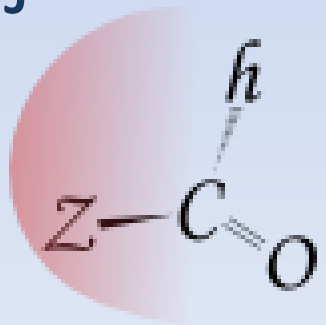
SYNTEZA ASYMETRYCZNA

Dr inż. Tomasz Rowicki

ZAKŁAD CHEMII ORGANICZNEJ

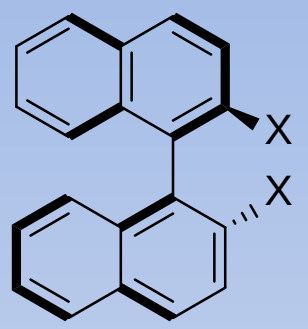


Konsultacje: pon. 14^{15}-16^{00}, pok. 135, G.Ch.

Zagadnienia na dziś

1. Katalizatory „uprzywilejowane”
2. Reakcje syntezy asymetrycznej w warunkach niekonwencjonalnych

Katalizatory „uprzywilejowane”

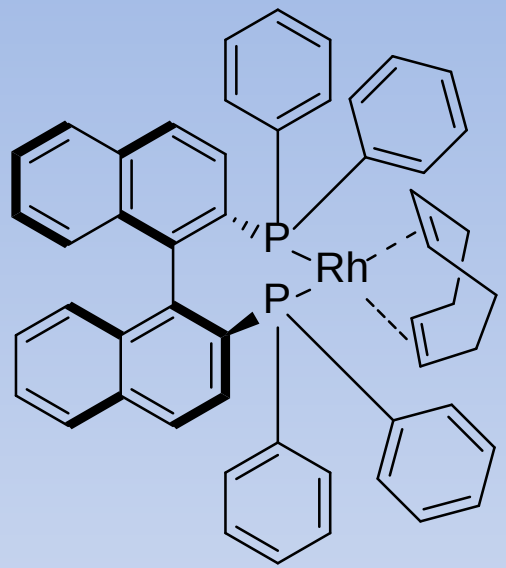


X = OH BINOL
X = PPh_2 BINAP

Pochodne binaftolu

- Cykloaddycja Dielsa-Adlera
- Reakcja aldolowa Mukaiyamy
- Allilowanie aldehydów
- Izomeryzacja alkenów
- Reakcja Hecka

