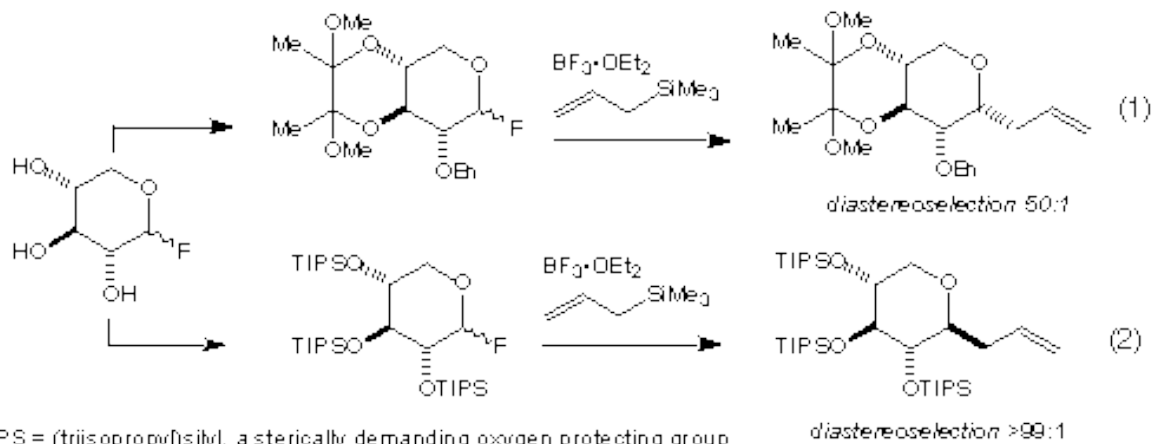


## Dr. Andreana Group Meeting – Fun Problem Set ☺

(Credit: Dr. Evans CCB Problem Sets)

### Problem 1 (Choose Part A or B)

The stereochemical course of C-glycosidation may be controlled by the judicious choice of protecting groups (*Angew. Chem. Int. Ed.* 2003, 1021-3).

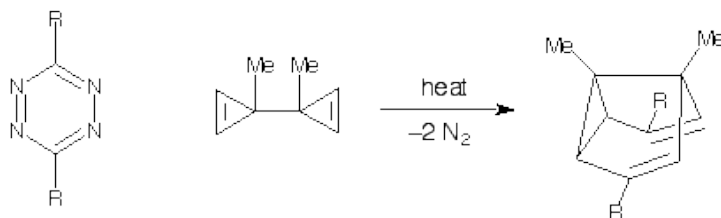


Part A. Using conformational drawings, rationalize the stereochemical outcome of the allylation illustrated in Eq 1.


Part B. Using conformational drawings, rationalize the stereochemical outcome of the allylation illustrated in Eq 2.

### Problem 2a

The following "one-pot" synthesis of semibulvalene was recently reported by J. Sauer (*Eur. J. Chem.* 2002, 791-801).

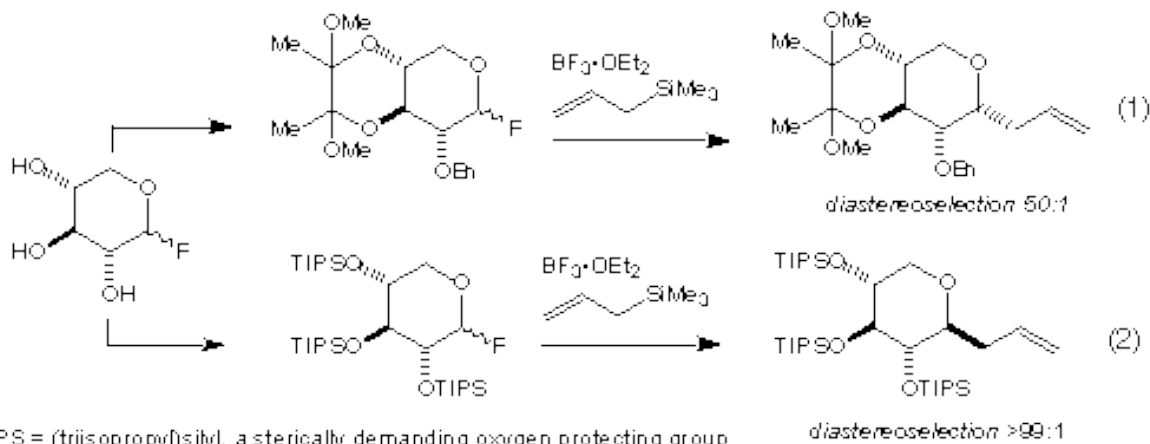


Provide a plausible mechanism for this transformation in the space below:

