

# Catalytic strategies for the conversion of CO<sub>2</sub> into cyclic carbonates

Paolo P. Pescarmona



# Groningen



Ben Feringa  
2016 Nobel Prize in Chemistry



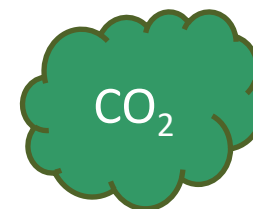
# CO<sub>2</sub> fixation by its conversion to valuable chemicals

CO<sub>2</sub> as feedstock: carbon dioxide is produced in large amounts from industrial processes and fuel combustion.

↳ inexpensive, widely-available, renewable and non-toxic (→ green) C<sub>1</sub>-feedstock .



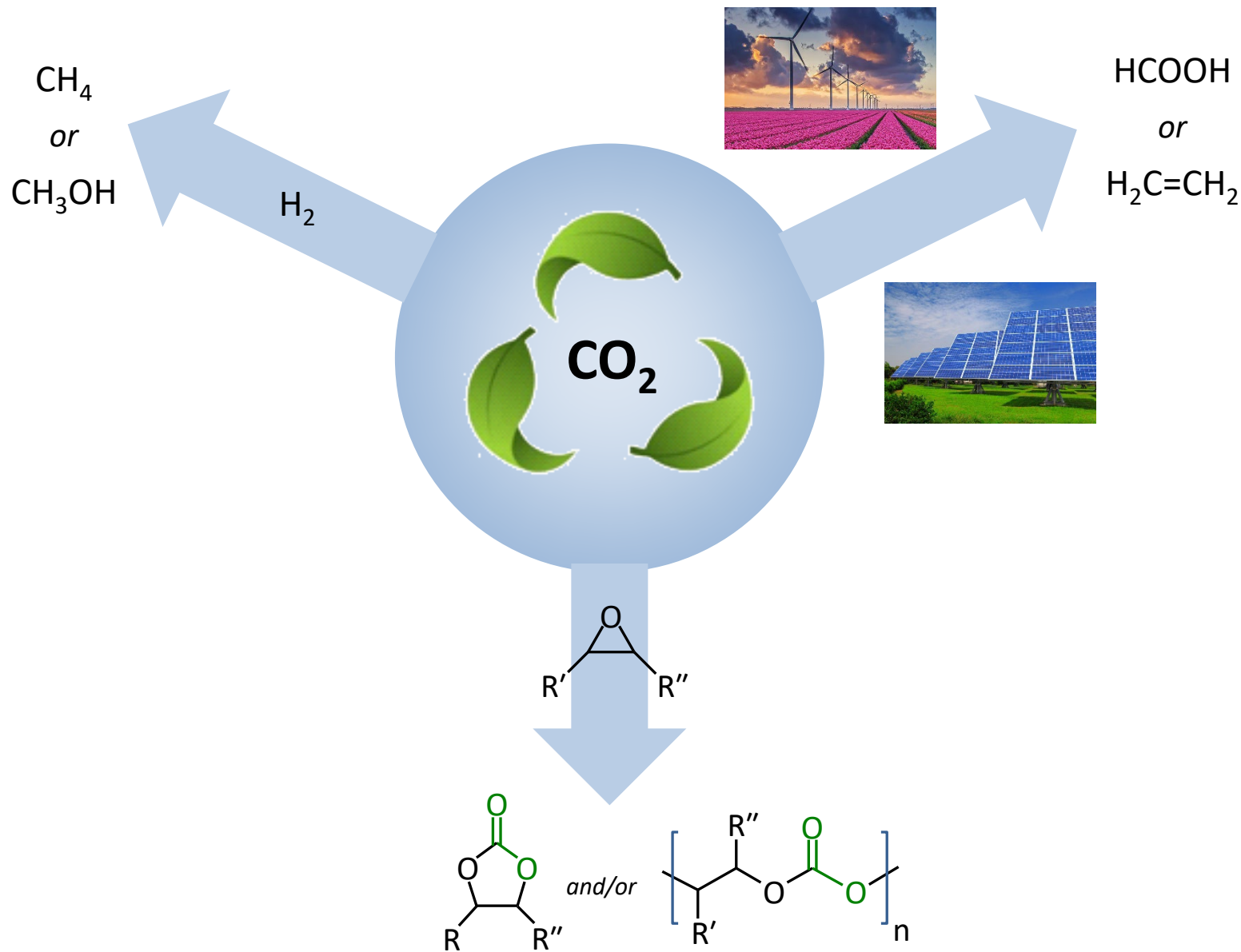
- Power plants
- Cement industry
- Steel industry
- NH<sub>3</sub> production



## Challenge:

Conversion of a thermodynamically highly stable molecule as CO<sub>2</sub>.

