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]。

Green Chemistry
綠色化學

工業界綠色永續合成實例

Cases of Green, Sustainable Synthesis in Industrial World

2010 綠色/永續合成化學講習會
December 3, 2010, 化學會年會，台灣大學

朝陽科技大學　　周德璋

Green Chemistry

The design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment.

[為縮減或淘汰對人類健康和環境具有危害性的物質的使用與產生，而進行化學產品和製造過程的設計、開發與執行。]

Anastas PT, Warner JC, editors.
Green Chemistry: theory and practice.
Oxford: Oxford University Press; 1998.

Anastas PT, Kirchhoff MM,
Origins, Current Status, and Future Challenges of Green Chemistry
Acc. Chem. Res. 2002, 35. 686.

The Twelve Principals of Green Chemistry

1. Prevent waste
2. Design safer chemicals and products
3. Design less hazardous chemical syntheses
4. Use renewable feedstocks
5. Use catalysts, not stoichiometric reagents
6. Avoid chemical derivatives
7. Maximize atom economy
8. Use safer solvents and reaction conditions
9. Increase energy efficiency
10. Design chemicals and products to degrade after use
11. Analyze in real time to prevent pollution
12. Minimize the potential for accidents

Anastas PT, Warner JC, editors. *Green Chemistry: theory and practice.* Oxford: Oxford University Press; 1998.

John C. Warner

Research chemist at Polaroid (1988)
Professor at the UMass, Boston (1996),
-- established first doctoral program in green chemistry
Professor at UMass, Lowell (2004)
-- founded Center for Green Chemistry

Chief technology officer and chairman of the board of Warner Babcock Institute for Green Chemistry (2007)

"Green chemistry
is the mechanics of doing
sustainable chemistry,"

Warner:
"By focusing on green chemistry, it puts us in a different innovative space. It is a science that presents industries with an incredible **opportunity for continuous growth** and **competitive advantage**."

Chemical & Engineering News, 88(40), October 04, **2010**

Paul T. Anastas

Professor of chemistry for the environment at Yale University,
Director of Yale's Center for Green Chemistry & Green Engineering,
Widely regarded as one of the fathers of "green chemistry,"
The Environmental Protection Agency assistant administrator for the Office of R&D,

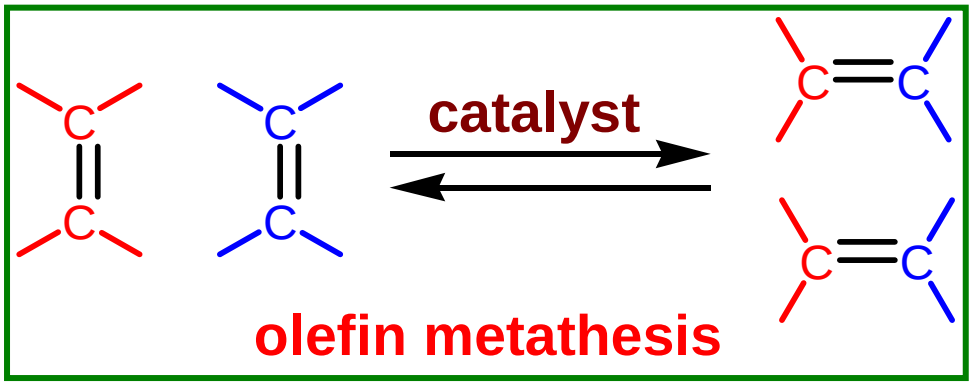
"Why did you become a chemist?"
Some are excited by the **intellectual challenges of chemistry**.
Others want to use chemistry and chemical engineering to solve problems and **make the world a better place**.

Anastas:
"The world needs both. Building a sustainable world is the most taxing intellectual exercise we have ever engaged in. It is also the most important for the future of the world."

Robert H. Grubbs, Richard R. Schrock, and France's Yves Chauvin

won the 2005 Nobel Award for their development of the **metathesis** method in organic synthesis.

"This represents a great step forward for **green chemistry**, reducing potentially hazardous waste through smarter production. **Metathesis** is an example of how important basic science has been applied for the benefit of mankind, society, and the environment,……"



綠色化學

Green Chemistry is focused on the design, manufacture, and the use of chemicals and chemical processes that have little or no pollution potential or environmental risk.

Sustainable Chemistry not only includes the concepts of green chemistry, but also expands the definition to a larger system than just the reaction. Also considers the effect of processing, materials, energy, and economics.

永續化學

綠色化學的終極目的是縮減或淘汰對人類健康和環境具有危害性的物質的使用與產生，因此任何化學產品及其相關活動—製造過程的設計、開發、與實行，當然包含化學合成，都要秉持此認知而思考。

Anastas and Warner:
"In virtually every aspect in society,
it has long been acknowledged that preventing a problem
is superior to trying to solve it once it has been created."

green chemistry
seeks to reduce and prevent pollution at its source.

⬇

綠色永續合成

What is the ideal synthesis

1. Convenient and practical -- Simple
2. High yield (100%!)
3. Short (1 step! // 1-pot!)
4. Mild conditions (room temperature or 37 ^{o}C)
5. Starting materials easy to obtain (natural or commercial)
6. Available controlled stimulus (mild reagents or catalysts)
7. Cheap and safe solvent (water!)
8. Easy isolation of products
9. Isolation of intermediates unnecessary (one-pot reaction)
10. Display novel chemistry or new applications

As Mother Nature Does!


高
原子
效率
原料易取
簡便實用
綠色永續
合成
安全
少步驟
(一步)
節能
減廢
環境友善

Sitagliptin

The active ingredient in **Januvia**™ -- medication for type 2 diabetes.

Disodium iminodiacetate (DSIDA)

A key intermediate in the production of Roundup® herbicide

Ibuprofen

One of core non-steroidal anti-inflammatory medicines

Cytovene® [ganciclovir]

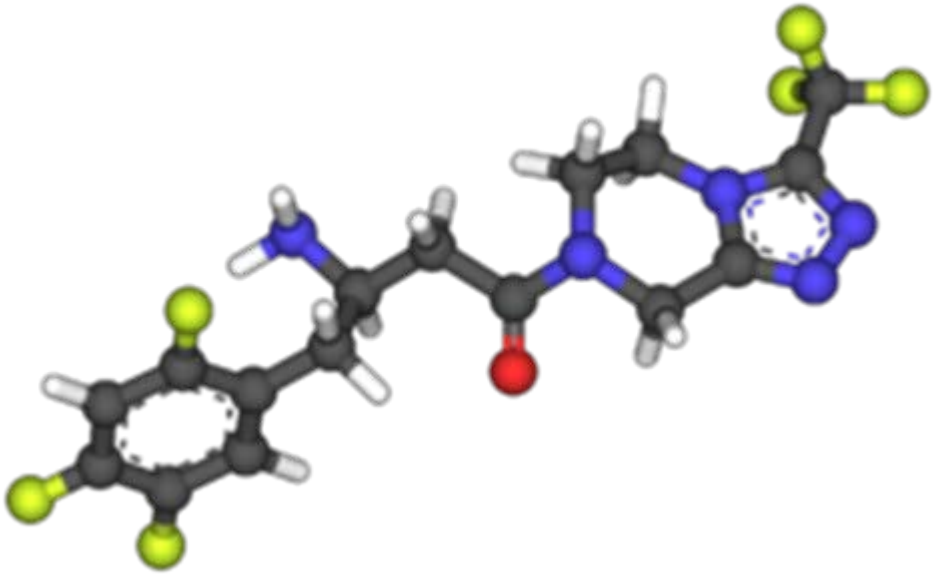
A prescription medication as “antivirals”.

Polyaspartate

Biodegradable Alternative to Polyacrylate

Case 1. 實例1

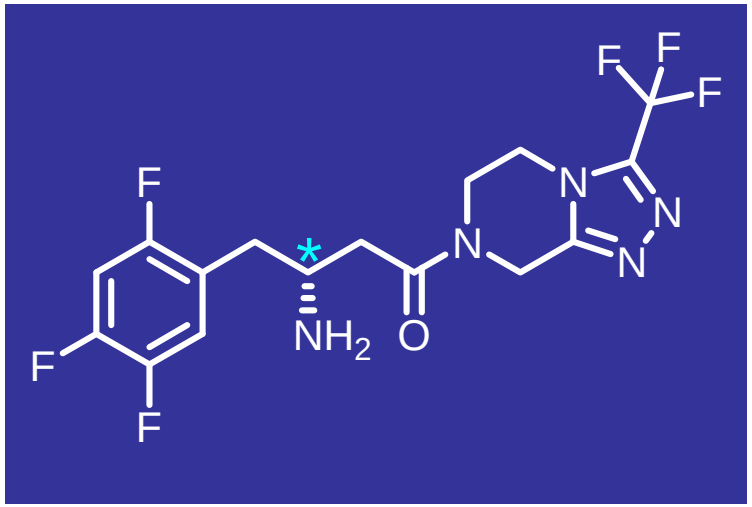
sitagliptin



US Presidential Green Chemistry Challenge Awards:

Greener Synthetic Pathways Award **2006**

What is Sitagliptin?



(*R*)-4-oxo-4-[3-(trifluoromethyl)-5,6-dihydro[1,2,4]triazolo[4,3-*a*]pyrazin-7(8*H*)-yl]-1-(2,4,5-trifluorophenyl)butan-2-amine

Sitagliptin•H_3PO_4

- the active ingredient in **Januvia**™.

Januvia (sitagliptin)

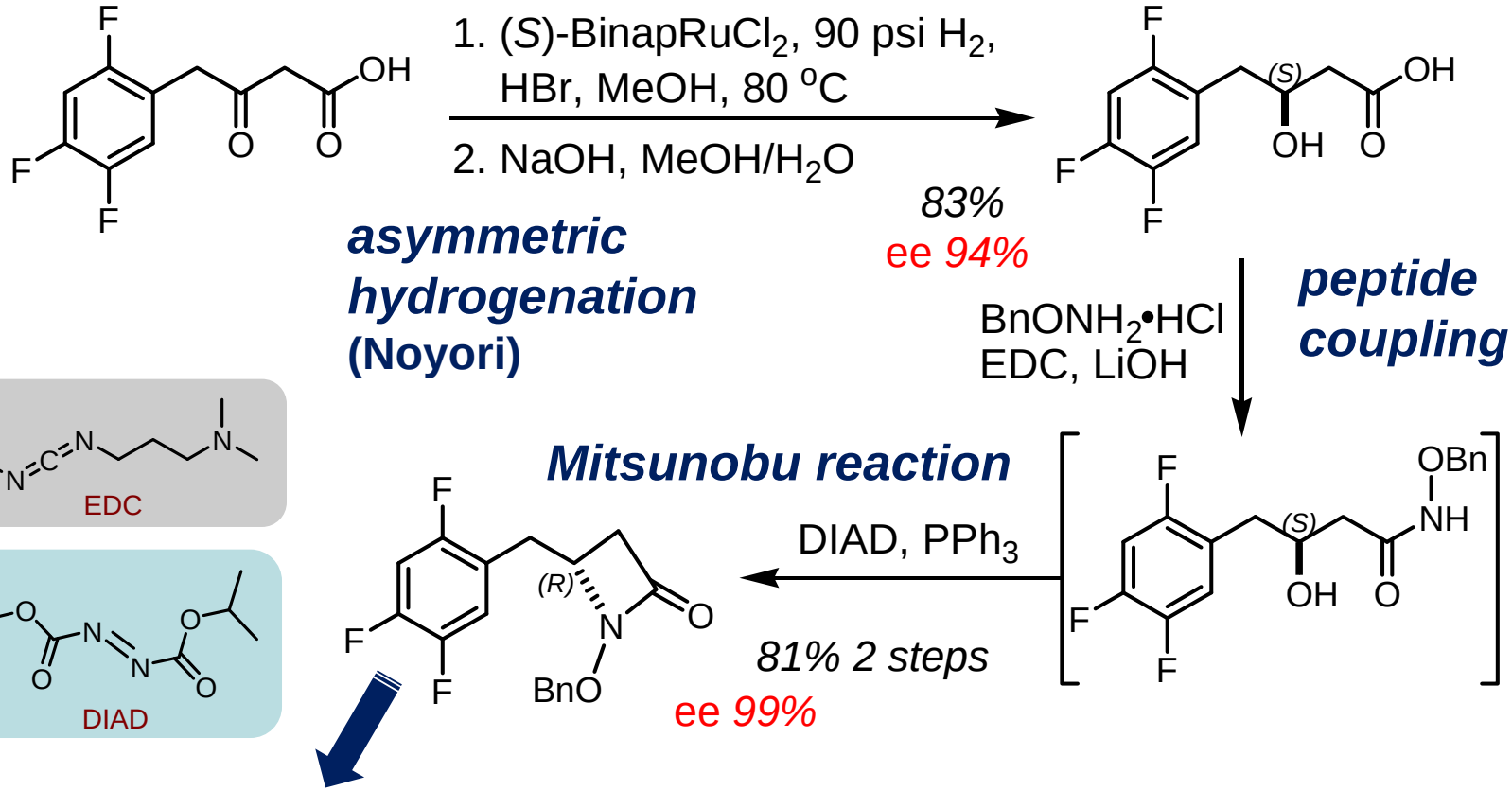
MERCK

- 具效力和選擇性的dipeptidyl peptidase type 4(DPP-4)抑制劑，治療二型糖尿病（type 2 diabetes）的藥劑。
- 2006年10月成為第一個通過美國FDA核准的糖尿病藥。
- 抑制DPP-4對腸泌素激素的水解作用，進而提高glucagonlike peptide-1（GLP-1）與glucose-dependent insulinotropic polypeptide（GIP）的濃度。

