 7.1, 1.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.13, 137.18, 132.70, 129.10, 127.87, 126.49, 123.66, 38.30.[12]

1-[(tert-butoxy)carbonyl]-1,2,3,6-tetrahydropyridine-4-carboxylic acid (**2l**): White solid, 143.1 mg obtained, yield 63% from **1l**; 131.7 mg obtained, yield 58% from **3l**. R_f: 0.4 (PE/EA=3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1H), 6.98 (s, 1H), 4.08 (s, 2H), 3.50 (t, *J* = 5.5 Hz, 2H), 2.40 – 2.33 (m, 2H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.93, 154.76, 137.50 (d, *J* = 63.6 Hz), 128.57, 80.28, 43.62 (d, *J* = 46.5 Hz), 39.90 (d, *J* = 126.2 Hz), 28.38, 24.09.[13]

2-phenylacrylic acid (**2m**): Orange solid, 121.4 mg obtained, yield 82%. R_f: 0.3 (PE/EA=10:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.86 (s, 1H), 7.46 – 7.28 (m, 5H), 6.24 (s, 1H), 5.96 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.22, 141.97, 137.18, 128.57, 128.47, 128.42, 126.53.[14]

***(E)*-4-ethoxy-4-oxobut-2-enoic acid** (**2n**): White solid, 109.5 mg obtained, yield 76%. R_f: 0.4 (PE/EA=10:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.24 (s, 1H), 6.70 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.18, 165.01, 135.01, 133.10, 61.44, 14.38.[15]

4-phenylcyclohex-1-ene-1-carboxylic acid (**2o**): White solid, 175.8 mg obtained, yield 87%. R_f: 0.3 (PE/EA=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.27 (s, 1H), 7.35-7.39 (m, 2H), 7.26-7.28 (m, 4H), 2.92 – 2.80 (m, 1H), 2.56-2.64 (m, 2H), 2.34-2.44 (m, 2H), 2.08-2.13 (m, 1H), 1.73-1.87 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.08, 145.88, 141.97, 129.73, 128.59, 126.85, 126.42, 39.06, 33.97, 29.33, 24.48.[16]

4,4-difluorocyclohex-1-ene-1-carboxylic acid (**2p**): Unknown compound. White solid, 136.1 mg obtained, yield 84%. R_f: 0.5 (PE/EA=5:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.50 (s, 1H), 6.74 – 6.67 (m, 1H), 2.70-2.80 (m, 2H), 2.39-2.44 (m, 2H), 1.97-2.11 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.58, 133.87, 129.90, 123.66 (t, J = 239.37 Hz), 34.75 (t, J = 27.27 Hz), 29.70 (t, J = 24.24 Hz), 22.99 (t, J = 5.05 Hz). ^{19}F NMR (471 MHz, DMSO-d_6) δ -94.98 (pd, J = 14.6, 3.1 Hz). **HRMS**: calculated for $C_7H_7F_2O_2[M-H]^-$ 161.041959, found 161.04159.

3,3,5,5-Tetramethyl-cyclohexen-carbonsaeure (**2q**): Unknown compound. White solid, 142.1 mg obtained, yield 78%. R_f: 0.3 (PE/EA=10:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.17 (s, 1H), 6.61 (s, 1H), 1.92 (d, J = 1.7 Hz, 2H), 1.31 (s, 2H), 1.03 (s, 6H), 0.92 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.06, 146.90, 127.02, 49.11, 37.67, 33.37, 30.81, 30.50, 29.94. **HRMS**: calculated for $C_{11}H_{17}O_2[M-H]^-$ 181.123403, found 181.123380.

3,6-dihydro-2H-pyran-4-carboxylic acid (**2r**): Unknown compound. White solid, 107.6 mg obtained, yield 84%. R_f: 0.4 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.40 (s, 1H), 6.85 (p, J = 2.3 Hz, 1H), 4.18 (q, J = 2.9 Hz, 2H), 3.68 (t, J = 5.5 Hz, 2H), 2.21 (tq, J = 5.2, 2.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.51, 137.82, 128.27, 64.92, 63.64, 24.67. **HRMS**: calculated for $C_6H_8NaO_3[M+Na]^+$ 151.036565, found 151.03658.

