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]。

Some Non-biological catalysts in Sustainable Chemistry

劉廣定
(ktliu@ntu.edu.tw)

Catalysis heads toward sustainability

Environmental problems

Grassian, *Environmental Catalysis*, Taylor & Francis, **2005**

Sanghi and Singh (ed), *Green Chemistry for Environmental Remediation*, Wiley, **2012**

Green Chemistry and Societal Sustainability

Green Lab Technologies

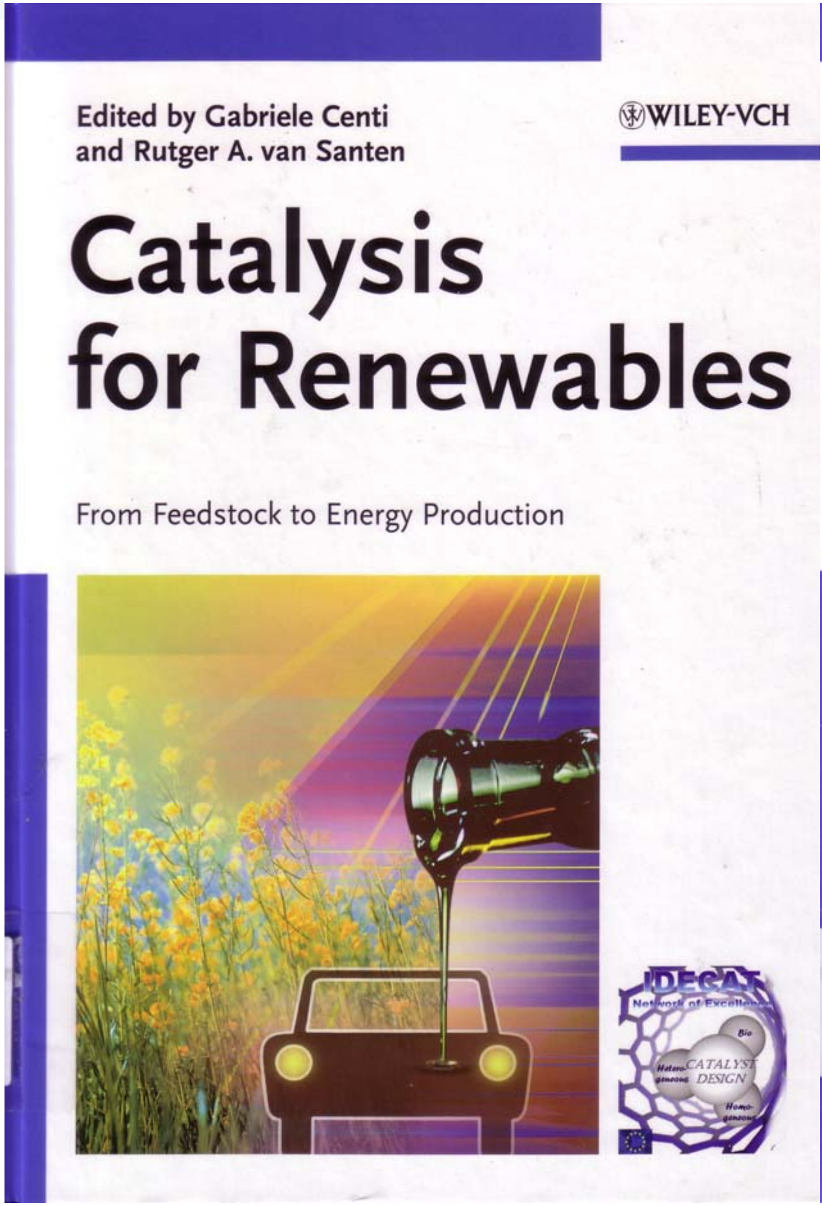
Green Bio-energy Sources

Green Solution for Remediation

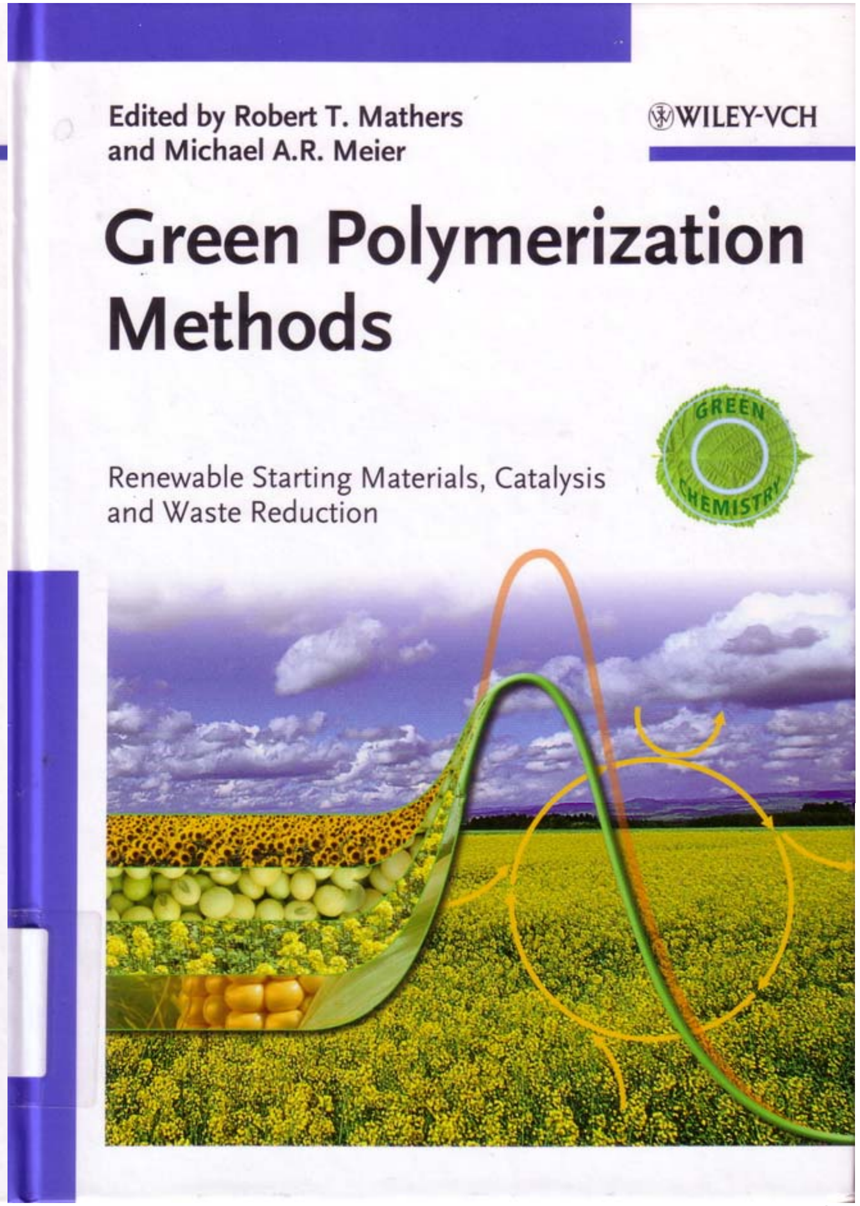
Renewable catalytic technology

Centi and van Santan (ed), *Catalysis for Renewables*, Wiley-VCH, **2007**

Mathers and Meier (ed), *Green Polymerization Methods,* Wiley-VCH, **2011**



(A **2007** publication)



(A **2011** publication)

唯有永續化學
能使化學永續

For the purpose of synthesis

∗ Selectively catalyzed processes are superior to Stoichiometric processes (＃9 of the 12 principles)

∗ Measure catalyst and solvent losses in air and aqueous effluents (＃4 of the 12 more principles)

Employ catalyst to enhance the efficiency and to reduce E-factor as possible

Industry sector	Production/metric tons year^{-1}	E-factor/kg waste kg product^{-1}
Oil refining	10^6–10^8	<0.1
Bulk chemicals	10^4–10^6	<1–5
Fine chemicals	10^2–10^4	5–50
Pharmaceuticals	10–10^3	25–100

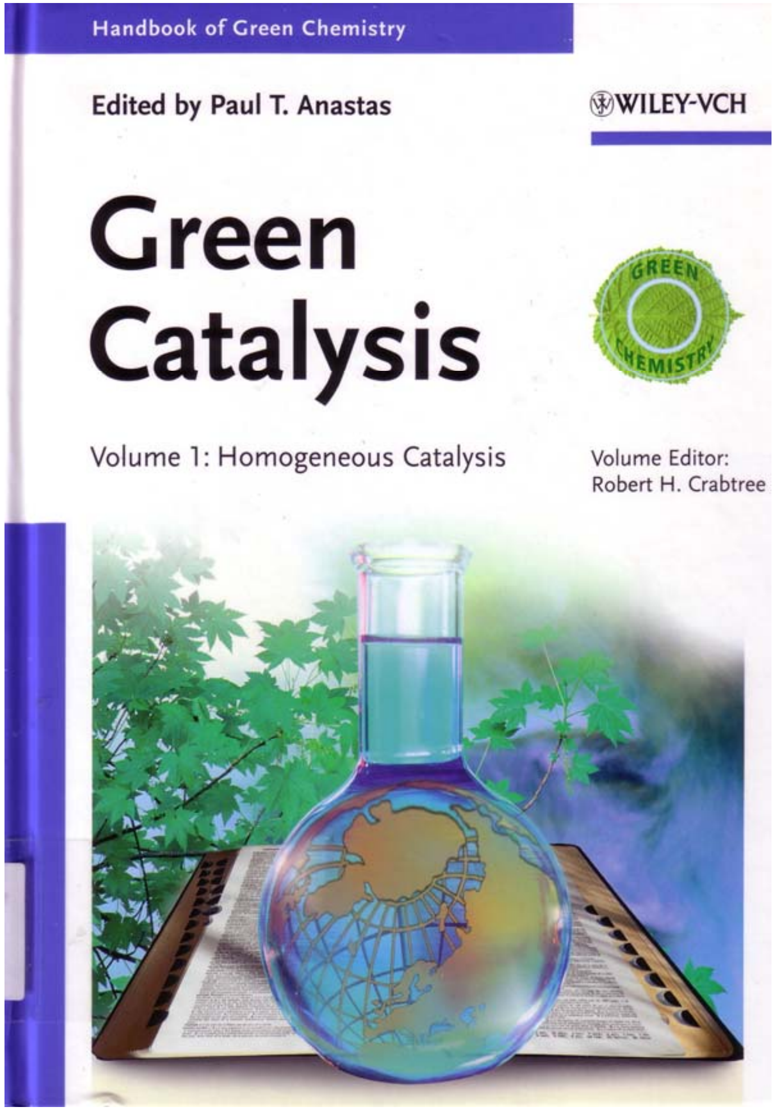
Characteristics for ideal chemical synthesis toward sustainability

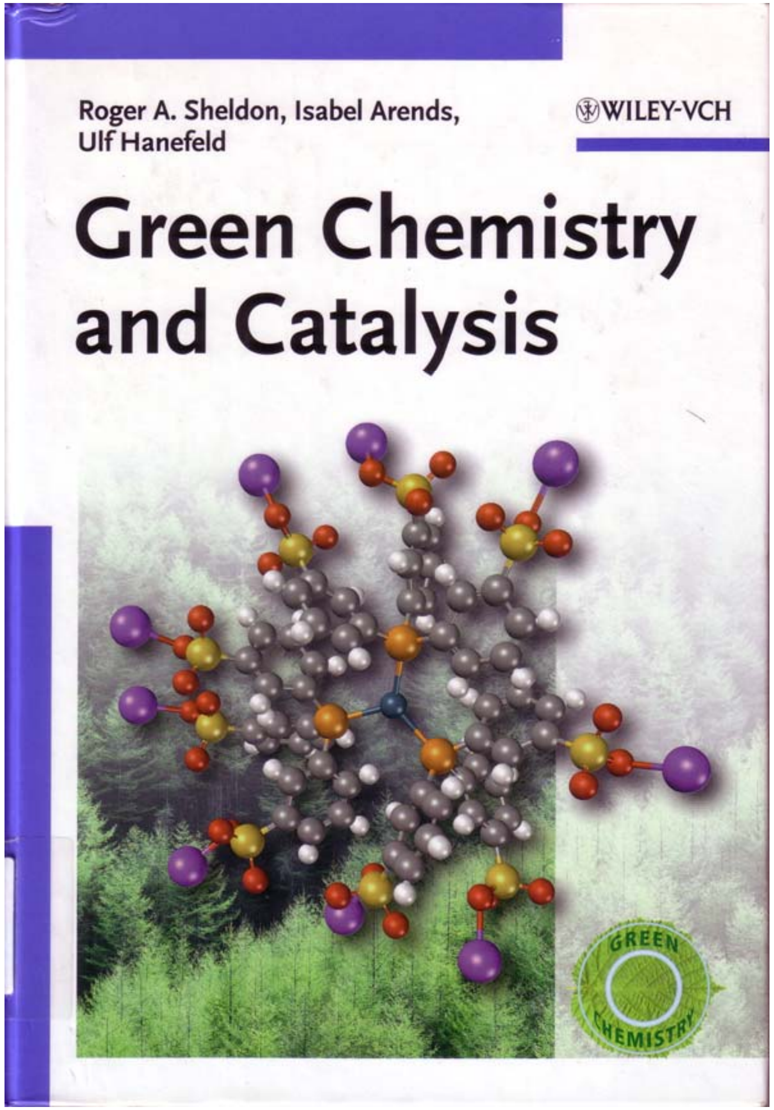
- Simplicity
- Safety, environmentally benign processes
- High yield and selectivity, material efficiency
- Low E-factor, less wastes
- Energy efficiency
- Use of renewable and recyclable reagents
- Use of renewable and recyclable solvents

……

A variety of approaches

- **Better methods of chemical activation**: photo-, electro-, high pressure, ultrasound, microwave, mechano-chemistry
- **More effective methodologies:** multicomponent reactions, **new catalysts**, continuous flow and micro-reactors
- **Solvent alternatives**：replacement of petroleum-based, and volatile organic compounds (VOCs); switchable systems
- etc.





Vol. 1, *Homogeneous Catalysis*
Vol. 2, *Heterogeneous Catalysis*
Vol. 3, *Biocatalysis*
(2009 Publications)

(A 2007 publication)

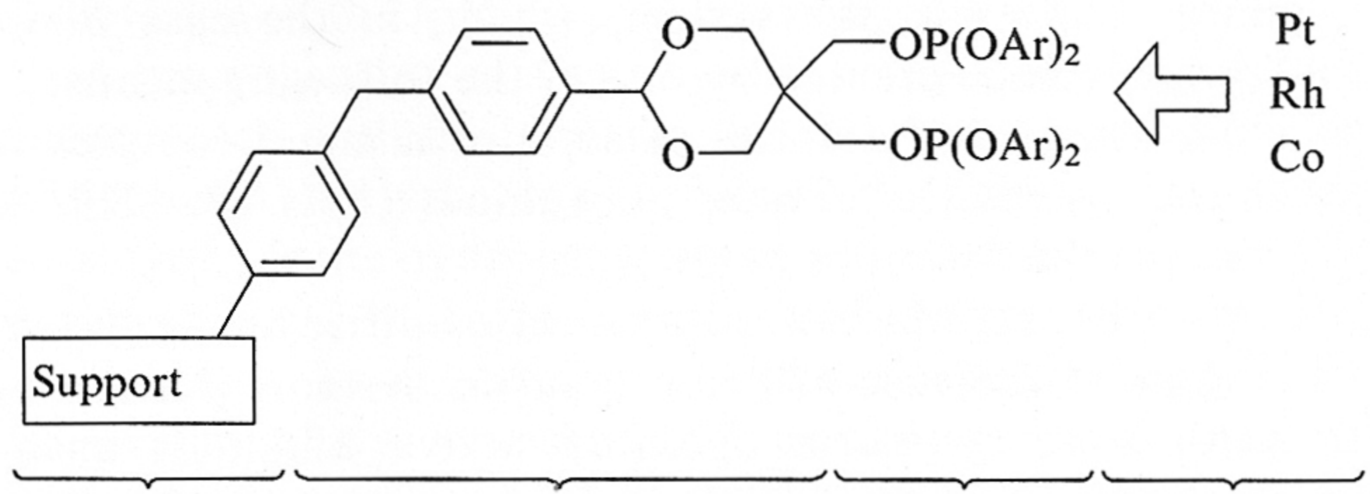
Homogeneous vs Heterogeneous catalysts

(Lancaster, p. 93)

Heterogeneous	*Homogeneous*
Usually distinct solid phase	Same phase as reaction medium
Readily separated	Often difficult to separate
Readily regenerated and recycled	Expensive/difficult to recycle
Rates not usually as fast as homogeneous	Often very high rates
May be diffusion limited	Not diffusion controlled
Quite sensitive to poisons	Usually robust to poisons
Lower selectivity	High selectivity
Long service life	Short service life
Often high-energy process	Often takes place under mild conditions
Poor mechanistic understanding	Often mechanism well understood

Other classifications: Asymmetric catalysts (enantioselective)
Metal triflate catalysts (Lewis acid)
Phase transfer catalysts
Biocatalysts
Photo-catalysts
etc.

