

Nickel-Catalyzed Hydroboration of Styrenes

By

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A thesis submitted in partial fulfillment of
the requirement for the degree of

Bachelors of Science with Honors
(Chemistry)

At the

UNIVERSITY OF WISCONSIN-MADISON

2016

Abstract

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First-row transition metal catalysis offers a cheaper, more environmentally sustainable alternative to second and third-row transition metal catalysts. Nickel has shown great promise as a tool for the borylation of alkenes to yield boronic esters, but it is challenging to control the regiochemistry of reactions of simple olefins. Herein, we report the synthesis of benzyl boronic esters via nickel-catalyzed hydroboration. A series of novel N-heterocyclic carbene (NHC)-phosphine nickel complexes were synthesized to optimize this transformation. New heteroleptic NHC-phosphine complexes were found to display a broad substrate scope and maintain the integrity of yield and regioselectivity when challenged with substrates bearing increased steric hindrance. The heteroleptic complexes also tolerate both electron-withdrawing and electron-donating groups better than previously investigated bisphosphine and Ni(0) complexes.

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List of Abbreviations

Ac	acetyl
aq	aqueous
Ar	aryl
Bcat	catacholborane
Bpin	4,4,5,5-tetramethyl-1,3,2-dioxaborolane
C	Celsius
cod	cyclooctadiene
Cp	Cyclopentadienyl
Cy	Cyclohexyl
d	doublet
dd	doublet of doublets
dt	doublet of triplets
ee	enantiomeric excess
equiv	equivalent
Et	ethyl
Et ₃ P	triethylphosphine
EtOAc	ethyl acetate
g	gram
h	hour
Hz	hertz
IMes	1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2 <i>H</i> -imidazol-2-ylidene
IMesHCl	1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride

IPr	1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2 <i>H</i> -imidazol-2-ylidene
IPrHCl	1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride
<i>J</i>	spin-spin coupling constant in hertz
KOtBu	potassium tert-butoxide
M	molar
m	multiplet
Me	methyl
mg	milligram
min	minute
mL	milliliter
mM	millimolar
mmol	millimol
mol	moles
nBu ₃ P	tributylphosphine
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance spectroscopy
OAc	acetate
OMe	methoxy
PCy ₃	tricyclohexylphosphine
Ph	phenyl
PPh ₃	triphenylphosphine
ppm	parts per million
Pr	normal-propyl

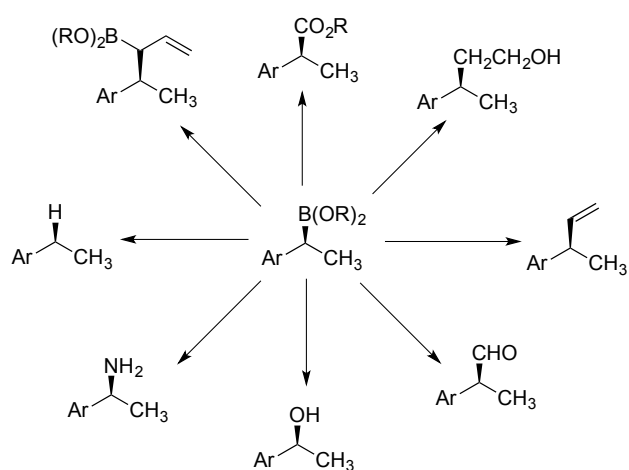
q	quartet
rt	room temperature
s	singlet
tBu	<i>tert</i> -butyl
tBu ₂ MeP	di- <i>tert</i> -butylmethylphosphine
tBu ₃ P	tri- <i>tert</i> -butylphosphine
td	triplet of doublets
THF	tetrahydrofuran
δ	chemical shift in ppm
μL	microliter

Chapter 1: Introduction to Transition Metal-Catalyzed Borylations

1.1 Synthetic Utility of Organoborons

A long standing challenge for organic chemists has been the direct functionalization of sp^3 hybridized C-H and C-C bonds. Developing methodology for the borylation of sp^3 hybridized C-C and C-H bonds has become an intensive field of research, as carbon-boron bonds have proven themselves as exceptional functional handles for a variety of organic transformations. Carbon-boron bonds, due to their slight elongation, ease processes of substitution, but still exhibit enough stability such that organoboron functionalities can be carried throughout multiple synthetic steps.¹ This stability also lends itself to stereoselective installation and maintaining the resulting chiral center without risk of epimerization.² The vacant p-orbital in sp^2 hybridized intermediates such as boronic acids and esters makes for an excellent Lewis acid. This makes sp^2 hybridized boron atoms capable of coordinating other Lewis bases and nucleophiles. Metal insertion into the carbon-boron bond can be facilitated by simply changing boron from its Lewis acidic sp^2 hybridization to the more Lewis basic sp^3 hybridization.³ Thanks to this wide array of electronic behavior accessible to boron, organoboron intermediates promise to display a variety of unusual and novel reactivity.

Scheme 1.1. Transformation of the carbon-boron bond



Perhaps the seminal demonstration of the utility of organoboron compounds is the cross coupling of aryl boronic acids and aryl halides to produce biaryls.³ However, the field of organoboron functionalization is not limited simply to Suzuki couplings. In recent years, sp^3 carbon-boron bonds have been directly converted to C-C,⁴ C-O,⁵ and C-N bonds.⁶

Moreover, these conversions can be used to install a range of functional groups such as alcohols,⁷ amines,⁶ carbonyls,⁸ and arenes⁹ (**Scheme 1.1**). Potential substrates are diverse, ranging from macromolecular saturated polymers to small aromatic molecules. However, accessing many aliphatic secondary and tertiary organoboron intermediates for functionalization is not trivial. Many of the desired borylation precursors are typically small molecules with limited reactivity. As such, the use of transition metal catalysis to synthesize organoboron species is required.

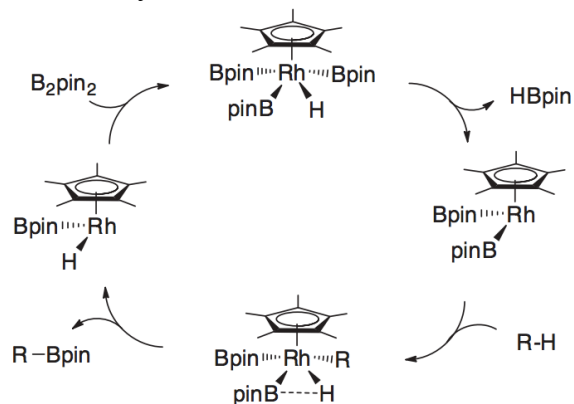
1.2 Strategies for Introducing sp^3 Carbon-Boron Bonds

1.2.1 C-H Borylation

Accessing sp^3 carbon-boron bonds has proven to be a challenge for chemists that wish to use simple aliphatic substrates devoid of π -systems. The first report of C-H borylation of a saturated sp^3 hybridized carbon was reported by Hartwig and coworkers.¹⁰ This initial report used a tungsten catalyst under photochemical conditions to borylate pentane at the terminal carbon. Cyclopentadienyl rhodium catalysts capable of catalyzing the C-H borylation under high heat without the assistance of photolytic cleavage shortly followed.¹¹ Several chemoselective variants have been made on the reaction.¹²

Most C-H borylations on straight chained alkanes result in borylation of the terminal carbon exclusively.¹³ Little to no branched borylation is observed presumably due to the high energy barrier of secondary C-H bond cleavage to yield the necessary rhodium alkylhydride intermediate (**Scheme 1.2**).¹⁴ Additionally, steric bulk around the secondary carbon hinders C-B formation. As such, regioselectivity has proven

Scheme 1.2 Mechanism of Rh-catalyzed alkane borylation



difficult to reverse using this mechanism of borylation. Stereoselective C-H borylation remains a point of investigation as well. Benzylic C-H borylations are also accessible using alkylphosphine rhodium catalysts. While this method provides direct access to benzyl boronic esters, the chemistry is less developed and yields suffer compared to aliphatic substrates.¹⁵

Since these initial reports, intensive exploration into developing catalysts and conditions for alkyl C-H borylation has persisted. However, while significant progress has been made, chemists are still mostly confined to the use of rhodium, iridium, and ruthenium catalysts under harsh reaction conditions and limited substrate scope.

