Boron Chemistry : Non-metal Catalyzed Borylation of Unsaturated C-C Bond

Reporter: Bo Xing

1. Background

2. Organocatalyzed borylation

   2.1 hydroborylation of unsaturated carbonyl compounds

   2.2 diborylation of unactivated alkenes and alkynes

3. Summary

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Organoboronic compounds —— a crucial reagent for C-C bond formation

Until 2009, C-B bond formation remained exclusively in the domain of metal-based catalysis.

Pt, Rh, Ni, Cu…… largely limited to reactions of acyclic substrates!

New and complementary method is in need

—— focus on the organocatalyst

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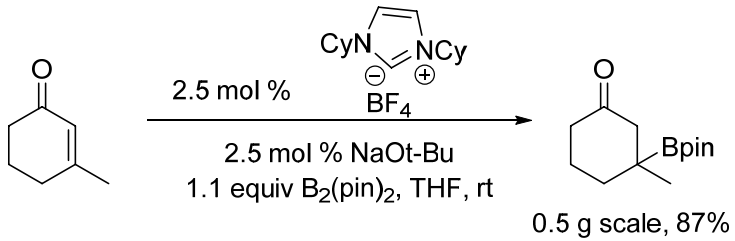
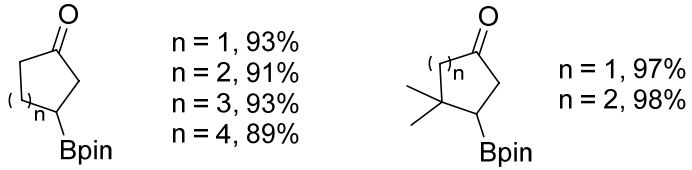
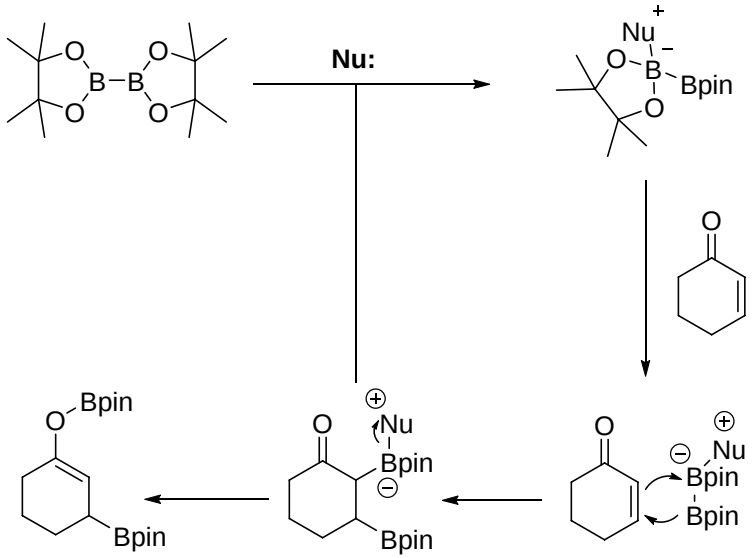
First report



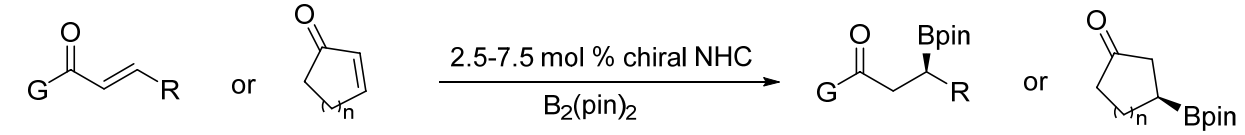


Proposed model for borylation:



J. Am. Chem. Soc., 2009, 131, 7253

Efforts for enantioselective C-B bond formation

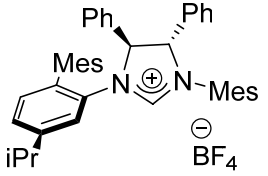


G = alkyl, aryl, alkoxy, amino or H
R = alkyl or aryl

n = 1-3

base assisted: 20 % DBU
additives: 20 equiv MeOH

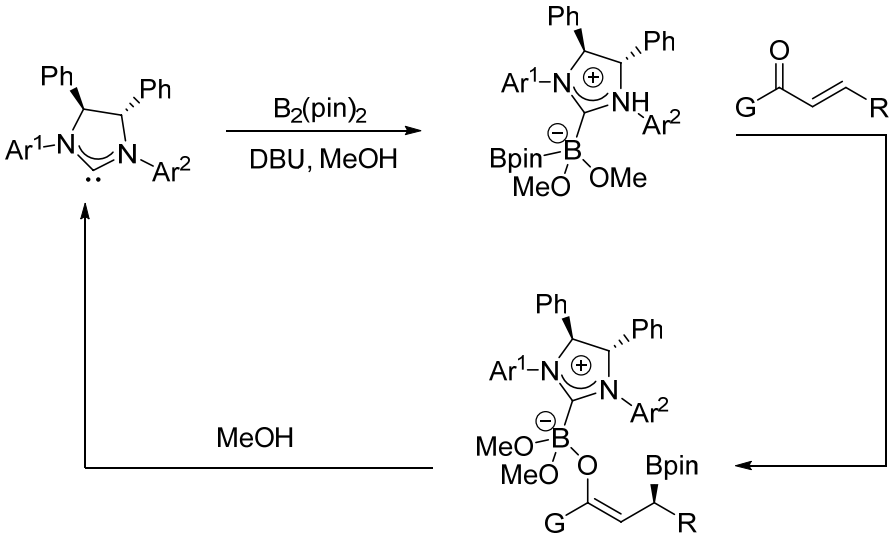
broad substrate scope ?
efficiency ?
enantioselectivity ?



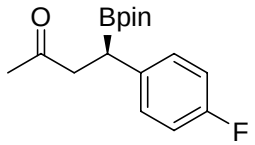
G = Me, Ph, i-Pr, n-Bu, MeO, H, Weinerb amine
mild conditions, rt or 60-70 °C
moderate to good yield,
high enantioselcetive excess

J. Am. Chem. Soc., 2012, 134, 8277

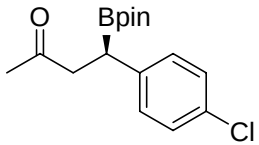
Impact of DBU and MeOH



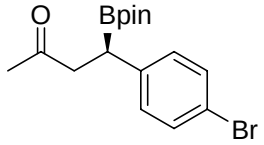
20 mol% vs 100 mol% DBU



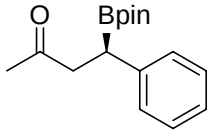
with 20 mol % DBU:
27% conv, 18% yield, 98:2 ee
with 100 mol % DBU:
> 98% conv, 91% yield, > 98:2 ee



with 20 mol % DBU:
34% conv, 19% yield, 91:9 ee
with 100 mol % DBU:
> 98% conv, 65% yield, 95:5 ee



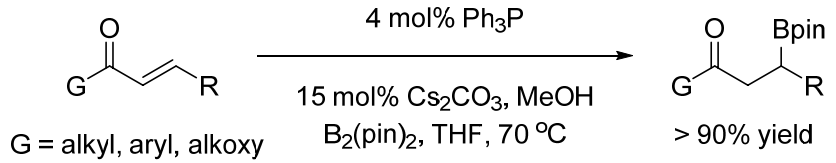
with 20 mol % DBU:
60% conv, 43% yield, 92:8 ee
with 100 mol % DBU:
> 90% conv, 62% yield, 93:7 ee

