

Fast, Selective and Tolerant Polymerisation Catalysts for the Synthesis of Low Molecular Weight Polyester and Polycarbonate Polyols



Edward John Karl Shellard



Keble College
Department of Inorganic Chemistry
University of Oxford
April 2025

A thesis submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy in Chemistry

For my family

“The end of the melody is not its goal”

- Friedrich Nietzsche

Declaration

The work described in this thesis was conducted between October 2021 and April 2025 at the University of Oxford. This is the work of the author unless otherwise stated.

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes, and that they do not alter, transform or build-upon it. For any reuse or distribution, researchers must make clear to others the licence terms of this work.

A handwritten signature in blue ink, appearing to read 'E. Shellard', with a stylized, cursive script.

Edward J. K. Shellard

Abstract

This thesis describes the development of novel Al(III)/K(I) heterodinuclear catalysts for use in the synthesis of low molecular weight polyesters and polycarbonates by the ring-opening copolymerisation (ROCOP) of epoxides/anhydrides and epoxides/carbon dioxide (CO₂), respectively.

Chapter 1 introduces these two ROCOP reactions outlining their mechanisms and catalyst development. The use of protic compounds as chain transfer agents (CTA) to control the polymer molecular weight and the challenges associated with designing catalysts stable to high CTA loading is discussed.

Chapter 2 presents a series of Al(III)/K(I) catalysts, assessing the impact of modifications to the ancillary ligand on the ROCOP of cyclohexene oxide (CHO) with phthalic anhydride (PA). Catalysts are compared by rate constants, turn over frequencies (TOF), and polyester selectivity. The lead catalyst is then tested for CTA loading tolerance, revealing an increase in activity with increased alcohol (CTA) loading achieving optimal rate at 200 equiv. CTA with TOF = 1890 h⁻¹. This represents a 4.4x increase in rate over the reaction without CTA, a remarkable result for epoxide/anhydride ROCOP.

Chapter 3 explores the same catalyst series, as in Chapter 2, but for CHO/CO₂ ROCOP. The same parameters are compared between the catalysts, suggesting a different lead catalyst, with a promising rate compared with other literature Al(III)-based polycarbonate ROCOP catalysts. Through kinetic experimentation the polymerisation rate law is established and an equilibrium for CO₂ insertion is revealed and then quantified.

Chapter 4 investigates further the rate law and kinetic influence of CTA on the Al(III)/K(I) catalysed ROCOP. A first order rate dependence on each of: catalyst, epoxide and CTA is deduced from kinetic experimentation. Subsequent CTA scope, kinetic isotope effect reactions and tests on CTA binding to the catalyst imply that the rate enhancement occurs from coordination of alcohol end-capped chain ends to the K(I) which labilises the propagating nucleophile (carboxylate).

Chapter 5 summarises the main findings of this thesis and its implications. An outlook section suggests directions for future research that can build upon the work presented here.

Chapter 6 provides experimental details for Chapters 2-4.

An Appendix is included, presenting all the supplementary figures and data that complement the discussion throughout Chapters 2-4.

Acknowledgements

First of all, I'd like to thank Professor Charlotte Williams for the opportunity to carry out my DPhil under her supervision in her research group. I've greatly appreciated your leadership, insightfulness and encouragement throughout.

I've had the privilege of working alongside a dynamic team of gifted scientists from whom I have learnt so much. Special thanks go to Dr Wilf Diment, Dr Ryan Kerr, Dr Diego Resendiz-Lara, Dr Nora Jannsen and Dr Gemma Fereday-Trott for all your support and guidance. I'm particularly grateful to Nora and Gemma for their help in proof-reading this thesis. Then to everyone else, you've all been such a pleasure to work alongside so thank you all: Kat, Maddie, Mantas, Thom, Greg, George, Sandy, Victor, James, Lukas, Fran, Kam, Kira, Freya, Kristian, Thomas, Balu, Fer, Holly, Rosie, Ploy, Philipp, Brad, Mati, Bonny, David, Kate, Arron, Wouter, Gloria, Hui.

To all those that I have met here in Oxford, however our paths may have crossed, I'm glad that they did; thank you for making this such a wonderful time with so many memories that I will forever cherish.

Finally, a special thank you goes to my family. To Grandmummy and Omi, I have felt your love and prayers always, no matter how far apart we may have been. To my siblings, William, Julian and Eleanor, thank you for always providing healthy competition – I'm so proud of all of you. And, finally, to my parents. Without your unwavering love, support and belief in me, I would not be where I am today. So thank you, this is for you.

List of Publications

Al(III)/K(I) Heterodinuclear Polymerization Catalysts Showing Fast Rates and High Selectivity for Polyester Polyols

Shellard, E. J. K., Diment, W. T., Resendiz-Lara, D. A., Fiorentini, F., Gregory, G. L., Williams, C. K. *ACS Catal.* **2024**, 14 (3), 1363-1374. DOI: [10.1021/acscatal.3c05712](https://doi.org/10.1021/acscatal.3c05712)

Al(III)/K(I) Heterodinuclear Complexes for the Ring Opening Copolymerization of Carbon Dioxide with Epoxides

Shellard, E. J. K., Jannsen, N., Williams, C. K. *Manuscript in preparation*

Investigations into Alcohol-Induced Rate Enhancement of Epoxide/Anhydride Ring Opening Copolymerizations

Shellard, E. J. K., Jannsen, N., Williams, C. K. *Manuscript in preparation.*

Terpene Sourced Epoxides as a Versatile Platform to Achieve Fully Biobased Polyesters with a Wide T_g Range

Holzmüller, P., Resendiz-Lara, D. A., **Shellard, E. J. K.**, Frey, H., Williams, C. K. *Manuscript in preparation.*

Abbreviations

Å	Angstrom
A	Pre-Exponential Factor
AGE	Allyl glycidyl ether
ATR-IR	Attenuated Total Reflectance-Infrared Spectroscopy
BDI	β -diiminate
BDM	Benzene-1,4-dimethanol
BnOD	Deuterated benzyl alcohol
BnOH	Benzyl alcohol
BTM	1,3,5-benzenetrimethanol
Bu	Butyl
°C	Degrees Centigrade
CDCl ₃	<i>d</i> -Chloroform
CHC	Cyclohexene carbonate
CHD	<i>trans</i> -1,2-Cyclohexanediol
CHO	Cyclohexene Oxide
Conv.	Conversion
Cp	Cyclopentadienyl
CPMA	Carbic Anhydride
CTA	Chain Transfer Agent
Cy	Cyclohexyl
δ	NMR Shift
Δ	Change/Difference
$\bar{D}$	Dispersity

D	Diffusion Coefficient
DEC	Diethyl Carbonate
DFT	Density Functional Theory
DGA	Diglycolic Anhydride
dm	Decimeter
DNP	2,4-dinitrophenolate
DOSY NMR	Diffusion Ordered Magnetic Resonance Spectroscopy
DP	Degree of Polymerisation
E_a	Activation Energy
EA	Elemental Analysis
<i>e.g.</i>	for example
Epox.	Epoxide
Equiv.	Equivalents (text)
Eq.	Equivalents (figure)
Et	Ethyl
<i>et al.</i>	and others
g	gram
G	Gibbs Free Energy
$\Delta G^\ddagger$	Transition State Barrier
GEO	Glycerol Ethoxylate
GPC	Gel Permeation Chromatography
h	hour
$\Delta H^\ddagger$	Enthalpy of Activation
HMBC	Heteronuclear Multiple Bond Correlation

HSQC	Heteronuclear Single Quantum Coherence
<i>i.e.</i>	that is
IR	Infrared
J	Joules
k	Rate Constant
K	Kelvin
K_a	Association Constant
kcal	kilocalorie
K_{eq}	Equilibrium Constant
kg	kilogram
K.I.E	Kinetic Isotope Effect
kJ	kilojoule
k_{obs}	Observed Rate Constant
k_p	Polymerisation Rate Coefficient
L	Litres
LO	Limonene oxide
m	minute
M	mol dm^{-3}
M	Metal
MALDI-ToF	Matrix-Assisted Laser Desorption/Ionization – Time of Flight
Me	Methyl
min	minute
mL	millilitre
MM	Michaelis-Menten

mmol	millimole
M_n	Number Average Molecular Weight
mol	mole
MW	Molecular Weight
NBA	Norbornene Anhydride
NMR	Nuclear Magnetic Resonance
no.	number
<i>o</i>	<i>ortho</i>
OAc	Acetate
OH	Hydroxyl Functionality
<i>p</i>	Pressure
PA	Phthalic Anhydride
PCHC	Poly(Cyclohexene Carbonate)
PCHCPE	Poly(Cyclohexene Oxide- <i>alt</i> -Phthalate)
PE	Polyester
Ph	Phenyl
pK_a	Acid Dissociation Constant
PLF	Polymers in Liquid Formulations
PO	Propylene Oxide
PPN	Bis(triphenylphosphine)iminium
Pr	Propyl
PS	Polystyrene
PU	Polyurethane
R	Generic Substituent

R	Universal Gas Constant
r.d.s	Rate Determining Step
ROCOP	Ring Opening Copolymerisation
ROP	Ring Opening Polymerisation
s	second
$\Delta S^\ddagger$	Entropy of Activation
select.	selectivity
T	Temperature
TCA	Tricyclic Anhydride
T_g	Glass Transition Temperature
THF	Tetrahydrofuran
TOF	Turnover Frequency
Tol.	Toluene
TON	Turnover Number
μL	microlitres
V	Volume
vCHO	4-Vinyl-1-cyclohexene oxide
vs.	versus
VT NMR	Variable Temperature Nuclear Resonance Spectroscopy
X	Generic Coligand
XRD	X-ray Diffraction

List of Figures and Tables

Chapter 1: Introduction

- Figure 1.1** ROCOP reaction of epoxides with either anhydrides or CO₂ to produce polyesters and polycarbonates, respectively.
- Figure 1.2** The proposed polymerisation mechanism for epoxide/anhydride ROCOP.
- Figure 1.3** Schematic of epoxide/CO₂ ROCOP, showing the propagation cycle and the side reactions that can occur.
- Figure 1.4** Diagrams representing different groups of catalysts tested.
- Figure 1.5** Some of the first ROCOP catalysts were Al porphyrins that showed activity for PO/CO₂ and PO/PA ROCOP.
- Figure 1.6** Highly active M(III) salen catalysts reported by Darensbourg and Coates and co-workers.
- Figure 1.7** The ligands and metals tested by Duchateau and co-workers for epoxide/anhydride ROCOP.
- Figure 1.8** Bicomponent catalyst systems whose activity with CTA is of interest.
- Figure 1.9** First example of a tethered ROCOP catalyst.
- Figure 1.10** Highly active Co(III) catalysts, with tethered quaternary ammonium salts.
- Figure 1.11** Al(III) porphyrin with tethered cocatalyst showing improved activity for epoxide/CO₂ ROCOP.
- Figure 1.12** (salen)Al(III)X with tethered cocatalyst showing improved loading tolerance and tolerance to CTA.
- Figure 1.13** A (salcy)Co(III)X₂ catalyst that requires water for initiation.
- Figure 1.14** A series of Zn(BDI) catalysts showing intermetallic cooperativity as dimers. Proposed transition state involving two Zn centres.
- Figure 1.15** Highly active *tri*-Cr(III) catalyst with salphen-based ligand.
- Figure 1.16** Highly active *di*-Zn catalysts reported by Rieger and co-workers.
- Figure 1.17** Bottlebrush polymeric Al(III) porphyrin catalysts.
- Figure 1.18** Bimetallic complexes held within a macrocyclic ancillary ligand.

Figure 1.19	A <i>di</i> -Zn(II) catalyst with an <i>ortho</i> -vanillin-based ancillary ligand.
Figure 1.20	Co(III)K(I) catalysts with 'closed' and 'open' ligands.
Figure 1.21	Scheme showing the CO ₂ insertion equilibrium and its influence on polymer propagation.
Figure 1.22	Highly active Al(III)K(I) catalyst with Schiff base ancillary ligand for epoxide/anhydride ROCOP.
Figure 1.23	Proposed 'aluminate' reaction mechanism in rate determining step of epoxide ring opening.
Figure 1.24	The aims and objectives of this thesis – the synthesis of Al(III)K(I) catalysts for the ROCOP of epoxide/anhydride and epoxide/CO ₂ with diol to produce low MW polyesters and polycarbonates.

Chapter 2: Synthesis, Characterisation and Polymerisation Catalysis of Heterodinuclear Al(III)/K(I) *ortho*-Vanillin derived Schiff Base Complexes

Figure 2.1	(a) The series of Al(III)/K(I) heterobimetallic catalysts differing by imine linker groups. (b) Catalyst synthesis.
Figure 2.2	¹ H NMR Spectrum of complex 1 (CDCl ₃ (#), 298 K, 400 MHz)
Figure 2.3	(a) Molecular structure of complex 1 obtained from X-ray diffraction experiments. Overall structure is polymeric. (b) Schematic showing a repeat unit (monomer) of the polymeric structure.
Table 2.1	Selected bond lengths for L _{C2Me2} AlK(OAc) ₂ 1
Figure 2.4	(a) Molecular structure of complex 2 obtained from X-ray diffraction experiments. Overall structure is polymeric. (b) Schematic showing a repeat unit (monomer) of the polymeric structure. (c) Molecular structure showing connectivity.
Figure 2.5	(a) Molecular structure of complex 5 obtained from X-ray diffraction experiments. Overall structure is polymeric. (b) Schematic showing a repeat unit (monomer) of the polymeric structure.
Table 2.2	Polymerisation data for CHO/PA ROCOP with catalysts 1-6 .
Table 2.3	Rates for CHO/PA ROCOP by complex 4 .
Figure 2.6	Graph of [PA] against time for CHO/PA ROCOP using catalyst 1 and 2 .

Figure 2.7	(a) Plot of change in polymer molar mass and dispersity with PA conversion for catalyst 1 . (b) GPC trace of PCHPE at full conversion produced by catalyst 1 .
Figure 2.8	Plot of computed reaction profile for epoxide ring-opening for 1 and 4 showing a slightly lower energy barrier for 1 .
Table 2.4	Data for the CHO/PA ROCOP with variable loadings of diol (CHD) using catalyst 1 .
Figure 2.9	(a) Evolution of molar mass, at full PA conversion, vs. the amount of diol added (0-200 equiv.) as illustrated by the GPC data. (b) Plot of polyester M_n at full conversion vs. $1/[\text{HO-R-OH}]$.
Figure 2.10	MALDI-ToF of PCHPE obtained with complex 1 . Conditions: $[\mathbf{1}]:[\text{CHD}]:[\text{PA}]:[\text{CHO}] = 1:20:400:2000$
Figure 2.11	MALDI-ToF of PCHPE obtained with complex 1 . Conditions: $[\mathbf{1}]:[\text{CHD}]:[\text{PA}]:[\text{CHO}] = 1:100:400:2000$
Figure 2.12	Plot of k_{obs} vs. $[\text{HO-R-OH}]$ and vs. CHD equivalents.
Figure 2.13	Graph of TOF against Degree of Polymerisation (DP).
Figure 2.14	A pictorial representation of DP = 10 at two different CTA concentrations.
Table 2.5	Table showing catalyst activity Air/N ₂ atmospheres and with purified monomers or unpurified monomer.
Table 2.6	Table showing catalyst activity at different catalyst loadings.
Figure 2.15	Graph showing TOF for different monomer combinations.
Table 2.7	Data for epoxide/anhydride ROCOP monomer scope using catalyst 1 .
Figure 2.16	The organometallic Al(III)K(I) complex reported by Diment <i>et al.</i>

Chapter 3: Al(III)/K(I) Heterobimetallic Complexes for the Ring-Opening Copolymerisation of Epoxides with CO₂

Figure 3.1	Schematic of epoxide/CO ₂ ROCOP, showing the propagation cycle and the side reactions that can occur.
Figure 3.2	The scope of Al(III)/K(I) complexes tested in this study. The diamine backbone of the ancillary ligand has been varied.

Table 3.1	Polymerisation data for CHO/CO ₂ ROCOP with catalysts 1-6 .
Table 3.2	Polymerisation results for CHO/CO ₂ ROCOP at high CO ₂ pressures.
Figure 3.3	(a) GPC trace of polymer produced from [2]:[CHO] = 1:2000. (b) GPC trace of polymer produced from [2]:[CHD]:[CHO] = 1:20:4000.
Table 3.3	Epoxide scope using 2 .
Figure 3.4	(a) Plot of $\ln([CHO]_t/[CHO]_0)$ vs. time for CHO/CO ₂ ROCOP. (b) Plot of k_{obs} vs. [cat] for CHO/CO ₂ ROCOP catalysed by 2 (c) Plot of $\ln[k_{obs}]$ vs. $\ln[cat]$ with gradient of 1.3. (d) Plot of TOF at 20 % conversion vs [CHO]/[2].
Figure 3.5	(a) Graph of k_{obs} vs. $p(CO_2)$ for CHO/CO ₂ ROCOP catalysed by 2 at 5 - 30 bar CO ₂ . (b) Graph of k_{obs} vs [CO ₂] where [CO ₂] is calculated from $p(CO_2)$ by linear calibration
Figure 3.6	Graph of PCHC selectivity vs. $p(CO_2)$ for CHO/CO ₂ ROCOP catalysed by 2 at 5 - 30 bar CO ₂ .
Figure 3.7	Concentration vs. time data for experimentally determined values and the calculated values using COPASI kinetic modelling of pressure dependent rate law. (a) 12.5 bar CO ₂ pressure. (b) 25 bar CO ₂ pressure.
Figure 3.8	Scheme showing the CO ₂ insertion equilibrium and its influence on polymer propagation.
Figure 3.9	Concentration vs. time data for experimentally determined values and the calculated values using COPASI kinetic modelling of unified rate law. (a) 12.5 bar CO ₂ pressure. (b) 25 bar CO ₂ pressure.
Figure 3.10	Diagram showing catalytic propagation cycle and off-cyclic back-biting.
Figure 3.11	Plot of $\ln(k_p/T)$ vs. $1/T$ for the forward polymerisation of CHO/CO ₂ ROCOP catalysed by 2 over the temperature range 90-110 °C.
Figure 3.12	Plot of $\ln(k_p/T)$ vs. $1/T$ for backbiting of polycarbonate to form <i>trans</i> -cyclic carbonate catalysed by 2 over the temperature range 105-120 °C.

Chapter 4: Investigations into Alcohol-Induced Rate Enhancement

- Figure 4.1** CHO/PA polymerisation (i) $[1]:[PA]:[CHO] = 1:400:2000$ (ii) $t = 25$ mins, $V(\text{BnOH or Tol}) = 25.7 \mu\text{L}$ (50 equiv.) added.
- Figure 4.2** Plot of PCHPE production given as conversion (%) against t (min) for $[1]:[PA]:[CHO] = 1:400:2000$; $t = 25$ mins, $V(\text{BnOH or Tol}) = 25.7 \mu\text{L}$ (50 equiv.) added.
- Figure 4.3** (a) GPC plot of PCHPE at full conversion from $[1]:[PA]:[CHO] = 1:400:2000$; $t = 25$ mins, 50 equiv. BnOH added. (b) MALDI-ToF of same PCHPE sample.
- Figure 4.4** The series of alcohols tested: benzyl alcohol (BnOH), benzene-1,4-dimethanol (BDM) and 1,3,5-benzenetrimethanol (BTM).
- Figure 4.5** Graph showing rate of reaction, k_{obs} ($\times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$), against no. of hydroxyl groups in CTA.
- Figure 4.6** Graph showing M_n (g mol^{-1}) at full conversion against number of hydroxyl groups in CTA.
- Table 4.1** Additional CTA scope.
- Figure 4.7** Plot of rate of reaction, k_{obs} against $[\text{BnOH}]$.
- Figure 4.8** Plot of rate of reaction, k_{obs} against $[\text{BnOH}]$ overlayed with baseline rate $k_{\text{obs}} = 3.90 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ from very high purity monomers and no BnOH.
- Figure 4.9** Plot of $[\text{PA}]$ against time.
- Figure 4.10** Plot of $\ln([CHO]_t/[CHO]_0)$ against t .
- Figure 4.11** Plot of k_{obs} against $[\text{cat}]$.
- Figure 4.12** Plot of $\ln(k_{\text{obs}})$ against $\ln([\text{cat}])$.
- Figure 4.13** Plot of concentration against time for the reaction $[1]:[PA]:[CHO] = 1:400:2000$. Experimental values and COPASI model.
- Figure 4.14** Plot of concentration against time for the reaction $[1]:[\text{BnOH}]:[PA]:[CHO] = 1:25:400:2000$. Experimental values and COPASI model.
- Figure 4.15** Plot of rate of reaction, k_{obs} , against $[\text{BnOH}]$ overlayed with rates obtained by COPASI kinetic modelling.
- Figure 4.16** Proposed mechanism of PA/CHO ROCOP catalysed by **1** with CTA, showing two pathways (1 & 2) where $k_2 > k_1$.

Figure 4.17	Diagrams indicating possible interactions of alcohol in the transition state that could lower the energy barrier for epoxide ring opening. (a) Hydrogen bonding to coordinated epoxide. (b) Coordination of O to K(I).
Table 4.2	Rate, k_{obs} , and activity, TOF, for BnOH and BnOD for $[1]:[\text{BnOH/D}]:[\text{PA}]:[\text{CHO}] = 1:50:400:2000$
Figure 4.18	(a) Graph of $[\text{PA}]$ against time for BnOH and BnOD for $[1]:[\text{BnOH/D}]:[\text{PA}]:[\text{CHO}] = 1:50:400:2000$. (b) Graph comparing rate of reaction, k_{obs} .
Figure 4.19	Equilibrium between 1 and 1 •BnOH.
Figure 4.20	^1H NMR spectra (CDCl_3 (#), 298 K, 400 MHz) of 1 with increasing equiv of BnOH (0 – 400).
Figure 4.21	Plot of NMR shift, δ , of proton g against equivalents of BnOH added ($[\text{BnOH}]/[\mathbf{1}]$) for binding studies.
Figure 4.22	Plot of estimated mole fraction of bound vs. unbound of 1 for varying equivalents of BnOH ($[\text{BnOH}]/[\mathbf{1}]$). Calculated by Bindfit.
Figure 4.23	Molecular structure of complex 1 with H_2O bound at the K(I), obtained from X-ray diffraction experiments.
Table 4.3	Selected bond lengths for $[\mathbf{1}\cdot\text{H}_2\text{O}]$

Chapter 5: Conclusions and Outlook

Figure 5.1	Thesis summary.
Figure 5.2	(a) Al(III)K(I) catalyst ligand modification for further catalyst optimisation. (b) Ligand backbone modifications for potential improvements on existing epoxide/ CO_2 ROCOOP catalysts.
Figure 5.3	(a) Future alcohol rate enhancement studies for epoxide/ CO_2 ROCOP and lactone ROP. (b) Upscaling the catalysis for production of PLFs.

Table of Contents

Declaration	3
Abstract	4
Acknowledgements	6
List of Publications	7
List of Abbreviations	8
List of Figures and Tables	13
Table of Contents	19
Chapter 1: Introduction	23
1.1 Polyesters/carbonates and their Industrial Production	24
1.2 Epoxide/Heteroallene Ring-Opening Copolymerisation	25
1.2.1 Polymerisation Mechanisms	26
1.2.2 Catalysts	30
1.3 Early Discovery and Development of ROCOP Catalysts	30
1.4 Monometallic Complexes with Cocatalyst	31
1.4.1 Porphyrins	31
1.4.2 Metal(salen)X Catalysts	33
1.4.3 Role of Cocatalyst	35
1.4.4 Al(III) Catalysts for Epoxide/CO ₂ ROCOP	35
1.4.5 CTA Tolerance of Bicomponent Catalyst Systems	35
1.5 Multifunctional Catalysts	37
1.5.1 Tethered Cocatalyst	37
1.5.2 Improved Catalyst Loading Tolerance	39
1.5.3 CTA Tolerance of Bifunctional Catalysts	41
1.6 Multi-Homometallic Complexes	43
1.6.1 β -Diiminate Zinc Catalysts	43
1.6.2 Tethered Monometallic Complexes	44
1.6.3 Bottlebrush Polymeric Aluminium Porphyrin Catalysts	46
1.6.4 Bimetallic Complexes with Macrocyclic Ancillary Ligands	48
1.7 Multi-Heterometallic Complexes	51
1.7.1 Intermetallic Synergy	51

1.7.2	Dinuclear Metallate ROCOP Mechanism for M(III)M(I/II) Catalysts	51
1.7.3	CO ₂ Insertion Equilibrium, K_{eq}	52
1.7.4	Co(III)M(I/II), s-Block Metal Lewis Acidity-Activity Trends	54
1.7.5	Heterodinuclear Al(III) Catalysts	55
1.8	Aims and Objectives	57
1.9	References	60
Chapter 2: Synthesis, Characterisation and Polymerisation Catalysis of Heterodinuclear Al(III)/K(I) <i>ortho</i>-Vanillin derived Schiff Base Complexes		68
2.1	Introduction and Aims	69
2.2	Synthesis and Characterisation	71
2.2.1	Synthesis	71
2.2.2	NMR Spectroscopy	72
2.2.3	X-ray Crystallography	74
2.3	Epoxide/Anhydride ROCOP Catalysts	77
2.3.1	Catalyst Series	77
2.3.2	Kinetic Runs of Lead Catalysts	81
2.3.3	DFT Studies into Effect of Catalyst Backbone	83
2.4	Using Chain Transfer Agent to Control MW and Enhance Polymerisation Rate	84
2.5	Catalyst Stability Tests	91
2.6	Monomer Scope	94
2.7	Conclusions and Outlook	96
2.8	References	99
Chapter 3: Al(III)/K(I) Heterobimetallic Complexes for the Ring-Opening Copolymerisation of Epoxides with CO₂		102
3.1	Introduction and Aims	103
3.2	Catalyst Scope Tests	105
3.2.1	Al(III)/K(I) Low CO ₂ Pressure Tests	105
3.2.2	High-Pressure Polymerisations and Discussion	108
3.2.3	Monomer Scope	111
3.3	Kinetic Analysis of $L_{Cyc}AlK(OAc)]_2$ (2)	113
3.3.1	Determining k_{obs}	113

3.3.2	Order in [CHO]	114
3.3.3	Order in [cat]	115
3.3.4	Order in [CO ₂]	115
3.3.5	Proposed Rate Law	117
3.4	Towards a Unified Rate Law with K_{eq}	118
3.5	Eyring Analysis	124
3.5.1	Polycarbonate Reaction Barrier	125
3.5.2	Cyclic Carbonate Barrier	125
3.5.3	Discussion	127
3.6	Conclusions and Outlook	128
3.7	References	129
Chapter 4: Investigations into Alcohol-Induced Rate Enhancement		133
4.1	Introduction and Aims	134
4.2	Polymerisation Rate Enhancement Tests	135
4.2.1	Addition of CTA Partway Through Polymerisation	135
4.2.1.1	Rates of Polymerisation	135
4.2.1.2	GPC M_n of Polymers Produced	137
4.2.2	Chain Transfer Agent Scope	139
4.2.2.1	CTA Functionality Test	139
4.2.2.2	CTA Further Scope	141
4.3	Reaction Kinetics	142
4.3.1	Reaction Order in Chain Transfer Agent	142
4.3.2	Overall Reaction Kinetics	145
4.3.3	Proposed Rate Equation	147
4.3.4	Kinetic Modelling using Rate Law	148
4.3.5	Proposed Reaction Mechanism	152
4.3.6	Proposed Methods for Rate Enhancement in Transition State	153
4.4	Diagnostic Tests into the Nature of Alcohol in Rate Determining Steps	154
4.4.1	Kinetic Isotope Effect	154
4.4.2	Binding Studies	157
4.4.3	X-ray Crystallography of Proposed Intermediates	160
4.5	Conclusions and Outlook	162

4.6	References	163
Chapter 5: Conclusions and Outlook		165
5.1	Thesis Summary	166
5.2	Outlook	169
5.2.1	Heterodinuclear Catalysts	169
5.2.2	Alcohol Acceleration of Polymerisation Rates	171
5.3	References	173
Chapter 6: Experimental Details		175
6.1	General Considerations	176
6.2	Monomer and CTA Purification Procedures	176
6.3	Methods	177
6.4	General Polymerisation Procedures	179
6.5	Binding Studies	183
6.6	Characterising Data for Chapter 2	183
6.7	COPASI Modelling Parameters	190
6.8	References	191
Appendix		193
	Supplementary Figures and Tables for Chapter 2	198
	Supplementary Figures and Tables for Chapter 3	244
	Supplementary Figures and Tables for Chapter 4	255
	References	261

Chapter 1

Introduction

1.1 Polyesters/carbonates and their Industrial Production

Plastics have had a transformational impact on society and are pervasive in almost all areas of daily life. Global plastics production has steadily increased year on year, however, only just over 9 % of plastics are recycled, with 0.7 % being bio-based whilst around 22.5 % of plastic waste is considered mismanaged.^{1, 2} Plastic production and disposal also contributed to 3.3 % of global CO₂eq emissions in 2019.³ This has to change in order to reduce plastic waste entering the environment and the detrimental climate impact its production and consumption has.^{4, 5} This requires a radical transformation of the lifecycle of plastics with an emphasis on recyclability and biodegradability whilst ensuring renewable feedstocks or CO₂ are used. A recent perspective by Vidal *et al.* concluded that in order to meet global climate targets, a 50 % reduction in plastic use, the entire avoidance of fossil-based feedstocks and a 95 % recycling rate are required.⁴ In order to facilitate a high rate of (bio)chemical recyclability, polymers with cleavable bonds should be widely used.^{6, 7} Two classes of polymers that show particular promise in this regard are polyesters and polycarbonates.⁸⁻¹⁰

This thesis will focus more specifically on the production of low molecular weight (MW) polymers, targeted for use in liquid formulations (PLFs) and pre-polymers for use in polyurethane (PU) or resin. PLFs are a broad group of polymers that typically have low molecular weights of between 2 - 10 kg mol⁻¹. PLFs are found in a wide range of formulated products including those for household cleaning, personal care, cosmetics, medicine, agriculture, coatings, paints, and sealants, where they act as thickeners, emulsifiers or stabilizers.^{7, 11} The combined value of the markets that PLFs are used in is \$1.3 trillion and annually 36 million metric tonnes are produced.¹¹ The nature of their application means that it is very challenging to recover PLFs after use and they often leach

into the environment. The future direction towards sustainable PLF production and use must focus on de-fossilising their feedstocks used and ensuring that there is full degradation into non-toxic metabolites at the end of use.^{7, 10, 12, 13} The delivery of such PLFs requires improvements to the production of degradable polymers; this work focusses on polyesters and polycarbonates.^{10, 14} These types of polymers are selected because many of the monomers can be derived from renewable feedstocks (or CO₂) and a range of enzymes, both natural and modified are known and continue to be discovered for ester hydrolysis and, in some cases, biodegradation.^{10, 14, 15} Furthermore, the by-products of such degradations – diol and diacids – are often metabolites and/or show low toxicity.¹⁴ The challenge for sustainable PUs or resins is on recyclability and on reducing the overall lifecycle CO₂ emissions.^{7,11,16}

Today, the industrial production of both polyesters and polycarbonates generally applies step-growth polycondensation reactions: polyesters by combining diesters/diacids with diols or using hydroxyl acids, and polycarbonates by diols typically with phosgene.^{17, 18} These reactions are energy intensive, requiring high temperatures and reduced pressures or high airflow and they rely on petrochemicals, some of which are toxic. An alternative synthesis route that shows great promise is the ring-opening copolymerisation (ROCOP) of epoxides with either anhydrides or CO₂. These controlled polymerisations will be the focus of the thesis.

1.2 Epoxide/Heteroallene Ring-Opening Copolymerisation

Heterocycle/heteroallene ring-opening copolymerisation is a catalytically controlled polymerisation resulting in the sequential ring opening of epoxides with either cyclic anhydrides or CO₂ to produce polyesters and polycarbonates, respectively (Figure 1.1).

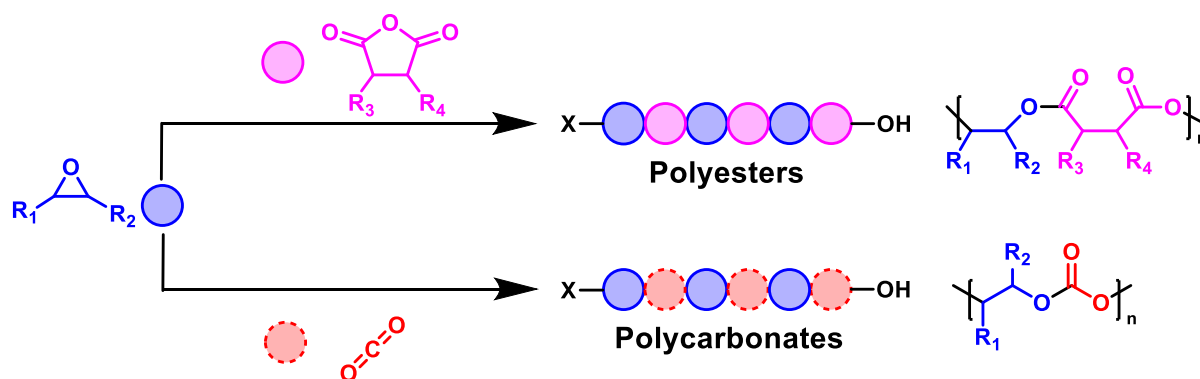


Figure 1.1 ROCOP reaction of epoxides with either anhydrides or CO_2 to produce polyesters and polycarbonates, respectively.

Epoxide/anhydride and epoxide/ CO_2 ROCOP benefits from being atom economical and having a broad monomer scope, allowing for diverse polymer properties.^{19, 20} Many epoxides and anhydrides are already commercial, and many more have viable synthesis routes from bio-renewable sources, as well as sequestering, if only temporarily, CO_2 into the polymer.^{13, 15} Studies have shown that widespread use of CO_2 in polycarbonate production could contribute to a 10-50 Mt yr⁻¹ reduction in CO_2 emissions by 2050, and, in polypropylene carbonate production, for every 1 kg CO_2 used, there is a net 3 kg CO_2 eq GHG emissions reduction for that polyol.^{21, 22} ROCOP has already been implemented commercially, primarily to produce polycarbonates, and has a well-established academic history.^{5,15,19} All-in-all, ROCOP is effective at delivering aliphatic, semi-aromatic, functionalised and/or polar polyesters and carbonates with exceptional end group and MW control and narrow dispersities.^{10, 20}

1.2.1 Polymerisation Mechanisms

The general mechanistic scheme for ROCOP is commonly accepted but there are recent and ongoing discoveries that improve understanding of the catalysis, in particular, insights into factors that control the polymerisation rate and selectivity. The mechanisms

for polyester and polycarbonate production are apparently quite similar but it is not always the case that the same catalysts are effective for both reactions.²³⁻²⁵

Firstly, the polyester mechanism is discussed, which involves the sequential ring opening of an epoxide and an anhydride (Figure 1.2):

The polymerisation starts with an **initiation**. An initiating catalyst refers to a coligand being able to start the polymerisation. In this work, acetates will be used as the initiating coligands; such metal-carboxylates undergo nucleophilic attack at the epoxide causing it to ring open, forming a metal-alkoxide that goes on to further react. This initiation process is typically fast, however, choice of catalyst and coligand can impact its rate.²⁶

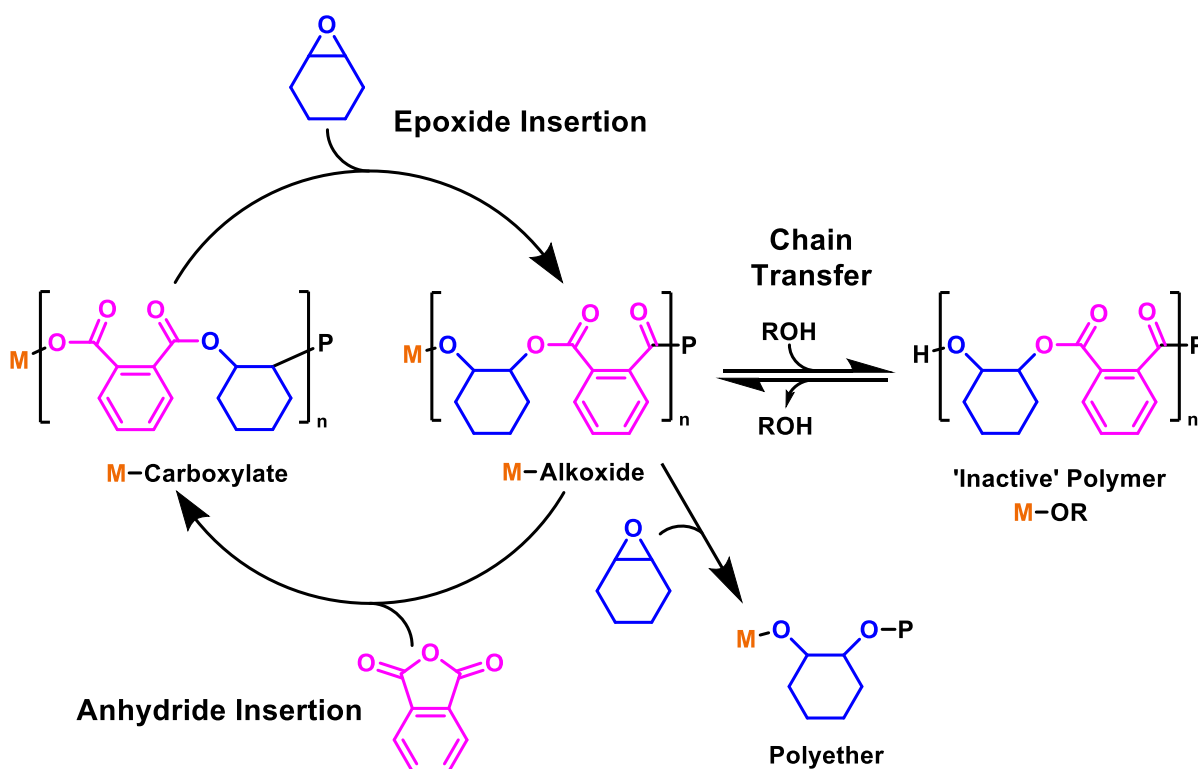


Figure 1.2 The proposed polymerisation mechanism for epoxide/anhydride ROCOP, illustrating propagation steps for phthalic anhydride (PA) and cyclohexene oxide (CHO) insertions, along with fast and reversible chain transfer reactions with alcohols.

The **propagation** step, as mentioned above, involves the sequential cycling between metal alkoxide (from epoxide ring opening on the metal and subsequent insertion) and metal-carboxylate (from an analogous process with the anhydride) intermediates.²⁷ This cycling leads to a perfectly alternating polyester. When the catalysis is studied, the epoxide ring opening is often rate-limiting, resulting in a first-order rate dependence. The polymerisations are usually zero order in anhydride, suggesting anhydride insertion occurs more rapidly than epoxide ring opening.²⁸ Therefore, reactions are often run in neat epoxide which acts as a solvent as well as a reactant.

Chain transfer is a rapid off-cycle equilibrium involving proton exchange, or a chain transfer reaction, between the metal-alkoxide intermediates and inactive 'free' polymer chains that are end-capped with alcohols. A chain transfer agent (CTA), often an alcohol, initiates this process and the quantity added is used to regulate polymer molecular weight (M_n), made possible because chain transfer typically occurs faster than polymerisation propagation.²⁹⁻³¹ It also allows for control of the polymer chain end group identity. This is used to greatest effect when targeting low molar mass hydroxyl telechelic polyesters (from diols), allowing for minimal catalyst loading to be used. Conversely, this means that any water can react with epoxides to form diol impurities which then act as chain transfer agents, resulting in the need for very pure monomers and anhydrous conditions when synthesising high MW polymers. Unfortunately, many catalysts become inactive or show severely diminished rates when applied with excess diols or other protic chain transfer agents.^{5,19,20} This occurs both by catalyst decomposition (by ancillary ligand decompositions) and by coordination to the metal, that competitively inhibits monomer binding.³²

An unwanted side reaction is the formation of **ether** linkages. This is when two epoxides ring open sequentially without an anhydride in between. A few catalysts can selectively control the amount of ether linkages within the polymer, but this is beyond the scope of this study.^{33, 34} When benchmarking catalysts for ROCOP, selectivity for the alternating polymer is usually reported and often the goal.

The catalytic cycle for epoxide/ CO_2 ROCOP to produce polycarbonates is shown in Figure 1.3. This follows an analogous reaction pathway, with initiation, propagation and chain transfer, as well as off-cycle ether linkage formation. CO_2 insertion is considered reversible, giving rise to an equilibrium that is governed by CO_2 pressure, with high pressure favouring M-carbonate formation.^{24, 25, 35, 36}

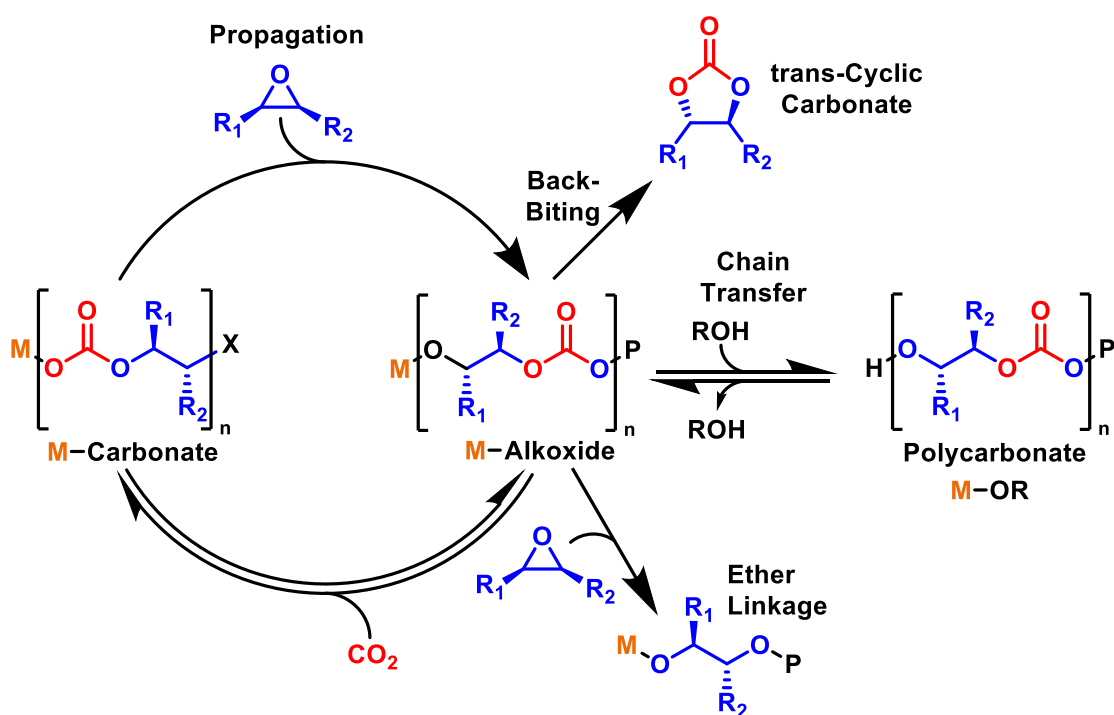


Figure 1.3 Schematic of epoxide/ CO_2 ROCOP, showing the propagation cycle and the side reactions that can occur, including reversible chain transfer, back-biting to form cyclic carbonate and subsequent epoxide insertions to produce ether linkages.

Backbiting is a side reaction that produces cyclic carbonate instead of polymer. This can happen from either the M-carbonate or the M-alkoxide intermediate; many catalysts show that most cyclic carbonate forms from the metal-alkoxide intermediate. The cyclic carbonate is the thermodynamic product of epoxide/CO₂ coupling and so is favoured at high temperatures. Low CO₂ pressures also favour cyclic carbonate formation since the CO₂ insertion equilibrium shifts towards the alkoxide intermediate. This cyclic carbonate side reaction should be suppressed because these products are challenging to remove from the final polymer product and reduce the overall atom-economy of the process.

1.2.2 Catalysts

The best ROCOP catalysts combine fast rates, with high selectivity for the alternating polymer, operating at low catalyst loadings and offering good polymerisation control. Ideally, catalyst synthesis should be straightforward, using earth-abundant, non-toxic, and inexpensive metals.^{27,37-39} There is still significant potential for improving the catalyst CTA tolerance.³² Several classes of catalyst will be considered here (Figure 1.4). These include bicomponent catalyst systems (Section 1.4), with a mono-metallic complex and cocatalyst, multifunctional catalysts (Section 1.5), where a cocatalyst is tethered to the ancillary ligand of a monometallic complex, and finally multi-metallic complexes, that can be either homonuclear (Section 1.6) or heteronuclear (Section 1.7).

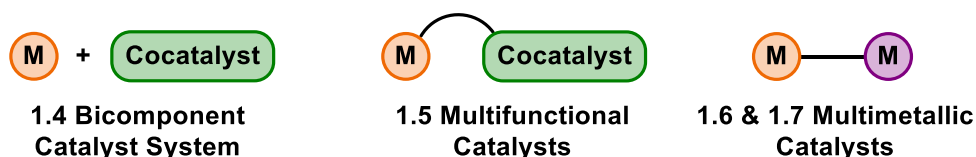


Figure 1.4 Diagrams representing different groups of catalysts tested.

1.3 Early Discovery and Development of ROCOP Catalysts

The first homogeneous epoxide/anhydride ROCOP catalysts were simple bases, discovered as a consequence of using anhydrides as cross-linkers for epoxy resins in 1954.^{40, 41} The polymers were produced from phthalic anhydride and phenyl glycidyl ether and contained both ester and ether linkages in the polymer backbone. The addition of a tertiary amine was first shown to improve the quantity of ester versus ether crosslinkers for the epoxy resins, and was then also shown to suppress polyether formation in ROCOP which led to the production of linear polyesters.⁴²⁻⁴⁴ At this stage, there was still limited understanding of reaction mechanism but it had been identified that protic impurities limited the resultant polymer MW.⁴⁴

A few years later, Inoue and co-workers discovered the copolymerisation of the epoxide propylene oxide (PO) with CO₂ using diethylzinc and water (ZnEt₂/H₂O) to produce a polycarbonate.⁴⁵ In this study, triethylaluminium (AlEt₃) was also tested but it resulted in mainly polyether.⁴⁵ Later work successfully used AlEt₃ to produce an alternating copolymer by adding a Lewis base to the polymerisation.⁴⁶

These two revolutionary polymerisations paved the way for decades of further catalyst development and mechanistic exploration in order to best harness the potential of producing polyesters and polycarbonates by the ROCOP of epoxides with anhydrides and CO₂.

1.4 Monometallic Complexes with Cocatalyst

1.4.1 Porphyrins

Pioneering work, by Inoue and co-workers, reported that Al-porphyrins could catalyse ROCOP.^{47, 48} Firstly, this was shown for PO/CO₂ in 1978 [1.1]⁴⁷ and then in 1985 with a different porphyrin ligand [1.2] PO/PA ROCOP was performed (Figure 1.5).⁴⁸ The catalysis for PO/PA ROCOP by [1.2] had a turnover frequency (TOF) = 4-7 day⁻¹ (4 % vs. PA; *T* = 25 °C), required an Et₄NX cocatalyst, and yielded polymers with a narrow dispersity (*D* = 1.1) but still relatively low *M_n* (3,000 g mol⁻¹).

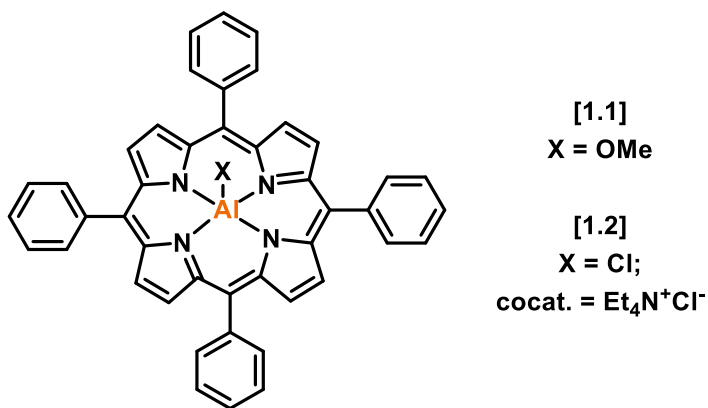


Figure 1.5 Some of the first ROCOP catalysts were Al(III) porphyrins that showed activity for PO/CO₂ and PO/PA ROCOP.^{29, 47}

In this study, ¹³C{¹H} Nuclear Magnetic Resonance (NMR) experiments revealed that the carboxylate of the (porphinato)aluminium was much more abundant in the polymerisation mixture than the alkoxide, and so from this it was inferred that the anhydride ring opening from the alkoxide occurred faster than the ring opening of the epoxide from the carboxylate.⁴⁸ ¹H NMR experiments, where cocatalyst Et₄N⁺RCOO⁻ was progressively added, suggested that there was an equilibrium leading to the formation of a structure where the carboxylate groups coordinate axially on the Al and the Et₄N⁺ is closely bound.⁴⁸ Further work examined a (porphyrin)Al(III)Cl/MeOH & EtOH system

for epoxide ring opening polymerisation (ROP) and demonstrated that chain transfer was occurring.²⁹

Other metals, such as (porphyrin)Cr(III)Cl, were also somewhat active for epoxide/anhydride and CO₂ ROCOP, but the addition of a cocatalyst was essential for the polymerisation to occur.^{19, 49-51}

1.4.2 Metal(salen)X Catalysts

Metal(salen)X complexes are important catalysts that have been extensively investigated for epoxide/CO₂ and epoxide/anhydride ROCOP producing both polycarbonates and polyesters.⁵²⁻⁵⁵

An early study by Darensbourg and co-workers identified a (salen)Cr(III)Cl/*N*-methyl imidazole catalyst system for CHO/CO₂ ROCOP to form poly(cyclohexene carbonate) (PCHC).⁵⁶ Subsequent iteration on this catalyst system, in particular altering the cocatalyst added to [PPN⁺N₃⁻] (PPN is Bis(triphenylphosphine)imine), resulted in a very active epoxide/CO₂ ROCOP catalyst system **[1.3]** (TOF = 1150 h⁻¹; >99 % PCHC; **[1.3]**: [PPN⁺N₃⁻]: [CHO] = 1:1:2300; *p*(CO₂) = 35 bar; *T* = 80 °C) (Figure 1.6).⁵⁷

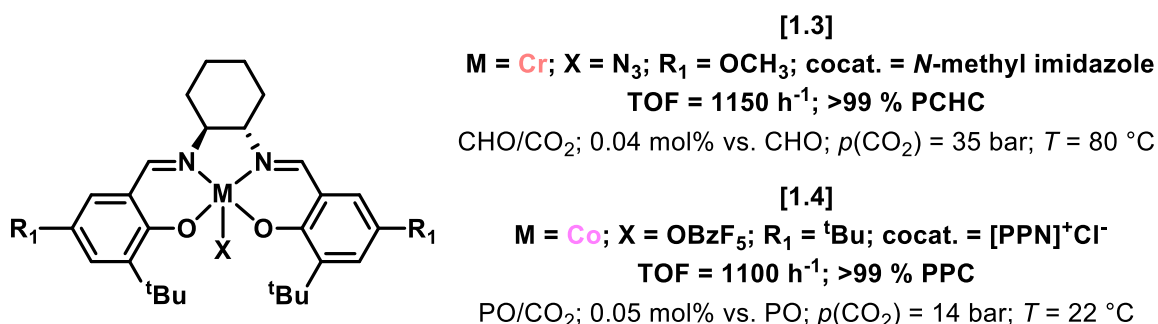


Figure 1.6 Highly active M(III) salen catalysts reported by Darensbourg⁵⁷ and Coates⁵⁸ and co-workers.

A (salen)CoX catalyst [**1.4**], reported by Coates and co-workers, showed high activities for PO/CO₂ ROCOP (TOF = 1100 h⁻¹; >99 % PPC; [**1.4**]:[PPNCl]:[PO] = 1:1:2000; *p*(CO₂) = 14 bar; *T* = 22 °C) (Figure 1.6).⁵⁸ The cocatalyst added, consisting of a bulky non-coordinating cation and a nucleophilic anion ([PPN]Cl or [PPN][OBzF₅]), showed improvements in not only reaction rate, but also regio- and stereoselectivity of the polymers produced.

A study on the ROCOP of epoxides with anhydrides by (salen)M(III)X was conducted by Duchateau and co-workers, comparing catalytic activity with different ligand backbones, metals (Al, Cr, Co) and cocatalysts (Figure 1.7).⁵⁴ The lead catalyst was a (salophen)Cr(III)X ([**1.5**], Figure 1.7) since it showed the most consistent high activity across the anhydrides tested (TOF = 235 h⁻¹; [**1.5**]:[PPNCl]:[PA]:[CHO] = 1:1:250:250; *T* = 110 °C).⁵⁴

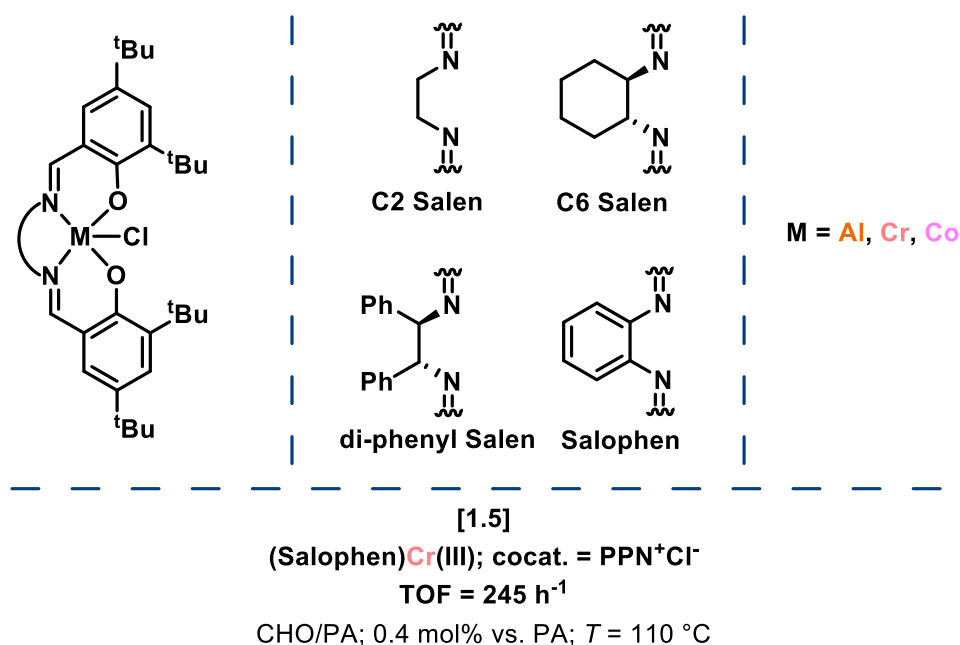


Figure 1.7 The ligands and metals tested by Duchateau and co-workers for epoxide/anhydride ROCOP.⁵⁴

Ligand backbones with the greatest steric bulk had a negative impact on rate, whereas those that were less sterically encumbered (ethylenediamine and cyclohexyldiamine)

had near identical rates. The cocatalyst (PPNCl) loading of 1 equiv. relative to the catalyst was required to reach optimum activity. When used as a cocatalyst, phosphines and *N*-heterocyclic nucleophiles both needed to be added in higher quantities (vs. metal complex) to achieve peak activity and these polymerisations were almost always slower than when using salt cocatalysts.

1.4.3 Role of Cocatalyst

Further kinetic insights looking specifically at the cocatalyst revealed that the catalyst and cocatalyst operate as a cooperative ion pair.³⁸ This meant that at high loadings, there was a pseudo first order for the catalytic pair, but a second order behaviour at much lower loadings. This results in a dilution effect where, as the catalyst system concentration is dropped, a drastic drop in catalytic activity is observed. From this work and others, it is now believed that there is a pre-equilibrium of epoxide binding, and then the rate determining step is the ring opening of a M-coordinated epoxide by a carboxylate that is stabilised by the cocatalyst.^{38, 59}

1.4.4 Al(III) Catalysts for Epoxide/CO₂ ROCOP

Al(III) complexes are interesting for use in ROCOP catalysts due to Al's earth abundance, low cost and low toxicity.⁶⁰ One challenge most evident in epoxide/CO₂ ROCOP is that replacing Co(III) or Cr(III) with Al(III) in the same ancillary ligand almost always significantly reduces the catalytic activity. This lower activity for Al(III) complexes is clearly seen for porphyrins,¹⁹ salens,^{54, 61} and amino-phenolates.⁶² In later sections of this chapter (Section 1.5), a few examples of catalyst design will be discussed that have a positive effect on catalytic activity of Al(III) complexes.

1.4.5 CTA Tolerance of Bicomponent Catalyst Systems

In addition to metal choice, tolerance to chain transfer agent will be of important consideration in this thesis since the objective is to make polymers for formulations ($2 < M_n < 10 \text{ kg mol}^{-1}$). Generally, catalyst tolerance to a large excess of CTA is either not directly explored or unreported. This is especially the case for bicomponent catalyst systems, because they are overwhelmingly deactivated by the presence of protic impurities.³²

A notable study into why alcohols/protic compounds deactivate catalysts was conducted by Coates and co-workers.³⁰ The authors reported that for a (salen)Al(III)Cl/PPNCl bicomponent catalyst ([**1.6**], Figure 1.8), there was a 64 % decrease in TOF when just 10 equiv. of 1-adamantanecarboxylic acid was added to the polymerisation ([**1.6**]:[carbocyclic anhydride (CPMA)] = 1:1,200; $T = 60 \text{ }^{\circ}\text{C}$).³² The choice of cocatalyst did not solve the deactivation problem. From Lineweaver-Burk analysis of catalyst-alcohol coordination, there appeared to be mixed mechanisms for the inhibition. The interpretation of the results was that the polymer chain ends being able to directly compete with the epoxide binding by coordinating to the Al(III), whilst also deactivating the carboxylate nucleophile (needed to attack the epoxide) by hydrogen-bonding to these anionic chain ends (when they dissociate to enable epoxide binding to the metal centre in the rate limiting step).

