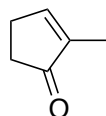


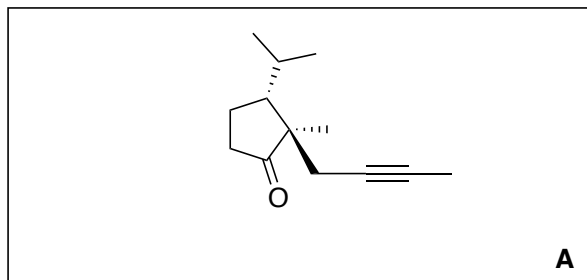
Synthesis Challenge 112

AG Wegner

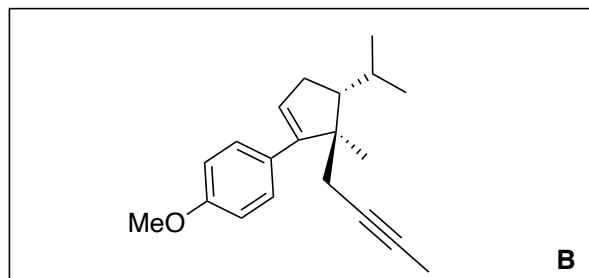
Total Synthesis of (–)-Psathyrin A Enabled by Radical Cyclization,
W. Zhao, R. Al-Ahmad, M. Dai, *J. Am. Chem. Soc.* **2025**, *147*, 32365–32369
23.10.2025



1

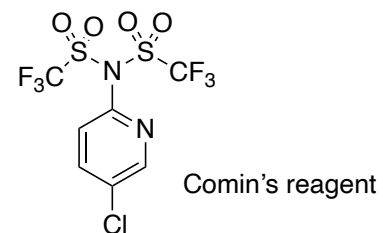
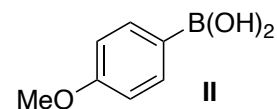
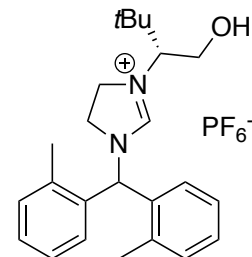


2-3

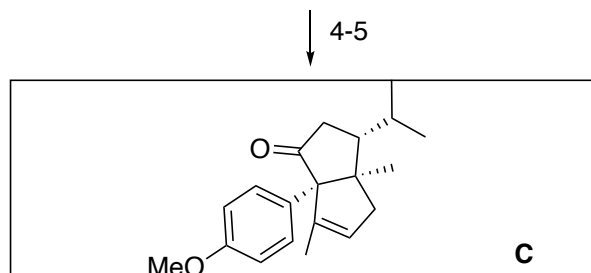


1) $\text{Cu}(\text{OTf})_2$, **I**, iPrMgBr , Et_2O , then, HMPA,
30 min, 1-bromo-2-butyne, 12 h

2) KHMDS, Comin's reagent, THF, 10 min
3) **II**, $\text{PdCl}_2(\text{dppf})$, K_3PO_4 , DMF, H_2O



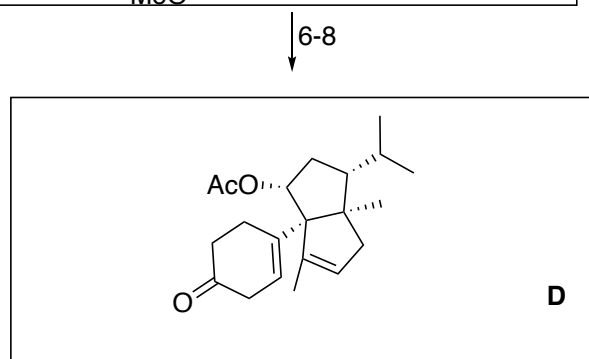
Step 3: Suzuki cross coupling reaction



- 4) *m*CPBA, CH₂Cl₂, 30 min, then pTsOH, 10 min
 5) AuCl(PPh₃), AgOTf, toluene 30 min

