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
(ktliu@ntu.edu.tw)

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, O_2(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.

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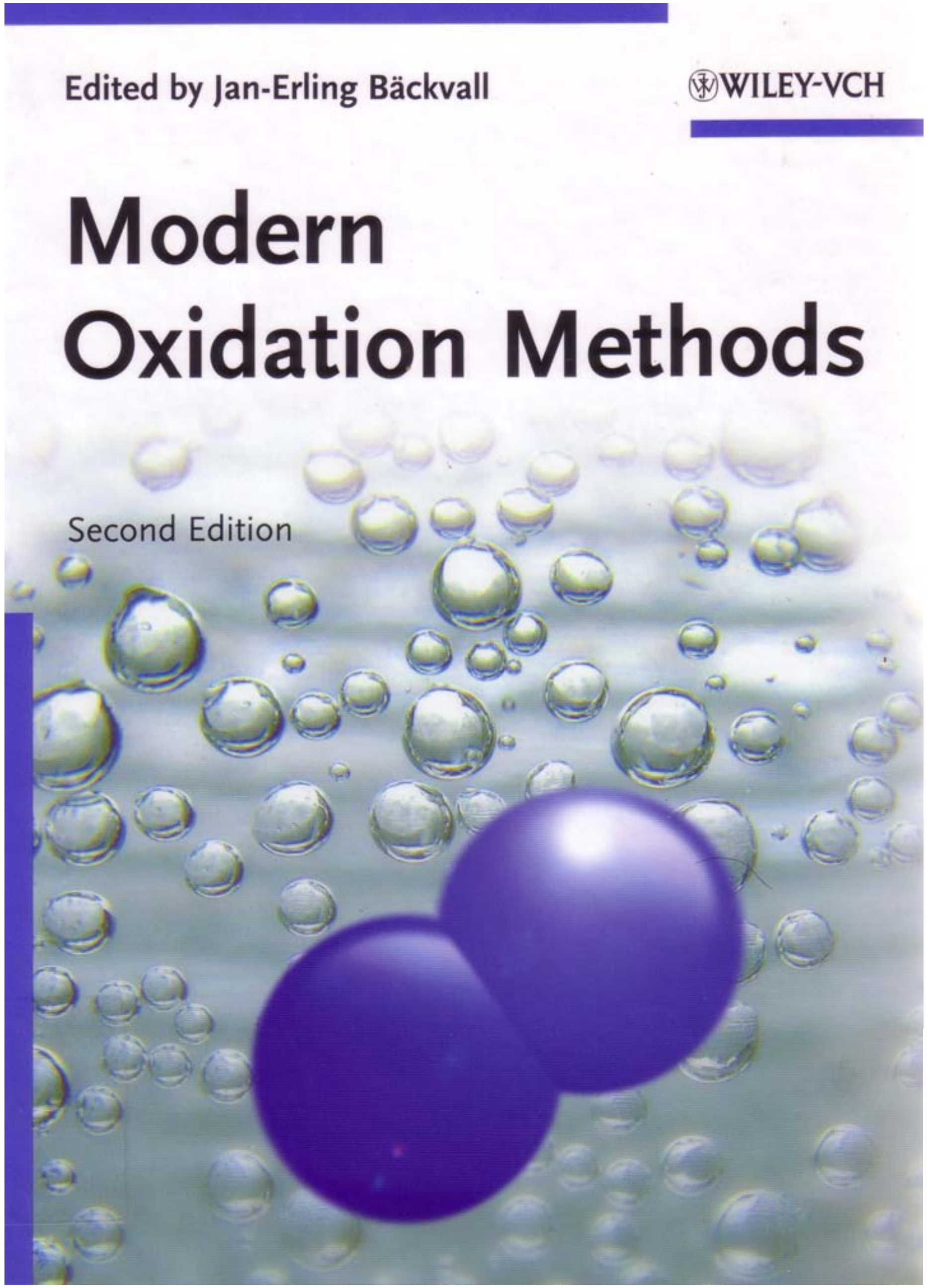
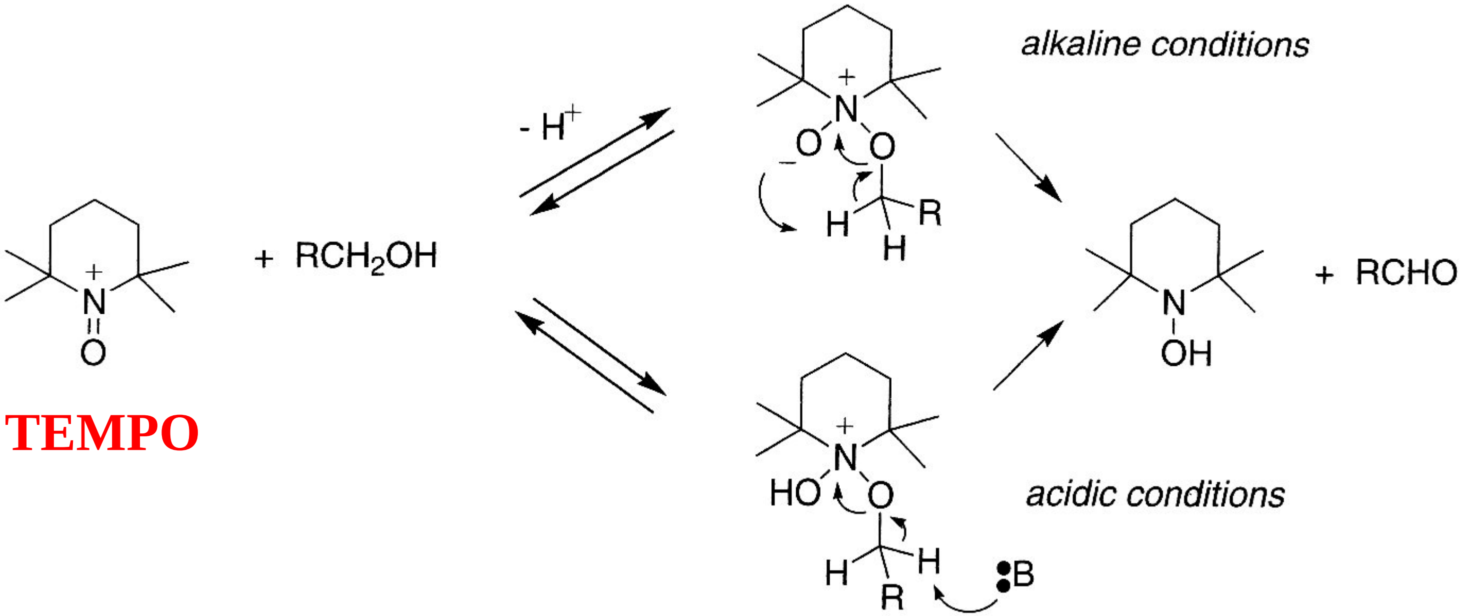
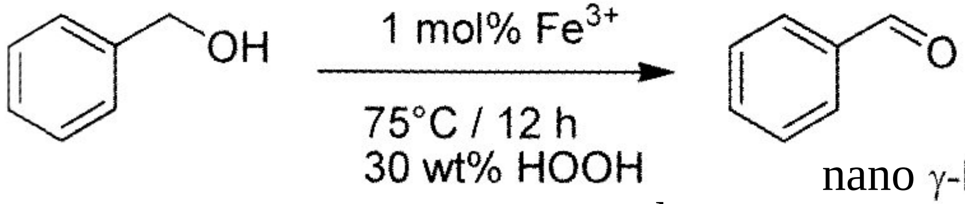
A 2010 reference book (1st Ed, 2004)



The use of TEMPO



TEMPO



	TON	Selectivity
nano γ-Fe_2O_3	32	97%
homogeneous $Fe(NO_3)_3$	25	35%

…… (with 226 references)

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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 CO_2 (50-60 bar, rt); SC CO_2(＞74 bar, ＞31℃)**]

易除去或回收再用

故可用為溶劑及反應試劑

Recent literatures

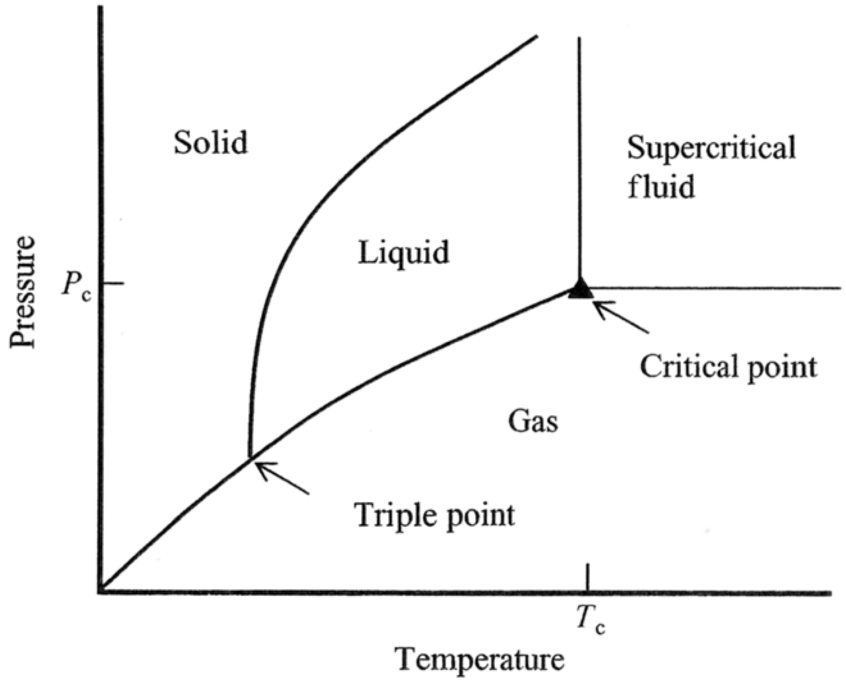
Transition-metal-catalyzed C-C bond formation through the fixation of CO_2
Chem. Soc. Rev. **2011**, *40*, 2435-2452

Use of CO_2 in chemical syntheses via lactone intermediate *Green Chem*. **2011**, *13*, 25-39

Adaptive Process Optimization for Continuous Methylation of Alcohols in SC CO_2, *Org. Proc. Res. Dev.* **2011**, *15*, 932-938

Ionic Liquids and Dense CO_2: A Beneficial Biphasic System for Catalysis, *Chem. Rev*. **2011**, *111*, 322-363.

