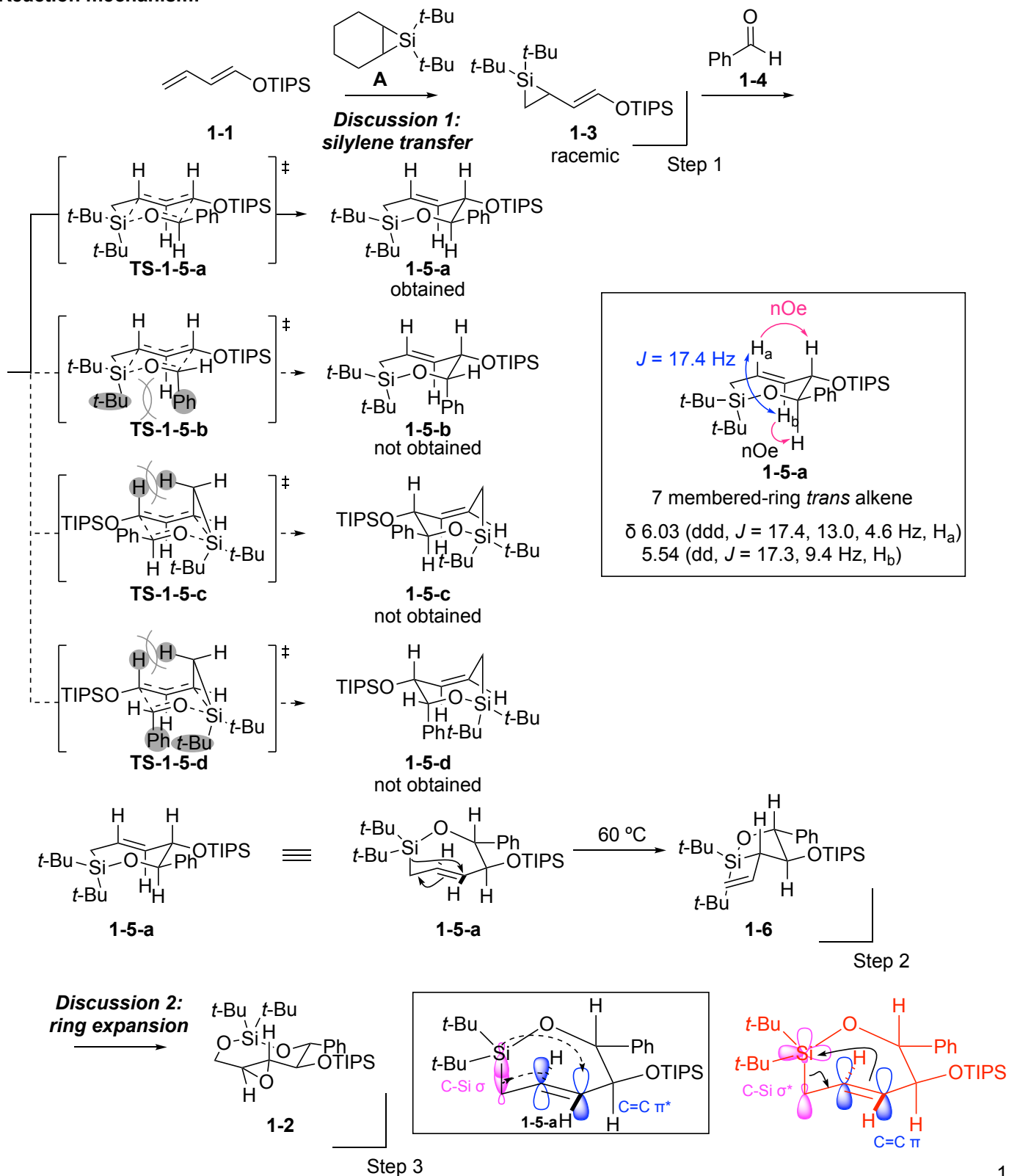
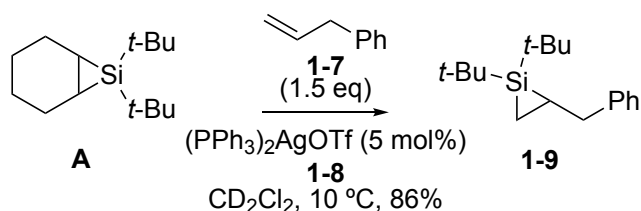


**Reaction mechanism:**

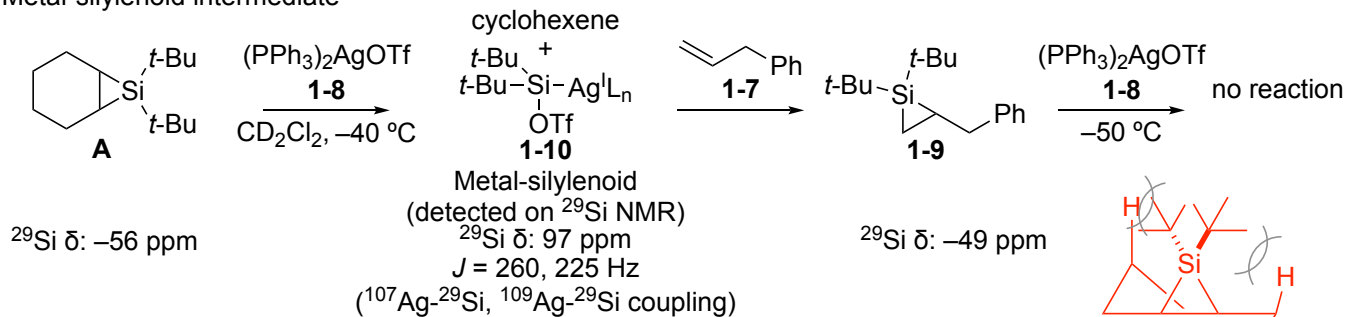


## Discussion 1: silylene transfer

### 1.1. Mechanistic study



#### • Metal-silylenoid intermediate



$^{29}\text{Si}$   $\delta$ : -56 ppm

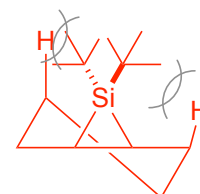
Metal-silylenoid  
(detected on  $^{29}\text{Si}$  NMR)