1,4-dioxaspiro[4.5]dec-7-ene-8-carboxylic acid (**2s**): White solid, 134.4 mg obtained, yield 73%. R_f: 0.3 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.23 (s, 1H), 6.72-6,70 (m, 1H), 3.89 (s, 4H), 2.36-2.30 (m, 4H), 1.68 (t, J = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.15, 136.72, 130.15, 106.97, 64.26, 36.04, 30.70, 23.83.[17]

1-benzyloxycarbonyl-1,2,3,6-tetrahydropyridine-4-carboxylic acid (**2t**): Unknown compound. White solid, 216.7 mg obtained, yield 83%. R_f: 0.2 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.50 (s, 1H), 7.38-7.31 (m, 5H), 6.86 – 6.79 (m, 1H), 5.11 (s, 2H), 4.12 – 4.03 (m, 2H), 3.50 (d, J = 8.1 Hz, 2H), 2.29-2.25 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.57, 154.95, 137.30, 135.50, 135.26, 129.22, 128.89, 128.34, 128.10, 66.76, 43.66, 24.32. **HRMS**: calculated for $C_{14}H_{16}NO_4[M+H]^+$ 262.107384, found 262.107522.

4-((tert-butoxycarbonyl)amino)cyclohex-1-ene-1-carboxylic acid (**2u**): Unknown compound. White solid, 127.8 mg obtained, yield 53%. R_f: 0.3 (PE/EA=3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.18 (s, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.75-6.73 (m, 1H), 2.41-2.30 (m, 2H), 2.21-1.99 (m, 2H), 1.81-1.71 (m, 1H), 1.45-1.39 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.28, 155.45, 137.43, 130.35, 78.01, 45.48, 31.98, 28.72, 28.55, 23.76. **HRMS**: calculated for $C_{12}H_{18}NO_4[M-H]^-$ 240.124132, found 240.123703.

***(E)*-4-ethyl cinnamic acid** (**2v**): White solid, 149.7 mg obtained, yield 85%. R_f: 0.3 (PE/EA=10:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.38 (s, 1H), 7.61 (s, 1H), 7.57 (d, J = 16.0 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 6.48 (d, J = 15.9 Hz, 1H), 2.62 (q, J = 7.6 Hz, 2H), 1.18 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.19, 146.84, 144.43, 132.22, 128.81, 128.76, 118.61, 28.53, 15.85.[18]

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Keywords: • Copper catalyst • Carbon dioxide • Carboxylation • Alkenyl boron compounds

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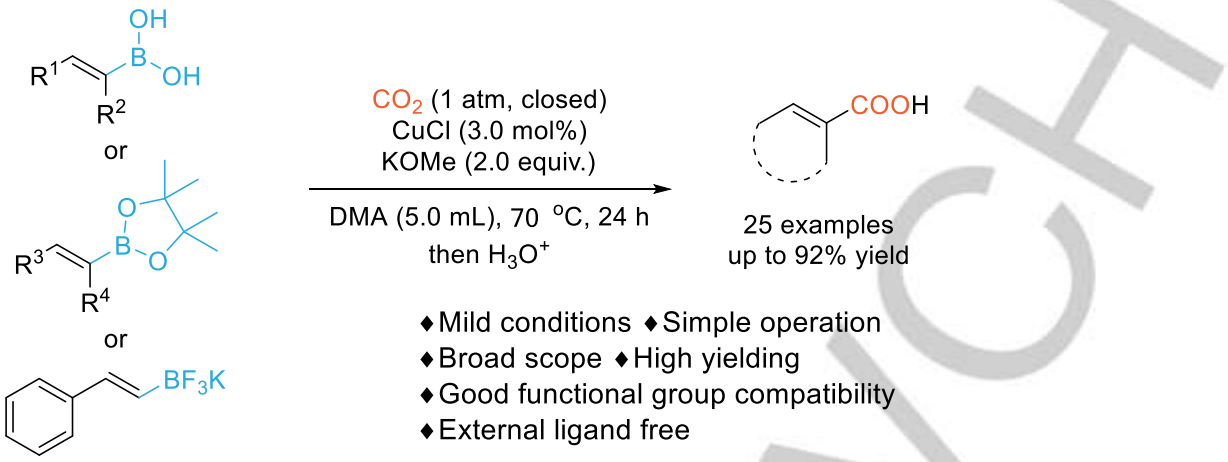

Three kinds of alkenyl boron compounds were effetively transformed into the corresponding α, β-unsaturated carboxylic acids in moderate to high yield through cuprous halide-catalysted carboxylation with CO_2. The advantages of this method include low cost, mild conditions, simple operation, broad scope and external ligand free.