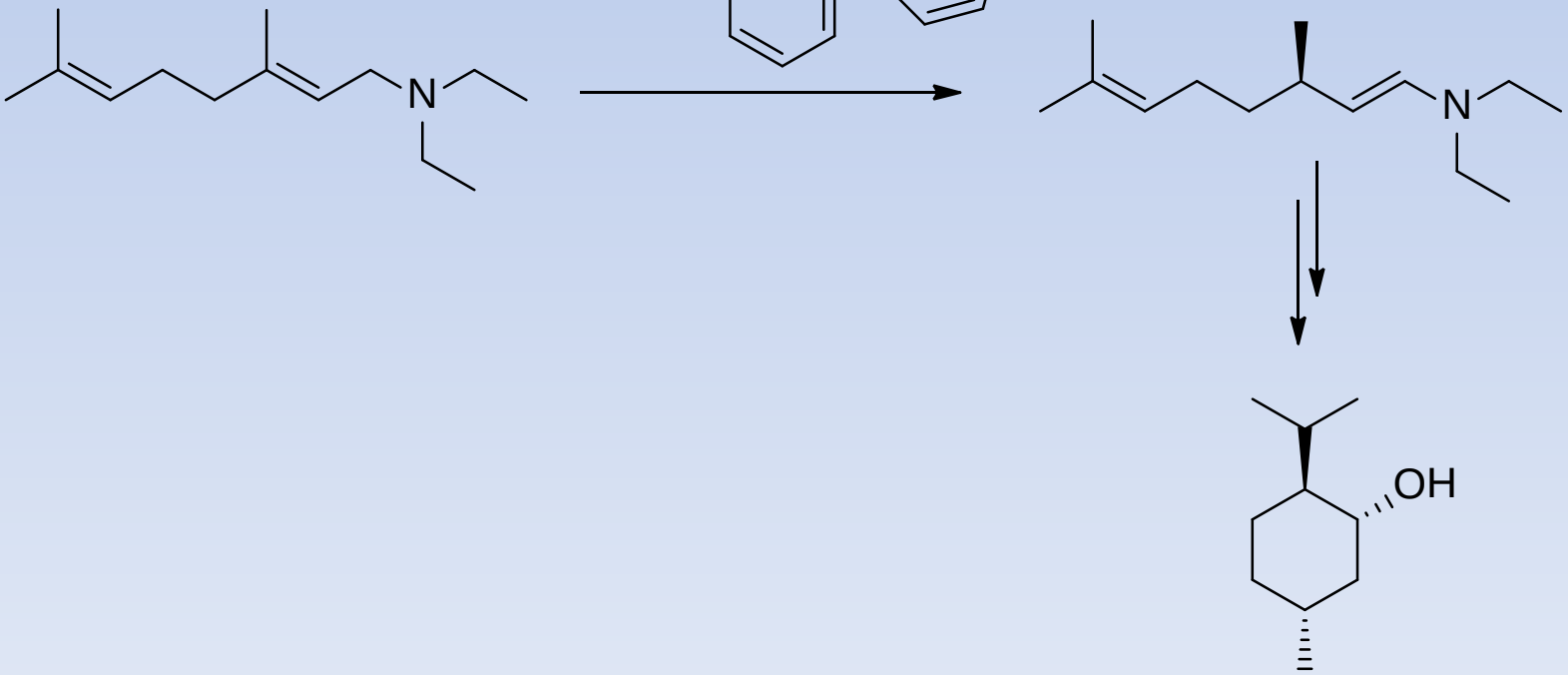
Pochodne binaftolu - izomeryzacja



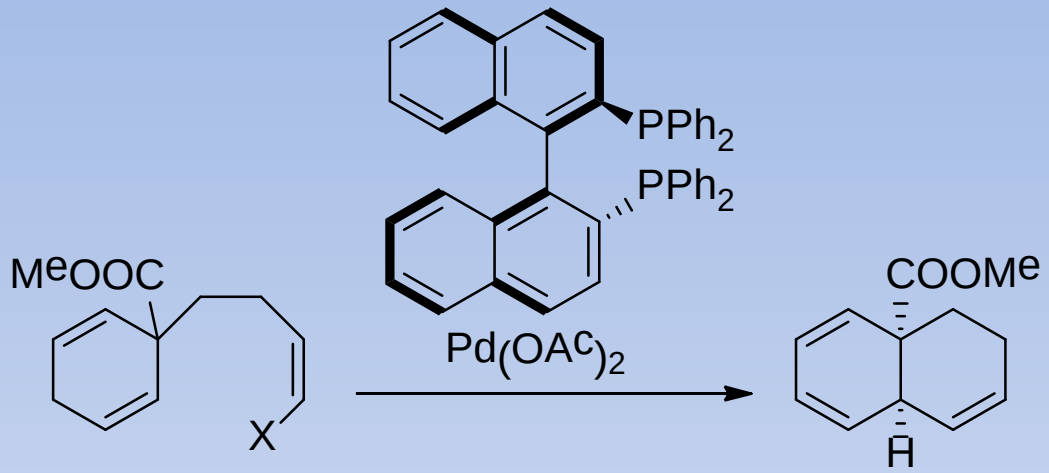
Proces Takasago

- 3000 ton/rok

Ryōji Noyori – nagroda Nobla 2001



Pochodne binaftolu – reakcja Hecka



X = I

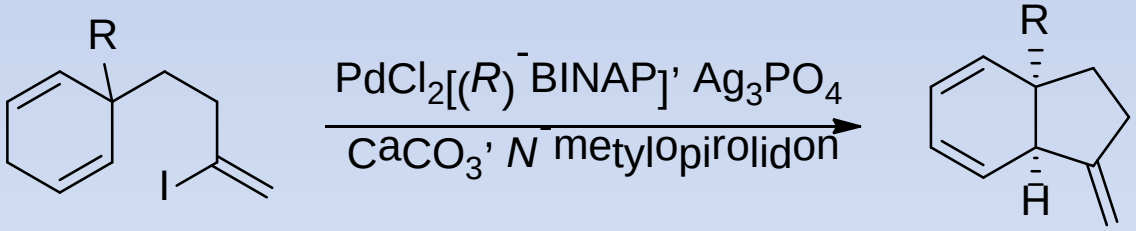
Ag_2CO_3, N-metylopirolidon, 60°C

e.e. = 46%

X = OTf

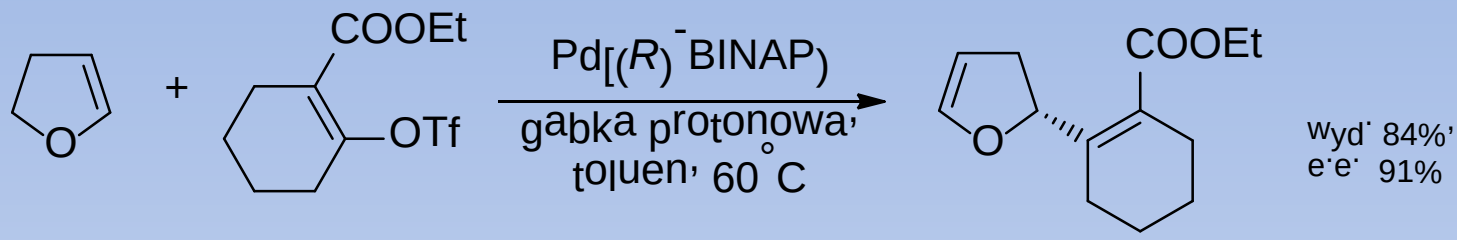
K_2CO_3, toluen, 60°C

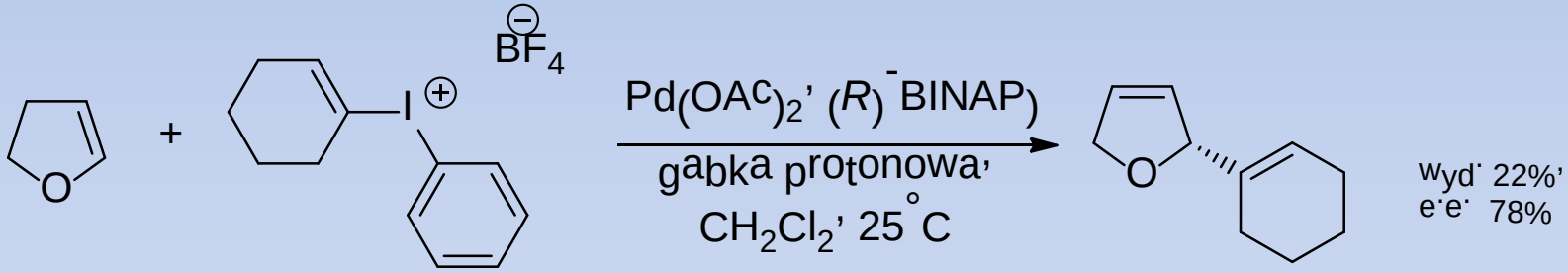
e.e. = 91%

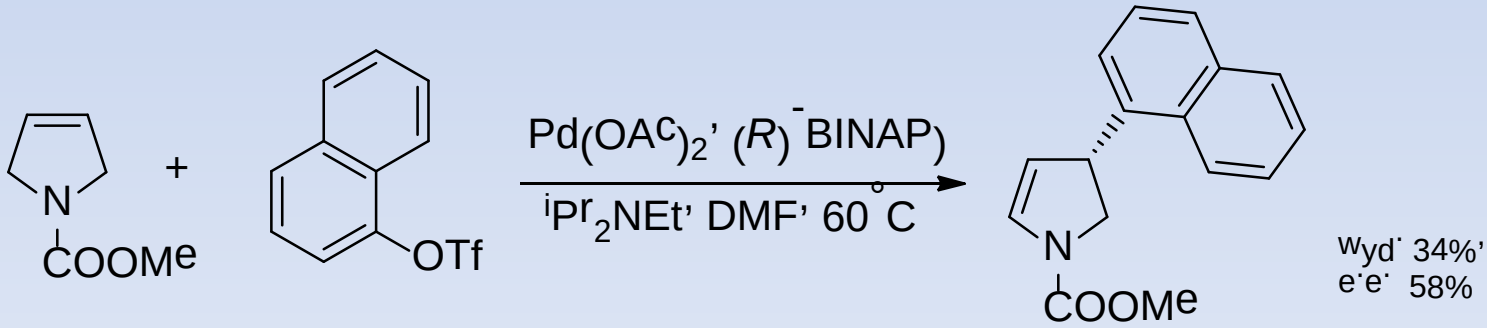