$^{29}\text{Si}$   $\delta$ : 97 ppm

$J = 260, 225$  Hz

( $^{107}\text{Ag}$ - $^{29}\text{Si}$ ,  $^{109}\text{Ag}$ - $^{29}\text{Si}$  coupling)

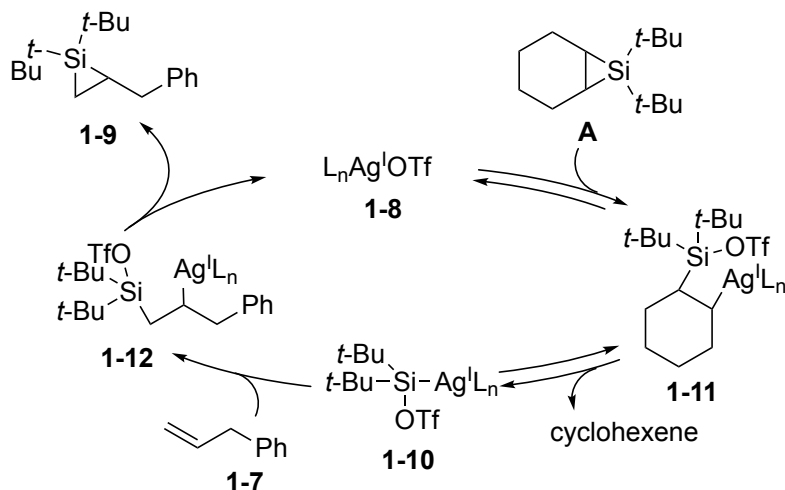
$^{29}\text{Si}$   $\delta$ : -49 ppm



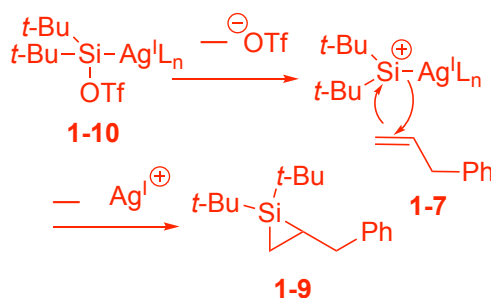
low field shift of  $^{29}\text{Si}$  shift  $\longrightarrow$  silylenoid is electrophilic.

**A** is less stable than **1-9** due to the steric hindrance between *t*-Bu group and H.

#### • catalytic cycle

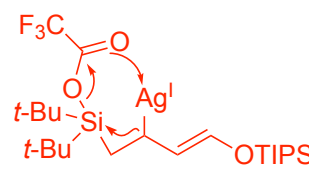
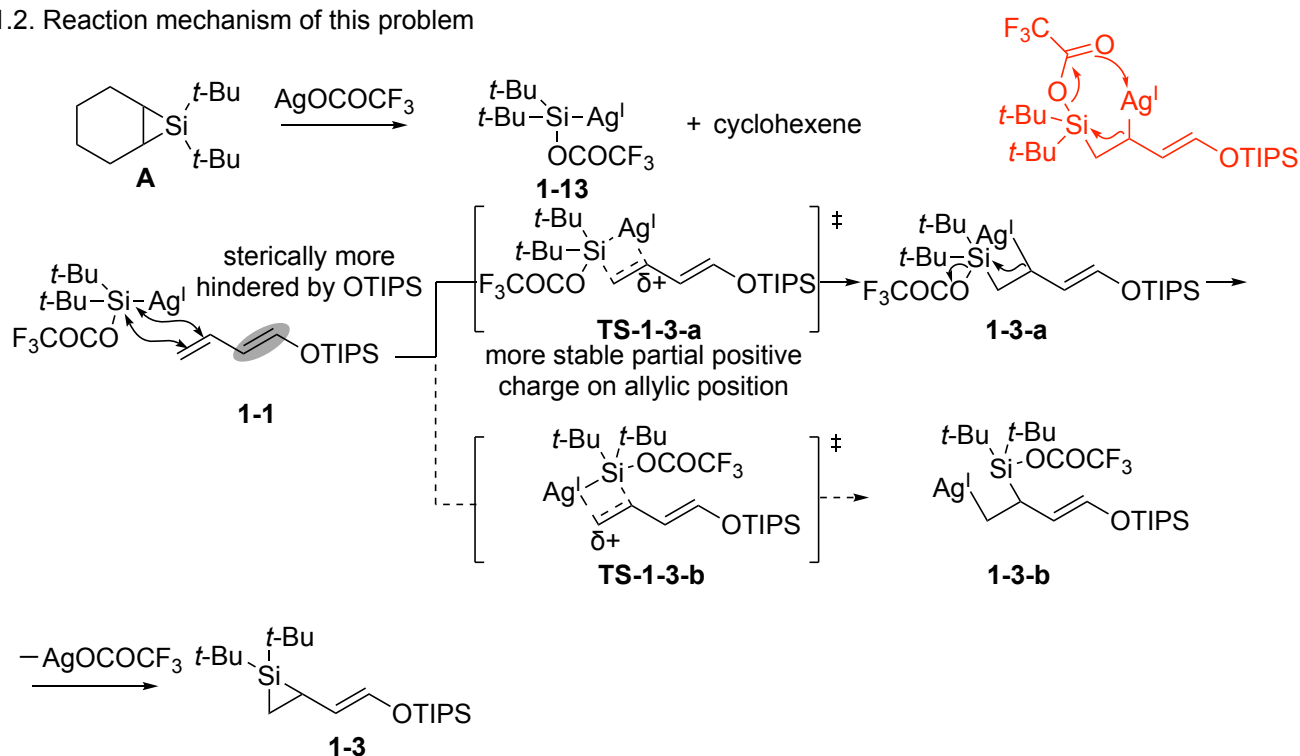


