
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]。

永續化學合成(5)

非傳統試劑與永續化學合成

劉廣定

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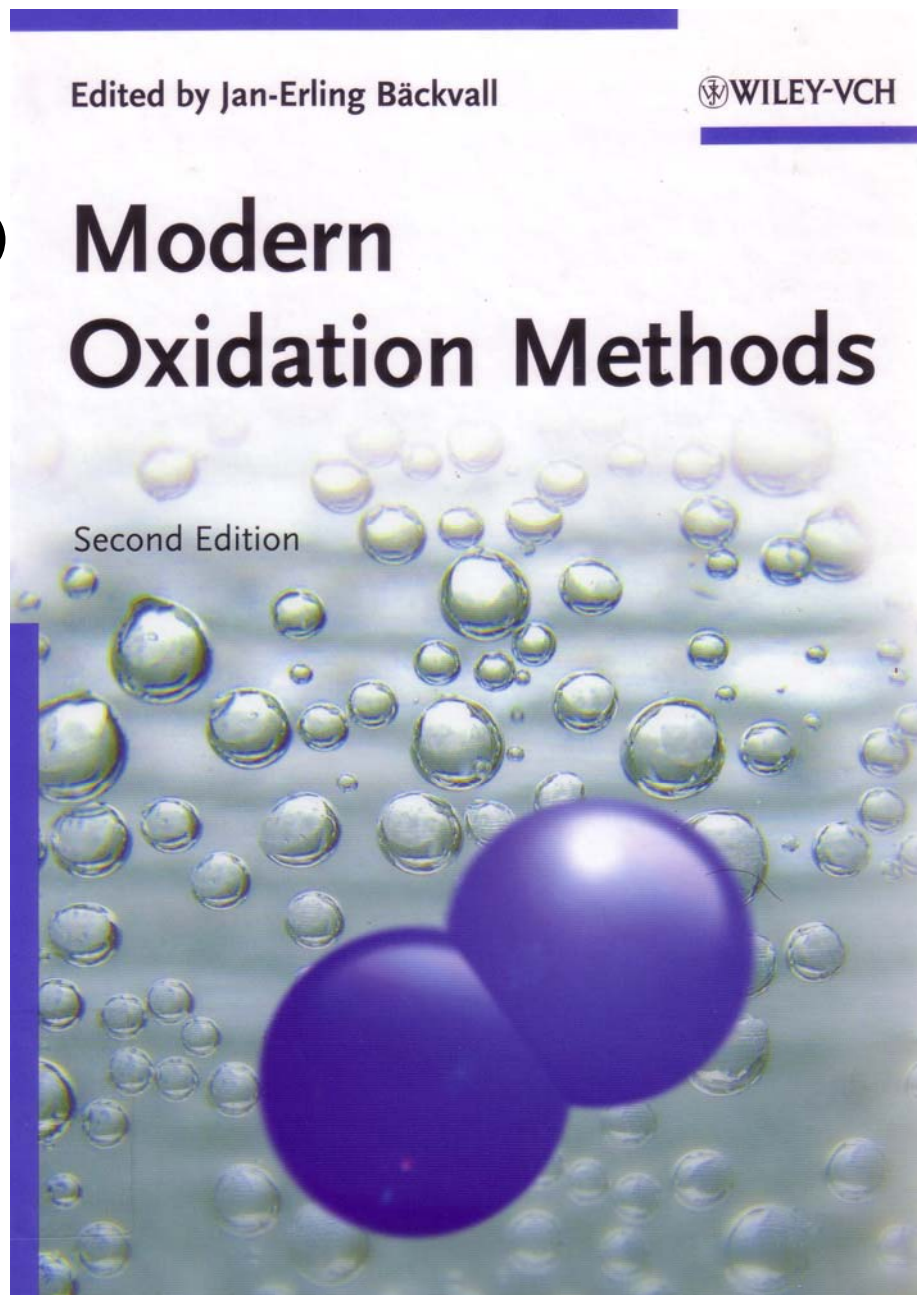
December 2, 2011

Criteria of chemicals and solvents used in sustainable chemistry

- Naturally abundant and easily regenerate
- From renewable sources
- Environmentally benign
- Recyclable (reusable)
- (Bio)Degradable
- etc.

- Naturally abundant and easily regenerate,
- H_2O , CO_2 , $\text{O}_2(\text{air})$, CaCO_3 , etc.
- From renewable sources,
- carbohydrates, fatty acids and glycerol, terpenes, lignin, amino acids, etc.
- Environmentally benign,
- H_2O_2 , SC-CO_2 , organic carbonates, supported reagents, etc.
- Recyclable, manganese salts, etc.
- Biodegradable
- etc.

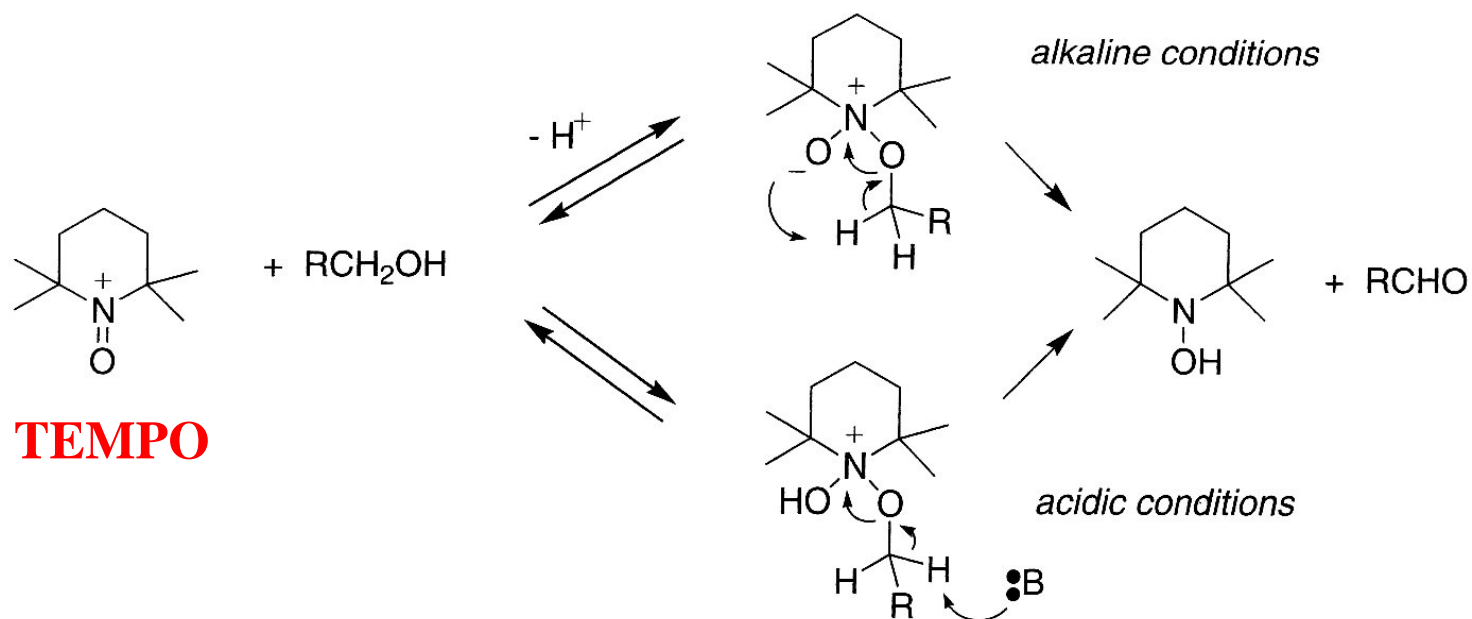
**A 2010 reference
book (1st Ed, 2004)**



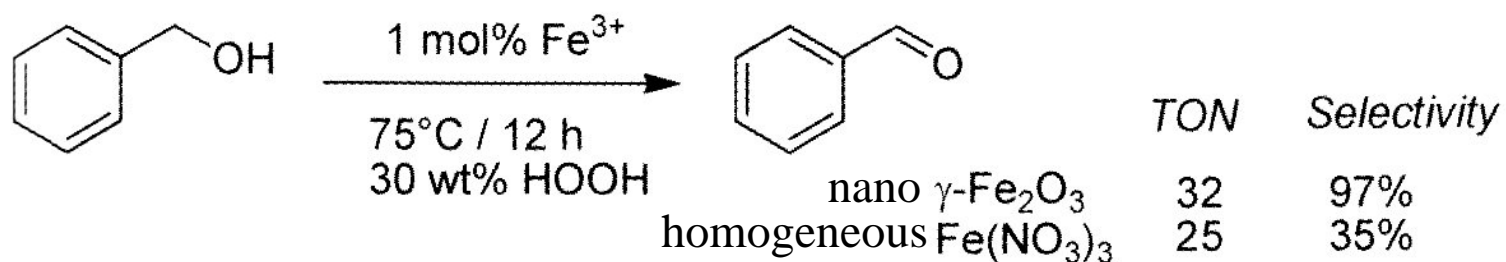
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The use of TEMPO



TEMPO



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Green Polymerization Methods (2011)

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二氧化碳

無毒(但能令人窒息)

不自燃也不助燃

有廉價之高純度商品

液態或超臨界態 [Liq CO₂ (50-60 bar, rt); SC CO₂ (>74 bar, >31°C)]

易除去或回收再用

故可用為溶劑及反應試劑

Recent literatures

Transition-metal-catalyzed C-C bond formation through the fixation of CO₂

Chem. Soc. Rev. **2011**, *40*, 2435-2452

Use of CO₂ in chemical syntheses via lactone intermediate *Green Chem.*

2011, *13*, 25-39

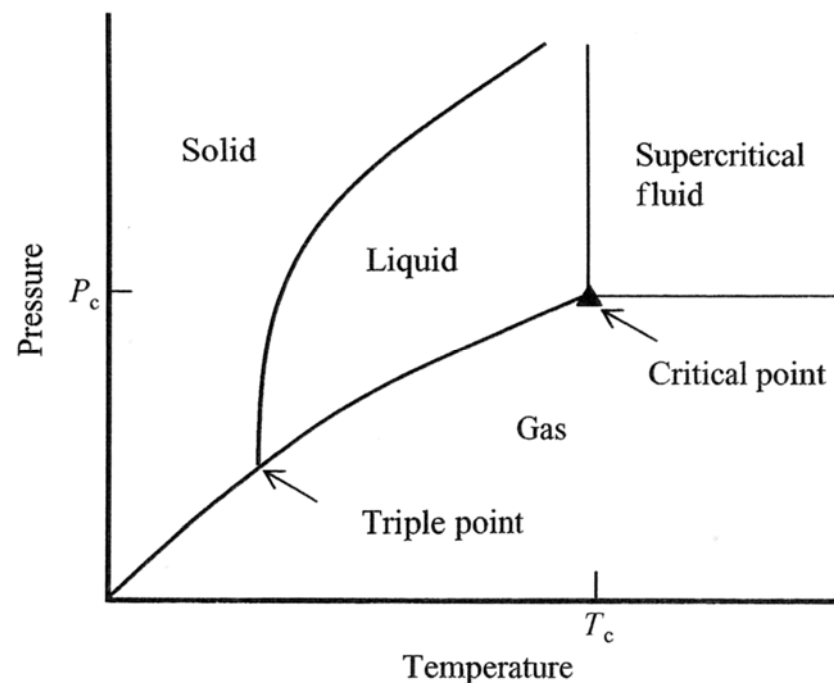
Adaptive Process Optimization for Continuous Methylation of Alcohols in

SC CO₂, *Org. Proc. Res. Dev.* **2011**, *15*, 932-938

Ionic Liquids and Dense CO₂: A Beneficial Biphasic System for Catalysis,

Chem. Rev. **2011**, *111*, 322-363.

