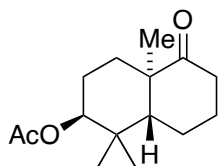
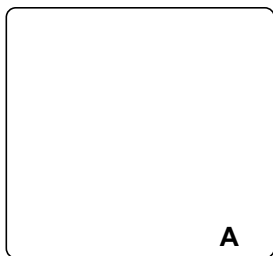


# Total Syntheses of Highly Oxidized ent-Kaurenoid Pharicin A, Pharicin B, 7-O-Acetylpseurata C, and Pseurata C: A [5+2] Cascade Approach

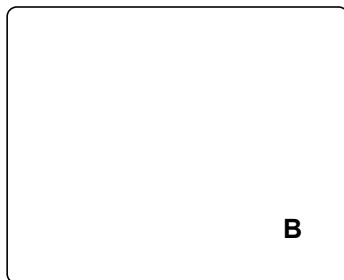
Chi He, Jialei Hu, Yubing Wu, Hanfeng Ding  
*J. Am. Chem. Soc.*, **2017**, *139*, 6098–6101.



1-4

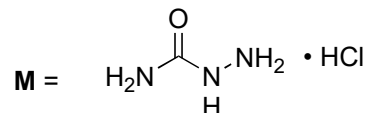


5-7

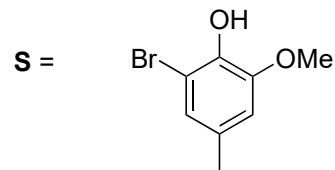


8-12

- 1) IBX, DMSO/toluene, 85 °C
- 2) H<sub>2</sub>O<sub>2</sub>, NaOH, MeOH, 0 °C
- 3) **M**, NaOAc, EtOH, H<sub>2</sub>O, 30 °C
- 4) Pb(OAc)<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C



- 5) Pd/CaCO<sub>3</sub>, H<sub>2</sub>, silica gel, hexane
- 6) **S** (1.3 equiv), *n*-BuLi (2.5 equiv), THF, -78 °C
- 7) K<sub>2</sub>CO<sub>3</sub>, PhI(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, HFIP, 0 °C



- 8) DMP, NaHCO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C
- 9) NaBH<sub>4</sub> (4 equiv), MeOH, RT
- 10) Ac<sub>2</sub>O (1.5 equiv), Et<sub>3</sub>N, DMAP, RT
- 11) NaHCO<sub>3</sub>, TBACl, TEMPO, NCS, CH<sub>2</sub>Cl<sub>2</sub>, 30 °C
- 12) *p*-TsOH, CH<sub>2</sub>Cl<sub>2</sub>, 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.

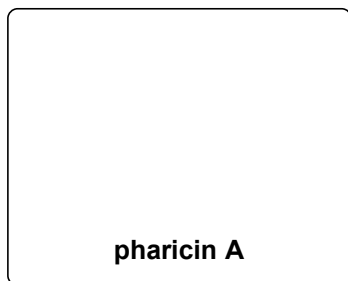
Hint: Steps 11 till 14 serve a single purpose.



13-15

13) L-Selectride, THF,  $-78\text{ }^{\circ}\text{C}$   
14)  $\text{O}_2$ , methylene blue,  $\text{CH}_3\text{CN}$ ,  $0\text{ }^{\circ}\text{C}$   
15) TCCA,  $\text{CH}_2\text{Cl}_2$ , RT

Step 14/15: Propose a mechanism for these steps



16a) LiOH  
THF/ $\text{H}_2\text{O}$ , RT

16b)  $\text{PhI}(\text{OAc})_2$ , TEMPO,  $\text{CH}_2\text{Cl}_2$ , RT\*  
17b)  $\text{Me}_3\text{SnOH}$ ,  $(\text{CH}_2\text{Cl})_2$ ,  $85\text{ }^{\circ}\text{C}$

\* The product is called 7-O-acetylpsaurata C