R	CO2Me	CH_2OTBS	CH_2OAc	$CH_2OTBDPS$	CH_2OPiv
e.e. (%)	83	82	84	73	80

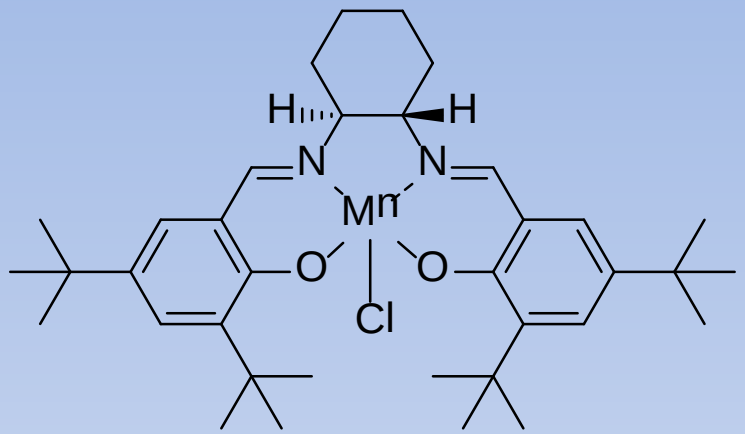
Pochodne binaftolu – reakcja Hecka







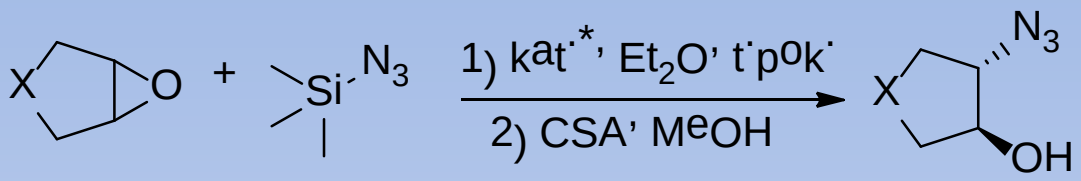
Katalizatory „uprzywilejowane”

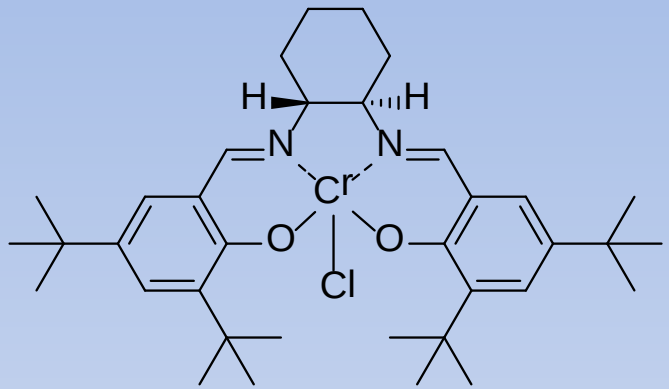


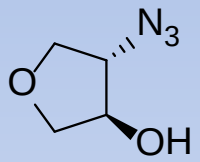
Kompleksy SALEN-owe

- Epoksydowanie alkenów
- Otwieranie epoksydów
- Cykloaddycja Dielsa-Adlera
- Reakcja Streckera
- Reakcja Michaela