Supercritical fluids and critical points



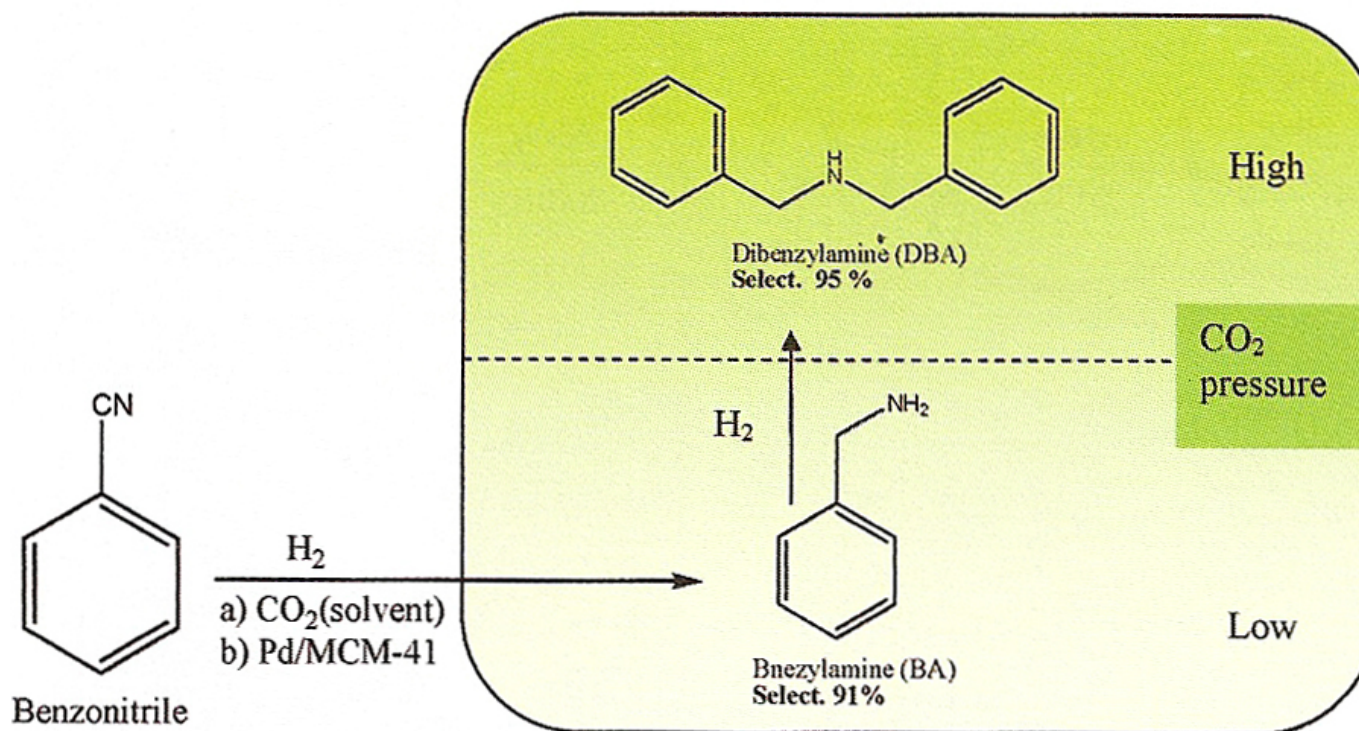
<i>Material</i>	T_c (°C)	P_c (bar)
Ammonia	132.4	113.2
<u>Carbon dioxide</u>	31.1	73.8
Ethane	32.2	48.7
Ethene	9.2	50.4
Fluoroform	25.9	48.2
Propane	96.7	42.5
<u>Water</u>	374.2	220.5

A versatile lab to pilot scale continuous rxn system for SCF processing, *Org. Process Res Dev.* **2011**, *15*, 1275-1280

Hydrogenation of nitrile in scCO₂: a tunable approach to amine selectivity

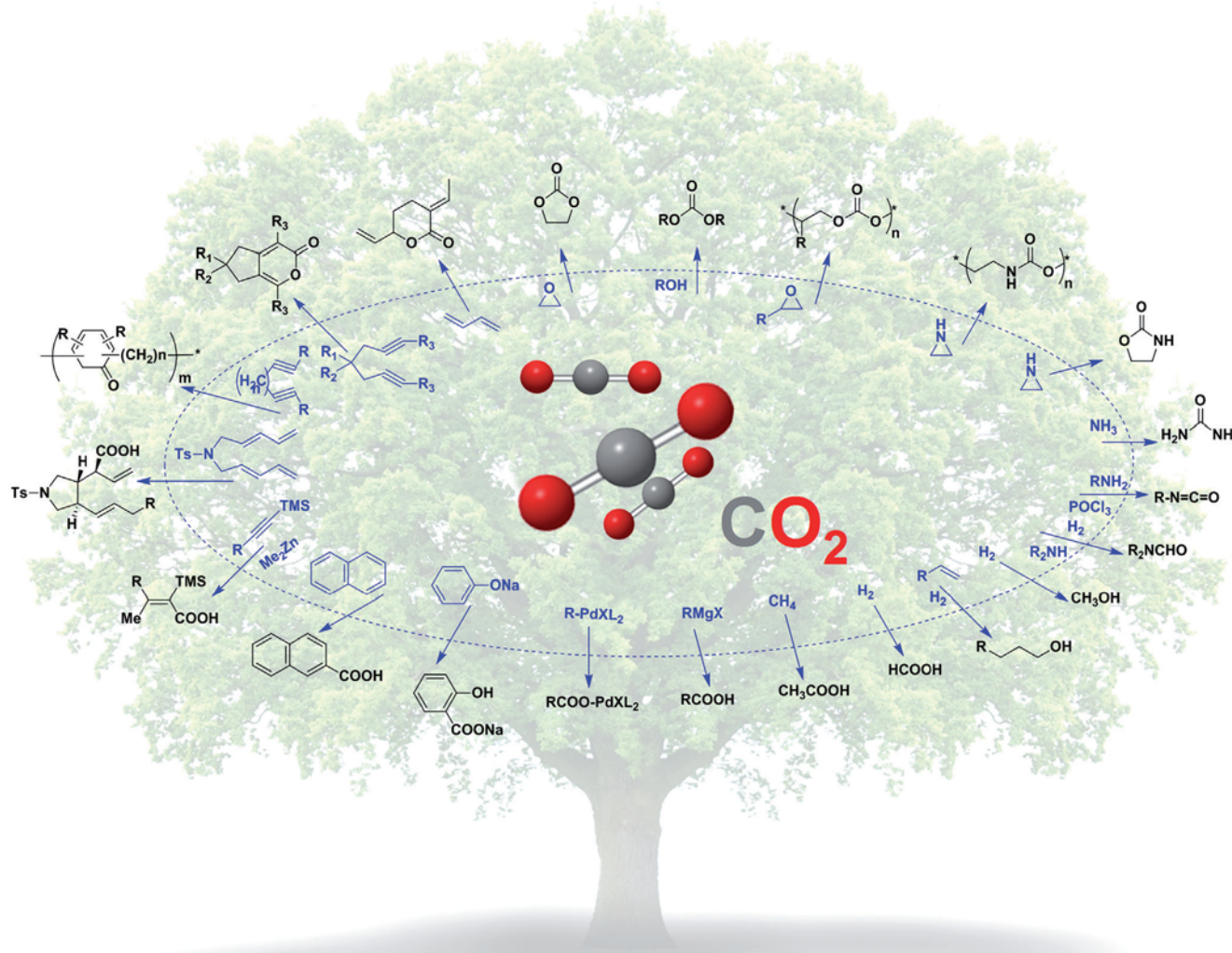
Green Chem. **2010**, *12*, 87-93

By **tuning the CO₂ pressure** changes the product selectivity (more than 90%) from benzylamine to dibenzylamine, with 90+% conversion.



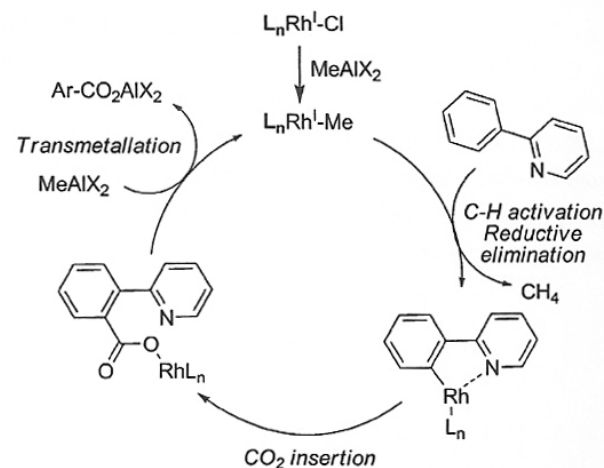
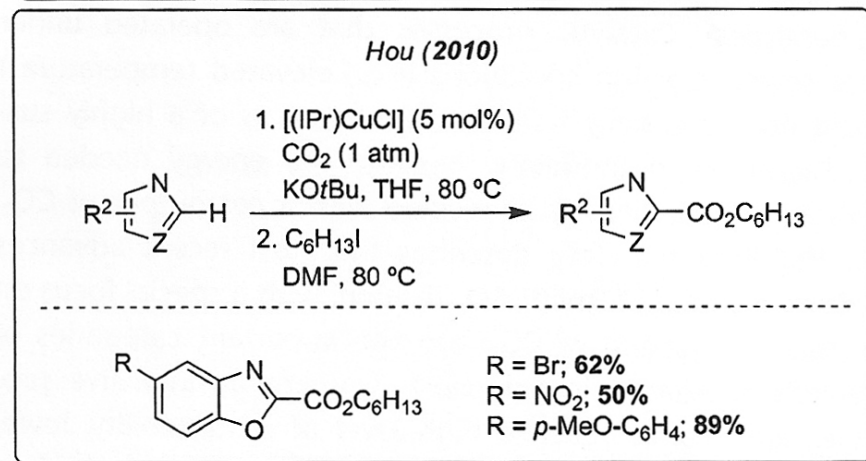
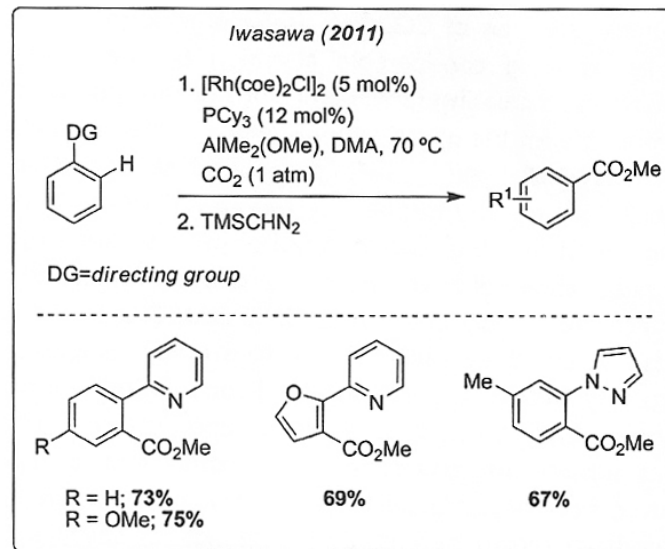
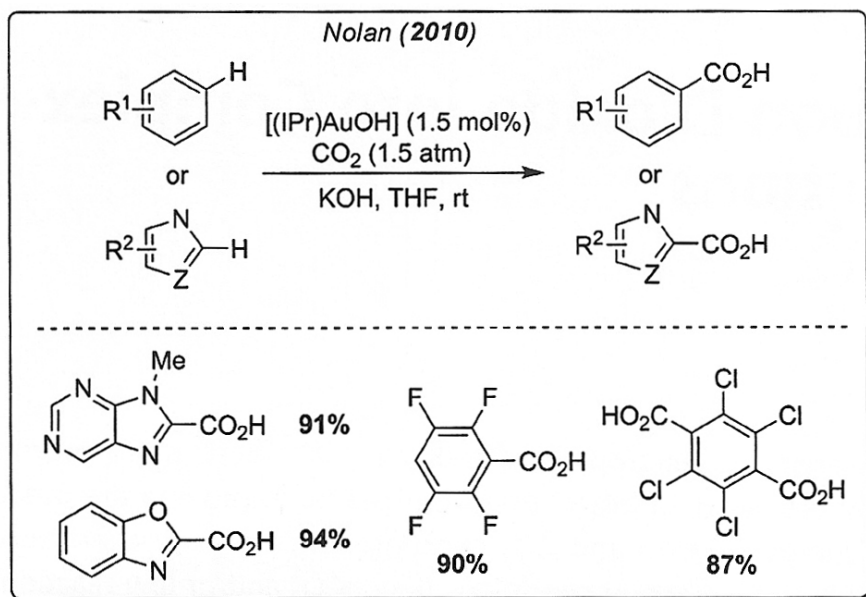
Chemical Technologies for Exploiting and Recycling Carbon Dioxide into the Value Chain

