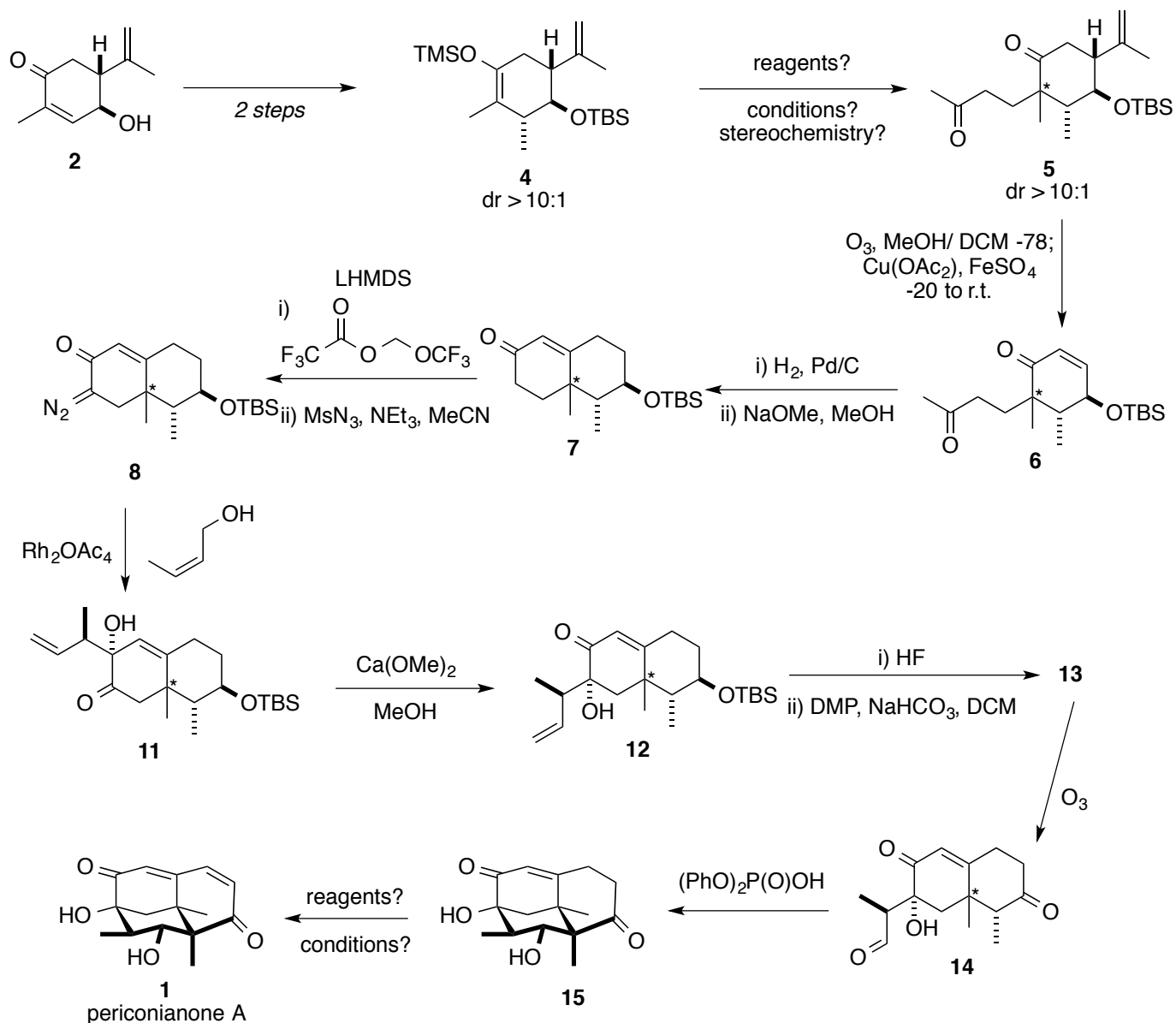


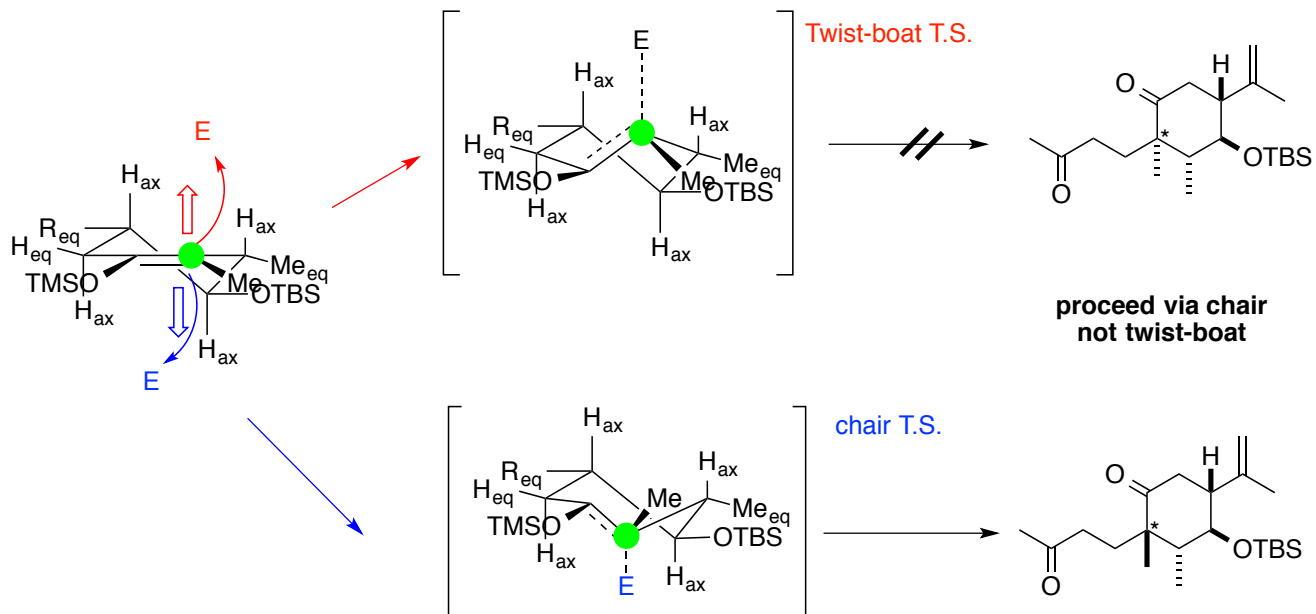