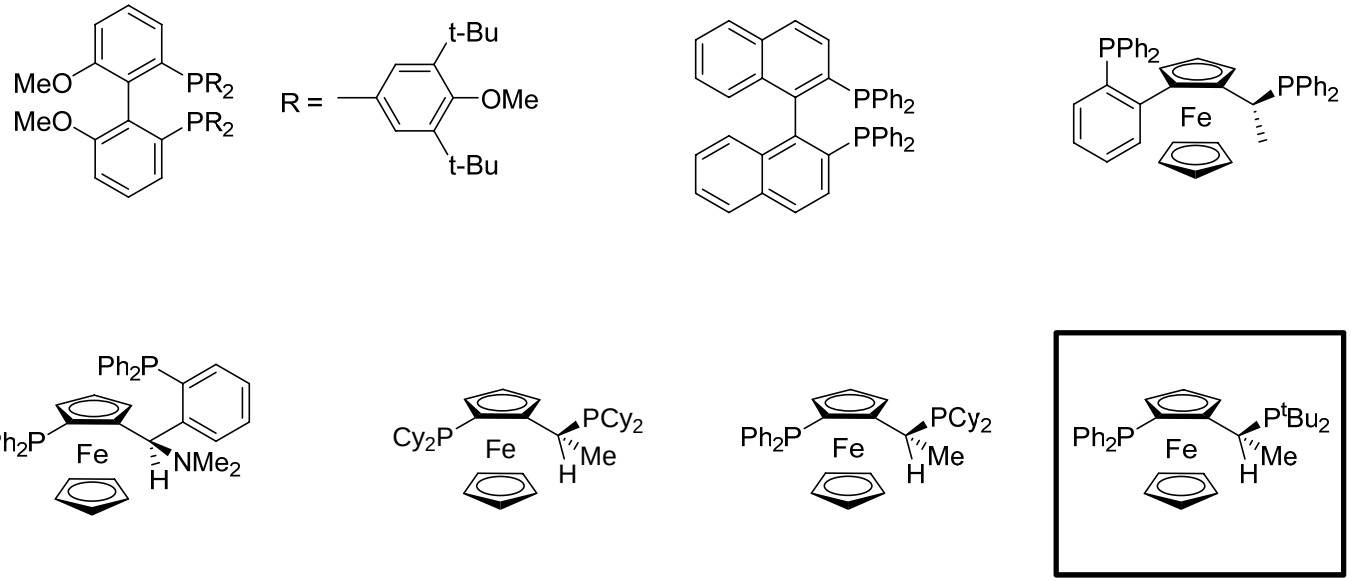


with 20 mol % DBU:
82% conv, 72% yield, 93.5:6.5 ee
with 100 mol % DBU:
> 98% conv, 80% yield, 93.5:6.5 ee

