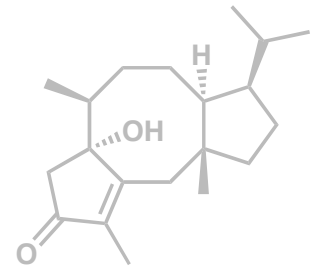
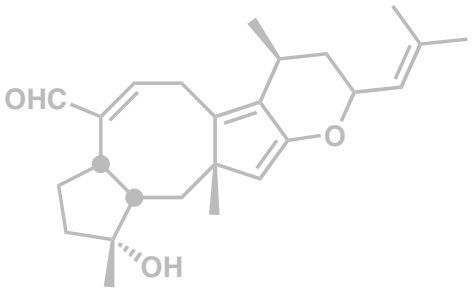
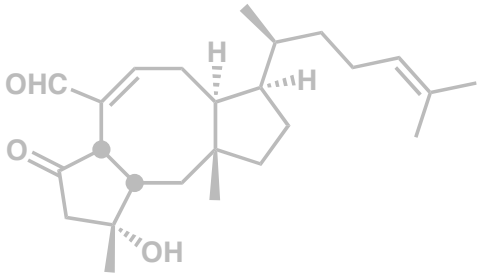


(+)-fusicoauritone



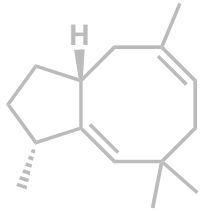
ophiobolin E



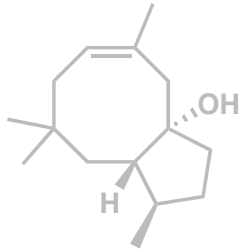
ophiobolin C

Cyclooctanoid Natural Products

Synthesis of eight-membered ring containing terpenoids



precapnelladiene



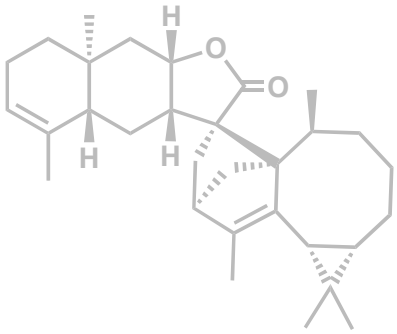
dactylol

Chris Henry

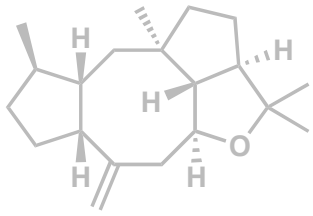
Stoltz Group Literature Presentation

June 15th, 2008

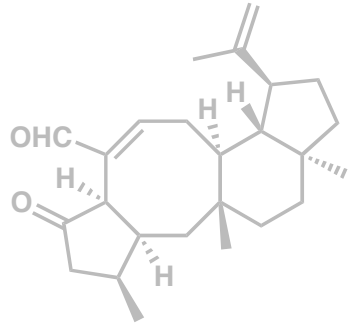
147 Noyes, 8:00 PM



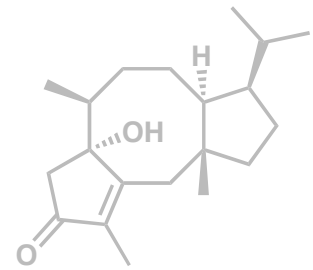
plagiospirolide E



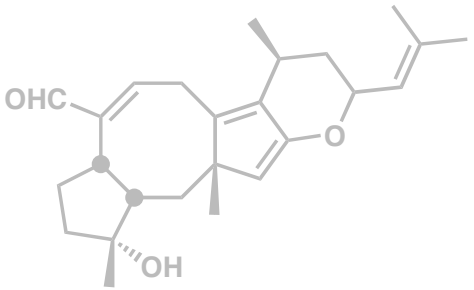
(+)-epoxydictymene



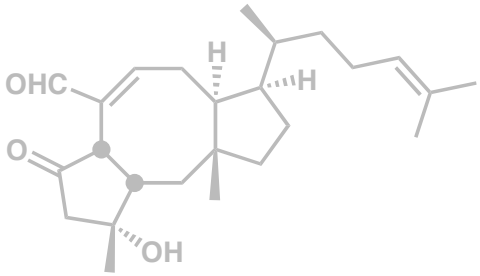
variecolin



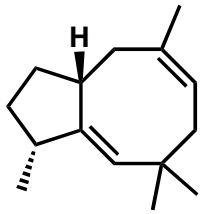
(+)-fusicoauritone



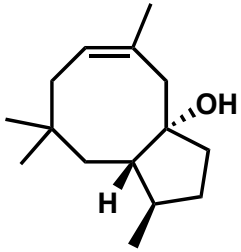
ophiobolin E



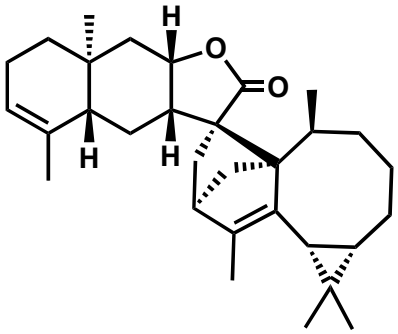
ophiobolin C



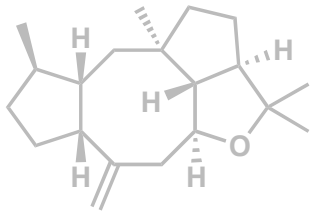
precapnelladiene



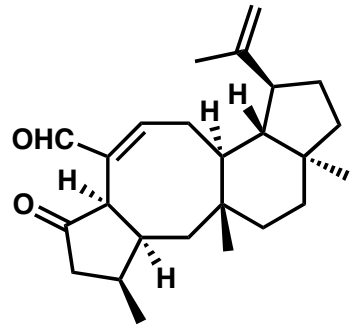
dactylol



plagiospirolide E

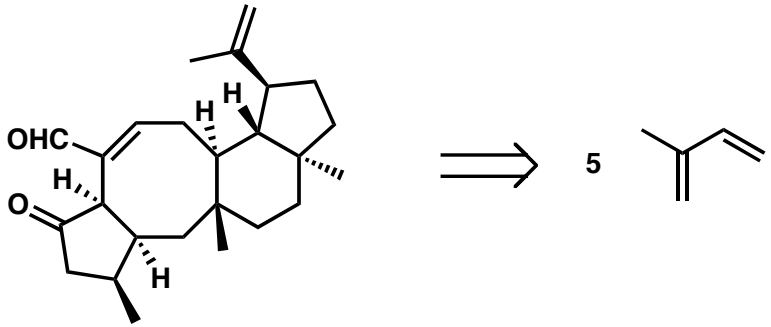


(+)-epoxydictymene



variecolin

Other types of cyclooctanoid natural products

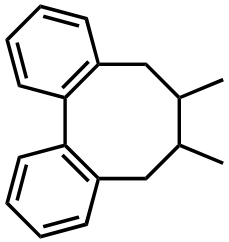


variecolin

sesterterpenoid

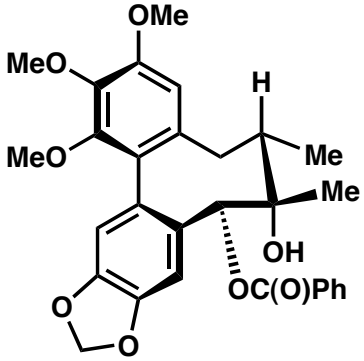
isoprene

Dibenzocyclooctadiene Lignans



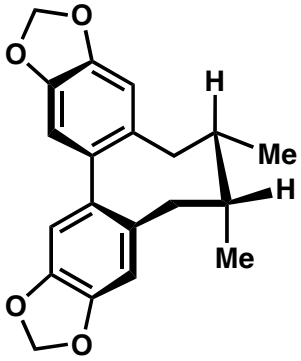
C6 – C6' linkage

(dibenzocyclooctadiene)



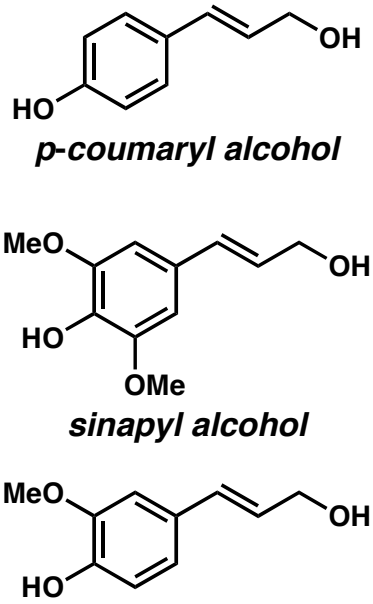
gomisin G

anti-HIV activity



wuweizisu C

antihepatotoxic activity



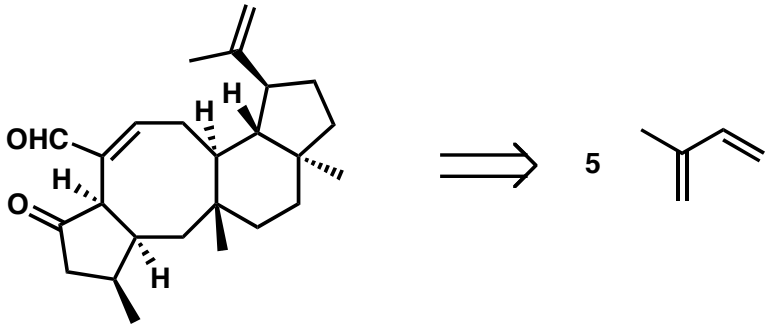
p-coumaryl alcohol

sinapyl alcohol

coniferyl alcohol

Chang. *Chem. Rev.* **2005**, *105*, 4581.

Other types of cyclooctanoid natural products



variecolin

sesterterpenoid

isoprene

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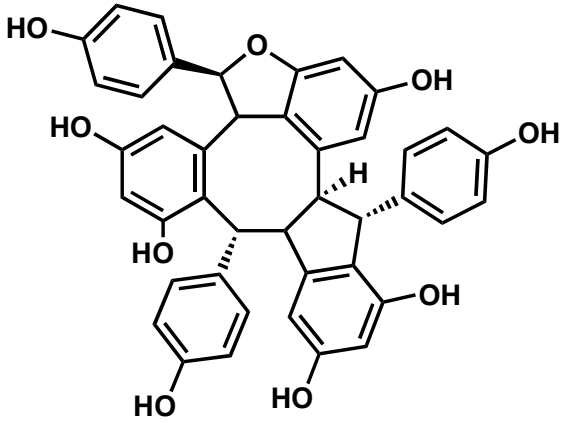
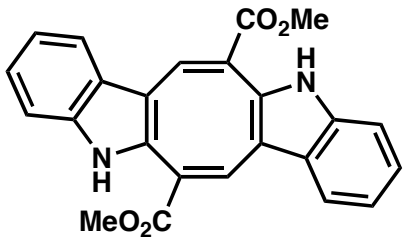
polyphenol lignans

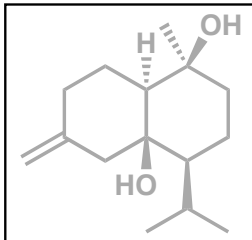
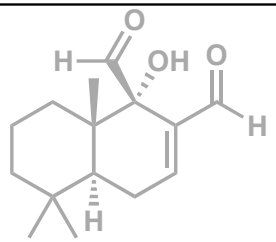
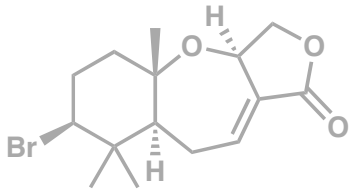
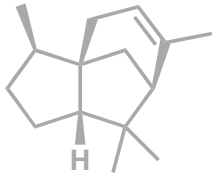
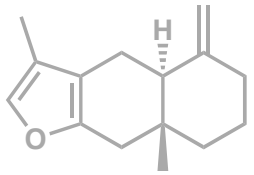
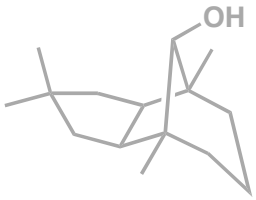
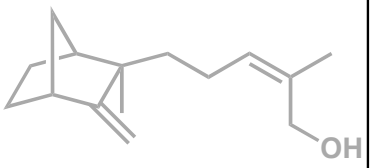


distichol

indoles

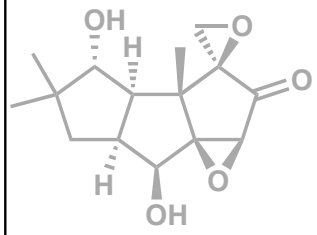


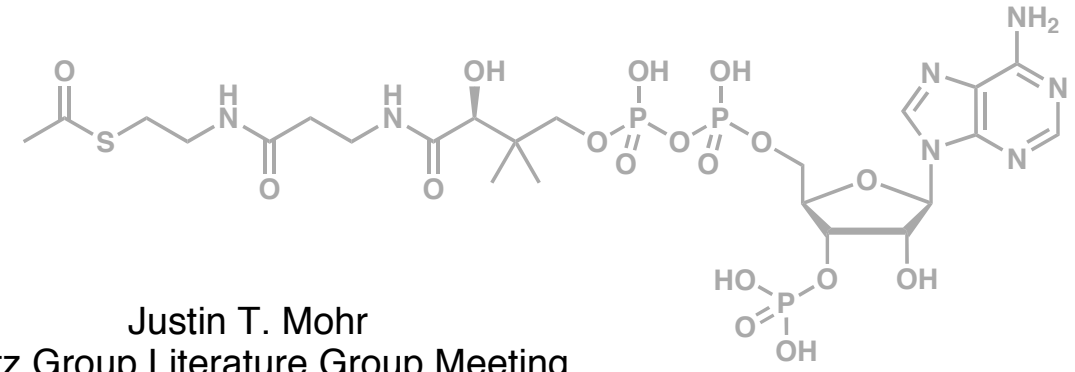
caulerpin

Sesquiterpenoids

Biosynthesis and Total Synthesis



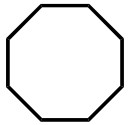

Justin T. Mohr
Stoltz Group Literature Group Meeting
2 April 2007

Strategies for the Construction of Medium-Sized Rings

Pamela Tadross
Stoltz Group Literature Presentation

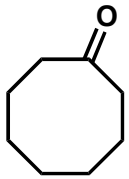
March 3, 2008
147 Noyes, 8:00 PM

Cyclooctane & Cyclooctanone



Chemical Formula: C_8H_{16}
Molecular Weight: 112.21
Density: 0.834
mp: 9–14 °C
bp: 149 °C (1 atm)

___
100g – $33.80
500g – $83.70



Chemical Formula: $C_8H_{14}O$
Molecular Weight: 126.20
Density: 0.958
mp: 32–41 °C
bp: 159–197 °C

____
25g – $25.00
100g – $70.40

Conformations of eight-membered rings

three major families

boat–chair

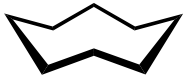
boat–chair

twist boat–chair

chair

twist chair

chair–chair



crown

chair–chair

twist chair–chair

boat–boat

boat–boat

twist boat–boat

boat

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reviewed in:

Petasis. *Tetrahedron* **1992**, *48*, 5757.