Supported homogeneous catalysts

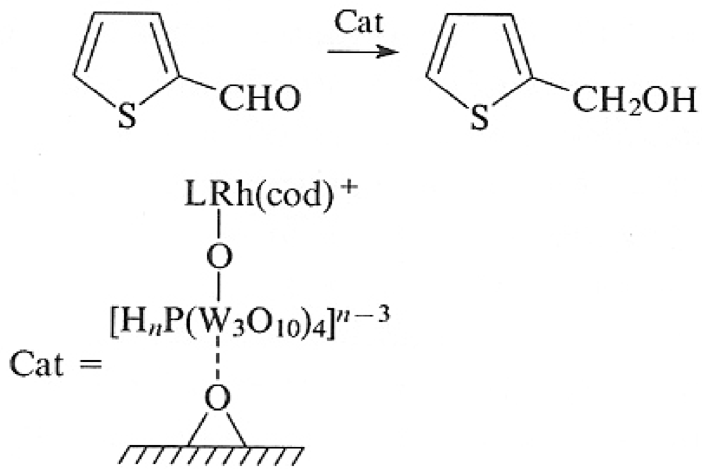


Various types of support:
Polymers
Cellulose
Oxides
Zeolites
Carbon materials

Various types of 'spacer'

Various types of ligands (anchors)

Various types of metals



Green Catalysts

Ideal Green catalysts are eco-friendly catalysts which

- are highly efficient;
- are recyclable;
- are biodegradable;
- are non-toxic;
- can be made from renewable sources;
- can convert toxic substances into less or non-toxic ones;
- can be used in environmentally benign media.

Catalysis as an important tool of Green Chemistry

Russ. Chem. Rev. **2010**, *79*, 441-461

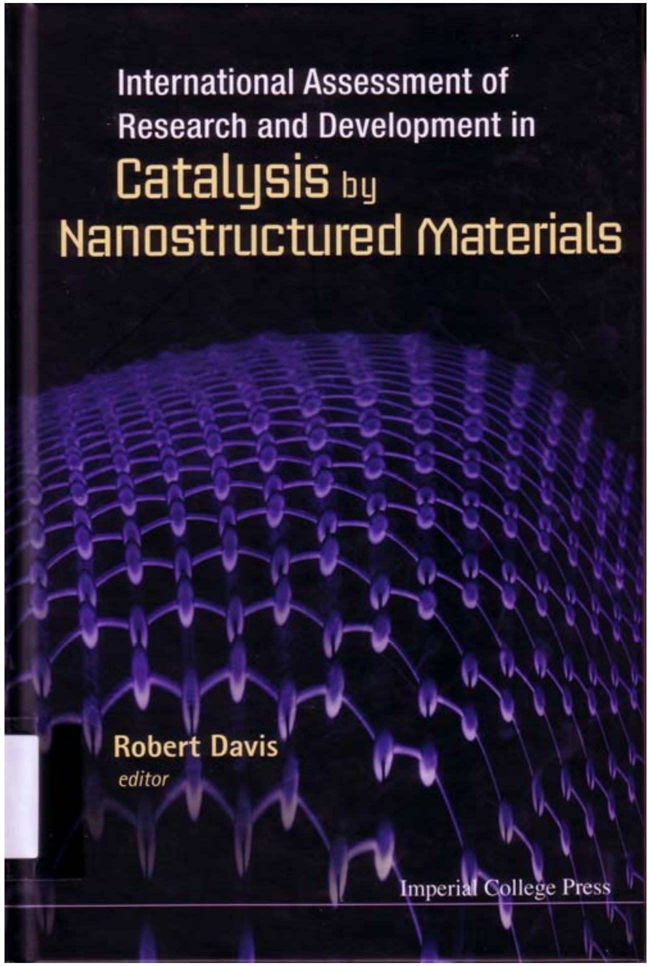
Important parameters that impact on both the commercial viability and the inherent greenness for a catalyst

1. **Selectivity** – the amount of substrate converted to the desired product as a percentage of total consumed substrate.
2. **Turnover frequency** – the number of moles of product produced per mole of catalyst per second. (**TOF**, efficiency of a catalyst)
3. **Turnover number** – the amount of product per mole of catalyst. (**TON**, lifetime of a catalyst)

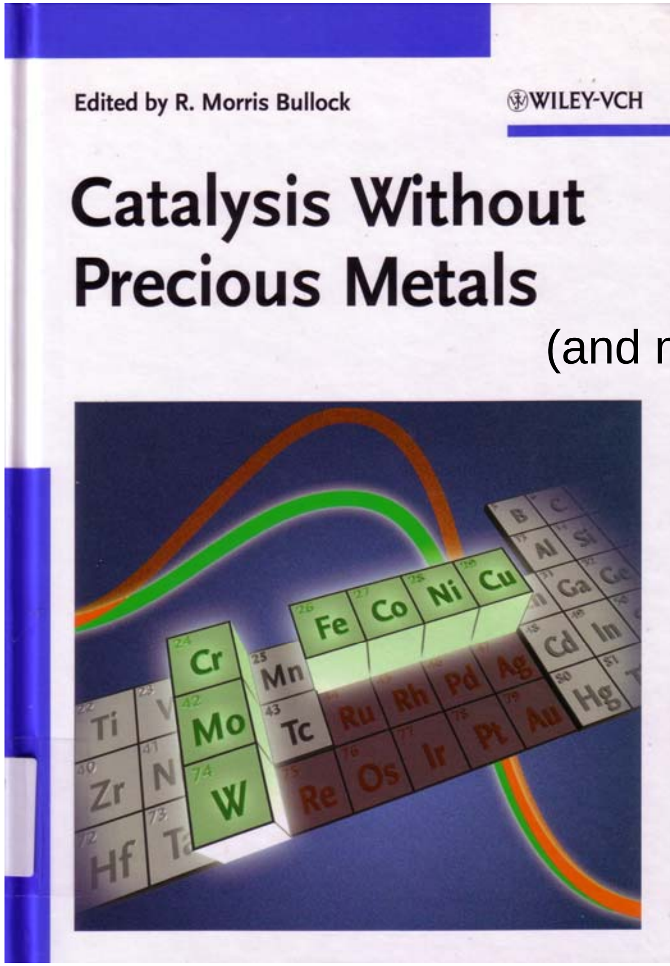
Lancaster p.92

唯有永續化學
能使化學永續

Recent approaches



(A **2011** publication)



(and metal-free)

(A **2010** publication)

☆**Nanocatalyst and Prospects of Green Chemistry**, *ChemSusChem*, **2012**, *5*, 65-76

Applications of TAML®-Fe(III) activated H_2O_2

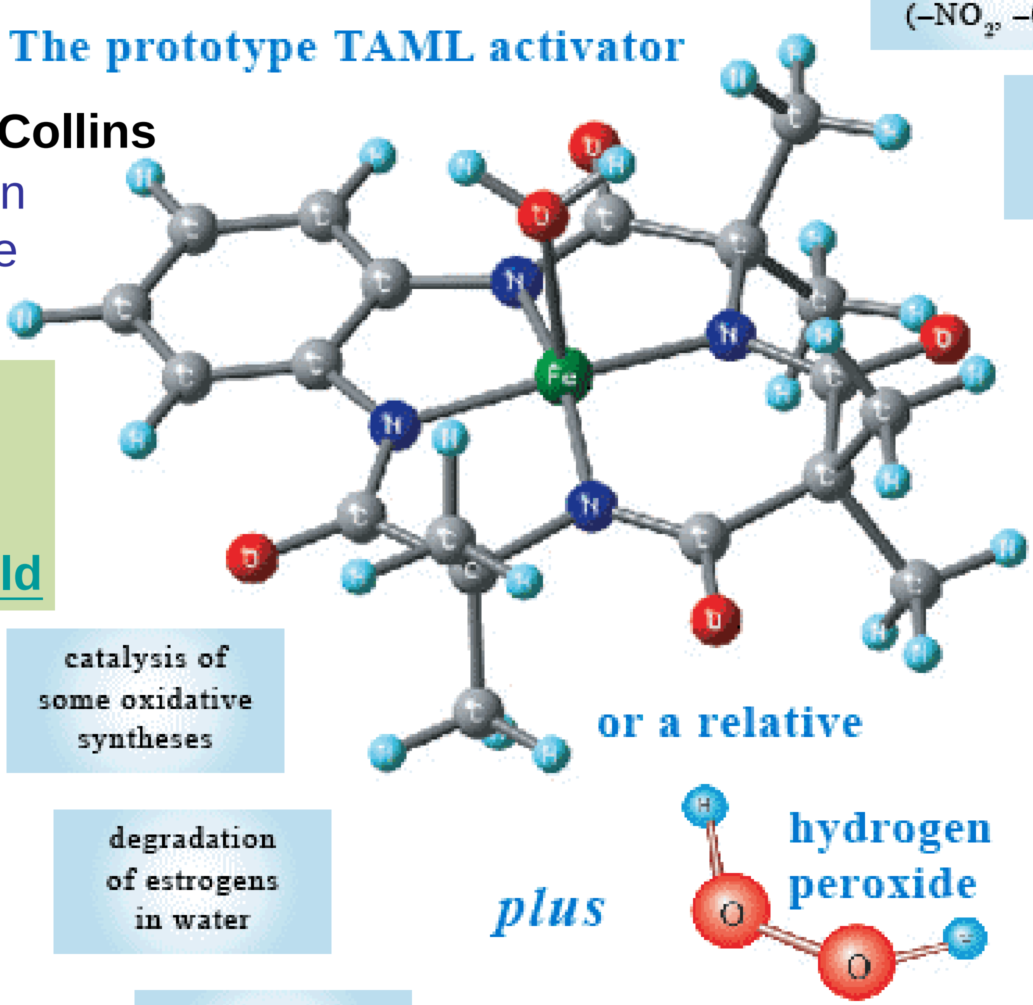
唯有永續化學
能使化學永續

(http://www.chem.cmu.edu/groups/Collins/)

Professor Terry Collins
(Institute for Green Science, Carnegie Mellon U.)

PGCC Award 1999

- Industrial
- Household
- Medical
- Military/Battlefield

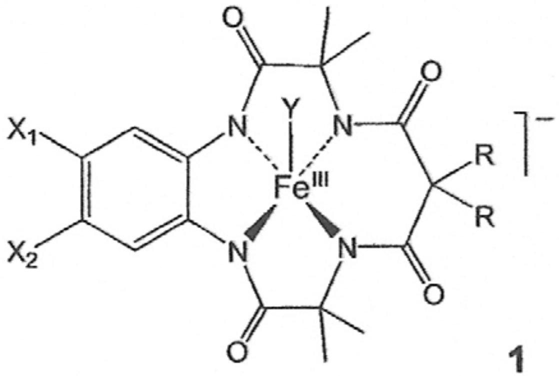


- degradation in water of phenols ($-NO_2$, –CL…)
- mitigation of pulp and paper effluent color
- mitigation of pulp and paper mill smells
- rapid killing of biological warfare agents
- detoxification of chemical warfare agents
- inhibition of laundry process dye transfer
- degradation in water of many other organics
- eliminates thiophosphate pesticide toxicity
- catalysis over a wide pH range, including > 14
- bleaching of dyes in textile mill effluent
- degradation of estrogens in water
- catalysis of some oxidative syntheses

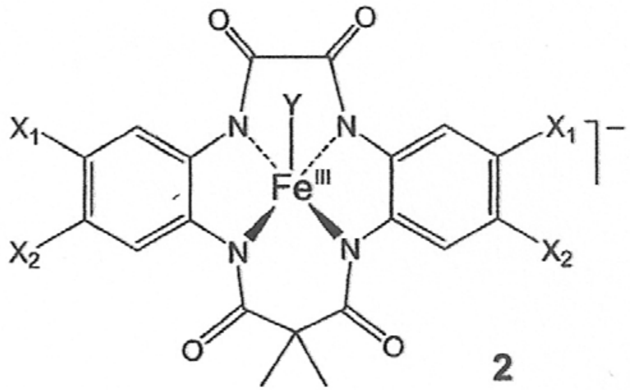
唯有永續化學
能使化學永續

Green Oxidation Catalysts for Purifying Environmental Waters

J. Am. Chem. Soc., **2010**, *132 (28)*, 9774–9781



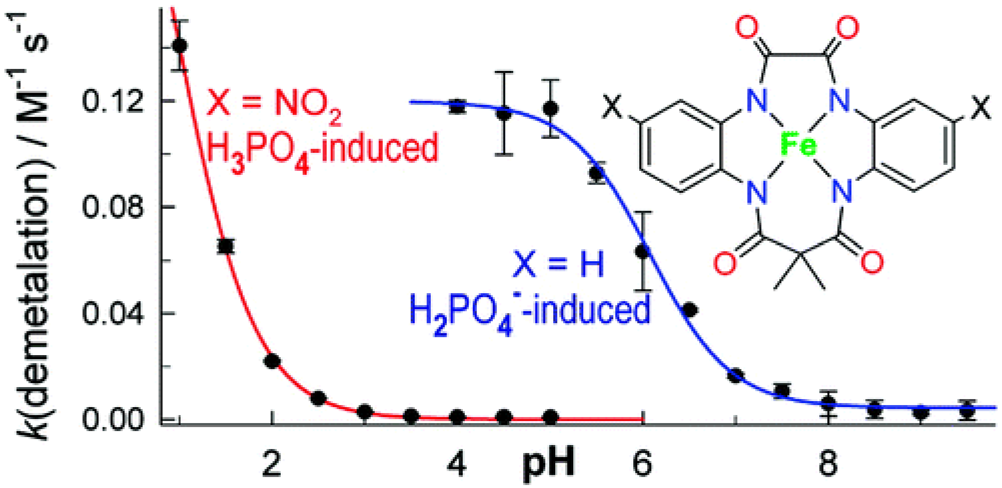
1



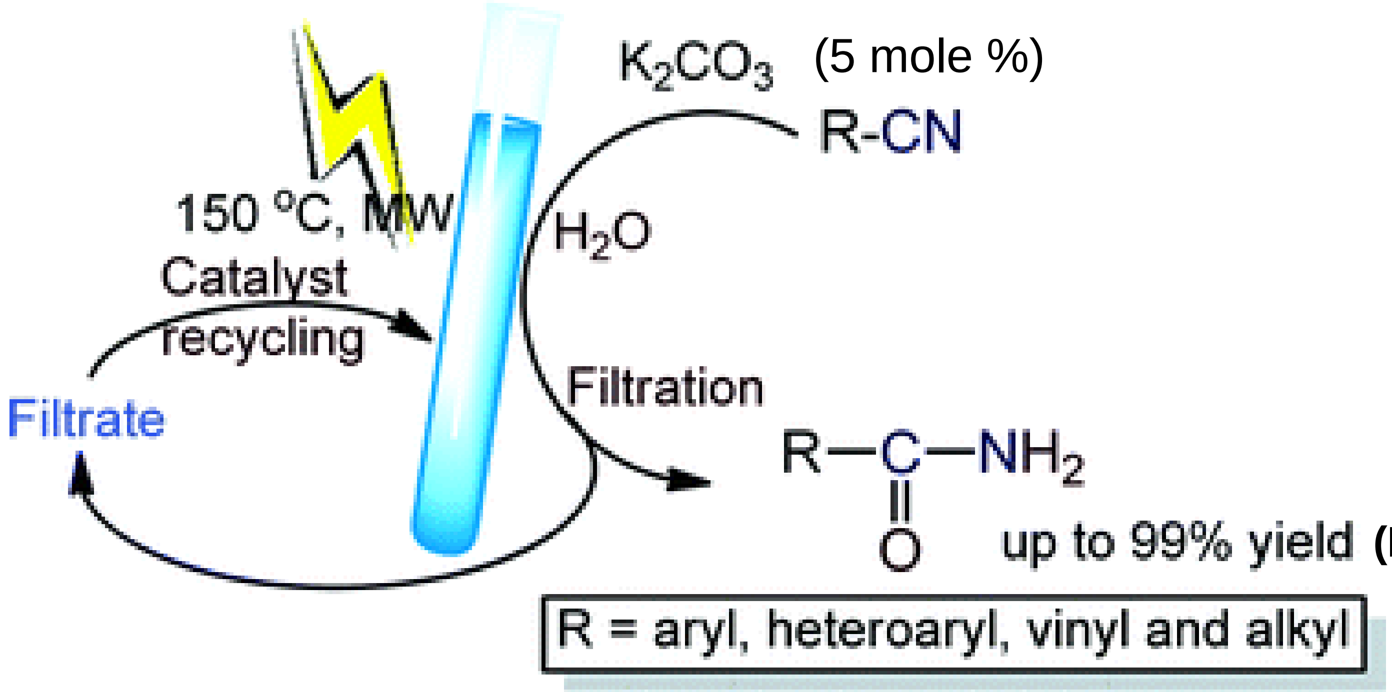
2

(**a**) $X_1 = X_2 = H$, $R = CH_3$
(**b**) $X_1 = X_2 = Cl$, $R = F$
(**c**) $X_1 = NO_2$, $X_2 = H$, $R = F$

(**d**) $X_1 = X_2 = H$
(**e**) $X_1 = NO_2$, $X_2 = H$
(**f**) $X_1 = X_2 = Cl$



Efficient and practical transition metal-free hydration of nitriles



(In general ca 90%)

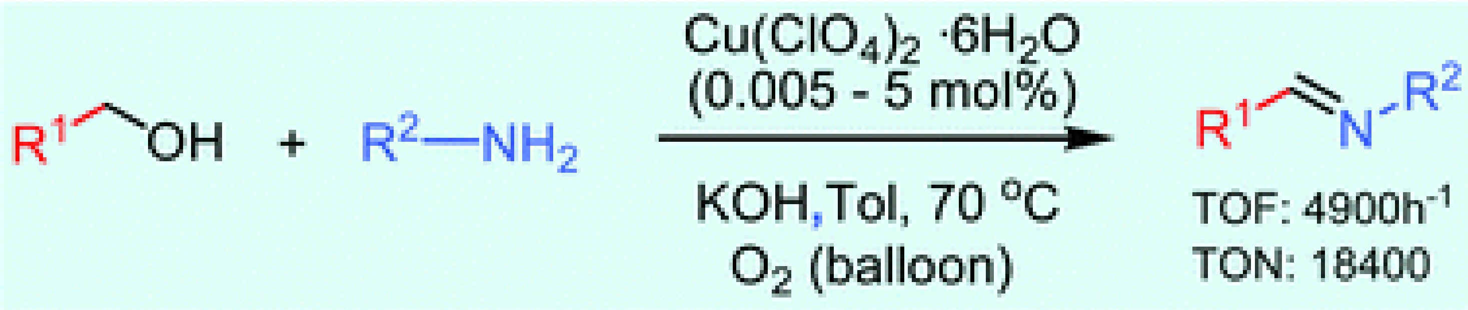
A practical, atom-economical, and straightforward transition metal-free hydration of nitriles to various amides was realized by using **K_2CO_3 as an efficient catalyst under microwave irradiation.**

Green Chem., 2012, **14**, 921-924

Copper-catalyzed highly efficient aerobic oxidative synthesis of imines from alcohols and amines

Green Chem., 2012, **14**, 1016-1019

A highly efficient and green tandem imine synthesis from alcohol and amine with dioxygen as oxidant was achieved.



