UNIVERSITY of York

Green Chemistry
Centre of Excellence

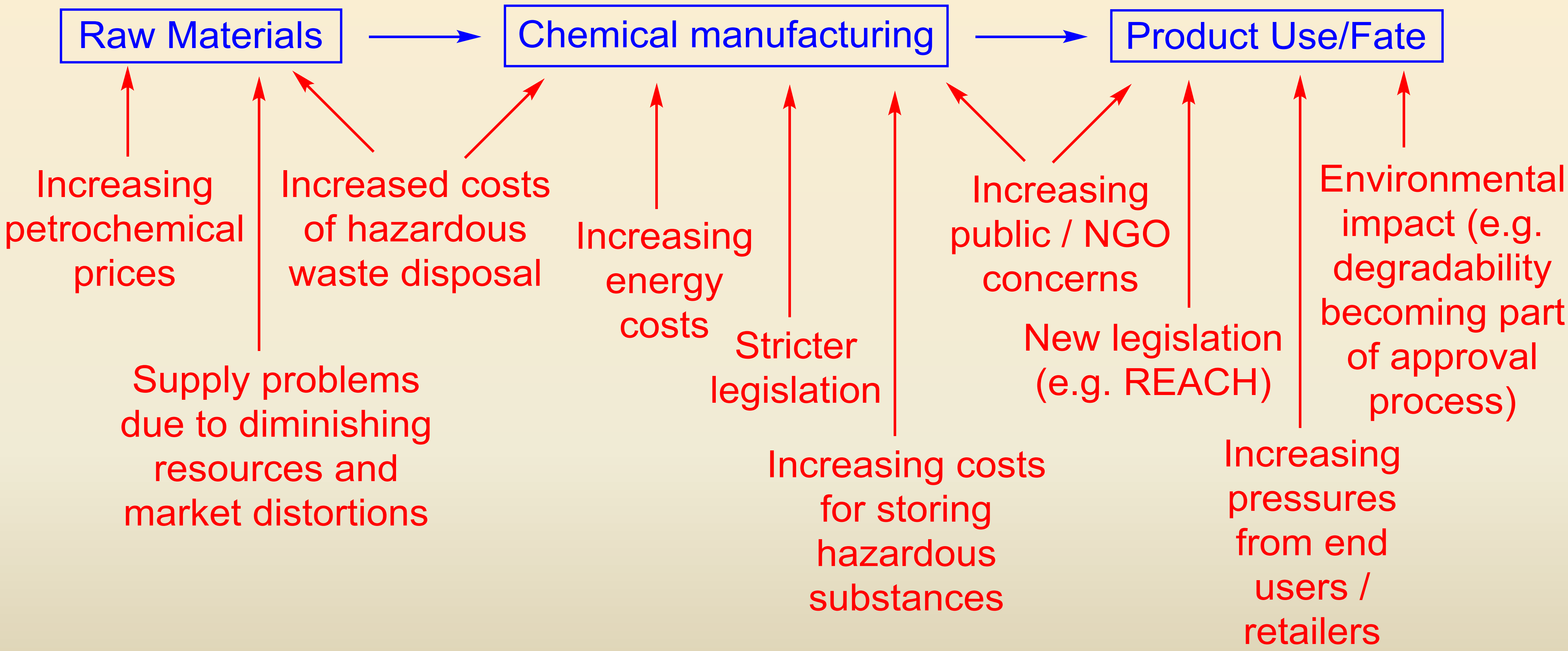
CO_2 related chemistry

Professor Michael North

August 2014

CO2 Chem
An EPSRC Grand Challenge Network
Fine Chemicals
Process Engineering
Catalysis
Carbon Capture
Biosynthesis
Bulk Chemicals
Social Impact

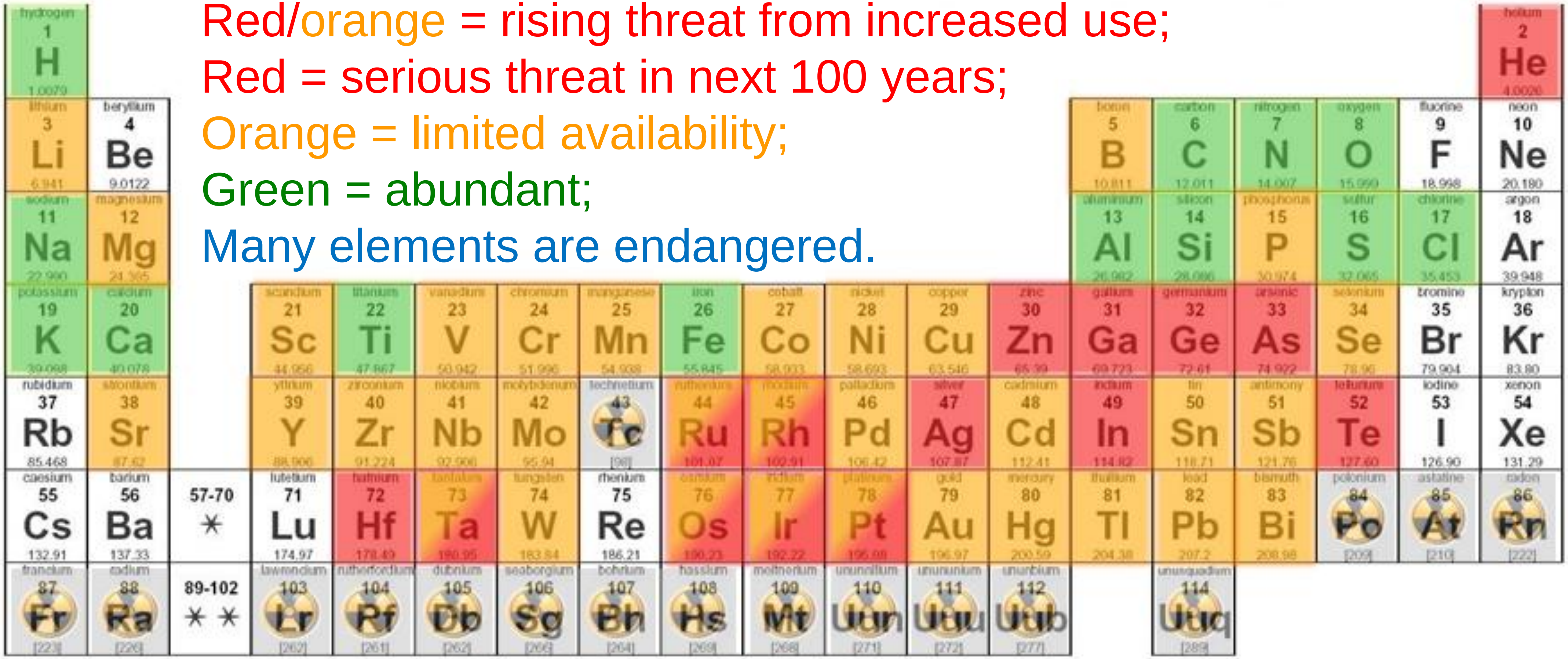
Pressures on chemicals across the lifecycle



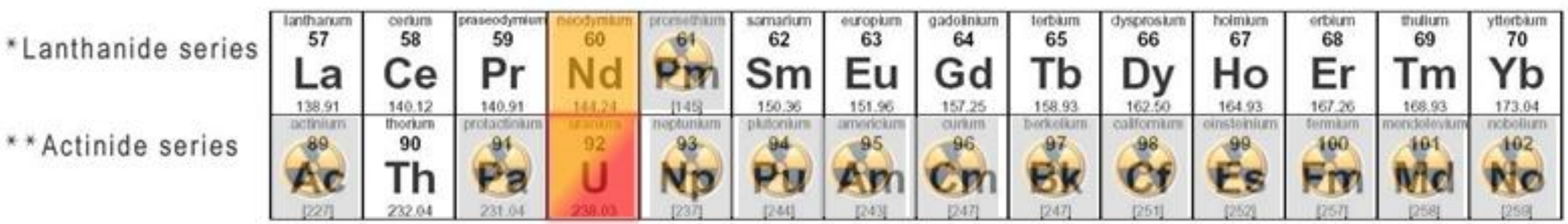
We need alternative, sustainable starting materials for the chemicals industry and CO_2 is one such sustainable resource.

Sustainable catalysts

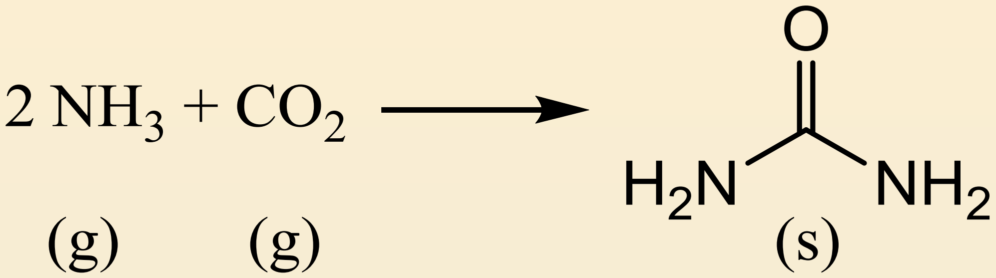
Red/orange = rising threat from increased use;
Red = serious threat in next 100 years;
Orange = limited availability;
Green = abundant;
Many elements are endangered.



