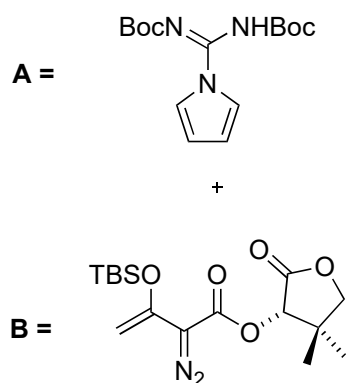


## A concise synthesis of (+)-batzelladine **B** from simple pyrrole-based starting materials

Parr, B.T.; Economou, C.; Herzon, S. *Nature* **2015**, *525*, 507-510.



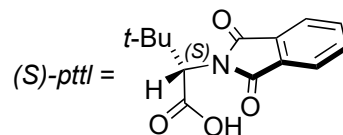
1-3



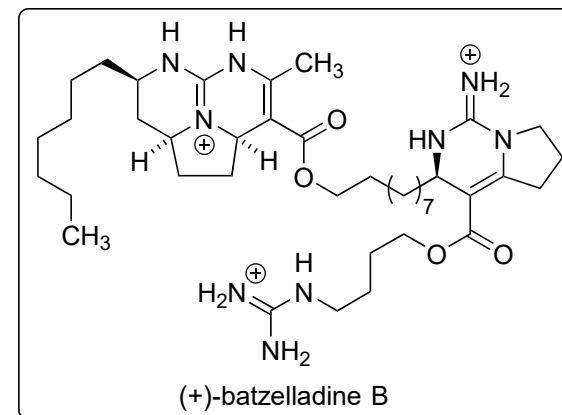
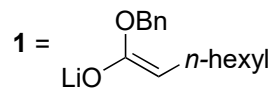
4-6



- 1) slow addition of **B**  
Rh<sub>2</sub>[(*S*)-pttl]<sub>4</sub> (0.5 mol%), pentane, reflux, 3 h
- 2) H<sub>2</sub> (30 bar), ClRh(PPh<sub>3</sub>)<sub>3</sub> (2 mol%), rt, 24 h
- 3) TMS-EBX (1.2 eq.), TBAF (2.4 eq.),  
THF/CH<sub>2</sub>Cl<sub>2</sub>, -78 °C, 3 h



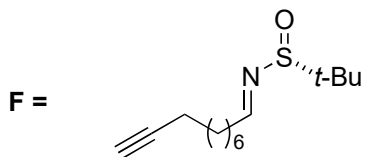
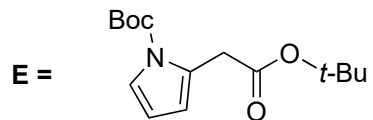
- 4) *n*-BuLi (1.0 eq), THF, -78 °C, 1 h,  
then **1** (1.8 eq), -78 °C, 3 h,  
then DMPU, -78 °C, 30 min
- 5) H<sub>2</sub>, Pd/C, THF, rt, 6 h
- 6) LiOH, THF/H<sub>2</sub>O, 0 °C, 1 h



*Step 1: Reaction type?*

*Step 3: Structure of TMS-EBX? Reaction Mechanism?*

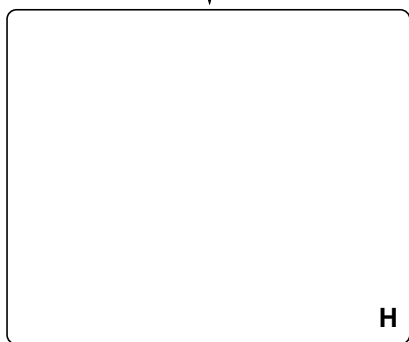
*Mechanism of Step 4?*



7-9

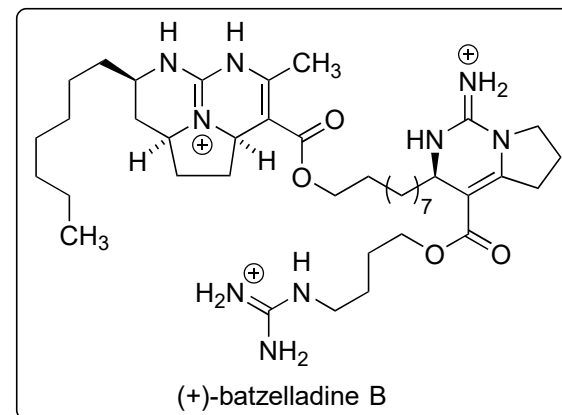
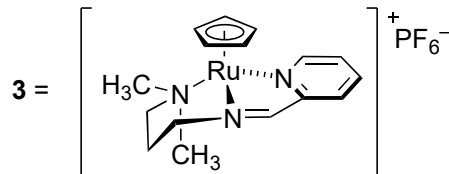
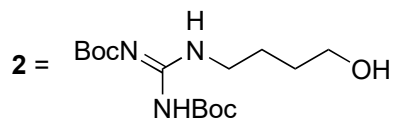


10-13



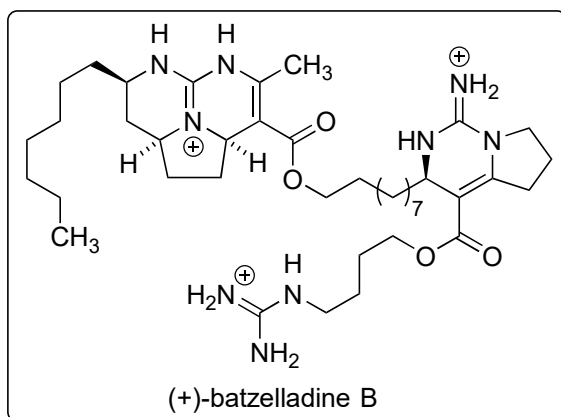
- 7) LDA, Ti(O*i*-Pr)<sub>3</sub>Cl, THF, -78 °C, 2 h
- 8) HCl, MeOH/dioxane, 0 °C, 2 h
- 9) (ClSnBu<sub>2</sub>)<sub>2</sub>O, PhCH<sub>3</sub>, 100 °C, 2 h

- 10) EtOTf, 2,4,6-tri-*t*-butylpyrimidine, CH<sub>2</sub>Cl<sub>2</sub>, rt, 43 h
- 11) DMBNH<sub>3</sub>, EtOH, 70 °C, 5 days
- 12) TMSOTf, 2,6-lutidine, CH<sub>2</sub>Cl<sub>2</sub>, rt, 40 h  
then EDC·HCl, **2**, 2 h
- 13) **3** (15 mol%), HCO<sub>2</sub>H (4 eq.), *p*-TSA (1 eq), NMP/H<sub>2</sub>O, rt, 72 h



D + H

↓ 14, 15



14) EDC•HCl, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, rt, 14 h

15) TFA, Pd/C, 0 °C to rt, 1 h  
then H<sub>2</sub>, rt, 15 h