1.2.2 Halide Borylation

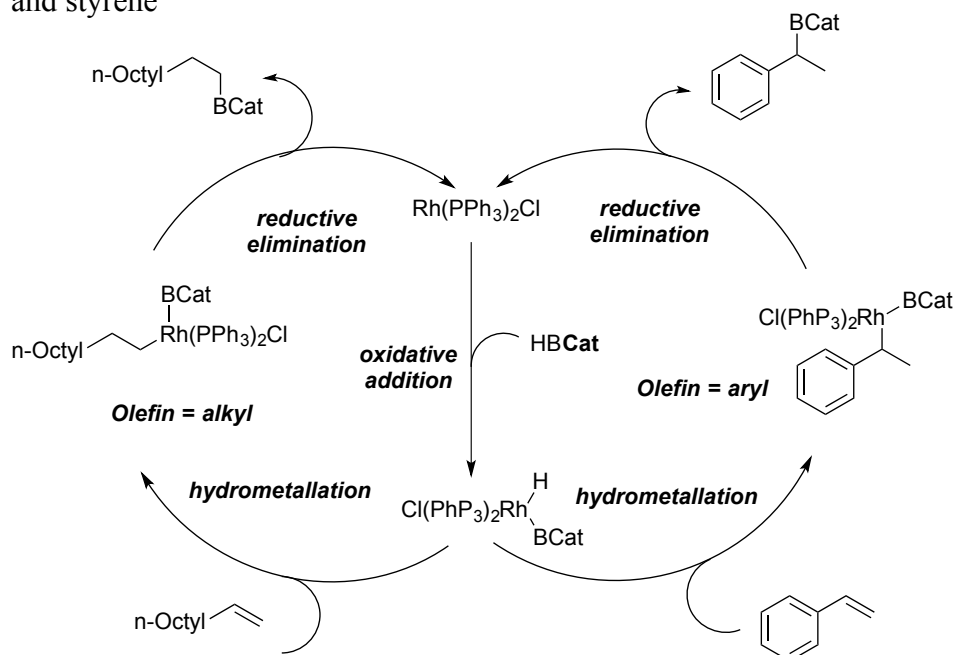
Currently, methods for borylating saturated sp^3 C-H bonds requires expensive precious metal catalysts and high temperatures or photolytic cleavage. Conversely, borylation of alkyl halides can be carried out with a broad range of inexpensive first-row transition metal catalysts including manganese,¹⁶ copper,¹⁷ zinc,¹⁸ iron,¹⁹ and nickel.²⁰ These transformations are also typically carried out under mild conditions with minimal catalyst loading. Though it offers itself as a more economically feasible alternative for accessing sp^3 carbon-boron bonds, the primary advantage of alkyl halide borylation is the wide range of accessible substrates. Alkyl halide borylation can be performed on primary, secondary, and tertiary carbon centers.¹⁶⁻²⁰ Additionally, the transformation is tolerant to a variety of functional groups such as ethers, amides, and esters.¹⁶⁻²⁰ Overall, halide borylation is a much more synthetically useful pathway for accessing sp^3 carbon-boron bonds than past methods.

1.2.3 Transition Metal-Catalyzed Hydroboration

In sophomore organic, it is taught that uncatalyzed hydroborations can install a C-B bond at the least sterically hindered carbon of an olefin.⁵ While this transformation is useful in theory,

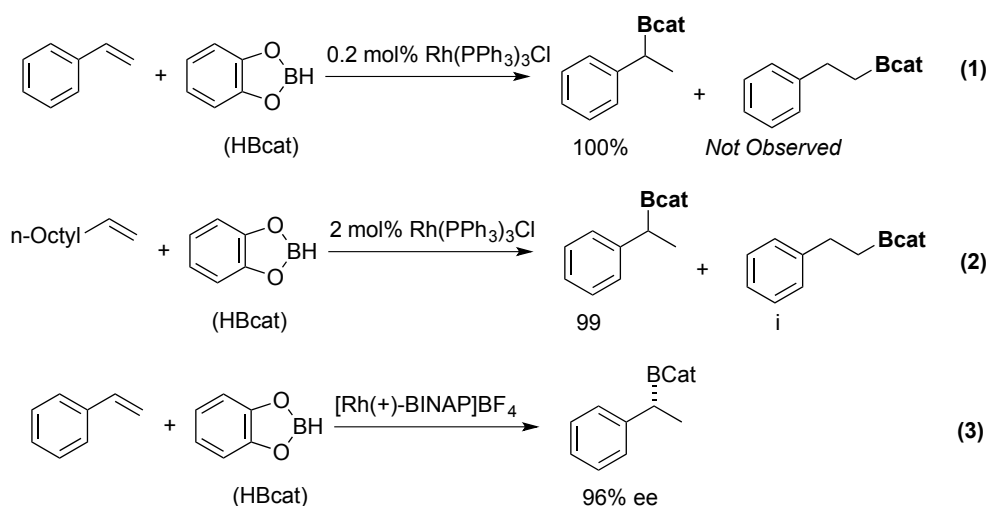
its synthetic applications are limited. Traditional hydroboration boron reagents like BH_3 and 9-BBN are Lewis acidic enough to coordinate to any accessible heteroatoms present on a substrate rather than target the alkene.²¹ However, boronic esters exhibit diminished Lewis acidity due to electron donation by the adjacent oxygen atoms. This makes boronic esters excellent borylation reagents for performing borylations on substrates more complex than simple hydrocarbons. Mannig reported one of the first transition metal-catalyzed hydroborations of a heteroatom bearing olefin using rhodium and catecholborane.²¹ The synthetic utility of transition metal-catalyzed hydroborations has only grown since. An example of one of the most well-developed and selective transition metal-catalyzed hydroborations is rhodium-catalyzed hydroboration.