J. Am. Chem. Soc., 2012, 134, 8277

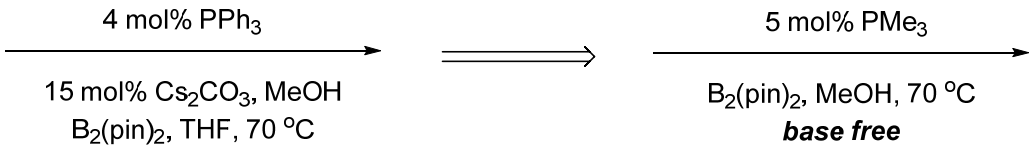
Phosphine——as another organocatalyst



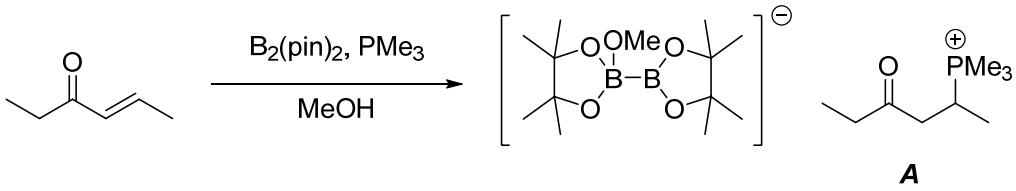


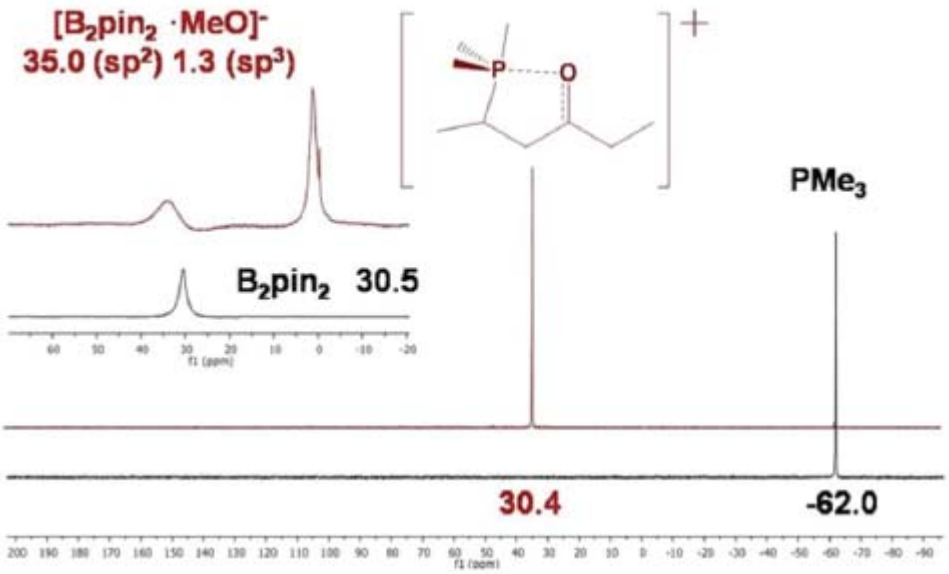
Angew. Chem. Int. Ed., 2010, 49, 5130

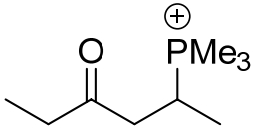
Conditions further optimized



Mechanism research



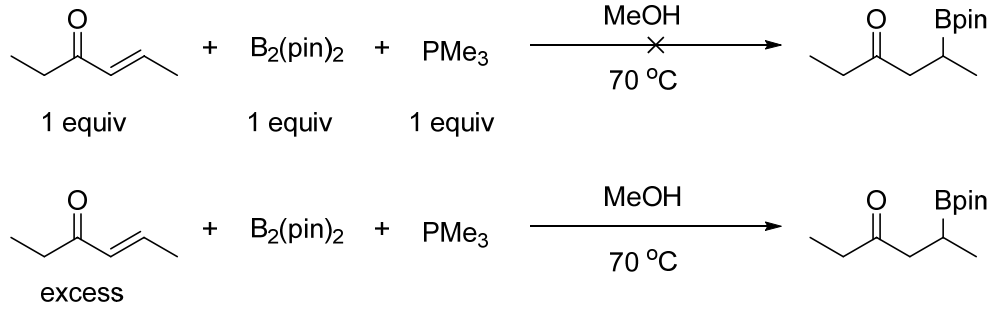


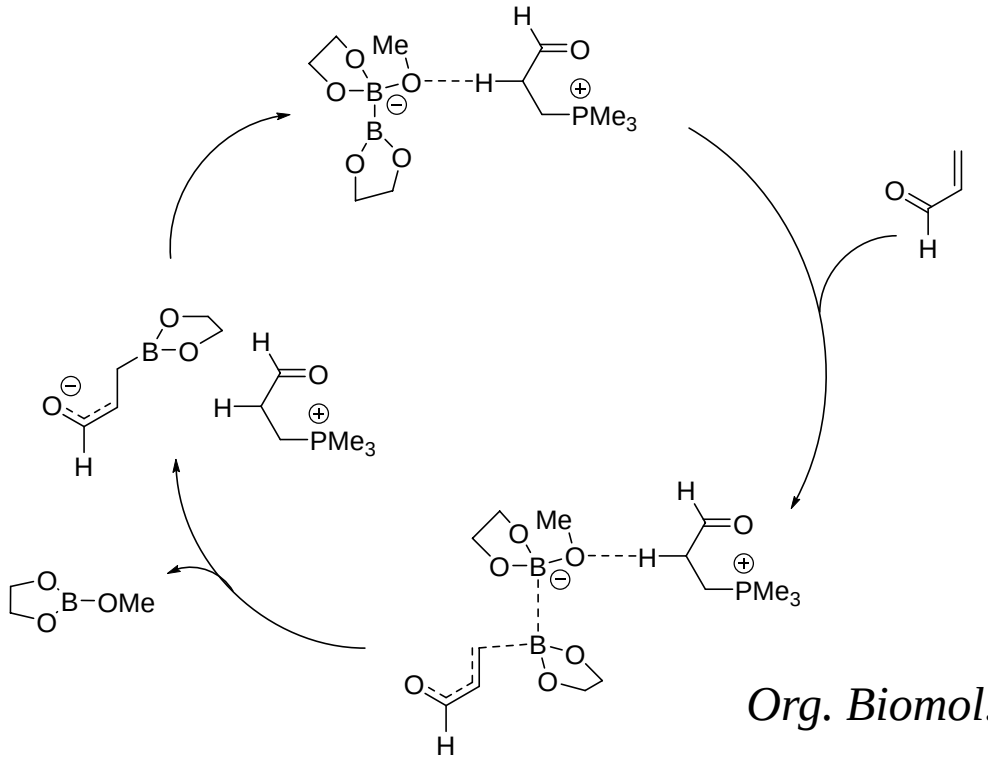


confirmed by ^{31}P-^{1}H NMR

Org. Biomol. Chem., 2012, 10, 9677

