

UNIVERSITY *of York*



**Green
Chemistry**
Centre of Excellence



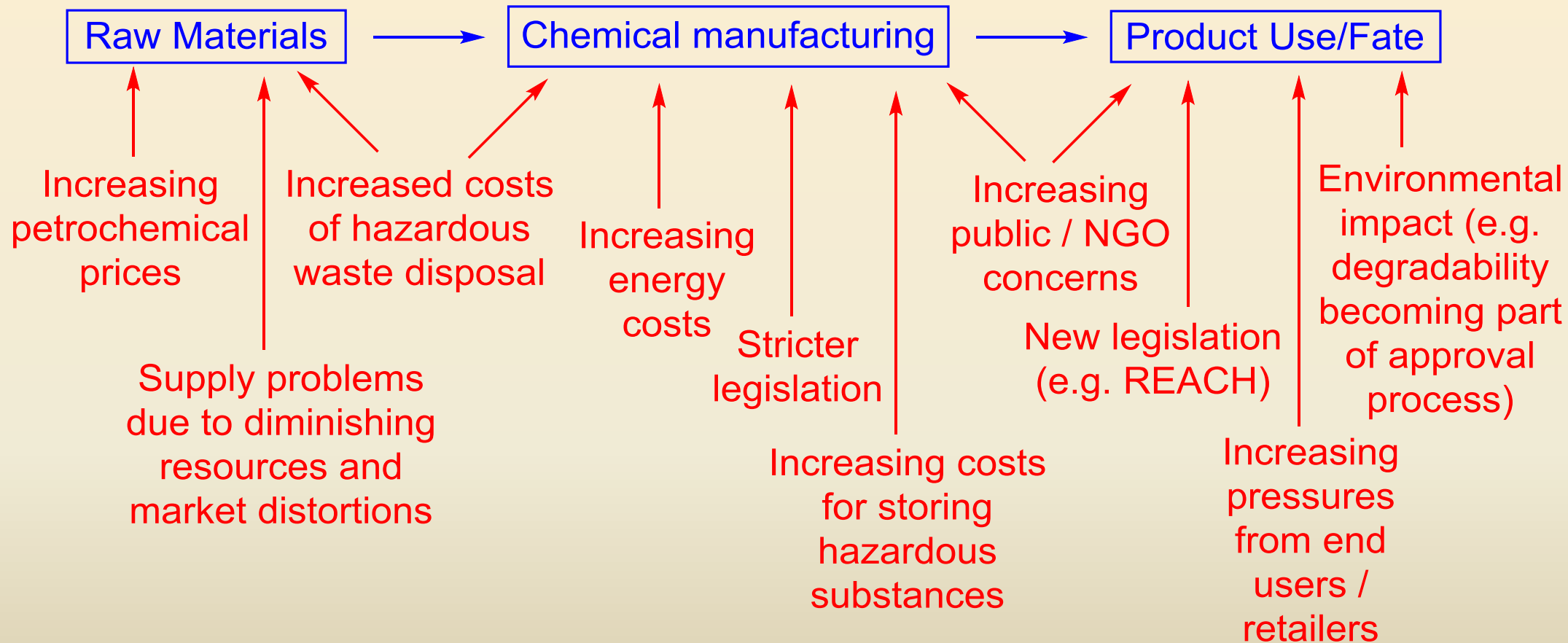
CO₂ related chemistry

Professor Michael North

August 2014



Pressures on chemicals across the lifecycle



We need alternative, sustainable starting materials for the chemicals industry and CO₂ 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.

hydrogen 1 H 1.0079																	helium 2 He 4.0026																
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180										
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948										
potassium 19 K 39.098	calcium 20 Ca 40.078																	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selecnium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62																	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]															
francium 87 Fr [223]	radium 88 Ra [226]	89-102 **	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununium 110 Uun [271]	ununium 111 Uuu [272]	unbibium 112 Uub [277]						ununquadium 114 Uuq [289]															

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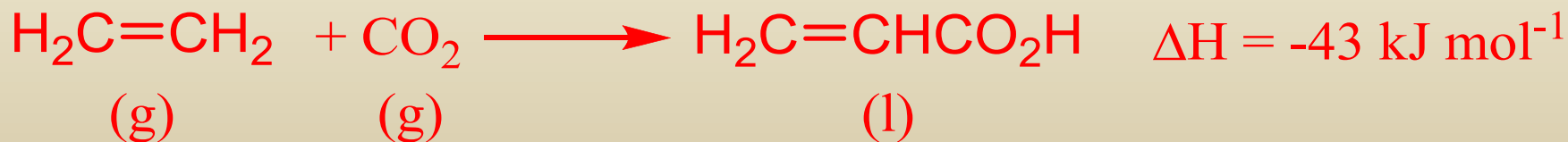
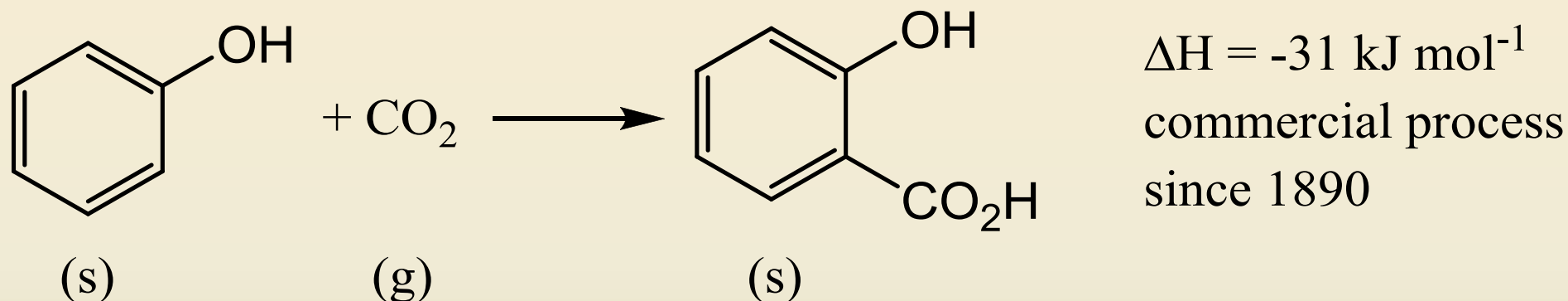
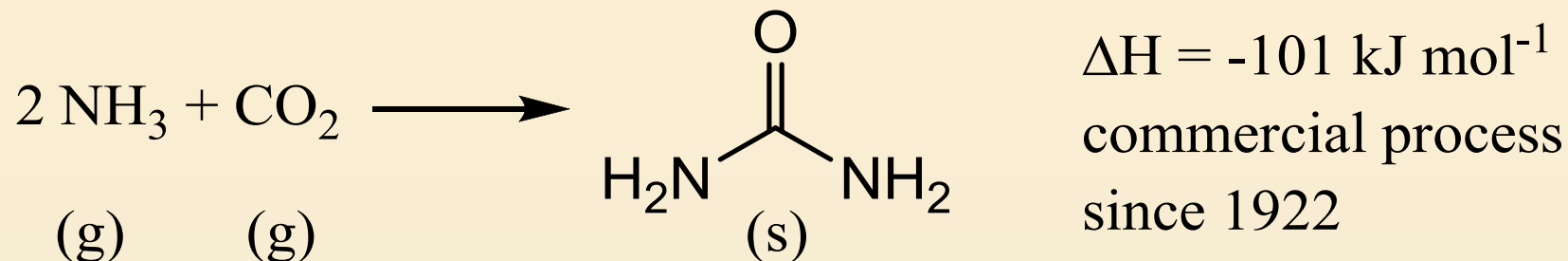
<http://www.chemistryinnovation.co.uk/>

* Lanthanide series

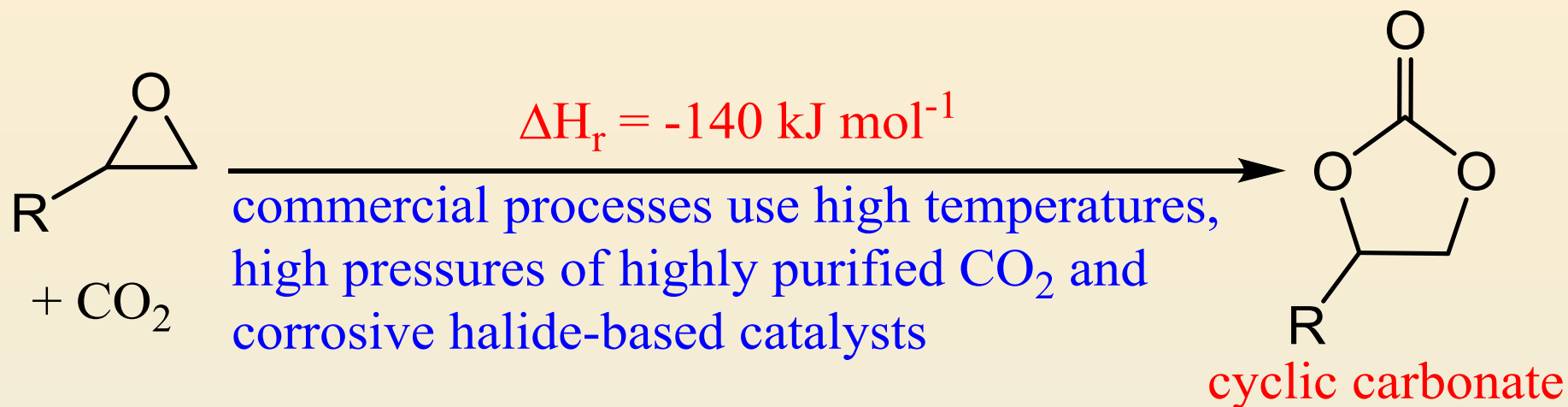
** Actinide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Use of CO₂ as a starting material



