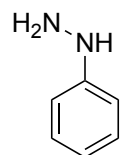


Enantioselective Total Synthesis of (+)-Flavisiamine F via Late-Stage Visible-Light-Induced Photochemical Cyclization

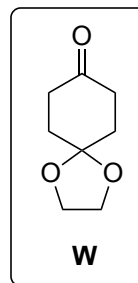
X. Tong, B. Shi, K. Liang, Q. Liu, C. Xia
Angew. Chem. Int. Ed. **2019**, *58*, 5443–5446.



1-4



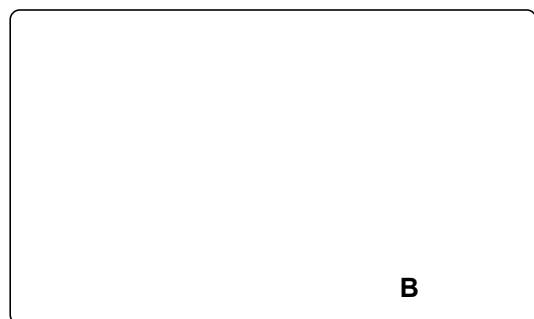
- 1) **W**
- 2) ethylene glycol 190°C
- 3) NaOH, *n*-Bu₄N⁺ SO₄⁻, PhSO₂Cl
- 4) *p*-TsOH·H₂O



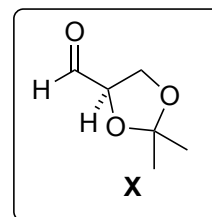
Name of step 1 and 2? Mechanism?

Name three different general ways to access this class of compounds. What are the starting materials/conditions?

5-8



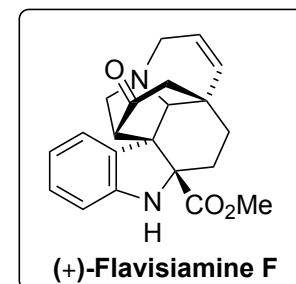
- 5) LHMDS, PhNTf₂, HMPA:THF (1:10)
- 6) CrCl₂, NiCl₂ (5 mol%), **X**, 1:1 d.r.
- 7) IBX
- 8) LiBHEt₃, 35:1 d.r.
- 9) NaH, Cl₃CCN, 25 °C
- 10) TMSOTf, DIPEA
- 11) K₂CO₃, PhCl, reflux, then 1 molL⁻¹ HCl



Name of step 6? Mechanism?

Name of step 9?

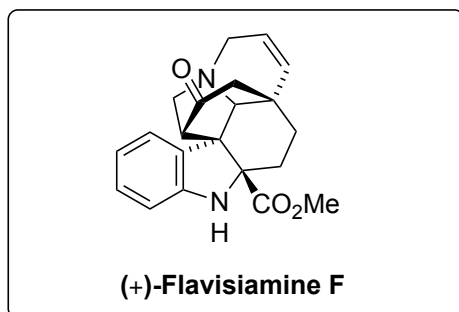
Name of step 11?



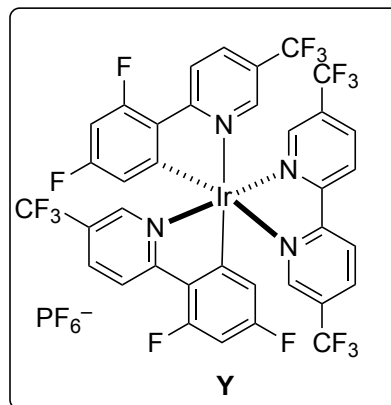
9-13



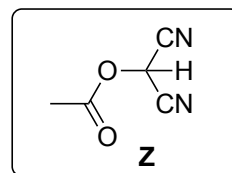
14-17



- 12) Ag_2O , MeI
- 13) KHMDS, TBSCl
- 14) DIBAL
- 15) K_2CO_3 , allyl bromide
- 16) aq. HCHO/EtOH, *then* 1N HCl
- 17) *p*-TsOH, Grubbs^{2nd} generation catalyst
- 18) LiHMDS, I_2



- 19) Et_3N , **Y** (5 mol%), air, blue LED, DMF, 77% yield
- 20) imidazole, **Z**
- 21) K_2CO_3 , H_2O_2
- 22) HCl, MeOH, reflux



Name of step 16)

Structure of Grubbs 2nd generation catalyst?

20) hint: Instead of directly introducing the methoxy carbonyl, a nitrile was isolated