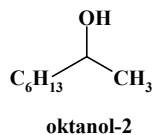
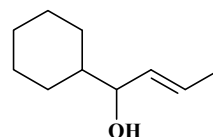


Wykład 7 STEREOCHEMIA ORGANICZNA Sławomir Jarosz

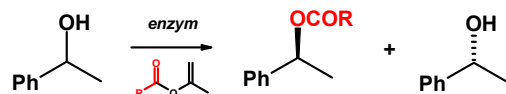
Klasyczny rozdział racematu



Kinetyczny rozdział racematu



Dynamiczny rozdział racematu

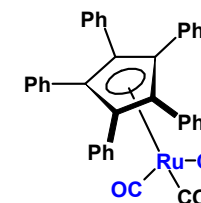


Enzymatyczny rozdział: Bäckvall and co-workers,
Chem. Eur. J. **2006**, *12*, 225-232
Ogólnie o enzymach w biotransformacjach:
K. Faber, *Angew.* **2008**, *47*, 8782-8793

enantioselektywne
właściwości enzymu

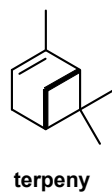
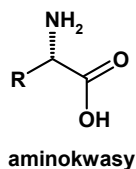
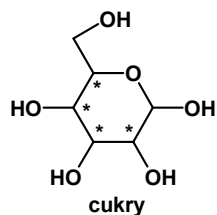
$$E = \frac{\ln[1 - c(1 + ee_p)]}{\ln[1 - c(1 - ee_p)]}$$

c = konwersja,
ee_p - nadmiar
enantjomeryczny
produktu



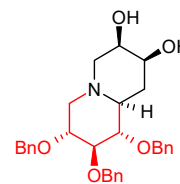
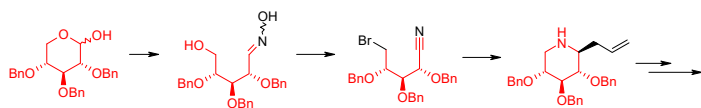
Przeniesienie chiralności z łatwo dostępnych optycznie czystych związków naturalnych na produkt(y)

Chiron approach



Jak otrzymać związki optycznie czynne?

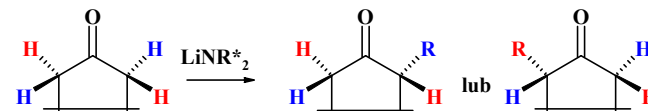
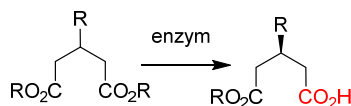
Chiron approach



Ze związków achiralnych

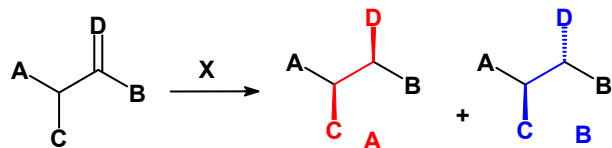
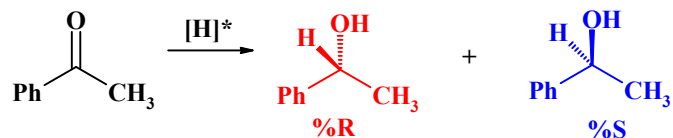
Synteza asymetryczna, Kataliza (w tym organokataliza), Reakcje diastereoselektywne z użyciem pomocników chiralnych

Desymetryzacja związków symetrycznych

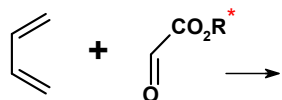
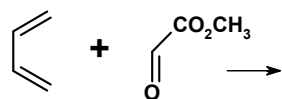
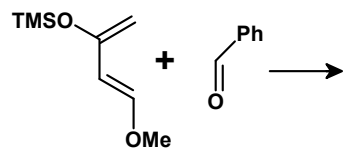
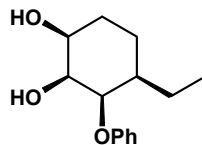