**Dr. Andrea Group Meeting – Fun Problem Set**   
**(Credit: Dr. Evans CCB Problem Sets)**

**Problem 1 (Choose Part A or B)**

The stereochemical course of C-glycosidation may be controlled by the judicious choice of protecting groups (*Angew. Chem. Int. Ed.* 2003, 1021-3).

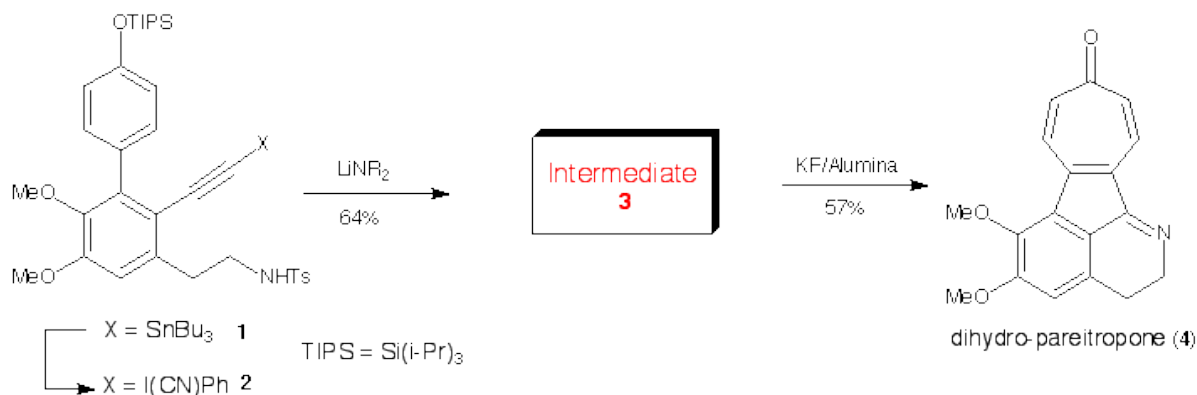


**Part A.** Using conformational drawings, rationalize the stereochemical outcome of the allylation illustrated in Eq 1.

**Part B.** Using conformational drawings, rationalize the stereochemical outcome of the allylation illustrated in Eq 2.

**Problem 2b**

An elegant synthesis of pareitropone (**5**) was recently reported by Feldman (*J. Am. Chem. Soc.* **2002**, 124, 11600). The first reaction was staged by the generation of the iodoacetylide **2** which was treated with  $\text{LiNR}_2$  without purification to form intermediate **3** which was immediately transformed into the dihydro-pareitropone (**4**) in with KF and alumina. The synthesis of **5** was completed by air oxidation of **4**.

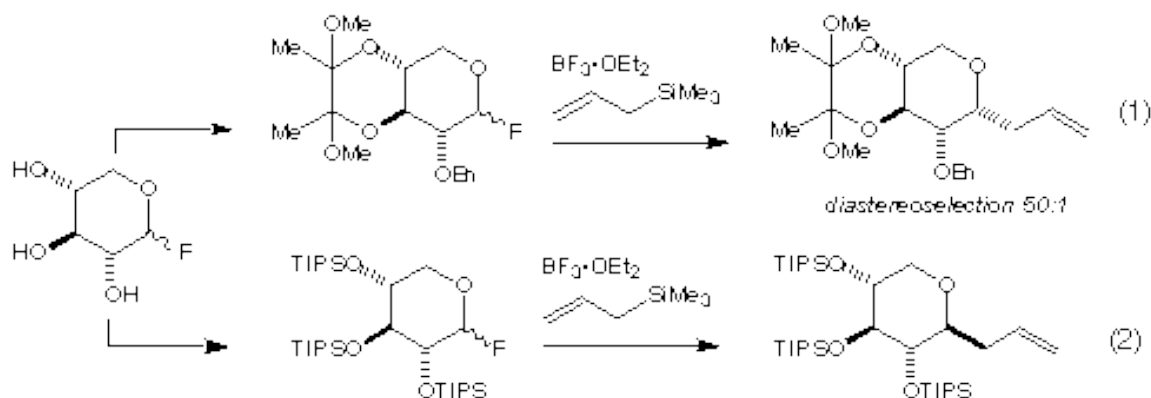


Provide a plausible mechanism for the conversion of **2** to **4** and identify the structure of **intermediate 3**.

