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。[如本頁取材自〇〇〇教授演講內容]。

永續化學合成(4)

可再生性資源在合成上的利用

劉廣定

(ktliu@ntu.edu.tw)

(December 3, 2010)

The use of chemicals and solvents from renewable resources

永續化學十二原則 (Anastas and Warner, 1998)

7. A raw material or feedstock should be renewable rather than depleting, whenever technically and economically practicable.

永續工程十二原則(Anastas and Zimmerman, 2003)

7. Material and energy inputs should be renewable rather than depleting.

永續十律 Ten commandments of sustainability (Manahan, 2005)

7. Material demand must be drastically reduced; materials must come from renewable resources, be recyclable and, if discarded to the environment, be degradable.

Renewable resources and reagents

- **Chemicals from renewable feedstock**
- **CO_2, water, carbohydrates and products**
- **Terpene (essential oils) and lignin**
- **Fatty acids from fats and oils**
- **Glycerol as starting materials and solvents**
- **Organic carbonate and other green substitutes**
- **etc.**

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); SCF CO_2(＞74 bar, ＞31℃)**]

易除去或回收再用

故可用為溶劑及反應試劑

Green Chemistry Using Liquid and Supercritical Carbon Dioxide (DeSimone and Tumas, Ed., Oxford, **2003**)

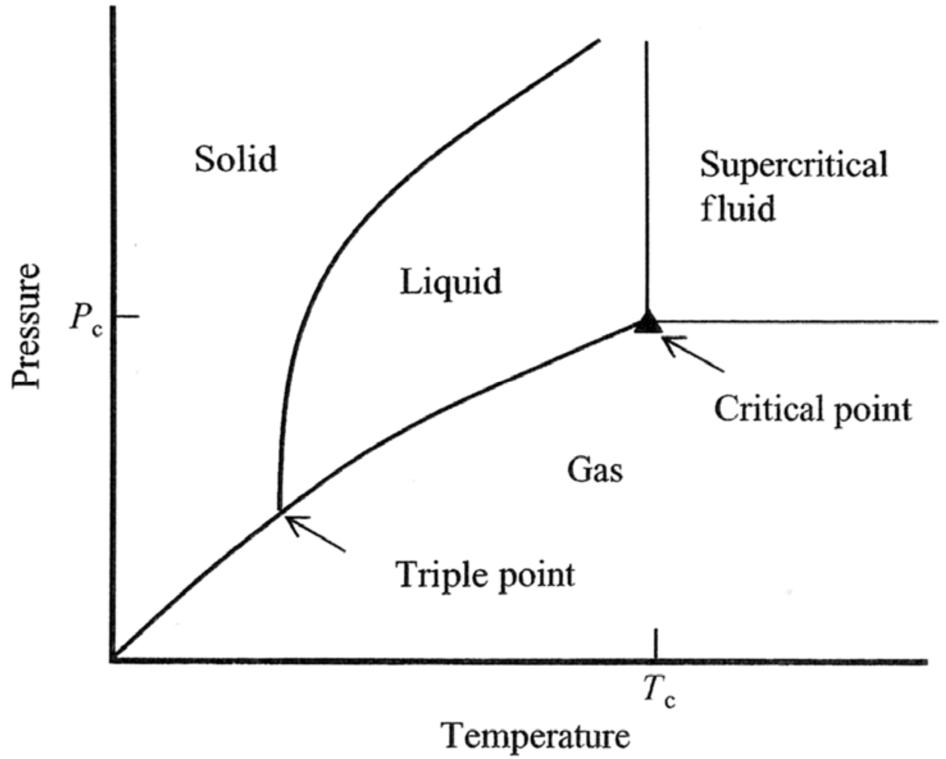
Green Reaction Media in Organic Synthesis **(**Mikami, Ed., Chapter 4, Blackhill, **2005)**

The Potential of CO_2 in Synthetic Organic Chemistry **(**Rayner, *Org. Proc. Res. Dev.* **2007**, *11*, 121-132)

Alternative Solvents for Green Chemistry (Kerton, Chapter 4, RSC, 2009)

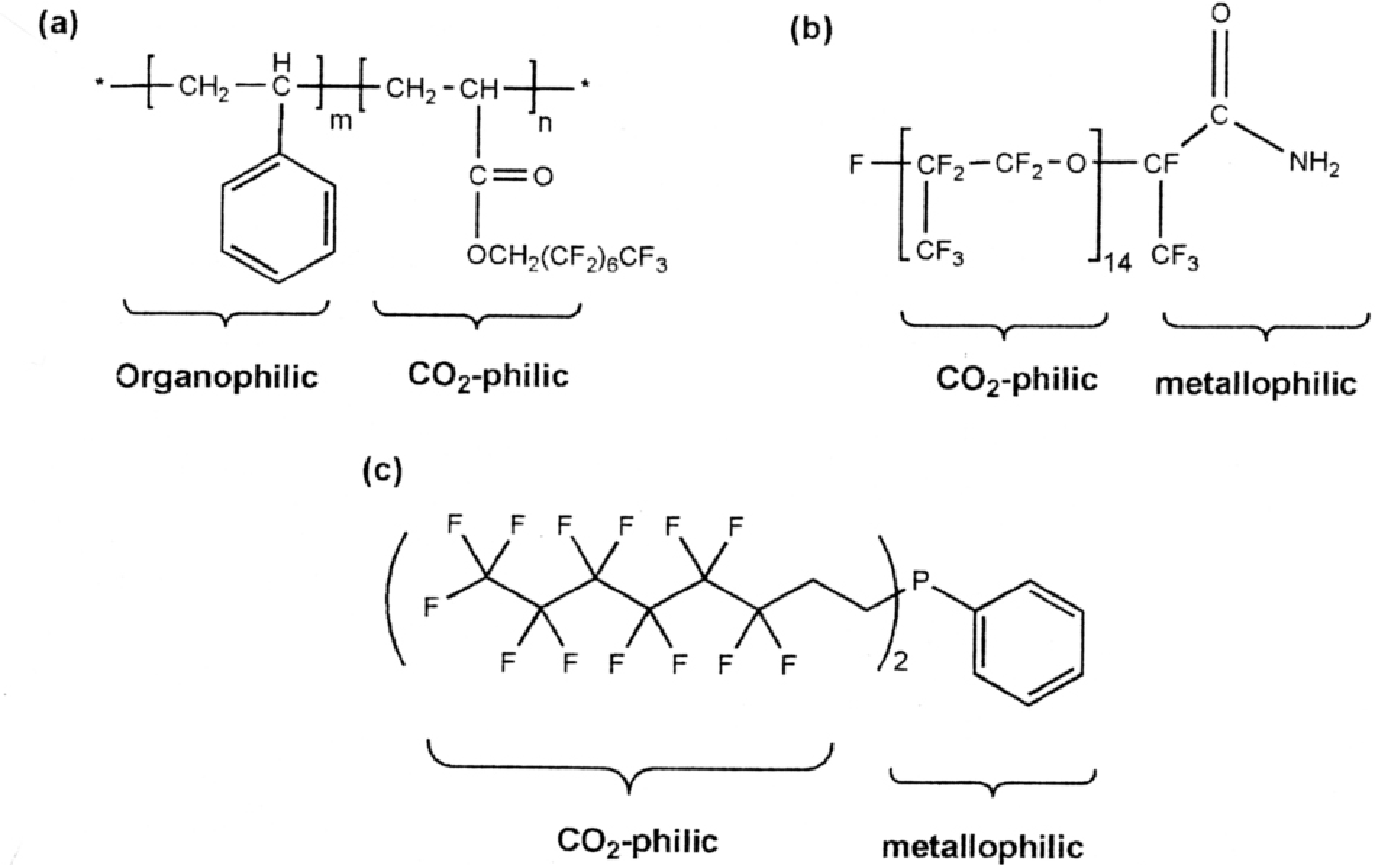
Utilization of CO_2(Darensbrough, *Inorg. Chem*. **2010**, *49*, 10765-10781)

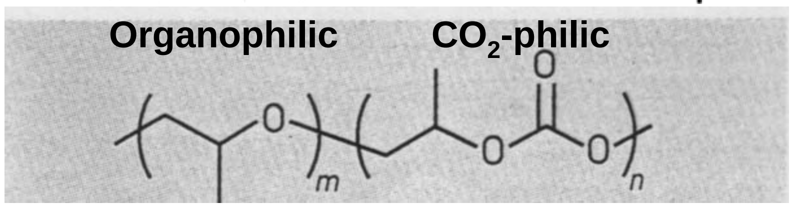
Phase diagram and critical points



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

Surfactants for SCF-CO_2

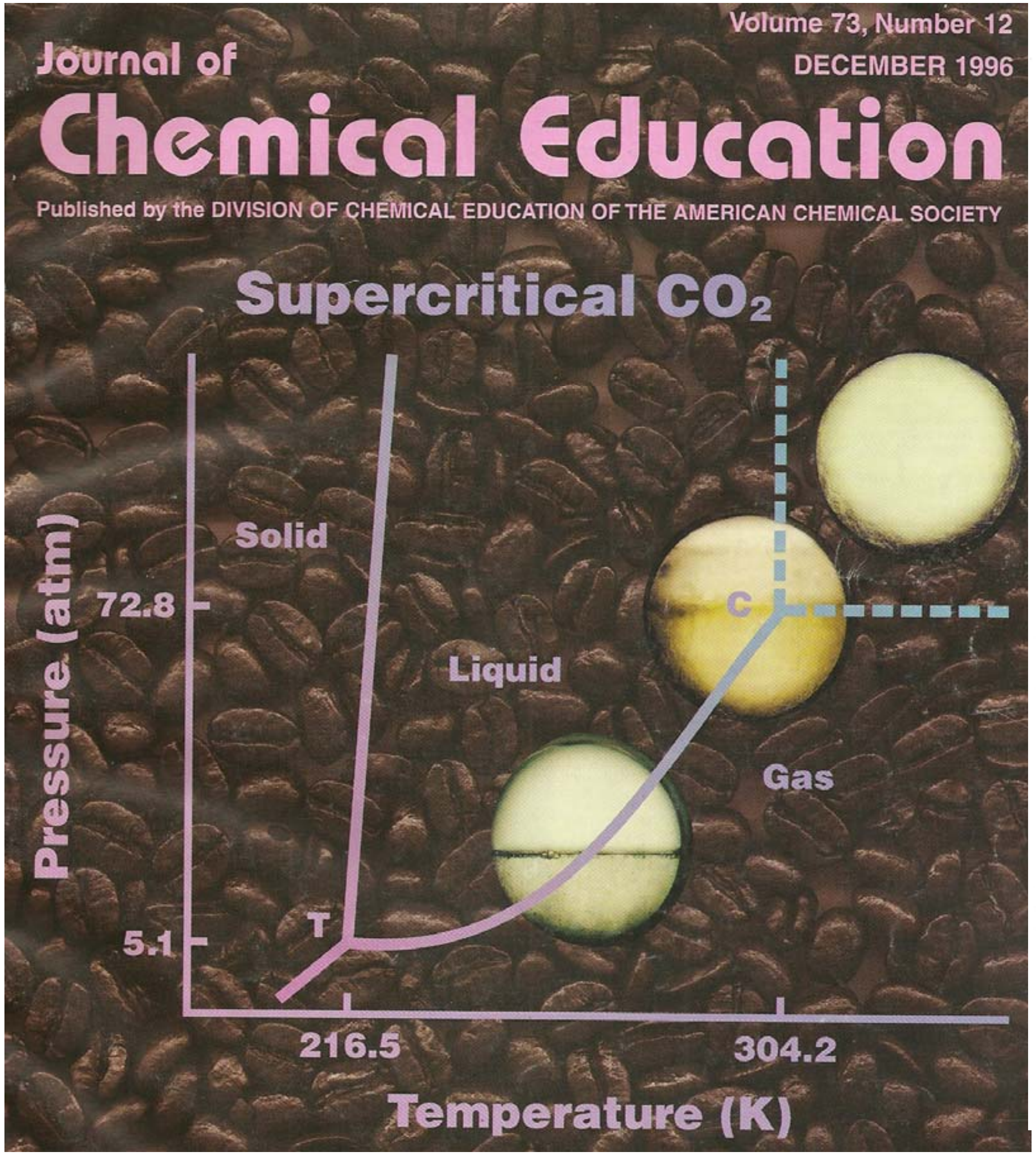




Non-fluorinated (ether-carbonate) copolymer by Beckman and coworkers at U. of Pittsburgh. **PGCC Award of 2002**

(*J. Phys. Chem. B*, **2009**, *113*, 14971-14980)

“老”技術



Chemical reactions in supercritical carbon dioxide
C. M. Wai, *J. Chem. Educ*. **1996**, *75*, 1641-1645

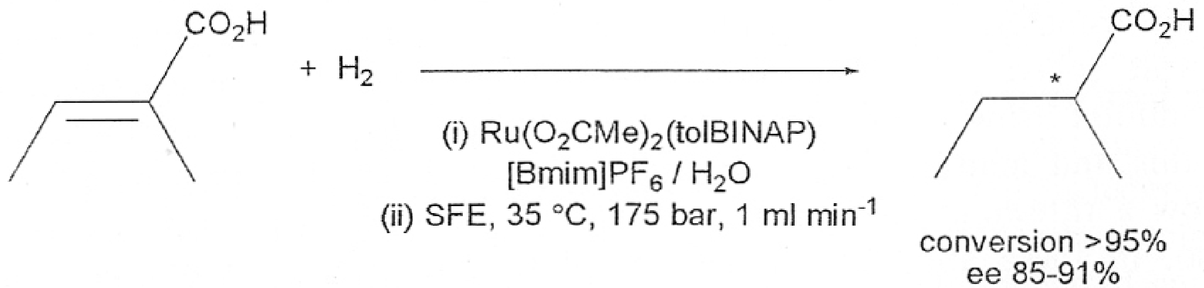
化工技術

1998年10月號／第67期

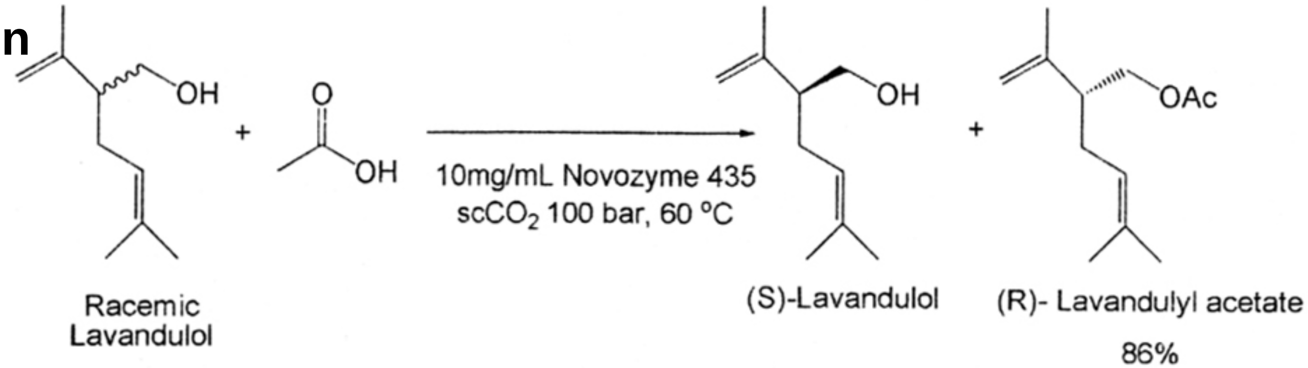
超臨界流體技術　專輯　　　談駿嵩主編

Examples

Hydrogenation in Biphasic IL-scCO$_2$ system



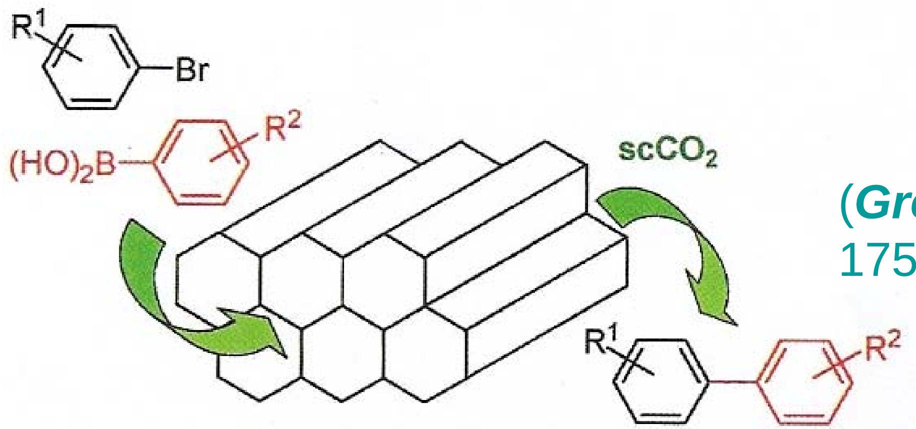
Biocatalytic esterification



(Kerton, pp. 81-82)

Suzuki coupling

90^{o}C, 20MPa, 24h
61-99% yield



Ph-SBA-15-PPh$_3$-Pd
(can be used at least 7 times)

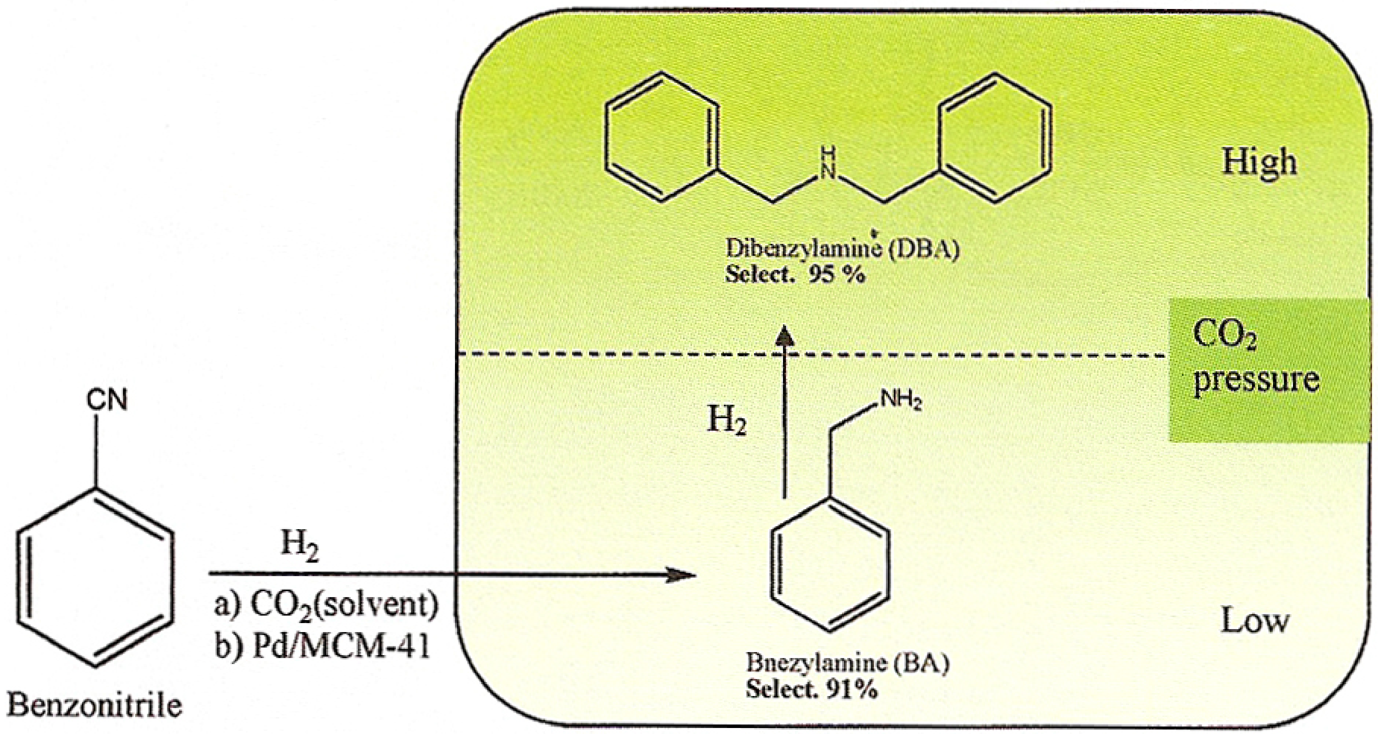
(*Green Chem*. **2010**, *12*, 1758-1766)

Courtesy of Professor C. M. Wai, U. Idaho.