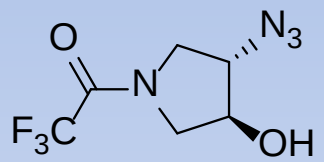
Kompleksy SALEN - otwieranie epoksydów



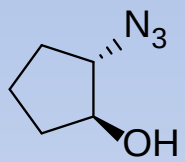




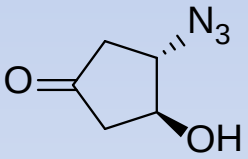
wyd. 96%
e.e. 97%



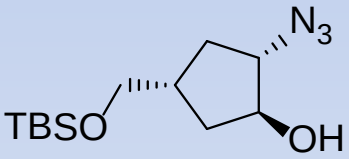
wyd. 87%
e.e. 95%



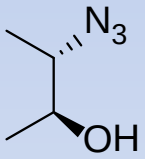
wyd. 97%
e.e. 93%



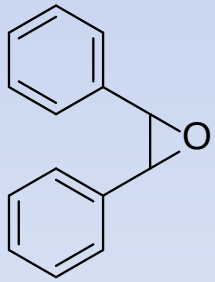
wyd. 77%
e.e. 94%

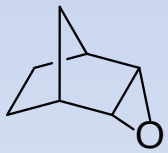


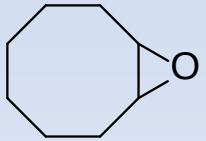
wyd. 77%
e.e. 94%

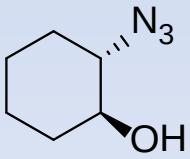


wyd. 65%
e.e. 82%

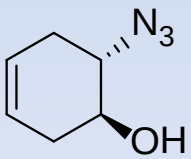




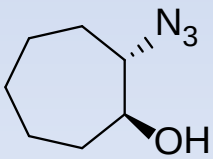




wyd. 95%
e.e. 85%

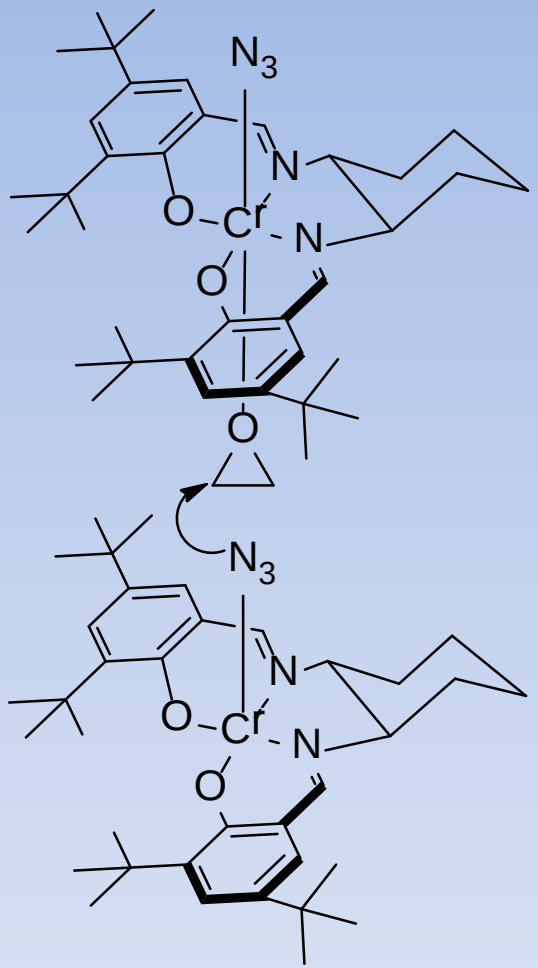


wyd. 85%
e.e. 92%



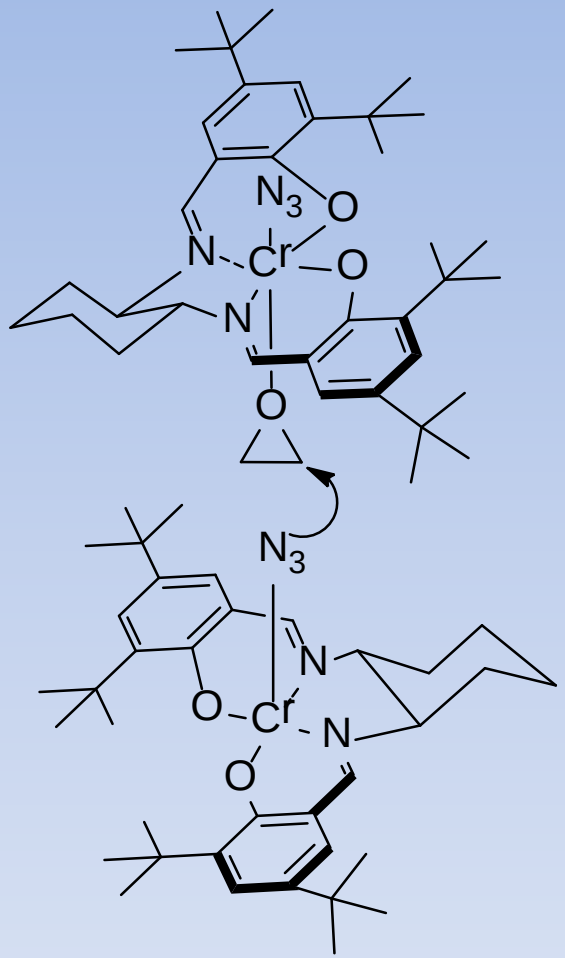
wyd. 99%
e.e. 42%

Kompleksy SALEN - otwieranie epoksydów



„głowa do głowy”

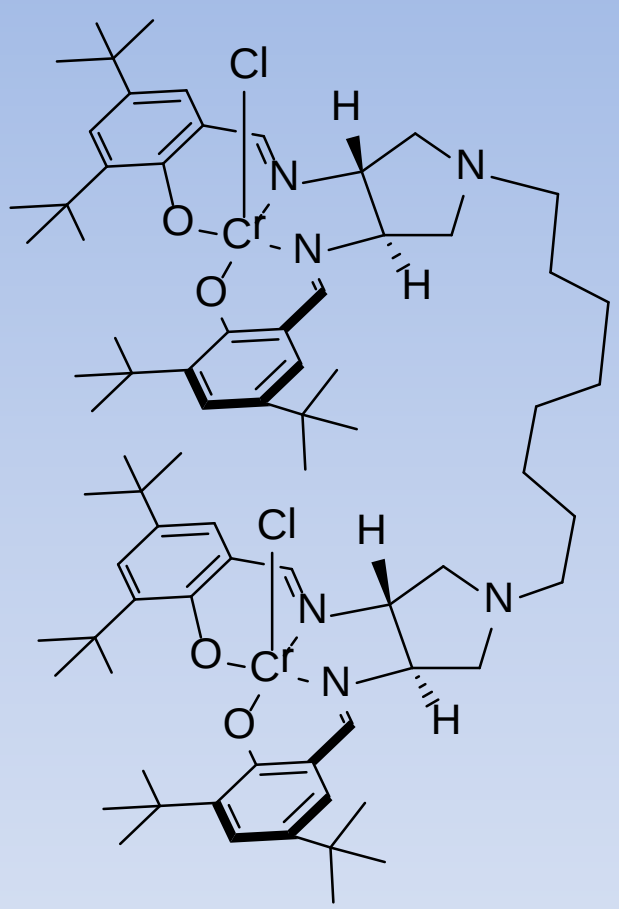
- **nie**aktywny

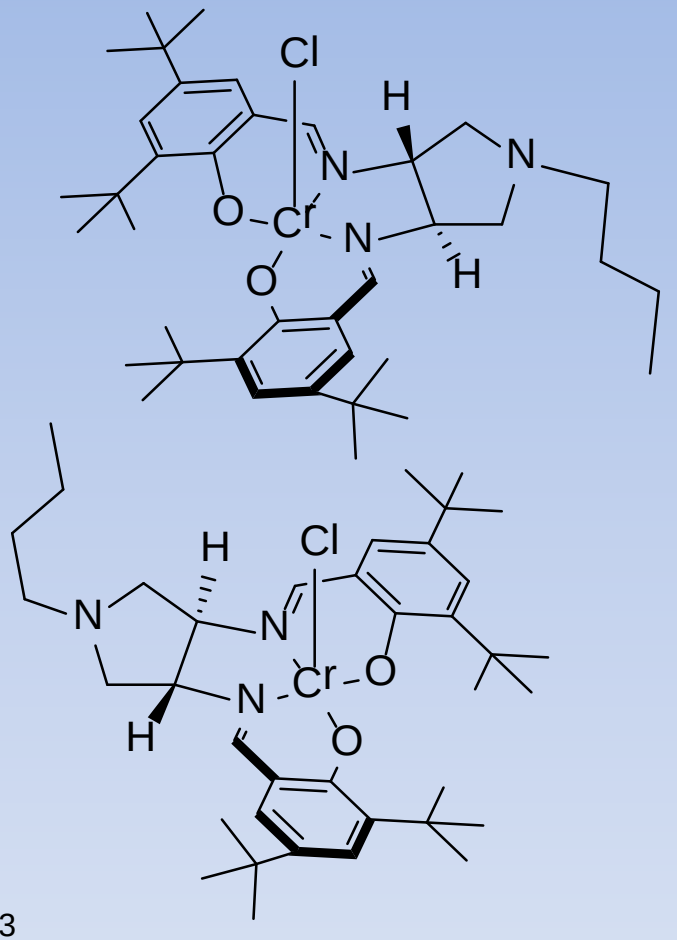


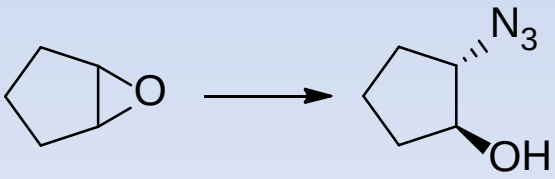
„głowa do ogona”

