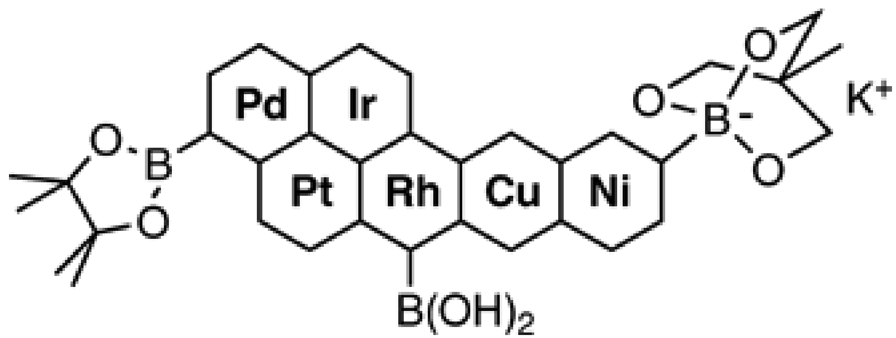
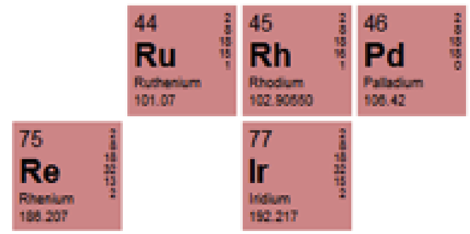
C-H Activation
for the Construction of C-B bonds

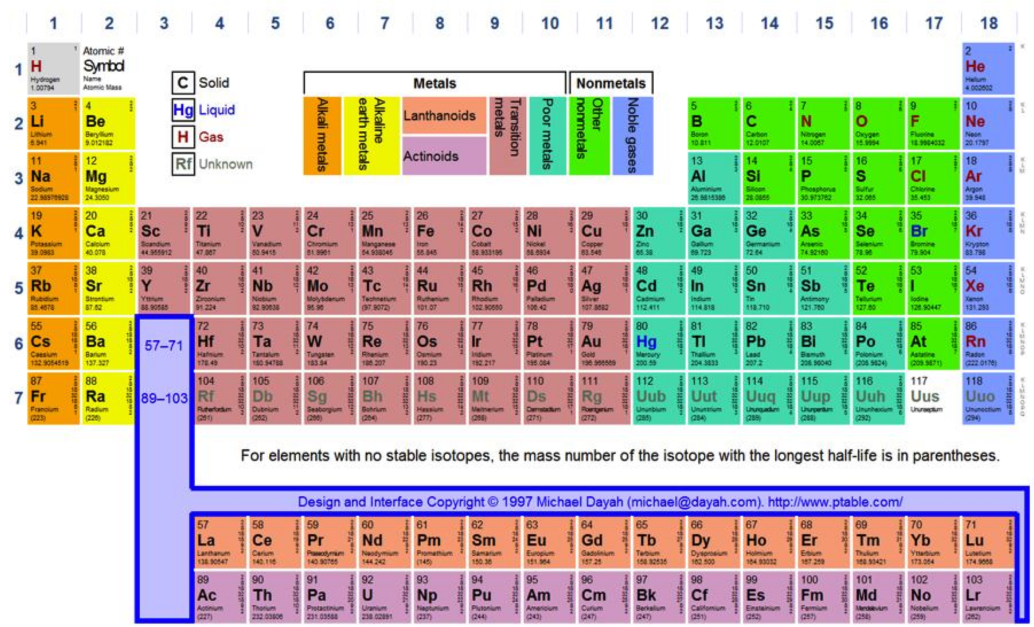


2012. 4.18
Haye Min Ko

Contents



44 Ru Ruthenium 101.07
45 Rh Rhodium 102.90550
46 Pd Palladium 106.42
75 Re Rhenium 186.207
77 Ir Iridium 192.217



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Atomic #
Symbol
Name
Atomic Mass
C Solid
Hg Liquid
H Gas
Rf Unknown
Metals
Nonmetals
Alkali metals
Alkaline earth metals
Lanthanoids
Actinoids
Transition metals
Poor metals
Other nonmetals
Noble gases
57–71
89–103
For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.
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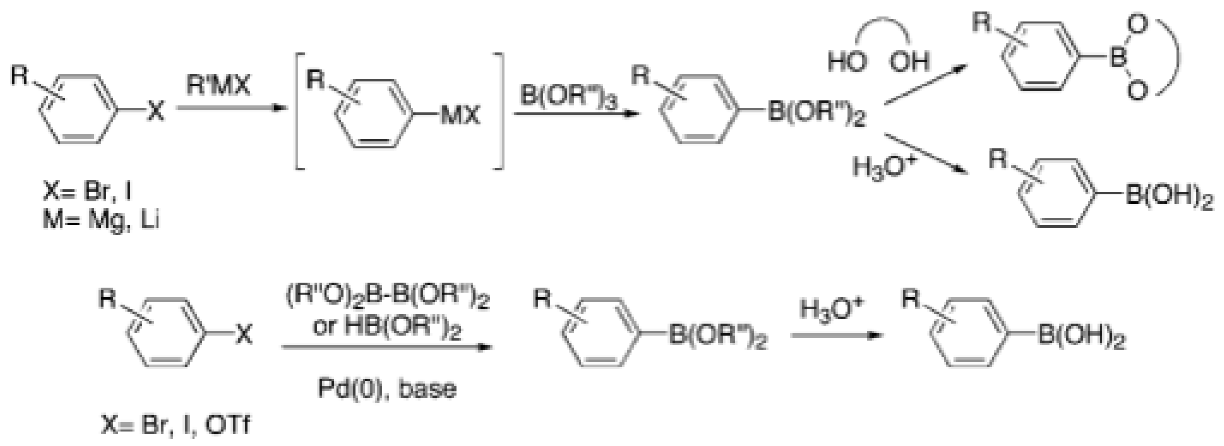
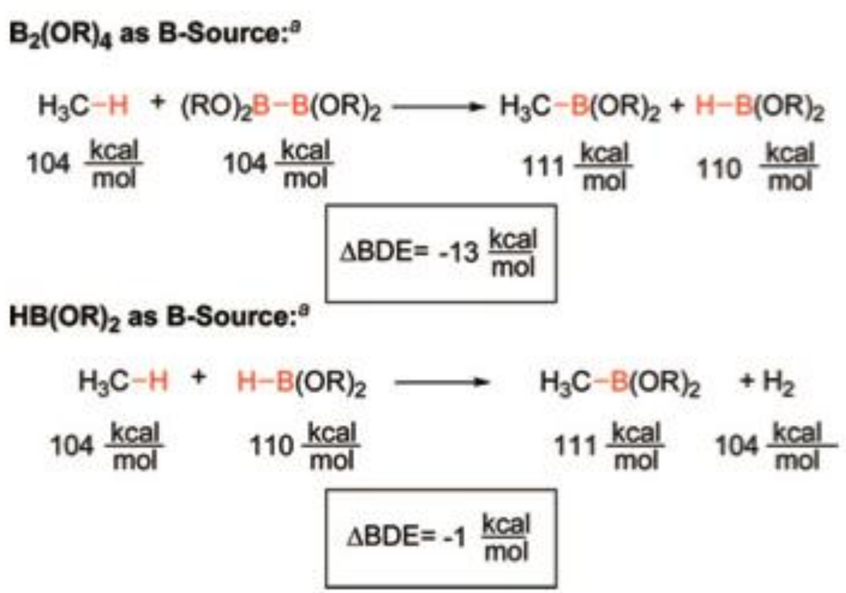
1. Introduction

