# Radical-Induced 1, 2-Migrations of Boron Ate Complexes

Speaker： Shutao Qi

Supervisor: Prof. Junliang Zhang

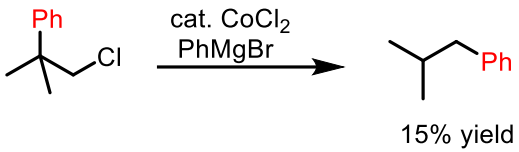
# Content

# Content

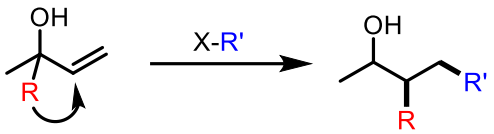
# Introduction

## *Radical-induced 1,2-migrations*

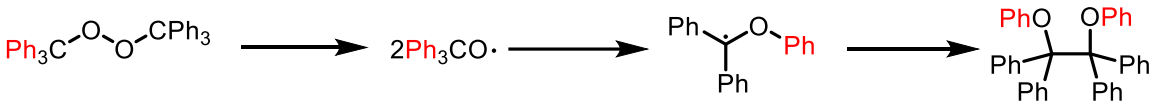
***Neophyl rearrangement***



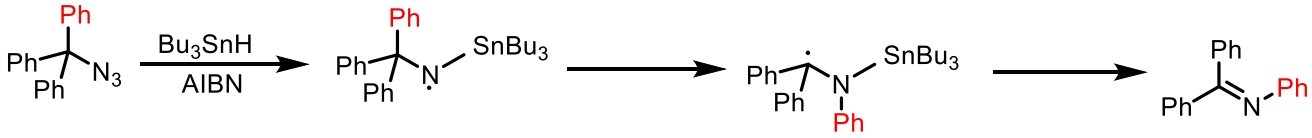

***semi-pinacol rearrangement***




***Radical 1,2-aryl migrations between carbon and oxygen***




***Radical 1,2-aryl migration from carbon to nitrogen***



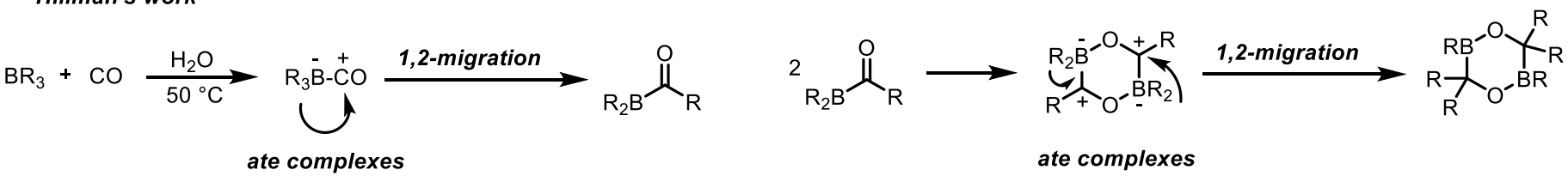


M. S. Kharasch et al, *J. Am. Chem. Soc*., **1944**, *66*, 1438.
H. Wieland et al, *Chem. Ber*., **1911**, *44*, 2550.
J. Y. Do et al, *Chem. Commun*., **1995**, 1607.
Y.-Q. Tu et al, *Chem. Soc. Rev*. **2015**, *44*, 5220

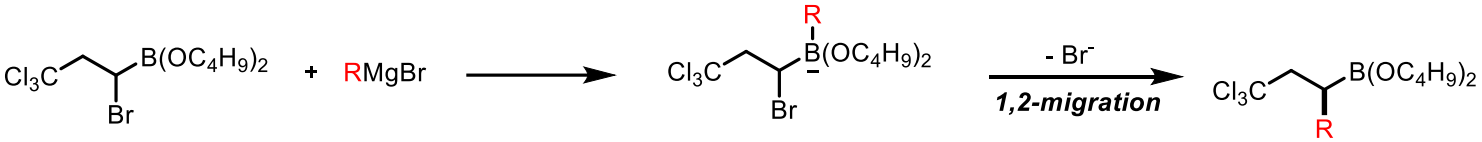
# Introduction

## *1,2-Metalate migrations of boron ate complexes*

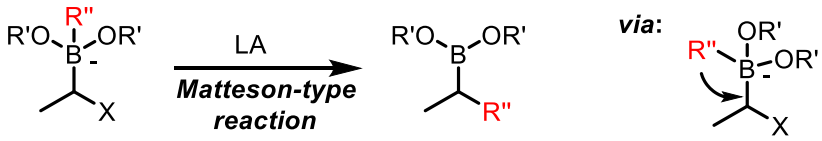
***Hillman's work***



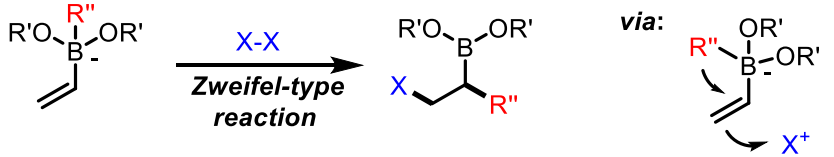

***Matteson's work***




***Lewis acid-induced 1,2-boron ate migrations to $sp^3$ carbons:***




***Electrophile-induced 1,2-boron ate migrations to $sp^2$ carbons:***



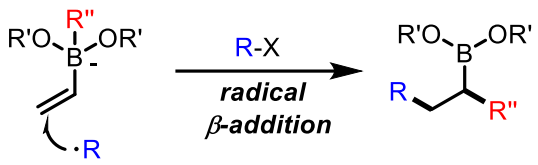


M. E. D. Hillman, *J. Am. Chem. Soc*. **1962**, *84*, 4715.
D. S. Matteson et al, *J. Am. Chem. Soc*. **1963**, *85*, 2599.
D. S. Matteson, R. Ray, *J. Am. Chem. Soc*. **1980**, *102*, 7590
G. Zweifel et al, *J. Am. Chem. Soc*. **1967**, *89*, 3652

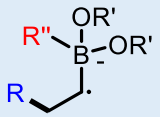
# Introduction

## *Radical-induced 1,2-migrations of boron ate complexes*

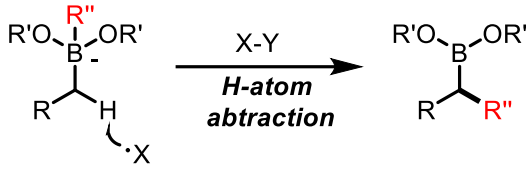
***Radical-induced 1,2-boron ate migrations to $sp^2$ carbons:***



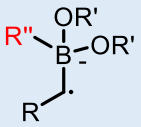

***via*:**




***Radical-induced 1,2-boron ate migrations to $sp^3$ carbons:***

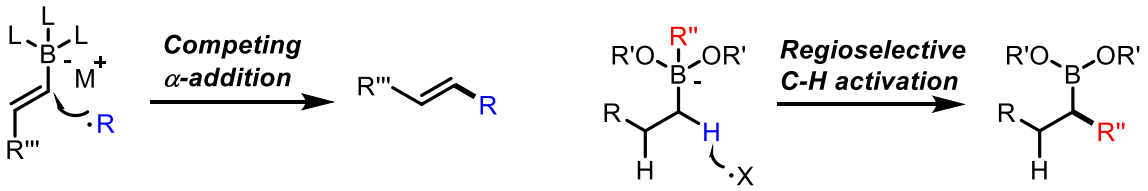



***via*:**

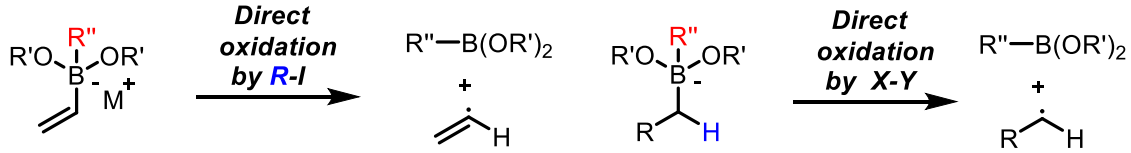



***Main challenges:***

(I)



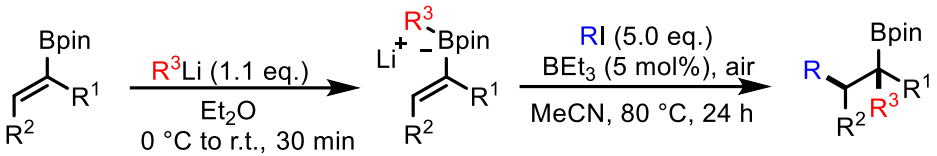

(II)