#### other possible mechanism



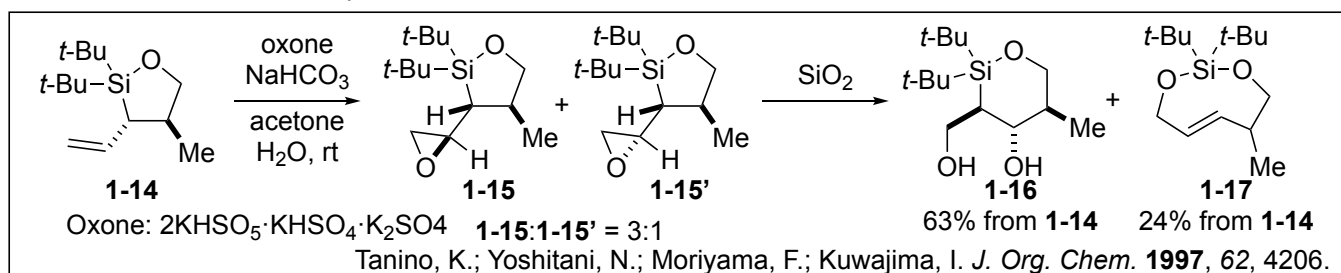
Tom, G. D.; Woerpel, K. A. *J. Am. Chem. Soc.* **2004**, 126, 9993-10002.