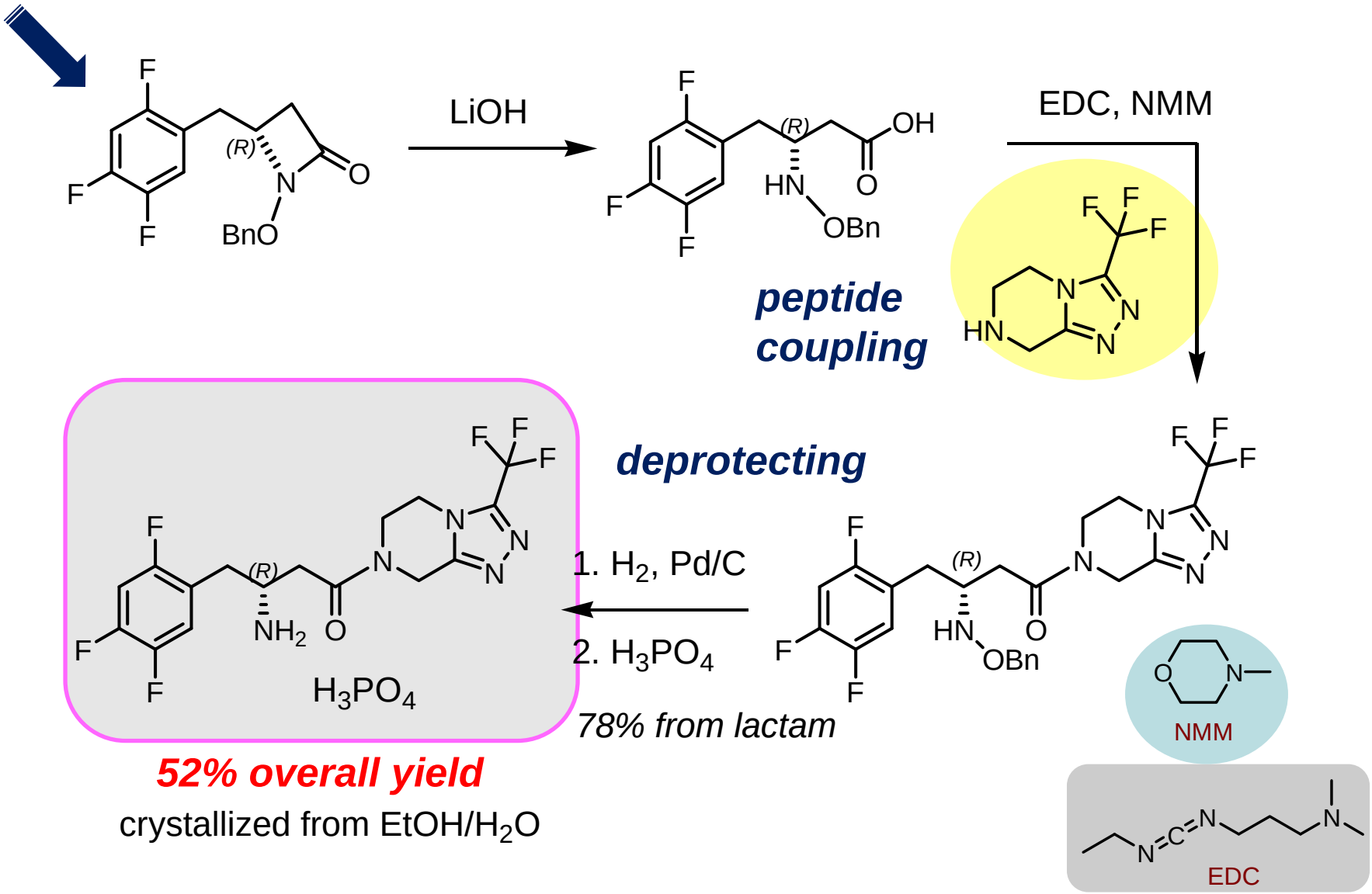
[Review: Drucker, *Cell Metab.*, 2006, 3, 153]

synthesis

- first-generation synthesis of sitagliptin (Old process)



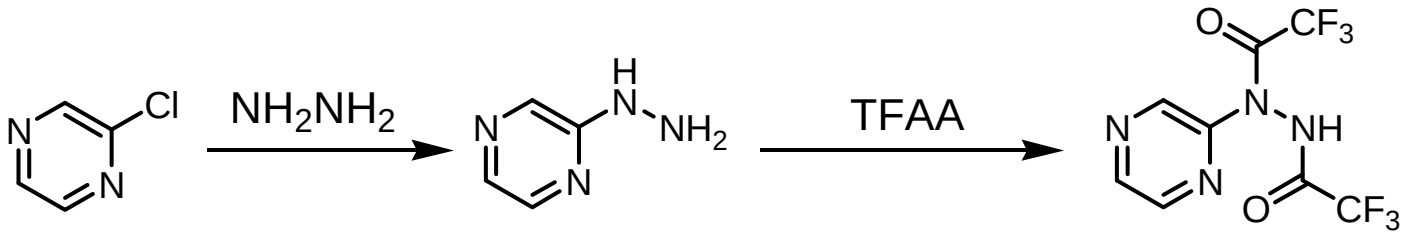
K. B. Hansen, *et. al*., *Organic Process Research & Development* **2005,** *9*, 634-639.

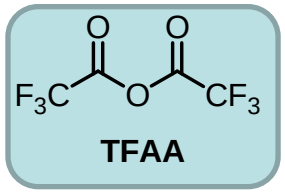


52% overall yield

crystallized from EtOH/H_2O

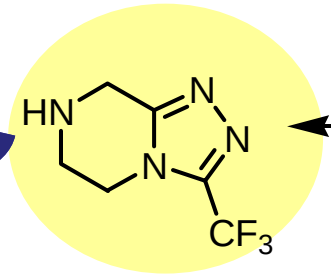
K. B. Hansen, *et. al*., *Organic Process Research & Development* **2005,** *9*, 634-639.



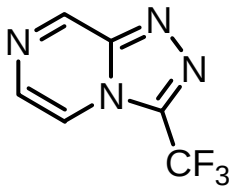


Synthesis of 3-(trifluoromethyl)-5,6,7,8-tetrahydro-[1,2,4]triazolo [4,3-a]pyrazine

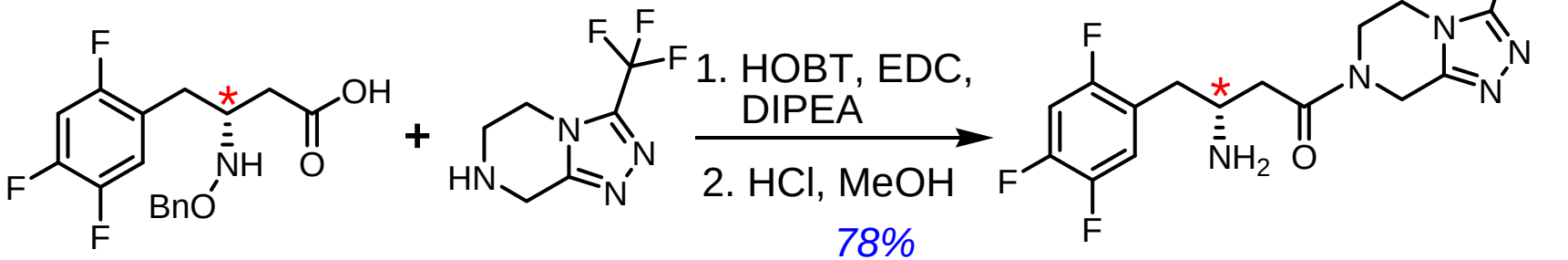
26% overall yield

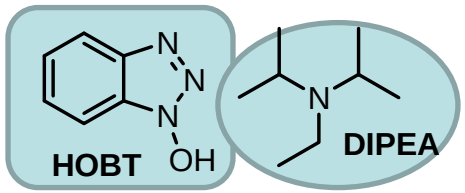


triazolopiperazine



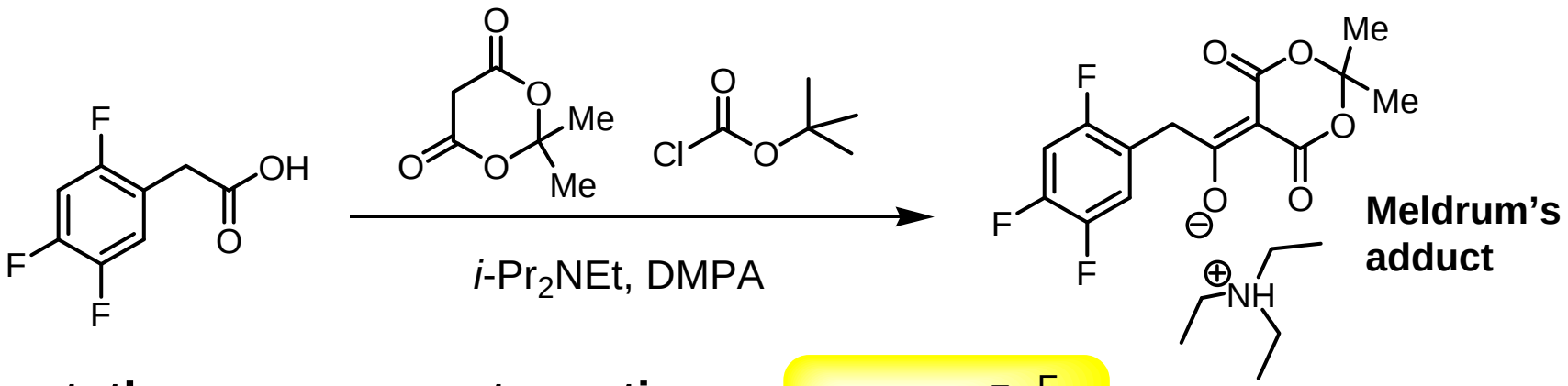
peptide coupling



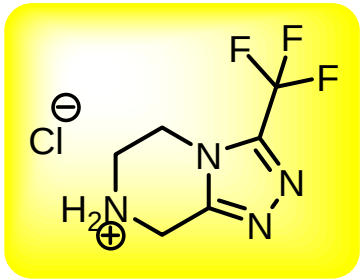


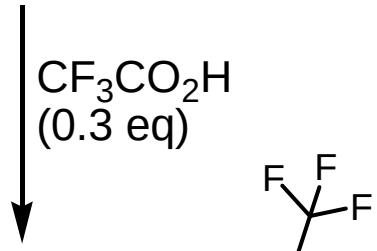
D. Kim, *et. al.*, *J. Med. Chem.* ***2005,*** 48, 141-151.

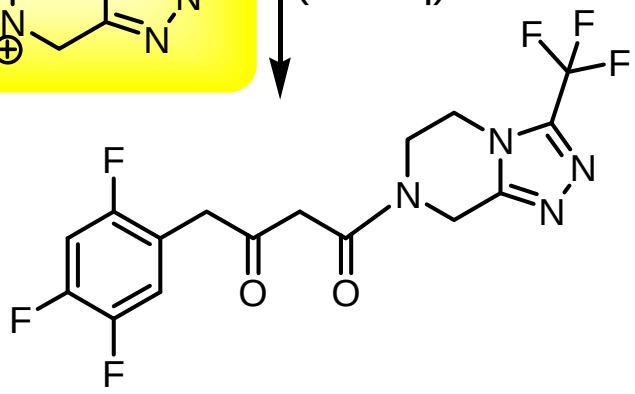
second-generation synthesis of sitagliptin (New process – Green route)

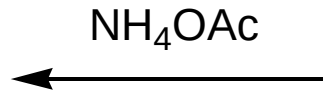


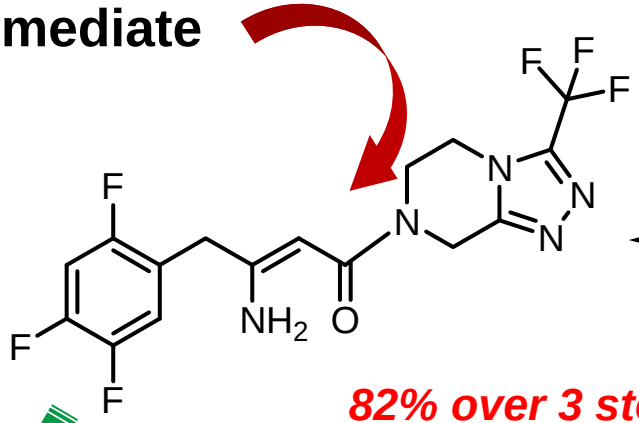
One-pot, three-component reaction to key β-enamino amide intermediate







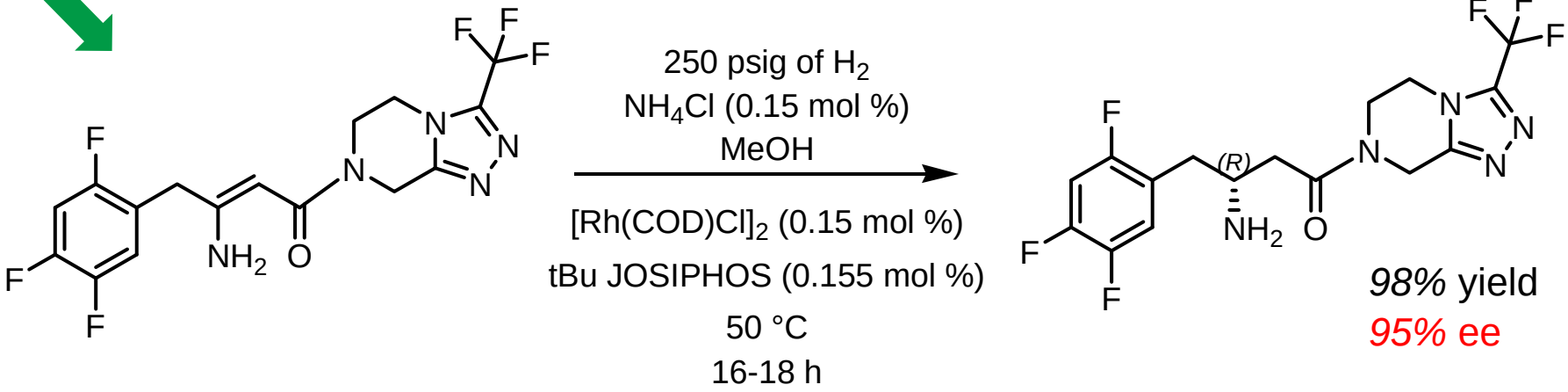




82% over 3 steps

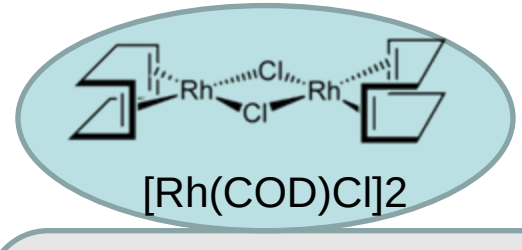
K. B. Hansen, *et. al*., *J. Am. Chem. Soc*. **2009**, *131*, 8798–8804

