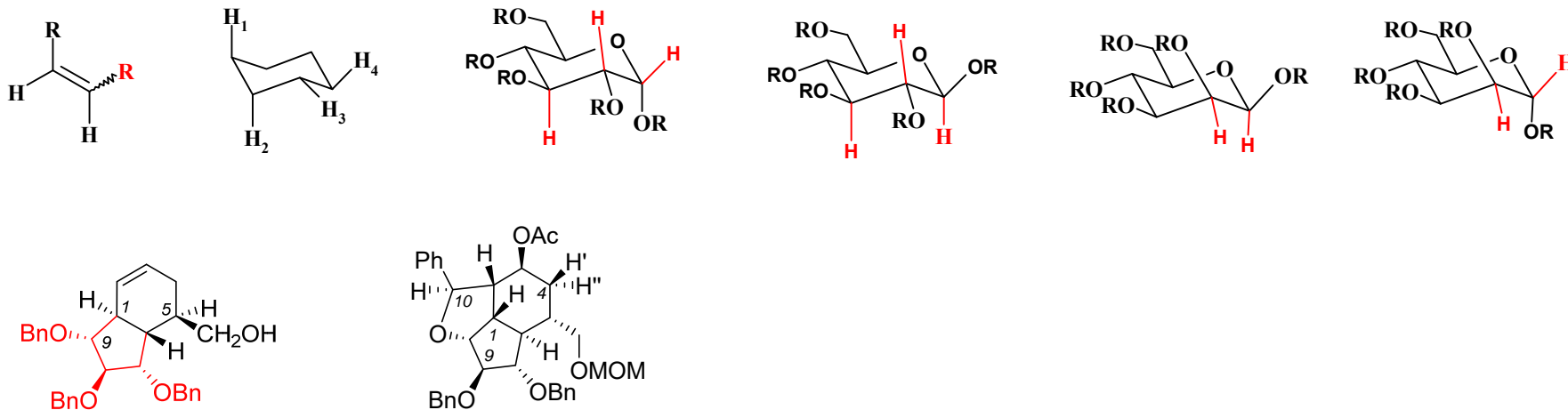
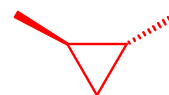


Wyznaczanie konfiguracji względnej poprzez analizę spektralną: STAŁE SPRZĘŻENIA  $^1\text{H}$  NMR

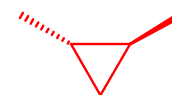


Metody chemiczne

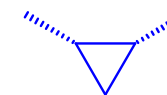
Jak łatwo rozróżnić te związki ???



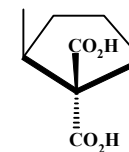
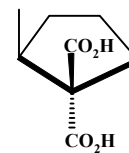
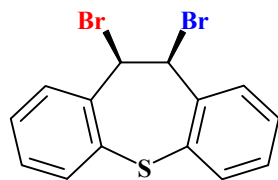
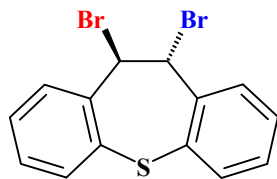
*trans*



*trans*



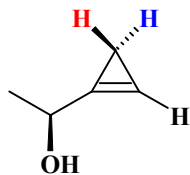
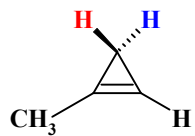
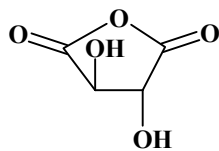
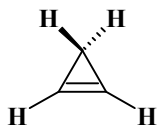
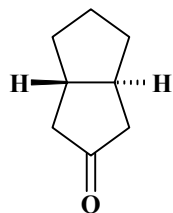
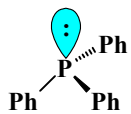
*cis*



### Podział grup wg topowości

1. Homotopowe
2. Enancjotopowe
3. Diastereotopowe

## przykłady



Czy związek achiralny może mieć grupy diastereotopowe??

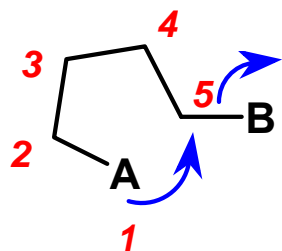
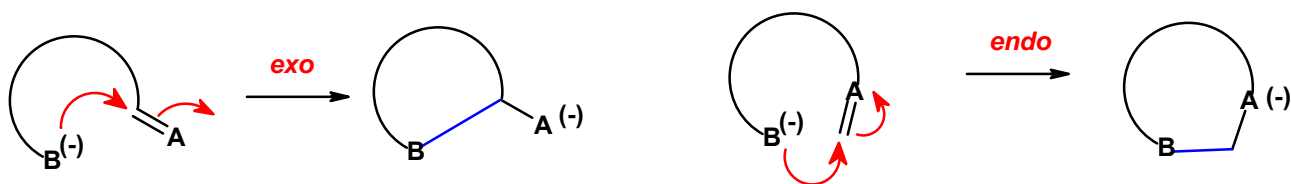
## test zastępowania

---

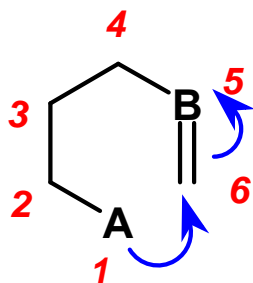
Przykład cukrowy

## **Topowość grup – symetria (podsumowanie)**

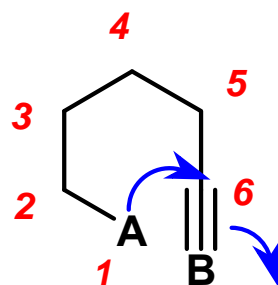
## Reguły Baldwina



5-exo-tet



6-endo-trig



6-exo-dig

Procesy: 3-7-exo-Tet są uprzywilejowane. 5-6-Endo-Tet nie

3-7-exo-Trig oraz 6-7-Endo-Trig są uprzywilejowane. 3-5-Endo-Trig nie

5-7-exo-Dig oraz 3-7-Endo-Dig są uprzywilejowane. 3-4-Exo-Dig nie

J. E. Baldwin, *J. Chem. Soc., Chem. Commun.* **1976**, 734; J. E. Baldwin, J. Cutting, W. Dupont, L. Kruse, L. Silberman, R. C. Thomas, *J. Chem. Soc., Chem. Commun.* **1976**, 736; J. E. Baldwin, R. C. Thomas, L. Kruse, L. Silberman, *J. Org. Chem.*, **1977**, 42, 3846; K. Gilmore, R.K. Mohamed, I.V. Alabugin, *WIREs Comput Mol Sci* **2016**, 6:487 (doi: 10.1002/wcms.1261)

# Reakcje pericykliczne

## 1. cykloaddycja

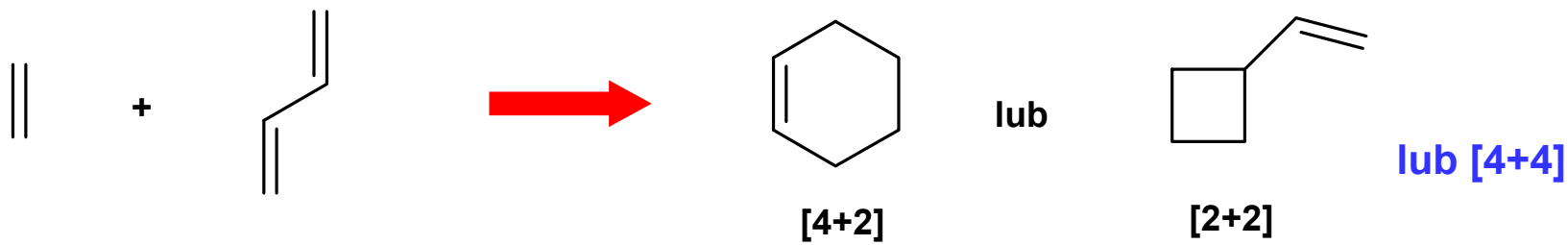
[2+2], [4+2], [4+4], [8+2] [6+4] itd

dipolarna [1,3]

