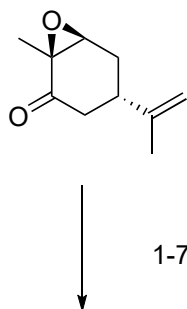
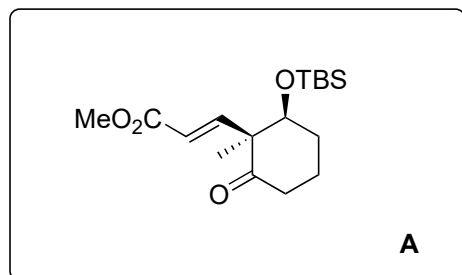


A Convergent Approach to Phragmalin-Type Limonoids: Total Synthesis of Thagraanatin P

Jaehoo Lee, Spencer C. Davis, Amber Sheu, Jacqueline W. Gu, and Timothy R. Newhouse

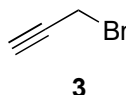
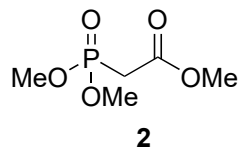
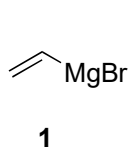


1-7

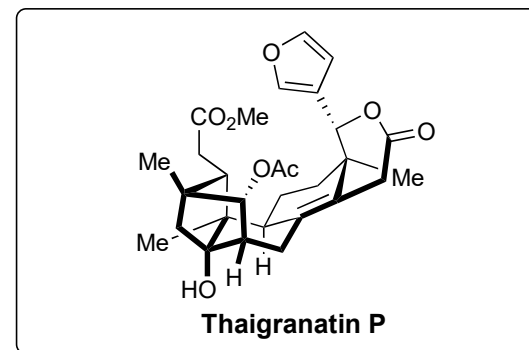


8-17

- 1) O_3 , MeOH, *then* PhSH, $FeSO_4 \cdot 7H_2O$
- 2) $TsNHNH_2$
- 3) **1**, THF, $-78^\circ C$
- 4) TBSOTf, 2,6-lutidine
- 5) $CuCl_2$ (cat.), hydroxyacetone, benzene
- 6) OsO_4 , NMO, $NaIO_4$
- 7) **2**, NaHMDS



- 8) KHMDS, $ZnCl_2$, *then* CH_2O
- 9) **3**, Al, $HgCl_2$
- 10) Bu_3SnH , AIBN, *then* PPTS
- 11) $(COCl)_2$, DMSO, Et_3N
- 12) Sml_2 , MeOH, HMPA, THF, reflux
- 13) DMP
- 14) $LiBH_4$
- 15) TFA, *then* TMSCl, imidazole, *then* DMP
- 16) $CH_2=PPh_3$ (salt-free)
- 17) Ac_2O , pyridine

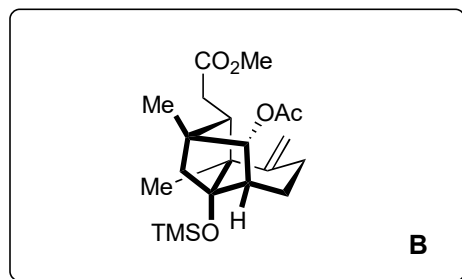


10) Provide a mechanism. What PPTS is needed for?

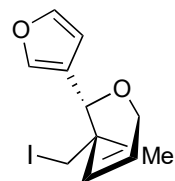
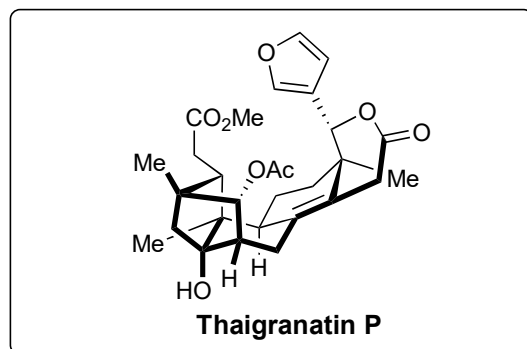
Starts with an attack of tin radical to alkyne followed by 1,4-attack of newly formed radical onto Michael system

12) From now on draw as natural product

15) 2 TMS protected and 1 free alcohol



18-22



18) SeO_2 , H_2O , DCE, 60°C

19) **4**, $t\text{-BuLi}$, $\text{CuI-Me}_2\text{S}$, *then* Comins' reagent

20) CrO_3 , 3,5-DMP

21) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, Et_3N , DMF, 100°C ,
then 1M HCl

22) Sml_2 , PhSH, HMPA, THF, reflux

21) What is the name of the reaction?

Intramolecular Heck

Hint: tertiary alcohol deprotection at this step