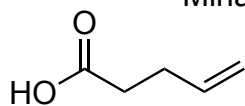


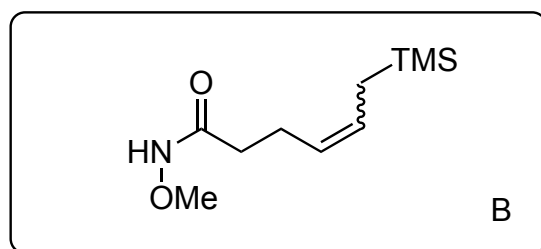
Synthesis Challenge #10 AG Wegner

Total Synthesis of (+-)-Gephyrotoxin by Amide-Selective Reductive Nucleophilic Addition, K. Shirokane, T. Wada, M. Yoritate, R. Minamikawa, N. Takayama, T. Sato, N. Chida, *Angew. Chem. Int. Ed.* **2014**, *53*, 512–516
16.01.2014



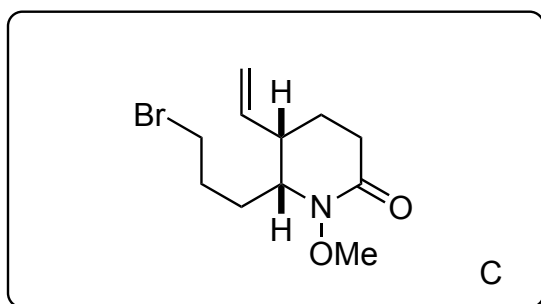
A

1-2



B

3

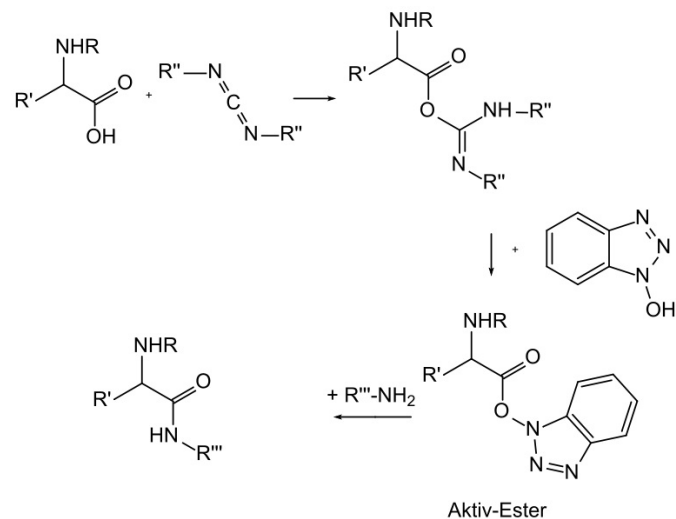


C

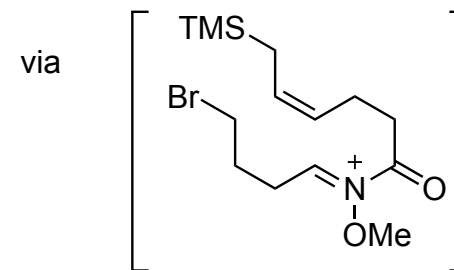
- 1) $\text{H}_2\text{NOMe}\cdot\text{HCl}$, EDCI, HOBT, Et_3N
- 2) Grubbs II, $\text{CH}_2=\text{CHCH}_2\text{TMS}$

- 3) $\text{Br}(\text{CH}_2)_3\text{CHO}$, $\text{BF}_3\cdot\text{Et}_2\text{O}$

Please, provide a detailed Mechanism for step 1).