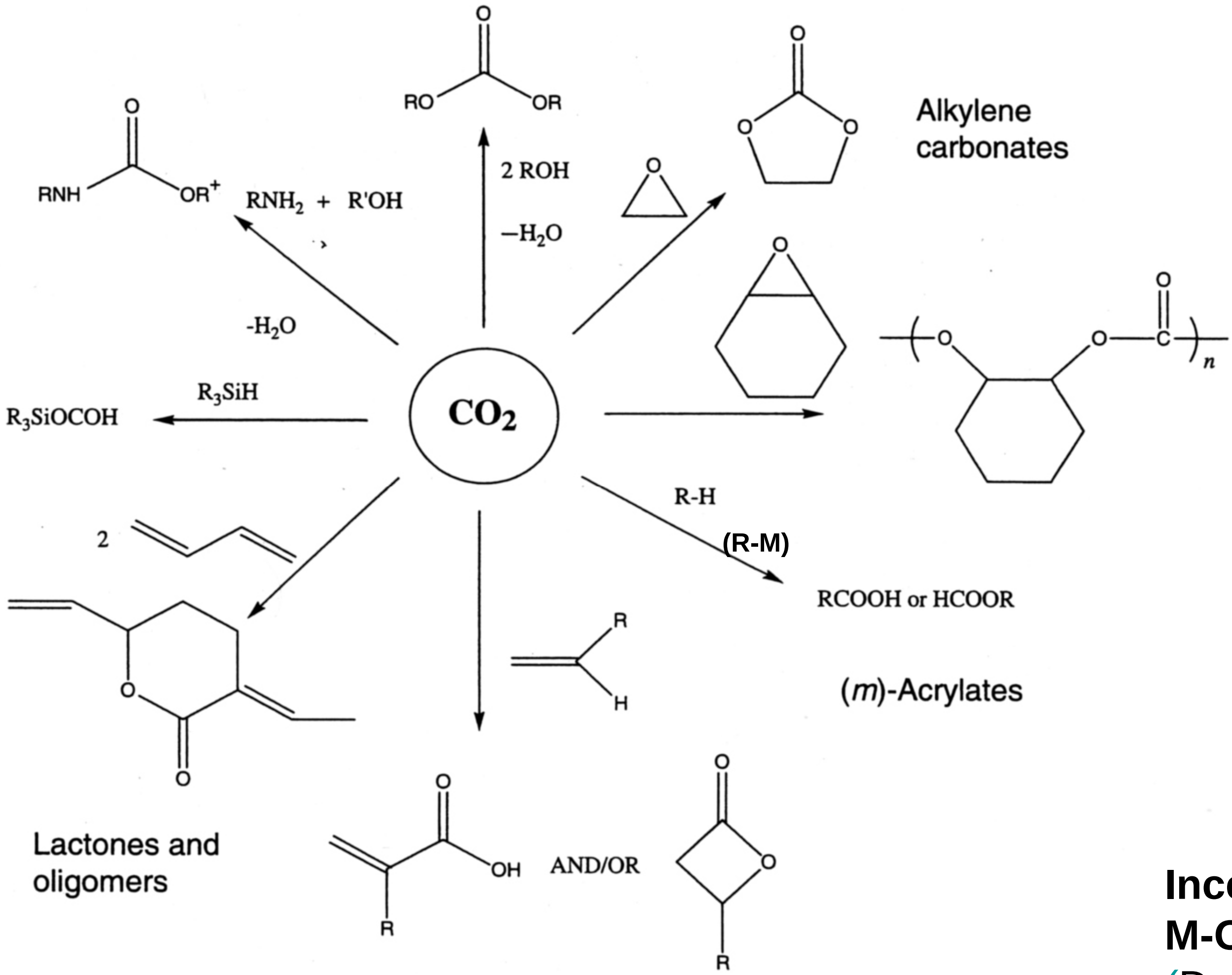
Hydrogenation of nitrile in $scCO_2$: a tunable approach to amine selectivity

Chatterjee, *et al. Green Chem*. **2010**, *12*, 87-93

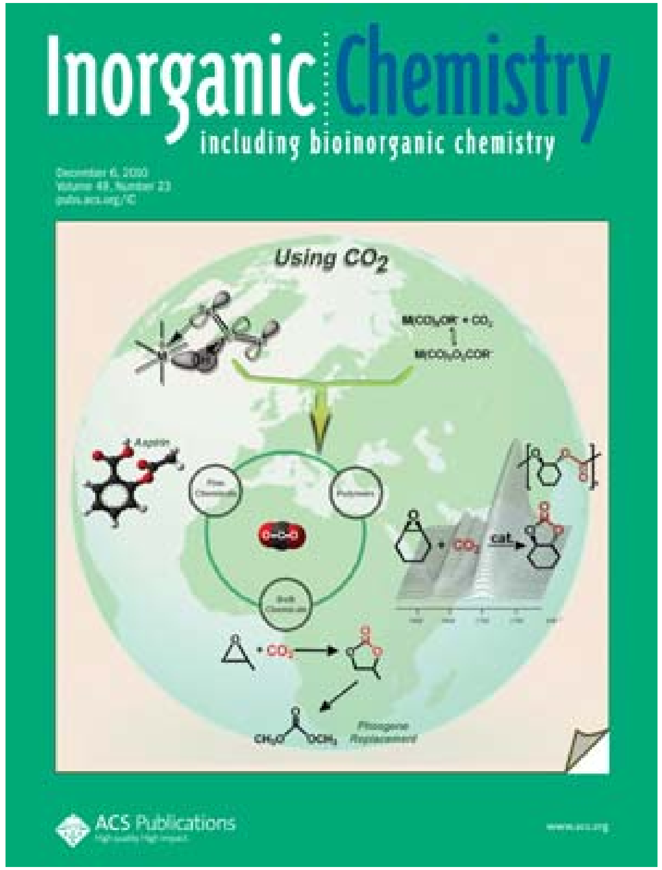
By tuning the CO_2 pressure changes the product selectivity (more than 90%) from benzylamine to dibenzylamine, with 90+% conversion.



CO_2 Transformations



(Sakakura, et al., *Chem. Rev.* **2007**, *107*, 2365-2387)



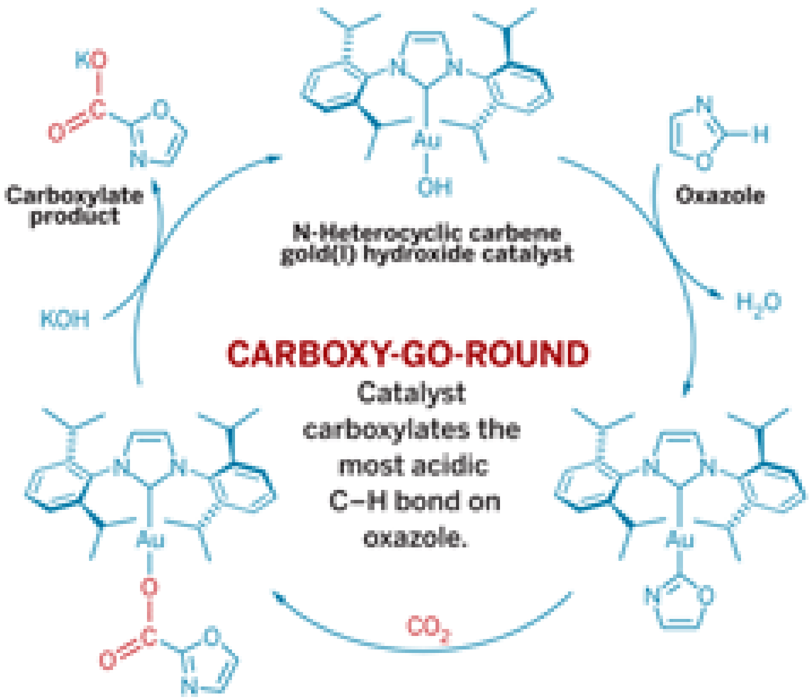
Incertion of CO_2 into M-H, M-C and M-O bonds
(Darensbourg *Inorg. Chem*. **2010**, *49*, 10765-10780)

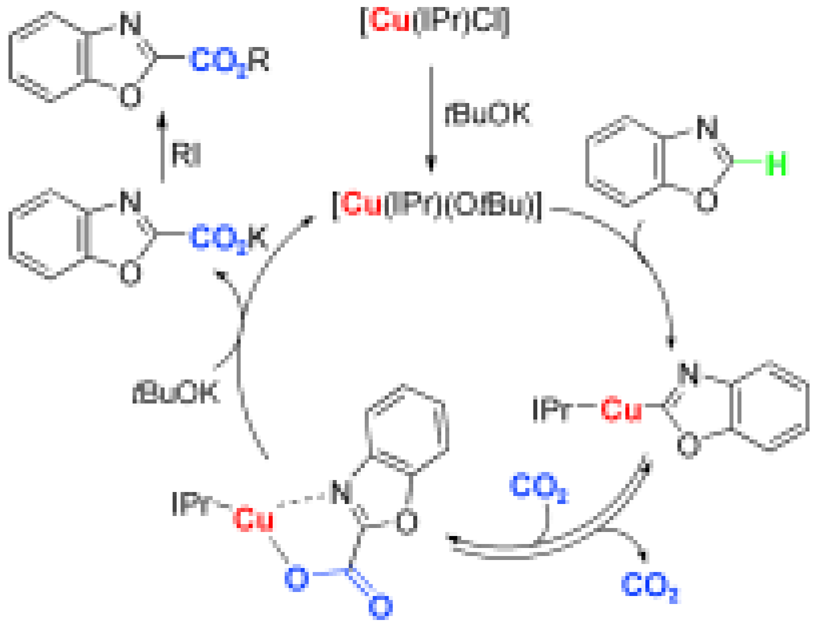
Direct carboxylation with CO_2

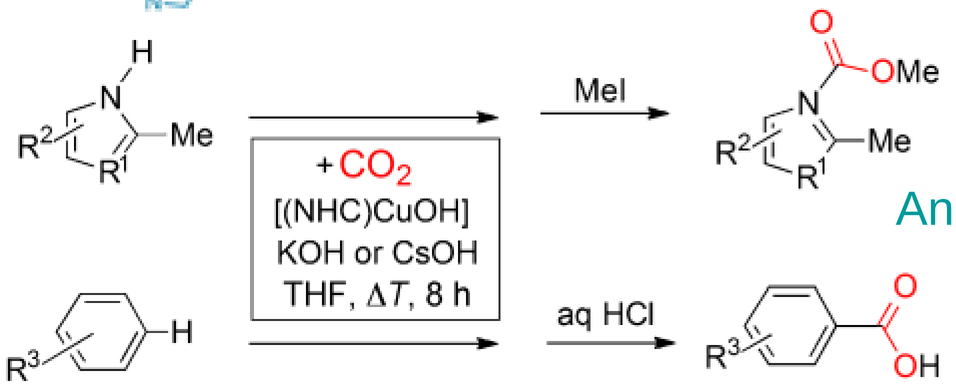
Greenhouse gas makes good

Nolan, *JACS* **2010**, *132*, 8858-8859

Hou, Angew. Chem. **2010**, *49*, 8670-8673



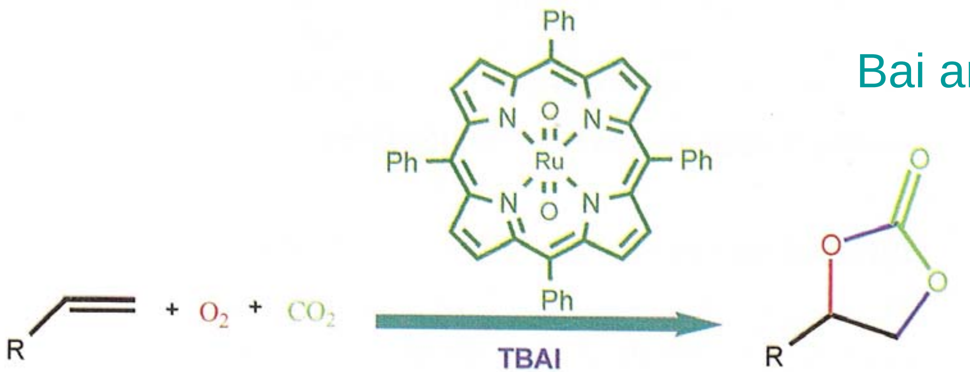




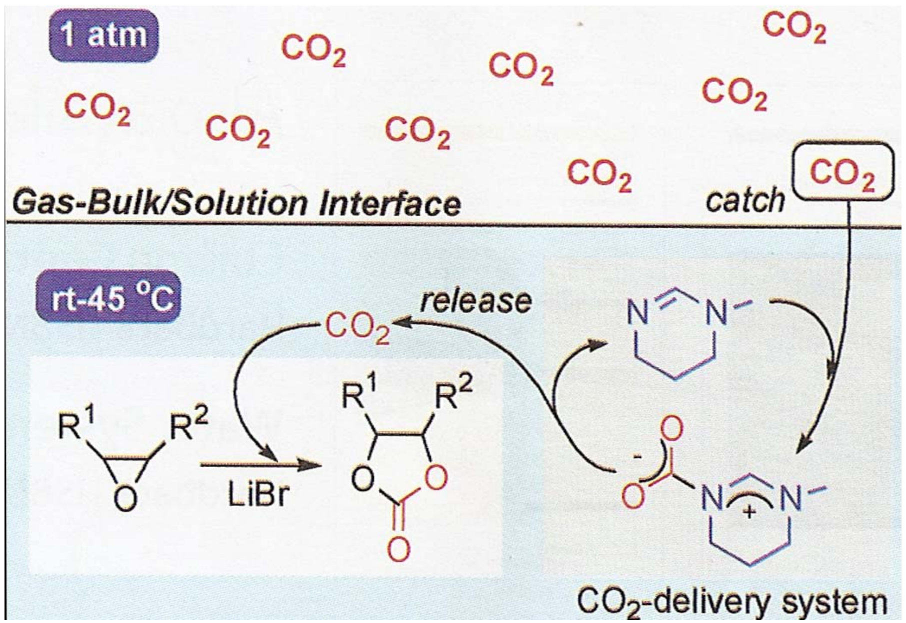
Angew. Chem. **2010**, *49*, 8674-8677

Aerobic oxidative carboxylation of olefins with metalloporphyrin catalysts

Bai and Jing, *Green Chem*. **2010,** *12,* 39-41



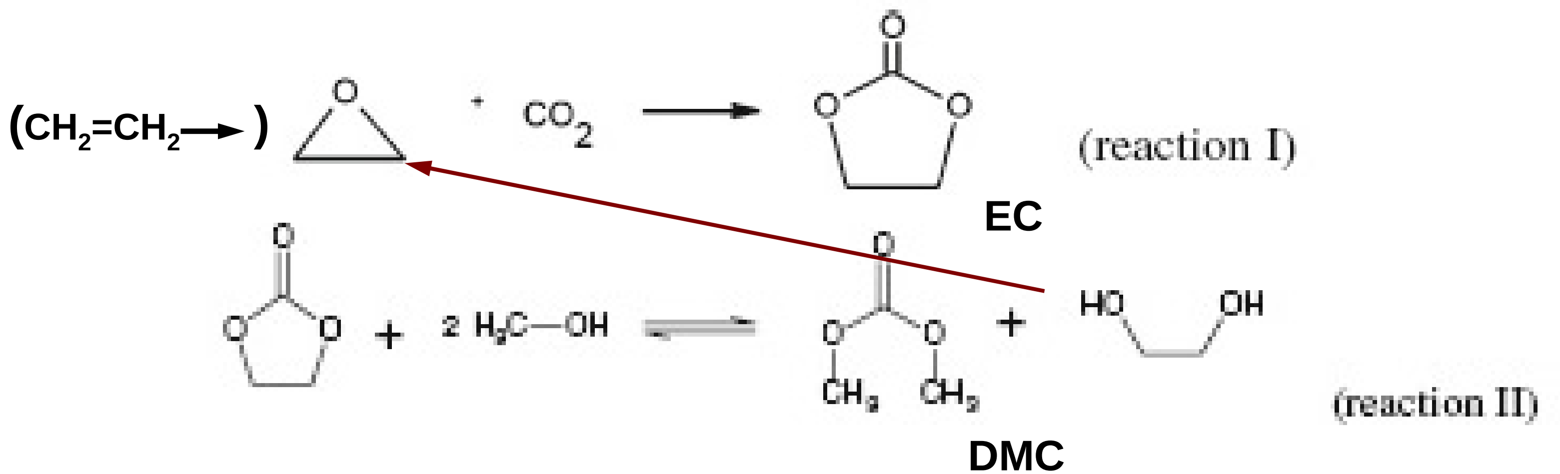
Amidine-mediated delivery of CO_2 from gas phase to reaction system for highly efficient synthesis of cyclic carbonates from epoxides



Barkakaty, et al., *Green Chem*. **2010,** *12,* 42-44

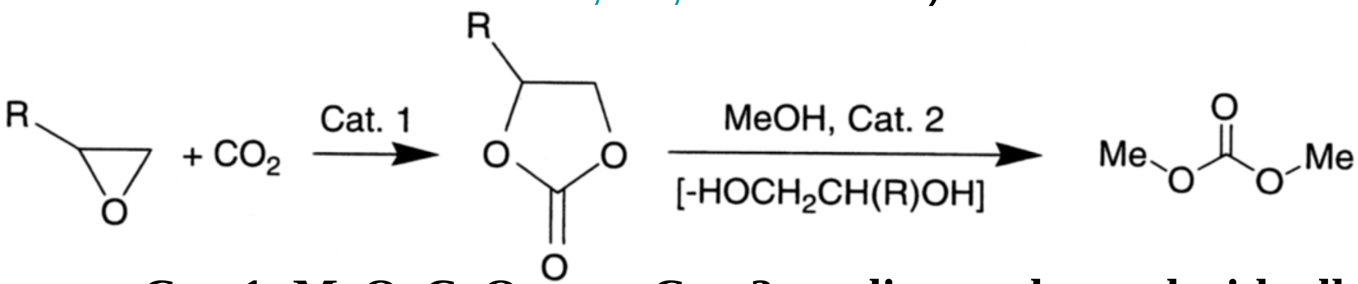
Production of Dimethyl carbonate (DMC) from ethylene oxide and CO_2 as a more effective way for the reuse of CO_2

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



Cyclic carbonates from epoxides and CO_2

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



Cat. 1: MgO, CaO

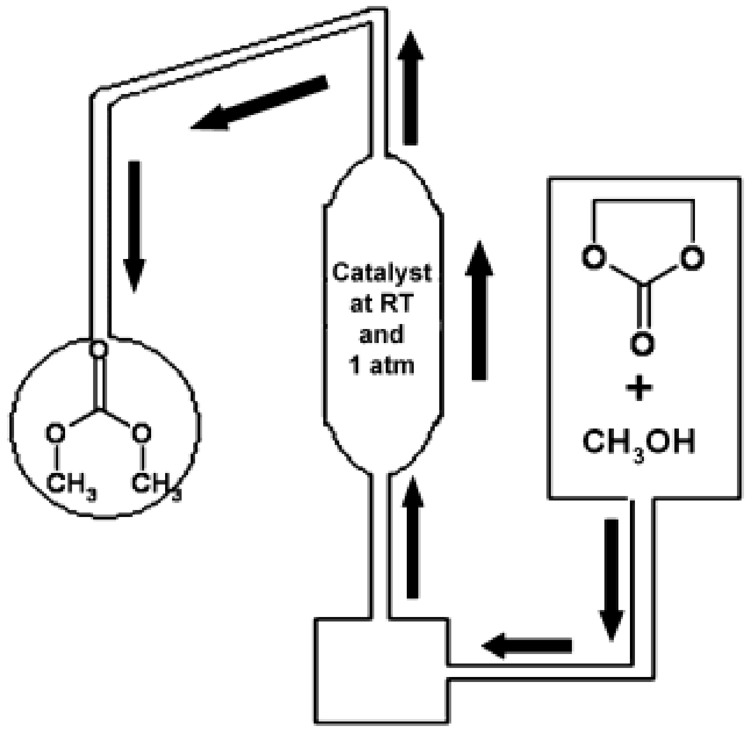
Cat. 2: zeolites exchanged with alkali or alkali earth metal ions

Transesterification of Cyclic Carbonates to Dimethyl Carbonate Using Solid Oxide Catalyst at Ambient Conditions: Environmentally Benign Synthesis

(*ChemSusChem* **2010**, *3*, 575-578)

Continuous synthesis at ambient conditions:

Dimethyl carbonate (DMC) is an important methylating and carbonylating agent. Transesterification of cyclic carbonates using methanol for the synthesis of DMC is environmentally benign. CaO–ZnO catalysts, prepared by a wet impregnation method, are effective catalysts for the transesterification of ethylene carbonate using methanol in batch and in continuous reactors. Yields of *ca.* 84 % DMC can be achieved at ambient conditions



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

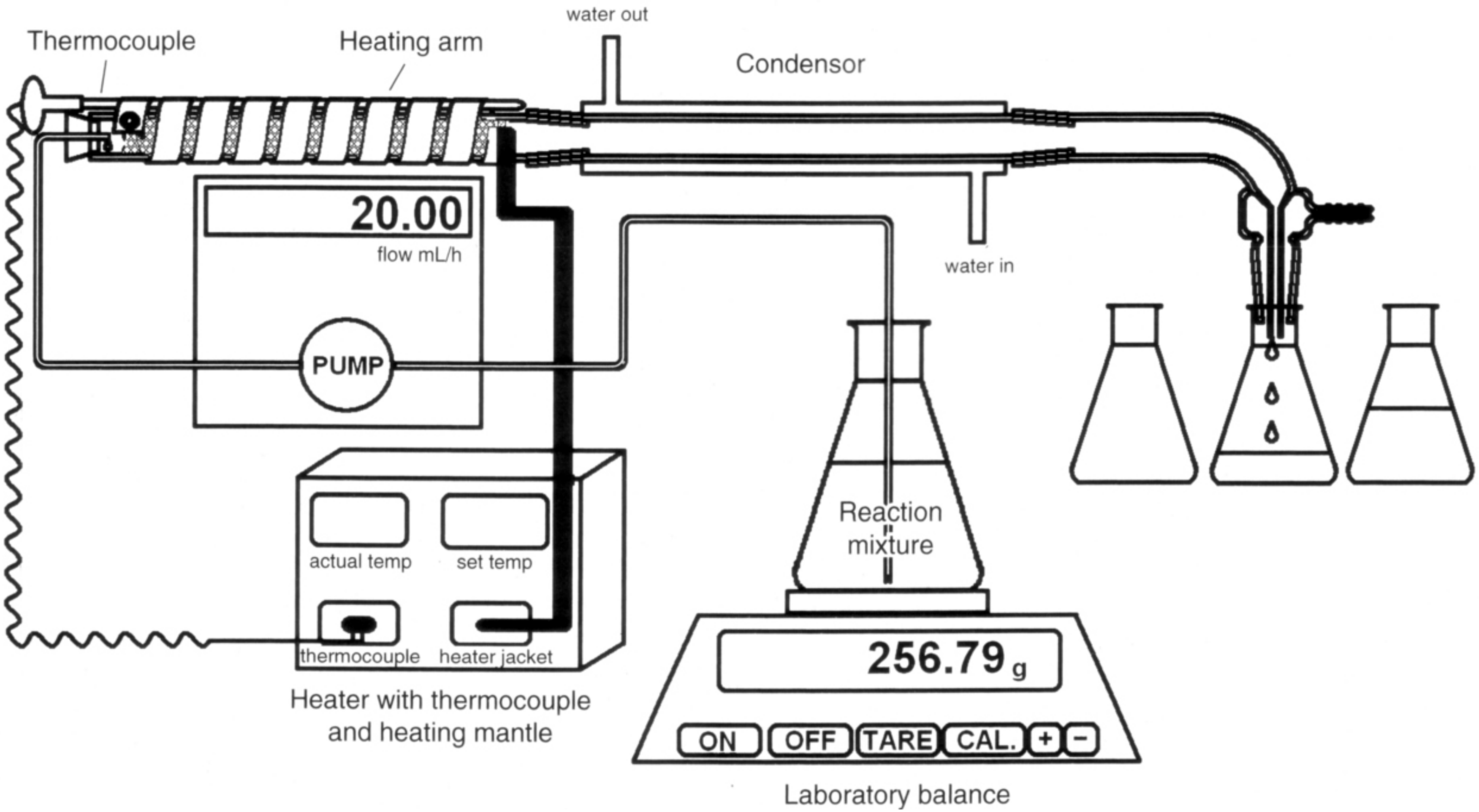
Useful methylation and alkoxycarbonylation agents

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

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

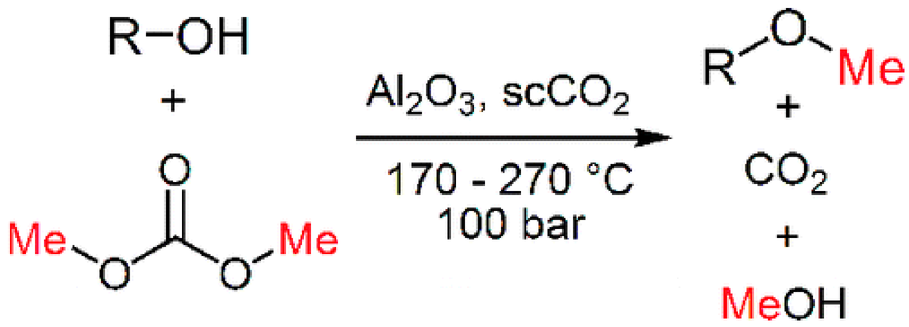
(Tundo and Selva, in *Methods and Reagents for Green Chemistry*, pp. 77-102)

Methylation of 2-naphthol using dimethyl carbonate under continuous-flow gas-phase conditions



Tundo, et al. *J. Chem. Educ.*, **2010**, *87*(11), 1233-1335

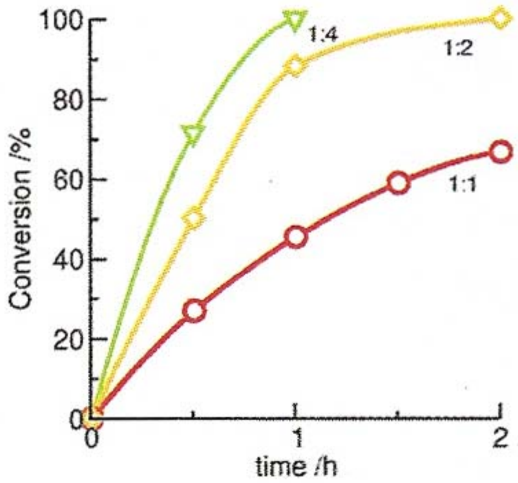
Continuous Acid-Catalyzed Methylations in Supercritical CO_2: Comparison of Methanol, Dimethyl Ether and Dimethyl Carbonate as Methylating Agents

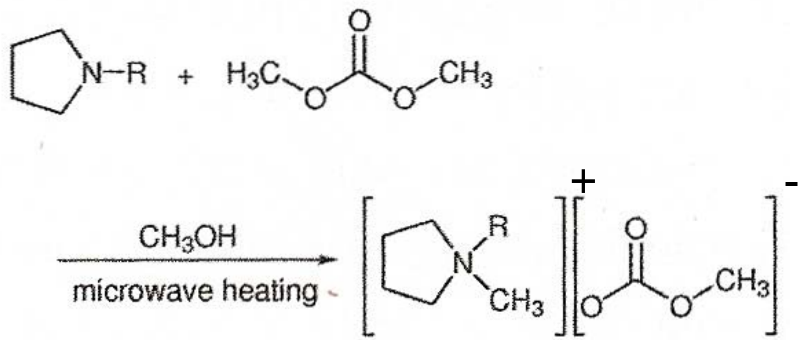


Org. Proc. Res. Dev. **2010**, *14*, 411-416
(Poliakoff and coworkers)

Optimised MW-assisted synthesis of methylcarbonate salts: a convenient methodology to prepare intermediates for ionic liquids

Holbrey, et al., *Green Chem*. **2010,** *12*, 407-410





100% yield at 130℃ for 1 hr, R = Bu

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]

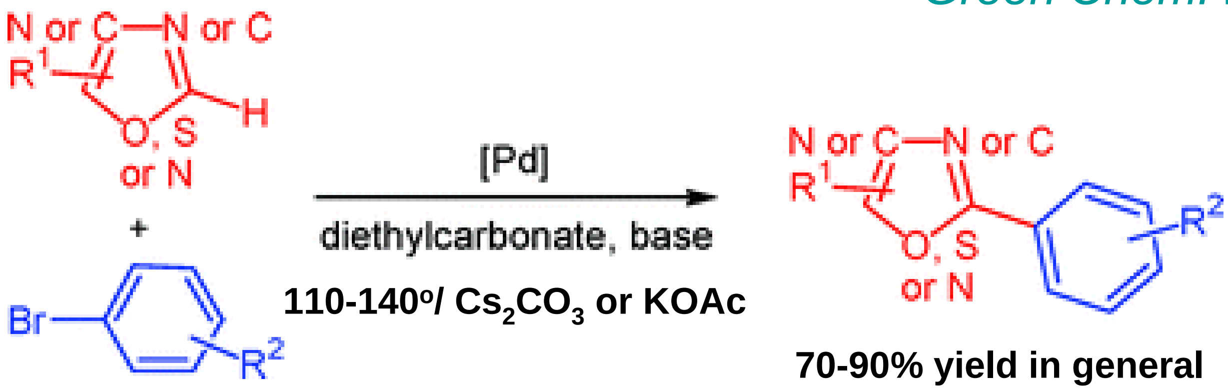
Acetone 0.320 cP

Water 0.891 cP

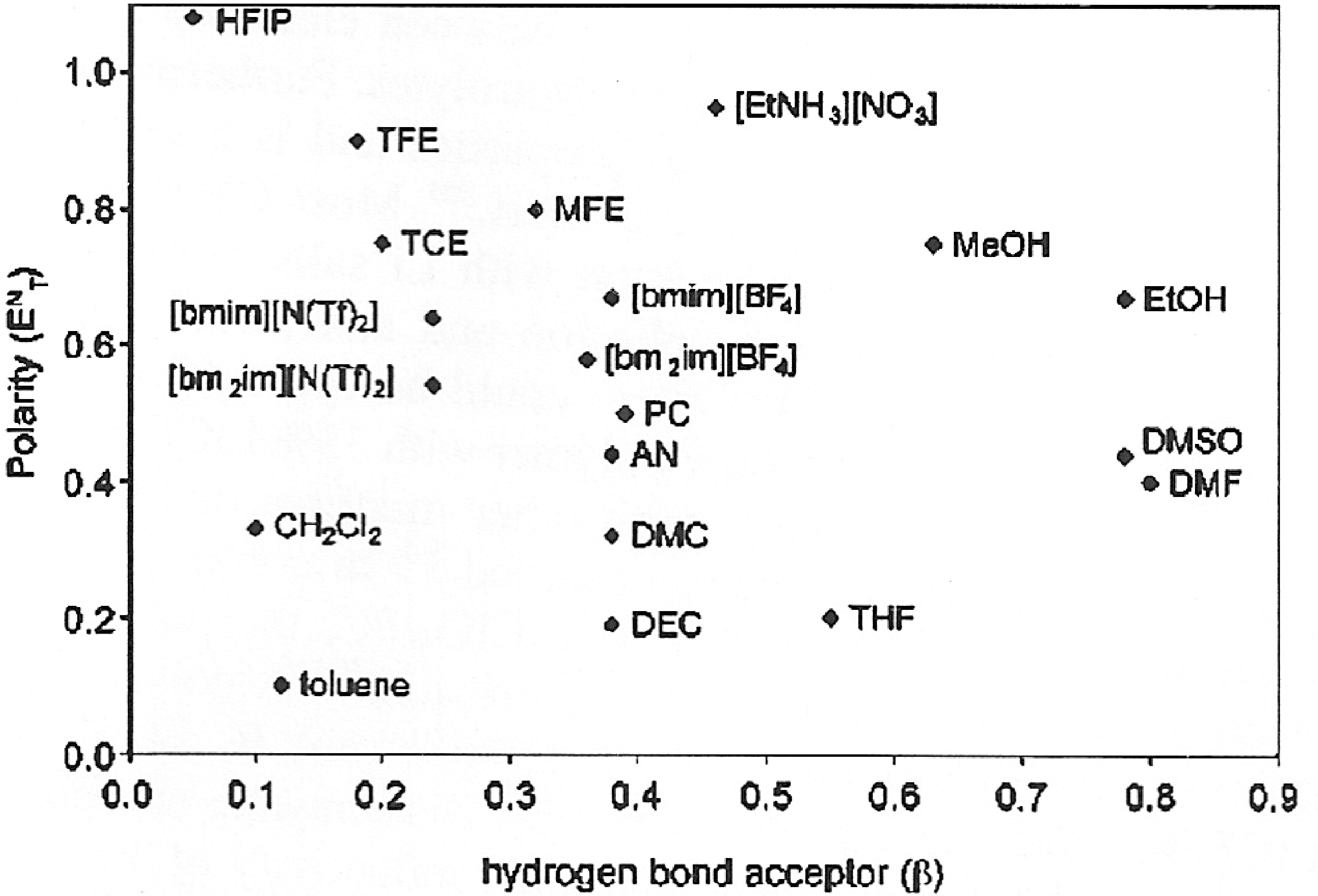
1-butanol 2.99 cP

The palladium-catalysed direct 2-, 4- or 5-arylation of a wide range of **heteroaromatics** with aryl halides proceed in moderate to good yields using the **eco-friendly solvents carbonates.**

Green Chem. **2010**, *12*, 2053-2063



Polarities and basicity of some solvents



Chem. Rev. **2010**, *110*, 4564

Organic reactions in aqueous media

Reference books and **review articles**:

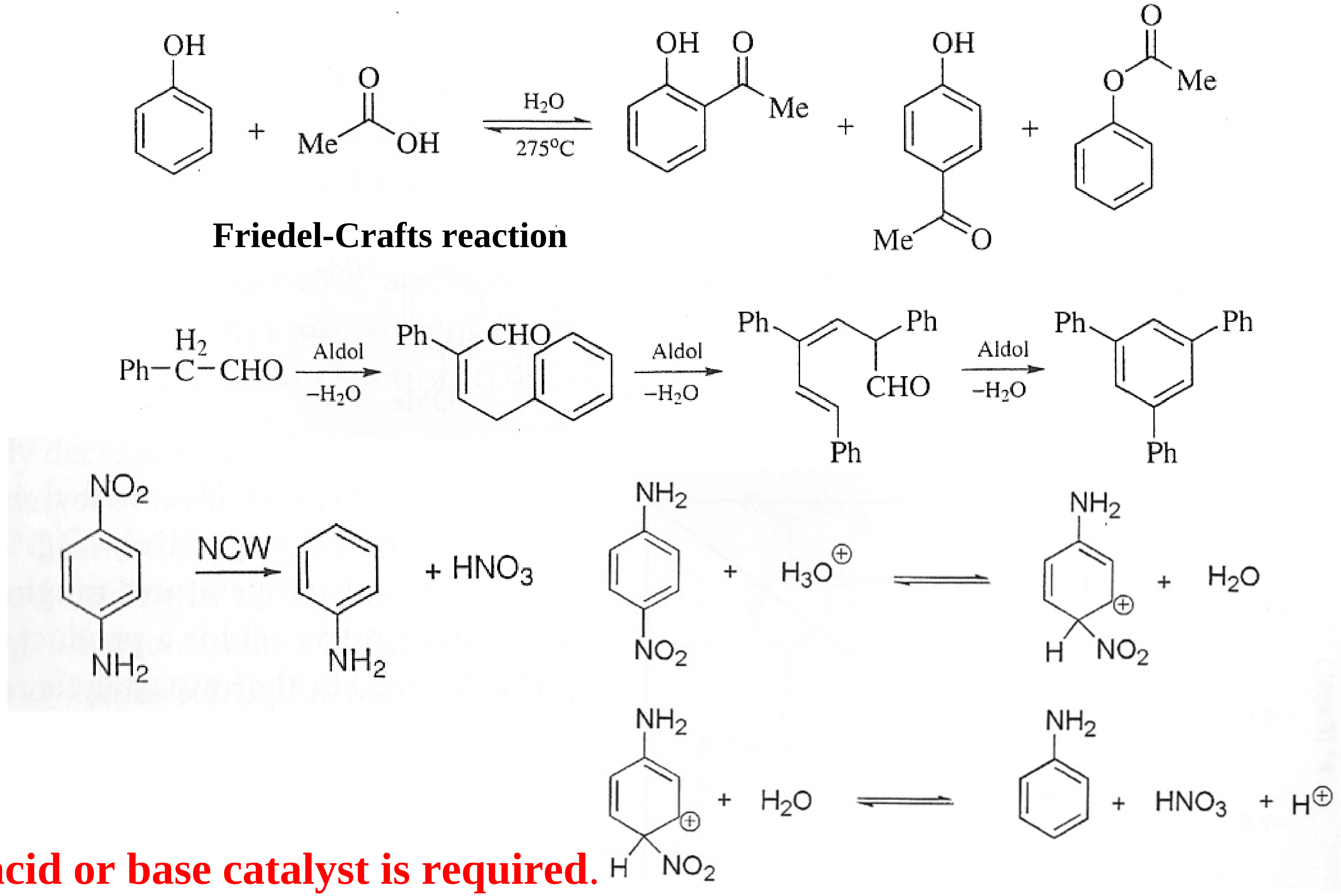
- Adams, et al., *Chemistry in Alternative Reaction Media*, **2004** , Wiley
- Lindström Ed., *Organic Reactions in Water*, **2007** , Blackwell
- Li and Chan, *Comprehensive Organic Reactions in Aqueous Media,* 2nd Ed, **2007**, Wiley
- Herrerias, *et al.*, *Chem. Rev*. **2007**, *107*, 2546-62 (Reaction of C-H)
- Dallinger and Kappe, *Chem. Rev*. **2007**, *107*, 2563-91 (MW assisted)
- Hailes, *Org. Proc. Res. Dev*. **2007**, *11*, 114-120 (general discussions)
- Kerton, *Alternative Solvents for Green Chemistry,* Chapter 3, **2009** , RSC
- Minakata and Komatsu, *Chem. Rev*. **2009**, *109*, 711-724 (on silica)
- Chanda and Fokin, *Chem. Rev*. **2009**, *109*, 725-748 (on water)
- Polshettiwan and Verma, Ed. *Aqueous Microwave Assisted Chemistry: Synthesis and Catalysis*, **2010**, RSC

Dielectric and ionization constants

	Ambient	Near-critical	Supercritical
Temperature, °C	25	275 (200-300)	400 (375)
Pressure, bar	1	60	230 (221)
Density, g per cc	1	0.7	0.1
Dielectric constant	80	20	2 (6)
Relative ionization constant[a]	1	1,000	<0.01

[a] K_w/K_w(25℃)

Reactions in near-critical water (NCW)

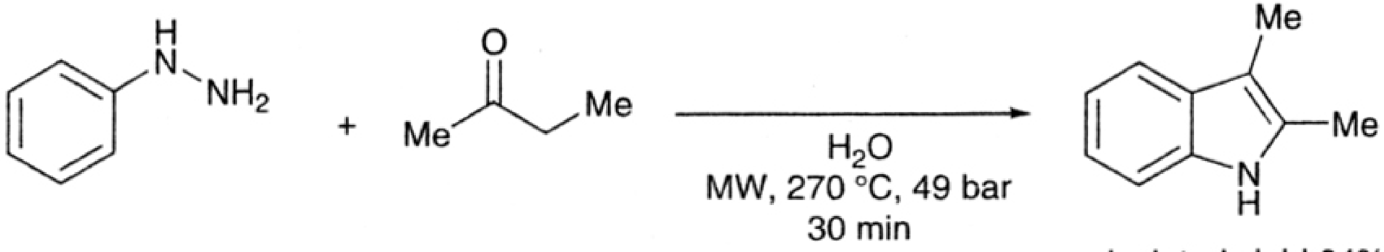


No acid or base catalyst is required.

Also for other hydrolysis, hydration, elimination, rearrangement, etc

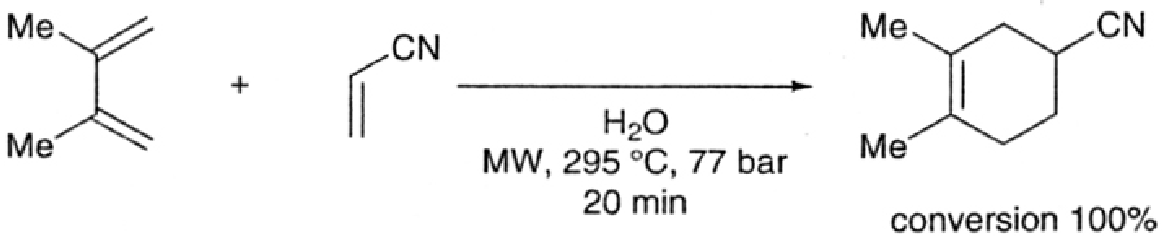
Some microwave assisted reactions at NCW

Fischer indole synthesis



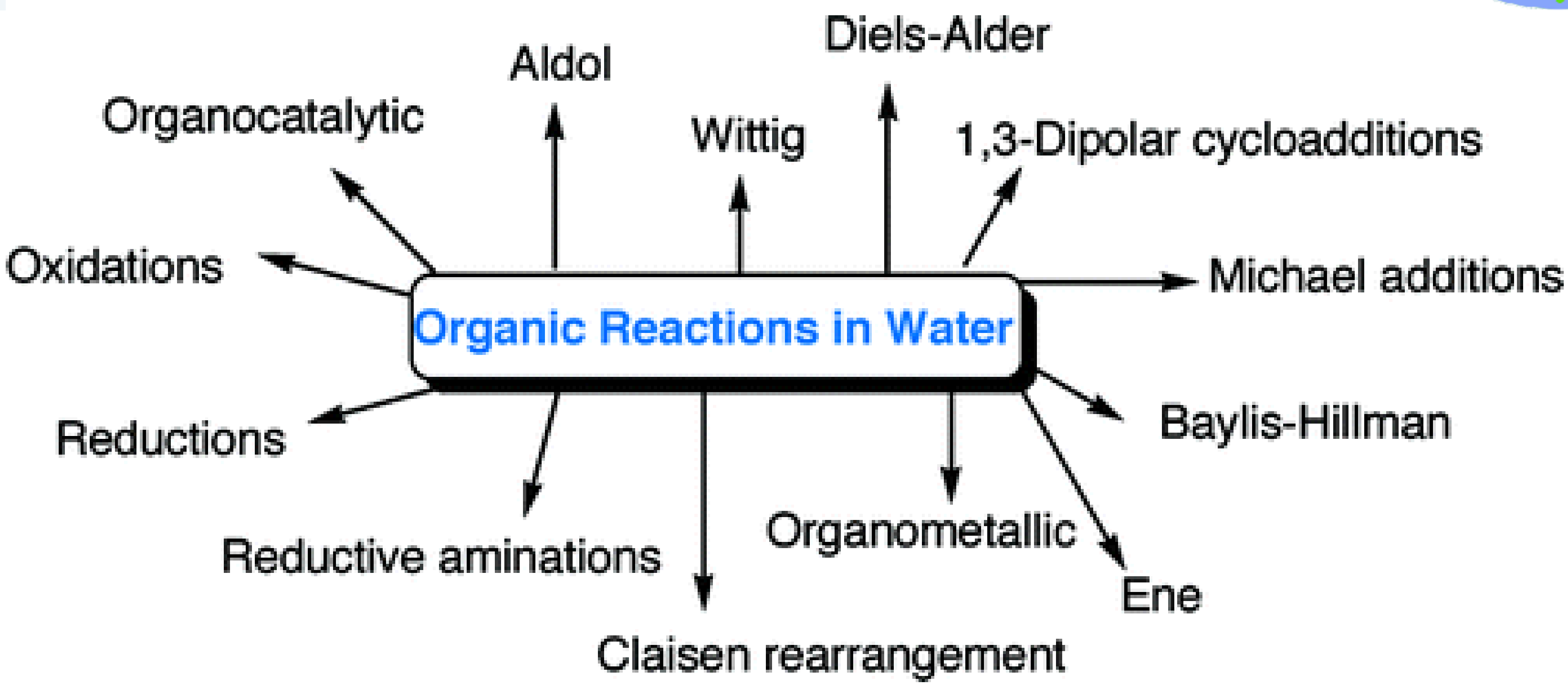
isolated yield 64%
(column chromatography, CH_2Cl_2)

Diels-Alder reaction



conversion 100%
isolated yield 65%
(extraction, Et_2O
chromatography, CH_2Cl_2)

(Kerton, p. 88)



Hailes, *Org. Process Res. Dev*. **2007,** *11*, 114-120

This short review focuses on the potential use of water as a reaction solvent, highlighting advantages and the range of reactions that can be carried out in water.

Hydrophobic Effects

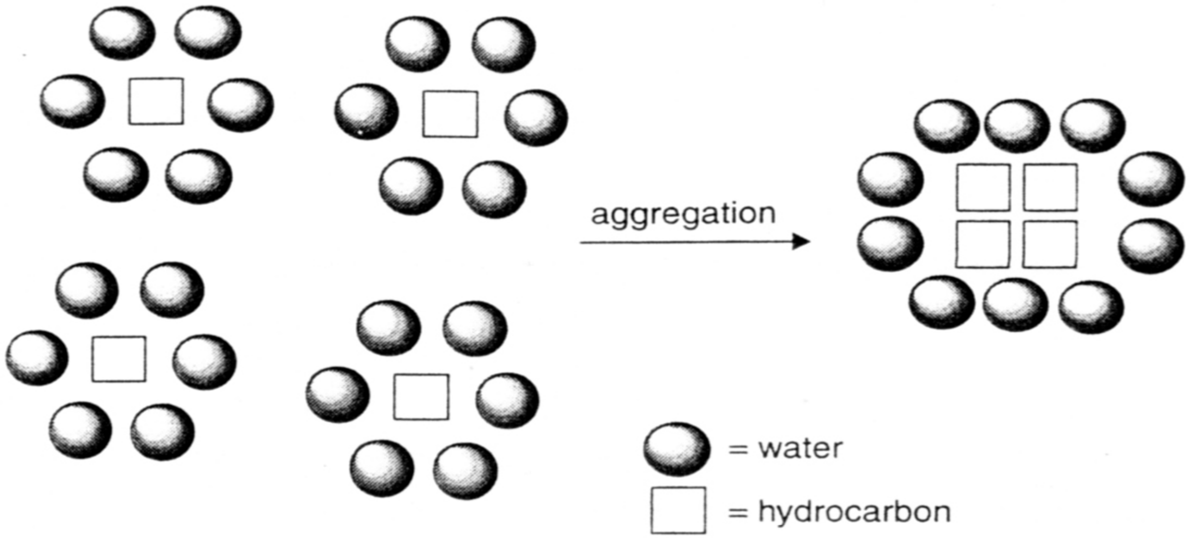
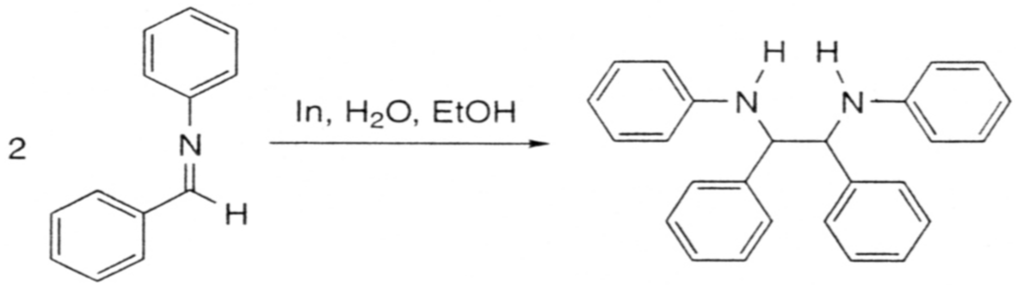


Figure 5.5 The hydrophobic effect. Aggregation of hydrocarbon molecules in water reduces the number of molecules with restricted motion

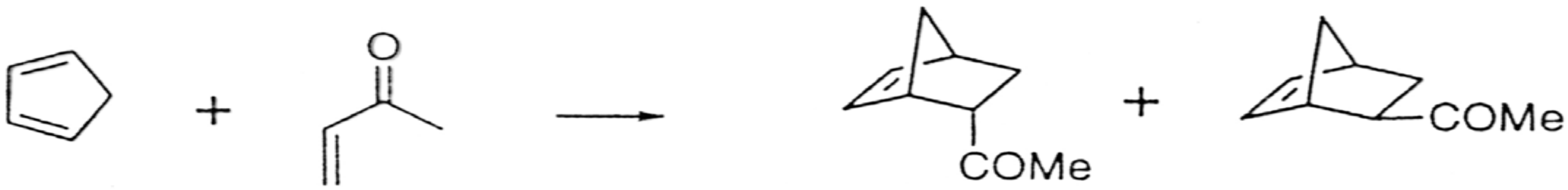


Scheme 5.1 Indium mediated imine coupling

(Adams, p.101)

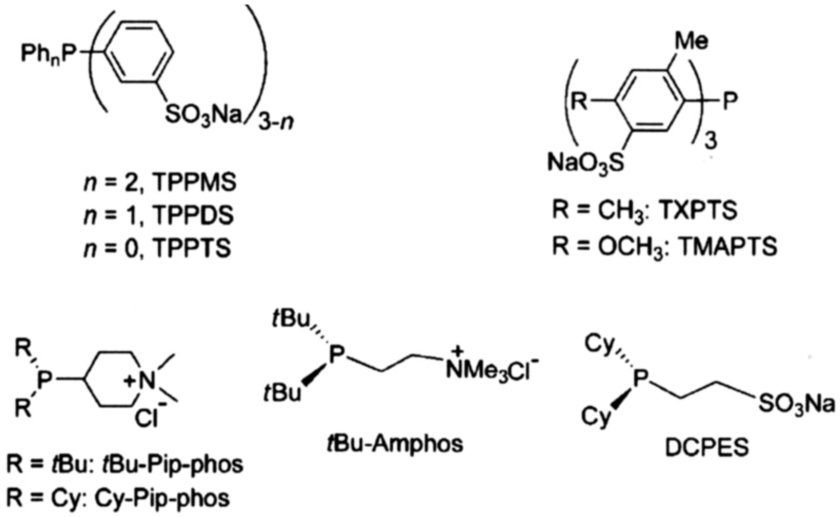
Diels-Alder Reaction

Enhanced Selectivity and Reactivity

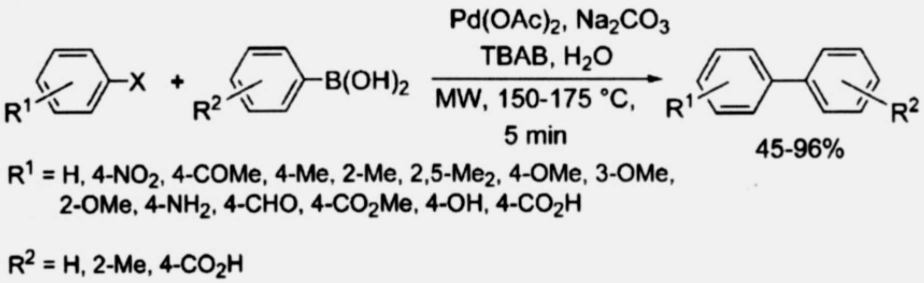


solvent	kinetics 10^5 k ($M^{-1}s^{-1}$)	selectivity endo/exo ratio
isooctane	5.94[a]	
methanol	75.5[a]	8.5[c]
formamide	318[b]	8.9[b]
ethylene glycol	480[b]	10.4[b]
water	4400[a]	25[d]
water (LiCl 4.86 M)	10800[a]	28[d]
water ($(NH_2)_3CCl$ 4.86 M)	4300[a]	22[d]
β-cyclodextrin (10 mM)	10900[a]	
α-cyclodextrin (10 mM)	2610[a]	

Suzuki–Miyaura Cross-Coupling Reactions in Aqueous Media: Green and Sustainable Syntheses of Biaryls



Scheme 2. Water-soluble phosphine ligands employed in Suzuki–Miyaura reactions.



