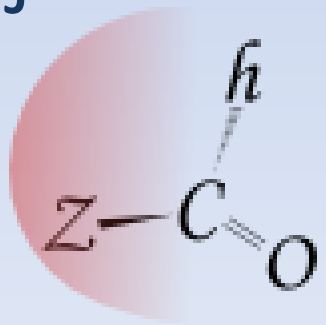
SYNTEZA ASYMETRYCZNA

Dr inż. Tomasz Rowicki

ZAKŁAD CHEMII ORGANICZNEJ



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

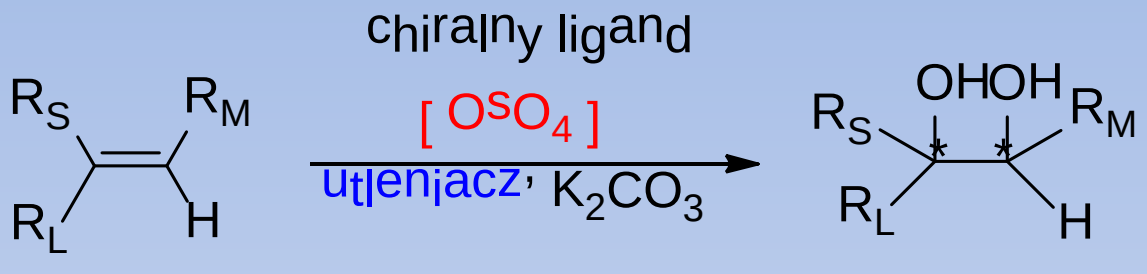
Zagadnienia na dziś

1. Utlenianie wiązań podwójnych C=C

   - asymetryczne dihydroksylowanie

   - asymetryczne aminohydroksylowanie

Dihydroksylowanie Sharpless'a



OsO_4

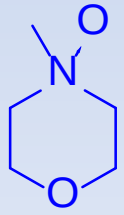
NDS 0,002 mg/m³ ,NDSCh 0,006 mg/m³ !!!

