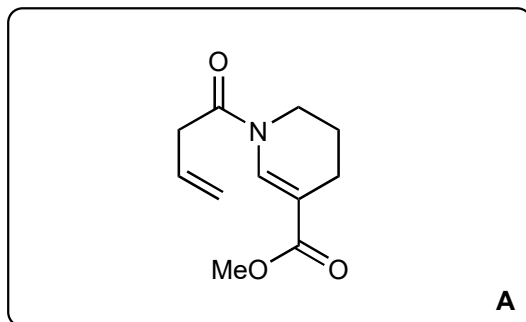
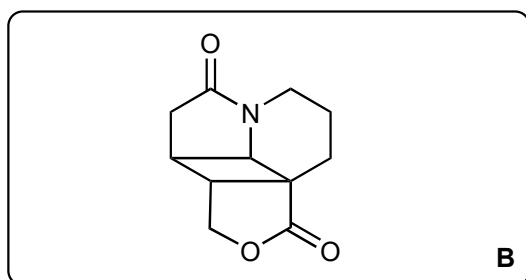


Synthesis of Aspidodispermine via Pericyclic Framework Reconstruction

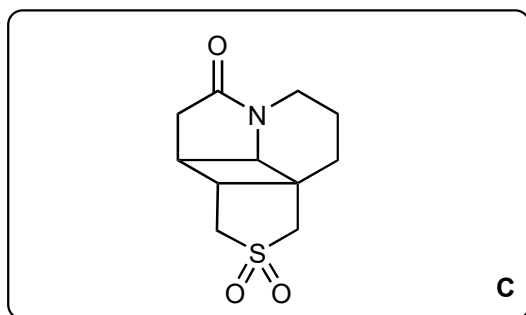
F. Reuß, P. Heretsch *Org. Lett.* **2020**, *22*, 3956–3959.



1–3



4–7

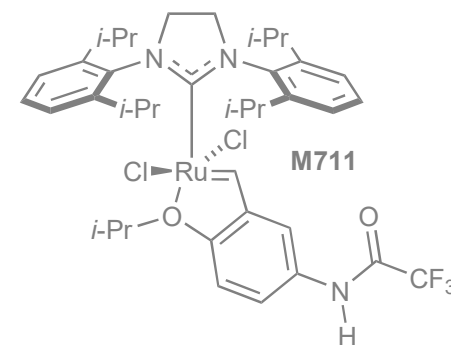


- 1) Allyl-OH, CuI, **M711**
- 2) hv, acetone
- 3) TFA

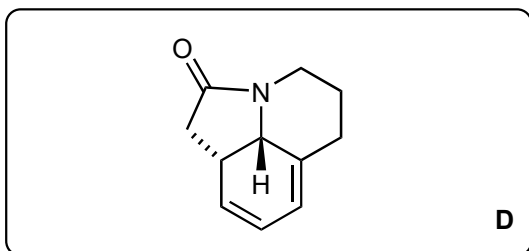
- 4) NaBH₄, NaOMe
- 5) MsCl, Et₃N (excess)
- 6) Na₂S (1 equiv)
- 7) *m*-CPBA (excess)

Structure of Umicore catalyst **M711**?
(Draw HG-II, change the NHC to SIPr and add a trifluoroacetamide-group *para* to the oxygen bridge)

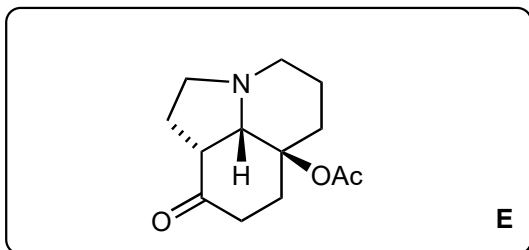
Step 2: Classify this reaction. **[2+2]-cycloaddition**
Role of acetone? **photosensitizer and solvent**



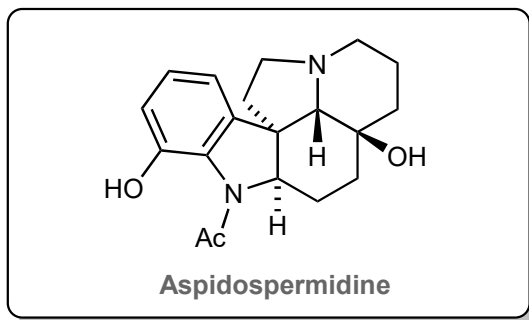
8-10



11-14



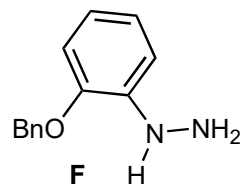
15-19



- 8) SO_2Cl_2 , pyridine
- 9) $\text{KO}t\text{Bu}$
- 10) PhH, 110 °C

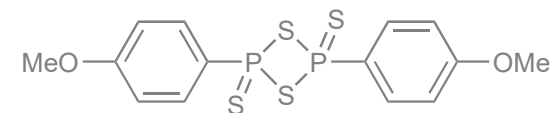
- 11) O_2 , TPP, hv then Et_3N
- 12) Ac_2O , Et_3N , DMAP
- 13) Lawesson's reagent
- 14) NaBH_4 , NiCl_2

- 15) Hydrazine **F** then AcOH
- 16) NaBH_4
- 17) Ac_2O , pyridine
- 18) DIBAL-H
- 19) H_2 , Pd/C



Step 9: Name the reaction and come up with a mechanism.
Ramberg-Bäcklund ring-contraction
Step 10: Classify the reaction.
[4π]-electrocyclic ring-opening

Step 11: Classify this reaction. **[4+2]-cycloaddition**
What is TPP? **Tetraphenylporphyrin**
Alternatives for TPP? **Methylene Blue, Rose Bengal**
Step 13: Structure of Lawesson's reagent? Alternative? **P_4S_{10}**



Step 15: Name this reaction. **Fischer Indol Synthesis**
Come up with two other methods to prepare the product of this step. **Bartoli, Gassmann, Larock etc.**