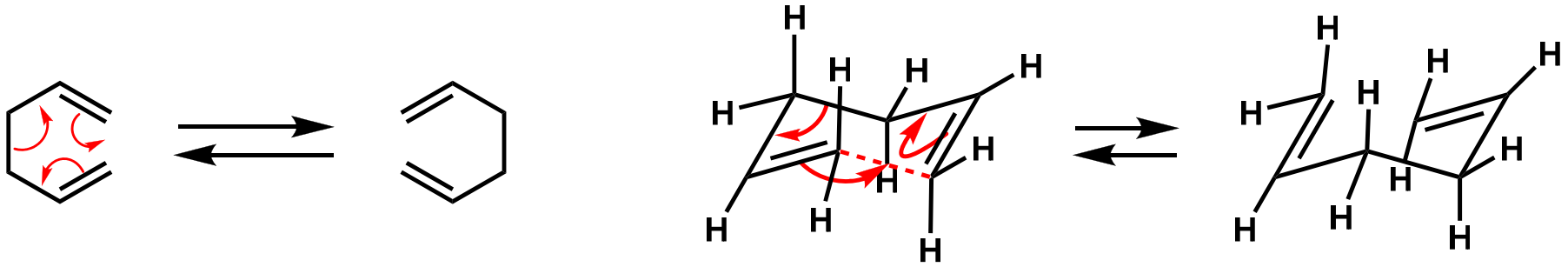
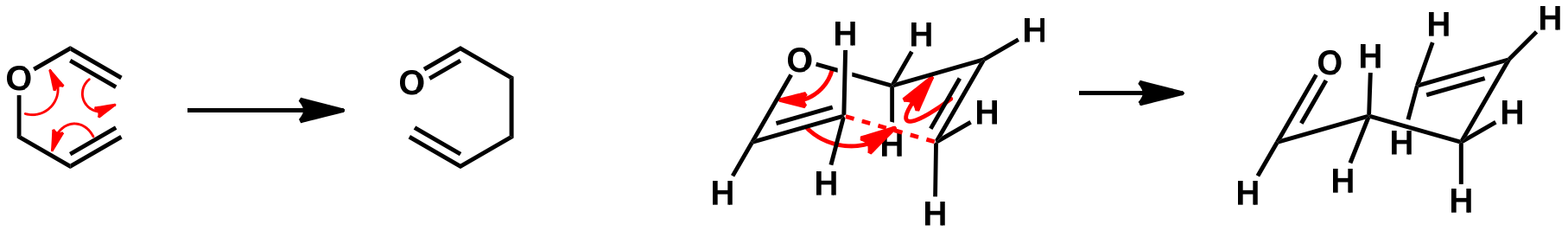
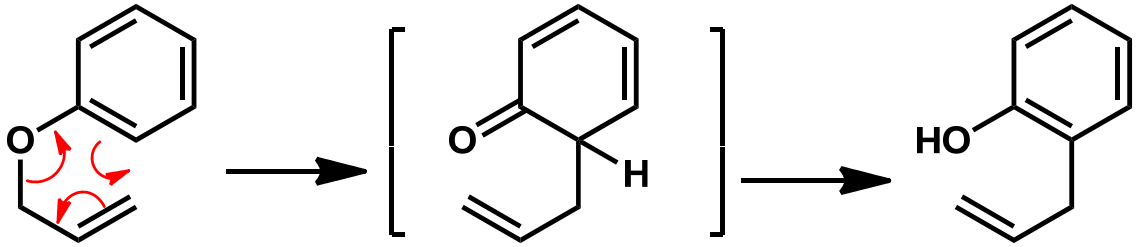
[3,3]-Sigmatropic Rearrangement

Cope rearrangement

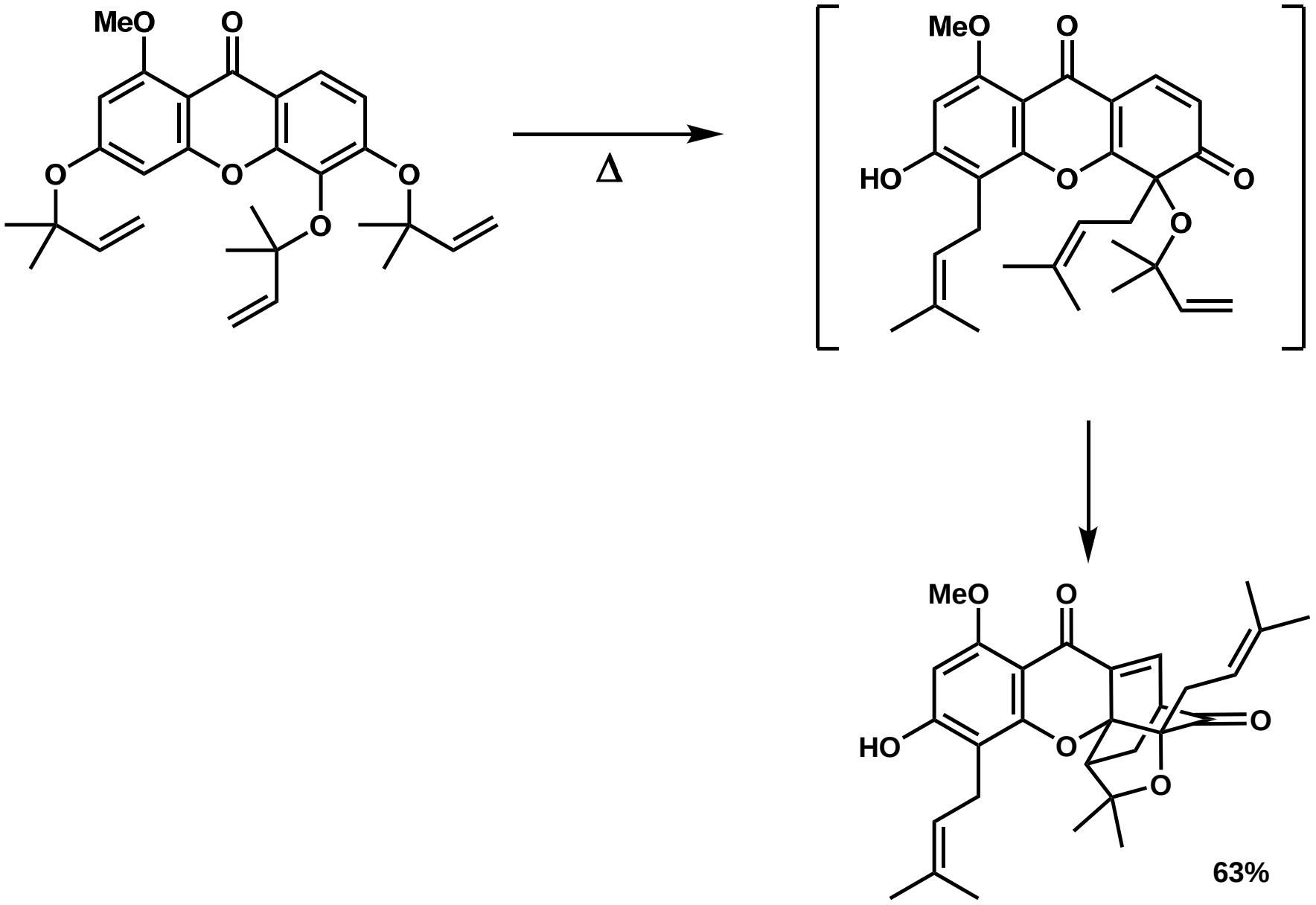


Claisen rearrangement



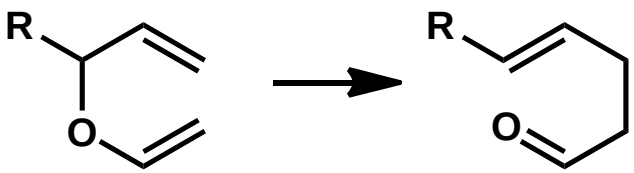


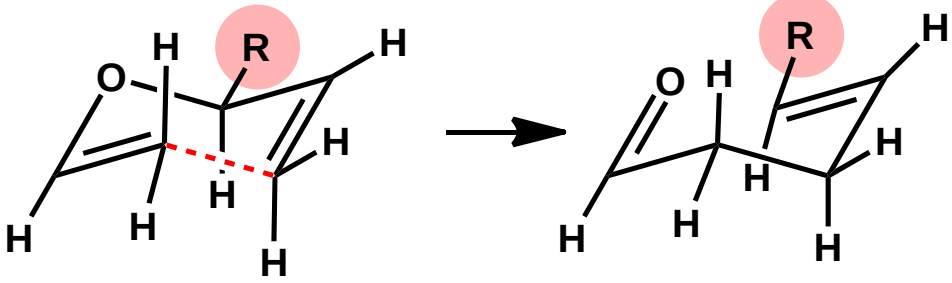
Claisen Rearrangement

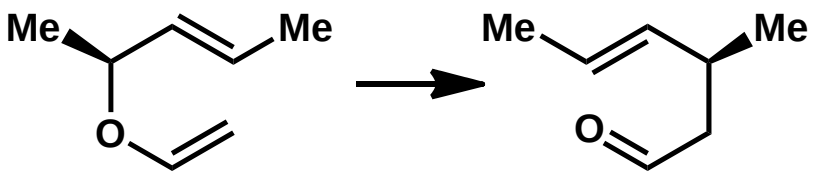


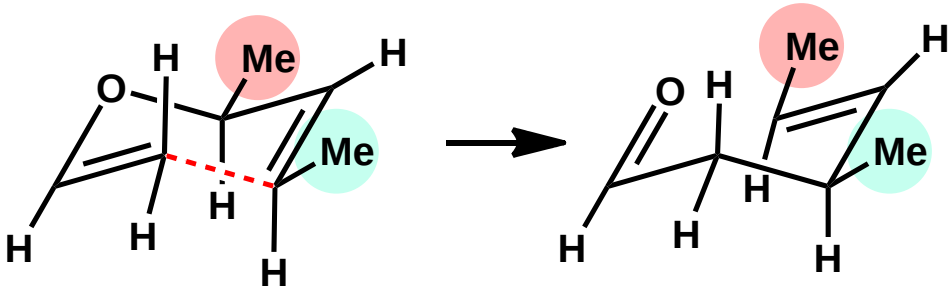
Nicolaou, K. C.; Li, J. *Angew. Chem. Int. Ed.* **2001**, *40*, 4264.