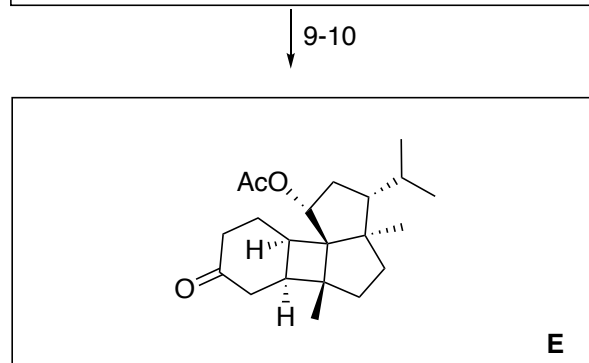
Step 4: Epoxidation, followed by Meinwald rearrangement

Step 5: Conia-Ene reaction



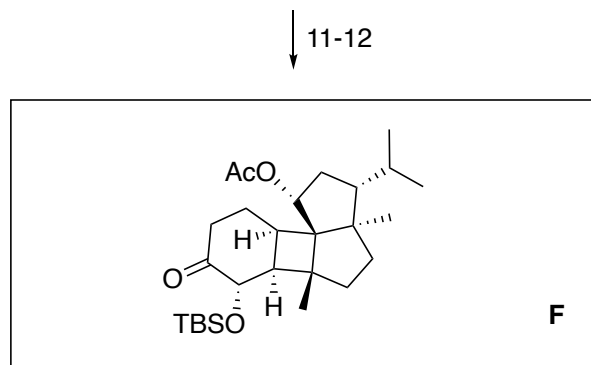
- 6) LiAlH₄, THF, 20 min
 7) Li, NH₃ (l), EtOH/THF, then 1 M HCl, 30 min
 8) Ac₂O, Et₃N, DMAP, CH₂Cl₂, 3h

Step 7: Birch reduction



- 9) HCl (1.0M in Et₂O), THF, 6h
 10) Fe(acac)₃, PhSiH₃, Et₂O 1.5h

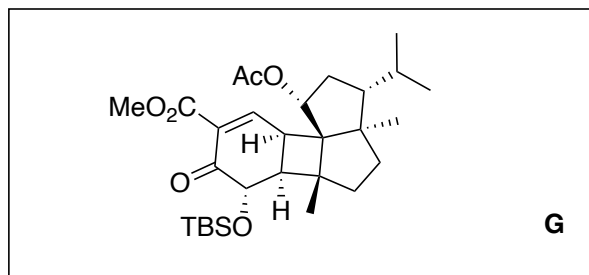
Step 9: **M**etal-catalyzed **h**ydrogen **t**ransfer (MHAT) Reaction



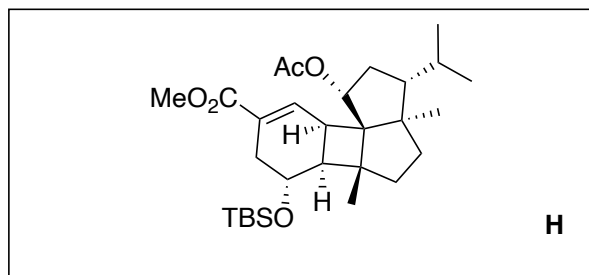
- 11) TBAF (2 mol%), HMDS, TMS-imidazole, THF, then OsO₄, 30 min
 12) TBSOTf, 2,6-lutidine, CH₂Cl₂

Step 11: Rubottom oxidation

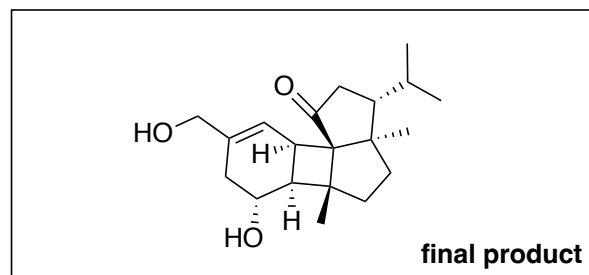
↓ 13-14



↓ 15-17



↓ 18-19



13) LiHMDS, CNCO₂Me, Et₂O, 30 min
14) PhSeBr, pyridine, CH₂Cl₂, then H₂O₂, 30 min

15) CeCl₃·7H₂O, NaBH₄, MeOH, 10 min
16) NaH, CS₂, THF, then MeI, 30 min
17) AIBN, nBu₃SnH, toluene, 30 min

18) DIBAL-H, CH₂Cl₂, then potassium sodium tartrate, 1 h, then TBSCl, imidazole
19) IBX, DMSO, 30 min, then HF·pyridine, THF, 30 min

Step 15: Luche reduction
Step 16/17: Barton-McCombie deoxygenation