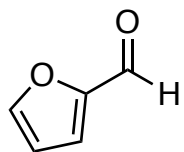
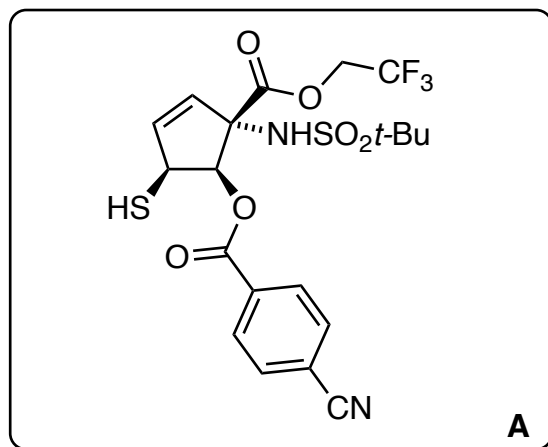


Total Synthesis of Tagetitoxin

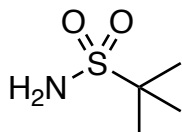
He, C.; Chu, H.; Stratton, T. P.; Kossler, D.; Eberle, K. J.; Flood, D. T.; Baran, P. S.
J. Am. Chem. Soc. **2020**, *142*, 13683–13688.



1–7

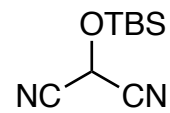


8–10



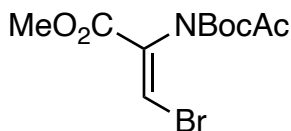
1

- 1) **1**, amberlyst 15, Δ
- 2) **2**, Et₃N then 2,2,2-trifluoroethanol, TBAF
- 3) methylene blue, O₂, h ν then Me₂S, SiO₂
- 4) 4-cyanobenzoyl chloride, DMAP
- 5) CeCl₃·7H₂O, NaBH₄
- 6) 1,1'-thiocarbonyldiimidazole
- 7) BHT, 115 °C then *p*-TsOH, H₂O



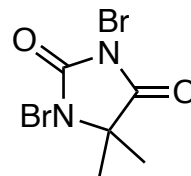
2

- 3) Please provide a mechanism.
See below
- 5) Please name the reaction.
Luche reduction
- 7) Please classify the reaction.
[3,3]-sigmatropic rearrangement



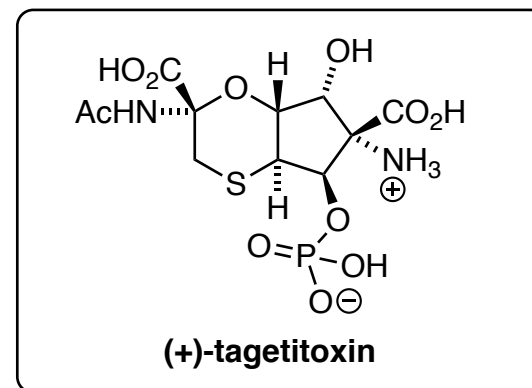
3

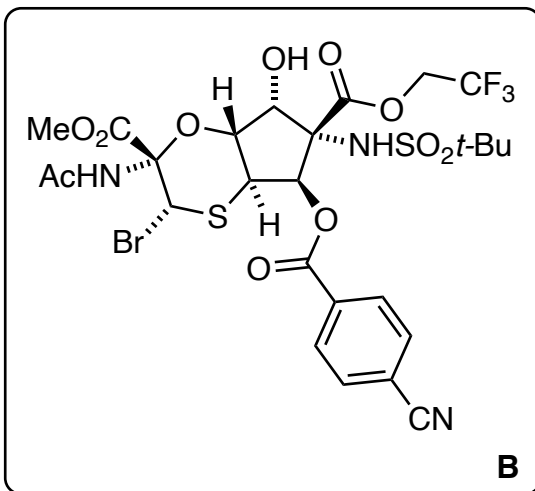
- 8) **3**, Et₃N
- 9) OsO₄, NMO, citric acid then HCl
- 10) **4**, AcOH, Δ



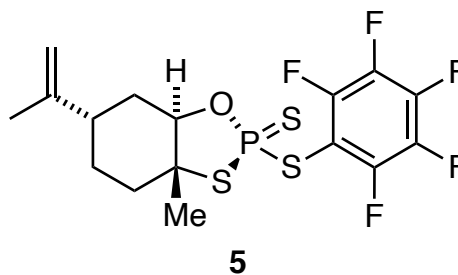
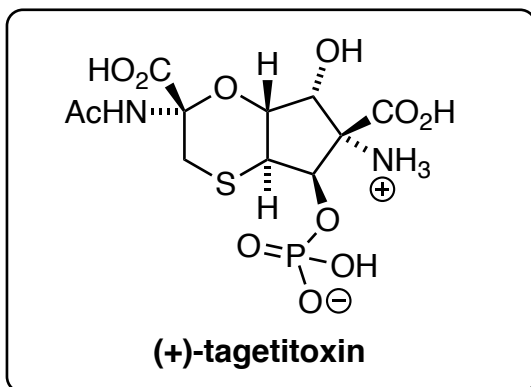
4

- 9) Hint: The most labile protective group is lost.





11–15



- 11) TfOH, anisole
- 12) *n*-Bu₃SnH, AIBN *then* acetone, *p*-TsOH
- 13) MeOH, Et₃N *then* **5**, DBN; separation of diastereomers
- 14) SeO₂
- 15) TMSOK, H₂O *then* MeONH₂·HCl

11) Hint: Monodeprotection.

13) Hint: 2 eq of MeOH are consumed.

solution to step 3:

overall: Piancatelli-type rearrangement