Common Syntheses of Arylboronate Esters and Acids



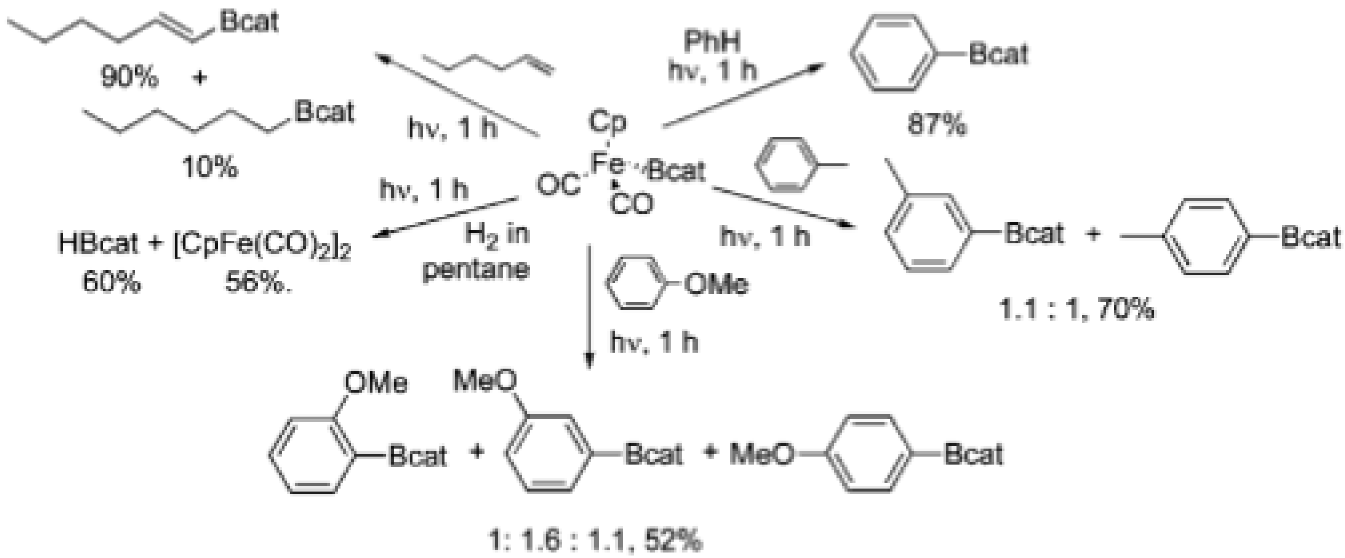


Thermodynamic of Methane Borylation with $B_2(OR)_4$ or $HB(OR)_2$

2. Stoichiometric Borylation

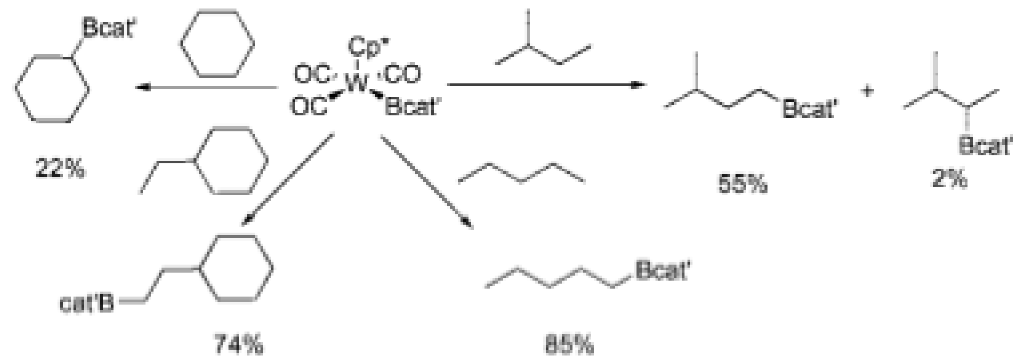
2.1. Iron

- Summary of the Reactions of the Iron Boryl Complex $CpFe(CO)_2(Bcat)$

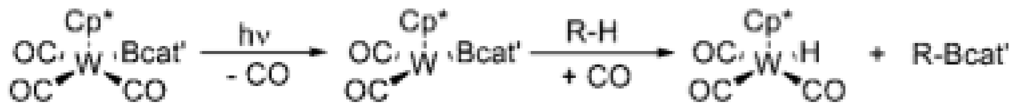


2.2. Tungsten

- Reactions of $Cp^*W(CO)_3(Bcat')$ with Various Alkanes



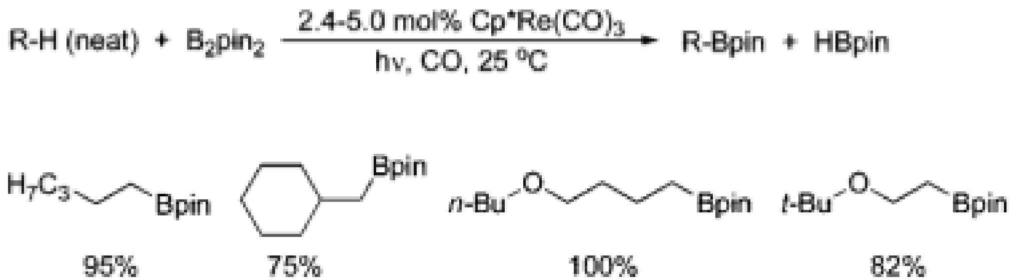
- Proposed mechanism for the reaction of $Cp^*W(CO)_3(Bcat')$ with alkanes



