

# DIENY A POLYENY



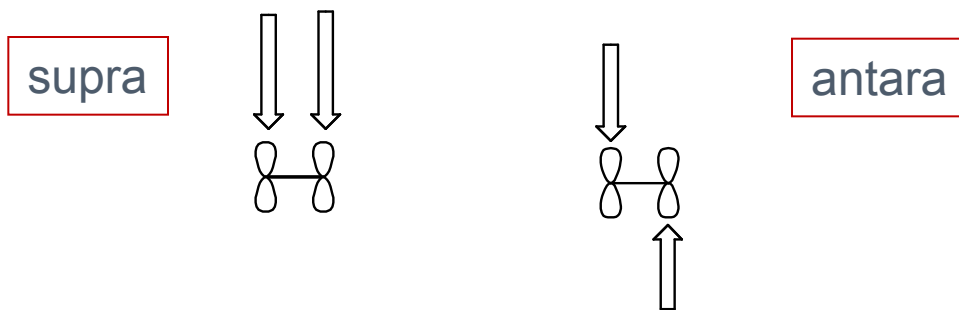
# Pericyklické reakce

## Woodward – Hoffmann

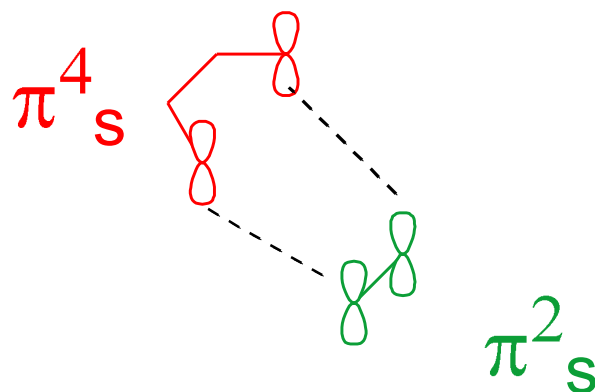
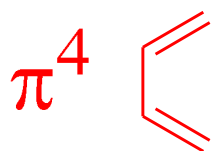
pravidla odvozena na základě korelace mezi molekulovými orbitaly reaktantů a produktů s využitím pravidla zachování orbitalové symetrie

$$(4q + 2)_s + (4r)_a$$

P. reakce je termicky povolena, je-li celkový počet suprafaciálně reagujících  $(4q+2)$  elektronových komponent a antarafaciálně reagujících  $(4r)$  elektronových komponent lichý ( $q, r$  jsou celá kladná čísla)



# Pericyklické reakce



máme jednu  $(4q + 2)_s$

Liché číslo



$(4q + 2)_s + (4r)_a$

nemáme žádnou  $(4r)_a$



## **K. Fukui**

Teorie interakce hraničních molekulových orbitalů

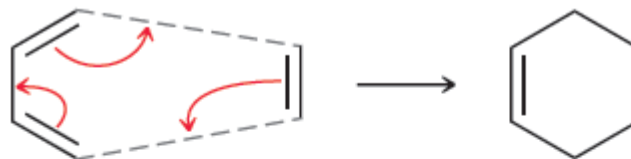
## **H. Zimmermann**

Aromatický a antiaromatický tranzitní stav



# Pericyklické reakce

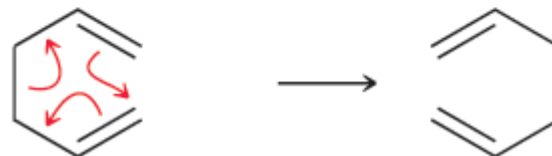
## 1) Cykloadiční reakce



## 2) Elektrocyklizační reakce



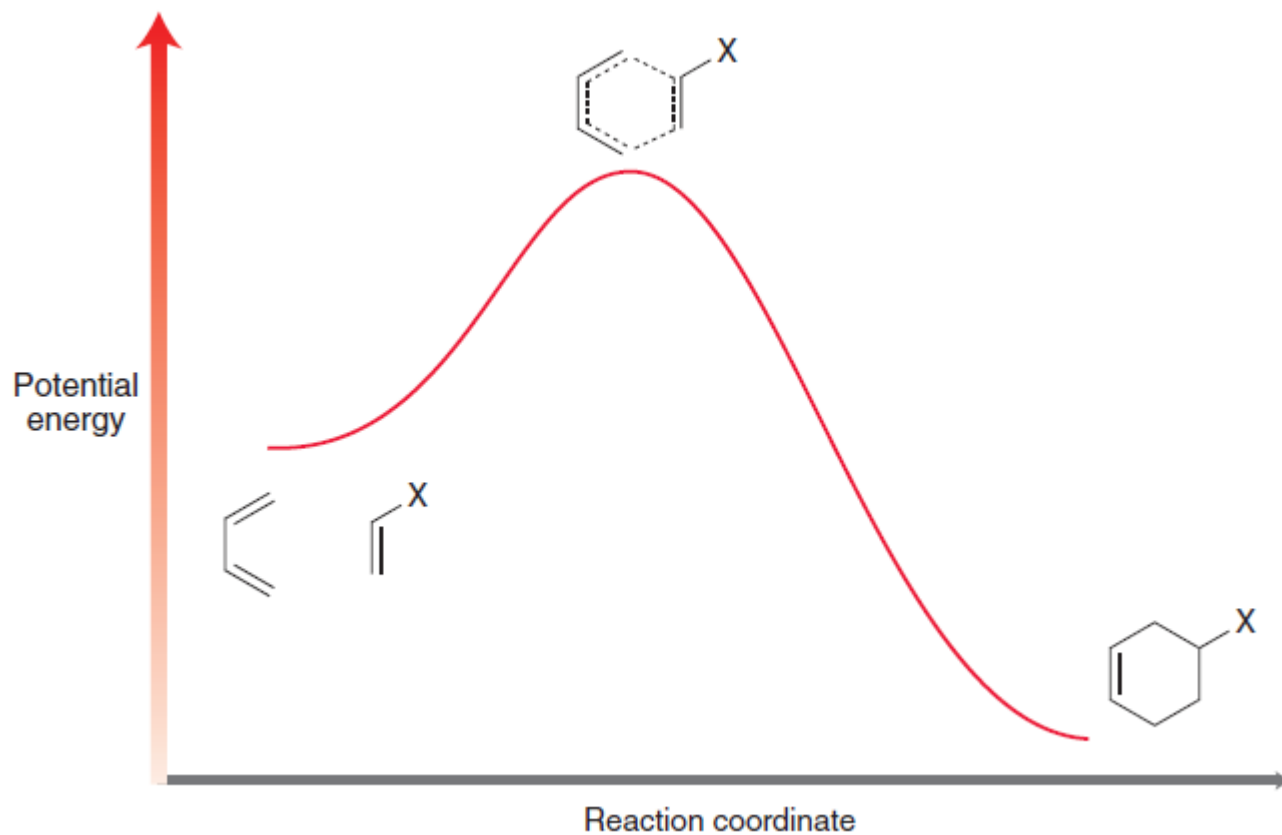
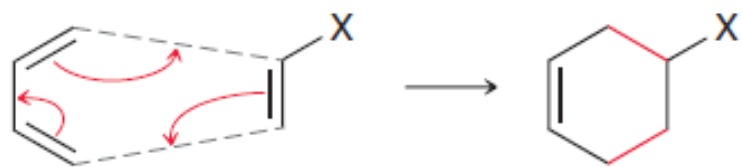
## 3) Sigmatropní přesmyky

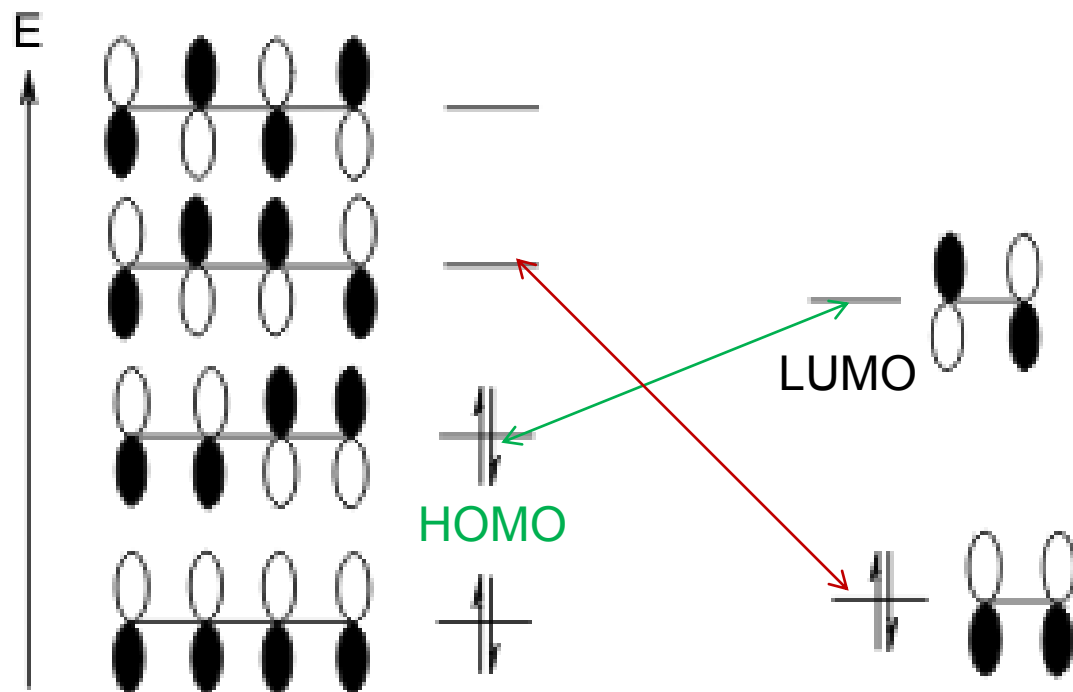
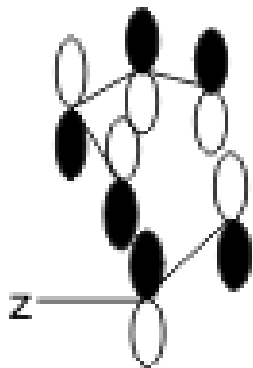


změna v počtu $\sigma$ vazeb	změna v počtu $\pi$ vazeb
+ 2	- 2
+ 1	- 1
0	0



# Diels-Alderova reakce

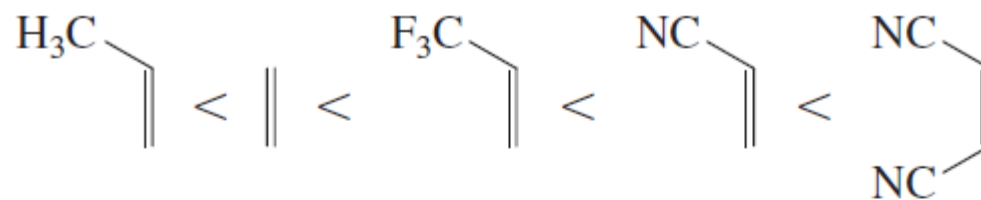




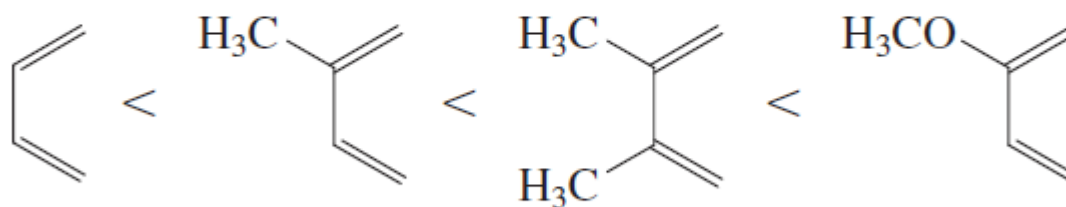
dien

dienofil






**Dienophile**



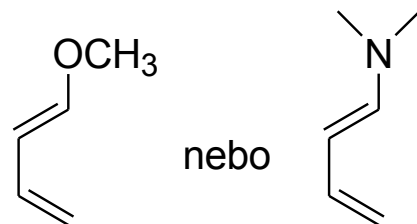
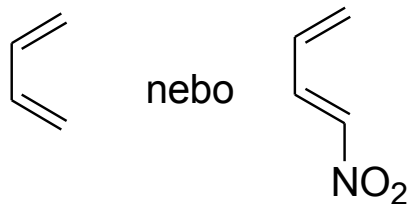
**Diene**

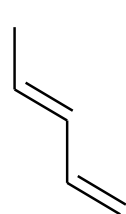
Increasing reactivity 



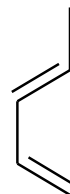


Který dien bude při D. - A. reakci s benzochinonem reaktivnější?

