
聲明

本檔案之內容僅供下載人自學或推廣化學教育之非營利目的使用。並請於使用時註明出處。

[如本頁取材自○○○教授演講內容]。

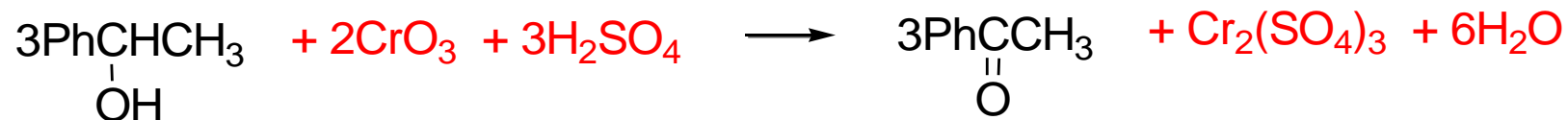
觸媒在綠色/永續化學的應用

蔡蘊明
台大化學系

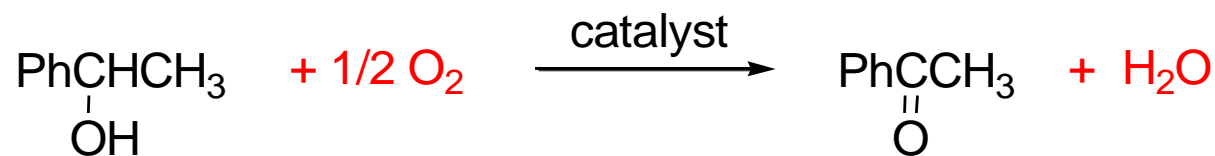
Outline

- Introduction
- Solid acid and base catalysts
- Recycling of metal catalysts
- Organocatalysis
- Catalytic hydrogenation
- Green oxidation reagents
- Biocatalysis

Catalyst and atom efficiency

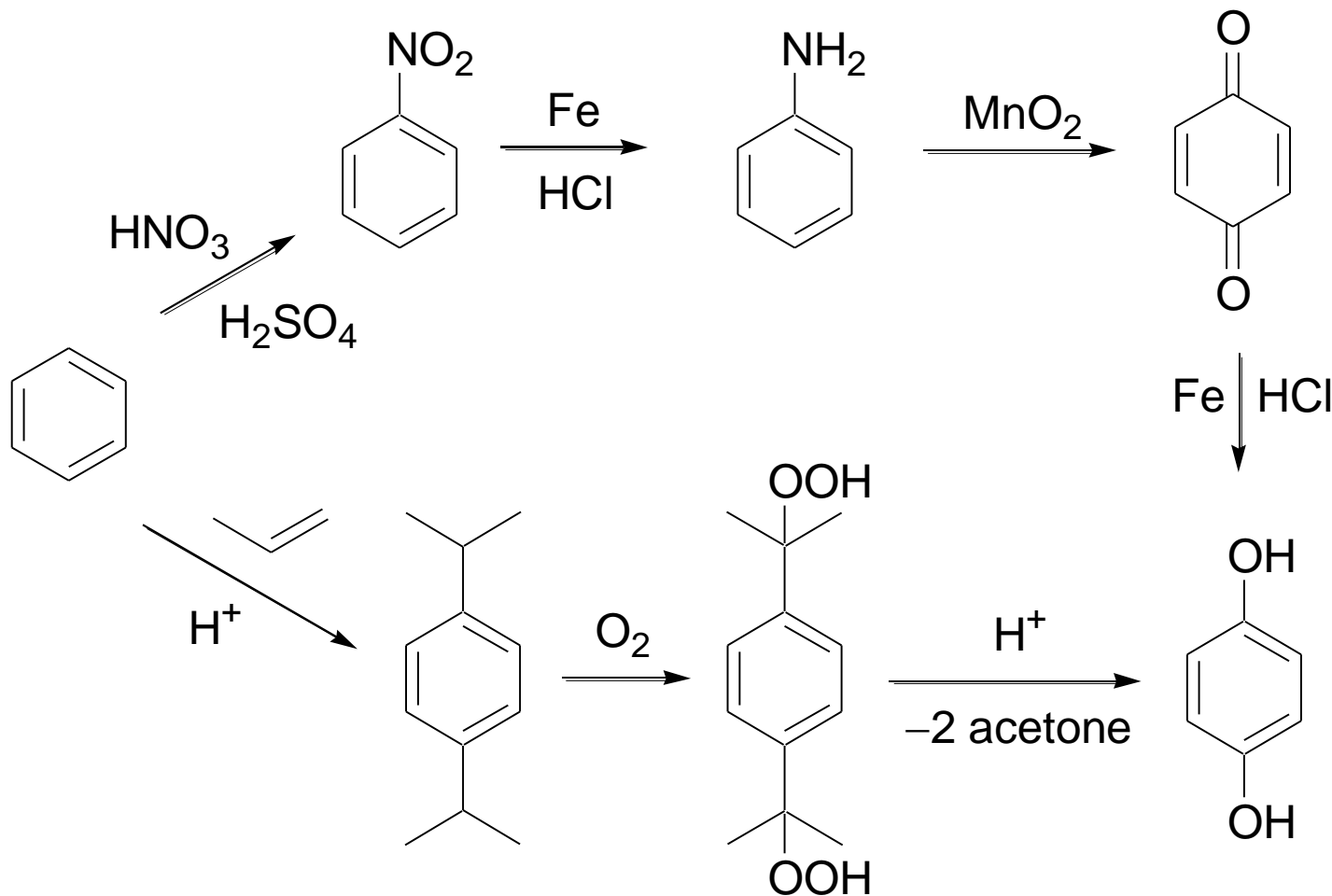


$$\text{Atom efficiency} = 360/860 = 42\%$$



$$\text{Atom efficiency} = 120/138 = 87\%$$

Classical approach \Rightarrow High salt formation



Catalytic approach

Per Kg:
>10 Kg vs <1Kg

Green solutions

- Catalysis by solid acids and bases
- Catalytic reduction
- Catalytic oxidation
- Catalytic C-C bond formation
- Biocatalysis
- Enantioselective catalysis

Ref.

Sheldon, R. A.; Arends, I.; Hanefeld, U

Green Chemistry and Catalysis

Wiley,2007.

Solid acids as catalysts

Advantages

- Easy separation and recycling
- Safer and easier to handle
- Less contamination

Three major categories

- Acidic clays
- Zeolites
- Acidic group linked to solid surface

◎ Acidic clays

amorphous, layered structures

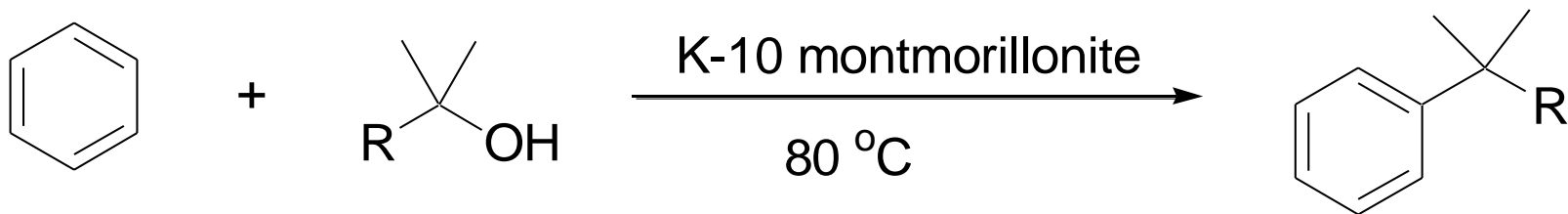
Basic building blocks

SiO_4 tetrahedra and MO_6 octahedra

($\text{M} = \text{Al}^{3+}, \text{Mg}^{2+}, \text{Fe}^{3+}, \text{Fe}^{2+}, \text{etc}$)

Interlamellar exchangeable cation

responsible for the Brønsted or Lewis acidity



Shortcoming

limited thermo stability

◎ Zeolites

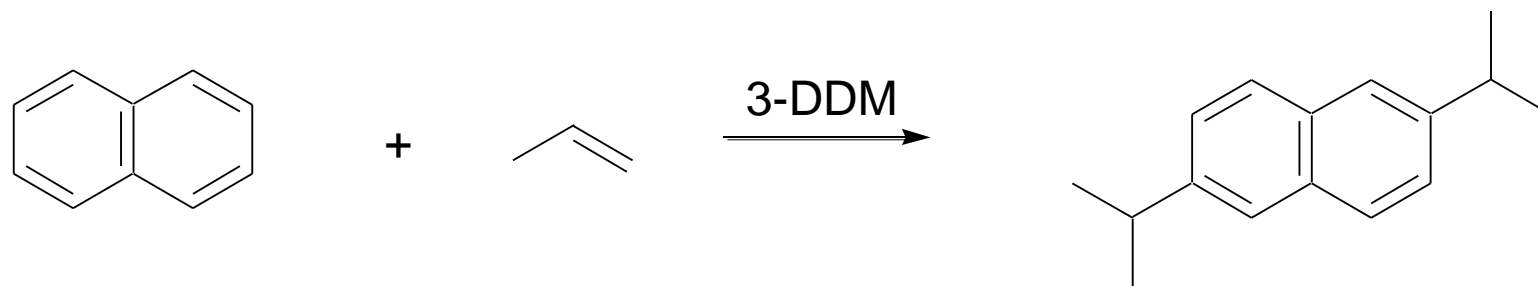
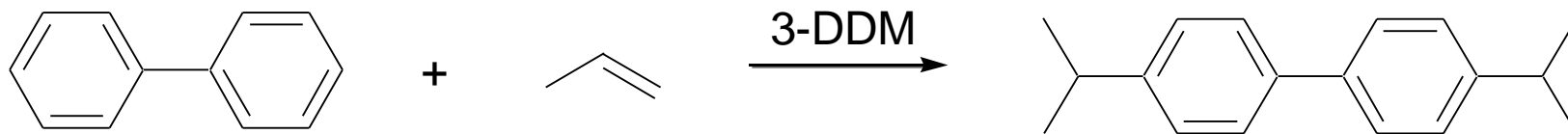
crystalline aluminosilicates

containing corner-sharing SiO_4 and AlO_4^- tetrahedra

Extraframework cation (maintain electroneutrality)
exchangeable and responsible for the acidity

Important features

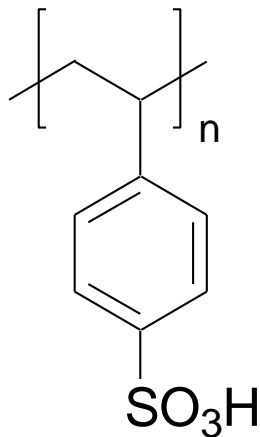
- uniform internal structure
- large internal surface area
- tunable pores
- tunable acidity
 - Si/Al ratio, ion exchange, post-modification
- framework substitution by transition elements
- strong electric fields within the confined space



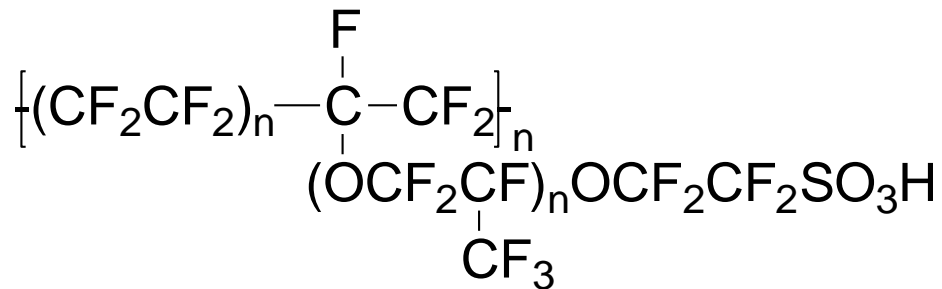
3-DDM = 3-dimensional dealuminated Mordenite (Si/Al = 100-1000)

