

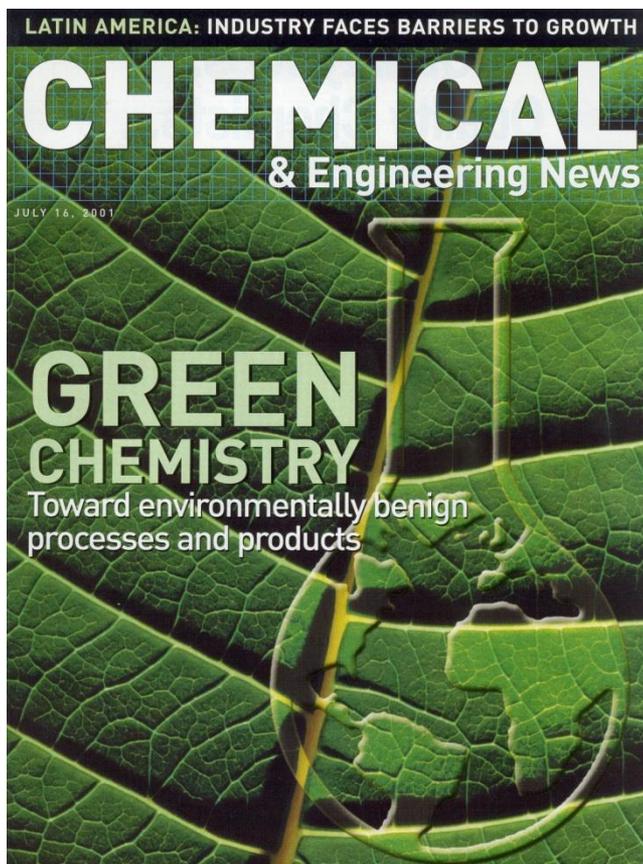
The Role of Green Chemistry in Sustainability

Mary M. Kirchhoff

EPA Region 6 QA Conference

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Green Chemistry



Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

Sustainable Development



Development that meets the needs of the present without compromising the ability of future generations to meet their own needs.

Brundtland Commission

Presidential Green Chemistry Challenge Awards



- The Presidential Green Chemistry Challenge was established to *recognize and promote* fundamental and innovative chemical technologies that accomplish pollution prevention through source reduction and that are useful to industry.



Award Categories



- Greener synthetic pathways
- Greener reaction conditions
- Design of greener chemicals
- Small business
- Academic
- Specific environmental benefit: Climate change

2015 Award Winner



- Ethanol and green crude from algae
 - Bio-engineered cyanobacteria
 - High conversion (80%) to ethanol
 - Ethanol purified via Vapor Compression Steam Stripping
 - Residual biomass converted to green crude
 - 70% reduction in CO₂ emissions relative to gasoline

Algenol

12 Principles



1. Prevention
2. Atom economy
3. Less hazardous chemical syntheses
4. Designing safer chemicals
5. Safer solvents and auxiliaries
6. Energy efficiency
7. Renewable feedstocks
8. Reduce derivatives
9. Catalysis
10. Design for degradation
11. Real-time analysis for pollution prevention
12. Inherently safer chemistry

Principle 1



It is better to prevent waste than to treat or clean up waste after it is formed.