### 1.2. Reaction mechanism of this problem

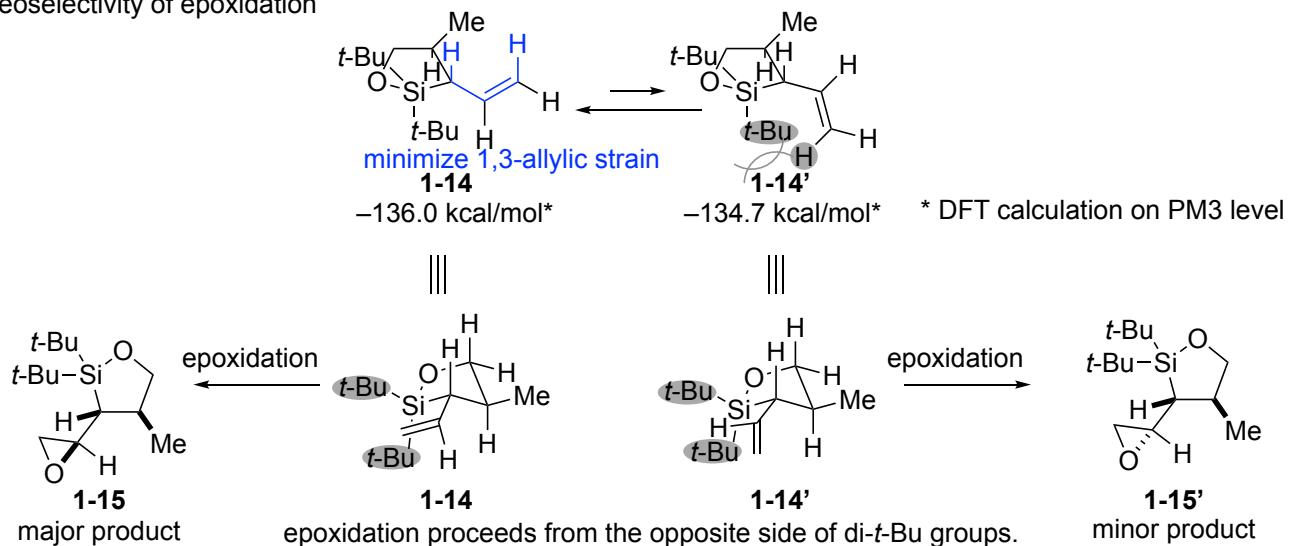


## Discussion 2: Ring expansion

### 2.1. Other results of similar compound

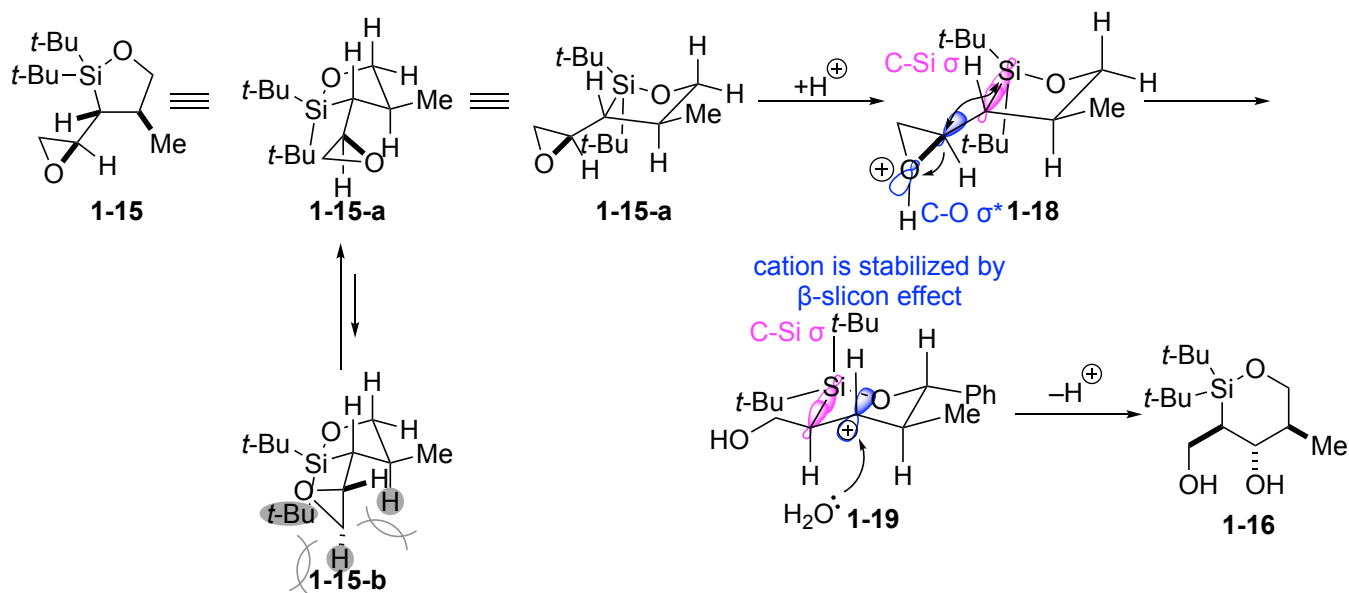


#### i) Stereoselectivity of epoxidation

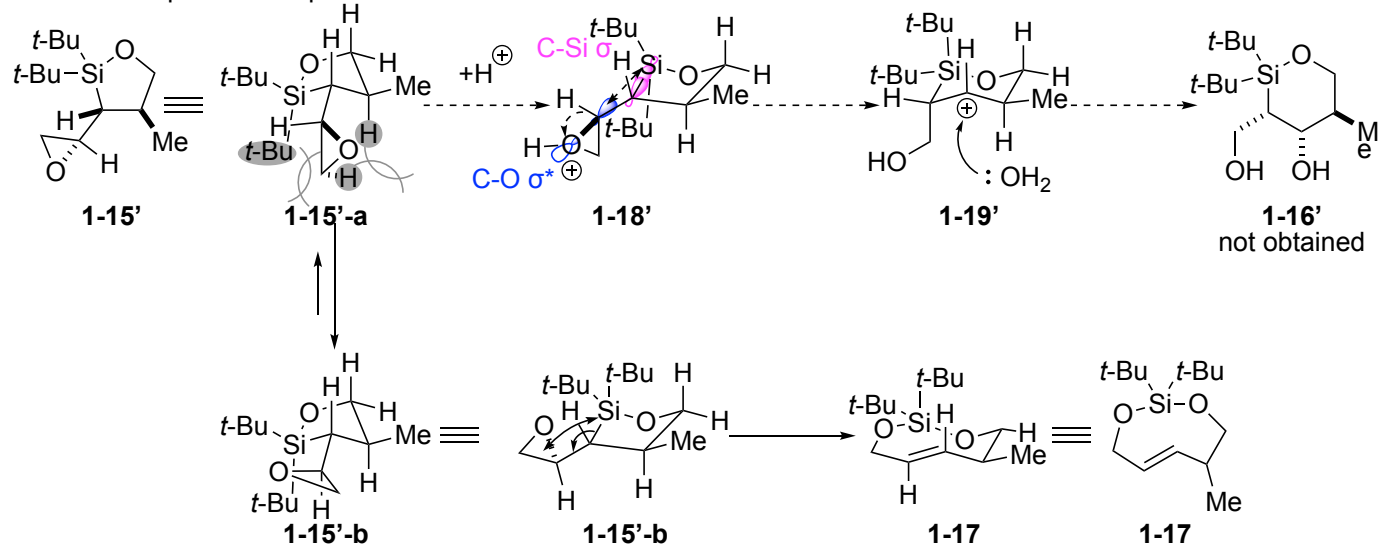