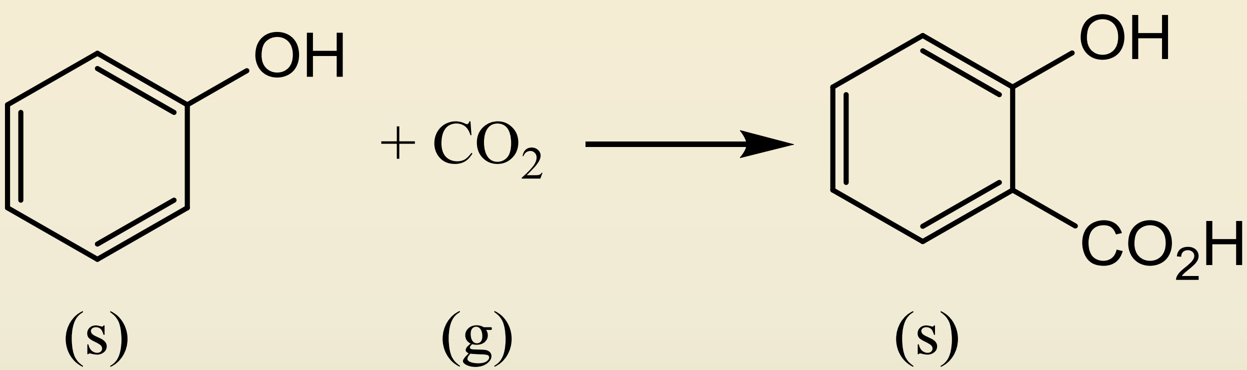
http://www.chemistryinnovation.co.uk/



Use of CO_2 as a starting material



$\Delta H = -101\ \mathrm{kJ\ mol^{-1}}$
commercial process
since 1922

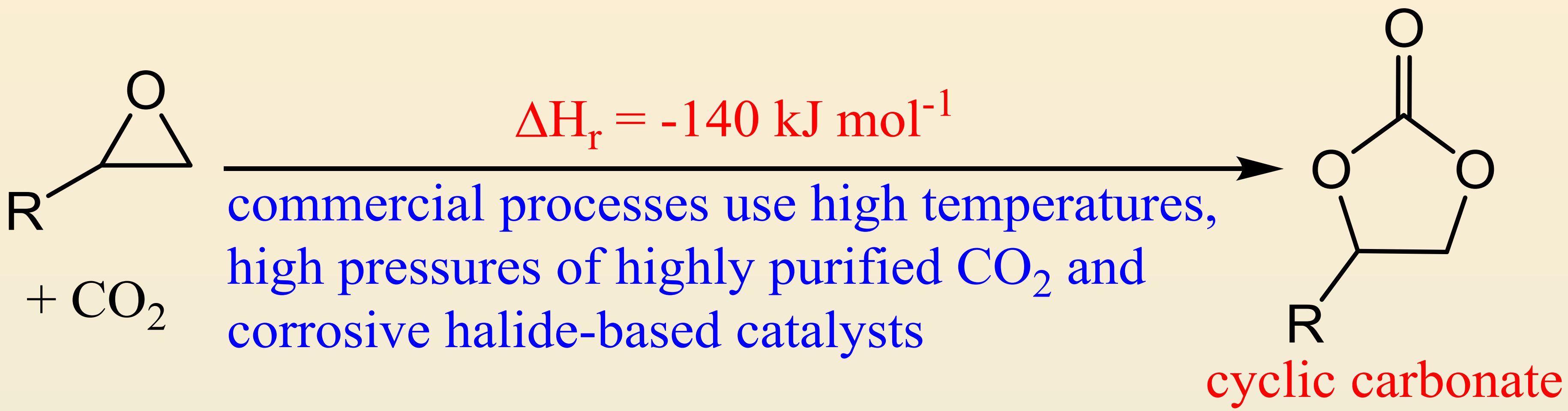


$\Delta H = -31\ \mathrm{kJ\ mol^{-1}}$
commercial process
since 1890

$$\underset{(g)}{H_2C{=}CH_2} + \underset{(g)}{CO_2} \longrightarrow \underset{(l)}{H_2C{=}CHCO_2H} \qquad \Delta H = -43\ \mathrm{kJ\ mol^{-1}}$$

Review *Chem. Today* **2004**, *98*, 455–462.

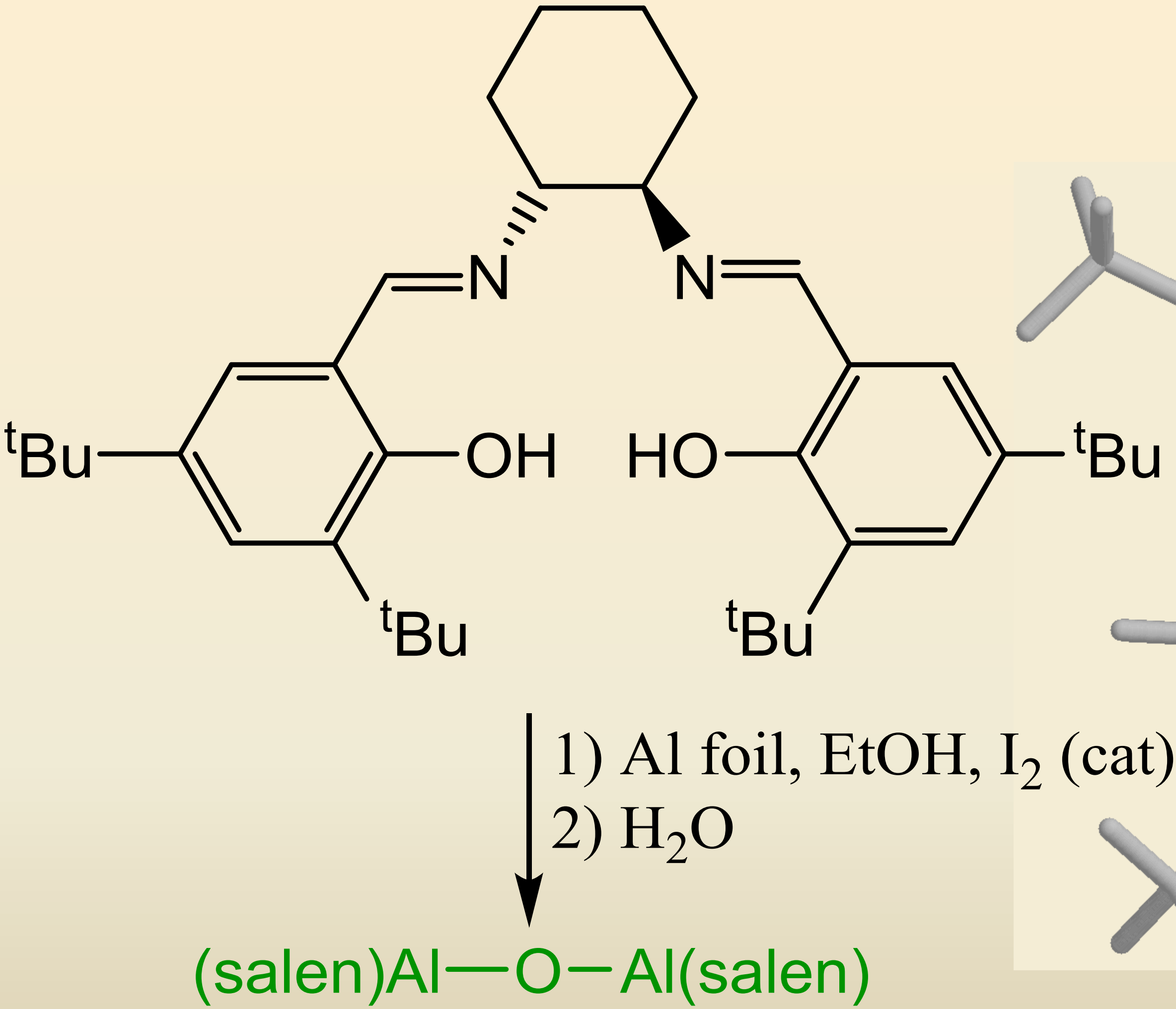
Synthesis of cyclic carbonates



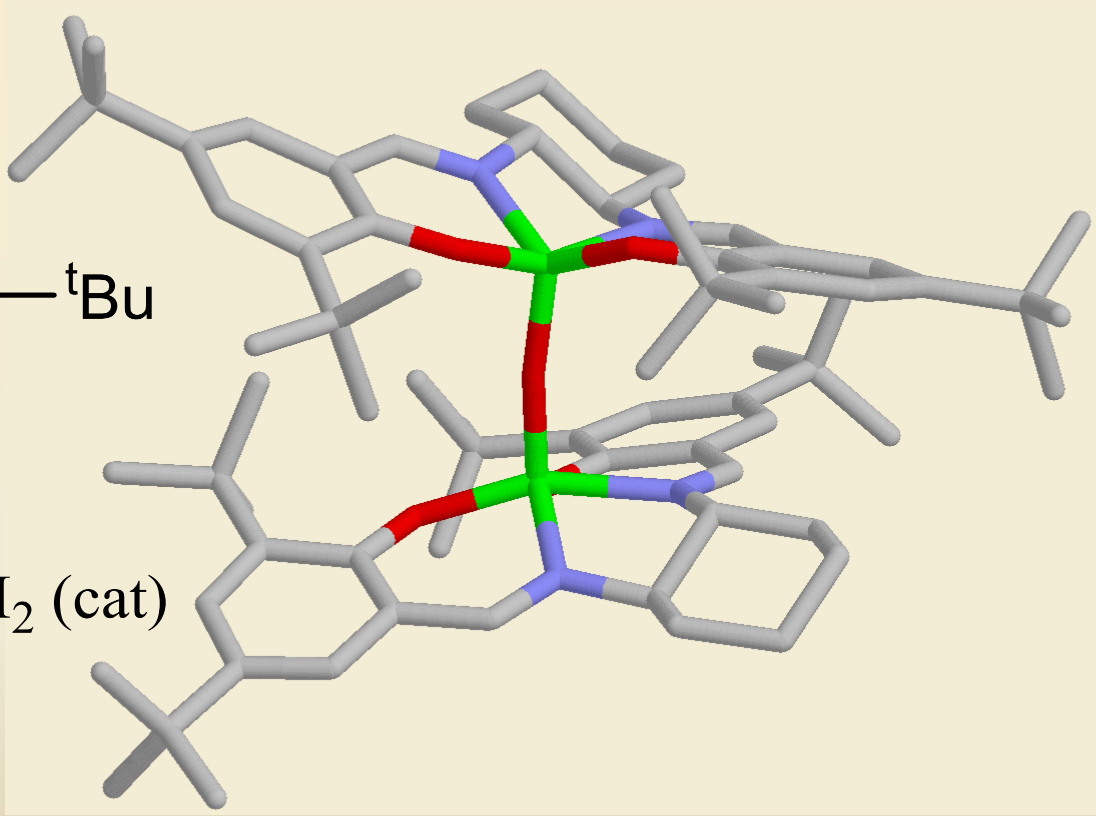
Applications: Electrolyte for lithium ion battery
Polar aprotic solvent
Chemical intermediate (e.g. for dimethyl carbonate)
Polymer synthesis

Reviews: *Ind. Eng. Chem. Res.* **2003**, *42*, 663–674; *Green Chem.* **2010**, *12*, 1514–1539.

A bimetallic aluminium(salen) catalyst

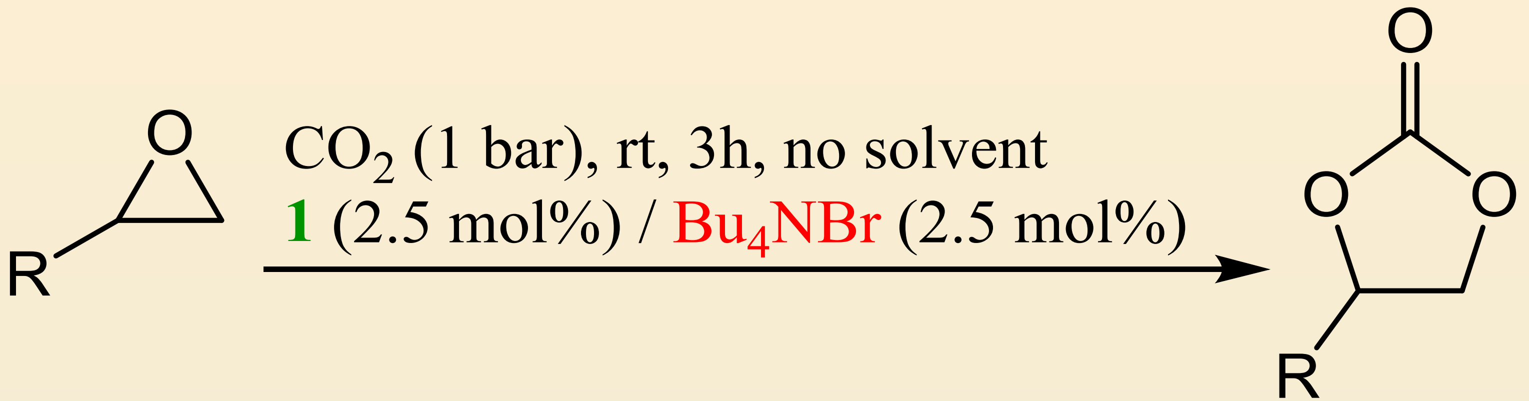


1 bimetallic catalyst



M. North *et al.*, *Eur. J. Inorg. Chem.* **2007**, 3323–3326;
Chem. Eur. J. **2010**, *16*, 6828–6843; Patent WO/2008/132474.

