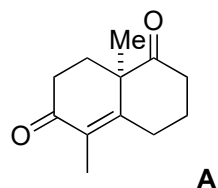
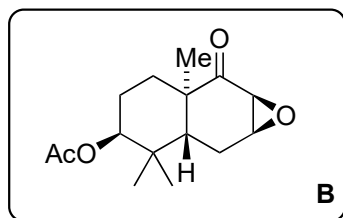


# Total Syntheses of Highly Oxidized *ent*-Kaurenoids Pharicin A, Pharicinin B, 7-*O*-Acetylpsaurata C, and Psaurata C: A [5+2] Cascade Approach

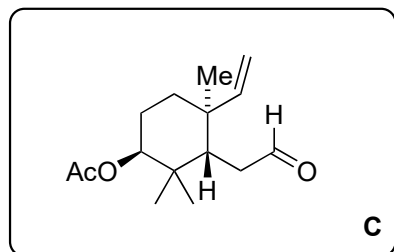
C. He, J. Hu, Y. Wu, H. Ding, *J. Am. Chem. Soc.* **2017**, *139*, 6098



1-6

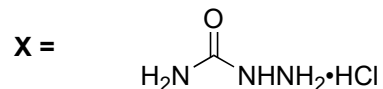


7-9

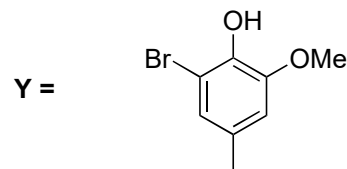


10-13

- 1) ethylene glycol, *p*-TSA·H<sub>2</sub>O, PhH, 80 °C
- 2) Li, NH<sub>3</sub>, MeI, -78 to 45 °C
- 3) L-selectride *then* HCl
- 4) Ac<sub>2</sub>O, Et<sub>3</sub>N, DMAP
- 5) IBX, DMSO, PhH, 85 °C
- 6) H<sub>2</sub>O<sub>2</sub>, NaOH, 0 °C



- 7) **X**, NaOAc
- 8) Pb(OAc)<sub>4</sub>
- 9) H<sub>2</sub>, SiO<sub>2</sub>, Lindlar cat.



- 10) **Y**, *n*-BuLi
- 11) PDC, SiO<sub>2</sub>
- 12) NaBH<sub>4</sub>
- 13) PhI(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, HFIP, 0 °C

Name of Reaction in **Step 6**.

Scheffer–Weitz epoxidation

Please provide the name and mechanism of the reaction effected during **Step 7, 8**.

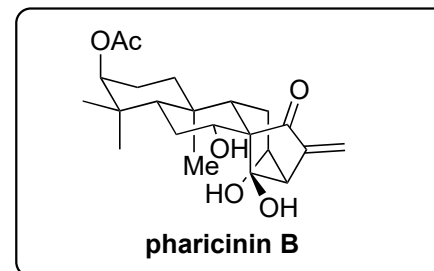
**Hint:** Standard conditions use *p*-toluenesulfonylhydrazide instead of **X** and Pb(OAc)<sub>4</sub>.

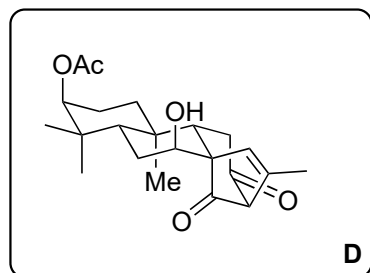
Eschenmoser–Tanabe fragmentation

**Key Step.** Please provide the mechanism of **Step 13**.

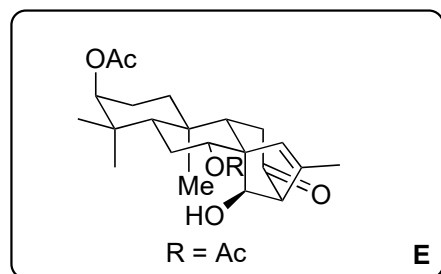
**Hint:** After formation of an initial intermediate a migration takes place. Please classify the migration.