There are two notable catalyst exceptions to the general rule that alcohols/acids deactivate (Figure 1.8). In 2022, Fieser and co-workers reported that the hydrated $\text{YCl}_3(\text{H}_2\text{O})_6$ /PPNCl [**1.7**] catalyst system showed an increase in activity over the anhydrous variant (i.e. $\text{YCl}_3(\text{THF})_3$ /PPNCl), under similar reaction conditions; a useful result since it allowed for use of unpurified monomers and for the polymerisation to be

carried out in air.⁶³ Recently, Chen *et al.*, reported a (bipyridine bisphenolate)Al(III)(Cl)/PPNCl **[1.8]** catalyst that maintained ~85% of its rate when applied with up to 100 equivalents of maleic acid.⁶⁴ Tests seem to indicate this was due to improved stability of the M-alkoxide reaction intermediate to high concentrations of CTA, and it did not decompose by loss of Al(III) from the ligand by protonolysis.

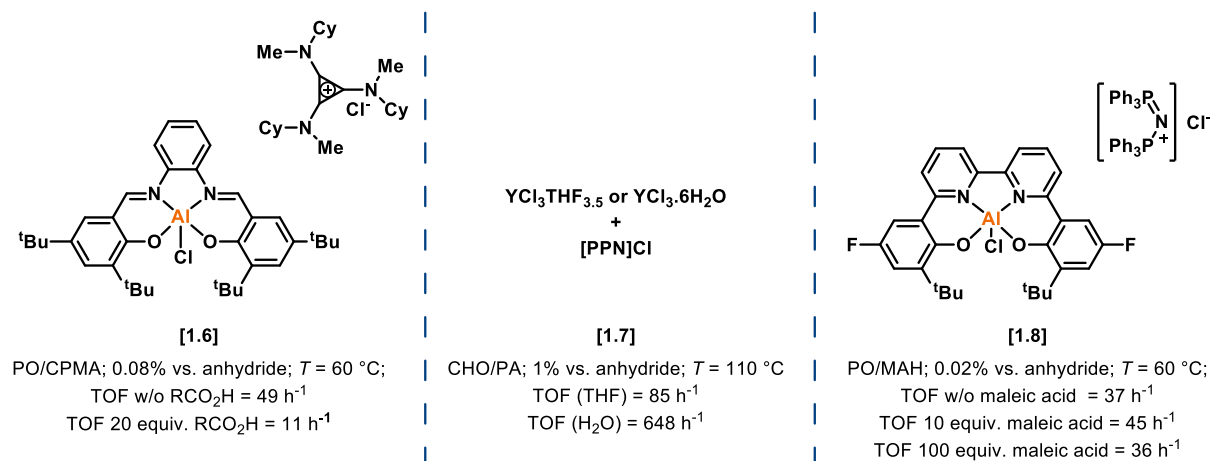


Figure 1.8 Bicomponent catalyst systems whose activity with CTA is of interest.^{32, 63, 64}

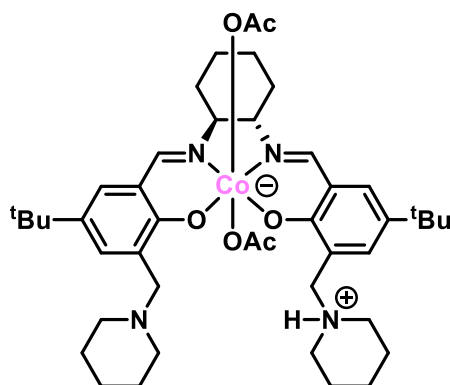
1.5 Multifunctional Catalysts

1.5.1 Tethered Cocatalyst

Improvements to monometallic catalyst loading tolerance and selectivity were achieved by tethering either a cationic or Lewis Basic cocatalyst onto the ligand framework.³⁷ This was first done by Nozaki and co-workers in 2006 for epoxide/ CO_2 ROCOP using a $[(\text{salen})\text{Co}(\text{III})^+\text{X}_2^-]$ complex (**[1.9]**, Figure 1.9) where one arm of the ligand bore a piperidinium group and the other was capped with a piperidinyl group (TOF = 130 h^{-1} ; 99 % PPC; **[1.9]**: $[\text{PO}] = 1:2000$; $p(\text{CO}_2) = 14\text{ bar}$; $T = 25\text{ }^{\circ}\text{C}$).⁶⁵

This modification gave improvements, particularly in suppressing backbiting, which allowed the polymerisation to be run to completion without formation of cyclic

carbonate. This is believed to occur because the two piperidinyll groups moderate the nucleophilicity of the carbonate chain end by protonation, thus disfavouring backbiting.



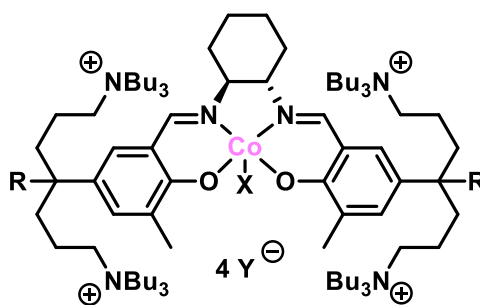
[1.9]

TOF = 130 h⁻¹; 99 % PPC

PO/CO₂; 0.05 mol% vs. PO; *p*(CO₂) = 14 bar; *T* = 25 °C

Figure 1.9 First example of a tethered ROCOP catalyst.⁶⁵

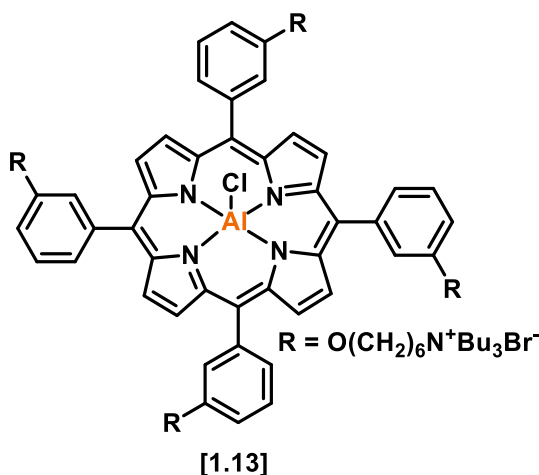
Tethering the cocatalyst has been used to great effect by Lee and co-workers when they attached a quaternary ammonium salt to a (salcy)Co(III)X catalyst with X = 2,4-dinitrophenolate ([DNP]⁻) ([1.10], Figure 1.10).⁶⁶ An impressive TOF of 26,000 h⁻¹ was achieved for PO/CO₂ ROCOP at very low catalyst loadings (>99 % PPC; [1.10]:[PO] = 1:50,000; *p*(CO₂) = 20 bar; *T* = 80 °C). Indeed, this is the fastest catalyst in the field and it was also useful for PO/PA polymerisation.⁶⁷



[1.10]	[1.11]	[1.12]
X = Y = [DNP] ⁻	X = [BF ₄] ⁻ , Y = [DNP] ⁻	X = CH ₃ CO ₂ ⁻ , Y = [NO ₃] ⁻
R = H	R = Me	R = Me
TOF = 26,000 h ⁻¹ ; >99 % PPC	TOF = 16,000 h ⁻¹ ; >99 % PPC	TOF = 15,000 h ⁻¹ ; >99 % PPC
PO/CO ₂ ; 0.004 mol% vs. PO;	PO/CO ₂ ; 0.001 mol% vs. PO;	PO/CO ₂ ; 0.001 mol% vs. PO;
<i>p</i> (CO ₂) = 20 bar; <i>T</i> = 80 °C	<i>p</i> (CO ₂) = 20 bar; <i>T</i> = 75 °C	<i>p</i> (CO ₂) = 25 bar; <i>T</i> = 75 °C

Figure 1.10 Highly active Co(III) catalysts, with tethered quaternary ammonium salts.^{66, 68, 69}

For epoxide/CO₂ ROCOP, Al(III) catalysts were typically not very active, *vide supra*. However, Ema, Nozaki, Hasegawa and co-workers reported a (porphyrin)Al(III)Cl with a tethered quaternary ammonium salt ([**1.13**], Figure 1.11), that reached activities of 10,000 h⁻¹ (>99 % PCHC; [**1.13**]:[CHO] = 1:40,000; *p*(CO₂) = 20 bar; *T* = 120 °C).⁷⁰



TOF = 10,000 h⁻¹; >99 % PCHC

CHO/CO₂; 0.0025 mol% vs. CHO; *p*(CO₂) = 20 bar; *T* = 120 °C

Figure 1.11 Al(III) porphyrin with tethered cocatalyst showing improved activity for epoxide/CO₂ ROCOP.⁷⁰

Density functional theory (DFT) computational modelling of this catalyst suggested that its activity is inversely related to the energy difference between the bound carbonate and the bound epoxide.^{70, 71} This was interpreted to mean that the catalyst has greater affinity for the epoxide, hence promoting the propagation of the polymer.

1.5.2 Improved Catalyst Loading Tolerance

There is also a significant benefit of a tethered cocatalyst on overall catalyst loading tolerance. A cocatalyst tethered to the ancillary ligand is proposed to prevent the polymer chain from diffusing away from the metal catalyst, encouraging intramolecular epoxide ring opening. This would obviate the dilution effects experienced by the bicomponent catalyst systems.^{37, 38}

Coates and co-workers compared two (salen)Al(III)Cl catalysts, one requires an additional cocatalyst (PPNCl) [1.6] and the other is a bifunctional catalyst, with an aminocyclopropenium incorporated into the salen ligand ([1.14], Figure 1.12).³⁸

This comprehensive study demonstrated that, for PO/CPMA ROCOP, there was no significant drop in catalyst activity, when the loading of catalyst [1.14] was varied from 0.5 mol% to 0.025 mol%, indicating a first order rate dependence ([1.14]:[CPMA]:[PO] = 1:200:1000 – 1:4000:20,000, $T = 60\text{ }^{\circ}\text{C}$).³⁸ The binary system [1.6], *vide supra*, exhibits first order behaviour at high catalyst loadings ([1.6]:[PPNCl]:[PO] = 1:1:1000 – 1:1:4000) and then transitions to second order at lower loadings ([1.6]:[PPNCl]:[PO] = 1:1:6000 – 1:1:20,000).³⁸ Notably, good catalyst loading tolerance offers several advantages: it reduces the amount of a costly catalyst required, reduces the amount of catalyst to be removed from the final polymer and it facilitates the synthesis of higher MW polymers.

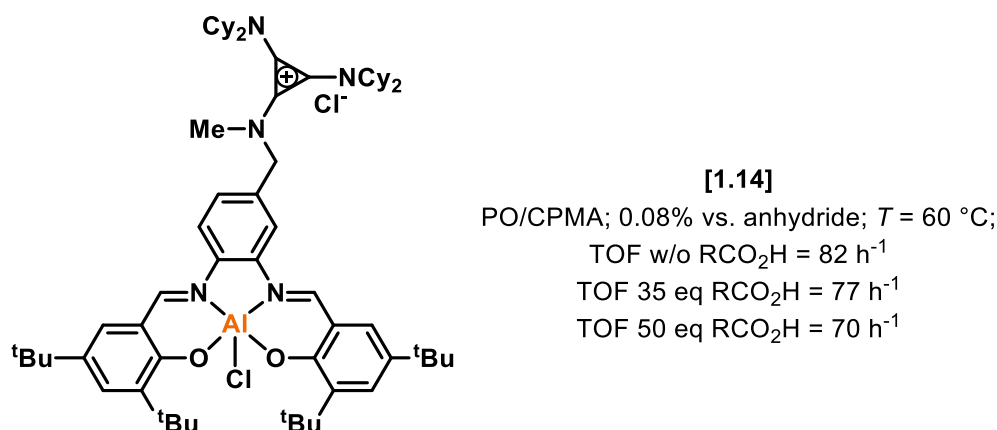


Figure 1.12 (salen)Al(III)X with tethered cocatalyst showing improved loading tolerance and tolerance to CTA.^{32, 38}

1.5.3 CTA Tolerance of Bifunctional Catalysts

An additional significant benefit of the tethered cocatalyst, is in relation to CTA loading tolerance. Some bifunctional catalysts show better tolerance to CTA, allowing for better targeted molecular weights to be achieved.³² For example, Coates and co-workers compared the same catalysts as above ([**1.6**] & [**1.14**]) and showed that a TOF of around 80 h⁻¹ was maintained when using up to 35 equiv. of acidic CTA ([**1.14**]:[CPMA] = 1:1200; CTA = 1-adamantanecarboxylic acid; *T* = 60 °C).³² It was proposed that the proximity enforced by the tethered cocatalyst in [**1.14**] favoured the active hexacoordinate complex, where the chain ends remain coordinated at the metal centre, which avoids competitive binding of the alcohol chain ends. It was also proposed to prevent hydrogen-bonding by the CTA to anionic polymer chain ends.

Further exploration of complexes similar to [**1.10**], by Lee and co-workers investigated the influences of changing the counter anions of the complex. They reported a tetrafunctional (salen)Co(III)X catalyst, containing [DNP]⁻ anions, ([**1.11**], Figure 1.10) that showed very high TOFs for PO/CO₂ ROCOP (TOF = 16,000 h⁻¹; >99 % PPC; [**1.11**]:[PO] = 1:100,000; *p*(CO₂) = 20 bar; *T* = 75 °C).⁶⁸ The catalyst showed a significant increase in induction time in the presence of water or methanol impurities (1 – 10 h), with no polymerisation initiation occurring when using more than 20 equiv. of either CTA. It should be noted that the rate of polymerisation, once initiated, was unaffected. It is believed that hydrogen bonding from the water stabilised the DNP⁻ anion, preventing it from initiating the polymerisation by inhibiting its nucleophilic attack on PO. Changing the counter anion to NO₃⁻ ([**1.12**], Figure 1.10) solved the deactivation, resulting in polymerisation at high rates (TOF = 15,000 h⁻¹; >99 % PPC; [**1.12**]:[PO] = 1:100,000; *p*(CO₂) = 25 bar; *T* = 75 °C), even when using up to 200 equiv. adipic acid as CTA.⁶⁹ High activity was even observed at loadings of 600 equiv. of acid resulting in a slightly lower

TOF of, TOF = 7,300 h⁻¹. Surprisingly, there was a small increase in TOF up to 50 equiv. adipic acid (10 equiv., TOF = 14,800 h⁻¹; 50 equiv., TOF = 18,900 h⁻¹).⁶⁹ No comment was made as to whether this change in TOF reflects merely a decrease in initiation time or whether it is due to an increase in polymerisation activity. Note that this report concerned epoxide/CO₂ ROCOP but such a phenomenon was not replicated for epoxide/anhydride ROCOP.

Darensbourg and co-workers reported a (salcy)Co(III)X₂ catalyst, with an amino tether group and DNP⁻ as counter-anion ([**1.15**], Figure 1.13) for epoxide (*tert*-butyl 3,4-epoxybutanoate)/CO₂. This catalyst only functioned when water was present.⁷² The authors argued that a weakly basic nucleophile was required to initiate the polymerisation, which could only be generated from hydrolysis or chain transfer reactions. These literature examples show the influence of CTA on the initiation of a polymerisation and how this can be influenced both positively and negatively.

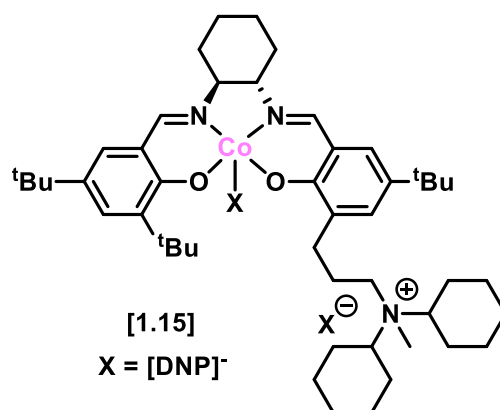


Figure 1.13 A (salcy)Co(III)X₂ catalyst that requires water for initiation.⁷²

These bifunctional catalysts are effective at low catalyst loadings, reducing side reactions and expanding monomer scope. Some challenges remain, namely synthetic accessibility, industrial viability, and catalyst efficiency at ambient conditions.

1.6 Multi-Homometallic Complexes

1.6.1 β -Diiminate Zinc Catalysts

In 2003, Coates and co-workers reported a series of *di*-Zn β -diiminate (BDI) catalysts ([**1.16**], [**1.17**] & [**1.18**], Figure 1.14).⁷³

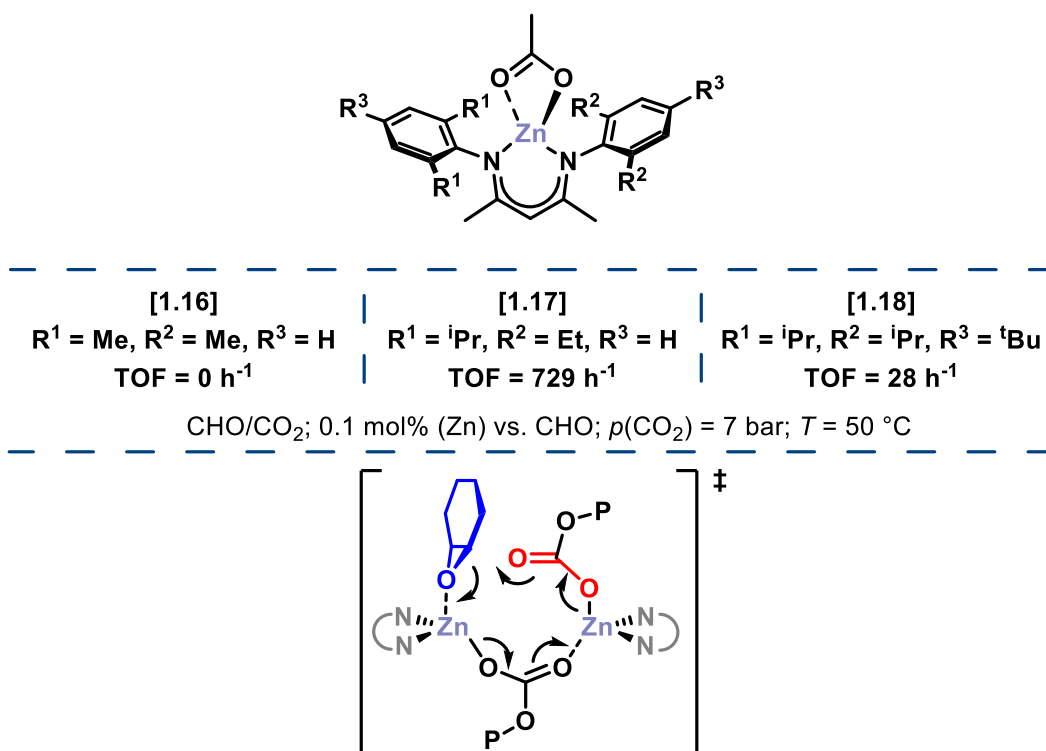


Figure 1.14 A series of Zn(II)(BDI) catalysts showing intermetallic cooperativity as dimers. Proposed transition state involving two Zn centres.⁷³

These dimers have different activities depending on the nature of the BDI ligand. Tightly bound dimeric complexes, formed due to low steric bulk on the ligand [**1.16**], have low rates (Figure 1.14). Slightly increasing the ligand's bulkiness [**1.17**] (Figure 1.14) enhances the rate because the catalyst can now function as a dimeric initiator with μ, η^2 -O₂CR or μ, η^2 -O₂COR bridging groups. However, too high steric bulk [**1.18**] (Figure 1.14) decreases rates again because they are more sterically encumbered and cannot access the bimetallic transition state. Kinetic analysis of the lead complex [**1.17**] gave the following rate law at 50 $^\circ\text{C}$:

$$\frac{d[P]}{dt} = k_p[\text{CHO}]^1[\text{CO}_2]^0[\text{Zn}]_{\text{tot}}^{1.73}$$

The order in Zn was temperature dependant and varied between 1.0 – 1.8 across the different complexes. The higher reaction order in catalyst meant that at higher T and lower concentration, the rate of reaction was significantly decreased, consistent with a dimeric transition state (Figure 1.14). From the ligand sterics, the authors concluded that the dimer must be loosely bound and it is believed that an optimum intermetallic proximity controls the rate enhancement.⁷³ These same catalysts were later shown to also be active for some epoxide/anhydride polymerisations, displaying high polyester selectivity and mechanistic studies revealed an analogous transition state.⁷⁴

1.6.2 Tethered Monometallic Complexes

A common approach in multimetallic catalysts is to tether two or more of a monometallic complex together.⁷⁵⁻⁷⁸ Early examples of *di*-Cr(III) catalysts coordinated by salen or salphen ligands suggested that intermetallic cooperativity was essential for the best rates.^{75, 76} More recently, Cui *et al.* explored a *tri*-Cr(III) series of complexes ([**1.19**], Figure 1.15) for epoxide/anhydride ROCOP.⁷⁷

These *tri*-Cr(III) complexes reached very high TOFs of 2560 h⁻¹ ([Cr]:[PPNCl]:[PA]:[CHO]=1:1:400:2000; $T = 60\text{ }^{\circ}\text{C}$) which was a nearly 50x increase in rate compared with the monometallic analogue under the same conditions (TOF = 56 h⁻¹). It should be noted that these polymerisations still required the presence of 1 equiv. cocatalyst (PPNCl) per metal centre to suppress polyether formation.

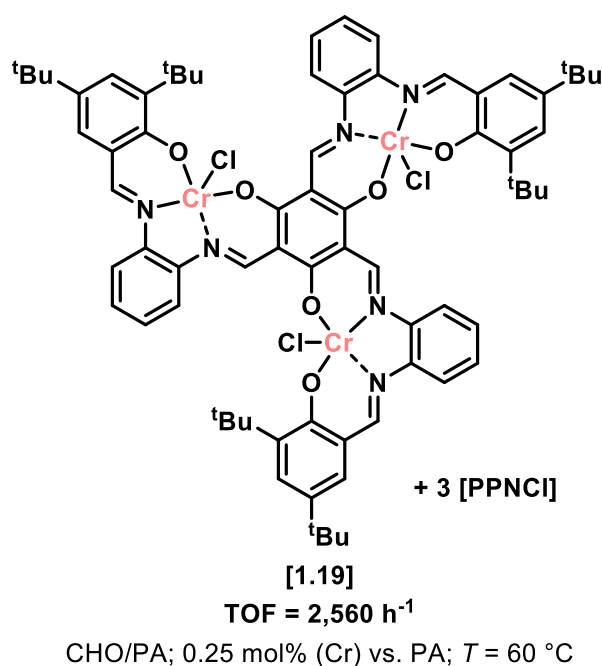


Figure 1.15 Highly active *tri*-Cr(III) catalyst with salphen-based ligand.⁷⁷

Bimetallic ((salen)Al(III)X)₂ complexes gave high TOFs (TOF = 750 h⁻¹, [Al]:[PPNCl]:[PA]:[CHO]=1:1:125:500, T = 50 °C) and also allowed for the asymmetric copolymerisation of *meso*-epoxides.⁷⁸ Nozaki and co-workers investigated *di*-Co(III) catalysts for PO/CO₂ ROCOP. The authors suggested that cooperativity between the Co(III) metal centres accounted for their performance.⁷⁹ The catalytic activity depended upon the ligand linker length between the two Co(III) centres, indicating that there is an optimal intermetallic separation to achieve the fastest rates.

This intermetallic separation was further investigated by Rieger and co-workers on a *di*-Zn(II) catalyst ([1.20], Figure 1.16).³⁵ DFT studies on this catalyst suggest that the separation between the Zn(II) sites may change over the course of the polymerisation catalytic cycle.³⁵ From a resting state separation of 7.77 Å, the two Zn(II) centres get closer to a distance of 5.31 Å in the rate determining transition state.³⁵ Adding the electron withdrawing group -CF₃ to the ligand [1.21] was proposed to increase the Lewis

acidity of the Zn(II) leading to high rates for CHO/CO₂ ROCOP (TOF = 155,000 h⁻¹; >99 % PCHC; [1.21]:[CHO] = 1:8000; *p*(CO₂) = 30 bar; *T* = 100 °C).⁸⁰

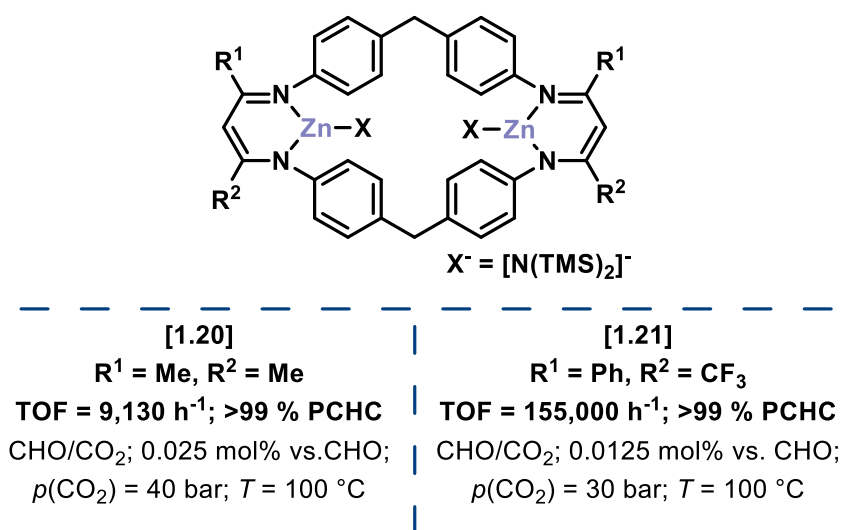


Figure 1.16 Highly active *di*-Zn catalysts reported by Rieger and co-workers.^{35, 80}

1.6.3 Bottlebrush Polymeric Aluminium Porphyrin Catalysts

A class of highly active Al(III) catalysts for epoxide/CO₂ ROCOP were achieved by tethering multiple Al porphyrins together into oligomeric or dimeric structures (Figure 1.17).⁸¹⁻⁸³

The first polymeric aluminium porphyrin catalyst was prepared by Cao *et al.*⁸¹ It showed a trend of increased activity (relative to each Al(III) centre) and selectivity with increasing catalyst chain length (i.e. more Al(III) centres per oligomer chain). PPnCl as a cocatalyst was still necessary, but only 0.25 equiv. (relative to Al(III) centre) was required for optimal polymer selectivity. Further optimisation of the catalyst ([1.22], Figure 1.17) resulted in a TOF of 3,110 h⁻¹, and 99 % selectivity, for polymer for PO/CO₂ ROCOP ([Al]:[PPnCl]:[PO] = 1:0.5:10,000, *p*(CO₂) = 30 bar, *T* = 70 °C). However, there were only 46 % carbonate linkages.⁸² The catalysts also appeared to be stable in the presence of

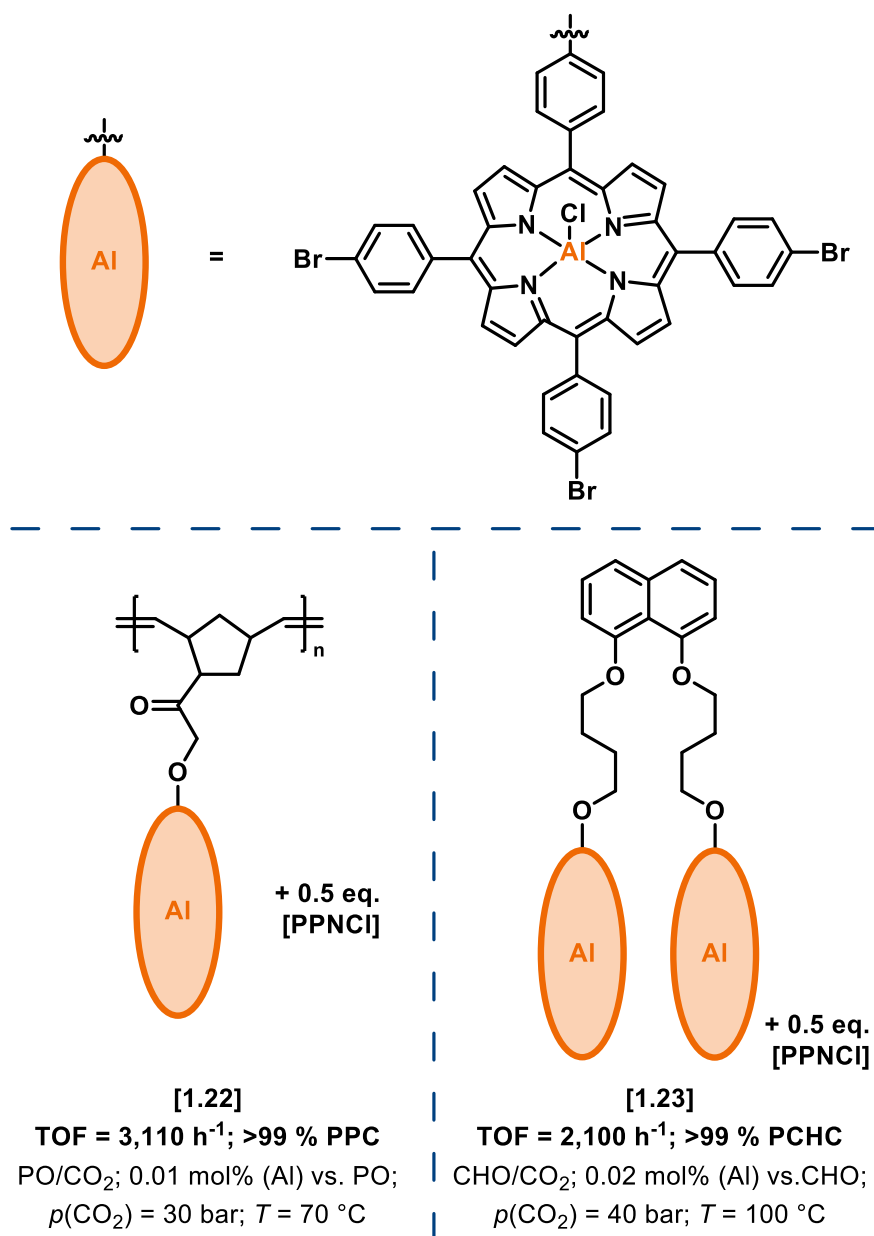


Figure 1.17 Bottlebrush polymeric Al(III) porphyrin catalysts.⁸¹⁻⁸⁴

around 8000 equiv. CTA which was used to produce ultra-low MW polycarbonates with narrow dispersities.⁸³ The TOF appeared to trend down, the more CTA was added, although these are very impressive loadings. The dimeric equivalent of these catalysts ([1.23], Figure 1.17) was tested for CHO/CO₂ ROCOP and gave a maximum activity of TOF = 2,100 h⁻¹ with >99 % selectivity for polymer vs. cyclic and >99 % for carbonate uptake into the polymer ([Al]:[PPNCl]:[CHO] = 1:0.5:5000, $p(\text{CO}_2) = 40 \text{ bar}$, $T = 100 \text{ }^\circ\text{C}$).⁸⁴ The reaction rate increased with greater intermetallic separation, likely due to the steric

hinderance from adjacent bulky porphyrin rings inhibiting CHO insertion. Although never reported, this may be a draw-back for the bottlebrush polymeric aluminium porphyrin catalysts when using for the synthesis of PCHC.

1.6.4 Bimetallic Complexes with Macrocyclic Ancillary Ligands

Williams and co-workers investigated bimetallic complexes for ROCOP with the first example a *di*-Zn(II) complex coordinated by a macrocyclic ancillary ligand ([**1.24**], Figure 1.18).⁸⁵ This catalyst gave perfectly alternating PCHC, with 95 % polycarbonate selectivity, at just 1 bar CO₂ pressure in unoptimized conditions ([**1.24**]:[CHO] = 1:1,000; *p*(CO₂) = 1 bar; *T* = 100 °C), an impressive step forward over other bimetallic complexes at the time. A maximum TOF of 140 h⁻¹ was achieved at 10 atm pressure, without further improvements in polycarbonate selectivity ([**1.24**]:[CHO] = 1:10,000, *p*(CO₂) = 10 bar, *T* = 100 °C). Kinetic analysis revealed the following rate law across CO₂ pressures of 1 bar ≤ *p*(CO₂) ≤ 40 bar:⁸⁶

$$\frac{d[P]}{dt} = k_p [CHO]^1 [CO_2]^0 [1.24]^1$$

This suggested a rate limiting CHO insertion step with a fast CO₂ insertion step. The proposed mechanism was a chain shuttling propagation, whereby CHO is coordinated to one of the Zn(II) centres and there is a polymeric carbonate species on the other. The carbonate performs a nucleophilic ring opening attack on the CHO, forming an alkoxide that then rapidly reacts with CO₂ to reform a carbonate. This mechanism was also in agreement with DFT calculations.⁸⁷ The intermetallic separation of ~3.0 Å was proposed to be crucial for enabling successful catalysis without any cocatalyst. A *di*-Mg(II) catalyst, coordinated by the same macrocycle ([**1.25**], Figure 1.18), was six times more active than

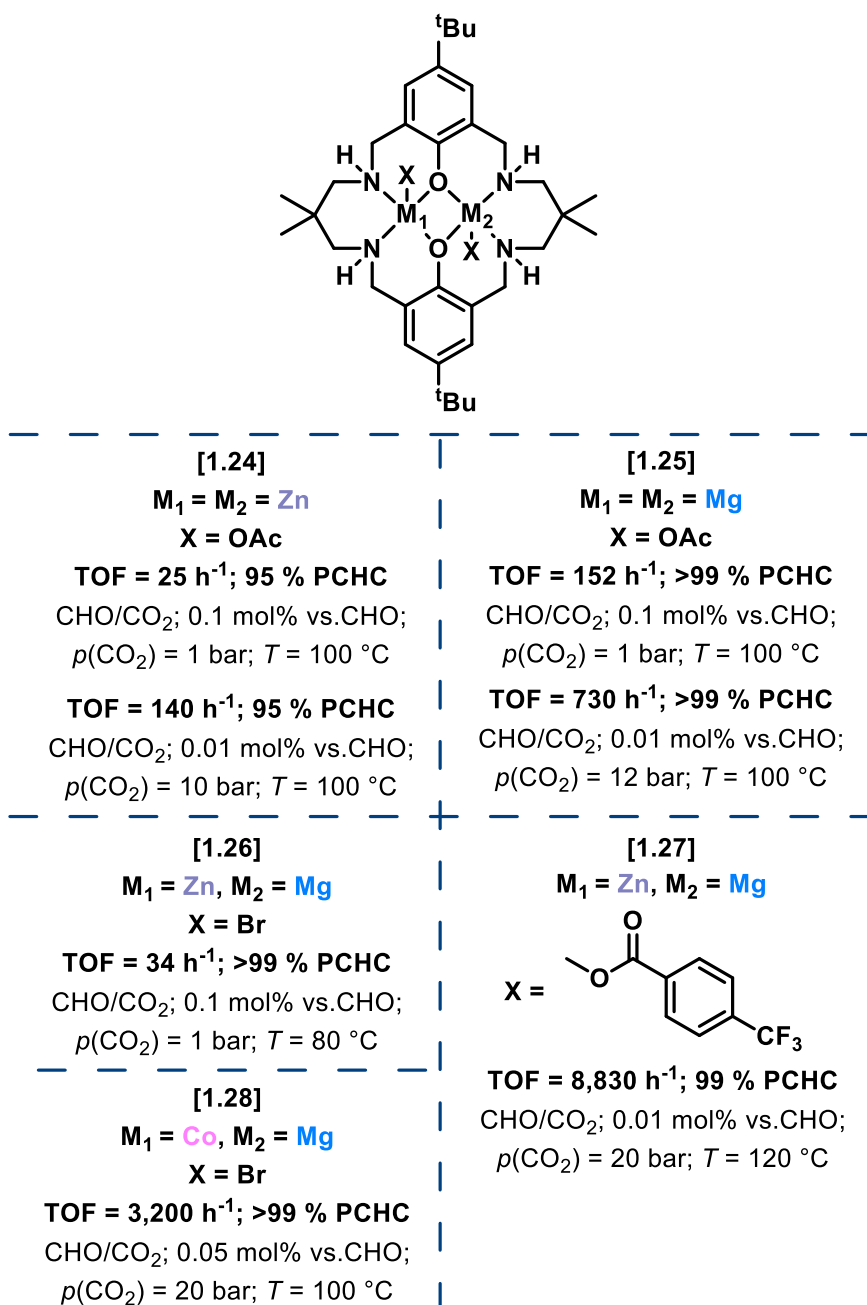
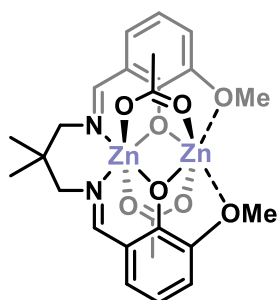


Figure 1.18 Bimetallic complexes held within a macrocyclic ancillary ligand.^{23, 26, 85, 88, 89}

[1.24], this result being particularly interesting because the molar mass of Mg is a third of that of Zn and it has far greater earth abundance.⁸⁸ Note, however, that these catalysts showed some deactivation in the presence of water as a CTA, with a 10x drop in rate when 30 equiv. H₂O was added. Both these catalysts even showed activity when polymerising CO₂ captured from a UK coal power station and showed very good tolerance to a range of impurities.⁹⁰ A benefit of these bimetallic complexes, where the metals are coordinated

adjacent to one another in an ancillary ligand, is that an intermetallic separation of around 3-4 Å is enforced, in contrast to tethered alternatives where active metal sites can be quite far away.

Williams and co-workers also tested a series of Schiff-base ancillary ligands, derived from *ortho*-vanillin which can be extracted from plants. A series of *di*-Zn(II) catalysts ([**1.29**], Figure 1.19) featuring different diamine linkers were investigated.⁹¹



[**1.29**]

TOF = 200 h⁻¹

CHO/PA; 1 mol% vs. PA; *T* = 100 °C

Figure 1.19 A *di*-Zn(II) catalyst with an *ortho*-vanillin-based ancillary ligand.⁹¹

For PA/CHO ROCOP, the catalyst with a 2,2-dimethyl-1,3-propanediamine backbone gave the fastest rate (TOF = 200 h⁻¹, [**1.29**]:[PA]:[CHO] = 1:100:800, *T* = 100 °C).⁹¹ The rate was almost 3x less when replacing the backbone with a more rigid alternative, (*±*)-*trans*-1,2-diaminocyclohexane. Also, reducing the Schiff base imine to an amine gave even more drastic drops in TOF, down 20x from the fastest catalyst. This shows the significant impact of the di-imine linker on catalytic activity.

1.7 Multi-Heterometallic Complexes

1.7.1 Intermetallic Synergy

In 2015, Williams and co-workers reported a Zn(II)Mg(II) macrocyclic complex ([**1.26**], Figure 1.18) that showed intermetallic synergy.⁸⁹ This heterometallic catalyst gave a TOF of 34 h⁻¹ (>99 % PCHC; [**1.26**]:[CHO] = 1:1,000; *p*(CO₂) = 1 bar; *T* = 80 °C) which was faster than either of the homonuclear complexes and faster than a 1:1 mixture of the *di*-Zn(II) and *di*-Mg(II) catalysts (TOF([**1.25**]) = 15 h⁻¹; TOF([**1.24**]) = 0 h⁻¹; TOF(1:1) = 7 h⁻¹).⁸⁹ The heterometallic Zn(II)Mg(II) catalyst was further optimised, by changing the coligand ([**1.27**], Figure 1.18) and reaction conditions, to reach a TOF of 8,830 h⁻¹ (99 % PCHC; [**1.27**]:[CHO] = 1:10,000; *p*(CO₂) = 20 bar; *T* = 120 °C).²⁶

This finding prompted further investigations into intermetallic synergy, a notable study being on a Mg(II)Co(II) complex, with the same macrocycle ([**1.28**], Figure 1.18).^{23,27} Again, the heterometallic Mg(II)Co(II) catalyst showed significantly faster rates than either of the homonuclear analogues. The key output and proposal from the kinetic investigations was that the Mg(II) reduced the transition state entropy whilst the Co(II) reduced the transition state enthalpy. The two metals were proposed to have distinct roles, Mg(II) for coordinating CHO whilst Co(II) provides the carbonate nucleophile to attack the activated CHO in the chain shuttling mechanism.²³

1.7.2 Dinuclear Metallate ROCOP Mechanism for M(III)M(I/II) Catalysts

Williams and co-workers have also investigated catalyst comparisons of M(III) with other s-block metals, notably those in Group I. A different macrocyclic ligand was introduced containing a Schiff base pocket, for the M(III), and an ether pocket, that coordinates the M(I). This resulted in the discovery of a PO/CO₂ ROCOP catalyst, with a

Co(III)K(I) metal combination ([**1.30**], Figure 1.20).⁹² It achieved, a TOF of 800 h⁻¹ for PO/CO₂ ROCOP, without any polyether and with 93 % polycarbonate selectivity ([**1.30**]:[1,2-*trans*-cyclohexane diol(CHD)]:[PO]=1:20:4000, *p*(CO₂) = 30 bar, *T* = 70 °C). It also showed tolerance to CTA up to 250 equiv. of diol. The kinetic and DFT studies suggest that the Co(III) activates the epoxide and the K(I) provides the carbonate nucleophile (intermetallic separation = 3.698 Å).^{24, 92} This mechanism has been termed a ‘metallate’ mechanism, primarily because X-ray crystallography reveals that, in the resting state, the Co(III) coordinates the acetate as a cobalate.⁹²

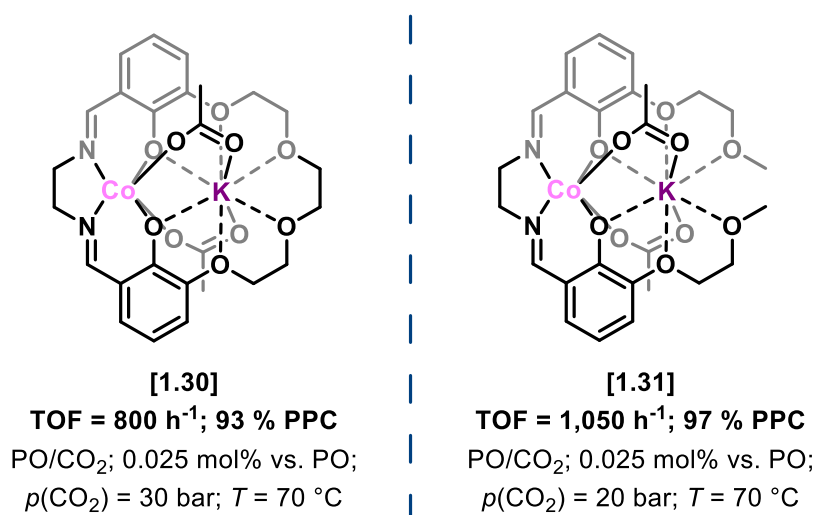


Figure 1.20 Co(III)K(I) catalysts with ‘closed’ and ‘open’ ligands.^{25, 92}

1.7.3 CO₂ Insertion Equilibrium, *K*_{eq}

Additional work using the Co(III)K(I) catalyst revealed that when an ‘open’ ligand is used ([**1.31**], Figure 1.20), an increase in rate and polycarbonate selectivity could be achieved. The new Co(III)K(I) catalyst has a TOF([**1.31**], open) = 1050 h⁻¹ (PPC select.([**1.31**], open) = 97 %; [cat]:[CHD]:[PO] = 1:20:4000; *p*(CO₂) = 20 bar; *T* = 70 °C) vs. the closed analogue TOF([**1.30**], closed) = 800 h⁻¹ (PPC select.([**1.30**], closed) = 93 %).²⁵

This work also involved extensive kinetic studies trying to probe the rate dependence on $p(\text{CO}_2)$. In two different pressure ranges, different rate laws were determined.

$$\text{Rate} = k_p[\text{Cat}]^1[\text{PO}]^1[\text{CO}_2]^1, \quad P \leq 12 \text{ bar} \quad (1)$$

$$\text{Rate} = k_p[\text{Cat}]^1[\text{PO}]^1[\text{CO}_2]^0, \quad P \geq 12 \text{ bar} \quad (2)$$

Beyond a threshold CO_2 pressure, there was a zero order rate dependence on $p(\text{CO}_2)$, the ‘plateau’ region, however below it, there appeared to be a first order rate dependence, the ‘linear’ region. Similar results were also reported when using a *di*-Zn(II) complex [1.20] (Figure 1.16), *vide supra*, but there was no interpretation that suggested a CO_2 insertion equilibrium.³⁵ The investigation into catalyst [1.31] combined these two different CO_2 pressure regimes into a single rate expression, by introducing a pre-equilibrium of CO_2 insertion. It was hypothesised that the CO_2 insertion is reversible, and so the relative concentrations of the alkoxide and carbonate intermediates are governed by an equilibrium (K_{eq}) (Figure 1.21).²⁴

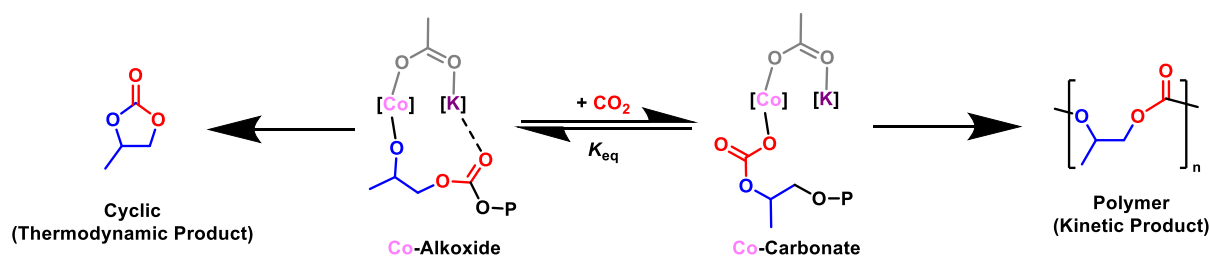


Figure 1.21 Scheme showing the CO_2 insertion equilibrium and its influence on polymer propagation.

This has implications on both the rate and polycarbonate selectivity (over cyclic carbonate). The expression for K_{eq} is as follows:

$$K_{\text{eq}} = \frac{[\text{carbonate}]}{[\text{alkoxide}][\text{CO}_2]} \quad (3)$$

This was then incorporated into the rate law giving the following unified rate equation:

$$Rate = k_p K_{eq} [alkoxide]^1 [PO]^1 [CO_2]^1 \quad (4)$$

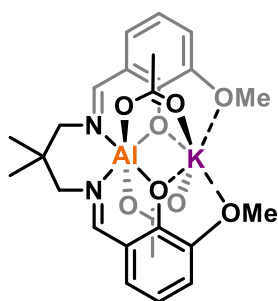
The CO₂ insertion equilibrium and rate law was shown to be relevant to the catalyst [1.31] and to other literature catalysts (where data was re-interpreted).²⁵ This is the basis for the proposed mechanism shown in Figure 1.3.

1.7.4 Co(III)M(I/II), s-Block Metal Lewis Acidity-Activity Trends

Catalysts with the 'closed' ligand were prepared using different s-block metals to form Co(III)M(I/II) ([1.30], Figure 1.20). Two studies were undertaken looking at the influence of the choice of s-block metal on reaction activity and selectivity, using the acid dissociation constant (pK_a) of $[M(OH_2)_m]^{n+}$ as a measure for the s-block metal Lewis acidity.^{93, 94} For both PO/CO₂ and CHO/CO₂ ROCOP, there was an increase in the observed rate constant (k_{obs}) against decreasing metal Lewis acidity (increasing pK_a). The rate relationship is exponential for PO/CO₂ but linear in PPC selectivity (%).^{93, 94} The clear result was that K(I) was the best performing catalyst of the scope. A similar exponential increase of k_{obs} against decreasing s-block metal Lewis acidity was seen for PO/PA and CHO/PA ROCOP, with the same catalysts.^{93, 94} The rationalisation, for both polymerisations, is that the least Lewis acidic s-block metal results in the most destabilised M-carbonate/carboxylate intermediates which are key intermediates in the rate determining step. With regards to selectivity, the same rationale results in a destabilised alkoxide intermediate which then favours CO₂ insertion to form the carboxylate. This reduces the concentration of the alkoxide intermediate which can backbite to form cyclic carbonate.⁹³

1.7.5 Heterodinuclear Al(III) Catalysts

Finally, the Schiff base ligand used to make *di*-Zn(II) catalyst **[1.29]** was also very effective at coordinating Al(III) in the Schiff-base *N,N,O,O* pocket. An Al(III) catalyst, could achieve a TOF of 350 h⁻¹ for PA/CHO, but required 1 equiv. PPNCl ([cat]:[PPNCl]:[CHD]:[PA]:[CHO] = 1:1:2:100:500, *T* = 100 °C).⁹⁵ Adding a group I metal into the *O,O,O,O* pocket avoided the need for a cocatalyst and, the resulting Al(III)K(I) catalyst (**[1.32]**, Figure 1.22) achieved a TOF = 1072 h⁻¹ (**[1.32]**: [PA]:[CHO] = 1:400:2000, *T* = 100 °C).²⁸



[1.32]

TOF = 1,070 h⁻¹

CHO/PA; 0.025 mol% vs. PA; *T* = 100 °C

Figure 1.22 Highly active Al(III)K(I) catalyst with Schiff base ancillary ligand for epoxide/anhydride ROCOP.²⁸

The activity trend (at least for Na(I) and K(I)) matched that which was reported for the Co(III)M(I) complexes, *vide supra*.⁹³ The same rationale, of weakly Lewis acidic group I metals enhancing activity, is believed to explain this trend as well. The Al(III)K(I) catalyst **[1.32]** was highly active for a number of different monomers. A full kinetic investigation was carried out, resulting in a rate law of:

$$Rate = k_{obs}[\mathbf{1.32}]^1[\text{CHO}]^1[\text{PA}]^0$$

It was suggested that the rate determining step is the ring opening of epoxide, by attack from the K(I)-carboxylate. DFT calculations supported a dinuclear ‘metalate’ mechanism

(Figure 1.23), as above, and again the X-ray crystal structure showed that the acetates coordinated to form an aluminate in the solid state.

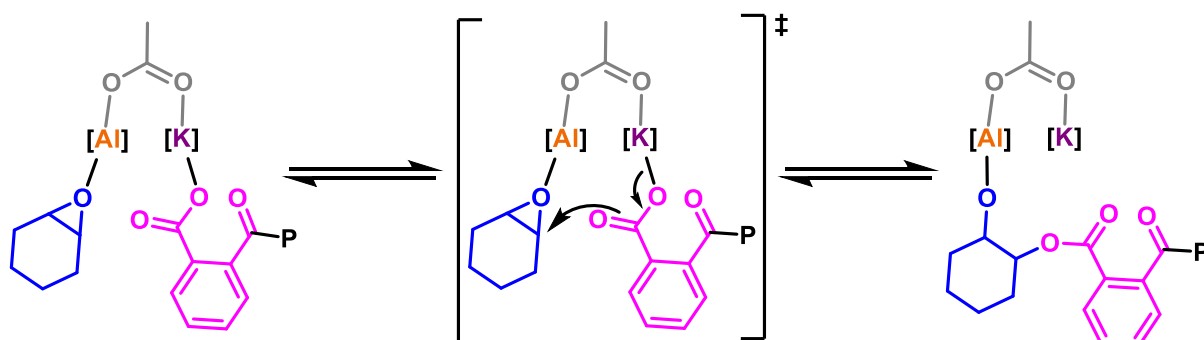


Figure 1.23 Proposed ‘aluminate’ reaction mechanism in rate determining step of epoxide ring opening.²⁸

DFT calculations suggested that the lowest energy transition state was where the carboxylate is coordinated to the K(I), whilst the Al(III), coordinates and activates the epoxide. This attack is both kinetically and thermodynamically favoured. The intermetallic distance is roughly 3.5 Å.

This catalyst was also tested for CHO/CO₂ ROCOP, revealing a high activity but reduced selectivity (TOF = 510 h⁻¹, PCHC select. = 88 %, [cat]:[CHO] = 1:4000, *p*(CO₂) = 20 bar, *T* = 100 °C); the was selectivity improved by increasing the CO₂ pressure.^{28, 96} Improvements to these Al(III)/K(I) catalysts for CHO/CO₂ ROCOP were achieved with the “open” ligand in **[1.31]** (Al(III) replacing the Co(III)).⁹⁷ This led to an activity of 1080 h⁻¹ (PCHC select. = 97 %, [cat]:[CHD]:[CHO] = 1:20:4000, *p*(CO₂) = 20 bar, *T* = 100 °C).⁹⁷

The use of Al(III) and K(I) in these catalysts is particularly desirable. Both metals are earth abundant and relatively inexpensive, without major toxicity concerns. It is, therefore, worthwhile to try to improve the performance of catalysts featuring these metals.

1.8 Aims and Objectives

The focus of this thesis will be on polymerisation catalysis for epoxide/anhydride and epoxide/CO₂ ROCOP. There are promising results from recent catalyst development but there is still much to be explored and understood.

1. Catalyst performance. The first report of an Al(III)K(I) ROCOP catalyst was by Diment *et al.* which showed that it was highly active for epoxide/anhydride ROCOP.²⁸ Modifications with the intention of improving catalytic activity, especially to enable epoxide/CO₂ ROCOP, are very worthwhile due to the favourable metal combination in this catalyst. An area that remains to be explored is finding the optimum structure for the ancillary ligand and observing its influence over catalyst activity. In addition to this, it is still necessary to understand the polymerisation mechanisms and how catalyst structure-performance relationships apply between different processes.

2. Low molecular weight polyesters. The production of low MW polyesters requires catalyst tolerance to high alcohol (CTA) loadings, since such conditions should decrease the resultant polyester MW whilst minimising the catalyst loading. The development of catalysts that tolerate high alcohol loadings for epoxide/anhydride ROCOP catalysis is still a major challenge. The objective is to develop Al(III)K(I) catalysts whose rates are enhanced by high alcohol loadings. Gaining insight into how catalysis may be accelerated by alcohols would be valuable for guiding future catalyst design.

Chapter 2 will focus on improving the Al(III)K(I) catalyst ROCOP performance. This work will be on epoxide/anhydride ROCOP, investigating whether catalyst performance can be improved through ligand derivatization. Specifically, a series of Al(III)K(I) catalysts with different Schiff-base ancillary ligands will be examined focussing on the diimine linkers. These complexes will be characterised by NMR spectroscopy, Infrared (IR) spectroscopy, X-ray Diffraction (XRD) Crystallography, Matrix-Assisted Laser Desorption/Ionization – Time of Flight (MALDI-ToF) and Elemental Analysis (EA). Their catalytic activities will be compared to the ROCOP of PA with CHO, since these monomers are benchmarks in the field and tolerate high temperatures. Additionally, experiments will test the epoxide and anhydride monomer scope and evaluate catalyst tolerance to CTA as a means to deliver polymer MW control.

Chapter 3 will target the same series of Al(III)K(I) catalysts for epoxide/CO₂ ROCOP. It aims to determine whether the ligand structure-performance relationships are the same or different to those uncovered for epoxide/anhydride ROCOP. The catalysts will be benchmarked for CHO/CO₂ ROCOP. Kinetic studies will be conducted to elucidate the reaction mechanism, with a particular focus on the rate dependence on [CO₂].

Chapter 4 will build on the groundwork of Chapter 2, exploring the mechanistic roles that CTA plays in the ROCOP of epoxide/anhydride when catalysed by an Al(III)K(I) catalyst. This study will begin with kinetic experiments to determine a rate law, with particular focus on establishing the reaction order in [CTA]. Once this has been determined, additional investigations, including kinetic isotope effect studies, binding studies and crystallography will be conducted to identify any additional mechanistic roles CTA plays in the rate determining step, beyond the standard chain transfer.

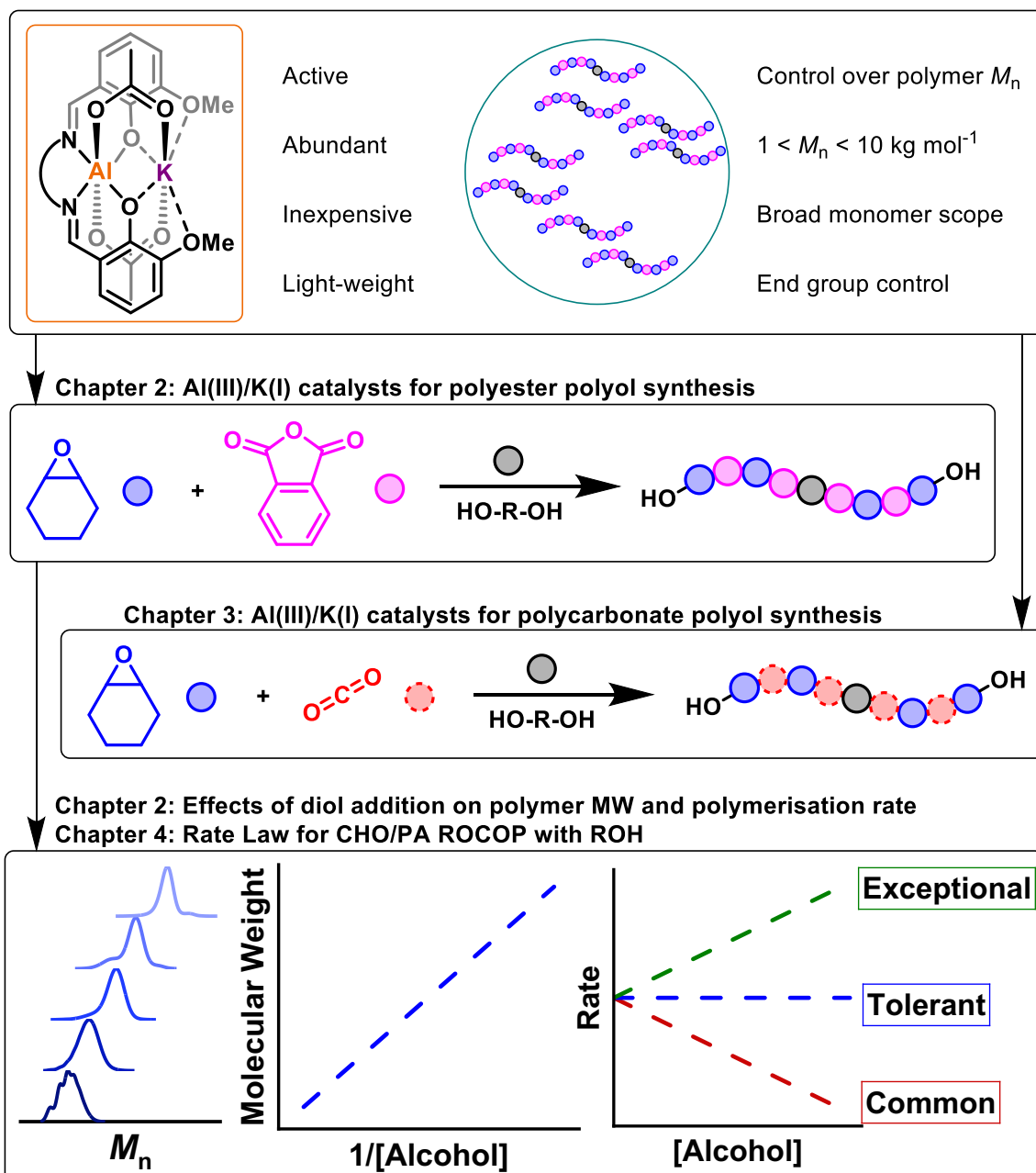


Figure 1.24 The aims and objectives of this thesis – the synthesis of Al(III)K(I) catalysts for the ROCOP of epoxide/anhydride and epoxide/ CO_2 with diol to produce low MW polyesters and polycarbonates.

