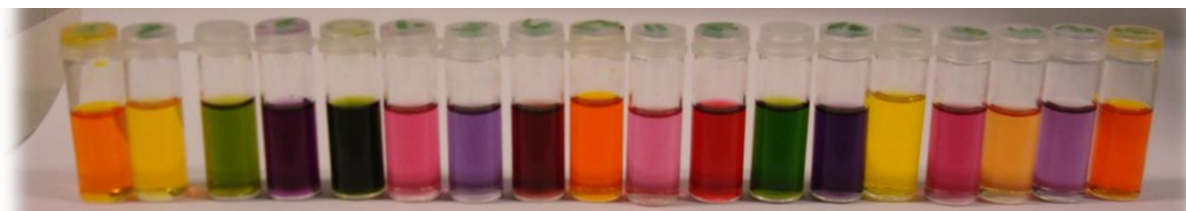
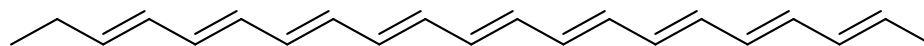
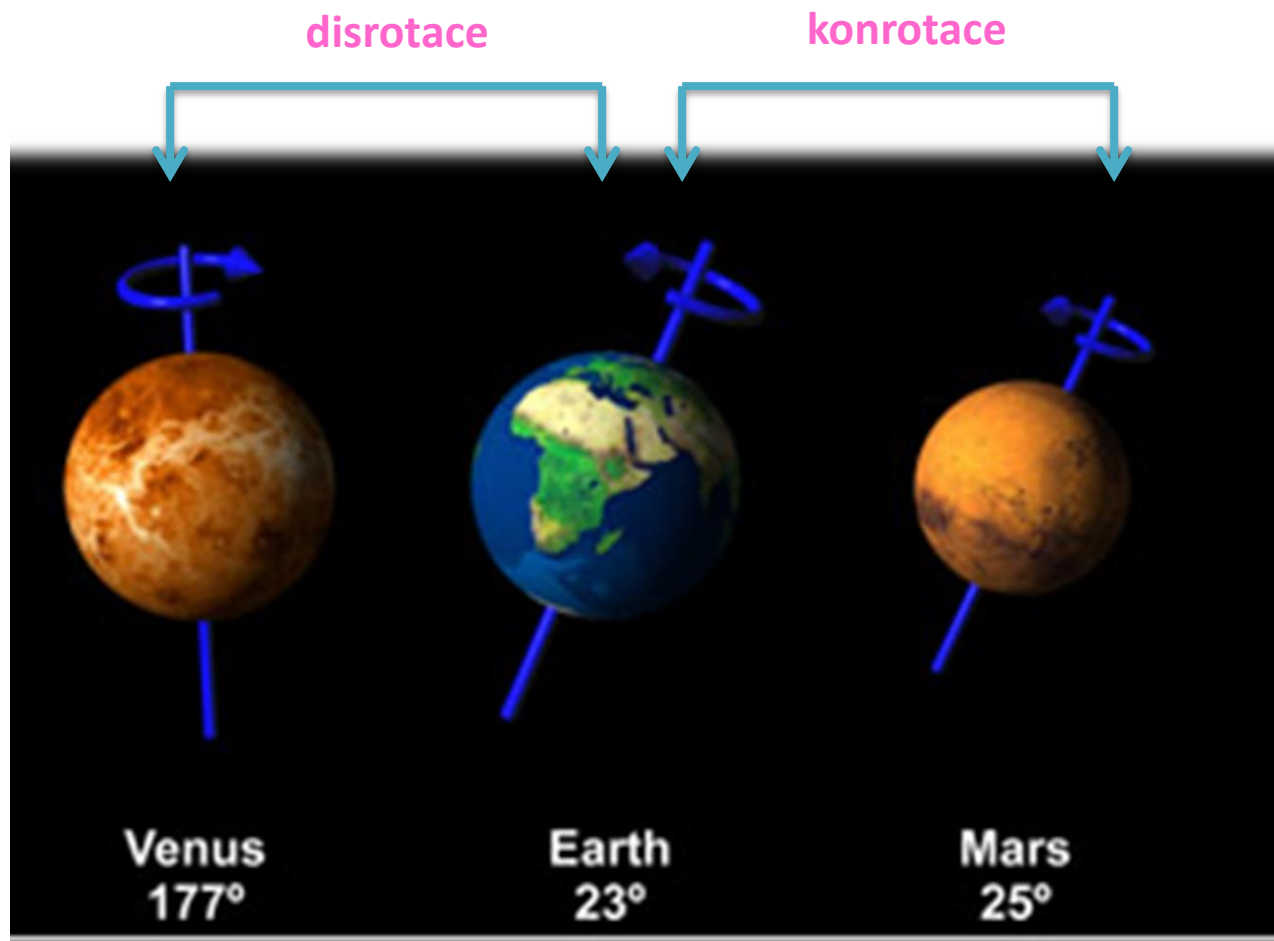
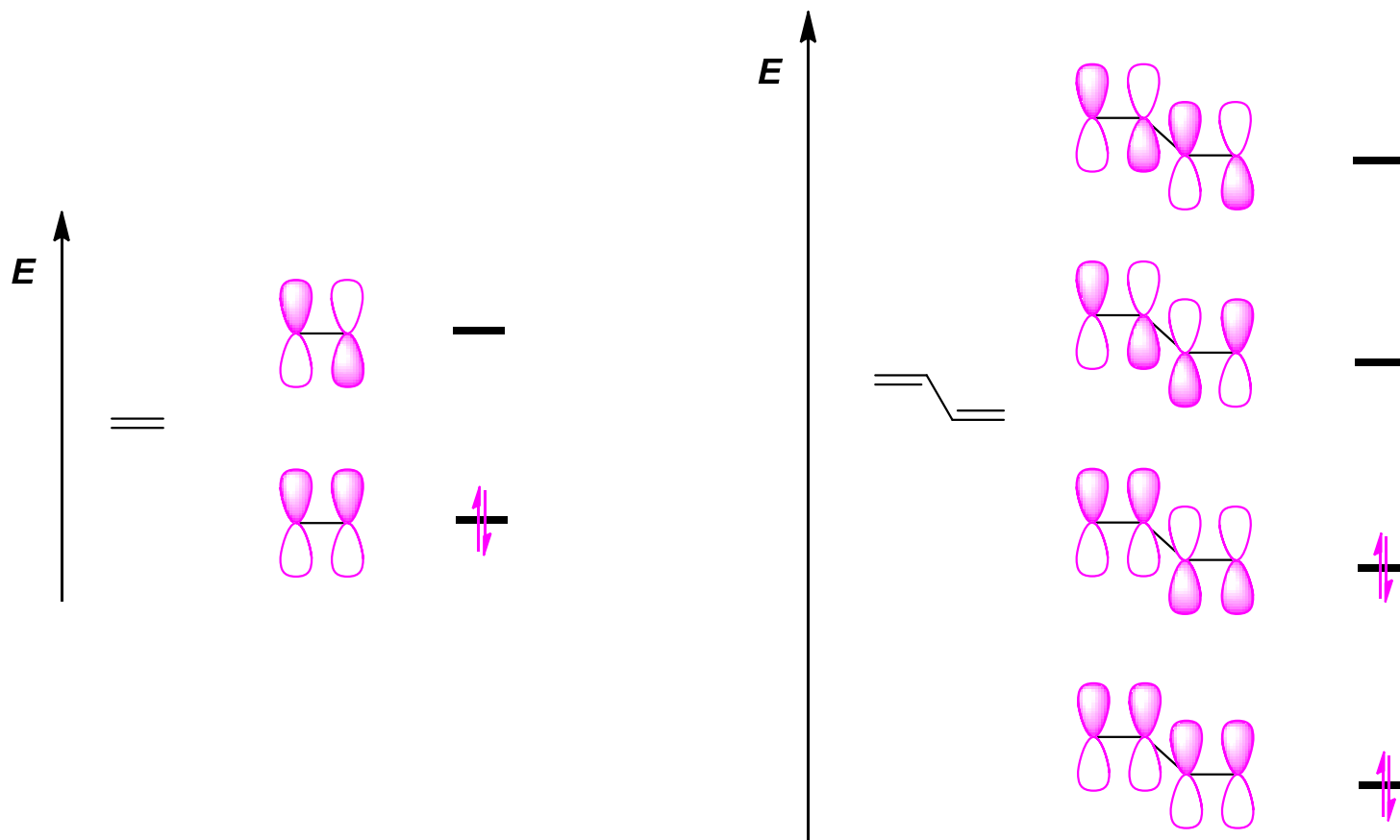