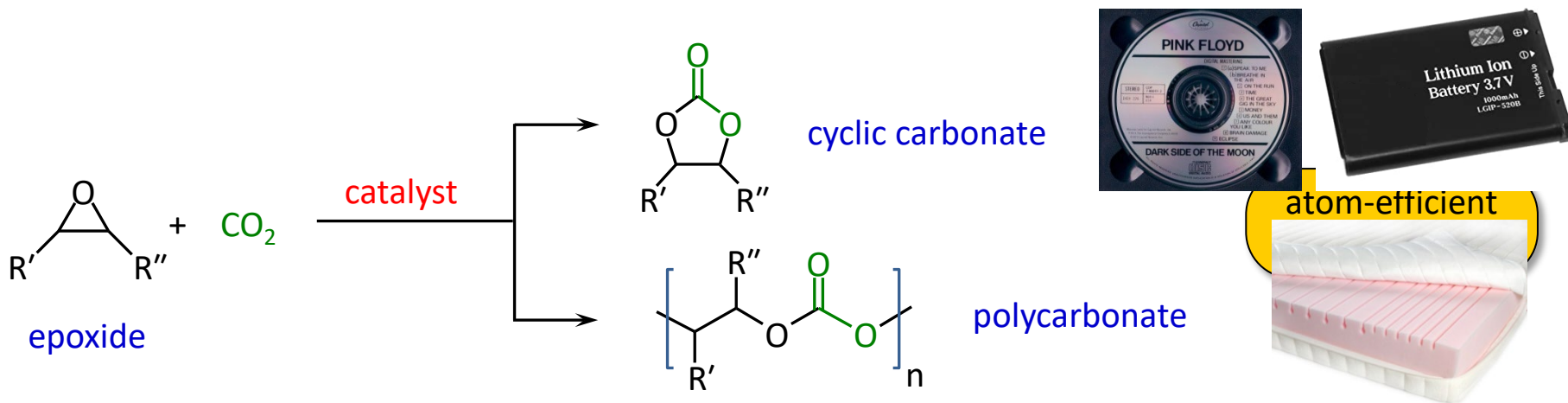
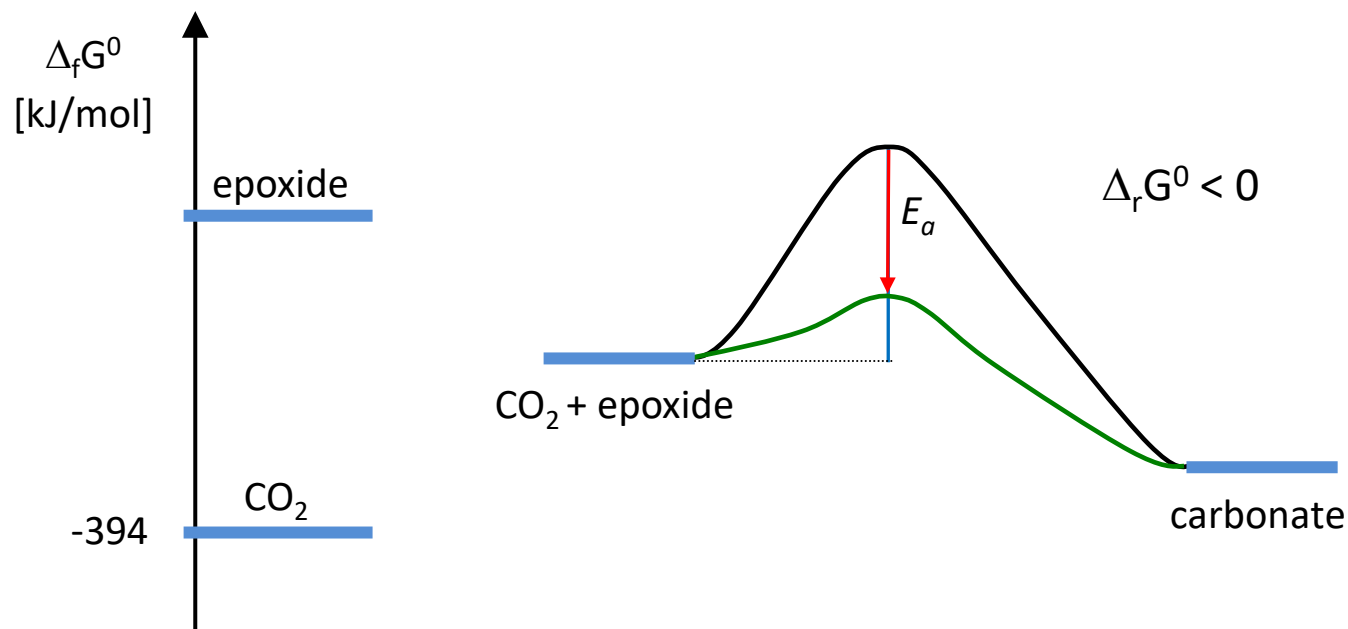
# CO<sub>2</sub> as feedstock





