Workshop 1: **Catalysis for CO_2 Conversion**

“Catalysis”

Dr. Christopher J. Whiteoak

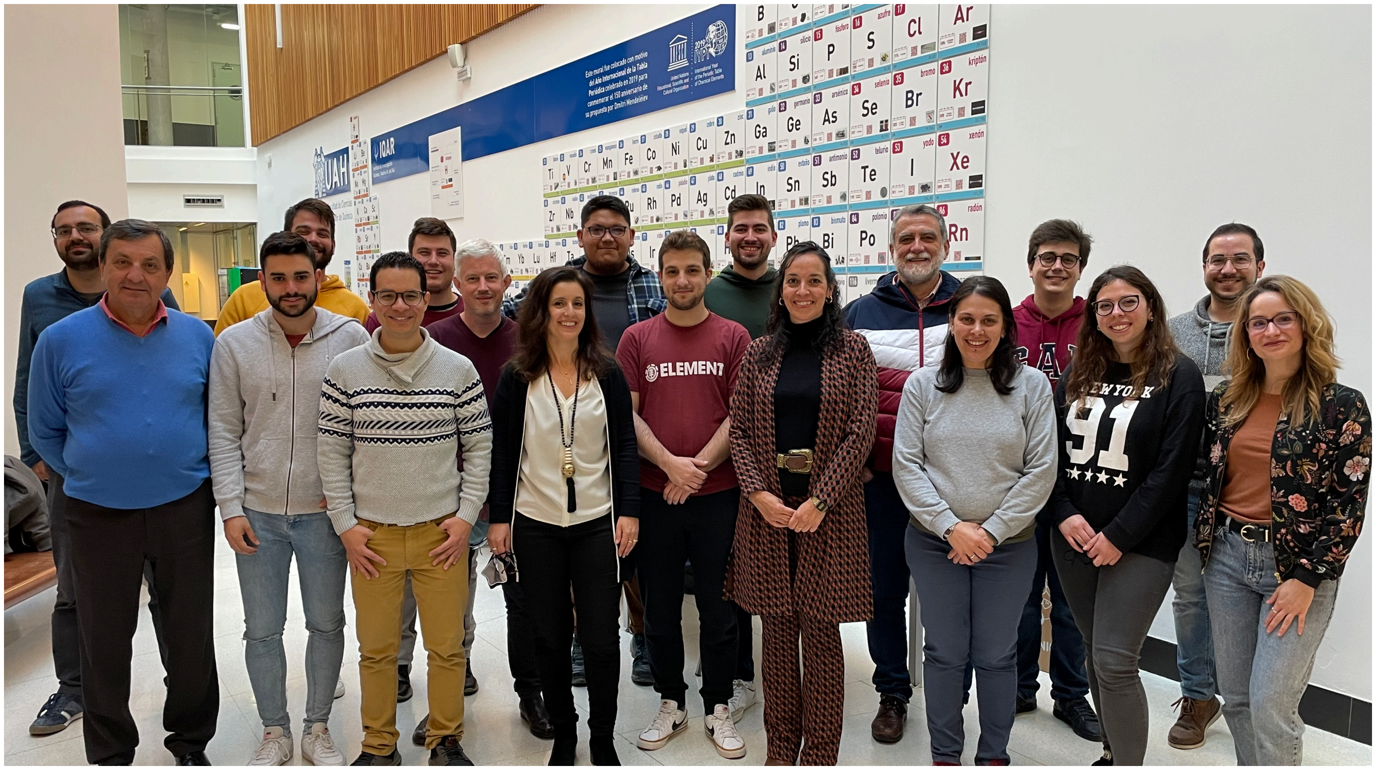
ICIQ, Tarragona, Thursday, 25 January 2024

SOSCATCOM

Universidad de Alcalá

Alcalá de Henares

SOSCATCOM Research Group



SOSCATCOM

Group leaders:

Prof. Marta E. G. Mosquera

Prof. Gerardo Jiménez

https://soscatcom.es/

Sustainable Catalytic Processes with Organometallic Compounds

Overlap

There will be overlap…

Organic chemistry		*Polymer chemistry*
	Catalysis	

Catalysis is essential in organic chemistry and polymer chemistry!

(maybe the organic chemistry community have adopted Pd…)

Overview

[1] Catalysis in general – where are we?

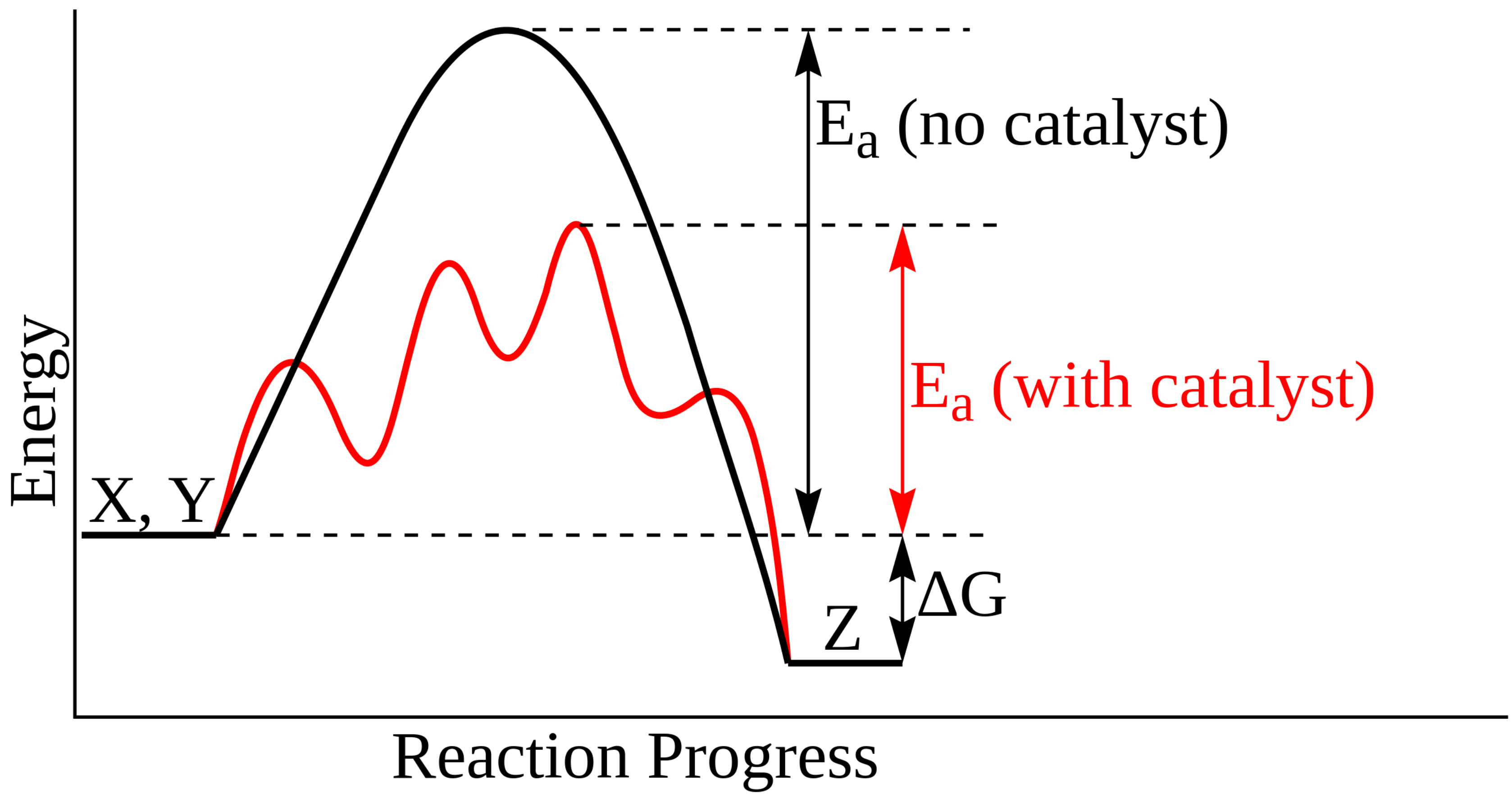
[2] Consider where starting materials come from…

[3] How we can use CO_2 as a reagent (specific examples of cyclic and polycarbonates)

[4] End of life concerns of plastics – approaches to recycling using catalysis

[5] Specific examples of catalytic recycling of polycarbonates

Catalysis: reducing energy requirements



Energy: *the current situation*

Global direct CO_2 emissions from primary chemical production were 941 megatons of CO_2 in 2019. The manufacturing of chemicals is **energy-intensive**

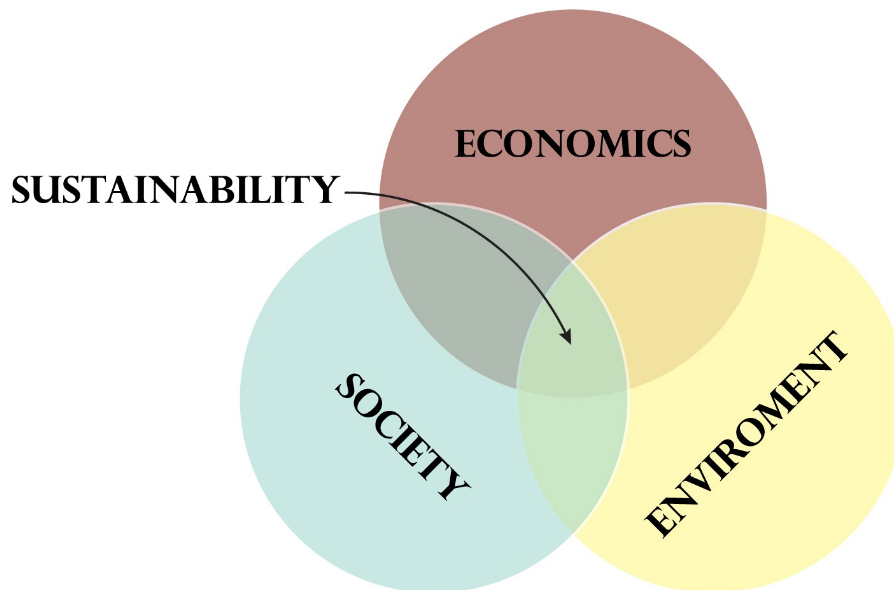
EIA (2021) Chemicals. https://www.iea.org/reports/chemicals. Accessed January 2024.

"Reducing carbon emissions in the chemical industry focuses on innovations in process and chemical engineering, including utilization of big data and supercomputing, and advances in materials science, process design, sensors, analytics and catalysts"

T. Taseska, W, Yu, M. K. Wilsey, C. P. Cox, Z. Meng, S. S. Ngarnim, A. M. Müller, "Analysis of the Scale of Global Human Needs and Opportunities for Sustainable Catalytic Technologies", *Top. Catal.*, **2023**, *66*, 338.

"Catalysis contributes to more than 30% of the total GDP of European economies, and catalytic processes are involved in 80% of all manufactured goods"

"it enables materials to be made that sustain society as we know it"



C. R. Catlow C., M. Davidson, C. Hardacre, G. J. Hutchings, "Catalysis making the world a better place", *Phil. Trans. R. Soc. A.*, **2016**, *374*, 20150089.

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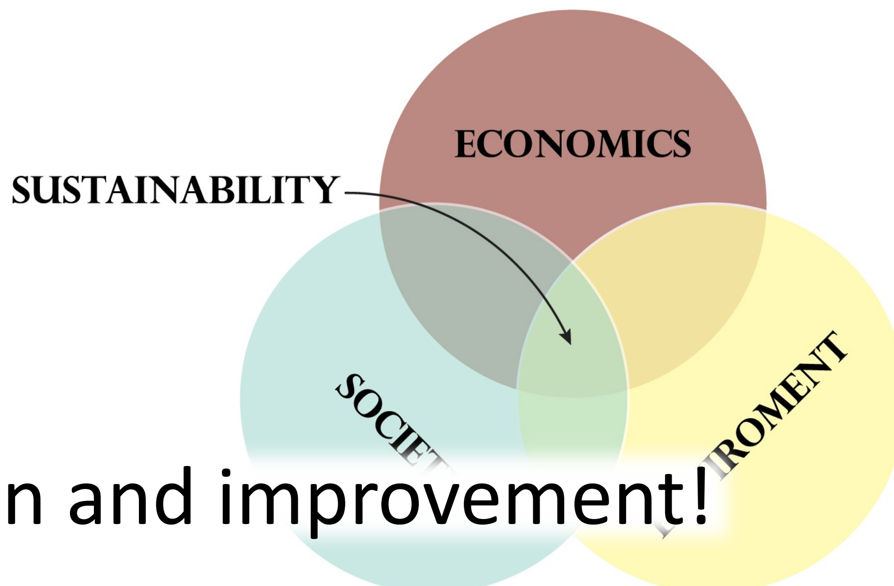


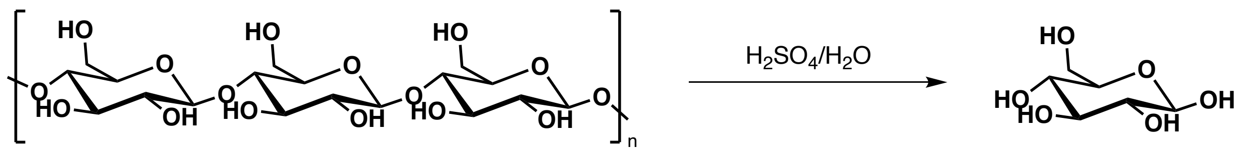
Still room for innovation and improvement!

C. R. Catlow C., M. Davidson, C. Hardacre, G. J. Hutchings, "Catalysis making the world a better place", *Phil. Trans. R. Soc. A.*, **2016**, *374*, 20150089.

The first chemical reaction in chemistry knowingly using a catalyst was reported in 1811 by Gottlieb Kirchhoff:

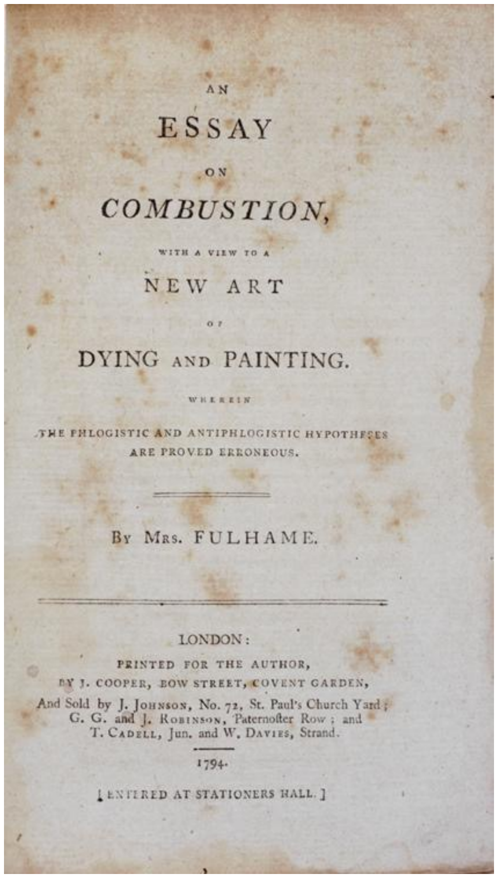
“the acid-catalyzed conversion of starch to glucose”

Starch was heated with sulfuric acid (aq.):



Since the sulfuric acid was not consumed, it was the first documented example of catalysis

The first chemical reaction in chemistry knowingly using a catalyst was reported in 1811 by Gottlieb Kirchhoff:



AN ESSAY ON COMBUSTION, WITH A VIEW TO A NEW ART OF DYING AND PAINTING. WHEREIN THE PHLOGISTIC AND ANTIPHLOGISTIC HYPOTHESES ARE PROVED ERRONEOUS.

BY MRS. FULHAME.

LONDON: PRINTED FOR THE AUTHOR, BY J. COOPER, BOW STREET, COVENT GARDEN, And Sold by J. JOHNSON, No. 72, St. Paul's Church Yard; G. G. and J. ROBINSON, Paternoster Row; and T. CADELL, Jun. and W. DAVIES, Strand.

1794.

[ENTERED AT STATIONERS HALL.]

Oddly enough the concept of catalysis was invented before…

1794: Elizabeth Fulhame

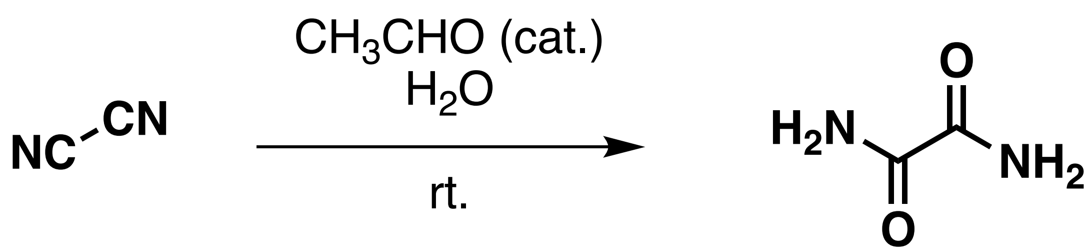
Possibly one of the greatest "forgotten" scientists? (also discovered photoreduction)

*The concept of "**catalysts**":*

Jöns Jacob Berzelius.

"chemicals facilitating a reaction without undergoing any change themselves" was **formalized** in 1836 by Jöns Jacob Berzelius (40 years after Elizabeth Fulhame)

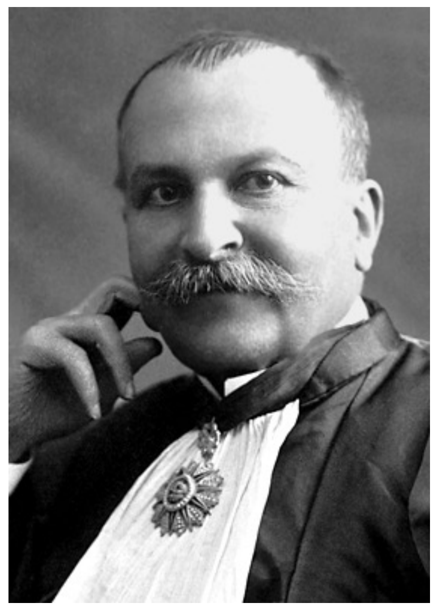
Organo-catalysis was first formerly introduced by Justus von Liebig in 1860



Recognition

Catalysis is frequently recognized by the Nobel prize - Important

F. Wilhelm Ostwald received the Nobel Prize in 1909 for his work on “***catalysis and on the fundamental principles governing chemical equilibria and rates of reaction***”



Paul Sabatier was honored in 1912 for his work on “***improving the hydrogenation of organic species in the presence of metals***”

Heterogeneous or homogeneous catalysis?

homogeneous catalysis

Advantages

- ✓ Homogeneous catalysts are "*traditionally*" more selective than heterogeneous catalysts
- ✓ For exothermic processes, homogeneous catalysts transfer excess heat into the solvent
- ✓ Homogeneous catalysts are easier to characterize precisely, so their reaction mechanisms are amenable to rational design/manipulation

Disadvantages

- ✗ The separation of homogeneous catalysts from products can be challenging. In cases involving highly activity catalysts, the catalyst is often not removed from the product. In other cases, organic products are often and can be separated by distillation
- ✗ Homogeneous catalyst often have limited thermal stability compared to heterogeneous catalysts. Many organometallic complexes degrade >100 °C.

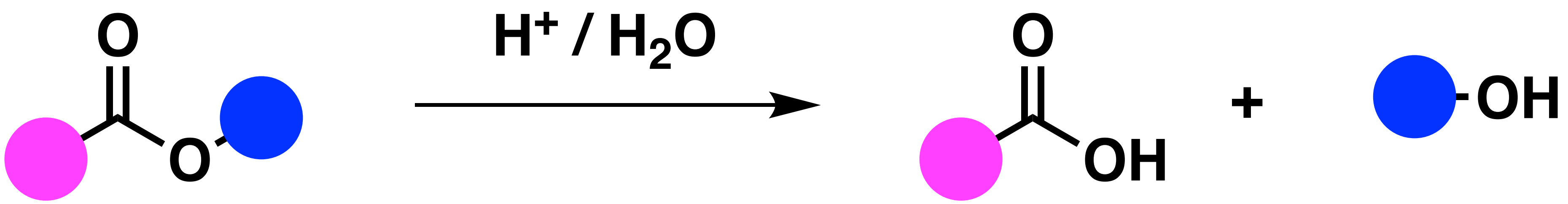
… there are many more to discuss

Examples of catalysis

[1] Non-metal-based catalysis

The proton (H^+) is is capable of catalysis (as already seen with starch):

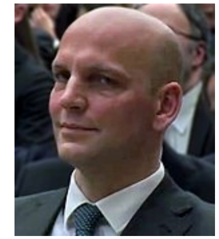
e.g. Hydrolysis of esters



Note: At neutral pH, aqueous solutions of most esters do not hydrolyze at practical rates

Examples of catalysis

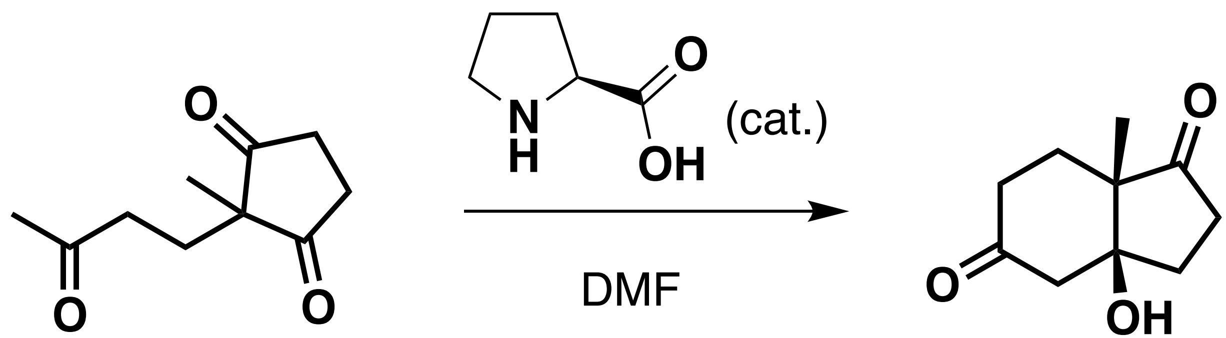
[1] Non-metal-based catalysis



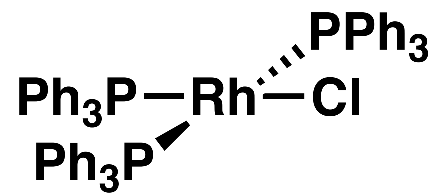
Chiral proline as catalyst (first reported in the 1970's)

Nobel prize 2021: Benjamin List & David M. C. MacMillan for the "***development of asymmetric organocatalysis***"

e.g. Hajos–Parrish–Eder–Sauer–Wiechert reaction (catalyzed asymmetric aldol reaction)



Examples of catalysis

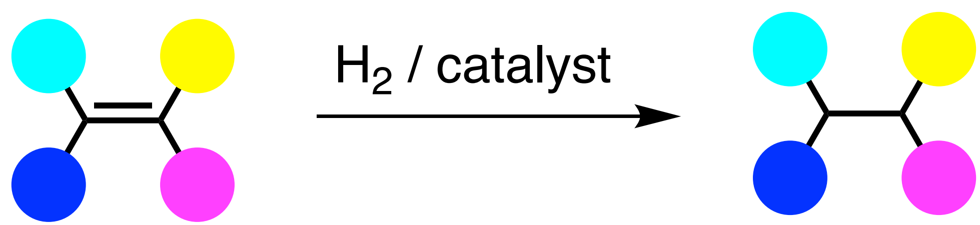


Wilkinson catalyst

[2] Transition metal catalysis

(a) Hydrogenation:

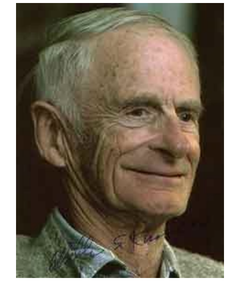
H_2 is added to unsaturated substrates. A related methodology, transfer hydrogenation, involves by transfer of hydrogen from one substrate (the hydrogen donor) to another (the hydrogen acceptor)



Note: Most large-scale industrial hydrogenations – margarine, ammonia, benzene-to-cyclohexane – are conducted with heterogeneous catalysts. Fine chemical syntheses, however, often rely on homogeneous catalysts

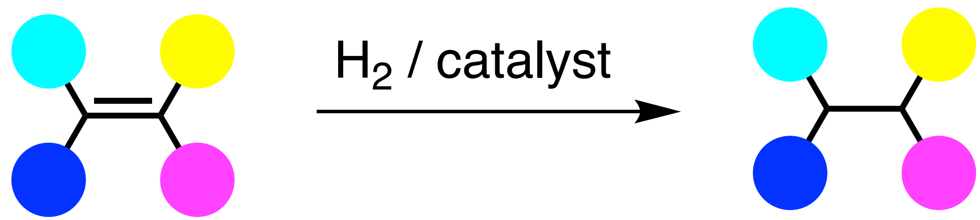
Examples of catalysis

[2] Transition metal catalysis



Nobel prize 2001: Ryōji Noyori & William S. Knowles for their work on "***chirally catalysed hydrogenation reactions***"

(a) Hydrogenation and related reactions:



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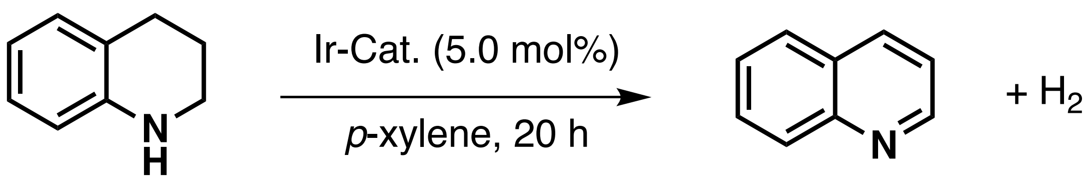
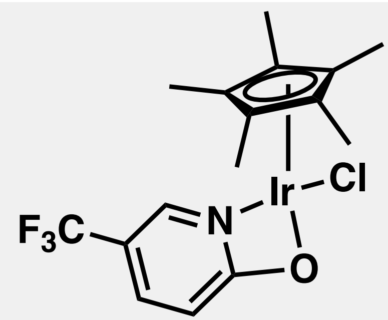
Examples of catalysis

[2] Transition metal catalysis

The reverse: Dehydrogenation



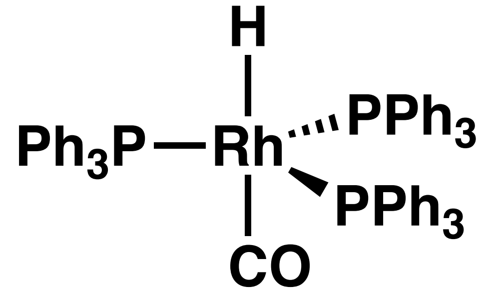


Ir-Cat.

Yamaguchi/Fujita (2009)

R. Yamaguchi, C. Ikeda, Y. Takahashi, K.-I. Fujita, “Homogeneous Catalytic System for Reversible Dehydrogenation-Hydrogenation Reactions of Nitrogen Heterocycles with Reversible Interconversion of Catalytic Species”, *J. Am. Chem. Soc.*, **2009**, *131*, 8410.

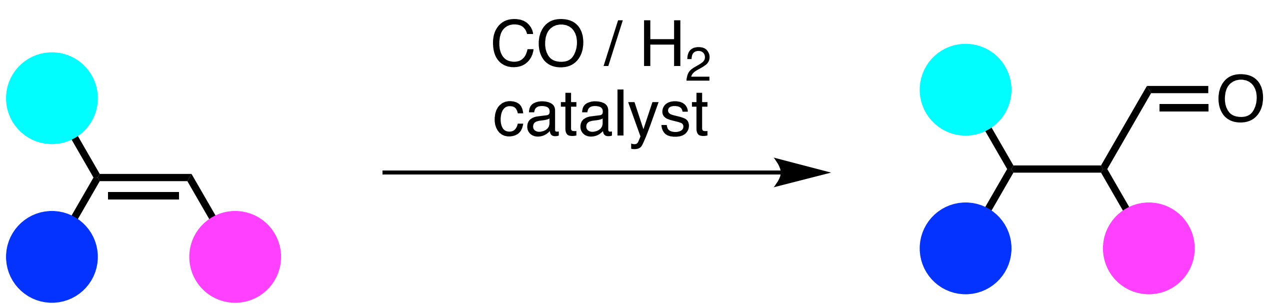
Examples of catalysis



[2] Transition metal catalysis

(b) Carbonylations:

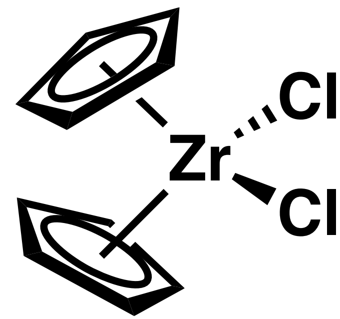
Hydroformylation, a prominent form of carbonylation, involves the addition of “H” and "C(O)H" across a double bond.