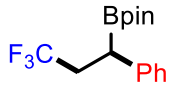
# Content

# 1, 2-Migration to $sp^2$ Carbons

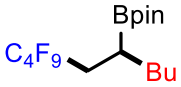
***First example***



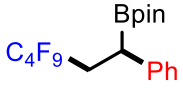

***Selected examples***



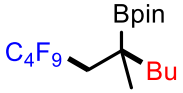

23%



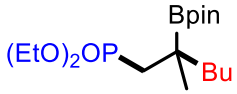

66%



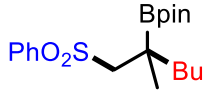

68%



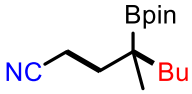

86%



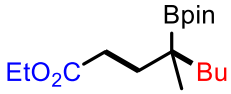

71%



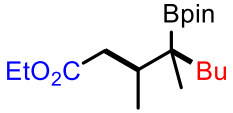

92%




68%




92%




65%, *dr* = 1.6:1

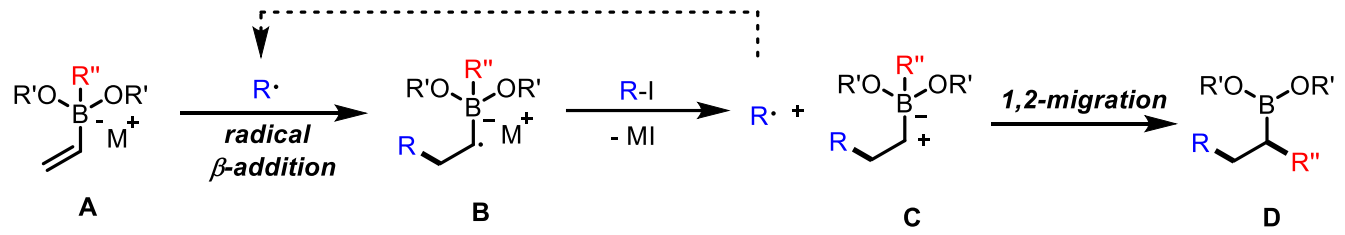


A. Studer et al, *Science,* **2017**, *355*, 936

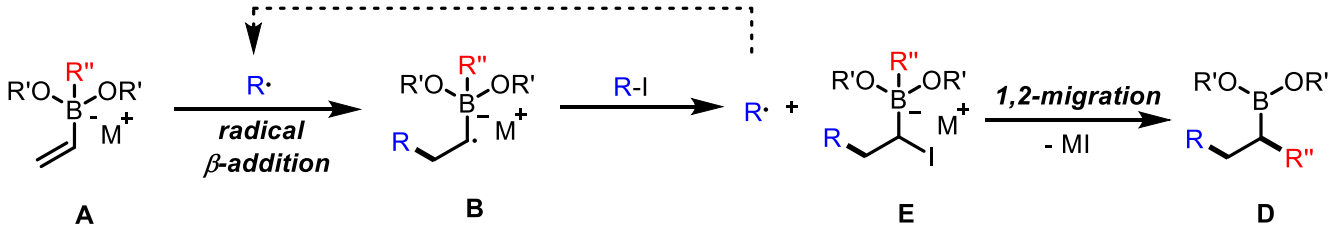
# 1, 2-Migration to $sp^2$ Carbons

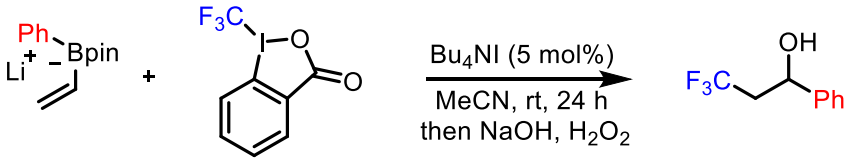
***Mechanistic study***

***a) Electron catalysis, outer-sphere ET:***




***b) Atom transfer addition, inner-sphere ET:***



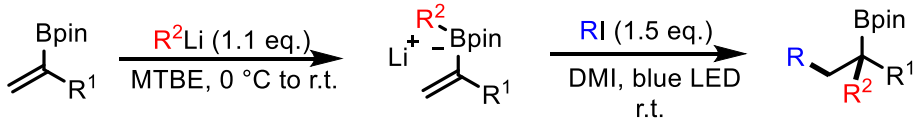





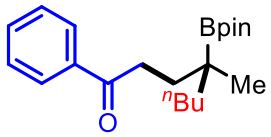

A. Studer et al, *Science,* **2017**, *355*, 936

# 1, 2-Migration to $sp^2$ Carbons

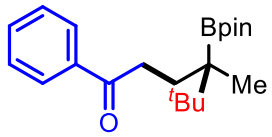
***Light initiation***



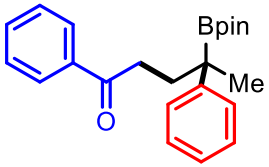

***Selected examples***



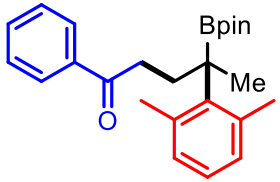

88%



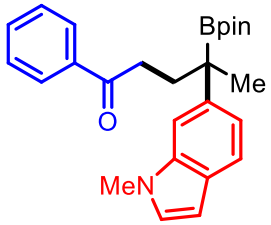

74%



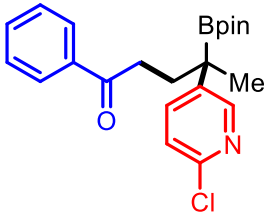

81%