# Reaction of CO<sub>2</sub> with epoxides

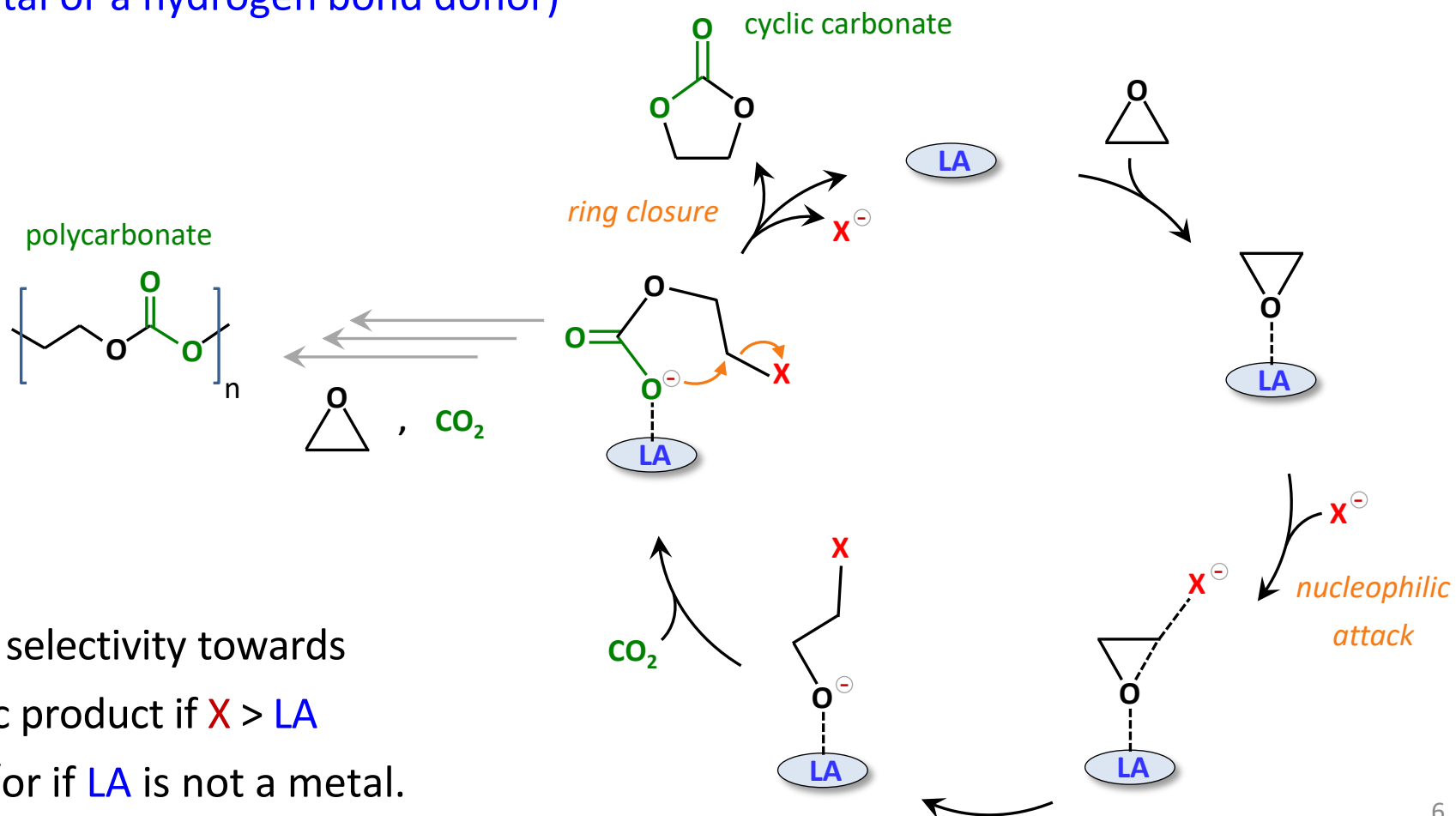
**Viable approach:** reaction of CO<sub>2</sub> with high free energy compounds (H<sub>2</sub>, epoxides, amines)



# Catalytic conversion of CO<sub>2</sub> to cyclic and polymeric carbonates

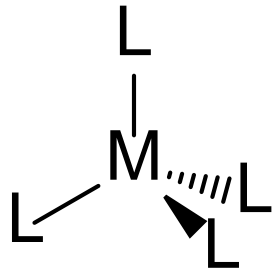
The reaction of epoxides with CO<sub>2</sub> is typically catalysed by a combination of:

- A nucleophile (X<sup>-</sup>).
- A Lewis acid (LA) site  
(a metal or a hydrogen bond donor)

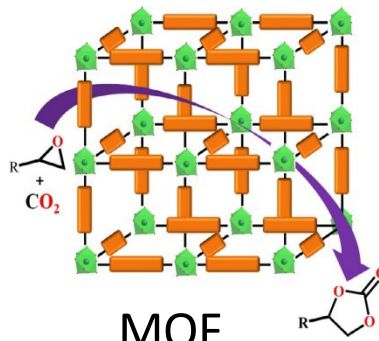


# Metal-based vs. metal-free catalysts

Most catalysts for the conversion of CO<sub>2</sub> to cyclic and polymeric carbonates are metal-based.



Metal complexes



MOF

Advantage of metal-based catalysts:  
high activity

Periodic Table of the Elements

Periodic Table of the Elements																			
1 IA		2 IIA												3 IIA	4 IVA	5 VA	6 VIA	7 VIIA	8 VIIIA
Atomic Number																			
Symbol																			
Name																			
Atomic Mass																			
1 H Hydrogen 1.008	2 He Helium 4.003	3 Li Lithium 6.941	4 Be Beryllium 9.012	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180	11 Na Sodium 22.990	12 Mg Magnesium 24.305	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948		
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.09	35 Br Bromine 79.904	36 Kr Krypton 84.80		
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29		
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [209]	86 Rn Radon [222]		
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium [278]	114 Fl Flerovium [289]	115 Uup Ununpentium [289]	116 Lv Livermorium [293]	117 Uus Ununseptium [293]	118 Uuo Ununoctium [294]		

Limitations of metal catalysts:

- Expensive
- Sensitive to moisture and air
- Possibly toxic
- Need for a co-catalyst

Can we develop metal-free catalysts for the conversion of CO<sub>2</sub>?