Related reactions: The conversion of alcohols to carboxylic acids. MeOH and CO to give acetic acid (Monsanto and Cativa processes)

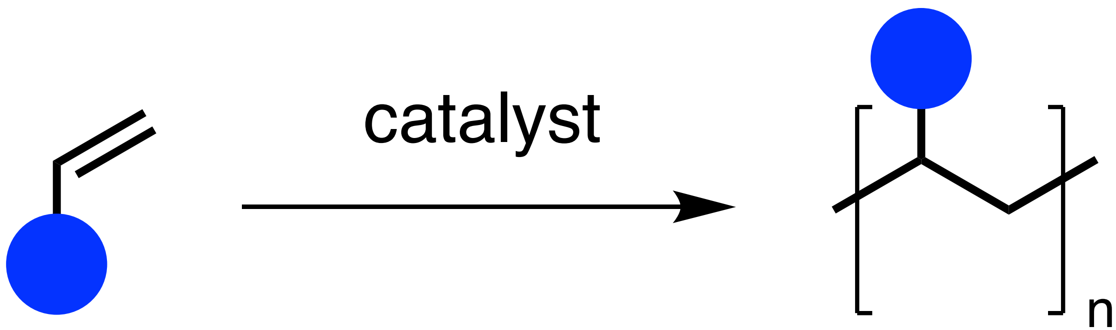
Examples of catalysis

[2] Transition metal catalysis



(c) Polymerization and metathesis of alkenes:

Polyethylene and polypropylene are produced from ethylene and propylene by Ziegler-Natta catalysis



Examples of catalysis

[2] Transition metal catalysis


Nobel prize 1963: Karl Ziegler & Giulio Natta for the “***discoveries in the field of the chemistry and technology of high polymers***”

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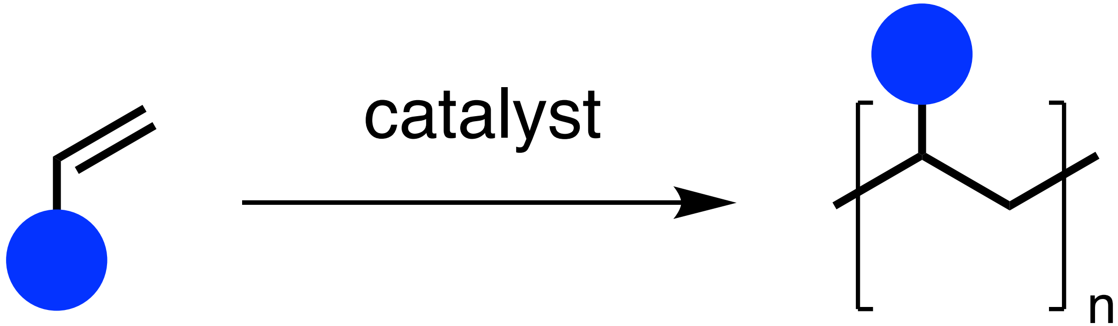

Examples of catalysis

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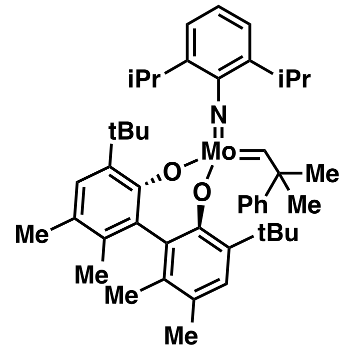
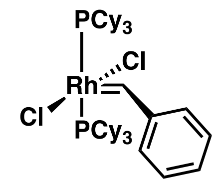
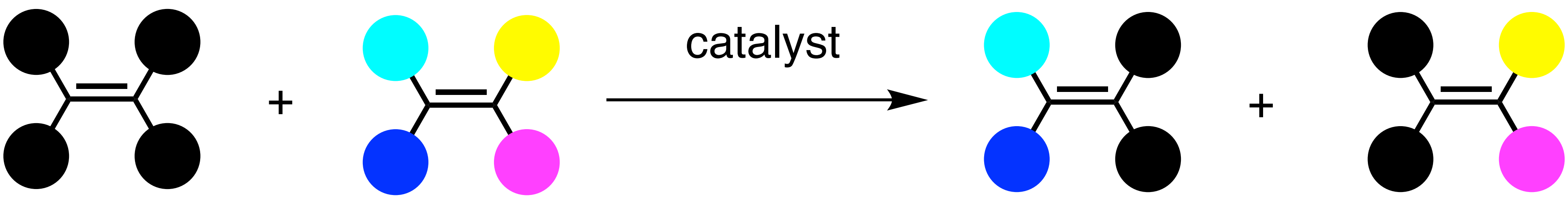


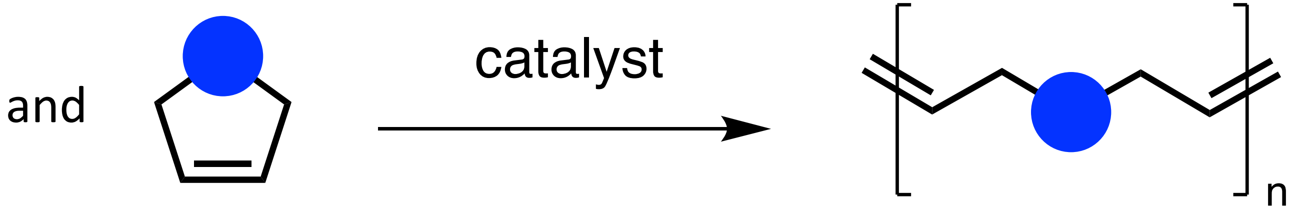
Schrock catalyst



Grubbs catalysts

Olefin metathesis y ring-opening metathesis polymerization



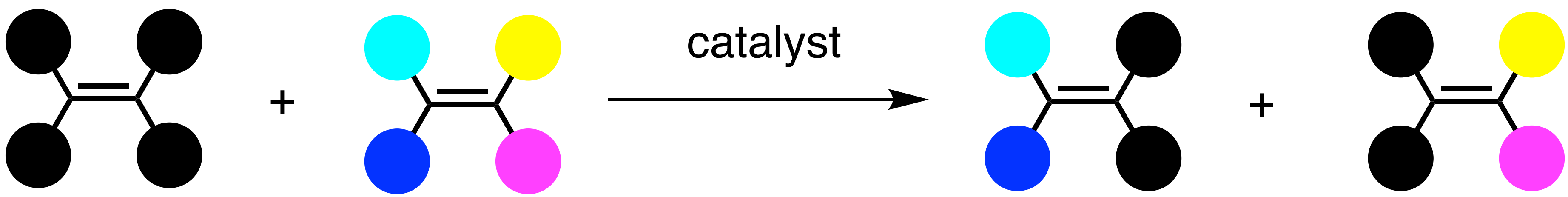


Examples of catalysis

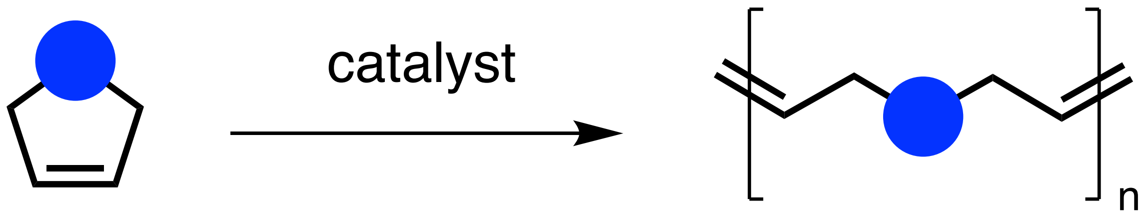
[2] Transition metal catalysis

Nobel prize 2005: Yves Chauvin, Robert H. Grubbs & Richard R. Schrock for the "***development of the metathesis method in organic synthesis***"

(c) Polymerization and metathesis of alkenes:



and

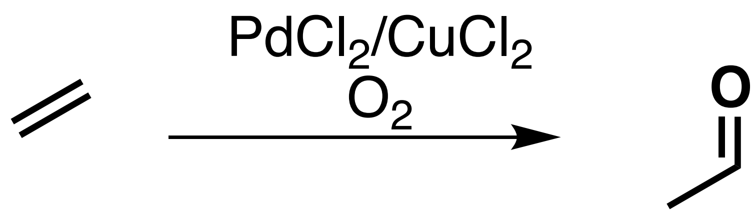


Examples of catalysis

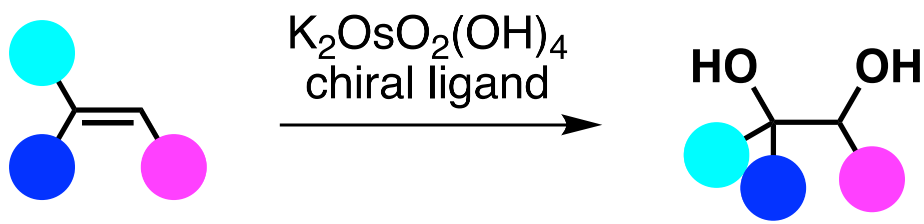
[2] Transition metal catalysis

(d) Oxidations:

Homogeneous catalysts are also used in a variety of oxidations. In the Wacker process, acetaldehyde can be produced from ethene and oxygen



Alkenes can be dihydroxylated by metal complexes, e.g. Sharpless dihydroxylation

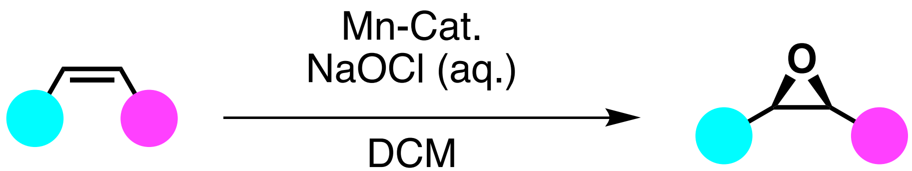


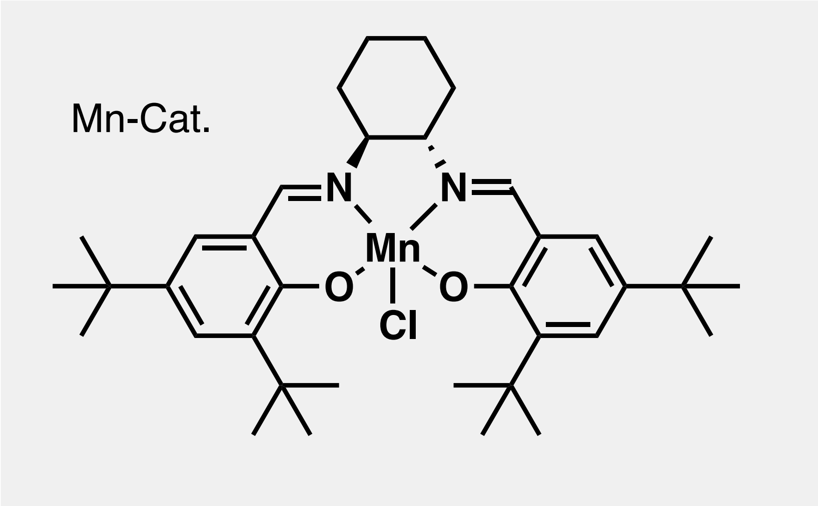
Examples of catalysis

[2] Transition metal catalysis

(d) Oxidations:

Jacobsen epoxidation:



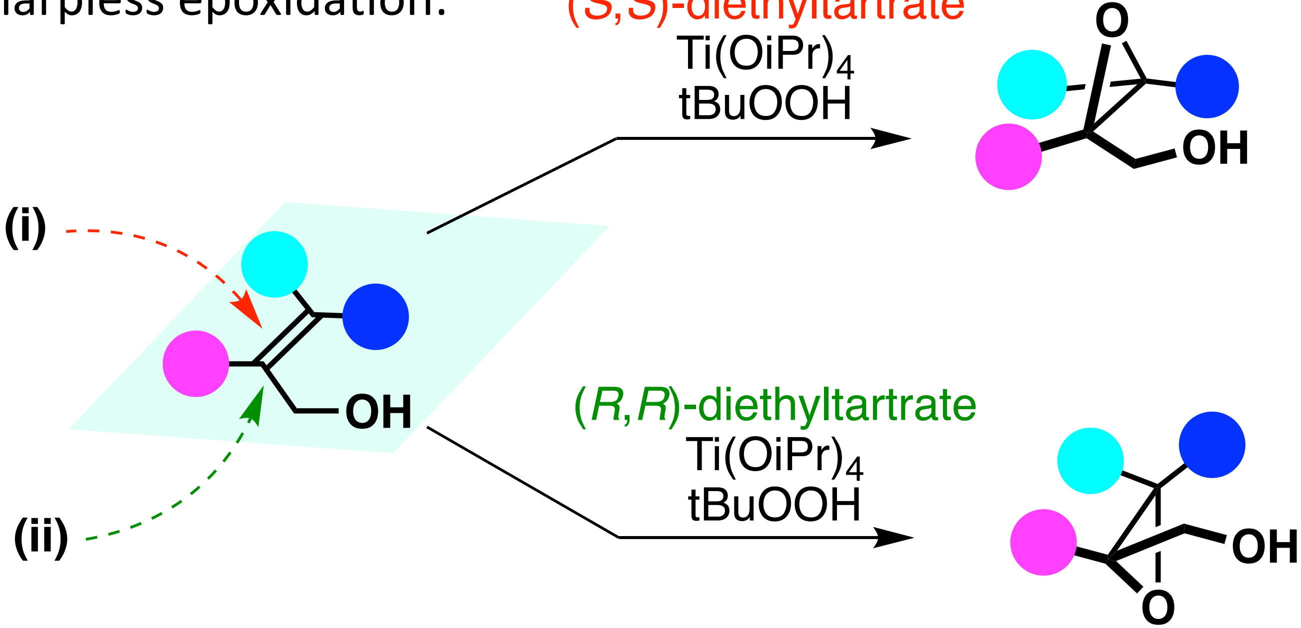


Examples of catalysis

[2] Transition metal catalysis

(d) Oxidations:

Sharpless epoxidation:



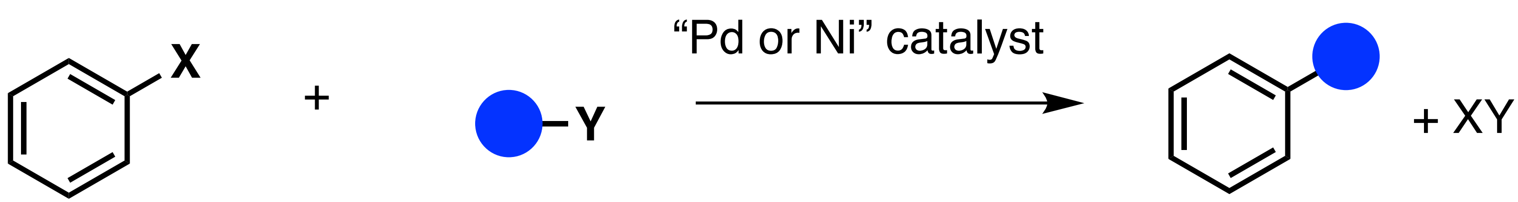
Nobel prize 2001: Barry Sharpless for his work on ***"chirally catalysed oxidation reactions"***

Examples of catalysis

[2] Transition metal catalysis

(e) Cross-coupling:

For the synthesis of new C-C and C-X bonds



X = eg. halide/triflate Y = eg. MgX, $B(OR)_2$, ZnX

Extensively applied and novel C-H bond activations alternative for Ar-X substrates

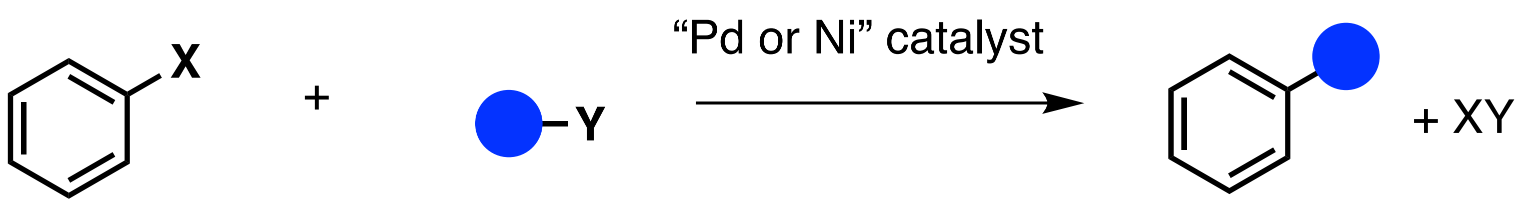
Examples of catalysis

[2] Transition metal catalysis

(e) Cross-coupling:

Nobel prize 2010: Richard F. Heck, Ei-Ichi Negishi & Akira Suzuki for development of "***palladium-catalyzed cross couplings in organic synthesis***".

For the synthesis of new C-C and C-X bonds



X = eg. halide/triflate   Y = eg. MgX, $B(OR)_2$, ZnX

Extensively applied and novel C-H bond activations alternative for Ar-X substrates

We have a toolbox available!

With selectivity…

Where does all this fit with the 12 principles of green chemistry?

1. WASTE PREVENTION

Prioritize the prevention of waste, rather than cleaning up and treating waste after it has been created. Plan ahead to minimize waste at every step.

2. ATOM ECONOMY

Reduce waste at the molecular level by maximizing the number of atoms from all reagents that are incorporated into the final product. Use atom economy to evaluate reaction efficiency.

3. LESS HAZARDOUS CHEMICAL SYNTHESIS

Design chemical reactions and synthetic routes to be as safe as possible. Consider the hazards of all substances handled during the reaction, including waste.

4. DESIGNING SAFER CHEMICALS

Minimize toxicity directly by molecular design. Predict and evaluate aspects such as physical properties, toxicity, and environmental fate throughout the design process.

5. SAFER SOLVENTS & AUXILIARIES

Choose the safest solvent available for any given step. Minimize the total amount of solvents and auxiliary substances used, as these make up a large percentage of the total waste created.

6. DESIGN FOR ENERGY EFFICIENCY

Choose the least energy-intensive chemical route. Avoid heating and cooling, as well as pressurized and vacuum conditions (i.e. ambient temperature & pressure are optimal).

7. USE OF RENEWABLE FEEDSTOCKS

Use chemicals which are made from renewable (i.e. plant-based) sources, rather than other, equivalent chemicals originating from petrochemical sources.

8. REDUCE DERIVATIVES

Minimize the use of temporary derivatives such as protecting groups. Avoid derivatives to reduce reaction steps, resources required, and waste created.

9. CATALYSIS

Use catalytic instead of stoichiometric reagents in reactions. Choose catalysts to help increase selectivity, minimize waste, and reduce reaction times and energy demands.

10. DESIGN FOR DEGRADATION

Design chemicals that degrade and can be discarded easily. Ensure that both chemicals and their degradation products are not toxic, bioaccumulative, or environmentally persistent.

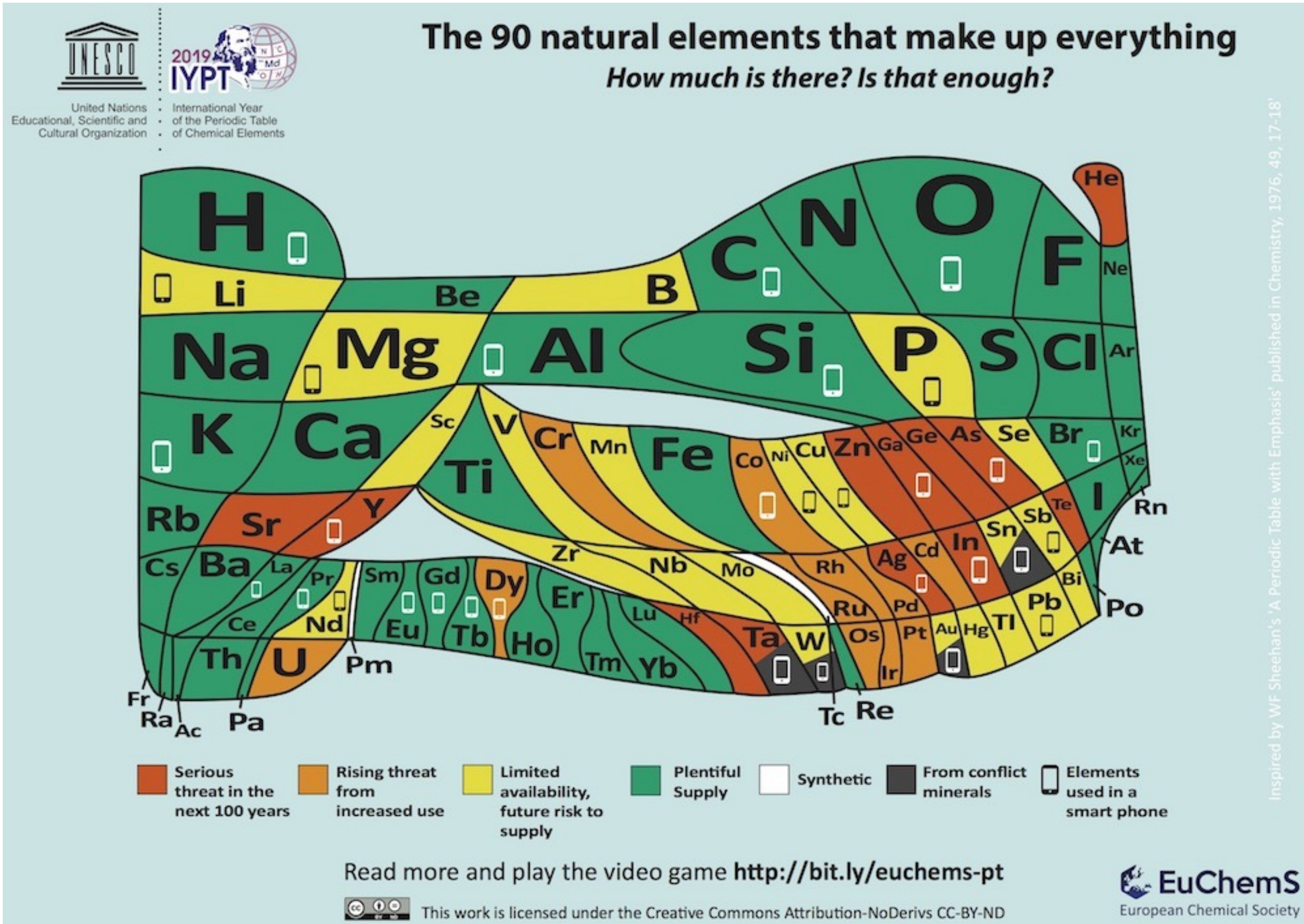
11. REAL-TIME POLLUTION PREVENTION

Monitor chemical reactions in real-time as they occur to prevent the formation and release of any potentially hazardous and polluting substances.

12. SAFER CHEMISTRY FOR ACCIDENT PREVENTION

Choose and develop chemical procedures that are safer and inherently minimize the risk of accidents. Know the possible risks and assess them beforehand.

Other things to consider?



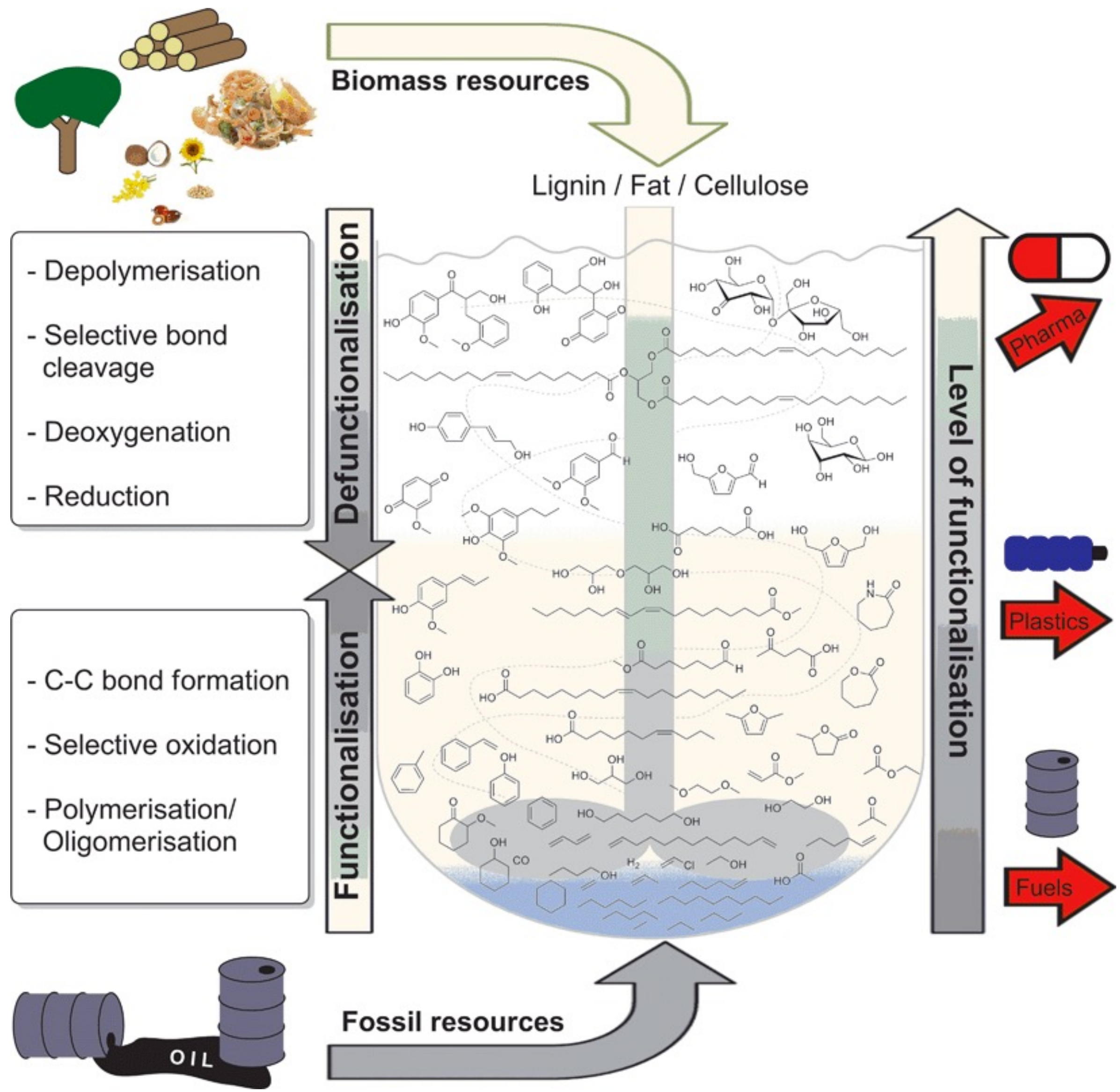
An overview of the current situation:

Defunctionalisation

vs.

Functionalisation

…different approaches required



P. J. Deuss, K. Barta, J. G. de Vries, "Homogeneous catalysis for the conversion of biomass and biomass-derived platform chemicals", *Catal. Sci. Technol.*, **2014**, *4*, 1174. B. M. Stadler, C. Wulf, T. Werner, S. Tin, J. G. de Vries, "Catalytic Approaches to Monomers for Polymers Based on Renewables", *ACS Catal.*, **2019**, *9*, 8012.

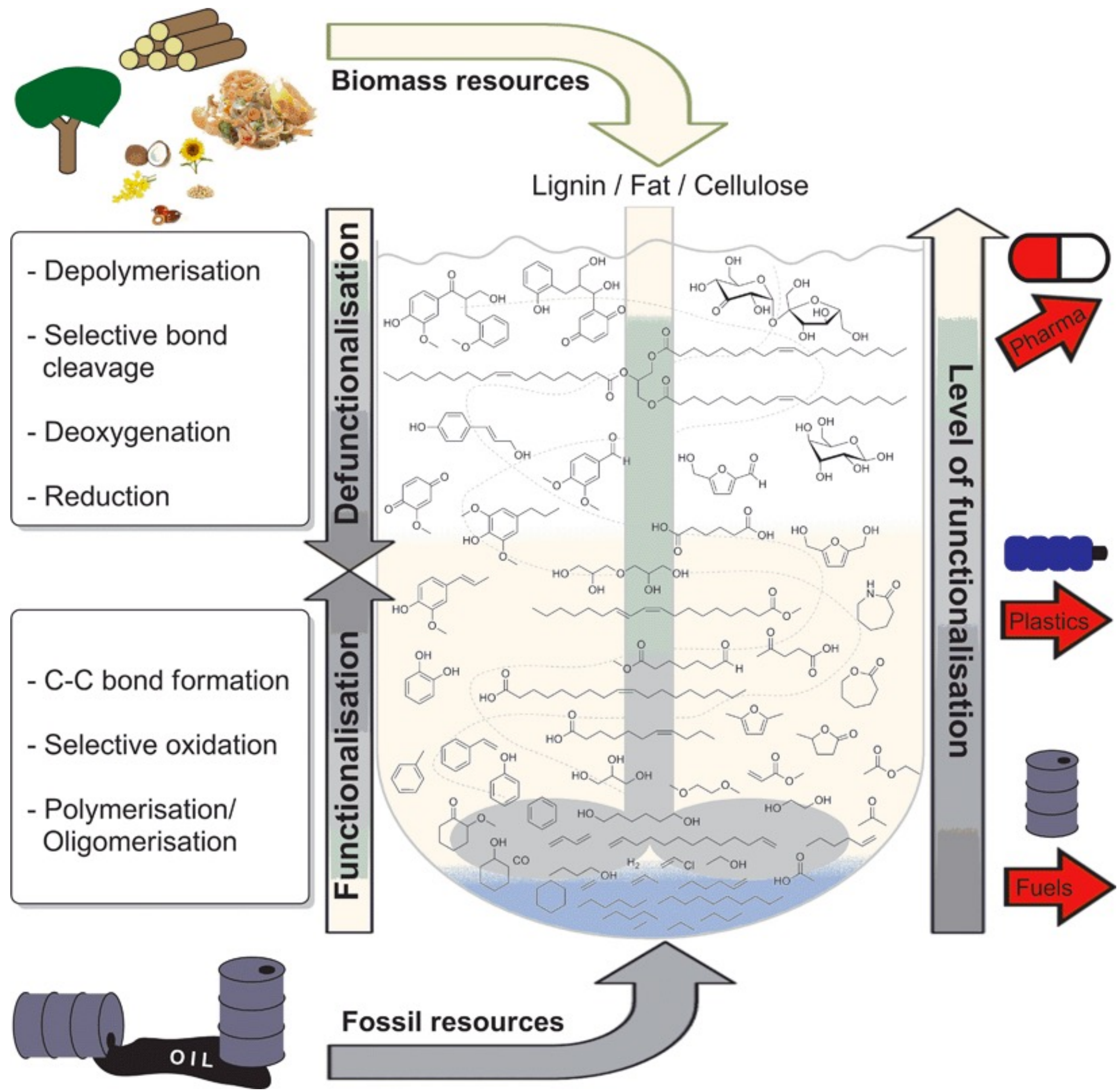
An overview of the current situation:

Defunctionalisation

vs.