Anet. Top. Curr. Chem. **1974**, *45* 169.

Conformations of eight-membered rings

three major families

boat–chair

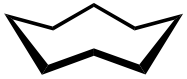
boat–chair

twist boat–chair

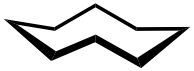
chair

twist chair

chair–chair



crown



chair–chair

twist chair–chair

boat–boat

boat–boat

twist boat–boat

boat

---

reviewed in:

Petasis. *Tetrahedron* **1992**, *48*, 5757.

Anet. Top. Curr. Chem. **1974**, *45* 169.

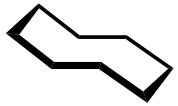
Conformations of eight-membered rings

three major families

boat–chair

boat–chair

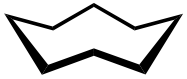
twist boat–chair



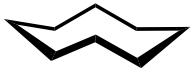
chair

twist chair

chair–chair



crown



chair–chair

twist chair–chair

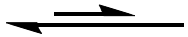
boat–boat

boat–boat

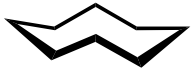
twist boat–boat

boat

"boat–chair"



room temperature



"chair-chair"

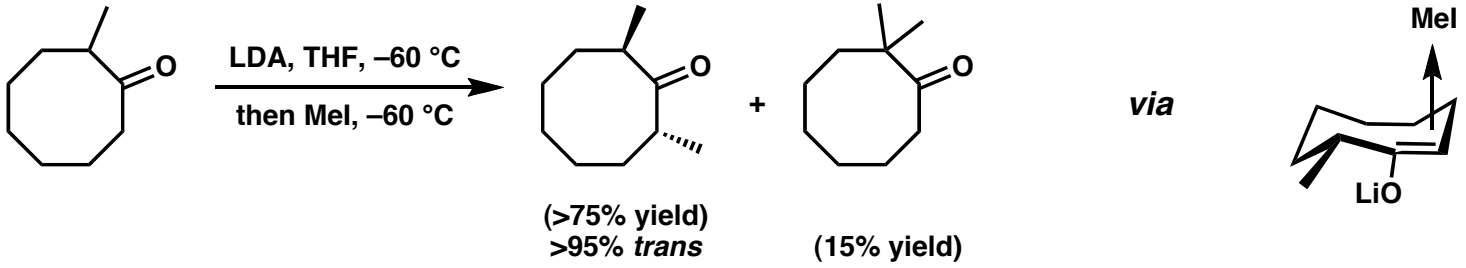
94 : 6

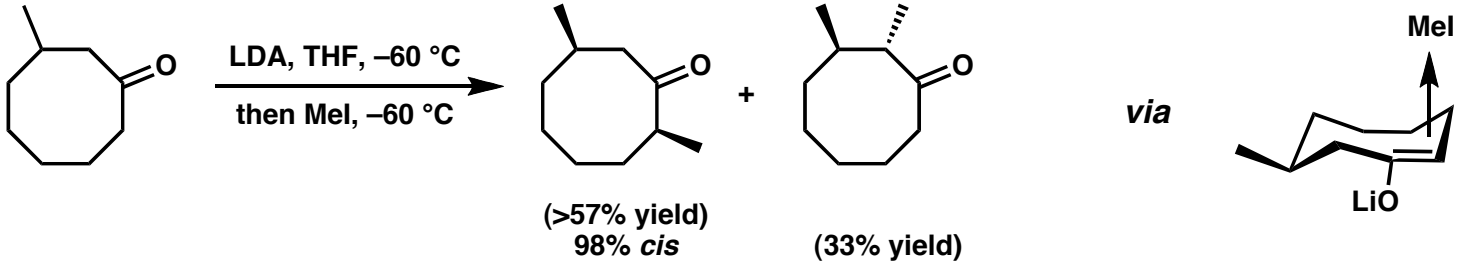
reviewed in:

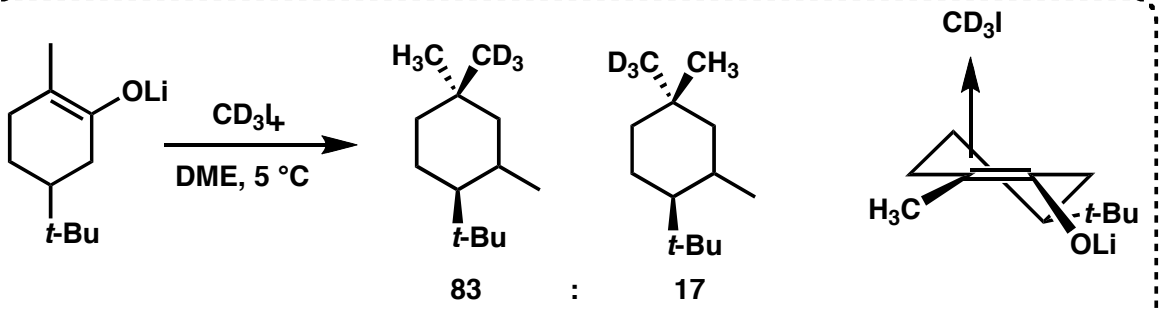
Petasis. *Tetrahedron* **1992**, *48*, 5757.
Anet. Top. Curr. Chem. **1974**, *45* 169.

"Chemical consequences of conformation"

Diastereoselection in eight-membered rings





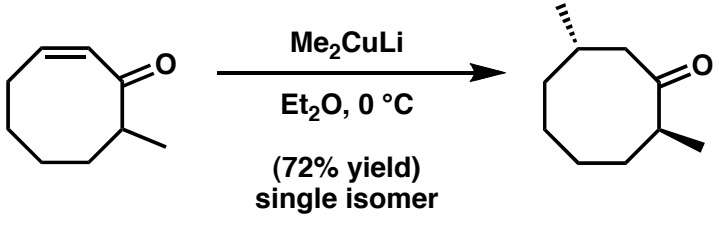


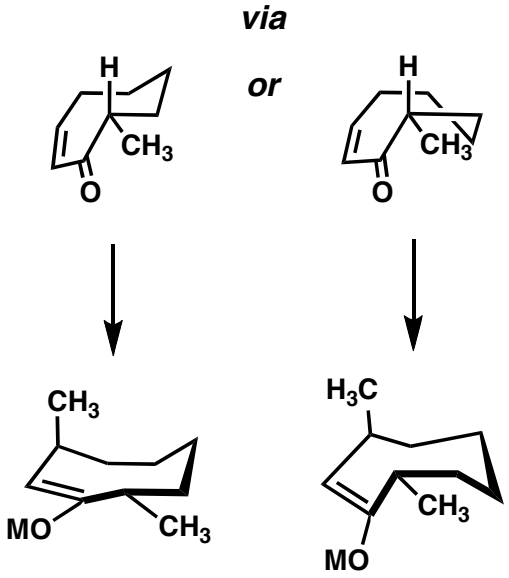
House. *J. Org. Chem.* **1973**, *38*, 1000.

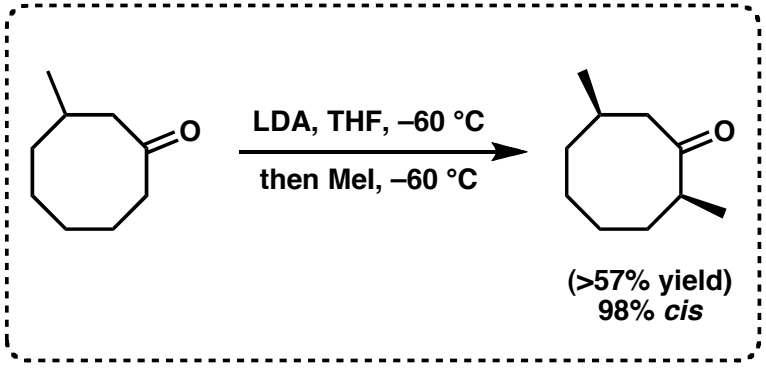
Still. *Tetrahedron.* **1981**, *37*, 3981.

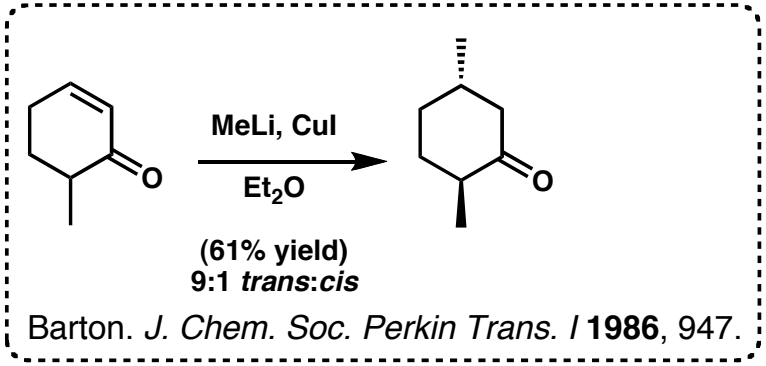
"Chemical consequences of conformation"

Diastereoselection in eight-membered rings







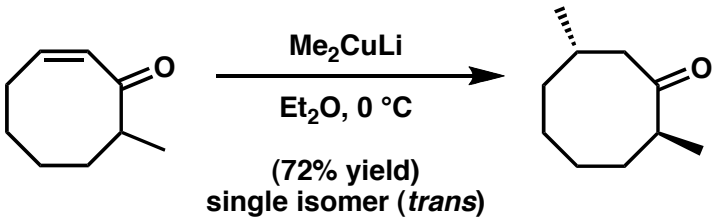


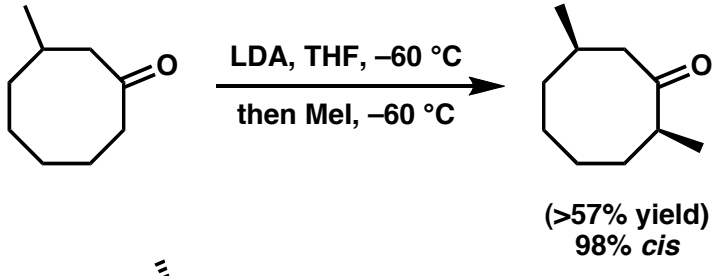
Barton. *J. Chem. Soc. Perkin Trans. I* **1986**, 947.

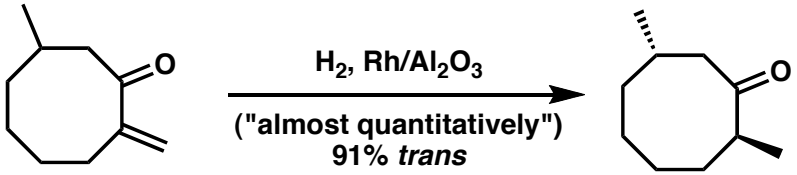
Still. *Tetrahedron.* **1981**, *37*, 3981.

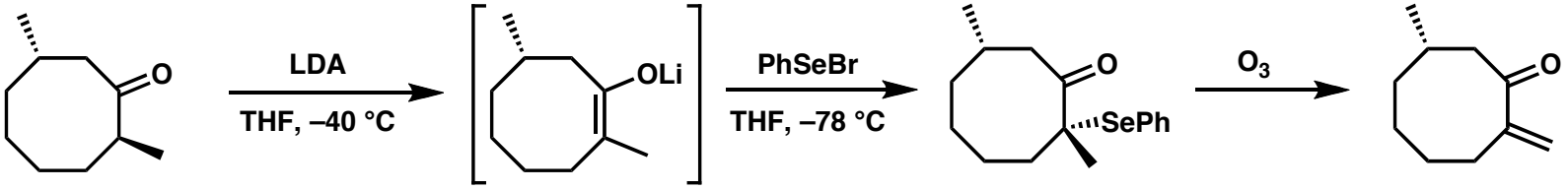
"Chemical consequences of conformation"

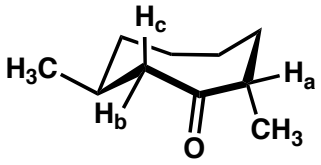
Diastereoselection in eight-membered rings









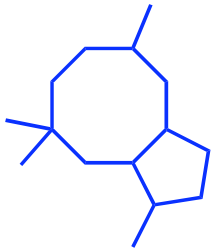


lowest energy conformation
by MM2 force field calculation

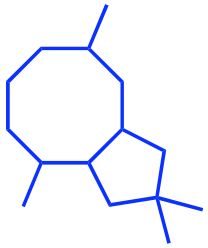
Still. *Tetrahedron.* **1981**, *37*, 3981.

