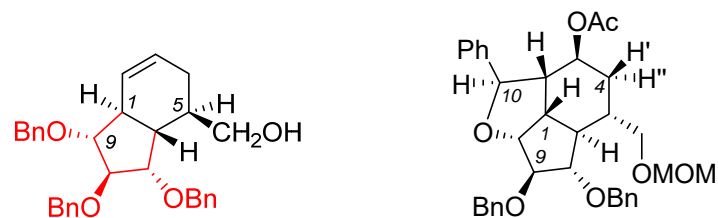
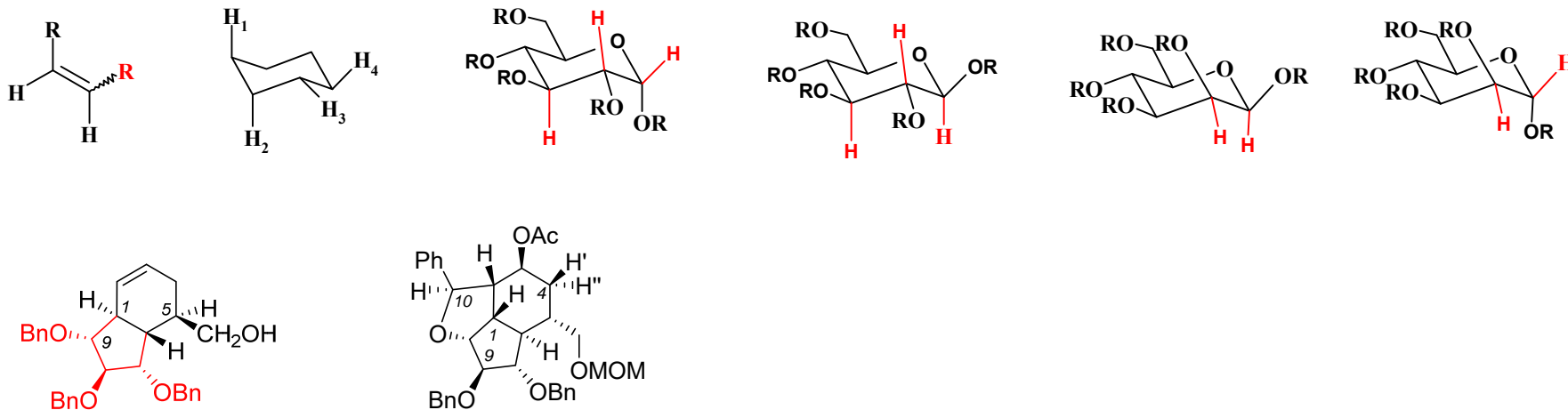


Wyznaczanie konfiguracji względnej poprzez analizę spektralną: STAŁE SPRZĘŻENIA ^1H NMR

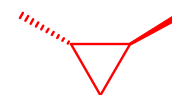


Metody chemiczne

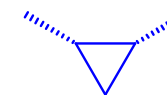
Jak łatwo rozróżnić te związki ???



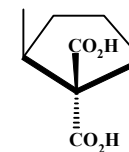
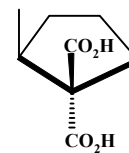
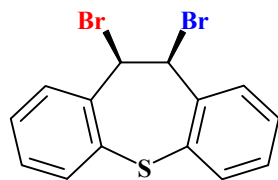
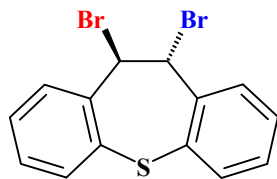
trans



trans



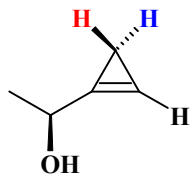
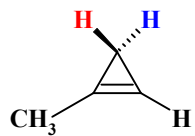
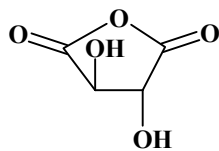
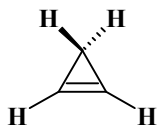
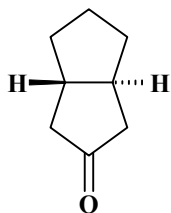
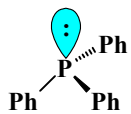
cis



Podział grup wg topowości

1. Homotopowe
2. Enancjotopowe
3. Diastereotopowe

przykłady



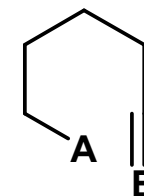
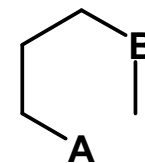
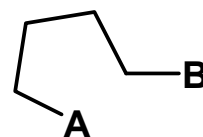
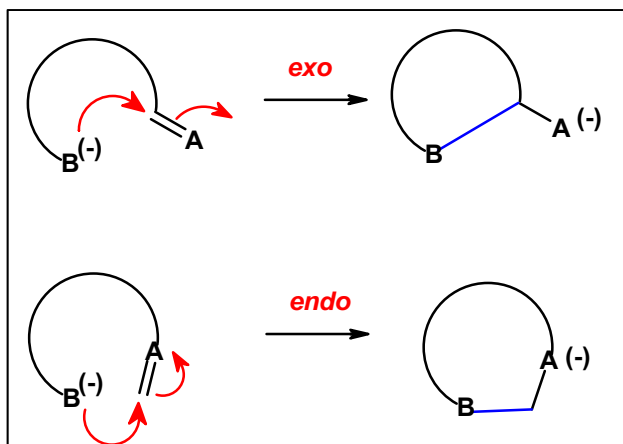
Czy związek achiralny może mieć grupy diastereotopowe??

test zastępowania

Przykład cukrowy

Topowość grup – symetria (podsumowanie)

Reguły Baldwina



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

	EXO			ENDO		
	Tet	Trig	Dig	Tet	Trig	Dig
3	Tak	Tak	Nie		Nie	Tak
4	Tak	Tak	Nie		Nie	Tak
5	Tak	Tak	Tak	Nie	NIE	Tak
6	Tak	Tak	Tak	Nie	Tak	Tak
7	Tak	Tak	Tak		Tak	Tak

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

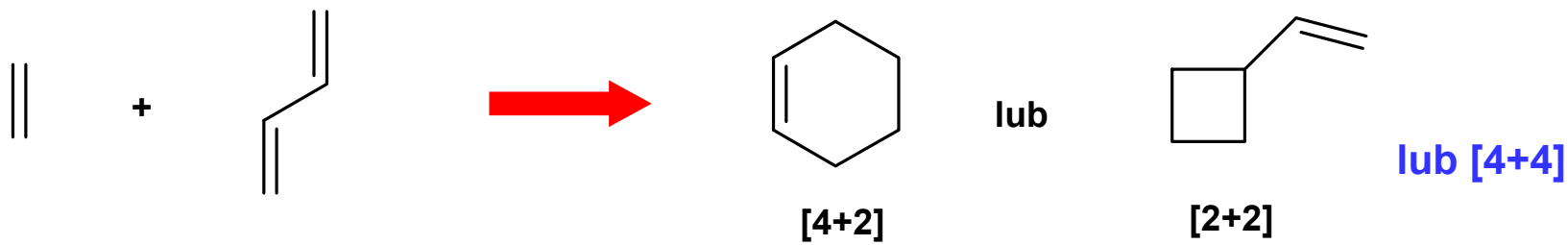
[2+2], [4+2], [4+4], [8+2] [6+4] itd

dipolarna [1,3]

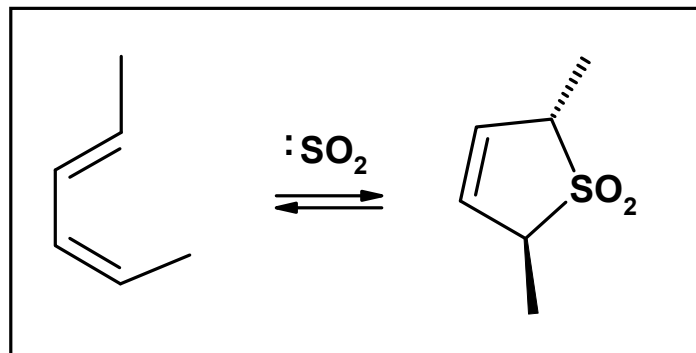
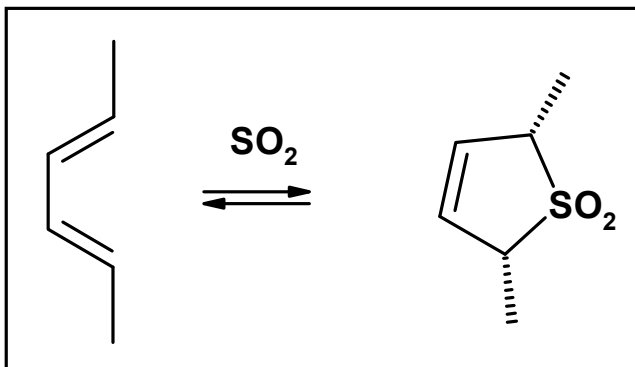
2. reakcje cheletropowe