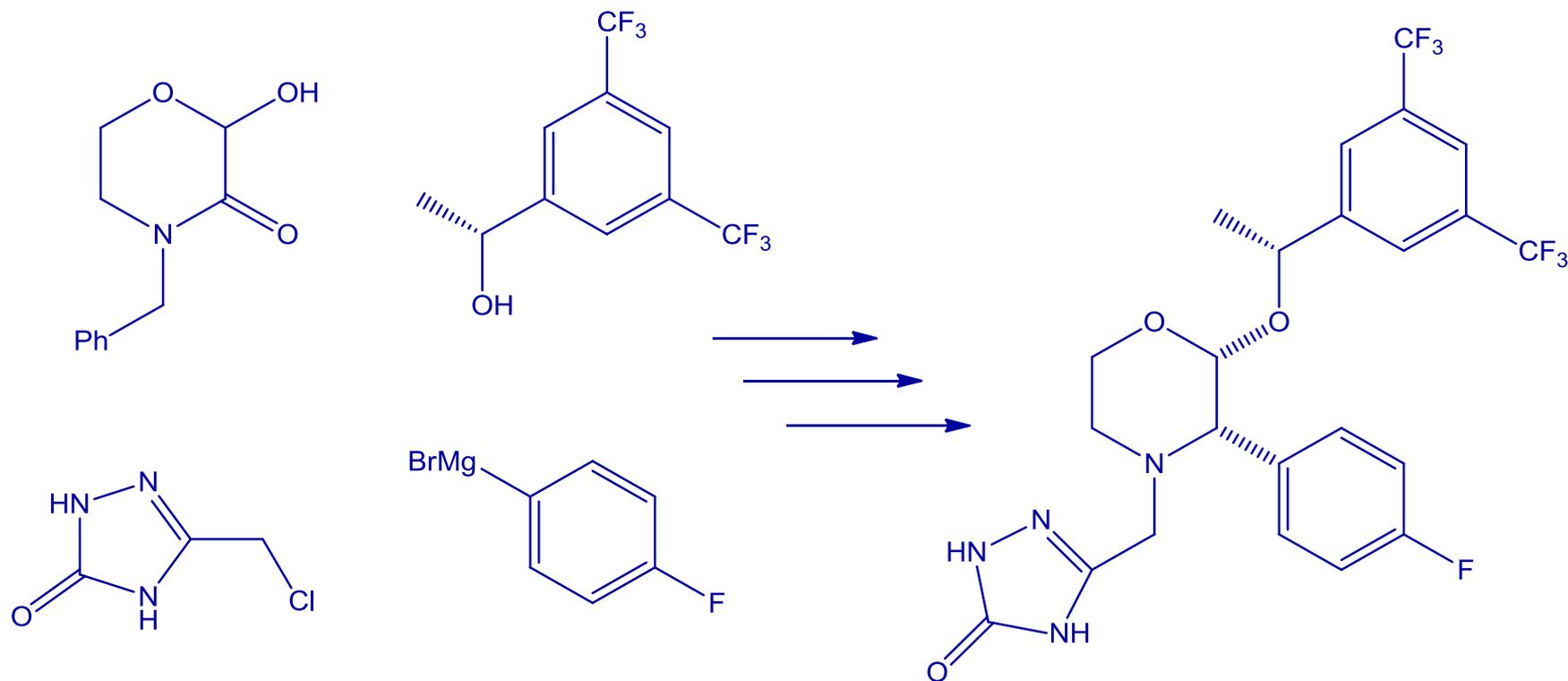
E-factor

- Weight of byproducts/weight of desired product
 - Oil refining 0.1
 - Bulk chemicals <15
 - Fine chemicals 5-50
 - Pharmaceuticals 25-100+

Sheldon, *ChemTech*, **1994**, 24, 38.

Aprepitant Synthesis

- Doubles yield
- Eliminates 340,000 L waste/ton of product



Aprepitant Statistics

- 85% reduction in raw materials usage
- 80% reduction in water usage
- 85% reduction in waste
- 75% lower manufacturing costs
- E-factor
 - Reduced from 477 to 66

Merck & Co

Principle 2

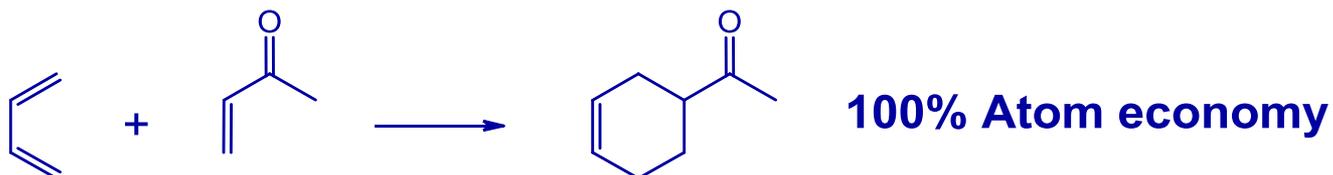


Synthetic methods should be designed to maximize the incorporation of all materials used into the final product.

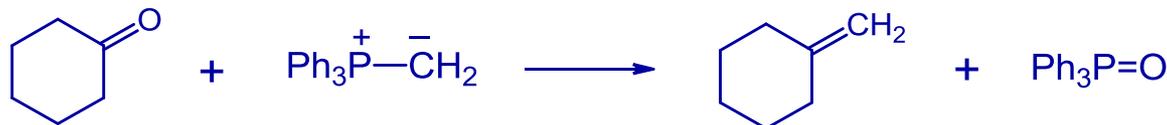
Atom Economy

$$\text{Atom economy} = \frac{\text{MW of desired product}}{\text{Sum of MWs of all substances produced}}$$

