Synthetic Approaches to Eight Membered Rings via Carbon-Carbon Bond Manipulation

D. H. B. Ripin 11/95

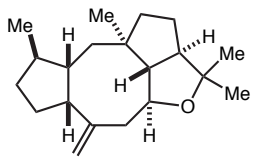
I. The synthetic challenge

II. Intramolecular cyclization

III. Ring contraction of larger rings

IV. Fragmentations of bicyclic ring systems

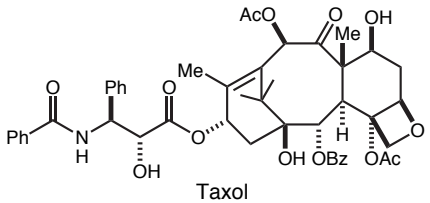
V. Ring expansion of smaller rings



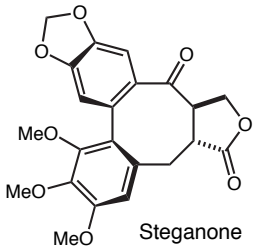
(+) epoxydictymene

Leading References:

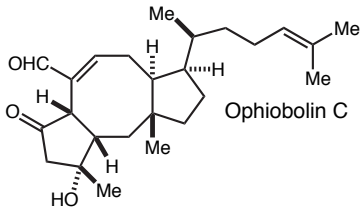
Petasis, Patane *Tetrahed.* **1992**, 5757
Swindell *Org. Prep. Proc. Int.* **1991**, 465.
Oare *Evans Group Seminar* **1991**.



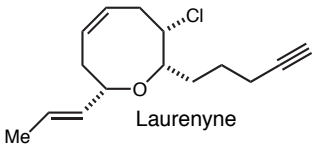
Taxol



Steganone



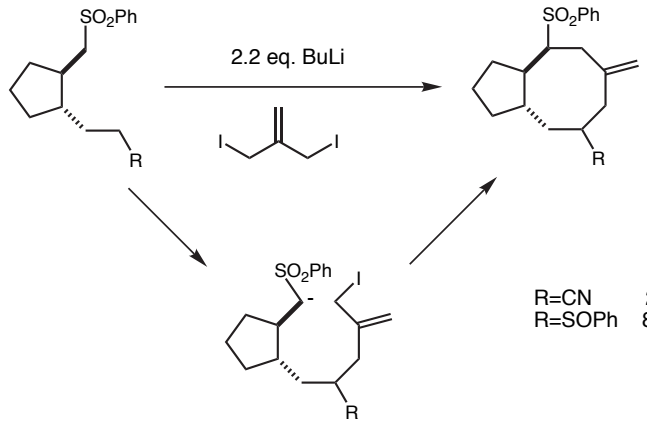
Ophiobolin C



Laurenyne

Intramolecular cyclization routes to eight membered rings

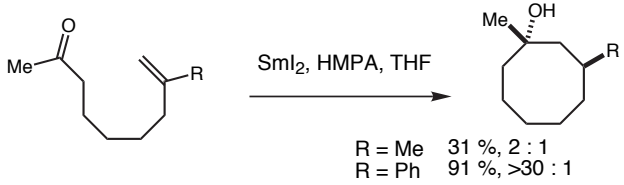
Sulfone alkylation:



■ cis olefins, fused rings, and large substituents facilitate the gauche relationships required for cyclization.

Lansbury *TL* **1990**, 3965.

Radical cyclization

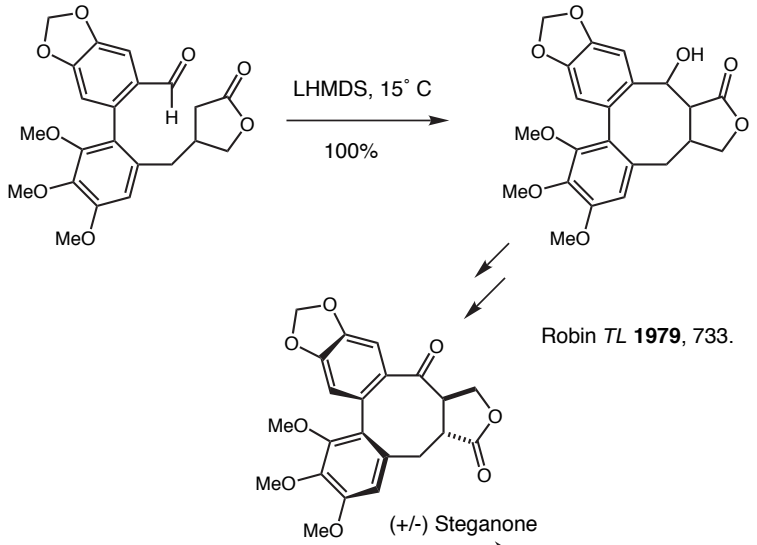


8-endo trig closure preferred over 7-exo.

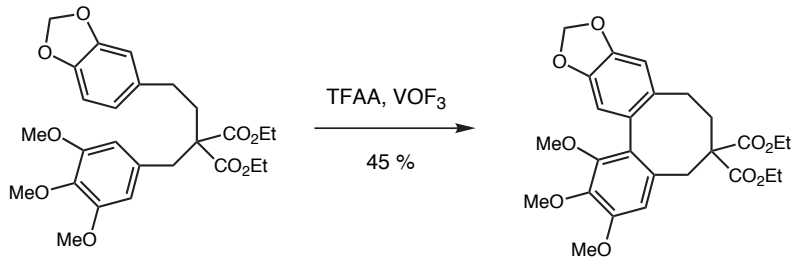
Molander *JOC* **1994**, 3189.

