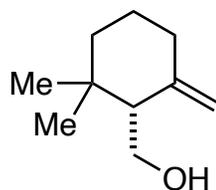


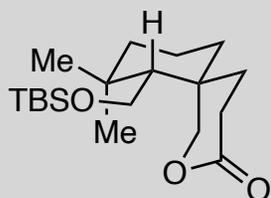
# A Concise Total Synthesis of (-)-Maoecrystal Z

Cha, J. Y.; Yeoman, J. T. S.; Reisman, S. E.

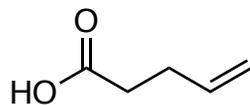
*J. Am. Chem. Soc.* **2011**, *133* (38), 14964-14967.



1-3

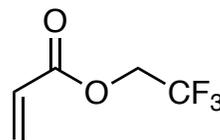


A



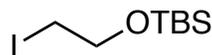
4-7

- 1) TBSCl, imidazole,  $\text{CH}_2\text{Cl}_2$
- 2) *m*-CPBA,  $\text{NaHCO}_3$ ,  $\text{CH}_2\text{Cl}_2$
- 3) **1**,  $\text{Cp}_2\text{TiCl}_2$ ,  $\text{Zn}^0$ , 2,4,6-collidine·HCl, THF, rt



1

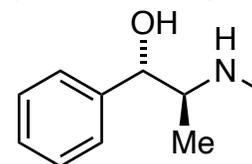
- 4) PivCl,  $\text{Et}_3\text{N}$ , THF, *then* (*S,S*)-pseudoephedrine
- 5) **2**, LDA, LiCl, THF
- 6)  $\text{BH}_3\cdot\text{NH}_3$ , LDA, THF
- 7)  $\text{I}_2$ ,  $\text{PPh}_3$ , imidazole,  $\text{CH}_2\text{Cl}_2$



2

- 1) How would you make the starting material?
- 3) Hint: Loss of trifluoroethanol

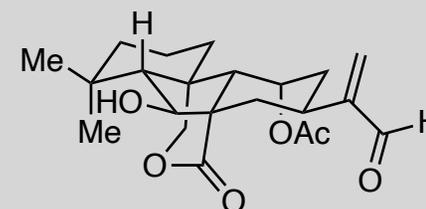
- 4) Structure of pseudoephedrine?



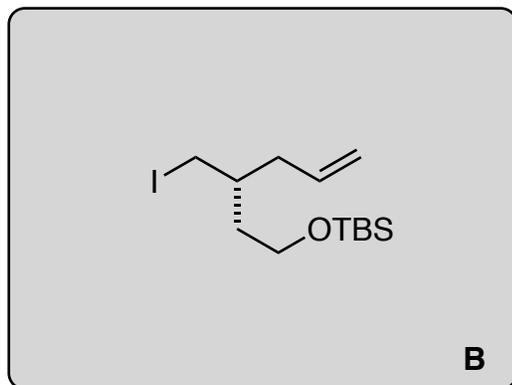
(*S,S*)-pseudoephedrine

- 7) Name of reaction?

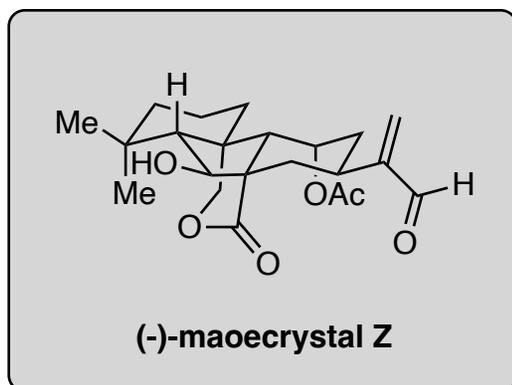
Appel reaction



(-)-maoecrystal Z



8-16

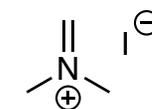


- 8) **A**, LiHMDS, *then* **B**, 4:1 THF/HMPA, 0 to 23 °C
- 9) KHMDS, PhSeBr, -78 °C, *then* H<sub>2</sub>O<sub>2</sub>
- 10) H<sub>2</sub>SiF<sub>6</sub>, CH<sub>3</sub>CN
- 11) DMP, CH<sub>2</sub>Cl<sub>2</sub>
- 12) Sml<sub>2</sub>, LiBr, *t*-BuOH, THF, -78 °C
- 13) Ac<sub>2</sub>O, TMSOTf, CH<sub>2</sub>Cl<sub>2</sub>
- 14) O<sub>3</sub>, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>
- 15) Eschenmoser's salt, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>
- 16) 1M NaOH, 1:1 MeOH/H<sub>2</sub>O

10) Hint: 3.7 eq H<sub>2</sub>SiF<sub>6</sub>

12) Hint: two rings formed

15) Structure of Eschenmoser's salt?



Eschenmoser's salt