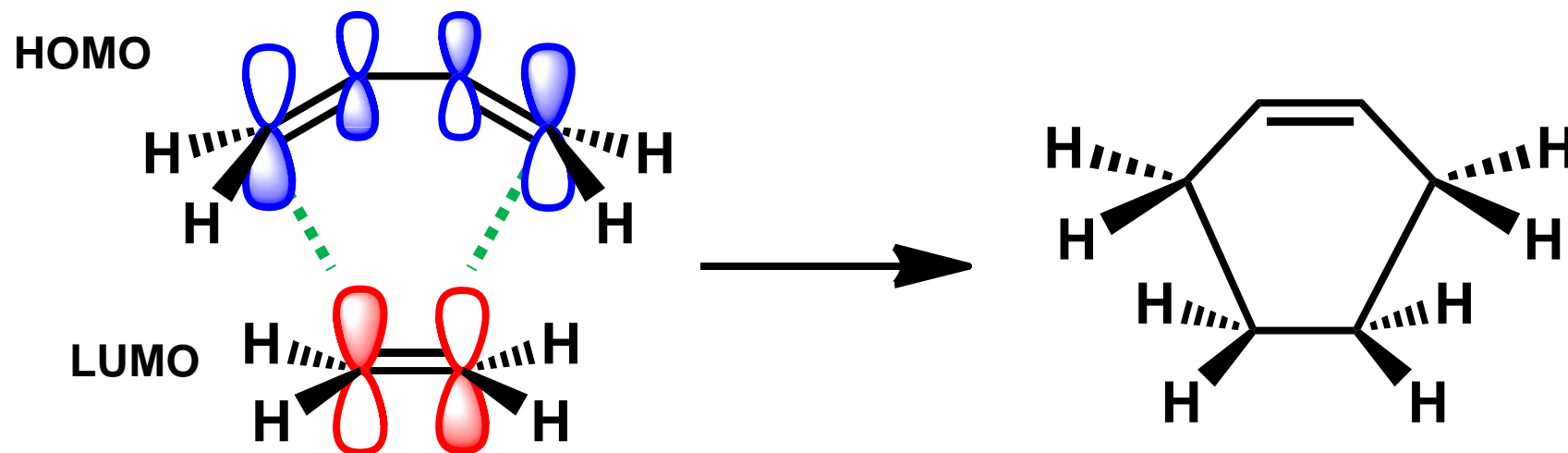
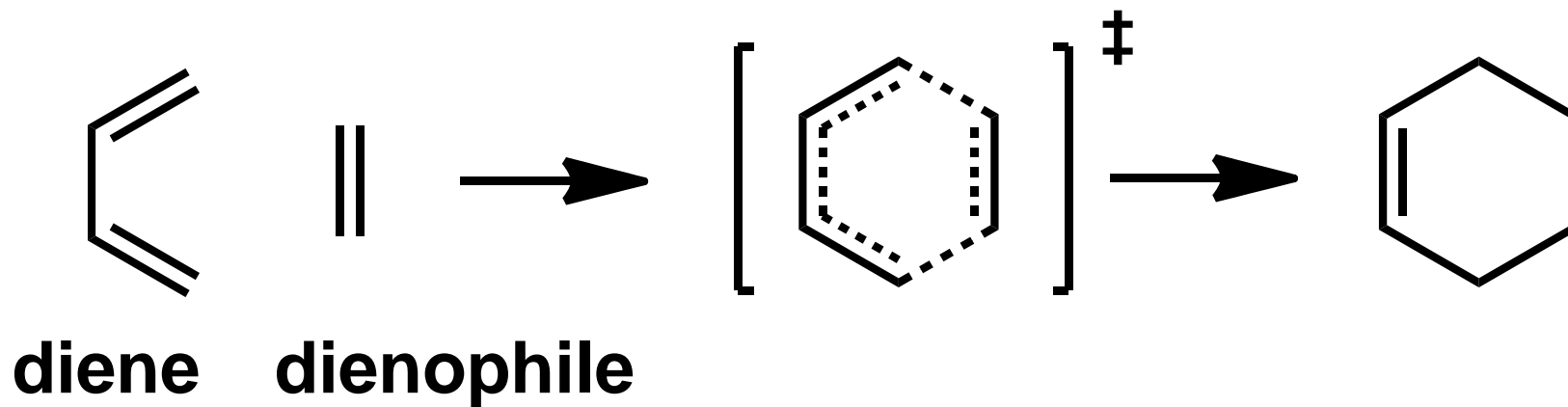
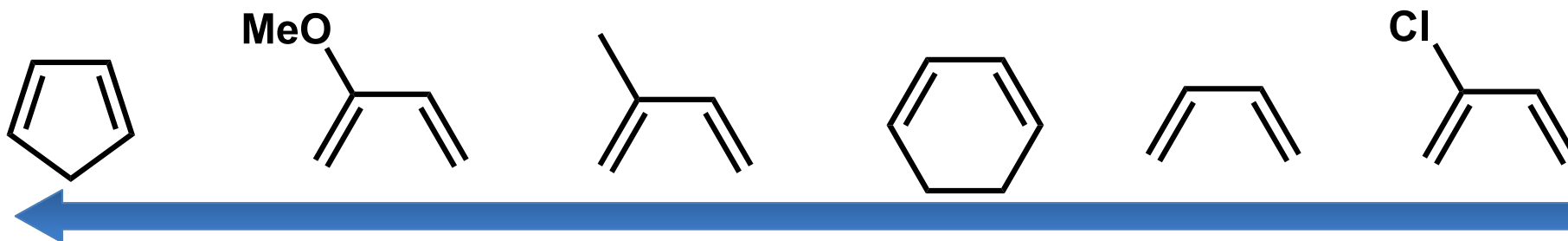
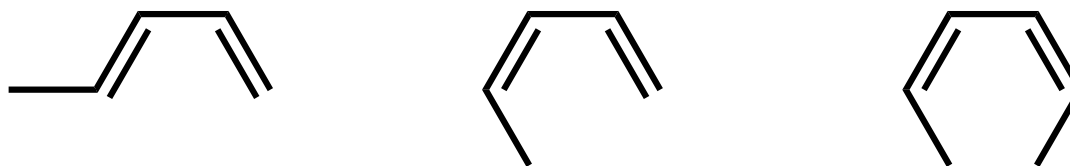
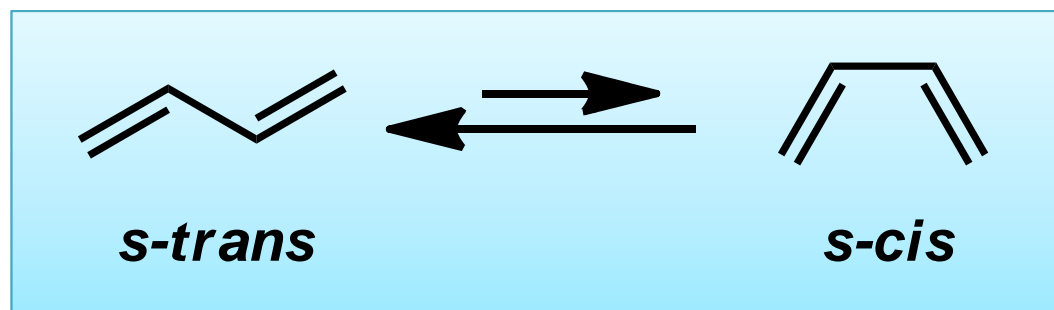


# Diels–Alder Reaction

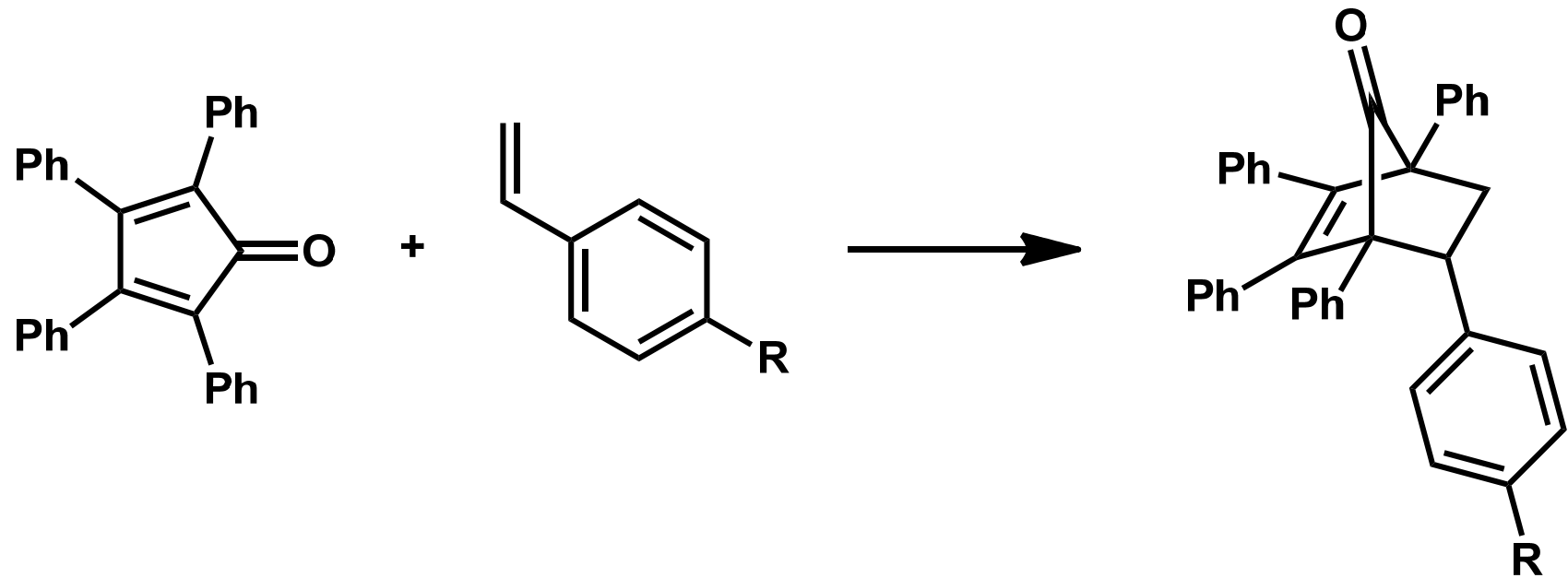


**diene**

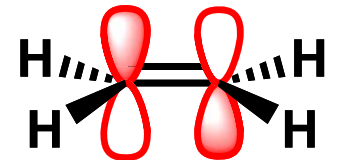
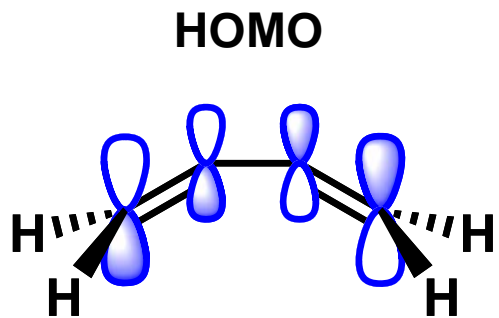