3. reakcje elektrocykliczne

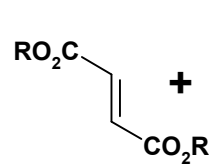
4. przegrupowanie sigmatropowe



Reakcje cheletropowe



Reakcja Dielsa-Aldera

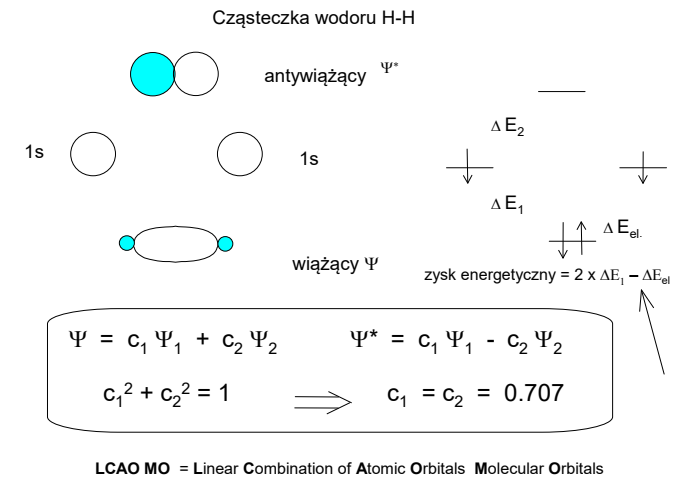
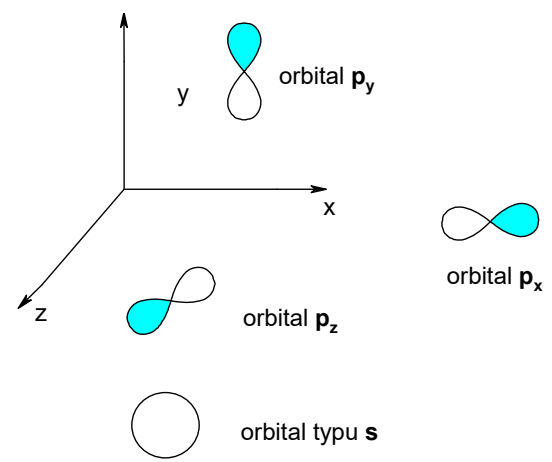


Stereospecyficznosc, Stereoselektywnosc



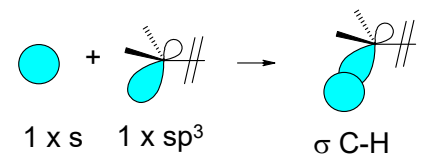
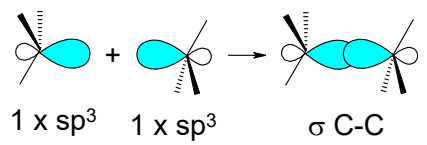
selektywnosc wielu reakcji mozna przewidziec za pomoca **TEORII ORBITALI
FRONTALNYCH**

Typy orbitali

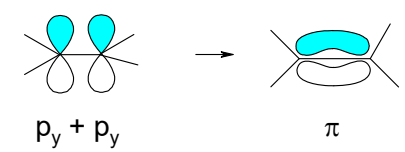
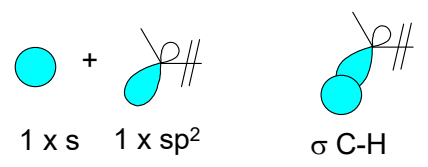
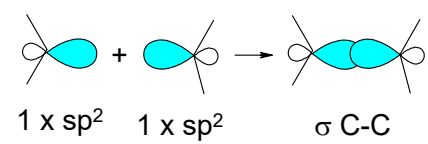


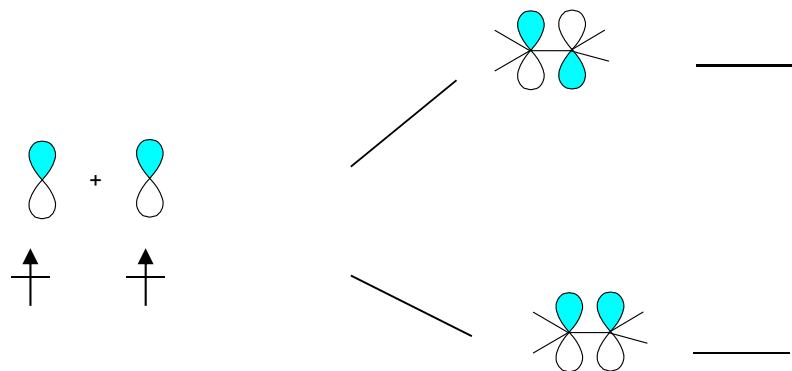
Hybrydyzacja

etan

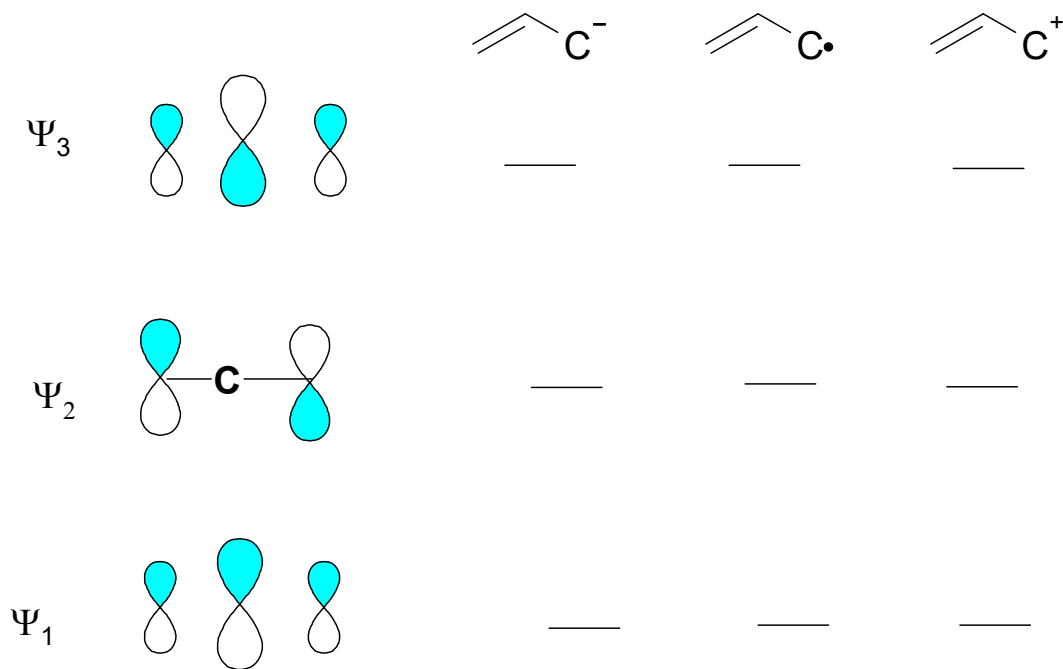
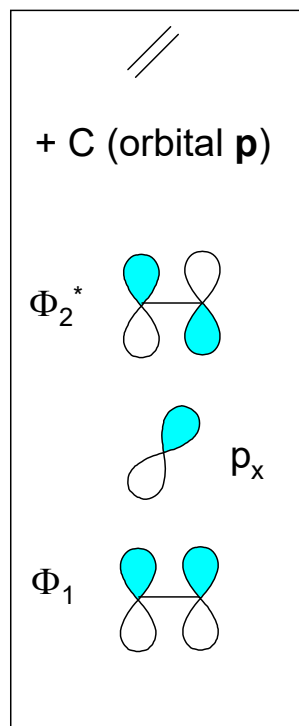


etylen

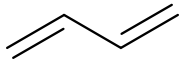




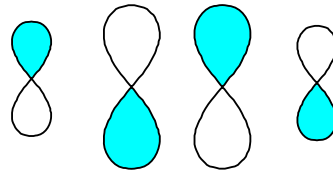
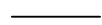
Allil



butadien



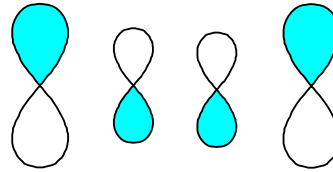
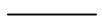
Ψ_4



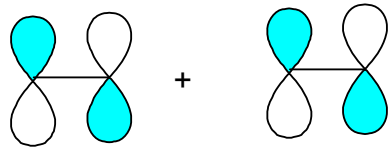
$$c_1\Phi_1 - c_2\Phi_2 + c_3\Phi_3 - c_4\Phi_4$$