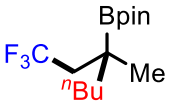

80%



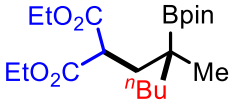

80%




25%




68%



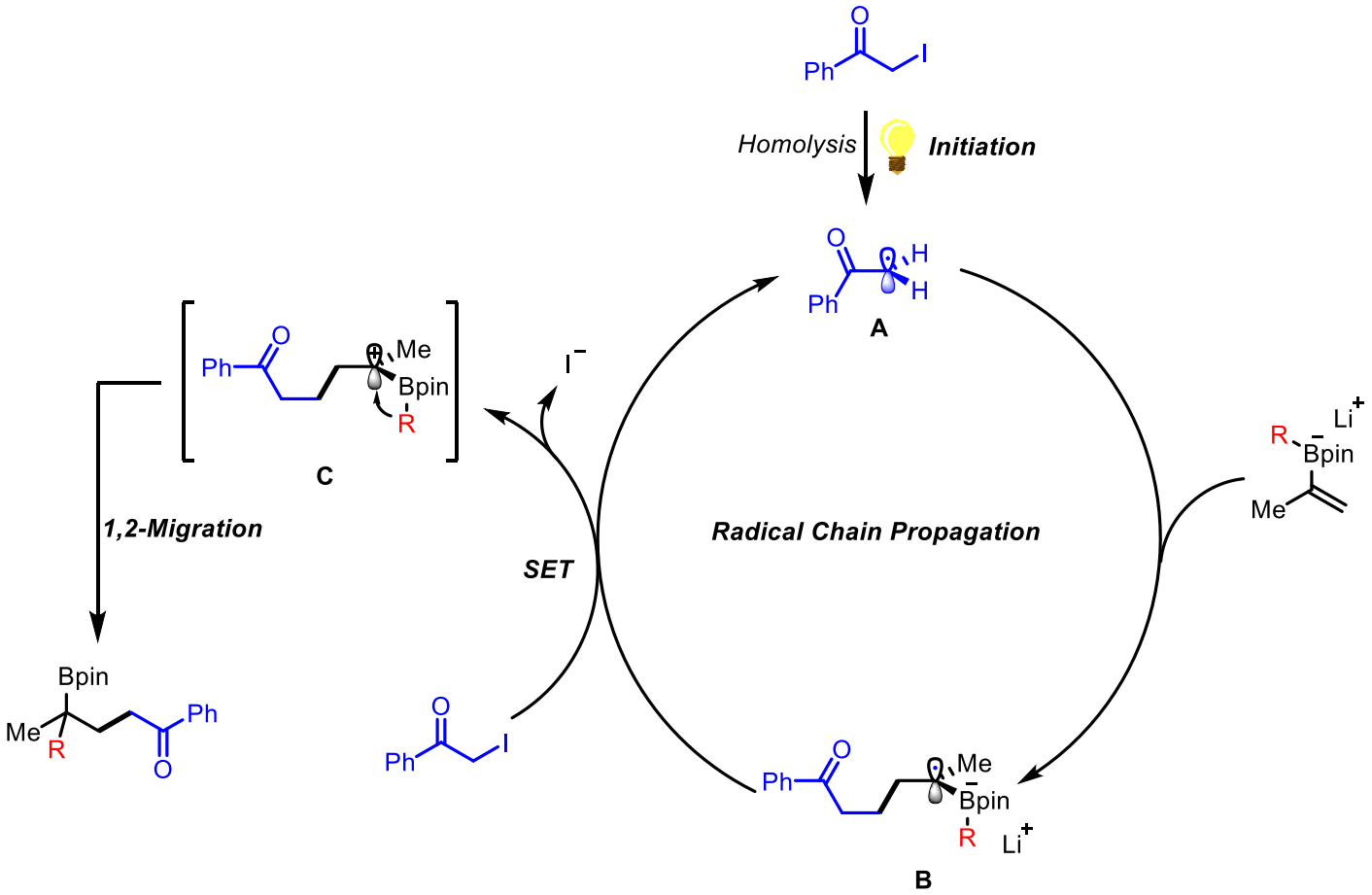

70%



V. K. Aggarwal et al, *J. Am. Chem. Soc*. **2017**, *139*, 5736

# 1, 2-Migration to $sp^2$ Carbons

***Proposed mechanism***

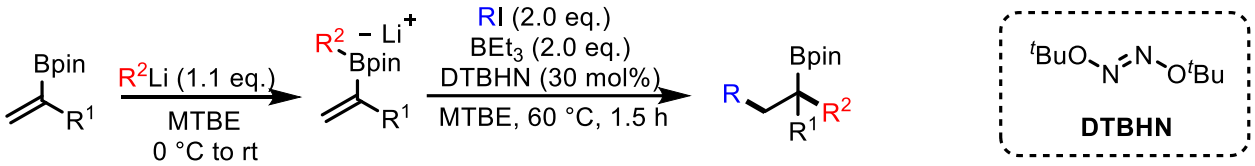




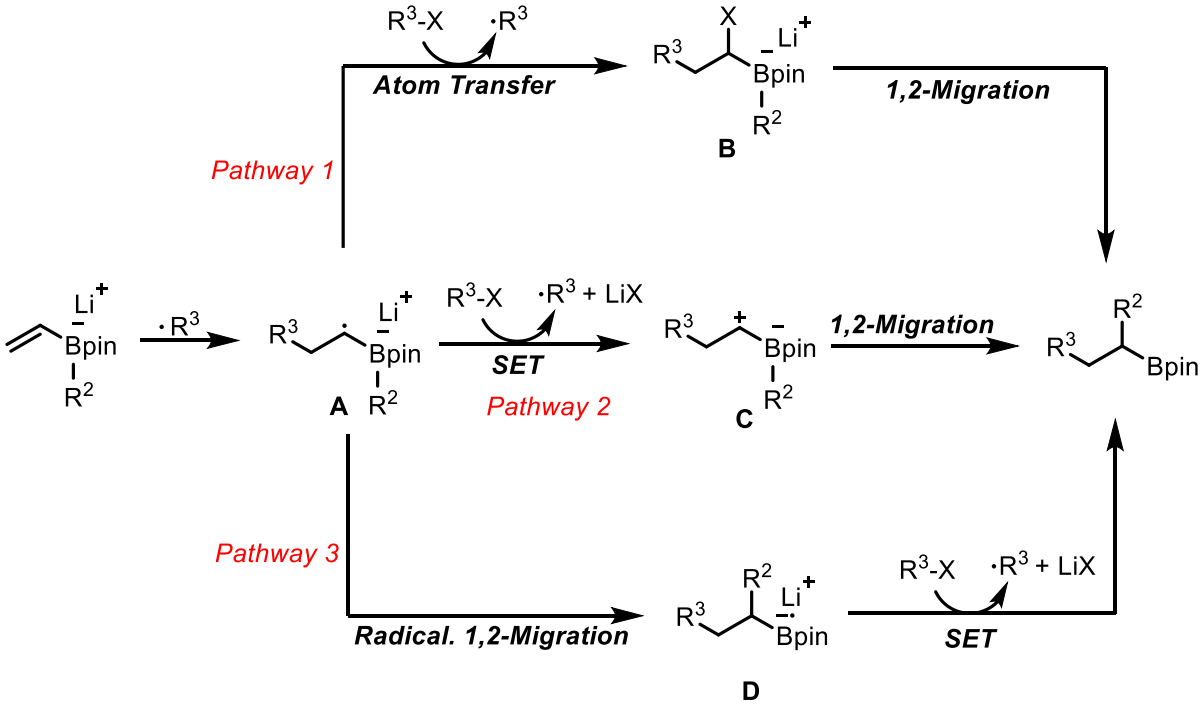

V. K. Aggarwal et al, *J. Am. Chem. Soc*. **2017**, *139*, 5736

# 1, 2-Migration to $sp^2$ Carbons

***Mechanistic study***




***Proposed mechanism***

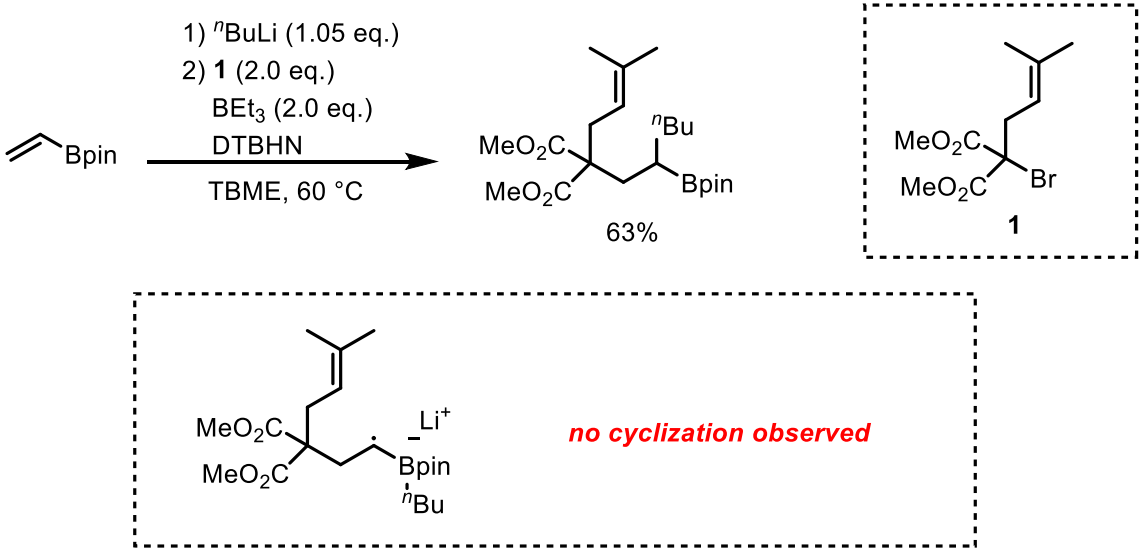




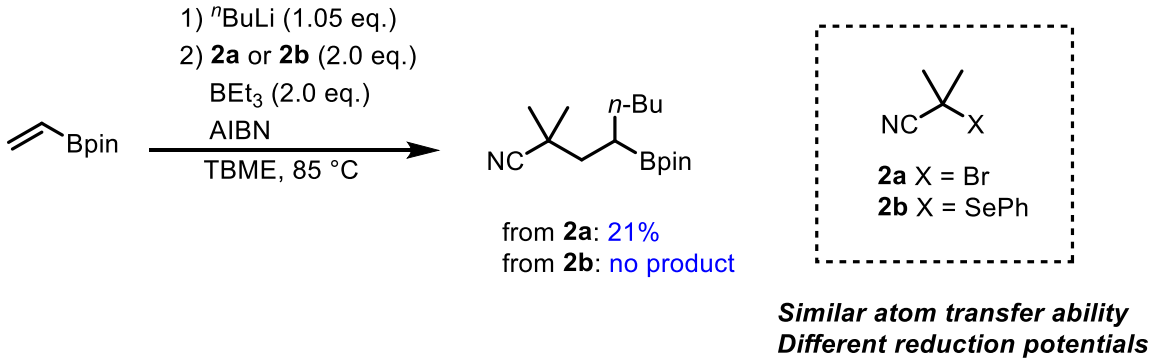

P. Renaud et al, *Chem. Eur. J.* **2018**, *24*, 11498

# 1, 2-Migration to $sp^2$ Carbons

***Radical clock experiment***




***Atom transfer experiment***



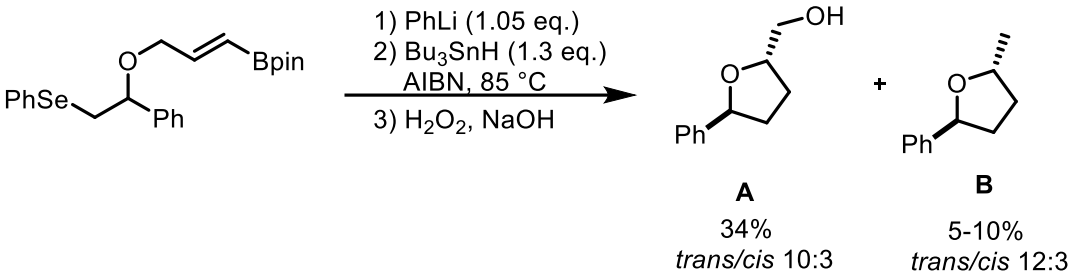

***Similar atom transfer ability***
***Different reduction potentials***

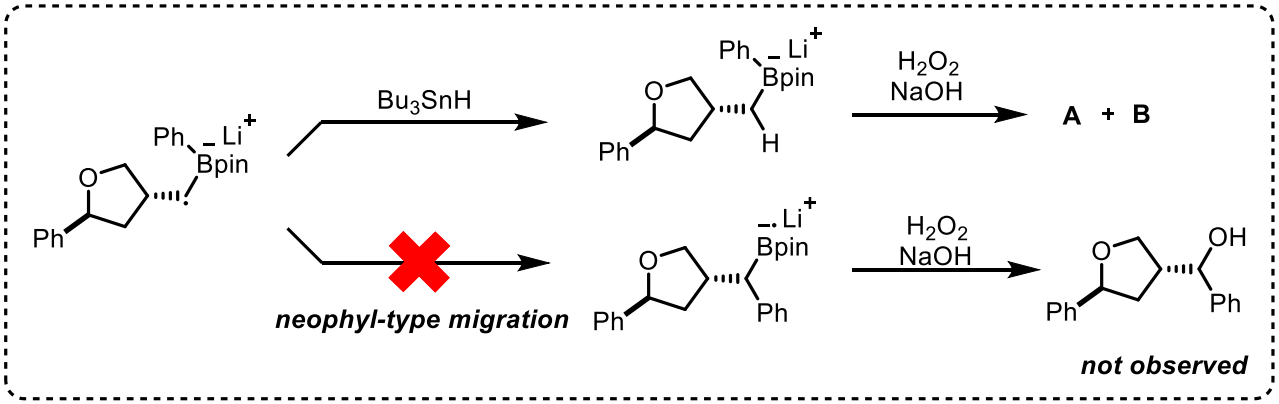


P. Renaud et al, *Chem. Eur. J.* **2018**, *24*, 11498

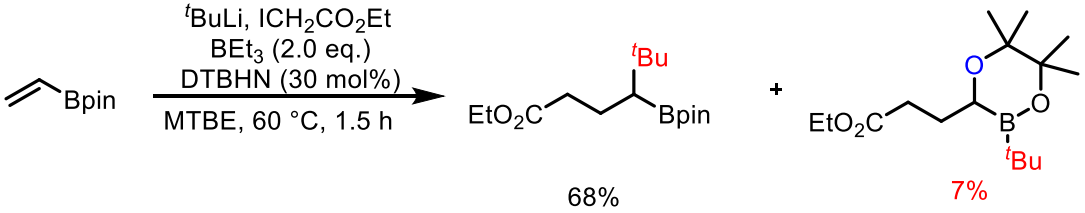
# 1, 2-Migration to $sp^2$ Carbons

***Radical 1,2-migration experiment***




***Oxygen 1,2-migration experiment***



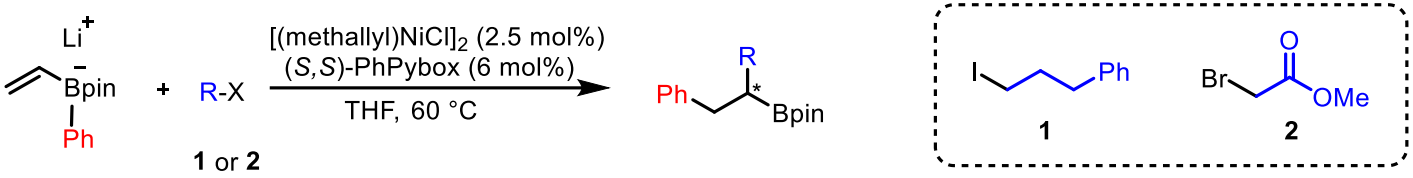

***B-O bond is much stronger than a B-C bond***



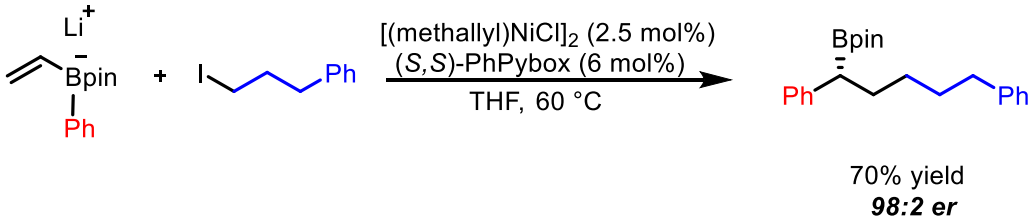
P. Renaud et al, *Chem. Eur. J.* **2018**, *24*, 11498

