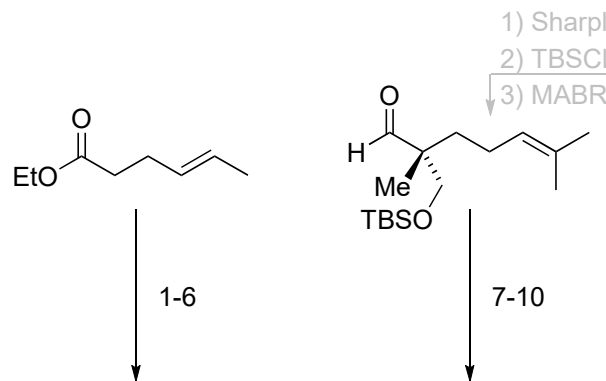


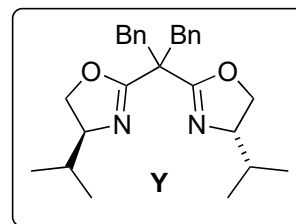
## Enantioselective Total Synthesis of Cotylenin A

M. Uwamori, R. Osada, R. Sugiyama, K. Nagatani, M. Nakada\* *J. Am. Chem. Soc.* **2020**, *142*, 5556–5561.



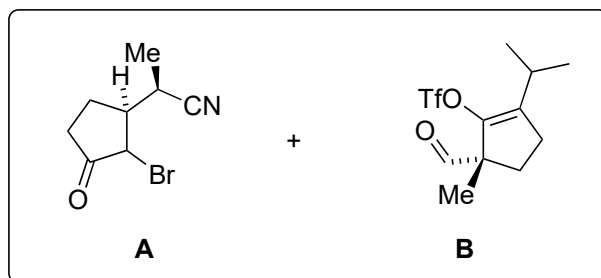
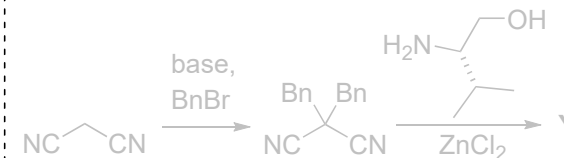
*Tetrahedron* **1991**, *47*, 6983–6998.

- 1) MeSO<sub>2</sub>Mes, *n*-BuLi
- 2) TsN<sub>3</sub>, NEt<sub>3</sub>
- 3) CuPF<sub>6</sub>(MeCN)<sub>4</sub>, **Y**
- 4) NaCN
- 5) Sml<sub>2</sub>, CIP(O)(OEt)<sub>2</sub>
- 6) NBS, THF/H<sub>2</sub>O
- 7) *tert*-C<sub>12</sub>H<sub>25</sub>SH, TBHP, CuCl, 2,2'-bipyridyl
- 8) PhNTf<sub>2</sub>, LDA
- 9) NEt<sub>3</sub> · 3HF
- 10) DMP



step 2: Name and mechanism of the reaction?  
Regitz diazo transfer; mechanism below

step 3: Name of the ligand class?  
BOX ligands (bisoxazoline ligands)  
How would you prepare the ligand?



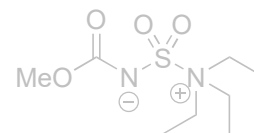
step 11: Name and mechanism of the reaction?  
Utimoto coupling; mechanism below

Structure of Burgess reagent?

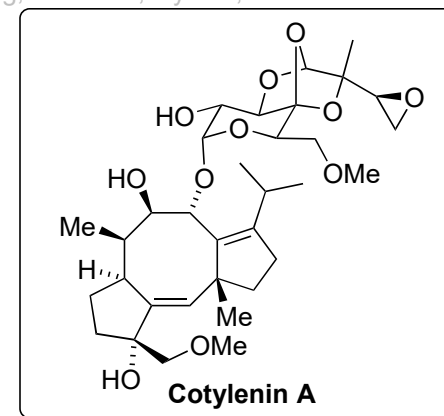
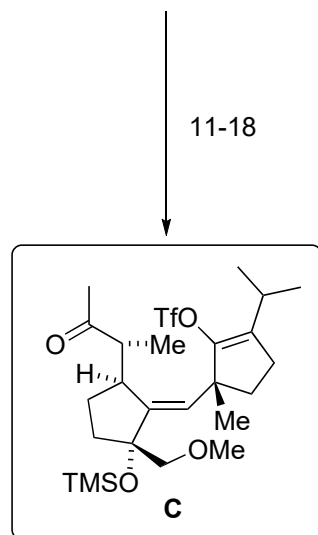
step 13: Name of the reaction? Takai–Lombardo olefination