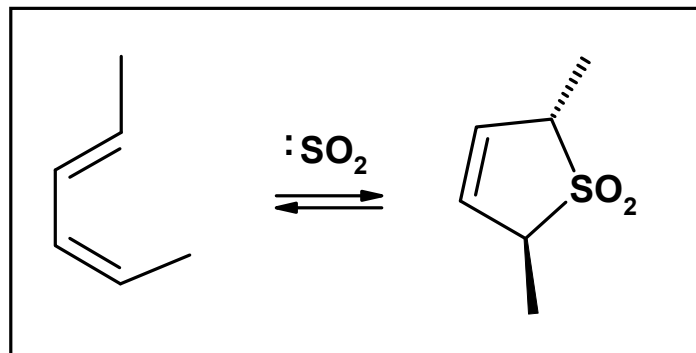
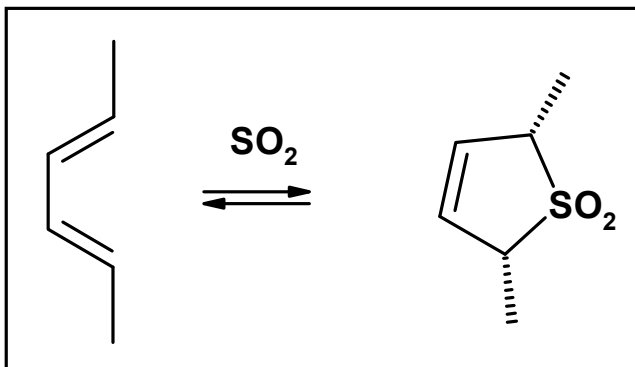
## 2. reakcje cheletropowe

## 3. reakcje elektrocykliczne

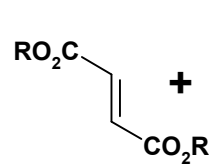
## 4. przegrupowanie sigmatropowe



### Reakcje cheletropowe



## Reakcja Dielsa-Aldera



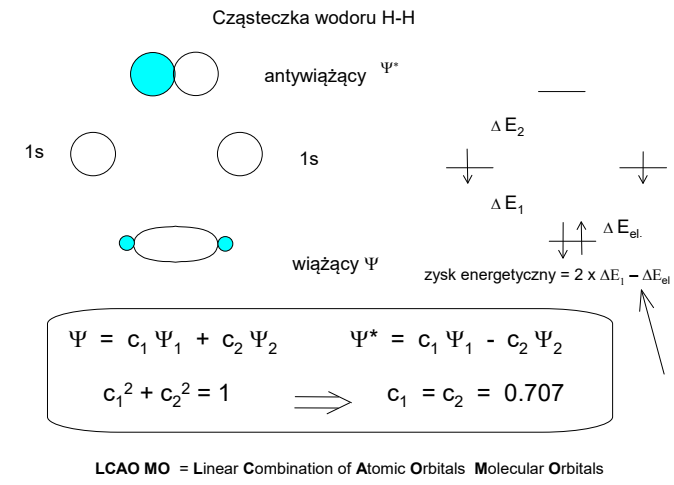
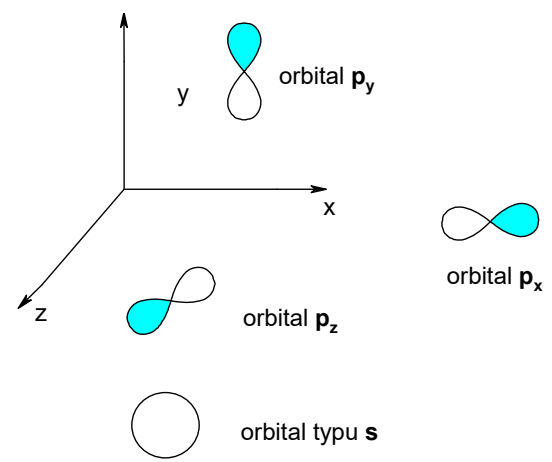
## Stereospecyficznosc, Stereoselektywnosc



selektywnosc wielu reakcji mozna przewidziec za pomoca **TEORII ORBITALI  
FRONTALNYCH**

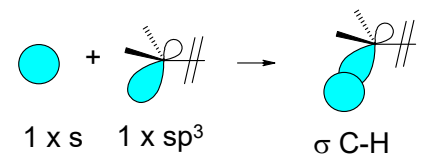
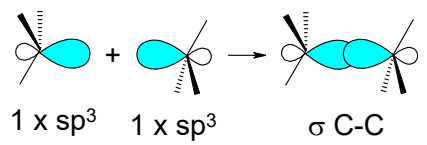


# Typy orbitali

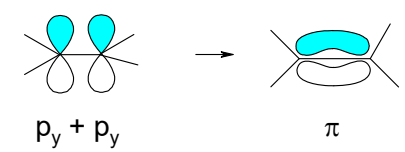
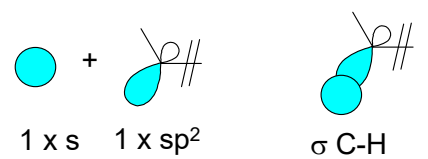
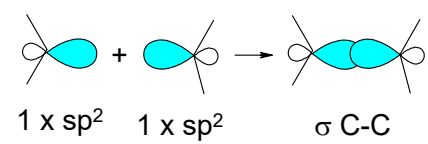


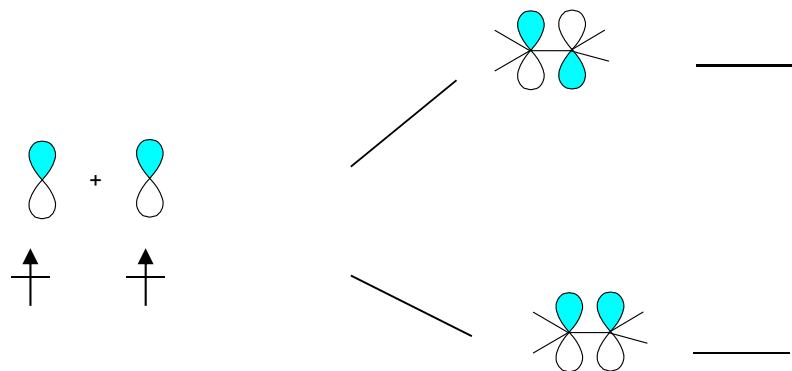
## Hybrydyzacja

### etan

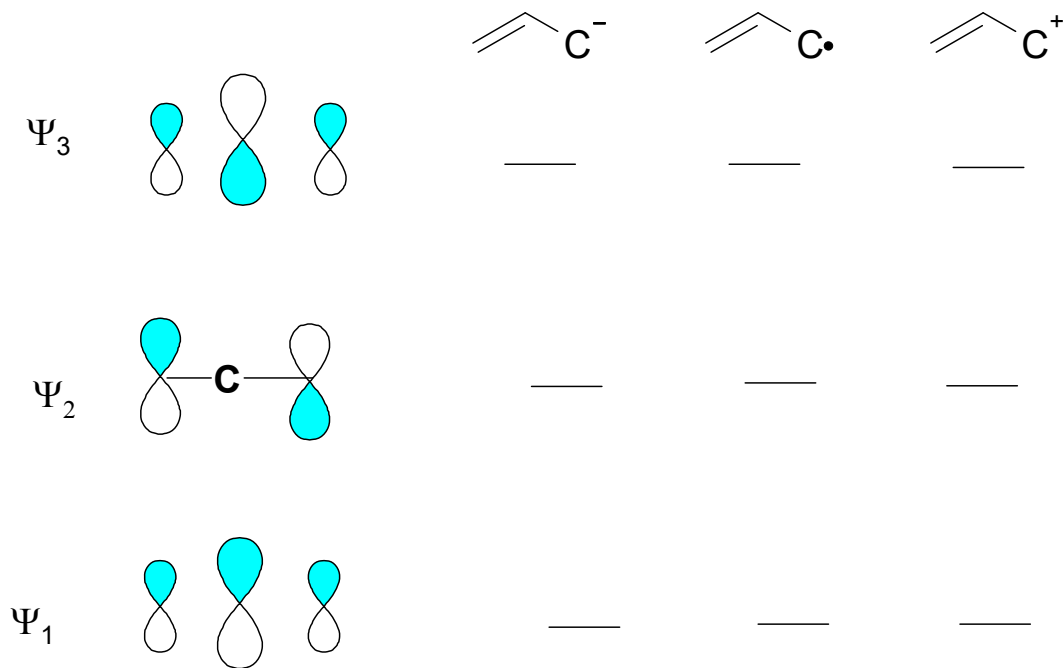
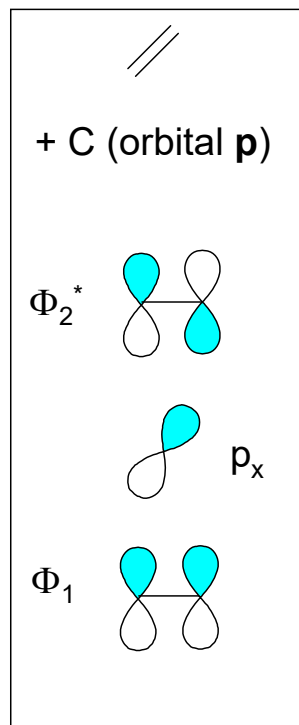


