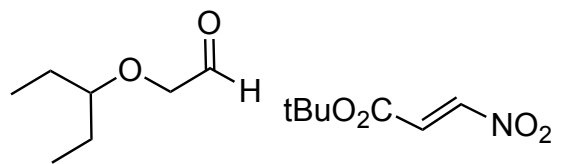


### Synthesis Challenge #8 AG Wegner

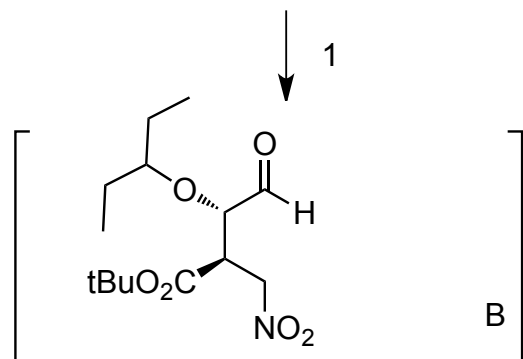
T. Mukaiyama, H. Ishikawa, H. Koshino, Y. Hayashi, *Chem. Eur. J.* **2013**, ASAP, DOI:

10.1002/chem.201302371

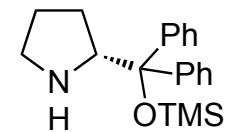
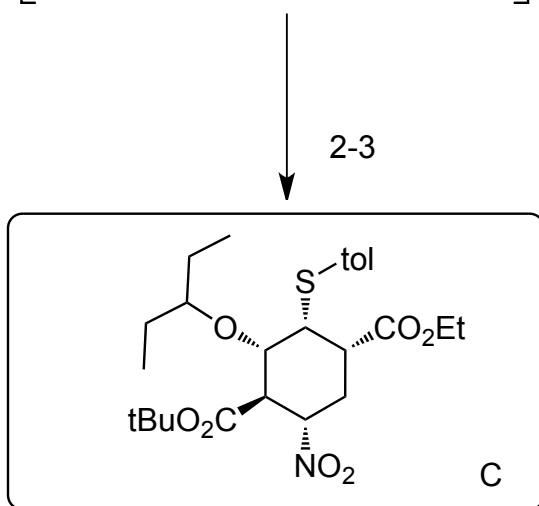
05.12.2013



