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$FeCl_2$-Catalyzed Hydroboration of Aryl Alkenes with Bis(pinacolato)diboron

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The first ligand-free ferrous chloride catalyzed anti-Markovnikov hydroboration of un-activated aryl alkenes with bis(pinacolato)diboron (B_2pin_2) has been reported. Reactions proceed smoothly with high regioselectivity for a large range of aryl alkenes with wide functional-group compatibility and low catalyst loading under mild conditions.

Introduction

Alkylboronates are among the most versatile building blocks in organic synthesis. They are not only widely used in Suzuki–Miyaura cross-coupling reaction with aryl and alkyl halides but can also be readily converted into the corresponding alcohols, aldehydes, amines, *etc.*.[1] An advantage of alkylboronates over other common C(sp^3) organometallic nucleophiles like Grignard reagent is their stability. Many of them can be stored in air and readily purified as common organic compounds by chromatography.[1d] For this reason, the synthesis of alkylboronates with diverse functional group is especially meaningful.

Traditionally, alkylboronates are prepared by the reactions of suitable boron reagents with Grignard reagent or organolithium reagents.[1a,2] However, these methods are limited due to poor functional-group compatibility and atom economy. Recently, transition metal-catalyzed borylations of alkanes,[3] alkenes,[4-8] alkyl halides and pseudohalides,[9] as an alternative method for the preparation of alkylboronates, have become one of the most active research topics. Among them, transition metal-catalyzed hydroboration of alkenes is a useful method for the preparation of alkylboronates, owing to wide functional-group compatibility and mild conditions. Significant progress has been made recently in such transformations catalyzed by rhodium,[5] iridium,[5b,5f,5i,6] copper,[7] cobalt,[8] *etc.*.

In consideration of sustainable and green chemistry, iron-based catalytic systems have received significant growing interests because iron salts are earth-abundant, inexpensive, environment-friendly and less toxic.[10] Beyond the traditional iron-catalyzed reactions, such as Friedel–Crafts reaction, oxidation, *etc.*, the good performance of iron-catalysts on hydrosilylation,[11] hydrogenation,[12] cross-coupling,[13] C-H activation,[14] cyclization,[15] addition of unsaturated C-C bonds[16] has made it a rising star in catalyst. However, there are only several examples of iron-catalyzed borylation reactions of alkenes. Ritter and co-workers[17] discovered the first iron-catalyzed hydroboration of 1,3-dienes to afford linear (E)-γ-disubstituted allylboranes with pinacolborane (HBpin). In recent years, Huang,[18] Thomas,[19] Chirik,[20] Lu,[21] Szymczak,[22] Darcel[23] and co-workers successively reported iron-catalyzed hydroboration of alkenes with HBpin. However, most of these synthetic methods need adding reductant, like $NaBHEt_3$ or Grignard reagent. In addition, the use of ligands or complicated iron complex increased their cost in application. Fernández and co-workers[24] reported a commercially available iron salts catalyzed hydroboration of electron-deficient olefins with B_2pin_2. However, the substrates are limited to α,β-unsaturated esters, ketones, and imines. Thus, the commercially available iron salt catalyzed hydroboration of simple alkenes with B_2pin_2 is still highly desirable. In this context, we report a ferrous chloride catalyzed hydroboration of aryl alkenes with B_2pin_2 in the absence of ligands.

Results and discussion

Our studies were initiated by choosing hydroboration of styrene (**1a**) with B_2pin_2 (**2**) as the model reaction (Table 1). Fortunately, the first catalytic reaction performed with $FeCl_2$ as catalyst upon addition of ^{t}BuOK and ^{t}BuOH in THF stirring at 65 °C for 12 h afforded 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (**3a**) in 100% yield (Table 1, entry 1) with high regioselectivity. Three control experiments were performed to ensure this reaction was catalyzed by iron salt (Table 1, entries 2-4). Using high-purity (99.99%) $FeCl_2$ as catalyst can also afford a quantitative yield (Table 1, entry 2). When $FeCl_3$ was used, a slightly declining yield was observed in 90% (Table 1, entry 3). It is not surprising that there was almost no reaction in absence of iron salt (Table 1, entry 4). So, this reaction catalyzed by iron salt was identified. At lower temperature, the reaction can also proceed but was significantly slow. Only 24%

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yield was achieved at room temperature even for 24 h (Table 1, entry 5).

The fact that the addition of alcohols or water is essential in the hydroboration of alkenes has been confirmed by previous reports.[7e] Consequently, the effect of alcohols or water was investigated. If no additional alcohols or water was added, the yield of **3a** was very low (Table 1, entry 10). When 1 equivalent of alcohols or water was added, the yield of **3a** increased sharply (Table 1, entry 1 and entries 6-9). In general, alcohols were better than water, and the best result was achieved by ^{t}BuOH.