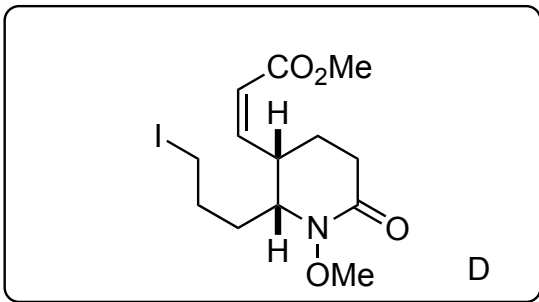


Please, provide a detailed mechanism for step 3).

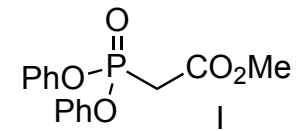


OMe-group increases electrophilicity of N.

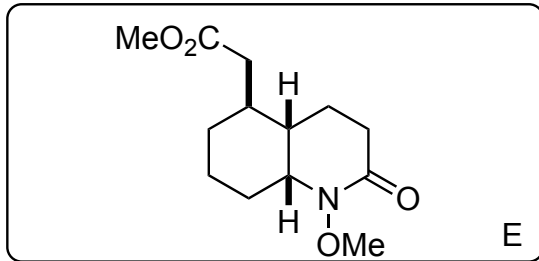
4-5



4) O₃, MeOH, -78°C, Me₂S, RT
5) I, DBU, NaI

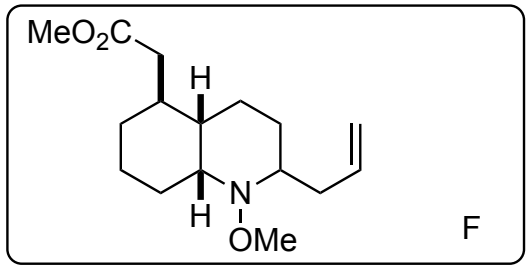


6



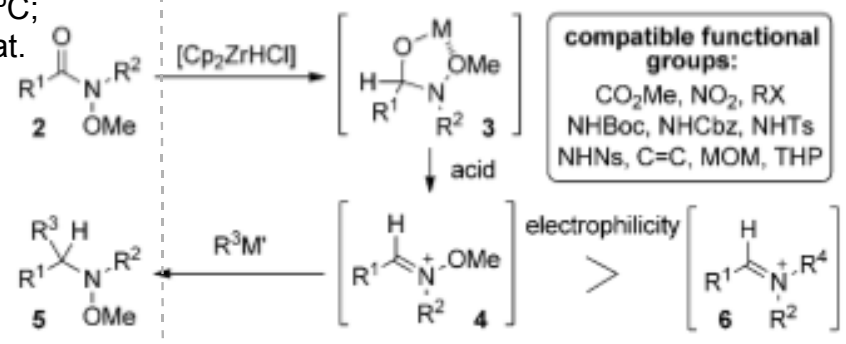
6) AIBN, Bu₃SnH, Toluene, 80°C

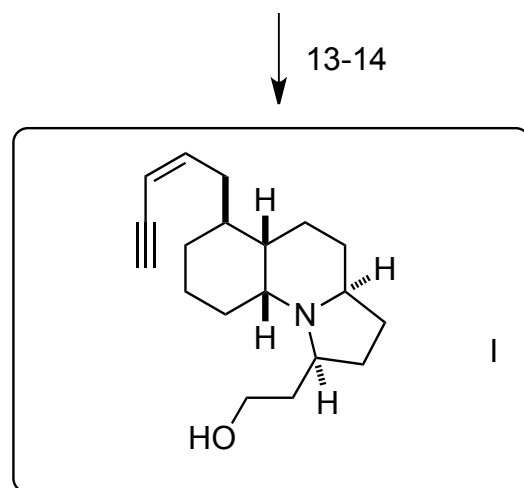
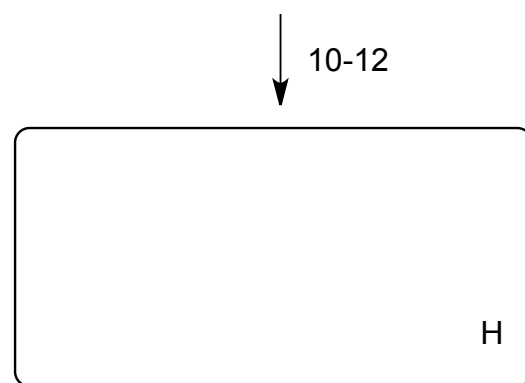
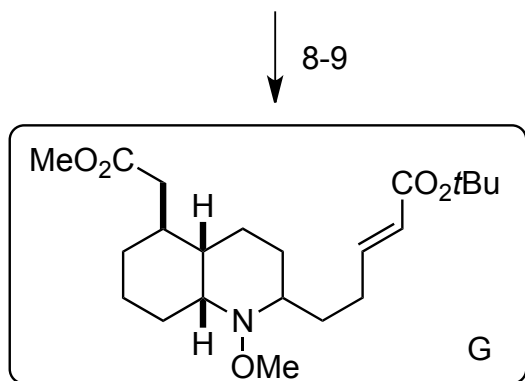
7