6. Dieny a polyeny





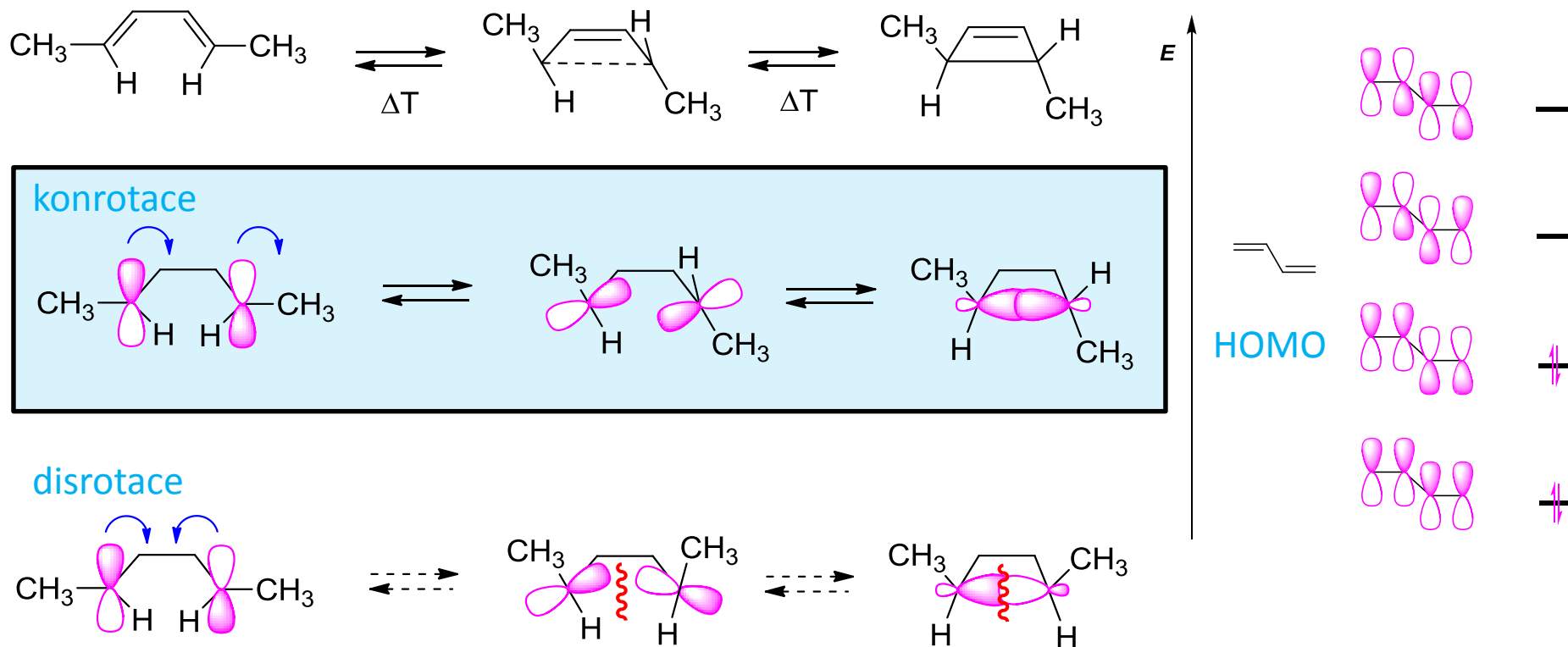


Se zvyšující se energií se mění symetrie molekulových orbitalů.

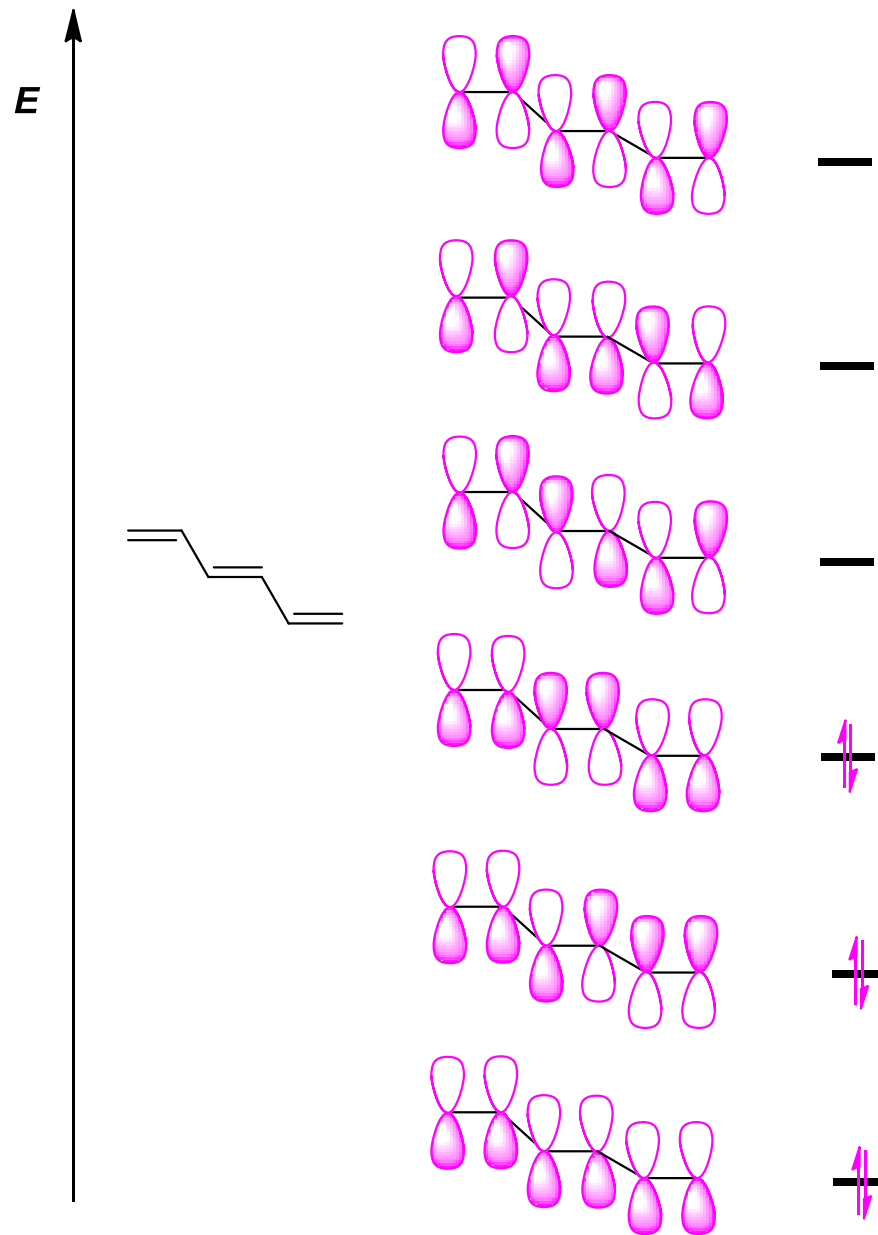
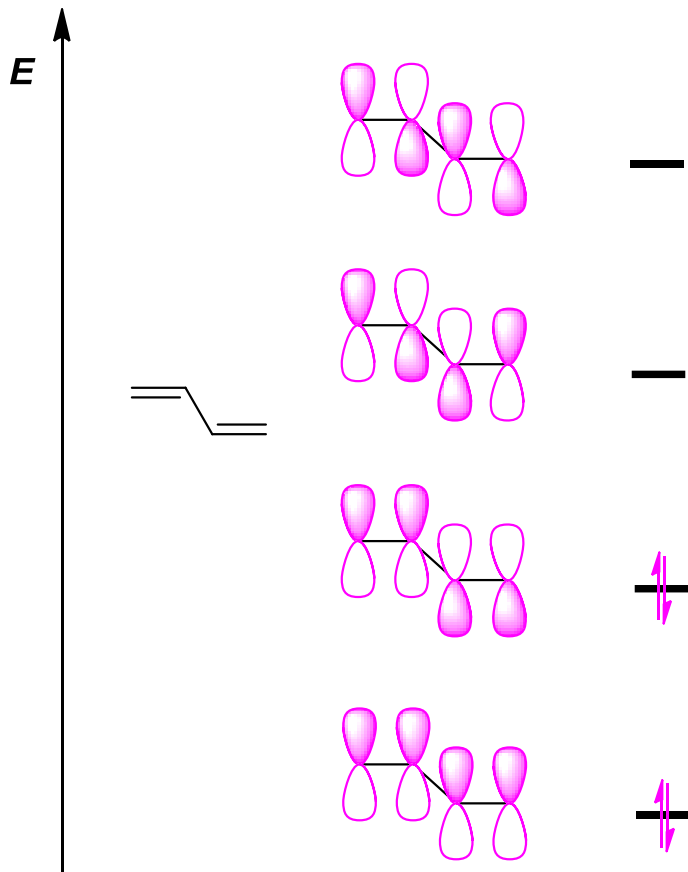
Při termických electrocylizačních reakcích zvažujeme symetrii HOMO.