1) **I** (1 mol%),  $\text{ClCH}_2\text{CO}_2\text{H}$  (20 mol%), Toluene

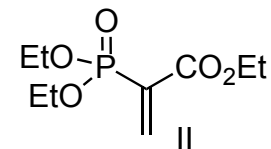


2) **II**,  $\text{CsCO}_3$   
3) TolSH

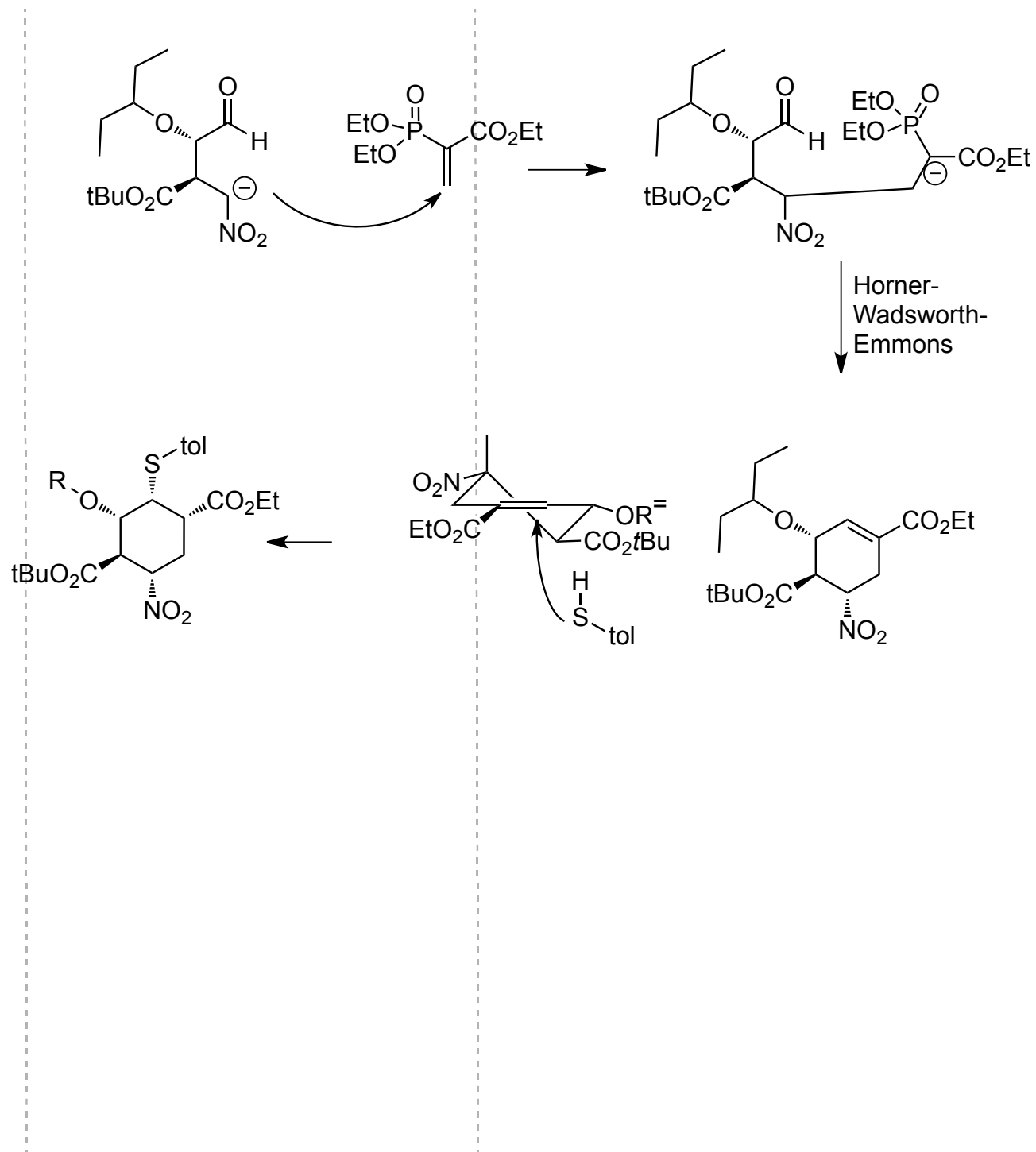


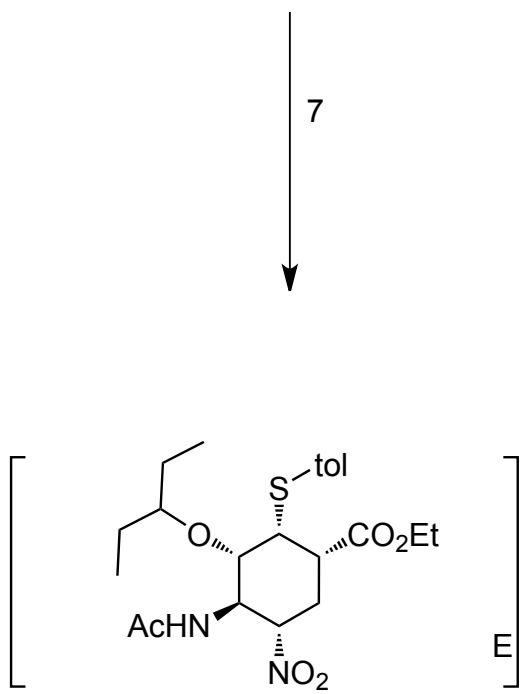
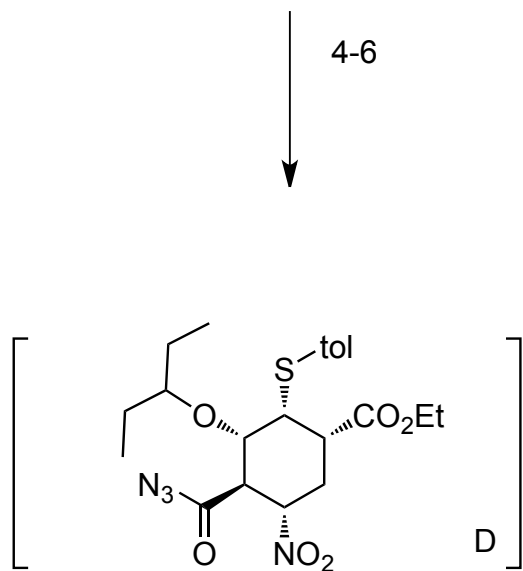
Please, provide a detailed mechanism for step 1).