Supercritical fluids and critical points



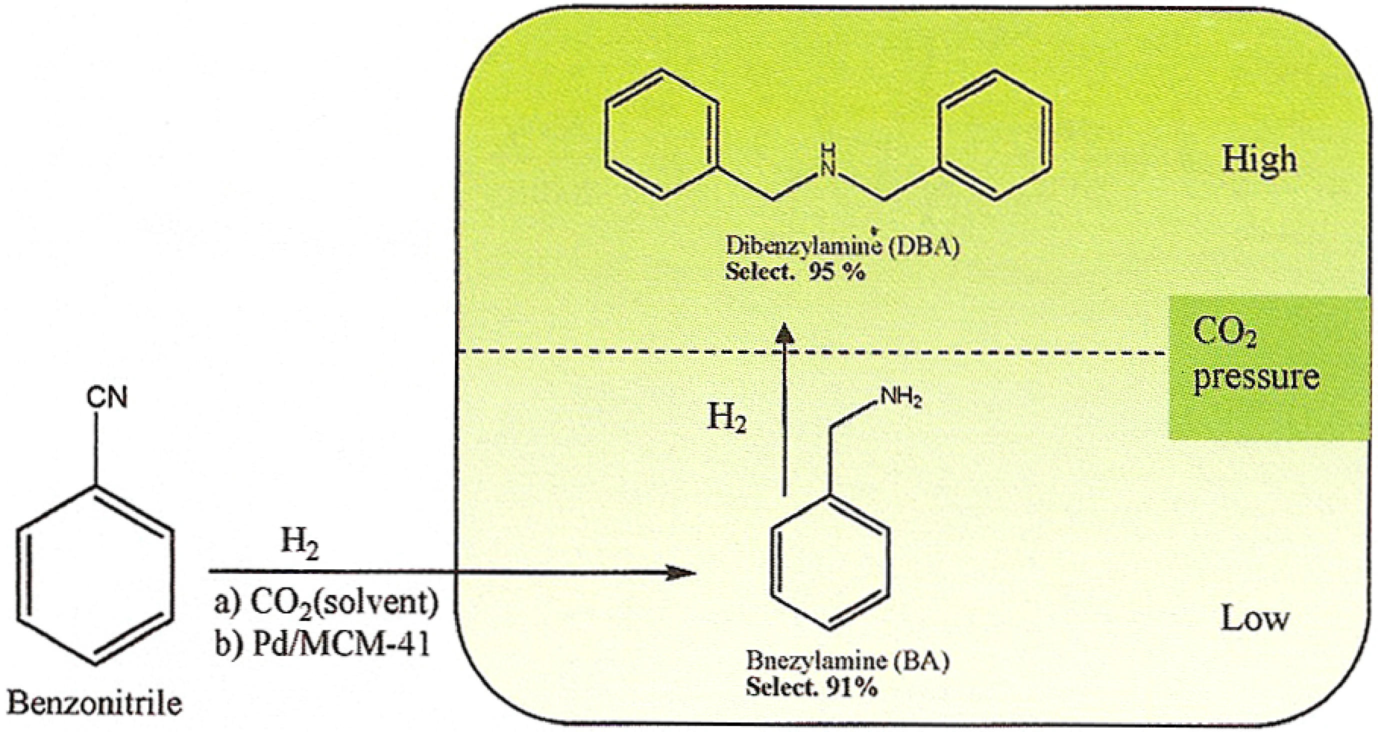
Material	T_c *(°C)*	P_c *(bar)*
Ammonia	132.4	113.2
Carbon dioxide	31.1	73.8
Ethane	32.2	48.7
Ethene	9.2	50.4
Fluoroform	25.9	48.2
Propane	96.7	42.5
Water	374.2	220.5

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

Hydrogenation of nitrile in $scCO_2$: a tunable approach to amine selectivity

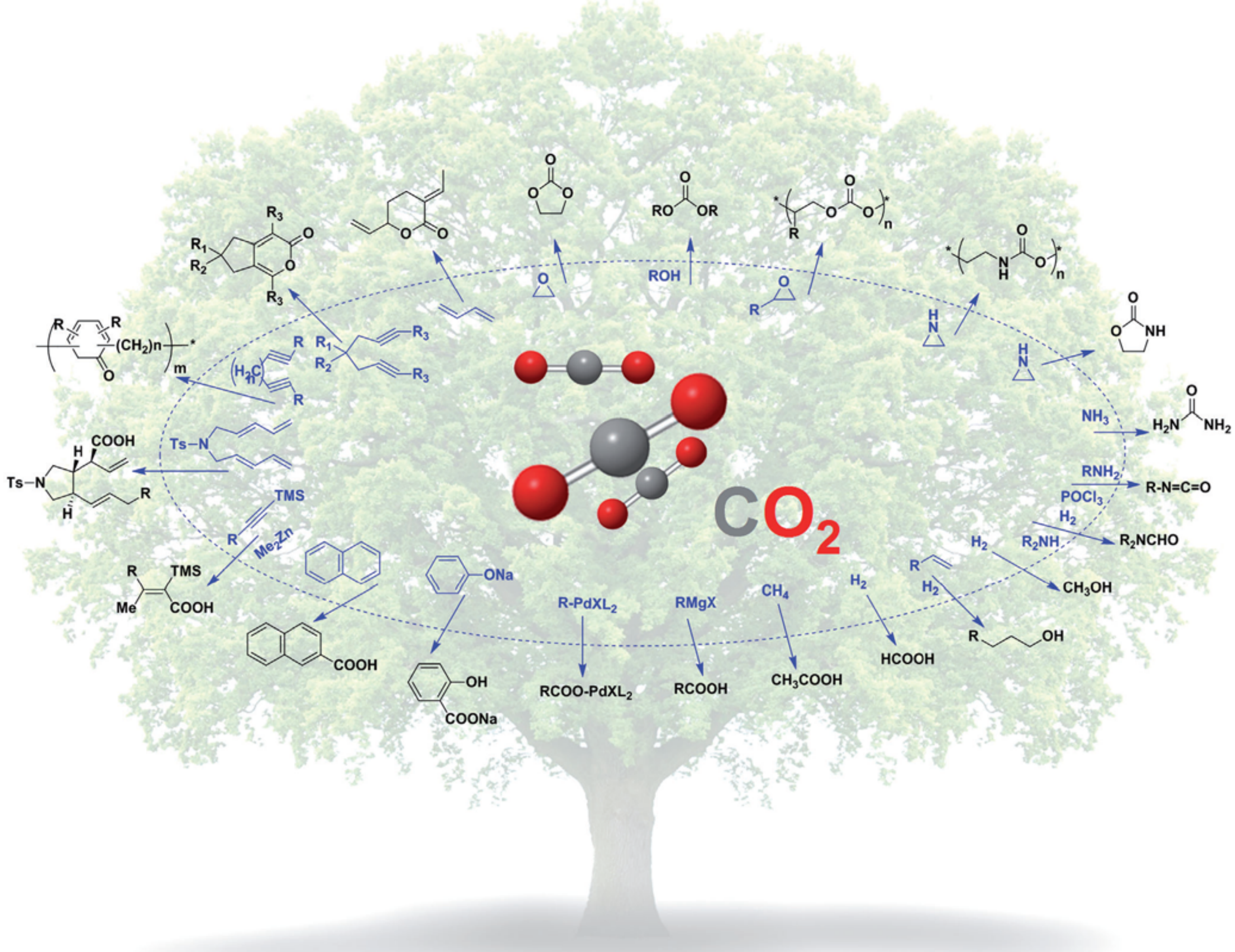
Green Chem. **2010**, *12*, 87-93

By tuning the CO_2 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

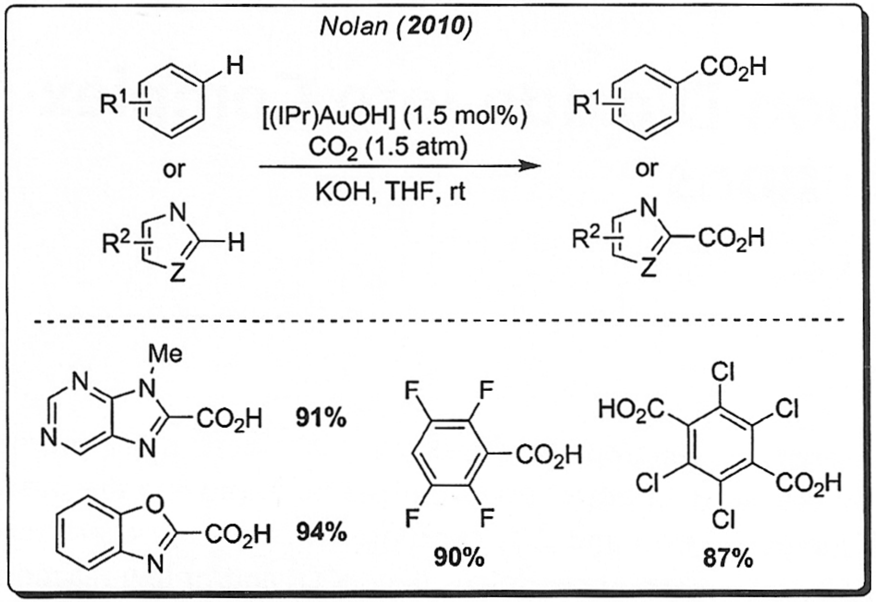
ChemSusChem **2011**. *4*. 1216-1240

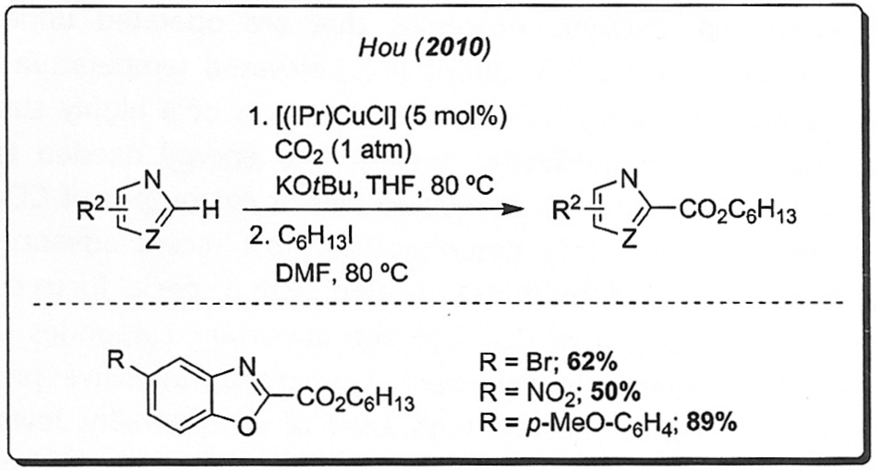


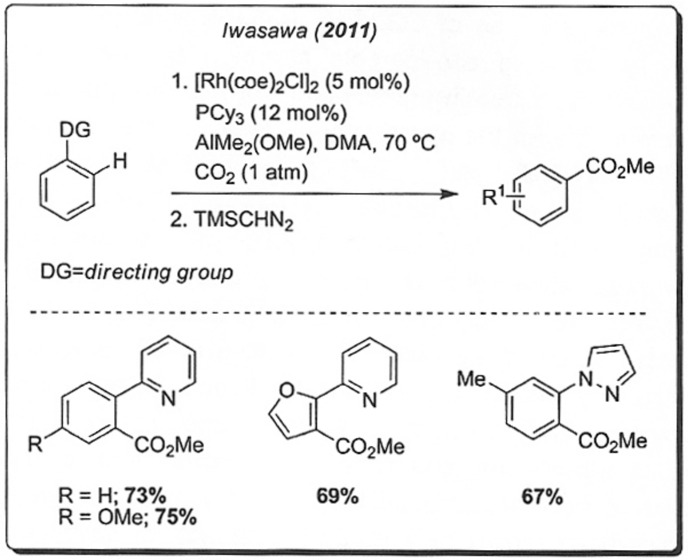
See also: Aresta, Ed., Carbon Dioxide as Chemical Feedstock, **2010**, Wiley-VCH

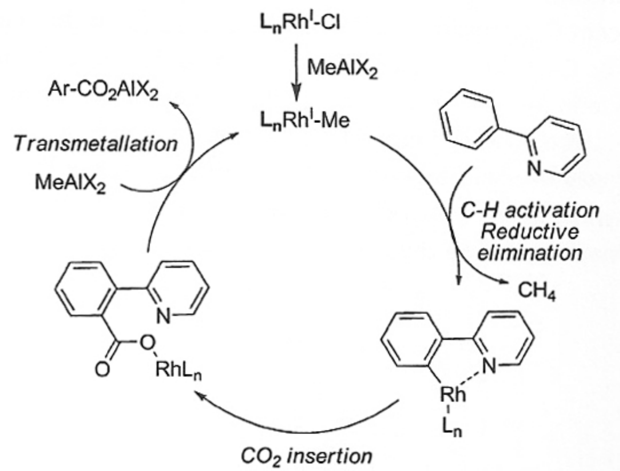
Fixation of CO_2 into Complex Organic Matter under Mild Conditions