# Homogeneous organocatalysts

---

## First strategy

[Hopefully soon available as a publication]



# Homogeneous vs. heterogeneous catalysts

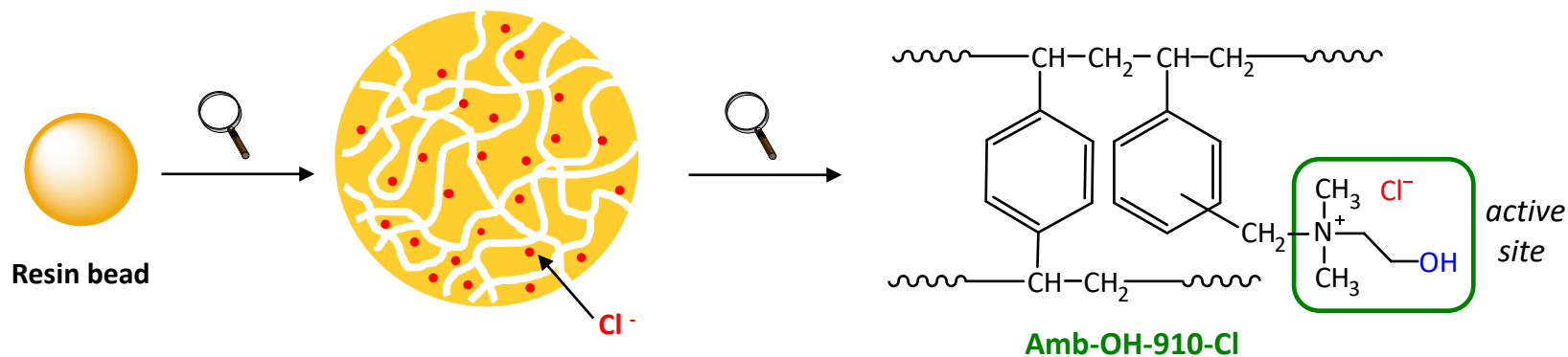
## Second strategy

Can we have a similar combination of active sites in a metal-free heterogeneous catalyst?

- A nucleophile ( $X^-$ ).
- A hydrogen bond donor as (mild) Lewis acid (LA) site

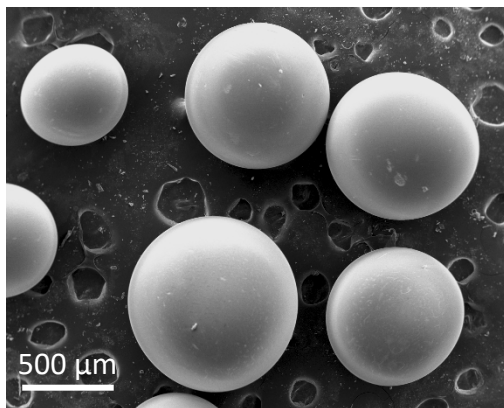


Inexpensive, commercial anion-exchange resin beads

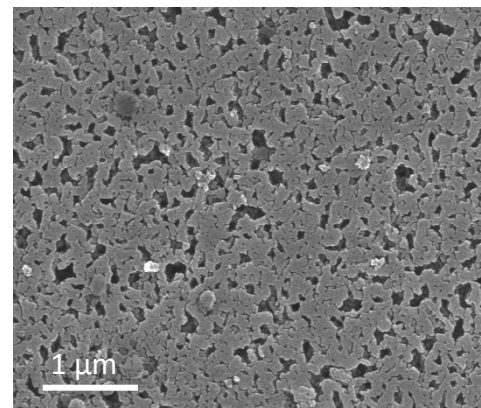


# Resin beads as catalysts for the conversion of CO<sub>2</sub> to cyclic carbonates

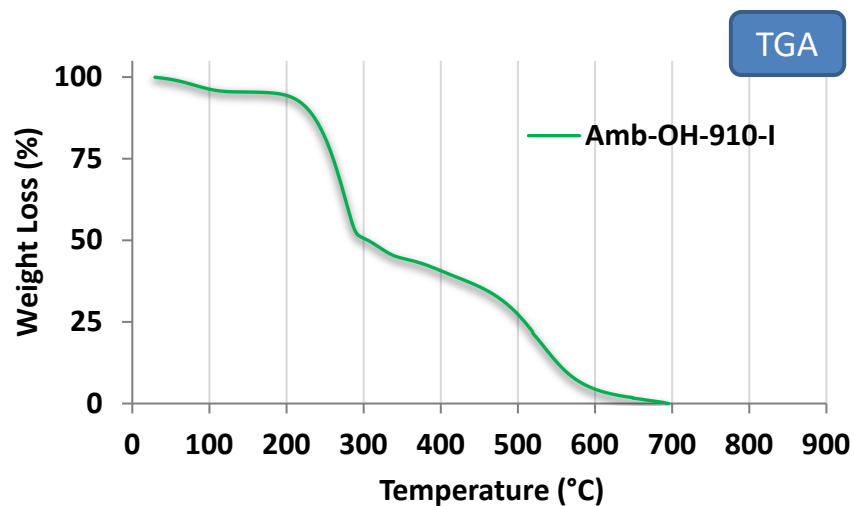
Macroscopic porous Amberlite resin beads



