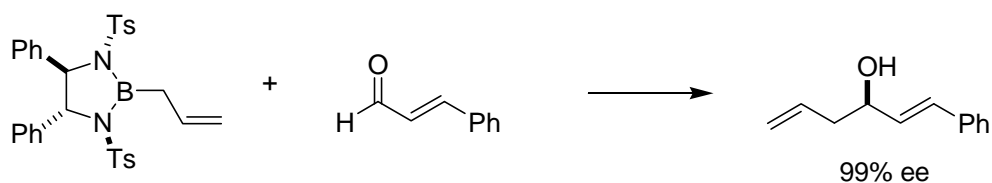


Problem Set No. 7 (4.6.2013)

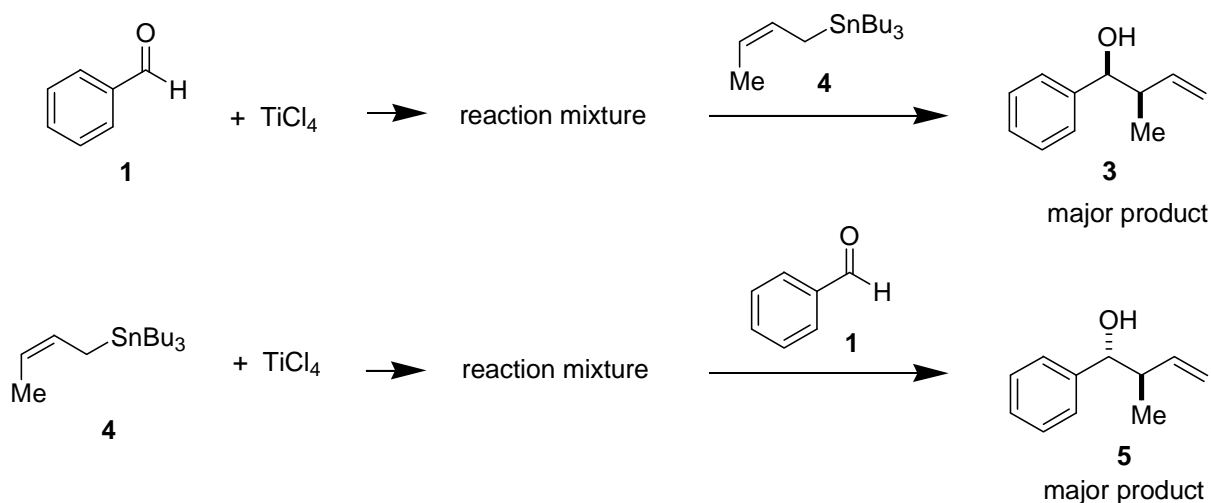
1. a) E.J. Corey proposed a new chiral allylation reagent for the enantioselective addition to aldehydes. Draw the two possible transition states (attack from front or back) for this reaction explaining why one side of the aldehyde is attacked preferentially.



b) Which enantiomer of *N,N*-dibenzyl-protected 2-amino-3-phenylpropanal should be used to have a matched situation? Draw the transition state of this reaction and the product with three contiguous stereocenters.

2. Explain the  $\beta$ -effect involved in the reactions of allyl stannanes and propargyl stannanes with electrophiles!

3. Diastereomer **3** is obtained when adding (*Z*)-crotylstannane **4** to a reaction mixture consisting of benzaldehyde **1** and titanium tetrachloride at  $-78\text{ }^{\circ}\text{C}$ . However, if (*Z*)-crotylstannane **4** is mixed with titanium tetrachloride at  $0\text{ }^{\circ}\text{C}$ , then cooled to  $-78\text{ }^{\circ}\text{C}$  and finally treated with benzaldehyde **1** isomer **5** is observed to be the major product. Give an explanation for this observation! How can stannane **4** be prepared?



4. React allyl(tributyl)stannane with (*S*)-2-benzyloxypropanal under chelate control! What is a suitable Lewis acid and which major product do you expect? Draw the respective transition state.

5. Explain the mechanism of the Johnson-Claisen-rearrangement as given in the lecture in full detail (including stereochemistry)! Hint: a chair-like transition state is also assumed for this process.