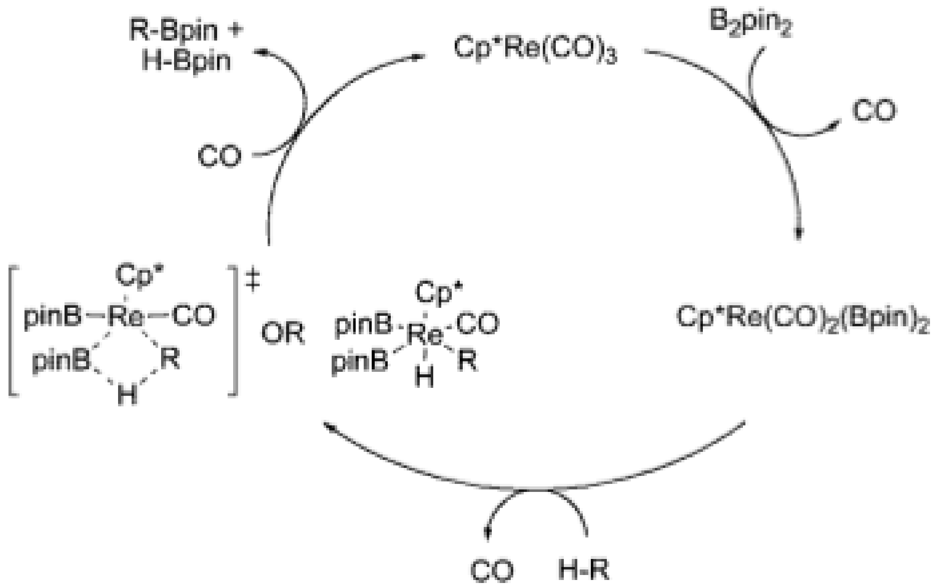
3. Metal-catalyzed Borylation

3.1. Rhenium

- Cp*Re-Catalyzed Borylation of Alkanes

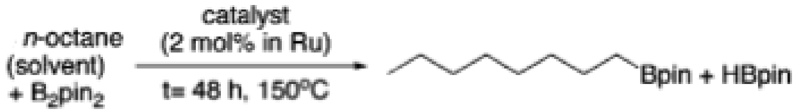


- Proposed mechanism for Cp*Re-Catalyzed Alkanes Borylation



3.2. Ruthenium

- Borylation of Octane with B_2pin_2 catalyzed Ru complexes

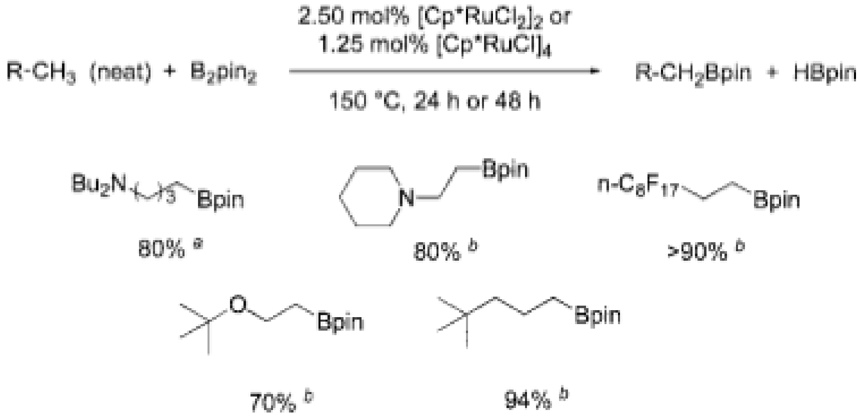


catalyst	yield[a]	conversion[a]
$[Cp^*RuCl_2]_2$	98% (75%)[b]	99%
$[Cp^*RuCl]_4$[c]	65%	99%
Cp*Ru(H)(COD)	58%	80%
Cp*Ru(Cl)(TMEDA)	95%	98%
$[Cp^*Ru(OMe)]_2$	7%	65%
$(COD)Ru(2\text{-methylallyl})_2$	7%	59%
$Ru(acac)_3$	4%	76%

[a] Determined by GC. [b] Isolated yield in parentheses. [c] 5 mol % Ru used.

The reaction of arenes with B_2pin_2 in the presence of Cp*Ru-complexes did not form functionalized products in good yields.

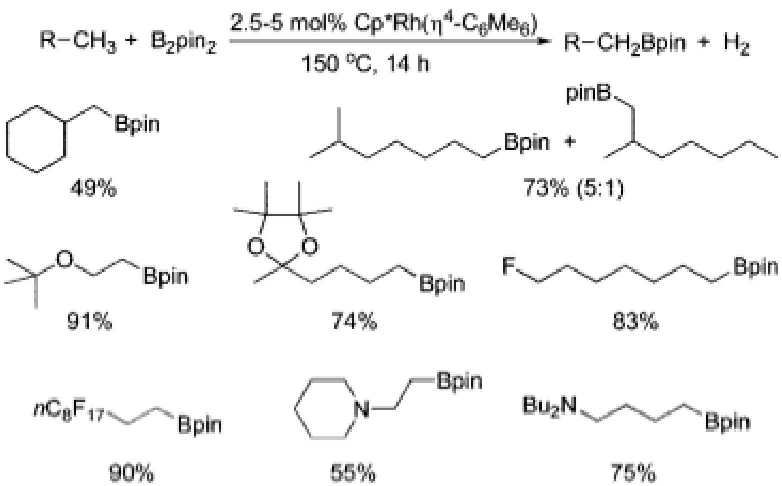
- Ru-Catalyzed Terminal Borylation of Heteroatom-Containing Substrates



[a] Conditions: $[Cp^*RuCl]_4$ neat, 150 °C, 24 h, yield determined by GC.
[b] Conditions: $[Cp^*RuCl_2]_2$ neat, 150 °C, 48 h, yield determined by GC.

3.3. Rhodium

- Rh-catalyzed Borylation of Aliphatic Substrates

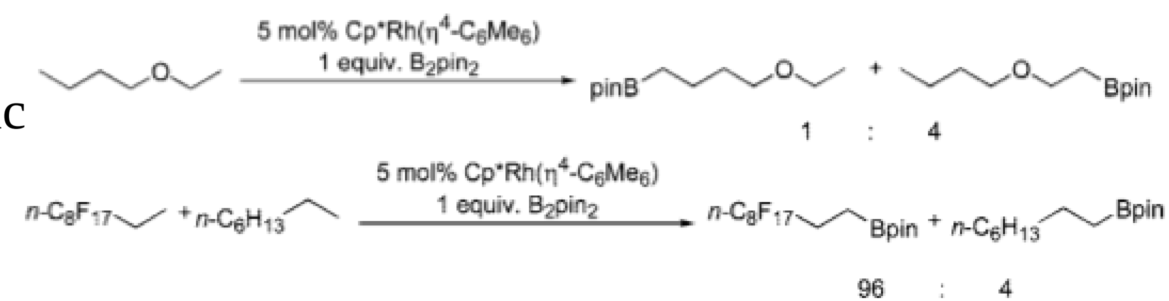


[a] Conditions: 2.5−5 mol % Cp*Rh(η^4-C_6Me_6), 1 equiv of B_2pin_2 in neat substrate, 150 °C, 24 h. yields were determined by GC analysis.

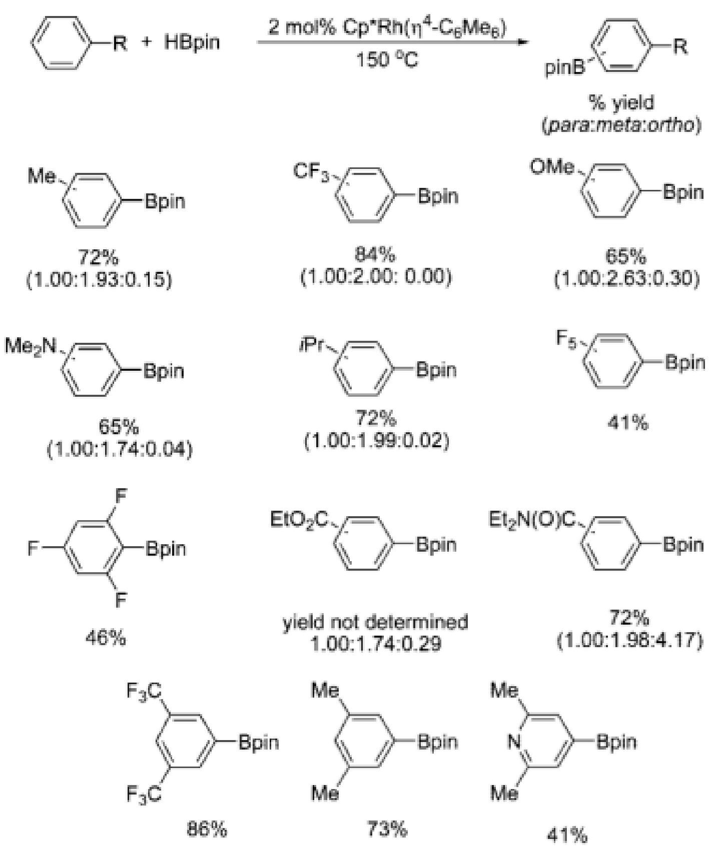
More electron-deficient C-H bonds in aliphatic substrates undergo borylation catalyzed by Cp*Rh(η^4-C_6Me_6) faster than more electron-rich C-H bonds.