ChemSusChem 2011, 4, 1216-1240

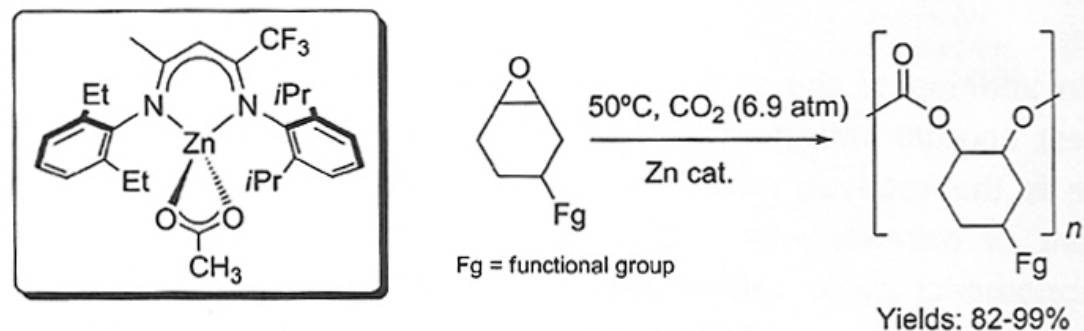


Fixation of CO₂ into Complex Organic Matter under Mild Conditions

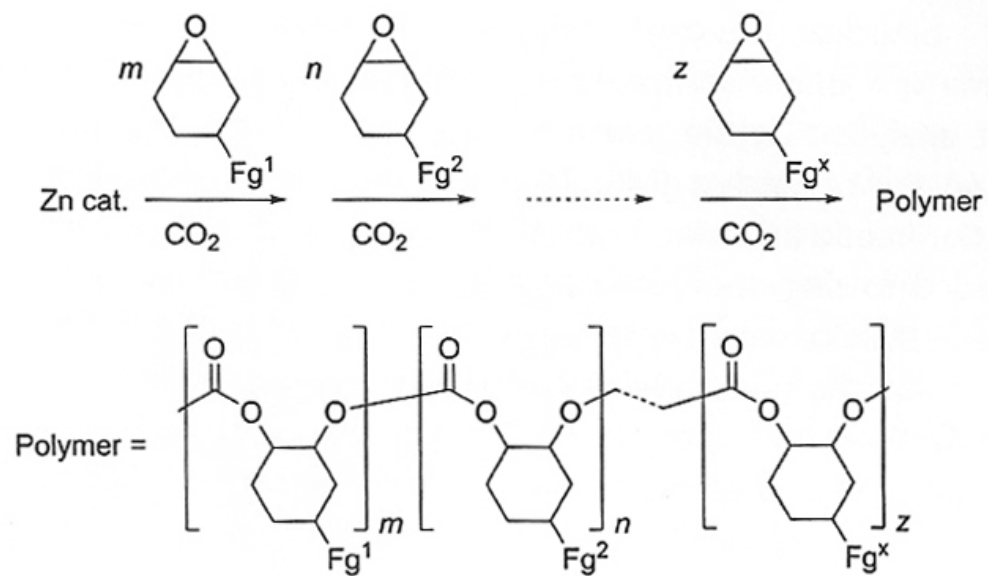
ChemSusChem 2011, 4, 1259-1263



Coates (2011)



Multiblock CHO copolymers:



Yields: 87-99%
 Up to six different CHO monomers

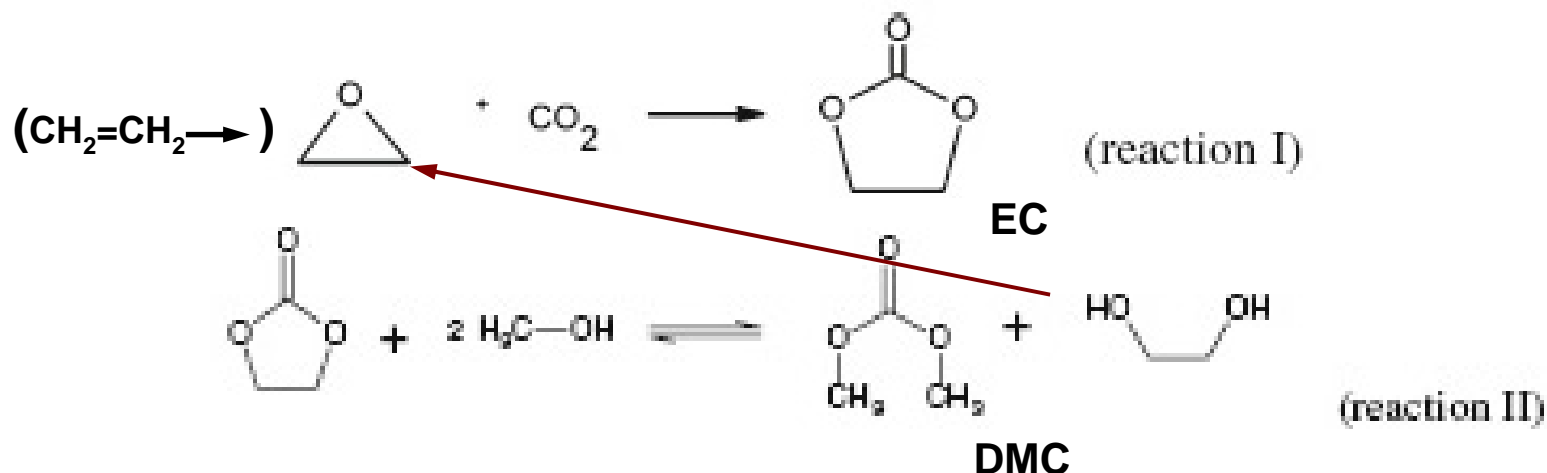
Preparation of flame retarding polymers was demonstrated by using immortal CO₂/propylene oxide copolymerization in the presence of phosphorous-containing chain transfer agents.



Green Chem. **2011**, *13*, 3469-3475

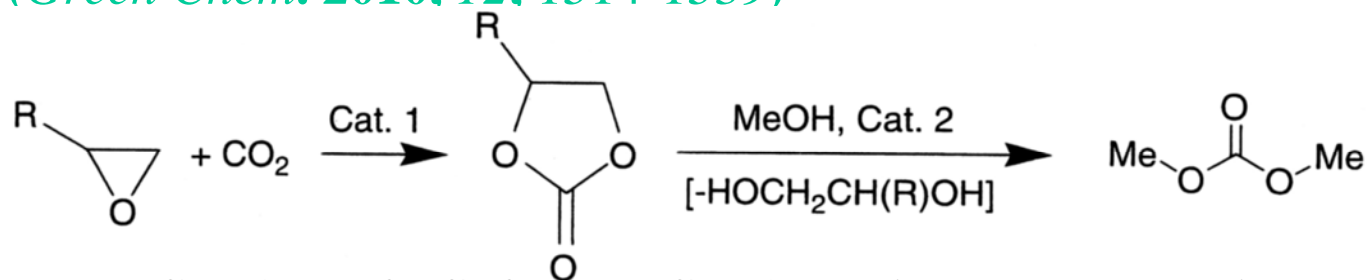
Production of **Dimethyl carbonate** (DMC) from ethylene oxide and CO₂ as a more effective way for the **reuse of CO₂**

(Clean Technologies and Environ. Policy 2009, 11(4), 459-472)



Cyclic carbonates from epoxides and CO₂

(Green Chem. 2010, 12, 1514-1539)



Cat. 1: MgO, CaO

**Cat. 2: zeolites exchanged with alkali
 or alkali earth metal ions**

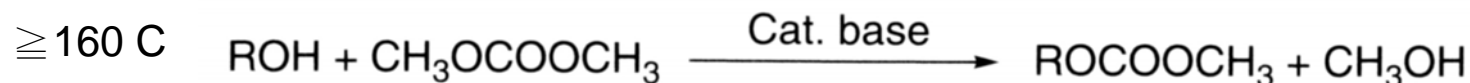
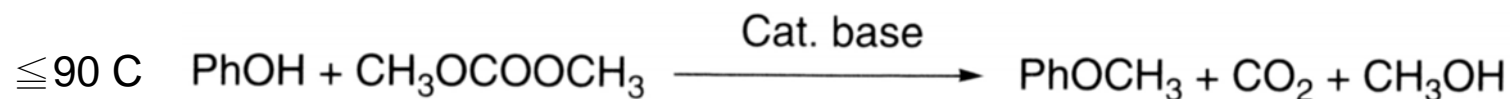
Dimethyl Carbonate as a Green Reagent

Low toxicity, no mutagenic or irritating effect.

Biodegradable (> 90% in 28 days)

Melting point (°C)	4.6
Boiling point (°C)	90.3
Density (d ₄ ²⁰)	1.07
Viscosity (μ ²⁰ , cps)	0.625
Flashing point (°C, O.C.)	21.7
Dielectric constant (ε ²⁵)	3.087
Dipol moment (μ, D)	0.91
ΔH vap (kcal/kg)	88.2
Solubility H ₂ O (g/100 g)	13.9
Azeotropical mixtures	With water, alcohols, hydrocarbons

Useful methylation and alkoxy-carbonylation agents

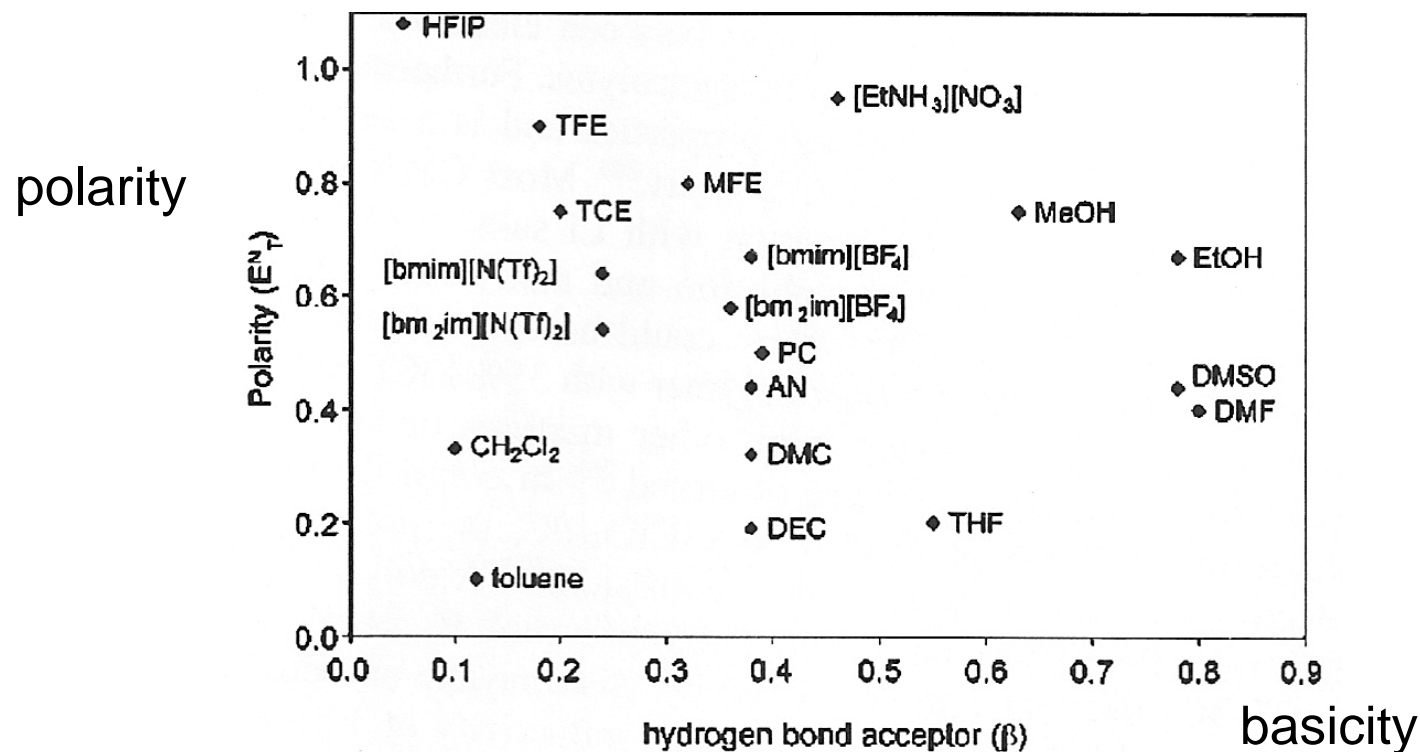


Organic carbonates as solvents

(*Chem. Rev.* 2010, 110, 4554-4581)