#### ii) Reaction mechanism of ring expansion

- From major product of epoxidation

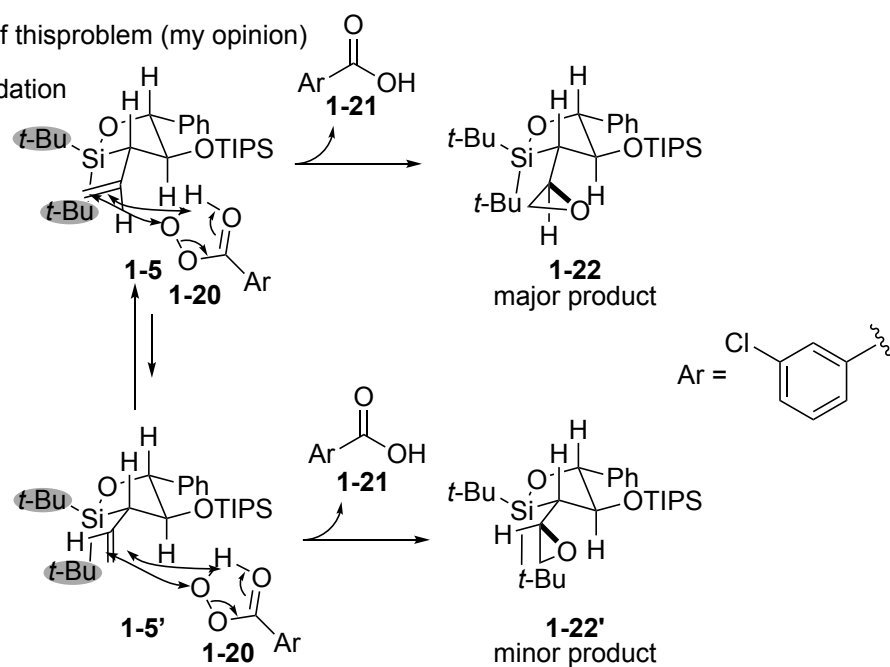


• From minor product of epoxidation



## 2.2. Reaction mechanism of this problem (my opinion)

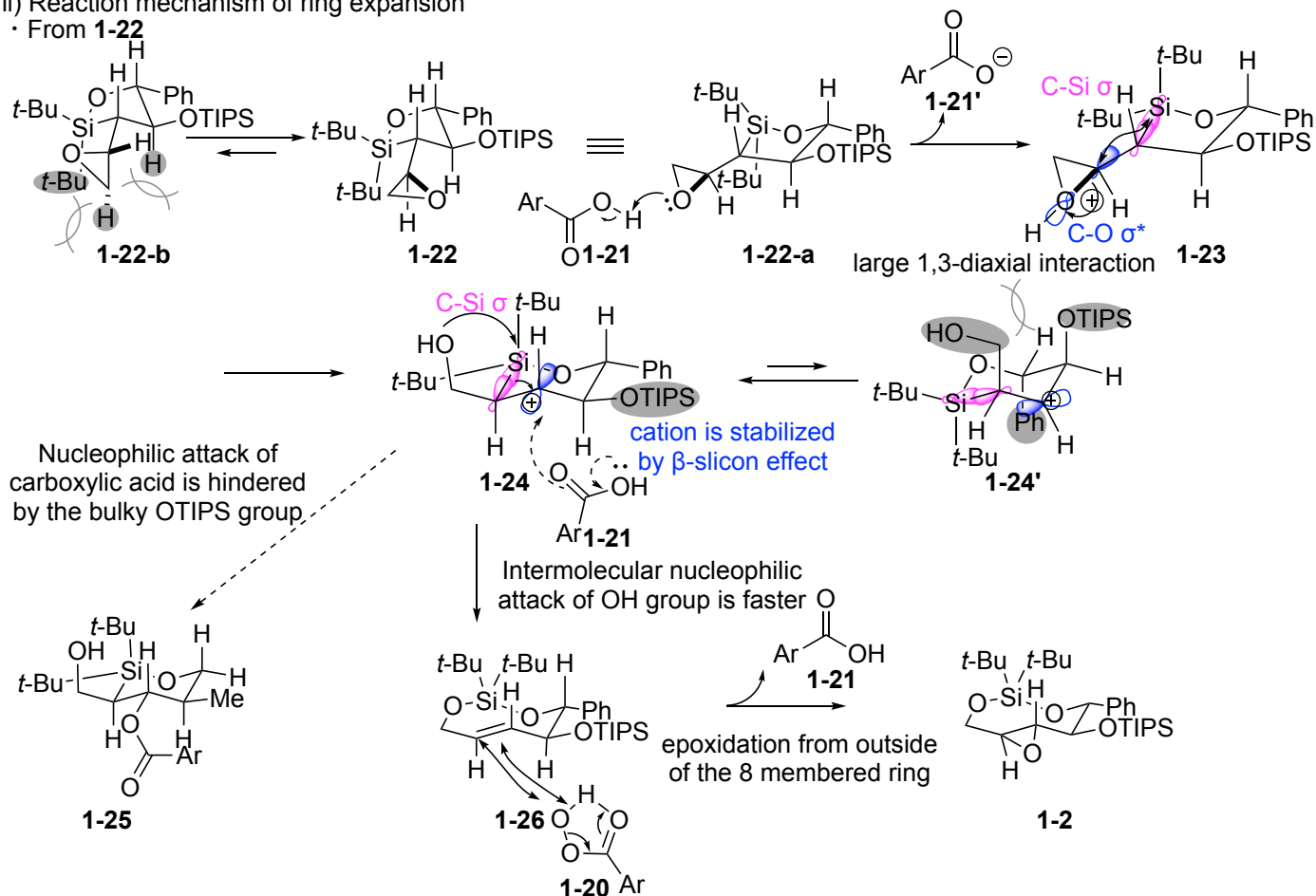
i) Stereoselectivity of epoxidation



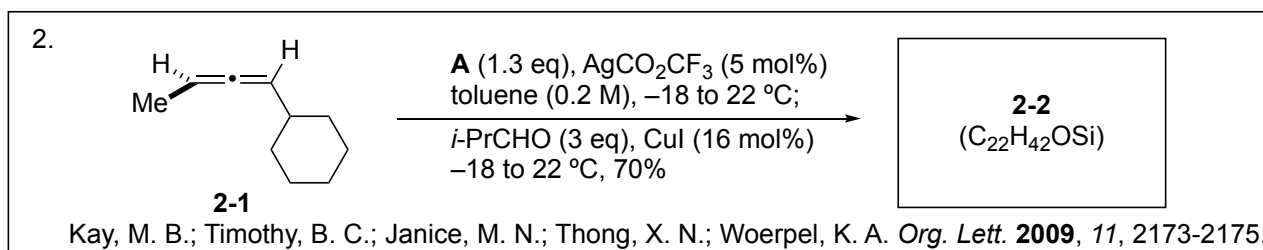
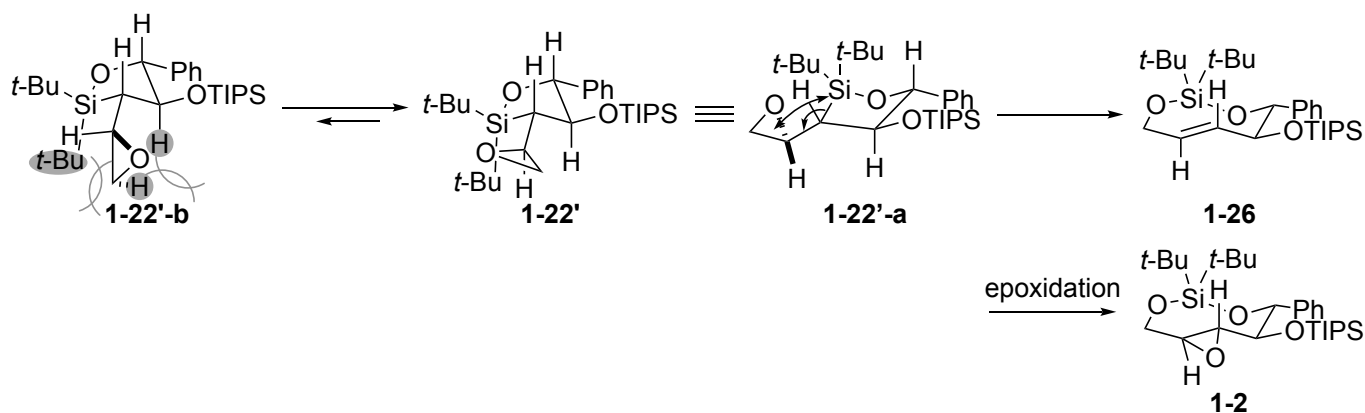
