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Grignard reagents-catalyzed hydroboration of aldehydes and ketones

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ABSTRACT

Simple, commercially available Grignard reagents have been used as highly efficient precatalysts for the hydroboration of a wide range of aldehydes and ketones. The reaction employs very low catalyst loadings (aldehydes: 0.05 mol%, ketones: 0.5 mol%), and proceeds rapidly (aldehydes: 10 min, ketones: 20 min) under neat condition at room temperature. The Grignard reagent catalyst demonstrated good substrate scope, functional group tolerance, and high chemoselectivity in the carbonyl hydroboration. DFT calculations were performed to investigate the possible reaction mechanism. In contrast to the traditional stoichiometric use of Grignard reagents, this newly developed protocol provides a catalytic application of these reagents for molecular transformations.

1. Introduction

Since their discovery by Victor Grignard in 1900, Grignard reagents have proved to be an extremely powerful and ubiquitous synthetic tool in synthetic chemistry due to their ease of preparation and broad application in organic and organometallic synthesis [1,2]. Over the past 100 years and more since their discovery, considerable efforts have been made to investigate the formation, structure, reactivity, application, and mechanism of Grignard reagents [3–6]. Grignard reagents, especially the classical magnesium-based Grignard reagents (RMgX), are probably the most widely used organometallic reagents in inorganic, organic and organometallic chemistry to date. Nevertheless, the development of organomagnesium chemistry is still vital and full of surprises for their easy accessibility, high reactivity, improvement of atom economy and widespread application. Not only do they find extensive use on a small scale in many research laboratories worldwide but they also have been prepared and utilized on a larger scale in diverse industrial processe [7–12]. For example, one of the most important uses of the Grignard reagent is the reaction with aldehydes and ketones to form alcohols. When reacted with another halogenated compound in the presence of a suitable catalyst, they can also be used as transfer reagents for alkyl and aryl moieties in the C–C cross-coupling reaction to increase the carbon chain length of products [13–16], and even reacted with carbon dioxide to generate the corresponding carboxylic acid containing one more carbon atom than that of the starting material [17]. However, to our surprise, the amount of Grignard reagents employed in these protocols are stoichiometric and very few catalytic applications of Grignard reagents have been reported to date [18,19].

Hydroboration of carbonyl compounds is an attractive organic transformation among the various carbonyl reduction methodologies available because boron hydrides are relatively stable and helps to circumvent the use of highly flammable and pressurized hydrogen gas and stoichiometric amounts of metal hydride reagents. In addition, the resultant borate esters are versatile synthetic intermediates which can be further hydrolyzed to various functional alcohols [20–23]. Until now, the catalytic hydroboration of aldehydes and ketones is achieved with numerous catalysts based on transition metals and main group elements [24]. Among main group elements, literature reports about the earth-abundant and inexpensive alkaline earth metal catalyzed hydroboration of carbonyls are relatively few [25–33]. In most instances, these

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catalysts stabilized by sterically hindered ligands are expensive and relatively difficult to synthesize. Recently, Hreczycho and co-workers reported catalyst-free and solvent-free hydroboration of aldehydes. However, this protocol requires higher temperature and longer reaction time to get better conversions. More importantly, this method is completely ineffective for ketones and gave only trace amounts of the desired boronic esters even at elevated temperature [34]. Quite recently, Ma et al. reported hydroboration of ketones in the absence of a catalyst, however, it also requires excessive HBpin and higher temperature [35]. Therefore, it is essential to develop a convenient and easily attainable alkaline earth metal-based catalyst for hydroboration of both aldehydes and ketones at ambient temperature which will offer a powerful and sustainable alternative.