The presence of heteroatoms, such as nitrogen and oxygen, are known to activate the C-H bond α to the heteroatom toward cleavage by many metal complexes. However this property of the heteroatoms did not override the preference of the catalyst for the functionalization of the least hindered of the primary C-H bonds.

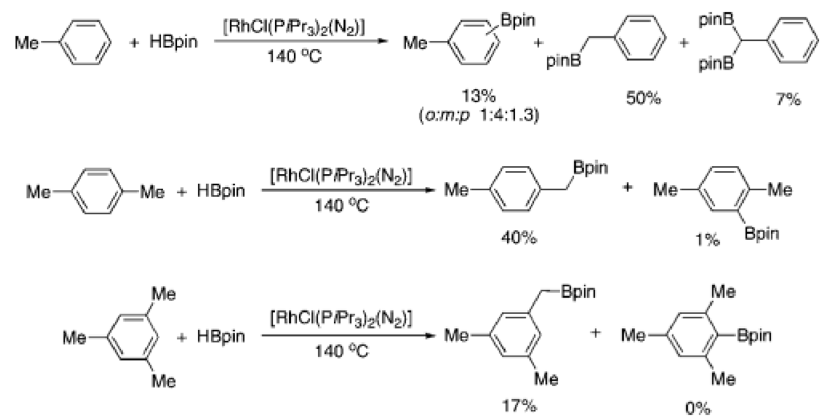
- Electronic Effect on Aliphatic Borylation



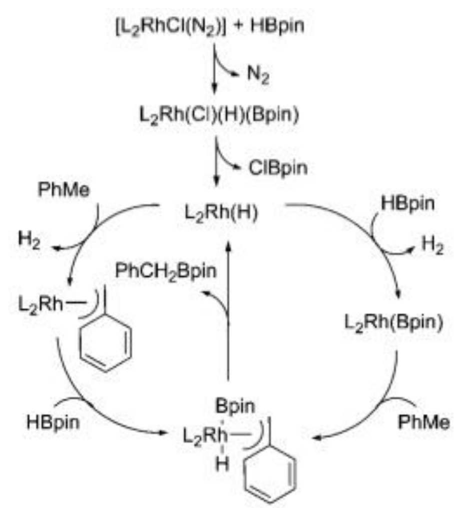
- Rh-catalyzed Borylation of Arenes



- Rh-Catalyzed Benzylic Borlation of Toluene



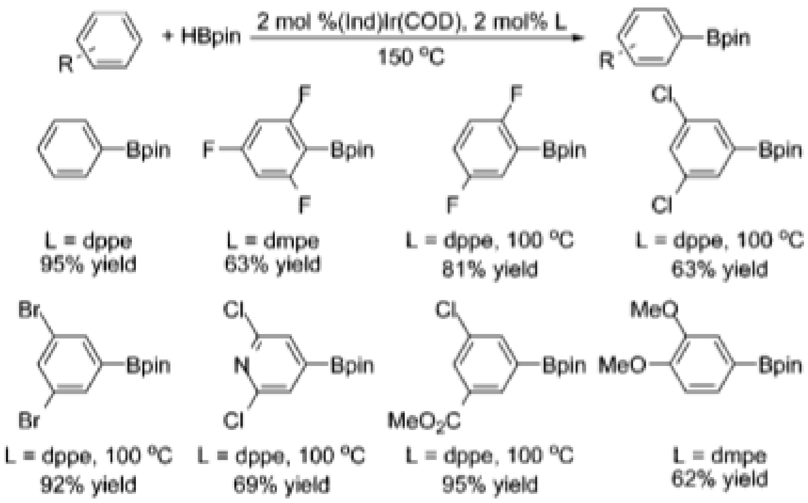
- Two Potential Mechanisms

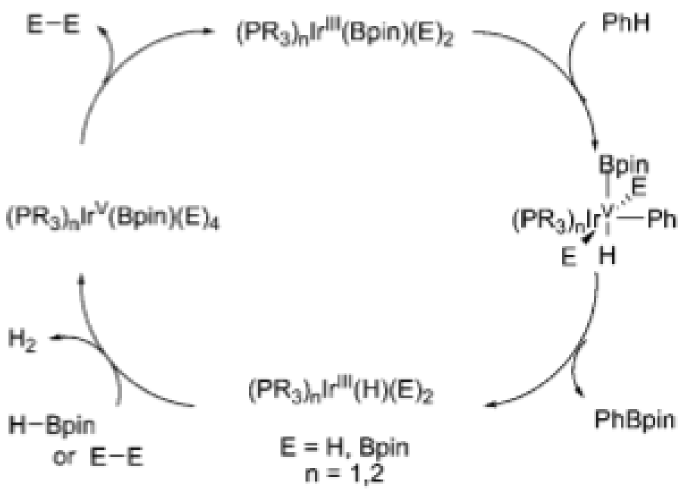


3.4. Iridium

- Arene Borylation

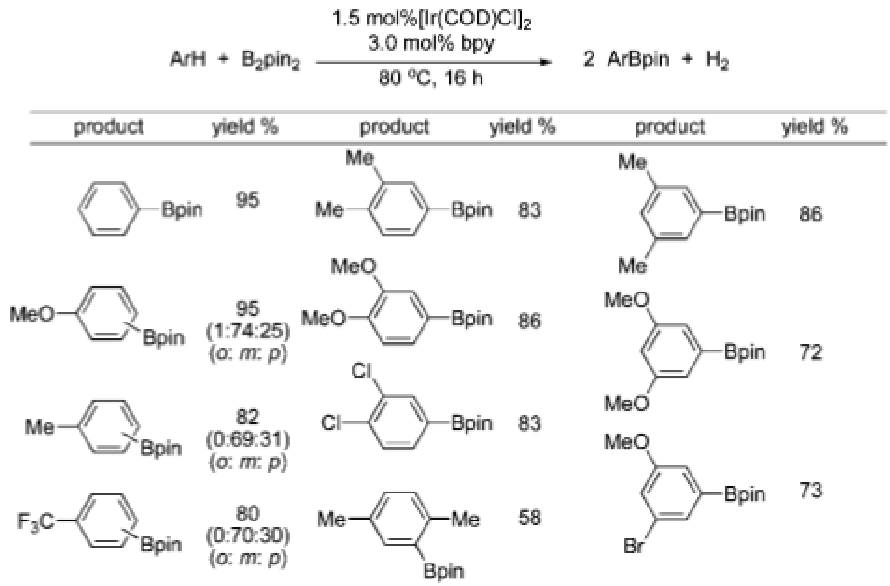
I. Arene Borylation with Iridium catalysts containing Phosphine Ligands