# 1, 2-Migration to $sp^2$ Carbons

***Metal-induced 1,2-migration***

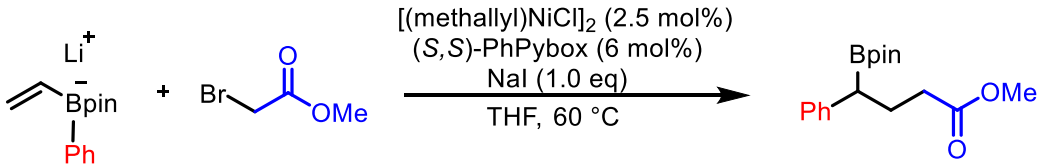



***For non-active alkyl halide***




70% yield
***98:2 er***

***For active alkyl halide***



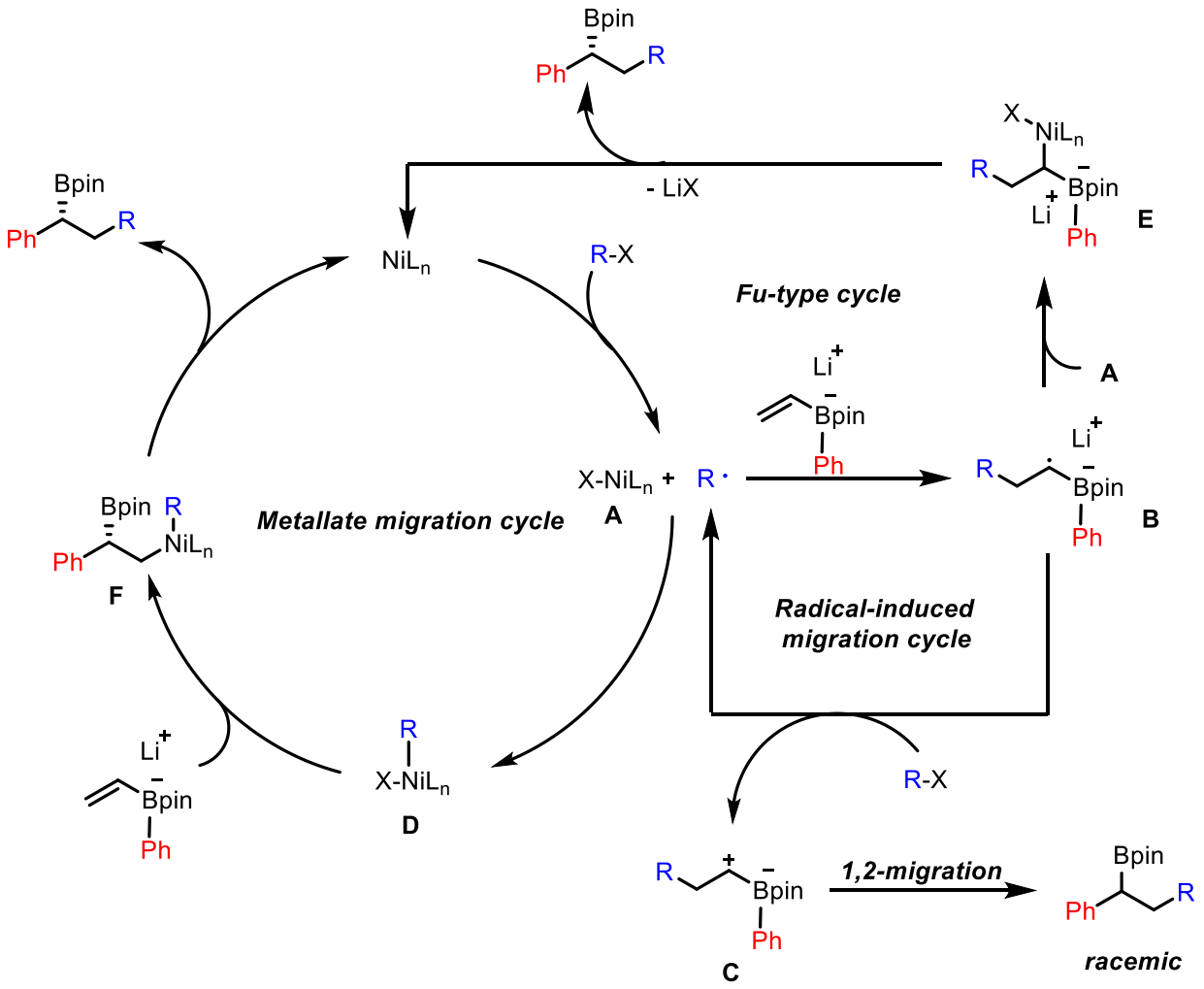

92% yield
***racemic***



J. P. Morken et al, *J. Am. Chem. Soc*. **2017**, *139*, 17293

# 1, 2-Migration to $sp^2$ Carbons

***Proposed mechanism***

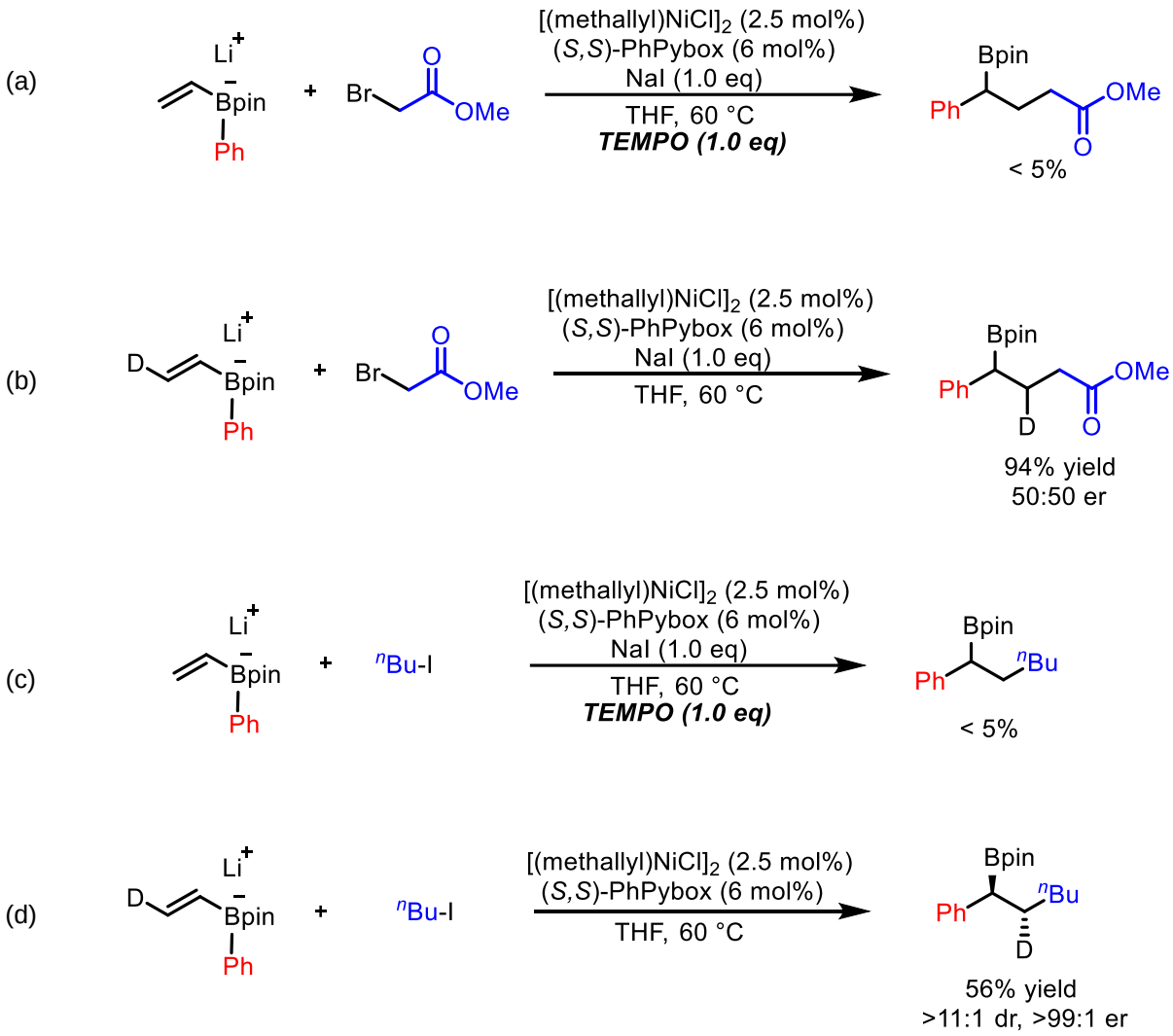





J. P. Morken et al, *J. Am. Chem. Soc*. **2017**, *139*, 17293

# 1, 2-Migration to $sp^2$ Carbons

***Control experiment***

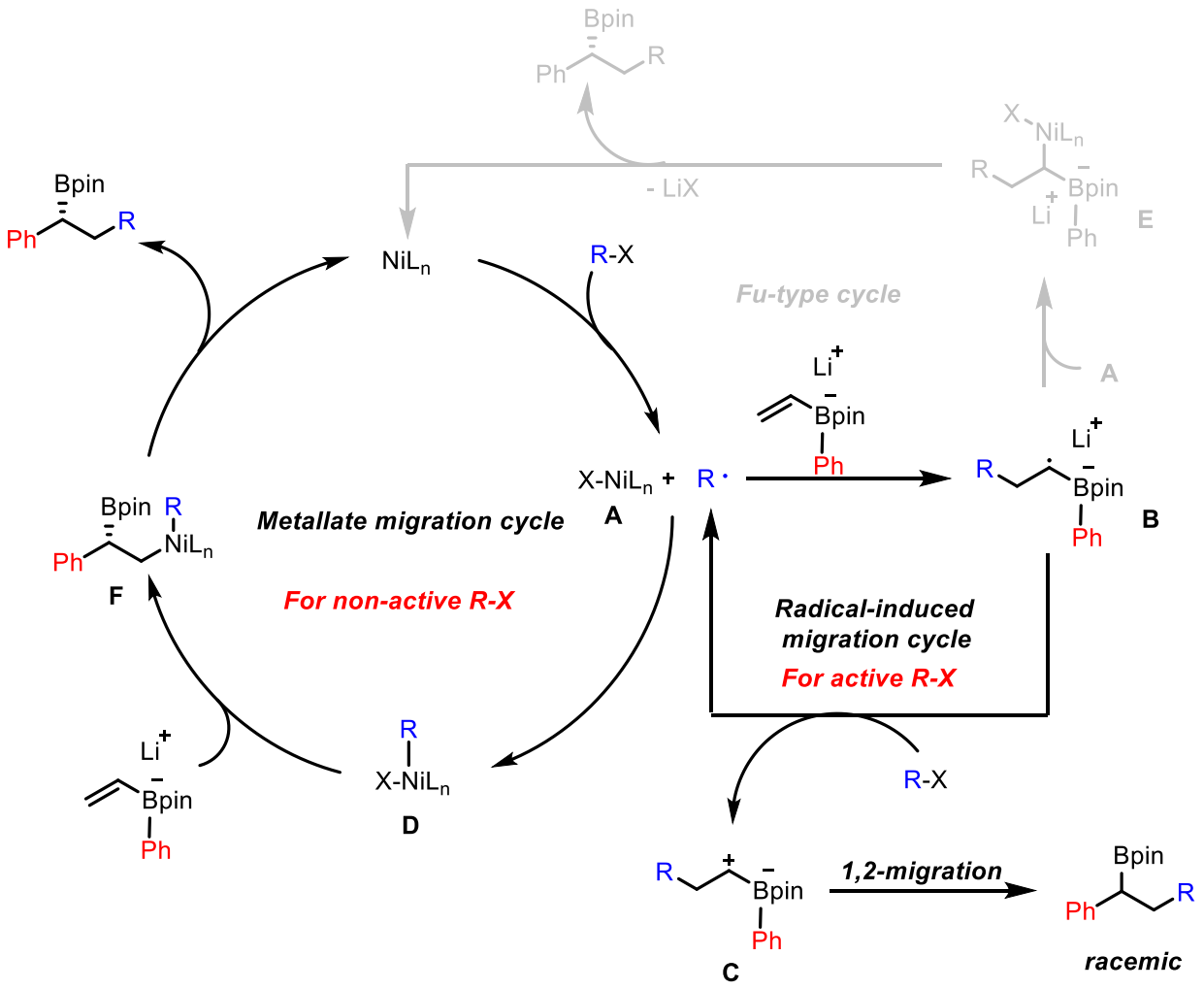





J. P. Morken et al, *J. Am. Chem. Soc*. **2017**, *139*, 17293

# 1, 2-Migration to $sp^2$ Carbons

***Proposed mechanism***

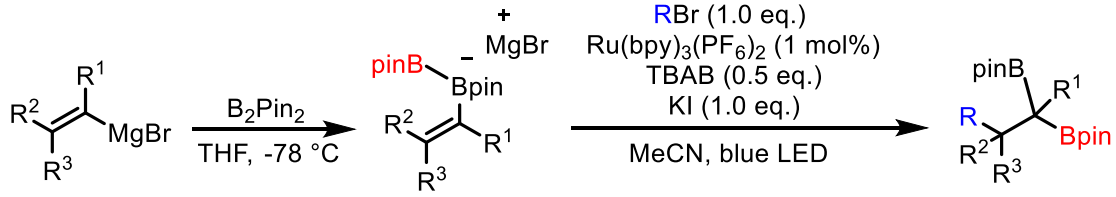




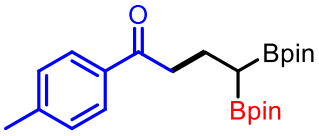

J. P. Morken et al, *J. Am. Chem. Soc*. **2017**, *139*, 17293

# 1, 2-Migration to $sp^2$ Carbons

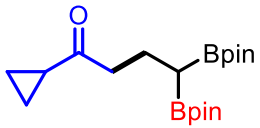
***Boron migration***



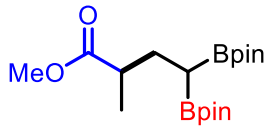

***Selected examples***



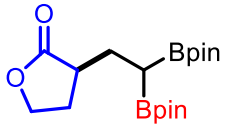

77%



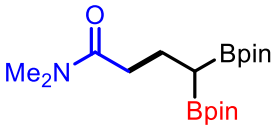

74%