Functionalisation

...but significant opportunities!



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Examples of compounds that can be obtained:

Lots…

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Examples of compounds that can be obtained:

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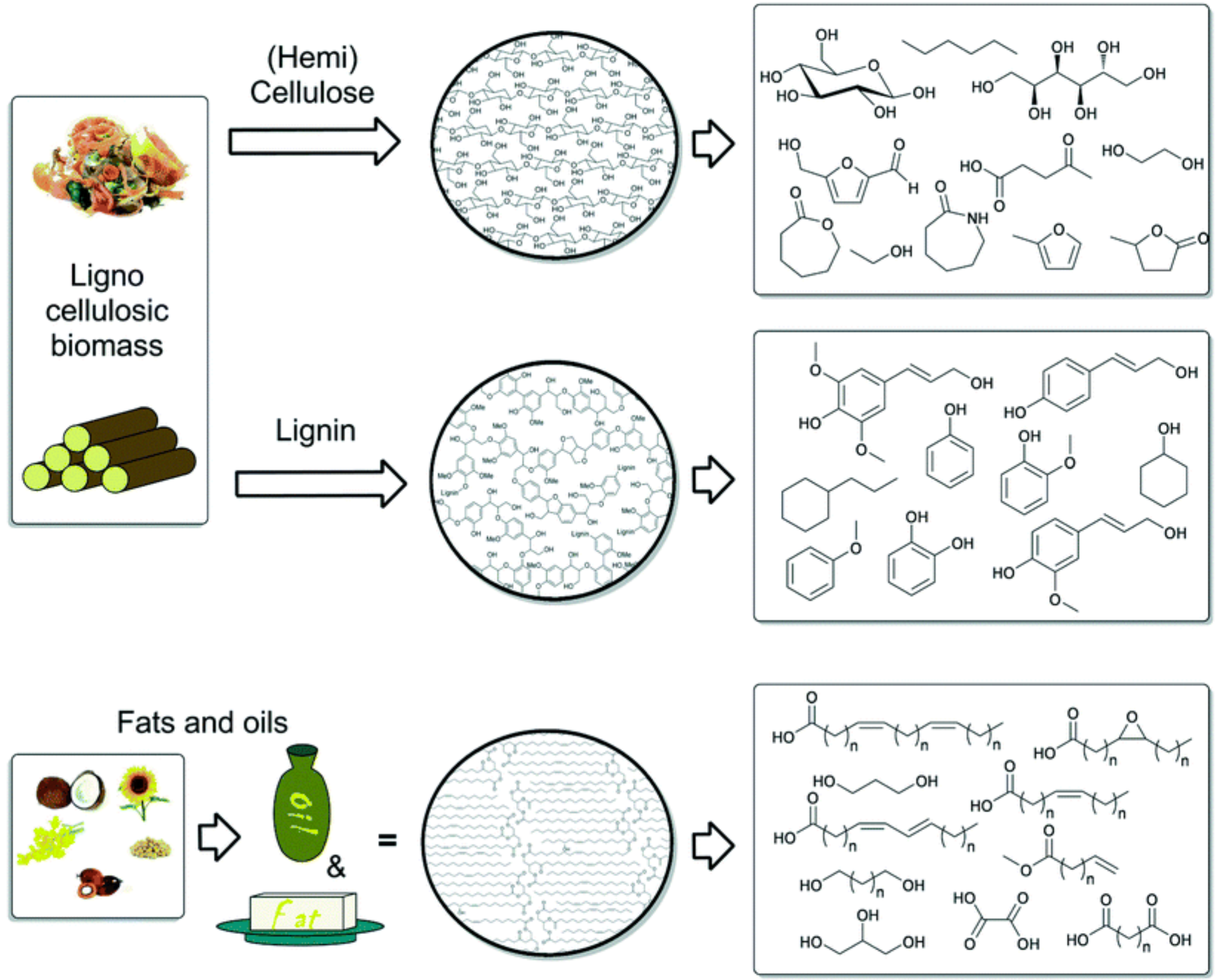
vs.



Fewer…

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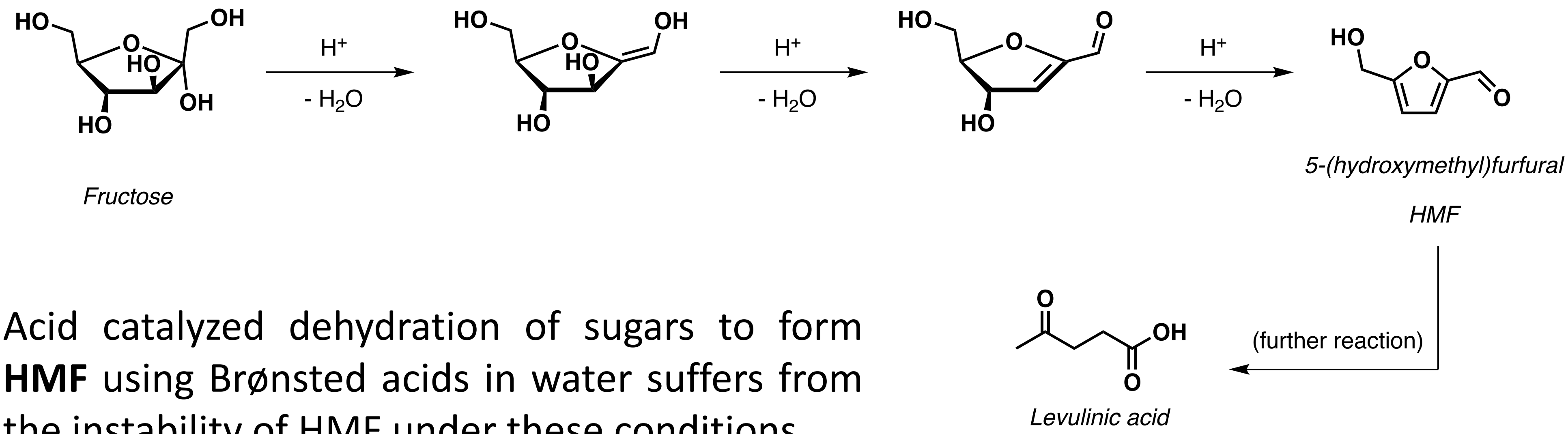
Some examples:



Acid catalyzed dehydration of sugars to form **HMF** using Brønsted acids in water suffers from the instability of HMF under these conditions

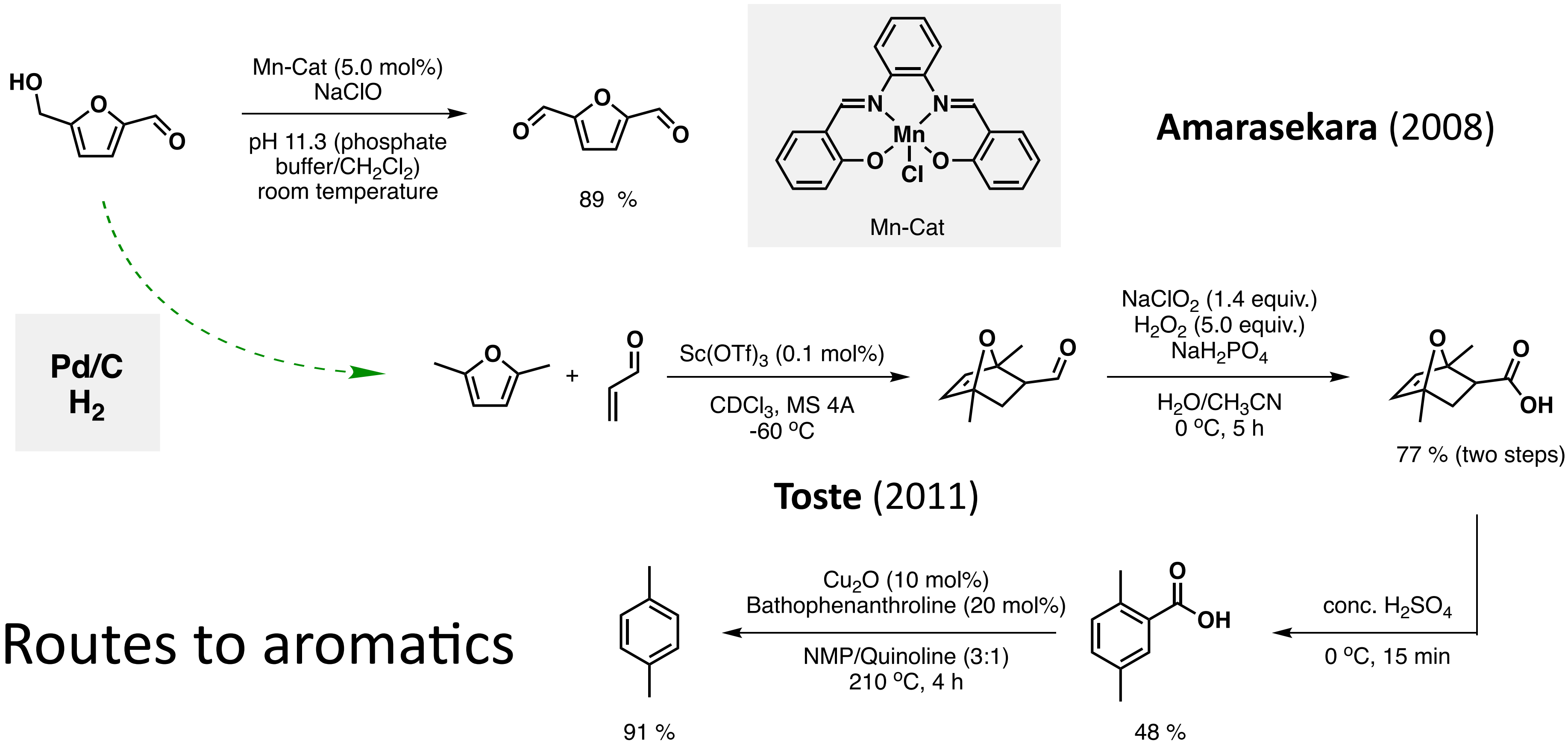
It is rehydrated and forms levulinic acid. To suppress the side reaction, protocols have been developed e.g. use of soluble Lewis acid catalysts in dipolar aprotic solvents ($LaCl_3$)

Acid catalysis again!

R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, "Hydroxymethylfurfural, A Versatile Platform Chemical Made from Renewable Resources", *Chem. Rev.* **2013**, *113*, 1499. A. A. Rosatella, S. P. Simeonov, R. F. M. Frade, C. A. M. Alfonso, "5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications", *Green Chem.*, **2011**, *13*, 754.

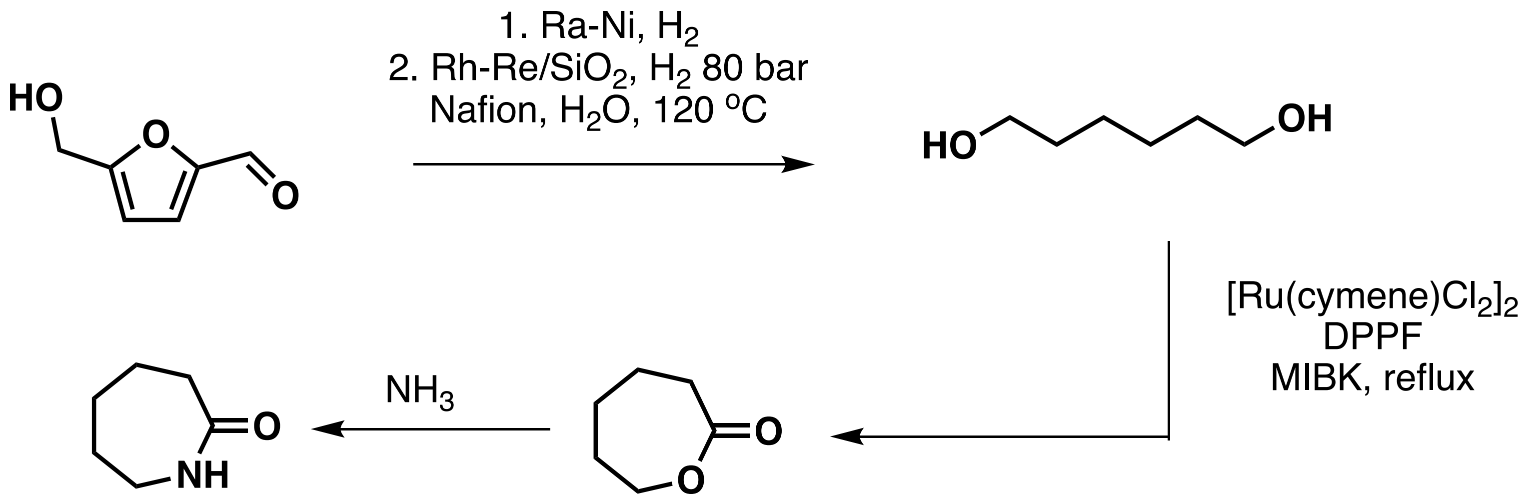
Why all the fuss? …upgrading of HMF (selected catalyzed examples):

Oxidation to other functional groups (also possible to form dicarboxylic acid)



(i) A. S. Amarasekara, D. Green, E. McMillan, "Efficient oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran using Mn(III)–salen catalysts", *Catal. Commun.*, **2008**, *9*, 286. (ii) M. Shiramizu, F. D. Toste, "On the Diels–Alder Approach to Solely Biomass-Derived Polyethylene Terephthalate (PET): Conversion of 2,5-Dimethylfuran and Acrolein into p-Xylene", *Chem. Eur. J.*, **2011**, *17*, 12452.

Why all the fuss? …upgrading of HMF (selected catalyzed examples):



De Vries/Heeres (2011)

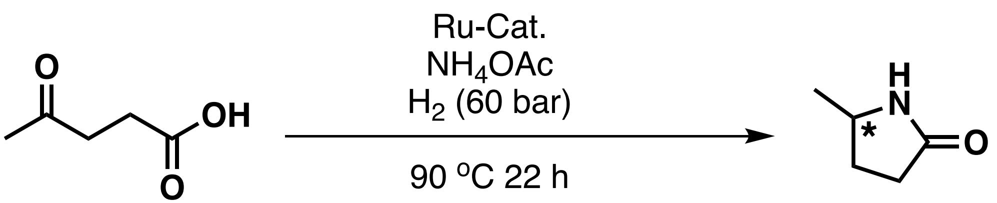
Monomers for Ring-Opening Polymerisation (ROP)

Sometimes the combination of heterogeneous and homogeneous catalysis steps can be highly beneficial – avoid working in isolation!

T. Buntara, S. Noel, P. H. Phua, I. Melián-Cabrera, J. G. de Vries, H. J. Heeres, " Caprolactam from Renewable Resources: Catalytic Conversion of5-Hydroxymethylfurfural into Caprolactone", *Angew. Chem., Int. Ed.*, **2011**, *50*, 7083.

And the levulinic acid?

Can also be upgraded to useful (and even chiral) compounds using appropriate catalysts:



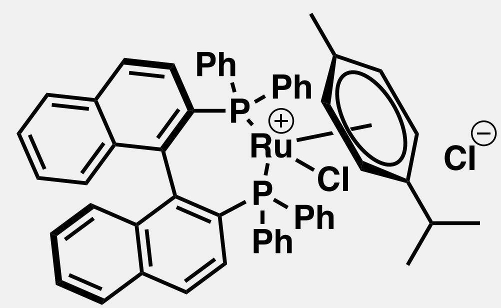
Levulinic acid

"reductive amination"

85 % yield (isolated)

Tin/de Vries (2023)

3 : 97 e.r. Ru-Cat 1
93 : 7 e.r. Ru-Cat 2

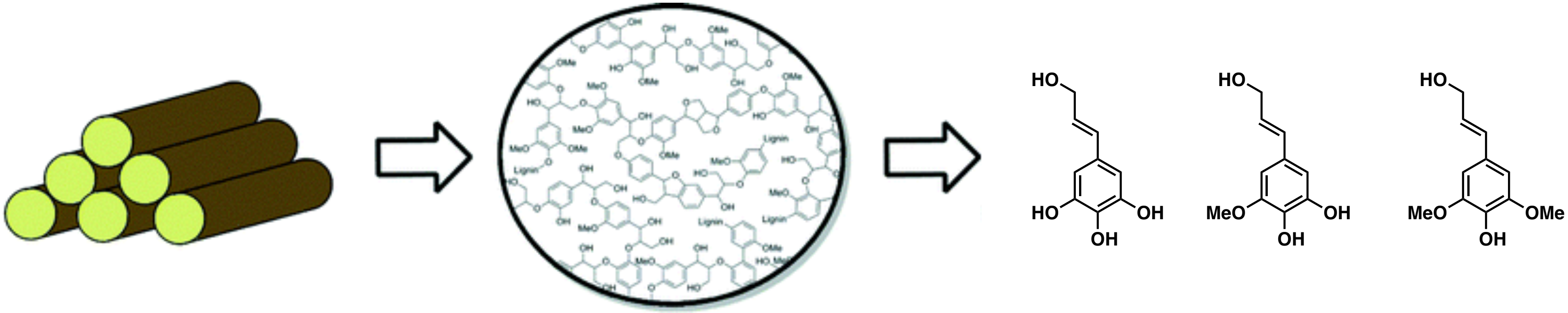


Ru-Cat 1 = (*R*)
Ru-Cat 2 = (*S*)

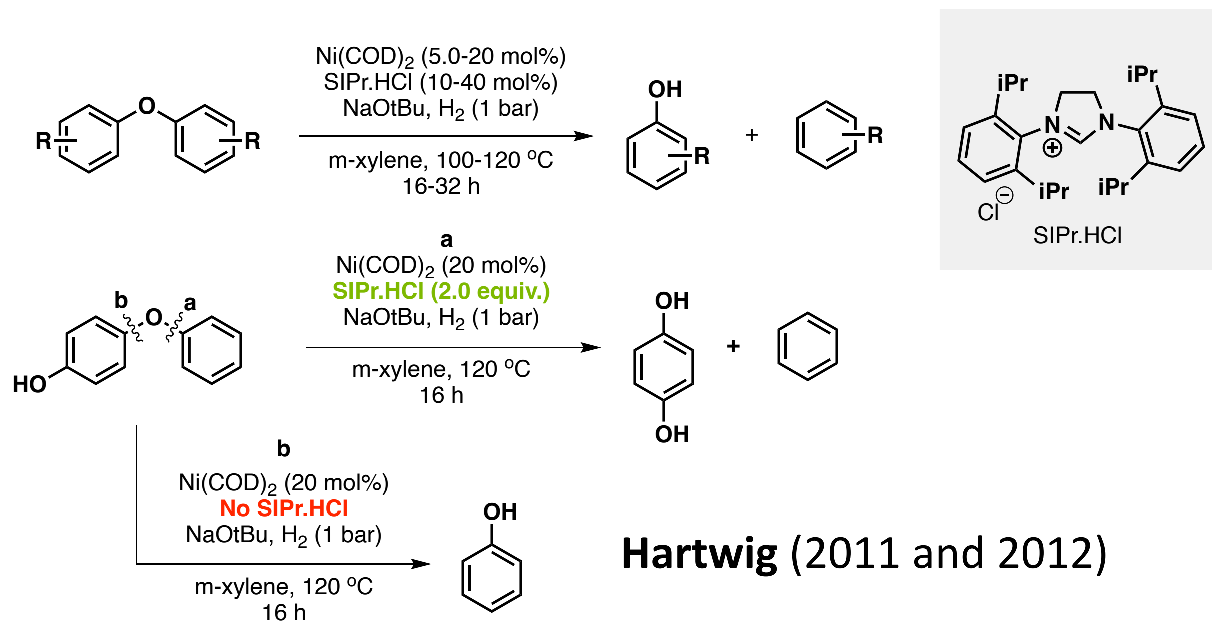
Easy access to useful enantiomerically pure pyrrolidinones!

S. Chakraborty, S. Zheng, F. Kallmeier, E. Baráth, S. Tin, J. G. de Vries, "Ru Catalyzed Direct Asymmetric Reductive Amination of Bio-Based Levulinic Acid and Ester for the Synthesis of Chiral Pyrrolidinone", *ChemSusChem*., **2023**, *16*, e202202353. J. J. Bozell, L. Moens, D. C. Elliot, Y. Wang, G. G. Neuenscwander, S. W. Fitzpatrick, R. J. Bilski, J. L. Jarnefeld, *Resour. Conserv. Recycl.*, **2000**, *28*, 227.

From lignin (a highly complex compound – source of aromatics)



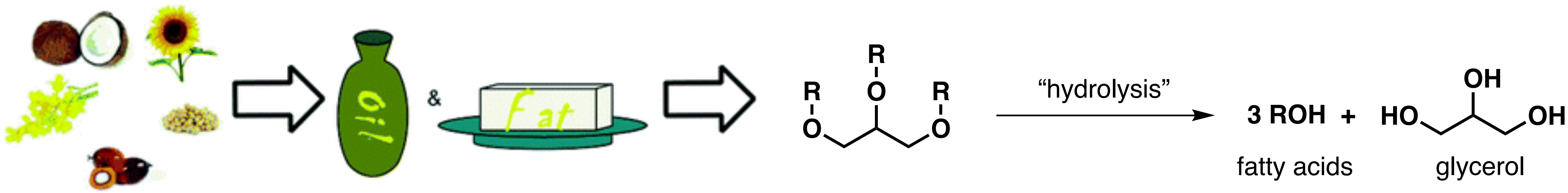
Selective breaking of bonds to obtain useful aromatic compounds using catalysis



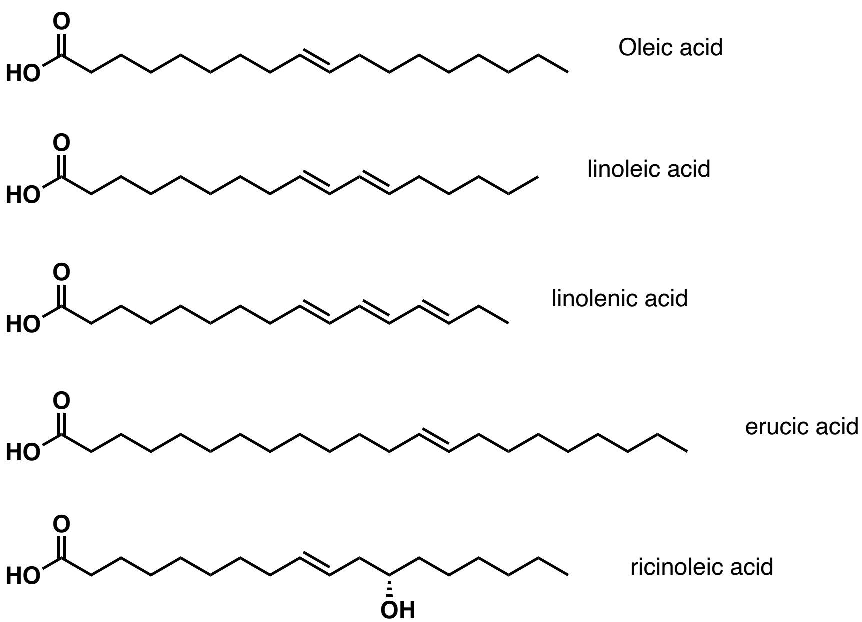
Hartwig (2011 and 2012)

A. G. Sergeev, J. D. Webb, J. F. Hartwig, "A Heterogeneous Nickel Catalyst for the Hydrogenolysis of Aryl Ethers without Arene Hydrogenation", *J. Am. Chem. Soc.*, **2012**, *134*, 20226. A. G. Sergeev, J. F. Hartwig, "Selective, Nickel-Catalyzed Hydrogenolysis of Aryl Ethers", *Science*, **2011**, *332*, 439.

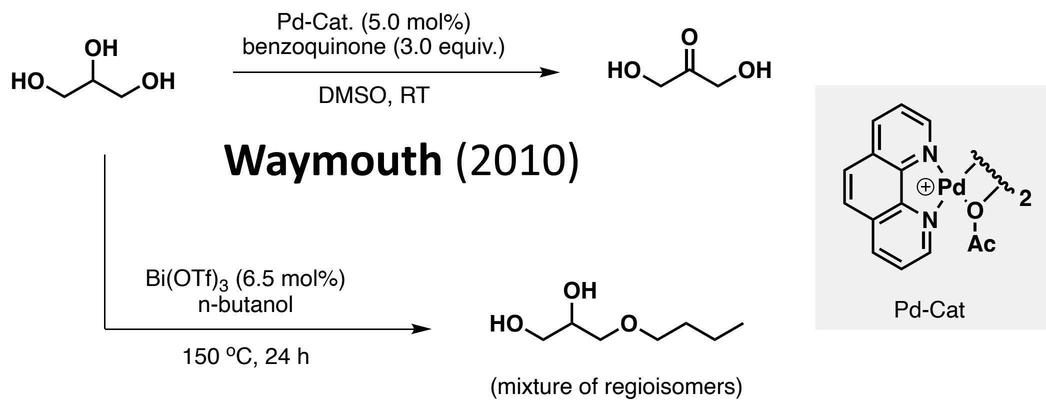
From oils (access to fatty acids and glycerol)



Examples of common fatty acids:



Glycerol can be further upgraded:



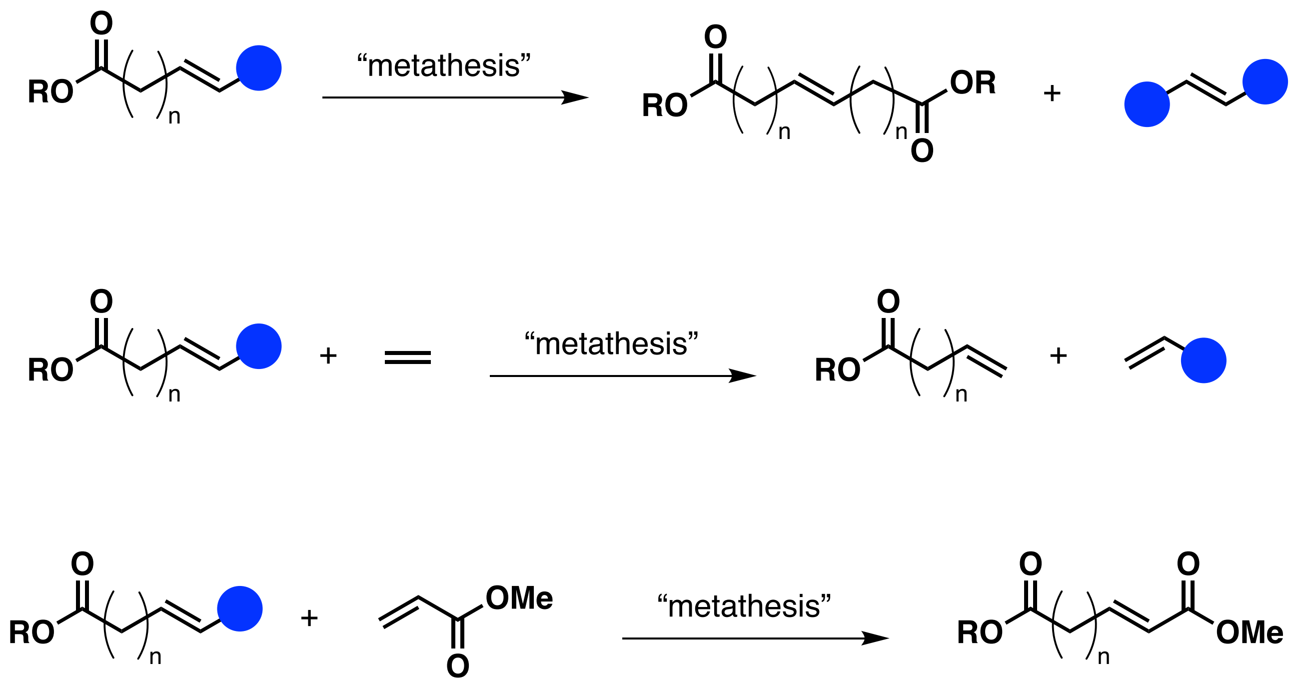
Waymouth (2010)

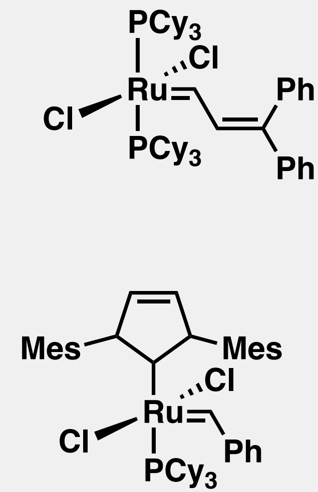
Jérôme (2013)

R. M. Painter, D. M. Pearson, R. M. Waymouth, "Selective Catalytic Oxidation of Glycerol to Dihydroxyacetone", *Angew. Chem., Int. Ed.*, **2010**, *49*, 9456. F. Liu, K. De Oliviera Vigier, M. Pera-Titus, Y. Pouilloux, J.-M. Clacens, F. Decampo, F. Jérôme, "Catalytic etherification of glycerol with short chain alkyl alcohols in the presence of Lewis acids", *Green Chem.*, **2013**, *15*, 901.