▪ Analýza pomocí molekulových orbitalů

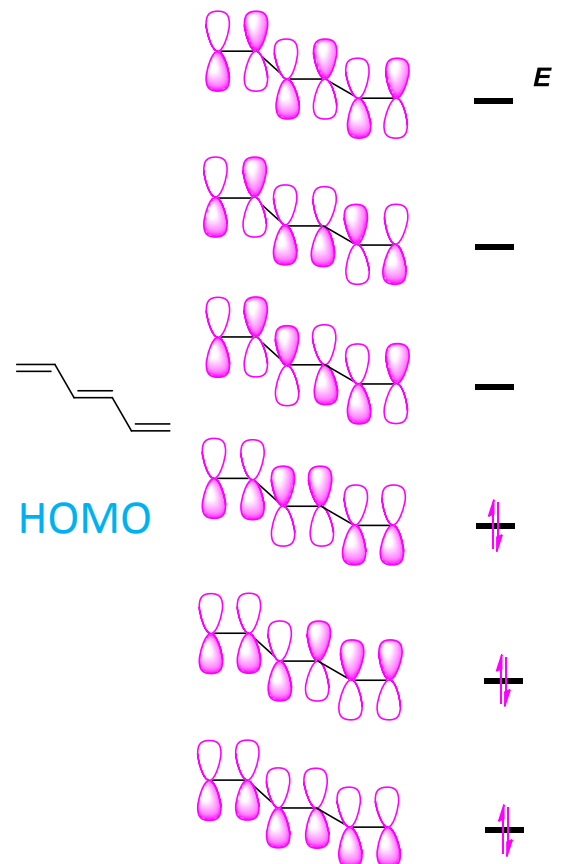
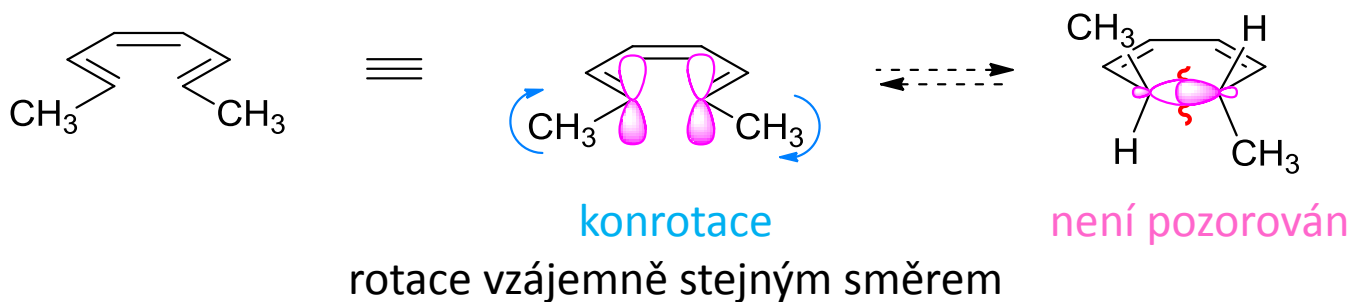
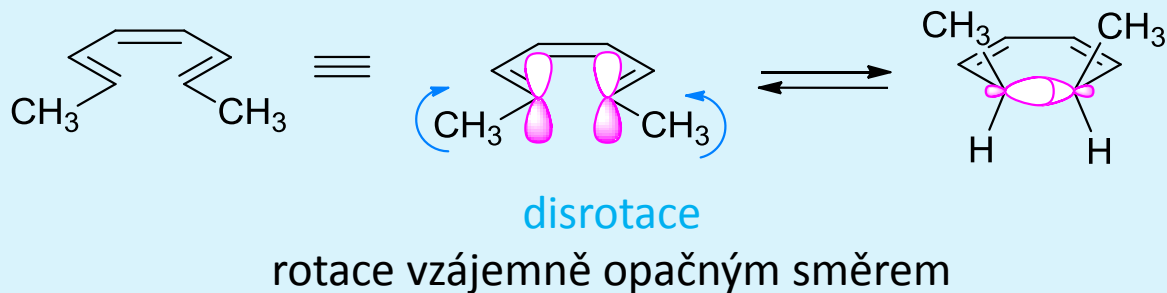


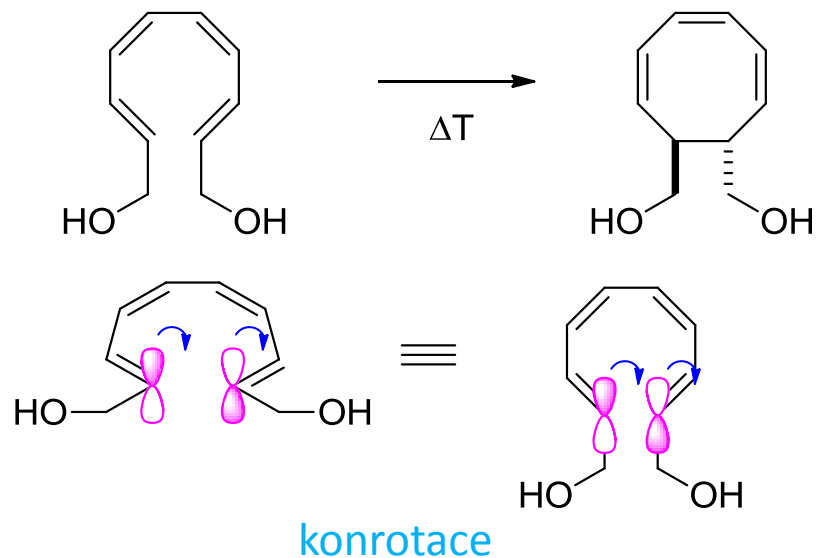
Elektrocyclizace je rovnovážná reakce a lze její mechanismus analyzovat v obou směrech (**princip mikroskopické reversibility**).