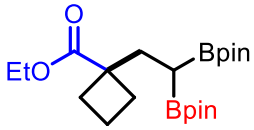

52%



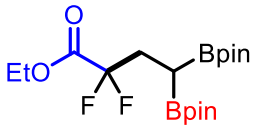

81%



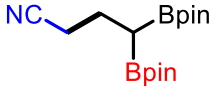

71%



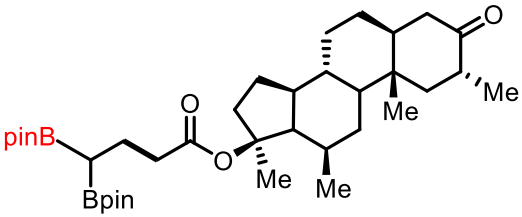

51%




42%

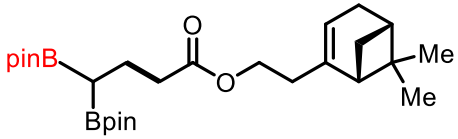



69%




**from 17a-Methyl-Drostanolone**

52%




**from Nopol**

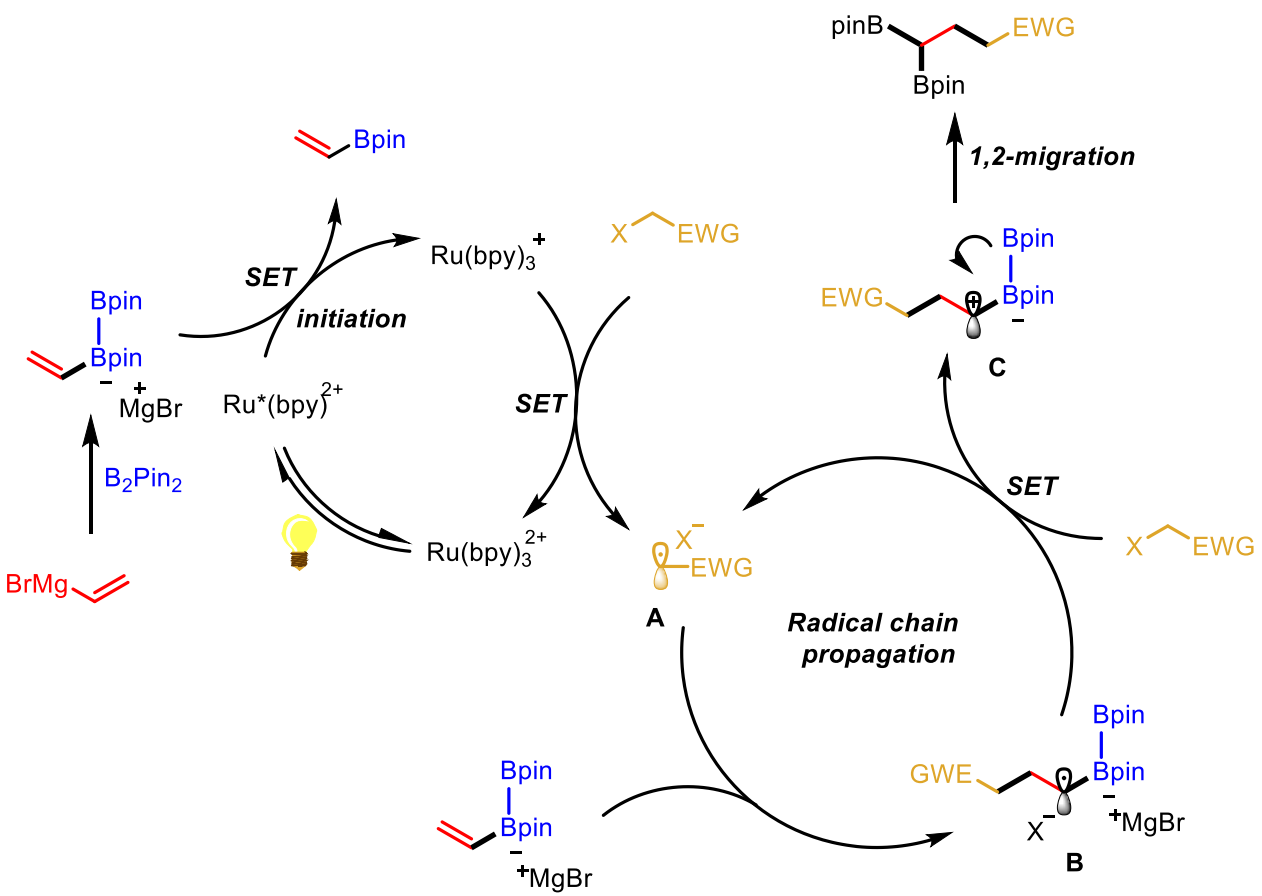
70%



Z. Shi et al, *Angew. Chem. Int. Ed*. **2019**, *58*, 9448

# 1, 2-Migration to $sp^2$ Carbons

***Proposed mechanism***

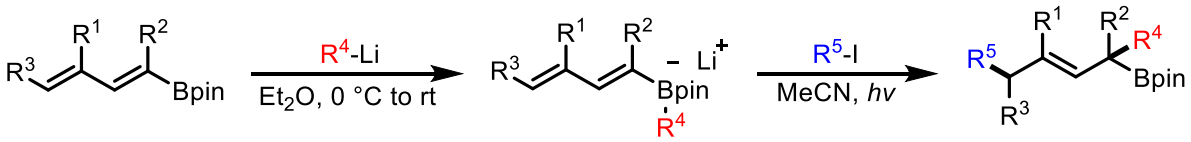




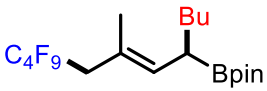

Z. Shi et al, *Angew. Chem. Int. Ed*. **2019**, *58*, 9448

# 1, 2-Migration to $sp^2$ Carbons

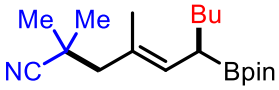
***1,4-Diene ate complexes***



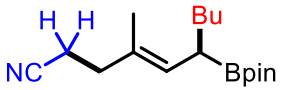

***Selected examples***



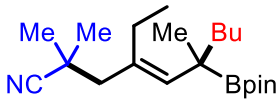

69%, E/Z = 9:1



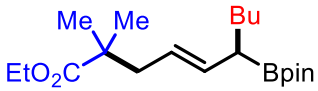

82%, E/Z = 26:1



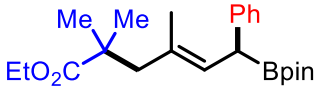

68%, E/Z = 9:1




64%, E/Z = 4:1

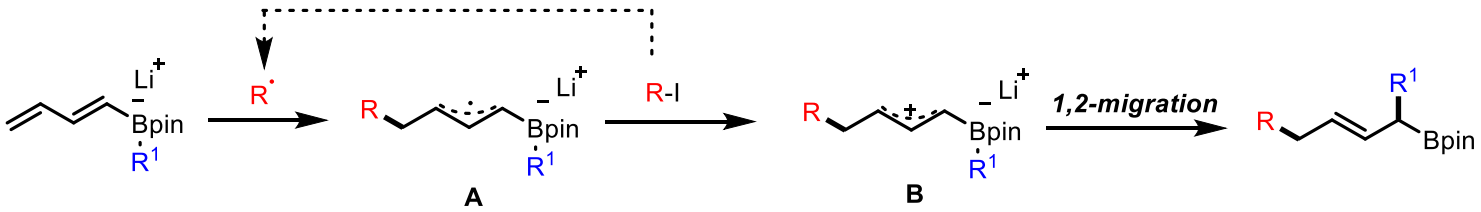



60%, E/Z = 23:1




81%, E/Z = 9:1

***Proposed mechanism***

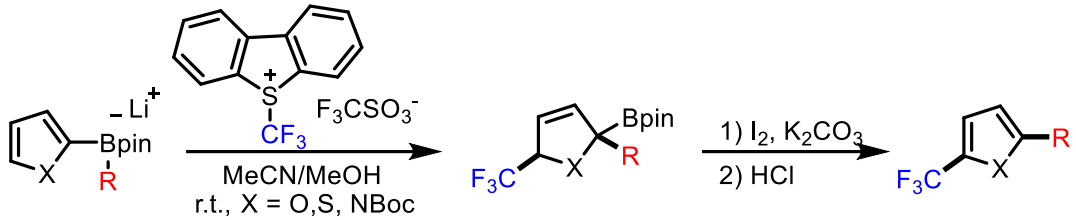




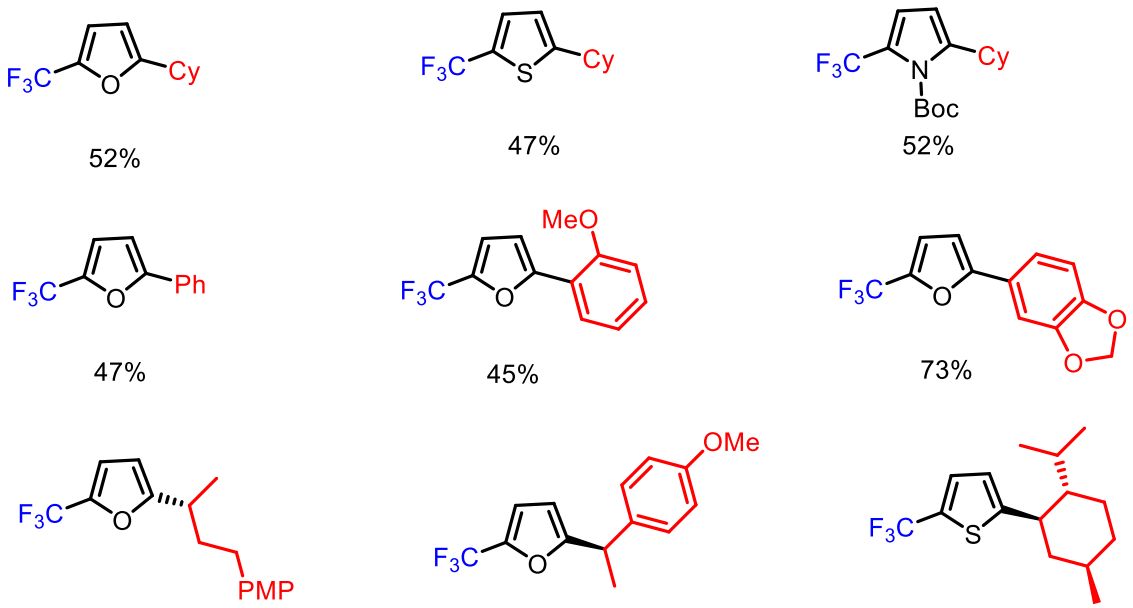