Bead format ⇒ easy separation



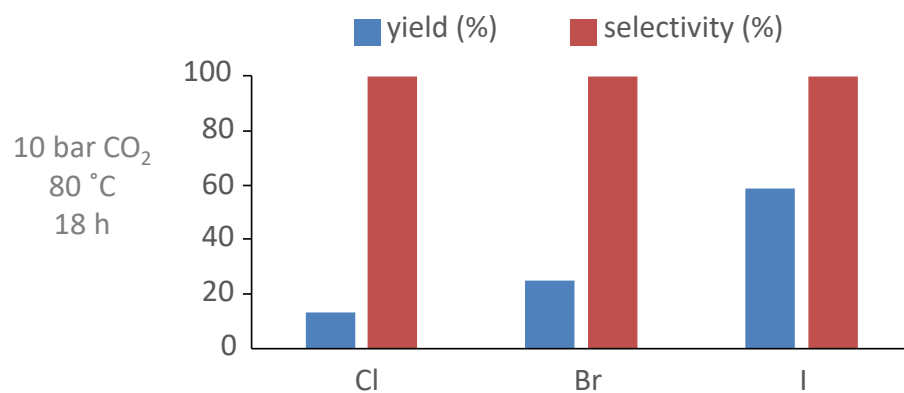
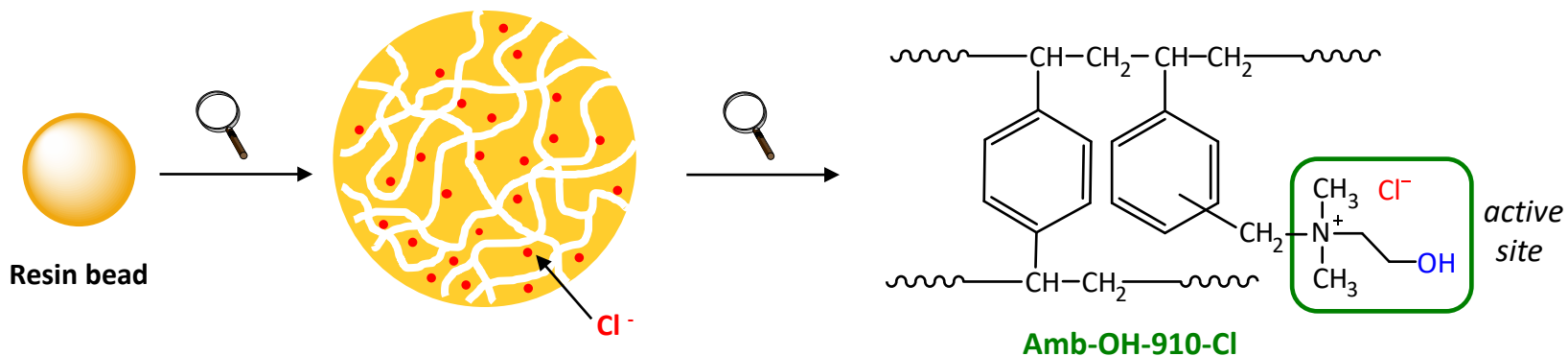
Porous structure ⇒ accessibility to the active sites



Thermal stability well above the reaction T

# Resin beads as catalysts for the conversion of CO<sub>2</sub> to cyclic carbonates

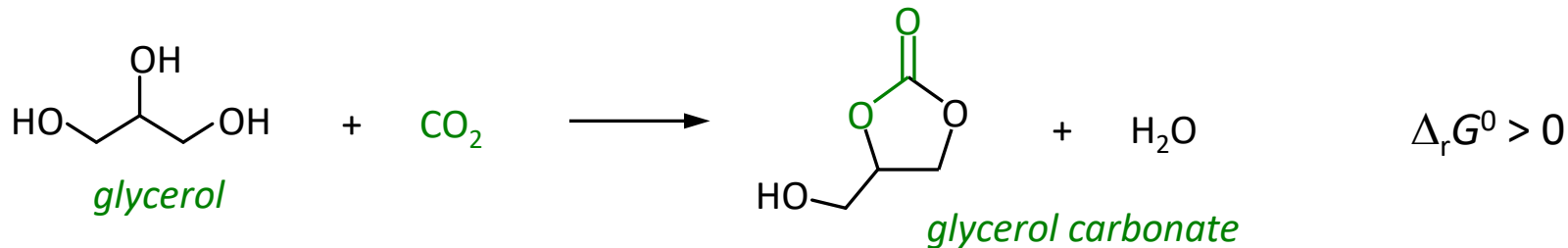
The catalytic activity can be tuned by ion-exchange of the halide ion acting as nucleophilic catalytic species.



*halide (Cl, Br, I)  
can be tuned*

Amb-OH-910 in iodide form gives highest activity in the synthesis of cyclic carbonates.

# Glycerol carbonate

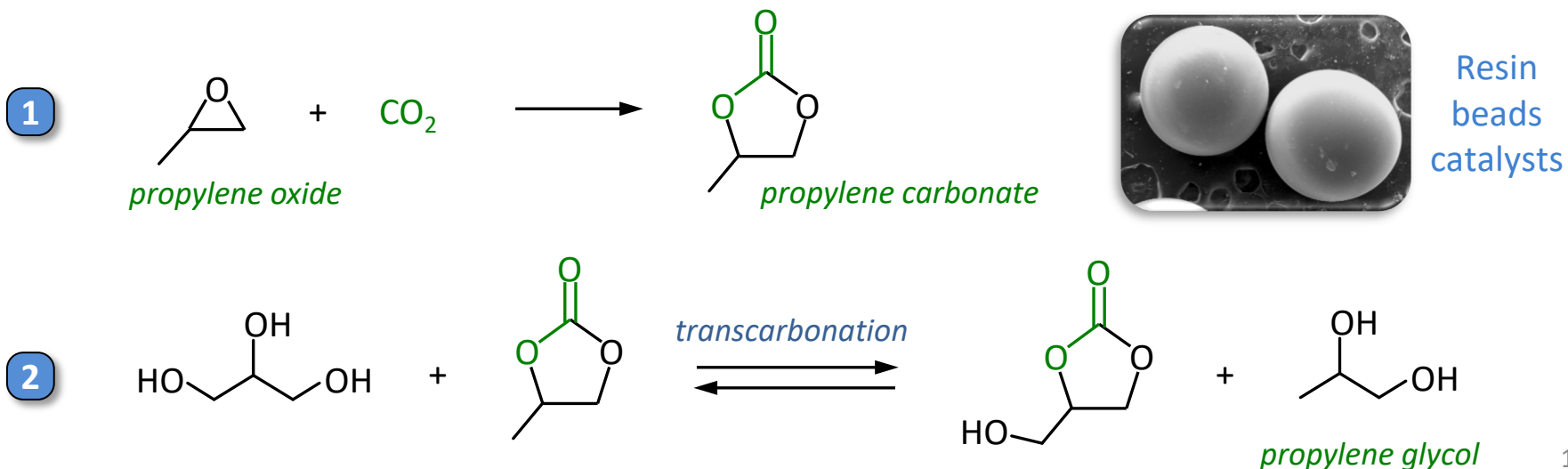


Direct carbonation is thermodynamically unfavourable.