Enantioselective hydrogenation of unprotected β-enamine amide



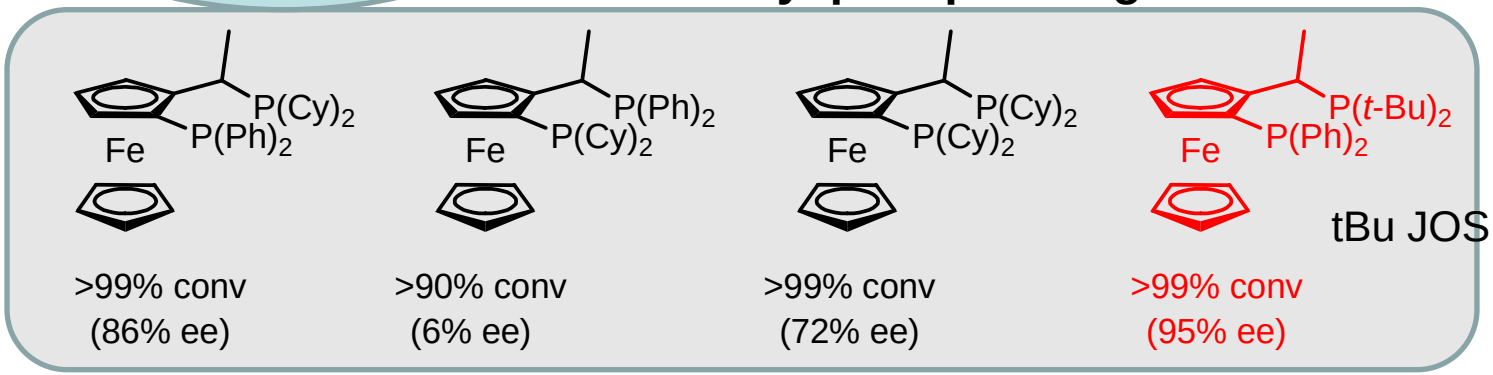
98% yield
95% ee

recrystallized as the phosphoric acid salt



[Rh(COD)Cl]2

JOSIPHOS
ferrocenyl phosphine ligands



tBu JOSIPHOS

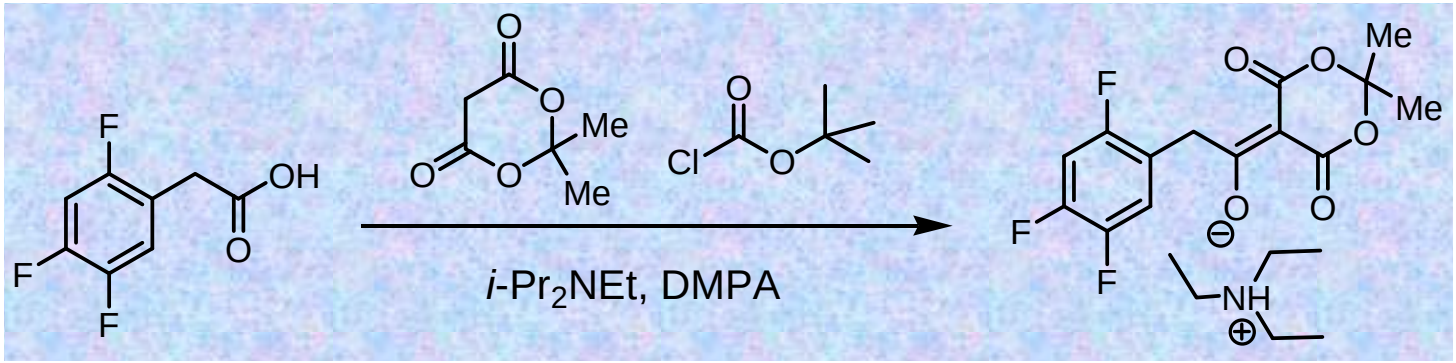
>99% conv (86% ee)	>90% conv (6% ee)	>99% conv (72% ee)	>99% conv (95% ee)

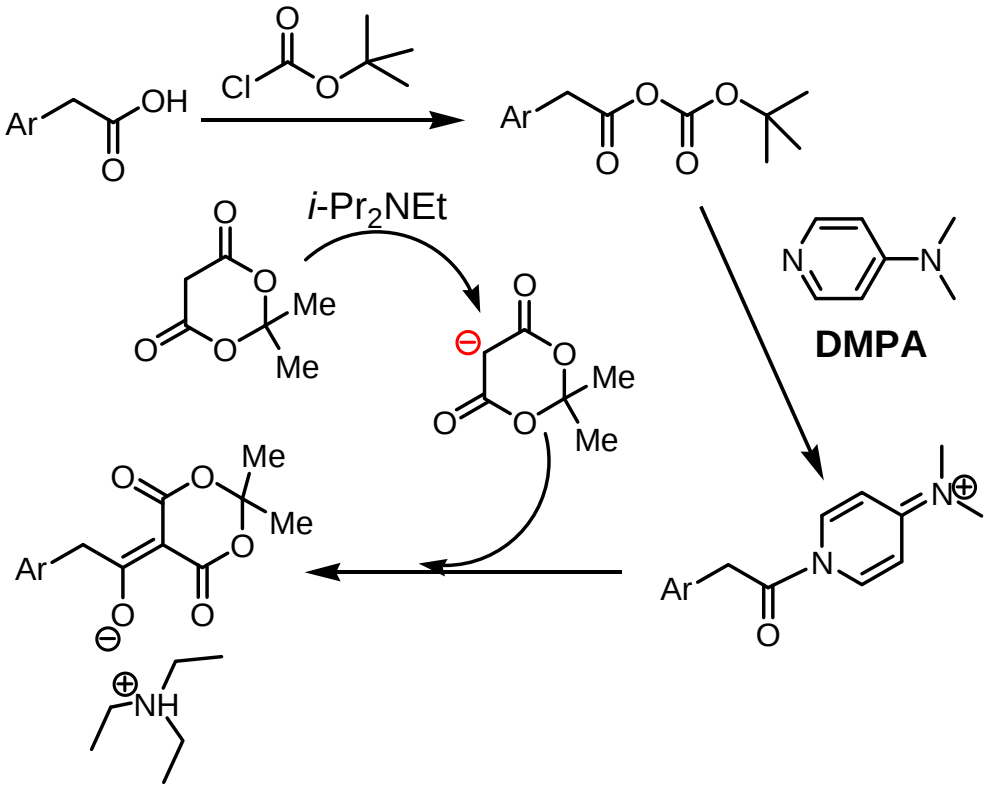
K. B. Hansen, *et. al*., *J. Am. Chem. Soc*. **2009**, *131*, 8798–8804

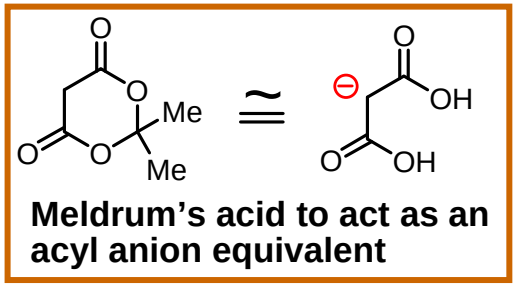
The "greener" features

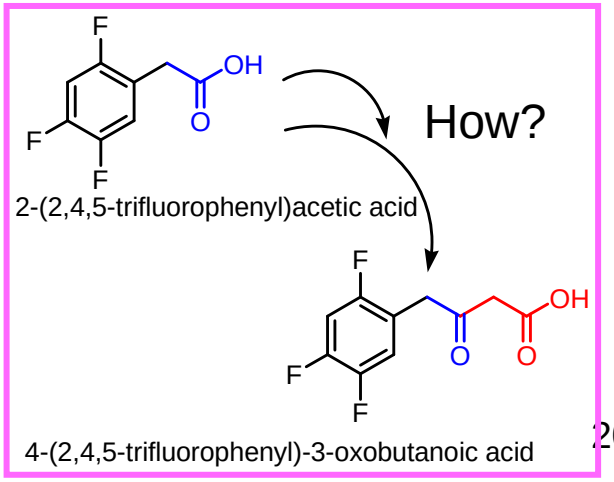
- **Fewer steps (4 vs 8):**
  elimination Mitsunobu reaction
  elimination one peptide coupling
  ***No** protection-deprotection of the amine nitrogen*
- **Increases yield (65% vs 52%)**
- **Waste reduction (>80%):**
  Eliminate 60 L of aqueous waste per kg of product
  (prevent formation of 150,000 metric tons of solid and aqueous process waste over the lifetime of Januvia)
- **Unprecedented efficient hydrogenation of an unprotected enamine.**
  an excellent example of a scientific innovation resulting in benefits to the environment!

How is the Meldrum's adduct formed?

