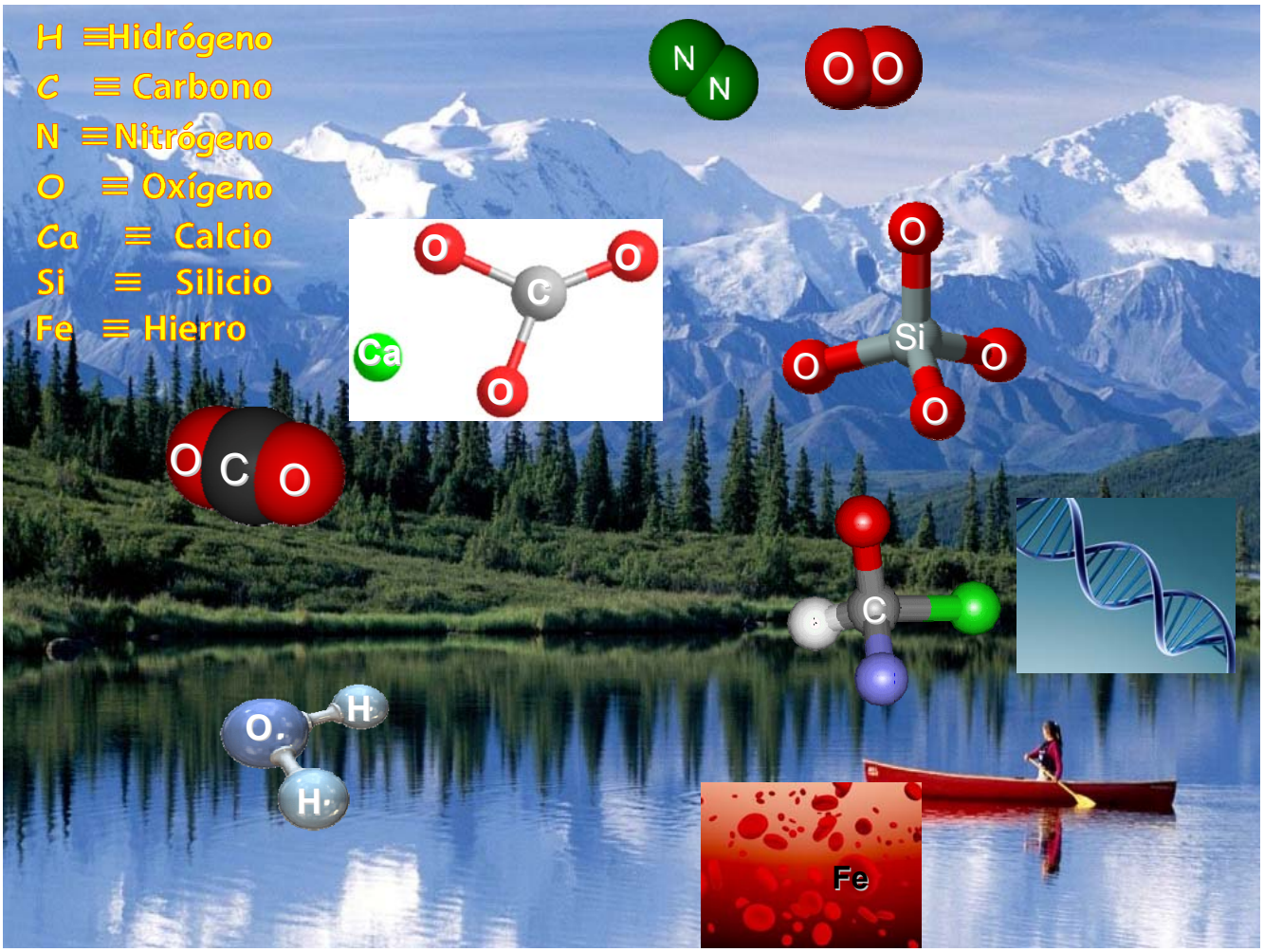
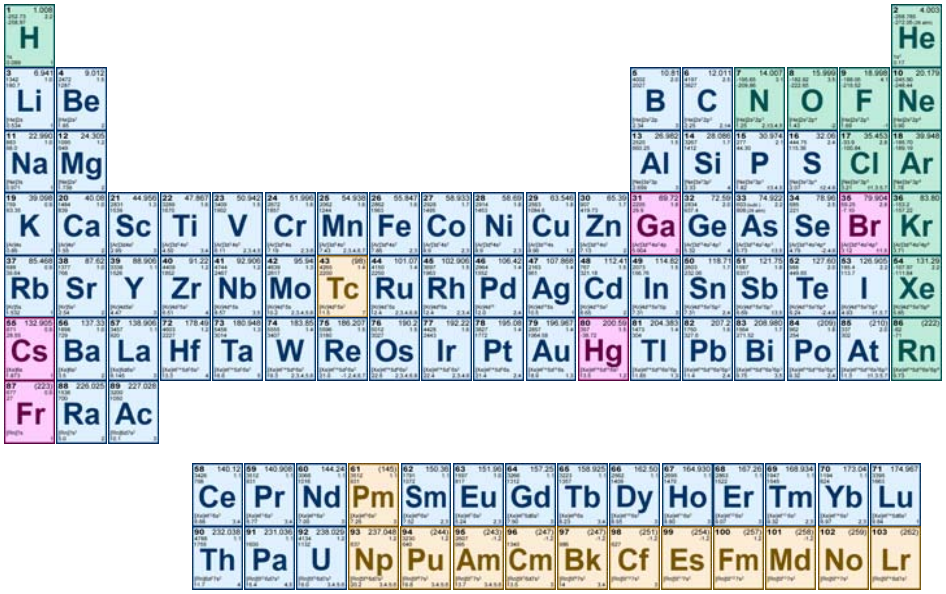
La Química, la catálisis y la vida

Ernesto Carmona Guzmán

Universidad de Sevilla – Consejo Superior de Investigaciones Científicas

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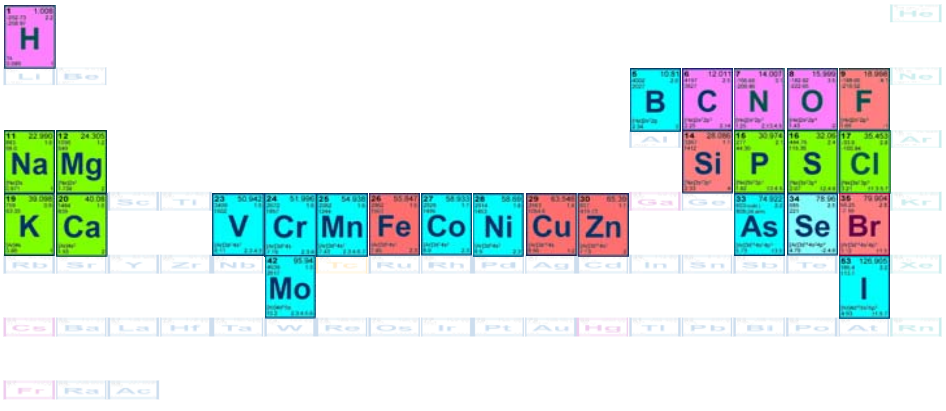
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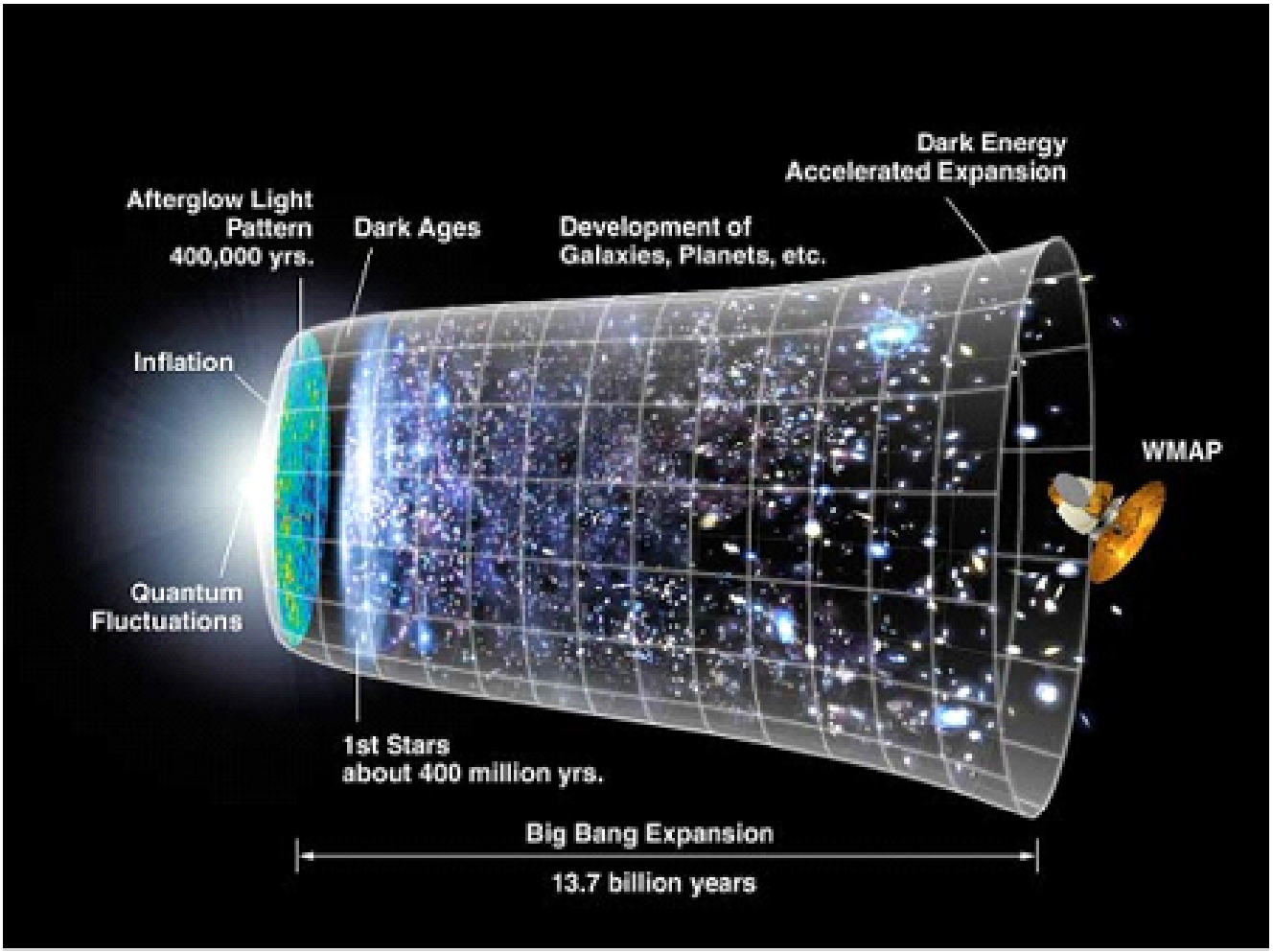
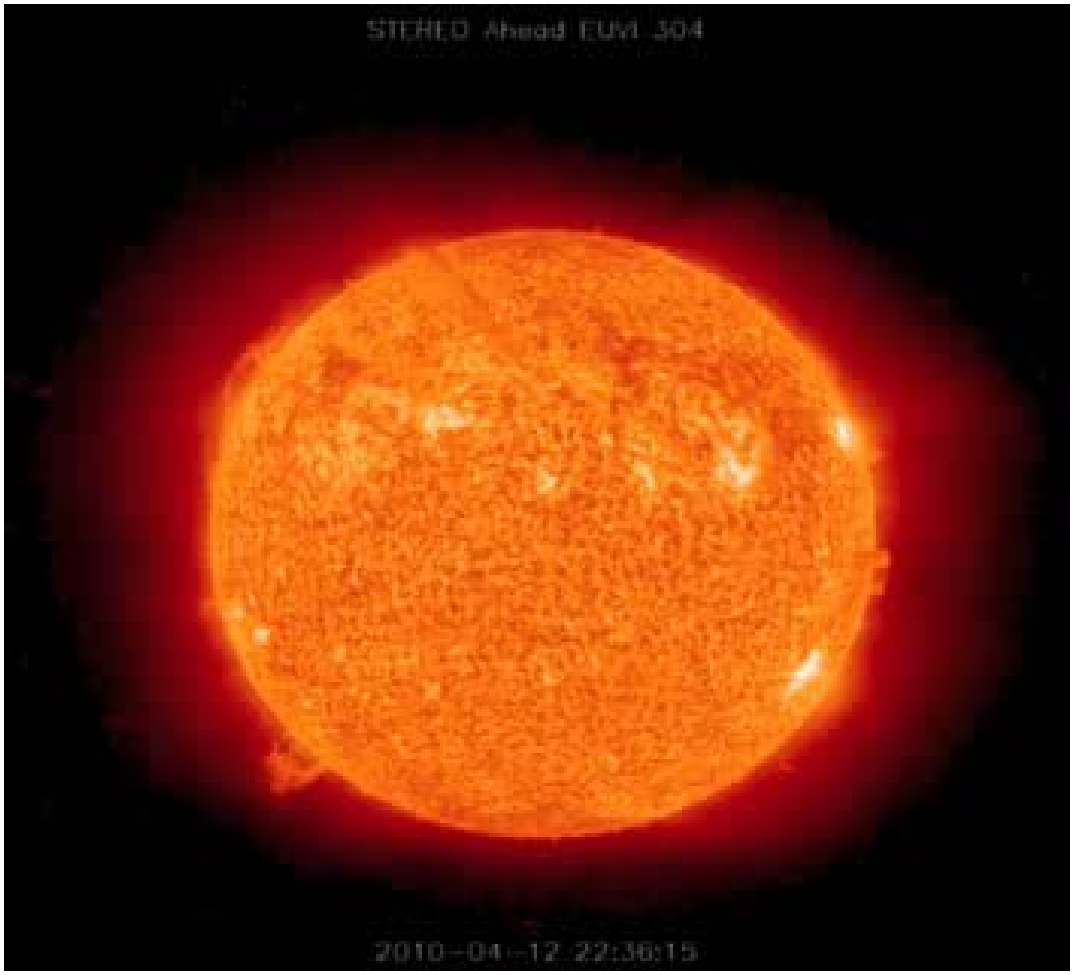