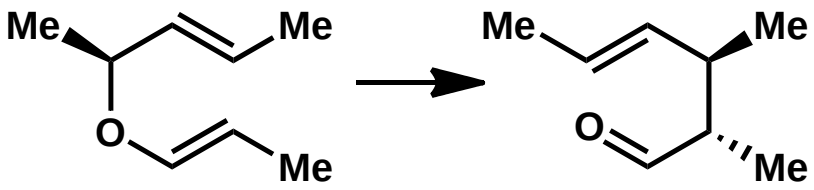
Stereochemistry

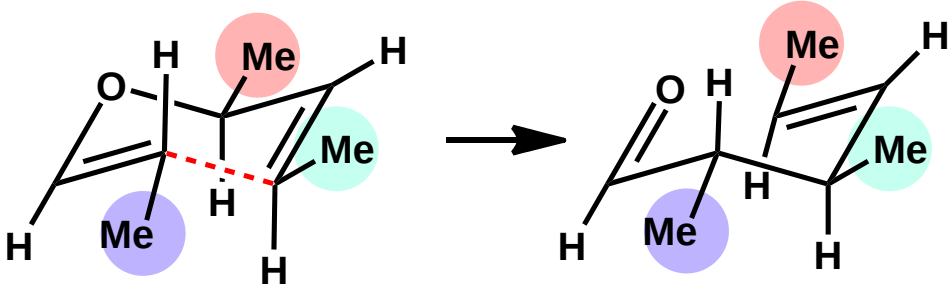


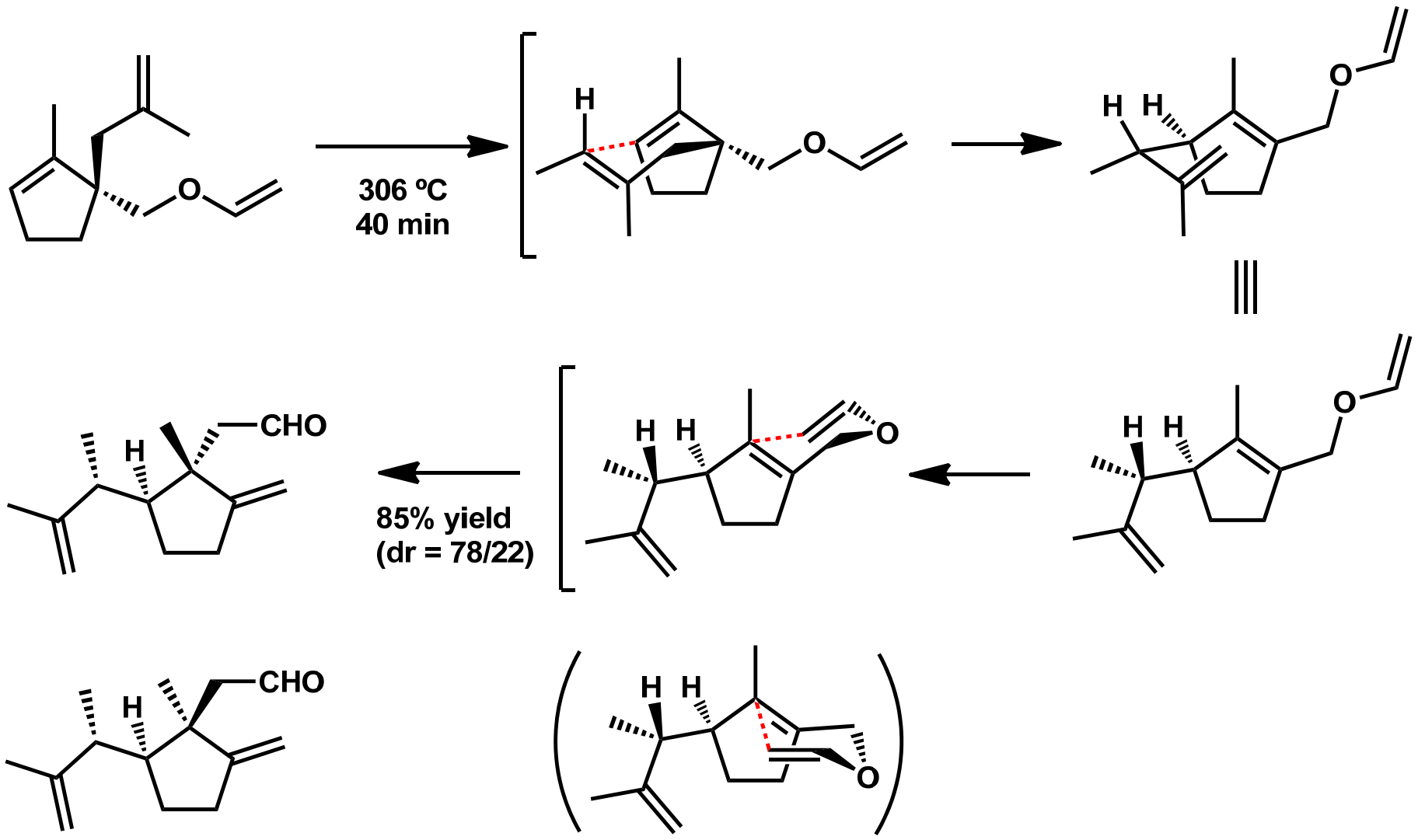






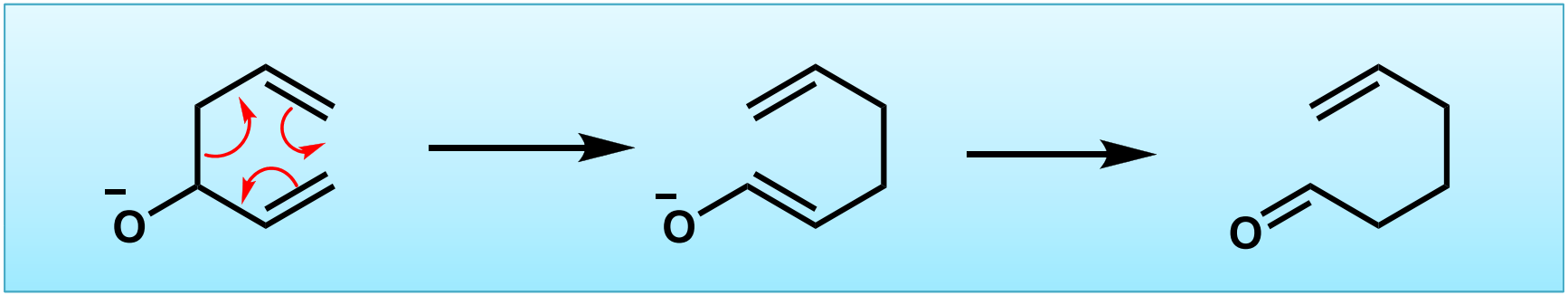


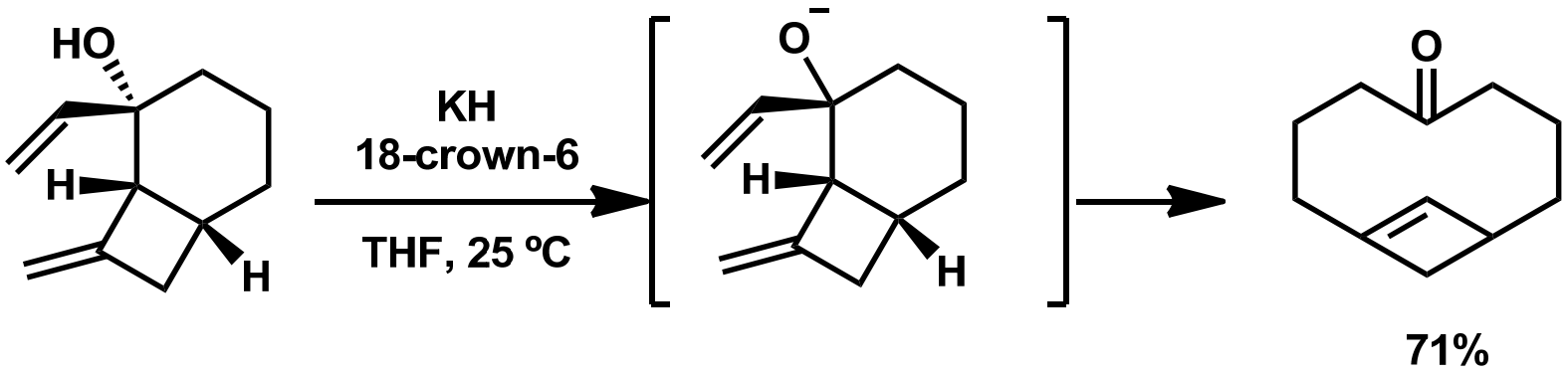




Ziegler, F. E.; Piwinski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 7181.