Φ_3 i Φ_4

Ψ_3



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



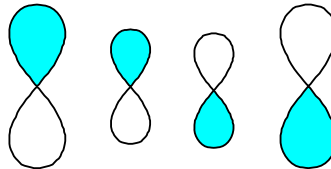
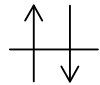
LUMO



HOMO

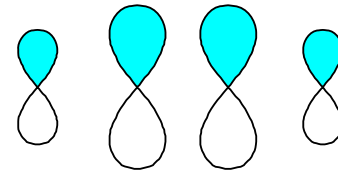
Φ_1 i Φ_2

Ψ_2



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

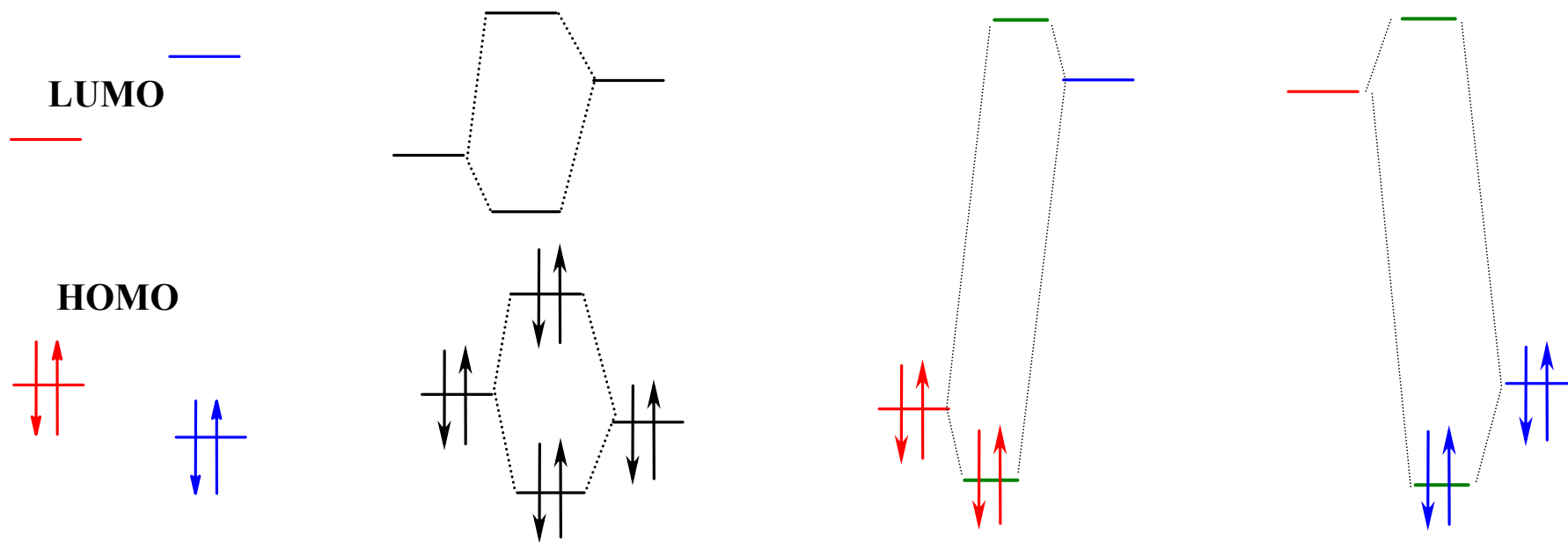
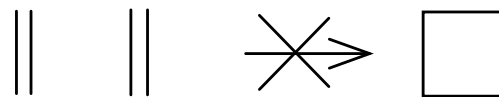
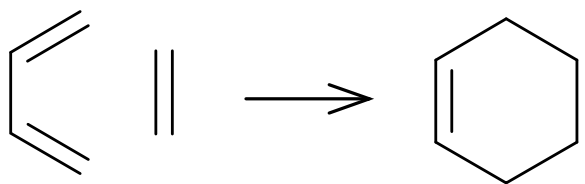
Ψ_1

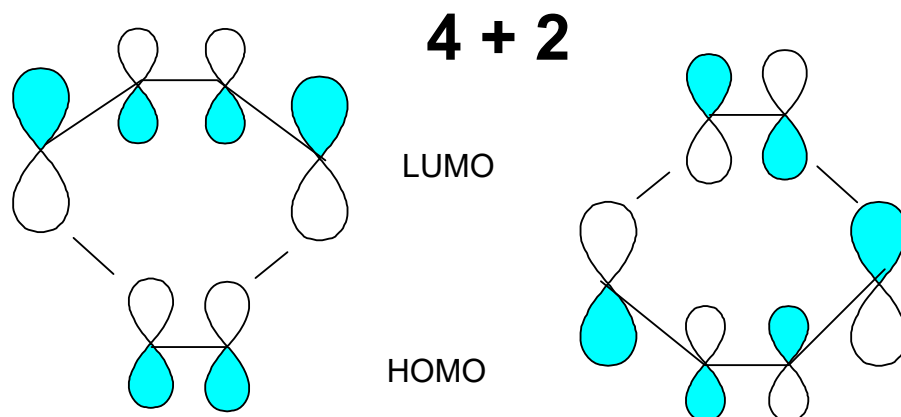
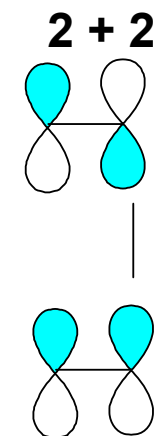
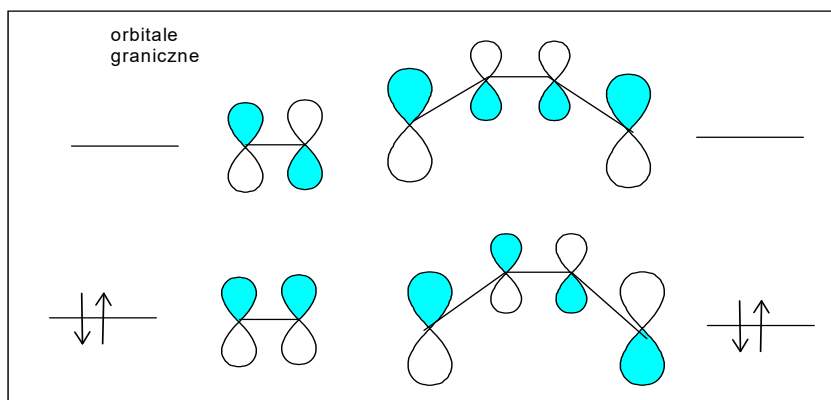
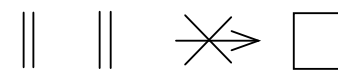
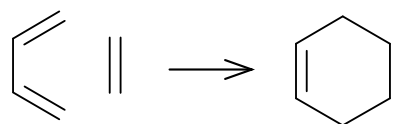


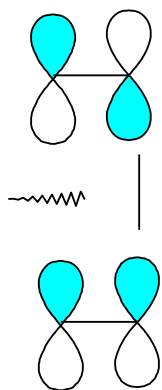
$$c_1\Phi_1 + c_2\Phi_2 + c_3\Phi_3 + c_4\Phi_4$$

$$\Sigma c^2 = 1$$

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



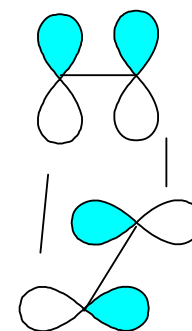
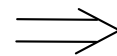




proces suprafacjalny
tu jest niekorzystny

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

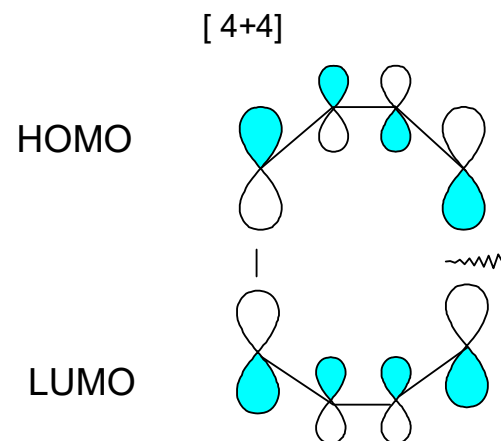
albo musi być



proces antarafacjalny

Liczba par
elektronowych

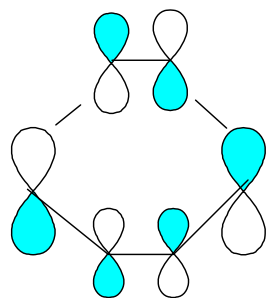
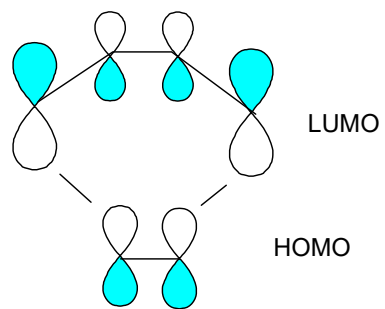
$$2 = 2n$$



