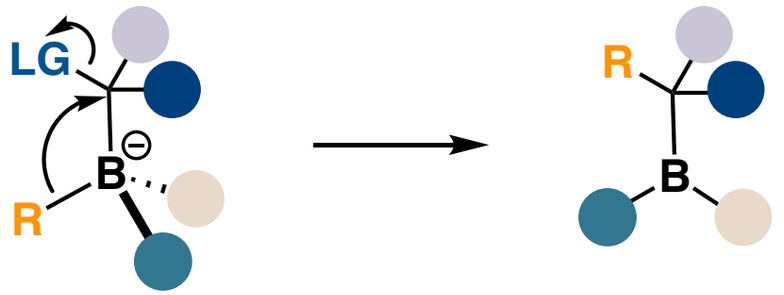
Boron Homologation



Boron Enabled Assembly Line synthesis

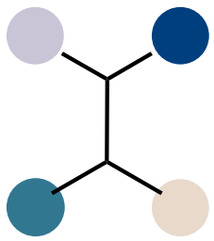
Zhe Dong

MacMillan Research Group

Group Meeting

Feb 14th, 2019

Continuous Carbon Chiral Center Synthesis



Unsolved Problem

- ***Quick access to starting materials***
- ***Reactivity: overcoming the steric bulk***
- ***Selectivity: facile synthesis of all 4 enantiomers***

Stereospecific or Stereoconvergent?

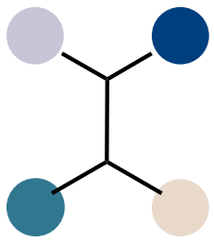
M = Li, Mg, Zn, B, Sn

Stereoconvergent?

No asymmetric report
No access to all 4 enantiomers

Lucas, E. L.; Jarvo, E. R. *Nat. Rev. Chem.* **2017**, 1, 65.

Continuous Carbon Chiral Center Synthesis



Unsolved Problem

- ***Quick access to starting materials***
- ***Reactivity: overcoming the steric bulk***
- ***Selectivity: facile synthesis of all 4 enantiomers***

Stereospecific or Stereoconvergent?

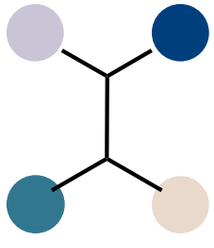
M = Li, Mg, Zn, B, Sn

Stereospecific

No good way to generate chiral nucleophile
Match and mismatch issue

Lucas, E. L.; Jarvo, E. R. *Nat. Rev. Chem.* **2017**, 1, 65.

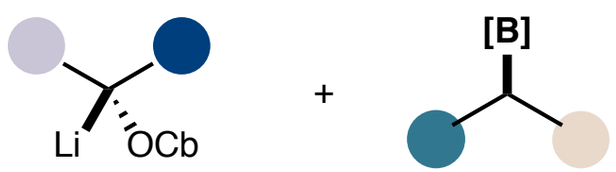
Continuous Carbon Chiral Center Synthesis



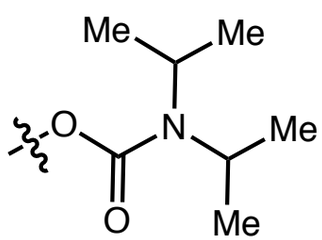
Unsolved Problem

- ***Quick access to starting materials***
- ***Reactivity: overcoming the steric bulk***
- ***Selectivity: facile synthesis of all 4 enantiomers***

- ***Stereospecific Reaction without Catalysis***



One Step from chiral alcohol



OCb

Solve all the mentioned issues in both seactivity/ selectivity

Problem: functional group tolerance/ low temperature

Leonori D.; Aggarwal V.K. *Acc. Chem. Res.*, **2014**, 47, 3174

Boron Homologation via 1,2-Metallate Rerrangments

Non-Catalyzed Boron Homologation

Matteson Homologation

Zweifel Olefination

Aggarwal Homologation

Real-World Application

Assembly Line Synthesis

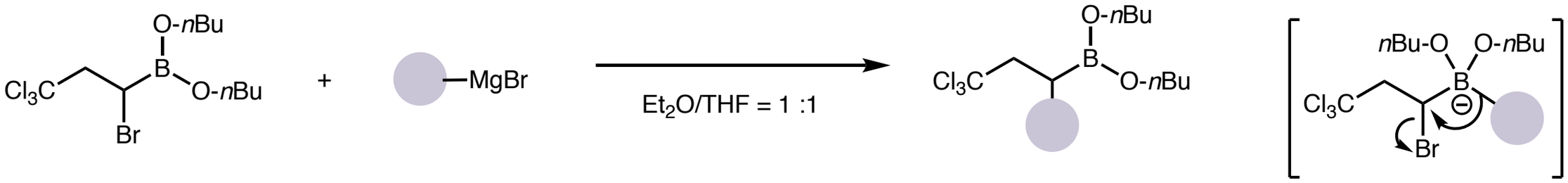
Heteroatom Issue

Catalyzed Boron Homologation

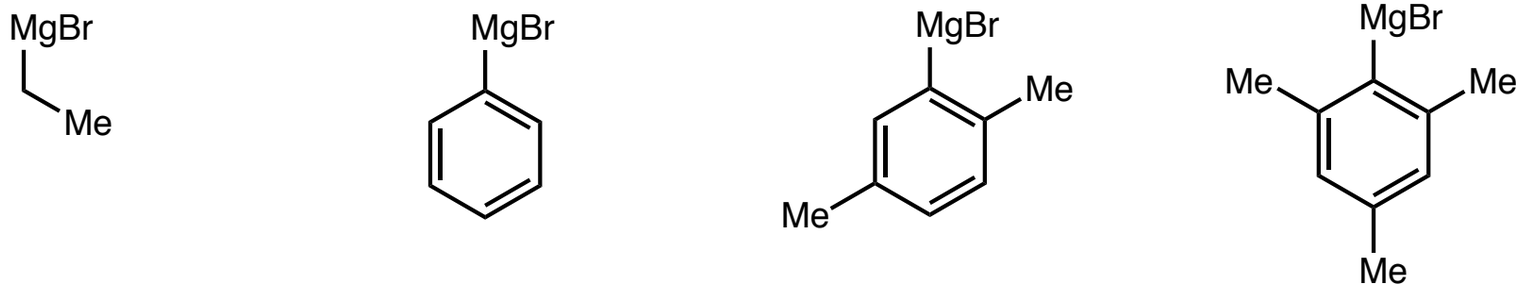
Double Electron Transfer Initiated Reaction

Single Electron Transfer Initiated Reaction

Matteson Homologation: Reaction Discovery



Scope and Conditions

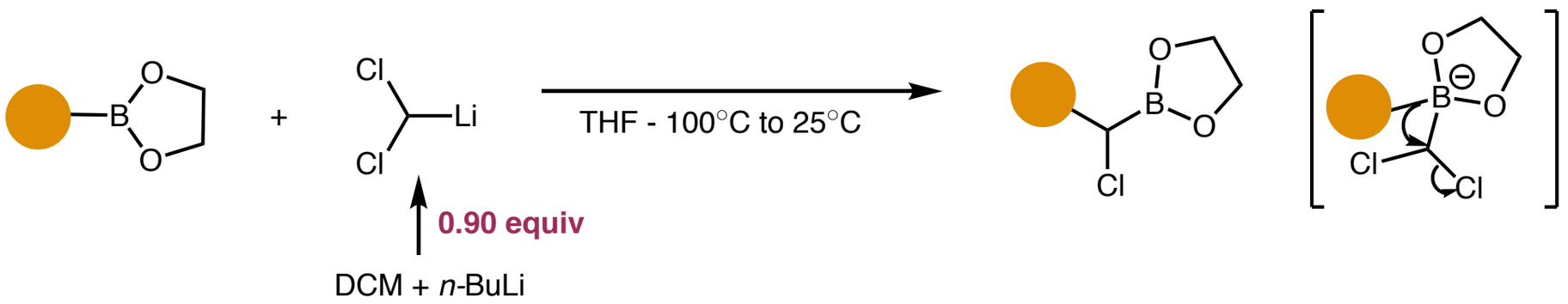


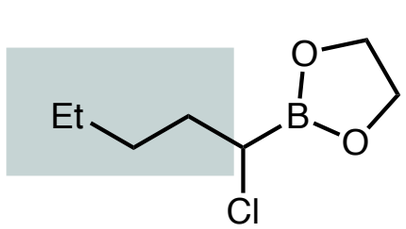
25°C 22h 90% IY	25°C 22h 91% IY	25°C 2h 80% IY	-70°C 2h 63% IY

More hindered group easier to migrate: ***More Bulky, More Reactive***

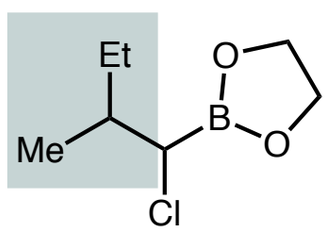
Matteson, D. S.; Mah, R. W. H. *J. Am. Chem. Soc.* **1963**, *85*, 2599.

α–Chlorol-alkyl Lithium Reagents for Homologation

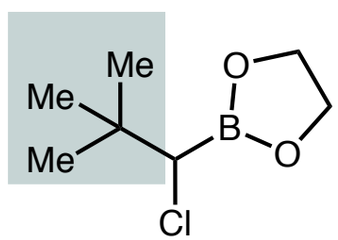




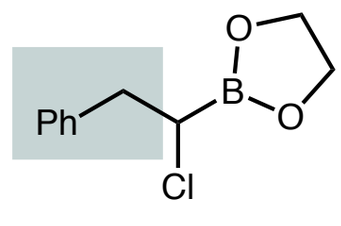
80% IY



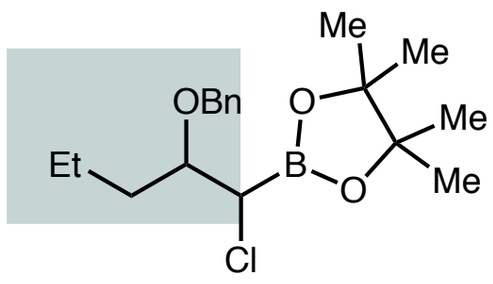
77% IY



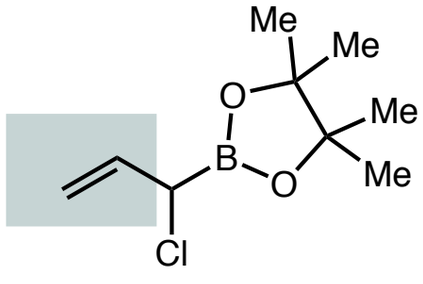
78% IY



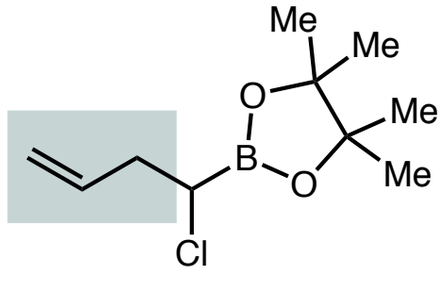
84% IY



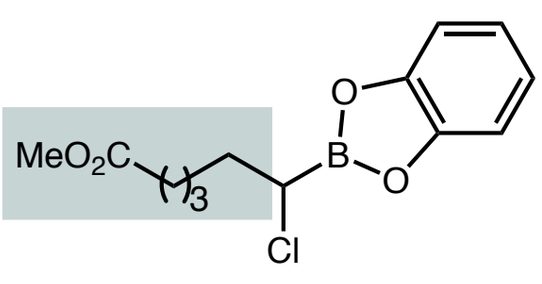
81% IY



90% IY



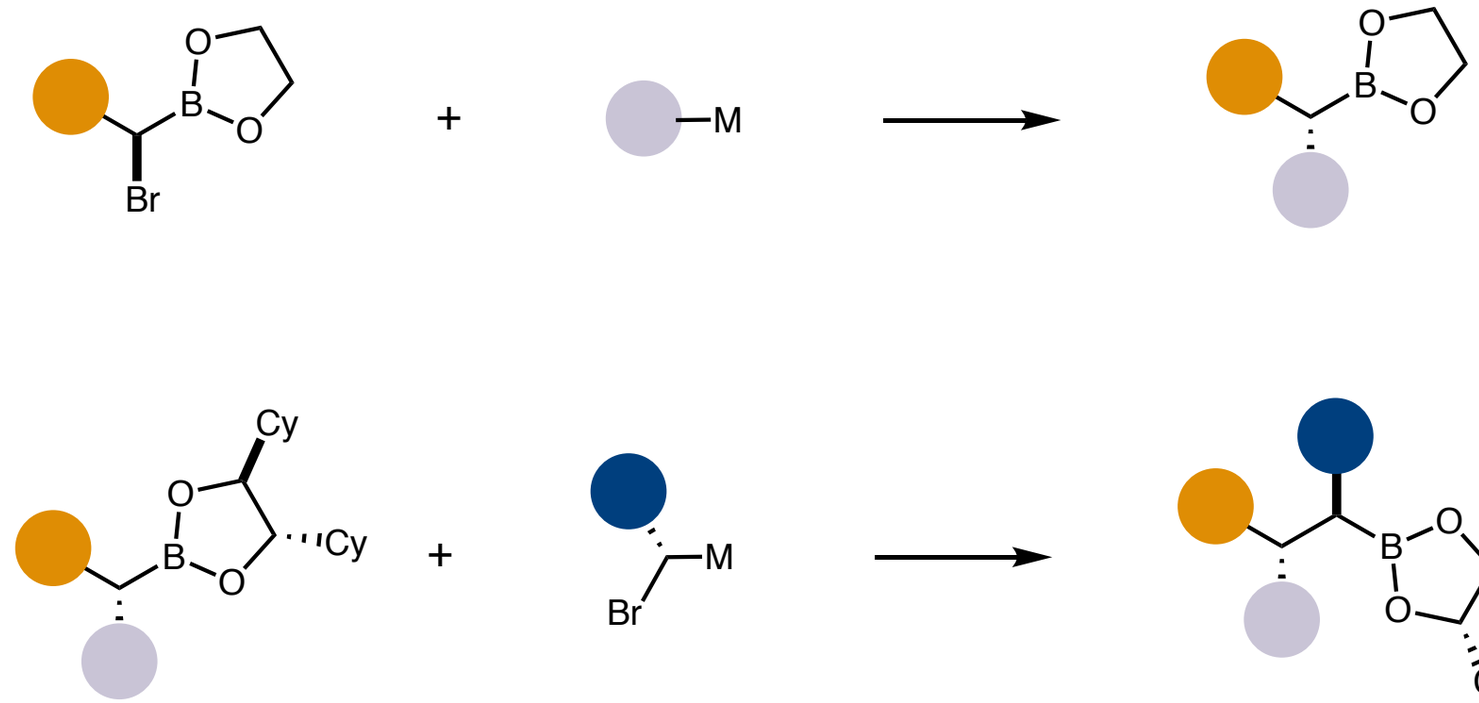
87% IY



67% IY

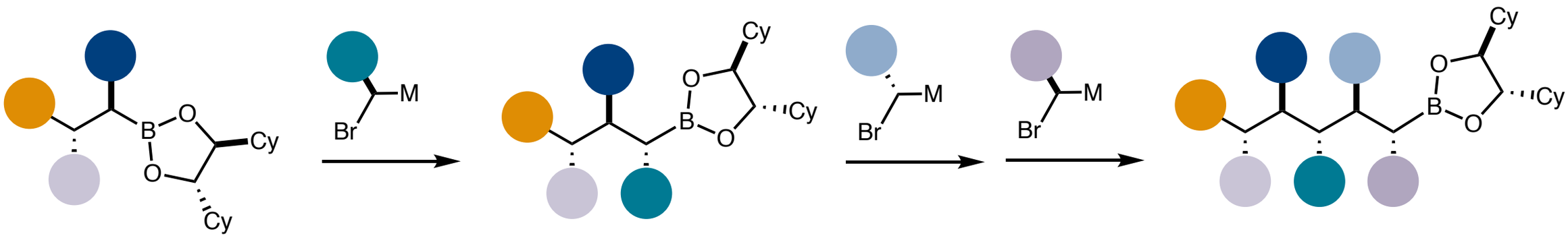
Matteson, D. S.; Majumdar, D. *J. Am. Chem. Soc.* **1980**, *102*, 7588.

Matteson Homologation: Iterative Version



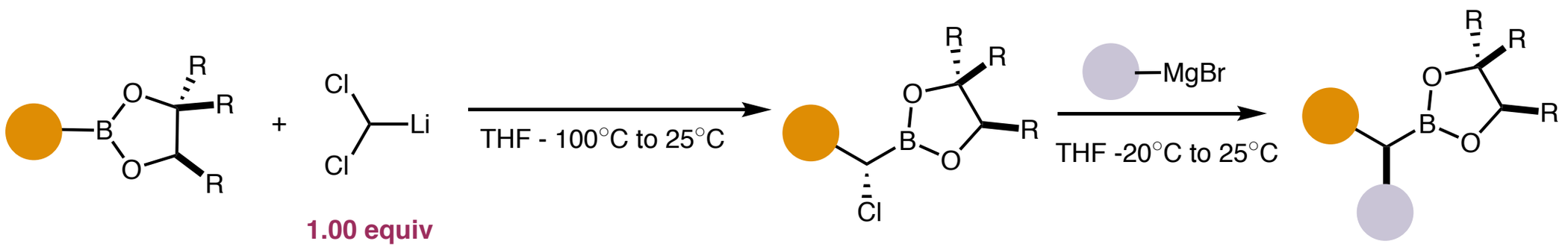
Type I : Form S_N2

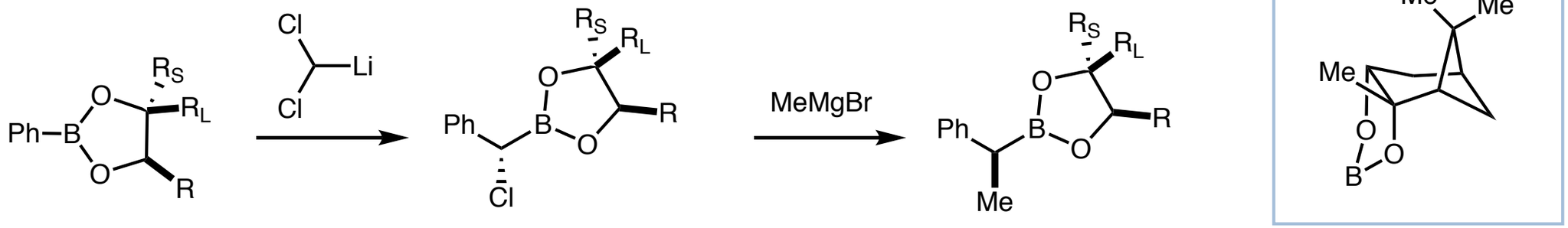
Type II: Homologation

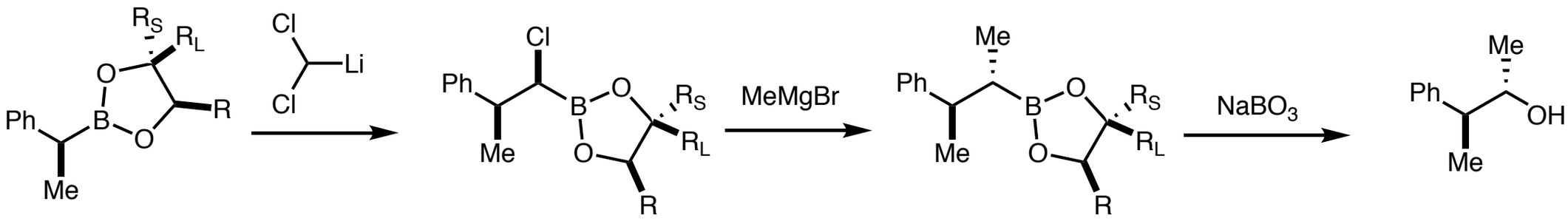


Iterative Synthesis

Chiral Diol as Auxiliary for Diastereoselective Homologation





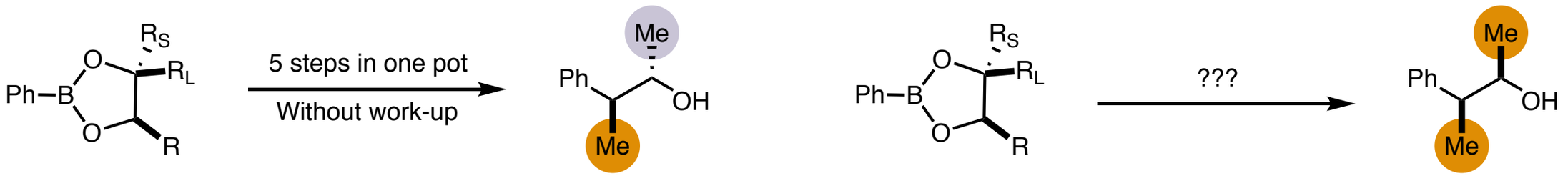


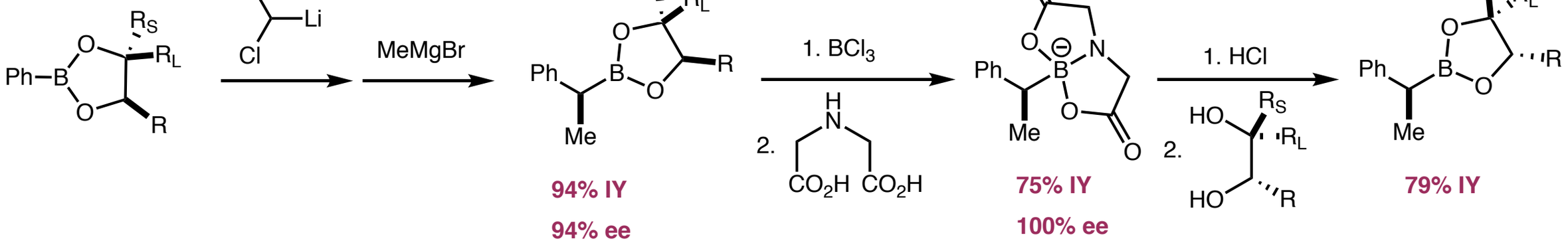
90% IY for 5 steps

97% ee. 9:1 d.r.

Matteson, D. S.; Ray, R. *J. Am. Chem. Soc.* **1980**, *102*, 7590.

Chiral Diol as Auxiliary : Painful Access to Diastereomer





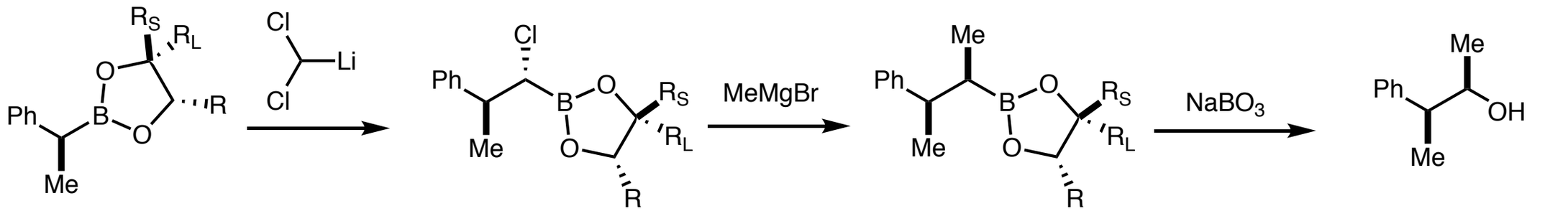
94% IY

94% ee

75% IY

100% ee

79% IY

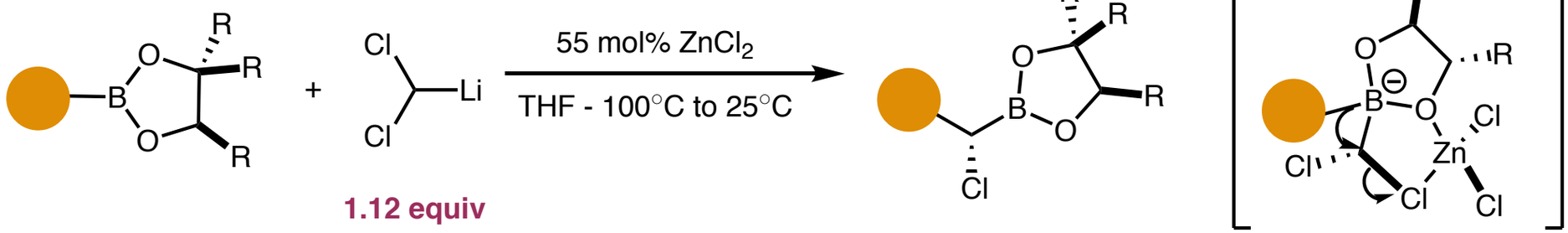


93% IY for 3 steps

100% ee. 15:1 d.r.

Matteson, D. S.; Ray, R. *J. Am. Chem. Soc.* **1980**, *102*, 7590.

Chiral Diol as Auxiliary : Improvement on Selectivity



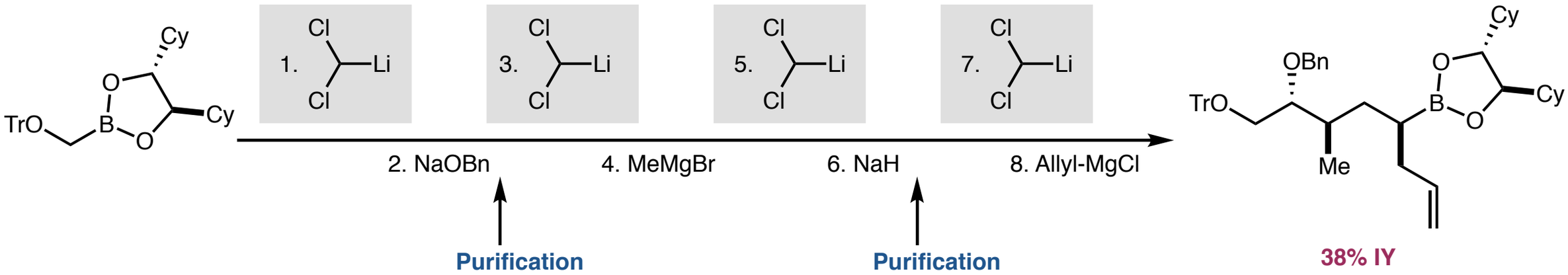
1.12 equiv

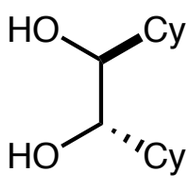
	Me, [B], Cl	Et, [B], Cl	Me, Me, [B], Cl	Ph, [B], Cl
W/O $ZnCl_2$	**57% IY 74% es**	**61% IY 90% es**	**30% IY 88% es**	**75% IY 92.5% es**
W $ZnCl_2$	**83% IY 95.7% es**	**86% IY 98.5% es**	**89% IY 99.5% es**	**99% IY 99.5% es**

Matteson, D. S.; Sadhu, K. M. *J. Am. Chem. Soc.* **1983**, *105*, 2077.

