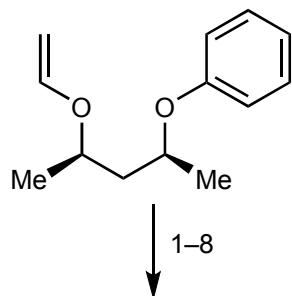
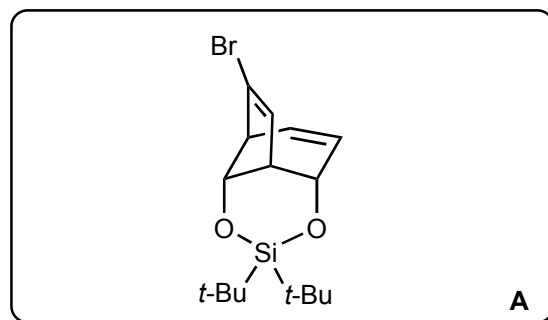


Total Syntheses of the C19 Diterpenoid Alkaloids (-)-Talatisamine, (-)-Liljestrandisine, and (-)-Liljestrandinine by a Fragment Coupling Approach

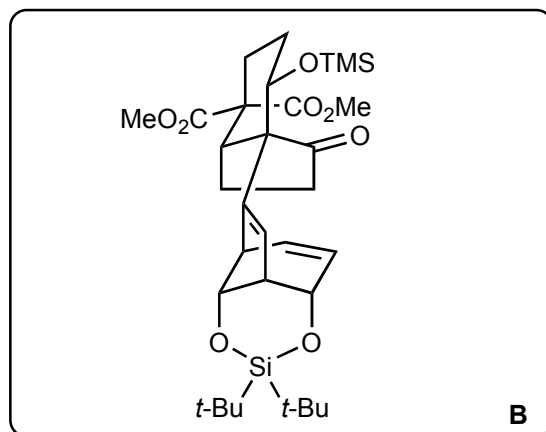
A. R. Wong, N. J. Fastuca, V. W. Mak, J. K. Kerkovius, S. M. Stevenson and S. E. Reisman
ACS Cent. Sci. **2021**, *7*, 1311–1316



1–8

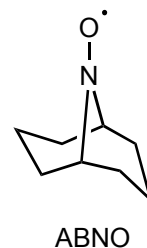
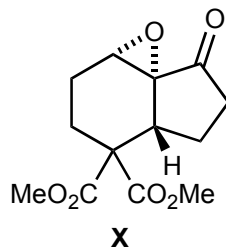


9–10



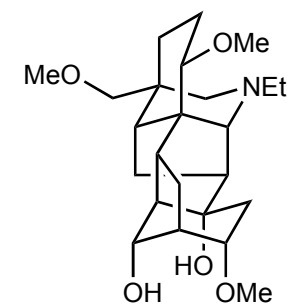
- 1) $h\nu$ (254 nm)
- 2) *m*-CPBA then aq. HCl (2 M)
- 3) NaBH₄, CeCl₃ · 7 H₂O
- 4) *t*-Bu₂Si(OTf)₂, 2,6-lutidine
- 5) Cu(MeCN)₄OTf, *N*-methylimidazole, ^{MeO}bpy, ABNO, open to air, then K₂CO₃, MeOH
- 6) Cu(MeCN)₄OTf, NMI, ^{MeO}bpy, ABNO, open to air
- 7) KHMDS, Comins' reagent
- 8) Ni(OAc)₂ · 4 H₂O, *N*-methylimidazole, Zn, LiBr

- 9) *t*-BuLi then **X** then TMSCl
- 10) TMSNTf₂, 2,6-*t*-Bu-4-MePy



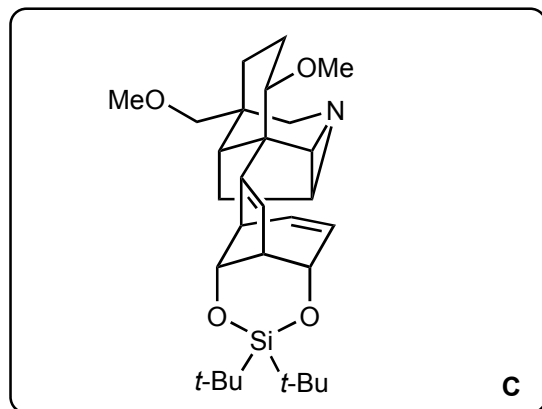
- 1) Mechanism?
hint: it's a meta-arene-alkene cycloaddition
- 2) Mechanism?
- 5) Mechanism?
hint: the second step is an E1CB elimination