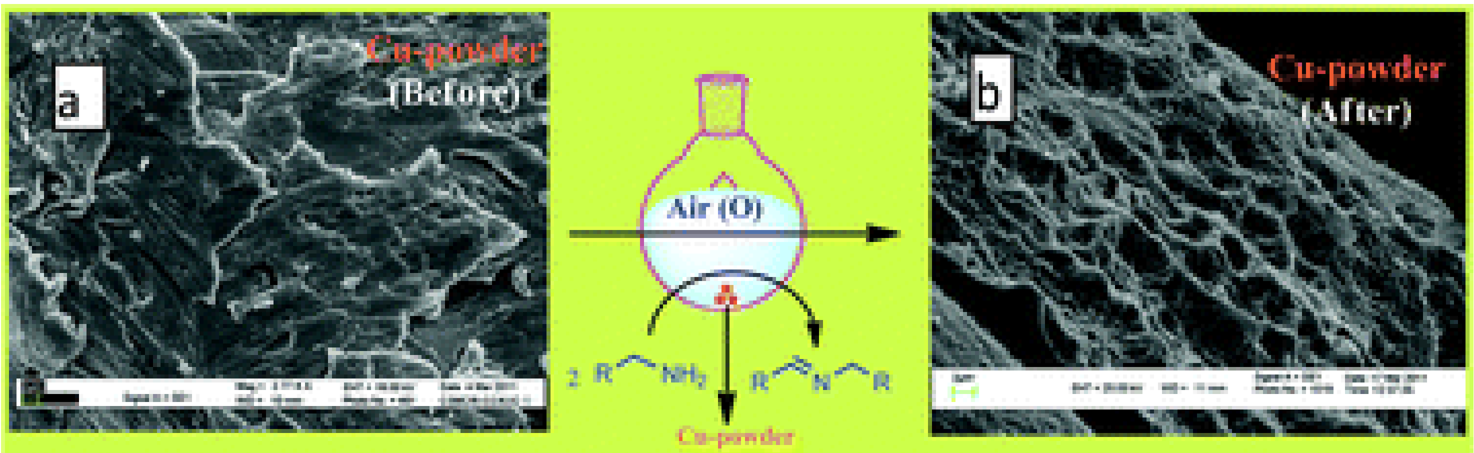
~90% yield in 72 hr

唯有永續化學
能使化學永續

Copper(0)-catalyzed aerobic oxidative synthesis of imines from amines under solvent-free conditions

RSC Adv., 2012,**2**, 5119-5122

A copper(0)-catalyzed direct synthesis of imines from amines under solvent-free aerobic conditions is described. The method is applicable for the synthesis of various imines from corresponding amines such as benzylic, aliphatic, cyclic secondary and heteroaromatic amines. Being solvent free, using air as a benign oxidant, and the easy separation and easy availability of the catalyst (copper powder) are the vital advantages of present protocol.



Cu powder (0.5 mole%) 90^{o}C, 20 hr, yield ~ 99%

唯有永續化學
能使化學永續

Nano-layered manganese oxides as low-cost, easily synthesized, environmentally friendly and efficient catalysts for epoxidation of olefins

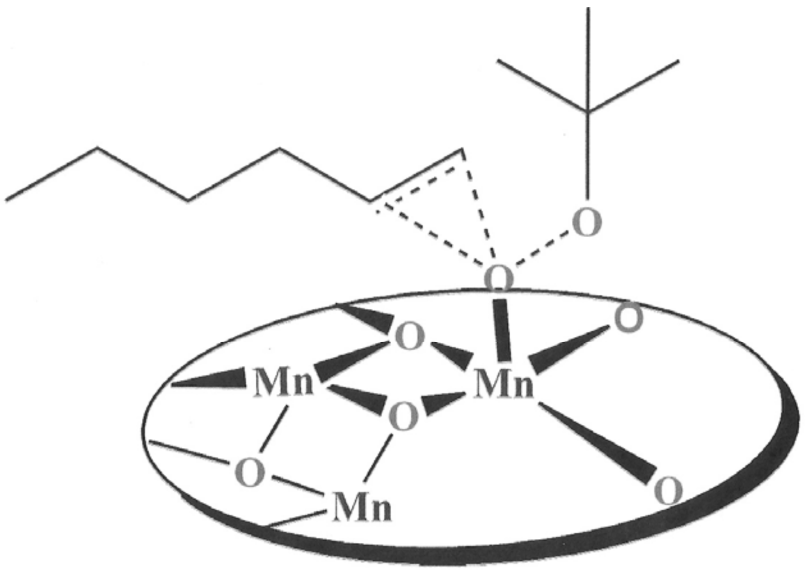
RSC Adv., 2012,2, 3654-3657

Incorporation of calcium(II), zinc(II) and aluminium(III) to manganese oxides greatly improved the activity of manganese oxide towards the epoxidation of olefins (methanol-CH_2Cl_2)in the presence of anhydrous *tert*-butyl hydroperoxide as an oxidant.

With 0.05 mole% of catalyst

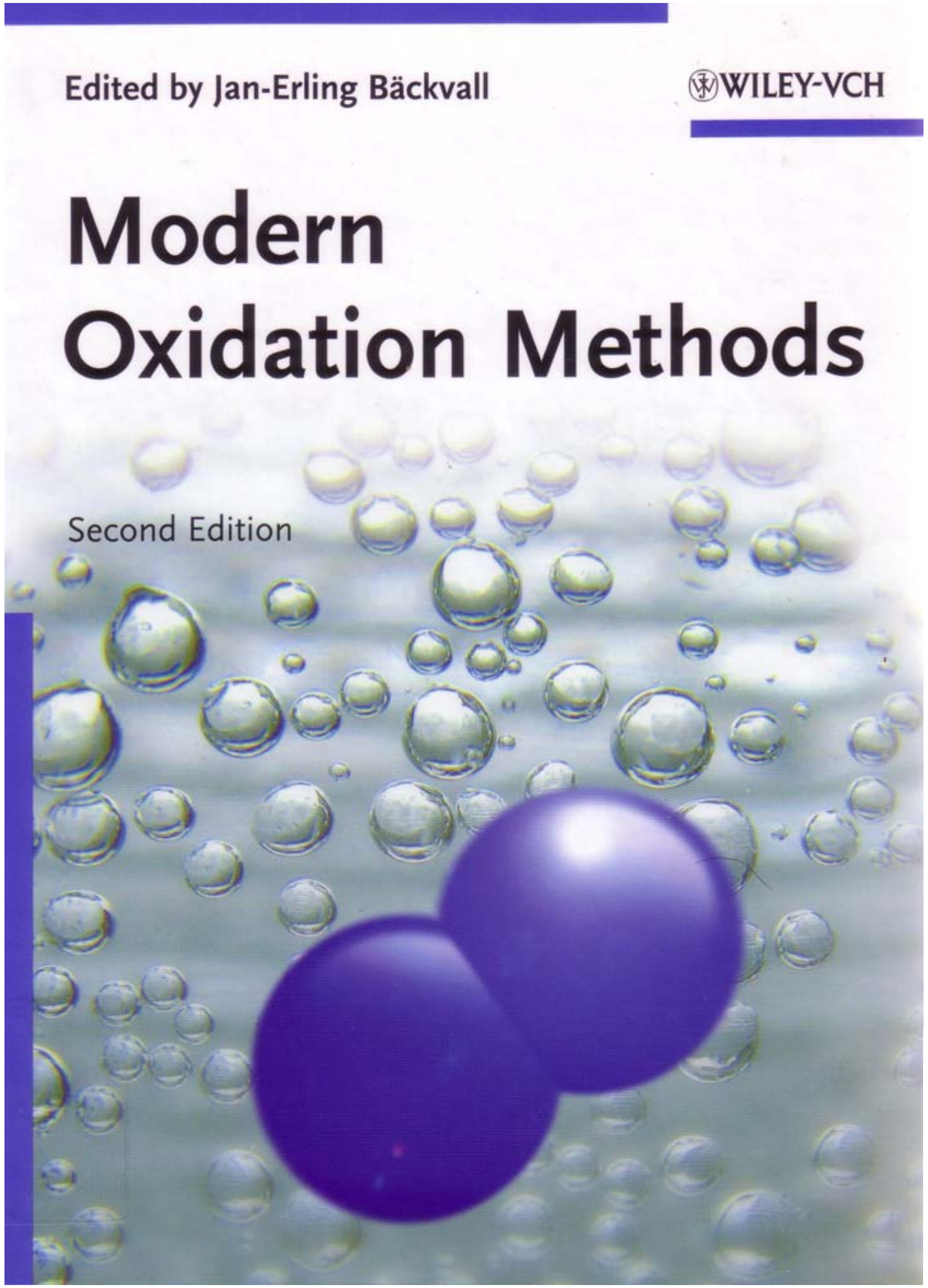
80-90% conversion at 70^{o}C

for 2 hr.



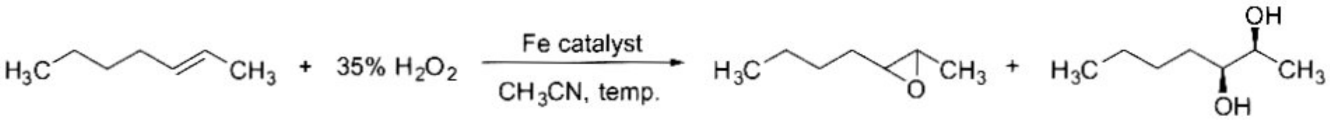
Scheme 2 Proposal mechanism for epoxidation of olefins by manganese oxides.

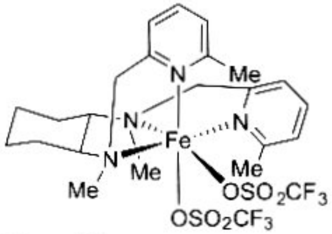
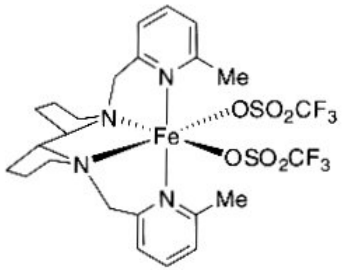
A 2010 reference book (1st Ed, 2004)



1 **Recent Developments in Metal-catalyzed Dihydroxylation of Alkenes** *1*
Man Kin Tse, Kristin Schröder, and Matthias Beller
1.1 Introduction *1*
1.2 Environmentally Friendly Terminal Oxidants *3*
1.2.1 Hydrogen Peroxide *3*
1.2.2 Hypochlorite *5*
1.2.3 Chlorite *8*
1.2.4 Oxygen or Air *9*
1.3 Supported Osmium Catalyst *16*
1.3.1 Nitrogen-group Donating Support *16*
1.3.2 Microencapsulated OsO_4 *17*
1.3.3 Supports Bearing Alkenes *19*
1.3.4 Immobilization by Ionic Interaction *21*
1.4 Ionic Liquid *22*
1.5 Ruthenium Catalysts *23*
1.6 Iron Catalysts *26*
1.7 Conclusions *32*
References *32* **(85 references)**

Iron catalyst



Entry	Catalyst	Alkene:H_2O_2	Temp. (°C)	Epoxide[a)]	*cis*-diol[a)]	*ee* (%)[b)]
1	 10 mol%	50 : 1[c)]	30	7%	49%	79
2	 10 mol%	50 : 1[d)]	r.t.	2%	52%	97

a) Yield based on the limiting reagent.
b) Enantiomeric excess of *cis*-2,3-heptanediol.
c) 50% H_2O_2 was used.
d) Concentration of H_2O_2 was not mentioned.

Que, *Angew. Chem*. **2008**, *47*, 1887

5 **Modern Oxidation of Alcohols using Environmentally Benign Oxidants** *147*

Isabel W.C.E. Arends and Roger A. Sheldon

5.1 Introduction *147*

5.2 Oxoammonium based Oxidation of Alcohols – TEMPO as Catalyst *147*

5.3 Metal-Mediated Oxidation of Alcohols – Mechanism *151*

5.4 Ruthenium-Catalyzed Oxidations with O_2 *153*

5.5 Palladium-Catalyzed Oxidations with O_2 *163*

5.5.1 Gold Nanoparticles as Catalysts *169*

5.6 Copper-Catalyzed Oxidations with O_2 *170*

5.7 Other Metals as Catalysts for Oxidation with O_2 *174*

5.8 Catalytic Oxidation of Alcohols with Hydrogen Peroxide *176*

5.8.1 Biocatalytic Oxidation of Alcohols *179*

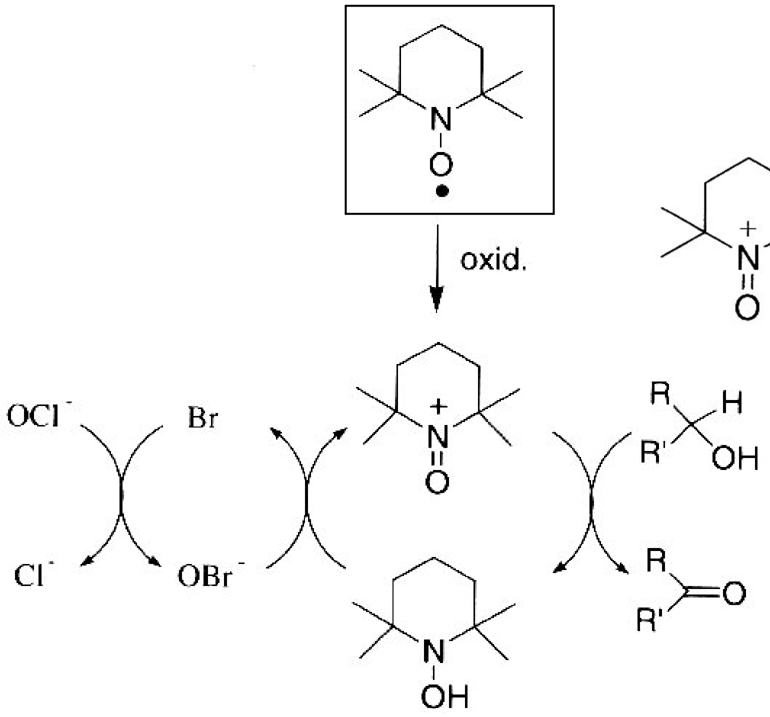
5.9 Concluding Remarks *180*

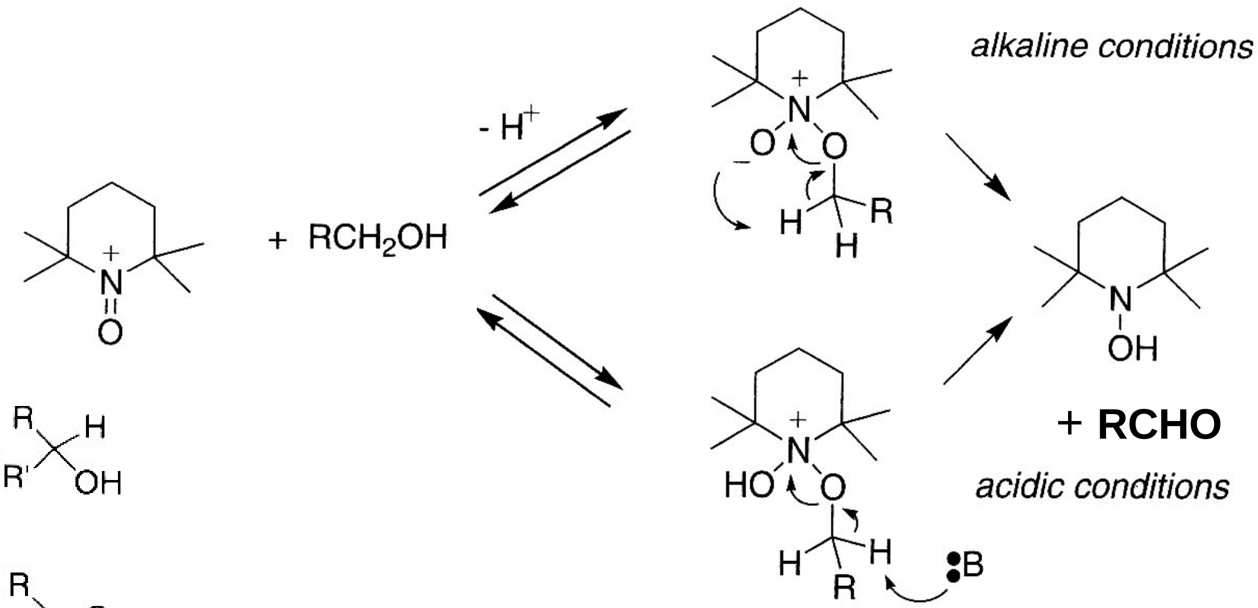
References *180* **(148 references)**

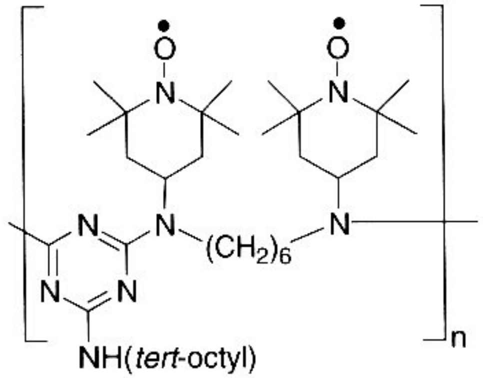
11 Manganese-catalyzed Oxidation with Hydrogen Peroxide