Pinacol-type 1,2-acyl migration

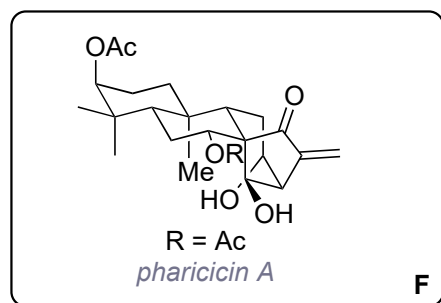




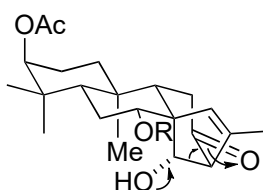
14–18



19, 20



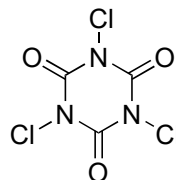
Retro-Aldol/Aldol



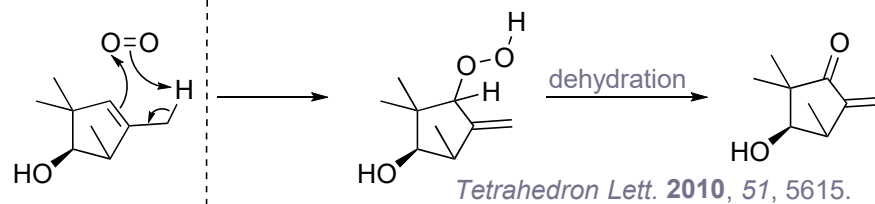
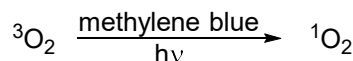
R = Ac

- 14) DMP, NaHCO<sub>3</sub>
- 15) NaBH<sub>4</sub>
- 16) Ac<sub>2</sub>O, DMAP
- 17) NCS, TBACl, TEMPO
- 18) cat. *p*-TSA·H<sub>2</sub>O

TCCA =

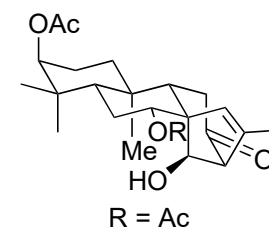
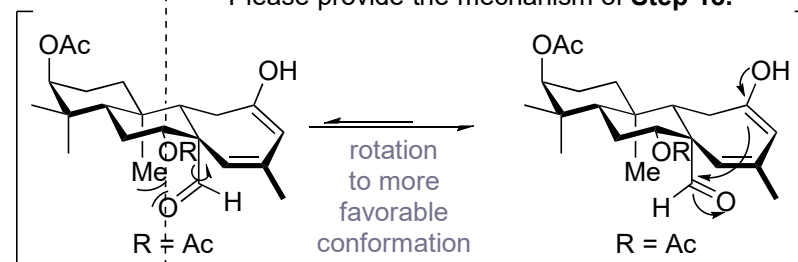


- 19) L-selectride
- 20) methylene blue, O<sub>2</sub>, hν, MeCN *then* TCCA



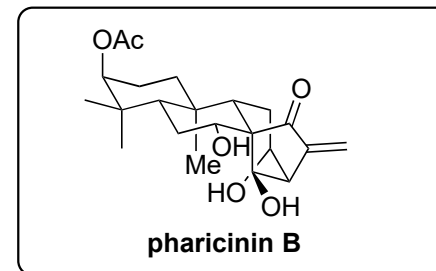
*Angew. Chem., Int. Ed.* **1996**, *35*, 477.

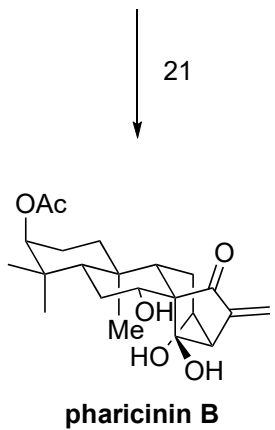
Please provide the mechanism of **Step 18**.