**dienophile**

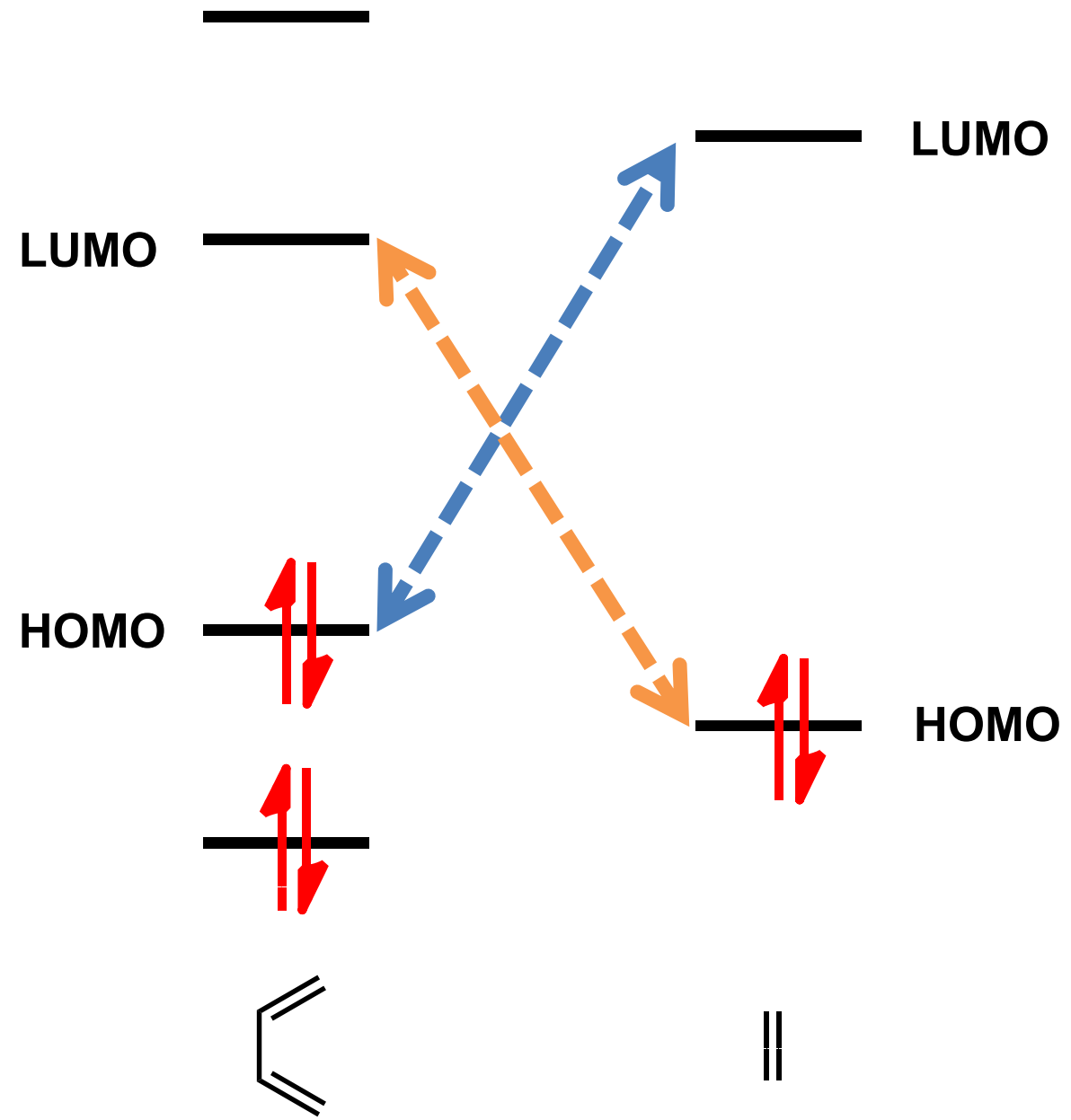
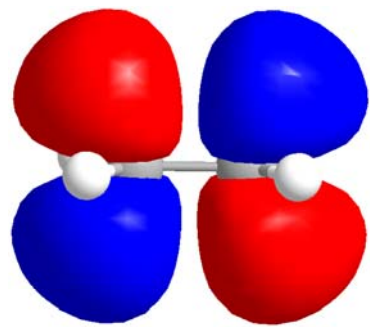


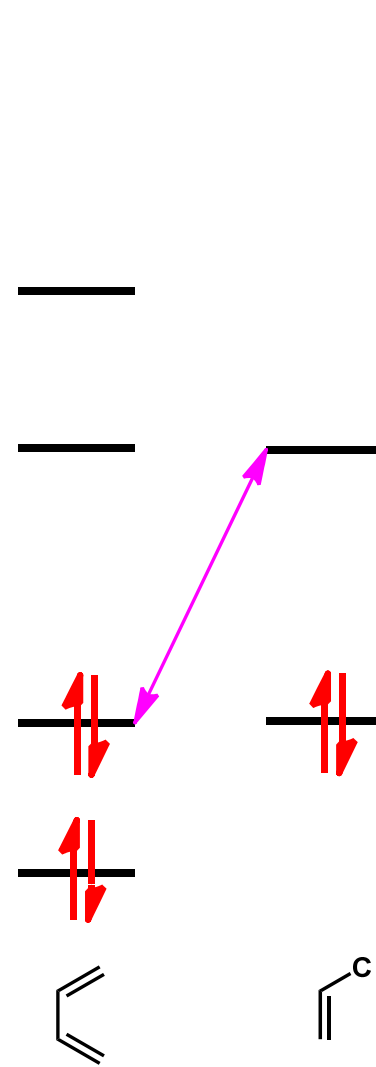
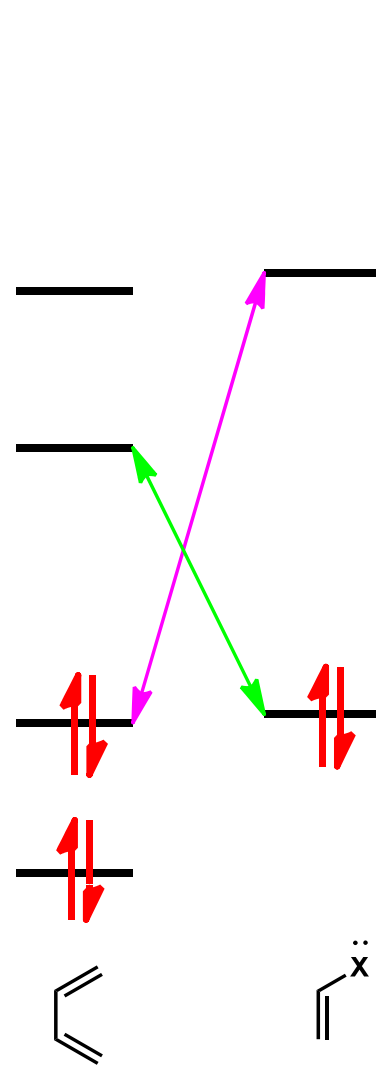
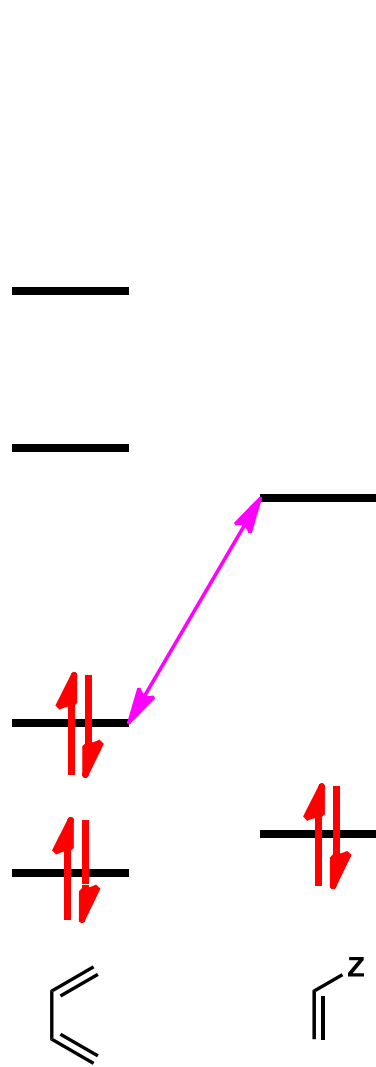
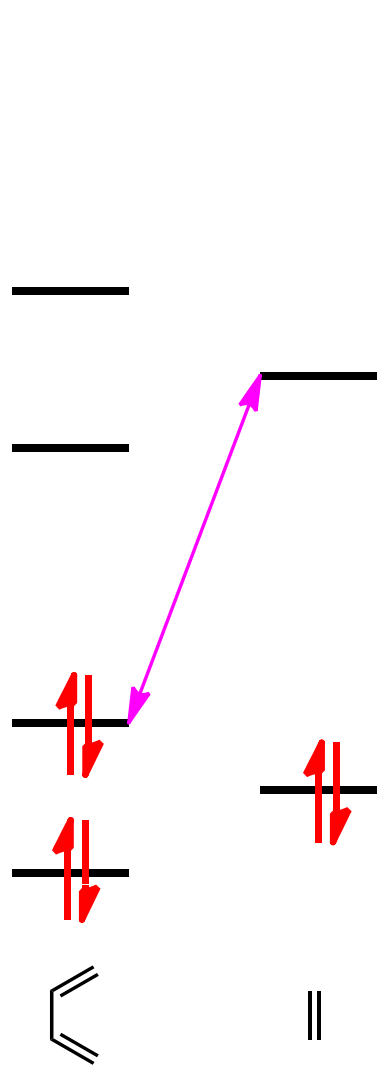