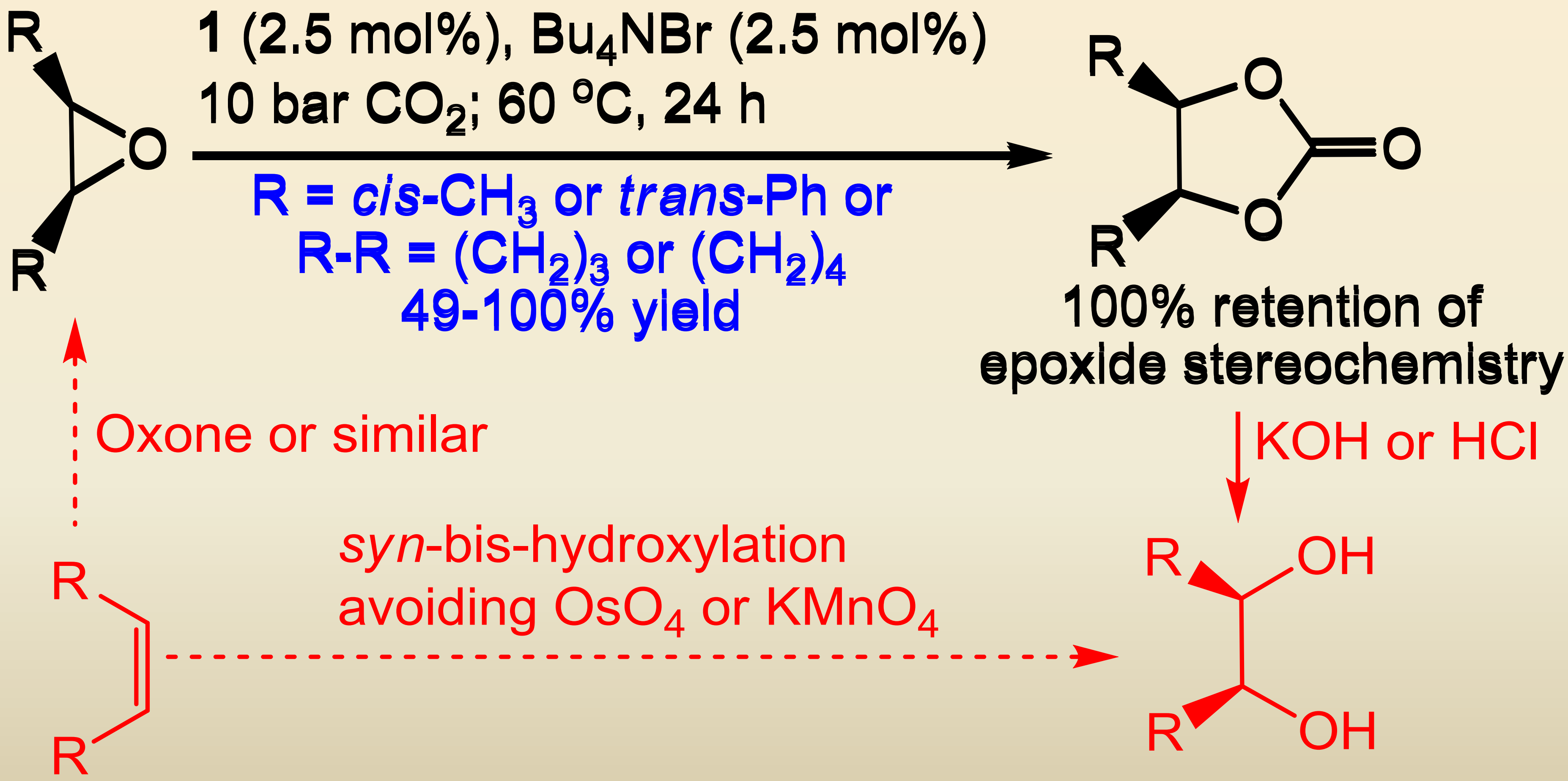
Batch results with terminal epoxides



R	Yield	R	Yield	R	Yield
Ph	62%	Me	77%	CH_2OCOMe	34%
$PhCH_2$	44%	H	76%	CH_2OCOPh	58%
Bu	87%	CH_2OH	36%	4-MeC_6H_4	77%
C_8H_{17}	64%	CH_2Cl	60%	3-$MeOC_6H_4$	48%
CH_2O^tBu	50%	CH_2OPh	55%	4-ClC_6H_4	42%

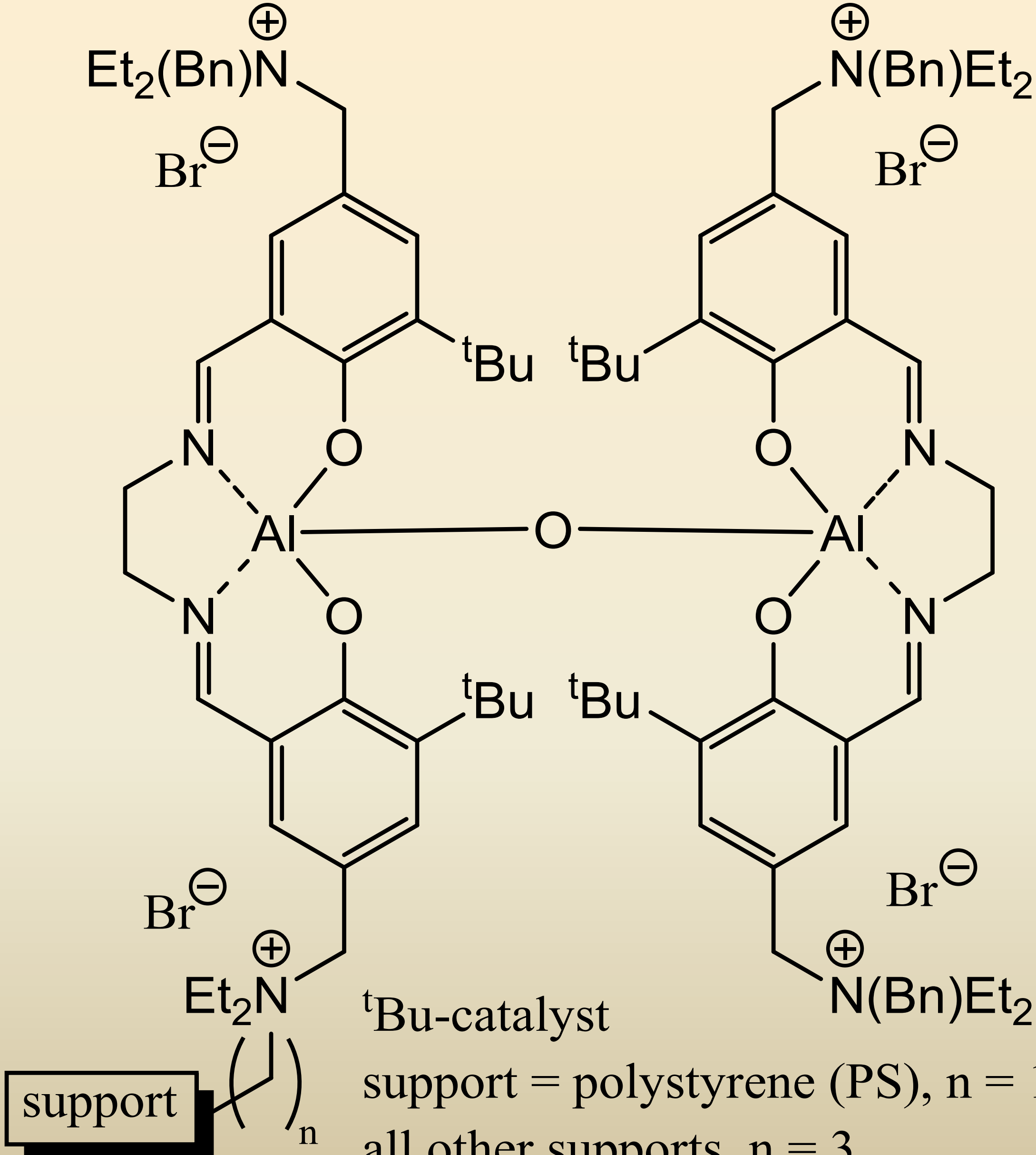
M. North *et al.*, *Eur. J. Inorg. Chem.* **2007**, 3323–3326; *Chem. Eur. J.* **2010**, *16*, 6828–6843.

