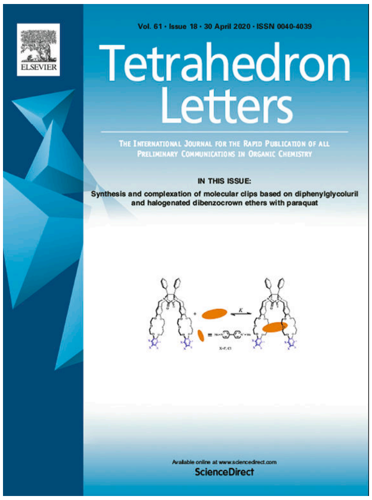

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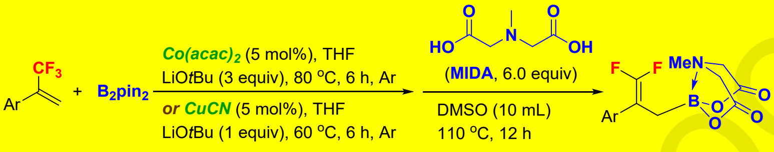

- Ligand-free
- Good FG tolerance
- Facile product isolation and purification

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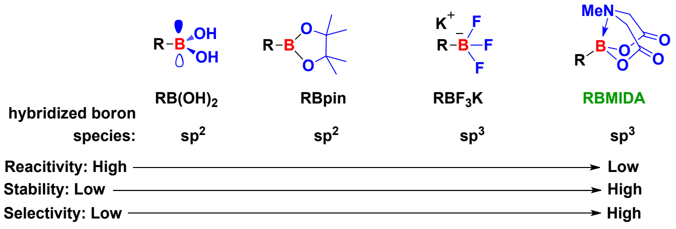
ABSTRACT

A novel two-step synthesis of *gem*-difluoroallyl MIDA boronates, which are air- and moisture-stable fluorine-containing building blocks for potential applications in iterative cross-couplings, was developed. The first step involves cobalt- or copper-catalyzed defluoroborylation of α-trifluoromethyl alkenes with B_2pin_2 in the absence of ligand. Next, without further purification, the resulting *gem*-difluroallylboronic acid pinacol ester was converted to *gem*-difluoroallyl MIDA boronates by heating in the presence of MIDA.

gem-Difluoroalkenes are recognized as important architectural units widely found in agrochemicals, pharmaceuticals as well as organic materials.[1] Furthermore, they are useful synthetic intermediates for the synthesis of a variety of fluorine-containing or non-fluorinated organic molecules due to their high polarization of the carbon–carbon double bond and the good leaving-group ability of the fluoride ion.[2] Therefore, the synthesis of various *gem*-difluoroalkenes has attracted increasing attention in recent years.[3] Numerous methods have been developed thus far for the synthesis of *gem*-difluoroalkene derivatives.[4] One of the most commonly used method for the synthesis of functionalized *gem*-difluoroalkenes involves the S_N2' reaction of 2-trifluoromethyl-1-alkenes with oxygen, sulfur, nitrogen nucleophiles and organometallic reagents.[5]

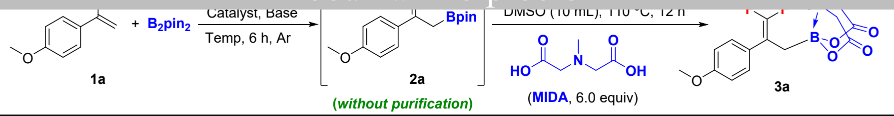
Boronic acids ($RB(OH)_2$), boronate esters such as pinacol boronates (RBpin), potassium organotrifluoroborates (RBF_3K) and *N*-methyliminodiacetic acid (MIDA) boronates are four main organoboron reagents (Scheme 1).[6] They are indispensable and versatile coupling partners in transition-metal-catalyzed C−C and C−heteroatom bond formation.[7] Among the various available organoboron compounds, MIDA boronates are especially attractive because they have found wide applications in the synthesis of small-molecule natural products through the iterative cross-coupling (ICC) strategy.[8] The MIDA boronates are stable towards many types of chemical transformations and also stable to storage on the bench top under air without noticeable decomposition for several months.[9] Furthermore, they are generally highly crystalline, free-flowing solids and could be easily purified by recrystallization from solvent without the use of column chromatography.[10] As a consequence, increasing efforts have been devoted to the synthesis of structurally diverse MIDA boronates in recent years.[11]