- **aktywny**

Kompleksy SALEN - otwieranie epoksydów



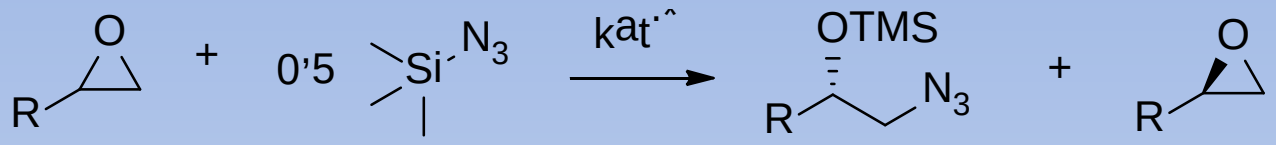


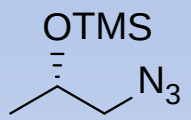


e.e. = 8%

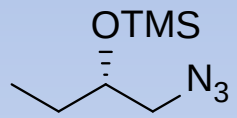
e.e. = 90%

Kompleksy SALEN - otwieranie epoksydów

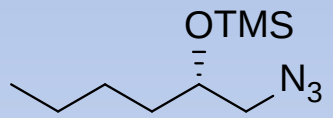




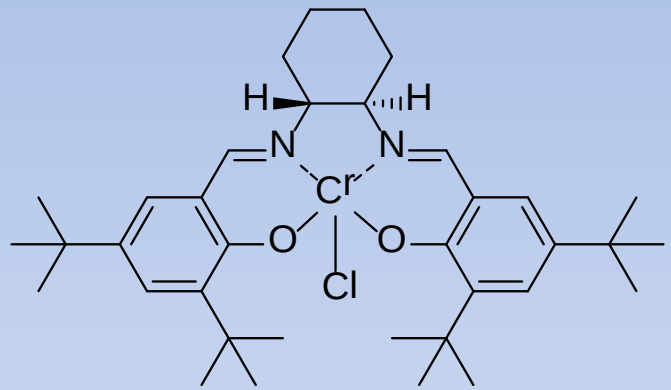
e·e· = 97%

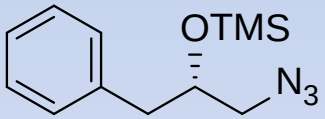


e·e· = 97%

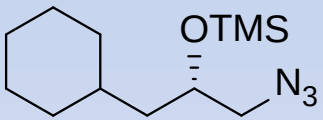


e·e· = 97%

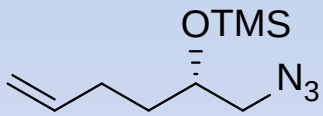




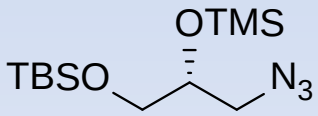
e·e· = 93%



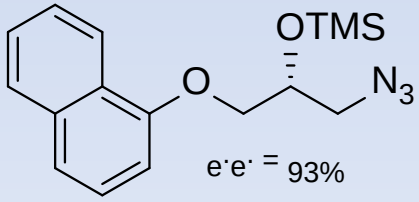
e·e· = 97%



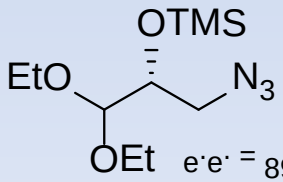
e·e· = 98%



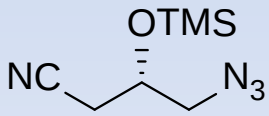
e·e· = 96%



e·e· = 93%

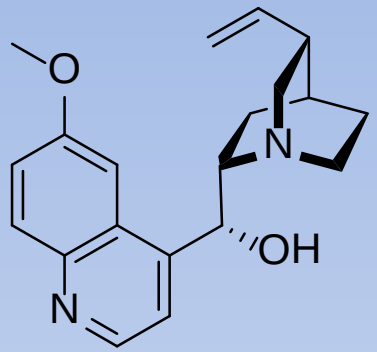


e·e· = 89%

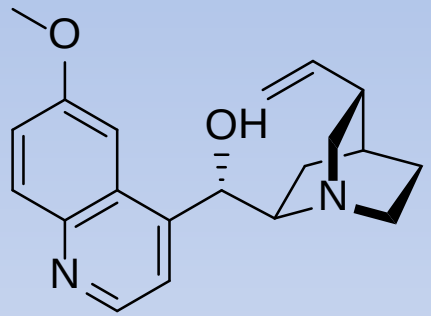


e·e· = 92%

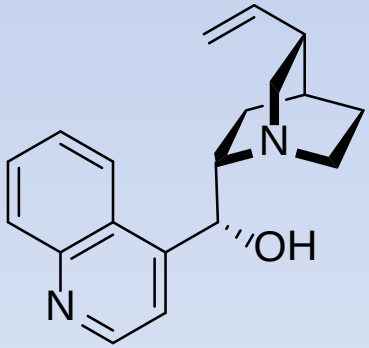
Katalizatory „uprzywilejowane”