ChemSusChem **2011**, *4*, 1259-1263

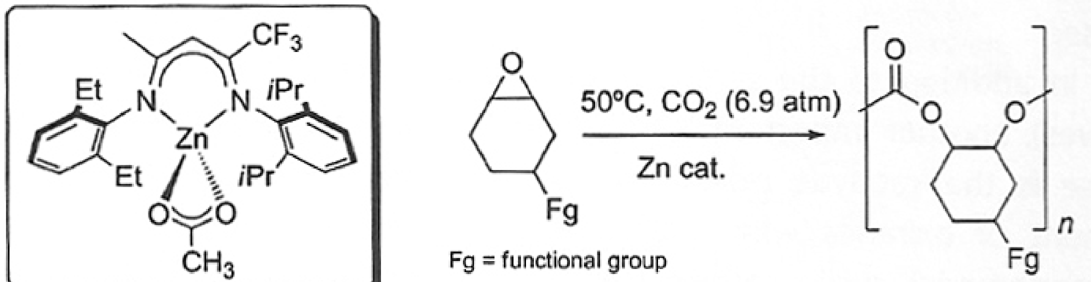






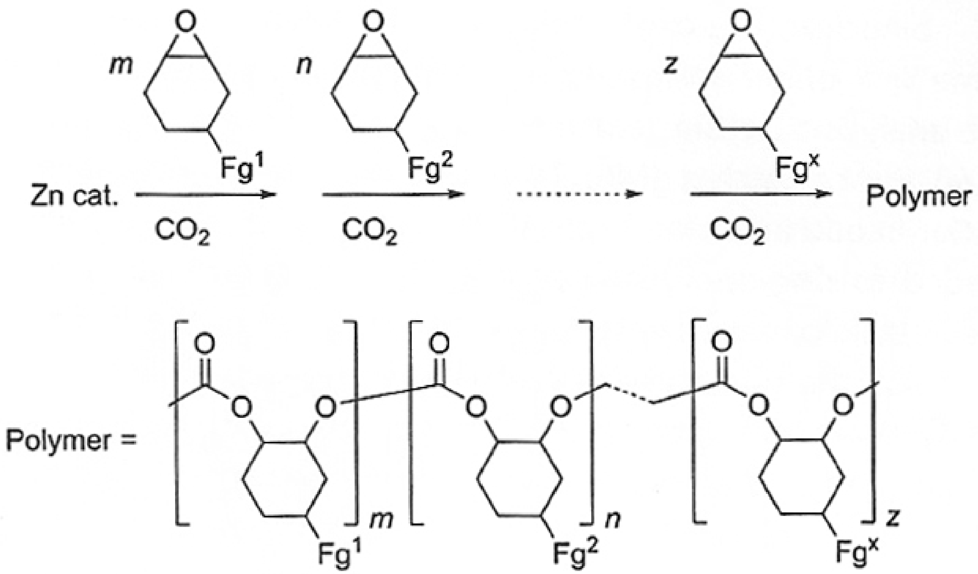


Coates (**2011**)



Yields: 82-99%

Multiblock CHO copolymers:



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

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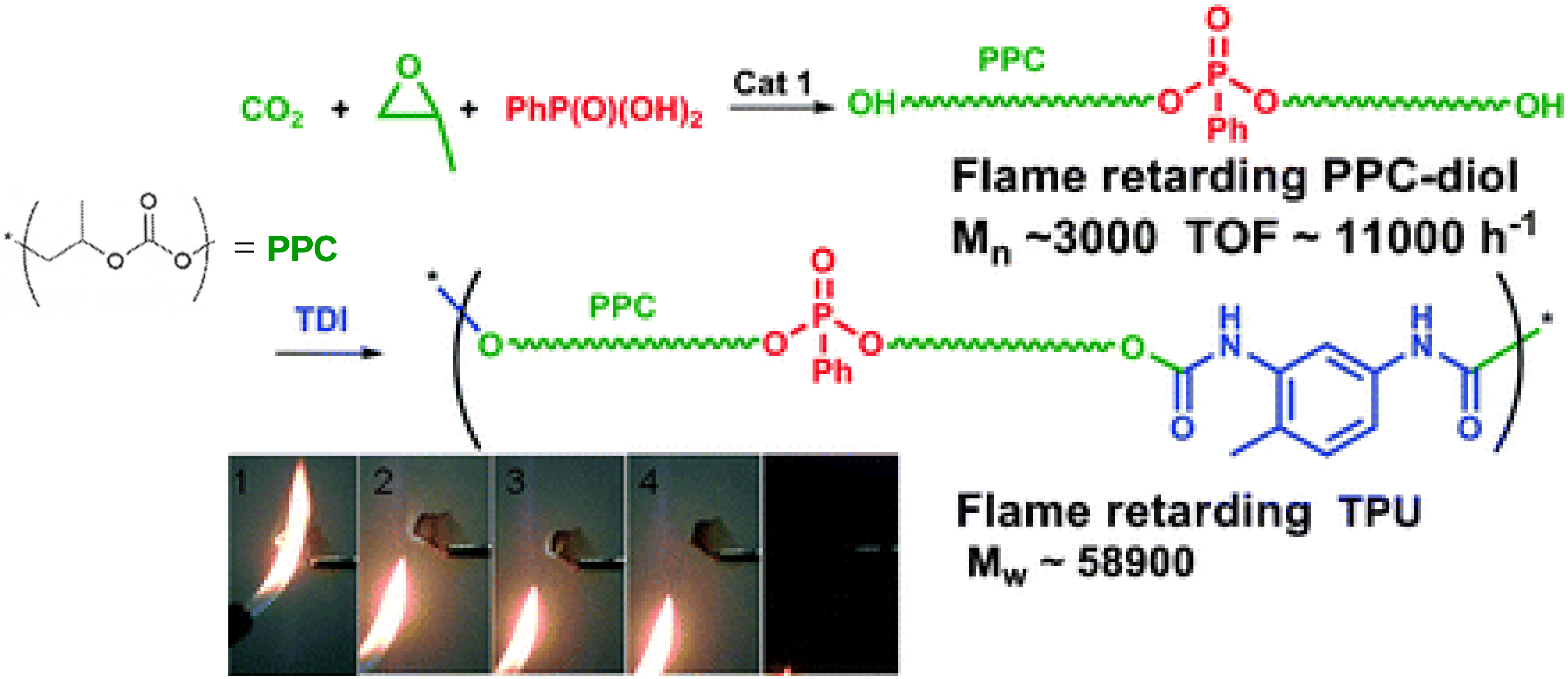
Preparation of flame retarding polymers was demonstrated by using immortal CO_2/propylene oxide copolymerization in the presence of phosphorous-containing chain transfer agents.



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

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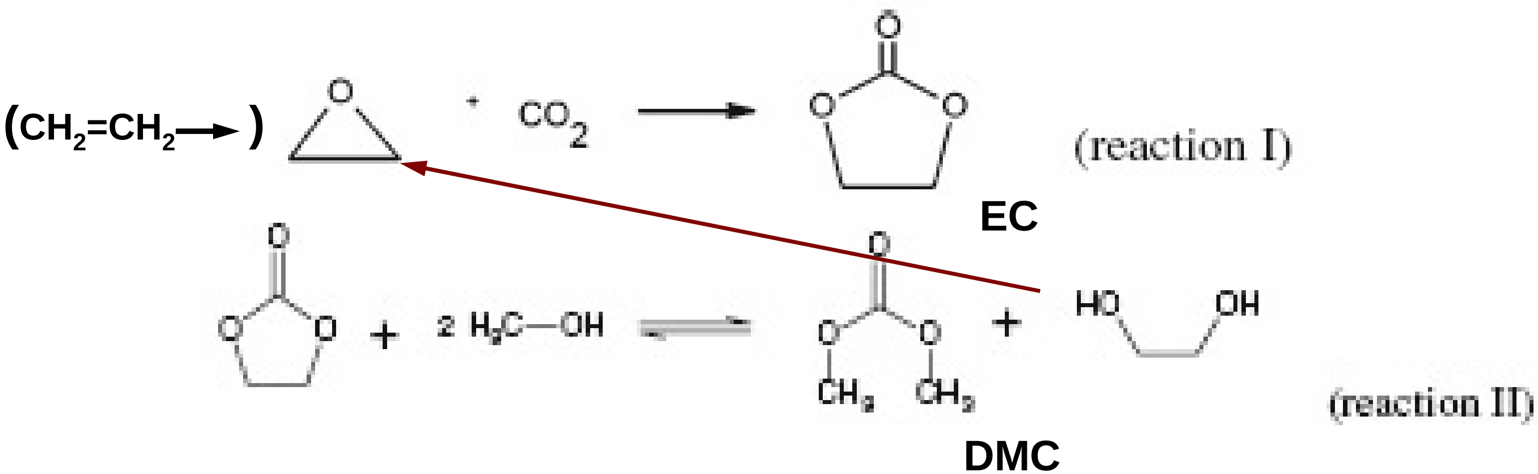
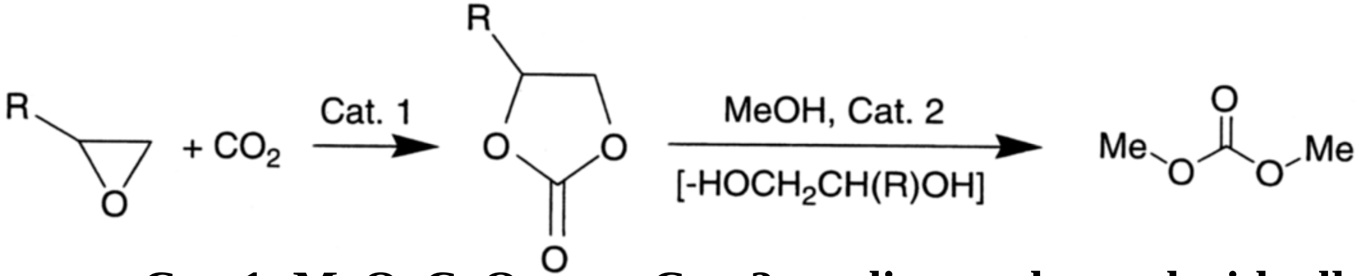
Production of Dimethyl carbonate (DMC) from ethylene oxide and CO_2 as a more effective way for the reuse of CO_2

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



Cyclic carbonates from epoxides and CO_2

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



Cat. 1: MgO, CaO

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

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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_2O (g/100g)	13.9
Azeotropical mixtures	With water, alcohols, hydrocarbons

Useful methylation and alkoxycarbonylation agents

≦90 C $$PhOH + CH_3OCOOCH_3 \xrightarrow{\text{Cat. base}} PhOCH_3 + CO_2 + CH_3OH$$

≧160 C $$ROH + CH_3OCOOCH_3 \xrightarrow{\text{Cat. base}} ROCOOCH_3 + CH_3OH$$

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Organic carbonates as solvents

