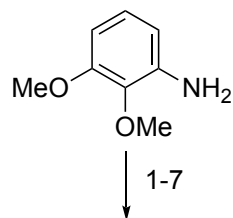
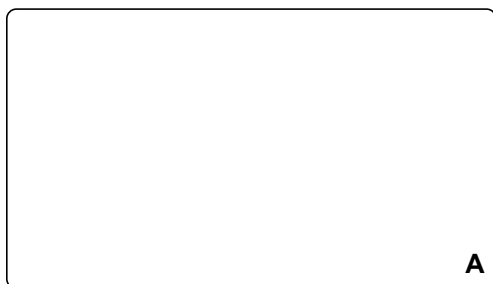


Unified Divergent Total Synthesis of Discorhabdin B, H, K, and Aleutianamine via the Late-Stage Oxidative N,S-Acetal Formation

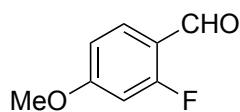
M. Shimomura, K. Ide, J. Sakata, H. Tokuyama*
J. Am. Chem. Soc. **2023**, *145*, 33, 18233–18239



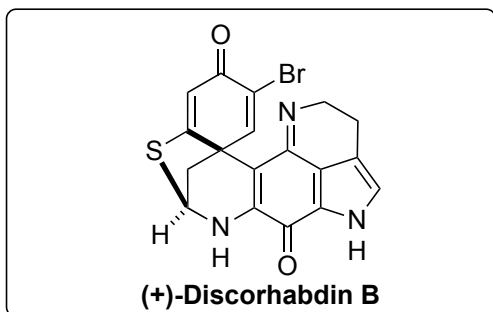
1-7



A

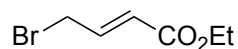


8-14

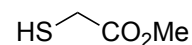


(+)-Discorhabdin B

- 1) ICl, Na₂CO₃
- 2) **1**, NaHCO₃
- 3) Pd(OAc)₂ P(*o*-tolyl)₃, NEt₃
- 4) LAH
- 5) DPPA, DIAD, PPh₃
- 6) TsCl, KOTBu
- 7) PIFA, TMSOTf, HFIP:H₂O stop here for **A**



1



2

- 8) **2**, K₂CO₃, DMF
- 9) Mg, AcOH, MeOH
- 10) NaOH, MeOH
- 11) DPPA, NEt₃, tBuOH, Δ
- 12) Na, NH₃
- 13) PivCl, NEt₃
- 14) 4M HCl in dioxane
- 15) **A**, MeOH
- 16) PIFA, TFE, air
- 17). PyHBr₃
- 18) CuBr₂ cat., air
- 19) NaOMe, MeOH

- 1) Hint: ICl gives *o*-anilines
- 5) Name of reaction?

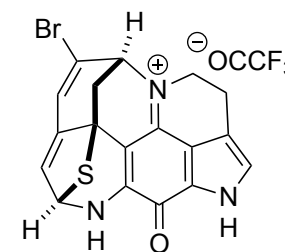
- 7) Hint: start with coordination of PIFA to the
- 8) Name of heterocycle?

- 9) These conditions can reduce α,β-esters

- 11) Name of rearrangement?

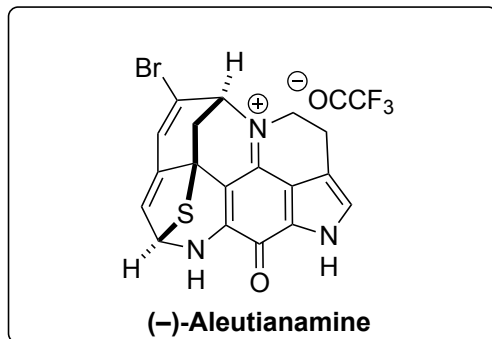
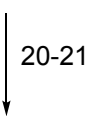
- 12) Hint: It is not a Birch reduction, there is a bond that is easier to cleave.

- 15–21) TFA is used to aid in isolation as a salt.



(-)-Aleutianamine

18



Start with **intermediate 18**
20) NaBH₄, CeCl₃·7H₂O *then* HPLC H⁺
21) NaOMe, MeOH