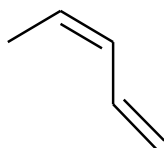




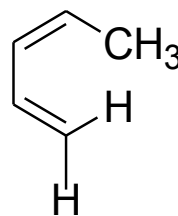
**s-trans**



**s-cis**  
reagující konformace



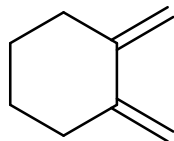
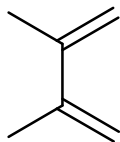
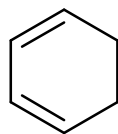
**s-trans**



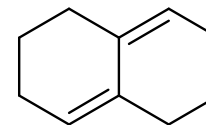
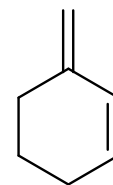
**s-cis**  
reagující konformace  
částečná stérická zábrana

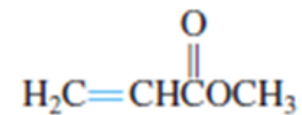
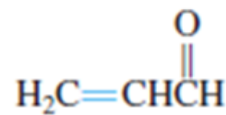
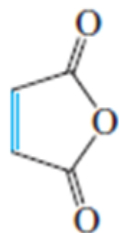
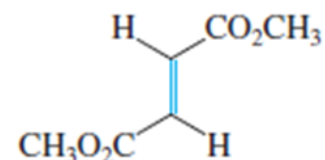
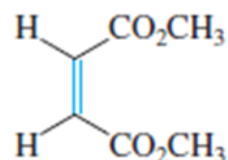
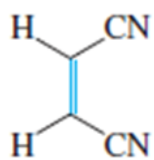
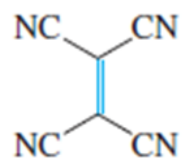
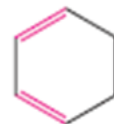
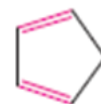
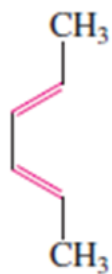
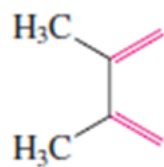