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

Table 1. Transport and Thermodynamic Properties

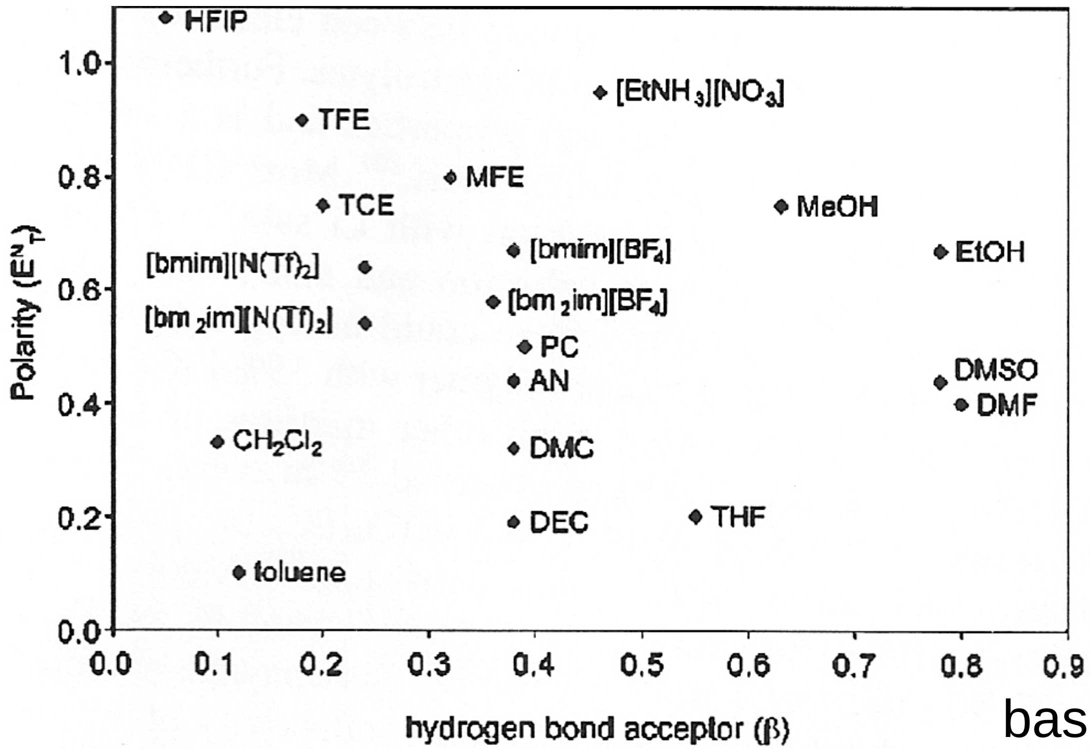
organic carbonate	bp [K]	*d* (293 K) [g/cm^3]	viscosity (298 K) [cP]
DMC	363^b	1.07^b	0.590^b
DEC	399^b	0.98^b	0.753^c
EC	521^d	1.34^{a,d}	2.56^{a,d}
PC	515^d	1.20^d	2.50^d
BC	524^d	1.14^d	3.14^c

Acetone 0.320 cP

Water 0.891 cP

1-butanol 2.99 cP

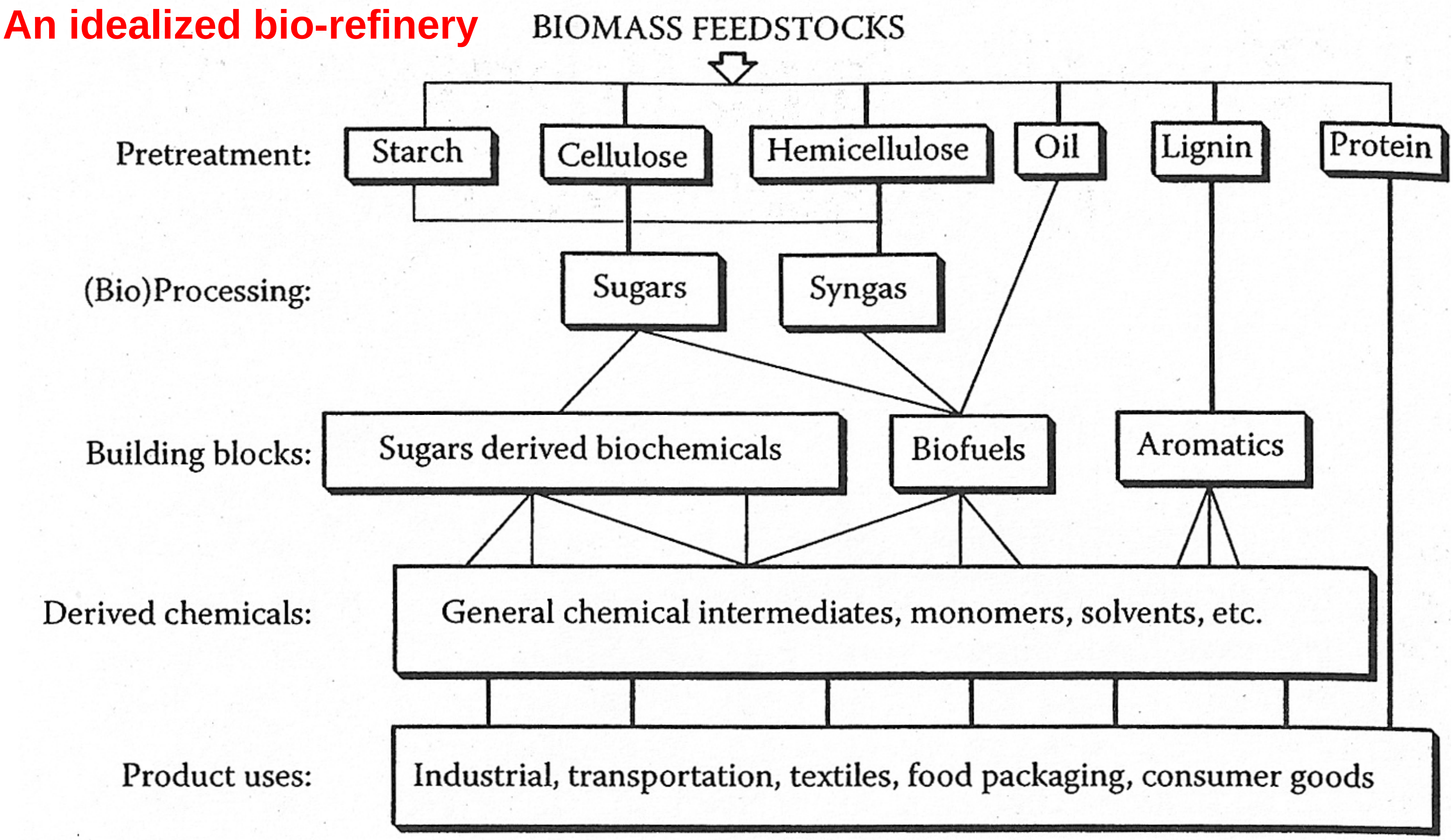
polarity



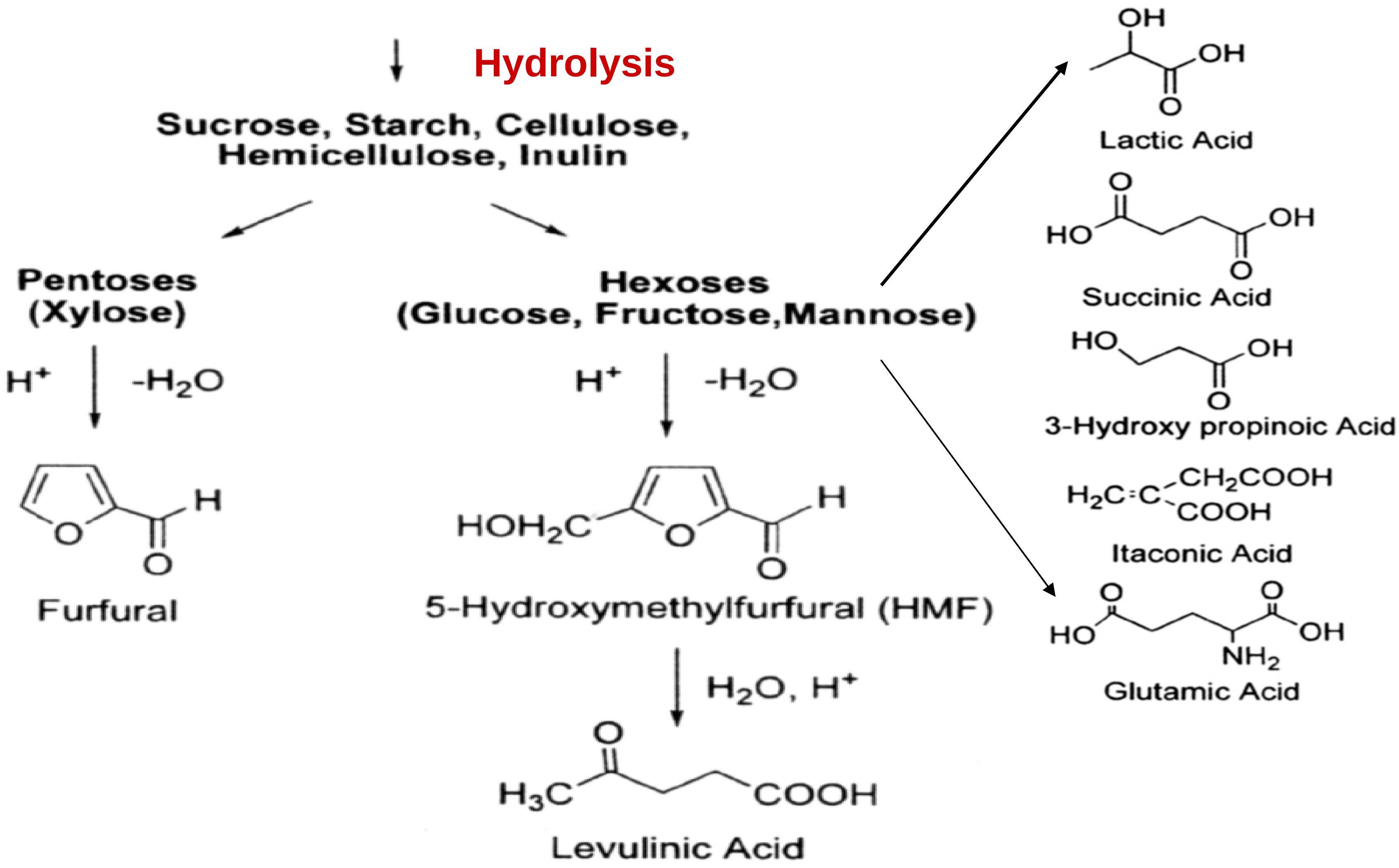
basicity

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

An idealized bio-refinery

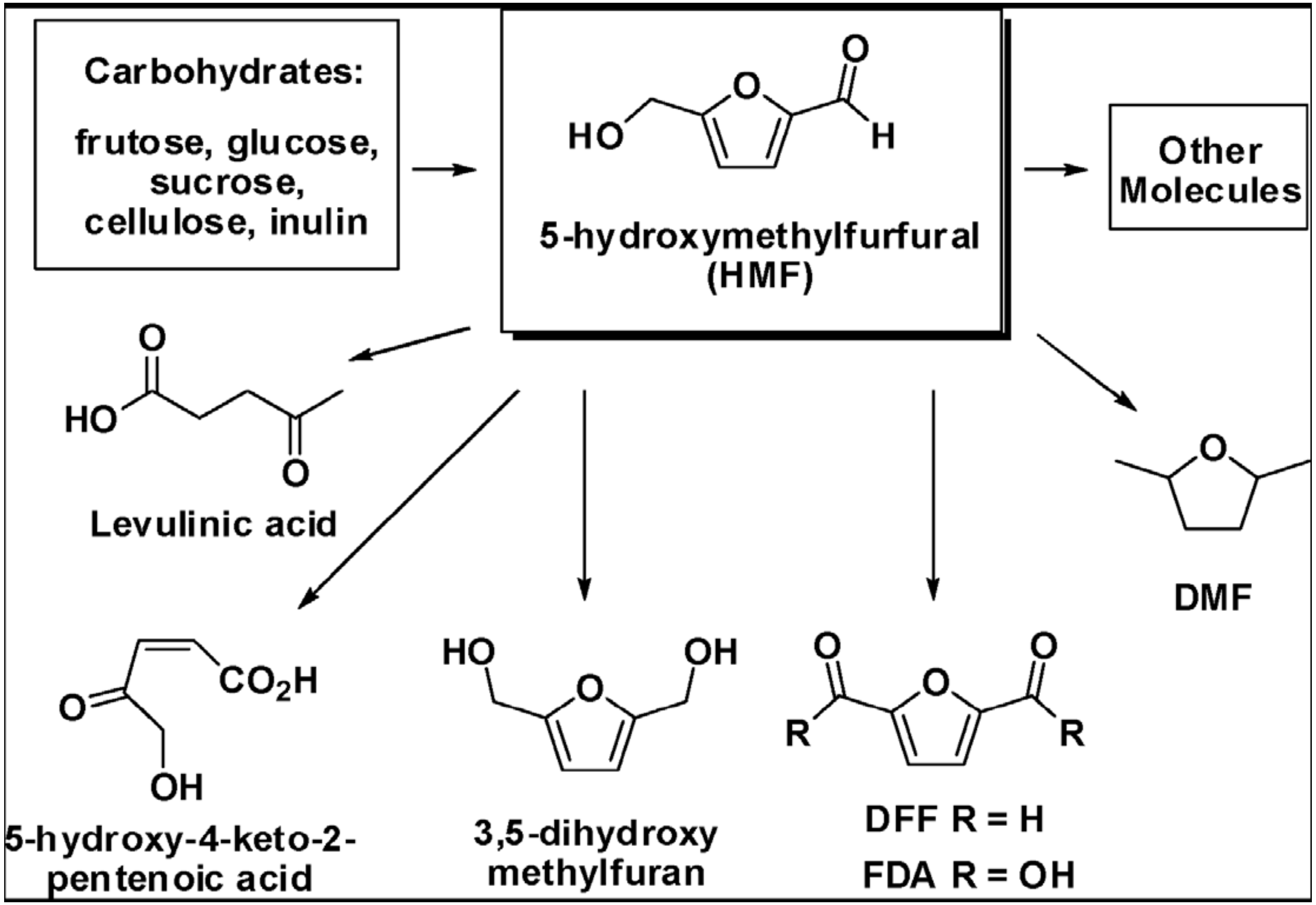


From polysaccharides (vegetal biomass)