◎ Solid acids containing surface SO₃H

Amberlyst[®] -15



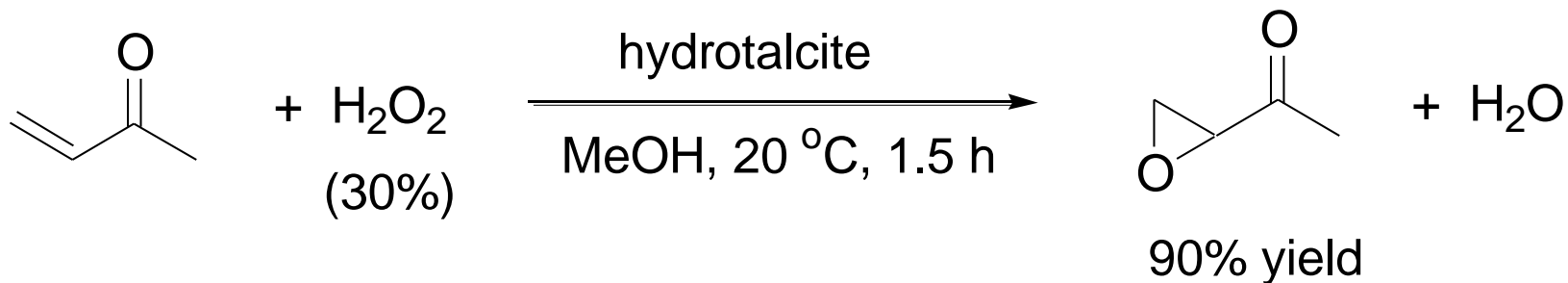
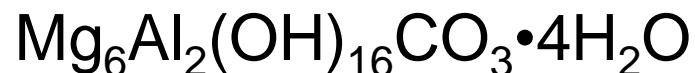
Nafion[®]



Solid bases as catalysts

⊙ Anionic clays: Hydrotalcites

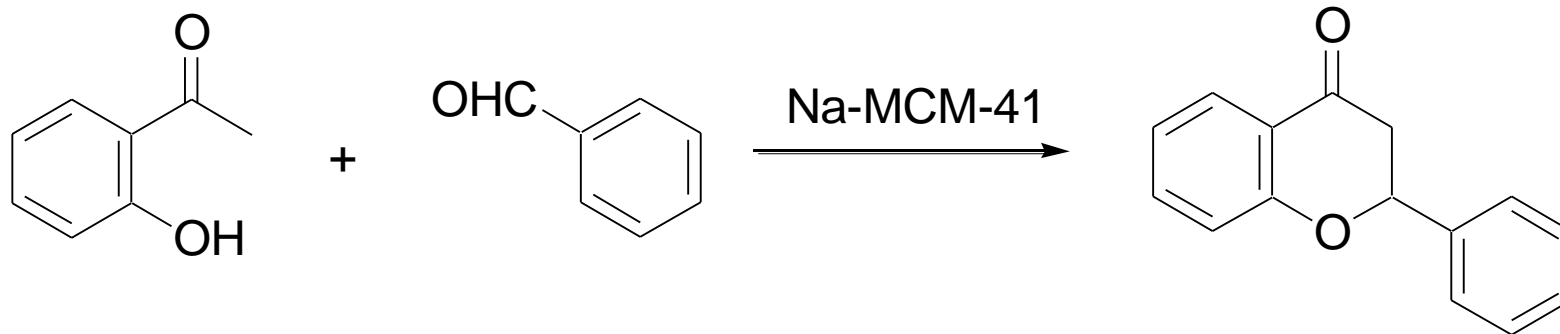
a natural mineral of ideal formula



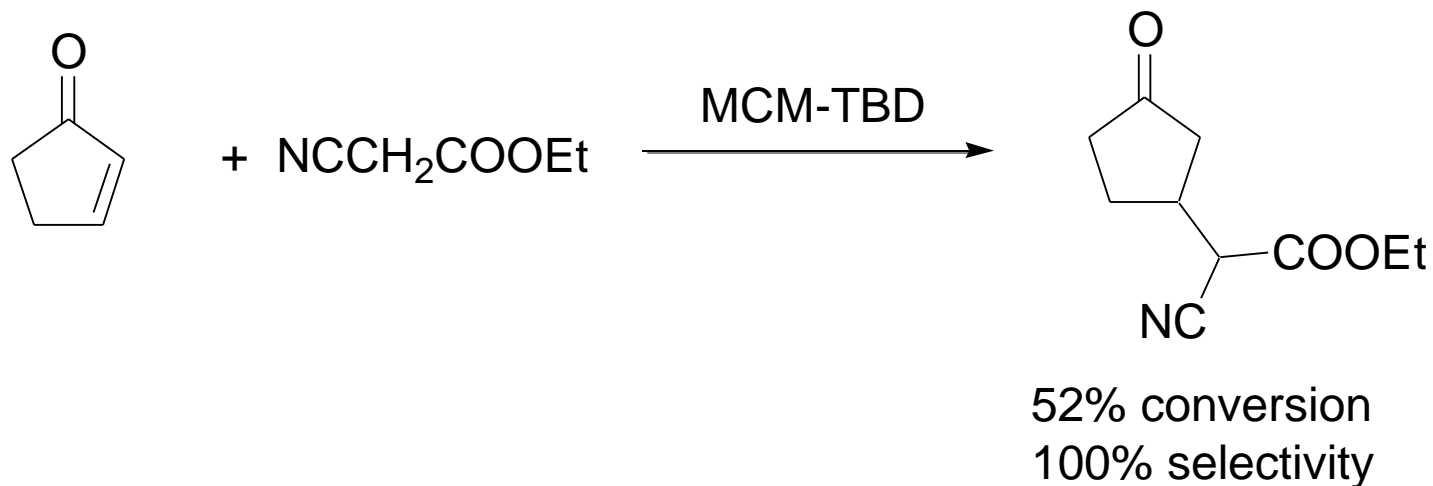
◎ Basic zeolites

by alkaline metal exchange with proton

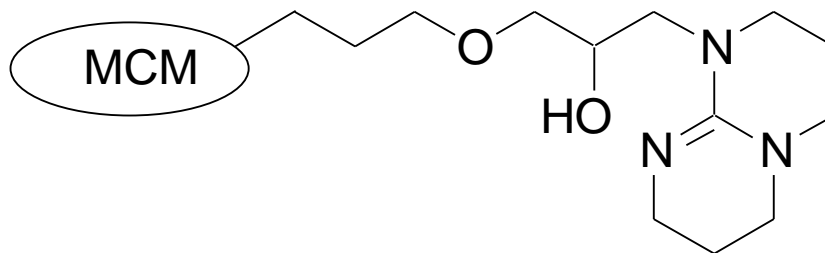
by generation of metal oxide nanoparticles in cavities



⊙ Organic base attached to mesoporous silicates



MCM-TBD:



Recyclable Palladium Catalysts

Heterogeneous

Supports used

Silica

Ordered mesoporous silica materials

Other inorganic supports

Polymeric materials

Type of active Pd

Nanoparticles

Complexes

Homogeneous

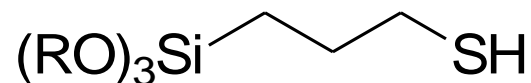
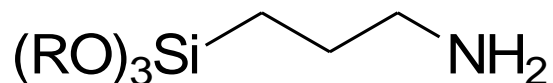
Ionic liquid

Fluorous ligands

Molnar, A. *Chem. Rev.* **2011**, *111*, 2251–2320

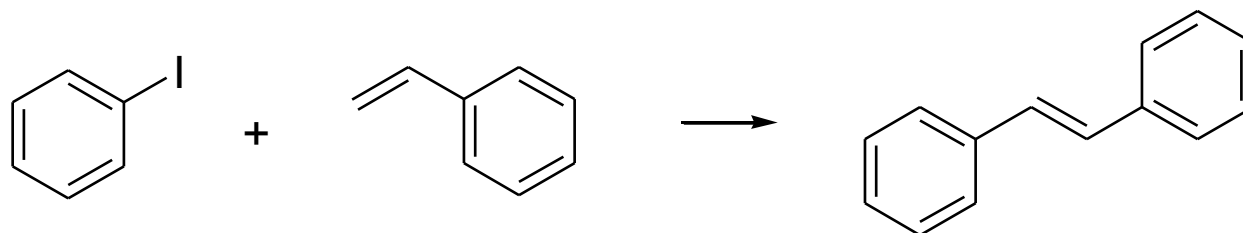
© Support on silica

Postsynthetic modification by grafting



Sol-gel process

Tetraethyl orthosilicate (TEOS)
Functionalized trialkoxysilane
and/or Templating agent



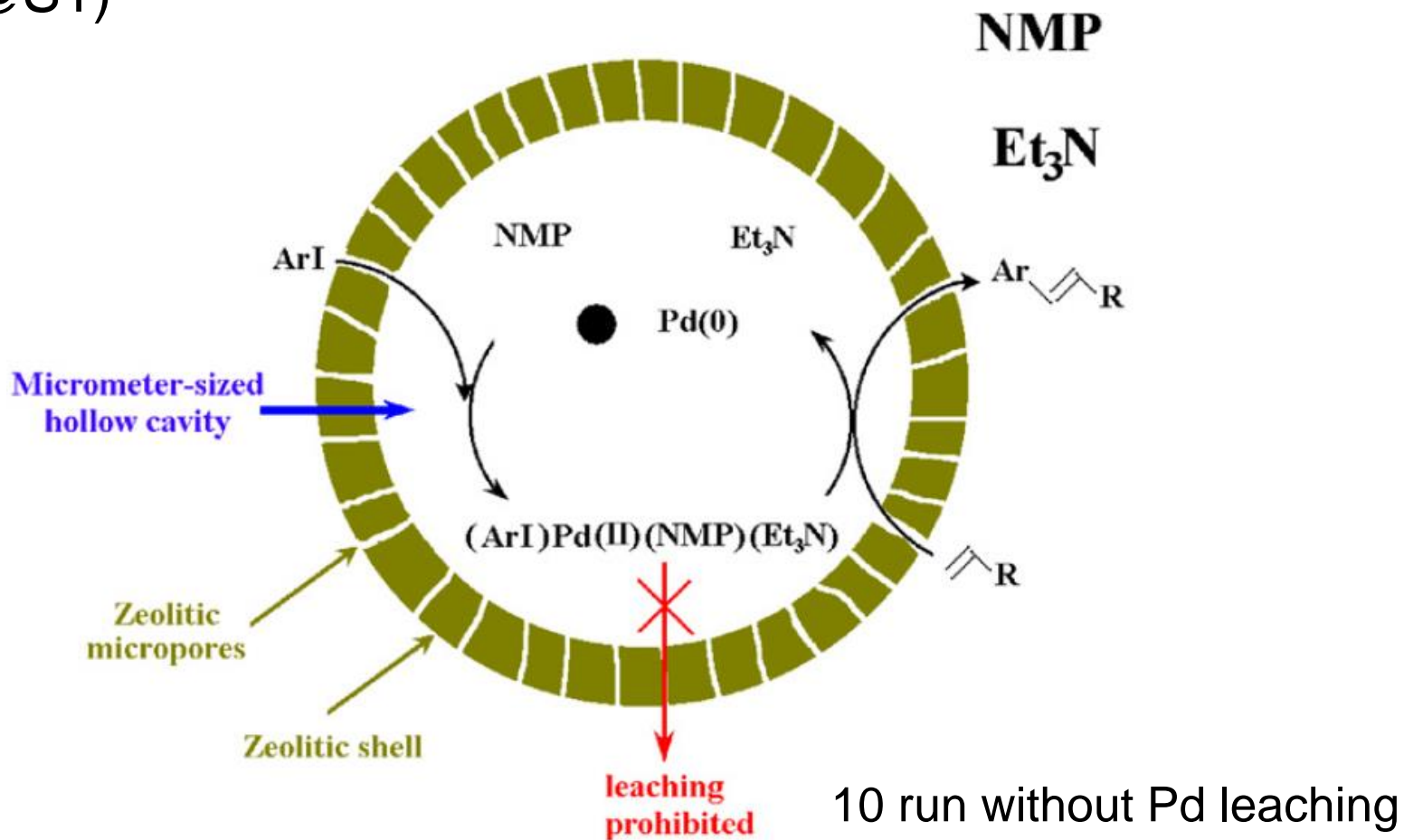
4.1% Pd-grHS-Si(HIPE) (0.004)