A. Studer et al, *Org. Lett*. **2018**, *20*, 3666

# 1, 2-Migration to $sp^2$ Carbons

***Heterocycle ate complexes***




***Selected examples***

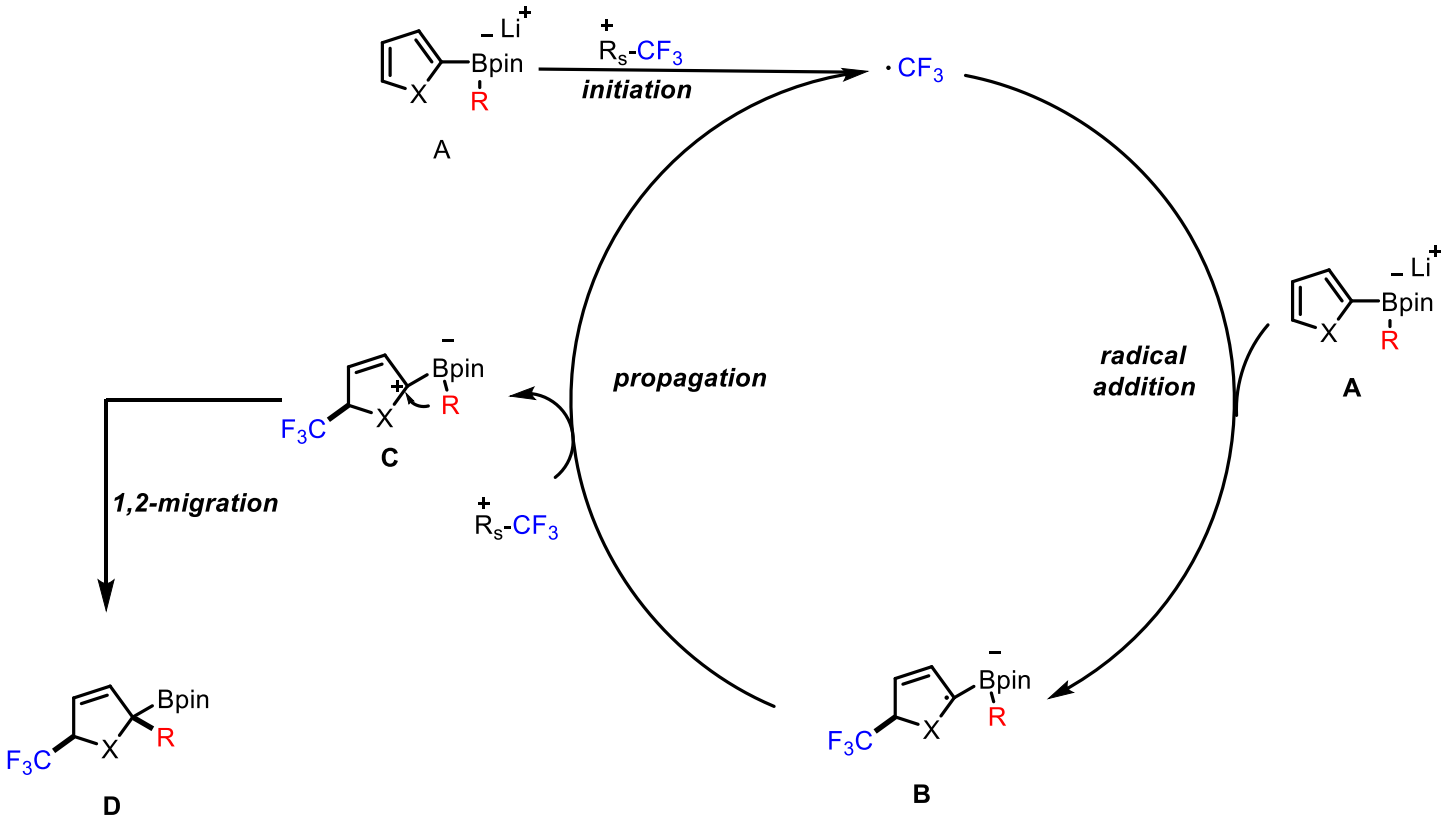





V. K. Aggarwal et al, *Angew. Chem. Int. Ed*. **2017**, *56*, 1810.

# 1, 2-Migration to $sp^2$ Carbons

***Proposed mechanism***

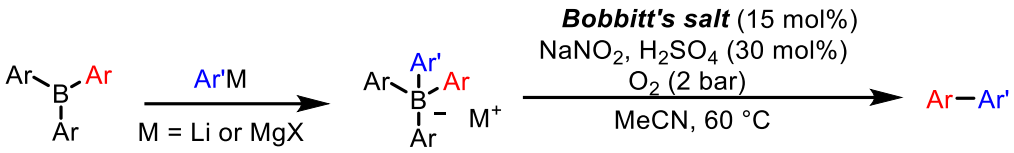


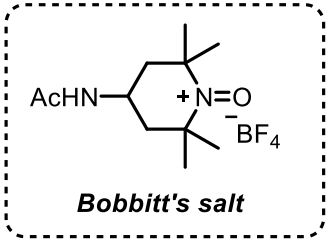



V. K. Aggarwal et al, *Angew. Chem. Int. Ed*. **2017**, *56*, 1810.

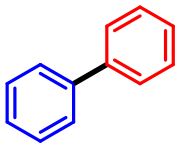
# 1, 2-Migration to $sp^2$ Carbons

***Aryl-aryl coupling***

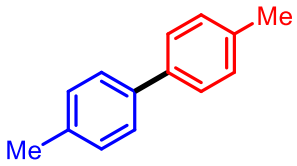


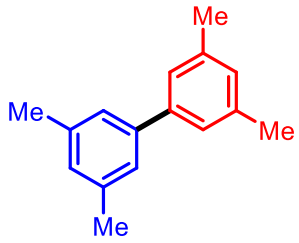

***Selected examples***



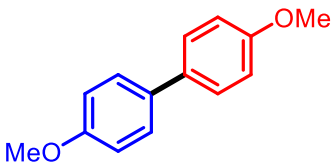
88%



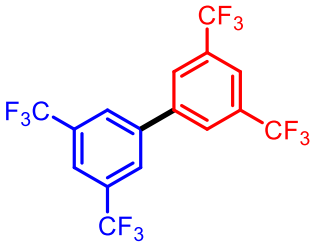

88%




88%

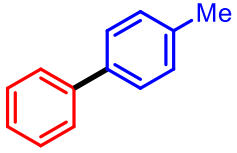



75%

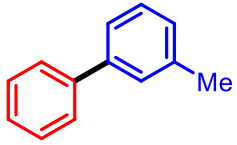



trace

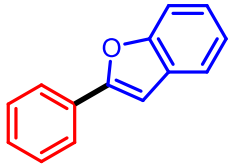

50%




74%




60%



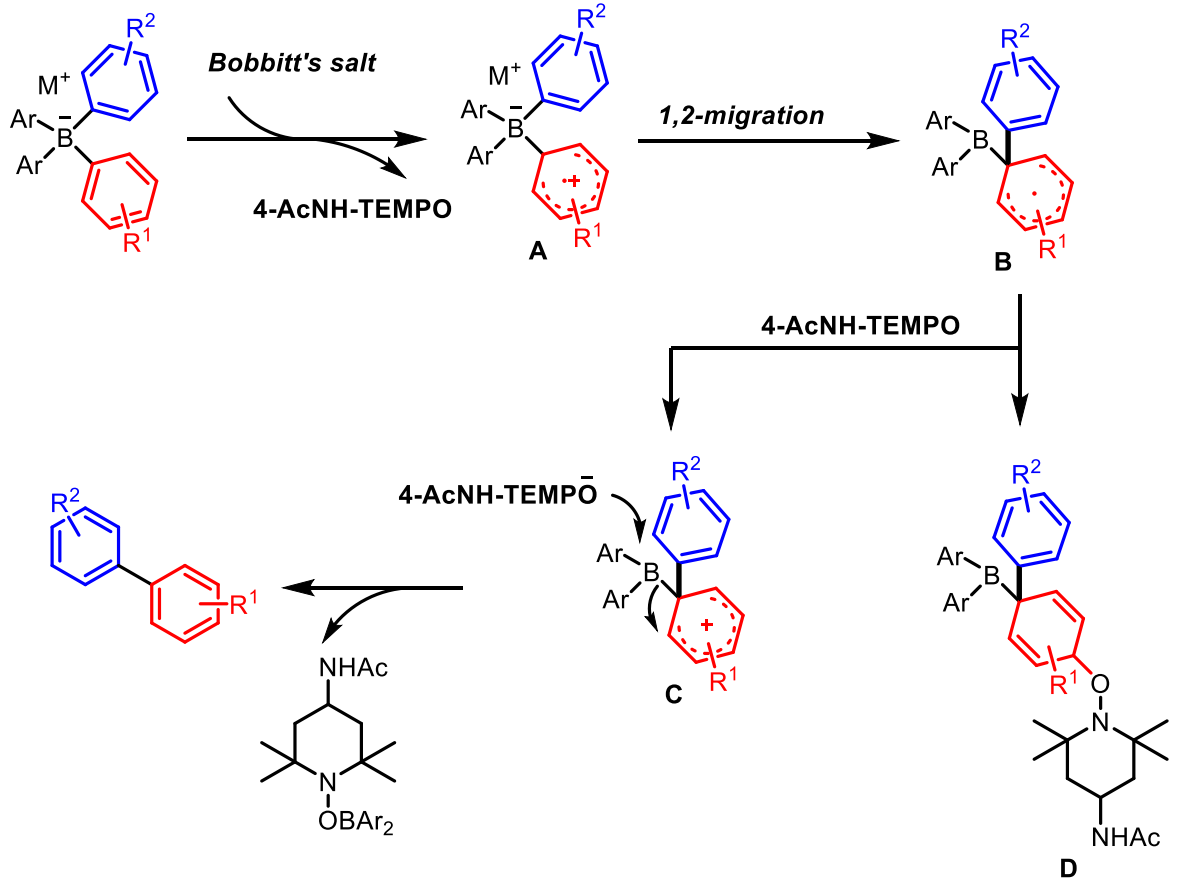

51%



A. Studer et al, *Angew. Chem. Int. Ed*. **2020**, *59*, 15468

# 1, 2-Migration to $sp^2$ Carbons

***Proposed mechanism***



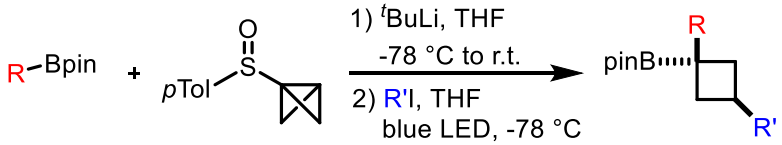