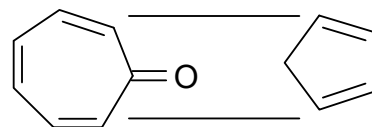
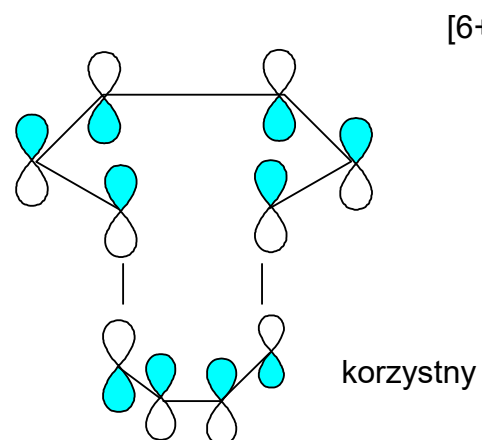
Liczba par
elektronowych

$$4 = 2n$$

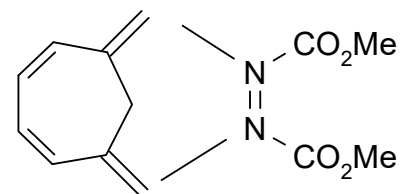
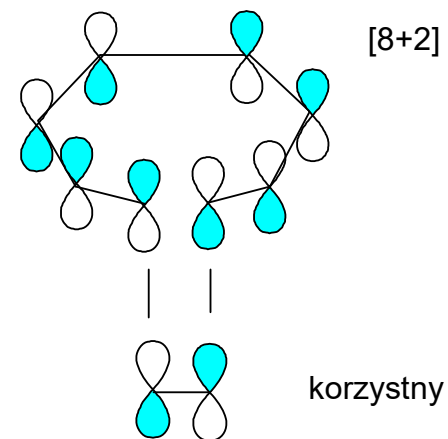
inne (uzgodnione) procesy cykloaddycji



$$3 = 2n + 1$$

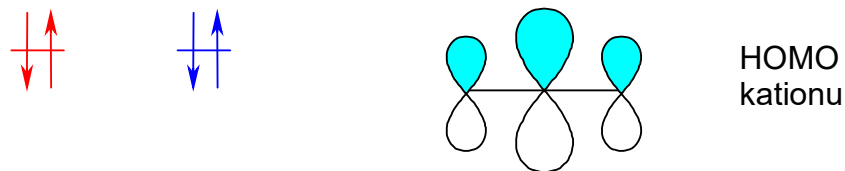
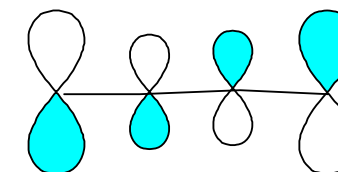
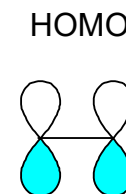
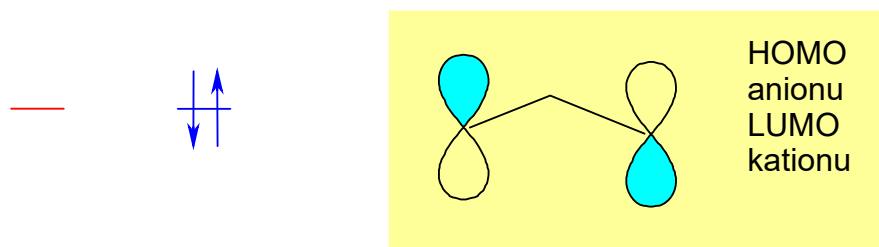
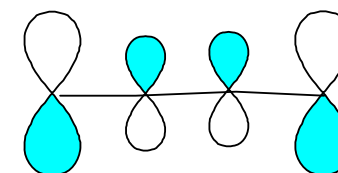
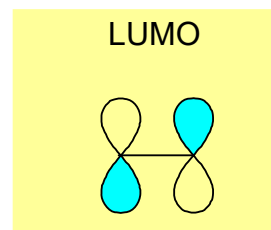
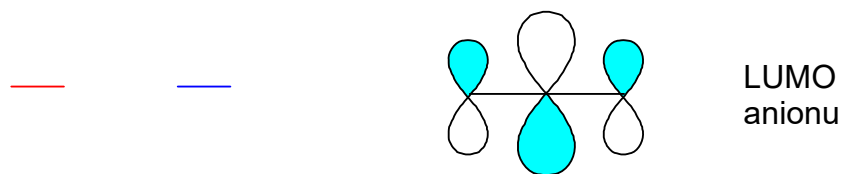
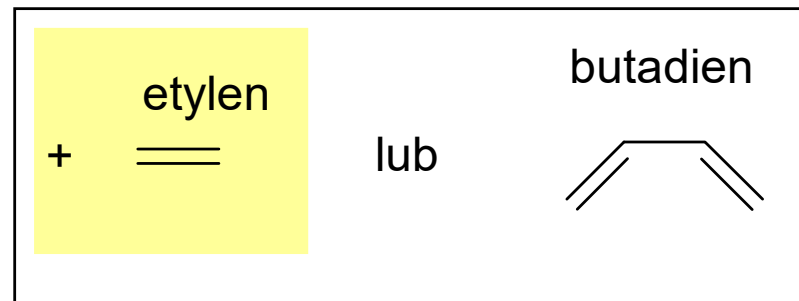


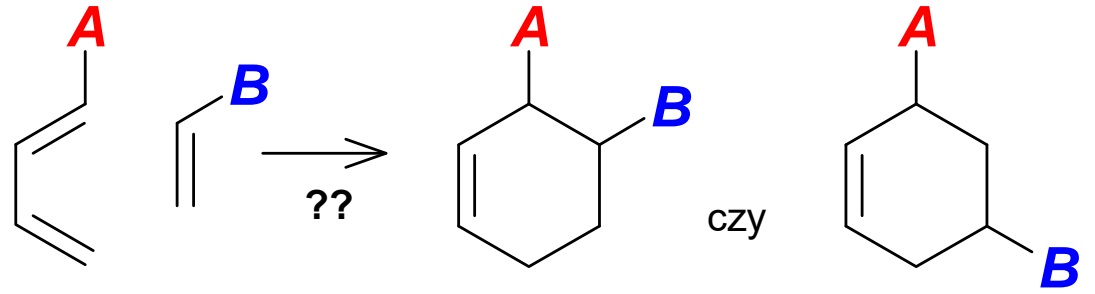
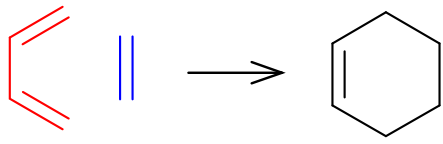
$$5 = 2n + 1$$



$$5 = 2n + 1$$

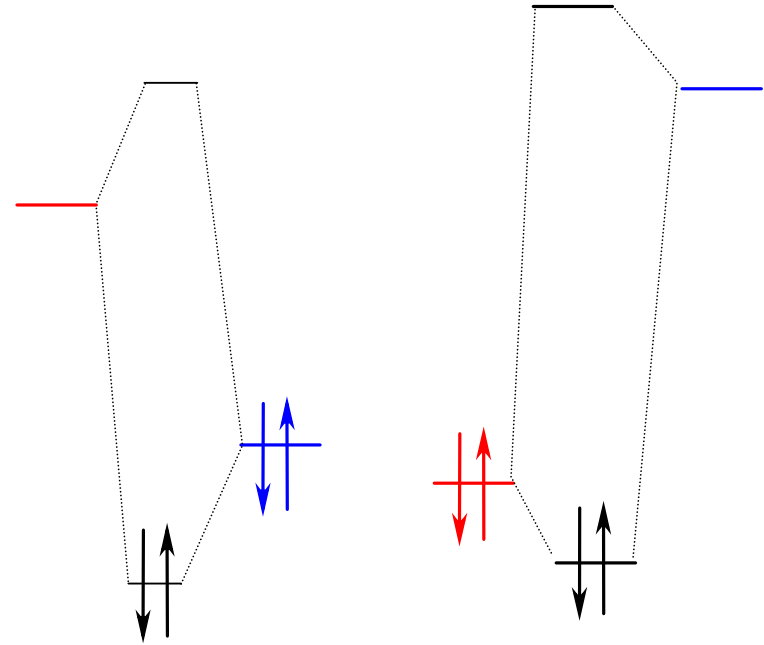
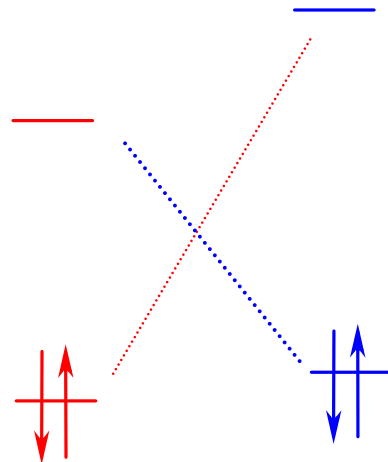
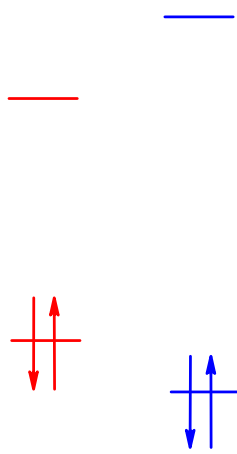
Jakie reakcje zaobserwujemy??