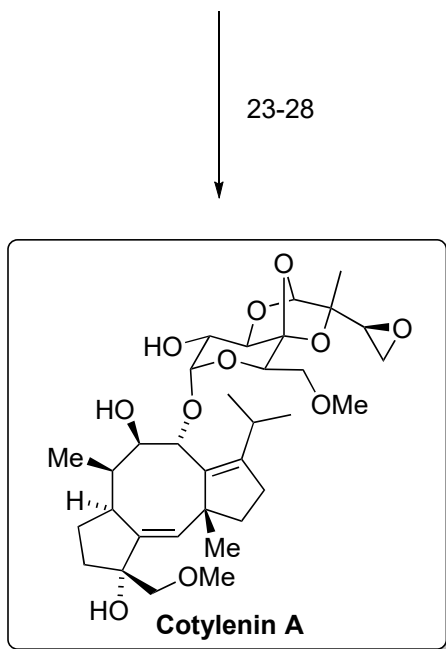
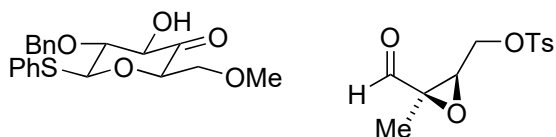
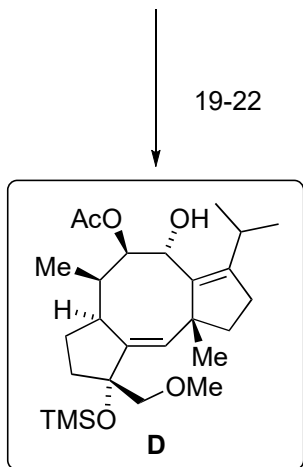
Possible alternatives? e.g. Tebbe, Petasis, Wittig, Peterson, Nysted, Lebel olefination

Burgess reagent:

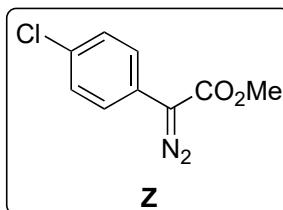


- 11) BEt<sub>3</sub>, Ph<sub>3</sub>SnH
- 12) Burgess reagent
- 13) CH<sub>2</sub>I<sub>2</sub>, Zn, ZrCl<sub>4</sub>, PbCl<sub>2</sub>
- 14) K<sub>2</sub>OsO<sub>4</sub> · 2H<sub>2</sub>O, NMO
- 15) Me<sub>3</sub>OBF<sub>4</sub>, 2,6-*t*-Bu<sub>2</sub>-4MePy, then TMSCl, pyridine
- 16) DIBAL
- 17) MeMgBr
- 18) DMP



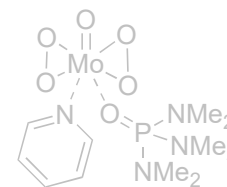


- 19)  $\text{PdCl}_2(\text{PCy}_3)_2$ , PhOK
- 20) LHMDS, LiCl, MoOPH
- 21)  $\text{Me}_4\text{NBH}(\text{O}_2\text{C}i\text{-Pr})_3$
- 22)  $\text{Ac}_2\text{O}$ , py