Intramolecular cyclization routes to eight membered rings

Aldol:



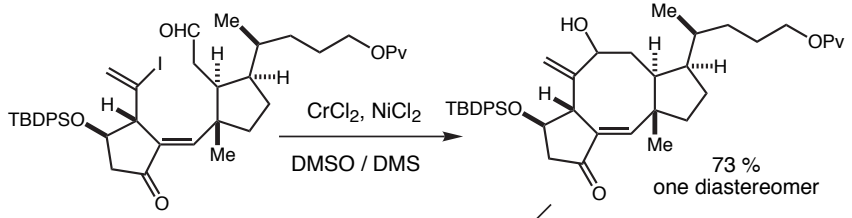
Biaryl coupling:



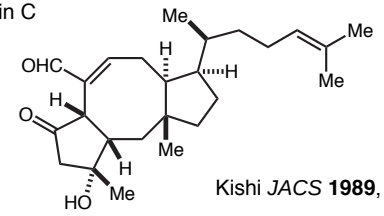
Kende *JACS* **1976**, 267.

Intramolecular cyclization routes to eight membered rings

Nickel-Chromium coupling

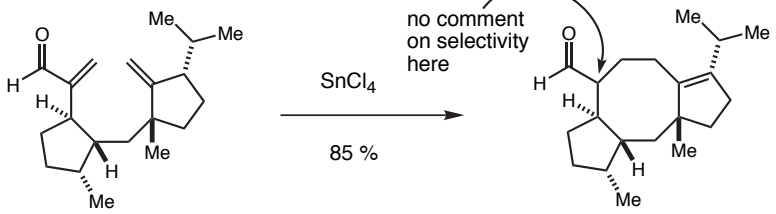


Ophiobolin C



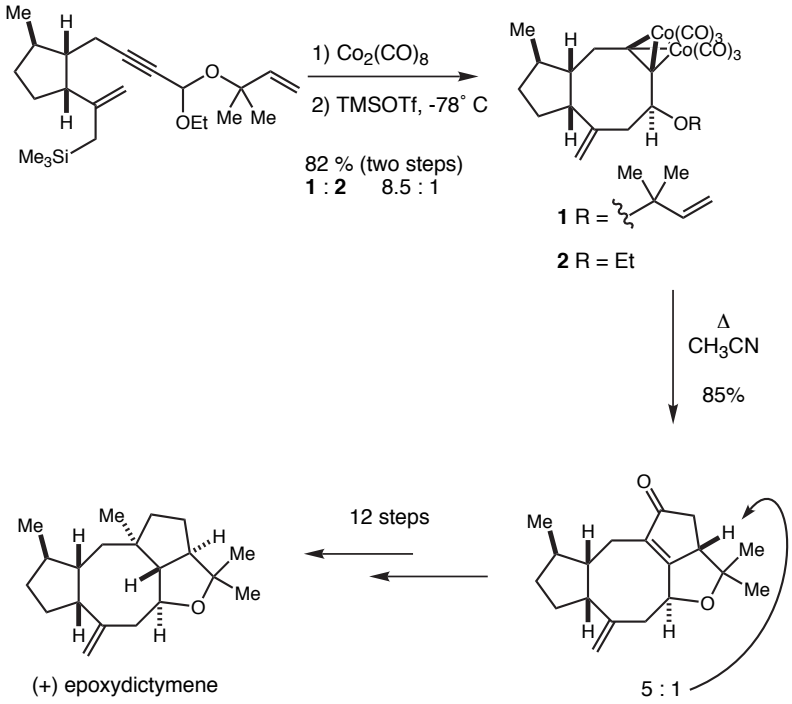
Kishi *JACS* **1989**, 2735.

Conjugate ene rxn.



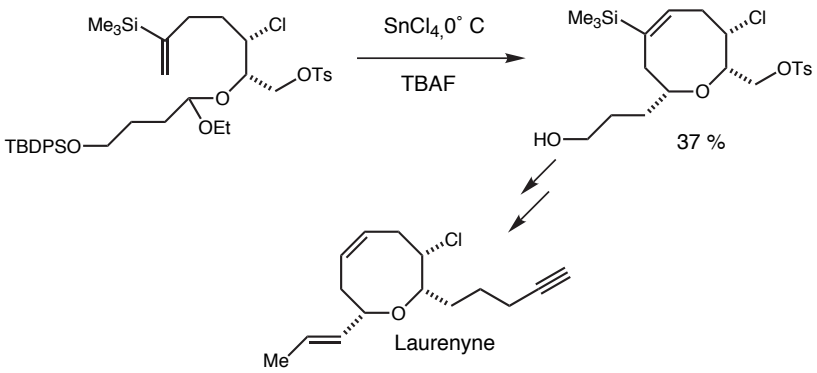
Kato *Chem. Lett.* **1989**, 91.

Intramolecular cyclization routes to eight membered rings

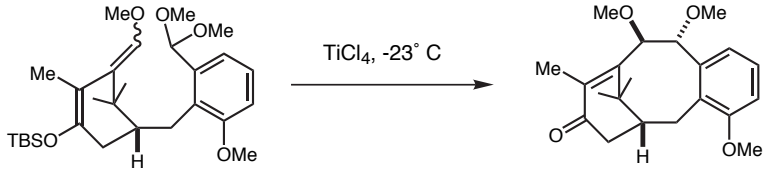


Schreiber *JACS* **1994**, 5505.

Intramolecular cyclization routes
to eight membered rings



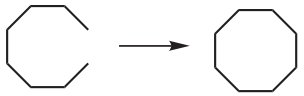
Overman *JACS* **1988**, 2248.