R	$k_{\text{rel}}$
NMe <sub>2</sub>	4.6
OMe	1.4
H	1
Cl	1.07
NO <sub>2</sub>	1.2



LUMO





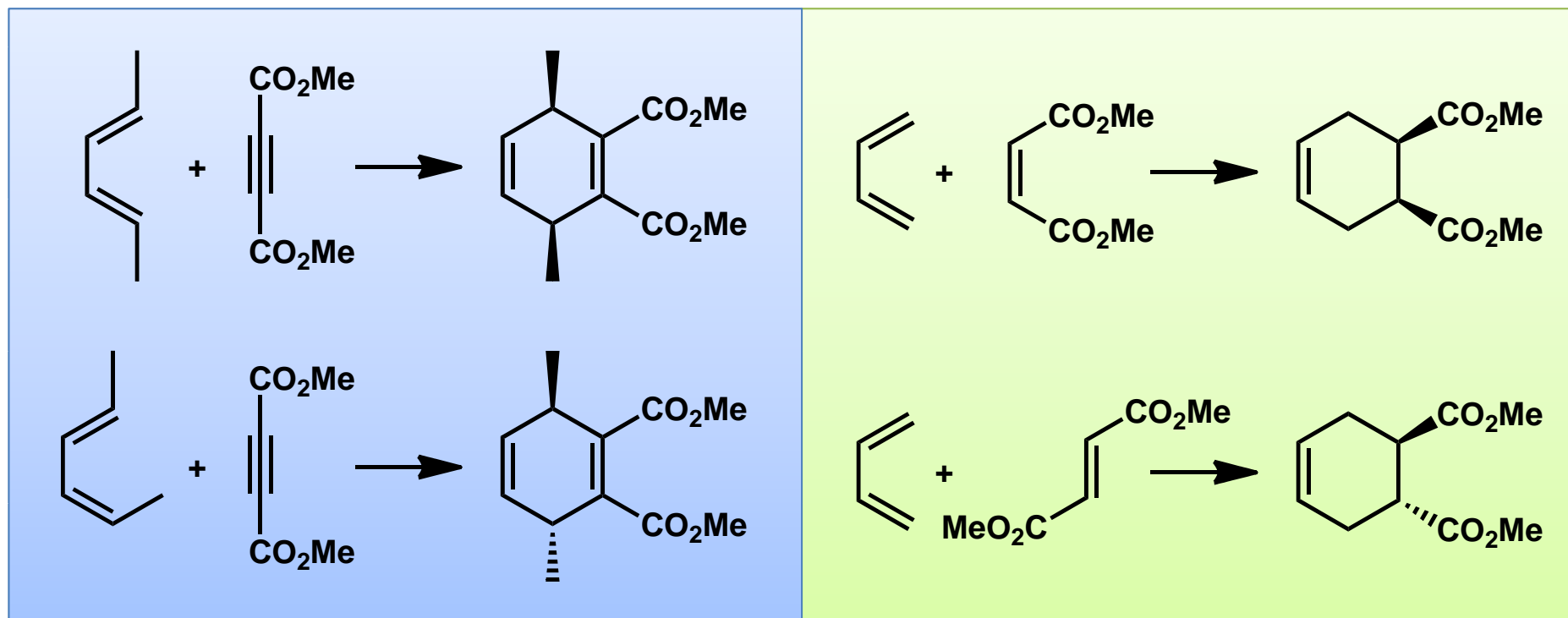
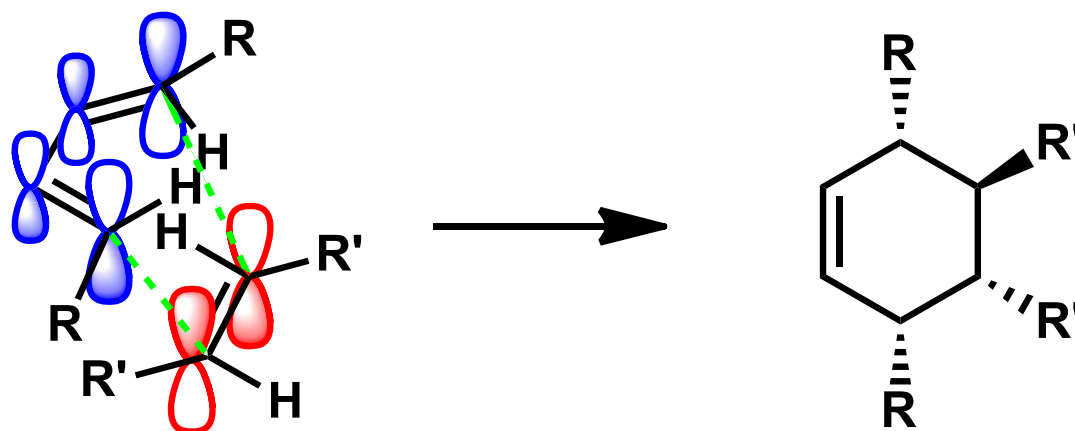
normal electron-demand