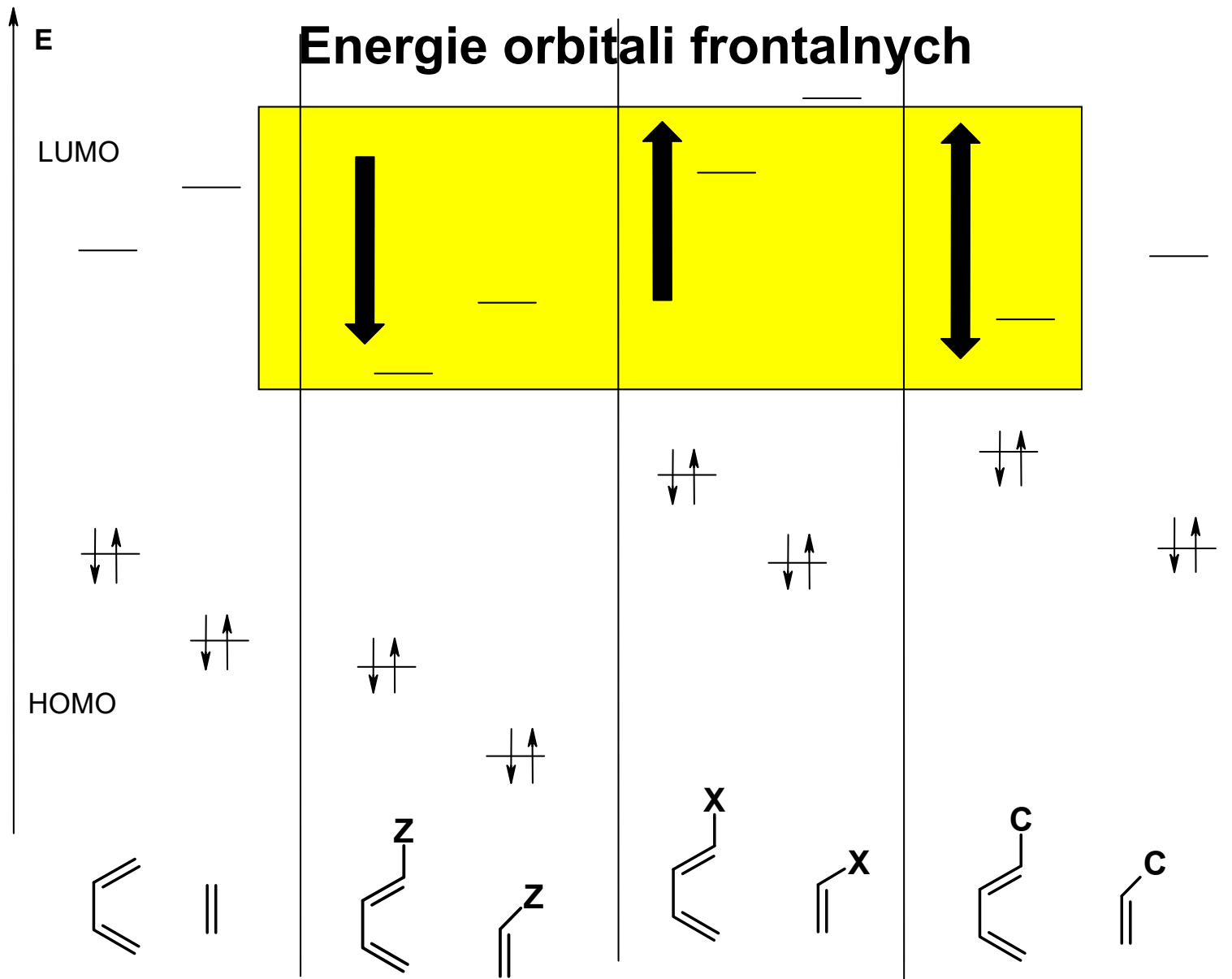




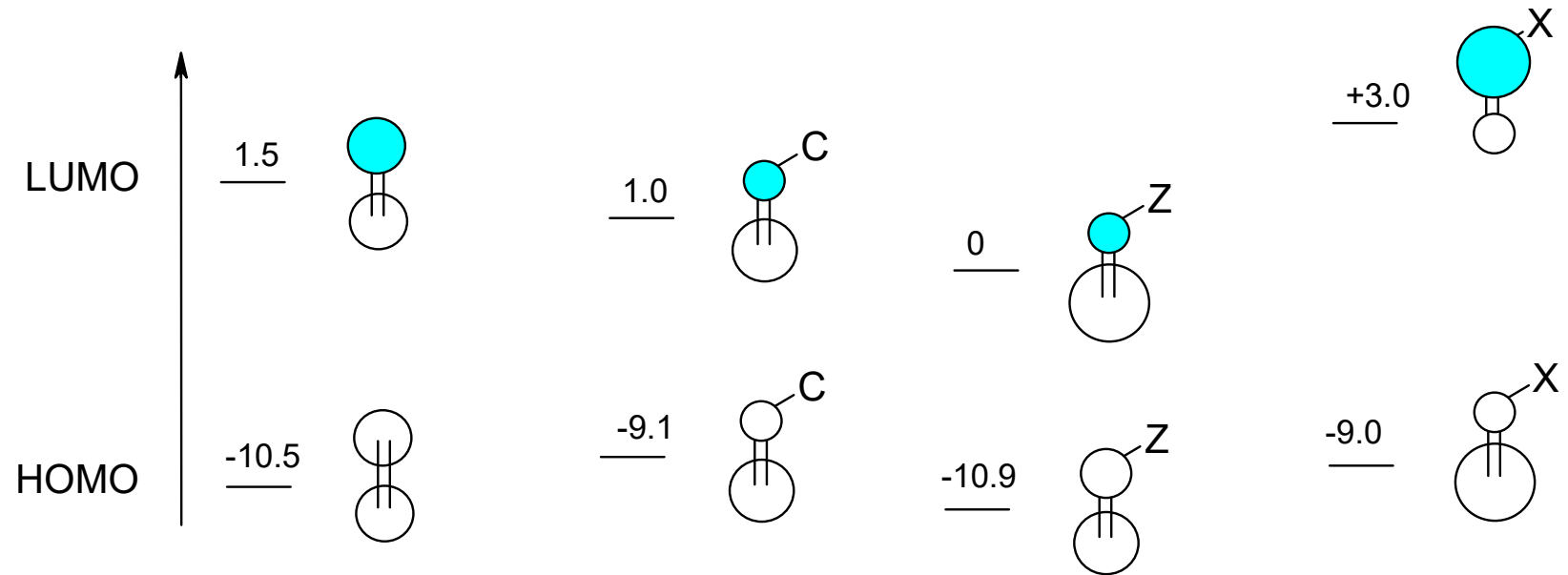
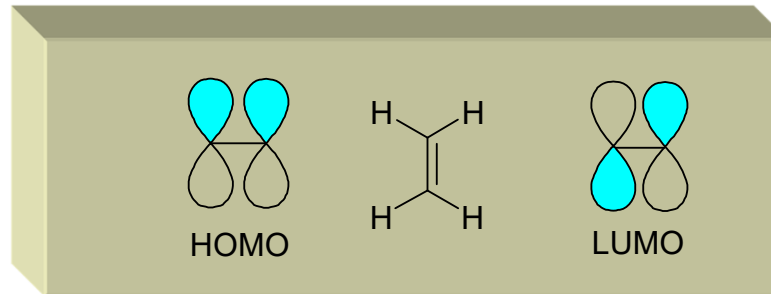
LUMO