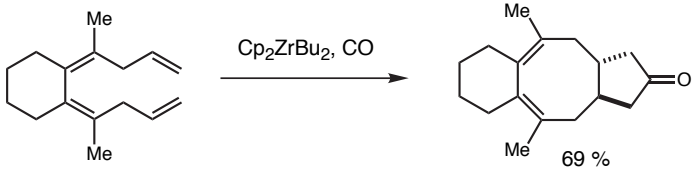
84 % one isomer

Kuwajima *TL* **1993**, 345.

Intramolecular cyclization routes
to eight membered rings

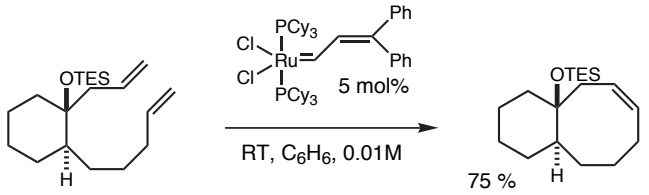


Negishi cyclization



Takahashi *Organomet*.**1994**, 4183.

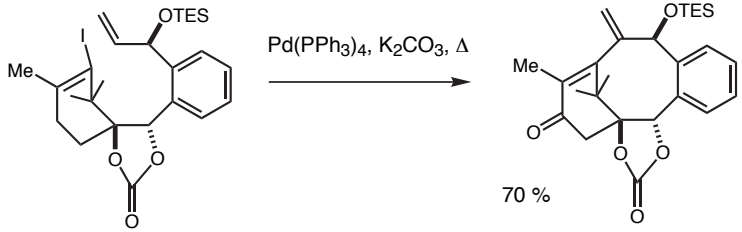
Ring Closing Metathesis



Grubbs *JACS* **1995**, 2108.

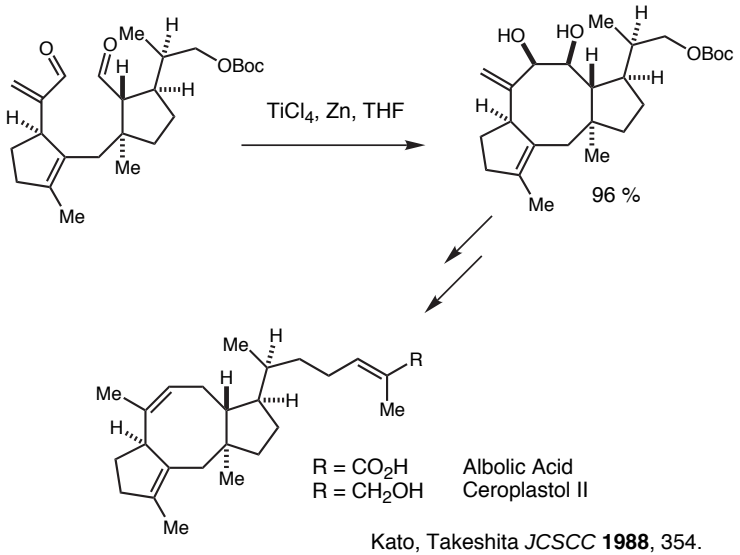
Intramolecular cyclization routes
to eight membered rings

Heck Reaction:



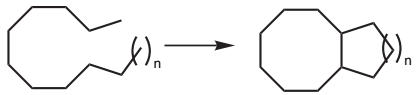
Danishefsky *JACS* **1995**, 5229.

McMurray Rxn.

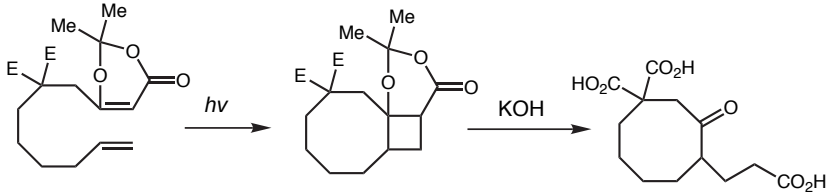


Kato, Takeshita *JCSCC* **1988**, 354.

Intramolecular cycloaddition routes
to eight membered rings

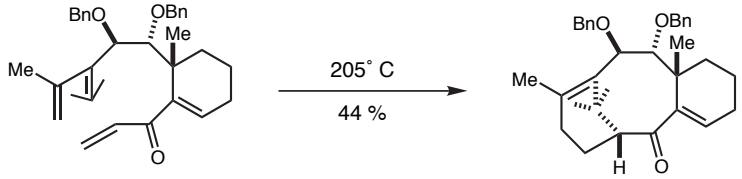


[2+2]



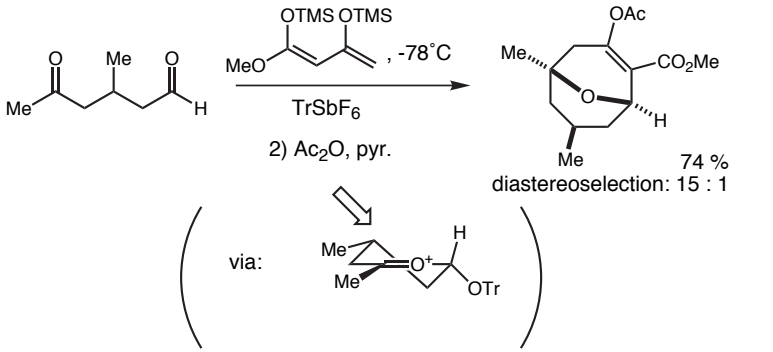
Winkler *Heterocycles* **1987**, 55.