1.9 References

- (1) *Plastics - the Fast Facts 2024*. Plastics Europe, 2024. <https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2024/> (accessed 2025 Feb 25).
- (2) *Annual plastic waste by disposal method*. Our World in Data, 2023. <https://ourworldindata.org/grapher/plastic-fate> (accessed 2025 Feb 25).
- (3) Ritchie, H. *How much of global greenhouse gas emissions come from plastics?* 2023. <https://ourworldindata.org/ghg-emissions-plastics> (accessed 2025 Feb 25).
- (4) Vidal, F.; van der Marel, E. R.; Kerr, R. W. F.; McElroy, C.; Schroeder, N.; Mitchell, C.; Rosetto, G.; Chen, T. T. D.; Bailey, R. M.; Hepburn, C.; et al. Designing a circular carbon and plastics economy for a sustainable future. *Nature* **2024**, 626 (7997), 45–57. DOI: 10.1038/s41586-023-06939-z.
- (5) Haque, F. M.; Ishibashi, J. S. A.; Lidston, C. A. L.; Shao, H.; Bates, F. S.; Chang, A. B.; Coates, G. W.; Cramer, C. J.; Dauenhauer, P. J.; Dichtel, W. R.; et al. Defining the Macromolecules of Tomorrow through Synergistic Sustainable Polymer Research. *Chem. Rev.* **2022**, 122 (6), 6322–6373. DOI: 10.1021/acs.chemrev.1c00173.
- (6) Hong, M.; Chen, E. Y. X. Chemically recyclable polymers: a circular economy approach to sustainability. *Green Chem.* **2017**, 19 (16), 3692–3706. DOI: 10.1039/c7gc01496a.
- (7) Kelly, C. L. Addressing the sustainability challenges for polymers in liquid formulations. *Chem. Sci.* **2023**. DOI: 10.1039/d3sc90086j.
- (8) Shi, C.; Quinn, E. C.; Diment, W. T.; Chen, E. Y. X. Recyclable and (Bio)degradable Polyesters in a Circular Plastics Economy. *Chem. Rev.* **2024**, 124 (7), 4393–4478. DOI: 10.1021/acs.chemrev.3c00848.
- (9) Brannigan, R. P.; Dove, A. P. Synthesis, properties and biomedical applications of hydrolytically degradable materials based on aliphatic polyesters and polycarbonates. *Biomater. Sci.* **2017**, 5 (1), 9–21. DOI: 10.1039/c6bm00584e.
- (10) Cywar, R. M.; Rorrer, N. A.; Hoyt, C. B.; Beckham, G. T.; Chen, E. Y. X. Bio-based polymers with performance-advantaged properties. *Nat. Rev. Mater.* **2021**, 7 (2), 83–103. DOI: 10.1038/s41578-021-00363-3.
- (11) *Polymers in Liquid Formulations. Technical report: A landscape view of the global PLFs market* Royal Society of Chemistry, 2021.
- (12) Sanford, M. J.; Peña Carrodegua, L.; Van Zee, N. J.; Kleij, A. W.; Coates, G. W. Alternating Copolymerization of Propylene Oxide and Cyclohexene Oxide with Tricyclic Anhydrides: Access to Partially Renewable Aliphatic Polyesters with High Glass Transition Temperatures. *Macromol.* **2016**, 49 (17), 6394–6400. DOI: 10.1021/acs.macromol.6b01425.
- (13) Poland, S. J.; Darensbourg, D. J. A quest for polycarbonates provided via sustainable epoxide/CO₂ copolymerization processes. *Green Chem.* **2017**, 19 (21), 4990–5011. DOI: 10.1039/c7gc02560b.

- (14) Rosenboom, J.-G.; Langer, R.; Traverso, G. Bioplastics for a circular economy. *Nat. Rev. Mater.* **2022**, *7* (2), 117–137. DOI: 10.1038/s41578-021-00407-8.
- (15) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable polymers from renewable resources. *Nature* **2016**, *540* (7633), 354–362. DOI: 10.1038/nature21001.
- (16) Backer, S. A.; Leal, L. Biodegradability as an Off-Ramp for the Circular Economy: Investigations into Biodegradable Polymers for Home and Personal Care. *Acc. Chem. Res.* **2022**, *55* (15), 2011–2018. DOI: 10.1021/acs.accounts.2c00336.
- (17) Zhang, X.; Fevre, M.; Jones, G. O.; Waymouth, R. M. Catalysis as an Enabling Science for Sustainable Polymers. *Chem. Rev.* **2017**, *118* (2), 839–885. DOI: 10.1021/acs.chemrev.7b00329.
- (18) Odian, G. *Principles of Polymerization*, 4th Ed.; 2004.
- (19) Longo, J. M.; Sanford, M. J.; Coates, G. W. Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides with Discrete Metal Complexes: Structure–Property Relationships. *Chem. Rev.* **2016**, *116* (24), 15167–15197. DOI: 10.1021/acs.chemrev.6b00553.
- (20) Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. Ring-opening copolymerization (ROCOP): synthesis and properties of polyesters and polycarbonates. *Chem. Commun.* **2015**, *51* (30), 6459–6479. DOI: 10.1039/c4cc10113h.
- (21) Hepburn, C.; Adlen, E.; Beddington, J.; Carter, E. A.; Fuss, S.; Mac Dowell, N.; Minx, J. C.; Smith, P.; Williams, C. K. The technological and economic prospects for CO₂ utilization and removal. *Nature* **2019**, *575* (7781), 87–97. DOI: 10.1038/s41586-019-1681-6.
- (22) von der Assen, N.; Bardow, A. Life cycle assessment of polyols for polyurethane production using CO₂ as feedstock: insights from an industrial case study. *Green Chem.* **2014**, *16* (6), 3272–3280. DOI: 10.1039/c4gc00513a.
- (23) Deacy, A. C.; Kilpatrick, A. F. R.; Regoutz, A.; Williams, C. K. Understanding metal synergy in heterodinuclear catalysts for the copolymerization of CO₂ and epoxides. *Nat. Chem.* **2020**, *12* (4), 372–380. DOI: 10.1038/s41557-020-0450-3.
- (24) Deacy, A. C.; Phanopoulos, A.; Lindeboom, W.; Buchard, A.; Williams, C. K. Insights into the Mechanism of Carbon Dioxide and Propylene Oxide Ring-Opening Copolymerization Using a Co(III)/K(I) Heterodinuclear Catalyst. *J. Am. Chem. Soc.* **2022**, *144* (39), 17929–17938. DOI: 10.1021/jacs.2c06921.
- (25) Eisenhardt, K. H. S.; Fiorentini, F.; Lindeboom, W.; Williams, C. K. Quantifying CO₂ Insertion Equilibria for Low-Pressure Propene Oxide and Carbon Dioxide Ring Opening Copolymerization Catalysts. *J. Am. Chem. Soc.* **2024**, *146* (15), 10451–10464. DOI: 10.1021/jacs.3c13959.
- (26) Trott, G.; Garden, J. A.; Williams, C. K. Heterodinuclear zinc and magnesium catalysts for epoxide/CO₂ ring opening copolymerizations. *Chem. Sci.* **2019**, *10* (17), 4618–4627. DOI: 10.1039/c9sc00385a.

- (27) Diment, W. T.; Lindeboom, W.; Fiorentini, F.; Deacy, A. C.; Williams, C. K. Synergic Heterodinuclear Catalysts for the Ring-Opening Copolymerization (ROCOP) of Epoxides, Carbon Dioxide, and Anhydrides. *Acc. Chem. Res.* **2022**, *55* (15), 1997–2010. DOI: 10.1021/acs.accounts.2c00197.
- (28) Diment, W. T.; Gregory, G. L.; Kerr, R. W. F.; Phanopoulos, A.; Buchard, A.; Williams, C. K. Catalytic Synergy Using Al(III) and Group 1 Metals to Accelerate Epoxide and Anhydride Ring-Opening Copolymerizations. *ACS Catal.* **2021**, *11* (20), 12532–12542. DOI: 10.1021/acscatal.1c04020.
- (29) Asano, S.; Aida, T.; Inoue, S. 'Immortal' polymerization. Polymerization of epoxide catalysed by an aluminium porphyrin–alcohol system. *J. Chem. Soc., Chem. Commun.* **1985**, (17), 1148–1149. DOI: 10.1039/c39850001148.
- (30) Aida, T.; Maekawa, Y.; Asano, S.; Inoue, S. Immortal Polymerization - Polymerization of Epoxide and Beta-Lactone with Aluminum Porphyrin in the Presence of Protic Compound. *Macromol.* **1988**, *21* (5), 1195–1202. DOI: DOI 10.1021/ma00183a001.
- (31) Inoue, S. Immortal polymerization: The outset, development, and application. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38* (16), 2861–2871. DOI: 10.1002/1099-0518(20000815)38:16<2861::Aid-pola20>3.0.Co;2-1.
- (32) Lidston, C. A. L.; Abel, B. A.; Coates, G. W. Bifunctional Catalysis Prevents Inhibition in Reversible-Deactivation Ring-Opening Copolymerizations of Epoxides and Cyclic Anhydrides. *J. Am. Chem. Soc.* **2020**, *142* (47), 20161–20169. DOI: 10.1021/jacs.0c10014.
- (33) Kerr, R. W. F.; Williams, C. K. Zr(IV) Catalyst for the Ring-Opening Copolymerization of Anhydrides (A) with Epoxides (B), Oxetane (B), and Tetrahydrofurans (C) to Make ABB- and/or ABC-Poly(ester-alt-ethers). *J. Am. Chem. Soc.* **2022**, *144* (15), 6882–6893. DOI: 10.1021/jacs.2c01225.
- (34) Yang, G.-W.; Xu, C.-K.; Xie, R.; Zhang, Y.-Y.; Lu, C.; Qi, H.; Yang, L.; Wang, Y.; Wu, G.-P. Precision copolymerization of CO₂ and epoxides enabled by organoboron catalysts. *Nat. Synth.* **2022**, *1* (11), 892–901. DOI: 10.1038/s44160-022-00137-x.
- (35) Lehenmeier, M. W.; Kissling, S.; Altenbuchner, P. T.; Bruckmeier, C.; Deglmann, P.; Brym, A. K.; Rieger, B. Flexibly Tethered Dinuclear Zinc Complexes: A Solution to the Entropy Problem in CO₂/Epoxide Copolymerization Catalysis? *Angew. Chem. Int. Ed.* **2013**, *52* (37), 9821–9826. DOI: 10.1002/anie.201302157.
- (36) Kernbichl, S.; Reiter, M.; Mock, J.; Rieger, B. Terpolymerization of β -Butyrolactone, Epoxides, and CO₂: Chemoselective CO₂-Switch and Its Impact on Kinetics and Material Properties. *Macromol.* **2019**, *52* (21), 8476–8483. DOI: 10.1021/acs.macromol.9b01777.
- (37) Lidston, C. A. L.; Severson, S. M.; Abel, B. A.; Coates, G. W. Multifunctional Catalysts for Ring-Opening Copolymerizations. *ACS Catal.* **2022**, 11037–11070. DOI: 10.1021/acscatal.2c02524.
- (38) Abel, B. A.; Lidston, C. A. L.; Coates, G. W. Mechanism-Inspired Design of Bifunctional Catalysts for the Alternating Ring-Opening Copolymerization of Epoxides and Cyclic

- Anhydrides. *J. Am. Chem. Soc.* **2019**, *141* (32), 12760–12769. DOI: 10.1021/jacs.9b05570.
- (39) Bhat, G. A.; Darensbourg, D. J. Progress in the catalytic reactions of CO₂ and epoxides to selectively provide cyclic or polymeric carbonates. *Green Chem.* **2022**, *24* (13), 5007–5034. DOI: 10.1039/d2gc01422j.
- (40) Shechter, L.; Wynstra, J. Glycidyl Ether Reactions with Alcohols, Phenols, Carboxylic Acids, and Acid Anhydrides. *Ind. Eng. Chem.* **1956**, *48* (1), 86–93. DOI: 10.1021/ie50553a028.
- (41) Fisch, W.; Hofmann, W. Über den Härtungsmechanismus der äthoxylinharze. *J. Polym. Sci.* **1954**, *7*, 497–502.
- (42) Dearborn, E. C.; Fuoss, R. M.; White, A. F. Acid acceleration of epoxide condensations. *J. Polym. Sci.* **1955**, *16* (82), 201–208. DOI: 10.1002/pol.1955.120168210.
- (43) Weiss, H. Anhydride Curing Agents for Epoxy Resins. *Ind. Eng. Chem.* **1957**, *49* (7), 1089–1090. DOI: 10.1021/ie50571a024.
- (44) Fischer, R. F. Polyesters from epoxides and anhydrides. *J. Polym. Sci.* **1960**, *44* (143), 155–172. DOI: 10.1002/pol.1960.1204414314.
- (45) Inoue, S.; Koinuma, H.; Tsuruta, T. Copolymerization of carbon dioxide and epoxide. *J. Polym. Sci., Part B: Polym. Lett.* **1969**, *7* (4), 287–292. DOI: 10.1002/pol.1969.110070408.
- (46) Koinuma, H.; Hirai, H. Copolymerization of carbon dioxide and some oxiranes by organoaluminium catalysts. *Makromolekul. Chem.* **1977**, *178* (5), 1283–1294. DOI: 10.1002/macp.1977.021780507.
- (47) Takeda, N.; Inoue, S. Polymerization of 1,2-epoxypropane and copolymerization with carbon dioxide catalyzed by metalloporphyrins. *Makromolekul. Chem.* **1978**, *179* (5), 1377–1381. DOI: 10.1002/macp.1978.021790529.
- (48) Aida, T.; Inoue, S. Catalytic reaction on both sides of a metalloporphyrin plane. Alternating copolymerization of phthalic anhydride and epoxypropane with an aluminum porphyrin-quaternary salt system. *J. Am. Chem. Soc.* **1985**, *107* (5), 1358–1364. DOI: 10.1021/ja00291a041.
- (49) Trott, G.; Saini, P. K.; Williams, C. K. Catalysts for CO₂/Epoxide Ring-Opening Copolymerization. *Philos. Trans. R. Soc., A* **2016**, *374* (2061). DOI: 10.1098/rsta.2015.0085.
- (50) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. Copolymerization of CO₂ and 1,2-Cyclohexene Oxide Using a CO₂-Soluble Chromium Porphyrin Catalyst. *Macromol.* **1999**, *33* (2), 303–308. DOI: 10.1021/ma991162m.
- (51) Bernard, A.; Chatterjee, C.; Chisholm, M. H. The influence of the metal (Al, Cr and Co) and the substituents of the porphyrin in controlling the reactions involved in the copolymerization of propylene oxide and cyclic anhydrides by porphyrin metal(III) complexes. *Polymer* **2013**, *54* (11), 2639–2646. DOI: 10.1016/j.polymer.2013.02.033.

- (52) DiCiccio, A. M.; Coates, G. W. Ring-Opening Copolymerization of Maleic Anhydride with Epoxides: A Chain-Growth Approach to Unsaturated Polyesters. *J. Am. Chem. Soc.* **2011**, *133* (28), 10724–10727. DOI: 10.1021/ja203520p.
- (53) Huijser, S.; HosseiniNejad, E.; Sablong, R.; de Jong, C.; Koning, C. E.; Duchateau, R. Ring-Opening Co- and Terpolymerization of an Alicyclic Oxirane with Carboxylic Acid Anhydrides and CO₂ in the Presence of Chromium Porphyrinato and Salen Catalysts. *Macromol.* **2011**, *44* (5), 1132–1139. DOI: 10.1021/ma102238u.
- (54) Hosseini Nejad, E.; van Melis, C. G. W.; Vermeer, T. J.; Koning, C. E.; Duchateau, R. Alternating Ring-Opening Polymerization of Cyclohexene Oxide and Anhydrides: Effect of Catalyst, Cocatalyst, and Anhydride Structure. *Macromol.* **2012**, *45* (4), 1770–1776. DOI: 10.1021/ma2025804.
- (55) Darensbourg, D. J.; Poland, R. R.; Escobedo, C. Kinetic Studies of the Alternating Copolymerization of Cyclic Acid Anhydrides and Epoxides, and the Terpolymerization of Cyclic Acid Anhydrides, Epoxides, and CO₂ Catalyzed by (salen)Cr(III)Cl. *Macromol.* **2012**, *45* (5), 2242–2248. DOI: 10.1021/ma2026385.
- (56) Darensbourg, D. J.; Yarbrough, J. C. Mechanistic Aspects of the Copolymerization Reaction of Carbon Dioxide and Epoxides, Using a Chiral Salen Chromium Chloride Catalyst. *J. Am. Chem. Soc.* **2002**, *124* (22), 6335–6342. DOI: 10.1021/ja012714v.
- (57) Darensbourg, D. J.; Mackiewicz, R. M.; Billodeaux, D. R. Pressure Dependence of the Carbon Dioxide/Cyclohexene Oxide Coupling Reaction Catalyzed by Chromium Salen Complexes. Optimization of the Comonomer-Alternating Enchainment Pathway. *Organometallics* **2004**, *24* (1), 144–148. DOI: 10.1021/om049454l.
- (58) Cohen, C. T.; Chu, T.; Coates, G. W. Cobalt Catalysts for the Alternating Copolymerization of Propylene Oxide and Carbon Dioxide: Combining High Activity and Selectivity. *J. Am. Chem. Soc.* **2005**, *127* (31), 10869–10878. DOI: 10.1021/ja051744l.
- (59) Fieser, M. E.; Sanford, M. J.; Mitchell, L. A.; Dunbar, C. R.; Mandal, M.; Van Zee, N. J.; Urness, D. M.; Cramer, C. J.; Coates, G. W.; Tolman, W. B. Mechanistic Insights into the Alternating Copolymerization of Epoxides and Cyclic Anhydrides Using a (Salph)AlCl and Iminium Salt Catalytic System. *J. Am. Chem. Soc.* **2017**, *139* (42), 15222–15231. DOI: 10.1021/jacs.7b09079.
- (60) Cao, H.; Liu, S.; Wang, X. Environmentally benign metal catalyst for the ring-opening copolymerization of epoxide and CO₂: state-of-the-art, opportunities, and challenges. *Green Chem. Eng.* **2022**, *3* (2), 111–124. DOI: 10.1016/j.gce.2021.11.005.
- (61) Darensbourg, D. J.; Billodeaux, D. R. Aluminum Salen Complexes and Tetrabutylammonium Salts: A Binary Catalytic System for Production of Polycarbonates from CO₂ and Cyclohexene Oxide. *Inorg. Chem.* **2005**, *44* (5), 1433–1442. DOI: 10.1021/ic048508g.
- (62) Plommer, H.; Stein, L.; Murphy, J. N.; Ikpo, N.; Mora-Diez, N.; Kerton, F. M. Copolymerization of CHO/CO₂ catalyzed by a series of aluminum amino-phenolate complexes and insights into structure–activity relationships. *Dalton Trans.* **2020**, *49* (20), 6884–6895. DOI: 10.1039/d0dt00726a.

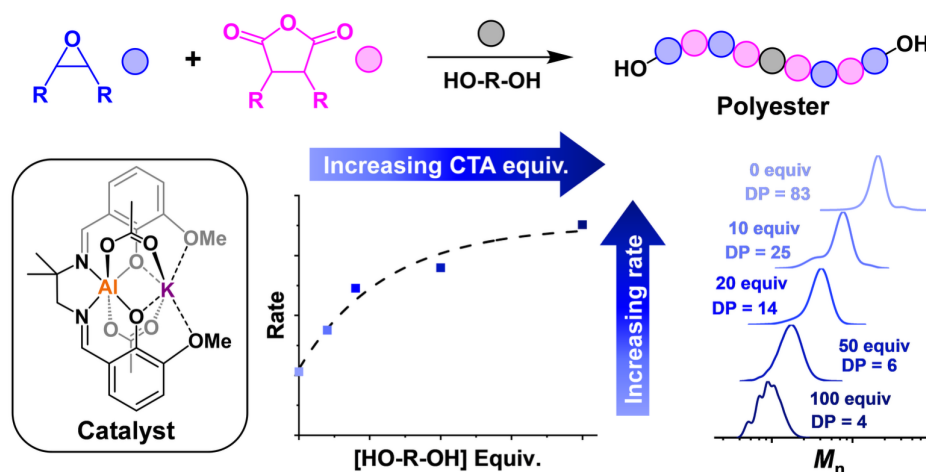
- (63) Wood, Z. A.; Assefa, M. K.; Fieser, M. E. Simple yttrium salts as highly active and controlled catalysts for the atom-efficient synthesis of high molecular weight polyesters. *Chem. Sci.* **2022**, *13* (35), 10437–10447. DOI: 10.1039/d2sc02745c.
- (64) Chen, X.-L.; Wang, B.; Pan, L.; Li, Y.-S. Synthesis of Unsaturated (Co)polyesters from Ring-Opening Copolymerization by Aluminum Bipyridine Bisphenolate Complexes with Improved Protonic Impurities Tolerance. *Macromol.* **2022**, *55* (9), 3502–3512. DOI: 10.1021/acs.macromol.2c00034.
- (65) Nakano, K.; Kamada, T.; Nozaki, K. Selective Formation of Polycarbonate over Cyclic Carbonate: Copolymerization of Epoxides with Carbon Dioxide Catalyzed by a Cobalt(III) Complex with a Piperidinium End-Capping Arm. *Angew. Chem. Int. Ed.* **2006**, *45* (43), 7274–7277. DOI: 10.1002/anie.200603132.
- (66) S, S.; Min, J. K.; Seong, J. E.; Na, S. J.; Lee, B. Y. A Highly Active and Recyclable Catalytic System for CO₂/Propylene Oxide Copolymerization. *Angew. Chem. Int. Ed.* **2008**, *47* (38), 7306–7309. DOI: 10.1002/anie.200801852.
- (67) Jeon, J. Y.; Eo, S. C.; Varghese, J. K.; Lee, B. Y. Copolymerization and terpolymerization of carbon dioxide/propylene oxide/phthalic anhydride using a (salen)Co(III) complex tethering four quaternary ammonium salts. *Beilstein J. Org. Chem.* **2014**, *10*, 1787–1795. DOI: 10.3762/bjoc.10.187.
- (68) Na, S. J.; S, S.; Cyriac, A.; Kim, B. E.; Yoo, J.; Kang, Y. K.; Han, S. J.; Lee, C.; Lee, B. Y. Elucidation of the Structure of a Highly Active Catalytic System for CO₂/Epoxide Copolymerization: A salen-Cobaltate Complex of an Unusual Binding Mode. *Inorg. Chem.* **2009**, *48* (21), 10455–10465. DOI: 10.1021/ic901584u.
- (69) Cyriac, A.; Lee, S. H.; Varghese, J. K.; Park, E. S.; Park, J. H.; Lee, B. Y. Immortal CO₂/Propylene Oxide Copolymerization: Precise Control of Molecular Weight and Architecture of Various Block Copolymers. *Macromol.* **2010**, *43* (18), 7398–7401. DOI: 10.1021/ma101259k.
- (70) Deng, J.; Ratanasak, M.; Sako, Y.; Tokuda, H.; Maeda, C.; Nozaki, K.; Hasegawa, J. Y.; Ema, T. Aluminum porphyrins with quaternary ammonium halides as catalysts for copolymerization of cyclohexene oxide and CO₂: metal-ligand cooperative catalysis. *Chem. Sci.* **2020**, *11* (22), 5669–5675. DOI: 10.1039/d0sc01609h.
- (71) Ohkawara, T.; Suzuki, K.; Nakano, K.; Mori, S.; Nozaki, K. Facile Estimation of Catalytic Activity and Selectivities in Copolymerization of Propylene Oxide with Carbon Dioxide Mediated by Metal Complexes with Planar Tetradentate Ligand. *J. Am. Chem. Soc.* **2014**, *136* (30), 10728–10735. DOI: 10.1021/ja5046814.
- (72) Tsai, F.-T.; Wang, Y.; Darensbourg, D. J. Environmentally Benign CO₂-Based Copolymers: Degradable Polycarbonates Derived from Dihydroxybutyric Acid and Their Platinum-Polymer Conjugates. *J. Am. Chem. Soc.* **2016**, *138* (13), 4626–4633. DOI: 10.1021/jacs.6b01327.
- (73) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. Mechanism of the Alternating Copolymerization of Epoxides and CO₂ Using β -Diiminate Zinc Catalysts: Evidence for a Bimetallic Epoxide Enchainment. *J. Am. Chem. Soc.* **2003**, *125* (39), 11911–11924. DOI: 10.1021/ja030085e.

- (74) Jeske, R. C.; DiCiccio, A. M.; Coates, G. W. Alternating Copolymerization of Epoxides and Cyclic Anhydrides: An Improved Route to Aliphatic Polyesters. *J. Am. Chem. Soc.* **2007**, *129* (37), 11330–11331. DOI: 10.1021/ja0737568.
- (75) Klaus, S.; Vagin, S. I.; Lehenmeier, M. W.; Deglmann, P.; Brym, A. K.; Rieger, B. Kinetic and Mechanistic Investigation of Mononuclear and Flexibly Linked Dinuclear Complexes for Copolymerization of CO₂ and Epoxides. *Macromol.* **2011**, *44* (24), 9508–9516. DOI: 10.1021/ma201387f.
- (76) Liu, Y.; Ren, W. M.; Liu, J.; Lu, X. B. Asymmetric Copolymerization of CO₂ with meso-Epoxides Mediated by Dinuclear Cobalt(III) Complexes: Unprecedented Enantioselectivity and Activity. *Angew. Chem. Int. Ed.* **2013**, *52* (44), 11594–11598. DOI: 10.1002/anie.201305154.
- (77) Cui, L.; Ren, B. H.; Lu, X. B. Trinuclear salphen–chromium(III)chloride complexes as catalysts for the alternating copolymerization of epoxides and cyclic anhydrides. *J. Polym. Sci.* **2021**, *59* (16), 1821–1828. DOI: 10.1002/pol.20210334.
- (78) Li, J.; Liu, Y.; Ren, W.-M.; Lu, X.-B. Asymmetric Alternating Copolymerization of Meso-epoxides and Cyclic Anhydrides: Efficient Access to Enantiopure Polyesters. *J. Am. Chem. Soc.* **2016**, *138* (36), 11493–11496. DOI: 10.1021/jacs.6b07520.
- (79) Nakano, K.; Hashimoto, S.; Nozaki, K. Bimetallic mechanism operating in the copolymerization of propylene oxide with carbon dioxide catalyzed by cobalt–salen complexes. *Chem. Sci.* **2010**, *1* (3). DOI: 10.1039/c0sc00220h.
- (80) Kissling, S.; Lehenmeier, M. W.; Altenbuchner, P. T.; Kronast, A.; Reiter, M.; Deglmann, P.; Seemann, U. B.; Rieger, B. Dinuclear zinc catalysts with unprecedented activities for the copolymerization of cyclohexene oxide and CO₂. *Chem. Commun.* **2015**, *51* (22), 4579–4582. DOI: 10.1039/c5cc00784d.
- (81) Cao, H.; Qin, Y.; Zhuo, C.; Wang, X.; Wang, F. Homogeneous Metallic Oligomer Catalyst with Multisite Intramolecular Cooperativity for the Synthesis of CO₂-Based Polymers. *ACS Catal.* **2019**, *9* (9), 8669–8676. DOI: 10.1021/acscatal.9b02741.
- (82) Zhuo, C.; You, H.; Gao, F.; Liu, S.; Wang, X.; Wang, F. Bottlebrush polymeric catalyst: Boosting activity for CO₂/epoxide copolymerization. *Fuel* **2023**, *333*. DOI: 10.1016/j.fuel.2022.126434.
- (83) Zhuo, C.; Cao, H.; Wang, X.; Liu, S.; Wang, X. Polymeric aluminum porphyrin: Controllable synthesis of ultra-low molecular weight CO₂-based polyols. *Chin. Chem. Lett.* **2023**, *34* (8). DOI: 10.1016/j.ccllet.2022.108011.
- (84) Fan, P.; Liu, S.; Zhang, R.; Zhuo, C.; Gao, F.; Pang, X.; Chen, X.; Wang, X. Rigid-Flexible Binuclear Catalysts: Boosting Activity for Copolymerization of CO₂ and Propylene Oxide. *Macromol.* **2024**, *57* (12), 5702–5711. DOI: 10.1021/acs.macromol.4c00887.
- (85) Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K. Highly Active Dizinc Catalyst for the Copolymerization of Carbon Dioxide and Cyclohexene Oxide at One Atmosphere Pressure. *Angew. Chem. Int. Ed.* **2009**, *48* (5), 931–933. DOI: 10.1002/anie.200803896.

- (86) Jutz, F.; Buchard, A.; Kember, M. R.; Fredriksen, S. B.; Williams, C. K. Mechanistic Investigation and Reaction Kinetics of the Low-Pressure Copolymerization of Cyclohexene Oxide and Carbon Dioxide Catalyzed by a Dizinc Complex. *J. Am. Chem. Soc.* **2011**, *133* (43), 17395–17405. DOI: 10.1021/ja206352x.
- (87) Buchard, A.; Jutz, F.; Kember, M. R.; White, A. J. P.; Rzepa, H. S.; Williams, C. K. Experimental and Computational Investigation of the Mechanism of Carbon Dioxide/Cyclohexene Oxide Copolymerization Using a Dizinc Catalyst. *Macromol.* **2012**, *45* (17), 6781–6795. DOI: 10.1021/ma300803b.
- (88) Kember, M. R.; Williams, C. K. Efficient Magnesium Catalysts for the Copolymerization of Epoxides and CO₂; Using Water to Synthesize Polycarbonate Polyols. *J. Am. Chem. Soc.* **2012**, *134* (38), 15676–15679. DOI: 10.1021/ja307096m.
- (89) Garden, J. A.; Saini, P. K.; Williams, C. K. Greater than the Sum of Its Parts: A Heterodinuclear Polymerization Catalyst. *J. Am. Chem. Soc.* **2015**, *137* (48), 15078–15081. DOI: 10.1021/jacs.5b09913.
- (90) Chapman, A. M.; Keyworth, C.; Kember, M. R.; Lennox, A. J. J.; Williams, C. K. Adding Value to Power Station Captured CO₂: Tolerant Zn and Mg Homogeneous Catalysts for Polycarbonate Polyol Production. *ACS Catal.* **2015**, *5* (3), 1581–1588. DOI: 10.1021/cs501798s.
- (91) Thevenon, A.; Garden, J. A.; White, A. J.; Williams, C. K. Dinuclear Zinc Salen Catalysts for the Ring Opening Copolymerization of Epoxides and Carbon Dioxide or Anhydrides. *Inorg. Chem.* **2015**, *54* (24), 11906–11915. DOI: 10.1021/acs.inorgchem.5b02233.
- (92) Deacy, A. C.; Moreby, E.; Phanopoulos, A.; Williams, C. K. Co(III)/Alkali-Metal(I) Heterodinuclear Catalysts for the Ring-Opening Copolymerization of CO₂ and Propylene Oxide. *J. Am. Chem. Soc.* **2020**, *142* (45), 19150–19160. DOI: 10.1021/jacs.0c07980.
- (93) Fiorentini, F.; Diment, W. T.; Deacy, A. C.; Kerr, R. W. F.; Faulkner, S.; Williams, C. K. Understanding catalytic synergy in dinuclear polymerization catalysts for sustainable polymers. *Nat. Commun.* **2023**, *14* (1). DOI: 10.1038/s41467-023-40284-z.
- (94) Butler, F.; Fiorentini, F.; Eisenhardt, K. H. S.; Williams, C. K. Structure-Activity Relationships for s-Block Metal/Co(III) Heterodinuclear Catalysts in Cyclohexene Oxide Ring-Opening Copolymerizations. *Angew. Chem. Int. Ed.* **2025**. DOI: 10.1002/anie.202422497.
- (95) Diment, W. T.; Stößer, T.; Kerr, R. W. F.; Phanopoulos, A.; Durr, C. B.; Williams, C. K. Ortho-vanillin derived Al(III) and Co(III) catalyst systems for switchable catalysis using ϵ -decalactone, phthalic anhydride and cyclohexene oxide. *Catal. Sci. Technol.* **2021**, *11* (5), 1737–1745. DOI: 10.1039/d0cy02164d.
- (96) Diment, W. T. Catalyst Development for the Ring-Opening Copolymerisation of Epoxides and Anhydrides. DPhil. Thesis, University of Oxford, 2021.
- (97) Eisenhardt, K. H. S.; Fiorentini, F.; Williams, C. K. Understanding the Effect of M(III) Choice in Heterodinuclear Polymerization Catalysts. *Inorg. Chem.* **2024**. DOI: 10.1021/acs.inorgchem.4c04430.

Chapter 2

Synthesis, Characterisation and Polymerisation Catalysis of Heterodinuclear Al(III)/K(I) ortho- Vanillin derived Schiff Base Complexes



Work described in this chapter appears in “Al(III)/K(I) Heterodinuclear Polymerization Catalysts Showing Fast Rates and High Selectivity for Polyester Polyols”
Shellard, E. J. K., Diment, W. T., Resendiz-Lara, D. A., Fiorentini, F., Gregory, G. L.,
Williams, C. K.,
ACS Catal. **2024**, 14 (3), 1363-1374

2.1 Introduction and Aims

The design of catalysts for epoxide/anhydride ROCOP may be improved by understanding structure-activity relationships of these catalysts. This chapter examines catalyst design, with the target being a ROCOP catalyst that combines high rates and selectivity, whilst operating at low catalyst loadings and showing high levels of polymerisation control.¹⁻³ Many successful current catalyst systems require PPNX co-catalysts that are expensive and may be toxic and corrosive to steel.²

Recent development in heterodinuclear catalysts, exploiting intermetallic synergy, has resulted in catalysts with very high activities and operating without any co-catalyst.³ For example, in 2021 an Al(III)/K(I) complex, with a diphenolate Schiff base ligand, showed a TOF of 1072 h⁻¹ (0.25 mol% vs. anhydride, 100 °C, CHO/PA).^{3,4} This catalyst is of particular interest since it is unique in that it fits well within the constraints of having a ligand that is straightforward to synthesise along with metals that are earth-abundant, low/non-toxic and inexpensive.⁵ The rate law of the catalysis was determined to be first order in catalyst and epoxide concentrations, *i.e.* rate = $k[\text{L}_{\text{van}}\text{Al(III)K(I)(OAc)}_2][\text{CHO}]^1[\text{PA}]^0$. The rate law, supported by experiments and DFT calculations, was rationalised by a dinuclear metallate polymerisation mechanism.⁴

In the catalysis, the polyester polyol molar masses, and end-groups, are controlled by adding specific but excess quantities of diols (*vs.* catalyst), known as the chain transfer agent (CTA), to the polymerisation.^{6,7} The diols are proposed to undergo proton exchange, or chain transfer reactions, with the alkoxide-chain intermediates, liberating ‘free’ polymer chains end-capped with alcohols. These chain transfer reactions usually occur faster than chain propagation, producing polyesters where the overall molar mass values depend upon the amount of diol added to the reaction.⁸⁻¹⁰ Unfortunately, few

catalysts tolerate excess alcohol being present, *i.e.* operate at equivalent rates to when it is absent, with many showing diminished activities, and thus performance evaluations are typically conducted at rather low excesses of alcohol, *e.g.* ~ 10 equivalents vs. catalyst, which is often insufficient for adequate polymer chain end-group control and limits access to the oligomers.^{6, 11-13}

This chapter investigates a series of Al(III)/K(I) catalysts, where systematic variations to the diamine backbone linker of the ligand are made to identify trends between ligand structure with activity, ester linkage selectivity and polymerisation control. This catalyst series is tested for the copolymerisation of CHO and PA, a common benchmark polymerisation. In order to assess the catalyst viability for the formation of hydroxyl end-capped oligoesters, polymerisations with varying quantities of hydroxyl containing additives (acting as CTAs) are run with a particular focus on the M_n of the polymers produced and the catalytic activity. It is important to also establish whether the catalyst can be applied for the synthesis of a range of polyesters, and therefore a number of epoxides and anhydrides of different properties are copolymerised using the most active and selective catalyst.

2.2 Synthesis and Characterisation

To understand the catalyst structure-performance relationships, the ligand backbone was systematically varied. The 'imine' linker groups were selected due to their proximity to the active site, Al(III), allowing for them to impart electronic and steric influences, which should moderate both ground/transition state energies in the rate determining step. Catalyst **1.32** features a 2,2-dimethyl propylene linker⁴ and serves as a point of comparison with a series of C_2 : 2,2-dimethylethylene (**1**), (1*R*,2*R*)-(-)-1,2-cyclohexylene (**2**), (1*R*,2*R*)-(-)-1,2-diphenylethylene (**3**), 1,2-phenylene (**4**), ethylene (**6**) and another C_3 , 1,3-propylene (**5**), linker group (Figure 2.1).

2.2.1 Synthesis

The ligands were all successfully synthesised by Schiff base condensation reactions between *ortho*-vanillin and the different diamines (see Chapter 6: Experimental for experimental details).⁴ The Al(III)/K(I) catalysts, **1-6**, were prepared by first reacting the ligand with triethylaluminium, then adding acetic acid to yield the Al(III) acetate complex that was isolated. Subsequent addition of one equiv. of KOAc yielded the air-stable Al(III)/K(I) heterobimetallic complex (Figure 2.1).

Catalysts **1-6** were isolated as (light) yellow powders in good yields and were characterized by NMR spectroscopy and, in some cases, by single crystal X-ray diffraction (Figures S2.1 – S2.41, Tables S2.1 – S2.3). Further confirmation of identity and purity was achieved by IR spectroscopy, MALDI-ToF and Elemental Analysis (Figures S2.42 – S2.53).

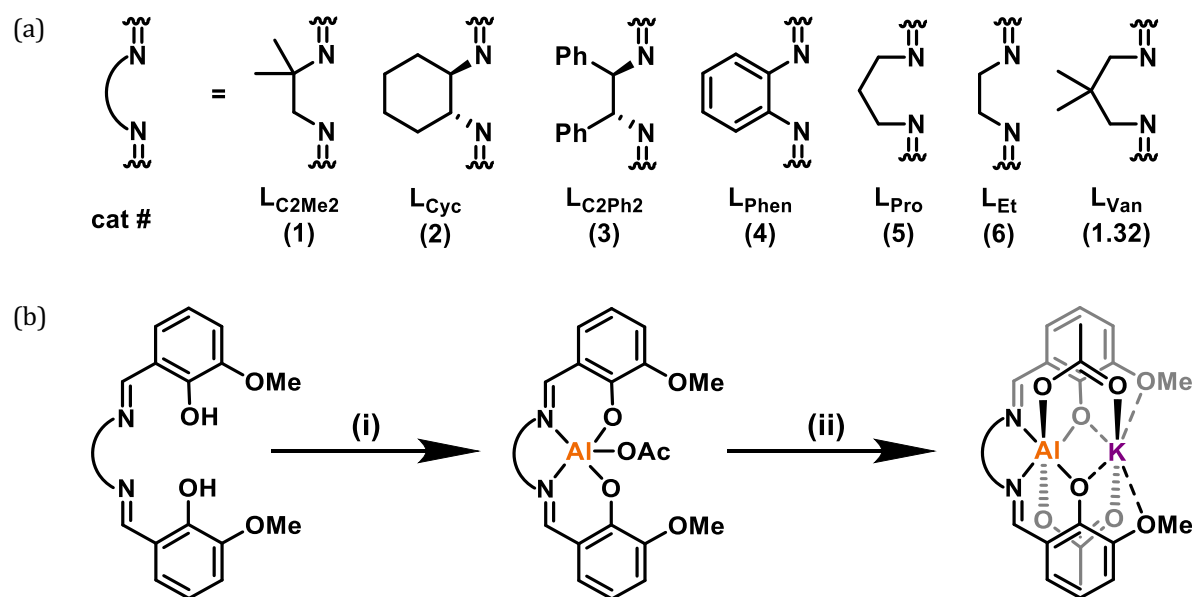


Figure 2.1. (a) The series of Al(III)/K(I) heterobimetallic catalysts differing by imine linker groups. (b) Catalyst synthesis. Reaction conditions: (i) 1.05 equiv. $AlEt_3$, toluene, 5 h, 25 °C, then 2.0 equiv. AcOH, toluene, 4 h, 100 °C, then 12 h, 25 °C. Yields = 75 % (1), 80 % (2), 65 % (3), 68 % (4), 81 % (5), 98 % (6). (ii) 1.0 equiv. KOAc, $CHCl_3$, 16 h, 25 °C. Yields = 99 % (1), 99 % (2), 99 % (3), 93 % (4), 88 % (5), 93 % (6).

2.2.2 NMR Spectroscopy

All complexes (1-6) were characterised by 1H , ^{13}C and ^{27}Al NMR and show chemical shifts consistent with the successful formation of the heterodinuclear complexes. Complex 1 is used as an exemplar for discussion (Figure 2.2).

The formation of complex 1 (2,2-dimethylethylene) was monitored by NMR spectroscopy (Figure S2.2), observing the disappearance of the ligand phenol peaks (13.75 and 14.37 ppm) upon reaction with triethylaluminium, followed by a new acetate resonance (1.87 ppm) upon reaction with acetic acid (Figure 2.2). After the final step, the increased relative acetate peak integral (6H) is consistent with the complex having two acetate ligands and the decrease in chemical shift of the $-OCH_3$ protons (g & l) suggests coordination of a second metal.

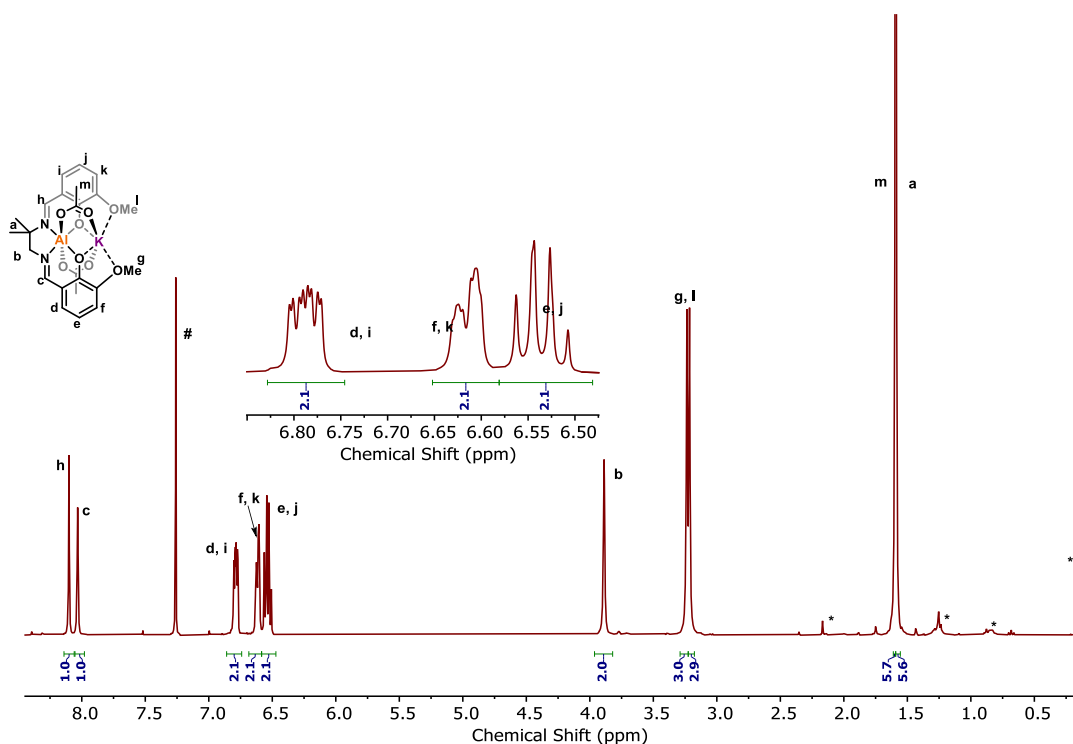


Figure 2.2. ^1H NMR Spectrum of complex **1** (CDCl_3 (#), 298 K, 400 MHz) *: minor impurities from acetone, hexane and grease.

The asymmetric backbone of the ligand results in 13 distinct proton environments, although there is overlap of the shifts with protons on the aromatic rings. In contrast, the acetate ligands show a singlet resonance which indicates that the complex adopts a structure in which the acetates are equivalent, on an NMR timescale, at room temperature.

The ^{27}Al NMR spectra of complex **1** (in CDCl_3) shows a broad singlet, from 0 - 10 ppm, on top of the broad background from the probe, consistent with a hexacoordinate Al(III), albeit with asymmetry in its coordination chemistry (Figure S2.4). This is consistent for all complexes with ligand backbone lengths of two carbons. For complex **5**, the ^{27}Al NMR spectrum shows a sharp peak at around 0 ppm, indicating higher symmetry around the hexacoordinate Al(III). Indeed, a similar spectrum was observed for complex **1.32**.⁴ The three-carbon backbone appears to enable a more symmetric conformation of the ligand around the Al(III) centre.

2.2.3 X-ray Crystallography

X-ray diffraction experiments were conducted using single crystals, prepared by vapor diffusion of hexane into chloroform solutions. The structures reported were solved by Dr Francesca Fiorentini and Dr Nora Janssen (University of Oxford) (Tables 2.1 & S2.1 – S2.3, Figures 2.3 – 2.5). The structure of complex **1** is shown in Figure 2.3 with selected bond lengths (Table 2.1) and refinement data (Table S2.3).

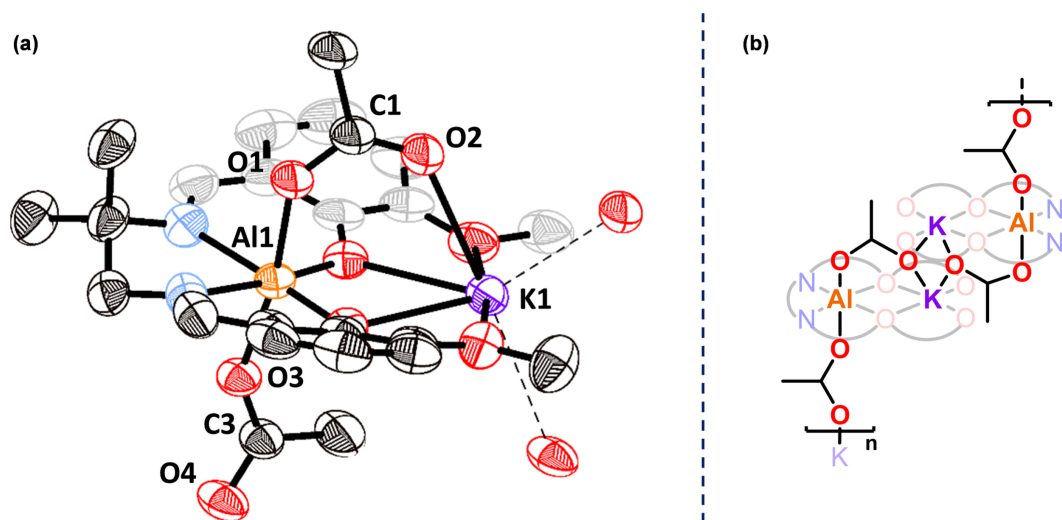


Figure 2.3. (a) Molecular structure of complex **1** obtained from X-ray diffraction experiments, with thermal ellipsoids presented at 50% probability and H atoms omitted for clarity (atom colour scheme: Al (orange), K (purple), O (red), N (blue), C (black/greyscale)). Overall structure is polymeric. (b) Schematic showing a repeat unit (monomer) of the polymeric structure.

Table 2.1 Selected bond lengths for $\text{LC}_2\text{Me}_2\text{AlK}(\text{OAc})_2$ (**1**)

Bond	Bond Length (Å)
K(1)-Al(1)	3.5789(8)
K(1)-O(2)	2.6641(18)
K(1)-O(4)	2.9294(18)
Al(1)-O(1)	1.9174(17)
Al(1)-O(3)	1.8915(15)
O(1)-C(1)	1.271 (3)
O(2)-C(1)	1.226(3)
O(3)-C(3)	1.273(2)
O(4)-C(3)	1.229(3)

In the solid state, complex **1** forms an extended polymeric structure in which each Al(III) centre is hexacoordinate, within a distorted octahedral coordination geometry, consistent with the observed ^{27}Al NMR spectrum (Figures 2.3 & S2.4). The Al(III) is speciated as an aluminate, with the two acetate oxygen atoms being coordinated anionically to it. The aluminate speciation was confirmed by the different acetate ligand C-O bond lengths; the oxygen atoms coordinated to the aluminium have longer C-O bonds, indicating that they are more single bond in nature [$\text{O}(1)\text{-C}(1) = 1.271(3) \text{ \AA}$, $\text{O}(2)\text{-C}(1) = 1.226(3) \text{ \AA}$, $\text{O}(3)\text{-C}(2) = 1.273(2) \text{ \AA}$, $\text{O}(4)\text{-C}(2) = 1.229(3) \text{ \AA}$] (Table 2.1). The Al-O bonds are considerably shorter than the K-O bonds, consistent with the larger ionic radius of the latter [$\text{K}(1)\text{-O}(2) = 2.6641(18) \text{ \AA}$, $\text{K}(1)\text{-O}(4) = 2.9294(18) \text{ \AA}$, $\text{Al}(1)\text{-O}(1) = 1.9174(17) \text{ \AA}$, $\text{Al}(1)\text{-O}(3) = 1.8915(15) \text{ \AA}$] (Table 2.1).

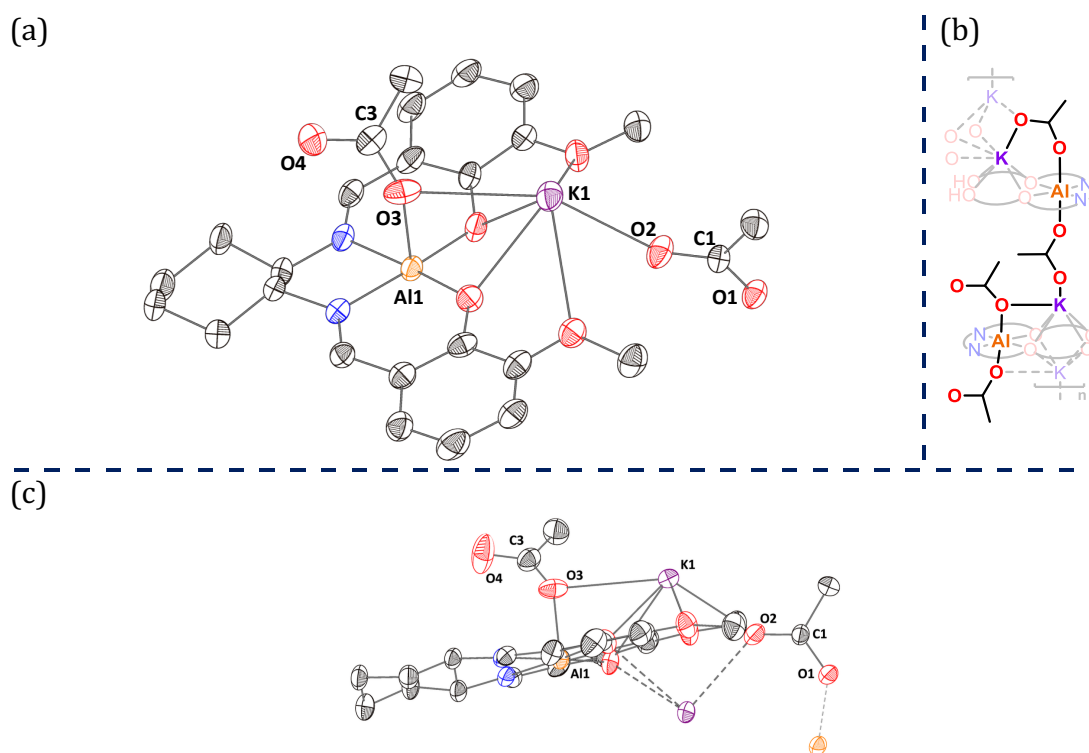


Figure 2.4 (a) Molecular structure of complex **2** obtained from X-ray diffraction experiments, with thermal ellipsoids presented at 50% probability and all H atoms omitted for clarity (atom colour scheme: Al (orange), K (purple), O (red), N (blue), C (black)). Overall structure is polymeric. (b) Schematic showing a repeat unit (monomer) of the polymeric structure. (c) Molecular structure showing connectivity.

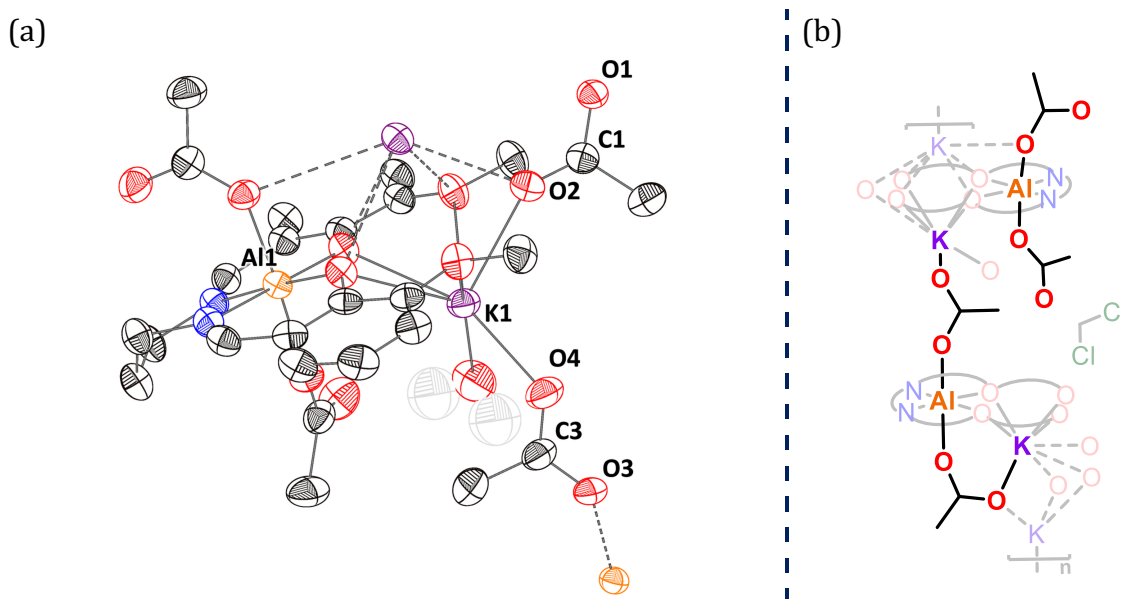


Figure 2.5 (a) Molecular structure of complex **5** obtained from X-ray diffraction experiments, with thermal ellipsoids presented at 50% probability and all H atoms omitted for clarity (atom colour scheme: Al (orange), K (purple), O (red), N (blue), C (black), Cl (grey)). Overall structure is polymeric. (b) Schematic showing a repeat unit (monomer) of the polymeric structure.

For **1**, the Al(1)-K(1) separation is 3.5789(8) Å, similar to that reported for **1.32** (Al(1)-K(1) = 3.665 Å) which demonstrated intermetallic synergy in the catalysis.⁴ In addition, the Al(I)-K(I) distances for complexes **2** and **5** are also within this region as well, being 3.603(2) Å and 3.744(2) Å respectively (Tables S2.1 & S2.2). Interestingly however, in both of these complexes, the K(1) is out of the plane of the *O,O,O,O* binding pocket with a distances of 1.408 Å for **2** and 1.415 Å for **5**. This is in contrast to **1** which is on the mean plane of that binding pocket.

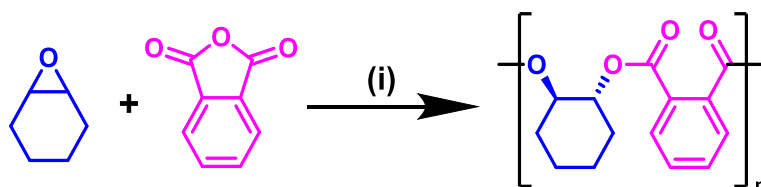
Catalyst **1** was analysed by DOSY NMR spectroscopy in methanol-*d*₄ at room temperature and the hydrodynamic radius obtained is consistent with it remaining dimeric in solution (Figure S2.54). The ROCOP reactions are conducted at higher temperatures (100 °C) which may favour (entropically) dissociation to monomers under the conditions of the catalysis, but a catalytically active dimer cannot be ruled out either.