### etylen

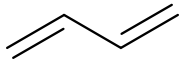




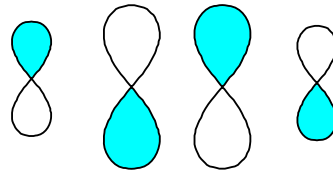
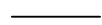
**Allil**



butadien



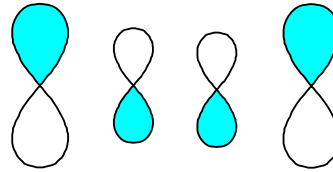
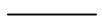
$\Psi_4$



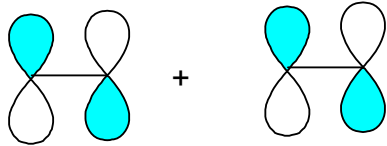
$$c_1\Phi_1 - c_2\Phi_2 + c_3\Phi_3 - c_4\Phi_4$$

$\Phi_3$  i  $\Phi_4$

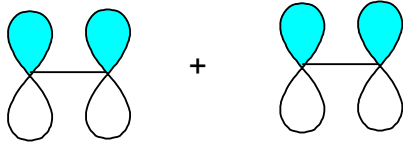
$\Psi_3$



$$c_1\Phi_1 - c_2\Phi_2 - c_3\Phi_3 + c_4\Phi_4$$



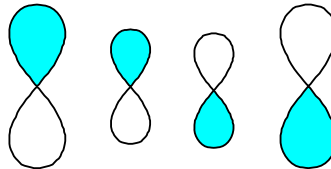
LUMO



HOMO

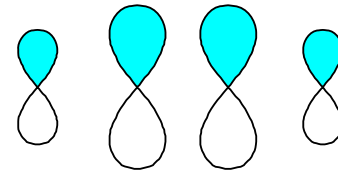
$\Phi_1$  i  $\Phi_2$

$\Psi_2$



$$c_1\Phi_1 + c_2\Phi_2 - c_3\Phi_3 - c_4\Phi_4$$

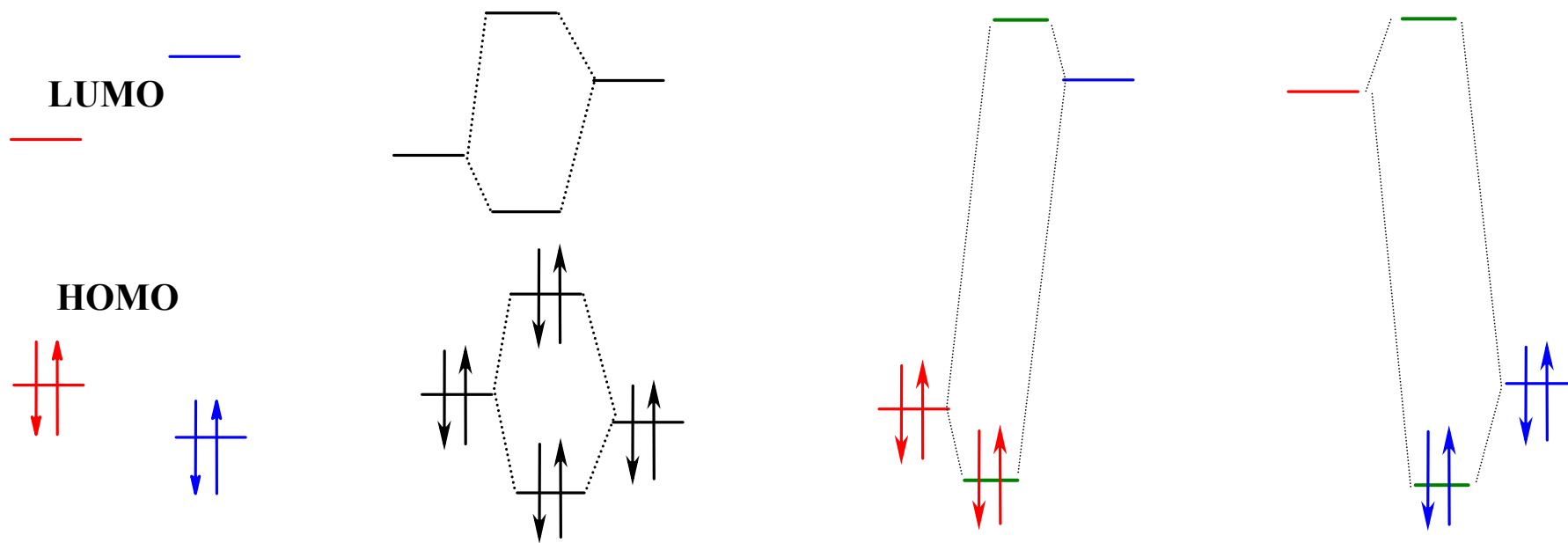
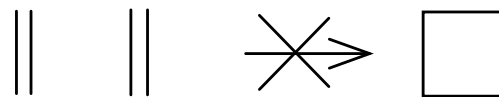
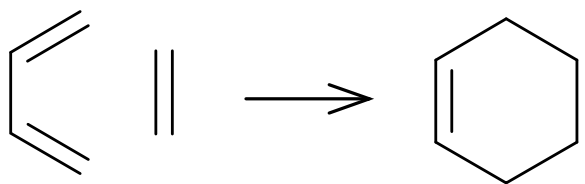
$\Psi_1$

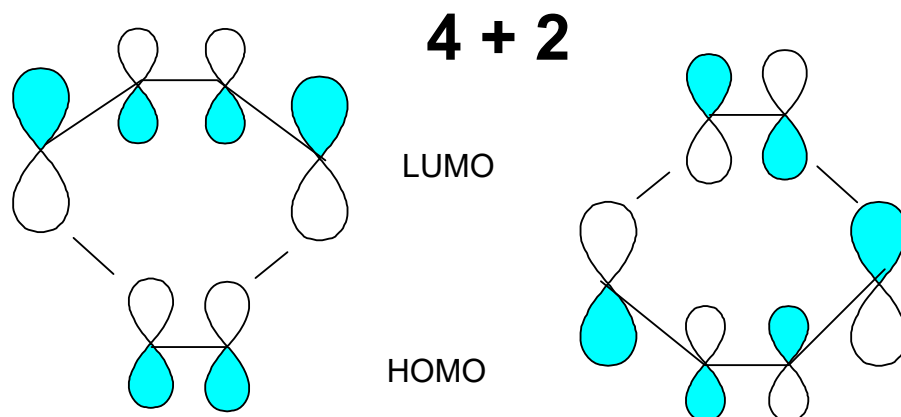
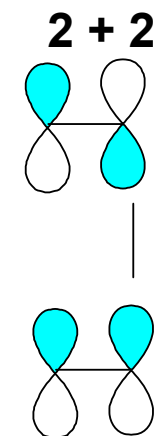
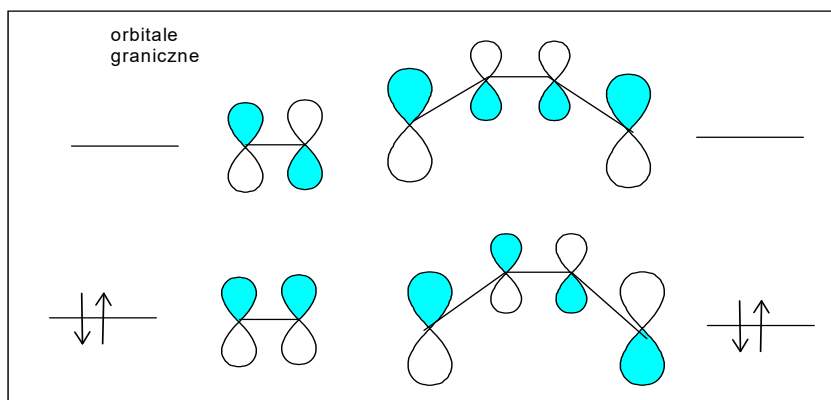
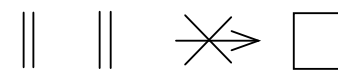
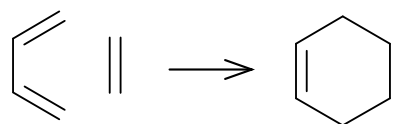


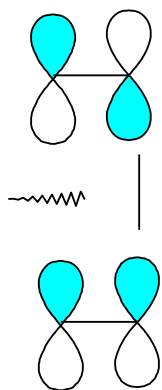
$$c_1\Phi_1 + c_2\Phi_2 + c_3\Phi_3 + c_4\Phi_4$$

$$\Sigma c^2 = 1$$

$$c = 0.600 \text{ lub } c = 0.371$$



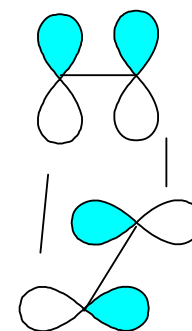
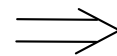




proces suprafacjalny  
tu jest niekorzystny

reakcja może być albo  
'stepwise'  
(wtedy nie jest  
uzgodniona  
- 'concerned')

