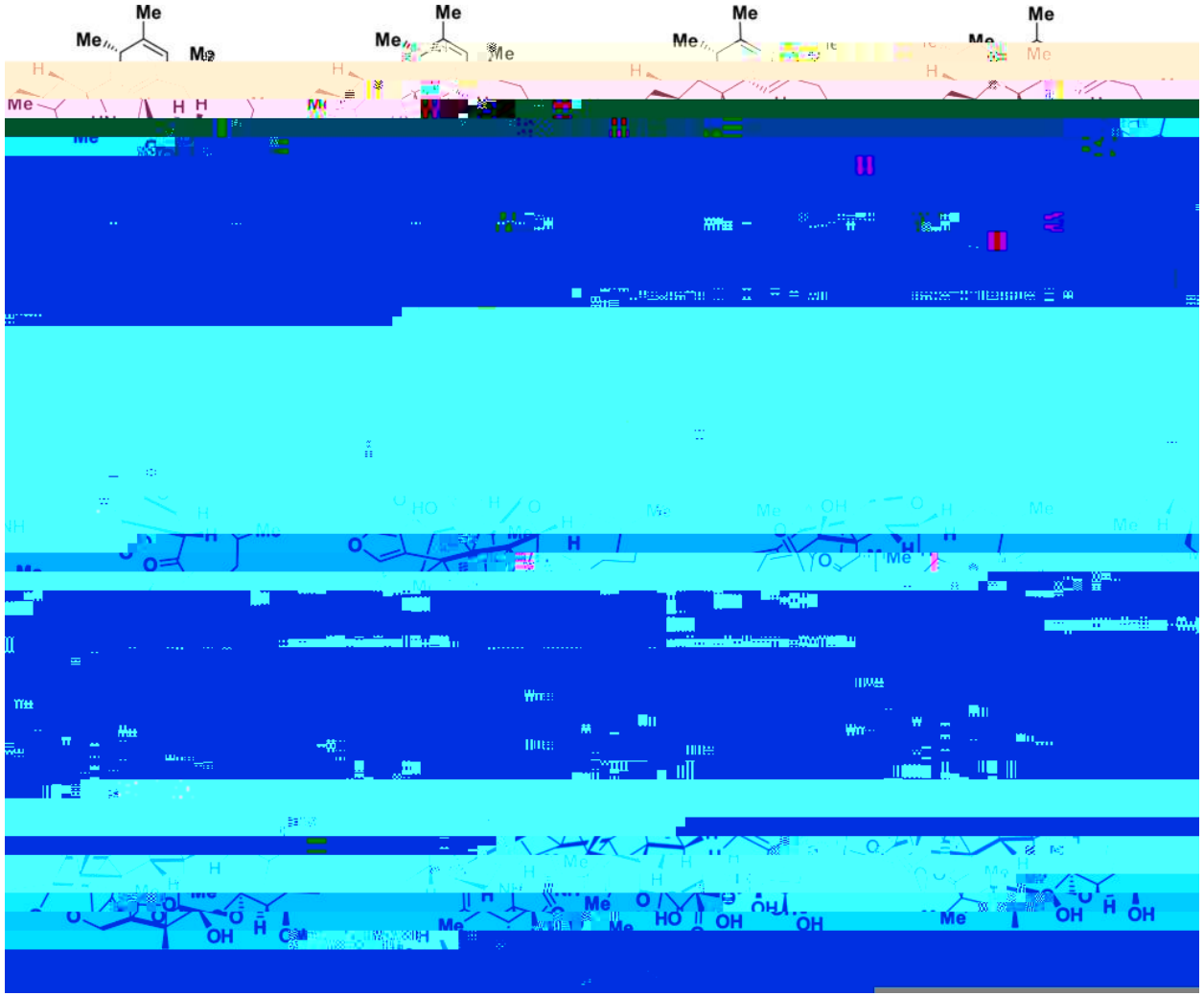
Total Syntheses of Asperchalasines A-E

Bao R. etc. *Angew. Chem. Int. Ed.* , *57*, 14216



Asperchalasines is a collection of merocytochalasans from fermentation broth of Aspergillus flavipes