## Answer Key

### Problem 1

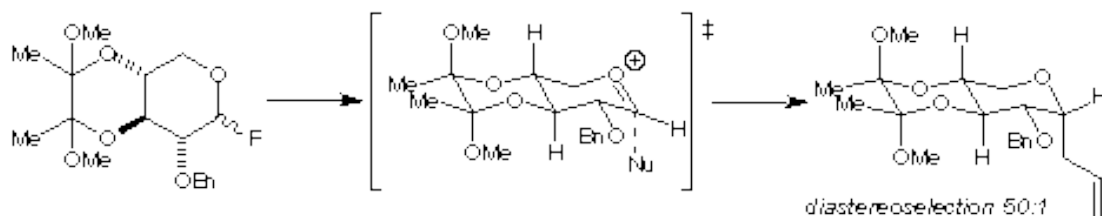
The stereochemical course of C-glycosidation may be controlled by the judicious choice of protecting groups (*Angew. Chem. Int. Ed.* 2003, 1021-3).



TIPSO = (triisopropyl)silyl, a sterically demanding oxygen protecting group

diastereoselection >99:1

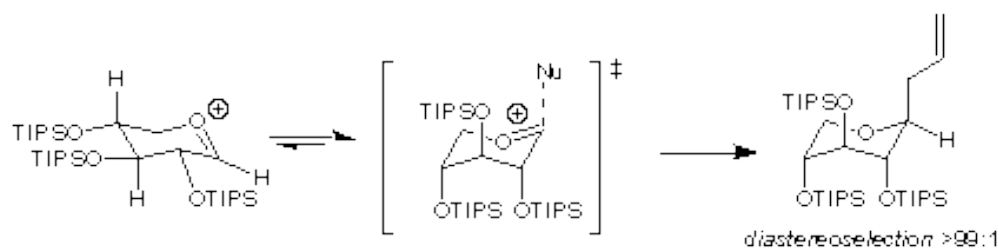
Part A. Using conformational drawings, rationalize the stereochemical outcome of the allylation illustrated in Eq. 1.



This substrate is conformationally locked.

Axial attack on oxocarbenium ion is stereoelectronically favored as is syn attack to the vicinal cis OBn substituent (Woerpel, *JACS* 2000, 122, 168).

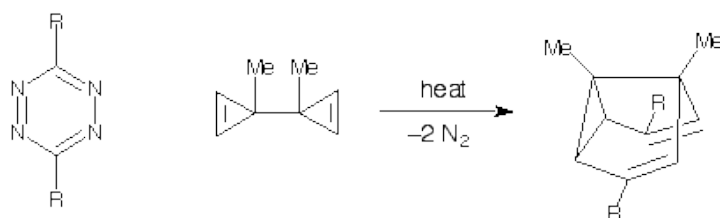
Part B. Using conformational drawings, rationalize the stereochemical outcome of the allylation illustrated in Eq. 2.