Synthesis of cyclic carbonates



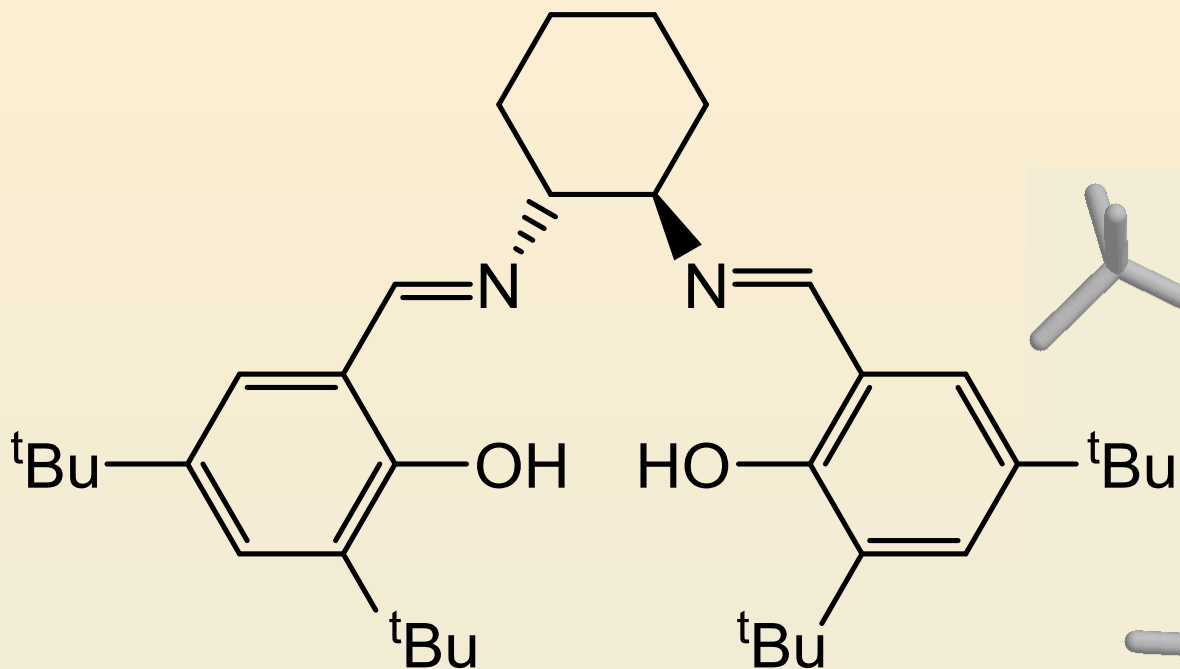
Applications: Electrolyte for lithium ion battery

Polar aprotic solvent

Chemical intermediate (e.g. for dimethyl carbonate)