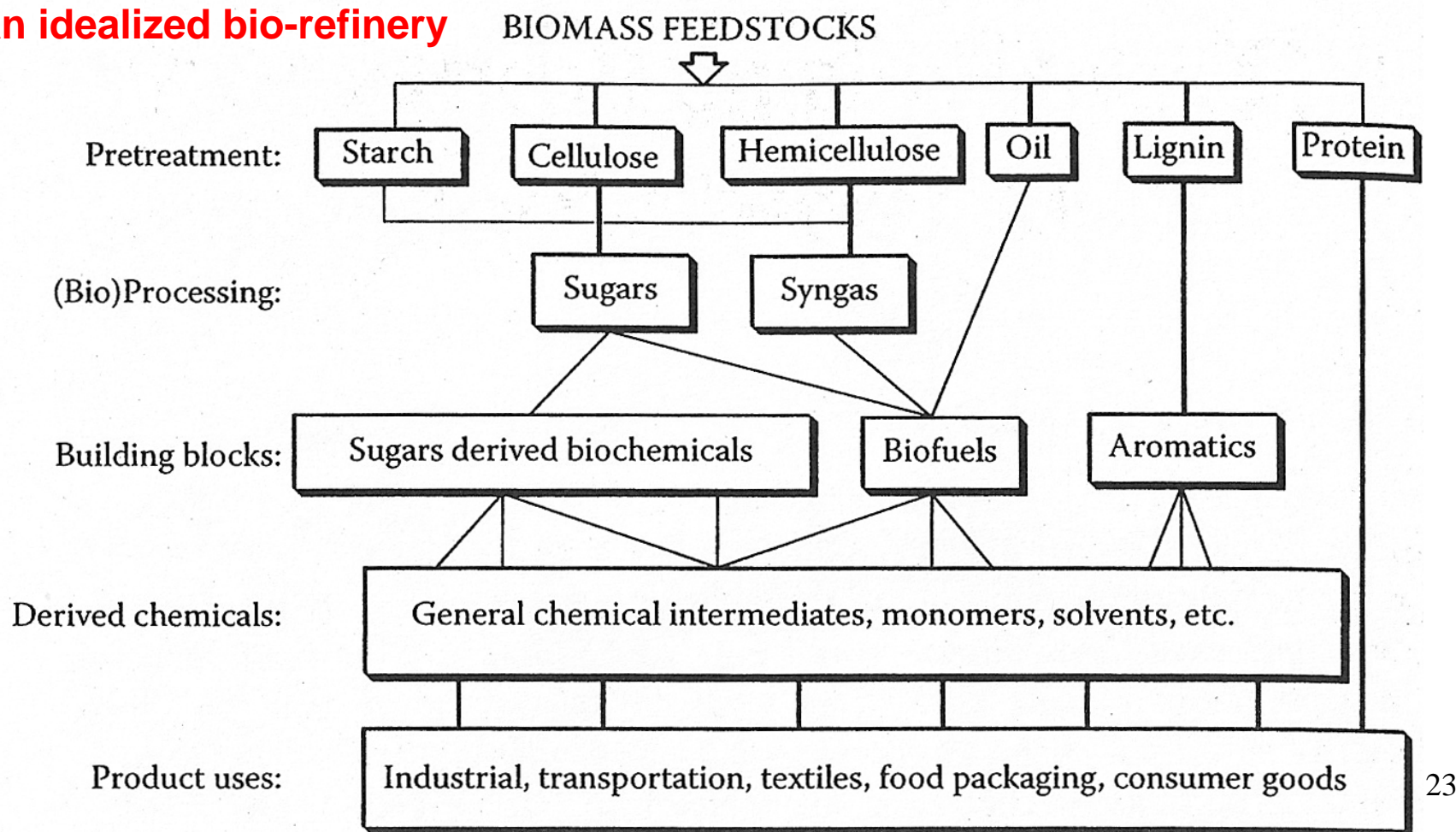
Table 1. Transport and Thermodynamic Properties

organic carbonate	bp [K]	d (293 K) [g/cm ³]	viscosity (298 K) [cP]		
DMC	363 ^b	1.07 ^b	0.590 ^b	Acetone	0.320 cP
DEC	399 ^b	0.98 ^b	0.753 ^c	Water	0.891 cP
EC	521 ^d	1.34 ^{a,d}	2.56 ^{a,d}	1-butanol	2.99 cP
PC	515 ^d	1.20 ^d	2.50 ^d		
BC	524 ^d	1.14 ^d	3.14 ^c		

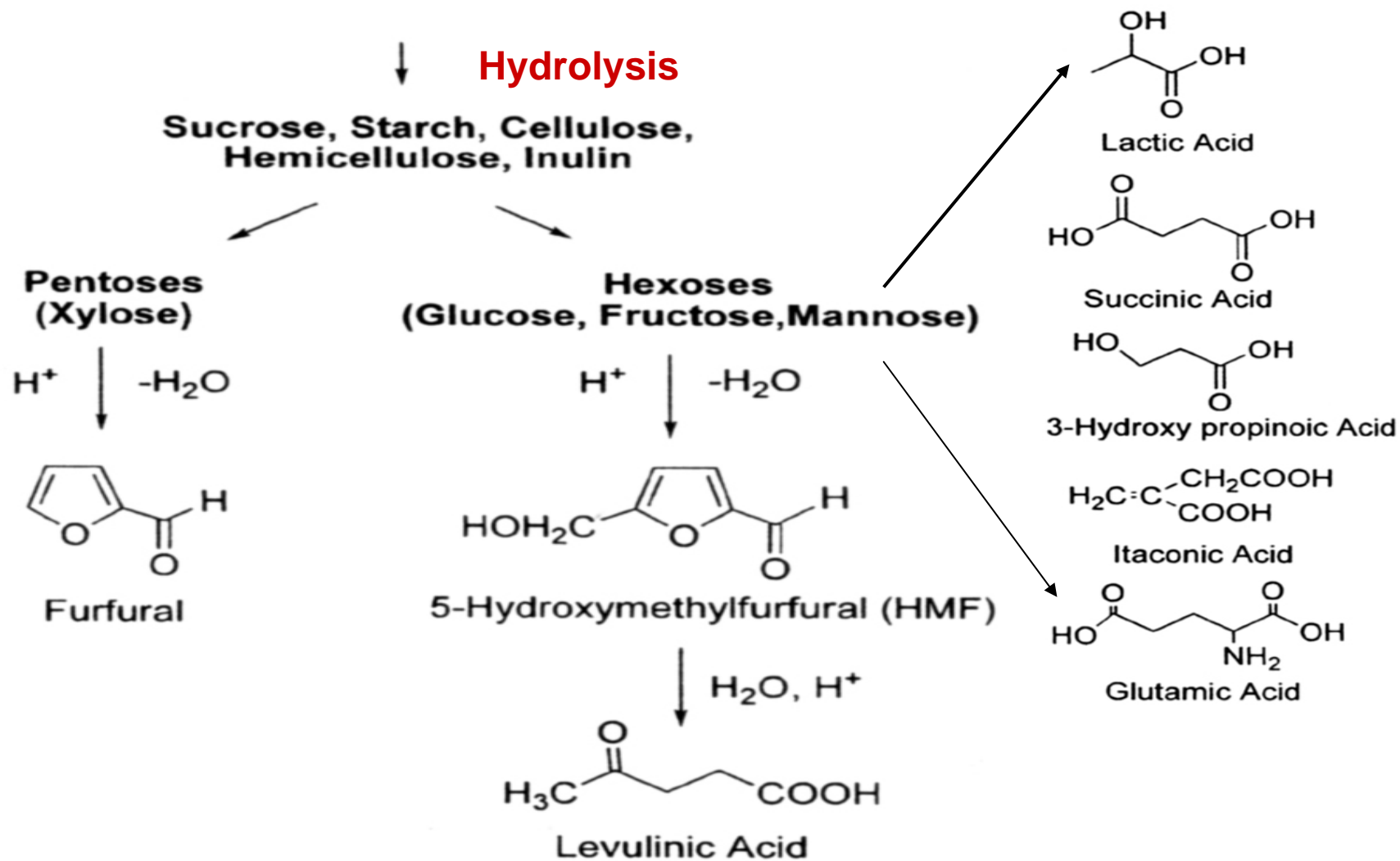


Renewable resources: Carbohydrates (sugar, starch, cellulose, etc.), 75%
 Lignin, 20%
 Fats and oils, proteins, terpenes, etc., 5%

An idealized bio-refinery

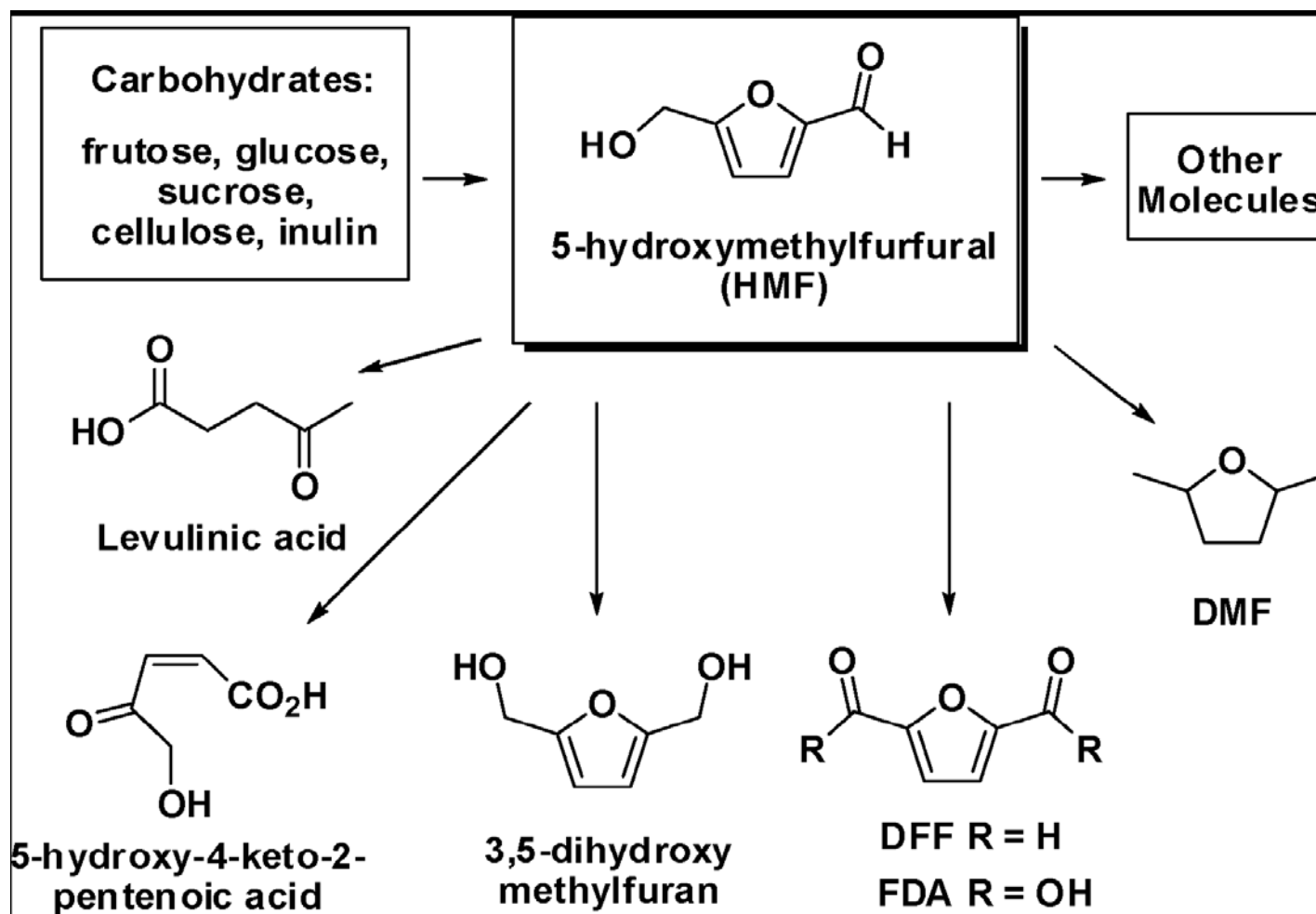


From polysaccharides (vegetal biomass)