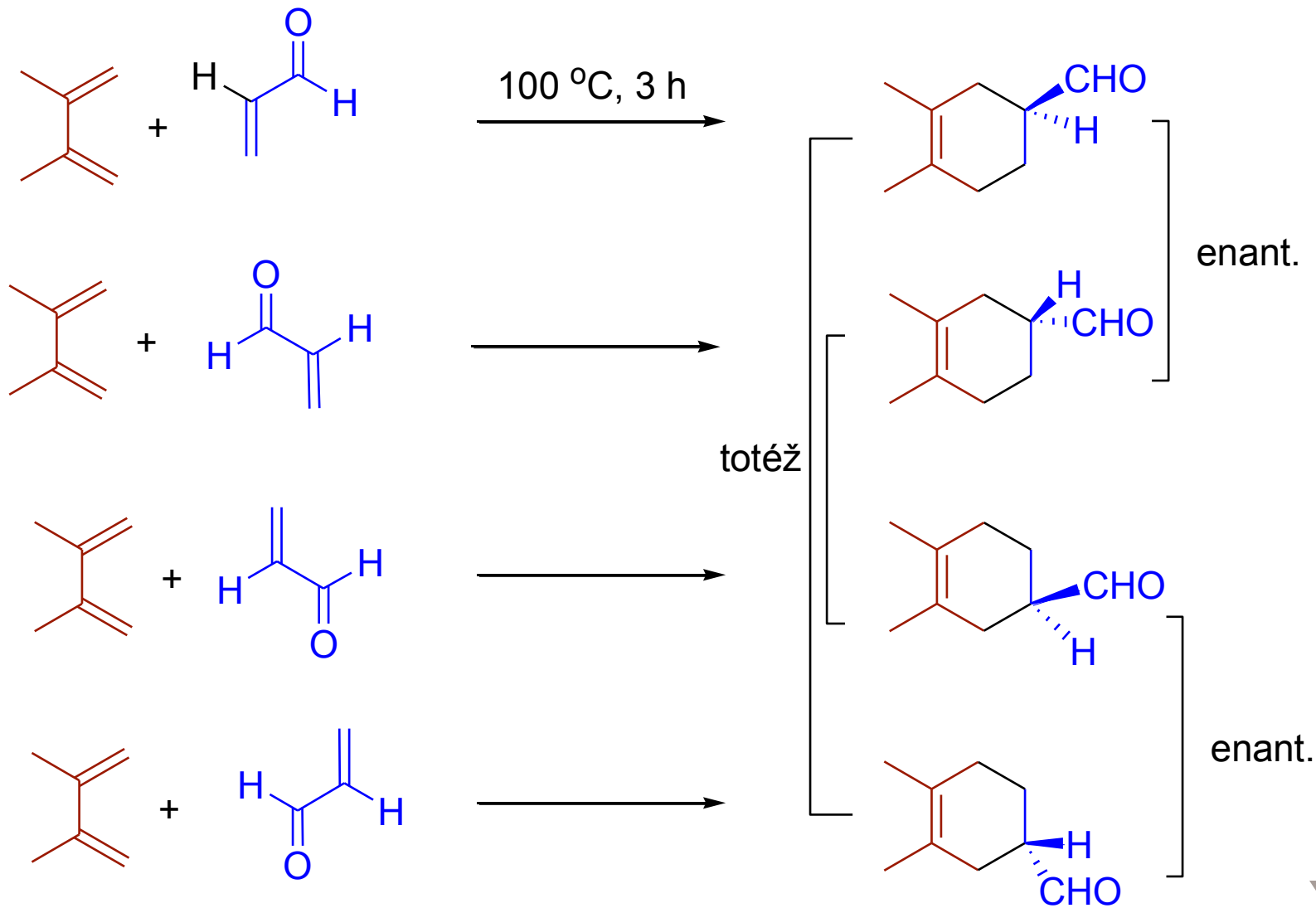
## reaktivní dieny

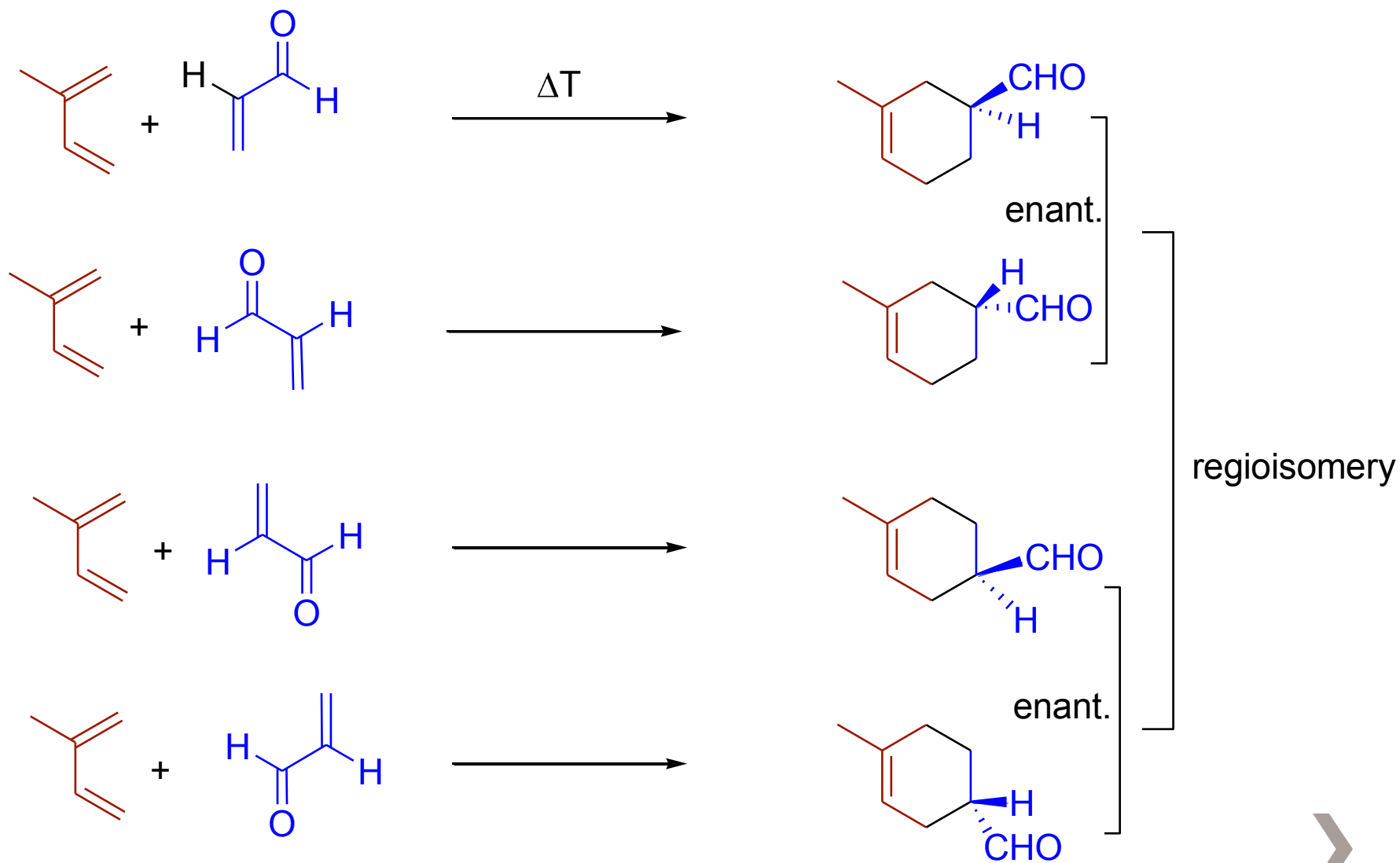


## nereaktivní dieny

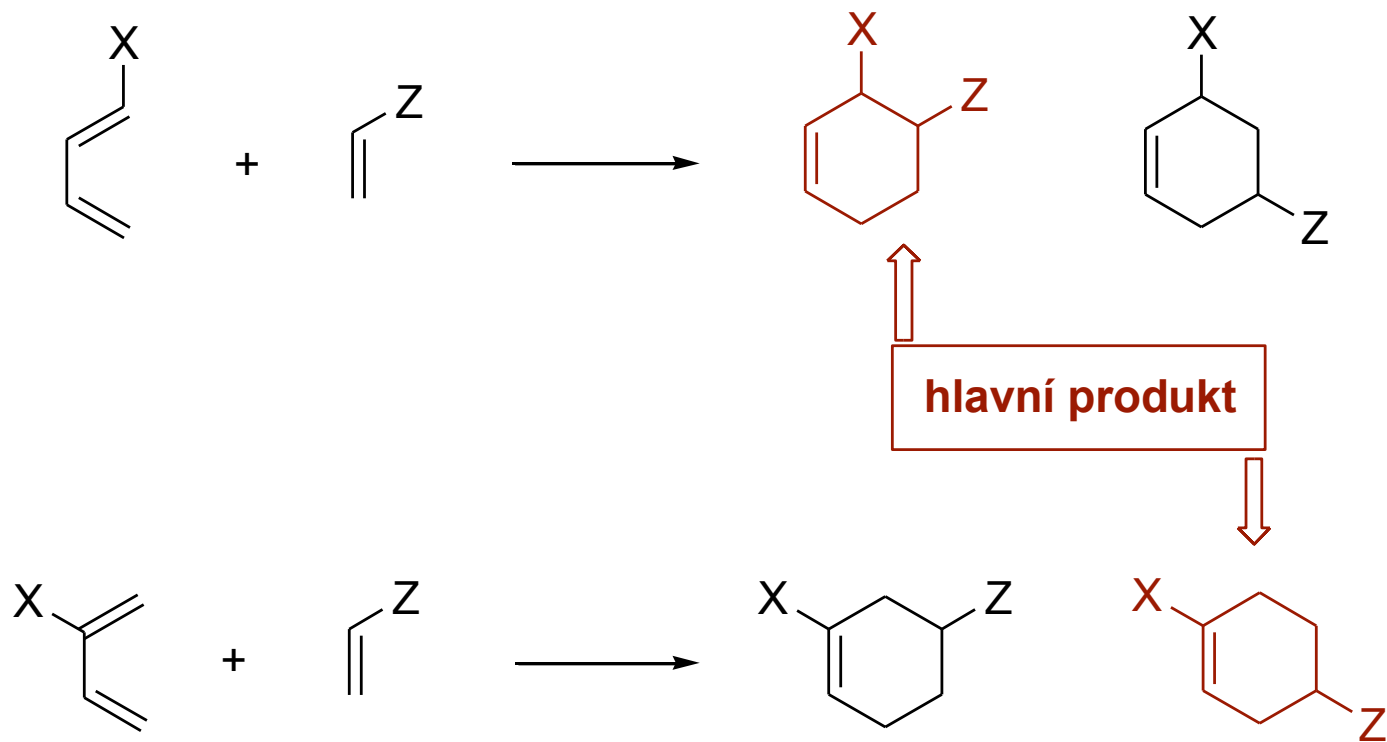


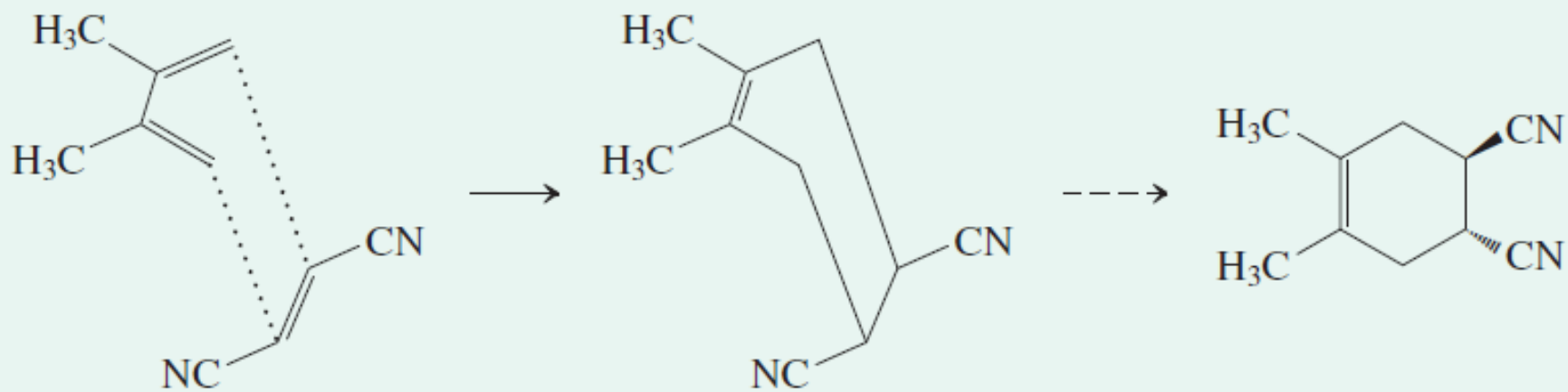
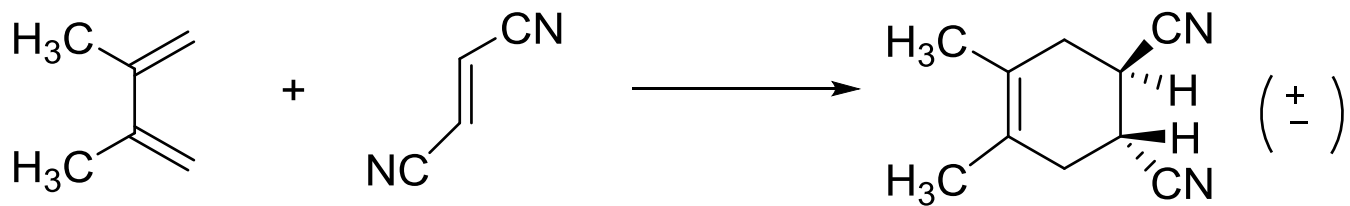




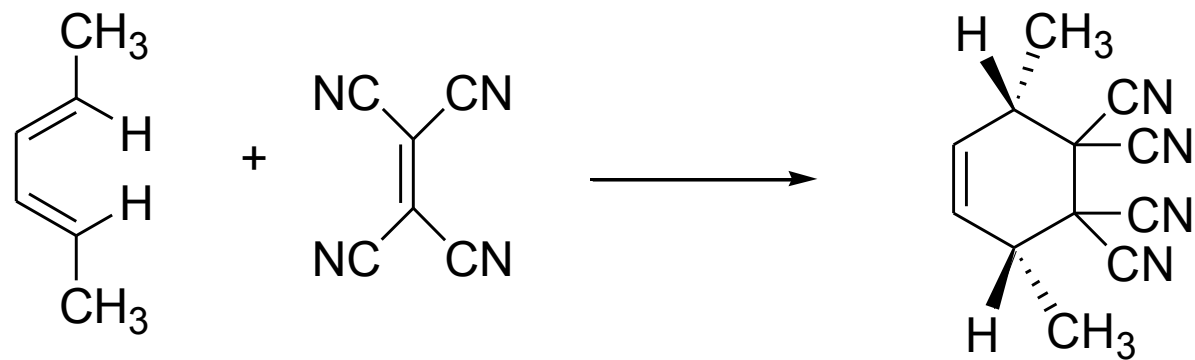


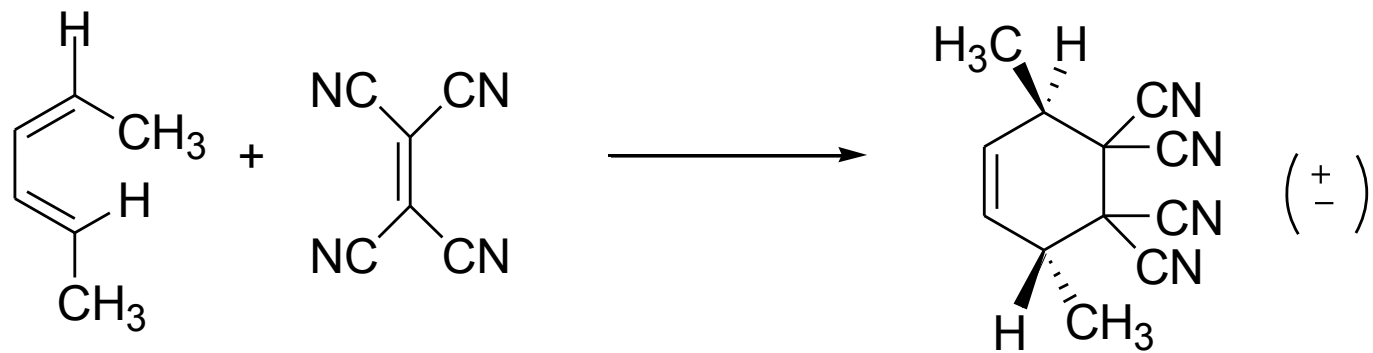
## Regioisomery u Diels-Alderovy reakce

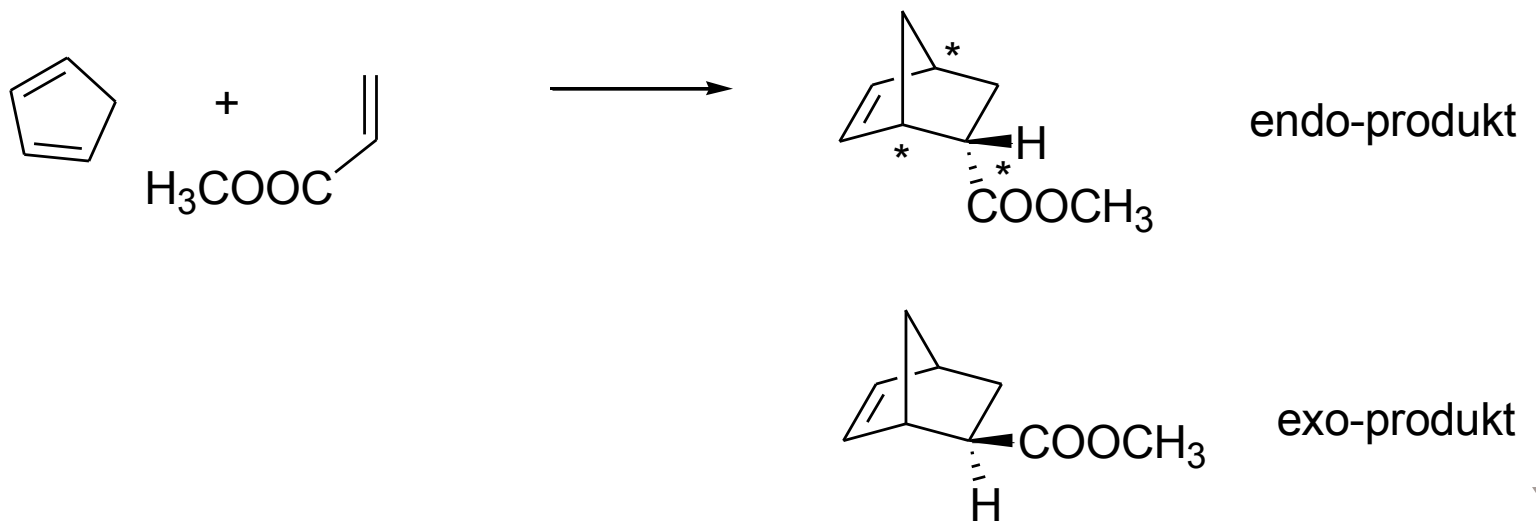
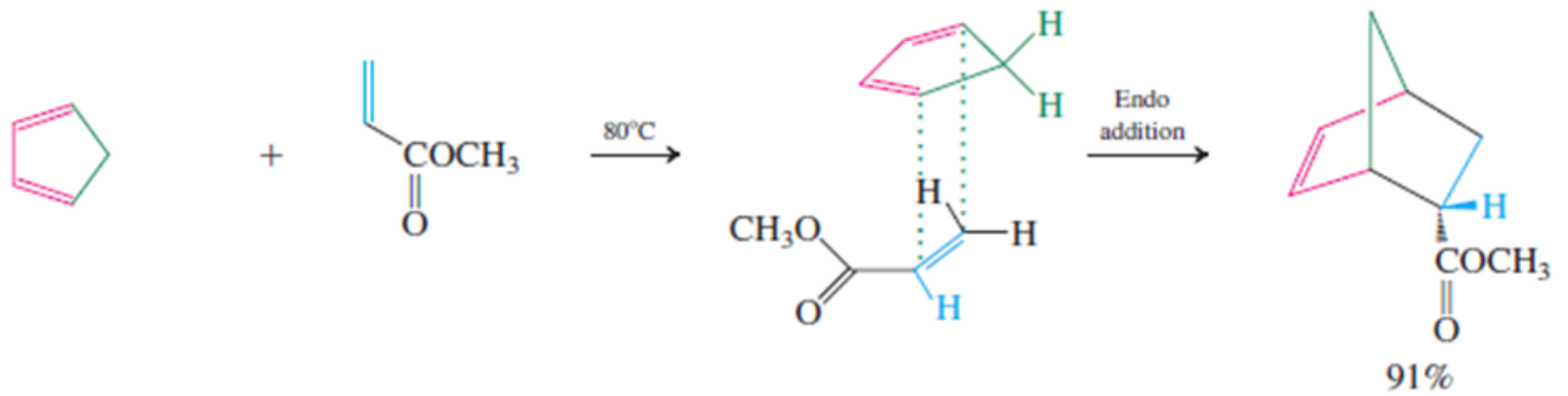


