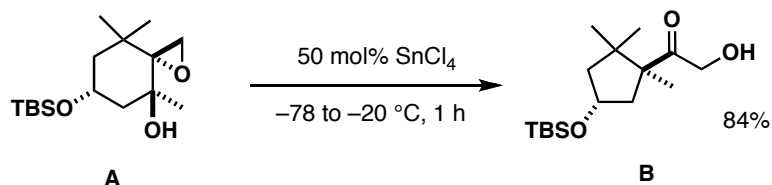
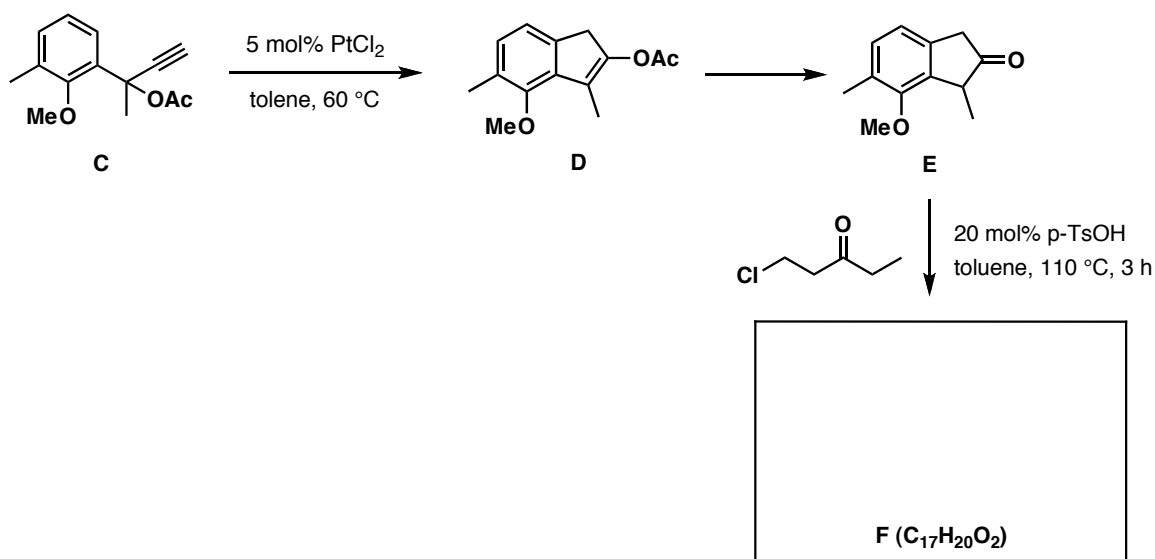


Organic Cumulative Examination (December 1, 2011)
Daesung Lee

1. (10 points) The rearrangement of epoxides catalyzed by a variety of Lewis acids has been extensively utilized in the construction of oxygenated molecular frameworks. In a recent study, a highly functionalized epoxide **A** was shown to undergo selective rearrangement to the corresponding hydroxyketone **B**. Draw a reasonable arrow-pushing mechanism for this transformation.

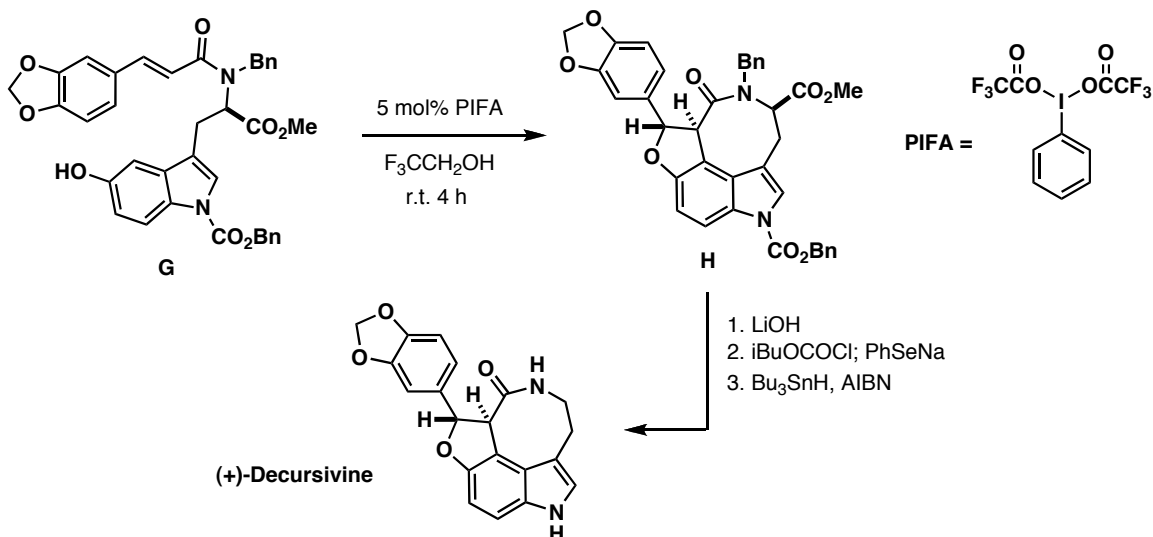


2. Compare to conventional Lewis acids, which typically activate molecules containing functionality with lone-pair electrons as illustrated above, π -Lewis acids such as platinum and gold complexes promote reactions of alkyne-containing molecules as shown in the transformation of **C** to **D**.



