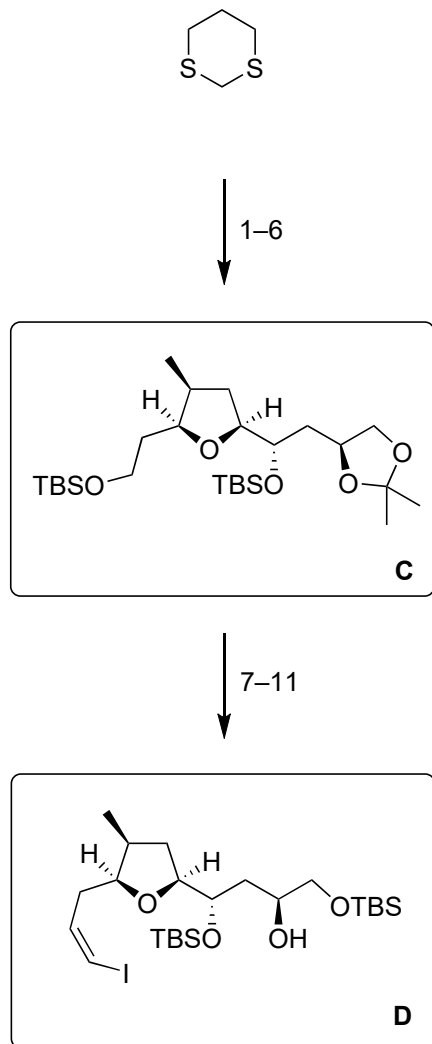


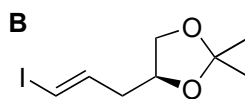
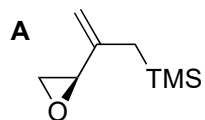
Total Synthesis of (-)-Mandelalide A Exploiting Anion Relay Chemistry (ARC): Identification of a Type II ARC/CuCN Cross-Coupling Protocol

Minh H. Nguyen, Masashi Imanishi, Taichi Kurogi, and Amos B. Smith, III

JACS 2016, 138, 3675



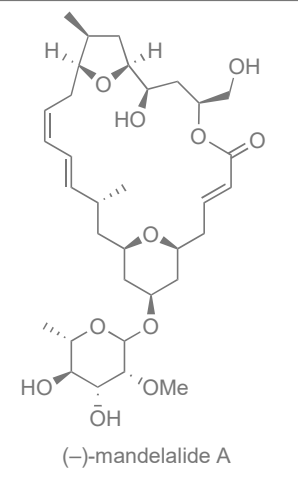
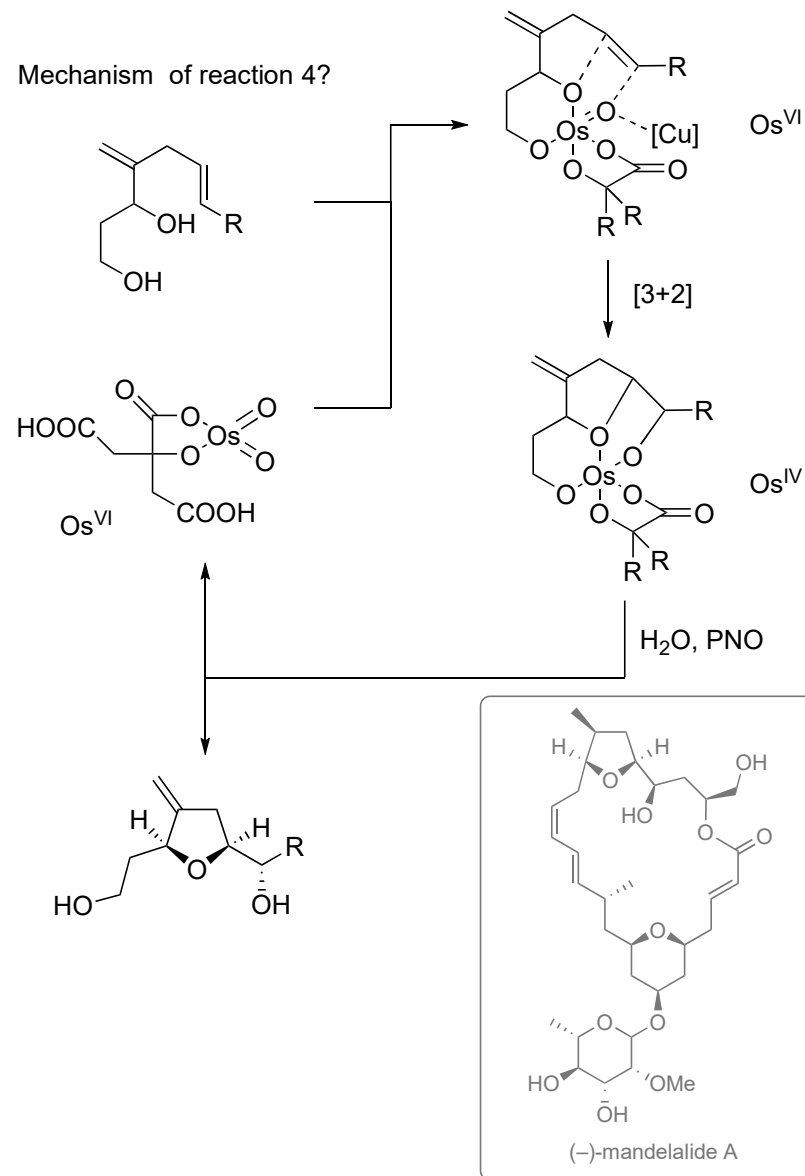
- 1) *n*BuLi, then **A**, then **B**, CuCN (0.75 eq.) then TBAF
- 2) MeI, CaCO₃, 65 °C
- 3) NaBH₄
- 4) K₂OsO₄·2H₂O, pyridine-N-oxide, Cu(OTf)₂, citric acid, pH = 6.5 phosphate buffer/MeCN
- 5) TBSOTf, 2,6-Lutidine
- 6) (PPh₃)₃RhCl, H₂