Diels-Alder Reaction



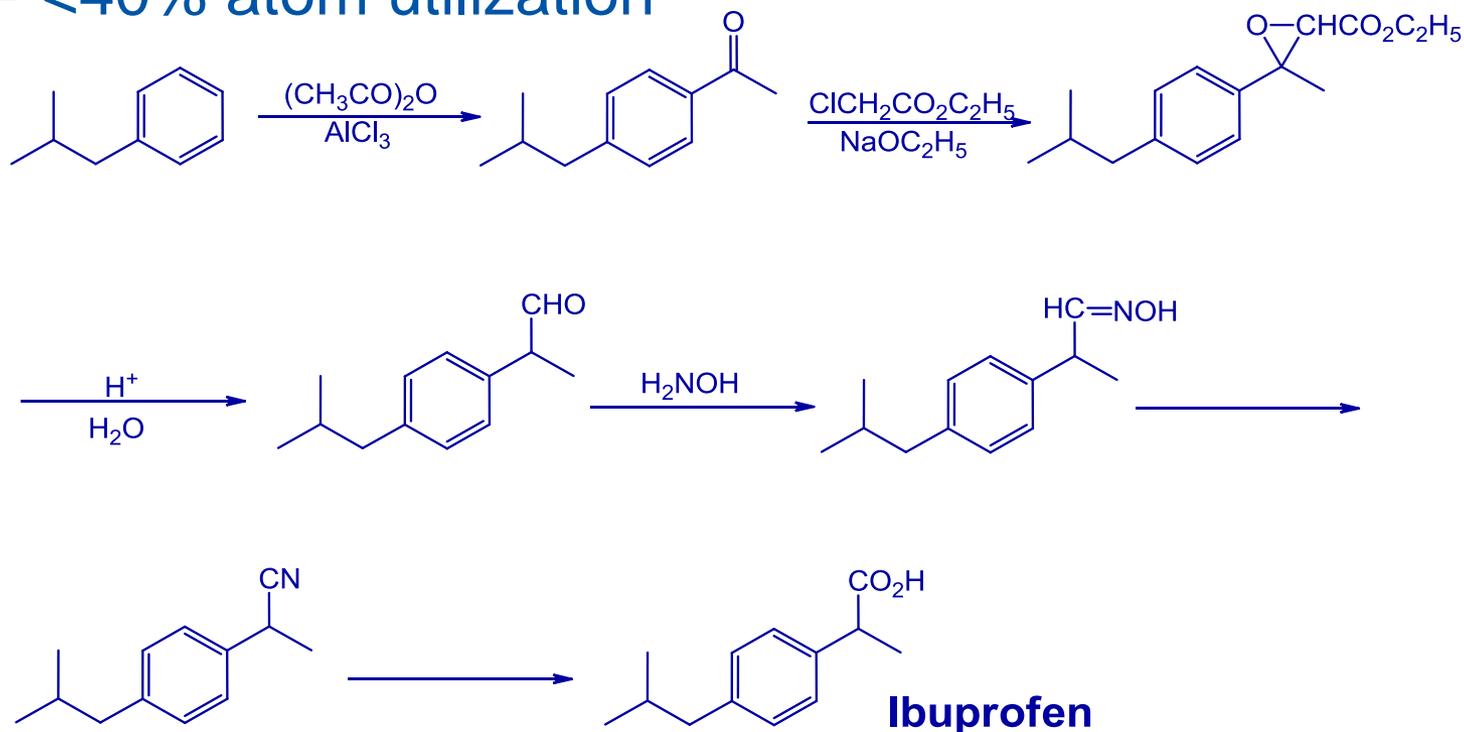
Wittig Reaction



35% Atom economy

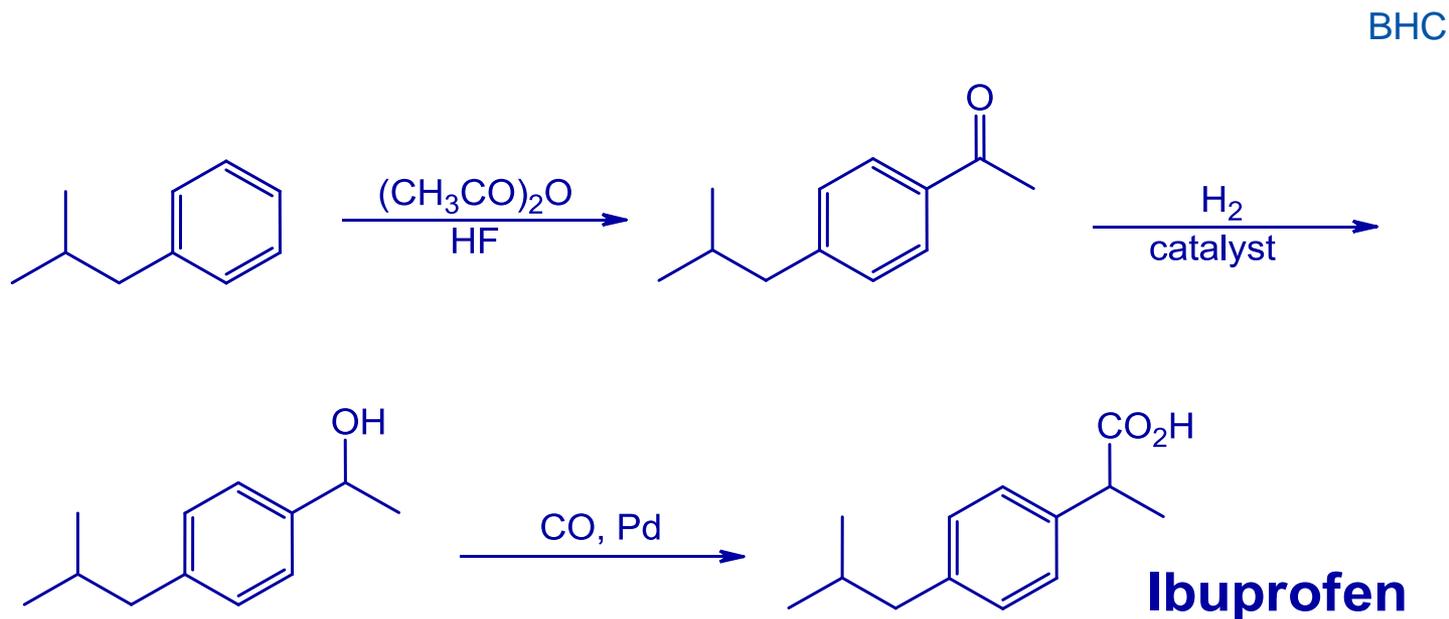
Ibuprofen Synthesis

- Traditional synthesis of ibuprofen
 - 6 stoichiometric steps
 - <40% atom utilization



Ibuprofen Synthesis

- Catalytic synthesis of ibuprofen
 - 3 catalytic steps
 - 80% atom utilization (99% with recovered acetic acid)



How Green is Green?



- Metrics
 - Atom economy
 - E-factor
 - Life Cycle Analysis (LCA)
 - Energy usage
 - Solvent selection
 - Quantifying and characterizing waste

Principle 3

Wherever practicable,
synthetic methodologies
should be designed to use
and generate substances
that possess little or no
toxicity to human health and
the environment.

RE-HEALING™ Foam