In addition, the base is also essential for this reaction. There was almost no reaction in absence of ^{t}BuOK (Table 1, entry 11). Further study showed that a slight excess ^{t}BuOK and B_2pin_2 were beneficial for the conversion (Table 1, entry 1 and entries 12-15), and the best result was obtained with 1.2 equivalent of ^{t}BuOK and 1.5 equivalent of B_2pin_2 (Table 1, entry 1). The catalytic activity of $FeCl_2$ was so high that an excellent isolated yield of 92% was achieved even when the amount of catalyst was reduced to 1 mol% (Table 1, entry 16), and using high-purity (99.99%) $FeCl_2$ as catalyst can also afford a high isolated yield (Table 1, entry 18). But further reducing of the catalyst resulted in the sharp decrease in yield (Table 1, entry 17).

Table 1 should be inserted here.

Solvents play an important role in affecting reactivity (Table 2). Good yield was obtained with THF but not for dioxane and ^{t}BuOMe (Table 2, entries 1-3). Alcohol solvents show a tremendous difference in yield (Table 2, entries 4 and 5). Nonpolar solvents such as CCl_4 and toluene were not suitable for the reaction (Table 2, entries 6 and 7). Polar solvents like MeCN, DMSO and DMF led to a moderate to excellent yield (Table 2, entries 8-10).

Table 2 should be inserted here.

The scope of this reaction was explored as the optimized conditions identified. A range of substituted aryl alkenes were initially surveyed (Table 3). Both electron-donating and electron-withdrawing groups were tolerated in this reaction. A variety of *para*-substituted functional groups, such as methyl, methoxyl, cyano, amine, ester and halogen were compatible to generate desired alkylboronates (**3b**-**3k**) in good to excellent yields. Besides, a chloro substituent was tolerated at all the positions on the benzene ring (**3h**, **3j** and **3k**) without any dehalogenated byproducts. However, reaction of 4-bromostyrene (**1i**) as substrate under the optimized condition gave both the desired product (**3i**) and dehalogenation byproduct (**3a**). In order to get higher yield, the reaction time was decreased to 3 h, and the desired product was afforded in 80% yield. The polysubstituted styrene, thienyl alkene, furyl alkene and naphthyl alkenes also proceeded smoothly with **2** to afford moderate to good yields of product independently. In addition, 1,3-divinylbenzene could be employed as substrate to give outstanding yield of the corresponding product (**3o**) with diploid loading of other reagents and catalyst but not reaction time. To our delight, the hydroboration of 1,1-disubstituted alkenes also took place smoothly to give the product (**3p**-**3r**) in excellent yield. Furthermore, internal alkenes, including furyl alkene, phenyl alkene and naphthyl alkene provided the desired product in moderate to good yields (**3s**-**3v**). Finally, another series of cyclic aryl alkenes, such as indene and 1,2-dihydronaphthalene, can also undergo reaction to obtain desired products in high yield (**3w** and **3x**). Unfortunately, under the optimized condition, the reaction almost no occurred when using cyclohexene as a substrate. Using 1-octene as a substrate, the product was afforded in low isolated yield of 31%, with a low regioselectivity of 30% of the branched isomer and 70% of the linear isomer.

Table 3 should be inserted here.

On the basis of the above information and previous reports,[7l,17,18a,25] a putative reaction pathway for the iron-catalyzed hydroboration of aryl alkenes with B_2pin_2 is shown in Scheme 1. First, complex **A** was generated via addition of ^{t}BuOK 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 aryl alkene to the intermediate **B** followed by the insertion of aryl alkene to the Fe-B bond. Finally, intermediate **C** was protonated with ^{t}BuOH to generate *anti*-Markovnikov products and the iron catalyst. In order to verify the proton supplied with additive, isotope labeling experiment was performed under the standard reaction conditions but the ^{t}BuOH was replaced by CD_3OD (Scheme 2). The deuterated product (**3a-D**) was isolated with a good yield of 85% and high deuterated ratio in 99%. ^{t}BuOK did not consume in our proposed catalytic cycle, but 1.2 equivalent of ^{t}BuOK was needed for high yield of the product in the best condition. Our simulative argument is that a high concentration of intermediate **B** is essential to generate species **C**. And the result also showed that a yield of 82% was achieved when 0.6 equivalent of ^{t}BuOK was used (Table 1, entry 14). That means the stoichiometric ^{t}BuOK is not essential for the reaction. It agrees with our proposed mechanism.

Scheme 1 should be inserted here.
Scheme 2 should be inserted here.

Experimental section

Materials and Methods

Unless otherwise noted, all reactions were performed under argon using Schlenk line techniques with magnetic stirring. Solvents were dried by passage through an activated alumina column under argon. Column chromatography was performed on silica gel (200~300 mesh) or aluminum oxide (neutral, 200~300 mesh). All ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) or ^{13}C NMR (125 MHz) were recorded on Bruker AVANCE II-400 or Bruker AVANCE III-500 spectrometer with chemical shifts reported as ppm (in $CDCl_3$, with TMS as an internal standard).

High resolution mass spectra (HRMS) (EI) were recorded on a Micromass GCT spectrometer.