Dark Energy
Accelerated Expansion
Afterglow Light
Pattern
400,000 yrs.
Dark Ages
Development of
Galaxies, Planets, etc.
Inflation
WMAP
Quantum
Fluctuations
1st Stars
about 400 million yrs.
Big Bang Expansion
13.7 billion years


H
C
N
O



$^1H + {}^1H = {}^2H + e^+ + \nu$ (1)

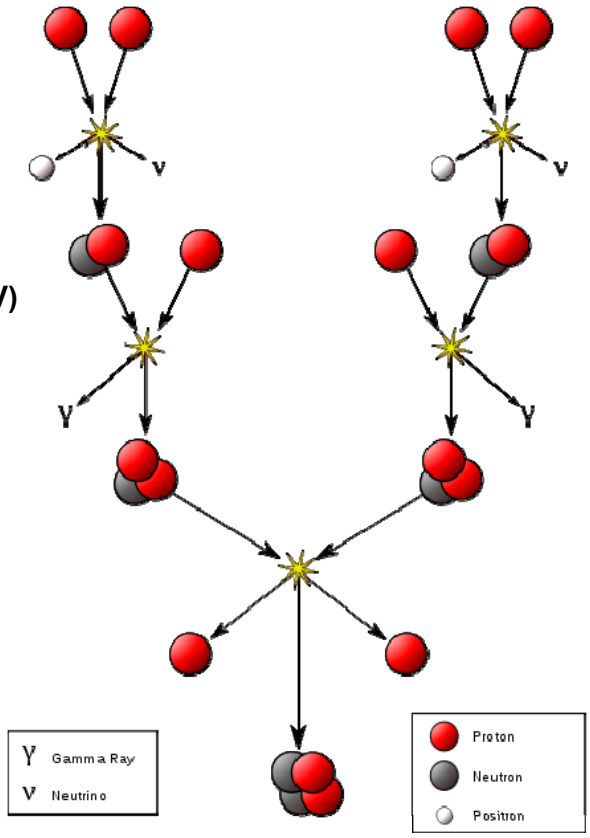
$^2H + {}^1H = {}^3H + \gamma$ (2)

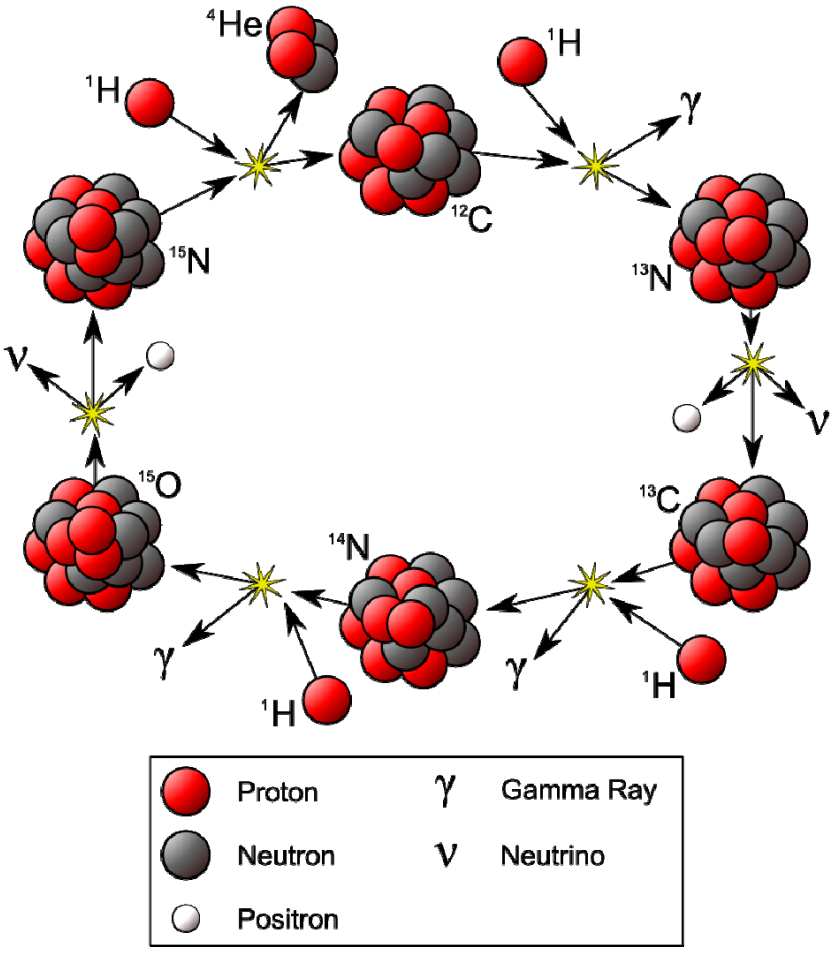
$^3H + {}^3H = {}^4H + 2\,{}^1H$ (3)

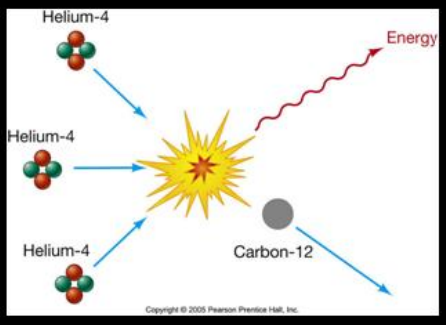
$4\,{}^1H \longrightarrow {}^4He + 2e^+ + 2\nu$ (26,72 MeV)