- Firefighting foam that contains hydrocarbon surfactants, water, solvent, complex carbohydrates, a preservative, and a corrosion inhibitor
 - Effective for flame knockdown, fire control, extinguishment, and burn-back resistance
 - Eliminates fluorinated surfactants (PBT)

The Solberg Company

Principle 4

Chemical products should be designed to preserve efficacy of function while reducing toxicity.

EVOQUE Polymer

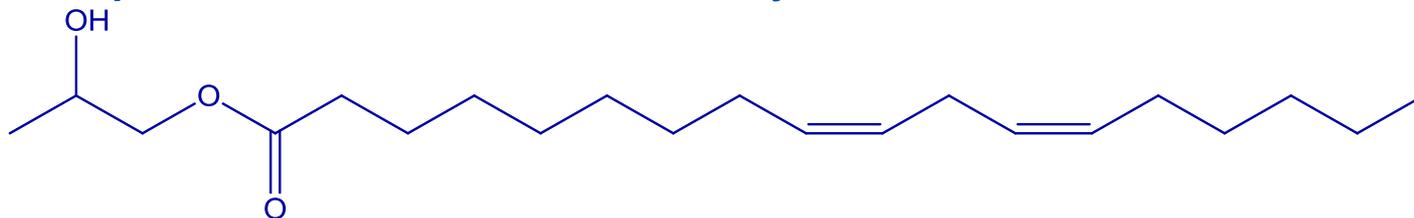


- Binder technology that reduces TiO_2 use in paints
 - TiO_2 most commonly used paint pigment due to its ability to scatter and reflect incident light
 - Most expensive and energy intensive component
- EVOQUE polymers provide improved coverage at lower TiO_2 levels
 - Reduced carbon emissions and water consumption