Disubstituted epoxides and stereochemistry



M. North *et al.*, *J. Org. Chem.* **2013**, *78*, 419–426.

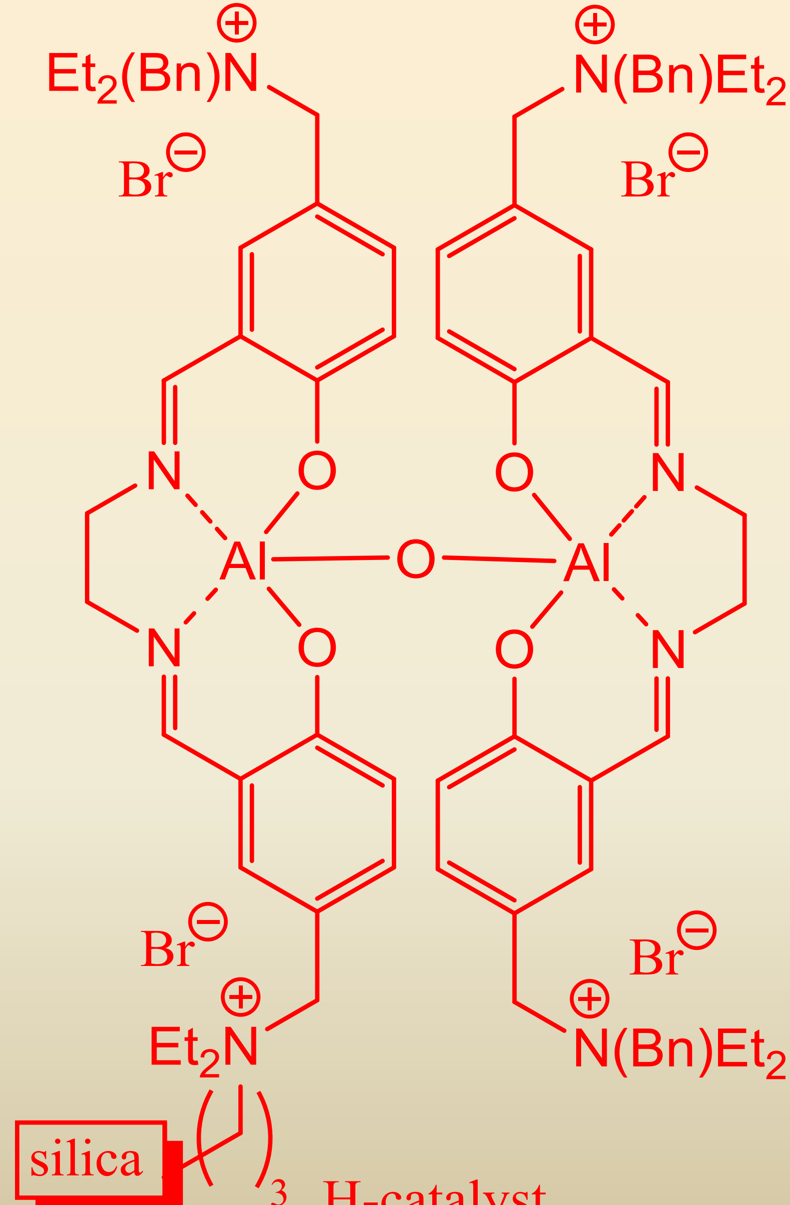
Supported catalyst structures



^{t}Bu-catalyst

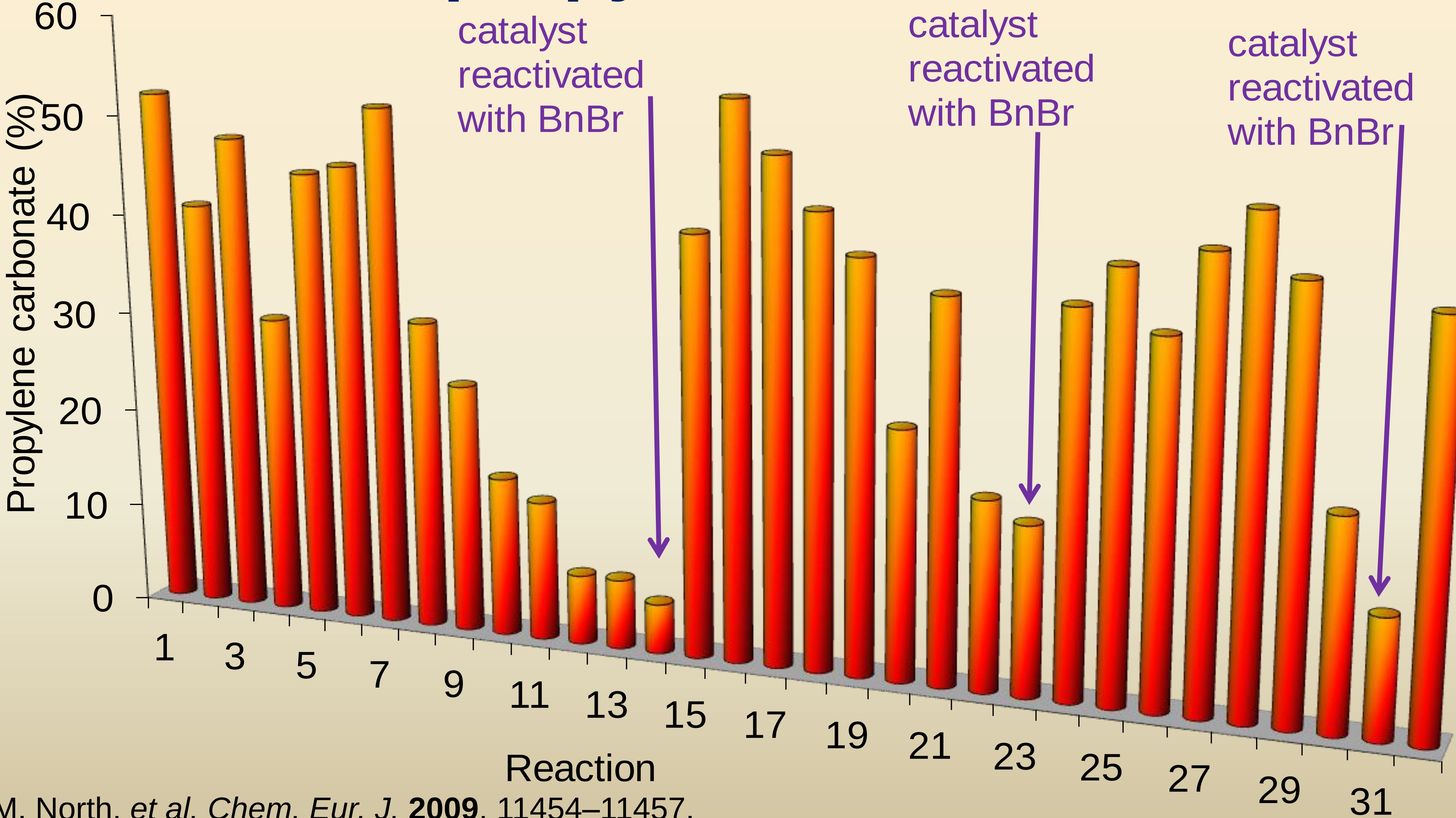
support = polystyrene (PS), n = 1

all other supports, n = 3



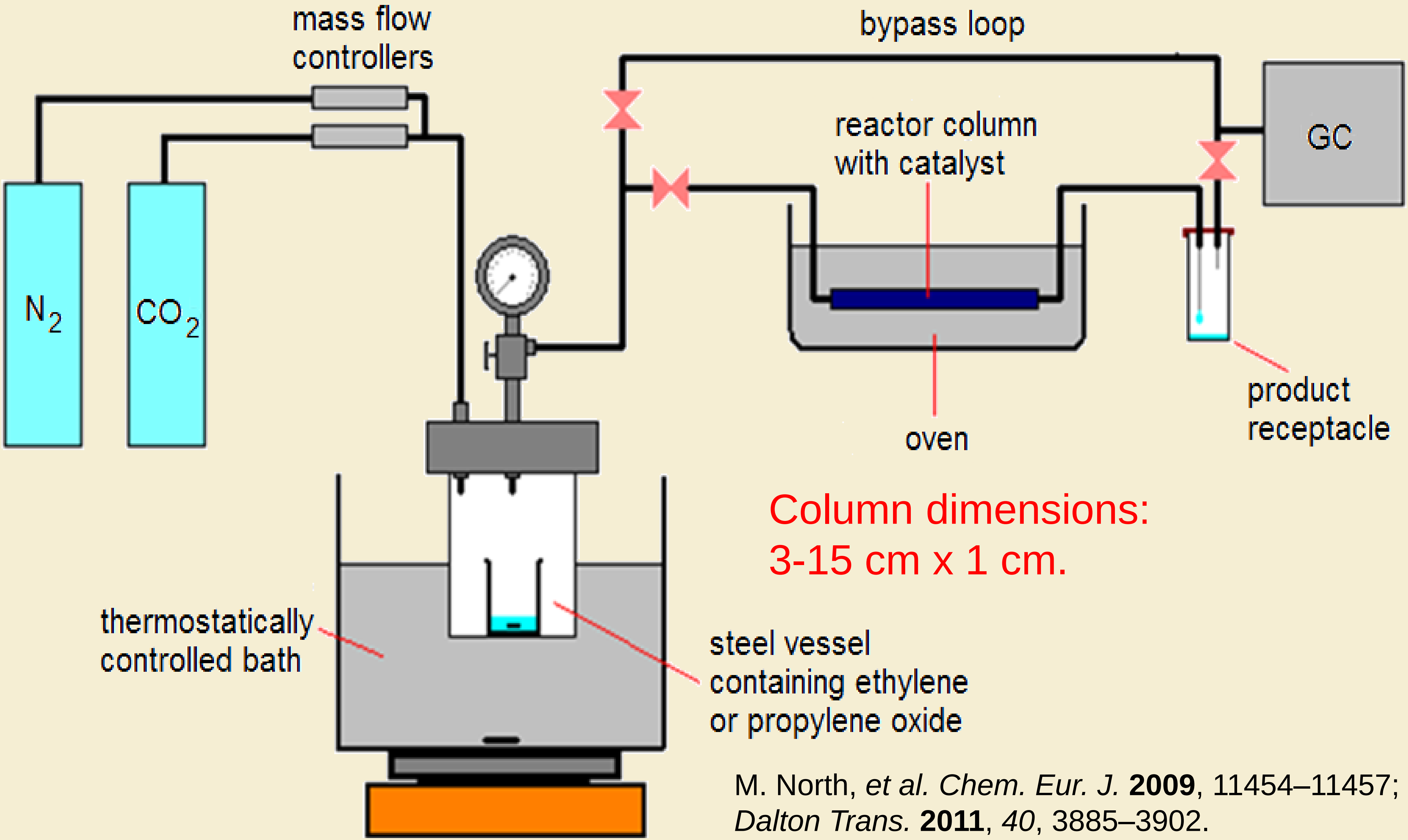
H-catalyst

Reuse of silica-supported catalyst with propylene oxide



M. North, *et al. Chem. Eur. J.* **2009**, 11454–11457.

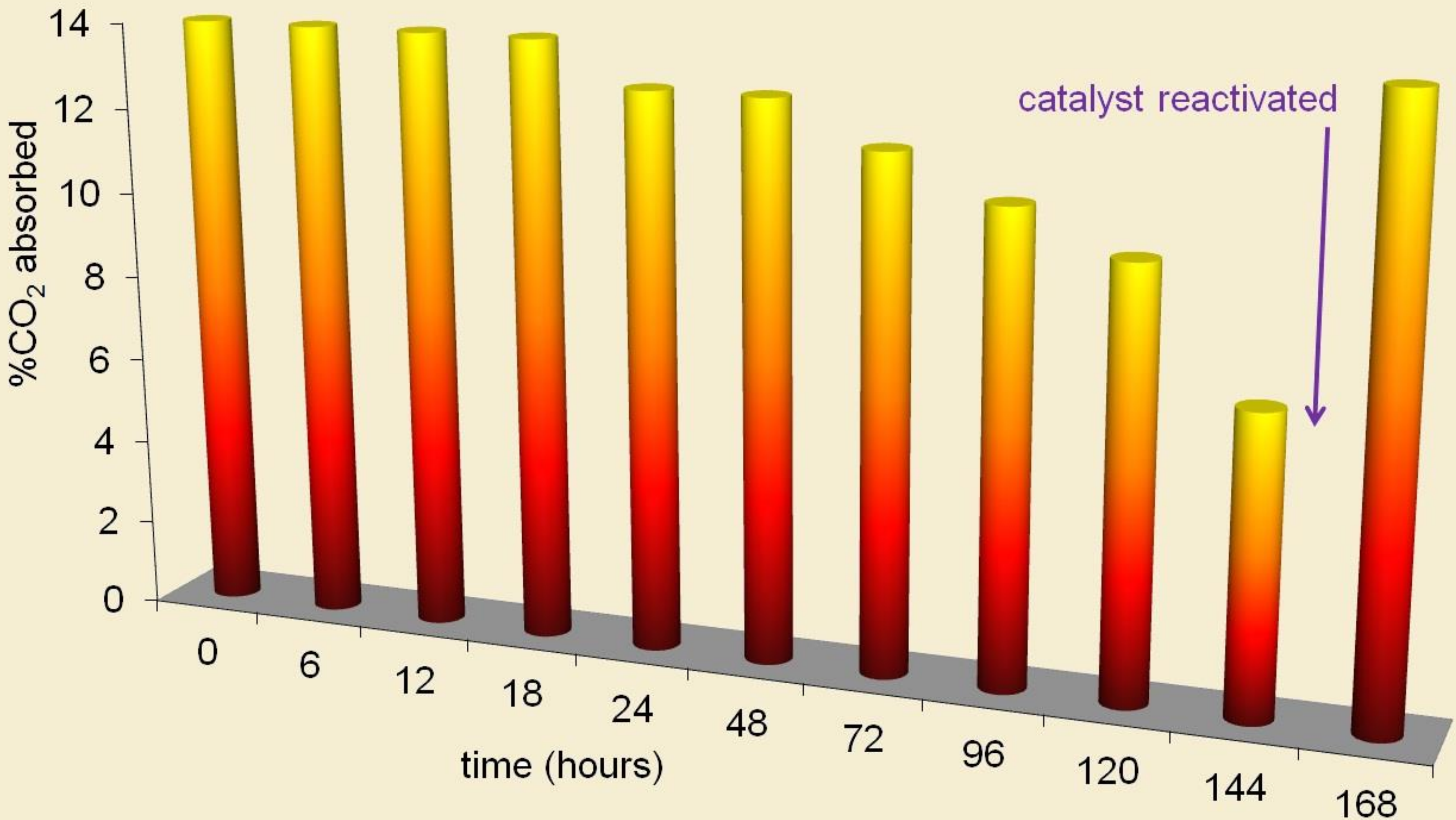
Gas phase flow reactor



Column dimensions:
3-15 cm x 1 cm.

M. North, *et al. Chem. Eur. J.* **2009**, 11454–11457; *Dalton Trans.* **2011**, *40*, 3885–3902.

Continuous flow results at 100 ºC



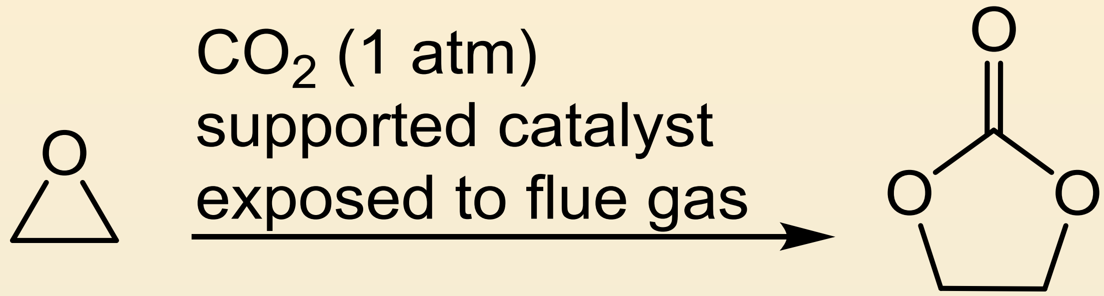
M. North, *et al. Chem. Eur. J.* **2009**, 11454–11457; *Dalton Trans.* **2011**, *40*, 3885–3902.