Polymer synthesis

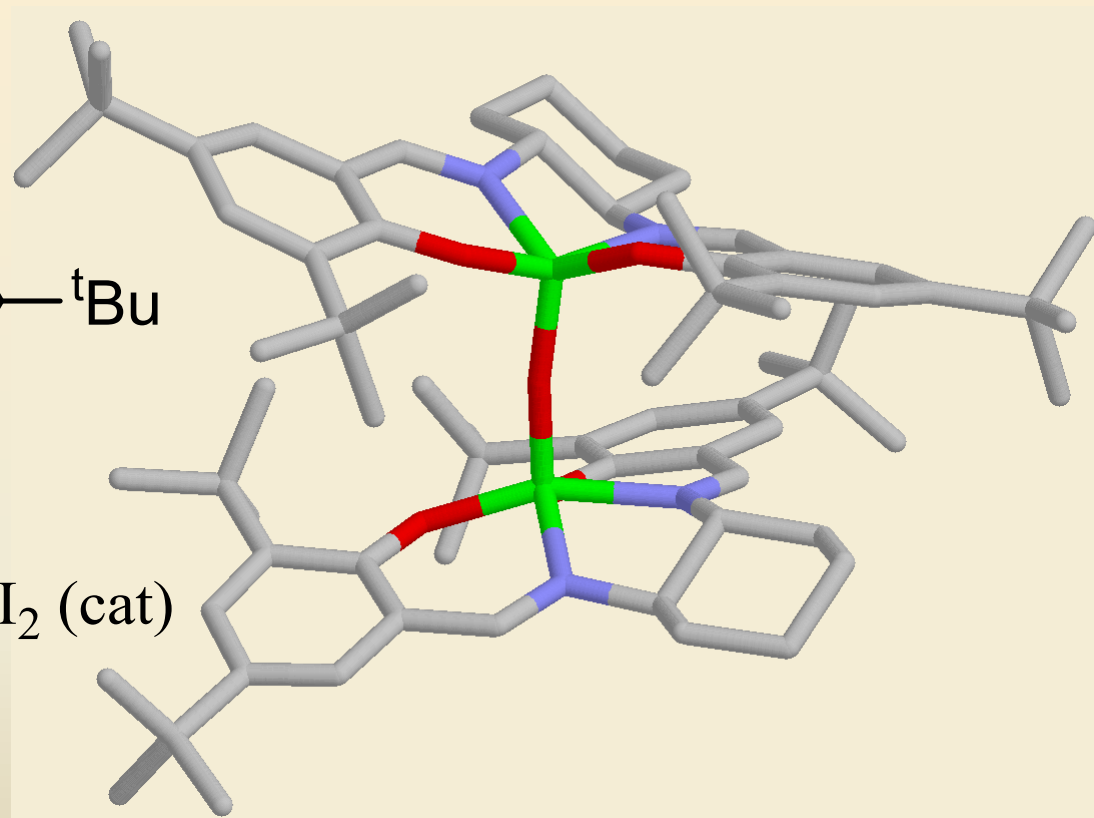
A bimetallic aluminium(salen) catalyst



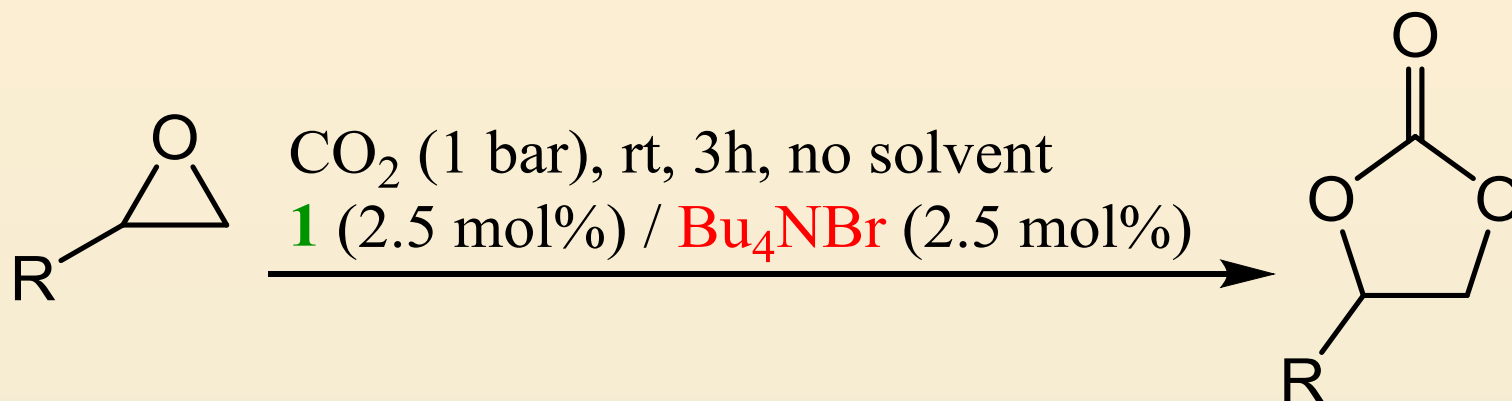
1) Al foil, EtOH, I₂ (cat)
2) H₂O



1 bimetallic catalyst

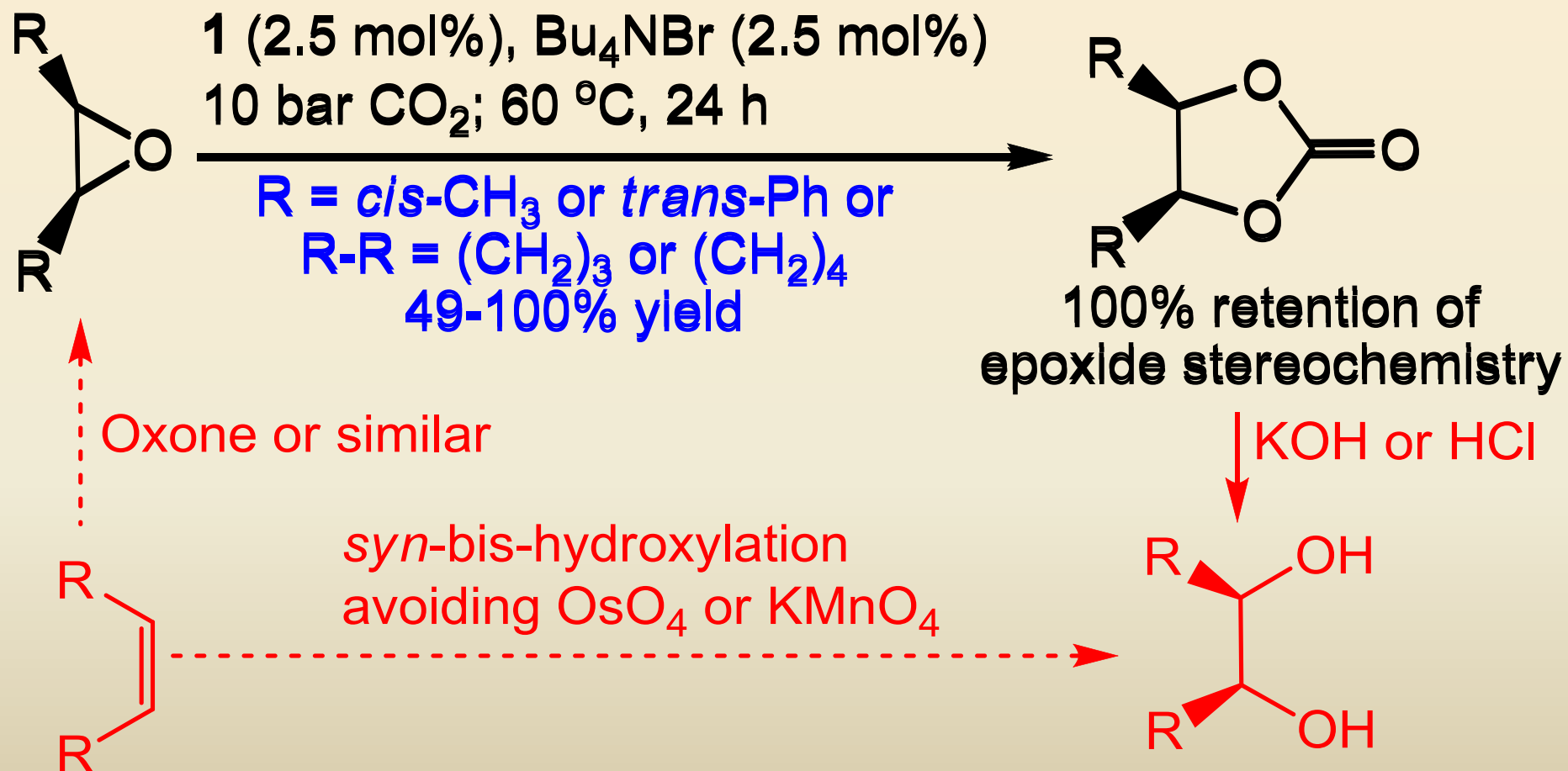


Batch results with terminal epoxides

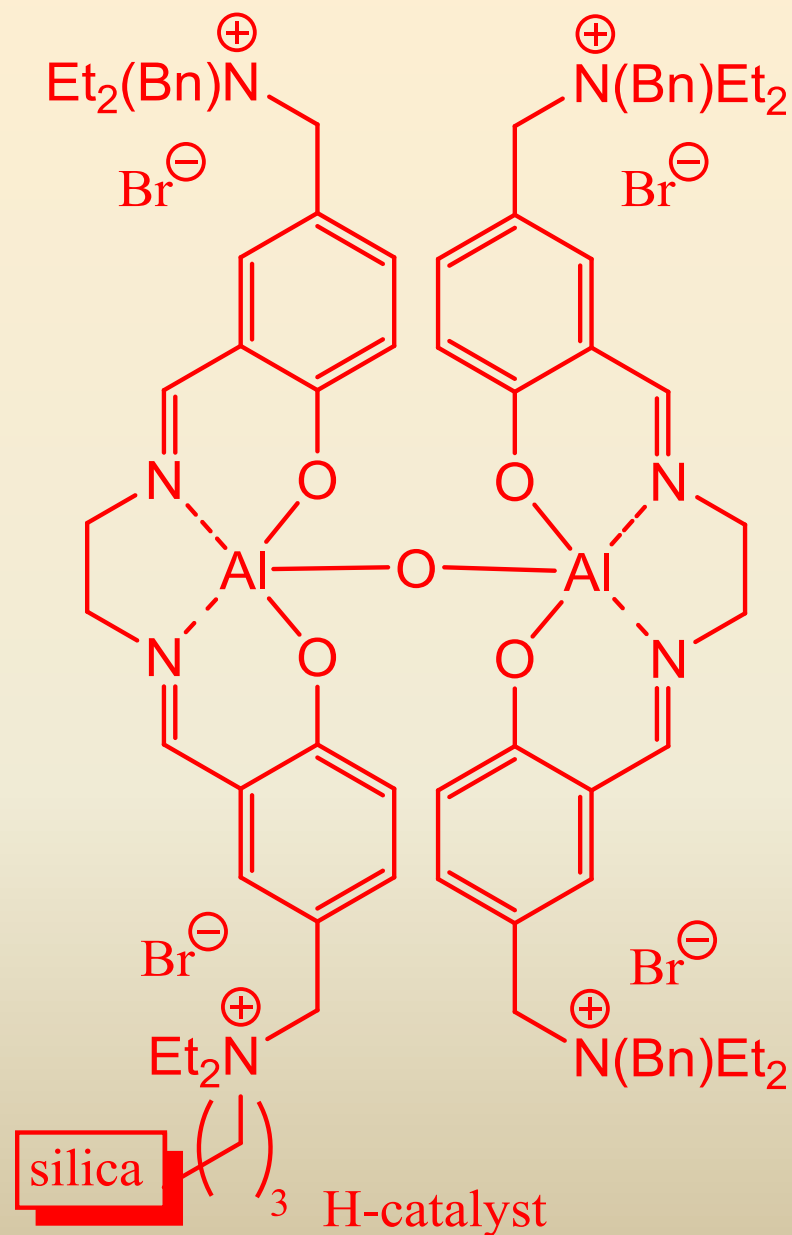
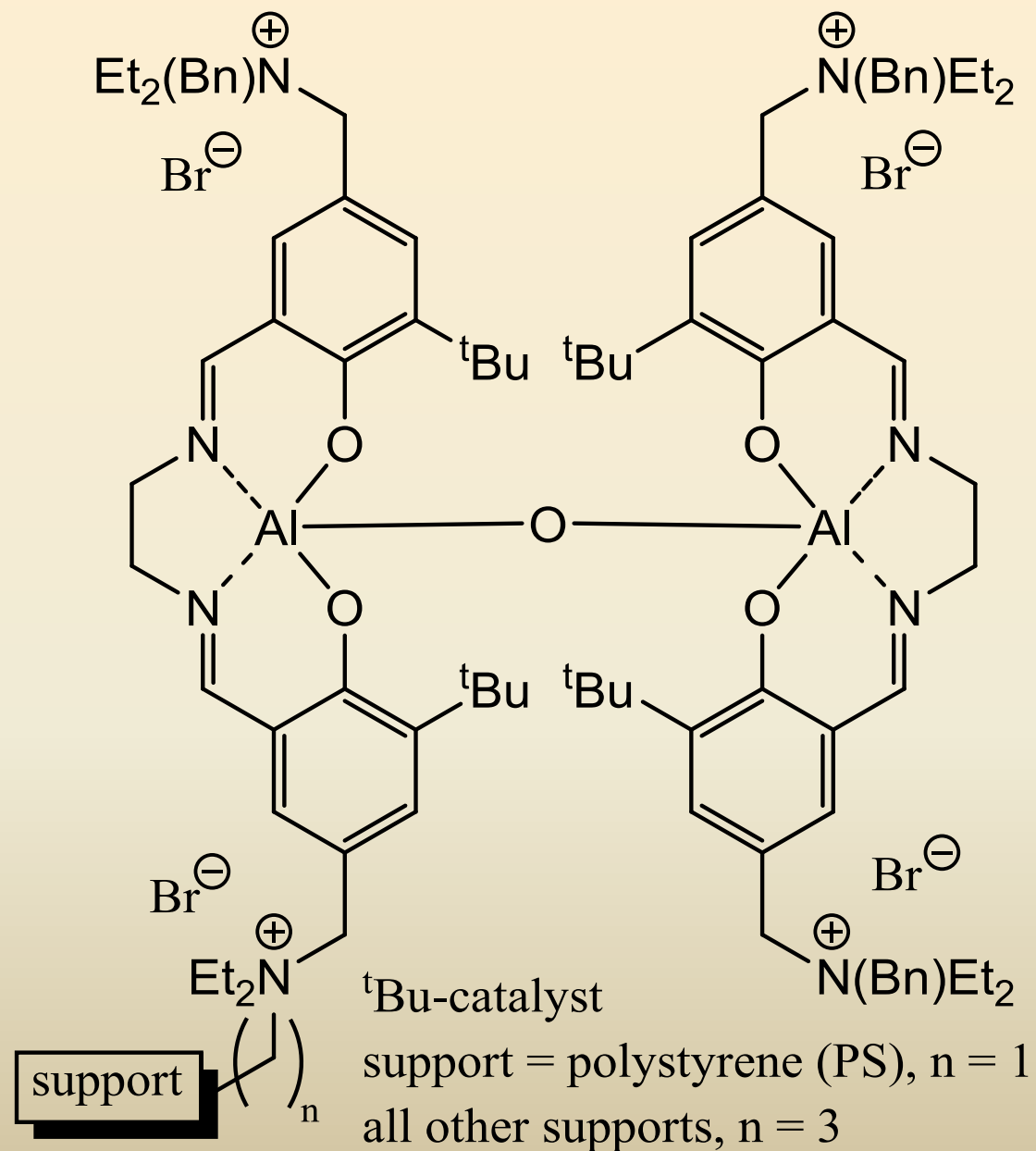