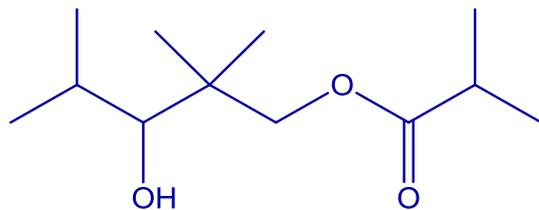
Reduced VOC Paints

- Coalescent: added to paint to provide a smooth, continuous finish
- 120 billion pounds volatile coalescents lost to the atmosphere in the U.S. each year

ADM



Archer RC propylene glycol monoester



2, 2, 4-trimethyl-1, 3-pentanediol monoisobutyrate

Principle 5

The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.

Non-Traditional Solvents

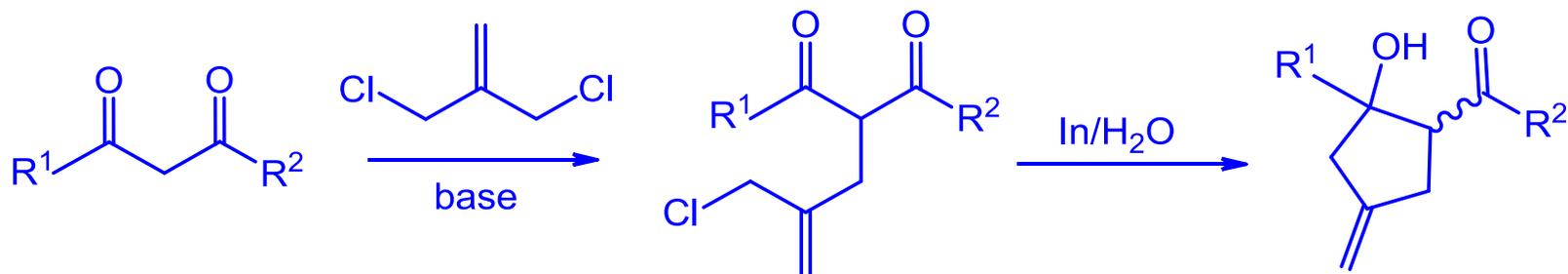


- Supercritical CO₂
- CO₂-expanded liquids
- Ionic liquids
- Liquid polymers (PEG)
- Switchable solvents
- Water

Benign Solvents: H₂O

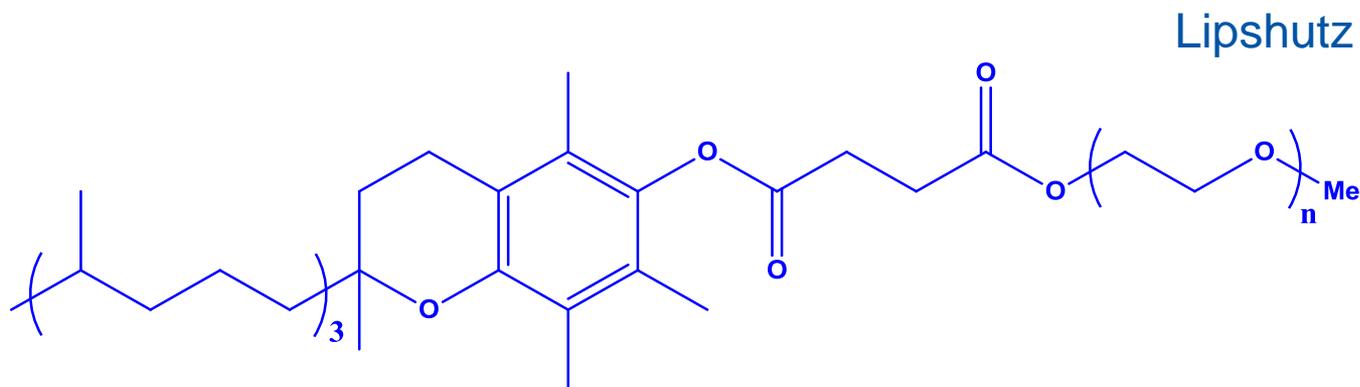
- Carbon-carbon bond formation in water
 - Diels-Alder, Barbier-Grignard
- Indium-mediated cyclopentanoid formation

Li



Micellar Catalysis

- Amphiphilic surfactant (TPGS-750-M) enables metal-catalyzed organic reactions in water
 - Surfactant composed of vitamin E, succinic acid, and MPEG-750
 - Eliminates large volumes of organic solvents



TPGS-750-M

Principle 6

Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

Renewable Fuel

- Biofene®
 - Genetically engineered baker's yeast converts sugarcane into β -farnesene
 - Catalytic hydrogenation yields farnesane (Amyris Diesel), a drop-in replacement for petroleum diesel
 - Benefits relative to petroleum diesel: higher cetane number, lower SO_x and particulate emissions

Amyris Inc.