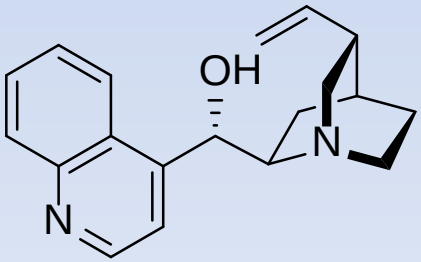
chininа



chinidyna



cynchonidyna

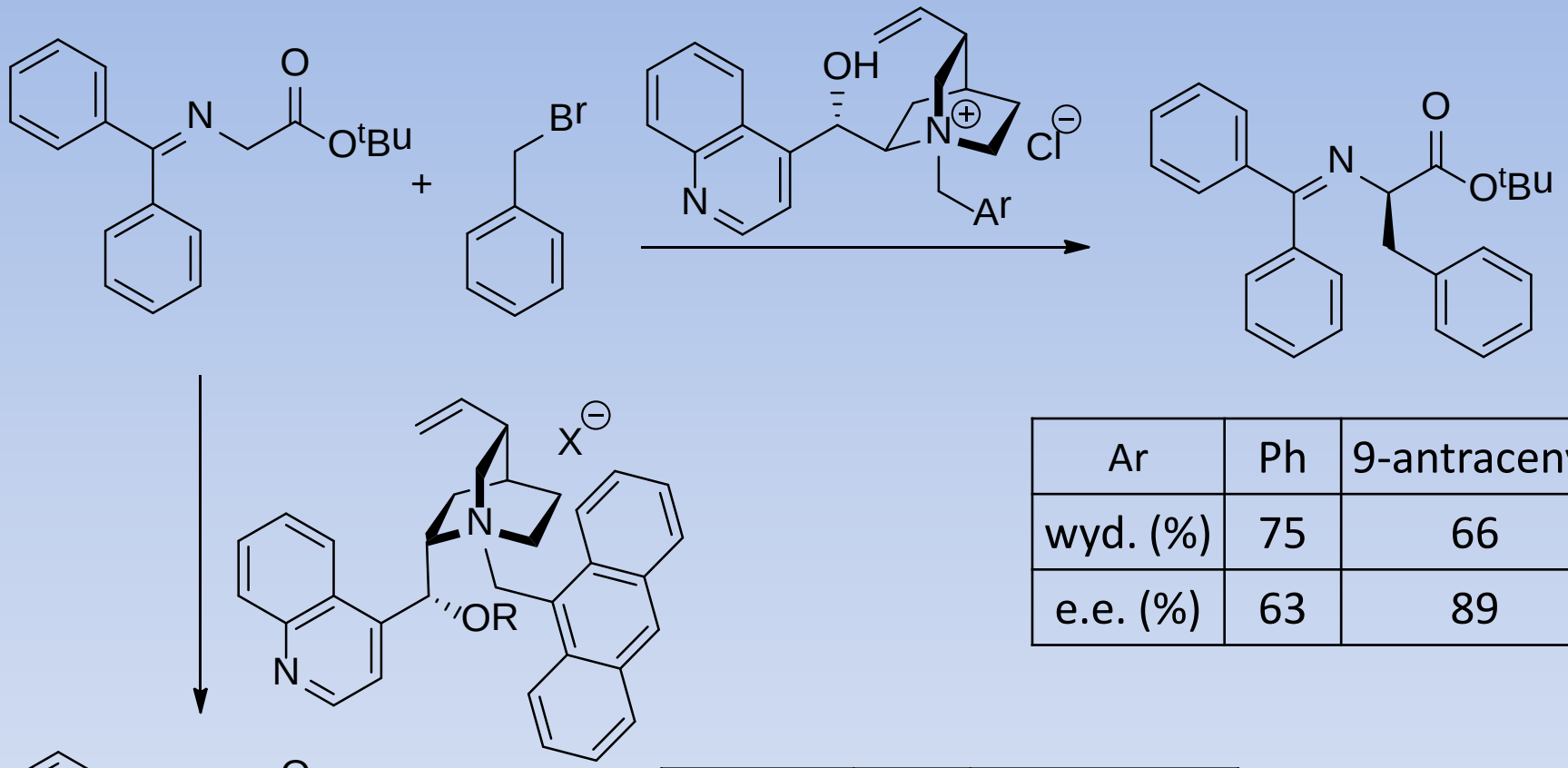


cynchonina

Alkaloidy chinowca i ich pochodne

- Dihydroksylowanie alkenów
- Acylowanie
- Redukcja w układzie heterofazowym
- Kataliza przeniesienia międzyfazowego

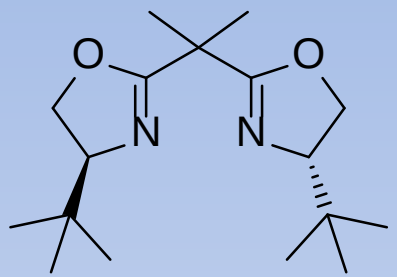
Pochodne alkaloidów chinowca



Ar	Ph	9-antracenyl
wyd. (%)	75	66
e.e. (%)	63	89

R	H	allil
X	Cl	Br
wyd. (%)	68	91
e.e. (%)	84	94

Katalizatory „uprzywilejowane”

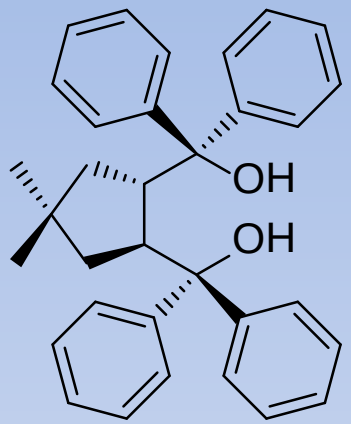


Bis(oksazoliny)

Bis(oksazoliny) „Box-y”

- Cykloaddycja Dielsa-Adlera
- Reakcja aldolowa Mukaiyamy
- Reakcja Michaela
- Synteza cyklopropanów
- Synteza azyrydyn

Katalizatory „uprzywilejowane”

