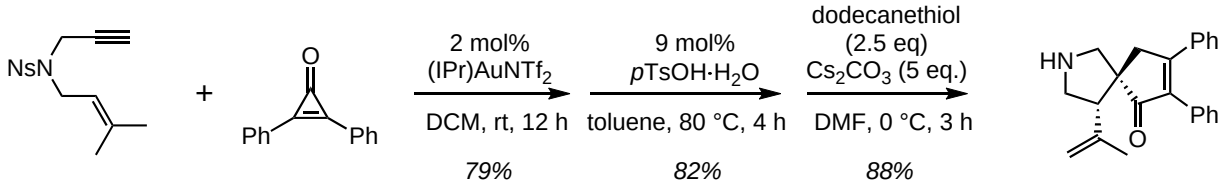
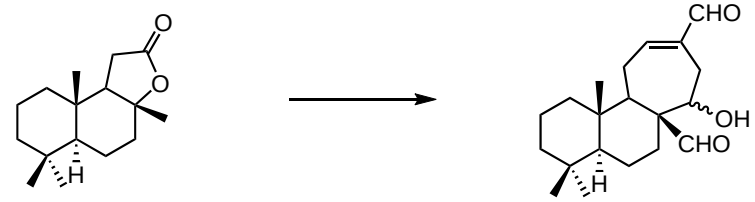
20140517

1. Propose reaction mechanisms for the following reactions.



T. Matsuda *et al. JOC* **2014**, *79*, 2739.

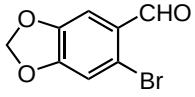
2. Propose a synthesis of galanal from (+)-sclareolide.



(+)-sclareolide

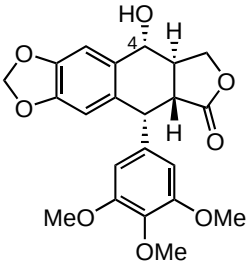
garanal A: α-OH
galanal B: β-OH

R.-J. Chein *et al. Org. Lett*. **2014**, ASAP.



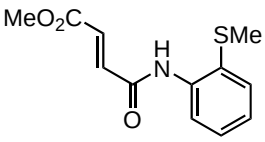
1) Me_3SI (2.7 eq.), $BnNEt_3Cl$ (4 mol%)
CH_2Cl_2/19M NaOH (1:1), 0 ºC to rt
2) *n*BuLi (1.2 eq.), Et_2O/THF (10:3), –78 ºC
then $MgBr_2$ (2 eq.), –78 to 0 ºC, >50% (2 steps)

3) **A** (0.5 eq.), KHMDS (2.2 eq.), THF, –78 to 0 ºC
then $LiEt_3BH$ (4 eq.), –78ºC
4) *p*TsOH (10 mol%)
2,2-dimethoxypropane/THF (2:1), 41% (2 steps)
5) $Pd(OAc)_2$ (15 mol%), **B** (2 eq.), K_2CO_3 (1.5 eq.)
$(BnO)_2P(O)OH$ (0.4 eq.), *t*AmylOH, 58%
6) TFA/THF/H_2O (1:1:1), 43% (4-epimer 33%)

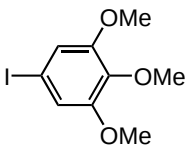


Podophyllotoxin

A:



B:



Ting, C. P.; Maimone, T. J. *Angew. Chem. Int. Ed.* **2014***, 53*, 3115.