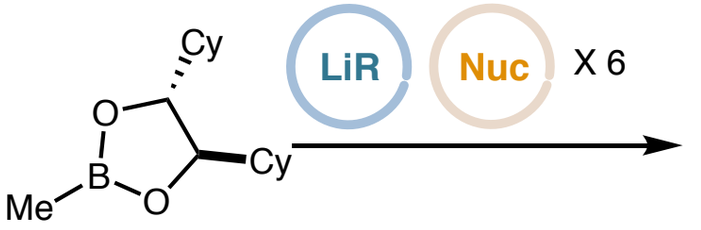
Matteson, D. S.; Sadhu, K. M.; Peterson, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 810.

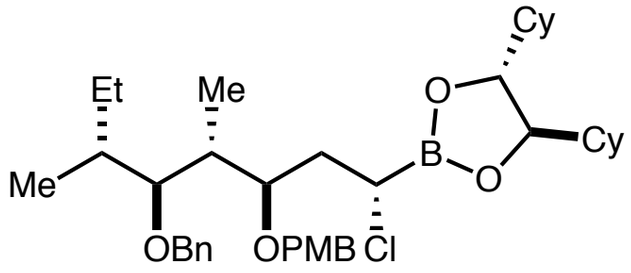
Matteson Homologation: State of Art



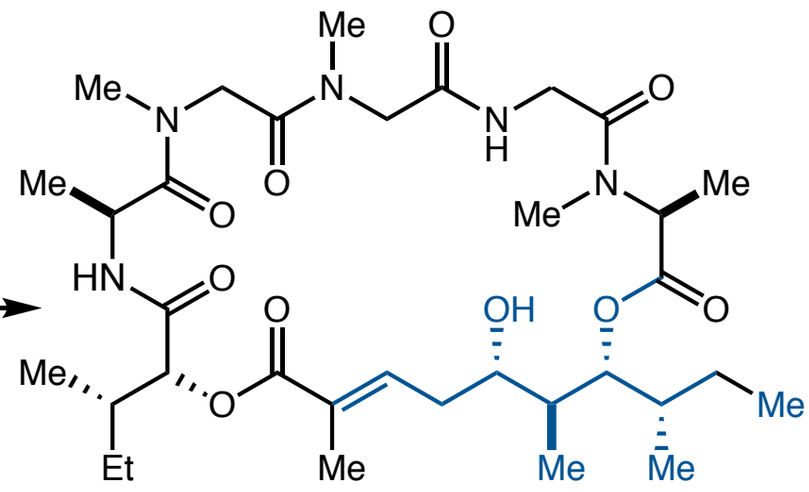


- *Easy to install*
- *Easy to deprotect/switch*





45% IY for 12 chemical step

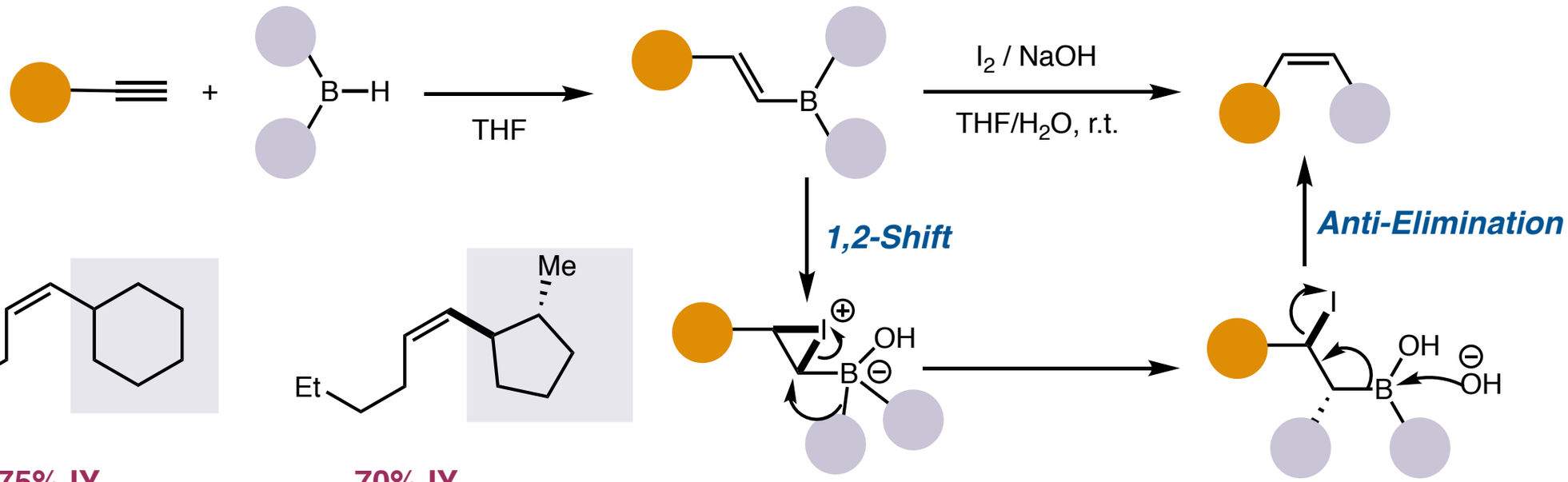


Lagunamide A

Matteson, D. S.; Soundararajan, R.; Ho, O. C.; Gatzweiler, W. *Organometallics* **1996**, *15*, 152.

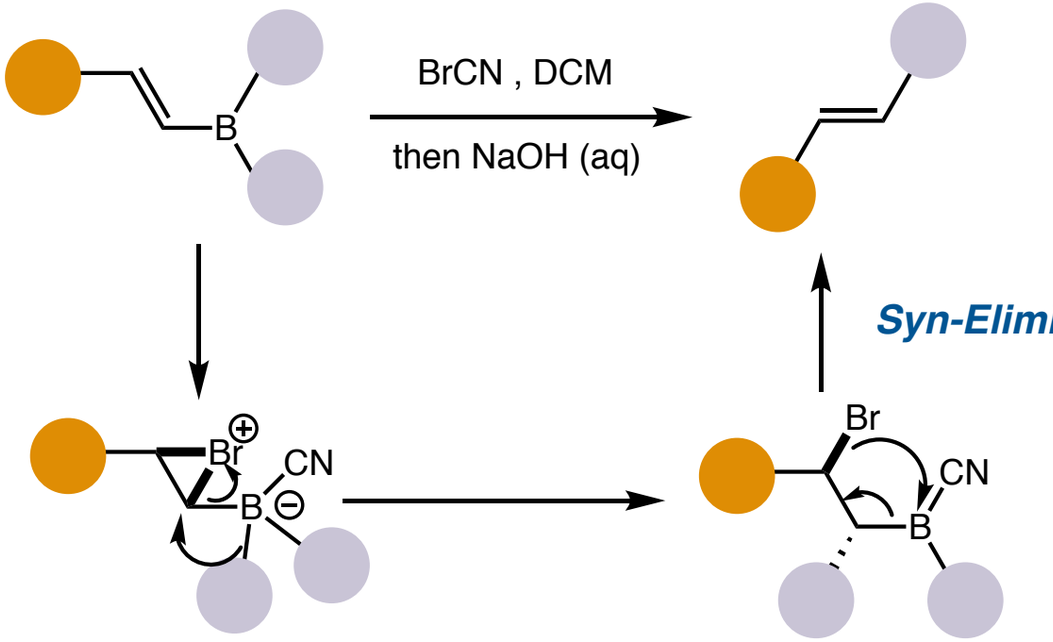
Gorges, J.; Kazmaier, U. *Org. Lett.* **2018**, *20*, 2033.

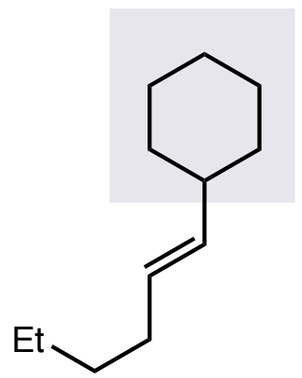
Zweifel Olefination: Reaction Discovery



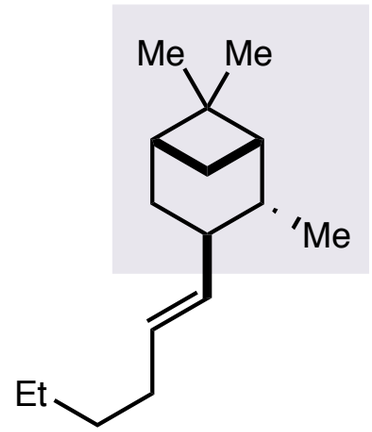
75% IY
99:1 Z/E

70% IY
85:15 Z/E





69% IY
96:4 E/Z

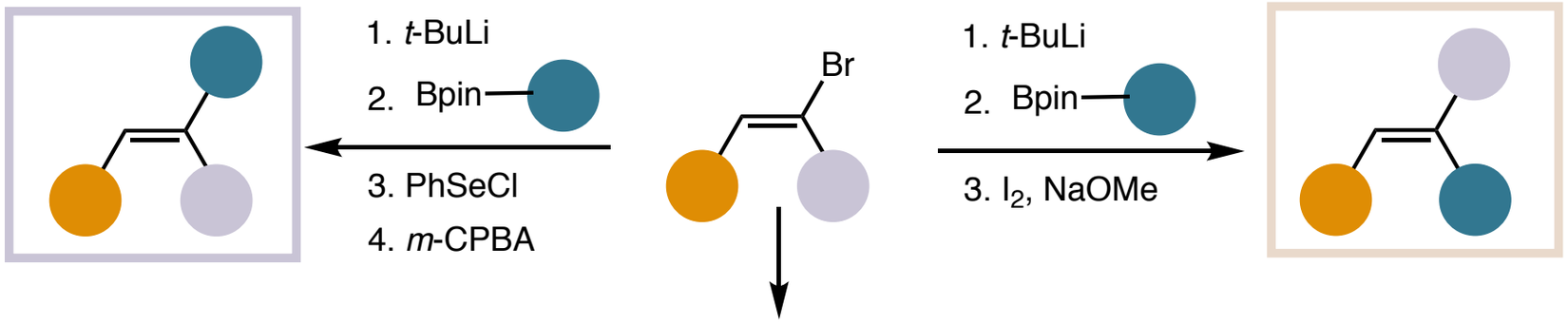


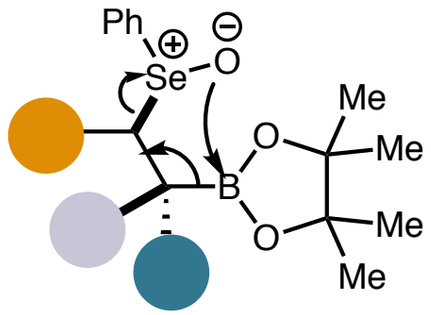
75% IY
98:2 E/Z

Zweifel, G.; Arzoumanian, H.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 3652.

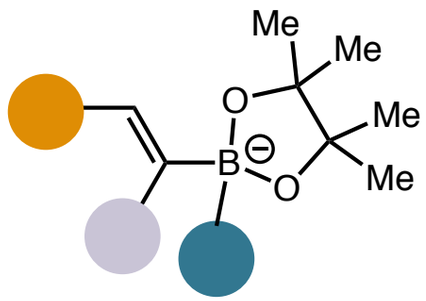
Zweifel, G.; Fisher, R. P.; Snow, J. T.; Whitney, C. C. *J. Am. Chem. Soc.* **1972**, *94*, 6560.

Zweifel Olefination: State of Art

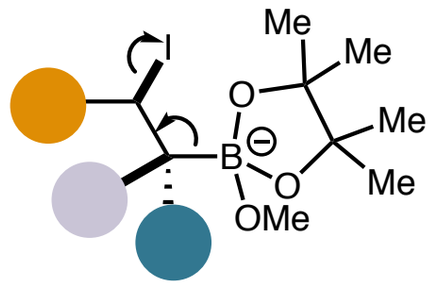


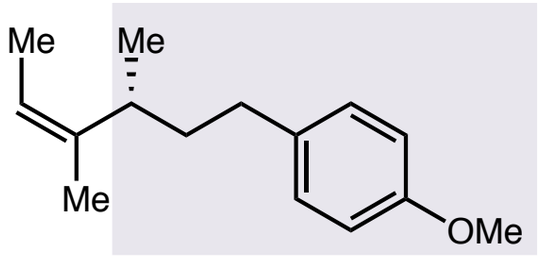


- *Excellent Syn Elimination*



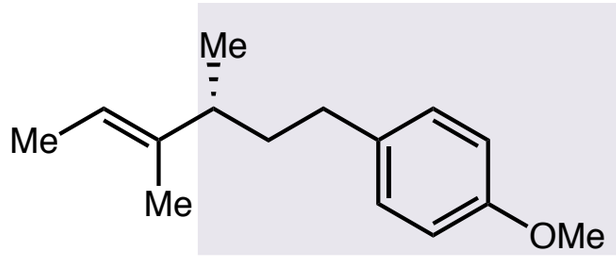
- *High Reactive Olefin*





95% IY 100% es

> 98:2 Z/E

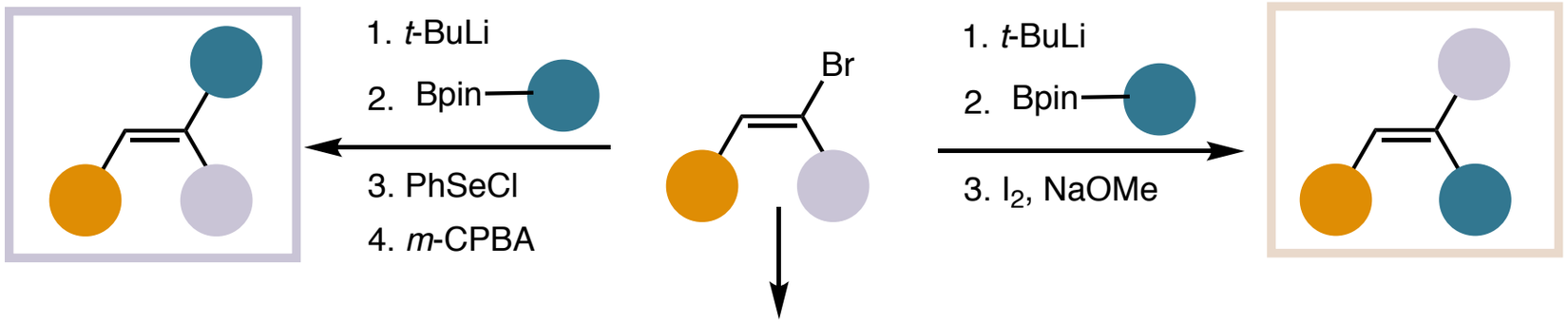


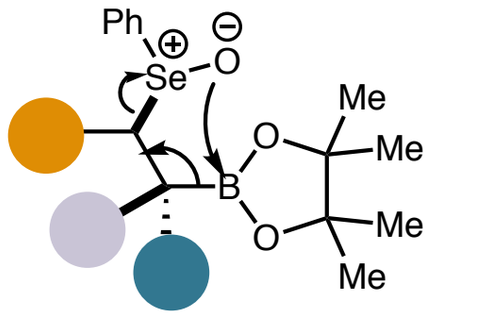
83% IY 100% es

96:4 E/Z

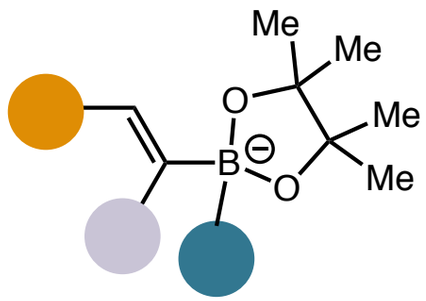
Armstrong, R. J.; García-Ruiz, C.; Myers, E. L.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2017**, *56*, 786.

Zweifel Olefination: State of Art

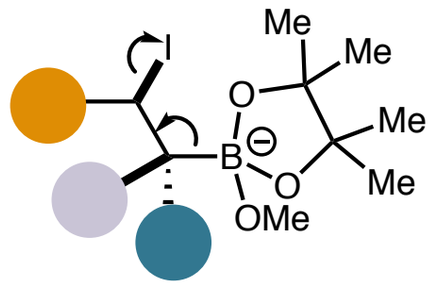


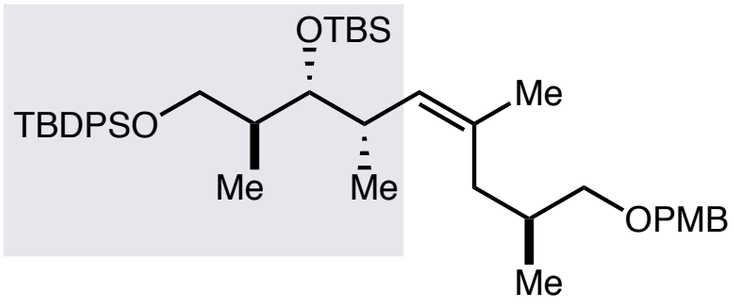


- *Excellent Syn Elimination*



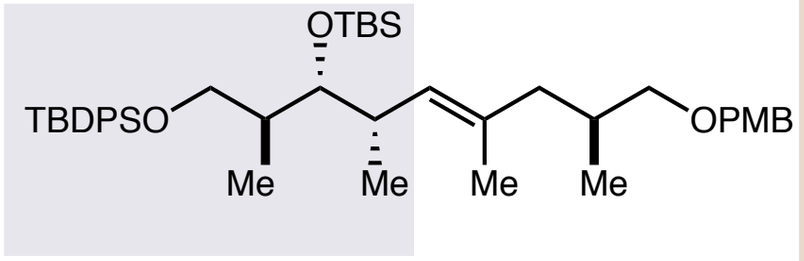
- *High Reactive Olefin*





45% IY > 20:1 d.r.

98:2 Z/E

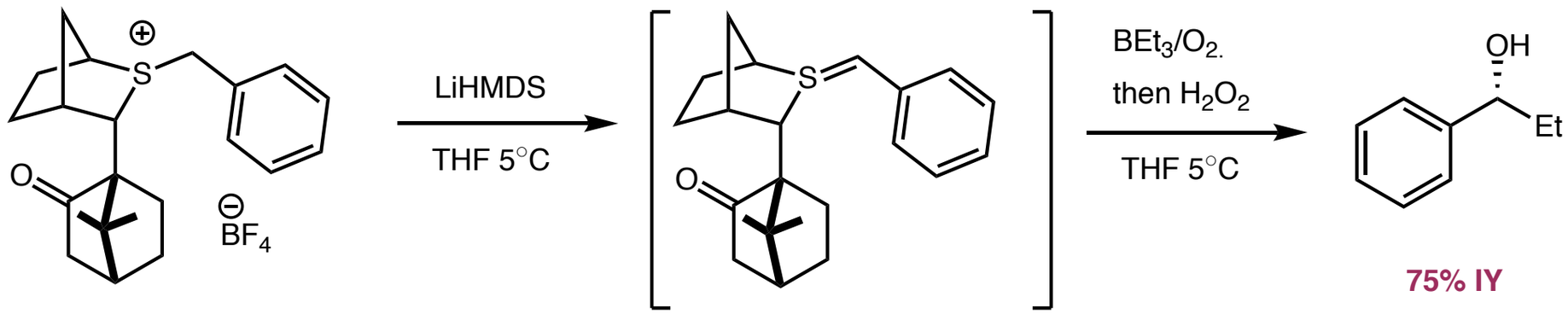


52% IY > 20:1 d.r.

98:2 Z/E

Armstrong, R. J.; García-Ruiz, C.; Myers, E. L.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2017**, *56*, 786.

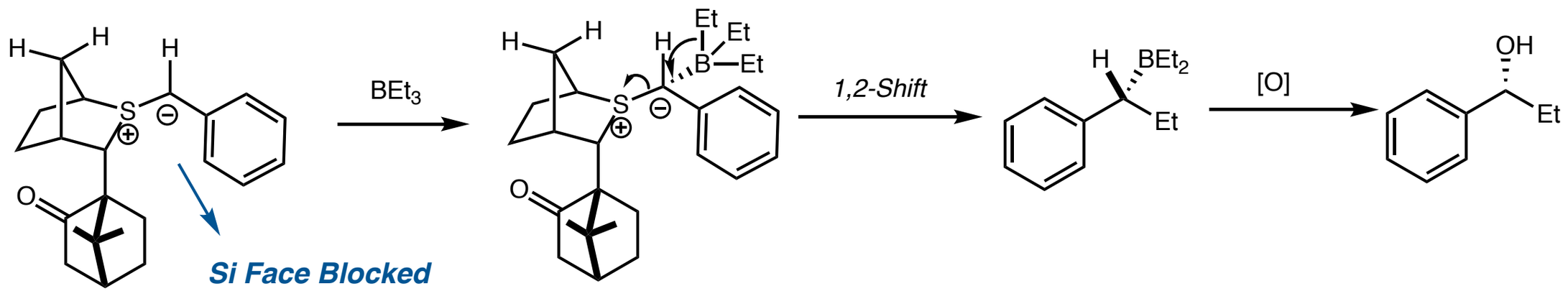
Aggarwal Homologation: Accidental Discovery?



75% IY

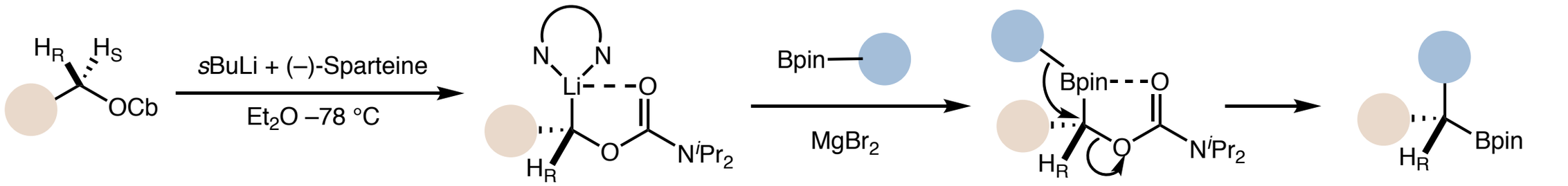
98% ee

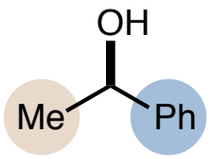
Proposed Mechanism



Aggarwal, V. K.; Fang, G. Y.; Schmidt, A. T. *J. Am. Chem. Soc.* **2005**, *127*, 1642.

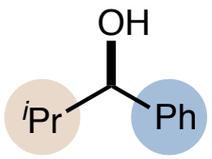
Aggarwal Homologation: New Leaving Group





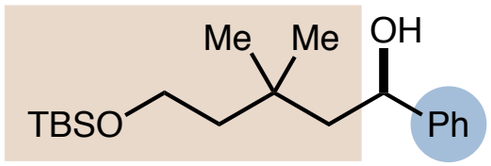
70% IY

94% ee



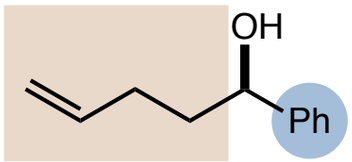
70% IY

96% ee



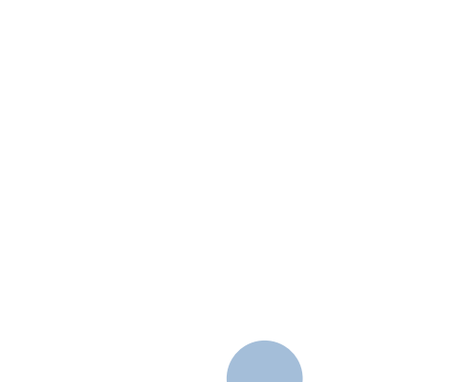
64% IY

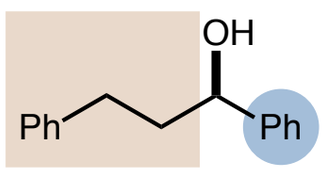
96% ee



73% IY

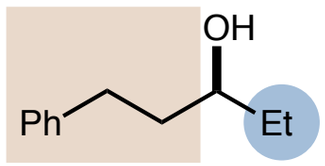
96% ee





94% IY

94% ee



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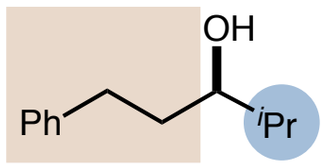
96% ee



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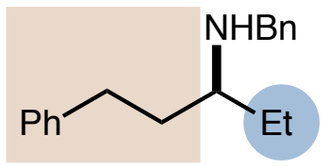
96% ee



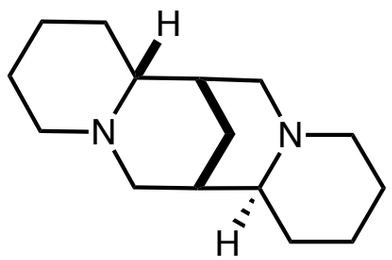
BCl_3/BnN_3 work up

63% IY

96% ee

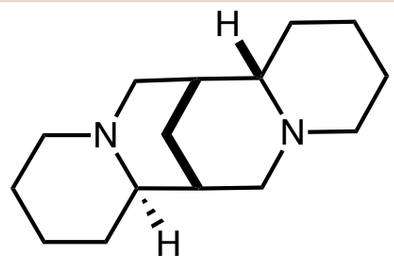
Stymiest, J. L.; Dutheuil, G.; Mahmood, A.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2007**, *46*, 7491.