2.3 Epoxide/Anhydride ROCOP Catalysis

2.3.1 Catalyst Series

Complexes **1-6** were each tested as polymerisation catalysts and, to allow comparisons with the broader literature, the commonly used ‘benchmark monomers’ phthalic anhydride (PA) and cyclohexene oxide (CHO) were selected for these initial tests (Table 2.2). Polymerisations were conducted using [cat]:[PA]:[CHO] of 1:100:500 and at 100 °C.

Table 2.2. Polymerisation data for CHO/PA ROCOP with catalysts **1-6**. Polymerisation Conditions: (i) [Cat]₀: [PA]₀: [CHO]₀ = 1:100:500, *T* = 100 °C.



Entry	Conditions		Polymerisation Results				
	Catalyst	<i>t</i> (min)	Conv. (%) ^a	TOF (h ⁻¹) ^a	PE Select. (%) ^b	<i>M</i> _{n, GPC} (g mol ⁻¹) [<i>D</i>] ^c	<i>M</i> _{n, Theory} (g mol ⁻¹) ^d
a	1 (L _{C2Me2})	10	74	440	>99	6,000 [1.13]	9,200
b	2 (L _{Cyc})	15	69	280	>99	6,200 [1.13]	8,500
c	3 (L _{C2Ph2})	15	64	260	93	4,900 [1.15]	7,900
d	4 (L _{Phen})	90	69	46	59	3,500 [1.57]	8,500
e	5 (L _{Pro})	10	60	360	93	2,100 [1.13]	4,400
f	6 (L _{Et})	15	83	330	>99	5,000 [1.26]	10,200
g ^{e, 4}	1.32 (L _{C3Me2})	15	67	1070	>99	-	-

^a Turnover frequency = TON/time(h). TON determined *via* Conversion*equiv.(monomer). Conversion determined by ¹H NMR (298 K, 400 MHz, CDCl₃) spectroscopy; comparison of PA monomer peaks (8.06-8.00 and 7.94-7.88 ppm) to polymer peaks (7.63-7.52 and 7.44-7.34 ppm) (Table S2.4, Figure S2.55). ^b Selectivity for polyester over ether linkage formation. Determined by ¹H NMR spectroscopy (298 K, 400 MHz, CDCl₃) by comparison of polyester peaks (5.22-5.04 ppm) vs. any ether linkages (3.8-3.2 ppm). ^c Determined by GPC in THF, 30 °C, calibrated using PS standards. ^d Determined according to *M*_{n, Theory} = (TON**M*_{n, repeatunit})/(2*equiv.(cat)) + *M*_{n, OAc}. ^e Loading at [cat]₀: [PA]₀: [CHO]₀ = 1:400:2000.

The polymerisations were monitored by regular removal of aliquots, which were used to determine the conversion (TON), selectivity (%; ester linkages) and molar mass (M_n , $[\eta]$) vs. time relationships. Whilst these tests were run under a N_2 atmosphere, the catalyst is air stable and the polymerisation can successfully be run in air (Section 2.5).

Catalysts **1**, **2** & **6** showed quantitative ester linkage selectivity and high activities, with $TOF(\mathbf{1}) = 440\text{ h}^{-1}$, $TOF(\mathbf{2}) = 280\text{ h}^{-1}$ and $TOF(\mathbf{6}) = 330\text{ h}^{-1}$; catalyst **1** had the highest activity of the series (Table 2.2, a & b). Catalysts **3** and **5** were also active, with TOFs of 260 h^{-1} and 360 h^{-1} , respectively, however both showed slightly lower ester linkage selectivity (93%, Table 2.2, c & e).

Catalyst **4** showed the lowest rate and selectivity (Table 2.2, d), with over 40 % ether linkages in the polymer. When tested, this catalyst did not yield any polyether in neat epoxide, however. Curiously, the ester linkage selectivity was consistent at all conversions but was catalyst loading dependent (Table 2.3). DOSY NMR of the resulting polymer revealed a single copolymer species; these findings may indicate alternative monomer sequences during enchainment (Figure S2.56).¹⁴ The loss of polymer selectivity when catalyst loading is decreased could indicate that catalyst decomposition by loss of the K(I) is occurring. Monometallic complexes typically produce polymers with low polyester selectivities when used in absence of a cocatalyst.

The more selective catalysts, **1-3**, **5** & **6**, all showed very good polymerisation control with reasonable agreement between theoretical and experimental molar mass values; all the polyesters showed narrow molar mass distributions.

Table 2.3. Rates for CHO/PA ROCOP by complex **4**.

Entry	Conditions		Polymerisation Results				
	[cat] : [PA] : [CHO]	t (h)	Conv. (%) ^b	TOF (h ⁻¹) ^c	PE Select. (%) ^d	$M_{n, GPC}$ (g mol ⁻¹) [D] ^e	$M_{n, Theory}$ (g mol ⁻¹) ^f
a	1:100:500	1.5	69	46	59	3,500 [1.57]	8,500
b	1:0:500	2.5	<1	0	-	-	-
c ^a	1:1000:5000	9.8	90	92	36	23,000 [1.66]	110,000

^a Scale of reaction doubled, V(CHO) = 2 mL. ^b Determined by ¹H NMR (298 K, 400 MHz, CDCl₃) spectroscopy; comparison of PA monomer peaks at 8.06-8.00 and 7.94- 7.88 ppm to polymer peaks at 7.63-7.52 and 7.44-7.34 ppm. ^c Turnover frequency = TON/time(h). TON determined *via* Conversion*equiv.(monomer). ^d Selectivity for polyester over polyether formation. Determined by ¹H NMR spectroscopy (298 K, 400 MHz, CDCl₃); polyester 5.22-5.04 ppm vs. ether linkages 3.8-3.2 ppm. ^e Determined by GPC in THF, 30 °C, calibrated using PS standards. ^f Determined using (TON* M_n (repeatunit))/equiv.(cat).

It is observed that increasing the backbone linker rigidity reduced the catalytic rate and selectivity, as apparent from comparing the activity for **1**, **2** and **4** (Table 2.2, a, b & d). A similar conclusion can be drawn when comparing C_2 and C_3 backbone activity, where **1.32**, the C_3 backbone, is over twice as fast as **1**, the C_2 backbone (Table 2.2, a & g). Indeed, previously in lactide ROP, differences in rates between catalysts were often attributed to ligand rigidity.^{15, 16}

Comparing the most active Al(III)/K(I) catalysts, **1**, **5**, **6** and **1.32**, showed that imine linkers featuring two methyl groups improved both polymerisation activity and selectivity. Catalyst **1** (1,1-dimethyl ethylene backbone) showed the highest rates of the complexes featuring C_2 -backbones, it was 1.3 times faster than **6** (ethylene backbone). Further, the methyl substituent rate enhancement was also observed for the C_3 backbone catalysts, where catalyst **1.32** (2,2-dimethylpropylene) was three times as fast as **5** (1,3-propylene linker) (Table 2.2, a, e-g). To investigate whether this trend was also related to ligand conformational fluxionality, VT NMR spectroscopy was conducted using catalysts **1.32** and **5** (Figures S2.57 & S2.58). Both complexes show averaged ligand

backbone conformations at room temperature, with a particular focus on the ligand-Al(III) six membered ring as this is where the dimethyl substituent is most likely to have an impact. On stepwise cooling down to -80 °C, both samples gave the same response to temperature. The peaks at shifts relating to the N-CH (H^f , amine) and -OC(=O)H₃ (H^h , acetate) protons for both complexes gradually disappeared with two new peaks each emerging in their place. This is not a peak splitting that would be indicative of freezing out of ligand fluxionality but rather appears to be some form of a phase transition. What this phase transition is, is not clear, perhaps the complexes form some polymeric-like structure at these low temperatures.

Ultimately, the VT experiment did not reveal any difference in temperature response between the two complexes, suggesting that the dimethyl functionality may not have a significant enough impact on the fluxionality of the ligand-Al(III) six membered ring to impact the rate of reaction. Thus, it appears that other possible scenarios, such as an influence on the electron density at the Al(III) active site by the methyls or angle compression of the dimethyl groups affecting the geometry of the ligand, could be more significant contributing factors.

Comparing **1**, **2**, **5** and **1.32** for which solid state crystal structures have been solved, there appears no clear trend between catalytic activity and intermetallic separation. The complexes (**2** & **5**) with the K(I) out of plane from the *O,O,O,O* pocket have both slower rates and, in the case for **5** lower selectivities than **1** and **1.32** where, in both instances, the K(I) is in the plane. Perhaps, as discussed for **4**, there may be some debonding of the K(I) which could lead to a loss of intermetallic synergy and reduce selectivity.

2.3.2 Kinetic Runs of Lead Catalysts

Complexes **1** and **2** are two of the best performing catalysts from this series and hence were applied at lower loadings (catalyst:PA:CHO = 1:400:2000, $T = 100\text{ }^{\circ}\text{C}$) with conversions vs. time plotted (Figure 2.6 & S2.59). The reactions were run in triplicate with errors at each point calculated as $\pm\sigma/\sqrt{n}$, where σ is the experimental standard deviation and n is the number of measurements.

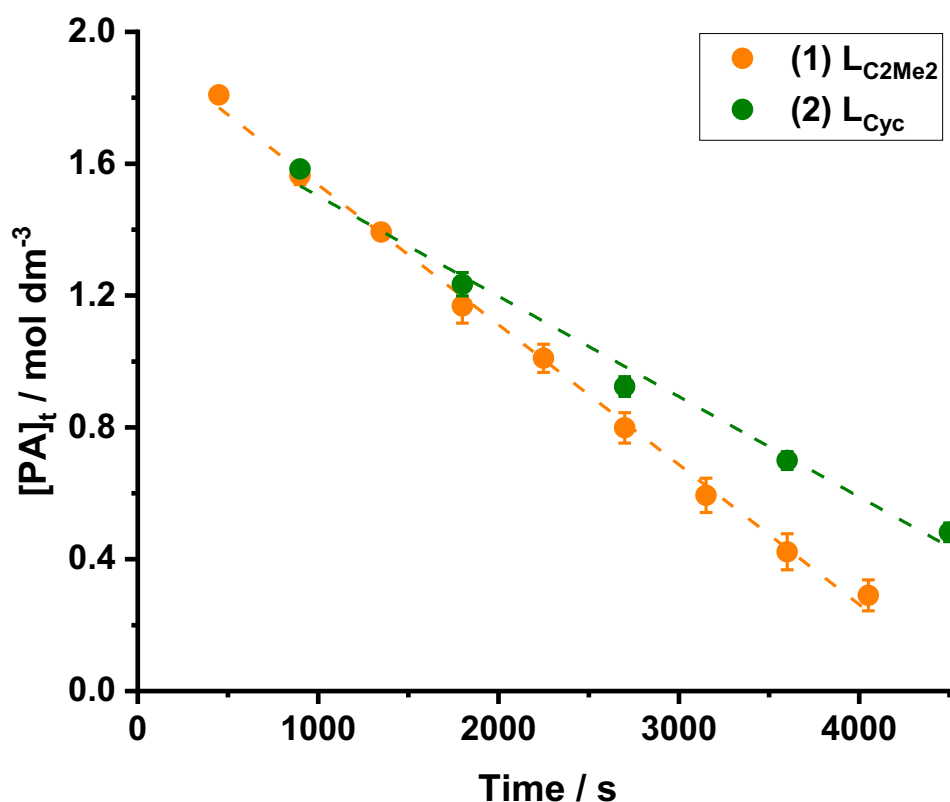


Figure 2.6. Graph of [PA] against time for CHO/PA ROCOP using catalyst **1** (orange) and **2** (green). Conditions: [cat]:[PA]:[CHO] = 1:400:2000, $T = 100\text{ }^{\circ}\text{C}$. Reactions carried out in triplicate, with aliquots at regular time intervals.

A pseudo zero order rate constant, k_{obs} could be calculated from the gradient of linear plots of [PA] vs. time.

$$\frac{d[\text{PA}]}{dt} = -k_{\text{obs}} \quad (2.1)$$

Catalyst **1** maintained its good performance and when monitoring the rate of anhydride consumption showed a constant, high pseudo zero order rate constant,

$k_{\text{obs}} = 4.25 \pm 0.09 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ (Figure 2.6). Complex **2** showed slightly better loading tolerance but was slower than **1**, with $k_{\text{obs}} = 3.0 \pm 0.2 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ under equivalent conditions (Figure 2.6). Complex **3** was also tested, but showed signs of decomposition at these lower loadings, with the rate tailing off after 45 minutes at higher conversions (Figure S2.59), see discussion on this *vide supra*.

The polyester molar mass values, determined from aliquots analysed by GPC, showed a linear increase vs. PA conversion which is consistent with a well-controlled/living polymerisation (Figure 2.7a, S2.60 & S2.61). The GPC of the poly(cyclohexene oxide-*alt*-phthalate) (PCHPE) showed narrow dispersity however with a slight high-weight shoulder (Figure 2.7b). This is attributed to chain-transfer with residual diols in the purified monomers; the major peak was initiated by the acetate ligands on the catalyst. Polymer chain initiation and molecular weight control will be discussed *vide infra* in Section 2.4.

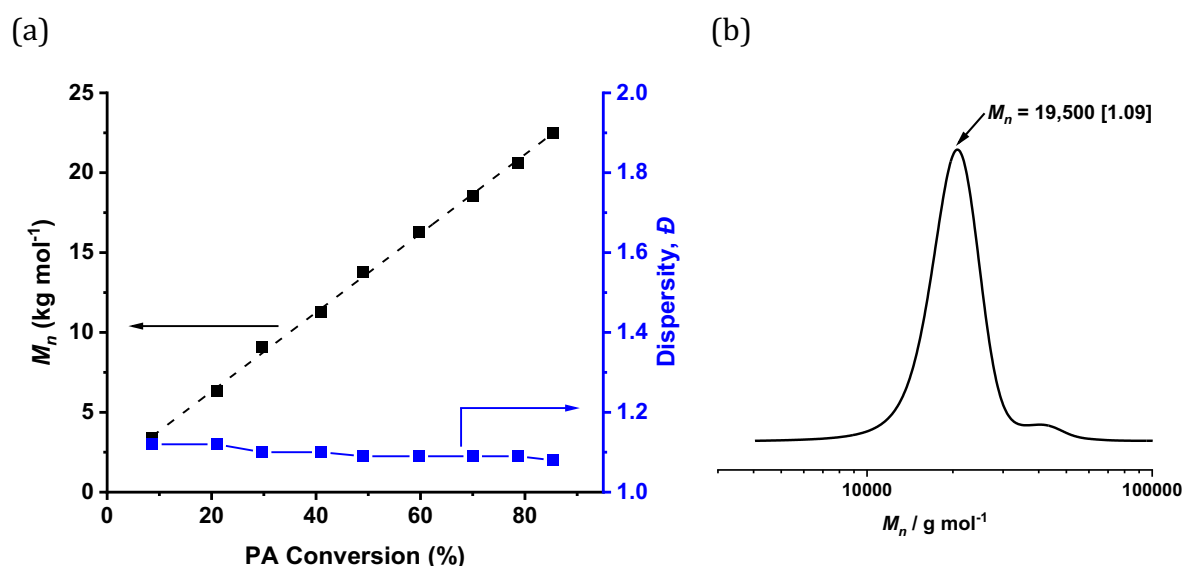


Figure 2.7. (a) Plot of change in polymer molar mass and dispersity with PA conversion for catalyst **1**. Conditions: [cat]:[PA]:[CHO] = 1:400:2000, $T = 100^\circ\text{C}$. (b) GPC trace of PCHPE at full conversion produced by catalyst **1**.

2.3.3 DFT Studies into Effect of Catalyst Backbone

To complement the Al(III)K(I) catalyst scope and the related discussion, DFT calculations were undertaken to see if the experimentally observed trends could be rationalised (Figure 2.8).

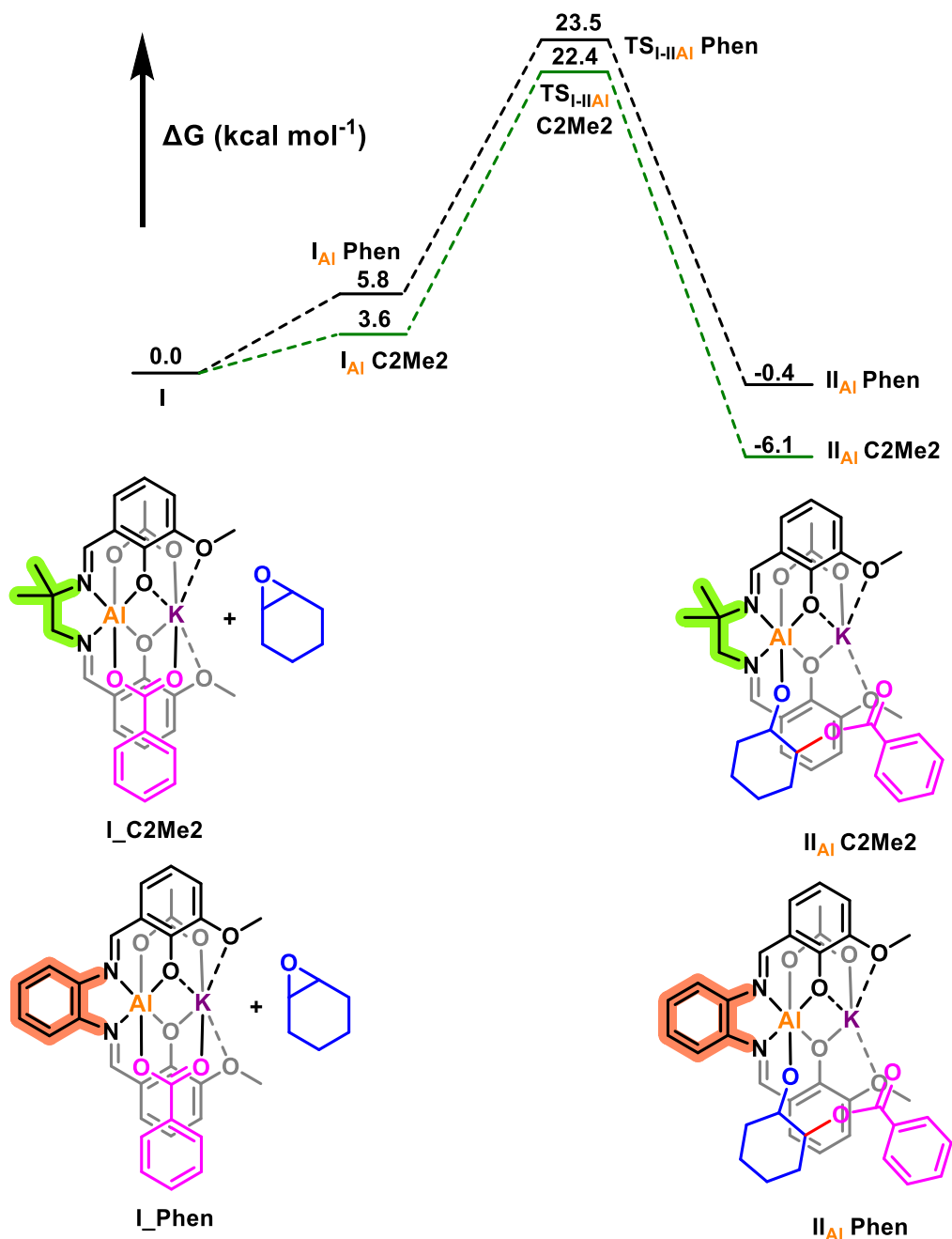


Figure 2.8. Plot of computed reaction profile for epoxide ring-opening for **1** and **4** showing a slightly lower energy barrier for **1**. $\omega\text{b97xD/C H} = 6\text{-}31\text{+g(d,p)}/\text{K Al O N} = 6\text{-}311\text{+g(d)}/\text{solvent} = \text{modified THF eps}=16$ epsinf=1.867 (cpcm).

The fastest and slowest catalysts of the scope were tested, $\text{L}_{\text{C2Me2}}\text{AlK}(\text{OAc})_2$ (**1**) (TOF = 440 h^{-1}) and $\text{L}_{\text{Phen}}\text{AlK}(\text{OAc})_2$ (**4**) (TOF = 46 h^{-1}), to give the greatest contrast for comparison. Work on this was conducted equally with Dr Georgina Gregory (University of Oxford). A summary of the computed values can be found in the Appendix (Tables S2.5 & S2.6). The functional ωb97xD and basis set choices were based on previous published work on ROCOP catalysis, and they provide sufficient sensitivity for use in transition state calculations.⁴

The calculations show that the ring opening of the epoxide is both more kinetically [$\Delta G(\text{I-TS}_{\text{I-IIAl}}\text{Phen}) = +23.5 \text{ kcal mol}^{-1}$ vs. $\Delta G(\text{I-TS}_{\text{I-IIAl}}\text{C2Me2}) = +22.4 \text{ kcal mol}^{-1}$] and thermodynamically [$\Delta G(\text{I-IIAl}\text{Phen}) = -6.2 \text{ kcal mol}^{-1}$ vs. $\Delta G(\text{I-IIAl}\text{C2Me2}) = -9.7 \text{ kcal mol}^{-1}$] favoured to occur with catalyst **1** (Figure 2.8). This is in agreement with the observed experimental trends. The differences are subtle however and just within the error of DFT calculations.

Calculations comparing energies for epoxide activation on the Al(III) versus on the K(I) yielded compelling results favouring epoxide activation on the Al(III), with the carboxylate attacking from the K(I) (Figures S2.62 - S2.64). This is as was observed previously when similar calculations were run for catalyst **1.32**.⁴

2.4 Using Chain Transfer Agent to Control MW and Enhance Polymerisation Rate

To target the production of polyester polyols, the lead catalyst (**1**) was tested for PA/CHO ROCOP conducted with controlled quantities of diol, *trans*-1,2-cyclohexanediol (CHD), as the chain transfer agent.

The CHD was added at 10-400 equivalents vs. catalyst and all reactions were conducted with removal of regular reaction aliquots ([**1**]:[CHD]:[PA]:[CHO] = 1:10-400:400:2000, $T = 100\text{ }^{\circ}\text{C}$, Table 2.4 & S2.7, Figure 2.9). All polymerisations were run until complete anhydride consumption and linear plots of [PA] vs. time indicated zeroth orders in anhydride concentration and allowed for determination of both point TOF values and rate constants, k_{obs} (Table 2.4 & S2.7, Figure S2.65).

Table 2.4. Data for the CHO/PA ROCOP with variable loadings of diol (CHD) using catalyst **1**.

Entry	CHD equiv. (#)	t (min)	TON ^a	TOF (h ⁻¹) ^b	k_{obs} (x 10 ⁻³ mol dm ⁻³ s ⁻¹) ^c	$M_{\text{n, GPC}}$ (g mol ⁻¹) [$\bar{D}$] at full conv. ^d	$M_{\text{n, Theory}}$ (g mol ⁻¹) ^e
a	0	30	213	426	0.425	20,400 [1.08]	49,000
b	10	15	180	730	0.702	6,100 [1.19]	8,300
c	20	15	232	926	0.982	3,500 [1.14]	4,600
d	50	15	311	1240	1.12	1,600 [1.13]	2,000
e	100	10	284	1700	1.41	880 [1.11]	1,100
f	200	10	315	1890	1.83	530 [1.10]	600
g	400	5	145	1740	1.83	400 [1.06]	360

Polymerisation conditions are [**1**]:[CHD]:[anhydride] = 1:#:400, using 1 mL CHO such that [**1**] = 4.9 mmol, 100 °C. ^aTON = (conversion (%) / 100 (%)) * ([anhydride] / [**1**]). Conversion determined by ¹H NMR spectroscopy (298 K, 400 MHz, CDCl₃) by comparison of the normalized integrals of PA peaks, at 8.06-8.00 and 7.94-7.88 ppm, vs. equivalent polymer peaks, 7.63-7.52 and 7.44-7.34 ppm. ^bTurnover frequency = TON/time(h). TON determined by Conversion*equiv.(monomer). ^cDetermined as the gradient of fits to plots of [PA] (mol dm⁻³) vs. time (s). ^dDetermined by GPC, in THF at 30 °C, with the instrument calibrated using PS standards. ^eDetermined using $M_{\text{n, Theory}} = (\text{TON} * M_{\text{n, repeat unit}}) / (2 * \text{equiv.}(\text{cat}) + \text{equiv.}(\text{CHD})) + M_{\text{n, CHD}}$.

The catalyst showed unusually high tolerance to chain transfer agent, allowing access to oligomers, with degrees of polymerisation (DP) < 10, and with experimental molar mass values in very good agreement with theoretical values (Table 2.4, Figure 2.9). The polymerisation catalyst remained active and controlled when 200 equiv. of diol was used and, under these conditions, the resulting oligomer had an average DP of just 2. The polymer molar masses were inversely proportional to the quantities of diol added, as seen by the linear fit to the plot of polyester molar mass vs. 1/[diol] (Figure 2.9b), once again consistent with a well-controlled polymerisation.⁷ The data demonstrates that the

catalyst is very well suited to the production of the low molar mass polyesters required for liquid formulations, in every case showing excellent control and predictable molar mass values.

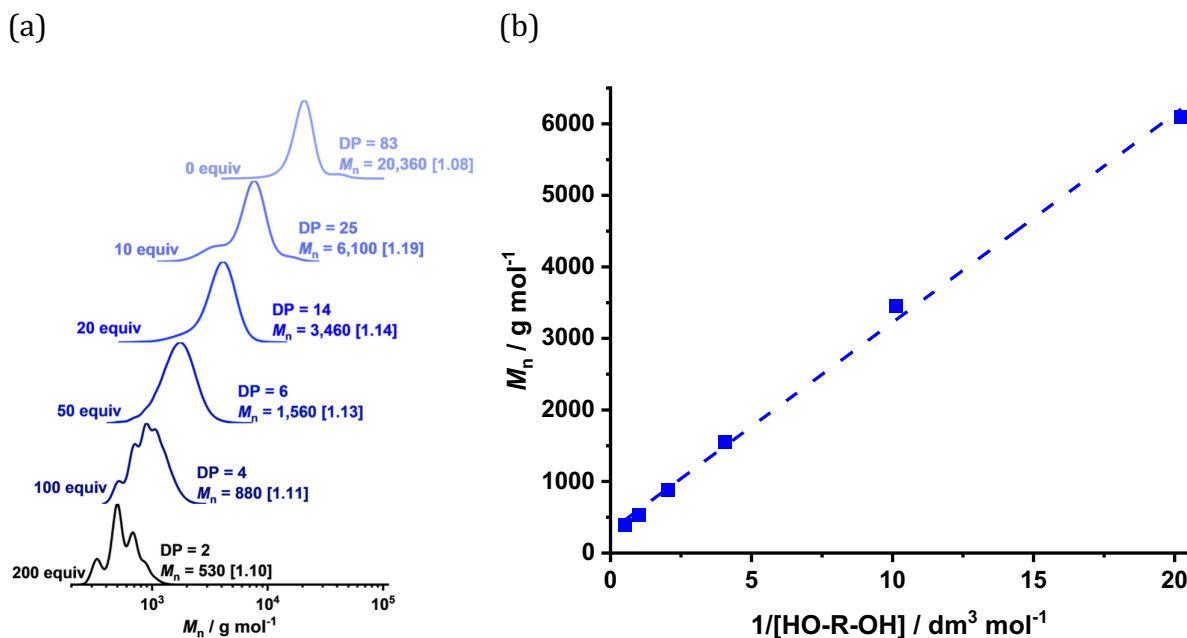


Figure 2.9. (a) Evolution of molar mass, at full PA conversion, vs. the amount of diol added (0-200 equiv.) as illustrated by the GPC data. Conditions: [1]:[CHD]:[PA]:[CHO] = 1:0-200:400:2000, at 100 °C. (b) Plot of polyester M_n at full conversion vs. 1/[HO-R-OH].

For polymerisation with only catalyst, in absence of added CTA, initiation occurred primarily from the acetate ligands but when diol (CHD) was added, initiation also occurred from the alcohol groups (Figure 2.9a). Adding progressively greater quantities of CHD into the polymerisations resulted in the polyester molar mass being reduced, and a low dispersity of the distributions was maintained. After 20 equiv. CHD, a single, monomodal distribution was observed consistent with the majority of chains being diol initiated. The multiple peaks in the GPC at very high CHD loadings are due to individual oligomers being resolved.

MALDI-ToF was used to confirm these claims about chain initiation. Figure 2.10 is the resultant polymer from when 20 equiv. CHD was added and shows two distinct trends of

peaks, one at high weight caused by CHD initiation and one at lower weight, which calculations suggest is initiated by the acetate ligands from the catalyst. When the loading of CHD is increased further to 100 equiv., then only one trend is observed, that of CHD initiation (Figure 2.11).

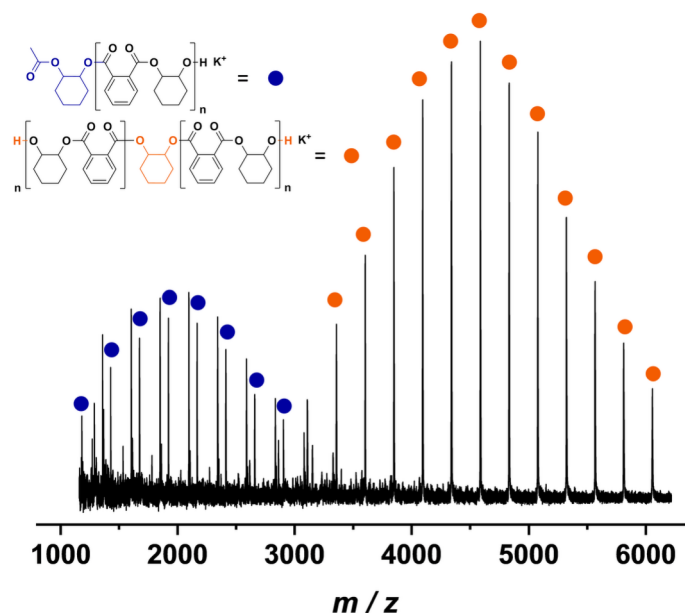


Figure 2.10. MALDI-ToF of PCHPE obtained with complex **1**. Conditions: $[\mathbf{1}]:[\text{CHD}]:[\text{PA}]:[\text{CHO}] = 1:20:400:2000$, 45 min, $T = 100\text{ }^{\circ}\text{C}$. $M_{n,\text{calc}}(\text{repeat unit}) = 245.98\text{ g mol}^{-1}$, $M_{n,\text{theoretical}}(\text{repeat unit}) = 246.26\text{ g mol}^{-1}$. $M_{n,\text{calc}}(\text{end group = blue}) = 197.71\text{ g mol}^{-1}$, $M_{n,\text{theoretical}}(\text{end group = AcOH} + \text{K}^+) = 197.06\text{ g mol}^{-1}$. Orange distribution attributed to CHD initiating species.

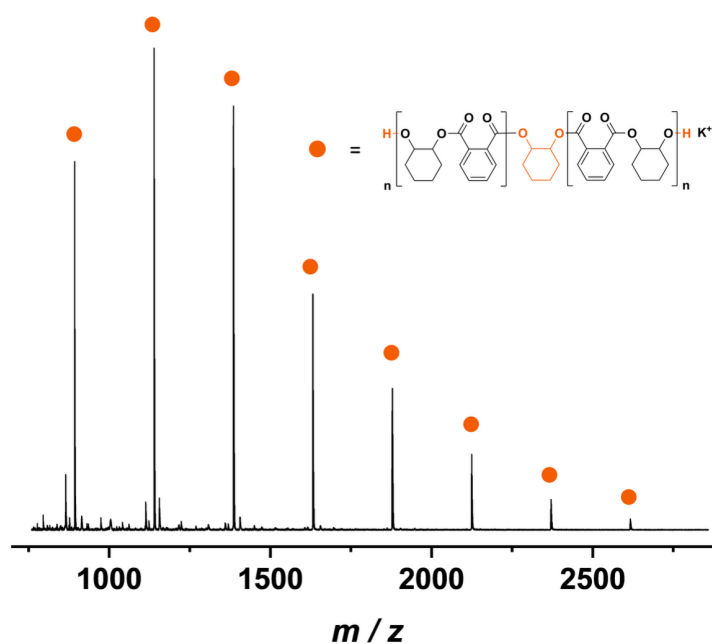


Figure 2.11. MALDI-ToF of PCHPE obtained with complex **1**. Conditions: $[\mathbf{1}]:[\text{CHD}]:[\text{PA}]:[\text{CHO}] = 1:100:400:2000$, 26 min, $T = 100\text{ }^{\circ}\text{C}$. $M_{n,\text{calc}}(\text{repeat unit}) = 246.07\text{ g mol}^{-1}$, $M_{n,\text{theoretical}}(\text{repeat unit}) = 246.26\text{ g mol}^{-1}$. $M_{n,\text{calc}}(\text{end group = orange}) = 155.08\text{ g mol}^{-1}$, $M_{n,\text{theoretical}}(\text{end group = CHD} + \text{K}^+) = 155.05\text{ g mol}^{-1}$.

Surprisingly, the polymerisation rates and TOF values also correlated with the quantity of diol, and rates increased as progressively greater quantities of diol were added (Figure 2.12, Table 2.4). Accordingly, adding 50 equiv. of alcohol resulted in ~3x higher activity and adding 200 equiv. of alcohol resulted in ~4.5x rate enhancement compared to the reaction run without any added alcohol, reaching a TOF of 1890 h⁻¹. The ester linkage selectivity remained at >99 % and in all cases perfectly alternating polyesters were produced (Table S2.7). Such an effect has been observed for the ROCOP of epoxide/CO₂ and ROP of lactones but this has not been reported for epoxide/anhydride ROCOP and no attempts to rationalise this phenomenon have been made.

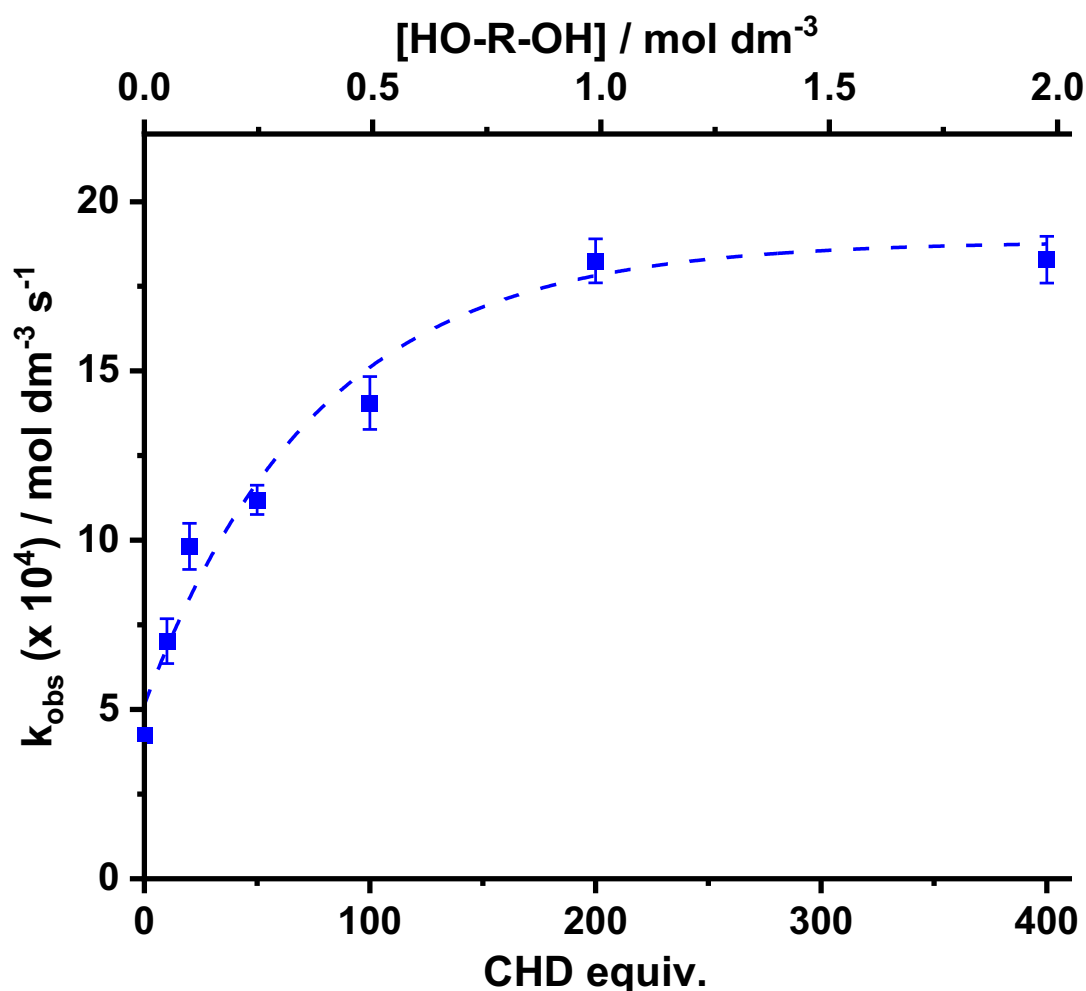


Figure 2.12. Plot of k_{obs} vs. $[\text{HO-R-OH}]$ and vs. CHD equivalents. Errors derived from fits of $[\text{PA}]$ (mol dm⁻³) vs. t (s) (Table S2.7). Conditions: $[\text{1}]:[\text{CHD}]:[\text{PA}]:[\text{CHO}] = 1:0\text{-}400:400:2000$, $T = 100$ °C. The non-linear curve fit is an exponential decay (Origin ExpDec1). $y = A1 \cdot \exp(-x/t1) + y0$. $y0 = 18.8$; $A1 = -13.7$; $t1 = 0.379$.

In order to investigate these beneficial effects of diol addition upon the polymerisation rate, it's important to consider whether any changes to the overall solution viscosity could be responsible. Generally during polymerisations, the viscosity increases and at higher conversions reactions may become diffusion controlled. In this work, analysis of the polymerisation aliquots showed that rates remained constant throughout polymerisations (from 10-75 % conversion) even when producing high molar mass polyesters, as suggested by a linear conversion-time plot (Figure S2.65). In each polymerisation, the degree of polymerisation increased with conversion, thus, rates were not influenced by any changes in viscosity with increasing chain length.

In addition, comparing polymerisations conducted with different diol concentrations but producing polyesters with the same DP showed different rates. For example, a polymerisation using **1** without any diol was stopped at 9 % conversion, resulting in a polyester with DP = 14 and TOF = 277 h⁻¹. The same reaction was conducted using 10 equiv. of diol and stopped at 46 % conversion, resulting in the same polyesters with DP = 11 but showing a much higher TOF of 730 h⁻¹ (Figure 2.13). In these two polymerisation solutions, the polymers are of the same DP yet have very different rates. In fact, the reaction with the diol has a 6x greater concentration of polymer present, as calculated by the number of initiators (Figure 2.14). Therefore, were there any difference in viscosity between the reactions, it is expected that the reaction with 10 equiv. CHD present would have a greater viscosity. This indicates that the rate trends do not correlate with any potential viscosity effects.

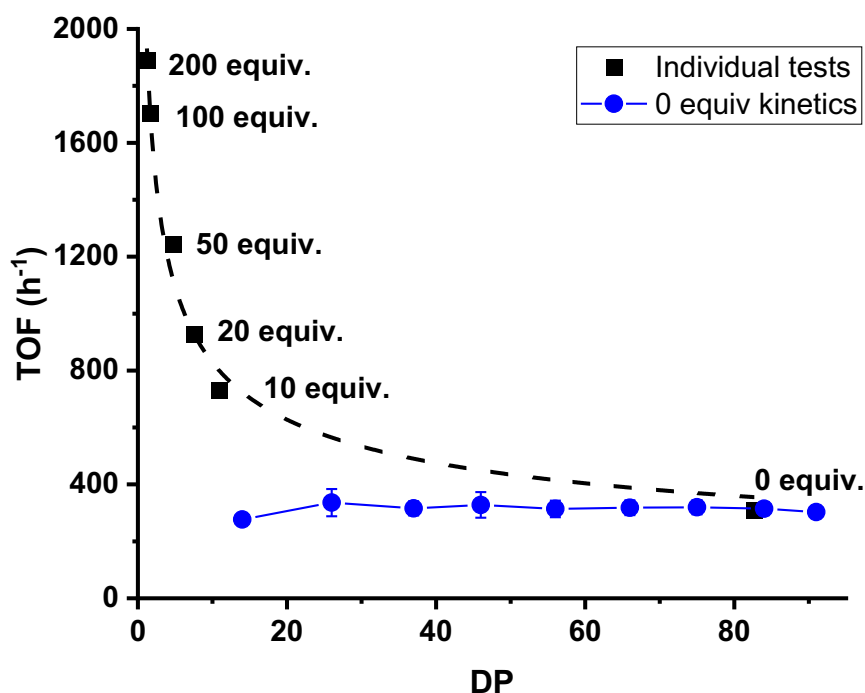
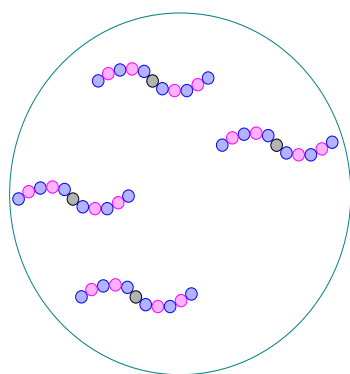


Figure 2.13. Graph of TOF against Degree of Polymerisation (DP). The points represent individual point TOFs and the corresponding DP for that aliquot. The black squares are individual tests at different CHD loadings. The blue circles come from aliquots from the kinetic study at 0 equiv. CHD loading. This shows that TOF remains constant across a range of DPs with a given CHD loading (blue), contrary to the trend observed when CHD loading is varied (black).

(a)



(b)

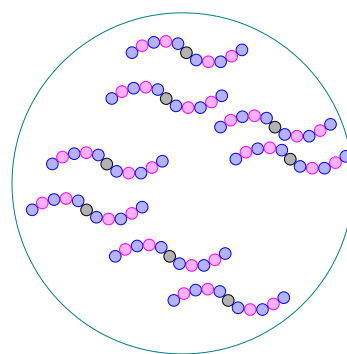


Figure 2.14. A pictorial representation of DP = 10 at two different CTA concentrations. This shows that, a higher concentration of CTA but the same DP, results in a higher concentration of polymer chains and thus, presumably, a higher viscosity.

Next, the influences of diol upon the polymerisation rate were investigated using a different catalyst in the series, **1.32** (featuring a 2,2-dimethylpropylene backbone) (Table S2.8). Once again, the catalytic activity increased with alcohol addition, although the magnitude of the increase was lower than for catalyst **1**. In the case of **1.32**, polymerisations were ~1.6x faster when 100 equivalents of diol were added, whereas using **1**, under the same conditions, resulted in a 4x greater TOF (Table 2.4, a & e, and Table S2.8, a & c). These experiments indicate a ‘molecular’ rationale for the rate increases since the resulting polymer chains are identical (Table 2.4 & S2.8). These rates increase but eventually plateau for **1** but for **1.32**, they even begin to decrease after a maximum at 200 equiv. CHD (Table 2.4 & S2.8). These differences in polymerisation rate in response to alcohol loading do not reflect a difference in stability to alcohol, since both catalysts were stable at 100 °C for 30 min in the presence of macromolecular triol, glycerol ethoxylate (GEO) (Figures S2.66 – S2.69).

It is important to appreciate that, while the rates level off when using an equimolar amount of alcohol and anhydride monomer, the reaction can no longer be considered a polymerisation. This means that the limits of the catalysis occur when only a single ring-opening reaction occurs, yielding products with DP = 1. Under conditions where useful polyols are produced, *i.e.* using 10-100 equiv. alcohol, the rates increase significantly with alcohol concentration for both.^{17, 18}

2.5 Catalyst Stability Tests

Catalyst **1** is very tolerant to high levels of CTA in the reaction, but it’s wider stability to different reaction conditions still should be probed.

Firstly, a comparison was made between a reaction run in a nitrogen atmosphere with purified monomers and one run in air with unpurified monomers (Table 2.5). The reaction set up and catalyst loading was the same ($[1]:[PA]:[CHO] = 1:400:2000$, $T = 100\text{ }^{\circ}\text{C}$) to give the best comparison.

Table 2.5. Table showing catalyst activity Air/N₂ atmospheres and with purified monomers or unpurified monomer. $[1]_0:[PA]_0:[CHO]_0 = 1:400:2000$, $T = 100\text{ }^{\circ}\text{C}$.

Entry	Conditions			Polymerisation Results				
	Air / N ₂ atm.	Purified mon.	t (min)	Conv. (%) ^a	TOF (h ⁻¹) ^b	PE Select. (%) ^c	$M_{n, \text{GPC}}$ (g mol ⁻¹) [D] ^d	$M_{n, \text{Theory}}$ (g mol ⁻¹) ^e
a	N ₂	Y	30	49	390	>99	13,800 [1.09]	48,000
b	Air	N	30	75	600	>99	1,600 [1.14]	74,000

^a Conversion determined by ¹H NMR (298 K, 400 MHz, CDCl₃) spectroscopy; comparison of PA monomer peaks (8.06-8.00 and 7.94-7.88 ppm) to polymer peaks (7.63-7.52 and 7.44-7.34 ppm). ^b Turnover frequency = TON/time(h). TON determined via Conversion*equiv.(monomer). ^c Selectivity for polyester over ether linkage formation. Determined by ¹H NMR spectroscopy (298 K, 400 MHz, CDCl₃) by comparison of polyester peaks (5.22-5.04 ppm) vs. any ether linkages (3.8-3.2 ppm). ^d Determined by GPC in THF, 30 °C, calibrated using PS standards. ^e Determined according to $M_{n, \text{Theory}} = (\text{TON} * M_{n, \text{repeat unit}}) / (2 * \text{equiv.}(\text{cat})) + M_{n, \text{OAc}}$.

From Table 2.5, it can be clearly seen that the catalyst retains its activity after being left in air and there are no issues running the polymerisation under a normal atmosphere. In fact, the rate of reaction seems to have substantially increased by 50 %. This is attributed to the fact that the unpurified monomers have high levels of residual CTA in them, which would act to enhance the rate of reaction, as has been seen in Section 2.4. This also impacts the observed molecular weight however, with $M_{n, \text{GPC}}$ being just over 2 % of the $M_{n, \text{Theory}}$ (Table 2.5, b). As expected with a large quantity of CTA, the dispersity is narrow and the distribution is monomodal.

Catalyst loading tolerance was also investigated. It is of commercial importance that the polymerisation reaction can be run at very low catalyst loadings, since it reduces cost

and there is less catalyst to remove from the final polymer (removal of **1** is done on the lab scale using a silica plug). However, many catalysts in the ROCOP field struggle with loading tolerance, particularly bi-component catalysts that need a co-catalyst, since these are vulnerable to dilution effects.¹⁹ This is an inherent advantage of bimetallic catalysts, where this issue is less pronounced, as demonstrated by catalyst **1.32**.⁴ For catalyst **1**, the loading tolerance was tested with CTA present (in this case, benzyl alcohol (BnOH)). The concentrations of BnOH, PA and CHO were all kept the same, whilst [**1**] was progressively dropped, down to 0.0125 mol% relative to anhydride (Table 2.6).

Table 2.6. Table showing catalyst activity at different catalyst loadings. [Cat]₀: [BnOH]₀: [PA]₀: [CHO]₀ = #:50:400:2000, *T* = 100 °C.

Entry	Conditions		Polymerisation Results			
	[cat] (mol%) ^a	[BnOH] (equiv.) ^b	TOF (h ⁻¹) ^c	<i>k</i> _{obs} (x10 ⁻⁴ mol dm ⁻³ s ⁻¹) ^d	PE Select. (%) ^e	<i>M</i> _{n, GPC} (g mol ⁻¹) [<i>Đ</i>] at full conv. ^f
a	0.25	50	719	9.88	>99	1,400 [1.12]
b	0.125	100	805	5.54	>99	1,500 [1.13]
c	0.0125	1000	1054	0.73	>99	1,300 [1.13]

^a Relative to [PA]. ^b Relative to [cat]. ^c Turnover frequency = TON/time(h). TON determined via Conversion*equiv.(PA). Conversion determined by ¹H NMR (298 K, 400 MHz, CDCl₃) spectroscopy; comparison of PA monomer peaks (8.06-8.00 and 7.94-7.88 ppm) to polymer peaks (7.63-7.52 and 7.44-7.34 ppm). ^d *k*_{obs} calculated by the gradient of [PA] vs. time. ^e Selectivity for polyester over ether linkage formation. Determined by ¹H NMR spectroscopy (298 K, 400 MHz, CDCl₃) by comparison of polyester peaks (5.22-5.04 ppm) vs. any ether linkages (3.8-3.2 ppm). ^f Determined by GPC in THF, 30 °C, calibrated using PS standards. ^g Determined according to $M_{n, \text{Theory}} = (\text{TON} * M_{n, \text{repeat unit}}) / (2 * \text{equiv.}(\text{cat})) + M_{n, \text{OAc}}$.

Remarkably, the TOF remained more or less constant, despite this very low catalyst loading. Looking at the CTA loading relative to catalyst, it goes to as high as 1000 equiv. which is the highest CTA loading reported for epoxide/anhydride ROCOP. Because the CTA to monomer ratio was kept the same, the $M_{n, \text{Theory}} = 2,000 \text{ g mol}^{-1}$ and the M_n of the final polymers were almost identical, despite having very different catalyst loadings (Table 2.6).

2.6 Monomer Scope

Catalyst **1** was tested using different monomer combinations to produce a range of polyester polyols (Figure 2.15 & Table 2.7). Vinyl cyclohexene oxide (vCHO) and allyl glycidyl ether (AGE) were selected because they contain alkene moieties which could, in future, be post-functionalised to moderate hydrophilicity, pH, rheology or to install specific functional groups or ions.²⁰ All these features could be relevant to future applications in liquid formulations. Diglycolic anhydride (DGA) is a bio-based monomer producing aliphatic polyesters with flexible backbones and low glass transition temperatures.²¹ Rigid, bio-based monomers norbornene anhydride (NBA)²² and tricyclic anhydride (TCA)²³ were selected for the opposite reason – they yield polyesters with more ‘rigid’ backbones and higher T_g values. Finally, propylene oxide (PO) was used since it is one of the most widely produced epoxides globally and its polymers are already widely applied in surfactant applications.²⁴ In all cases, epoxide/anhydride ROCOP was conducted using 20 equiv. of diol (CHD) to produce hydroxyl telechelic polyesters with DP values from 11-22, and molar mass values in the polyol range (2-5 kg mol⁻¹), in most cases with narrow distributions.

All monomer combinations were successfully enchainned producing polyesters with molar mass values in close agreement with the theoretical values; minor variations occur because the values are determined by GPC measurements calibrated against polystyrene standards (Figures S2.70-S2.83). All monomer combinations were polymerised to yield perfectly alternating polyesters, without any ether linkages, within the detection limits of NMR spectroscopy (Table 2.7). Catalyst **1** showed high activity for ROCOP using vCHO/PA, CHO/PA and CHO/DGA, reaching TOF values of ~900 h⁻¹ (Table 2.7, a,b&g).

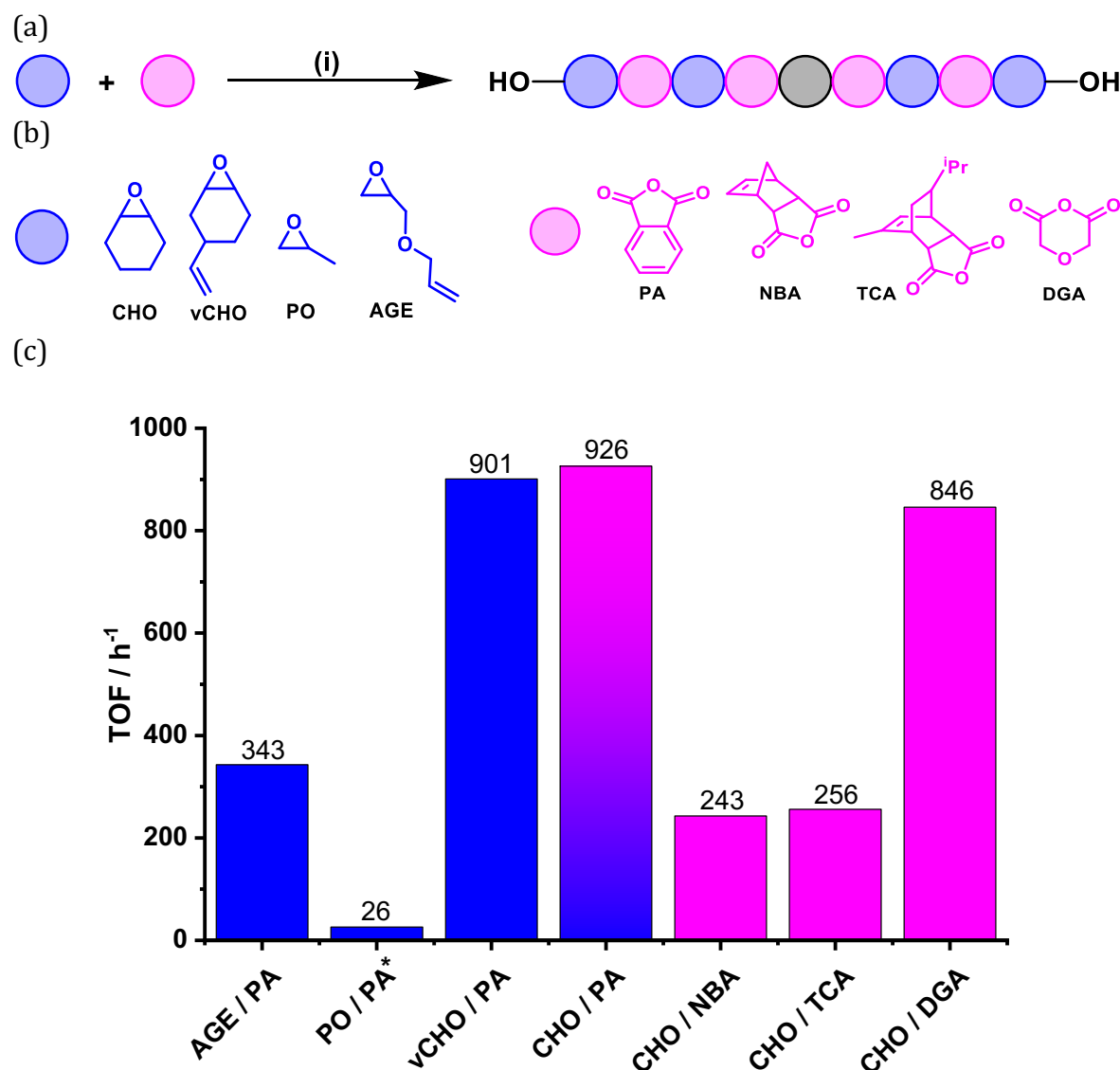


Figure 2.15. (a) Polymerisation conditions: (i) $[1]: [\text{CHD}]: [\text{anhydride}] = 1:20:400$, 1 mL epoxide such that $[1] = 4.9 \text{ mmol}$, $T = 100^\circ\text{C}$. (b) Epoxide and anhydride scope. (c) Graph showing TOF for different monomer combinations. *PO/PA run at $T = 60^\circ\text{C}$.

The rates were slightly slower using alkylene/glycidyl ether oxides, particularly where lower temperature conditions were necessary due to monomer volatility ($\text{TOF}(\text{PO}) = 26 \text{ h}^{-1}$ at 60°C ; $\text{TOF}(\text{AGE}) = 343 \text{ h}^{-1}$ at 100°C , Table 2.7, c & d). The resulting polyesters showed regio-random distributions, as determined by quantitative ^{13}C NMR spectroscopy (Figure S2.84). The catalyst was also active for sterically hindered anhydrides showing activity values within the range expected for such monomers, *e.g.* CHO/NBA ($\text{TOF} = 243 \text{ h}^{-1}$) and CHO/TCA ($\text{TOF} = 256 \text{ h}^{-1}$, Table 2.7, e & f).

Table 2.7. Data for epoxide/anhydride ROCOP monomer scope using catalyst **1**.^a

Entry	Conditions		Polymerisation Results				
	Monomers	time (min)	TON ^c	Activity TOF (h ⁻¹) ^d	Polyester selectivity (%) ^e	$M_{n, GPC}$ (g mol ⁻¹) [$\bar{D}_M$] at full conversion ^f	$M_{n, Theory}$ (g mol ⁻¹) ^g
a	CHO/PA	15	232	926	>99	3,500 [1.14]	4,500
b	vCHO/PA	15	225	901	>99	4,600 [1.11]	5,000
c ^b	PO/PA	420	182	26	>99	4,700 [1.13]	3,800
d	AGE/PA	30	172	343	>99	4,500 [1.15]	4,800
e	CHO/NBA	30	121	243	>99	3,600 [1.11]	4,800
f	CHO/TCA	30	128	256	>99	3,700 [1.15]	6,000
g	CHO/DGA	15	212	846	>99	2,600 [1.32]	3,900

^aPolymerisation conditions: (i) [**1**]: [CHD] : [anhydride]: = 1:20:400, 1 mL epoxide such that [**1**] = 4.9 mmol, 100 °C. ^bReaction conducted at 60 °C. ^cTON = (conversion (%) / 100 (%)) * ([anhydride] / [**1**]). Conversion determined by ¹H NMR spectroscopy (Figures S2.70-S2.76). ^dTurnover frequency = TON/time(h). TON determined *via* Conversion*equiv.(anhydride). ^eDetermined by ¹H NMR spectroscopy (Figures S2.70-S2.76) by comparison of resonances from ester vs. ether linkages. ^fDetermined by GPC, in THF at 30 °C, calibrated using PS standards. ^g Calculated from (TON* $M_{n repeat unit}$)/equiv.(cat + diol).

