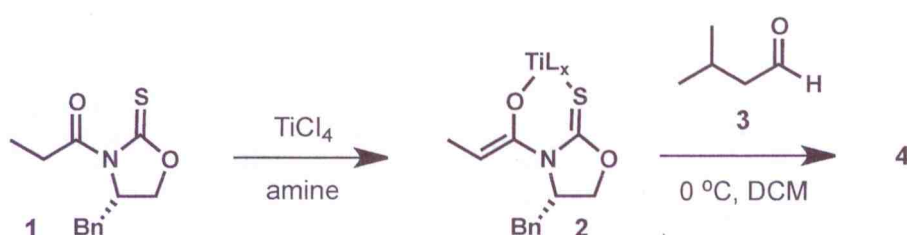


ROC 2012-2013 Mid-term test

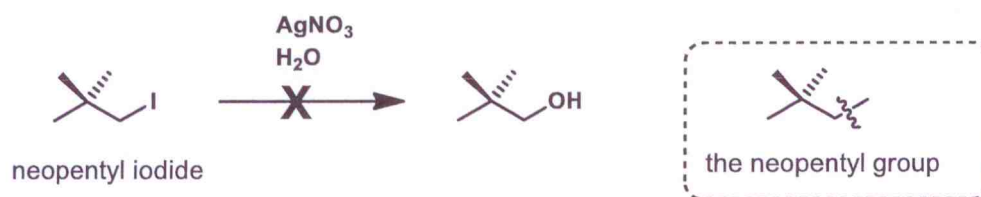
Problem 1

N-acyloxazolidinethiones (such as **1**), “sulfur equivalents of the Evans aldol auxiliaries”, can effectively be used in chiral aldol condensation reactions. Taking into account that the titanium Lewis acid used in this reaction coordinates to the chiral sulfur auxiliary, the enolate and the aldehyde simultaneously, predict the structure of compound **4** (after aqueous work up), including the stereochemistry.



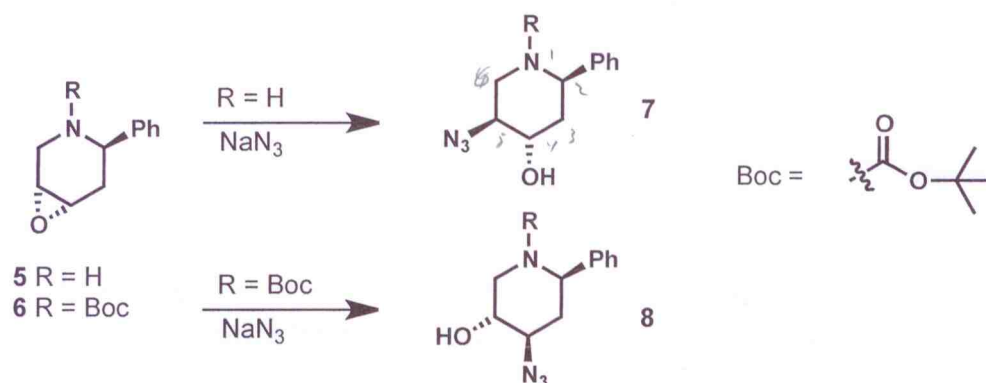
Problem 2

Substitution reactions on neopentyl systems proceed very sluggishly. Provide an explanation for this fact considering both $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ -mechanisms. In the description of the $\text{S}_{\text{N}}2$ -process, use a Newman projection to indicate steric interactions.



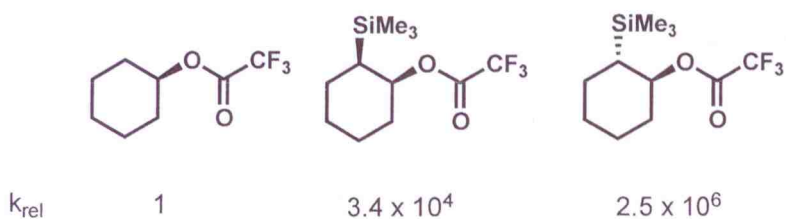
Problem 3

The regiochemistry of the nucleophilic epoxide ring opening in piperidine epoxides **5** and **6** depends on the presence (or absence) of 1,3-allylic strain of the phenyl group present on the piperidine epoxides. Provide a mechanistic rationale for the regio- and stereochemistry observed in the transformations depicted below.



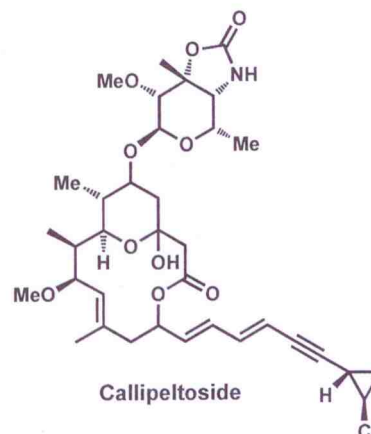
Problem 4

The solvolysis of the trifluoroacetates in trifluoroethanol depicted below proceeds with the relative rate constants given. Explain the trend observed for the rate constants.



Problem 5

Callipeltoside A, is a cytotoxic glycosidic macrolide isolated from the shallow water sponge, *Callipelta* sp. Because of its intriguing structure, several total syntheses of this compound have been reported. A part of one these syntheses is depicted below.



- Provide the mechanism for the formation of **11** from **9** and **10** (you may ignore stereochemistry issues).
- The reduction of ketone **12**, proceeds stereoselectively to provide, after silylation, product **13**. Which stereoisomer at C-3 is formed and why?
- Provide a mechanism for the transformation of **14** into **15**. Which stereoisomer at C-1 is formed and why?