Planowanie syntez związków optycznie czynnych

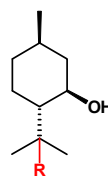
Wykorzystanie reakcji enancjoróżnicujących i diastereoróżnicujących



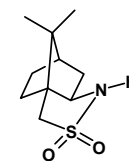
Planowanie syntez związków optycznie czynnych



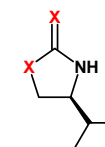
Pomocniki chiralne (chiral auxiliary)



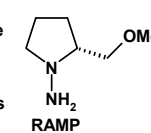
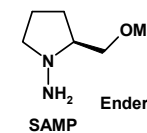
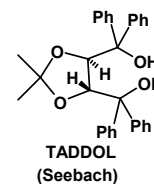
R = H (mentol)
R = Ph 8-fenyliomentol (Corey, 1978)



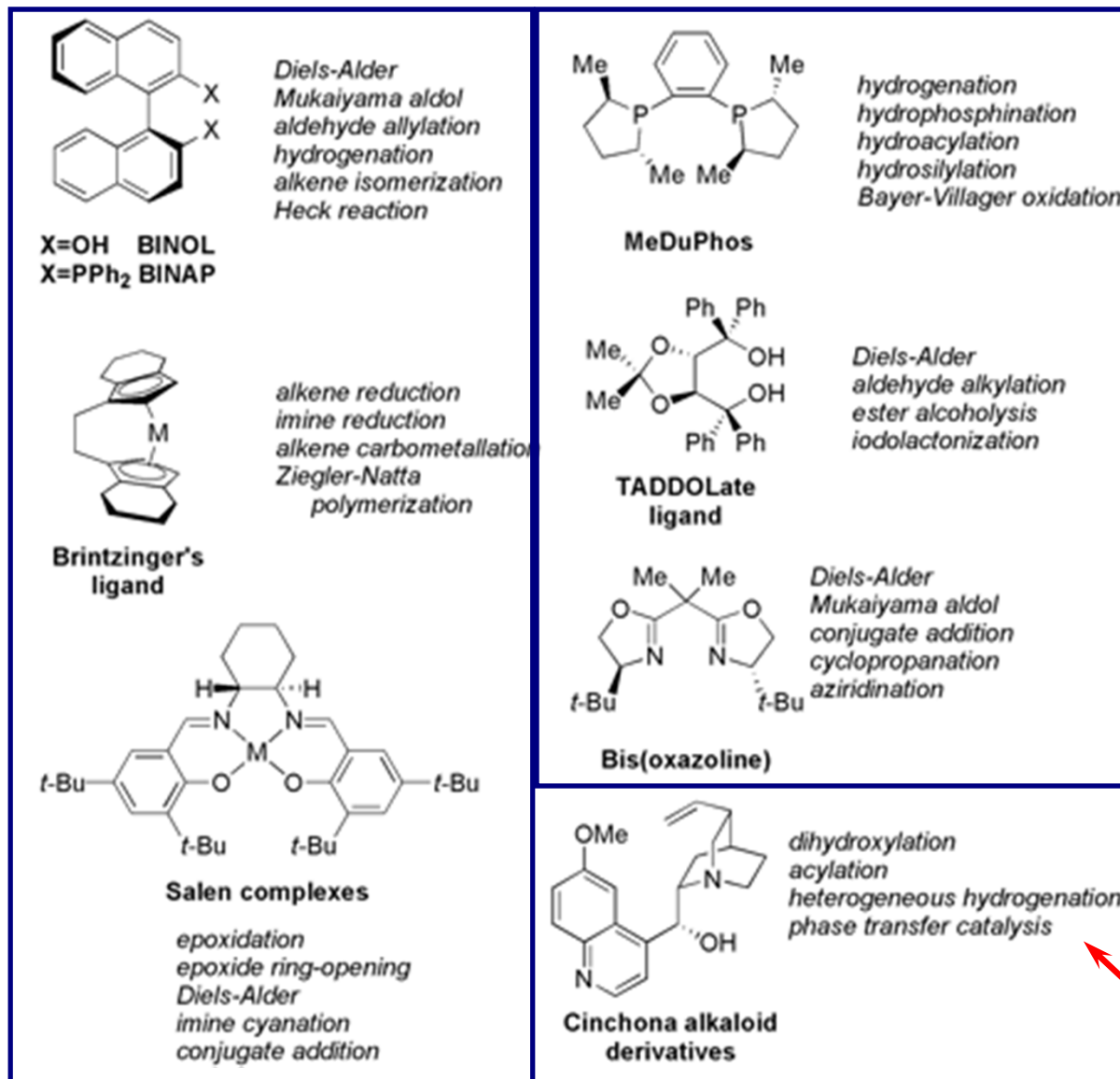
sultam Oppolzera



Evans aux.
X = O, S



Synteza asymetryczna (privileged catalysts)



Symetria C₂

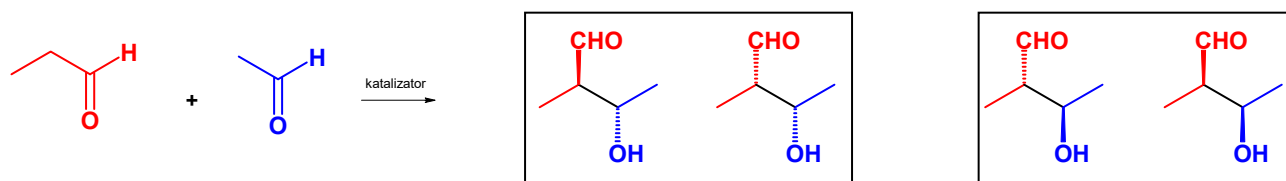
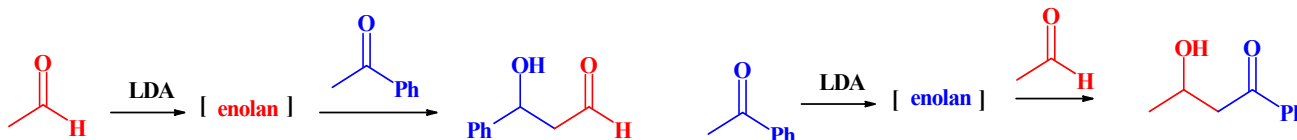
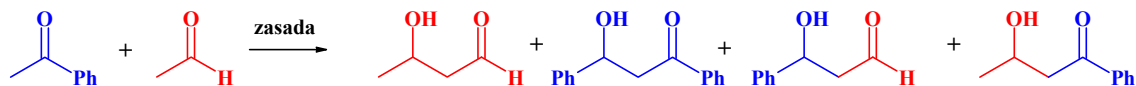
Symetria C₁

K. Maruoka, T. Ooi
Chem. Rev. 2003, 3013

Small-Molecule C-H donors in Asymmetric Catalysis; A.G. Doyle, E.N. Jacobsen, *Chem. Rev.* **2007**, 107 (12), 5713-5743

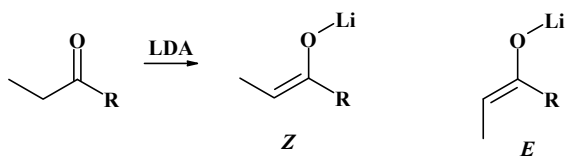
Caly zeszyt 12 Chem. Rev. 2007 rok

Reakcja aldolowa

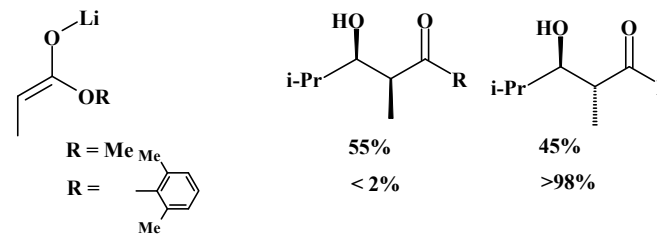
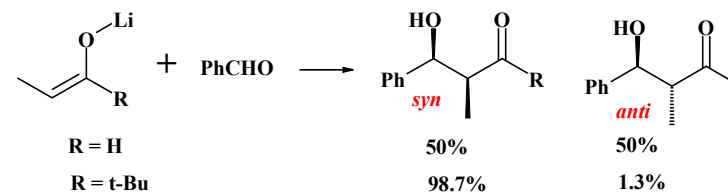