Aryl alkenes **1e**, **1l**, **1o**, **1s** (mixture of *cis*- and *trans* isomers), **1t** (mixture of *cis*- and *trans* isomers), **1u** (mixture of *cis*- and *trans* isomers) and **1v** (mixture of *cis*- and *trans* isomers) were prepared by Wittig olefination of the corresponding aldehyde followed the examples of previously reported procedures.[26] Other aryl alkenes were purchased and used as received.

The following chemicals were purchased and used as received: $FeCl_3$ (98 %, J&K), ^tBuOK (99 %, J&K), Bis(pinacolato)diboron (>99 %, TCI), high-purity $FeCl_2$ (beads, 99.99 %, Sigma-Aldrich, powder was prepared using a mortar and pestle in a glovebox).

$FeCl_2$ was prepared from $FeCl_3$ (50 g) in chlorobenzene (450 mL) at 130 °C for 8 h under argon followed the example of previously reported procedures.[27]

General Procedure for the Synthesis of Alkylboronates

To a Schlenk tube equipped with a magnetic stir bar and charged with $FeCl_2$ (2.6 mg, 0.02 mmol) was added THF (20 mL), followed by aryl alkene (2 mmol), bis(pinacolato)diboron (762 mg, 3 mmol), ^tBuOK (269 mg, 2.4 mmol), ^tBuOH (150 mg, 2 mmol). The resulting solution was stirred at 65 °C for 12 h. The solution of the crude product was concentrated in vacuum, brine (20 mL) was added and the aqueous layer was extracted with EtOAc (3×20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography using the appropriate gradient of petroleum ether and EtOAc.

4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (3a)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (430 mg, 92 %); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.20-7.27 (m, 4H, ArH), 7.13-7.16 (m, 1H, ArH), 2.75 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.22 (s, 12H, $2C(CH_3)_2$), 1.14 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 128.3, 128.1, 125.6, 83.2, 30.1, 24.7. These spectroscopic data correspond to reported data.[7m]

4,4,5,5-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (3b)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (421 mg, 86 %); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.04-7.12 (m, 4H, ArH), 2.70 (t, J = 8.0 Hz, 2H, $ArCH_2$), 2.30 (s, 3H, $ArCH_3$), 1.23 (s, 12H, $2C(CH_3)_2$), 1.12 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 134.6, 128.8, 127.8, 82.8, 29.5, 24.7, 20.9. These spectroscopic data correspond to reported data.[7m]

2-(4-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:5). Colorless oil (464 mg, 89 %); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.13 (d, J = 8.0 Hz, 2H, ArH), 6.81 (d, J = 8.0 Hz, 2H, ArH), 3.78 (s, 3H, OCH_3), 2.69 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.22 (s, 12H, $2C(CH_3)_2$), 1.11 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 136.5, 128.8, 113.6, 83.0, 55.2, 29.1, 24.8. These spectroscopic data correspond to reported data.[7m]

2-(4-Cyanophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:7). Colorless oil (497 mg, 97 %); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.55 (d, J = 8.0 Hz, 2H, ArH), 7.31 (d, J = 8.0 Hz, 2H, ArH), 2.79 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.21 (s, 12H, $2C(CH_3)_2$), 1.14 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 132.0, 128.9, 119.2, 109.4, 83.3, 30.1, 24.8. These spectroscopic data correspond to reported data.[28]

4,4,5,5-Tetramethyl-2-(4-dimethylaminophenethyl)-1,3,2-dioxaborolane (3e)

Title compound was isolated by flash chromatography on aluminum oxide eluting with petroleum ether/ethyl acetate (100:1-100:7). Pale yellow oil (460 mg, 84 %); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.10 (d, J = 8.0 Hz, 2H, ArH), 6.69 (d, J = 8.0 Hz, 2H, ArH), 2.90 (s, 6H, $N(CH_3)_2$), 2.66 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.23 (s, 12H, $2C(CH_3)_2$), 1.11 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 133.0, 128.5, 113.1, 83.1, 41.1, 29.0, 24.9; HRMS-EI: calc for $C_{16}H_{26}O_2BN$, 275.2057; found, 275.2061.

2-(4-Methoxycarbonylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:15). Colorless oil (396 mg, 68 %); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.93 (d, J = 8.0 Hz, 2H, ArH), 7.28 (d, J = 8.0 Hz, 2H, ArH), 3.89 (s, 3H, OCH_3), 2.79 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.21 (s, 12H, $2C(CH_3)_2$), 1.15 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 149.9, 129.6, 128.0, 127.6, 83.2, 51.8, 30.0, 24.8. These spectroscopic data correspond to reported data.[28]

2-(4-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (495 mg, 99 %); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.13-7.18 (m, 2H, ArH), 6.90-6.96 (m, 2H, ArH), 2.71 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.21 (s, 12H, $2C(CH_3)_2$), 1.11 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2 (d, J = 241.6 Hz), 140.0 (d, J = 3.1 Hz), 129.4 (d, J = 7.6 Hz), 114.8 (d, J = 20.9 Hz), 83.1, 29.2, 24.8.