$K_2OsO_2(OH)_4$

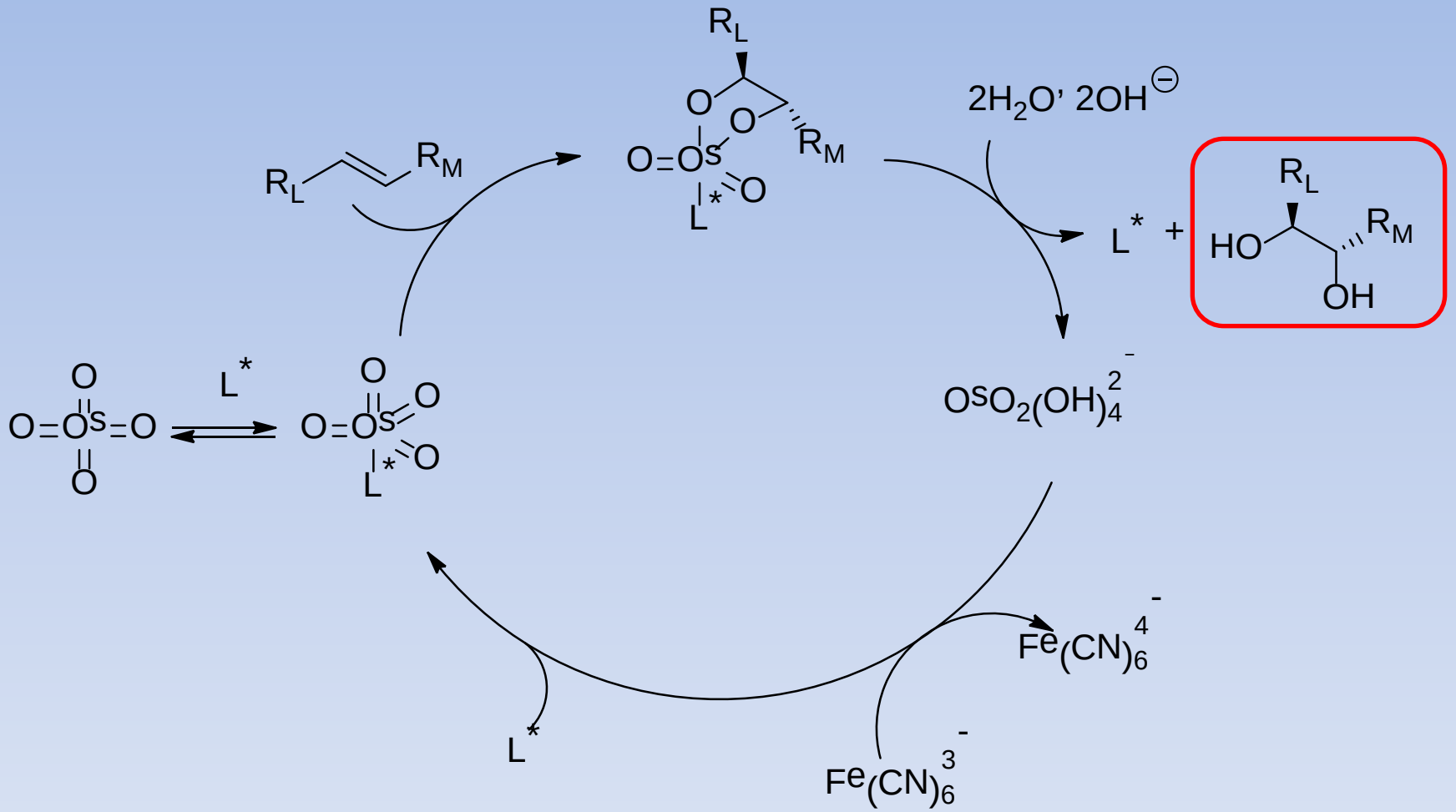
utleniacz

$K_3Fe(CN)_6$, N-tlenek-N-metylomorfoliny

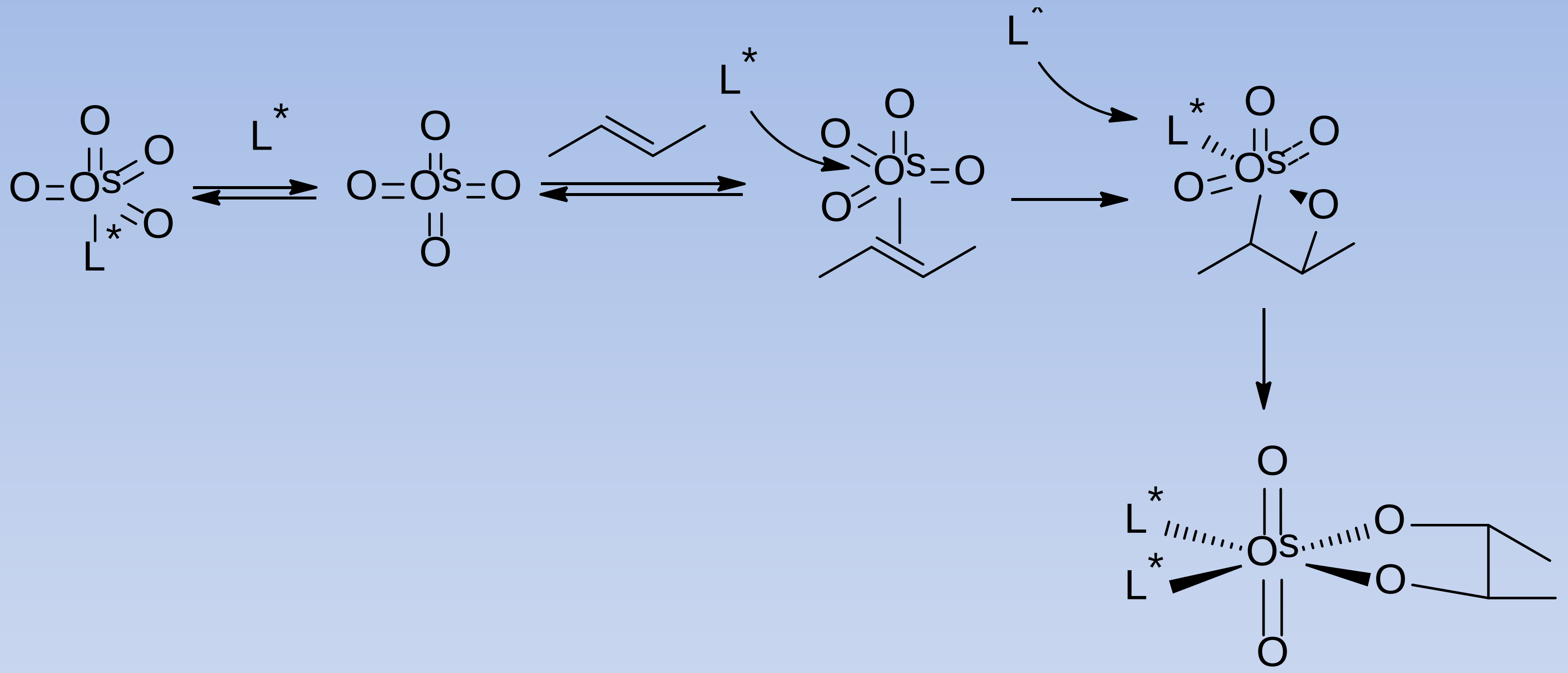
KCN NDSP 5 mg/m³

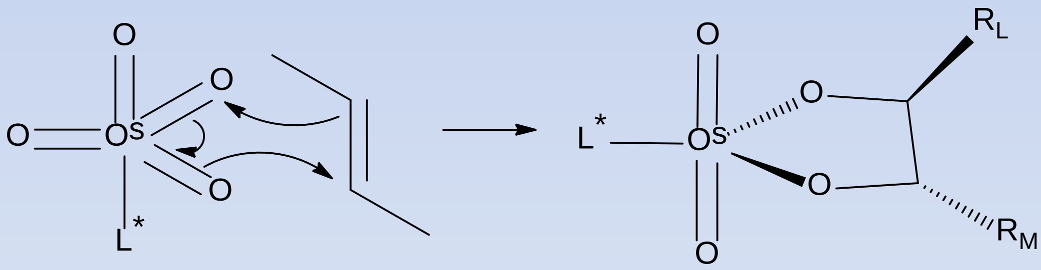


Dihydroksylowanie Sharpless'a

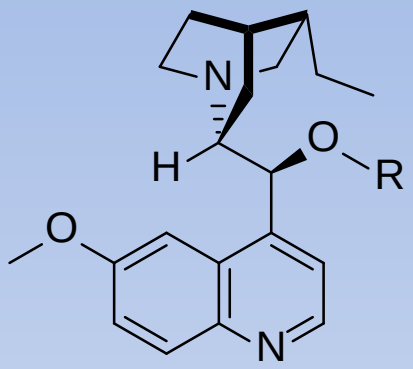


Dihydroksylowanie Sharpless'a

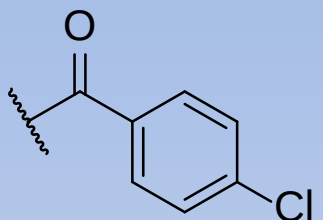




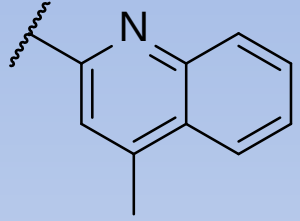