Energy



- Conversion of industrial waste gases via a microbial process into ethanol and chemicals
 - 70% reduction in greenhouse gas emissions compared to fossil fuel gasoline
 - Reduction in particulate and NO_x emissions
 - Three pre-commercial facilities (steel mills) operating in China

LanzaTech

- MAX HT™ Bayer Sodalite Scale Inhibitor
 - Bayer process converts bauxite ore to alumina
 - Problem: aluminosilicate crystals build up in heat exchangers/pipes
 - Decreases efficiency of heat exchange
 - Requires cleaning with H_2SO_4
- MAX HT™ inhibits crystal formation
- Annual savings per plant: \$2-20 M, 9.5-47.5 trillion BTU

Cytec

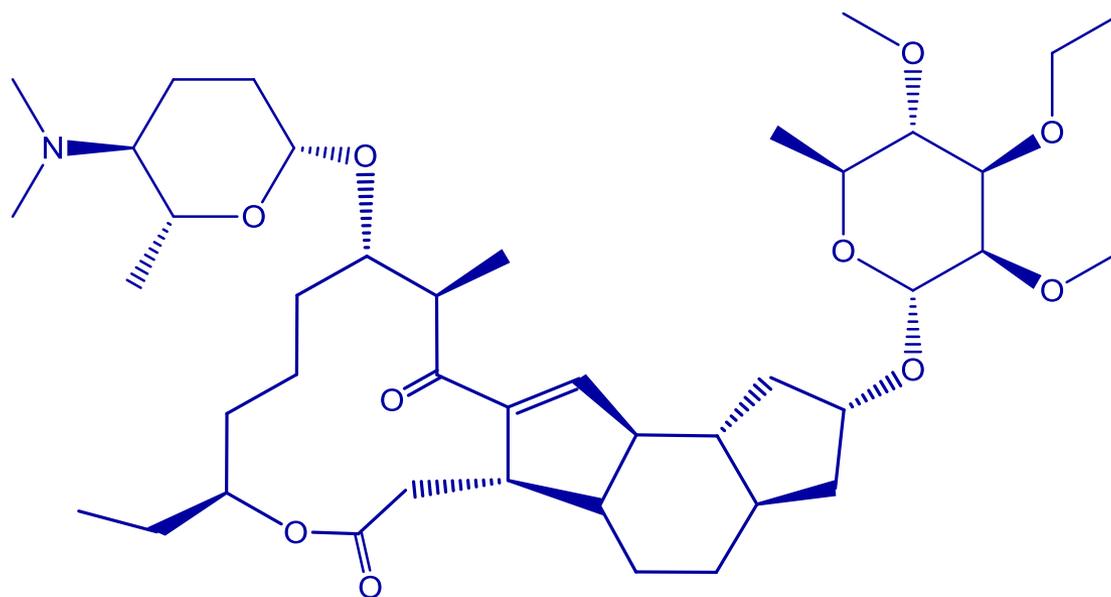
Principle 7



A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.

Spinetoram

- Produced by fermentation of renewable feedstocks using *Saccharopolyspora spinosa*



Spinetoram
3'-O-5,6-dihydro spinosyn J

Evolution of a Greener Technology



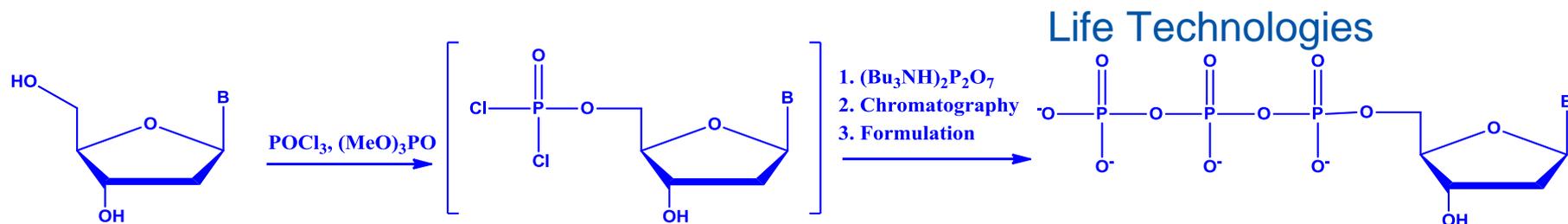
- 1999: Spinosad (Dow AgroSciences)
 - Selective, environmentally-friendly insecticide
- 2008: Spinetoram (Dow AgroSciences)
 - Controls wider range of pests at lower use rates than spinosad
- 2010: Natular™ Larvicide (Clarke)
 - Spinosad-based mosquito larvicide that slowly releases in water (Sequential Plaster Matrix)

