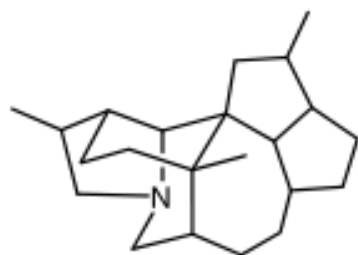
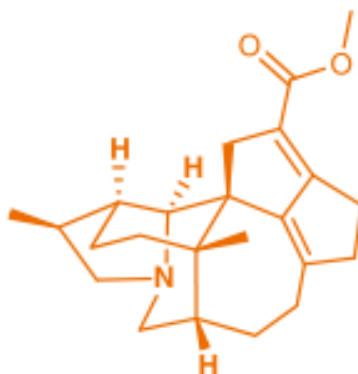


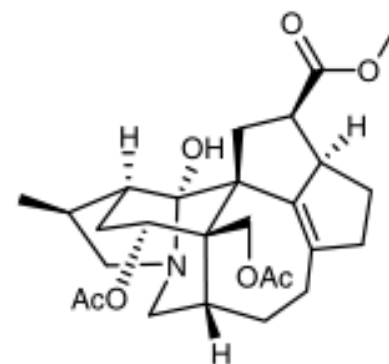
# Asymmetric Total Synthesis of Yuzurimine-type Daphniphyllum alkaloid (+)-Caldaphnidine J



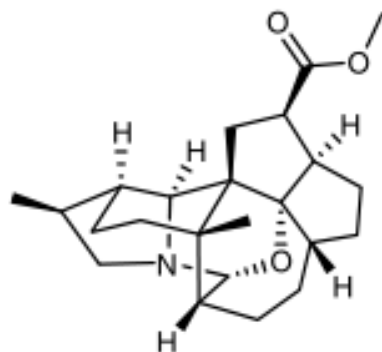
Common skeleton of  
Yuzurimine-type alkaloids