Dihydroksylowanie Sharpless'a



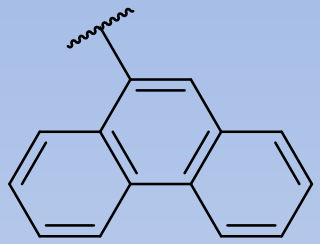
DHQD



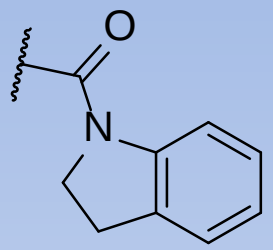
CLB



MEQ

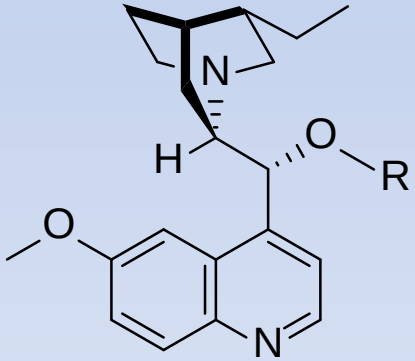


PHN



IND

R dla katalizatorów I-ej generacji



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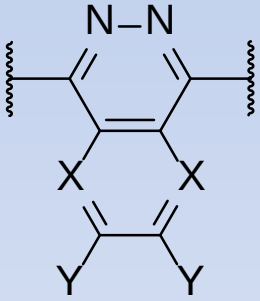
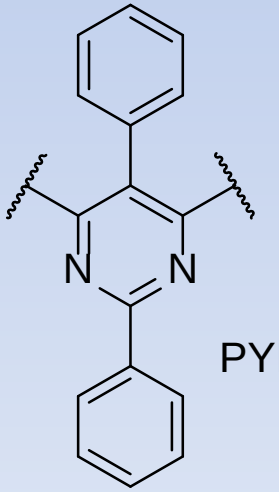
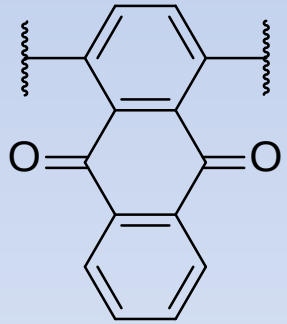


