Stereochemistry **Name:**
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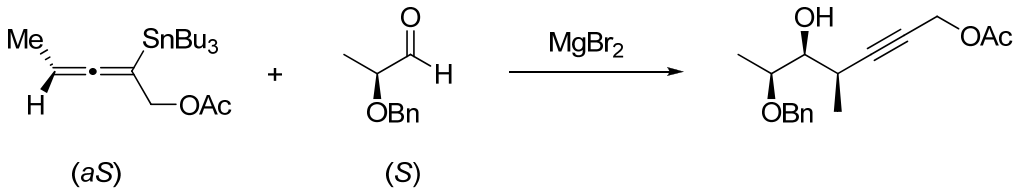
Problem Set No. 8 (18.6.2013)

1. a) Explain the formation of the addition product of the (*aS*) allenyl stannane to a chiral aldehyde by drawing a suitable transition state!



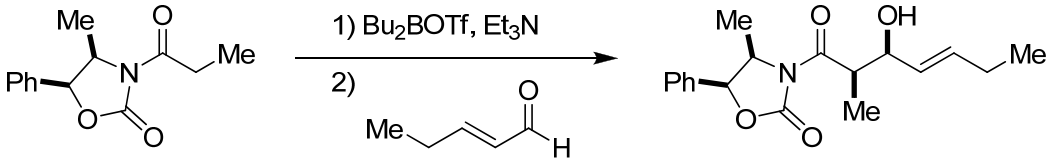
(*aS*) (*S*)

b) Using the (*aR*) allene and BF_3 as Lewis acid provides another diastereomer (ratio 97:3). Suggest a transition state and the configuration of this new product!

2. a) Generate the silyl enol ether from cyclohexanone and $ClSiMe_3$ (conditions?).

b) Which major aldol addition product of the BF_3-promoted addition of benzaldehyde to this silyl enol ether do you expect based on the transition state presented in the lecture (with *Z*-configured silyl enol ethers)? Draw the transition state of this reaction!

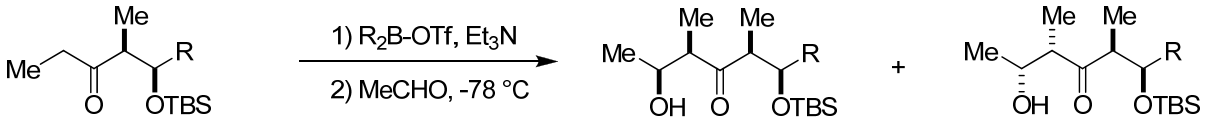
3. In their total synthesis of cytovaricin, Evans et al. used a diastereoselective aldol reaction.
a) Explain the observed diastereoselectivity by providing a representation of the product-forming transition state.



b) Suggest a pathway for the synthesis of the enantiopure precursor oxazolidinone!

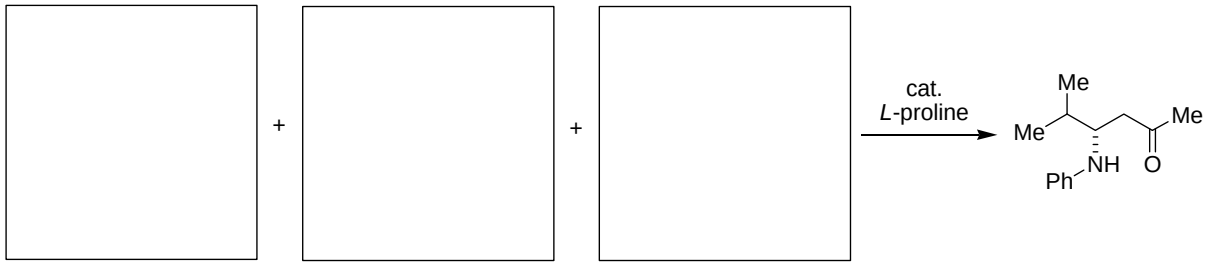
c) Convert the aldol product into the corresponding carboxylic acid!