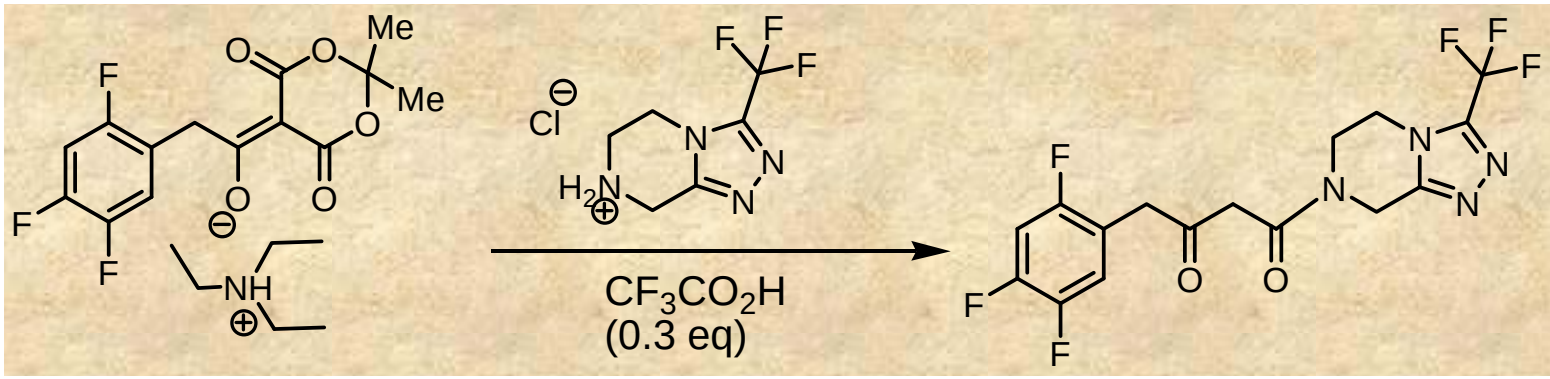


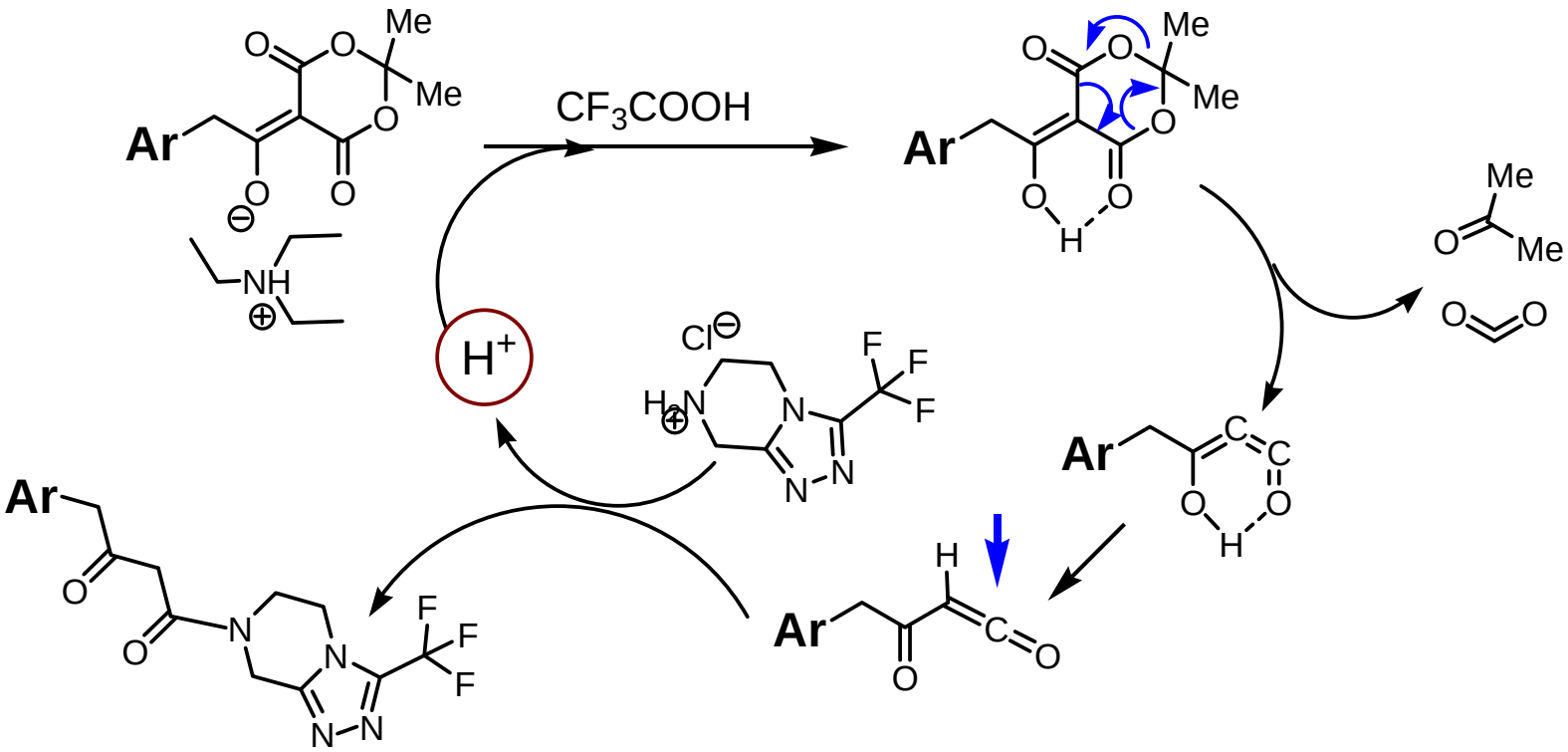


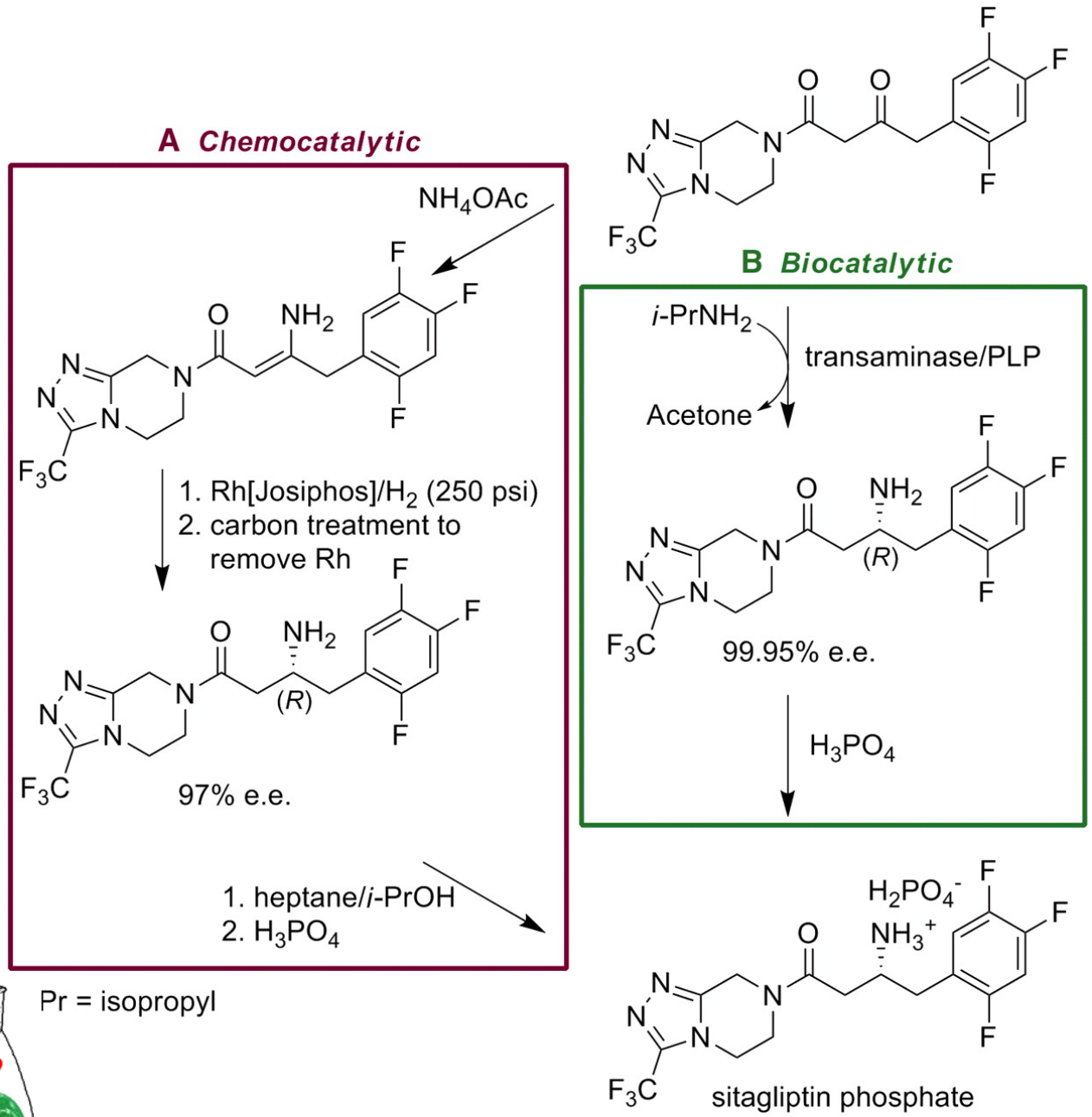




How is the β-ketoamide formed?







Biocatalytic Transamination

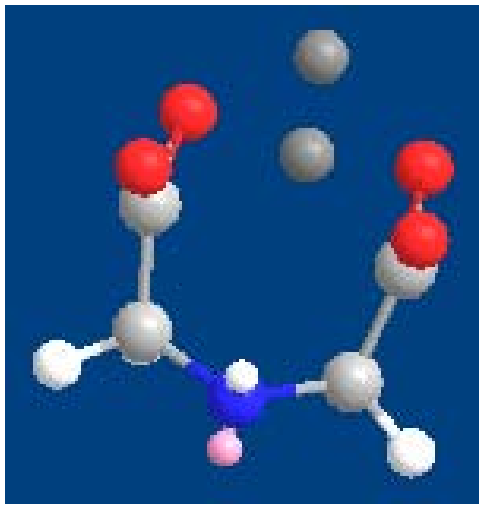
Science
AAAS

C K Savile et al. *Science* *2010*;329:305-309

Presidential Green Chemistry Challenge Award
Greener Reaction Conditions Award
2010

Case 2. 實例2

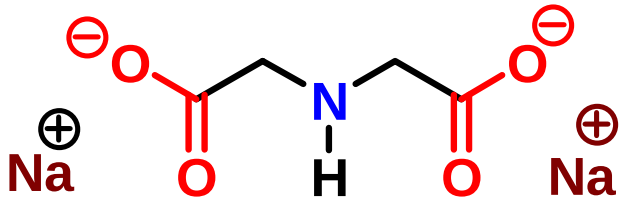
Disodium iminodiacetate (DSIDA)



US Presidential Green Chemistry Challenge Awards:

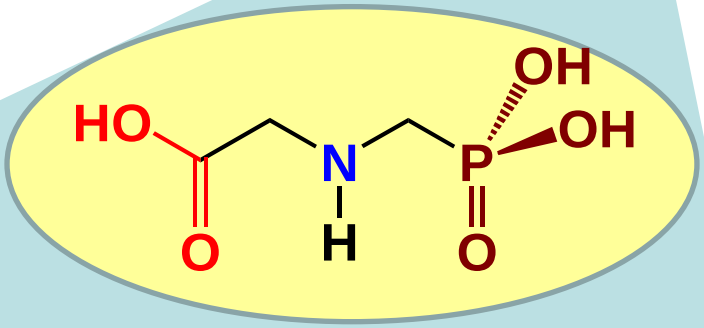
Greener Synthetic Pathways Award **1996**

What is Disodium iminodiacetate (DSIDA)?



sodium 2,2'-azanediyldiacetate
disodium 2-[(2-oxido-2-xoethyl)amino]acetate

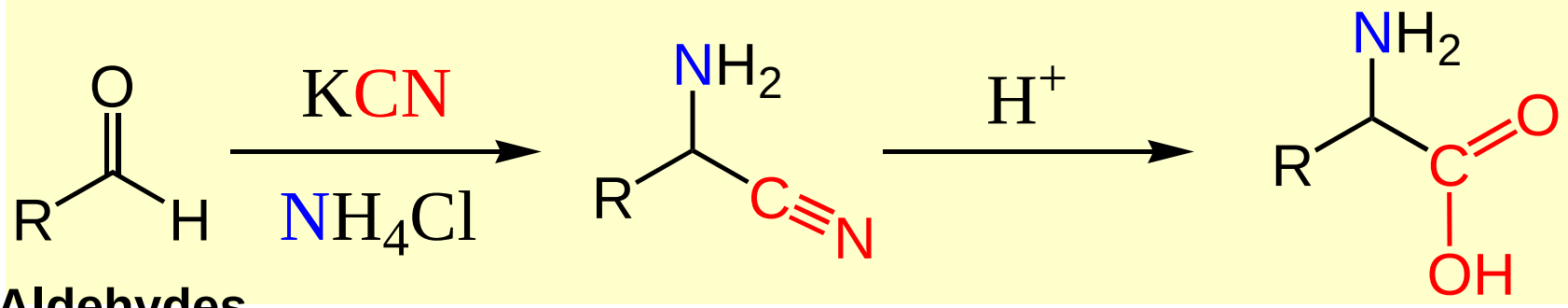
a key intermediate in the production of Monsanto's Roundup® herbicide



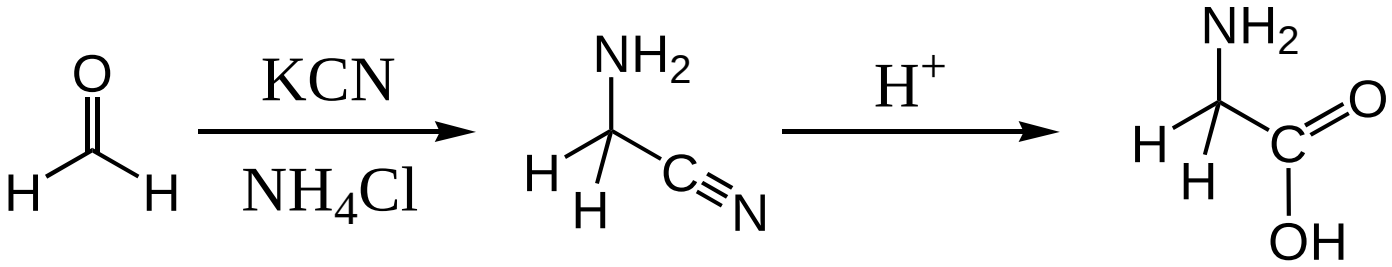
Glyphosate: *N*-(phosphonomethyl)glycine in the form of its isopropylamine salt (41%)

Roundup® agricultural herbicides are the flagship of Monsanto's agricultural chemicals business.

Strecker amino acid synthesis



Aldehydes (or Ketones)

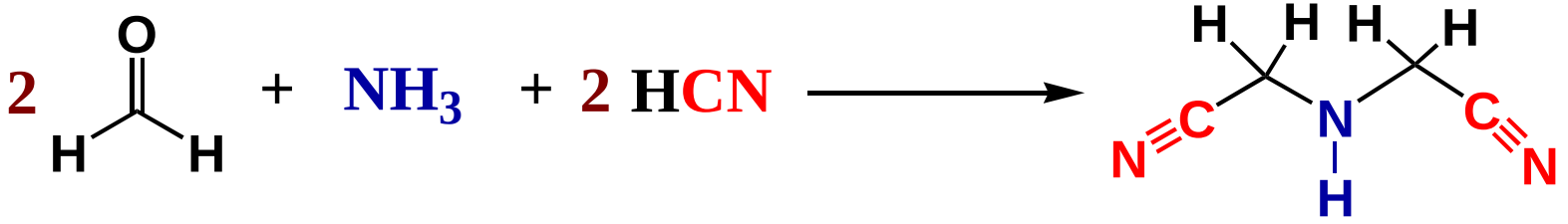


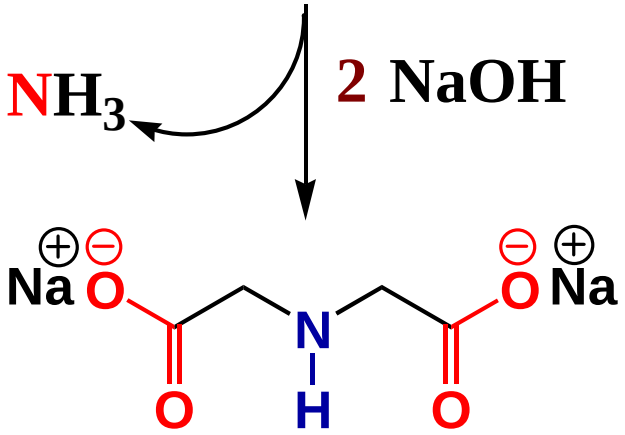
glycine

2-aminoacetic acid

Traditionally, the Strecker process has been used to manufacture DSIDA. It requires formaldehyde, ammonia, hydrogen cyanide, and hydrochloric acid.

The Strecker process for synthesizing DSIDA





disodium iminodiacetate

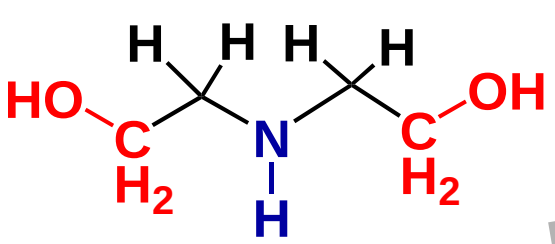
hydrogen cyanide:
extremely toxic;
requires special handling

exothermic reaction
generating potentially unstable intermediates.

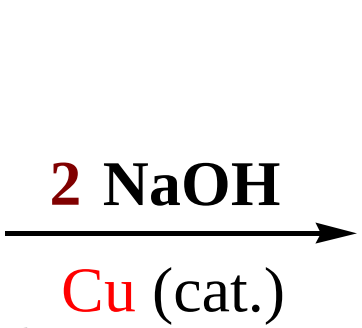
waste: *1 kg for every 7 kg of product.*

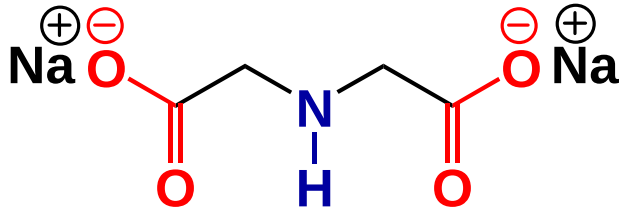
Green process for synthesizing DSIDA

copper-catalyzed dehydrogenation of diethanolamine



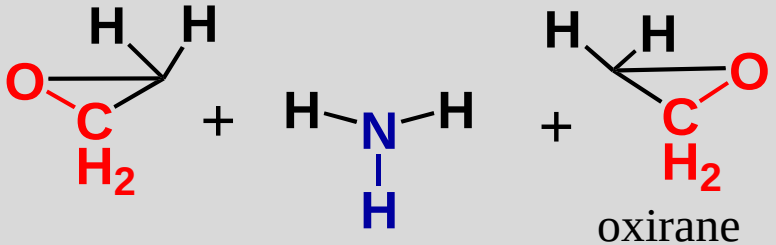
diethanolamine
2,2'-azanediyldiethanol





disodium iminodiacetate

+ 4 H_2



oxirane
ethylene oxide

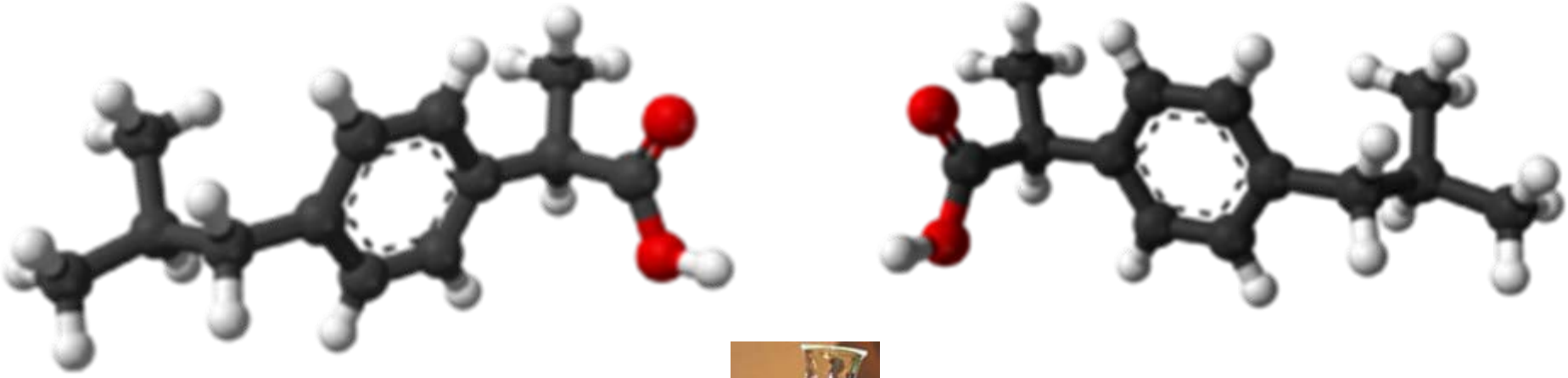
Greener Synthetic Pathways Award 1996

- ***the dehydrogenation reaction is endothermic;***
  avoid the use of cyanide and formaldehyde;
- ***fewer process steps, higher overall yield;***
  no purification or waste cut is necessary;
- ***recover catalyst by filtration, ready for subsequent use in the manufacture of* Roundup*;***
- ***This catalysis technology is applicable in the production of other amino acids and***
- ***becomes a general method for conversion of primary alcohols to carboxylic acid salts.***

1. Prevent Waste
2. Increase Atom Economy
3. Design Less Hazardous Chemical Syntheses
4. Design Safer Chemicals
9. Use Catalysts

Case 3. 實例3

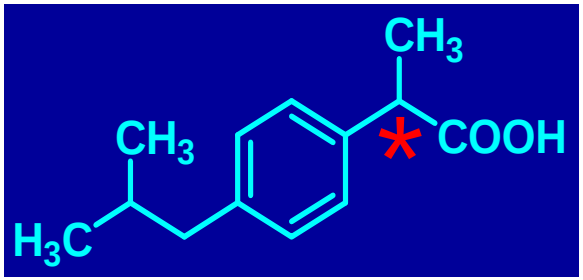
Ibuprofen

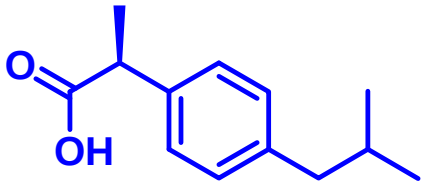


US Presidential Green Chemistry Challenge Awards:

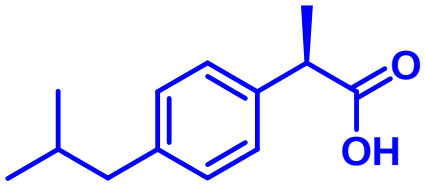
Greener Synthetic Pathways Award **1997**

What is ibuprofen?