They are series of fungal secondary metabolites consisting of two types of subunits :

and

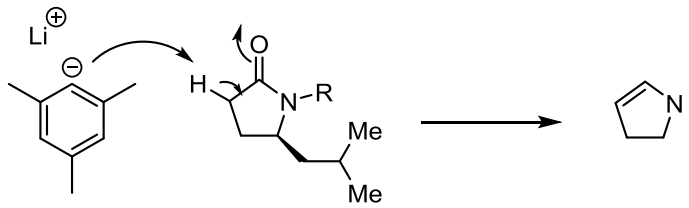
Some of

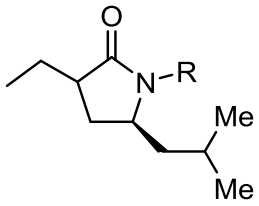
Synthetic strategy mainly built on biosynthetic origin:

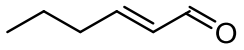
Two common precursors, aspochalasinB ( ) and epicoccine( )

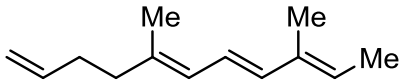
Due to underlying endo/exo selectivity and regioselectivity, the Diels-

Sequential selenylation and oxidative elimination



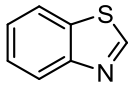


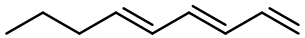




Sequential selenylation and oxidative elimination

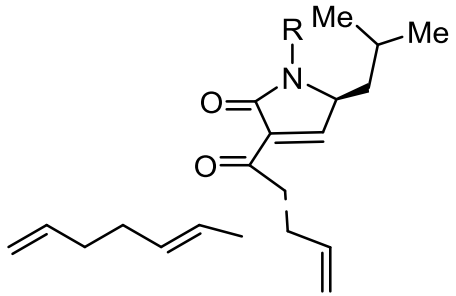
Julia Olefination

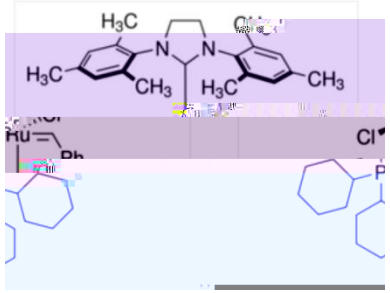




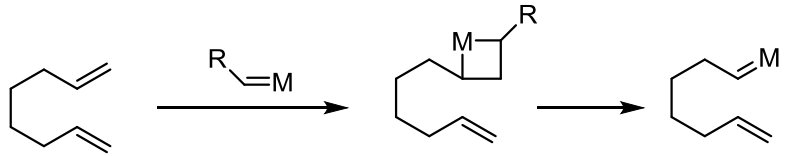
+

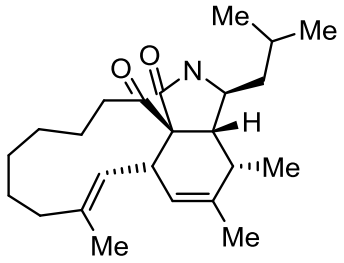
Lewis acid-promoted Diels-Alder reaction:



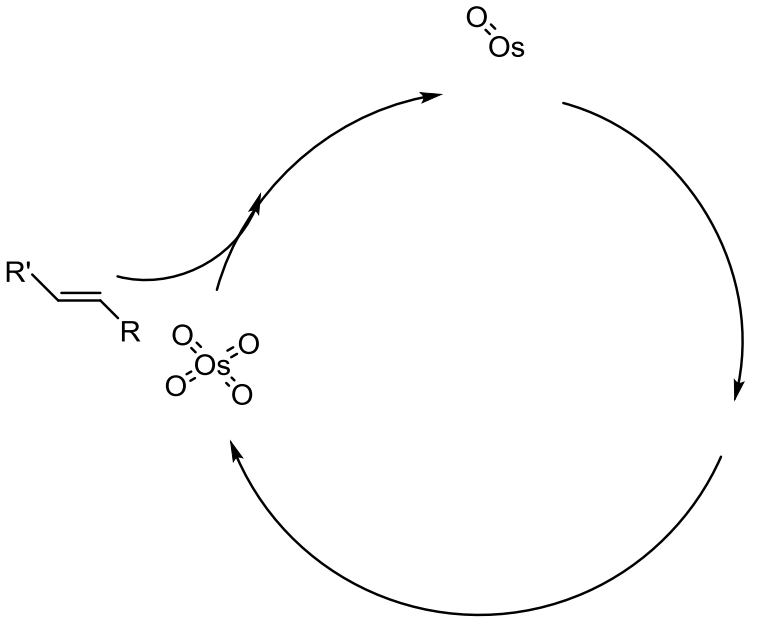


Grubb's second generation Catalyst catalyzed Ring Closing metathesis:

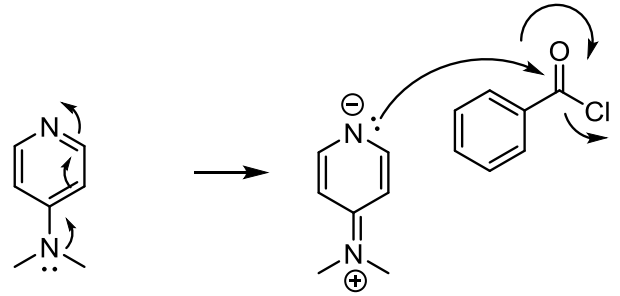


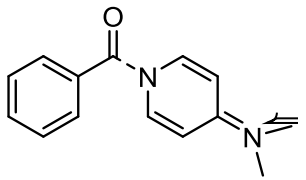


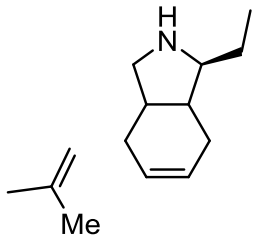
Upjohn dihydroxylation



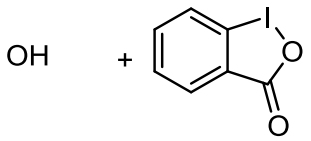
Selective 17-OH protection



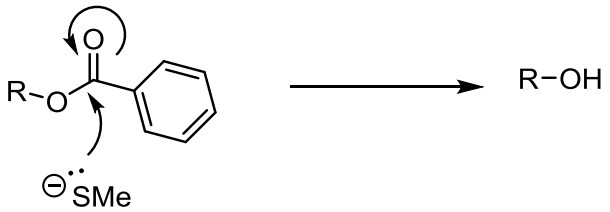




Dess-Martin Oxidation



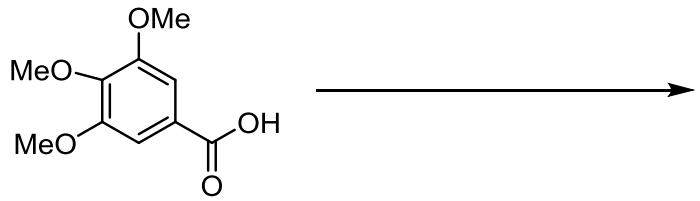
Benzoyl group deprotection



Another sequential selenylation and oxidative elimination:

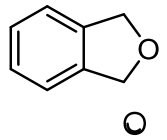
Forming unsaturated carbonyl (mechanism see before)

Syntheses of epicoccine part

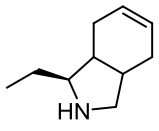


Blanc Chloromethylation and dechlorination

Trauner D. *Angew. Chem. Int. Ed.* ,*126*,13632



Finishing syntheses
Of asperchalasine A



Back-up mechanism of last page:

Diels-Alder reaction forming :

Hydrogenolysis of benzyl group: