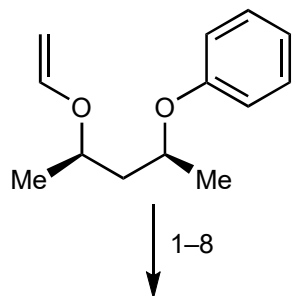


**Total Syntheses of the C19 Diterpenoid Alkaloids (-)-Talatisamine,  
(-)-Liljestrandisine, and (-)-Liljestrandinine by a Fragment Coupling  
Approach**

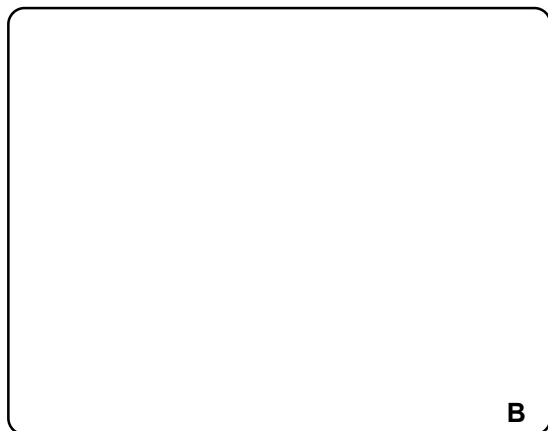
A. R. Wong, N. J. Fastuca, V. W. Mak, J. K. Kerkovius, S. M. Stevenson and S. E. Reisman  
*ACS Cent. Sci.* **2021**, ASAP



1-8



9-10



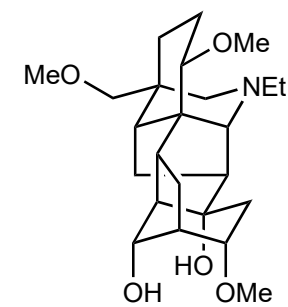
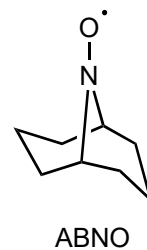
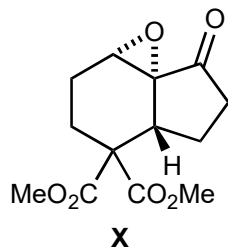
- 1)  $h\nu$  (254 nm)
- 2) *m*-CPBA then aq. HCl (2 M)
- 3) NaBH<sub>4</sub>, CeCl<sub>3</sub> · 7 H<sub>2</sub>O
- 4) *t*-Bu<sub>2</sub>Si(OTf)<sub>2</sub>, 2,6-lutidine
- 5) Cu(MeCN)<sub>4</sub>OTf, NMI, <sup>MeO</sup>bpy, ABNO, open to air then K<sub>2</sub>CO<sub>3</sub>, MeOH
- 6) Cu(MeCN)<sub>4</sub>OTf, NMI, <sup>MeO</sup>bpy, ABNO, open to air
- 7) KHMDS, Comins' reagent
- 8) Ni(OAc)<sub>2</sub>·4 H<sub>2</sub>O, NMI, Zn, LiBr

2) Mechanism?

5) Mechanism?

- 9) *t*-BuLi then **X** then TMSCl
- 10) TMSNTf<sub>2</sub>, 2,6-*t*-Bu-4-MePy

10) Name the reaction

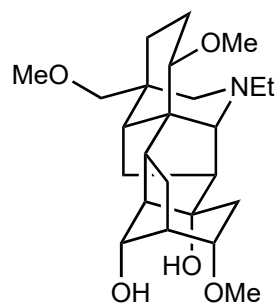


**(-)-Talatisamine**

11–19

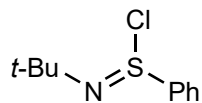


20–29



- 11) TCA *then*  $K_2CO_3$ , MeOH
- 12) KHMDS, Comins' reagent
- 13)  $Pd(OAc)_2$ ,  $PPh_3$ ,  $HCO_2H$ ,  $NEt_3$
- 14)  $(allyl)NH_2 \cdot HCl$ , Na-2-ethylhexanoate
- 15)  $LiBHET_3$
- 16)  $Me_3OBF_4$ , Proton Sponge, 4Å MS
- 17)  $[Ir(COE)_2Cl]_2$ ,  $Et_2SiH_2$  *then*  $LiBHET_3$
- 18)  $Pd(PPh_3)_4$ , 1,3-dimethylbarbituric acid
- 19)  $PhI(OAc)_2$ ,  $K_2CO_3$ ,  $SiO_2$

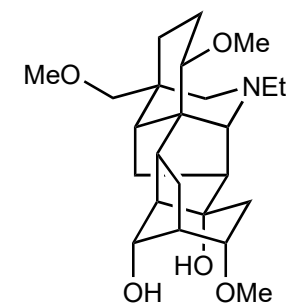
- 20) AcBr
- 21)  $HF \cdot py$
- 22)  $Cu(MeCN)_4OTf$ , NMI,  $MeO$ bpy, ABNO
- 23) MOMCl, DIPEA, TBAI
- 24) AIBN,  $H_2SnBu_3$
- 25)  $H_2$ , Pd/C
- 26) LHMDS, **Y** *then*  $H_2O$ , py
- 27) RedAl
- 28)  $BF_3 \cdot OEt_2$ ,  $Me_3OBF_4$ , 2,6-*t*-Bu-4-MePy
- 29) aq.  $H_2SO_4$  (0.5 M)



**Y**

16) Structure of Proton Sponge?

27) Structure of RedAl?



**(-)-Talatisamine**