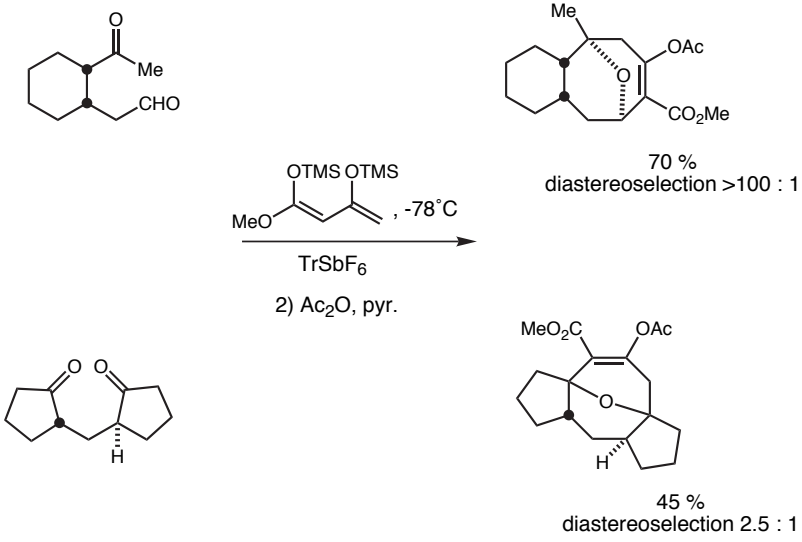
[4+2]



Shea *TL* **1994**, 1317.

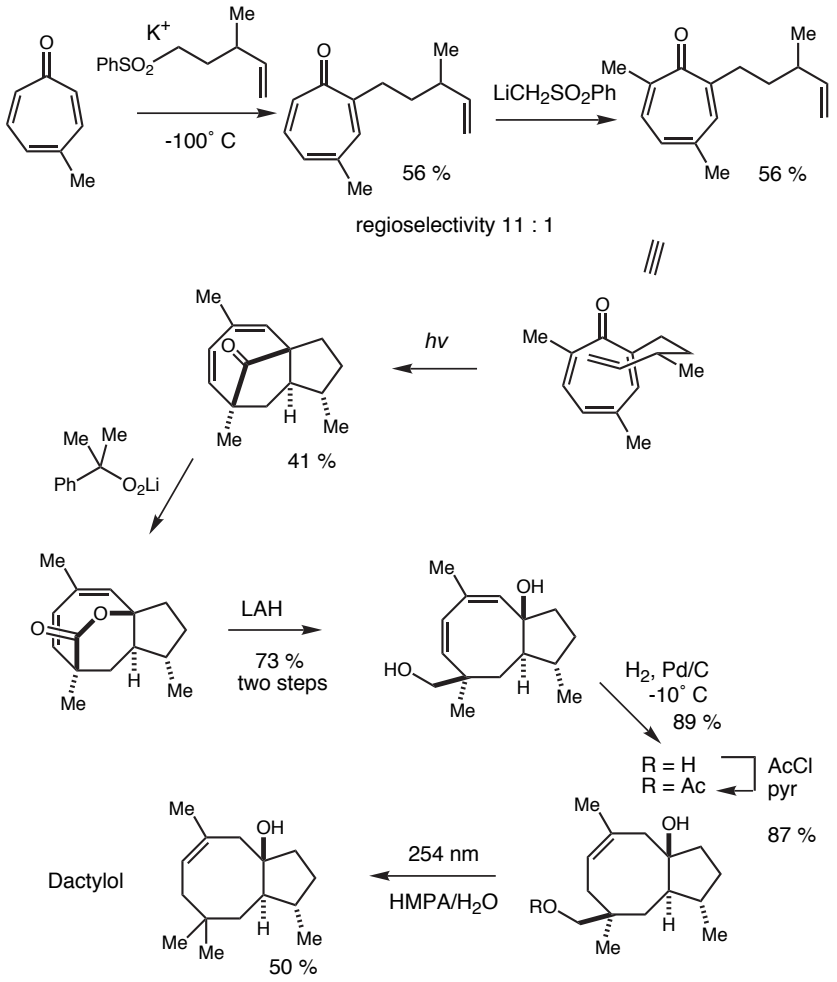
"[3 + 5]" Annulation routes
to eight membered rings





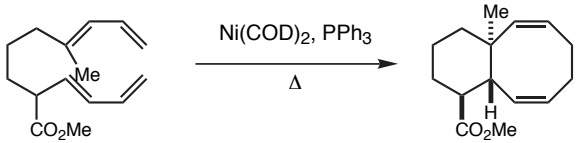
Molander *JOC* **1993**, 5931.

[2 + 6] Cycloaddition routes
to Dactylol



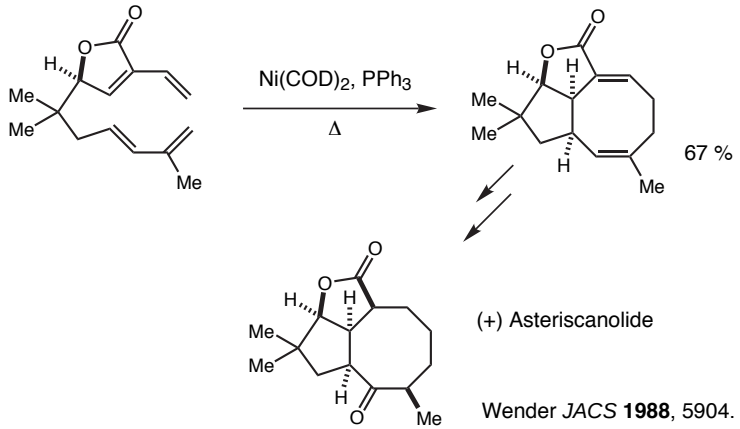
Feldman *JACS* **1989**, 6457.

