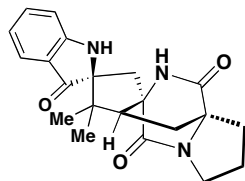
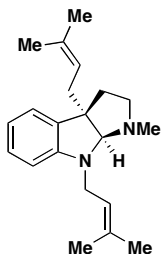


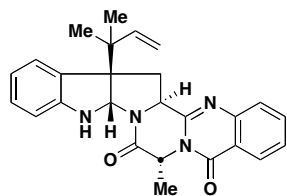
Syntheses Discussed:



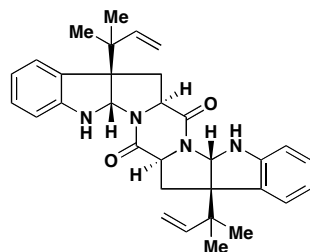
ent-Brevianamide B
Williams, *JACS*, 1990, 808



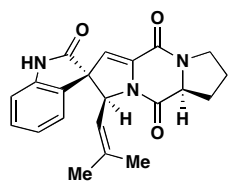
ent-Debromoflustramine B
Crich, *JOC*, 1994, 5543



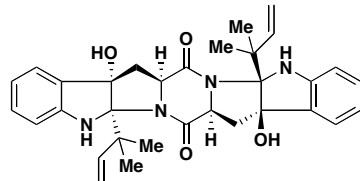
Ardeemin
Danishefsky, *JACS*, 1999, 11953



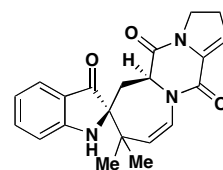
Amauromine
Danishefsky, *JACS*, 1999, 11953



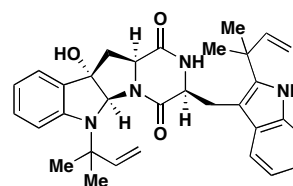
Spirotryprostatin B
Williams, *JACS*, 2000, 5666
Danishefsky, *ACIEE*, 2000, 2175
Carreira, *ACIEE*, 2003, 694
Horne, *ACIEE*, 2004, 5357



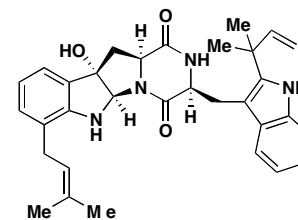
Gypsetin
Danishefsky, *JACS*, 1999, 11964



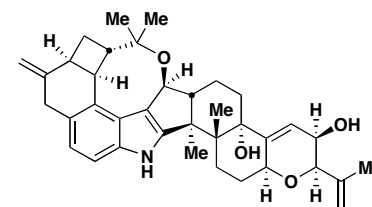
Austamide
Corey, *JACS*, 2002, 7904



Okaramine C
Ley, *OBC*, 2004, 2415

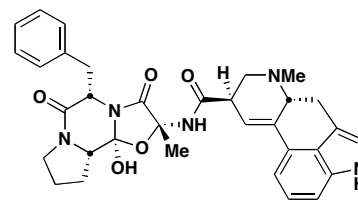


Okaramine J
Ganesan, *OL*, 2003, 2825

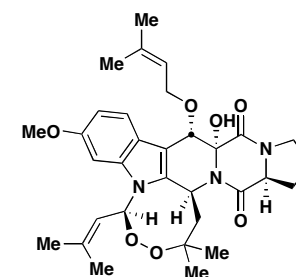


Penitrem D
Smith, *JACS*, 2000, 11254

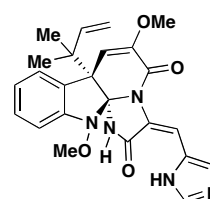
For your consideration:



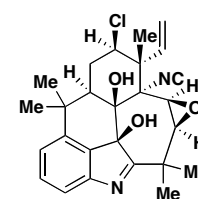
Ergotamine



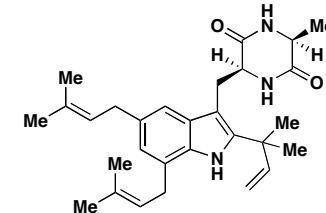
Fumitremorgin A



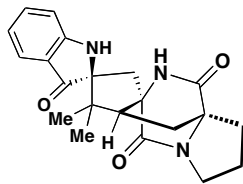
Oxaline



Ambiguine D
isonitrile

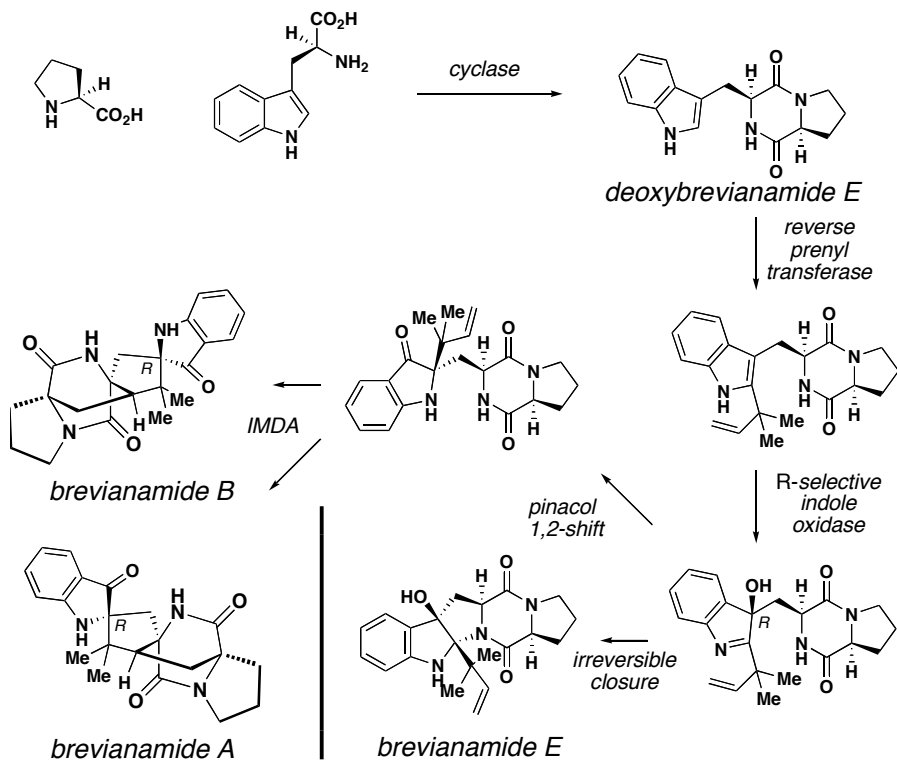


Echinulin

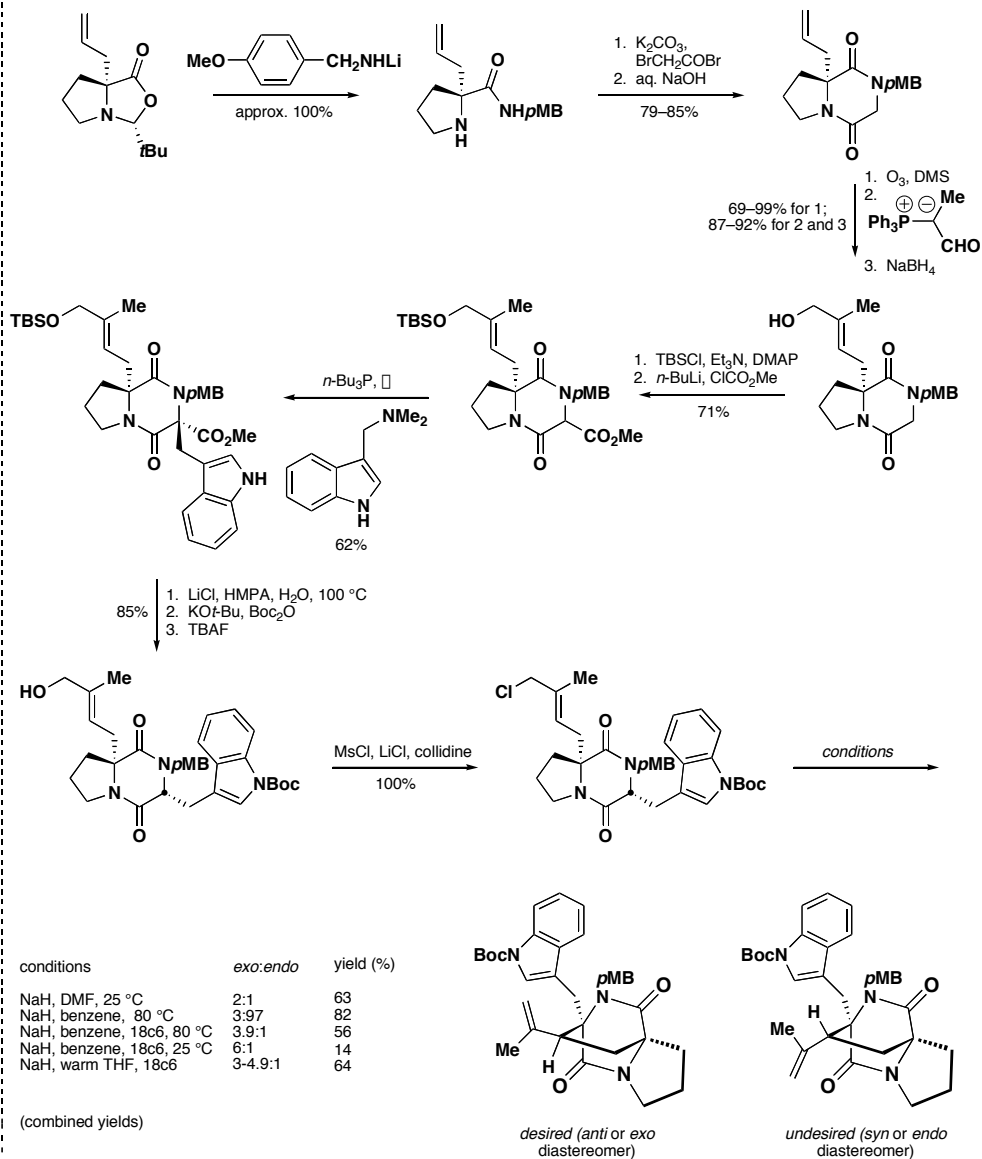


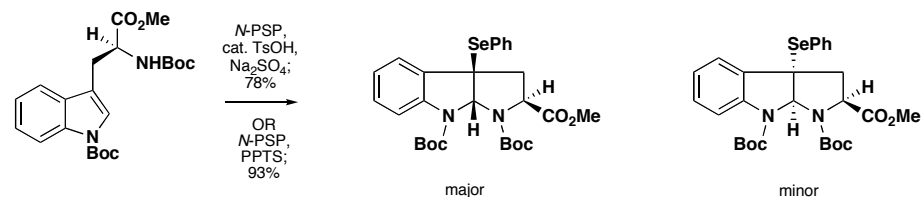
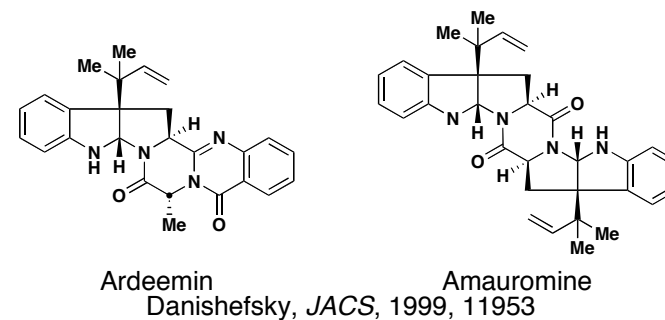
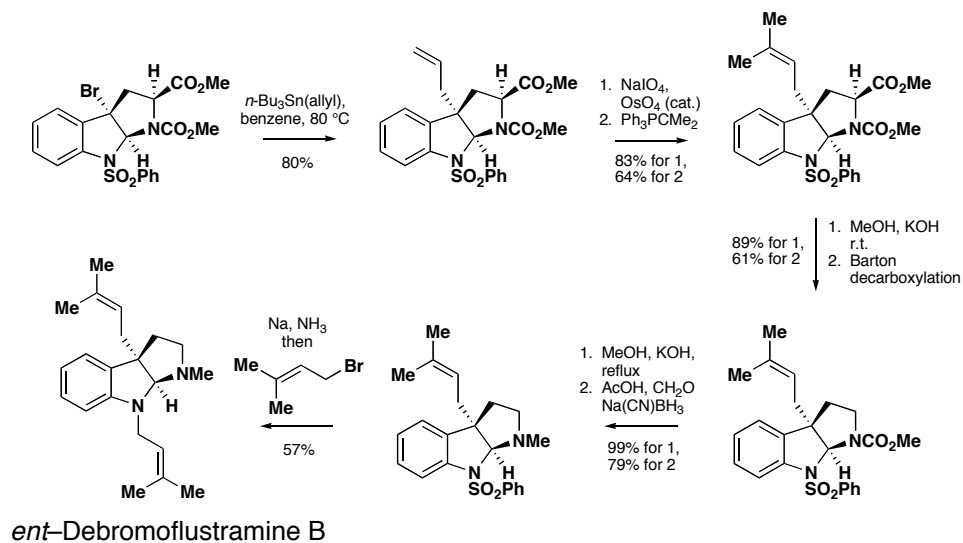
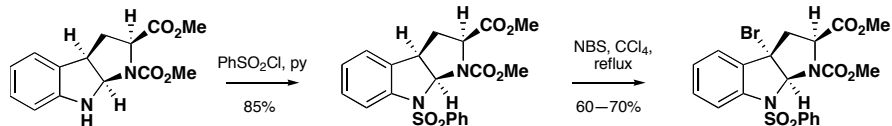
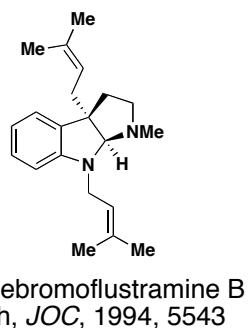
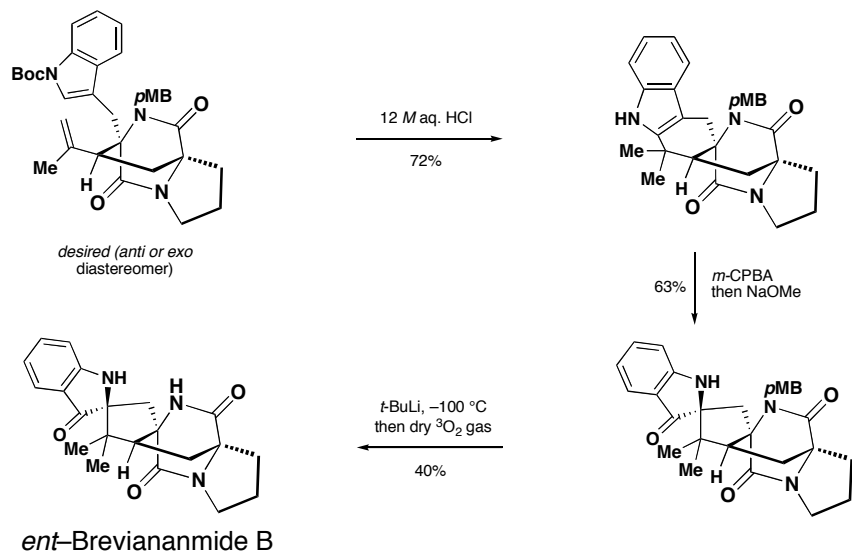