Et₃N, DMF, 155 °C

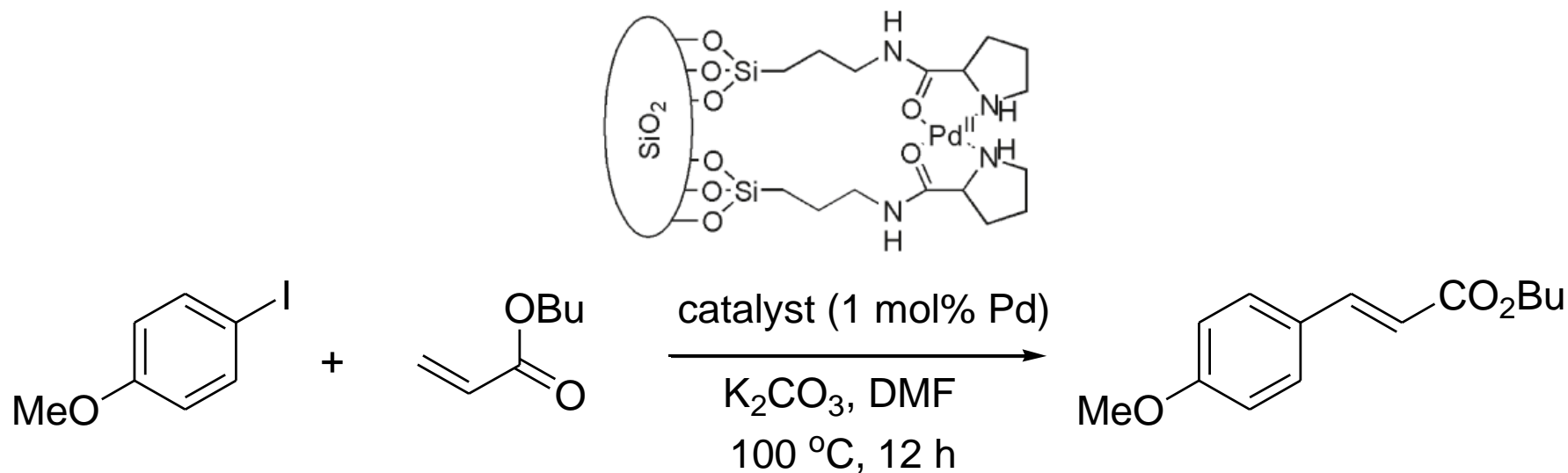
7 runs, average yield: 97, *E/Z*: 96/4

Ungureanu, S.; Deleuze, H.; Sanchez, C.; Popa, M. I.; Backov, R. *Chem. Mater.* **2008**, *20*, 6494–6500

Nanopalladium-entrapped zeolitic microcapsular reactor (Pd@S1)



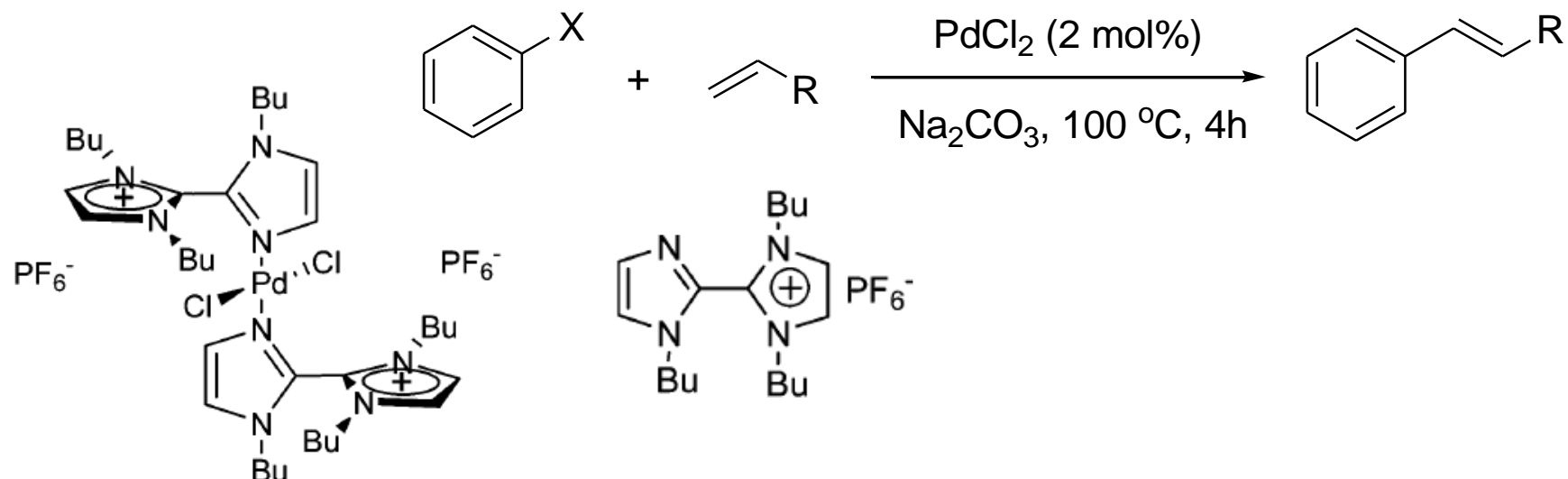
Ren, N.; Yang, Y.-H.; Zhang, Y.-H.; Wang, Q.-R.; Tang, Y.
J. Catal. **2007**, *246*, 215.



14 runs with yields 99-91%, <0.1 ppm leaching each run

Liu, H.; Wang, L.; Li, P. *Synthesis* **2008**, 2405-2411

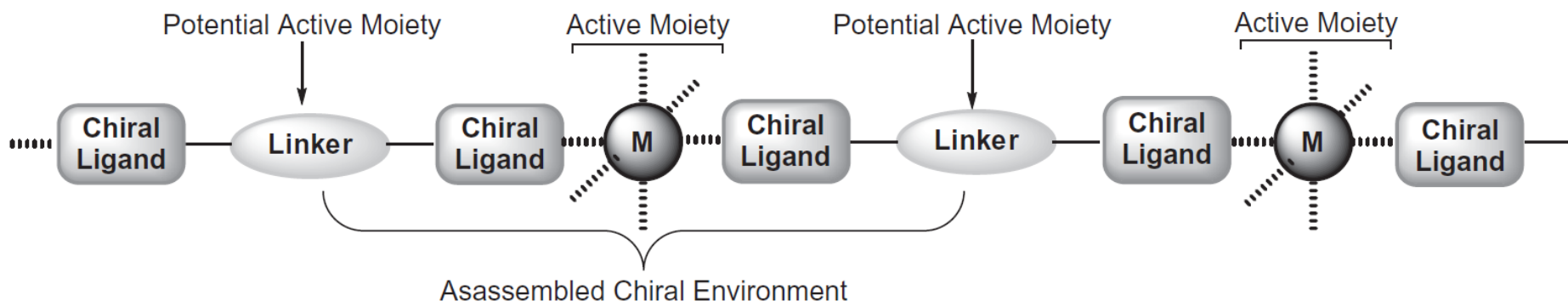
⊙ Ionic liquids



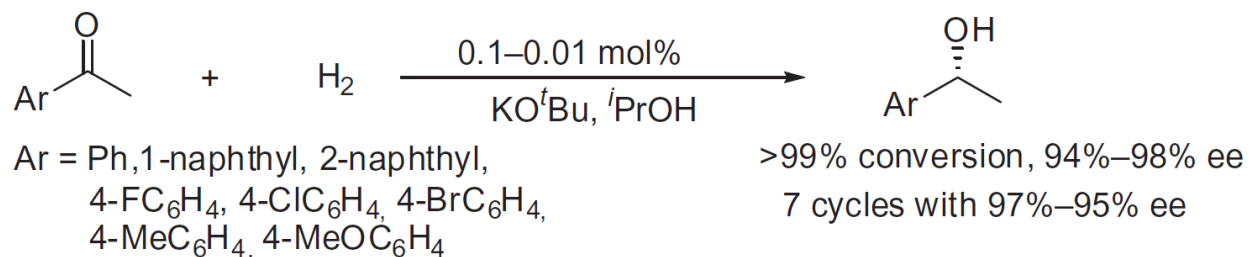
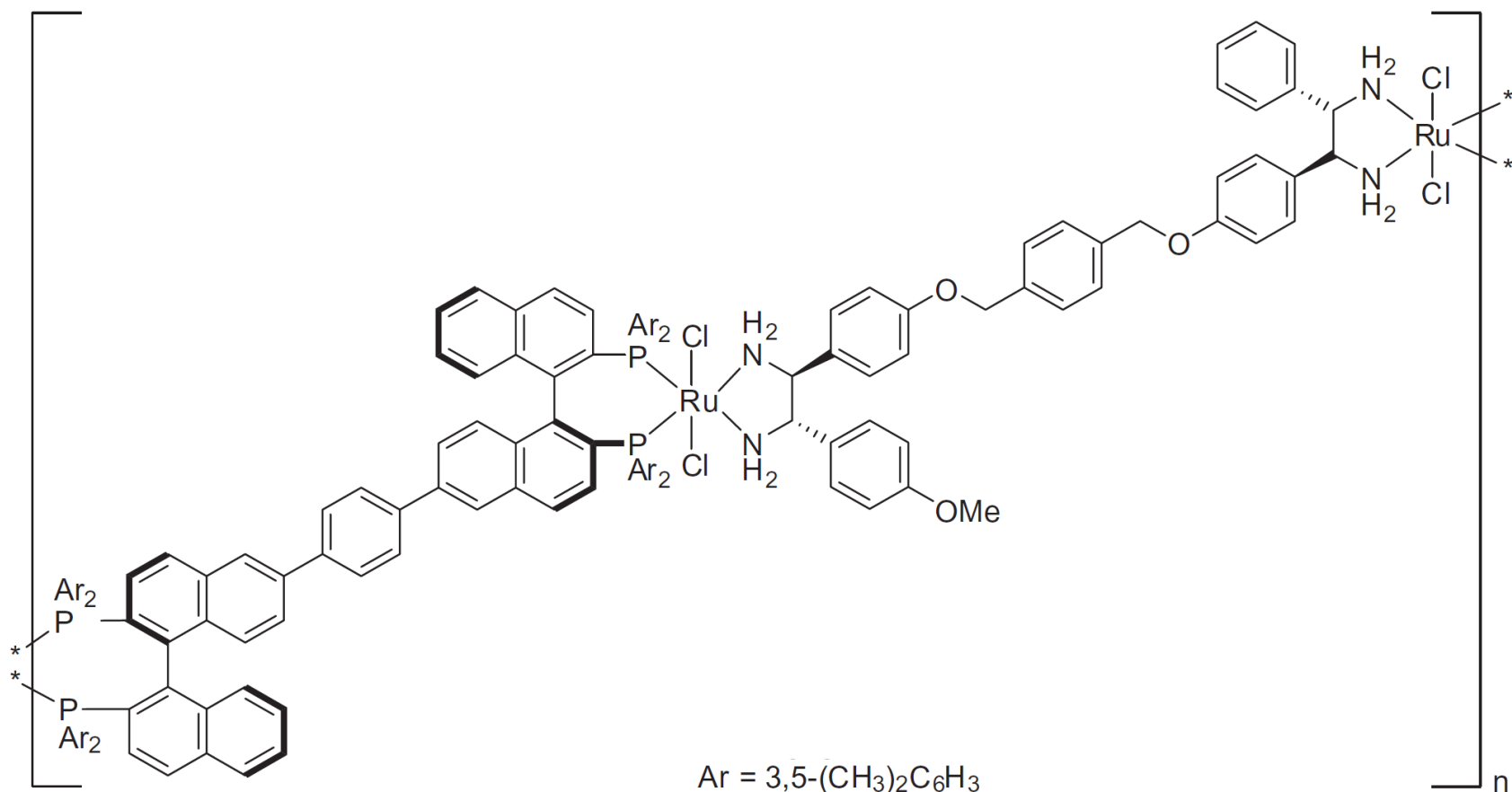
X	R	cycle	yield ^a (%)	cycle	yield ^a (%)
I	CO ₂ Me	1	92	4	91
		2	90	5	91
		3	94		
Cl	CO ₂ Me	6	70	8	75
		7	78		
Cl	Ph	9	86	11	83
		10	81		

Xiao, J.-C.; Twamley, B.; Shreeve, J. M. *Org. Lett.* **2004**, *6*, 3845–3847

Self-supported catalysts



Kuo, H.; Ding, K. in *Catalytic Methods in Asymmetric Synthesis: Advanced Materials, Techniques, and Applications*, 1st Ed., Chapter 5, pp257–290; Gruttadauria, M.; Giacalone, F., Eds.
John Wiley & Sons, 2011.



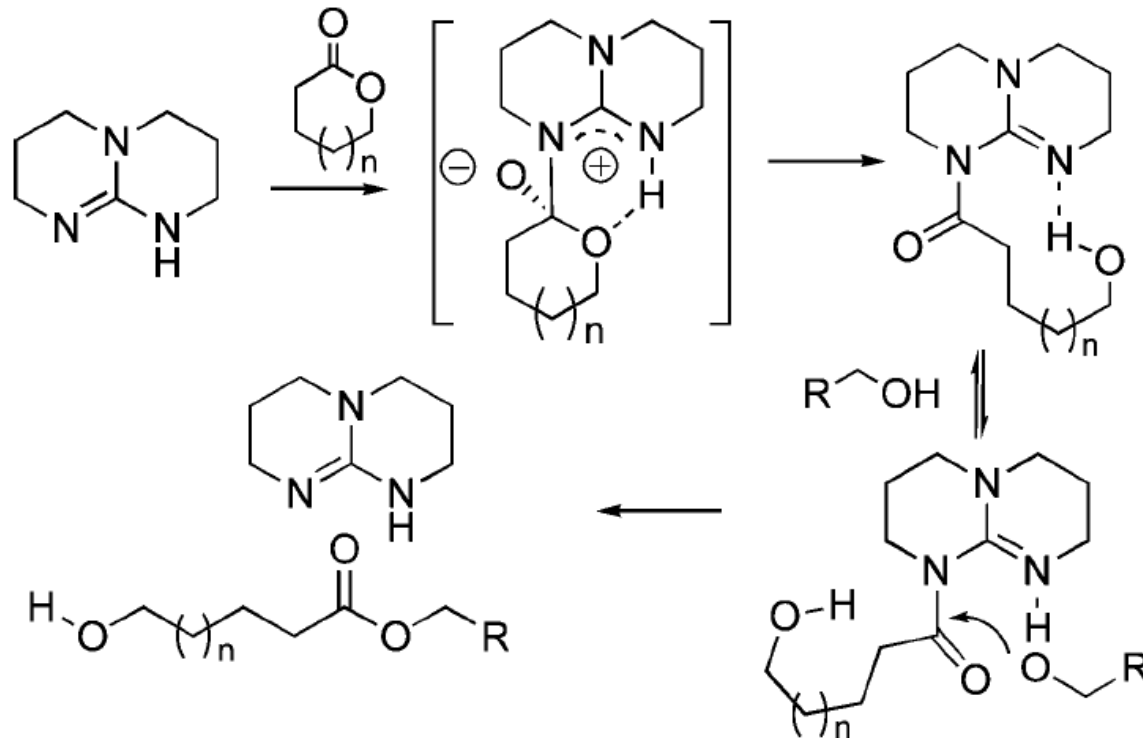
Guo, H.; Ding, K. in *Catalytic Methods in Asymmetric Synthesis: Advanced Materials, Techniques, and Applications*, Gruttadauria, M.; Giacalone, F. (Eds); Wiley & Sons, 2011

Organocatalysts

2012 Presidential Green Chemistry Challenge *Academic Award*

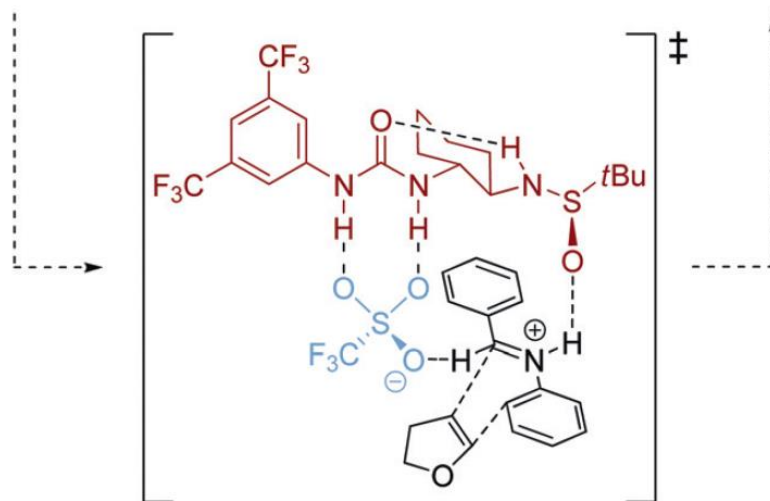
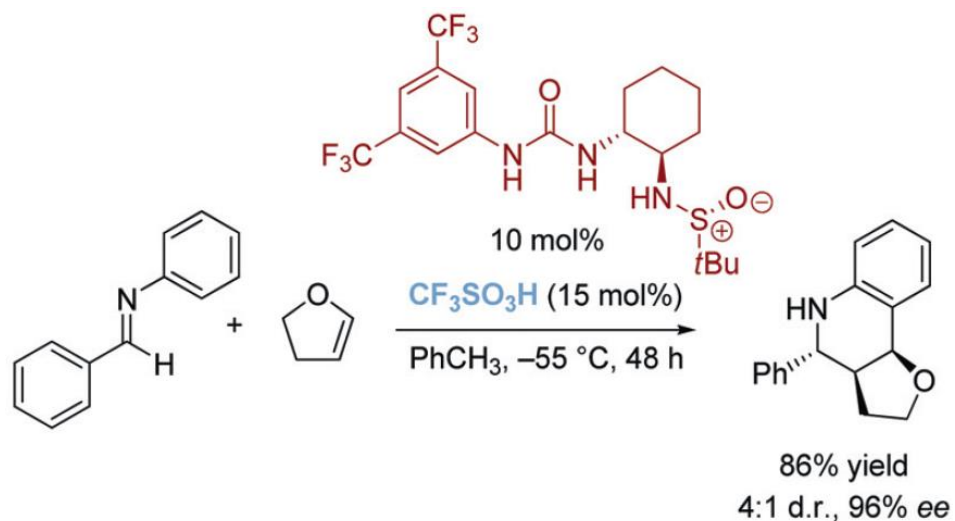
Prof. R. M. Waymouth (Stanford), Dr. J. L. Hedrick (IBM)

Discovered metal-free catalysts that are highly active and able to make a wide variety of plastics



J. Am. Chem. Soc. **2006**, 128, 4556

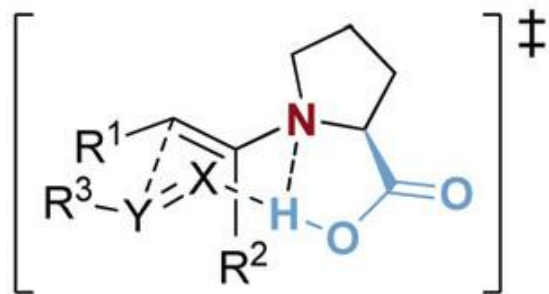
Cooperative catalysis



Xu, H.; Zuend, S. J.; Woll, M. G.; Tao, Y.; Jacobsen, E. N. *Science*, **2010**, 327, 986.

Multifunctional catalyst

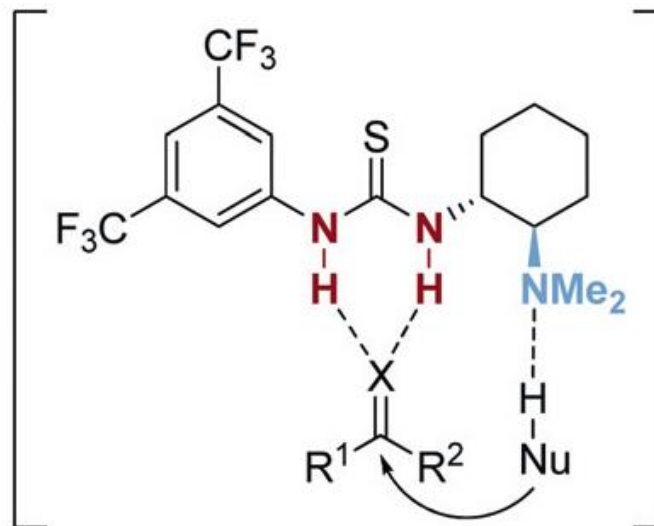
L-Proline



$R^1, R^2, R^3 = \text{H, alkyl, aryl}$
 $X = \text{O, NR}$; $Y = \text{C, N, O, S}$
 $\text{Nu} = \text{nucleophile}$

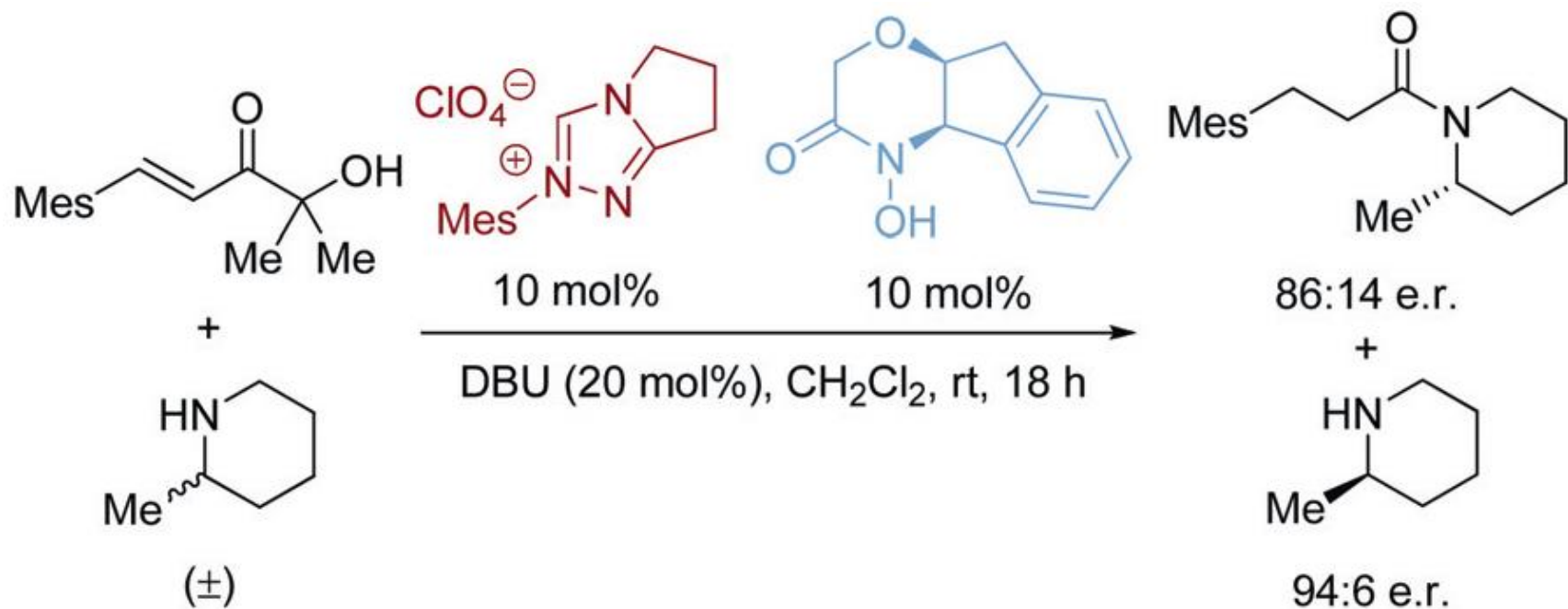
List, B. *Tetrahedron* **2002**, *58*, 5573

Takemoto's catalyst

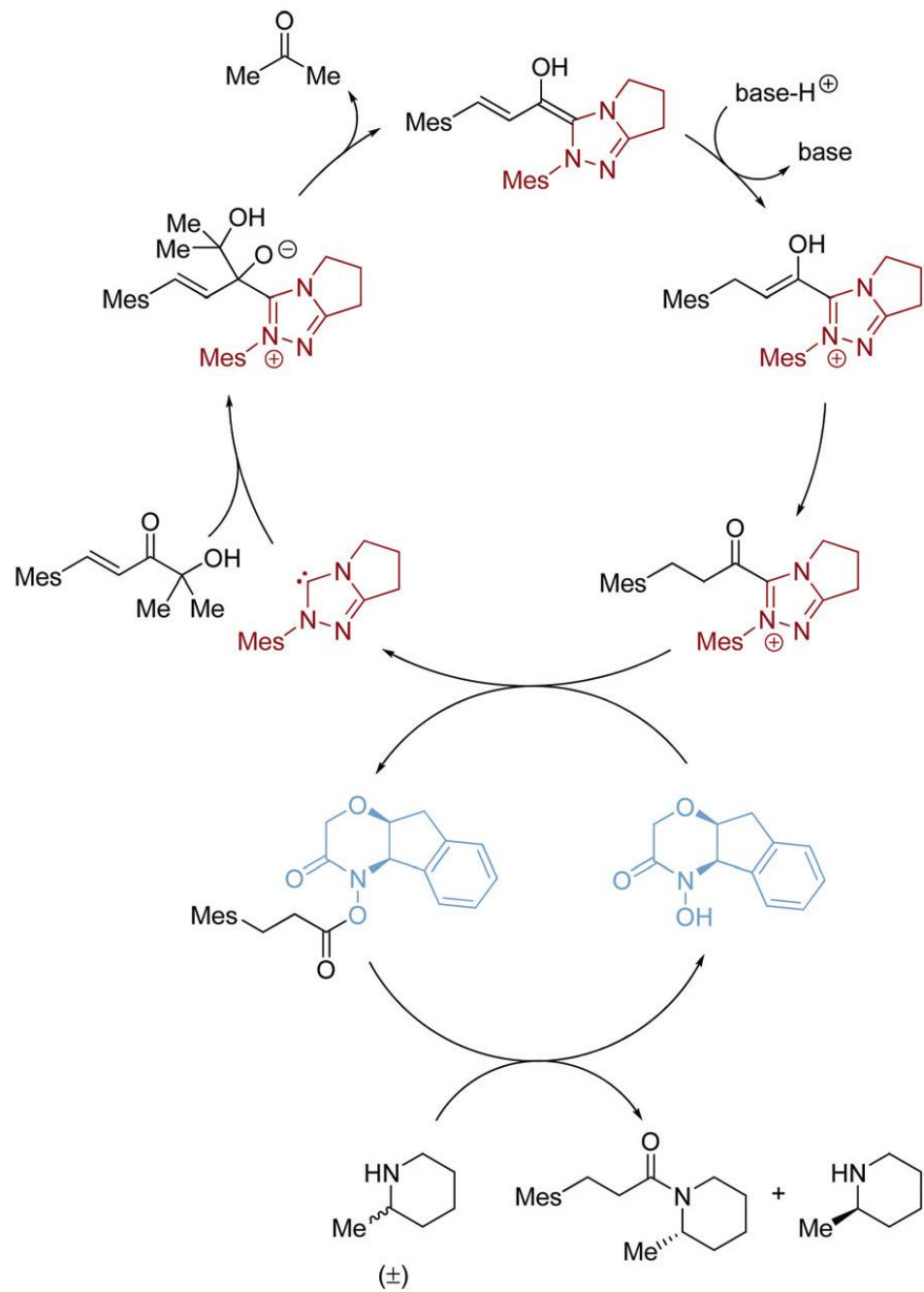


Panday, S. K. *Tetrahedron: Asymmetry* **2011**, *22*, 1817

Dual catalysis / Synergistic catalysis



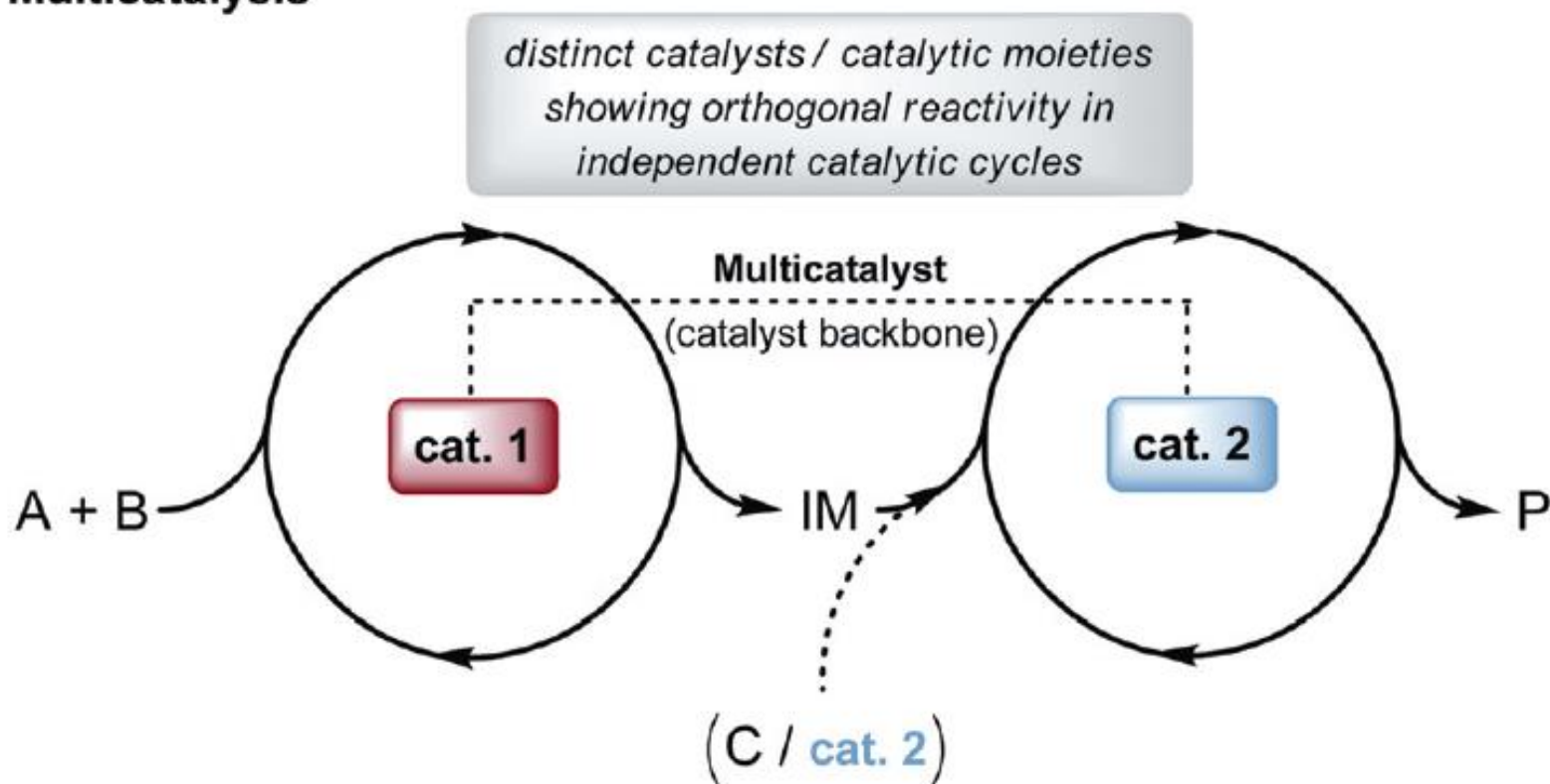
Binanzer, M.; Hsieh, S.-Y.; Bode, J. W. *J. Am. Chem. Soc.* **2011**, *133*, 19698



Organomulticatalysis

Wende, R. C.; Schreiner, P. R. *Green Chem.* **2012**, *14*, 1821

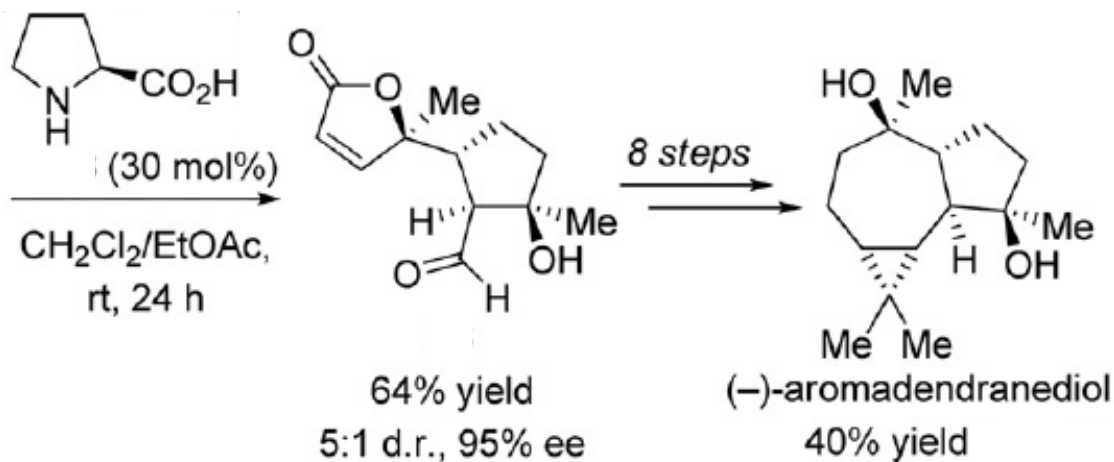
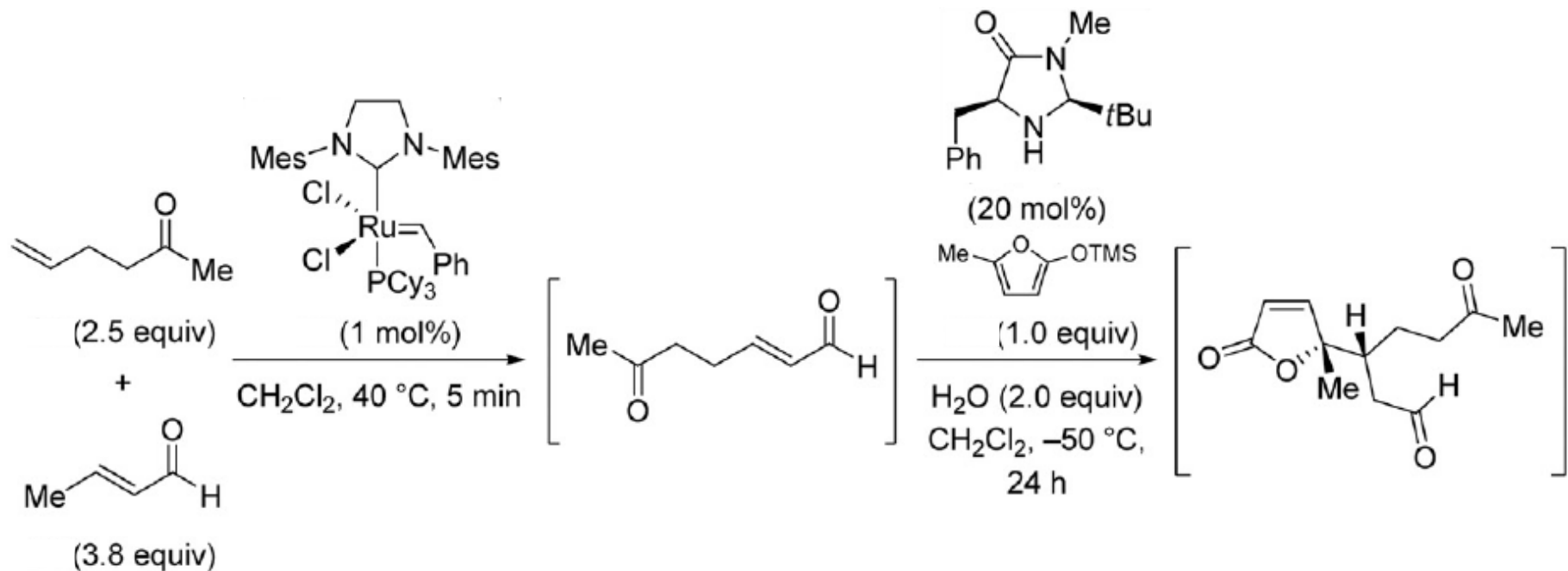
Multicatalysis



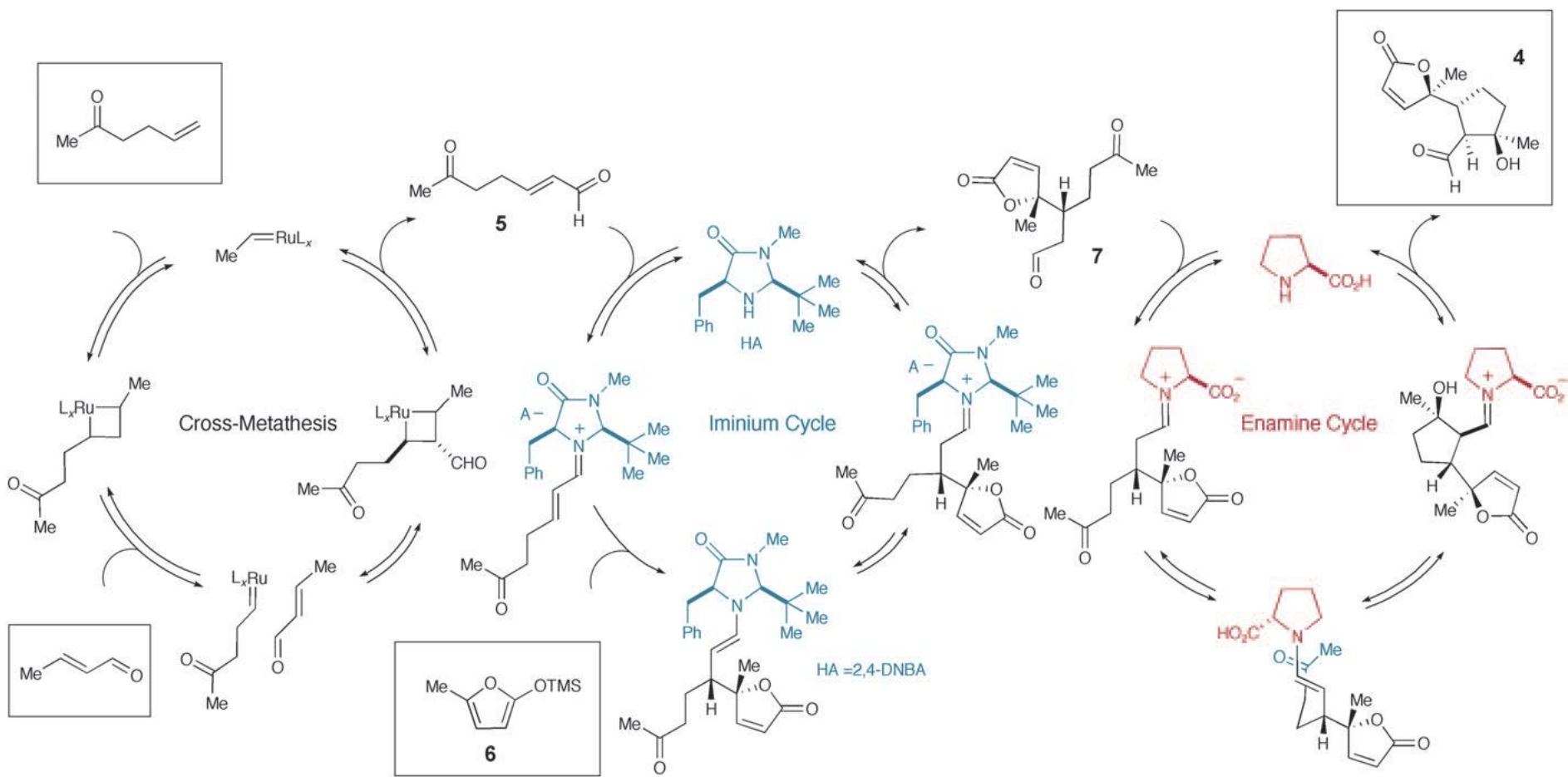
- 1.) **Sequential multicatalysis:** addition of **cat. 2**, reagents, or change in reaction conditions after completion of the 1st catalytic cycle
- 2.) **Tandem / Relay catalysis:** no change in reaction conditions required

Multicatalysis

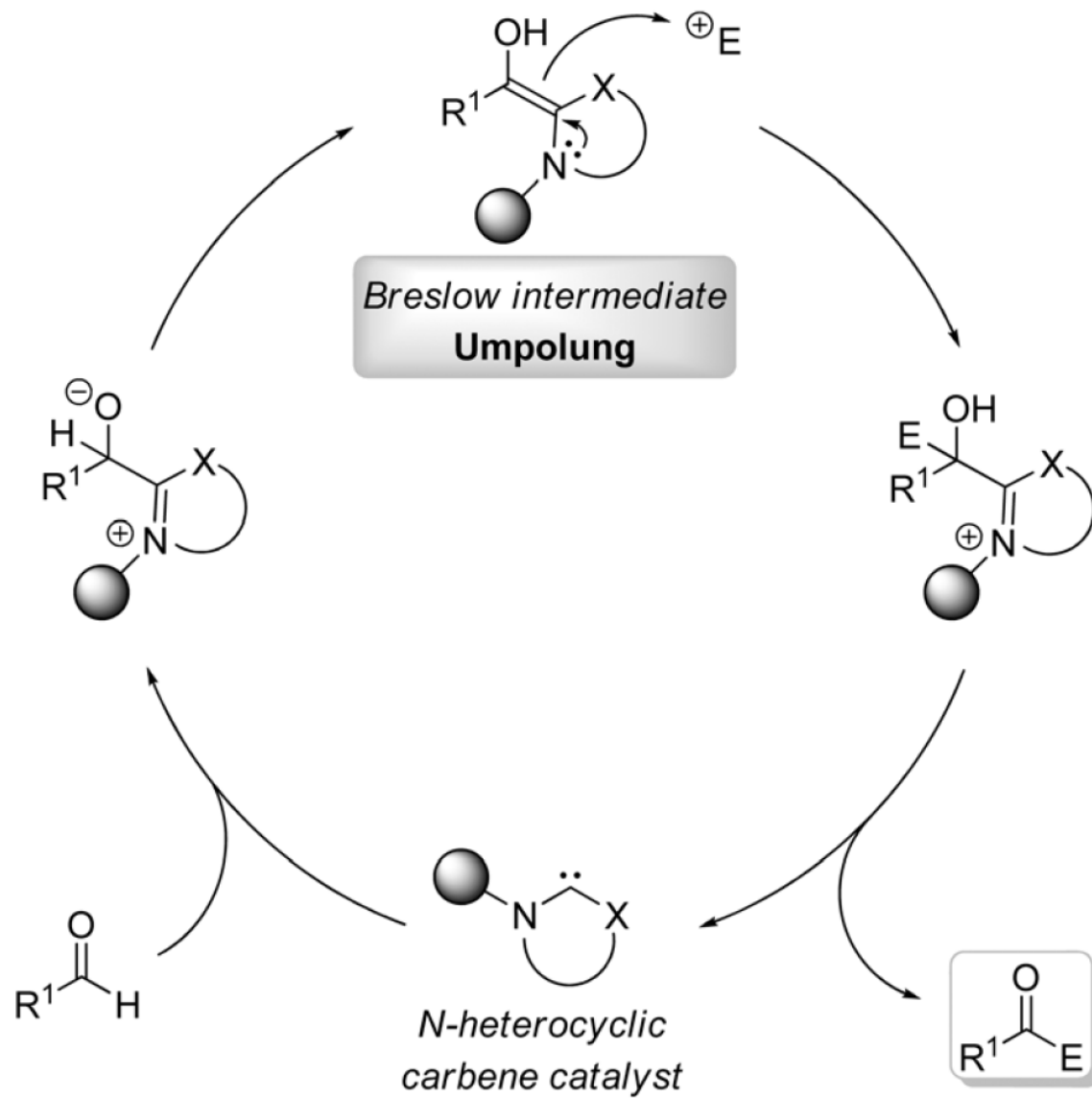
- Low E-factor
- High pot economy
- Equilibrium driving
- Less side reaction
- Avoid stability and toxicity problems
- Amplify enantioselectivity
- Rate enhancement



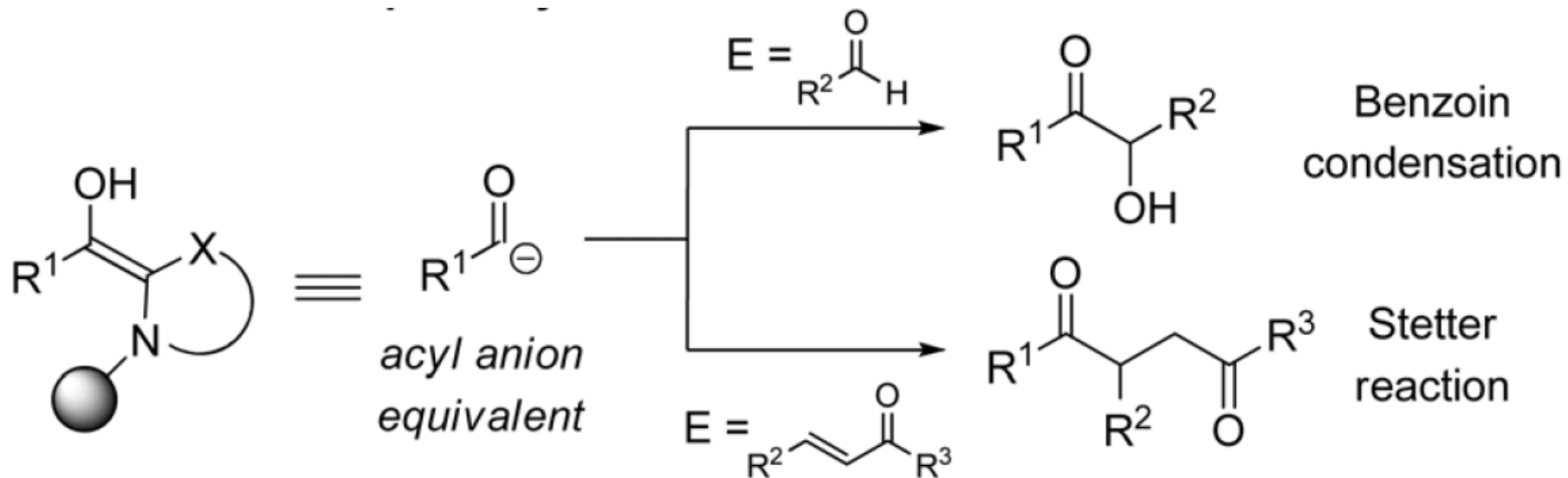
Simmons, B.; Walji, A. M.;
 MacMillan, D. W. C.
Angew. Chem., Int. Ed.
2009, 48, 4349



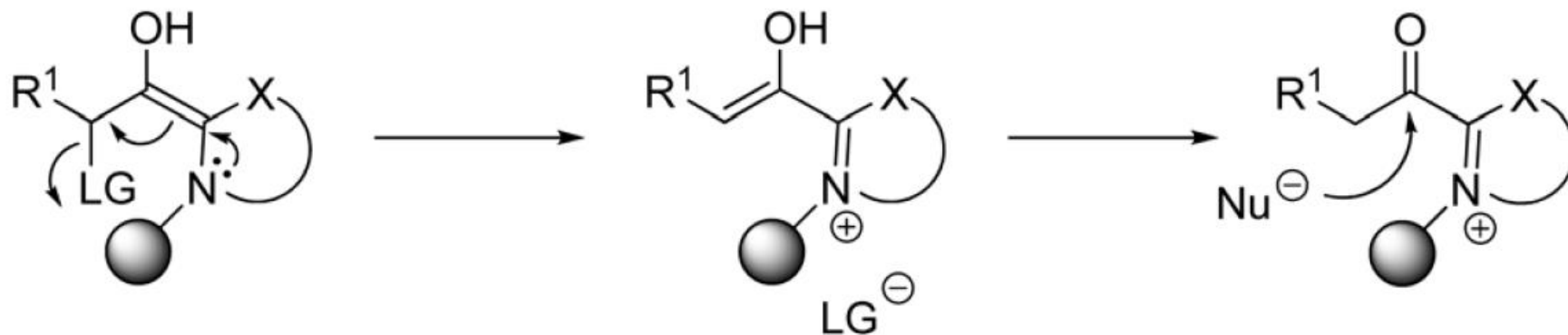
N-Heterocyclic carbene catalysts



Two possibilities



Extended Umpolung



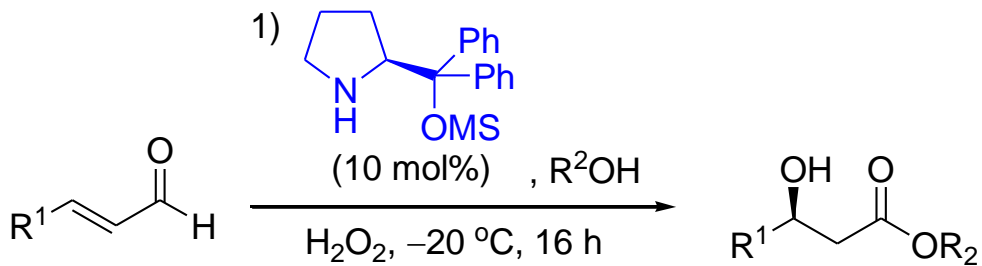
intramolecular redox reaction (extended Umpolung)