(S)-ibuprofen



(R)-ibuprofen

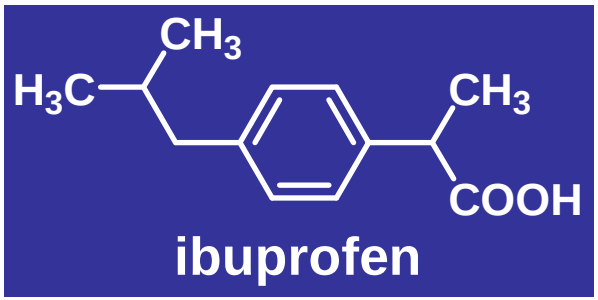
(S)-2-(4-isobutylphenyl)propanoic acid, (S)-ibuprofen, is active form both *in vitro* and *in vivo*.

(S)-ibuprofen ⇌ **(R)-ibuprofen**

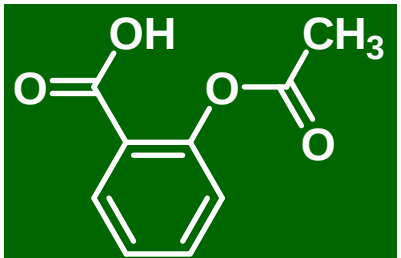
2-arylpropionyl-CoA epimerase (isomerase)

marketed as racemic mixtures.

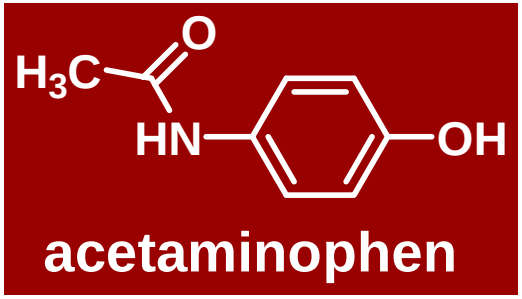
- One of core non-steroidal anti-inflammatory medicines (非類固醇消炎藥) in the World Health Organization's "Essential Drugs List", which is a list of minimum medical needs for a basic health care system ---- *Over-the-Counter (不需處方可出售的) medicine.* [others: aspirin, paracetamol (acetaminophen)]



ibuprofen



aspirin



acetaminophen

- Discovered by S. Adams, with J. Nicholson, A. R. M. Dunlop, J. B. Wilson & C. Burrows (Boots Company), and was patented in 1961. Dr. Adams initially tested the drug on a hangover（宿醉）.

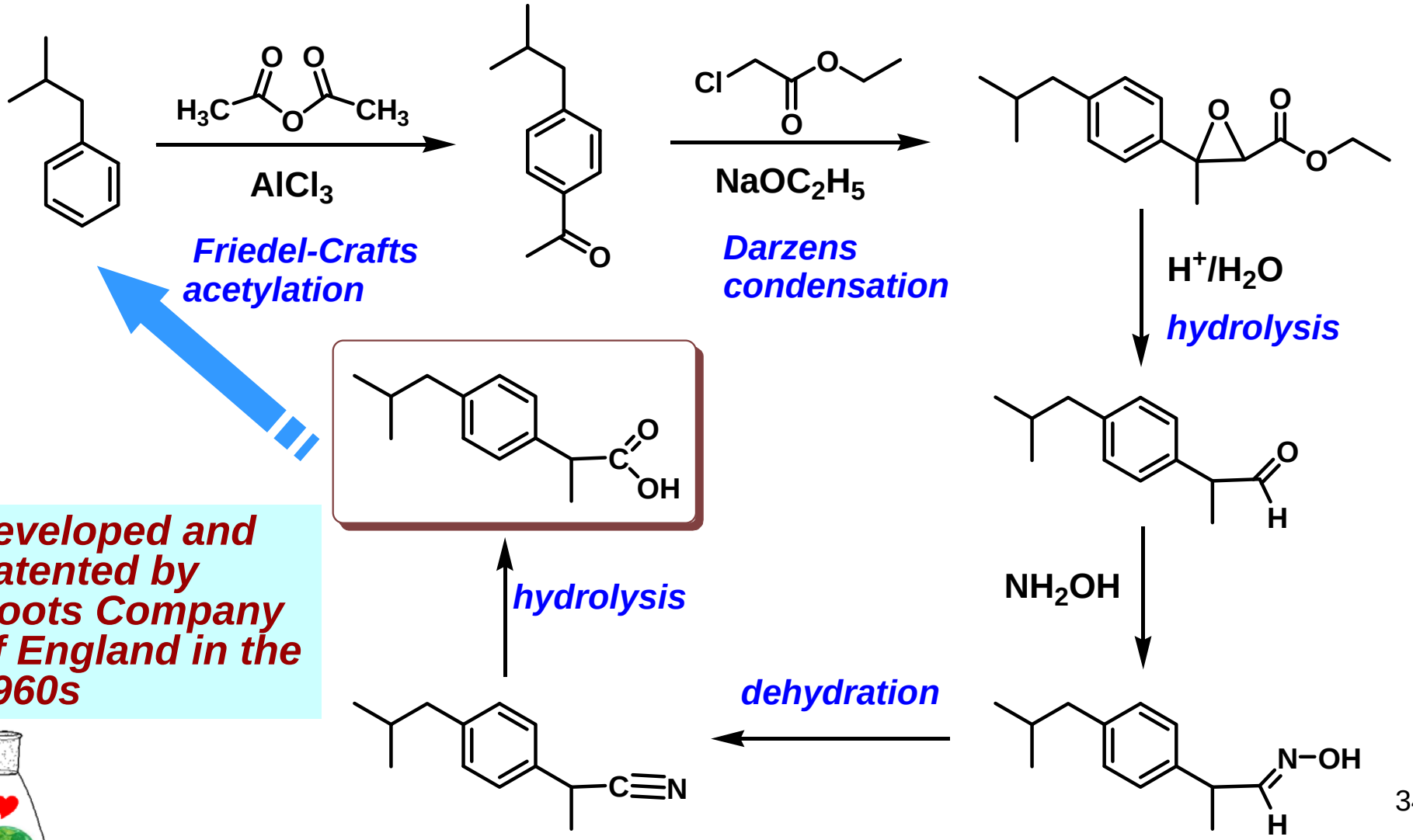
- It was launched in 1969 as a medication for the treatment of rheumatoid arthritis [風濕性關節炎] in the UK and in 1974 in the USA.
- The Boots Group was awarded ***Queen's Award for Technical Achievement*** for the development of ibuprofen in 1987.
- 具解熱、消炎和鎮痛的作用，可治療發燒、疼痛和發炎。
- 減輕關節炎(arthritis)，原發型痛經(primary dysmenorrhea)，發燒 (fever)，等症狀；作為止痛劑（analgesic)；具抑制血小板凝集效應（antiplatelet effect）。
- Active ingredient in “Motrin”, “Advil”, Medipren”….，“炎熱消”（水液），“普服芬”(錠劑), 宜痛炎錠, 伊普®鎮痛, ….

synthesis

- The industrial synthesis was developed and patented by Boots Company of England in 1961. ***--- brown synthesis***
- A new greener industrial synthesis was developed and implemented by the BHC Company (now BASF Corporation) in 1991. ***--- green synthesis***
- BHC won Presidential Green Chemistry Challenge Awards (USA) **---- Greener Synthetic Pathways Award in 1997.**

BHC = Boots + Hoechst Celanese

Boots synthesis of ibuprofen
--- brown synthesis



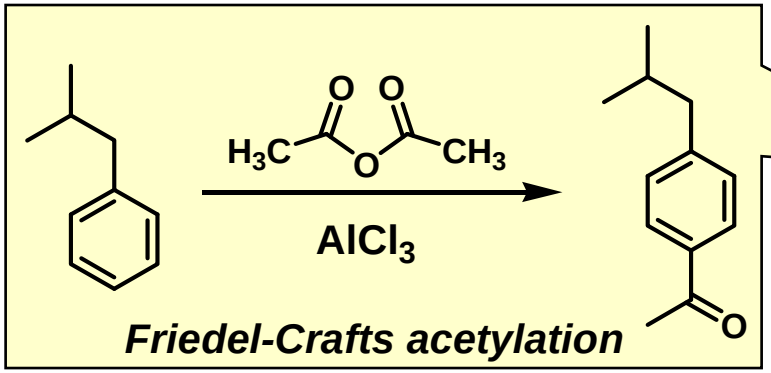
developed and patented by Boots Company of England in the 1960s

	Reagent		Used in ibuprofen		Unused in ibuprofen	
	Formula	**Mw**	**Formula**	**Mw**	**Formula**	**Mw**
1	$C_{10}H_{14}$	134	$C_{10}H_{13}$	133	H	1
	$C_4H_6O_3$	102	C_2H_3	24	$C_2H_3O_3$	75
2	$C_4H_7ClO_2$	122.5	CH	13	$C_3H_6ClO_2$	109.5
	C_2H_5ONa	68		0	C_2H_5ONa	68
3	H_3O	19		0	H_3O	19
4	NH_3O	33		0	NH_3O	33
6	H_4O_2	36	HO_2	33	H	3
	Total		**Ibuprofen**		**Waste products**	
	$C_{20}H_{42}NO_{10}ClNa$	514.5	$C_{13}H_{18}O_2$	206	$C_7H_{24}NO_8ClNa$	308.5

▸ = (206)/(514.5) x 100 = **40%**

Table 1. Atom economy in the Boots' synthesis of ibuprofen

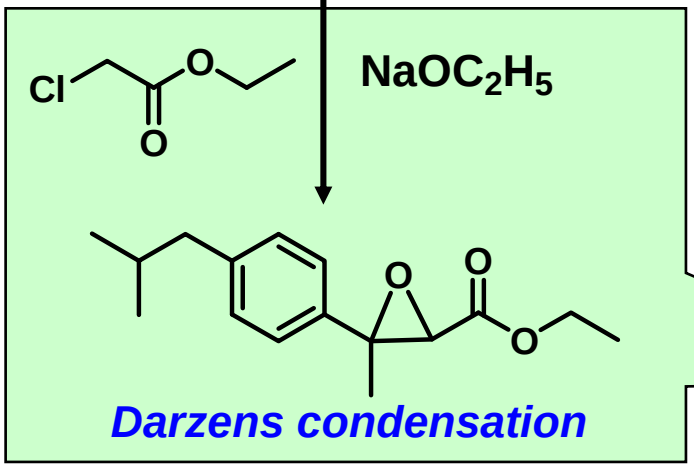
Problems with Boots synthesis of ibuprofen



HCl AcOH Al

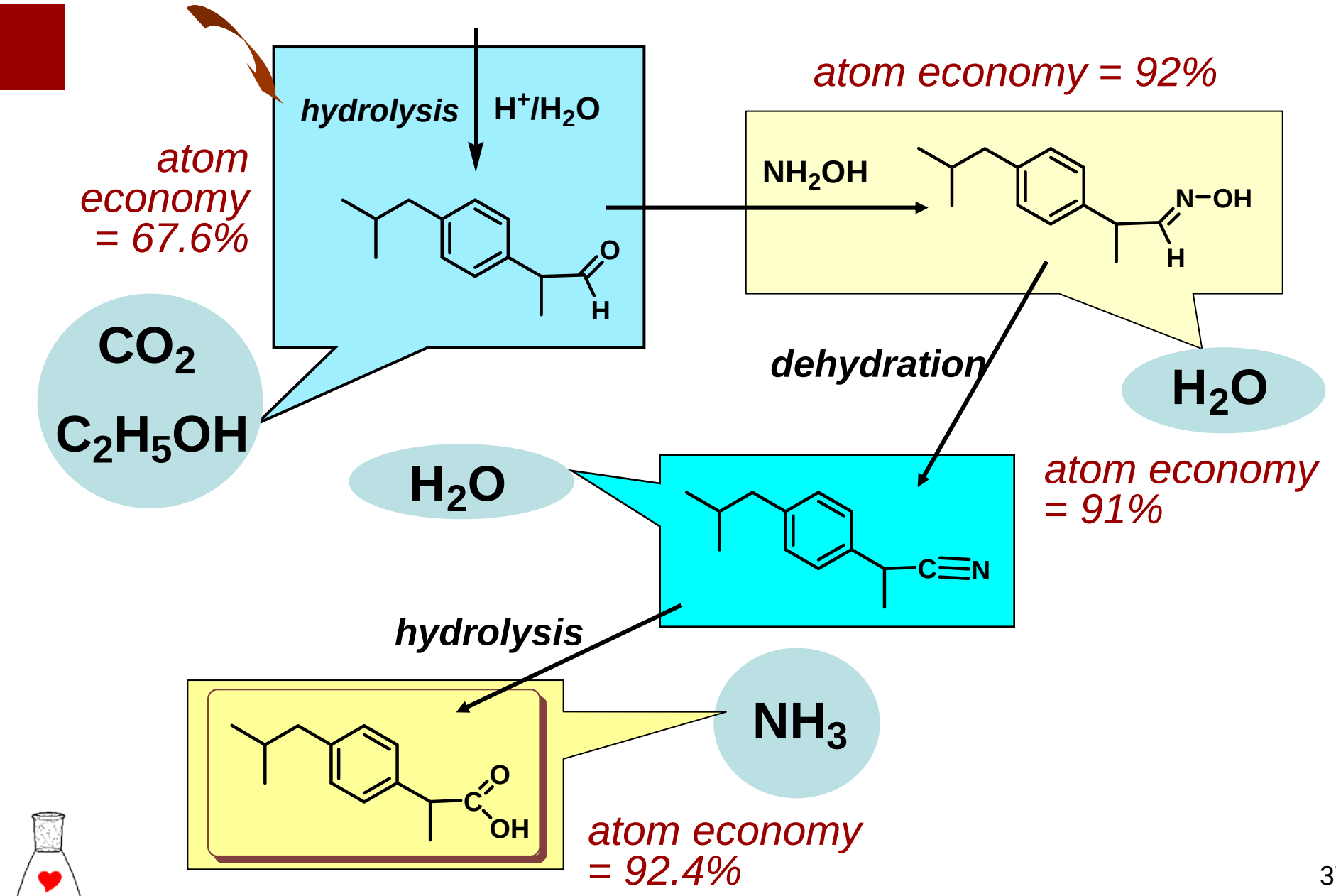
atom economy = 74.5%

aluminium trichloride, **$AlCl_3$**, is not a true catalyst. it is changed into a hydrated form, $Al(OH)_3/H_2O$, that has to be disposed of – usually in landfill sites.