Occurance in terpenoid ring systems

Sesquiterpenoid ring systems



precapnellane



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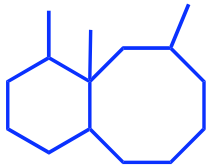
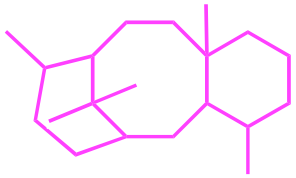


neolemnane

Diterpenoid ring systems



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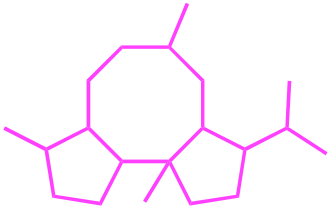
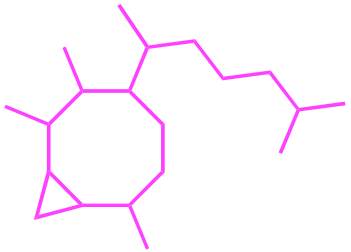
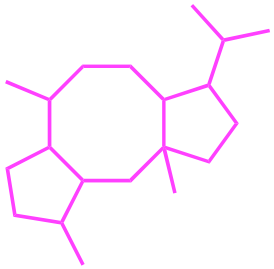


basmane

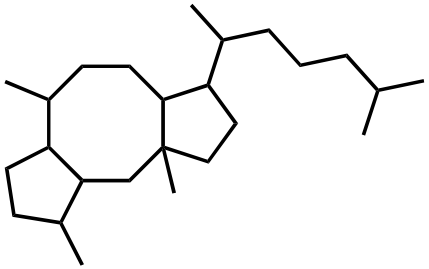


crenulane

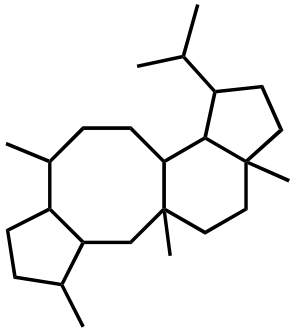
Sesterterpenoid ring systems



fusicoccane



ophiobolane



variecolin family

reviewed in:

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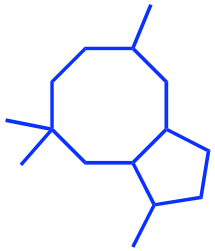
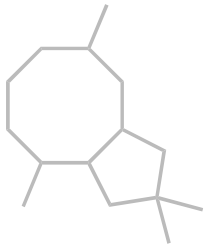
Occurance in terpenoid ring systems

Sesquiterpenoid ring systems



precapnellane



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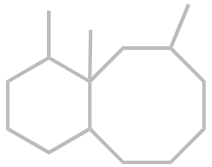
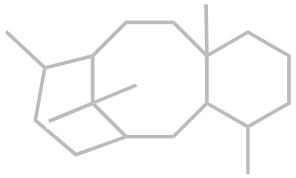


neolemnane

Diterpenoid ring systems



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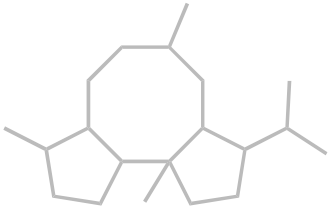
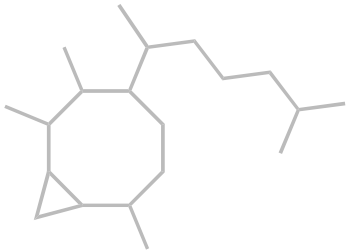
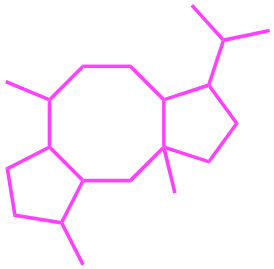


basmane

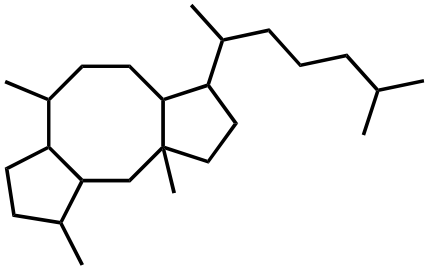


crenulane

Sesterterpenoid ring systems



fusicoccane



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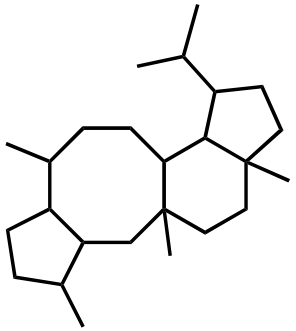
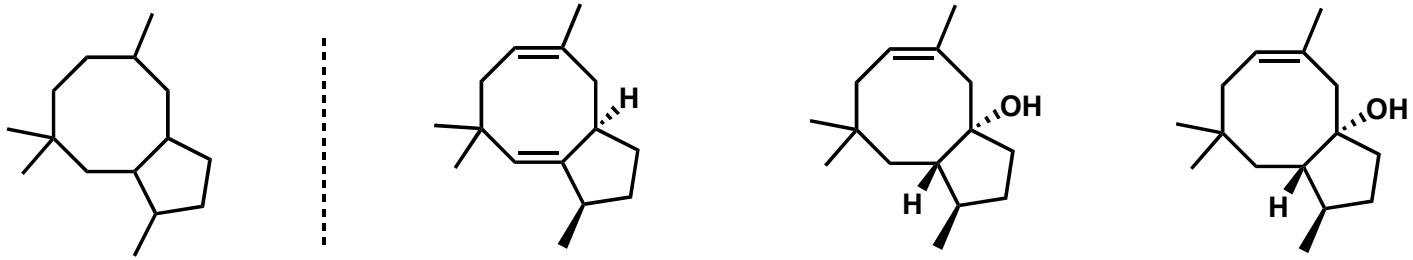


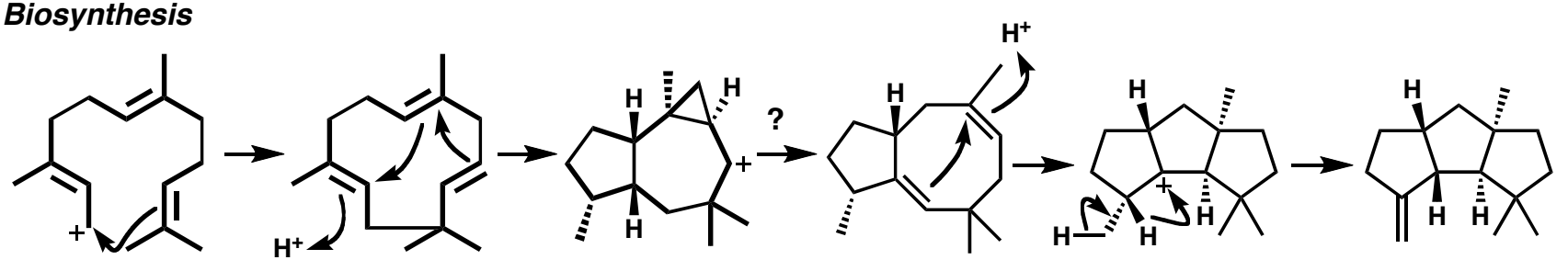
variecolin family

Precapnellane sesquiterpenoids



precapnellane ***precapnelladiene*** ***dactylol*** ***poitediol***

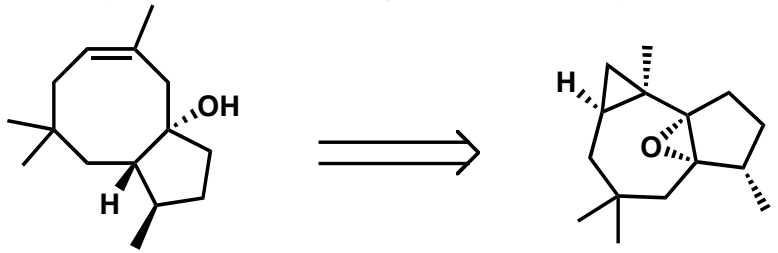
Biosynthesis



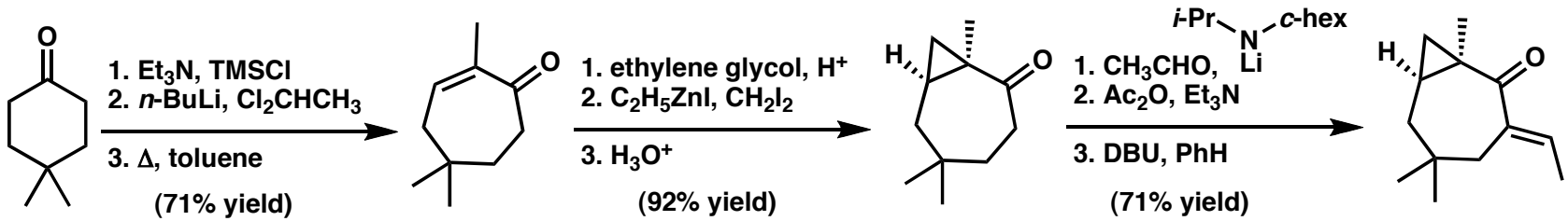
trans,trans-farnesyl *humulene* *africane* *precapnelladiene* ***$\Delta^{9(12)}$-capnellene***

Strategies in cyclooctanoid synthesis

Fragmentation of [5,1,0] systems



dactylol



Paquette. *J. Am. Chem. Soc.* **1987**,*109*, 3025.

Strategies in cyclooctanoid synthesis

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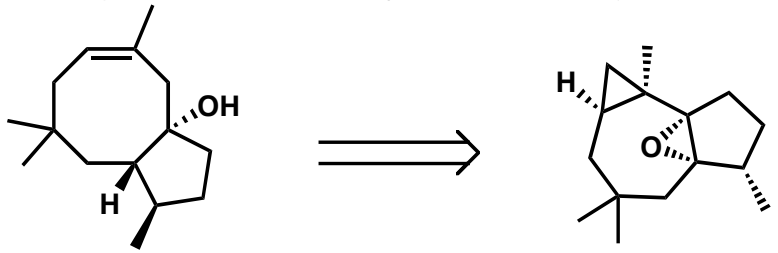

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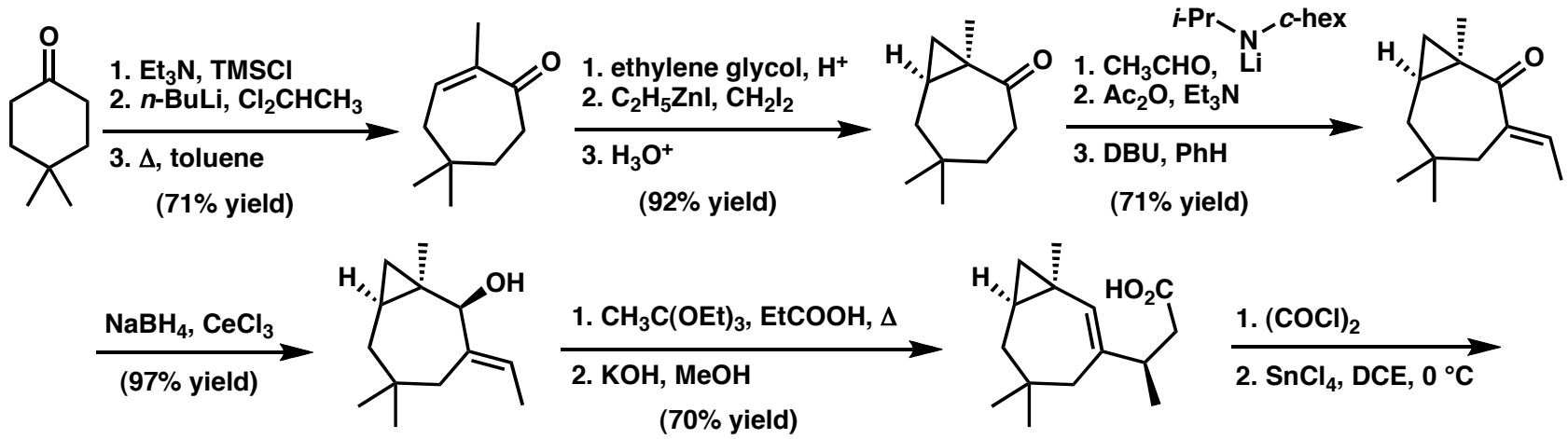

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Strategies in cyclooctanoid synthesis