These spectroscopic data correspond to reported data.[7m]

2-(4-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (523 mg, 98 %); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.22 (d, J = 8.0 Hz, 2H, ArH), 7.14 (d, J = 8.0 Hz, 2H, ArH), 2.71 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.21 (s, 12H, $2C(CH_3)_2$), 1.11 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 131.2, 129.4, 128.2, 83.2, 29.3, 24.8. These spectroscopic data correspond to reported data.[7m]

2-(4-Bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)

Prepared by general procedure, but the reaction time was reduced to 3 h. Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (496 mg, 80 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.37 (d, J = 8.0 Hz, 2H, ArH), 7.08 (d, J = 8.0 Hz, 2H, ArH), 2.69 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.21 (s, 12H, $2C(CH_3)_2$), 1.11 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 131.3, 129.9, 119.3, 83.3, 29.5, 24.9. These spectroscopic data correspond to reported data.[7m]

2-(2-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (520 mg, 98 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.25-7.32 (m, 2H, ArH), 7.08-7.18 (m, 2H, ArH), 2.84 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.24 (s, 12H, $2C(CH_3)_2$), 1.15 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 133.9, 129.8, 129.4, 127.1, 126.7, 83.2, 27.9, 24.9; HRMS-EI: calc for $C_{14}H_{20}O_2BCl$, 266.1245; found, 266.1256.

2-(3-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (520 mg, 98 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.07-7.24 (m, 4H, ArH), 2.72 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.22 (s, 12H, $2C(CH_3)_2$), 1.12 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 133.9, 129.4, 128.3, 126.3, 125.7, 83.2, 29.7, 24.8; HRMS-EI: calc for $C_{14}H_{20}O_2BCl$, 266.1245; found, 266.1238.

2-(3,4,5-Trimethoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:7). White solid (622 mg, 97 %); m.p. 61-63 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 6.44 (s, 2H, ArH), 3.83 (s, 6H, $2OCH_3$), 3.81 (s, 3H, OCH_3), 2.69 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.22 (s, 12H, $2C(CH_3)_2$), 1.14 (t, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 140.3, 135.9, 104.9, 83.2, 60.9, 56.0, 30.4, 24.9; HRMS-EI: calc for $C_{17}H_{27}O_5B$, 322.1952; found, 322.1959.

2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-thiophene (3m)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Pale yellow oil (315 mg, 66 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.07-7.09 (m, 1H, ArH), 6.88-6.90 (m, 1H, ArH), 6.79-6.80 (m, 1H, ArH), 2.96 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.24-1.20(m, 14H, $2C(CH_3)_2$ + BCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 126.5, 123.4, 122.6, 83.2, 24.8, 24.4. These spectroscopic data correspond to reported data.[9a]

4,4,5,5-Tetramethyl-2-(2-(naphthalen-1-yl)ethyl)-1,3,2-dioxaborolane (3n)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (500 mg, 89 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 8.09 (d, J = 8.0 Hz, 1H, ArH), 7.84 (d, J = 8.0 Hz, 1H, ArH), 7.65-7.71 (m, 1H, ArH), 7.44-7.52 (m, 2H, ArH), 7.36-7.41 (m, 2H, ArH), 3.21 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.29 (t, J = 8.0 Hz, 2H, BCH_2), 1.25 (s, 12H, $2C(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 133.9, 131.8, 128.7, 126.4, 125.7, 125.6, 125.4, 125.1, 124.0, 83.2, 27.0, 24.9; HRMS-EI: calc for $C_{18}H_{23}O_2B$, 282.1791; found, 282.1790.

1,3-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzene (3o)

To a Schlenk tube equipped with a magnetic stir bar and charged with $FeCl_2$ (5.1 mg, 0.04 mmol) was added THF (20 mL), followed by 1,3-divinylbenzene (2 mmol), bis(pinacolato)diboron (1524 mg, 6 mmol), ^{t}BuOK (538 mg, 4.8 mmol), ^{t}BuOH (300 mg, 4 mmol). The resulting solution was stirred at 65 °C for 12 h. The solution of the crude product was concentrated in vacuo, brine (20 mL) was added and the aqueous layer was extracted with EtOAc (3×20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent removed under reduced pressure. Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:7). White solid (741 mg, 96 %); m.p. 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.15 (t, J = 8.0 Hz, 1H, ArH), 7.06 (s, 1H, ArH), 7.01(d, J = 8.0 Hz, 2H, 2ArH), 2.70 (t, J = 8.0 Hz, 4H, $2PhCH_2$), 1.22 (s, 24H, $4C(CH_3)_2$), 1.12 (t, J = 8.0 Hz, 4H, $2BCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 128.0, 127.8, 125.2, 83.0, 29.9, 24.8; HRMS-EI: calc for $C_{22}H_{36}O_4B_2$, 386.2800; found, 386.2806.