NaCl C_2H_5OH

atom economy = 71.6%


hydrolysis
H^+/H_2O
atom economy = 92%
atom economy = 67.6%
NH_2OH
N−OH
H
O
H
CO_2
C_2H_5OH
dehydration
H_2O
H_2O
atom economy = 91%
C≡N
hydrolysis
NH_3
C
O
OH
atom economy = 92.4%

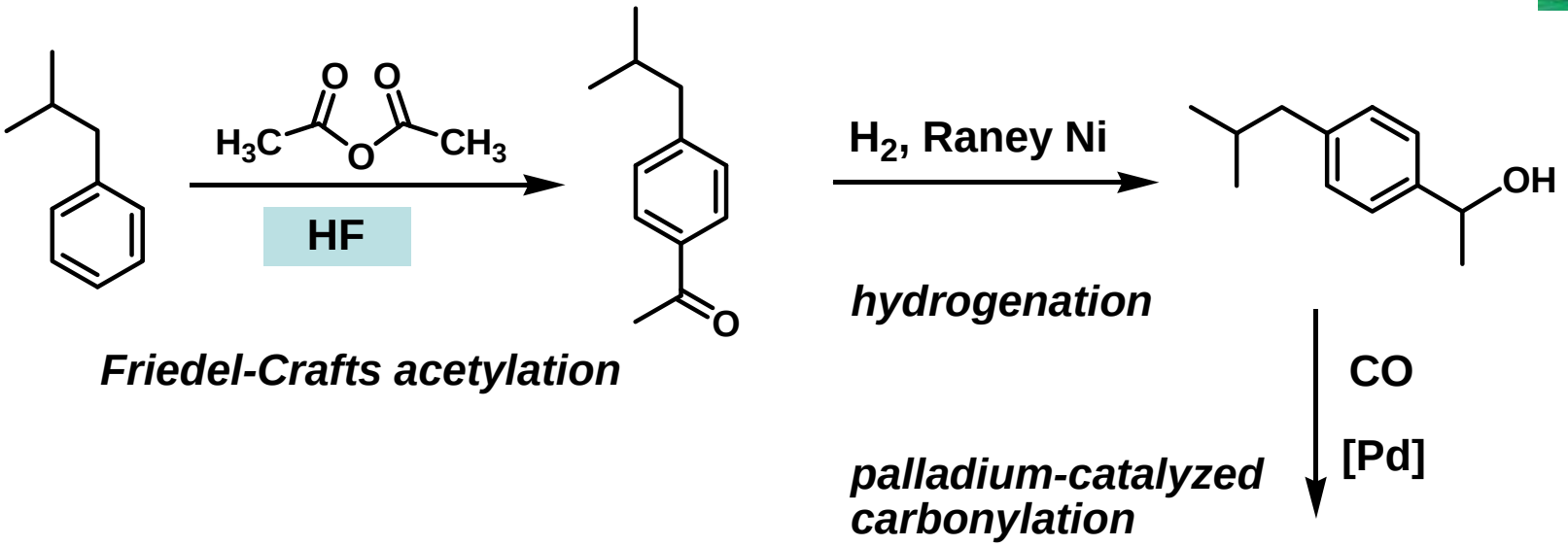
- **6 steps!**
  If 90% yield for each step, then overall yield is 53%.
- **atom economy is 40%!**
  thus every 1 kg of ibuprofen produced is accompanied with more than 1.5 kg of waste.
- **UK market for ibuprofen is about 3,000,000 kg per year!**
  - *about 4,500,000 kg of waste are produced.*
  - *a typical tablet contains 200 mg of ibuprofen, then 15,000,000,000 (1.5×10^{10}) tablets are produced.*

World population on November 2010 is estimated by the United States Census Bureau to be 6.884 billion (6,884,000,000).

BHC synthesis of ibuprofen --- green synthesis

(USA) Presidential Green Chemistry Challenge Awards

Greener Synthetic Pathways Award in 1997



developed and implemented by the BHC Company in 1991

	Reagent		Used in ibuprofen		Unused in ibuprofen	
	Formula	**Mw**	**Formula**	**Mw**	**Formula**	**Mw**
1	$C_{10}H_{14}$	134	$C_{10}H_{13}$	133	H	1
	$C_4H_6O_3$	102	C_2H_3O	43	$C_2H_3O_2$	59
2	H_2	2	H_2	2		0
3	CO	28	CO	28		0
	Total		**Ibuprofen**		**Waste products**	
	$C_{15}H_{22}O_4$	266	$C_{13}H_{18}O_2$	206	$C_2H_4O_2$	60
atom economy = (206)/(266) x 100 = **77.4%**						

Table 2. Atom economy in the BHC synthesis of ibuprofen

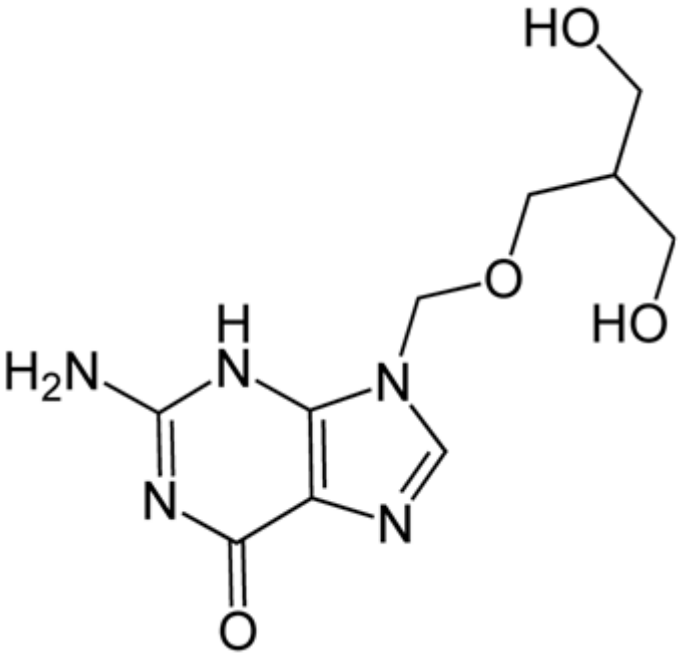
Economic and Environmental Advantages of BHC Synthesis

- Greater overall yield (three steps vs. six steps)
- Greater atom economy (uses less feedstocks)
- Fewer auxiliary substances (products and solvents separation agents)
- **Less waste:** greater atom economy, catalytic vs. stoichiometric reagents, recovery of byproducts and reagents, recycling, and reuse, lower disposal costs.

The BHC ibuprofen process is an innovative, efficient technology that has revolutionized bulk pharmaceutical manufacturing.

Case 4. 實例4

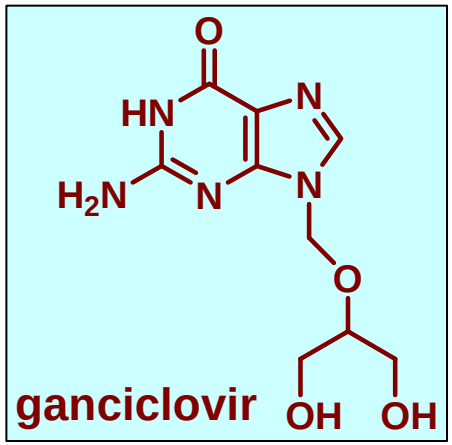
The Cytovene® [ganciclovir]



US Presidential Green Chemistry Challenge Awards:

Greener Synthetic Pathways Award **2000**

What is ganciclovir [“更昔洛韋”]?



Chemical Formula: $C_9H_{13}N_5O_4$
Exact Mass: 255.09675
Molecular Weight: 255.23062

IUPAC name:
2-amino-9-{[(1,3-dihydroxypropan-2-yl)oxy]methyl}-6,9-dihydro-3*H*-purin-6-one

- Ganciclovir is a prescription medication that belongs to the family of drugs known as “antivirals”.
[“更昔洛韋”是屬於抗病毒的處方藥劑]

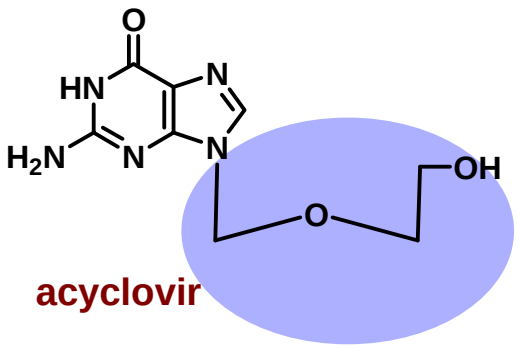
- Ganciclovir works by inhibiting cellular DNA polymerase that is associated with viral infections.

- Ganciclovir is used to treat for cytomegalovirus (CMV) retinitis infections in immunocompromised patients, including patients with acquired immunodeficiency syndrome (AIDS) or patients undergoing chemotherapy.
  ["更昔洛韋"是用於治療免疫損害患者中的巨細胞病毒 (CMV) 視網膜炎，包括獲得性免疫缺陷綜合征（愛滋病）或化療病人。]

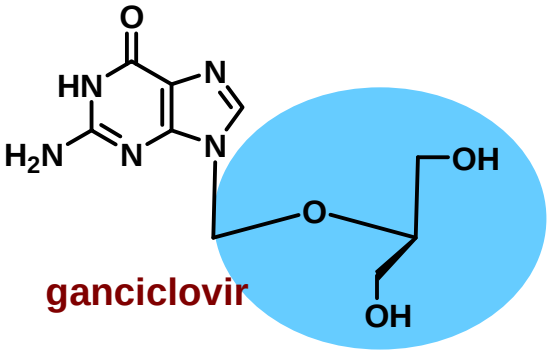
- Cytovene®, the registered trade name by the Roche Pharmaceuticals, contains ganciclovir sodium as the medicinal ingredient.

synthesis

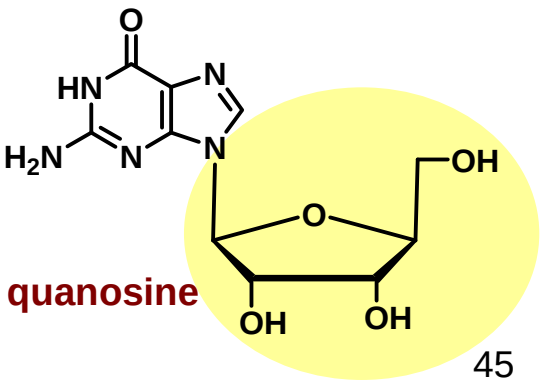
- In 1974, scientists at Wellcome discovered the potent antiviral agent acyclovir (Zovirax®) for the treatment of various viral infections including herpes viruses HSV-1 and HSV-2.
- In 1980, Dr. Kelvin Ogilvie and his research team at McGill University discovered Ganciclovir [*CAN. J. CHEM. 1982, 60, 3005*.], and developed by Verheyden and Martin at Syntex Research in 1980.
- The first commercially viable process for the manufacture of ganciclovir was developed by Roche Colorado Corporation, formerly known as Syntex Chemicals, in the early 1990s.
- The 1st generation process is known as **Persilylation Process**.



