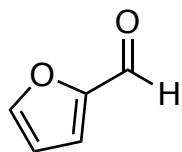


Total Synthesis of Tagetitoxin

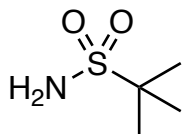
He, C.; Chu, H.; Stratton, T. P.; Kossler, D.; Eberle, K. J.; Flood, D. T.; Baran, P. S.
J. Am. Chem. Soc. **2020**, *142*, 13683–13688.



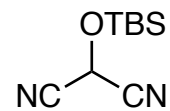
1–7



8–10

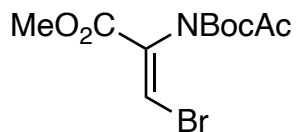


1

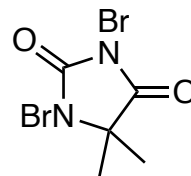


2

- 1) **1**, amberlyst 15, Δ
- 2) **2**, Et_3N then 2,2,2-trifluoroethanol, TBAF
- 3) methylene blue, O_2 , $h\nu$ then Me_2S , SiO_2
- 4) 4-cyanobenzoyl chloride, DMAP
- 5) $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, NaBH_4
- 6) 1,1'-thiocarbonyldiimidazole
- 7) BHT, 115°C then PTSA, H_2O



3



4

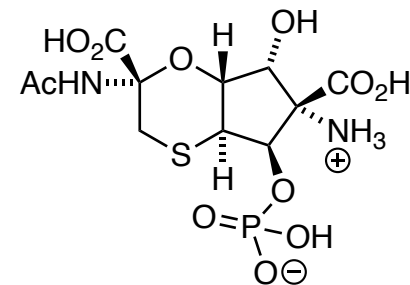
- 8) **3**, Et_3N
- 9) OsO_4 , NMO, citric acid then HCl
- 10) **4**, AcOH, Δ

3) Please provide a mechanism.

5) Please name the reaction.

7) Please classify the reaction.

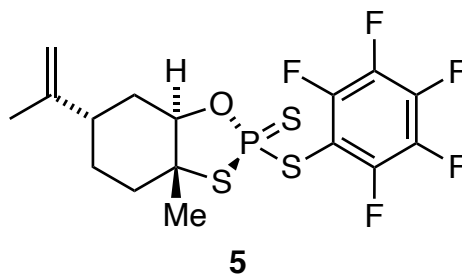
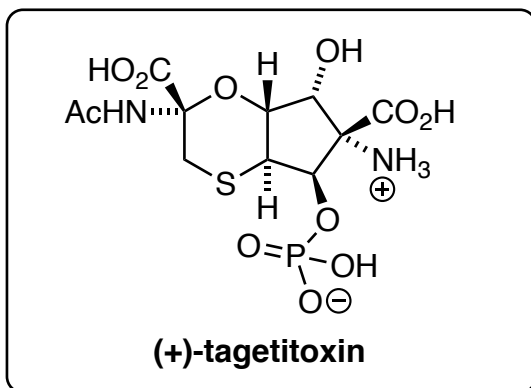
9) Hint: The most labile protective group is lost.



(+)-tagetitoxin



11–15



- 11) TfOH, anisole
- 12) *n*-Bu₃SnH, AIBN *then* acetone, PTSA
- 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.