CHEM – 750

Advance Organic synthesis

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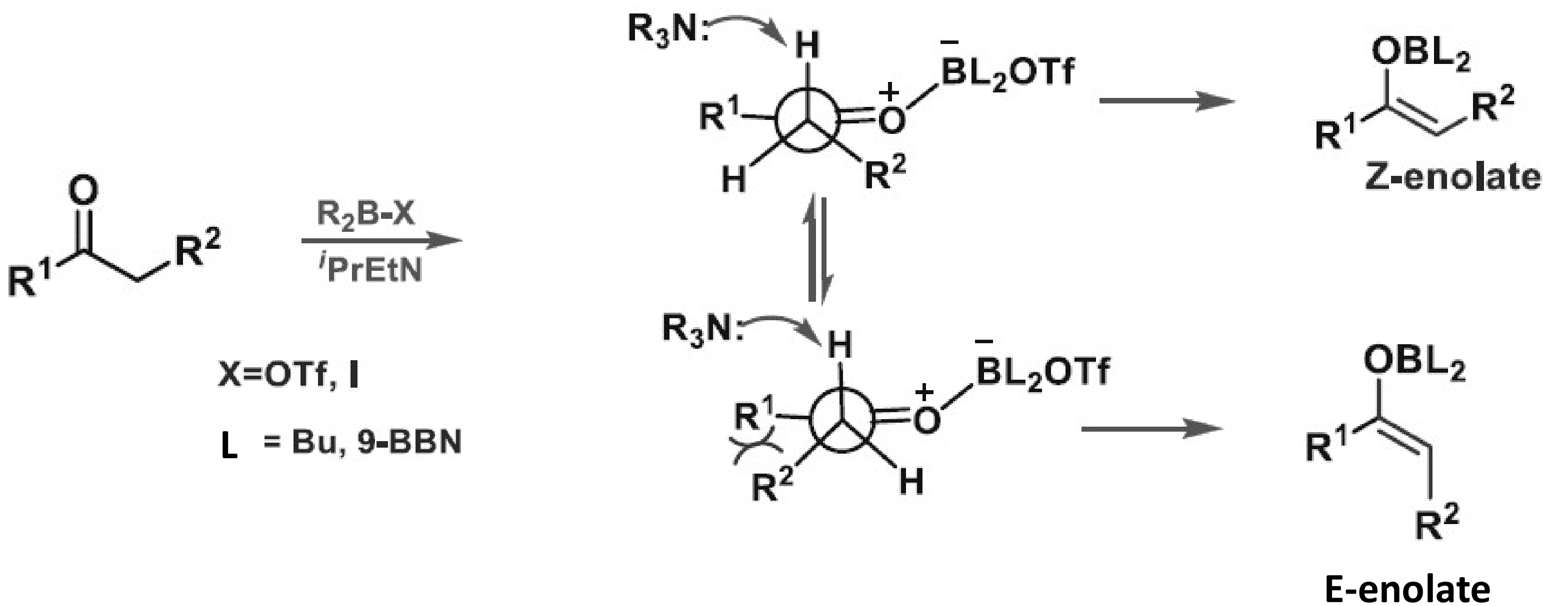
Boron Enolates

Alkali & alkaline earth metal enolates tend to be aggregates- complicates stereoselection models

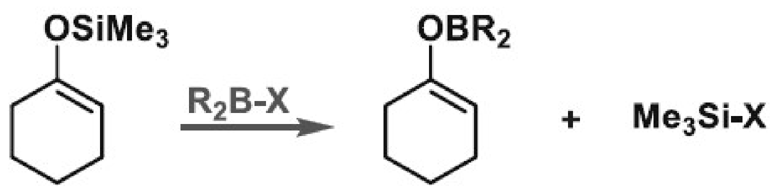
Boron enolates are monomeric and homogeneous

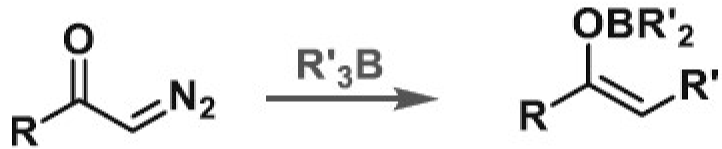
B-O and B-C bonds are shorter and stronger(more covalent character) than the corresponding Li-O and Li-C bonds- therefore tighter more organized transition state.