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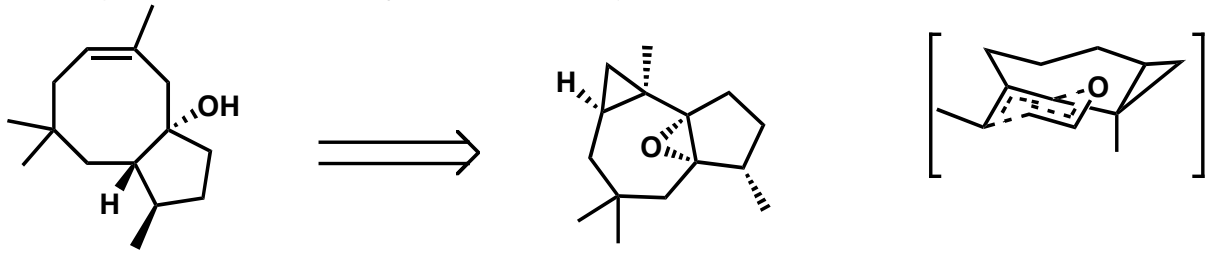
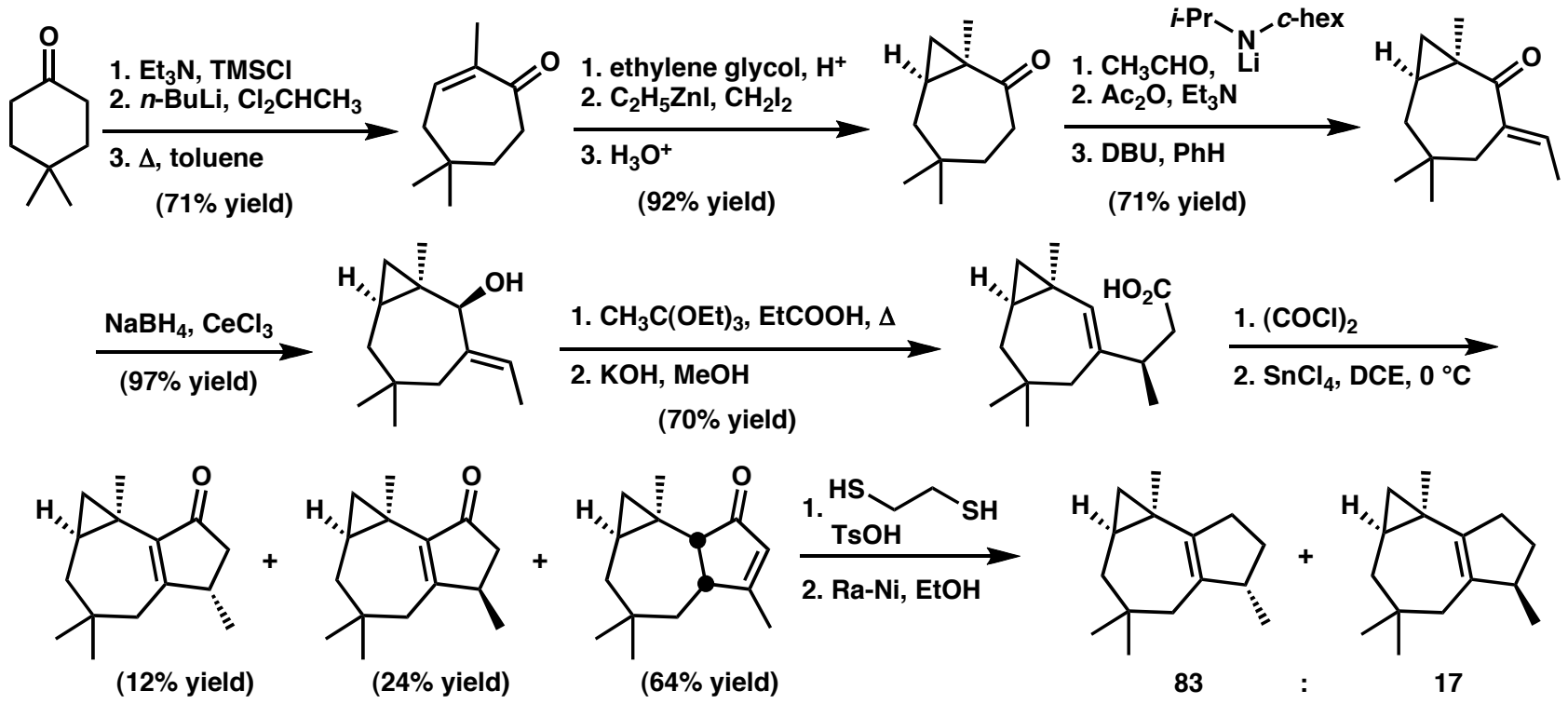


dactylol



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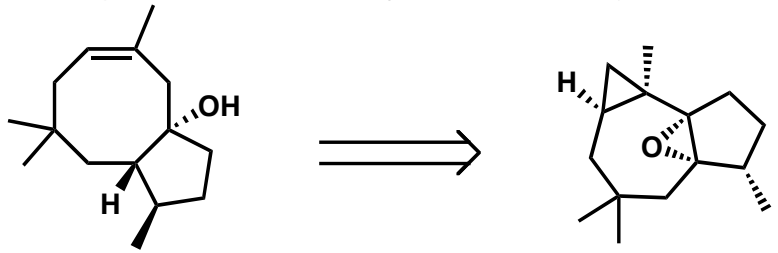
Strategies in cyclooctanoid synthesis

Fragmentation of [5,1,0] systems



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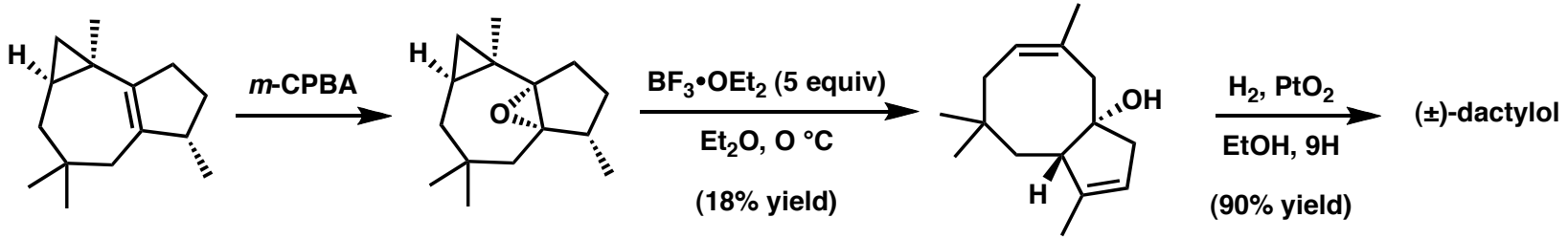

Matsumoto. *Tetrahedron Lett.* **1985**, 873.
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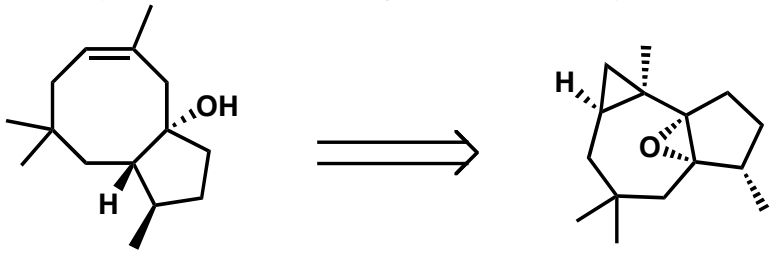
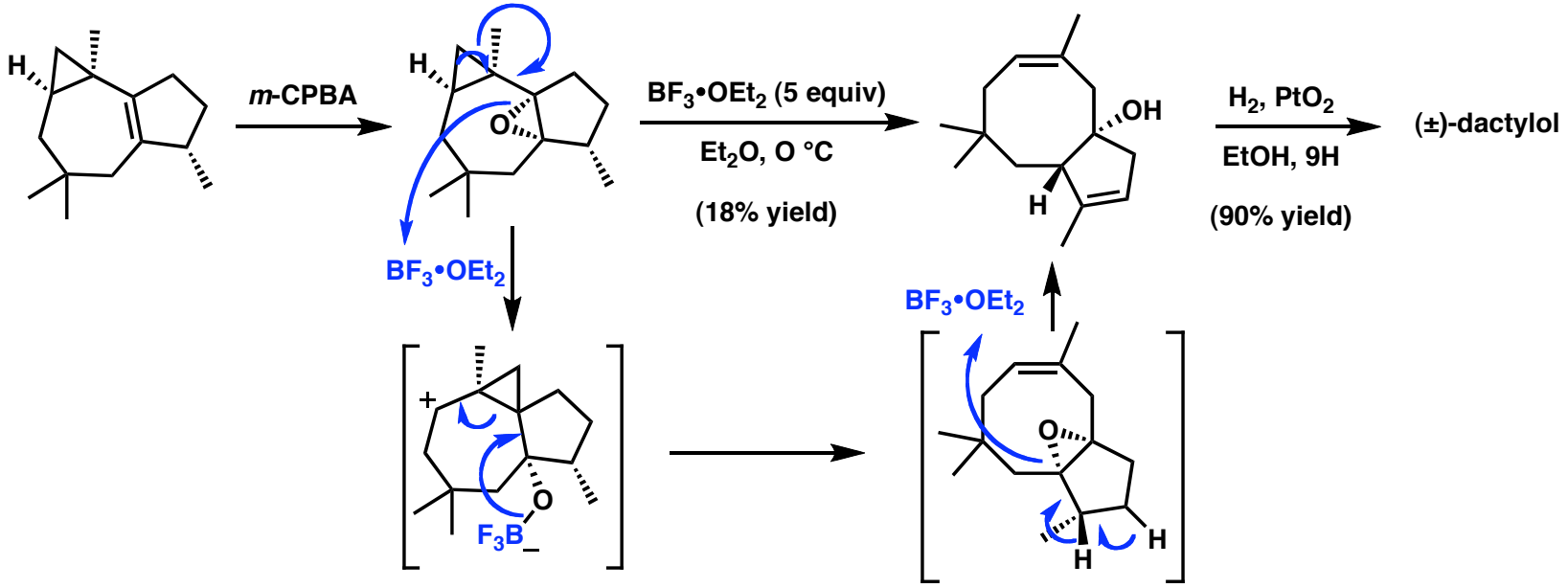
Strategies in cyclooctanoid synthesis

Fragmentation of [5,1,0] systems



dactylol



Matsumoto. *Tetrahedron Lett.* **1985**, 873.
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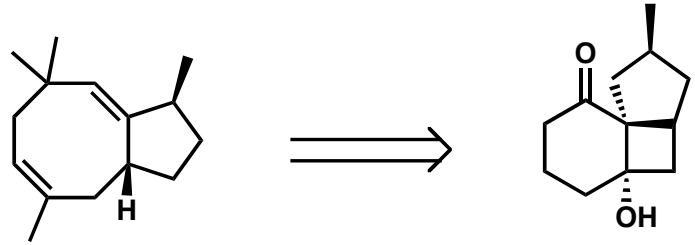
Strategies in cyclooctanoid synthesis

Fragmentation of [4,2,0] systems

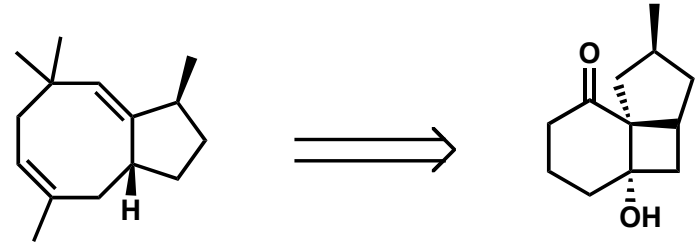


epi-precapnelladiene

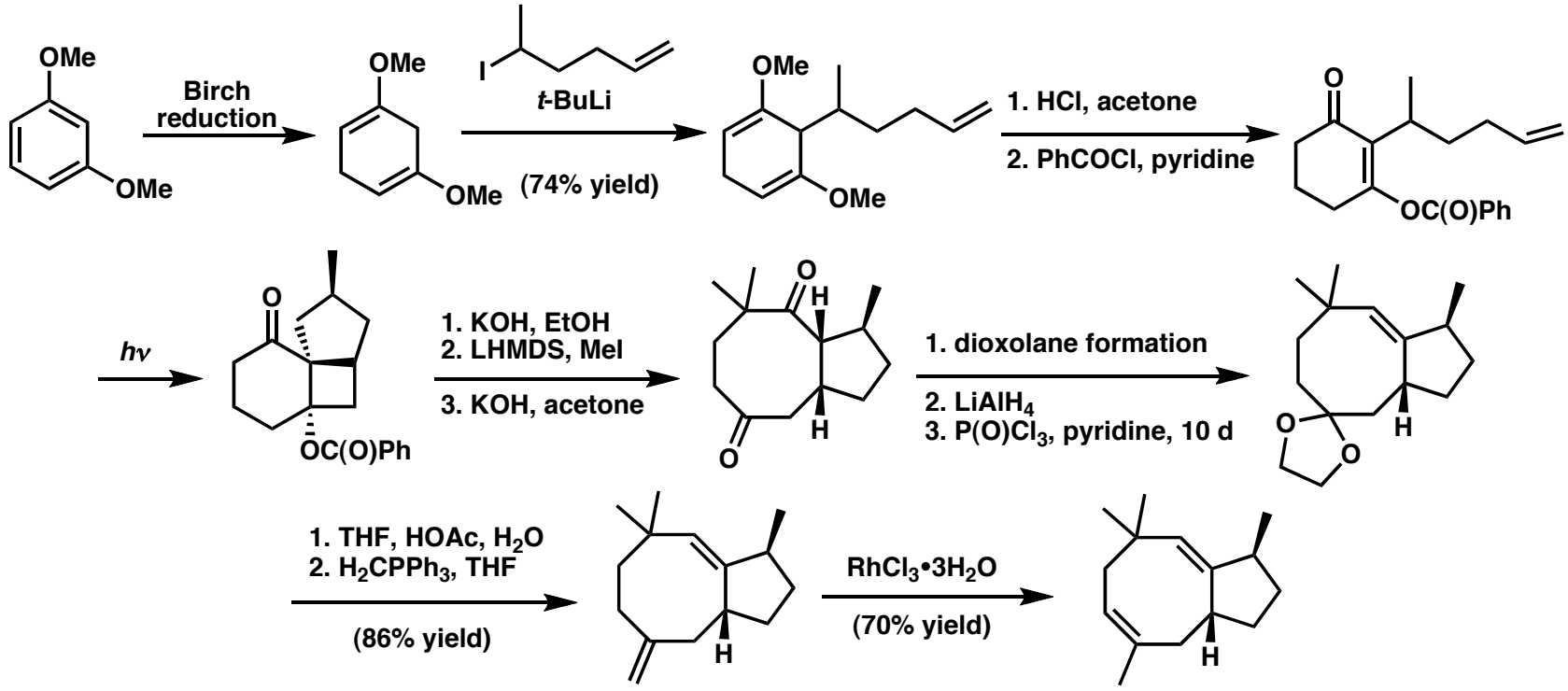
Pattenden. *J. Chem. Soc. Chem. Comm.* **1980**, 1195.