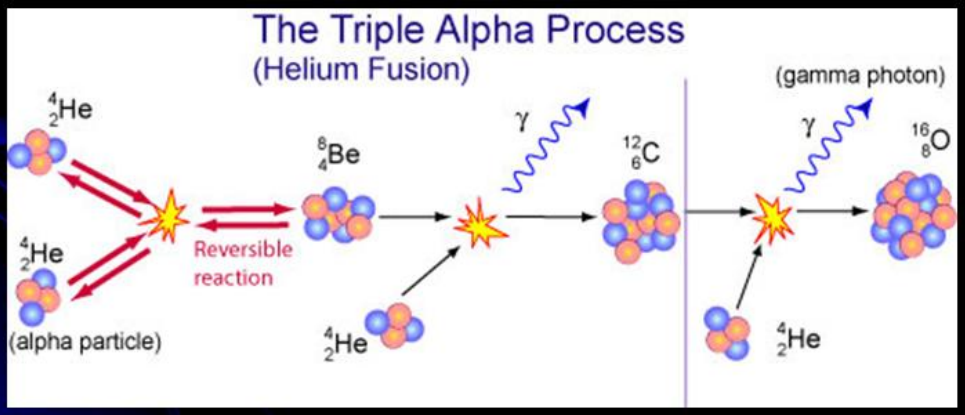
$^1H + {}^1H = {}^2He + \gamma$

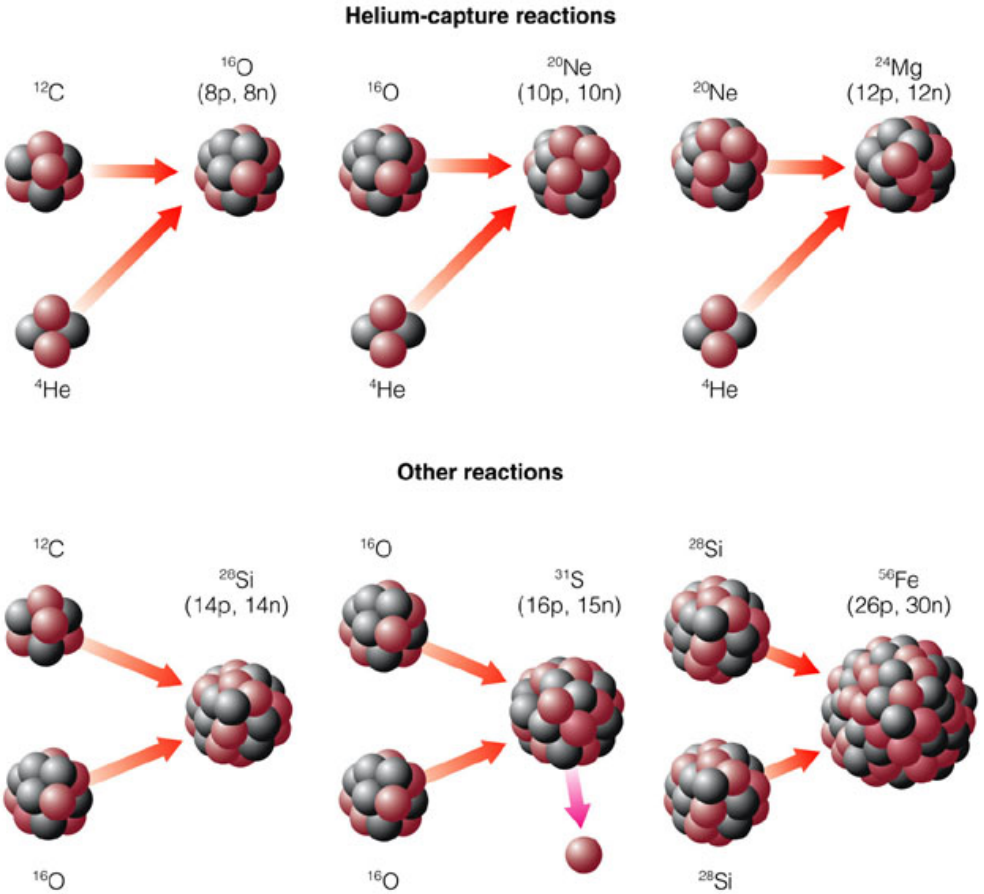
$^2He = {}^2H + e^+ + \nu$




^{4}He
^{1}H
^{12}C
^{1}H
γ
^{15}N
^{13}N
ν
ν
^{15}O
^{13}C
^{14}N
γ
γ
^{1}H
^{1}H
Proton
Neutron
Positron
γ Gamma Ray
ν Neutrino

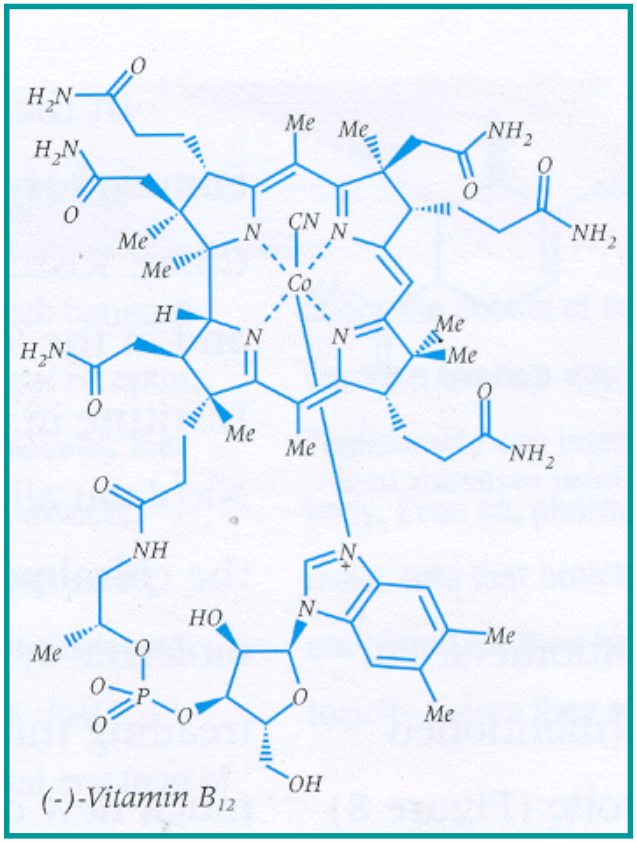

Helium-4
Energy
Helium-4
Helium-4
Carbon-12
Copyright © 2005 Pearson Prentice Hall, Inc.

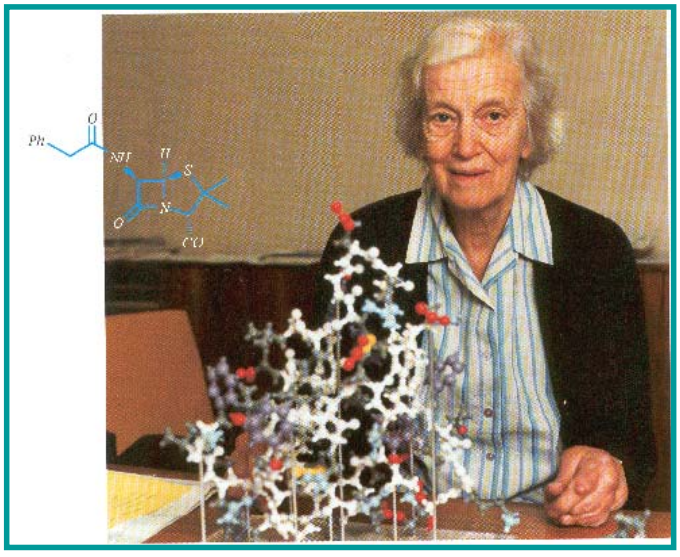

The Triple Alpha Process
(Helium Fusion)
(gamma photon)
$^{4}_{2}$He
$^{8}_{4}$Be
γ
$^{12}_{6}$C
γ
$^{16}_{8}$O
$^{4}_{2}$He
Reversible reaction
(alpha particle)
$^{4}_{2}$He
$^{4}_{2}$He



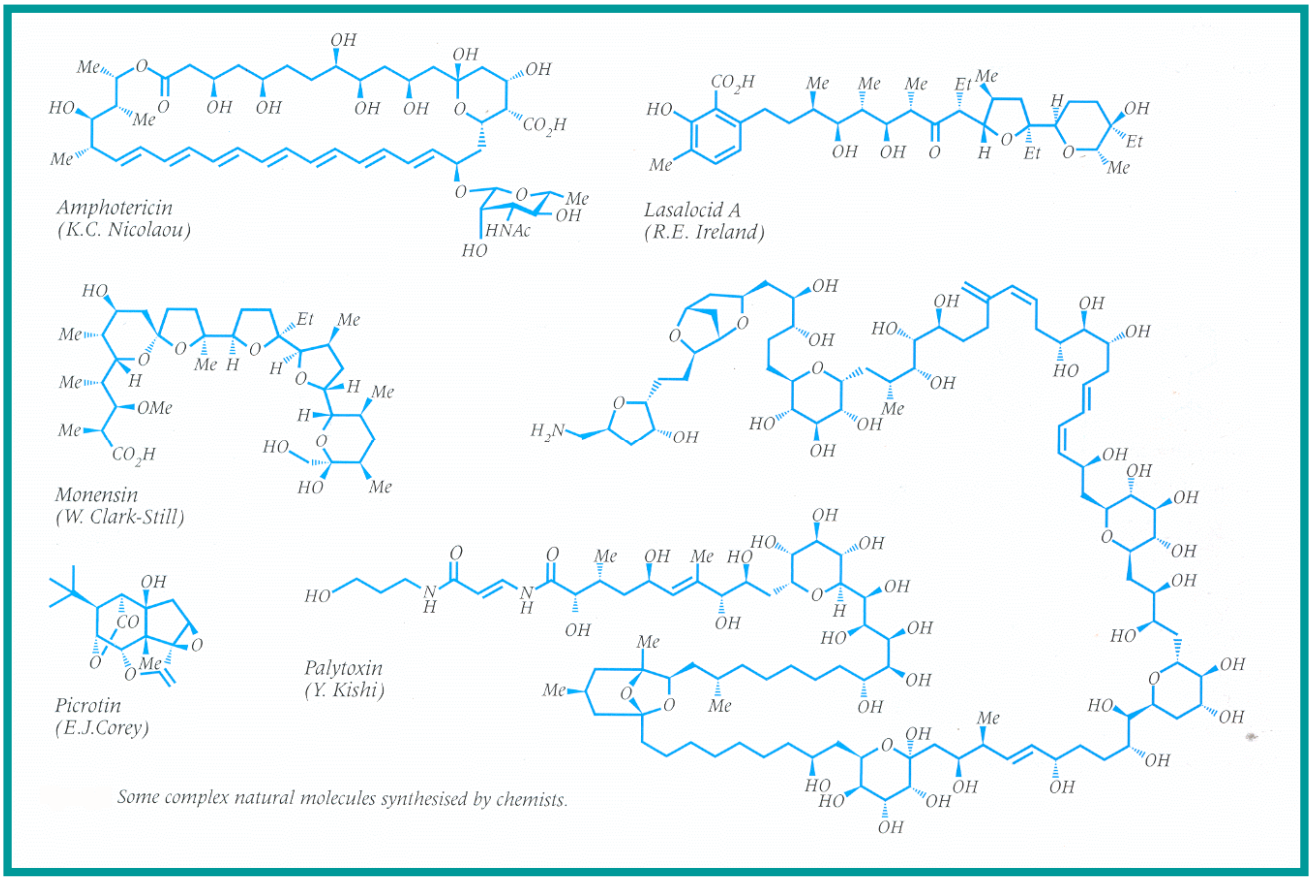
« Before the word for it (in any language) came to be, there was chemistry. For one defining aspect of human beings has always been the meld of mind and hands in transforming matter. »

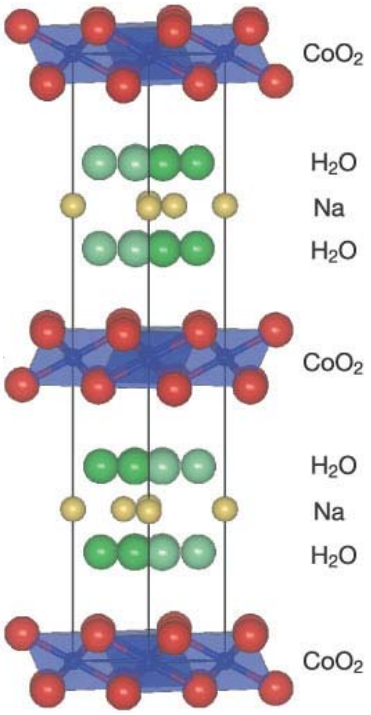
Roald Hoffmann
Premio Nobel de Química 1981.
The New Chemistry. N. Hall, Ed.
Cambridge Univ. Press, 2000