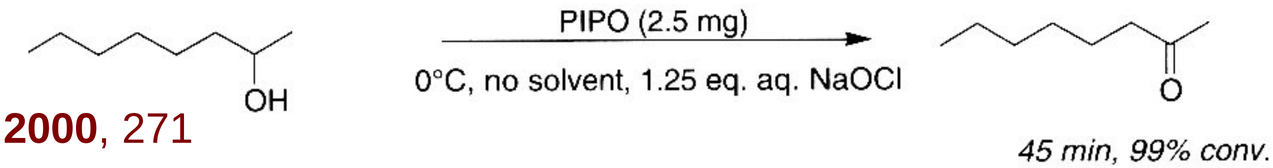
(156 references)

The use of TEMPO for oxidation







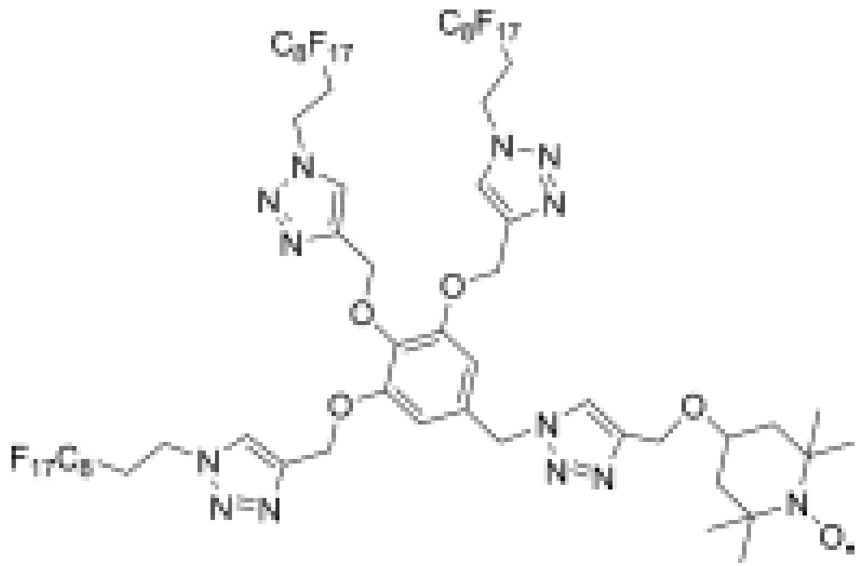


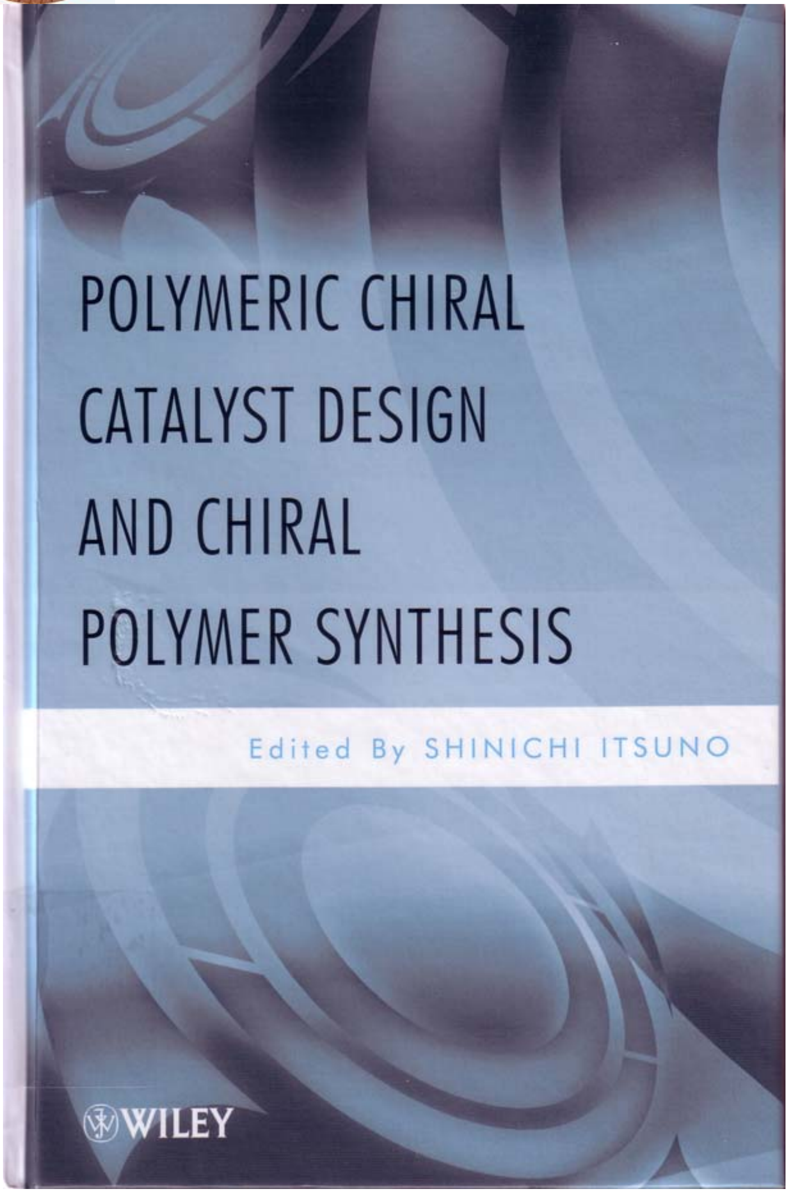
Sheldon, *Chem. Comm*. **2000**, 271

A Recyclable TEMPO Catalyst

(*ChemSusChem* **2010**, *3* (9),1040–1042)

The catalyst is active towards a wide range of substrates. In addition, it can be readily recovered by simple filtration and reused without loss of activity





(A **2011** publication)

2. Polymer-immobilized Chiral Organocatalyst

5. Continuous Flow System using Polymer- Supported Catalysts

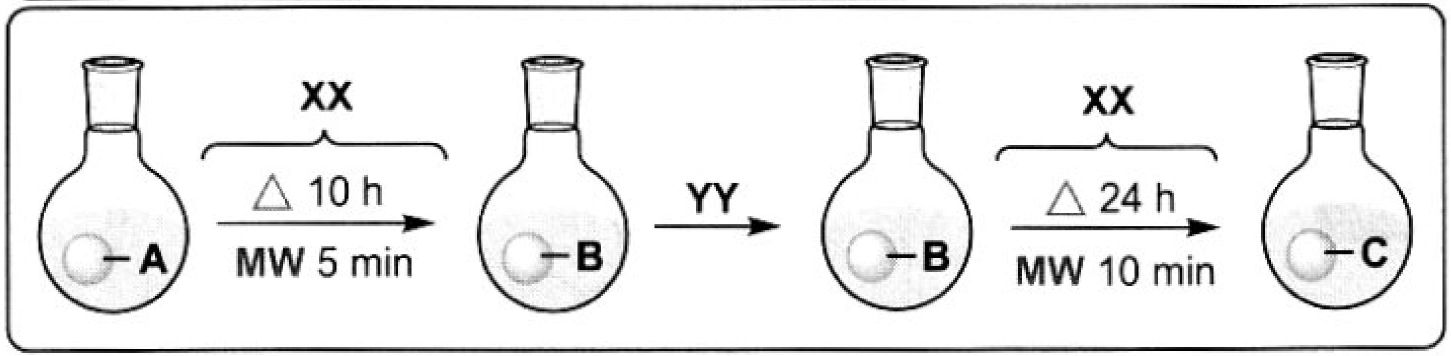
6. Chiral Synthesis on Polymer Support: A Combinatoral Approach

唯有永續化學
能使化學永續

PEG supported reagent

Two-Step PEG Supported Synthetic Process

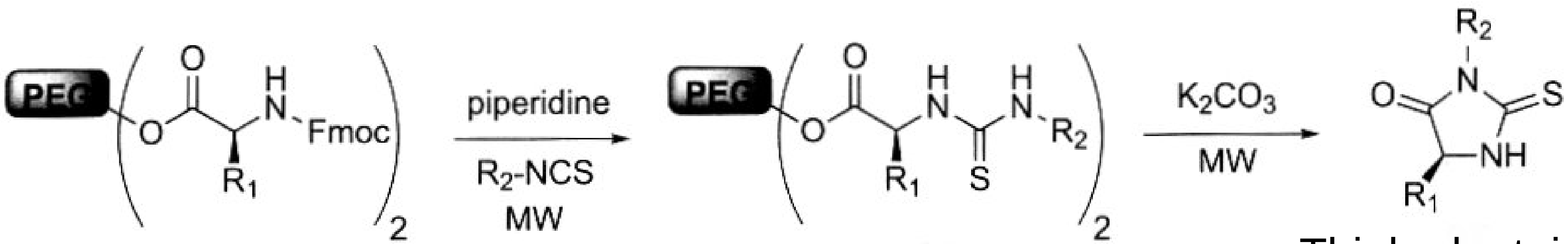
Conventional **versus Microwave**



XX : In-pot reaction time, **YY** : Reloading time

△ - Convntional heating, **MW** - Microwave irradiation

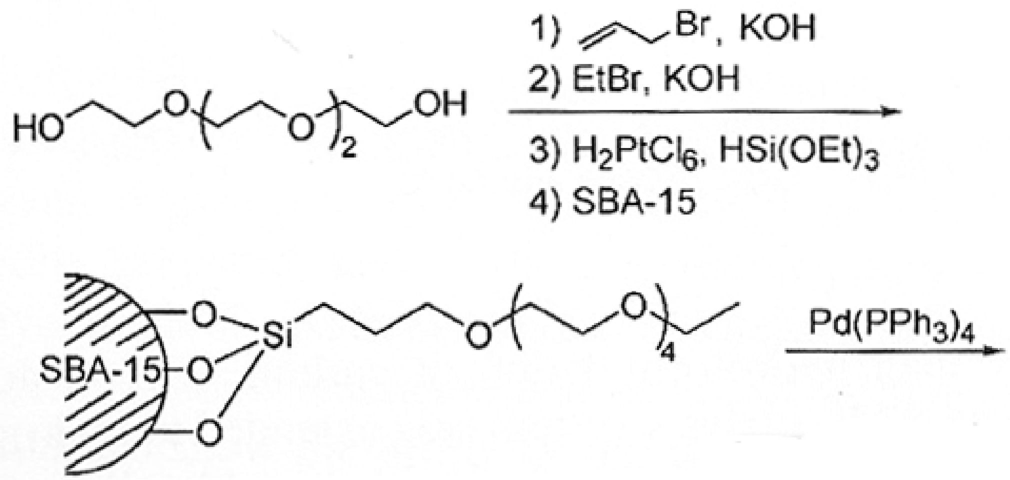
Over all in-pot reaction time : (△) = 34 h and (**MW**) = 15 min



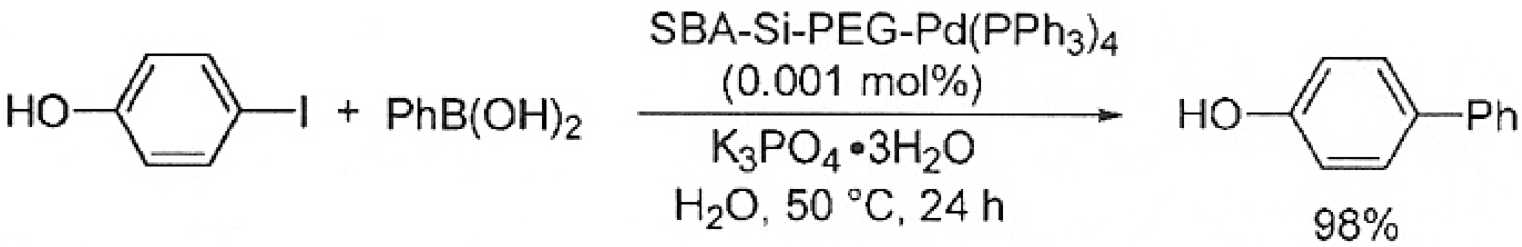
Thiohydantoin,81-99% HPLC yield

Lin and Sun, *Terahedron Lett.* **2003**, *44*, 8739-8742

Mesoporous Silica (SBA-15)**-supported catalyst** and Suzuki Coupling



SBA-Si-PEG-Pd(PPh$_3$)$_4$



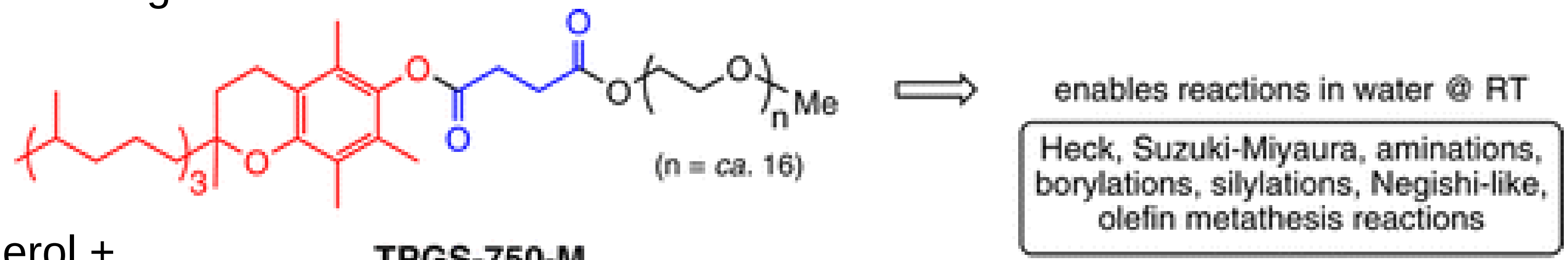
Minakata and Komatsu, *Chem. Rev*. **2009**, *109*, 711-724

PGCC Academic Award 2011

Professor Bruce H. Lipshutz, Department of Chemistry and Biochemistry, University of California, Santa Barbara

Innovation and Benefits

Most chemical manufacturing processes rely on organic solvents, which tend to be volatile, toxic, and flammable. Chemical manufacturers use billions of pounds of organic solvents each year, much of which becomes waste. Water itself cannot replace organic solvents as the medium for chemical reactions because many chemicals do not dissolve and do not react in water. Professor Lipshutz has designed a safe surfactant, **TPGS-750-M,** that forms tiny droplets in water. Organic chemicals dissolve in these droplets and react efficiently, allowing water to replace organic solvents.