Sources of waste CO_2

Source	Global CO_2 emissions (10^6 t CO_2 / year)	CO_2 purity (volume %)
Coal	14,200	12-15
Natural gas	6,320	3-5
Refineries	850	3-13
Cement production	2000	14-33
Ethylene production	260	12
Iron and steel production	1000	15
Natural gas production	50	5-70
Ammonia production	150	100

J. Wilcox *Carbon Capture* Springer, **2012**.

Testing with real flue gas

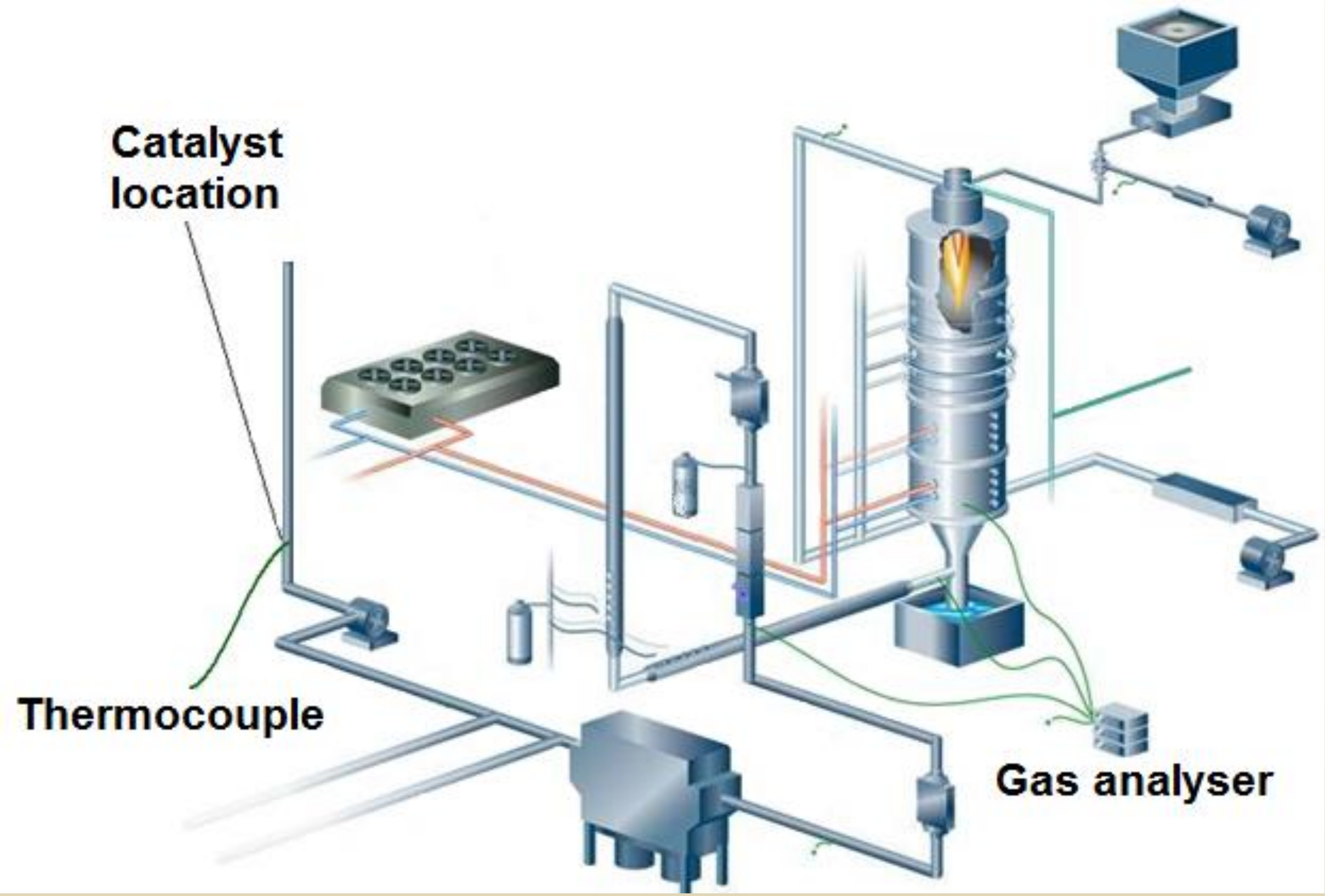


Five catalyst samples (all from same batch) used:

1. Never exposed to flue gas (control)
2. Exposed to flue gas from gas burn for 4 hours
3. Exposed to flue gas from coal burn for 4 hours
4. Exposed to flue gas from coal burn for 8 hours
5. Exposed to flue gas from coal burn for 16 hours

Catalysts then used in flow reactor

Doosan Power systems test facility



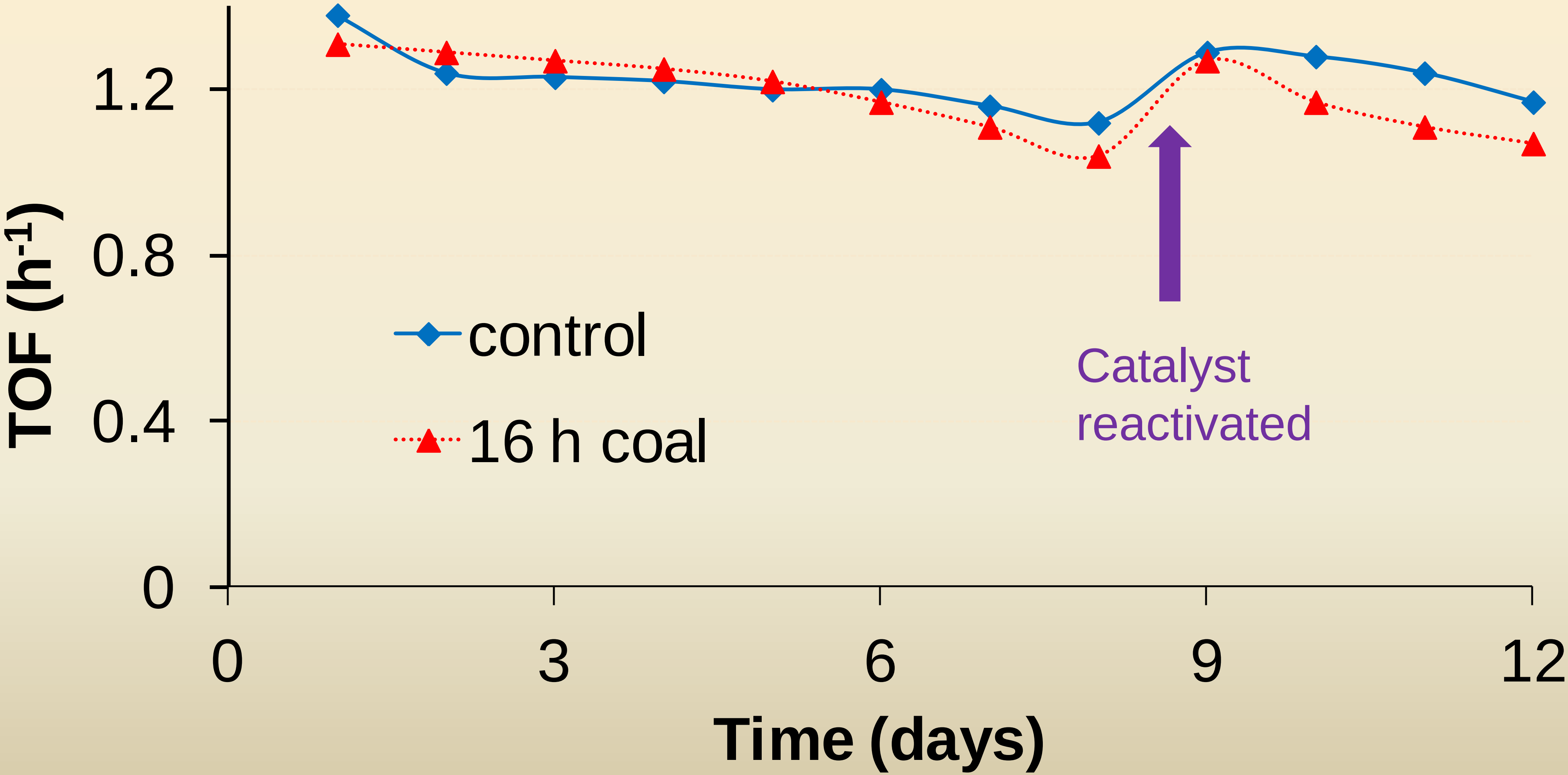
Flue gas composition
Flow rate 20 mL/min