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

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



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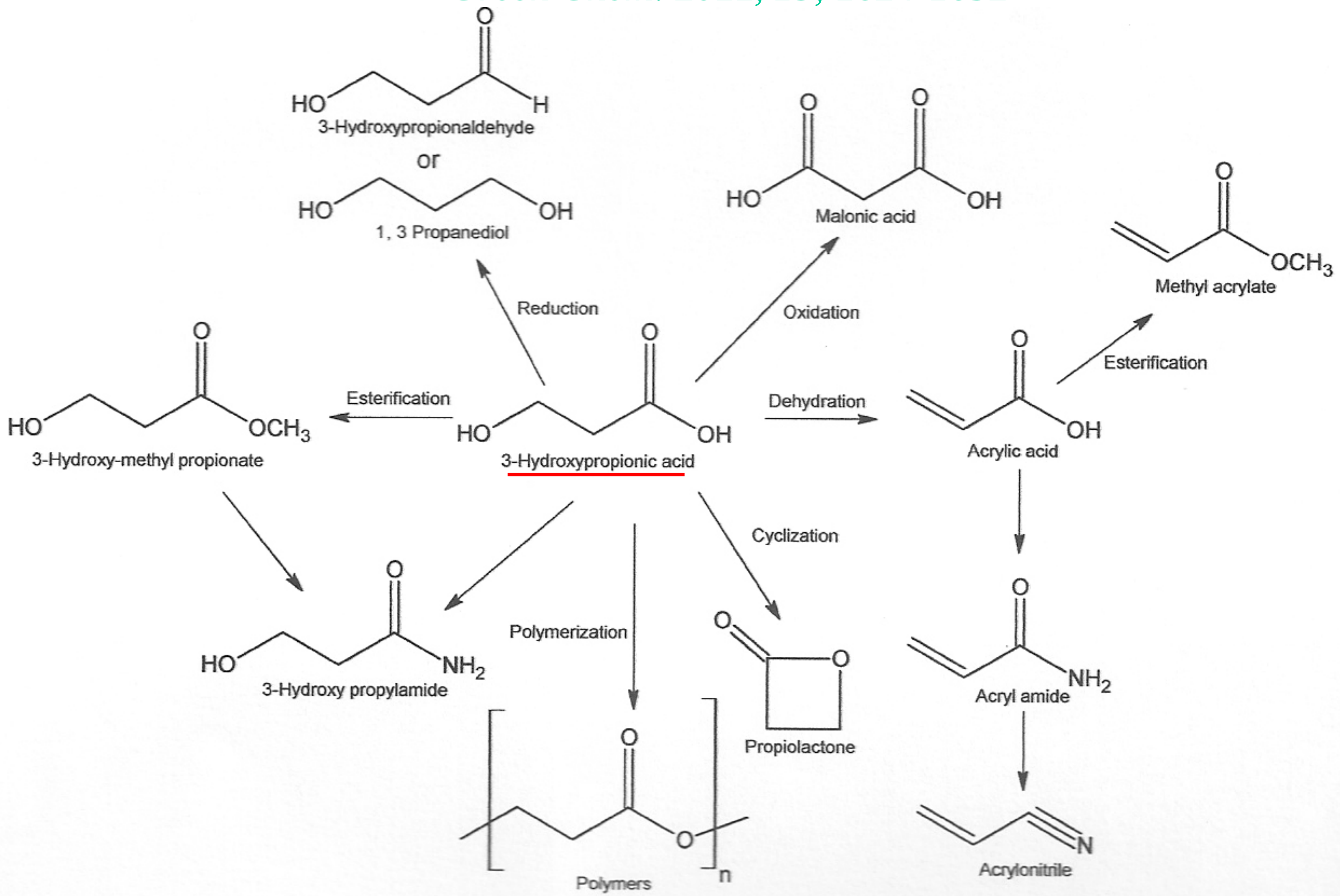
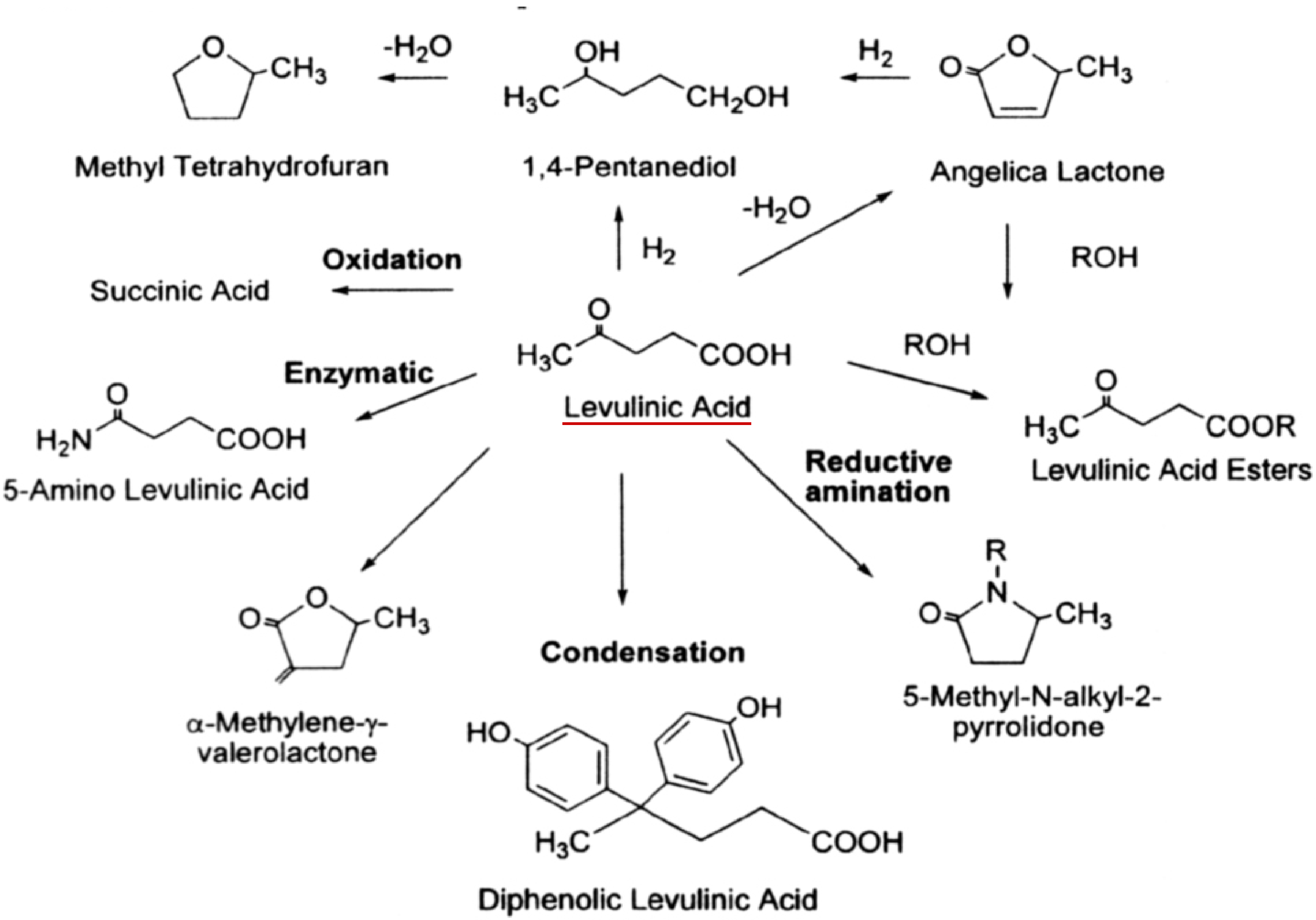
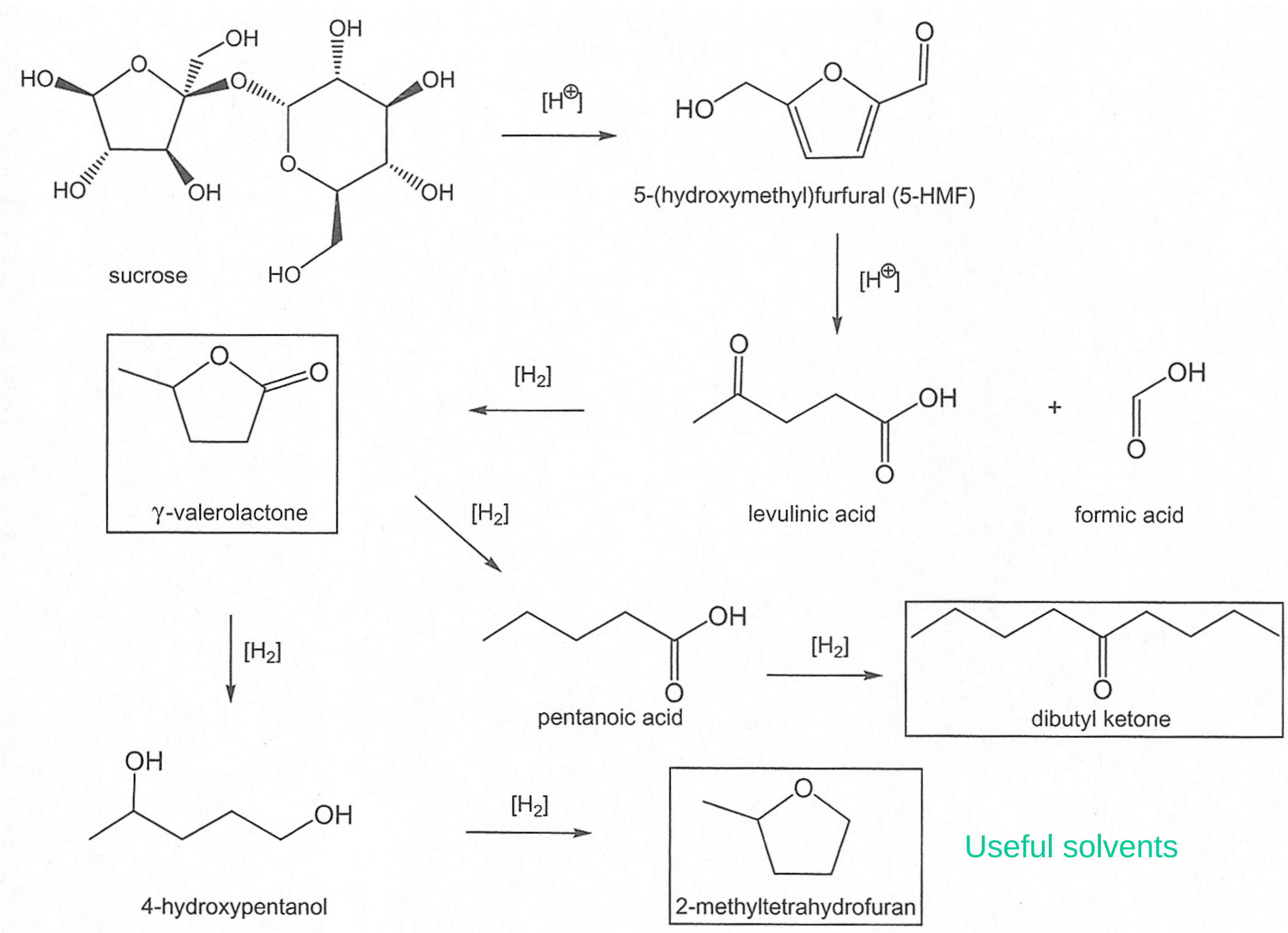
A green approach to chemical building blocks. The case of 3-hydroxypropanoic acid