ent-Brevianamide B
Williams, *JACS*, 1990, 808

Biosynthesis: Most of the brevianamides are comprised of a tryptophan-proline diketopiperazine and a single prenyl unit. Usually, the prenyl unit is attached to the indole in a reversed sense to C2 of indole. A set of events that explains both the abundance and results of feeding experiments is outlined below:

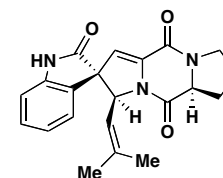
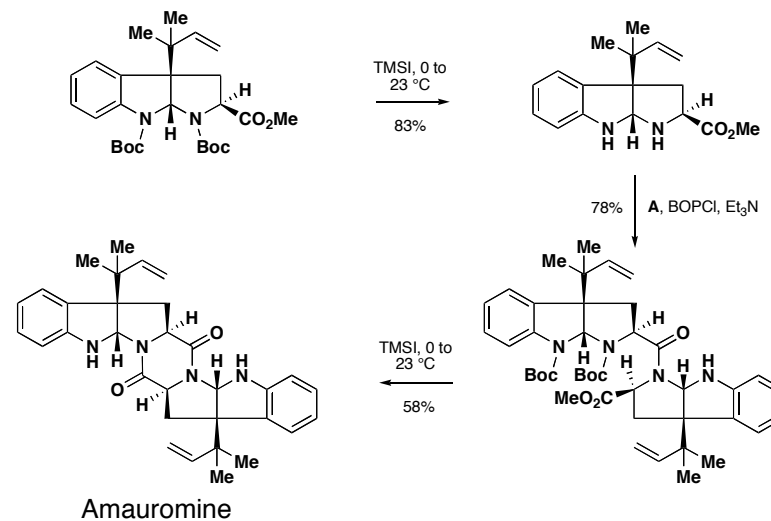
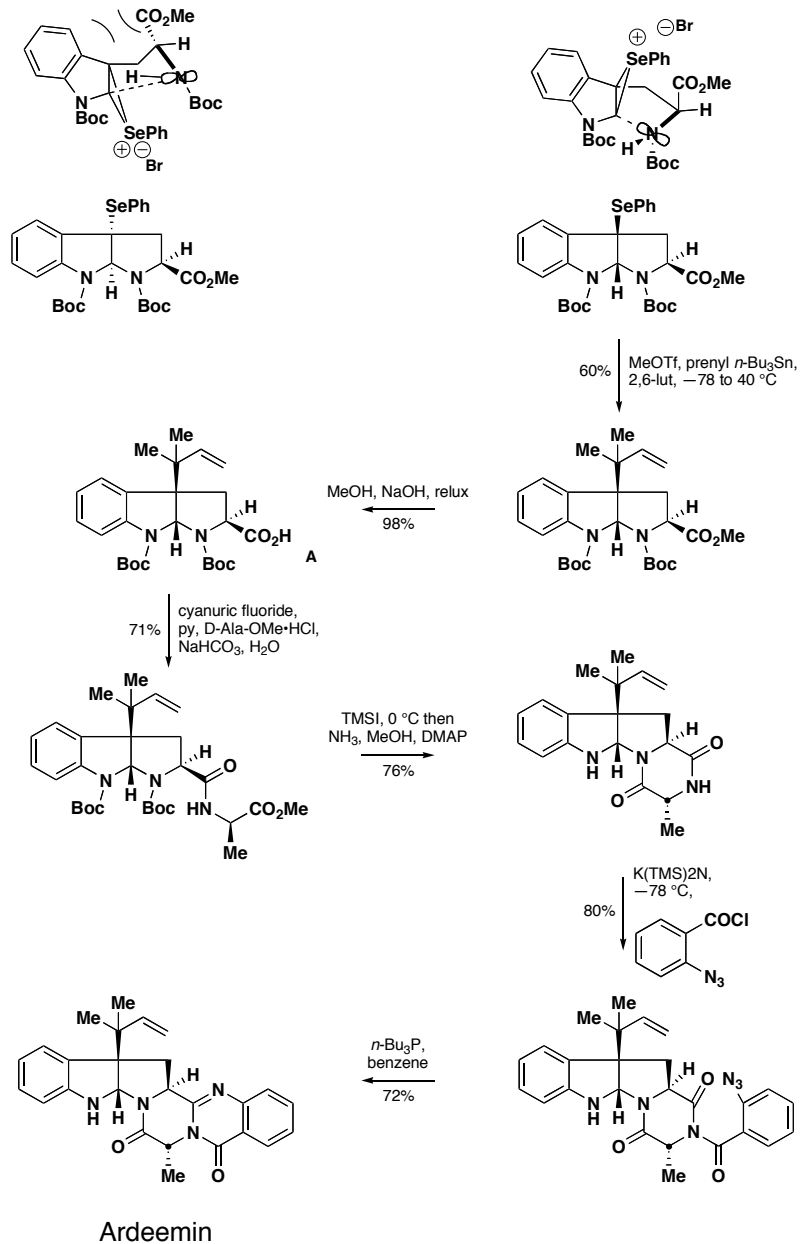
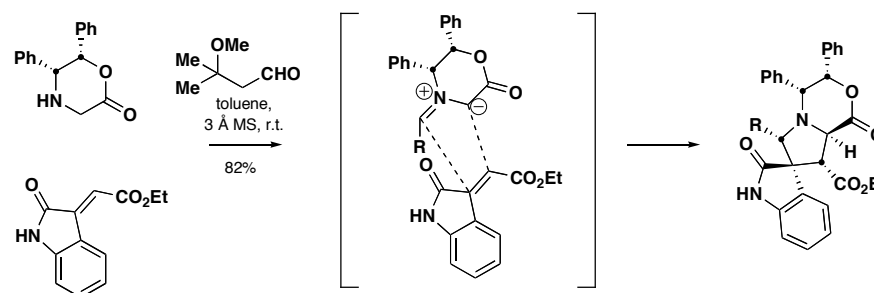


