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Synthesis of *gem*-Difluoroallylboronates via $FeCl_2$-Catalyzed Boration/β-Fluorine Elimination of Trifluoromethyl Alkenes

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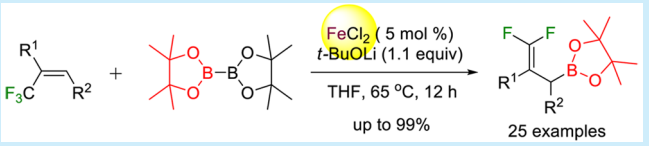
Supporting Information

ABSTRACT: The first ferrous chloride catalyzed boration/β-fluorine elimination of trifluoromethyl alkenes is described. Thus, a full range of *gem*-difluoroallylboronates were obtained in high yield under mild conditions. As an important fluorinated building block, *gem*-difluoroallylboronate can be readily converted into diverse difluoro-substituted species.



Introduction of fluorine atom(s) or fluorinated moieties into organic molecules can dramatically alter the reactivity, physical, chemical, and biological properties of the target molecule. As a consequence, fluorine-containing compounds are widely used in various fields such as material science and agricultural and pharmaceutical chemistry.[1] Among numerous fluorine-containing compounds, *gem*-difluorovinyl (1,1-difluoro-1-alkene) functionality is an important structural motif of many biologically active compounds. It appears in mechanism-based enzyme inhibitors[2] and is also considered as a bioisostere of the corresponding aldehyde and ketone in drug design.[3] Moreover, the *gem*-difluorovinyl is a useful monomer for the preparation of fluorinated polymers[4] and can be further converted into different fluorinated functionalities in organic synthesis.[5]

Over the past 50 years, owing to their important applications, a number of examples of the preparation of *gem*-difluorovinyls have been reported. First, the Wittig, Horner–Wadsworth–Emmons, and Julia–Kocienski reaction for the difluoroolefination of aldehydes or ketones are classical methods.[6] Recently, *gem*-difluoroolefination of diazo compounds as an efficient approach toward *gem*-difluorovinyl derivatives has also been reported.[7] Alternatively, *gem*-difluorovinyl derivatives have been prepared via a direct introduction of *gem*-difluorovinylidene unit with *gem*-difluorovinyl lithium, copper, zinc, tin, silicon, halogen, tosylate, or borane.[8] Finally, nucleophilic addition of nitrogen, sulfur, and carbon nucleophiles on trifluoromethylalkenes followed by β-fluorine elimination is also an efficient approach to *gem*-difluorovinyl derivatives.[9]

With the widely use in Suzuki–Miyaura cross-coupling reactions and conversion into the corresponding alcohols, aldehydes, amines, etc., alkylboronates have become one of the most versatile building blocks in organic synthesis.[10] Allylboronates are also known to be reagents of choice for allylation reactions.[11] Introducing an electron-donating boronate group into *gem*-difluorovinylidenes should therefore afford *gem*-difluoroallylboronates as versatile carbon nucleophilic units embedding a *gem*-difluorovinyl framework.

Surprisingly, the preparation of *gem*-difluoroallylboronates has scarcely been described. Their synthesis based on the stoichiometric reaction of iodomethylboronate with difluorovinyllithium was first reported by Ramachandran and co-workers.[12] More recently, Zhang and co-workers described the preparation of a shelf-stable β-tosyloxy-γ,γ-difluoroallylboronic acid pinacol ester through an analogous way.[13] However, the reaction conditions required for the preparation of difluorovinyllithium species and their homologation to the corresponding allylboronate limit the scope of this synthetic route. To the best of our knowledge, the sole example of the catalytic synthesis of *gem*-difluoroallylboronate was presented by Hoveyda and co-workers, showing that (3,3,3-trifluoroprop-1-en-2-yl)benzene could lead to the corresponding *gem*-difluoroallylboronate in a moderate yield by a copper-catalyzed boration/β-fluorine elimination using a *N*-heterocyclic carbene Cu catalyst.[14] Otherwise, the rhodium, iridium, or copper salt catalyzed reactions of HBpin or B_2pin_2 with trifluoroalkenes have been reported to deliver the expected 3,3,3-trifluoropropylboronates.[15]

Owing to its earth-abundance, low price and low toxicity, iron is an attractive metal for the development of new catalytic processes, and this field has received much attention.[16] In this context, we report the $FeCl_2$-catalyzed addition/β-fluorine elimination of trifluoromethyl alkenes leading to *gem*-difluoroallylboronates.