5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications

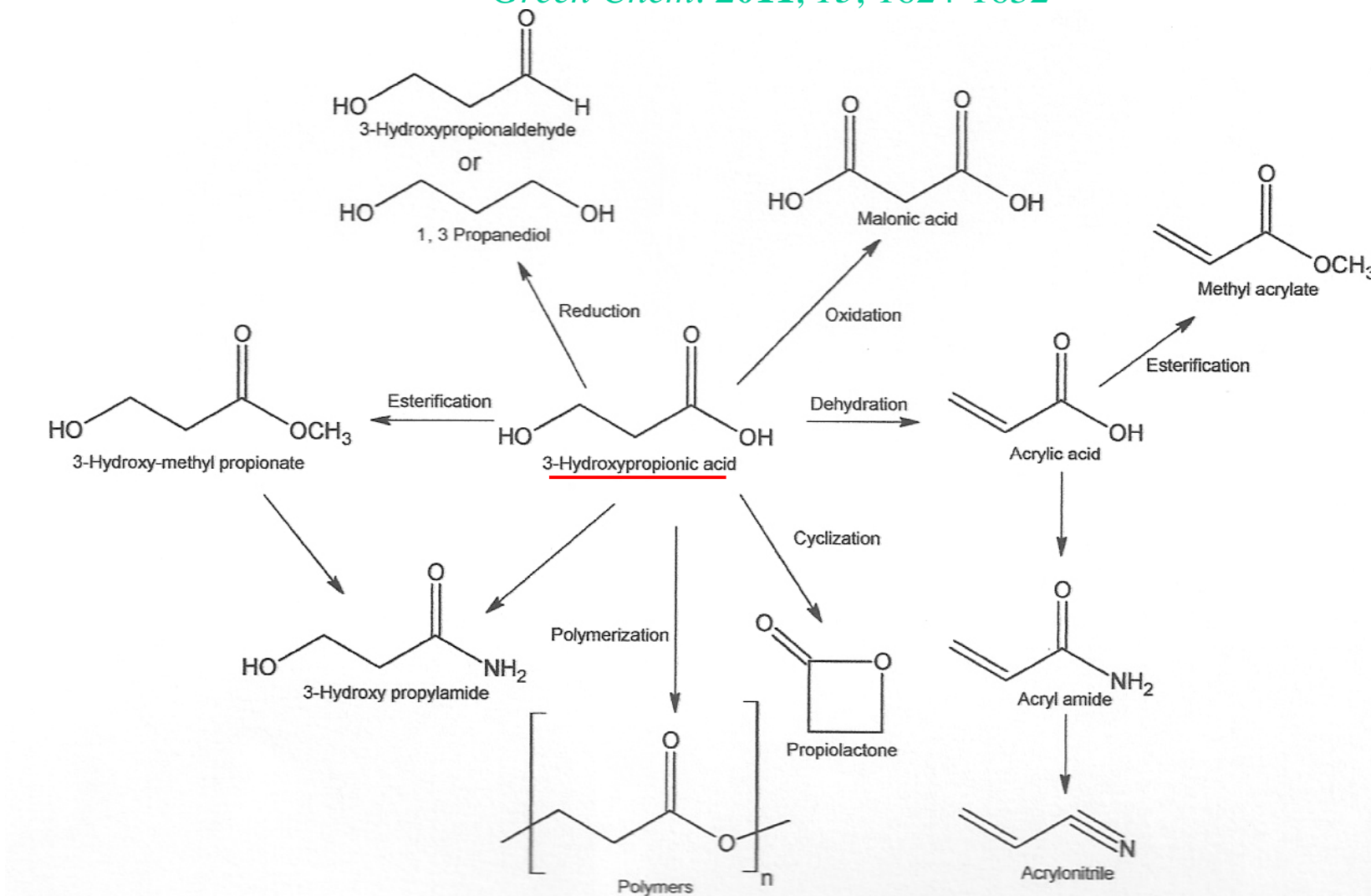
- *Green Chem.*, 2011, **13**, 754–793

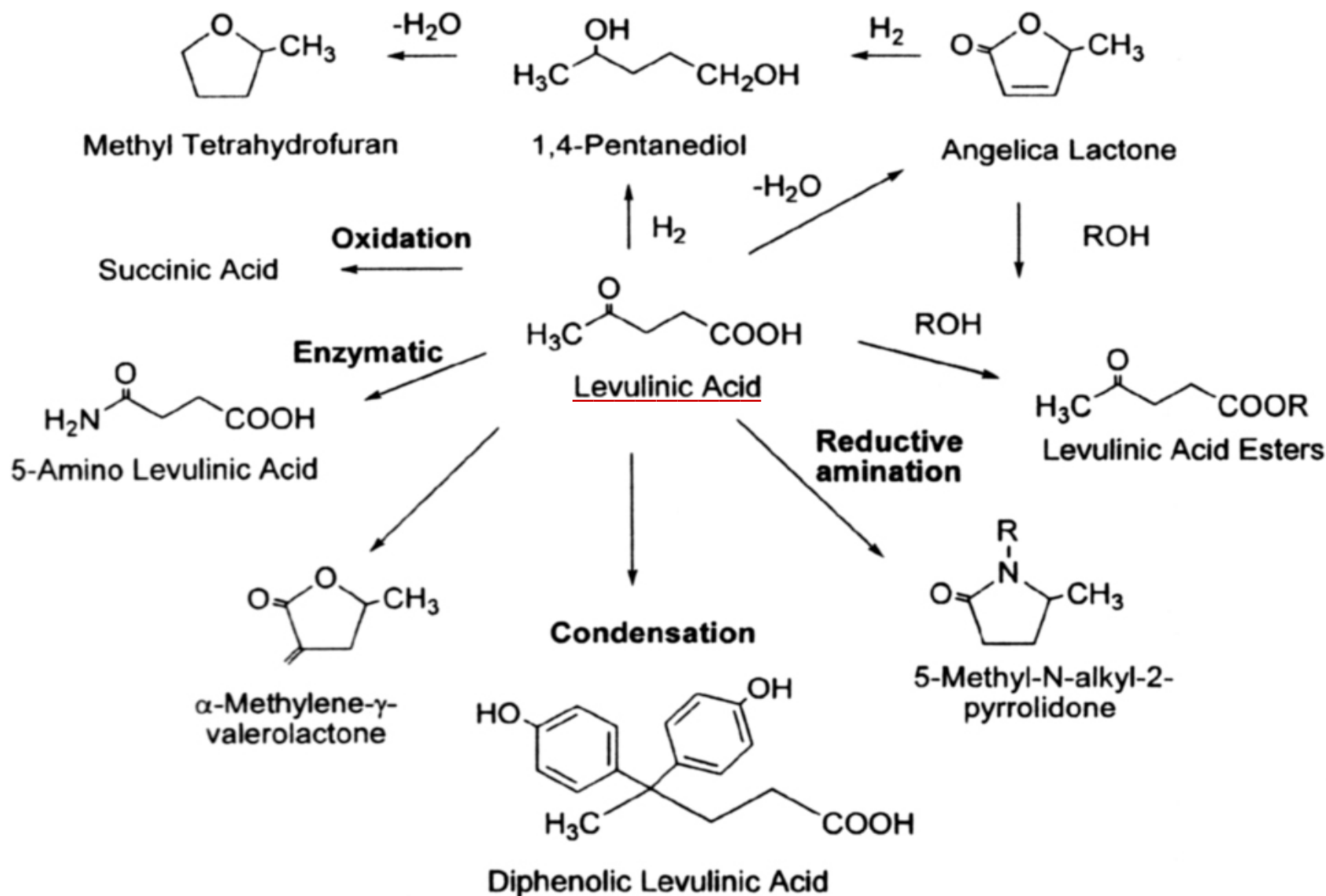


A green approach to chemical building blocks.