Scheme 1 The comparison of various organoboron reagents

gem-Difluoroallylboronates are useful precursors for further transformation into various difluorinated compounds.[12] Nowadays, the highly efficient copper or iron-catalyzed synthesis of β-substituted-γ,γ-difluoroallylboronic acid pinacol ester from trifluoromethyl alkenes and B_2pin_2 has received significant growing interests. In 2011, Hoveyda′ group disclosed the first example of Cu-catalyzed defluoroborylation of CF_3-substituted alkenes with B_2pin_2 in the presence of chiral or achiral imidazolinium salt. However, only one borylated *gem*-difluoroalkene was obtained (yields 54 and 20 %, respectively).[13] In 2017, Zhou and co-workers have reported the synthesis of *gem*-difluoroallylboronates via $FeCl_2$-catalyzed defluoroborylation of trifluoromethyl alkenes.[14] In 2018, Shi and Ito independently developed a novel approach for the synthesis of enantioenriched *gem*-difluoroallylboronates via the copper(I)-

Table 1. Optimization of reaction conditions.[a]



Entry	Catalyst (x mol%)	Base (x equiv)	Solvent	Temp (ºC)	**2a** (%)[b]
1	none	LiO*t*Bu (1)	THF	60	0
2	$Co(OAc)_2$ (10)	LiO*t*Bu (1)	THF	60	7
3	CoF_2 (10)	LiO*t*Bu (1)	THF	60	10
4	$CoCl_2(PPh_3)_4$ (10)	LiO*t*Bu (1)	THF	60	16
5	$CoBr_2$ (10)	LiO*t*Bu (1)	THF	60	22
6	$Co(acac)_2$ (10)	LiO*t*Bu (1)	THF	60	50
7	$Co(acac)_2$ (10)	None	THF	60	0
8	$Co(acac)_2$ (10)	CH_3ONa (1)	THF	60	13
9	$Co(acac)_2$ (10)	C_2H_5ONa (1)	THF	60	16
10	$Co(acac)_2$ (10)	KO*t*Bu (1)	THF	60	22
11	$Co(acac)_2$ (10)	NaO*t*Bu (1)	THF	60	30
12	$Co(acac)_2$ (10)	LiO*t*Bu (1)	Et_2O	60	7
13	$Co(acac)_2$ (10)	LiO*t*Bu (1)	CH_3CN	60	13
14	$Co(acac)_2$ (10)	LiO*t*Bu (1)	toluene	60	24
15	$Co(acac)_2$ (10)	LiO*t*Bu (1)	DMF	60	42
16	$Co(acac)_2$ (10)	LiO*t*Bu (2)	THF	60	61
17	$Co(acac)_2$ (10)	LiO*t*Bu (3)	THF	60	70
18	$Co(acac)_2$ (10)	LiO*t*Bu (3)	THF	80	90
19	$Co(acac)_2$ (5)	LiO*t*Bu (3)	THF	80	89
20	$Co(acac)_2$ (3)	LiO*t*Bu (3)	THF	80	60
21	CuOAc (10)	LiO*t*Bu (3)	THF	rt	10
22	CuOAc (10)	LiO*t*Bu (3)	THF	60	80
23	CuI (10)	LiO*t*Bu (3)	THF	60	88
24	CuBr (10)	LiO*t*Bu (3)	THF	60	87
25	CuSCN (10)	LiO*t*Bu (3)	THF	60	89
26	CuCN (10)	LiO*t*Bu (3)	THF	60	95
27	CuCN (5)	LiO*t*Bu (3)	THF	60	95
28	CuCN (5)	LiO*t*Bu (1)	THF	60	95
29	CuCN (5)	LiO*t*Bu (0.5)	THF	60	20

[a] Reaction conditions: **1a** (0.1 mmol), B_2pin_2 (0.12 mmol), solvent (1 mL).