The substituents on the boron atom (R) can be varied in order to control selectivity



Boron Enolates

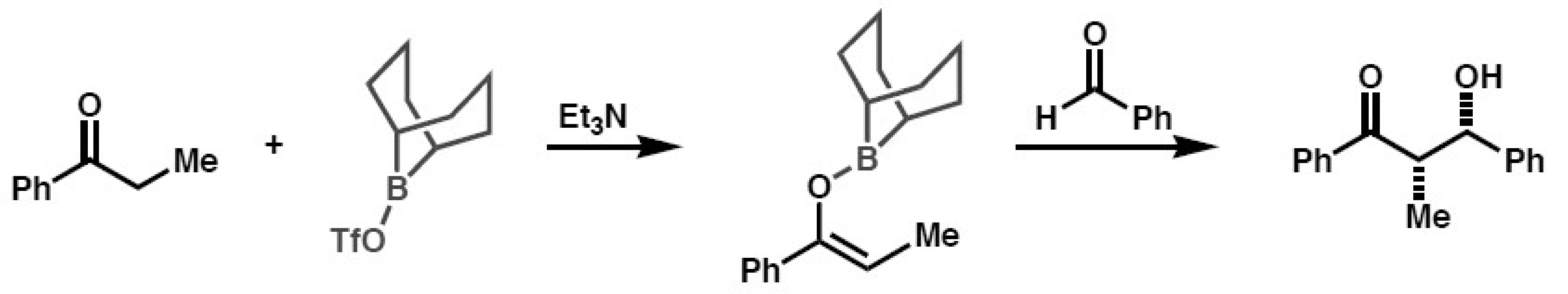




Hooz reaction

Mechanism !

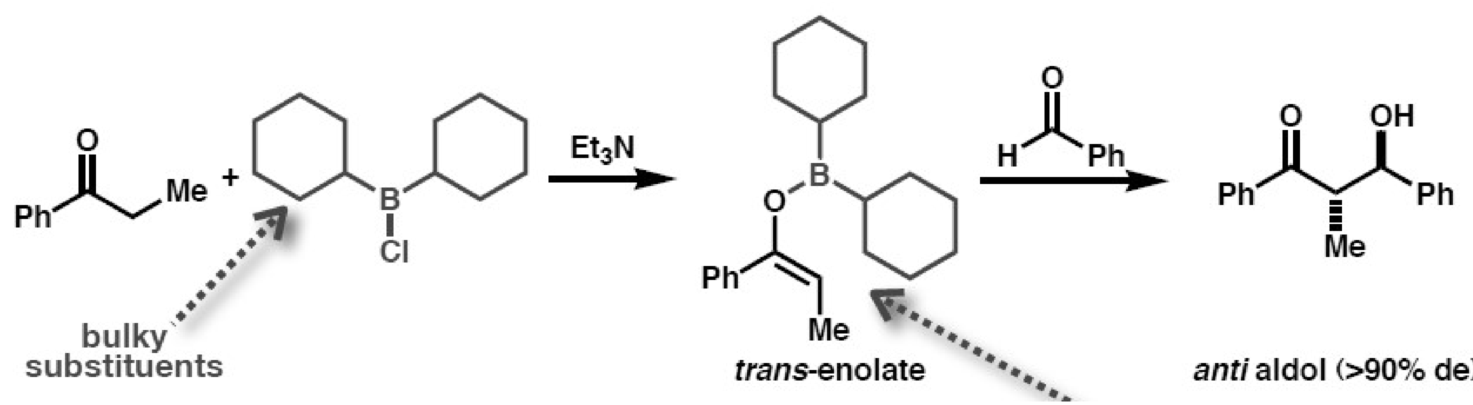
Boron Enolates



cis-enolate

syn aldol (96% de)

- 9-BBN (9-borabicyclononane) looks bulky
- But most of it is 'tied-back' behind boron thus allowing formation of the *cis*-enolate