acyclovir



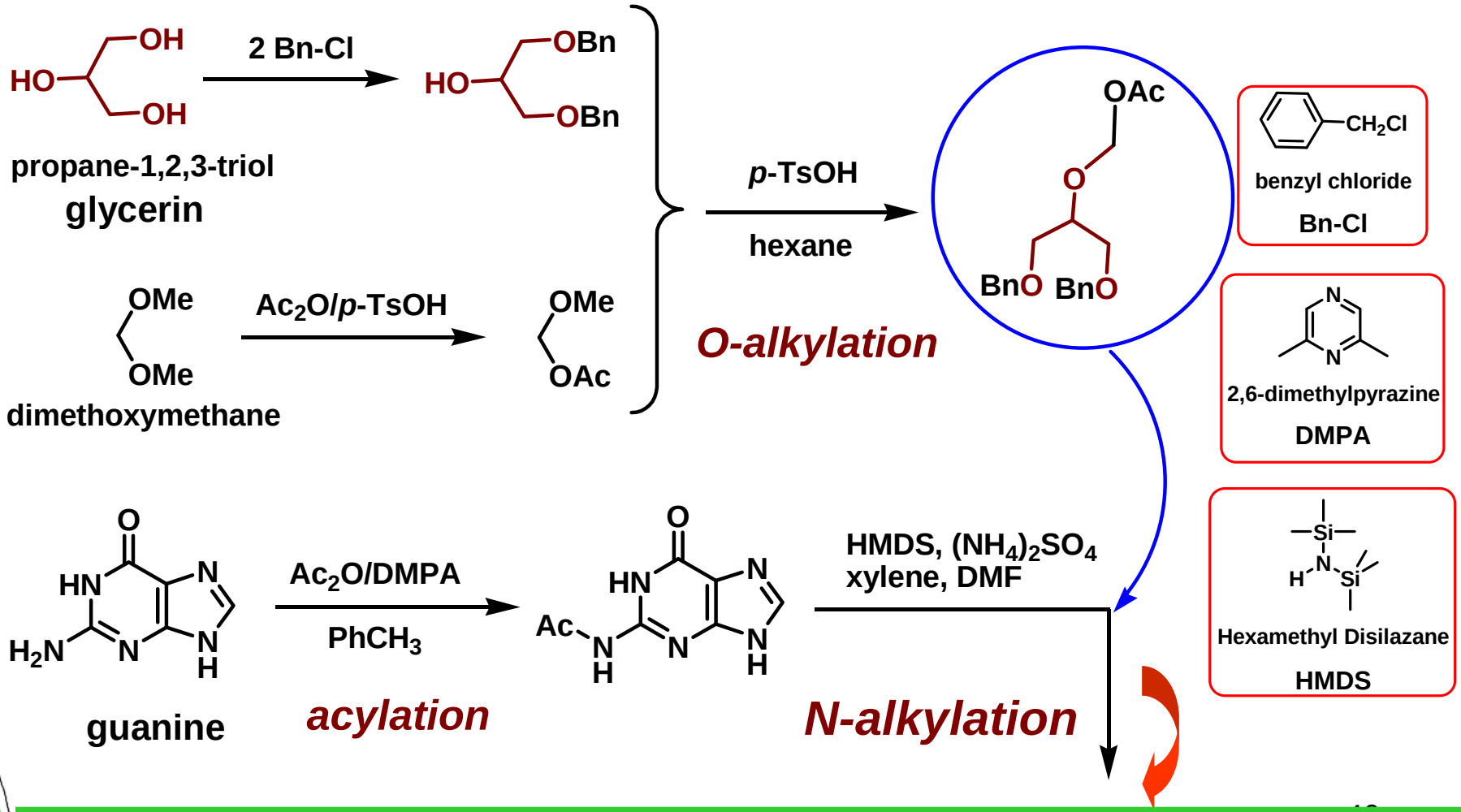
ganciclovir

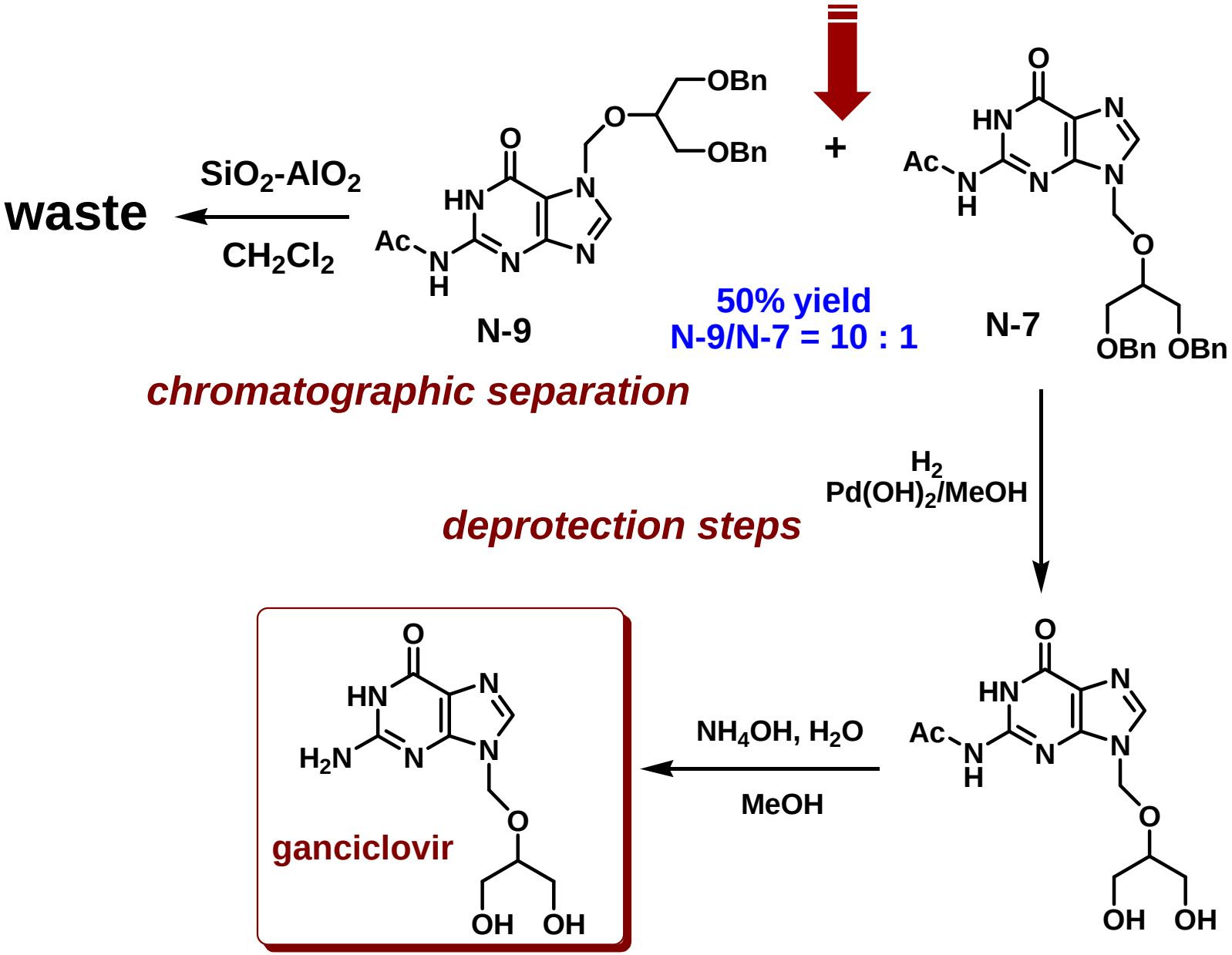


quanosine

Persilylation Process --- Brown process

U.S. Patent 4, 621,140, November 4, 1986.
U.S. Patent 4,803,271, February 7, 1989.




waste
SiO_2-AlO_2
CH_2Cl_2
N-9
+
N-7
50% yield
N-9/N-7 = 10 : 1
chromatographic separation
H_2
$Pd(OH)_2$/MeOH
deprotection steps
NH_4OH, H_2O
MeOH
ganciclovir

Problems with Persilylation Process

- A six-step process, in which 4-steps are protection-deprotection reactions.
- Involved 28 reagents and intermediates, and required the purification and isolation of 5 discrete intermediates.
- Involved at least 8 different kinds of solvents.
- Afforded specification grade ganciclovir in 54% yield.
- Involved a potentially hazardous palladium catalyzed hydrogenation step, which is needed to remove dibenzyl ether protecting group.
- Poor selectivity of key alkylation reaction, affording the desired N-7 isomer as minor product (N-7:N-9 = 1:10) and requiring costly and tedious chromatographic separation.

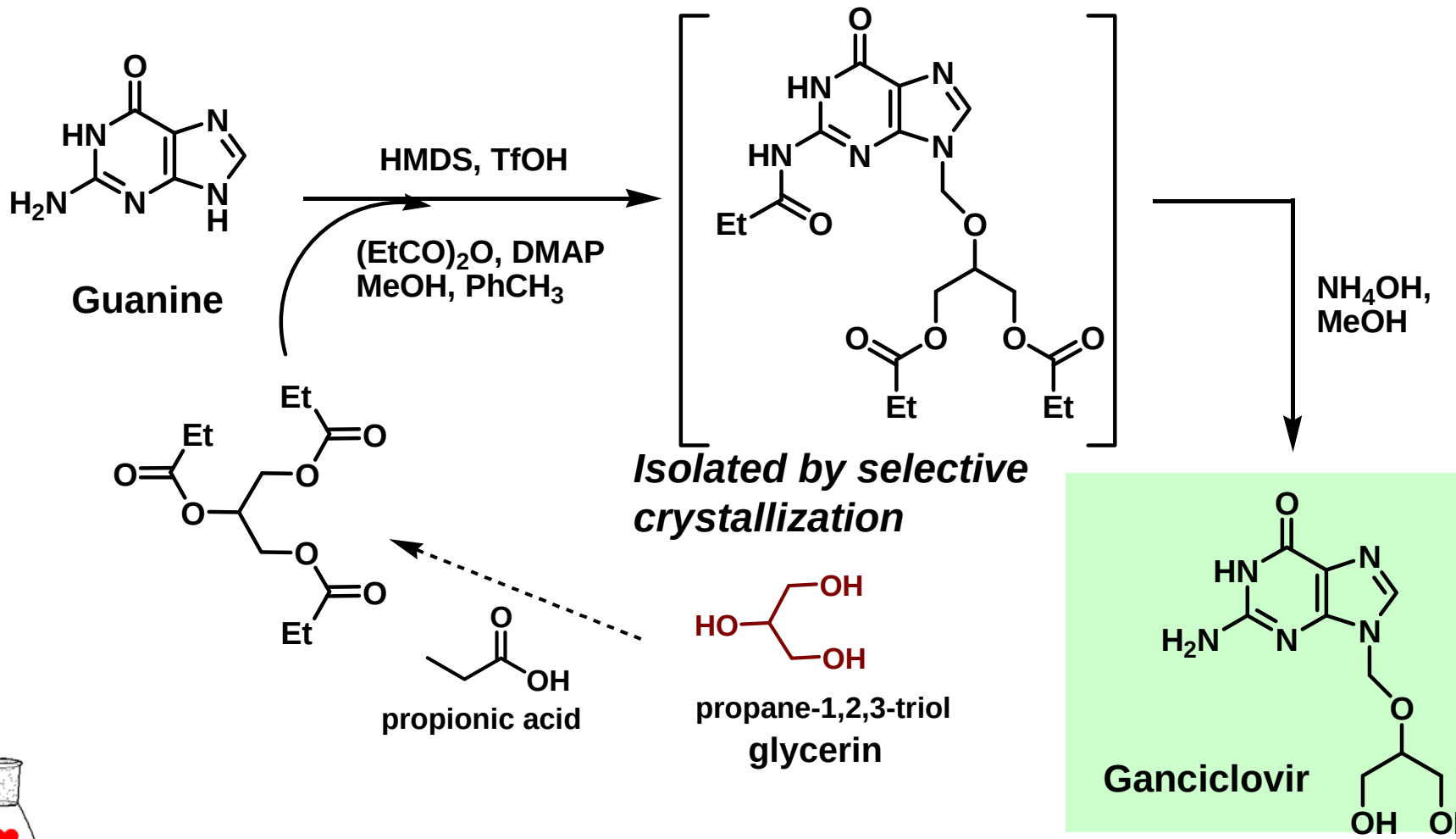
In 1993, the Boulder Technology Center of Roche Colorado Corporation completed the demonstration of a new and expedient process for the production of ganciclovir by (1) leveraging the **basic principles of molecular conservation** to minimize the creation and disposal of undesired wastes, and (2) formulating **efficient process engineering design** for streamlining process operation and the recycling of raw materials. The new (2nd generation) process is called

The Guanine TriEster (GTE) Process.

This technology was awarded the Presidential Green Chemistry Challenge Award [Greener Synthetic Pathways Award] in the U.S. in 2000.

The Guanine TriEster (GTE) Process

--- Green process



The "greener" features of the GTE process

- **Fewer process steps:**
  - The process demonstrates the potential for a "one step" process for the production of ganciclovir.
- **Waste quantity reduction/elimination:**
  - Reduced the number of chemical reagents and intermediates from 28 to 11.
  - Eliminated 2 hazardous solid waste streams (SiO_2-AlO_2 & $Pd(OH)_2$).
  - Eliminated 11 different byproducts from the liquid waste streams.
  - Efficiently recycled and reused 4 of the 5 raw materials not incorporated into the final product.

[*U.S. Patent 5, 565, 565, October 15, 1996*.]

- Involved virtually no protection-deprotection steps, and thus eliminated a potentially hazardous palladium catalyzed hydrogenation step.
- The process thus reduced air emissions by ~66% and liquid/solid waste generation by ~89%.

- **Yield improved:**

  The process provides more than a 25% increase in overall yield and a 100% increase in production throughput.

- **Greener:**

  The process achieves applying the principles of

  1. Prevent Waste
  2. Increase Atom Economy
  3. Design Less Hazardous Chemical Syntheses

- The process designed and used a 4-carbon triester coupling reagent, which generated innocuous byproduct (EtCOOH) via simple hydrolysis.
- The process demonstrated the novel design of the direct silylation of guanine, that gives rise to a highly regioselective alkylation and thus less unwanted alkylated byproduct.

For a review of synthetic approaches to N-9 substituted guanies.

- F. P. Clausen and J. Juhl-Christensen, *Organic Prep. & Proced. Intl*., 1993, 25, 375.
- V. V. N. K. V. Prasada Raju, et. al. *ARKIVOC* 2009 (xii) 296-301.
- K. Izawa* and H. Shiragami, *Pure & Appl. Chem.,*1998, *70*, 313-318.

For the study describing a possible approach to selective alkylation of guanines.

- D. Sing, M.J. Wani and A. Kumar, *J. Org. Chem*. 1999, 64, 4664.
- J. Boryski and B. Golankiewicz, *Synthesis*, 1999, 625.
- United States Patent 7078524, Issued on July 18, 2006.

References

- Development of an Environmentally Friendly, Cost Effective Process for the Production of cytovene® Antiviral Agent. *www.aspentech.com/publication_files/AICHE2000.pdf*
- Biologically active acyclonucleoside analogues. 11. The synthesis of 9-[[2-hydroxy-1-(hydroxymethyl)ethoxy]methyl]guanine (BIOLF-62). K. Ogilvieu, et. al., *Can. J. Chem*. **1982**, *60*, 3005.
- Synthesis of acyclovir, ganciclovir and their prodrugs: A review [Review], Gao, H.; Mitra, A. K. *Synthesis*, **2000**, 2000.
- Regioselective synthesis of various prodrugs of ganciclovir, Gao, H.; Mitra, A. K. *Tetrahedron Letters,* **2000**, *41*, 1131.
- A Facile Synthesis of 9-(1,3-Dihydroxy-2-propoxymethyl) guanine (Ganciclovir) from Guanosine, Boryski, et al., *Synthesis*, **1999**, 625.