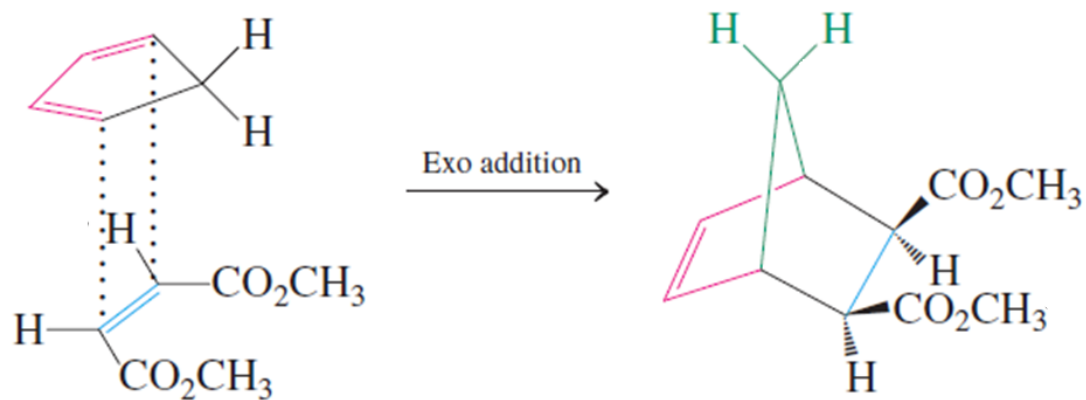
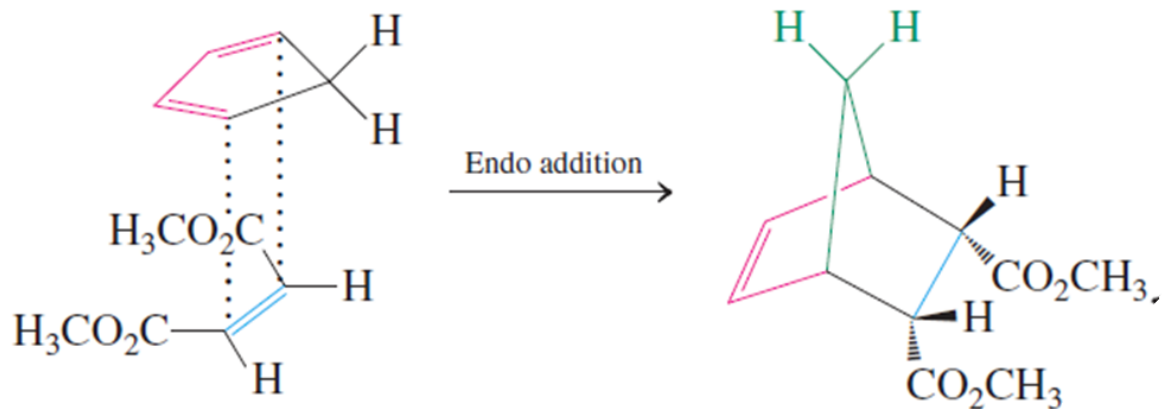
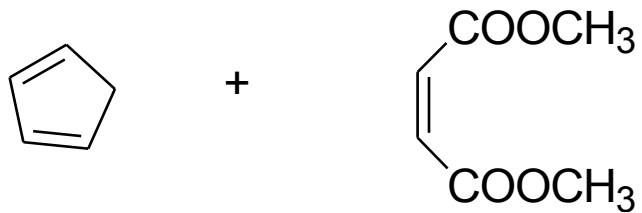




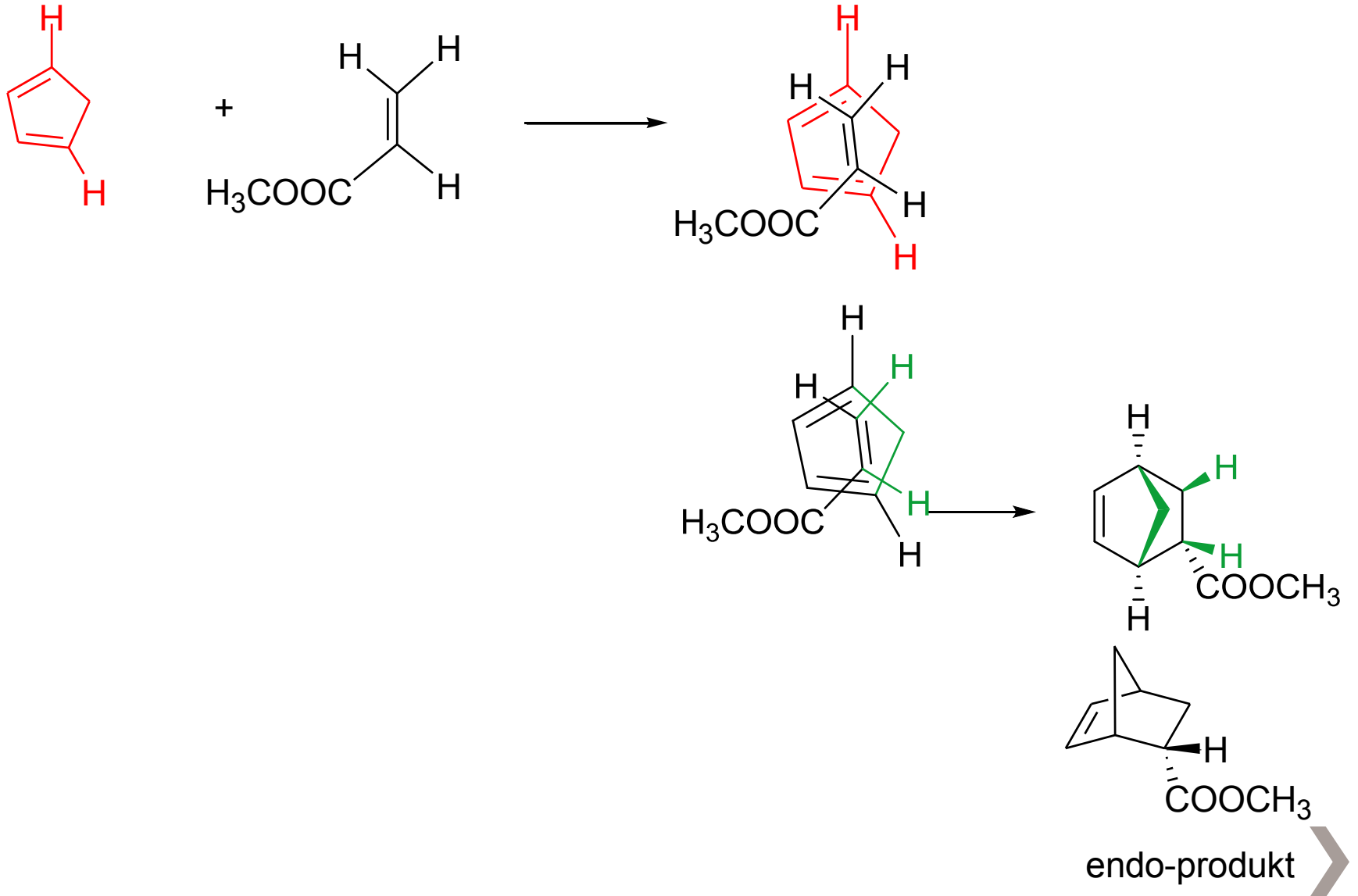


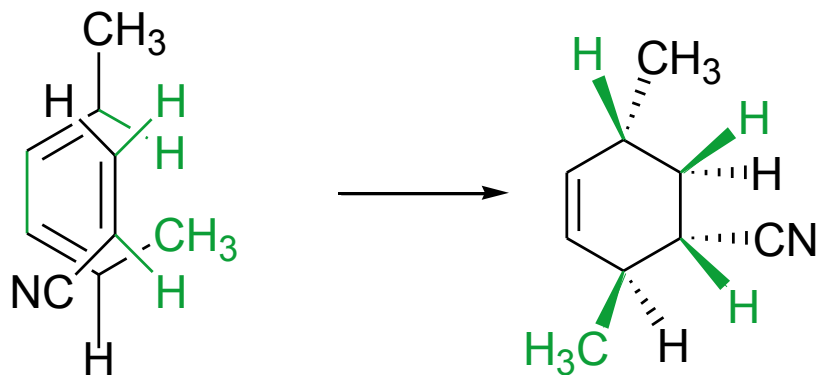
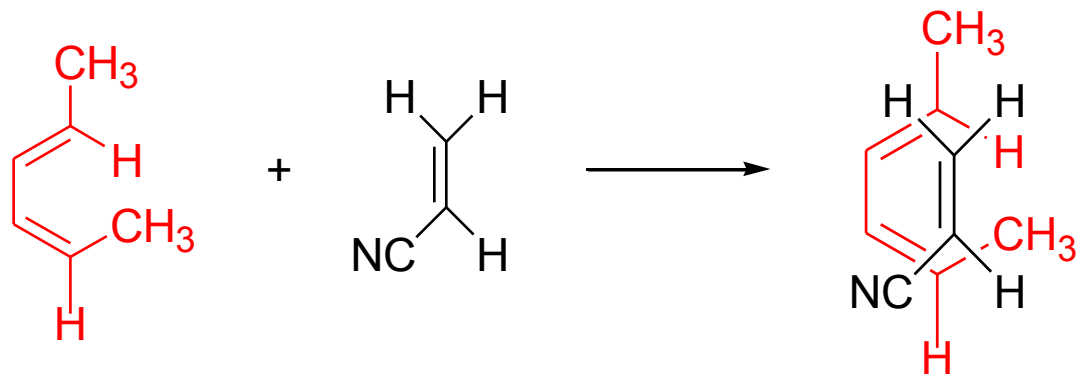


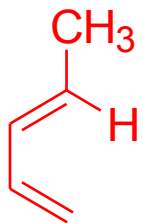




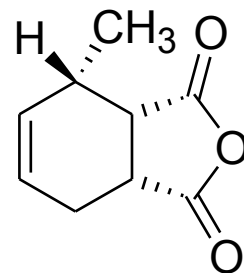
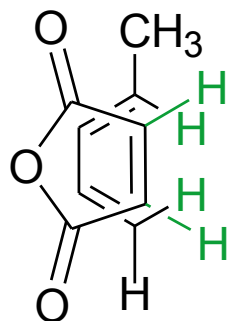
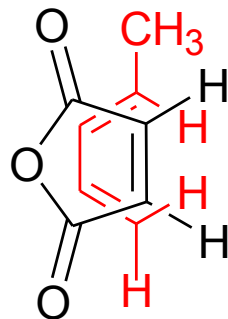
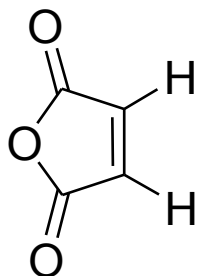
# Jak nakreslit *endo* produkt

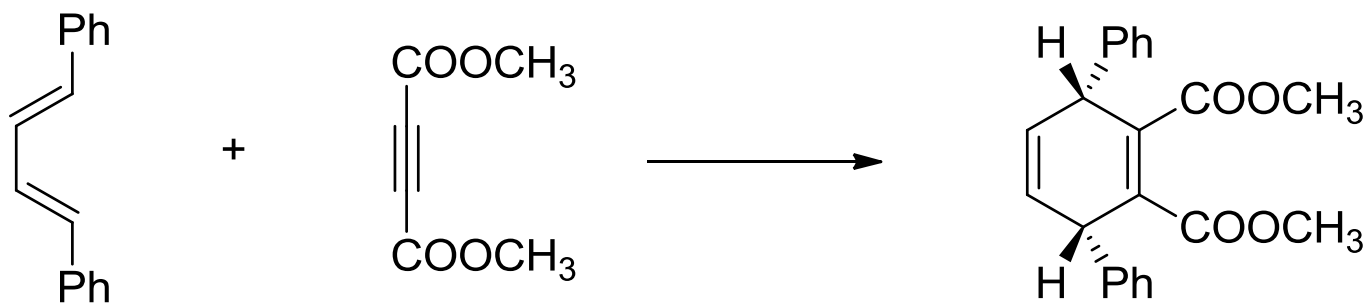
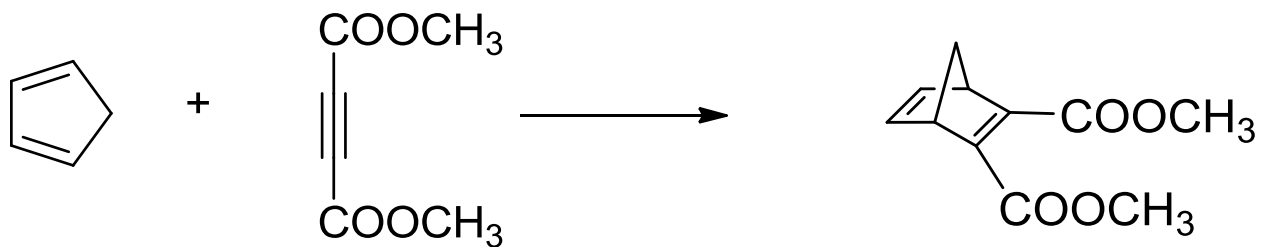




