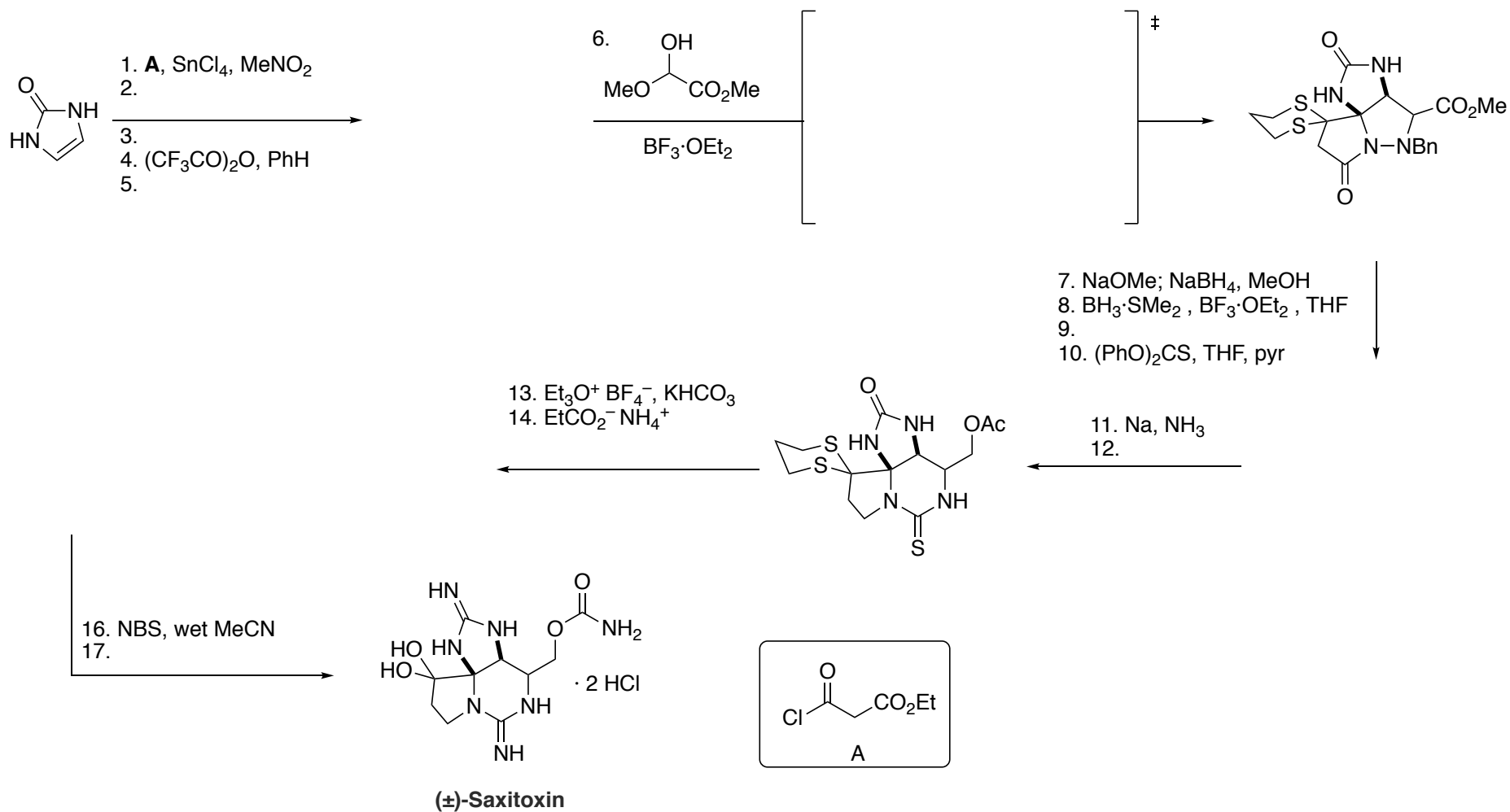


# E42: The Total Synthesis of Saxitoxin (STX)



P. A. Jacobi, M. J. Martinelli, S. Polanc, *J. Am. Chem. Soc.* **1984**, *106*, 5594.

1<sup>st</sup> Generation: J. J. Fleming, J. Du Bois, *J. Am. Chem. Soc.* **2006**, *128*, 3926.

2<sup>nd</sup> Generation: J. J. Fleming, M. D. McReynolds, J. Du Bois, *J. Am. Chem. Soc.* **2007**, *129*, 9964.

First TS: H. Tanino, T. Nakata, T. Kaneko, Y. Kishi, *J. Am. Chem. Soc.* **1977**, *99*, 2818.

Review: A. P. Thottumkara, W. H. Parsons, J. Du Bois, *Angew. Chem. Int. Ed.* **2014**, *53*, 5760.

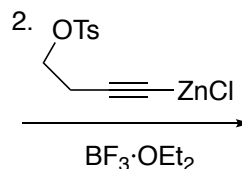


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# E42: The Total Synthesis of Saxitoxin (STX)

1.  $\text{Rh}_2(\text{esp})_2$  (0.3 mol%)  
 $\text{PhI}(\text{OAc})_2$   
 $\text{MgO}$ ,  $\text{CH}_2\text{Cl}_2$

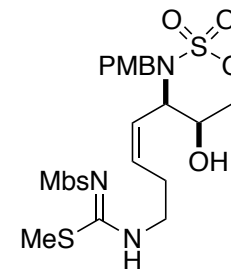


3.

4.

5.

6.  $\text{Me}_3\text{P}$ ,  $\text{H}_2\text{O}/\text{THF}$   
 7.  $\text{MbsN}=\text{C}(\text{Cl})\text{SMe}$ ,  $i\text{Pr}_2\text{NEt}$ ,  
 $\text{MeCN}$



Mbs = 4-Methoxybenzenesulfonyl

8.

9.

10.

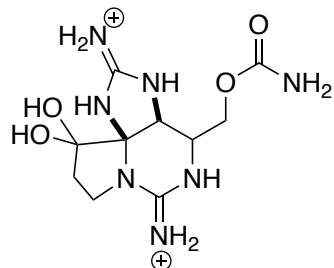
11.  $\text{MbsN}=\text{CCl}_2$ ,  $\text{KO}t\text{-Bu}$  then  
 $\text{TMS}_2\text{NH}$

12.  $\text{H}_2\text{O}$ ,  $\text{MeCN}$

nine-membered  
 ring guanidine

15.  $\text{Cl}_3\text{CC}(\text{O})\text{NCO}$   
 16.  $\text{K}_2\text{CO}_3$ ,  $\text{MeOH}$   
 17.  $\text{OsO}_4$ ,  $t\text{-BuOOH}$

18.  $\text{B}(\text{O}_2\text{CCF}_3)_3$   
 $\text{CF}_3\text{CO}_2\text{H}$   
 19.  $\text{DMSO}$ ,  $\text{DCC}$ ,  
 $\text{C}_5\text{H}_5\text{N}\cdot\text{HO}_2\text{CCF}_3$   
 HPLC with  $\text{C}_3\text{F}_7\text{CO}_2\text{H}$



(+)-Saxitoxin  
 $\cdot 2 (\text{C}_3\text{F}_7\text{CO}_2^-)$

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