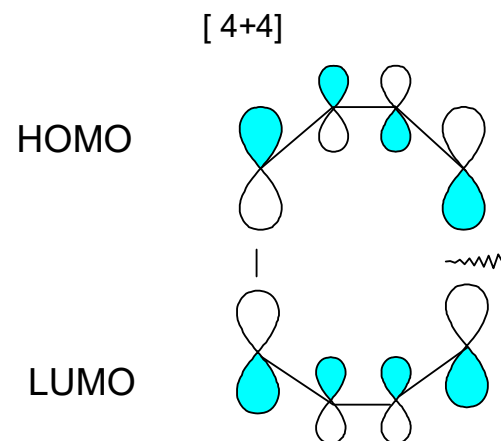
albo musi być



proces antarafacjalny

Liczba par  
elektronowych

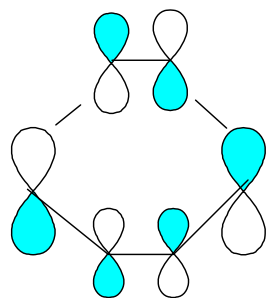
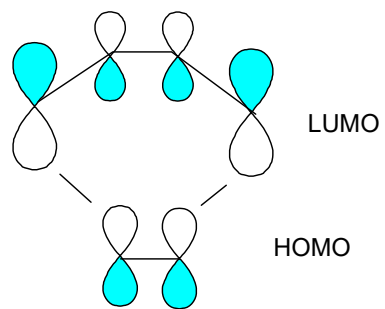
$$2 = 2n$$



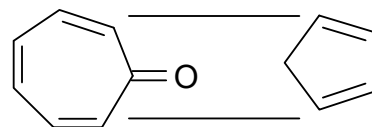
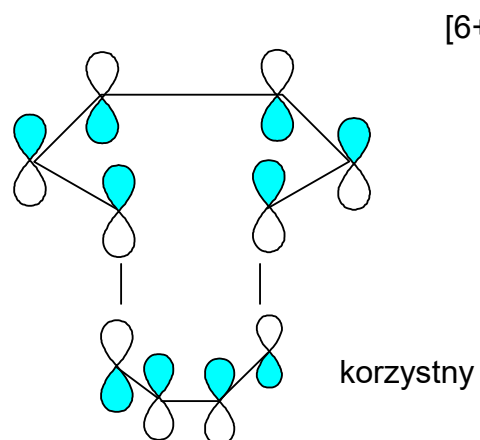
Liczba par  
elektronowych

$$4 = 2n$$

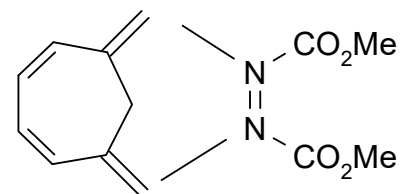
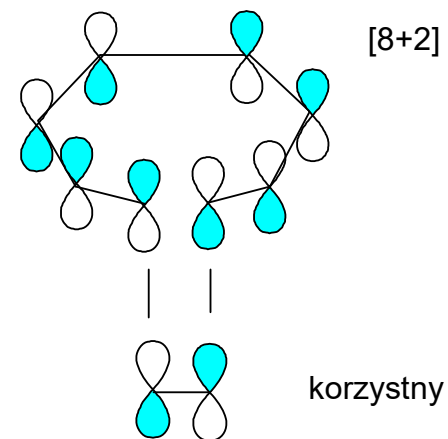
## inne (uzgodnione) procesy cykloaddycji



$$3 = 2n + 1$$

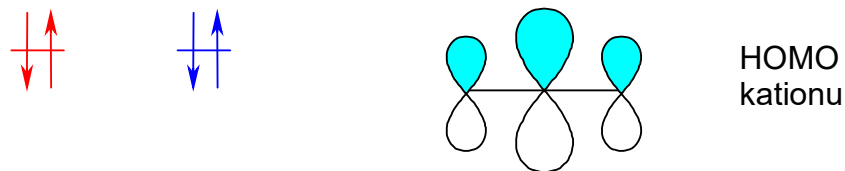
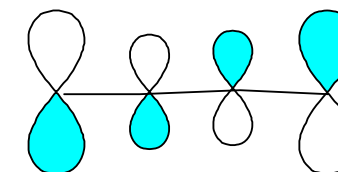
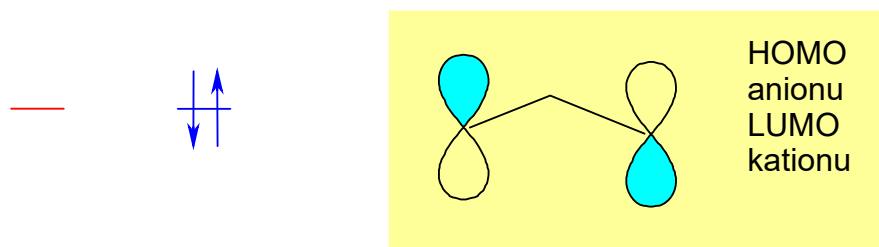
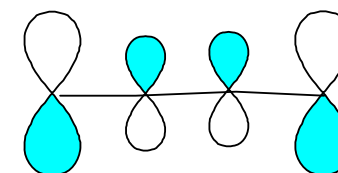
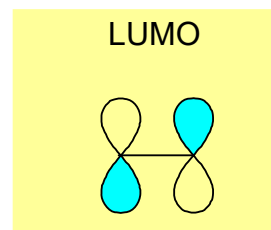
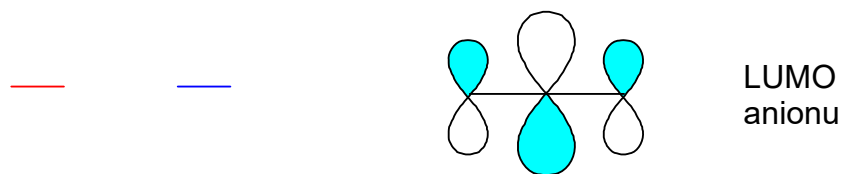
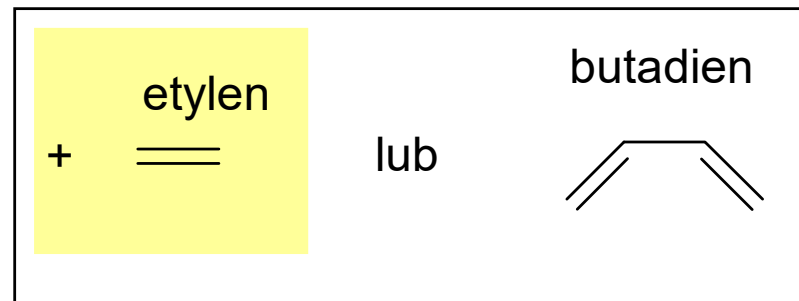


$$5 = 2n + 1$$

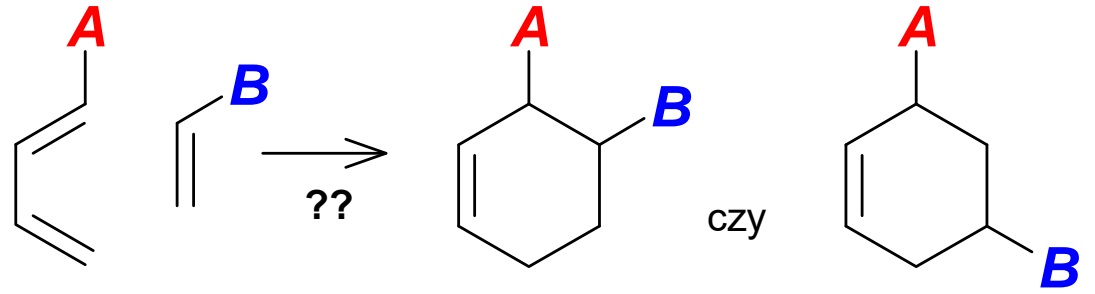
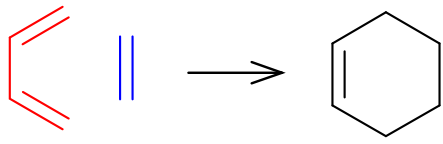


$$5 = 2n + 1$$

Jakie reakcje zaobserwujemy??