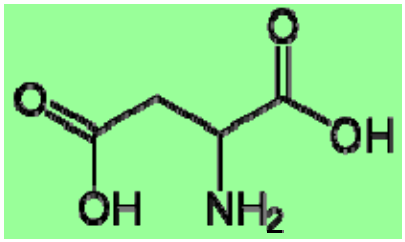
Case 5. 實例5

Polyaspartate

Biodegradable Alternative to Polyacrylate

US Presidential Green Chemistry Challenge Awards:

Award in the small business category 1996



Aspartic acid

天冬氨酸

2-Aminobutanedioic acid

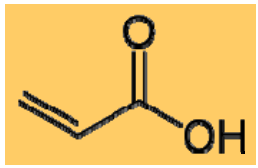
2-氨基丁酸

Acrylic acid

壓克力酸

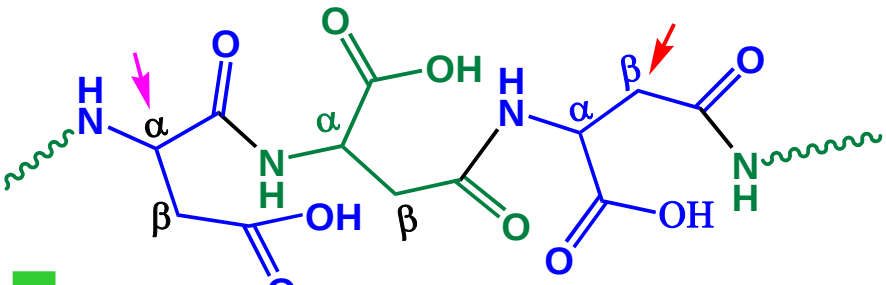
propenoic acid

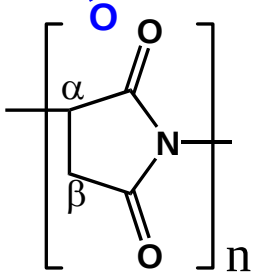
丙烯酸



Polyaspartic acid

聚天冬氨酸

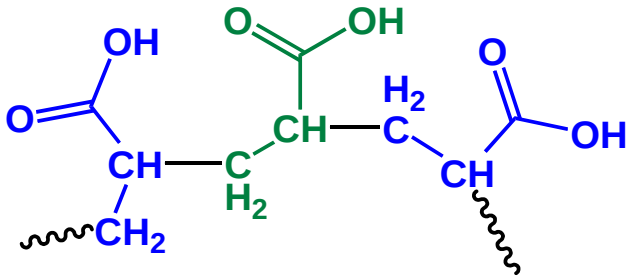




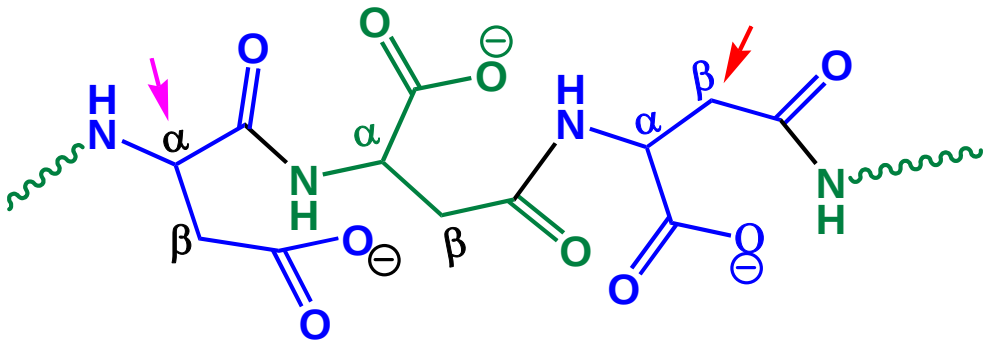
poly(succinimide)

Polyacrylic acid

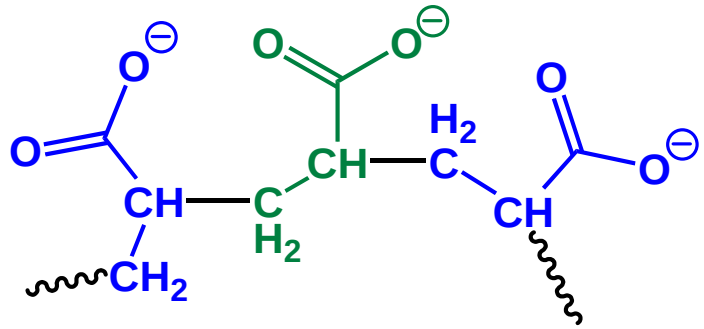
聚丙烯酸



Polyaspartate
聚天冬氨酸鹽

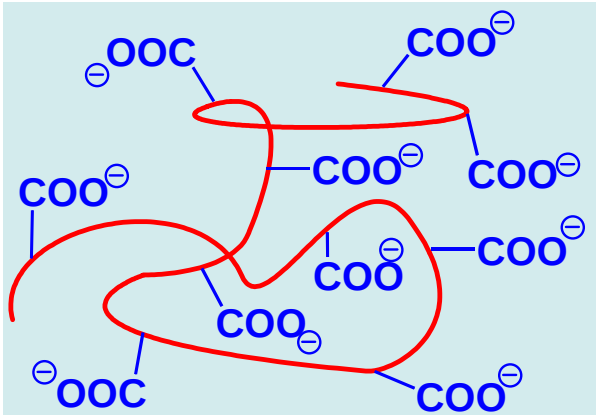


Polyacrylate
聚丙烯酸鹽



What are polyaspartate and polyacrylate in common?

Polyanion, Hydrophilic, Water soluble

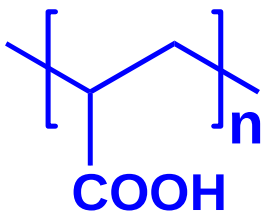


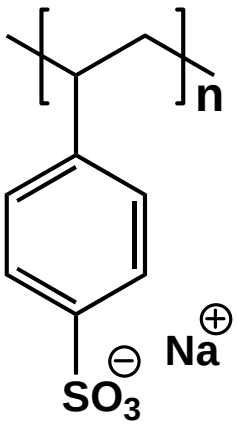
Polyelectrolytes

- polymers whose repeating units bear an electrolyte group, dissociating in aqueous solution (water) to generate positive or negative charge.
- also called macroions or polyions or polysalts.
- can be polyanions or polycations.
- generally water soluble polymers if their structure is linear.
- the polymer will be highly expanded in aqueous solution.
- can be modified to function as antiscalant（抗垢劑）and dispersant（分散劑）.

Examples

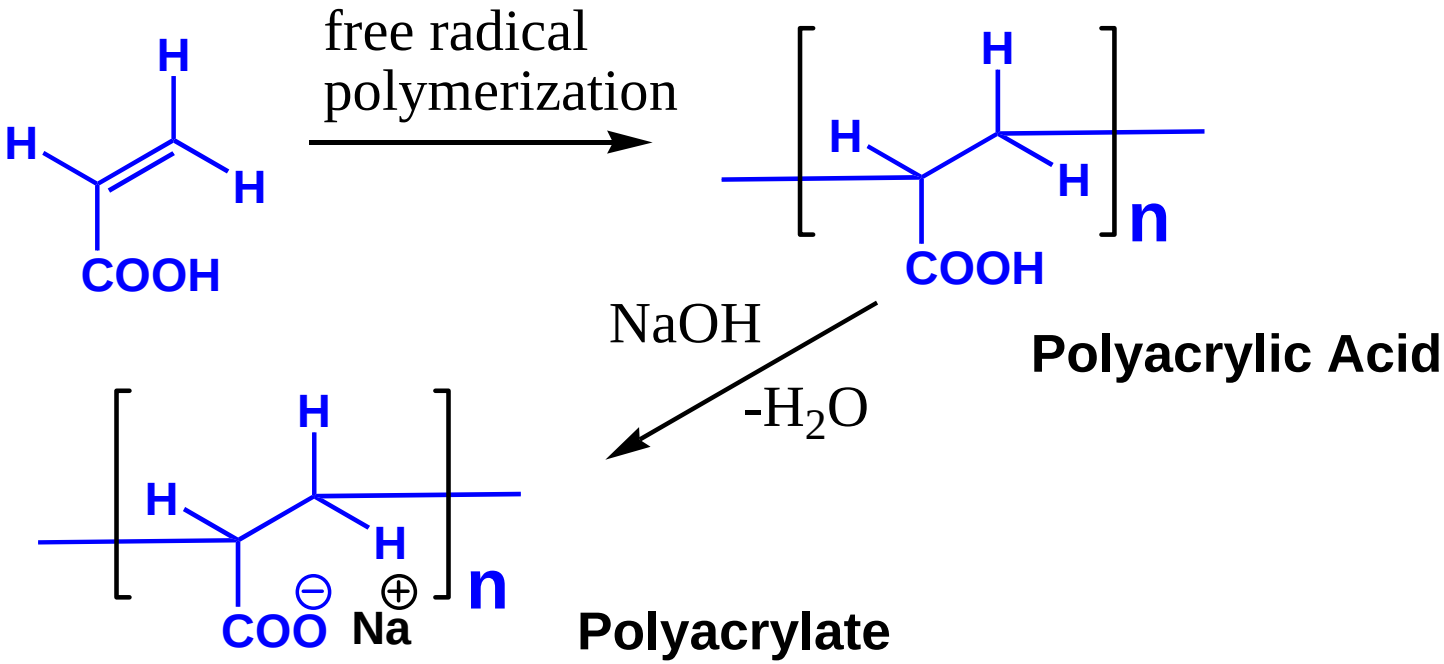
polypeptides (proteins), DNA,
poly(sodium styrene sulfonate, PSS),
polyacrylic acid (PAA).





Polyacrylate (PAC)

Synthesis



PAC can function as both an antiscalant（抗垢劑 ）and a dispersant（分散劑）.

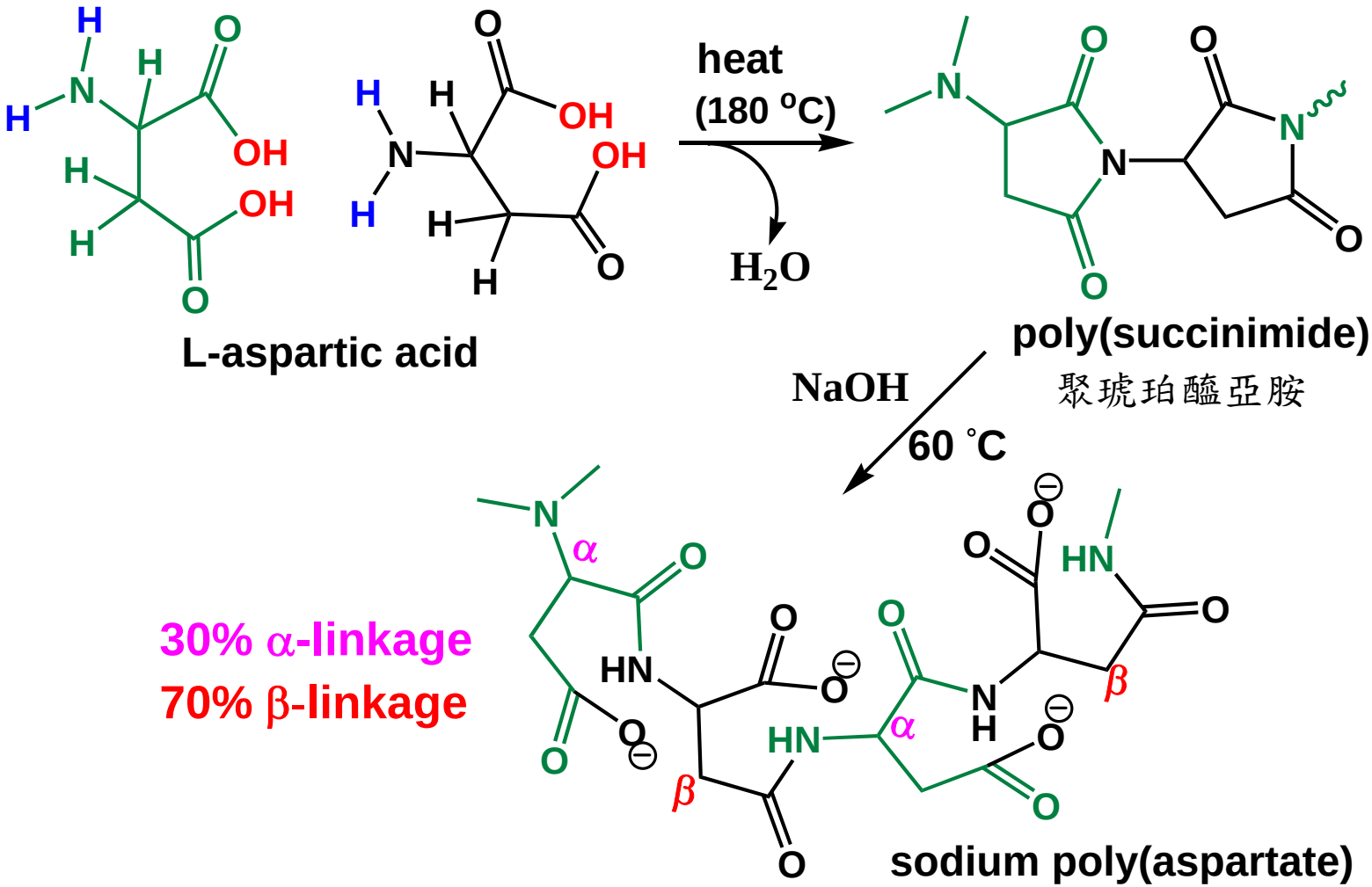
PAC and the Environment

- PAC is nontoxic and environmentally benign, **but it is not biodegradable.**
- Because it is widely used for many applications, it poses an environmental problem from a landfill perspective.
- When PAC is used as an antiscalant or a dispersant, it becomes part of wastewater.
- PAC is nonvolatile and not biodegradable, so the only way to remove it from the water is to precipitate it as an insoluble sludge.
- The sludge must then be landfilled.
- Feedstocks are made from fossil fuels.

Polyaspartate

- Polyaspartate has similar properties to the polyacrylates and so it can be used as a dispersant, or an antiscalant, or a superabsorber.
- Polyaspartate is **nontoxic**, **biodegradeable**（可生物分解的）, and environmentally safe.
- Biodegradation results in decomposition of TPA to environmentally benign products such as carbon dioxide and water.
- The Donlar Corporation developed an economic way to produce “thermal polyaspartate (TPA)” in high yield (~97%), that eliminates use of organic solvents, cuts waste, and uses less energy.
- Polyaspartate is a biopolymer synthesized from L-aspartic acid, a natural amino acid.

Synthesis of thermal polyaspartate (TPA)



Green Chemistry *in ACTION*

- In April 1997, Donlar opened the world's largest manufacturing facility for biodegradable polyaspartates, in Peru, Illinois, with a production capacity of more than 30 million pounds a year.
- The opening of this facility resulted in commercial availability of TPA.
- TPA is marketed and sold as a corrosion and scale inhibitor, a dispersing agent, a waste water additive, a superabsorber, and also as an agricultural polymer.
- As an agricultural polymer, TPA is used to enhance fertilizer uptake by plants. Less fertilizer is added to the soil and the environmental impact from fertilizer run-off is reduced.

- British Petroleum Exploration and others have achieved success with a TPA additive that helps to sustain the flow of crude from oil wells in North Sea offshore oil fields.

TPA is a green alternative to Polyacrylate and other currently used water soluble polymers!

References

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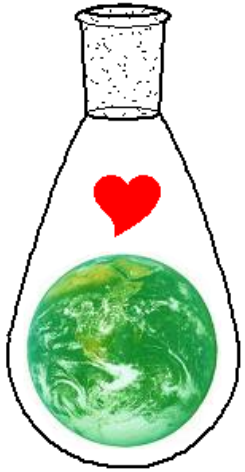
感謝您的聆聽，請指教



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