Principle 8

Unnecessary derivatization
(blocking group,
protection/deprotection,
temporary modification of
physical/chemical processes)
should be avoided whenever
possible.

PCR Reagents

- Deoxyribonucleotide triphosphates (dNTPs)
- One-pot synthesis eliminates need for protecting groups, improves yields, minimizes hazardous reagent and solvent usage, and decreases waste production
- E-factor drops from 3200 to 400



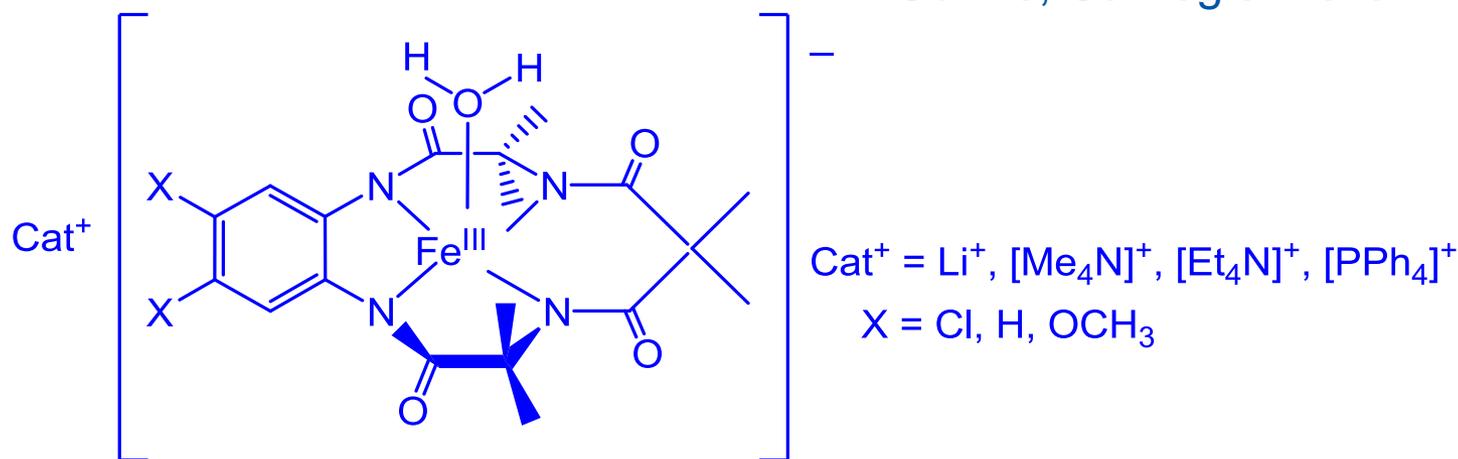
Principle 9

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

TAML Catalysts

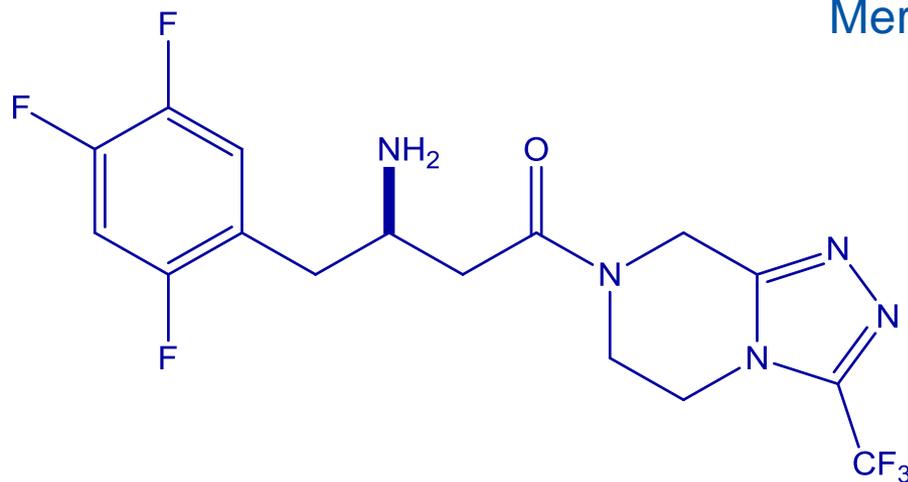
- Activate H_2O_2 for chlorine-free wood pulp bleaching (1999 PGCC)
- New application: Degrade endocrine disruptors in wastewater