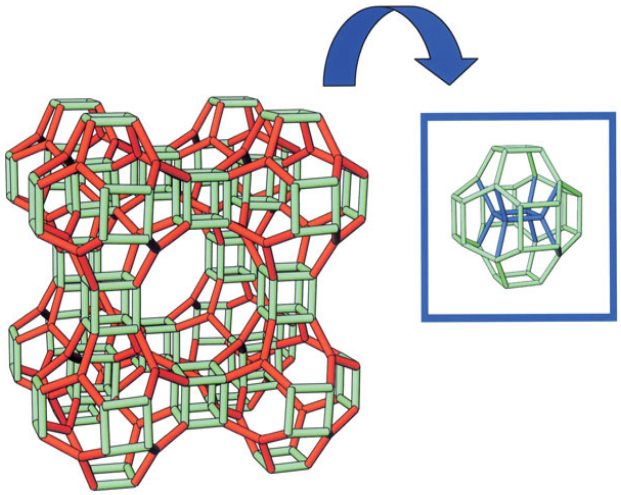


D. Hodgkin
Premio Nobel, 1964

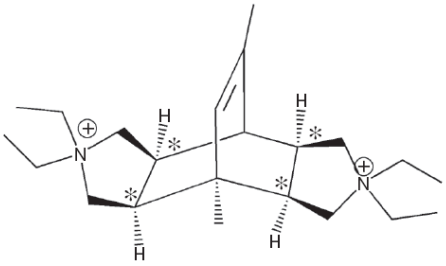




Nature, 2003, *422,* 53



Nature, 2002, ***418,*** **515**



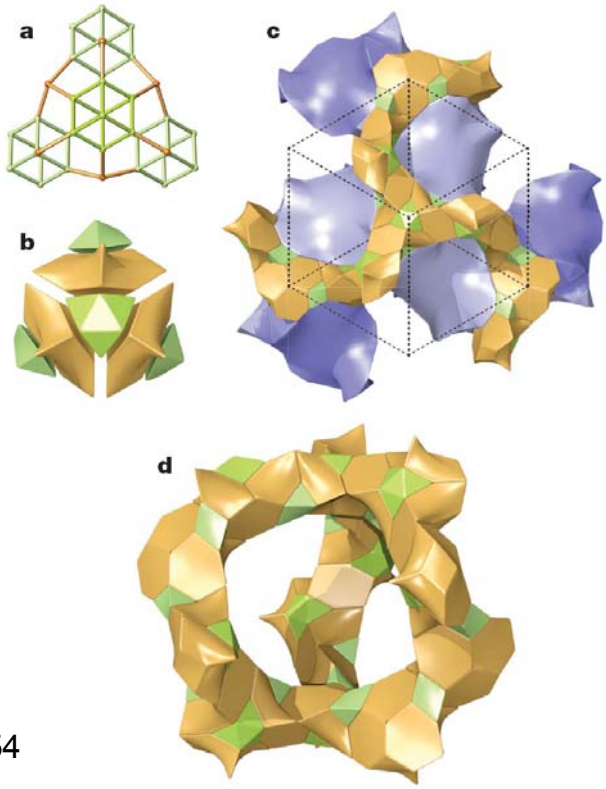


Figure 1 | Structure of SDA2 used for synthesizing the ITQ-37 zeolite. SDA2 contains four chiral centres (marked with asterisks) in a meso conformation, making the overall molecule achiral.

A. Corma, *et al. Nature* **2009**, *458*, 1154

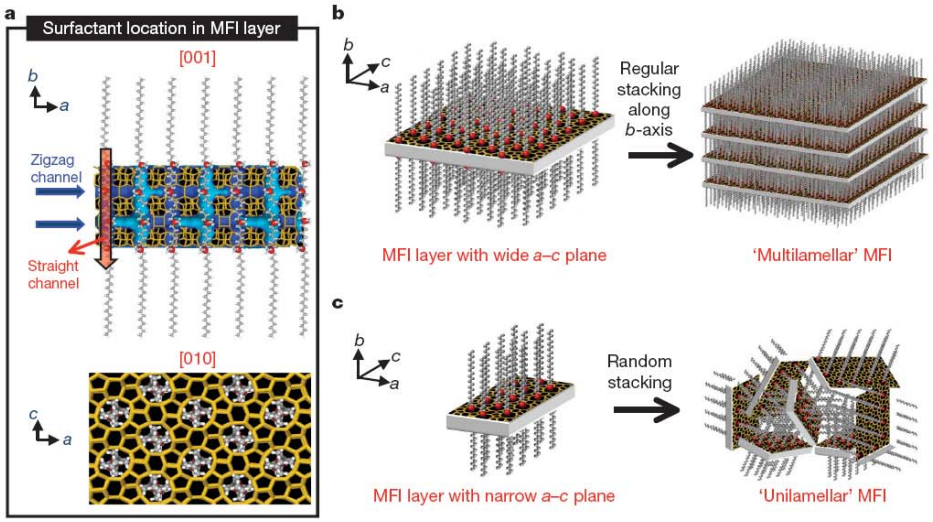
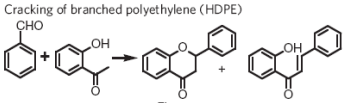
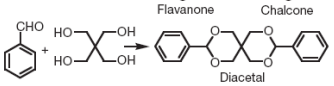


Figure 2 | Crystallization of MFI nanosheets. **a**, Proposed structure model for the single MFI nanosheet. Surfactant molecules are aligned along the straight channel of MFI framework. Two quaternary ammonium groups (indicated as a red sphere) are located at the channel intersections; one is inside the framework, and the other is at the pore mouth of the external surface. Many MFI nanosheets form either multilamellar stacking along the *b*-axis (**b**), or a random assembly of unilamellar structure (**c**).

Table 1 | Catalytic conversion of bulky molecules over MFI zeolites

Reactions	Conventional MFI (Si/Al = 41)	Multilamellar MFI nanosheets (Si/Al = 48)	Unilamellar MFI nanosheets (Si/Al = 53)
Cracking of branched polyethylene (HDPE)	27	45	85
 Flavanone Chalcone	16 (50/50/0)*	48 (62/28/10)*	76 (64/31/5)*
 Diacetal	42	86	86

Catalytic activities were compared on the basis of the same weight of catalyst (see Methods for reaction conditions). *The numbers in parentheses indicate percentage selectivity: (flavanone/chalcone/others). All other numbers indicate the percentage reactant conversion, reproducible within 3% over three runs. HDPE, high-density polyethylene.

M. Choi, K. Na *et al. Nature* **2009**, *461*, 246

$$N_2(g) + 3H_2(g) \overset{[cat]}{\rightleftharpoons} 2NH_3(g)$$

Industria Química

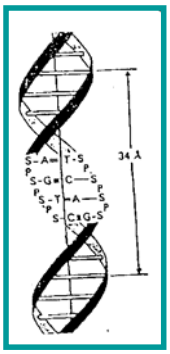
Polímeros, Cristales, Líquidos, Superconductores, otros materiales, Fármacos, pesticidas fragantes (quirales)

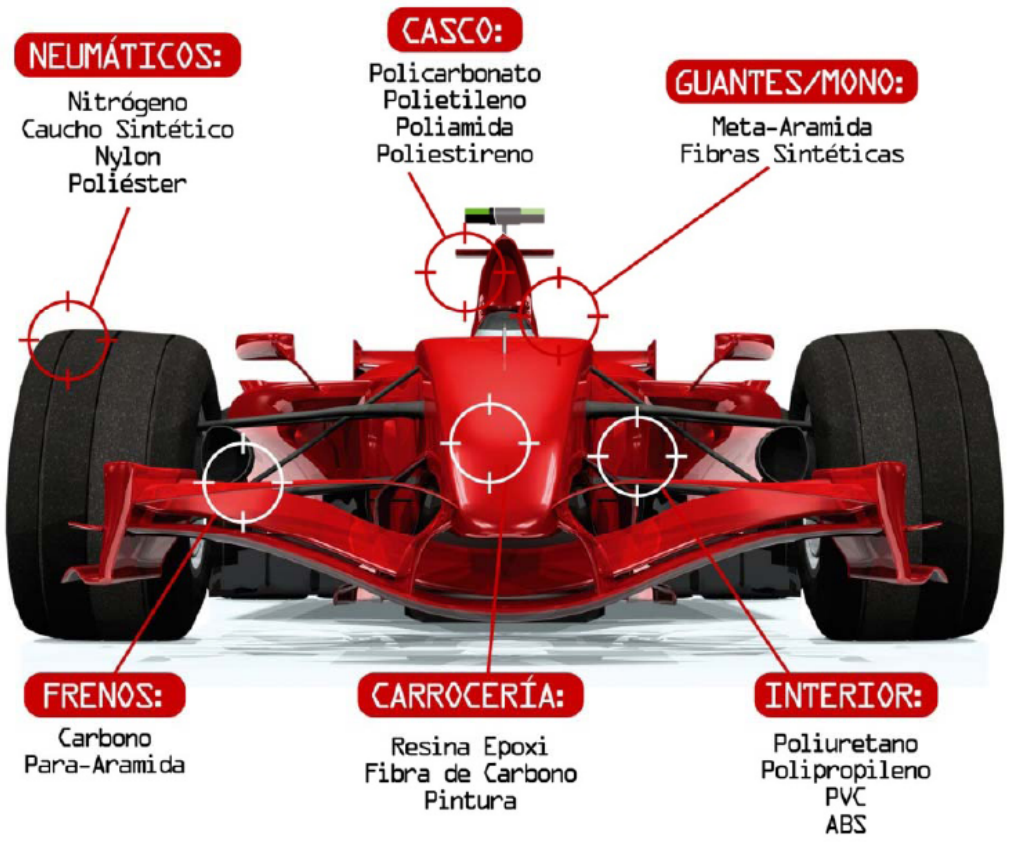
Átomos, Moléculas

SÍNTESIS QUÍMICA

Otras Moléculas, Compuestos, materiales,...

La Química de la Vida





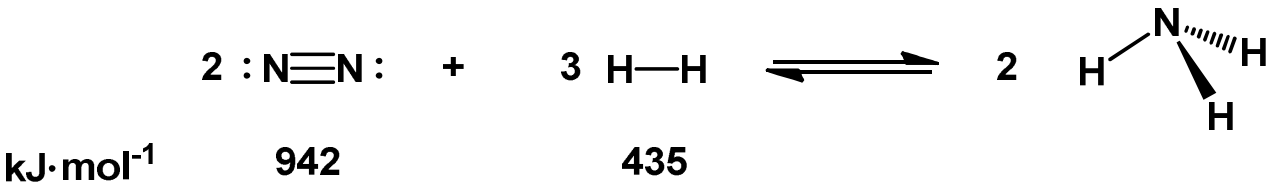
"A catalyst is a substance which affects the rate of a chemical reaction without being part of its end products"

W. Ostwald, 1900. Premio Nobel de Química, 1909.

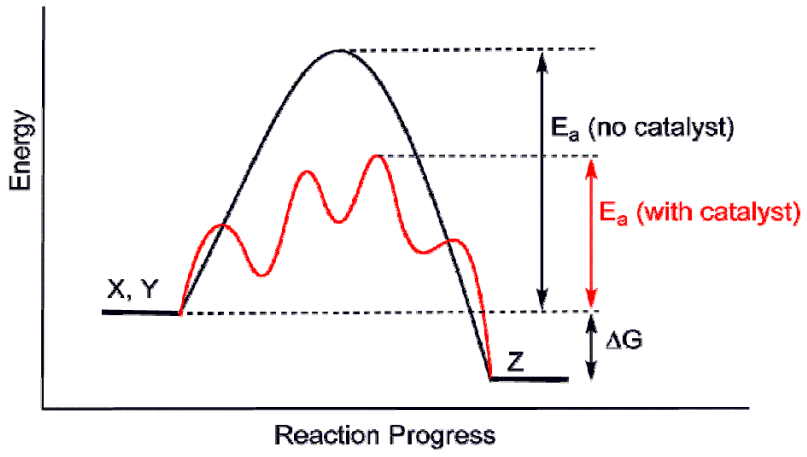
"A catalyst is a substance which increases the rate at which a chemical reaction approaches equilibrium without becoming itself permanently involved"

P. W. N. M. van Leewen, Homogeneous Catalysis

Kluwer Academic Publishers, Dordrecht, 2004.