R	Yield		R	Yield		R	Yield
Ph	62%		Me	77%		CH ₂ OCOMe	34%
PhCH ₂	44%		H	76%		CH ₂ OCOPh	58%
Bu	87%		CH ₂ OH	36%		4-MeC ₆ H ₄	77%
C ₈ H ₁₇	64%		CH ₂ Cl	60%		3-MeOC ₆ H ₄	48%
CH ₂ O ^t Bu	50%		CH ₂ OPh	55%		4-ClC ₆ H ₄	42%

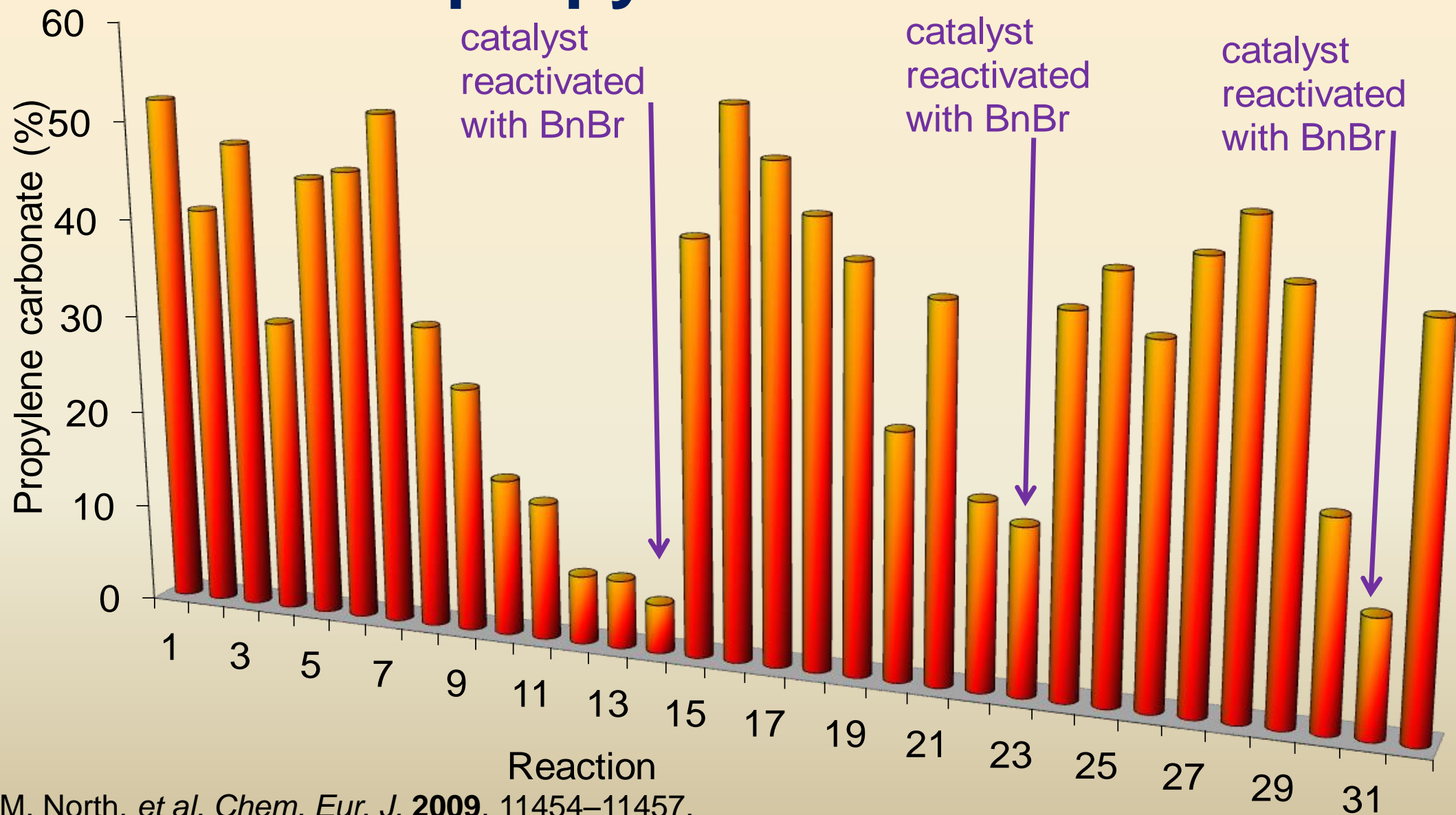
Disubstituted epoxides and stereochemistry