4,4,5,5-Tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (3p)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (490 mg, 99 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.22-7.28 (m, 4H, ArH), 7.13-7.16 (m, 1H, ArH), 2.98-3.07 (m, 1H, ArCH), 1.27 (d, 3H, $CHCH_3$), 1.14-1.16 (m, 14H, $2C(CH_3)_2$ + BCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 128.2, 126.6, 125.7, 82.9, 35.8, 25.0, 24.8, 24.7. These spectroscopic data correspond to reported data.[7m]

2-(2,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Pale yellow solid (577 mg, 94 %); m.p. 60-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.19-7.28 (m, 8H, ArH), 7.11-7.15 (m, 2H, ArH), 4.28 (t, J = 8.0 Hz, 1H, ArCH), 1.60 (d, J = 8.0 Hz, 2H, BCH_2), 1.05 (s, 12H, $2C(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 128.3, 127.8, 126.0, 83.2, 46.7, 24.7. These spectroscopic data correspond to reported data.[7m]

4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane (3r)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (555 mg, 94 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.78-7.82 (m, 3H, ArH), 7.69 (s, 1H, ArH) 7.40-7.48 (m, 3H, ArH), 2.21-3.30 (m, 1H, ArCH), 1.40 (d, J = 4.0 Hz, 3H, $CHCH_3$), 1.29 (t, J = 8.0 Hz, 2H, BCH_2), 1.17 (s, 12H, $2C(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 133.7, 132.2, 127.8, 127.7, 127.5, 126.0, 125.8, 125.0, 124.5, 83.1, 36.0, 24.9, 24.8, 24.8. These spectroscopic data correspond to reported data.[7i]

2-(1-(Furan-2-yl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (337 mg, 64 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.26 (d, J = 4.0 Hz,1H, ArH), 6.24 (t, J = 4.0 Hz,1H, ArH), 5.97 (d, J = 4.0 Hz,1H, ArH), 2.74 (dd, J = 8.0 Hz, J = 15.00 Hz, 1H, 1/2ArCH_2), 2.66 (dd, J = 8.0 Hz, J = 15.00 Hz, 1H, 1/2ArCH_2), 1.28-1.48 (m, 5H, BCH+CHCH_2+CH_3CH_2), 1.20 (s, 6H, 2*[1/2C(CH_3)$_2$]), 1.12 (s, 6H, 2*[1/2C(CH_3)$_2$]), 0.89 (t, J = 8.0 Hz, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 140.6, 110.0, 105.1, 83.1, 33.4, 29.6, 24.8, 24.8, 22.2, 14.4; HRMS-EI: calc for $C_{15}H_{25}O_3B$, 264.1897; found, 264.1899.

4,4,5,5-Tetramethyl-2-(1-phenylpentan-2-yl)-1,3,2-dioxaborolane (3t)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (500 mg, 91 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.19-7.25 (m, 4H, ArH), 7.11-7.16 (m, 1H, ArH), 2.71 (dd, J = 8.0 Hz, 13.56 Hz, 1H, 1/2ArCH_2), 2.66 (dd, J = 8.0 Hz, 13.6 Hz, 1H, 1/2ArCH_2), 1.45-1.48 (m, 5H, BCH+CHCH_2+CH_3CH_2), 1.16 (s, 6H, 2*[1/2C(CH_3)$_2$]), 1.12 (s, 6H, 2*[1/2C(CH_3)$_2$]), 0.89 (t, J = 8.0 Hz, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 128.8, 128.0, 125.5, 82.8, 37.4, 33.6, 24.8, 24.7, 22.3, 14.4; HRMS-EI: calc for $C_{17}H_{27}O_2B$, 274.2104; found, 274.2105.

4,4,5,5-Tetramethyl-2-(1-(naphthalen-1-yl)pentan-2-yl)-1,3,2-dioxaborolane (3u)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (512 mg, 79 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 8.08 (d, J = 12.0 Hz, 1H, ArH), 7.81-7.84 (m, 1H, ArH), 7.67-7.69 (m, 1H, ArH), 7.43-7.51 (m, 2H, ArH), 7.34-7.40 (m, 2H, ArH), 3.20 (dd, J = 8.0 Hz, 14.0 Hz, 1H, 1/2ArCH_2), 3.10 (dd, J = 8.0 Hz, 14.0 Hz, 1H, 1/2ArCH_2), 1.28-1.59 (m, 5H, BCH+CHCH_2+CH_3CH_2), 1.17 (s, 6H, 2*[1/2C(CH_3)$_2$]), 1.12 (s, 6H, 2*[1/2C(CH_3)$_2$]), 0.91 (t, J = 8.0 Hz, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 134.0, 132.2, 128.7, 126.5, 126.5, 125.6, 125.3, 125.3, 124.3, 83.0, 344.5, 34.2, 24.9, 24.7, 22.5, 14.6; HRMS-EI: calc for $C_{21}H_{29}O_2B$, 324.2261; found, 324.2258.

