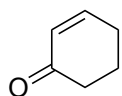


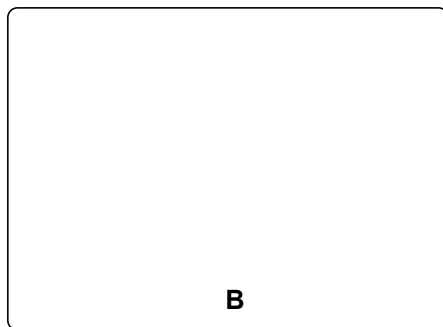
# Total Synthesis of Talatisamine

D. Kamakura, H. Todoroki, D. Urabe, K. Hagiwara, M. Inoue  
*Angew. Chem. Int. Ed.* **2020**, *59*, 479–486.



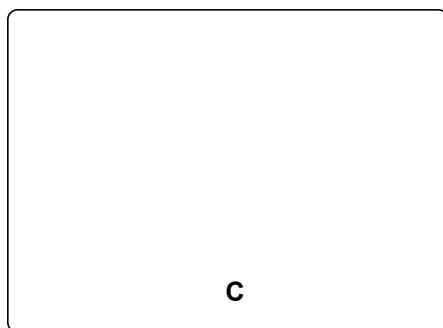
**A**

1-8



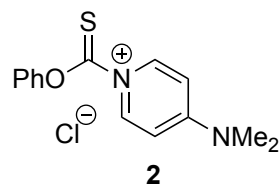
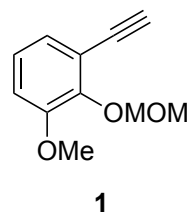
**B**

9-21



**C**

- 1)  $\text{Me}_2\text{PhSiCl}$ , Li,  $\text{Et}_2\text{Zn}$
- 2) NaH, KH,  $(\text{MeO})_2\text{CO}$
- 3)  $\text{LiN}(i\text{-Pr})_2$ ,  $\text{MeOCOCN}$
- 4) HCHO,  $\text{EtNH}_2$
- 5)  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$
- 6)  $\text{CF}_3\text{CO}_2\text{H}$ , AcOOH
- 7) TBSOTf
- 8) **1**,  $\text{EtMgBr}$



- 9) **2**, NaH
- 10) V-40,  $n\text{-Bu}_3\text{SnH}$
- 11)  $\text{H}_2$ , Pd/C
- 12) DIBAL (2 equiv.)
- 13)  $\text{NaN}(\text{TMS})_2$ , MeI
- 14)  $n\text{-Bu}_4\text{NF}$
- 15) NaH, MeI
- 16) DIBAL
- 17) DMP
- 18) Tebbe's reagent
- 19)  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $\text{Me}_2\text{S}$
- 20) HBr, DMSO
- 21) HCl,  $\text{PhI}(\text{OAc})_2$ , MeOH

Hint: 1,4 addition in step 1.

4) Which named reaction takes place?

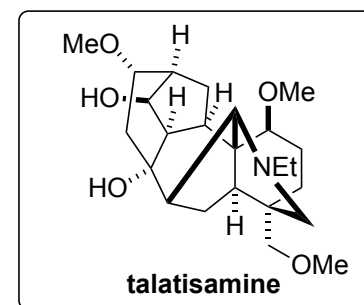
5-6) Please name the reaction sequence.

Hint: In step 8, the product is isolated as a mixture of diastereomers

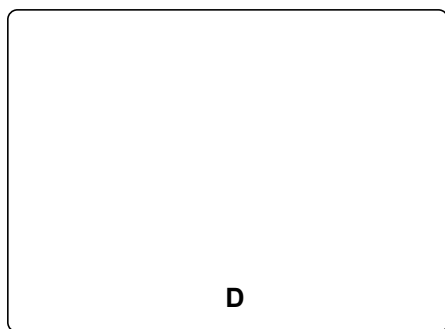
Hint: In step 12, selective reduction of one carbonyl.

18) Structure of Tebbe's reagent?

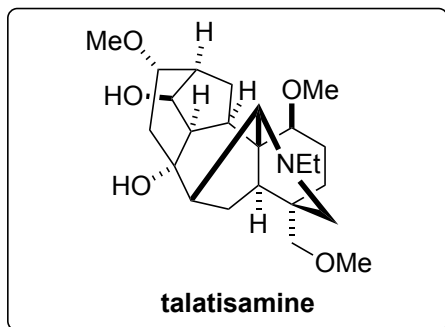
Hint: In step 20, bromination of phenol moiety.



22-28



29-35



- 22) PhMe, reflux
- 23) Ph<sub>3</sub>SnH, AIBN
- 24) DIBAL
- 25) Tf<sub>2</sub>O
- 26) DBU, DMSO
- 27) TIPSOTf, DMDO
- 28) (COCl)<sub>2</sub>, DMSO

- 29) TsNHNH<sub>2</sub>, then NaBH<sub>4</sub>, CeCl<sub>3</sub>·7H<sub>2</sub>O
- 30) catecholborane, NaOAc·3H<sub>2</sub>O
- 31) NaN(TMS)<sub>2</sub>, MeI
- 32) HCl
- 33) NaHCO<sub>3</sub>, NaBH<sub>4</sub>
- 34) Hg(OAc)<sub>2</sub>, AcOH
- 35) 1,4-dioxane, H<sub>2</sub>O, 90 °C

22) Name the reaction and discuss the role of the bromide in the reaction

Hint: In step 29, NaBH<sub>4</sub> does not reduce the hydrozone.

Hint: In step 30, a sigmatropic rearrangement occurs.

30) Structure of catecholborane?

Which reaction takes place in step 34?