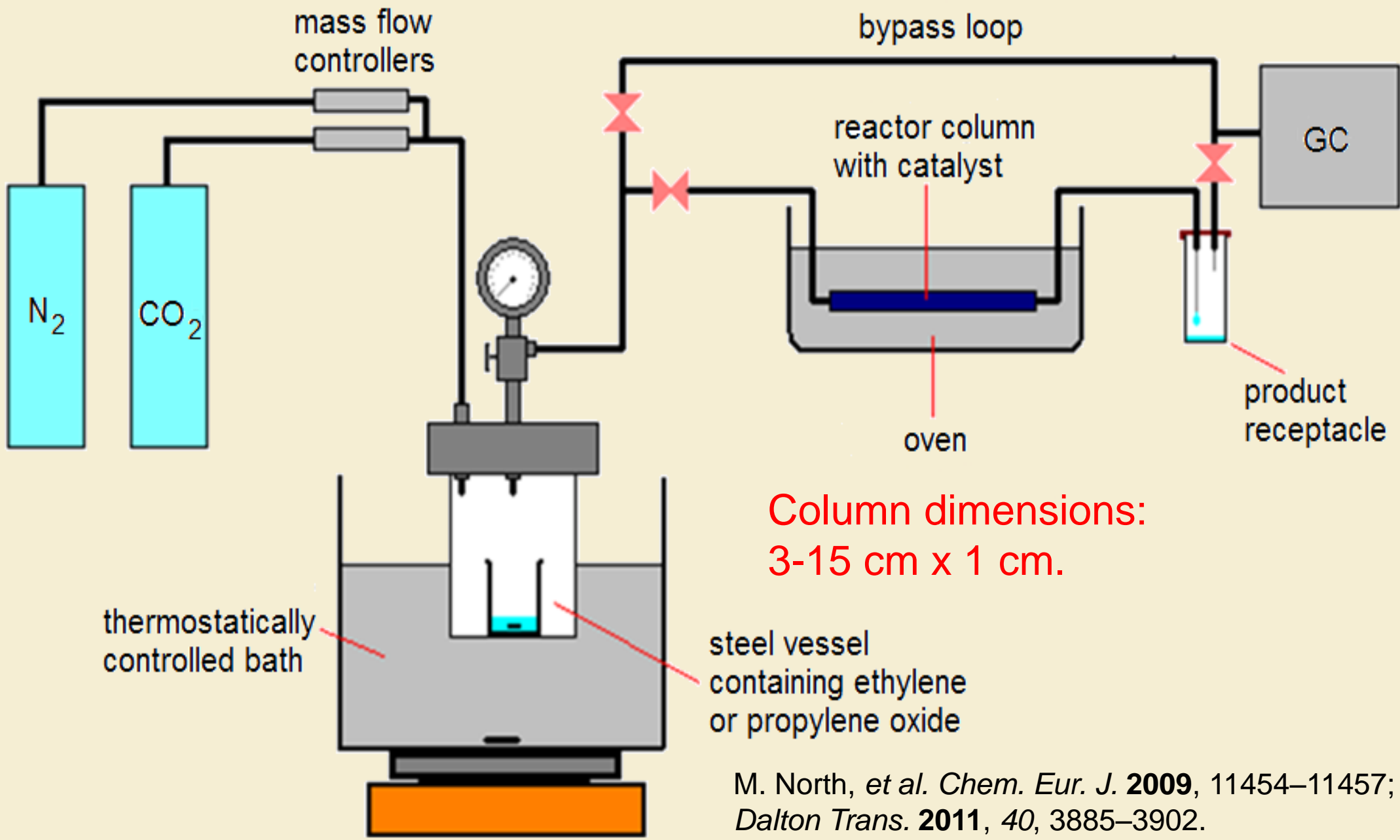
Supported catalyst structures



Reuse of silica-supported catalyst with propylene oxide

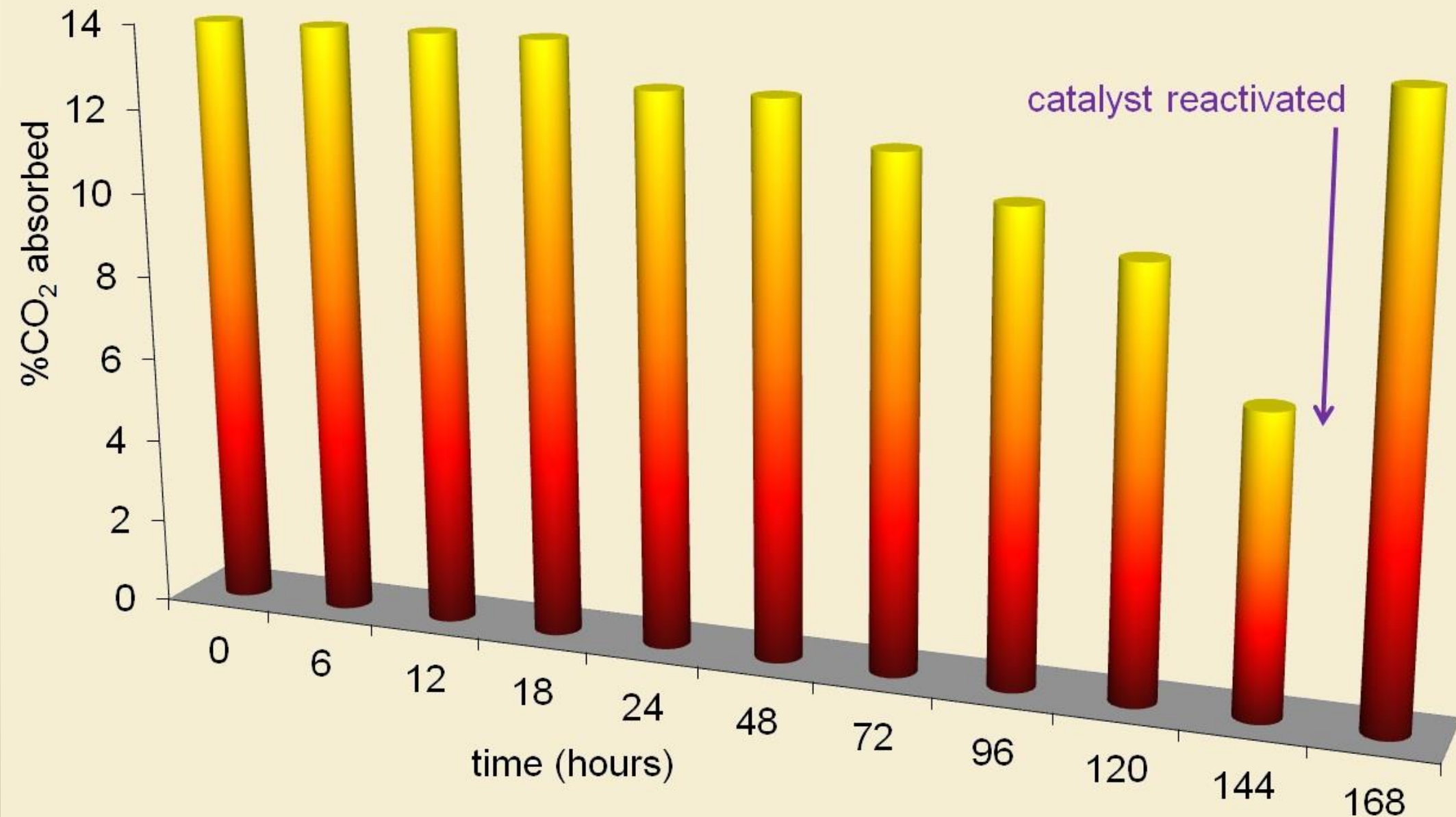


Gas phase flow reactor



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

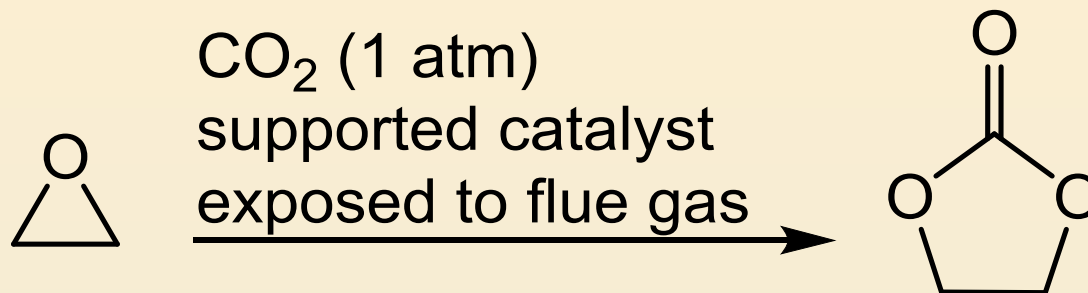
Continuous flow results at 100 °C



Sources of waste CO₂

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

Testing with real flue gas

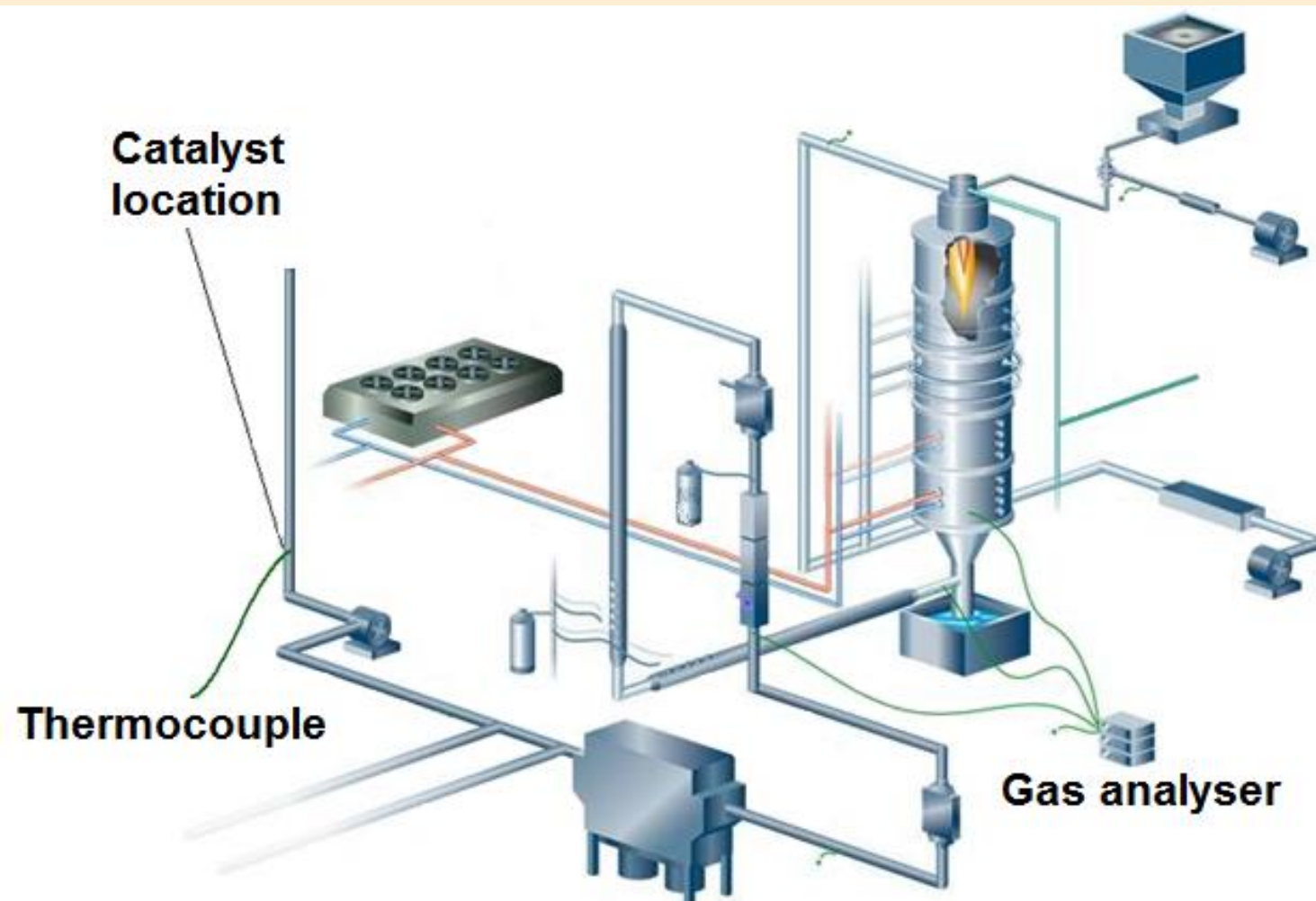


Five catalyst samples (all from same batch) used:

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

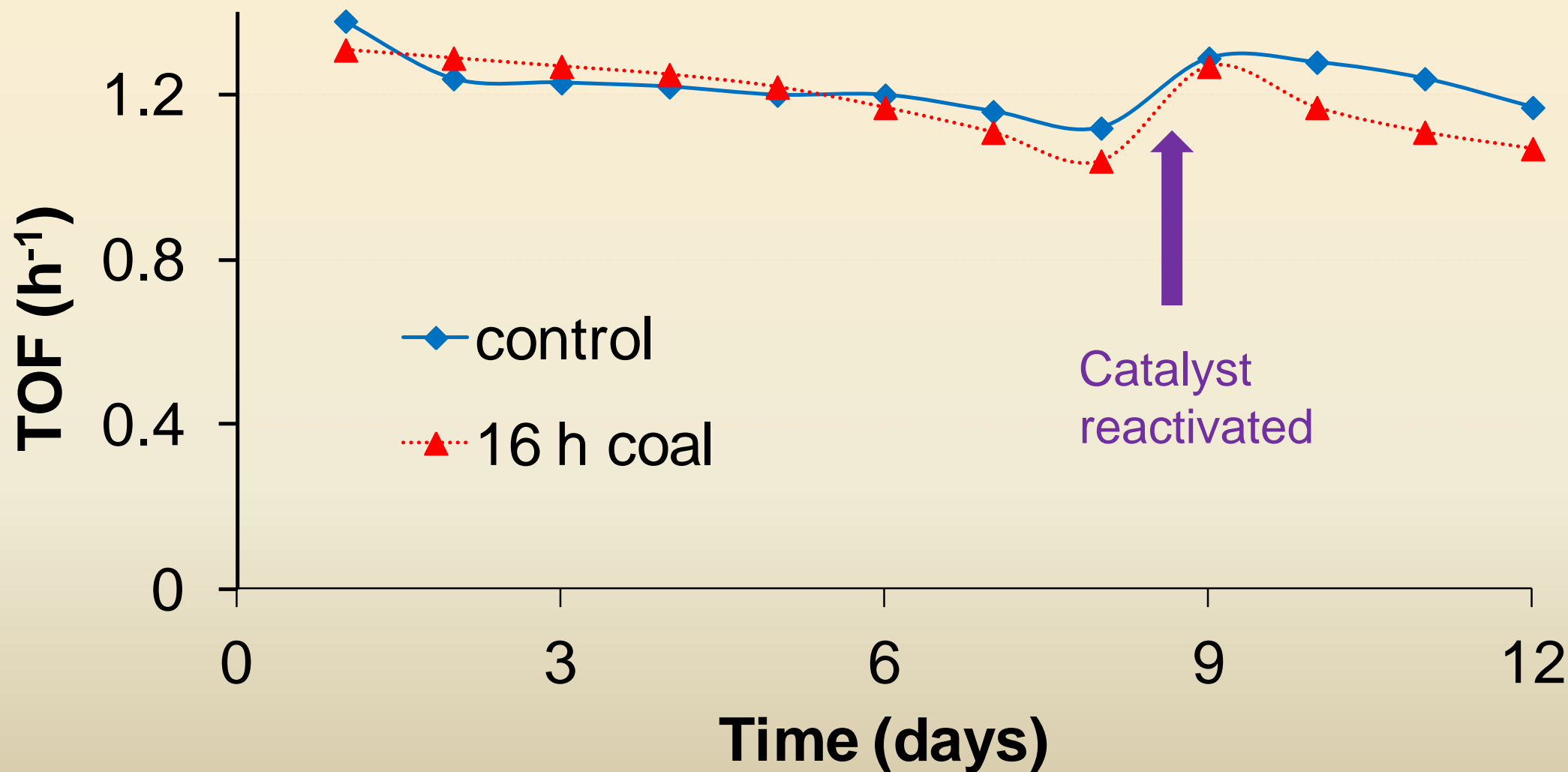


Flue gas composition
Flow rate 20 mL/min

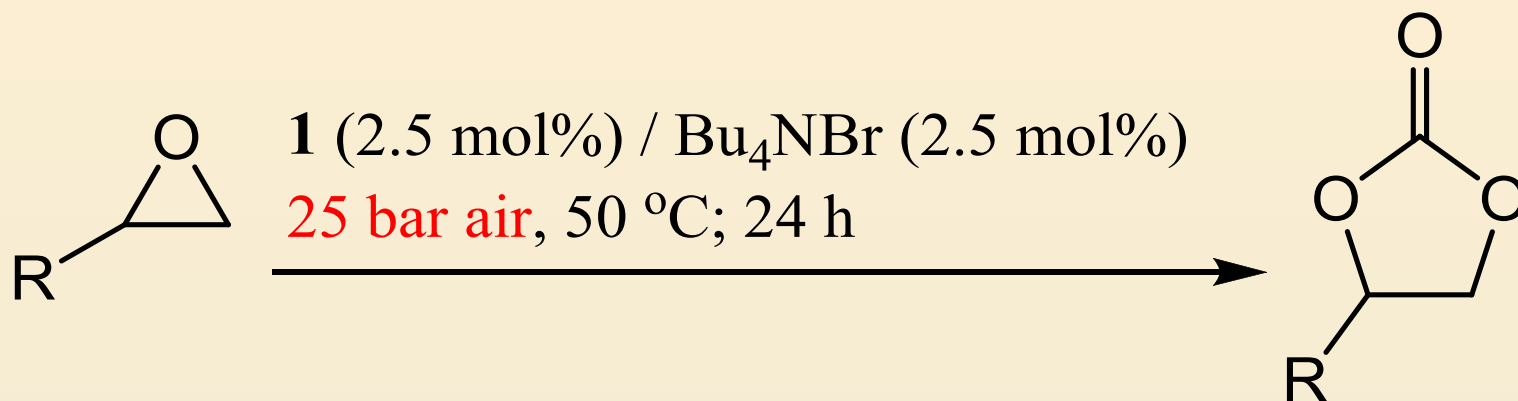
T	52 °C
CO ₂	15%
O ₂	3%
SO ₂	291ppm
CO	40ppm
NO _x	443ppm

Used El Cerrejon coal (typical hard coal):
74%C; 0.5%S; 1.5%N; 5%H; 7% H₂O

Real flue gas flow reactor results with ethylene oxide

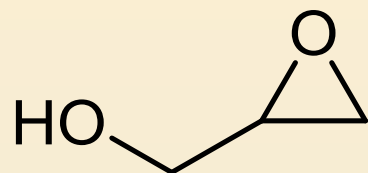


Use of compressed air

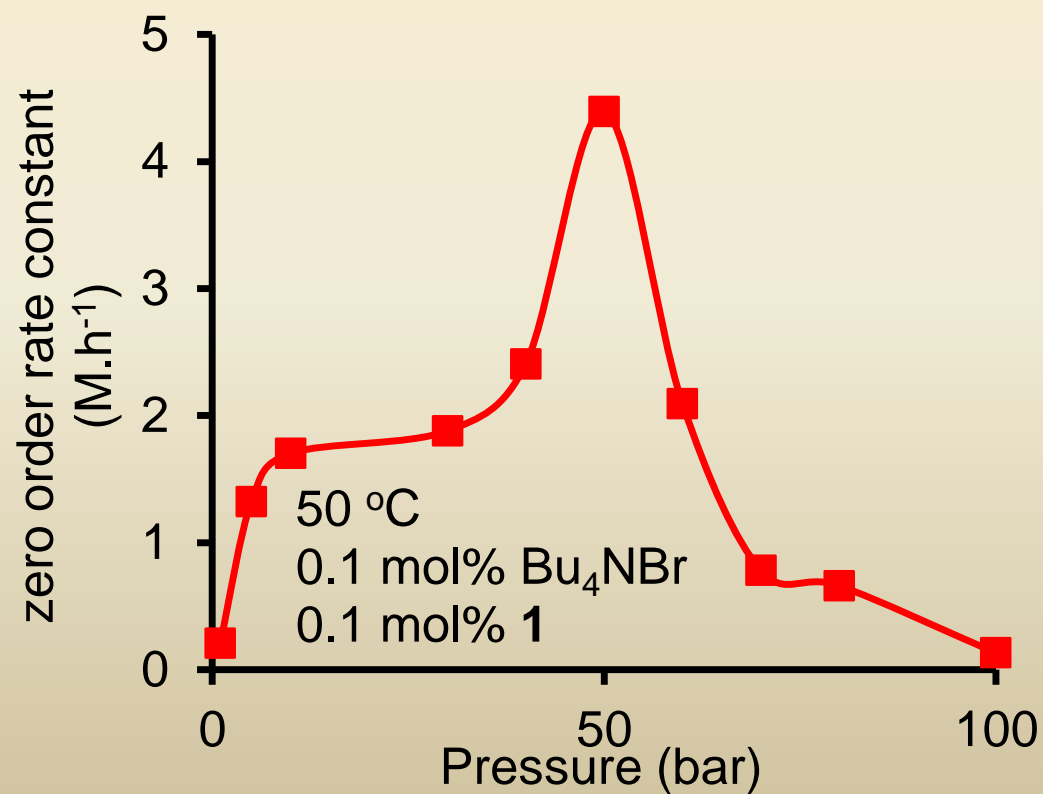
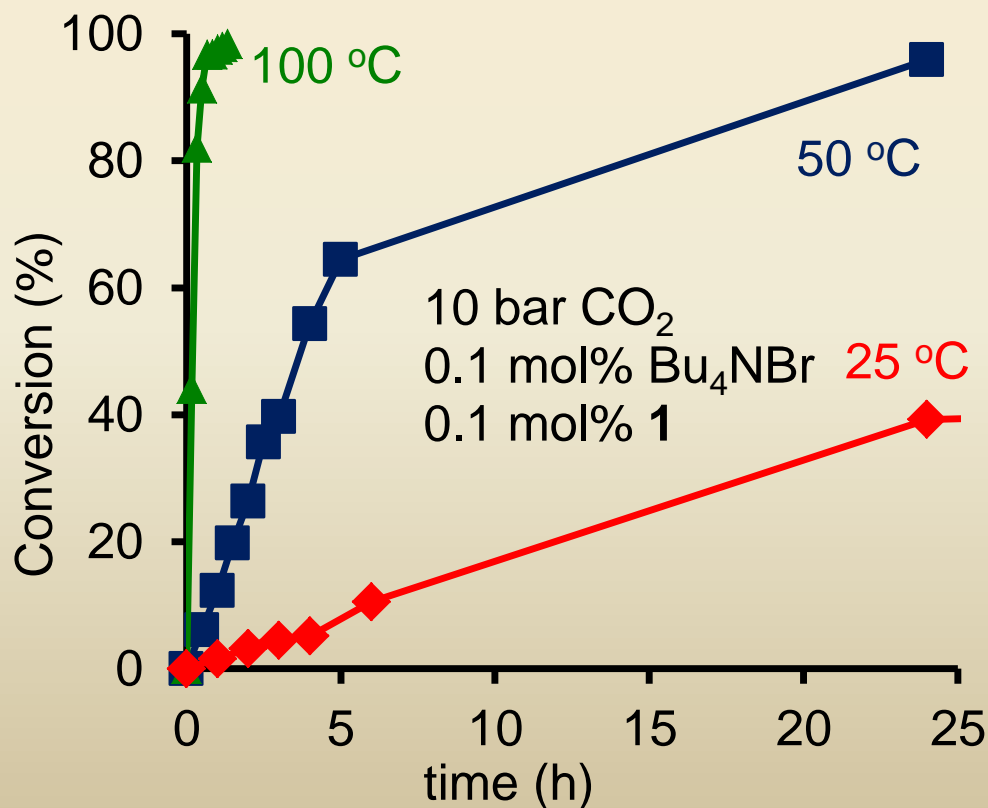
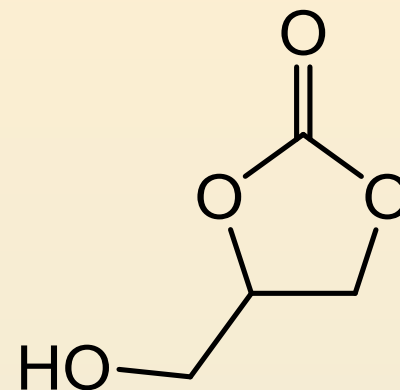