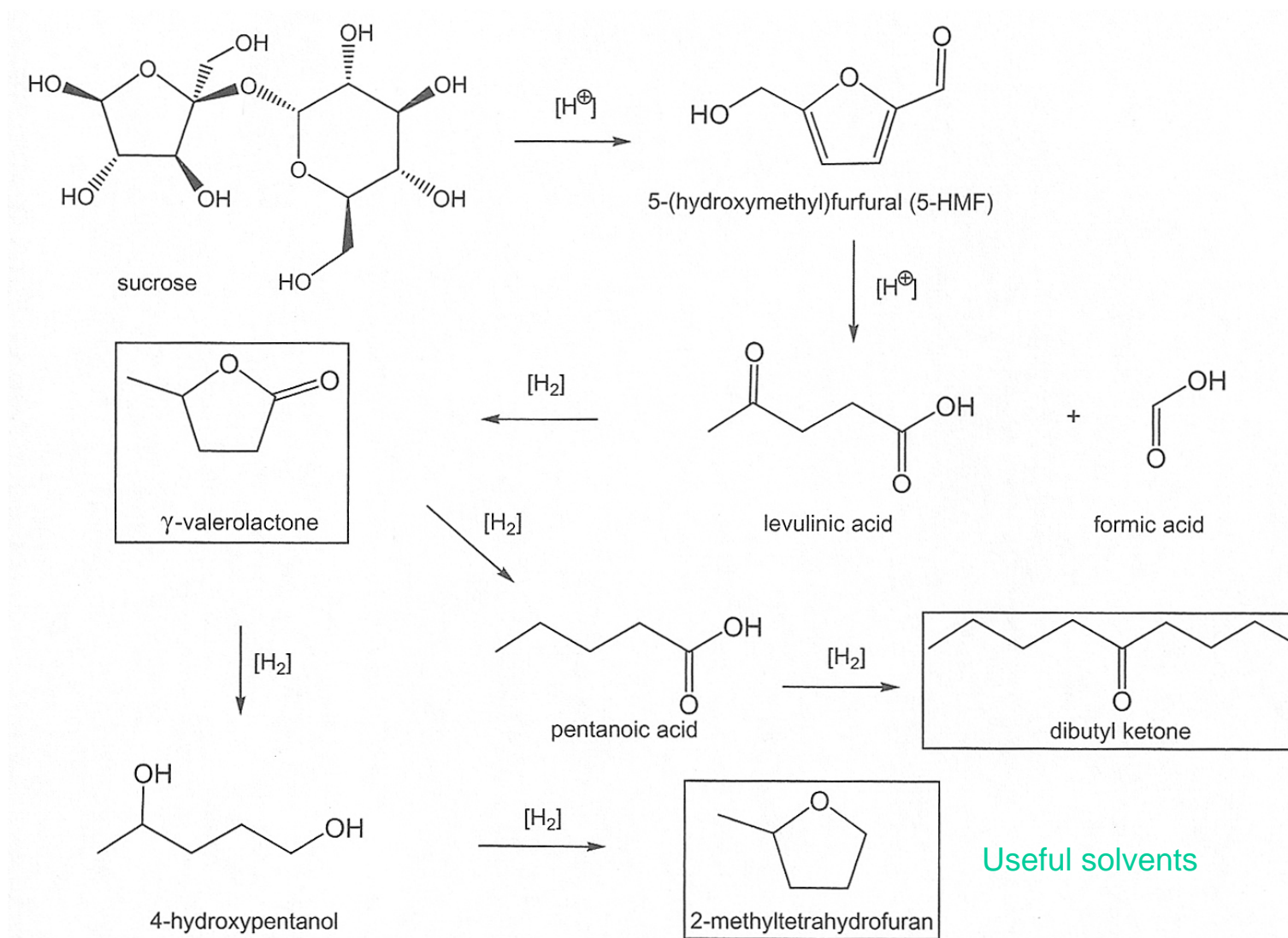
The case of 3-hydroxypropanoic acid

Green Chem. **2011**, *13*, 1624-1632

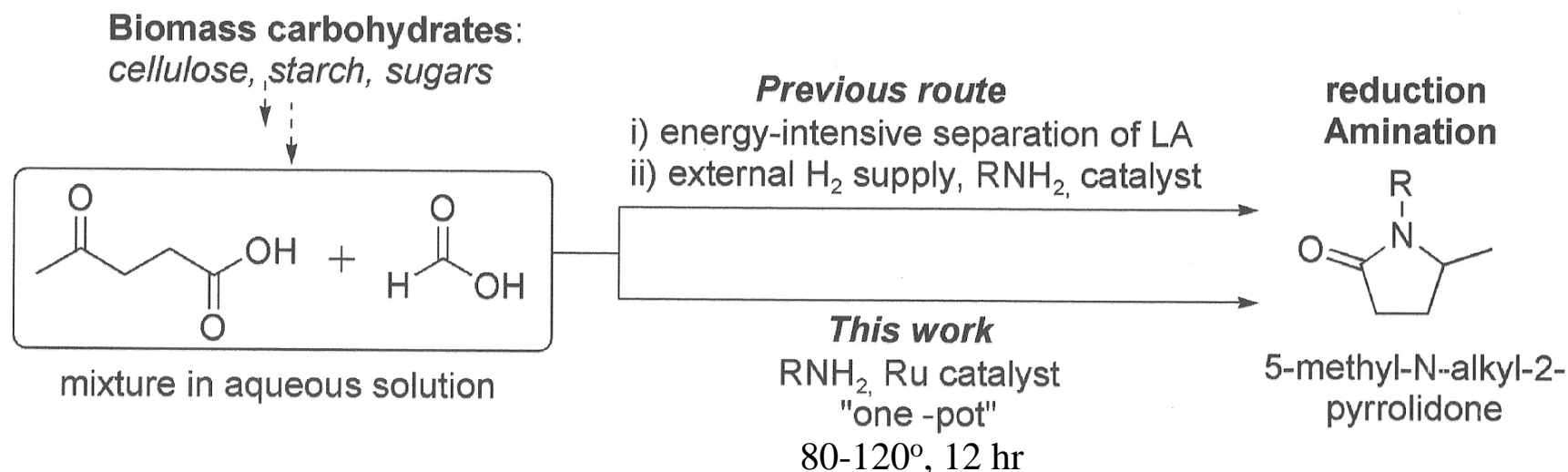




1999 PGCC Award of Small Business — Biofine process to make levulinic acid from paper mill sludge, agricultural residues, waste wood and papers. 27



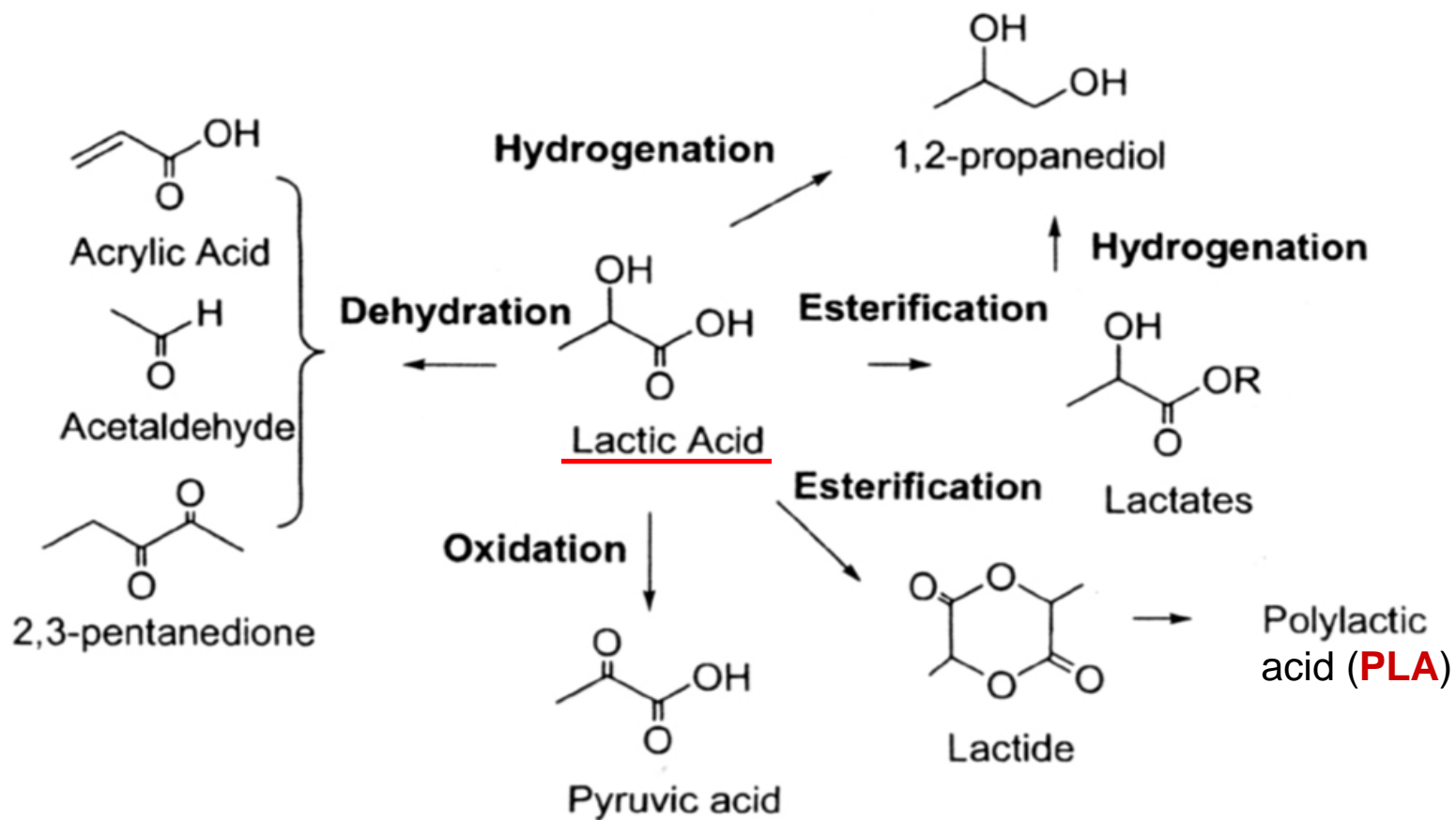
Levulinic acid to pyrrolidines



Alkylamines, Conditions A: LA (1 mmol), FA (1 mmol), H₂O (150 mg), amine (1 mmol), 1 (0.5 mol%) t-Bu₃PHBF₄ (1.5 mol%), 80°C, 12 h.

Arylamines, Conditions B: LA (2 mmol), FA (2 mmol), H₂O (250 mg), amine (1 mmol), 1 (1mol%) t-Bu₃PHBF₄ (3 mol%) 120°C, 12 h.

Lactic acid and ethyl lactate

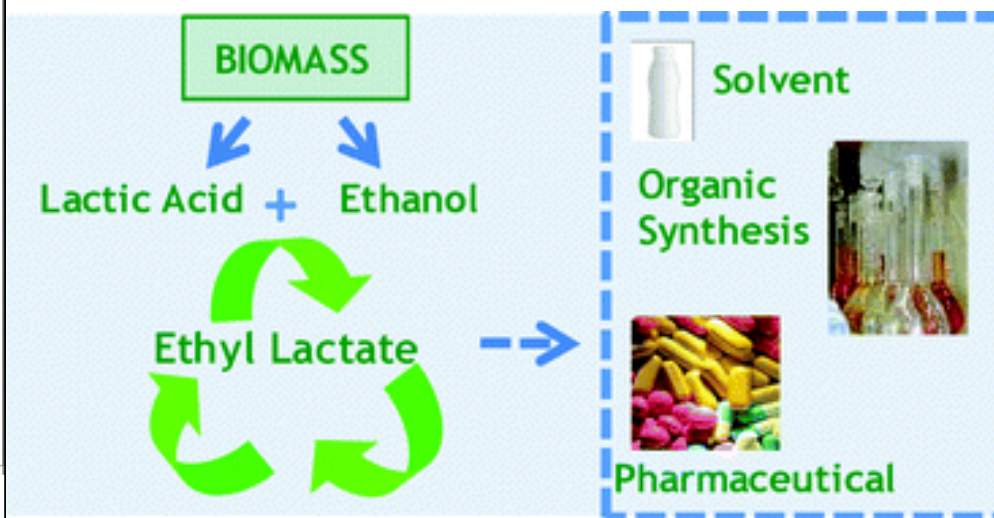
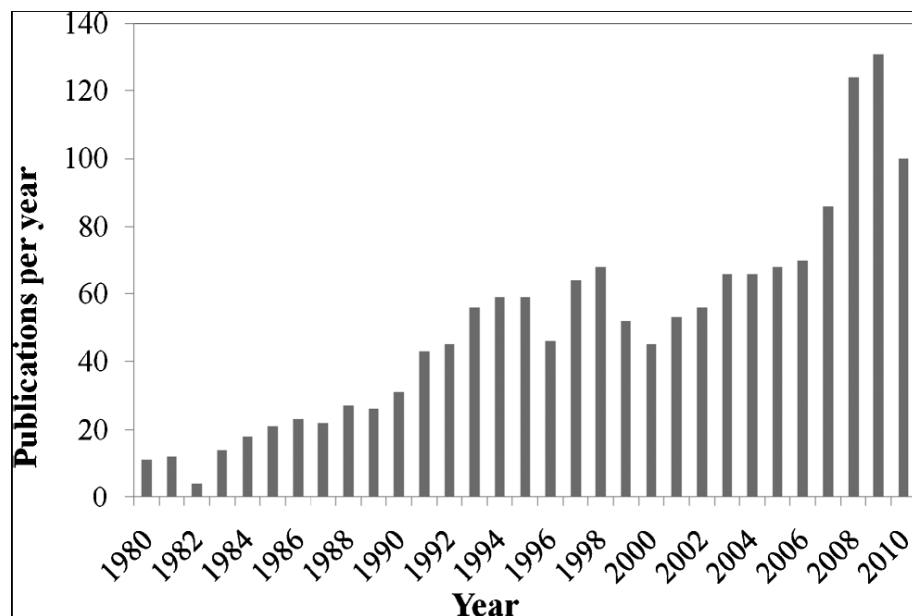


Ethyl lactate is a very useful solvent.

Ethyl lactate as a solvent: Properties, applications and production processes – a review

Green Chem. 2011, 13, 2658-2671

This review summarizes the main properties of ethyl lactate and its applications, as well as its synthesis and production processes, with emphasis on reactive/separation processes.



Data were obtained from ISI Web of Knowledge on 5th of July 2011.