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





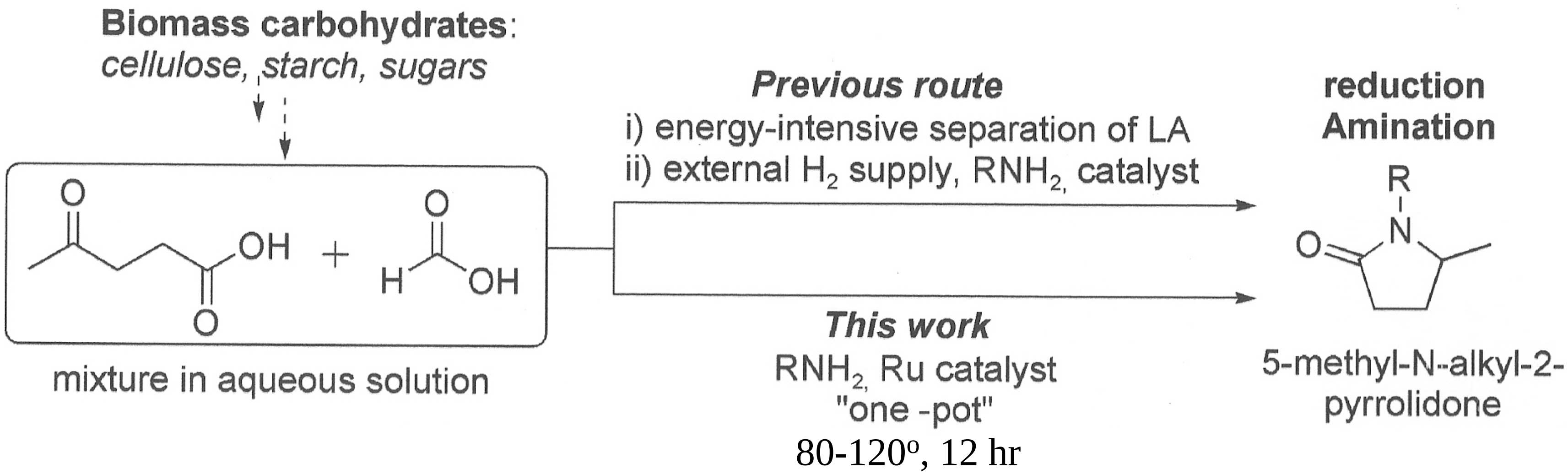
1999 PGCC Award of Small Business——Biofine process to make levulinic acid from paper mill sludge, agricultural residues, waste wood and papers.



Useful solvents

(Winterton, *Chemistry for Sustainable Technologies*, **2011**, p.385)

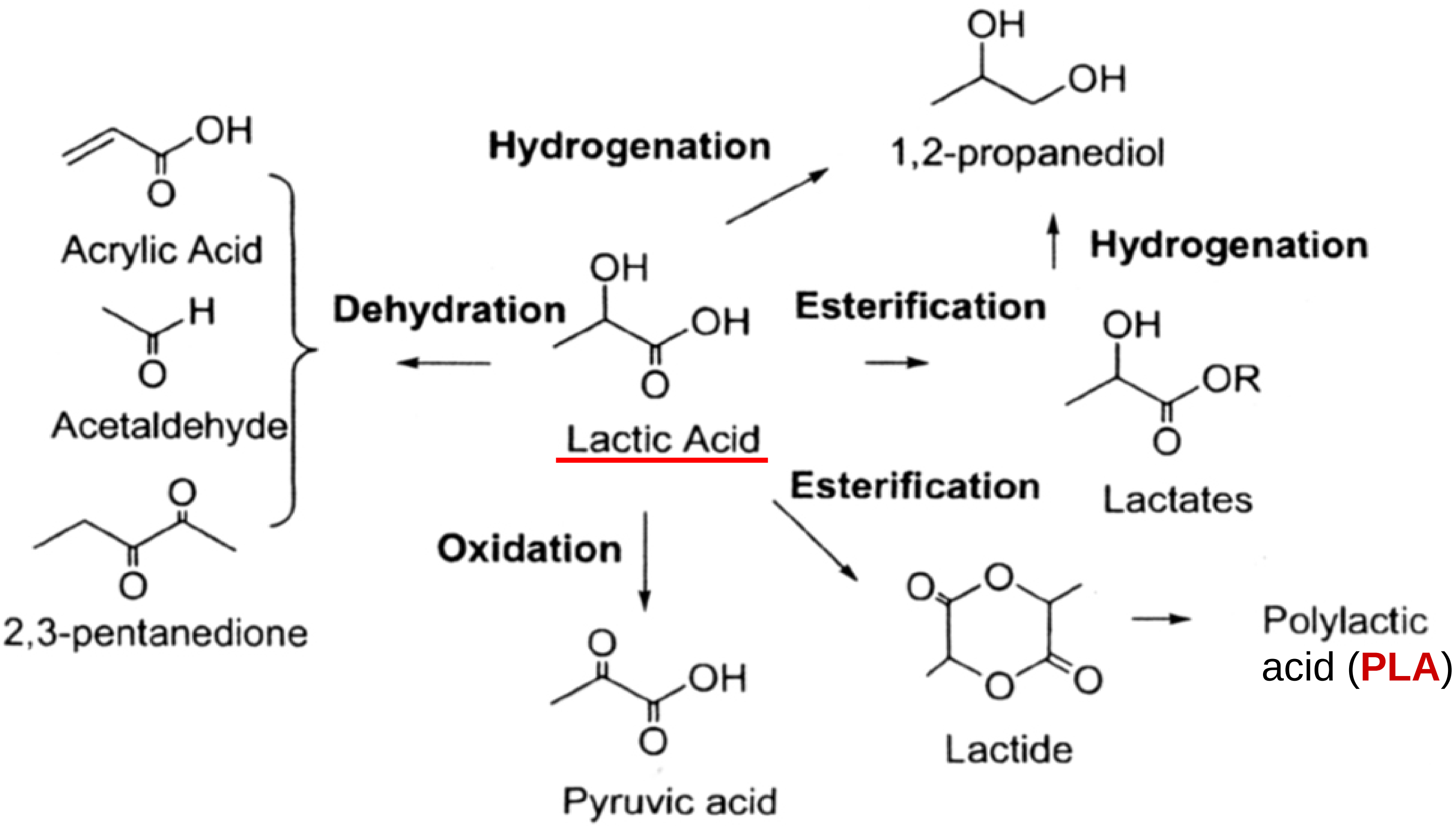
Levulinic acid to pyrrolidines



Alkylamines, Conditions A: LA (1 mmol), FA (1 mmol), H_2O (150 mg), amine (1 mmol), 1 (0.5 mol%) t-Bu_3PHBF_4 (1.5 mol%), 80^{o}C, 12 h.
Arylamines, Conditions B: LA (2 mmol), FA (2 mmol), H_2O (250 mg), amine (1 mmol), 1 (1mol%) t-Bu_3PHBF_4 (3 mol%) 120^{o}C, 12 h.

ChemSusChem **2011**, *4*, 1578-1581.

Lactic acid and ethyl lactate

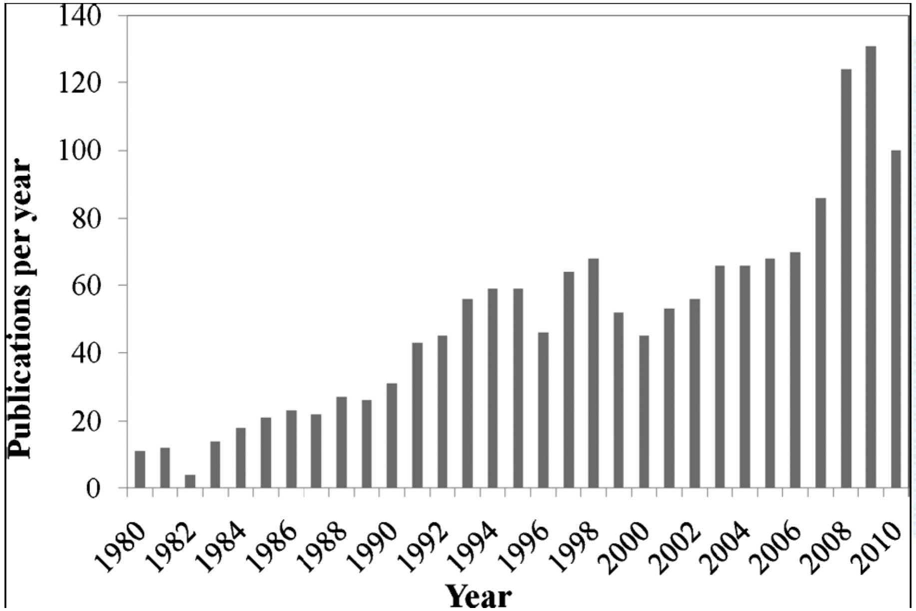


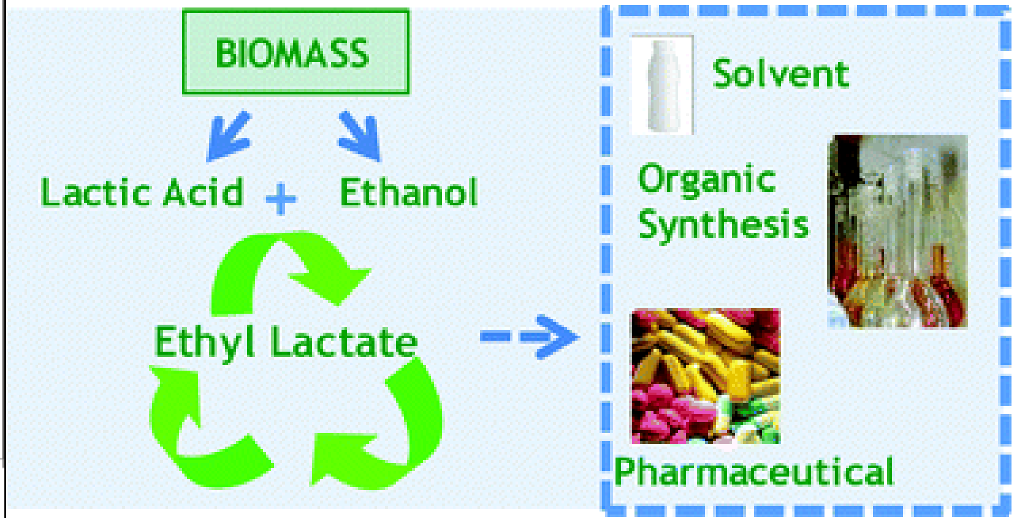
Ethyl lactate is a very useful solvent.

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.