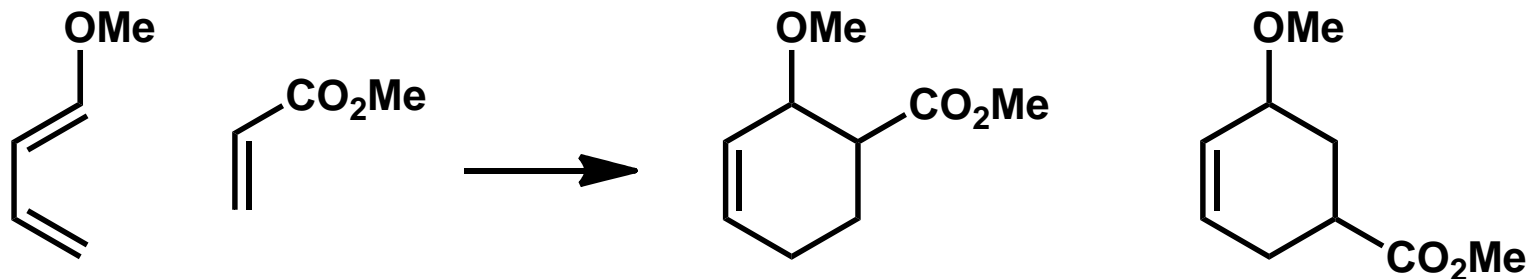
reverse electron-demand



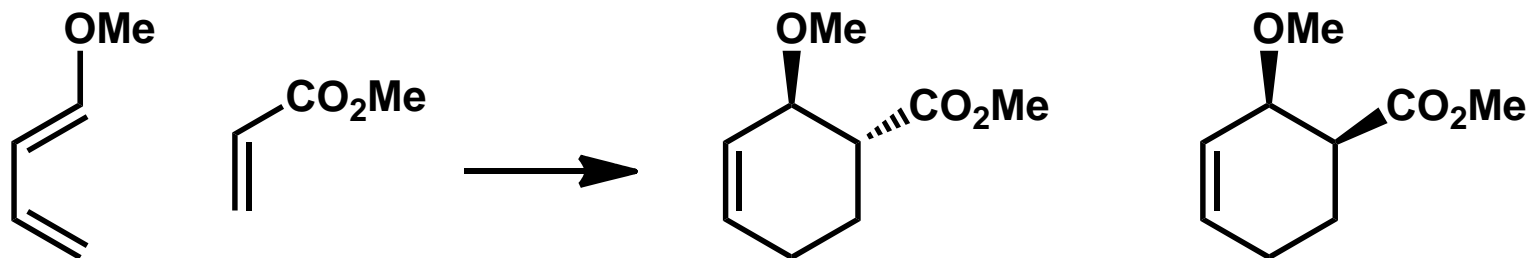
# Stereospecificity



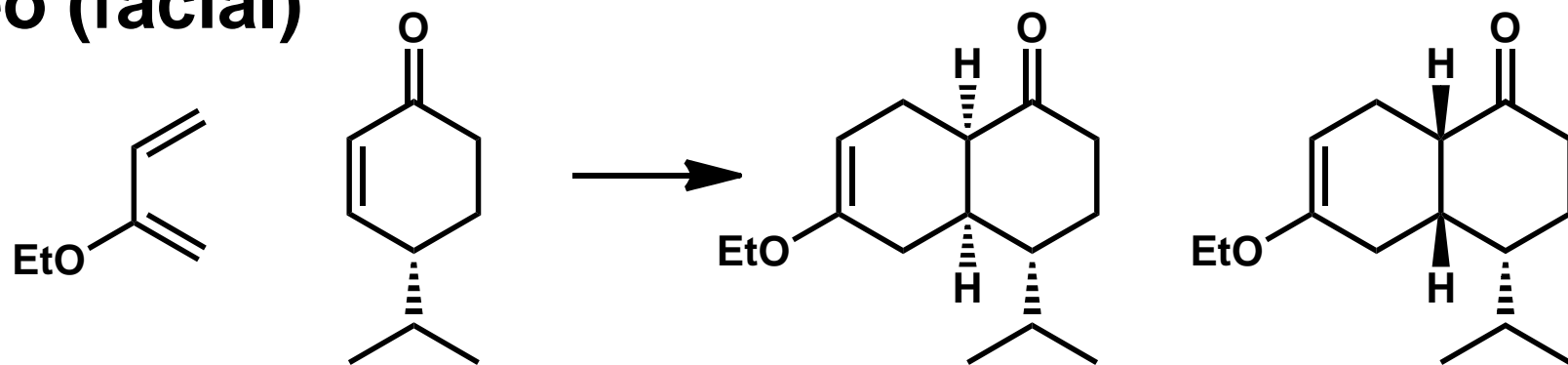
**regio**



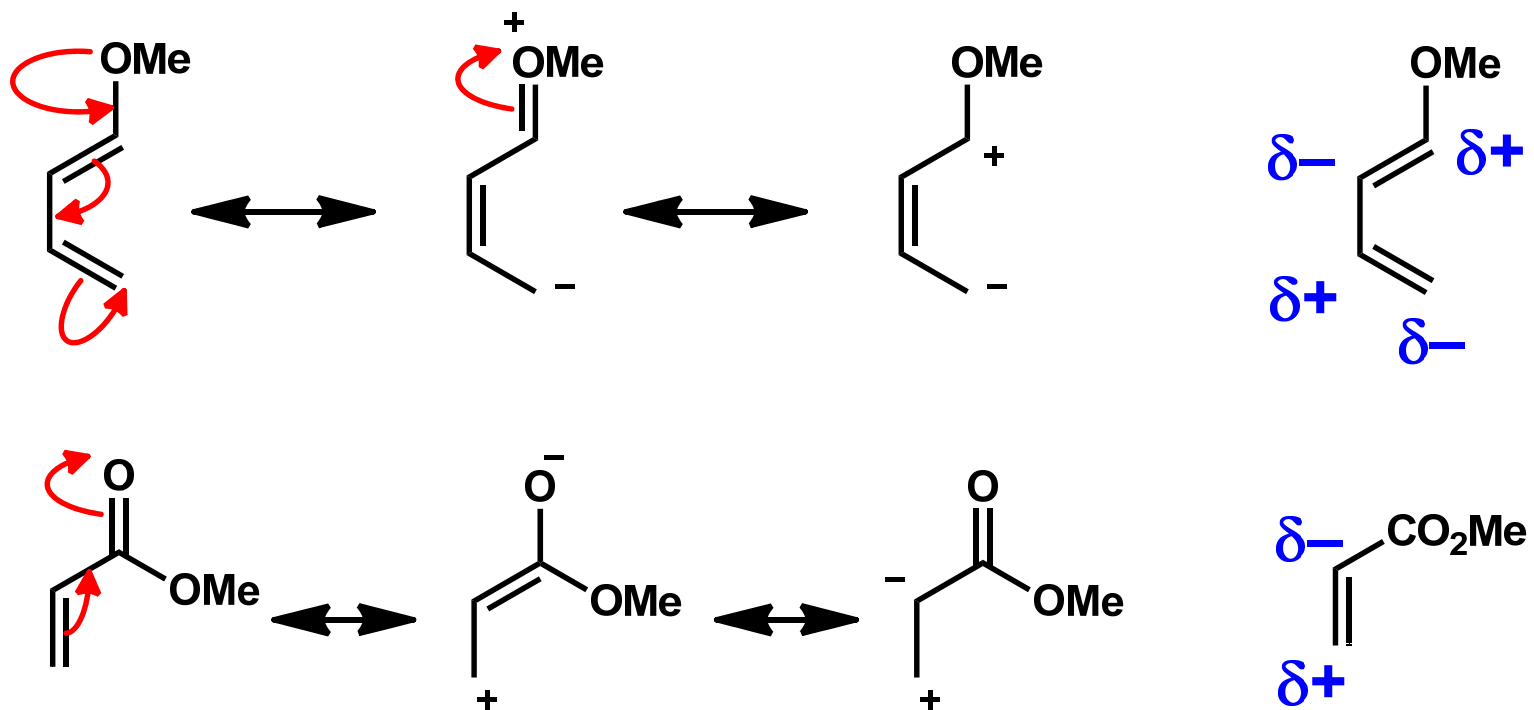
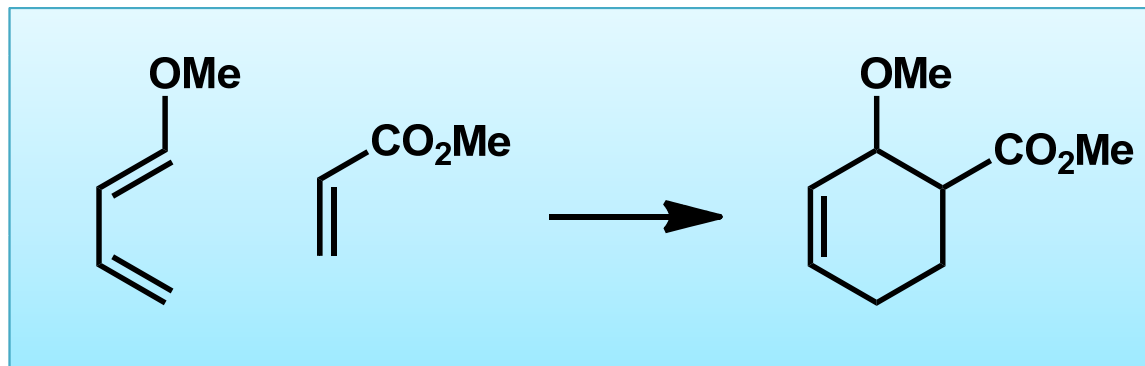
**endo/exo**



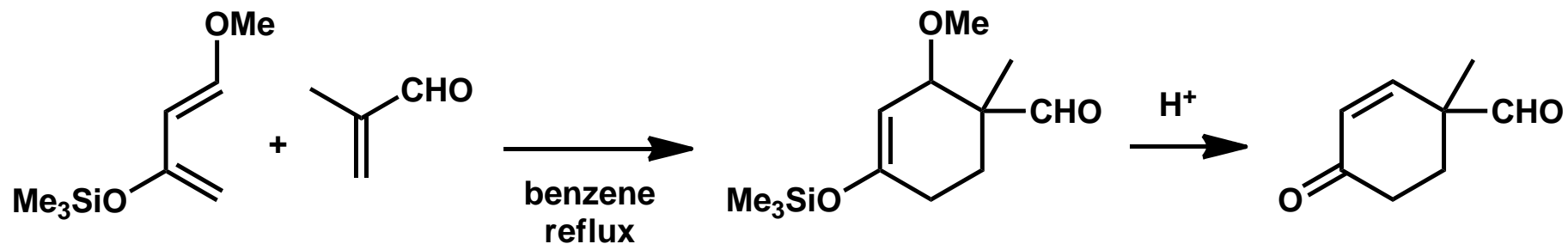
**stereo (facial)**



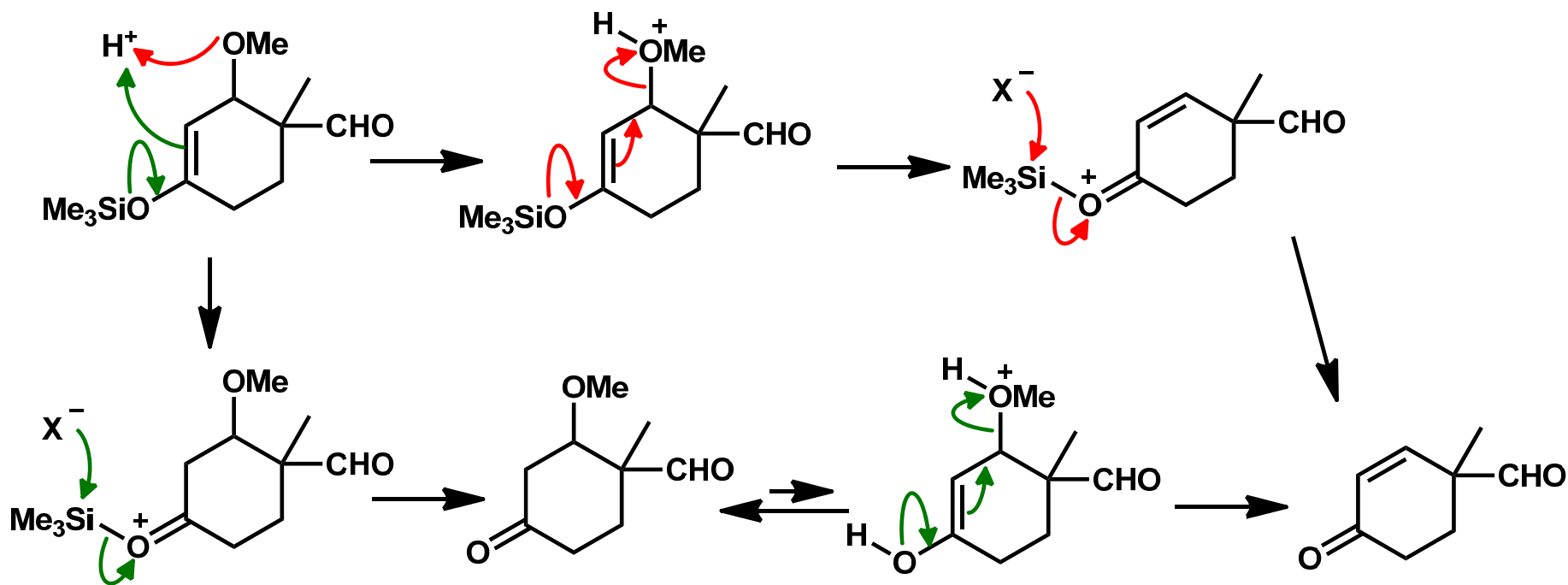
# Regioselectivity



# Danishefsky's diene

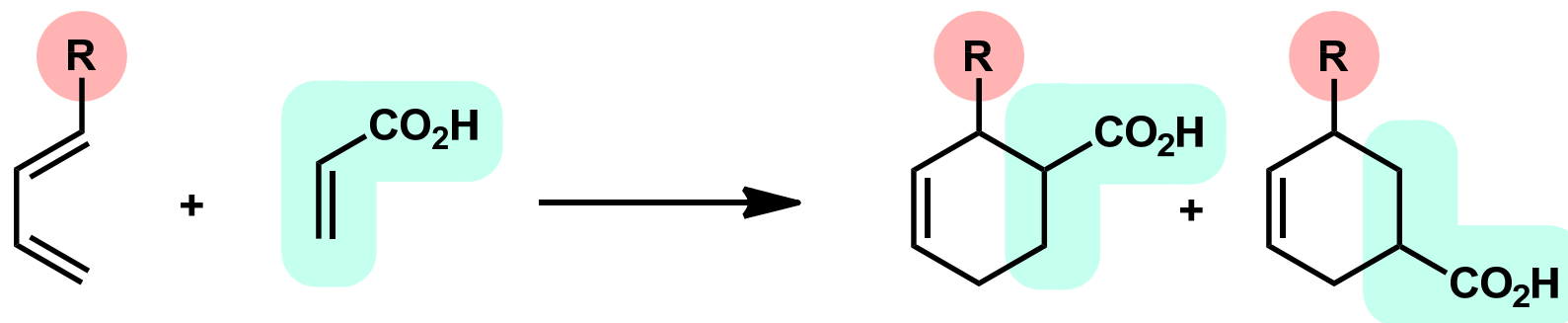


Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807.