Upgrading fatty acids:

Unsaturated fatty acids: Metathesis (with/without other olefins)





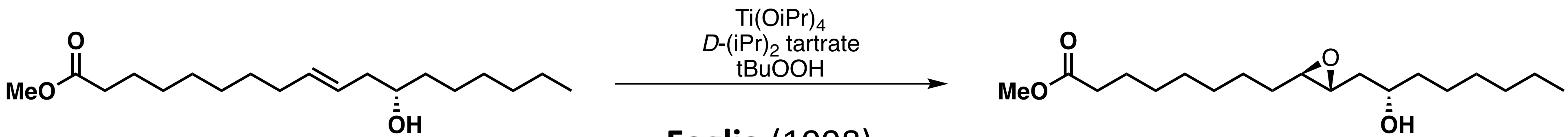
catalysts

The catalysts already exist – new application!

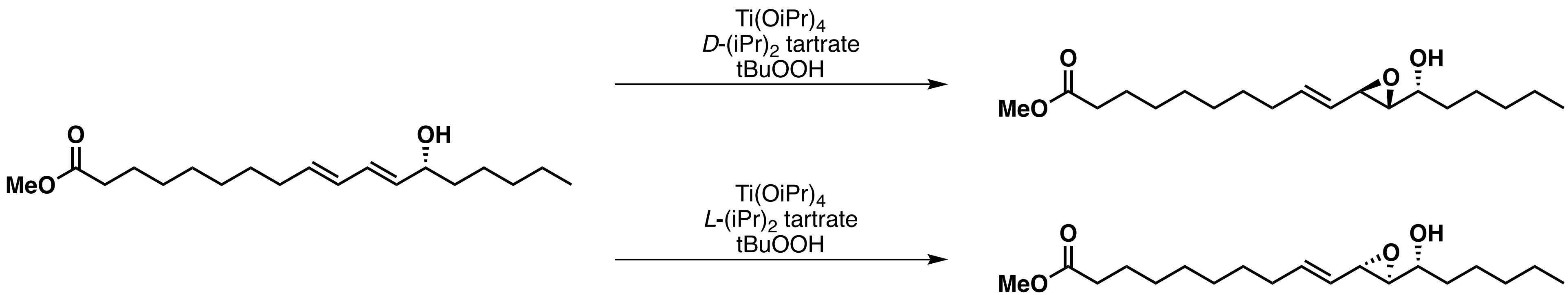
M. A. R. Meier, "Metathesis with Oleochemicals: New Approaches for the Utilization of Plant Oils as Renewable Resources in Polymer Science", *Macromol. Chem. Phys.*, **2009**, *210*, 1073.

Upgrading fatty acids:

Oxidations are very common:



Foglia (1998)



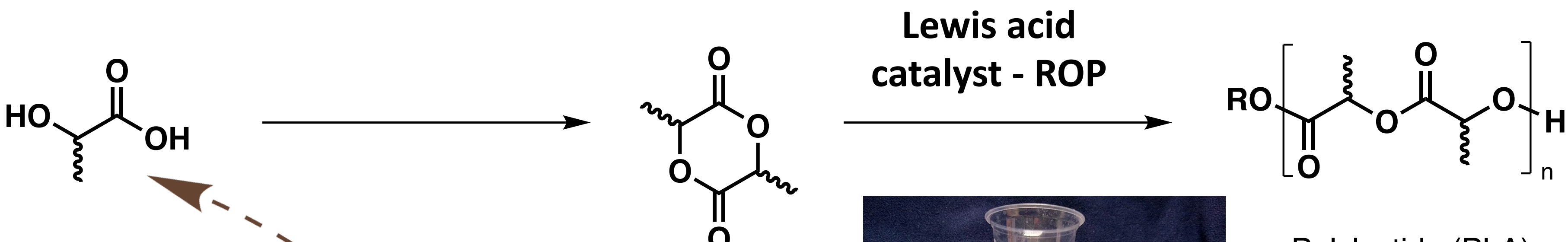
Omar (2003)

Note: If only obtaining epoxide is important – use *m*-CPBA

T. A. Foglia, P. E. Sonnet, A. Nunez, R. L. Dudley, "Selective oxidations of methyl ricinoleate: Diastereoselective epoxidation with titanium[IV] catalysts", *J. Am. Oil Chem. Soc.*, **1998**, *75*, 601. M. Nor Omar, H. A. Moynihan, R. J. Hamilton, "Asymmetric Sharpless epoxidation of 13*S*-hydroxy-9*Z*,11*E*-octadecadienoic acid (13*S*-HODE)", *Eur. J. Lipid Sci. Technol.*, **2003**, *105*, 43.

Other wastes

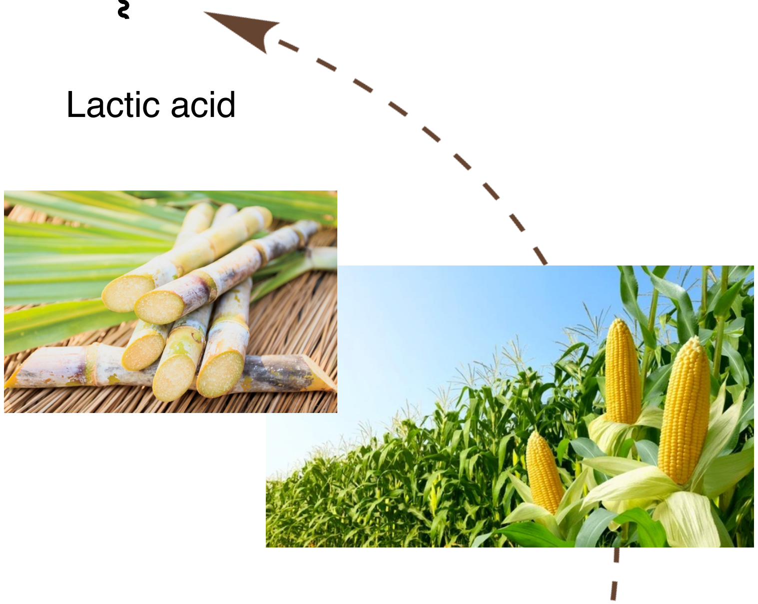
Lactic acid – Lactide:



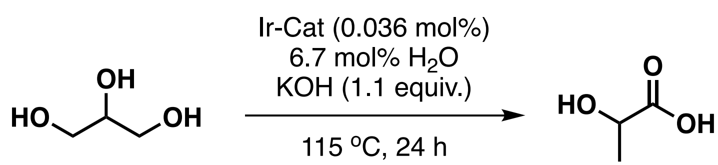
Lactic acid

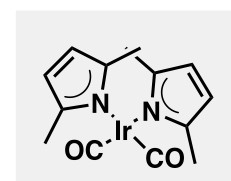
Lactide

Polylactide (PLA)



(Fermentation of wastes)





Ir-Cat.

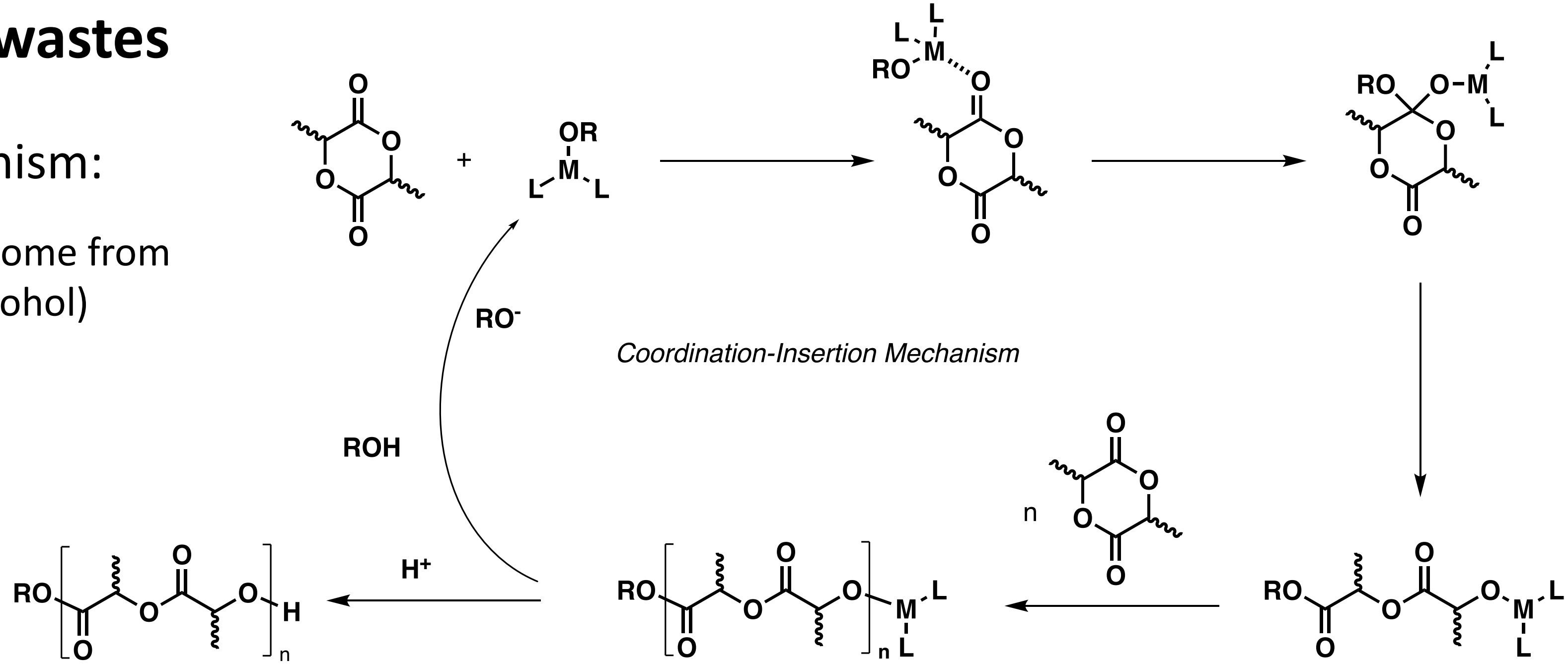
Campos/Crabtree (2014)

L. S. Sharninghausen, J. Campos, M. G. Manas, R. H. Crabtree, "Efficient Selective and Atom Economic Catalytic Conversion of Glycerol to Lactic Acid", *Nat. Commun.*, **2014**, *5*, 5084.

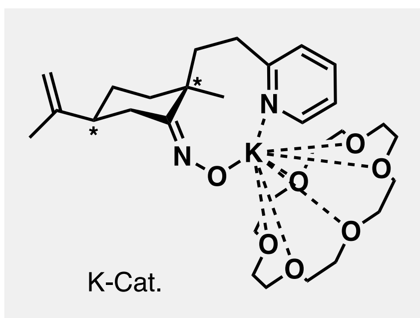
Other wastes

Mechanism:

(RO- can come from benzyl alcohol)

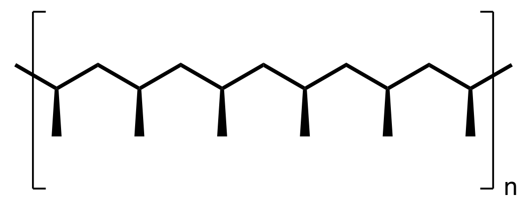


Example from our research group:



(ligand derived from limonene)

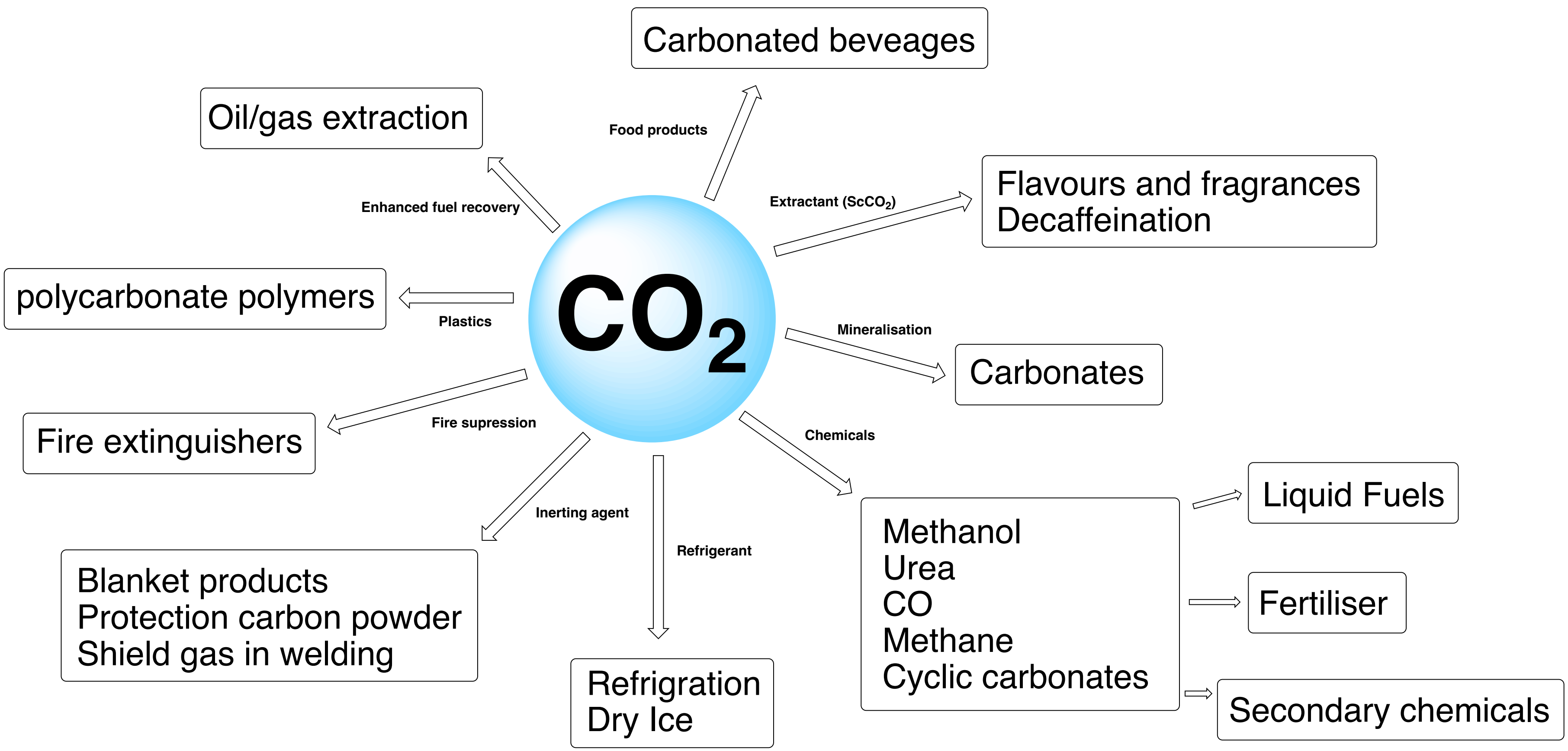
Can promote *rac*-lactide isoselective polymerization to give highly isotactic polymers



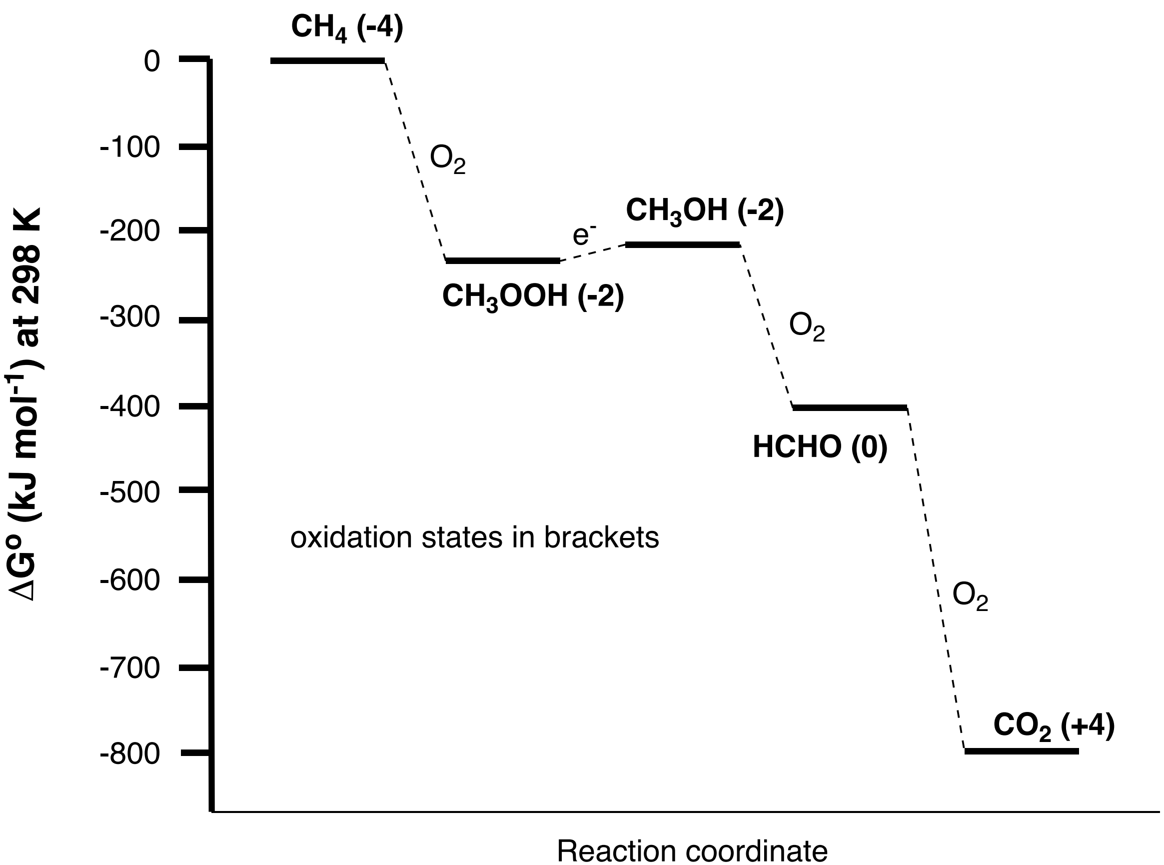
M. Fernández-Millán, P. Ortega, T. Cuenca, J. Cano, M. E. G. Mosquera, "Alkali-Metal Compounds with Bio-Based Ligands as Catalysts for Isoselective Lactide Polymerization: Influence of the Catalyst Aggregation on the Polymerization Control", *Organometallics*, **2020**, *39*, 2278.

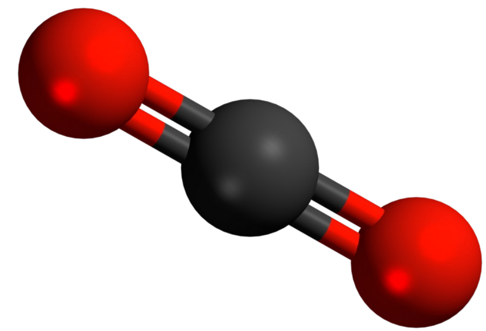
Moving on to CO_2…

CO_2 is a problem – but it has also found many applications



Oxidation states of carbon and energy:



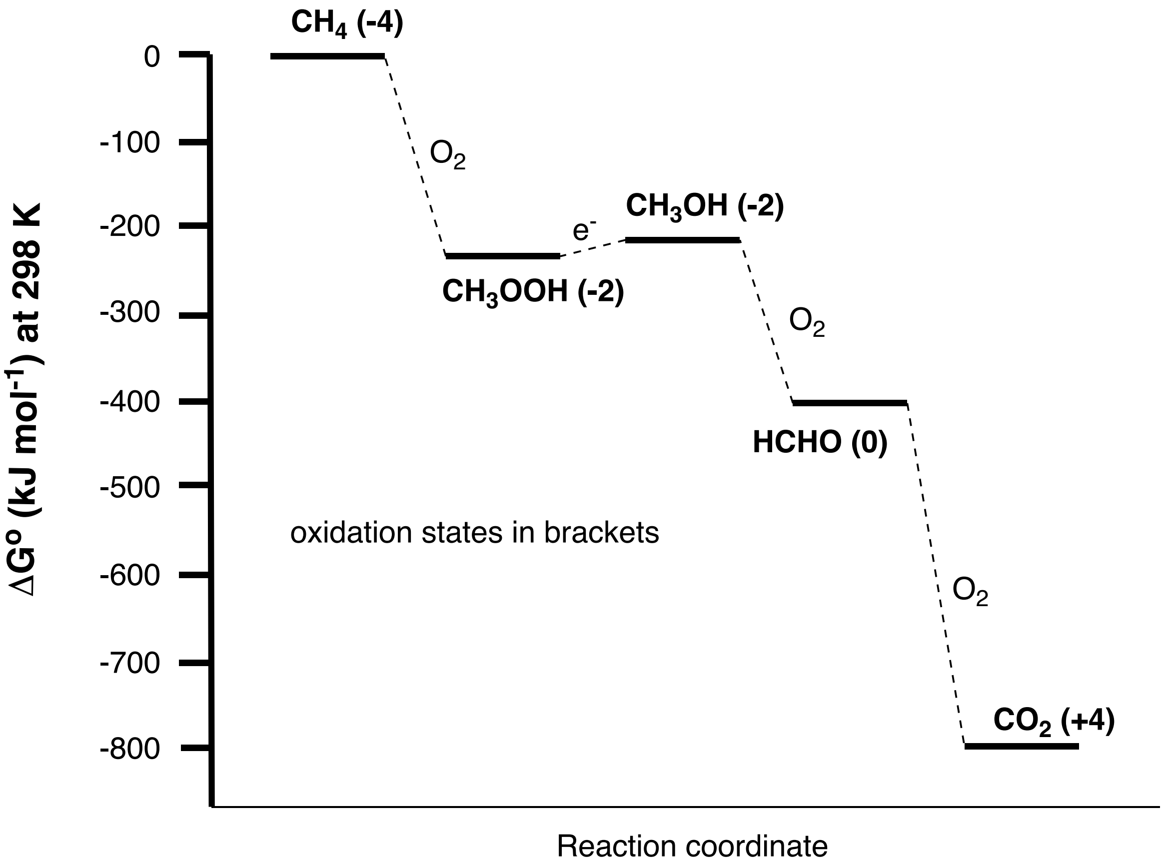


CO_2 is essentially an energy sink and rather demanding to convert into other compounds...

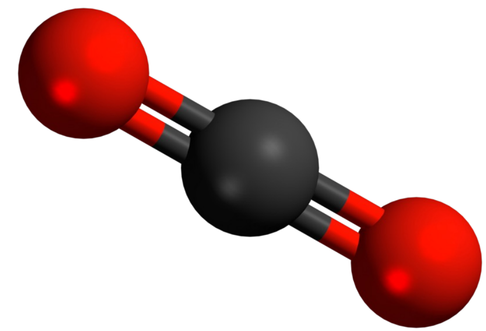
Approximate Gibbs free energy (ΔGº) for some carbon compounds at different oxidation states of carbon

Y. Fan, W. Zhou, X. Qiu, H. Li, Y. Jiang, Z. Sun, D. Han, L. Niu, Z. Tang, "Selective photocatalytic oxidation of methane by quantum-sized bismuth vanadate", *Nat. Sustain*., **2021**, *4*, 509.

Oxidation states of carbon and energy:



Approximate Gibbs free energy (ΔG°) for some carbon compounds at different oxidation states of carbon

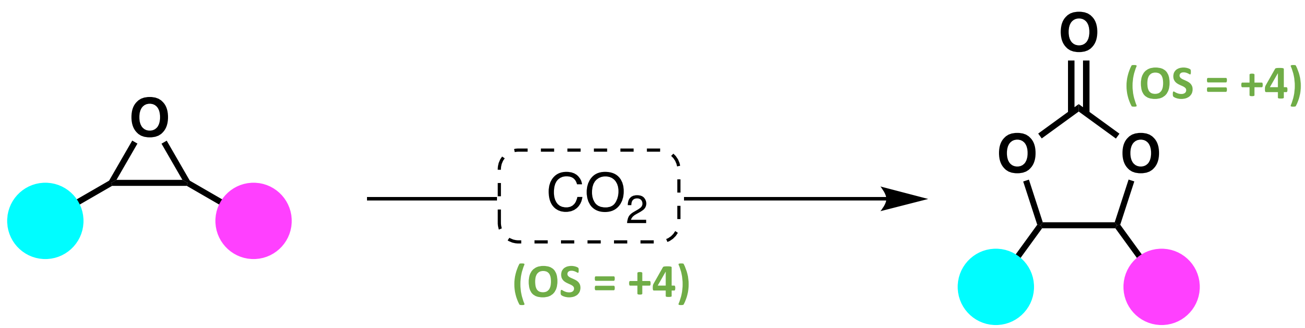


CO_2 is essentially an energy sink and rather demanding to convert into other compounds…

Non-reductive applications would be very attractive from an energy point of view

Y. Fan, W. Zhou, X. Qiu, H. Li, Y. Jiang, Z. Sun, D. Han, L. Niu, Z. Tang, "Selective photocatalytic oxidation of methane by quantum-sized bismuth vanadate", *Nat. Sustain*., **2021**, *4*, 509.