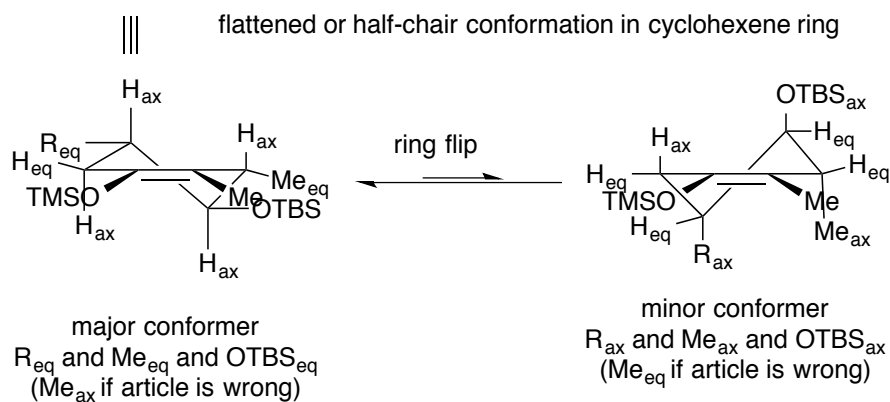
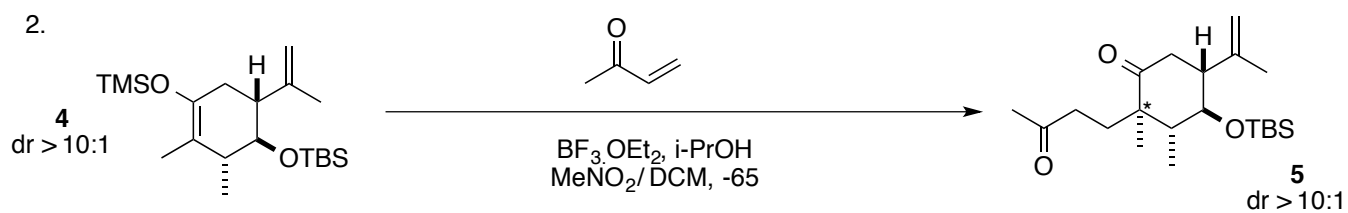