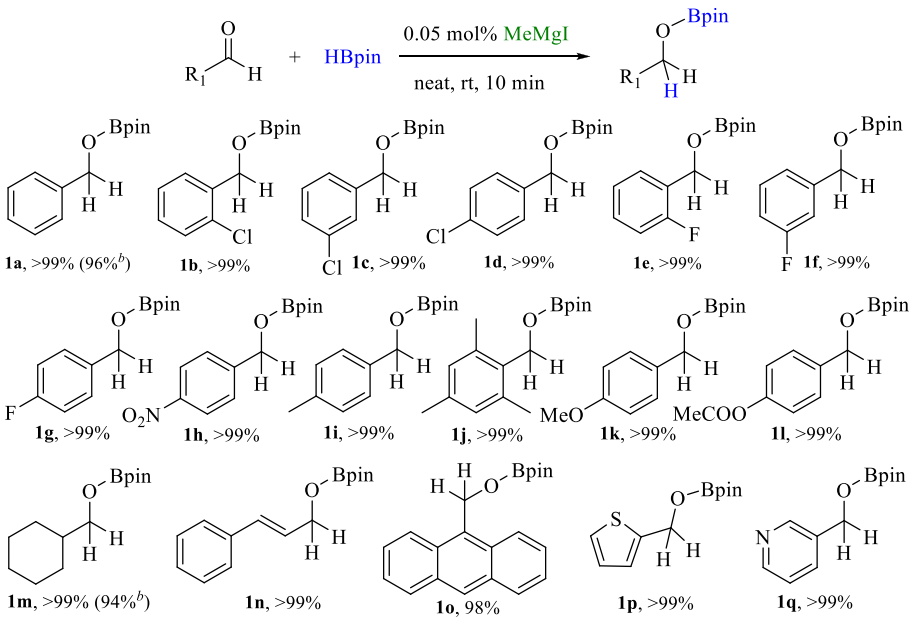
Herein, we report the highly efficient hydroboration of aldehydes and ketones with HBpin catalyzed by simple, commercially available and inexpensive Grignard reagents in truly catalytic amounts.

2. Results and discussion

We began our investigations into a plausible catalytic application of Grignard reagents with the addition of only 0.05 mol% of MeMgI as a catalyst to the mixture of benzaldehyde and HBpin under neat condition. To our surprise, the corresponding borate ester product was observed in a quantitative yield after 10 min at room temperature (Table S1, entry 1). Other commercially available Grignard reagents have been screened as well. All tested Grignard reagents showed excellent catalytic activity that gave almost full conversions under the same conditions (Table S1, entries 2–5). It needs to be highlighted that the catalytic performance of these Grignard reagents is better than most of transition metal catalysts, and could be comparable to that of rare-earth metal-based catalysts [36–40]. In addition, the reactivity of Grignard reagent is indeed better than that of most reported alkaline earth metal-based complexes [25–33](e.g. MeMgI: 0.05 mol%, 10 min, 99% yield *vs* magnesium alkyl complex [CH{C(Me)NAr}$_2$-Mg^{n}Bu] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$): 0.05 mol%, 15 min, in C_6D_6, 95% yield; [Mg(thf)$_6$][HBPh$_3$]$_2$: 0.01 mol%, 12 h, in THF-d$_8$, 78% yield; [PhC(N^{i}Pr)$_2$CaI]: 0.5 mol%, 40 min, in benzene, 83% yield). When organic solvents such as $CDCl_3$, C_6D_6 and CD_3CN were added into the above reaction under the same conditions, only trace conversion was observed (Table S1, entries 6–8).

With the optimized reaction conditions in hand, namely 0.05 mol% of MeMgI under neat condition at room temperature for 10 min, we explored the scope of the Grignard reagent catalyzed hydroboration of aldehydes. The position of halogen on the phenyl ring has no obvious effect on the reactivity as demonstrated by the clean hydroboration of 2/3/4-chlorobenzaldehyde and 2/3/4-fluorobenzaldehyde (Table 1, 1b–1g). This result is different from the rare-earth ytterbium catalyst reported previously by Ma group, wherein the substituent position (*o, m, p*) on the benzene ring has significant impact on the reactivity [38]. Both reactions employing benzaldehydes bearing electron-withdrawing as well as those with electron-donating substituents such as O_2N-, Me-, MeO- and MeCOO- proceeded rapidly and gave quantitative yields (Table 1, 1h–1l). Even the sterically bulky mesitaldehyde gave an excellent yield (Table 1,1j). When 4-acetyloxy substituted benzaldehyde was used, the ester moiety was retained intact during the hydroboration process (Table 1, 1l). This trend is consistent with the fact that hydroboration of esters is more difficult than that of aldehydes due to their steric and electronic factors [41]. Aliphatic aldehydes such as cinnamaldehyde and 9-anthraldehyde as well as heterocyclic aldehydes such as 2-thiophenecarboxaldehyde and 3-pyridinecarboxaldehyde all afforded the corresponding borate ester products in very high yields (Table 1,1m–1q). To our delight, cinnamaldehyde underwent hydroboration exclusively at the carbonyl group leaving the olefinic functionality intact when

Table 1
Hydroboration of Aldehydes Catalyzed by MeMgI[a].