- lubricants
- adhesives
- surfactants
- green solvent
- monomer

## Third strategy

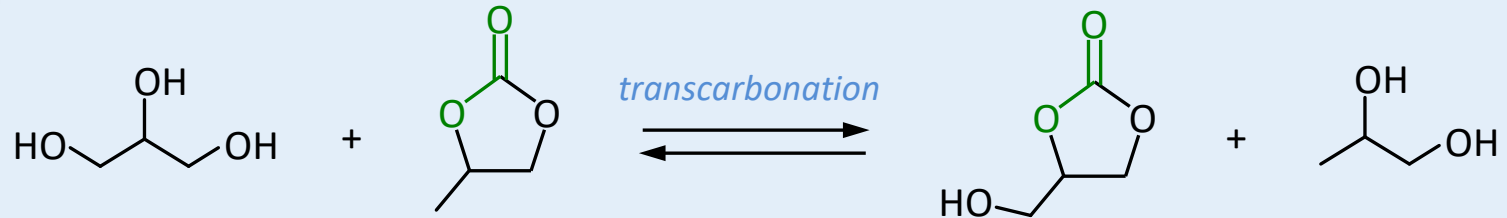
A thermodynamically viable alternative:



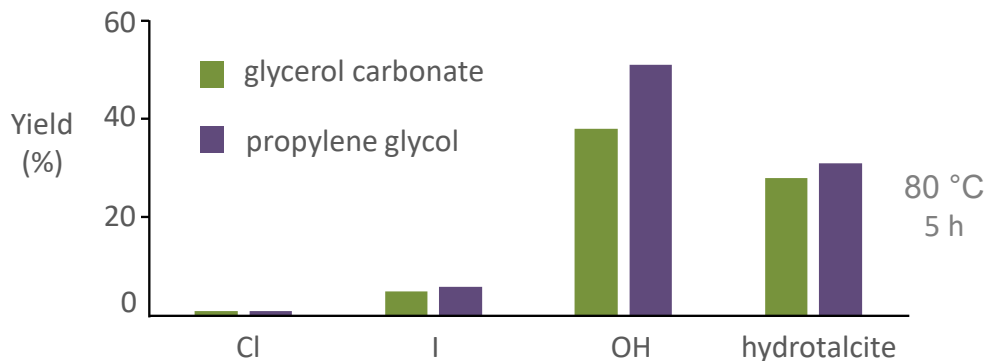
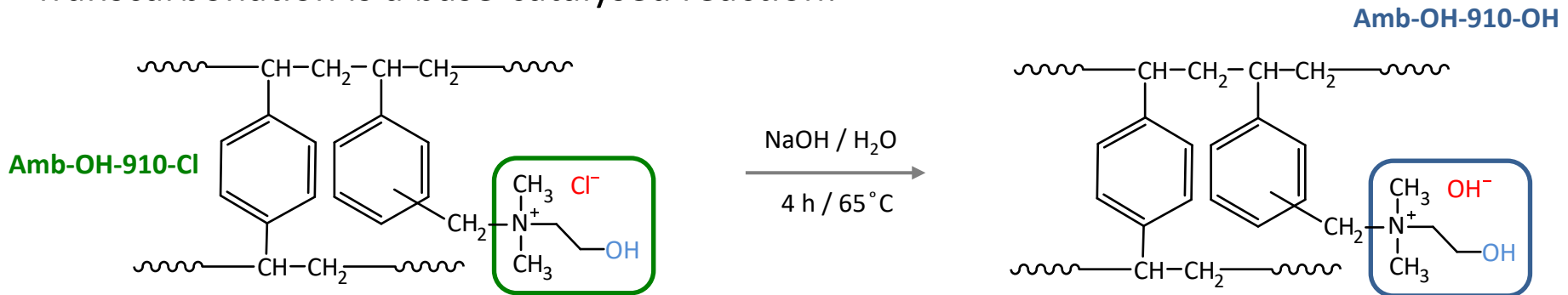
# Transcarbonation

Can we use an Amberlite resin bead to catalyse the transcarbonation reaction?