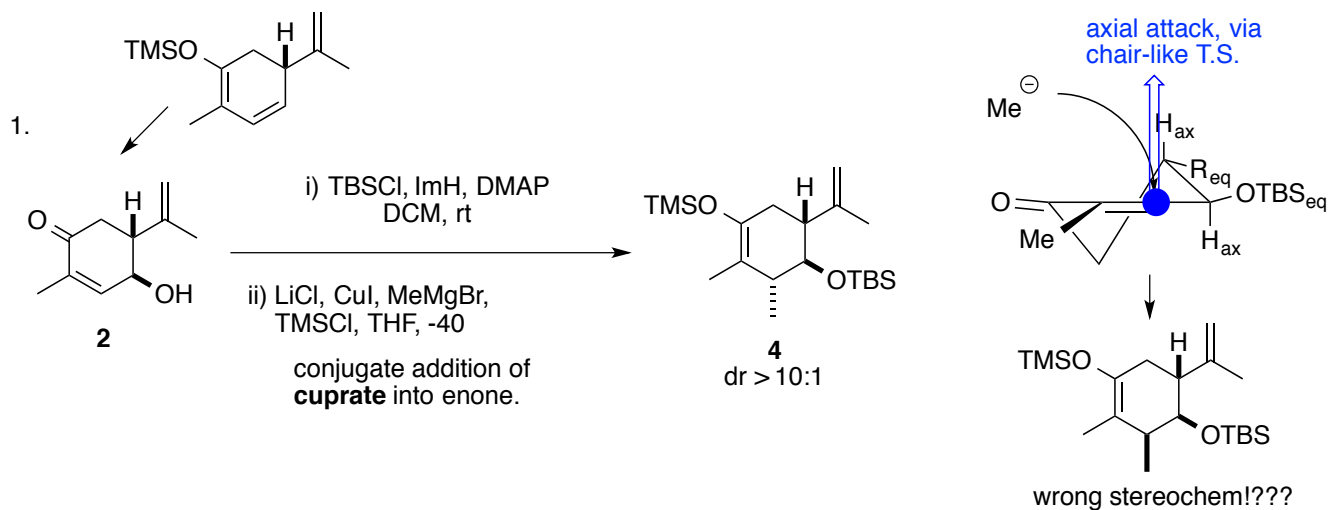
Total Synthesis of Periconianone A