New discovery





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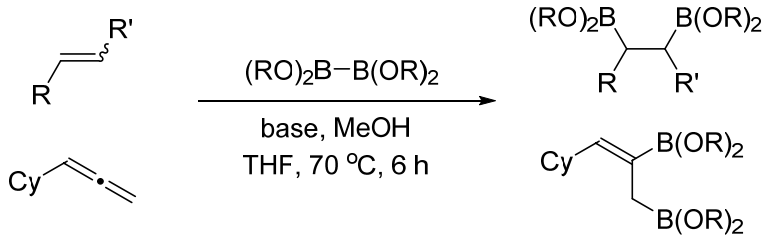
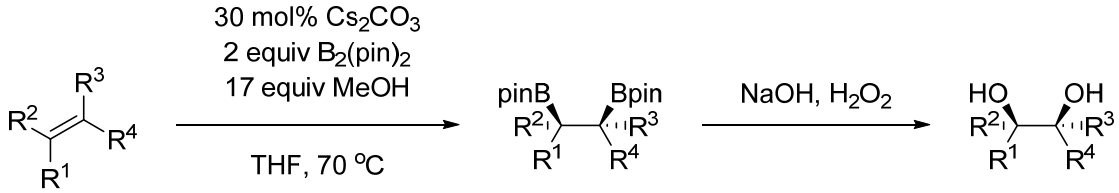


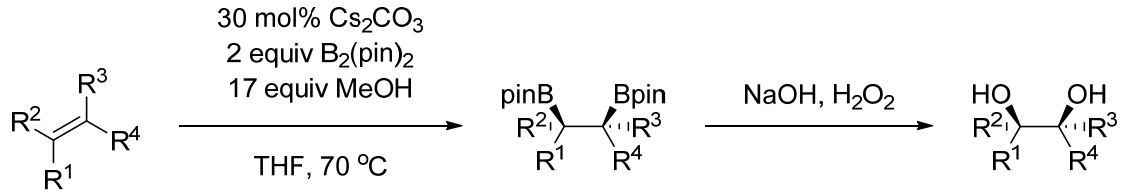
Angew. Chem. Int. Ed., 2011, 50, 7158

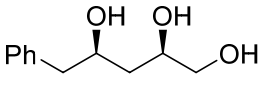
Hydroxyl-directed

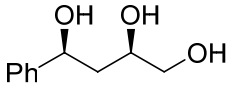


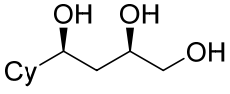
J. Am. Chem. Soc., 2014, 136, 9264

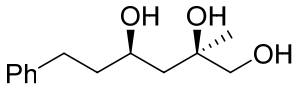
Hydroxyl-directed diborylation of alkenes

