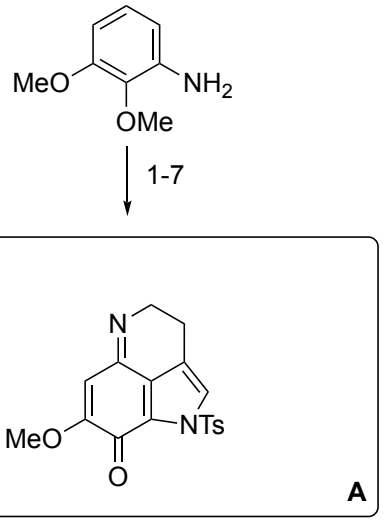
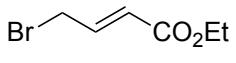
# Unified Divergent Total Synthesis of Discorhabdin B, H, K, and Aleutianamine via the Late-Stage Oxidative N,S-Acetal Formation

M. Shimomura, K. Ide, J. Sakata, H. Tokuyama*

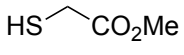
*J. Am. Chem. Soc.* **2023**, *145*, 33, 18233–18239




1) ICl, $Na_2CO_3$
2) **1**, $NaHCO_3$
3) $Pd(OAc)_2$ P(*o*-tolyl)$_3$, $NEt_3$
4) LAH
5) DPPA, DIAD, $PPh_3$
6) TsCl, KOtBu
7) PIFA, TMSOTf, HFIP:$H_2O$ stop here for **A**




**1**




**2**

8) **2,** $K_2CO_3$, DMF
9) Mg, AcOH, MeOH
10) NaOH, MeOH
11) DPPA, $NEt_3$, tBuOH, $\Delta$
12) Na, $NH_3$
13) PivCl, $NEt_3$
14) 4M HCl in dioxane
15) **A,** MeOH
16) PIFA, TFE, air
17). $PyHBr_3$
18) $CuBr_2$ cat., air
19) NaOMe, MeOH

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

7) Hint: start with coordination of PIFA to the azide

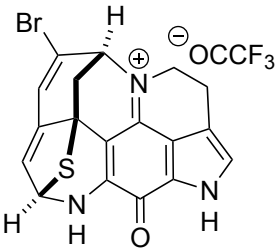
8) Name of heterocycle?
Benzothiophene

9) These conditions can reduce $\alpha,\beta$-unsaturated esters

11) Name of rearrangement?
Curtius

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

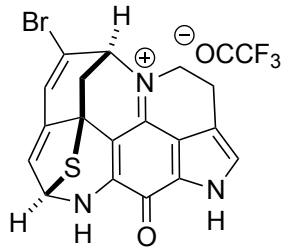
15–21) TFA is used to aid in isolation as a salt.




**(–)-Aleutianamine**

**18**

20-21



**(–)-Aleutianamine**

Start with **intermediate 18**
20) $NaBH_4$, $CeCl_3 \cdot 7H_2O$ *then* HPLC $H^+$
21) NaOMe, MeOH