7) [Cp₂ZrHCl], CH₂Cl₂, 0°C;
CH₂=CHCH₂SnBu₃, cat.
Sc(OTf)₃

Please, provide mechanism for step 7)





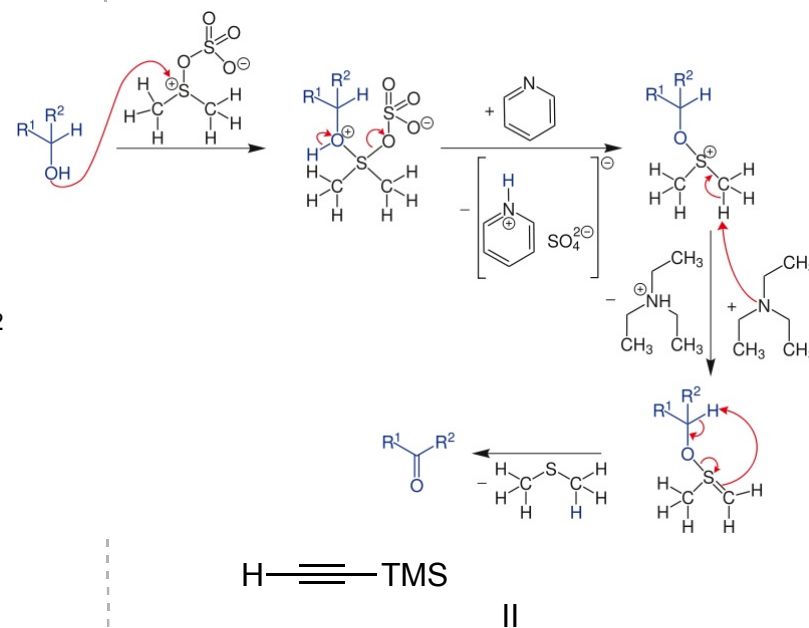
8) hexylborane, THF, 0°C;
NaBO₃, RT
9) SO₃*Py, *i*Pr₂NEt,
DMSO/CH₂Cl₂, RT;
Ph₃P=CHCO₂*t*Bu

10) Zn, AcOH/H₂O
11) NaAlH(O*t*Bu)/Bu₂
12) Ph₃P⁺CH₂I⁻, NaN(TMS)₂
THF/HMPA, -78°C to RT

13) II, [Pd(PPh₃)₄], CuI, Et₃N, RT;
K₂CO₃, MeOH, RT
14) DIBALH, Et₂O, -78°C;
NaBH₄, MeOH

What is the name of the reaction in step 9)?

Parikh-Doering oxidation, followed by
Wittig olefination



What is the name of the reaction in step 13? What is the purpose of CuI?

Sonogashira reaction, Complexation of
the acetylene to facilitate deprotonation
for the formation of the Cu-acetylide in
situ, which act as the coupling agent