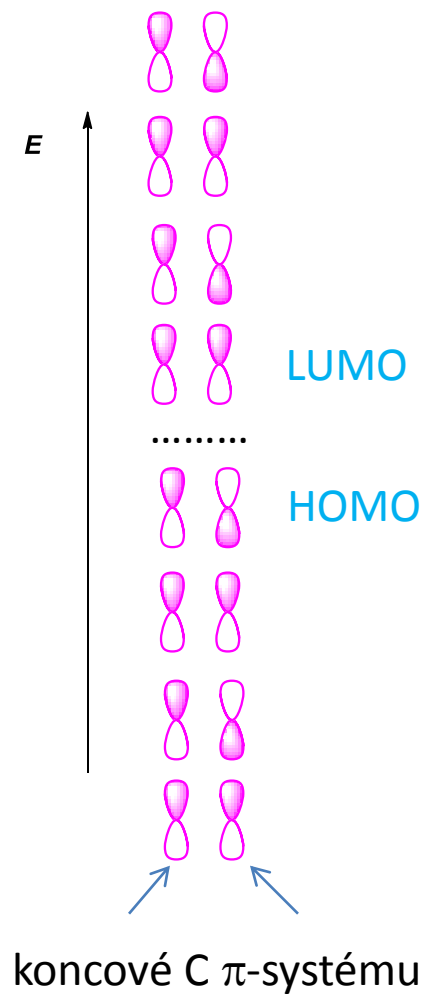


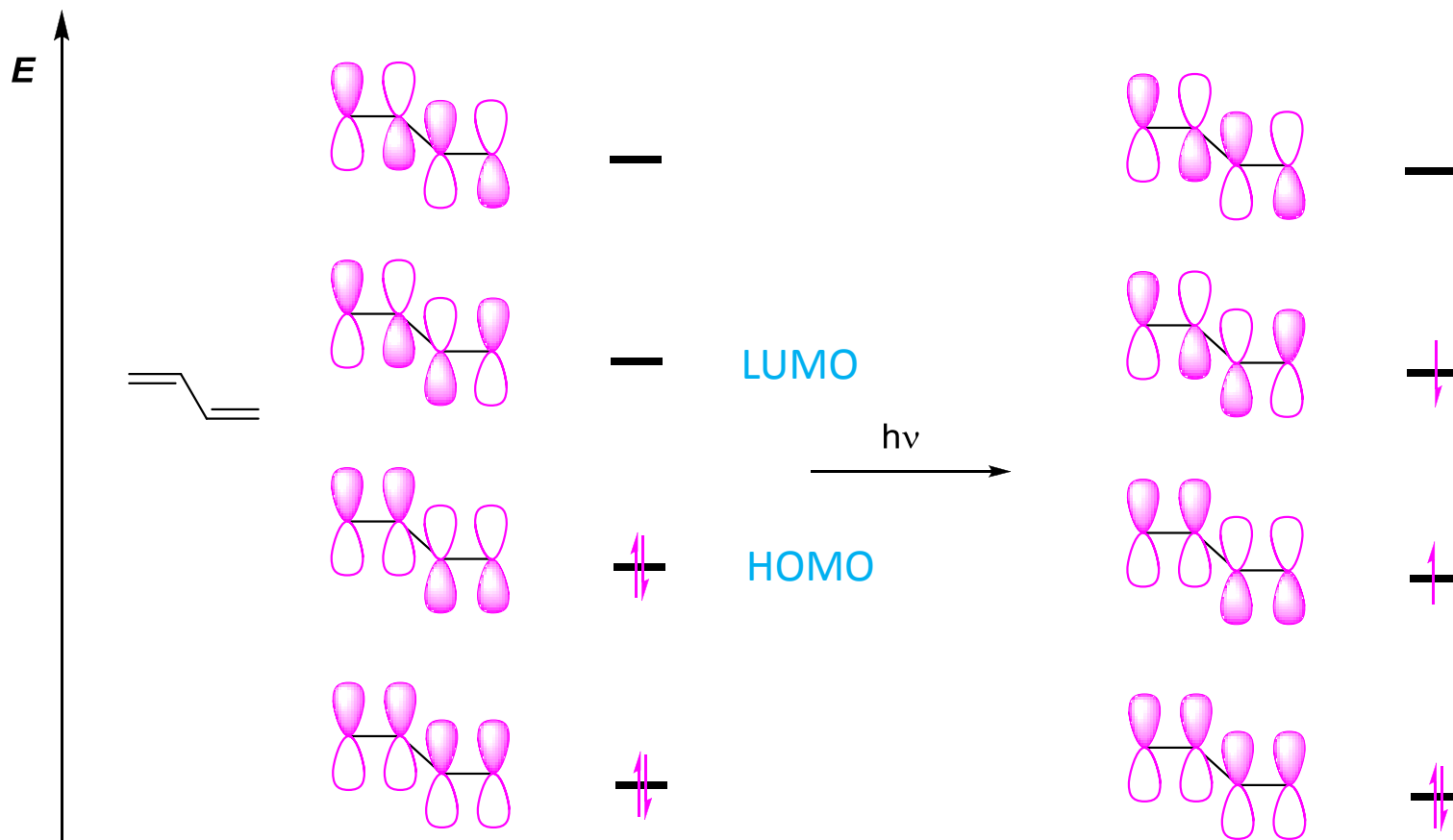
- Analýza pomocí molekulových orbitalů
- Experimentální pozorování ...





- termický proces
 - HOMO
 - symetrie orbitalů na koncových atomech
- 8π elektronů
 - 4 vazebné + 4 antivazebné MO

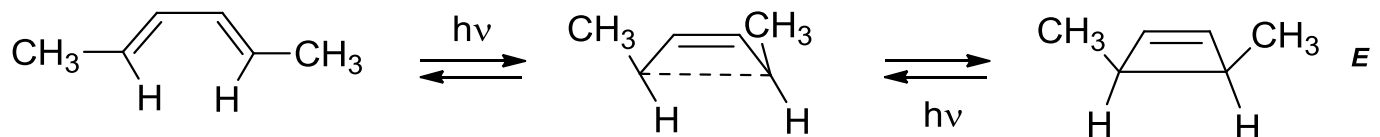




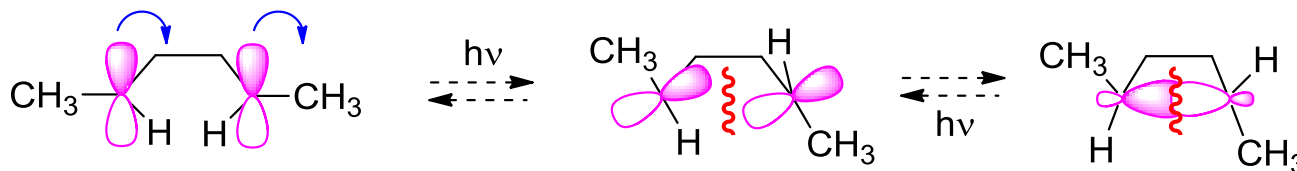
Při fotochemických electrocylizačních reakcích zvažujeme symetrii LUMO.