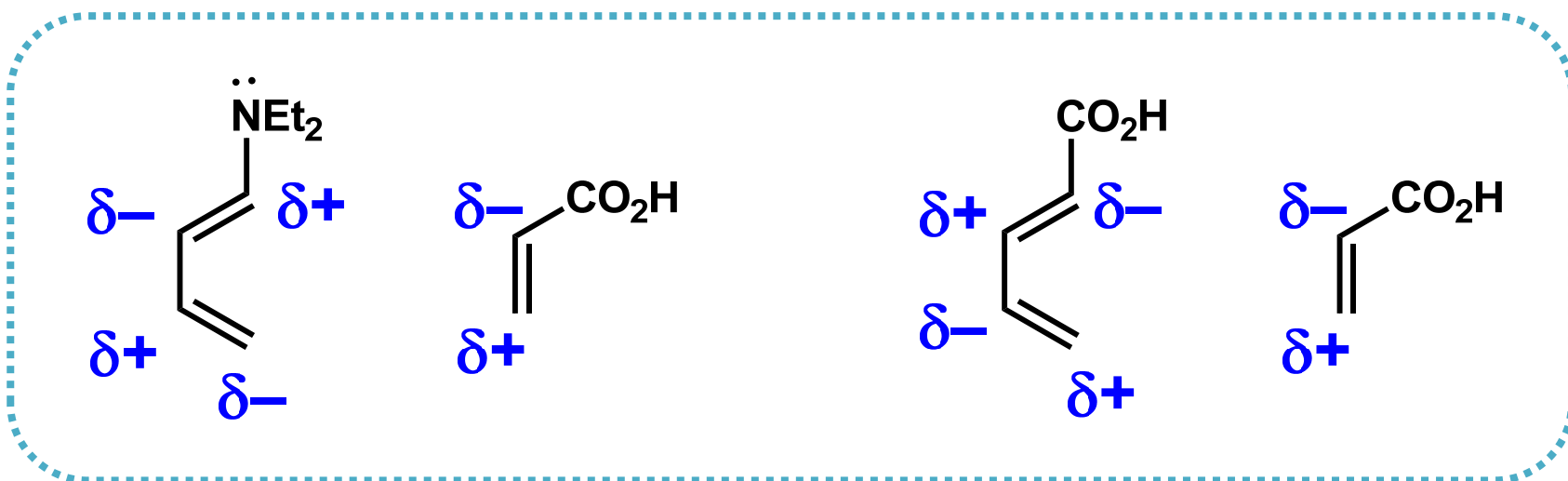




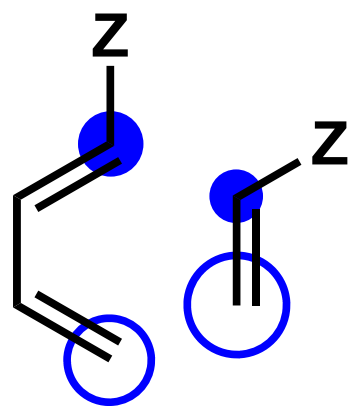
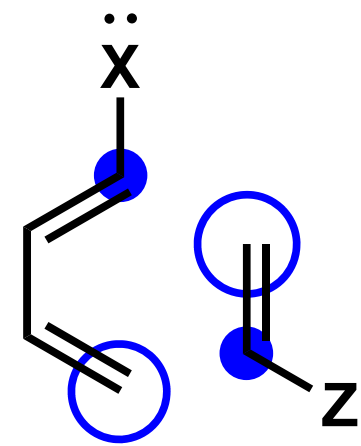
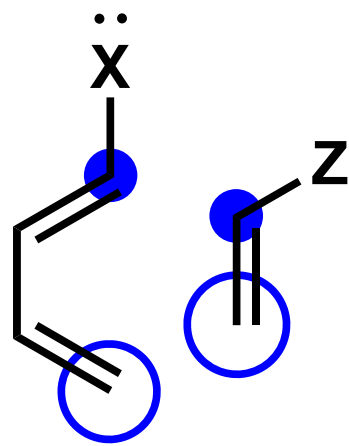
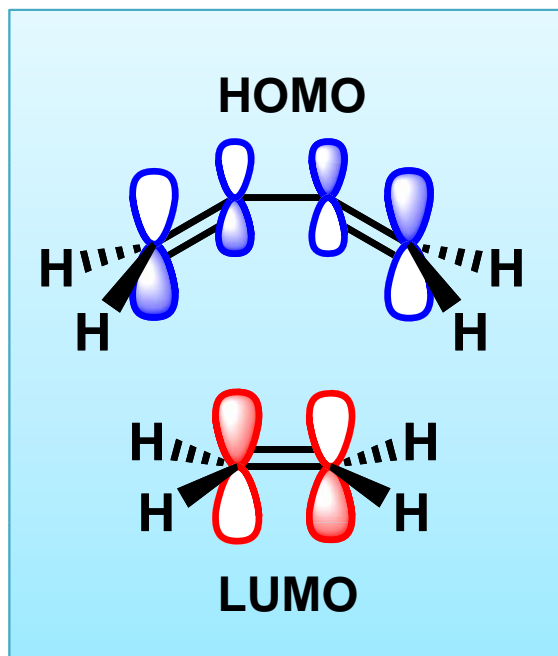
# Regioselectivity



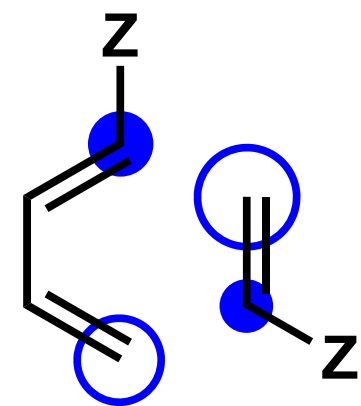
R	temp.	ratio
NEt <sub>2</sub>	20 °C	100 : 0
CH <sub>3</sub>	20 °C	95 : 5
CO <sub>2</sub> H	70 °C	91 : 9