HOMO

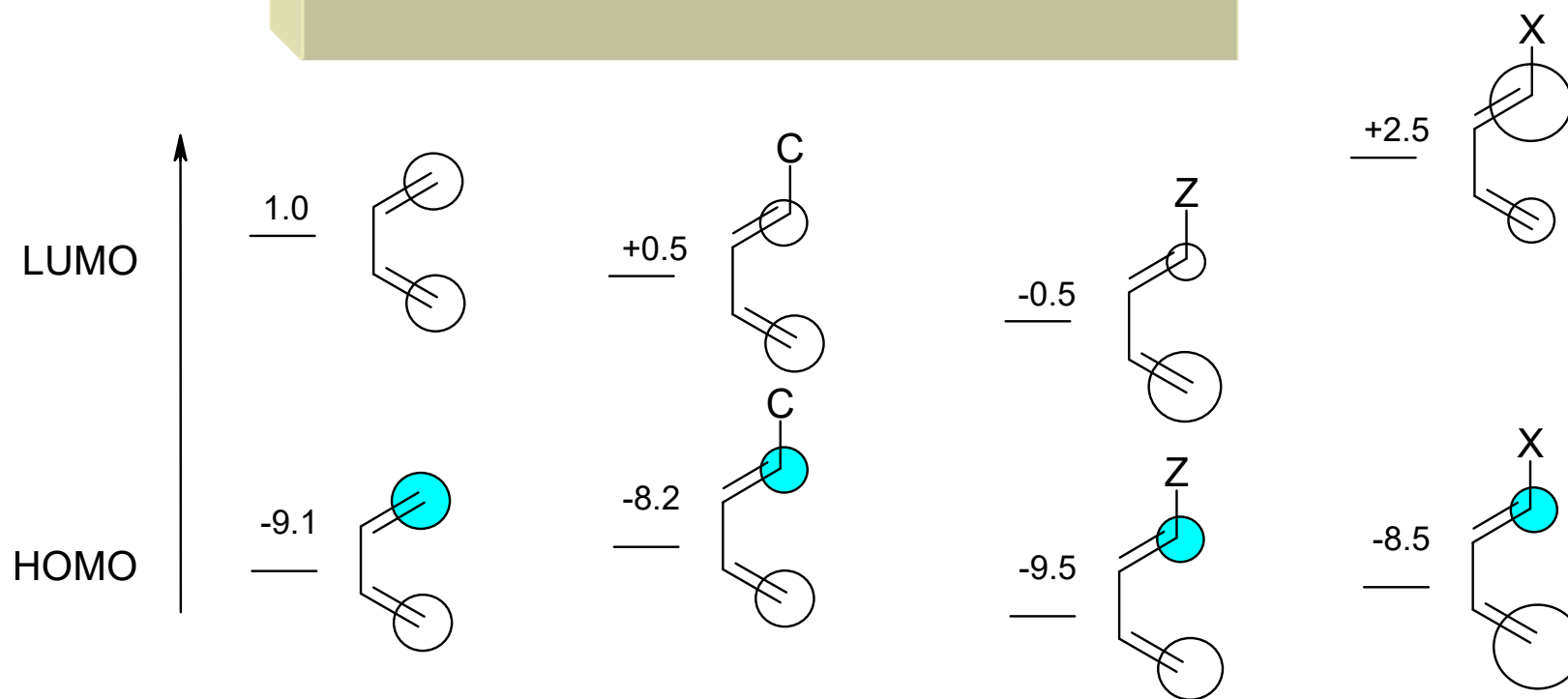
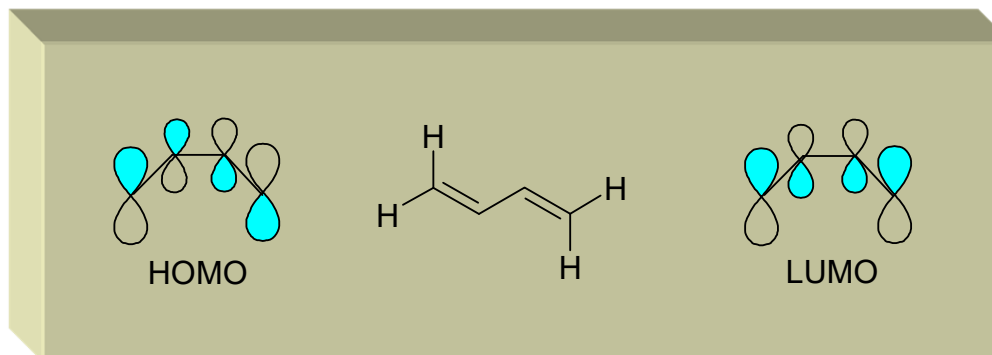




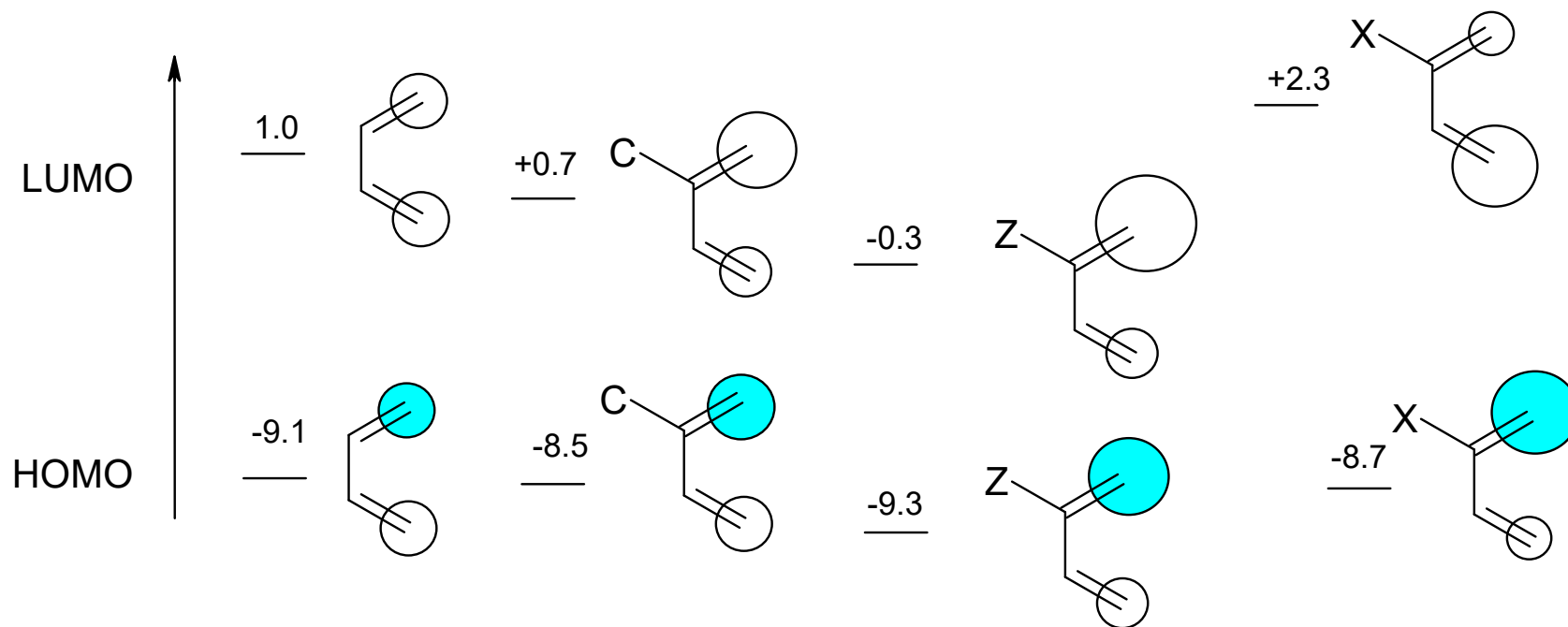
Typowe energie (eV) i współczynniki orbitalne