4. Analyse the stereochemical outcome of the following aldol reaction. Explain why the three boron reagents lead to differences in selectivity.

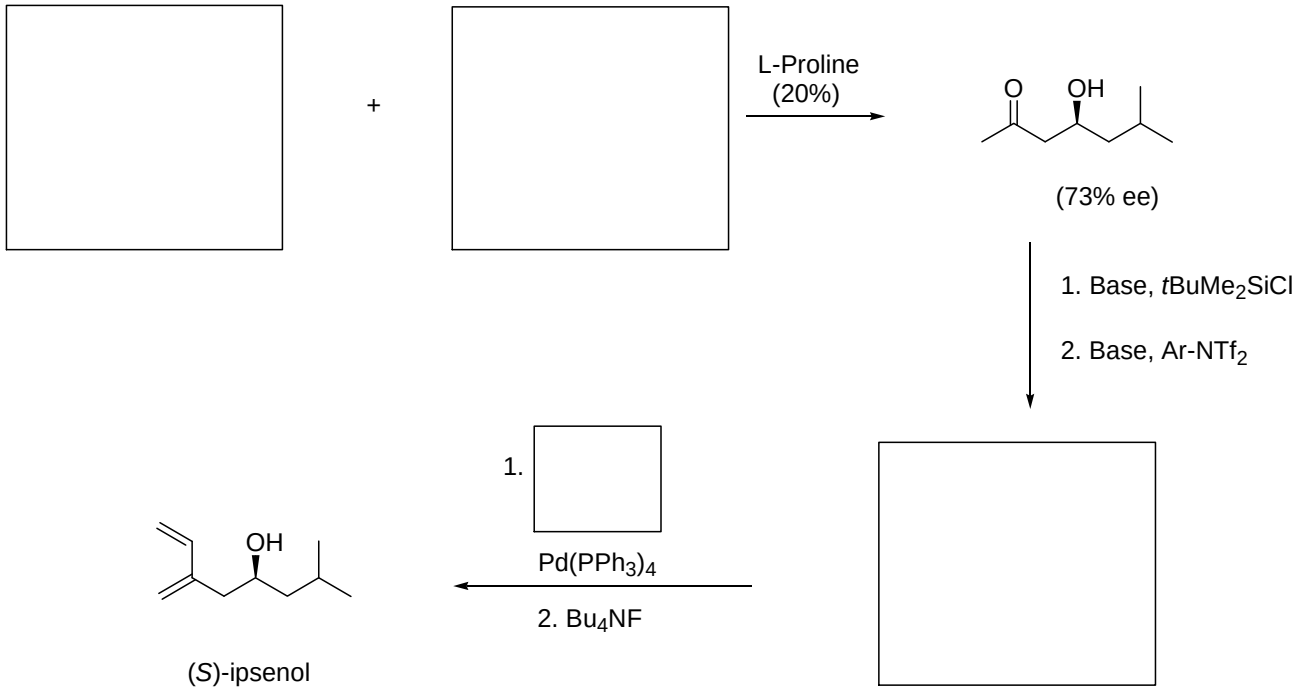


R_2B-OTf			
9-BBN-OTf	92	:	8
(+)-(IpC)$_2$BOTf	98	:	2
(-)-(IpC)$_2$BOTf	75	:	25

5. The following reactions involve organocatalysis.
a) Provide suitable starting materials and key intermediates for the following synthesis of a chiral secondary amine. Draw the transition state of this Mannich reaction!



b) The natural product ipsenol has been prepared in an enantio-enriched form as shown below. Supplement the equations (no mechanism), but draw the transition state explaining the outcome of the first step!



c) The reaction of an aldehyde and diethyl azodicarboxylate in the presence of L-proline also occurs in an enantioselective fashion. Supplement the equations! Give the transition state for the reaction.