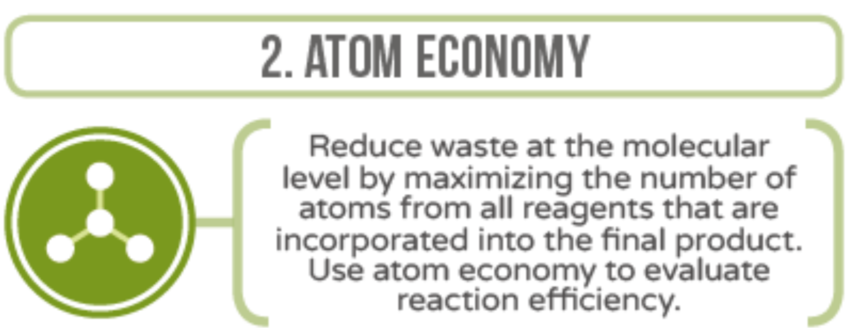
(Non-reductive) addition of CO_2 to epoxides to produce cyclic carbonates:

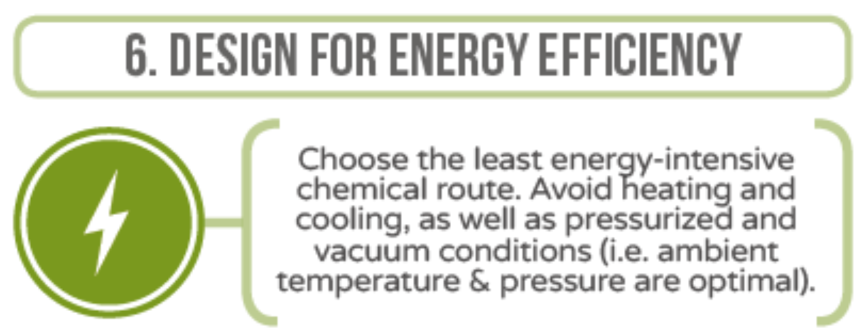


No need to change the oxidation state…

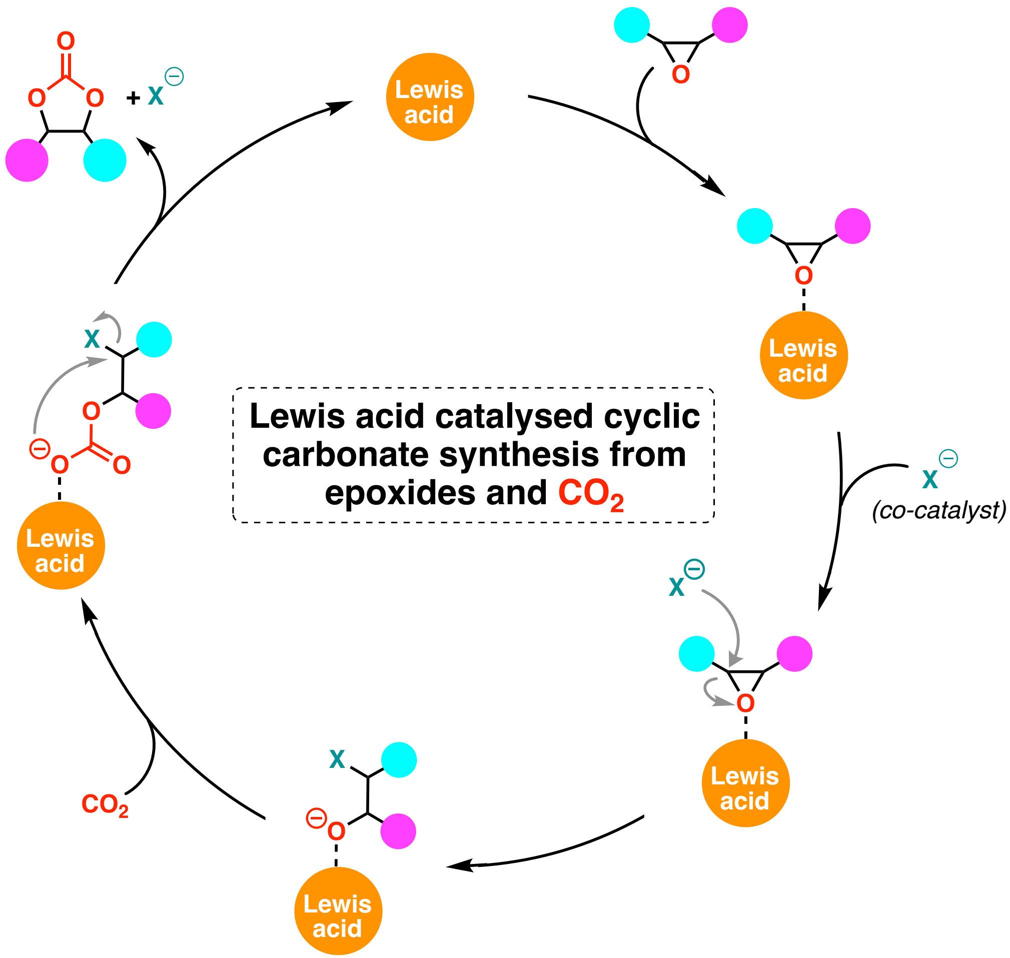
Attractive reaction for use of CO_2

12 principles of green chemistry:





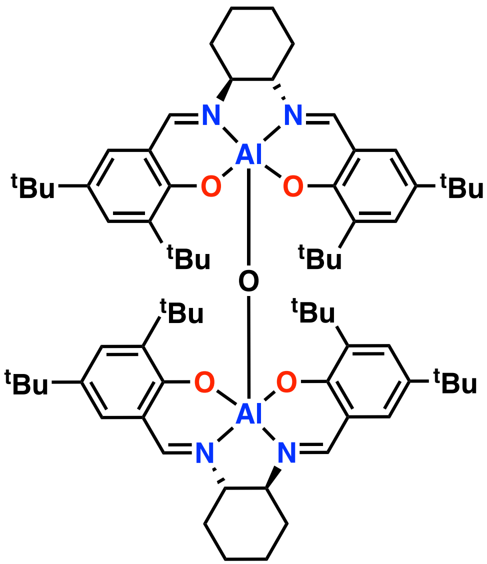
Mechanism for the formation of cyclic carbonates using a catalyst:



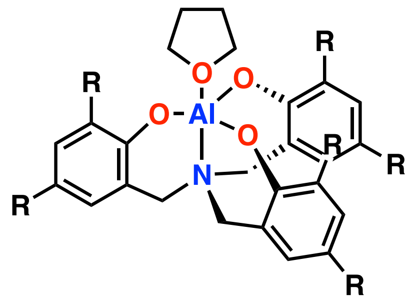
Redox neutral mechanism (non-reductive coupling)

Lewis acid approach highlighted (other types of catalysis, *eg*. Bronsted acid also reported)

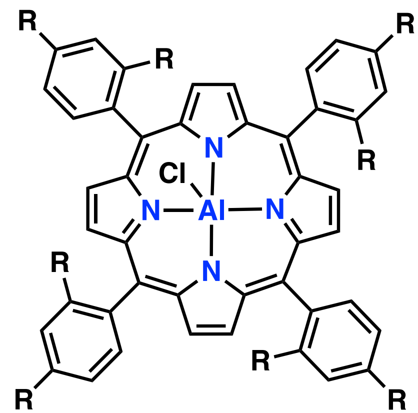
Many highly active group 13 catalysts have been developed:



North (2010)

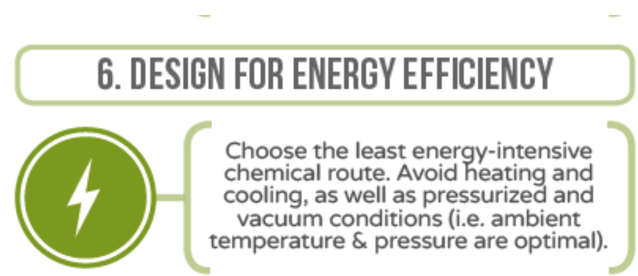


Kleij (2013)



Qin/Wang (2015)

Operative at room temperature…



W. Clegg, R. W. Harrington, M. North, R. Pasquale, "Cyclic Carbonate Synthesis Catalysed by Bimetallic Aluminium–Salen Complexes", *Chem. Eur. J.*, **2010**, *16*, 6828. C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, "A Powerful Aluminum Catalyst for the Synthesis of Highly Functional Organic Carbonates", *J. Am. Chem. Soc.*, **2013**, *135*, 1228. Y. Qin, H. Guo, X. Sheng, X. Wang, F. Wang, "An aluminum porphyrin complex with high activity and selectivity for cyclic carbonate synthesis", *Green Chem.*, **2015**, *17*, 2853.

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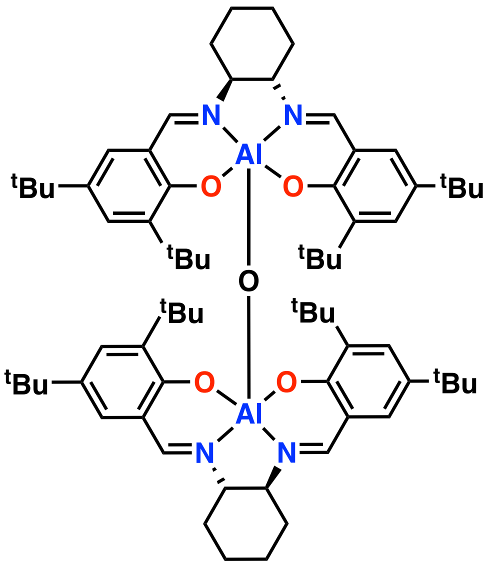
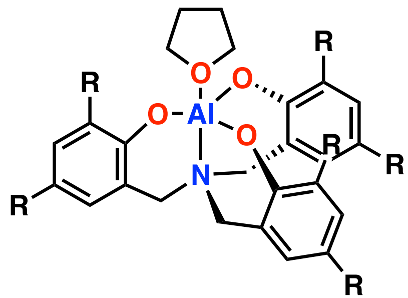
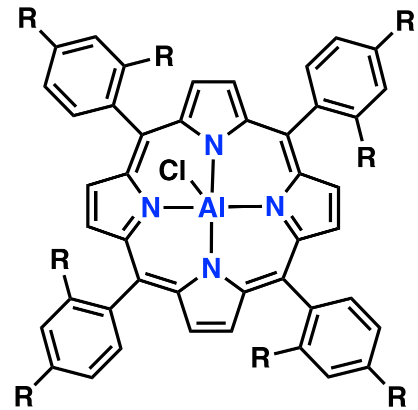


North (2010)



Kleij (2013)



Qin/Wang (2015)

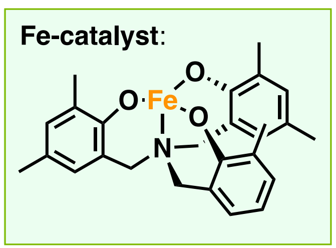
We have catalysts…

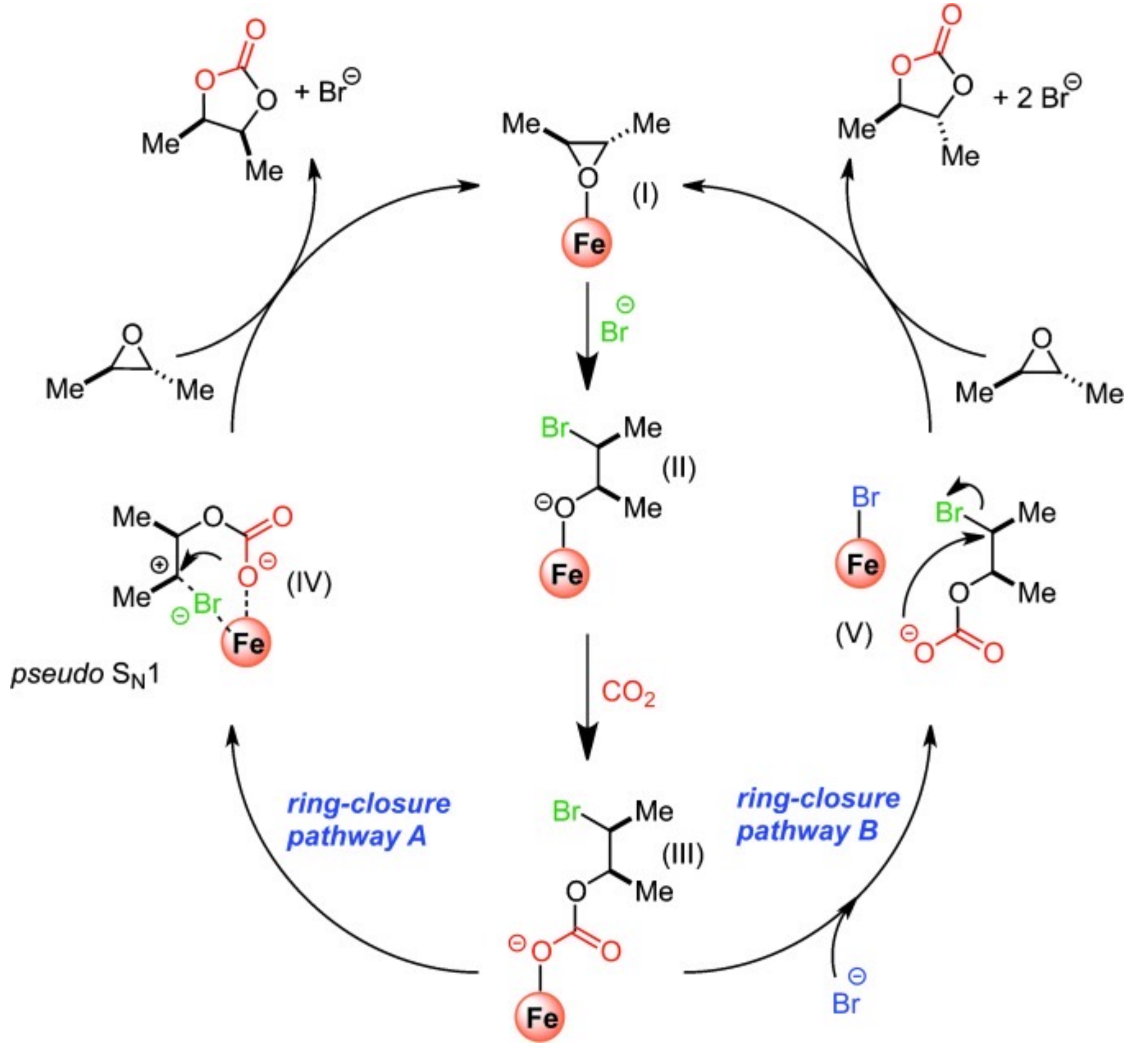
W. Clegg, R. W. Harrington, M. North, R. Pasquale, "Cyclic Carbonate Synthesis Catalysed by Bimetallic Aluminium–Salen Complexes", *Chem. Eur. J.*, **2010**, *16*, 6828. C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, "A Powerful Aluminum Catalyst for the Synthesis of Highly Functional Organic Carbonates", *J. Am. Chem. Soc.*, **2013**, *135*, 1228. Y. Qin, H. Guo, X. Sheng, X. Wang, F. Wang, "An aluminum porphyrin complex with high activity and selectivity for cyclic carbonate synthesis", *Green Chem.*, **2015**, *17*, 2853.

Mechanistic “oddities”

Stereoselectivity:

Can control the outcome!





More or less co-catalyst…

C. J. Whiteoak, E. Martin, E. Escudero-Adán, A. W. Kleij, “Stereochemical Divergence in the Formation of Organic Carbonates Derived from Internal Epoxides”, *Adv. Synth. Catal.*, **2013**, *355*, 2233.

Conversion of bio-derived epoxides:

Question: *where do bio-derived epoxides come from?*

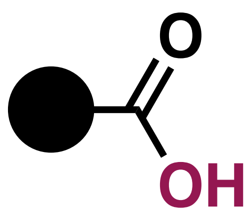
Traditional approach:

Conversion of bio-derived epoxides:

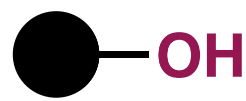
Question: *where do bio-derived epoxides come from?*

Traditional approach:

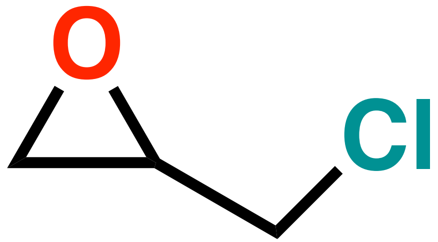
✖ Limited number of alkenes available – other functional groups/methods?



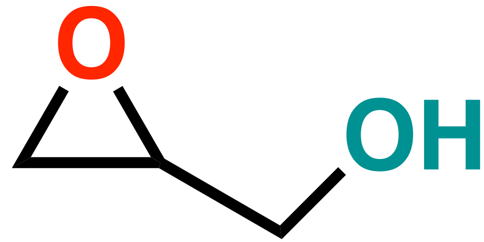
Carboxylic acids



Alcohols



Solvay, ABT, Korea Kumho Petro Chemical Group and may others…

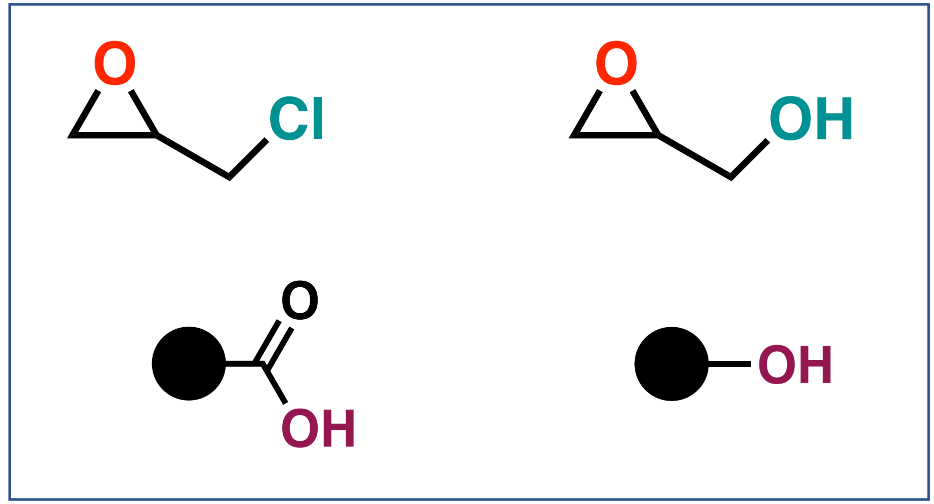


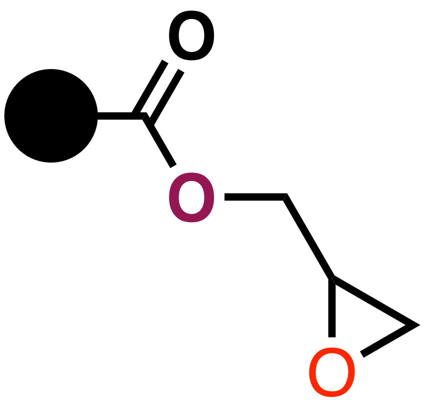
Green Lizard Technologies, Blue Bear Chemicals…

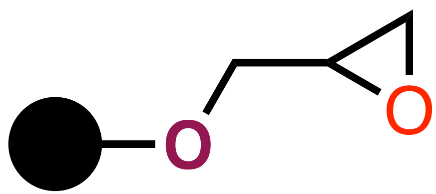
Both can be derived from glycerol

Question: Can we make use of them?

Use of glycidol and epichlorohydrin:





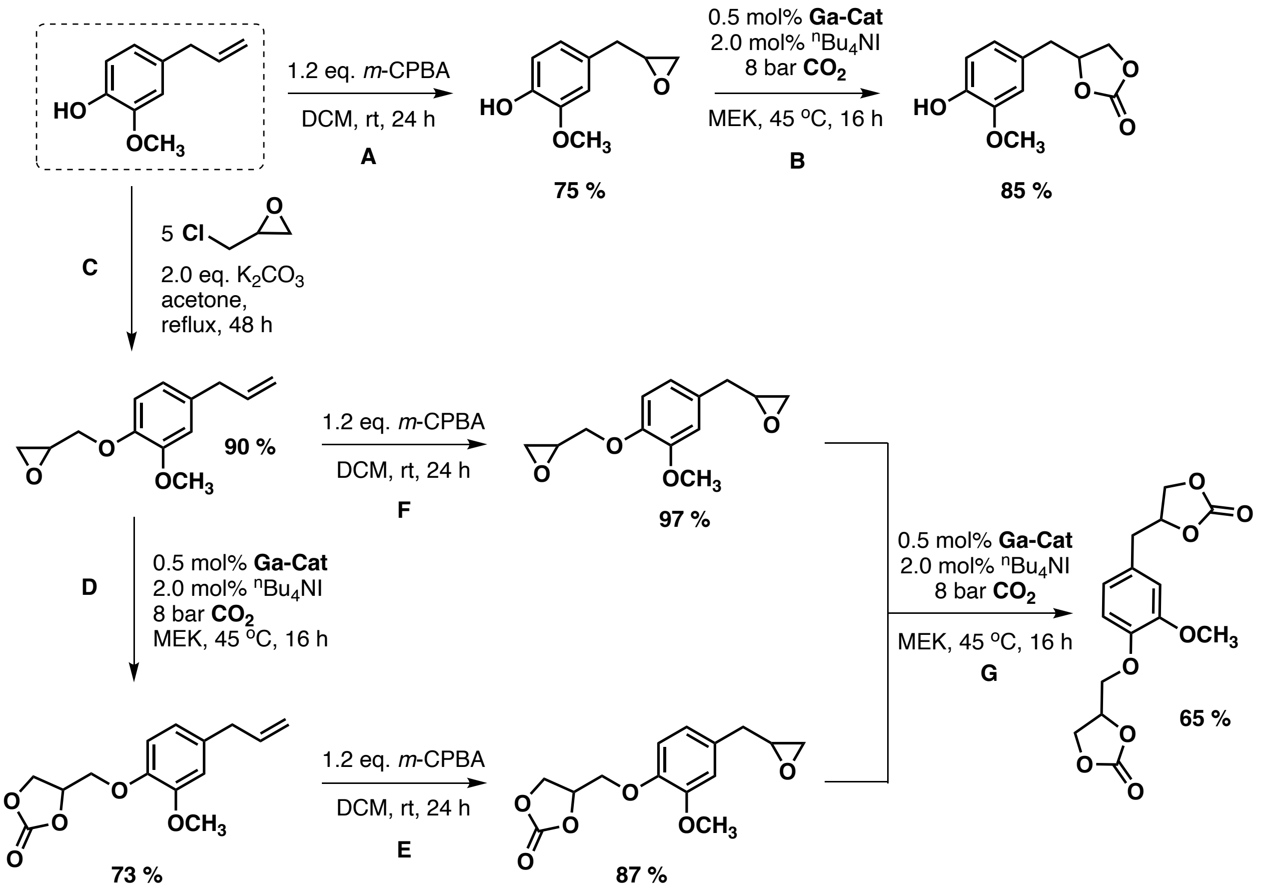


New opportunities…

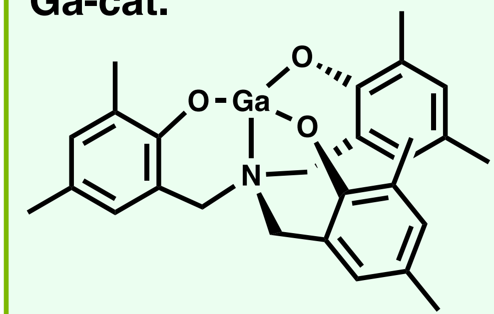
(Coupling *via* use of base or Steglich reaction)

Examples of bio-derived cyclic carbonates from our research

From eugenol



Ga-cat.



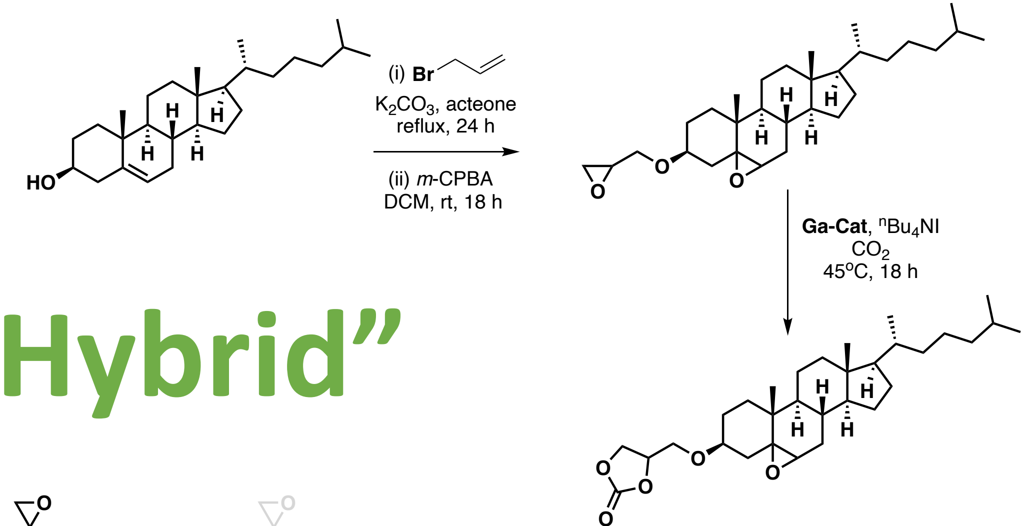
✔ New opportunities…

Examples of bio-derived cyclic carbonates from our research

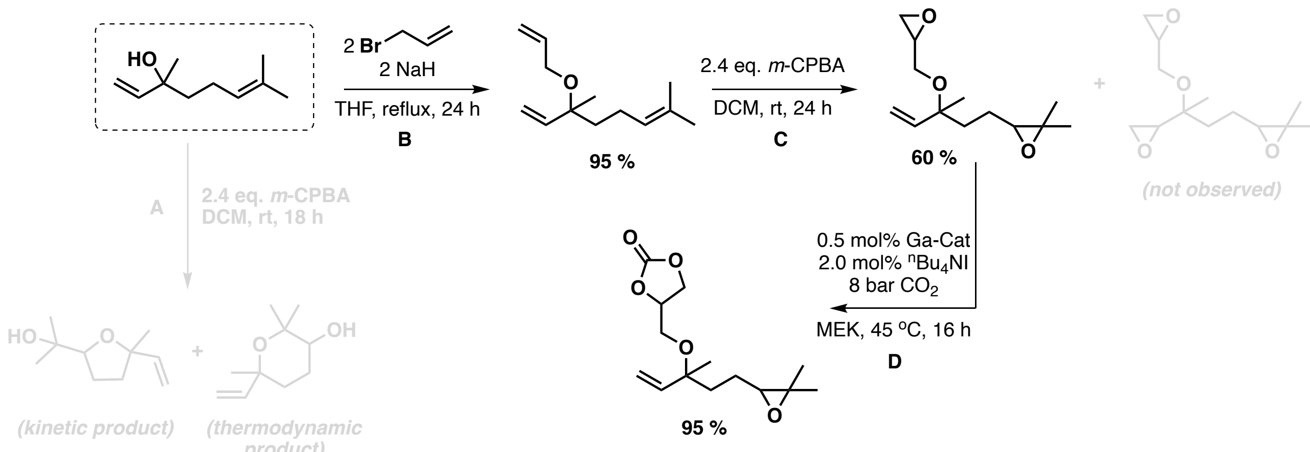
Also react with allyl bromide and then oxidise:

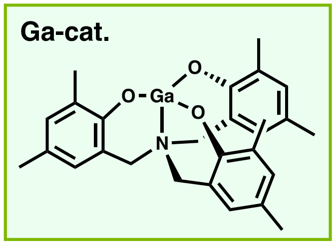
“Hybrid”

From cholesterol



From linalool

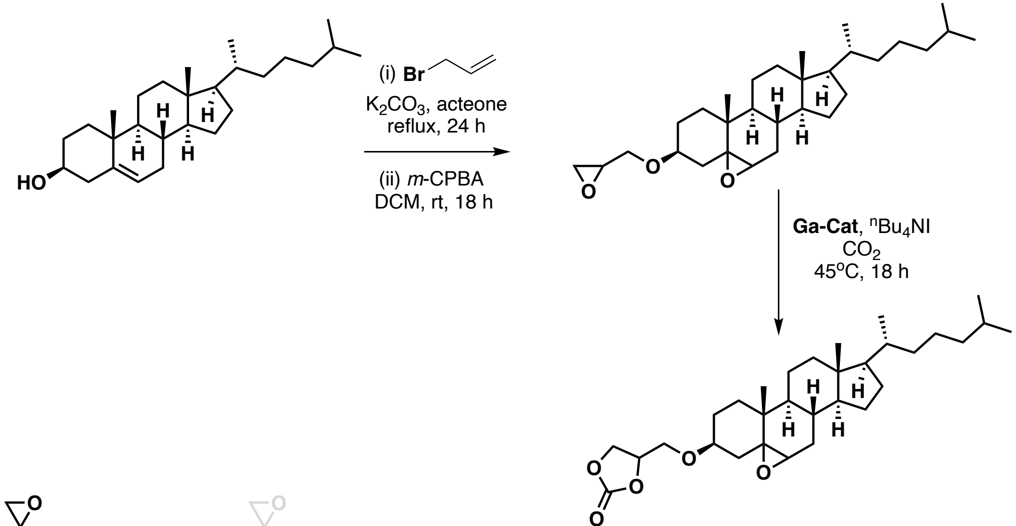




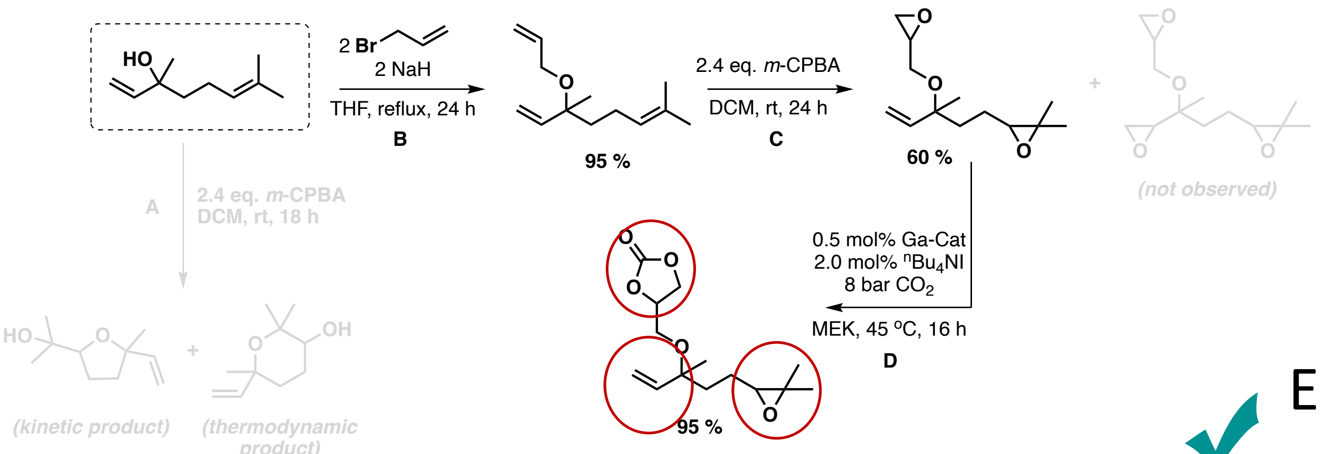
Examples of bio-derived cyclic carbonates from our research