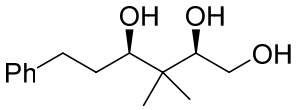


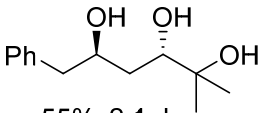

74%, 13:1 dr

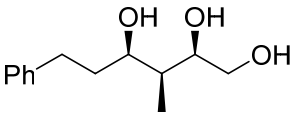

84%, 14:1 dr

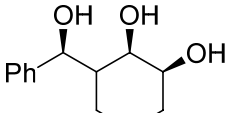

51%, 5:1 dr

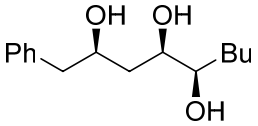

64%, 17:1 dr

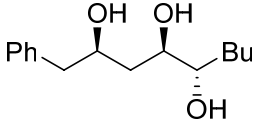

69%, 20:1 dr

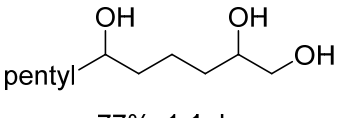

55%, 2:1 dr

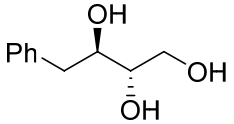

80%, 7:1 dr


94%, 20:1 dr


64%, 5:1 dr
from E alkene


79%, 9:1 dr
from Z alkene


77%, 1:1 dr


47%, 1.8:1 dr

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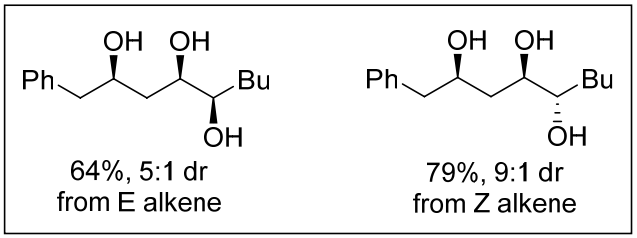
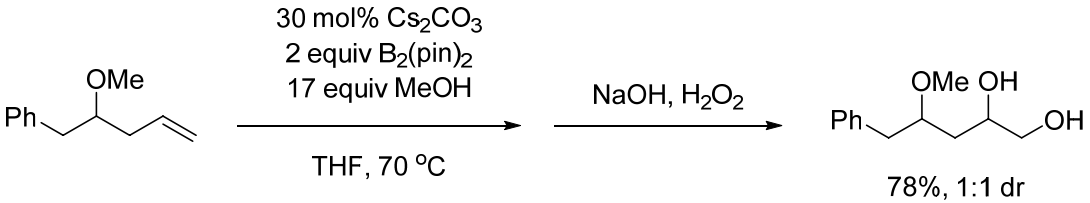
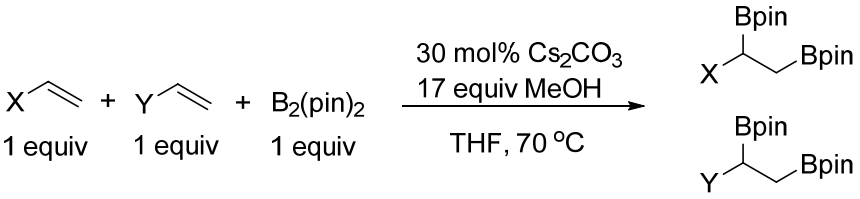
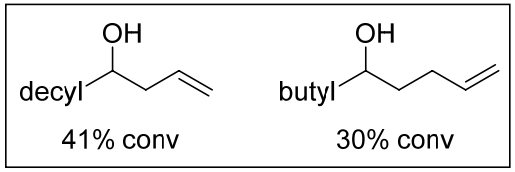
Stereochemical model