[a]Aldehydes (1 equiv), HBpin (1.1 equiv), yield was determined by ^{1}H NMR spectroscopy.
[b]Isolated yields of the corresponding alcohols.

catalyzed by 0.05 mol% of MeMgI under neat condition at room temperature for 10 min (Table 1,1n).

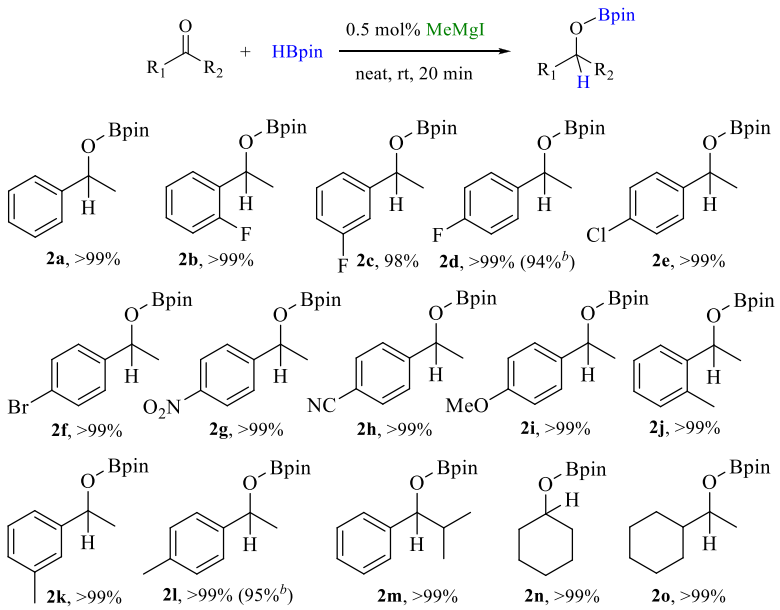
Encouraged by the above results from the aldehyde hydroboration reaction, we extended the substrate scope to a wide range of ketones. As expected, a relatively higher catalyst loading and slightly longer reaction time was required for hydroboration of the more sterically bulky ketonic carbonyl functionality when compared with aldehydes in order to achieve similar results. This trend is in line with reported literatures [24]. The preliminary investigation was carried out on the hydroboration of acetophenone with HBpin catalyzed by different catalyst loadings of MeMgI with/without solvent at room temperature for 20 min. Upon increasing catalyst loading, the hydroboration yield was gradually increased. Acetophenone was cleanly converted into the corresponding borate ester at 0.5 mol% catalyst loading within 20 min under neat condition (Table S2, entries 1–4). Similar to what was observed for aldehyde when an organic solvent such as $CDCl_3$, C_6D_6 and CD_3CN was employed, only trace yield was obtained under the same conditions as that employed for the MeMgI-catalyzed aldehyde hydroboration (Table S2, entries 5–7).

Similarly, various aromatic ketones and aliphatic ketones all underwent the hydroboration process smoothly with 0.5 mol% of MeMgI under neat condition at room temperature for 20 min. It should be noted that the catalytic activity of MeMgI was indeed more efficient than that of most of previous reported cases [24]. It was also demonstrated that acetophenone substrates with electron-withdrawing or electron-donating groups such as F-, Cl-, Br-, O_2N-, NC-, MeO- and Me-underwent full conversions (Table 2, 2b–2l). Once again, no obvious substituent effect was found in the hydroboration of (*o, m, p*)-F-substitutes and (*o, m, p*)-Me-substituted analogues. Changing the methyl moiety of acetophenone to isopropyl also produced the corresponding borate ethers in excellent yield (Table 2, 2m). The hydroboration of alkyl ketones could also be completed in high yield (Table 2, 2n, 2).