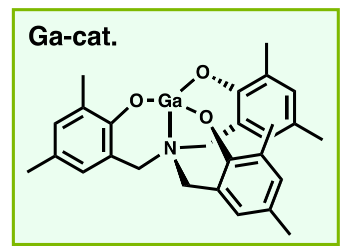
Also react with allyl bromide and then oxidise:

From cholesterol



From linalool





Exploiting the selective activity of the catalyst

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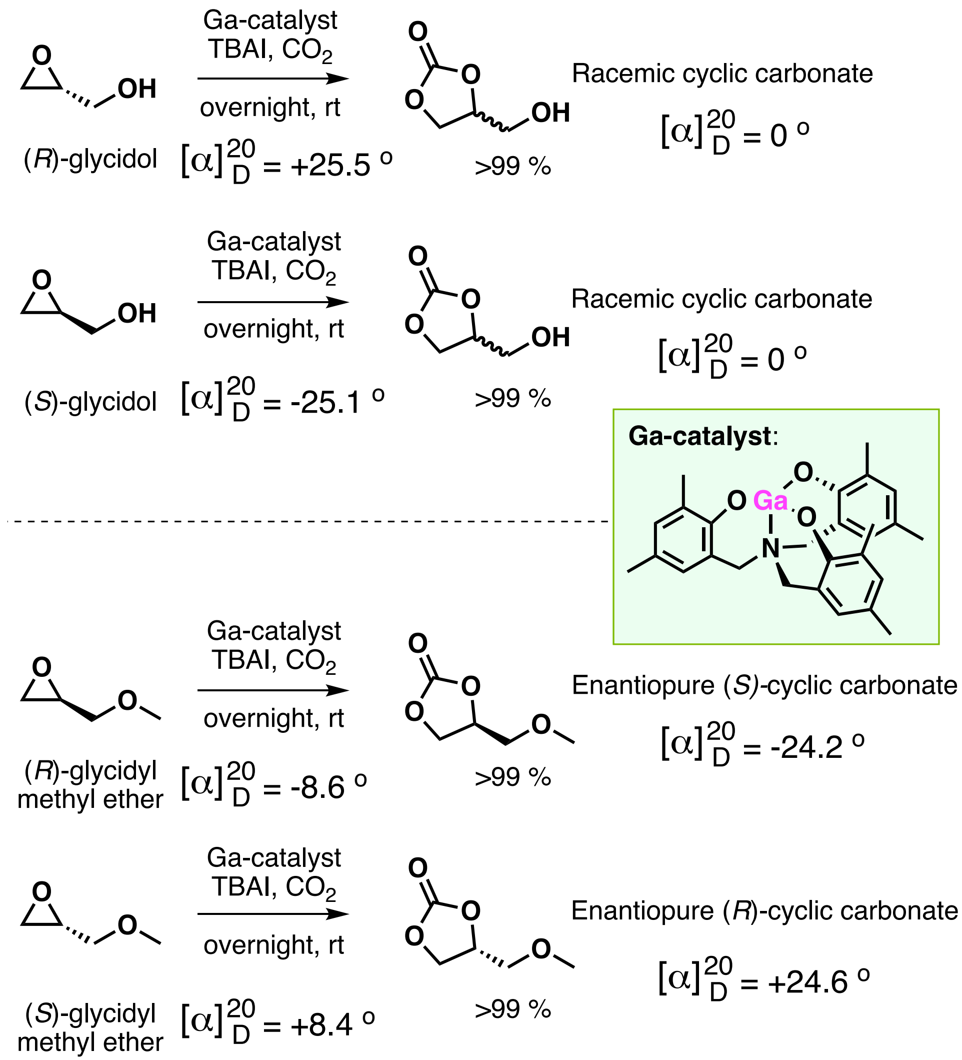
Retention of original stereochemistry is possible:

Difference between glycidol and “protected” glycidol…

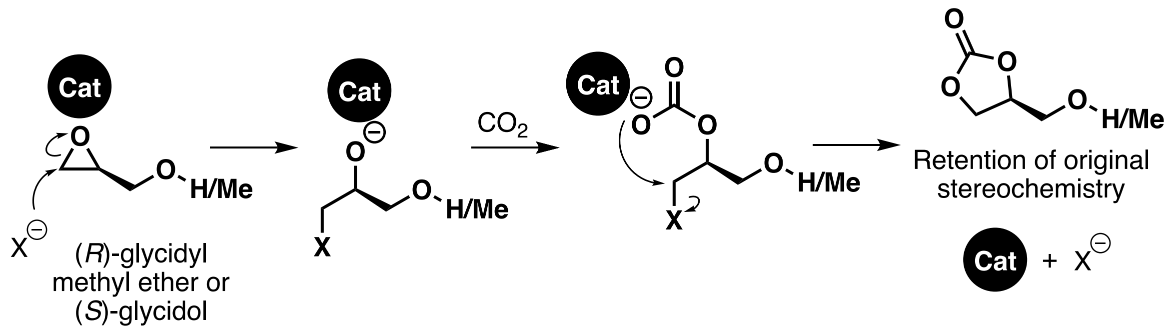


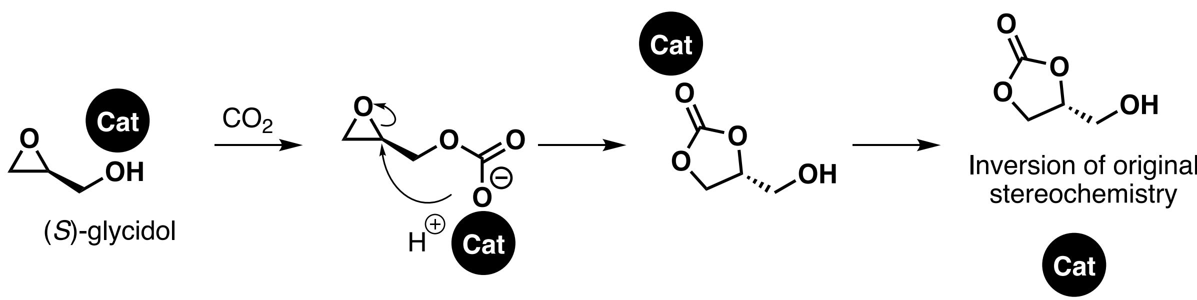
D. Jaraba Cabrera, L. Álvarez-Miguel, A. Hernando Rodríguez, A. Hamilton, M. E. G. Mosquera, C. J. Whiteoak, “submitted manuscript”.

Conversion of bio-derived epoxides:

Why???

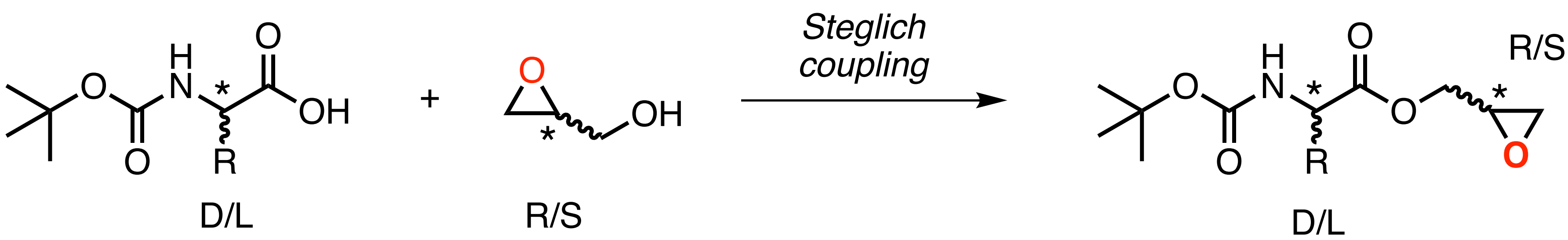
Again the mechanism is key...

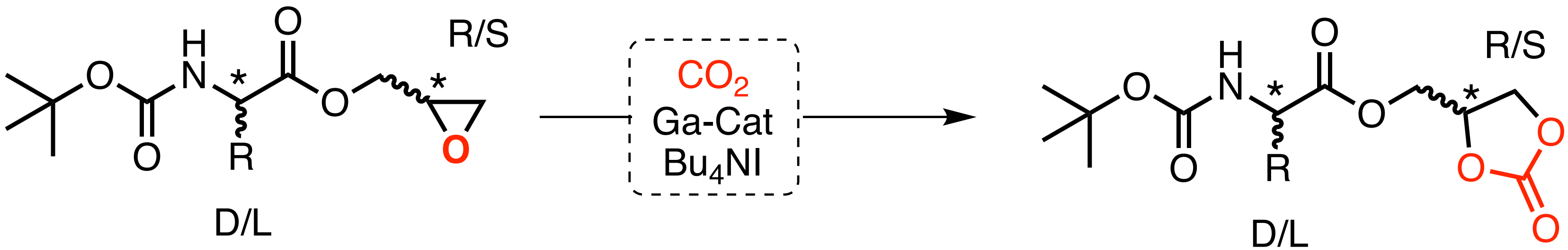




Cat = Catalyst

More complex substrates - *use of amino acids*:





D. Jaraba Cabrera, L. Álvarez-Miguel, A. Hernando Rodríguez, A. Hamilton, M. E. G. Mosquera, C. J. Whiteoak, "submitted manuscript".

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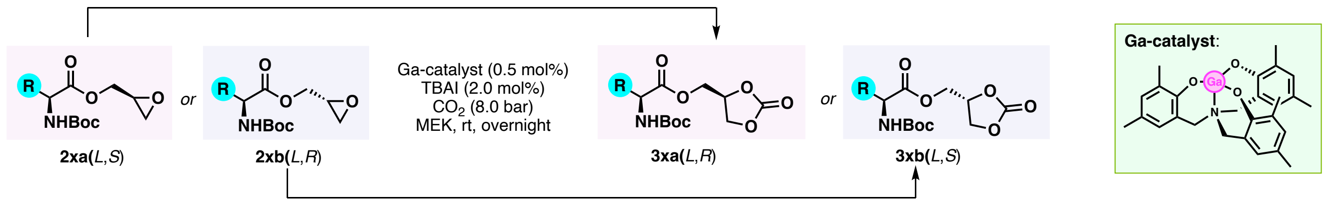
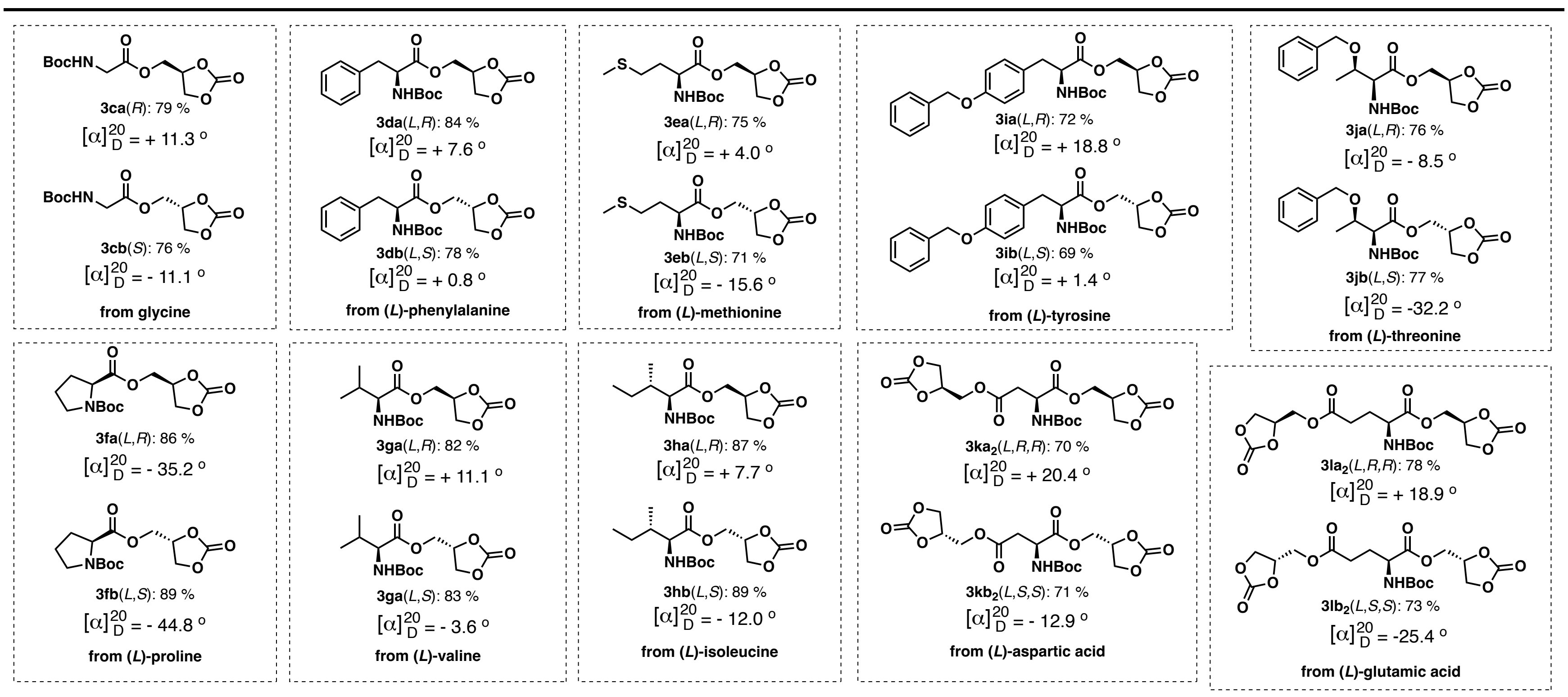
Use of amino acids:

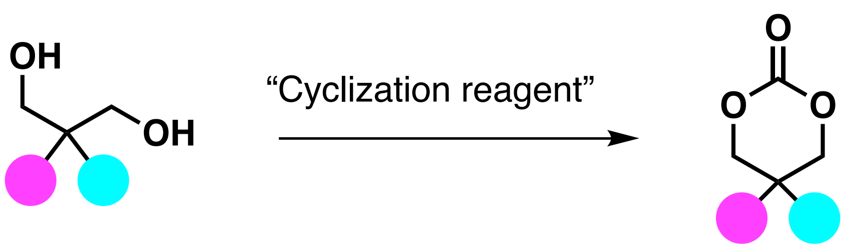


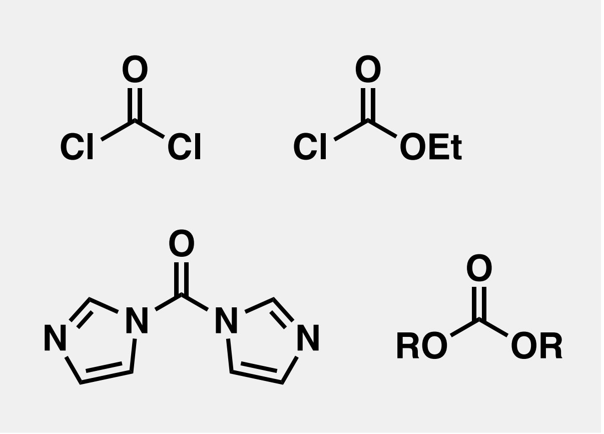


D. Jaraba Cabrera, L. Álvarez-Miguel, A. Hernando Rodríguez, A. Hamilton, M. E. G. Mosquera, C. J. Whiteoak, “submitted manuscript”.

Beyond 5-membered cyclic carbonates – 6-membered variants

Traditional stoichiometric approaches
to 6-membered cyclic carbonates:

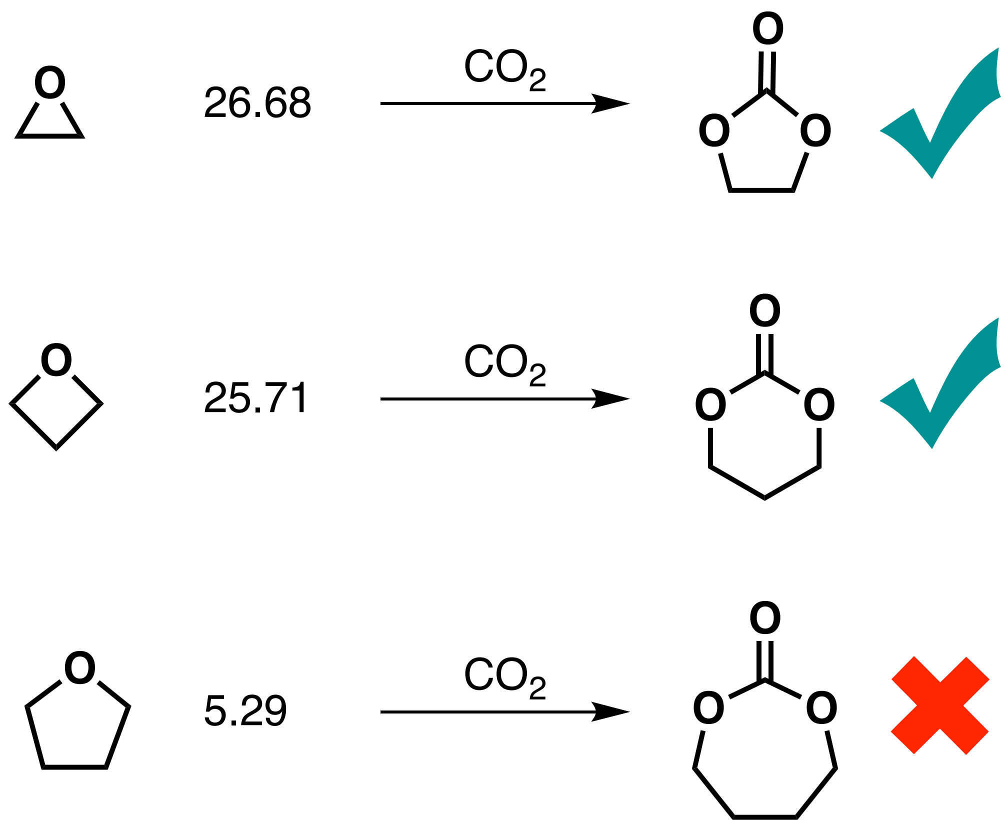




There must be a better way?

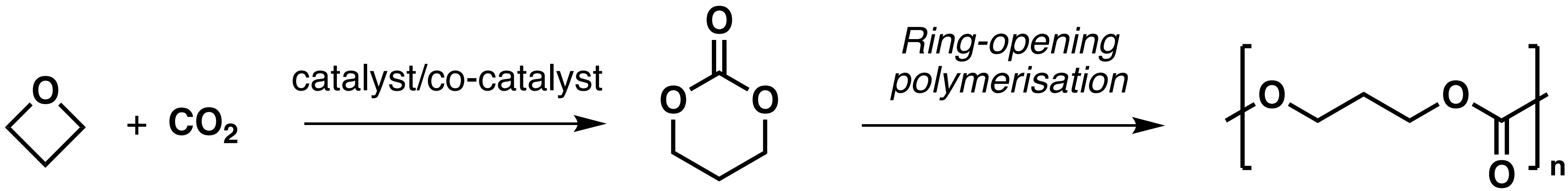
Beyond epoxides – from oxetanes (more sustainable?)

Ring strain (kcal mol^{-1}): **Ring strain?**

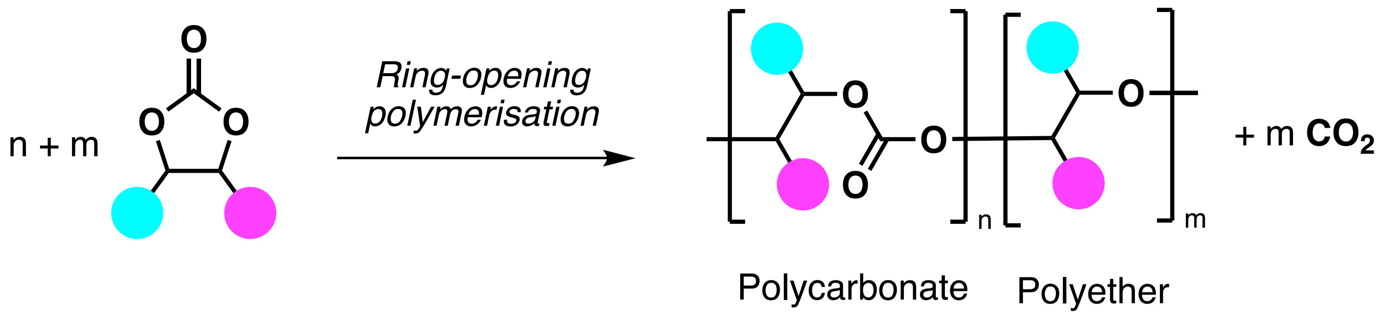


Does the reaction work with four-membered cyclic ethers?

Formation of six-membered cyclic carbonates and polycarbonates



Rather distinct from the 5-membered cyclic carbonates which tend to lose CO_2 (*up to 30 %*)



L. Álvarez-Miguel, M. D. G. Billacura, M. E. G. Mosquera, C. J. Whiteoak, "Catalytic Synthesis of Polycarbonates using Carbon Dioxide" in Biopolymers: Synthesis, Properties, and Emerging Applications (eds. V. Sessini, S. Ghosh and M. E. G. Mosquera), ISBN 9780323909396. A. Hosseinian, S. Farshbaf, R. Mohammadi, A. Monfared, E. Vessally, "Advancements in six-membered cyclic carbonate (1,3-dioxan-2-one) synthesis utilizing carbon dioxide as a C1 source", *RSC Adv.*, **2018**, *8*, 17976.

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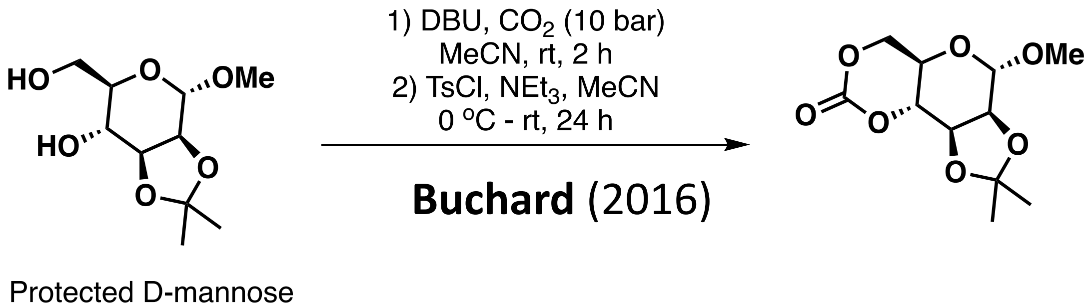
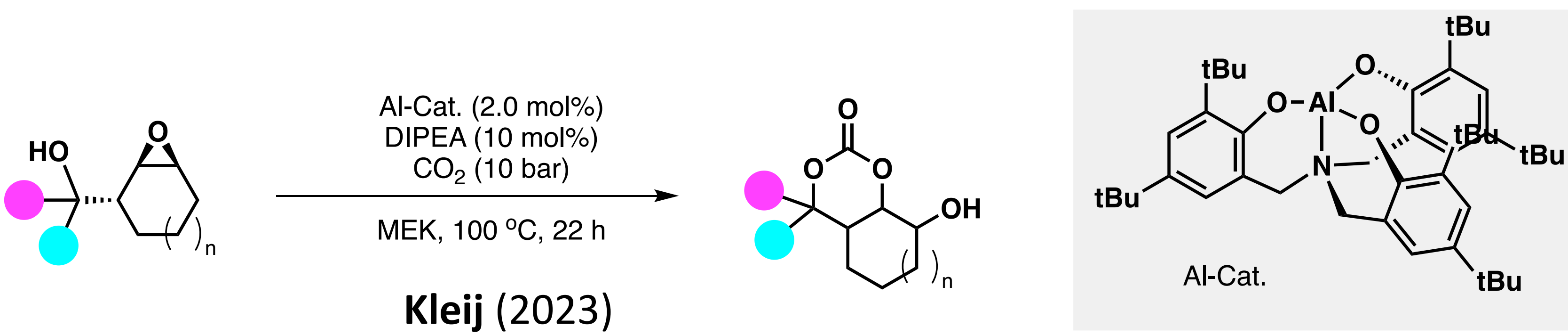
Other approaches using CO_2:



(although needs 1.0 equiv. DBU)

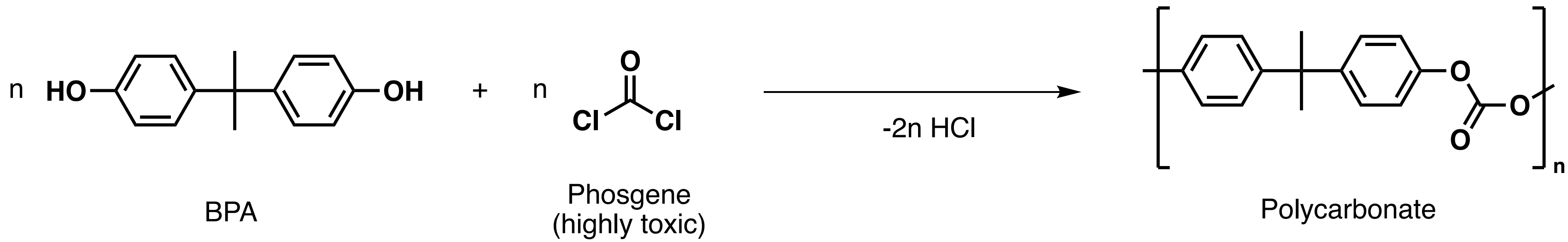


If the OH is capped, these compounds can be easily polymerized forming polycarbonates using a TBD/BnOH ROP approach

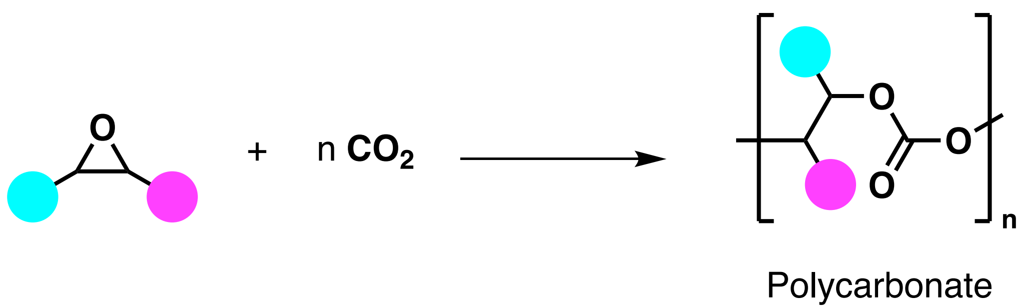
G. L. Gregory, L. M. Jenisch, B. Charles, G. Kociok-Kohn, A. Buchard, "Polymers from Sugars and CO_2: Synthesis and Polymerization of a D-Mannose-Based Cyclic Carbonate", *Macromolecules*, **2016**, *49*, 7165. C. Qiao, W. Shi, A. Brandolese, J. Benet-Buchholz, E. C. Escudero-Adán, A. W. Kleij, "A Novel Catalytic Route to Polymerizable Bicyclic Cyclic Carbonate Monomers from Carbon Dioxide", *Angew. Chem.Int. Ed.*, **2022**, *61, e202205053*. J. Ni, M.Lanzi, D. H. Lamparelli, A. W. Kleij, "Ring-opening polymerization of functionalized aliphatic bicyclic carbonates", *Polym. Chem*., **2023**, *14*, 4748.

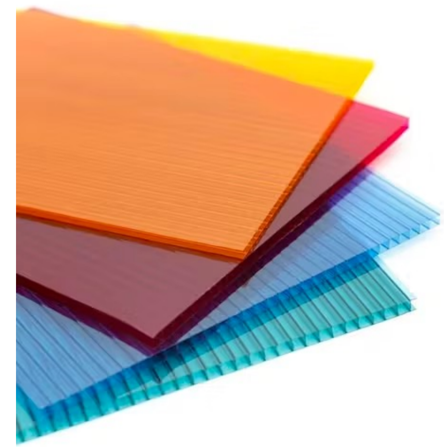
Direct formation of polycarbonates (co-polymerization of epoxides and CO_2)

Traditional approach:



Alternative approach:

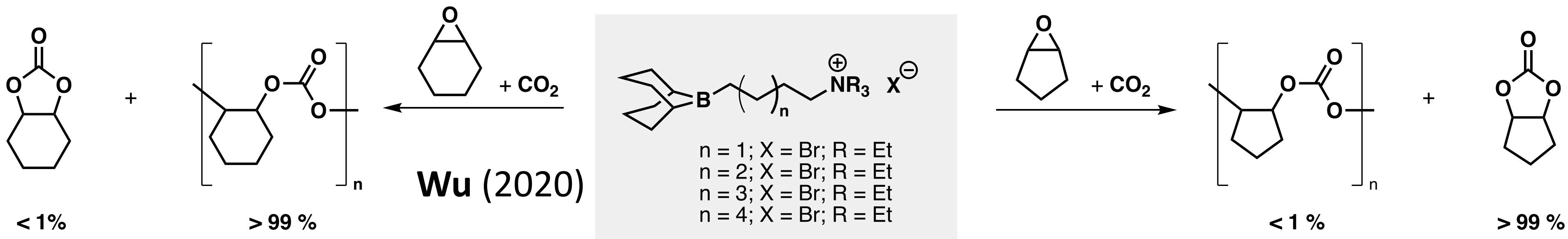




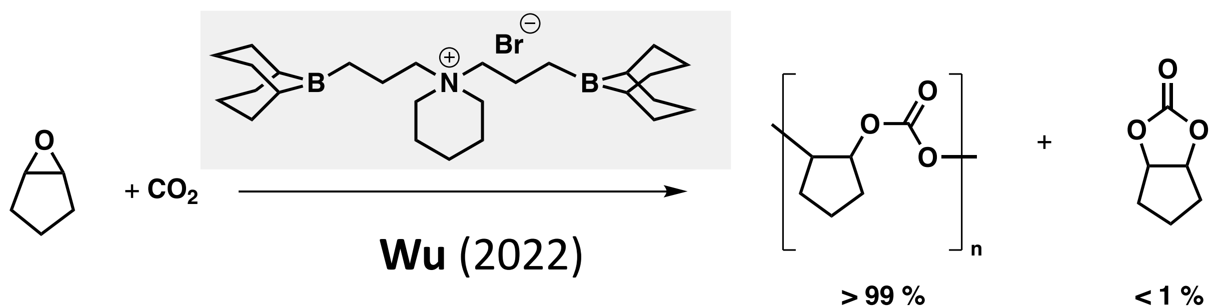
L. Álvarez-Miguel, M. D. G. Billacura, M. E. G. Mosquera, C. J. Whiteoak, "Catalytic Synthesis of Polycarbonates using Carbon Dioxide" in Biopolymers: Synthesis, Properties, and Emerging Applications (eds. V. Sessini, S. Ghosh and M. E. G. Mosquera), ISBN 9780323909396.