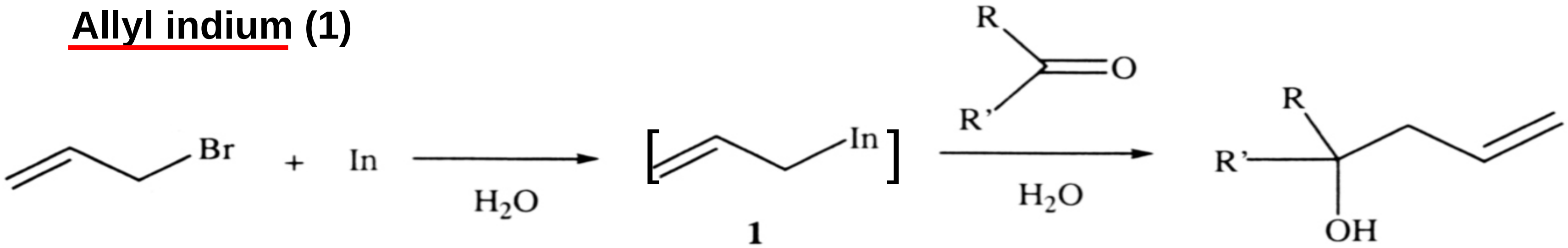
Scheme 29. Microwave-mediated Suzuki–Miyaura coupling in water using $Pd(OAc)_2$.

Suzuki–Miyaura reactions are among the most widely used protocols for the formation of carbon–carbon bonds. These reactions are generally catalyzed by soluble palladium complexes with various ligands. However, the use of toxic organic solvents remains a scientific challenge and an aspect of economical and ecological relevance. This review will summarize various recently developed significant methods by which the Suzuki–Miyaura coupling was conducted in aqueous media, and analyzes if they are "real green" protocols.

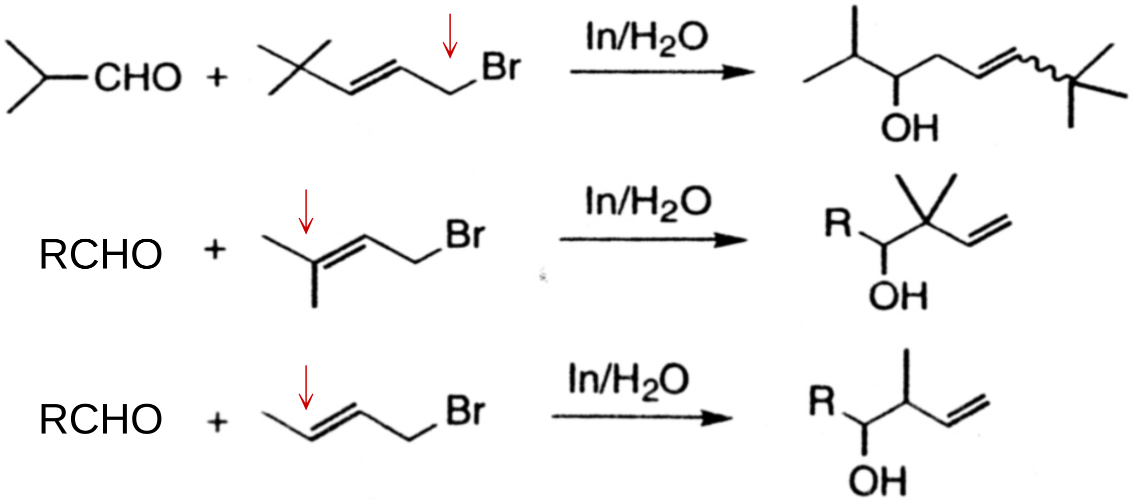
(*ChemSusChem* **2010**, *3*, 502–522)

Grignard-type Reactions

Allyl indium (1)

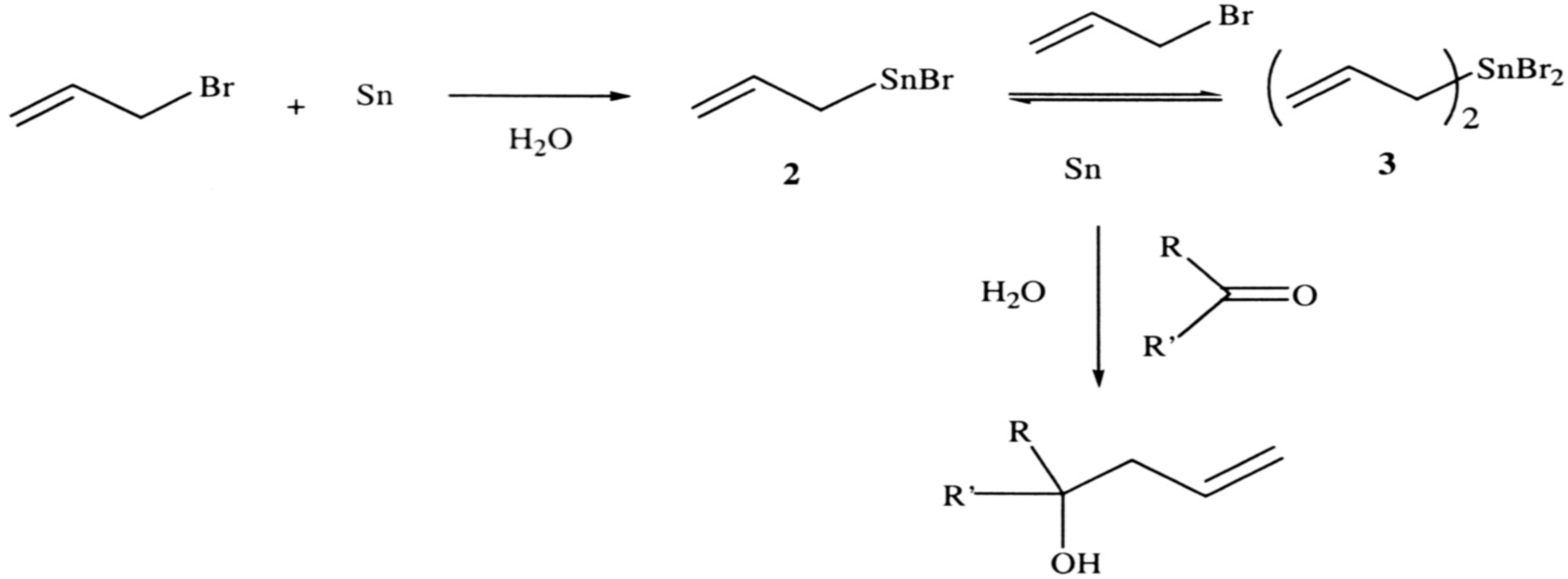


Indium has low first ionization potential (5.70 eV), and is not sensitive to water or base.
The regioselectivity is governed by the bulkiness of the substituent on the C=C.

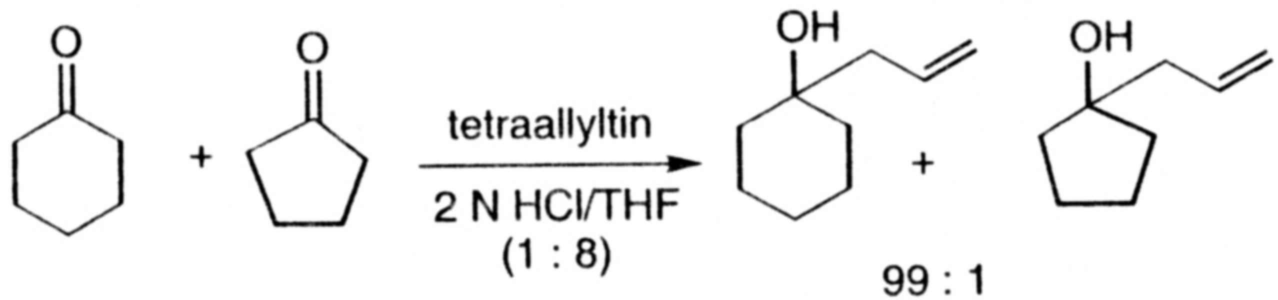


Grignard-type Reactions

Similarly, in the tin-mediated allylation reaction, allyltin intermediates are generated (13). Both allyltin(II) bromide (**2**) and diallyltin(IV) dibromide (**3**) are formed, and can be observed by NMR in the aqueous media (Scheme 3).



High chemoselectivity



99 : 1

Organic Reactions on Silica in Water

Minakata and Komatsu, *Chem. Rev*. **2009**, *109*, 711-724

Heterogenization of homogeneous catalytic reaction allows for the facile recovery and recycling of catalysts. Two basic approaches have been developed.

1. Immobilization of catalysts on silica supports in a water-only phase.
2. To employ a biphasic system:

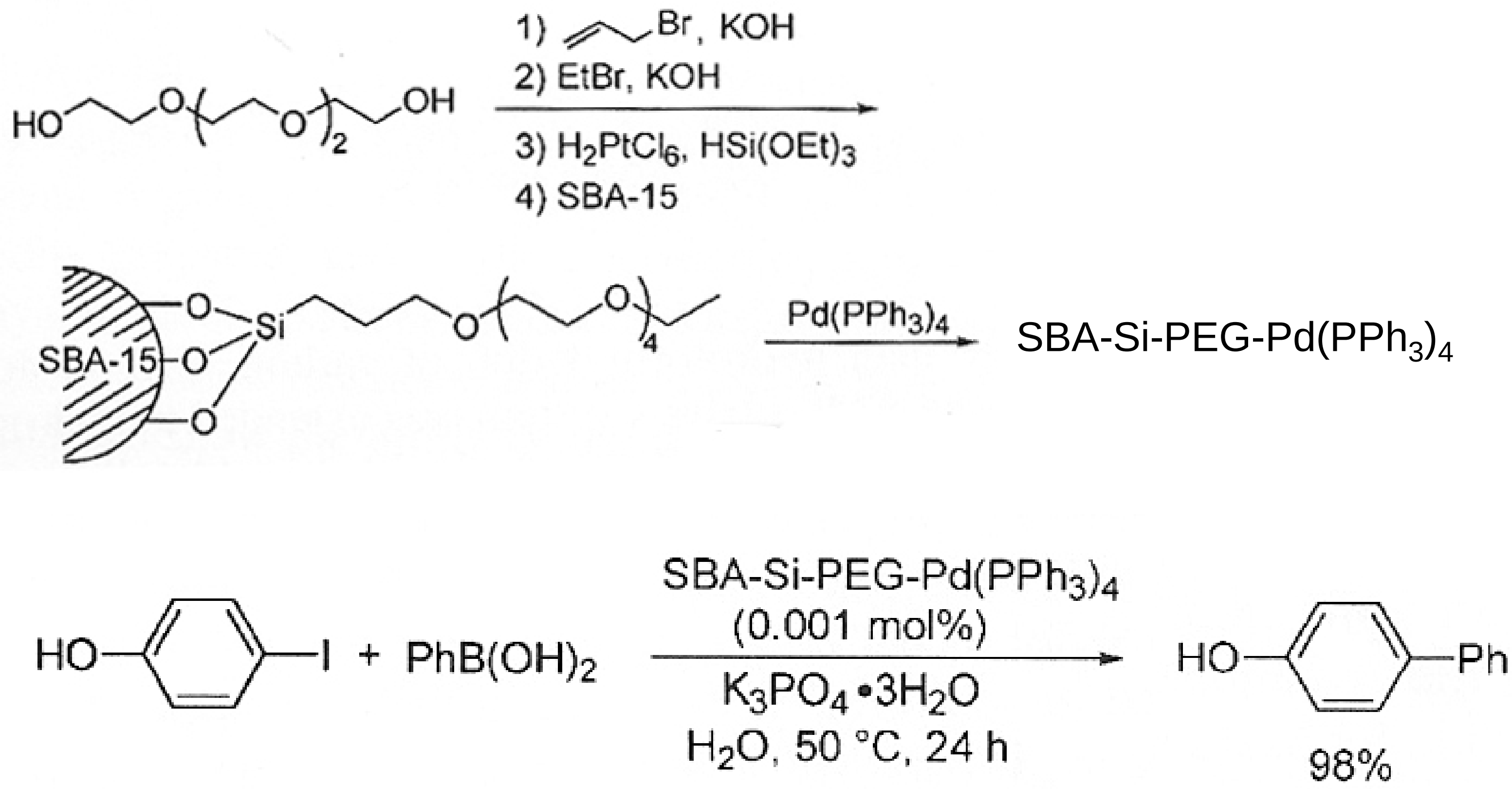
   Water – organic solvent

   Water – ionic liquid

   Fluorous reverse-phase silica and water

Silica without modification is also generally used.

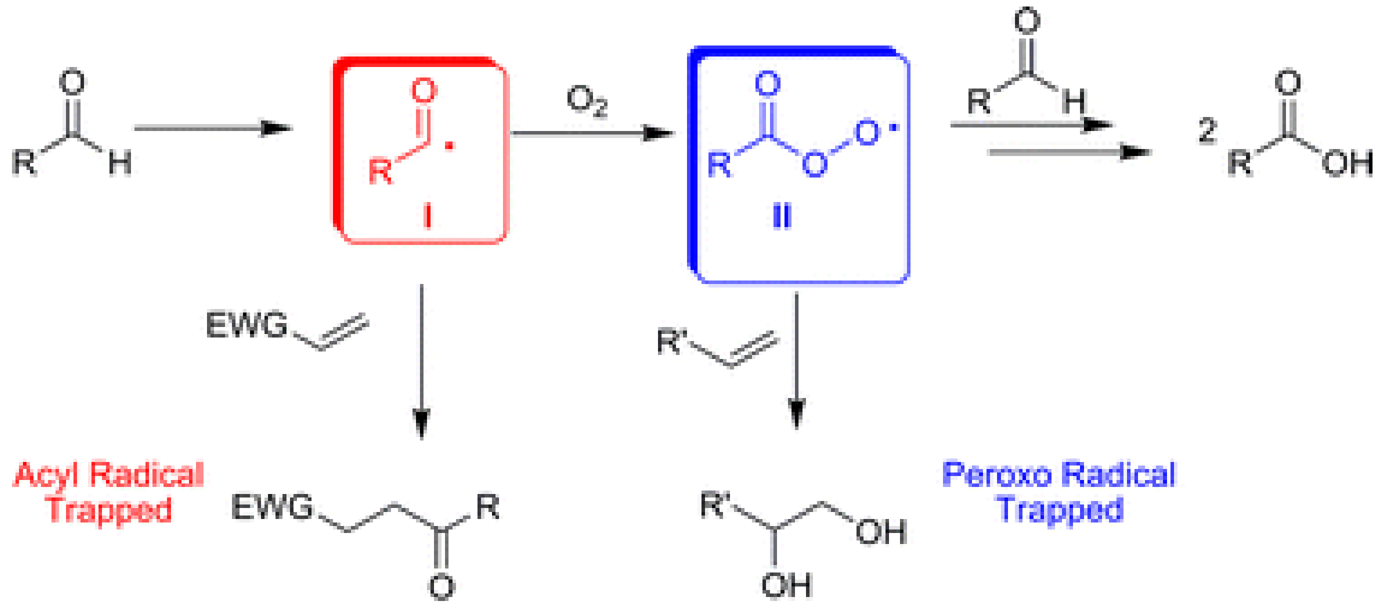
Mesoporous Silica-supported catalyst and Suzuki Coupling



Straightforward radical organic chemistry in neat conditions and on water

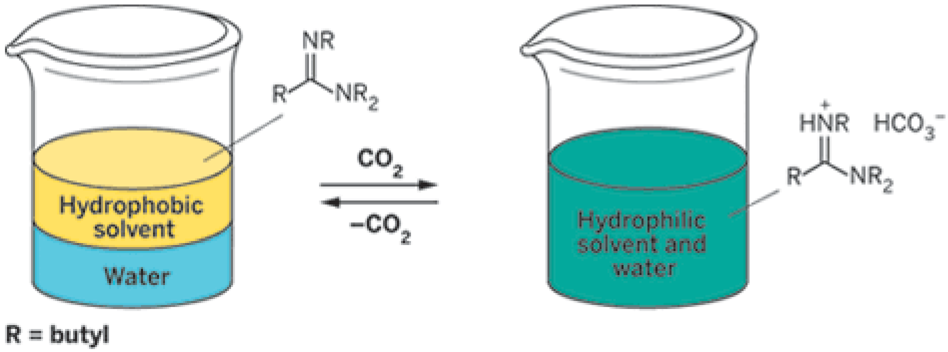
Shapiro et al., *Green Chem.*, **2010**, *12*, 582 - 584

Radicals generated during aldehyde oxidation to carboxylic acids can be efficiently trapped under environmentally friendly conditions, either in neat conditions or "on water."

