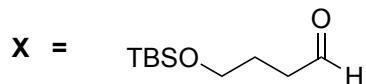
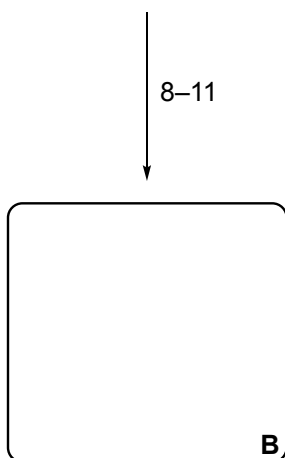
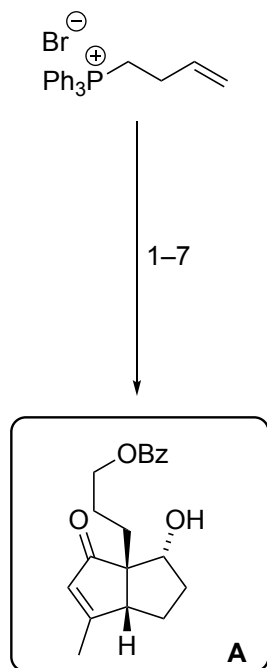
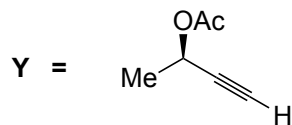


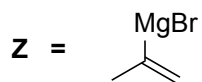
Total Synthesis of (-)-Merochlorin A
 Brandstätter, M.; Freis, M.; Huwlyer, N.; Carreira, E. M.
Angew. Chem. Int. Ed. **2019**, *58*, 2490–2494



- 1) LiBr (2.0 eq), PhLi (1.0 eq) *then X* *then* PhLi (1.1 eq) *then* 1,2-diiodoethane
- 2) **Y**, PdCl₂(PPh₃)₂, CuI, NEt₃
- 3) 9-BBN *then* NaBO₃•4 H₂O
- 4) BzCl, pyridine
- 5) TBAF
- 6) (COCl)₂, DMSO *then* NEt₃
- 7) Au(MeCN)(JohnPhos)SbF₆, H₂O (cat.)



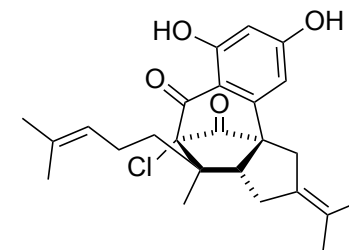
- 8) Tf₂O, 2,6-lutidine *then* DBU
- 9) PdCl₂, CuCl, O₂, DMF/H₂O
- 10) LaCl₃•2 LiCl (5.0 eq), **Z**
- 11) BF₃•OEt₂ (1.5 eq), Et₃SiH (excess)



Step 1: Please provide the name of the reaction.

Hint: Think about the intermediates and what effect additional PhLi has to arrive at the correct product.

Step 7 – Key step: Please provide a reasonable mechanism that accounts for the formation of **A**. **Hint:** Several named reactions take place in this cascade.

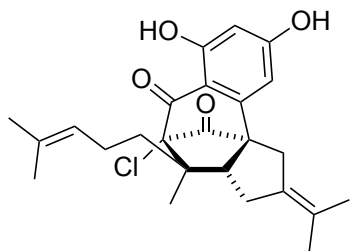


(-)-merochlorin A

12–16

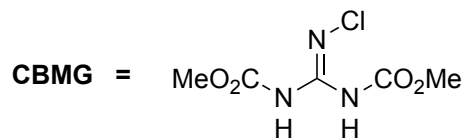
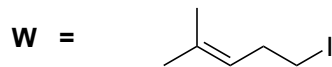


17–22

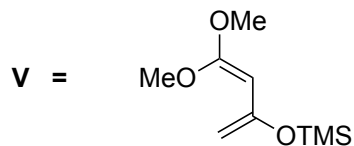
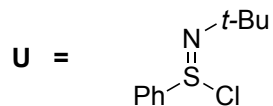


(-)-merochlorin A

- 12) **W**, *t*-BuLi then LiCu(CN)(2-thiofurenyl) then **B**, BF₃•OEt₂
13) NEt₃, TMSOTf then **CBMG**
14) K₂CO₃, MeOH/THF
15) PDC, DMF
16) Ac₂O (neat), NaOAc, 140 °C



- 17) DIBAL-H (1.3 eq), PhMe
18) PCC, celite
19) LDA, then **U**
20) **V**, 110 °C then 1 M HCl
21) NEt₃, TMSOTf, then Pd(OAc)₂ (1.5 eq)
22) LiCl, 135 °C



Step 17: The product formed can be seen as the product of a formal [1,3]-rearrangement. Please explain formation of the product.