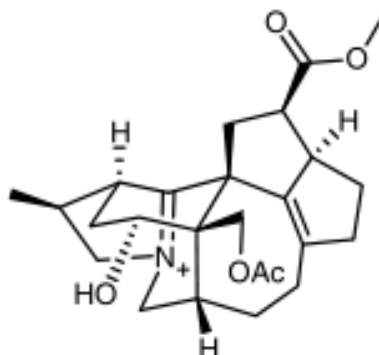
Caldaphnidine J



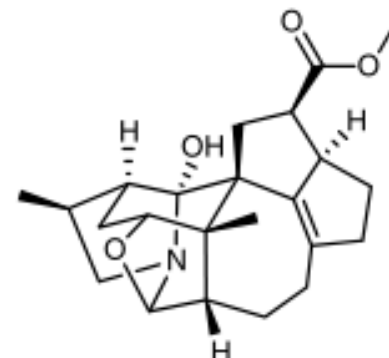
Yuzurimine



Daphcalycine

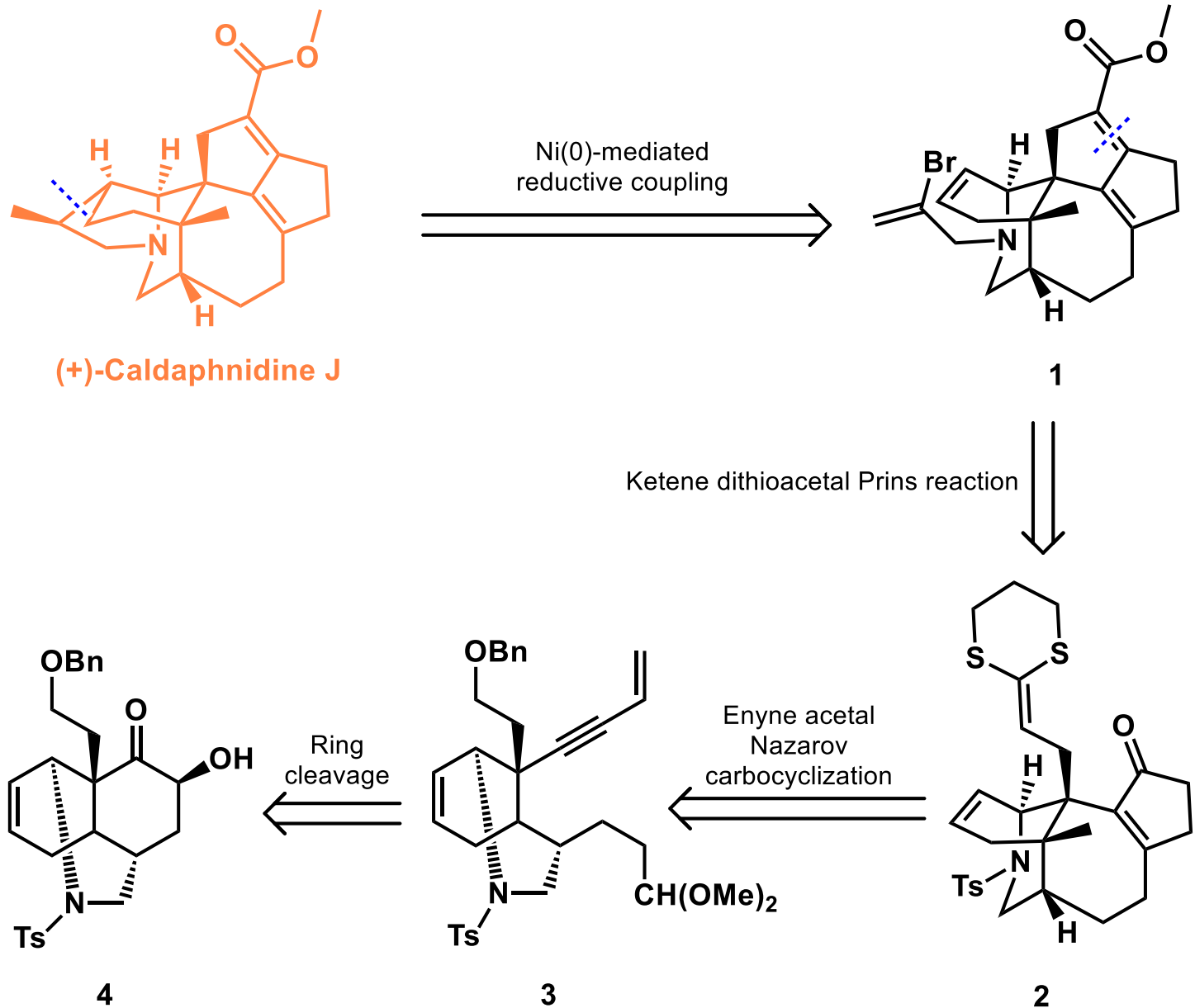


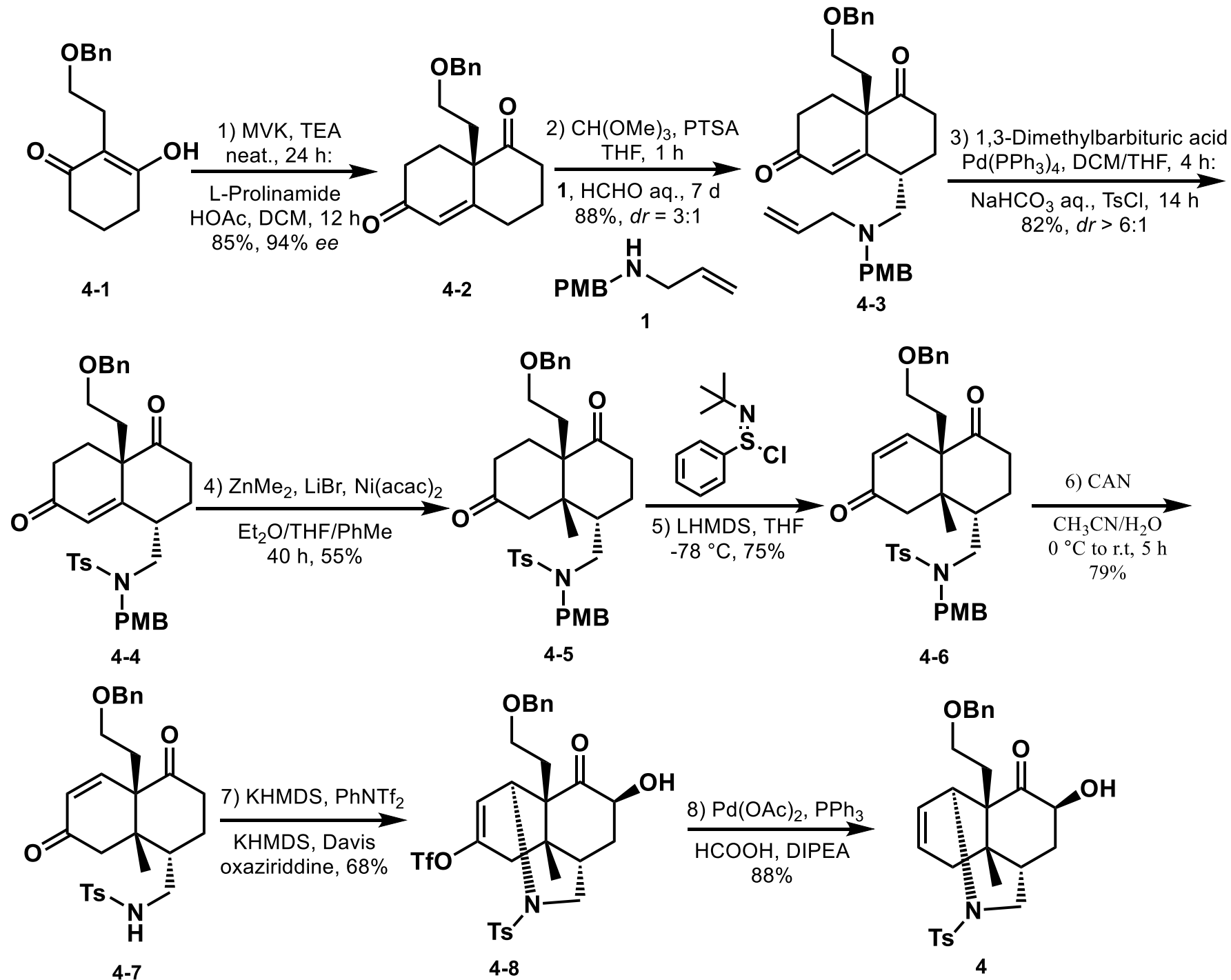