Same as the results in the box, I think that both 1-22 and 1-22' are generated, and 1-22 would be a major product.

ii) Reaction mechanism of ring expansion

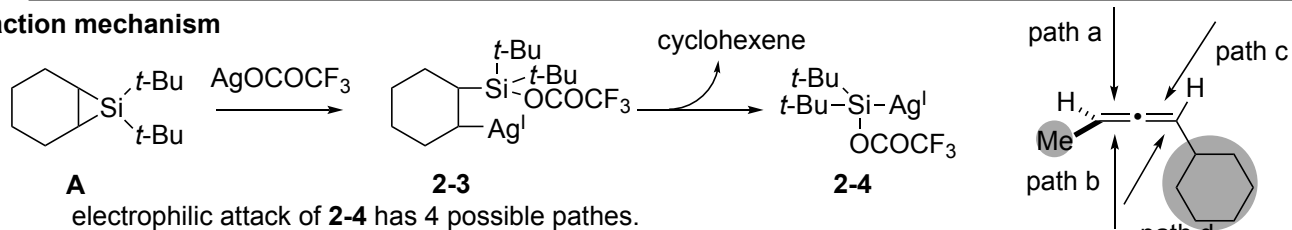
• From **1-22**



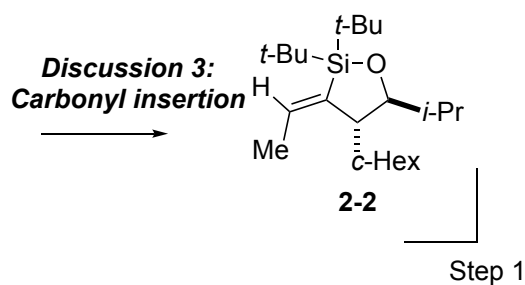
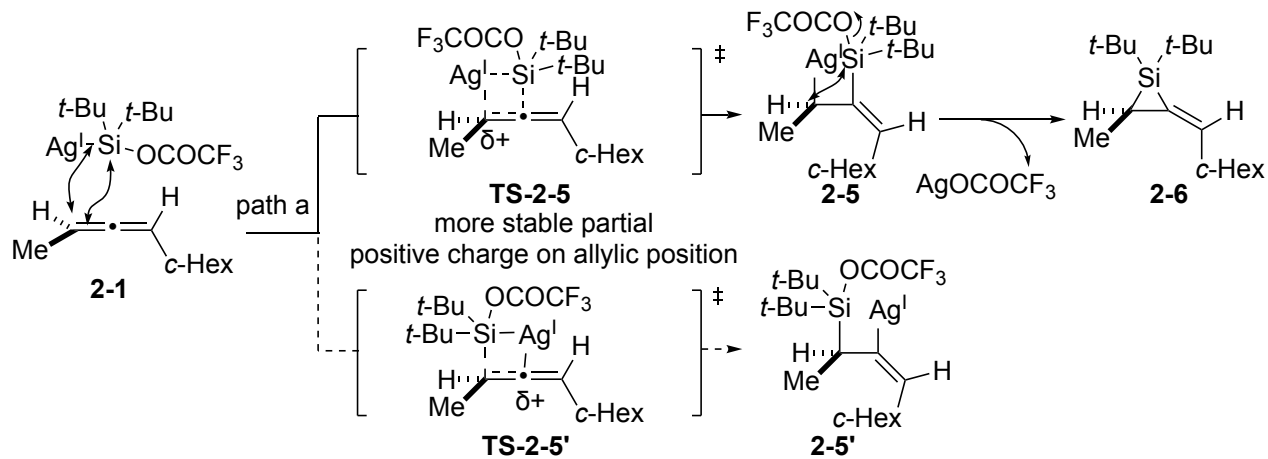
• From **1-22'**



Reaction mechanism

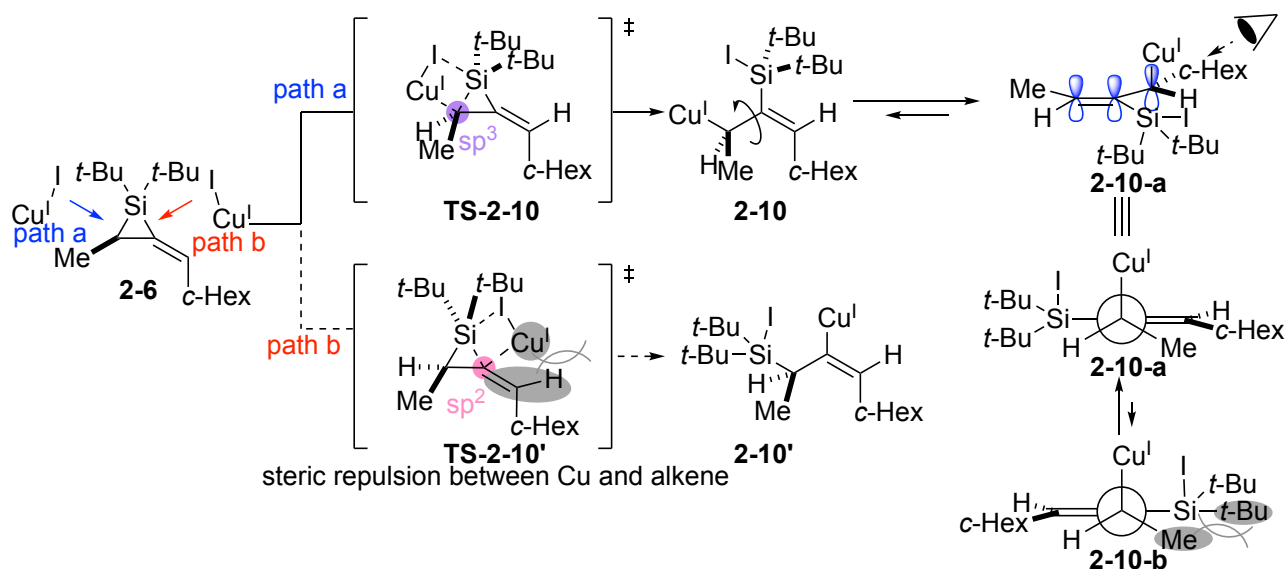
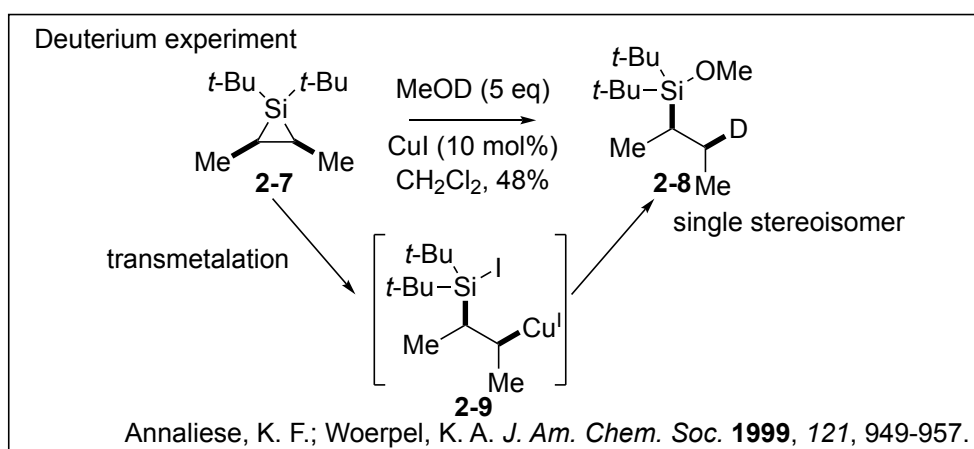


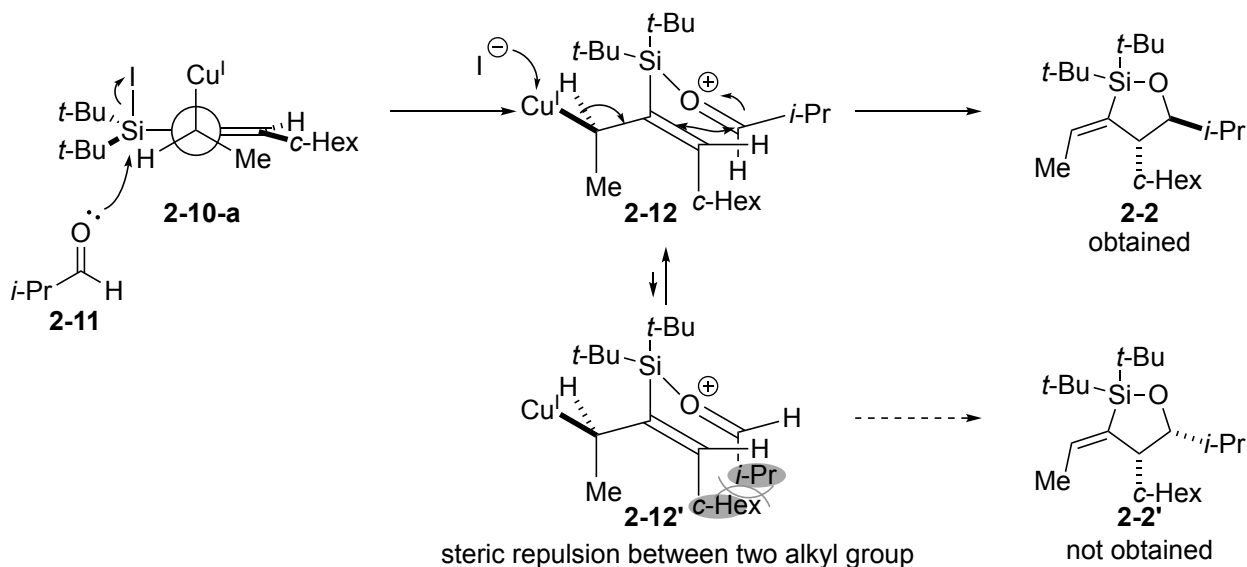
- i) Me vs. *c*-Hex: **2-4** reacts with the olefin containing a less bulky Me group. → path a and b  
 ii) *c*-Hex vs. H: **2-4** attacks from the same side of the smaller H atom. → path a is the most favored.