R	Conversion (%)	R	Conversion (%)
Ph	79	CH ₂ Cl	31
Et	60	CH ₂ OPh	53
Bu	57	4-ClC ₆ H ₄	54
Oct	73	4-BrC ₆ H ₄	28
Dec	39		

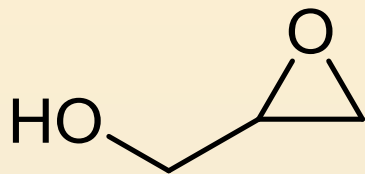
Variable temperature and pressure kinetics



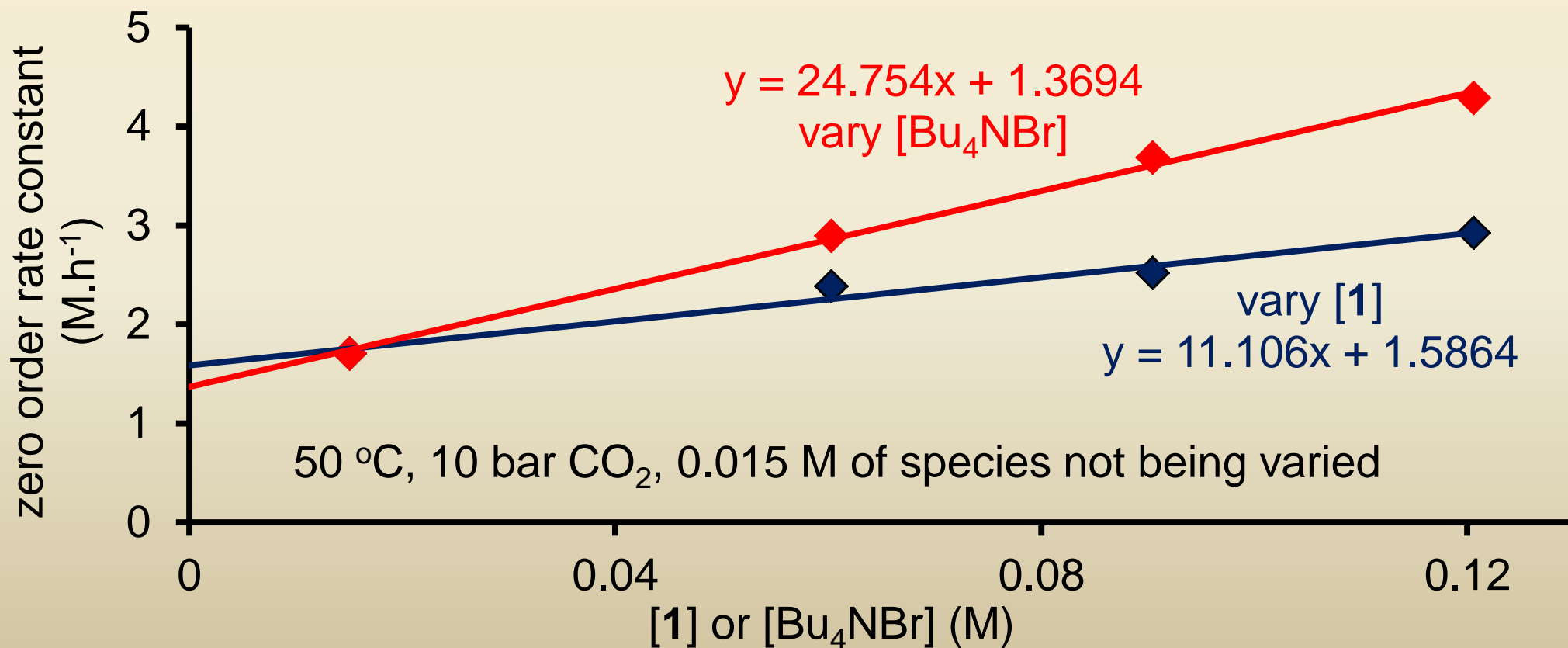
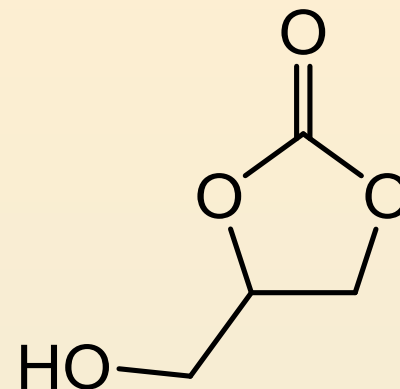
CO₂ (1-100 bar), 20-100 °C,
no solvent, **1** (0-2.5 mol%) /
Bu₄NBr (0-2.5 mol%)



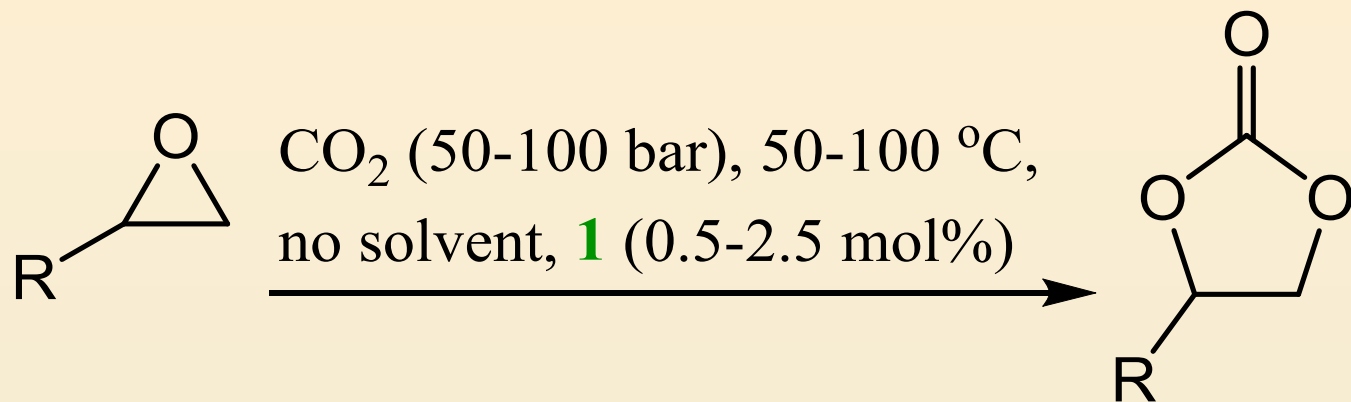
Varying [1] or [Bu₄NBr]



CO₂ (1-100 bar), 20-100 °C,
no solvent, **1** (0-2.5 mol%) /
Bu₄NBr (0-2.5 mol%)

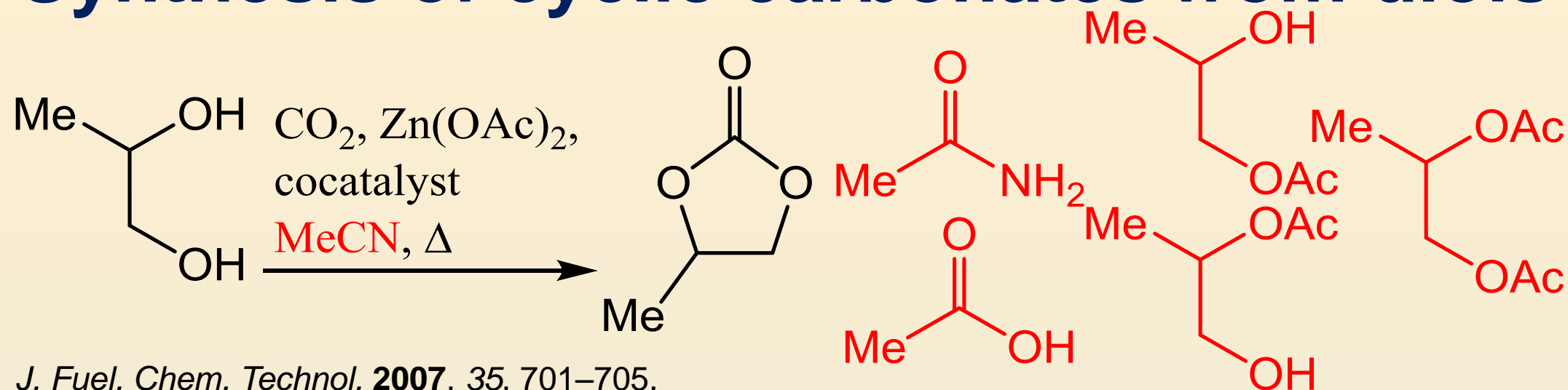


Reactions without Bu₄NBr



R	1 (mol%)	T (°C)	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 ₆ H ₄	0.5	50	50	73
4-BrC ₆ H ₄	1.0	100	50	70
CH ₂ OH	0.5	50	50	77
PhOCH ₂	2.5	50	10	85