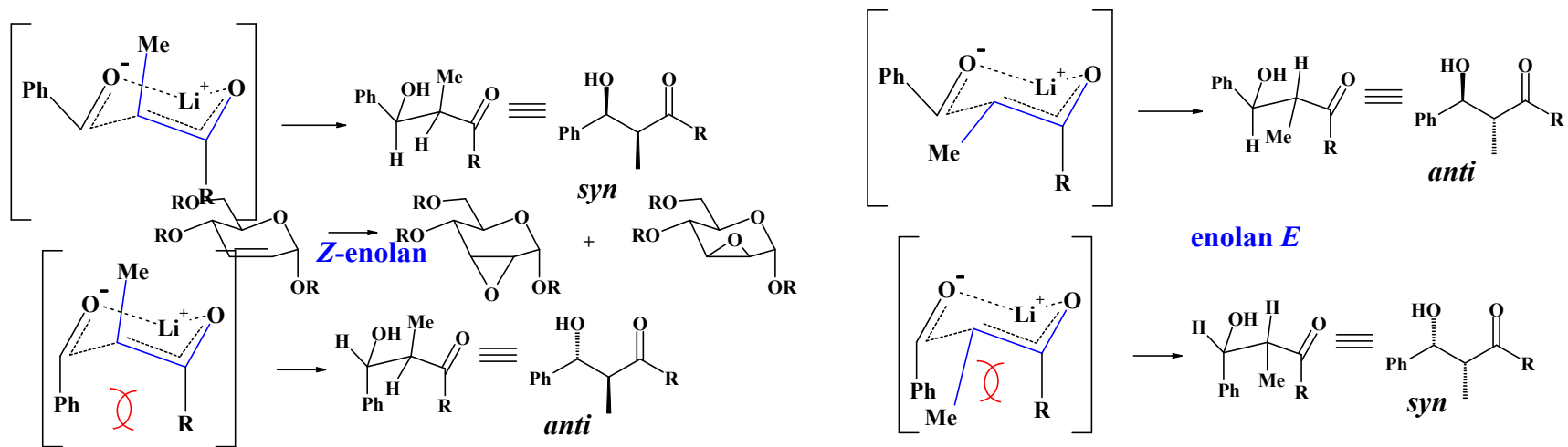
tworzenie enolanów

kontrola kinetyczna szbciej tworzą się izomery Z
szczególnie gdy mamy duże (stosunkowo) podstawniki