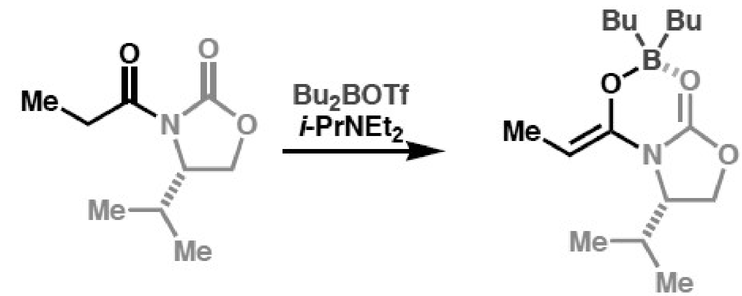


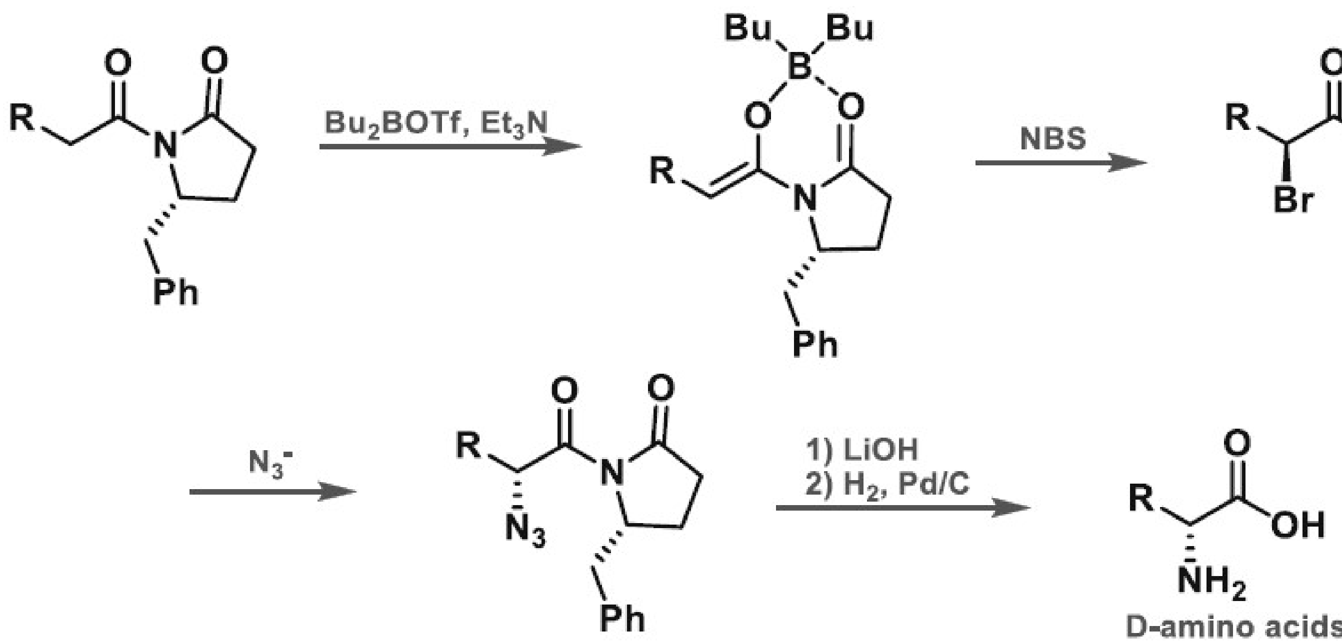
trans-enolate

anti aldol (>90% de)

