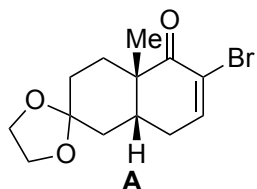


Total Synthesis of (-)-Batrachotoxinin A: A Local-Desymmetrization Approach

Y. Guo, Z. Guo, J.-T. Lu, R. Fang, S.-C. Chen, T. Luo

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1 - 3

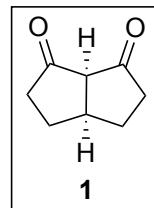


4/5



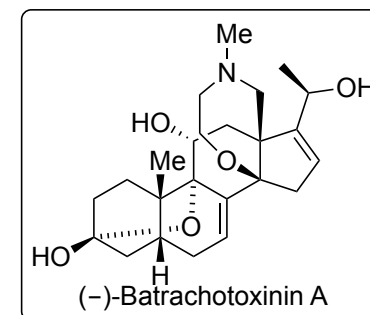
- 1) *t*-BuLi, ethyl vinyl ether, *then A*, *then* aq. HCl
- 2) (+)-CSA, MeOH
- 3) TMSOTf, TEA, *then* NBS

- 4) Ru(bpy)₃Cl₂·6H₂O (2 mol%), H₂NCH₂CH₂NMe₂·HOTf, **1**, NaHCO₃, 65W CFL
- 5) *t*-BuLi, *then* MeOH



step 1: How would you prepare **A** from the Hajos-Parrish ketone?

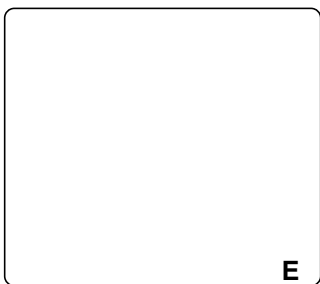
Hint step 2: a 6-membered acetal is formed



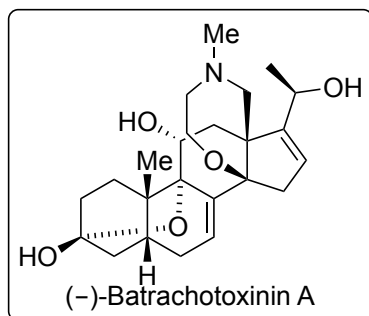
6 - 9



9 - 11



12 - 15



- 6) TMSOTf, TEA
- 7) Pd(OAc)₂
- 8) DIBAL, then LAH
- 9) *p*TsOH, (MeO)₂CMe₂, then O₃, MeOH then NaBH₄

- 10) *p*TsOH (0.01 equiv), then *o*-NO₂PhSeCN, PBU₃, then H₂O₂
- 11) (+)-CSA, MeOH, then NaIO₄

- 12) NaBH(TFA)₃, MeNH₂, ClCH₂COCl, then EtONa
- 13) ¹O₂, then Ac₂O
- 14) MeMgBr
- 15) LAH, then aq. HCl

step 6/7: name reaction?

Hint step 8: a total of 2 [H] and 1 deprotection occur

Hint step 9: a 6-membered heterocycle forms

step 10: name reaction?

Hint step 10: a re-acetalization occurs

step 13: name reaction?