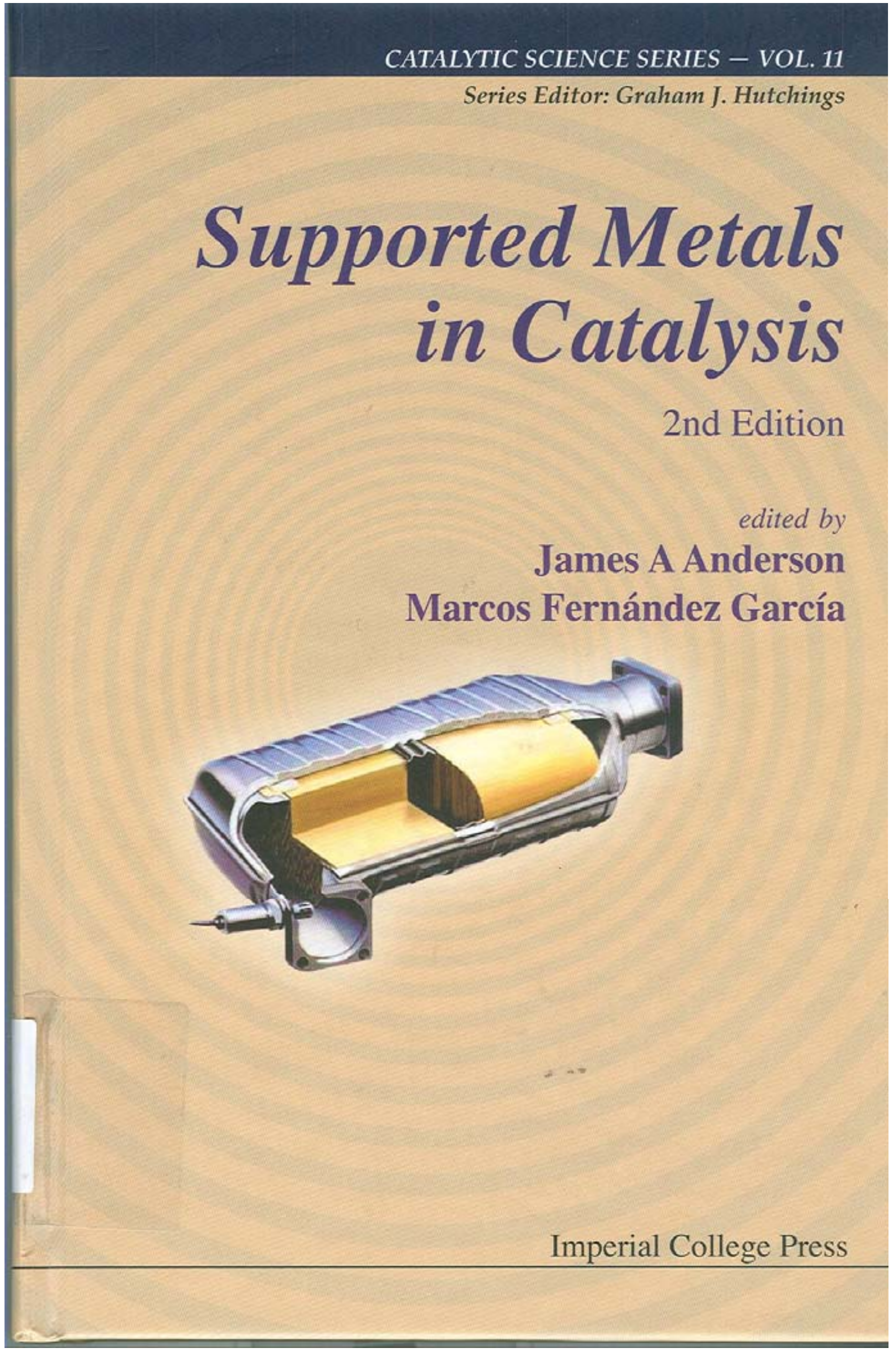


α-tocopherol + $(CH_2CO)_2O$, then PEG-750-M

TPGS-750-M

Lipschutz, *et al. J. Org. Chem.*, **2011**, *76*, 4379-4391.

唯有永續化學
能使化學永續



5. For Fine Chemical Synthesis

8. Production of hydrogen

9. Application in Fuel Cells

10. Vehicle Emision Control

2012 edition with 566pp (2005 edition with 368pp)

唯有永續化學
能使化學永續

Methyl methacrylate manufacture

Shell process

1-Propyne + CO + MeOH + Pd catalyst ⟶ MMA

↑

Newer process (EverNu Technology, 2008)

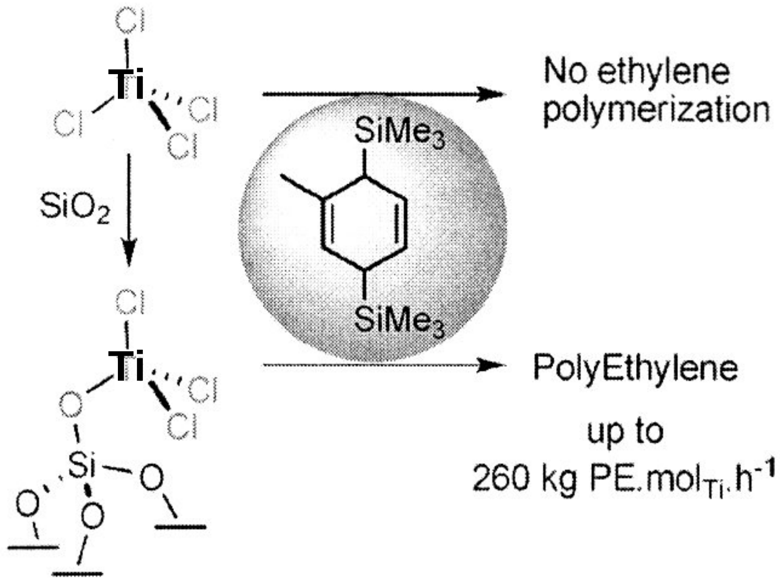
Isobutane + air (O_2) + mixed metal in capsules ⟶ MAA (methacrylic acid)

2008 PGCC Small Business Awards Entries.

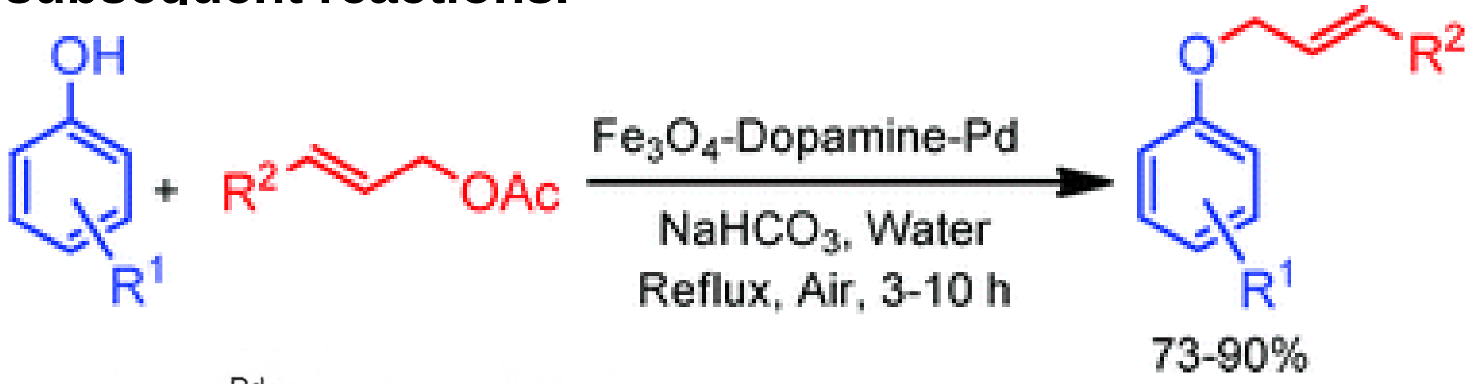
Award was given to SiGNa Chemistry, Inc. for "New Stabilized Alkali metals (encapsulating within porous, sand-like powders made of metal oxides) for safer, sustainable synthesis.

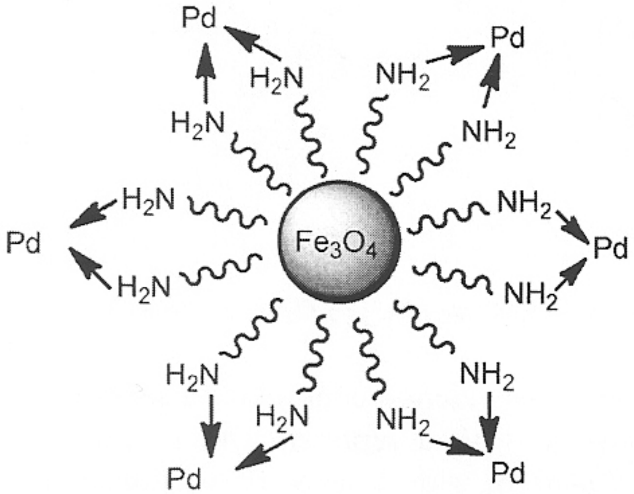
More example of supported catalysts

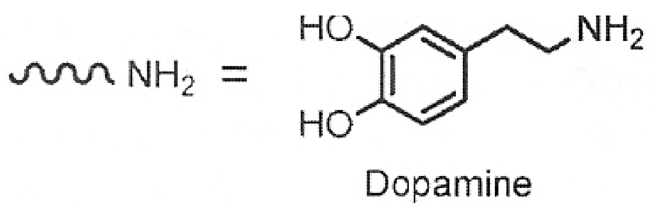
Silica-supported titanium(IV) chloride is readily reduced by Mashima and co-workers' reagent (1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene) to afford materials active in ethylene polymerisation without need of aluminum alkyl cocatalyst.



[*Macromol. Rapid Commun*. **2011**, 32, 1921-1924]

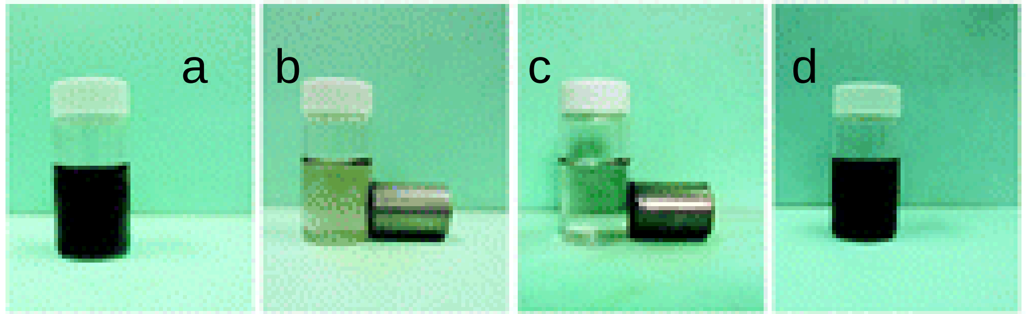
- **A magnetically recoverable heterogeneous Pd catalyst has been used for an eco-friendly synthesis of allylic ethers in water *via O*-allylation of phenols with allylic acetates under a normal air atmosphere. The catalyst was efficiently recycled in subsequent reactions.**
- 





[*Green Chem*. **2012**, *14*, 67-71]

Novel magnetic-separable and efficient Au/Fe–Al–O composite for the lactonization of 1,4-butanediol to γ-butyrolactone (*RSC Advances*, **2012**, *2*, 3801–3809)



Progressive separation of $Au/Fe_2O_3@A_{l2}O_3$ from the suspension (a) without magnet, (b) upon application of a magnet for 1 min, (c) upon application of a magnet for 10 min and (d) re-dispersion by shaking after removing the magnet.

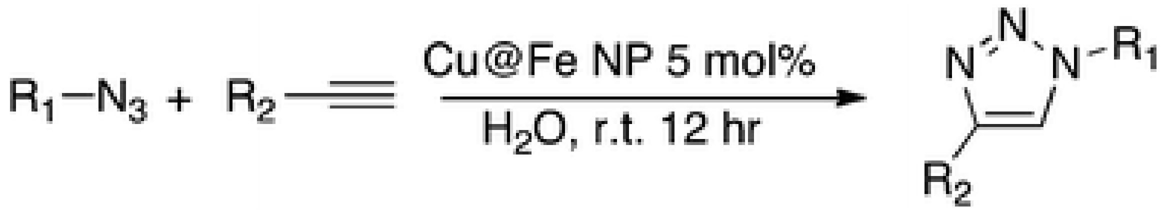
At 140℃, 1.25 MPa air in Tri-butyl phosphate solvent, for 4 hr.

99% conversion, 87% selectivity and 86% yield were observed.

唯有永續化學
能使化學永續

Magnetic copper–iron nanoparticles as simple heterogeneous catalysts for theazide–alkyne click reaction in water

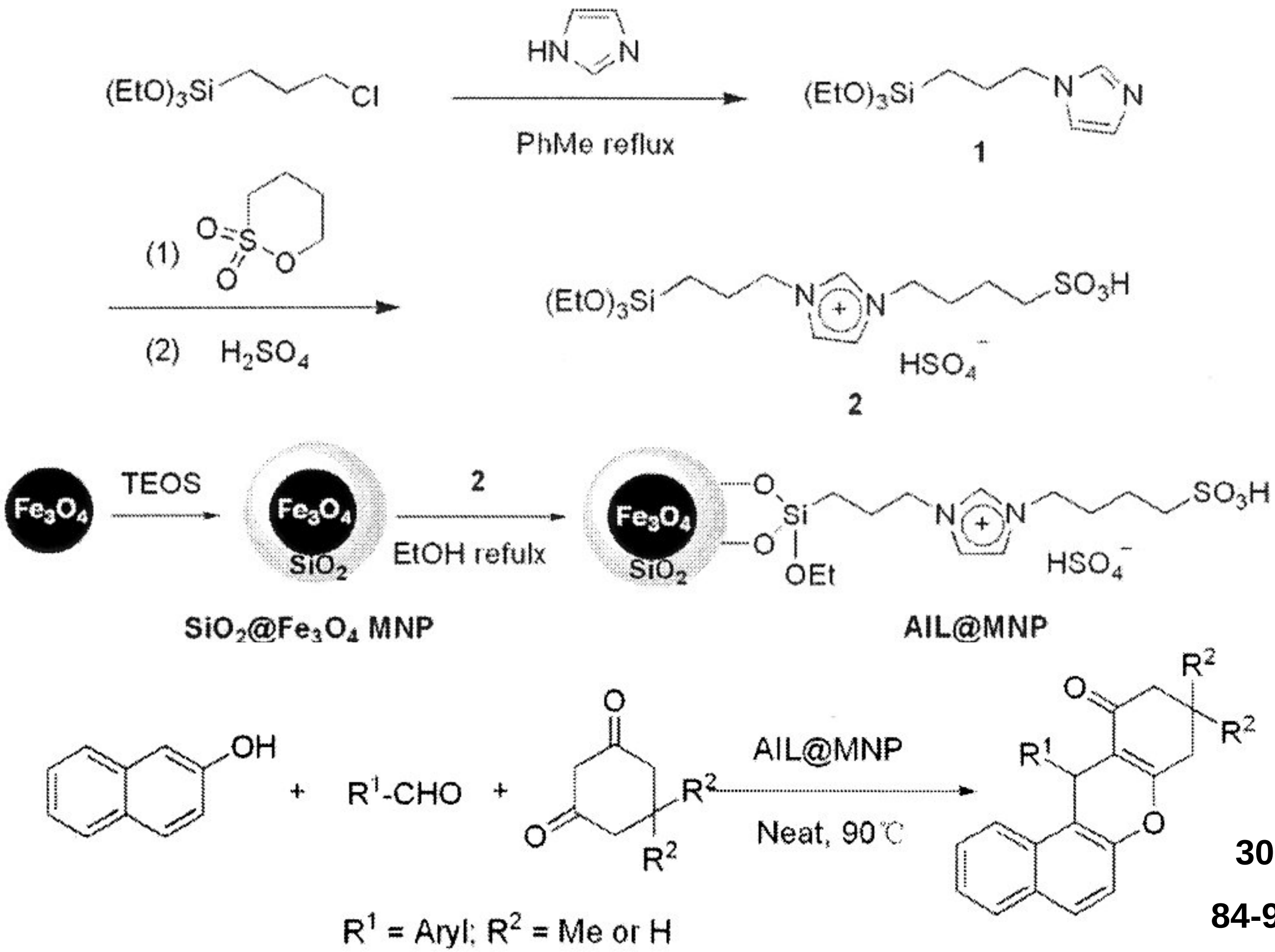
The development of a novel bimetallic copper–iron nanoparticle synthesis provides a recoverable heterogeneous catalyst for the azide–alkyne “click” reaction in water. The nanoparticles catalyze theproductionof a diverse range of triazoles (49-93% yield), while separation and reuse proved to be easy.