Typowe energie (eV) i współczynniki orbitalne



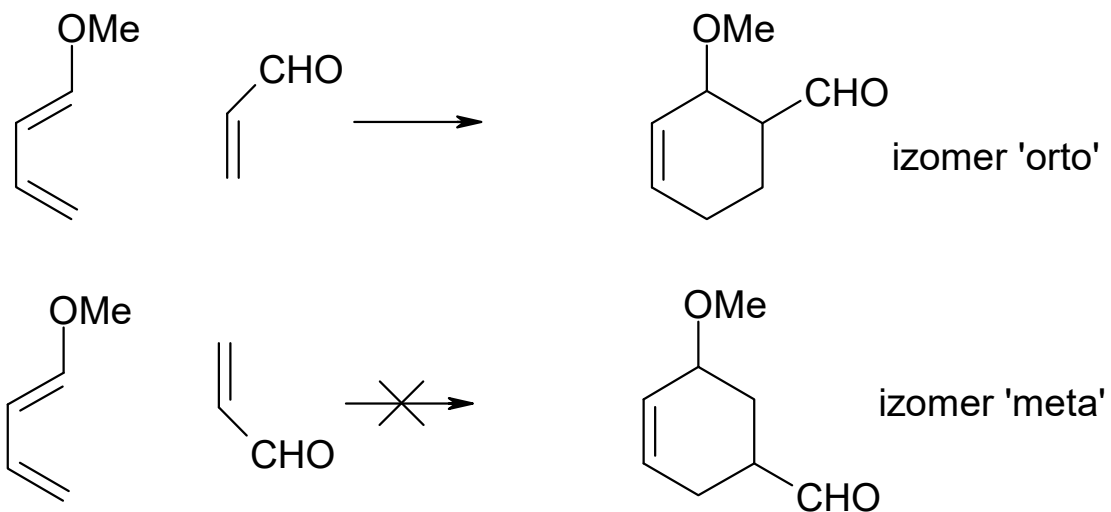
Typowe energie (eV) i współczynniki orbitalne



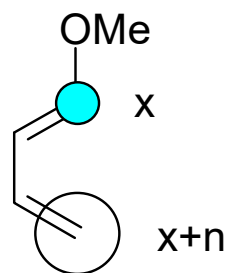
Reakcja Dielsa - Aldera



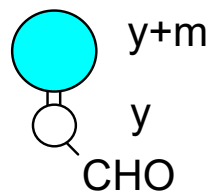
Regioselektywność w reakcjach Dielsa-Aldera



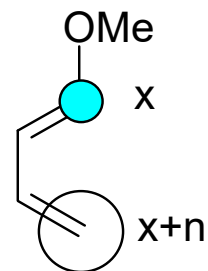
Homo dienu (typ X) i LUMO dienofila (typ Z)



HOMO
(-8.5 eV)

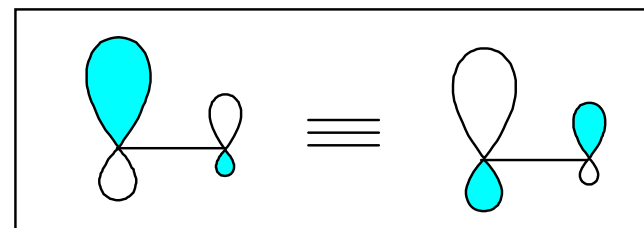
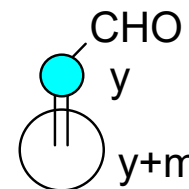


LUMO
(~0 eV)



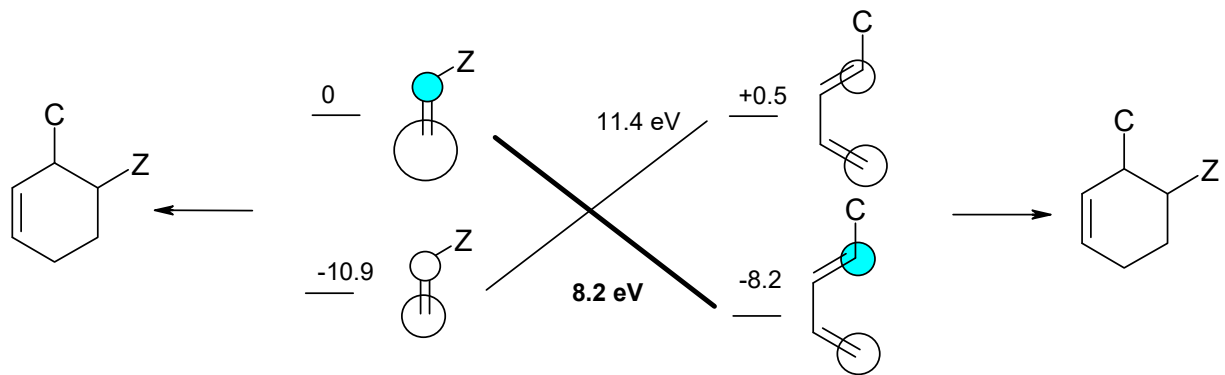
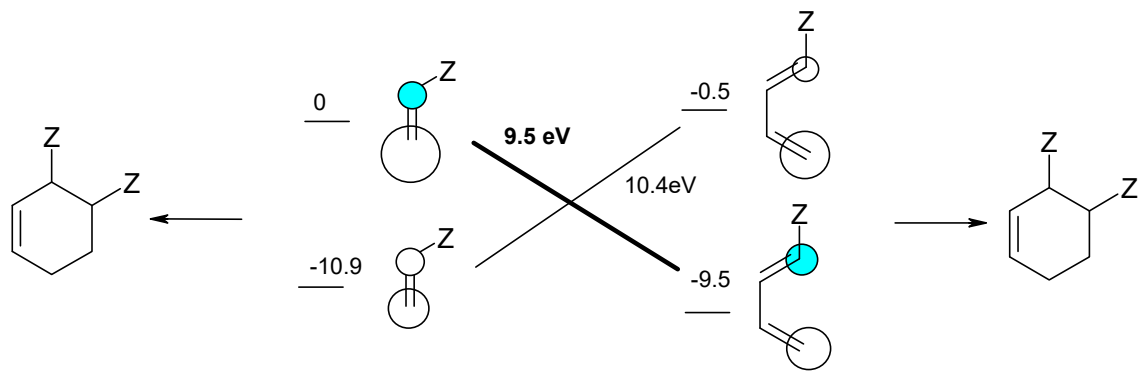
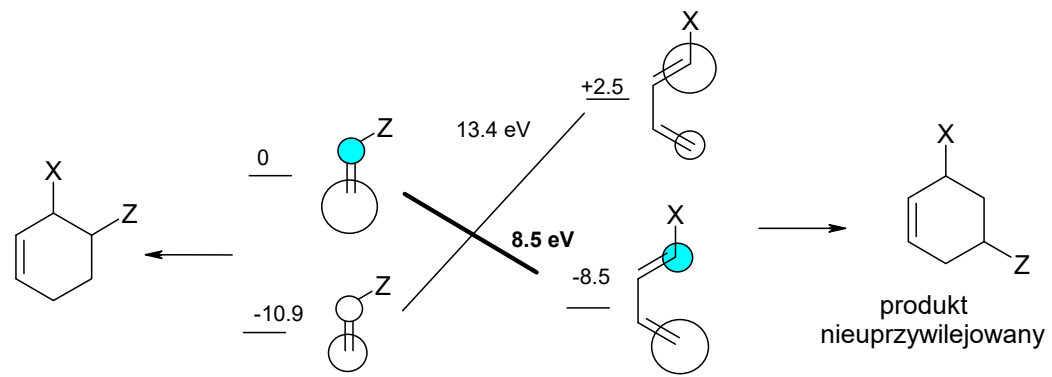
LUMO
(+2.5 eV)

HOMO
(-10.9 eV)