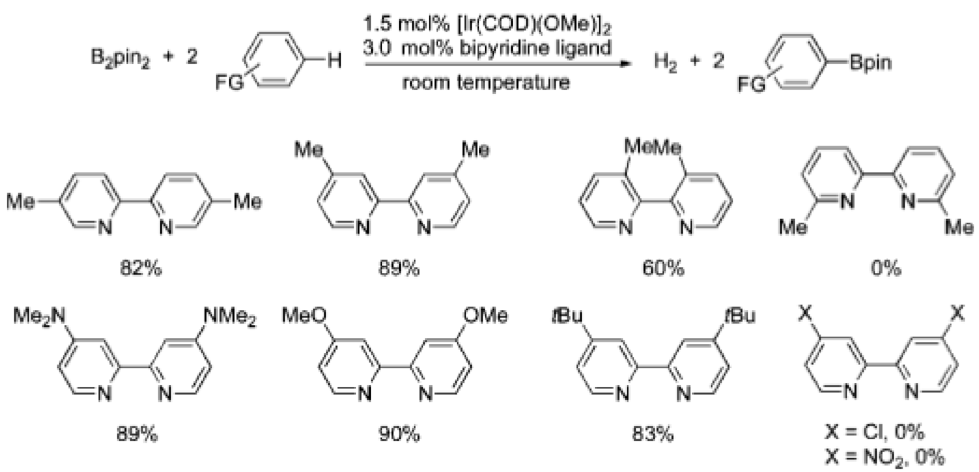




Proposed Mechanism

II. Arene Borylation with Iridium catalysts containing Bipyridine Ligands

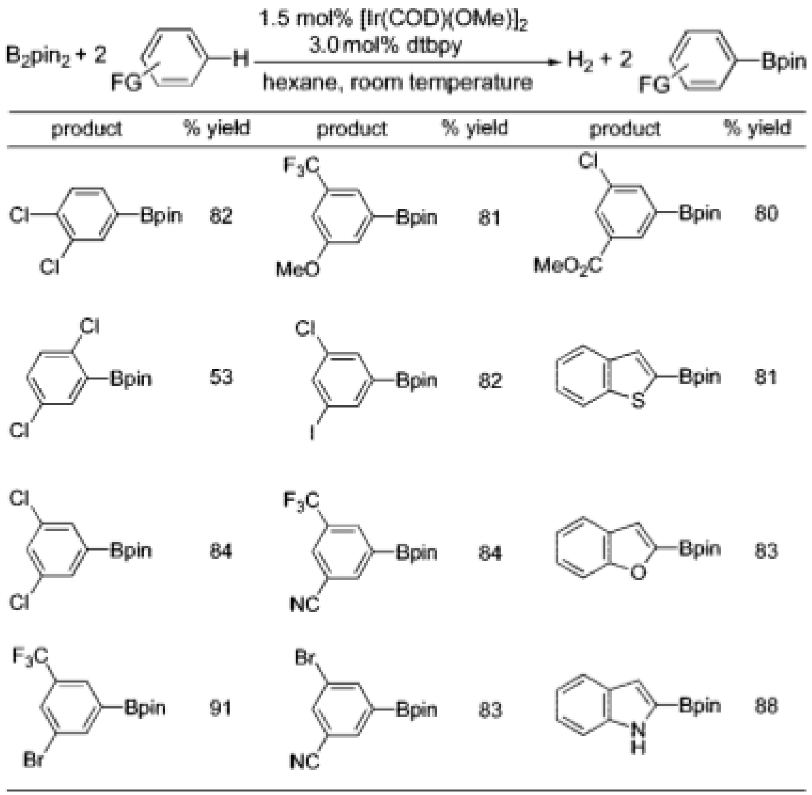




Steric effect

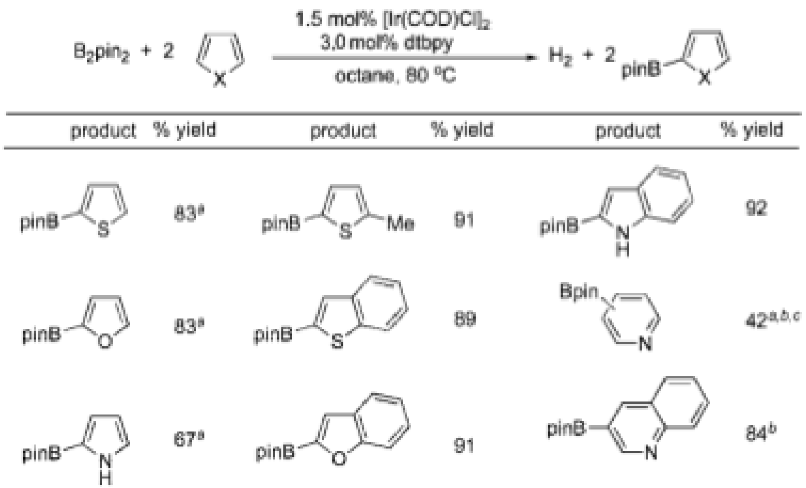
Electronic effect

II. Arene Borylation with Iridium catalysts containing Bipyridine Ligands

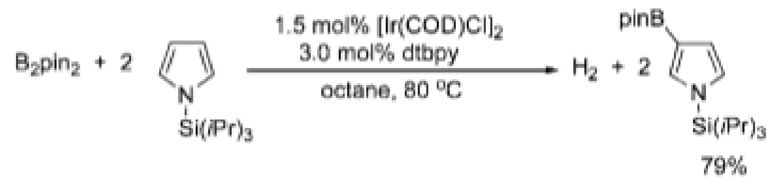


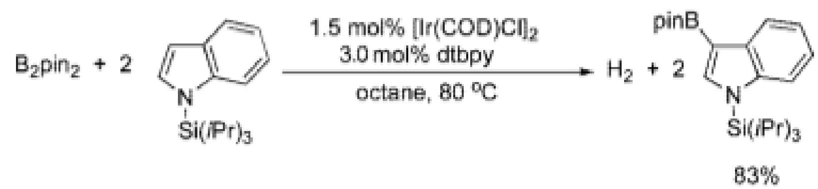
It was faster in nonploar solvents, such as hexane, than in more coordination, more polar solvents, such as dimethyl ether (DME), and dimethyl formamide (DMF).