4,4,5,5-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane (3v)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (460 mg, 94 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.13-7.25 (m, 5H, ArH), 2.81 (dd, J = 8.0 Hz, 13.6 Hz, 1H, 1/2ArCH_2), 2.54 (dd, J = 8.0 Hz, 13.6 Hz, 1H, 1/2ArCH_2), 1.31-1.40 (m, 1H, BCH), 1.19 (s, 6H, 2*[1/2C(CH_3)$_2$]), 1.18 (s, 6H, 2*[1/2C(CH_3)$_2$]), 0.96 (d, J = 8.0 Hz, 3H, CHCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 128.9, 128.0, 125.6, 83.0, 39.1, 24.8, 15.3. These spectroscopic data correspond to reported data.[7m]

2-(2,3-Dihydro-1*H*-inden-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3w)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (455 mg, 93 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.19-7.23 (m, 2H, ArH), 7.09-7.14 (m, 2H, ArH), 2.94-3.10 (m, 4H, 2ArCH_2), 1.82-1.93 (m, 1H, BCH), 1.27 (s, 12H, 2C(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 126.0, 124.3, 83.3, 35.2, 24.9. These spectroscopic data correspond to reported data.[7e]

4,4,5,5-Tetramethyl-2-(1,2,3,4-tetrahydro-2-naphthalenyl)-1,3,2-Dioxaborolane (3x)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (482 mg, 94 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.04-7.09 (m, 4H, ArH), 2.72-2.89 (m, 4H, 2ArCH_2), 1.99-2.06 (m, 1H, 1/2CHCH_2), 1.60-1.71 (m, 1H, 1/2CHCH_2), 1.29-1.38 (m, 1H, BCH), 1.26 (s, 6H, 2*[1/2C(CH_3)$_2$]), 1.26 (s, 6H, 2*[1/2C(CH_3)$_2$]); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 137.1, 129.2, 129.0, 125.4, 83.2, 30.8, 29.8, 24.9, 24.8, 24.8. These spectroscopic data correspond to reported data.[7e]

4,4,5,5-Tetramethyl-2-phen(1-D)ethyl-1,3,2-dioxaborolane (3a-D).

To a Schlenk tube equipped with a magnetic stir bar and charged with $FeCl_2$ (5 mg, 0.04 mmol) was added THF (5 mL), followed by styrene (41 mg, 0.4 mmol), bis(pinacolato)diboron (150 mg, 0.6 mmol), ^{t}BuOK (53 mg, 0.48 mmol), CD_3OD (72mg, 2 mmol). The resulting solution was stirred at 65 °C for 12 h. The solution of the crude product was concentrated in vacuo, brine (5 mL) was added and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried (Na_2SO_4) and the solvent removed under reduced pressure. Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (79 mg, 85 %); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.20-7.28 (m, 4H, ArH), 7.13-7.17 (m, 1H, ArH), 2.73 (t, J = 8.0 Hz, 1H, ArCH), 1.22 (s, 12H, 2C(CH_3)$_2$), 1.13 (d, J = 8.0 Hz, 2H, BCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 128.2, 128.0, 125.5, 83.1, 77.4, 77.2, 76.9, 29.8, 29.7, 29.5, 24.8. These spectroscopic data correspond to reported data.[7m]

Conclusions

In conclusion, we have developed the first ferrous chloride catalyzed hydroboration of un-activated aryl alkenes with B_2pin_2 in the absence of ligands. The reaction proceeded smoothly in the presence of ferrous chloride, ^{t}BuOK and ^{t}BuOH, and the alkylboronates were obtained in high yield with high selectivity. Both substituted aryl ethylenes and internal alkenes gave good yield. The functional groups such as halogen, ester, amine, alkoxy, cyano *etc.* were tolerated well in the reaction. Employing air and moisture-stable B_2pin_2, using only 1 mol% of cheap and environment-friendly ferrous chloride, avoiding air and moisture-sensitive reductant and ligands make it a practical method for the preparation of alkylboronates.

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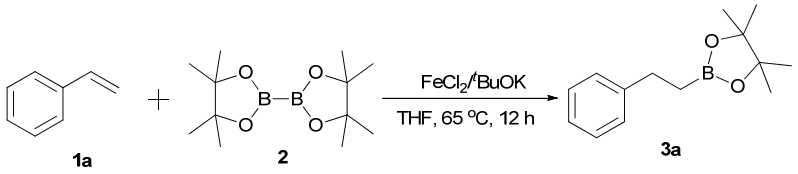
Table 1 Optimization of reaction conditions for hydroboration of styrene[a]