Scheme 1.3. Mechanism of Rh-catalyzed hydroboration of both 1-decene and styrene



For decades, rhodium has been the seminal metal to use for transition metal-catalyzed hydroborations, and for good reason. Catalyst loadings have been reported in the sub 1.0 mol% range, reaction conditions are usually mild, and quantitative yields are not unusual. A collection of rhodium catalysts have been synthesized to meet the needs of synthetic chemists who wish to have complete control over the site and stereochemistry of the borylation. Using only 0.2 mol%

catalyst loading, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ can exclusively install a benzyl boronic ester on styrene in quantitative yield (Equation 1).²² Interestingly, performing the same transformation using 1-decene as the olefin source provides the terminal boronic ester with 99:1 regioselectivity (Equation 2).²² This suggests that proximity to the aromatic π -system may offer extra stability to any boron-rhodium adducts present in the mechanism (Scheme 1.3). The hydroboration can be made enantioselective up to 96% ee while maintaining yield by taking advantage of the axial chirality of BINAP and using $[\text{Rh}(+)\text{-BINAP}]\text{BF}_4$ as the catalyst (Equation 3).²³



Despite the success chemists have had with rhodium catalyzed hydroborations, the desire for alternative catalysts remains. Iridium has gained popularity,²⁴ but other late transition metals such as Pd ²⁵ and Ru ²⁶ have only yielded nominal results. This lack of success has motivated chemists to turn towards first-row transition metals as potential hydroboration catalysts.

1.3 Nickel as a Synthetically Useful Tool for Coupling Reactions

While catalysis with palladium and platinum has provided a bountiful field of research for organometallic chemists, the search for cheaper, more reactive alternatives to these precious metals remains. Catalysis using nickel has proven to be an attractive alternative to precious metal catalysis and as such, has become an area of intensive research over recent decades. Efforts have not only

encompassed reproducing transformations traditionally performed by precious metals, but on discovering new reactions and mechanistic pathways inaccessible to palladium and platinum.

Conveniently, many of the same mechanistic steps present in precious metal catalysis are preserved in nickel-catalyzed reactions. Those general steps being oxidative addition, transmetallation, β -hydride elimination, and reductive elimination. This transfer of mechanistic behavior has allowed nickel to catalyze many classic organometallic transformations such as Suzuki and Heck-type couplings.^{3,27} Compared to palladium or platinum however, nickel is a much smaller and relatively more electropositive metal. This increased comfort bearing a positive charge allows nickel to undergo oxidative addition much more readily than its group 10 counterparts.²⁸ Consequently, facile oxidative addition allows nickel access to cross-coupling electrophiles that are considerably less or completely unreactive under palladium-catalyzed conditions such as phenol derivatives,²⁹ aromatic nitriles,³⁰ and aryl fluorides.³¹ Nickel also offers opportunity for new mechanistic pathways. The few catalytically active oxidation states of palladium have mostly limited reaction mechanisms to Pd(0), Pd(II), and Pd(IV) catalytic cycles consisting of two-electron transfers. Conversely, nickel is not limited by a small number of catalytically active oxidation states nor simple two-electron transfers. Indeed, Ni(0), Ni(I), Ni(II), Ni(III), and even Ni(IV) have precedence as catalytically active species.³² While one-electron radical pathways between these species are certainly possible, two-electron conversions between Ni(0)/Ni(II) are the most easily accessible and most widely used in the development of catalytic cycles. Researchers have been taking advantage of these properties to develop novel transformations.

1.4 Conclusions and Outlook

Recent advances in catalysis allows for the borylation of a wide variety of aliphatic, olefinic, alkynyl, and heteroatom bearing substrates. In spite of this progress however, most of these methodologies require the use of high cost precious metals and harsh reaction conditions for only moderate to good results. It is prudent for today's organometallic chemists to search for cheaper, higher yielding alternatives that maintain reactivity and selectivity in the face of diverse substrate classes. One alternative that has shown promise is using first-row transition metals to access synthetically useful organoboron intermediates.

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Chapter 2: Nickel-Catalyzed Hydroboration of Styrenes

2.1 Introduction to Nickel-catalyzed Borylations

First-row transition metal catalysis offers a cheaper, more environmentally sustainable alternative to using second and third-row transition metals for organometallic transformations. While these advantages have sparked significant effort to functionalize first-row transition metals for use performing transformations classically carried out by their lower-transition metal counterparts, success has been limited. Boundaries to success have been partly due to the differing electronic structures of first-row transition metals that result in reduced electronegativity and harder Lewis acidic behavior. Additionally, first-row transition metals can more easily access difficult to control radical pathways.¹ These behaviors are not as pronounced in second and third-row transition metals.¹ Despite the challenges, the potential advantages first-row transition metal catalysis offers makes it prudent for us as organometallic chemists to tame these species.

One transformation that has received much attention in recent years is metal-catalyzed borylations. This is because boronic esters can serve as functional handles to access a wide array of carbon-carbon and carbon-heteroatom bond-forming transformations. Classically, lower-row transition metals such as rhodium, platinum, and iridium have been used to accomplish such transformations.² In recent years however, nickel has increasingly shown great promise as a robust borylation catalyst, with successful reactions including the coupling between aryl and alkyl halides to produce boronic esters,³ diboration,⁴ and 1,4-hydroboration.⁵ However, despite recent progress methodology for carrying out these reactions on simple olefins in a regioselective manner remains elusive. Currently, there are only two reports where nickel is used to catalyze the hydroboration of simple olefins. Kabalka used nickel powder to catalyze the hydroboration of a few olefins, notably styrene, but with limited to no selectivity.⁶ Srebnik demonstrated two examples where

$\text{CpNiPPh}_3(\text{Cl})$ was used to catalyze the hydroboration of olefins.⁷ When performed on styrene with pinacolborane, Srebnik's catalyst provided excellent yield and selectivity to form the linear boronic ester. A synthetic demand then arises, as currently there are no such methods published that describe the use of nickel to selectively generate the branched boronic ester via hydroboration of simple olefins. Herein, we report the synthesis of benzyl boronic esters via nickel-catalyzed hydroboration of styrenes.

2.2 Optimization of Nickel-catalyzed Hydroboration

The investigation into nickel-catalyzed hydroboration began with the identification of promising nickel catalysts. We first turned to the nickel complexes $(\text{Cy}_3\text{P})_2\text{NiCl}_2$ and $\text{Ni}(\text{cod})_2$ (Table 2.1), both of which have well documented precedence as synthetically useful catalysts for a wide variety of transformations. In the presence of pinacolborane and potassium tert-butoxide, both of these complexes produced the desired branched boronic ester in good to excellent yields (entries 1 and 2). However, these results did not come without limitations. $\text{Ni}(\text{cod})_2$ demonstrated excellent yields and selectivity for branched borylation on unsubstituted styrene, but yields faltered dramatically and became unreproducible as soon as substitutions were made that altered the substrate electronics (Table 2.2). Encouragingly, $(\text{Cy}_3\text{P})_2\text{NiCl}_2$ seemed to tolerate a wider variety of functional group substitutions while maintaining regioselectivity and producing more consistent yields. In an effort to improve this reactivity, a series of alkyl bis-phosphine complexes were synthesized. Increasing the sterics of the phosphine ligands reduced the yield (Table 2.1, entries 3 and 4) while a reduction in ligand bulk shut down reactivity entirely (entries 5 and 6). The influence of phosphine bulk or minute differences in lability on this trend is a potential point of interest.