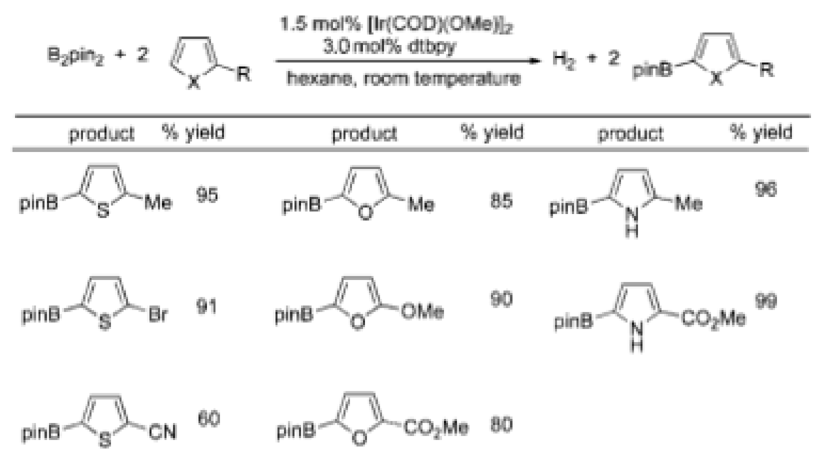
- Heteroarene Borylation



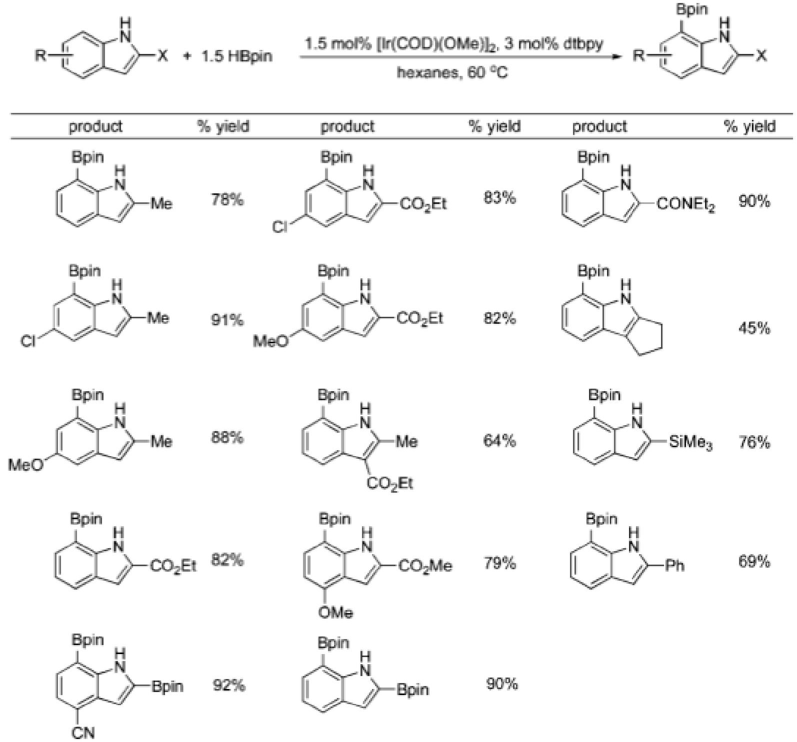
[a] Diborylated products were produced in 12−17% yield. [b] Reaction conducted at 100 °C. [c] Ratio of 3- and 4-boryl pyridine was 67:33.

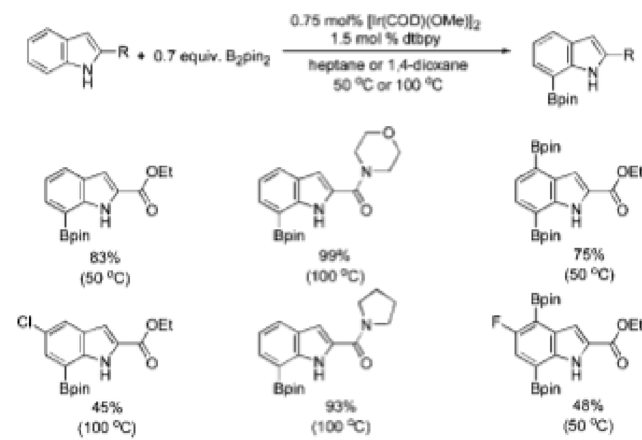




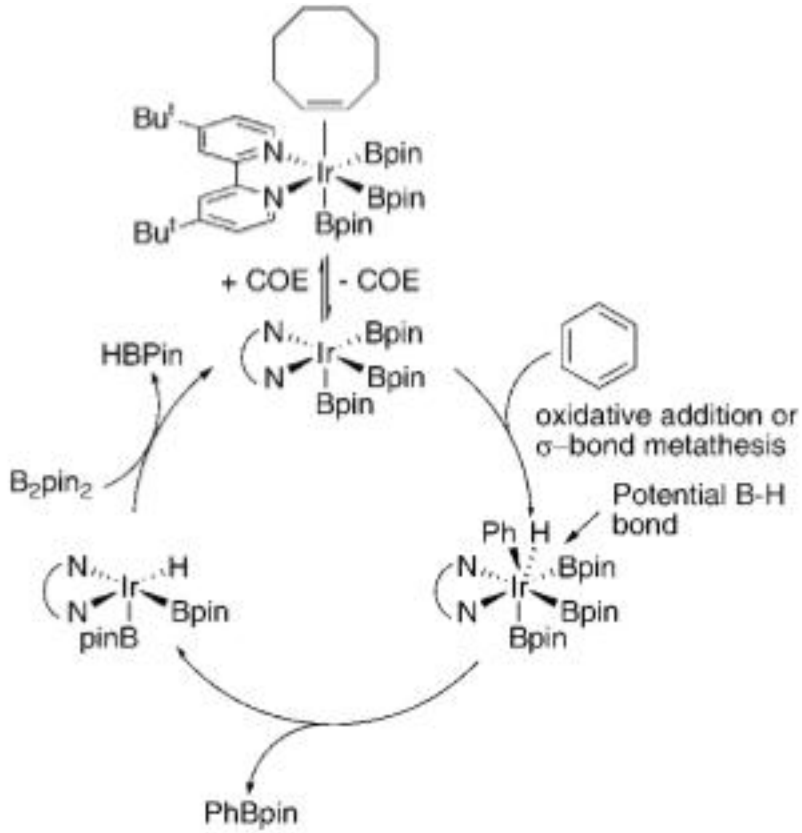


- Indole Borylation





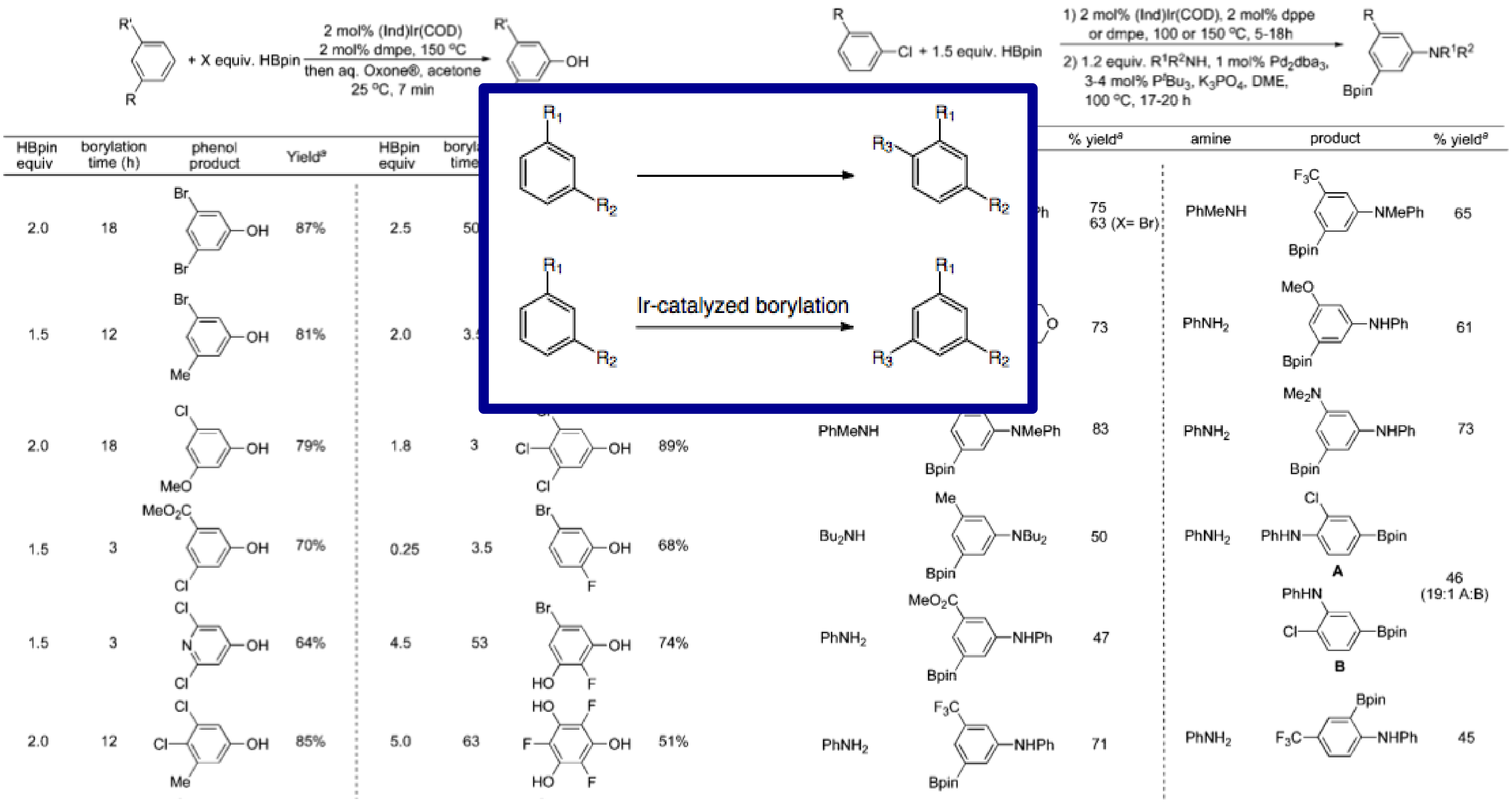
- Proposed Mechanism for the Iridium-Catalyzed Borylation of Arenes