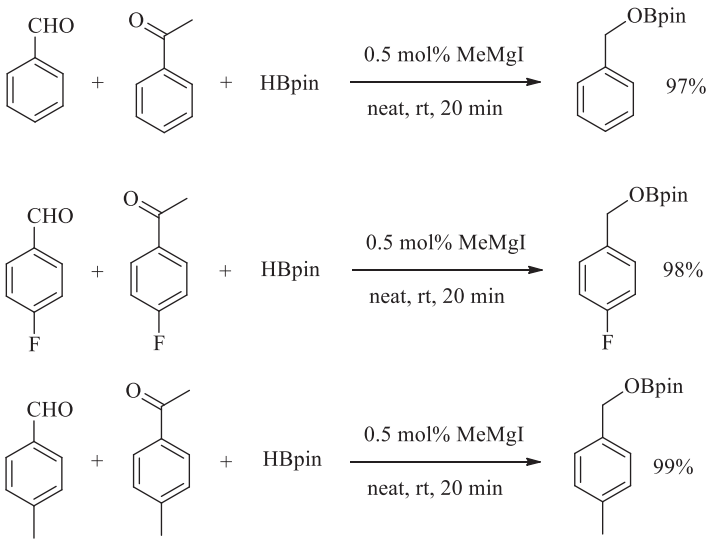
Subsequently, we also examined the chemoselective hydroboration of aldehydes over ketones. Equimolar amounts of benzaldehyde, acetophenone and pinacolborane were treated with 0.5 mol% MeMgI under neat condition at room temperature. It resulted in 97% conversion of benzaldehyde in 20 min while acetophenone remained almost unreacted (>98%). Similar chemoselectivity was also observed in the competitive catalytic hydroboration reactions of 4-fluorobenzaldehyde over 4-fluoroacetophenone and 4-methylbenzaldehyde over 4-methylacetophenone (Scheme 1). Lastly, a large-scale hydroboration of benzaldehyde/acetophenone (15 mmol) with HBpin (15.2 mmol) was performed with 0.05/0.5 mol% of MeMgI under neat condition at room temperature for 30 min/1 h respectively. Pleasingly, the conversions in both cases were successfully achieved with 99% yields (Scheme 2).

In addition, we used DFT calculations (M06–2X [42,43]) to investigate the possible mechanistic pathway of the hydroboration of PhCHO with HBpin in the presence of MeMgI (see **SI** for computational details). The computed free energy profile and transition states are displayed in Scheme 3 respectively (the optimized structures of minimum species are shown in Fig. S2, the cartesian coordinates of all optimized structures are also provided in **SI**). The whole pathway consists of the following six stages: (1) The magnesium atom of the catalyst (MeMgI) associates with one oxygen atom of HBpin to form an encounter complex (**Int1**), which is exergonic by 1.6 kcal/mol. Then, the methyl group is likely to attack the boron center to generate the zwitterionic intermediate **A** via **TS1** (being endothermic of 4.5 kcal/mol and the barrier is 12.6 kcal/mol, relative to **Int1**). (2) **A** binds with a benzaldehyde molecule driven by coordination interaction between the magnesium and oxygen atoms to form **Int2**, which is exergonic of 11.7 kcal/mol. Subsequently, the hydride transfers from boron to benzaldehyde to generate the intermediate **B** via **TS2**. This process involves a barrier of 4.3 kcal/mol and is exergonic by 29.2 kcal/mol

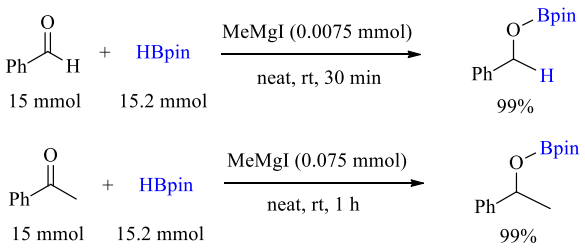
Table 2
Hydroboration of Ketones Catalyzed by MeMgI[a].



[a]Ketones (1 equiv), HBpin (1.1 equiv), yield was determined by ^{1}H NMR spectroscopy. [b]Isolated yields of the corresponding alcohols.

