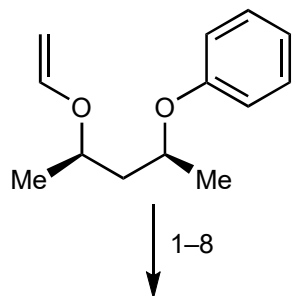
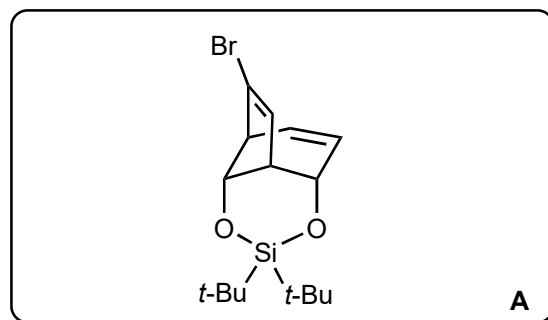


Total Syntheses of the C19 Diterpenoid Alkaloids (-)-Talatisamine, (-)-Liljestrandisine, and (-)-Liljestrandinine by a Fragment Coupling Approach

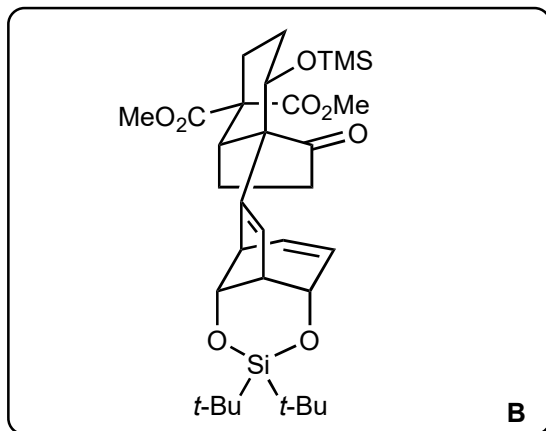
A. R. Wong, N. J. Fastuca, V. W. Mak, J. K. Kerkovius, S. M. Stevenson and S. E. Reisman
ACS Cent. Sci. **2021**, ASAP



1-8



9-10



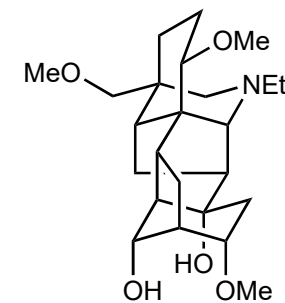
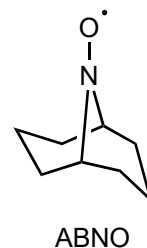
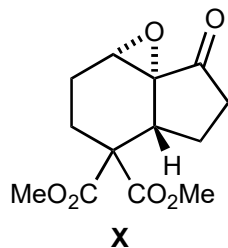
- 1) $h\nu$ (254 nm)
- 2) *m*-CPBA then aq. HCl (2 M)
- 3) NaBH_4 , $\text{CeCl}_3 \cdot 7 \text{H}_2\text{O}$
- 4) $t\text{-Bu}_2\text{Si}(\text{OTf})_2$, 2,6-lutidine
- 5) $\text{Cu}(\text{MeCN})_4\text{OTf}$, NMI, MeO^ibpy , ABNO, open to air then K_2CO_3 , MeOH
- 6) $\text{Cu}(\text{MeCN})_4\text{OTf}$, NMI, MeO^ibpy , ABNO, open to air
- 7) KHMDS, Comins' reagent
- 8) $\text{Ni}(\text{OAc})_2 \cdot 4 \text{H}_2\text{O}$, NMI, Zn, LiBr

2) Mechanism?

5) Mechanism?

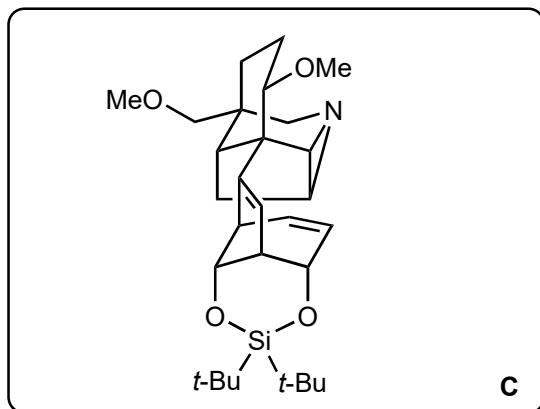
- 9) $t\text{-BuLi}$ then **X** then TMSCl
- 10) TMSNTf_2 , 2,6-*t*-Bu-4-MePy