[4 + 4] Cycloaddition routes
to eight membered rings



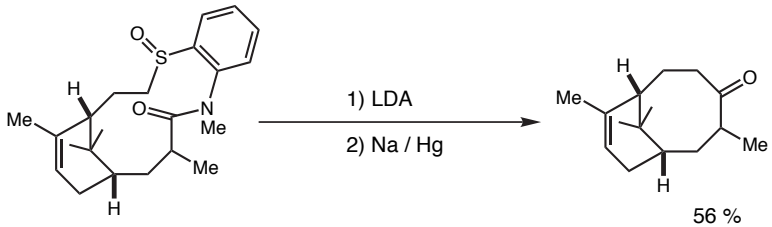
92 %
diastereoselection 97 : 3

Wender *TL* **1987**, 2221.



Wender *JACS* **1988**, 5904.

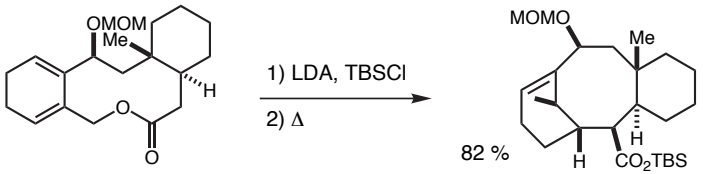
Ring contraction routes to eight membered rings



56 %

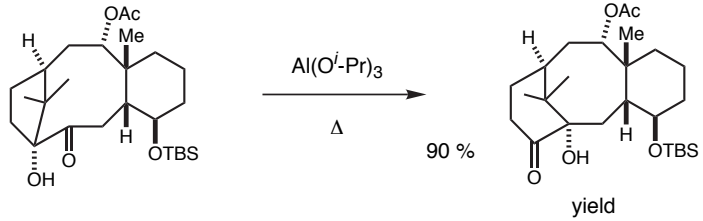
Ohtsuka, Oishi *TL* **1986**, 203.

Ireland-Claisen



Funk *JOC* **1988**, 4141.

Pinacol

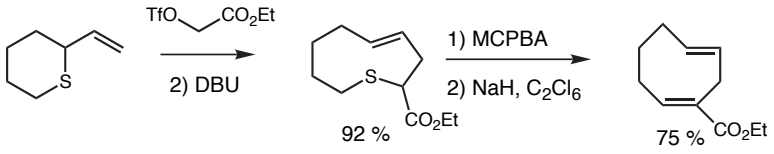


yield

Paquette *TL* **1991**, 6679.

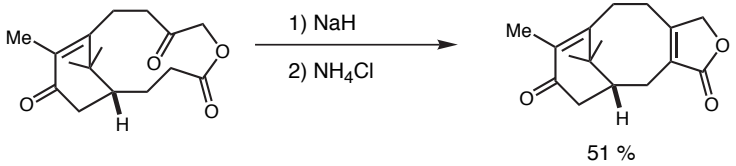
Ring contraction routes to eight membered rings

Ramberg-Backlund



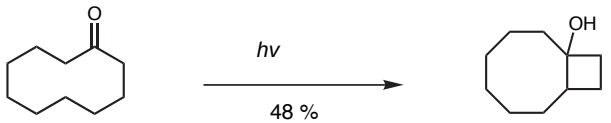
Vedejs *JOC* **1978**, 4884.

Transannular Aldol



Sampson *JOC* **1993**, 6807.

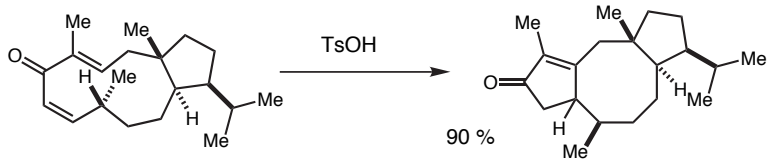
Norrish Type II



Sauers *TL* **1990**, 5709.

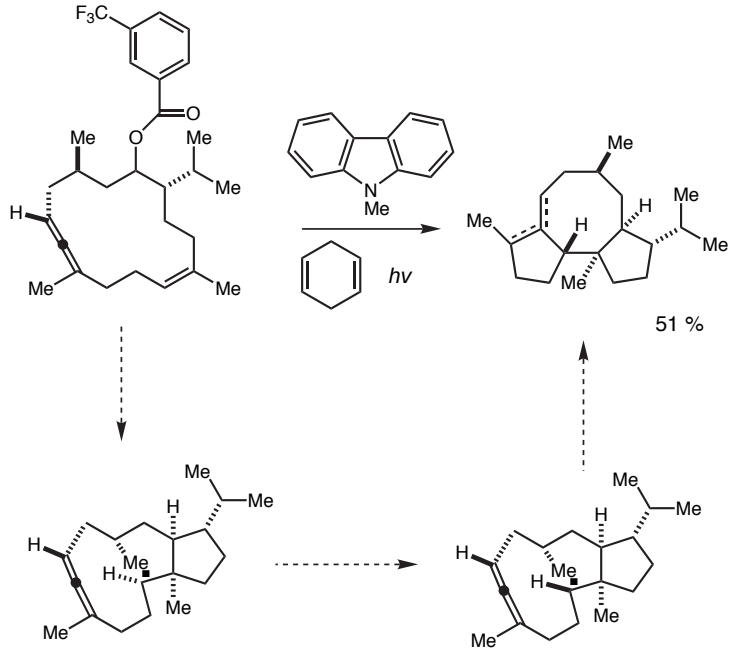
Ring contraction routes to eight membered rings

Transannular Nazarov Cyclization



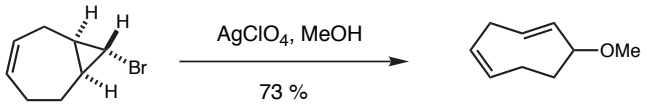
Williams *PJ Coleman Evening Seminar* 10/4/1994

Transannular radical cyclization

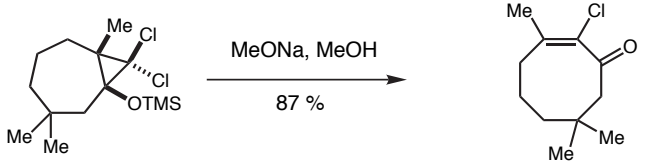


Myers *JACS* **1993**, 7926.