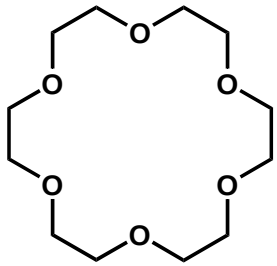
(Anionic) Oxy-Cope Rearrangement





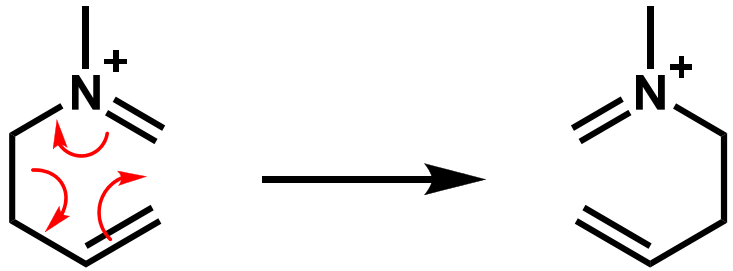
71%

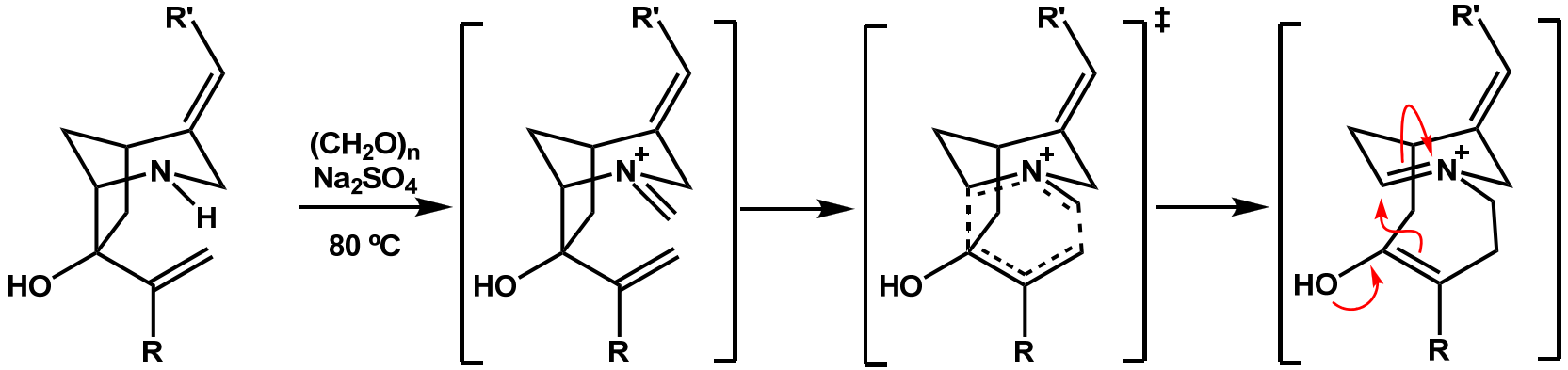
Schreiber, S. L.; Santini, C. *Tetrahedron Lett.* **1981**, *22*, 4651.



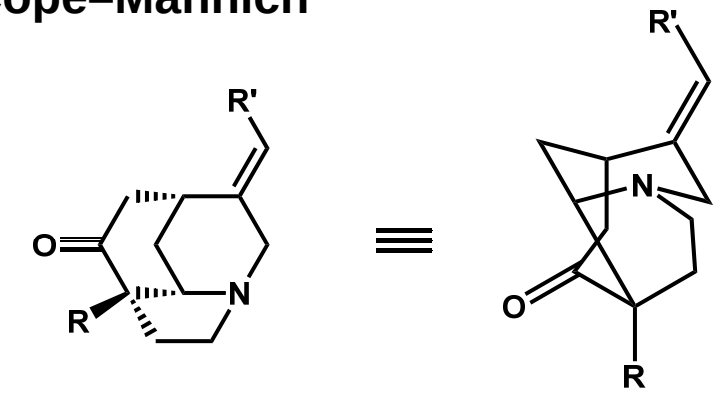
18-crown-6

Aza-Cope Rearrangement



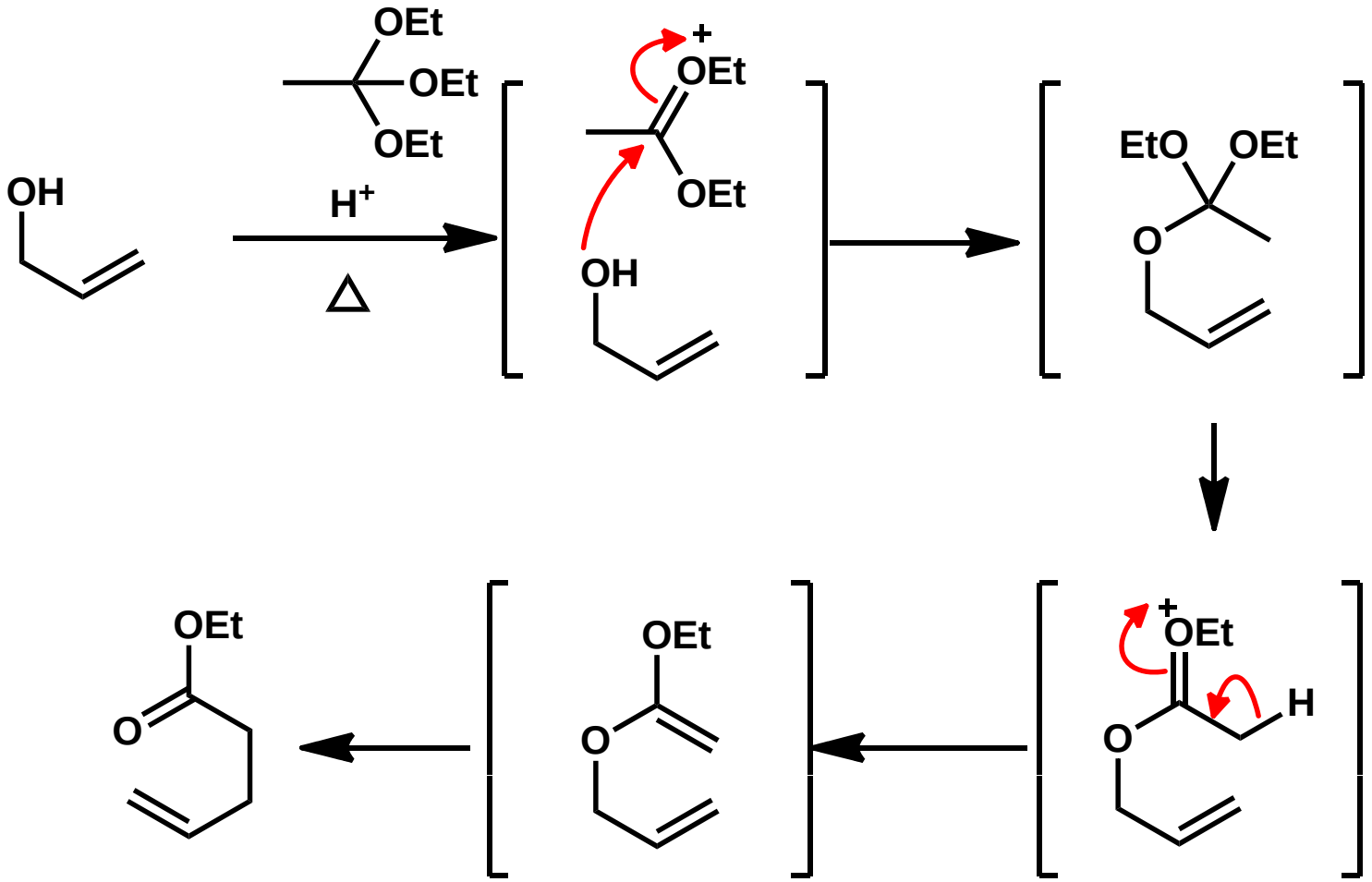


aza-Cope–Mannich



Knight, S. D.; Overman, L. E.; Pairaudeau, G.
J. Am. Chem. Soc. **1995**, *117*, 5776.