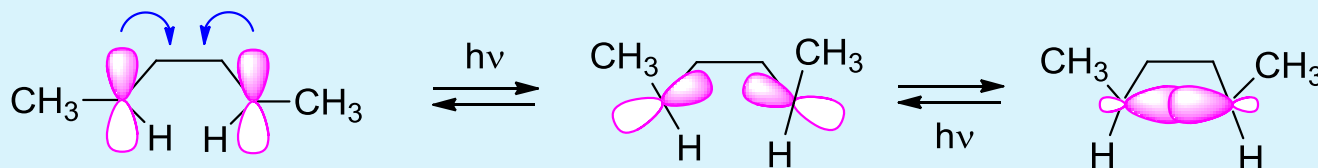
▪ Analýza pomocí molekulových orbitalů



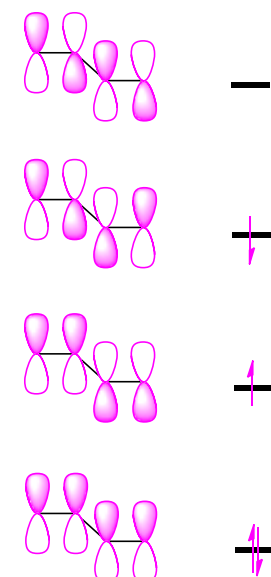
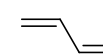
konrotace



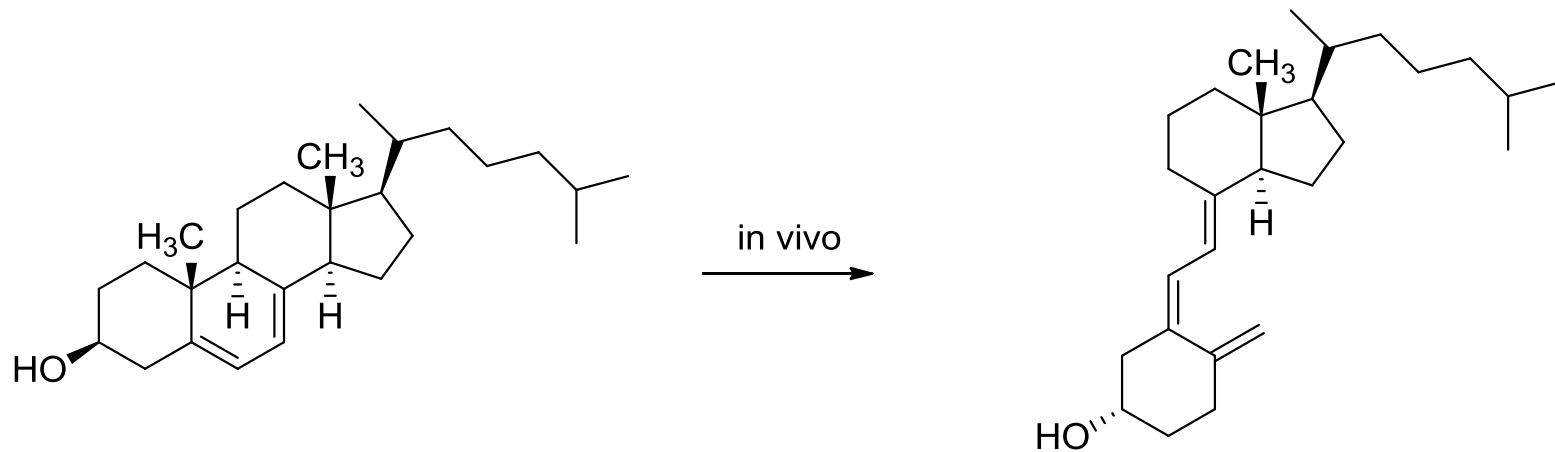
disrotace



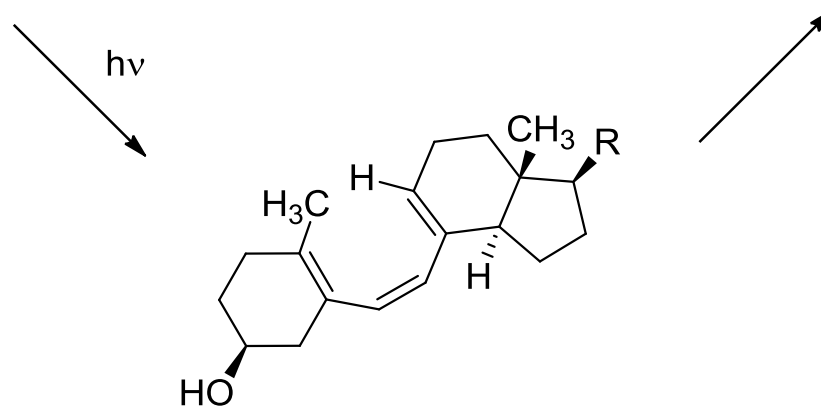
LUMO

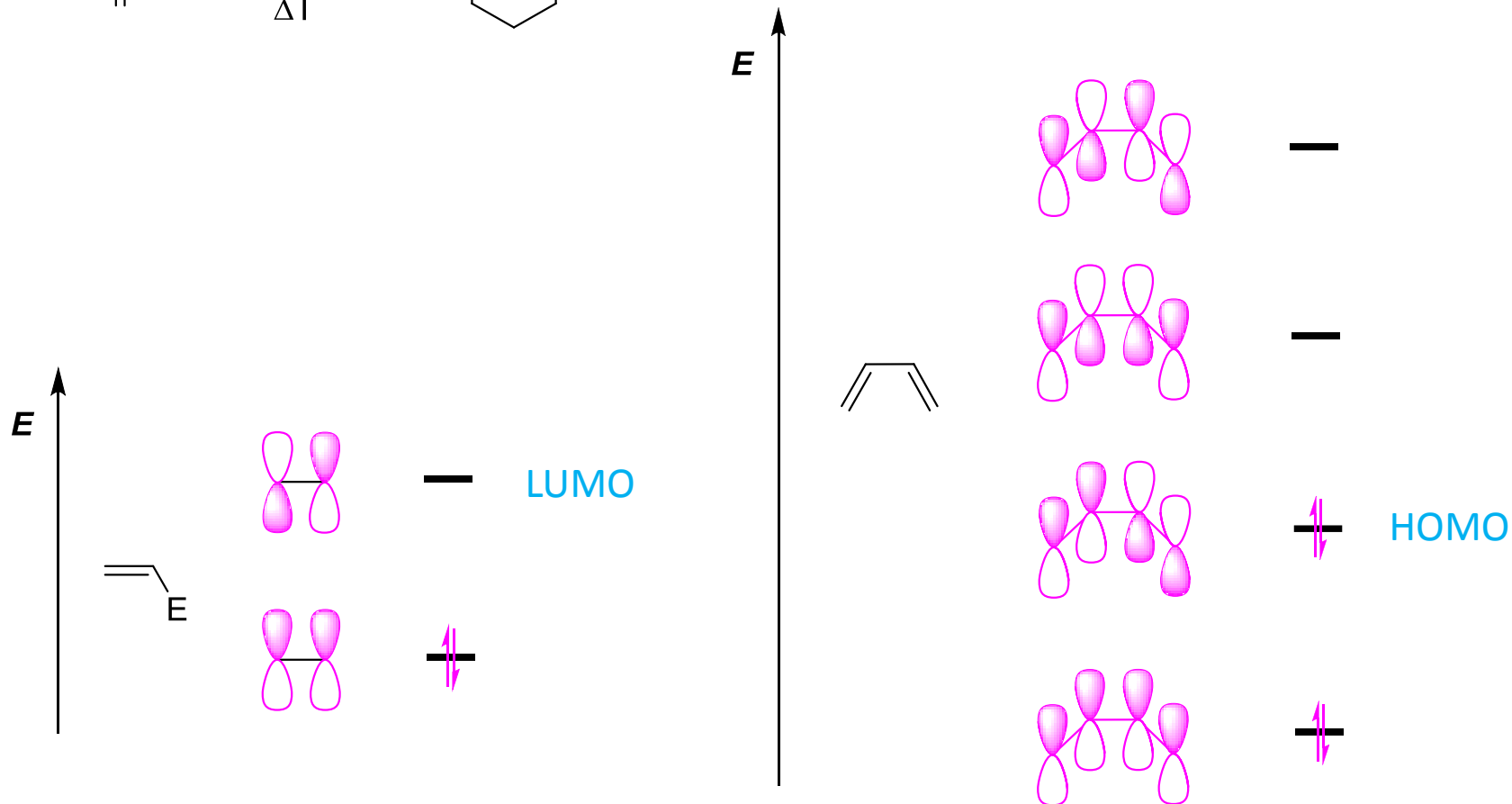


Elektrocyclizace je rovnovážná reakce a lze její mechanismus analyzovat v obou směrech (princip mikroskopické reversibility).

