

CHEM 8321/4321

November 7, 2022

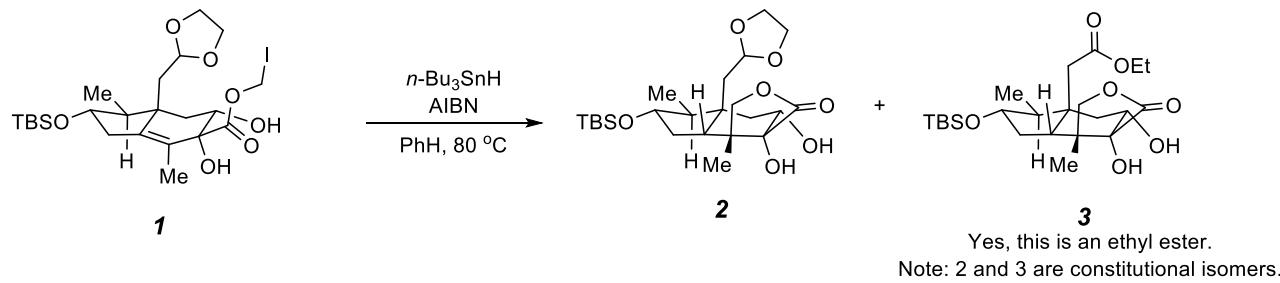
## Problem Set #9

T. R. Hoye

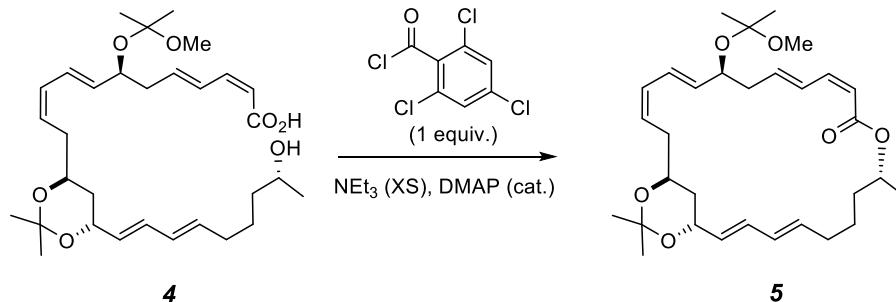
**Due in class, Monday November 14, 2021**

**Detailed Mechanism** Provide a detailed mechanism [i.e., explicitly show (using curly arrows) *EVERY* intermediate, formal charge (where relevant), equilibrium, and bond-making and -breaking step] to account for the following transformations:

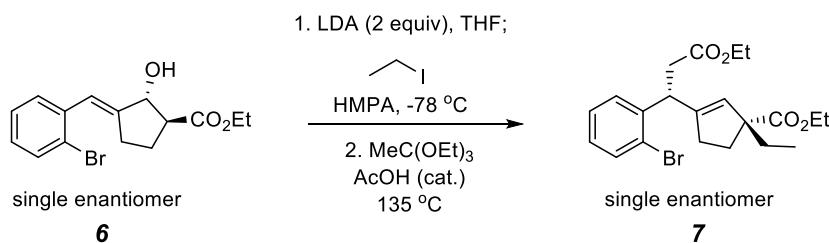
- a) The formation of lactones **2** and **3** through a radical cyclization of primary iodide **1**. (Hint: the first two steps are the same to make both products.)



- b)** The cyclization of **4** to furnish **5**. This is a Yamaguchi Macrolactonization reaction.

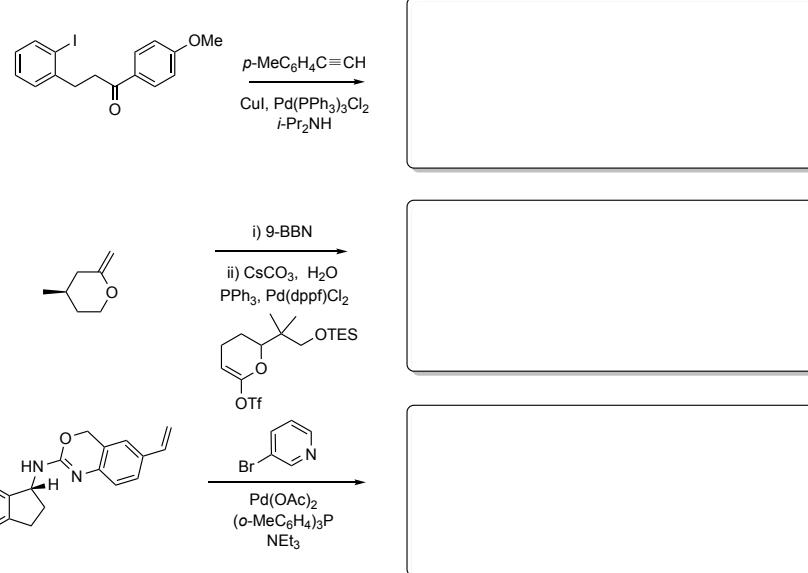


- c) The formation of alkylated diester **7** by treating ethyl ester **6** with LDA and ethyl iodide, followed by treatment with triethyl orthoformate to effect a Johnson-Claisen rearrangement. Account for the configuration of the ethyl bearing carbon in the product and provide a detailed mechanism for step 2.

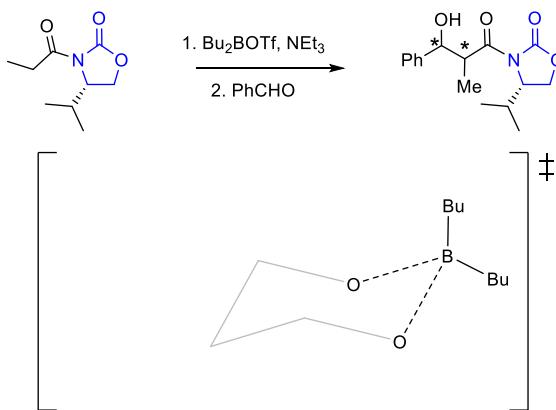


**Other Problems**

**1.** Predict the major product of each metal catalyzed transformation



**2.** The Evans asymmetric aldol reaction utilizes an **oxazolidinone** as a chiral auxiliary that contains a stereocenter to obtain high diastereoselectivity in an aldol addition reaction. Deduce the configuration of the starred stereogenic carbon atoms by drawing the fully elaborated, six-membered transition state structure.



**3.** The conversion of alcohol **8** to cycloheptanone **9** occurs via an oxyanionic-Cope rearrangement within the vicinal pi-pi system, followed by an *in situ* S<sub>N</sub>2' cyclization. Indicate the relative configuration of each of the three newly formed stereogenic centers **marked in red** by assuming a chair-like transition state for each of the two steps (use a *trans*-decalin scaffold as a guide).