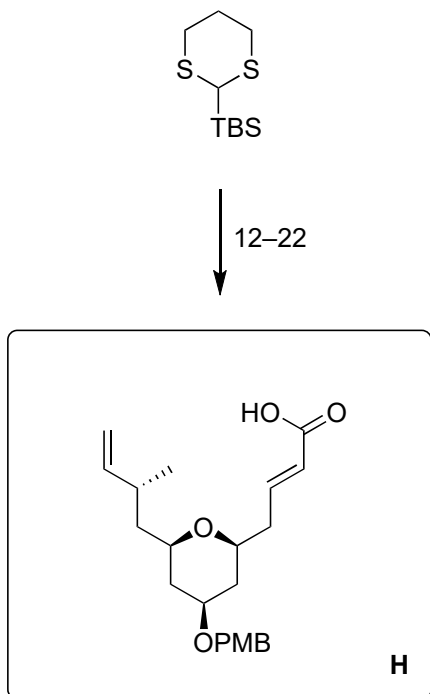


- 7) HF, pyridine
- 8) DMP
- 9) Ph₃PCH₂I₂, NaHMDS
- 10) CeCl₃·7H₂O, (COOH)₂
- 11) TBSCl, imidazole

Hint: Only one position reacts in step 7 and also in step 11.

Mechanism of reaction 4?

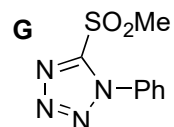
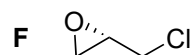
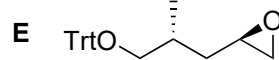




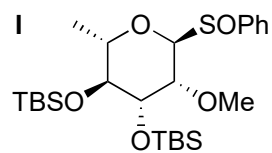
23-27

(-)-mandelalide A

- 12) *n*BuLi
then **E**,
then HMPA
then **F**
then CH₂=CH-MgBr, CuI
- 13) MsCl, Et₃N
- 14) TBAF, reflux
- 15) MeI, CaCO₃
- 16) NaBH₄
- 17) PMBBR
- 18) PPTS
- 19) H₂C=CH-COOMe, Grubbs I
- 20) DMP
- 21) **G**, NaHMDS
- 22) LiOH

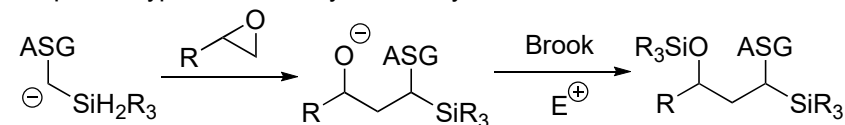


- 23) 2,4,6-trichlorobenzoyl chloride
DMAP, Et₃N, **D**
- 24) DDQ
- 25) **I**, Tf₂O, MS 4Å
2,6-di-*t*Bu-4-Me-pyridine
- 26) Pd(OAc)₂, Cs₂CO₃, Et₃N, DMF
- 27) HF, pyridine

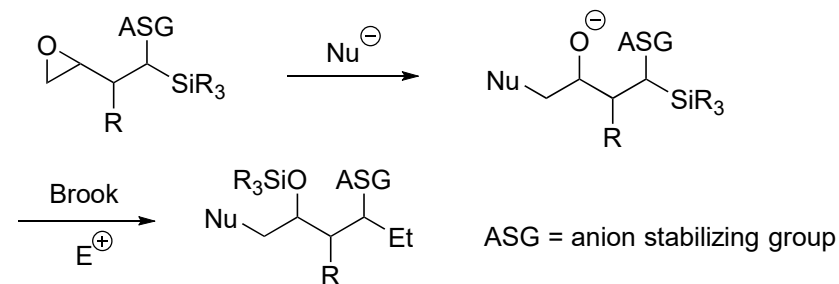


Compare and classify step 1 and step 12

Step 12 - Type I anion relay chemistry tactic



Step 1 - Type II anion relay chemistry tactic



Name of reaction 25?
Kahne glycosylation