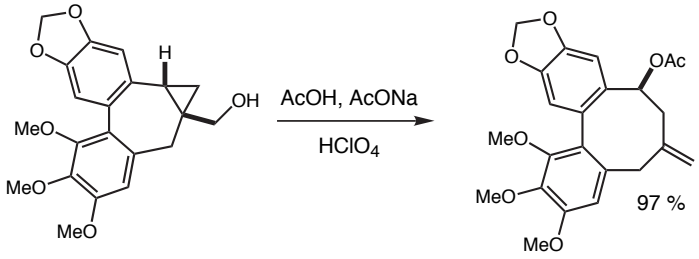
Fragmentation of bicyclic ring systems



Reese *JCSCC* **1970**, 1644.

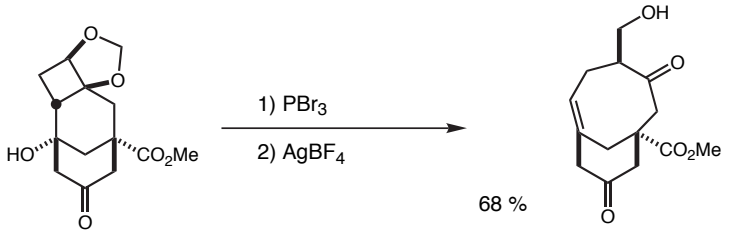


Wenkert *JOC* **1990**, 1185.

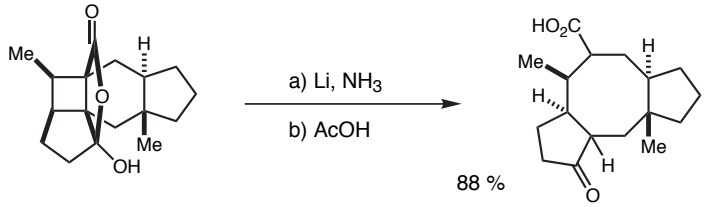


Magnus *JCSCC* **1984**, 1179.

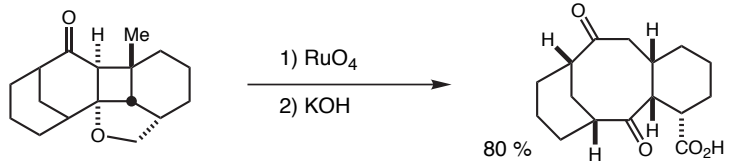
Fragmentation of bicyclic ring systems



Kraus *Synlett* **1993**, 71.

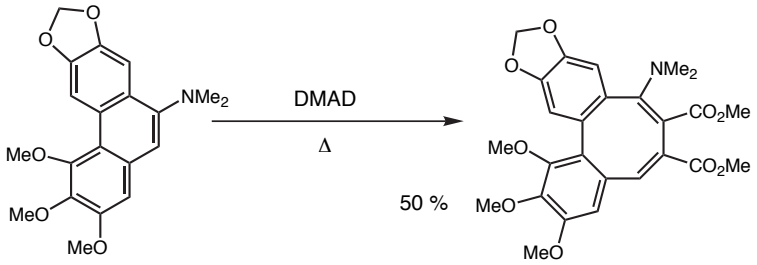


Coates *JACS* **1985**, 3541.

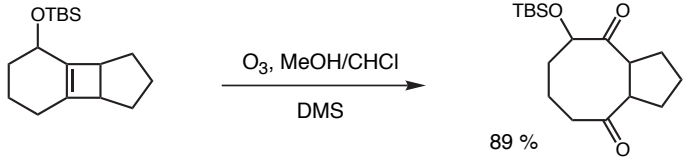


Berkowitz *TL* **1985**, 3665.

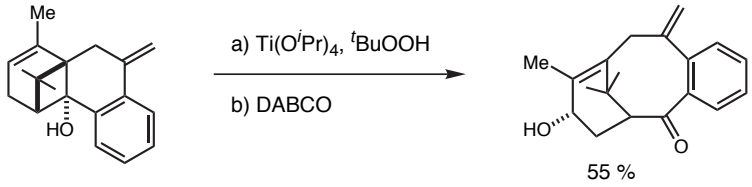
Fragmentation of bicyclic ring systems



Krow *JOC* **1978**, 3950.

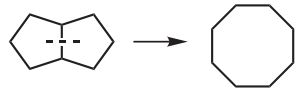


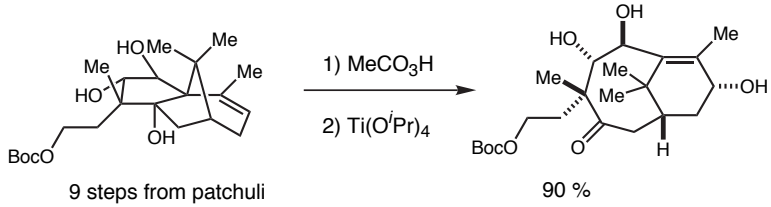
Galatsis *Tetrahed*. **1995**, 665.