X = CH, Y = H: PHAL
X = CH, Y = Ph: DP PHAL
X = N, Y = Ph: DPP



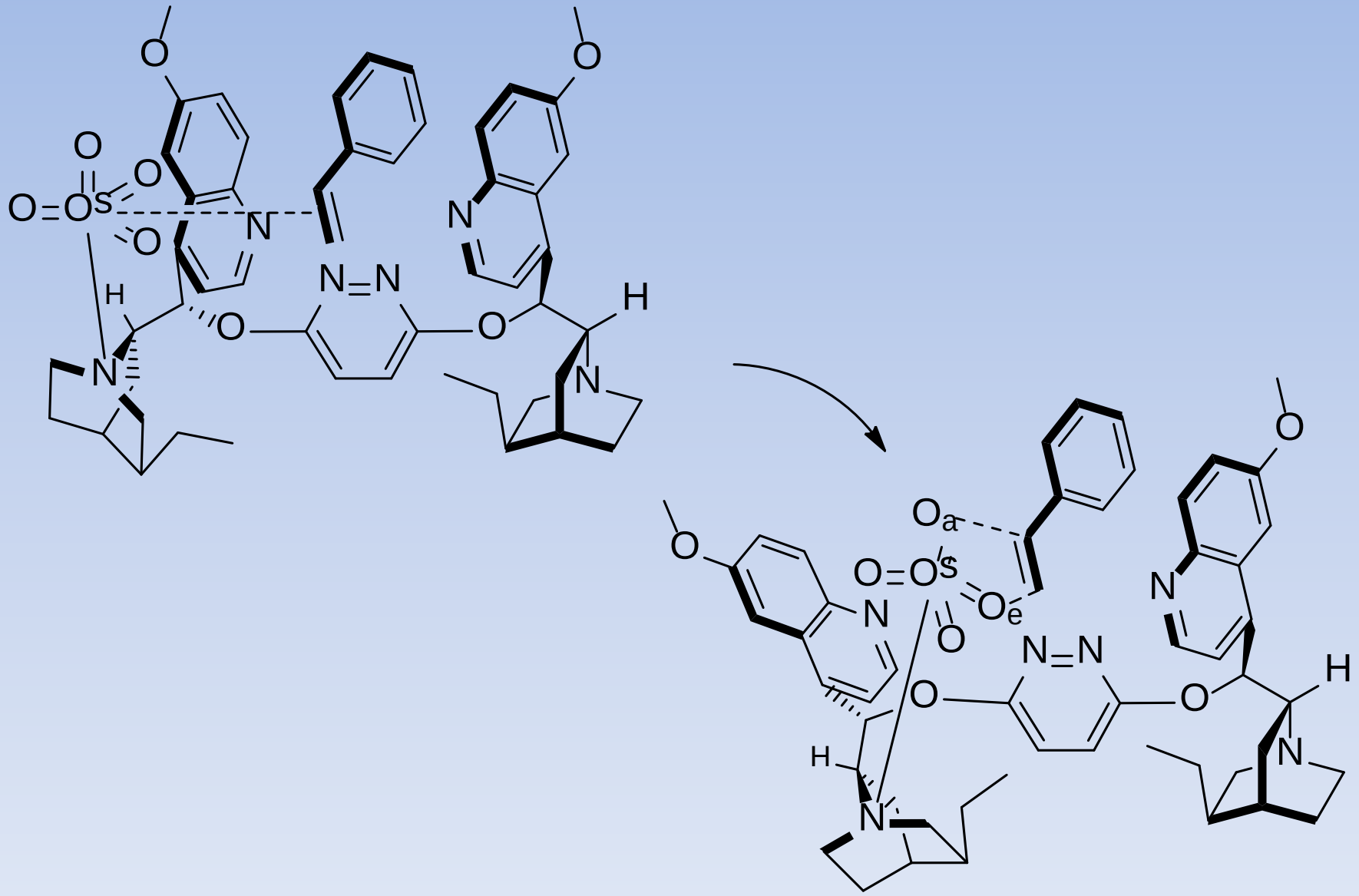
PYR



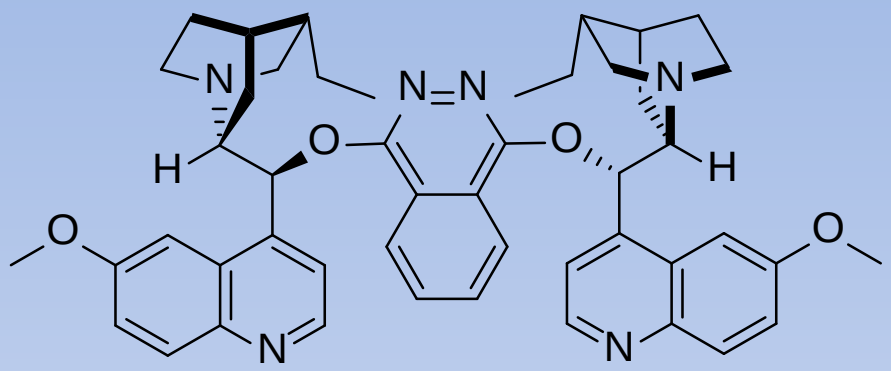
AQN

R dla katalizatorów II-ej generacji

Dihydroksylowanie Sharpless'a



Dihydroksylowanie Sharpless'a



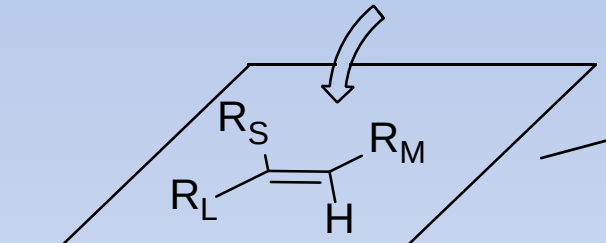
pochodna chinidyny

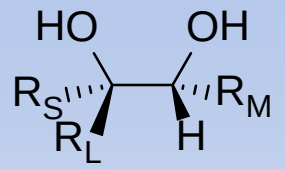
$(DHQD)_2$-PHAL

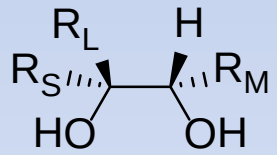
$K_2OSO_2(OH)_4$

$K_3Fe(CN)_6$, K_2CO_3

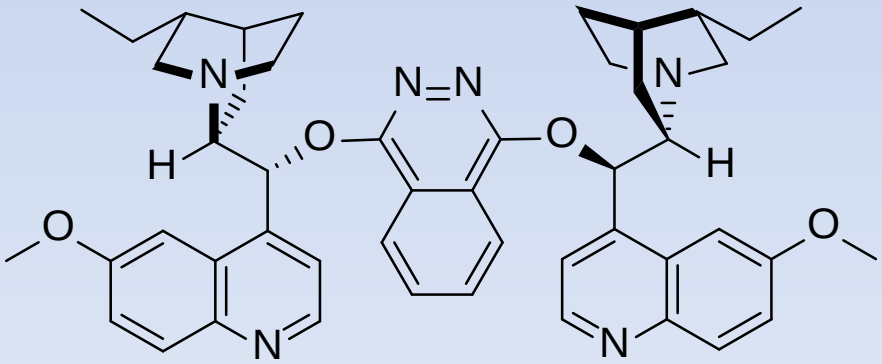
$AD\text{-}mix\text{-}\beta$







pochodna chininy



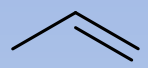
$AD\text{-}mix\text{-}\alpha$

$(DHQ)_2$-PHAL

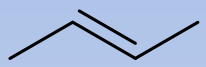
$K_2OSO_2(OH)_4$

$K_3Fe(CN)_6$, K_2CO_3

Dihydroksylowanie Sharpless'a