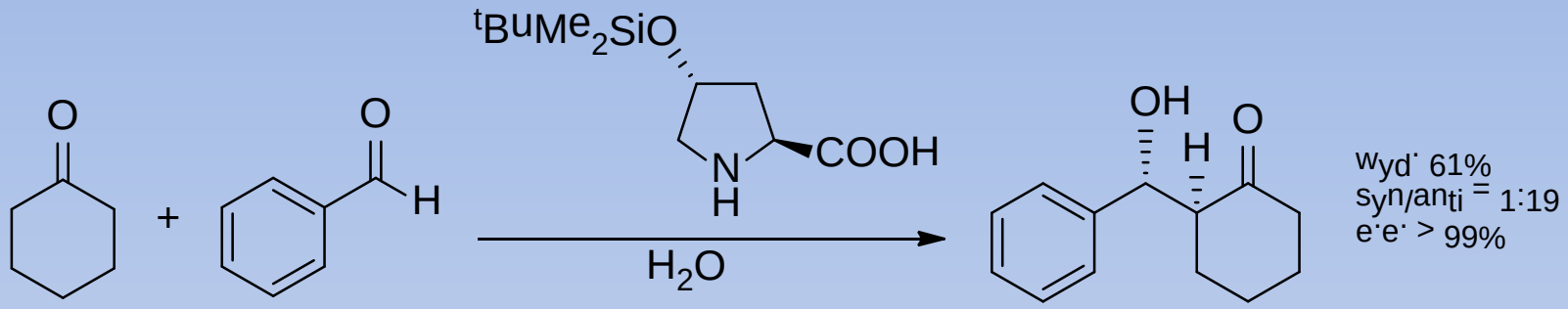


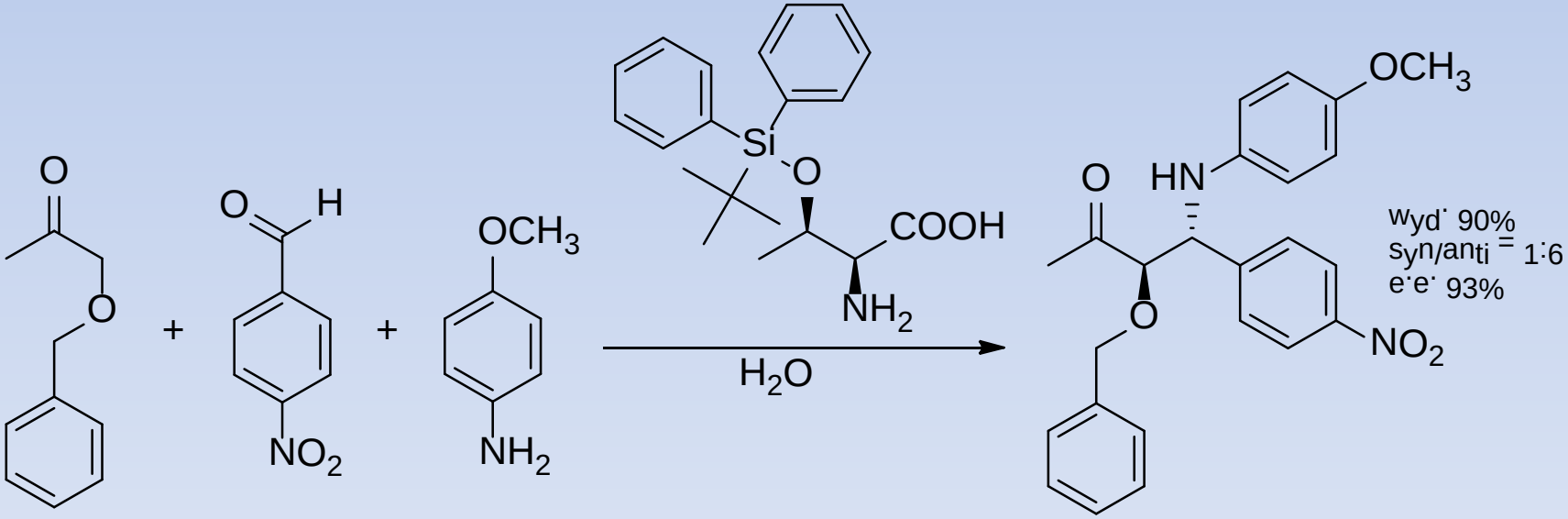
TADDOL

TADDOL i jego pochodne

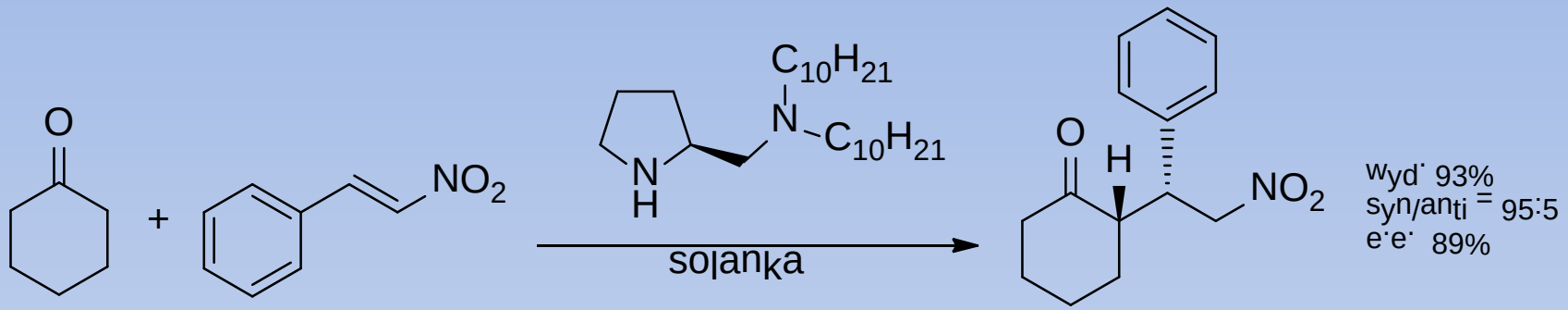
- Cykloaddycja Dielsa-Adlera
- Alkilowanie aldehydów
- Alkoholiza estrów
- Jodolaktonizacja