It is also notable that there were, once again, rate enhancements using the different monomer combinations through adding the diol. For example, vCHO/PA ROCOP conducted using catalyst **1** with 20 equiv. of alcohol showed 5x greater activity compared to the equivalent polymerisation conducted without any diol (Table S2.9, a&b). PO/PA ROCOP showed a 1.4x rate increase when 20 equivalents of alcohol were used compared to reactions without any diol (Table S2.9, c-e).

2.7 Conclusions and Outlook

In summary, a series of heterodinuclear Al(III)/K(I) catalysts showed very high rates, control and selectivity for cyclohexene oxide/phthalic anhydride ring opening copolymerisations. When alcohols were added as chain transfer agents, the catalysts showed unprecedented rate enhancements, even at very low catalyst loadings, whilst maintaining an equivalently high polymerisation control. The catalysts and diols were

used to selectively produce polyester polyols showing degrees of polymerisation from 1-83, in all cases with predictable molar mass values and monomodal, narrow dispersity, molar mass distributions. The best catalysts showed significant rate enhancements after alcohol addition, achieving TOF values of $\sim 1900 \text{ h}^{-1}$ when using 200 equivalents of alcohol. This corresponds to a 4.5x increase in rate compared to reactions without the alcohol. The acceleration of rates upon the addition of excess alcohol is very unusual and contrasts with most other catalysts in this field. The lead catalysts were also fast, selective and controlled in other epoxide/anhydride polymerisations producing low molar mass, hydroxyl telechelic polyesters in all cases.

Catalysts such as these that can be applied to different ROCOP monomers and show significant promise in the preparation of oligomeric polyesters, which are important products for future applications in liquid formulations as well as for polyurethane and resin production. Therefore, it is worthwhile to obtain a better mechanistic understanding of this novel phenomenon so that it may be possible to guide future catalyst design.

Further iterations to this catalyst design could be targeted. The backbone modifications have focused on sterics and conformation, showing significant influence, correlating an increase in flexibility with an increase in rate. But electronics play a very crucial role as well. Modifications to the *ortho*-vanillin aromatic ring to change its electron density could lead to further catalyst optimisation.

The metal in the complex is also a crucial component as it is the essential Lewis Acid that activates the epoxide for ring opening. A recent report from Williams and co-workers presented an Fe(III)K(I) catalyst, with an Schiff-base ligand, that showed excellent

activities and temperature tolerance.²⁵ Iron is cheap and abundant and so further studies into using this metal as the primary Lewis acid in the catalyst would be worthwhile.

Finally, the catalysis presented here uses large quantities of CTA to target low M_n polymers but this same principle of molecular weight control can be employed for the production of high MW polyesters. The requirement for this is that a non-initiating catalyst is used, which ensures that the molecular weight remains entirely independent of the catalyst loading. In the case of the low weight polyesters produced in this study, the CTA swamps the catalyst initiation, making this less of a concern. Diment *et al.* reported catalyst **2.1** – with Et and Cp coligands in place of the acetates – which was successfully employed for the synthesis of high molecular weight polyesters (Figure 2.16).²⁶

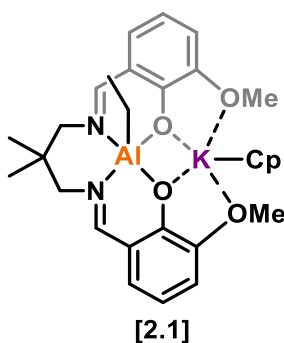


Figure 2.16. The organometallic Al(III)K(I) complex reported by Diment *et al.*²⁶

A non-initiating version of catalyst **1** could be synthesised and compared with **2.1**. Comparisons should also be made for the ROP of lactones. This would hopefully reveal a suitable catalyst for the synthesis of complex polymeric structures, such as multiblocks, by making use of switch chemistry.

2.8 References

- (1) Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. Ring-opening copolymerization (ROCOP): synthesis and properties of polyesters and polycarbonates. *Chem. Commun.* **2015**, 51 (30), 6459–6479. DOI: 10.1039/c4cc10113h.
- (2) Lidston, C. A. L.; Severson, S. M.; Abel, B. A.; Coates, G. W. Multifunctional Catalysts for Ring-Opening Copolymerizations. *ACS Catal.* **2022**, 11037–11070. DOI: 10.1021/acscatal.2c02524.
- (3) Diment, W. T.; Lindeboom, W.; Fiorentini, F.; Deacy, A. C.; Williams, C. K. Synergic Heterodinuclear Catalysts for the Ring-Opening Copolymerization (ROCOP) of Epoxides, Carbon Dioxide, and Anhydrides. *Acc. Chem. Res.* **2022**, 55 (15), 1997–2010. DOI: 10.1021/acs.accounts.2c00197.
- (4) Diment, W. T.; Gregory, G. L.; Kerr, R. W. F.; Phanopoulos, A.; Buchard, A.; Williams, C. K. Catalytic Synergy Using Al(III) and Group 1 Metals to Accelerate Epoxide and Anhydride Ring-Opening Copolymerizations. *ACS Catal.* **2021**, 11 (20), 12532–12542. DOI: 10.1021/acscatal.1c04020.
- (5) Andrea, K. A.; Plommer, H.; Kerton, F. M. Ring-opening polymerizations and copolymerizations of epoxides using aluminum- and boron-centered catalysts. *Eur. Polym. J.* **2019**, 120. DOI: 10.1016/j.eurpolymj.2019.08.029.
- (6) Sanford, M. J.; Van Zee, N. J.; Coates, Geoffrey W. Reversible-deactivation anionic alternating ring-opening copolymerization of epoxides and cyclic anhydrides: access to orthogonally functionalizable multiblock aliphatic polyesters. *Chem. Sci.* **2018**, 9 (1), 134–142. DOI: 10.1039/c7sc03643d.
- (7) Darensbourg, D. J. Chain transfer agents utilized in epoxide and CO₂ copolymerization processes. *Green Chem.* **2019**, 21 (9), 2214–2223. DOI: 10.1039/c9gc00620f.
- (8) Asano, S.; Aida, T.; Inoue, S. 'Immortal' polymerization. Polymerization of epoxide catalysed by an aluminium porphyrin–alcohol system. *J. Chem. Soc., Chem. Commun.* **1985**, (17), 1148–1149. DOI: 10.1039/c39850001148.
- (9) Aida, T.; Maekawa, Y.; Asano, S.; Inoue, S. Immortal Polymerization - Polymerization of Epoxide and Beta-Lactone with Aluminum Porphyrin in the Presence of Protic Compound. *Macromol.* **1988**, 21 (5), 1195–1202. DOI: DOI 10.1021/ma00183a001.
- (10) Inoue, S. Immortal polymerization: The outset, development, and application. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, 38 (16), 2861–2871. DOI: 10.1002/1099-0518(20000815)38:16<2861::Aid-pola20>3.0.Co;2-1.
- (11) DiCiccio, A. M.; Coates, G. W. Ring-Opening Copolymerization of Maleic Anhydride with Epoxides: A Chain-Growth Approach to Unsaturated Polyesters. *J. Am. Chem. Soc.* **2011**, 133 (28), 10724–10727. DOI: 10.1021/ja203520p.
- (12) Nejad, E. H.; Paoniasari, A.; van Melis, C. G. W.; Koning, C. E.; Duchateau, R. Catalytic Ring-Opening Copolymerization of Limonene Oxide and Phthalic Anhydride: Toward

Partially Renewable Polyesters. *Macromol.* **2013**, *46* (3), 631–637. DOI: 10.1021/ma301904y.

- (13) Jeon, J. Y.; Eo, S. C.; Varghese, J. K.; Lee, B. Y. Copolymerization and terpolymerization of carbon dioxide/propylene oxide/phthalic anhydride using a (salen)Co(III) complex tethering four quaternary ammonium salts. *Beilstein J. Org. Chem.* **2014**, *10*, 1787–1795. DOI: 10.3762/bjoc.10.187.
- (14) Kerr, R. W. F.; Williams, C. K. Zr(IV) Catalyst for the Ring-Opening Copolymerization of Anhydrides (A) with Epoxides (B), Oxetane (B), and Tetrahydrofurans (C) to Make ABB- and/or ABC-Poly(ester-alt-ethers). *J. Am. Chem. Soc.* **2022**, *144* (15), 6882–6893. DOI: 10.1021/jacs.2c01225.
- (15) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; Pugh, R. I.; White, A. J. P. Study of ligand substituent effects on the rate and stereoselectivity of lactide polymerization using aluminum salen-type initiators. *Proc. Natl. Acad. Sci.* **2006**, *103* (42), 15343–15348. DOI: 10.1073/pnas.0602765103.
- (16) Pang, X.; Chen, X.; Du, H.; Wang, X.; Jing, X. Enolic Schiff-base aluminum complexes and their application in lactide polymerization. *J. Organomet. Chem.* **2007**, *692* (25), 5605–5613. DOI: 10.1016/j.jorganchem.2007.09.014.
- (17) Lidston, C. A. L.; Abel, B. A.; Coates, G. W. Bifunctional Catalysis Prevents Inhibition in Reversible-Deactivation Ring-Opening Copolymerizations of Epoxides and Cyclic Anhydrides. *J. Am. Chem. Soc.* **2020**, *142* (47), 20161–20169. DOI: 10.1021/jacs.0c10014.
- (18) Chen, X.-L.; Wang, B.; Pan, L.; Li, Y.-S. Synthesis of Unsaturated (Co)polyesters from Ring-Opening Copolymerization by Aluminum Bipyridine Bisphenolate Complexes with Improved Protonic Impurities Tolerance. *Macromol.* **2022**, *55* (9), 3502–3512. DOI: 10.1021/acs.macromol.2c00034.
- (19) Abel, B. A.; Lidston, C. A. L.; Coates, G. W. Mechanism-Inspired Design of Bifunctional Catalysts for the Alternating Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides. *J. Am. Chem. Soc.* **2019**, *141* (32), 12760–12769. DOI: 10.1021/jacs.9b05570.
- (20) Yi, N.; Chen, T. T. D.; Unruangsri, J.; Zhu, Y.; Williams, C. K. Orthogonal functionalization of alternating polyesters: selective patterning of (AB)_n sequences. *Chem. Sci.* **2019**, *10* (43), 9974–9980. DOI: 10.1039/c9sc03756j.
- (21) Jeske, R. C.; DiCiccio, A. M.; Coates, G. W. Alternating Copolymerization of Epoxides and Cyclic Anhydrides: An Improved Route to Aliphatic Polyesters. *J. Am. Chem. Soc.* **2007**, *129* (37), 11330–11331. DOI: 10.1021/ja0737568.
- (22) Han, B.; Zhang, L.; Liu, B.; Dong, X.; Kim, I.; Duan, Z.; Theato, P. Controllable Synthesis of Stereoregular Polyesters by Organocatalytic Alternating Copolymerizations of Cyclohexene Oxide and Norbornene Anhydrides. *Macromolecules* **2015**, *48* (11), 3431–3437. DOI: 10.1021/acs.macromol.5b00555.
- (23) Dakshinamoorthy, D.; Weinstock, A. K.; Damodaran, K.; Iwig, D. F.; Mathers, R. T. Diglycerol-Based Polyesters: Melt Polymerization with Hydrophobic Anhydrides. *ChemSusChem* **2014**, *7* (10), 2923–2929. DOI: 10.1002/cssc.201402249.

- (24) Baer, H.; Bergamo, M.; Forlin, A.; Pottenger, L. H.; Lindner, J. Propylene Oxide. In *Ullmann's Encyclopedia of Industrial Chemistry*, 2012.
- (25) Diment, W. T.; Rosetto, G.; Ezaz-Nikpay, N.; Kerr, R. W. F.; Williams, C. K. A highly active, thermally robust iron(iii)/potassium(i) heterodinuclear catalyst for bio-derived epoxide/anhydride ring-opening copolymerizations. *Green Chem.* **2023**, 25 (6), 2262–2267. DOI: 10.1039/d2gc04580j.
- (26) Diment, W. T.; Williams, C. K. Chain end-group selectivity using an organometallic Al(iii)/K(i) ring-opening copolymerization catalyst delivers high molar mass, monodisperse polyesters. *Chem. Sci.* **2022**, 13 (29), 8543–8549. DOI: 10.1039/d2sc02752f.

Chapter 3

Al(III)/K(I) Heterobimetallic Complexes for the Ring-Opening Copolymerisation of Epoxides with CO₂

Work described in this chapter appears in "*Al(III)/K(I) Heterobimetallic Complexes for the Ring-Opening Copolymerisation of Epoxides with CO₂*"

Shellard, E. J. K., Janssen, N., Williams, C. K.

Manuscript in preparation

3.1 Introduction and Aims

The use of carbon dioxide as a chemical feedstock can reduce the lifecycle emissions of the material produced by reducing the need for virgin petrochemicals as carbon sources and adds value to this greenhouse gas that would otherwise be treated as waste.¹ This chapter explores the use of CO₂ in the production of polycarbonates by copolymerisation with epoxides (Figure 3.1).

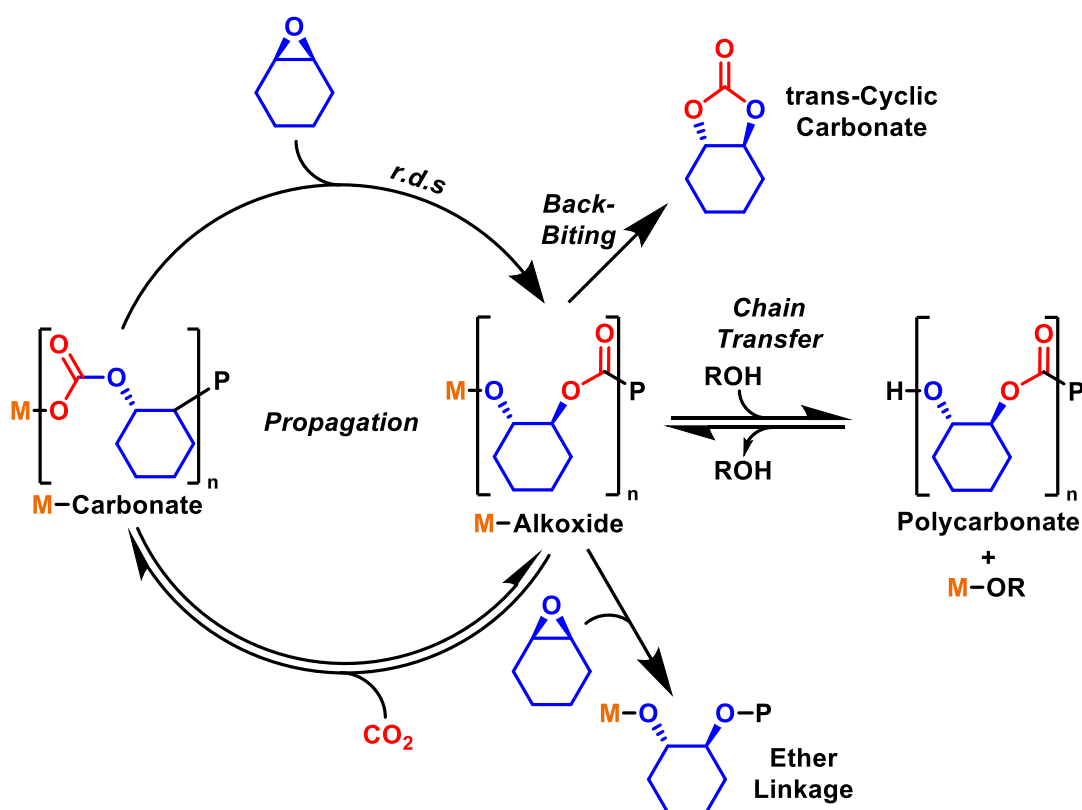


Figure 3.1 Schematic of epoxide/CO₂ ROCOP, showing the propagation cycle and the side reactions that can occur, including reversible chain transfer, back-biting to form cyclic carbonate and subsequent epoxide insertions to produce ether linkages.

There have been a number of highly active catalysts reported for the ROCOP of epoxides with CO₂. These contain metals such as Co(III),²⁻⁶ Zn(II),⁷ Ni(II),⁸ Mg(II),⁵ and Cr(III).⁹ Previous work in our group has explored (hetero)bimetallic complexes for these ROCOP reactions and revealed that intermetallic synergy can, for some metal combinations, lead to a significant increase in catalytic activity.^{5,10} These bimetallic

catalysts also avoid the need to add a cocatalyst; these latter additives make a catalyst system that is susceptible to dilution effects and the cocatalysts are corrosive, expensive and toxic.^{5, 11}

Many of the metals employed in the field's most active catalysts are expensive and uncommon, in particular Co(III). Aluminium complexes, therefore, are worthwhile candidates to investigate as catalysts for epoxide/CO₂ ROCOP, since it is the most abundant metal.¹² There is some precedent for Al(III) catalysts in epoxide/CO₂ ROCOP, but there remains scope to further improve catalytic activity.¹³⁻¹⁷ Of these Al(III) catalysts, Al(III)-porphyrins are by far the most active, with the lead Al(III) catalyst for CHO/CO₂ being reported by Nozaki and coworkers (TOF = 10,000 h⁻¹, [cat]:[CHO] = 1:40,000; *p*(CO₂) = 20 bar; *T* = 120 °C).¹⁵ Al(III)-porphyrins as pendant groups on low-DP (*DP* = 4-7) norbornene or methacrylate oligomers also showed high activity, this time for PO/CO₂ ROCOP.^{16, 17}

Our group recently reported an Al(III)K(I) catalyst that was active for CHO/CO₂ ROCOP (1:2000 cat:CHO, *p*(CO₂) = 20 bar, *T* = 100 °C), although its activity and selectivity (TOF = 500 h⁻¹, PCHC select. = 87 %) was less impressive than its function as an epoxide/anhydride ROCOP catalyst.¹⁸ Additionally, our team also recently reported a series of M(III)K(I) catalysts (M(III) = Co, Al & Fe), coordinated by a different Schiff-base ancillary ligand, revealing that the Al(III) catalyst was active for CHO/CO₂ ROCOP (TOF = 1083 h⁻¹; 97 % PCHC; [cat]:[CHD]:[CHO]=1:20:4000; *p*(CO₂) = 20 bar; *T* = 100 °C).¹⁹

The work in this chapter follows directly on from Chapter 2 with the Al(III)K(I) catalysts and ligand backbone scope (Figure 3.2).²⁰ Herein, the efficacy of Al(III)K(I) catalysts for epoxide/CO₂ ROCOP is determined, with the lead catalyst showing significant improvements in rate and polycarbonate selectivity (TOF = 1400 h⁻¹, 97 % selectivity, *p*(CO₂) = 20 bar, *T* = 110 °C). The rate law of this catalyst was determined, by

full kinetic investigation, revealing that the order dependence on CO₂ varies with pressure, with an increase in rate with pressure at low $p(\text{CO}_2)$, but the rate then plateaus above a certain threshold pressure. Kinetic modelling and Eyring analysis were also conducted to complement the mechanistic understanding of this Al(III) catalyst.

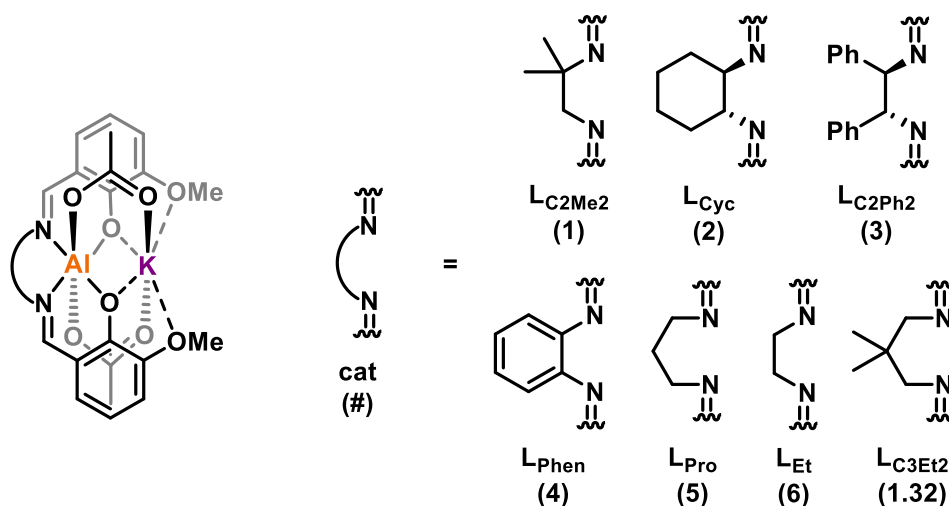


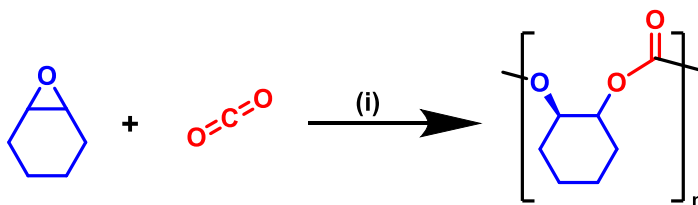
Figure 3.2 The scope of Al(III)K(I) complexes tested in this study. The diimine backbone of the ancillary ligand has been varied.

3.2 Catalyst Scope Tests

3.2.1 Al(III)K(I) Low CO₂ Pressure Tests

For the initial catalyst scope, the reactions were carried out in neat epoxide in absence of chain transfer agent or cocatalyst ($[\text{cat}]:[\text{CHO}] = 1:2000$, $V(\text{CHO}) = 1.6 \text{ mL}$, $p(\text{CO}_2) = 1 \text{ bar}$, $T = 100 \text{ }^\circ\text{C}$). The polymers produced were analysed to provide activity, selectivity for CO₂ in the polymer (carbonate linkage), selectivity for polymer over cyclic carbonate and molecular weights for each of the polymerisations (Table 3.1).

Table 3.1 Polymerisation data for CHO/CO₂ ROCOP with catalysts **1-6**;
(i) [cat]:[CHO] = 1:2000, V(CHO) = 1.6 mL, p(CO₂) = 1 bar, T = 100 °C



Entry	Conditions		CHO conv. (%) ^a	CO ₂ select. (%) ^a	PCHC select. (%) ^a	TON ^b	TOF (h ⁻¹) ^c	<i>M</i> _{n,GPC} (kg mol ⁻¹) [<i>D</i>] ^d
	Cat (#)	<i>t</i> (h)						
a	1	5	31	>99	91	628	126	6.8 [1.23]
b	2	5	29	>99	93	588	118	10.5 [1.13]
c	3	5	24	>99	95	484	97	5.9 [1.23]
d	4	16.5	4	>99	79	75	5	0.8 [1.12]
e	5	5	<1	-	0	4	1	-
f	6	5.25	4	>99	83	85	16	0.7 [1.10]
g ¹⁸	1.32	1	6	>99	50	116	116	3.5 [1.18]

^a CHO conversion, CO₂ selectivity, polycarbonate linkage selectivity and TON all determined by ¹H NMR (298 K, 400 MHz, CDCl₃) spectroscopy; comparison of CHO peak 3.05 ppm, PCHC backbone peak 4.65 ppm, Cyclic carbonate peaks 4.00 & 4.68 ppm and polyether peak 3.45 ppm. (See Figure S3.1 & Table S3.1).

^b TON determined by Conversion (of CHO)*equiv.(CHO). ^c Turnover frequency = TON/time(h). ^d Determined by GPC in THF, 30 °C, calibrated using PS standards (Figures S3.2 – S3.6).

Catalysts **1-3** were the best catalysts within the series with activities around 100 h⁻¹ (Table 3.1, a-c). Catalyst **1** being the most active of these three (TOF = 126 h⁻¹). These fastest catalysts did not show much variation in rate or polycarbonate selectivity so it is difficult to differentiate between them, despite very different ligand backbones. Catalysts **4-6**, on the other hand, gave poor catalytic activity, with catalyst **5** showing no evidence of any polycarbonate production, only a trace amount of cyclic carbonate was detectable by NMR spectroscopy (Table 3.1, d-f).

The fastest catalysts (**1-3**) (Table 3.1, a-c), were also the most selective, with selectivities of over 91 % in favour of polycarbonate production over that of trans-cyclic carbonate. This result showed promise since these high selectivities were achieved at 1 bar pressure, and polycarbonate selectivity commonly increases with pressure.³ No

ether linkages were formed in any of these polymerisations, intriguingly even for catalyst **4**, which did produce polyether for epoxide/anhydride ROCOP.²⁰

The PCHC molar mass, M_n , as assessed by GPC, was lower than theoretical values at these conversions, likely due to residual diol in the epoxide or water from the CO₂ that will act as a CTA.²¹ This was indicated by a significant high-weight shoulder in the GPCs (Figures S3.2 – S3.6). Complex **2** gave the highest M_n and narrowest dispersity of the catalysts tested (Table 3.1, b). In contrast, catalyst **1** has a higher conversion, yet significantly lower M_n and broader dispersity. This indicates that catalyst **2** exerts better control over the polymerisation process.

Comparing catalysts **5** and **6** with **1** and **1.32** (Table 3.1, a & e-g), reveals that the presence of dimethyl functional groups on the backbone is important for these heterodinuclear Al(III)K(I) catalysts to operate at an appreciable rate. The same can be said for the polycarbonate selectivity, where the methylene groups lead to an increase in selectivity. This same effect on rate was also observed in epoxide/anhydride ROCOP for these catalysts which was attributed to the electronic effects from the methyl groups.²⁰ This was because VT NMR experiments showed that there was no difference in temperature response between **5** & **1.32** (Figures S2.57 & S2.58), which would have been expected were the methyls to have an effect on fluxionality.²⁰ It should be noted that all catalysts were soluble in CHO under reaction conditions. What is unusual about these trends, especially for **6**, is that the ethylene backbone is widely used in catalysts in the field and in structure-activity relationships, often it is found that catalysts with this backbone are the most active.^{3,22} Perhaps, methylating the ethylene backbone of a number of the field's most active catalysts could lead to a further rate and selectivity enhancement. In contrast to the trends observed for epoxide/anhydride ROCOP, reducing

the backbone linker length from three carbons to two led to increases in both rate and selectivity.²⁰

Overall, these results are promising, especially because the high polycarbonate selectivity is a big improvement over catalyst **1.32**.

3.2.2 High-Pressure Polymerisations and Discussion

Catalysts **2** & **3** of the series, the fastest, most selective, and affording the best polymer control, were tested at high CO₂ pressure (20 bar). These polymerisations were conducted in neat epoxide with cyclohexane diol (CHD) as a CTA to control the MW of the polymers produced (1:20:4000 = [cat]:[CHD]:[CHO], $T = 100\text{ }^{\circ}\text{C}$).²³ The reactions were monitored on a high pressure ReactIR spectrometer, allowing for *in-situ* measurements of CHO conversion against time (Table 3.2).

At $p(\text{CO}_2) = 20\text{ bar}$, there was a significant increase in polymerisation rate compared with polymerisations at low pressure; notably, there was a 7x activity increase for **2**, and for **3**, there was a 3x increase in activity (Table 3.2, b & d). Intriguingly, when an initial test was run for **2** without CHD, there was a lower selectivity than the 1 bar run (Table 3.2, a & Table 3.1, b). The different reaction setup, with larger volumes and less efficient stirring could well have contributed to this. However, addition of 20 equiv. of CHD improved selectivity up to 96 % and led to slight increase in TOF to 890 h^{-1} as well. It is not immediately clear why the addition of CTA has such an effect, but a similar trend, where both activity and selectivity increase together, was seen with decreasing Lewis acidity of the s-block metal in a Co(III)M(I/II) complex.¹¹ In that study, it was proposed that a M(I/II) with a lower Lewis acidity had a weaker M(I/II)-carbonate bond, which made the carbonate more nucleophilic, leading to a higher rate. In a similar way, possibly

the coordination of hydroxyl polymer chain ends to the K(I) could weaken the K(I)-carbonate bond, leading to these observed improvements in rate and selectivity. Detailed investigation into the role of CTA in reaction rate enhancement is discussed in Chapter 4.

Table 3.2 Polymerisation results for CHO/CO₂ ROCOP at high CO₂ pressures

Entry	Conditions				CHO conv. (%) ^a	CO ₂ select. (%) ^a	PCHC select. (%) ^a	TOF (h ⁻¹) ^c	<i>k</i> _{obs} x 10 ⁵ (s ⁻¹) ^d	<i>M</i> _{n, GPC} (kg mol ⁻¹) [<i>D</i>] ^e
	Cat	Time (h)	[cat] (%)	CHD equiv.						
a	2	2.9	0.05	0	51	>99	89	820	13.0	16.2 [1.28]
b	2	3.6	0.025	20	48	>99	96	890	7.6	7.1 [1.14]
c ^f	2	1.3	0.025	20	39	>99	93	1410	10.9	5.6 [1.20]
d	3	4.4	0.025	20	40	>99	96	430	3.1	5.8 [1.10]
e ¹⁸	1.32	2	0.05	0	51	>99	88	510	-	23.4 [1.21]

Polymerisation conditions: [cat]:[CHD]:[CHO] = 1:20:4000, *V*(CHO) = 6 mL, *p*(CO₂) = 20 bar, *T* = 100 °C ^a CHO conversion, CO₂ selectivity, polycarbonate linkage selectivity and TON all determined by ¹H NMR (298 K, 400 MHz, CDCl₃) spectroscopy; comparison of CHO peak 3.05 ppm, PCHC backbone peak 4.65 ppm, Cyclic carbonate peaks 4.00 & 4.68 ppm and polyether peak 3.45 ppm (Table S3.1). ^b TON determined from conversion(of CHO)*equiv.(CHO). ^c TOF = TON/time(h). Calculated at 20 % conversion. Except for d (23%) and e (51%). ^d *k*_{obs} calculated from linear fit of ln([CHO]_t)/ln([CHO]₀) vs. *t* (s) within the region of 5-25% CHO conversion. (Figures S3.7 & S3.8) ^e Determined by GPC in THF, 30 °C, calibrated using PS standards. ^f *T* = 110 °C.

In comparison with catalyst **1.32**, both **2** & **3** have superior polycarbonate selectivity and rate (Table 3.2, a & d-e). Since the metal used is Al, it is tolerant to high operating temperatures, with thermal stability demonstrated in air up to 200 °C (Figure S3.9), so the reaction temperature could be raised to 110 °C (Table 3.2, c). This gave a TOF of 1410 h⁻¹ at 20 % conversion. However, the polycarbonate selectivity dropped to 93 % at this temperature, and this loss in selectivity is only amplified at higher temperatures, which limits the maximum operating temperature for which **2** can be an effective polymerisation catalyst.

Upon the addition of CTA to the reaction mixture, as discussed in Chapter 2, there is better control over the resultant polymer *M*_n and distributions become more monomodal with a narrower dispersity (Figure 3.3).

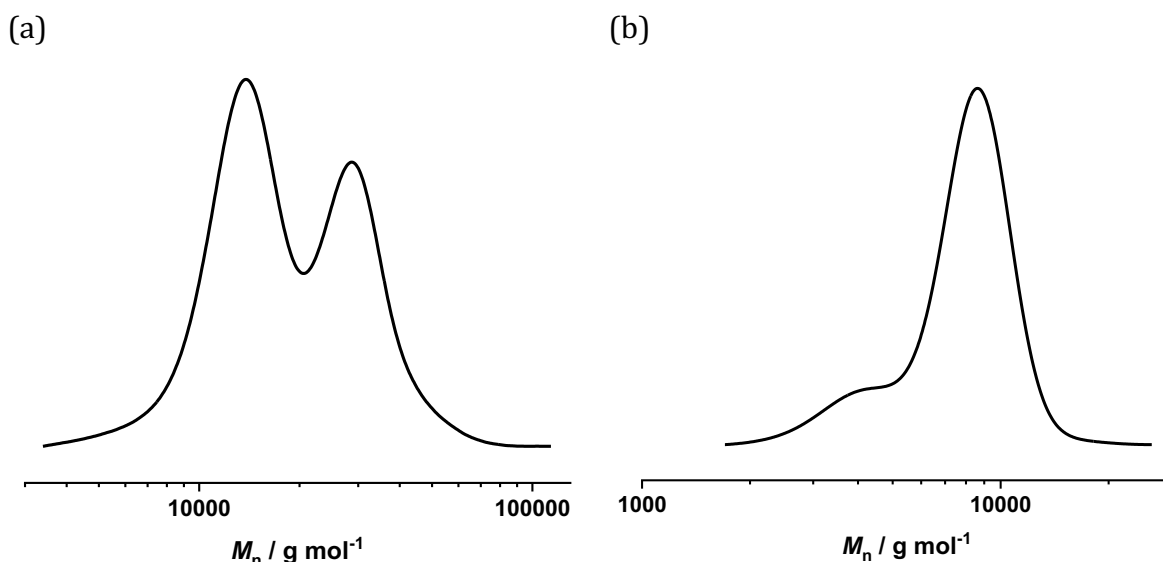


Figure 3.3 (a) GPC trace of polymer produced from entry a in Table 3.2 ([**2**]:[CHO] = 1:2000; $p(\text{CO}_2)$ = 20 bar CO_2 ; T = 100 °C). (b) GPC trace of polymer produced from entry b in Table 3.2 ([**2**]:[CHD]:[CHO] = 1:20:4000; $p(\text{CO}_2)$ = 20 bar CO_2 ; T = 100 °C). This shows how adding an excess of diol greatly increases the high-weight peak of the polymer trace and lowers the overall molecular weight.

It is worthwhile to see how this novel catalyst is placed within the wider field. Cobalt often leads to the fastest catalysts and Williams and co-workers reported a Mg(II)Co(II) catalyst that reached a $\text{TOF} = 3,200 \text{ h}^{-1}$ (>99 % PCHC; [cat]:[CHD]:[CHO] = 1:20:2000; T = 100 °C; $p(\text{CO}_2)$ = 20 bar) and a Co(III)Na(I) catalyst with $\text{TOF} = 1,590 \text{ h}^{-1}$ (>99 % PCHC; [cat]:[CHD]:[CHO] = 1:10:4000; $p(\text{CO}_2)$ = 20 bar; T = 100 °C).^{5, 22} These are 2-4 times more active than **2** under the same conditions. There was also a report of a *di*-Zn(II) catalyst by Rieger and co-workers that stands out because of the high activity reported, $\text{TOF} = 155,000 \text{ h}^{-1}$ (>99 % PCHC; [cat]:[CHO] = 1:8000; $p(\text{CO}_2)$ = 30 bar; T = 100 °C).⁷

The use of Al(III) presents clear advantages, particularly over metals such as cobalt, due to its high abundance and low toxicity. Therefore, a more relevant and informative comparison is between **2** and other Al(III) catalysts in the field. Al(III) amino-phenolate catalysts have been reported to be active for CHO/ CO_2 polymerisation however with moderate catalytic activities.¹⁴ Al(III)-salen catalysts have also been reported, with moderate activities, $\text{TOF} = 35 \text{ h}^{-1}$, at 80 °C and 35 bar and requiring PPNCl as a

cocatalyst.¹³ By far the most active Al(III) catalysts are porphyrin-based. There have been a number reported but, so far, the most active is an Al(III)-porphyrin with four tethered quaternary ammonium halide groups reported by Nozaki, Ema and co-workers that had a very high TOF of 10,000 h⁻¹ (>99 % PCHC; [cat]:[CHO] = 1:40,000; *p*(CO₂) = 20 bar; *T* = 120 °C).¹⁵ Work by Wang and co-workers has looked at tethering Al(III)-porphyrin complexes to form oligomers containing 4-7 Al(III) centres. These oligomers show high activities for PO/CO₂ over an analogous single Al(III)-porphyrin complex which is attributed to multi-metallic synergy, albeit whilst still requiring a PPnCl cocatalyst.^{12, 24} A dimeric equivalent of this catalyst could be used for CHO/CO₂ ROCOP and gave a rate of TOF = 2,100 h⁻¹ with >99 % polymer selectivity and >99 % carbonate linkages in the polymer ([Al]:[PPnCl]:[CHO] = 1:0.5:500, *p*(CO₂) = 40 bar, *T* = 100 °C).²⁵ The complex porphyrin ligands, and even more so the oligomers, require an involved synthesis, which could be a potential drawback, although the catalyst may be recyclable. Overall, catalyst **2** sits at the upper-end of Al(III) catalysts in terms of rate and selectivity and has the added benefit of a synthesis pathway that is straightforward and reasonably high-yielding (65% including ligand synthesis).²⁰

3.2.3 Monomer Scope

It is important to test the versatility of a novel catalyst for the synthesis of a number of polycarbonates, and thus catalytic activity for a few different monomers was tested. These were vCHO, with a useful vinyl group for polymer functionalisation, PO, a widely-used commercial epoxide, and limonene oxide (LO), a very desirable monomer to use because it can be derived from cyclic monoterpene limonene which is naturally occurring. All reactions were run in neat epoxide, unless otherwise stated, and at 20 bar CO₂ pressure (Table 3.3).

Table 3.3 Epoxide scope using **2**.

Entry	Conditions				epox. conv. (%) ^c	polym. select. (%) ^d	CO ₂ select. (%) ^e	TON of epox. ^f	TOF of epox. (h ⁻¹) ^g
	Epoxide	cat loading, # (mol%)	<i>T</i> (°C)	<i>t</i> (h)					
a	CHO	0.05	100	0.5	20	95	>99	404	807
b	^a vCHO	0.05	100	44	63	^b -	>99	630	14
c	PO	0.05	60	47	14	3	32	280	6
d	LO	0.1	150	48	0	-	-	-	-

Polymerisation conditions: [2]:[CHD] = 1:20, **2** loading given in table as # (mol %). *p*(CO₂) = 20 bar. All reactions carried out in neat epoxide (6 mL), unless otherwise stated. ^a Polymerisation conditions: [2]:[PEG-17]:[vCHO] = 1:98:1000, *V*(vCHO) = 4 mL, additional *V*(Toluene) = 2 mL, *p*(CO₂) = 20 bar (Figure S3.10) ^b Unable to confidently determine. ^c Epoxide conversion in reaction, determined by ¹H NMR ^d Proportion of polycarbonate vs. cyclic carbonate, determined by ¹H NMR ^e Proportion of carbonate vs. ether linkages, determined by ¹H NMR ^f TON of epoxide = % conversion / mol % of catalyst. ^g TOF = TON / *t* (h).

Catalyst **2** was shown to be active for vCHO but with a much lower TOF than for CHO (Table 3.3, a&b). It should be noted that the conditions for the vCHO/CO₂ copolymerisation were very different to that for CHO/CO₂, so drawing comparisons is difficult. vCHO was at a lower concentration and run to a higher conversion, meaning that [epoxide] would be significantly lower than for the CHO/CO₂ copolymerisation. Due to the first order relationship between rate and [epoxide], this would have led to a lower point TOF than if they were conducted under comparable conditions (Table 3.3, a & b). Overall, the fact that there was a successful polymerisation demonstrates the robustness of the catalyst to large excesses of a macroinitiator. For the PO/CO₂ reaction, very little polycarbonate was produced; the resultant polymer was mainly ether and the CO₂ had reacted to form cyclic carbonate (Table 3.3, c). Finally, a test with LO led to no observable product being formed (Table 3.3, d), this was despite high temperatures and catalyst loading. The copolymerisation of LO with CO₂ is very challenging because it is a sterically encumbered epoxide, meaning that coordination and/or nucleophilic attack is difficult. Interestingly, one of the few catalysts that is able to copolymerise the two is an Al(III) amino-triphenolate.²⁶

3.3 Kinetic Analysis of $\text{L}_{\text{Cyc}}\text{ALK}(\text{OAc})_2$ (**2**)

3.3.1 Determining k_{obs}

The polymerisation kinetics was tested for catalyst **2** in order to establish a rate law for the polymerisation. As above, the reactions were conducted in a steel reactor vessel and were continuously monitored *in-situ* by ATR-IR (1750 cm^{-1} for polycarbonate and 1820 cm^{-1} for cyclic carbonate) and under replenishing CO_2 flow. A pseudo first-order rate constant, k_{obs} , could be calculated from the linear fit of $\ln([\text{CHO}]_t)/\ln([\text{CHO}]_0)$ vs. time (s) within the region of 5 - 25 % CHO conversion (before viscosity limitations take effect) (Figure S3.8). This mathematical fit could be used based on the interpretation of a first-order rate dependence on [CHO]. This means that the reaction rate law takes the form:

$$\text{rate} = \frac{d[P]}{dt} = -\frac{d[\text{CHO}]}{dt} = k_{\text{obs}}[\text{CHO}] \quad (3.1)$$

where $k_{\text{obs}} = k_p[\mathbf{2}]^l$. Here, k_p is the polymerisation rate coefficient. This differential equation can then be rearranged and solved giving:

$$\begin{aligned} -\frac{d[\text{CHO}]}{dt} &= k_{\text{obs}}[\text{CHO}] \\ \int_{[\text{CHO}]_0}^{[\text{CHO}]_t} \frac{d[\text{CHO}]}{[\text{CHO}]} &= -k_{\text{obs}} \int_0^t dt \\ \ln\left(\frac{[\text{CHO}]_t}{[\text{CHO}]_0}\right) &= -k_{\text{obs}}t \end{aligned} \quad (3.2)$$

Hence a plot of $\ln\left(\frac{[\text{CHO}]_t}{[\text{CHO}]_0}\right)$ vs. time gives a linear trend, the gradient of which is $-k_{\text{obs}}$. Reporting k_{obs} gives a better representation of the rate of reaction as opposed to taking a point TOF which is influenced by the conversion at which the test is made and also any initiation effects.

3.3.2 Order in [CHO]

This first order trend is most visible when the CHO is diluted allowing higher conversions to be reached before viscosity exerts too great an influence. In this case, diethyl carbonate (DEC) was used such that $[\text{CHO}] = 3.33 \text{ M}$ and $[\text{cat}]:[\text{CHD}]:[\text{CHO}] = 1:20:4000$. The plot of $\ln([\text{CHO}]_t/[\text{CHO}]_0)$ vs. t gave a linear correlation indicating a first order dependence on CHO (Figure 3.4, a).

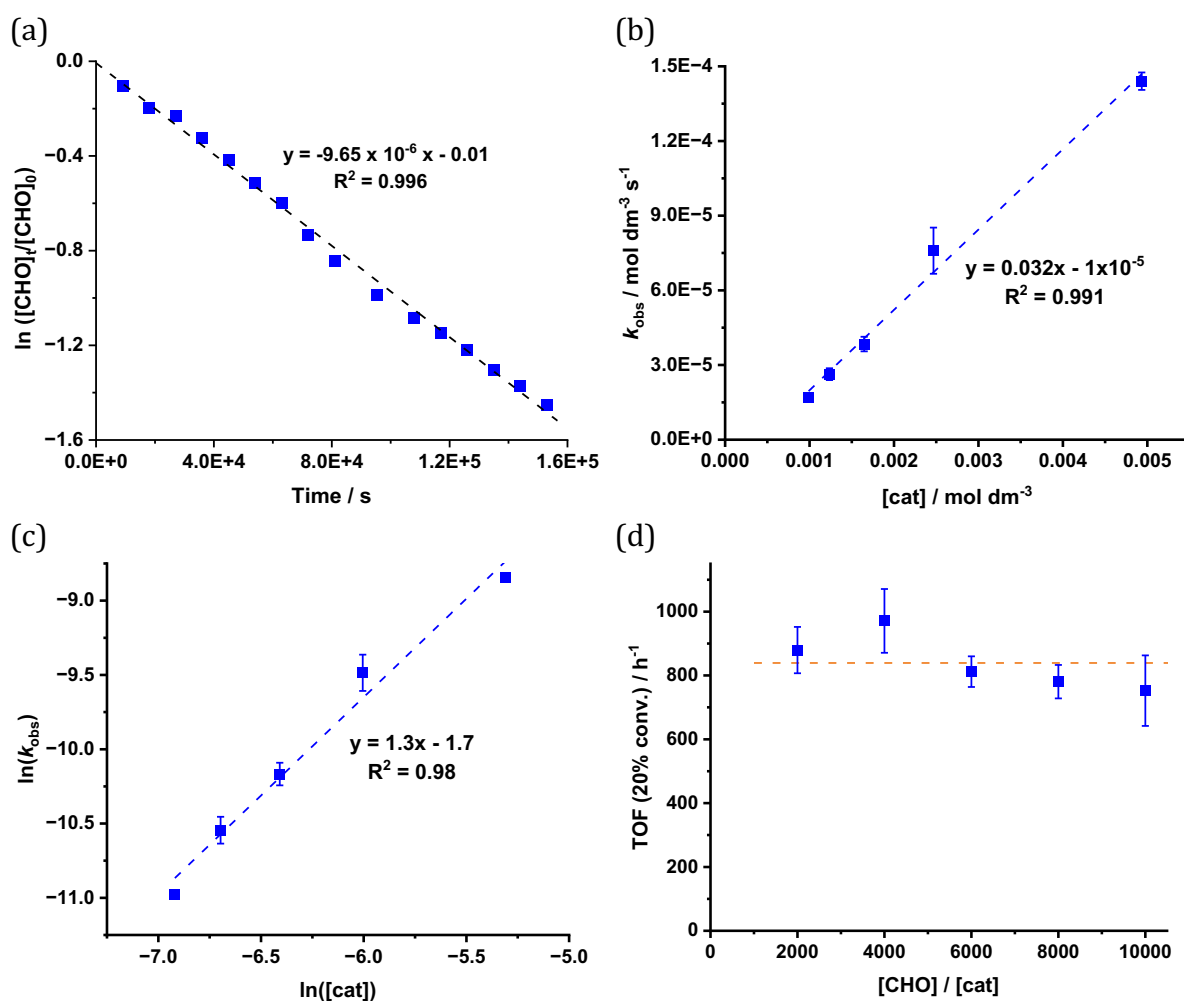


Figure 3.4 (a) Plot of $\ln([\text{CHO}]_t/[\text{CHO}]_0)$ vs. time for CHO/CO₂ ROCOP at $p(\text{CO}_2) = 20 \text{ bar}$, $T = 100 \text{ }^\circ\text{C}$. $[\text{2}]:[\text{CHD}]:[\text{CHO}] = 1:20:4000$, where $[\text{CHO}] = 3.33 \text{ M}$ in $V(\text{DEC}) = 6.8 \text{ mL}$. (b) Plot of k_{obs} vs. $[\text{cat}]$ for CHO/CO₂ ROCOP catalysed by **2** at $p(\text{CO}_2) = 20 \text{ bar}$, $T = 100 \text{ }^\circ\text{C}$. $[\text{2}]:[\text{CHD}]:[\text{CHO}] = 1:20:2000\text{--}10000$. k_{obs} obtained from gradient of linear fit between $\ln([\text{CHO}]_t/[\text{CHO}]_0)$ vs. t (s) for conversions 5–25 %. (c) Plot of $\ln[k_{\text{obs}}]$ vs. $\ln[\text{cat}]$ with gradient of 1.3. (d) Plot of TOF at 20 % conversion vs. $[\text{CHO}]/[\text{2}]$.

3.3.3 Order in [cat]

Next, the order in catalyst was determined by varying the catalyst loading from 0.05 - 0.01 mol% ([2]:[CHD]:[CHO] = 1:20:2000-10,000; $T = 100\text{ }^{\circ}\text{C}$; $p(\text{CO}_2) = 20\text{ bar}$) (Figure 3.4, b, Table S3.2); note the very low catalyst loadings achieved in these tests (Table S3.2, e). The rate dependence is governed by the following rate law:

$$k_{obs} = k[2]^l[CO_2]^n \quad (3.3)$$

$$\ln(k_{obs}) = \ln(k[2]^l[CO_2]^n)$$

$$\ln(k_{obs}) = l \cdot \ln([2]) + \ln(k[CO_2]^n) \quad (3.4)$$

Therefore, with a first order rate dependence on catalyst, there should be a linear correlation between k_{obs} and [2] when $p(\text{CO}_2)$ is constant, as is observed (Figure 3.4, b). A plot of $\ln(k_{obs})$ vs. $\ln([2])$ had a gradient of 1.3 (Figure 3.4, c). The TOF, representing catalytic activity, was calculated, using the final aliquot TON and interpolating using the IR traces to 20% conversion, for all runs and these remained constant irrespective of catalyst loading (Figure 3.4, d). This indicates that there is a close to first order rate dependence.

3.3.4 Order in [CO₂]

Finally, the order in [CO₂] was determined. From the k_{obs} vs. $p(\text{CO}_2)$ plot (Figure 3.5, a), it is clear that the rate of reaction increases steadily with $p(\text{CO}_2)$ before flattening out and reaching a plateau with rate of $6.9 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$. The drop in rate at 30 bar relative to 20 and 25 bar could be attributed to gas expansion, where the volume of the liquid phase increases, diluting the reactants.⁹

The $p(\text{CO}_2)$ was converted to $[\text{CO}_2]$ by a linear extrapolation of a set of calibration data that correlated $[\text{CO}_2]$ in CHO to $p(\text{CO}_2)$ at 100 °C (Figure 3.5, b & S3.11, Table S3.3).²⁷ The lower pressures from the calibration data were used in the linear fit, that was necessarily set to pass through the origin, since these are most likely to reliably follow the linear relationship of Henry's Law.

Recently, our group reported a study investigating the rate dependence on $[\text{CO}_2]$ for a Co(III)K(I) catalyst for PO/ CO_2 ROCOP.³ It used a simple model, splitting the trend into a tangential region, where the rate increase with $[\text{CO}_2]$ is approximated to be linear, and a plateau region, where the rate of reaction is assumed independent of $[\text{CO}_2]$, with a transition pressure between these two regions.

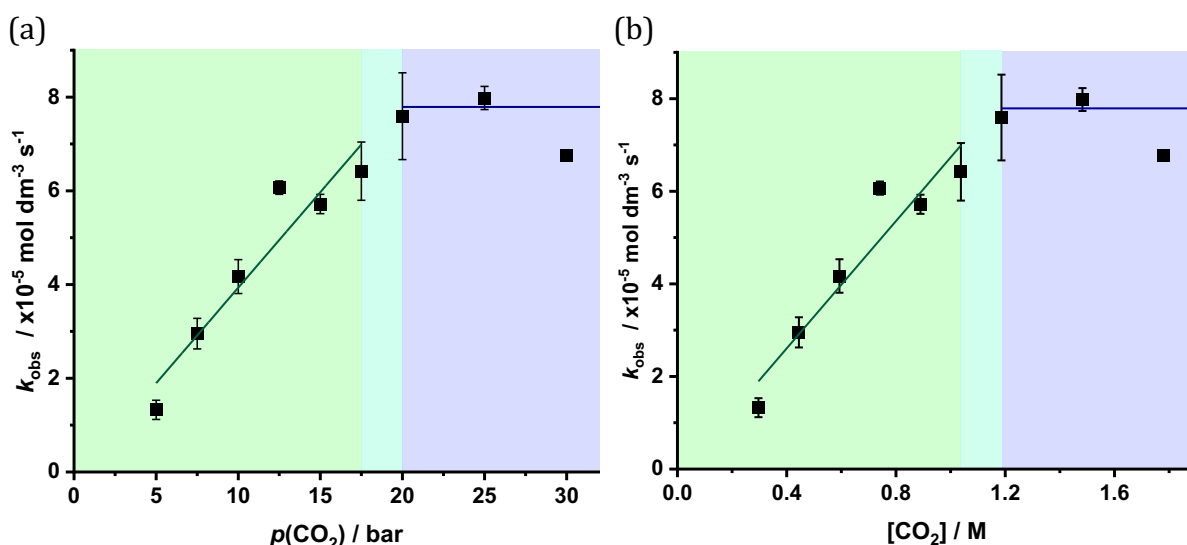


Figure 3.5 (a) Graph of k_{obs} vs. $p(\text{CO}_2)$ for CHO/ CO_2 ROCOP catalysed by **2** at 5 - 30 bar CO_2 , $T = 100$ °C. $[\text{2}]:[\text{CHD}]:[\text{CHO}] = 1:20:4000$. k_{obs} obtained from gradient of linear fit between $\ln([\text{CHO}]_t/[\text{CHO}]_0)$ vs. t (s) for conversions 5-25 %. (b) Graph of k_{obs} vs. $[\text{CO}_2]$ where $[\text{CO}_2]$ is calculated from $p(\text{CO}_2)$ by linear calibration (Figure S3.11 & Table S3.3).

Since similar trends were observed with **2**, these same approximations can be applied to interpret this kinetic data (Figure 3.5). If a linear tangential approximation is used for the low pressure runs ($5 \leq p(\text{CO}_2) < 20$ bar), one could interpret this as a first order rate dependence on $[\text{CO}_2]$. At higher pressures ($p(\text{CO}_2) \geq 20$ bar), the trend levels off, such

that $[\text{CO}_2]$ appears to be zero order relative to rate. Similar levelling off behaviour is also seen in the polycarbonate vs. cyclic carbonate selectivity trend for the same reaction (Figure 3.6).

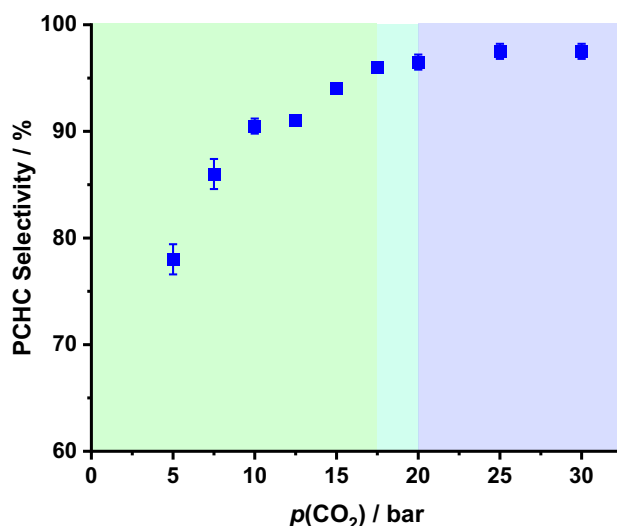


Figure 3.6 Graph of PCHC selectivity vs. $p(\text{CO}_2)$ for CHO/ CO_2 ROCOP catalysed by **2** at 5 - 30 bar CO_2 , $T = 100^\circ\text{C}$. $[\mathbf{2}]:[\text{CHD}]:[\text{CHO}] = 1:20:4000$. Selectivity determined by NMR looking at PCHC backbone peak 4.65 ppm and cyclic carbonate peaks 4.00 & 4.68 ppm

3.3.5 Proposed Rate Law

Overall, the data, along with the interpretations regarding the order in $[\text{CO}_2]$, give the following set of two rate laws:

$$\text{Rate} = k[\text{Cat}]^1[\text{CHO}]^1[\text{CO}_2]^1, \quad p(\text{CO}_2) < 20 \text{ bar} \quad (3.5)$$

$$\text{Rate} = k_p[\text{Cat}]^1[\text{CHO}]^1[\text{CO}_2]^0, \quad p(\text{CO}_2) \geq 20 \text{ bar} \quad (3.6)$$

To confirm that these rate laws are in good agreement with the data, the kinetic modelling software, COPASI, was used to simulate these rate laws.²⁸ The calculated values of both $[\text{CHO}]_t$ and $[\text{PCHC}]_t$ were overlayed onto the IR data for $p(\text{CO}_2) = 12.5$ & 25 bar (Figure 3.7). Visually, there was close agreement between the model and the data at both pressures, indicating that splitting the rate law into two regimes, before and after a

transition pressure (20 bar) is a sensible approach (Figure 3.7). However, this simplified model should be considered a first approximation to the underlying trend because there are likely other factors influencing the emergence of the high pressure plateau, such as gas expansion.

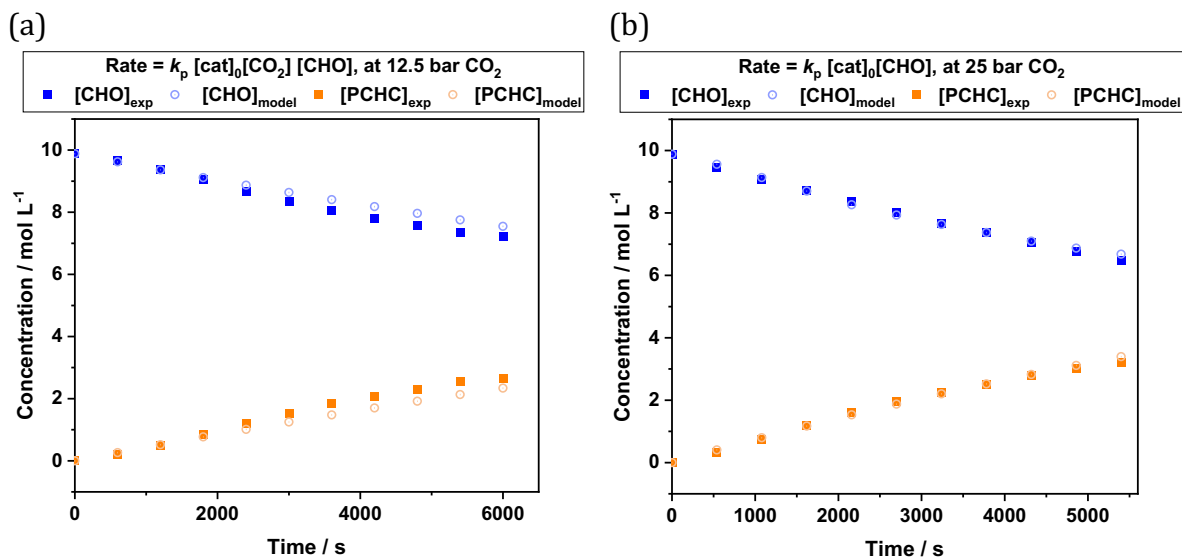


Figure 3.7 Concentration vs. time data for experimentally determined values (squares) and the calculated values using COPASI kinetic modelling (circles). (a) Experimental (squares) and modelled (circles) data for experiments conducted at 12.5 bar CO₂ pressure, where rate = $k_p [\text{cat}]_0 [\text{CHO}] [\text{CO}_2]$, $k = 0.0246 \text{ M}^{-2} \text{ s}^{-1}$, $[\text{cat}]_0 = 2.47 \text{ mM}$, $[\text{CHO}]_0 = 9.88 \text{ M}$, $[\text{CO}_2] = 0.741 \text{ M}$. (b) Experimental (squares) and modelled (circles) data for experiments conducted at 25 bar CO₂ pressure, where rate = $k_p [\text{cat}]_0 [\text{CHO}]_0$, $k_p = 0.0315 \text{ M}^{-1} \text{ s}^{-1}$, $[\text{cat}]_0 = 2.47 \text{ mM}$, $[\text{CHO}]_0 = 9.88 \text{ M}$.