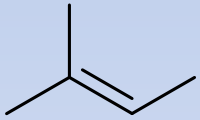


mono



trans-di

gem-di

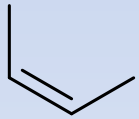


tri

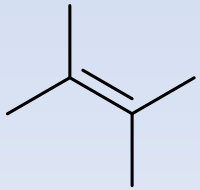
Dobre rezultaty

asymetrycznego dihydroksylowania

metodą Sharpless'a



cis-di



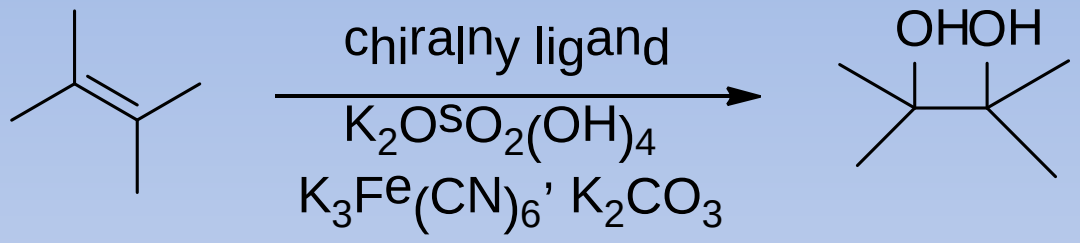
tetra

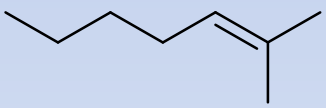
Słabe rezultaty

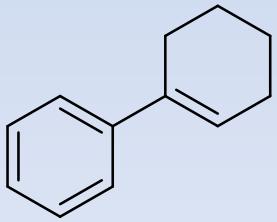
asymetrycznego dihydroksylowania

metodą Sharpless'a

Dihydroksylowanie Sharpless'a

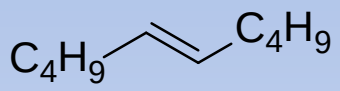


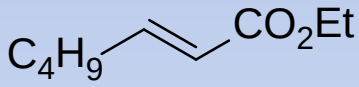


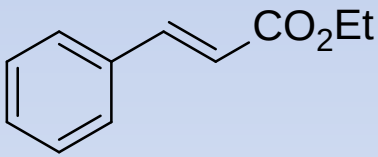


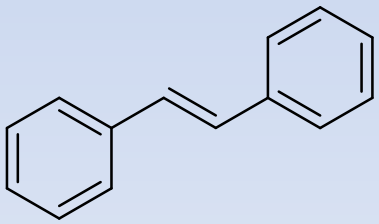
AD-mix-α [$(DHQ)_2$-PHAL]		**AD-mix-β [$(DHQD)_2$-PHAL]**	
% e.e.	konfiguracja	% e.e.	konfiguracja
95	(*S*)	98	(*R*)
97	(*S,S*)	99	(*R,R*)