Daphnezomine J

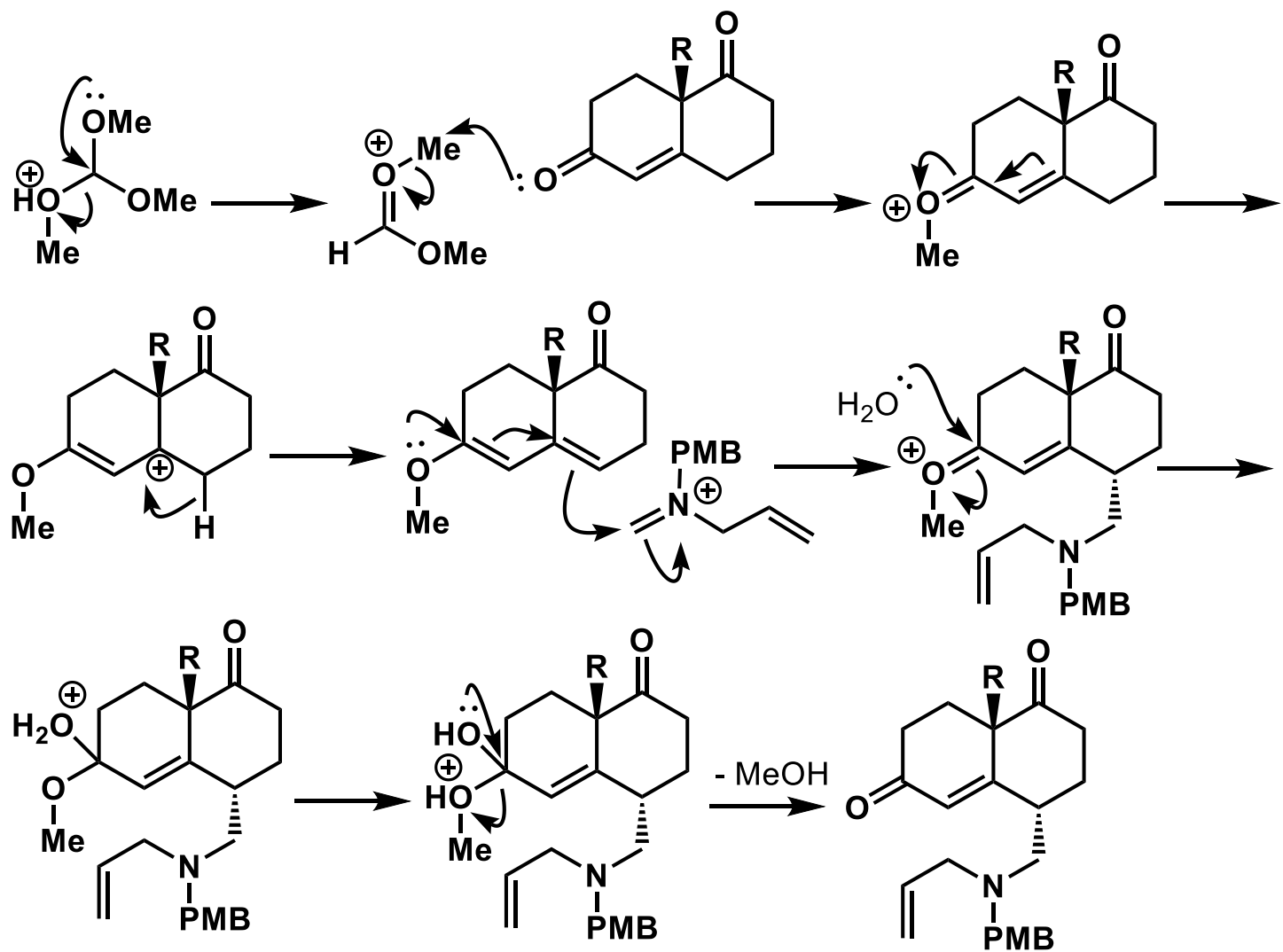


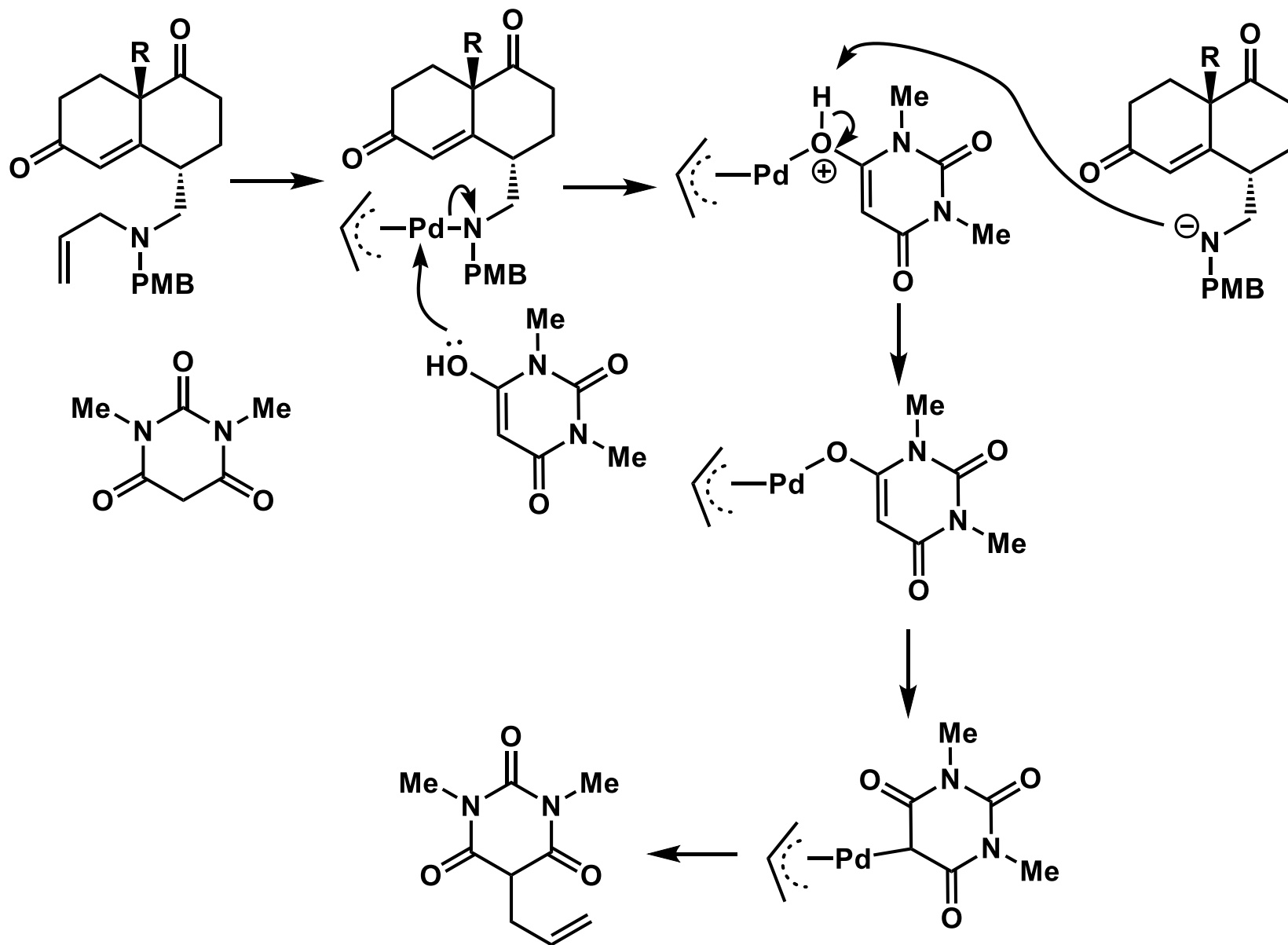
Yunnandaphnine E

# Retrosynthetic analysis of (+)-caldaphnidine J

