

**Problem Set No. 5 (29.5.2012)**

1. Draw the reactive conformations of (*S*)-2-benzyloxypropanal in the absence of a Lewis acid according to the Felkin-Anh model and in the presence of  $\text{TiCl}_4$ ! Which side of the carbonyl group will be attacked by nucleophiles with preference? Assign these faces of the carbonyl group by *Re* and *Si*!

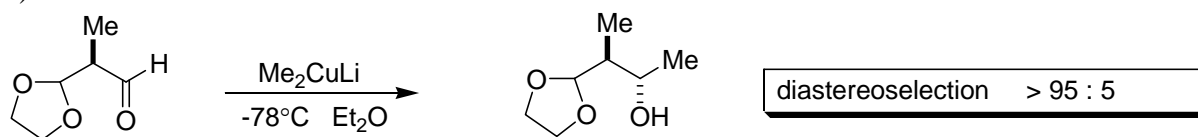
2. a) Propose a synthetic route to the *N,N*-dibenzyl-protected (*S*)-2-amino-3-phenylpropanal!

b) The addition of  $\text{Allyl-Ti}(\text{NEt}_2)_3$  to this chiral aldehyde provides at  $-78\text{ }^\circ\text{C}$  the product in an *anti/syn* ratio of 93:7. Explain this result! What is the energy difference of the two transition states?

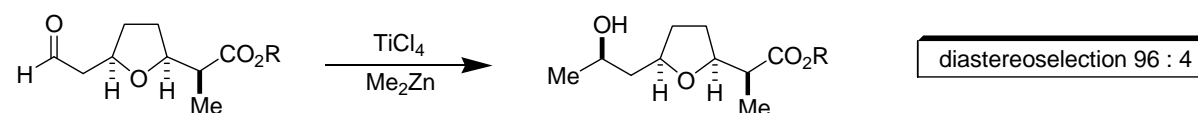
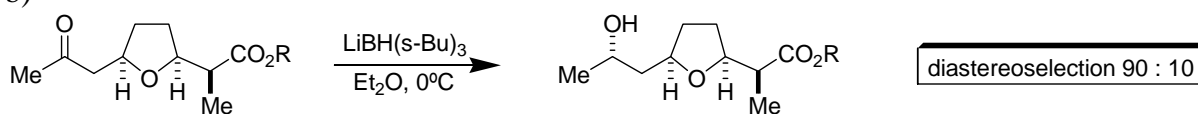
c) Deprotect the obtained product to the free primary amine!

2. Provide an explanation for the stereochemical outcome of the following reactions:

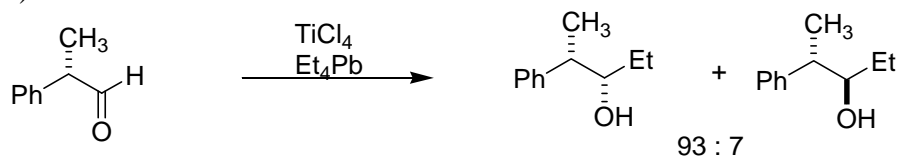
a)



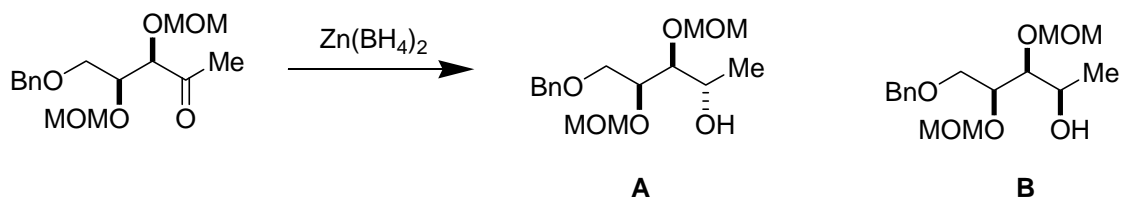
b)



c)



3) The two diastereomers are formed in a 93:7 (A:B) ratio. Which of the stereocenters present in the starting material determines the outcome in this case? L-Selectride provides the 2 diastereomers in reversed 8:92 ratio. Provide an account for these results.



4) Suggest two alternative methods to enantioselectively prepare (*R*)-1-phenylpropan-1-ol!