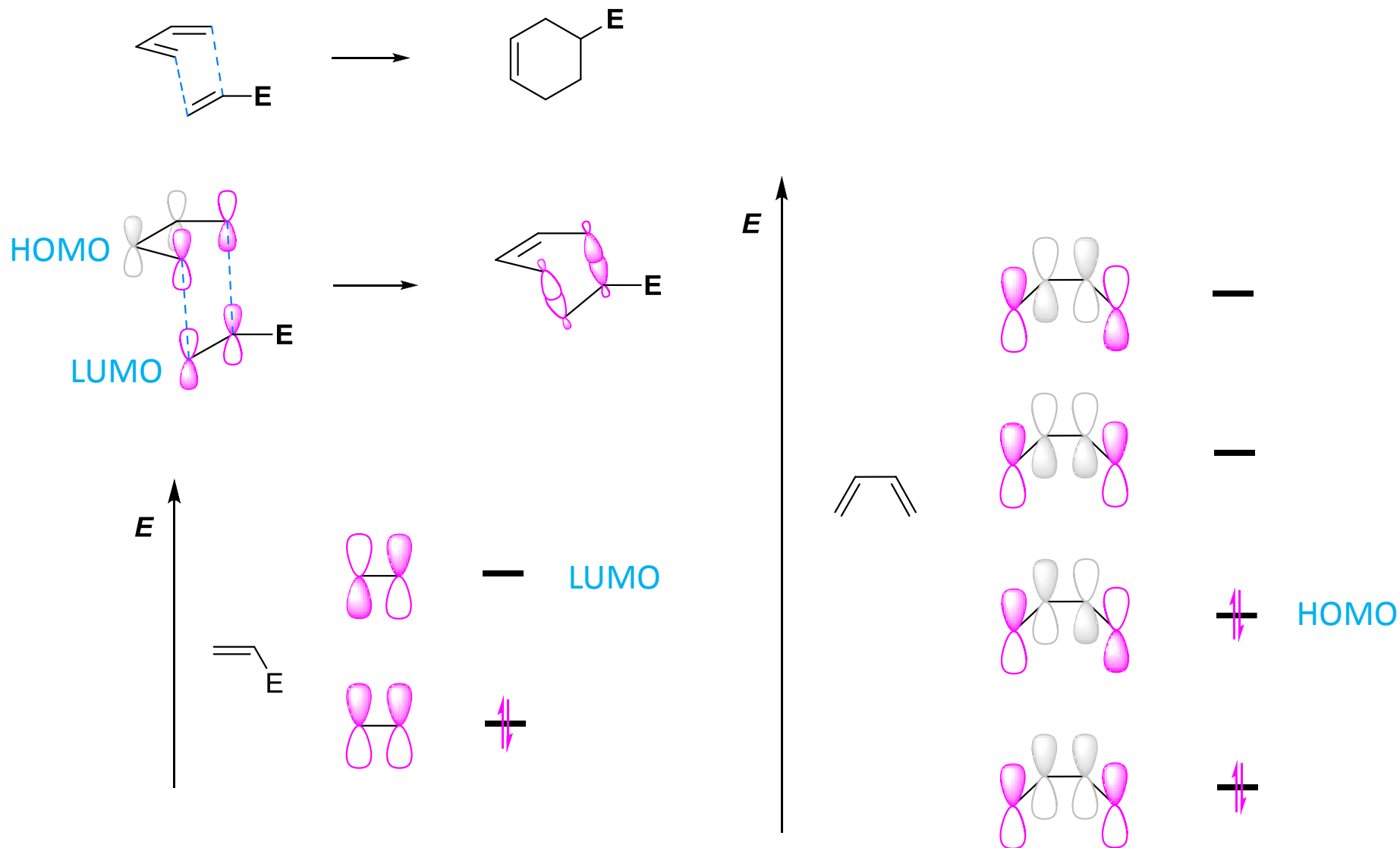


7-dehydrocholesterol

vitamin D₃provitamin D₃



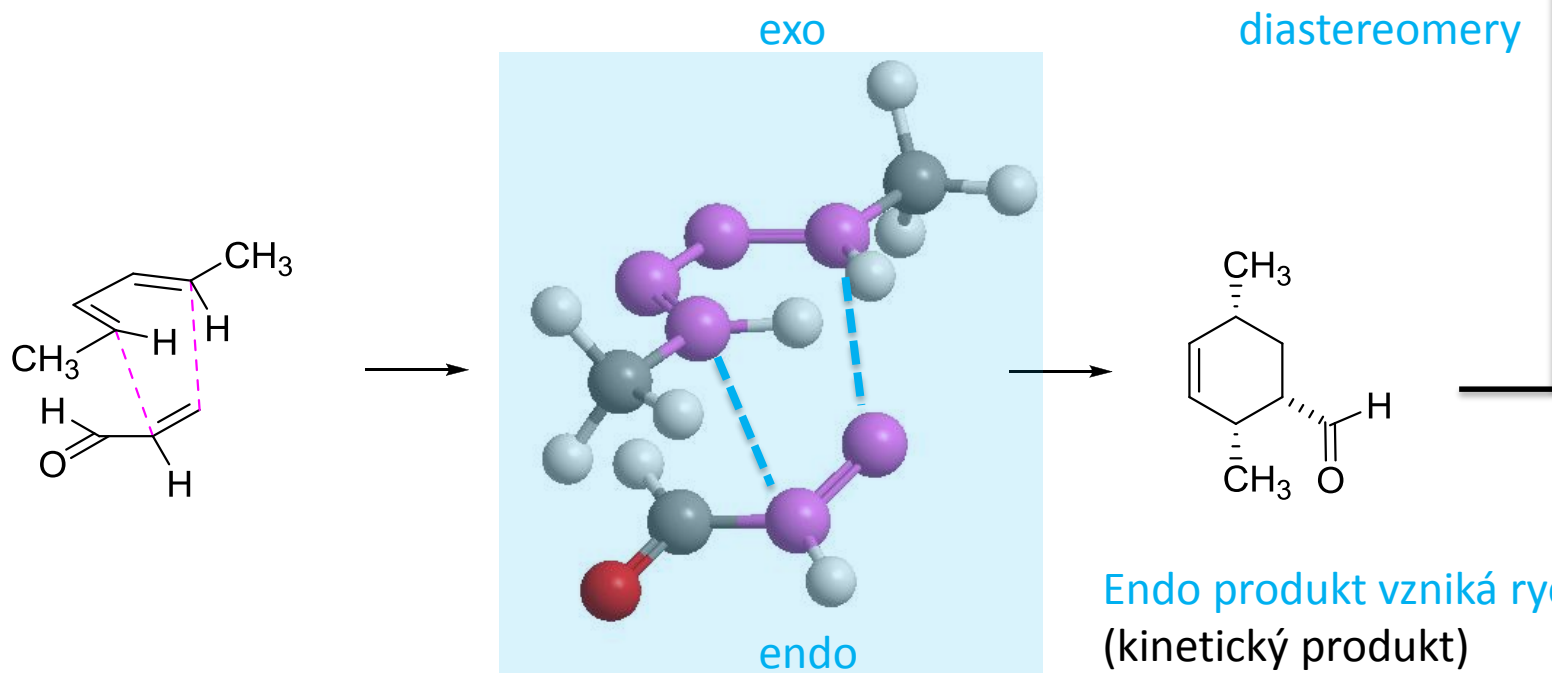
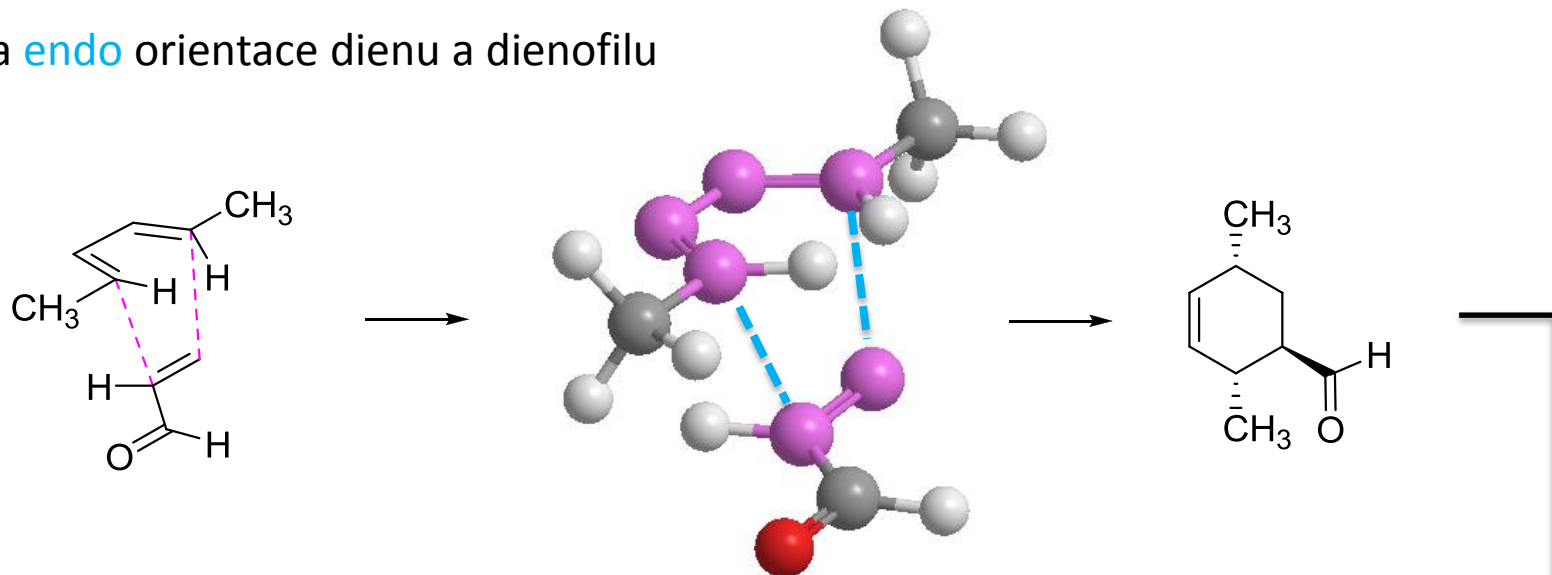
reakce probíhá na terminálních atomech alkenu a dienu