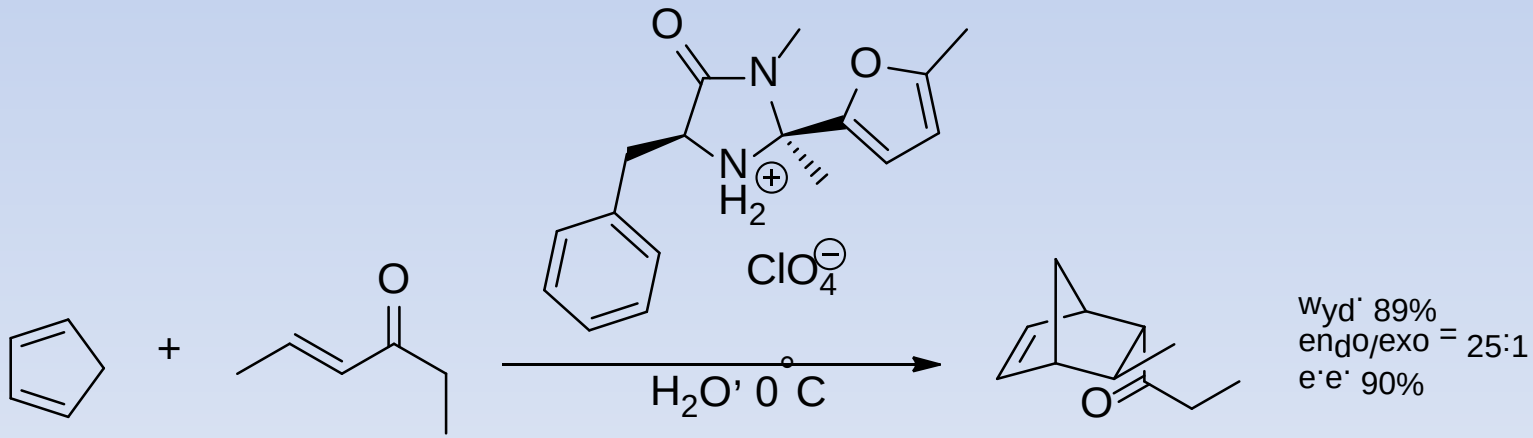
Synteza asymetryczna w wodzie



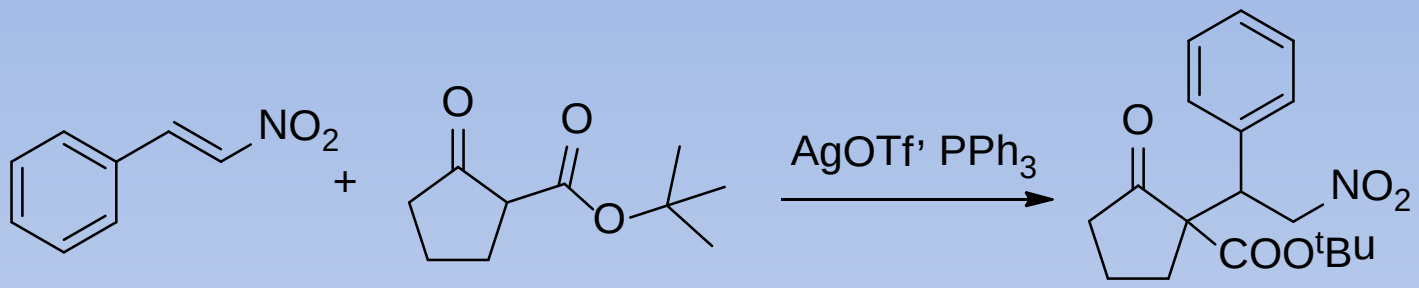


Synteza asymetryczna w wodzie



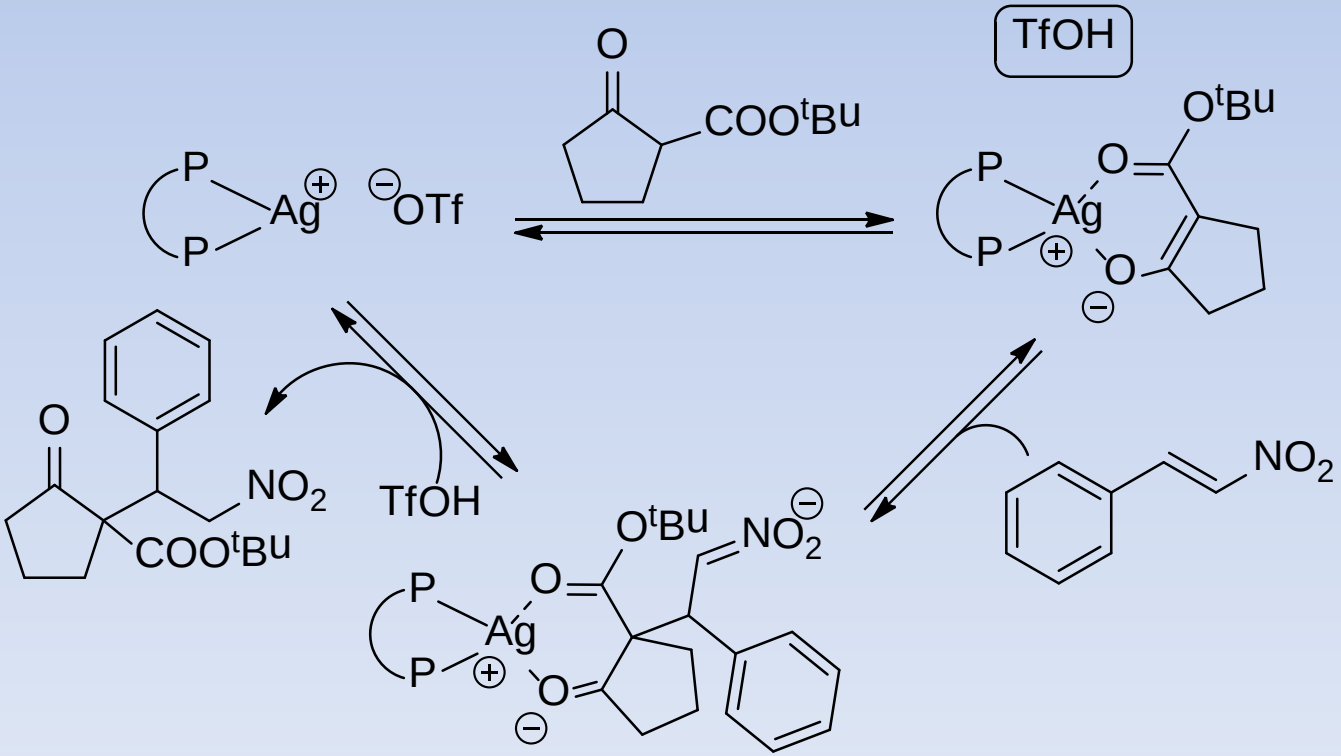


Synteza asymetryczna w wodzie

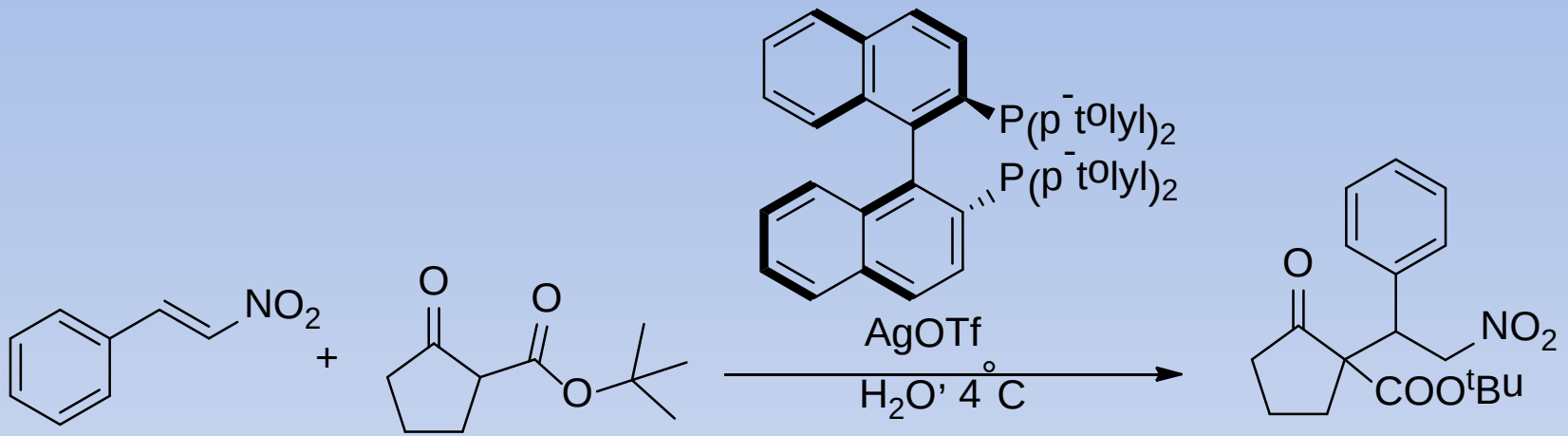


H_2O wyd. = 90%

CH_2Cl_2 lub THF, lub bez rozp. wyd. < 10%



Synteza asymetryczna w wodzie



wyd. 71%
d.r. = 77:23
e.e. 78%

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SYNTEZA ASYMETRYCZNA

Dziękuję za uwagę

Konsultacje: pon. 14^{15}-16^{00}, pok. 135, G.Ch.