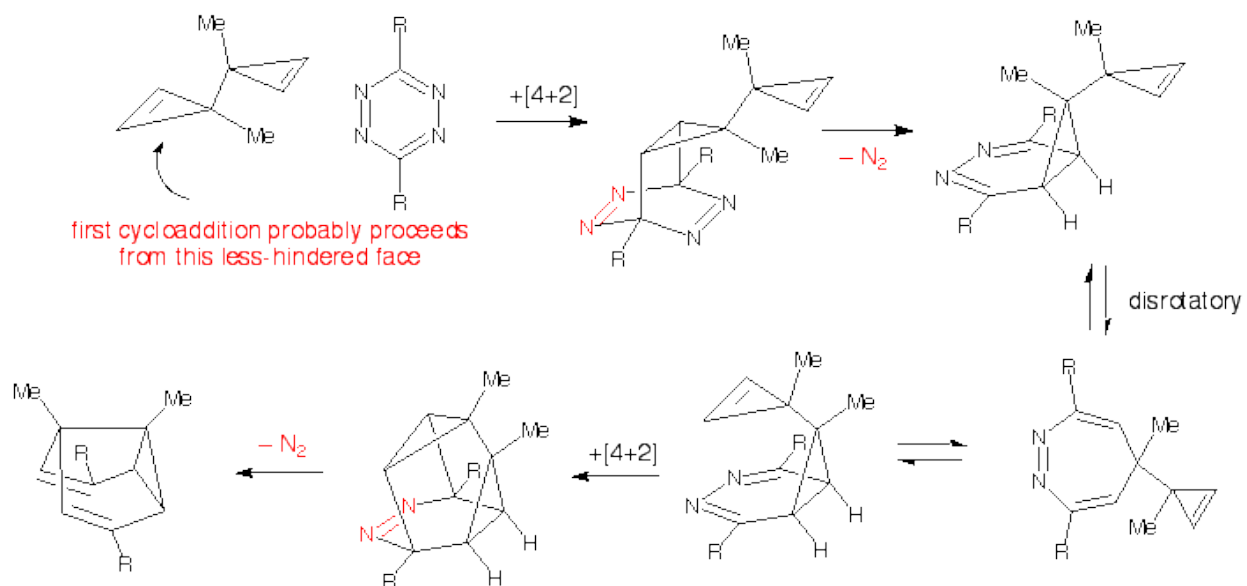
Vicinal bulky diequatorial silyl ethers cannot accommodate diequatorially; forced diaxial alignment and stereoelectronically favored axial nucleophilic addition

## Problem 2a

The following "one-pot" synthesis of semibulvalene was recently reported by J. Sauer (*Eur. J. Chem.* **2002**, 791-801).

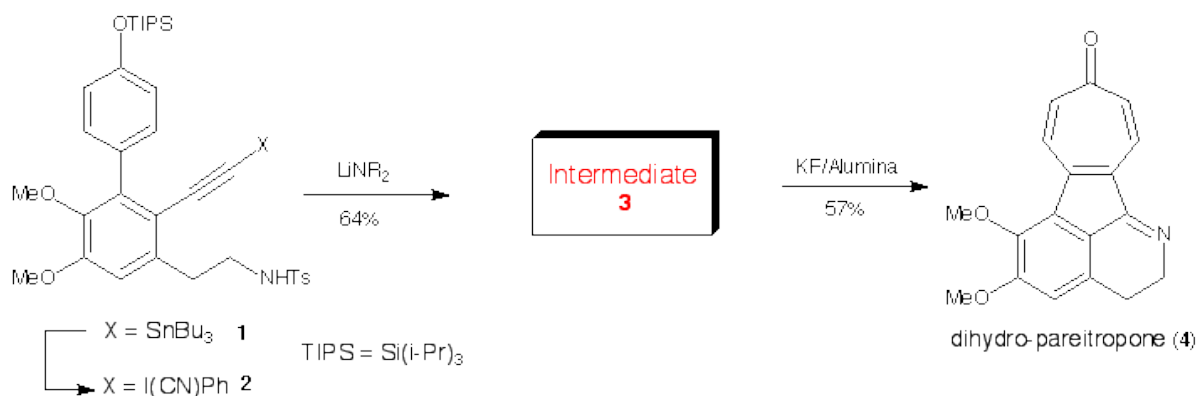


Provide a plausible mechanism for this transformation in the space below:



## Problem 2b

An elegant synthesis of pareitropone (**5**) was recently reported by Feldman (*J. Am. Chem. Soc.* **2002**, *124*, 11600). The first reaction was staged by the generation of the iodoacetylide **2** which was treated with  $\text{LiNR}_2$  without purification to form intermediate **3** which was immediately transformed into the dihydro-pareitropone (**4**) in with  $\text{KF}$  and alumina. The synthesis of **5** was completed by air oxidation of **4**.



Provide a plausible mechanism for the conversion of **2** to **4** and identify the structure of **intermediate 3**.