Controlled Ring-Opening Polymerization of *L*-Lactide Triggered by Supramolecular Organocatalytic Systems

(From Chapter 10 of *Renewable and Sustainable Polymers*, ACS, 2011)

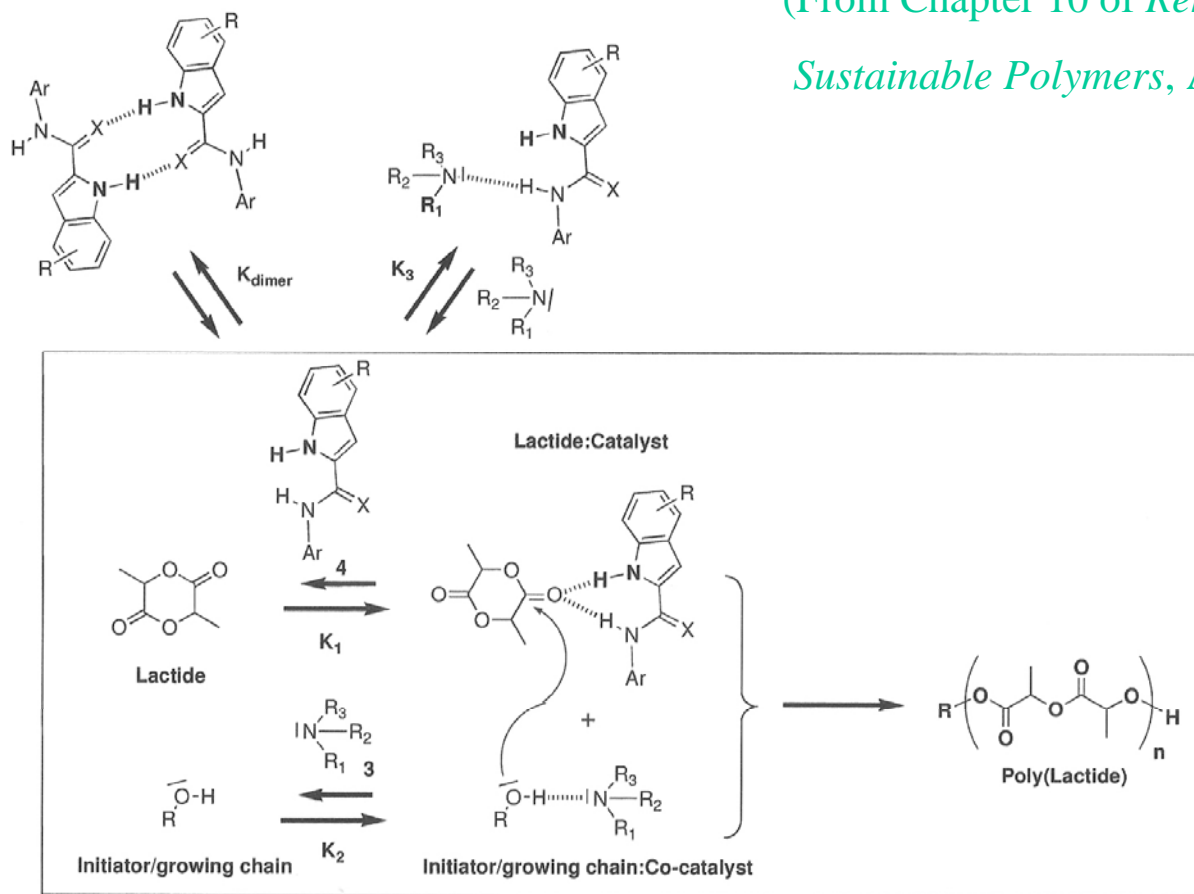
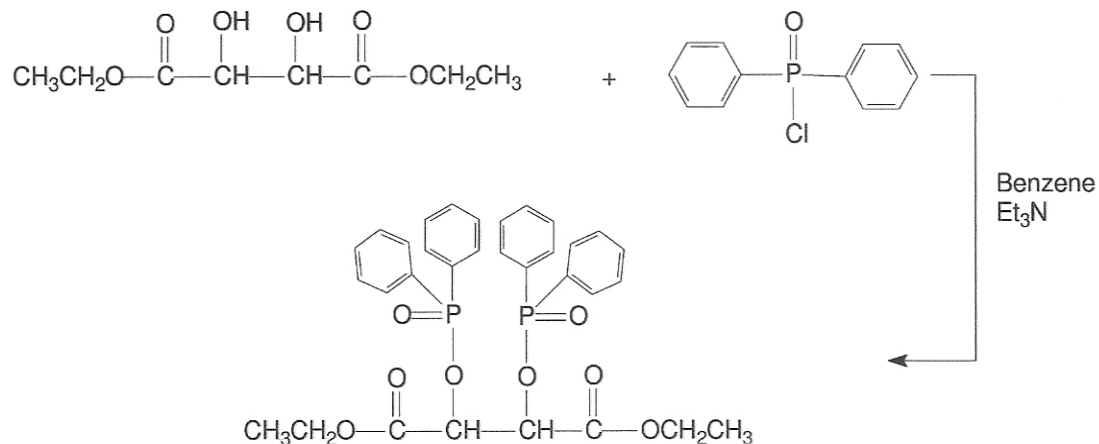
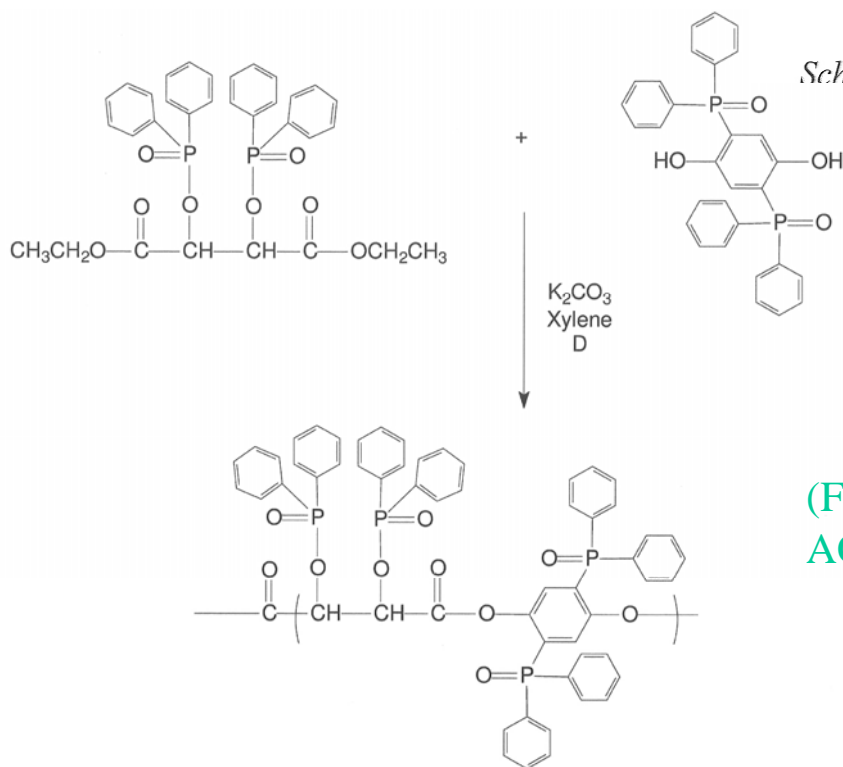


Figure 2. Multiple H-bonding equilibria involving reactants and catalysts **4** + **3** during the Ring Opening Polymerization of lactide.

Polycarbonates as Flame Retardants Based on Tartaric Acid: A potential C4 building block

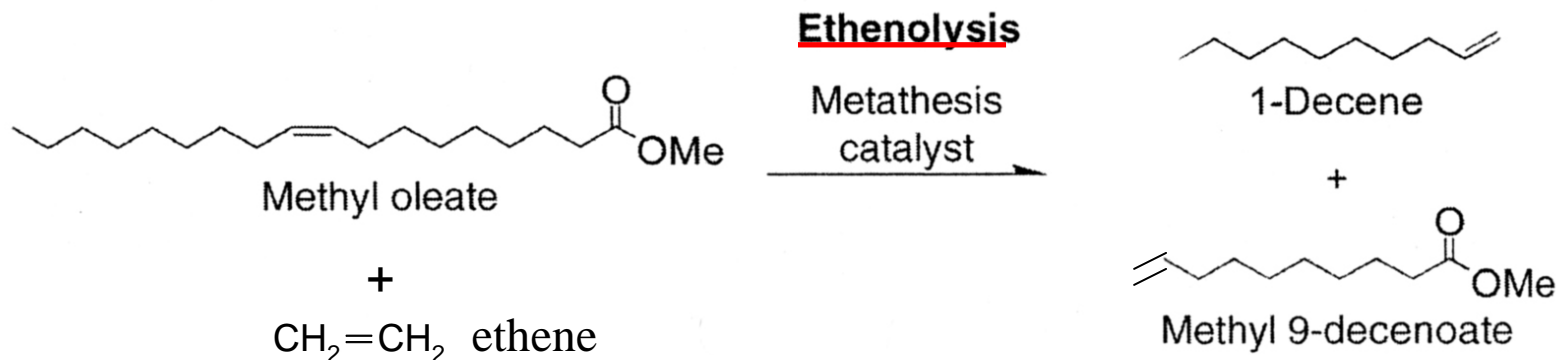
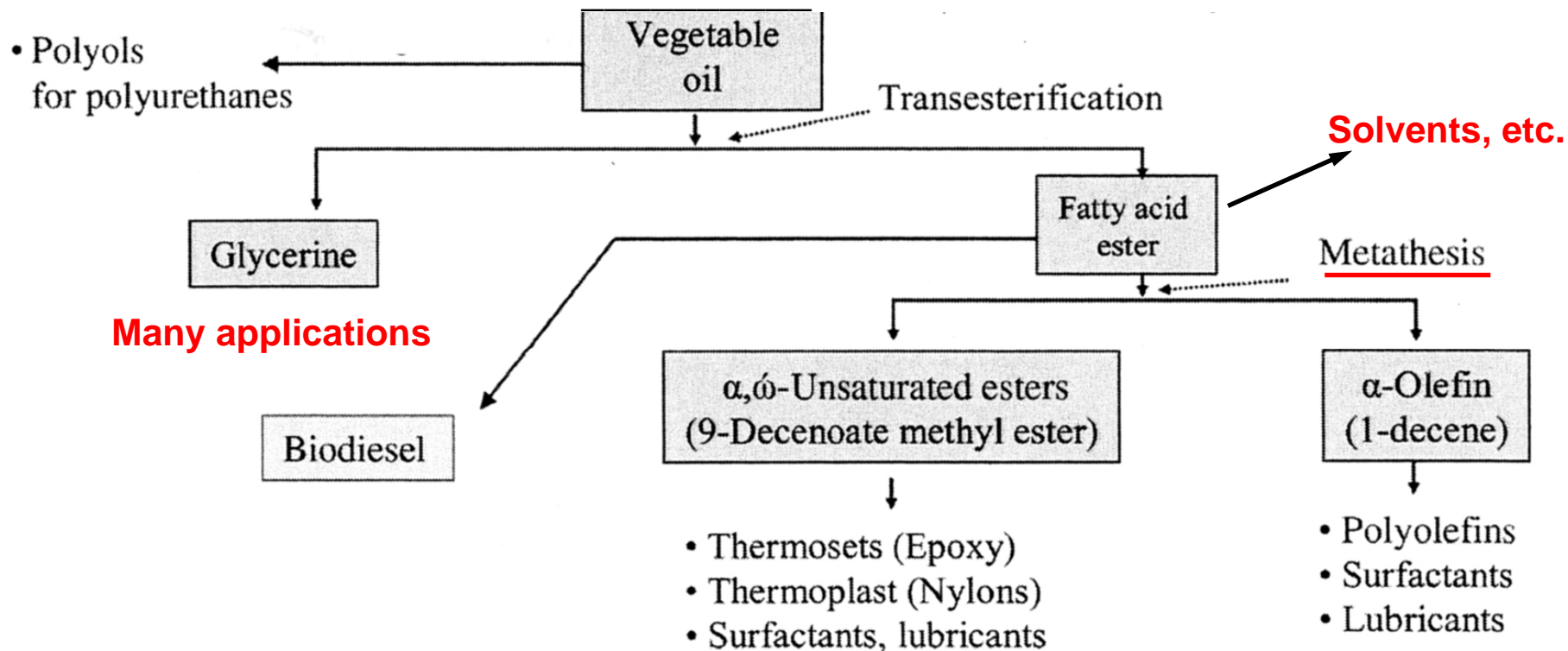


Scheme 1. Synthesis of diethyl 2,3-diphenylphosphinato-1,4-butanedioate



(From Chapter 9 of *Renewable and Sustainable Polymers*, ACS, 2011)