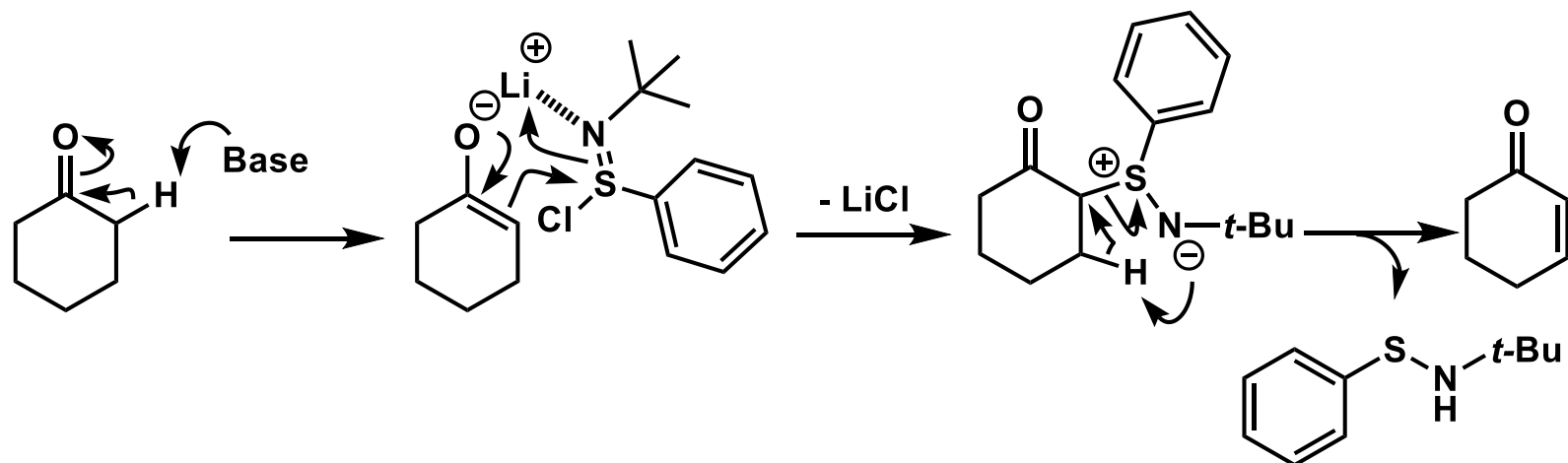






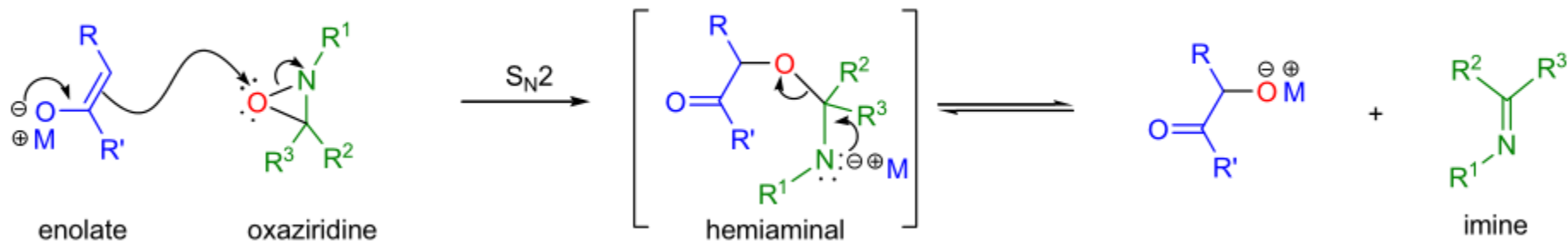


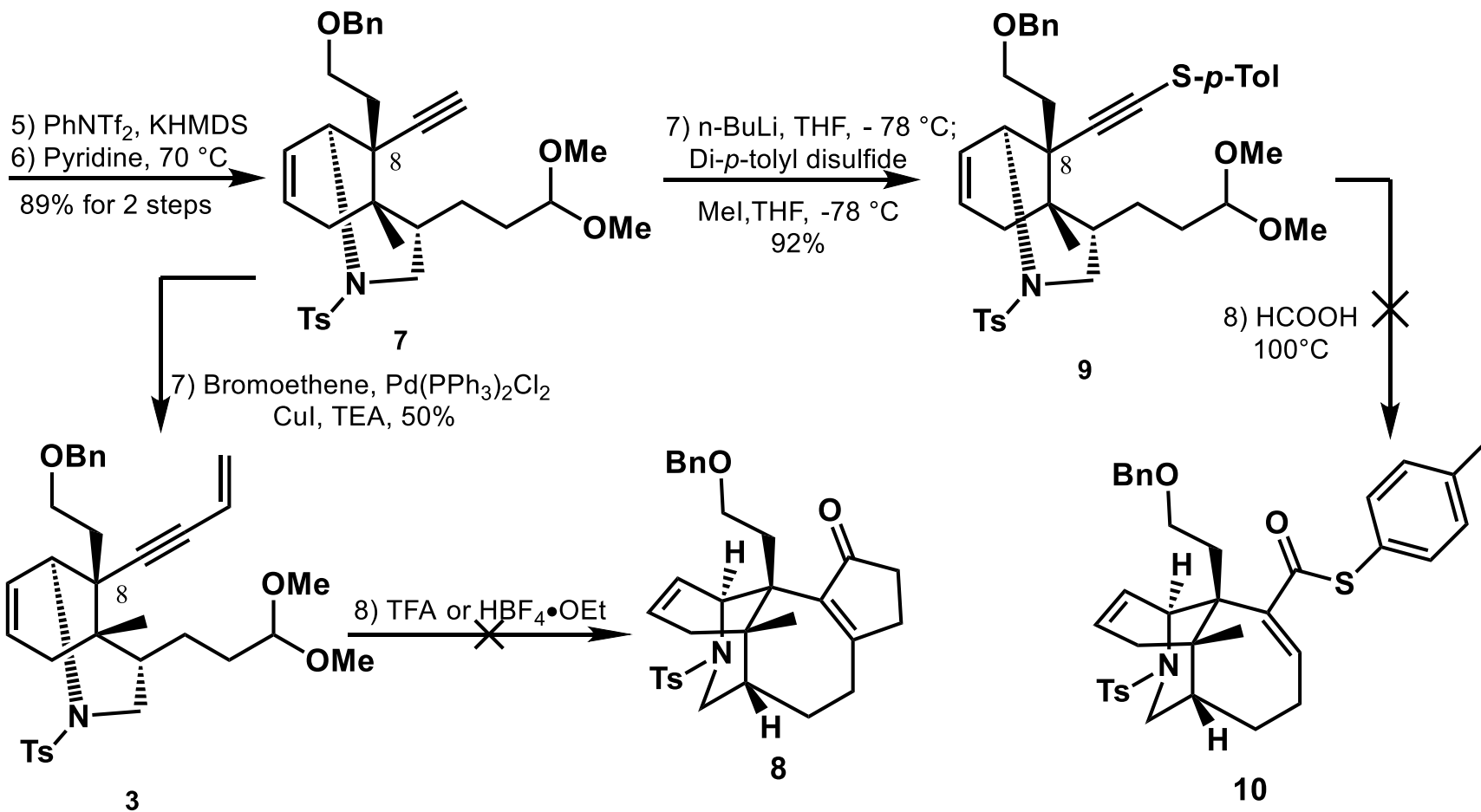
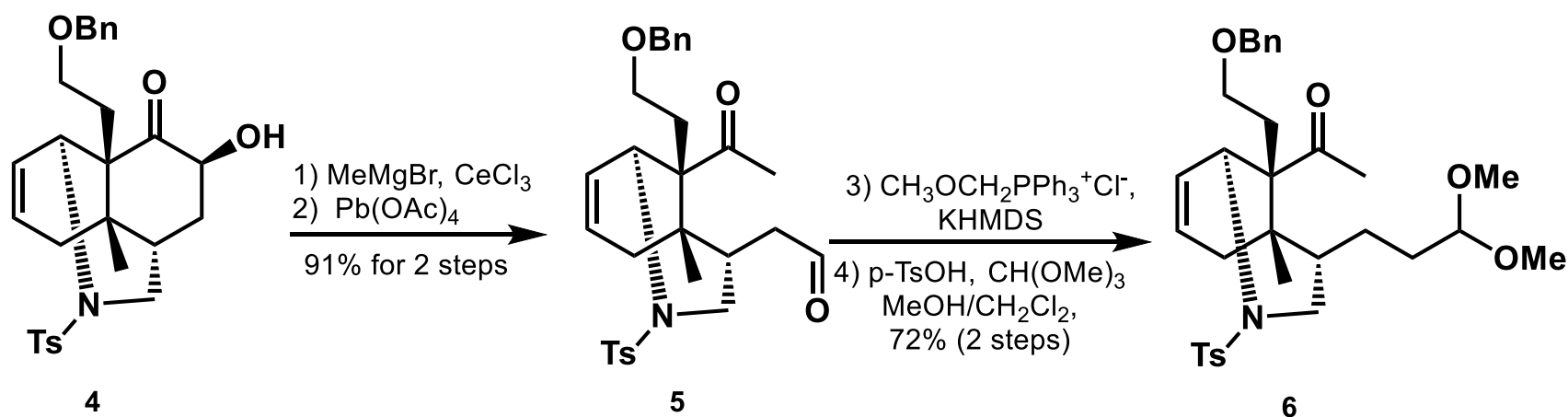
# Mukaiyama dehydrogenation