T	52 ^{o}C
CO_2	15%
O_2	3%
SO_2	291ppm
CO	40ppm
NO_x	443ppm

Used El Cerrejon coal (typical hard coal):
74%C; 0.5%S; 1.5%N; 5%H; 7% H_2O

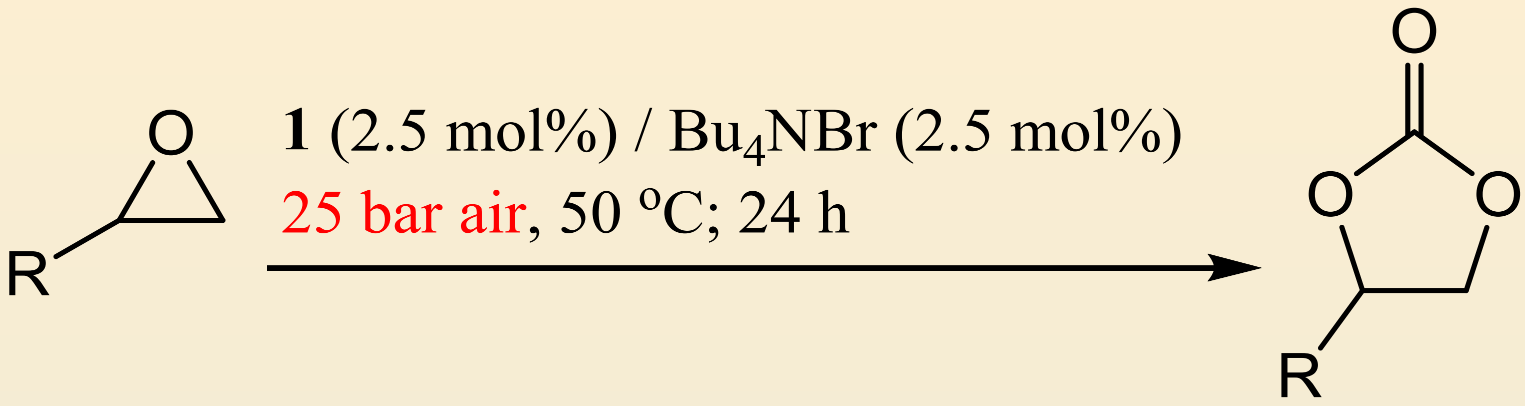
M. North *et al. Energy Environ. Sci.*, **2011**, *4*, 4163–4170.

Real flue gas flow reactor results with ethylene oxide



M. North, *et al. Energy Environ. Sci.*, **2011**, *4*, 4163–4170.

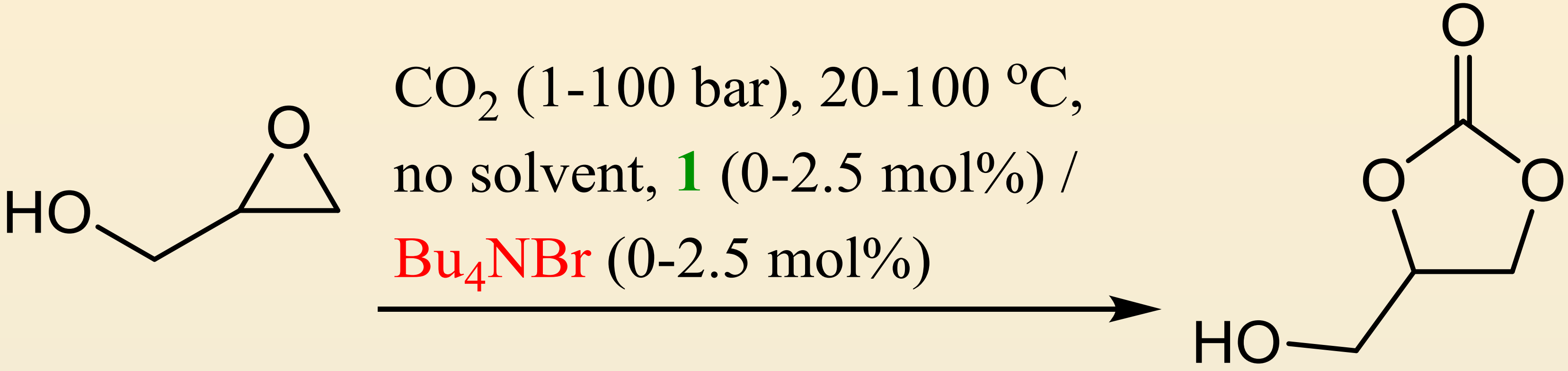
Use of compressed air

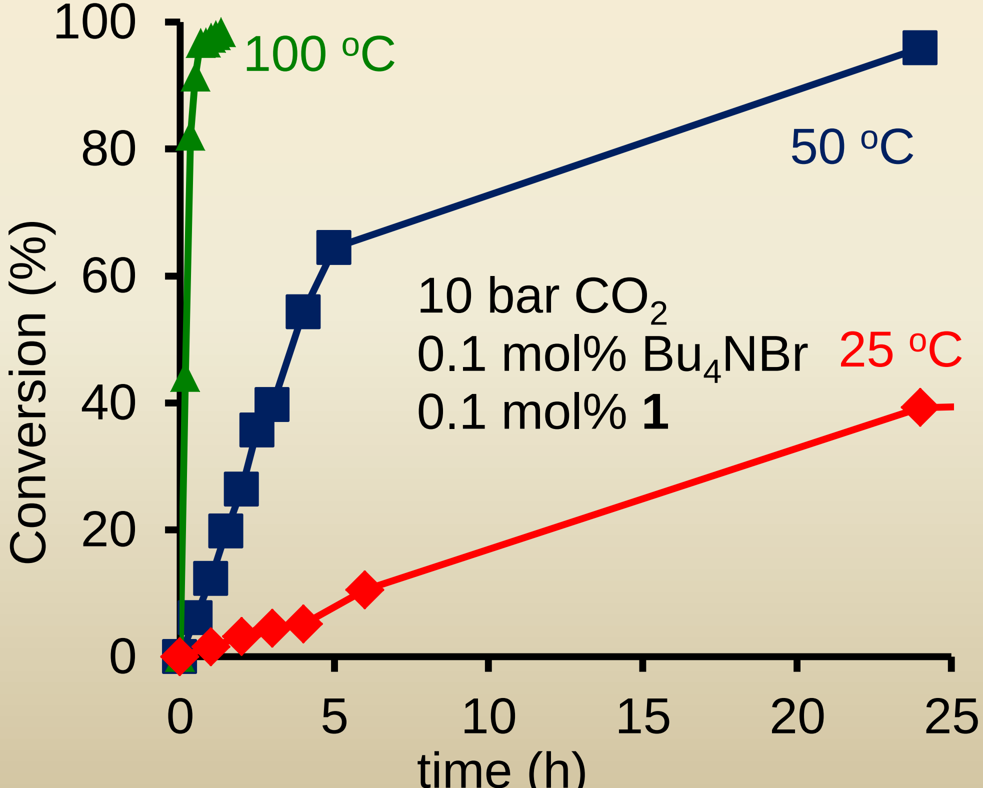


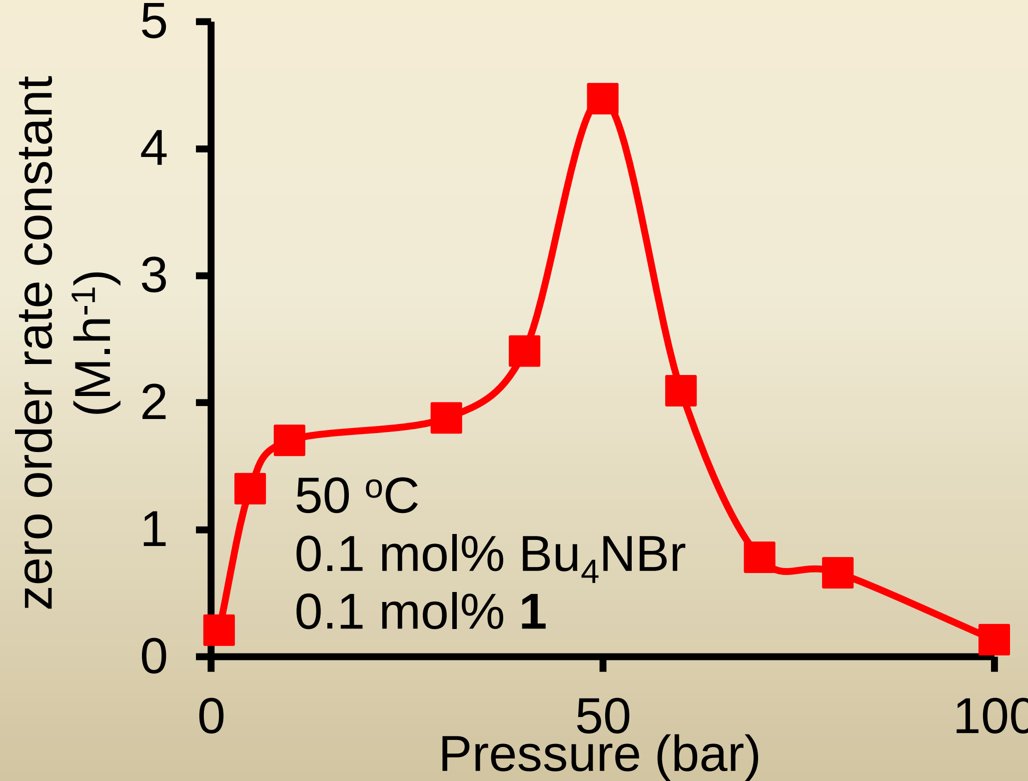
R	Conversion (%)	R	Conversion (%)
Ph	79	CH_2Cl	31
Et	60	CH_2OPh	53
Bu	57	4-ClC_6H_4	54
Oct	73	4-BrC_6H_4	28
Dec	39		