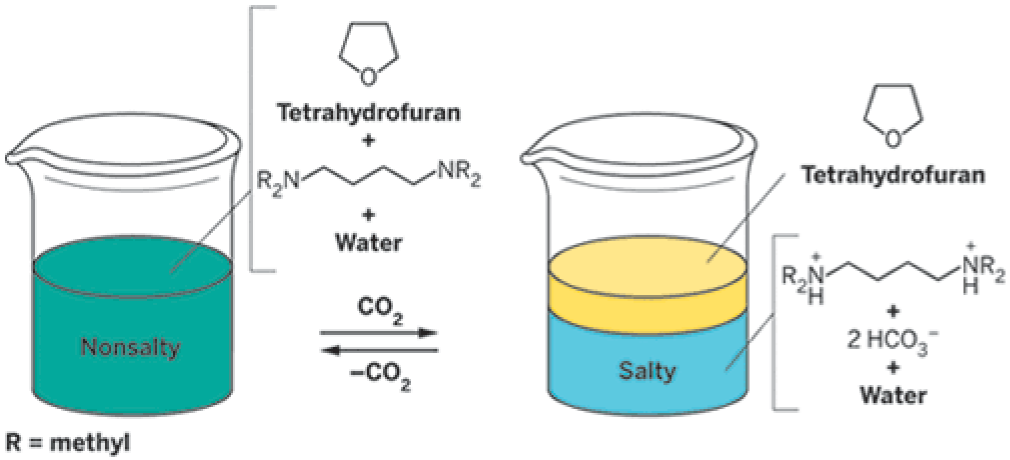


Switchable Water: Aqueous Solutions of Switchable Ionic Strength

Mercer and Jessop, *ChemSusChem* **2010**, *3*, 467-470



Switchable hydrophilicity solvent

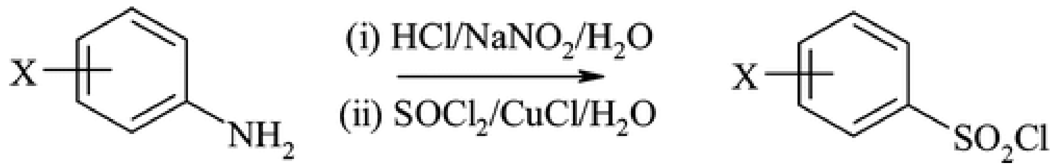


Switchable water

Aqueous Process Chemistry

The Preparation of Aryl Sulfonyl Chlorides

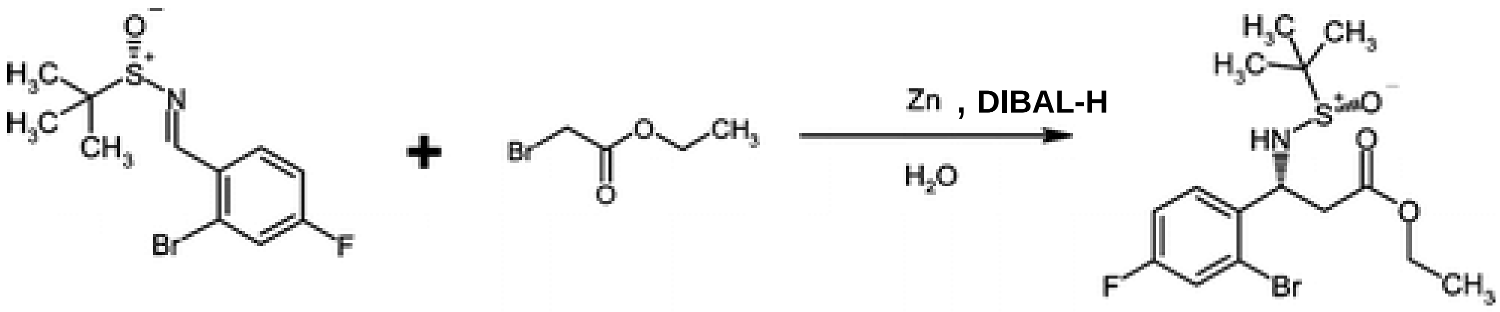
Hogan and Cox, *Org. Proc. Res. Dev.*, **2009**, *13*, 875–879



The method has been shown to be successful for a wide range of electron-deficient and electron-neutral aryl substrates., which results in their direct precipitation from the reaction mixture in >70% yields. **The aqueous process can be readily scaled up and has significant environmental benefits.**

A Scalable Zinc Activation Procedure Using DIBAL-H in a Reformatsky Reaction

Girgis, et al., *Org. Proc. Res. Dev.*, **2009**, *13*, 1094–1099



1 **2** **3**

Chemicals from renewable feedstocks

Monographs:

Renewable Resources and Renewable Energy, Ed. M Graziani and P. Fornasiero, CRC Press, **2007**

Catalysis for Renewables, Ed. G. Centi and R. A. van Santen, Wiley-VCH, **2007**

Introduction to Chemicals from Biomass, Ed. J. Clark and F. Deswarte, Wiley, **2008**

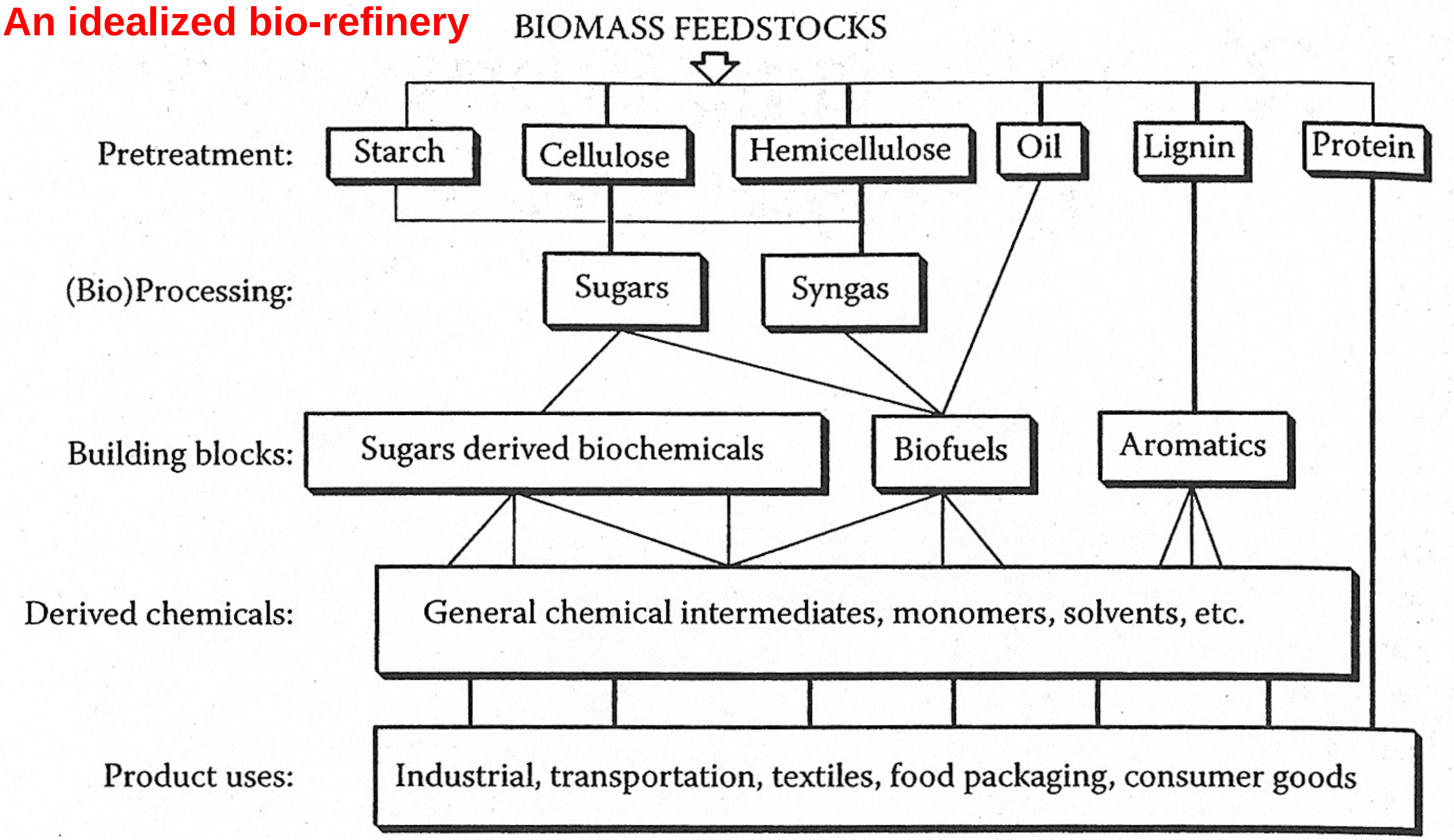
Review articles:

- *Chem. Rev*. **2007**, *107*, 2411-2502 (general)
- *Chem. Soc. Rev*. **2007**, *36*, 1788-1802 (polymers)
- *Green Chem*. **2008**, *10*, 13-30 (glycerol)
- *Chem. Soc. Rev.* **2008**, *37*,527-549 (glycerol, commodity chemicals)
- *Chem. Rev*. **2008**, *108*, 5253-5277 (glycerol, withdrawn Mar. 2010)
- *Green Chem*. **2009**, *11*, 13-26 (succinic acid)
- *ChemSusChem* **2009**, *2*, 1072-1095(myrcene)
- *Helv. Chim. Acta* **2009**, *92*, 1673-1719 (Monterpenes, thermal rearrangement)
- *Green Chem*. **2010**, *12*, 539-554 (biorefinery carbohydrates)
- *Chem. Rev*. **2010**,*110*, 3552-3599 (lignin)
- *Green Cnem*. **2010**,*12*, 1127-1138 (glycerol as solvents)
- *ChemSusChem.* **2010**, *3*, 1227-1235 (lignin)

Renewable resources:

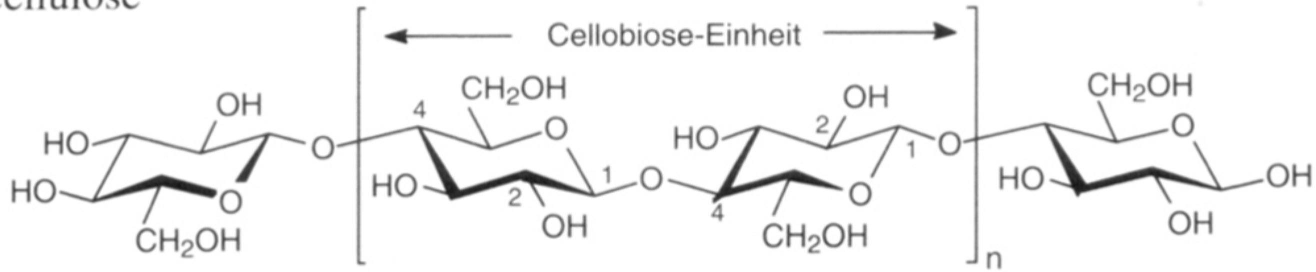
Carbohydrates (sugar, starch, cellulose, etc.), 75%
Lignin, 20%
Fats and oils, proteins, terpenes, etc., 5%

An idealized bio-refinery



Carbohydrates

Cellulose



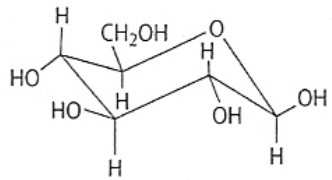
β**-1,4'-glycosidic linkage**

starch

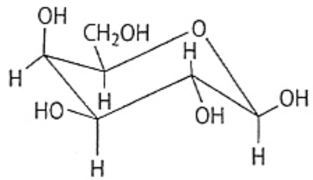
α**-1,4'-glycosidic linkage**

Hemicellulose (containing xylose, arabinose, glucose, etc.)

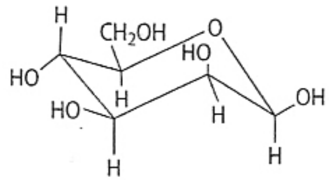
Sucrose (glucose and fructose)



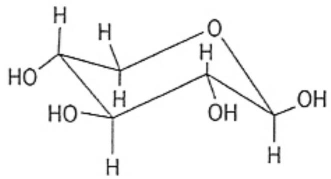
Glucose



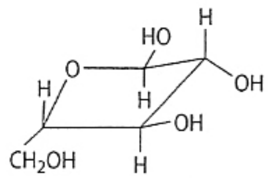
Galactose



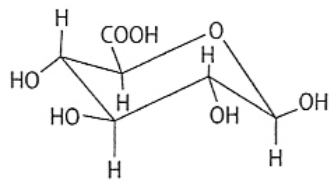
Mannose



Xylose



Arabinose

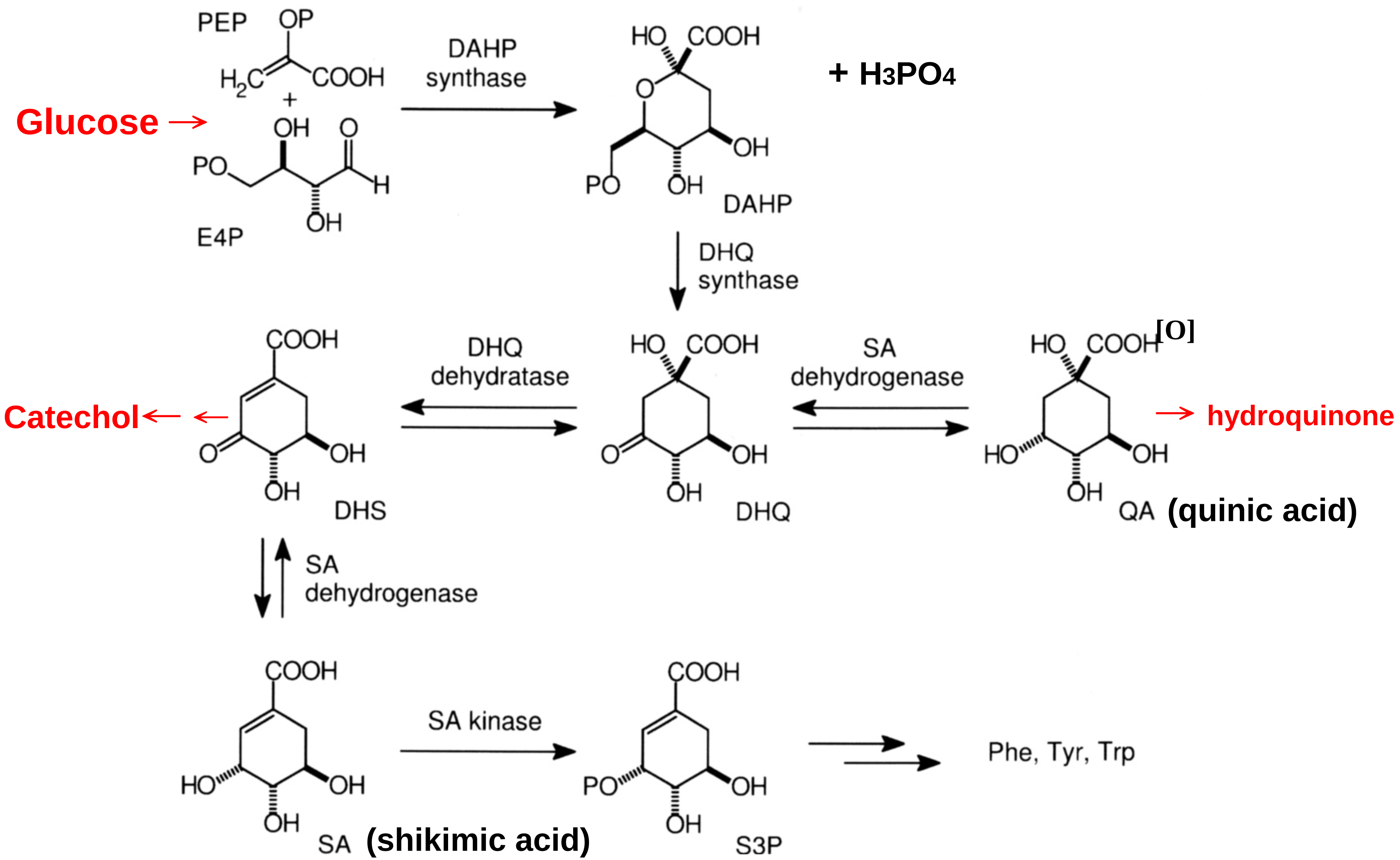


Glucuronic acid

醣類發酵產生乙醇：e.g. $C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH$(ethanol) $+ 2CO_2$