- (1) (10 points) Provide a reasonable mechanism for the conversion of **C** to **D** by showing appropriate intermediates and arrow-pushing.
- (2) (10 points) The resultant enol acetate **D** was transformed to ketone **E**, which then subjected to a simple reaction conditions as described above to produce a new product **F** in excellent yield. Draw the structure of **F** and a brief reaction mechanism for this transformation.

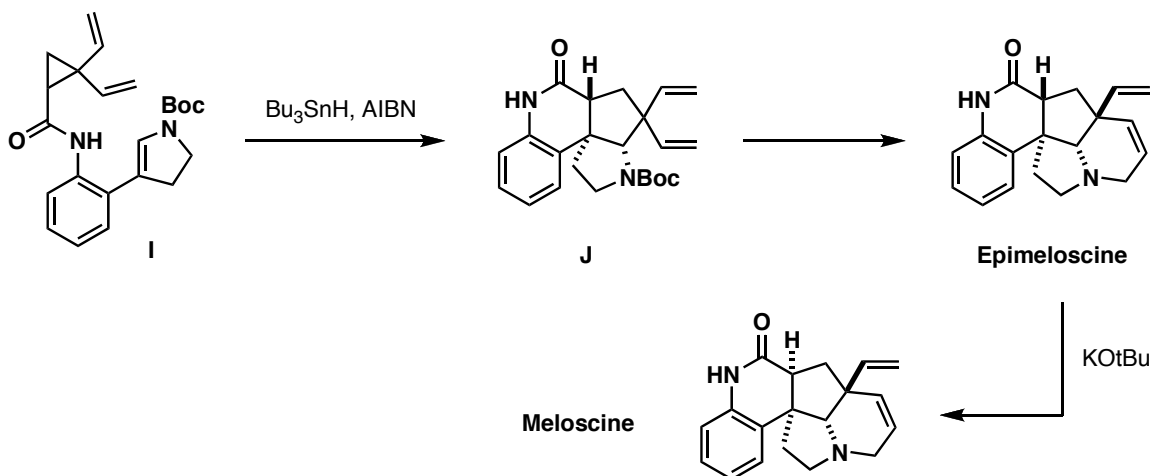
3. Recently, three total syntheses of indole-derived natural product decursivine were reported in the literature, and the key strategy in all three syntheses is quite similar if not identical. In one of the synthesis by Li et al. as shown below, an oxidation-promoted formal [3+2] cycloaddition of phenol with a tethered alkene was employed as the key step, which then was readily elaborated to (+)-decursivine through a three-step procedure.



(1) (15 points) Provide a detailed electron-pushing mechanism for the formation of **H** from **G**.

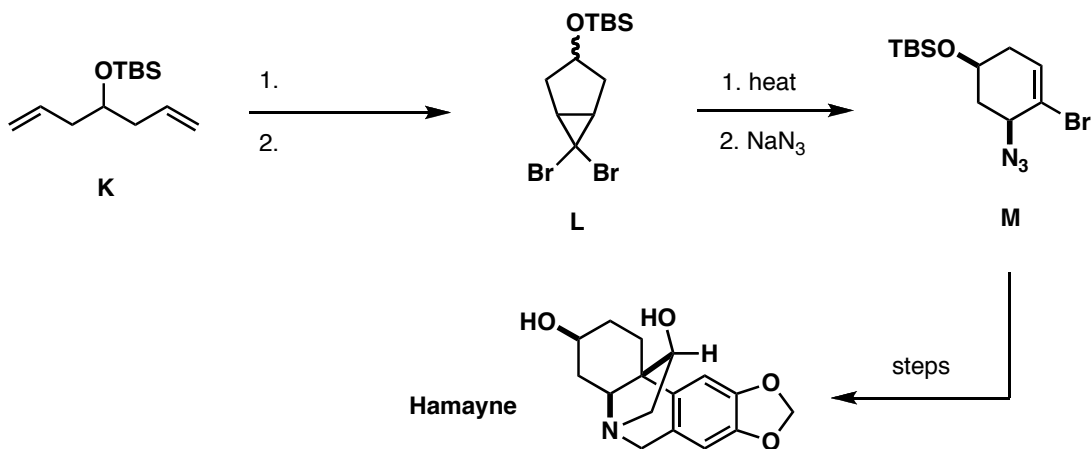
(2) (10 points) Briefly describe the decarboxylation process by drawing at least three intermediates according to the reaction conditions provided.

4. Various radical-mediated cascade reactions are powerful synthetic tools whereby complex molecular structures can be constructed in one synthetic operation. As an example, Curran et al. has employed a cascade radical annulation approach to the synthesis of epimeloscine and meloscine as shown below.



- (1) (15 points) Provide a detailed electron-pushing mechanism for the formation of **J** from **I**.
- (2) (10 points) How would you elaborate **J** to epimeloscine? On the basis of the structural characteristics, infer the three-step sequence that these authors employed or invent your own approach.

5. In their crinine alkaloid hamayne synthesis, Banwell and coworkers employed transformations to generate a pivotal intermediate **L** from **K**, which was further transformed to **M**.



- (1) (10 points) How would you synthesize **L** from **K**? Provide carbenoid/carbene-based reagents and reaction conditions to realize this via a two-step procedure.
- (2) (10 points) Provide an electron-pushing mechanism for the transformation of **L** to **M**. Unambiguously show stereochemistry whenever necessary.