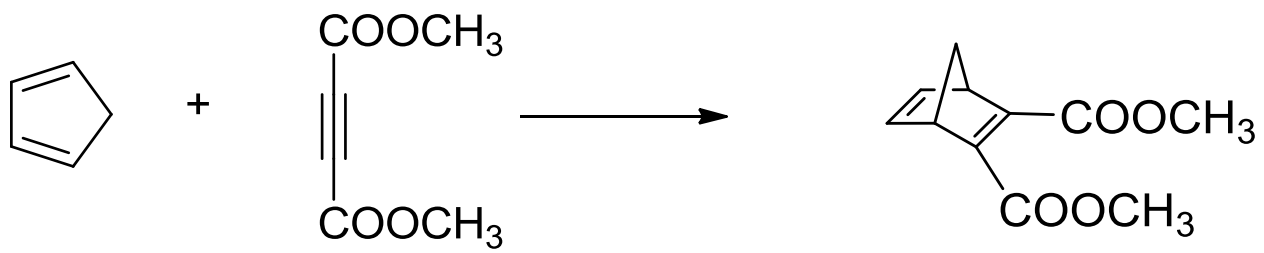


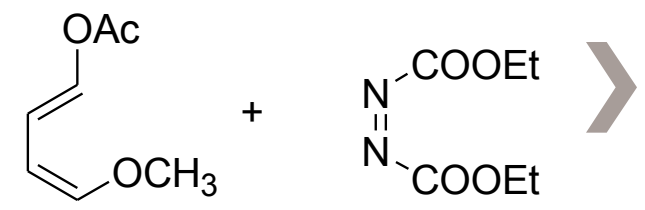
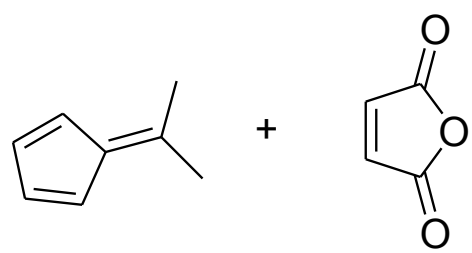
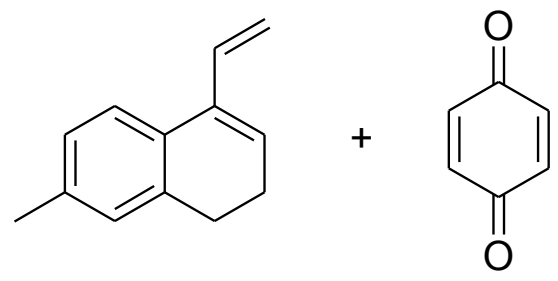
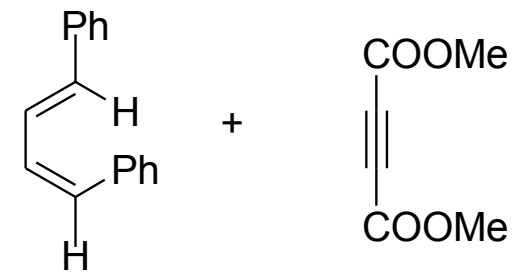
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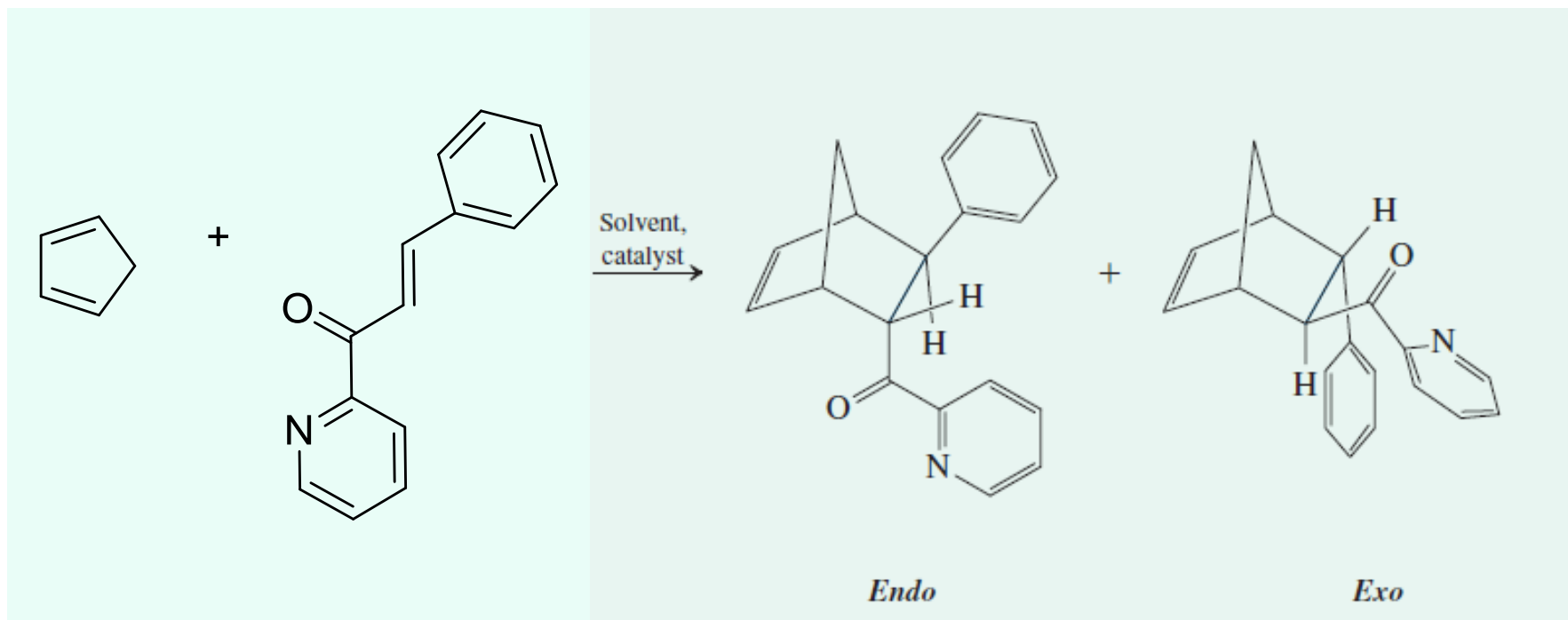
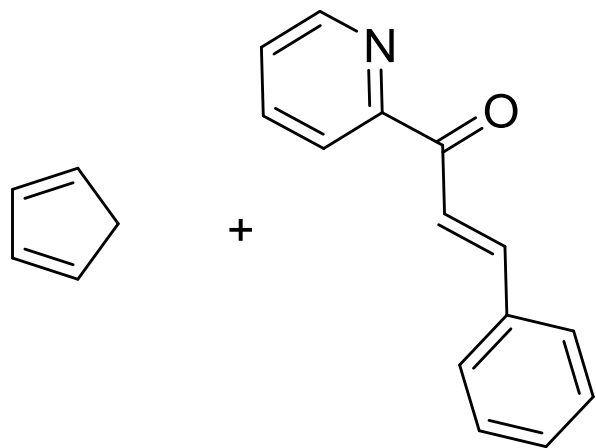


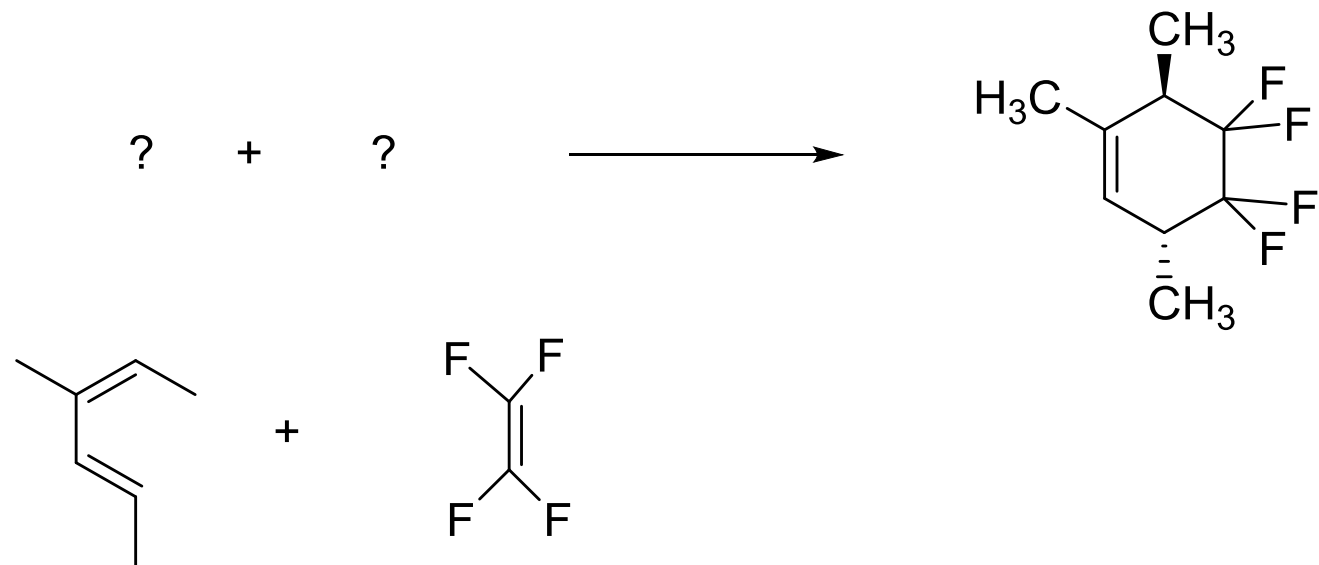


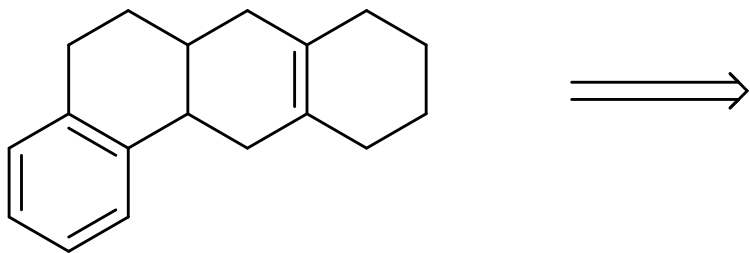
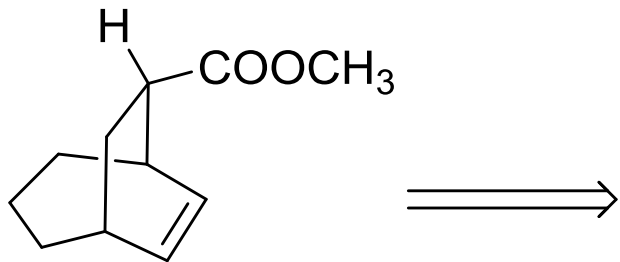


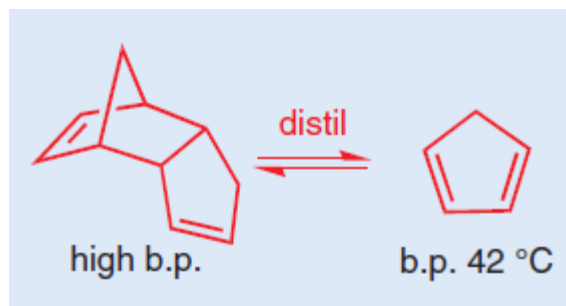
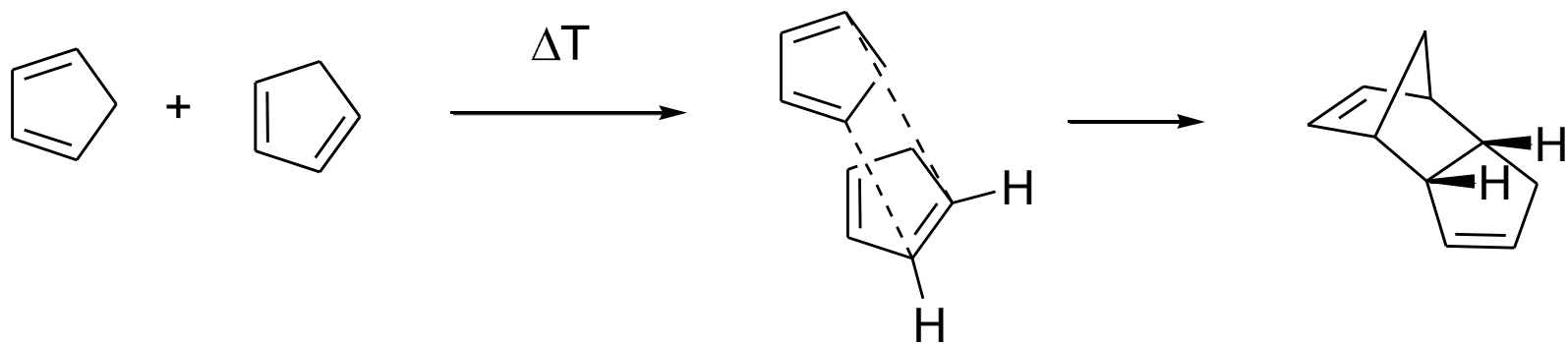