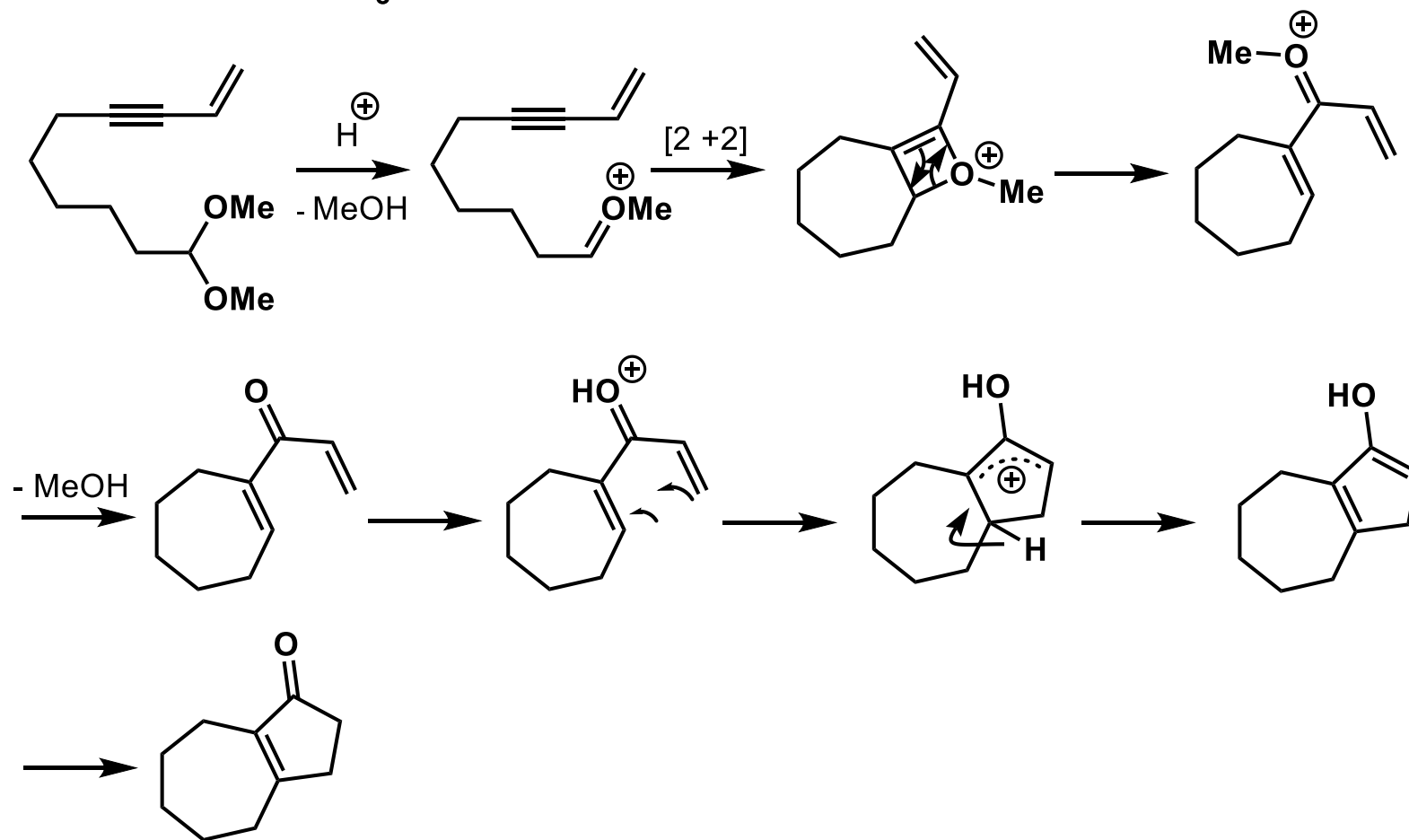
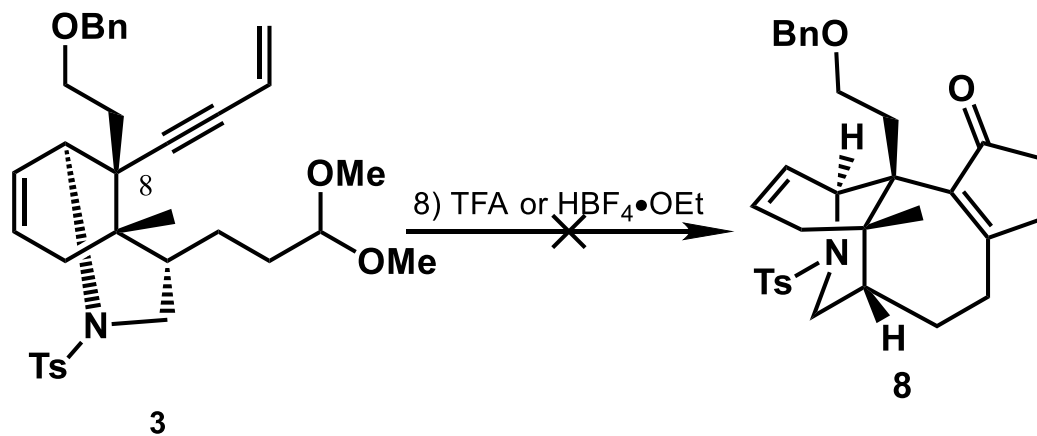