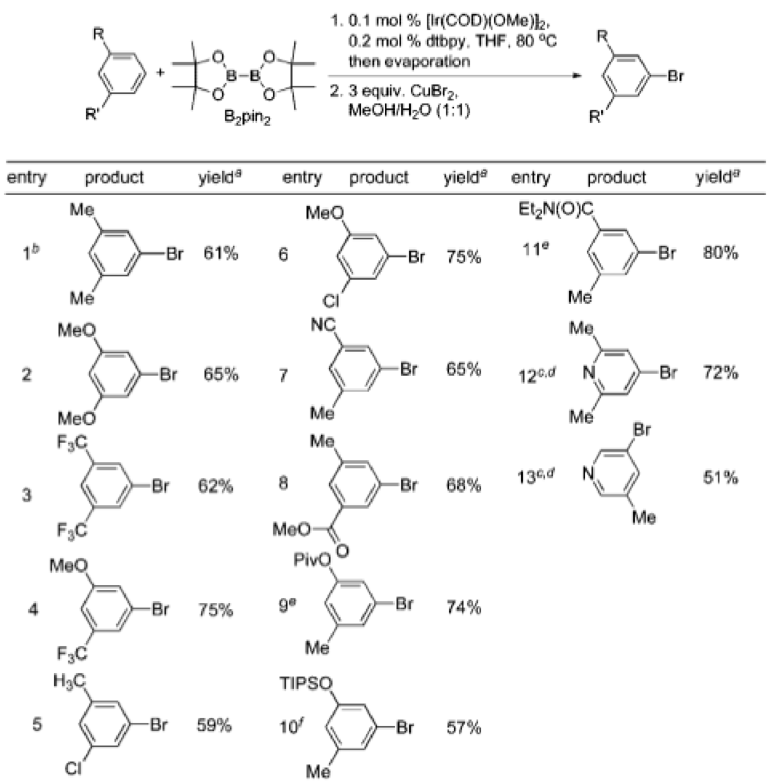
4. Application

- One-Pot Syntheses of Organic Compounds

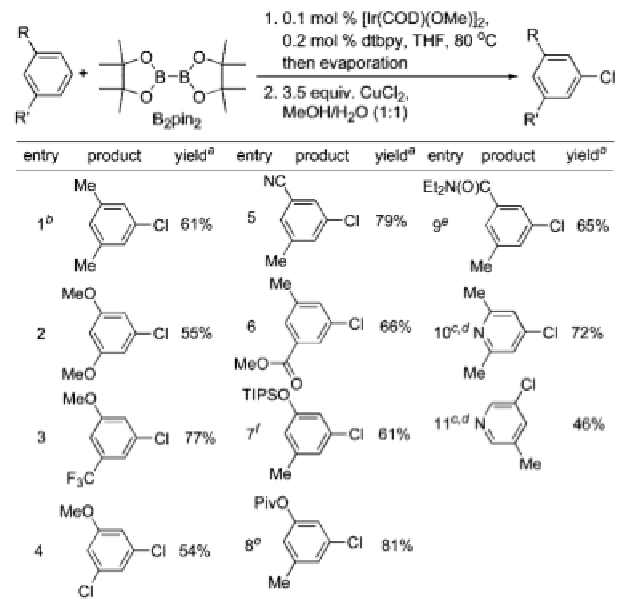
I. One-Pot Syntheses of Phenols and Arylamines



II. One-Pot Syntheses of Aryl Bromides and Aryl Chorides

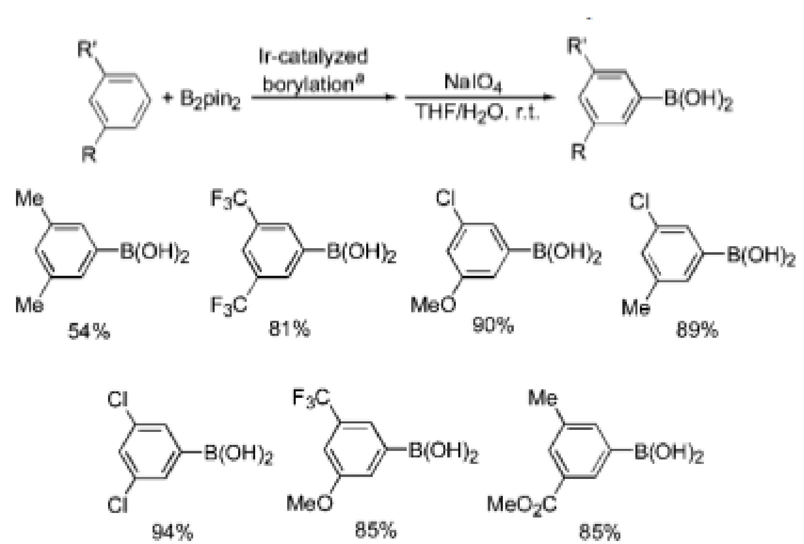


[a] Average isolated yield from two experiments. All reactions were run on a 2.0 mmol scale. [b] 0.5 mol % **1** and 1.0 mol % **2** used. [c] Contained 2% pinacol by ^{1}H NMR spectroscopy. [d] 3.0 mol % **1** and 6.0 mol % **2** used. [e] 1.0 mol % **1** and 2.0 mol % **2** used. [f] 2.0 mol % **1** and 4.0 mol % **2** used.