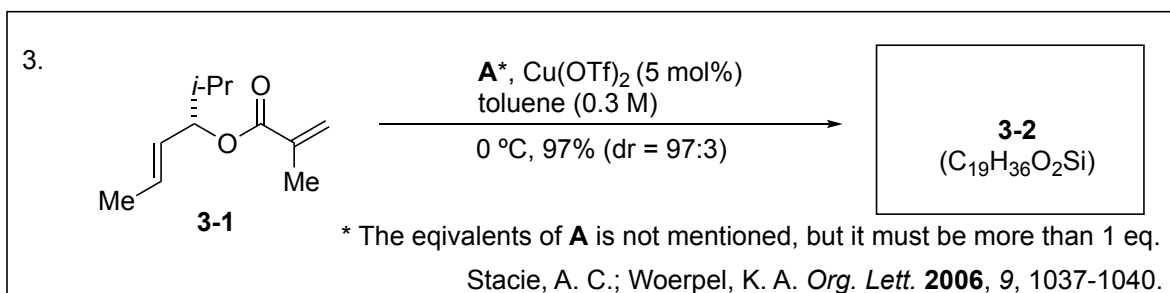
### Discussion 3: Carbonyl insertion

- Cu catalyzed reaction mechanism (my opinion)

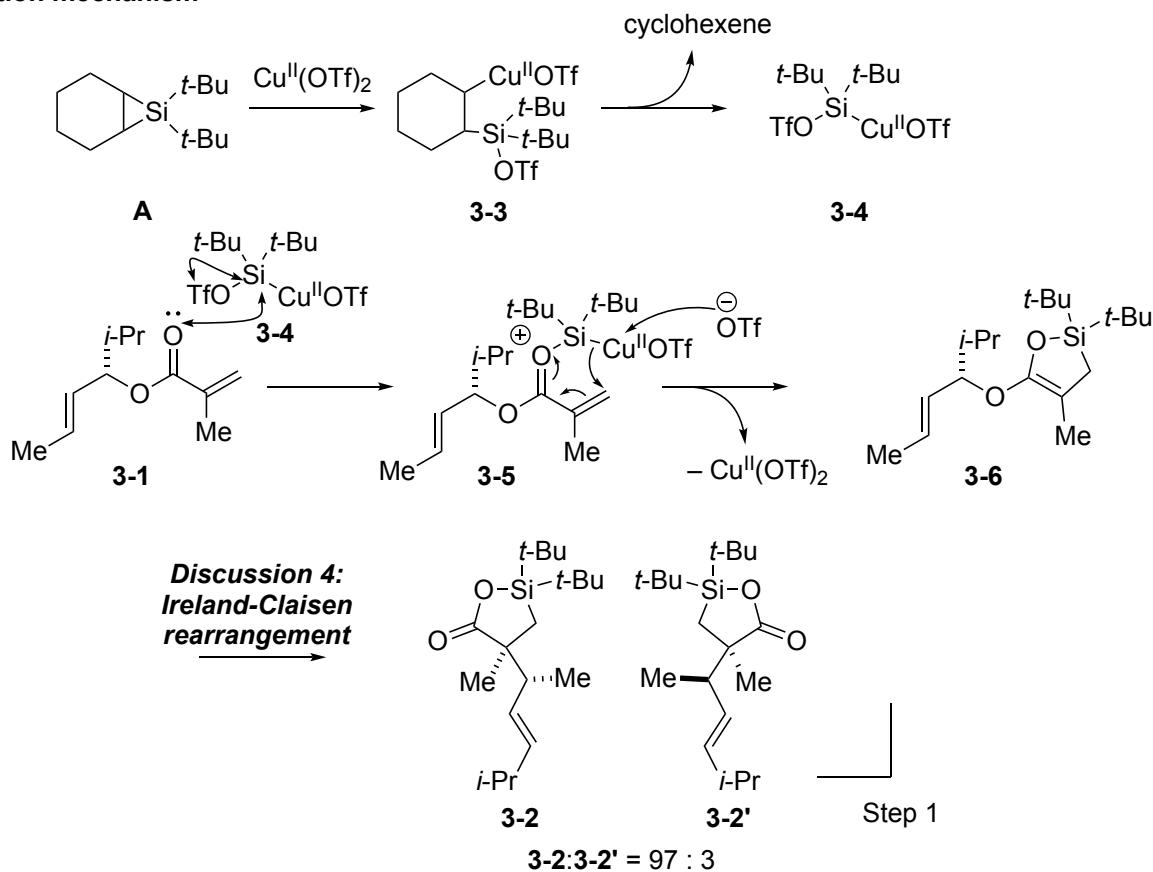




Nucleophilic attack of carbonyl to Si proceeds from the opposite side of I.



#### Reaction mechanism



**Discussion 4: Ireland-Claisen rearrangement**