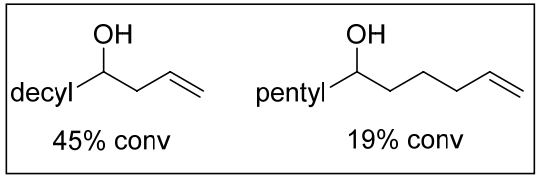


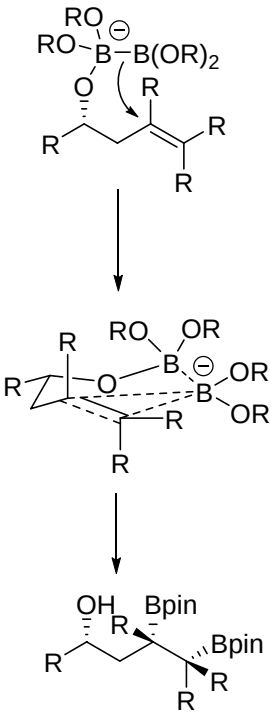
⟹ ***syn addition***











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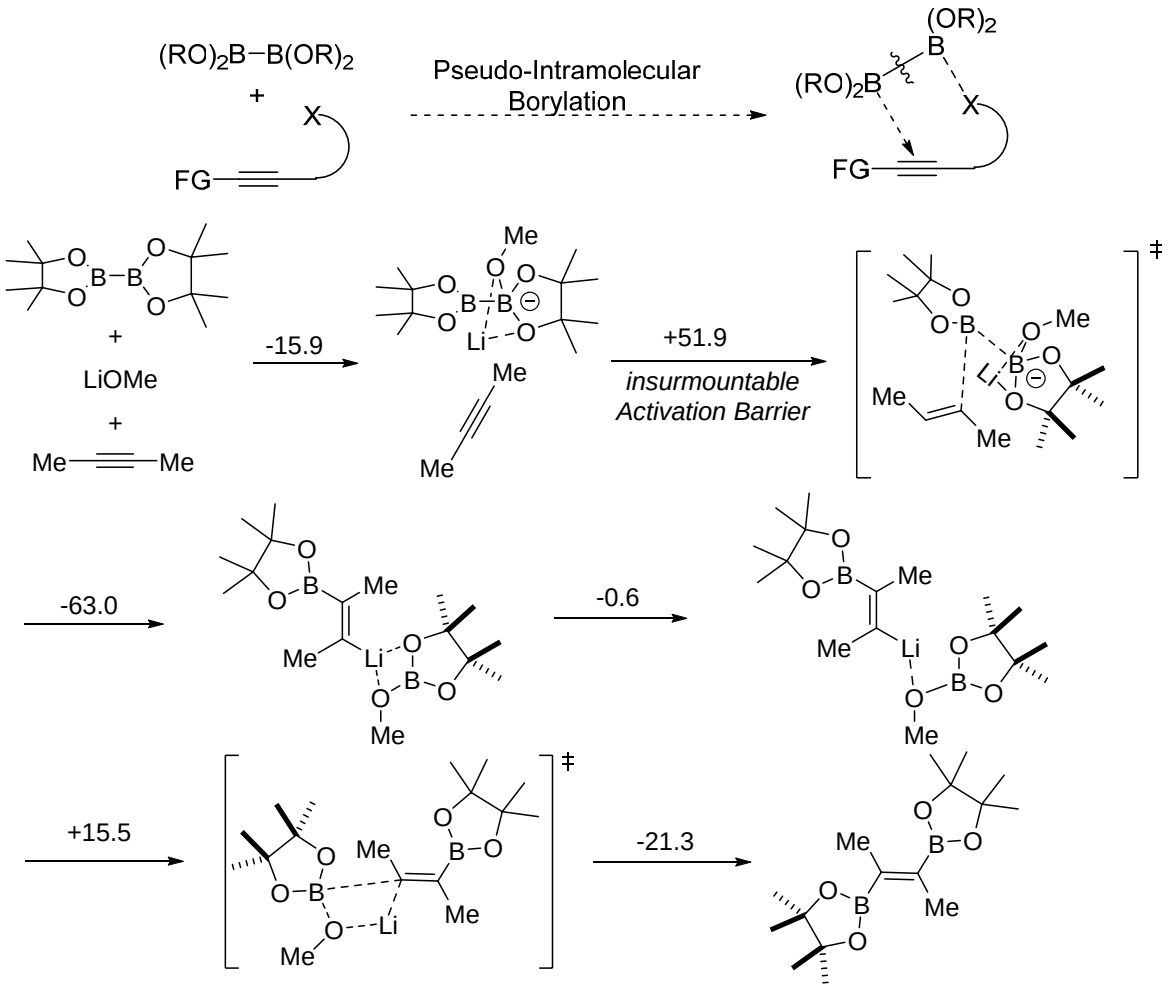
Trans diborylation of alkynes



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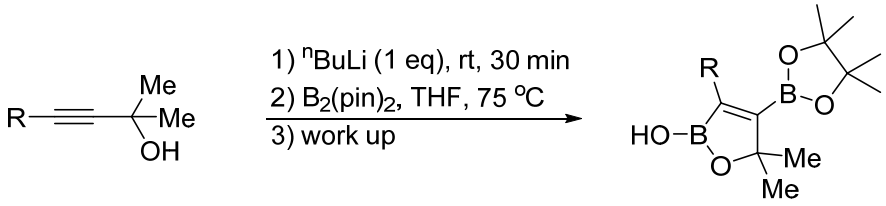
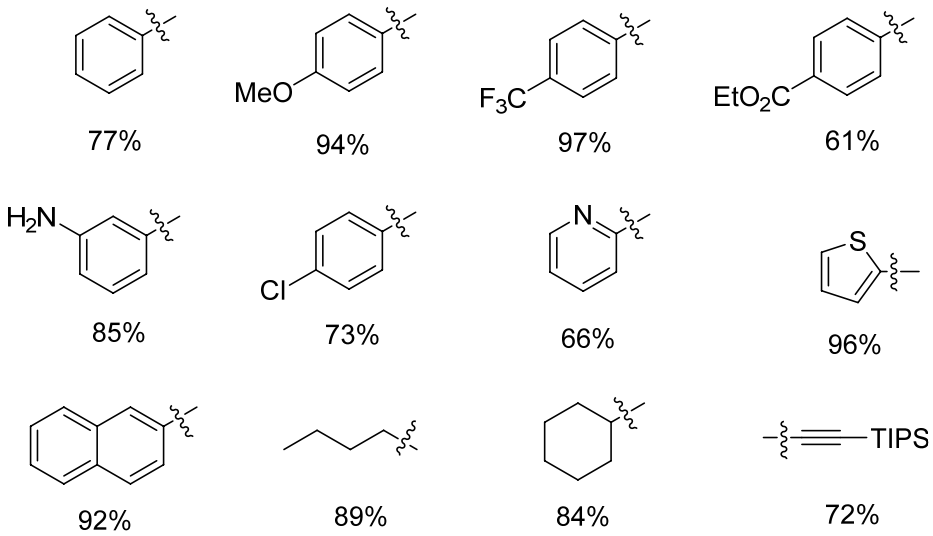
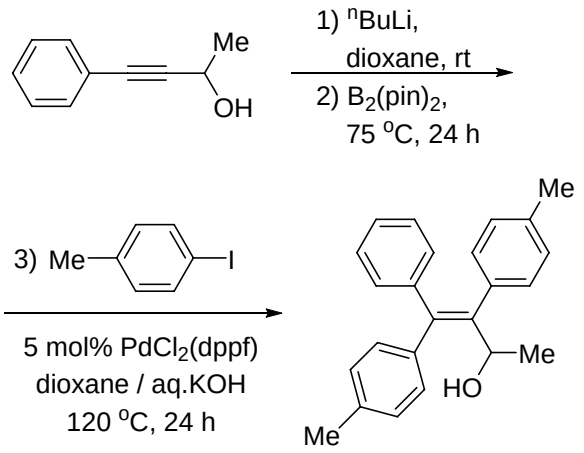
Trans diborylation of alkynes