3.4 Towards a Unified Rate Law with K_{eq}

It has previously been hypothesised that there exists an equilibrium between M-alkoxide and M-carbonate, governed by the equilibrium constant, K_{eq} (Figure 3.8, Equation (3.7)).²⁹ The position of this equilibrium is determined by the concentration of CO₂ in the polymerisation mixture. Since the activity of **2** appears to be responding to $p(\text{CO}_2)$ in this way, a previously reported approach was used to determine K_{eq} and establish a unified rate law.³

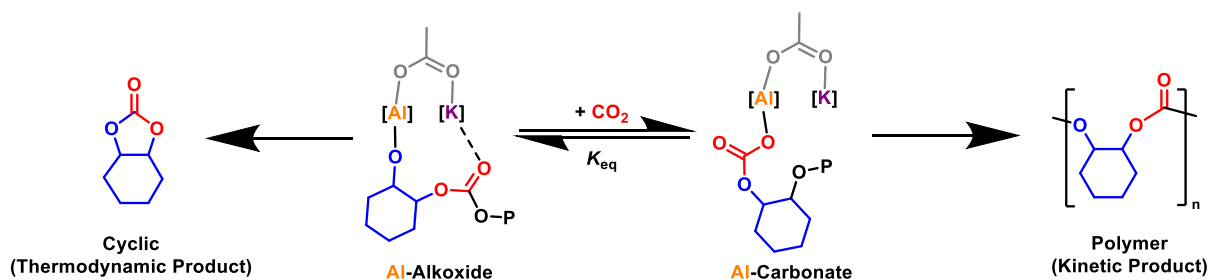


Figure 3.8 Scheme showing the CO₂ insertion equilibrium and its influence on polymer propagation.

$$K_{eq} = \frac{[\text{carbonate}]}{[\text{alkoxide}][\text{CO}_2]} \quad (3.7)$$

The [carbonate] was approximated by a proportional relationship between it and the rate of reaction in the linear regime, since, according to the mechanistic assumptions, this is the active species that contributes to propagation of the polymer chain. $Rate_{max}$ was the average rate of polymerisation in the plateau region (excluding 30 bar).

$$[\text{carbonate}]_p = [\text{cat}]_0 \times \frac{rate_p}{rate_{max}} \quad (3.8)$$

[Alkoxide]_p, could thus be calculated and for each pressure in the low-pressure regime, from $[\text{cat}]_0 - [\text{carbonate}]_p$. Using these concentrations and the calibrated [CO₂] for each pressure, a K_{eq} could be calculated from (3.7). The average of these values gives:

$$K_{eq} \text{ (2)} = 2.73 \pm 0.63 \text{ M}^{-1}$$

This gives a new rate law that should be universal across the CO₂ pressures tested:

$$Rate = k_p K_{eq} [\text{alkoxide}]^1 [\text{CHO}]^1 [\text{CO}_2]^1, \quad 5 \leq p(\text{CO}_2) \leq 30 \text{ bar} \quad (3.9)$$

This new collective rate law also showed excellent agreement between the experimental data and computational modelling, when tested using the COPASI software (Figure 3.9).²⁸

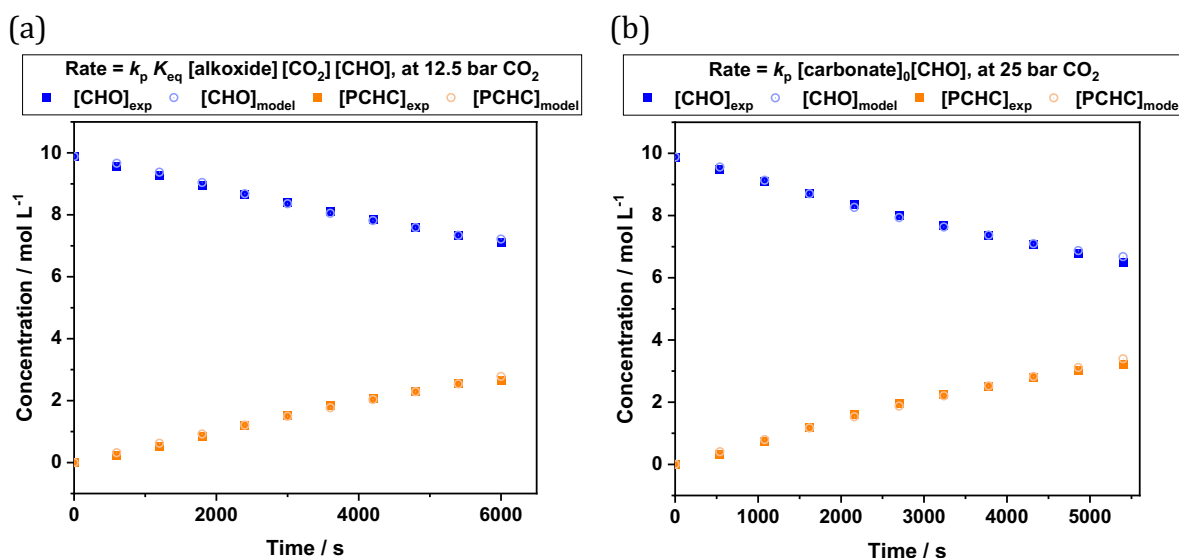


Figure 3.9 Concentration vs. time data for experimentally determined values (squares) and the calculated values using COPASI kinetic modelling (circles). (a) Experimental (squares) and modelled (circles) data for experiments conducted at 12.5 bar CO₂ pressure, where $\text{rate} = k_p K_{eq} [\text{alkoxide}] [\text{CO}_2] [\text{CHO}]_0$, $k_p = 0.0246 \text{ M}^{-1} \text{ s}^{-1}$, $K_{eq} = 2.73 \text{ M}^{-1}$, $[\text{carbonate}]_0 = 2.47 \text{ mM}$, $[\text{alkoxide}]_0 = 0 \text{ M}$, $[\text{CHO}]_0 = 9.88 \text{ M}$, $[\text{CO}_2] = 0.741 \text{ M}$. (b) Experimental (squares) and modelled (circles) data for experiments conducted at 25 bar CO₂ pressure, where $\text{rate} = k_p [\text{carbonate}] [\text{CHO}]_0$, $k_p = 0.0315 \text{ M}^{-2} \text{ s}^{-1}$, $[\text{carbonate}] \sim [\text{cat}]_0 = 2.47 \text{ mM}$, $[\text{CHO}]_0 = 9.88 \text{ M}$.

This approach very simply represents the effect on rate of $p(\text{CO}_2)$ and helps to identify the pressure above which the rate of polymerisation is effectively constant (the transition pressure). Therefore, the simplifications serve to improve the utility of the data gathered in relation to this trend. However, the pursuit of a more mathematically sound model to rigorously account for all the data would be worthwhile.

There is one key idiosyncrasy in the reasoning behind the ‘linear’/‘plateau’ interpretation and it comes from the determination of carbonate concentration based on its proportionality with rate (3.8). This would give a ‘linear’ relationship between $[\text{carbonate}]$ and $[\text{CO}_2]$, the same as that which is assumed to be between rate and $[\text{CO}_2]$; they are all proportional to each other. However, if it is assumed that K_{eq} obeys the equilibrium (3.7), it can be arranged to (3.10), which does not fit with the earlier ‘linear’ interpretation since $[\text{carbonate}]$ and $[\text{alkoxide}]$ are inextricably linked and K_{eq} is assumed constant.

$$[\text{carbonate}] = K_{eq}[\text{alkoxide}][\text{CO}_2] \quad (3.10)$$

This implies that there is a complication with the assumption of linearity between $[\text{CO}_2]$ and rate and so a potential solution could be to find an alternative relationship between the two. If, in equation (3.10), the $[\text{alkoxide}]$ is substituted by $[\text{cat}]_0 - [\text{carbonate}]$, the following relationship between $[\text{carbonate}]$ and $[\text{CO}_2]$ can be established:

$$[\text{carbonate}] = \frac{K_{eq} \cdot [\text{cat}]_0 \cdot [\text{CO}_2]}{1 + K_{eq} \cdot [\text{CO}_2]} \quad (3.11)$$

If equation (3.8) is inserted into this, the relationship between rate, k_{obs} , and $[\text{CO}_2]$ becomes:

$$k_{obs} = \frac{K_{eq} \cdot k_{max} \cdot [\text{CO}_2]}{1 + K_{eq} \cdot [\text{CO}_2]} \quad (3.12)$$

Rearranging yields:

$$\frac{1}{k_{obs}} = \frac{1}{k_{max}} + \frac{K_{eq}}{k_{max} \cdot [\text{CO}_2]} \quad (3.13)$$

This is a Michaelis-Menten (MM) relationship (3.12), which is used to represent enzymatically catalysed reactions that involve a preequilibrium. The CO_2 insertion equilibrium could be thought of in an analogous way. In general terms, an MM plot of reaction rate against substrate concentration represents a saturation kinetics trend, much like what is observed between polymerisation rate and $[\text{CO}_2]$: an initial increase in rate with $[\text{CO}_2]$ that then levels off at high $[\text{CO}_2]$. The ‘linear’ interpretation of the lower pressure data can be understood as taking the tangent to this line.

Equation (3.13) allows for the relevant parameters, k_{max} and K_{eq} , to be determined from a plot of $1/k_{obs}$ vs. $1/[\text{CO}_2]$ (Figure S3.12). Doing this for the data obtained and reported in section 3.3.4 gives the following:

$$k_{\max} = 22.2 \pm 8.6 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1} \text{ and } K_{\text{eq}} = 2.73 \pm 1.06 \text{ M}^{-1}$$

These parameters were then used with equation (3.12) to provide a prediction of k_{obs} from this MM model for the polymerisation data of **2** (Figure S3.13). This shows rather good agreement with the data however a 'plateau' region does not appear to have been reached yet. The calculated $k_{\max}$ is far greater than the maximum rates obtained in the experimental tests ($k_{\text{obs}} = 7.8 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$), but this is a theoretical maximum rate that could only hypothetically be achieved at very high pressures if effects such as gas expansion did not occur. This maximum rate is therefore a less useful value than that obtained from experimental values at commonly used pressures, as is the case when taking the average of rates at the 'plateau' region. Surprisingly though, the K_{eq} obtained from this MM methodology is exactly the same as that obtained from the initial 'linear'/'plateau' region approach. However, it is worth noting that underlying this correspondence are large errors associated with the estimation of the $k_{\max}$ and K_{eq} values. This is because the plot of $1/k_{\text{obs}}$ vs. $1/[\text{CO}_2]$ is very sensitive to anomalous results (outliers and other factors) and current data does not adequately represent the high $[\text{CO}_2]$ asymptotic regime.

There is also the possibility that this method may be limited by the lower selectivity of the polymerisation at low $p(\text{CO}_2)$, since the rate of CHO consumption is now governed by thermodynamic factors (surrounding cyclic carbonate formation) in addition to the kinetic ones that are being studied and interpreted here. At present, this MM model does not take this into account and so the actual polymerisation rate at low pressures may appear lower than expected by the model (as seen in Figure S3.13 for $p(\text{CO}_2) = 5 \text{ bar}$).

This MM approach can also be applied to published data for other catalysts where there is sufficient data on polymerisation rate dependence with $p(\text{CO}_2)$ over a wide range

of CO₂ concentrations. Plotting $1/k_{\text{obs}}$ vs. $1/[\text{CO}_2]$ for rate data for PO/CO₂ ROCOP catalysed by a Co(III)K(I) complex gives $k_{\text{max}} = 4.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ and $K_{\text{eq}} = 1.06 \text{ M}^{-1}$.³ These values are quite similar to those determined by the 'linear' method $k_{\text{max}} = 3.4 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ and $K_{\text{eq}} = 1.27 \text{ M}^{-1}$. It is expected that the MM-predicted maximum rate is higher than what can be observed at $p(\text{CO}_2) = 30 \text{ bar}$, so this difference isn't surprising. A plot of this data overlaid with the MM model shows quite close agreement with the overall trend of the scattered data (Figure S3.14).

The same MM modelling procedure was conducted on two different Zn-BDI catalysts (mono- and di-).^{30, 31} For the mono-catalyst, the general shape is similar, showing a very clear plateau, though there is only sparse data at low concentrations with large errors, so the actual values are only statistically consistent (Figure S3.15). On the other hand, for the di-Zn complex, the model provides a near-perfect prediction of the rate for most of the data points. This does lead to a different interpretation of the data though, with the MM model indicating that the 'plateau' region has not yet been attained within the pressures tested (Figure S3.16).

Ultimately, modelling the rate dependence on [CO₂] using a Michaelis Menten-like fit allows for a consistent interpretation of the data. However, at present this MM model has some clear limitations, since it does not yet account for certain effects such as the loss of polymer selectivity at low pressures and gas expansion at higher pressures. For this reason, it can appear to predict theoretical maximum rates that are not realistically attainable in the laboratory. The adoption of the simpler 'linear'/'plateau' methodology used in section 3.3 provides a phenomenological fit to what is actually obtained experimentally and so provides more practically relevant conclusions.

3.5 Eyring Analysis

Measurement of the transition state barrier ($\Delta G^\ddagger$) for the polymer propagation cycle forming PCHC and backbiting from the M-alkoxide to form cyclohexene carbonate (CHC) was conducted using the Eyring Equation (Figure 3.10, Equation (3.14)).

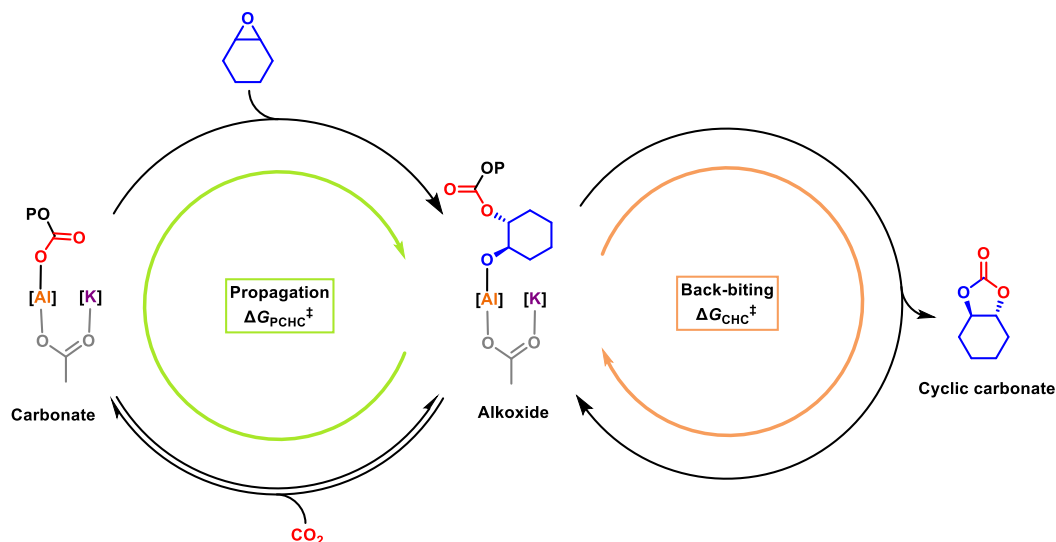


Figure 3.10 Diagram showing catalytic propagation cycle and off-cyclic back-biting.

This provides a mathematical relationship between the rate of reaction and the enthalpy and entropy of activation ($\Delta H^\ddagger$ and $\Delta S^\ddagger$ respectively):

$$k = \frac{k_B T}{h} e^{-\left(\frac{\Delta H^\ddagger}{RT}\right)} e^{\left(\frac{\Delta S^\ddagger}{R}\right)} \quad (3.14)$$

This can be rearranged by logarithmic manipulation into the linear form of the Eyring equation:

$$\ln \frac{k}{T} = \frac{-\Delta H^\ddagger}{R} \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \quad (3.15)$$

A plot of $\ln(k/T)$ vs. $1/T$ results in a gradient of $\frac{-\Delta H^\ddagger}{R}$ and a y-intercept of $\frac{\Delta S^\ddagger}{R} + \ln \frac{k_B}{h}$ from which both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ can be determined. The transition state Gibbs energy can thus be calculated for a given temperature:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (3.16)$$

3.5.1 Polycarbonate Reaction Barrier

The transition state barrier of PCHC formation $\Delta G_{\text{PCHC}}^\ddagger$ by **2** was found at high $p(\text{CO}_2)$ in order to suppress cyclic carbonate formation, and this complicates the interpretation of the kinetic data. Running the polymerisation at four temperatures between 90-110 °C and plotting $\ln(k_p/T)$ vs. $1/T$ (K^{-1}) enabled $\Delta H_{\text{PCHC}}^\ddagger$ and $\Delta S_{\text{PCHC}}^\ddagger$ to be calculated using the Eyring equation (Figure 3.11, Table S3.4). This gave, at typical reaction temperature of 100 °C, $\Delta G_{373, \text{PCHC}}^\ddagger = +103 \pm 13 \text{ kJ mol}^{-1}$ (24.6 kcal mol⁻¹).

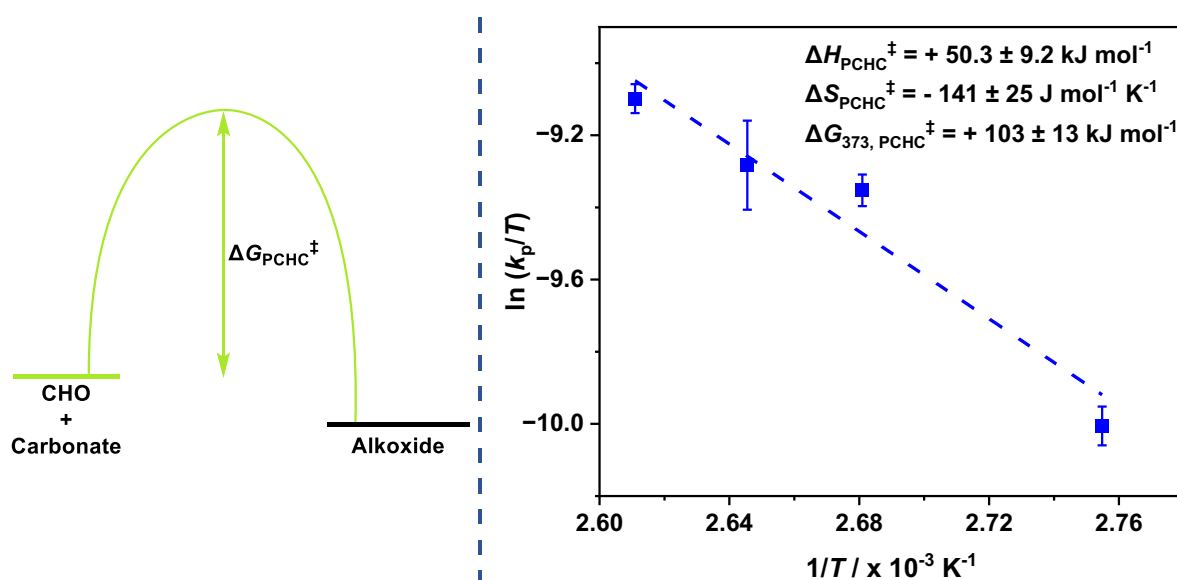


Figure 3.11 Plot of $\ln(k_p/T)$ vs. $1/T$ for the forward polymerisation of CHO/CO₂ ROCOP catalysed by **2** over the temperature range 90-110 °C.

3.5.2 Cyclic Carbonate Barrier

To determine the energy barrier to cyclic carbonate formation $\Delta G_{373, \text{CHC}}^\ddagger$, polymer backbiting experiments were conducted. This is because it is very challenging to separate the simultaneous differential equations representing the production of polycarbonate and cyclic carbonate in a polymerisation where significant quantities of both are being formed. Therefore, separating both reactions into their own individual experiments is the simpler approach.

The backbiting experiments were set up in the same reaction vessel as the polymerisation tests, filled with 6 mL CHO and a low concentration of polymer to avoid viscosity effects ($[2]:[\text{PCHC}] = 1:100$, $[2] = 2.47 \times 10^{-3} \text{ mol dm}^{-3}$, $V(\text{CHO}) = 6 \text{ mL}$). The same polymer sample was used throughout to ensure consistency between the runs because it is the concentration of polymer end-groups (and therefore the M_n of the polymer being used) that determines the rate of the reaction (since these rate comparisons are relative, an arbitrary M_n could be used, in this case 6,800 [1.13] g mol^{-1} , prepared using catalyst **2**).

As the polymer backbites to the cyclic carbonate, it is clear that the method of backbiting is from the chain-ends, as seen by an aliquot taken from one such reaction, showing that at 46 % conversion, the polymer $M_{n, \text{GPC}} = 4,100$ [1.14] g mol^{-1} which is 60 % of the original M_n whilst maintaining a narrow dispersity (Table S3.5). This is clear evidence that the polymer is being back-bitten from the chain ends in controlled manner, as opposed to depolymerisation by cleaving random carbonate linkages within the polymer, which would have led to a much wider dispersity and a much lower M_n . As a result, the reaction rate was modelled as pseudo-zero-order, since [endgroup], at least initially, will remain constant. It is important to note that, by analysis of the NMR spectrum, the backbiting experiments yielded *trans*-cyclic carbonate only (Figure S3.17).^{32,33} This indicates that the backbiting mechanism occurs from the alkoxide as opposed to the carbonate chain end.

These experiments, using the same plot of $\ln(k_p/T)$ vs. $1/T$ (K^{-1}), gives $\Delta G_{373, \text{CHC}^\ddagger} = +106 \pm 17 \text{ kJ mol}^{-1}$ (25.3 kcal mol^{-1}) (Figure 3.12, Table S3.6).

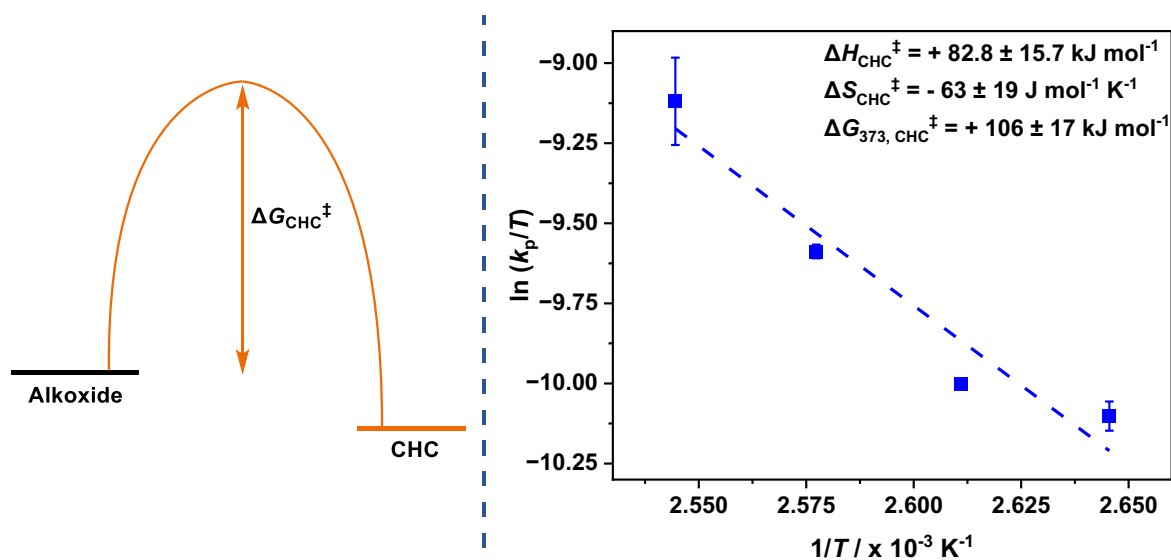


Figure 3.12 Plot of $\ln(k_p/T)$ vs. $1/T$ for backbiting of polycarbonate to form *trans*-cyclic carbonate catalysed by **2** over the temperature range 105-120 °C.

3.5.3 Discussion

The calculations reveal a backbiting transition state Gibbs Energy higher than that of the forward polymerisation reaction, in keeping with the experimental observation that the polymerisation is faster than cyclic carbonate formation. As temperature increases, the entropic driving force favouring cyclic becomes more prominent with a temperature of 417 K (144 °C), being where the $\Delta G^{\ddagger}$ are equivalent.

Comparison with the (porphyrin)Al(III)X catalyst ($\text{TOF} = 10,000 \text{ h}^{-1}$), reported by Nozaki, Ema, and co-workers, follows the expected experimental trend, since $\Delta G_{\text{PCHC}, 373}^{\ddagger} = + 92.5 \text{ kJ mol}^{-1}$, which is 10 kJ mol^{-1} lower than that calculated for **2**.¹⁵ Comparing with an (pheonalte)Al(III)X complex, the activation energy obtained by an Arrhenius plot was 149 kJ mol^{-1} , which is over 30 kJ mol^{-1} higher than **2**, which is consistent with its much lower rate of reaction ($\text{TOF} = 4 \text{ h}^{-1}$).¹⁴

3.6 Conclusions and Outlook

In summary, an active Al(III) catalyst (**2**) has been reported for CHO/CO₂ ROCOP showing fast rates and very good selectivity at both high and low pressures. The rate law reveals that it is the insertion of epoxide into the metal carbonate that is the rate determining step. Investigations into the effect of pressure on the catalytic activity revealed an equilibrium of CO₂ insertion, between the metal alkoxide and carbonate, governed by the equilibrium constant, $K_{eq} = 2.73 \pm 0.63 \text{ M}^{-1}$. Energy barriers were also calculated for the propagation and cyclic carbonate formation, allowing for comparison with other catalysts in the field.

This work highlights the potential that heterodinuclear Al(III) catalysts have, demonstrating excellent selectivity and amongst the highest rates reported for Al(III) epoxide/CO₂ catalysts whilst avoiding a complex synthesis process or the need for cocatalysts. This work contributes to the wider picture of heterodinuclear catalysts aiding ligand design considerations and further insights and refinements into rate dependence on $p(\text{CO}_2)$.

The insights gained from the backbone study could inspire similar modifications to other catalysts, potentially resulting in comparable improvements in activity. It would also be an interesting endeavour to, as was done in Chapter 2, test the CTA tolerance of catalyst **2** in CHO/CO₂ ROCOP. There is a better precedent for catalyst CTA tolerance in epoxide/CO₂ ROCOP,^{34, 35} but a specific study on this has yet to be conducted. Using the Al(III)K(I) metal combination for this, would allow for direct comparison between the two different copolymerisations.

3.7 References

- (1) Hepburn, C.; Adlen, E.; Beddington, J.; Carter, E. A.; Fuss, S.; Mac Dowell, N.; Minx, J. C.; Smith, P.; Williams, C. K. The technological and economic prospects for CO₂ utilization and removal. *Nature* **2019**, *575* (7781), 87–97. DOI: 10.1038/s41586-019-1681-6.
- (2) Deacy, A. C.; Moreby, E.; Phanopoulos, A.; Williams, C. K. Co(III)/Alkali-Metal(I) Heterodinuclear Catalysts for the Ring-Opening Copolymerization of CO₂ and Propylene Oxide. *J. Am. Chem. Soc.* **2020**, *142* (45), 19150–19160. DOI: 10.1021/jacs.0c07980.
- (3) Eisenhardt, K. H. S.; Fiorentini, F.; Lindeboom, W.; Williams, C. K. Quantifying CO₂ Insertion Equilibria for Low-Pressure Propene Oxide and Carbon Dioxide Ring Opening Copolymerization Catalysts. *J. Am. Chem. Soc.* **2024**, *146* (15), 10451–10464. DOI: 10.1021/jacs.3c13959.
- (4) Liu, Y.; Ren, W. M.; Liu, J.; Lu, X. B. Asymmetric Copolymerization of CO₂ with meso-Epoxides Mediated by Dinuclear Cobalt(III) Complexes: Unprecedented Enantioselectivity and Activity. *Angew. Chem. Int. Ed.* **2013**, *52* (44), 11594–11598. DOI: 10.1002/anie.201305154.
- (5) Deacy, A. C.; Kilpatrick, A. F. R.; Regoutz, A.; Williams, C. K. Understanding metal synergy in heterodinuclear catalysts for the copolymerization of CO₂ and epoxides. *Nat. Chem.* **2020**, *12* (4), 372–380. DOI: 10.1038/s41557-020-0450-3.
- (6) S, S.; Min, J. K.; Seong, J. E.; Na, S. J.; Lee, B. Y. A Highly Active and Recyclable Catalytic System for CO₂/Propylene Oxide Copolymerization. *Angew. Chem. Int. Ed.* **2008**, *47* (38), 7306–7309. DOI: 10.1002/anie.200801852.
- (7) Kissling, S.; Lehenmeier, M. W.; Altenbuchner, P. T.; Kronast, A.; Reiter, M.; Deglmann, P.; Seemann, U. B.; Rieger, B. Dinuclear zinc catalysts with unprecedented activities for the copolymerization of cyclohexene oxide and CO₂. *Chem. Commun.* **2015**, *51* (22), 4579–4582. DOI: 10.1039/c5cc00784d.
- (8) Su, Y.-C.; Tsui, C.-H.; Tsai, C.-Y.; Ko, B.-T. Highly active bimetallic nickel catalysts for alternating copolymerization of carbon dioxide with epoxides. *Polym. Chem.* **2020**, *11* (18), 3225–3236. DOI: 10.1039/d0py00174k.
- (9) Darensbourg, D. J.; Mackiewicz, R. M.; Billodeaux, D. R. Pressure Dependence of the Carbon Dioxide/Cyclohexene Oxide Coupling Reaction Catalyzed by Chromium Salen Complexes. Optimization of the Comonomer-Alternating Enchainment Pathway. *Organometallics* **2004**, *24* (1), 144–148. DOI: 10.1021/om049454l.
- (10) Garden, J. A.; Saini, P. K.; Williams, C. K. Greater than the Sum of Its Parts: A Heterodinuclear Polymerization Catalyst. *J. Am. Chem. Soc.* **2015**, *137* (48), 15078–15081. DOI: 10.1021/jacs.5b09913.
- (11) Fiorentini, F.; Diment, W. T.; Deacy, A. C.; Kerr, R. W. F.; Faulkner, S.; Williams, C. K. Understanding catalytic synergy in dinuclear polymerization catalysts for sustainable polymers. *Nat. Commun.* **2023**, *14* (1). DOI: 10.1038/s41467-023-40284-z.

- (12) Cao, H.; Liu, S.; Wang, X. Environmentally benign metal catalyst for the ring-opening copolymerization of epoxide and CO₂: state-of-the-art, opportunities, and challenges. *Green Chem. Eng.* **2022**, *3* (2), 111–124. DOI: 10.1016/j.gce.2021.11.005.
- (13) Darensbourg, D. J.; Billodeaux, D. R. Aluminum Salen Complexes and Tetrabutylammonium Salts: A Binary Catalytic System for Production of Polycarbonates from CO₂ and Cyclohexene Oxide. *Inorg. Chem.* **2005**, *44* (5), 1433–1442. DOI: 10.1021/ic048508g.
- (14) Plommer, H.; Stein, L.; Murphy, J. N.; Ikpo, N.; Mora-Diez, N.; Kerton, F. M. Copolymerization of CHO/CO₂ catalyzed by a series of aluminum amino-phenolate complexes and insights into structure–activity relationships. *Dalton Trans.* **2020**, *49* (20), 6884–6895. DOI: 10.1039/d0dt00726a.
- (15) Deng, J.; Ratanasak, M.; Sako, Y.; Tokuda, H.; Maeda, C.; Nozaki, K.; Hasegawa, J. Y.; Ema, T. Aluminum porphyrins with quaternary ammonium halides as catalysts for copolymerization of cyclohexene oxide and CO₂: metal-ligand cooperative catalysis. *Chem. Sci.* **2020**, *11* (22), 5669–5675. DOI: 10.1039/d0sc01609h.
- (16) Zhuo, C.; Cao, H.; Wang, X.; Liu, S.; Wang, X. Polymeric aluminum porphyrin: Controllable synthesis of ultra-low molecular weight CO₂-based polyols. *Chin. Chem. Lett.* **2023**, *34* (8). DOI: 10.1016/j.ccllet.2022.108011.
- (17) Zhuo, C.; You, H.; Gao, F.; Liu, S.; Wang, X.; Wang, F. Bottlebrush polymeric catalyst: Boosting activity for CO₂/epoxide copolymerization. *Fuel* **2023**, *333*. DOI: 10.1016/j.fuel.2022.126434.
- (18) Diment, W. T.; Gregory, G. L.; Kerr, R. W. F.; Phanopoulos, A.; Buchard, A.; Williams, C. K. Catalytic Synergy Using Al(III) and Group 1 Metals to Accelerate Epoxide and Anhydride Ring-Opening Copolymerizations. *ACS Catal.* **2021**, *11* (20), 12532–12542. DOI: 10.1021/acscatal.1c04020.
- (19) Eisenhardt, K. H. S.; Fiorentini, F.; Williams, C. K. Understanding the Effect of M(III) Choice in Heterodinuclear Polymerization Catalysts. *Inorg. Chem.* **2024**. DOI: 10.1021/acs.inorgchem.4c04430.
- (20) Shellard, E. J. K.; Diment, W. T.; Resendiz-Lara, D. A.; Fiorentini, F.; Gregory, G. L.; Williams, C. K. Al(III)/K(I) Heterodinuclear Polymerization Catalysts Showing Fast Rates and High Selectivity for Polyester Polyols. *ACS Catal.* **2024**, *14* (3), 1363–1374. DOI: 10.1021/acscatal.3c05712.
- (21) Wu, G.-P.; Darensbourg, D. J. Mechanistic Insights into Water-Mediated Tandem Catalysis of Metal-Coordination CO₂/Epoxide Copolymerization and Organocatalytic Ring-Opening Polymerization: One-Pot, Two Steps, and Three Catalysis Cycles for Triblock Copolymers Synthesis. *Macromol.* **2016**, *49* (3), 807–814. DOI: 10.1021/acs.macromol.5b02752.
- (22) Lindeboom, W.; Fraser, D. A. X.; Durr, C. B.; Williams, C. K. Heterodinuclear Zn(II), Mg(II) or Co(III) with Na(I) Catalysts for Carbon Dioxide and Cyclohexene Oxide Ring Opening Copolymerizations. *Chem. - Eur. J.* **2021**, *27* (47), 12224–12231. DOI: 10.1002/chem.202101140.

- (23) Darensbourg, D. J. Chain transfer agents utilized in epoxide and CO₂ copolymerization processes. *Green Chem.* **2019**, *21* (9), 2214–2223. DOI: 10.1039/c9gc00620f.
- (24) Cao, H.; Qin, Y.; Zhuo, C.; Wang, X.; Wang, F. Homogeneous Metallic Oligomer Catalyst with Multisite Intramolecular Cooperativity for the Synthesis of CO₂-Based Polymers. *ACS Catal.* **2019**, *9* (9), 8669–8676. DOI: 10.1021/acscatal.9b02741.
- (25) Fan, P.; Liu, S.; Zhang, R.; Zhuo, C.; Gao, F.; Pang, X.; Chen, X.; Wang, X. Rigid-Flexible Binuclear Catalysts: Boosting Activity for Copolymerization of CO₂ and Propylene Oxide. *Macromol.* **2024**, *57* (12), 5702–5711. DOI: 10.1021/acs.macromol.4c00887.
- (26) Peña Carrodegua, L.; González-Fabra, J.; Castro-Gómez, F.; Bo, C.; Kleij, A. W. AlIII-Catalysed Formation of Poly(limonene)carbonate: DFT Analysis of the Origin of Stereoregularity. *Chem. - Eur. J.* **2015**, *21* (16), 6115–6122. DOI: 10.1002/chem.201406334.
- (27) Foltran, S.; Cloutet, E.; Cramail, H.; Tassaing, T. In situ FTIR investigation of the solubility and swelling of model epoxides in supercritical CO₂. *J. Supercrit. Fluids.* **2012**, *63*, 52–58. DOI: 10.1016/j.supflu.2011.12.015.
- (28) Hoops, S.; Sahle, S.; Gauges, R.; Lee, C.; Pahle, J.; Simus, N.; Singhal, M.; Xu, L.; Mendes, P.; Kummer, U. COPASI—a COMplex PATHway Simulator. *Bioinformatics* **2006**, *22* (24), 3067–3074. DOI: 10.1093/bioinformatics/btl485.
- (29) Deacy, A. C.; Phanopoulos, A.; Lindeboom, W.; Buchard, A.; Williams, C. K. Insights into the Mechanism of Carbon Dioxide and Propylene Oxide Ring-Opening Copolymerization Using a Co(III)/K(I) Heterodinuclear Catalyst. *J. Am. Chem. Soc.* **2022**, *144* (39), 17929–17938. DOI: 10.1021/jacs.2c06921.
- (30) Lehenmeier, M. W.; Kissling, S.; Altenbuchner, P. T.; Bruckmeier, C.; Deglmann, P.; Brym, A. K.; Rieger, B. Flexibly Tethered Dinuclear Zinc Complexes: A Solution to the Entropy Problem in CO₂/Epoxide Copolymerization Catalysis? *Angew. Chem. Int. Ed.* **2013**, *52* (37), 9821–9826. DOI: 10.1002/anie.201302157.
- (31) Kernbichl, S.; Reiter, M.; Mock, J.; Rieger, B. Terpolymerization of β -Butyrolactone, Epoxides, and CO₂: Chemoselective CO₂-Switch and Its Impact on Kinetics and Material Properties. *Macromol.* **2019**, *52* (21), 8476–8483. DOI: 10.1021/acs.macromol.9b01777.
- (32) Singer, F. N.; Deacy, A. C.; McGuire, T. M.; Williams, C. K.; Buchard, A. Chemical Recycling of Poly(Cyclohexene Carbonate) Using a Di-MgII Catalyst. *Angew. Chem. Int. Ed.* **2022**, *61* (26). DOI: 10.1002/anie.202201785.
- (33) Wang, B.; Cao, X.; Wang, L.; Meng, X.; Wang, Y.; Sun, W. Co(II)-N₄ Catalysts for the Coupling of CO₂ with Epoxides into Cyclic Carbonates: Catalytic Activity, Computational and Kinetic Studies. *Inorg. Chem.* **2024**, *63* (20), 9156–9163. DOI: 10.1021/acs.inorgchem.4c00461.
- (34) Cyriac, A.; Lee, S. H.; Varghese, J. K.; Park, E. S.; Park, J. H.; Lee, B. Y. Immortal CO₂/Propylene Oxide Copolymerization: Precise Control of Molecular Weight and Architecture of Various Block Copolymers. *Macromol.* **2010**, *43* (18), 7398–7401. DOI: 10.1021/ma101259k.

- (35) Kuang, Q.; Zhang, R.; Zhou, Z.; Liao, C.; Liu, S.; Chen, X.; Wang, X. A Supported Catalyst that Enables the Synthesis of Colorless CO₂-Polyols with Ultra-Low Molecular Weight. *Angew. Chem. Int. Ed.* **2023**, 62 (35). DOI: 10.1002/anie.202305186.

Chapter 4:

Investigations into Alcohol-Induced Rate Enhancement

Work described in this chapter appears in "*Investigations into Alcohol-Induced Rate
Enhancement of Epoxide/Anhydride Ring Opening Copolymerisations*"

Shellard, E. J. K., Janssen, N., Williams, C. K.

Manuscript in preparation

4.1 Introduction and Aims

In epoxide/anhydride ring-opening copolymerisation (ROCOP), the development of catalysts tolerant to high protic compound loadings, that act as chain transfer agents (CTAs), is of particular importance for the production of low weight polyesters. It is also highly desirable to work to reduce the catalyst loading, especially if the catalyst must be removed from the polymer to allow for processing or use. In Chapter 2, it was reported that catalyst **1** was not only stable to alcohols as CTAs but the rate of reaction actually increased (by up to 5x) in the presence of excess alcohol functional group.¹ Reports of catalysts showing an enhanced activity for epoxide/anhydride ROCOP in the presence of protic compound CTA is extremely rare in the field, with this report being only the second example as far as it is possible to determine. The other catalyst is a Yttrium salt, $\text{YCl}_3\text{THF}_{3.5}$ or $\text{YCl}_3 \cdot 6\text{H}_2\text{O} + [\text{PPN}]\text{Cl}$, whose activity was noted to increase when the salt was hydrated and the reaction run in impure monomer.²

There are only a few other catalysts that have been noted to be tolerant to CTA. For example, a $[(\text{salph}[\text{CyPr}^+])\text{Al}(\text{III})(\text{Cl})](\text{Cl})^-$ complex, with a tethered cocatalyst on the ancillary ligand, was active when using 0 – 35 equivalents of CTA, but above that loading, the rate decreases.³ The authors investigated why the tethered cocatalyst appeared to improve CTA tolerance, over a binary catalyst system that was immediately deactivated. The bicomponent system is inhibited by competitive binding, of polymer hydroxyl chain ends to the Lewis acidic catalyst, and also hydrogen bonding, which disrupted anionic chain ends from ring opening the epoxide. Both of these effects are suppressed by tethering the cocatalyst.³ Another notable work, by Chen *et al.*, reports an $\text{Al}(\text{III})(\text{bipyridine bisphenolate})(\text{Cl})/\text{PPNCl}$ catalyst system that maintained a rate of around 85 % up to 100 equiv. of maleic acid.⁴

The work in this chapter follows on from the discovery reported in Chapter 2 and attempts to elucidate the causes of this rate enhancement. Firstly, test polymerisations were run with a timed addition of CTA to probe the rate enhancement. A CTA scope was also carried out. Next, a comprehensive kinetic study was conducted, to find the rate orders in catalyst, anhydride, epoxide, and, importantly, CTA. From this, a rate law could be determined. Finally, polymerisations with deuterated alcohol, along with tests investigating the nature of alcohol binding to the catalyst were conducted to investigate the origins of the rate enhancement based on a putative interaction between catalyst and alcohol in the rate determining step.

4.2 Polymerisation Rate Enhancement Tests

4.2.1 Addition of CTA Partway Through Polymerisation

4.2.1.1 Rates of Polymerisation

The first stage in establishing the origins of this CTA rate enhancement was to demonstrate that it was a chemical effect. That is to say that there is no purely physical phenomenon that could explain the change in rate, such as viscosity.

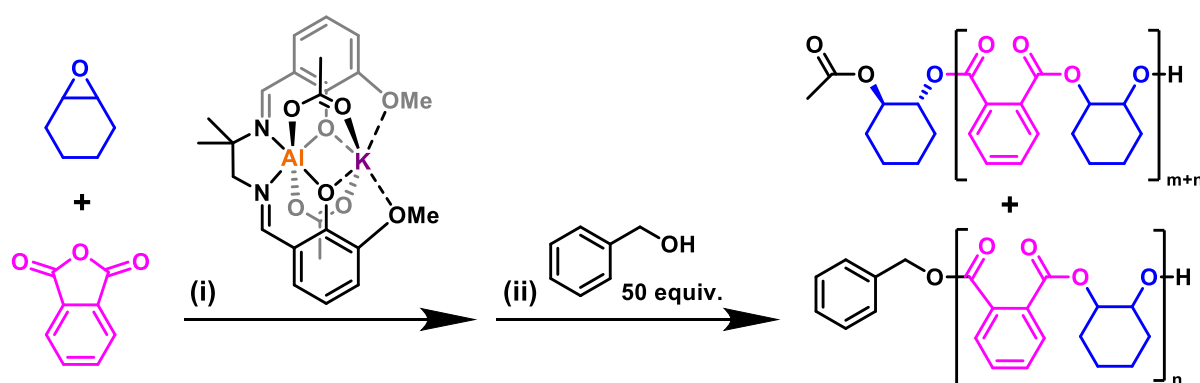


Figure 4.1 CHO/PA polymerisation (i) [1]:[PA]:[CHO] = 1:400:2000, $V(\text{CHO}) = 1 \text{ mL}$, $T = 100 \text{ }^{\circ}\text{C}$; (ii) $t = 25 \text{ mins}$, $V(\text{BnOH or Tol}) = 25.7 \text{ }\mu\text{L}$ (50 equiv.) added.

A ReactIR instrument was used to continuously monitor the reaction progression and speciation. The reaction was conducted with $[1]:[PA]:[CHO] = 1:400:2000$, $T = 100\text{ }^{\circ}\text{C}$, $V(\text{CHO}) = 1\text{ mL}$ and then, after 25 minutes, 50 equiv. (25.7 μL) of BnOH was injected into the polymerisation reaction mixture under N_2 flow (Figure 4.1). This led to an immediate change in rate (Figure 4.2). This same reaction was monitored by regular 5 min aliquots analysed by NMR spectroscopy (purple diamonds in Figure 4.2) which aligned very closely with the IR spectroscopy data. The gradient of the concentration/time graph (*i.e.* rate) before CTA addition was $2.6 \times 10^{-4}\text{ mol dm}^{-3}\text{ s}^{-1}$ (Figure S4.1). In the 20 mins after the CTA addition, the rate (*i.e.* gradient) almost doubled to $4.7 \times 10^{-4}\text{ mol dm}^{-3}\text{ s}^{-1}$ (Figure S4.2). This makes it clear that there is an instantaneous impact on rate by introducing 25x more hydroxyl groups into the polymerisation mixture.

A control reaction with an aprotic solvent, toluene, was carried out to confirm the change in absorbance was not an artefact of the probe. 25.7 μL of Tol (equivalent to the volume of BnOH added) was added at 25 mins to the reaction. This control experiment (green line in Figure 4.2) shows there is no perceivable change in rate when only toluene was added.

There is a sharp increase in conversion immediately after the 50 equiv. of BnOH are added to the polymerisation mixture (25 – 30 min), as indicated by the IR spectroscopy data. When calculating a TON from the magnitude of this jump in conversion, it is found to be roughly 50, possibly representing the 50 equiv. of BnOH added. In fact, a similar offset is also observed in the NMR spectroscopy data used to calibrate the *in-situ* conversion vs. time data. It is clear there is a significant initiation effect and it occurs very rapidly (faster than the 15s ReactIR timescale). It is tentatively proposed that the alcohol additive reacts rapidly and immediately to reduce [PA], perhaps via a molecular species.

In all subsequent work, the polymerisation rate is measured in the linear propagation regime (shown later to be valid), where all chains are assumed to have initiated.

The experiment clearly shows that BnOH has a chemical influence on the rate of reaction. It appears to rule out any significant contribution from viscosity, since the rate change occurs without any notable change to the reaction conditions, and the toluene control gives no change in reaction rate.

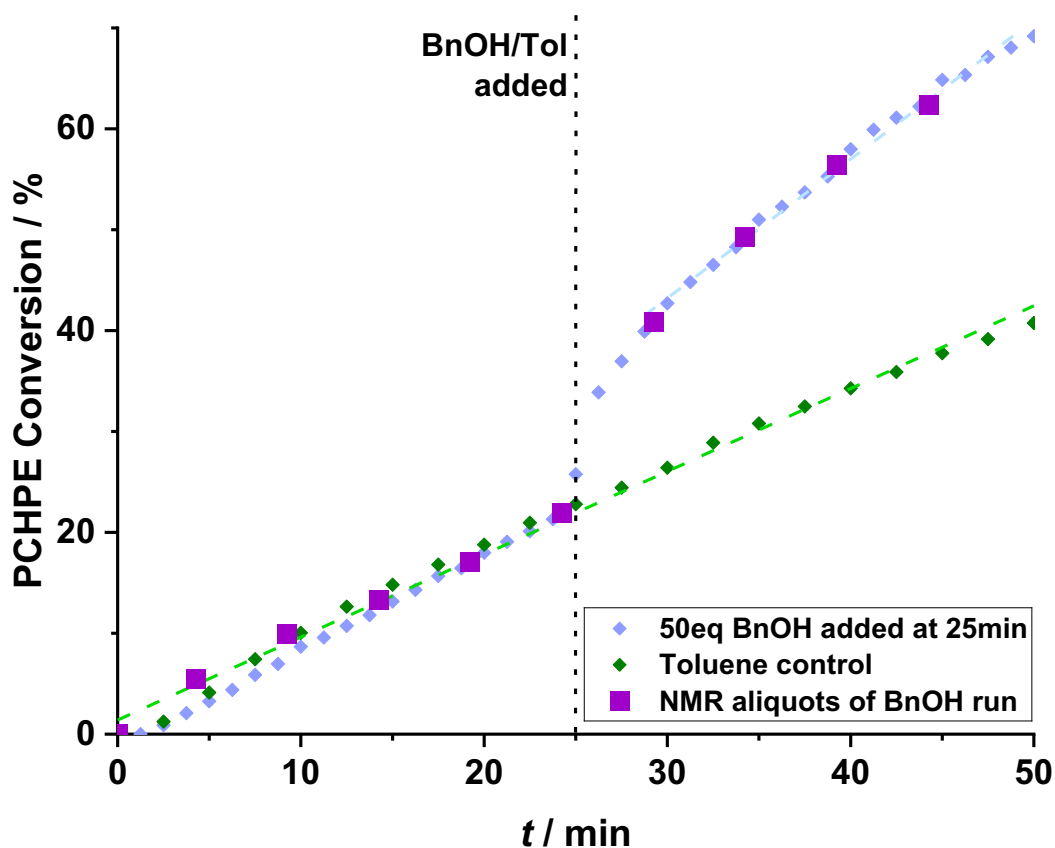


Figure 4.2 Plot of PCHPE production given as conversion (%) vs. t (min) for $[1]:[PA]:[CHO] = 1:400:2000$, $V(CHO) = 1$ mL, $T = 100$ °C; $t = 25$ mins, $V(\text{BnOH or Tol}) = 25.7$ μL (50 equiv.) added. With BnOH (purple line and diamonds (from NMR aliquots) and with Toluene (green line). ATR-IR peak at 1730 cm^{-1} was used for PCHPE production, and this matched the peak at 890 cm^{-1} for PA consumption.

4.2.1.2 GPC M_n of Polymers Produced

To characterise the polymers, GPC and MALDI-ToF data were collected. The GPC shown in Figure 4.3 (a) was obtained at full PA conversion in the BnOH partway addition

reaction detailed in 4.2.1.1 (or Figure 4.2) and shows a trimodal molar mass distribution. The two high M_n peaks are attributed to polymer chains initiated at the start of the reaction. The middle molecular weight distribution at $3,400 \text{ g mol}^{-1}$ is assigned to acetate end-capped chains, whereas the higher weight peak, $M_n = 7,600 \text{ g mol}^{-1}$, roughly double, is assigned to chains initiated from diol (as seen in Figure 2.10). A bimodal distribution is observed in the GPC of the toluene control reaction (Figure S4.3). The low weight peak at $M_n = 1,000 \text{ g mol}^{-1}$ originates from a distribution that is BnOH initiated, formed once the BnOH CTA was added. The M_n of this peak was sufficiently low to be detectable by MALDI-ToF which confirmed the initiating species (Figure 4.3, b).

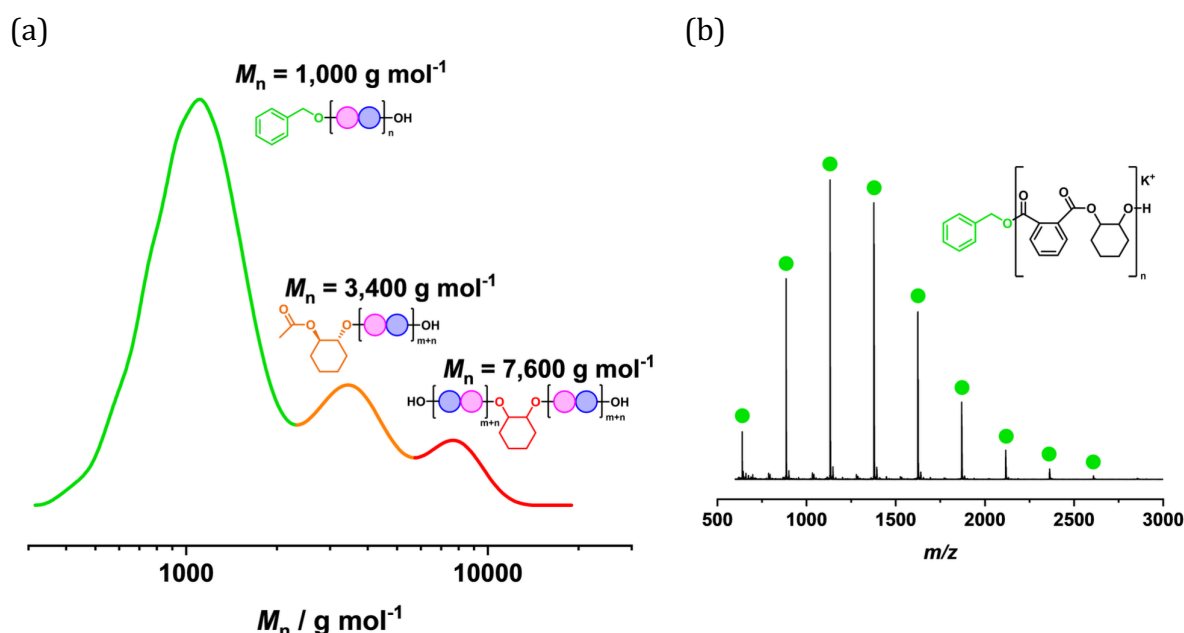


Figure 4.3 (a) GPC plot of PCHPE at full conversion from $[1]:[PA]:[CHO] = 1:400:2000$, $V(\text{CHO}) = 1 \text{ mL}$, $T = 100 \text{ }^\circ\text{C}$; $t = 25 \text{ mins}$, $V(\text{BnOH}) = 25.7 \text{ } \mu\text{L}$ (50 equiv.) with assignments of different M_n peaks. GPC in THF at $30 \text{ }^\circ\text{C}$, with instrument calibrated using PS standards (b) MALDI-ToF of same PCHPE sample. $M_{n,\text{calc}}(\text{repeat unit}) = 246.07 \text{ g mol}^{-1}$, $M_{n,\text{theoretical}}(\text{repeat unit}) = 246.26 \text{ g mol}^{-1}$. $M_{n,\text{calc}}(\text{end group} = \text{green}) = 147.21 \text{ g mol}^{-1}$, $M_{n,\text{theoretical}}(\text{end group} = \text{BnOH} + \text{K}^+) = 147.04 \text{ g mol}^{-1}$.

Since the M_n s of the two higher weight peaks are too high to be detectable by MALDI-ToF, an estimate of the DP was calculated from the GPC M_n to give an indication on assignments. The lowest weight peak, shown to be from BnOH initiation, gives $\text{DP}_2 = 4$ (calculated from $M_{n,\text{polymer}} / M_{n,\text{repeat unit}}$). This value is the number of repeat units on the end of each polymer chain since BnOH was added, which should be consistent across all

polymer chains. From this, DP_1 (number of repeat units in the polymer chain from before BnOH added) can be calculated using the middle peak, whose total $DP = DP_1 + DP_2 = 14$, implying that $DP_1 = 10$ (these polymers were initiated at the start of the reaction). It would then be expected that the highest weight peak has double the DP of the middle peak, since it is initiated at the start of the reaction from diol impurities, so $DP = 28$. From the $M_{n, GPC}$, the calculated DP is 31, which is very close to this approximation, substantiating the proposed assignment.

4.2.2 Chain Transfer Agent Scope

4.2.2.1 CTA Functionality Test

In another set of experiments, polymerisations were set up with different alcohol initiators (CTAs). BnOH, benzene-1,4-dimethanol (BDM), and 1,3,5-benzenetrimethanol (BTM) were used, since they all have similar chemical structures but each with a different number of hydroxyl functionalities. The reactions were set up with the quantities of the reagents altered such that $[-OH]$ remained constant throughout (Figure 4.4, $[1]:[PA]:[CHO] = 1:400:2000$; $[BnOH] = 50$, $[BDM] = 25$, $[BTM] = 16.7$; $T = 100\text{ }^{\circ}\text{C}$, $V(CHO) = 1\text{ mL}$).

With this adjustment for $[-OH]$, the rates across all three reactions were within error of each other (Figure 4.5). The final M_n of the products and their topologies (with three hydroxyl groups, BTM likely gives a star polymer) were all significantly different, with their molecular weights approximately proportional to the number of arms of the polymer (Figure 4.6). This indicates that regardless of the mass or topology of the polymer being produced, it is the hydroxyl functionality that influences the rate enhancement of the reaction.

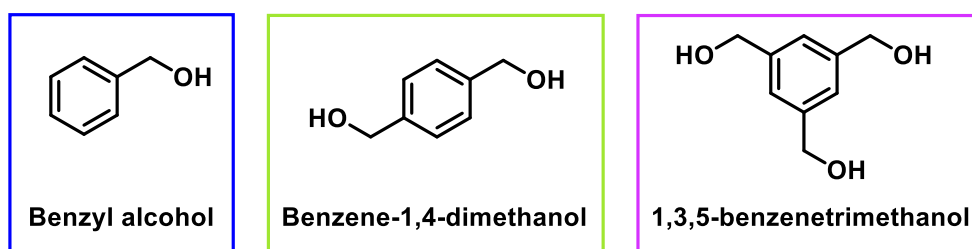


Figure 4.4 The series of alcohols tested: benzyl alcohol (BnOH), benzene-1,4-dimethanol (BDM) and 1,3,5-benzenetriethanol (BTM).

