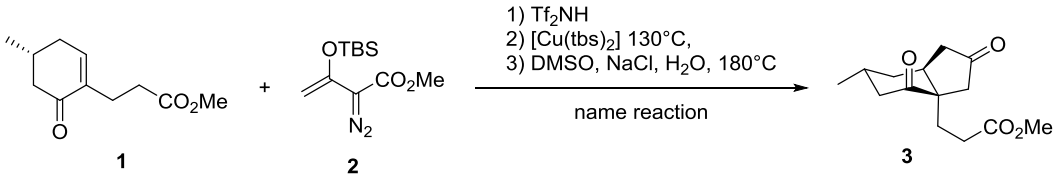
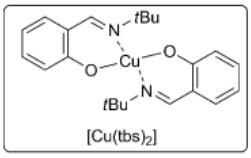
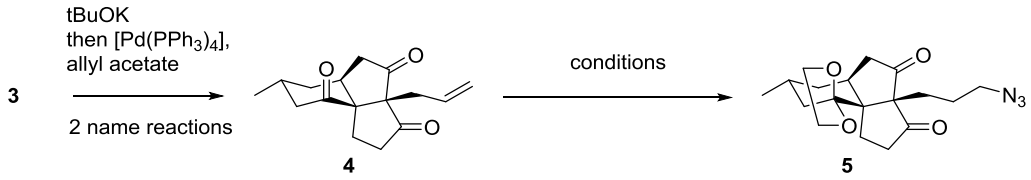
Problem Session **Submitted by Joséphine**

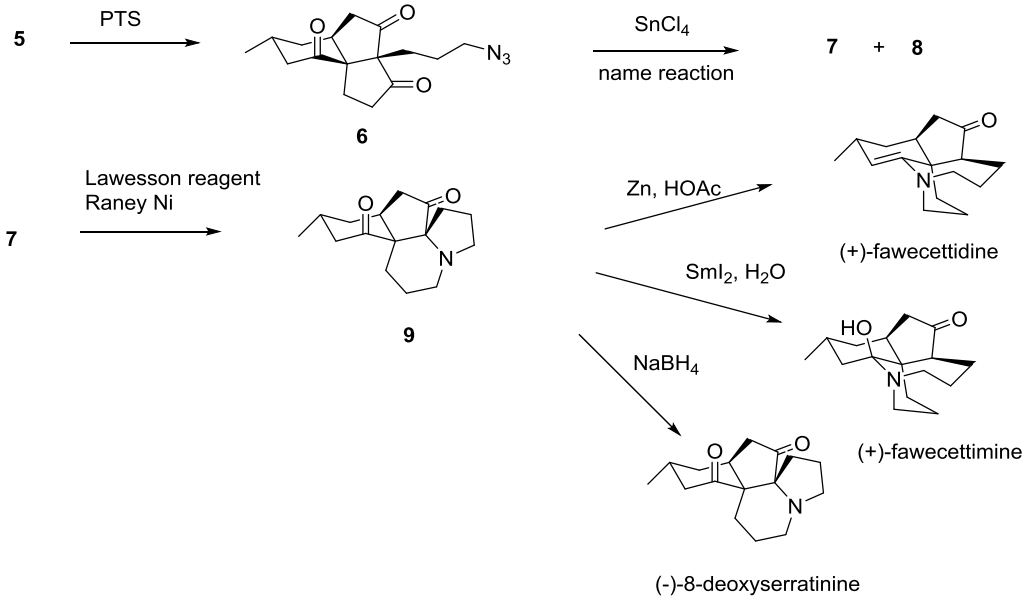
Synthesis of (+)-fawecettidine, (+)-fawecettimine and (-)-8-deoxyserratinine





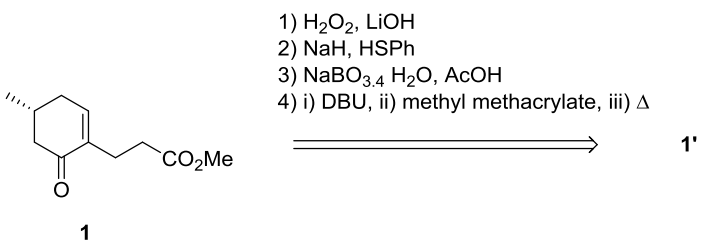


- Propose a mechanism for the formation of the cis-bicyclic dione **3** from **2** and **1** (2 pathways are possible!) and give the name reaction
- Give the 2 name reactions for the transformation of **4** from **3**
- Give the conditions for the preparations of **5** from **4**