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

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

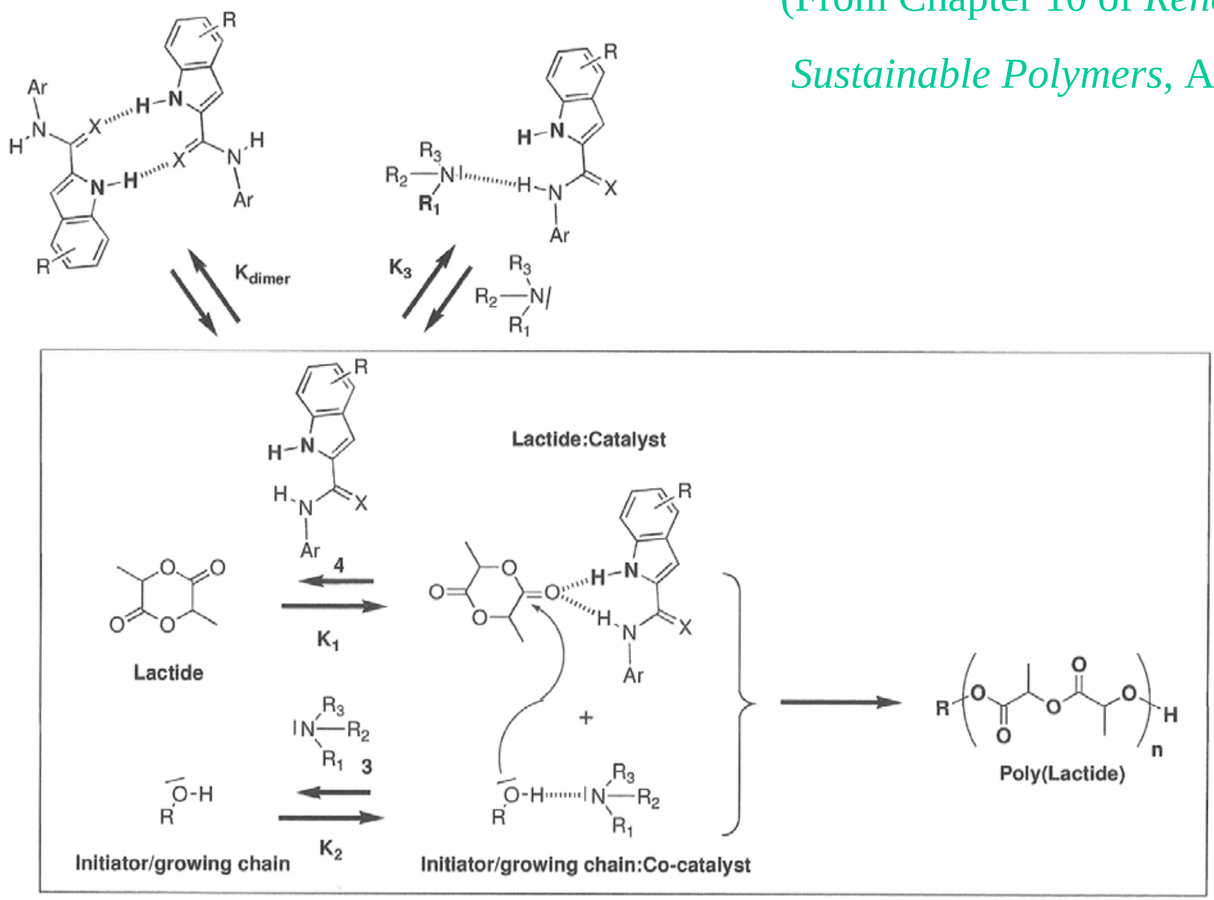

*Figure 2. Multiple H-bonding equilibria involving reactants and catalysts **4** + **3** during the Ring Opening Polymerization of lactide.*

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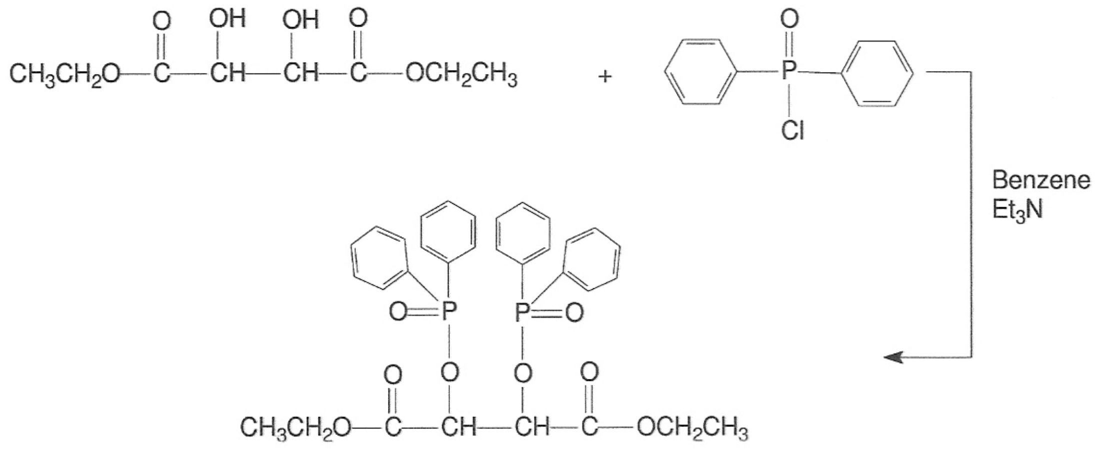
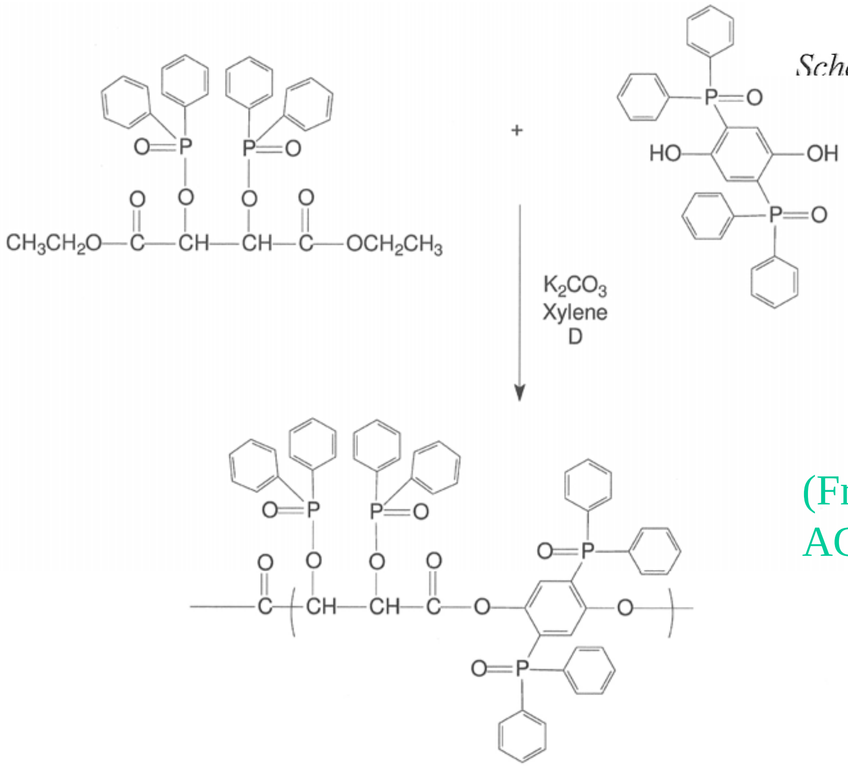
Polycarbonates as Flame Retardants Based on Tartaric Acid:

A potential C4 building block



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



Scheme 3. Generation of Oligomers Containing High Levels of Phospho

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

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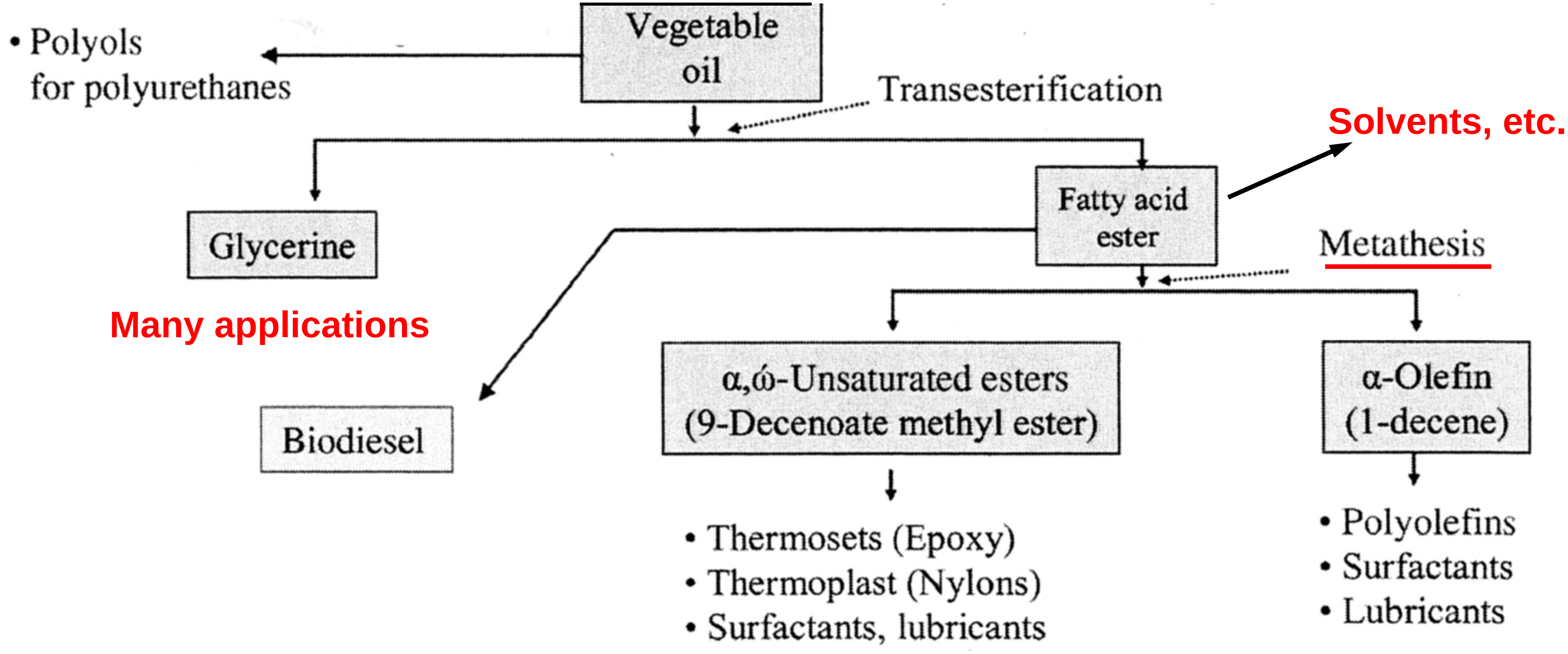
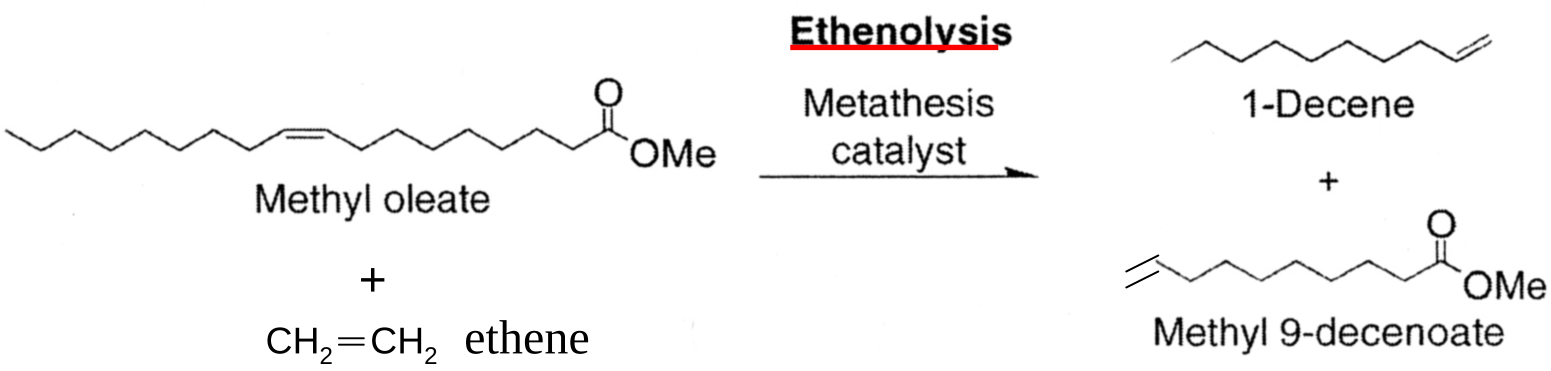
Bio-refinery of vegetable oils