submitted by Nick Tappin

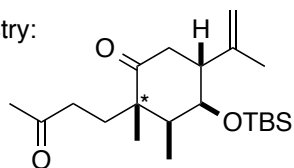
Did we see this in Villars 2017....?



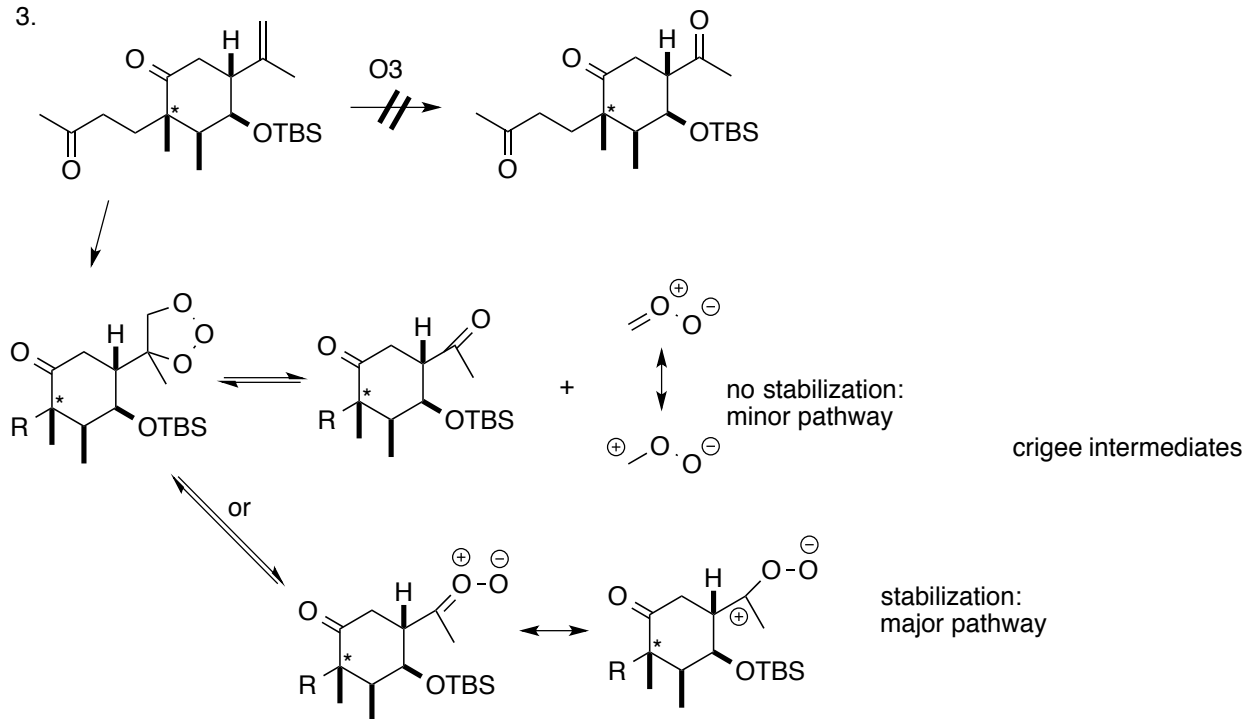
1. Suggest what could be the two steps leading to 4 from 2. Be careful with the choice of reagents (why?).
2. Provide reagents and conditions to affect the transformation from 4 to 5. Predict and rationalize the stereochemical outcome with aid of a model.
3. Explain 5 to 6.
4. Easy. Explain 6 to 7.
5. Provide a mechanism, with 3-D transition state to explain the formation of 11 from 8.
6. Easy. What happens from 11 to 12? Why is 12 the product and not 11? What is DMP? Predict structure 13.
7. What happens to give 15? Justify which through which carbon atom the reaction proceeds. Where is the diastereoselectivity coming from?
8. Easy. Suggest reagents for the final step.