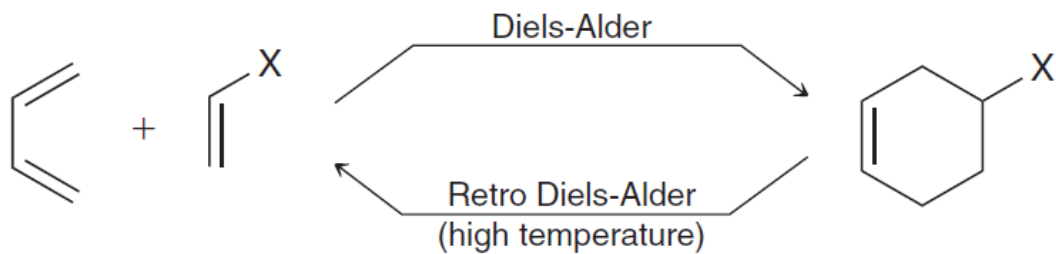
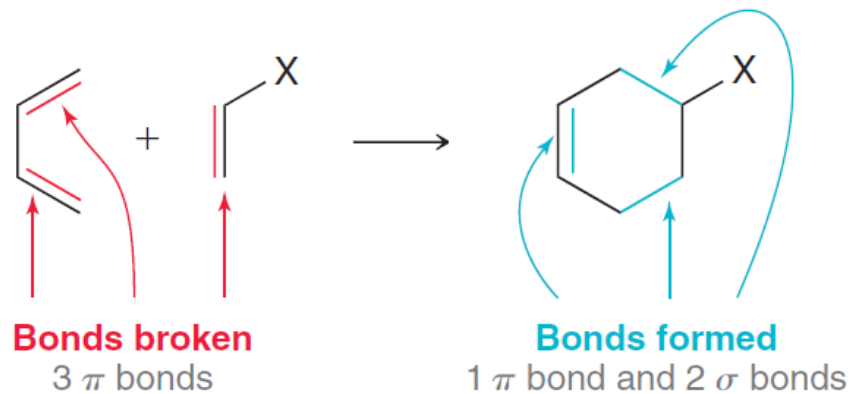






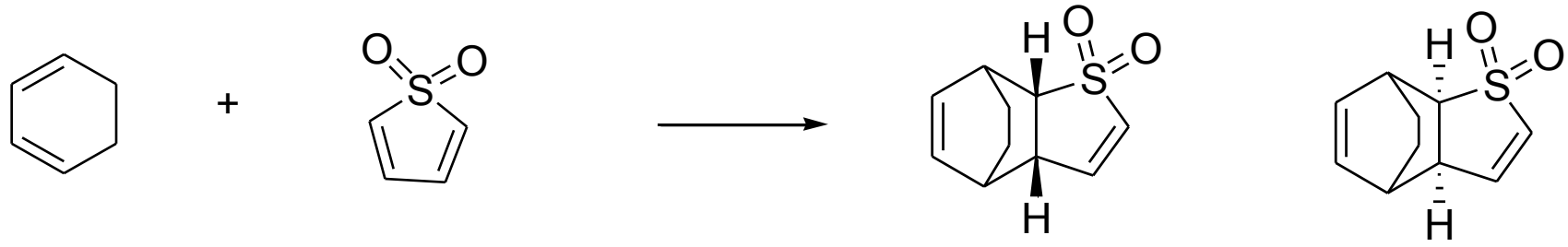
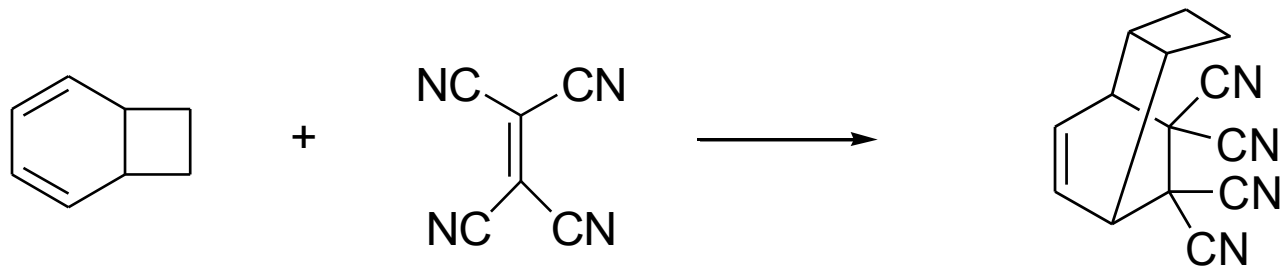


$$\Delta G = \underbrace{(\Delta H)}_{\text{Enthalpy term}} + \underbrace{(-T \Delta S)}_{\text{Entropy term}}$$

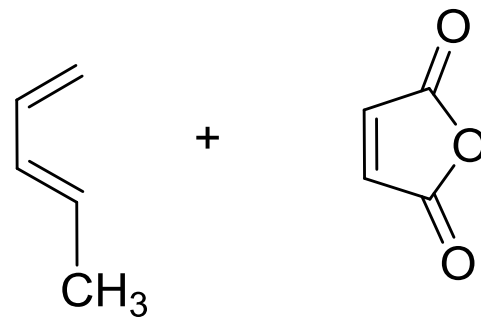
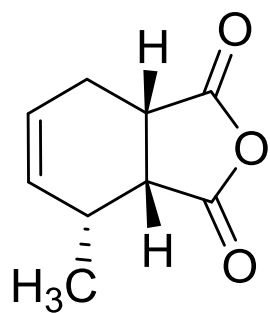
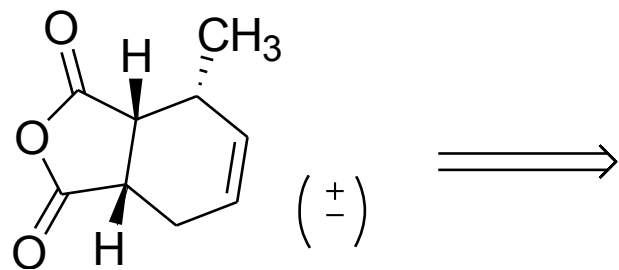


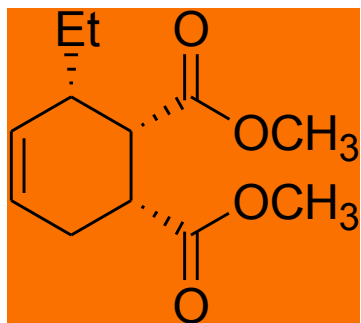
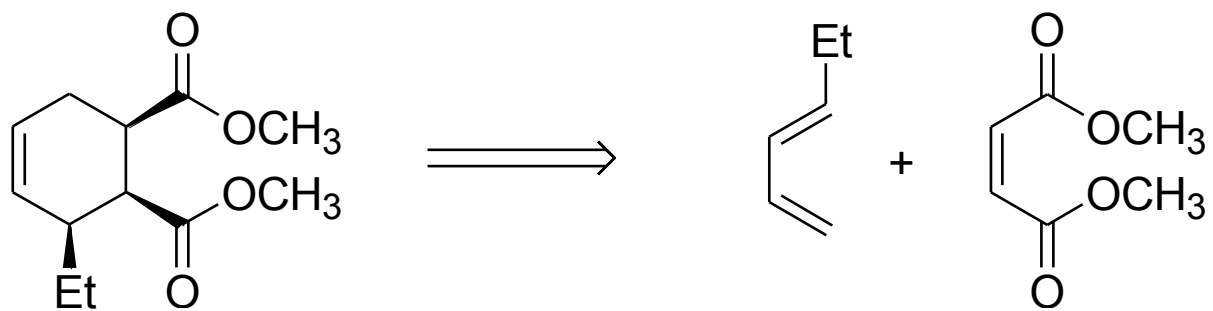
obvykle vyšší než 200 °C

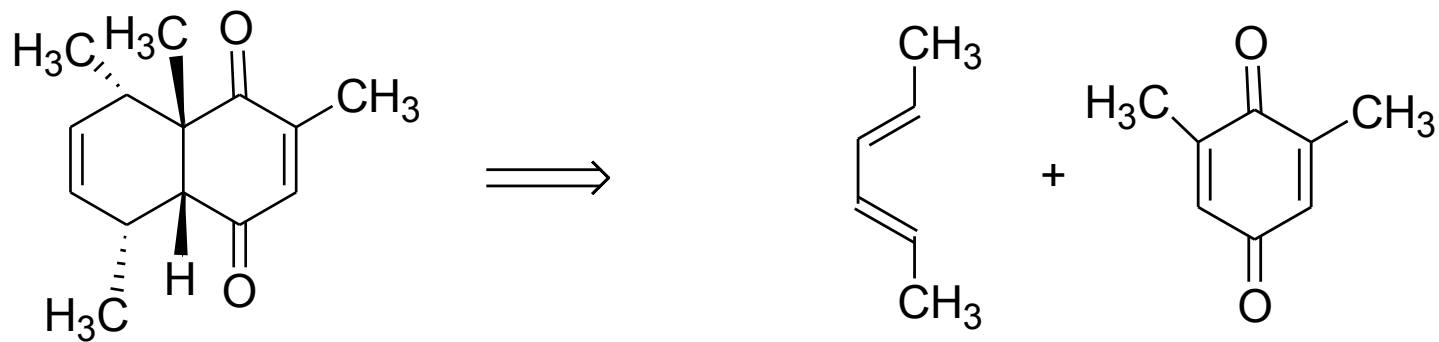




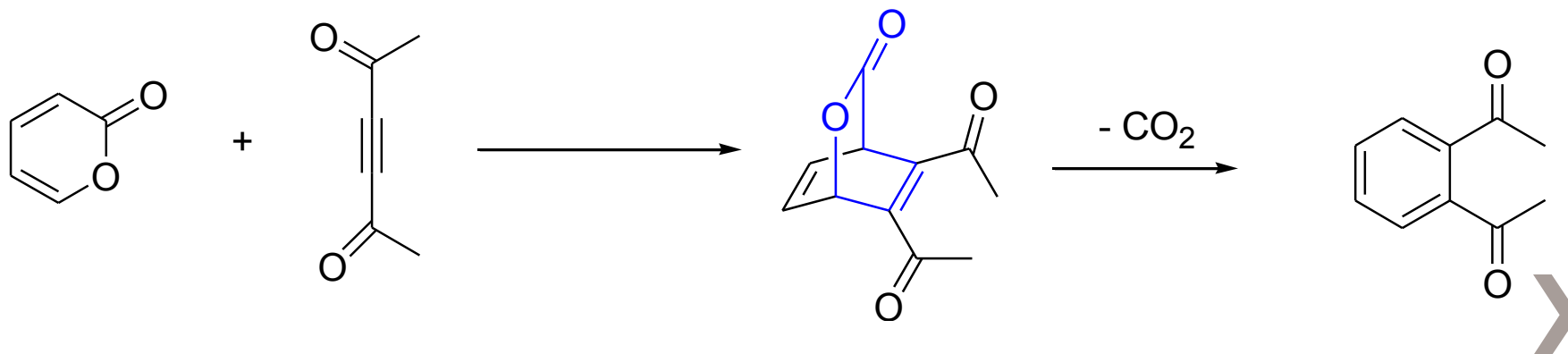
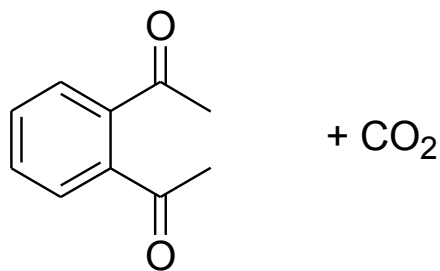
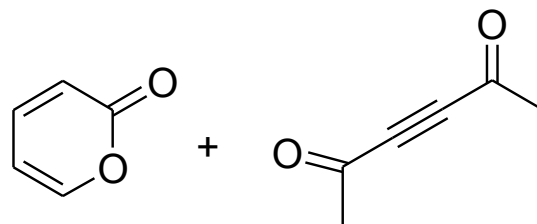




