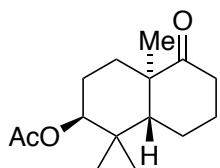
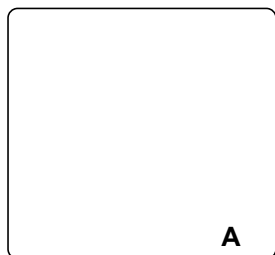


Total Syntheses of Highly Oxidized ent-Kaurenoid Pharicin A, Pharicin B, 7-O-Acetylpseurata C, and Pseurata C: A [5+2] Cascade Approach

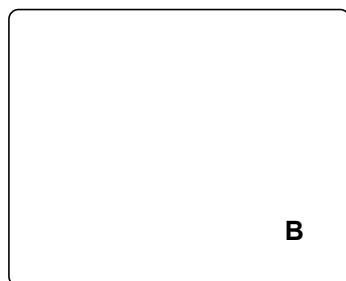
Chi He, Jialei Hu, Yubing Wu, Hanfeng Ding
J. Am. Chem. Soc., **2017**, *139*, 6098–6101.



1-4

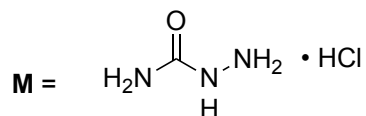


5-7

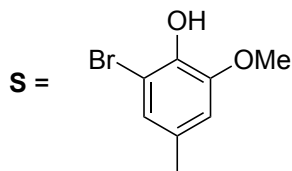


8-12

- 1) IBX, DMSO/toluene, 85 °C
- 2) H₂O₂, NaOH, MeOH, 0 °C
- 3) **M**, NaOAc, EtOH, H₂O, 30 °C
- 4) Pb(OAc)₄, CH₂Cl₂, 0 °C



- 5) Pd/CaCO₃, H₂, silica gel, hexane
- 6) **S** (1.3 equiv), *n*-BuLi (2.5 equiv), THF, -78 °C, then substrate
- 7) K₂CO₃, PhI(CF₃CO₂)₂, HFIP, 0 °C



- 8) DMP, NaHCO₃, CH₂Cl₂, 0 °C
- 9) NaBH₄ (4 equiv), MeOH, RT
- 10) Ac₂O (1.5 equiv), Et₃N, DMAP, RT
- 11) NaHCO₃, TBACl, TEMPO, NCS, CH₂Cl₂, 30 °C
- 12) *p*-TsOH, CH₂Cl₂, 30 °C

Step 3/4: Propose a mechanism for this two step procedure and name the heterocycles!

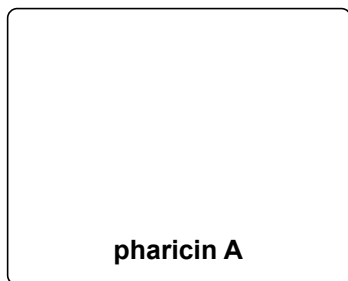
Step 7: It's a cascade of two reactions.

Hint: Steps 11 till 13 serve a single purpose.



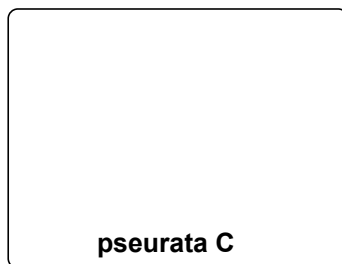
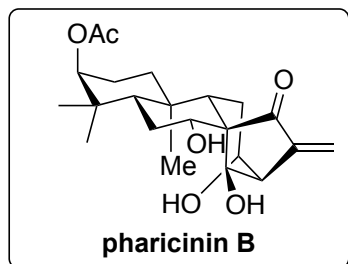
13-15

13) L-Selectride, THF, -78 °C
14) O₂, methylene blue, hv, CH₃CN, 0 °C
15) TCCA, CH₂Cl₂, RT



16a) LiOH
THF/H₂O, RT

16b) PhI(OAc)₂, TEMPO, CH₂Cl₂, RT*
17b) Me₃SnOH, (CH₂Cl)₂, 85 °C



Step 14/15: Propose a mechanism for these steps

* The product is called 7-O-acetylpseurata C