A. Studer et al, *Angew. Chem. Int. Ed*. **2020**, *59*, 15468

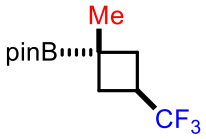
# Content

# 1, 2-Migration to $sp^3$ Carbons

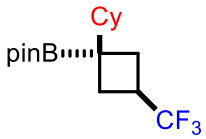
***BCB boron ate complexes***



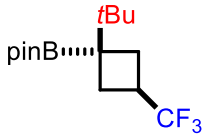

***Select examples***



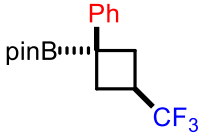

66%, dr = 11:1



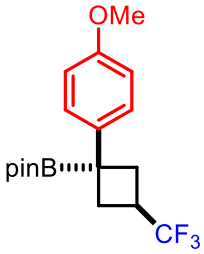

74%, dr > 20:1



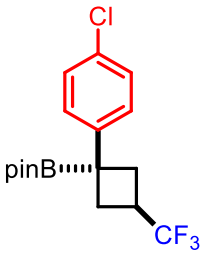

33%, dr > 20:1



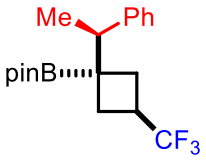

75%, dr = 4.5:1



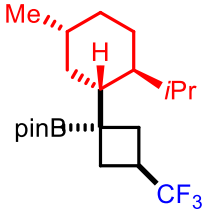

62%, dr = 6.8:1



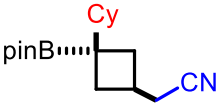

50%, dr = 2:1



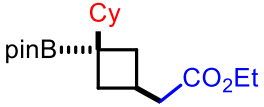

90%, dr > 20:1
es = 100%



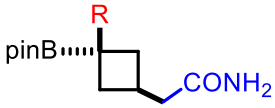

61%, es = 100%



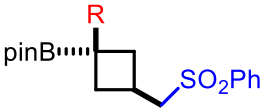

75%, dr = 3:1




64%, dr = 5.3:1




51%, dr = 6.5:1



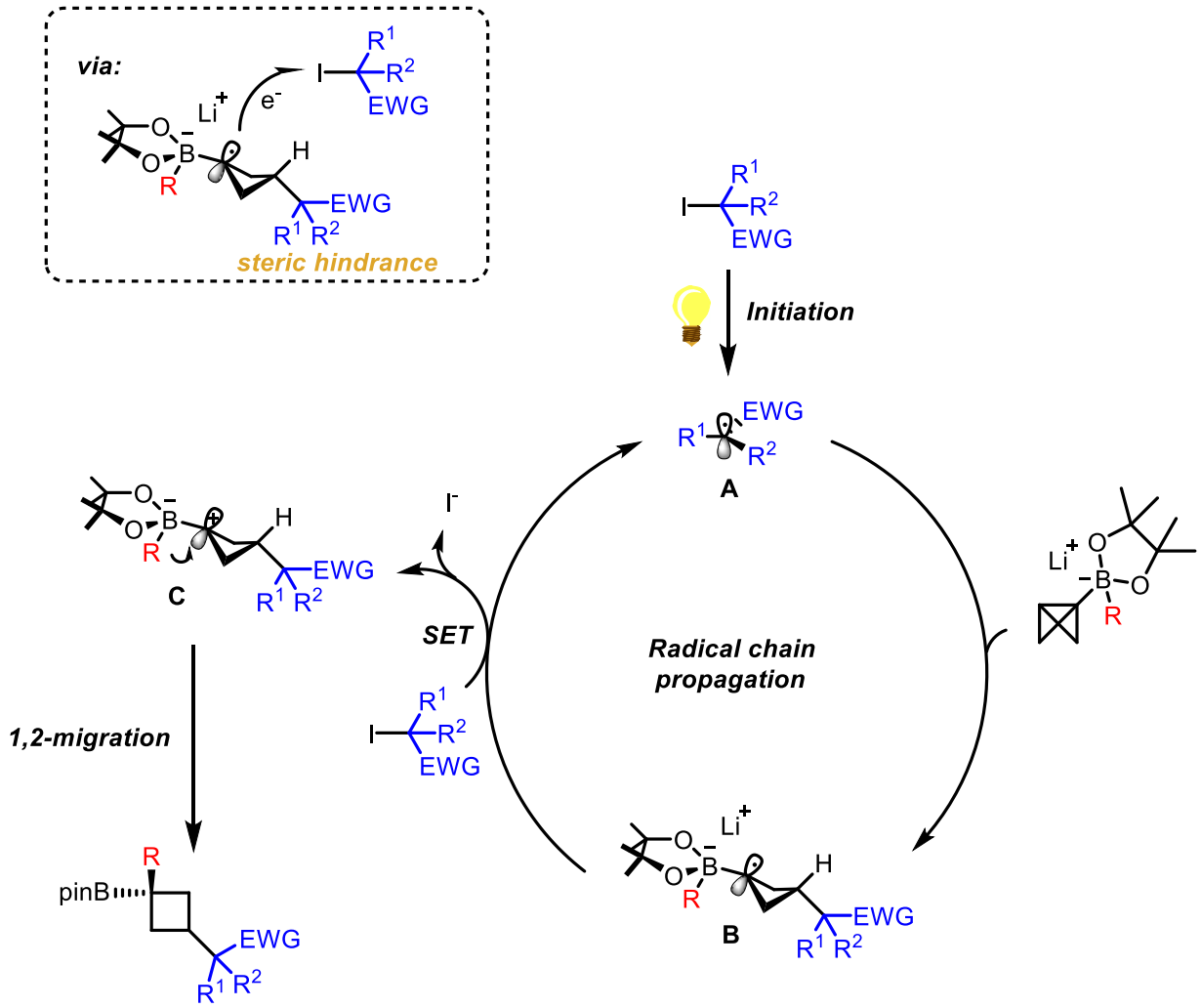

69%, dr = 8.4:1



V. K. Aggarwal et al, *J. Am. Chem. Soc*. **2019**, *141*, 9511

# 1, 2-Migration to $sp^3$ Carbons

***Proposed mechanism***

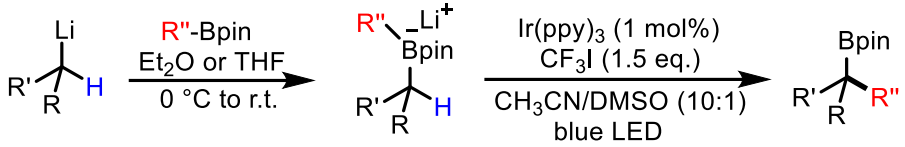




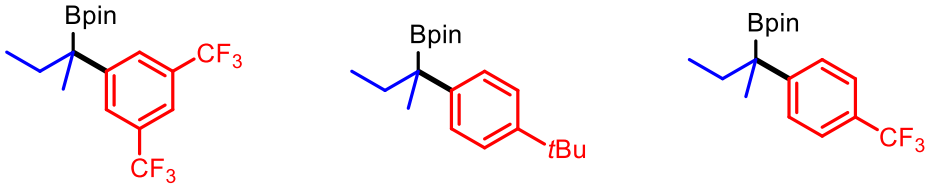