Dihydroksylowanie Sharpless'a



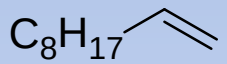
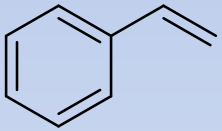
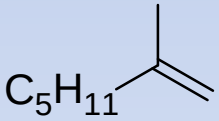
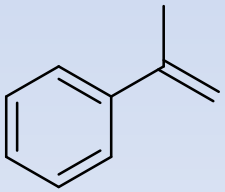




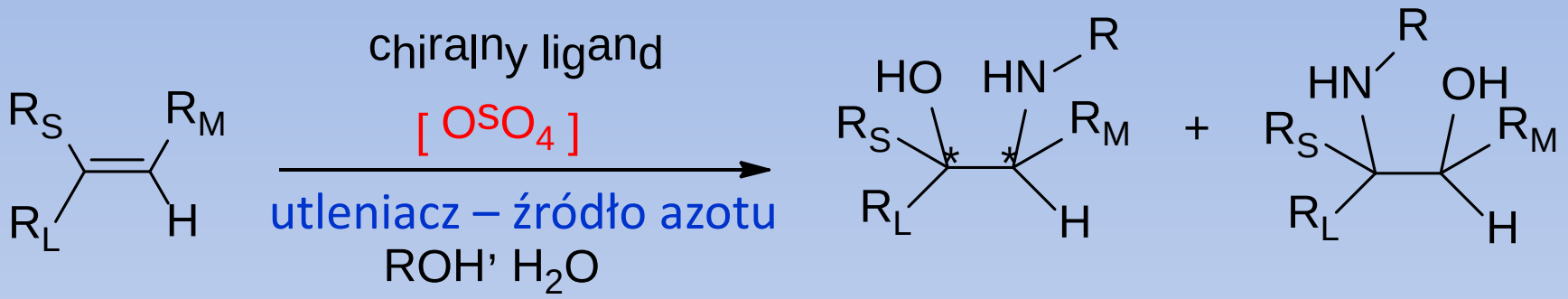


AD-mix-α [$(DHQ)_2$-PHAL]		**AD-mix-β [$(DHQD)_2$-PHAL]**	
% e.e.	konfiguracja	% e.e.	konfiguracja
93	(*S,S*)	97	(*R,R*)
96	(*2R,3S*)	99	(*2S,3R*)
95	(*2R,3S*)	97	(*2S,3R*)
>99,5	(*S,S*)	>99,5	(*R,R*)

Dihydroksylowanie Sharpless'a

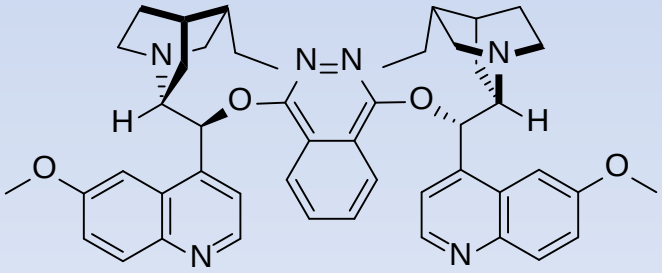
	AD-mix-α [$(DHQ)_2$-PHAL]		AD-mix-β [$(DHQD)_2$-PHAL]	
	% e.e.	konfiguracja	% e.e.	konfiguracja
	80	(*S*)	84	(*R*)
	97	(*S*)	97	(*R*)
	76	(*S*)	78	(*R*)
	94	(*S*)	93	(*R*)

Aminohydroksylowanie Sharpless'a

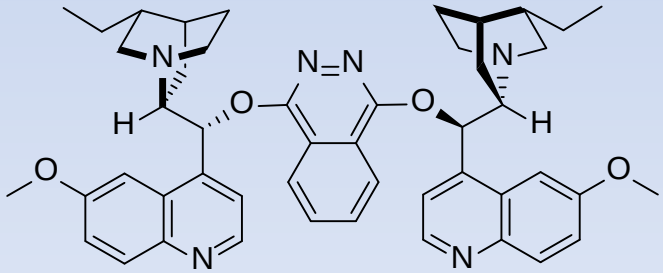


Chiralne ligandy

- Pochodne chininy i chinidyny jak w reakcji AD
- Katalizatory II-giej generacji: PHAL, DP PHAL, DPP, AQN, PYR