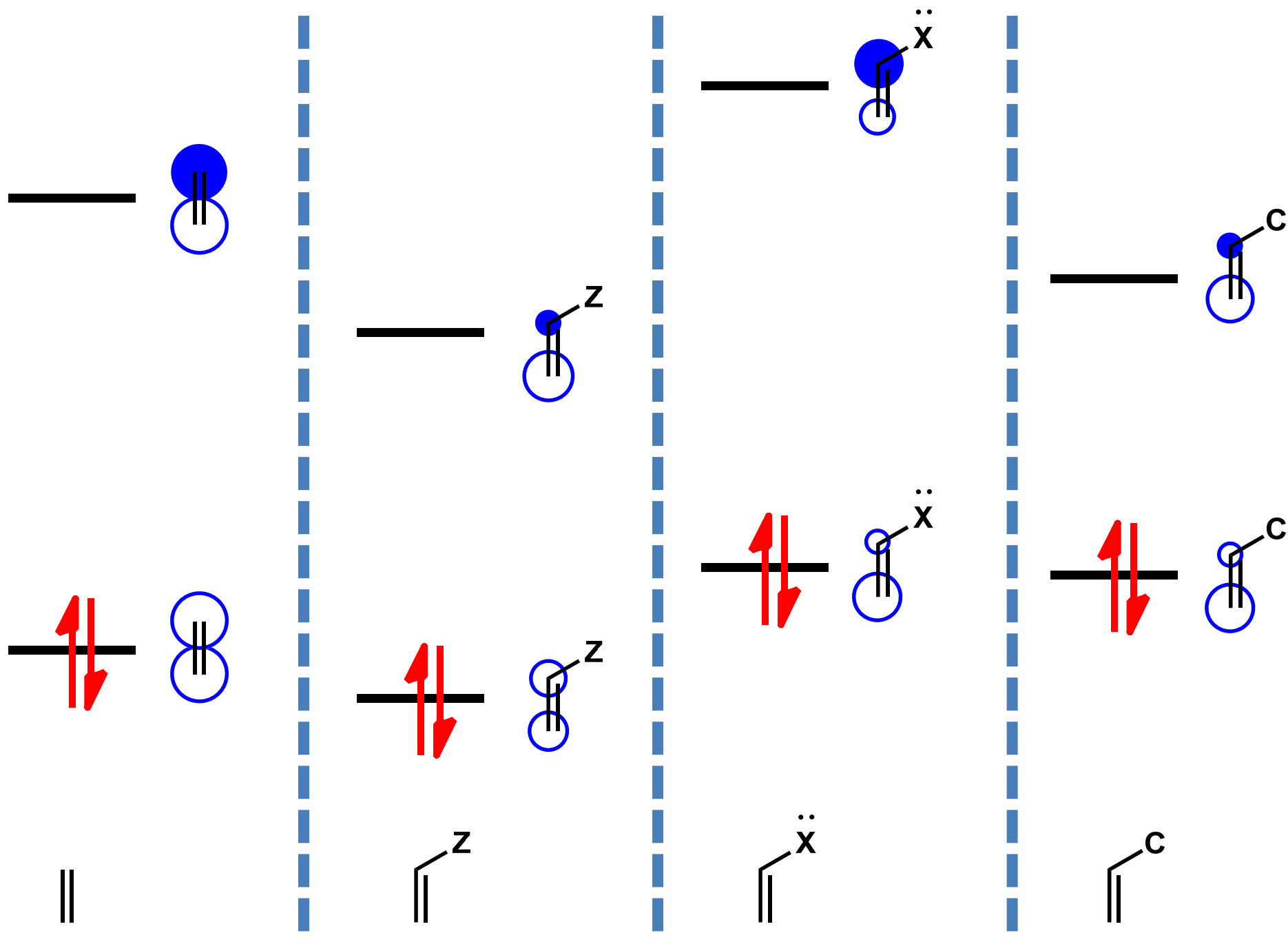
# Coefficients of Frontier Orbitals

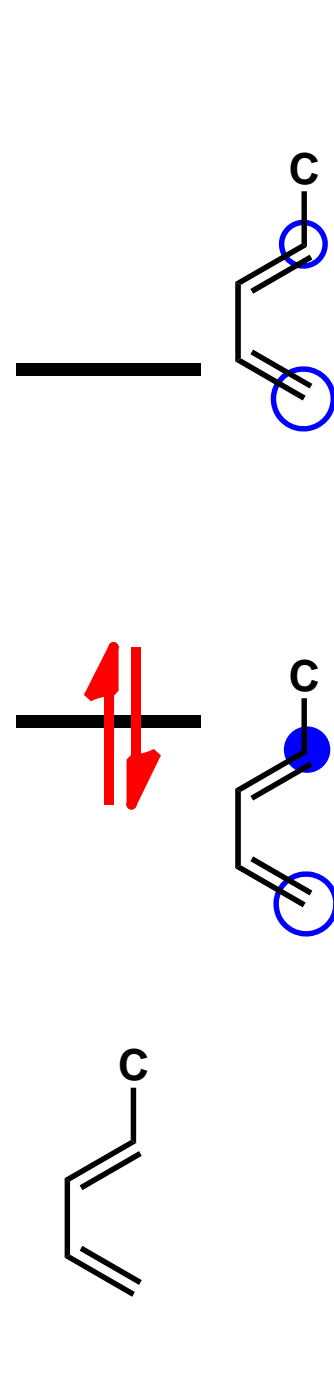
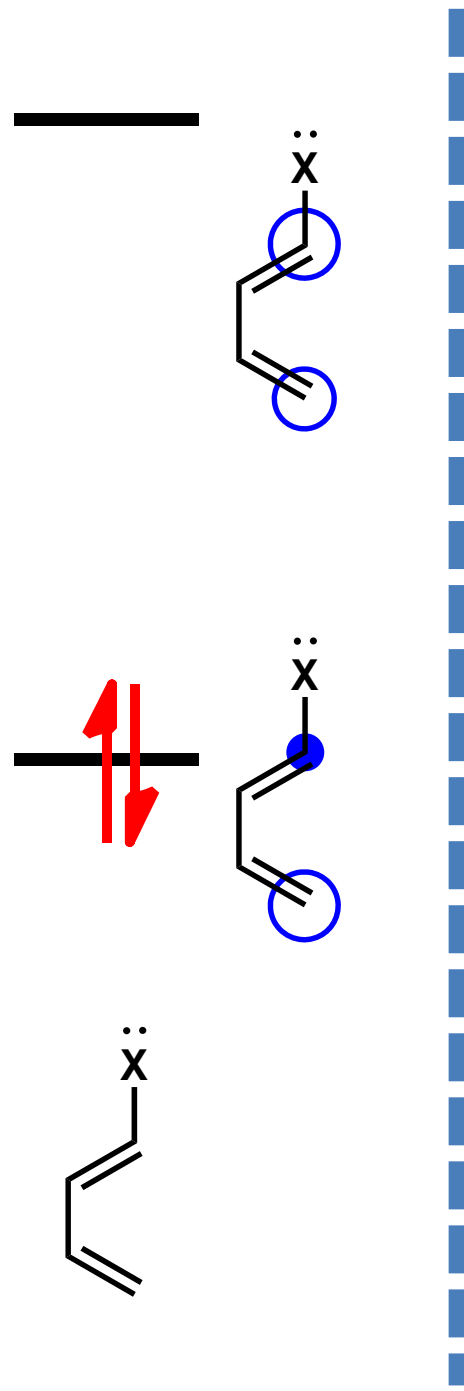
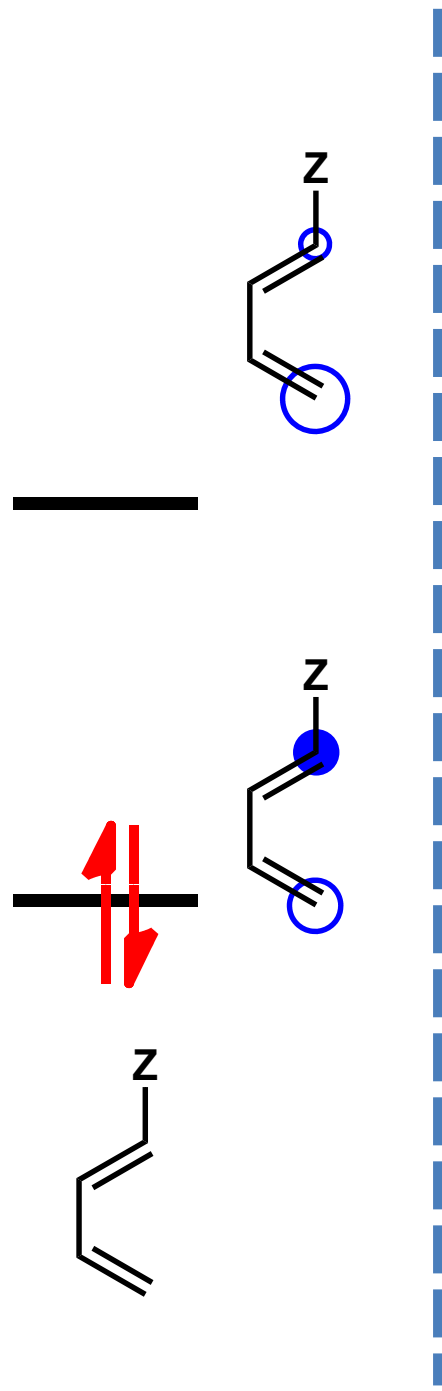
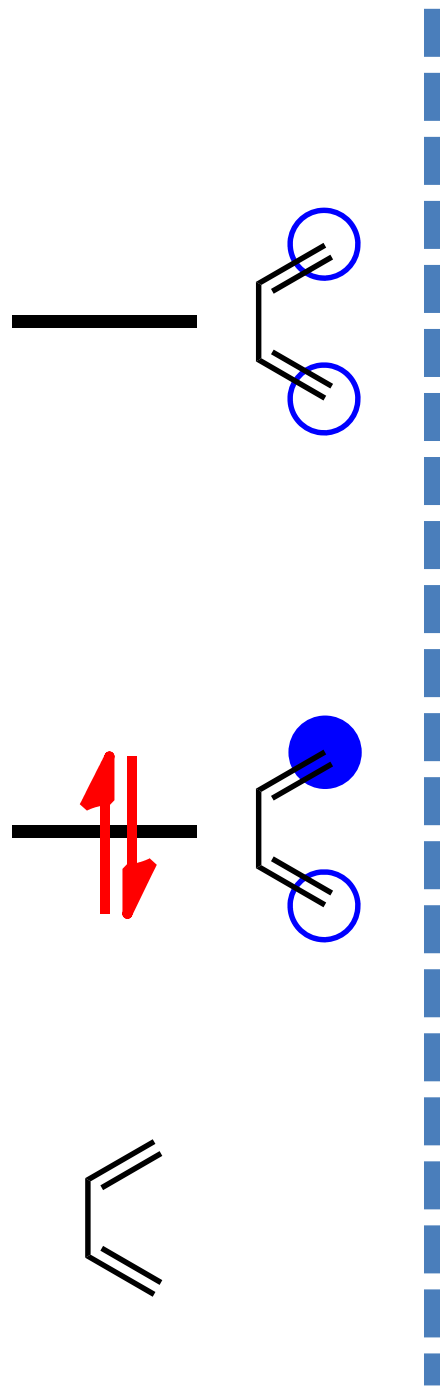


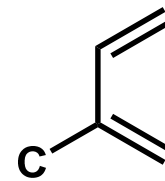
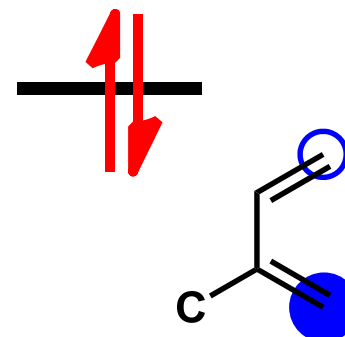
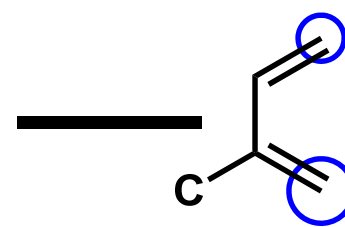
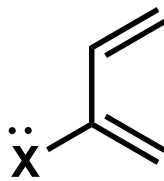
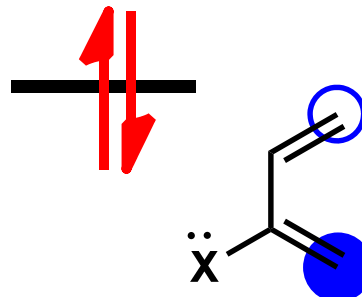
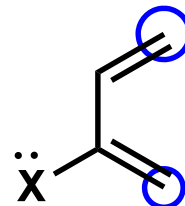
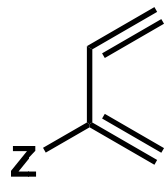
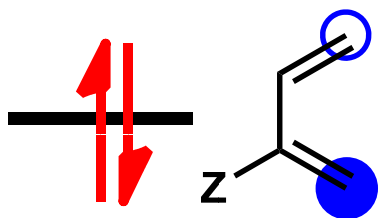
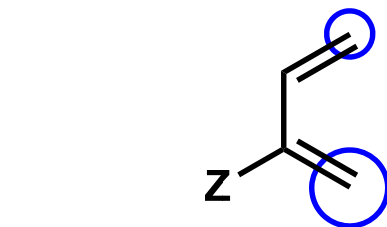
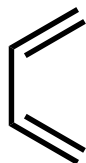
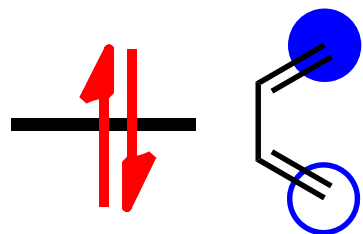
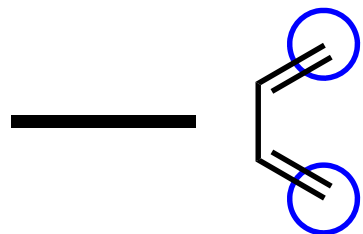
large-large  
small-small



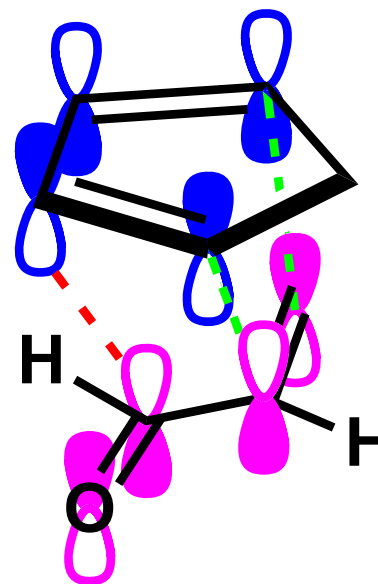
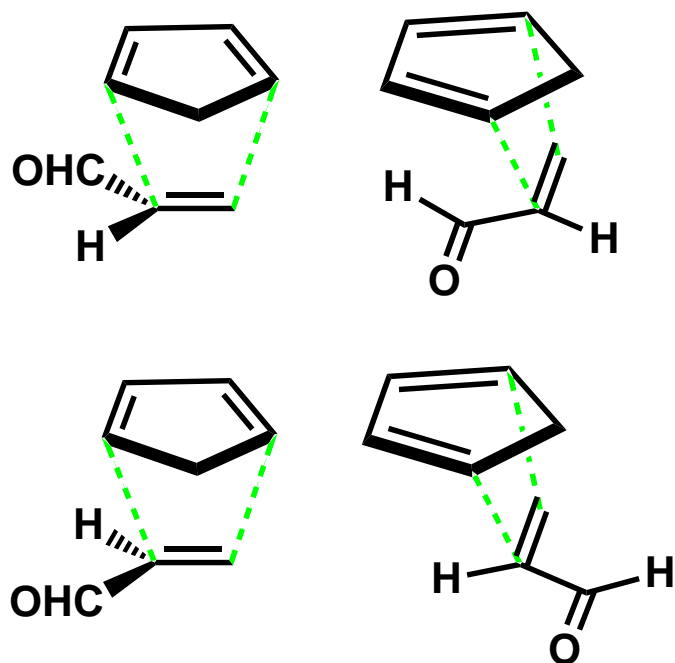
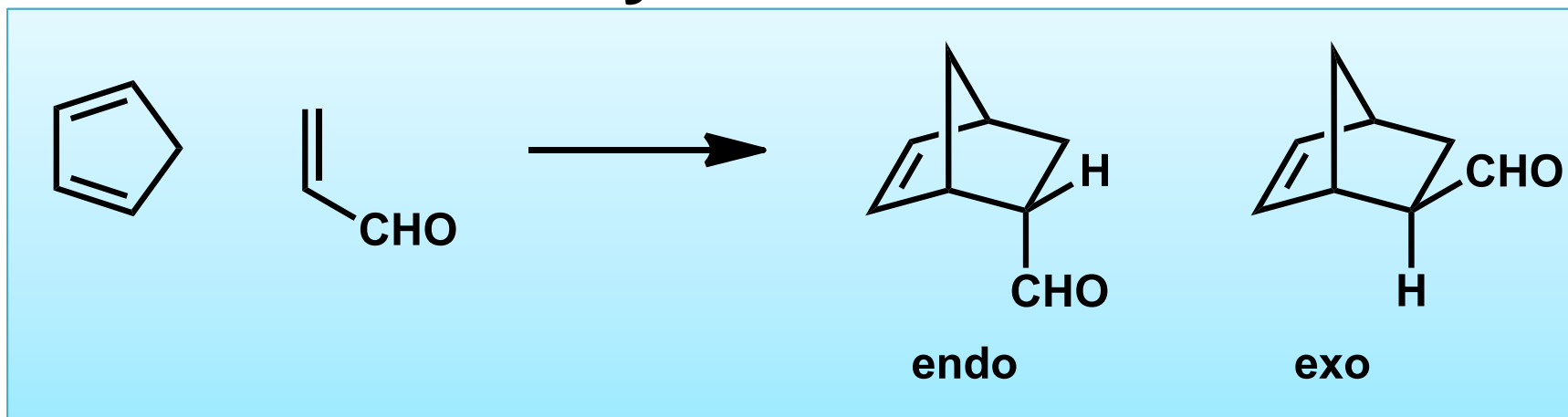
large-small  
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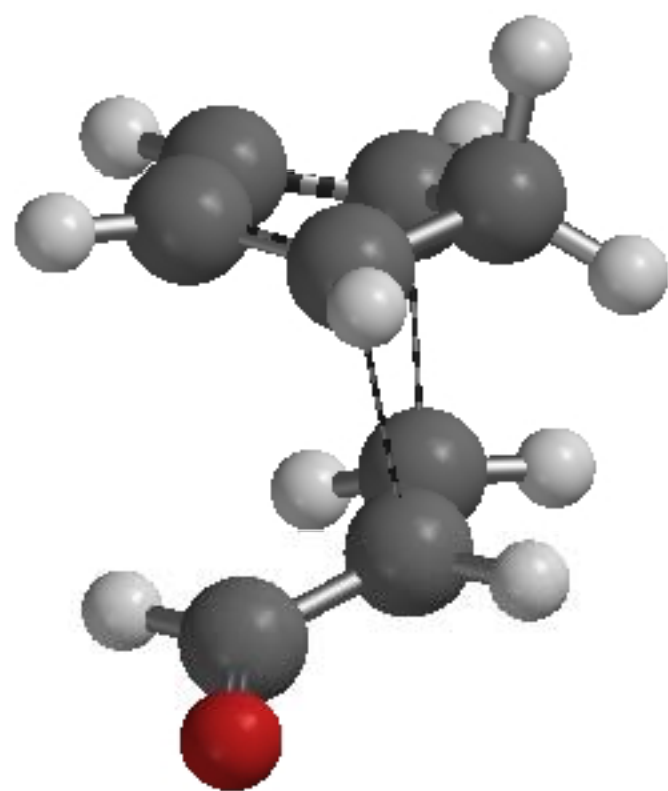