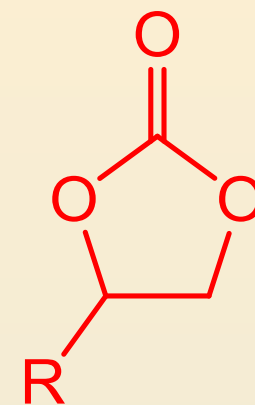
Synthesis of cyclic carbonates from diols



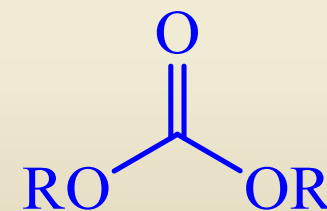
catalyst	cocatalyst	T (°C)	P (bar)	Time (h)	Yield (%)
Zn(OAc) ₂ 2.5 mol%	-	170	100	12	24
Zn(OAc) ₂ 2.5 mol%	-	145	60	16	21
Zn(OAc) ₂ 2.5 mol%	4-MeC ₆ H ₄ SO ₃ H	145	60	16	23
Zn(OAc) ₂ 5 mol%	4-MeC ₆ H ₄ SO ₃ H	145	60	16	29
Zn(OAc) ₂ 5 mol%	4-ClC ₆ H ₄ SO ₃ H	145	60	16	38
Zn(OTf) ₂ 5 mol%	-	135	40	16	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



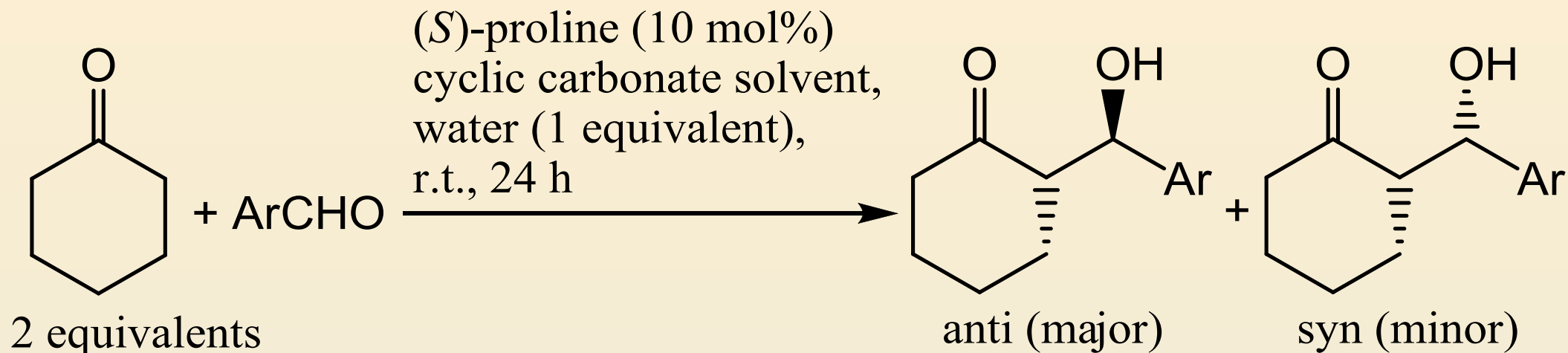
R = H, Me



R = Me, Et

Propylene carbonate: non-toxic, used in cosmetics

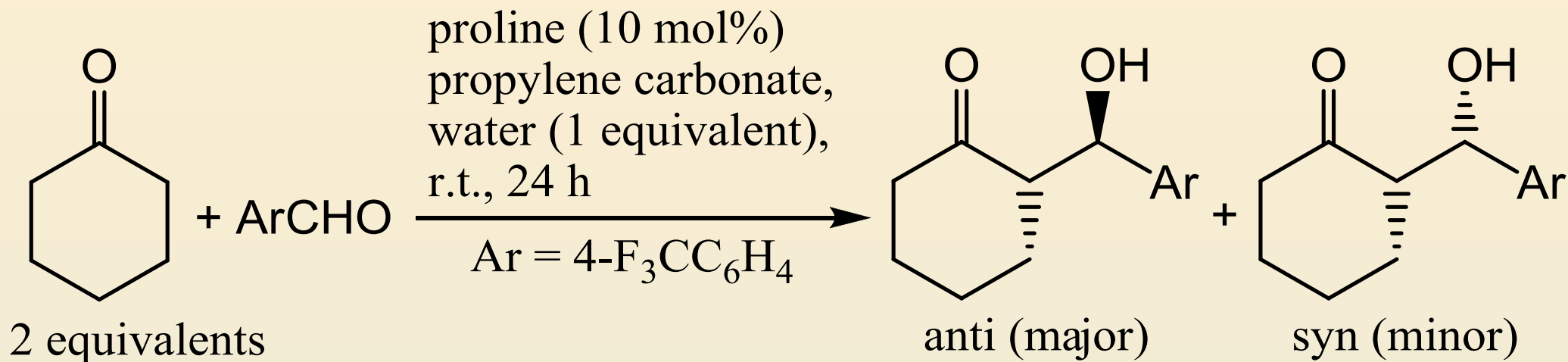
Amino acid catalysed reactions



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%

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)

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



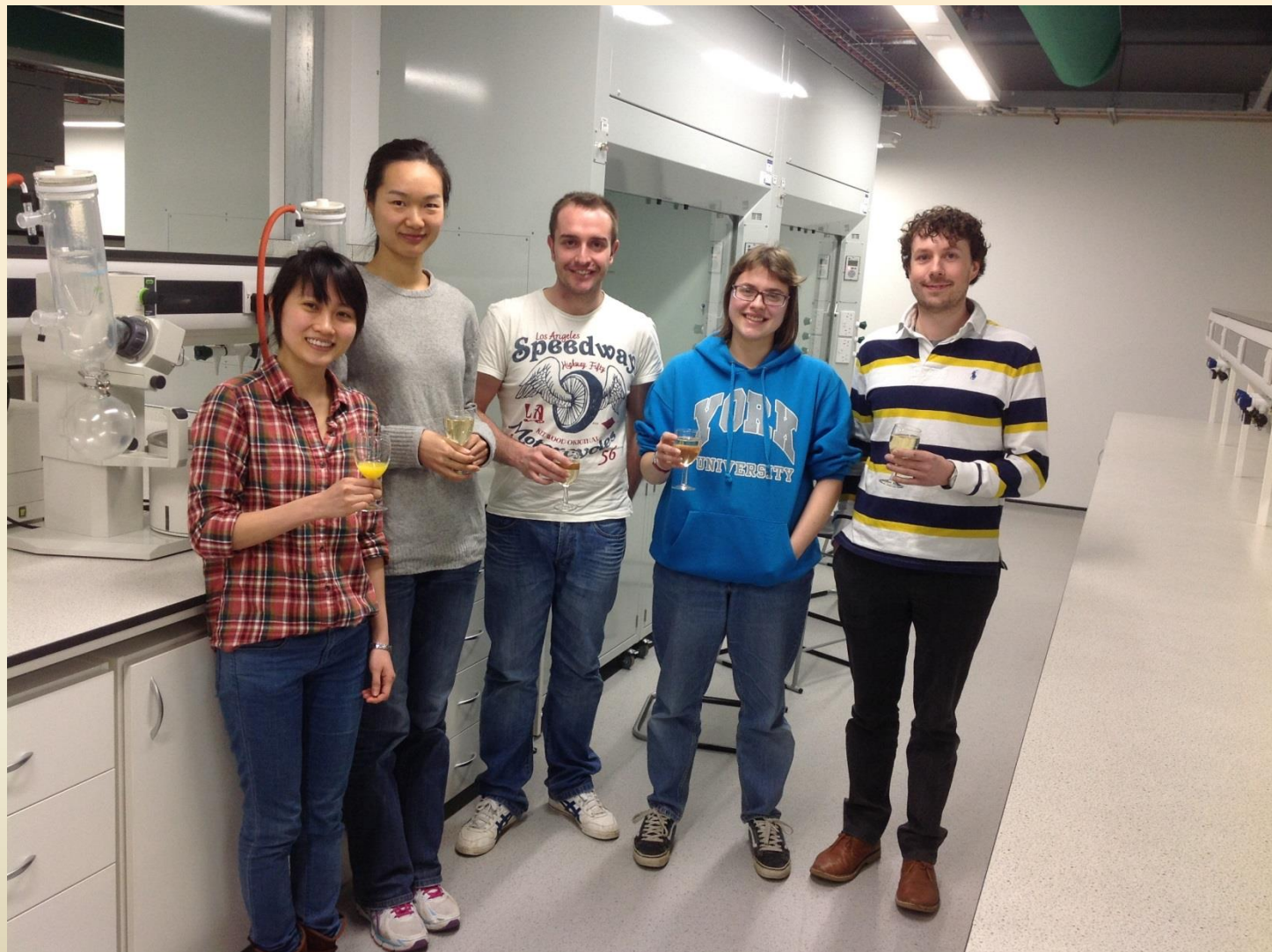
ca. €40M grants/investment in 2012-14 → new research and development buildings + new academic, research, technical, business development and admin staff.



CyclicCOR
Fine chemicals from CO₂

Acknowledgements

Dr. Riccardo Pasquale
Dr. Jaisiel Melendez
Dr. Pedro Villuendas
Dr. Carl Young
Dr. Jose Castro-Osma
Dr. Xiao Wu
Dr. James Comerford



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