1a 2 3a

Entry	Catalyst	^{t}BuOK	B_2pin_2	Additive	Yield(%)[b]
1	$FeCl_2$ (10 mol%)	1.2 eq	1.5 eq	^{t}BuOH	100
2	$FeCl_2$ (10 mol%)[c]	1.2 eq	1.5 eq	^{t}BuOH	100
3	$FeCl_3$ (10 mol%)	1.2 eq	1.5 eq	^{t}BuOH	90
4	-	1.2 eq	1.5 eq	^{t}BuOH	trace
5	$FeCl_2$ (10 mol%)	1.2 eq	1.5 eq	^{t}BuOH	24[d]
6	$FeCl_2$ (10 mol%)	1.2 eq	1.5 eq	MeOH	96
7	$FeCl_2$ (10 mol%)	1.2 eq	1.5 eq	EtOH	97
8	$FeCl_2$ (10 mol%)	1.2 eq	1.5 eq	^{i}PrOH	97
9	$FeCl_2$ (10 mol%)	1.2 eq	1.5 eq	H_2O	64
10	$FeCl_2$ (10 mol%)	1.2 eq	1.5 eq	-	10
11	$FeCl_2$ (10 mol%)	-	1.5 eq	^{t}BuOH	trace
12	$FeCl_2$ (10 mol%)	1.2 eq	0.6 eq	^{t}BuOH	42
13	$FeCl_2$ (10 mol%)	1.2 eq	1 eq	^{t}BuOH	76
14	$FeCl_2$ (10 mol%)	0.6 eq	1.5 eq	^{t}BuOH	82
15	$FeCl_2$ (10 mol%)	1 eq	1.5 eq	^{t}BuOH	93
16	$FeCl_2$ (1 mol%)	1.2 eq	1.5 eq	^{t}BuOH	92[e,f]
17	$FeCl_2$ (0.1 mol%)	1.2 eq	1.5 eq	^{t}BuOH	59[e,g]
18	$FeCl_2$ (1 mol%)[c]	1.2 eq	1.5 eq	^{t}BuOH	90[e,f]

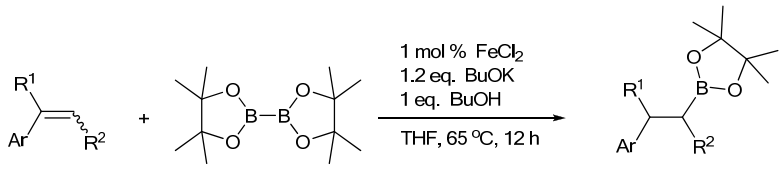
[a] Conditions: experiments were performed with **1a** (0.4 mmol), **2**, $FeCl_2$, ^{t}BuOK, additive (0.4 mmol, 1 eq.) in THF (5 mL) at 65 °C for 12 h. [b] Yield are determined by ^{1}H NMR with 2,2,2-trichloroethyl 2,2,2-trichloroacetate as an internal standard. [c] high-purity (99.99%) $FeCl_2$ was used. [d] Reaction was performed at 25 °C for 24 h. [e] Isolated yield. [f] **1a** (2 mmol), THF (20 mL). [g] **1a** (20 mmol), THF (100 mL).

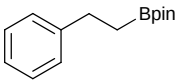
Table 2 Screening of solvents for hydroboration of styrene[a]

Entry	Solvent	Yield(%)[b]
1	THF	100
2	Dioxane	24
3	^{t}BuOMe	43
4	^{t}BuOH	95
5	MeOH	43
6	CCl_4	0
7	Toluene	50
8	MeCN	77
9	DMSO	70
10	DMF	95

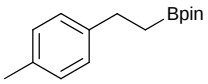
[a] Conditions: experiments were performed with **1a** (0.4 mmol), **2** (0.6 mmol), $FeCl_2$ (0.04 mmol), ^{t}BuOK (0.48 mmol), ^{t}BuOH (0.4 mmol) in solvent (5 mL) at 65 °C for 12 h. [b] Yield are determined by ^{1}H NMR with 2,2,2-trichloroethyl 2,2,2-trichloroacetate as an internal standard.

Table 3 Iron-catalyzed hydroboration of aryl alkenes with B_2pin_2[a, b]

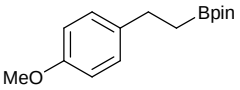




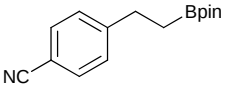
3a, 92%



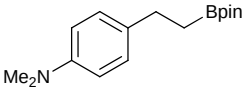
3b, 86%



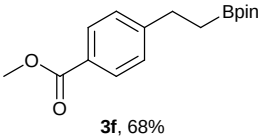
3c, 89%



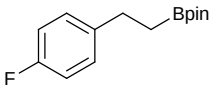
3d, 97%



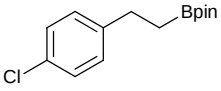
3e, 84%



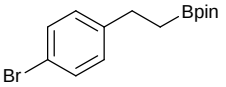
3f, 68%



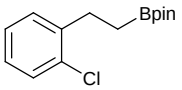
3g, 99%



3h, 98%



3i, 80%[c]



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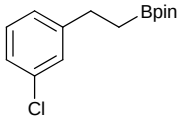

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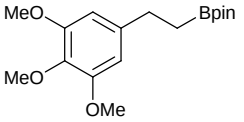
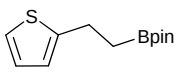
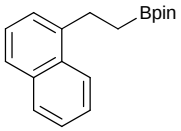