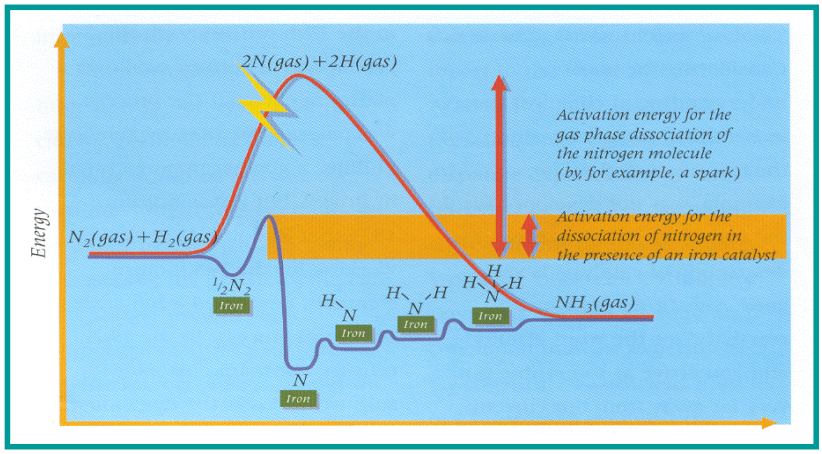


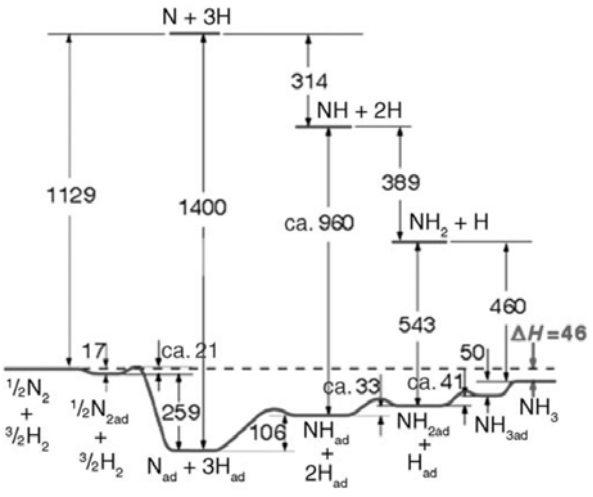
kJ·mol^{-1} 942 435



W. Crooks, 1898 (68th meeting of the British Association for the Advancement of Science):

"… all civilized nations stand in deadly peril of not having enough to eat… the fixation of atmospheric nitrogen is one of the great discoveries awaiting the ingenuity of chemists."





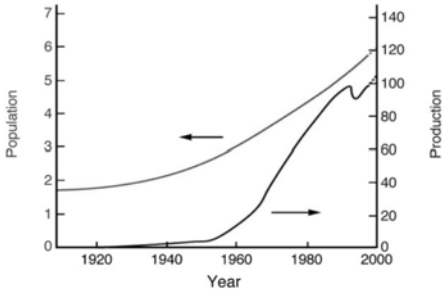
$N_2 \rightleftarrows N_{2ad} \rightleftarrows 2N_{ad}$

$H_2 \rightleftarrows 2H_{ad}$

$N_{ad} + H_{ad} \rightleftarrows NH_{ad}$

$NH_{ad} + H_{ad} \rightleftarrows NH_{2ad}$

$NH_{2ad} + H_{ad} \rightleftarrows NH_{3ad} \rightleftarrows NH_3$



Industry	Use
Fertilizer	Production of: ammonium sulfate, $(NH_4)_2SO_4$; ammonium phosphate, $(NH_4)_3PO_4$; ammonium nitrate, NH_4NO_3; urea, $(NH_2)_2CO$
Chemicals	Synthesis of: nitric acid, HNO_3 which is used in making explosives such as TNT (2,4,6-trinitrotoluene), nitroglycerine which is also used as a vasodilator (a substance that dilates blood vessels) and PETN (pentaerythritol nitrate); sodium hydrogen carbonate (sodium bicarbonate), $NaHCO_3$; sodium carbonate, Na_2CO_3; hydrogen cyanide (hydrocyanic acid), HCN; hydrazine, N_2H_4 (used in rocket propulsion systems).
Explosives	Ammonium nitrate, NH_4NO_3
Fibres & plastics	nylon, $-[(CH_2)_4\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}CO]-$, and other polyamides.
Refrigeration	Used for making ice, large scale refrigeration plants, air-conditioning units in buildings and plants.
Pharmaceuticals	Used in the manufacture of drugs such as sulfonamide which inhibit the growth and multiplication of bacteria that require *p*-aminobenzoic acid (PABA) for the biosynthesis of folic acids; anti-malarials and vitamins such as the B vitamins nicotinamide (niacinamide) and thiamine.
Pulp & paper	Ammonium hydrogen sulfite, NH_4HSO_3, enables some hardwoods to be used
Mining & metallurgy	Used in nitriding (bright annealing) steel; used in zinc and nickel extraction.

"for his studies of chemical processes on solid surfaces".

G. Ertl, Premio Nobel de Química 2007

"in recognition of their contributions to the invention and development of chemical high pressure methods"

C. Bosch, Premio Nobel de Química 1931 (F. Bergius)

"for the synthesis of ammonia from its elements"

F. Haber, Premio Nobel de Química 1918

Catalizadores de tres vías

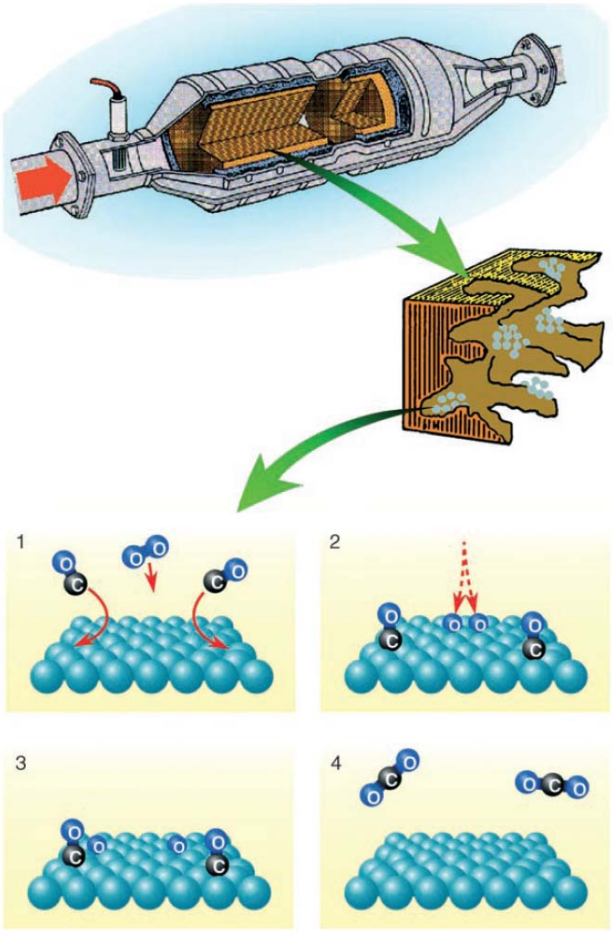
$$2\,NO_x \longrightarrow x\,O_2 + N_2 \qquad (1)$$

$$2\,CO + O_2 \longrightarrow 2\,CO_2 \qquad (2)$$

$$C_nH_{n+2} + \frac{3n+1}{2}\,O_2 \longrightarrow n\,CO_2 + (n+1)H_2O \qquad (3)$$

otras reacciones como:

$$2\,CO + 2\,NO \longrightarrow 2\,CO_2 + N_2 \qquad (4)$$



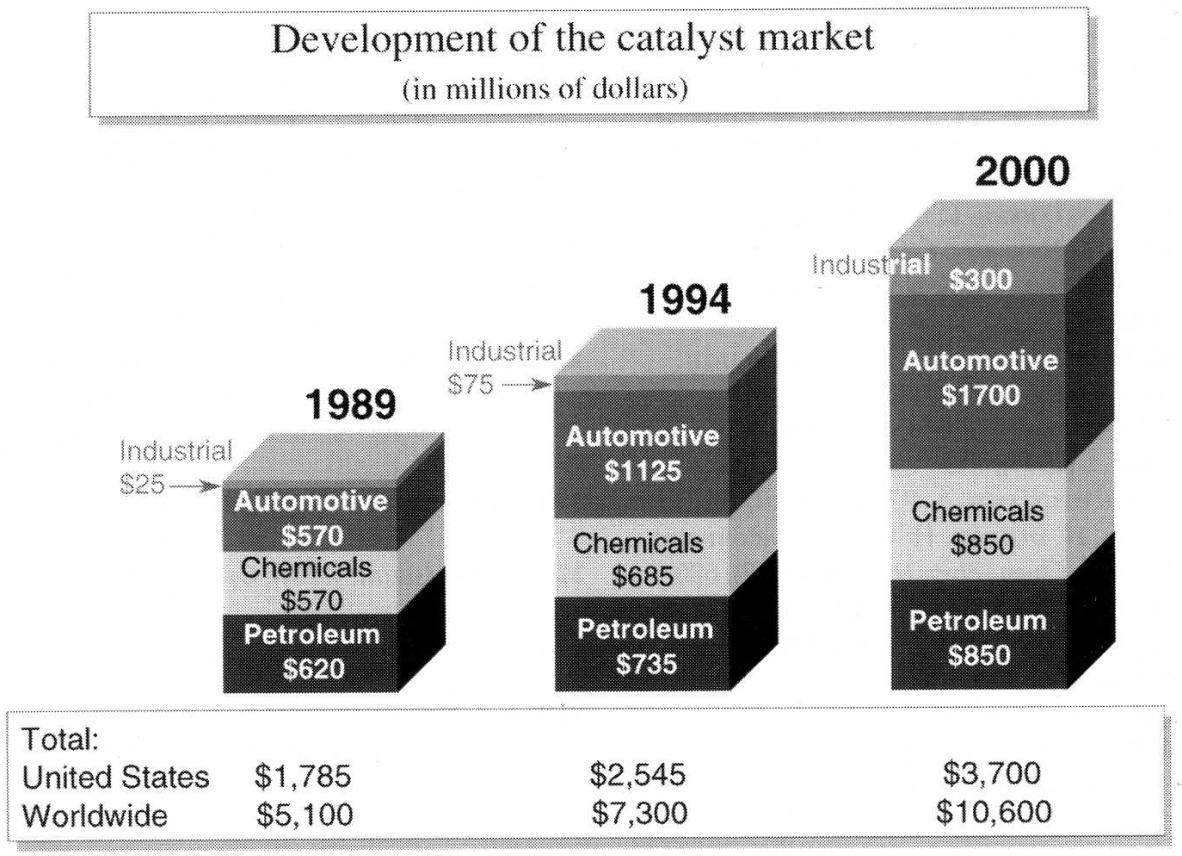


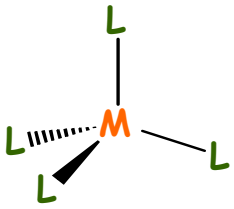
Fig. 4.13 Diagram showing the development of the catalyst market. [40]