(*Green Chem.*, **2012**, ***14***, 622-624)

唯有永續化學
能使化學永續

- **A magnetic nanoparticle supported dual acidic ionic liquid: a "quasi-homogeneous" catalyst for the one-pot synthesis of benzoxanthenes** [*Green Chem*. **2012**, *14*, 201-208]



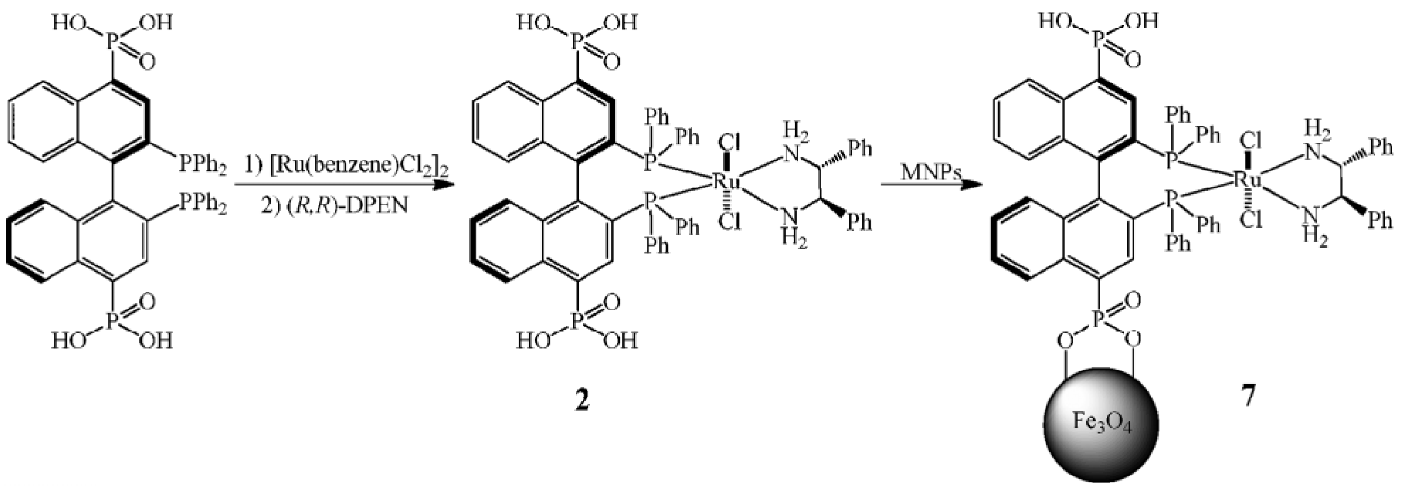
30-60 min

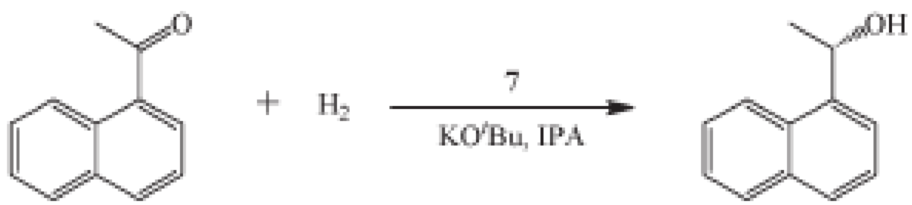
84-91% yield

唯有永續化學
能使化學永續

Immobilization of chiral catalysts on magnetite nanoparticles for highly enantioselective asymmetric hydrogenation of aromatic ketones

RSC Advances, **2012**, *2*, 2576–2580





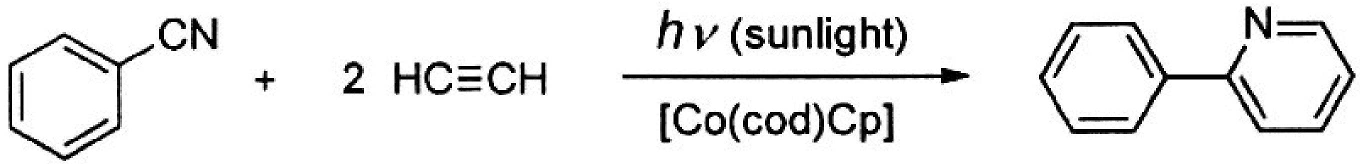
Run	1	2	3	4	5	6	7	8	9	10
ee%	98.1	97.2	97.4	97.5	98.0	98.0	98.0	97.9	98.0	97.1
conv.%	100	100	100	100	100	100	100	100	100	85

Homogeneous Photocatalytic Reactions

唯有永續化學
能使化學永續

24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu
42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag
74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au

CAT



9 1.27 mol in water- toluene

(ca. 0.5 mol%)

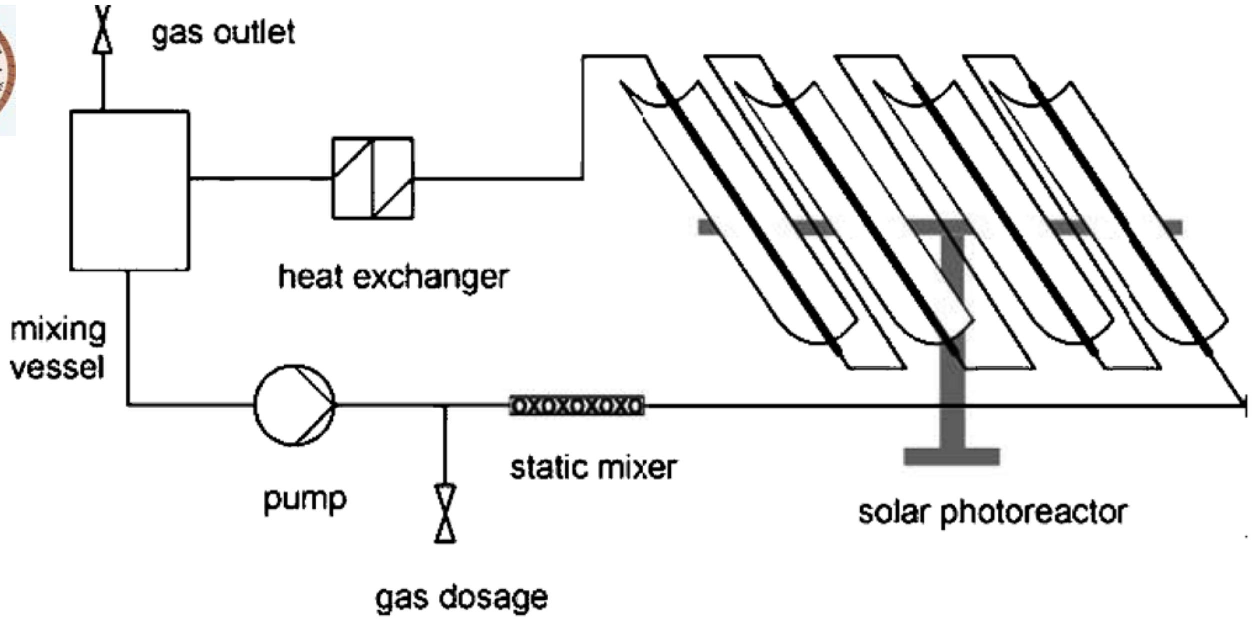
conversion: 40.7%
isolated yield: 39.3%
selectivity: 96.5%

10

6 hr of irradiation at 20℃

ChemSusChem **2012**, *5*, 352-371

唯有永續化學
能使化學永續



Photochem. Photobiol. Sci. **2005**, *2*, 409-411

PROPHIS-Solar reactor

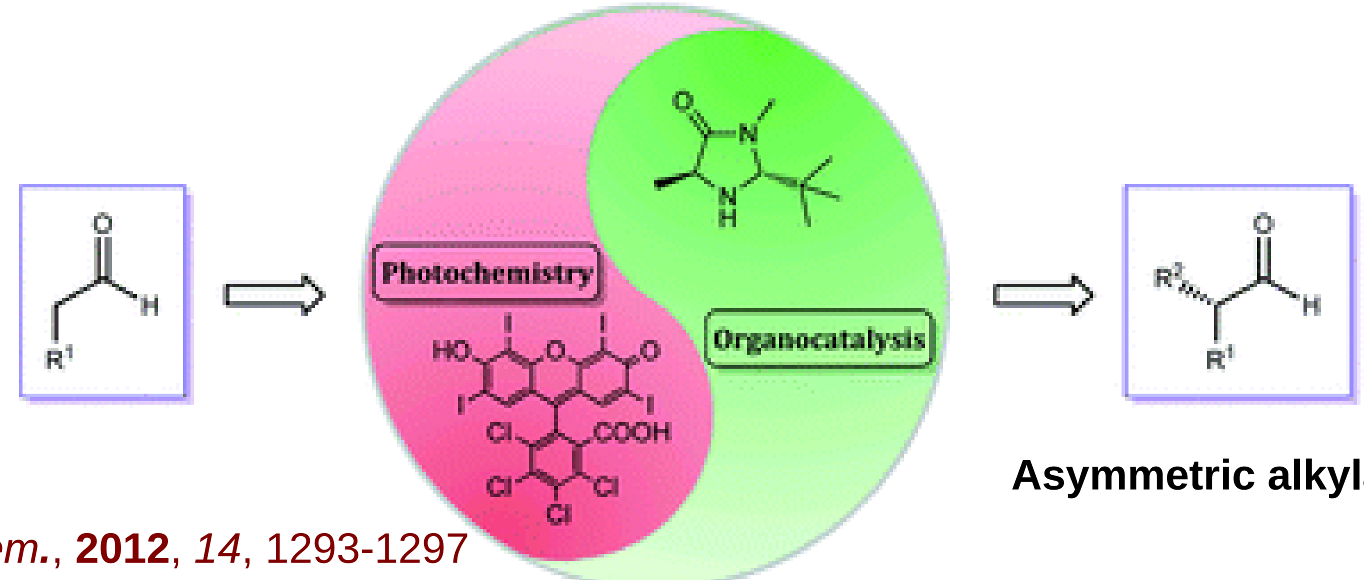
(*Pure Appl. Chem.* **2007,** *79,* 1939-1947)

- Highly efficient and selective sunlight-induced photocatalytic oxidation of cyclohexane on an eco-catalyst ($FeO@TiO_2$)under a CO_2 atmosphere

>99.9% selectivity to cyclohexanol + cyclohexanone, TON > 200 under CO_2

Ide, *et al. Green Chem*. **2012**, *14*, 1264-1267

- Visible Light Photoredox Organocatalysis with Rose Bengal (Hg 150W, LED 530 nm or Fluo 24W)



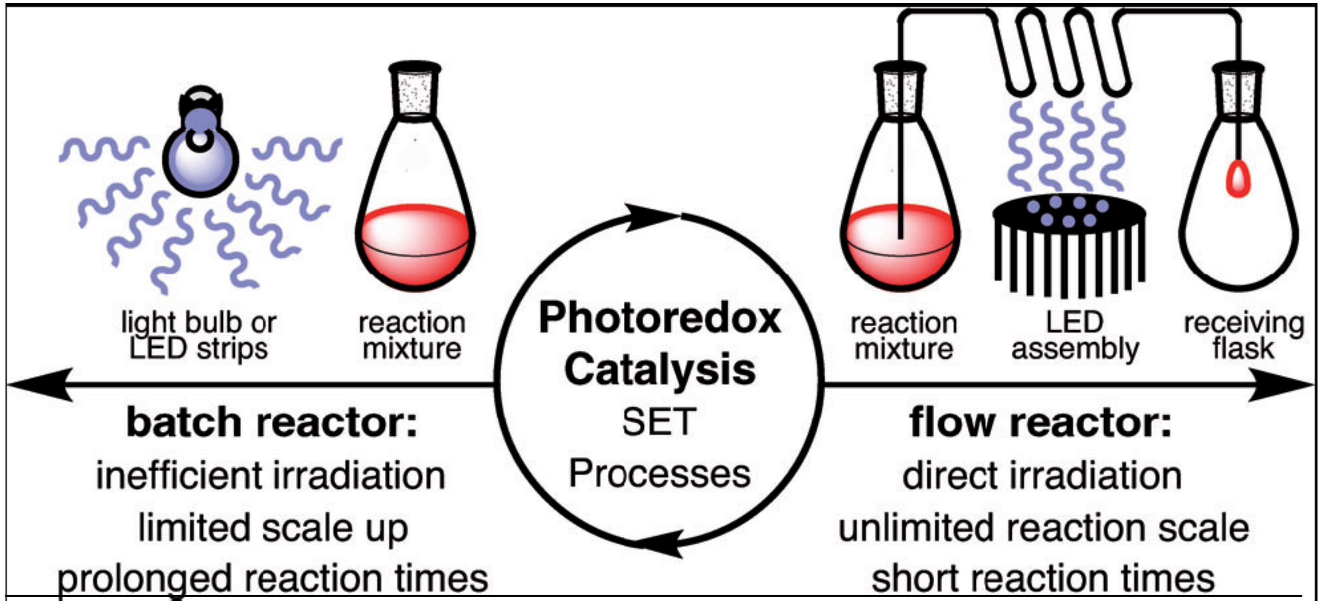
ca 80% ee

Asymmetric alkylation

Green Chem., **2012**, *14*, 1293-1297

Visible-Light Photoredox Catalysis in Flow

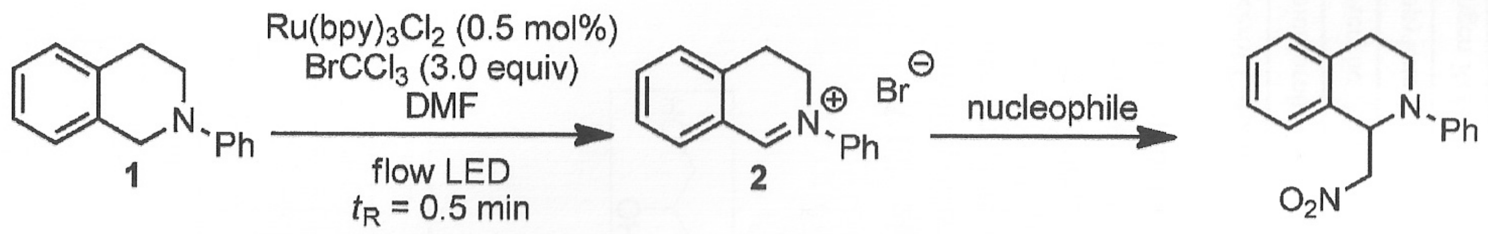
Angew. Chem. Int. Ed. **2012**, *51*, 4144 –4147



Photoredox catalysis in flow. Enabling increased efficiency by reactor technology SET=single-electron transfer.

A comparison with batch process

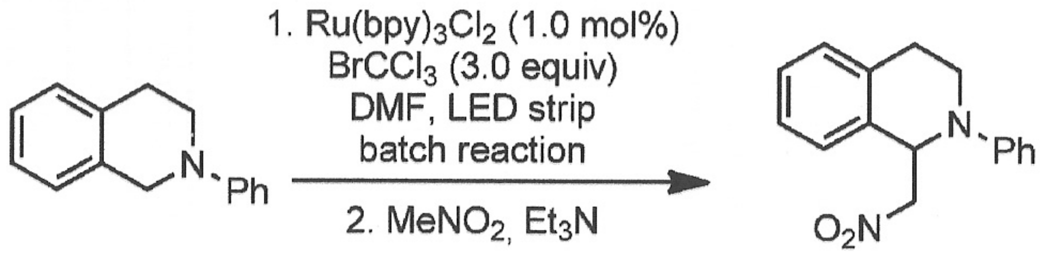
oxidative formation of iminium ions:



89%

t_R for iminium formation in flow:
0.5 min ⇒ 5.75 mmol h^{-1} (with a 479 μL reactor)

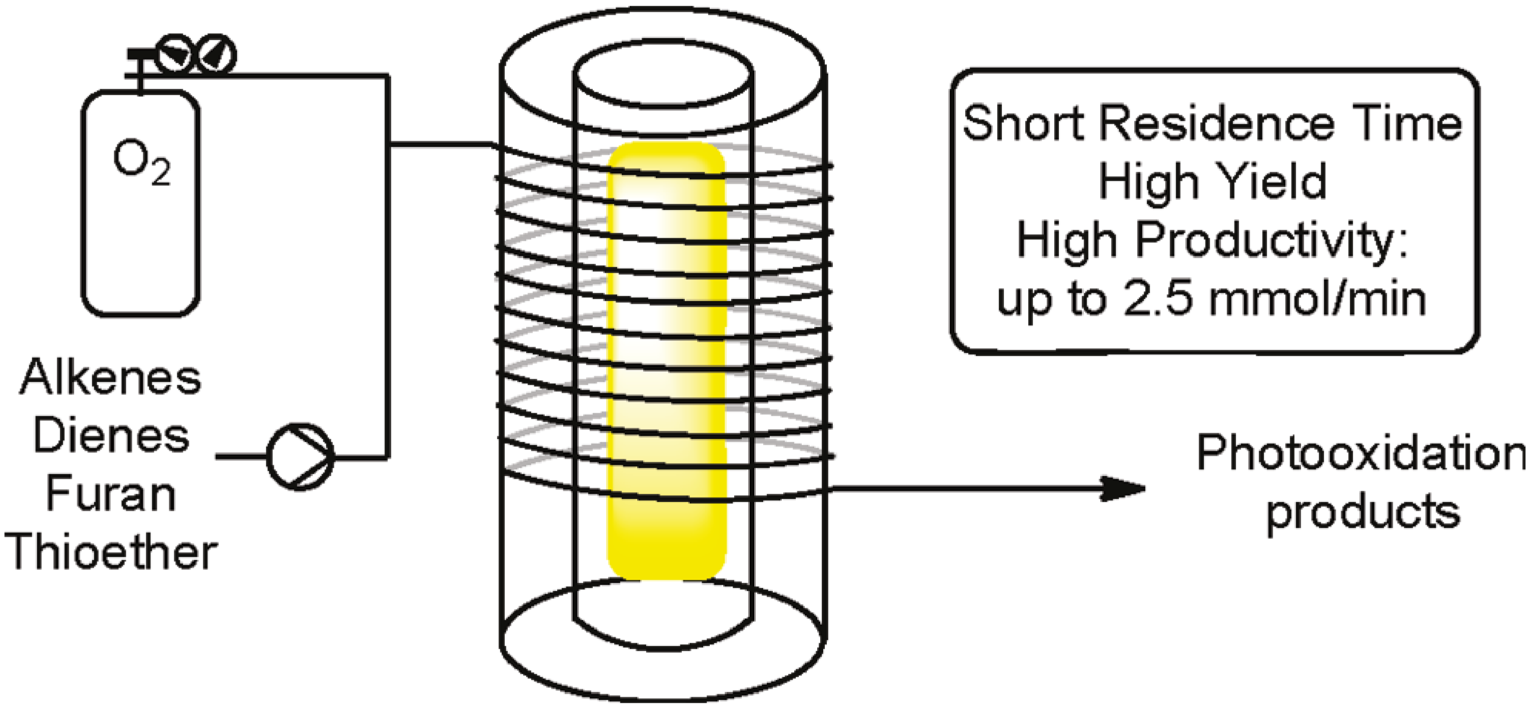
comparison with batch reaction:[9c]