We then wanted to integrate NHC's into our complexes due to their past success in nickel reactions.⁸ This was accomplished by the synthesis of a novel heteroleptic, NHC/phosphine nickel

complex, $\text{IPr}(\text{Cy}_3\text{P})\text{NiCl}_2$ using methods similar to that of Matsubara.⁸ This heteroleptic complex not only exhibited increased reactivity across a variety of styrenes, but also produced the most consistent and reproducible results (Table 2.2, entry 7). Further optimization of the carbene showed that $\text{IMes}(\text{Cy}_3\text{P})\text{NiCl}_2$ was the best pre-catalyst synthesized (Table 2.1, entry 8). We then synthesized a bis-NHC nickel complex. As expected, the complex displayed no reactivity as neither of the NHC ligands are labile (Table 5.1, entry 9). It is believed that the heteroleptic NHC/phosphine complexes perform better than either the bis-phosphine or bis-NHC complexes due to the complementary behavior between both ligands. Carbenes provide enhanced stability through strong sigma donation to the metal center while the alkyl phosphine ligands offer increased reactivity via their hemilability. Exchanging the Cy_3P ligand for other alkyl phosphine ligands could be used to fine tune the reactivity of these heteroleptic complexes due to small changes in phosphine lability.

Table 2.1. Optimization of Ni-catalyzed hydroboration.

R	$\text{Ni}(\text{cod})_2$	$(\text{Cy}_3\text{P})_2\text{NiCl}_2$	$\text{IPr}(\text{Cy}_3\text{P})\text{NiCl}_2$
H	99%	73%	77%
<i>o</i> -Me	27%	43%	72%
<i>p</i> -OMe	0%	10%	50%
<i>o</i> -CF ₃	58%	53%	55%

NMR yields determined using 1,1,1,2-tetrachloroethane as an internal standard.

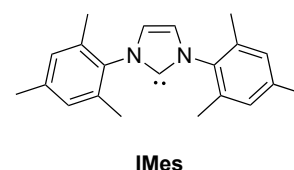
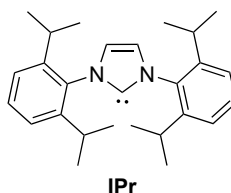
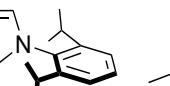
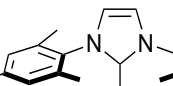


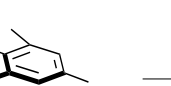
Table 2.2. Comparison of nickel complex reactivity



IPr(Cy₃P)NiCl₂



IMes(Cy₃P)NiCl₂



entry	Ni complex	yield
1	(Cy ₃ P) ₂ NiCl ₂	73%
2	Ni(cod) ₂	99%
3	(^t Bu ₃ P) ₂ NiCl ₂	10%
4	(^t Bu ₂ MeP) ₂ NiCl ₂	23%
5	(ⁿ Bu ₃ P) ₂ NiCl ₂	0%
6	(Et ₃ P) ₂ NiCl ₂	0%
7	IPr(Cy ₃ P)NiCl ₂	77%
8	IMes(Cy ₃ P)NiCl ₂	99%
9	(IMes) ₂ NiCl ₂	0%

NMR yields determined using 1,1,1,2-tetrachloroethane as an internal standard.

NMR yields determined using 1,1,1,2-tetrachloroethane as an internal standard.

2.3 Substrate Scope of Hydroboration

Using the IMes(Cy₃P)NiCl₂ as the nickel precatalyst, the following substrate scope was explored (Table 2.3). The reactivity of the precatalyst did not seem affected by substrate electronics as electron-rich styrenes (entries 2-5) and electron-deficient styrenes (entries 6-7) performed comparably. Proximity of arene substitution may play a role in reactivity, as para substituted variants of both electron-rich and electron-deficient styrenes (entries 4 and 7) performed better than their meta and ortho substituted counterparts that introduce bulk near the site of reaction (entries 2, 3, and 6). The reaction was tolerant of polyaromatics (entries 8-10) and unexpectedly successful with β substitutions on the olefin despite the large catalyst complex (entries 11 and 12). In all cases, selectivity for the branched boronic ester was maintained over formation of the linear boronic ester, with the latter appearing in only trace amounts for a handful of reactions (entries 4, 7, and 8). However, the substrate scope did have limitations. Reactivity faltered in the presence of halogen bearing substrates (entries 18-21) presumably due to oxidative addition into the C-X bond outcompeting hydrometallation. While ether-bearing styrenes performed well, esters dramatically reduced reactivity (entry 15). Amines, thioethers, and heterocyclic moieties shut down reactivity altogether (entries 13, 14, and 16-17).

Table 2.3. Substrate scope.

entry	substrate	yield ^a (NMR) ^b Branched	(NMR yield) ^b Linear	entry	substrate	yield ^a (NMR) ^b Branched	(NMR yield) ^b Linear
1		74(99)	---	7		80(68)	(5)
2		66	---	8		73	---
3		73	---	9		67	---
4		86 ^c (76)	(3)	10		82	---
5		70	---	11		89	(trace)
6		62	---	12		69	(trace)
<i>Poorly Performing Substrates:</i>							
entry	substrate	yield ^a (NMR) ^b Branched	(NMR yield) ^b Linear	entry	substrate	yield ^a (NMR) ^b Branched	(NMR yield) ^b Linear
13		---	---	18		8	---
14		---	---	19		13	---
15		13	---	20		10	---
16		---	---	21		45	---
17		---	---				

^aIsolated yield on a 1.0 mmol scale. ^bNMR yields shown in parentheses determined using 1,1,1,2-tetrachloroethane as an internal standard on a 0.25 mmol scale. ^c6mol% catalyst used

2.4 Impact of Steric Bulk of the Catalyst on Selectivity

For 4-OMe styrene, both $\text{IMes}(\text{Cy}_3\text{P})\text{NiCl}_2$ and $\text{IPr}(\text{Cy}_3\text{P})\text{NiCl}_2$ produced a mixture of branched and linear boronic esters (Table 2.4). While both precatalysts heavily favored formation of the branched boronic ester, the IMes complex favored production of the branched boronic ester more than the IPr complex. This apparent trend led us to hypothesize that steric bulk of the carbene may influence regioselectivity. Ultimately, we wondered if selectivity between branched and linear ester formation could be reversed by increasing bulk around the nickel center. To probe this hypothesis, we synthesized the sterically demanding nickel complex, $\text{IPr}^*(\text{Cy}_3\text{P})\text{NiCl}_2$, and used it as a precatalyst to screen a small series of styrenes (Table 2.5). Surprisingly, overall conversion of the starting material was mostly maintained despite the encumbering size of the nickel complex. While regioselectivity was not reversed by IPr^* , it increased the amount of linear boronic ester formation observed and confirmed that NHC ligand identity directly impacts regioselectivity.

Table 2.4. Effect of steric bulk on selectivity.

Reaction scheme showing the conversion of 4-methoxystyrene and HBpin to branched and linear boronic esters using $\text{IPr}^*(\text{Cy}_3\text{P})\text{NiCl}_2$ (3 mol%) and KO^tBu (6 mol%) in toluene at 60 °C for 18 h.

entry	Catalyst	branched	linear
1	$\text{Imes}(\text{Cy}_3\text{P})\text{NiCl}_2$	25	1
2	$\text{IPr}(\text{Cy}_3\text{P})\text{NiCl}_2$	8.3	1
3	$\text{IPr}^*(\text{Cy}_3\text{P})\text{NiCl}_2$	1.3	1

NMR yields determined using 1,1,1,2-tetrachloroethane as an internal standard.