# endo/exo-selectivity

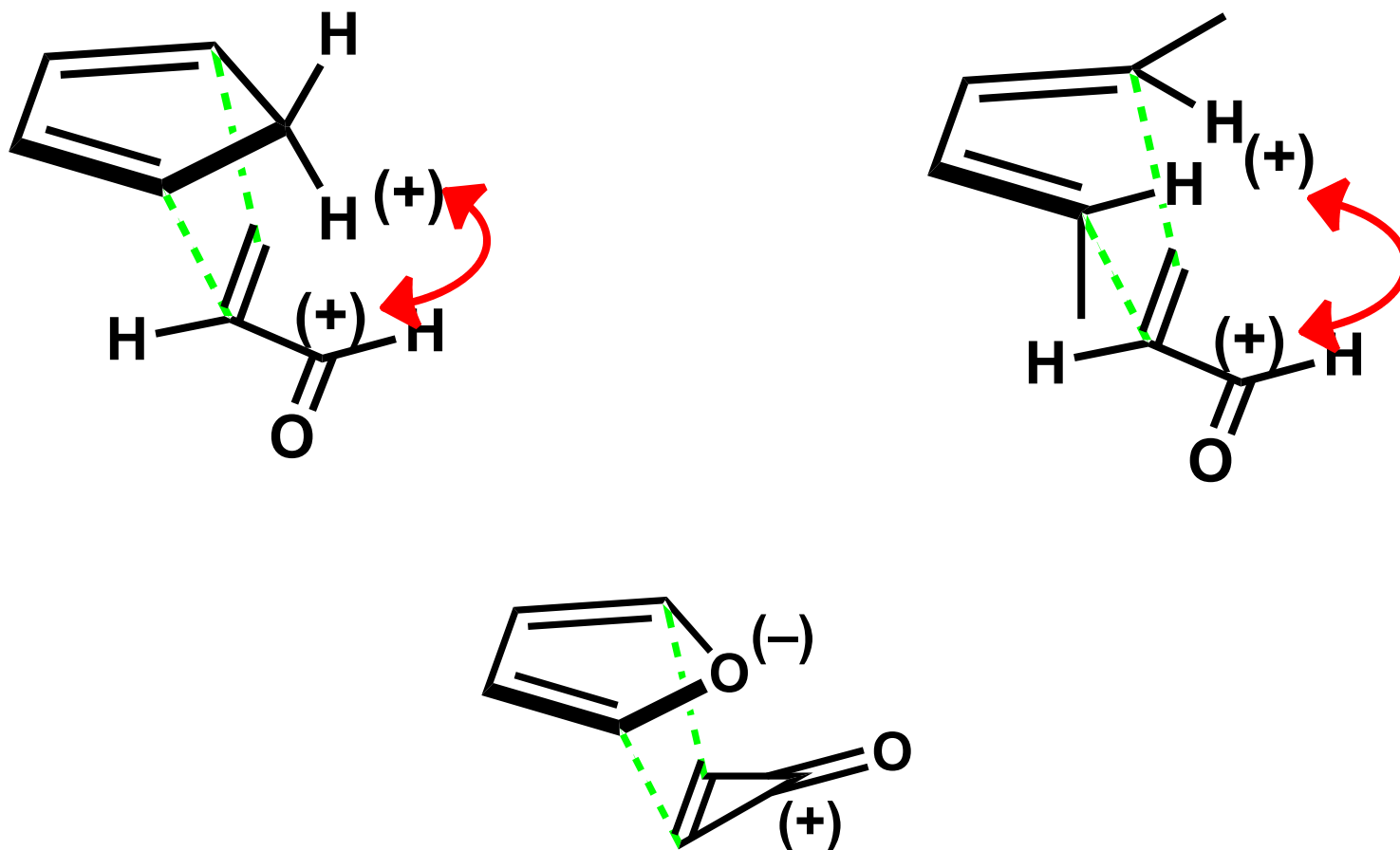


secondary orbital overlap

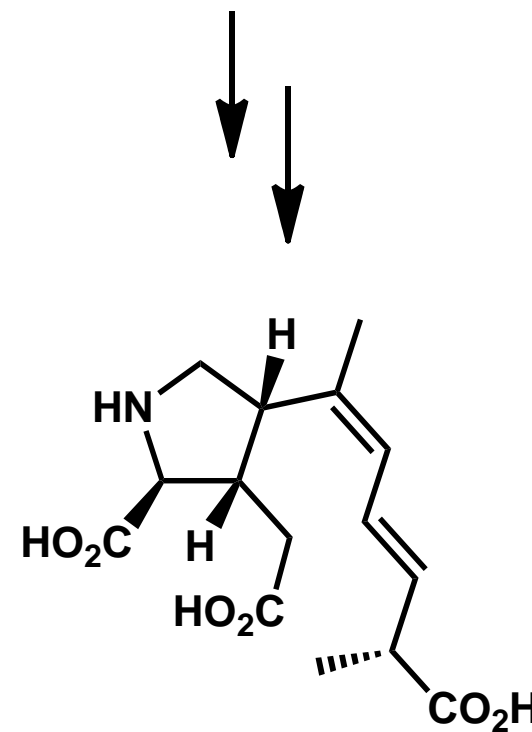
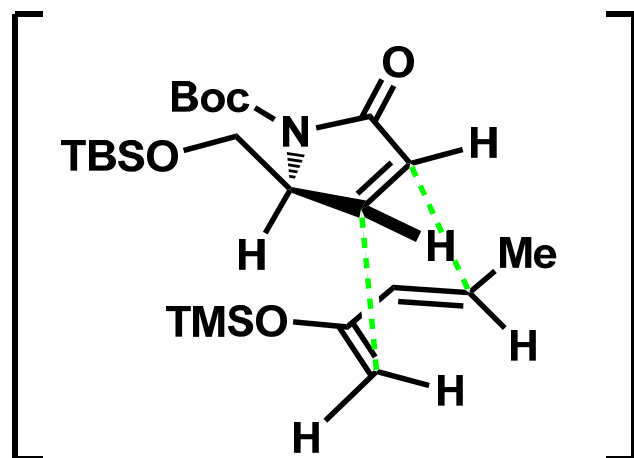
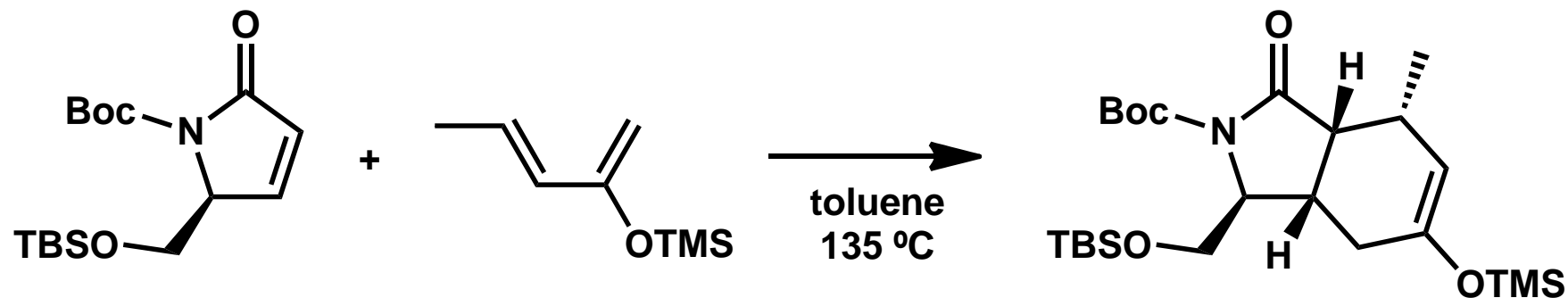


