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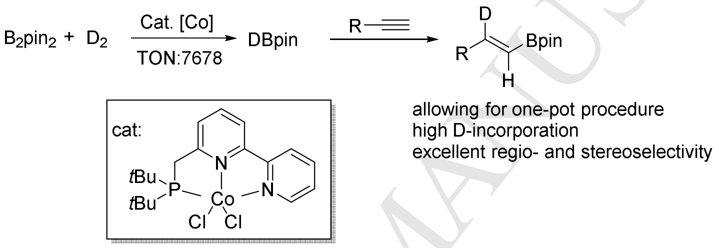
Lin Qiao [a,b], Lei Zhang[b], Guixia Liu [b,]*, Zheng Huang [b,]*
[a] *Department of Chemistry, Shanghai University, 99 Shang-Da Road, Shanghai 200444,China*
[b] *State Key laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Rd, Shanghai 200032, China*



allowing for one-pot procedure
high D-incorporation
excellent regio- and stereoselectivity

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[a] *Department of Chemistry, Shanghai University, 99 Shang-Da Road, Shanghai 200444,China*
[b]*State Key laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Rd, Shanghai 200032, China*

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ABSTRACT

Highly efficient hydrogenolysis and deuterogenolysis of diboron compounds have been realized by the use of a cobalt catalyst, affording TON up to 48201. Furthermore, a one-pot two-step procedure comprising sequential deuterogenolysis of diboron and deuteroboration of alkynes under the same cobalt catalyst has been developed for the efficient, atom-economical synthesis of deuterated vinylboronates with high deuterium incorporation and excellent regio- and stereoselectivity.

1. Introduction

Incorporation of deuterium into organic molecules can alter chemical and physical properties of the undeuterated counterparts because deuterium-carbon bonds are stronger than hydrogen-carbon bonds [1]. By taking advantage of this property, isotopically labeled compounds have been widely used in mechanistic studies by kinetic isotope effect measurements [2], and in pharmaceutical investigations [3]. As a result, there is great interest in facile synthesis of deuterated reagents and their application in site-specific deuterium incorporation into small molecules [4].

Pinacolborane (HBpin) is a versatile reagent in synthetic chemistry. In particular, hydroboration of functional groups such as alkenes and alkynes has provides a straightforward access to structurally diverse and synthetically useful organoboronates [5]. Given the high value of hydroboration reactions, mechanistic studies are important and deuterated pinacolborane (DBpin) is often essential for this purpose to track reaction pathway [6,7,8d,e]. On the other hand, DBpin could serve as a promising reagent to incorporate deuterium into small molecules through deuteroboration. Moreover, the resultant deuterated organoboronates could be potentially transformed to a range of isotope labelling compounds based on the versatile synthetic utility of organoborons. Despite the ubiquitous utility of HBpin, only a few methods have been reported to construction DBpin efficiently. The reaction of $BD_3{\cdot}THF$ with pinacol could afford DBpin (Scheme 1a) [7]. However, this methodology suffered from drawbacks including high cost of starting material and waste of two thirds of the deuterium content. Deuteration of pinacolborane under atmosphere of D_2 through H/D exchange could be achieved by the use of Ru, Ir, Rh and Co catalyst (Scheme 1b) [8]. Among them, a Co catalyst developed by the Chirik group represents the rare example of base-metal catalyzed process for this labelling reaction.[8d] However, the deuteration rate was only 83%. Considering the air- and moisture-sensitivity of HBpin, air stable and readily available B_2pin_2 [bis(pinacolato)diborane] [9] could be an ideal synthon for the synthesis of DBpin. Hartwig *et al.* have shown that the deuterogenolysis of B_2pin_2 could be accomplished with an Ir catalyst to afford DBpin in a good yield (Scheme 1c) [10].It is still desirable to develop a highly efficient catalyst system for this useful transformation, especially the catalyst based on inexpensive, sustainable and environmentally benign base-metal, such as cobalt.