Table 2.5. Substrate scope using $\text{IPr}^*(\text{Cy}_3\text{P})\text{NiCl}_2$.

Reaction scheme showing the conversion of a substituted styrene and HBpin to branched and linear boronic esters using $\text{IPr}^*(\text{Cy}_3\text{P})\text{NiCl}_2$ (3 mol%) and KO^tBu (6 mol%) in toluene at 60 °C for 18 h.

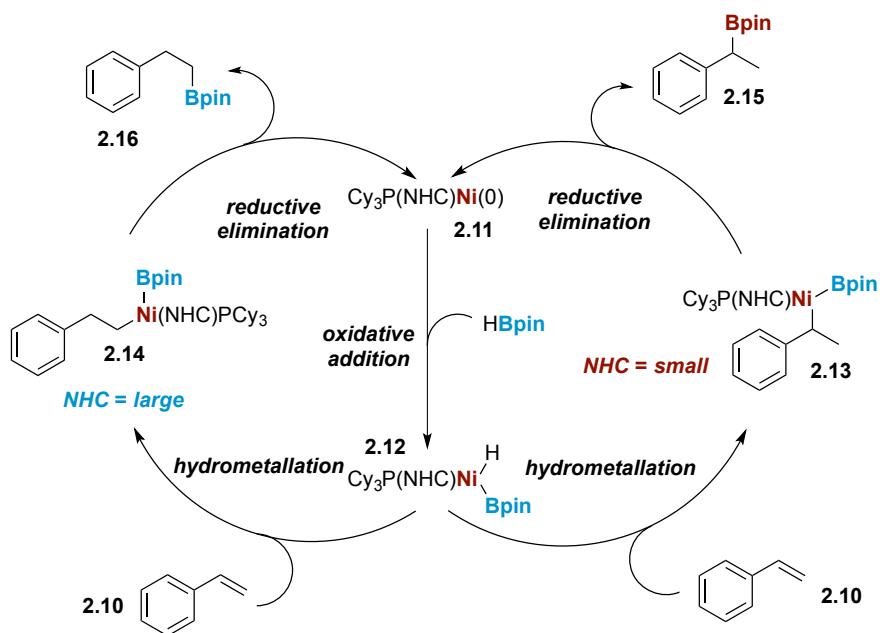
Structure of the $\text{IPr}^*(\text{Cy}_3\text{P})\text{NiCl}_2$ catalyst complex.

entry	substrate	SM	branched	linear
1	H	0%	48%	33%
2	4-OMe	20%	36%	27%
3	4-CF ₃	5%	39%	35%
4	4-Ph	17%	40%	31%

NMR yields determined using 1,1,1,2-tetrachloroethane as an internal standard.

2.5 Proposed Mechanism

A possible mechanism for the nickel-catalyzed hydroboration is shown in Scheme 2.1. Given that the Ni(0) precatalyst Ni(cod)₂ was able to catalyze the reaction, we hypothesize that the heteroleptic Ni(II) complexes go through a Ni(0) intermediate that serves as the active catalyst. Presumably the nickel complex chlorines are substituted by two tert-butoxides, which are then reduced by two equivalents of HBpin to generate H₂ gas and our reduced Ni(0) catalyst **2.11**. The Ni(0) catalyst then undergoes oxidative insertion into the B-H bond of HBpin to form a four-coordinate nickel borohydride complex **2.12**. The borohydride complex then needs to coordinate to the substrate olefin in order to hydrometallate. We predict that the phosphine ligand must dissociate at this point lest we create a five-coordinate Ni complex. Once the phosphine is dissociated and the olefin coordinated, the metal hydride can then insert itself into the olefin to produce the benzyl **2.13** or linear **2.14** nickel intermediate. As evidenced by our work, the preferred geometry of addition is that which produces the benzyl nickel. We suspect this is due to the increased stabilization offered by conjugation to the neighboring pi-system of the aromatic ring. This pi-system interaction is disfavored by steric repulsion between the substrate and catalyst, as evidenced by the decreased regioselectivity when IPr* is used as the carbene ligand. Subsequent reductive elimination of the nickel intermediate then produces the respective boronic ester product, **2.15** or **2.16**, and regenerates the active Ni(0) catalyst.

Scheme 2.1. Proposed catalytic cycle.

2.6 Conclusions

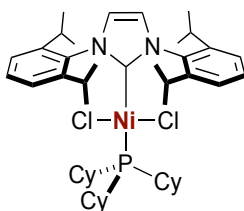
In conclusion, we have shown that nickel can effectively catalyze the hydroboration of styrenes and is a viable alternative to second or third-row transition metals that perform analogous transformations. The branched boronic ester can be exclusively accessed using a novel heteroleptic N-heterocyclic carbene/phosphine nickel complex. These complexes allow for a more variable substrate scope with both reproducible and increased yields not accessible using bis-phosphine or $\text{Ni}(0)$ catalysts. Increasing the steric bulk of the NHC ligand can dramatically influence the amount of linear boronic ester produced. Further studies include broadening the functional group tolerance and expanding the reaction to olefins other than styrenes. Additionally, using variants of chiral NHC's could make the hydroboration enantioselective. Performing mechanistic studies to further elucidate the catalytic cycle could help rationalize future catalyst design and candidates for reactions other than hydroboration.

2.7 Experimental Details

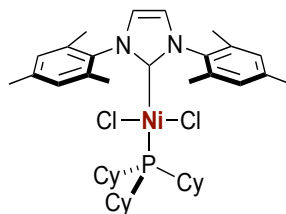
2.7.1 Preparation of Novel Nickel Complexes

Bis-phosphine nickel complexes were synthesized according to a previously reported procedure.⁹

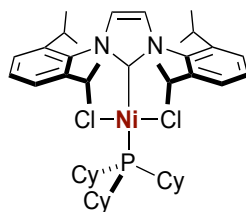
Heteroleptic complexes were prepared using a modified procedure.⁸



IPr(Cy₃P)NiCl₂. In a glovebox, a 100 mL round bottom flask was charged with 1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride (1.276 g; 3.00 mmol; 1.0 equiv), KO^tBu (0.404 g; 3.60 mmol; 1.2 equiv) 150 and 10 mL THF. The reaction was allowed to stir for 2.5 hours and then filtered through a pad of celite with a small amount of THF into a Schlenk flask containing (Cy₃P)₂NiCl₂ (2.072 g; 3.00 mmol; 1.0 equiv). The reaction was stirred overnight in the glovebox. The reaction was removed from the glovebox and transferred to a round bottom flask and the solvent was removed *in vacuo*. The resulting red solid was washed with hexanes and then filtered. The filtrate was evaporated to dryness and the red solid was dissolved in a minimal amount of toluene, layered on top of nitromethane, and allowed to slowly diffuse overnight. The resulting crystals of IPr(Cy₃P)NiCl₂ were isolated in 30% yield and were suitable for catalysis and X-ray crystallography. ¹H NMR (500 MHz, CDCl₃) δ 7.56 (t, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 4H), 6.99 (s, 2H), 3.09 (h, *J* = 6.8 Hz, 4H), 1.78 – 1.55 (m, 20H), 1.54 – 1.43 (m, 8H), 1.41 (d, *J* = 6.6 Hz, 12H), 1.32 – 1.10 (m, 5H), 1.07 (d, *J* = 7.0 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 166.8 (d, *J* = 123.4 Hz), 147.5, 135.9, 129.7, 123.9 (d, *J* = 3.8 Hz), 123.5, 30.9 (d, *J* = 17.4 Hz), 29.1, 28.7, 27.7 (d, *J* = 10.0 Hz), 26.6, 26.5, 22.6. ³¹P NMR (202 MHz, CDCl₃) δ 5.78.