2



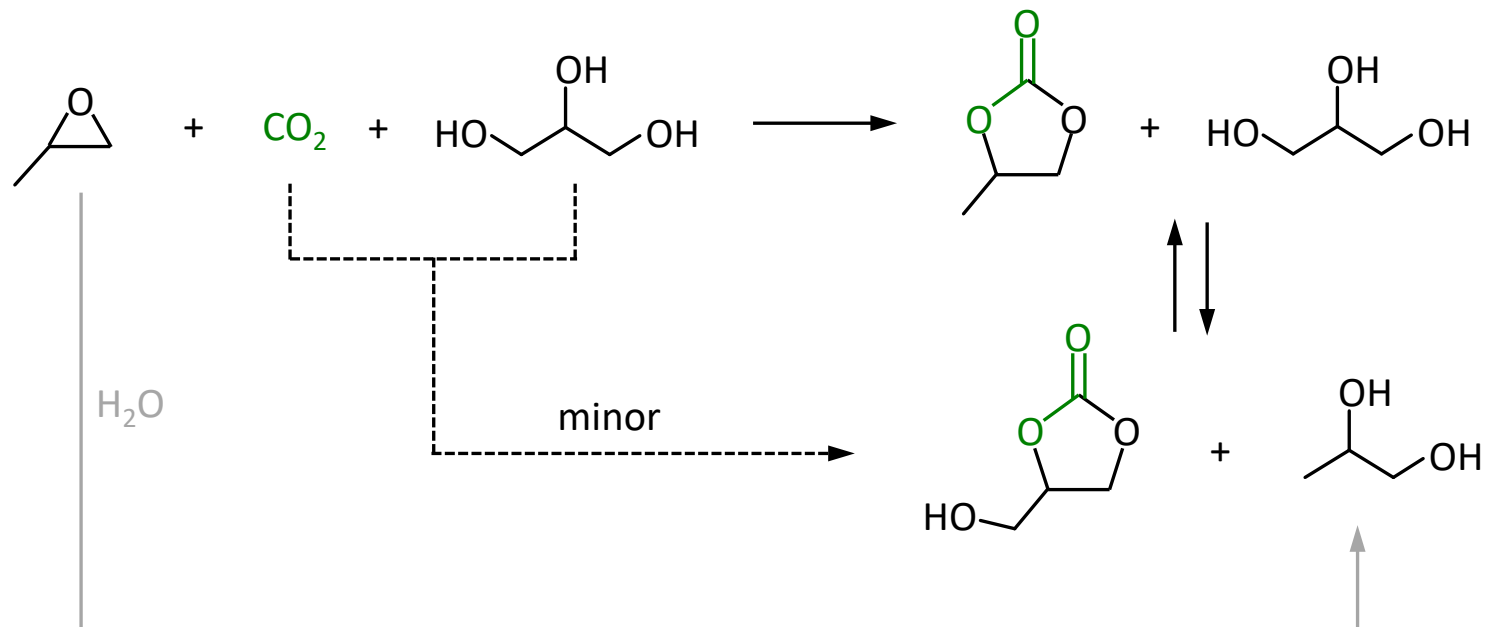
Transcarbonation is a base-catalysed reaction:



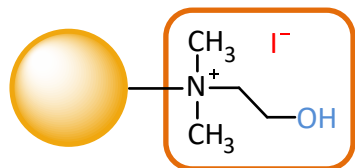
Highest activity with  
Amb-OH-910 in  
hydroxide form

# One-pot reaction

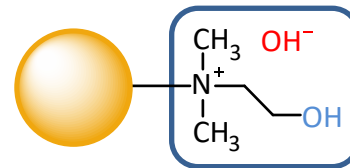
Can we perform the whole process in one pot?



Our initial strategy: combine the optimum catalyst for the **cycloaddition** of  $\text{CO}_2$  to the epoxide with the best catalyst for the **transcarbonation**.



Amb-OH-910-I



Amb-OH-910-OH



# One-pot reaction

Reality is less conventional than our expectations...

- Highest glycerol carbonate yield with Amb-OH-910-I alone
- Amb-OH-910-OH catalyses the hydrolysis of propylene oxide

Catalytic system I : OH ratio (%)	Yield (%)		
	Propylene carbonate	Propylene glycol	Glycerol carbonate
100:0	36	48	17
75:25	24	51	15
50:50	17	51	13
25:75	11	50	10
0:100	3	43	4

Reaction conditions: PO (20 mmol), aqueous glycerol (20 mmol), catalysts (95 mg), 115 °C, 20 bar CO<sub>2</sub>, 2h.

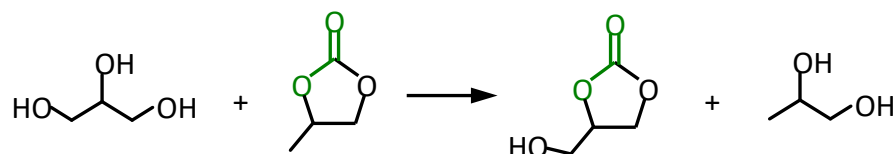
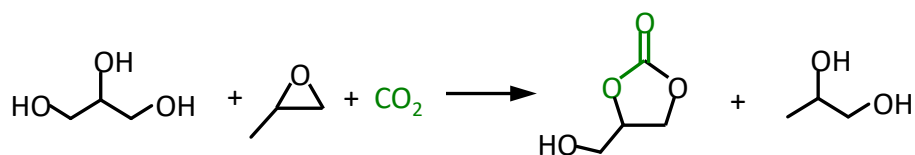
Glycerol carbonate yield can be increased using higher propylene oxide : glycerol ratio

Catalyst	PO:glycerol (mmol:mmol)	Yield (%)		
		Propylene carbonate	Propylene glycol	Glycerol carbonate
Amb-OH-910-I	20:0	76	0	0
Amb-OH-910-I	20:5	67	23	69
Amb-OH-910-I	20:10	51	33	50
Amb-OH-910-I	20:20	36	48	17
Amb-OH-910-I	20:40	32	53	8

Reaction conditions: glycerol: 115 °C, 20 bar CO<sub>2</sub>, 2h.