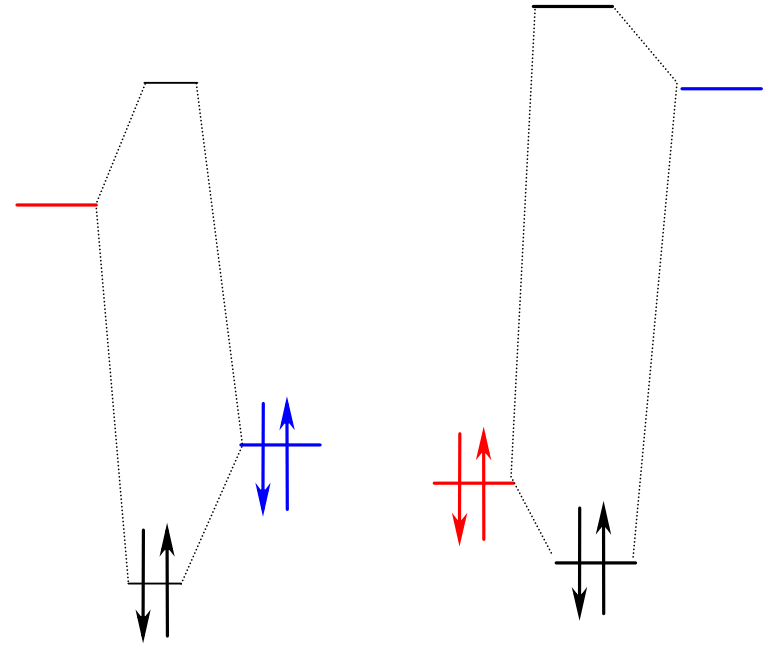
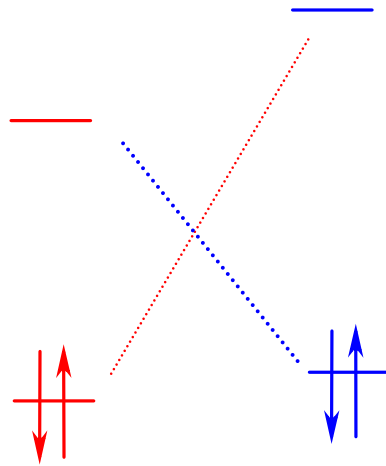
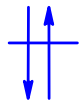
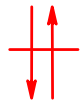


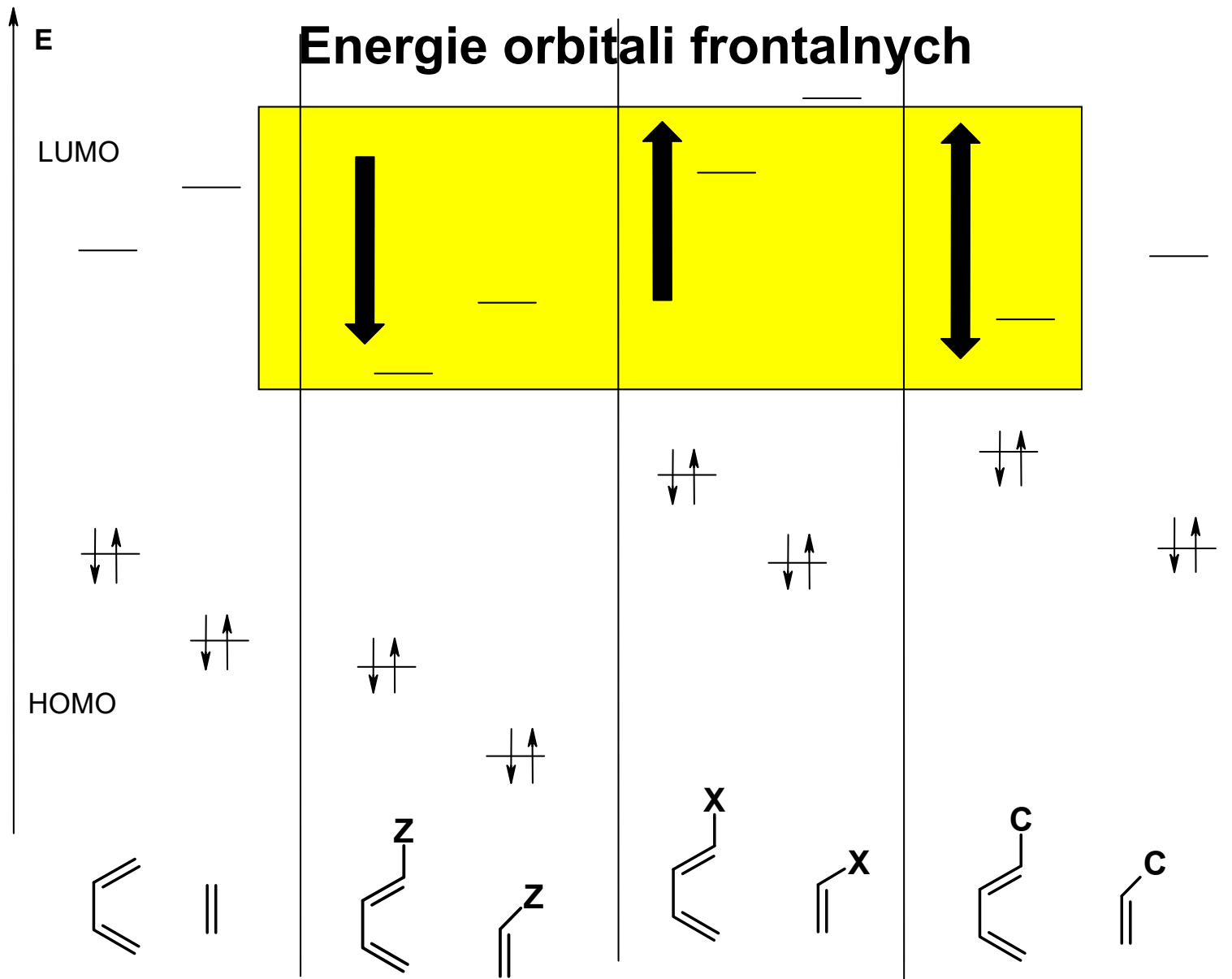


LUMO

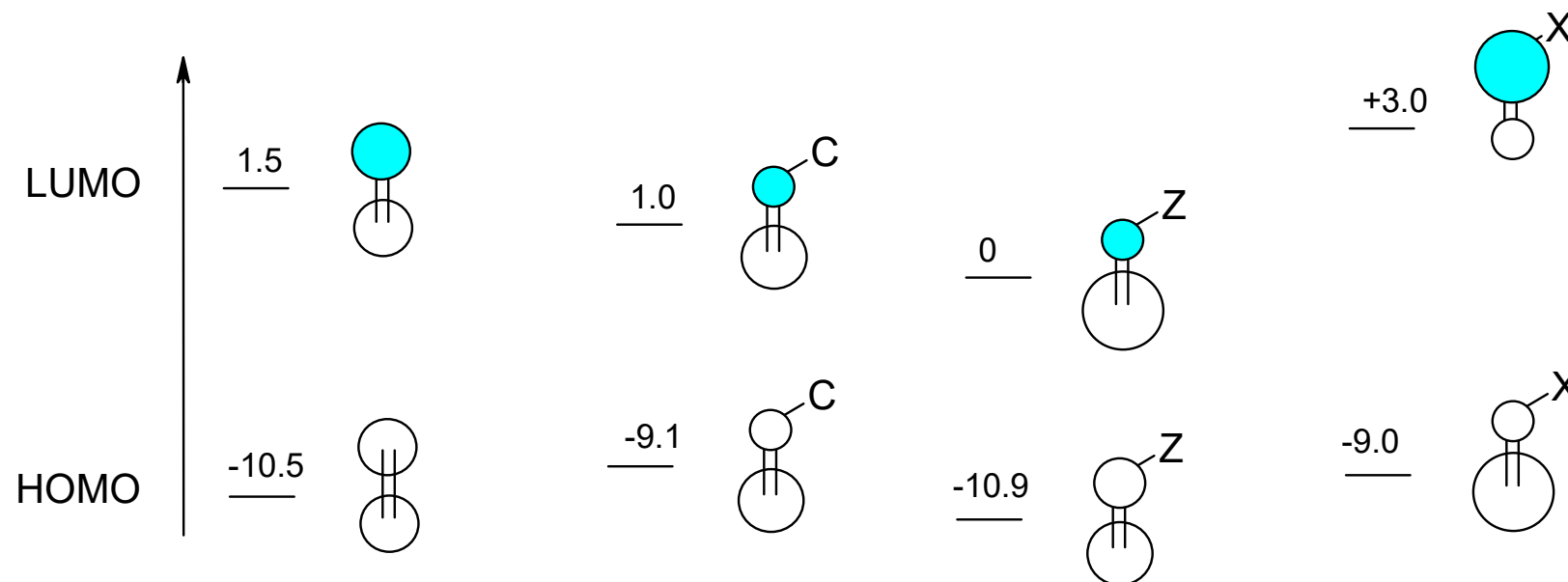
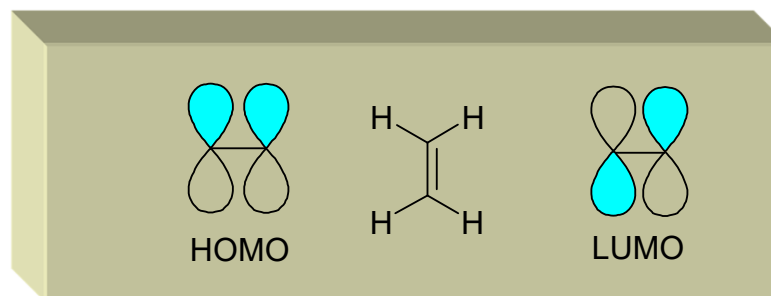