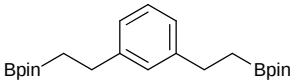
3l, 97%



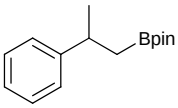
3m, 66%



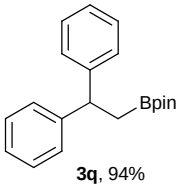
3n, 89%



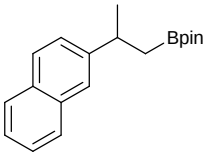
3o, 96%[d]



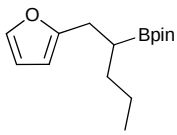
3p, 99%



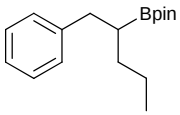
3q, 94%



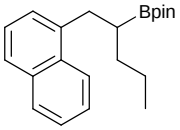
3r, 94%



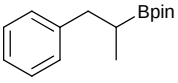
3s, 64%



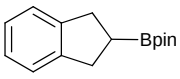
3t, 91%



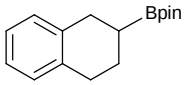
3u, 79%



3v, 94%



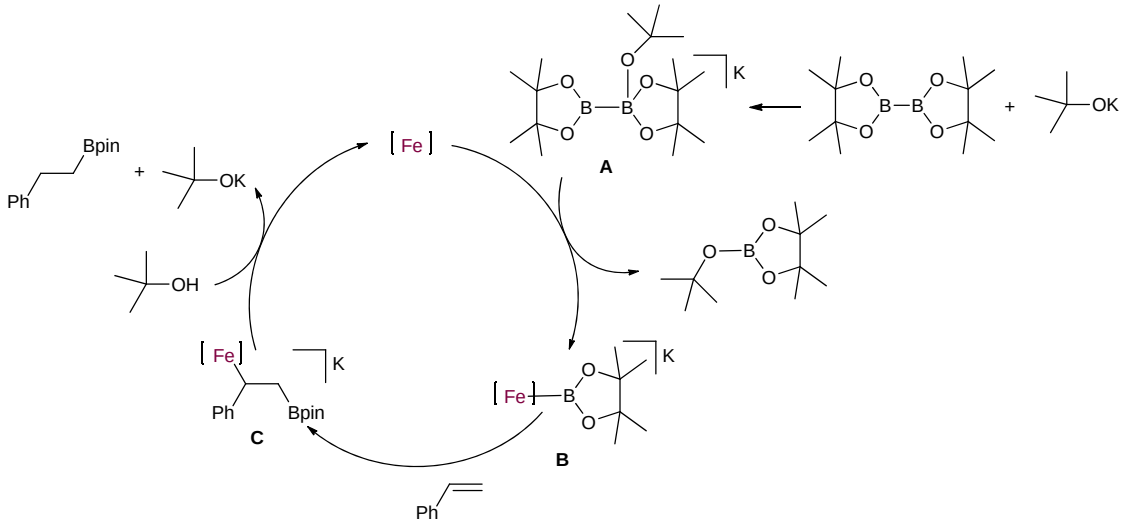
3w, 93%



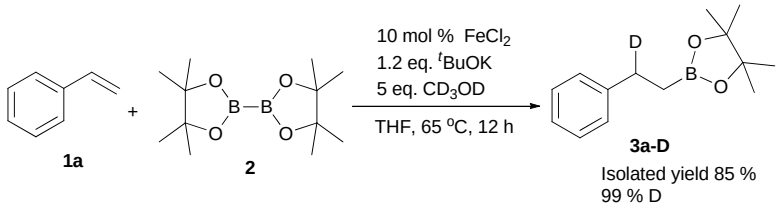
3x, 94%

[a] Conditions: experiments were performed with **1** (2 mmol), **2** (3 mmol), $FeCl_2$ (0.02 mmol), ^{t}BuOK (2.4 mmol), ^{t}BuOH (2 mmol) in THF (20 mL) at 65 °C for 12 h. [b] Isolated yields. [c] Reaction was performed for 3 h. [d] Reaction was performed with **1o** (2 mmol), **2** (6 mmol), $FeCl_2$ (0.04 mmol), ^{t}BuOK (4.8 mmol), ^{t}BuOH (4 mmol) in THF (30 mL) at 65 °C for 12 h.

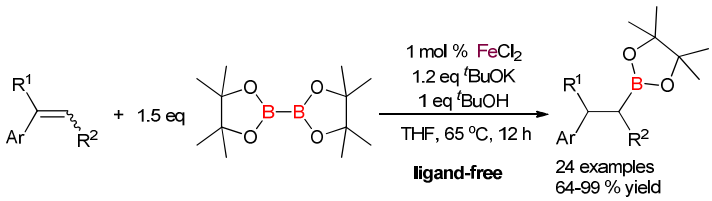
Scheme 1 Proposed mechanism for the iron-catalyzed hydroboration of aryl alkenes with B_2pin_2



Scheme 2 The deuterium labelling experiment



Graphical and textual abstract



Alkylboronates were synthesized by a ligand-free ferrous chloride catalyzed *anti*-Markovnikov hydroboration of un-activated aryl alkenes with bis(pinacolato)diboron.