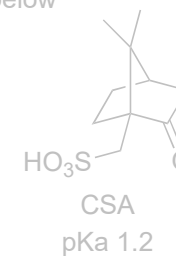


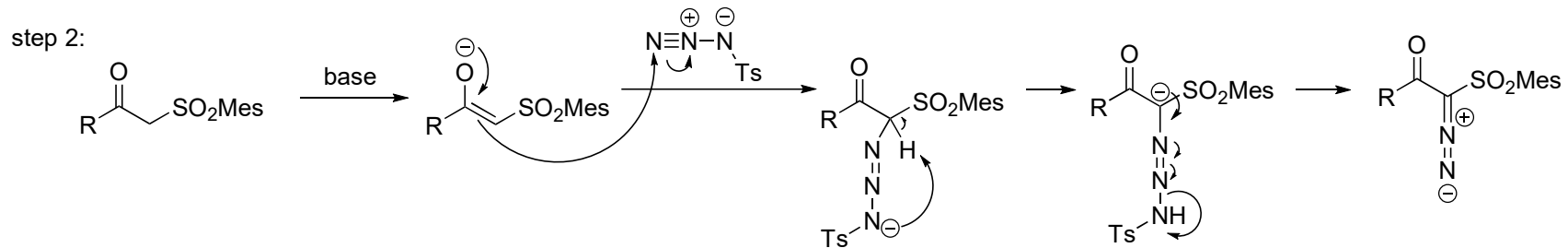
- 23) CSA
- 24) NaH
- 25) **Z**,  $\text{Rh}_2(\text{oct})_4$ , TfOH · DTBMP, **D**
- 26) MeLi
- 27) TBAF
- 28)  $\text{H}_2$ , Pd black

Structure of MoOPH?

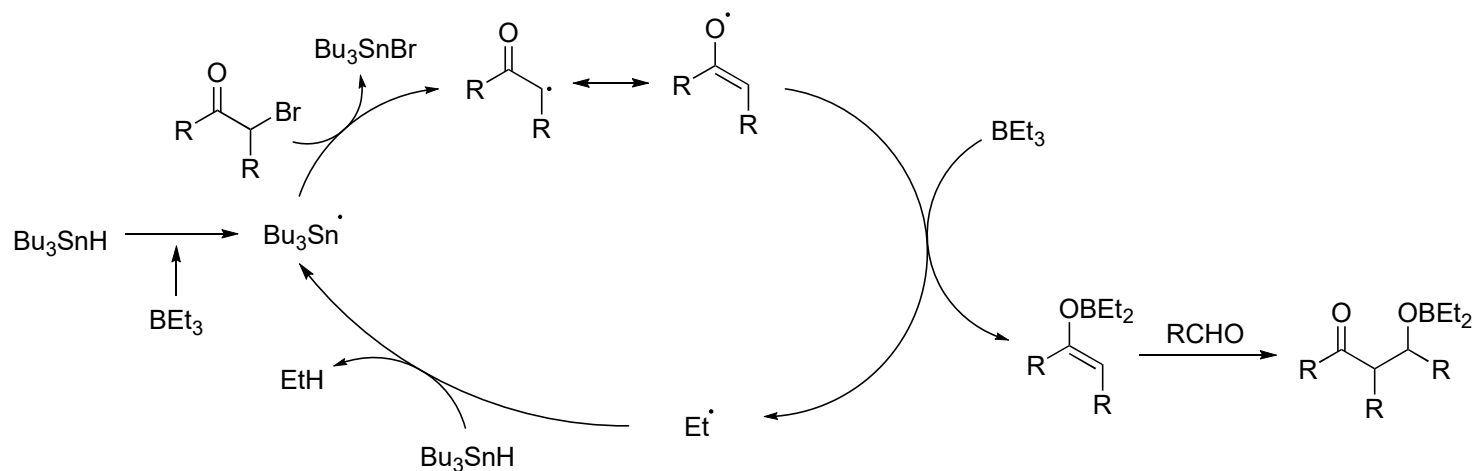


step 23: Mechanism? see below  
Structure and pKa of CSA?  
step 25: Mechanism? see below



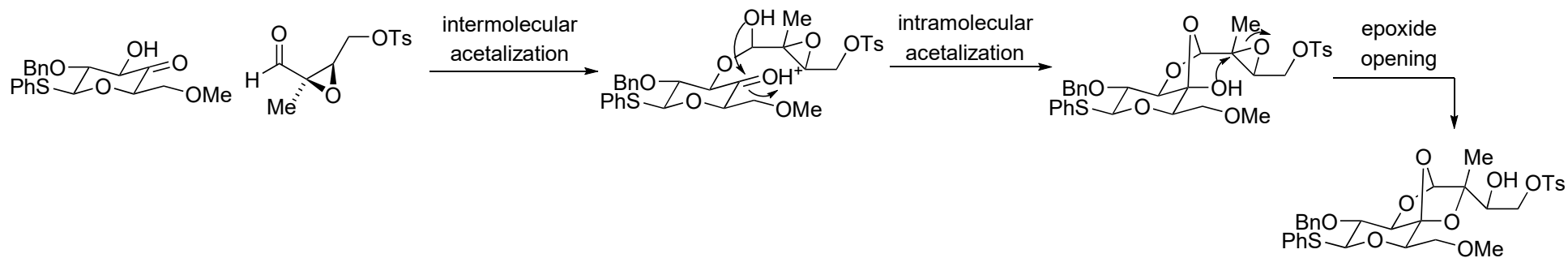


Mechanism step 11:

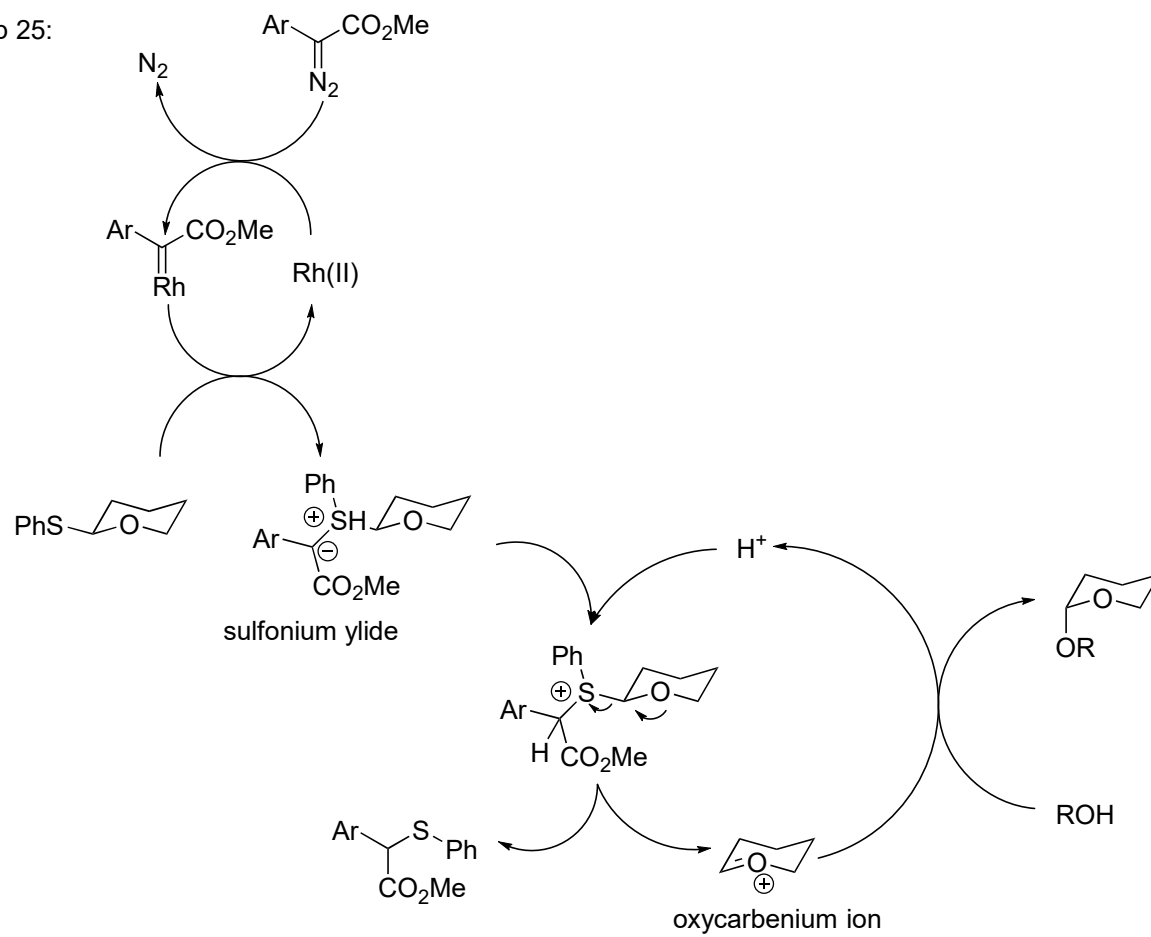


Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, 29, 1041.

step 23:



step 25:



*J. Am. Chem. Soc.* **2019**, *141*, 11775–11780.