HOMO

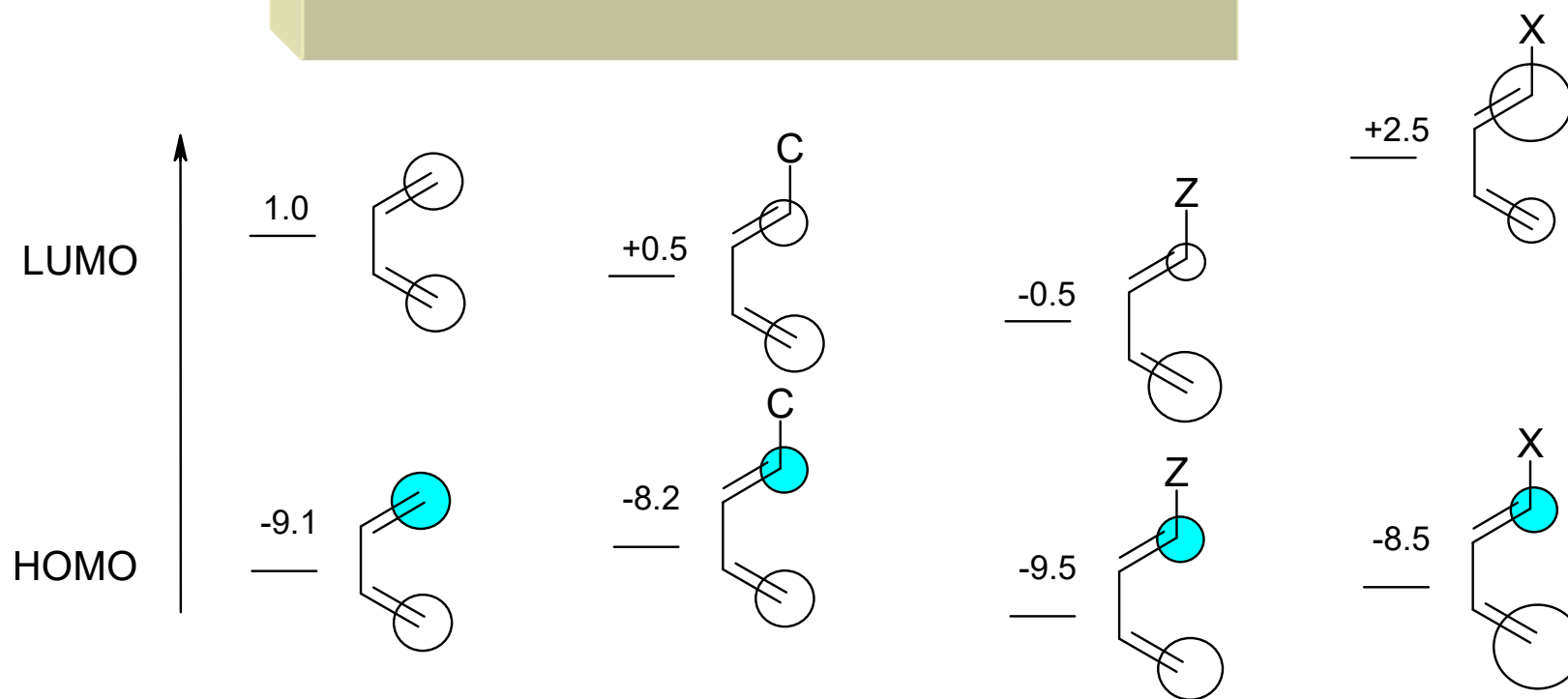
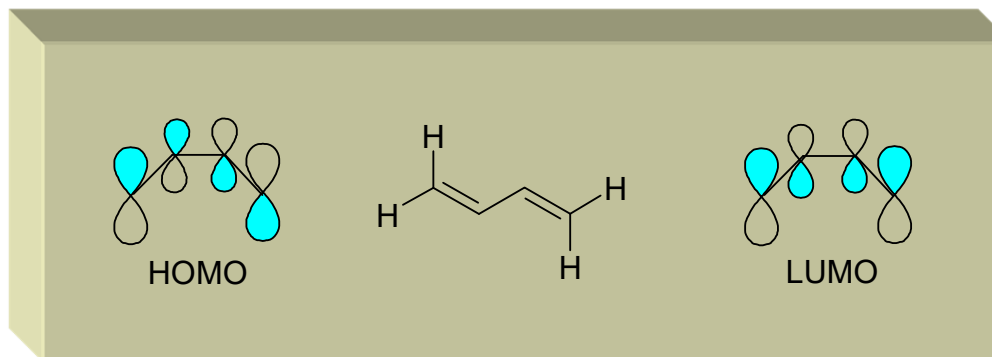




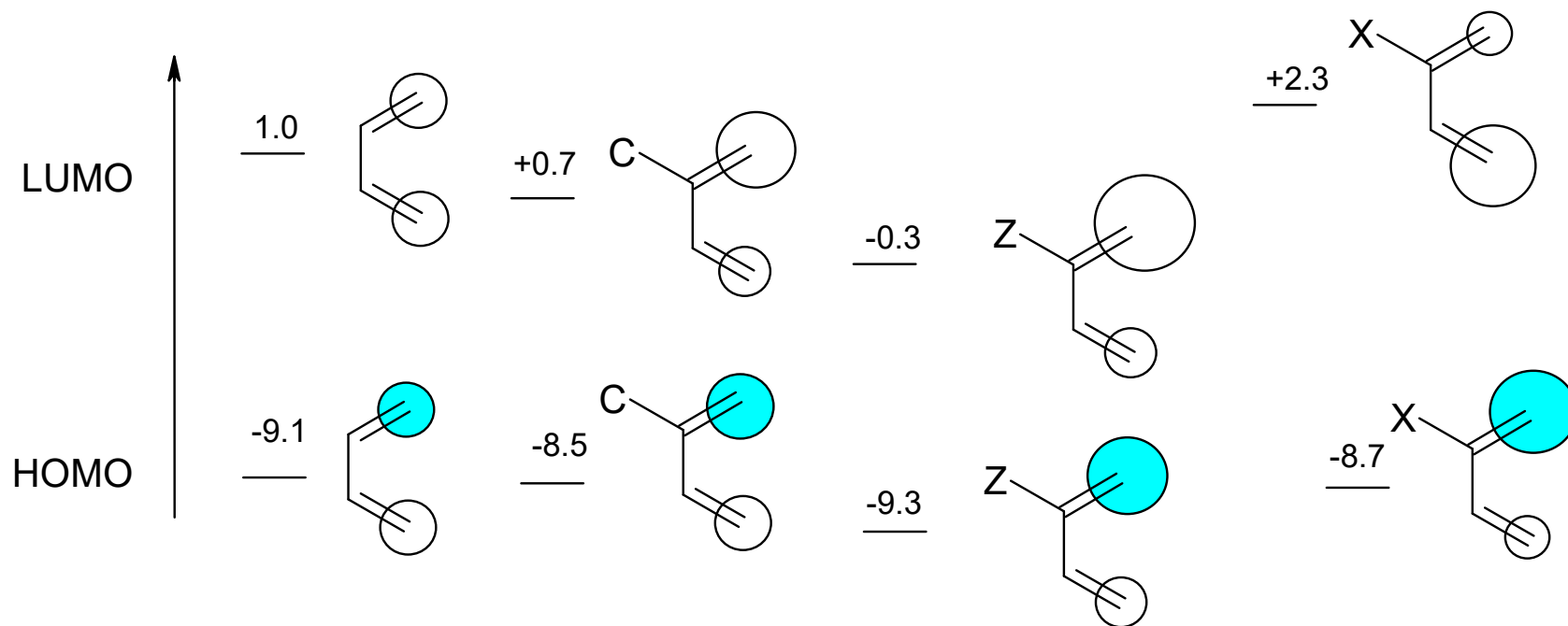
## Typowe energie (eV) i współczynniki orbitalne