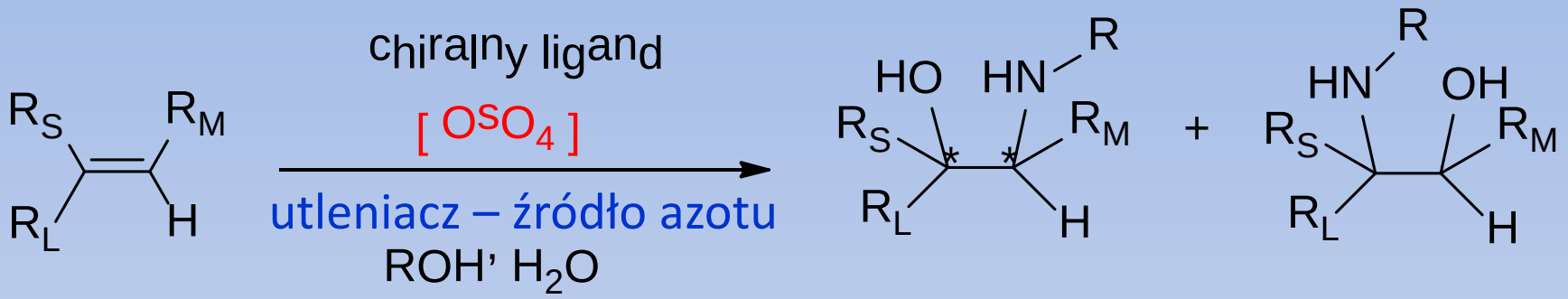


$(DHQD)_2$PHAL



$(DHQ)_2$PHAL

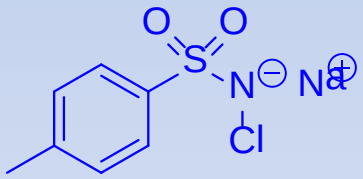
Aminohydroksylowanie Sharpless'a

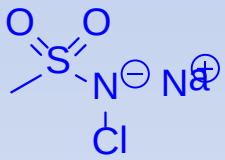


[**OsO_4**] – $K_2OsO_2(OH)_4$

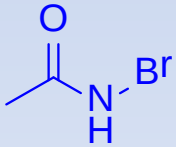
utleniacz – źródło azotu

- chloraminy (T, M)

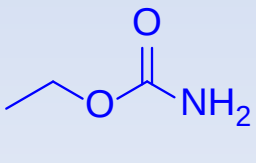


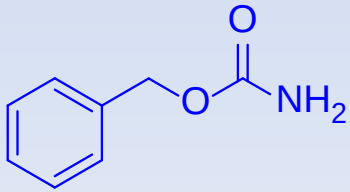


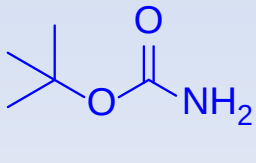
- N-halogeno amidy



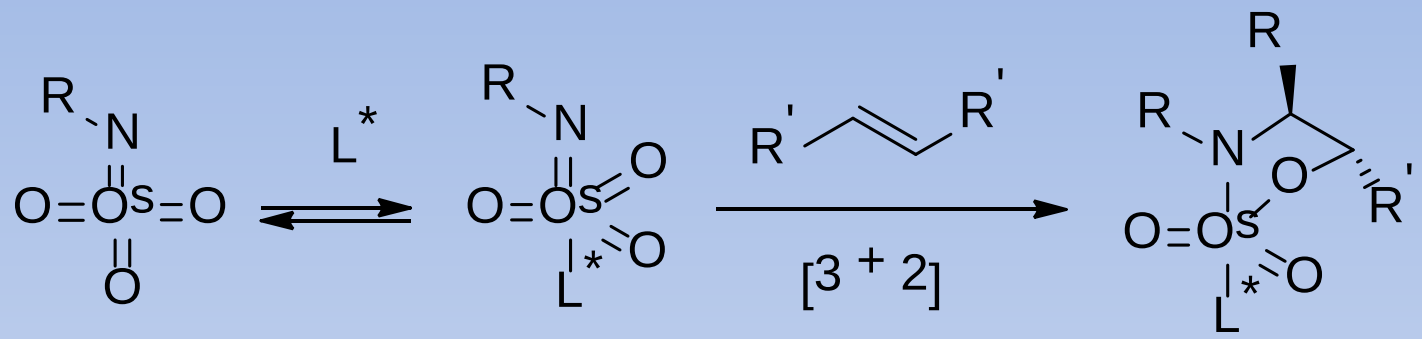
- karbaminiany
  + utleniacz np.: $^{t}BuOCl$