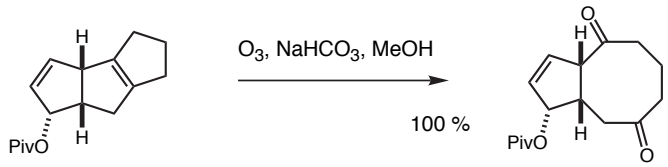
Wender *JACS* **1992**, 5878.

Fragmentation of bicyclic ring systems





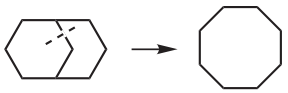
Holton *JACS* **1988**, 6558.

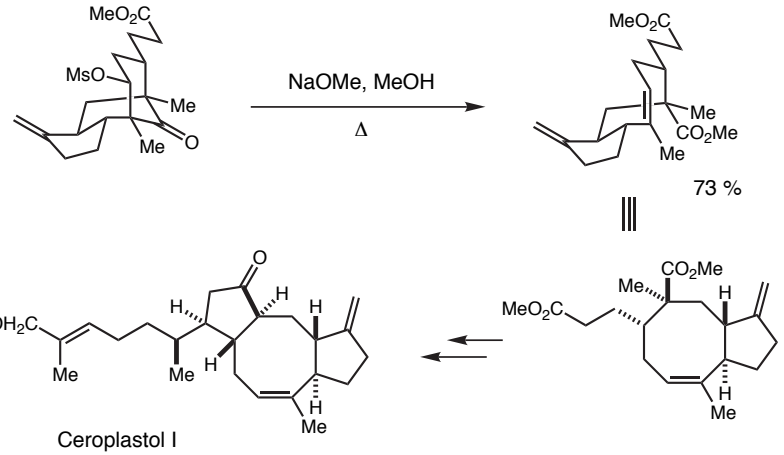


Trost *JOC* **1994**, 7568.

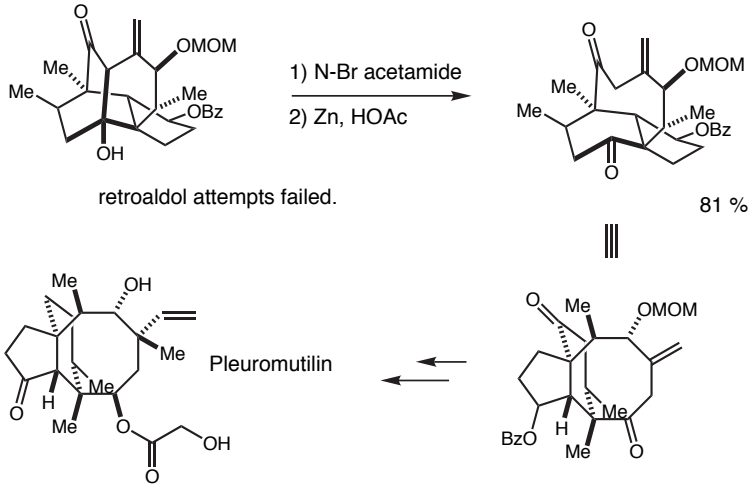
Trost *JACS* **1982**, 886.

Fragmentation of bicyclic ring systems



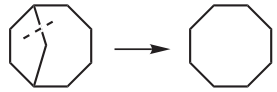


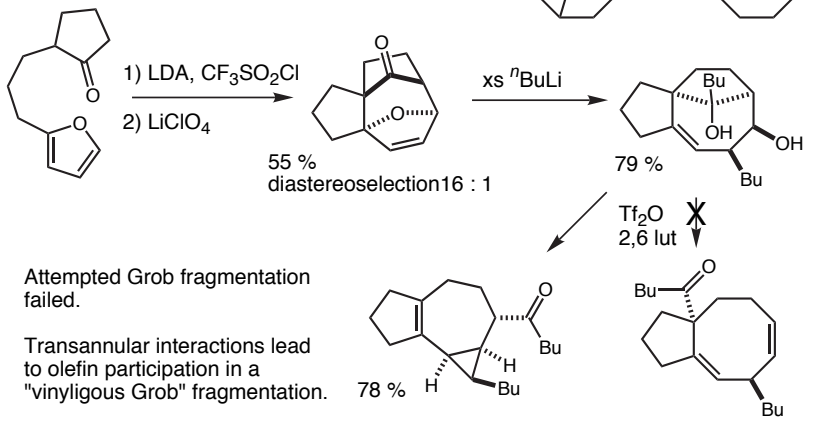
Boeckman *JACS* **1989**, 2737.



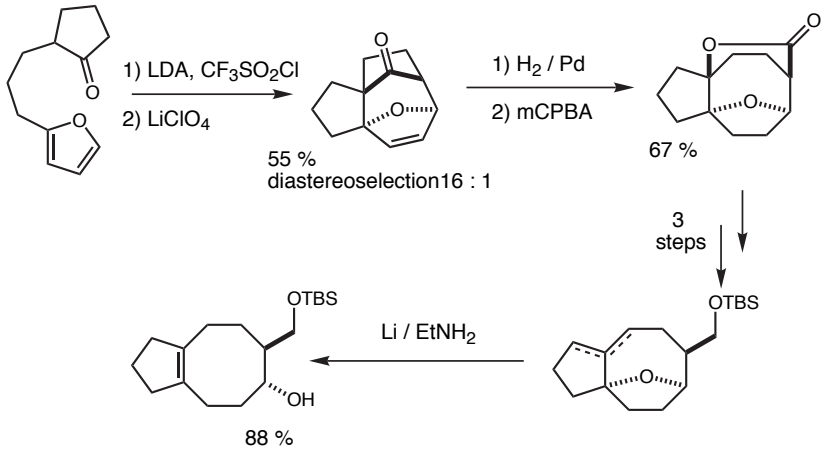
Gibbons, *JACS* **1982**, 1767

Fragmentation of bicyclic ring systems





Harmata *TL* **1993**, 789.