Michael addition of enamine derived from catalyst **I** and the aldehyde and the nitroolefine.

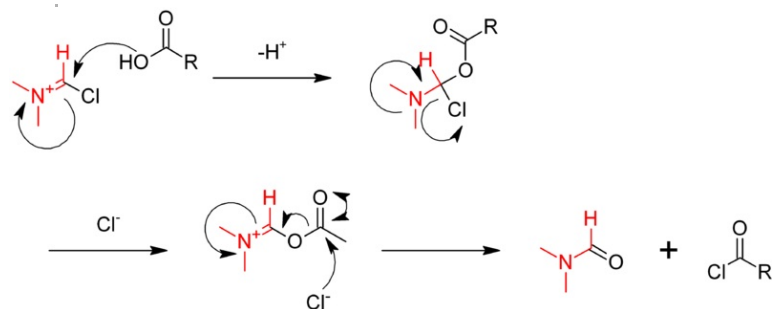
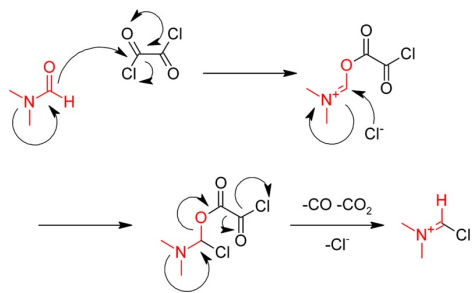


Please, provide a detailed mechanism for step 2) & 3).

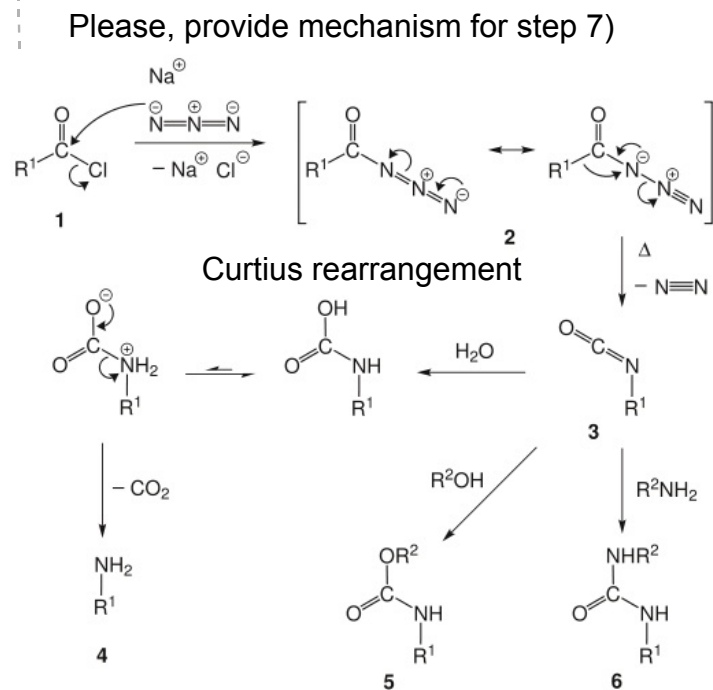




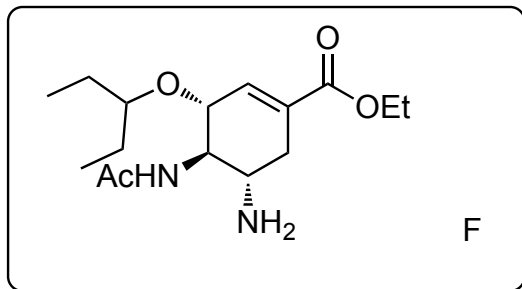
- 4) TFA, Toluene  
 5) (COCl)<sub>2</sub>, DMF (cat)  
 6) TMSN<sub>3</sub>, pyridine



- 7) AcOH, Ac<sub>2</sub>O



8-9



8) Zn, TMSCl, EtOH, 70°C, 2h;  
NH<sub>3</sub>, 0°C, 10 min  
9) K<sub>2</sub>CO<sub>3</sub>

Please, provide mechanism for step 9)

retro-Michael of toluenethiolgroup