Collins, Carnegie Mellon



Sitagliptin

- Active ingredient in Januvia™
 - Treatment for Type II diabetes
 - Controls blood sugar without significant side effects



Merck & Codexis

Sitagliptin

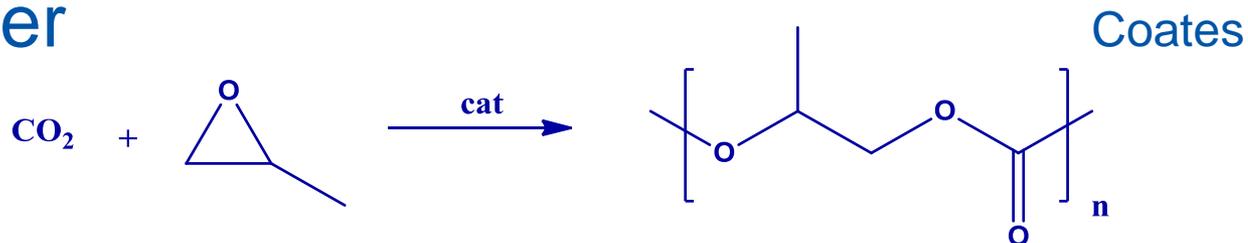
- Enzymatic transamination reaction
 - Eliminates high pressure and heavy metals
 - Generally applicable in converting ketones to chiral amines
- 1st generation: 8 steps, 44% overall yield
- New route: 3 steps, 50% increase in overall yield
 - 22,000 kg less waste per 1,000 kg product

Principle 10

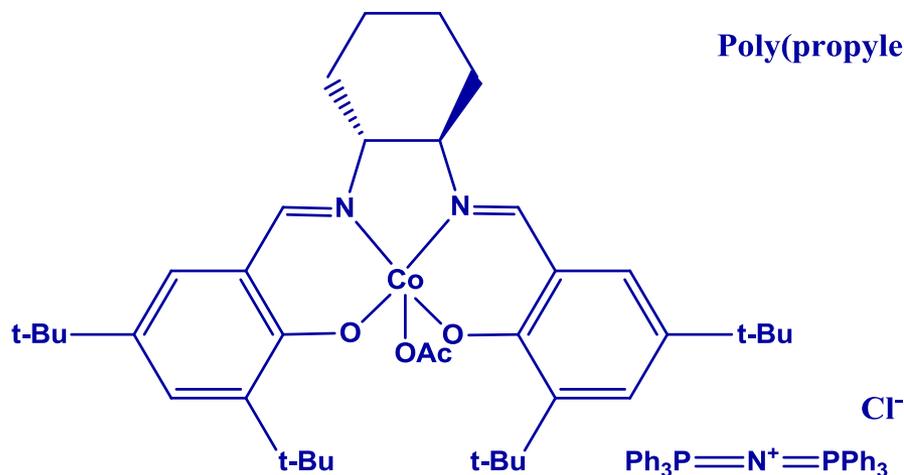
Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

Biodegradable Polymers

- CO and CO₂ used as monomers
- Catalyst exhibits high activity and high turnover number



Poly(propylene carbonate)



Principle 11

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

Protein Testing

- Automated protein tagging technique
 - Tags amino acids commonly found in proteins
 - Employs non-toxic solutions
 - Generates no hazardous waste
 - Does not bind to fillers and other sources of non-protein nitrogen
 - Replaces hazardous materials and high temperatures in traditional methods
 - Applications in the food and pet food sectors

CEM Corporation

Principle 12



Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Vegetable Oil Dielectric Insulating Liquid



- Envirotemp FR3 fluid
 - Made from vegetable oils, biodegradable, nontoxic, carbon neutral
 - Used in high voltage transformers
 - Lifetime of solid insulation system (paper, wood, paperboard) determines life of transformer
 - Fluid absorbs water as paper decomposes
 - Replaces mineral oil (low flash point)

Cargill, Inc.

Green Chemistry and Sustainability

- Green chemistry is a tool in achieving sustainability
 - Not a solution to all environmental problems
 - Fundamental approach to pollution prevention
 - Chemistry's unique contribution to sustainability