Aggarwal Homologation: Reagent Controlled Chiralty Transfer



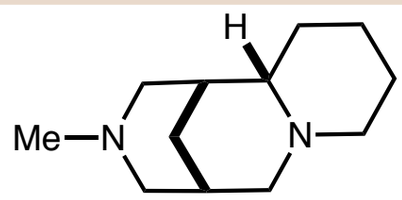
(–)-Sparteine

Used to be Widely Available



(+)-Sparteine

Not Available

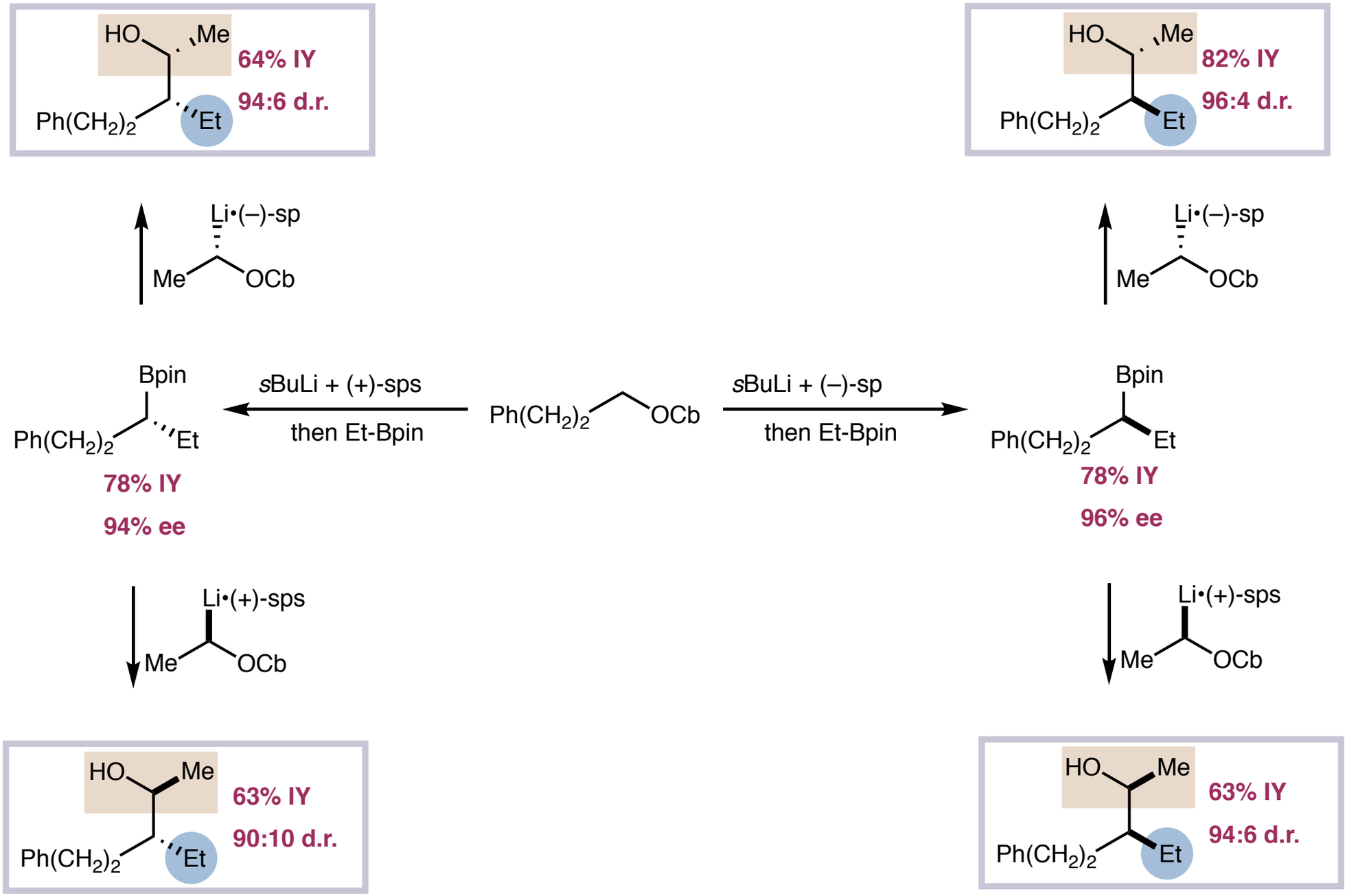


(+)-Sparteine Surrogate

Not Widely Commercial Available

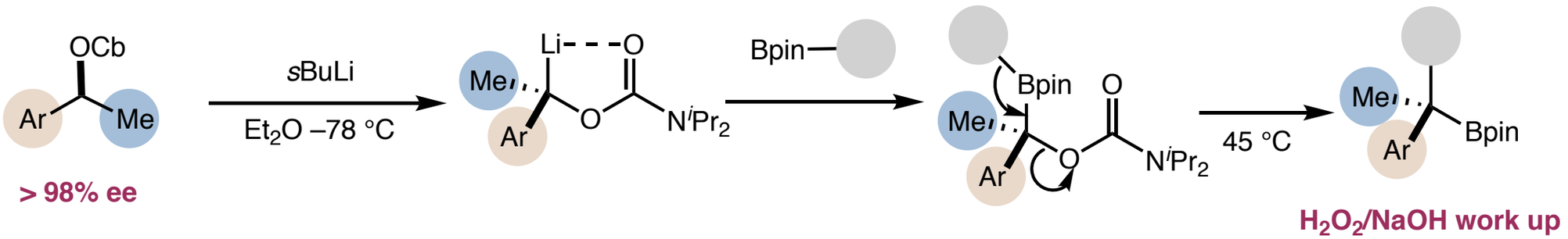
Stymiest, J. L.; Dutheuil, G.; Mahmood, A.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2007**, *46*, 7491.

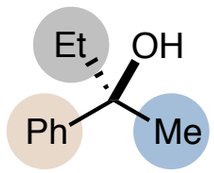
Aggarwal Homologation: Reagent Controlled Chiralty Transfer



Stymiest, J. L.; Dutheuil, G.; Mahmood, A.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2007**, *46*, 7491.

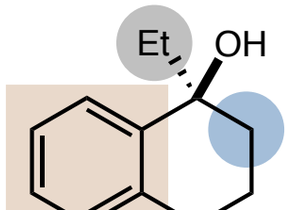
Transfer Alcohol Chirality to C-B bond





95% IY

100% es



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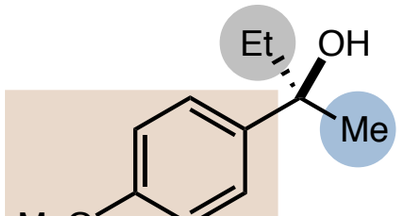
84% es



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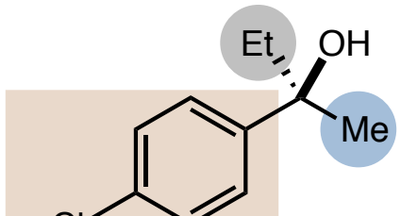
96% es



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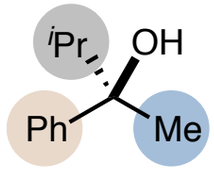

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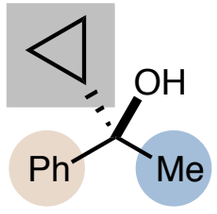

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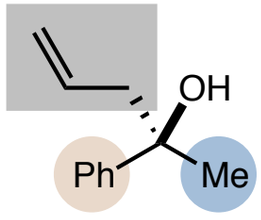

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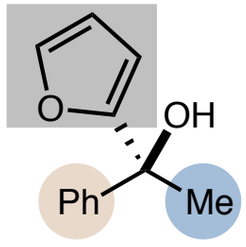
100% es

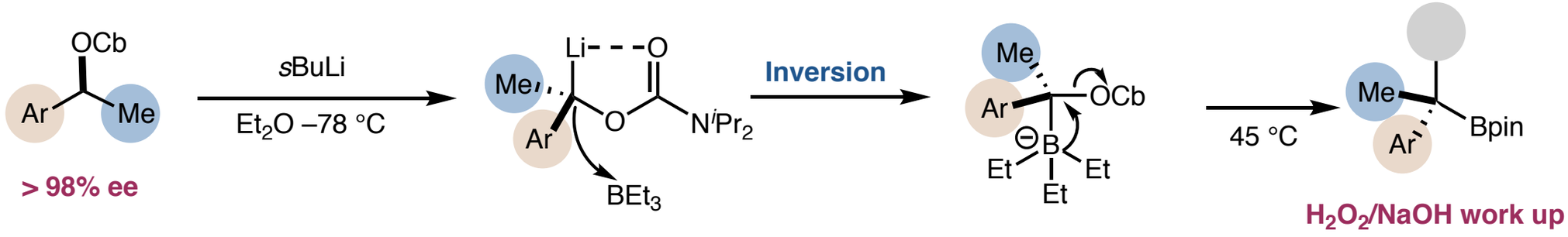


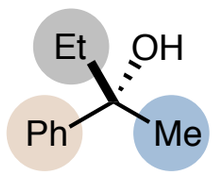
94% IY

98% es

Stymiest, J. L.; Bagutski, V.; French, R. M.; Aggarwal, V. K. *Nature* **2008**, *456*, 778.

Transfer Alcohol Chirality to C-B bond





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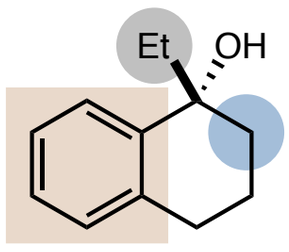

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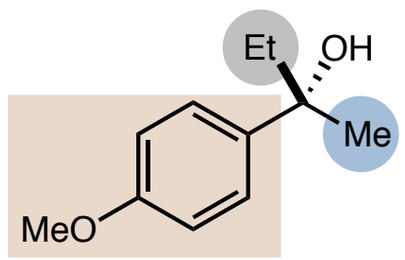

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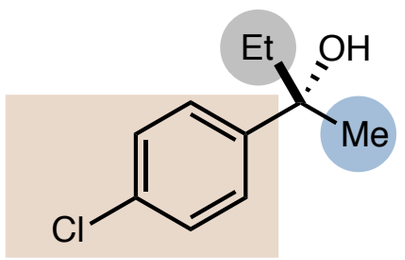

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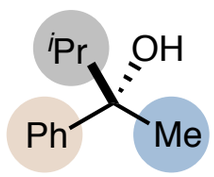


91% IY

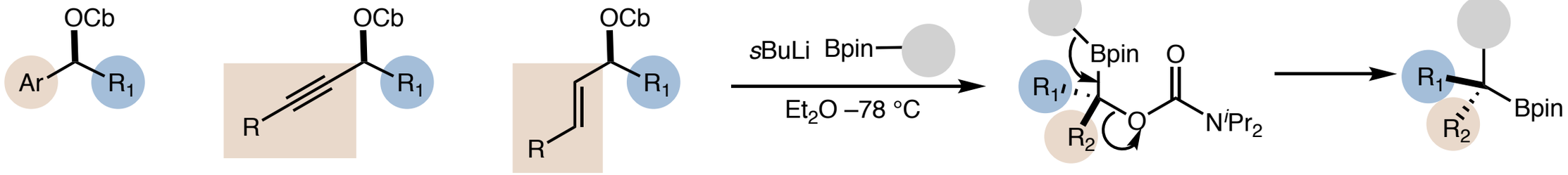
96% es

From ^{i}Pr-9-BBN

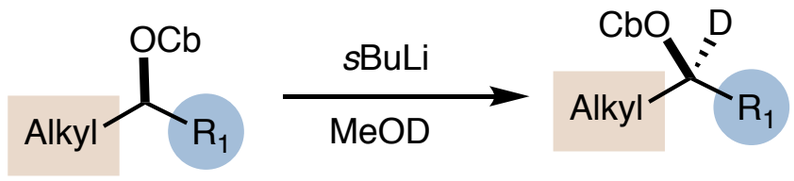
Inversion only happen when carbon-anion is benzylic

Stymiest, J. L.; Bagutski, V.; French, R. M.; Aggarwal, V. K. *Nature* **2008**, *456*, 778.

From Benzylic Alcohol to Normal Secondary Alcohol

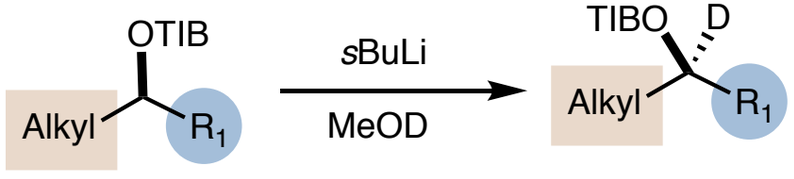


Acidlc C-H Bond

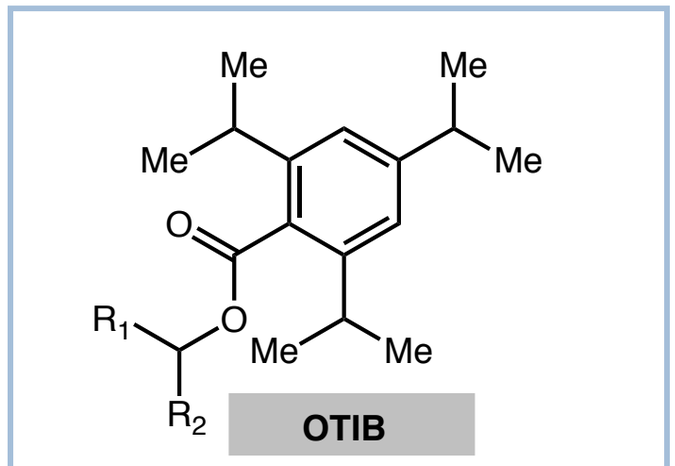


D <10%

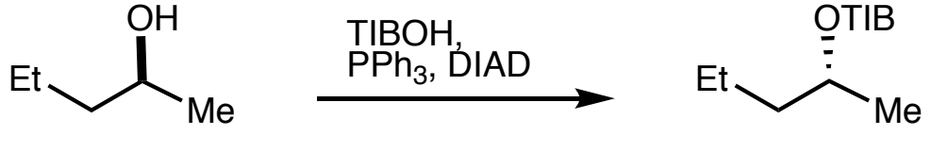
New leaving group required



D 92%



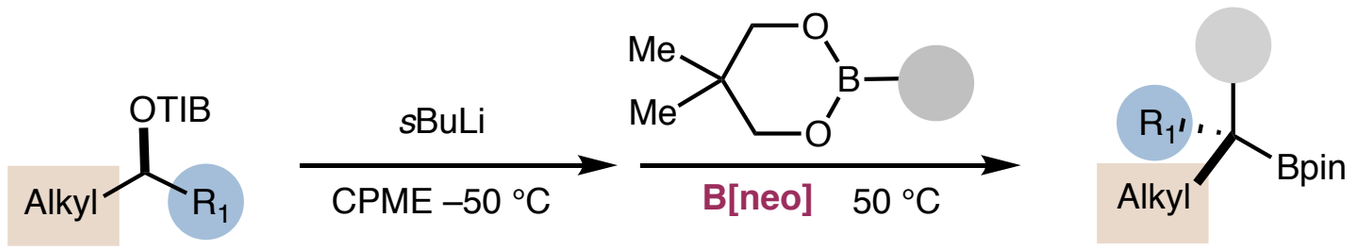
Installation:

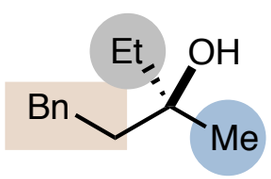


Pulis, A. P.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2012**, *134*, 7570.

Partridge, B. M.; Chausset-Boissarie, L.; Burns, M.; Pulis, A. P.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2012**, *51*, 11795.

From Benzylic Alcohol to Normal Secondary Alcohol





80% IY

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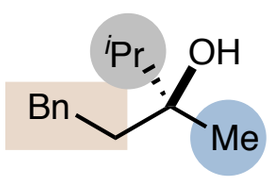

74% IY

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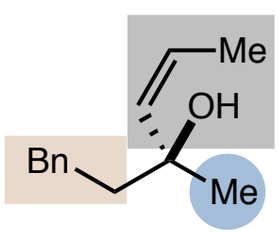

78% IY

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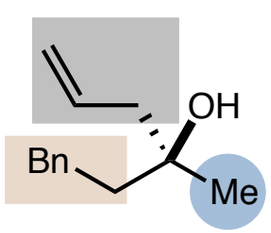

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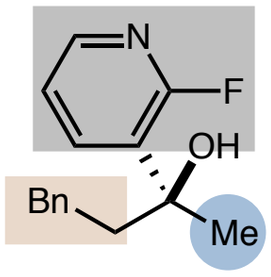

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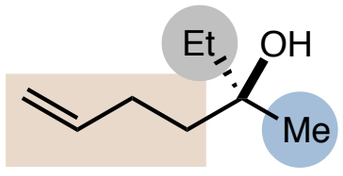

72% IY

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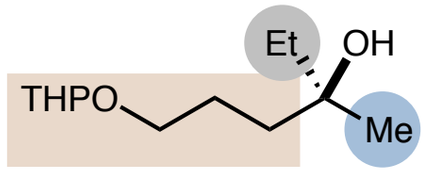
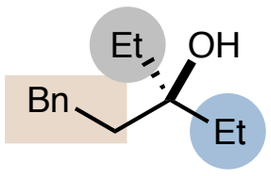


56% IY 93%brsm

98% es



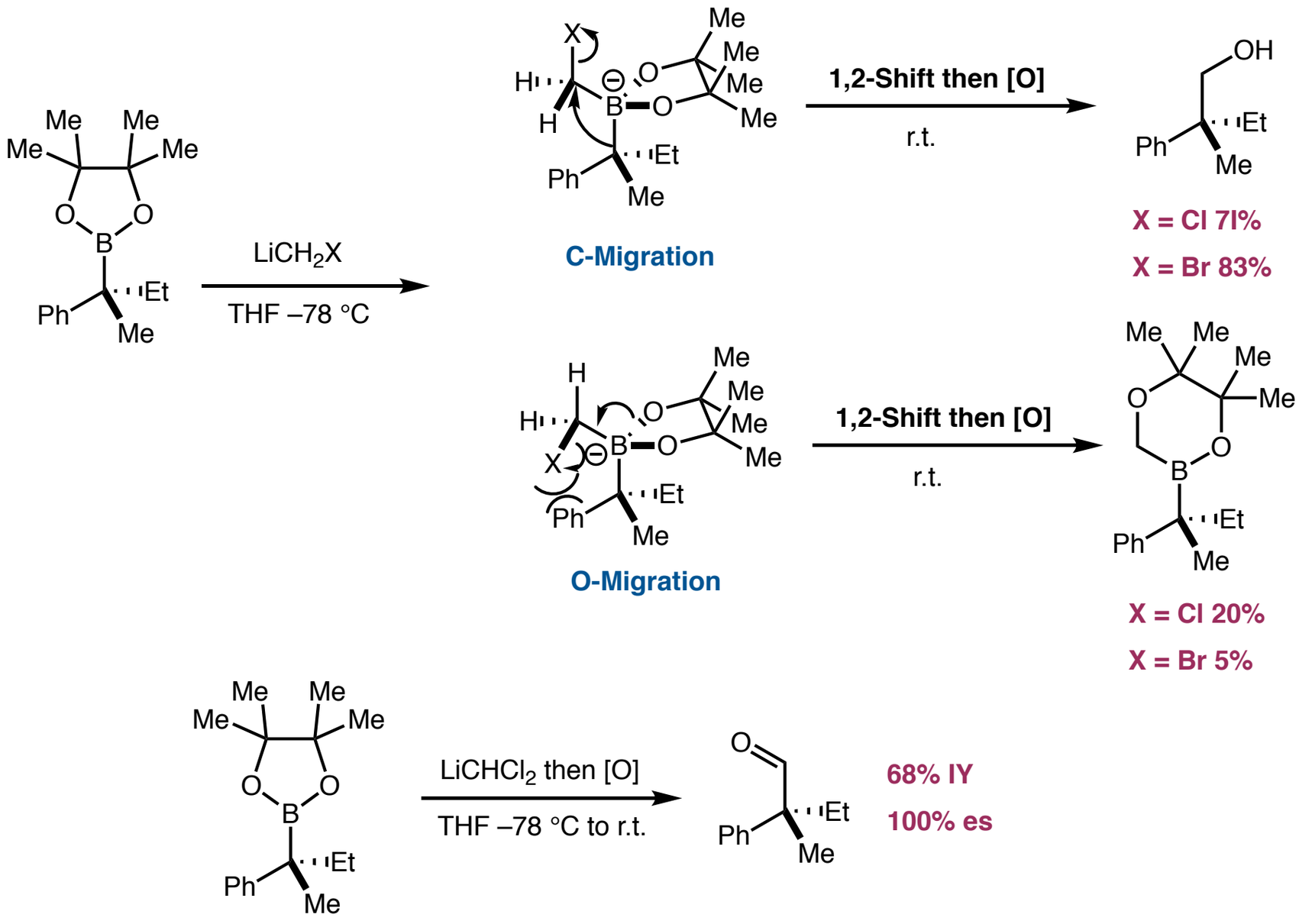
40% IY 78%brsm

100% es

Pulis, A. P.; Blair, D. J.; Torres, E.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2013**, *135*, 16054.

From Tertiary Boronic Acid to Quaternary Carbon Center

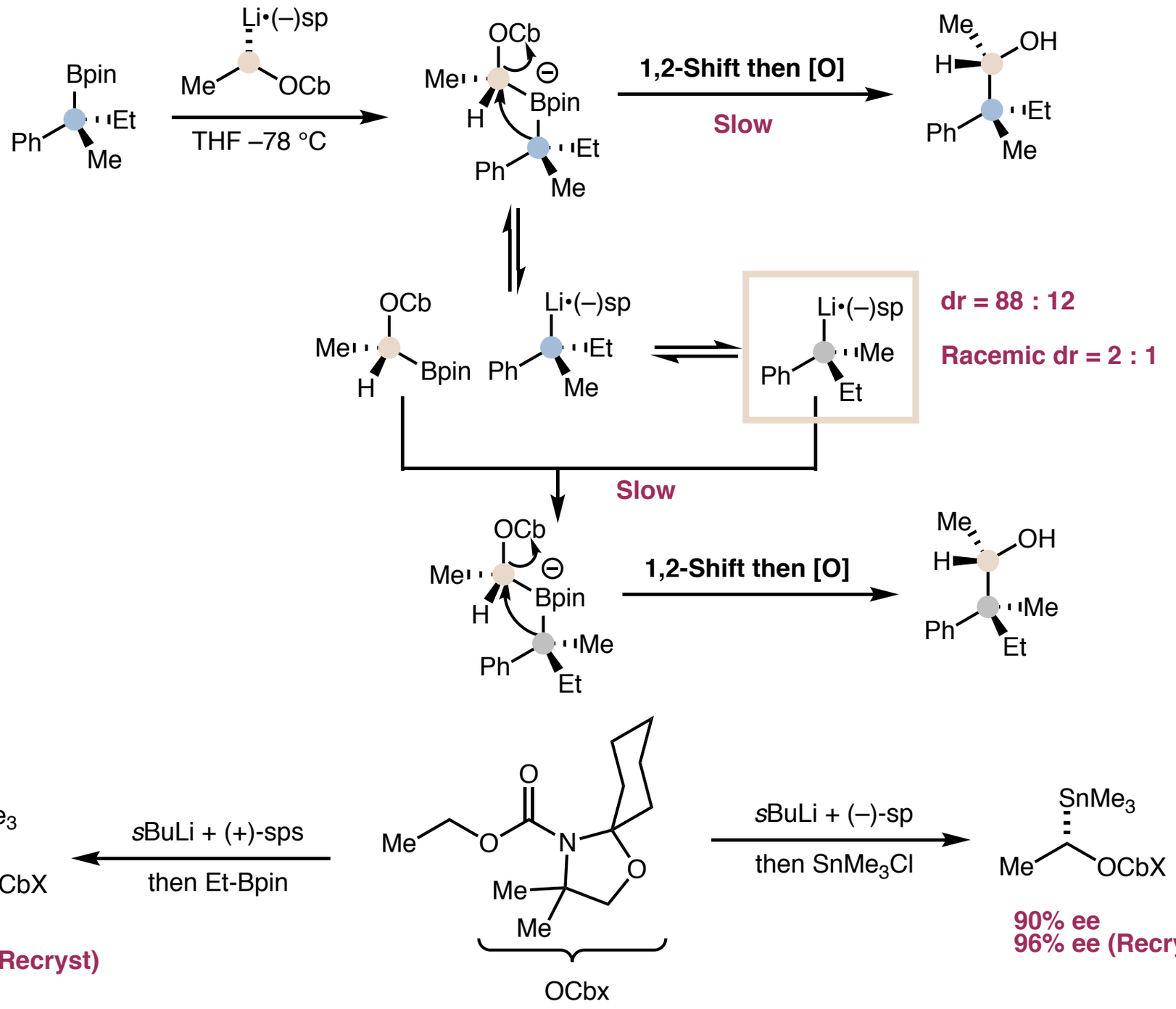
Quaternary Carbon + Methylene



Sonawane, R. P.; Jheengut, V.; Rabalakos, C.; Larouche-Gauthier, R.; Scott, H. K.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2011**, *50*, 3760.