Thorpe-Ingold effect

One-pot cross-coupling process



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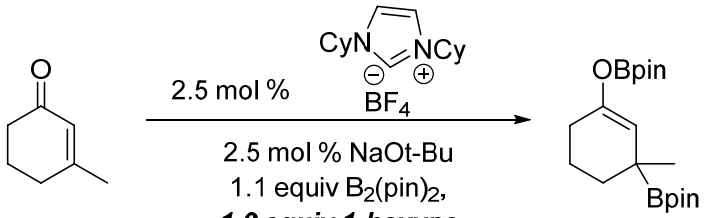
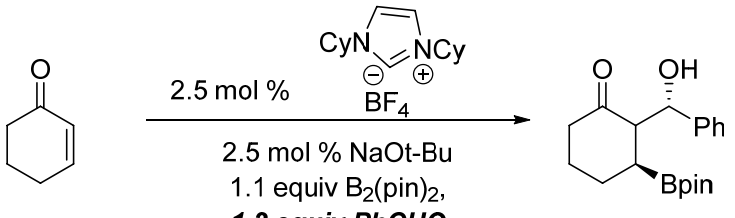
Hydroborylation of unsaturated carbonyl compounds:

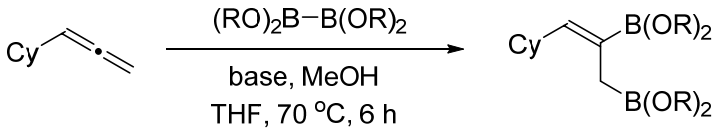


with 2.5 mol% CuOt-Bu: < 2% conv
without Cu salt: 85% conv, 81% yield

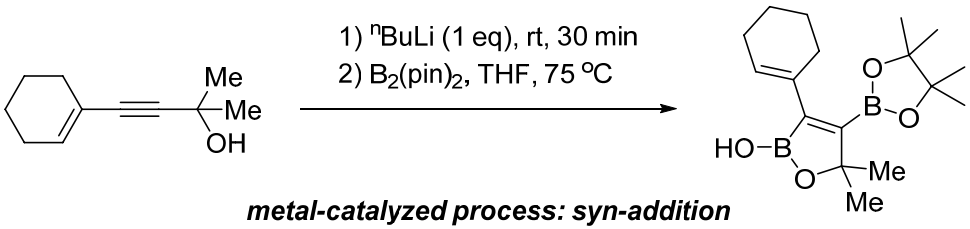


with 2.5 mol% CuOt-Bu: 31% yield
without Cu salt: 85% yield, 98:2 dr

Diborylation of unactivated alkenes and alkynes:



metal-catalyzed process: 2,3-selectivity
metal-free process: 1,2-selectivity



metal-catalyzed process: syn-addition
metal-free process: anti-addition

Thank you