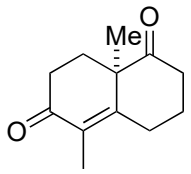
Total Syntheses of Highly Oxidized *ent*-Kaurenoids Pharicin A, Pharicinin B, 7-*O*-Acetylpseurata C, and Pseurata C: A [5+2] Cascade Approach

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



A

1–6

B

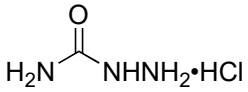
7–9

C

10–13

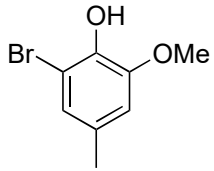
1) ethylene glycol, *p*-TSA•H_2O, PhH, 80 °C
2) Li, NH_3, MeI, –78 to 45 °C
3) L-selectride *then* HCl
4) Ac_2O, Et_3N, DMAP
5) IBX, DMSO, PhH, 85 °C
6) H_2O_2, NaOH, 0 °C

X =



7) **X**, NaOAc
8) $Pb(OAc)_4$
9) H_2, SiO_2, Lindlar cat.

Y =

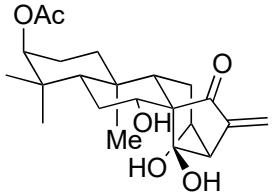


10) **Y**, *n*-BuLi
11) PDC, SiO_2
12) $NaBH_4$
13) $PhI(CF_3CO_2)_2$, K_2CO_3, HFIP, 0 °C

Name of Reaction in **Step 6.**

Please provide the name and mechanism of the reaction effected during **Step 7, 8.**
Hint: Standard conditions use *p*-toluenesulfonylhydrazide instead of **X** and $Pb(OAc)_4$.

Key Step. Please provide the mechanism of **Step 13.**
Hint: After formation of an initial intermediate a migration takes place. Please classify the migration.



pharicinin B

D

14–18

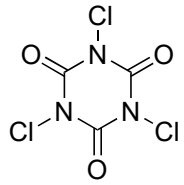
E

19, 20

pharicicin A **F**

14) DMP, $NaHCO_3$
15) $NaBH_4$
16) Ac_2O, DMAP
17) NCS, TBACl, TEMPO
18) cat. *p*-TSA•H_2O

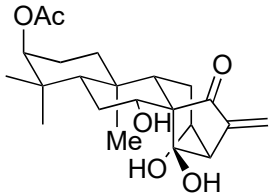
TCCA =



19) L-selectride
20) methylene blue, O_2, hν, MeCN *then* TCCA

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

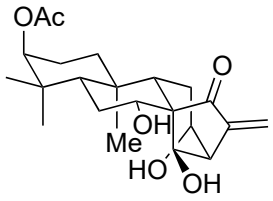
Please provide name and mechanism of the reaction in **Step 20.**



pharicinin B

21

21) LiOH, THF, H_2O



pharicinin B