Sorbitol, Xylitol $C_5H_{12}O_5$, $HOCH_2(CHOH)_3CH_2OH$ isomers

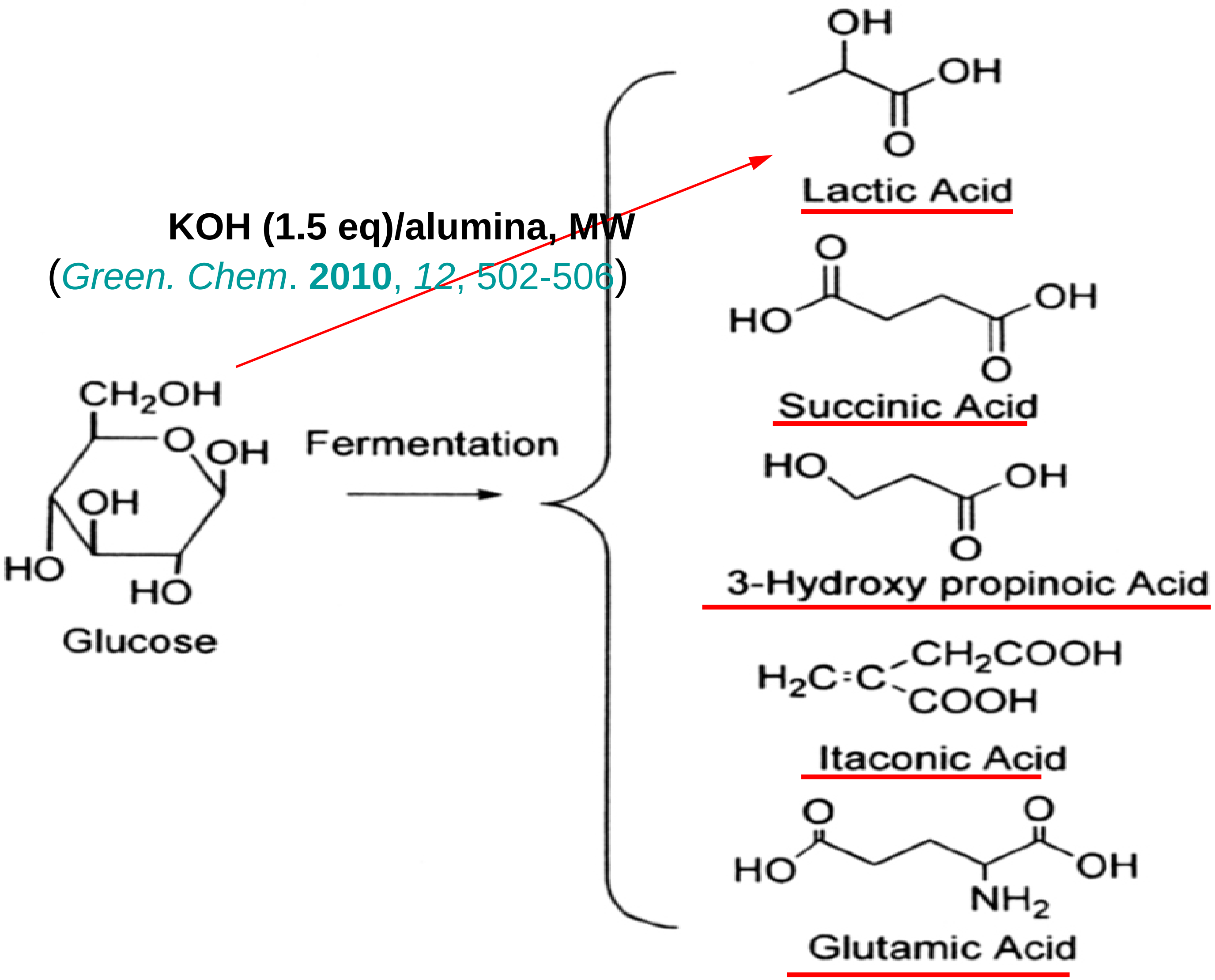
Glucose to other chemicals



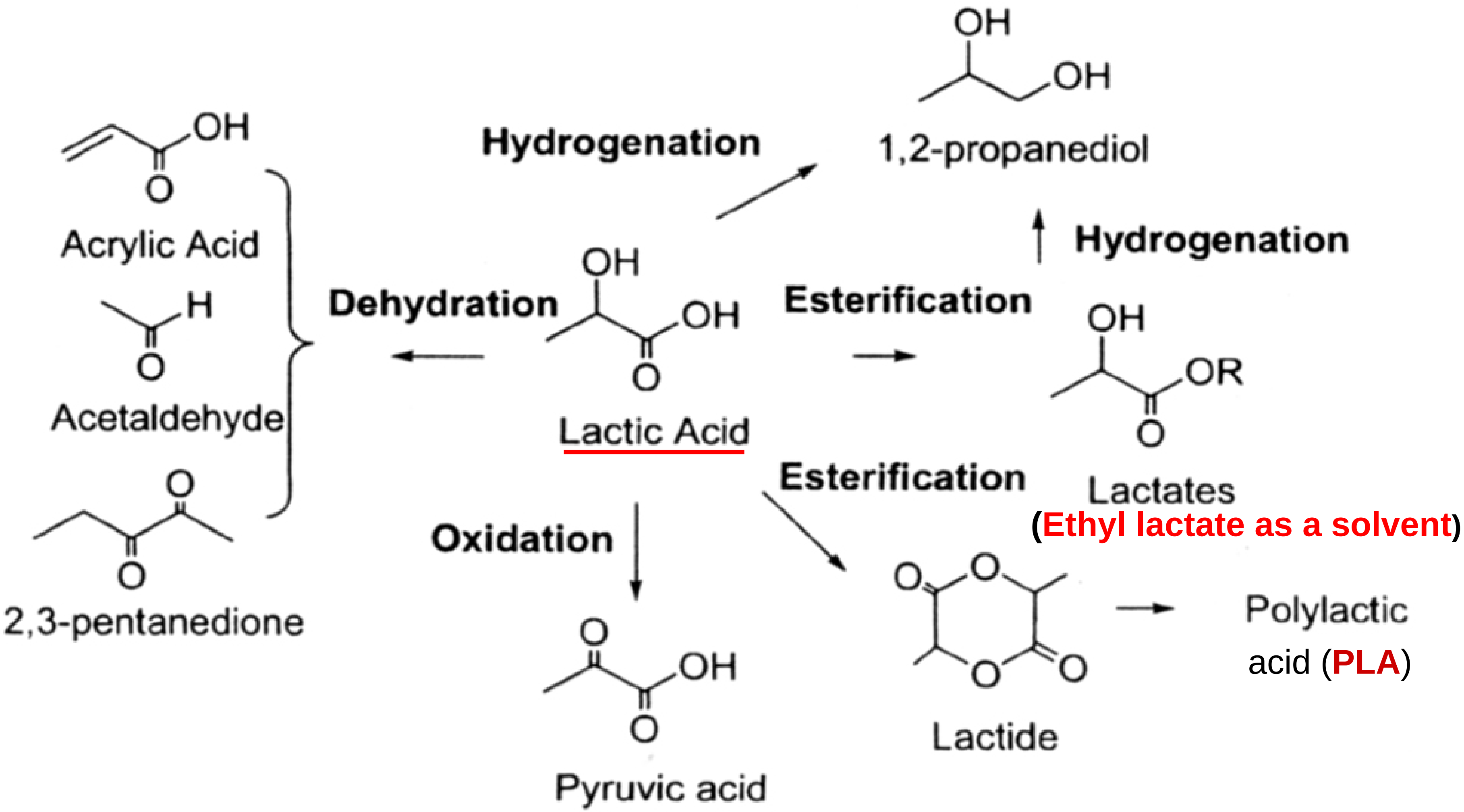
Darths and Frost (MSU), PGCC Award, 1998

More from fermentation of glucose

KOH (1.5 eq)/alumina, MW
(*Green. Chem.* **2010**, *12*, 502-506)

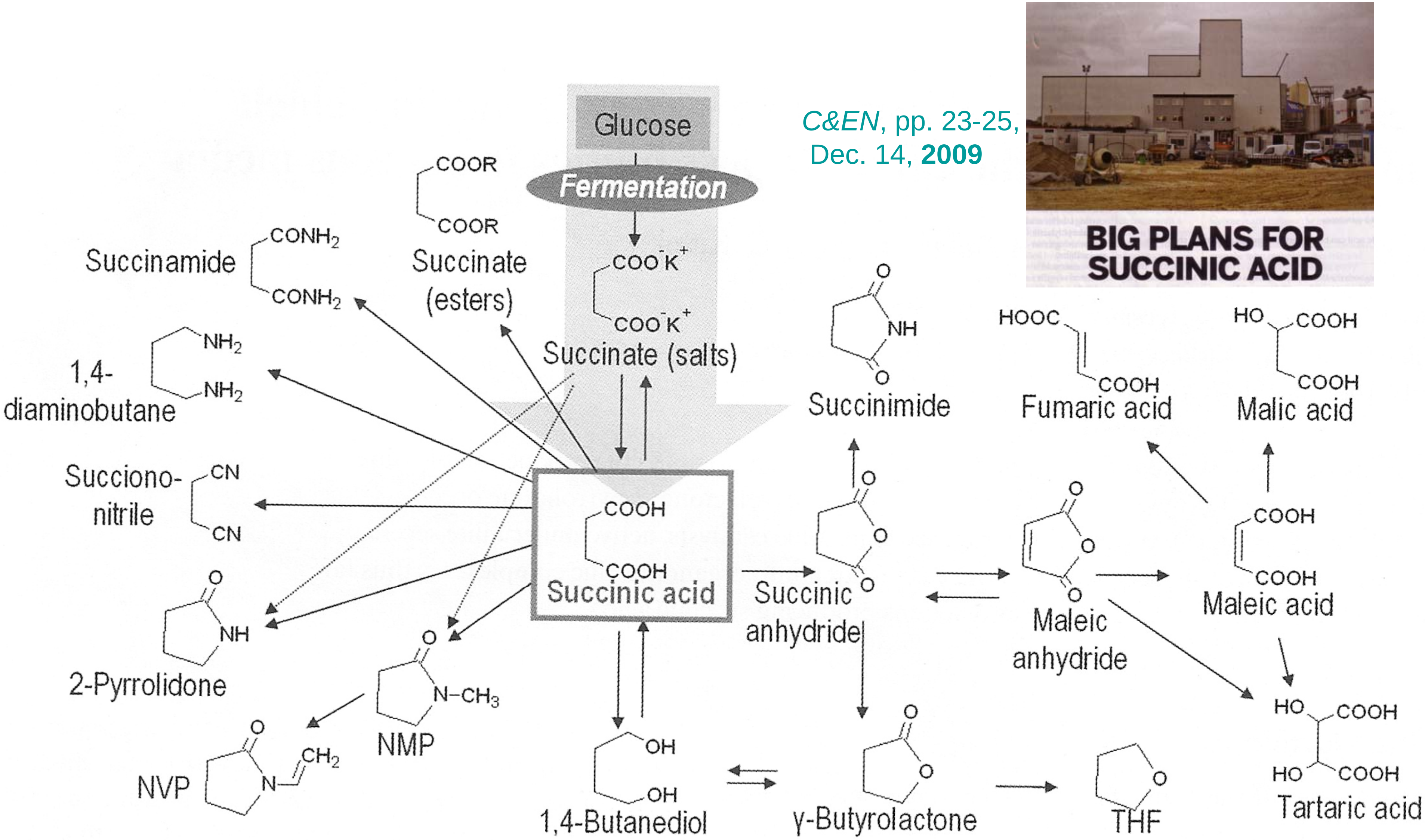


Important chemicals from lactic acid



Succinic acid as C-4 building block

C&EN, pp. 23-25, Dec. 14, **2009**



Green Chem. **2009**, *11*, 13-26

Top chemical opportunities from carbohydrates

DOE(USA, 2004)	Bozell and Peterson (suggested 2010)
Succinic, fumaric and malic acids	Ethanol
2,5-Furandicarboxylic acid (FDCA)	Furans (Furfural, HMF, FDCA)
3-Hydroxypropionic acid	Glucerol and derivtives
Aspartic acid	Biohydrocarbons (including isoprenes)
Glucaric acid	Lactic acid
Glutamic acid	Succinic acid
Itaconic acid	Hydroxypropionic acid/aldehyde
Levulinic acid	Levulinic acid
3-Hydroxybutyrolactone	Sorbitol
Glycerol	Xylitol
Sorbitol	
Xylitol	

Green Chem. **2010**, *12*, 539-554

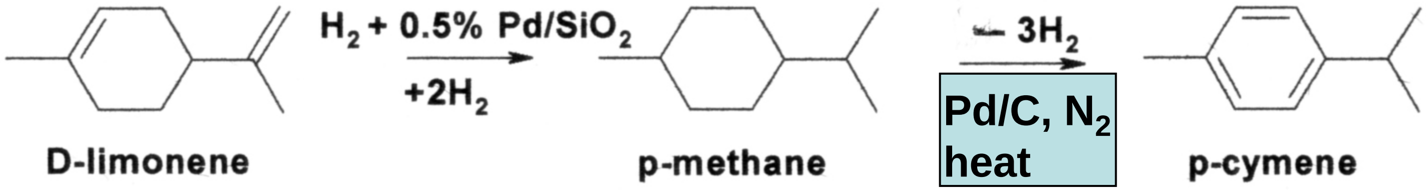
Inexpensive terpenes to useful chemicals

Limonene

- **a by-product of the juice industry (ca 50000 tpa)**
- **a good solvent to replace xylene in medical application**
- **to give *p*-cymene by hydrogenation and dehydrogenation**

***p*-cymene**

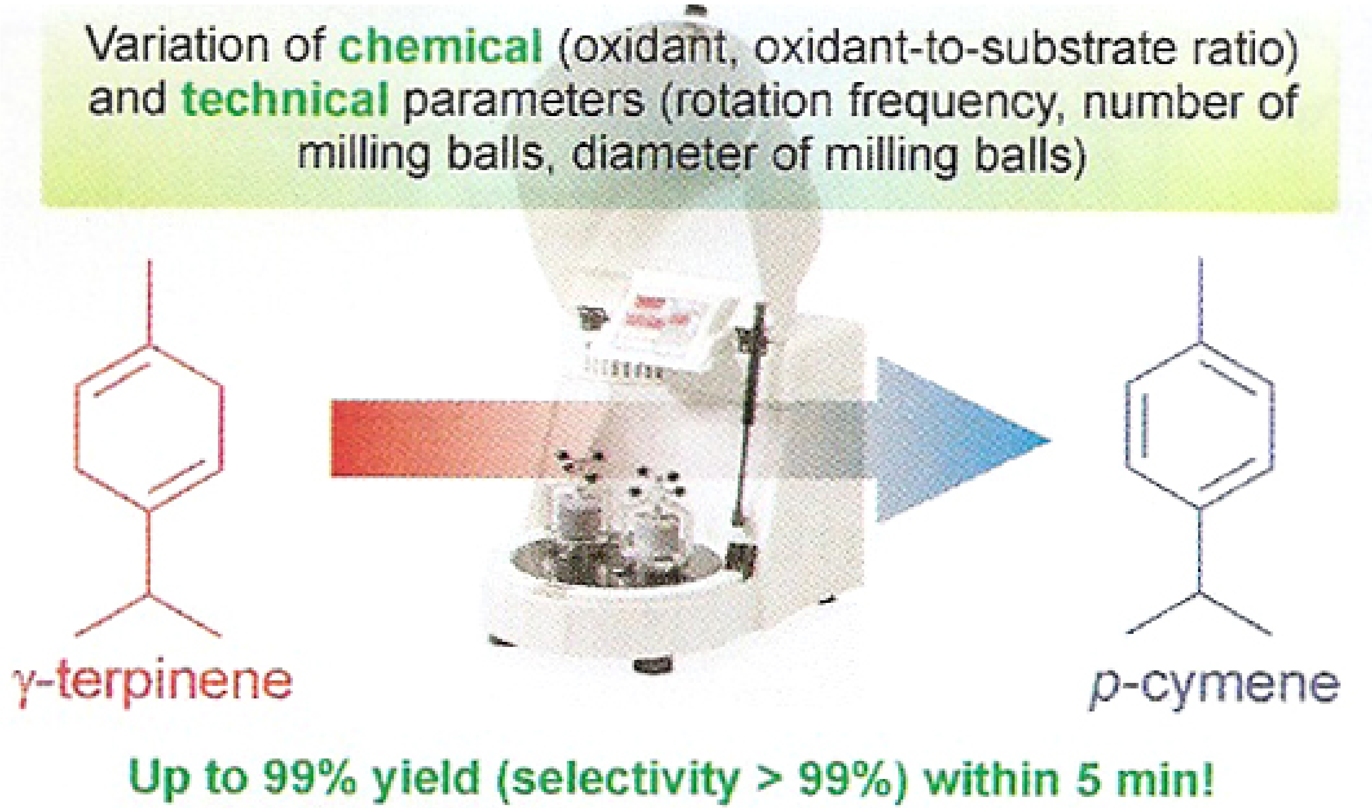
- a solvent
- an important intermediate chemical in the fragrance industry
- an intermediate **(to terephthalic acid)**
- a *p*-cresol intermediate
- a raw material for synthesis of non-nitrated musks



1,8-Cineole (eucalyptus oil) Pd/gamma-alumina at 250°C → p-cymene + H_2
(*Green Chem*. **2010**, *12*, 70-76)

Solvent-free dehydrogenation of γ-terpinene in a ball mill: investigation of reaction parameters

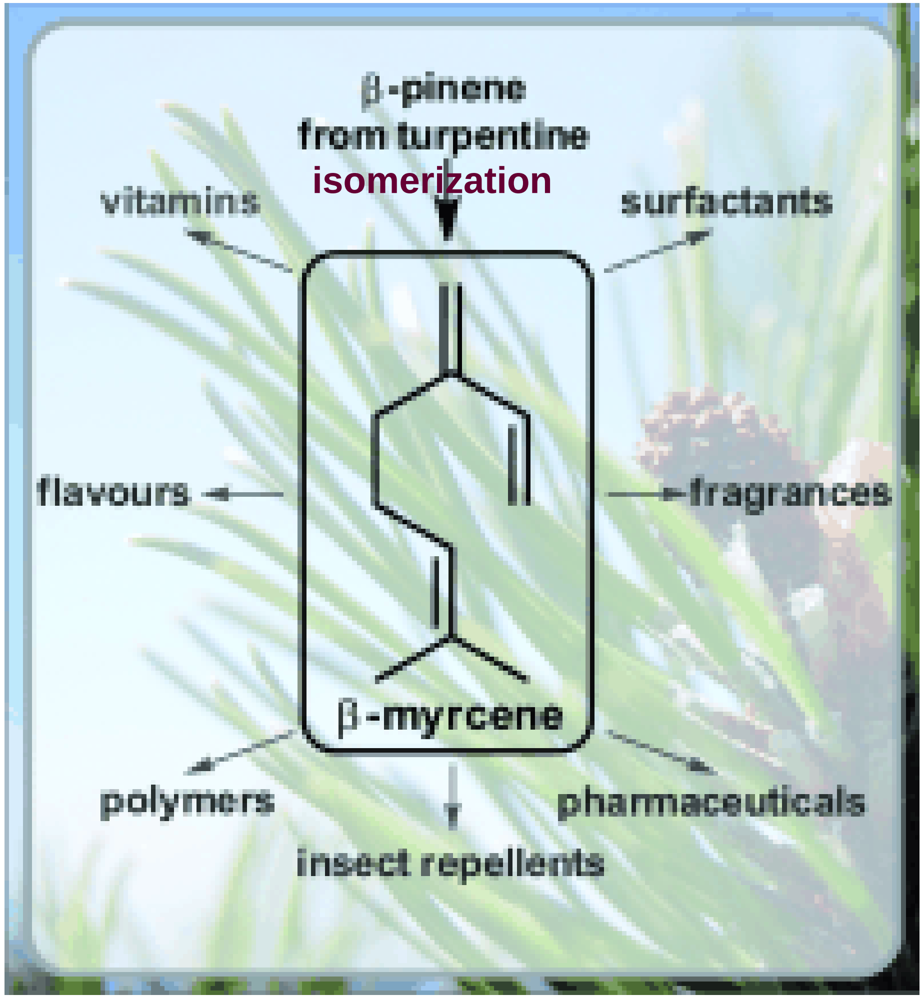
(Stolle, Ondruschka, *et al. Green Chem*. **2010**, *12*, 1288-1294)



$KMnO_4$ or $NaIO_4$
Alumina, 800 rpm

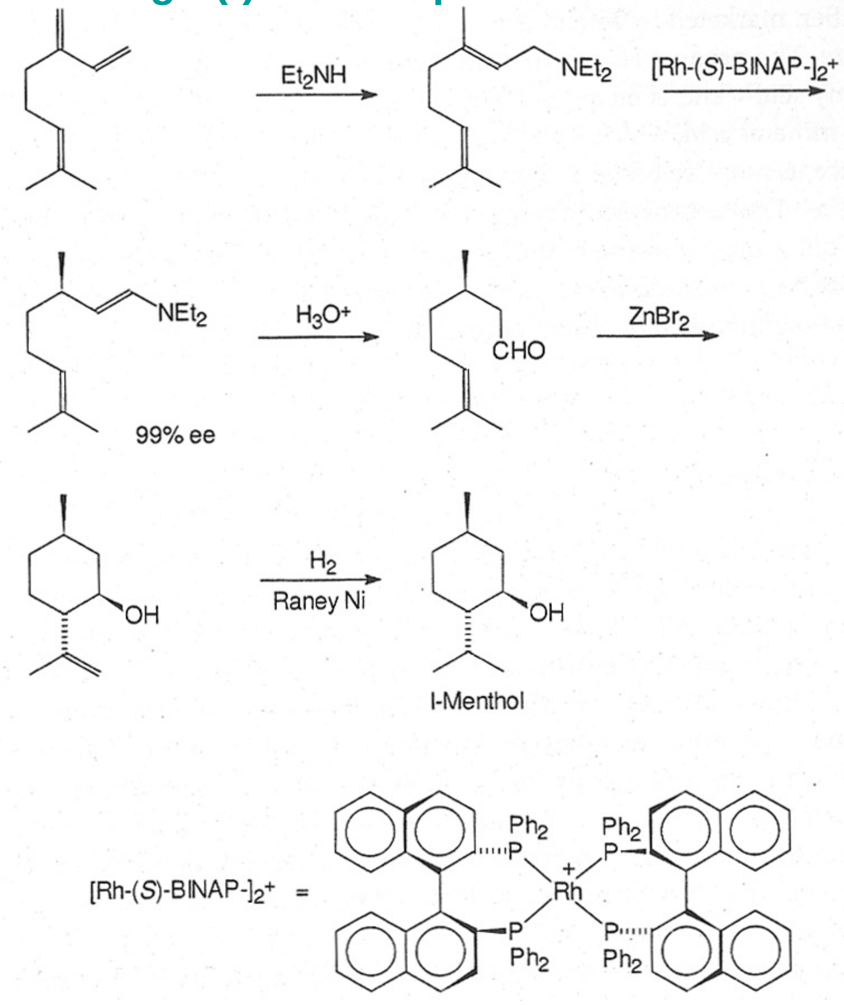
Size of balls has no difference (d: 2, 10, 15 mm)