Harmata *JOC* **1994**, 1241.

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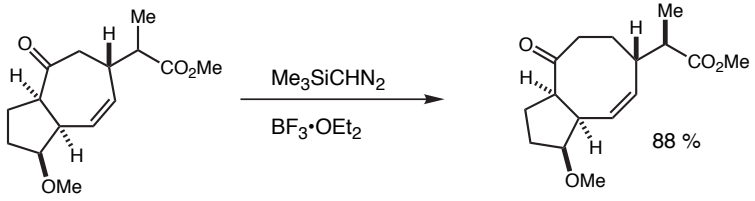
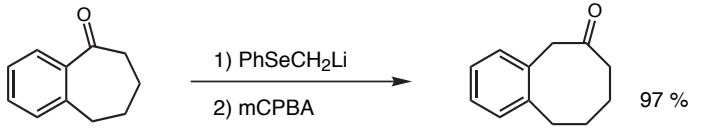
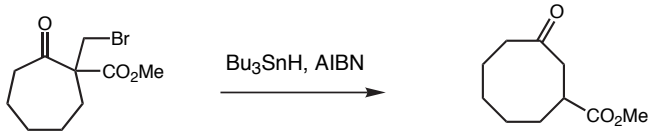


Rigby *JOC* **1987**, 4634.



Uemura *JCSCC* **1988**, 111.



Dowd *JACS* **1987**, 3493.

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Overman *JACS* **1989**, 1514.

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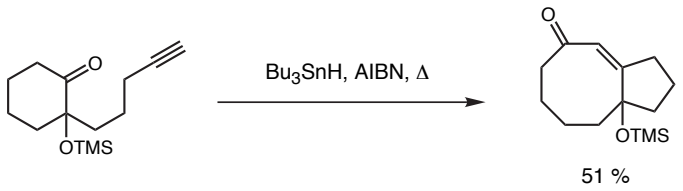
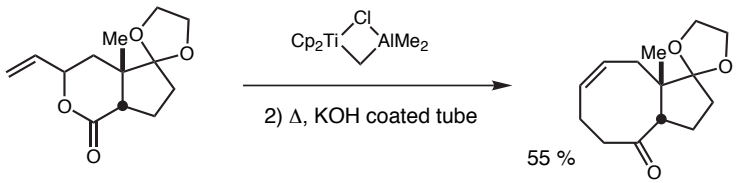
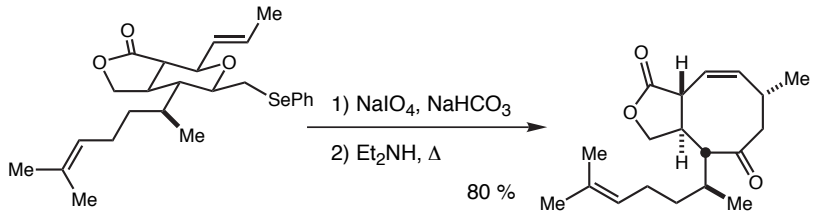


Nishida *JACS* **1990**, 902.



Paquette *JACS* **1993**, 1676.



Paquette *Helv. Chim. Acta* **1995**, 391.

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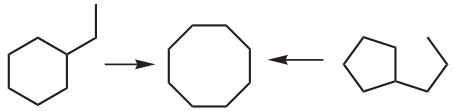
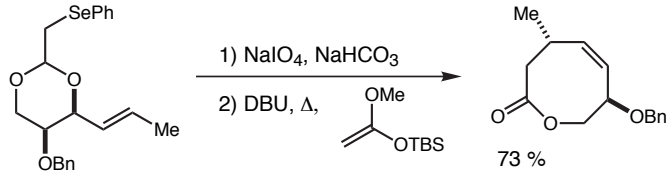
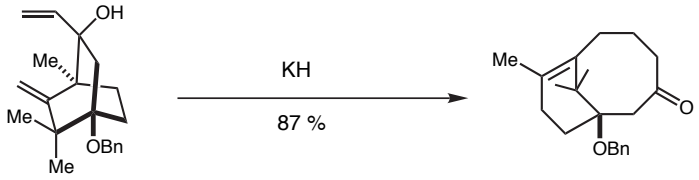
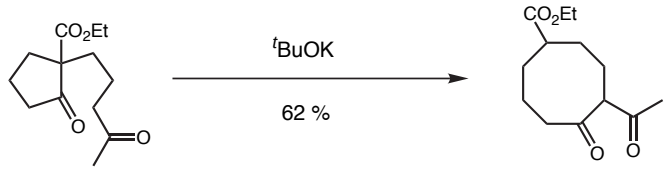




Holmes *JCSPTI* **1993**, 2743.



Martin *Tetrahed.* **1995**, 3455.



Sakai *JCSCC* **1988**, 612.

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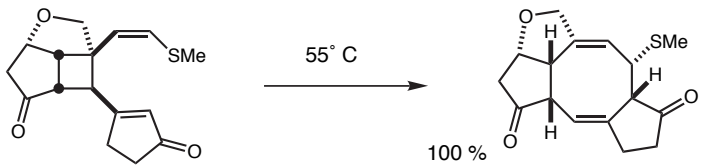
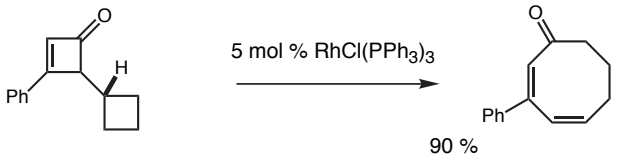


Jommi *TL* **1991**, 6969.



Liebeskind *JACS* **1993**, 4895.