From Tertiary Boronic Acid to Quaternary Carbon Center

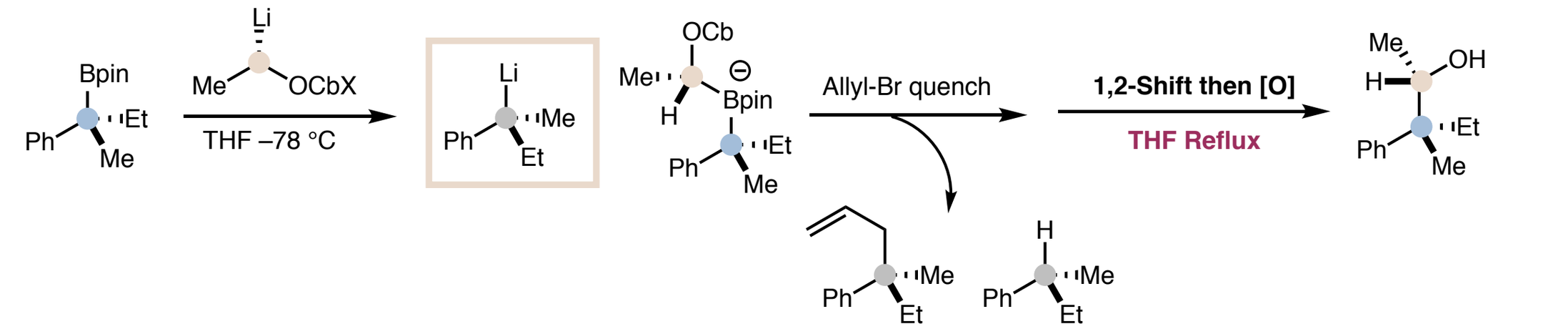
Quaternary Carbon + Methine

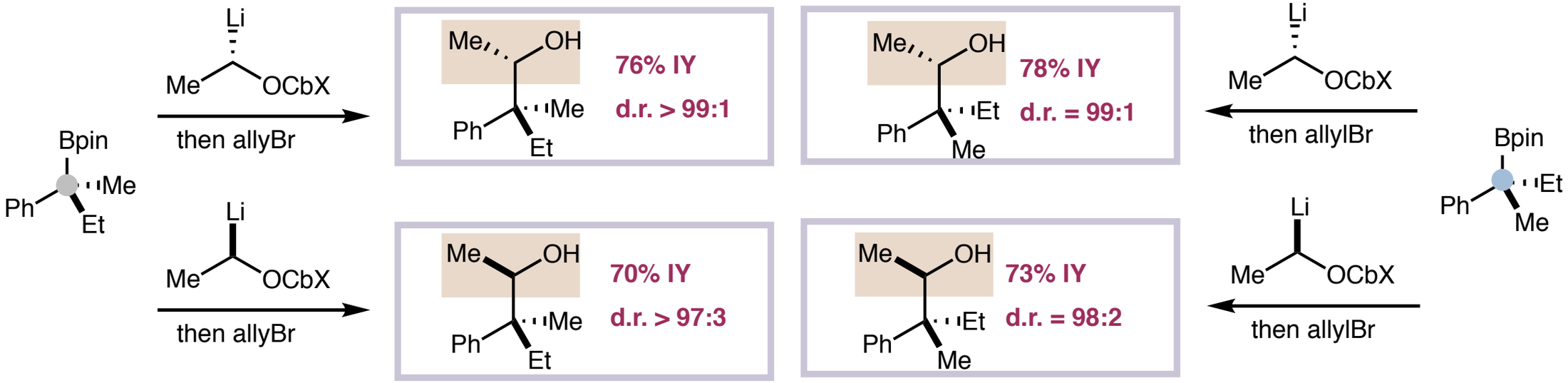


Blair, D. J.; Fletcher, C. J.; Wheelhouse, K. M. P.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2014**, *53*, 5552.

From Tertiary Boronic Acid to Quaternary Carbon Center

Quaternary Carbon + Methine

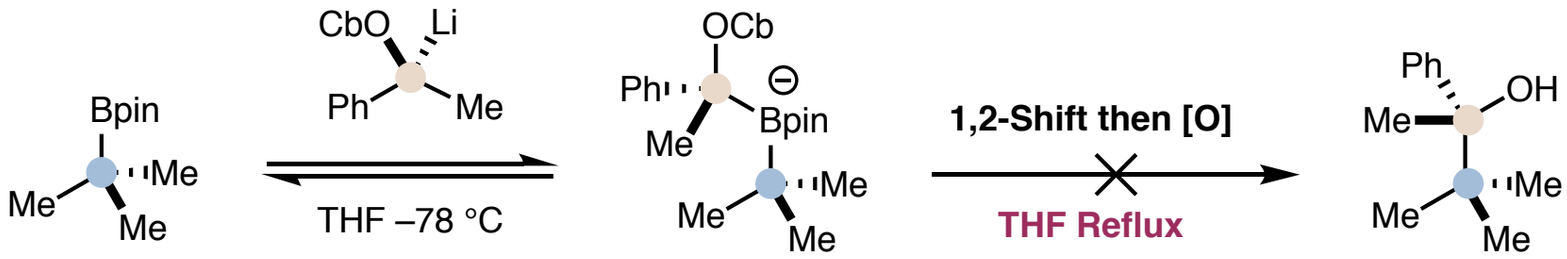


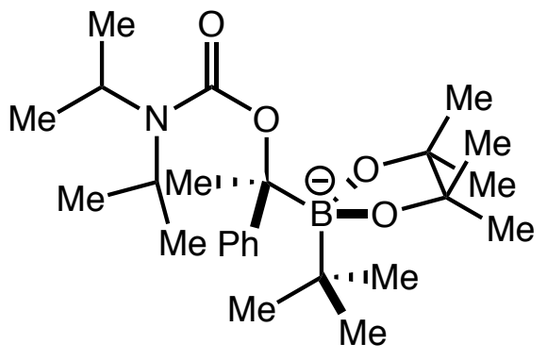


Blair, D. J.; Fletcher, C. J.; Wheelhouse, K. M. P.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2014**, *53*, 5552.

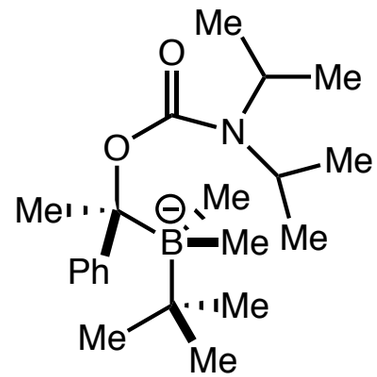
From Tertiary Boronic Acid to Quaternary Carbon Center

Quaternary Carbon + Quaternary Carbon



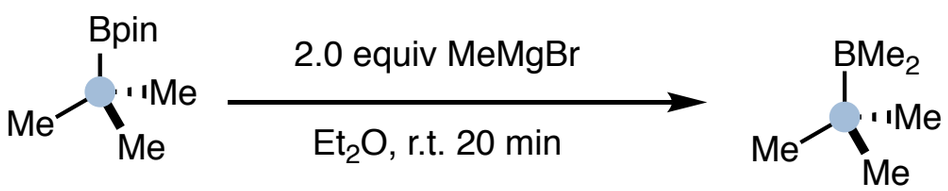


Too Hindered to form



tBuBMe$_2$

- *Reduced Steric Hinderance*
- *More Positve Boron Center*

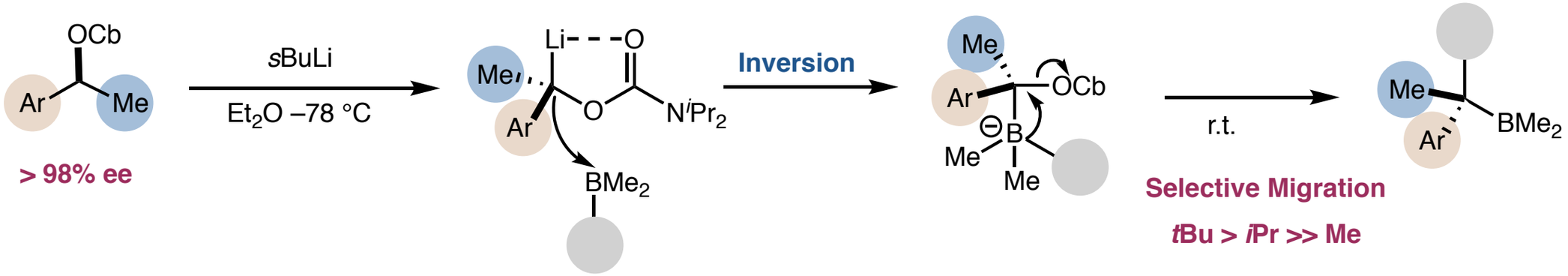


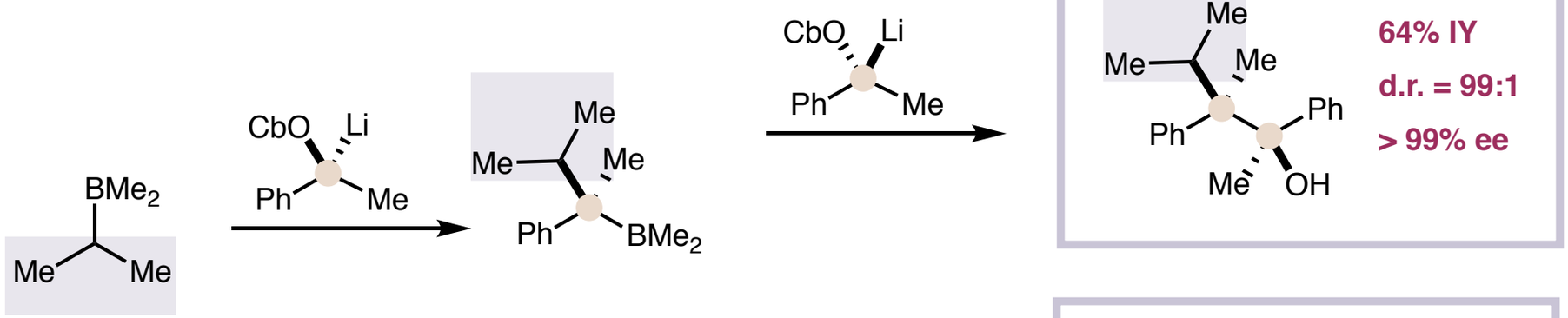
Purified by Distillation

Watson, C. G.; Balanta, A.; Elford, T. G.; Essafi, S.; Harvey, J. N.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2014**, *136*, 17370.

From Tertiary Boronic Acid to Quaternary Carbon Center

Quaternary Carbon + Quaternary Carbon





Watson, C. G.; Balanta, A.; Elford, T. G.; Essafi, S.; Harvey, J. N.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2014**, *136*, 17370.

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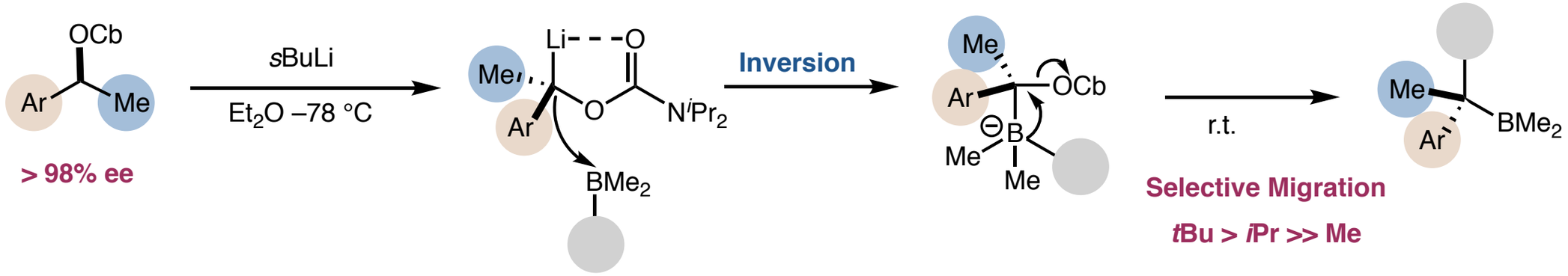
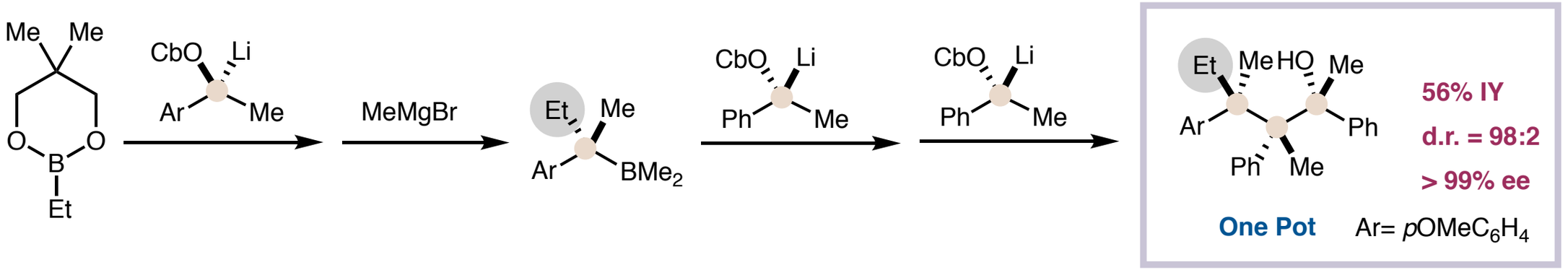
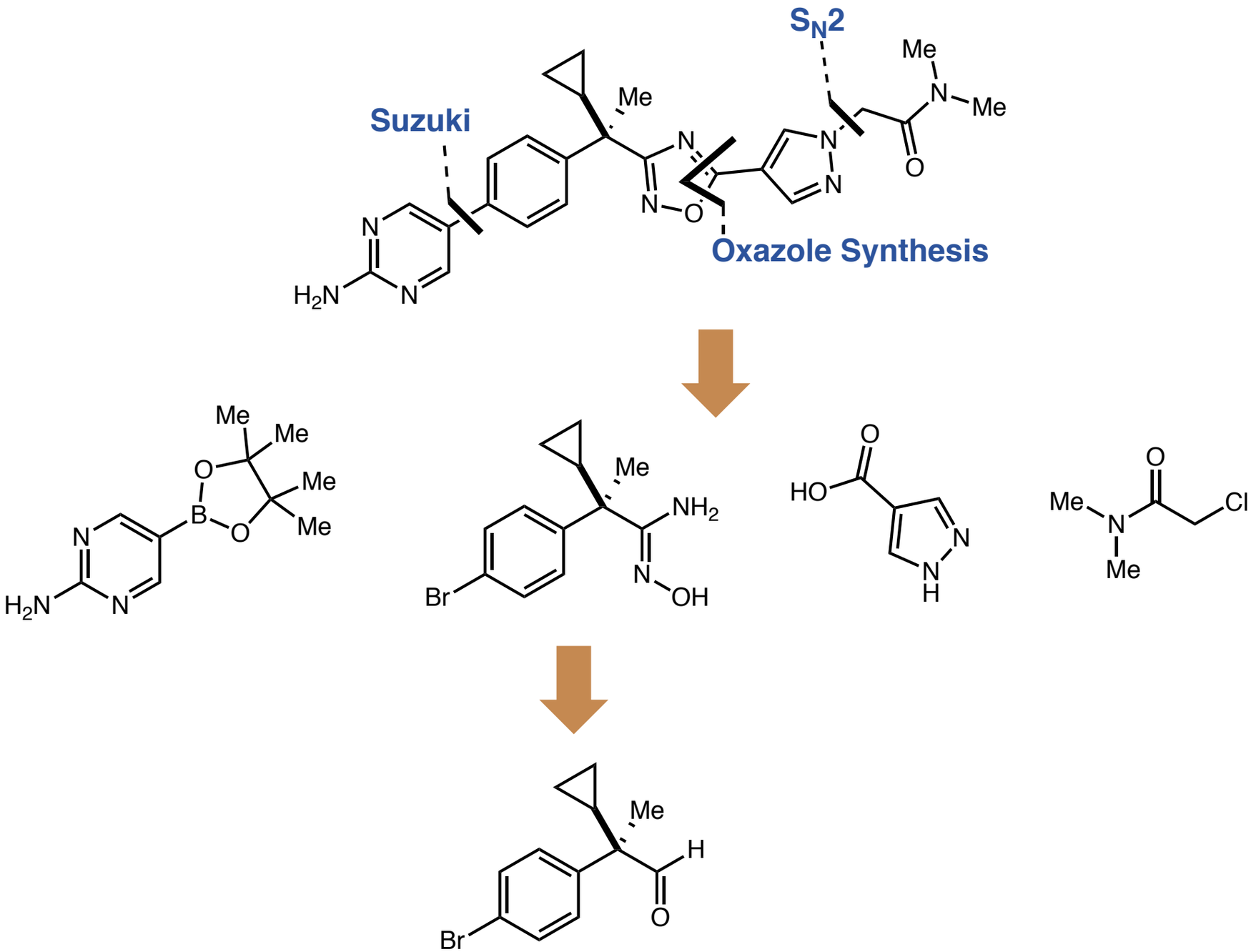




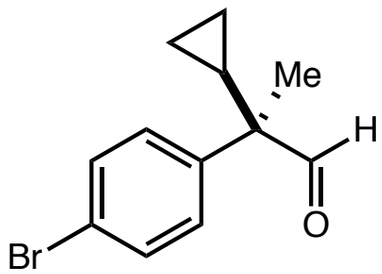
Watson, C. G.; Balanta, A.; Elford, T. G.; Essafi, S.; Harvey, J. N.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2014**, *136*, 17370.

Drug Candidate Synthesis

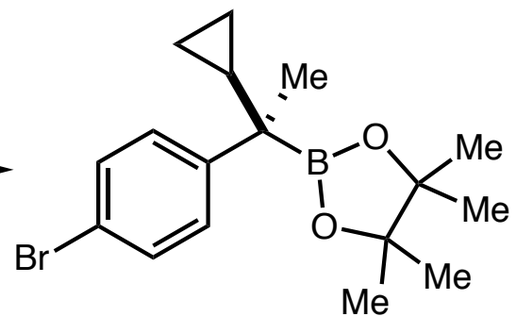


Senanayake, C. H. *et al. Org. Lett.* **2014**, *16*, 4360.

Drug Candidate Synthesis

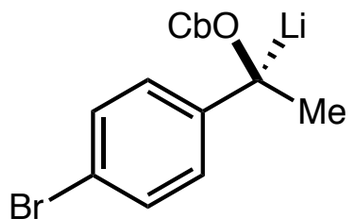


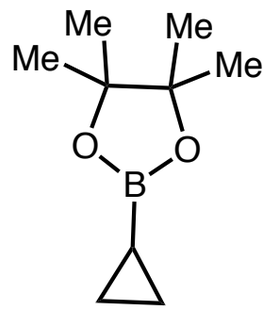
Matteson Homologation



Aggarwal Homologation

Route 1

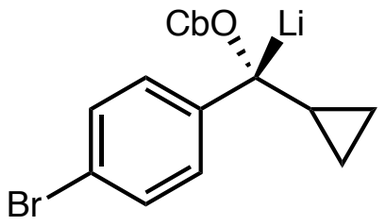


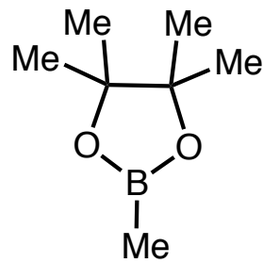


Deprotonation vs Li-Halogen Exchange

Cheap Chiral Alcohol

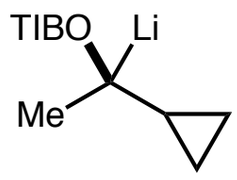
Route 2

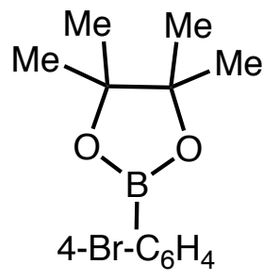




Me Migration is problem

Route 3



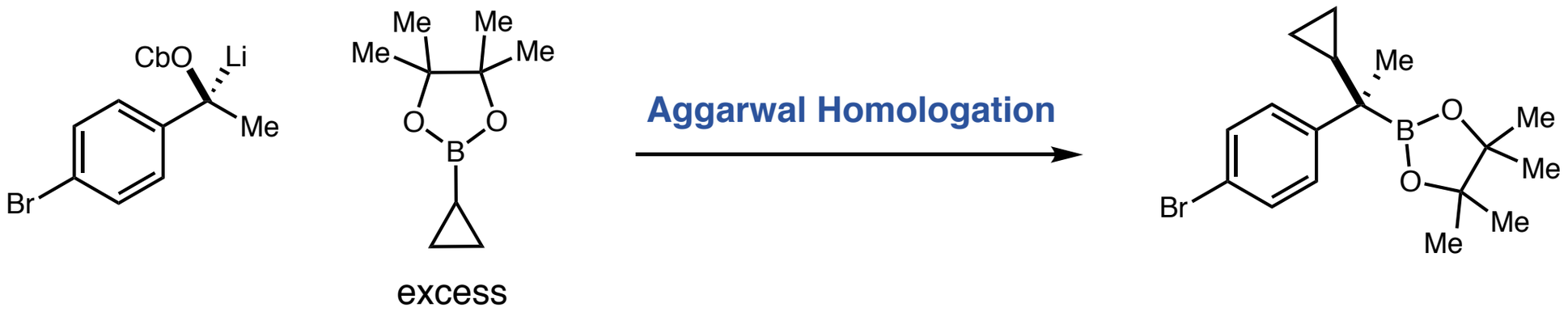


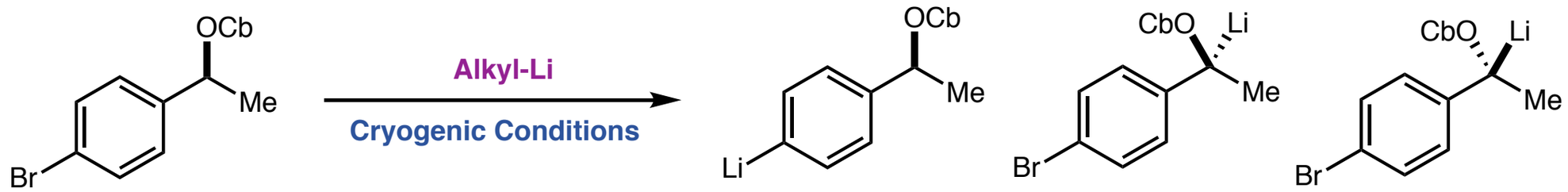
Chiral Alcohol is hard to access

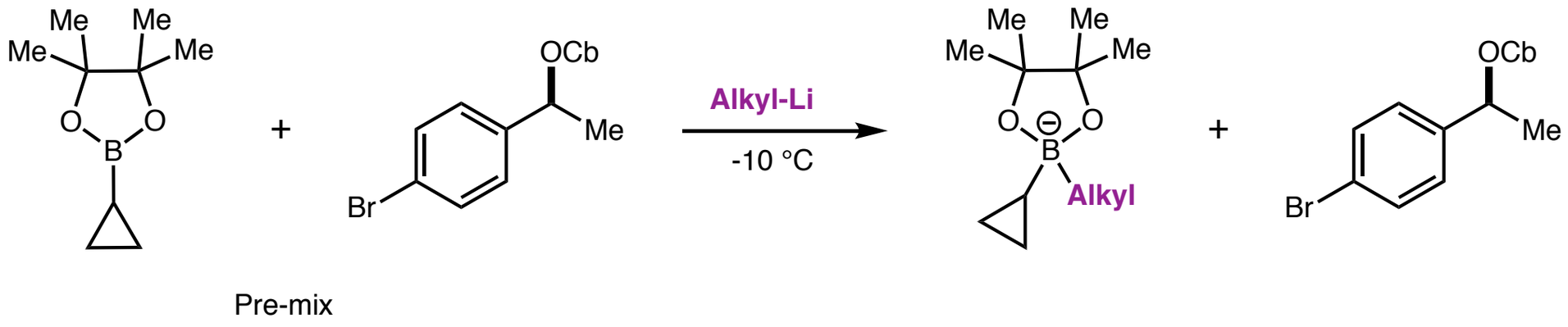
Senanayake, C. H. *et al. Org. Lett.* **2014**, *16*, 4360.

Senanayake, C. H. *et al. J. Org. Chem.* **2015**, *80*, 1651.

Drug Candidate Synthesis



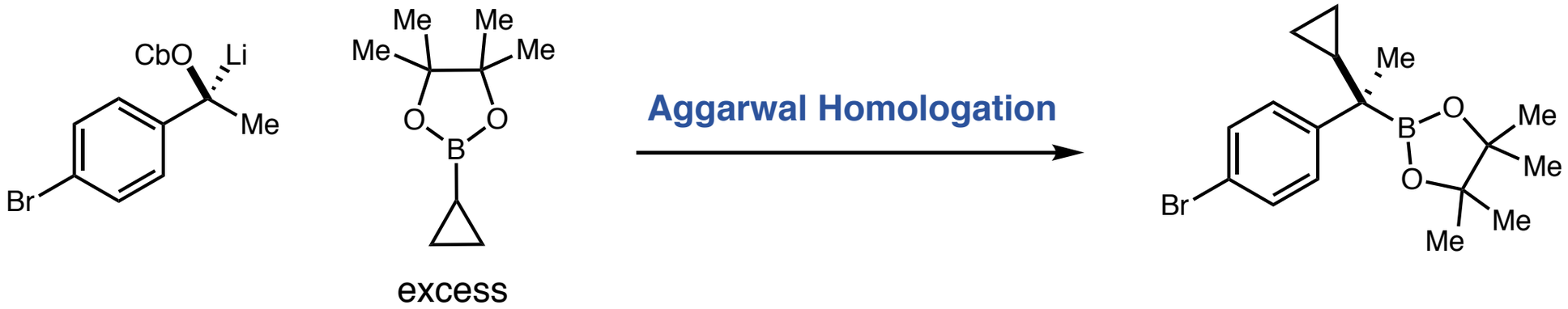


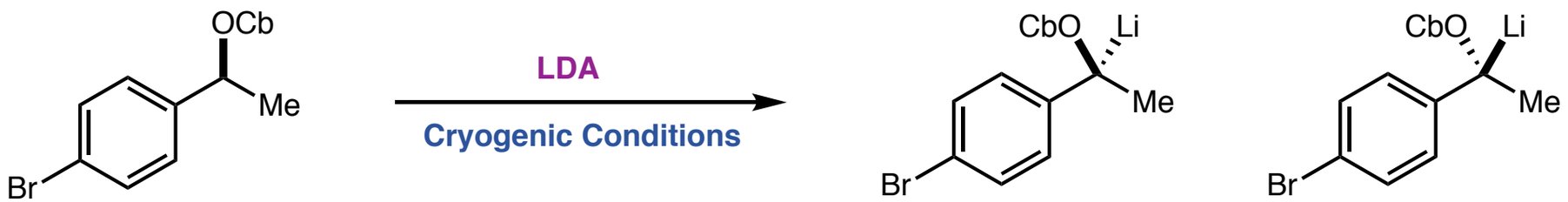


Senanayake, C. H. *et al. Org. Lett.* **2014**, *16*, 4360.