Our group has been interested in the discovery of catalytic transformations with well-defined base metal complexes as the

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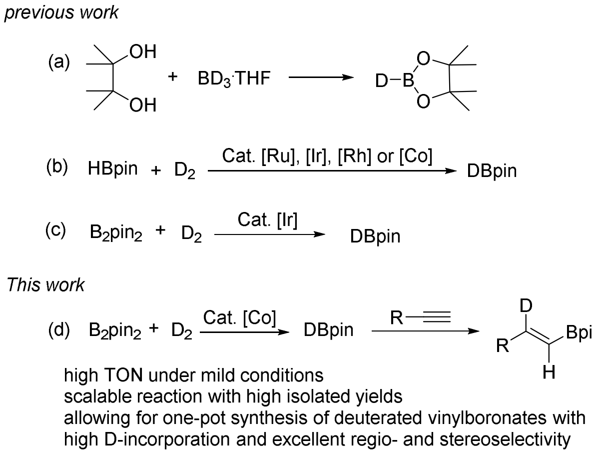
* Corresponding author. e-mail: guixia@sioc.ac.cn (G. Liu)

* Corresponding author. e-mail: huangzh@sioc.ac.cn (Z. Huang)

catalysts [11]. Previous studies from our laboratory have demonstrated that the bipyridyl-phosphine (PNN)Co complexes are highly active precatalysts for dehydrogenative borylation of 1-alkenes [11e]. The generation of HBpin by the interaction of Co-H with B_2pin_2 was involved in this process, suggesting that (PNN)Co may act as the effective catalyst for the synthesis of HBpin and DBpin from B_2pin_2 under the atmosphere of H_2 and D_2, respectively.

Here, we demonstrate that $(^{tBu}PNN)CoCl_2$ could serve as a powerful precatalyst in hydrolysis of diboron compounds with TON up to 48201, which could be tandemed with catalytic alkene hydroboration to afford alkylboronates in one pot. With D_2 as the reductant, deuterogenolysis of B_2pin_2 was accomplished with high efficiency. Remarkably, one pot synthesis of vinylboronate with high deuterium incorporation was realized by the sequence of deuterogenolysis of B_2pin_2 and alkyne deuteroboration.



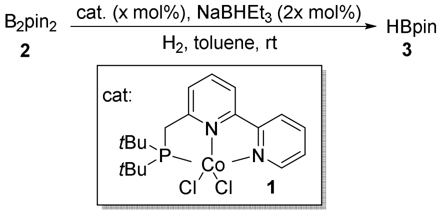
Scheme 1 Overview of synthetic methods for preparing DBpin

2. Results and Discussion

2.1. Hydrogenolysis of diboron compounds and one-pot synthesis of alkylboronates from B_2pin_2 and alkenes

Pioneering work by Marder group showed that heterogeneous catalytic B-B hydrogenolysis of diboron compounds reached TON up to 504 [12]. To develop highly active catalytic system for this transformation, we commenced our study by application of $(^{tBu}PNN)CoCl_2$ in the hydrogenolysis of B_2pin_2. Under 5 bar of H_2 at room temperature, the $(^{tBu}PNN)CoCl_2/NaBHEt_3$ system was so active that only 0.05 mol% of catalyst afforded HBpin in excellent yield with TON of 1942 in 3 h (Table 1, entry 1). Reducing the catalyst loading to 0.01 mol% improved the TON to 3981, but the yield was decreased to 40% (entry 2). Further optimization indicated the yield could be enhanced by conducting the reaction under higher pressure of H_2 (15 bar) with prolonged reaction time (entries 3-5). Other solvents such as pentane and Et_2O, gave comparable results. To facilitate the product separation, Et_2O was used as the optimal solvent due to its low boiling point. Under optimized conditions with 0.01 mol% of catalyst under 15 bar of H_2 in Et_2O, B_2pin_2 was readily converted to HBpin in a quantitative yield with a TON of 9994 (entry 6). Further reducing the catalytic loading to 0.001 mol% enhanced the TON significantly to 48201, albeit with reduced yield (entry 7).

Table 1 Optimization for Hydrogenolysis of B_2pin_2 Catalyzed by $(^{tBu}PNN)CoCl_2/NaBHEt_3$



entry	cat (x)	H_2 (bar)	*t* (h)	Yield (%)^b	TON (GC)
1^c	0.05	5	3	97	1942
2	0.01	5	3	40	3981
3	0.01	15	3	77	7698
4	0.01	15	6	93	9312
5	0.01	15	9	>98	9945
6^d	0.01	15	9	>98	9994
7^d	0.001	15	12	48	48201

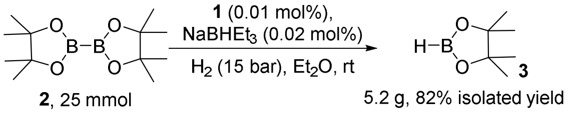
[a] Reaction conditions: on 25 mmol scale in toluene (10 mL) at rt.