$CoCl_3(NH_3)_6$ (amarillo)

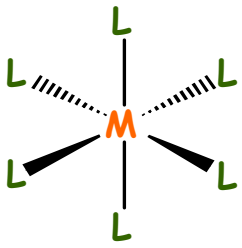
$CoCl_3(NH_3)_5$ (púrpura)

$CoCl_3(NH_3)_4$ (verde y violeta)

$CoCl_3(NH_3)_3$ (dos isómeros)



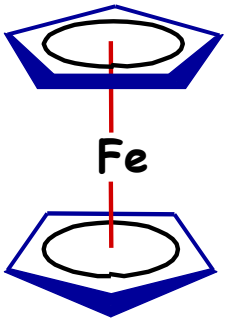
ML_4 (Td)

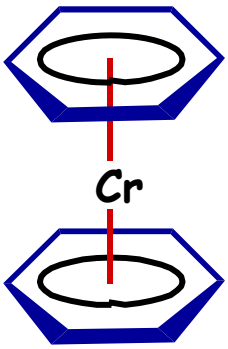


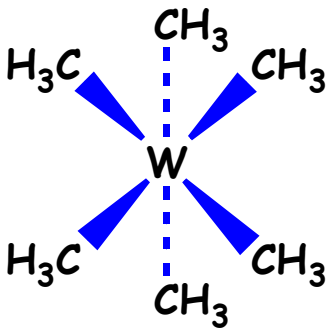
ML_6 (Oh)

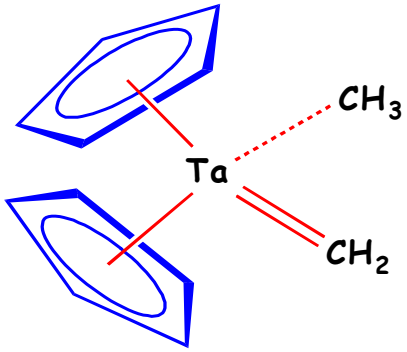
A. Werner.

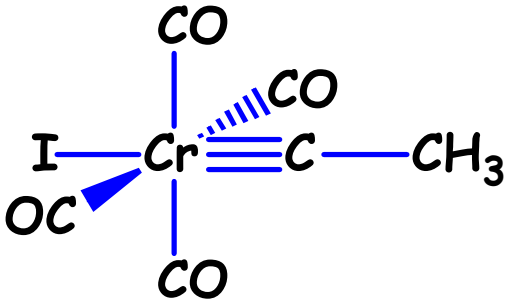
Premio Nobel de Química, 1913





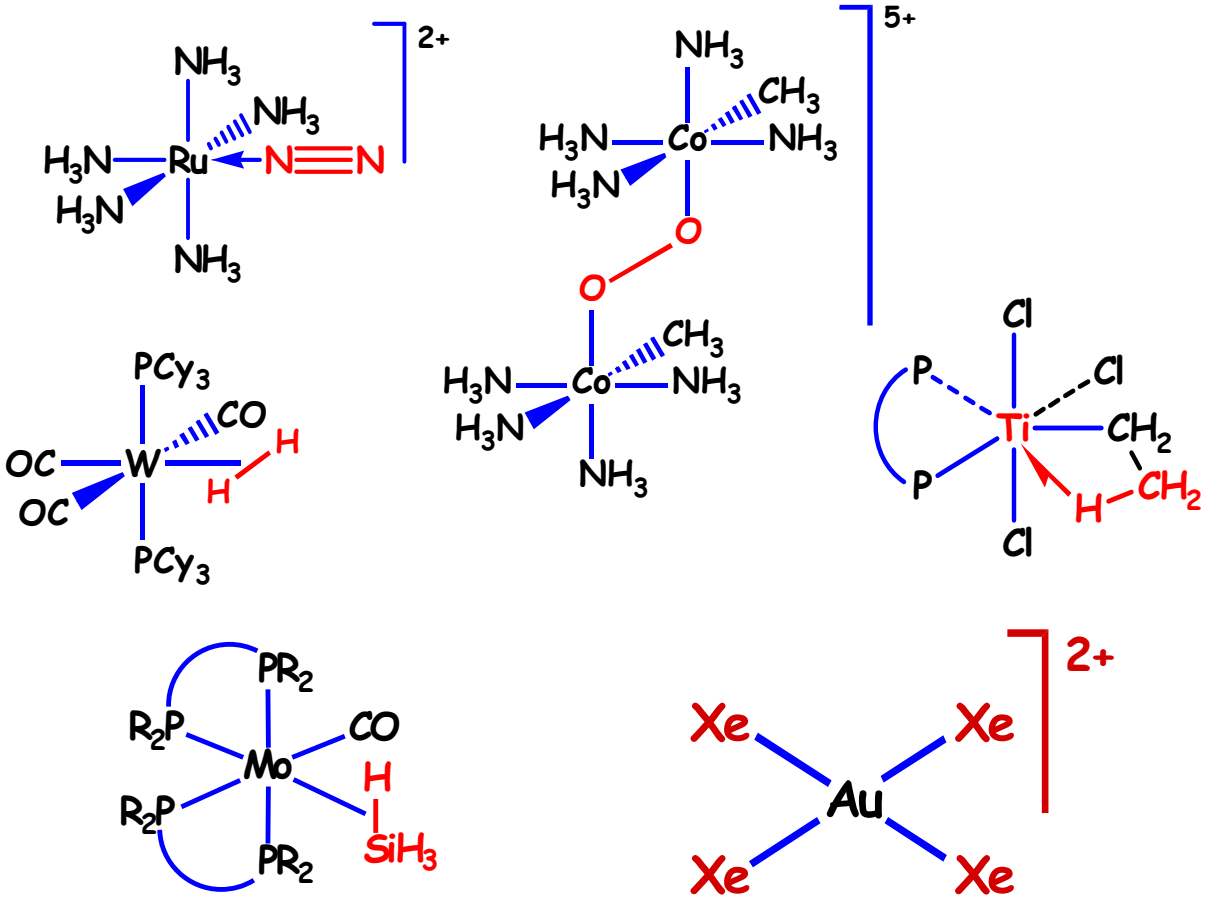






E.O. Fischer, G. Wilkinson.

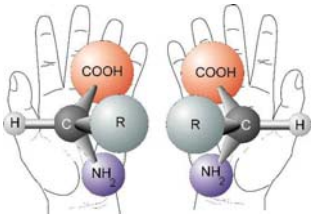
Premio Nobel de Química, 1973

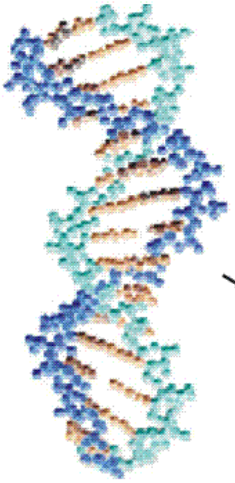


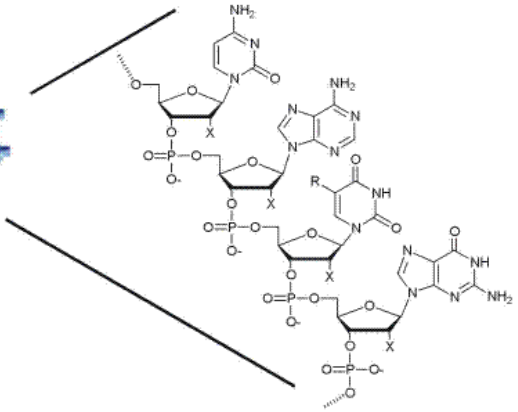
Algunos procesos catalíticos homogéneos

- Catálisis Ziegler – Natta para la producción de poliolefinas (metalocenos como catalizadores).
- Hidroformilación de alquenos catalizada mediante complejos de cobalto ($CoH(CO)_4$), o de rodio ($RhH(CO)(PPh_3)_3$). Síntesis de diversos productos oxigenados (alcoholes detergentes….).
- Síntesis del ácido acético: Monsanto (Rh) y Cativa (Ir)
- Metátesis de olefinas: carbenos de Schrock (Mo, W) y de Grubbs (Ru). **Premio Nobel de Química de 2005** (Y. Chauvin, R.H. Grubbs, R.R. Schrock).

La Quiralidad es un fenómeno común en la naturaleza:
Proteínas, Carbohidratos, Acidos Nucleicos

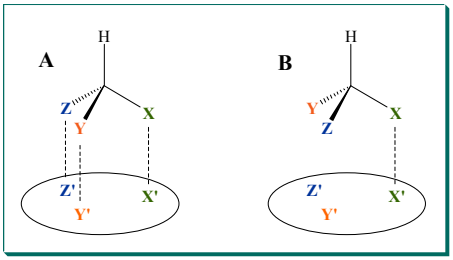




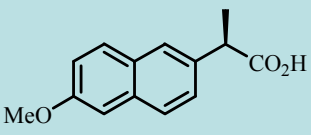


Las moléculas, como los objetos macroscópicos, tienen una estructura tridimensional.
La quiralidad de una molécula es una consecuencia de su estructura espacial.