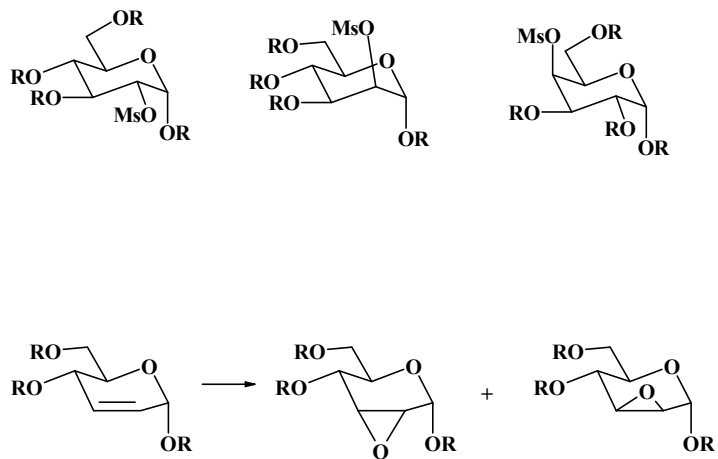


mały R = OMe Z = 3% E = 97%
duży R = Ph Z = 100% E = 0%

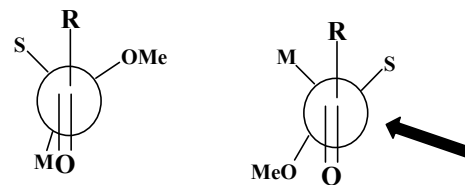
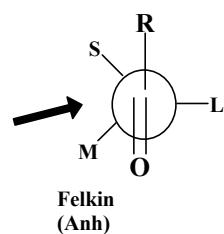
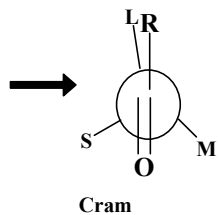
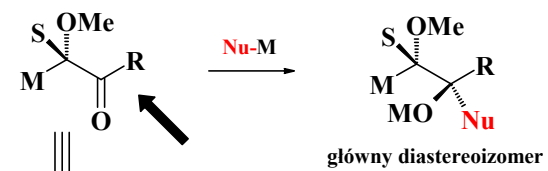
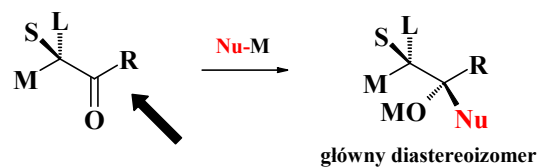




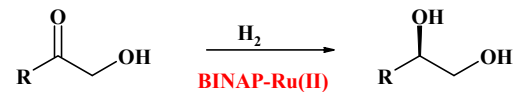
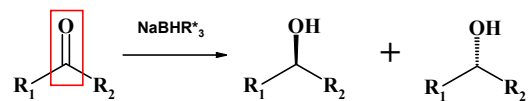
Reakcije substitucije – eliminacije



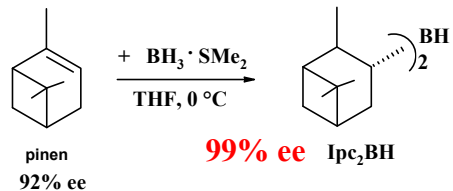
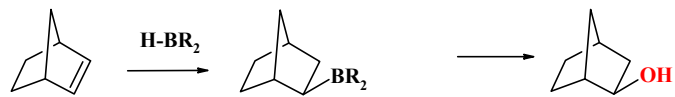
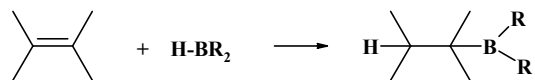
Addycja do grupy karbonylowej



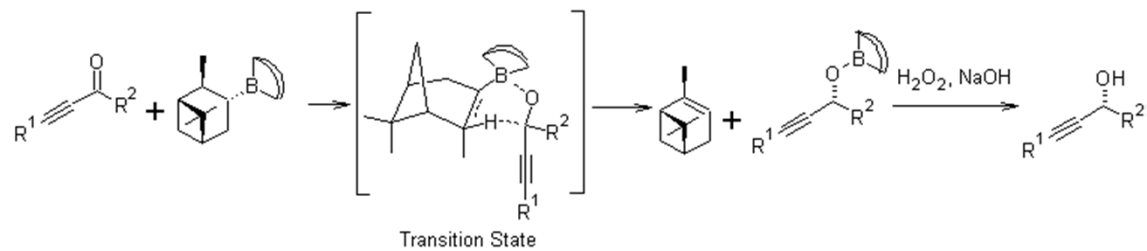
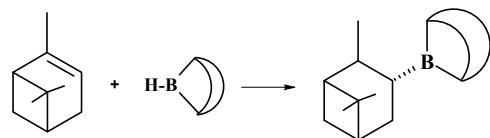
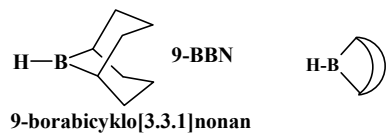
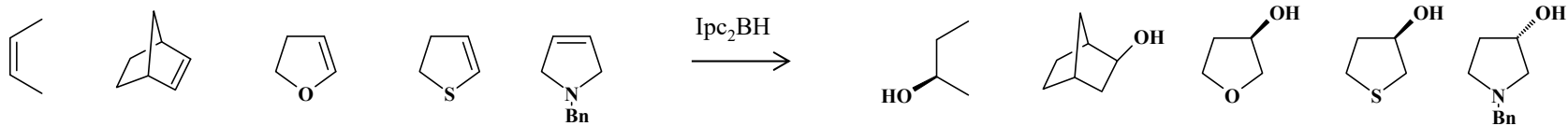
Jak dokonać asymetrycznej redukcji grupy karbonylowej ????