Co-polymerization of epoxides with CO_2

Cyclohexene oxide is a bit of a special case…



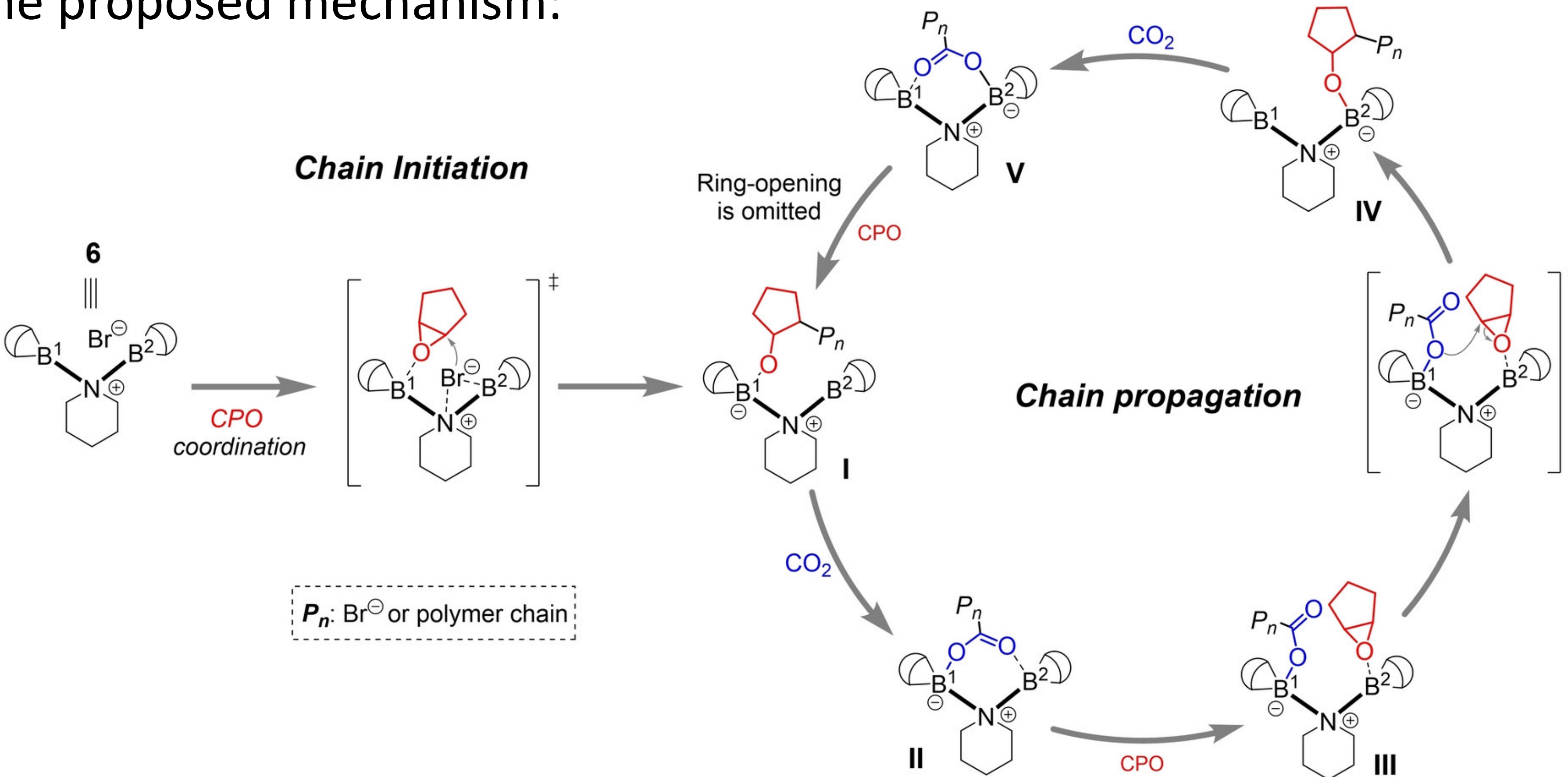
However, are two active centers better than one?



G.-W. Yang, Y.-Y. Zhang, R. Xie, G.-P. Wu, ”Scalable Bifunctional Organoboron Catalysts for Copolymerization of CO_2 and Epoxides with Unprecedented Efficiency”, *J. Am. Chem. Soc.*, **2022**, *142*, 12245. G.-W. Yang, Y. Wang, H. Qi, Y.-Y. Zhang, X.-F. Zhu, C. Lu, L. Yang, G.-P. Wu, “Highly Selective Preparation and Depolymerization of Chemically Recyclable Poly(cyclopentene carbonate) Enabled by Organoboron Catalysts”, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202210243.

Two active centers better than one (Catalyst design)?

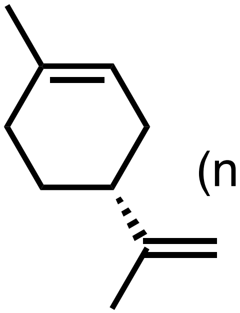
The proposed mechanism:



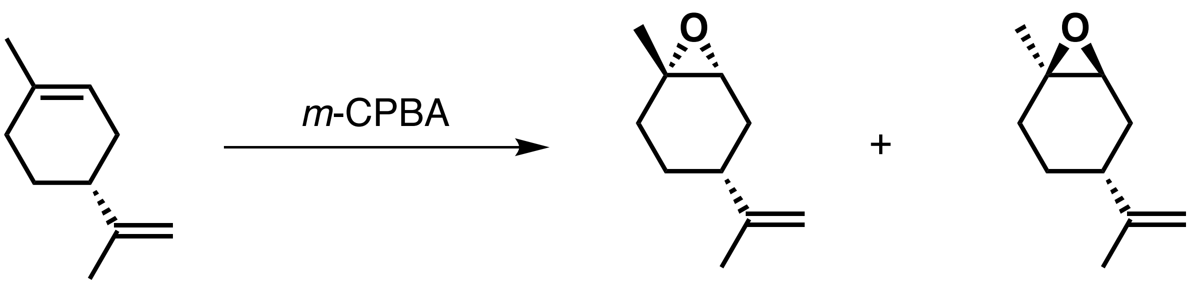
(There are many other examples…)

G.-W. Yang, Y. Wang, H. Qi, Y.-Y. Zhang, X.-F. Zhu, C. Lu, L. Yang, G.-P. Wu, "Highly Selective Preparation and Depolymerization of Chemically Recyclable Poly(cyclopentene carbonate) Enabled by Organoboron Catalysts", *Angew. Chem. Int. Ed.*, **2022**, *61*, e202210243.

The case of limonene oxide…



(R)-limonene
(naturally occuring)

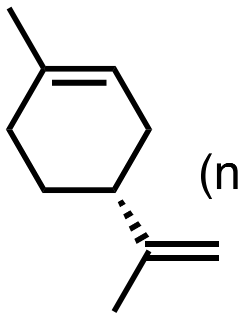


trans/cis-(R)-limonene oxide

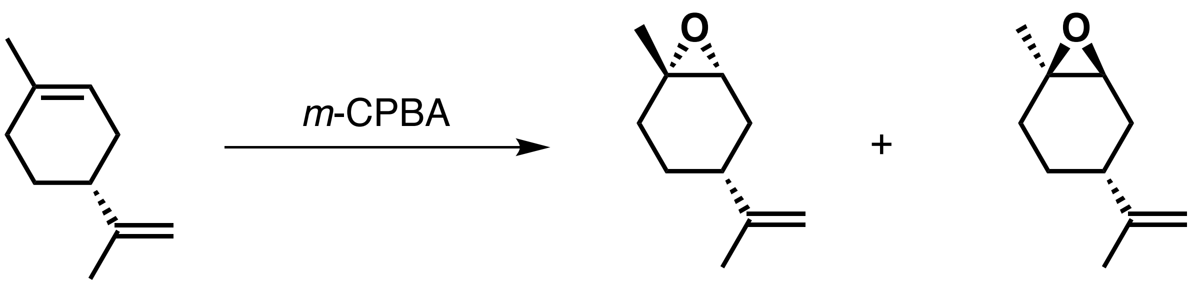
Can be separated and co-polymerized with CO_2

F. Parrino, A. Fidalgo, L. Palmisano, L. M. Ilharco, M. Pagliaro, R. Ciriminna, "Polymers of Limonene Oxide and Carbon Dioxide: Polycarbonates of the Solar Economy", *ACS Omega*, **2018**, *3*, 4884.

The case of limonene oxide…



(R)-limonene
(naturally occuring)



trans/cis-(R)-limonene oxide

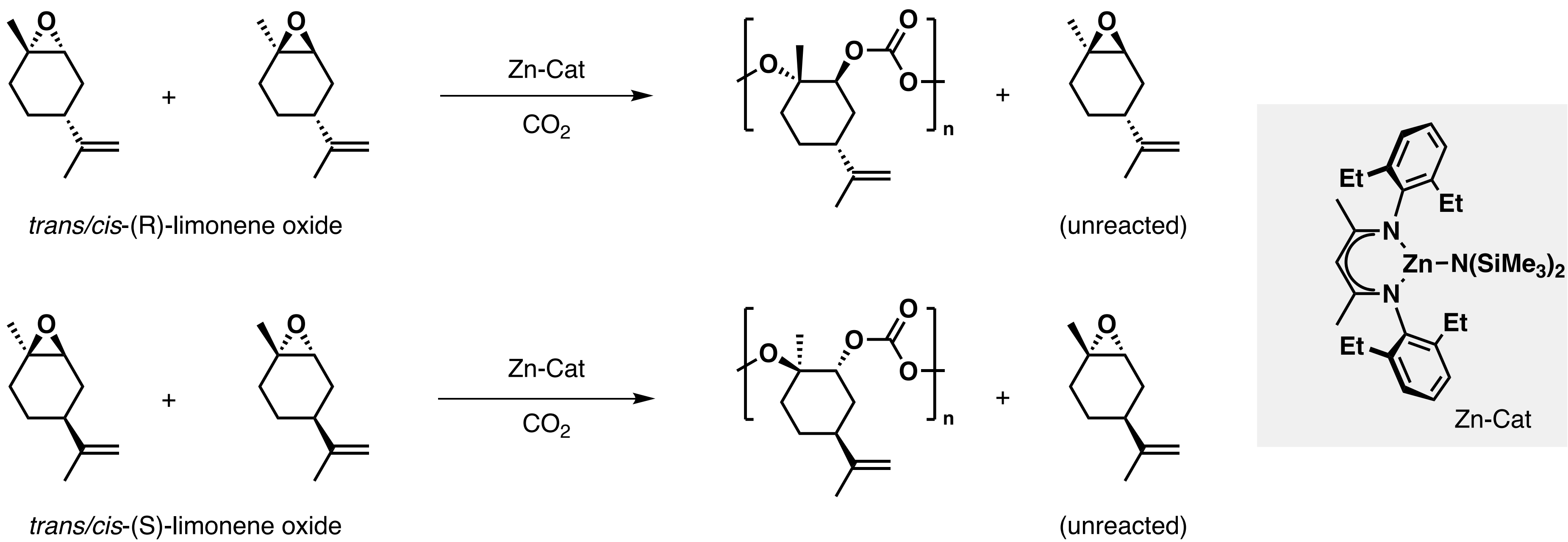
Can be separated and co-polymerized with CO_2

Or…

F. Parrino, A. Fidalgo, L. Palmisano, L. M. Ilharco, M. Pagliaro, R. Ciriminna, "Polymers of Limonene Oxide and Carbon Dioxide: Polycarbonates of the Solar Economy", *ACS Omega*, **2018**, *3*, 4884.

Example of polycarbonates from limonene oxide with interesting selectivity:

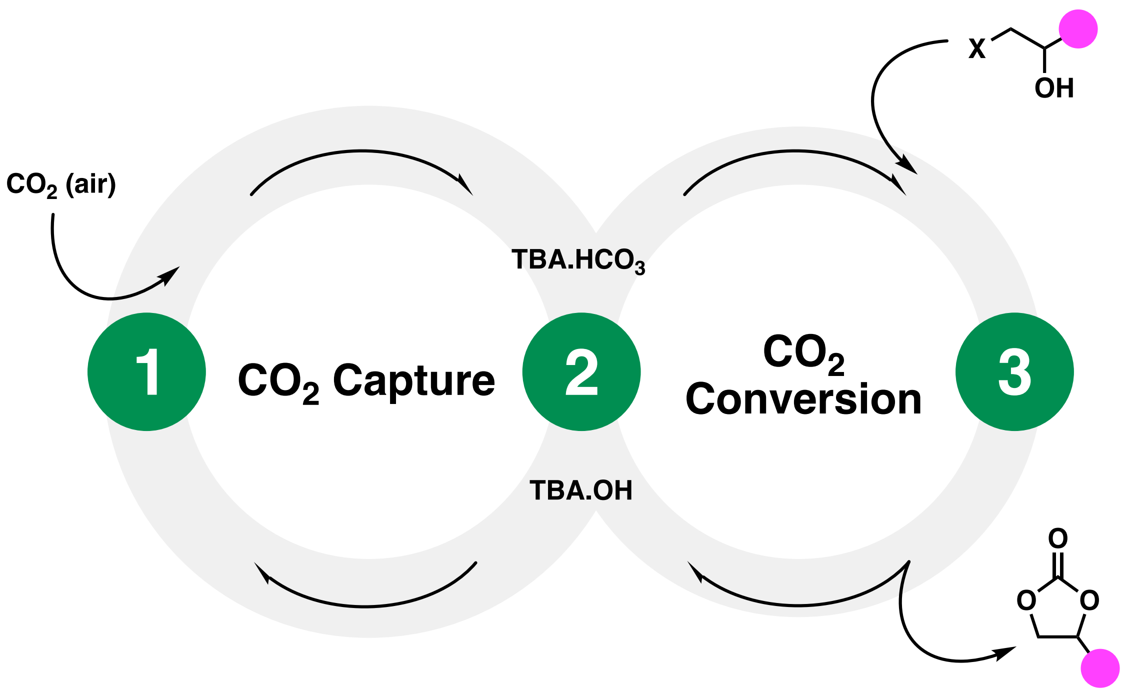
Auriemma/Coates (2015)

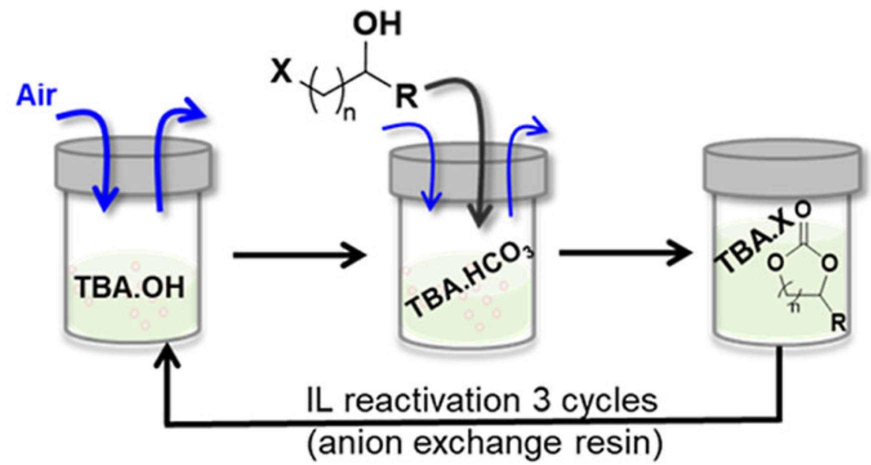


F. Auriemma, C. De Rosa, M. R. Di Caprio, R. Di Girolamo, W. C. Ellis, G. W. Coates, "Stereocomplexed Poly(Limonene Carbonate): A Unique Example of the Cocrystallization of Amorphous Enantiomeric Polymers", *Angew. Chem. Int. Ed.*, **2015**, *54*, 1215.

Where does CO_2 come from? Is this an opportunity for study?

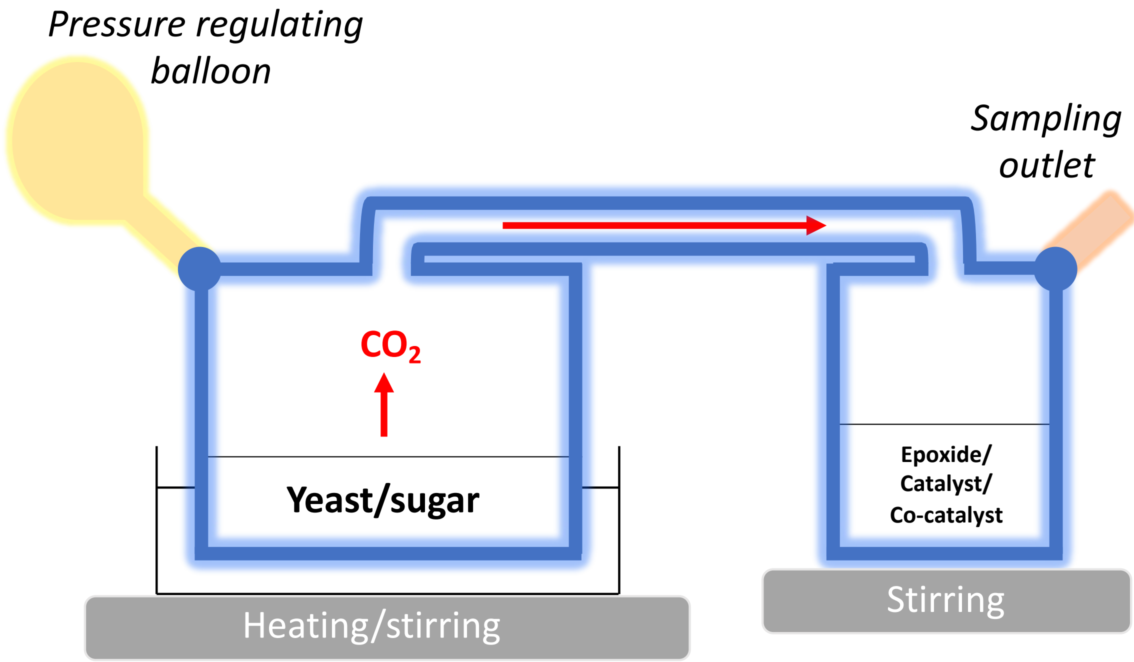
Directly from the air…

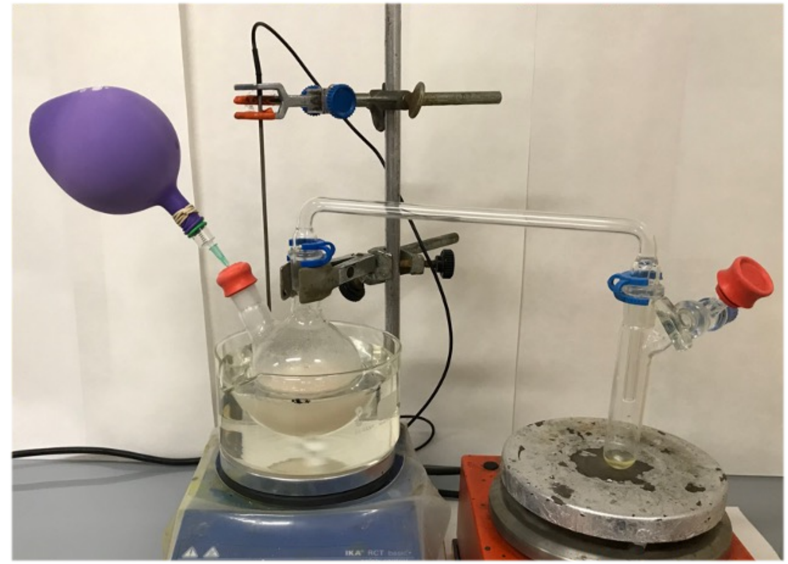




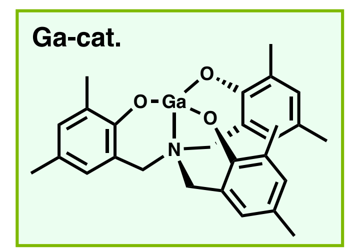
Zanatta/Sans (2023)

M. Zanatta, E. García-Verdugo, V. Sans, "Direct Air Capture and Integrated Conversion of Carbon Dioxide into Cyclic Carbonates with Basic Organic Salts", *ACS Sustainable Chem. Eng.*, **2023**, *11*, 9613.





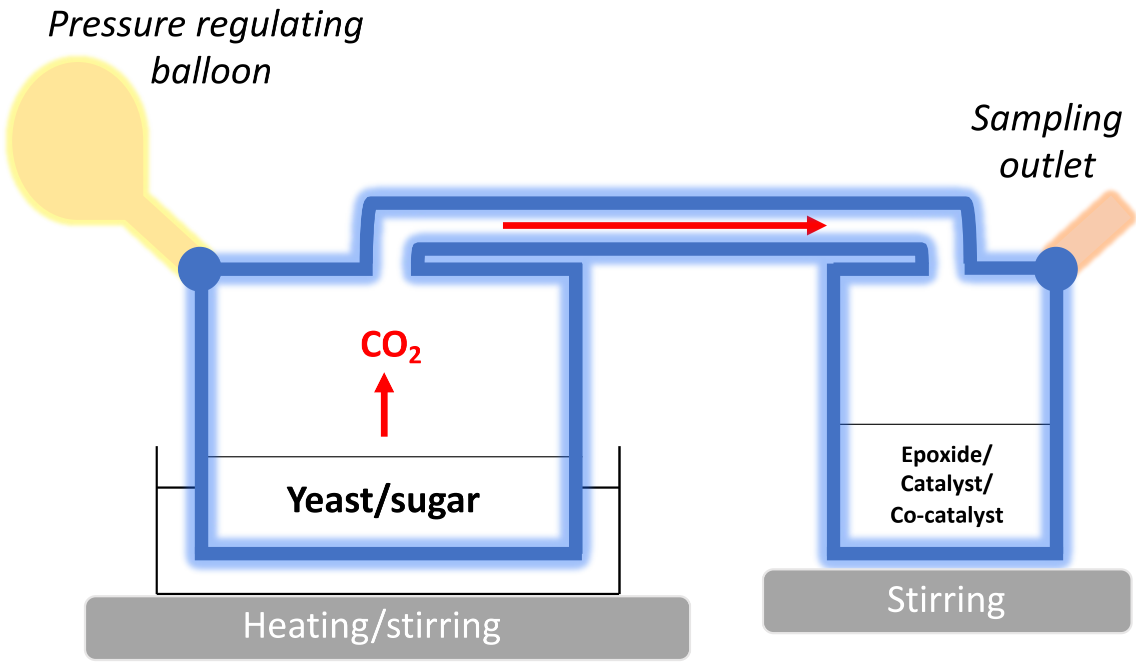
Whiteoak/Mosquera (2023)



✔ **Able to use very low pressure of CO_2 directly generated from fermentation!**

Yields of >99 %: 1.0 mol% Ga-Cat., 4.0 mol% Bu_4NI, rt, 18 h

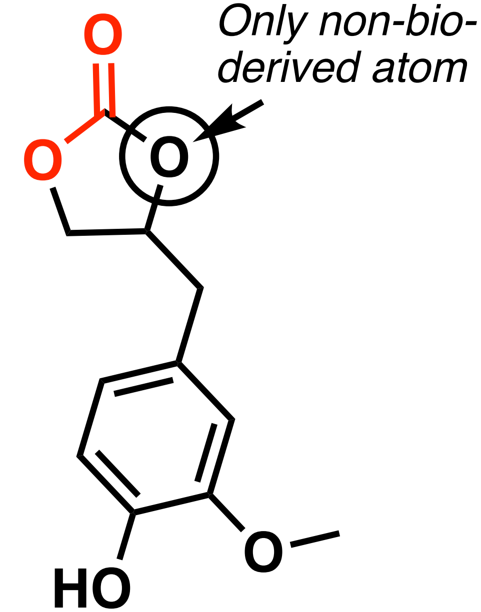
D. Jaraba Cabrera, L. Álvarez-Miguel, C. Díez-Poza, M. E. G. Mosquera, C. J. Whiteoak, "Combining Bio- and Chemo-Catalysis for Cyclic Carbonate Synthesis at Very Low Pressure: Efficient "Online" Utilization of CO_2 Obtained Directly from the Fermentation of Sugars", *Catal. Today*, **2023**, *114477*.



Whiteoak/Mosquera (2023)

✔ **Able to use very low pressure of CO_2 directly generated from fermentation!**

Bio-derived

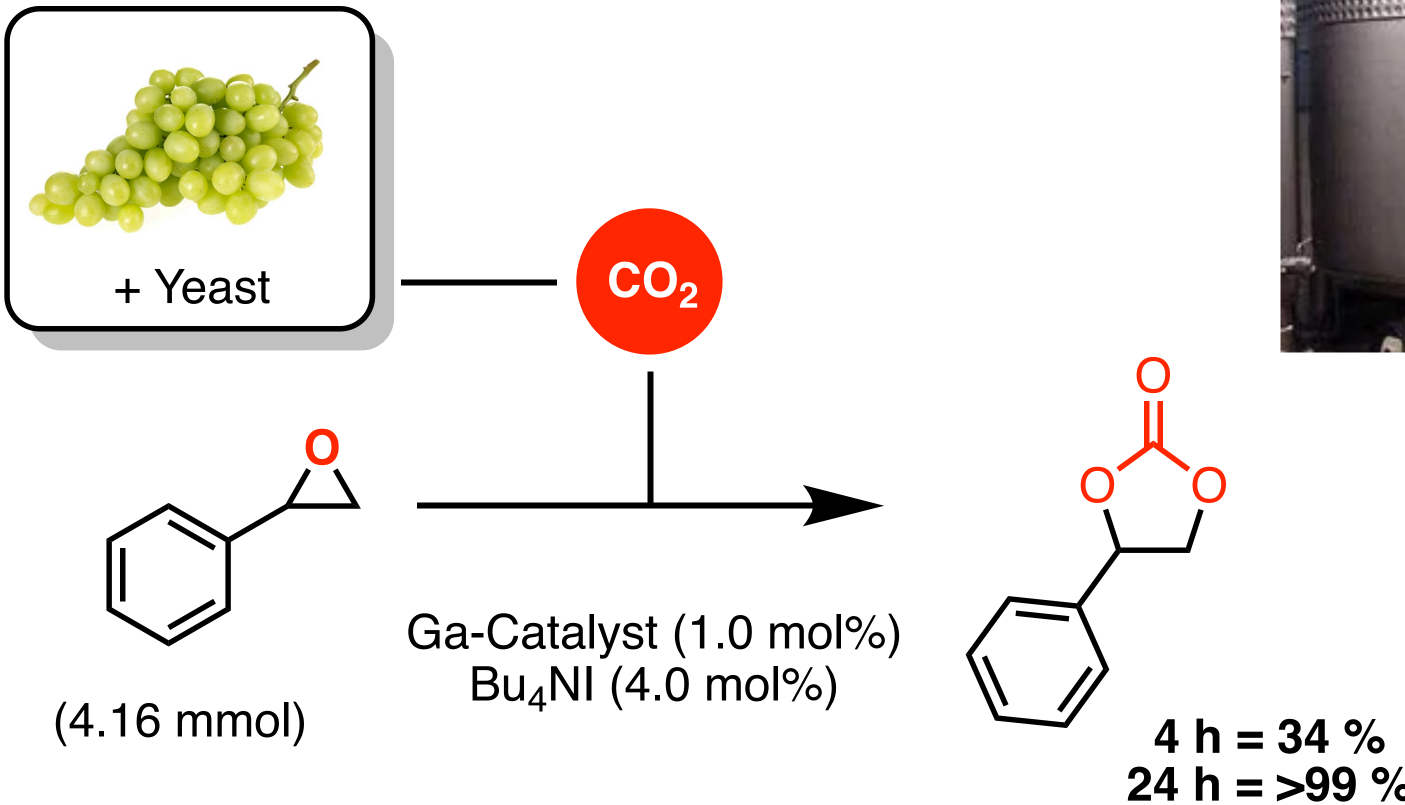


>99 % after 48 h

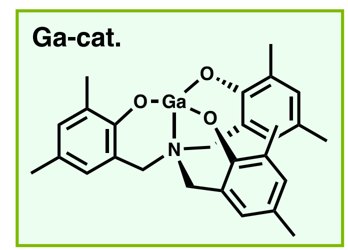
2 steps from eugenol

D. Jaraba Cabrera, L. Álvarez-Miguel, C. Díez-Poza, M. E. G. Mosquera, C. J. Whiteoak, "Combining Bio- and Chemo-Catalysis for Cyclic Carbonate Synthesis at Very Low Pressure: Efficient "Online" Utilization of CO_2 Obtained Directly from the Fermentation of Sugars", *Catal. Today*, **2023**, *114477*.