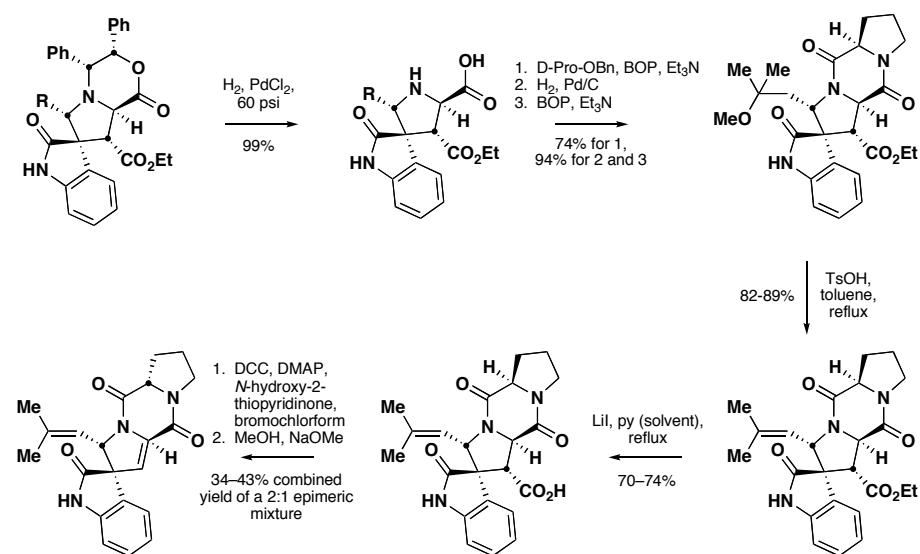
Synthesis:



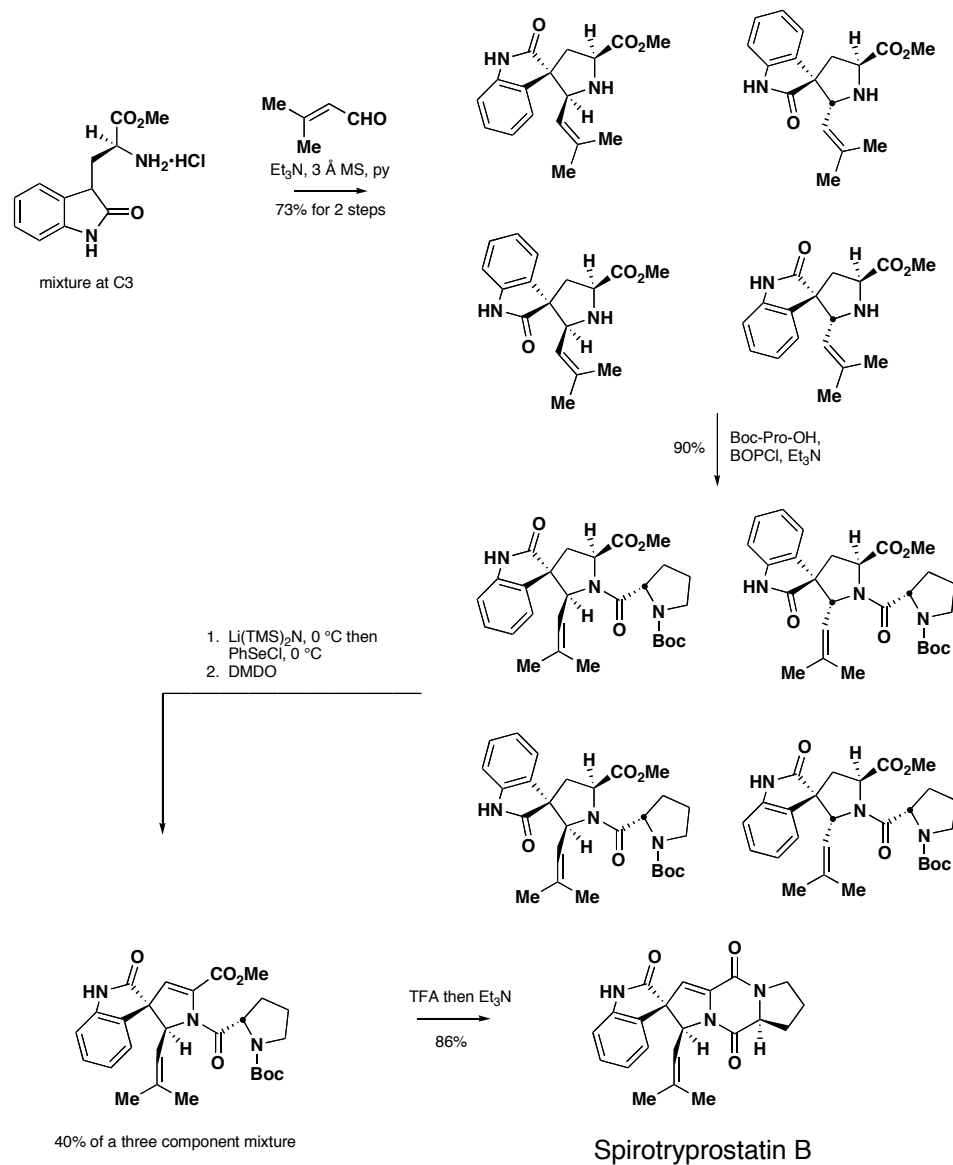
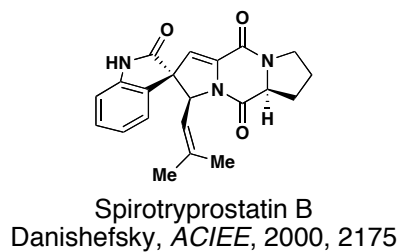


