

TOSTE GROUP MEETING PROBLEM SET  
JANUARY 20, 2003  
JOSHUA KENNEDY-SMITH

**DANISHEFSKY VS. NICOLAOU:  
THE GOLDEN YEARS OF TOTAL SYNTHESIS BATTLES**

PROBLEMS ATTACHED

- 1) NICOLAOU DEvised A CLEVER SEQUENCE FOR THE IODOARYL PORTION OF CALICHEAMICIN (THINK SYMMETRY AND STERICs), WHAT IS THE PRODUCT OF THE FOLLOWING REACTIONS?
- 2) FINISH AS MUCH OF THIS ROAD MAP AS YOU WANT AND EXPLAIN THE STEREOSELECTIVITY OF 6+7 to 8. (14 to 15 is tricky think lots of [O]:
- 3) i) EXPLAIN THE SELECTIVITY OF THIS DIELS-ALDER REACTION. ii) FOR BEN ONLY: WHAT ENZYME DOES THIS?
- 4) FOLLOW ALONG WITH THE DANISHEFSKY GROUP AS THEY BANG AWAY AT TAXOL...
- 5) ...AND FINISH IT...SORRY IF SOME OF THIS IS NOT SO OBVIOUS...
- 6) NICOLAOU STARTS ELEUTHEROBIN WITH CARVONE...
- 7) DANISHEFSKY STARTS ELEUTHEROBIN WITH PHELLANDRENE...
- 8) THIS IS HOW NICOLAOU FINISHES SARCODICTYIN