Johnson–Claisen Rearrangement



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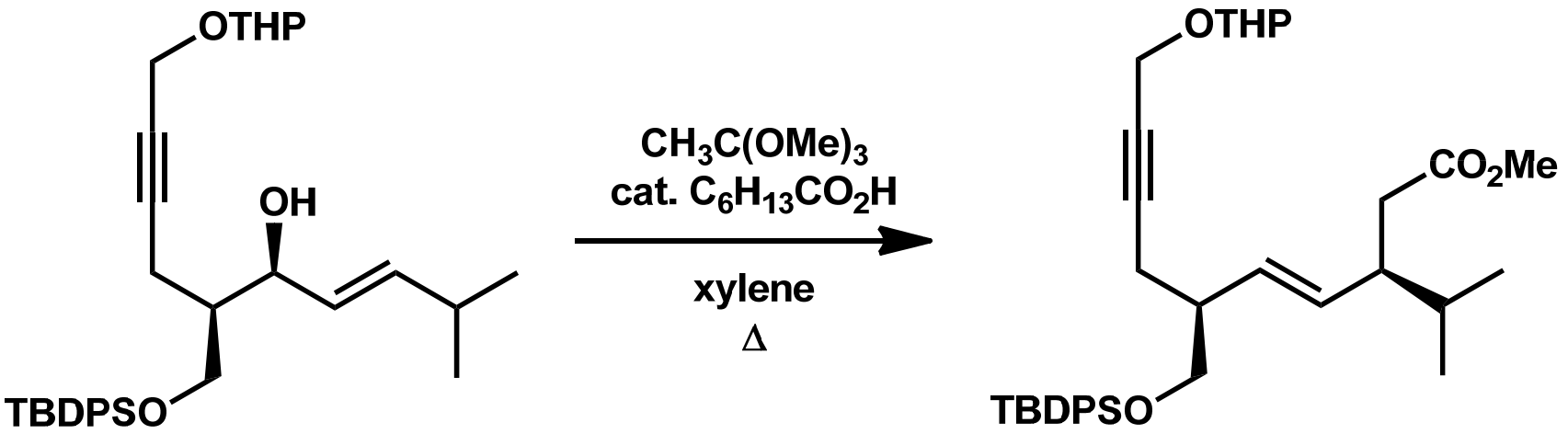
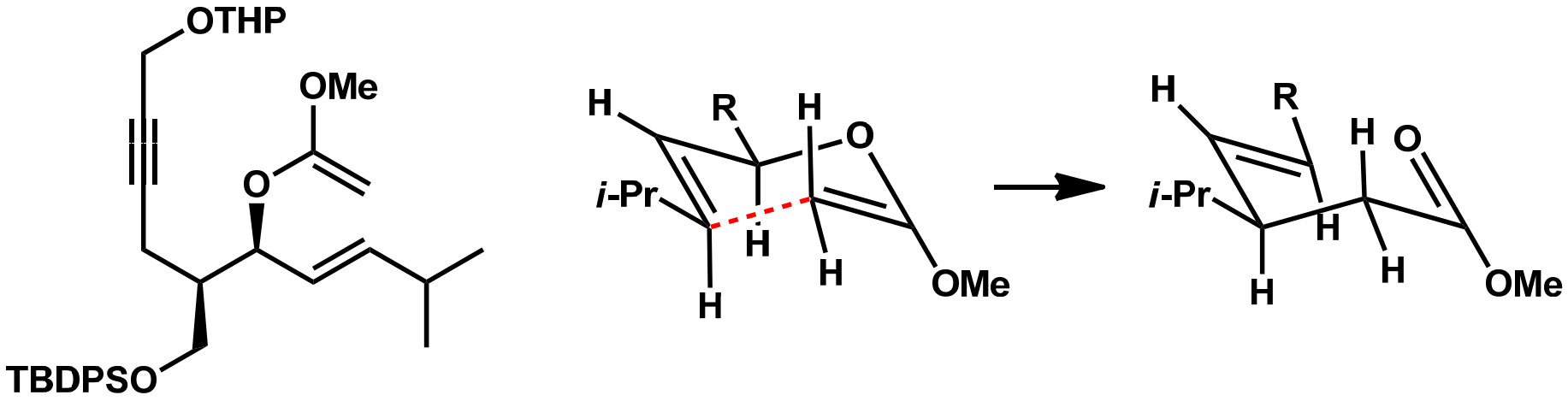
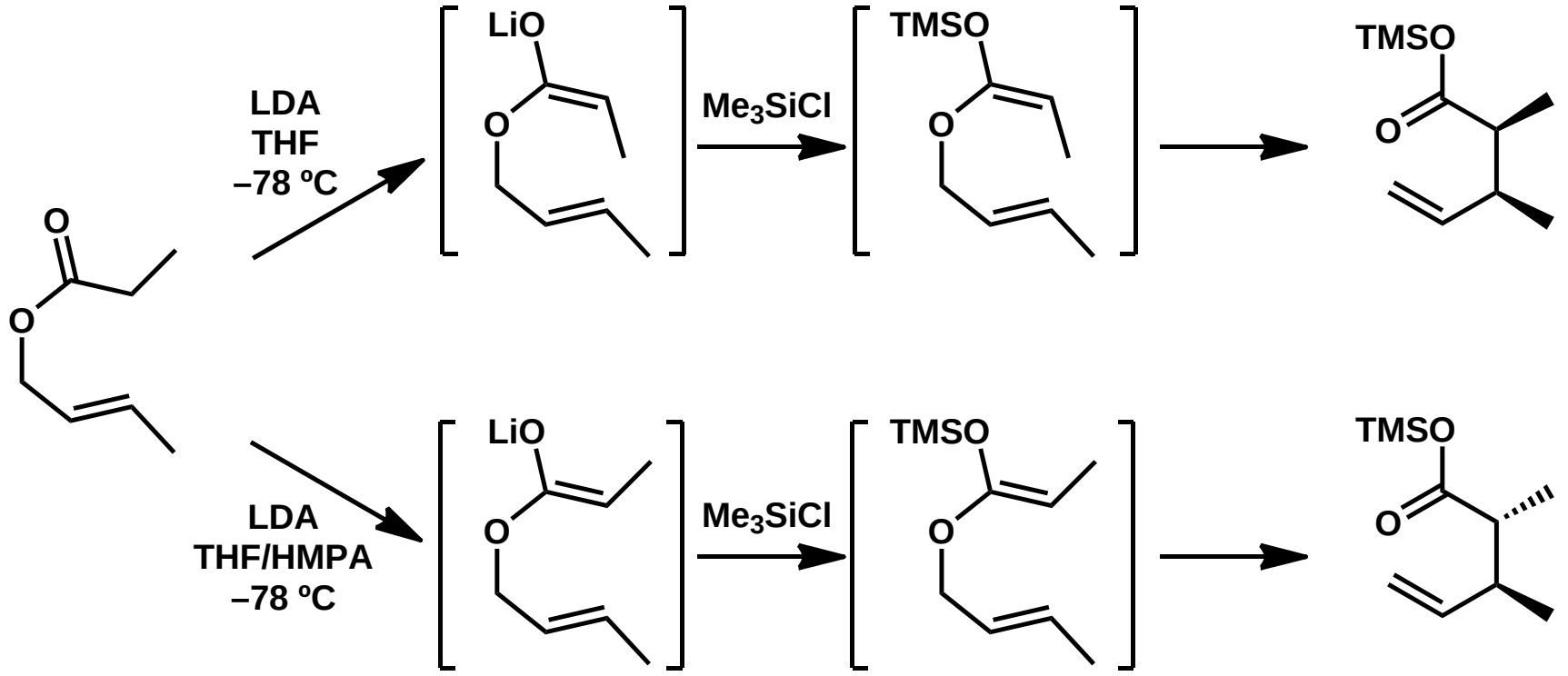


Takahashi, T. et al. *J. Org. Chem.* **1986**, *51*, 3393.

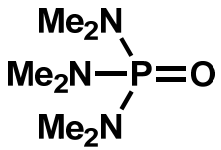


Ireland–Claisen Rearrangement

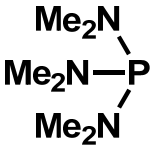


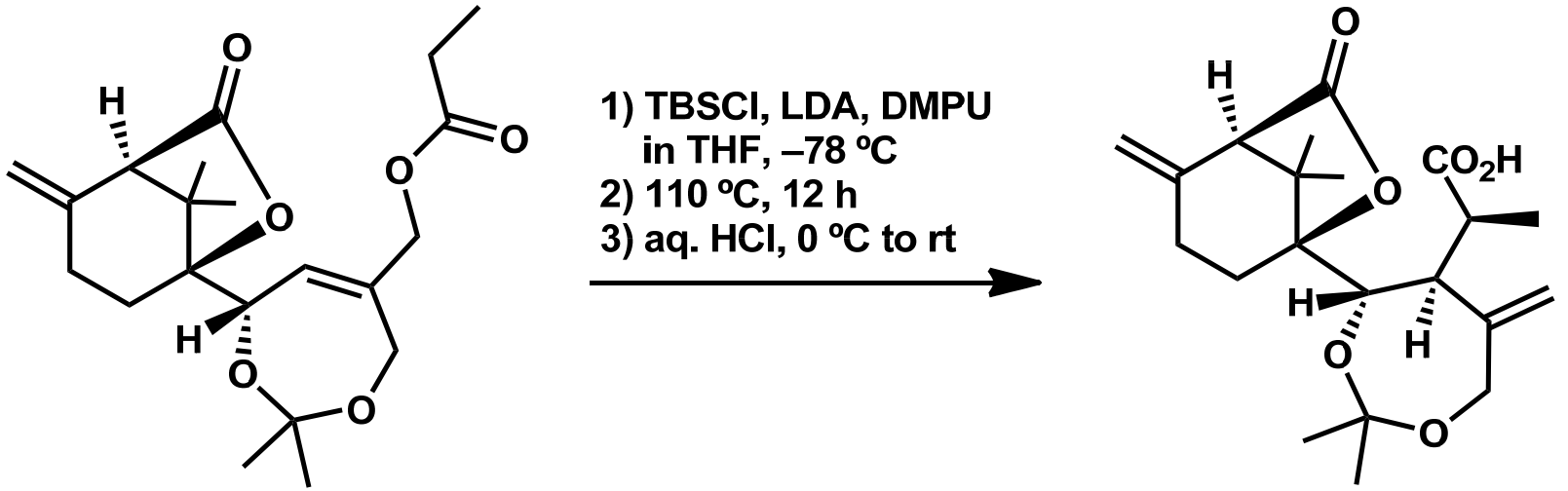
Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.