[b] Yields were determined by GC with mesitylene as an internal standard.

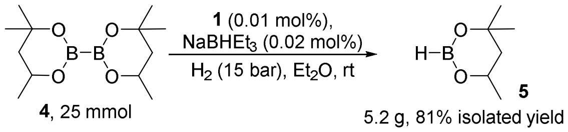
[c] 5 mmol of B_2pin_2 and 3 mL of toluene were used.

[d] Et_2O (10 mL) was used as the solvent.

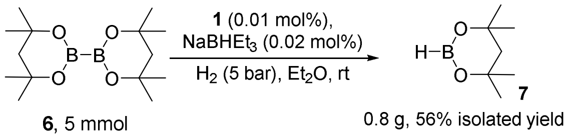
Under optimized conditions, HBpin could be isolated by distillation in gram scale (5.2 g, 82% yield) with a catalyst loading of 0.01 mol%, affording TON of 8201 (eq 1). The high efficiency and scalable feature of our protocol enable the facile synthesis of HBpin from stable and readily available B_2pin_2. The hydrogenolysis of other diboron compounds were also explored. When diboron compound **4** was subjected to the reaction conditions, the corresponding hydroborane **5** was furnished in 81% isolated yield (eq 2). Due to poor solubility of diboron compound **6**, the hydrogenolysis of **6** was less effective, delivering 56% yield of hydroborane **7** under 5 bar H_2 pressure (eq 3). Unfortunately, this (PNN)Co catalytic system was not effective for the synthesis of catecholborane (HBcat).



(1)



(2)

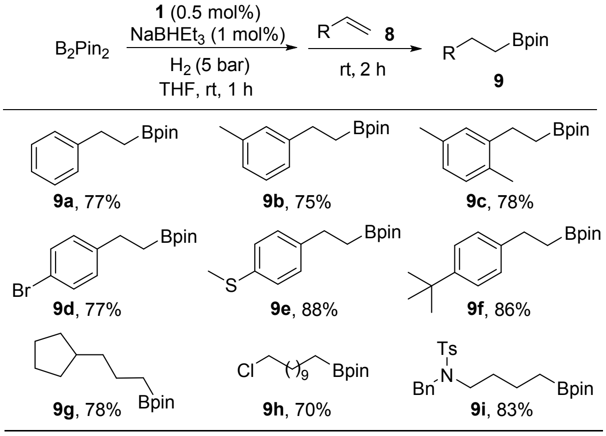


(3)

Since (PNN)Co complexes are very active for alkene hydroboration [11c], we reasoned that the HBpin generated in hydrogenolysis of B_2pin_2 could be added to the alkenes directly under the reaction conditions. Thus, a sequential B_2pin_2 hydrogenolysis/alkene hydroboration was developed and the scope of this one-pot two-step procedure was shown in Table 2. With catalyst loading of 0.5 mol% and 5 bar of H_2, a series of alkenes were transformed to alkyl boronates in high yields (70-88%) starting from B_2pin_2. Aryl alkenes (**9a-9f**) containing *orth*-, *meta*- and *para*-substituents at the aryl rings were smoothly hydroborated. This procedure was also applicable for alkyl alkenes (**9g-9i**). Several functional groups such as aryl bromide

(**9d**), thioether (**9e**), alkyl chloride (**9h**) and amine (**9i**) were well tolerated. While the formal hydroboration of unactivated alkenes with B_2pin_2 in literature [13] usually require basic conditions and a Brønsted acid as proton source, our procedure using H_2 as the hydrogen source is complementary to the known methods.

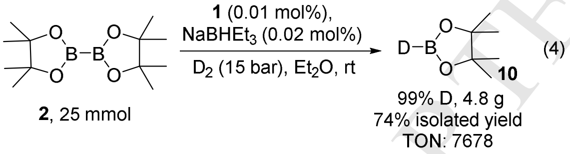
Table 2 One-pot preparation of alkyl boronates



Reaction conditions: B_2Pin_2 (0.375 mmol, 0.75 equiv), alkenes (0.5 mmol, 1 equiv), **1** (0.5 mol%), $NaBHEt_3$ (1 mol%) in THF (1 mL) at rt. Isolated yields.