95%

Batch reaction time for iminium formation:
3 h ⇒ 0.081 mmol h^{-1}

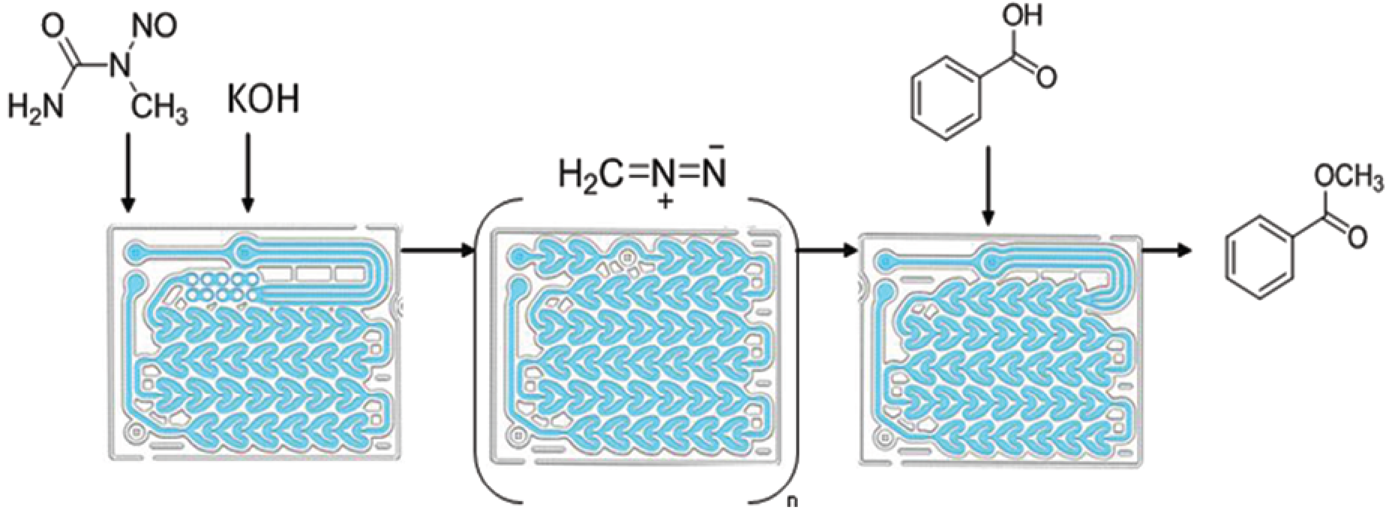
Highly Efficient Continuous Flow Reactions Using Singlet Oxygen



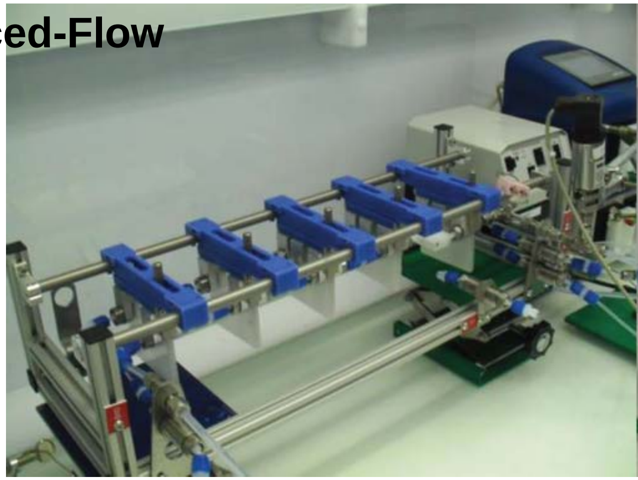
[*Org. Lett*. **2011**, *13*, 5008-5011]

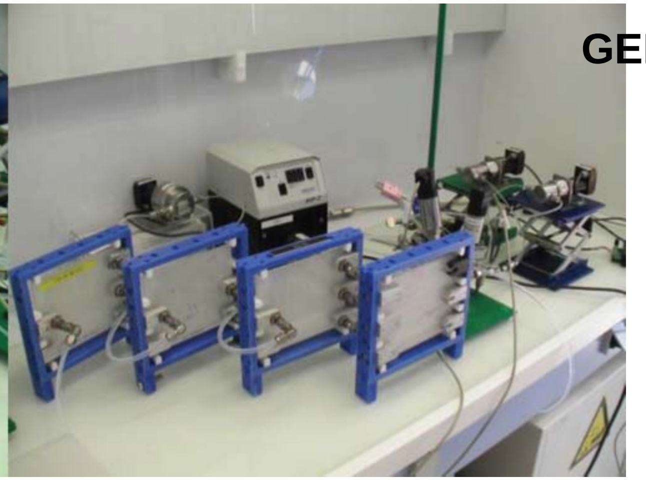
Scalable in Situ Diazomethane Generation in Continuous-Flow Reactors

Org. Proc. Res. Dev. **2012**, *16*, 1146–1149



Corning Advanced-Flow LowFlow

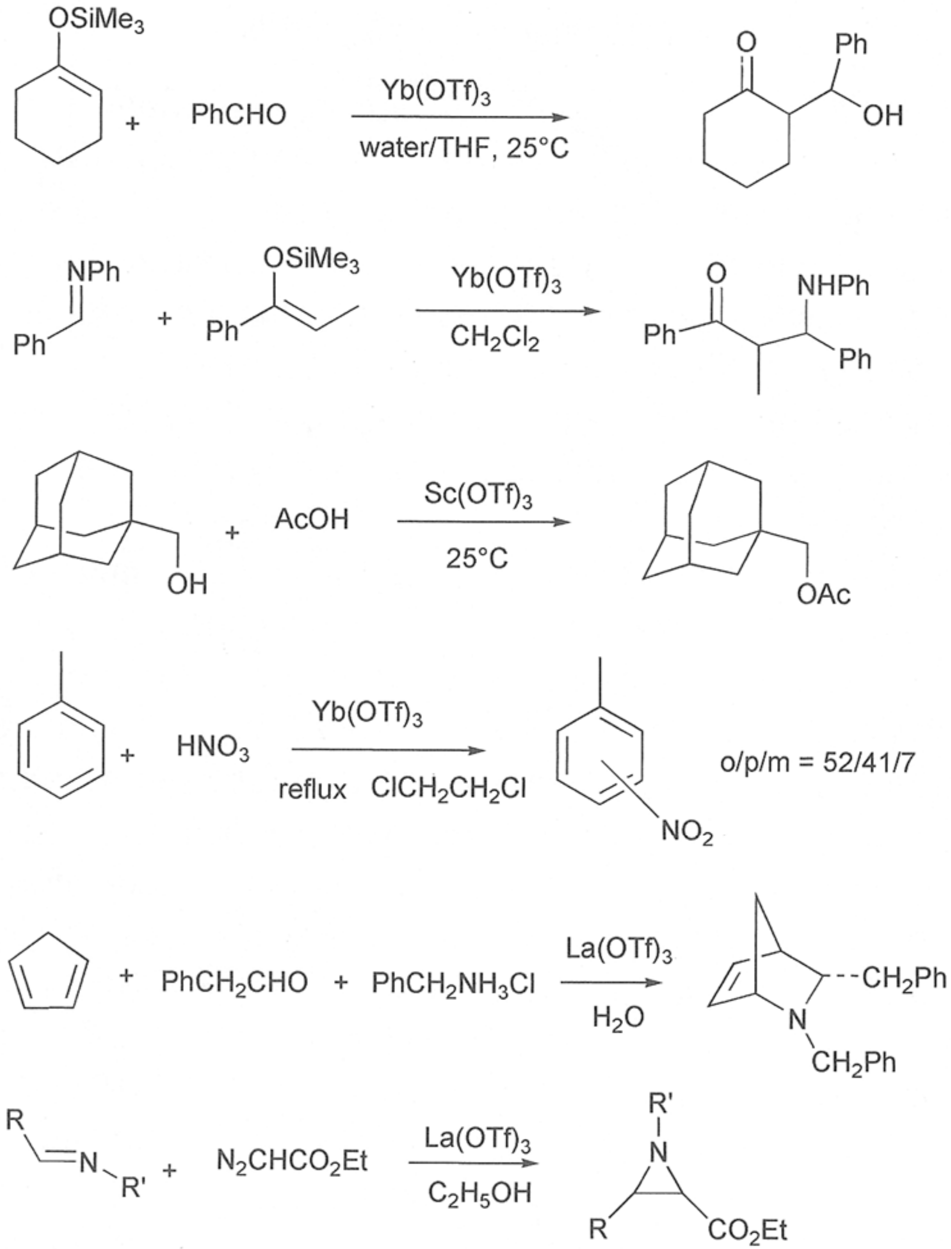




GEN1 reactors

Stable Lewis acid catalysts

Lanthanide and Lanthanide-like triflates are stable to water.



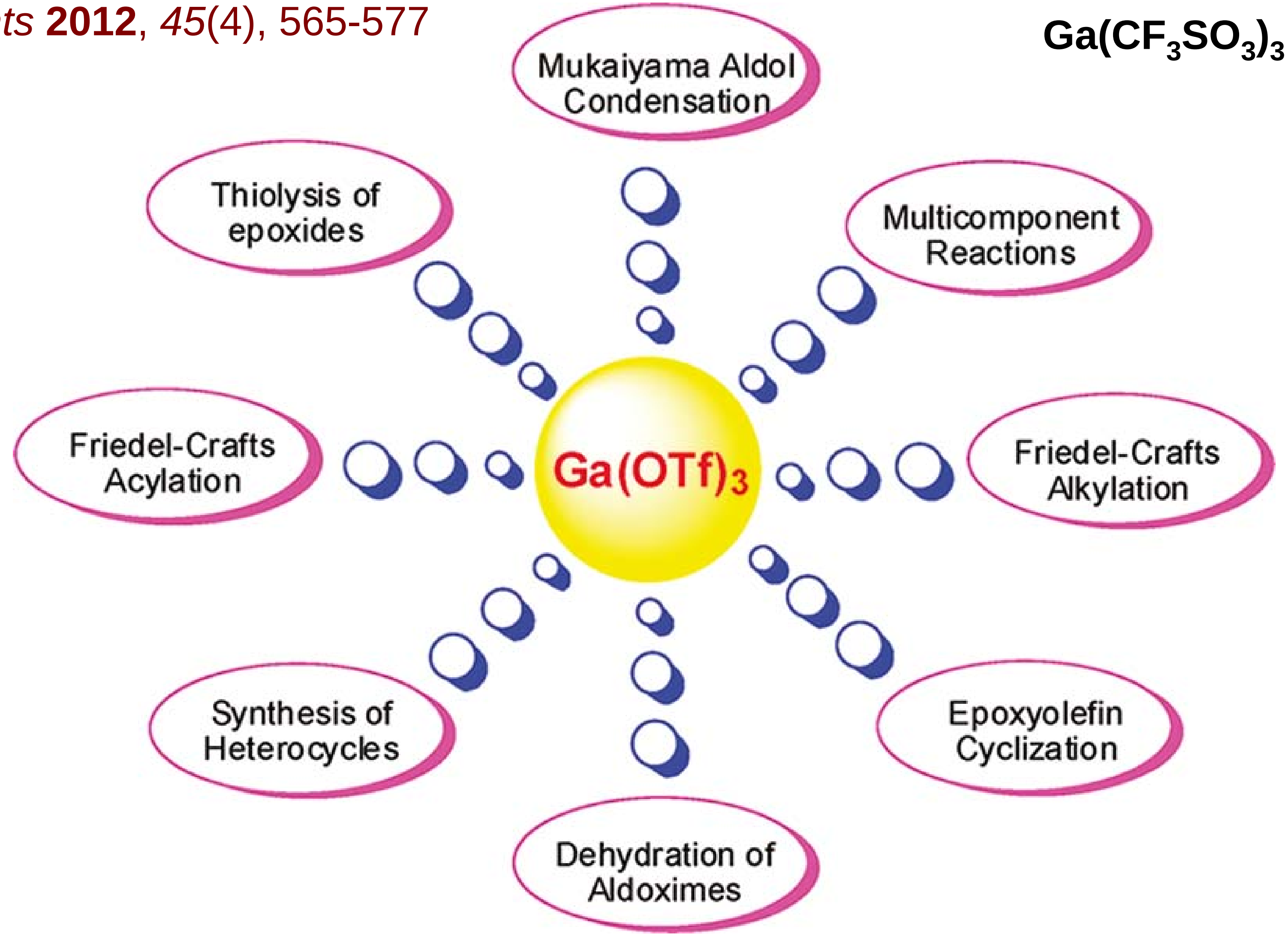
And enantiomer

唯有永續化學
能使化學永續

Gallium Triflate: An efficient and a sustainable Lewis acid Catalyst for organic synthetic transformations

Accounts **2012**, *45*(4), 565-577

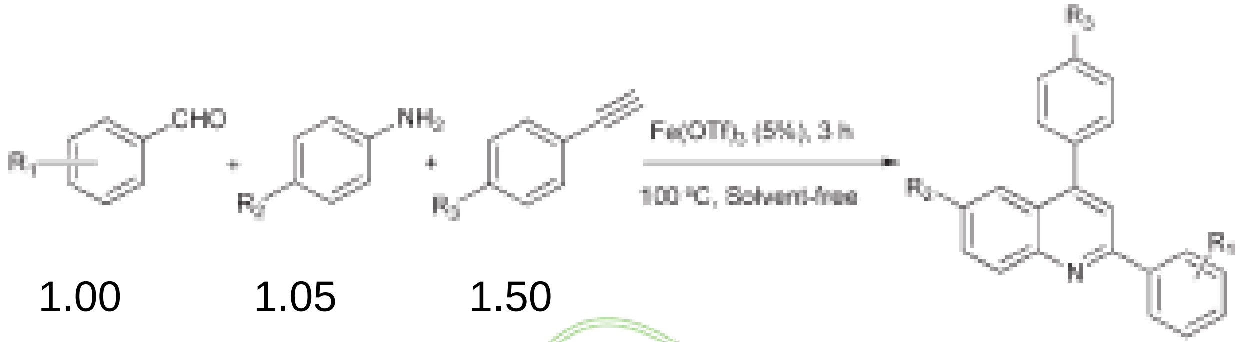
$Ga(CF_3SO_3)_3$



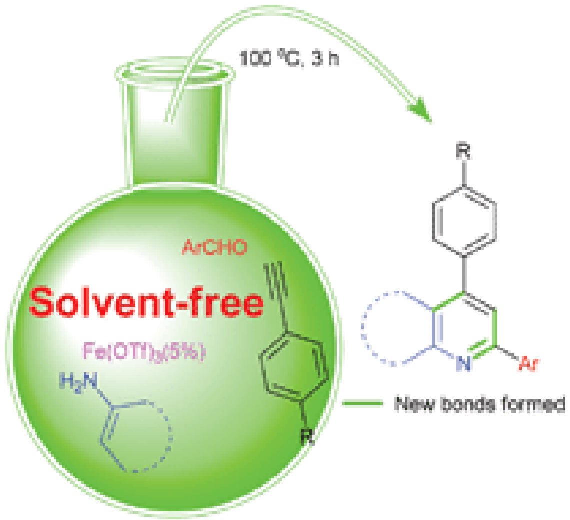
One-pot solvent-free synthesis of quinolines by C–H activation/C–C Bond formation catalyzed by recyclable iron(III) triflate

(*RSC Advances*, **2012**, *2*, 3759–3764)

Synthesis of quinolines using substituted anilines, phenylacetylenes and aldehydes.