[b] Yields are determined by GC analysis based on **1a**.

catalyzed asymmetric defluoroborylation of CF_3-substituted alkenes using (*R*,*S*)-Josiphos as the chiral ligand.[15] More recently, our group also reported an efficient method for the synthesis of *gem*-difluoroallylboronates via CuOAc-catalyzed defluorinative borylation of α-trifluoromethyl alkenes with B_2pin_2 using Xantphos as ligand and NaO*t*Bu as base.[16]

Although the above-mentioned approaches to the synthesis of *gem*-difluoroallylboronates are efficient and useful, these methods still suffer one or more drawbacks such as the use of complex and expensive ligands, limited substrate scope and tedious and time-consuming chromatographic separation. Therefore, there is a growing demand for more simple and efficient new catalytic system. Cobalt-catalyzed couplings are of interest in organic synthesis because cobalt catalysts are stable, inexpensive and low toxic.[17] To the best of our knowledge, defluoroborylation of trifluoromethyl alkenes employing Co-based catalysts have not been previously reported. In this letter, we reported a novel method for the synthesis of *gem*-difluoroallyl MIDA boronates through cobalt- or copper-catalyzed defluoroborylation of trifluoromethyl alkenes with B_2pin_2 in the absence of ligand, followed by treatment of the crude borylation products with *N*-methyliminodiacetic acid (MIDA).

We previously reported a copper-catalyzed synthesis of *gem*-difluoroallylboronates from α-trifluoromethyl alkenes and B_2pin_2 in the presence of Xantphos and NaO*t*Bu. During the course of our investigation on Cu-catalyzed defluoroborylation of trifluoromethyl alkenes, we found that the reaction could also provide the expected *gem*-difluoroallylboronate in 37% yield in the absence of ligand.[16] Encouraged by these preliminary results, we carried out this reaction without any additional ligand in the following investigation. We began our experiment by using the reaction of 1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene **1a** with B_2pin_2 as the model reaction to optimize the reaction conditions (Table 1). No desired product **2a** was detected in the absence of a metal catalyst (entry 1). The effect of the Co catalyst on the reaction was then examined. Among the various Co salts tested (entries 2–6), $Co(acac)_2$ was the most suitable for the reaction, giving the expected product **2a** in moderate yield, while other cobalt salts such as $Co(OAc)_2$, CoF_2, $CoCl_2(PPh_3)_4$ and $CoBr_2$ gave lower yields. Screening of different bases exhibited that LiO*t*Bu was effective for this reaction (entries 7–11), while small amounts of the borylated *gem*-difluoroalkenes were formed when CH_3ONa, C_2H_5ONa, KO*t*Bu or NaO*t*Bu was used as the base. Subsequently, the influence of solvent was investigated (entries 12–15). The results indicated that both THF and DMF could afford moderate yields of **2a**, whereas the yields were reduced when Et_2O, CH_3CN and toluene were used as solvent. Furthermore, an excess of LiO*t*Bu and higher temperature were found to be favorable for the reaction and afforded **2a** in high yield (entries 16–18). To our delight, decreasing the amount of $Co(acac)_2$ from 10 mol % to 5 mol % would also provide **2a** in good yield (entry 19). Further decreasing the amount of $Co(acac)_2$ led to significant decrease in the yield (60%, entry 20).

Inspired by the success in the Co-catalyzed defluoroborylation of α-trifluoromethyl alkenes, we focused on the defluoroborylation of trifluoromethyl alkenes using various Cu(I) cata

number of reaction conditions, such as the type of Cu(I) salt, catalyst and base amount, and reaction temperatures (entries 21–29). We found that the defluoroborylation of α-trifluoromethyl alkenes could proceed smoothly in the presence of 5 mol % CuCN and 1.0 equiv of LiO*t*Bu using THF as the solvent at 60 °C for 6 h (entry 28). When the amount of LiO*t*Bu was reduced from 1.0 to 0.5 equiv, the yield decreased sharply and only 20% of **3a** was obtained (entry 29).