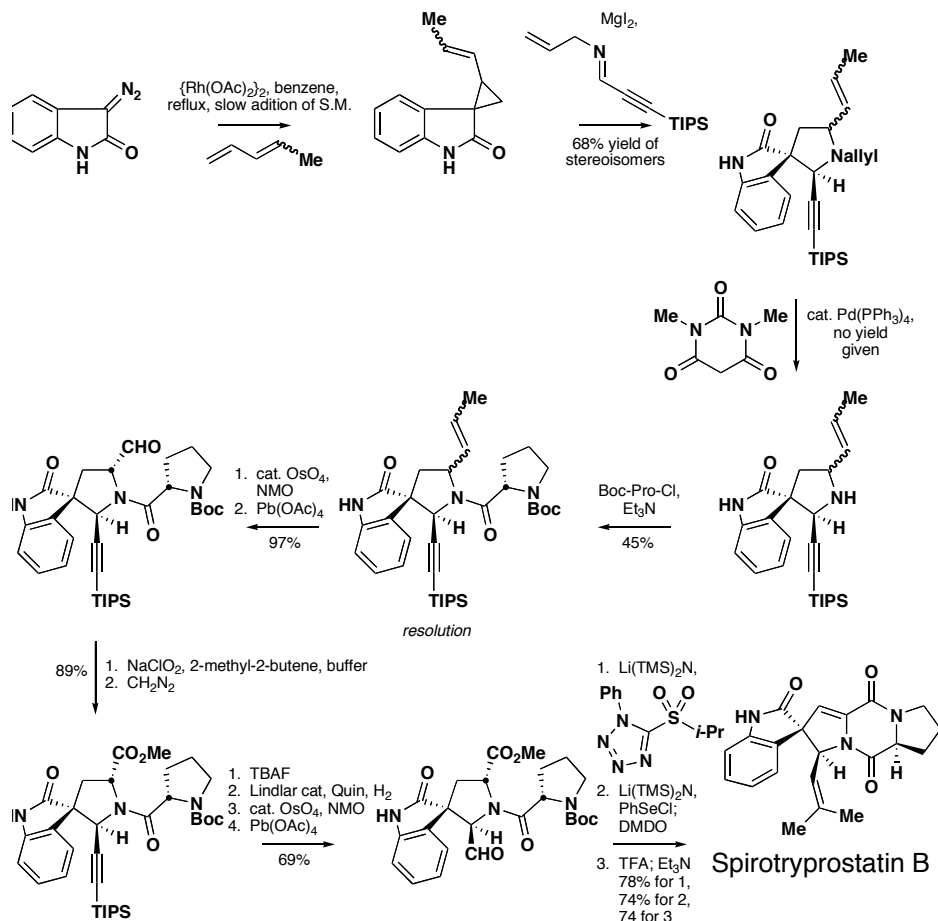
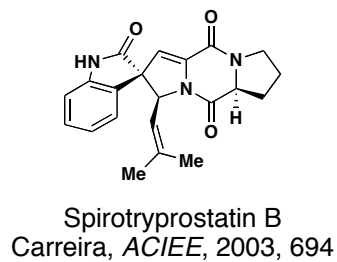
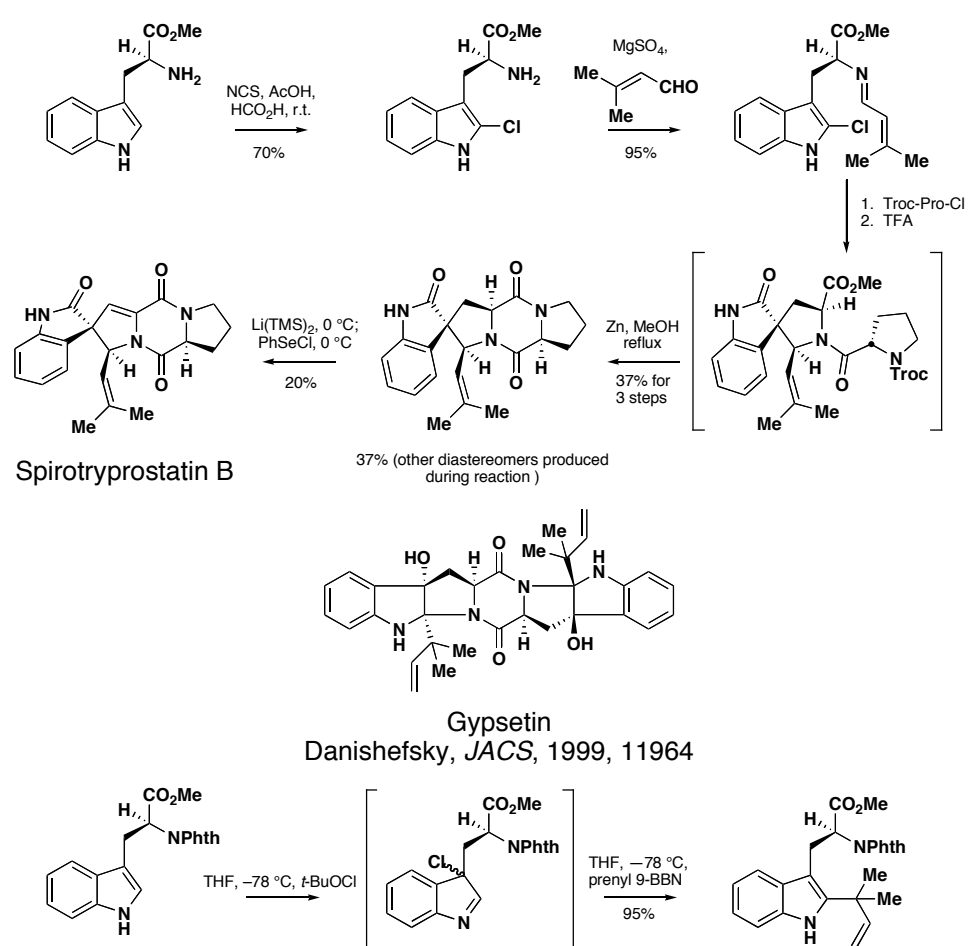
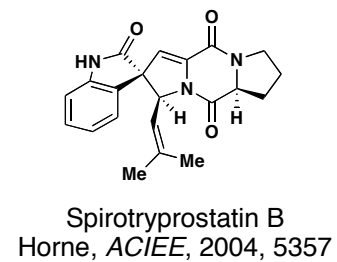
Rationalize the relative product distributions. Hint: the cyclization is irreversible under the reaction conditions.