1.00 1.05 1.50



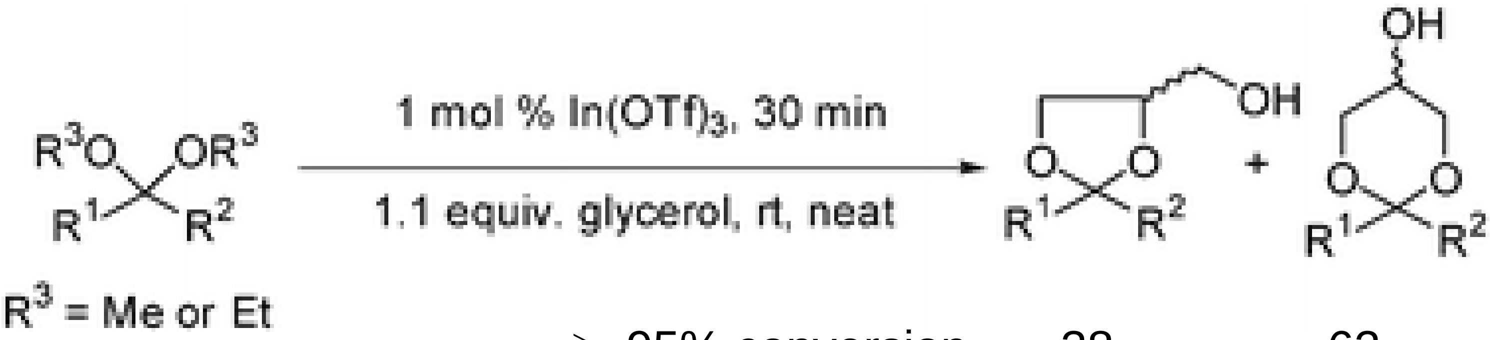
66-81% isolated

based on ArCHO

Metal triflate catalysed acetal exchange reactions of glycerol under solvent-free conditions

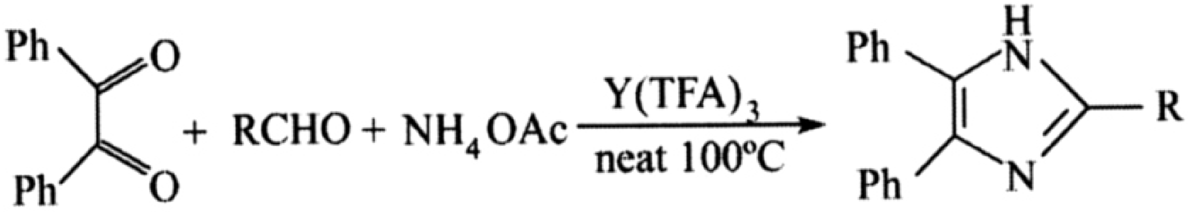
(*RSC Adv.*, **2012**, ***2***, 2702-2706)

Catalytic quantities of indium(III) triflate ($In(OTf)_3$) efficiently promote transacetalisation reactions of glycerol with acyclic acetals to generate the corresponding cyclic acetals under solvent-free reaction conditions.



> 95% conversion 38 62

Yttrium trifluoroacetate

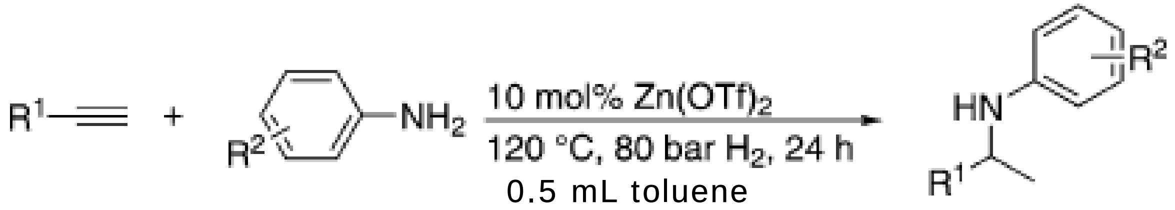


R	Isolated yield
C_6H_5	97
p-ClC_6H_4	97
2,4-$(Cl)_2$-C_6H_3	88
p-HOC_6H_4	99
p-$MeOC_6H_4$	96
p-MeC_6H_4	90
m-$NO_2C_6H_4$	93
2-ClC_6H_4	90
p-$NO_2C_6H_4$	93
$CH_3CH_2CH_2$	45

Green Chem. Lett. Rev. **2010**, *3*, 101-104

Development of New Hydrogenations of Imines and Benign Reductive Hydroaminations: Zinc Triflate as a Catalyst

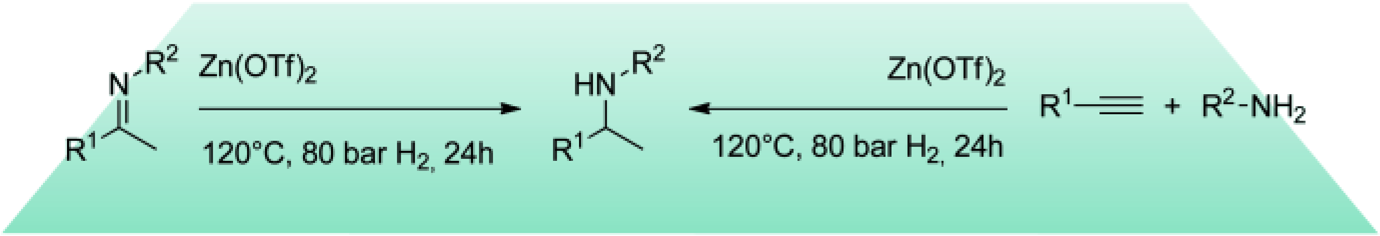
ChemSusChem **2012,** *5*, 777-782



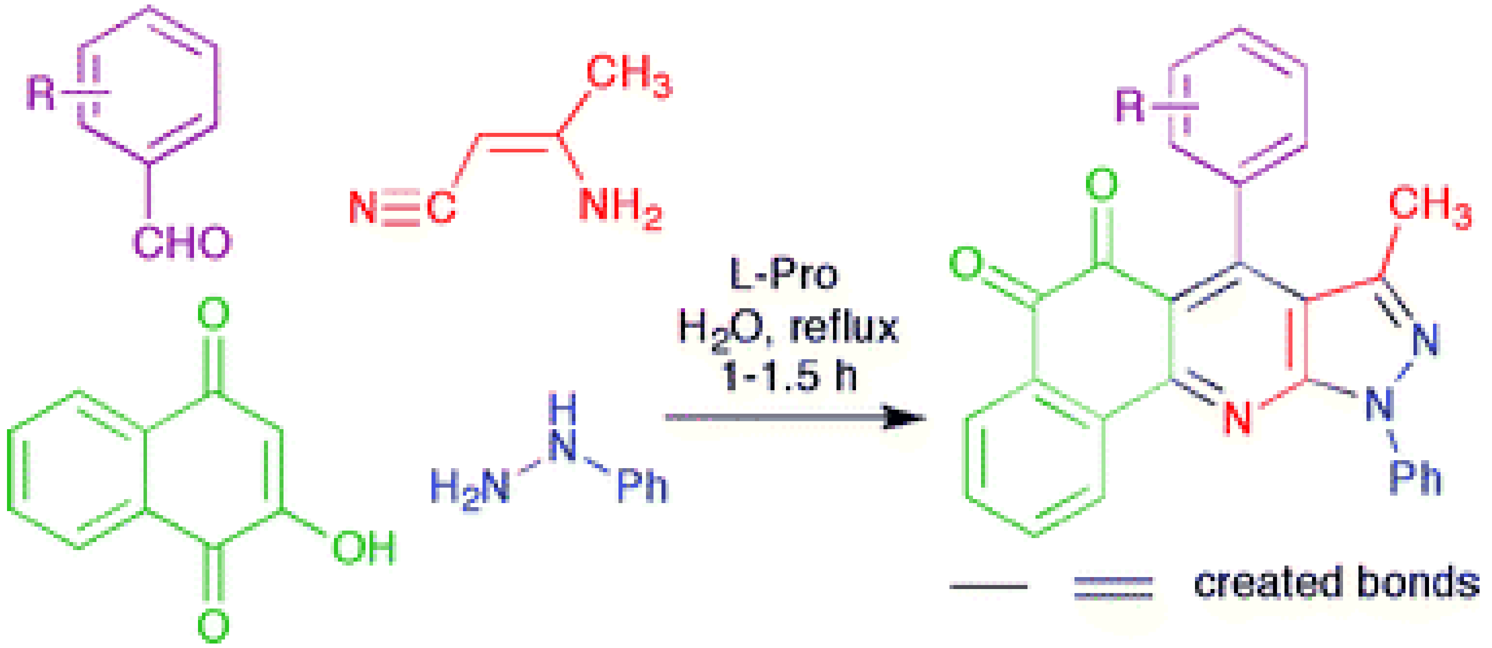
3 0.65 : **4** 0.50 mmol

2 55-88% yield

It's a triflate with zinc: The hydrogenation of imines and the reductive hydro-amination of alkynes with hydrogen and amines have been achieved by applying zinc triflate as a catalyst. This methodology is a convenient alternative to the use of precious metal-based catalysts and expensive silanes and Hantzsch ester dihydropyridines.



Some Organocatalysts for multi-component reactions (MCR)



A four-component, L-proline-catalyzed on-water synthesis of structurally complex polyheterocyclic *o*-quinones is described.

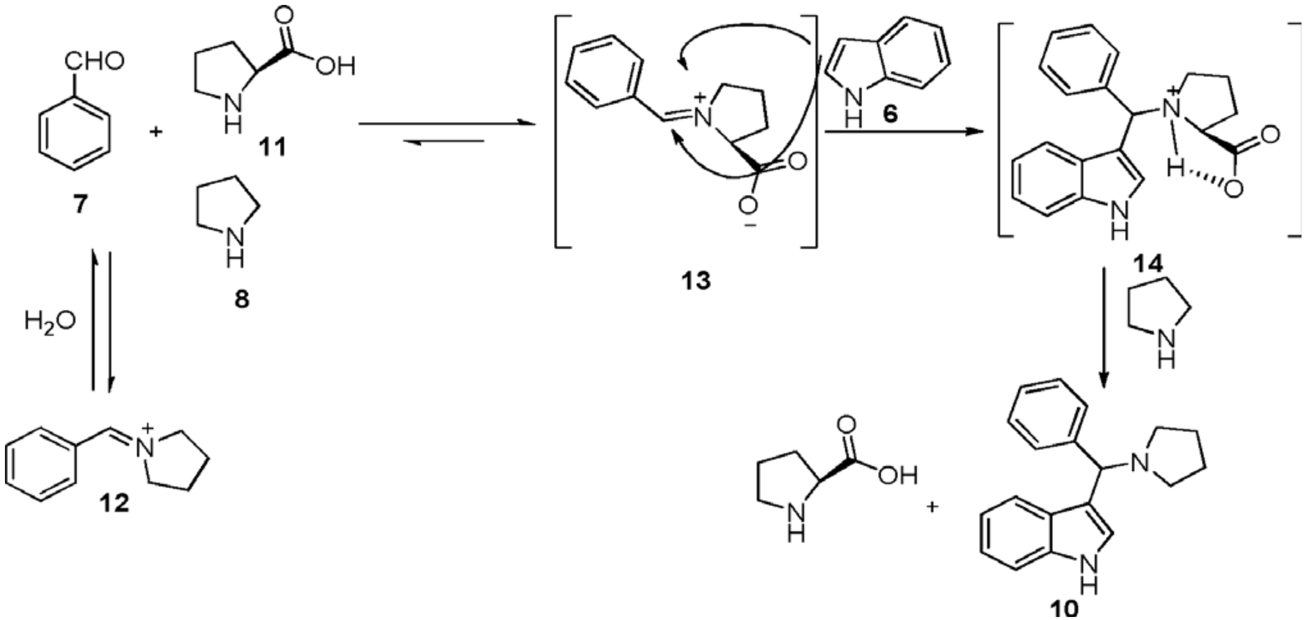
Green Chem. **2011**, *13*, 3248-3254

唯有永續化學
能使化學永續

More examples

L-Proline catalyzed multicomponent synthesis of the 3- amino-alkylated indole 10 (from 6, 7, 8)

[*Green Chem*. **2012**, *14*, 290-295]

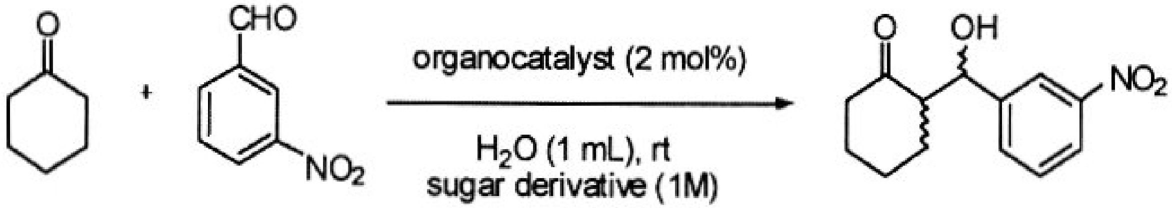


Room temp., 5.5 hr

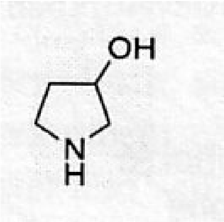
87% yield

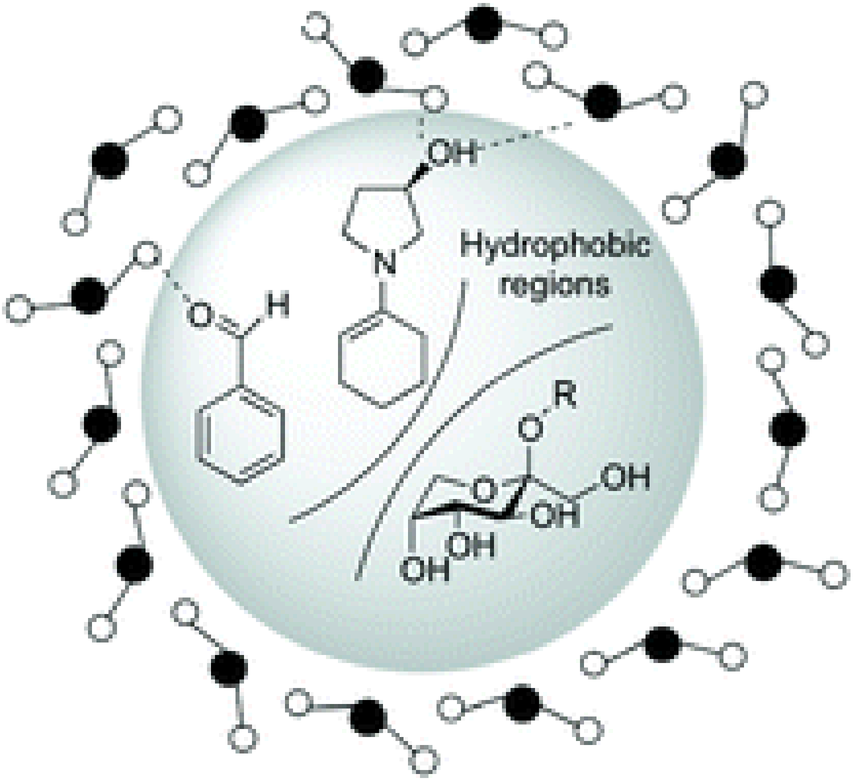
Organocatalyzed direct aldol reactions were efficiently performed in aqueous solutions of facial amphiphilic carbohydrates with high diastereoselectivity and yields.

（***Green Chem.***, 2012, **14**, 281-284 ）



Catalysts, *e.g.*



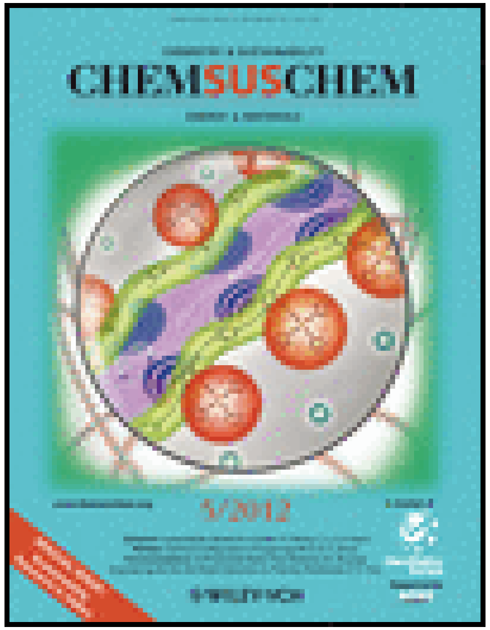


Specific catalysts designed and employed

- **Homogeneous and heterogeneous catalysts for multicomponent reactions [***RCS Adv*. **2012**, *2*, 16-58**]** (with 408 references)
- **Advances in catalytic metal-free reductions: from bio-inspired concepts to applications in the organocatalytic synthesis of pharmaceuticals and natural products** **[***Green Chem.* **2011***, 13,* 1084-1105] (with 129 references)

唯有永續化學
能使化學永續

ChemSusChem



Special Issue: Sustainability Research in Dalian

May 2012
Volume 5, Issue 5
Pages 801–955

The American Chemical Society plans to begin publishing **ACS Sustainable Chemistry & Engineering** in January 2013. The online-only journal will cover life cycle assessment, green chemistry, alternative energy, green innovative manufacturing, and harnessing waste as a resource (*C&EN*, May 2, 2012).

唯有永續化學能使化學永續

Sustainability of chemistry can only be achieved by sustainable chemistry

謝謝光臨 敬請指正

劉廣定
臺大化學系
(ktliu@ntu.edu.tw)