IMes(Cy₃P)NiCl₂. In a glovebox, a 100 mL round bottom flask was charged with 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride (3.086 g; 9.00 mmol; 1.0 equiv), KO^tBu (1.215 g; 10.8 mmol; 1.2 equiv) and 30 mL THF. The reaction was allowed to stir for 30 min. and then filtered through a pad of celite with a small amount of THF into a Schlenk flask containing (Cy₃P)₂NiCl₂ (6.215 g; 9.00 mmol; 1.0 equiv). The reaction was stirred overnight in the glovebox. The reaction was removed from the glovebox, filtered and washed with THF. The filtrate was concentrated *in vacuo*. The resulting red solid was with hexanes and then filtered. The orange solid that was isolated was the bis-NHC complex, IMes₂NiCl₂, in 53% yield (relative to the imidazolium salt). The complex was pure enough for catalysis. The filtrate was evaporated to dryness and the red solid was dissolved in a minimal amount of toluene, layered on top of nitromethane, and allowed to slowly diffuse overnight. The resulting crystals of IMes(Cy₃P)NiCl₂ were isolated in 8% yield and were suitable for catalysis and X-ray crystallography. ¹H NMR (500 MHz, CDCl₃) δ 7.12 (s, 4H), 6.92 (s, 2H), 2.43 (s, 6H), 2.37 (s, 12H), 1.81 – 1.62 (m, 18H), 1.61 – 1.48 (m, 6H), 1.31 – 1.13 (m, 3H), 1.13 – 0.96 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 165.2 (d, *J* = 121.3 Hz), 138.4, 151 136.7, 136.1, 128.8, 122.8 (d, *J* = 3.4 Hz), 30.5 (d, *J* = 17.6 Hz), 29.3, 27.7 (d, *J* = 10.0 Hz), 26.7, 21.2, 19.4. ³¹P NMR (202 MHz, CDCl₃) δ 7.03.

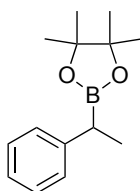


IPr*(Cy₃P)NiCl₂. IPr*HCl was prepared as previously reported.¹⁰ In a glovebox, a 100 mL round bottom flask was charged with IPr*HCl (1.84 g; 2.00 mmol; 1.0 equiv), KO^tBu (0.269 g; 2.40 mmol; 1.2 equiv) and 10 mL THF. The reaction was allowed to stir for 45 min. and then filtered through a pad of celite with a small amount of THF into a Schlenk flask containing (Cy₃P)₂NiCl₂ (1.90 g; 2.75 mmol; 1.4 equiv). The reaction was stirred overnight in the glovebox. The reaction was removed from the glovebox and transferred to a round bottom flask and the solvent was removed *in vacuo*. The resulting red solid was washed with hexanes and then filtered. The filtrate was evaporated to dryness and the red solid was dissolved in a minimal amount of toluene, layered on top of nitromethane, and allowed to slowly diffuse overnight. The resulting solid of IPr*(Cy₃P)NiCl₂ was isolated in 9.5% yield and were suitable for catalysis. The solid could then be crystallized by dissolving in a minimal amount of p-xylene, layered on top of nitromethane, and allowed to slowly diffuse overnight. The resulting crystals were suitable for X-ray crystallography. ¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, *J* = 7.6 Hz, 8H), 7.23 (t, *J* = 7.5 Hz, 8H), 7.18 (t, *J* = 7.2 Hz, 4H), 7.05 – 6.95 (m, 12H), 6.89 (s, 4H), 6.68 (d, *J* = 7.0 Hz, 8H), 5.91 (s, 4H), 4.10 (s, 2H), 2.30 (s, 6H), 1.95 – 1.77 (m, 9H), 1.66 – 1.54 (m, 15H), 1.21 – 1.03 (m, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 166.3 (d, *J* = 122.7 Hz), 145.6, 143.9, 143.8, 137.9, 135.5, 131.1, 129.6, 129.5, 127.7, 125.9, 125.9, 122.1, 122.1, 51.2, 31.2 (d, *J* = 17.1 Hz), 29.3, 27.8 (d, *J* = 10.0 Hz), 26.4, 21.9. ³¹P NMR (202 MHz, CDCl₃) δ 7.90.

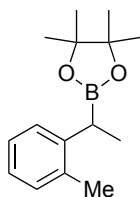
2.7.2 General Procedure for the Hydroboration of Styrenes.

All styrenes were purified by distillation or column chromatography before use. Substrate numbering is in reference to that in Table 2.3. Only branched boronic ester products are listed. It should be noted that none of the substrates listed in Table 2.3 under the category of “poorly

performing substrate” were isolated. All yields were determined by NMR and all coupling data was abstracted from crude ^1H NMR spectra, so appropriate caution should be exercised.

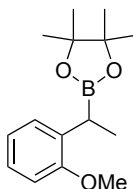


Compound 1. In a glovebox, a 10 mL round bottom flask was charged with IMes(Cy₃P)NiCl₂ (21 mg; 0.03 mmol; 3 mol%), KO^tBu (6.7 mg; 0.06 mmol; 6 mol%), and 2 mL of toluene. The flask was fitted a septum, removed from the glovebox and the mixture was allowed to stir for 10 minutes. Then, HBpin (0.18 mL; 1.24 mmol; 1.2 equiv) and then styrene (0.12 mL; 1.04 mmol; 1.0 equiv) was added. The reaction was allowed to stir overnight at 60 °C. The reaction was filtered through a plug of silica and washed with 10% EtOAc in hexanes and concentrated. The crude material was purified by column chromatography using isocratic 5% EtOAc in hexanes. NOTE: product decomposition occurs on silica, so the product should elute in 10 minutes or less. Compound **1** was isolated in 74% yield as a clear, colorless, viscous oil. ^1H NMR (500 MHz, CDCl₃) δ 7.26 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 7.13 (t, J = 7.2 Hz, 1H), 2.43 (q, J = 7.5 Hz, 1H), 1.33 (d, J = 7.5 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (126 MHz, CDCl₃) δ 145.0, 128.3, 127.8, 125.0, 83.3, 24.6, 17.0. HRMS (ESI) m/z calculated for C₁₄H₂₅BNO₂ [M+NH₄] + 249.2010, found 249.2013.