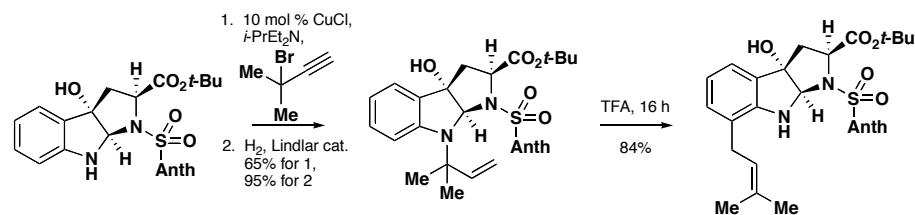
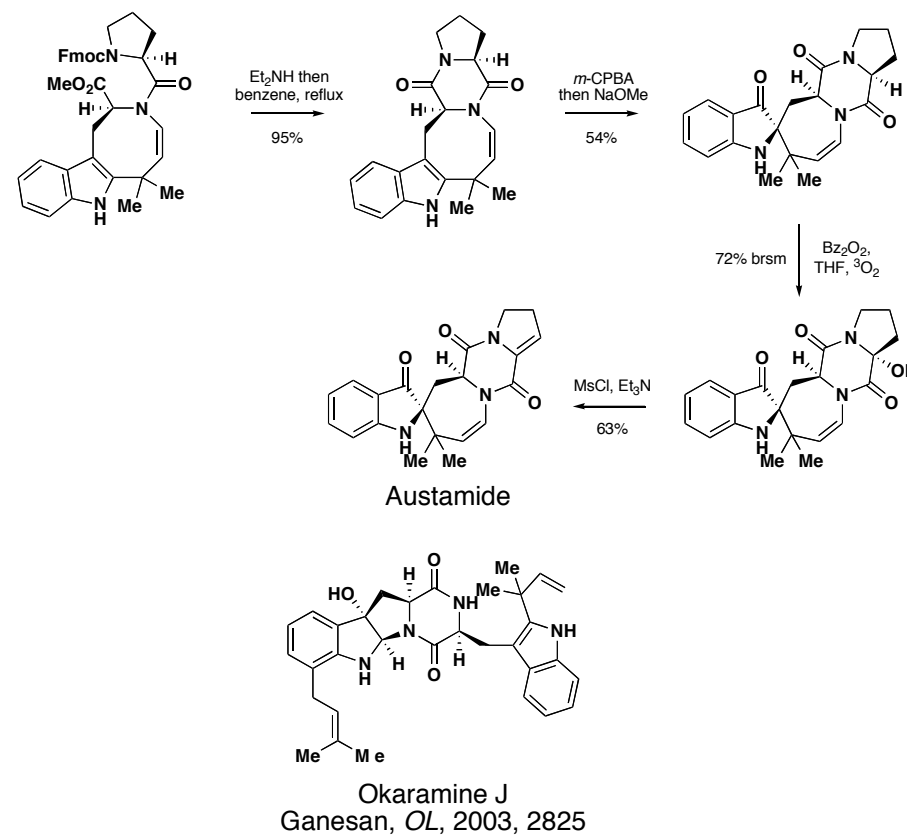
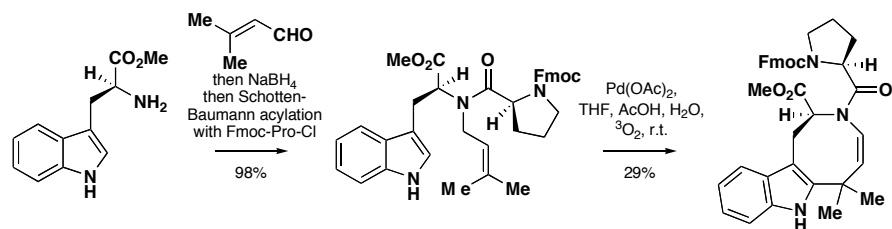
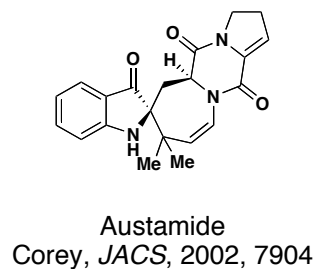
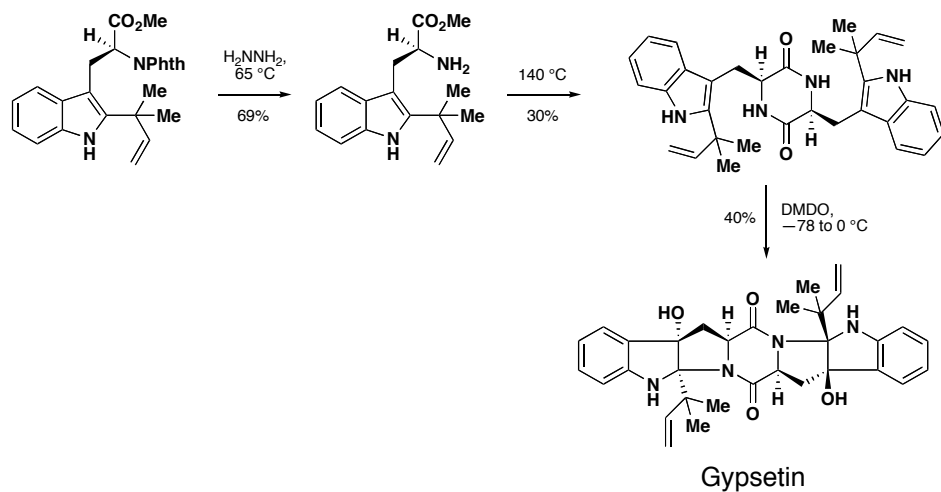
Williams, *JACS*, 2000, 5666