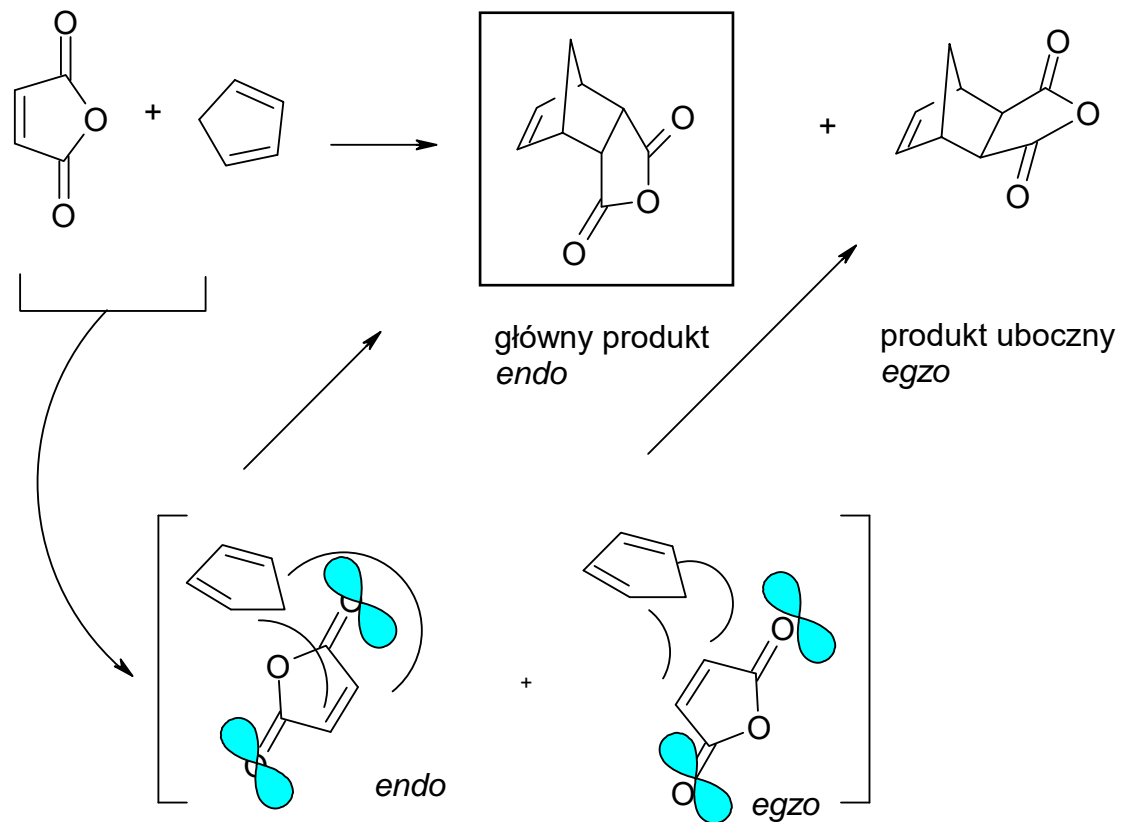


Warunek najlepszego nakładania orbitali $\Sigma c_{ij} = \max.$

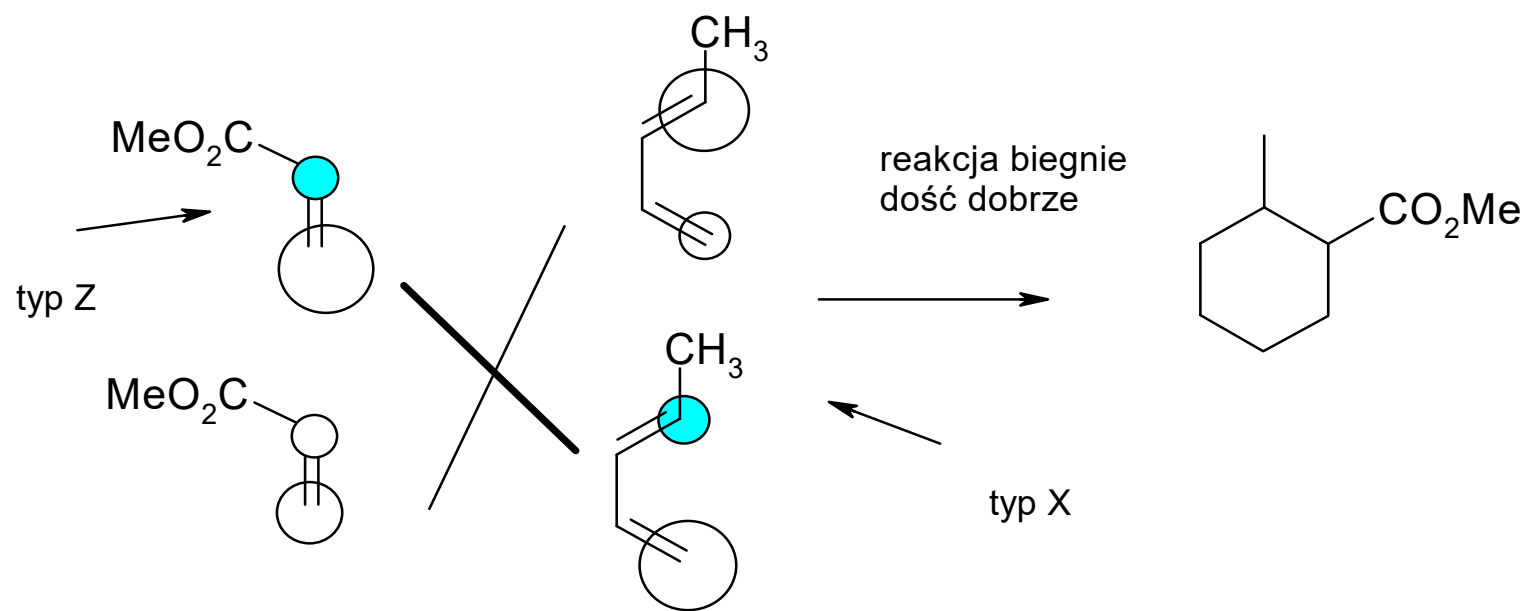
$$\Delta E \sim 1 / (E_1 - E_2)$$



Drugorzędowe efekty stereochemiczne reakcji pericyklicznych

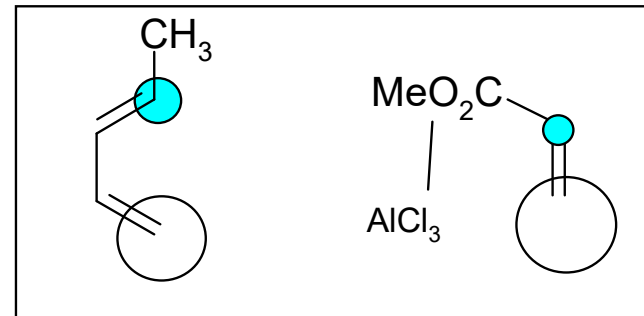
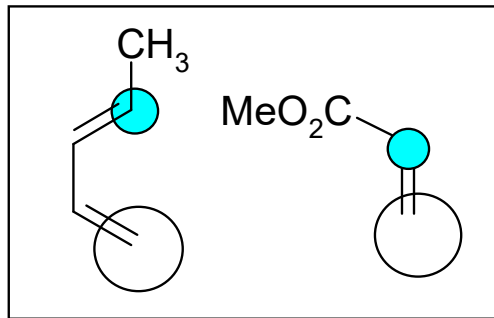
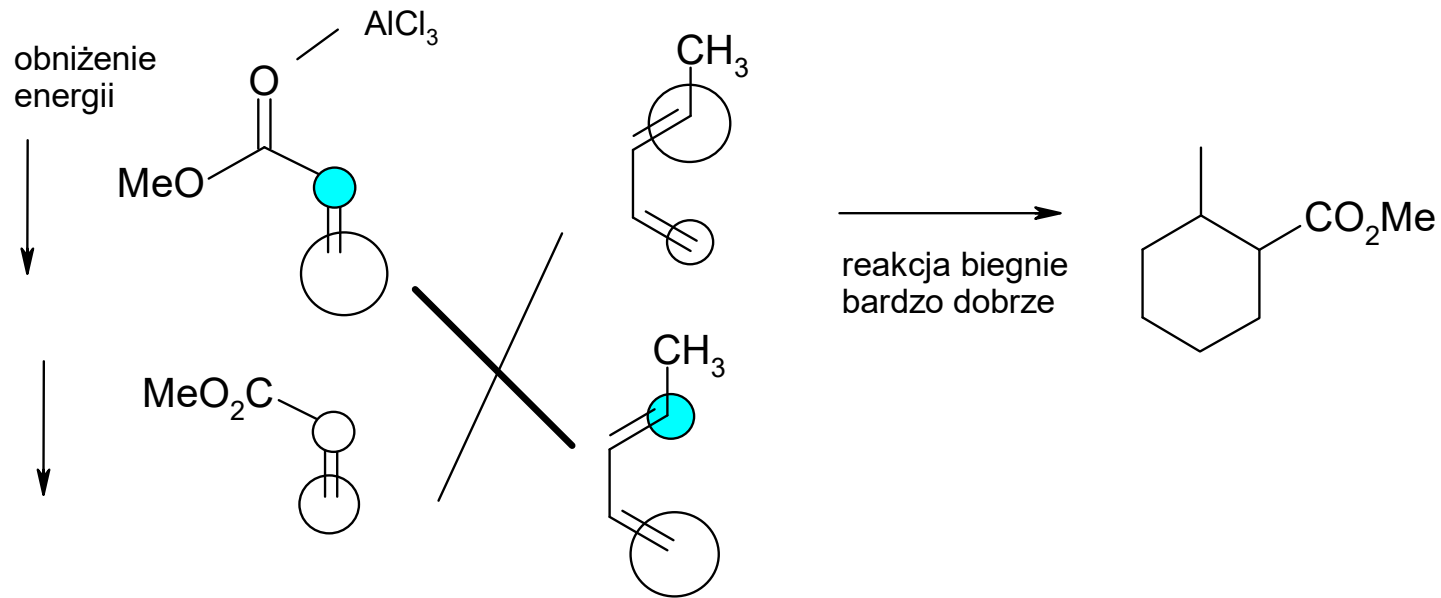


Kataliza reakcji Dielsa-Aldera kwasami Lewisa



+ 10% izomeru 'meta'

Kataliza reakcji Dielsa-Aldera kwasami Lewisa



+ 2% izomeru 'meta'