V. K. Aggarwal et al, *J. Am. Chem. Soc*. **2019**, *141*, 9511

# 1, 2-Migration to $sp^3$ Carbons

***HAT induced 1,2-migration***




***C($sp^2$)-C($sp^3$) coupling:***




67%



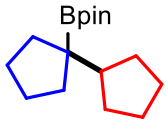

61%



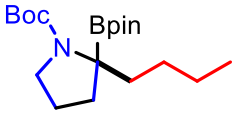

66%


61% (from δ–tocopherol)

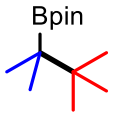
***C($sp^3$)-C($sp^3$) coupling:***



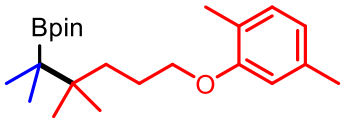

70%




58% rr = 32:1




50%



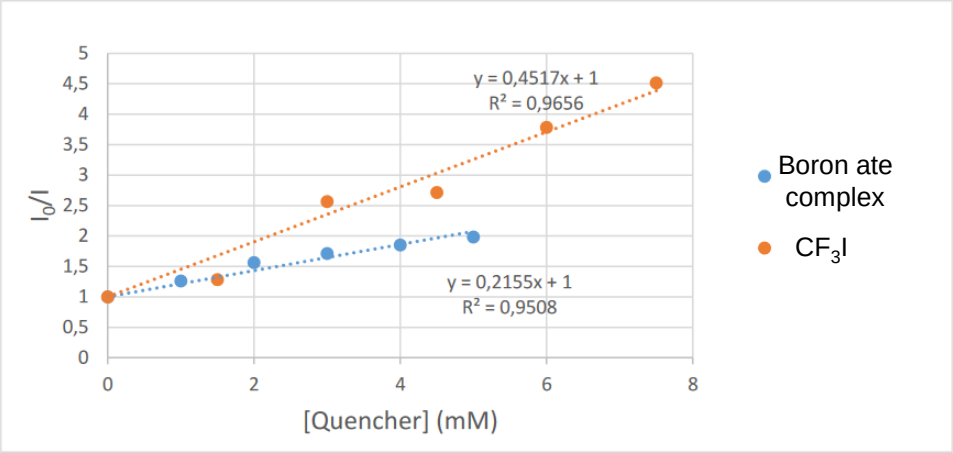

32% *(from gemfibrozil)*



A. Studer et al, *J. Am. Chem. Soc*. **2019**, *141*, 14126

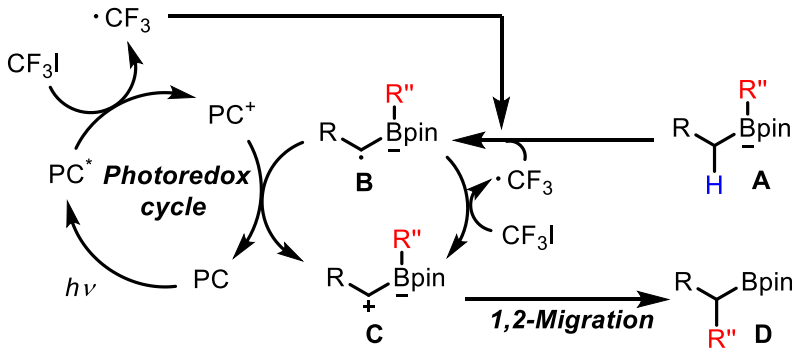
# 1, 2-Migration to $sp^3$ Carbons

***Stern-Volmer fluorescence quenching experiments***




Fac-Ir(ppy)$_3$ Solutions Quenched by Boron Ate Complex and $CF_3I$.

***Proposed mechanism***

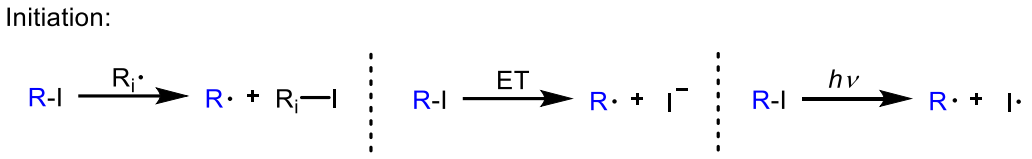


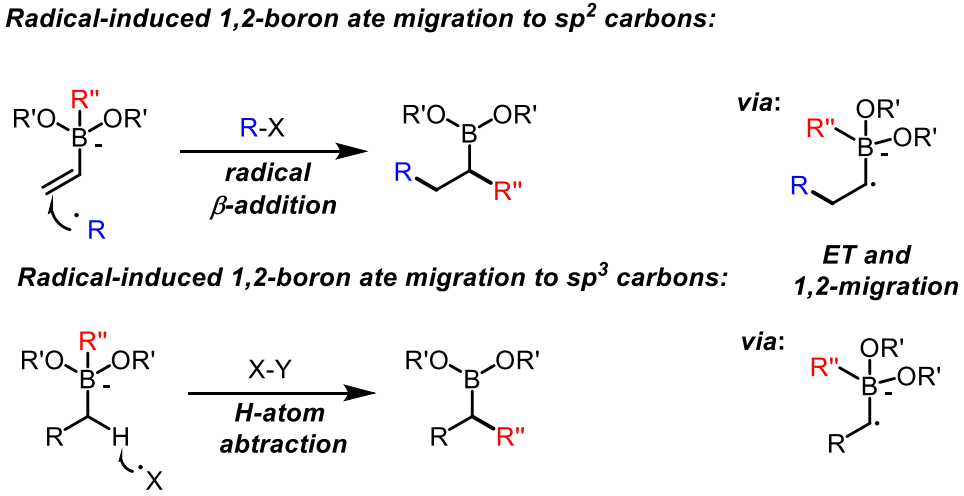



A. Studer et al, *J. Am. Chem. Soc*. **2019**, *141*, 14126

# Content

# Summary and Outlook




***Other migration groups such as heteroatom group?***
***Heteroatom-centered radicals as a reactant partner?***
***Enantioselective process?***

***Thanks For Your Attention***