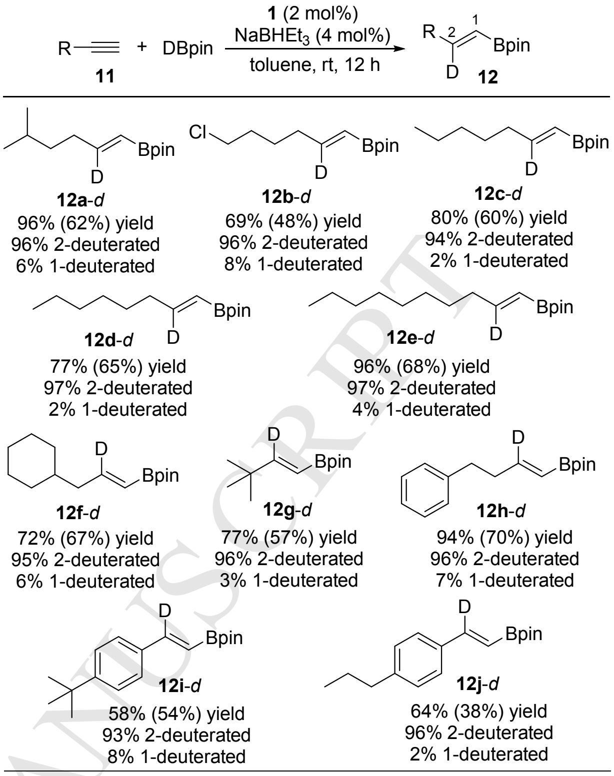
2.2. *Deuterogenolysis of B_2pin_2 and one-pot synthesis of deuterated vinylboronates*

The high efficiency of (PNN)Co in hydrogenolysis of diboron compounds intrigued us to investigate the deuterogenolysis of B_2pin_2 using D_2 as the hydrogen isotope source. Delightfully, the $(^{tBu}PNN)CoCl_2/NaBHEt_3$ catalytic system worked well for the deuterolysis of B_2pin_2 and the reaction could be easily scaled up. With a catalyst loading of 0.01 mol% and 15 bar of D_2, 4.8 g of DBpin (74% isolated yield) was obtained from 25 mmol of B_2pin_2. The deuterium incorporation was determined to be 99% by ^{1}H NMR spectroscopy.



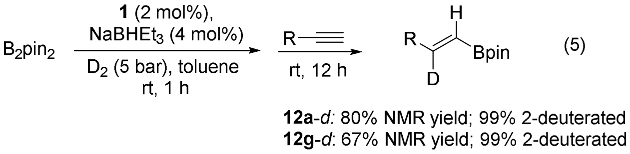
Given the high activity of (PNN)Co complex in deuterogenolysis of B_2pin_2, we next set out to explore the potential of this catalyst in alkyne deuteration to access deuterated vinylboronates, with the aim of combining the two reactions in a one-pot procedure catalyzed by one single catalyst. Although (PNN)Co complexes are very active for alkene hydroboration, their activity in alkyne hydroboration has not been studied. We found alkyne deuteroboration proceeded smoothly with $(^{tBu}PNN)CoCl_2$ as the precatalyst at room temperature (Table 3). A diverse scope of terminal alkynes were applicable in this transformation, in which DBpin was added across the triple bond in a regio- and stereo-selective way to afford vinylboronates with high deuteration (93%) at 2-position and less than 8% deuterium incorporation at 1-position. The deuteroboration of aliphatic alkynes gave good yields (72-96%), which were not obviously affected by the chain length. The alkyne containing a C(sp^3)-Cl bond was compatible with this deuteroboration protocol, as evidenced by the synthesis of **12b** in moderate yield. Sterically hindered alkyne **12g** with a *tert*-butyl substituent was suitable substrate giving 77% yield. Aryl alkynes (**12i** and **12j**) were also competent, leading to moderate yields of the desired products and small amount of aryl alkenes as the side products.

Table 3 Deuteroboration of alkynes



Reaction conditions: **11** (0.55 mmol, 1.1 equiv), DBpin (0.5 mmol, 1 equiv), **1** (2 mol%), $NaBHEt_3$ (4 mol%) in toluene (1 mL) at rt. Yields were determined by ^{1}H NMR spectroscopy with mesitylene as an internal standard. Isolated yields were shown in the parentheses. The rate of deuteration by was determined by ^{1}H NMR spectroscopy.