M. North *et al.*, *J. Org. Chem.* **2013**, *78*, 419–426.

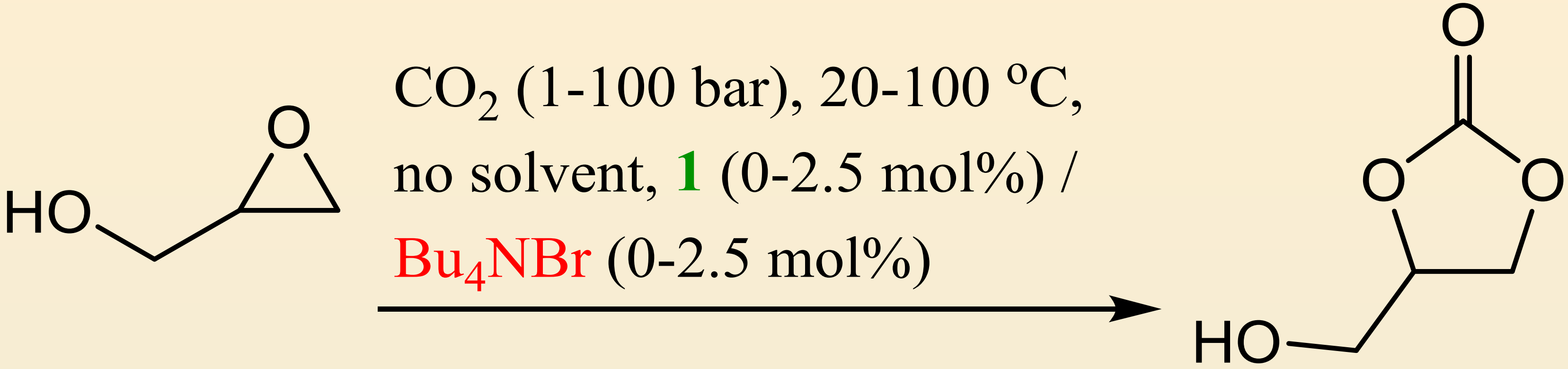
Variable temperature and pressure kinetics

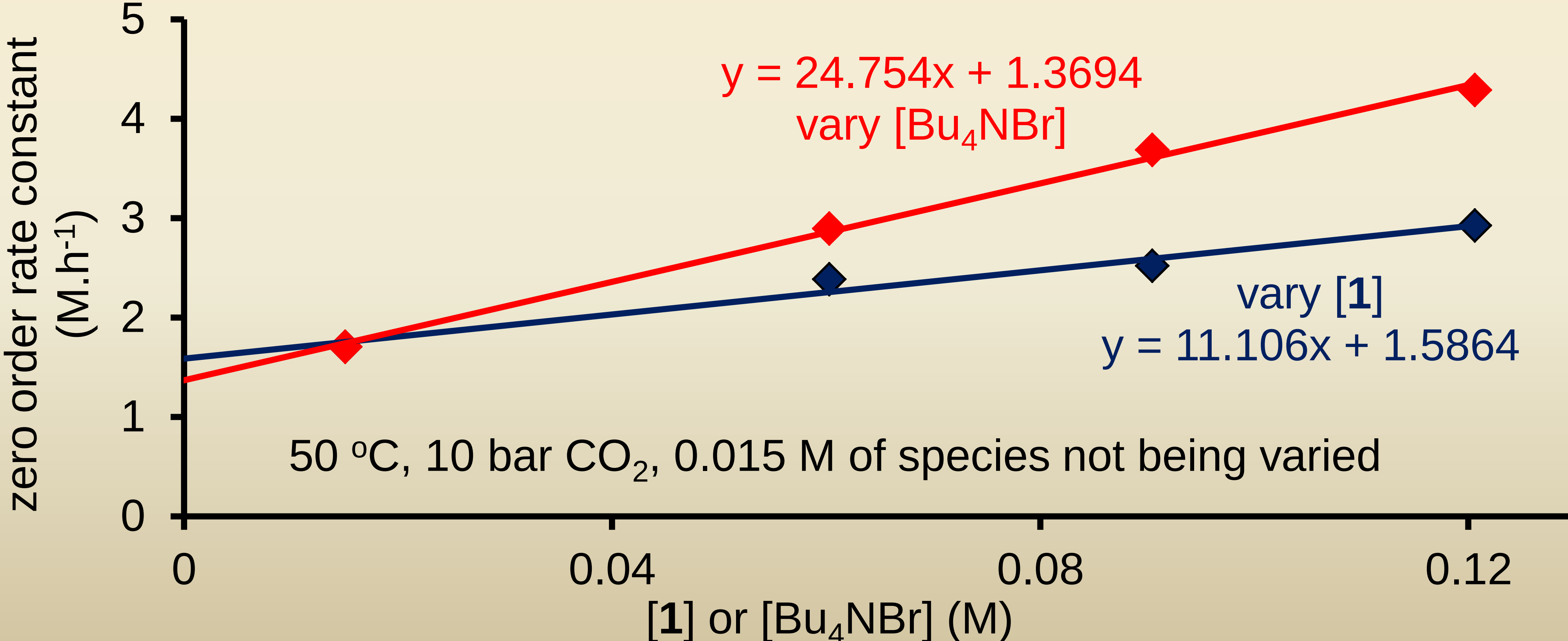




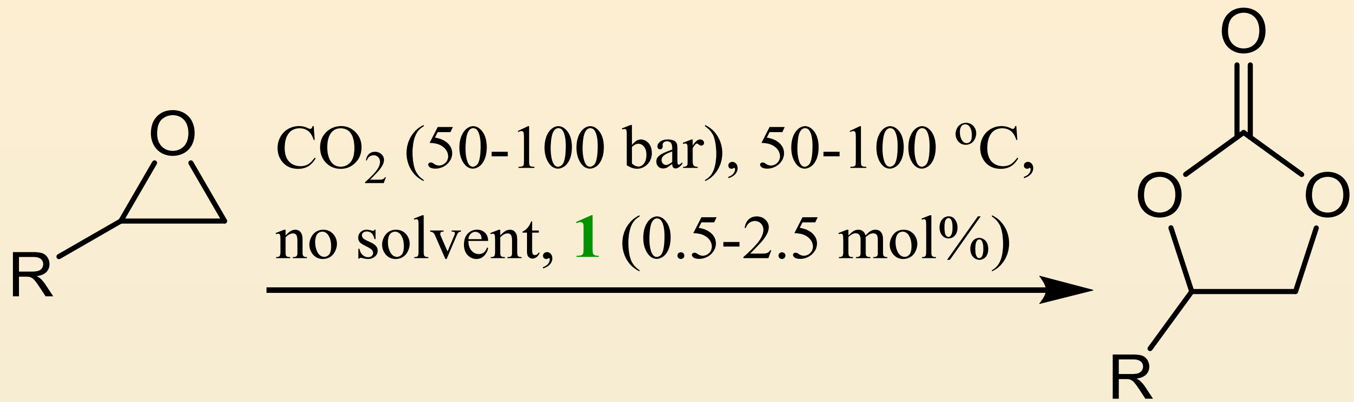


Varying [1] or [Bu_4NBr]



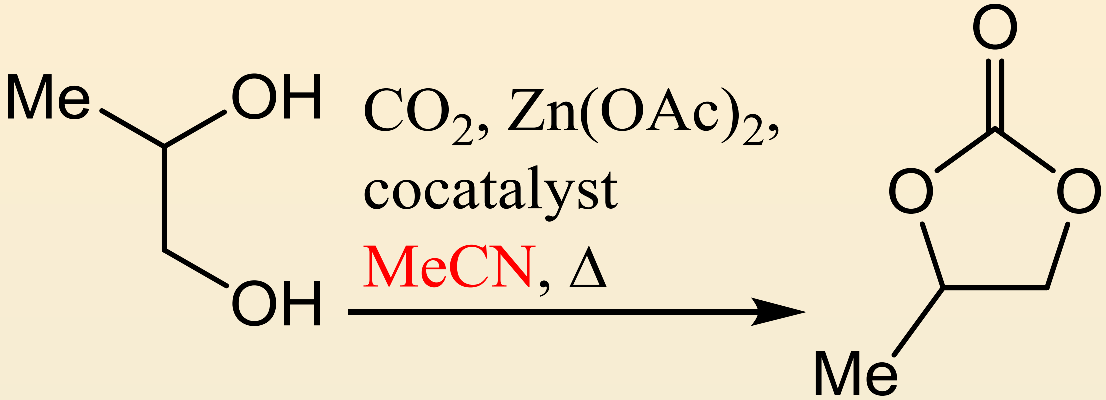


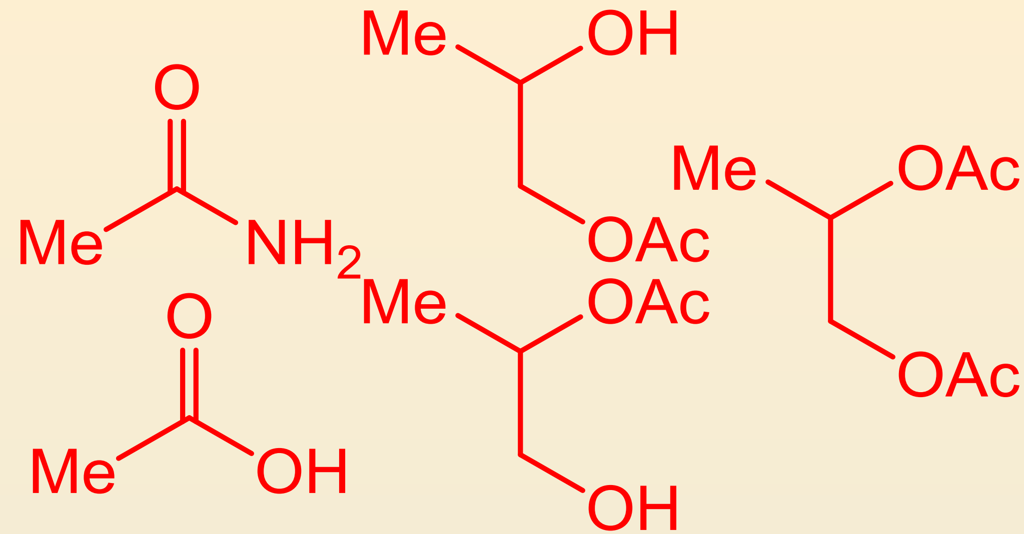
Reactions without Bu_4NBr



R	1 (mol%)	T (^oC)	P (bar)	Yield (%)
Me	0.5	50	50	50
nBu	0.5	50	10	82
nOct	2.5	50	10	89
Ph	0.5	50	50	78
4-ClC_6H_4	0.5	50	50	73
4-BrC_6H_4	1.0	100	50	70
CH_2OH	0.5	50	50	77
$PhOCH_2$	2.5	50	10	85