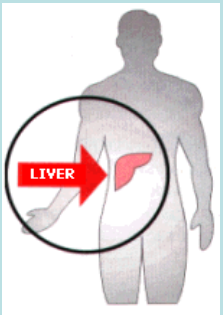
Productos Quirales: Efecto Biológico

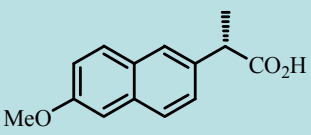


Enantiómeros y Propiedades Biológicas ⇨ *Naproxeno*

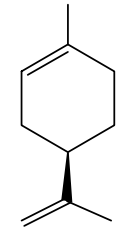


Tóxico

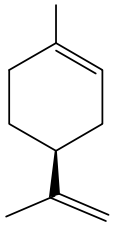




Naproxen
(Anti-inflamatorio)

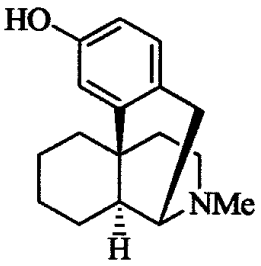


(*R*)-limonene

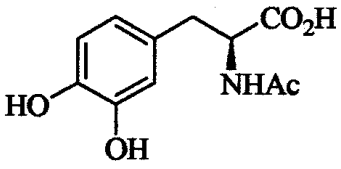


(*S*)-limonene

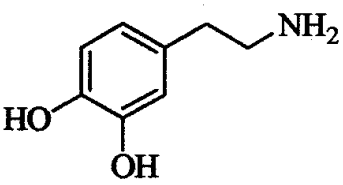
mirror plane



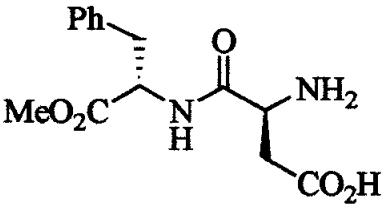
Dextrorfano



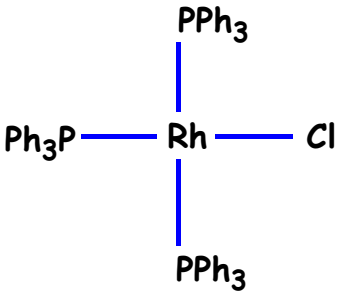
L-DOPA



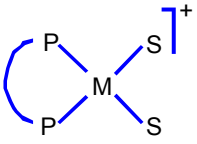
Dopamina



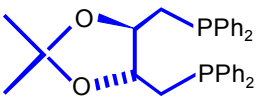
Aspartamo



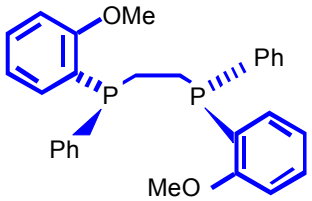
Catalizador de Wilkinson



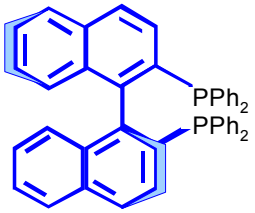
(Rh, Ir)
(Osborn, Schrock)



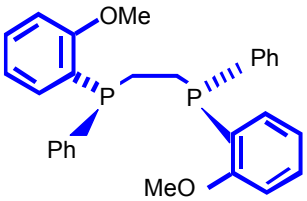
DIOP (Kagan)



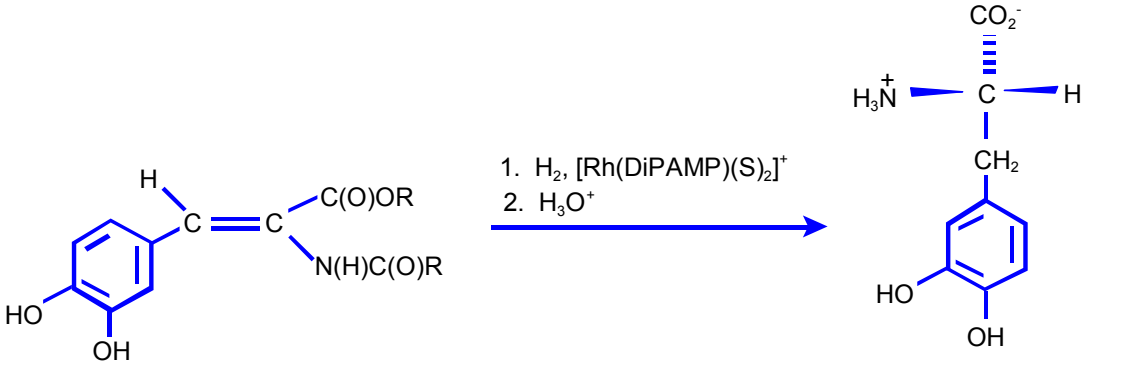
Di PAMP (Knowles)



BINAP (Noyori)

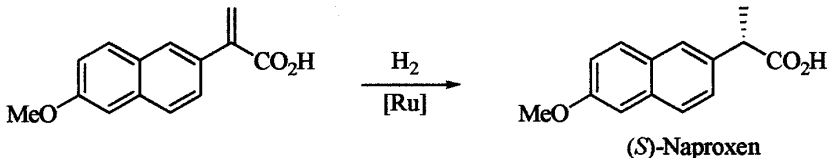


Di PAMP (Knowles)

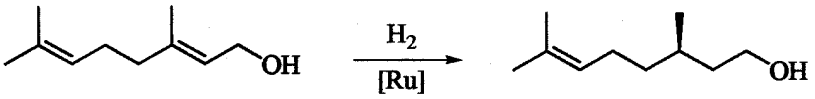


L-dihidroxifenilalanina (L-DOPA)

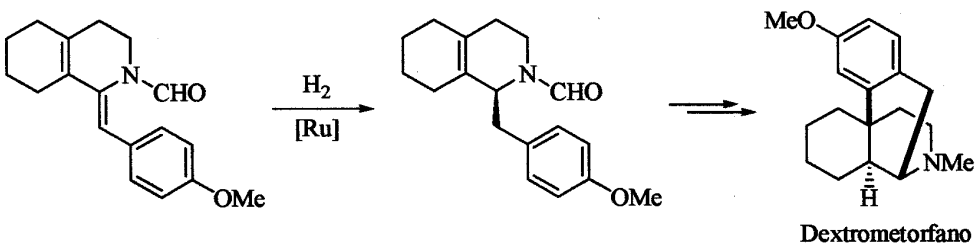
W. Knowles, Monsanto (1974)



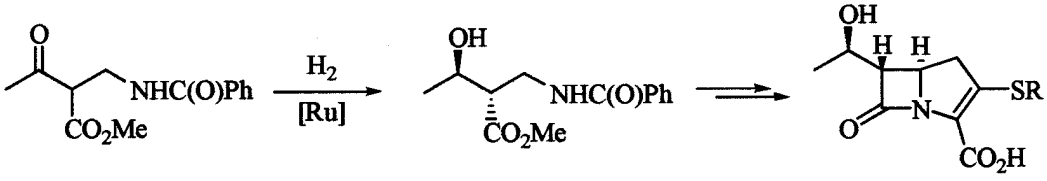
(*S*)-Naproxen



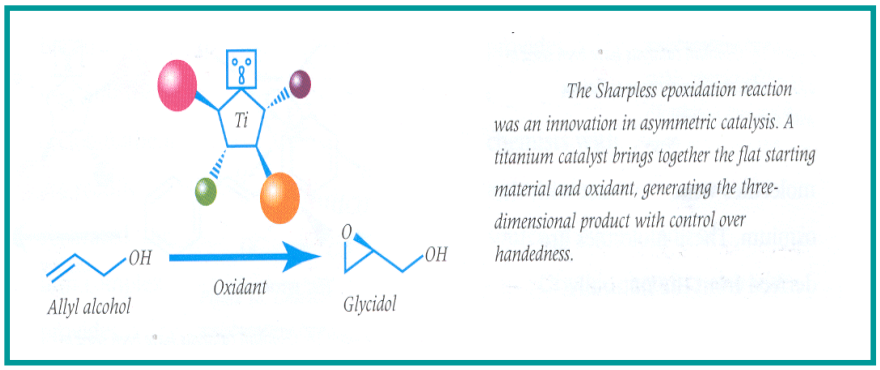
(*R*)-Citronelol



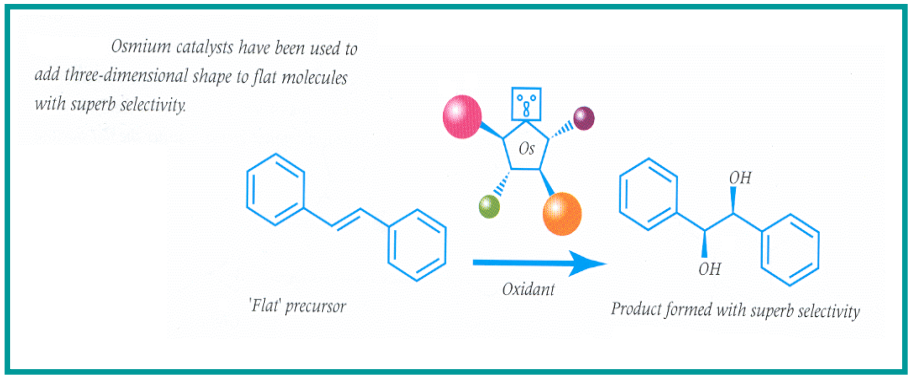
Dextrometorfano



R. Noyori



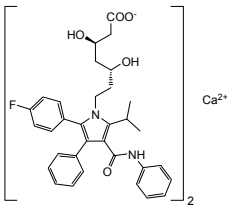
The Sharpless epoxidation reaction was an innovation in asymmetric catalysis. A titanium catalyst brings together the flat starting material and oxidant, generating the three-dimensional product with control over handedness.



W. Knowles, R. Noyori, B. Sharpless, Premio Nobel de Química, 2001.

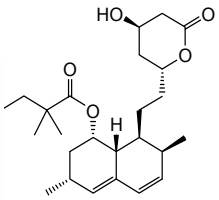
Importancia de los Productos Quirales en la Industria Farmacéutica

#1
LIPITOR
Treats: High cholesterol
Pfizer
$8.4 billion
+8%
Source: IMS Health, a healthcare information company. Twelve Months Ending December 2005



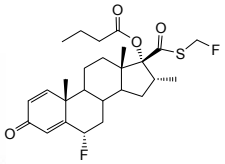
Atorvastatina

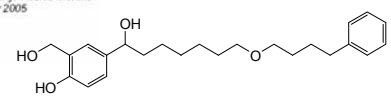
#2
ZOCOR
Treats: High cholesterol
Merck
$4.4 billion (2005 sales)
-5%
Source: IMS Health, a healthcare information company. Twelve Months Ending December 2005



Simvastatina

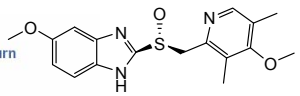
#5
ADVAIR DISKUS
Treats: Asthma
GlaxoSmithKline
$3.6 billion
+22%
Source: IMS Health, a healthcare information company. Twelve Months Ending December 2005





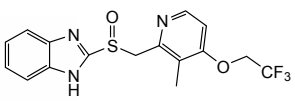
Fluticasona+Salmeterol

#3
NEXIUM
Treats: Heartburn
AstraZeneca
$4.4 billion
+15%
Source: IMS Health, a healthcare information company. Twelve Months Ending December 2005



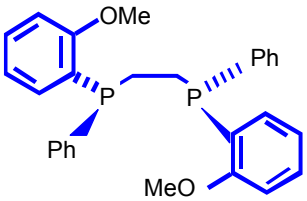
Esomeprazol

#4
PREVACID
Treats: Heartburn
Abbott & Takeda
$3.8 billion
-2%
Source: IMS Health, a healthcare information company. Twelve Months Ending December 2005