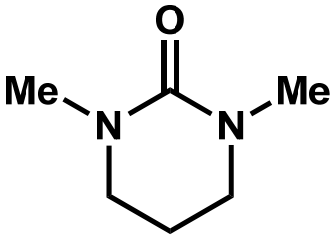
HMPA: hexamethylphosphoramide



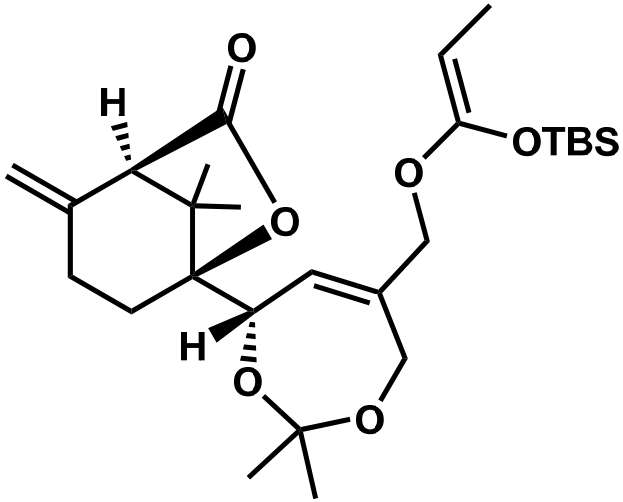
HMPT: hexamethylphosphorous triamide

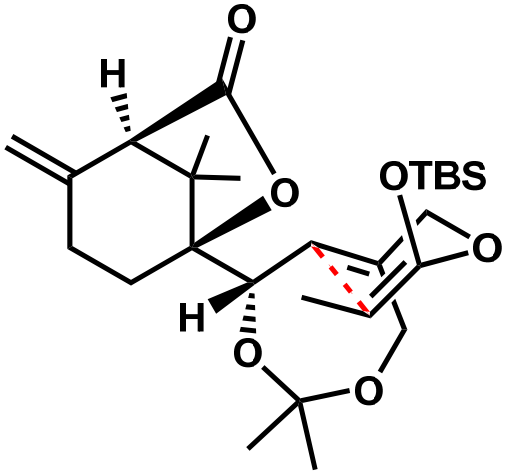






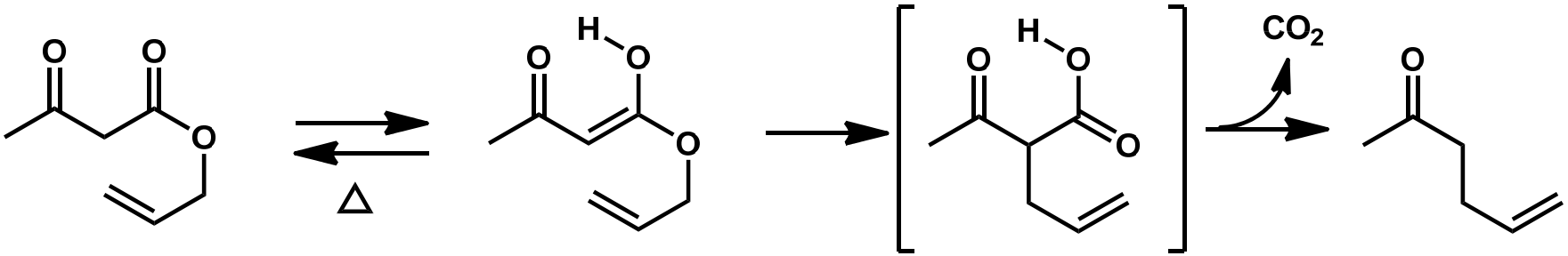
DMPU



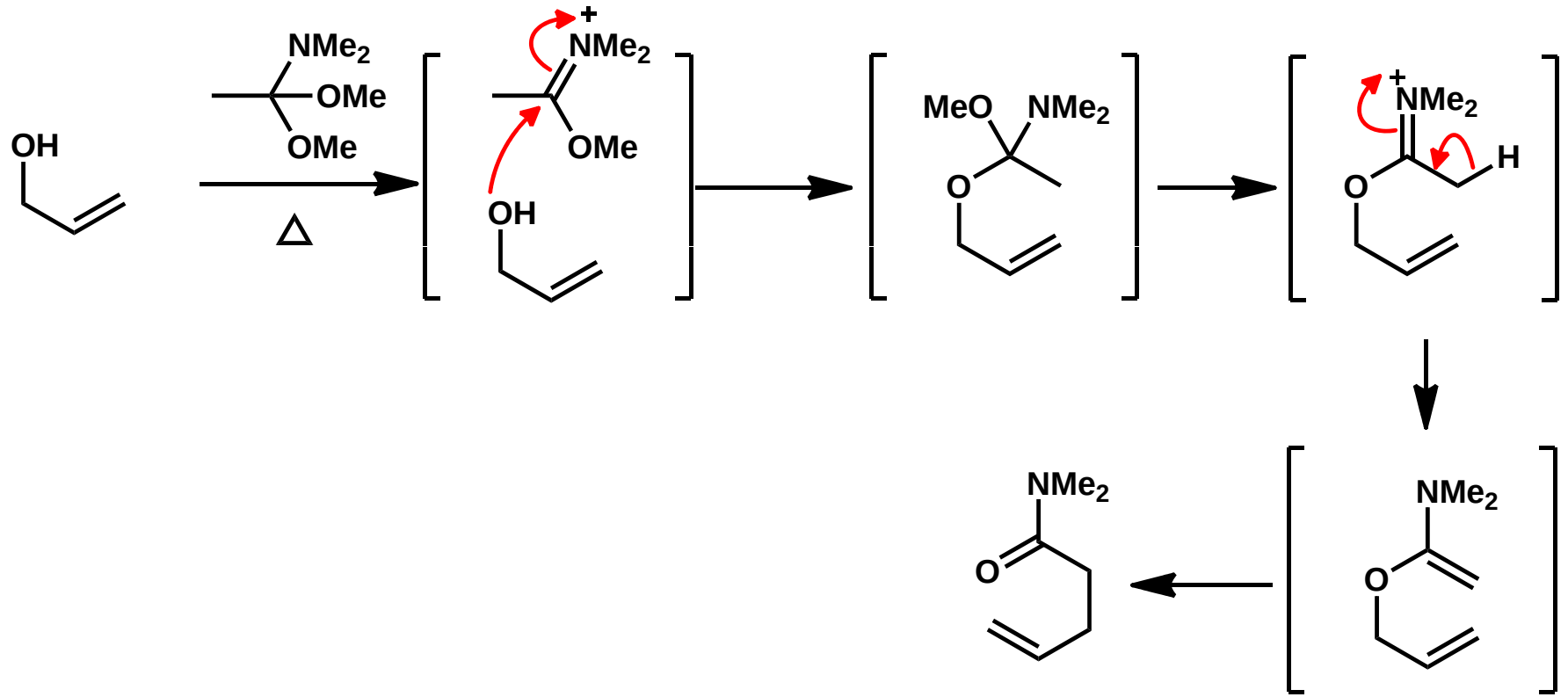


Stork, G. et al. *J. Am. Chem. Soc.* **1998**, *120*, 1337.

