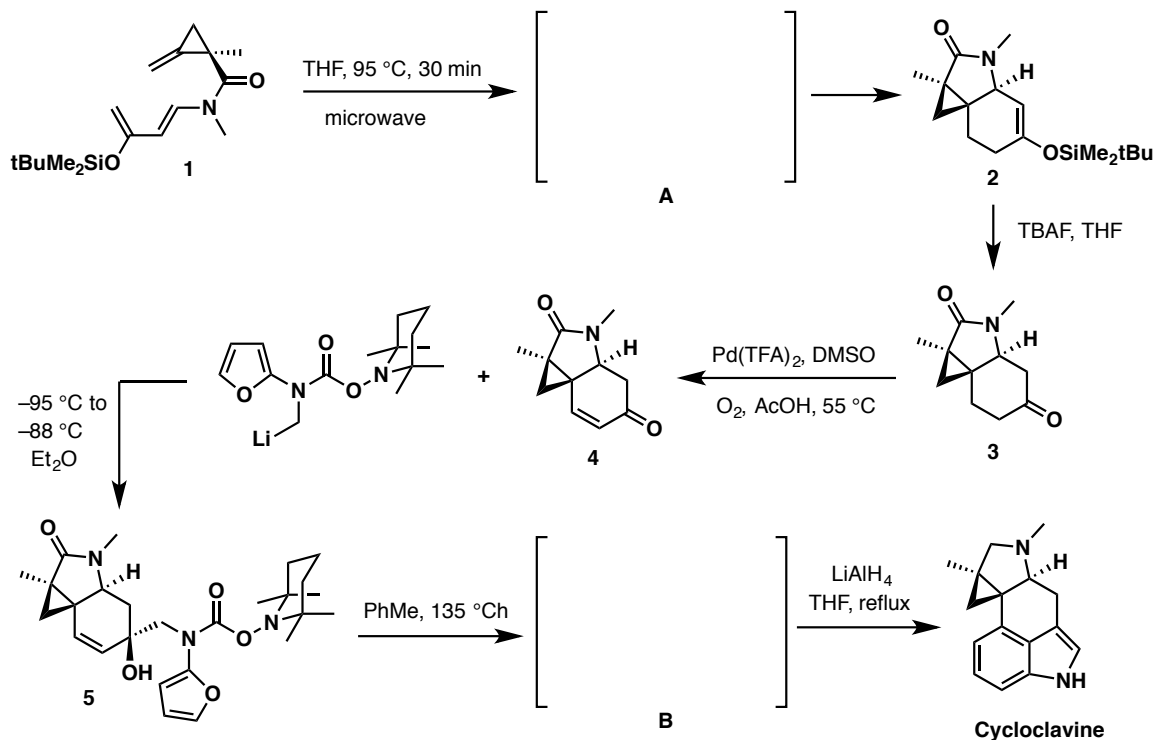


Organic Cumulative Exam (January 12, 2017)

Daesung Lee

1. (40 Points) Recently, Wipf and coworkers reported a highly concise total synthesis of (-)-cycloclavine relying on a key intramolecular Diels-Alder reaction as outlined below.



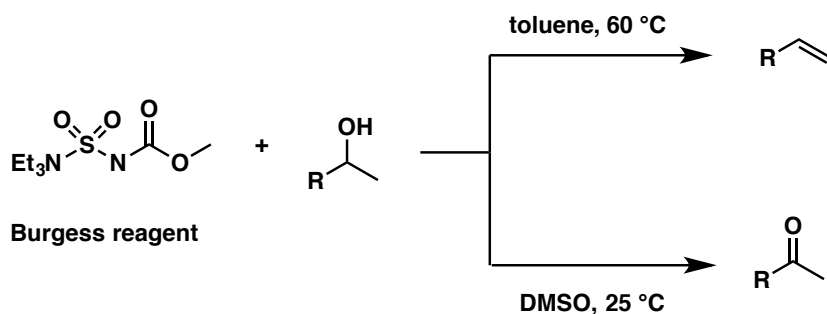
(a) (10 Points) Draw a reasonable transition state **A** in the conversion of **1** to **2**.