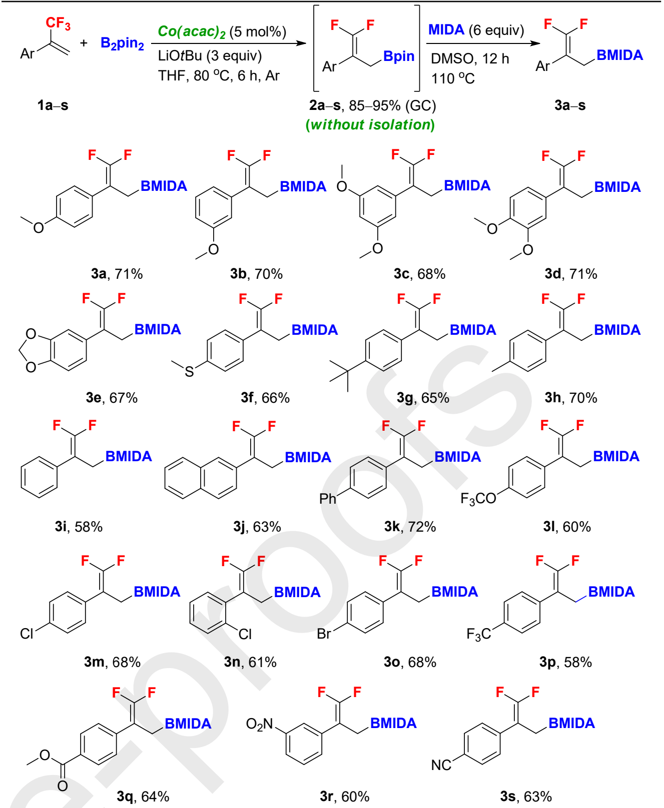
On the basis of our previous experimental observations, we found some *gem*-difluoroallylboronates are unstable during aqueous work-up and storage. Furthermore, some of them are sensitive or incompatible with silica gel chromatography and susceptible to decomposition during chromatographic isolation. To overcome these limitations, we next tried to convert pinacol boronic ester **2a** to MIDA-protected boronate **3a**. Delightfully, MIDA boronate **3a** could be synthesized by the reaction of trifluoromethyl alkene **1a** with B_2pin_2, followed by the addition of MIDA without the isolation of the intermediate *gem*-difluoroallylboronate **2a**. The *gem*-difluoroallyl MIDA boronates **3a** could be easily purified by recrystallization with Et_2O without the use of column chromatography.

With the optimized reaction conditions in hand (Table 1, entry 19), the scope and limitations of the Co-catalyzed synthesis of *gem*-difluoroallyl MIDA boronates was investigated. As shown in Table 2, in all cases, *gem*-difluroallylboronic acid pinacol esters **2a–s** could be obtained in high yields (85–95%, GC-MS). Both strong electron-donating (OMe, **3a**) and strong electron-withdrawing (NO_2, **3r** and CN, **3s**) groups attached to the aromatic ring of α-trifluoromethyl alkenes are compatible with the reaction conditions. This reaction exhibited a broad substrate scope and a variety of functional groups such as methoxy, methylthio, *tert*-butyl, trifluoromethoxy, chloro, bromo, trifluoromethyl, ester, nitro and cyano, groups were well tolerated under the optimized reaction conditions. The tolerance of the chloro, bromo, ester, nitro and cyano groups was particularly useful, which offered synthetic opportunities for further transformation. Notably, substrates bearing ester (**1q**), nitro (**1r**) or cyano (**1s**) groups worked well under the standard conditions. However, trifluoromethyl alkene **1q** failed to provide the expected product under our previously reported reaction conditions.[16] Meanwhile, defluorinative borylation of substrates **1r** and **1s** hardly proceeded under Zhou's reaction conditions.[14]

Without purification of the pinacol boronic esters **2a–s**, *N*-methyliminodiacetic acid (MIDA) was then directly added to the crude pinacol boronic esters.[18] To our delight, MIDA-protected boronates **3a–s** were obtained in moderate to good yields. All these *gem*-difluoroallyl MIDA boronates **3a–s** could be conveniently isolated in excellent purity by recrystallization with Et_2O and no chromatography was necessary. In addition, MIDA boronates **3a–s** are air-stable crystalline solids that can be stored on the bench top in air for more than three months without any detectable decomposition.