The $FeCl_2$-catalyzed reaction between 4-chloro-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1a**) and B_2pin_2 **2** was first selected as the model reaction for optimization of the reaction conditions. At the outset, several bases were examined (Table 1, entries 1–10). In contrast to our previous work on iron-catalyzed hydroboration of aryl alkenes,[17] low selectivity and yield were achieved in the presence of *t*-BuOK (Table 1, entry 1). Replacing *t*-BuOK with *t*-BuONa (Table 1, entry 2) or MeOLi (Table 1, entry 6) increased the selectivity, but only

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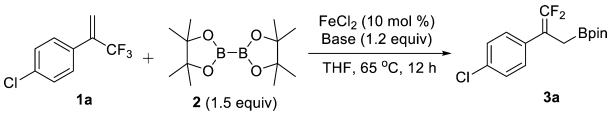
Table 1. Optimization of the Reaction Conditions[a,b]



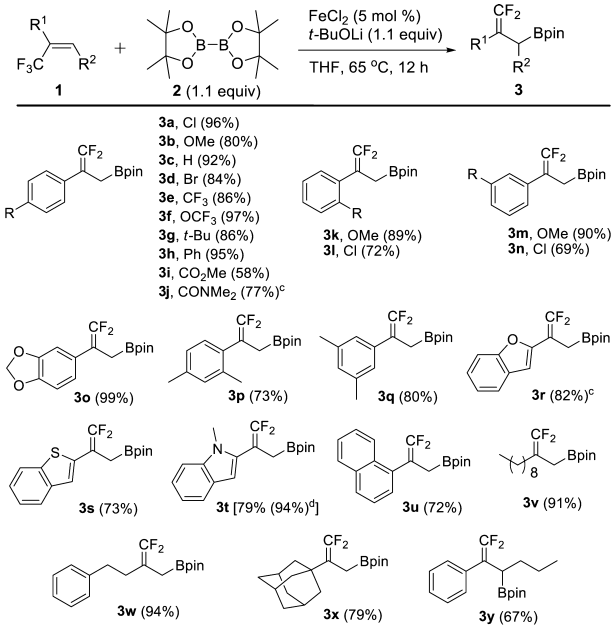
entry	base	conv (%)	yield (%)
1	*t*-BuOK	69	8
2	*t*-BuONa	59	55
3	*t*-BuOLi	100	99
4	MeOK	88	45
5	MeONa	23	4
6	MeOLi	43	41
7	KOH	39	10
8	Cs_2CO_3	21	5
9	K_2CO_3	22	5
10	K_3PO_4	25	3
11		33	0
12[c]	*t*-BuOLi	30	trace
13[d]	*t*-BuOLi	99	99
14[e]	*t*-BuOLi	93	90
15[f]	*t*-BuOLi	36	34
16[g]	*t*-BuOLi	74	59
17[h]	*t*-BuOLi	62	60
18[i]	*t*-BuOLi	99	99
19[j]	*t*-BuOLi	99	99
20[k]	*t*-BuOLi	98	98

[a]Reaction conditions: **1a** (0.4 mmol), **2** (0.6 mmol, 1.5 equiv), catalyst (10 mol %), base (0.48 mmol, 1.2 equiv), THF (6 mL), 65 °C, 12 h. [b]Conversion and yield were determined by ^{1}H NMR with 1,1,2,2-tetrachloroethaneas an internal standard. [c]No $FeCl_2$. [d]High-purity $FeCl_2$ (99.99%). [e]$FeCl_3$ as catalyst. [f]Reaction was performed at 25 °C for 24 h. [g]**2** (0.6 equiv). [h]*t*-BuOLi (0.6 equiv). [i]**2** (1.1 equiv), *t*-BuOLi (1.1 equiv). [j]$FeCl_2$ (5 mol %), **2** (1.1 equiv), *t*-BuOLi (1.1 equiv). [k]$FeCl_2$(99.99%, 5 mol %), **2** (1.1 equiv), *t*-BuOLi (1.1 equiv).