Carroll–Claisen Rearrangement

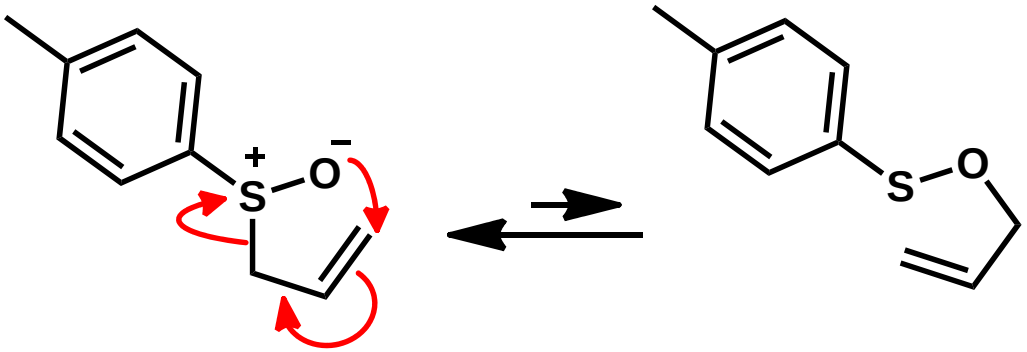


Eschenmoser–Claisen Rearrangement

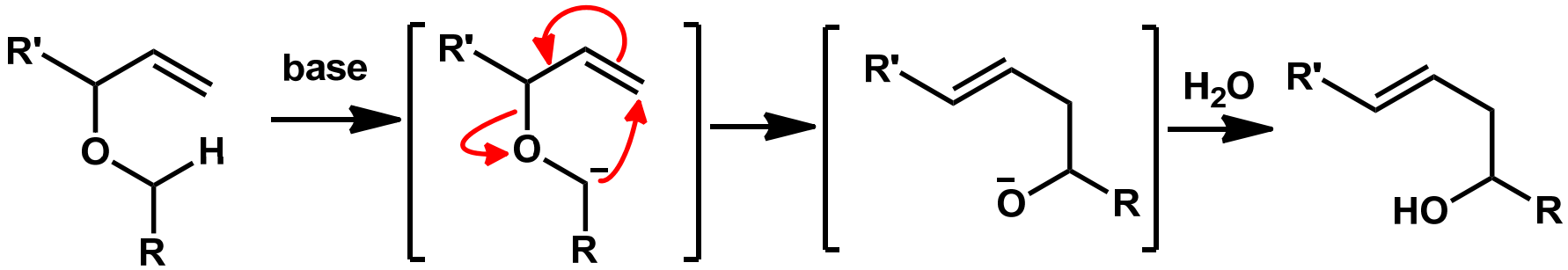


[2,3]-Sigmatropic Rearrangement

Mislow rearrangement

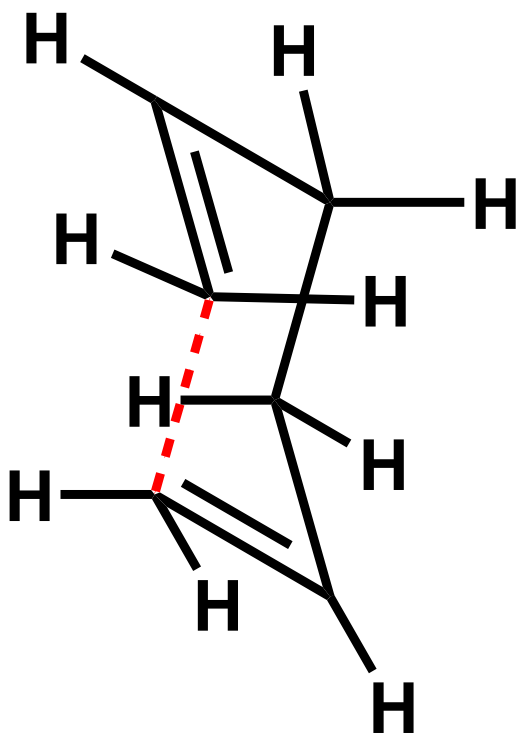


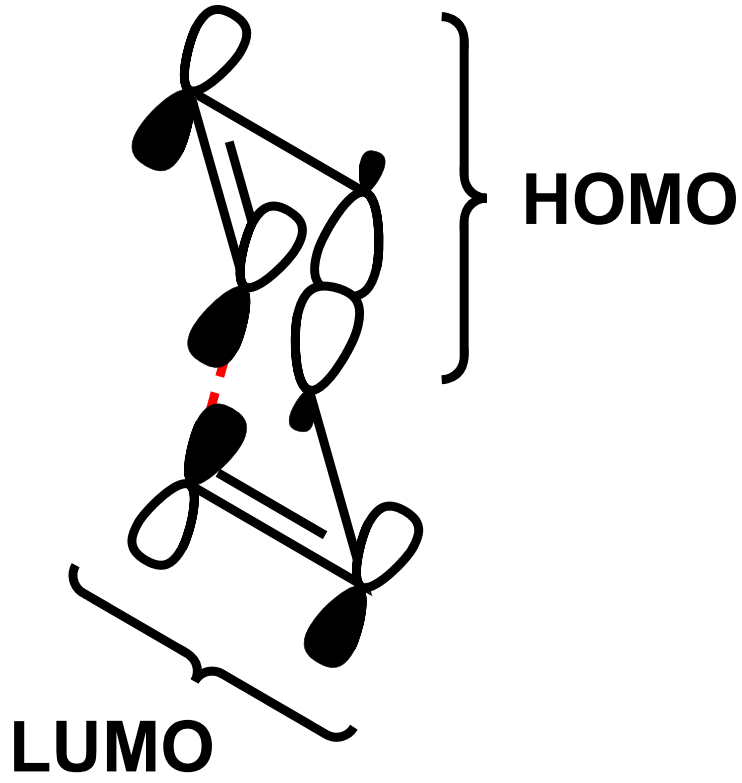
[2,3]-Wittig rearrangement

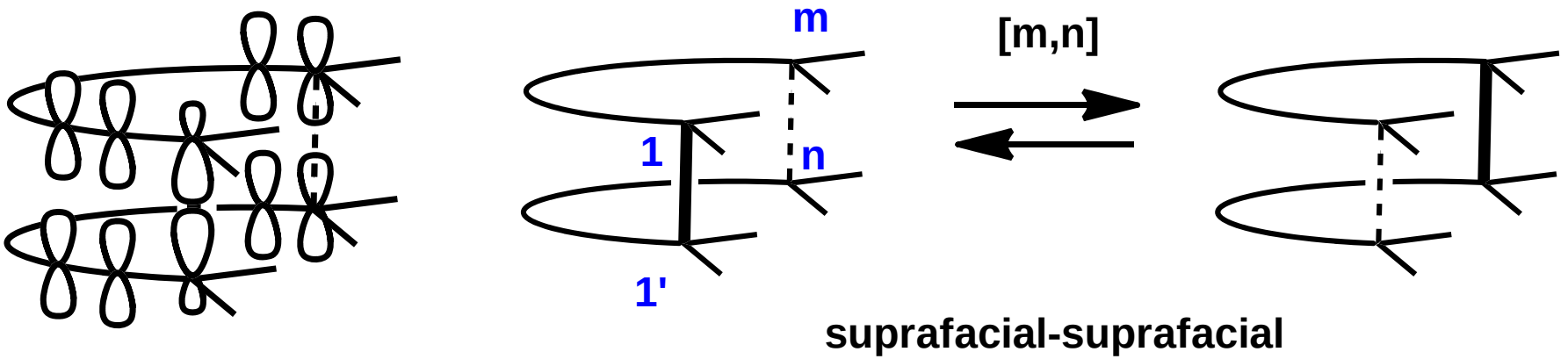


[3,3]-Sigmatropic Rearrangement

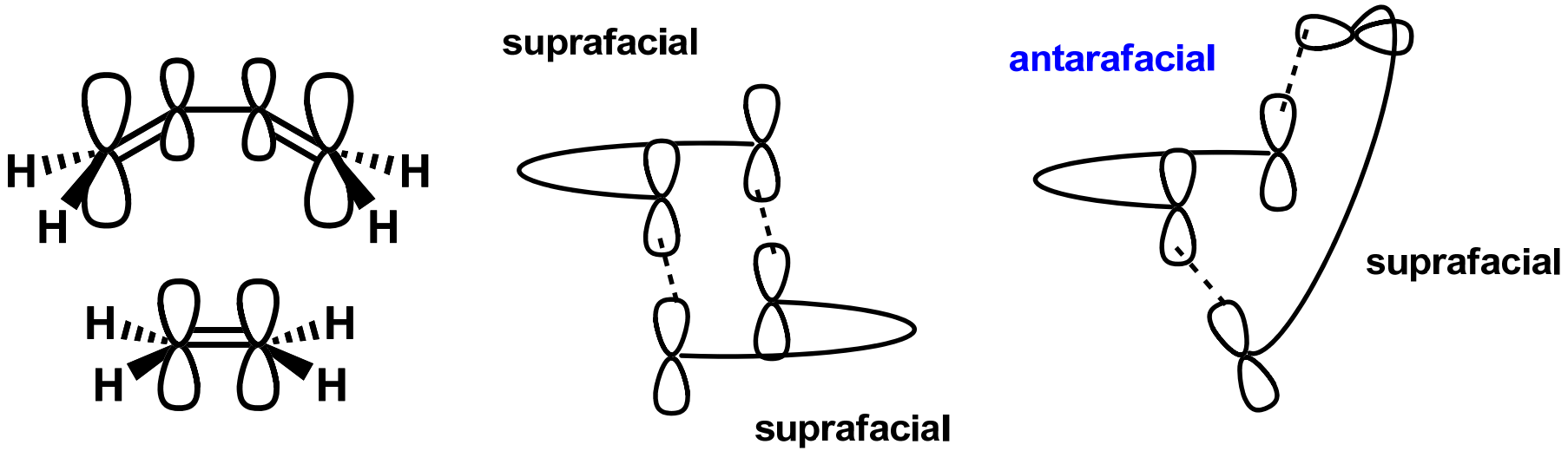
Cope rearrangement



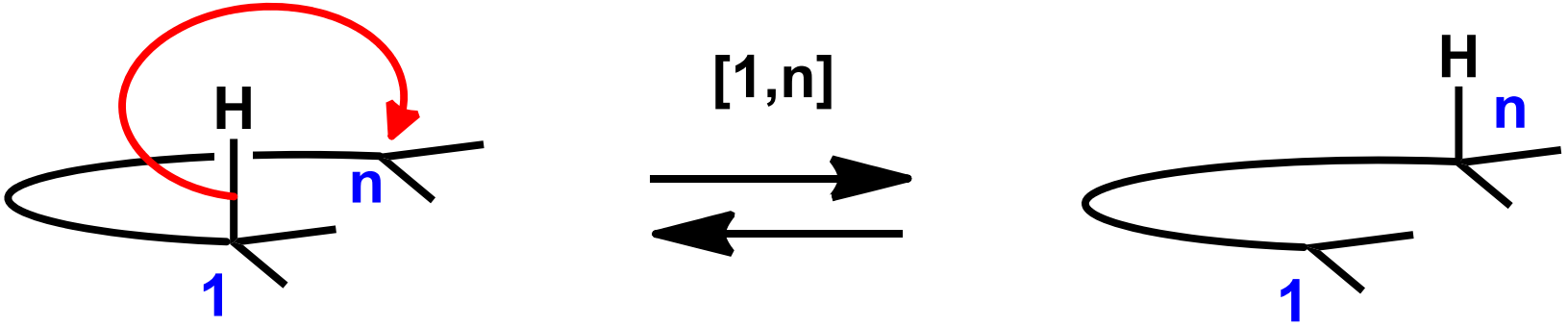


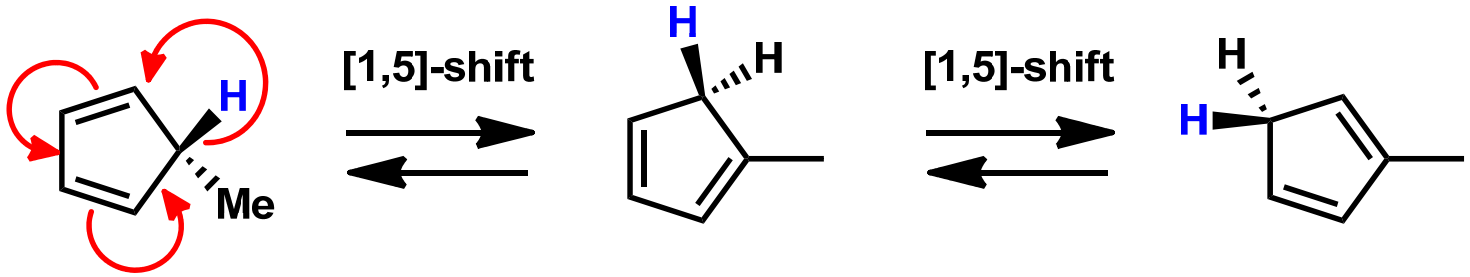