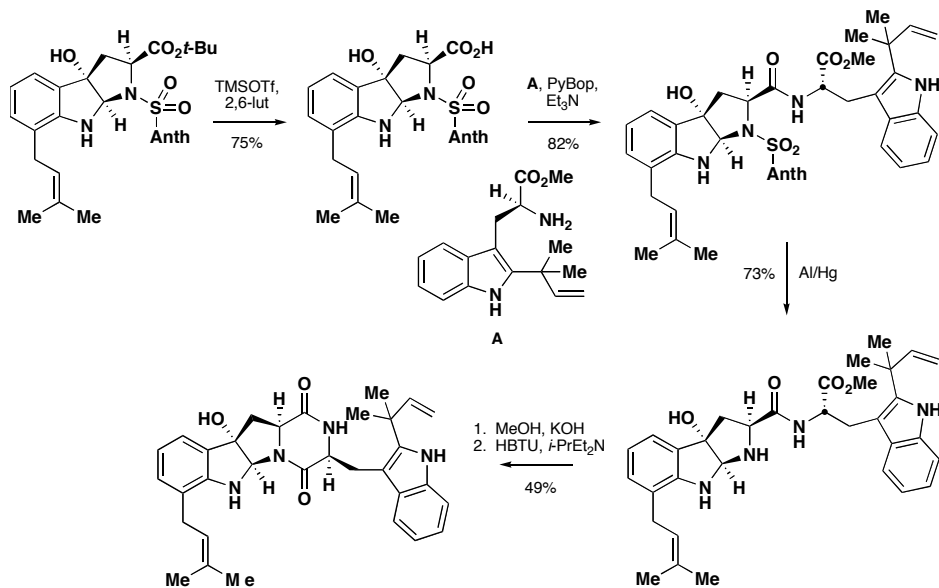


Spirotryprostatin B

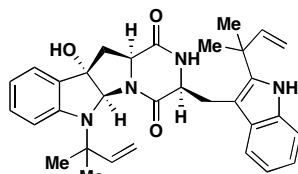
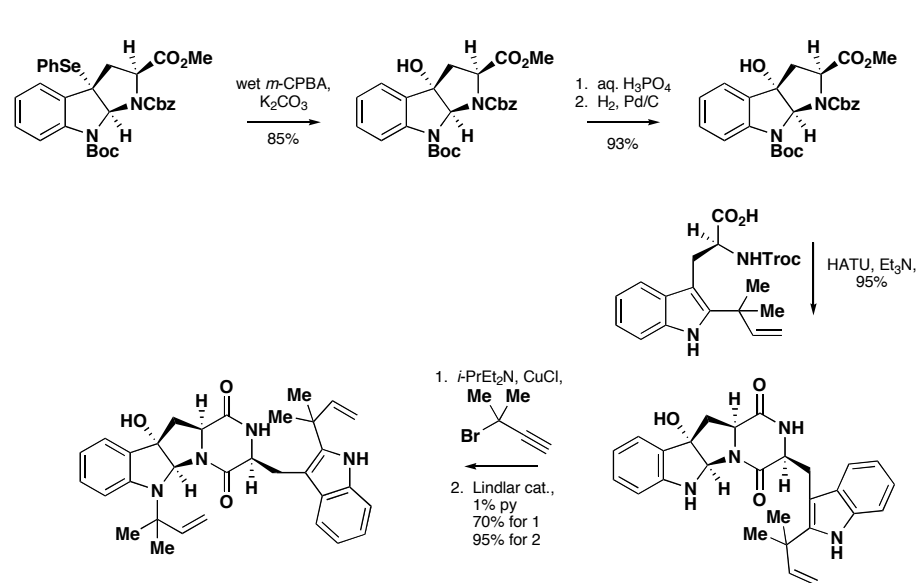
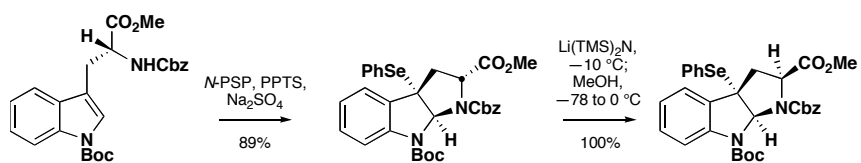


Carreira, *ACIEE*, 2003, 694Horne, *ACIEE*, 2004, 5357
Danishefsky, *JACS*, 1999, 11964