Asymetryczne borowodorowanie wiązań C=C



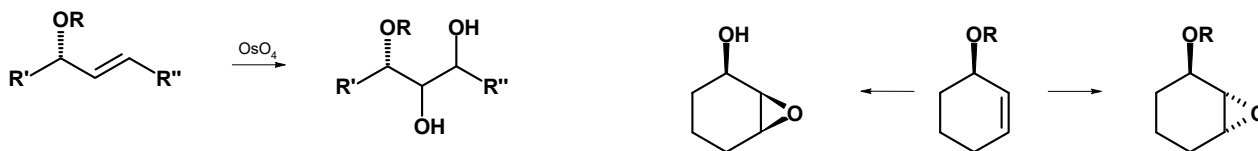
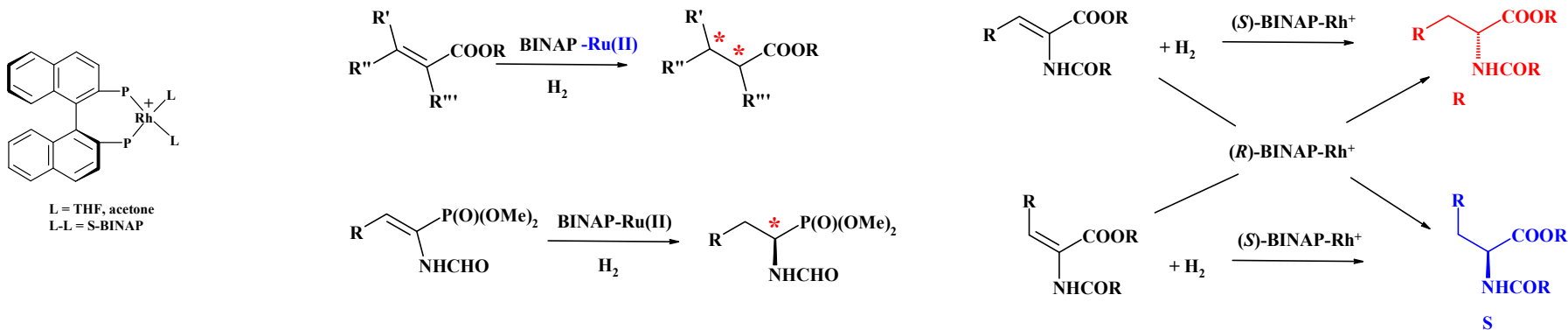
H.C. Brown, P.V. Ramachandran, *Pure Appl. Chem.*, 1994, 66, 201-212