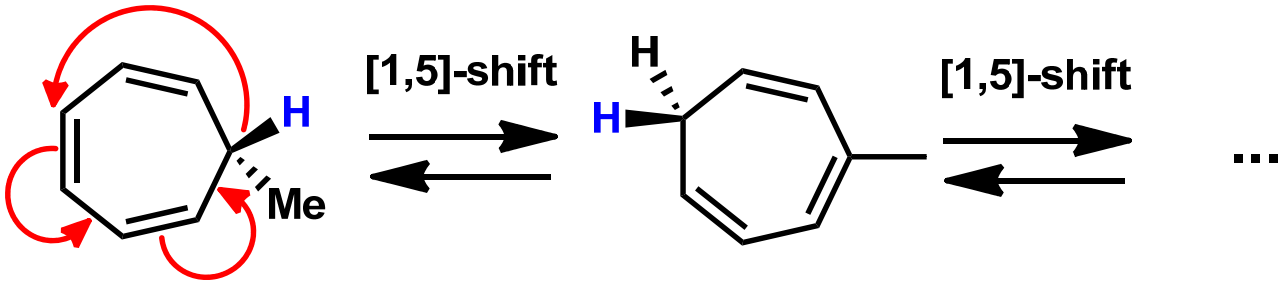
total number of electrons = (4n + 2) ..... allowed



[1,n]-Shift (Suprafacial Shift)....(4n + 2) electrons

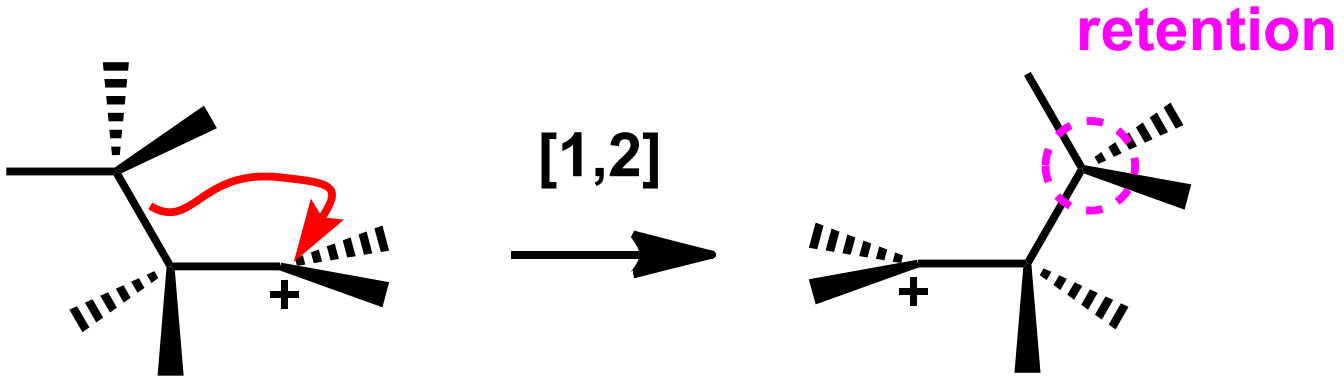






Fleming, I. Molecular *Orbitals and Organic Chemical Reactions,* John Wiley & Sons: West Sussex, 2009.

Wagner–Meerwein rearrangement



2 electrons

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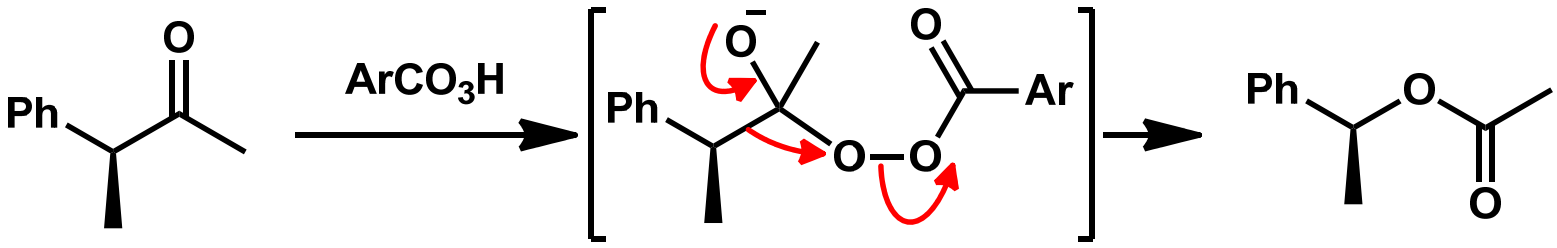
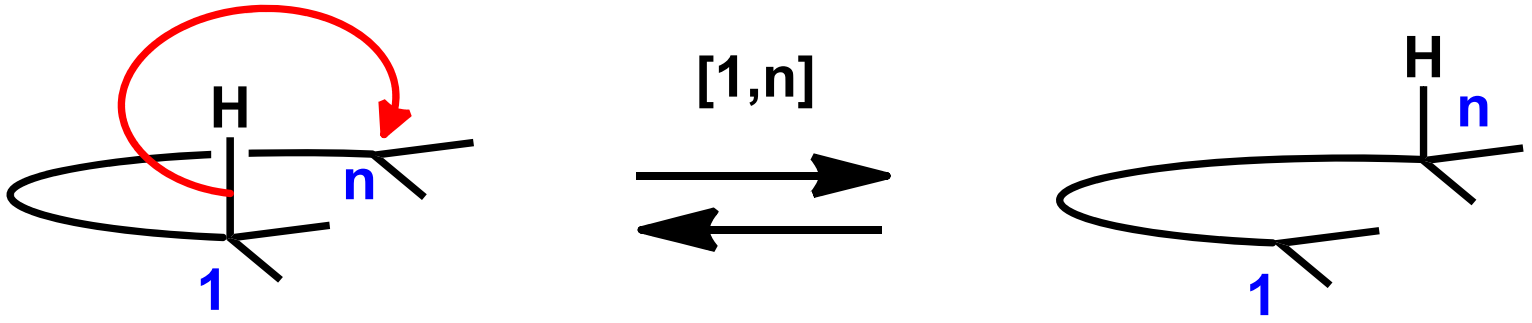
cf. Beckmann
Curtius
Baeyer–Villiger