Strategies in cyclooctanoid synthesis

Fragmentation of [4,2,0] systems



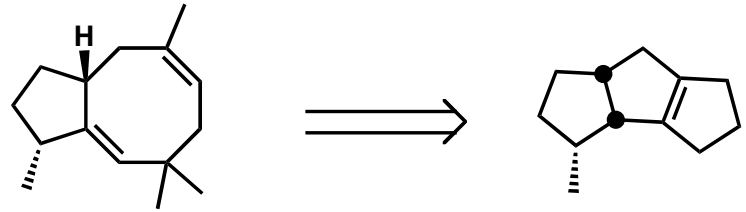
epi-precapnelladiene



Pattenden. *J. Chem. Soc. Chem. Comm.* **1980**, 1195.

Strategies in cyclooctanoid synthesis

Fragmentation of [3,3,0] systems

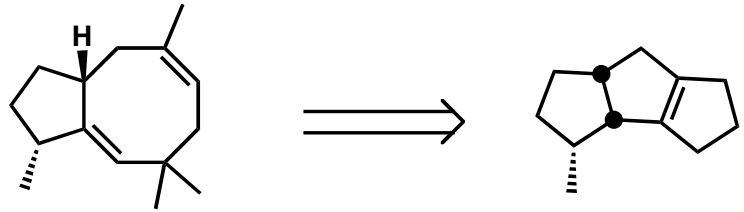


precapnelladiene

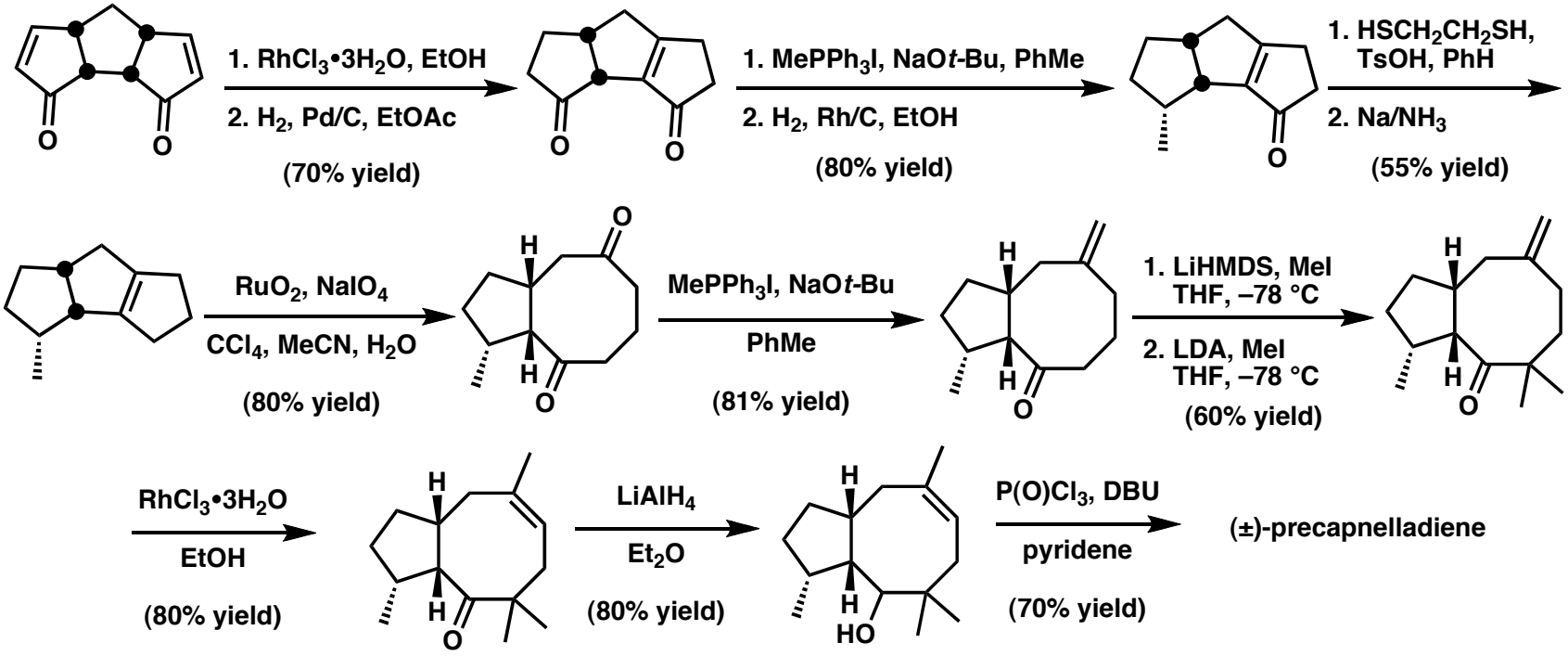
Mehta. *Tetrahedron* **1981**, *46*, 3936.
Mehta. *J. Chem. Soc. Chem. Comm.* **1984,** 1084.
Mehta. *J. Org. Chem.* **1987**, *52*, 2875.

Strategies in cyclooctanoid synthesis

Fragmentation of [3,3,0] systems



precapnelladiene



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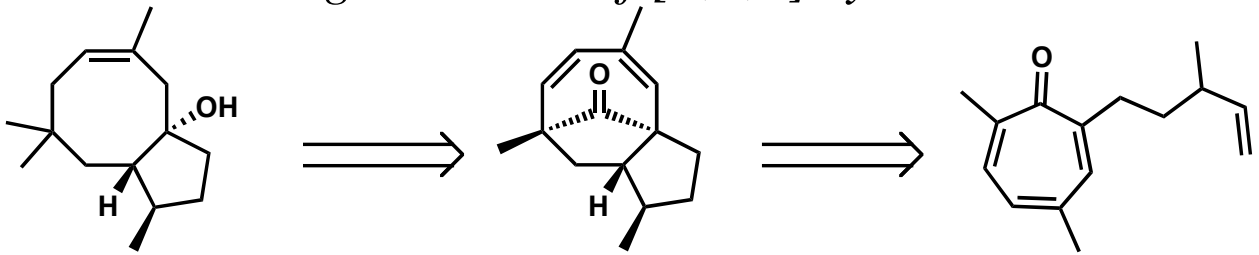
Strategies in cyclooctanoid synthesis

Fragmentation of [4,2,1] systems



dactylol

Feldman. *J. Am. Chem. Soc.* **1989**, *111*, 6457.
Feldman. *J. Am. Chem. Soc.* **1990**, *112*, 8490.

Strategies in cyclooctanoid synthesis

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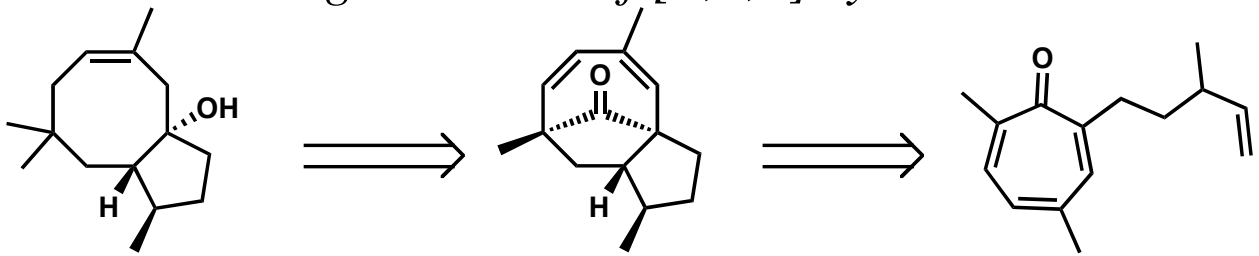

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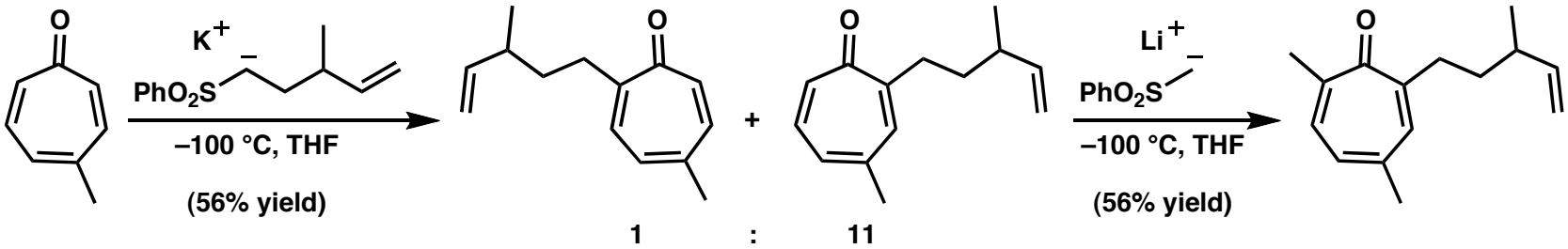

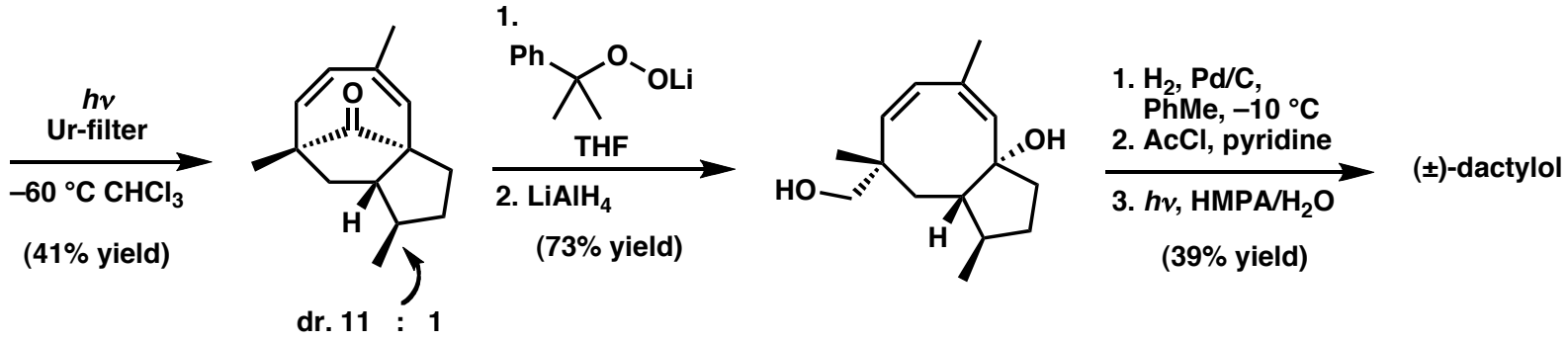

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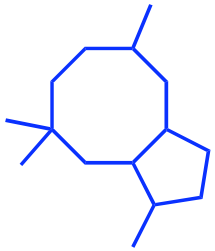
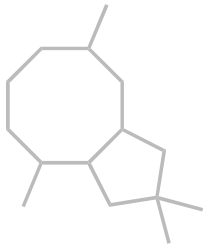
Occurance in terpenoid ring systems

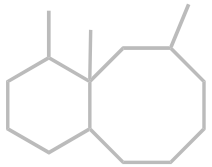
Sesquiterpenoid ring systems



precapnellane

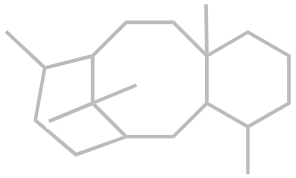


asteriscane

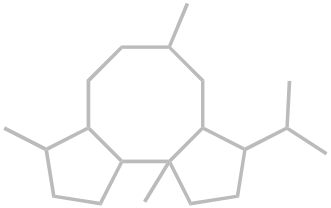


neolemnane

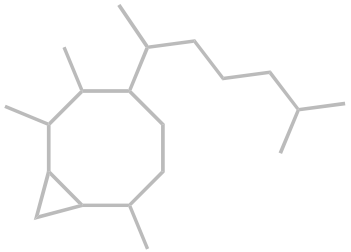
Diterpenoid ring systems



taxane

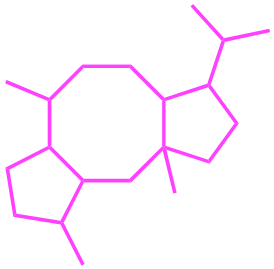


basmane

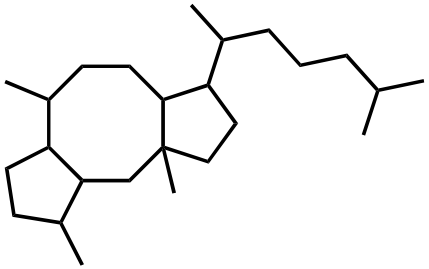


crenulane

Sesterterpenoid ring systems



fusicoccane



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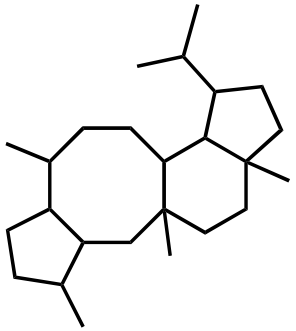
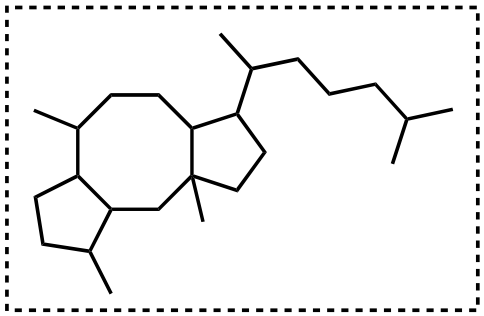


variecolin family



Sesterterpenoids

the ophiobolin family

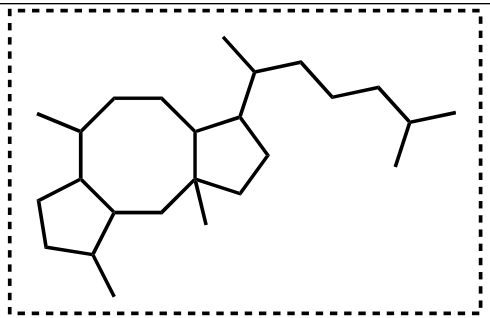
- **first isolated Ophiobolin A in 1957, 1961**