(b) (15 Points) Cyclohexanone **3** was then converted to the corresponding enone **4** through a catalytic version of the Saegusa–Ito oxidation. Propose a catalytic cycle for this oxidation process by drawing key intermediates.

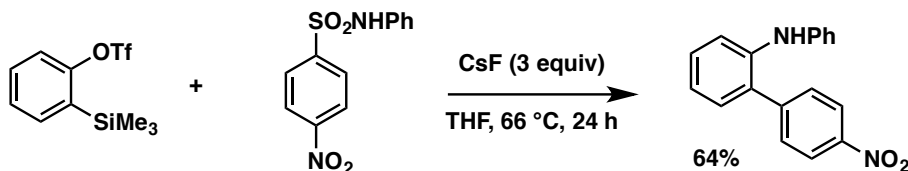
(c) (5 Points) Draw the structure of intermediate **B** formed from **5** under a thermal condition.

(d) (10 Points) Draw a mechanism that explain how **B** was converted to the final structure of cycloclavine under the given conditions.

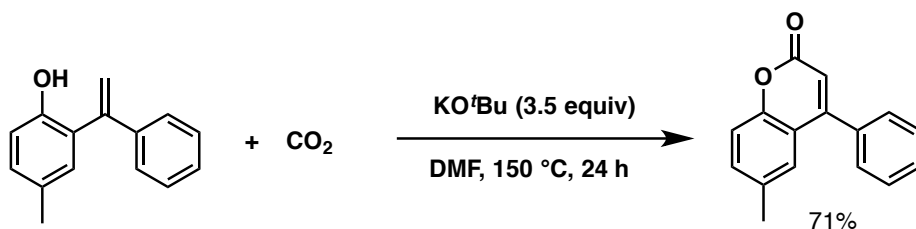
2. (20 Points) The Burgess reagent ([methoxycarbonylsulfamoyl] triethylammonium hydroxide) has historically found utility as a dehydrating agent. Recently, Bielawski and coworkers reported an alternative reactivity in DMSO. Draw mechanisms for both the transformation shown below.



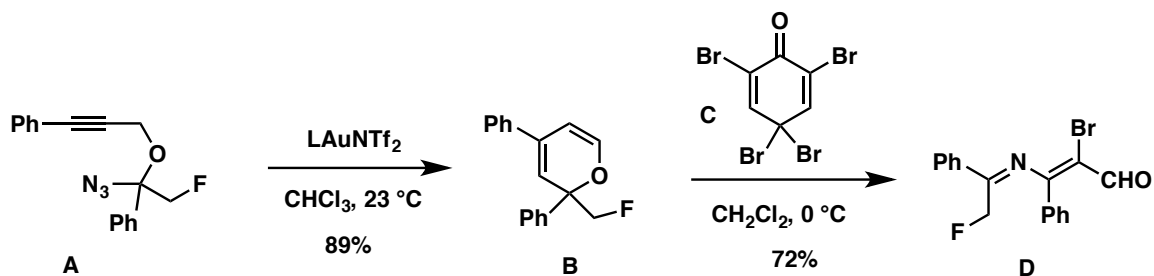
3. (15 points) The following transformation involves an electrophilic species called benzyne. Propose a reaction mechanism by drawing a series of key intermediates under the given conditions.



4. (10 points) An unusual carbonylation was achieved without a transition metal catalyst in the following transformation. Provide a reasonable reaction mechanism for this transformation.



5. (15 points) Treating azidoalkyne **A** with a cationic gold complex provided product **B** in high yield. Upon treating **B** with brominating agent **C**, aldehyde **D** was generated in good yield.



(a) (8 Points) Draw a reasonable mechanism for the conversion of **A** to **B**.

(b) (7 Points) Propose a mechanism for the conversion of **B** to **D** by drawing the key intermediates involved in the bond-making and breaking processes.