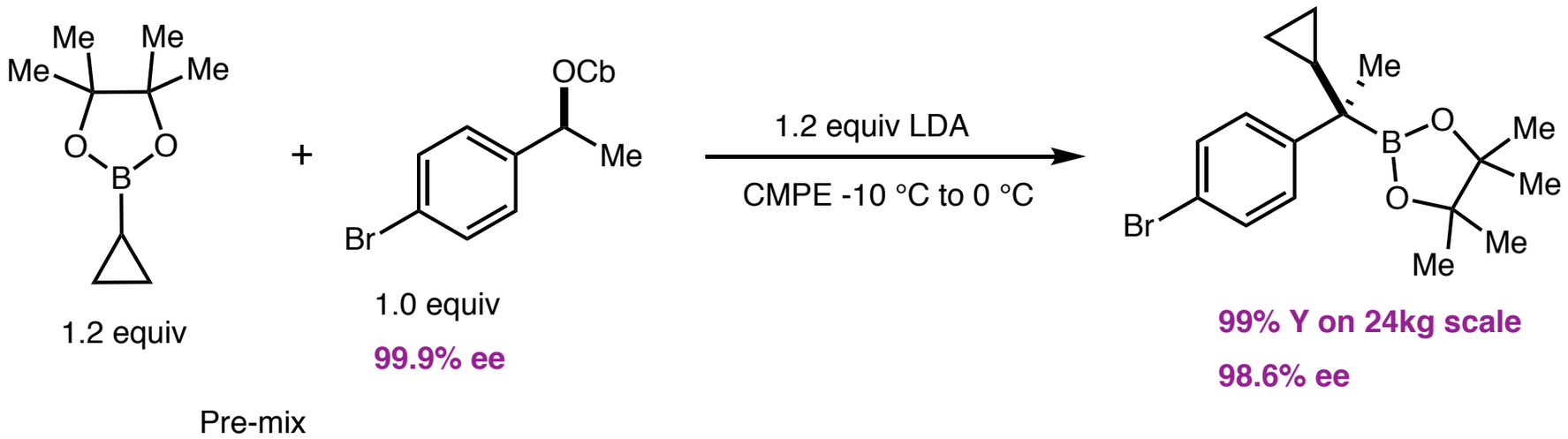
Senanayake, C. H. *et al. J. Org. Chem.* **2015**, *80*, 1651.

Drug Candidate Synthesis





Epimerization occurs before full conversion



Pre-mix

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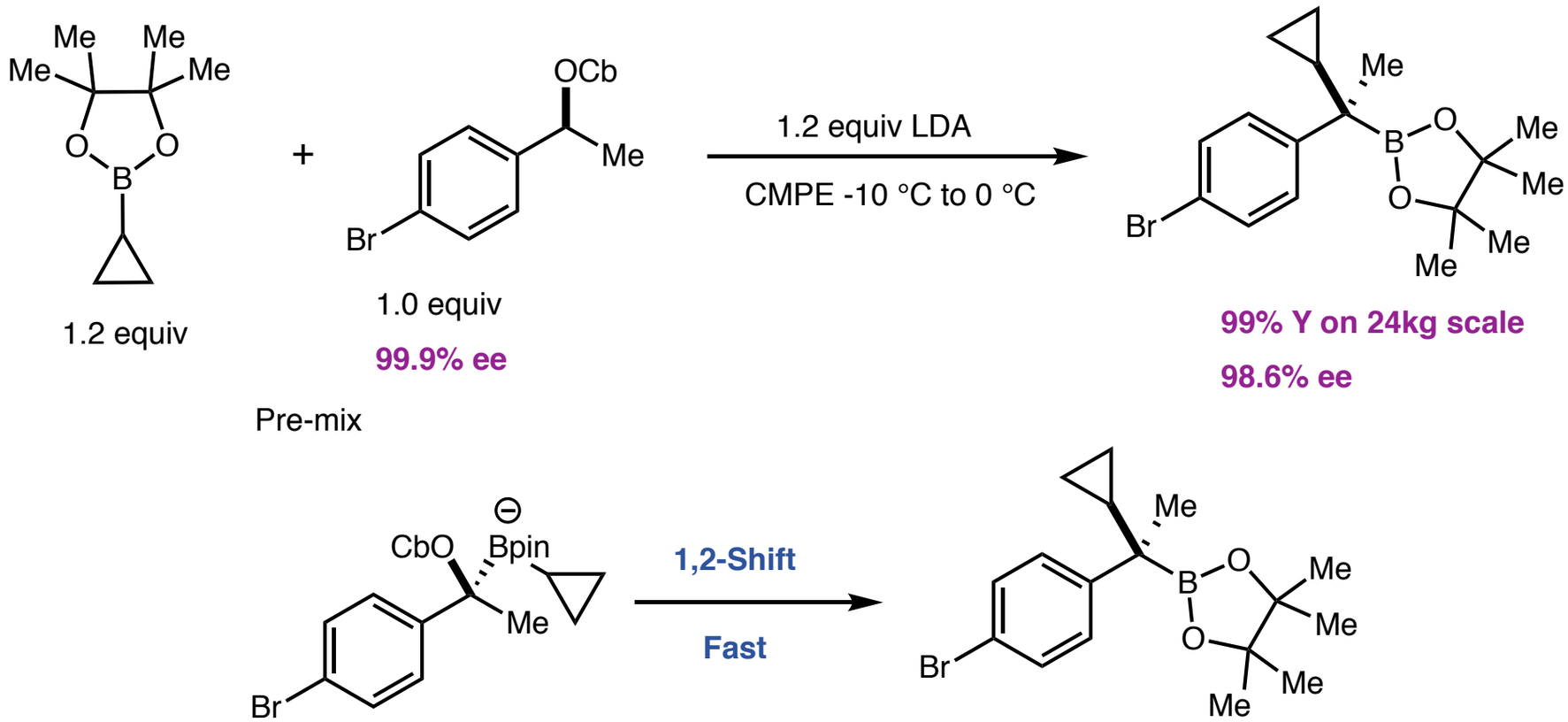
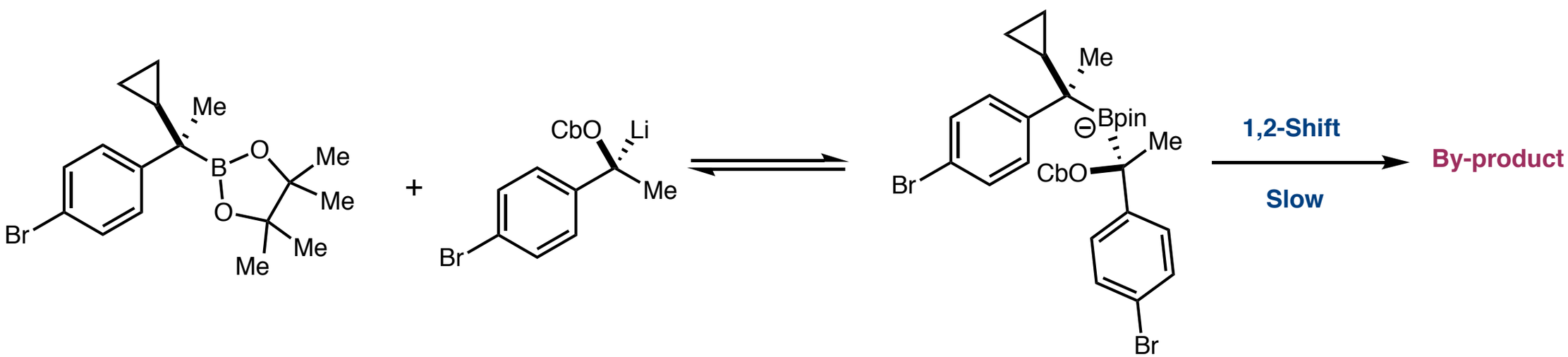
Senanayake, C. H. *et al. J. Org. Chem.* **2015**, *80*, 1651.

Drug Candidate Synthesis





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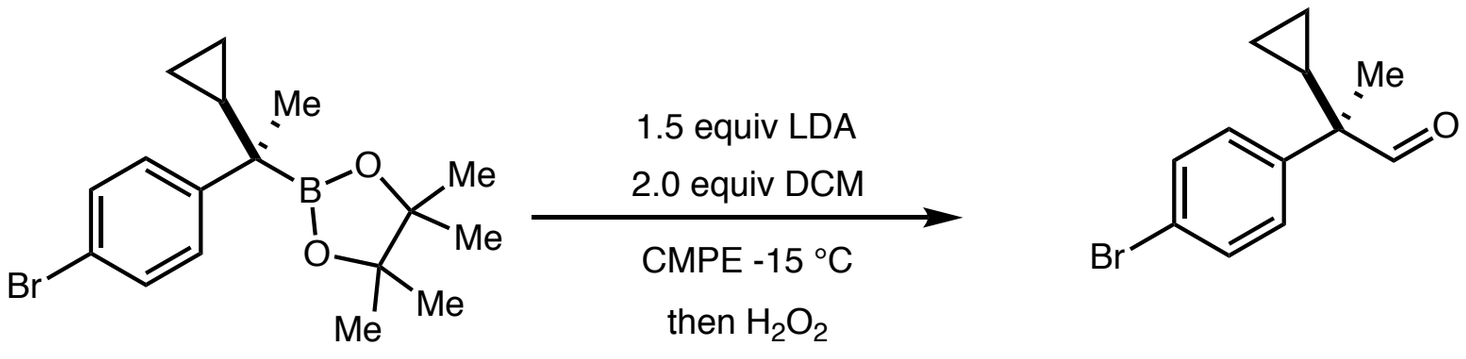
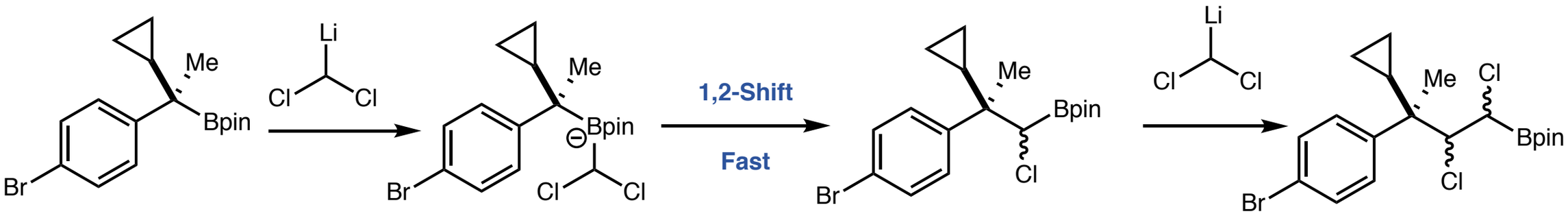
Drug Candidate Synthesis



LDA addtion time	Yield
< 1min	**93%**
35 min	**25%**

Problem : Muliple Homologation:



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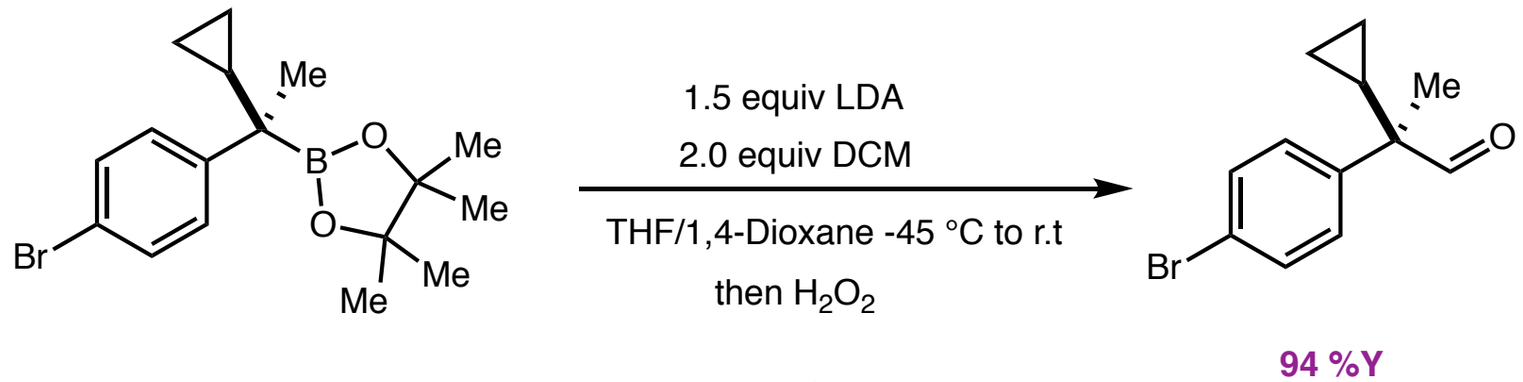
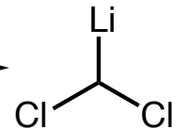
Drug Candidate Synthesis

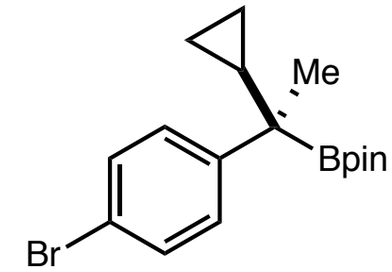


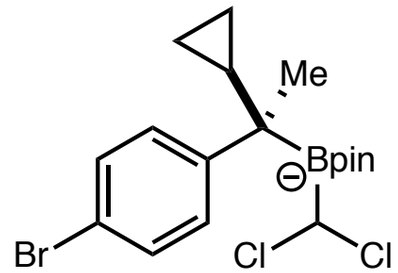
94 %Y

What is the trick?

-45 °C DCM LDA







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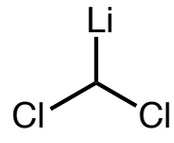
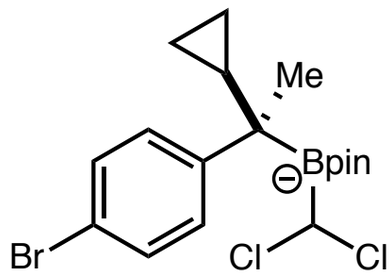
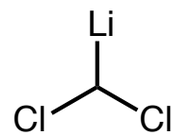


Excess

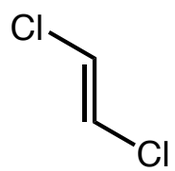
-25 °C



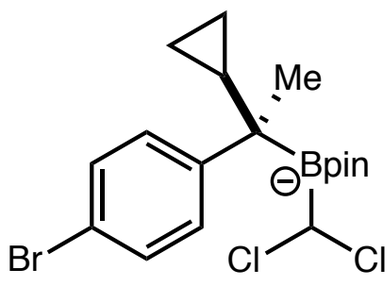
Inert



Fast Decomposion

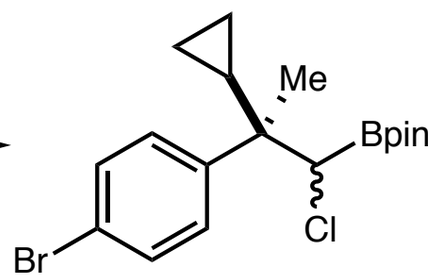


> -15 °C



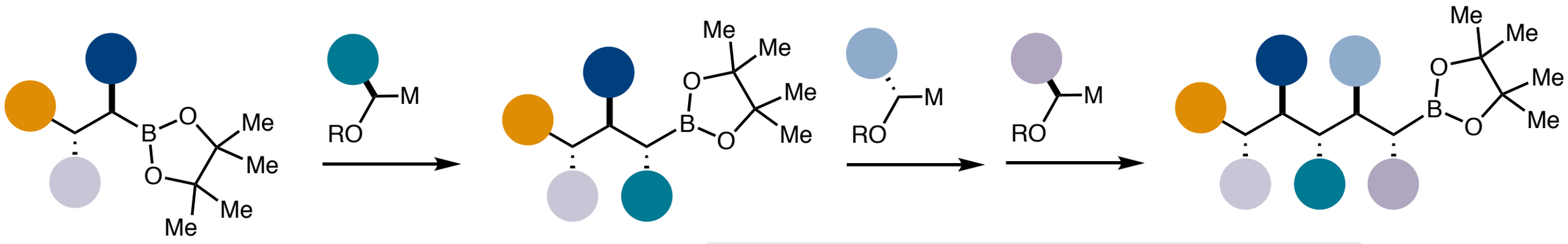
1,2-Shift

Fast



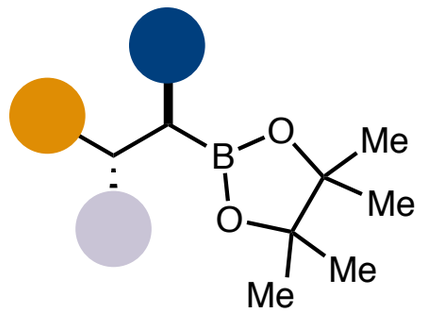
Senanayake, C. H. *et al. J. Org. Chem.* **2015**, *80*, 1651.

Programmable Temperature Enabled Assemble Line Synthesis



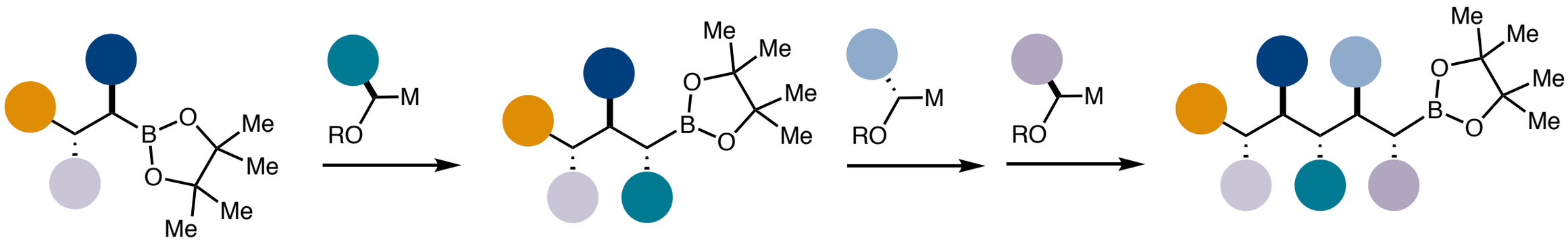
Auto Synthesis with Reagent Controlled Chirality

Working Hypothesis:



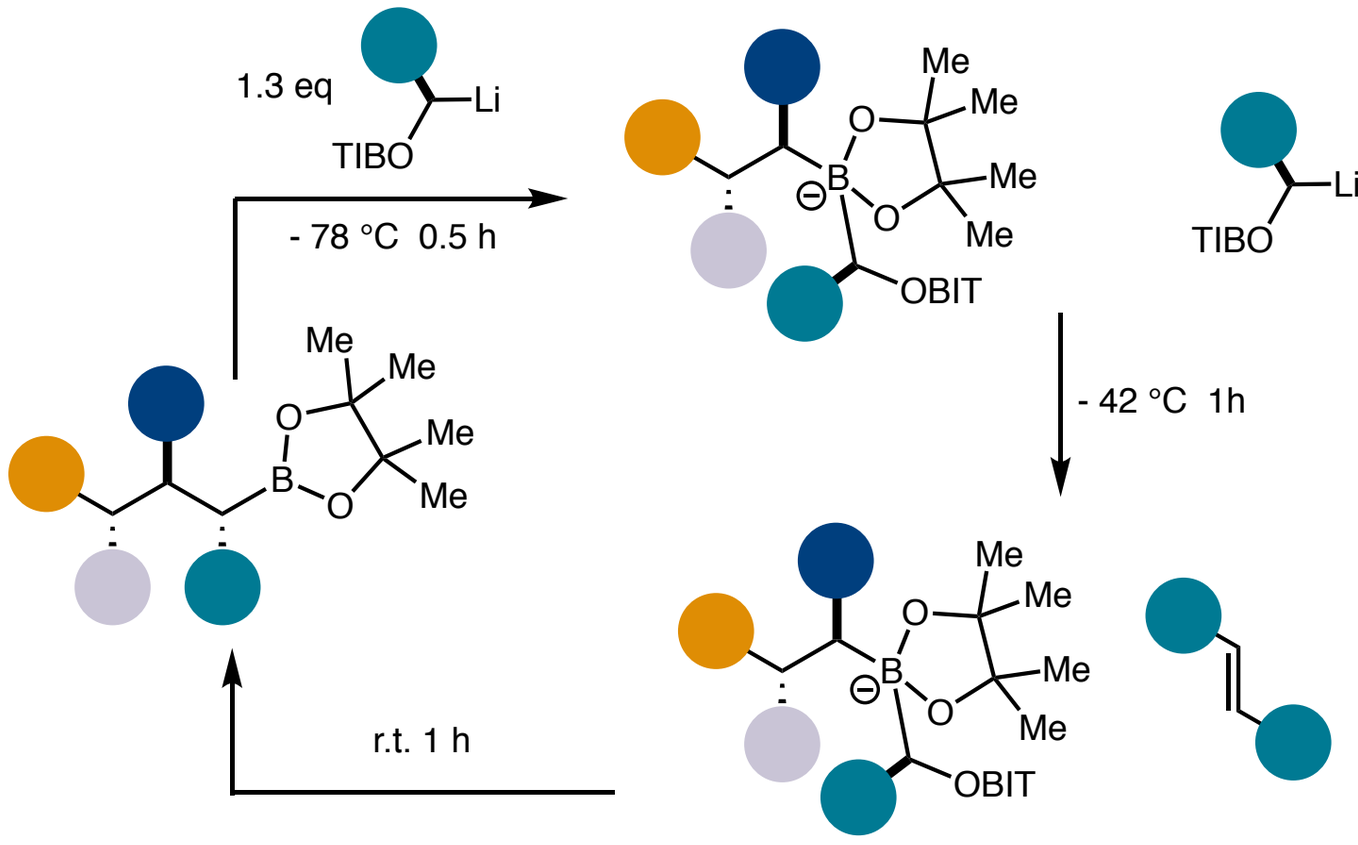
Burns, M.; Essafi, S.; Bame, J. R.; Bull, S. P.; Webster, M. P.; Balieu, S.; Dale, J. W.; Butts, C. P.; Harvey, J. N.; Aggarwal, V. K. *Nature* **2014**, *513*, 183

Programmable Temperature Enabled Assemble Line Synthesis



Auto Synthesis with Reagent Controlled Chirality

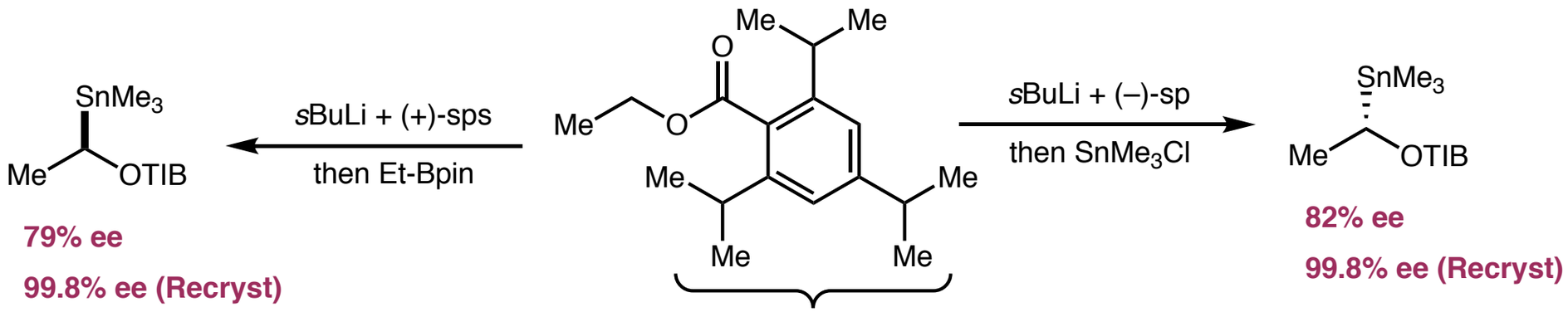
Working Hypothesis:



Burns, M.; Essafi, S.; Bame, J. R.; Bull, S. P.; Webster, M. P.; Balieu, S.; Dale, J. W.; Butts, C. P.; Harvey, J. N.; Aggarwal, V. K. *Nature* **2014**, *513*, 183

Programmable Temperature Enabled Assemble Line Synthesis

High Purity Reagents:



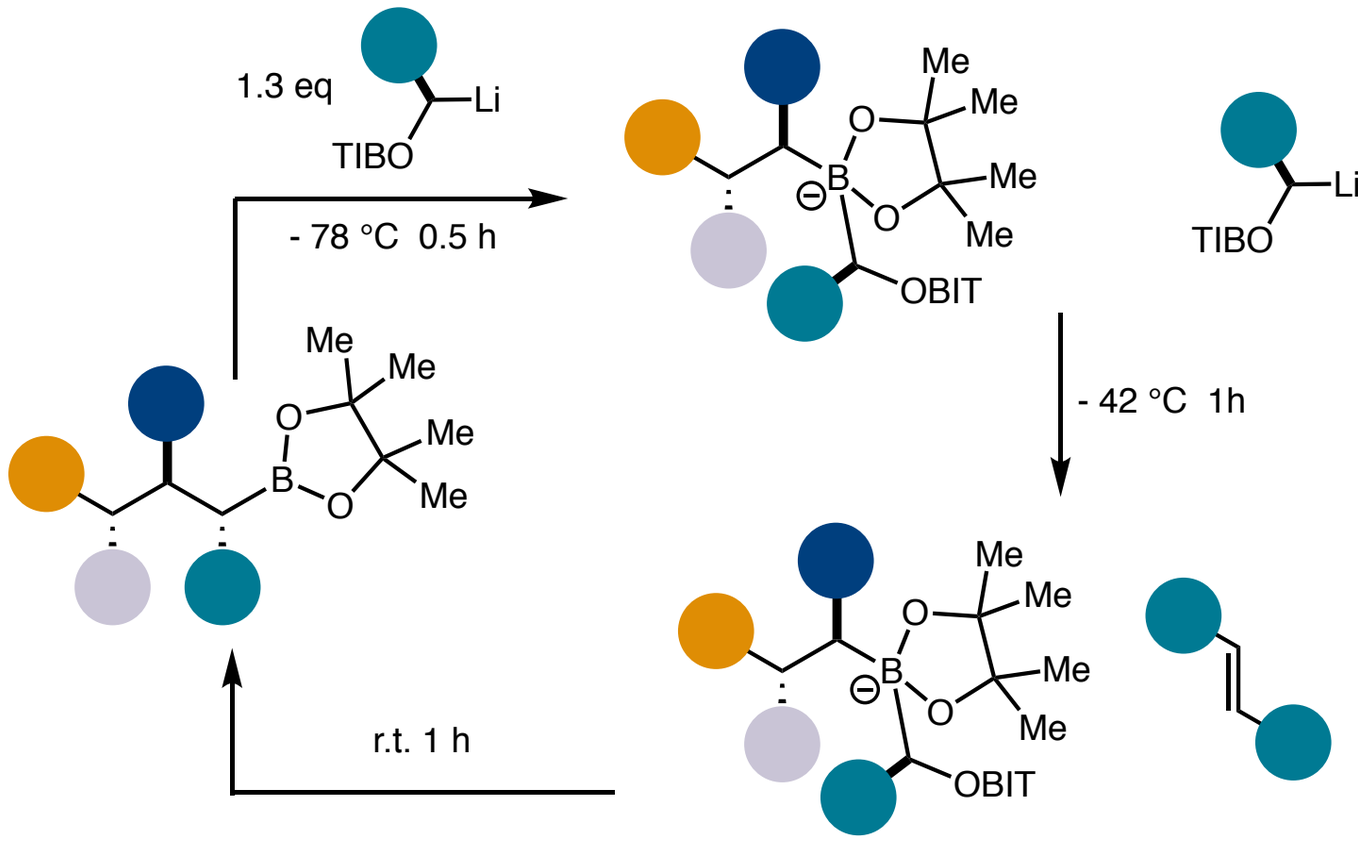
79% ee

99.8% ee (Recryst)

82% ee

99.8% ee (Recryst)

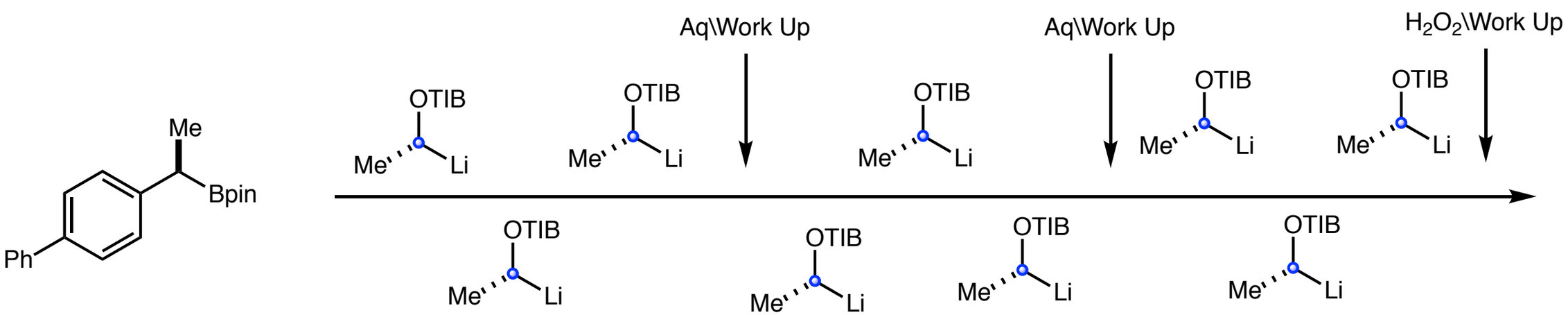
Working Hypothesis:

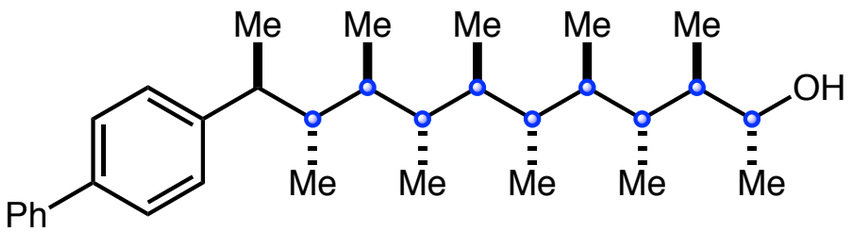


Burns, M.; Essafi, S.; Bame, J. R.; Bull, S. P.; Webster, M. P.; Balieu, S.; Dale, J. W.; Butts, C. P.; Harvey, J. N.; Aggarwal, V. K. *Nature* **2014**, *513*, 183

Programmable Temperature Enabled Assemble Line Synthesis

State of Art:





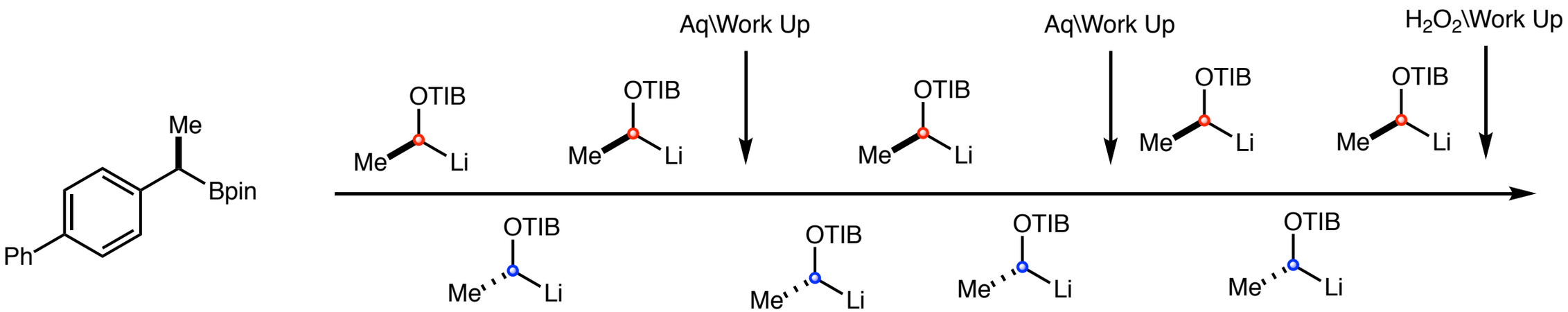
58% IY
> 99:1 d.r.

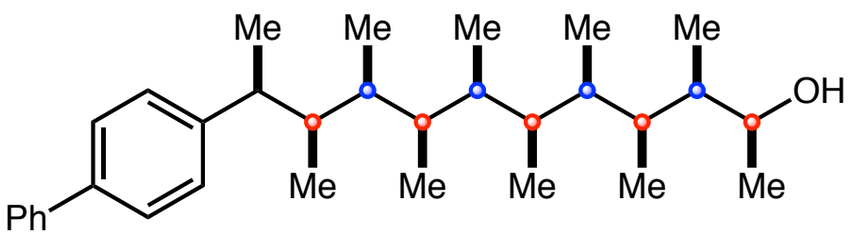
+ 8 C	**1**
+ 9 C	**97**
+ 10 C	**2**

Burns, M.; Essafi, S.; Bame, J. R.; Bull, S. P.; Webster, M. P.; Balieu, S.; Dale, J. W.; Butts, C. P.; Harvey, J. N.; Aggarwal, V. K. *Nature* **2014**, *513*, 183

Programmable Temperature Enabled Assemble Line Synthesis

State of Art:





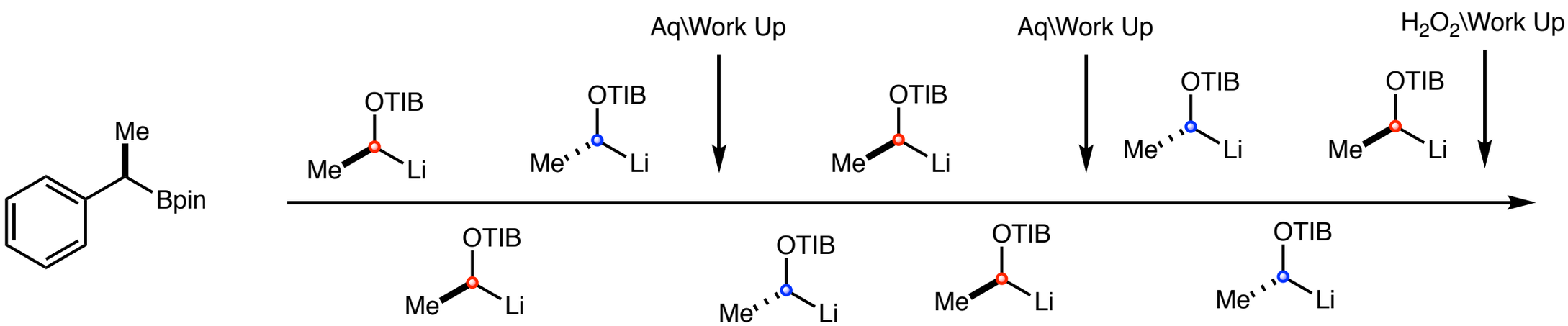
44% IY
> 99:1 d.r.

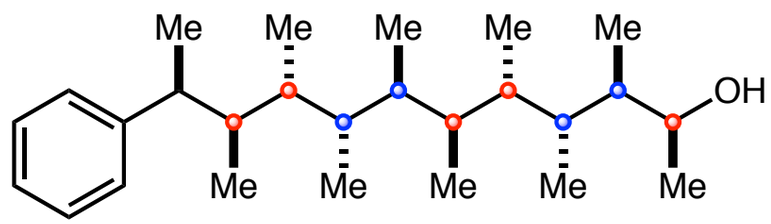
+ 8 C	**1**
+ 9 C	**94**
+ 10 C	**5**

Burns, M.; Essafi, S.; Bame, J. R.; Bull, S. P.; Webster, M. P.; Balieu, S.; Dale, J. W.; Butts, C. P.; Harvey, J. N.; Aggarwal, V. K. *Nature* **2014**, *513*, 183

Programmable Temperature Enabled Assemble Line Synthesis

State of Art:



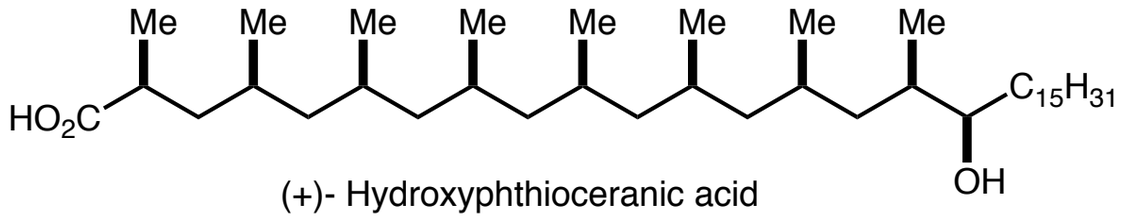


45% IY
> 99:1 d.r.

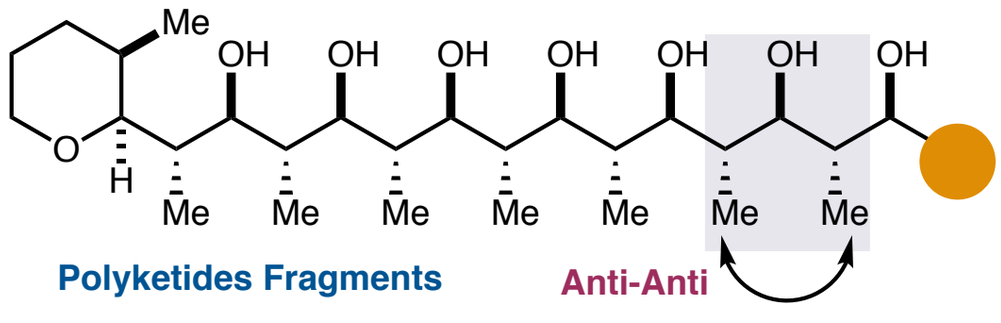
+ 8 C	**0**
+ 9 C	**97**
+ 10 C	**3**

Burns, M.; Essafi, S.; Bame, J. R.; Bull, S. P.; Webster, M. P.; Balieu, S.; Dale, J. W.; Butts, C. P.; Harvey, J. N.; Aggarwal, V. K. *Nature* **2014**, *513*, 183

From Hydrocarbon to Polypropionates

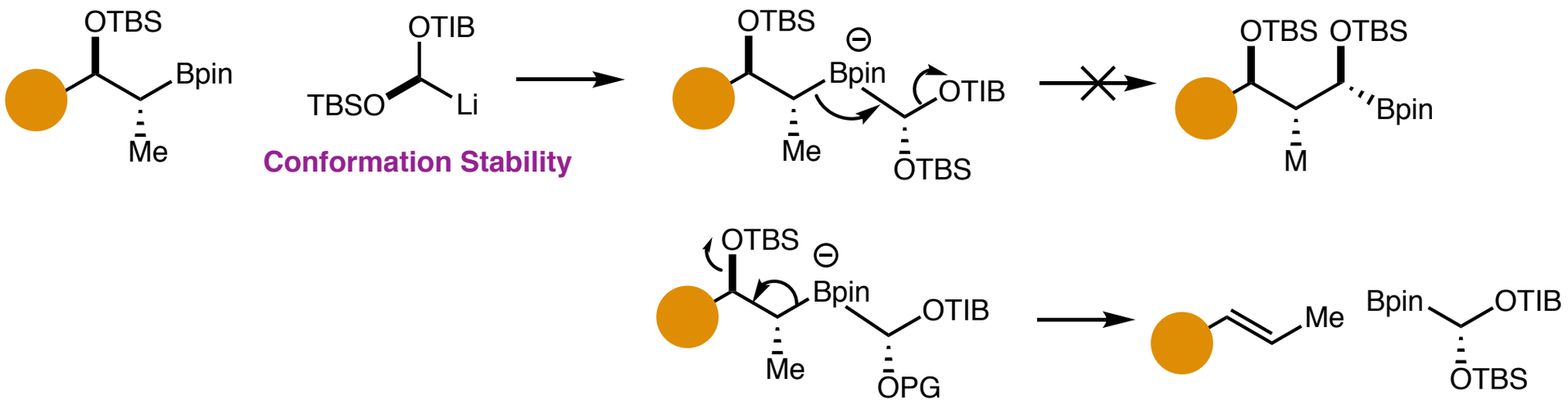


(+)- Hydroxyphthioceranic acid



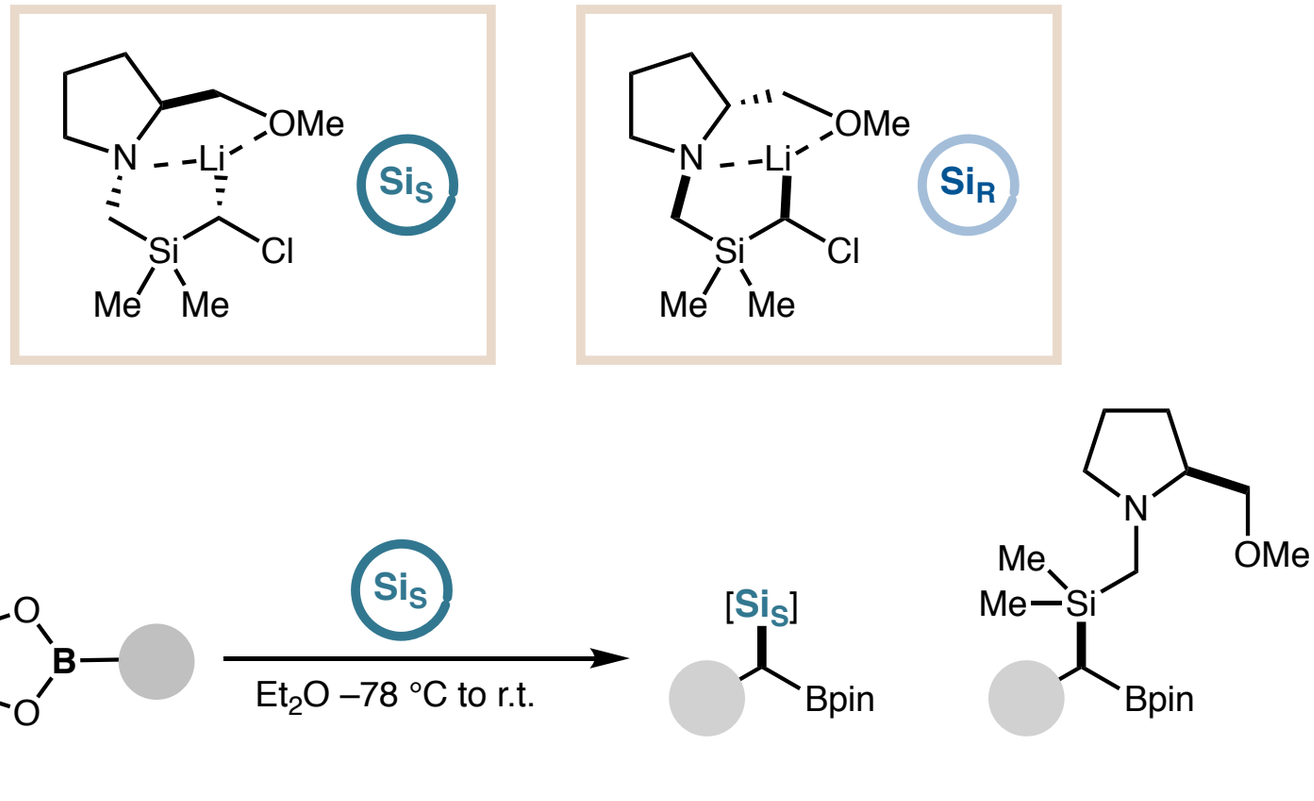
Polyketides Fragments **Anti-Anti**

Why Oxygen is difficult?



Bootwicha, T.; Feilner, J. M.; Myers, E. L.; Aggarwal, V. K. *Nat. Chem.* **2017**, *9*, 896.

Using Si Atom Instead of Oxygen



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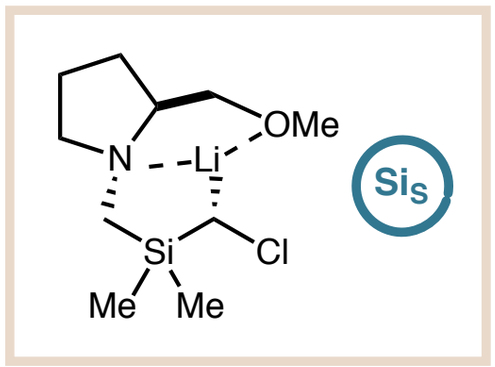
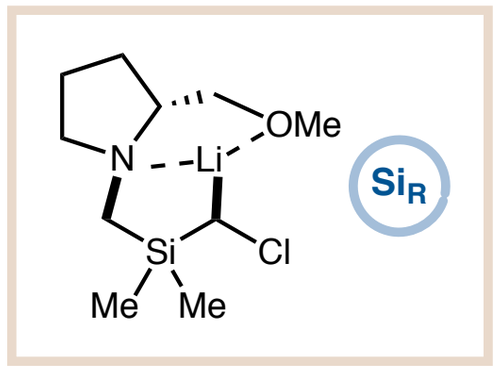
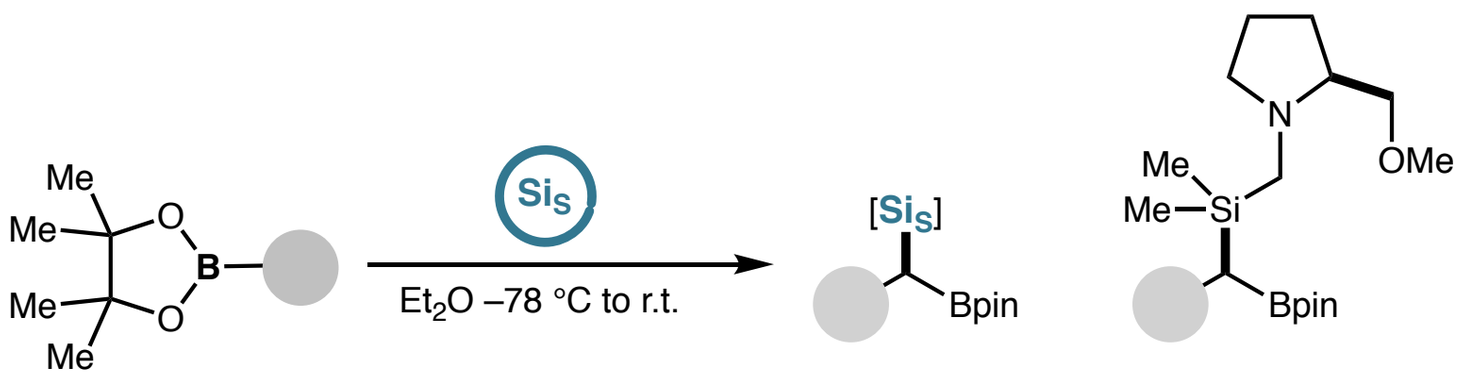
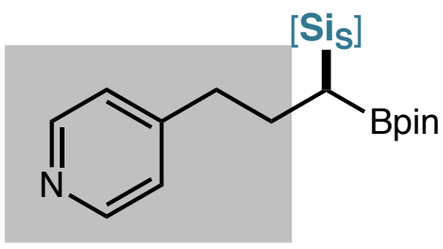
Using Si Atom Instead of Oxygen



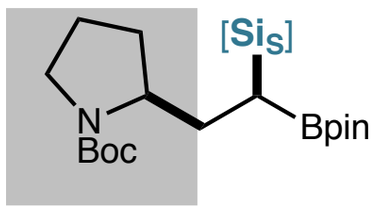






79% IY

92:8 d.r.



71% IY

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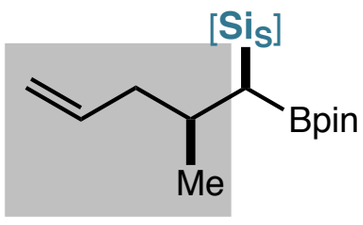

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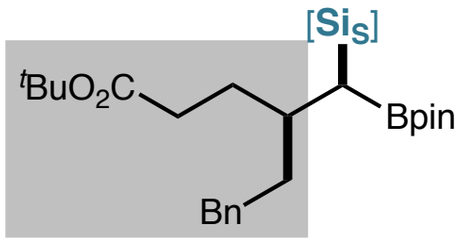
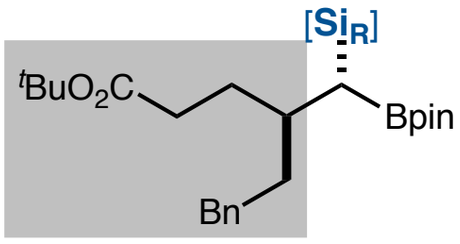
≥ 98:2 d.r.



77% IY

95:5 d.r.



79% IY

95:5 d.r.

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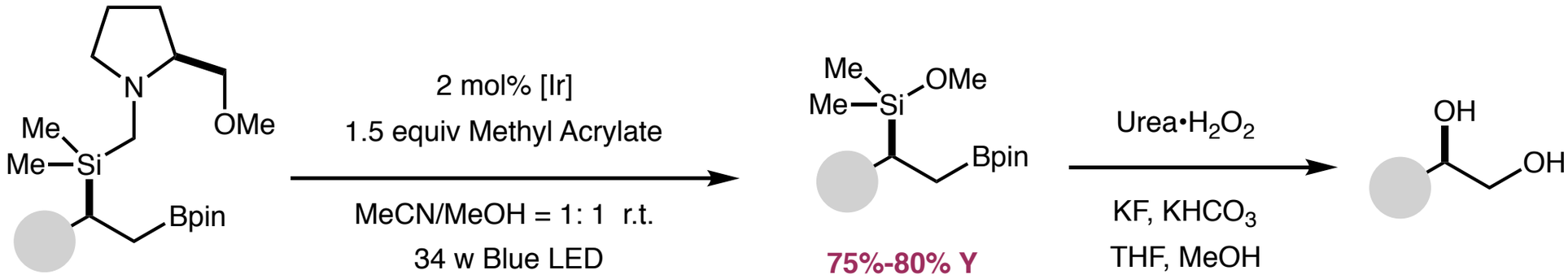
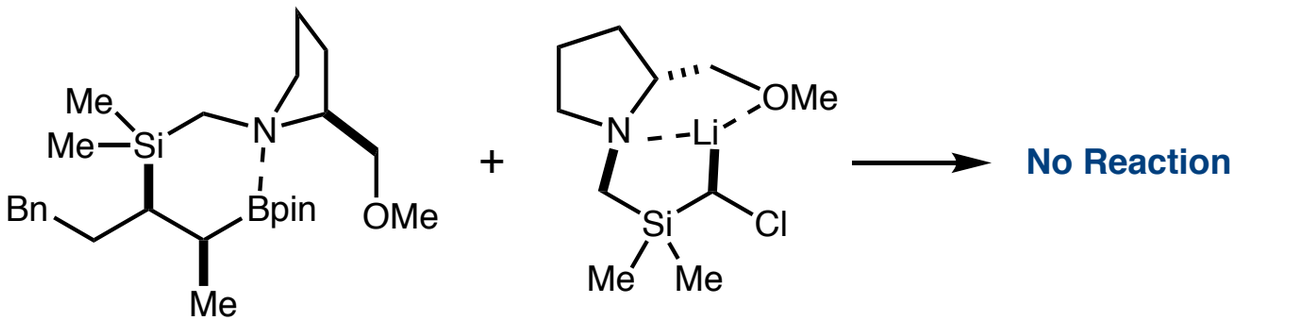
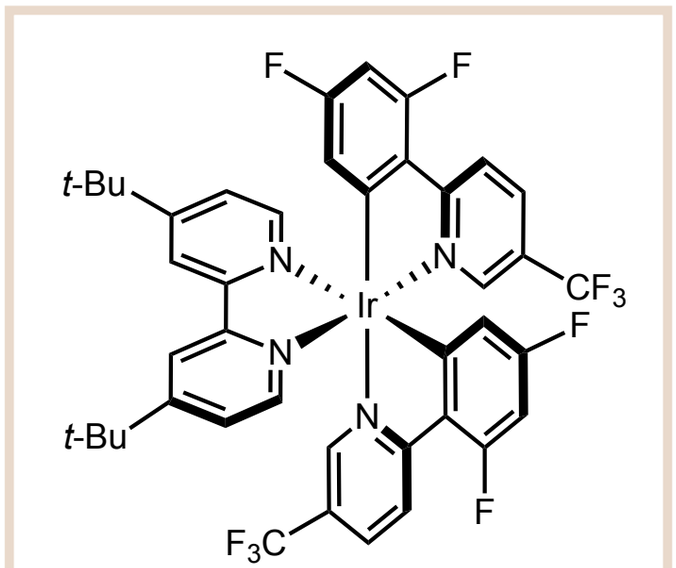
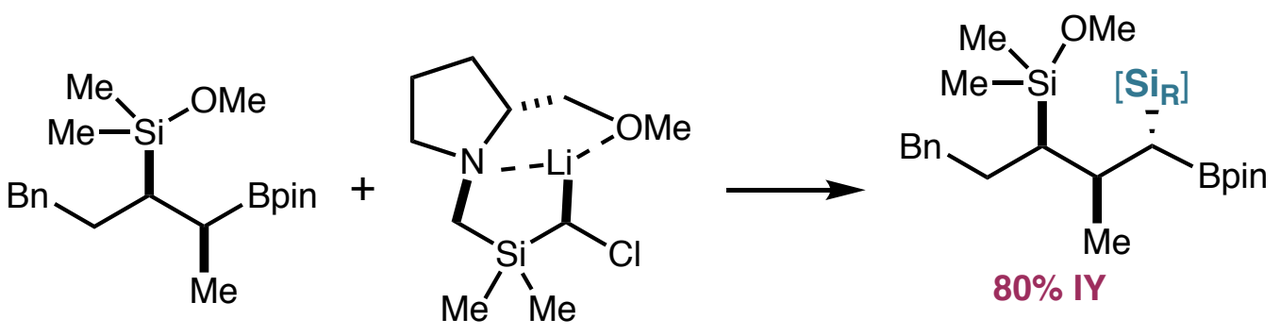
Transfer Si Atom to Oxygen



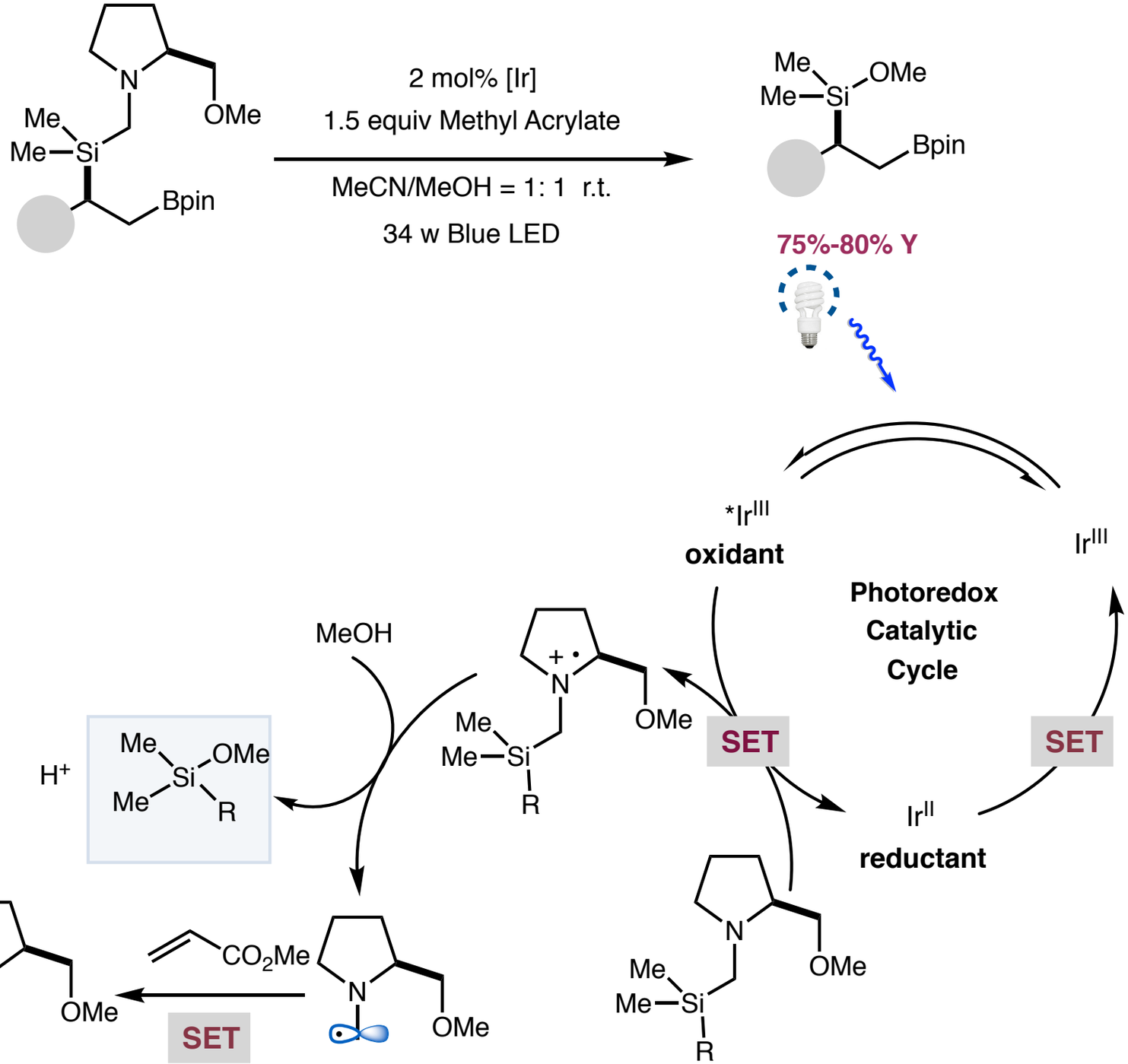






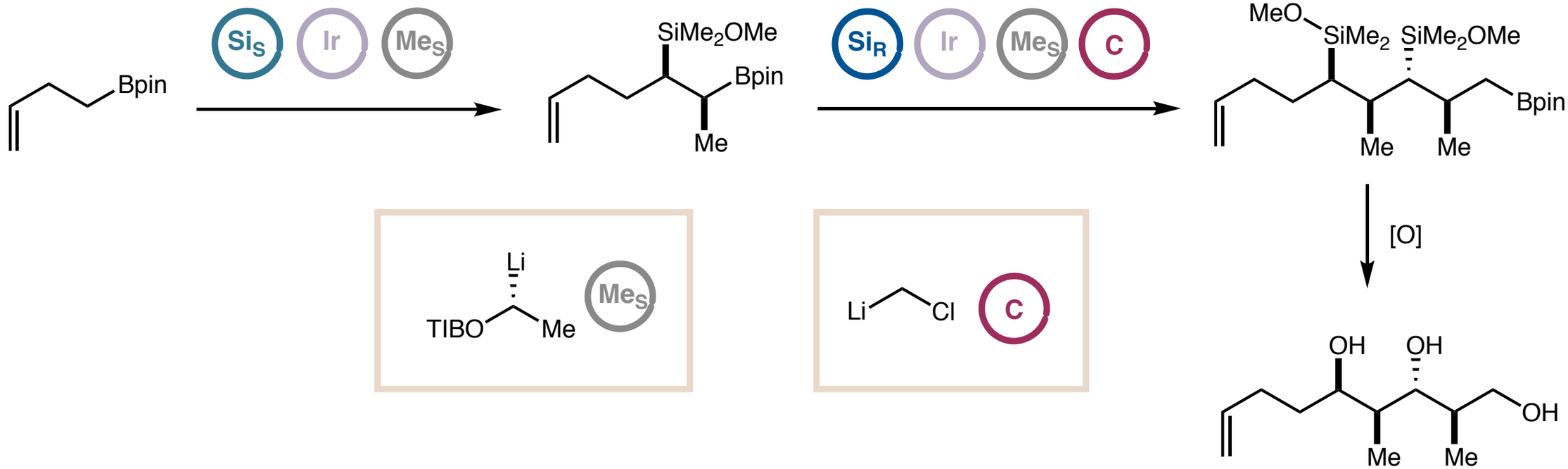
Bootwicha, T.; Feilner, J. M.; Myers, E. L.; Aggarwal, V. K. *Nat. Chem.* **2017**, *9*, 896.

Transfer Si Atom to Oxygen : Proposed Mechanism



Bootwicha, T.; Feilner, J. M.; Myers, E. L.; Aggarwal, V. K. *Nat. Chem.* **2017**, *9*, 896.

Iterative Assembly Line Synthesis of Polypropionate



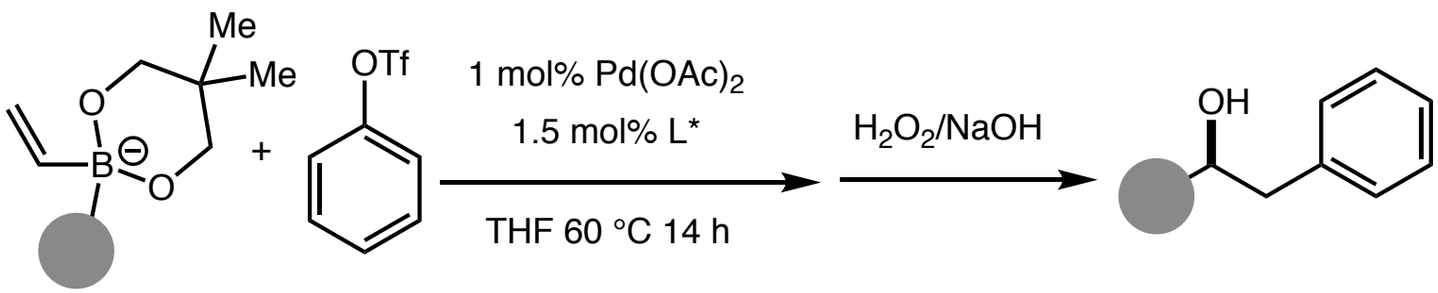
38% IY > 95:5 d.r.

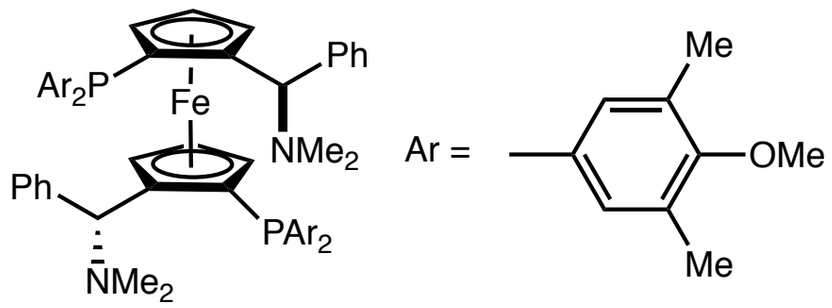
26% IY > 95:5 d.r.

29% IY > 95:5 d.r.

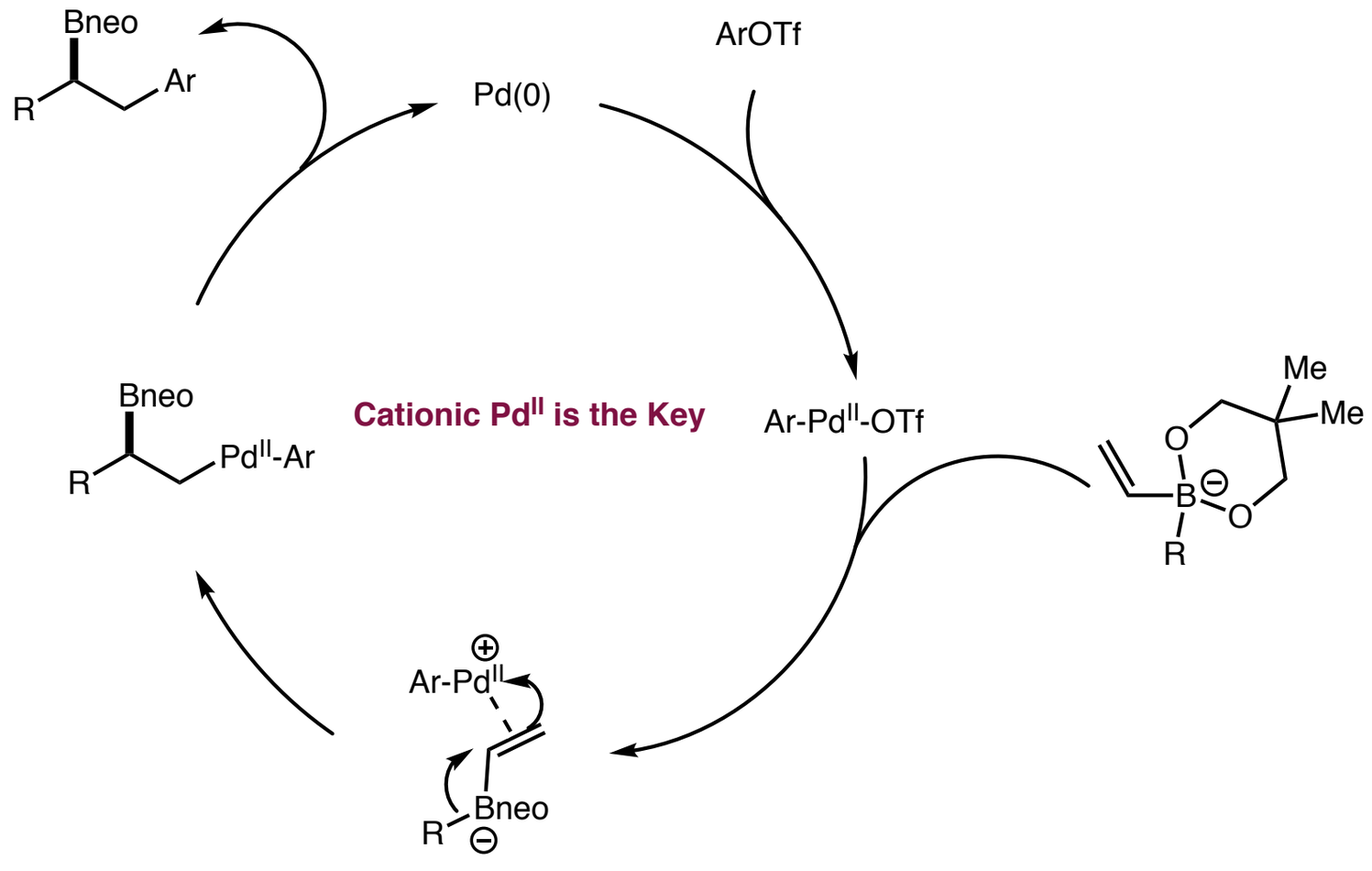
Bootwicha, T.; Feilner, J. M.; Myers, E. L.; Aggarwal, V. K. *Nat. Chem.* **2017**, *9*, 896.

Merging Pd Catalysis with Boron-1,2-Shift



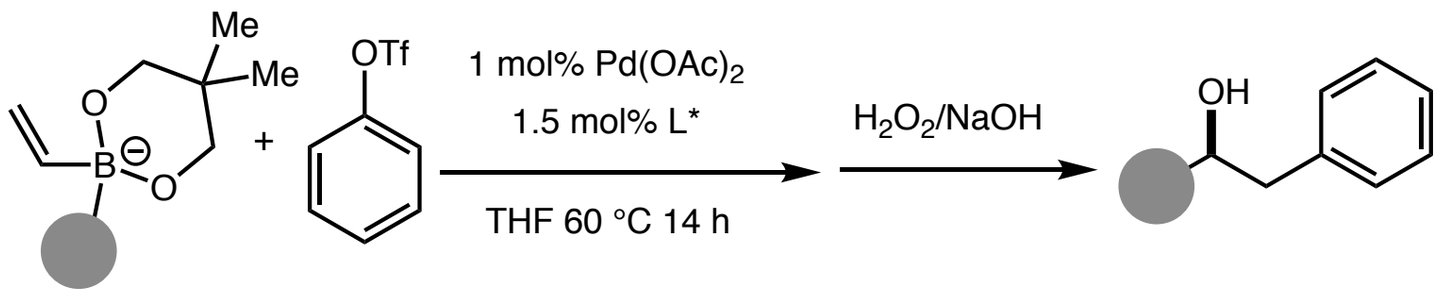


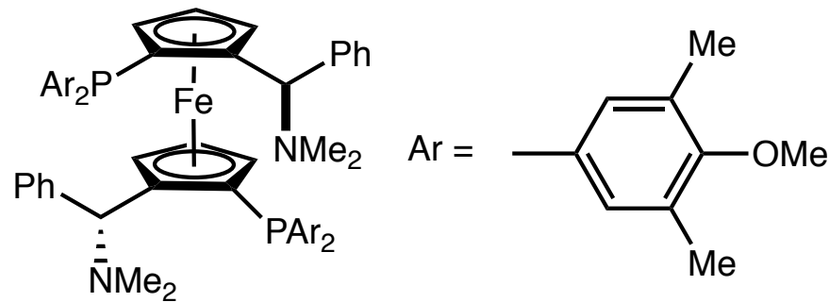
Chiral Ligand



Zhang, L.; Lovinger, G. J.; Edelstein, E. K.; Szymaniak, A. A.; Chierchia, M. P.; Morken, J. P. *Science* **2016**, *351*, 70.

Merging Pd Catalysis with Boron-1,2-Shift





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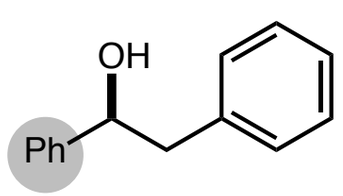
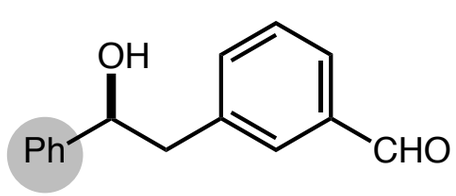


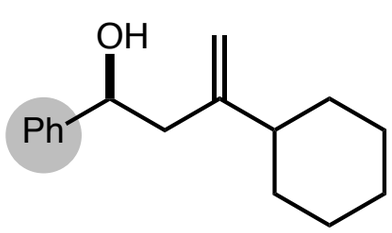
83% IY

94% es



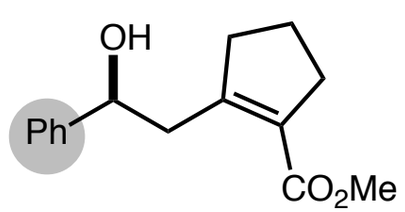
68% IY

92% ee



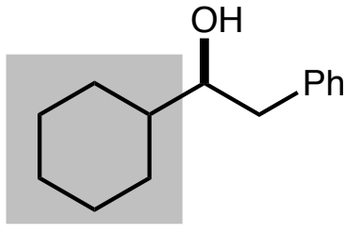
73% IY

90% ee



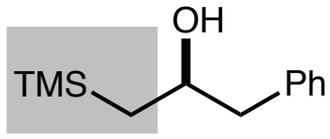
41% IY

80% ee



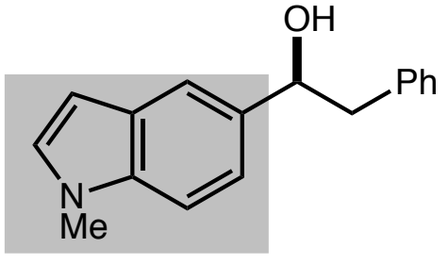
80% IY

90% ee



48% IY

76% ee



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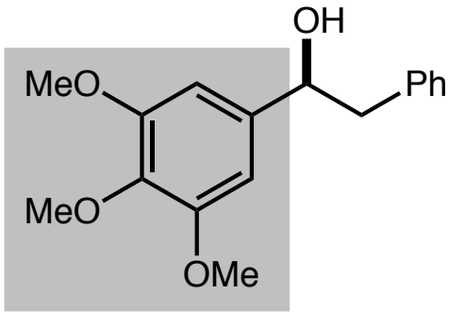
90% ee

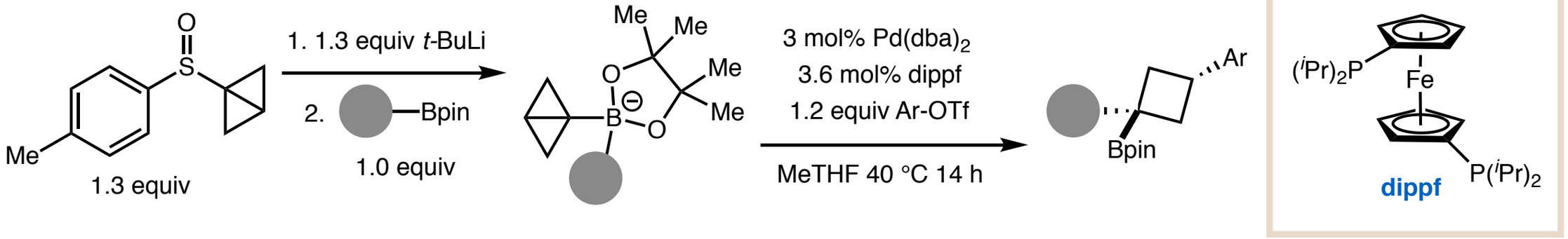


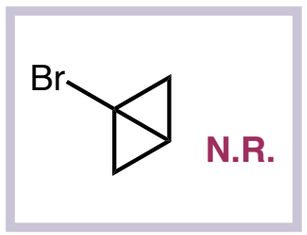
77% IY

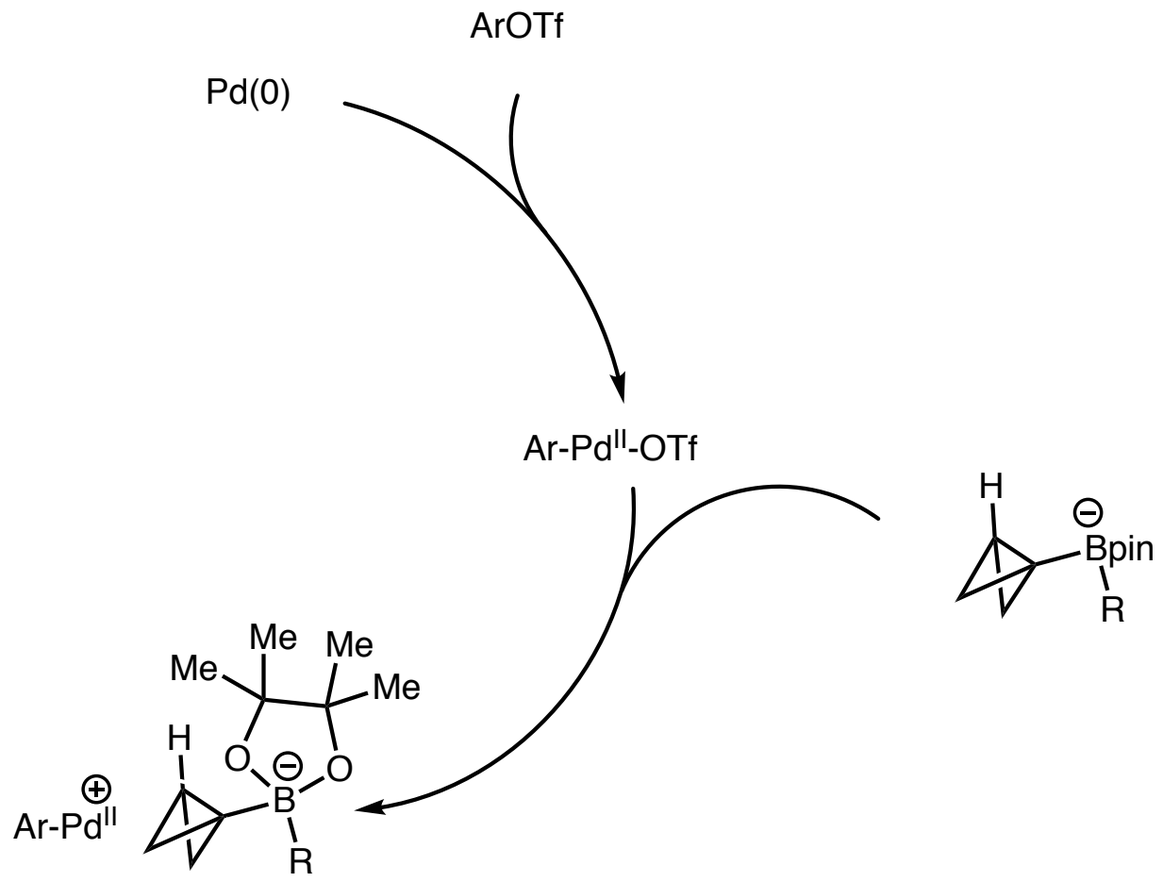
88% ee

Zhang, L.; Lovinger, G. J.; Edelstein, E. K.; Szymaniak, A. A.; Chierchia, M. P.; Morken, J. P. *Science* **2016**, *351*, 70.

Merging Pd Catalysis with Boron-1,2-Shift

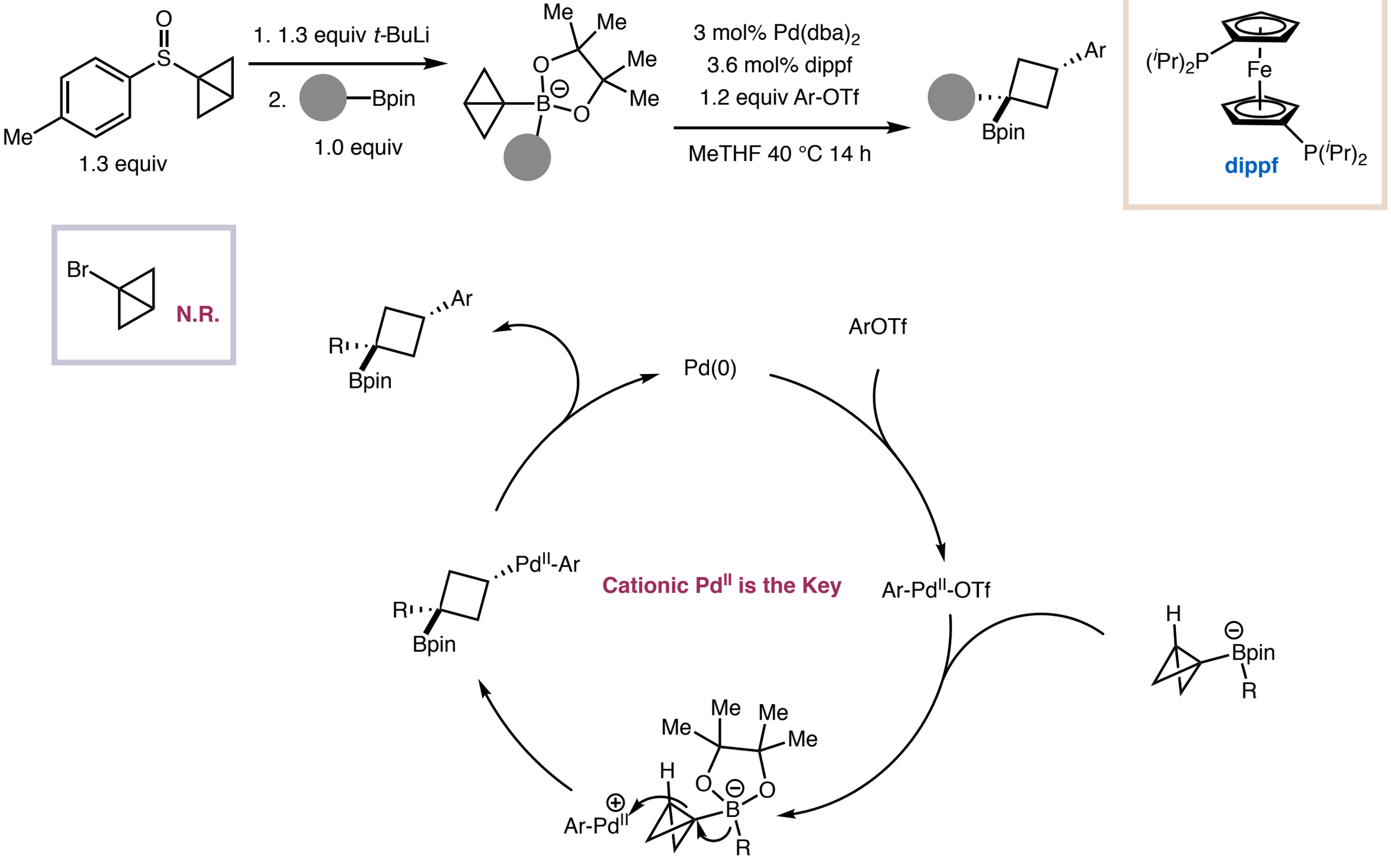






Fawcett, A.; Biberger, T.; Aggarwal, V. K. *Nat. Chem.* **2019**, *11*, 117.

Merging Pd Catalysis with Boron-1,2-Shift



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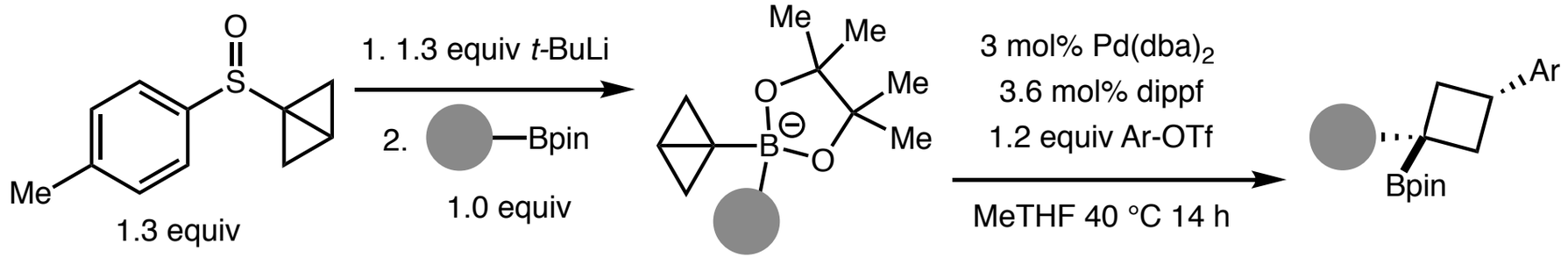
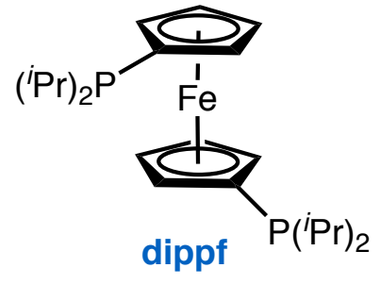
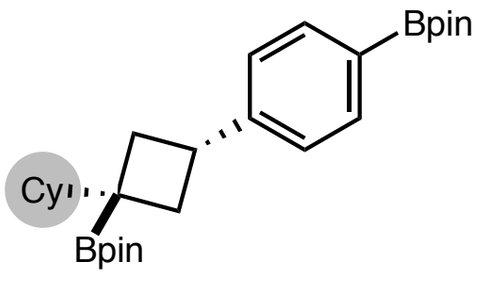
Merging Pd Catalysis with Boron-1,2-Shift







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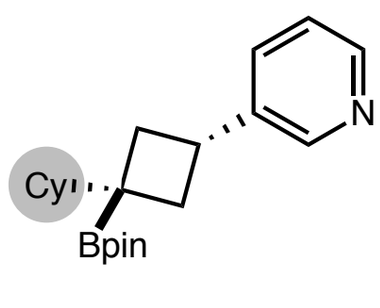

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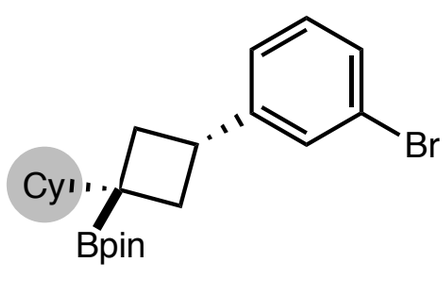

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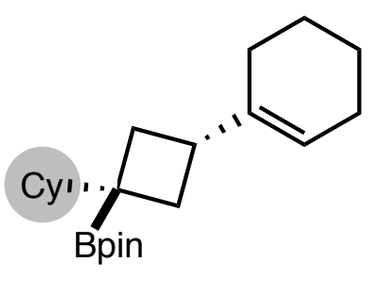

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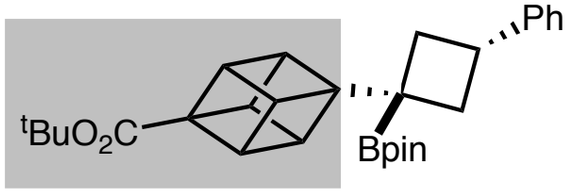

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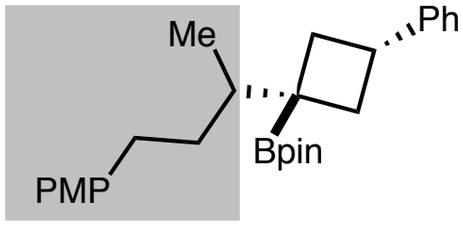

77% IY 100% es

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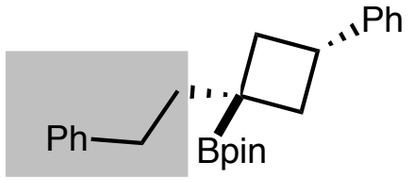

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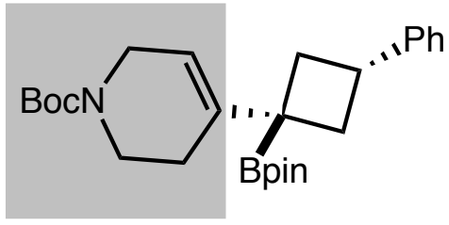

52% IY

>98:2 d.r.

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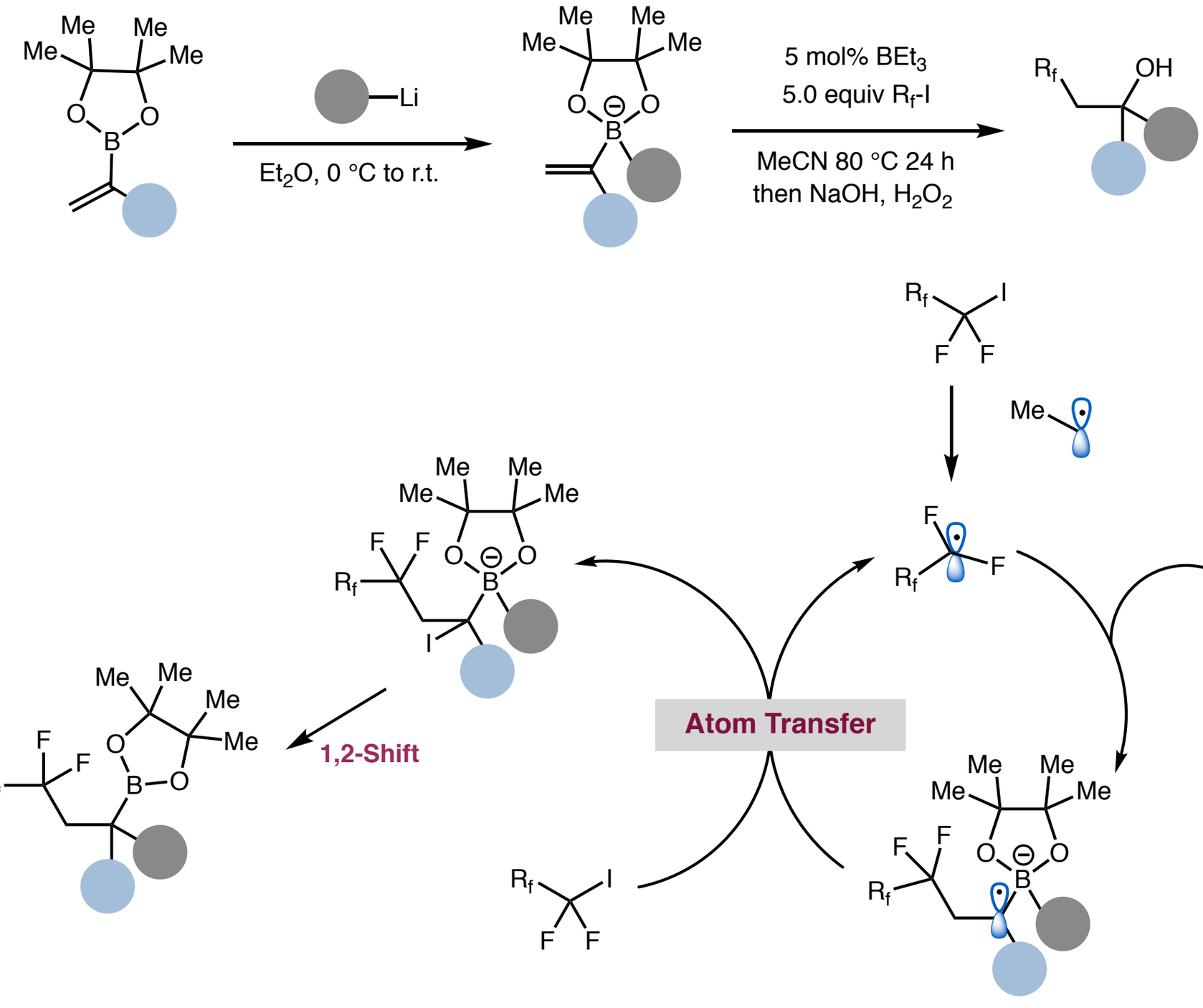
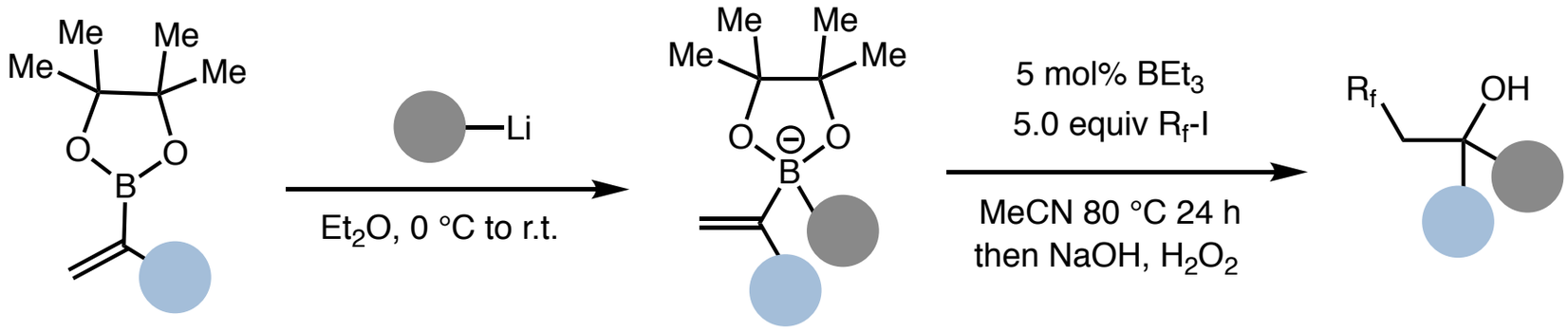
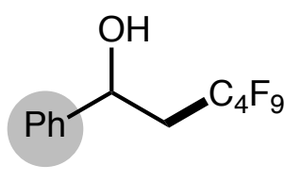
Merging Racical Reaction with Boron-1,2-Shift



Kischkewitz, M.; Okamoto, K.; Mück-Lichtenfeld, C.; Studer, A. *Science* **2017**, *355*, 936.

Merging Racical Reaction with Boron-1,2-Shift





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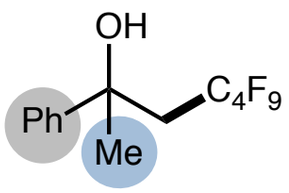

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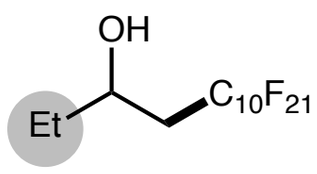

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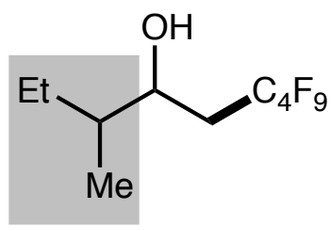

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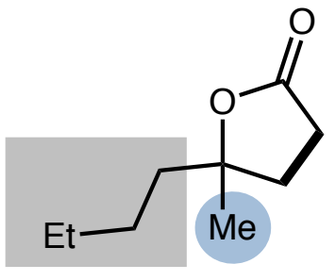

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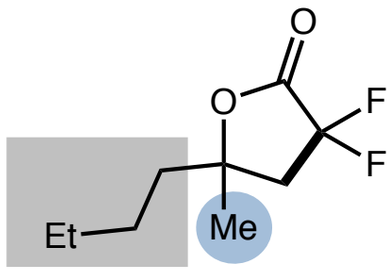

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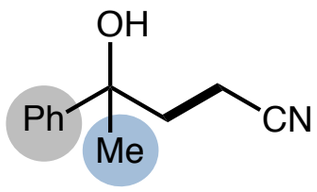

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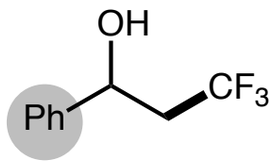

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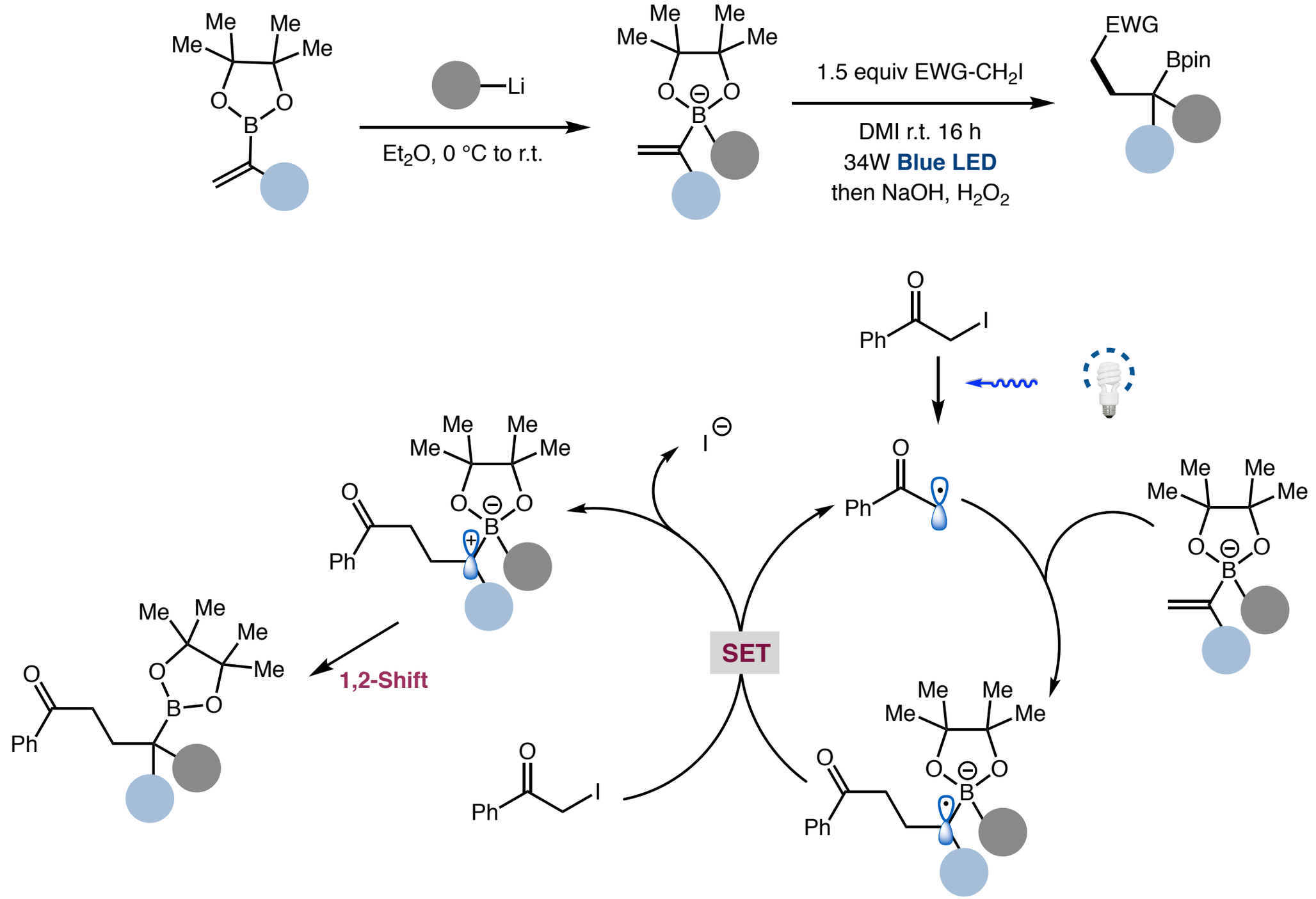
With Togni I

Kischkewitz, M.; Okamoto, K.; Mück-Lichtenfeld, C.; Studer, A. *Science* **2017**, *355*, 936.

Merging Racical Reaction with Boron-1,2-Shift



Silvi, M.; Sandford, C.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2017**, *139*, 5736.

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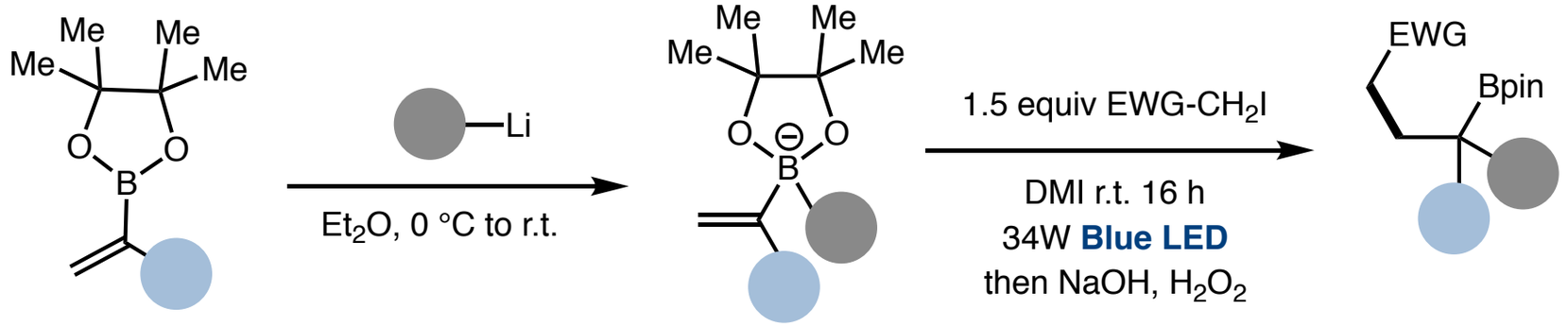
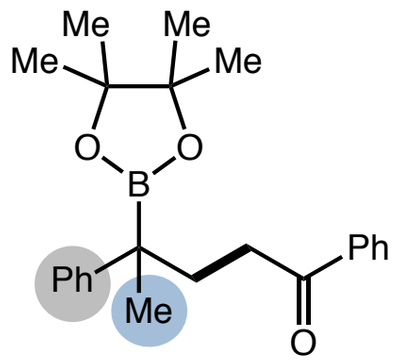
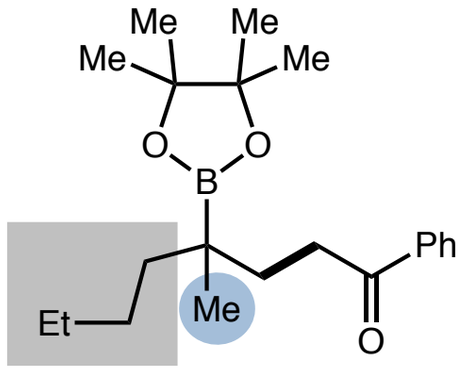
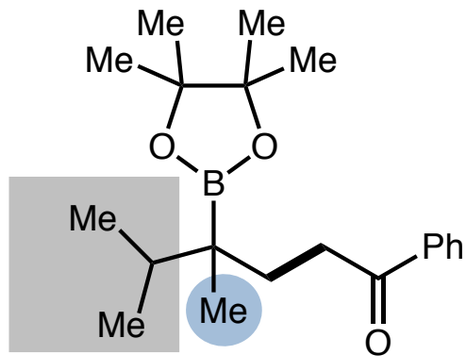




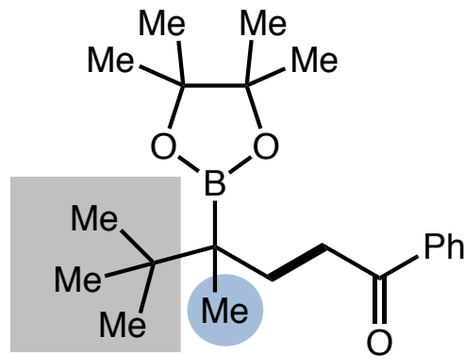
81% IY



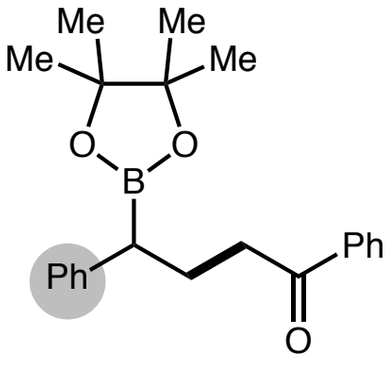
88% IY



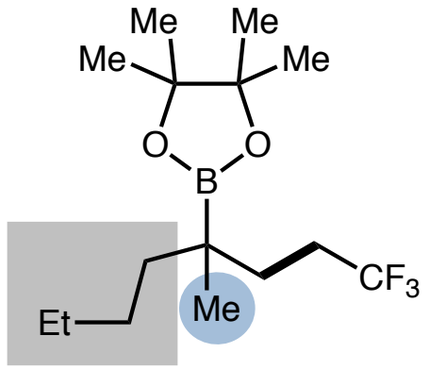
88% IY



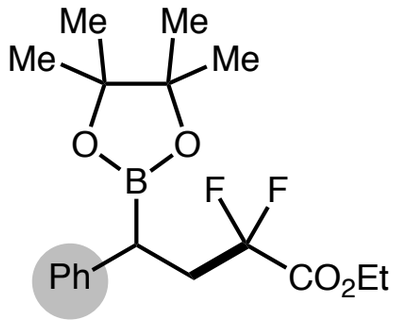
74% IY



65% IY

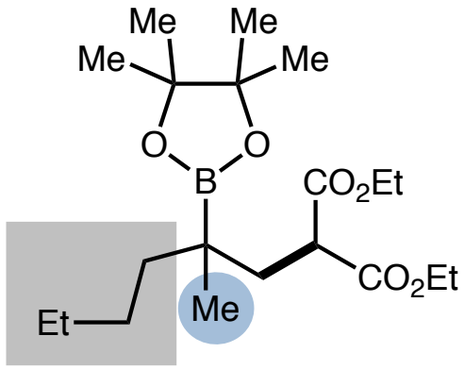


68% IY



69% IY

With 1 mol% $Ru[bpy]_3Cl_2$



70% IY

With 1 mol% $Ru[bpy]_3Cl_2$

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