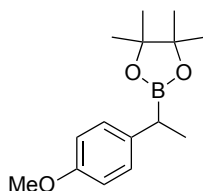


Compound 2. Compound **2** was prepared and purified in the same fashion as compound **1**. Compound **2** was isolated in 66% yield. ^1H NMR (500 MHz, CDCl₃) δ 7.20 (d, J = 7.7 Hz, 1H),

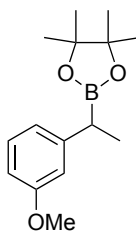
7.16 – 7.08 (m, 2H), 7.04 (t, $J = 7.4$ Hz, 1H), 2.58 (q, $J = 7.5$ Hz, 1H), 2.31 (s, 3H), 1.32 (d, $J = 7.4$ Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.4, 135.6, 123.0, 127.1, 126.0, 125.0, 83.2, 24.7, 19.9, 16.4. HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{28}\text{BNO}_2$ $[\text{M}+\text{NH}_4]^+$ + 263.2166, found 263.2163.



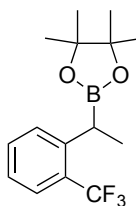
Compound 3. Compound **3** was prepared and purified in the same fashion as compound **1**. Compound **3** was isolated in 73% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.18 – 7.11 (m, 2H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 3.80 (s, 3H), 2.45 (q, $J = 7.5$ Hz, 1H), 1.28 (d, $J = 7.6$ Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 156.8, 133.9, 128.4, 126.2, 120.7, 109.7, 83.0, 54.9, 24.7, 15.1. HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{27}\text{BNO}_3$ $[\text{M}+\text{NH}_4]^+$ + 279.2115, found 279.2115. 153



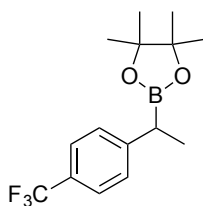
Compound 4. Compound **4** was prepared and purified in the same fashion as compound **1** except the amount of $\text{IMes}(\text{Cy}_3\text{P})\text{NiCl}_2$ and KO^tBu were doubled. Compound **4** was isolated in 86% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.13 (d, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 3.77 (s, 3H), 2.37 (q, $J = 7.5$ Hz, 1H), 1.29 (d, $J = 7.5$ Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 157.2, 137.0, 128.61, 113.8, 83.2, 55.2, 24.6, 17.4. HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{27}\text{BNO}_3$ $[\text{M}+\text{NH}_4]^+$ + 279.2115, found 279.2116.



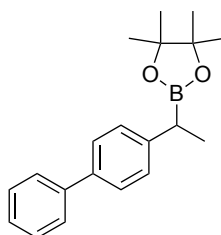
Compound 5. Compound **5** was prepared and purified in the same fashion as compound **1**. Compound **5** was isolated in 70% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.17 (t, $J = 7.9$ Hz, 1H), 6.81 (d, $J = 7.7$ Hz, 1H), 6.78 (t, $J = 2.5$ Hz, 1H), 6.68 (dd, $J = 8.2, 2.6$ Hz, 1H), 3.79 (s, 3H), 2.41 (q, $J = 7.5$ Hz, 1H), 1.32 (d, $J = 7.5$ Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.6, 146.6, 129.2, 120.3, 113.5, 110.5, 83.3, 55.1, 24.6, 17.0. HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{24}\text{BO}_3$ $[\text{M}+\text{H}]^+$ 262.1850, found 262.1853.



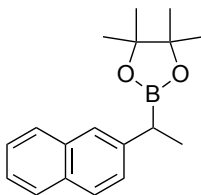
Compound 6. Compound **6** was prepared and purified in the same fashion as compound **1**. Compound **6** was isolated in 62% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.58 (d, $J = 7.9$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.8$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 2.84 (q, $J = 7.5$ Hz, 1H), 1.35 (d, $J = 7.4$ Hz, 3H), 1.21 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.6, 131.6, 129.6, 128.0 (q, $J = 29.0$ Hz), 125.7 (q, $J = 5.9$ Hz), 124.7 (q, $J = 273.8$ Hz), 124.9, 83.4, 24.6, 17.7. HRMS (ASAP) m/z calculated for $\text{C}_{15}\text{H}_{20}\text{BF}_3\text{O}_2$ $[\text{M}]^+$ 299.1540, found 299.1543.



Compound 7. Compound **7** was prepared and purified in the same fashion as compound **1**. Compound **7** was isolated in 80% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.51 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 2.50 (q, $J = 7.5$ Hz, 1H), 1.34 (d, $J = 7.5$ Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 149.3, 128.0, 127.4 (q, $J = 32.5$ Hz), 125.2 (q, $J = 3.8$ Hz), 124.5 (q, $J = 271.6$ Hz), 83.6, 24.6, 24.6, 16.7. HRMS (ASAP) m/z calculated for $\text{C}_{15}\text{H}_{20}\text{BF}_3\text{O}_2$ $[\text{M}]^+ 299.1540$, found 299.1539.

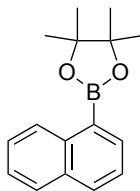


Compound 8. Compound **8** was prepared and purified in the same fashion as compound **1**. Compound **8** was isolated in 73% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.25 – 7.18 (m, 4H), 7.12 (t, $J = 7.1$ Hz, 1H), 2.29 (t, $J = 7.9$ Hz, 1H), 1.84 (dq, $J = 14.8, 7.8$ Hz, 1H), 1.64 (dq, $J = 14.7, 7.6$ Hz, 1H), 1.35 – 1.21 (m, 4H), 1.20 (s, 6H), 1.18 (s, 6H), 0.86 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.5, 128.4, 128.2, 125.0, 83.20, 32.3, 31.6, 24.6, 22.7, 14.0. HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{31}\text{BNO}_2$ $[\text{M}+\text{NH}_4]^+ 291.2479$, found 291.2478.

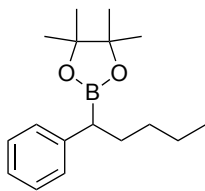


Compound 9. Compound **9** was prepared and purified in the same fashion as compound **1**. Compound **9** was isolated in 67% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.84 – 7.72 (m, 3H), 7.64 (s, 1H), 7.48 – 7.34 (m, 3H), 2.61 (q, $J = 7.5$ Hz, 1H), 1.42 (d, $J = 7.5$ Hz, 3H), 1.21 (s, 6H), 1.20

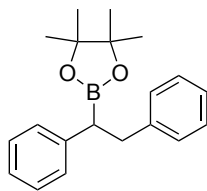
(s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.6, 133.8, 131.7, 127.6, 127.5, 127.4, 127.2, 125.6, 125.2, 124.7, 83.4, 24.6, 16.8. HRMS (ASAP) m/z calculated for $\text{C}_{18}\text{H}_{23}\text{BO}_2$ $[\text{M}]^+$ 281.1822, found 281.1818. 155



Compound 10. Compound **10** was prepared and purified in the same fashion as compound **1**. Compound **10** was isolated in 82% yield. ^1H NMR (500 MHz, CDCl_3) δ 8.10 (d, $J = 8.2$ Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.66 (d, $J = 7.9$ Hz, 1H), 7.50 – 7.35 (m, 4H), 3.11 (q, $J = 7.5$ Hz, 1H), 1.49 (d, $J = 7.4$ Hz, 3H), 1.20 (s, 6H), 1.19 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.4, 133.9, 132.0, 128.7, 125.8, 125.3, 125.2, 124.2, 124.0, 83.4, 24.7, 24.5, 16.4. HRMS (ESI) m/z calculated for $\text{C}_{18}\text{H}_{27}\text{BNO}_2$ $[\text{M}+\text{NH}_4]^+$ 299.2166, found 299.2165.