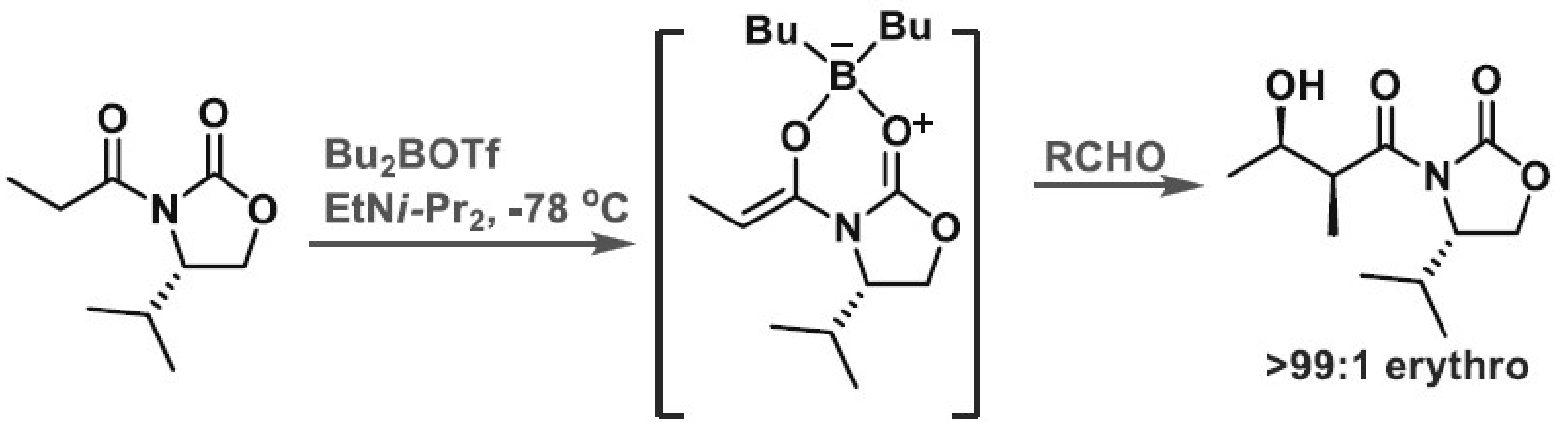
Boron Enolates

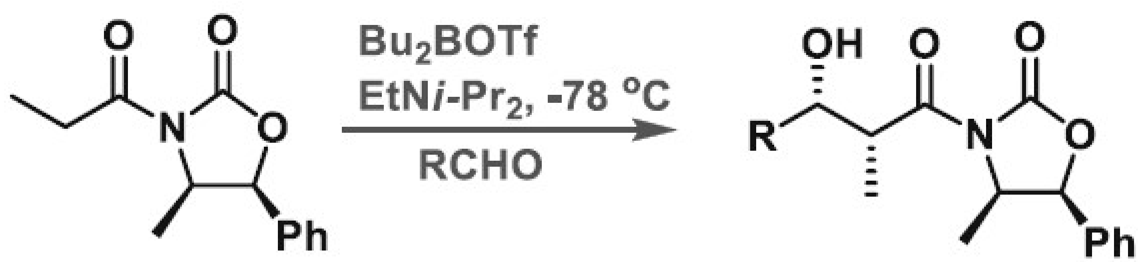
Li⁺ enolates give poor selectivity (1:1)
Boron and tin enolates give much improved selectivity





Aldol Condensation : Chiral Auxilaries





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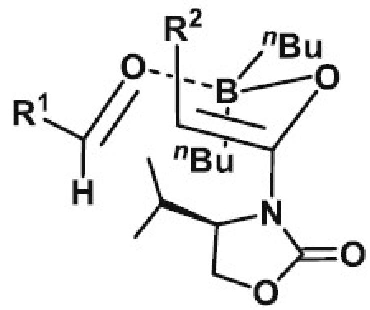
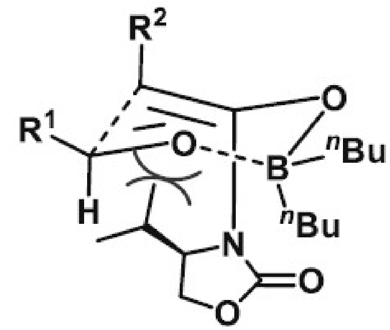
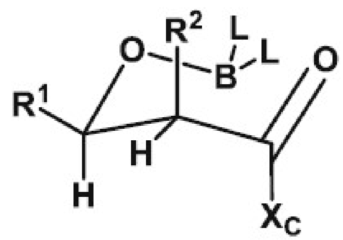
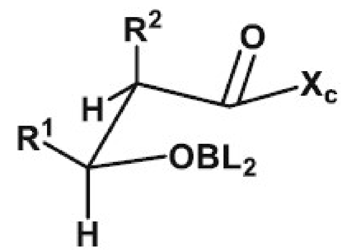
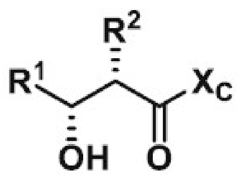




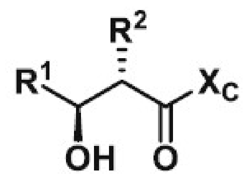




Draw Newman Projection !!