Bio-refinery of vegetable oils



Glycerol

The Future of Glycerol

by Pagliaro, et al., **1st Ed**(144 p), **2008**; **2nd Ed**(190 p), **2010**, RSC

Chapter 1 Glycerol: Properties and Production

Chapter 2 Reforming

Chapter 3 Selective Reduction

Chapter 4 Chlorination

Chapter 5 Dehydration

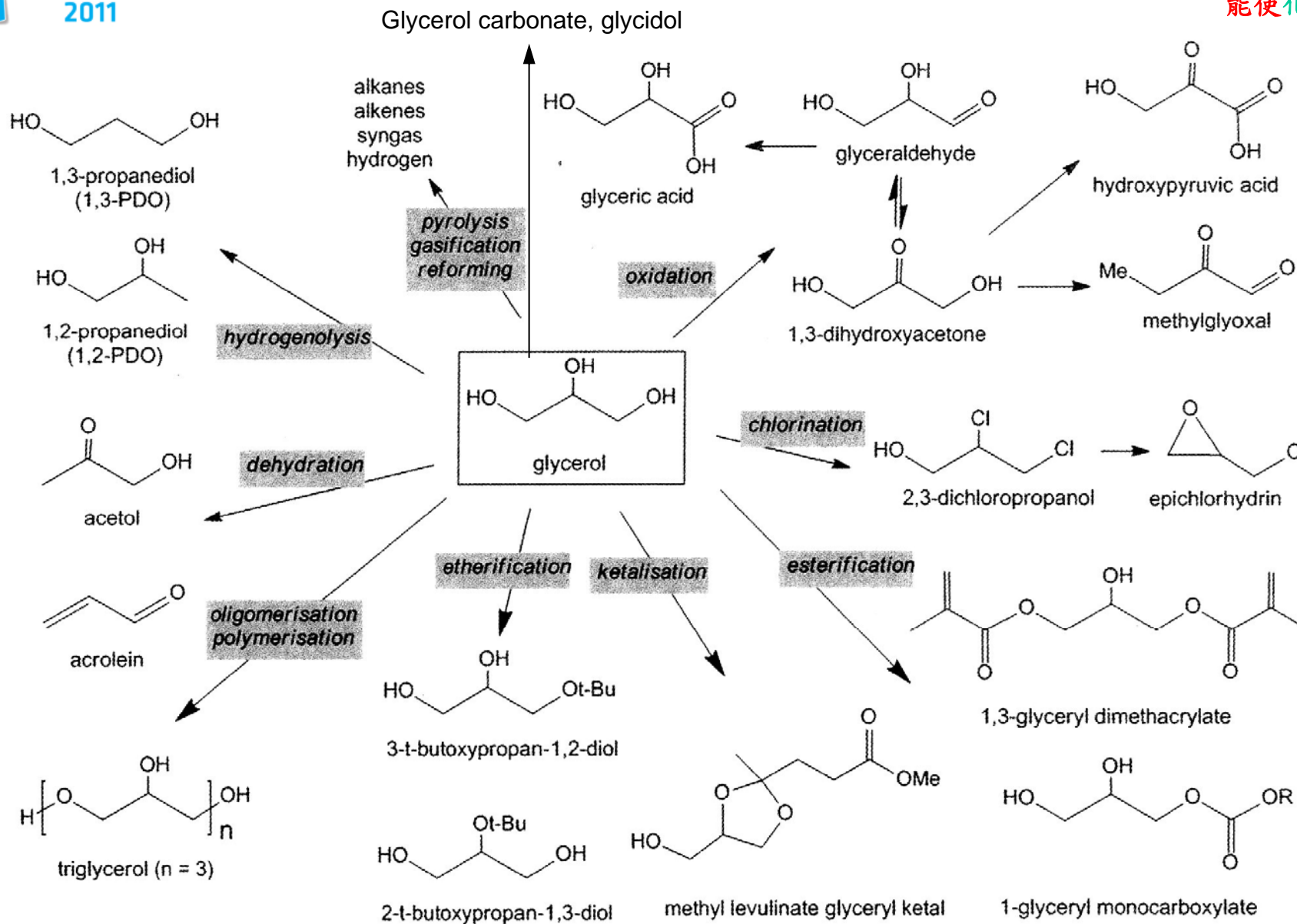
Chapter 6 Etherification

Chapter 7 Esterification

Chapter 8 Selective Oxidation

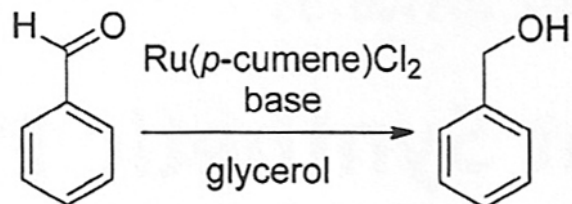
Chapter 9 Bioglycerol in the Construction Industry

Chapter 10 Sustainability of Bioglycerol



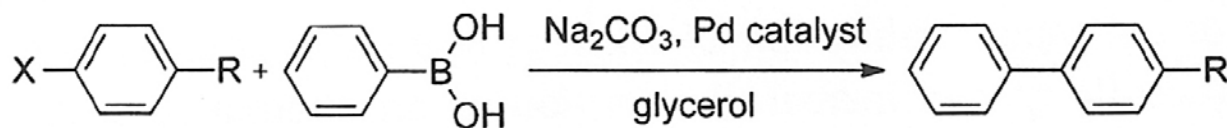
Synthesis in glycerol

(*ChemSusChem* 2011, 4, 1130-1134)



With Ultrasound/Microwave

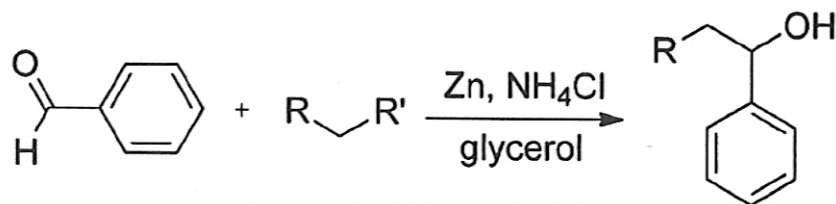
Benzaldehyde transfer hydrogenation reaction.



X= I, Br, Cl
 R= OCH₃, C(O)CH₃

With Ultrasound/Microwave

Suzuki cross-coupling reaction in glycerol.



R = C≡CH, HC=CH₂, CH₂CH₂C≡CH
 R'= Br, Cl

With Ultrasound

Barbier reaction in glycerol.

Table 1. Glycerol Feedstock Announcements

<i>Company</i>	<i>Product</i>	<i>Volume</i>	<i>Location</i>
ADM	Propylene Glycol	100,000 mt	Decatur, IL
Cargill/Ashland	Propylene Glycol	65,000 mt	Europe
Dow	Propylene Glycol	NA	Texas
Dow	Epichlorohydrin	150,000 mt	China
Huntsman	Glycerol Carbonate	NA	Texas
Solvay/Vinythai	Epichlorohydrin	100,000 mt	Thailand
Arkema	Acrylic Acid	NA	France
Synergy	Propylene Glycol	NA	NA
Linde	Hydrogen Reformation	Demonstration Plant	Germany

(From Chapter 6 of *Renewable and Sustainable Polymers*, ACS, 2011)

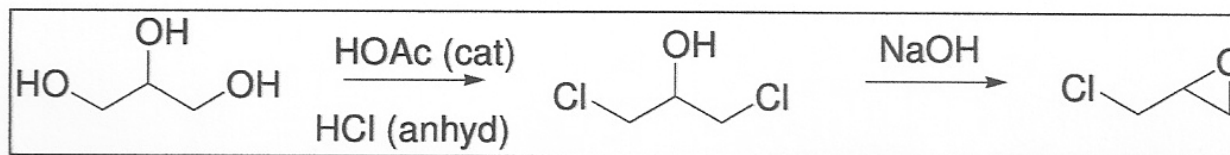
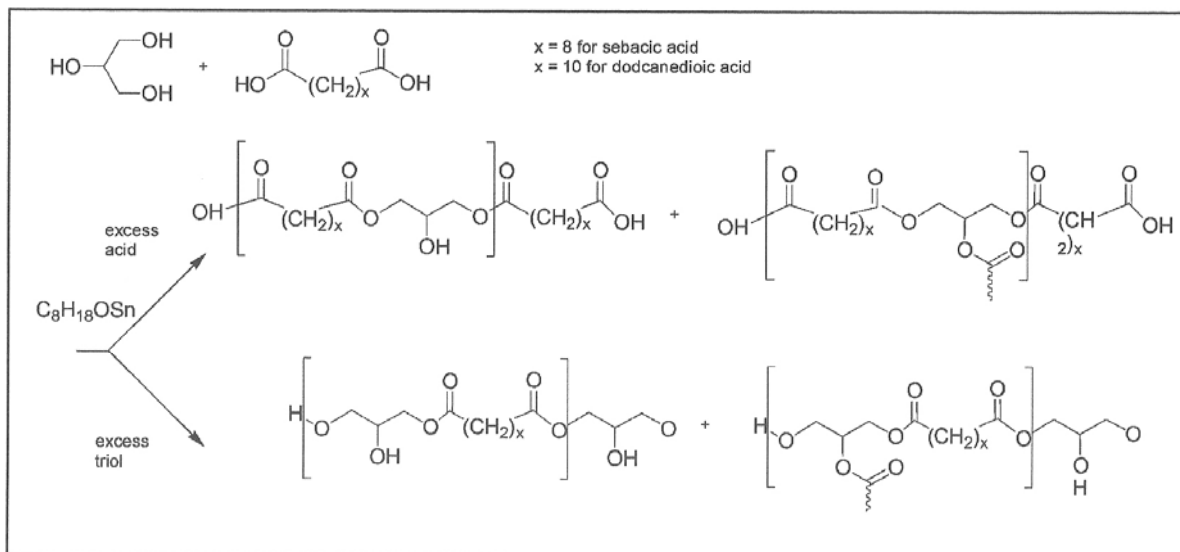


Figure 3. The Conversion of Glycerol to Epichlorohydrin.



Scheme 1. Step-Growth Polymerization of Glycerol with Either Sebacic Acid or Dodecanedioic Acid

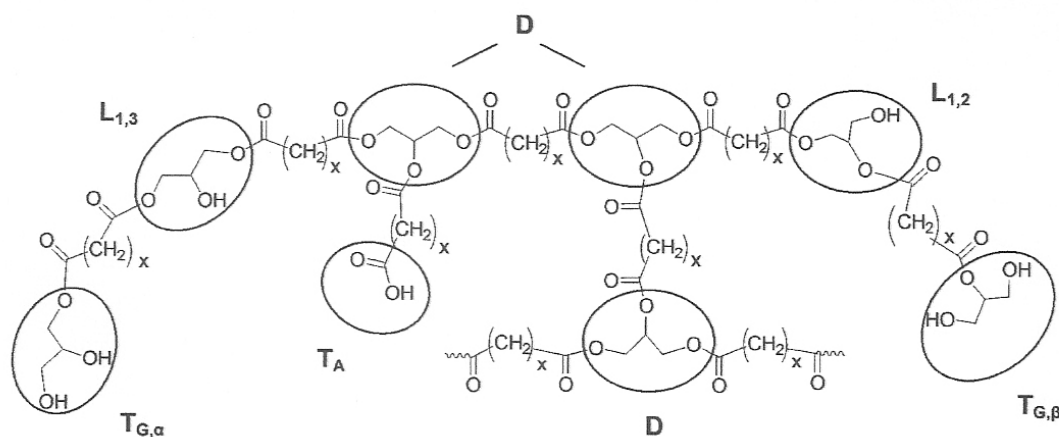


Figure 5. Types of structural units that can occur in copolyesters formed from glycerol with diacids ($x = 8$ for sebacic acid and $x = 10$ for dodecanedioic acid).

(From Chapter 2 of *Renewable and Sustainable Polymers*, ACS, 2011)

*Sustainable chemistry makes
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多謝聽講 歡迎討論

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