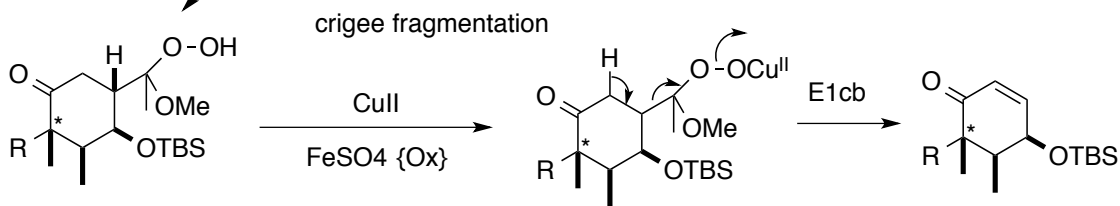
revised stereochemistry:



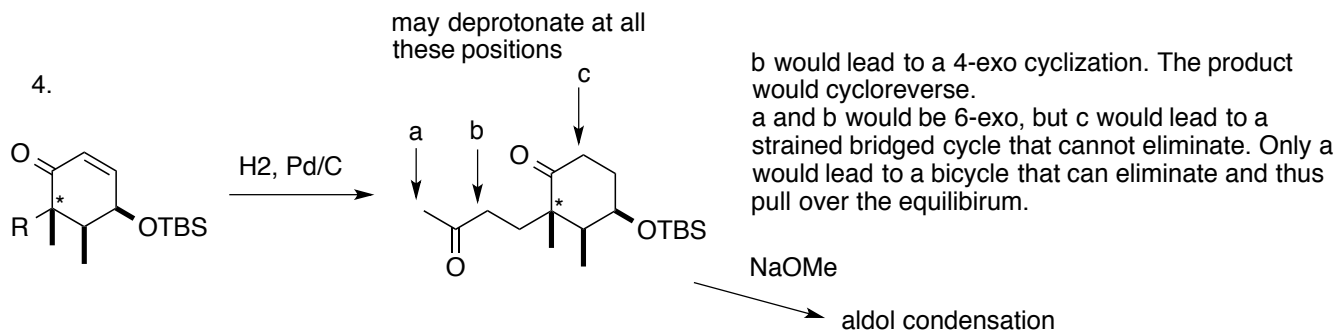
3.



MeOH
traps to give peroxy acetal



4.

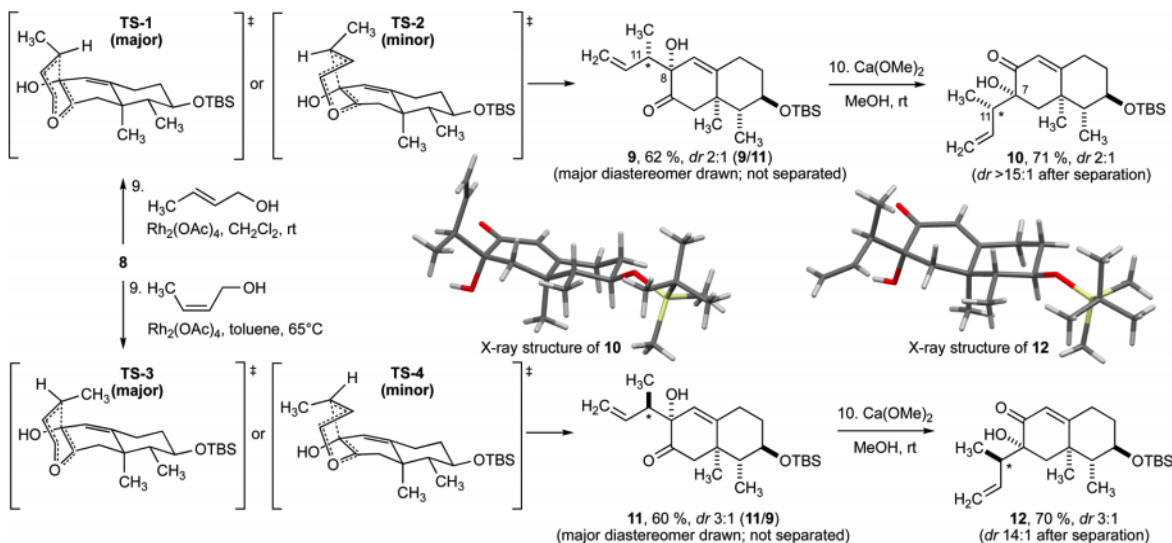
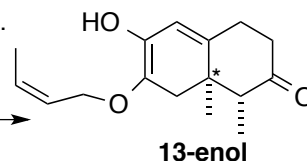