Synthesis of cyclic carbonates from diols



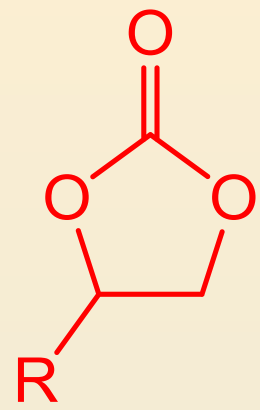


J. Fuel. Chem. Technol. **2007**, *35*, 701–705.

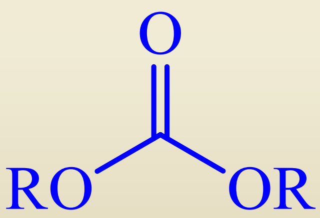
catalyst	cocatalyst	T (°C)	P (bar)	Time (h)	Yield (%)
$Zn(OAc)_2$ 2.5 mol%	-	170	100	12	24
$Zn(OAc)_2$ 2.5 mol%	-	145	60	16	21
$Zn(OAc)_2$ 2.5 mol%	$4\text{-}MeC_6H_4SO_3H$	145	60	16	23
$Zn(OAc)_2$ 5 mol%	$4\text{-}MeC_6H_4SO_3H$	145	60	16	29
$Zn(OAc)_2$ 5 mol%	$4\text{-}ClC_6H_4SO_3H$	145	60	16	38
$Zn(OTf)_2$ 5 mol%	-	135	40	16	42
$Zn(OTf)_2$ 10 mol%	-	135	40	16	44

Carbonates as aprotic solvents

Solvent	Bp (Mp)	Dielectric constant
MeCN	82 °C	38
DMF	153 °C	38
DMSO	189 °C	47
NMP	204 °C	32
HMPA	235 °C	30
Water	100 °C	80
Ethylene carbonate	248 °C (36 °C)	90
Propylene carbonate	242 °C (-49 °C)	64
Dimethyl carbonate	90 °C (2 °C)	3.2
Diethyl carbonate	128 °C (-43 °C)	2.9



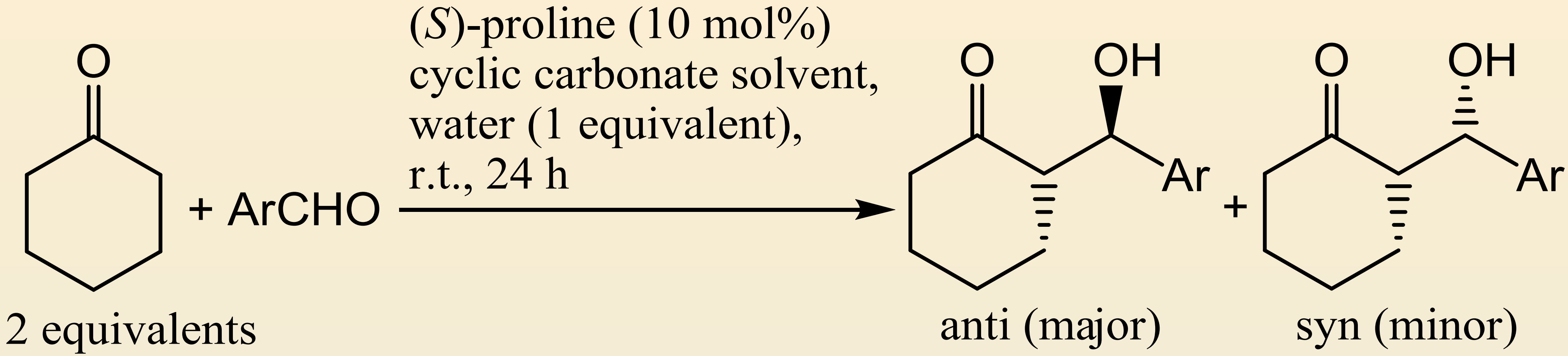
R = H, Me



R = Me, Et

Propylene carbonate: non-toxic, used in cosmetics

Amino acid catalysed reactions

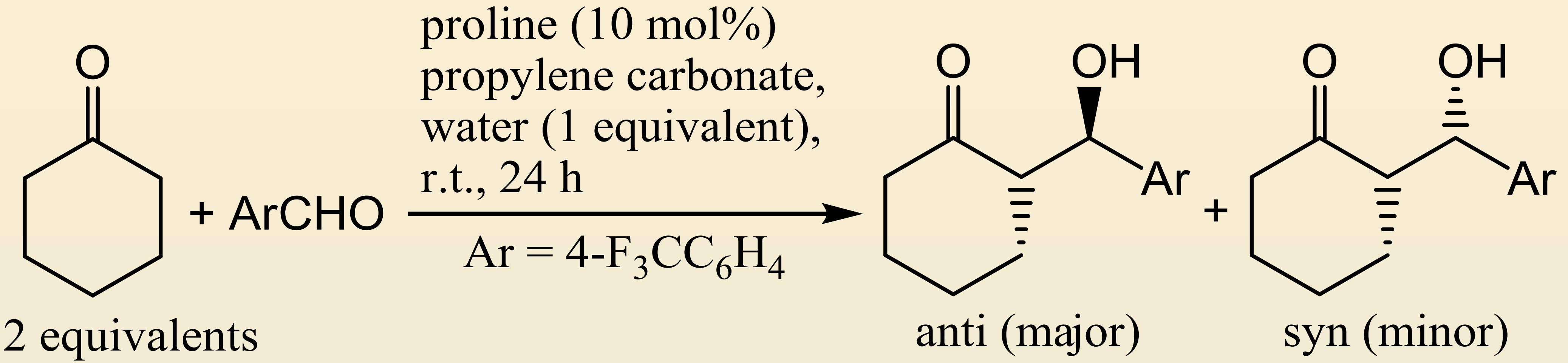


Results with 4-nitrobenzaldehyde

solvent	yield	dr	ee (anti)	ee (syn)
propylene carbonate	83%	8:1	98%	88%
ethylene carbonate	92%	9:1	98%	91%

M. North *et al. Tetrahedron: Asymmetry* **2010**, *21*, 1262–1271; *Synthesis* **2011**, 1918–1925.

Use of enantiomerically pure propylene carbonate



proline	solvent	yield	dr	ee (anti)	ee (syn)
S	*RS*-propylene carbonate	49%	5:1	93 (*S*,*R*)	68 (*S*,*S*)
S	*R*-propylene carbonate	26%	3:1	95 (*S*,*R*)	35 (*S*,*S*)
R	*R*-propylene carbonate	63%	6:1	96 (*R*,*S*)	98 (*R*,*R*)
RS	*R*-propylene carbonate	43%	6:1	6 (*S*,*R*)	9 (*S*,*S*)
S	ethylene carbonate	86%	9:1	98 (*S*,*R*)	89 (*S*,*S*)

M. North *et al.* *Org. Lett.* **2010**, *12*, 2378–2381.

York, the University and Green Chemistry at York

One of Europe's most beautiful and historic cities

University of York and its Chemistry department

- **Top 100 World-** and Top10 UK-ranked University. Times ‘Top Young University’
- **Top 5** UK-ranked Chemistry Department
- World-leading Green Chemistry Centre dedicated to creating genuinely sustainable supply chains for chemical and related products

ca. €40M grants/investment in 2012-14 → new research and development buildings + new academic, research, technical, business development and admin staff.

CyclicCO2R
Fine chemicals from CO_2

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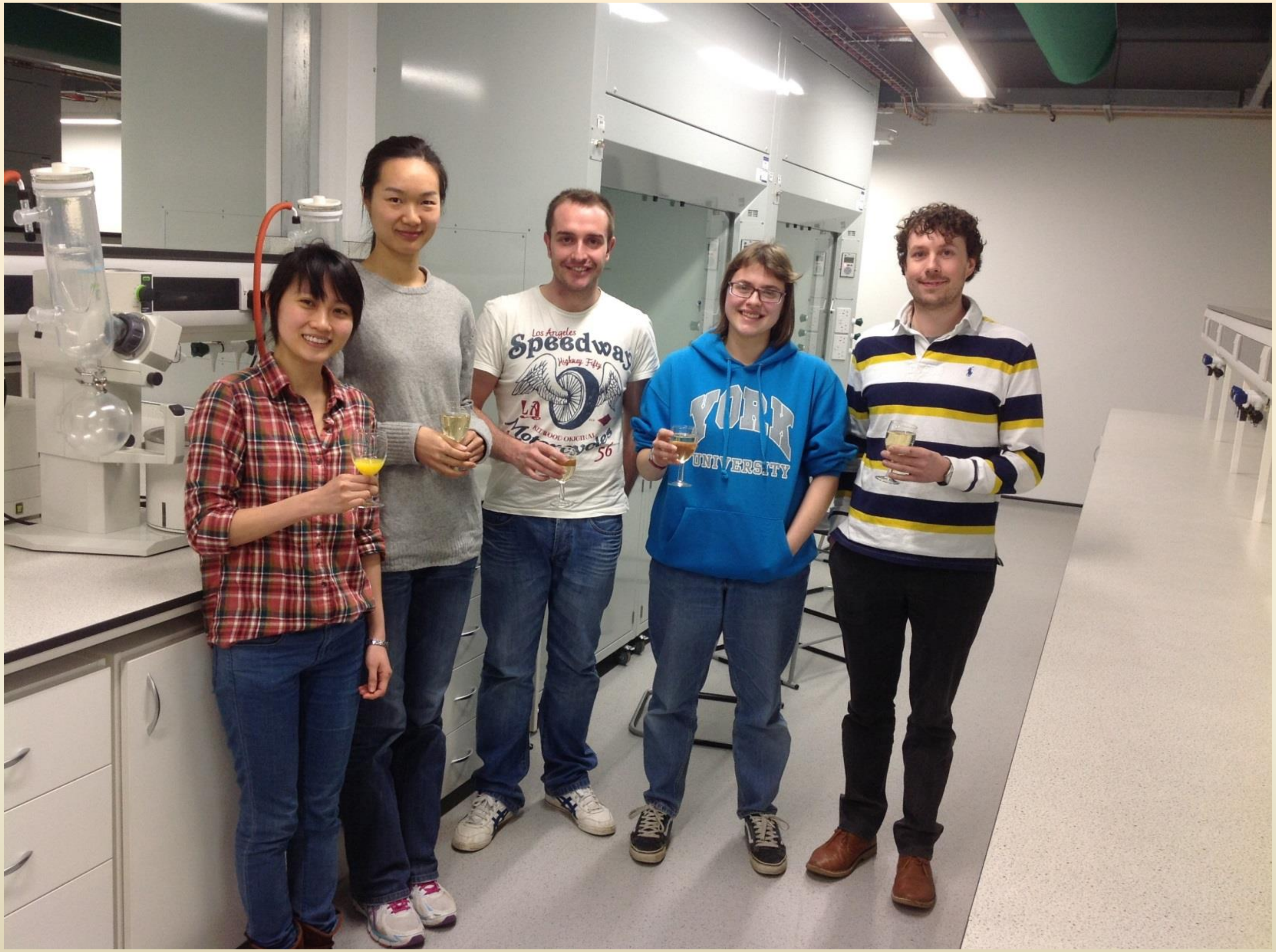

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CO2Chem
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EPSRC, TSB, SSE, DoosanBabcock,
EU, Sintef, CarbonConnections,