After demonstrating the catalytic performance of (PNN)Co in the deuteroboraiton of alkynes, a one-pot reaction was conducted for the efficient, atom-economical synthesis of deuterated vinylboronate directly from B_2pin_2 without the isolation of unstable DBpin. In the presence of 2 mol% of catalyst, B_2pin_2 was treated with 5 bar of D_2 at room temperature for 1 h. Subsequently, D_2 was released and alkyne was added. This procedure produced good yields of vinylboronates **12a** and **12g** with >98% D-incorporation at 2-position.



3. Conclusion

In conclusion, we have developed cobalt catalyzed hydrogenolysis and deuterogenolysis of diboron compounds for the synthesis of hydroboranes and deuterated pinacolbrane, respectively. The potential synthetic utility of our protocol was highlighted by the high efficiency and its scalable feature. Combined with Co-catalyzed alkene/alkyne hydroboration, one-pot two-step procedures were disclosed for synthesis of alkylboronates and deuterated vinylboronates from air stable and readily available B_2pin_2. The deuterated vinylboronates were obtained with high deuterium incorporation and excellent regio- and stereoselectiviy, which are attractive candidates for further transformation to access diverse isotope labelling compounds.

4. Experimental section

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. All manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. Ethyl ether (Et_2O), pentane, tetrahydrofuran (THF), toluene were distilled from sodium benzophenone ketyl prior to use. Alkenes and alkynes are were purchased from TCI, J&K, Aldrich and Alfa and were used as received. (^{tBu}PNN)$CoCl_2$ was synthesized according to our previously reported procedure.[11c]

NMR spectra were recorded on Agilent 400 MHz or Bruker 400 MHz or Agilent 600 MHz. ^{1}H NMR chemical shifts were referenced to residual protio solvent peaks or tetramethylsilane signal (0 ppm), and ^{13}C NMR chemical shifts were referenced to the solvent resonance. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The carbon bearing the boron is missing for all hydroboration products in the ^{13}C NMR spectra. GC analysis was acquired on Agilent 7820A gas chromatograph equipped with a flame-ionization detector. Elemental analyses and high resolution mass spectrometer (HR-MS) were carried out by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS).

4.1. General procedure for hydrogenolysis of diboron compounds

In a N_2 filled glovebox, $NaBHEt_3$ (5 μL, 1 M in THF, 5 μmol, 0.02 mol%) was added to a mixture of diboron compound (25 mmol) and complex **1** (1.1 mg, 2.5 μmol, 0.01 mol%) in Et_2O (10 mL) at 25 ºC in a 100 mL tube equipped with a magnetic stir bar. After the mixture was stirred for minutes, the color was changed from colorless to purple. The reaction tube was then placed in an autoclave. The autoclave was closed, purged three times with hydrogen (less than the pressure needed). The reaction mixture was stirred at 25 ºC under H_2 atmosphere (15 bar) for 9 h. After part of hydrogen was released, the autoclave was opened in a N_2 filled glovebox. The reaction mixture was transferred to a 100 mL flask equipped with a magnetic stir bar. The Et_2O solvent was removed via distillation under 1 atm of argon and the desired hydroborane was obtained by vacuum transfer as a clear, colorless liquid into an oven-dried, 50 mL flask.

4.2. General procedure for one-pot synthesis of alkyl boronates

In a N_2 filled glovebox, $NaBHEt_3$ (5 μL, 1 M in THF, 5 μmol, 1 mol%) was added to a mixture of B_2pin_2 (0.375 mmol, 0.75 equiv) and complex **1** (1.1 mg, 2.5 μmol, 0.5 mol%) in THF (1 mL) at 25 ºC in a 10 mL tube equipped with a magnetic stir bar. After the mixture was stirred for minutes, the color was changed from colorless to black. The reaction tube was then placed in an autoclave. The autoclave was closed, purged three times with hydrogen (less than the pressure needed). The reaction mixture was stirred at 25 ºC under H_2 atmosphere (5 bar) for 1 h. After release part of hydrogen, the autoclave was opened in a nitrogen glovebox. Then **8** (0.5 mmol, 1 equiv) was added to the mixture. The reaction mixture was stirred for another 2 h and then was quenched by exposing the reaction mixture to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel eluting with ethyl acetate/n-hexane (1:50) to give the product **9**.