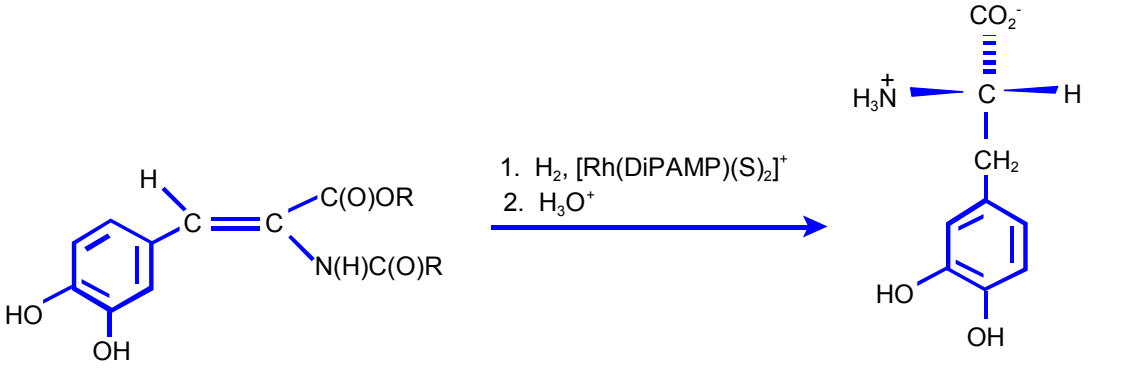


Lanzoprazol

Total ventas productos 1-5:
17.600 millones €



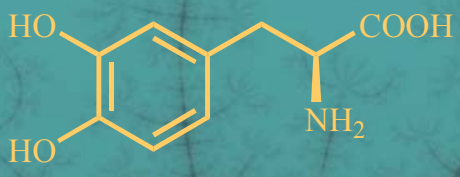
Di PAMP (Knowles)



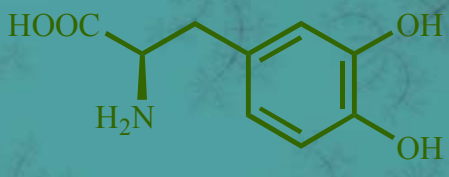
L-dihidroxifenilalanina (L-DOPA)

W. Knowles, Monsanto (1974)

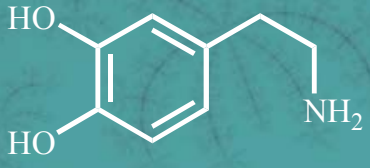
L-DOPA



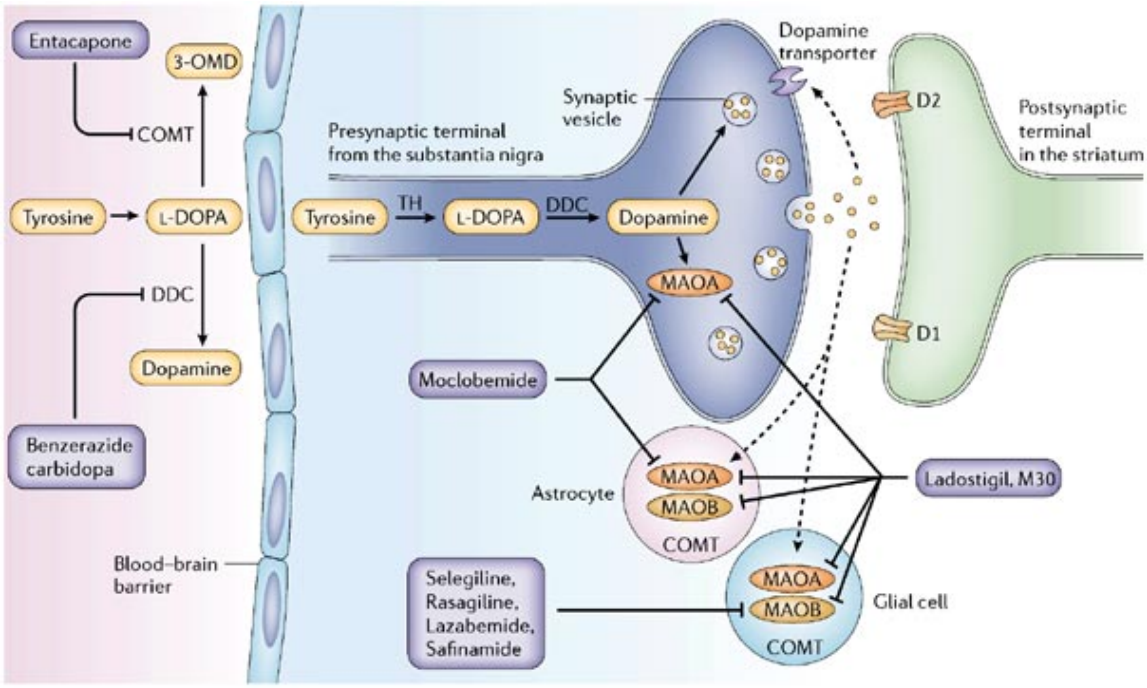
L-Dopa

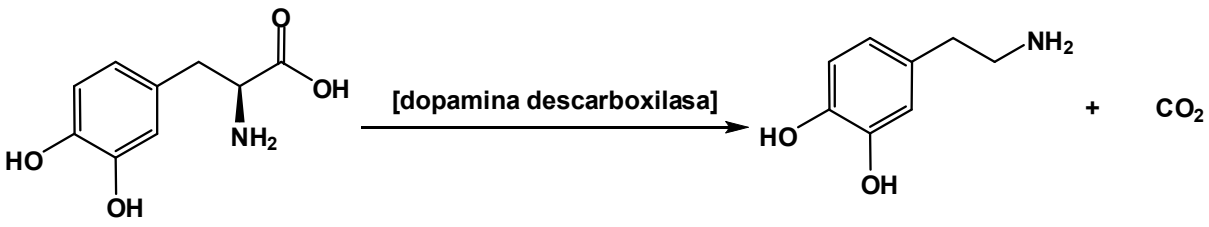


D-Dopa

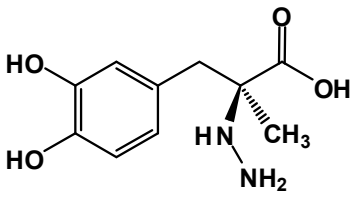


Dopamina

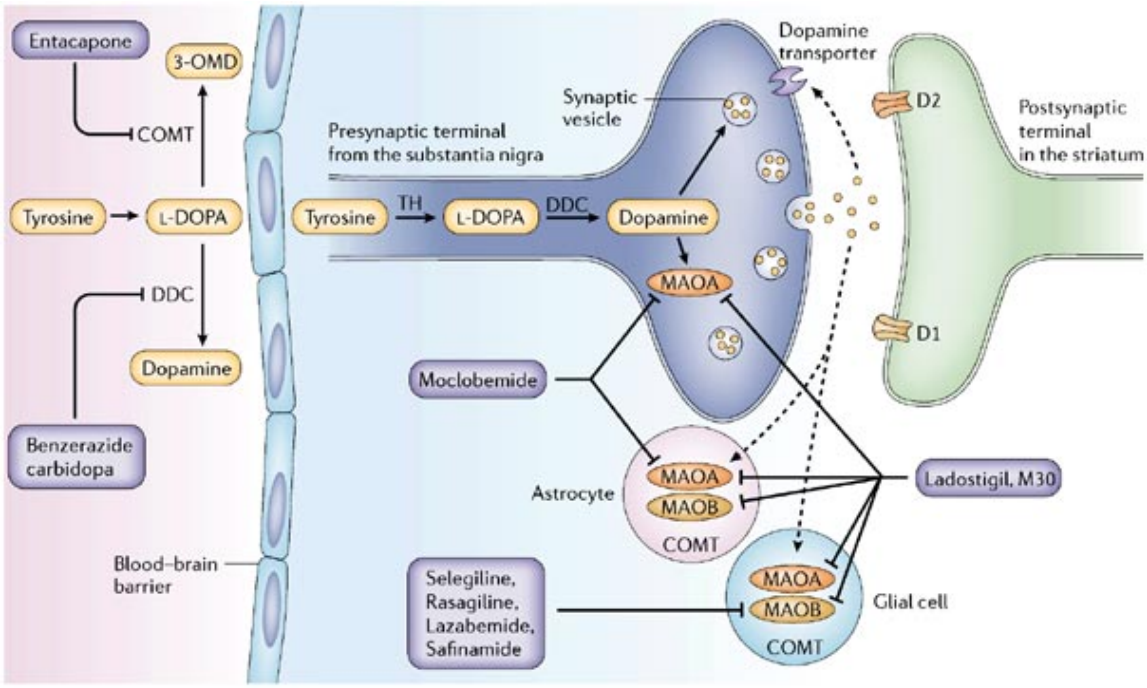




L-dopa **dopamina**



carbidopa

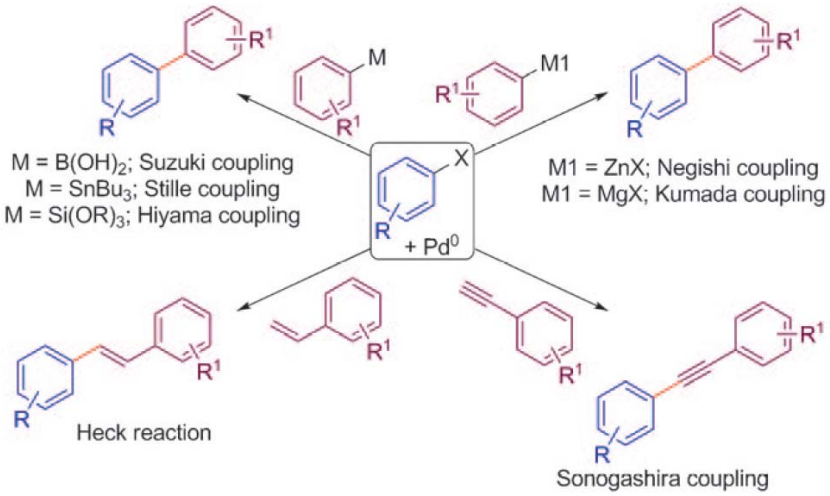


PREMIO NOBEL DE QUÍMICA 2010

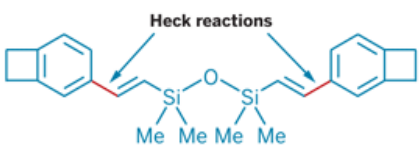
Richard F. Heck

Ei-ichi Negishi

Akira Suzuki

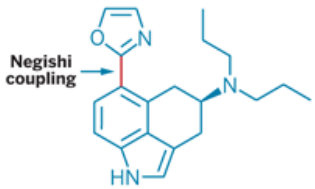


VERSATILITY Heck, Negishi, and Suzuki couplings have been used to make various fine chemicals.

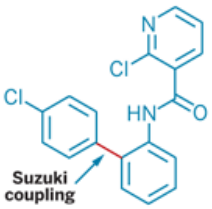


DVS-bis-BCB
(electronic resin monomer)

Me = methyl



Serotonin agonist



Boscalid
(fungicide)