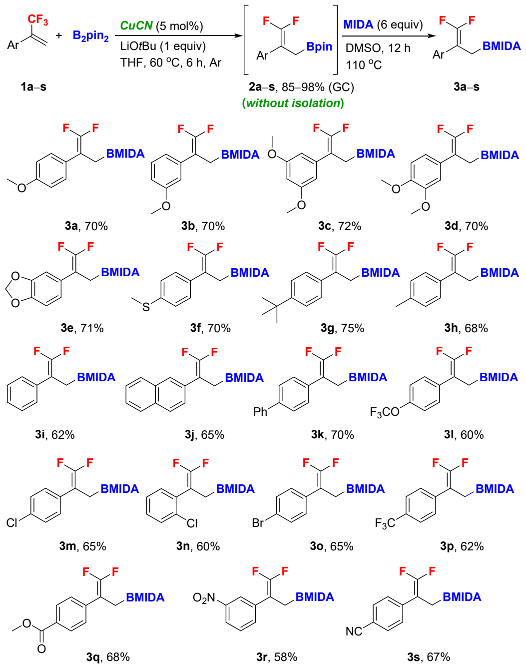
After the successful synthesis of a series of *gem*-difluoroallyl MIDA boronates under cobalt-catalyzed conditions, we next carried out the defluoroborylation of trifluoromethyl alkenes **1a–s** under the reaction conditions described for Table 1, entry 28 (5 mol% CuCN and 1.0 equiv of LiO*t*Bu), and sequential addition of MIDA without purification of the pinacol boronic esters **2a–s**. We were delighted to find that this copper-catalyzed two-step reaction also proceeded efficiently and afforded the corresponding products **3a–s** in comparable yields (Table 3).

DA boronates from α-trifluoromethyl alkenes.[a,b]



[a] Reaction conditions: 1) **1a–s** (1.0 mmol), B_2pin_2 (1.2 mmol), $Co(acac)_2$ (5 mol%), LiO*t*Bu (3 equiv), THF (5 mL), 80 °C, 6 h, Ar. 2) MIDA (6 equiv), DMSO (10 mL), 12 h, 110 °C, Ar.
[b] Isolated yields.

Table 3 Cu-catalyzed synthesis of *gem*-difluoroallyl MIDA boronates from α-trifluoromethyl alkenes.[a,b]



[a] Reaction conditions: 1) **1a–s** (1.0 mmol), B_2pin_2 (1.2 mmol), CuCN (5 mol%), LiO*t*Bu (1 equiv), THF (5 mL), 60 °C, 6 h, Ar. 2) MIDA (6 equiv), DMSO (10 mL), 110 °C, 12 h, Ar. [b] Isolated yields.

In summary, we have developed a novel two-step strategy for the synthesis of *gem*-difluoroallyl MIDA boronates through coba

alkenes with B_2pin_2 in the absence of ligand, followed by the addition of *N*-methyliminodiacetic acid (MIDA) without purification of the crude pinacol boronic esters. The difluoroallylation reaction exhibits good functional group compatibility and a variety of air- and moisture-stable *gem*-difluoroallyl MIDA boronates were obtained in moderate to good yields via this two-step procedure. Compared with the known protocols available, one of the notable advantages of this method is that the reaction is compatible with ester, nitro and cyano groups. Therefore, this method represents an efficient and valuable option for the synthesis of the important *gem*-difluoroallylboronates and *gem*-difluoroallyl MIDA boronates from α-trifluoromethyl alkenes. Further efforts to extend the applications of these fluorine-containing MIDA boronates in coupling reaction are underway in our laboratory.

Acknowledgments

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Supplementary Material

Supplementary data associated with this article can be found, in the online version, at

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights:

- MIDA boronates are versatile building blocks for organic synthesis.
- The functionalized *gem*-difluoroalkenes are valuable synthetic intermediates.
- Co- or Cu-catalyzed borylation of α-trifluoromethyl alkenes.
- Synthesis of *gem*-difluoroallyl MIDA boronates.

Graphical Abstract