## Typowe energie (eV) i współczynniki orbitalne



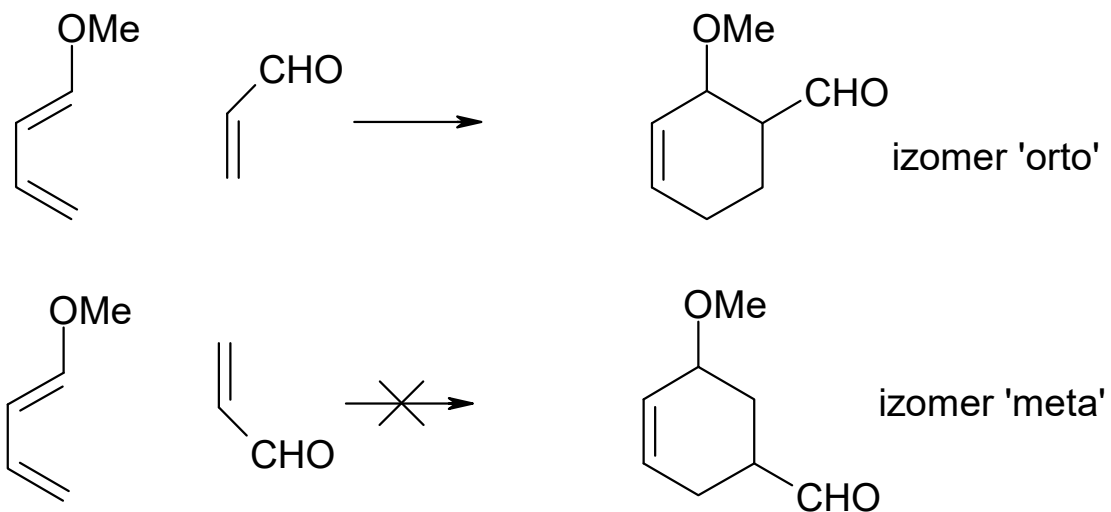
## Typowe energie (eV) i współczynniki orbitalne



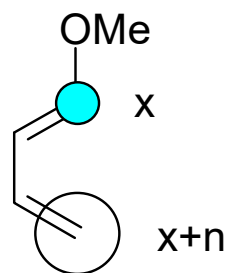
# Reakcja Dielsa - Aldera



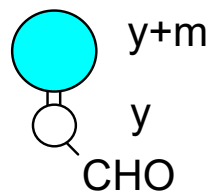
## Regioselektywność w reakcjach Dielsa-Aldera



Homo dienu (typ X) i LUMO dienofila (typ Z)



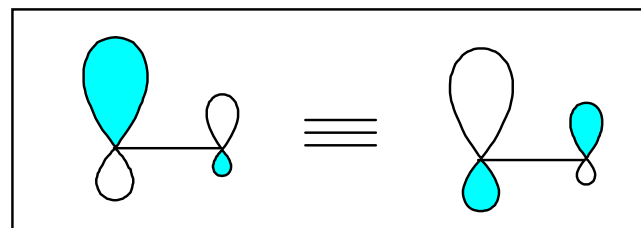
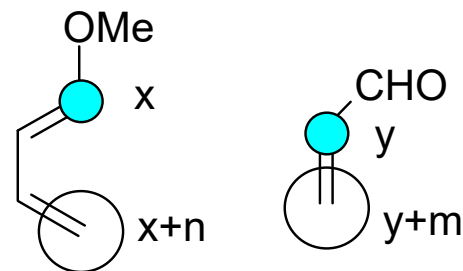
HOMO  
(-8.5 eV)



LUMO  
(~0 eV)

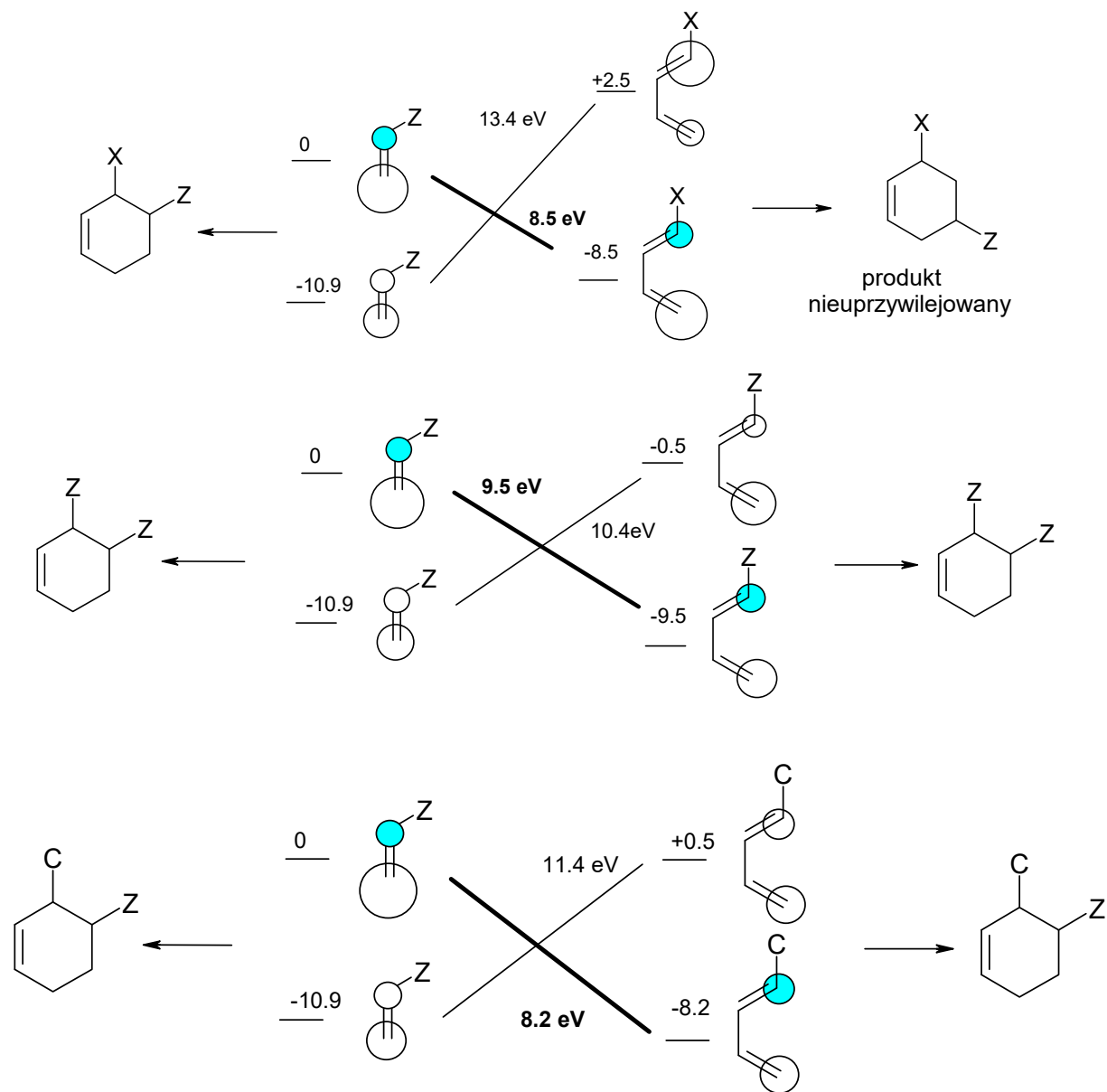
LUMO  
(+2.5 eV)

HOMO  
(-10.9 eV)



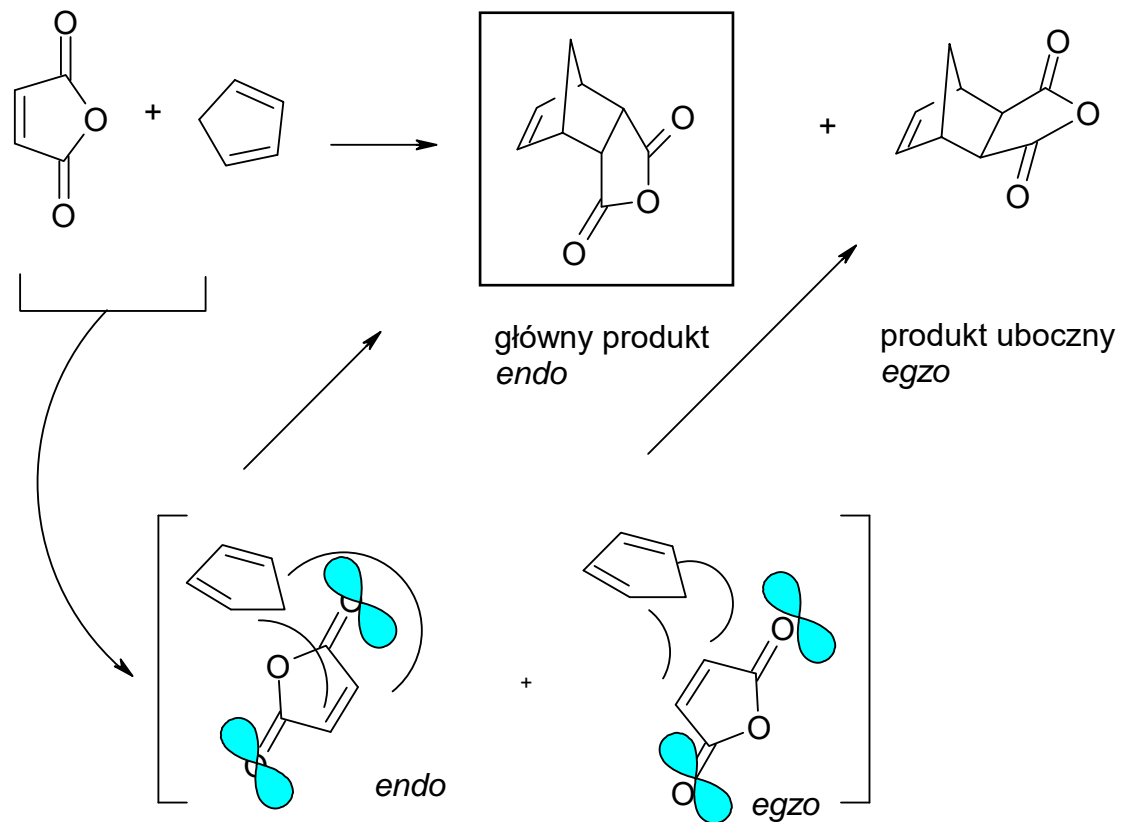
Warunek najlepszego nakładania orbitali  $\Sigma c_{ij} = \max.$