- **family members isolated from pathogenic fungi (Bipolaris oryzae, Aspergillus ustus, Cephalosporium caerulens, etc)**

- **Ophiobolin A was the first isolated sesterterpenoid (C25)**

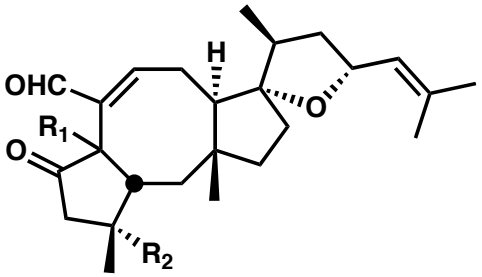
- **>25 members**

Image taken from: accessed 6/4/2009
http://www.knowledgebank.irri.org/IPM/diseaseDiagnosis/3.1.3._Brown_Spot_Bipolaris_oryzae.htm

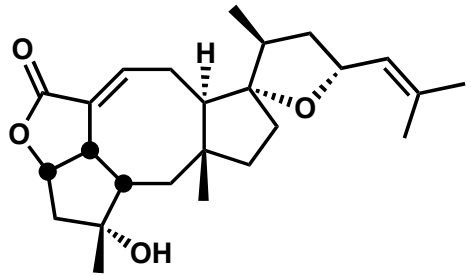


Sesterterpenoids

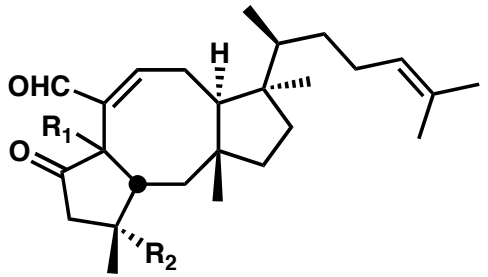
the ophiobolin family



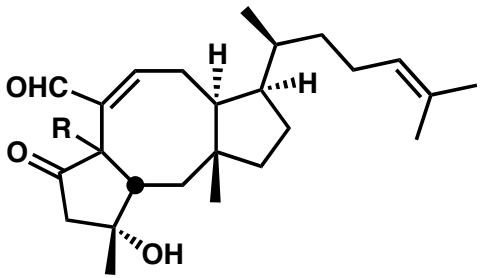
R_1 = βH, R_2 = OH, ophiobolin A
R_1 = βH, R_2 = H, 3-anhydroophiobolin A
R_1 = αH, R_2 = OH, 6-epiophiobolin A
R_1 = αH, R_2 = H, 3-anhydroophiobolin A



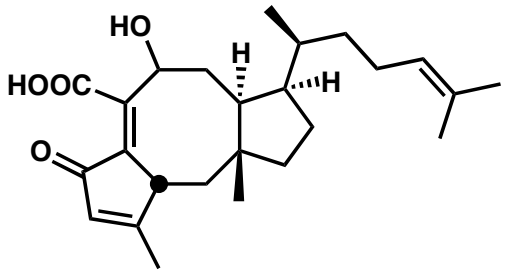
ophiobolin A lactone



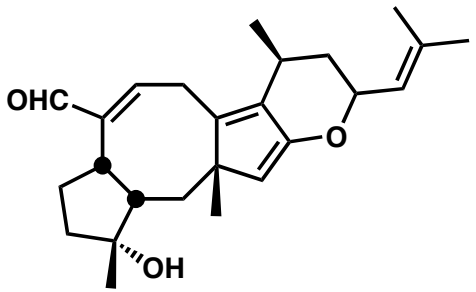
R_1 = βH, R_2 = OH, ophiobolin B
R_1 = αH, R_2 = H, 3-anhydroophiobolin B



R = βH, ophiobolin C
R = αH, 6-epiophiobolin C

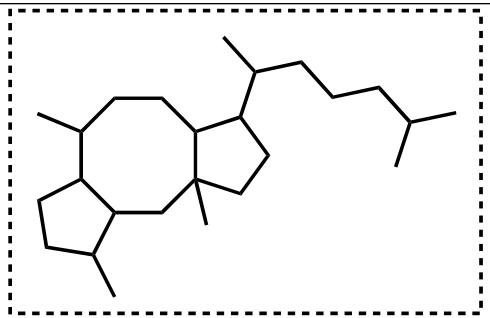


ophiobolin D



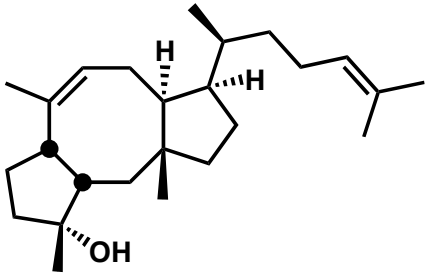
ophiobolin E

Reviewed in:
Leung. *Life Sciences* **2000**, *67*, 733.

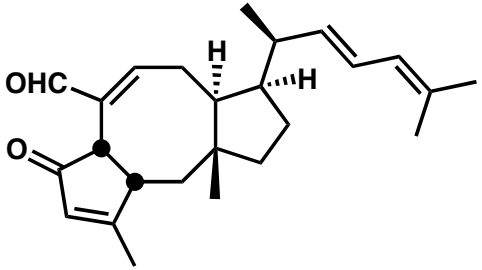


Sesterterpenoids

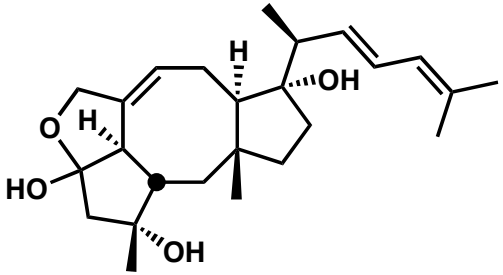
the ophiobolin family



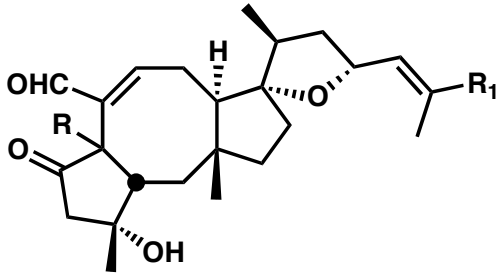
ophiobolin F



ophiobolin G

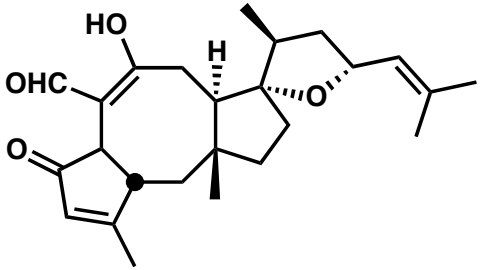


ophiobolin H

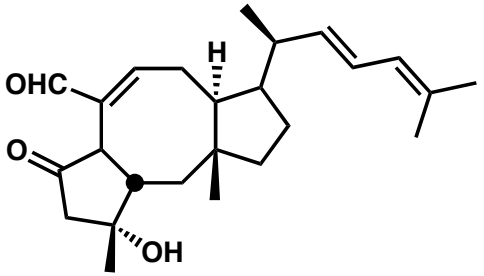


ophiobolin I

R_1 = Me, R_2 = βH, ophiobolin I
R_1 = CH_2OH, R_2 = βH, 25-hydroxyophiobolin I
R_1 = Me, R_2 = αH, 6-epiophiobolin I



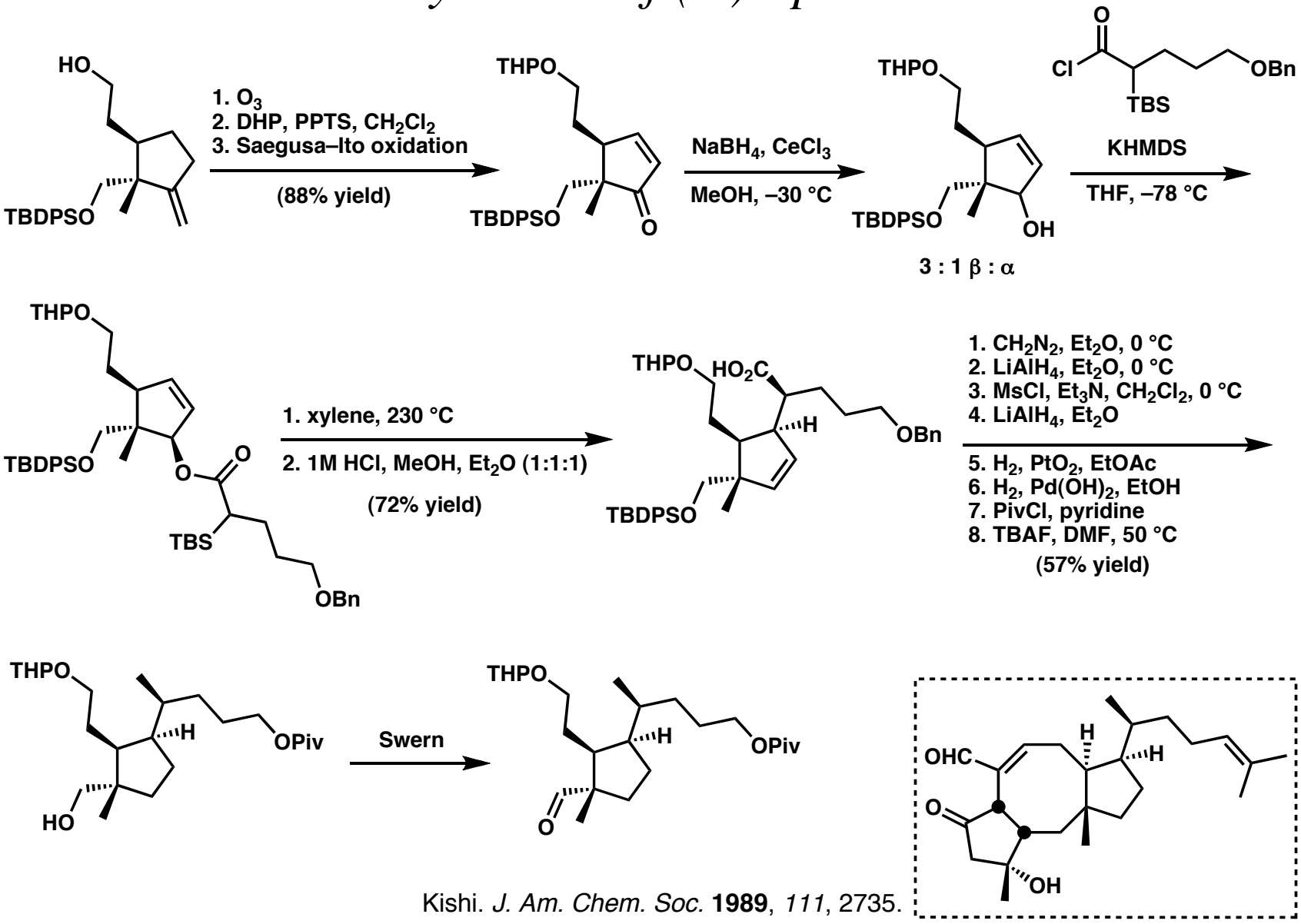
ophiobolin J



ophiobolin K

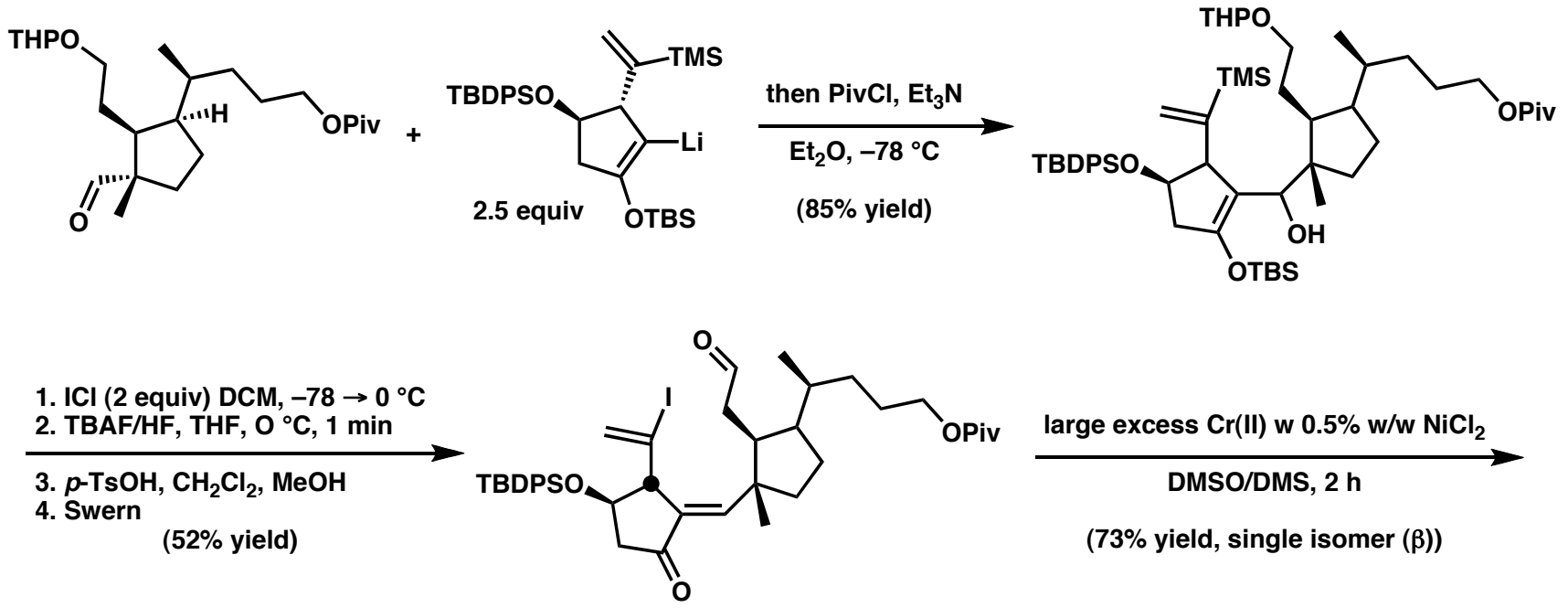
Reviewed in:
Leung. *Life Sciences* **2000**, *67*, 733.

