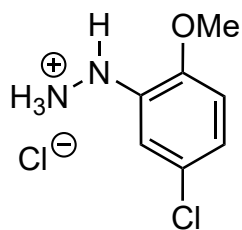


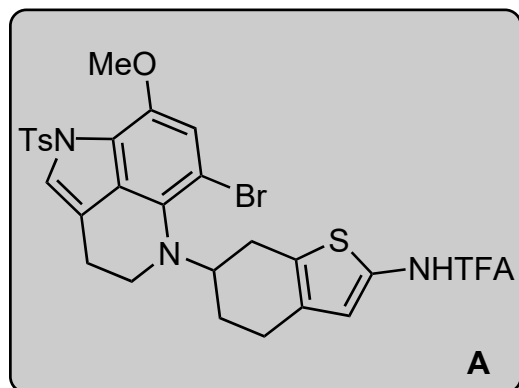
## Total Synthesis of Aleutianamine

H. Yu, Z. P. Sercel, S. P. Rezgui, J. Farhi, S. C. Virgil, B. M. Stoltz

*J. Am. Chem. Soc.* **2023**, *145*, 25533-25537.

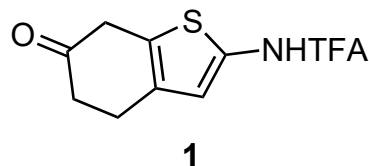


1-7



8 - 14

- 1) H<sub>2</sub>SO<sub>4</sub>, 2,3-dihydrofuran, DMA/H<sub>2</sub>O, 60°C
- 2) DIAD, PPh<sub>3</sub>, DPPA
- 3) TsCl, Bu<sub>4</sub>NHSO<sub>4</sub>, NaOH
- 4) PPh<sub>3</sub>, H<sub>2</sub>O, THF
- 5) BrettPhos Pd G<sub>4</sub>, BrettPhos, K<sub>3</sub>PO<sub>4</sub>
- 6) **1**, InCl<sub>3</sub>, Et<sub>3</sub>SiH
- 7) NBS



- 8) Pd(dba)<sub>2</sub>, XPhos, K<sub>2</sub>CO<sub>3</sub>, 100°C
- 9) TsCl, Py
- 10) NaOH, THF/EtOH, H<sub>2</sub>O, 75°C
- 11) TBSOTf, Et<sub>3</sub>N
- 12) DDQ, 2,6-lutidine, 0°C
- 13) OsO<sub>4</sub>, pyridine
- 14) CDI, DMAP

1) How could you make the starting material?

See solution at bottom of key

2) Name of the reaction?

Mitsunobu

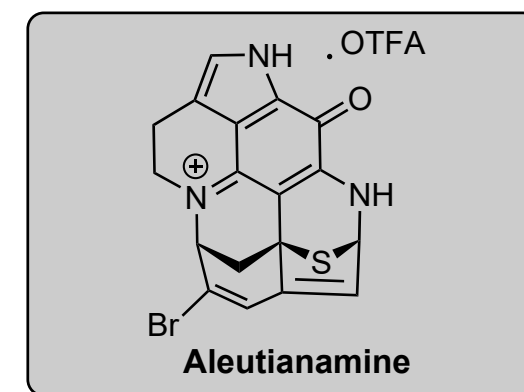
2) Structure of DIAD?

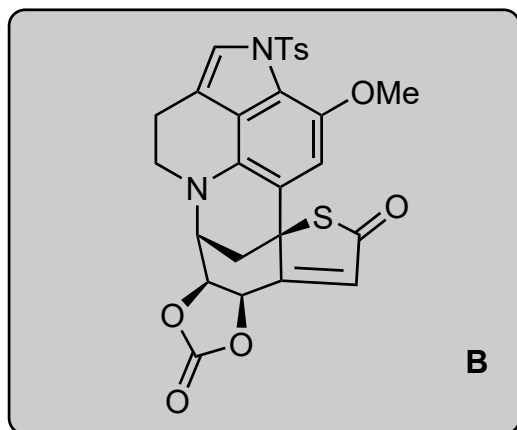
See solution at bottom of key

8) Hint: a new cycle is formed through dearomatization

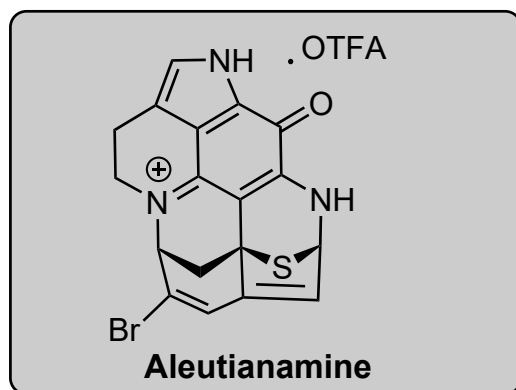
13) Name of the reaction?

Upjohn dihydroxylation

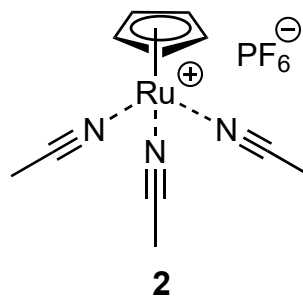




15-20

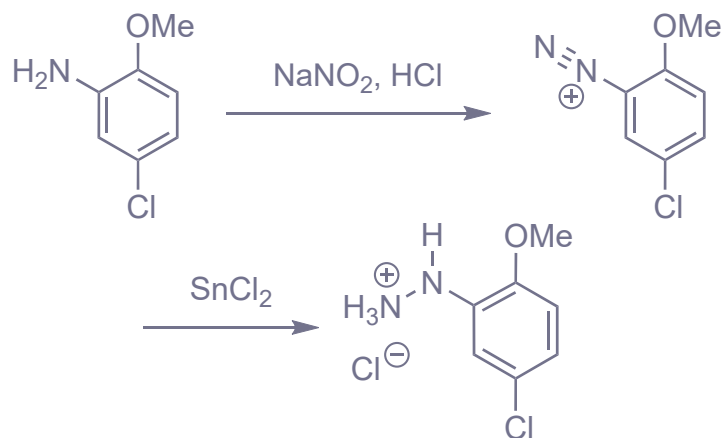


- 15) Pd(PPh<sub>3</sub>)<sub>4</sub>, dppe, 66°C
- 16) Tf<sub>2</sub>O, Et<sub>3</sub>N, -78°C
- 17) **2**, LiBr, NMP, 100°C
- 18) DIBAL-H, -78°C
- 19) CAN, MeCN, 0°C *then* NH<sub>4</sub>OH, O<sub>2</sub>, 0°C, *then* TFA
- 20) NaOMe, MeOH/THF, 0°C

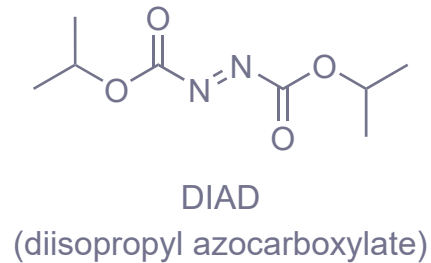


- 15) Suggest a mechanism  
See solution at bottom of key
- 17) Name of Ru catalyst (**2**)  
Shirakawa & Hayashi Ru-catalyst  
for triflate-halogen exchange

**solution to question 1:**



**solution to question 2b:**



**solution to question 15:**

Tsuji-Trost like reaction featuring  $\beta$ -hydride elimination instead of nucleophilic addition