$$\Delta E \sim 1 / (E_1 - E_2)$$

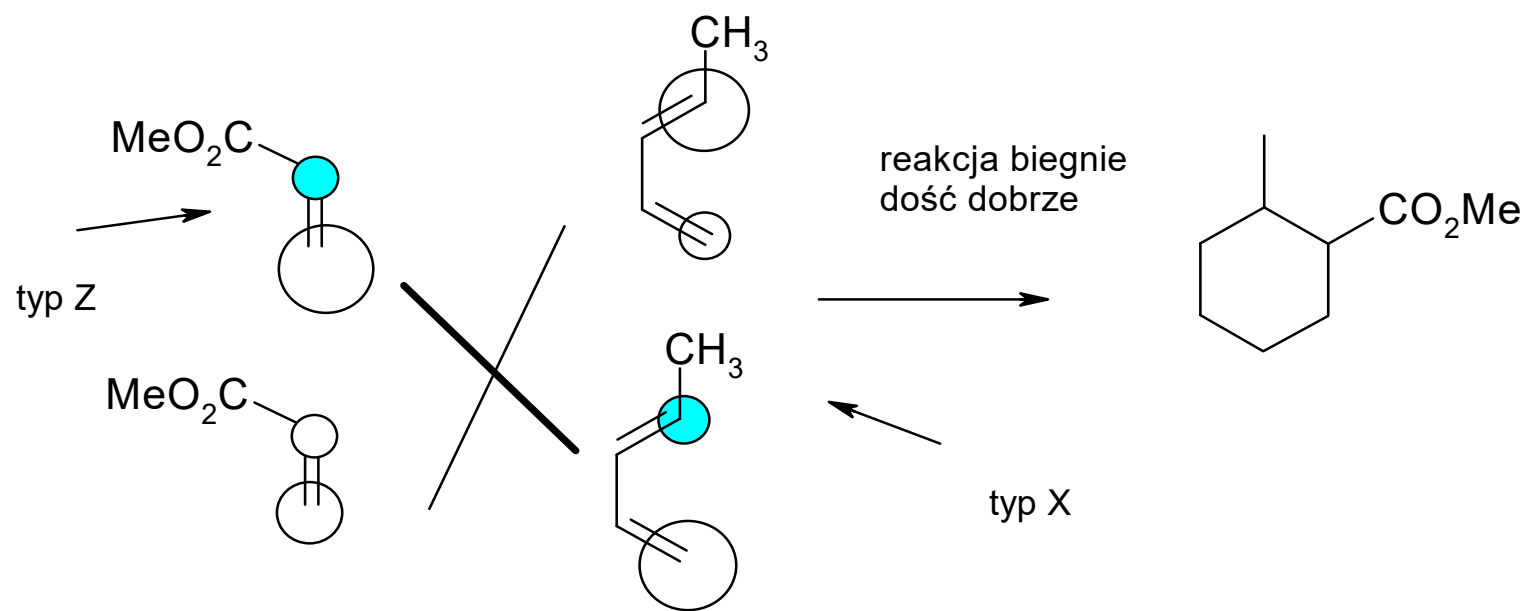




## Drugorzędowe efekty stereochemiczne reakcji pericyklicznych

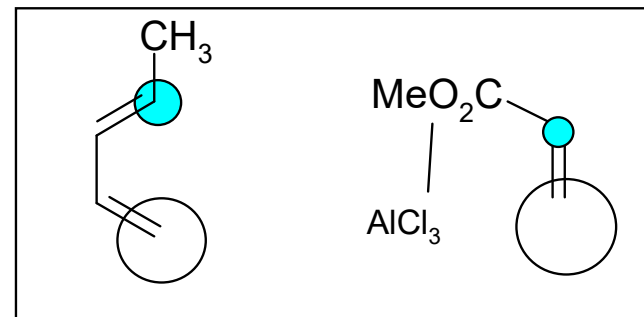
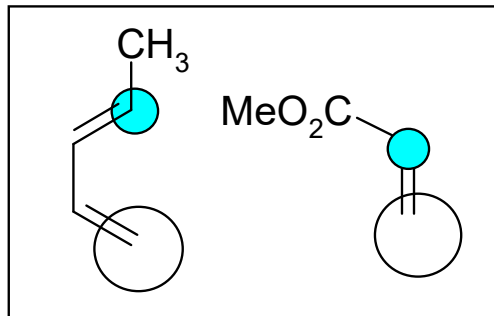
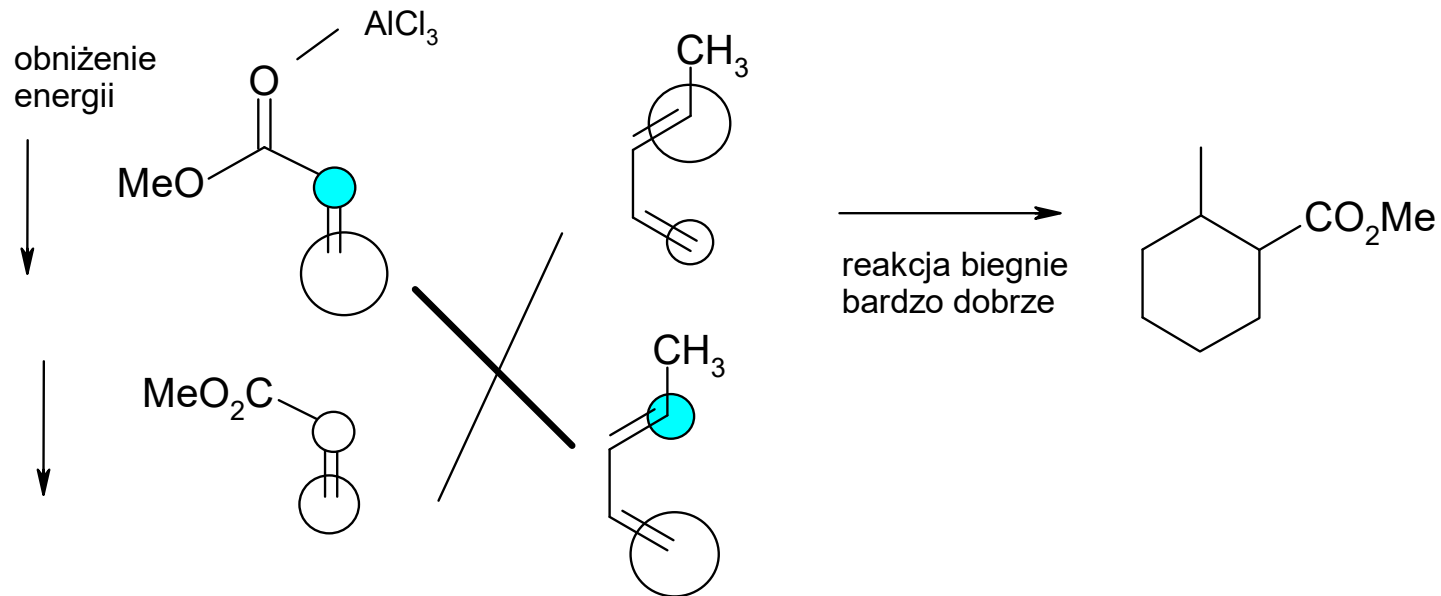


# Kataliza reakcji Dielsa-Aldera kwasami Lewisa



**+ 10% izomeru 'meta'**

## Kataliza reakcji Dielsa-Aldera kwasami Lewisa



**+ 2% izomeru 'meta'**