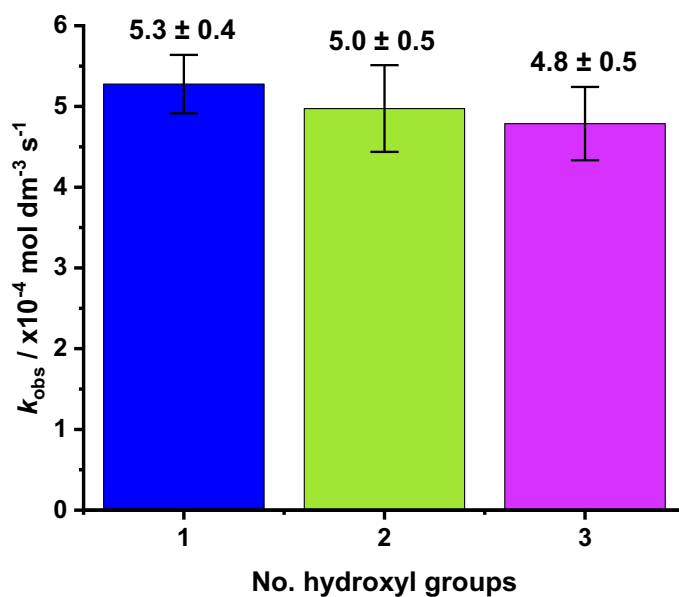


Figure 4.5 Graph showing rate of reaction, k_{obs} ($\times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$), against no. of hydroxyl groups in CTA for [1]:[PA]:[CHO] = 1:400:2000, $T = 100^\circ \text{C}$, $V(\text{CHO}) = 1 \text{ mL}$; [BnOH] = 50, [BDM] = 25, [BTM] = 16.7.

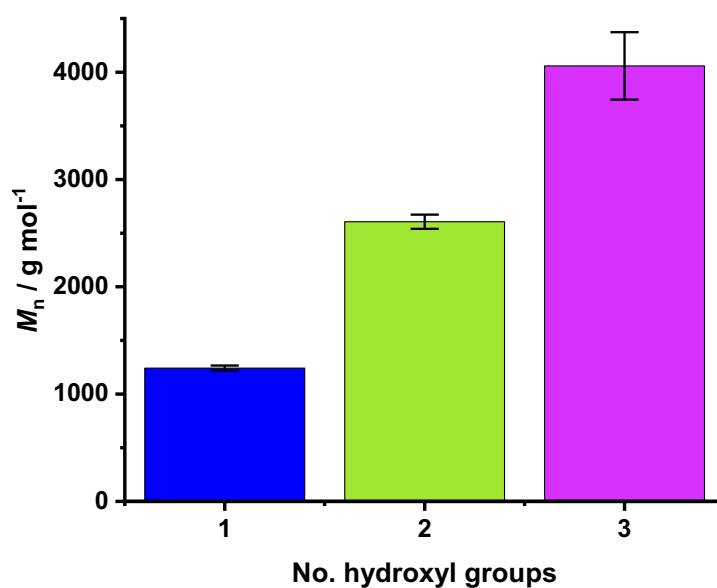
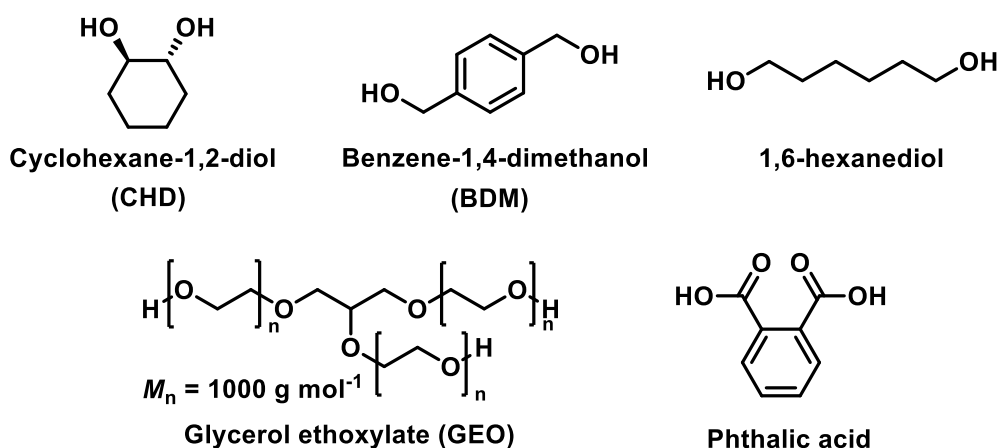


Figure 4.6 Graph showing M_n (g mol^{-1}) at full conversion against number of hydroxyl groups in CTA for [1]:[PA]:[CHO] = 1:400:2000, $T = 100^\circ \text{C}$, $V(\text{CHO}) = 1 \text{ mL}$; [BnOH] = 50, [BDM] = 25, [BTM] = 16.7.

4.2.2.2 CTA Further Scope

In addition to these kinetic tests, a scope of different alcohols and one di-acid was tested in order to demonstrate versatility of this catalyst. These runs were conducted under a reaction setup which only allowed point TOFs to be determined. The reactions were run at $[1]:[CTA]:[PA]:[CHO] = 1:20:400:2000$, $V(CHO) = 1$ mL, $T = 100$ °C (Table 4.1).

Table 4.1 Additional CTA scope.
Conditions: $[1]:[CTA]:[PA]:[CHO] = 1:20:400:2000$, $V(CHO) = 1$ mL, $T = 100$ °C.



Entry	Conditions		Polymerisation Data					
	CTA	t (min)	PA Conv. (%) ^a	PE Select. (%) ^b	TON ^c	TOF (h ⁻¹) ^d	$M_{n, GPC}$ (g mol ⁻¹) [$\bar{D}$] ^e	$M_{n, Theory}$ (g mol ⁻¹) ^f
a	CHD	20	66	>99	262	790	3,700 [1.14]	4,590
b	BDM	23	82	>99	330	860	2,520 [1.17]	4,620
c	1,6-hexanediol	26	89	>99	354	820	3,260 [1.14]	4,600
d	GEO	20	87	>99	350	1050	4,720 [1.17]	5,470
e	Phthalic acid	30	76	>99	302	600	2,920 [1.13]	4,640

Polymerisation conditions are $[1]:[CTA]:[PA]:[CHO] = 1:20:400:2000$, $V(CHO) = 1$ mL, $[1] = 4.9$ mM, $T = 100$ °C. ^a Conversion determined by ¹H NMR spectroscopy (298 K, 400 MHz, CDCl₃) by comparison of the normalised integrals of PA peaks, at 8.06-8.00 and 7.94-7.88 ppm, vs. equivalent polymer peaks, 7.63-7.52 and 7.44-7.34 ppm. ^b Selectivity for polyester over ether linkage formation. Determined by ¹H NMR spectroscopy (298 K, 400 MHz, CDCl₃) by comparison of polyester peaks (5.22-5.04 ppm) vs. any ether linkages (3.8-3.2 ppm). ^c TON = (conversion of PA (%) / 100 (%)) * ([anhydride] / [1]). ^d TOF = TON/time(h). ^e $M_{n, GPC}$ from GPC at full conversion, in THF at 30 °C, with instrument calibrated using PS standards. ^f $M_{n, Theory} = (TON * M_{n, repeat unit}) / (2 * \text{equiv. (Catalyst)} + \text{equiv. (CTA)}) + M_{n, CTA}$.

In all cases, the catalyst maintains a high activity when [CTA] = 20 equiv. was added to the polymerisation (Table 4.1), with all rates being at least around 50% more active than the catalyst without CTA (TOF = 430 h⁻¹, Table 2.2).¹ The trifunctional macroinitiator, GEO (Table 4.1, d), results in the highest catalytic activity in spite of its bulkiness, likely due to the three hydroxyl groups on the CTA instead of two, as discussed *vide supra*. A high TOF was also maintained in the presence of acid (phthalic acid) demonstrating that this polymerisation system is robust to a range of impurities (Table 4.1, e).

4.3 Reaction Kinetics

4.3.1 Reaction Order in Chain Transfer Agent

To carry out kinetic investigations, the previously reported Al(III)K(I) heterobimetallic complex, with the propylene diimine linker was used (Catalyst **1**, Figure 4.7). The CTA used in these studies was benzyl alcohol (BnOH), a monofunctional alcohol, such that [CTA] = [-hydroxyl groups], which simplifies interpretation of mechanistic results. BnOH loading tolerance tests were carried out, with a catalyst to monomer ratio of 1:400:2000 = [**1**]:[PA]:[CHO] (*V*(CHO) = 1 mL, *T* = 100 °C). The equivalents of BnOH compared to the catalyst were varied from 0 – 50 to cover a wide range of concentrations. These loadings ensure the product's theoretical DP remains over 8, staying in the polymeric regime and avoiding scenarios at very low DP where the reaction initiation may exert too much influence on the overall reaction rate. Removal of aliquots at regular time intervals from the reaction allowed for the PA conversion to be tracked over time.

From the linear correlation between polymer concentration (*i.e.* [PA]₀ – [PA]_t) and time, a rate constant, *k*_{obs}, was obtained from the gradient. This revealed that there was a first-order rate dependence on BnOH, as seen by the clear linear correlation between

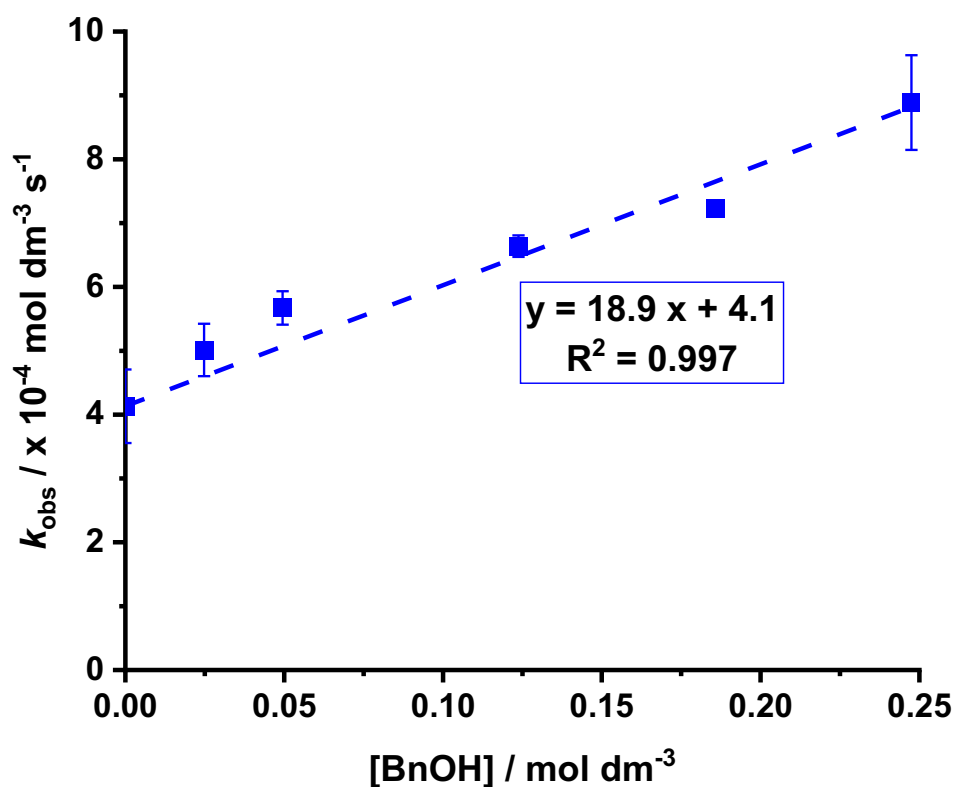


Figure 4.7 Plot of rate of reaction, k_{obs} ($\times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$), vs. $[\text{BnOH}]$ (mol dm^{-3}) for $[\mathbf{1}]:[\text{BnOH}]:[\text{PA}]:[\text{CHO}] = 1:(0-50):400:2000$, $V(\text{CHO}) = 1 \text{ mL}$, $[\mathbf{1}] = 4.94 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 100^\circ \text{C}$.

$[\text{BnOH}]$ and rate (Figure 4.7). No logarithmic plot could be plotted to further confirm this due to the non-zero intercept and significant discrepancies in perceived reaction order when attempting to factor in a y-axis offset. This finding implies a direct influence of the alcohol on the rate determining step.

The y-axis intercept is the rate of reaction in absence of any CTA ($k_{\text{obs}} = 4.1 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$) (Figure 4.7). An additional reaction was carried out using a batch of monomers, with very high purity, to try to determine this rate. This reaction gave a $k_{\text{obs}} = 3.9 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$, slightly lower than the intercept from the trend (Figure 4.8 & 4.9). This lower rate was expected because some additional residual diol in the monomers used for the other tests would also contribute to the rate enhancement (due to different purification).

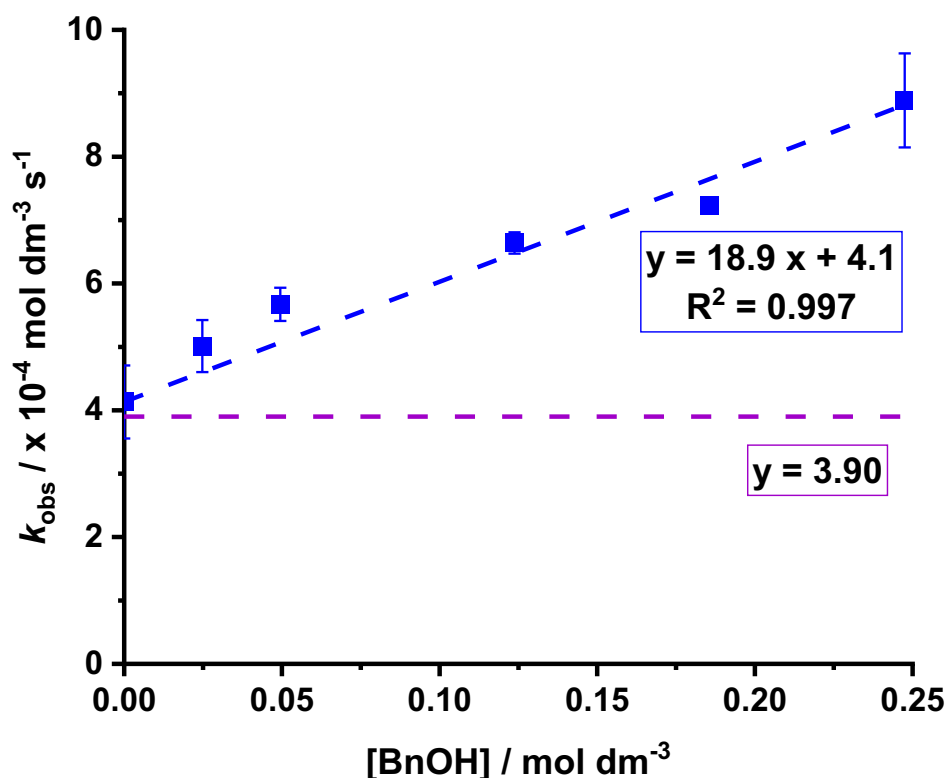


Figure 4.8 Plot of rate of reaction, k_{obs} ($\times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$), vs. $[\text{BnOH}]$ (mol dm^{-3}) as seen in Figure 4.7 (blue) overlaid with baseline rate $k_{\text{obs}} = 3.90 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ from very high purity monomers and no BnOH (purple).

Given the relatively small difference between the two rates, it was assumed that any residual diol present in the monomers is meaningfully lower than the BnOH added to probe the order in CTA, and therefore is not significantly impacting the observed trend. This non-zero rate in the absence of CTA also implies that there is a two-component rate law, one part that is dependent on $[\text{CTA}]$ and another part that is independent of the influence of $[\text{CTA}]$.

It may appear that this result is in contradiction with the trend reported earlier, in Chapter 2, for CHD (Figure 2.12). However, the range over which the CHD CTA studies were conducted went all the way to a 1:1 ratio of $[-\text{OH}]:[\text{anhydride}]$ which results in oligomerisation ($\text{DP} = 1$) rather than polymerisation. These low theoretical DPs mean that the rate reflects better the initiation rather than propagation of the copolymerisation. This composite of initiation and propagation could account for the

plateau in rates observed in Chapter 2 (Figure 2.12), and it reinforces the need to maintain a sufficiently high DP when assessing propagation rates.

4.3.2 Overall Reaction Kinetics

A rate law was then determined in order to probe the mechanism of the polymerisation. The zero order in PA was already confirmed by the linear conversion-time graph (Figure 4.9). It should be noted that the y-axis intercepts of those plots for these polymerisations were not exactly at $[PA]_0 = 1.98 \text{ M}$ (Figure S4.4). This is believed to be due to the same initiation effects caused by the presence of CTA as in the partway addition tests, as discussed *vide supra* in section 4.2.1.1. To avoid these initiation effects skewing the data, linear fits were mapped from the first aliquot onwards.

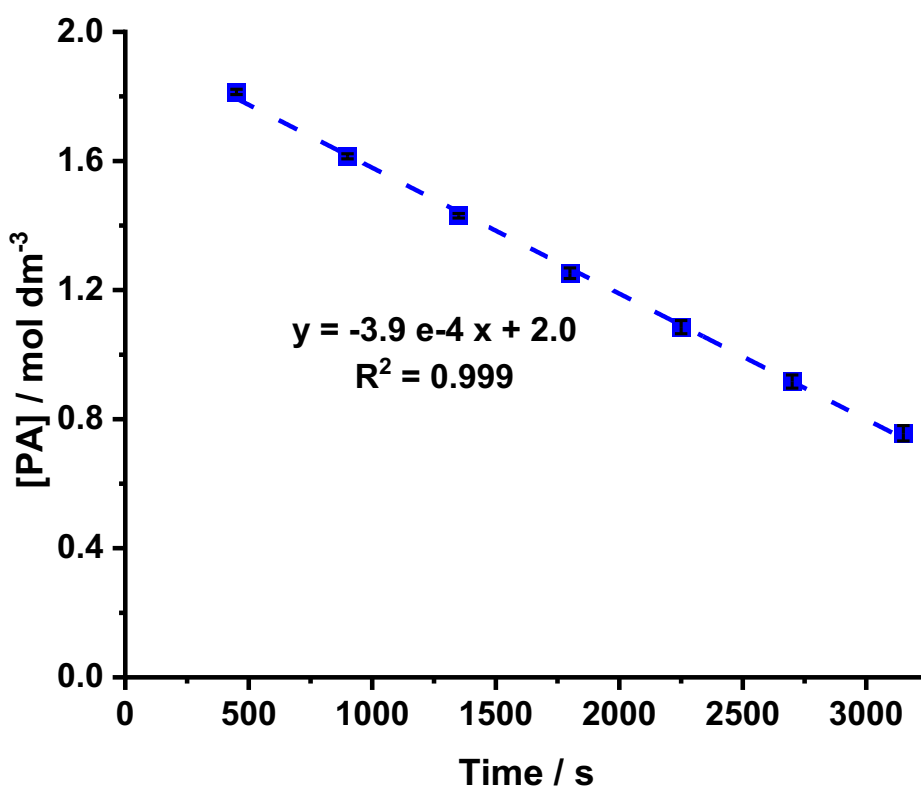


Figure 4.9 Plot of $[PA]$ (mol dm^{-3}) vs. time (s) for $[1]:[PA]:[CHO] = 1:400:2000$, $V(CHO) = 1 \text{ mL}$, $[1] = 4.94 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 100 \text{ }^{\circ}\text{C}$.

Running the polymerisation without excess CHO, by using toluene as the reaction solvent in substitute ($V(\text{CHO})/V(\text{Tol.}) = 0.33$, $[\mathbf{1}]:[\text{BnOH}]:[\text{PA}]:[\text{CHO}] = 1:25:400:500$, $[\mathbf{1}] = 4.94 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 100 \text{ }^{\circ}\text{C}$), led to an exponential decay in the PA conversion time graph. Plotting this as $\ln([\text{CHO}]_t/[\text{CHO}]_0)$ vs. time, gave a linear trend, indicating a first order dependence in CHO (Figure 4.10). These orders are typical for epoxide/anhydride ROCOP, as it is commonly found that epoxide ring opening is rate limiting, and that anhydride ring opening is fast. Indeed, this was found for the analogous Al(III)K(I) catalyst **1.32** with the L_{C3Me2} ligand (a dimethyl propane diamine) that was previously reported by Diment *et al.*⁵

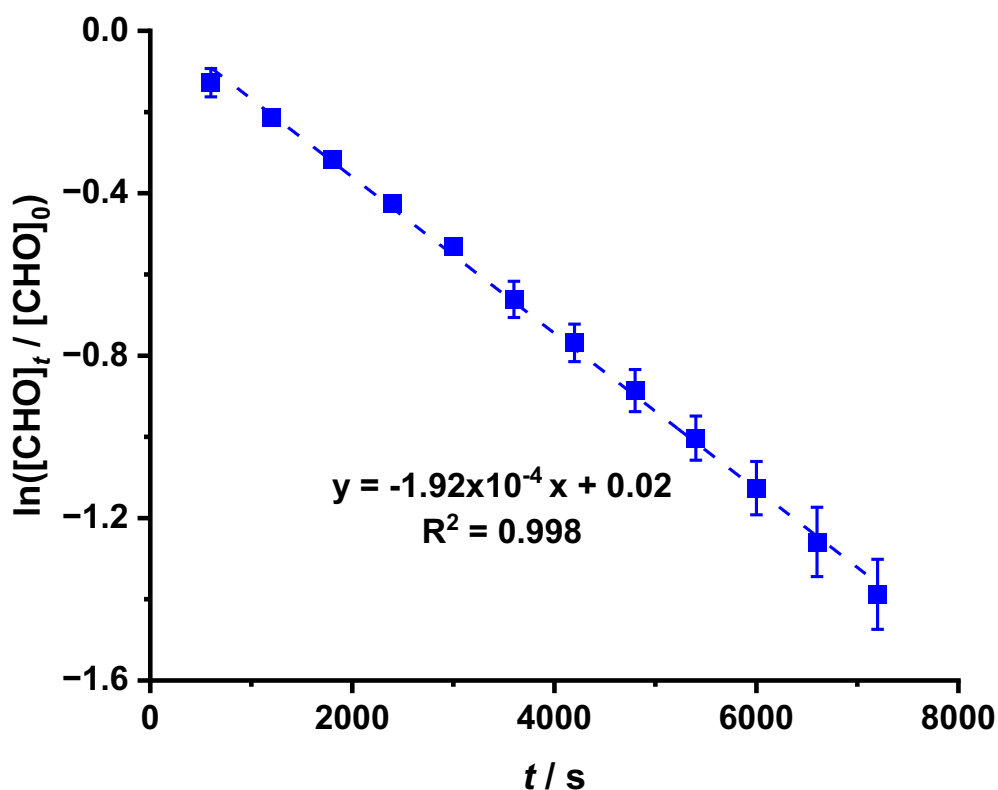


Figure 4.10 Plot of $\ln([\text{CHO}]_t/[\text{CHO}]_0)$ vs. t (s) for $[\mathbf{1}]:[\text{BnOH}]:[\text{PA}]:[\text{CHO}] = 1:25:400:500$, $V(\text{CHO}) = 0.25 \text{ mL}$, $V(\text{Tol}) = 0.75 \text{ mL}$, $[\mathbf{1}] = 4.94 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 100 \text{ }^{\circ}\text{C}$.

Finally, the order in catalyst was found through runs where $[\text{cat}]$ was varied by over more than an order of magnitude ($[\mathbf{1}] = 4.94 \times 10^{-4}$ to $2.47 \times 10^{-2} \text{ mol dm}^{-3}$). This gave a linear trend, when plotting k_{obs} vs. $[\text{cat}]$, passing through the origin (Figure 4.11). This

was exemplified further by plotting $\ln([k_{\text{obs}}])$ vs. $\ln([\text{cat}])$ which again gave a linear correlation, of gradient 1.0 (Figure 4.12). As detailed in 3.3.1, this value is the exponent of $[\text{cat}]$ in the rate law, hence first order.

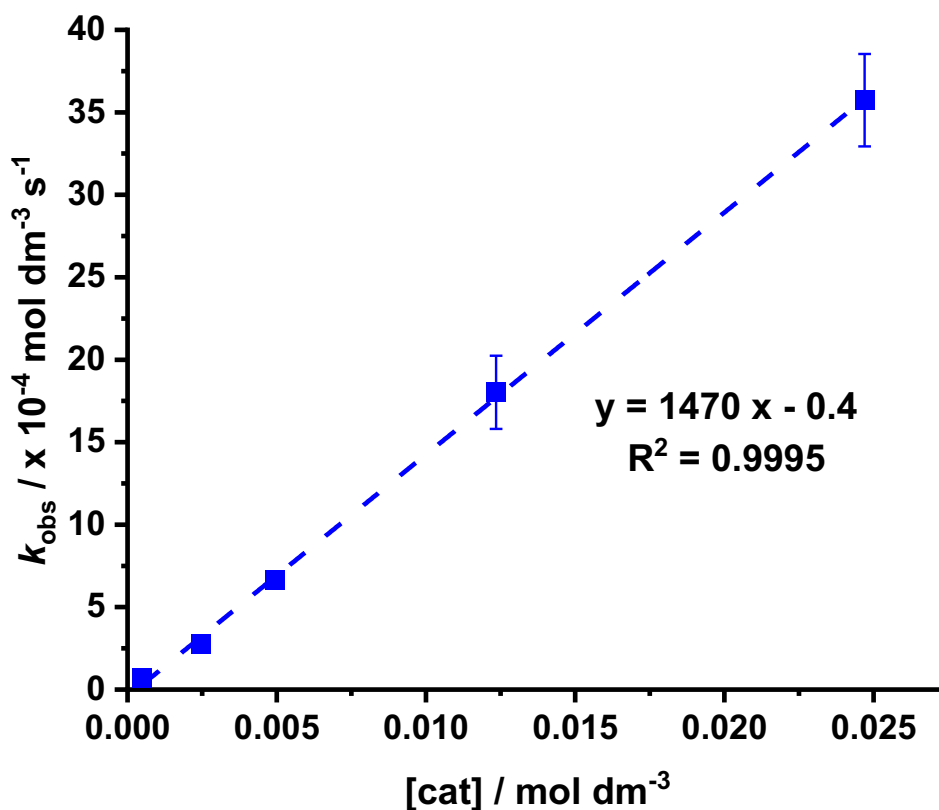


Figure 4.11 Plot of k_{obs} ($\times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$) vs. $[\text{cat}]$ (mol dm^{-3}).
 $[\text{1}]:[\text{BnOH}]:[\text{PA}]:[\text{CHO}] = (0.1\text{-}5):25:400:2000$, $V(\text{CHO}) = 1 \text{ mL}$,
 $[\text{1}] = 4.94 \times 10^{-4} - 2.47 \times 10^{-2} \text{ mol dm}^{-3}$, $T = 100^\circ \text{C}$.

4.3.3 Proposed Rate Equation

The result of these kinetic studies suggests the following rate law for polymer production:

$$\text{Rate} = \frac{d[\text{Polym}]}{dt} = k_1[\text{cat}][\text{CHO}] + k_2[\text{cat}][\text{CHO}][\text{ROH}]$$

Due to the non-zero y-intercept when studying the rate effect of ROH, as discussed before, the rate law has been split into two systems. Here, k_1 is the rate constant for the system governed with just a first order dependence on $[\text{cat}]$ and $[\text{CHO}]$, while k_2 is the

rate constant for the section of the rate law that additionally has a first order rate dependence on [ROH].

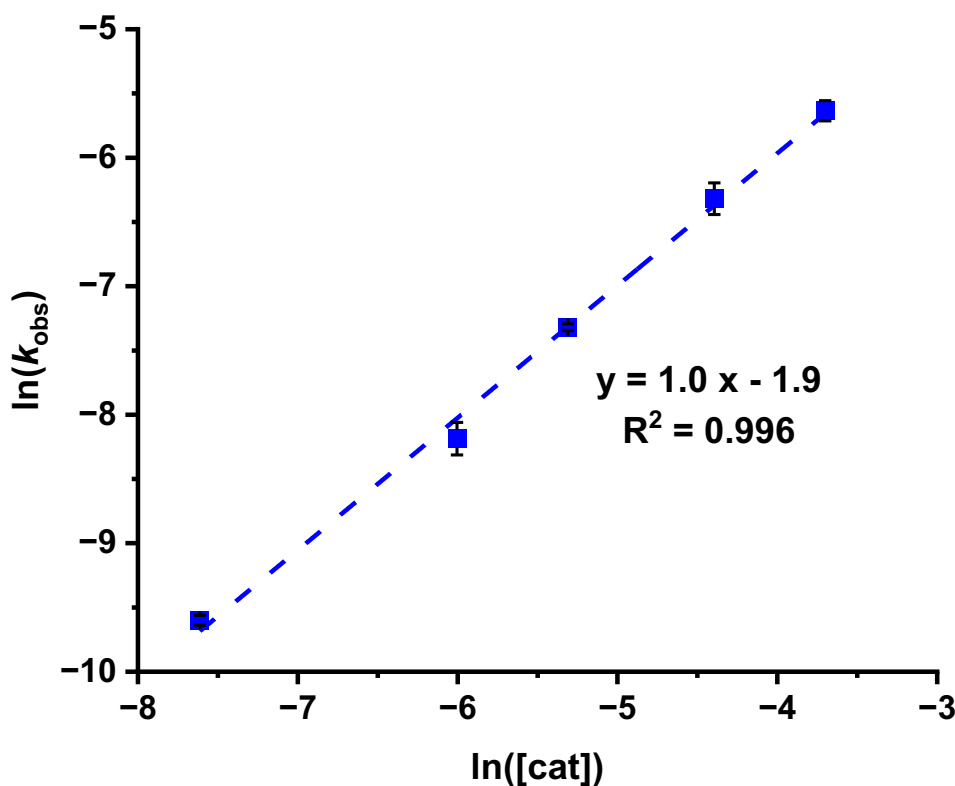


Figure 4.12 Plot of $\ln(k_{\text{obs}})$ vs. $\ln([\text{cat}])$ for $[\mathbf{1}]:[\text{BnOH}]:[\text{PA}]:[\text{CHO}] = (0.1\text{-}5):25:400:2000$, $V(\text{CHO}) = 1 \text{ mL}$, $[\mathbf{1}] = 4.94 \times 10^{-4} - 2.47 \times 10^{-2} \text{ mol dm}^{-3}$, $T = 100 \text{ }^{\circ}\text{C}$.

4.3.4 Kinetic Modelling using Rate Law

To assess whether the above rate law is an appropriate interpretation of the data observed, kinetic modelling using the kinetics software COPASI was carried out.⁶ In order to input the rate law as determined above, the rate constants k_1 and k_2 had to be calculated.

To find k_1 , the reaction rate at $[\text{BnOH}] = 0 \text{ M}$ was used. It should be noted that the rate was taken from the standard kinetics tests run (not the runs from when monomers were purified differently), in order to be consistent with the data from the main study

$([1]:[PA]:[CHO] = 1:400:2000, V(CHO) = 1 \text{ mL}, [1] = 4.94 \times 10^{-3} \text{ mol dm}^{-3}, T = 100 \text{ }^{\circ}\text{C})$.

Rearranging the rate equation, an expression for k_1 can be derived:

$$k_1 = \frac{\text{Rate}}{[\text{cat}][\text{CHO}]}$$

An important consideration has to be made on how $[\text{CHO}]$ is to be treated. The assumption has been made, that the rate can be fitted linearly, due to the zero order rate dependence of $[\text{PA}]$. However, this is not a perfectly linear fit since $[\text{CHO}]$ decreases by a total of 20% when the reaction is run to completion, so $[\text{CHO}]$ varies by a non-negligible amount over the course of the reaction, which may impact the calculated value of k_1 quite significantly. In the region where the kinetics are determined, which is up to around 60 % conversion of PA, the $[\text{CHO}]$ is expected to drop up to 12 %. Were $[\text{CHO}]_0$ used in the above expression, it would lead to an underestimate of the true value of k_1 . Therefore, whilst still applying the reasonable assumption that the excess of CHO is sufficient to interpret the data as linear, $[\text{CHO}]_{95\%}$ ($= 9.39 \text{ M}$) is used to calculate k_1 .

$$k_1 = \frac{\text{Rate}}{[\text{cat}][\text{CHO}]_{95\%}}$$

$$k_1 = 8.91 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

To determine k_2 , the rate dependence on $[\text{ROH}]$ was used, where k_2 is given by:

$$k_2 = \frac{d(\text{Rate})}{d([\text{BnOH}])} \times \frac{1}{[\text{cat}][\text{CHO}]_{95\%}}$$

$$k_2 = 0.0409 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

These two values were then inputted into the model on the software to then run simulations at different $[\text{BnOH}]$ to 50 % PA conversion in order to see how well the data and the model overlapped.

Firstly, the fit at 0eq BnOH was assessed. Observing [PA] vs. t , there is a very close agreement between the model and the experimental values (Figure 4.13). Comparing the rates of reaction, $k_{\text{obs, data}} = 4.13 \pm 0.58 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ and $k_{\text{obs, model}} = 4.10 \pm 0.03 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. This is a clear indicator that the rate constant was determined correctly, and that the rate law used in the model correlates well with the data when there is no BnOH in the reaction mixture.

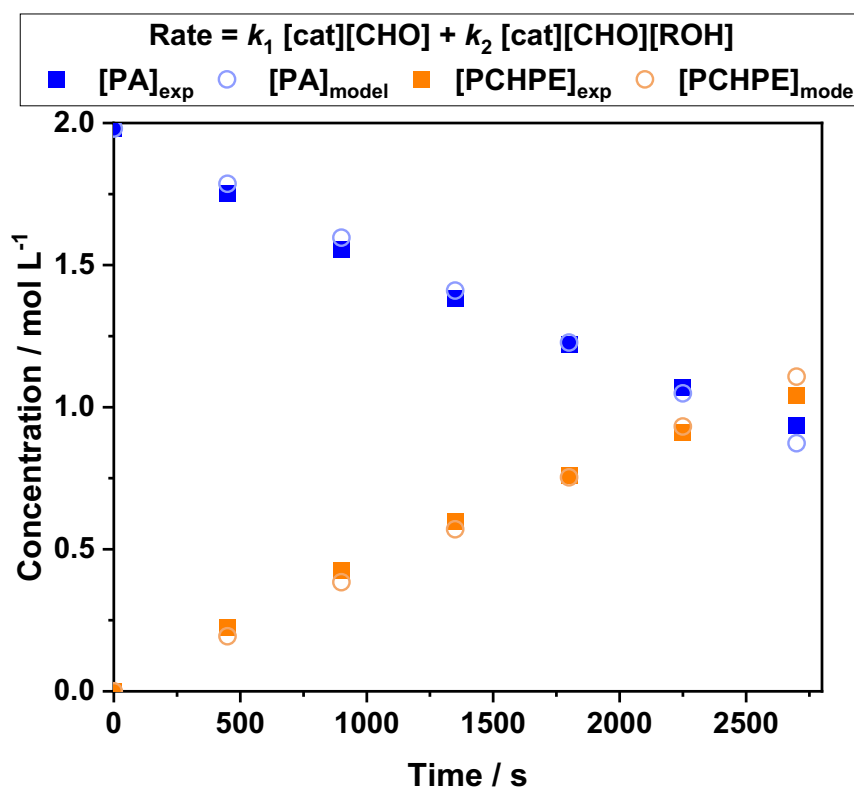


Figure 4.13 Plot of concentration (mol L^{-1}) against time (s) for the reaction [1]:[PA]:[CHO] = 1:400:2000, $V(\text{CHO}) = 1 \text{ mL}$, $[1] = 4.94 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 100^\circ \text{C}$. [PA] experimental (blue square), [PA] COPASI model (blue circle), [PCHPE] experimental (orange square), [PCHPE] COPASI model (orange circle).

When including BnOH into the model, the rapid initiation (*vide supra*) led to an offset between the conversions calculated by the model and the conversions obtained experimentally (Figure S4.5). This is because the model does not account for the initiation period, since this is not measured in the kinetic studies. To avoid this offset, $t = 0$ on the COPASI model was set at the conversion of the first aliquot (~10% conversion) because by then the system is in the polymerisation regime. Plotting this

gives a close fit between the model and the experimental data, such as in Figure 4.14 for the experiment with 25 equiv. BnOH.

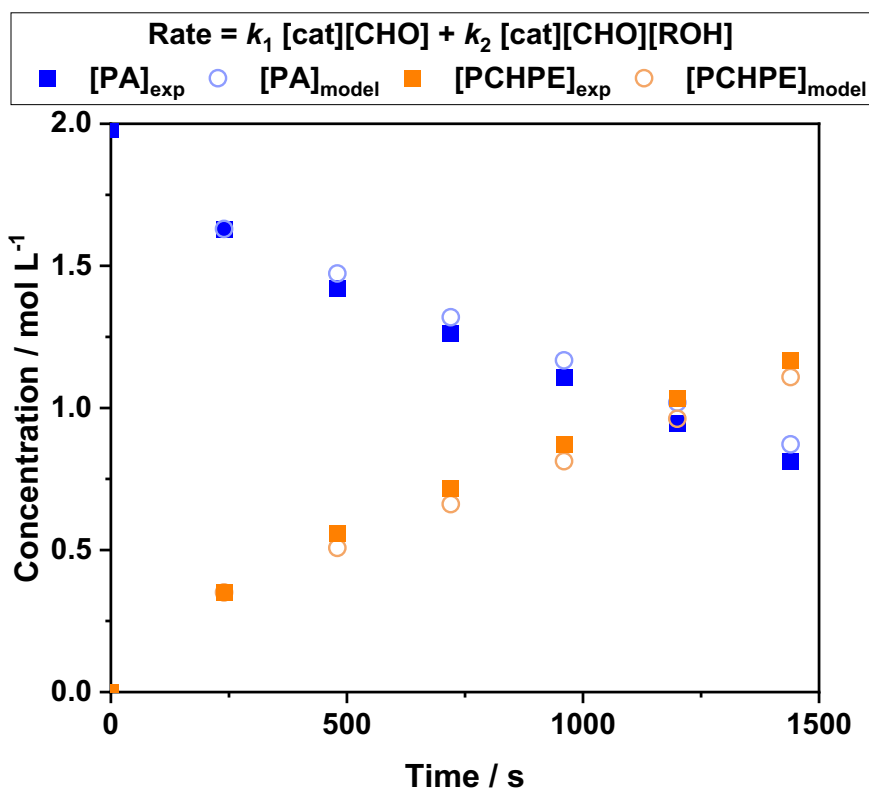


Figure 4.14 Plot of concentration (mol L⁻¹) against time (s) for the reaction [1]:[BnOH]:[PA]:[CHO] = 1:25:400:2000, $V(\text{CHO}) = 1 \text{ mL}$, $[1] = 4.94 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 100^\circ \text{C}$. [PA] experimental (blue square), [PA] COPASI model (blue circle), [PCHPE] experimental (orange square), [PCHPE] COPASI model (orange circle).

Notably, when comparing the experimentally determined rates and those from the model, there is close agreement again ($k_{\text{obs, data}} = 6.64 \pm 0.17 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$; $k_{\text{obs, model}} = 6.49 \pm 0.04 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$). When the rate of polymerisation is modelled for all [BnOH], the same linear rate dependence is observed (Figure 4.15. Table S4.1). Fitting this to a straight line, the gradient is 18.8 s^{-1} with an intercept of $4.15 \text{ mol dm}^{-3} \text{ s}^{-1}$, both of which are within error of the values obtained from the experimental runs (gradient = $18.9 \pm 1.1 \text{ s}^{-1}$; intercept = $4.13 \pm 0.22 \text{ mol dm}^{-3} \text{ s}^{-1}$). This would suggest that the two-component rate law put forward is a good representation of the experimental data.

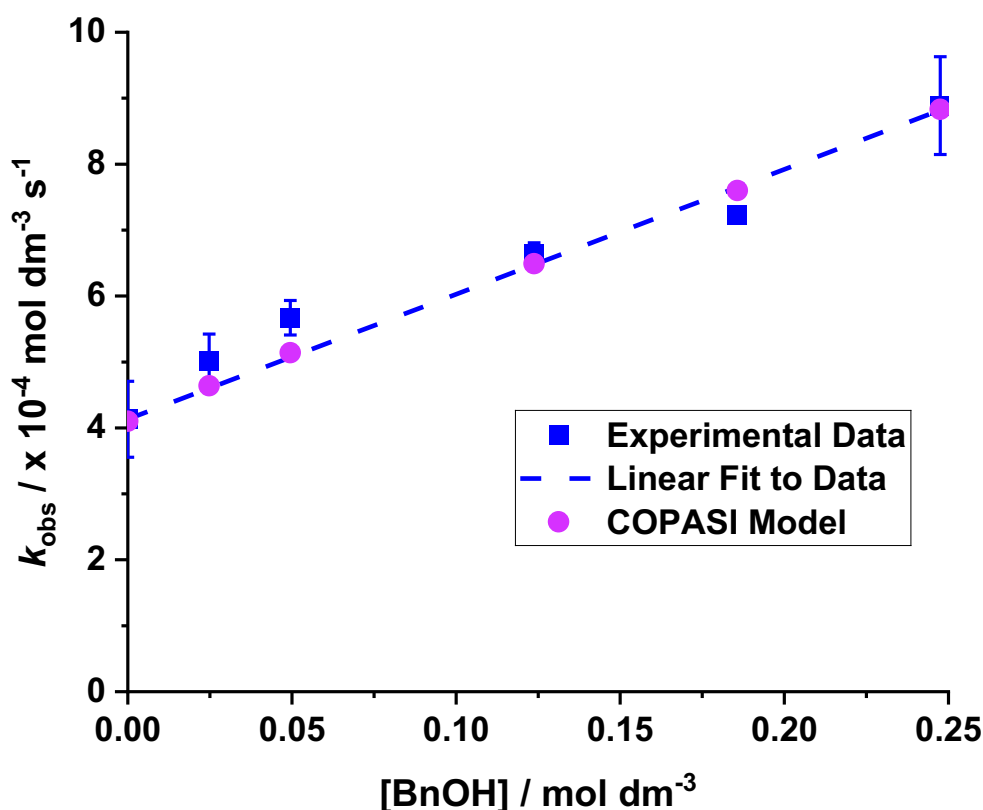


Figure 4.15 Plot of rate of reaction, k_{obs} ($\times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$), against $[\text{BnOH}]$ (mol dm^{-3}) as seen in Figure 4.7 (blue) overlaid with rates obtained by COPASI kinetic modelling (purple).

4.3.5 Proposed Reaction Mechanism

This two-component rate law implies that there are two reaction cycles in the mechanism (Figure 4.16). There is one standard cycle, pathway 1, with the usual sequence of fast anhydride and slow epoxide insertion, linked to k_1 . However, as the concentration of CTA increases, an alternative, more rapid reaction pathway is realised. In the rate determining step, the epoxide, catalyst and the alcohol come together and provide a faster alternative reaction cycle, pathway 2, linked to k_2 . It should be noted that the alcohol CTA reacts and polymerises and so the hydroxyl functional groups enacting this rate enhancement are not of the alcohol CTA but rather the hydroxyl polymer chain ends that are now in excess (due to reactions with the CTA present) (Figure 4.16).

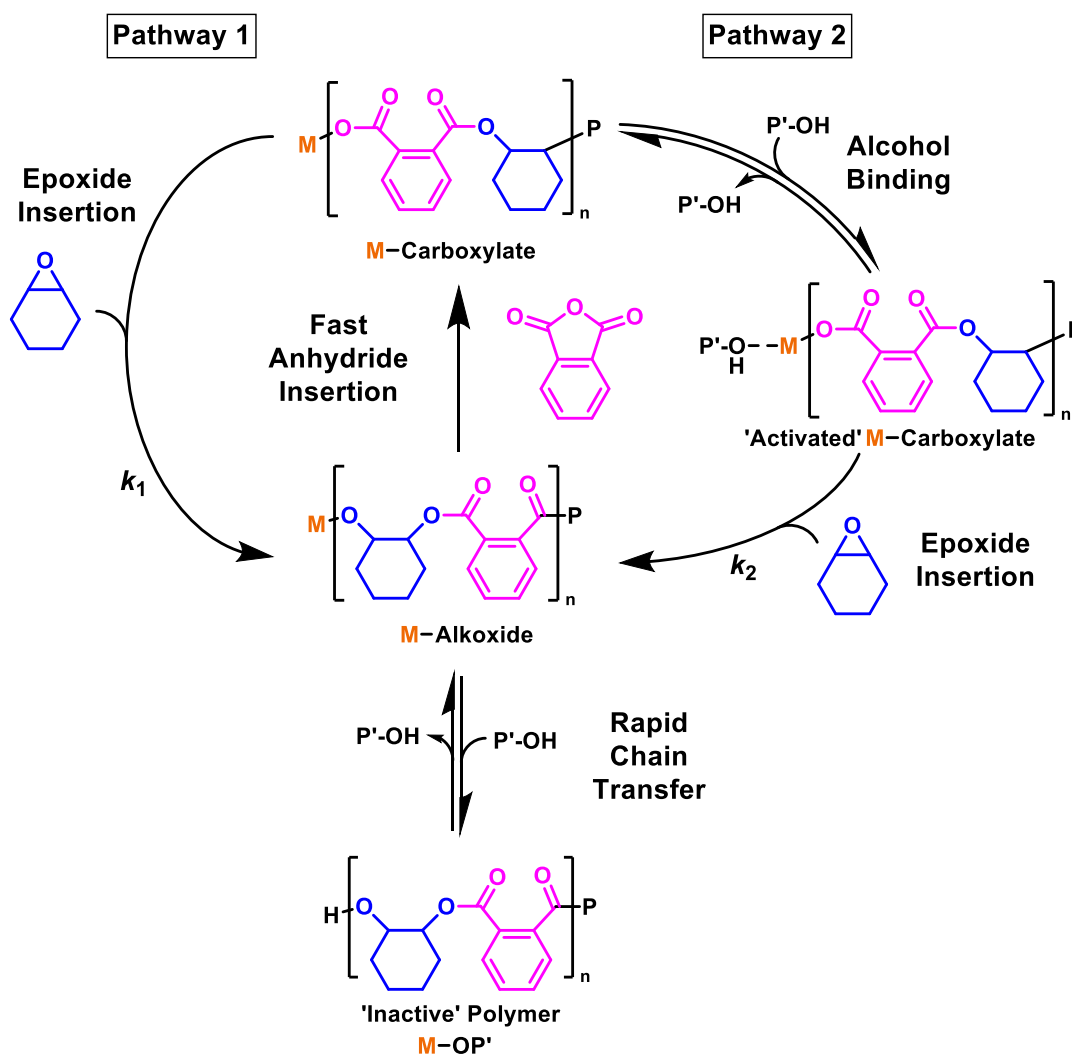


Figure 4.16 Proposed mechanism of PA/CHO ROCOP catalysed by **1** with CTA showing two pathways (1 & 2) where $k_2 > k_1$.

4.3.6 Proposed Methods for Rate Enhancement in Transition State

The alcohol's exact involvement in the rate determining step is still unclear after these tests and warrants further exploration. There are two likely hypotheses. One potential pathway is where the electrophile, the oxygen from the epoxide that is coordinated to Al(III), is activated by hydrogen bonding to the chain end alcohol group (Figure 4.17a). Alternatively, the hydroxyl chain ends could coordinate to the K(I), activating the carboxylate for nucleophilic attack on the epoxide (Figure 4.17b). It is also entirely possible that both interactions are occurring at the same time.

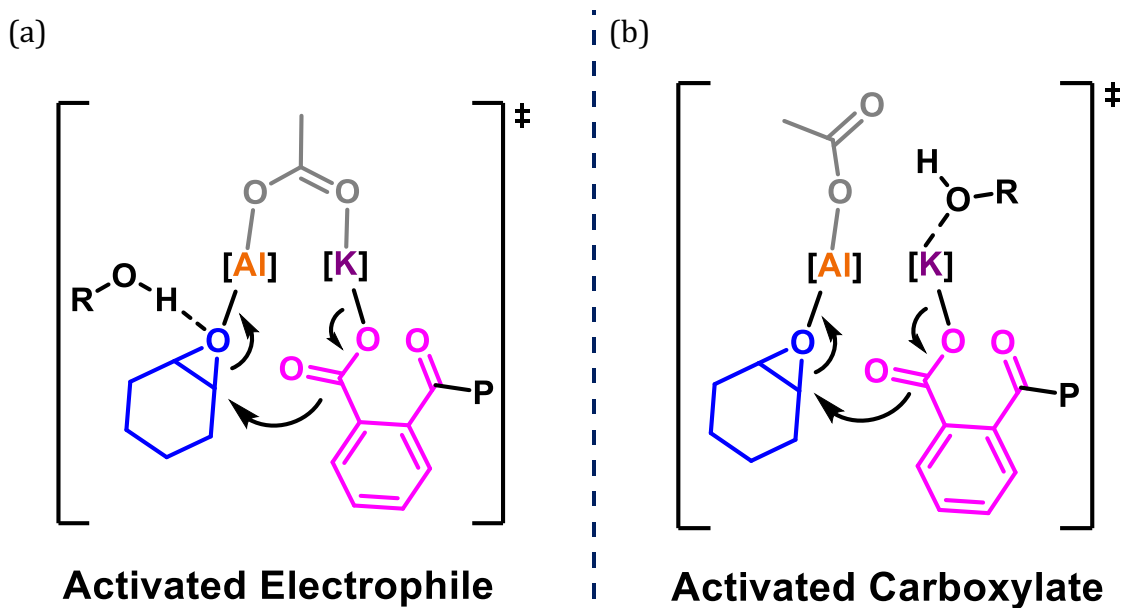


Figure 4.17 Diagrams indicating possible interactions of alcohol in the transition state that could lower the energy barrier for epoxide ring opening. (a) Hydrogen bonding to coordinated epoxide. (b) Coordination of O to K(I).

4.4 Diagnostic Tests into the Nature of Alcohol in Rate

Determining Steps

4.4.1 Kinetic Isotope Effect

Kinetic Isotope Effect (K.I.E) studies were carried out in order to investigate any possible role of the hydroxyl proton in the rate determining step (r.d.s). To achieve this, the activity of PA/CHO ROCOP with the addition of deuterated benzyl alcohol (BnOD) was compared to the previous kinetic analysis using protonated BnOH ([1]:[BnOH/D]:[PA]:[CHO] = 1:25:400:2000, $V(\text{CHO}) = 1 \text{ mL}$, $T = 100 \text{ }^{\circ}\text{C}$) (Table 4.2, Figure 4.18).

Table 4.2 Rate, k_{obs} ($\times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$), and activity, TOF (h^{-1}), for BnOH and BnOD for [1]:[BnOH/D]:[PA]:[CHO] = 1:25:400:2000, $T = 100^\circ \text{C}$, $V(\text{CHO}) = 1 \text{ mL}$.

CTA	$k_{\text{obs}} / \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$	TOF / h^{-1}
BnOH	5.3 ± 0.4	384 ± 26
BnOD	4.2 ± 0.1	307 ± 27

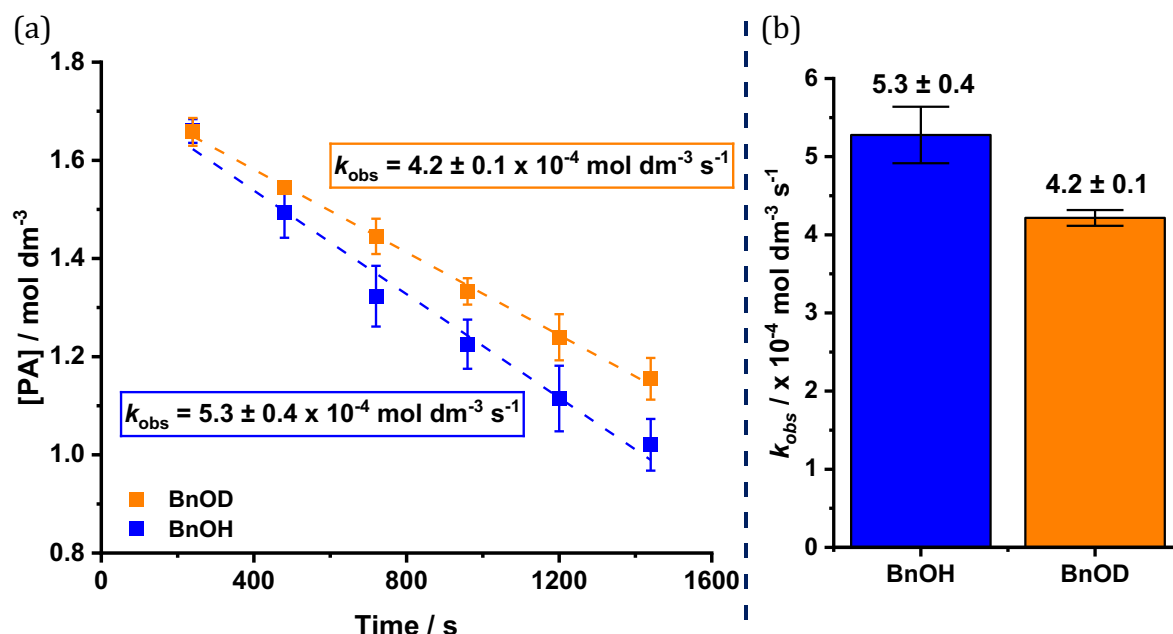


Figure 4.18 (a) Graph of [PA] (mol dm^{-3}) against time (s) for BnOH and BnOD for [1]:[BnOH/D]:[PA]:[CHO] = 1:25:400:2000, $T = 100^\circ \text{C}$, $V(\text{CHO}) = 1 \text{ mL}$. (b) Graph comparing rate of reaction, k_{obs} ($\times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$).

$$\frac{k_H}{k_D} = 1.3 \pm 0.2$$

This revealed that using BnOD as a CTA resulted in a slight decrease in reaction rate, as shown by a small positive K.I.E. = 1.3 ± 0.2 (Figure 4.18 & Table 4.2). Firstly, this is clear confirmation that no proton transfer is taking place in the r.d.s, since the value is much lower than what would be expected for a primary K.I.E (up to 7 or 8). This is in agreement with the rate law and proposed catalytic mechanisms. The cause of the small K.I.E. isn't immediately obvious, but its magnitude falls within the realms of a secondary K.I.E.

In the rate determining step, when the carboxylate attacks the coordinated epoxide, there is the flow of an electron pair from the K(I)-carboxylate to the newly-formed Al(III)-alkoxide. This may lead to a lower electron density around the K(I). Were the alcohol coordinated to the K(I) during this transformation (Figure 4.17b), it could result in a subtle change in the nature of its coordination to the K(I) which reciprocally could weaken the adjacent O-H(D) bond. This would, in effect, be a β secondary K.I.E: the proton is bonded to an atom (the O) that is adjacent to the atom where the bond is being broken (the K(I)). A K.I.E > 1, as measured here, would require the O-H(D) bond to be weakened by this transformation, which seems to be in agreement with the proposed transformation.

However, in the activated electrophile hypothesis (Figure 4.17a), where the alcohol acts as an H-bond donor to the coordinated epoxide, one might expect a similar K.I.E. to be observed. H-bonding is weaker for [O—D- - -O] compared with [O—H- - -O], and thus any potential rate enhancement caused by hydrogen bonding would be reduced in the deuterated species.⁷ The expected magnitude of this is hard to know for sure, but the effect would be slight.

Alternatively, this isotopic effect could be attributed to a Binding Isotope Effect.⁸ In the proposed mechanism, there exists an equilibrium where the alcohol binds to the complex to then activate it for epoxide ring-opening. Deuterating the alcohol could have an impact on the equilibrium constant governing this binding which would have an effect on the resultant rate of reaction. This very subtle effect has a range of magnitudes that covers this observed K.I.E, therefore this could be an alternative explanation.⁸

From this it is clear that both proposed transition states could account for the observed K.I.E behaviour, but it does not offer insights differentiating the two hypotheses.

4.4.2 Binding Studies

In order to determine if there was any notable interaction between an alcohol functionality and the catalyst, an NMR titration experiment was undertaken. In the experiment, alcohol (BnOH in this case), in a stock solution of CDCl₃, was incrementally added to a stock solution of **1**, also in CDCl₃, up to 400 equiv. relative to **1** (Figure 4.19). The ¹H NMR proton shifts were monitored for changes (Figure 4.20 & S4.6).

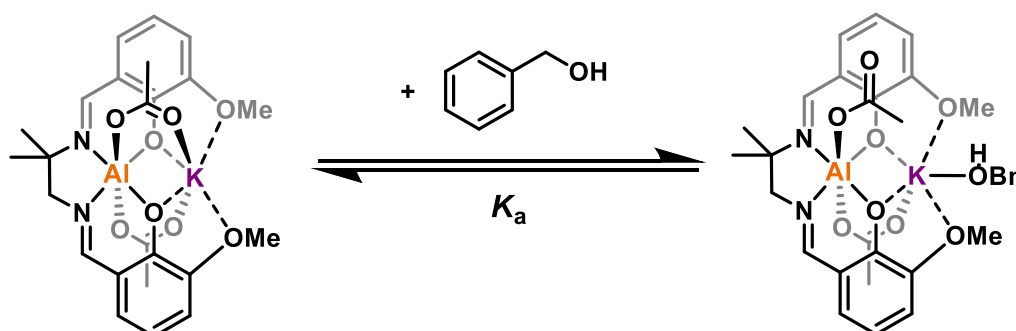


Figure 4.19 Equilibrium between **1** and **1**•BnOH.

$$K_a = \frac{[\text{cat} \cdot \text{BnOH}]}{[\text{BnOH}][\text{cat}]}$$

Figure 4.20 shows the overlaid ¹H NMR spectra at the different loadings of BnOH. It clearly shows that three proton environments on the catalyst shift; protons g, l, f & k experience shifts to higher values, whilst the two b protons shift to lower values. The protons that shift upwards are closest to the K(I), and this shift may represent an increase in deshielding, which could indicate that the BnOH is coordinating to the K(I). This would suggest a similar binding of ROH (R = polymer chain) could be taking place in the polymerisation mixture. It is then possible for the rate enhancement to occur via an activated carboxylate group, by ROH binding to K(I).

Quantifying these changes in chemical shift, along with the relative concentrations of both **1** (host) and BnOH (guest), a 1:1 stoichiometric association constant (K_a) was

calculated using the Bindfit program (Figure 4.21, Table S4.2).⁹⁻¹¹ The shifts of protons g & l, representing the -OMe protons close to the K(I), had a close agreement with the model fitting with low error and the 1:1 stoichiometric $K_a = 1.02 \text{ M}^{-1} (\pm 6.7 \%)$ (Figure 4.21). The value of this K_a indicates that a reasonable proportion of the catalyst would be bound by an alcohol at the loadings of the polymerisation reactions currently being carried out (5-50 equiv.).

