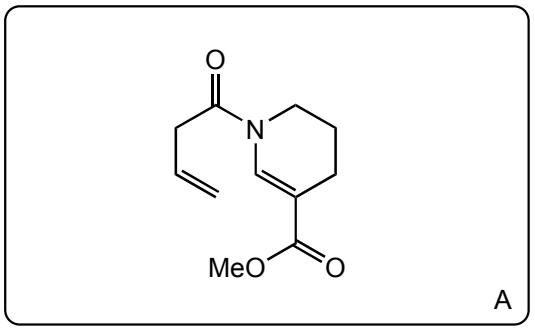
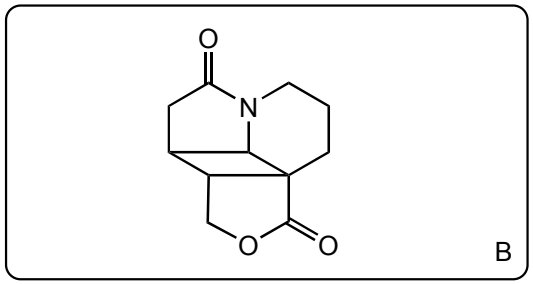
Synthesis of Aspidodispermine via Pericyclic Framework Reconstruction

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



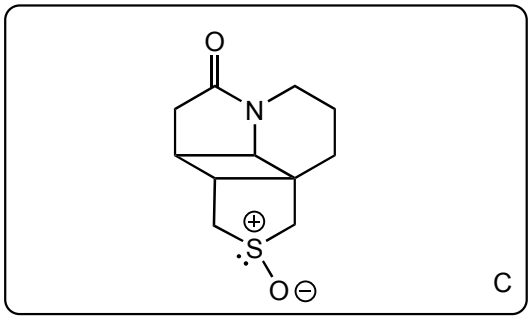
1–3

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



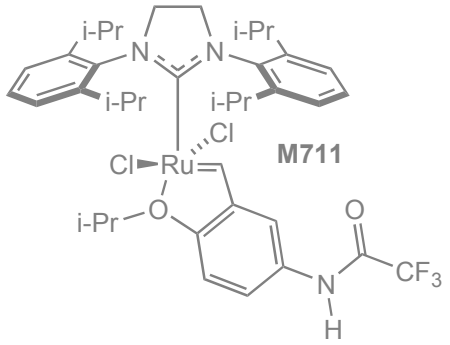
4–7

4) $NaBH_4$, NaOMe
5) MsCl, Et_3N (excess)
6) Na_2S (1 equiv)
7) *m*-CPBA (excess)

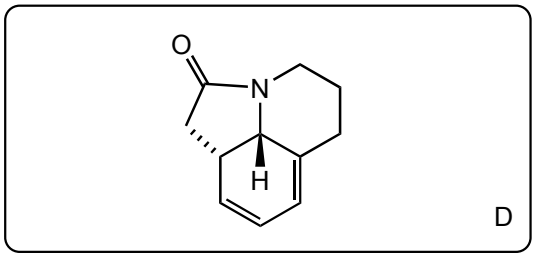


Structure of Umicore catalyst **M711**?
(Draw HG-II, change the NHC to SIPr and add a trifluoroacetamide-group *para* to the oxygen bridge)

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



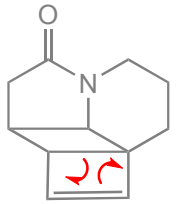
8–10



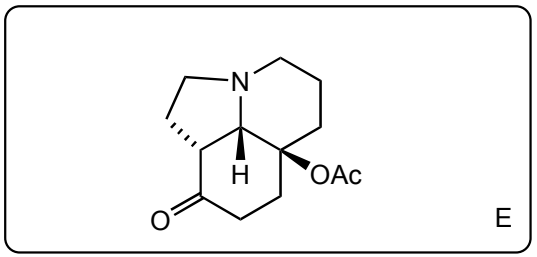
D

8) SO_2Cl_2, pyridine
9) KO*t*-Bu
10) PhH, 110 °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



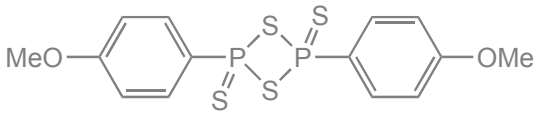
11–14



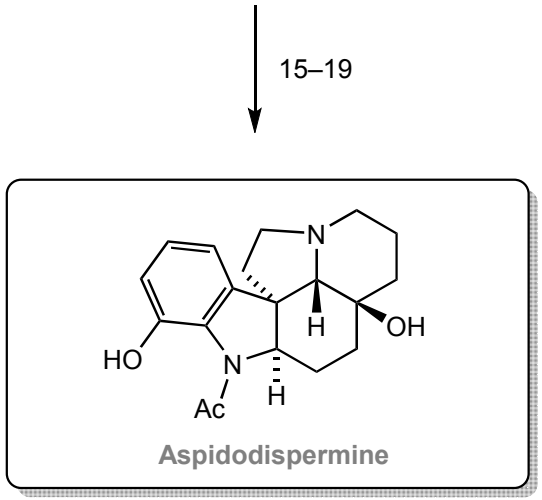
E

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

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}**

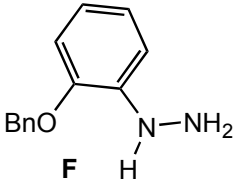


15–19



Aspidodispermine

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



F

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