moderate conversion was obtained. To our delight, excellent conversion and yield were achieved when *t*-BuOLi was used (Table 1, entry 3). Other bases such as MeOK, MeONa, KOH, Cs_2CO_3, K_2CO_3, and K_3PO_4 were found to be unfavorable (Table 1, entries 4, 5, and 7−10), while no product was obtained in the absence of a base (Table 1, entry 11). Use of a blank control experiment and high-purity (99.99%) $FeCl_2$ as catalyst ensured that this reaction was catalyzed by iron salt (Table 1, entries 12 and 13). Moreover, experiments involving trace metals present in $FeCl_2$ further support the involvement of iron (Tables S1 and S2).[18] A slightly lower yield was observed when $FeCl_3$ was used as a catalyst (Table 1, entry 14). The reaction was significantly slower at lower temperature. Only 34% yield was achieved at room temperature even for 24 h (Table 1, entry 15). In addition, several other solvents were explored (Table S3). THF is the optimized solvent, and ether solvents were more suitable for this reaction generally. Further study showed that a slight excess of *t*-BuOLi and B_2pin_2 was beneficial for the conversion (Table 1, entries 16−18). Slightly lower loading of $FeCl_2$ to 5 mol % still led to a high yield (Table 1, entry 19) and using high-purity (99.99%) $FeCl_2$ as catalyst gave similar results (Table 1, entry 20).

With the standard reaction conditions (Table 1, entry 19) in hand, we next explored the substrate scope of the reaction (Scheme 1). Substrates bearing electron-donating and electron-withdrawing groups in the *para* positions on the phenyl ring provided the corresponding products in moderate to excellent

Scheme 1. $FeCl_2$-Catalyzed Synthesis of *gem*-Difluorovinyl Derivatives[a,b]



[a]Reaction conditions: **1** (1.0 mmol), **2** (1.1 mmol, 1.1 equiv), $FeCl_2$ (5 mol %), *t*-BuOLi (1.1 mmol, 1.1 equiv), THF (8 mL), 65 °C, 12 h. [b]Isolated yields. [c]Reaction conditions: **1** (1.0 mmol), **2** (1.5 mmol, 1.5 equiv), $FeCl_2$ (10 mol %), *t*-BuOLi (1.2 mmol, 1.2 equiv), THF (8 mL), 65 °C, 18 h. [d]^{1}H NMR yield.

yields (**3a−j**). In addition, the electron-withdrawing group chloro substituent and electron-donating group methoxyl substituent were tolerated at all of the positions on the benzene ring (**3a,b,k−n**). The substrates with polysubstituted phenyl also proceeded smoothly with **2** to afford good to excellent yields (**3o−q**). In addition, heterocyclic and naphthyl substrates provided the desired products in good yields (**3r−t,u**). To our delight, alkyl substrates including bulky adamantyl group can also undergo the reaction to afford the desired products in high yields (**3v−x**). Finally, internal alkene provided the desired product in good yield too (**3y**). Unfortunately, cyano and nitro substituents were not tolerated in this reaction.

On the basis of the previous reports on the mechanism of boration[19] and addition/*β*-fluorine elimination of trifluoromethyl alkenes,[9h−j] a possible reaction pathway using **1a** as a representative substrate is proposed in Scheme 2. First, complex **A** was generated via addition of *t*-BuOLi to B_2pin_2. Then, upon the cleavage of B−B bond in complex **A**, the addition of $^-$Bpin anion to the iron center afforded intermediate **B**. Species **C** was formed by coordination of substrate to the intermediate **B** followed by the insertion of double bond to the Fe−B bond. Finally, intermediate **C** underwent *β*-fluorine elimination to generate the product and the iron catalyst.