5. Rh carbenoid inserts in to O-H bond, then there is a 3,3 σ ropic rearrangement.

Here we have the enantiomer!

diastereoselectivity is not an issue therefore

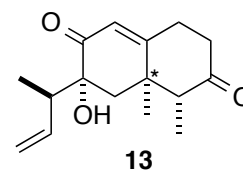
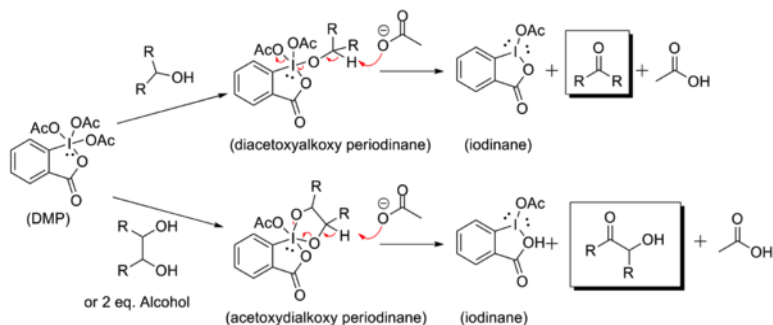
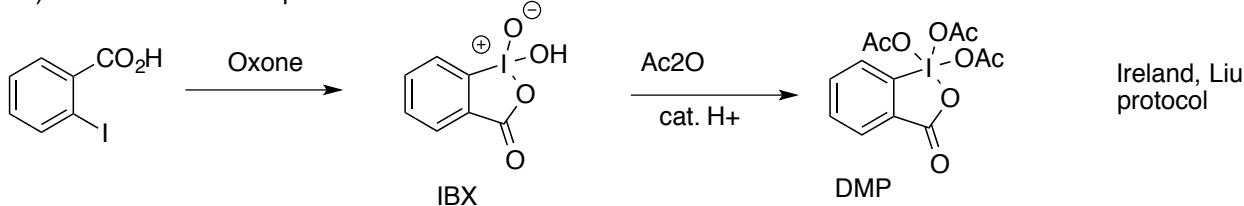
via:



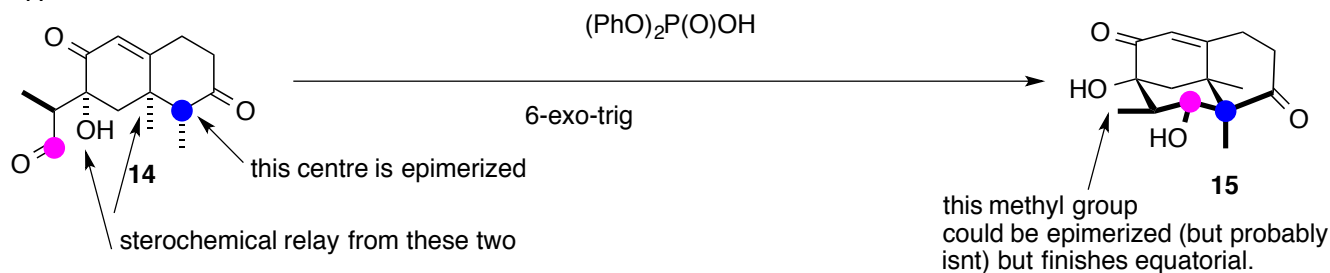
6. acylin rearrangement/ α -ketol rearrangement. Driving force is the migration that puts a double bond into conjugation with a carbonyl.

i) HF deprotects silyl protecting group on alcohol.

ii) DMP = Dess-Martin periodinane



7.



8.

LHMDS, PhSeCl; then NaIO₄