4.3. Procedure for deuterogenolysis of B_2pin_2

In a N_2 filled glovebox, $NaBHEt_3$ (5 μL, 1 M in THF, 5 μmol, 0.02 mol%) was added to a mixture of B_2pin_2 (25 mmol) and complex **1** (1.1 mg, 2.5 μmol, 0.01 mol%) in Et_2O (12 mL) at 25 ºC in a 100 mL tube equipped with a magnetic stir bar. After the mixture was stirred for minutes, the color was changed from colorless to purple. The reaction tube was then placed in an autoclave. The autoclave was closed, purged three times with D_2 (less than the pressure needed). The reaction mixture was stirred at 25 ºC under D_2 atmosphere (15 bar) for 9 h. After release part of gas, an autoclave was opened in a N_2 filled glovebox. The reaction mixture was transferred to a 100 mL flask equipped with a magnetic stir bar. The Et_2O solvent was removed via distillation under 1 atm of argon. Pure DBpin was obtained by vacuum transfer (4.77 g, 74%) as a clear, colorless liquid into an oven-dried, 50 mL flask. The rate of deuteration was obtained by ^{1}H NMR spectroscopy. D>99%. ^{1}H NMR (400 MHz, C_6D_6) δ 1.01 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 83.14, 24.95. ^{11}B NMR (128 MHz, C_6D_6) δ 28.36 (s). ^{2}H NMR (92 MHz, CH_2Cl_2) δ 4.03 (d, *J* = 30.8 Hz). HRMS-EI (m/z): Calcd for $[C_6H_{12}DBO_2]^+$: 128.1108; found: 128.1112.

4.4. General procedure for deuteroboration of alkynes with DBpin

In a N_2 filled glovebox, DBpin (0.5 mmol, 1 equiv) and **11** (0.55 mmol, 1.1 equiv) were added successively to a solution of complex **1** (4.4 mg, 10 μmol, 2 mol%) and $NaBHEt_3$ (20 μL, 1 M in THF, 20 μmol, 4 mol%) in toluene (1 mL) at 25 ºC in a 10 mL vial equipped with a magnetic stir bar. The reaction mixture was stirred at 25 ºC for 12 h and then was quenched by exposing the reaction mixture to air. The resulting mixture was filtered with short silica gel column and concentrated in vacuum. Yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard. Then the residue was purified by chromatography on silica gel eluting with ethyl acetate/n-hexane (1:50) to give the product **12**-*d*. The isolated yields were also obtained. The rate of deuterium incorporation was determined by comparing ^{1}H NMR spectroscopy with that of the corresponding hydroboration products [14].

4.5. General procedure for one-pot synthesis of deuterated vinylboronates

In a N_2 filled glovebox, $NaBHEt_3$ (20 μL, 1 M in THF, 20 μmol, 4 mol%) was added to a solution of B_2pin_2 (0.25 mmol, 0.5 equiv) and complex **1** (4.4 mg, 10 μmol, 2 mol%) in toluene (1 mL) at 25 ºC in a 10 mL tube equipped with a magnetic stir bar. After the mixture was stirred for minutes, the color was changed to from colorless to black. The reaction tube was then placed in an autoclave. The autoclave was closed, purged three times with D_2 (less than the pressure needed). The reaction mixture was stirred at 25 ºC under D_2 atmosphere (5 bar) for 1 h. After release part of gas, the autoclave was opened in a nitrogen glovebox. Then **11** (0.55 mmol, 1.1 equiv) was added to the mixture. The reaction mixture was stirred for another 12 h and then was quenched by exposing the reaction mixture to air. The resulting solution was filtered with short silica gel column and concentrated in vacuum. Yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard. Then the residue was purified by chromatography on silica gel eluting with ethyl acetate/n-hexane (1:50) to give the product **12**-*d*. The isolated yields were also obtained. The rate of deuterium incorporation was determined by comparing ^{1}H NMR spectroscopy with that of the corresponding hydroboration products.

Acknowledgments

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9. In addition to higher stability, B_2pin_2 is cheaper than HBpin. According to TCI, the price of HBpin is 1320 CNY /25g, while the price of B_2pin_2 is 450 CNY/25 g.
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14. To further confirm deuterium incorporation rate, quantitative ^{13}C NMR analysis of **12f**-*d* was conducted, which showed 96% D incorporated at 2-position. Please see the Supporting Information for the details.

Supplementary Material

Supplementary data to this article can be found online at