Myrcene as a Natural Base Chemical in Sustainable Chemistry



ChemSusChem **2009**, *2, 2072-2095*

Takasago (-)Menthol process

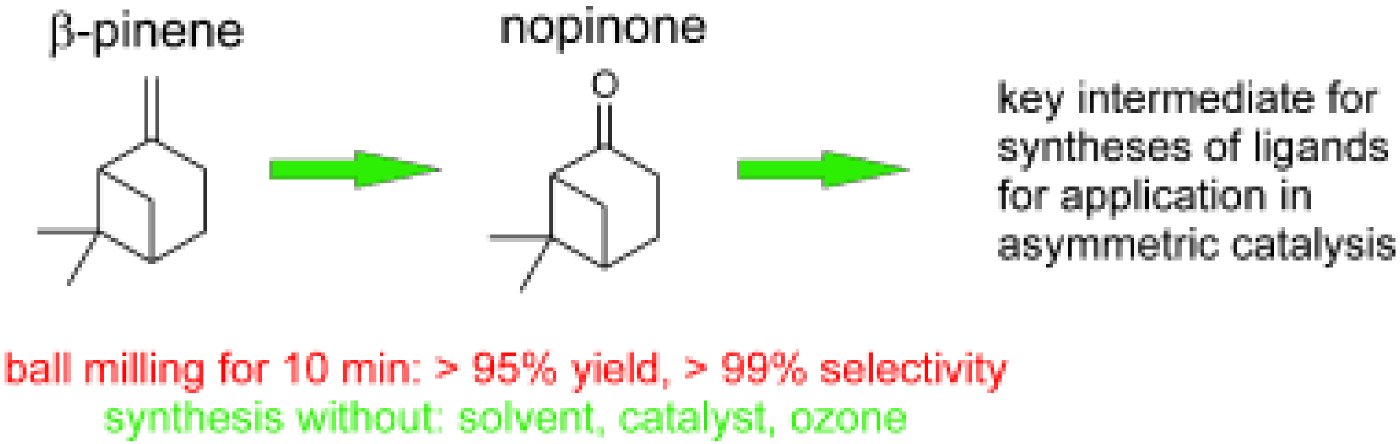


(*Catalysis for Renewables*, **2007**, p. 107)

Beta-Pinene to nopinone

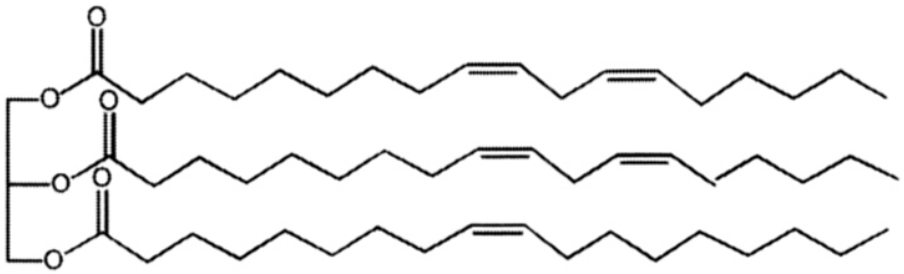
Stolle, Ondruschka, et al. *ChemSusChem* **2010**, *3*, 1181-1191

A solvent-free method for the synthesis of nopinone from the renewable monoterpene β-pinene in a ball mill is evaluated. The envisioned synthesis pathway uses non-hazardous reagents and is performed under ambient, non-inert reaction conditions. The influence of both technical and chemical reaction parameters on conversion, selectivity, and yield is assessed.

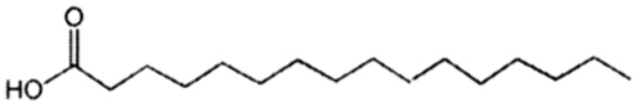


(Thermal rearrangements of monoterpenes, Stolle, Ondruschka, et al. *Helv. Chim. Acta* **2009**, *92*, 1673-1719)

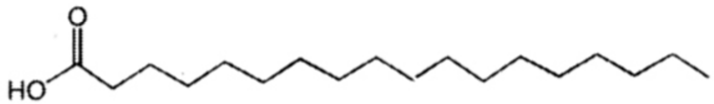
Fats and oils (Triglycerides)



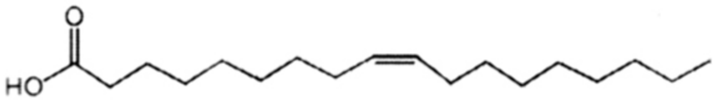
Soybean oil is a statistical mixture of glycerol esters of palmitic acid (10%), stearic acid (3%), oleic acid (23%), linoleic acid (55%), and linolenic acid (9%).



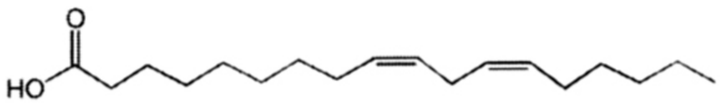
Palmitic acid



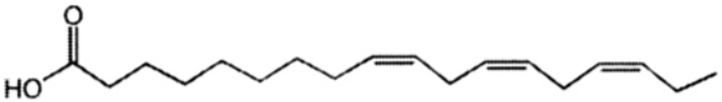
Stearic acid



Oleic acid



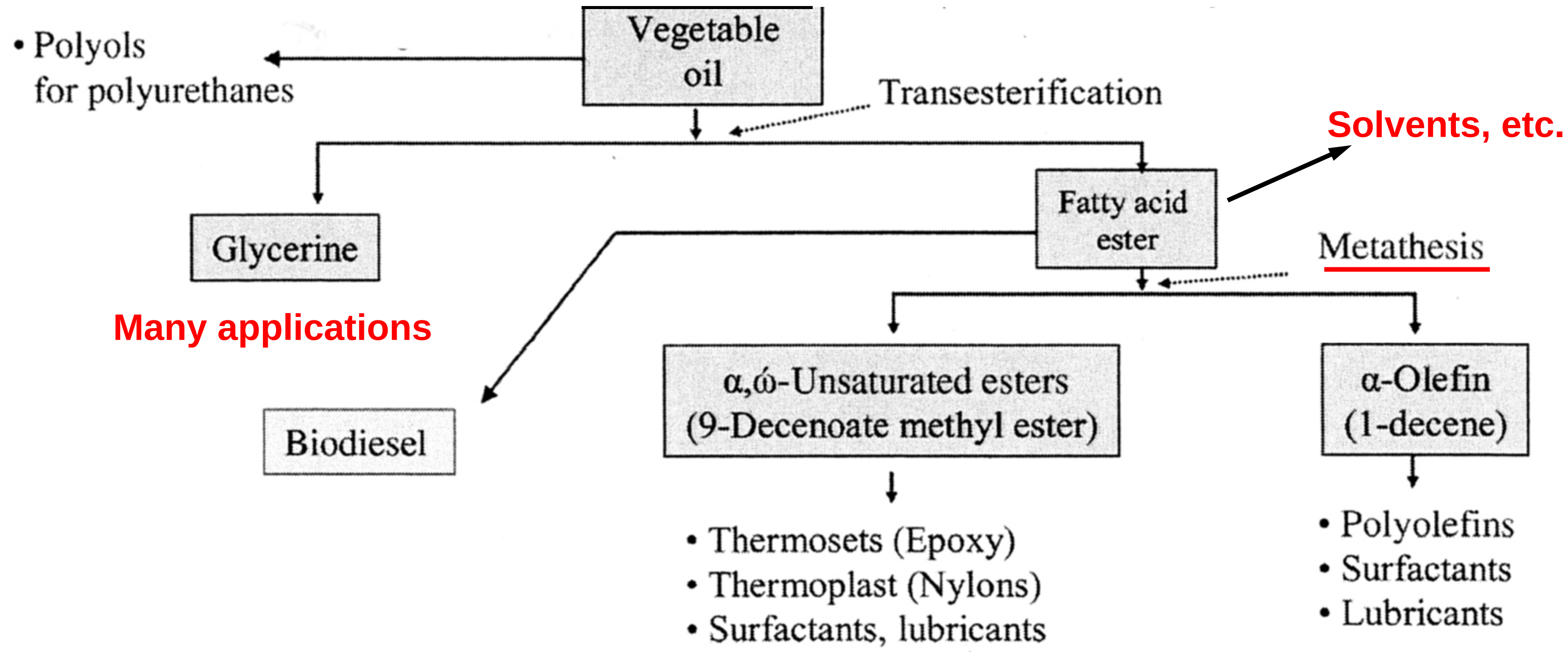
Linoleic acid

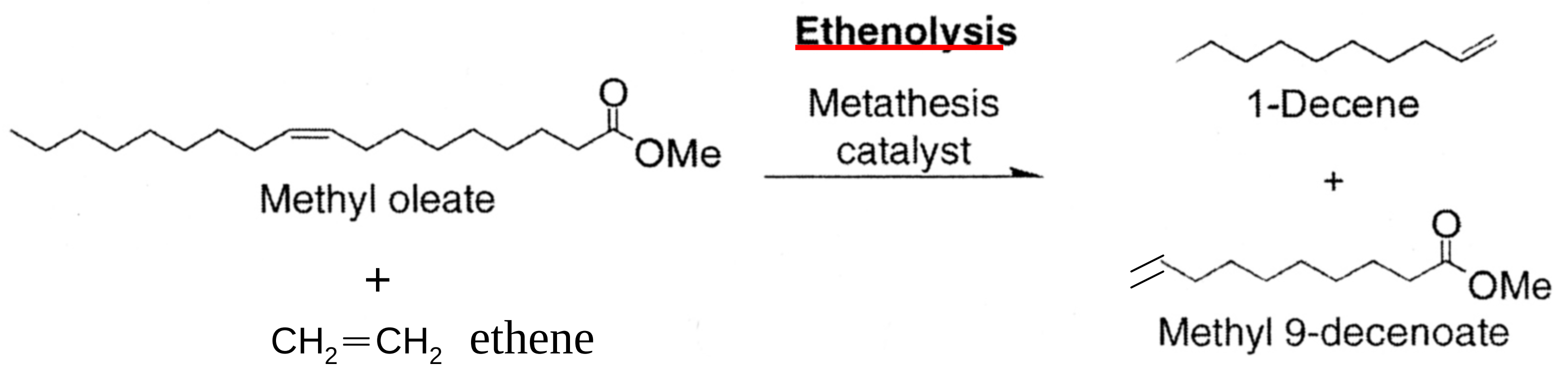


Linolenic acid

and glycerol (glycerin) $CH_2(OH)CH(OH)CH_2OH$

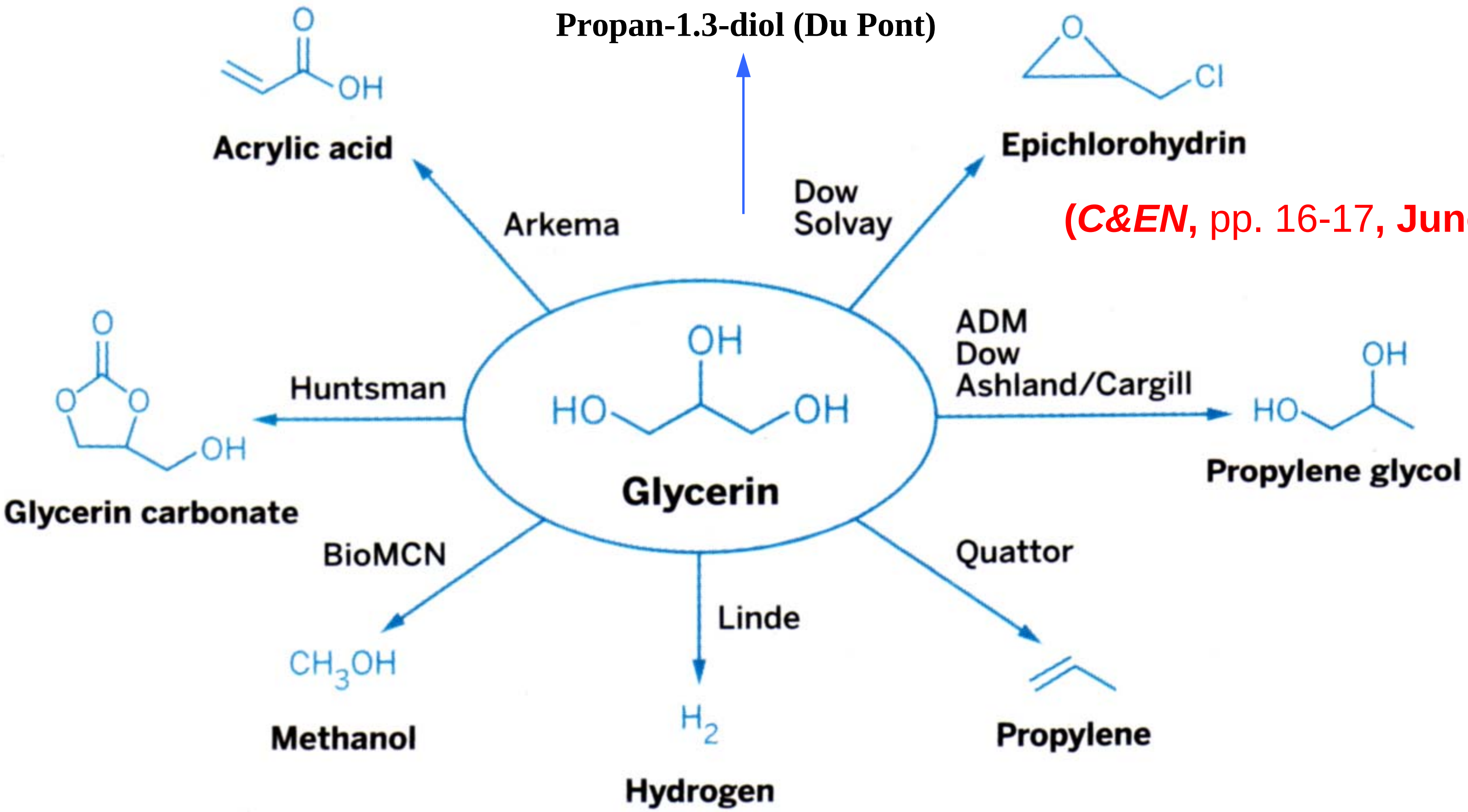
Bio-refinery of vegetable oils





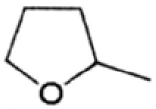
The use of fatty acids and glycerol

- The acidic function (COOH) can be modified.
- The alkene function (C=C) can be modified.
- Glycerol is a sustainable solvent (***Green Chem***. **2010**, *12*, 1127-1138)
- Glycerol (glycerin) is a potentially versatile feedstock.

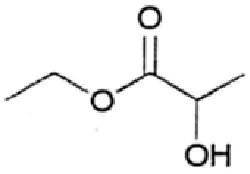


(***C&EN***, pp. 16-17**, June 16 , 2009)**

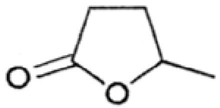
Solvents from renewable resources



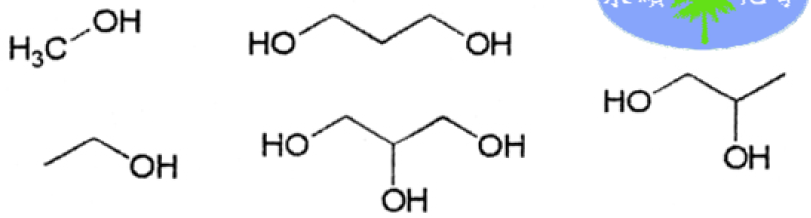
2-MeTHF



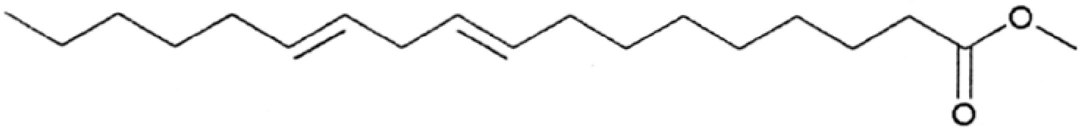
Ethyl lactate



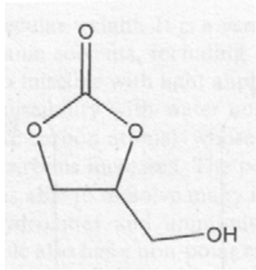
γ -Valerolactone



Alcohols and polyols



Fatty acid ester (Biodiesel component)



Glycerol carbonate (and other organic Carbontes)

Industrial uses of esteric green solvents

Solvent	*Industrial use*
Glycerol carbonate	Non-reactive diluent in epoxy or polyurethane systems
Ethyl lactate	Degreaser
	Photo-resist carrier solvent
	Clean-up solvent in microelectronics and semiconductor manufacture
2-Ethylhexyl lactate	Degreaser
	Agrochemical formulations
Fatty acid esters (and related compounds)	Biodegradable carrier oil for green inks
	Coalescent for decorative paint systems
	Agrochemical/pesticide formulations

唯永續化學能使化學永續

歡迎討論

劉廣定
(ktliu@ntu.edu.tw)