## DAVIS' OXAZIRIDINE OXIDATIONS

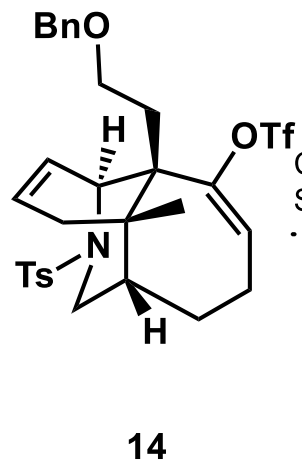
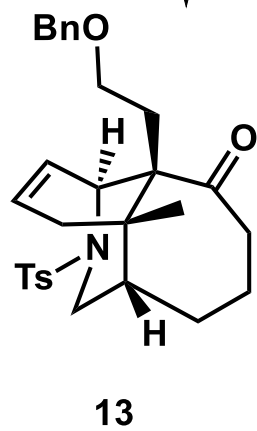
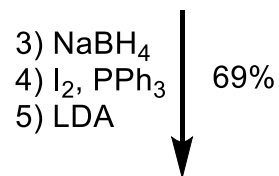
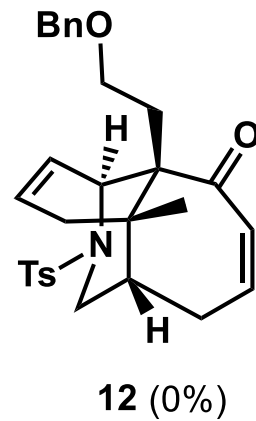
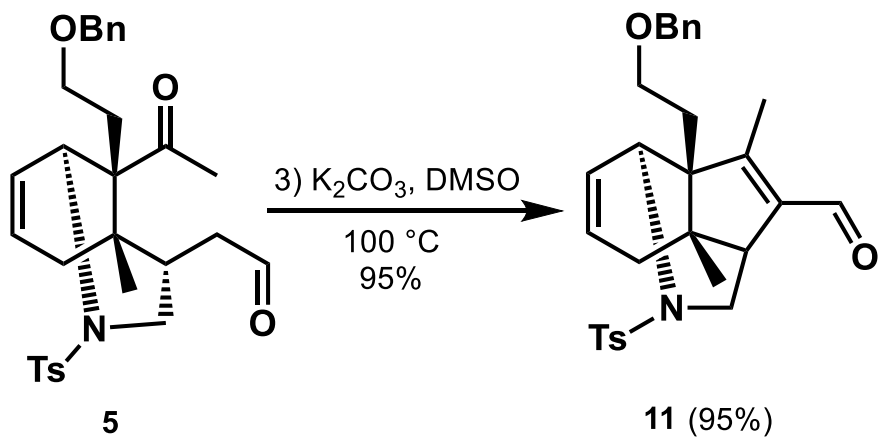
(References are on page 572)