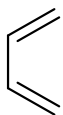
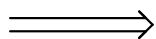
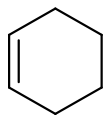


reakce probíhá na terminálních atomech alkenu a dienu



Exo a endo orientace dienu a dienofilu

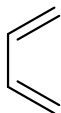
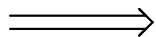
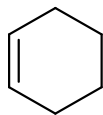




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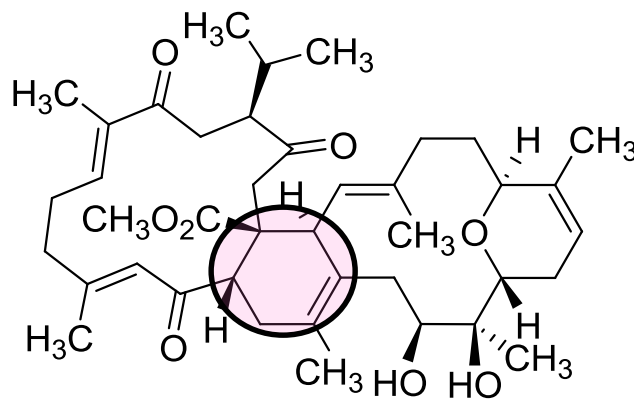
“retrosyntetické oko”



+



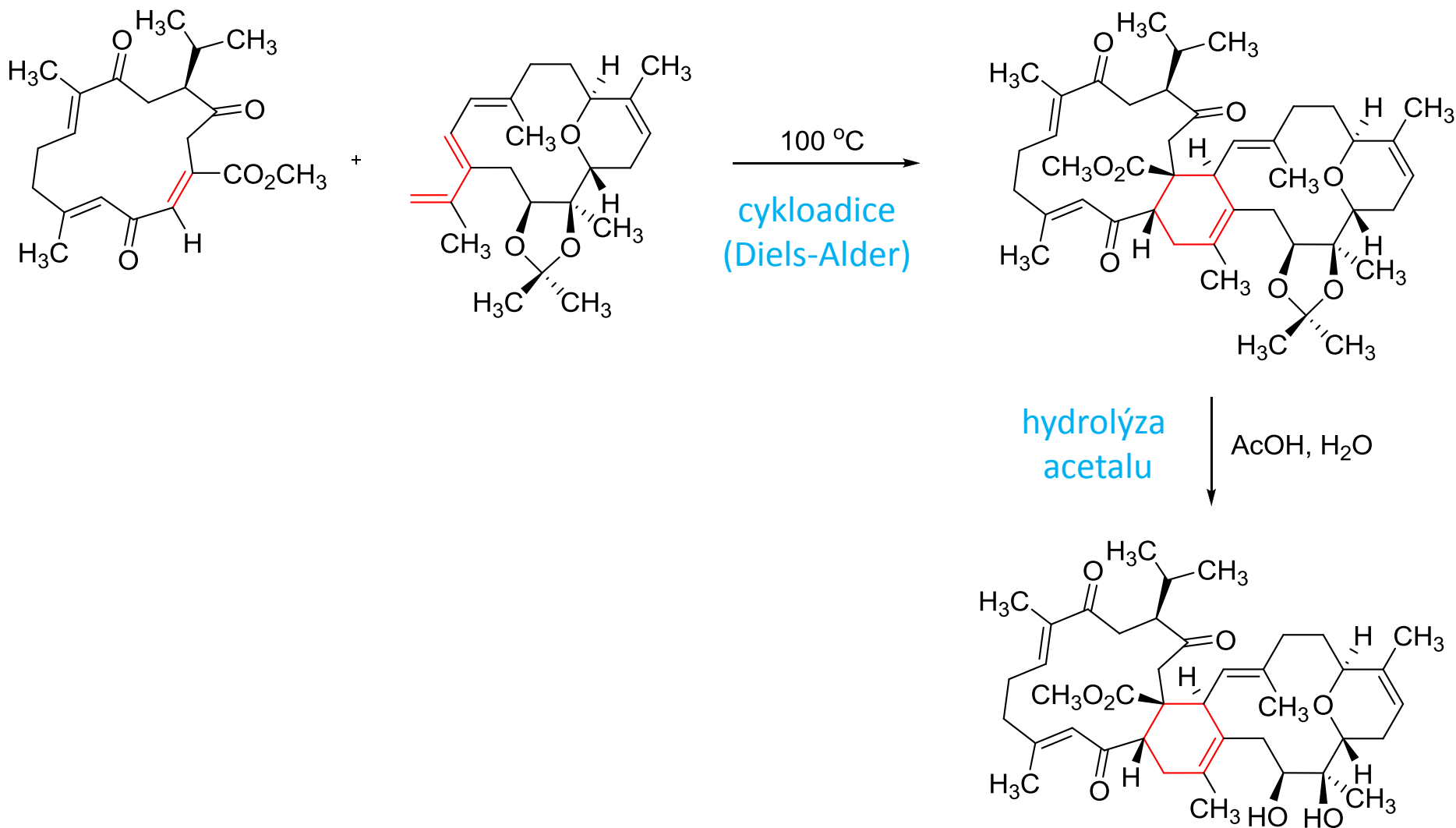
“retrosyntetické oko”