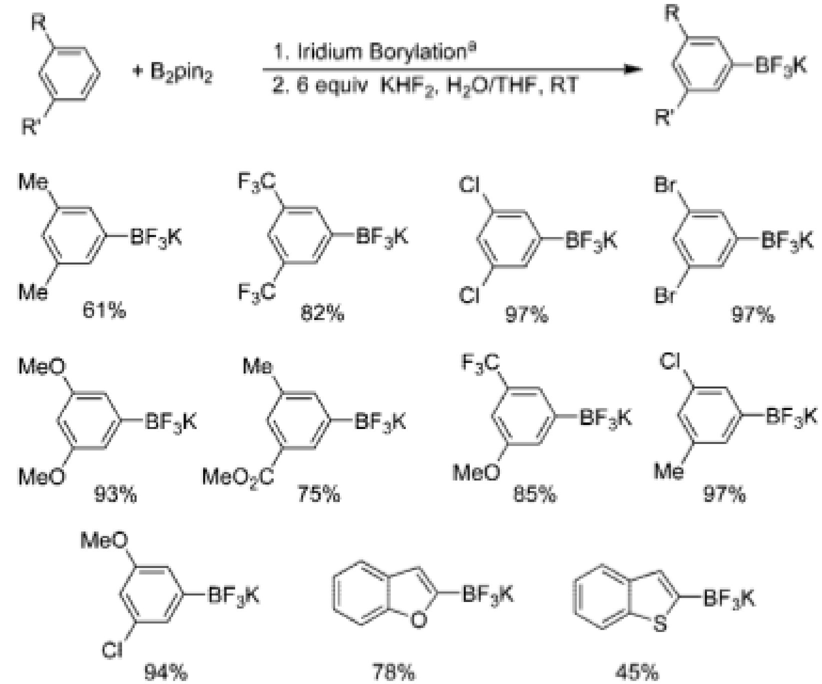


[a] Average isolated yield from two experiments. All reactions were run on a 2.0 mmol scale. [b] 0.5 mol % **1** and 1.0 mol % **2** were used. [c] Contained 2% pinacol by 1H-NMR spectroscopy. [d] 3.0 mol % **1** and 6.0 mol % **2** used. [e] 1.0 mol % **1** and 2.0 mol % **2** used. [f] 2.0 mol % **1** and 4.0 mol % **2** used.

III. Conversion of Arenes to Arylboronic Acids and Potassium Aryltrifluoroborates



[a] Borylation of arene was carried out on a 10 mmol scale using 0.1% $[Ir(COD)Cl]_2$ and 0.2% dtbpy in THF at 80 °C. $NaIO_4$ (15.0 mmol) was added to 5 mmol of crude ArBpin in a 4:1 THF/H_2O mixture. [b] Isolated yields on a 5 mmol scale of arene. Yields are the average of two reactions.



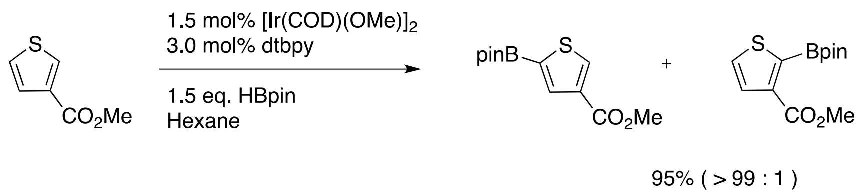
[a] Borylation of arene was carried out on a 10 mmol scale using 0.1% $[Ir(COD)Cl]_2$ and 0.2% dtbpy in THF at 80 °C. KHF_2 (5.7 mmol) was added to 5 mmol of crude ArBpin in a 4:1 THF/H_2O mixture. Isolated yields on a 5 mmol scale of arene.

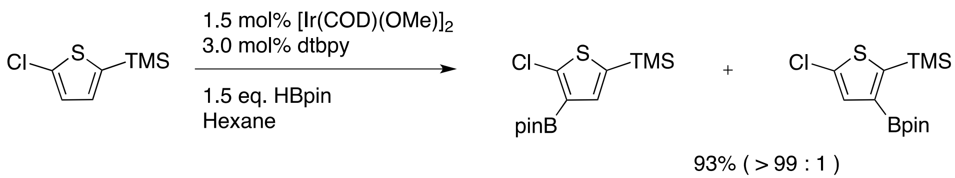
5. Conclusion

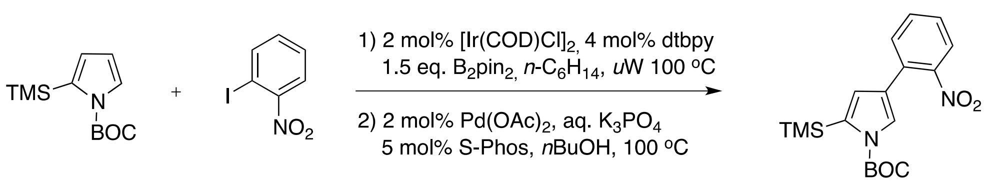
1. In contrast to many of these methods, the borylation of aryl C-H bonds occurs under mild conditions, with high turnover numbers and with a broad tolerance for functional groups.

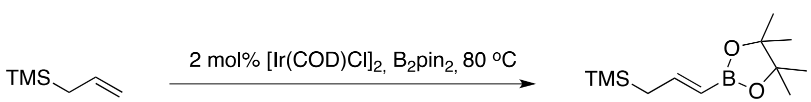
2. Considering the rapid development of this C-H borylation chemistry, one can anticipate that further advances will lead to C-H bond functionalizations with main group reagents that will lead, in turn, to additional, widely used synthetic methods.

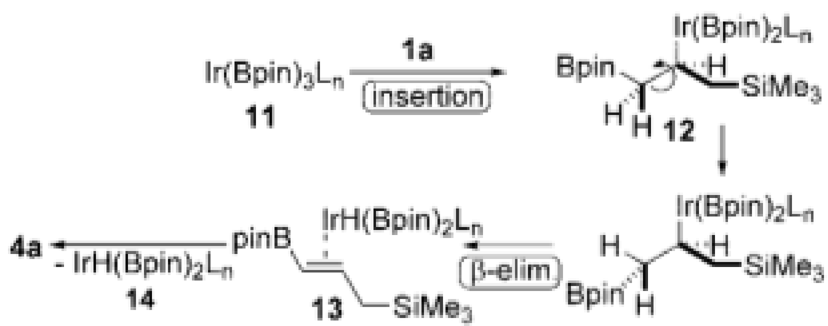
Thank you


S
CO2Me
1.5 mol% [Ir(COD)(OMe)]2
3.0 mol% dtbpy
1.5 eq. HBpin
Hexane
pinB
S
CO2Me
+
S
Bpin
CO2Me
95% (> 99 : 1)


Cl
S
TMS
1.5 mol% [Ir(COD)(OMe)]2
3.0 mol% dtbpy
1.5 eq. HBpin
Hexane
Cl
S
TMS
pinB
+
Cl
S
TMS
Bpin
93% (> 99 : 1)


TMS
N
BOC
+
I
NO2
1) 2 mol% [Ir(COD)Cl]2, 4 mol% dtbpy
1.5 eq. B2pin2, n-C6H14, uW 100 oC
2) 2 mol% Pd(OAc)2, aq. K3PO4
5 mol% S-Phos, nBuOH, 100 oC
NO2
TMS
N
BOC


TMS
2 mol% [Ir(COD)Cl]2, B2pin2, 80 oC
TMS
O
B
O


Ir(Bpin)3Ln
11
1a
insertion
Ir(Bpin)2Ln
Bpin
H
SiMe3
H
H
12
Ir(Bpin)2Ln
H
H
SiMe3
Bpin
H
β-elim
IrH(Bpin)2Ln
pinB
13
SiMe3
4a
- IrH(Bpin)2Ln
14