Synthesis of Aspidodispermine via Pericyclic Framework Reconstruction


1) Allyl-OH, Cul, 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
8) $\text{SO}_2\text{Cl}_2$, pyridine
9) KOtBu
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
11) $\text{O}_2$, TPP, hv then Et$_3$N
12) $\text{Ac}_2\text{O}$, Et$_3$N, DMAP
13) Lawesson's reagent
14) $\text{NaBH}_4$, 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
15) Hydrazine F then AcOH
16) $\text{NaBH}_4$
17) $\text{Ac}_2\text{O}$, pyridine
18) DIBAL-H
19) $\text{H}_2$, Pd/C

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.