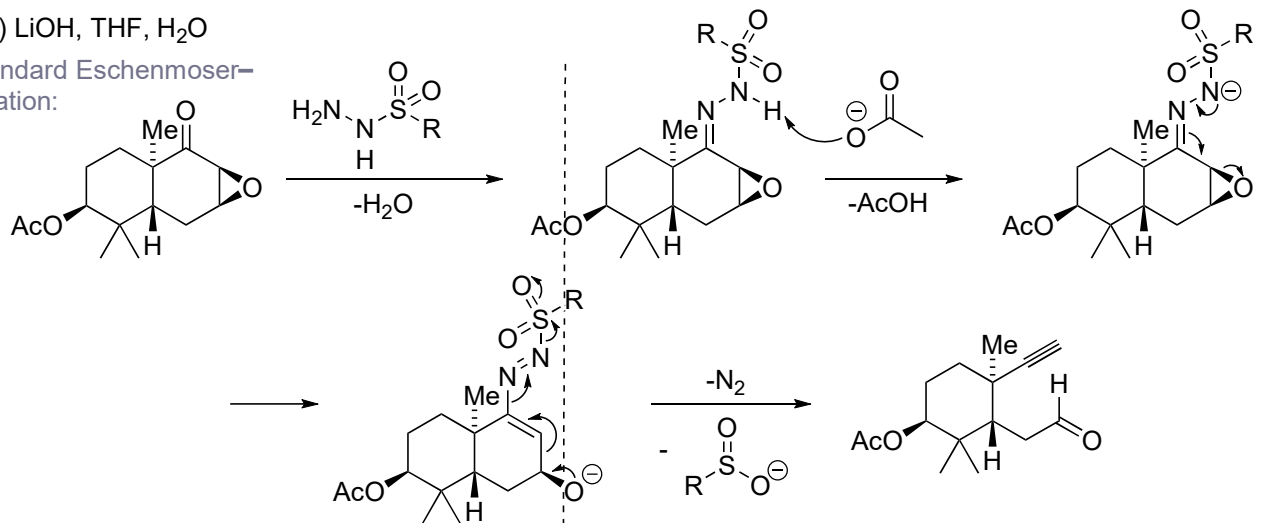
Please provide name and mechanism of the reaction in **Step 20**.

Singlet oxygen ene reaction/Schenk ene reaction

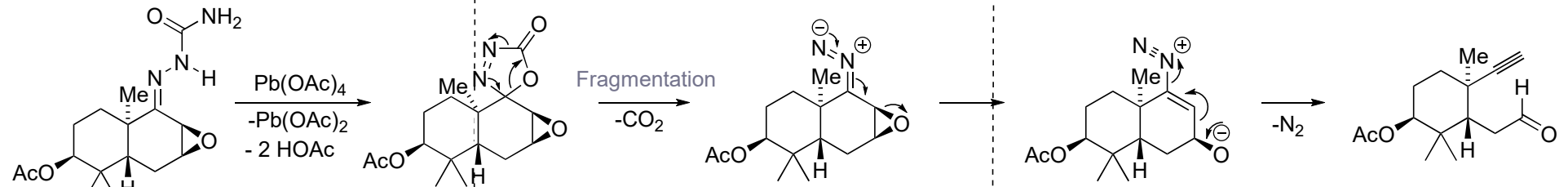




21) LiOH, THF, H<sub>2</sub>O  
 Mechanism of standard Eschenmoser-Tanabe fragmentation:



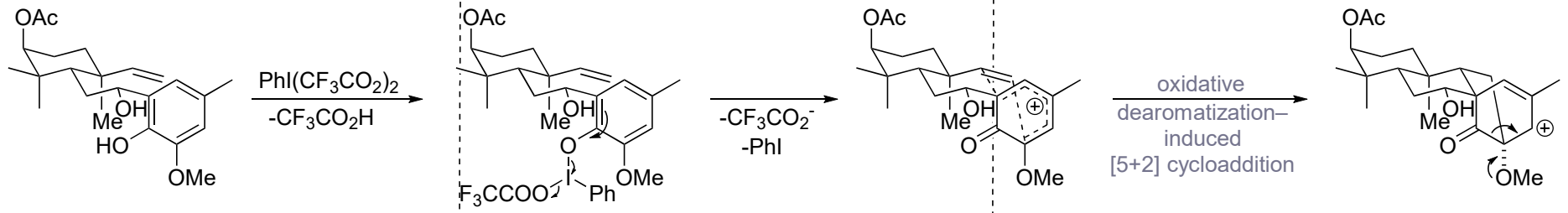
Possible Mechanism for Step 7, 8:



Oxidation of the semicarbazone to oxadiazoline and hydrolysis

*Can. J. Chem.* **1978**, 56, 308.  
*J. Am. Chem. Soc.* **2010**, 132, 1236.

Mechanism for Step 13



Dearomatization: *Tetrahedron* **2010**, 66, 2235. [5+2]: *J. Am. Chem. Soc.* **2011**, 133, 1603

pinacol-type  
 1,2-acyl migration