# One-pot reaction

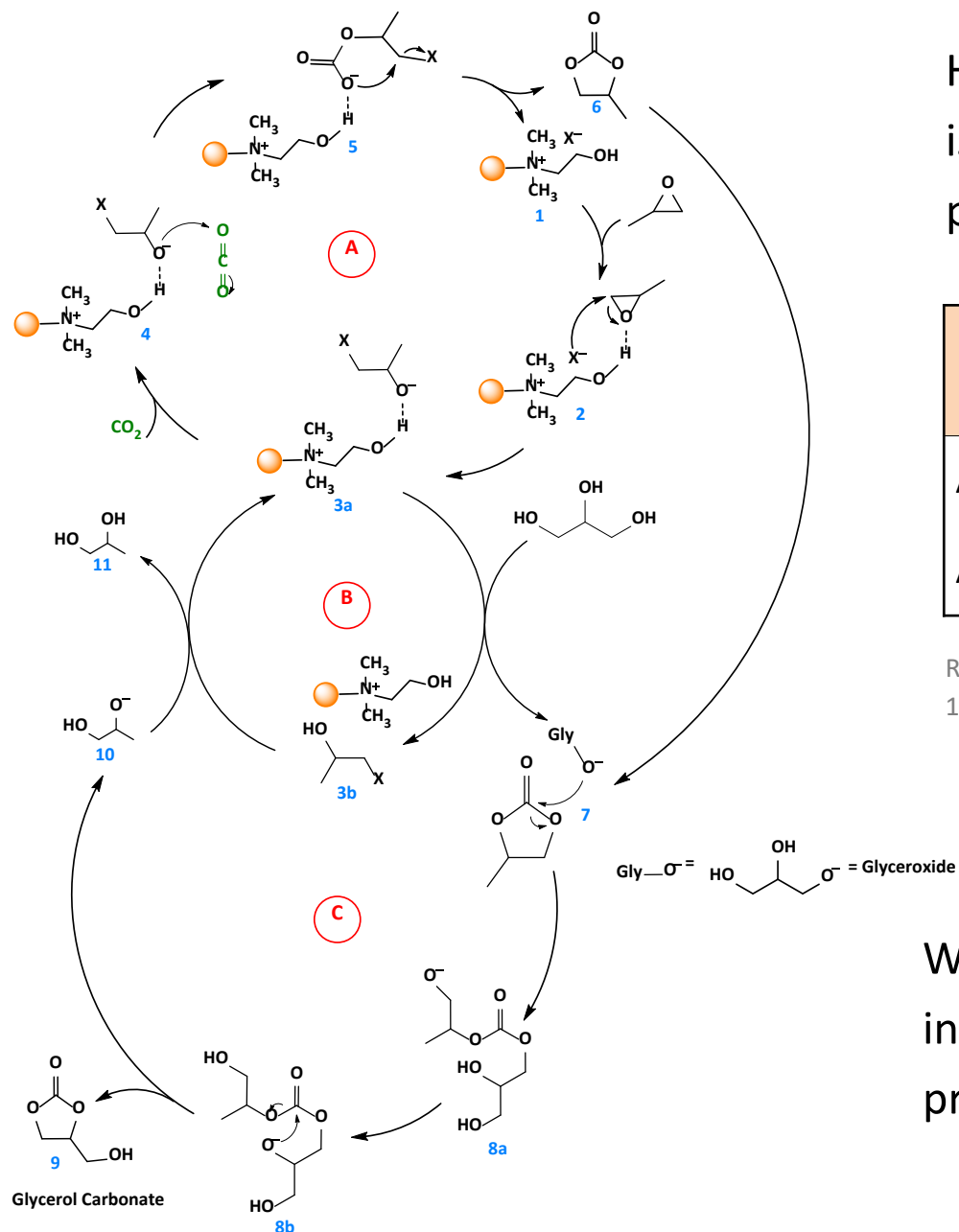
How can we explain that Amb-OH-910-I is more active in the whole one-pot process than in the second step alone?



Catalyst	Reactant	Yield (%)	
		Propylene glycol	Glycerol carbonate
Amb-OH-910-I	Propylene oxide	23	69
Amb-OH-910-I	Propylene carbonate	7	28

Reaction conditions: glycerol : propylene oxide (or carbonate) = 1: 4, 115 °C, 20 bar CO<sub>2</sub>, 2h.

# One-pot reaction mechanism



How can we explain that Amb-OH-910-I is more active in the whole one-pot process than in the second step alone?

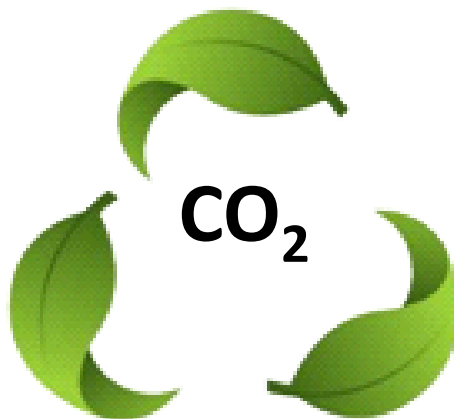
Catalyst	Reactant	Yield (%)	
		Propylene glycol	Glycerol carbonate
Amb-OH-910-I	Propylene oxide	23	69
Amb-OH-910-I	Propylene carbonate	7	28

Reaction conditions: glycerol : propylene oxide (or carbonate) = 1: 4, 115 °C, 20 bar CO<sub>2</sub>, 2h.

We propose a mechanism in which an intermediate of the cycloaddition can promote the transcarbonation reaction.

## Conclusions

- The fixation of CO<sub>2</sub> into cyclic carbonates is an attractive route to convert a waste gas into useful chemical products (global market: ~100 kton/year).
- Our group has developed active, selective, cost-effective, upscalable catalysts for producing cyclic carbonates.



# Acknowledgements



Jing Chen  
Dr. Yasser Alassmy

My whole group and  
colleagues in Groningen

**Thank you for your attention!**