X = NR, S

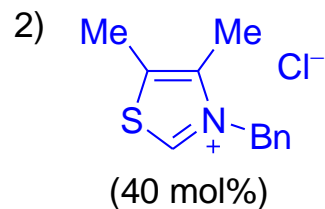
R¹, R², R³ = alkyl, aryl

LG = leaving group

E = electrophile; Nu = nucleophile



$R^1 =$ *n*-Pr
Me
n-Bu
Ph
4-ClPh
CO₂Et

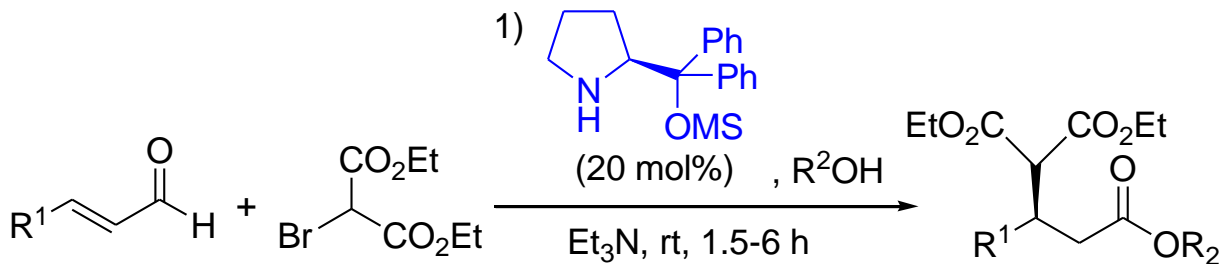


(40 mol%)
DIPEA (80%)
CHCl₃, 30 °C, 15 h

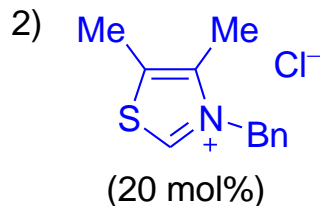
$R^2OH =$ EtOH, BnOH

59-82% yield
up to 95% ee

Zhao, G.-L.; Córdova, A.
Tetrahedron Lett.,
2007, 48, 5976



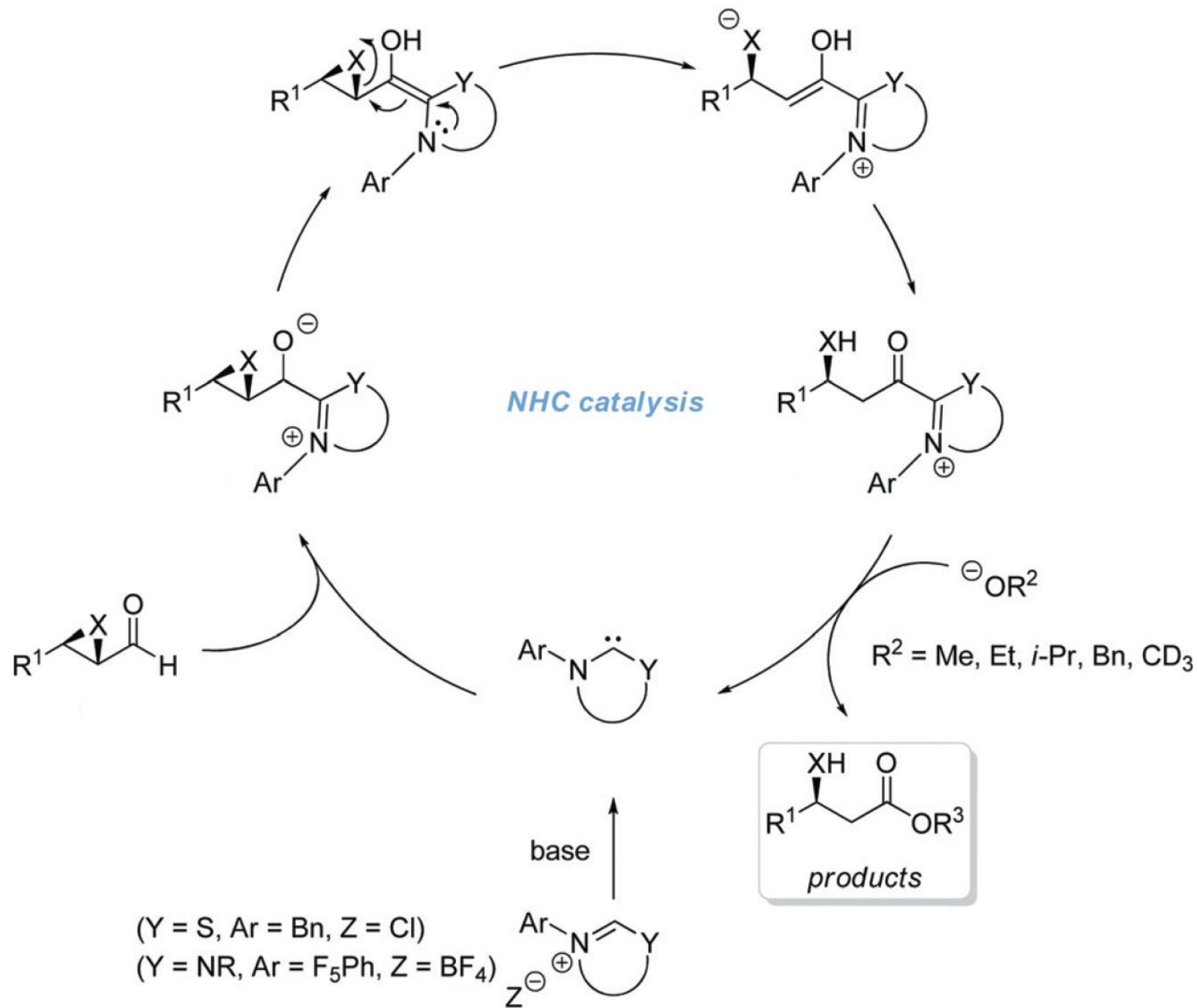
$R^1 =$ Ph
4-NO₂Ph
2-naphthyl

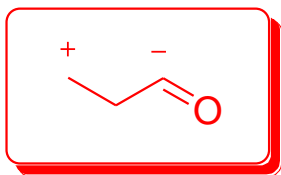


(20 mol%)
DIPEA (40%)
CHCl₃, 30 °C, 15 h

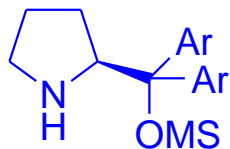
$R^2OH =$ MeOH, EtOH

56-74% yield
up to 97% ee

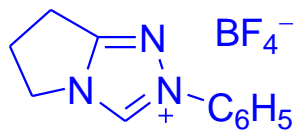




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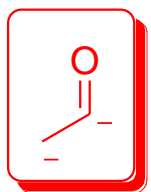
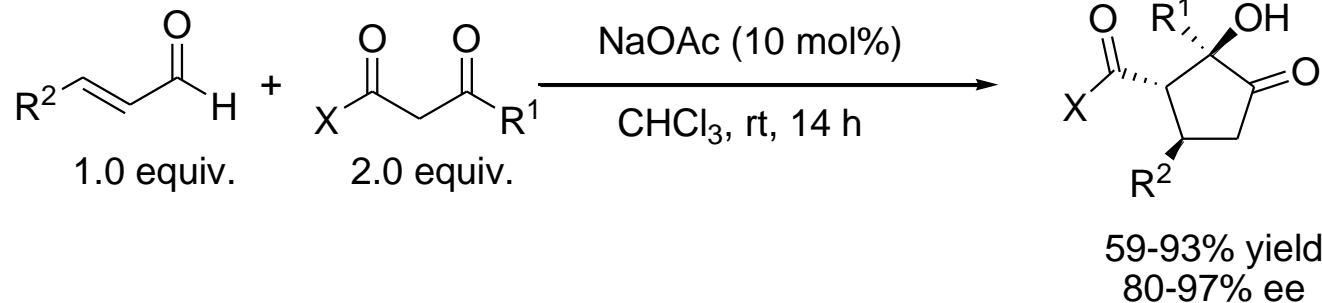


20 mol%

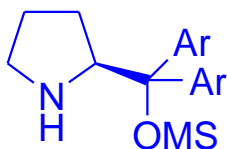


10 mol%

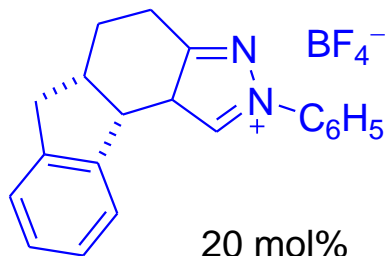
Lathrop, S. P.; Rovis, T.
J. Am. Chem. Soc.
2009, *131*, 13628



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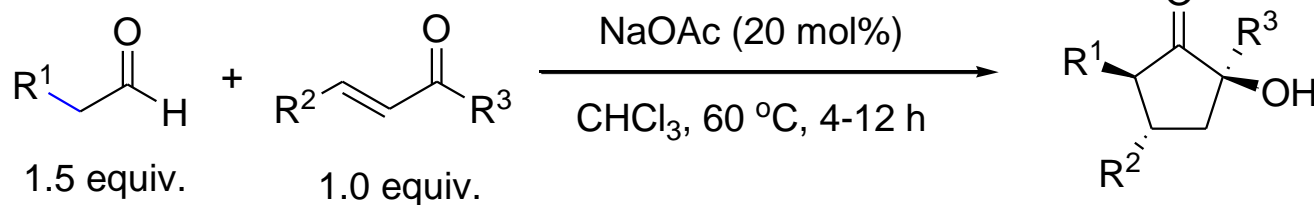


20 mol%



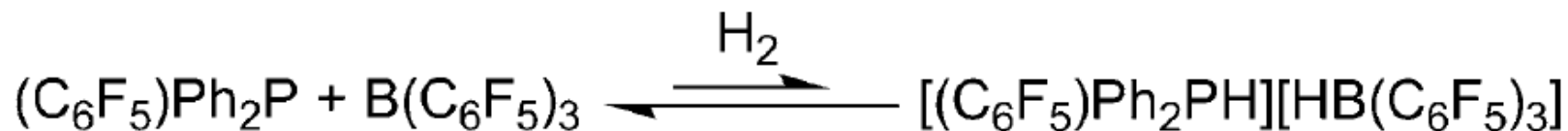
20 mol%

Ozboya, K. E.; Rovis, T.
Chem. Sci.
2011, *2*, 1835

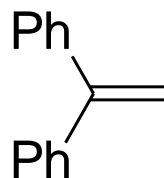


Catalytic hydrogenation: using organocatalyst

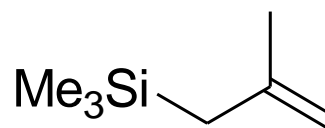
Frustrated Lewis Pairs (FLP)



20 mol%, 5 bar H₂, CH₂Cl₂, rt



99% (24 h)



95% (12 h)

(*p*-Tol)₂NMe

87% (40 h)

99% (12 h)

5 mol%

Greb, L.; OCa-Burgos, P.; Schirmer, B.; Grimme, S.; Stephan, D. W.; Paradies, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 10164

Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 46

Green oxidation reagent: O₂ catalyzed by transition metals

Traditional oxidation methods:

- Stoichiometric metal oxidation
- Nitric acid
- Swern oxidation
- Dess-Martin periodinane
- IBX
- TPAP/NMO

Problems:

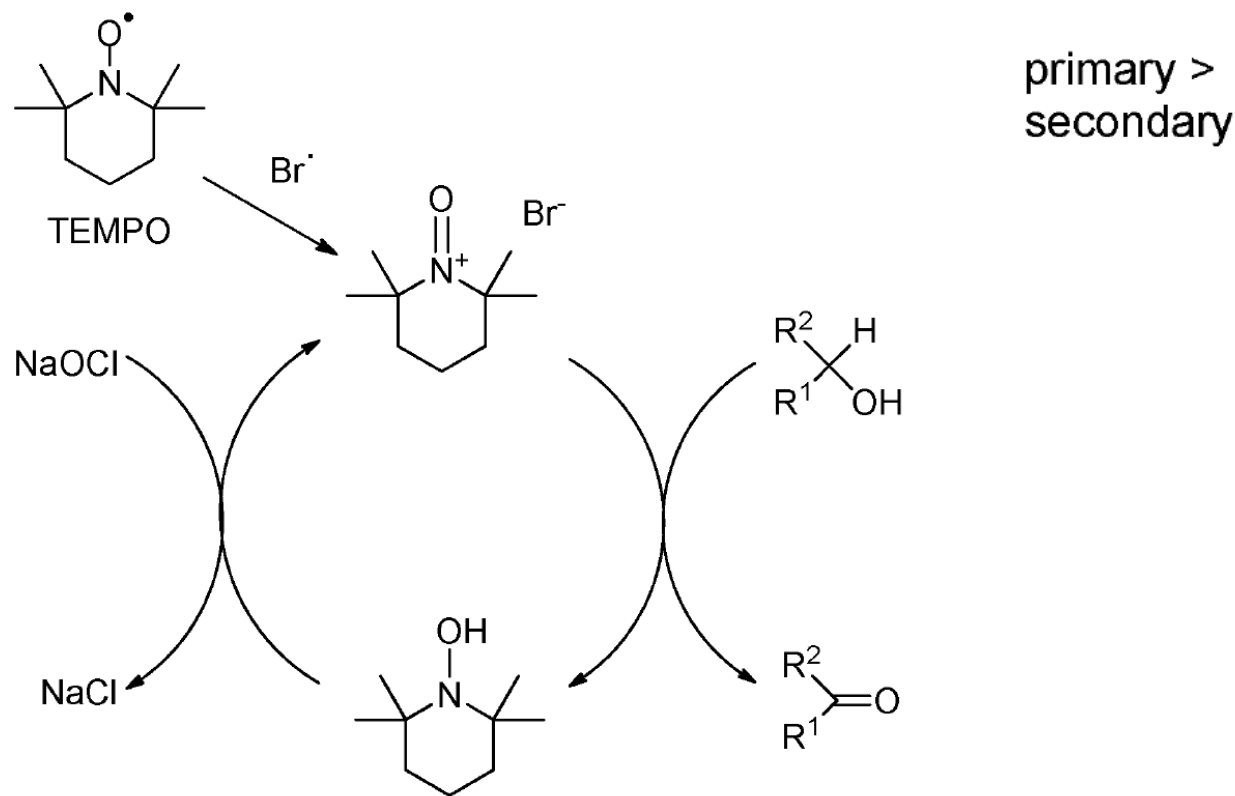
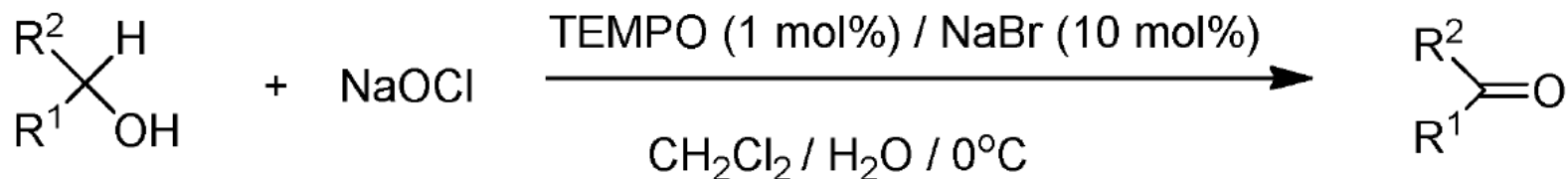
Heavy metal waste

Nitrogen oxides

Poor atom efficiencies

Difficult to scale-up

TEMPO catalysed oxidations with NaOCl



Anelli, L.; Biffi, C.; Montanari, F.; Quici, S. *J. Org. Chem.* **1987**, *52*, 2559
See also: Sheldon, R. A. *Chem. Soc. Rev.* **2012**, *41*, 1437

Biocatalysis

Advantages:

Highly efficient

Aqueous phase

Enantioselective

Regioselective

Chemoselective

Mild conditions

near neutral pH

low temperature

low pressure

Fewer byproducts

Simplified processing

Thayer, A. M. *C&EN* **2012**, 90, Issue 22, 13–18

Enabling technologies

Enzyme evolution methods

Microbial genomic sequencing

Bioinformatics

Protein engineering

DNA synthesis

Robotic screening

Established biocatalysts

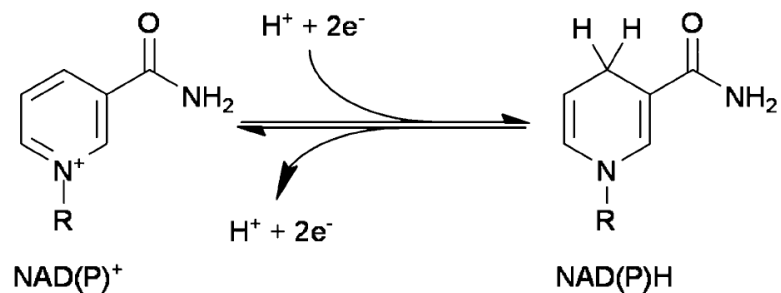
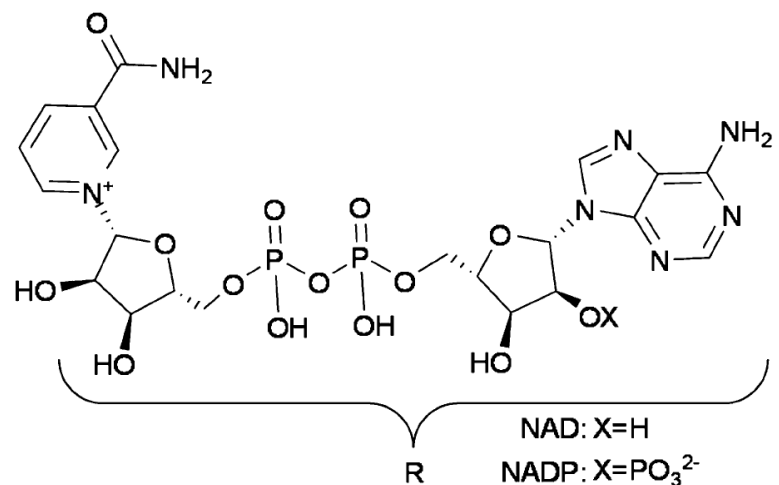
- Lipases
- Esterases
- Amidase
- Hydrolases
- Ketoreductases
- Transaminases

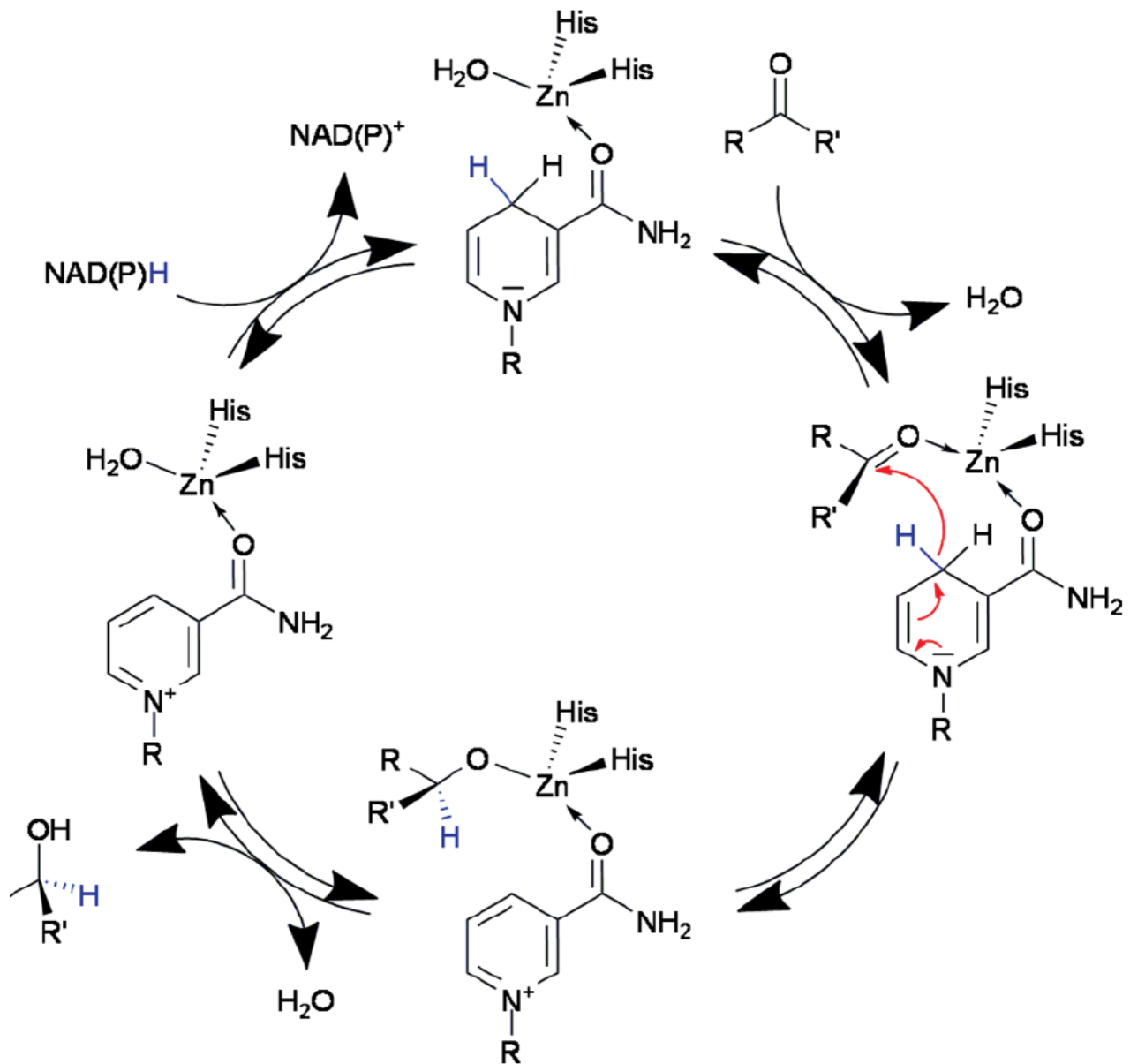
Clouthierzab, C. M.; Pelletier, J. N. *Chem. Soc. Rev.*, 2012, **41**, 1585

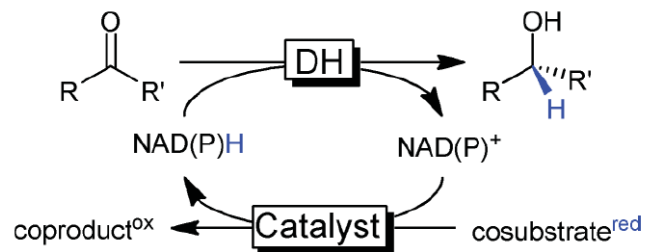
Enzymatic reductions

Hollmann, F.; Arends, I. W. C. E.; Holtmann, D. *Green Chem.*, **2011**, *13*, 2285

Alcohol dehydrogenases for carbonyl reductions







Cosubstrate	Coproduct	Catalyst	g (coproduct) mol (NAD(P)H) ⁻¹	$\Delta G'$ [kcal mol ⁻¹]
Glucose	Gluconic acid	GDH	196	-6.9
Isopropanol	Acetone	DH	58	-6.1
Ethanol	Acetic acid	ADH/AldDH	30	-12.9
Formic acid	CO ₂	FDH	44	-5.2
		Rh		
H ₃ PO ₃	H ₃ PO ₄	PDH	98	-15
		Rh		
H ₂	H ₂ O	Hase	18	-4.35
Cathode	—	Rh	0	Variable
		Hase/diaphorase		

GDH: glucose DH; ADH: alcohol DH (general); AldDH: aldehyde DH; FDH: formate DH; Rh: [Cp*Rh(bpy)(H₂O)]²⁺; Hase: hydrogenase.

Whole cells or isolated enzymes?

Whole cells

Advantage

No enzyme purification

No external cofactor regeneration

Disadvantage

Dependence on metabolic activity

Often low productivity

Reactant metabolization

Sometimes low selectivity

Isolated enzymes

Advantage

High volumetric productivities

Less side reactions

Disadvantage

Purification can be costly

Cofactor regeneration required

Stability can be an issue

Summary

Green chemistry technologies provide a number of benefits, including:

- Reduced waste, eliminating costly end-of-the-pipe treatments
- Safer products
- Reduced use of energy and resources
- Improved competitiveness of chemical manufacturers and their customers