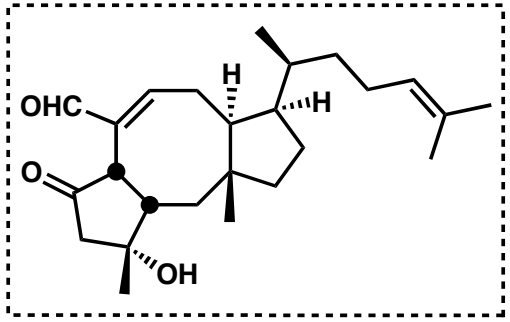
Kishi's synthesis of (+)-ophiobolin C



Kishi. *J. Am. Chem. Soc.* **1989**, *111*, 2735.

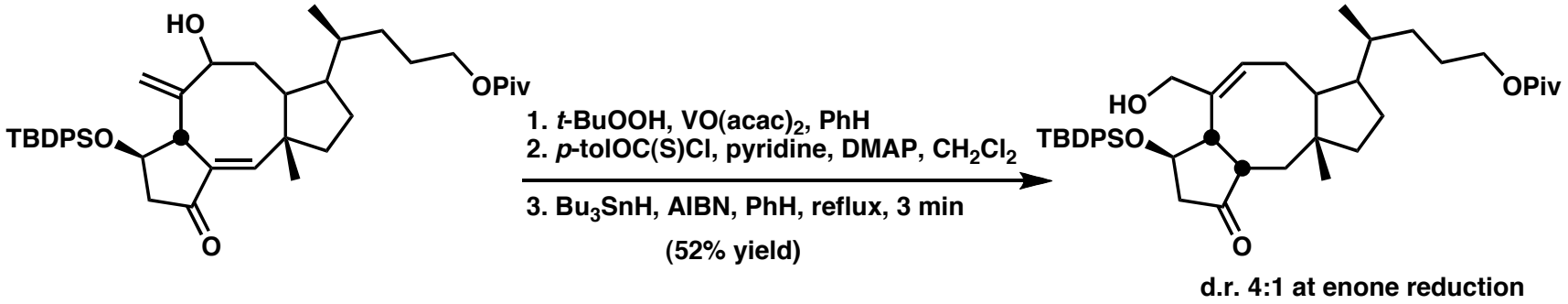
Kishi's synthesis of (+)-ophiobolin C



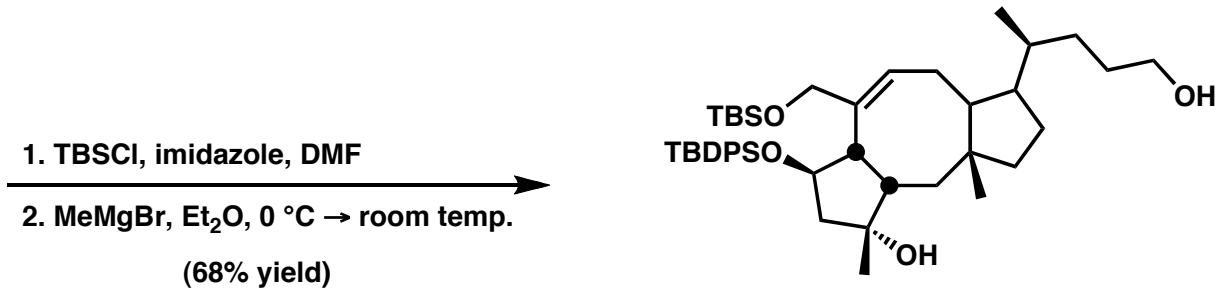


Kishi. *J. Am. Chem. Soc.* **1989**, *111*, 2735.

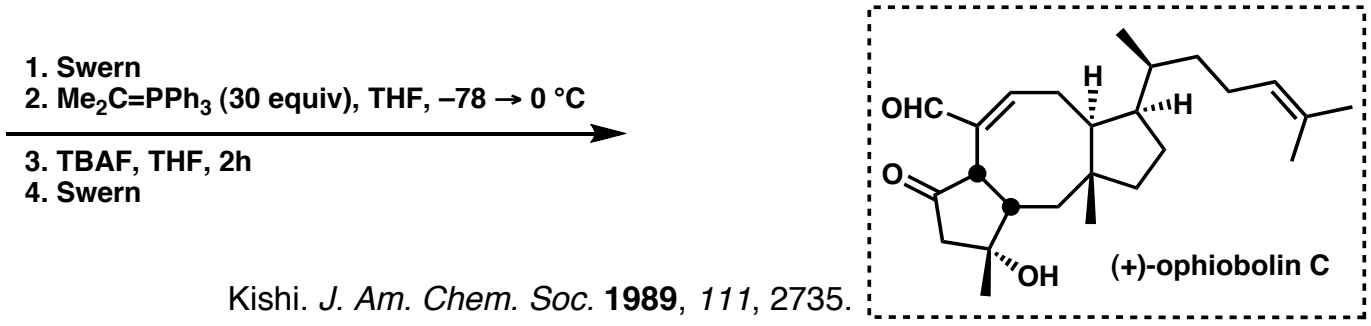
Kishi's synthesis of (+)-ophiobolin C



d.r. 4:1 at enone reduction



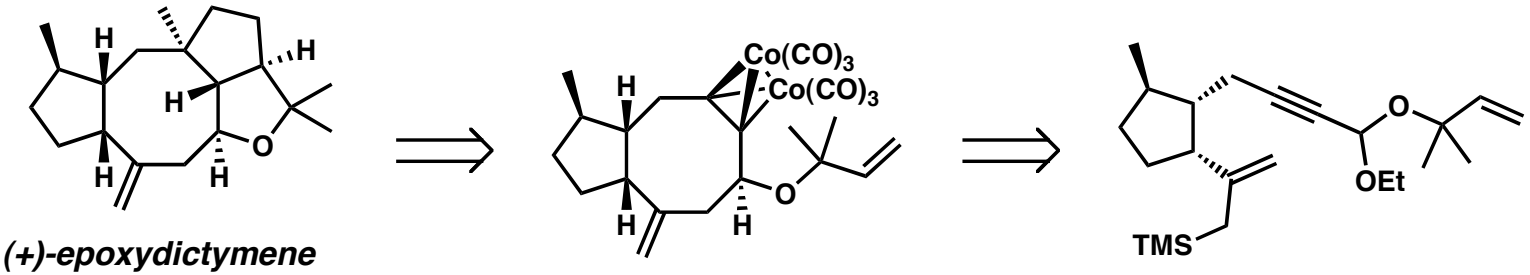
dr 13:1



Kishi. *J. Am. Chem. Soc.* **1989**, *111*, 2735.

C–C bond formation

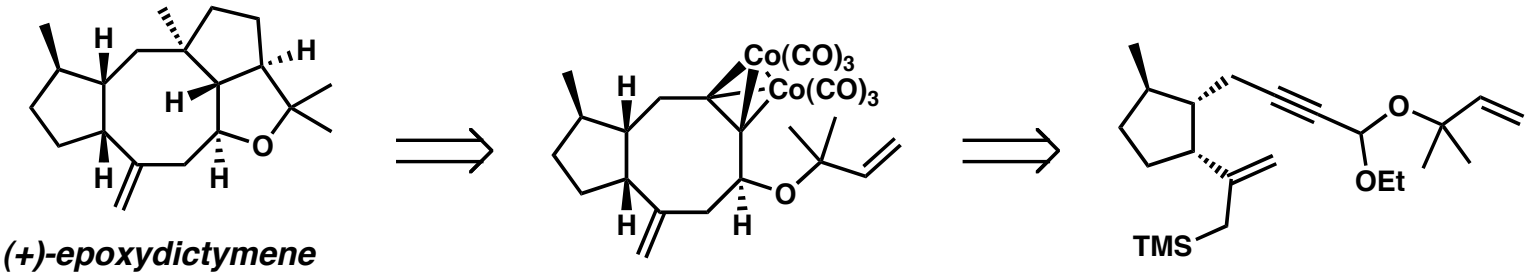
Synthesis of (+)-epoxydictymene



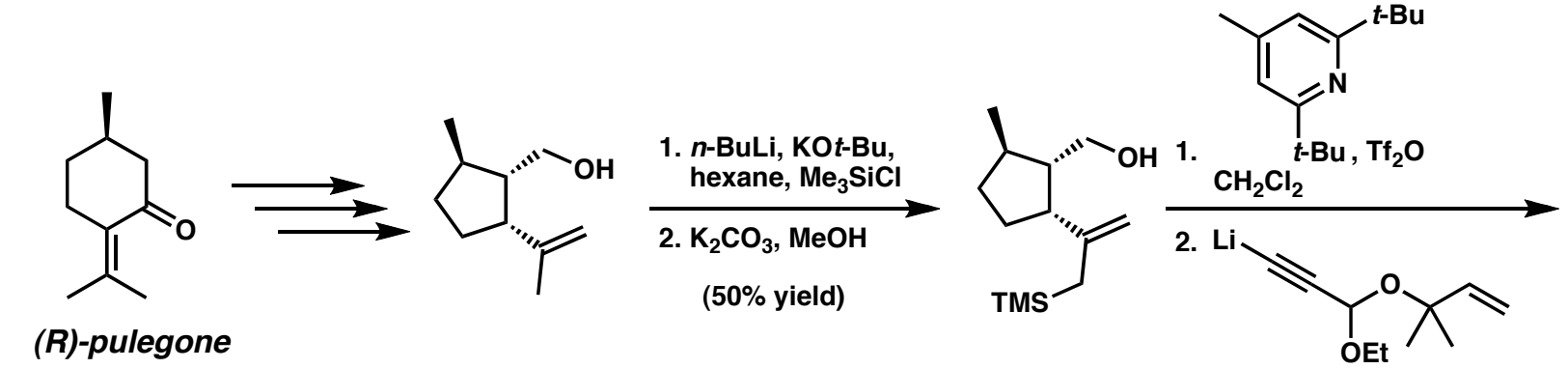
Schreiber. *J. Am. Chem. Soc.* **1994**, *116*, 5505.