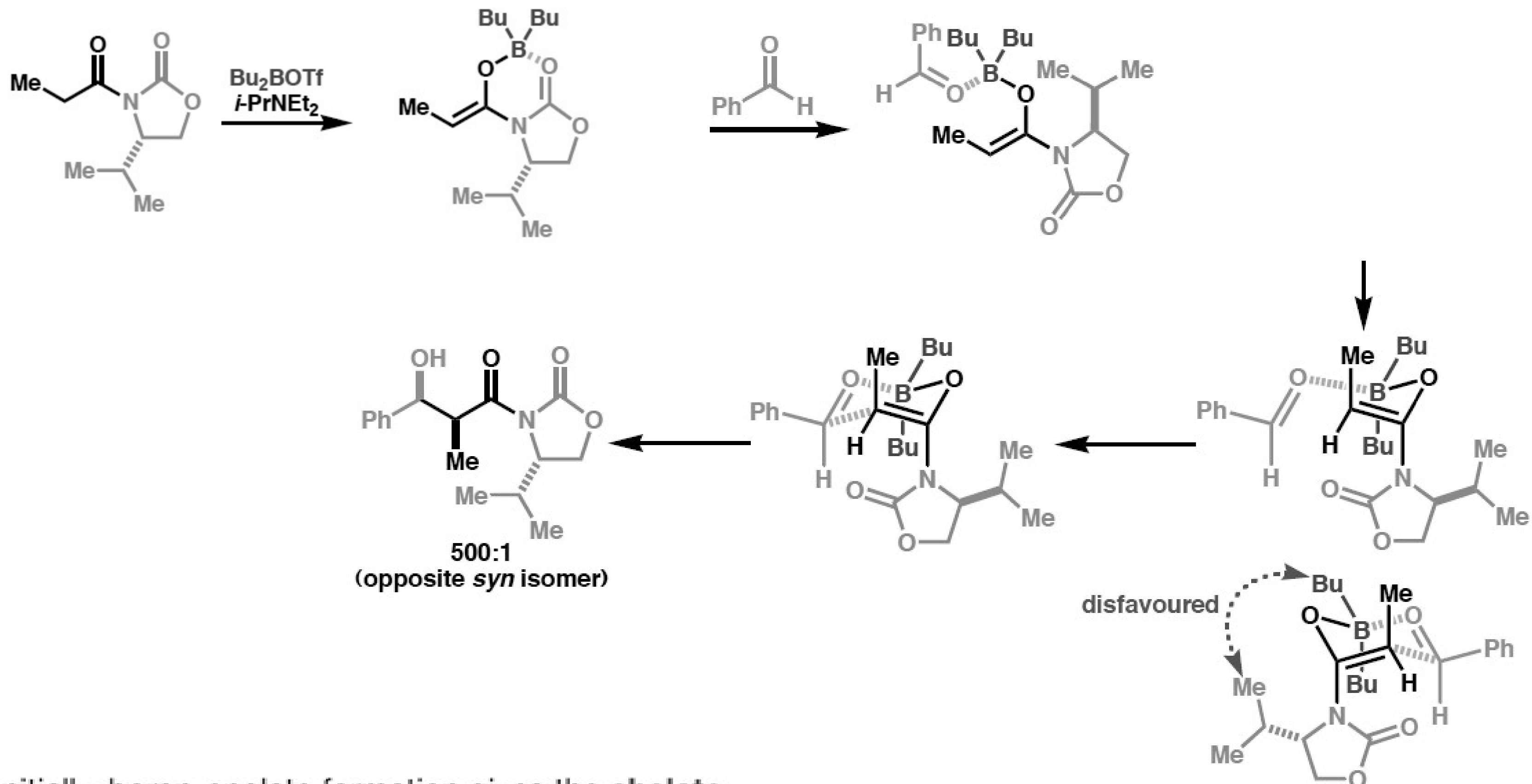


Syn



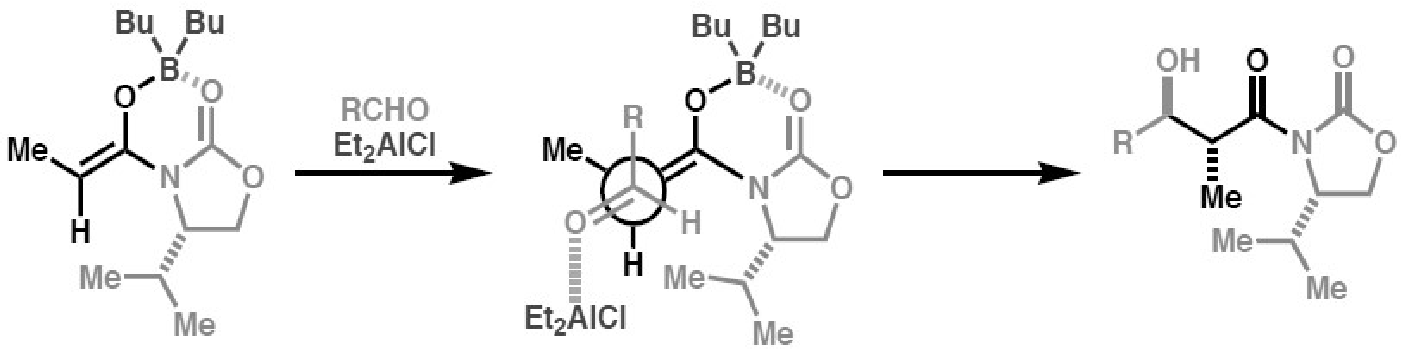
Anti

Chiral auxiliaries & the aldol reaction



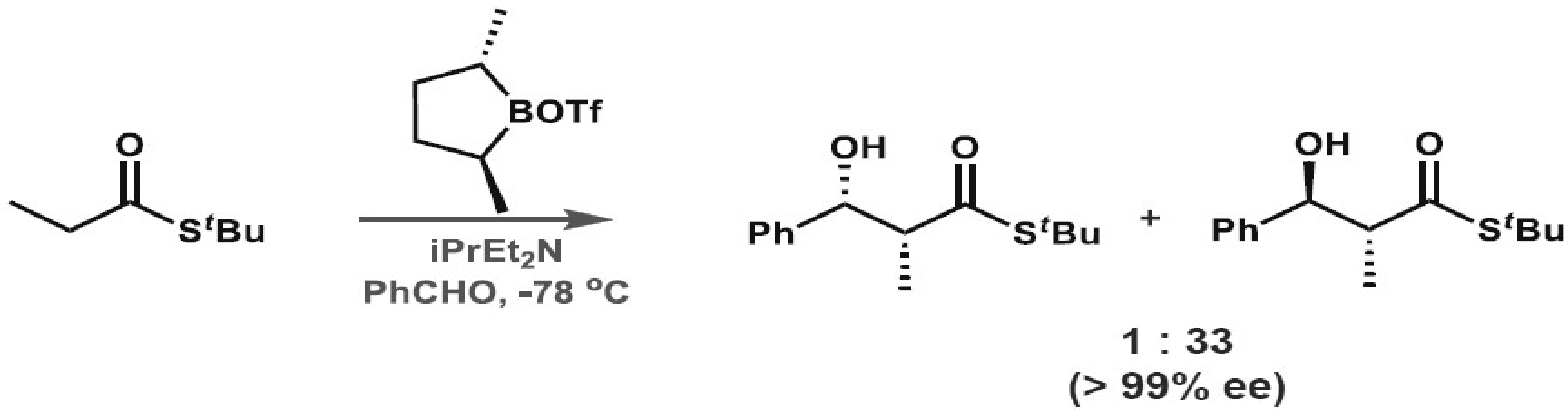
- Initially, boron-enolate formation gives the **chelate**
- This must be broken for the boron to chelate the aldehyde, a requirement of the aldol
- The auxiliary then rotates to minimise steric and electronic repulsions
- Aldehyde approaches from the opposite face to auxiliary

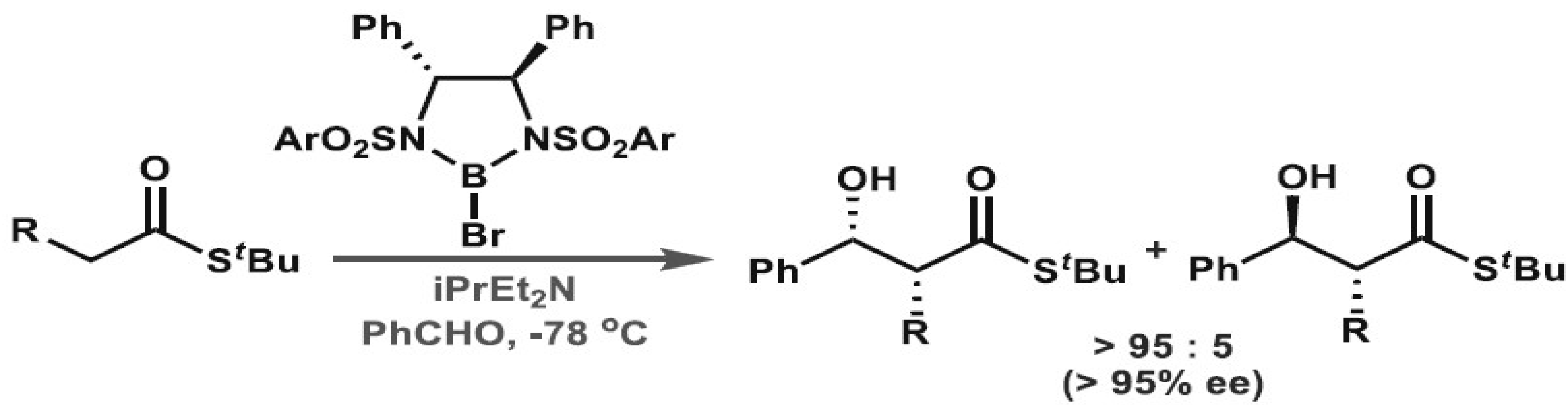
Reversal of diastereoselectivity



- The reaction can be made to favour *anti* diastereoisomer by forcing it to proceed *via* an 'open' transition state
- The **aluminium Lewis acid** preferentially coordinates to the aldehyde instead of the boron

Chiral Boron Enolates





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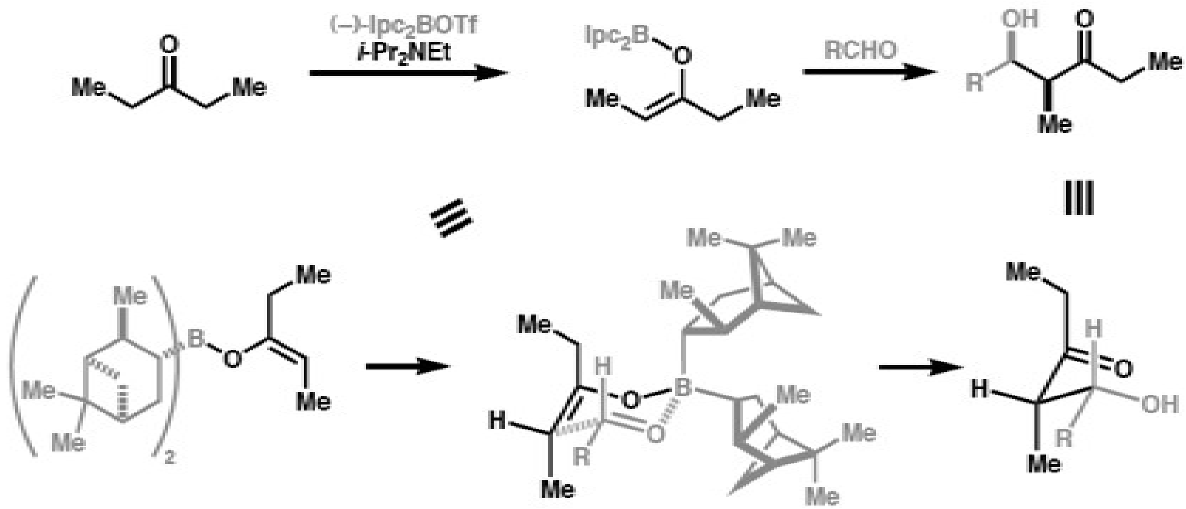

- Hopefully it is becoming clear that the use of **chiral reagents** is more efficient
- In this reaction, the standard pinene derivative is being utilised
- The transition state is analogous to that of Brown allylation
- Interaction between the enolate and the methyl group of the Ipc moiety is minimised