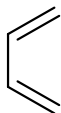
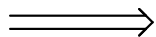
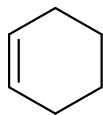


Methyl sarcophytoate



Syntéza

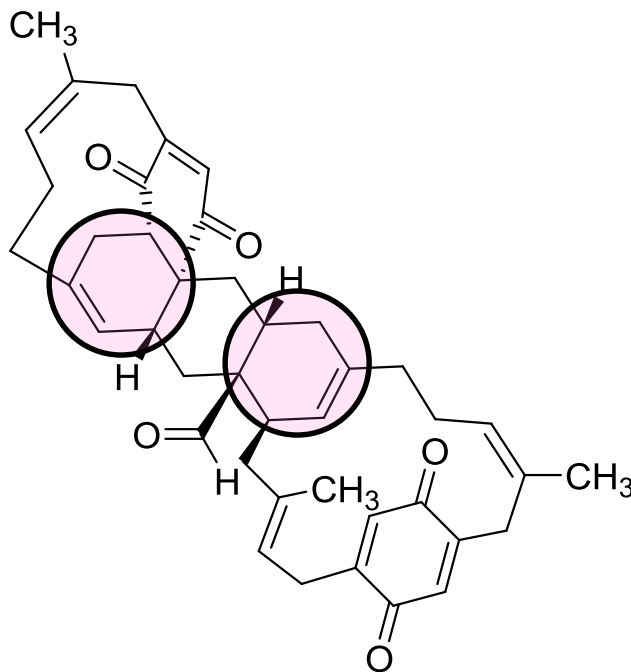




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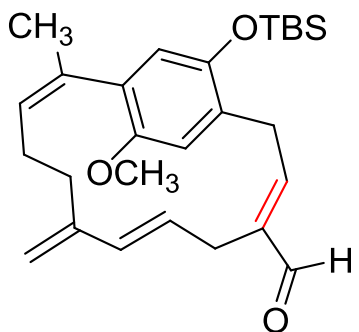
“retrosyntetické oko”



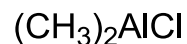
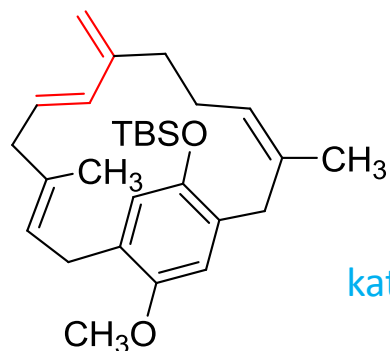
Longithorone A



Syntéza

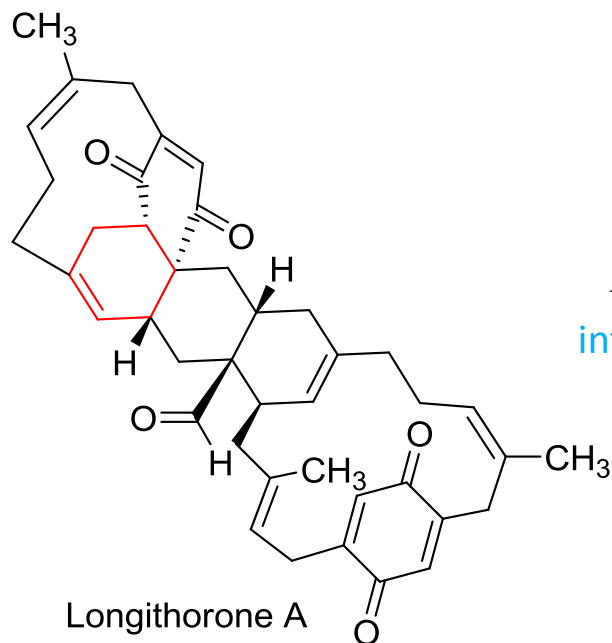
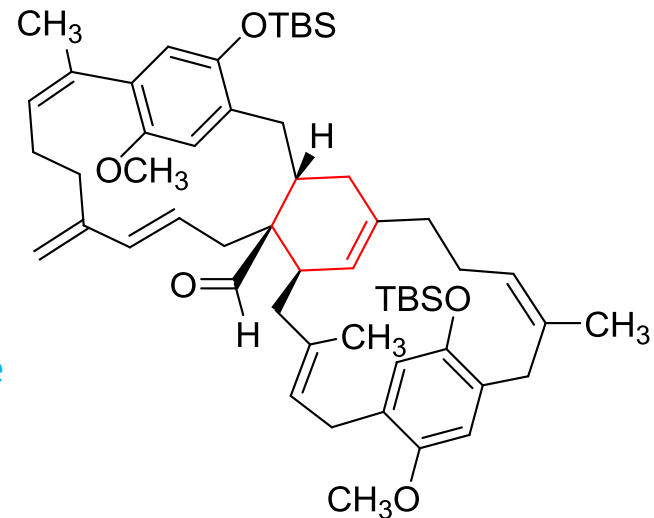


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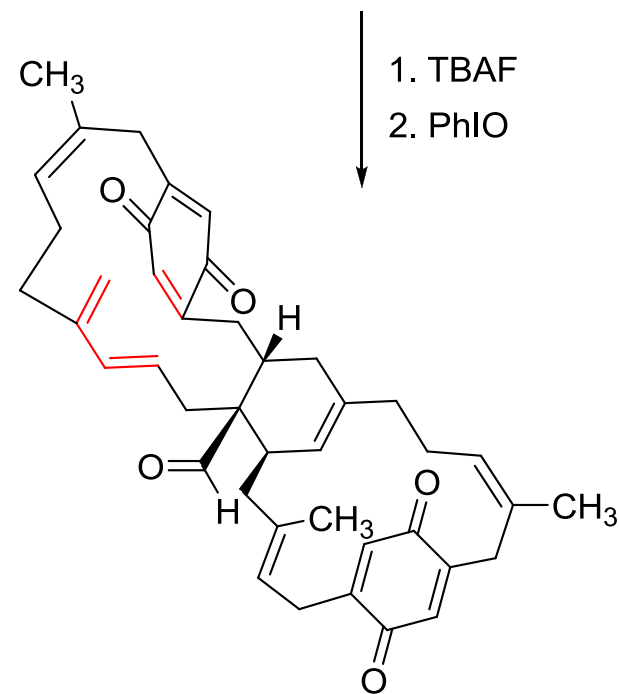
-20 °C

katalyzovaná cykloadice
(nižší teplota)



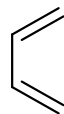
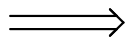
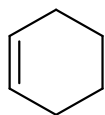
25 °C

intramolekulární
cykloadice





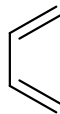
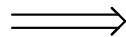
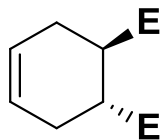
Retrosyntéza



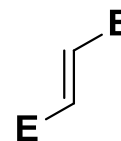
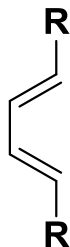
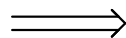
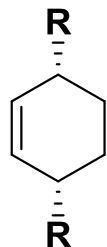
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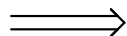
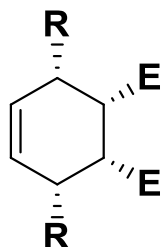
dien ... el. bohatý
dienofil ... el. deficitní

Stereochemie
dienofilu

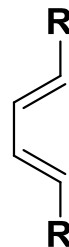
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Stereochemie
dienu

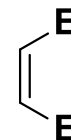
+

Stereochemie
dienofilu & dienu

endo



+



Endo preference