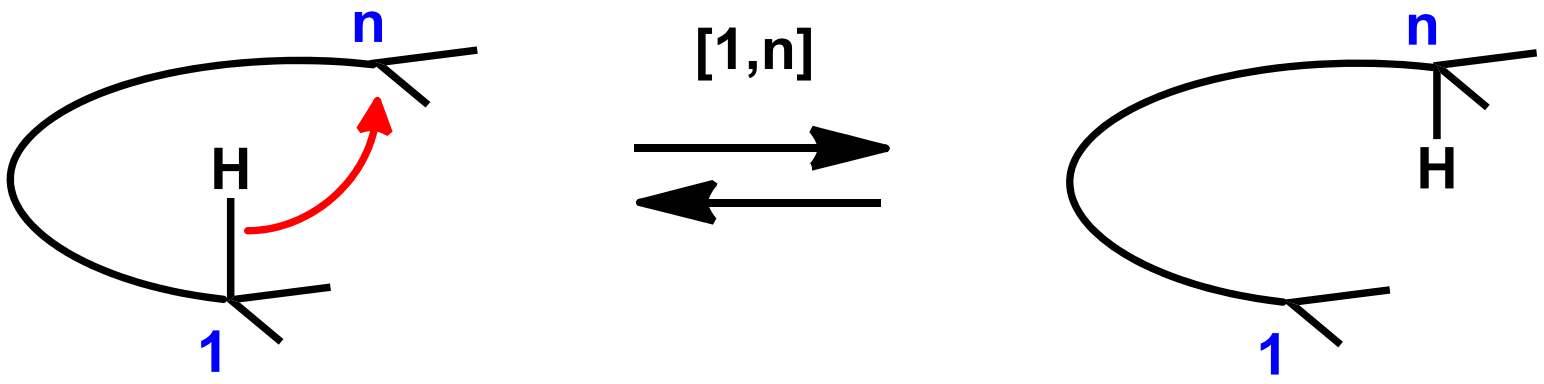


[1,n]-Shift

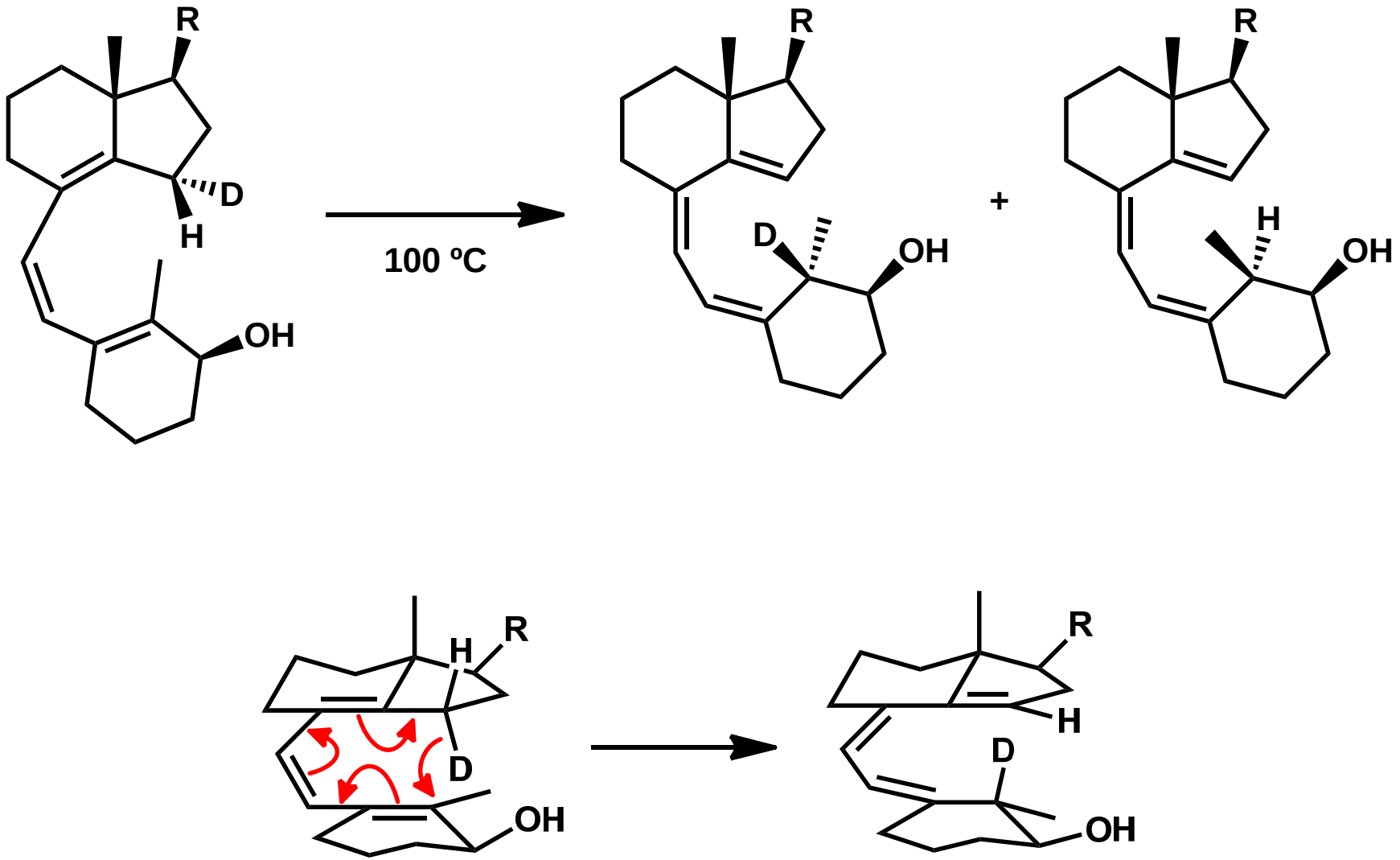
Suprafacial Shift....(4n + 2) electrons



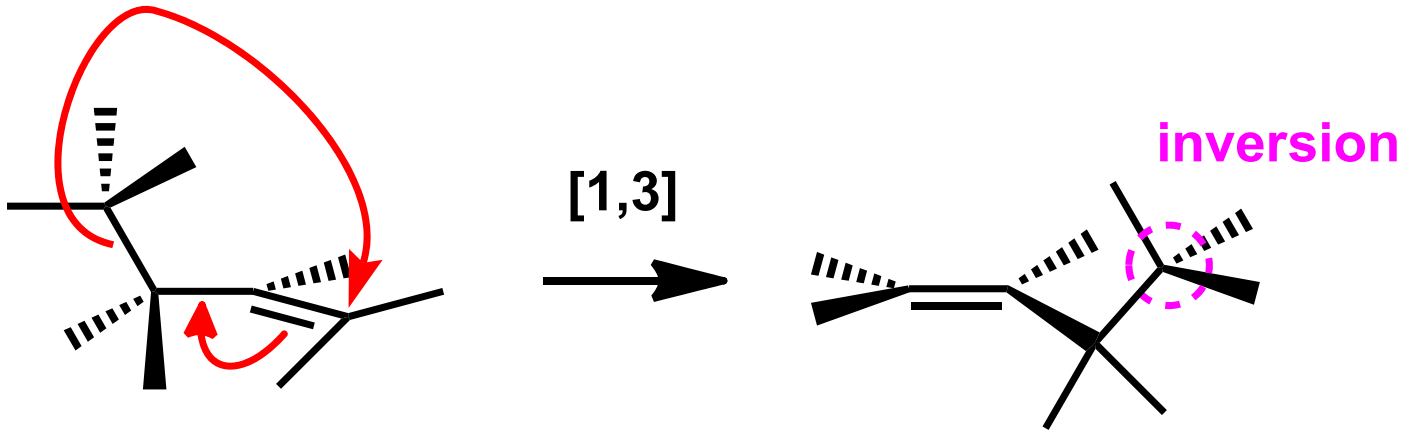
Antarafacial Shift....(4n) electrons



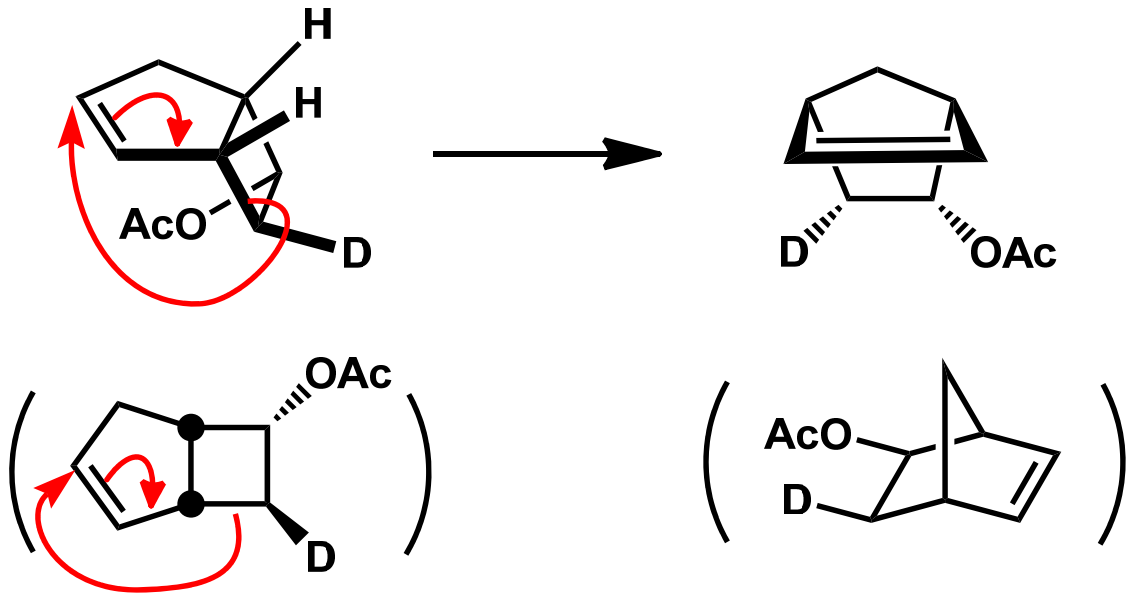
[1,7]-Shift



Hoeger, C. A.; Okamura, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 268.
Fleming, I. Molecular *Orbitals and Organic Chemical Reactions,* John Wiley & Sons: West Sussex, 2009.



4 electrons



Woodward–Hoffmann rule

A ground-state pericyclic change is symmetry-allowed when the total number of $(4q+2)_s$ and $(4r)_a$ components is odd.

Woodward, R. B.; Hoffmann, R. *Angew. Chem. Int. Ed.* **1969,** *8*, 781.