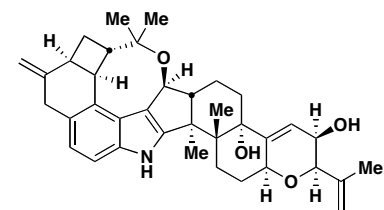
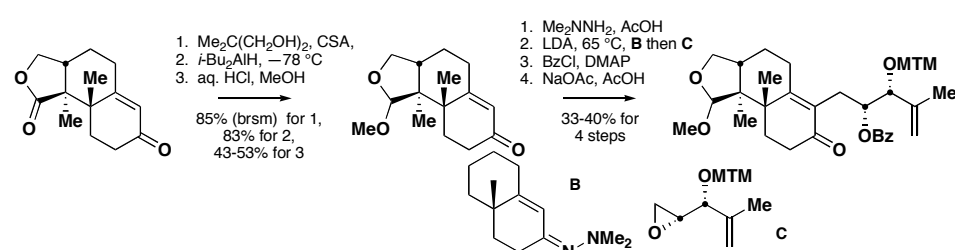


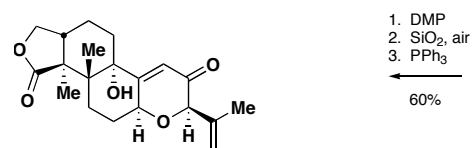
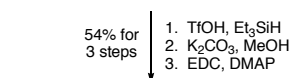
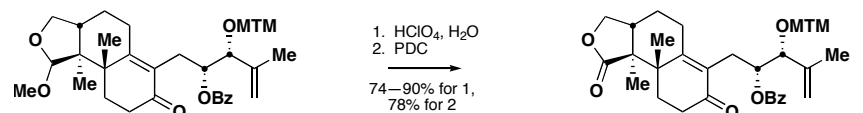


Okaramine J

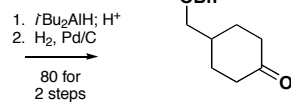
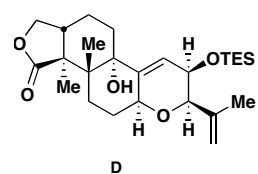
Okaramine C
Ley, *OBC*, 2004, 2415

Okaramine C

Penitrem D
Smith, *JACS*, 2000, 11254

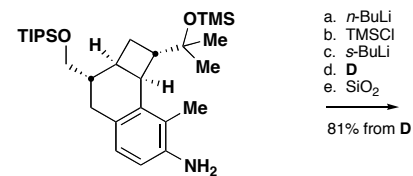
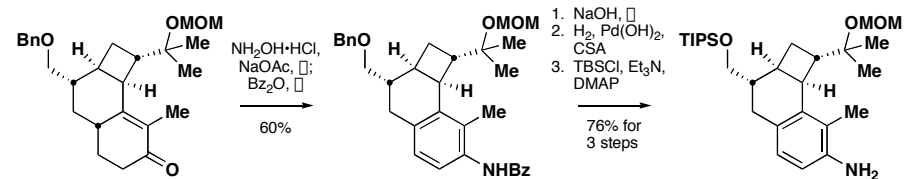
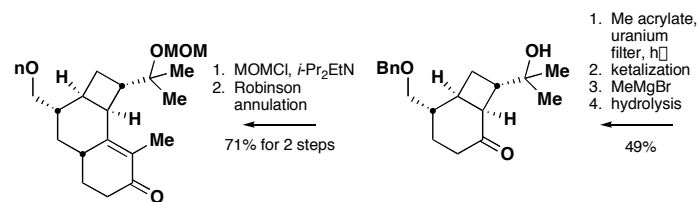


76% for
2 steps

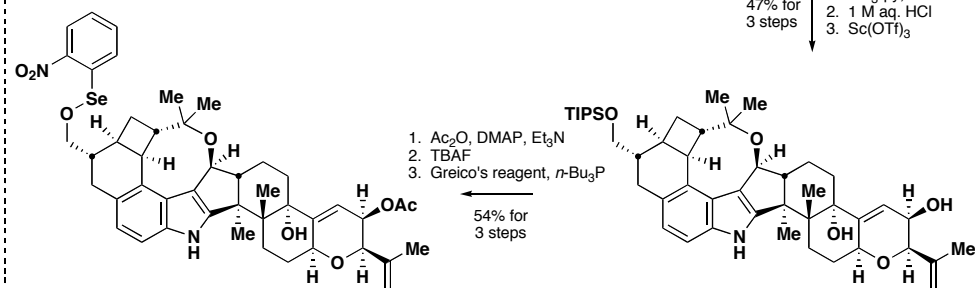
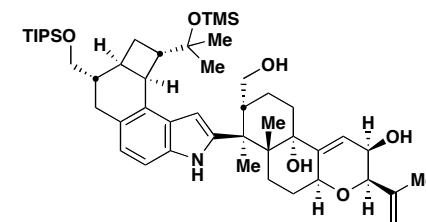


ca. 60%

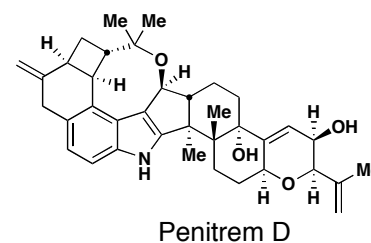
1. Scalemic amine,
 $n\text{-BuLi}$; TMSCl
2. $^1\text{O}_2$; PPh_3



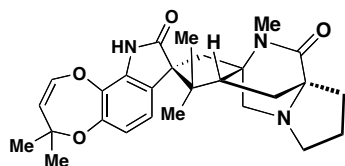
similarly prepared



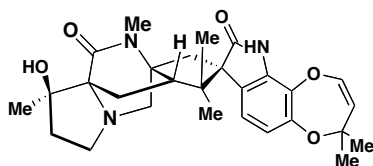
52% for
2 steps



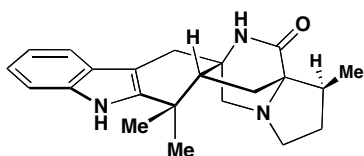
Other notable syntheses:



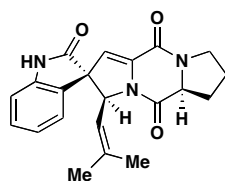
Paraherquamide B
Williams, *JACS*, 1996, 557



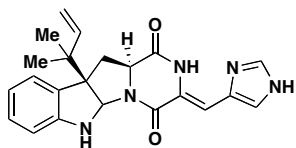
Paraherquamide A
Williams, *ACIEE*, 2000, 2540



VM5599
Williams, *JACS*, 2002, 2556



Spirotryprostatin B
Ganesan, *JOC*, 2000, 4685



Isoroquefortine C
Joullie, *JOC*, 2002, 620
Joullie, *PNAS*, 2004, 11971