# endo/exo-selectivity

## electrostatic repulsion

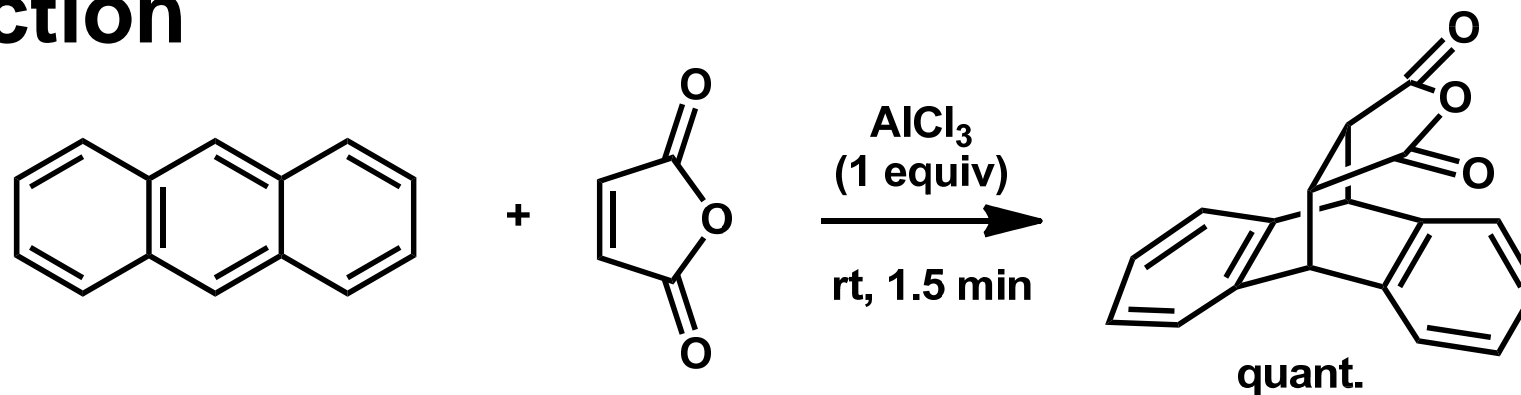


# regio-, endo/exo-, and facial selectivities



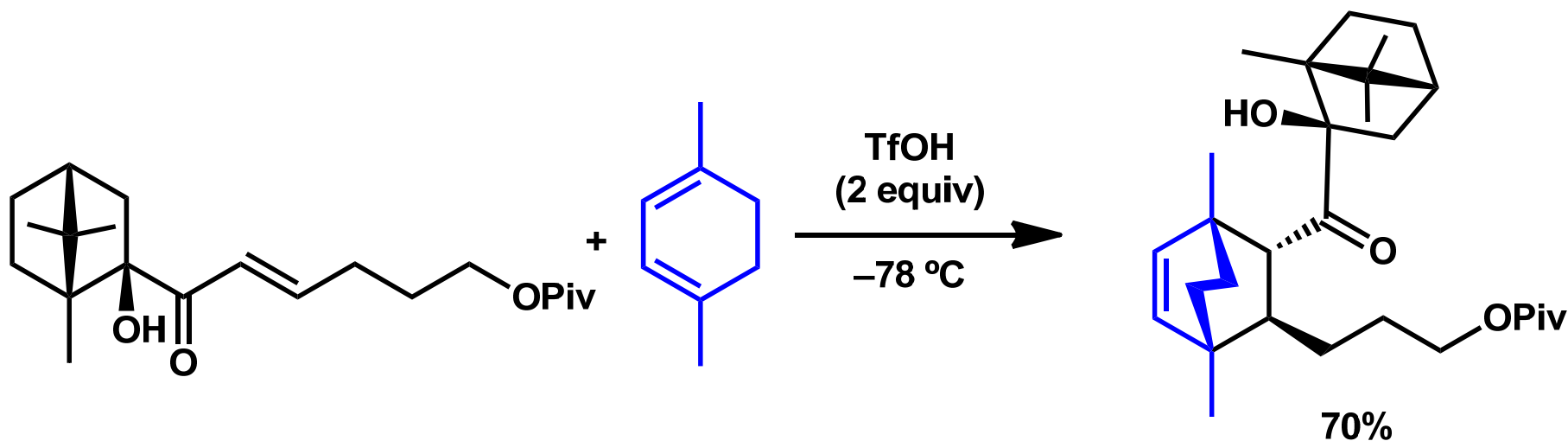
**(-)-domoic acid**

# Lewis (Brønsted) acid-accelerated Diels–Alder reaction

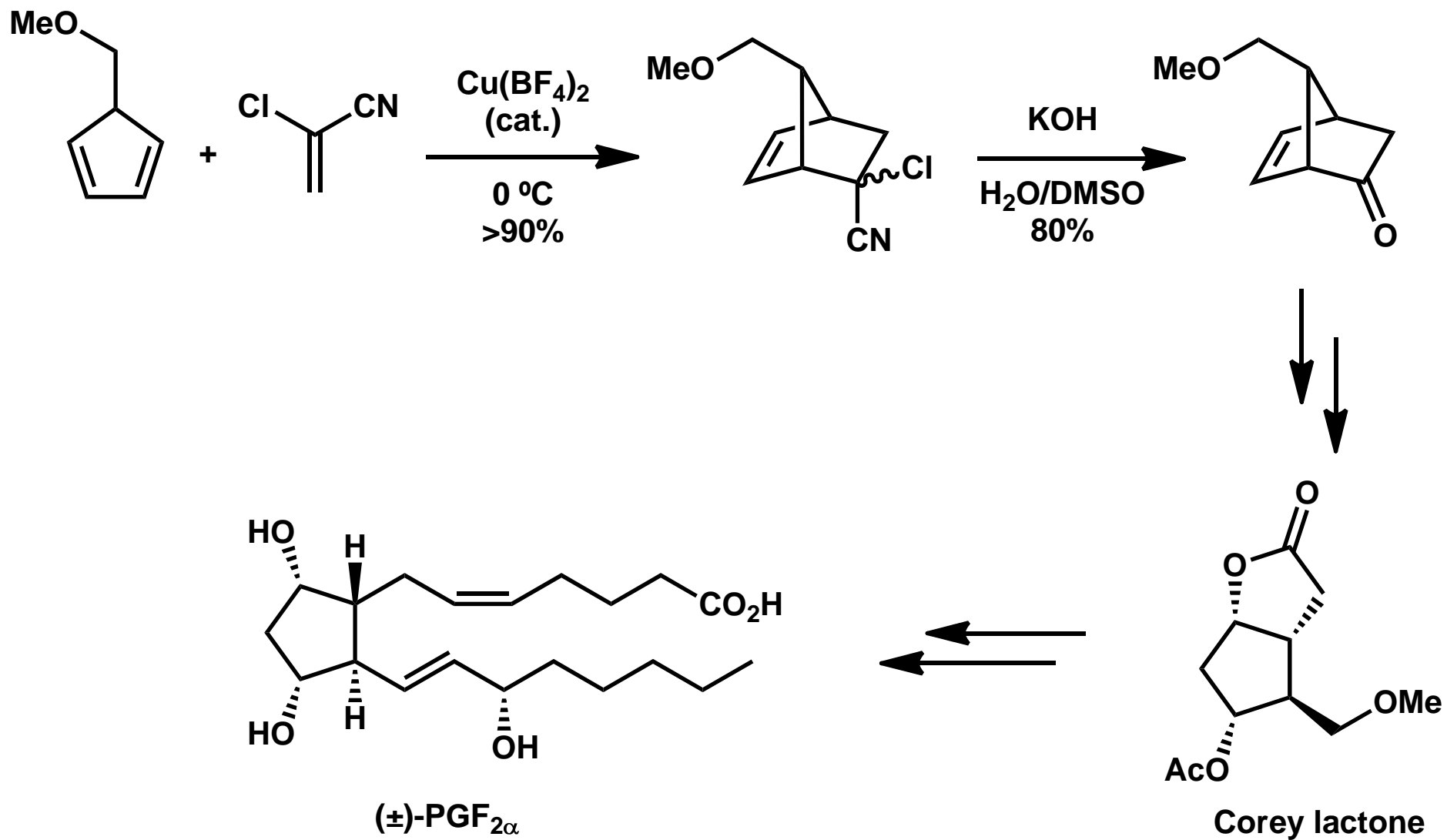


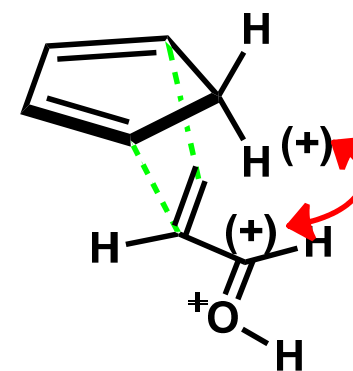
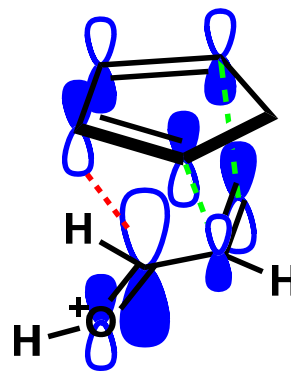
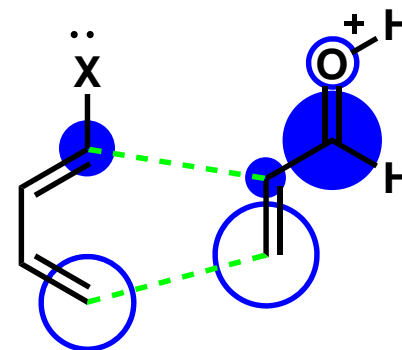
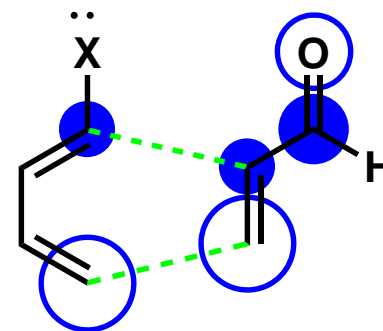
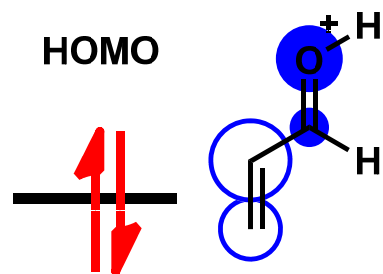
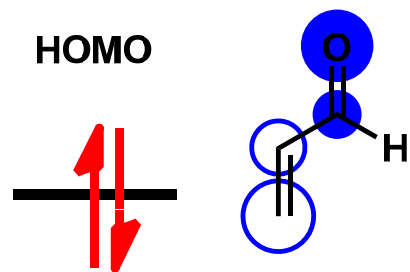
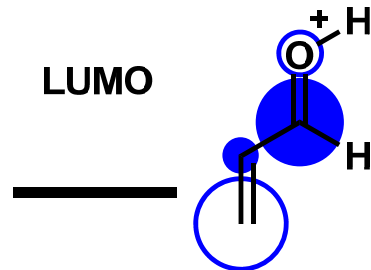
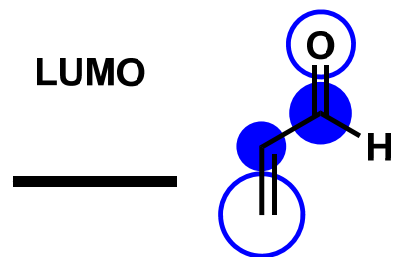
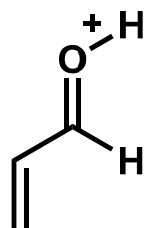
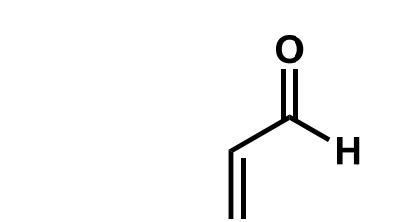
Without  $\text{AlCl}_3$ , 95% completion requires 4800 h.

Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436.



Pfeiffer, M. W. B.; Phillips, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 5334.





# Catalytic Asymmetric Diels–Alder Reaction