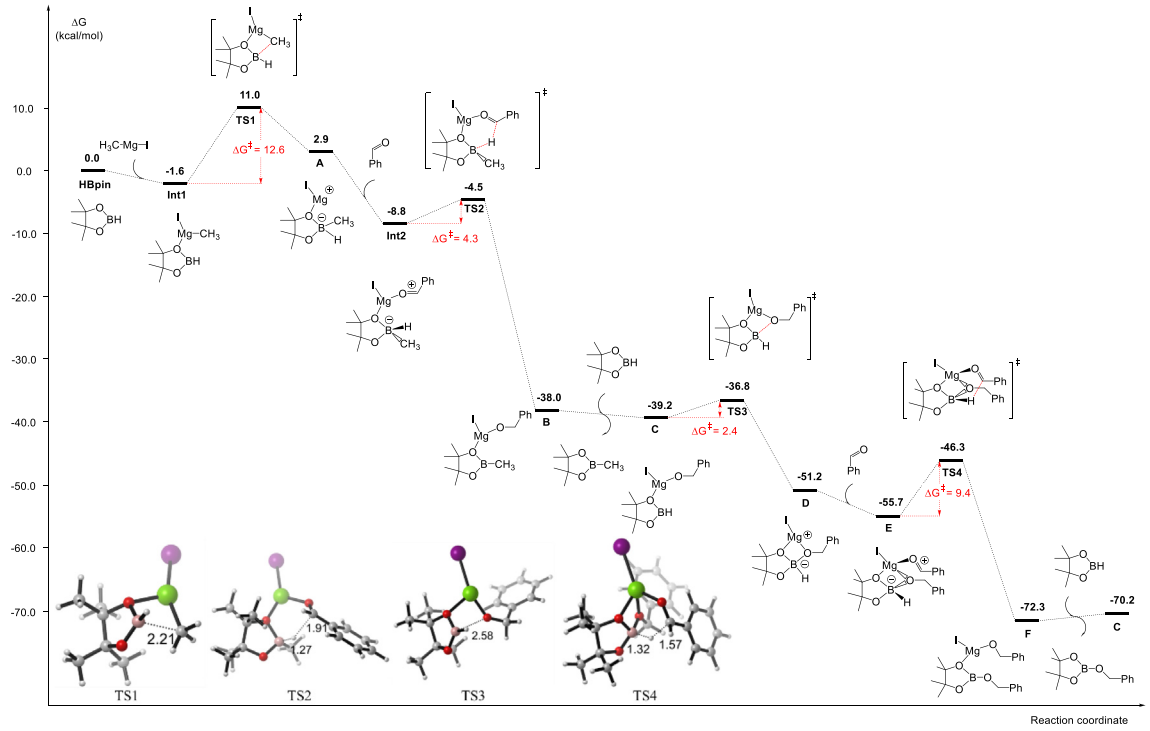


Scheme 1. Chemoselective Hydroboration of Aldehyde vs Ketone Catalyzed by MeMgI.



Scheme 2. Large-Scale Reaction of Benzaldehyde/Acetophenone with HBpin.

(relative to **Int2**). (3) Ligand exchange occurs between **B** and another HBpin molecule to generate the intermediate **C**, at the same time, release a Bpin-CH_3 molecule. This process is exergonic by 1.2 kcal/mol (4) The alkoxy group of **C** could nucleophilically attack the boron center to generate the zwitterionic intermediate **D** via the transition state **TS3**. This process involves a barrier of 2.4 kcal/mol and is exergonic by 12.0 kcal/mol (relative to **C**). (5) Similar to step (2), another molecule of benzaldehyde could bind with **D** to give the intermediate **E** (being exergonic by 4.5 kcal/mol), and a hydride migrate to the carbonyl carbon could follow to form the intermediate **F** (being exergonic by 16.6 kcal/mol and the barrier is 9.4 kcal/mol). (6) Starting from **F**, the final product could be



Scheme 3. Computed Gibbs Free Energy Profile of the MeMgI Catalyzed Hydroboration of PhCHO.