Glycerol

The Future of Glycerol

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

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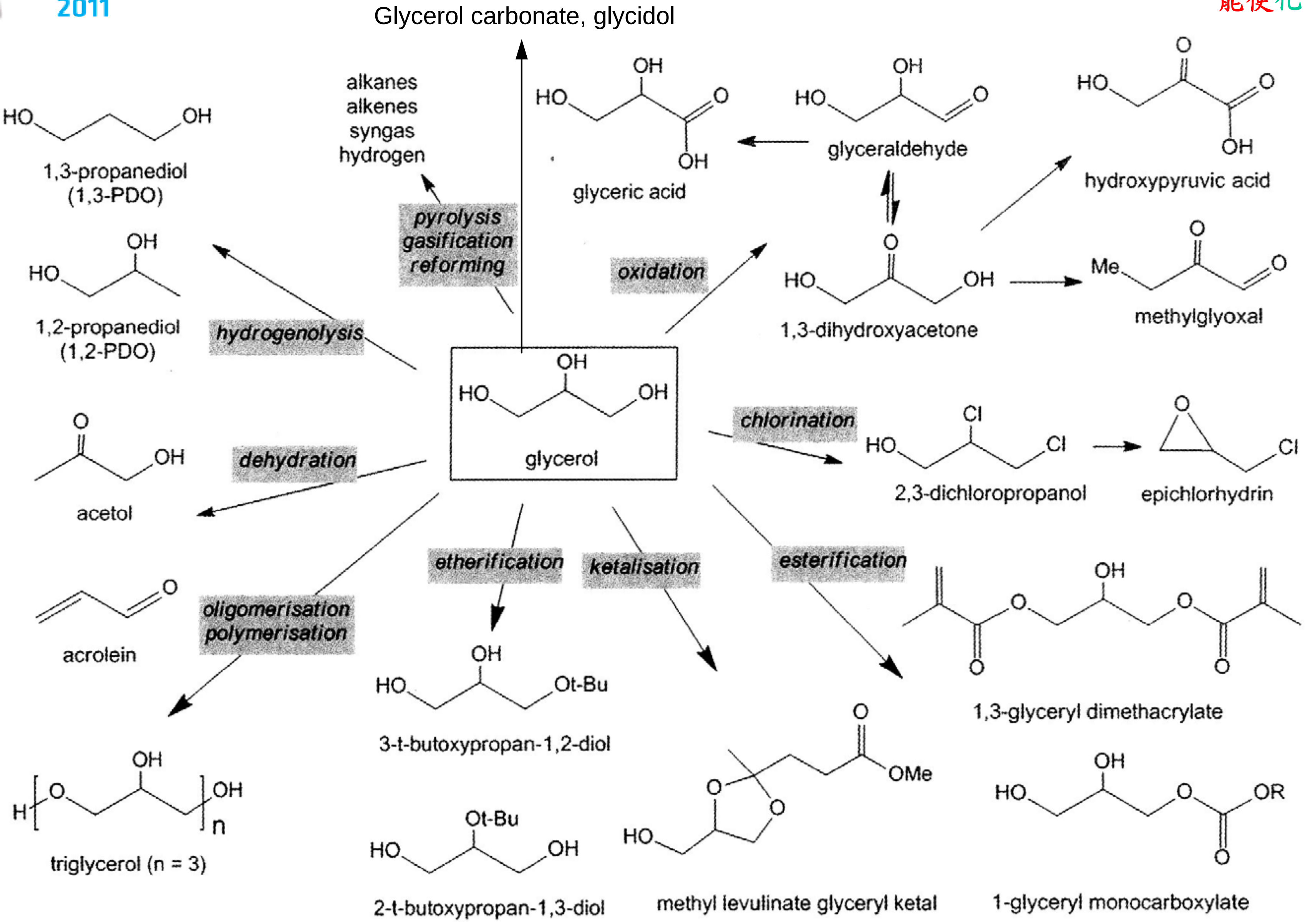

(Winterton, *Chemistry for Sustainable Technologies*, **2011**, p.386)

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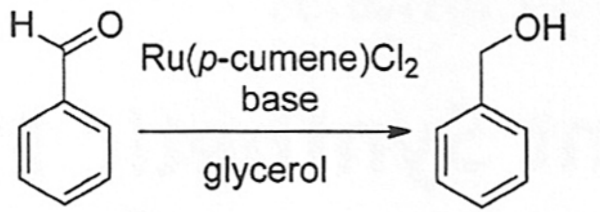
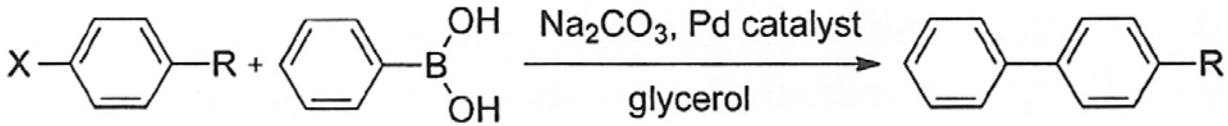
Synthesis in glycerol

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



With Ultrasound/Microwave

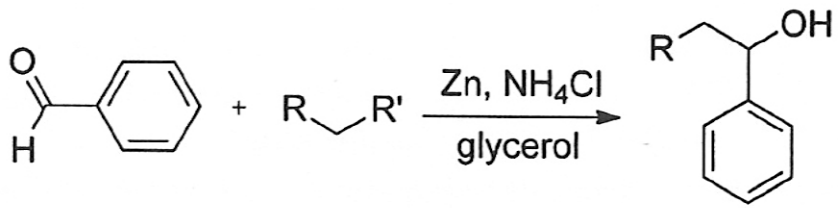
Benzaldehyde transfer hydrogenation reaction



X= I, Br, Cl
R= OCH_3, C(O)CH_3

With Ultrasound/Microwave

Suzuki cross-coupling reaction in glycerol.



With Ultrasound

R = C≡CH, HC=CH_2, CH_2CH_2C≡CH
R'= Br, Cl

Barbier reaction in glycerol.

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Table 1. Glycerol Feedstock Announcements

Company	*Product*	*Volume*	*Location*
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**)

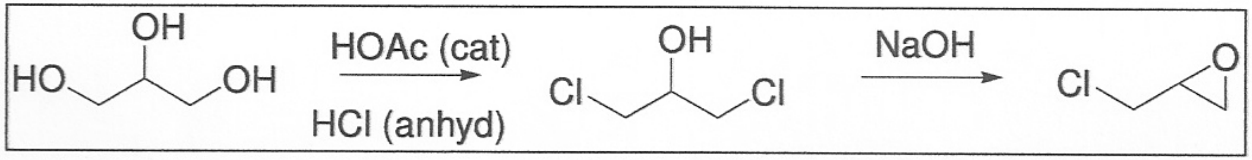
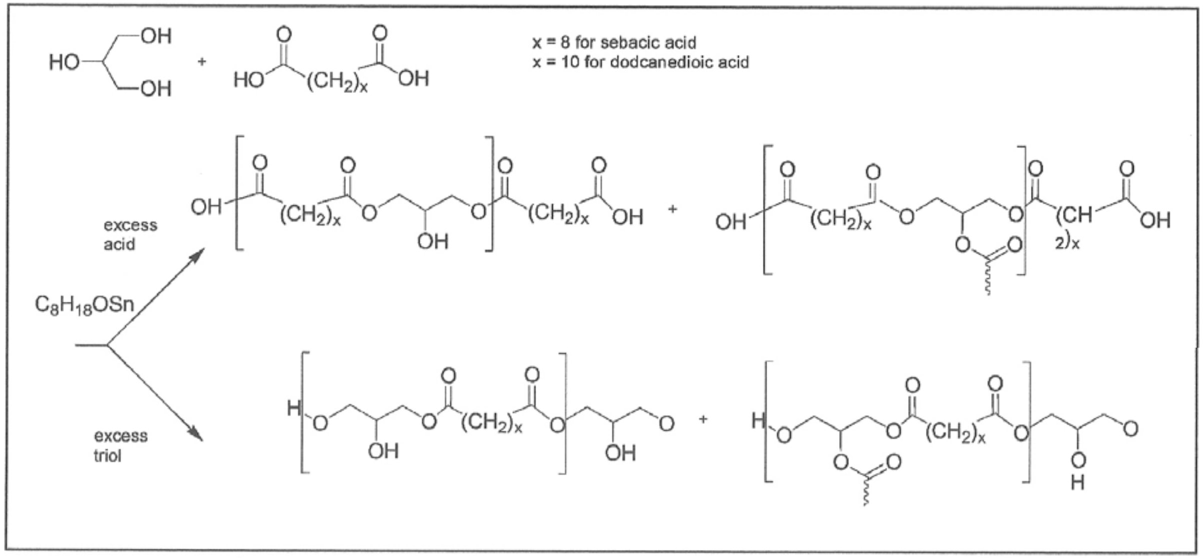


Figure 3. The Conversion of Glycerol to Epichlorohydrin.



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

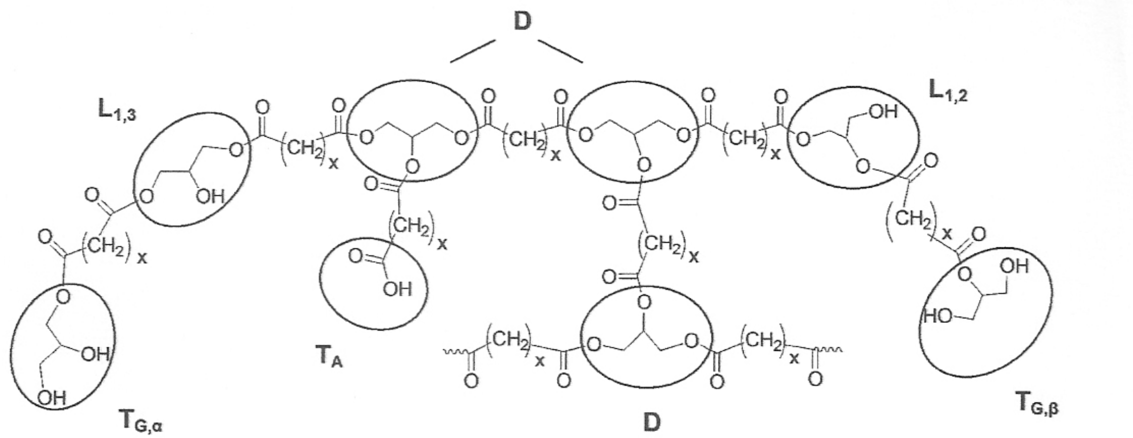


Figure 5. Types of structural units than can occur in copolyesters formed from glycerol with diacids (x = 8 for sebacic acid and x = 10 for dodecanedioic acid).

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

Sustainable chemistry makes chemistry sustainable

多謝聽講 歡迎討論

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