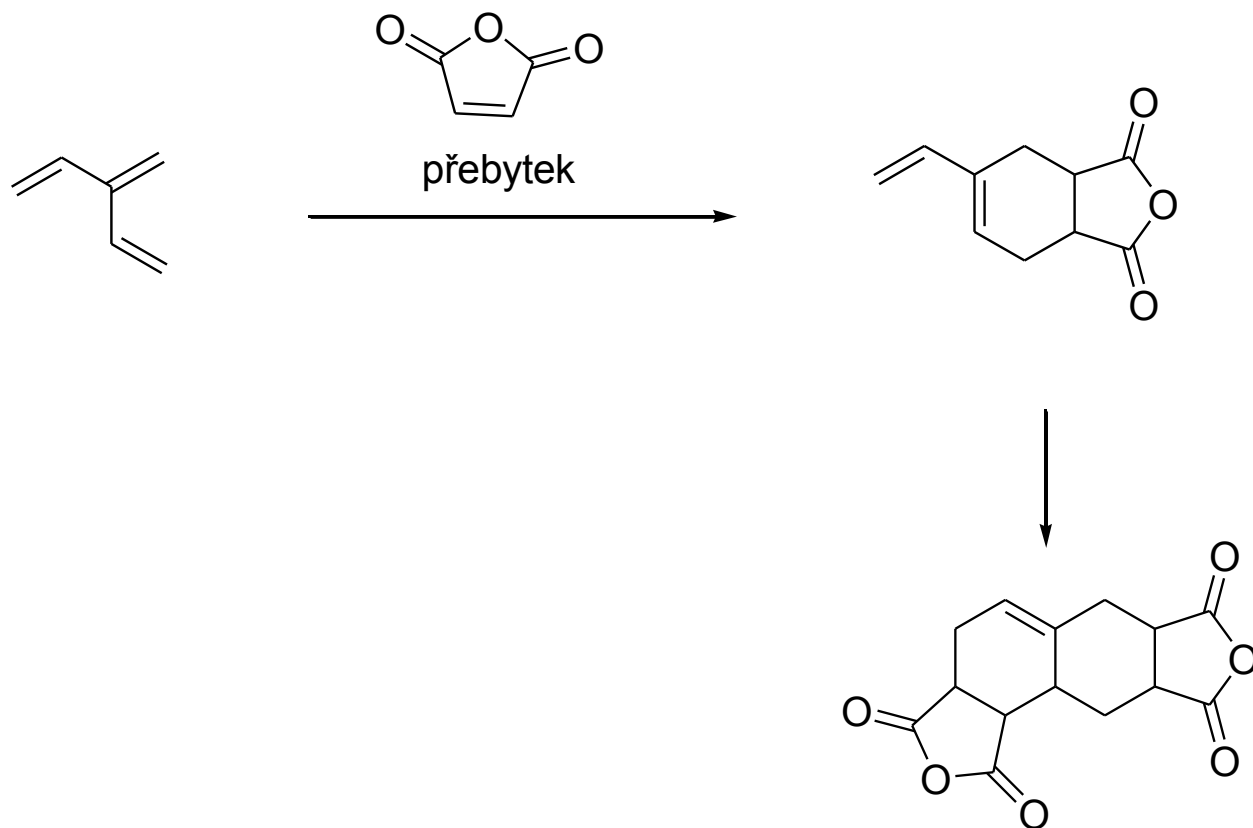




# Vysvětlete a zapište mechanismus



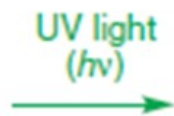
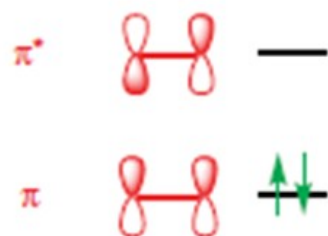
**Nakreslete produkt reakce (ignorujte stereochemii produktu)**



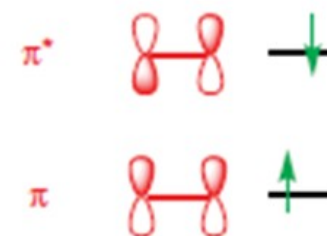
# Cykloadiční reakce



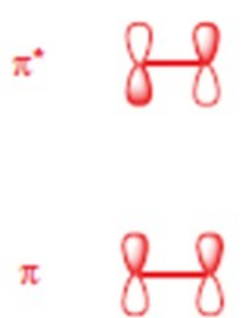
ground state of alkene



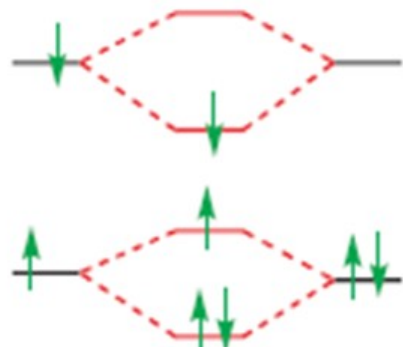
excited state of alkene



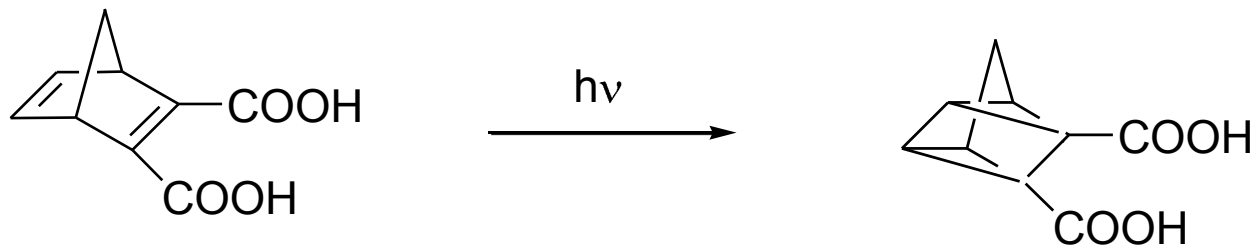
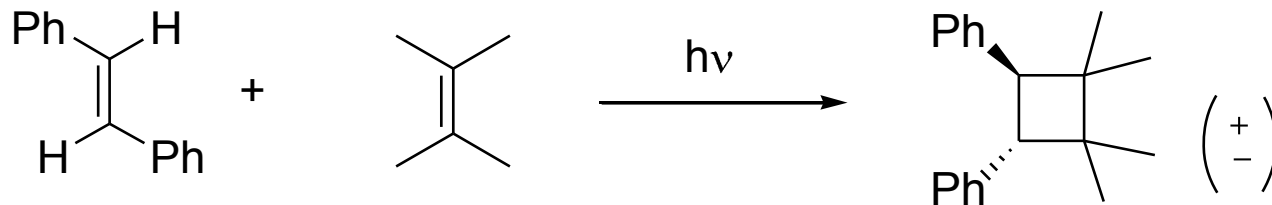
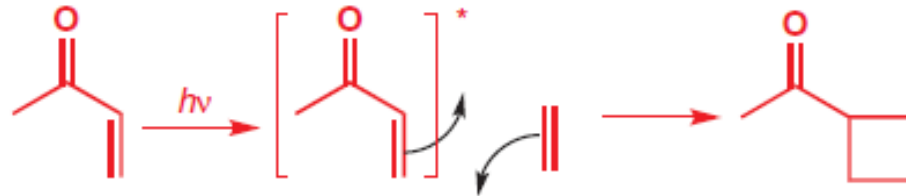
excited state of one alkene



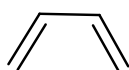
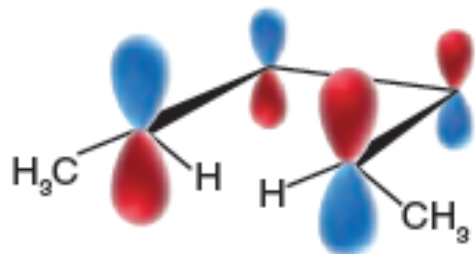
ground state of the other alkene



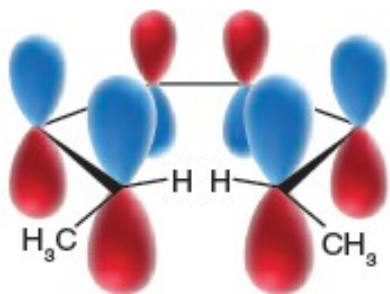
# Cykloadiční reakce



## Elektrocyclizační reakce



**HOMO**

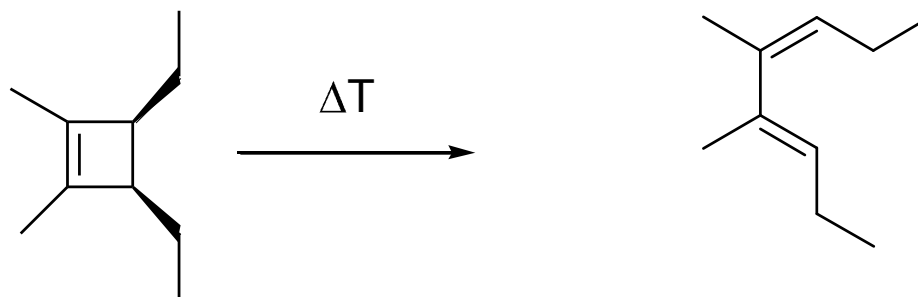
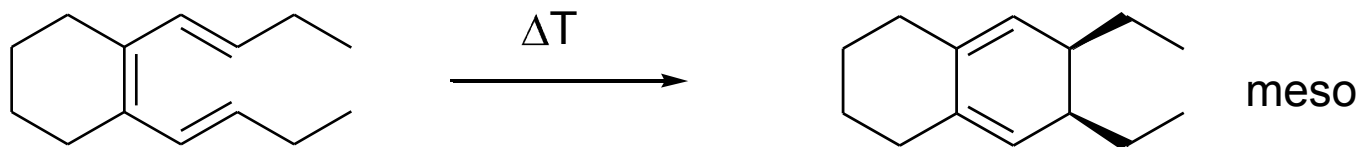


	$\Delta T$	$h\nu$
$4n$	konrotace antara	disrotace supra
$4n + 2$	disrotace supra	konrotace antara

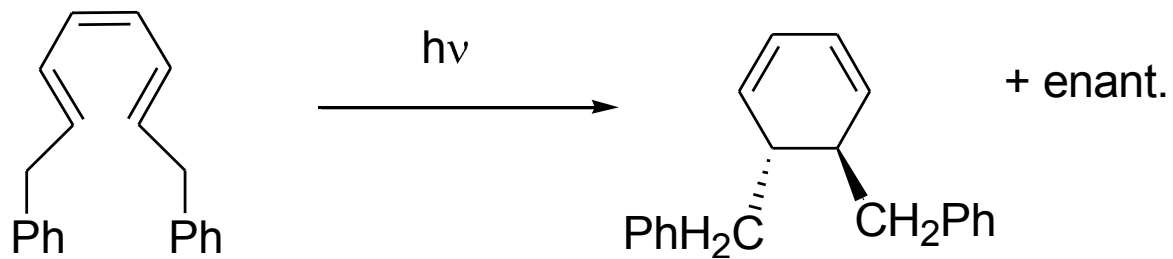
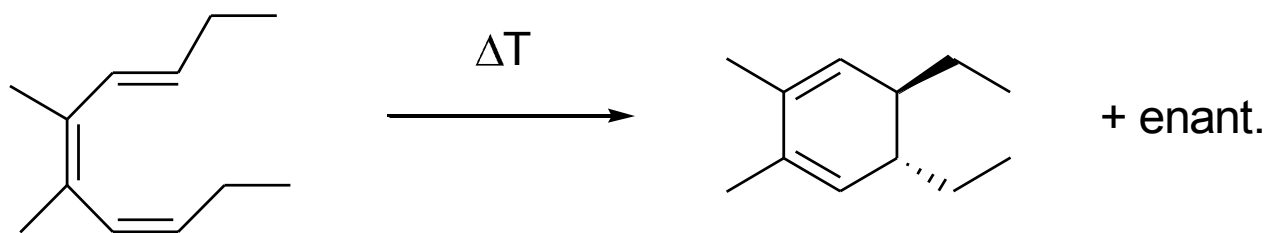