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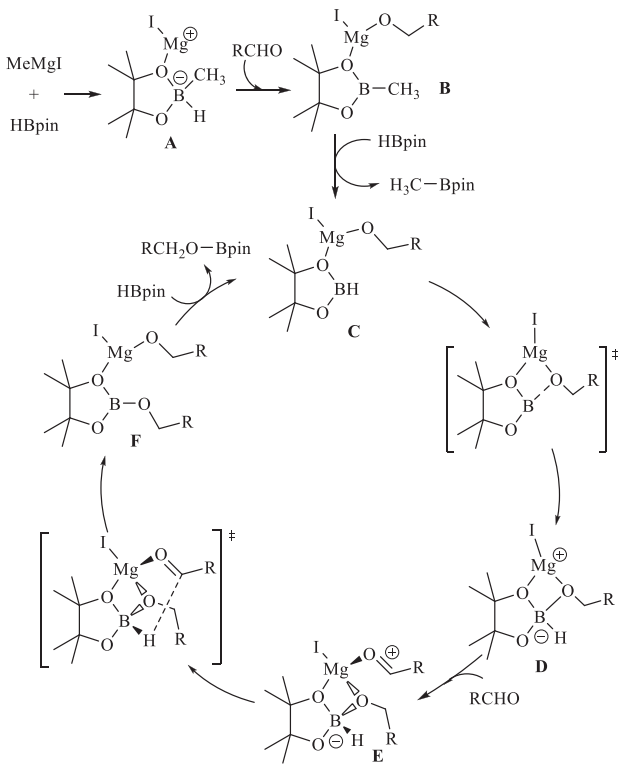

Scheme 4. Proposed Mechanistic Pathway.

obtained through ligand exchange with another HBpin molecule, at the same time, **C** is regenerated which is ready for the next catalytic cycle. This process is endothermic by 2.1 kcal/mol. The whole hydroboration of PhCHO with HBpin catalyzed with MeMgI is therefore exergonic by 70.2 kcal/mol (relative to the reactants HBpin, PhCHO and the catalyst MeMgI). This is consistent with the experimental phenomenon which the carbonyl hydroboration catalyzed by MeMgI is an exothermic reaction. These computational results suggest that this reaction is thermodynamically and kinetically feasible under the experimental conditions. According to the stoichiometric reaction and the DFT study, a possible mechanistic pathway is proposed in Scheme 4.

3. Summary

In summary, we have demonstrated that a series of simple, inexpensive, commercially available Grignard reagents can be employed in truly catalytic scale as efficient precatalysts for the hydroboration of a wide range of aldehydes and ketones with HBpin. The reaction proceeded rapidly with very low catalyst loading under neat condition at room temperature. It demonstrated high functional group tolerance for pyridine, ester, halides and nitro group etc. High chemoselectivity for aldehydes over ketones were also observed for the hydroboration reaction. Notably, a large-scale hydroboration was also carried out in very high yield under the optimized conditions and proceeded smoothly. In addition, DFT calculations were performed to investigate the possible reaction mechanism.

4. Experimental section

General Information. All reactions were performed under an atmosphere of nitrogen using glovebox technique. ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra were recorded at 25 °C on Bruker Avance III 600 MHz spectrometer in deuterated solvents and were referenced to the resonances of the solvent used. Chemicals were purchased from Sigma-Aldrich, Alfa Aesar, and Acros and used without further purification.

Experimental procedure. General procedure for catalytic hydroboration of aldehydes. To the mixture of aldehydes (0.2 mmol) and HBpin (0.22 mmol) in a 10 mL Schlenk flask equipped with a magnetic stir bar, a stock solution containing MeMgI (0.05 mol%, 0.04 mL) was added. Then the reaction mixture was stirred at 25 °C for 10 min. The progress of the reaction was monitored by ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopy which indicated the completion of the reaction by the disappearance of aldehyde (RCHO) proton and appearance of a new CH_2 resonance. Two examples (1a, 1 m) were selected to purify to get pure products: upon completion of the reaction, the combined organic layers were purified by silica gel column chromatography using ethyl acetate/hexane (1:9) mixture as eluents to obtain the corresponding pure alcohol products (96% and 94% yields respectively).

General procedure for catalytic hydroboration of ketones. To the mixture of ketones (0.2 mmol) and HBpin (0.22 mmol) in a 10 mL Schlenk flask equipped with a magnetic stir bar, a stock solution containing MeMgI (0.5 mol%, 0.04 mL) was added. Then the reaction mixture was stirred at 25 °C for 20 min. The progress of the reaction was monitored by ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopy which indicated the completion of the reaction by the appearance of a new CH resonance. Two examples (2d, 2l) were selected to purify to get pure products: upon completion of the reaction, the combined organic layers were purified by silica gel column chromatography using ethyl acetate/hexane (1:9) mixture as eluents to obtain the corresponding pure alcohol products (94 and 95% yields respectively).

Notes

The authors declare no competing financial interest.

Declaration of competing interest

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2020.131145.

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