Katalityczna enancjoselektywna redukcja wiązań C=C

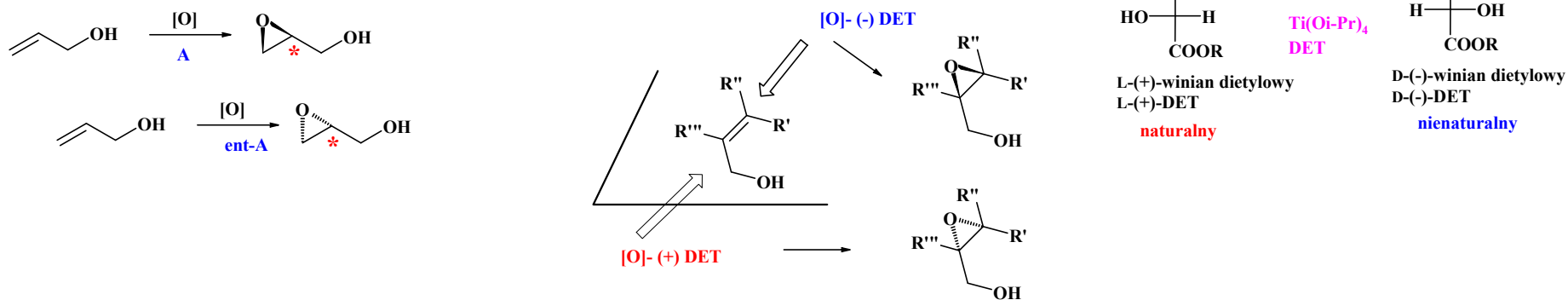
Kompleksy BINAP'u do **ENANCJOSELEKTYWNEJ** redukcji wiązań podwójnych

BINAP tworzy kompleksy z metalami przejściowymi, przenosząc na nie chiralność

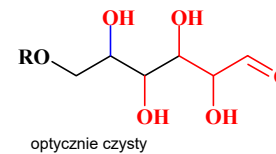
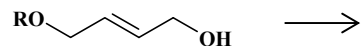


Kishi, et. al. Tetrahedron Lett. 1983, 3943; Tetrahedron, 1984, 2247

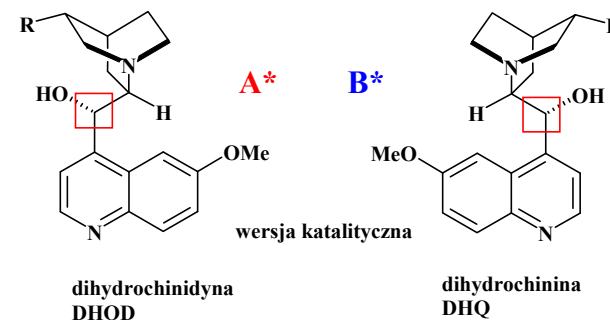
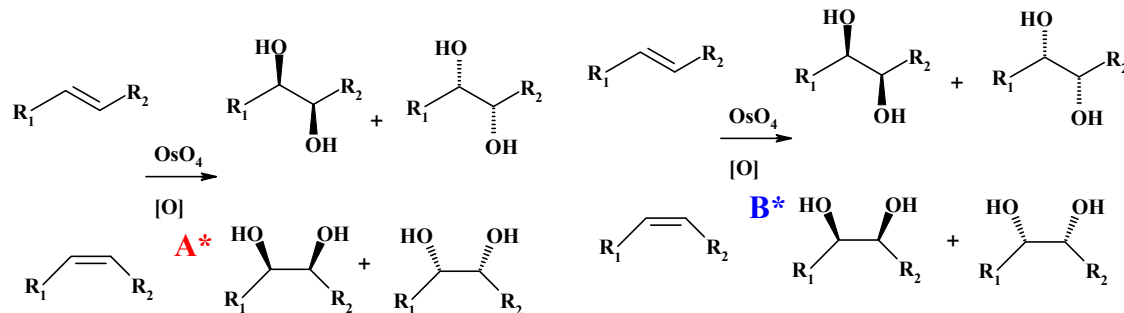
Asymetryczne epoksydowanie alkoholi allilowych



Synteza nienaturalnych cukrów (Sharpless Masamune)



Asymetryczna *cis*-hydroksylacja. Sharpless et al. Chem. Rev. 1994 2483-2547



wersja enancjoselektywna