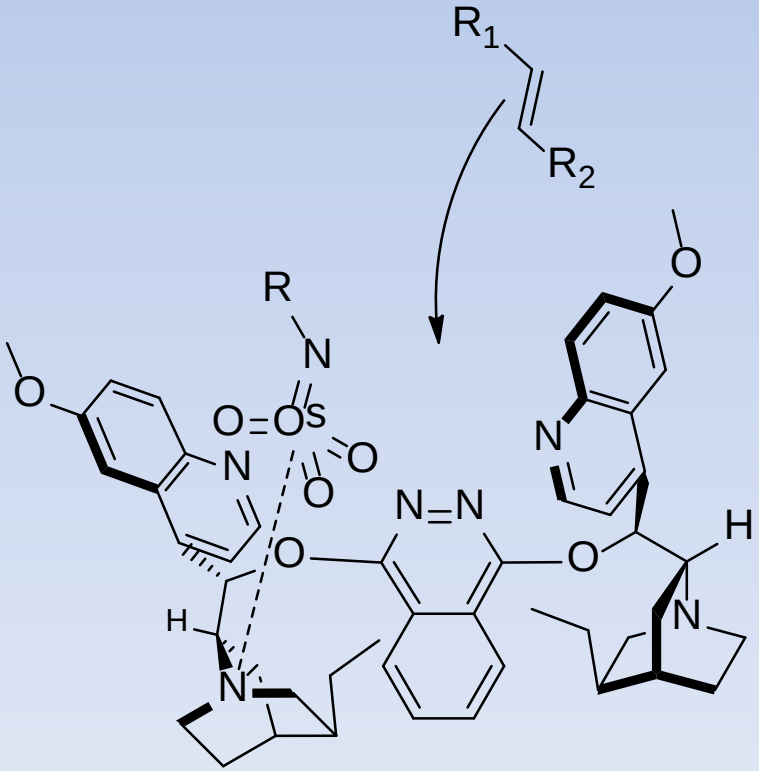


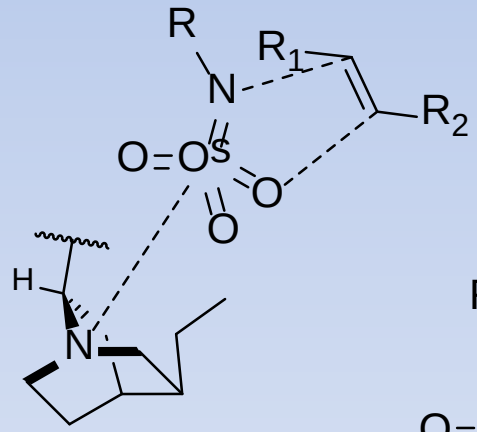


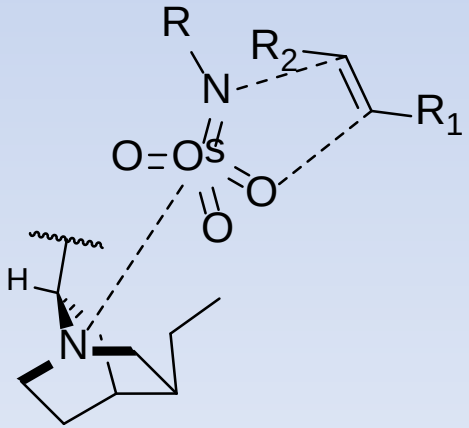


Aminohydroksylowanie Sharpless'a

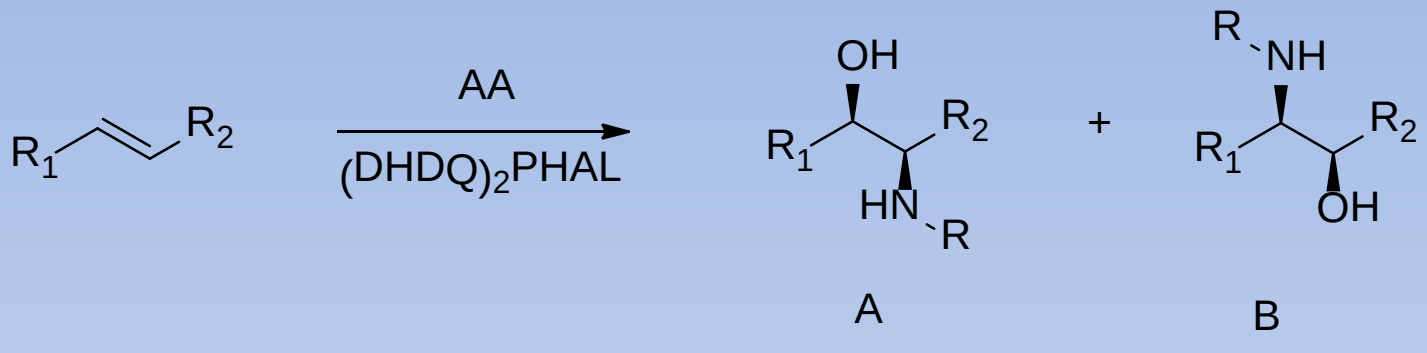








Aminohydroksylowanie Sharpless'a



substrat			produkt	
R	R_1	R_2	A	B
Ac	$TBDPSOCH_2CH_2$	H	20	1
Ac	$p\text{-}MeO\text{-}C_6H_4OCH_2CH_2$	H	1,2	1
Ts	Ph	CO_2Me	1	5
Ms	Ph	CO_2Me	9	91

Literatura do dzisiejszych zagadnień

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SYNTEZA ASYMETRYCZNA

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