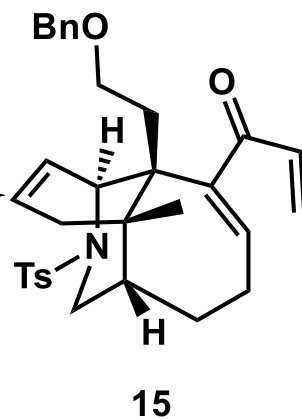




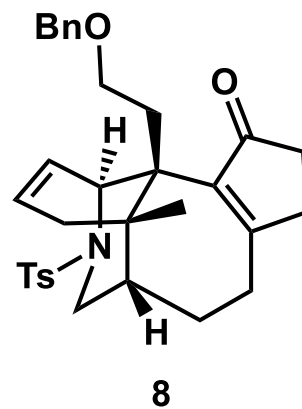


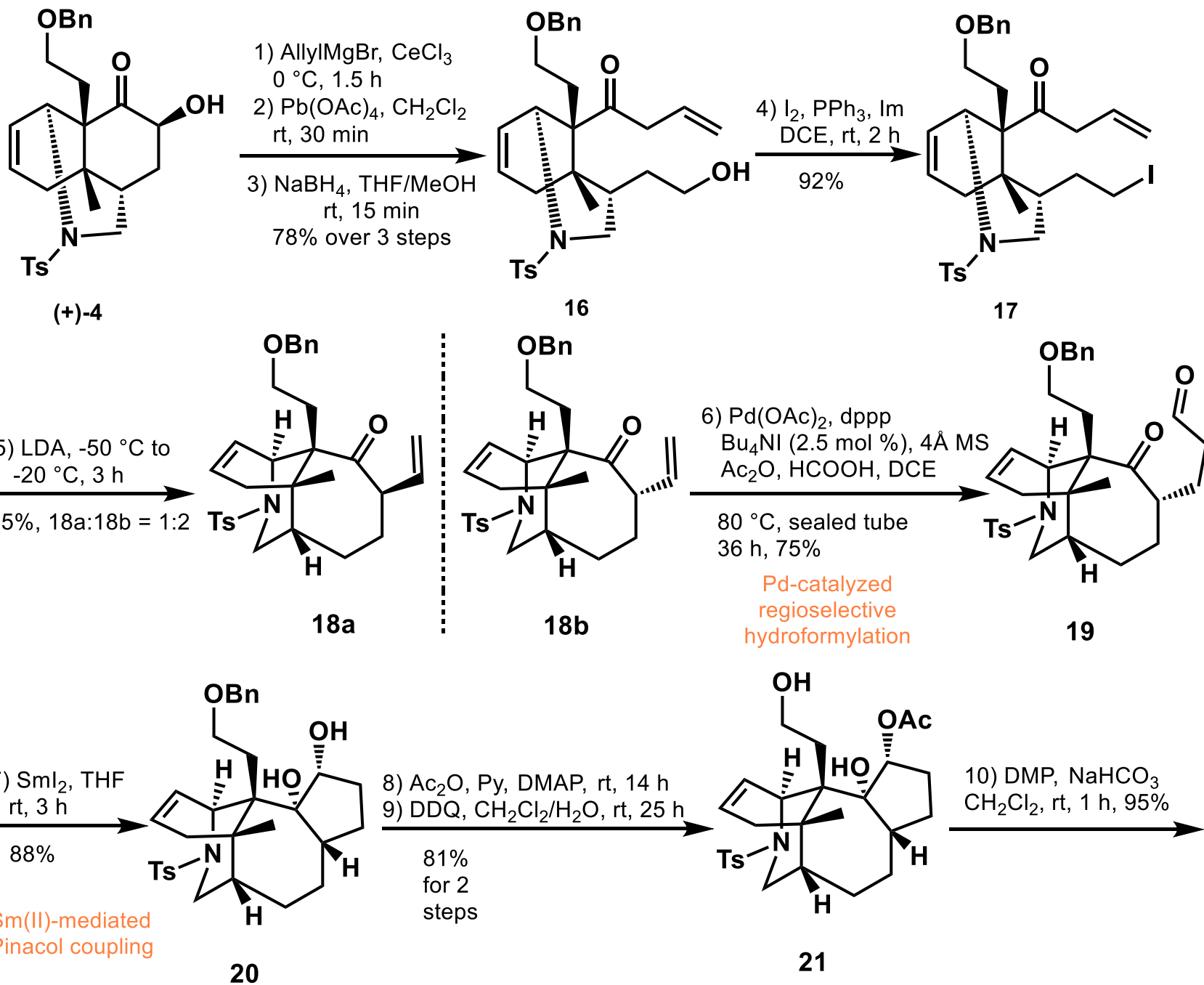


Carbonylative  
 Stille coupling

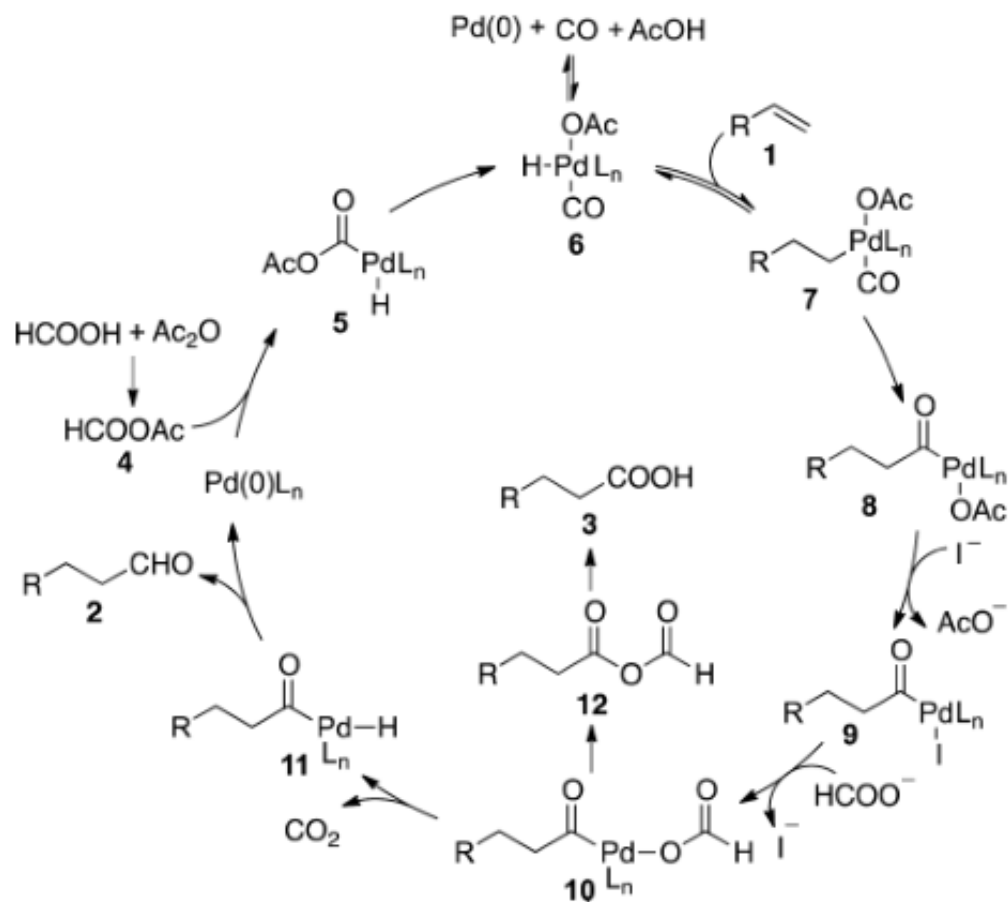


Nazarov

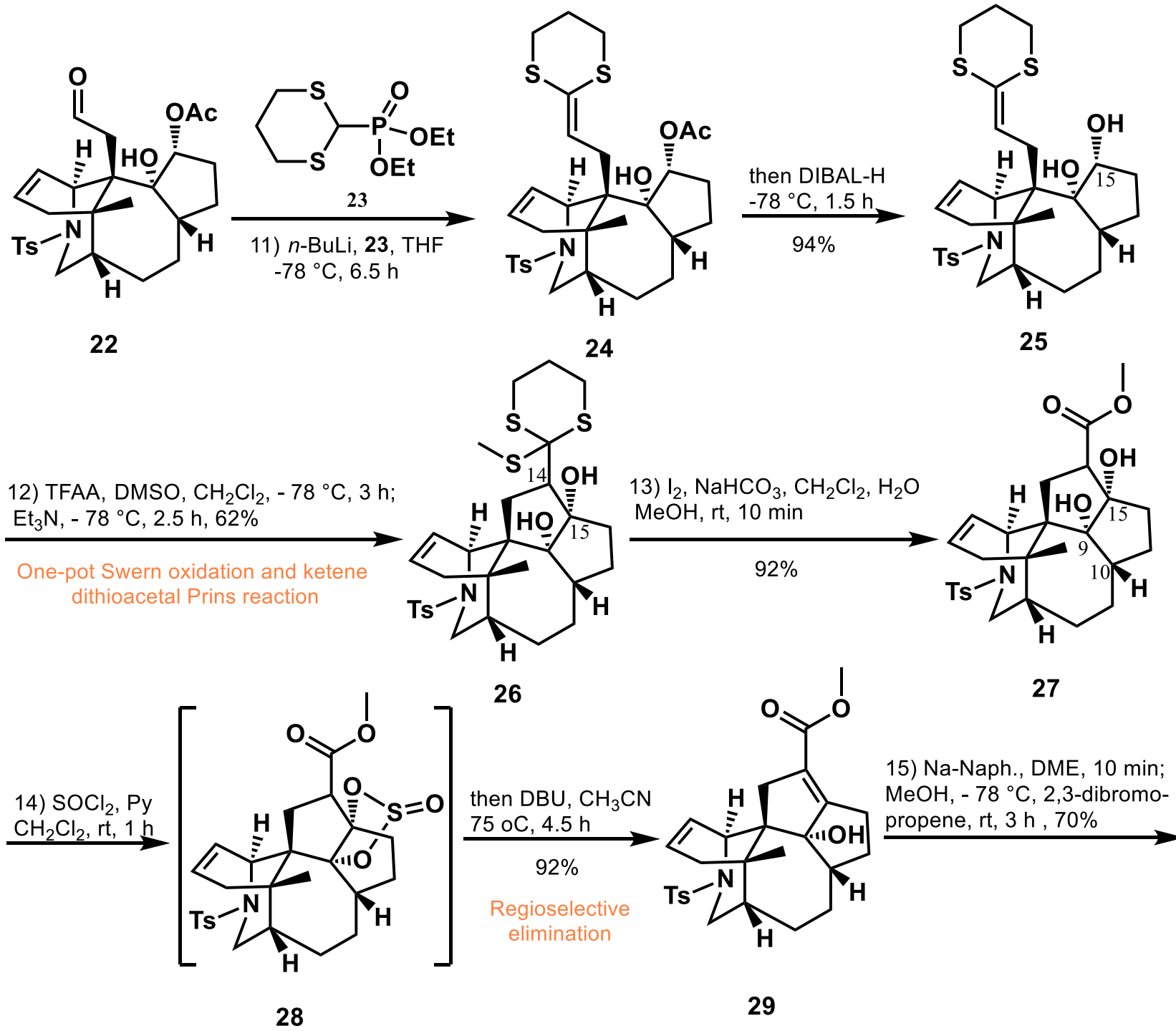


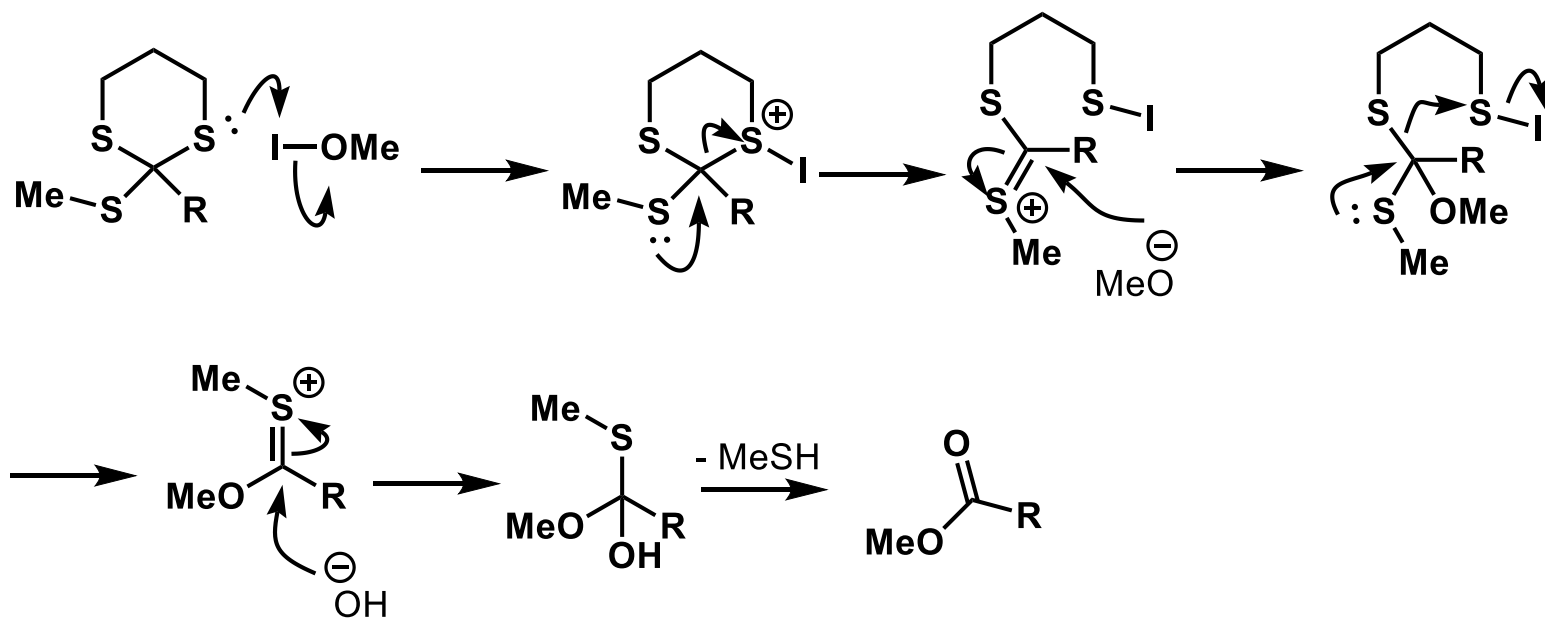


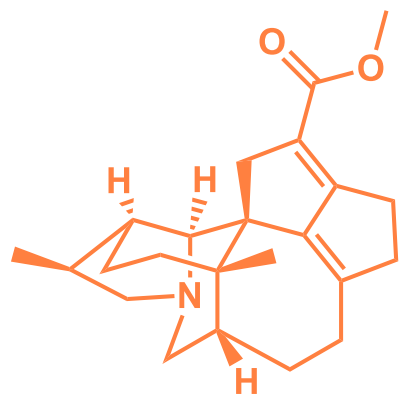
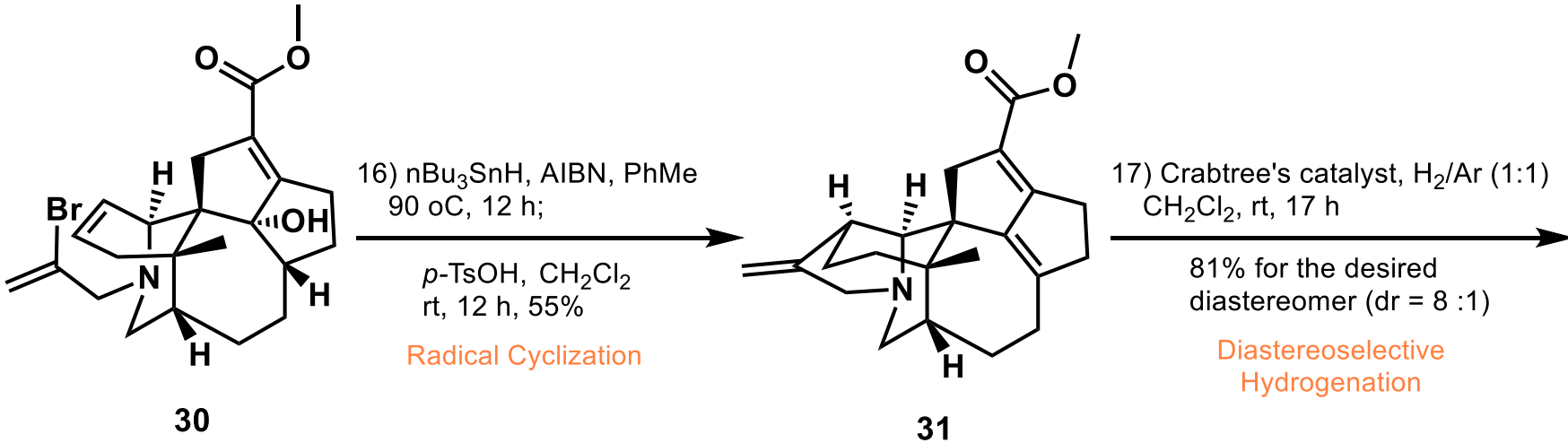
**Scheme 2. Proposed Catalytic Cycle for Regioselective Hydroformylation**



*J. Am. Chem. Soc.* 2016, **138**, 14864–14867







**(+)-Caldaphnidine J**

## The highlights of this synthesis:

- (1) A highly regioselective Pd-catalyzed hydroformylation reaction;
- (2) a Sm(II)-mediated pinacol coupling that produced a highly challenging 7/5 bicyclic system while all other attempts failed;
- (3) a one-pot Swern oxidation/ketene dithioacetal Prins reaction;
- (4) a regioselective elimination through a cyclic sulfite intermediate,
- (5) a radical cyclization reaction that rapidly constructed the tetrahydropyrrole motif.