	$\Delta T$	$h\nu$
<b>4n</b>	<b>konrotace</b>	<b>disrotace</b>
<b>4n + 2</b>	<b>disrotace</b>	<b>konrotace</b>

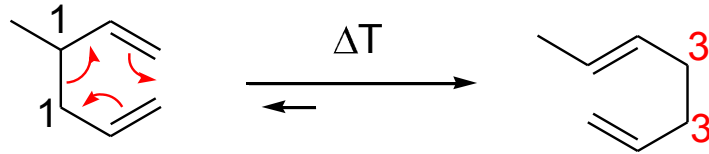


	$\Delta T$	$h\nu$
$4n$	konrotace	<b>disrotace</b>
$4n + 2$	<b>disrotace</b>	konrotace

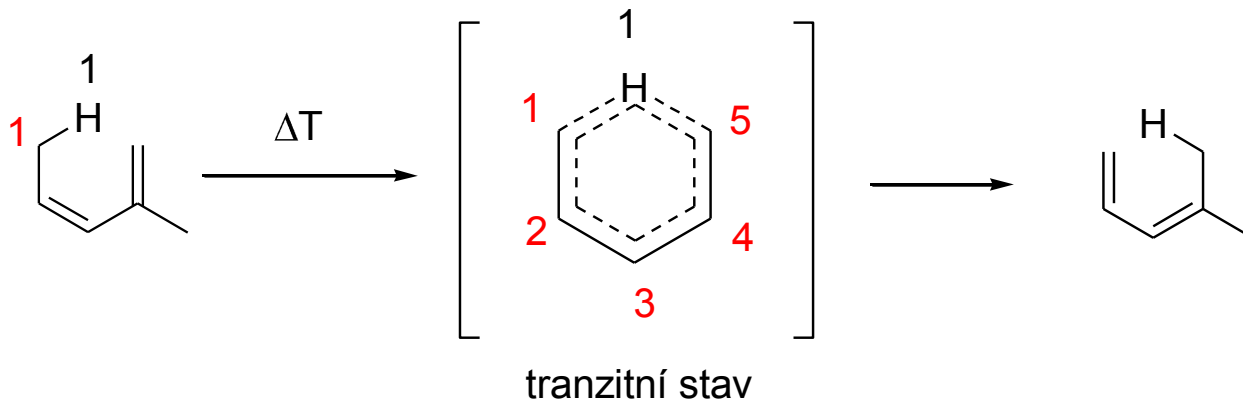
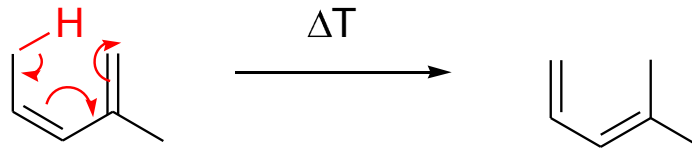


# Sigmatropní přesmyky

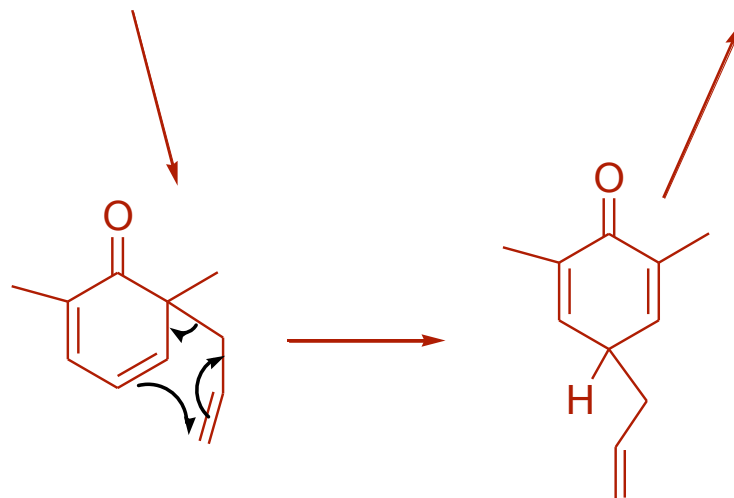
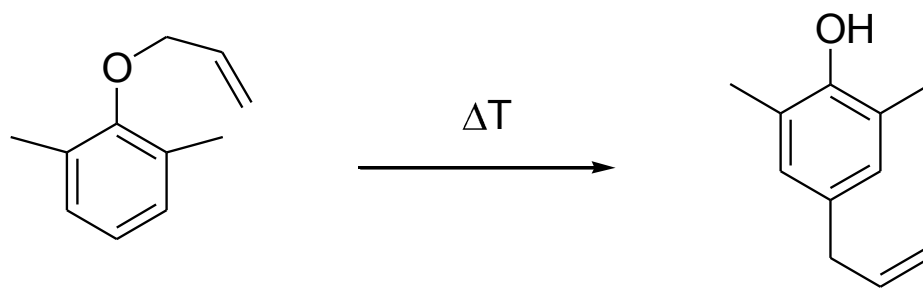
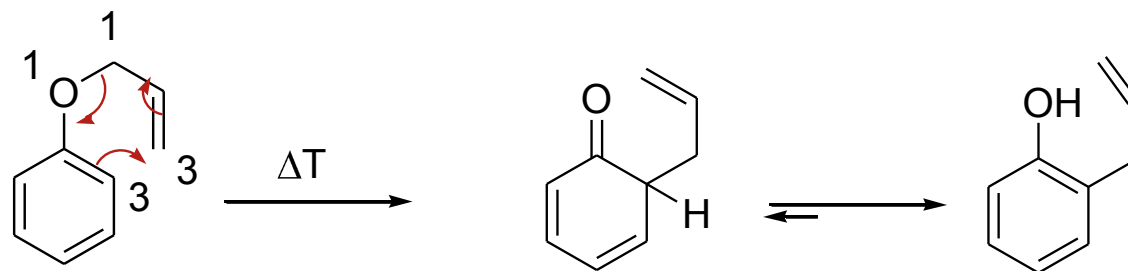
Copeho přesmyk

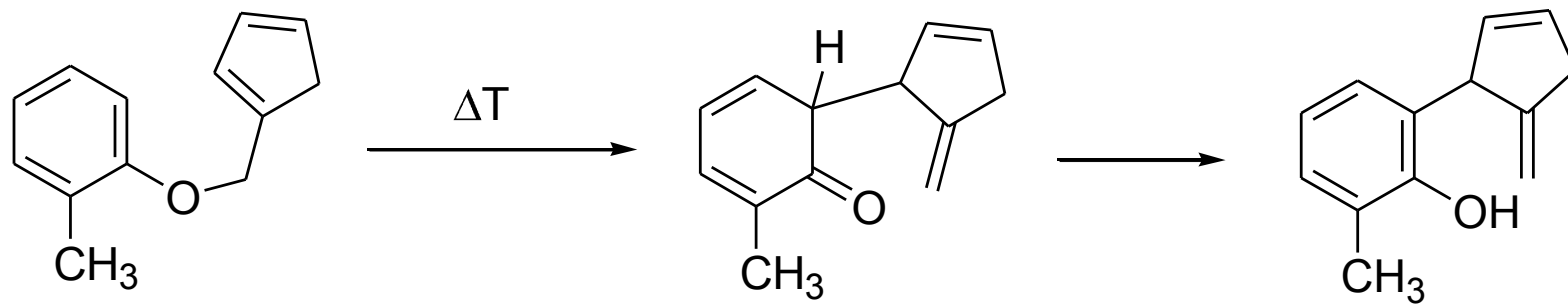
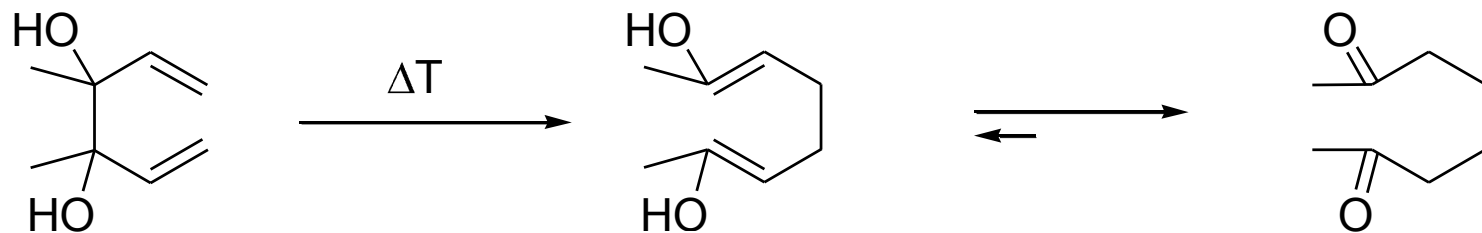


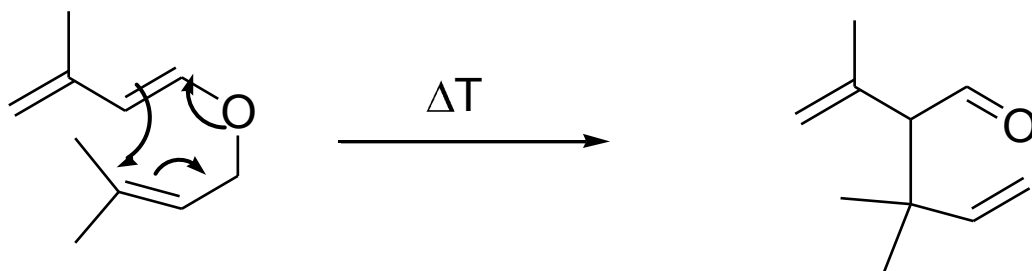
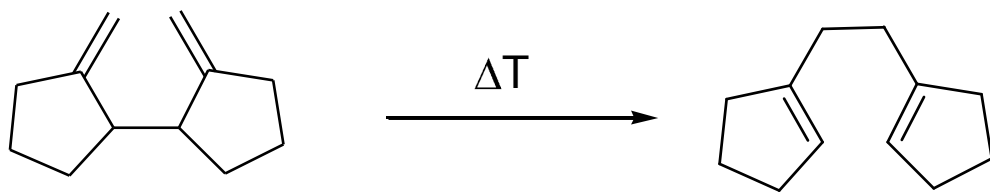
preferenze více substituovaného alkenu



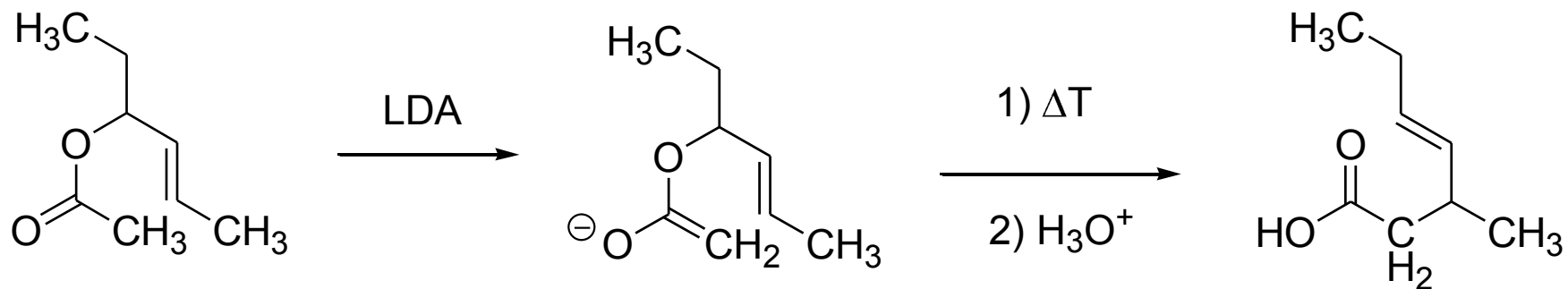
## Claisenův přesmyk







## Doplňte produkty reakcí



## Doplňte produkty a podmínky reakce