To demonstrate the practical utility of the ferrous chloride catalyzed boration/*β*-fluorine elimination process, a gram-scale reaction was conducted, and *gem*-difluoroallylboronate **3a** was obtained with maintained yield (Scheme 3). Bearing both *gem*-difluorovinyl and boronate groups, *gem*-difluoroallylboronate is an important fluorinated building block. It can be readily converted into the corresponding *gem*-difluoroallyl alcohol **4** (Scheme 4). Furthermore, compound **3c** can readily be

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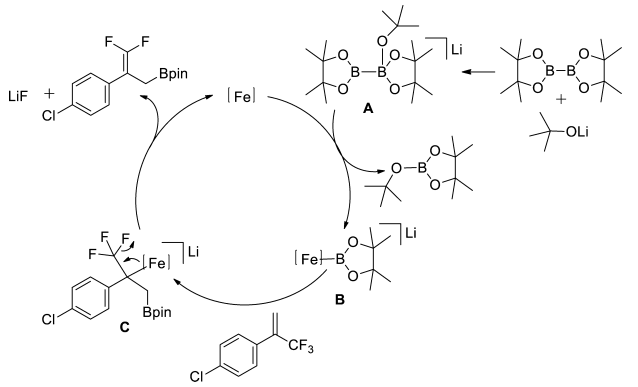
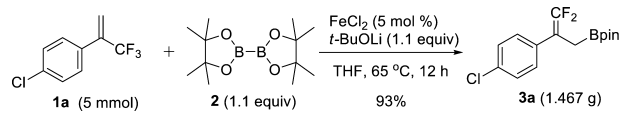
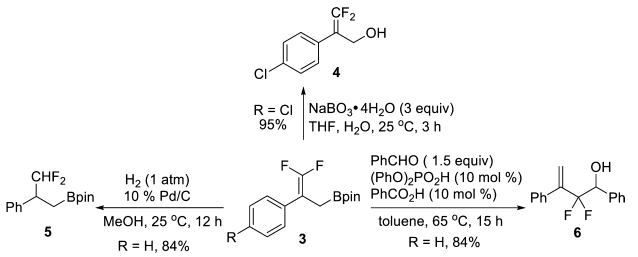
Scheme 2. Proposed Mechanism of the Reaction



Scheme 3. Gram-Scale Reaction



Scheme 4. Conversion of *gem*-Difluoroallylboronates

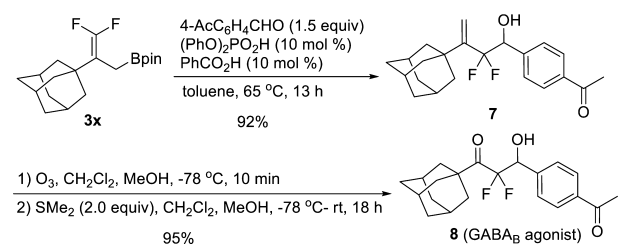


converted into the corresponding difluoromethylboronate **5** (Scheme 4) and reacts with benzaldehyde in the presence of acid catalyst to afford the homoallylic alcohol adduct **6** (Scheme 4) in 84% yield.

Finally, *gem*-difluoroallylboronates are extremely useful precursors and can be used to synthesize bioactive molecules. Recently, compound **8** was reported as a new agonist of the γ-aminobutyric acid type B ($GABA_B$) receptor by Colby and coworkers.[20] Herein, an alternative route for the synthesis of **8** based on the *gem*-difluoroallylboronate is presented. Compound **3x** reacted with 4-acetylbenzaldehyde to afford the homoallylic alcohol adduct **7** in 92% yield. Oxidation under ozone and reduction by dimethyl sulfide led to **8** in 95% yield (Scheme 5).

In conclusion, we have developed the first ferrous chloride catalyzed method for the synthesis of *gem*-difluoroallylboronates via boration/β-fluorine elimination of trifluoromethyl alkenes. Both substituted aryl and alkyl trifluoromethyl alkenes

Scheme 5. Synthesis of $GABA_B$ Receptor Agonist



gave good yields. Functional groups such as halogen, ester, trifluoromethyl, alkoxy, alkyl, etc. were tolerated well in the reaction. Furthermore, the *gem*-difluoroallylboronates can be readily converted into corresponding alcohols and difluoromethylboronates and used as intermediates for the synthesis of a $GABA_B$ receptor agonist.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00168.

Tables of reaction condition development, full experimental protocols, and characterization data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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