C–C bond formation

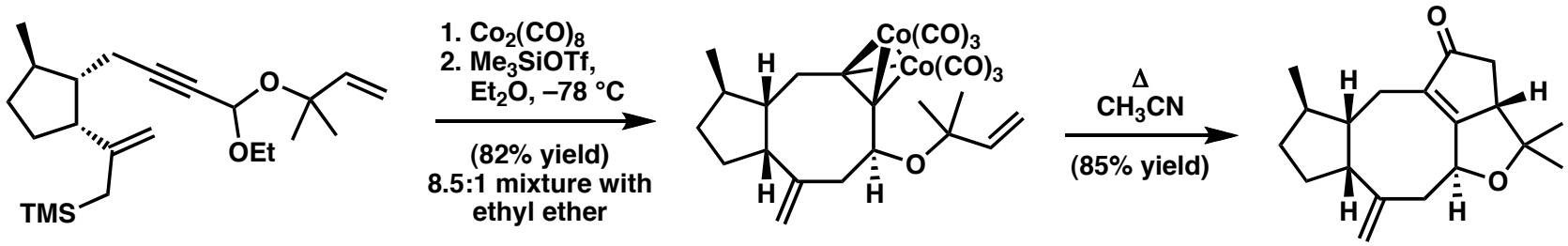
Synthesis of (+)-epoxydictymene



(+)-epoxydictymene



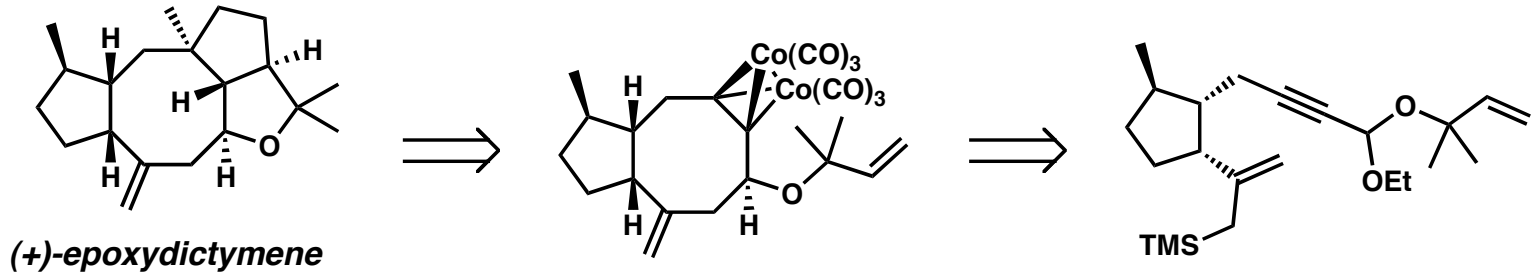
(R)-pulegone

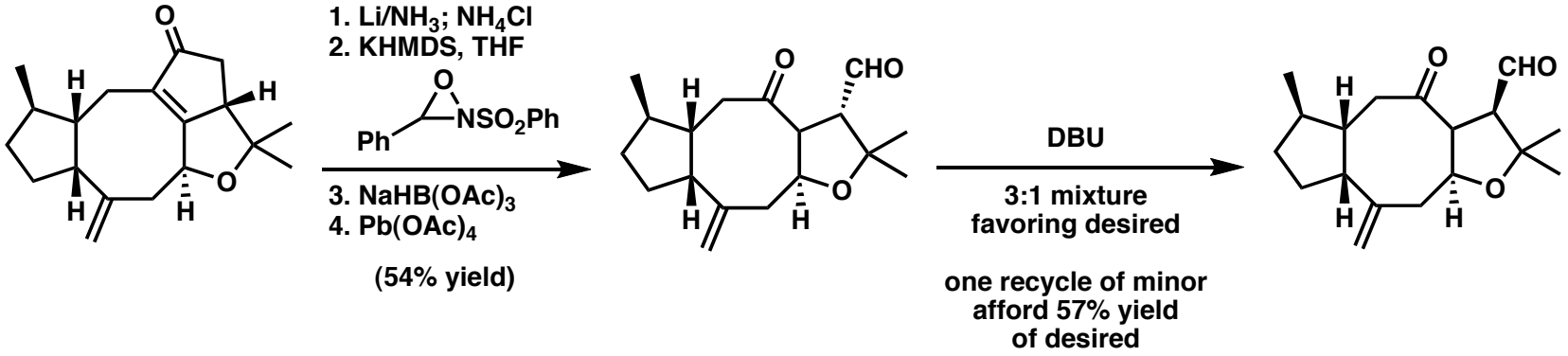


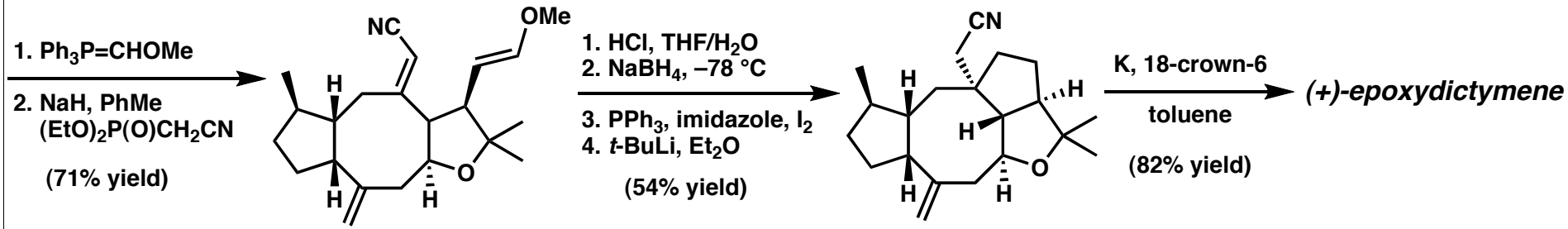
Schreiber. *J. Am. Chem. Soc.* **1994**, *116*, 5505.

C–C bond formation

Synthesis of (+)-epoxydictymene



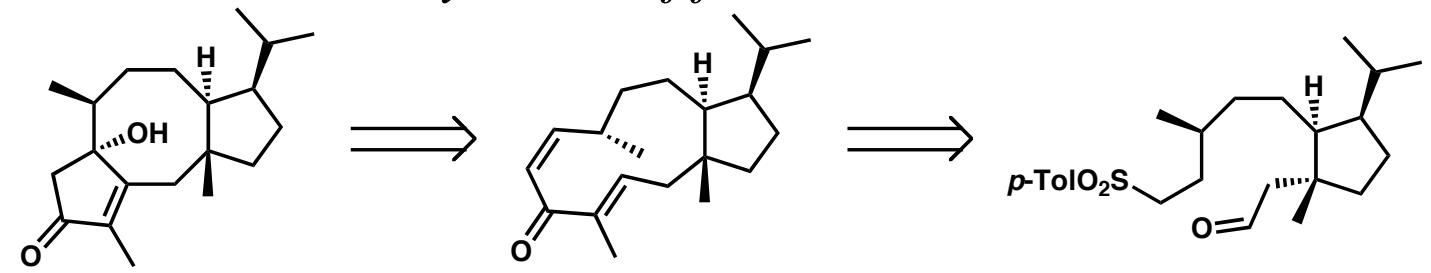




Schreiber. *J. Am. Chem. Soc.* **1994**, *116*, 5505.

C–C bond formation

Synthesis of fusicoauritone

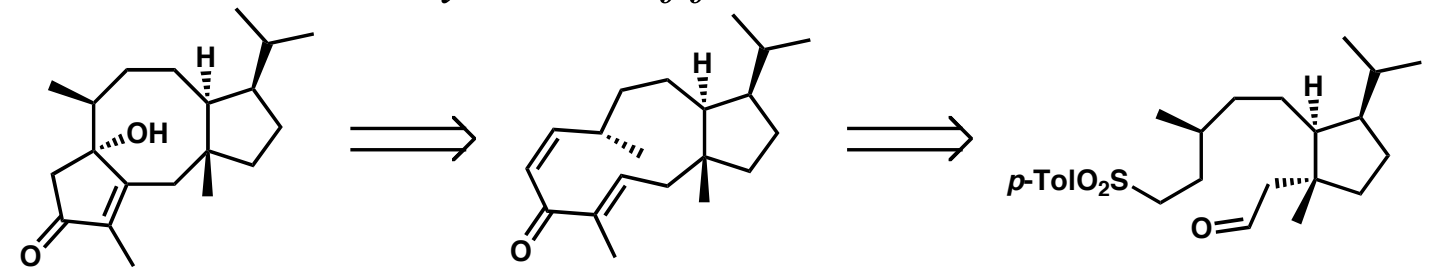


(+)-fusicoauritone

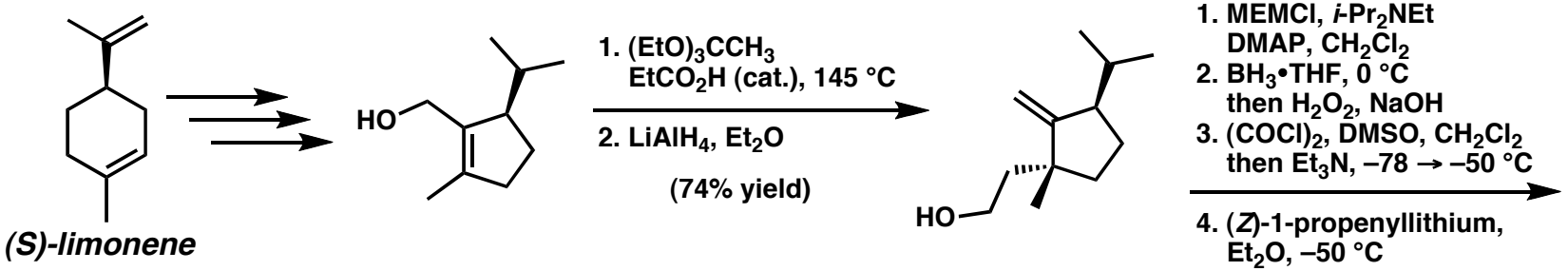
Williams. *Angew. Chem. Int. Ed.* **2007**, *46*, 915.

C–C bond formation

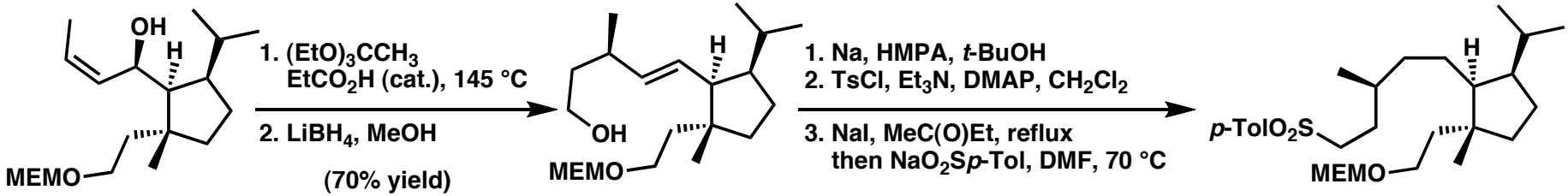
Synthesis of fusicoauritone



(+)-fusicoauritone



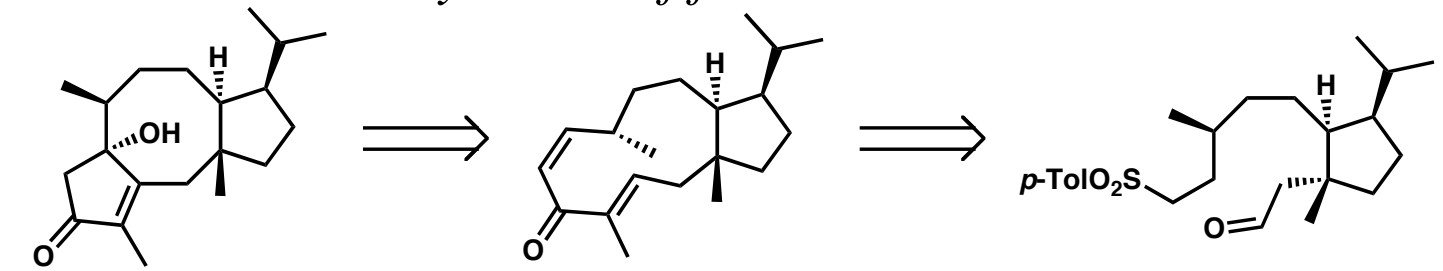
(S)-limonene



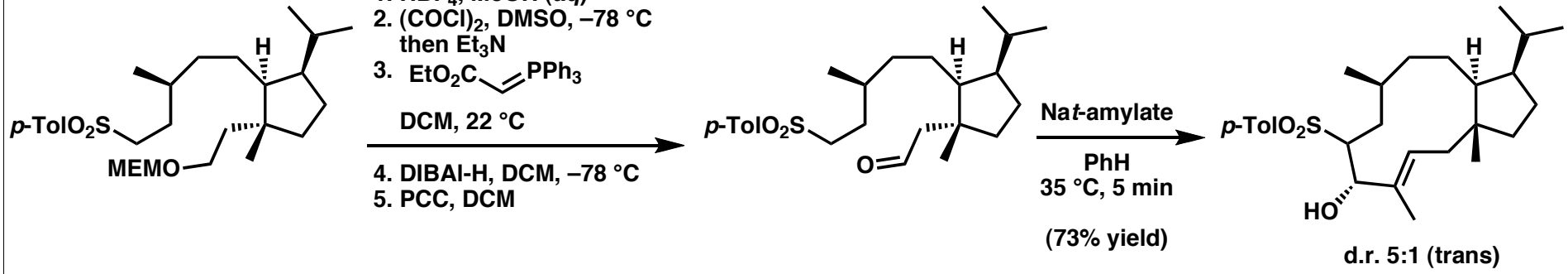
Williams. *Angew. Chem. Int. Ed.* **2007**, *46*, 915.

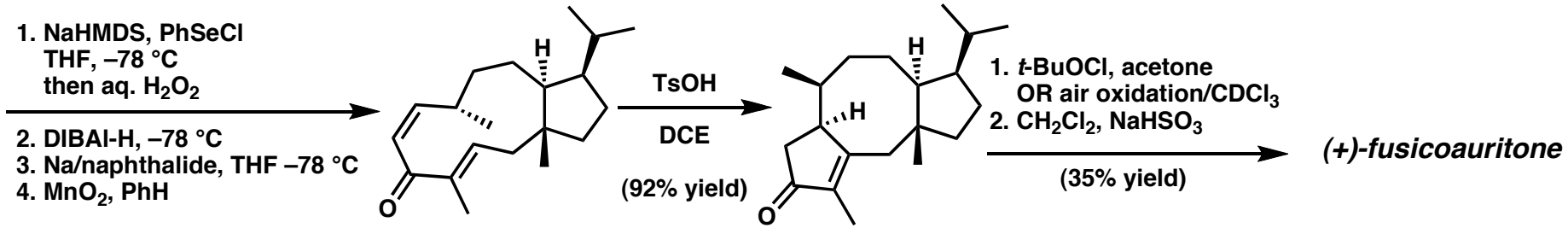
C–C bond formation

Synthesis of fusicoauritone



(+)-fusicoauritone





Williams. *Angew. Chem. Int. Ed.* **2007**, *46*, 915.