10) Name the reaction
 Semi-Pinacol rearrangement

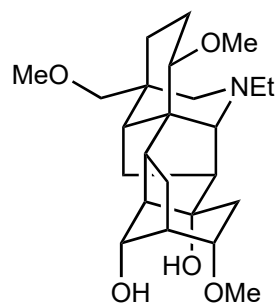


(-)-Talatisamine

11-19

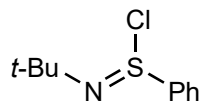


20-29



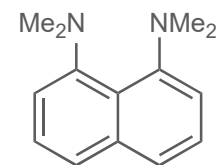
- 11) TCA *then* K₂CO₃, MeOH
- 12) KHMDS, Comins' reagent
- 13) Pd(OAc)₂, PPh₃, HCO₂H, NEt₃
- 14) (allyl)NH₂•HCl, Na-2-ethylhexanoate
- 15) LiBHET₃
- 16) Me₃OBF₄, Proton Sponge (excess)
- 17) [Ir(COE)₂Cl]₂, Et₂SiH₂ *then* LiBHET₃
- 18) Pd(PPh₃)₄, 1,3-dimethylbarbituric acid
- 19) PhI(OAc)₂, K₂CO₃, SiO₂

- 20) AcBr
- 21) HF•py
- 22) Cu(MeCN)₄OTf, NMI, MeO⁺bpy, ABNO
- 23) MOMCl, DIPEA, TBAI
- 24) AIBN, HSnBu₃
- 25) H₂, Pd/C
- 26) LHMDS, **Y** *then* H₂O, py
- 27) RedAl
- 28) BF₃•OEt₂, Me₃OBF₄, 2,6-*t*-Bu-4-MePy
- 29) aq. H₂SO₄ (0.5 M)



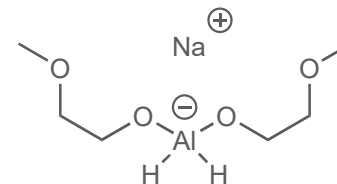
Y

16) Structure of Proton Sponge?

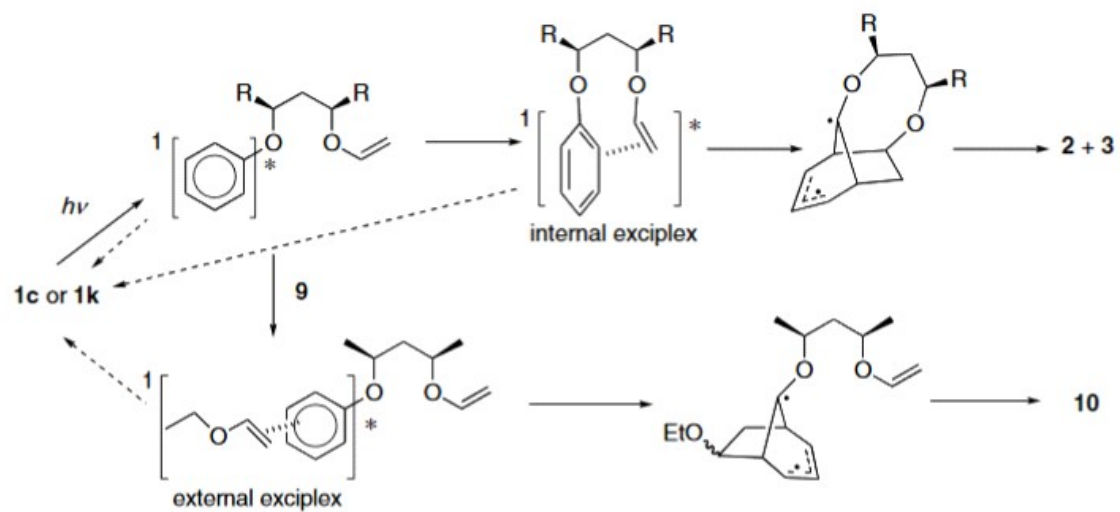


26) Name the reaction
Mukaiyama dehydrogenation

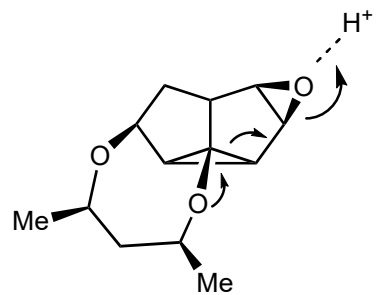
27) Structure of RedAl?



1) *Tetrahedron: Asymmetry* **2005**, 16, 675–683.



2) Grob-type fragmentation



5) *J. Am. Chem. Soc.* **2013**, 135, 15742–15745.