Use of other sugar sources:



Whiteoak/Mosquera (2023)



D. Jaraba Cabrera, L. Álvarez-Miguel, C. Díez-Poza, M. E. G. Mosquera, C. J. Whiteoak, "Combining Bio- and Chemo-Catalysis for Cyclic Carbonate Synthesis at Very Low Pressure: Efficient "Online" Utilization of CO_2 Obtained Directly from the Fermentation of Sugars", *Catal. Today*, **2023**, *114477*.

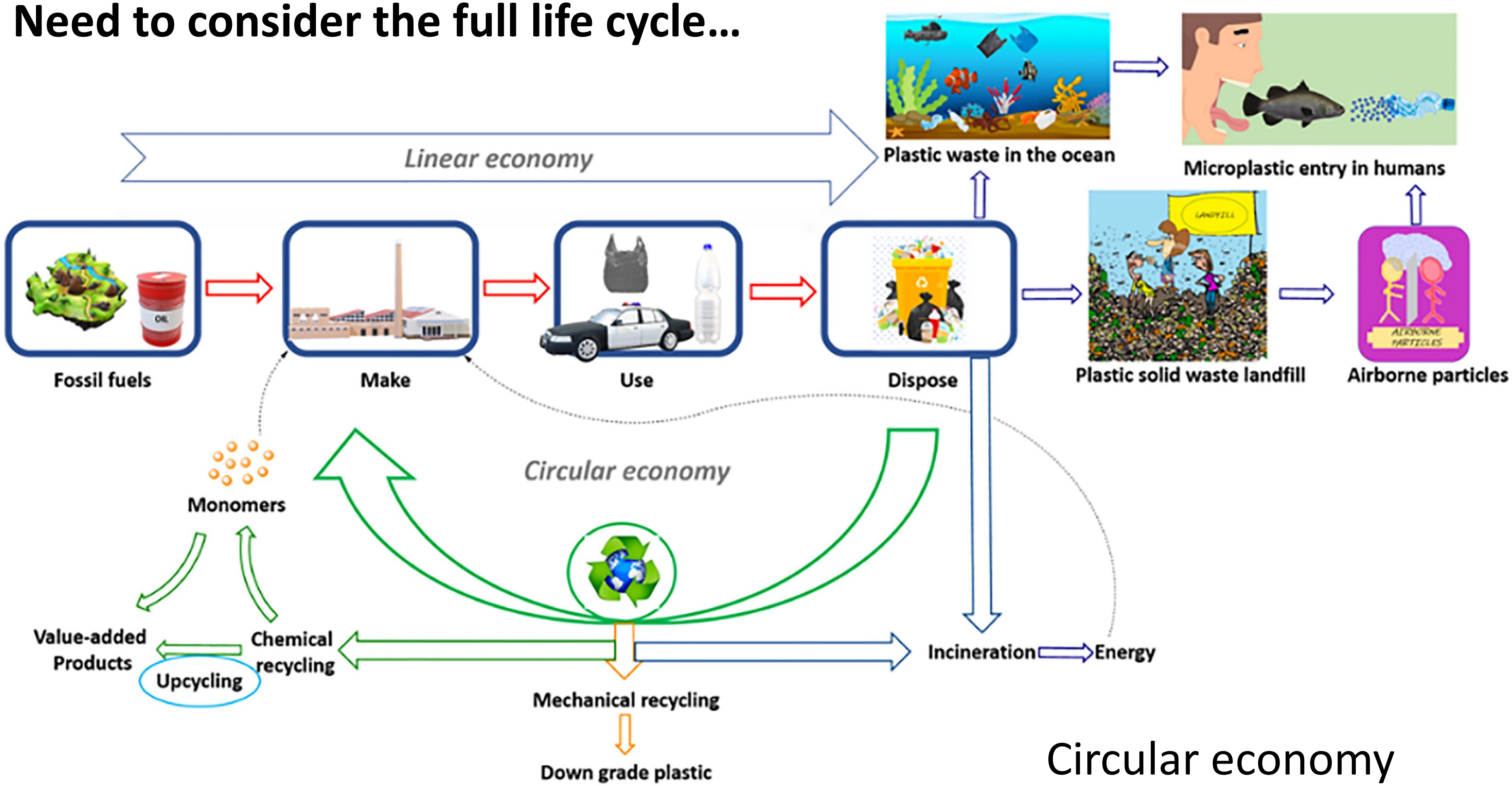
Spain pollution: Millions of plastic pellets wash up on coast

22 hours ago

https://www.bbc.com/news/world-europe-67921088

End of useful life is a concern...

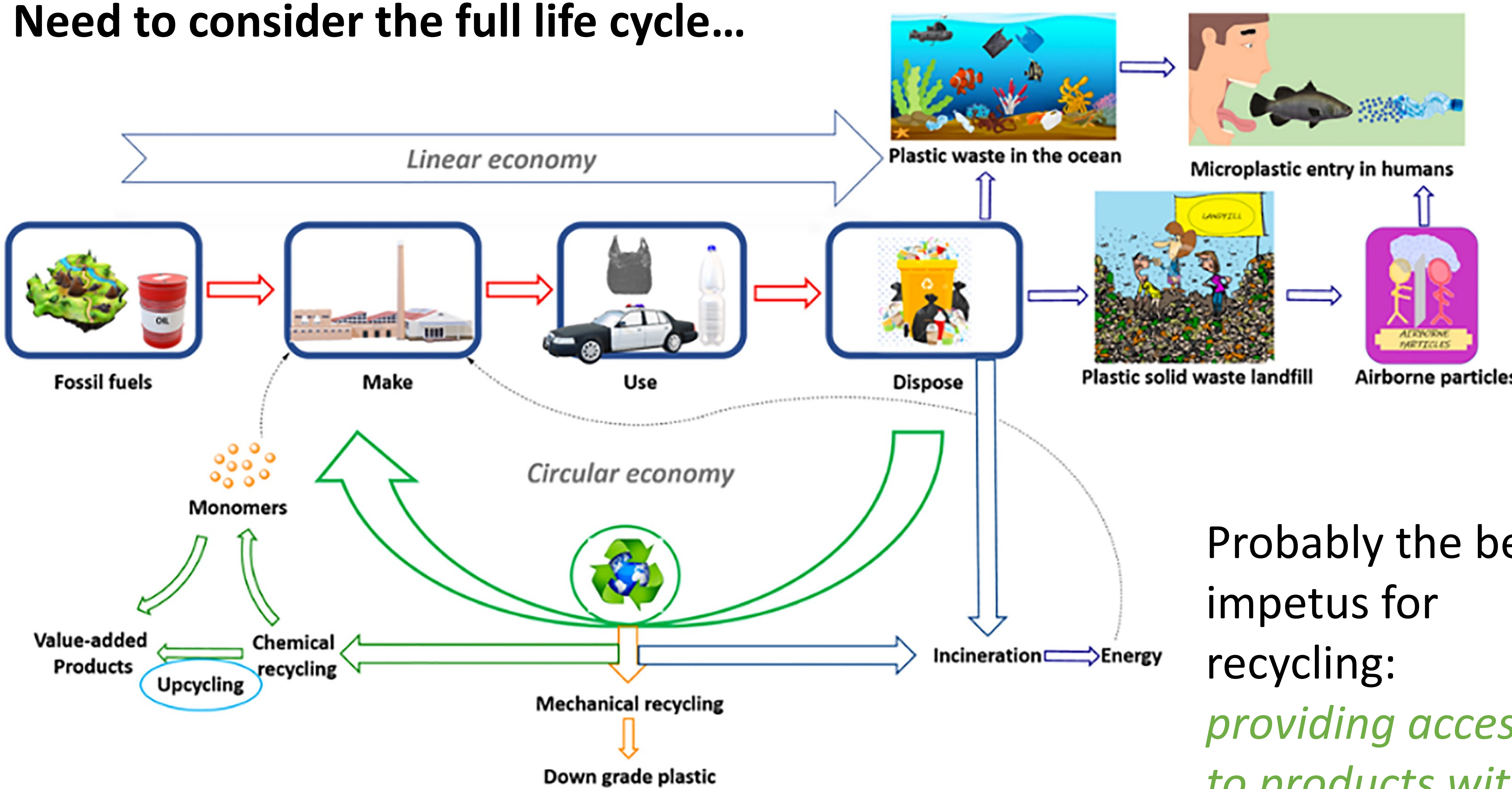
Need to consider the full life cycle…



Circular economy provides opportunities!

K. V. Khopade, S. H. Chikkali, N. Barsu, "Metal-catalyzed plastic depolymerization", *Cell Rep. Phys. Sci.*, **2023**, *4*, 101341.

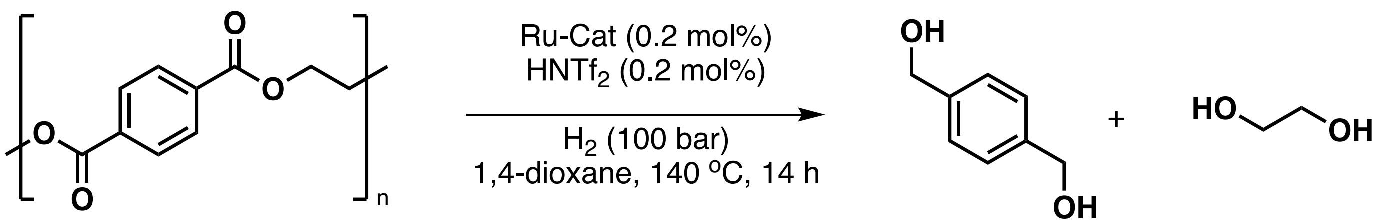
Need to consider the full life cycle...



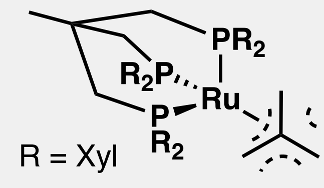
Probably the best impetus for recycling: *providing access to products with value...*

K. V. Khopade, S. H. Chikkali, N. Barsu, "Metal-catalyzed plastic depolymerization", *Cell Rep. Phys. Sci.*, **2023**, *4*, 101341.

Even with PET we can do things:



PET



Ru-Cat

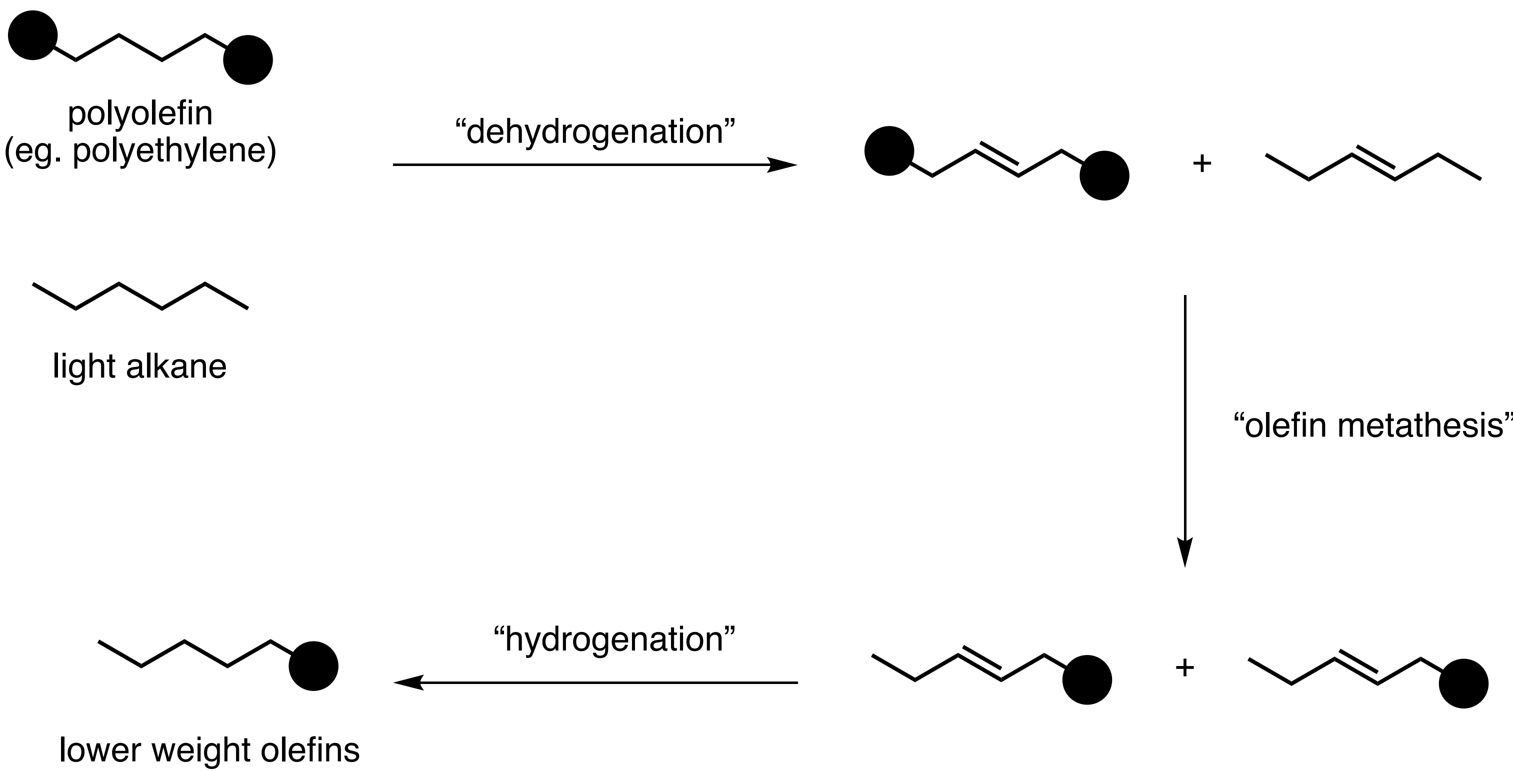
99 % conversion!

Klankermayer (2018)

However, the alcohol is not the original starting material (comes from the carboxylic acid)...

S. Westhues, J. Idel, J. Klankermayer, "Molecular catalyst systems as key enablers for tailored polyesters and polycarbonate recycling concepts", *Sci. Adv.*, **2018**, *4*, eaat9669.

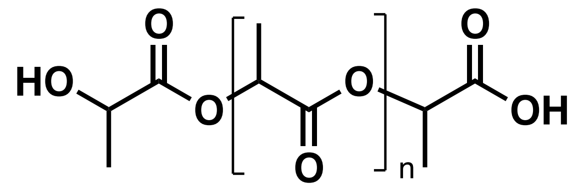
We can use some of the already established catalytic approaches to generate useful products:



(eg. fuels?)

K. V. Khopade, S. H. Chikkali, N. Barsu, "Metal-catalyzed plastic depolymerization", *Cell Rep. Phys. Sci.*, **2023**, *4*, 101341.

Returning to polylactide



Polylactide (PLA)

Recycling:

Can be either mechanically or **chemically** (through thermal or catalytic depolymerization) recycled.

Composting:

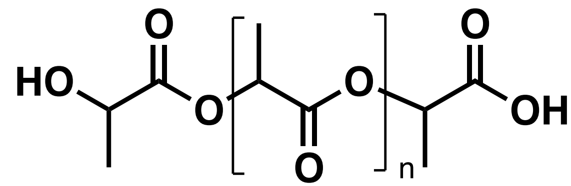
PLA is biodegradable (although "needs special conditions").
Actually, under natural conditions requires 100,000's of years ☹

Incineration:

Does not emit toxins during incineration (no Cl atoms etc)

P. McKeown, M. D. Jones, "The Chemical Recycling of PLA: A Review", *Sustain. Chem.*, **2020**, *1*, 1.

Returning to polylactide



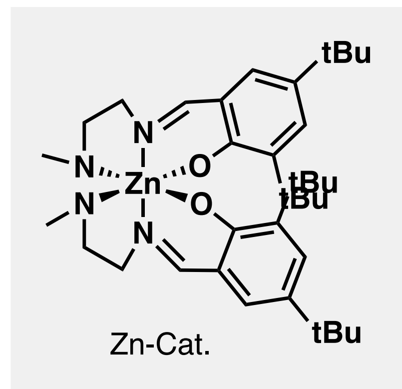
Polylactide (PLA)

Recycling:

Can be either mechanically or <u>chemically</u> (through thermal or catalytic depolymerization) recycled.

Polylactide (PLA)

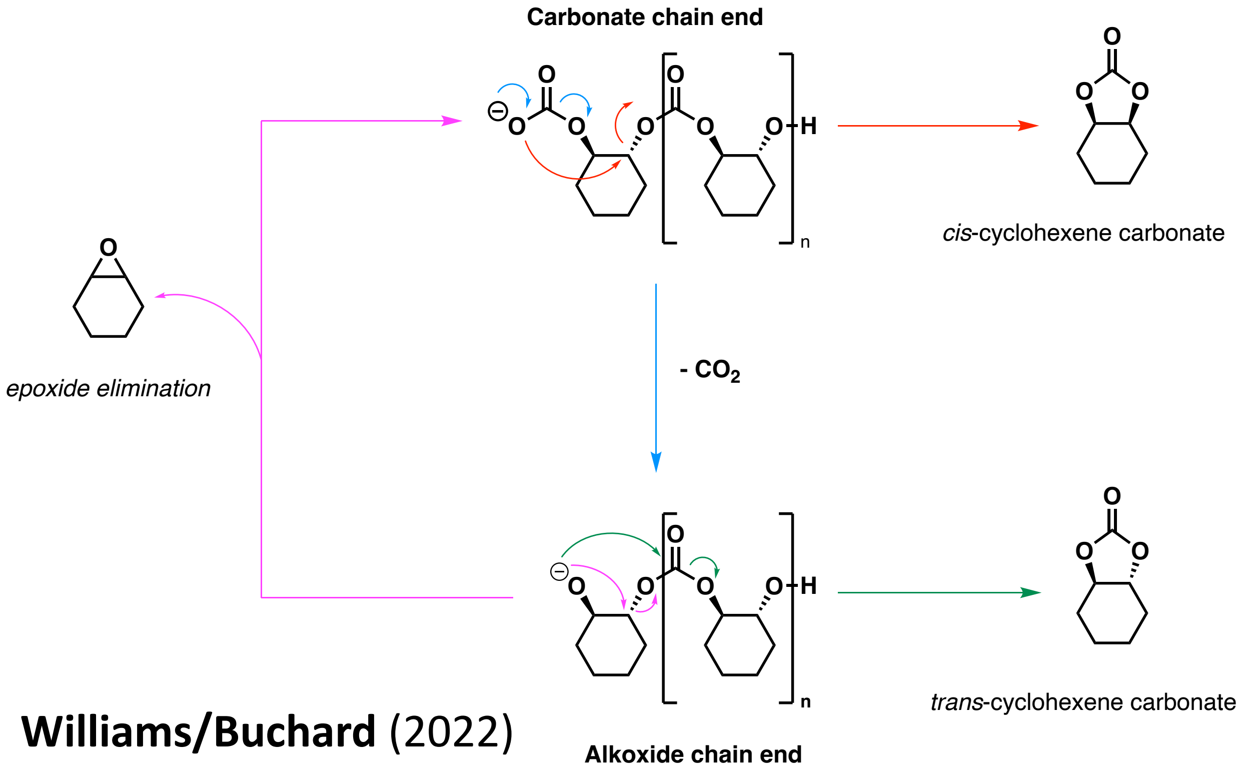
Alkyl lactide

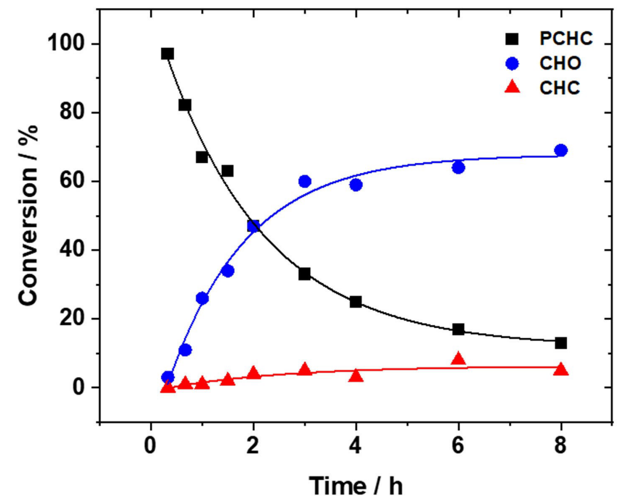


Jones/Wood (2019)

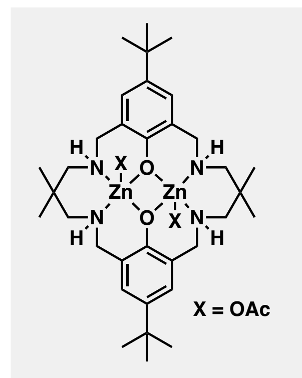
L. A. Román-Ramírez, P. Mckeown, M. D. Jones, J. Wood, “Poly(lactic acid) Degradation into Methyl Lactate Catalyzed by a Well-Defined Zn(II) Complex”, *ACS Catal.*, **2019**, *9*, 409.

What about polycarbonate recycling?

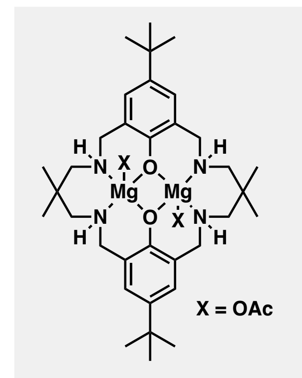




Williams/Buchard (2022)



39 % *trans*-cyclohexene carbonate
+ 61% cyclohexene oxide

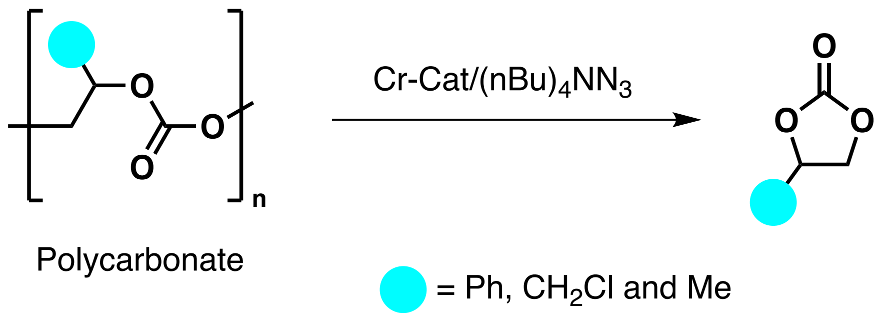


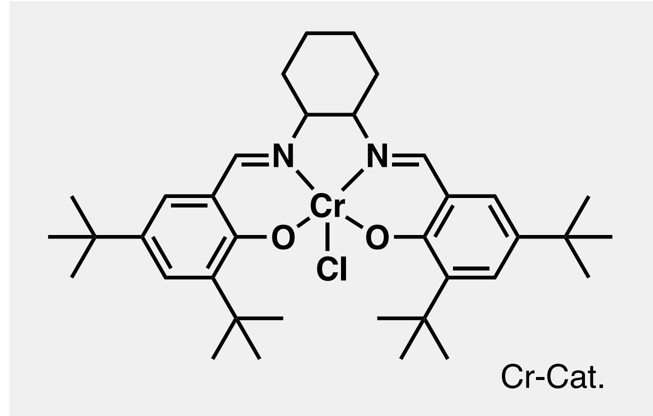
98 % cyclohexene oxide

Mg-alkoxide catalyzed epoxide extrusion being kinetically favourable compared to cyclic carbonate formation

F. N. Singer, A. C. Deacy, T. M. McGuire, C. K. Williams, A. Buchard, "Chemical Recycling of Poly(Cyclohexene Carbonate) Using a Di-Mg^{II} Catalyst", *Angew. Chem. Int. Ed.*, **2022**, *61*, e202201785.

Examples have been around for a “while”…





Darensbourg (2012)

Aliphatic polycarbonates were found to undergo quantitative conversion to the corresponding cyclic carbonate following deprotonation of their −OH end group by azide ion

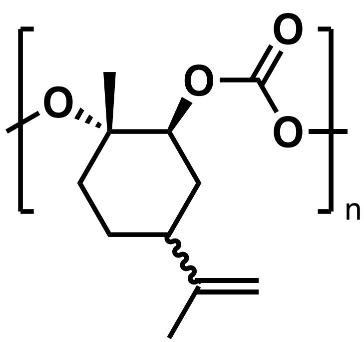
Involves the unzipping of the polymer in a backbiting fashion *leading to a steady decrease in the copolymer’s molecular weight while maintaining a narrow molecular weight distribution*

D. J. Darensbourg, S.-H. Wei, “Depolymerization of Polycarbonates Derived from Carbon Dioxide and Epoxides to Provide Cyclic Carbonates. A Kinetic Study”, *Macromolecules*, **2012**, *45,* 5916.

More recently a distinct example:

A new mechanism:

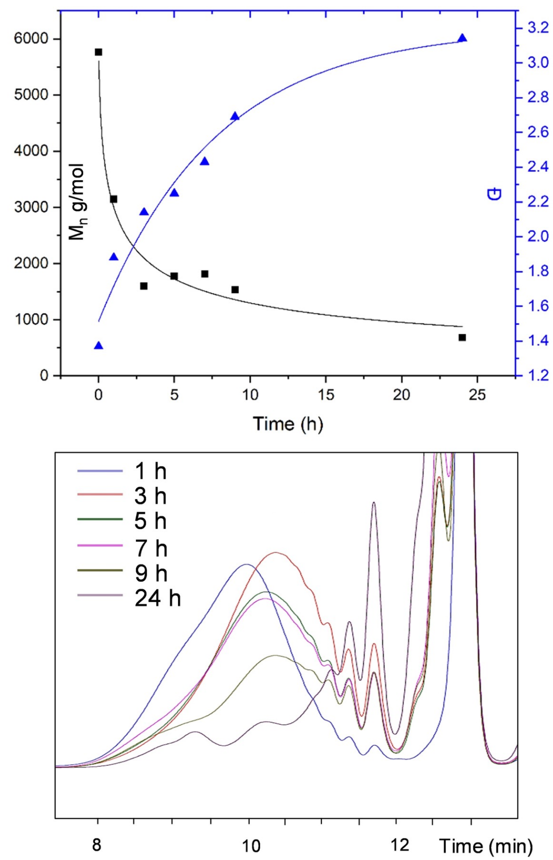
Scission in the middle of the main chain…



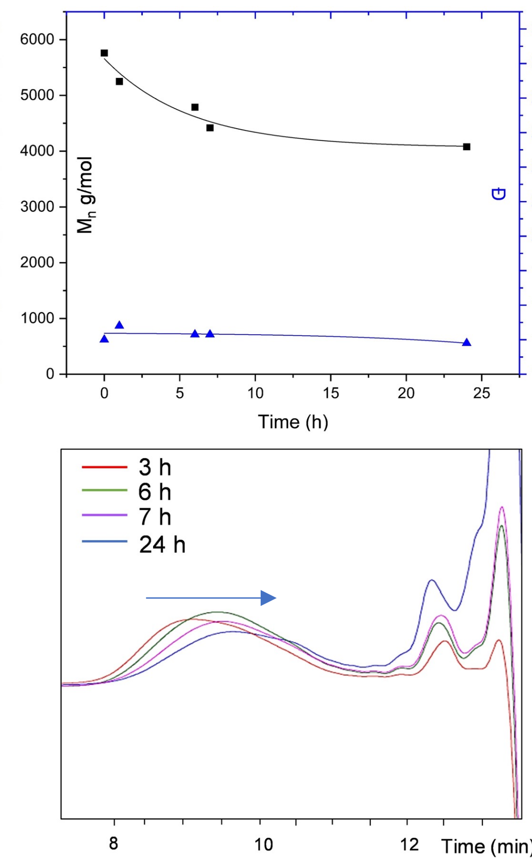
PLC

Bravo/Bo/Kleij (2023)

PLC-TBD



PLC-KOtBu (only end group depolymerization)



D. H. Lamparelli, A. Villar-Yanez, L. Dittrich, J. Rintjema, F. Bravo, C, Bo, A. W. Kleij, "Bicyclic Guanidine Promoted Mechanistically Divergent Depolymerization and Recycling of a Biobased Polycarbonate", *Angew. Chem. Int. Ed.*, **2023**, *62*, e202314659.

We have a toolbox available!

Catalysis will save the day!

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