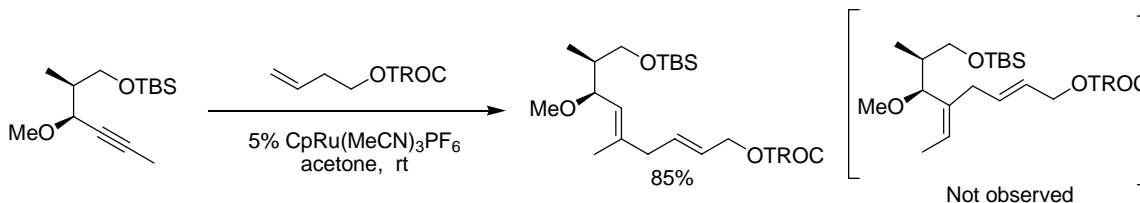
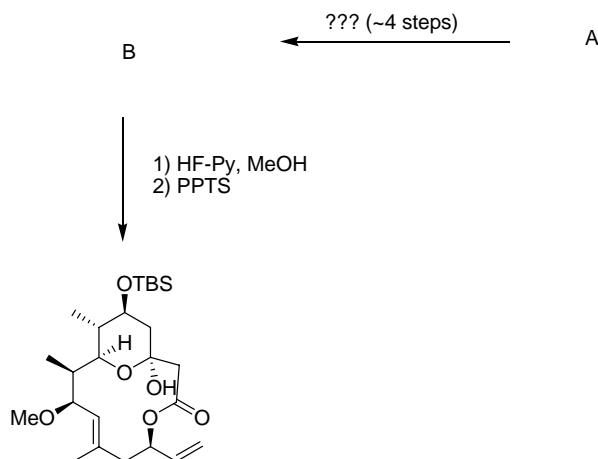
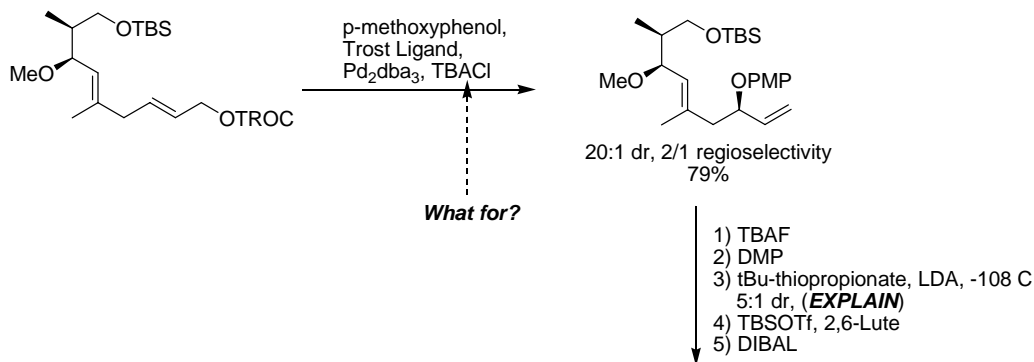


## And the Main Course... Janet's Callipelta Sponge, with a Side of Nauseating Shellfish

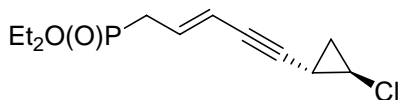
1) Regioselectivity in the alder-ene reaction is usually less than perfect. Not, however, when Janet is at the reins. Draw a catalytic cycle for the ruthenium catalyzed alder-ene reaction below, and account for the exceptional regioselectivity.



2) Remember that night that Dean made aflatoxin B lactone? Here is what Janet did that same night:



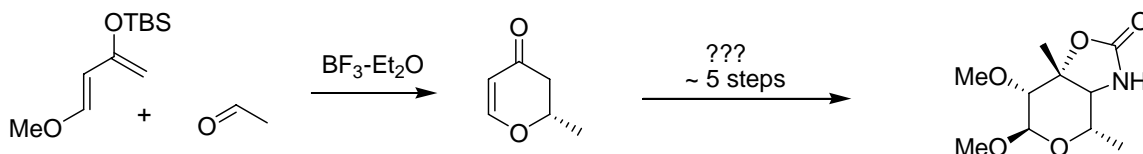
- 3) Propose an enantioselective synthesis of the Callipeltoside A side chain.



If you proposed an enantioselective Simmons-Smith reaction, don't.

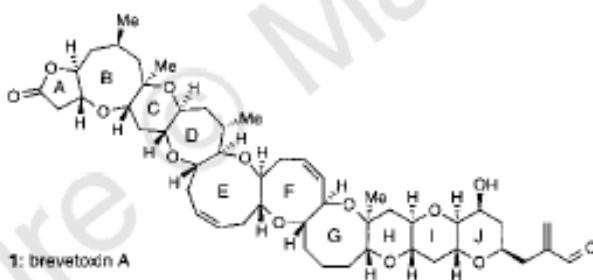
- 4) Janet and Co, referring to previously reported syntheses of callipeltose that utilize a chiral pool: "While this route proved productive... we sought a shorter route that might also provide easy access to either enantiomer."

4a) An asymmetric version of this exact hetero-Diels-Alder had been reported previously, therefore either enantiomer can easily be made. Janet accomplishes here the fastest synthesis of this sugar moiety yet. And those other schmucks started with sugars! How did she do it?



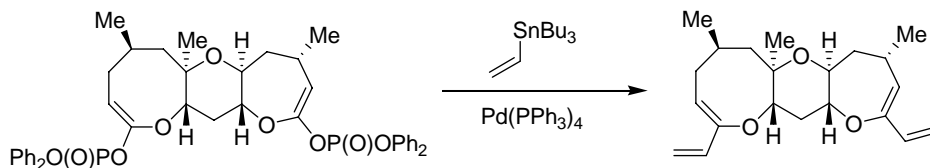
- 4b) This obviously doesn't apply here, but what would Dean say about 'access to both enantiomers' as a justification for racemic synthesis?

5) Propose a total synthesis of Brevotoxin A

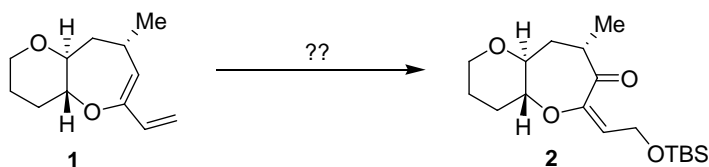


Ok not really.

The polycyclic ether framework of Brevotoxin A inspired a lot of innovation in the Nicolaou group. One of the most important methods developed (and used a number of times in the Brevotoxin A synthesis) was the use of ketene-acetal phosphates as coupling partners in cross coupling reactions. For example:



5a) Propose a way to convert **1** into **2**.



5b) Janet and friends come up with a new definition of pseudosymmetry: symmetry that is there only when you want it. Convert **3** into **4** using this beautiful concept.