- 10) Name the reaction
Semi-Pinacol rearrangement

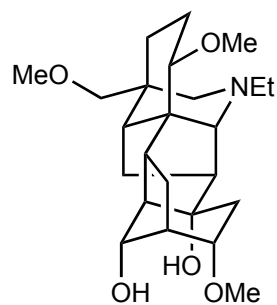


(-)-Talatisamine

11-19

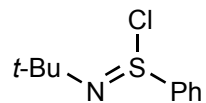


20-29



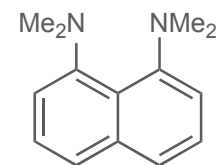
- 11) trichloroacetic acid *then* K_2CO_3 , MeOH
- 12) KHMDS, Comins' reagent
- 13) $Pd(OAc)_2$, PPh_3 , HCO_2H , NEt_3
- 14) $(allyl)NH_2 \cdot HCl$, Na-2-ethylhexanoate
- 15) $LiBHET_3$
- 16) Me_3OBF_4 , Proton Sponge (excess)
- 17) $[Ir(COE)_2Cl]_2$, Et_2SiH_2 *then* $LiBHET_3$
- 18) $Pd(PPh_3)_4$, 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^t bpy, ABNO
- 23) MOMCl, DIPEA, TBAI
- 24) AIBN, $HsSnBu_3$
- 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)



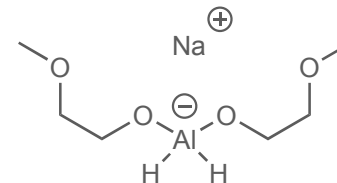
Y

16) Structure of Proton Sponge?

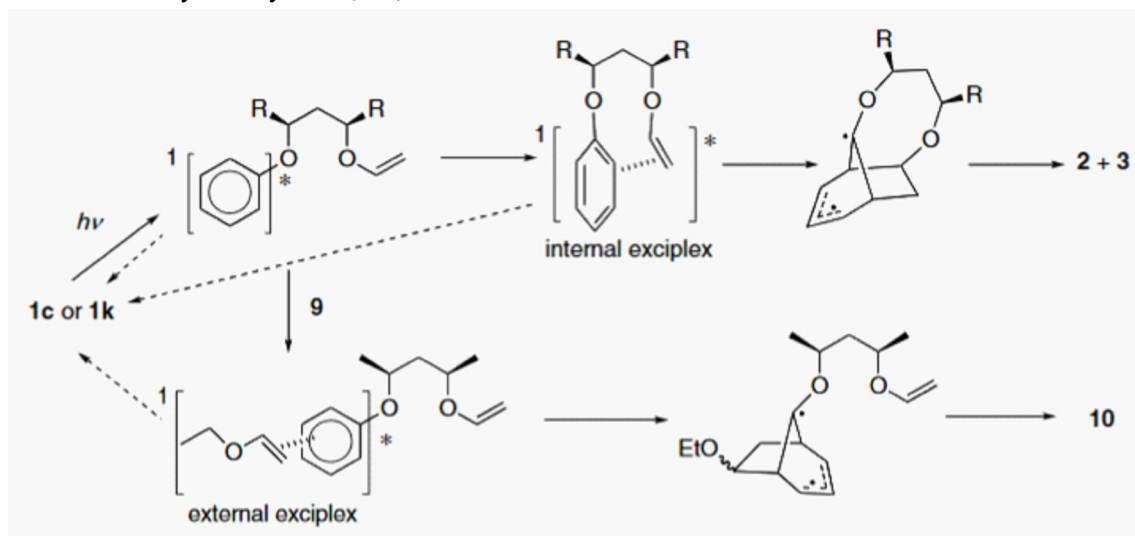


26) Name the reaction
Mukaiyama dehydrogenation

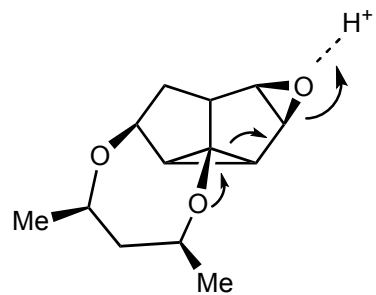
27) Structure of RedAl?



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



2) Grob-type fragmentation



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