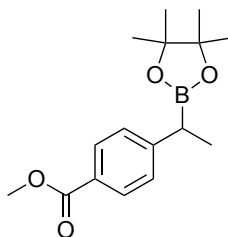


Compound 11. Compound **11** was prepared and purified in the same fashion as compound **1**. Compound **11** was isolated in 89% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.58 (d, $J = 7.6$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.33 – 7.27 (m, 3H), 2.48 (q, $J = 7.5$ Hz, 1H), 1.36 (d, $J = 7.5$ Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.2, 141.2, 137.9, 128.6, 128.2, 127.0, 126.9, 126.8, 83.4, 24.6, 17.1. HRMS (ESI) m/z calculated for $\text{C}_{20}\text{H}_{29}\text{BNO}_2$ $[\text{M}+\text{NH}_4]^+$ 325.2322, found 325.2317.



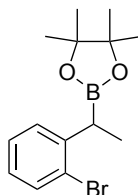
Compound 12. Compound **12** was prepared and purified in the same fashion as compound **1**.

The yield of Compound **12** was determined by NMR using a 1,1,2,2-tetrachloroethane internal standard. ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.10 (m, 11H), 3.15 (dd, J = 13.5, 9.8 Hz, 1H), 2.96 (dd, J = 13.5, 6.9 Hz, 1H), 2.68 (dd, J = 9.8, 6.9 Hz, 1H), 1.11 (s, 6H), 1.10 (s, 6H).



Compound 15. Compound **15** was prepared and purified in the same fashion as compound **1**.

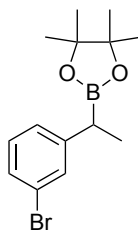
The yield of Compound **15** was determined by NMR using a 1,1,2,2-tetrachloroethane internal standard. ^1H NMR (400 MHz, CDCl_3) δ 7.24 (dd, J = 5.7, 2.7 Hz, 2H), 7.16 (dd, J = 7.8, 2.8 Hz, 2H), 3.89 (s, 3H), 2.51 (q, J = 7.3, 7.3, 7.1 Hz, 1H), 1.35 (d, J = 7.5 Hz, 3H), 1.18 (s, 6H), 1.17 (s, 6H).



Compound 18. Compound **18** was prepared and purified in the same fashion as compound **1**.

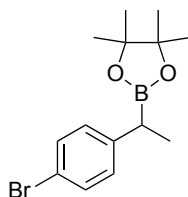
The yield of Compound **18** was determined by NMR using a 1,1,2,2-tetrachloroethane internal standard. ^1H NMR (400 MHz, Chloroform- d) δ 7.53 (dd, J = 7.9, 1.4 Hz, 4H), 7.27 (dd, J = 4.3,

1.1 Hz, 33H), 7.24 (d, $J = 7.8$ 31H), 7.09 (td, $J = 7.8$, 1.7 Hz, 16H), 2.64 (q, $J = 7.7$, 7.7, 7.6 Hz, 1H), 1.80 (d, $J = 6.8$ Hz, 3H), 1.34 (s, 6H), 1.33 (s, 6H).



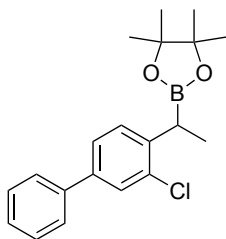
Compound 19. Compound **19** was prepared and purified in the same fashion as compound **1**.

The yield of Compound **19** was determined by NMR using a 1,1,2,2-tetrachloroethane internal standard. ^1H NMR (400 MHz CDCl_3) δ 7.40 – 7.05 (m, 68H), 2.40 (q, $J = 7.5$, 7.5, 7.4 Hz, 1H), 1.43 (d, $J = 7.0$ Hz, 3H), 1.19 (s, 6H), 1.18 (s, 6H).



Compound 20. Compound **20** was prepared and purified in the same fashion as compound **1**.

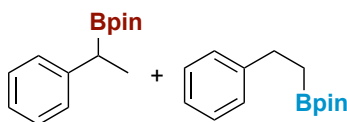
The yield of Compound **20** was determined by NMR using a 1,1,2,2-tetrachloroethane internal standard. ^1H NMR (400 MHz, Chloroform- d) δ 7.43 (d, $J = 8.5$ Hz, 20H), 7.25 (d, $J = 8.4$ Hz, 20H), 2.38 (q, $J = 7.5$, 7.5, 7.5 Hz, 1H), 1.42 (d, $J = 7.0$ Hz, 3H), 1.19 (s, 6H), 1.18 (s, 6H).



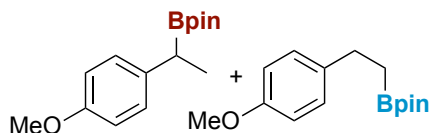
Compound 21. Compound **21** was prepared and purified in the same fashion as compound **1**.

The yield of Compound **21** was determined by NMR using a 1,1,2,2-tetrachloroethane internal standard. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.53 (m, 2H), 7.45 – 7.38 (m, 3H), 7.33 (dd, $J = 7.7, 6.0$ Hz, 3H), 2.79 (q, $J = 7.5, 7.5, 7.5$ Hz, 1H), 1.38 (d, $J = 7.5$ Hz, 3H), 1.25 (s, 12H).

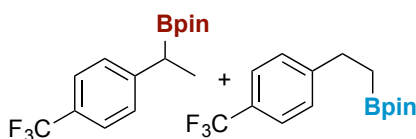
5.7.3 Effect of Sterics on Hydroboration.



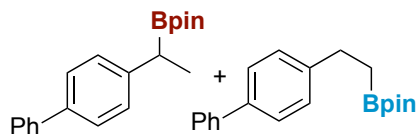
In a glovebox, a 5 mL vial was charged with $\text{IPr}^*(\text{Cy}_3\text{P})\text{NiCl}_2$ (9.9 mg; 7.5 μmol ; 3 mol%), KOtBu (1.7 mg; 15 μmol ; 6 mol%), and 0.5 mL of toluene. The vial was fitted a septum, removed from the glovebox and the mixture was allowed to stir for 10 minutes. Then, HBpin (44 μL ; 0.303 mmol; 1.2 equiv) and then styrene (29 μL ; 0.252 mmol; 1.0 equiv) was added. The reaction was allowed to stir overnight at 60 $^\circ\text{C}$. The reaction was filtered through a plug of silica and washed with 10% EtOAc in hexanes and concentrated. The crude material was dissolved in CDCl_3 and 10 μL of 1,1,1,2-tetrachloroethane was added. The product and starting material peaks were integrated against the standard. The standard was integrated such that integrations of one proton peaks would represent yield. 48% branched; 33% linear; 0% SM.



The mixture of branched and linear products were synthesized as described above. 36% branched; 27% linear; 20% SM.



The mixture of branched and linear products were synthesized as described above. 39% branched; 35% linear; 5% SM.



The mixture of branched and linear products were synthesized as described above. 41% branched; 31% linear; 17% SM.

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