- Give the 2 products **7** and **8** obtained from **6** and the name of the reaction
- Explain the mechanism of the formation of (+)-fawecettimine from **9**

Synthesis of starting material 1



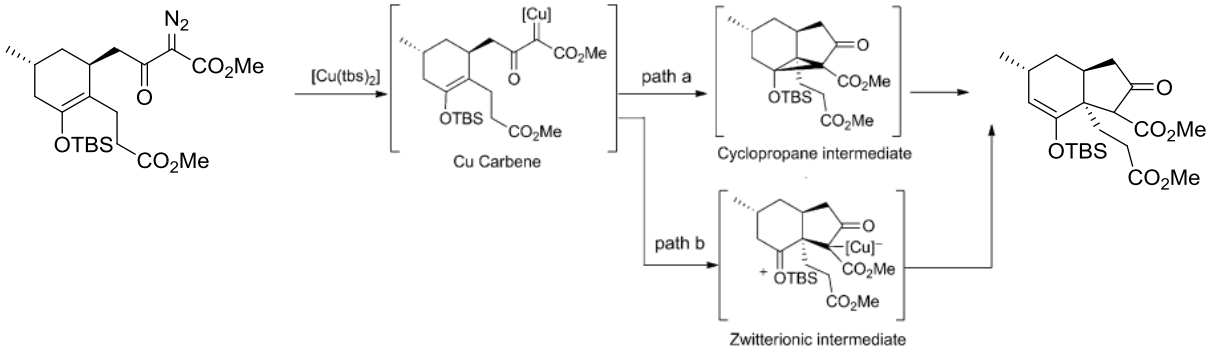
- What can be **1'** ?Give the mechanism for the synthesis of enone **1** from **1'**

Divergent and Efficient Syntheses of the *Lycopodium* Alkaloids (−)-Lycojaponicumin C, (−)-8-Deoxyserratinine, (+)-Fawcettimine, and (+)-Fawcettidine

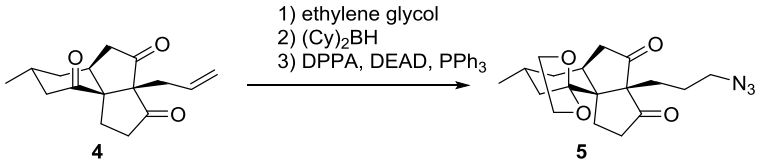
Tu et al. *Angew. Chem. Int. Ed.* **2013**, *52*, 11373 –11376

- Cis-bicyclic dione **3** from **2** and **1**:

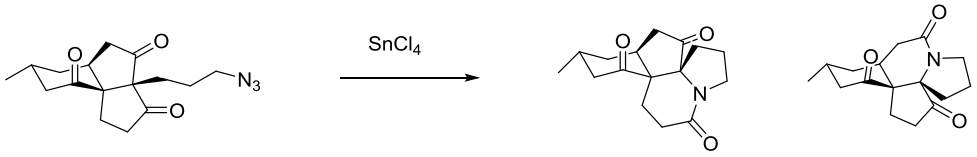
Mukaiyama– Michael addition from known enone and vinyl diazoacetate
carbene addition/cyclization
Proposed mechanism: Decomposition of diazo compound induced by [Cu(tbs)2] at 130°C to afford Cu carbene, which reacted with the enol silyl ether moiety to give the last intermediate via the cyclopropane intermediate or the zwitterionic intermediate



- **4** from **3 :** Dieckmann condensation / Tsuji-Trost allylation
- Conditions for formation of **5** (protection, hydroboration, Mitsunobu)



- 2 Products of the schmidt reaction cf Study of Aube on tether length and ring size (G. L. Milligan, C. J. Mossman, J. Aubé, *J. Am. Chem. Soc.* **1995**, *117*, 10449–10459)



6 membered ring favored over 7 mambered ring amide
Size of the ketone ring would not change selectivity (5 vs 6 memebere ring)

- Fragmentation with SmI_2 : Selective cleavage of the C-N bond of **9** with SmI_2 followed by a in situ aza-ketalization
  (T. Honda, *Heterocycles* 2011, **83**, 1–46)
- Starting material from (R)-(+)-Pulegone (J. A. Kozak, G. R. Dake, *Angew. Chem.* **2008**, *120*, 4289–4291)