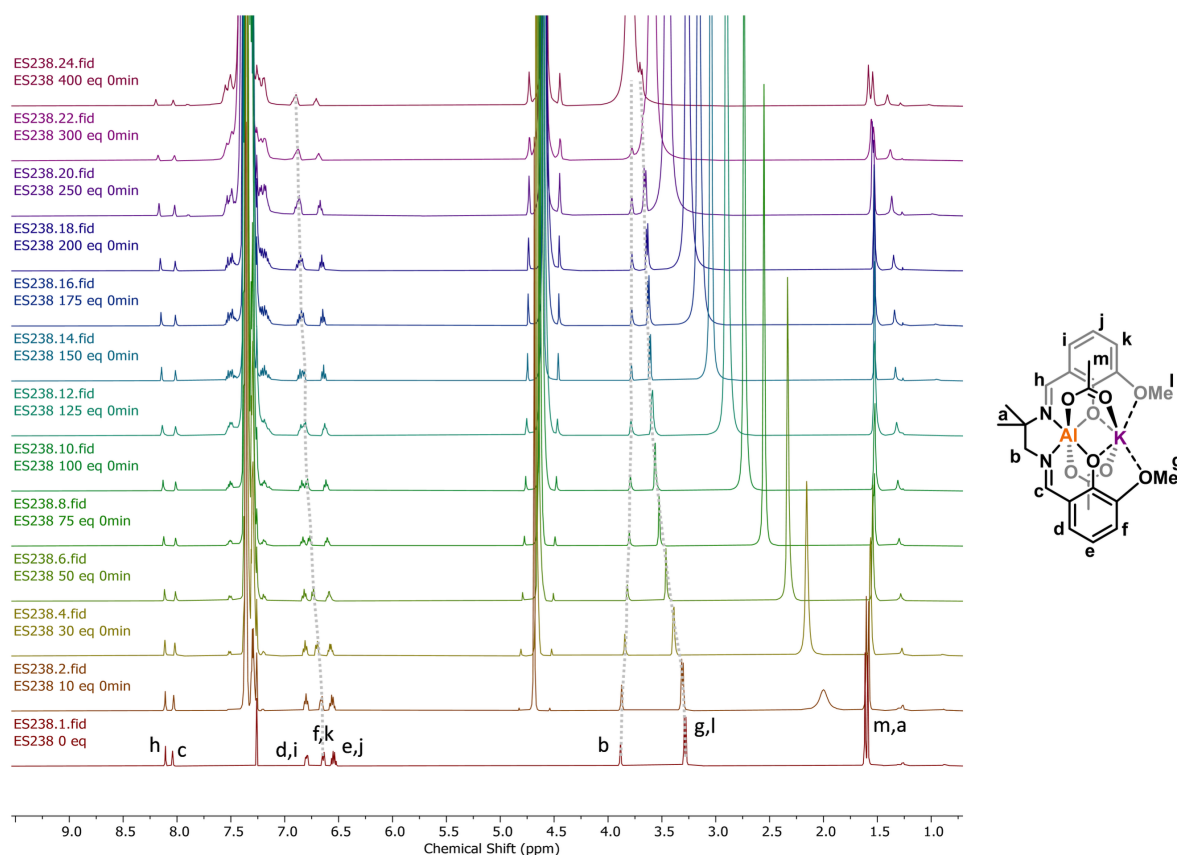


Figure 4.20 ^1H NMR spectra ($\text{CDCl}_3(\#)$, 298 K, 400 MHz) of **1** with increasing equiv of BnOH (0 – 400). Protons f, k and g, l shift upwards while b shifts down.

Using the plot, under the current conditions (25 °C in CDCl_3), 32% of the catalyst is expected to be bound by the alcohol if 50 equiv. is added (Figure 4.22). From just this study, it is hard to know how close this ratio is to what it would be under the reaction conditions, with a different solvent, higher temperature and different binding species. Bulkier binding species and higher temperatures may lead to a lowering of the proportion

that is bound. Overall though, the kinetic data reported earlier (in Section 4.3.1) follows a similar trend shown in the Mole fractions vs. Equivalent total $[G]/[H]$ plot (Figure 4.22) for the range that was tested. If this binding is truly the leading cause of the rate enhancement with CTA (Figure 4.17a), then it may mean that the observed rate dependence on $[ROH]$ is actually pseudo first order and that towards higher ROH loadings it follows a saturation kinetics trend, with the rate levelling off. It could be that this is what is being observed with CHD in Chapter 2, where this type of trend is seen (Figure 2.12) but it is still sensible to be cautious of over-interpreting that data due to the low DPs of the oligomers being produced. To properly probe this, kinetics at much lower catalyst loadings relative to PA and BnOH would have to be carried out, but it would, of course, impact rates.

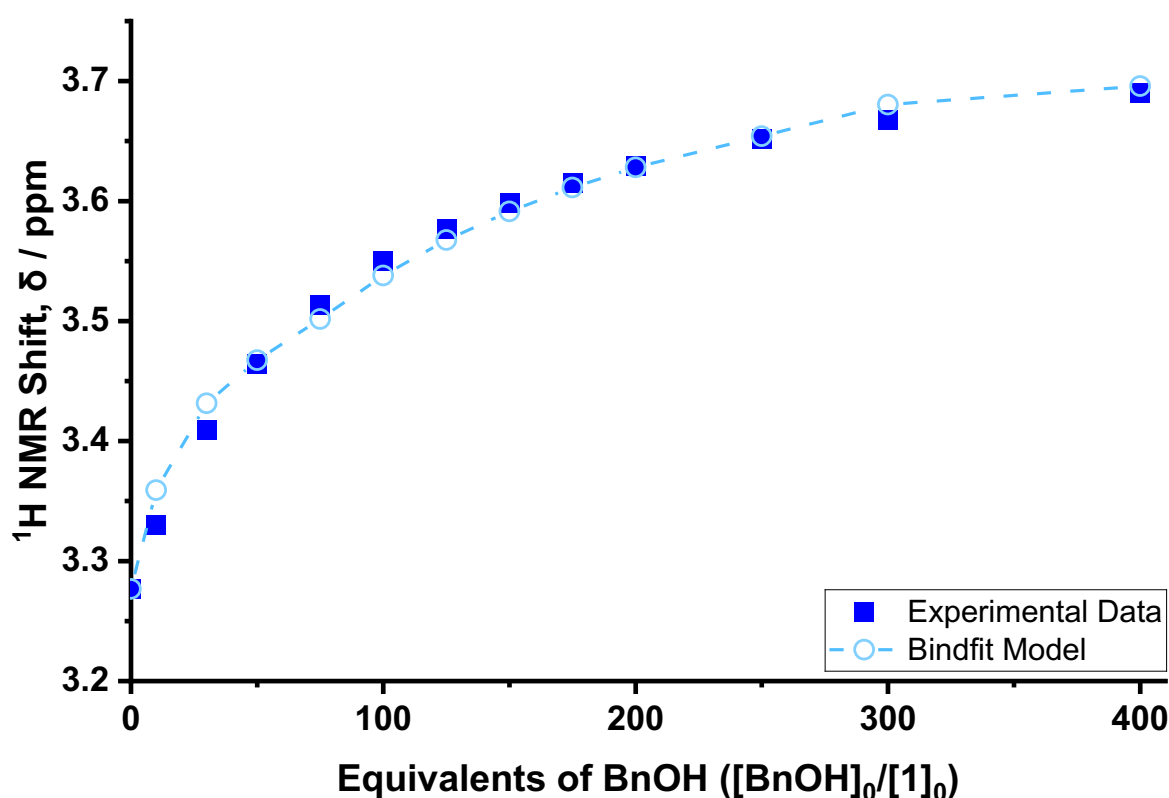


Figure 4.21 Plot of NMR shift, δ , of proton g (ppm) against equivalents of BnOH added ($[BnOH]/[1]$) for binding studies. Experimental data (dark blue points) and calculated fit (light blue circles with straight dashed lines between points). <http://app.supramolecular.org/bindfit/view/601a3cbf-3fdb-4e33-a93a-6a762d99b3d1>

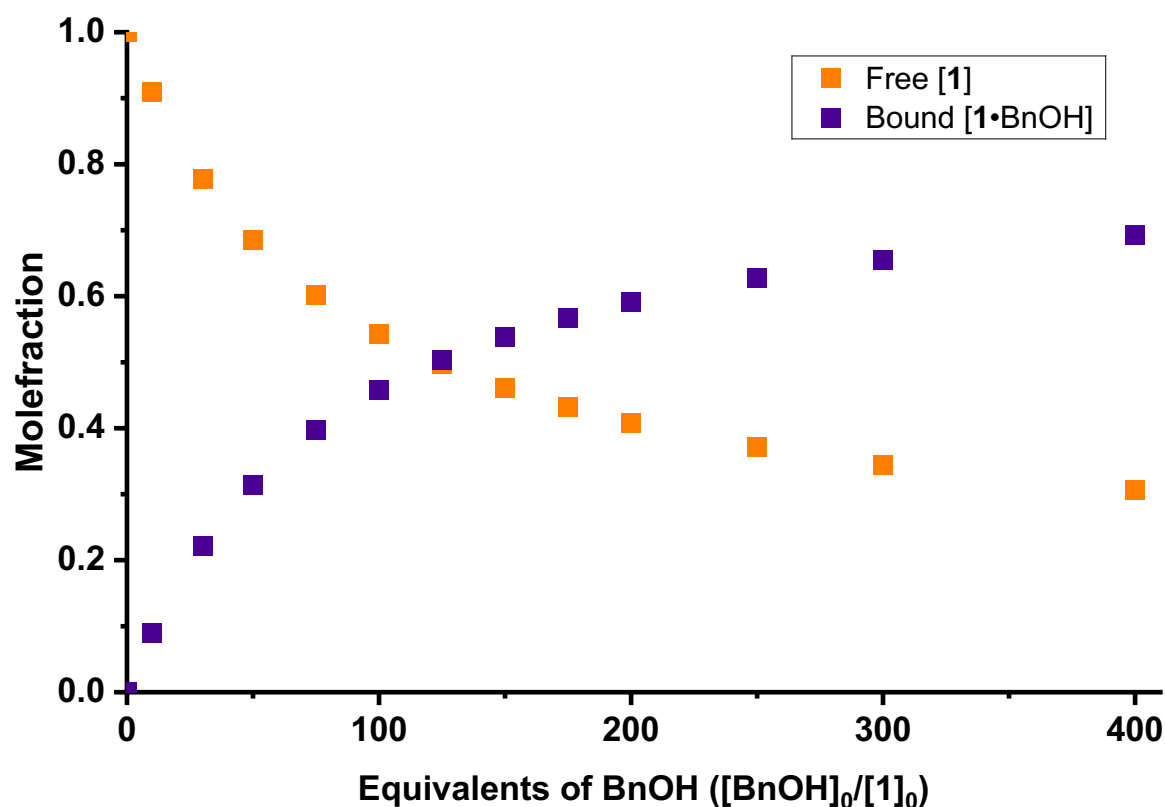


Figure 4.22 Plot of estimated mole fraction of bound vs. unbound of **1** ($[1]/([1]+[1\bullet\text{BnOH}])$, orange & $[1\bullet\text{BnOH}]/([1]+[1\bullet\text{BnOH}])$, purple) for varying equivalents of BnOH ($[\text{BnOH}]/[1]$). Calculated by Bindfit.

4.4.3 X-ray Crystallography of Proposed Intermediates

An X-ray diffraction experiment was conducted on crystals that were formed when **1** was dissolved along with excess BnOH, in CDCl_3 , and layered with hexane (Figure 4.23 & Table 4.3 & S4.3). The structure presented here was solved by Dr Nora Janssen (University of Oxford). Figure 4.23 shows the molecular structure, revealing that water was in fact bound to catalyst **1**. The species is a monomeric complex, as opposed to the solid state structure of **1** that was an extended polymer. The coordination of water at the K(I) centre is in agreement with the interpretations from the ^1H NMR binding studies which suggested that BnOH coordinates to the K(I) of complex **1** as well.

A solid-state structure is no perfect mimic of a solution state reaction intermediate, but comparison between the structures is still worthwhile. A particularly important bond

length to compare is that between K(1)-O(2). This mimics the bond between K(I) and the bound carboxylate in the hypothetical transition state. In complex **1** K(1)-O(2) = 2.6641(18) Å, but in complex **1**•H₂O K(1)-O(2) = 2.7088(18) Å (ref). This indicates that the coordination of water weakens this bond. Translating the finding to the proposed transition state, it may be that alcohol coordination to the K(I) weakens the K(I)-O(carboxylate) bond, thus “activating” the carboxylate, priming it to attack an adjacent coordinated epoxide.

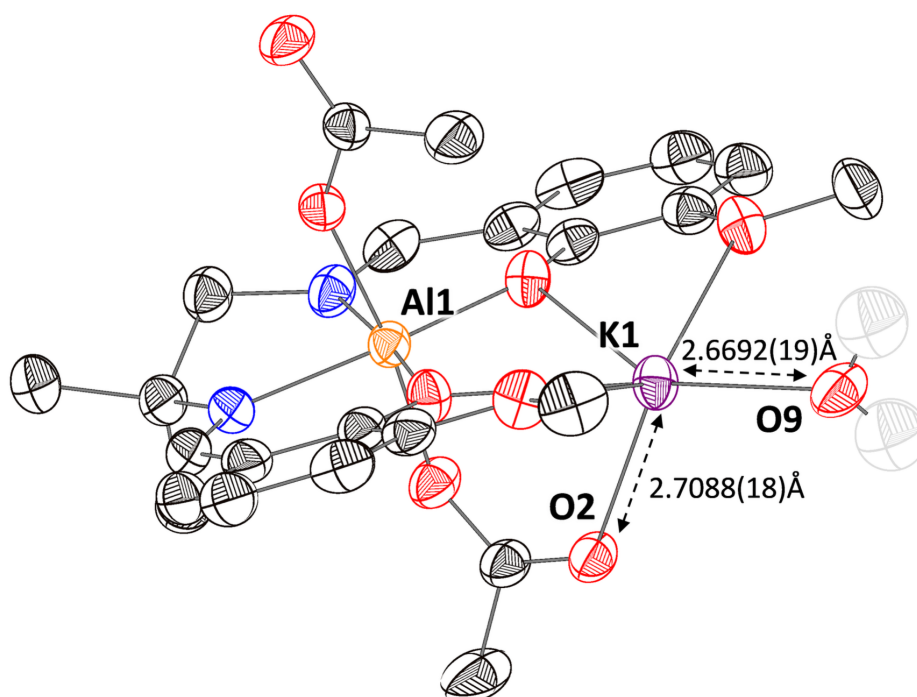


Figure 4.23 Molecular structure of complex **1** with H₂O bound at K1, obtained from X-ray diffraction experiments, with thermal ellipsoids presented at 50% probability and all H atoms aside from on water omitted for clarity (atom colour scheme: Al (orange), K (purple), O (red), N (blue), C (black), H (light grey)).

Table 4.3 Selected bond lengths for [**1**•H₂O]

Bond	Bond Length (Å)
K(1)-Al(1)	3.5580(8)
K(1)-O(2)	2.7088(18)
K(1)-O(9)	2.6692(19)
Al(1)-O(1)	1.9226(18)
Al(1)-O(3)	1.9146(17)
O(1)-C(1)	1.279(3)
O(2)-C(1)	1.235(3)
O(3)-C(3)	1.270(3)
O(4)-C(3)	1.238(3)

4.5 Conclusions and Outlook

In this Chapter, a range of approaches were taken to try to understand the remarkable phenomenon of catalytic rate enhancement with addition of alcohols or other protic species. This phenomenon was shown to have a chemical origin, as seen by the immediate change in rate upon addition of BnOH midway through a reaction. Testing a series of chain transfer agents revealed that rate scales with the amount of hydroxyl functionality. Also, the rate enhancement was observed using a variety of -OH containing molecules as CTAs.

Next, a full kinetic investigation into the orders of reaction for all components in the reaction mechanism was carried out and a complete rate law was established. The rate law revealed that there is a first order dependence on CTA in the reaction, as part of a dual cycle rate law.

The kinetic isotope influence was 1.3 – consistent with a secondary effect. Binding studies and an X-ray crystal structure showing a complex with water coordinated to K(I) support the rate acceleration from the K-carboxylate being activated by alcohol coordination at K(I).

In two recent studies, investigating Co(III)M(I/II) complexes for both epoxide/CO₂ ROCOP and cyclic ester ROP, it was revealed that the lower the Lewis acidity of the s-block metal, the faster the polymerisation.^{12, 13} The rationale was that, for the lower Lewis acidic metals, there was a weaker M(I/II)-carboxylate (or carbonate) bond. As mentioned in Section 3.2.2, a rate enhancement (and improvement in selectivity) was observed for an Al(III)K(I) catalyst (**2**) for CHO/CO₂ ROCOP with CTA. Therefore, with the same trends and a robust rationale, it seems very plausible that the hydroxyl functional groups present in the polymerisation, due to the addition of CTA, cause the observed rate

enhancement due to coordination to the K(I) which weakens the K(I)-carboxylate bond, promoting attack on the activated epoxide bound to the adjacent Al(III).

Overall, this work contributes to the understanding of how epoxide/anhydride ROCOP reaction rate is influenced by alcohols, suggesting a plausible method for rate enhancement. It is hoped that this work could facilitate the intentional design of other highly CTA tolerant catalysts and inspire investigations into the impact of CTA on other ROCOP and ROP polymerisations.

4.6 References

- (1) Shellard, E. J. K.; Diment, W. T.; Resendiz-Lara, D. A.; Fiorentini, F.; Gregory, G. L.; Williams, C. K. Al(III)/K(I) Heterodinuclear Polymerization Catalysts Showing Fast Rates and High Selectivity for Polyester Polyols. *ACS Catal.* **2024**, *14* (3), 1363–1374. DOI: 10.1021/acscatal.3c05712.
- (2) Wood, Z. A.; Assefa, M. K.; Fieser, M. E. Simple yttrium salts as highly active and controlled catalysts for the atom-efficient synthesis of high molecular weight polyesters. *Chem. Sci.* **2022**, *13* (35), 10437–10447. DOI: 10.1039/d2sc02745c.
- (3) Lidston, C. A. L.; Abel, B. A.; Coates, G. W. Bifunctional Catalysis Prevents Inhibition in Reversible-Deactivation Ring-Opening Copolymerizations of Epoxides and Cyclic Anhydrides. *J. Am. Chem. Soc.* **2020**, *142* (47), 20161–20169. DOI: 10.1021/jacs.0c10014.
- (4) Chen, X.-L.; Wang, B.; Pan, L.; Li, Y.-S. Synthesis of Unsaturated (Co)polyesters from Ring-Opening Copolymerization by Aluminum Bipyridine Bisphenolate Complexes with Improved Protonic Impurities Tolerance. *Macromol.* **2022**, *55* (9), 3502–3512. DOI: 10.1021/acs.macromol.2c00034.
- (5) Diment, W. T.; Gregory, G. L.; Kerr, R. W. F.; Phanopoulos, A.; Buchard, A.; Williams, C. K. Catalytic Synergy Using Al(III) and Group 1 Metals to Accelerate Epoxide and Anhydride Ring-Opening Copolymerizations. *ACS Catal.* **2021**, *11* (20), 12532–12542. DOI: 10.1021/acscatal.1c04020.
- (6) Hoops, S.; Sahle, S.; Gauges, R.; Lee, C.; Pahle, J.; Simus, N.; Singhal, M.; Xu, L.; Mendes, P.; Kummer, U. COPASI—a COMplex PATHway SIMulator. *Bioinformatics* **2006**, *22* (24), 3067–3074. DOI: 10.1093/bioinformatics/btl485.
- (7) Rao, C. N. R. Effect of deuteration on hydrogen bonds. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71* (0). DOI: 10.1039/f19757100980.

- (8) Świderek, K.; Paneth, P. Binding Isotope Effects. *Chem. Rev.* **2013**, *113* (10), 7851–7879. DOI: 10.1021/cr300515x.
- (9) *Bindfit*. <http://supramolecular.org> (accessed December 2024).
- (10) Thordarson, P. Determining association constants from titration experiments in supramolecular chemistry. *Chem. Soc. Rev.* **2011**, *40* (3), 1305–1323. DOI: 10.1039/c0cs00062k.
- (11) Brynn Hibbert, D.; Thordarson, P. The death of the Job plot, transparency, open science and online tools, uncertainty estimation methods and other developments in supramolecular chemistry data analysis. *Chem. Commun.* **2016**, *52* (87), 12792–12805. DOI: 10.1039/c6cc03888c.
- (12) Fiorentini, F.; Diment, W. T.; Deacy, A. C.; Kerr, R. W. F.; Faulkner, S.; Williams, C. K. Understanding catalytic synergy in dinuclear polymerization catalysts for sustainable polymers. *Nat. Commun.* **2023**, *14* (1). DOI: 10.1038/s41467-023-40284-z.
- (13) Butler, F.; Fiorentini, F.; Eisenhardt, K. H. S.; Williams, C. K. Structure-Activity Relationships for s-Block Metal/Co(III) Heterodinuclear Catalysts in Cyclohexene Oxide Ring-Opening Copolymerizations. *Angew. Chem. Int. Ed.* **2025**. DOI: 10.1002/anie.202422497.

Chapter 5

Conclusions and Outlook

5.1 Thesis Summary

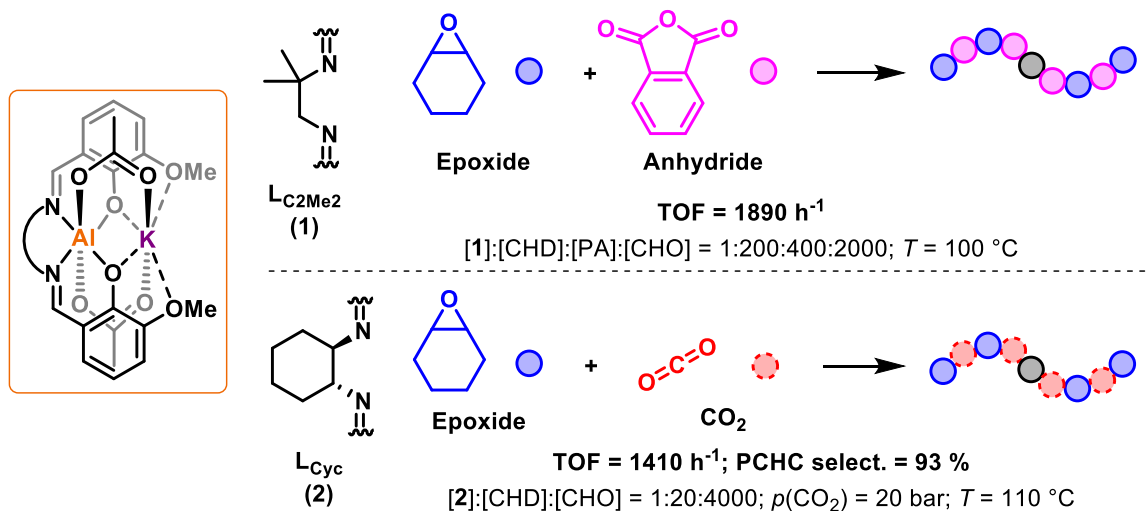
This thesis focuses on the development of Al(III)K(I) catalysts for the ring-opening copolymerisation (ROCOP) of epoxides with either anhydrides or CO₂ to produce polyesters and polycarbonates, respectively. A particular emphasis was taken on the synthesis of low MW polyesters, by the addition of large excesses of alcohol (diol) vs. catalyst so as to optimise production of oligomers and polymers for liquid formulations. This work particularly explored influences affecting catalyst performance and demonstrated improvements in the controlled synthesis of low MW polyesters:

1. To advance the understanding of catalyst structure-performance relationships, investigations were undertaken by varying the diimine linker of the ancillary Schiff base ligand for the Al(III)K(I) catalysts.¹ This class of catalysts was targeted because Al and K are both earth abundant and relatively cheap, with low toxicity. The ligand was simple to synthesise and used *ortho*-vanillin, which can be extracted from plants. This work revealed the significant influence of the ligand backbone chemistry on the rate of polymerisation. For epoxide/anhydride ROCOP, the best catalyst from the scope featured a 2C dimethyl backbone. This trend was attributed to a combination of its rigidity properties and electronic effects. Furthermore, it was observed that when alcohol was added to the reaction, the activity of the catalyst was greatly improved, a very unusual result in the field where catalysts are usually deactivated by protic compounds. The catalyst had a maximum activity at 200 equiv. alcohol with a TOF of 1890 h⁻¹. For epoxide/CO₂ ROCOP, a different trend in catalyst rate was observed with a maximum activity of 1410 h⁻¹ by a catalyst featuring a cyclohexyl backbone.² Its performance is high for an Al(III) catalyst and matches many of the top catalysts in the field. Overall, the catalysts with very rigid backbones or those without any substituents on the backbone

proved to be the slowest and least selective. Reaction kinetics determined for the lead catalyst revealed a CO₂ pressure dependant rate law which saturates at 20 bar, which is in agreement with recent reports for a few other leading catalysts.^{3, 4}

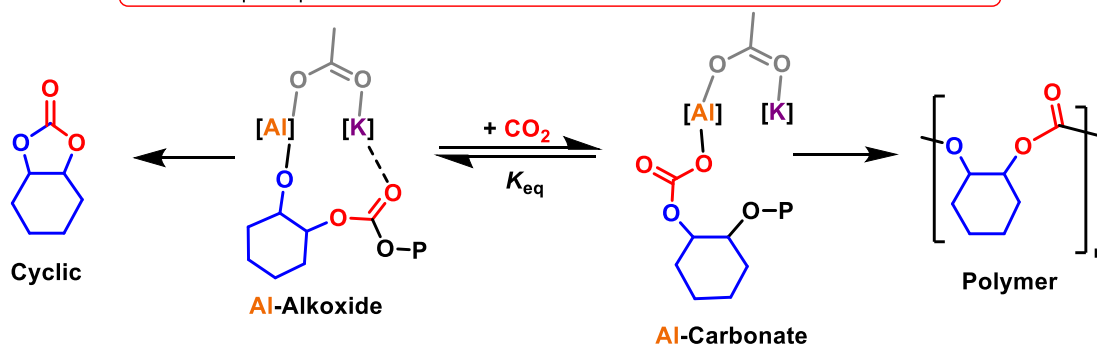
2. Following on from the discovery of the alcohol accelerated rate, studies investigating this phenomenon were conducted.⁵ Kinetic studies suggested that the polymerisation rate law was 1st order in catalyst, epoxide and alcohol concentrations. This result led to the proposal of a reaction pathway with two concurrent cycles, one of which requires the direct influence of the alcohol in the rate determining step. The nature of this direct effect from the alcohol was probed by ¹H NMR alcohol-catalyst binding studies, X-ray crystallography and by a kinetic isotope effect study. The data were rationalised by a mechanism in which the epoxide ring opening step occurs from a K(I)-carboxylate nucleophile. The alcohol was proposed to coordinate to the K(I), slightly decreasing the K(I) Lewis acidity and increasing the lability of the K(I)-carboxylate nucleophile. The generality of the alcohol rate acceleration is yet to be proven with other M(III)M(I/II) catalysts.

Chapters 2 & 3: Catalyst Ligand Modification Studies



Chapter 3: CHO/CO₂ ROCOP Kinetics

$$\text{Rate} = k_p K_{\text{eq}} [\text{alkoxide}] [\text{CHO}] [\text{CO}_2] \quad 5 < p(\text{CO}_2) < 30 \text{ bar}$$



Chapter 2 & 4: Understanding Alcohol Acceleration of Rates

$$\text{Rate} = k_1 [\text{cat}] [\text{CHO}] + k_2 [\text{cat}] [\text{CHO}] [\text{ROH}]$$

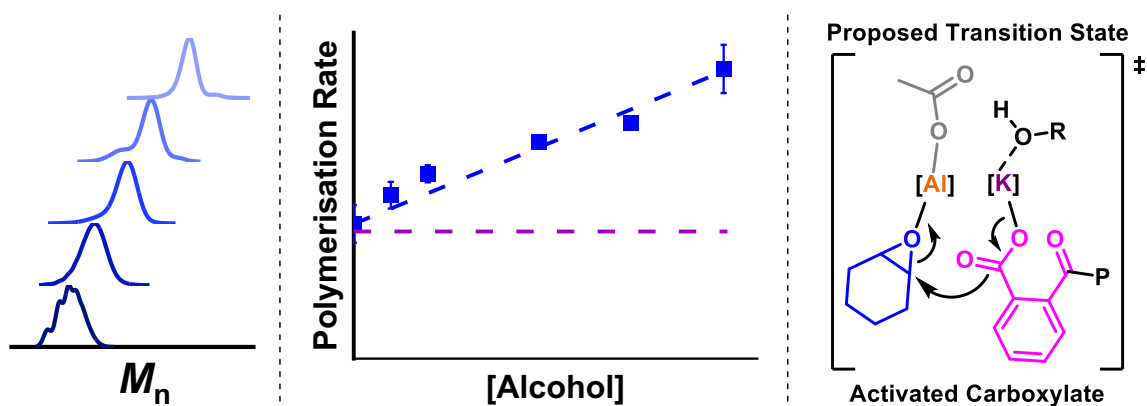


Figure 5.1 Thesis summary.

5.2 Outlook

5.2.1 Heterodinuclear Catalysts

This thesis demonstrates the potential of Al(III)K(I) heterodinuclear complexes as sustainable alternatives for ROCOP catalysts. Following on from the suggestions that have been made in Chapter 2, Section 2.7, there is a rich seam of possibilities for improving catalyst performance.

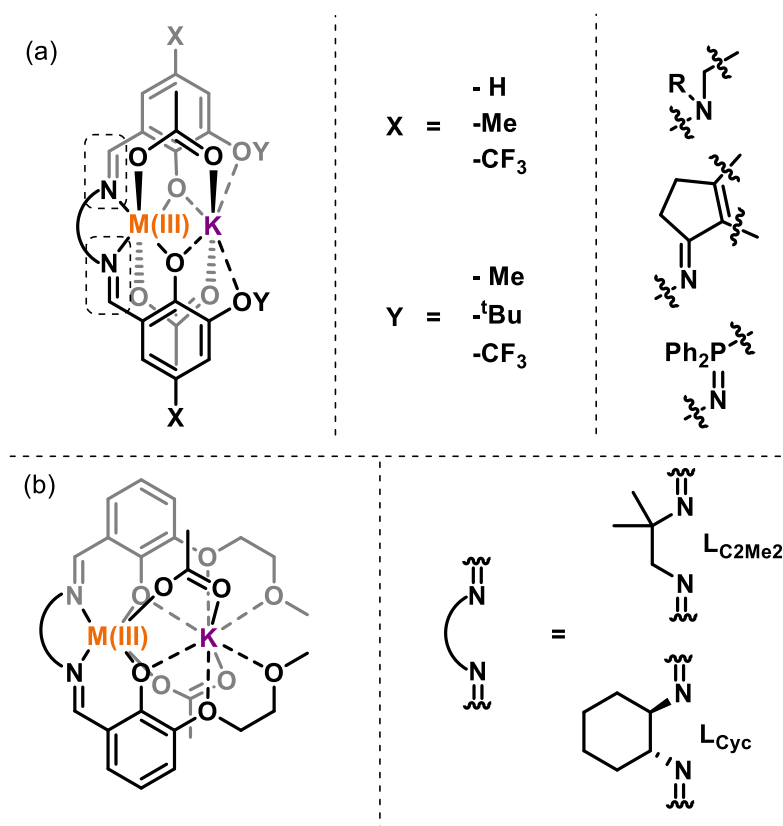


Figure 5.2 (a) Al(III)K(I) catalyst ligand modification for further catalyst optimisation. (b) Ligand backbone modifications for potential improvements on existing epoxide/ CO_2 ROCOP catalysts.

Prospects for further catalyst development include the following: Modifications to the ligand, beyond the di-imine backbone, remain to be fully explored. Another option would be to modify the phenolate-ethers. It is hypothesised that the Lewis acidity of the Al(III) metal is important for influencing catalyst activity since it affects to polarisation of the C-O bond in the epoxide.⁶ Therefore, having a ligand that is less electron donating, could

lead to enhanced rates. One way this could be achieved would be by adding fluorinated groups on to the phenolate, either as $-\text{CF}_3$ para to the $-\text{OH}$, or a $-\text{OCF}_3$ to replace the $-\text{OMe}$ that coordinates the K(I) (Figure 5.2a). One area to balance would be to prevent the formation of a strongly bound carbonate/carboxylate which could slow the reaction. Another approach to modifying the M(III) Lewis acidity would be to modify the imine donors, e.g. by replacing them with amines or even phosphoranes (Figure 5.2 a).^{7,8}

Tests in Chapter 3 revealed that the dimethyl ethylene di-imine backbone (L_{C2Me2}) led to higher rates and better control over the CHO/CO_2 polymerisation than the catalyst without the methyl groups present (L_{Et}). If this result is the same for other catalysts, then perhaps this would be a simple way to enhance their catalytic activity further, since many highly-active catalysts use the L_{Et} backbone in the ligand framework (Figure 5.2b). For example, the Al(III)K(I) catalyst, reported by Eisenhardt *et al.*, could be modified to introduce a di-methyl ethylene backbone which may lead to higher rates.⁶ It would also be worthwhile to test the cyclohexylene backbone on these catalysts, since this was the highest performing ligand of the series (Figure 5.2b).

With the intention of improving the sustainability of the epoxide/ CO_2 catalysts further, iron is a particularly important metal to target, due to it being earth abundant and environmentally benign. As with Al(III) catalysts, there are only limited prior examples of Fe catalysts. One successful example is the Fe(IV) -corrole complex, by Nozaki and co-workers, and an Fe(II)Mg(II) catalyst by Williams and co-workers.⁹⁻¹¹ Many of the ligand modifications mentioned above could also help to improve the activity of Fe(III)K(I) catalysts. The strategy would be to increase the Lewis acidity of the Fe(III) centre, and it would benefit from high T tolerance that can help drive rates higher.

5.2.2 Alcohol Acceleration of Polymerisation Rates

This thesis has established that some Al(III)K(I) catalysts are very effective at catalysing epoxide/anhydride ROCOP reactions in the presence of a large excess of alcohol. Chapter 4 investigated how and why this may be occurring. Seeking to take this work further would be to establish whether this alcohol rate-enhancement phenomenon occurs in epoxide/heterocumulene polymerisations and to demonstrate how effectively it could be applied on a larger scale.

Firstly, the Al(III)K(I) catalysts should be tested with alcohols for other polymerisations. These other reactions should include more epoxide/anhydride ROCOP, and also epoxide/CO₂ ROCOP and lactone ROP (Figure 5.3a). In Chapter 3, it was reported (in Section 3.2.3) that there was an improvement in rate and polymer selectivity when 20 equiv. of diol (CHD) was added to the polymerisation, and a rate enhancement has already been reported elsewhere in the field (as it appears to be the case for ROP as well).^{12, 13} Therefore, there is emerging evidence that alcohol-induced rate enhancement is a more general phenomenon. So far, a clear mechanism for this rate acceleration is lacking, so an in-depth investigation (akin to that in Chapter 4) could provide insightful results, especially if augmented with DFT modelling.

One of the key product classes applying low MW polymers are liquid formulations. Generally, polymers used in these products feature flexible backbones and oxygenated polymer chains to improve solubility in water. These PLFs require many different types of monomers, beyond the CHO/PA combination that has been the focus of this thesis. There have already been promising results from the monomer scope in Chapter 2, showing good catalytic activity when using allyl-glycidyl ether and diglycolic anhydride. In order to investigate this further, the monomer scope should be expanded to include

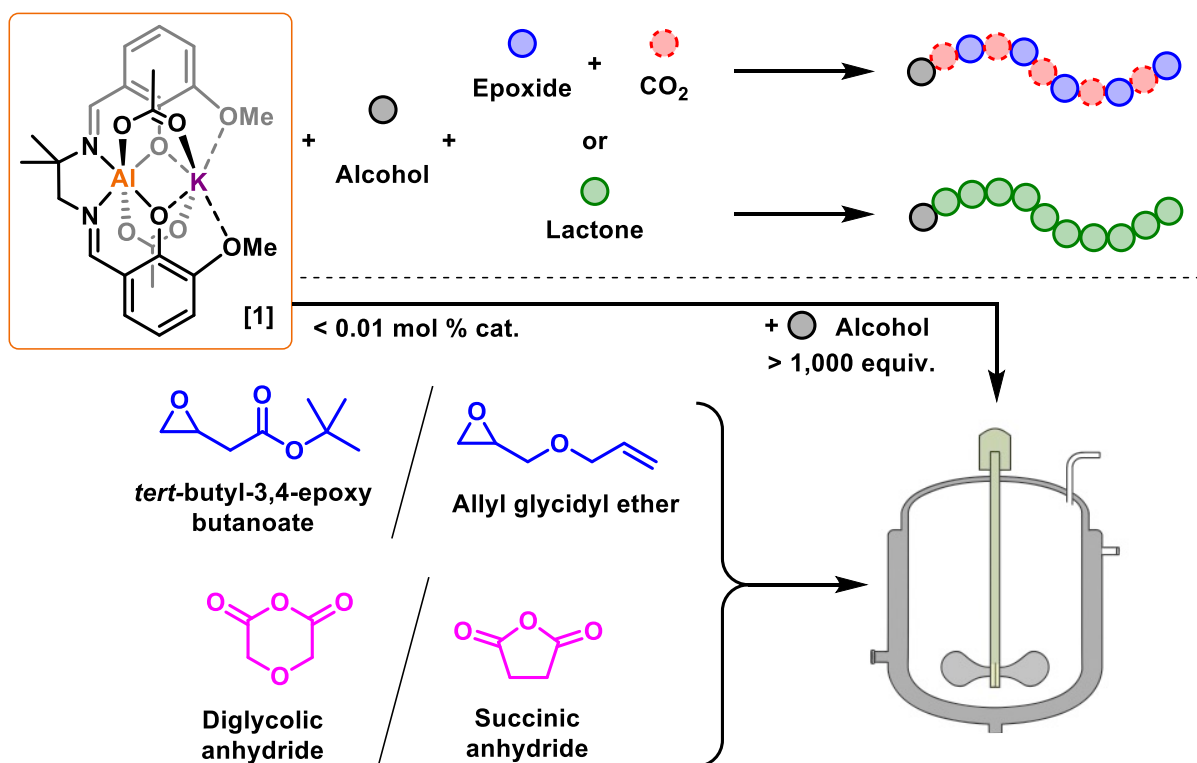


Figure 5.3 (a) Future alcohol rate enhancement studies for epoxide/CO₂ ROCOP and lactone ROP. (b) Upscaling the catalysis for production of PLFs.

glycidyl ethers and other anhydrides with flexible backbones (Figure 5.3b). Changing the alcohol could also be leveraged to influence chain-morphology and even end-group functionality, the latter plays a more important role the shorter the polymer/oligomer chains become.

Finally, it is worth considering the industrial relevance of these catalysts and their use with excess alcohol to target MW. One benefit for these polymerisations is the ability to minimise catalyst concentration and control both the rate and MW by inexpensive alcohol addition. This strategy has already been reported to be effective through work in Chapter 2. The Al(III)K(I) catalysts are also effectively removed at lab-scale by a silica plug, which was how polymers were purified and isolated in this work. Therefore, it would certainly be worthwhile to explore larger scale polymerisations and catalyst recycling (Figure

5.3b). To improve rate when optimising larger scale reactions, the high temperature tolerance of the Al(III)/K(I) catalyst is a potential benefit, as established in tests in Chapters 2 & 3. This may offer an avenue to use efficient ROCOP pathways to commercially produce sustainable polymers from bio-renewable feedstocks using cheap and environmentally benign metal catalysts.

5.3 References

- (1) Shellard, E. J. K.; Diment, W. T.; Resendiz-Lara, D. A.; Fiorentini, F.; Gregory, G. L.; Williams, C. K. Al(III)/K(I) Heterodinuclear Polymerization Catalysts Showing Fast Rates and High Selectivity for Polyester Polyols. *ACS Catal.* **2024**, *14* (3), 1363–1374. DOI: 10.1021/acscatal.3c05712.
- (2) Shellard, E. J. K., Jannsen, N., Williams, C. K. Investigations into Alcohol-Induced Rate Enhancement of Epoxide/Anhydride Ring Opening Copolymerisations. *Manuscript in preparation*.
- (3) Eisenhardt, K. H. S.; Fiorentini, F.; Lindeboom, W.; Williams, C. K. Quantifying CO₂ Insertion Equilibria for Low-Pressure Propene Oxide and Carbon Dioxide Ring Opening Copolymerization Catalysts. *J. Am. Chem. Soc.* **2024**, *146* (15), 10451–10464. DOI: 10.1021/jacs.3c13959.
- (4) Lehenmeier, M. W.; Kissling, S.; Altenbuchner, P. T.; Bruckmeier, C.; Deglmann, P.; Brym, A. K.; Rieger, B. Flexibly Tethered Dinuclear Zinc Complexes: A Solution to the Entropy Problem in CO₂/Epoxide Copolymerization Catalysis? *Angew. Chem. Int. Ed.* **2013**, *52* (37), 9821–9826. DOI: 10.1002/anie.201302157.
- (5) Shellard, E. J. K., Jannsen, N., Williams, C. K. Al(III)/K(I) Heterobimetallic Complexes for the Ring-Opening Copolymerisation of Epoxides with CO₂. *Manuscript in preparation*.
- (6) Eisenhardt, K. H. S.; Fiorentini, F.; Williams, C. K. Understanding the Effect of M(III) Choice in Heterodinuclear Polymerization Catalysts. *Inorg. Chem.* **2024**. DOI: 10.1021/acs.inorgchem.4c04430.
- (7) Thevenon, A.; Garden, J. A.; White, A. J.; Williams, C. K. Dinuclear Zinc Salen Catalysts for the Ring Opening Copolymerization of Epoxides and Carbon Dioxide or Anhydrides. *Inorg. Chem.* **2015**, *54* (24), 11906–11915. DOI: 10.1021/acs.inorgchem.5b02233.
- (8) Thevenon, A.; Cyriac, A.; Myers, D.; White, A. J. P.; Durr, C. B.; Williams, C. K. Indium Catalysts for Low-Pressure CO₂/Epoxide Ring-Opening Copolymerization: Evidence for a Mononuclear Mechanism? *J. Am. Chem. Soc.* **2018**, *140* (22), 6893–6903. DOI: 10.1021/jacs.8b01920.

- (9) Cao, H.; Liu, S.; Wang, X. Environmentally benign metal catalyst for the ring-opening copolymerization of epoxide and CO₂: state-of-the-art, opportunities, and challenges. *Green Chem. Eng.* **2022**, 3 (2), 111–124. DOI: 10.1016/j.gce.2021.11.005.
- (10) Nakano, K.; Kobayashi, K.; Ohkawara, T.; Imoto, H.; Nozaki, K. Copolymerization of Epoxides with Carbon Dioxide Catalyzed by Iron–Corrole Complexes: Synthesis of a Crystalline Copolymer. *J. Am. Chem. Soc.* **2013**, 135 (23), 8456–8459. DOI: 10.1021/ja4028633.
- (11) Reis, N. V.; Deacy, A. C.; Rosetto, G.; Durr, C. B.; Williams, C. K. Heterodinuclear Mg(II)M(II) (M=Cr, Mn, Fe, Co, Ni, Cu and Zn) Complexes for the Ring Opening Copolymerization of Carbon Dioxide/Epoxide and Anhydride/Epoxide. *Chem. - Eur. J.* **2022**, 28 (14). DOI: 10.1002/chem.202104198.
- (12) Cyriac, A.; Lee, S. H.; Varghese, J. K.; Park, E. S.; Park, J. H.; Lee, B. Y. Immortal CO₂/Propylene Oxide Copolymerization: Precise Control of Molecular Weight and Architecture of Various Block Copolymers. *Macromol.* **2010**, 43 (18), 7398–7401. DOI: 10.1021/ma101259k.
- (13) Kuang, Q.; Zhang, R.; Zhou, Z.; Liao, C.; Liu, S.; Chen, X.; Wang, X. A Supported Catalyst that Enables the Synthesis of Colorless CO₂-Polyols with Ultra-Low Molecular Weight. *Angew. Chem. Int. Ed.* **2023**, 62 (35). DOI: 10.1002/anie.202305186.

Chapter 6

Experimental Details

6.1 General Considerations

All manipulations were carried out in a nitrogen filled glovebox, or dual manifold nitrogen-vacuum Schlenk line. Solvents used for synthesis were collected from a solvent purification system (SPS), degassed with freeze-pump-thaw cycles and stored over activated 3 Å molecular sieves under an inert atmosphere, unless otherwise stated. All materials were stored under a nitrogen atmosphere, in a glovebox. Triethyl aluminium (93%) was purchased from Sigma-Aldrich and was used as received. Group 1 acetate salts were purchased from Sigma Aldrich or Acros Organics and were dried at 100 °C for 16 h before use.

6.2 Monomer and CTA Purification Procedures

6.2.1 Monomers

All epoxides (cyclohexene oxide (CHO, Acros Organics), propylene oxide (PO, Sigma Aldrich), vinyl-cyclohexene oxide (vCHO, Sigma Aldrich), allyl glycidyl ether (AGE, Sigma Aldrich)) were purified by stirring over calcium hydride followed by fractional distillation. Purification of phthalic anhydride (PA, Sigma Aldrich) was achieved through stirring in dry toluene. The supernatant was filtered, and the toluene subsequently removed *in vacuo*. The resultant white powder recrystallised from hot (60 °C) chloroform and subsequently sublimed under vacuum at 80 °C. Norbornene anhydride (NBA, Acros Organics) was purified through recrystallisation from dry ethyl acetate, followed by sublimation at 80 °C. Tricyclic anhydride (TCA) was synthesised according to a literature procedure, and was purified through crystallisation from hexane followed by sublimation at 80 °C.¹ Diglycolic anhydride (DGA, Alfa Aesar) was purified by recrystallising twice from acetic anhydride followed by two sublimations. Research-grade carbon dioxide

(BOC, CP grade, 99.995%) was dried by passing through two drying columns (VICI Metronics carbon dioxide purifier) in series, at 40 bar pressure, before use at lower pressures in the copolymerisations.

6.2.2 CTAs

trans-1,2-Cyclohexanediol (CHD, Sigma Aldrich) was purified by recrystallisation in chloroform and then dried at 100 °C for 16 h. Benzyl alcohol (BnOH, Sigma Aldrich) was purified by reduced pressure fractional distillation. Mono-deuterated benzyl alcohol (BnOD) was prepared by stirring BnOH in large excess of MeOD- d_4 at room temperature for 24 h. This was then separated and purified by fractional distillation.

6.3 Methods

NMR Spectroscopy: ^1H MNR and ^{27}Al spectra were obtained using a Bruker Avance III HD 400 NMR spectrometer. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained with either Bruker AV III HD 500 MHz NMR, Bruker NEO 600 MHz with broadband helium cryoprobe, or Bruker AVIII 700 MHz with inverse TCI $^1\text{H}/^{13}\text{C}/^{15}\text{N}$ cryoprobe spectrometers.

IR Spectroscopy: Carried out on a Shimadzu IRSpirit FT-IR spectrometer equipped with a single reflection ATR (attenuated total reflectance) accessory, in a nitrogen filled glovebox.

GPC analysis: Carried out using a Shimadzu LC-20AD instrument, equipped with a Refractive Index (RI) detector and two PSS SDV 5 μm linear M columns. The eluent used was HPLC-grade THF, heated to 30 °C, and with a flow rate of 1.0 mL min $^{-1}$.

Elemental Analysis: These were performed by the London Metropolitan University Elemental Analysis Service, 29 Hornsey Road, London, N7 7DD, UK.

MALDI-ToF: Carried out on a Bruker Autoflex Speed MALDI-ToF spectrometer. Polymer samples were prepared by a 1:4:1 solution of polymer (10 mg mL⁻¹ in THF), dithranol (10 mg mL⁻¹ in THF) and KTFA (10 mg mL⁻¹ in THF). Catalyst samples were prepared by a 1:4:1 solution of catalyst (10 mg mL⁻¹ in CHCl₃ (MeCN for **4**, MeOH for **6**)), trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (10 mg mL⁻¹ in THF) and KTFA or KI (10 mg mL⁻¹ in THF). This solution was spotted three times on a MALDI plate and allowed to dry completely before analysis was undertaken.

X-Ray Crystallography: Crystallographic data were collected, and structures solved, by either Dr Francesca Fiorentini or Dr Nora Janssen. Air sensitive crystalline samples were isolated in a nitrogen filled glovebox and immersed in fluorinated oil. Crystalline samples were mounted on a MiTeGen Micromount, and cooled to 150 K with dry nitrogen using an Oxford Cryosystem.² Data was collected using an Oxford Diffraction Supernova diffractometer using Cu K α (λ = 1.5417 Å) or Mo K α (λ = 0.7107 Å) radiation. The resulting reflection data was processed with CrysAlis Pro.³ The crystal structures were solved using the SHELXT program and least-square refined using the SHELXL program within the Olex2 system suite.⁴

Differential Scanning Calorimetry (DSC): Catalyst stability tests were conducted using a DSC25 (TA Instruments), equipped with the TRIOS software package. A DSC pan was loaded with 5 mg of the selected catalyst (both **1** and **2** tested). This was ramped at a rate of 10 °C min⁻¹ up to 100 °C and held isothermal for 1 h. The temperature was then ramped (rate 10 °C min⁻¹) to 160 °C, held for 1 h, then ramped (rate 10 °C min⁻¹) to 200 °C and held for a final 1 h.

Thermal gravimetric analysis (TGA): Data was collected on a TGA5500 System (TA Instruments), equipped with the TRIOS software package. A TGA pan was loaded with 5 mg of the selected catalyst (both **1** and **1.32** tested) and an additional 5 mg of MEO as a CTA. The temperature was quickly ramped up to 100 °C and held isothermal for 30 min.

6.4 General Polymerisation Procedures

6.4.1 Epoxide/Anhydride in Microwave Vial

The reaction was set up inside a nitrogen-filled glovebox. The catalyst (2.7 mg (for **1**), 4.9×10^{-3} mmol), PA (293 mg, 2.0 mmol) and CHO (9.9 mmol, 1 mL) were added to a 4 mL vial, with a rare-earth magnetic stirrer bar inside. A melamine cap containing a Teflon inlay, was used to seal the vial, with an additional layer of parafilm and then electrical insulation tape wrapped around the cap. The reaction mixture was heated at 100 °C, with stirring at 1400 rpm. At the times recorded, the reaction mixture was removed from heating and immediately cooled in an ice bath to slow the reaction rate such that polymerisation was effectively paused (TOF = 3 h^{-1} at RT). Aliquots were taken under inert atmosphere in a glovebox, but the ^1H NMR spectroscopy (2 mg crude product in 0.6 mL CDCl_3) and GPC (2 mg crude product in 1 mL THF and filtered) samples could be prepared in air.

6.4.2 Use of Low Pressure ReactIR for CHO/PA

In a nitrogen-filled glovebox, the catalyst (2.7 mg (for **1**), 4.9×10^{-3} mmol), BnOH (26 μL , 0.25 mmol), PA (293 mg, 2.0 mmol) and CHO (9.9 mmol, 1 mL) were added to a finger Schlenk. The Schlenk tube was sealed, taken out of the glovebox and cycled onto a

Schlenk line. The ReactIR probe was gently warmed with a heat gun to remove residual moisture then a background scan was taken. The probe was then inserted into the Schlenk tube under N₂ flow, and purged ten times. The Schlenk tube was lowered into a pre-heated oil bath, at 100 °C, with stirring, at 1000 rpm, and the IR scans were started, with a reading taken every 15 seconds. The crude product was analysed by ¹H NMR spectroscopy (2 mg crude product in 0.6 mL CDCl₃) and GPC (2 mg crude product in 1 mL THF and filtered). The samples could be prepared in air.

6.4.3 CTA Partway Addition Experiment

In a nitrogen-filled glovebox, the catalyst (2.7 mg (for **1**), 4.9 x 10⁻³ mmol), PA (293 mg, 2.0 mmol) and CHO (9.9 mmol, 1 mL) were added to a finger Schlenk. In a separate smaller Schlenk tube, excess amount of BnOH or Tol was added (50 µL). The two Schlenk tubes were sealed, taken out of the glovebox and cycled onto a Schlenk line. The ReactIR probe was gently warmed with a heat gun to remove residual moisture then a background scan was taken. The probe was then inserted into the Schlenk tube with catalyst and monomer in under N₂ flow and purged ten times. The Schlenk tube was lowered into a pre-heated oil bath at 100 °C with stirring at 1000 rpm and the IR scans were started, with a reading taken every 15 seconds. Reaction progression was monitored by 890 cm⁻¹ for PA consumption and 1730 cm⁻¹ for PCHPE production. At 25 mins, BnOH (26 µL, 0.25 mmol) or Tol control (26 µL) was added to the polymerisation mixture by removing the ReactIR probe briefly under N₂ flow and injecting from the top, before replacing it. The crude product was analysed by ¹H NMR spectroscopy (2 mg crude product in 0.6 mL CDCl₃) and GPC (2 mg crude product in 1 mL THF and filtered). The samples could be prepared in air.

6.4.4 Schlenk Aliquot Method

In a nitrogen-filled glovebox, the catalyst (2.7 mg (for **1**), 4.9×10^{-3} mmol), BnOH (26 μ L, 0.25 mmol), PA (293 mg, 2.0 mmol) and CHO (9.9 mmol, 1 mL) were added to a finger Schlenk. The Schlenk tube was sealed, taken out of the glovebox and cycled onto a Schlenk line. To start the reaction, the Schlenk tube was lowered into an oil bath preheated to 100 °C with stirring at 1400 rpm. Aliquots were taken using a glass pipette that had been purged by N₂ and heated with a heat gun for at least a minute. Under N₂ flow, the lid of the Schlenk tube was briefly removed and a small aliquot was taken using the pipette. The reaction was not stopped as the aliquots were taken. The aliquots were analysed by ¹H NMR spectroscopy (2 mg crude product in 0.6 mL CDCl₃) and GPC (2 mg crude product in 1 mL THF and filtered) and these samples were prepared in air.

6.4.5 Low Pressure CHO/CO₂

A solution of catalyst (4.5 mg (for **2**), 0.008 mmol) and CHO (1.6 mL, 15.8 mmol) was added to a Young's tap finger Schlenk tube along with a rare-earth magnetic stirrer bar, all within a nitrogen-filled glovebox. The Schlenk tube was cycled on to a triple manifold Young tap Schlenk line (N₂, CO₂ and vacuum). The solution was heated to 100 °C, stirred at 1000 rpm, and was left under a dynamic CO₂ atmosphere set to 1 bar. The reaction was quenched by addition of 1 M solution of benzoic acid, in CHCl₃. The samples were analysed by ¹H NMR spectroscopy (2 mg crude product in 0.6 mL CDCl₃) and GPC (2 mg crude product in 1 mL THF and filtered).

6.4.6 High Pressure Epoxide/CO₂

A solution of catalyst (8.4 mg (for **2**), 0.015 mmol) and cyclohexene diol (34 mg, 0.30 mmol) in CHO (6 mL, 59.3 mmol) was injected into a 100 mL Parr reactor, under a stream of dry CO₂. The reactor was fitted with a DiComp sentinel probe, attached to an ATR-IR spectrometer. Conversion to polycarbonate (PCHC) and cyclic carbonate (CHC) were followed using *in situ* ATR-IR spectroscopy by observing the development of peaks at 1750 cm⁻¹ and 1820 cm⁻¹ for PCHC and CHC, respectively. The reaction was stirred and the reactor was pressurised with CO₂ to the target reaction pressure and heated to the required temperature. Upon reaction completion, the reactor vessel was cooled to room temperature and depressurised. The catalyst was quenched by the addition of a 1 M solution of benzoic acid, in CHCl₃. A sample of the crude reaction mixture was removed for ¹H NMR spectroscopy (2 mg crude product in 0.6 mL CDCl₃) and GPC analysis (2 mg crude product in 1 mL THF and filtered).

6.4.7 Polycarbonate Backbiting Experiments

A solution of catalyst (8.4 mg (for **2**), 0.015 mmol) and poly(cyclohexene oxide carbonate) (210 mg, 1.5 mmol) in CHO (6 mL) was injected into a 100 mL Paar reactor, under a flow of dry N₂ in the same setup as the High Pressure polymerisations. The reactor was also fitted with a DiComp sentinel probe, attached to an ATR-IR spectrometer, which allowed for continual monitoring of PCHC consumption (1750 cm⁻¹) and cyclic carbonate formation (1820 cm⁻¹). The reaction was left under 1 bar N₂ pressure and heated to the desired temperature. Upon completion, the reaction was cooled and opened to air and a sample of the crude reaction mixture was removed for ¹H NMR spectroscopy (2 mg crude product in 0.6 mL CDCl₃).

6.4.8 Polymer Purification Method

Polymers were purified by precipitation from DCM into methanol or hexane. This precipitate was redissolved in DCM and passed through a silica plug. The DCM was then evaporated off and the polymer dried at 40 °C under vacuum for 16 h.

6.5 Binding Studies

All ^1H NMR spectroscopy titrations were performed on a Bruker Avance III 500 MHz NMR spectrometer, at 298 K, in CDCl_3 solvent. Initial sample volume of the NMR tube was 0.5 mL with a receptor (catalyst **1**) concentrations of 10 mM.

The BnOH solution had concentration of 5 M and the equivalents of BnOH (vs. catalyst) were as follows: 0, 10, 30, 50, 75, 100, 125, 150, 175, 200, 250, 300, 400. Binding was fast allowing the calculation association constants using Bindfit program available from <http://supramolecular.org>, accessed December, 2024.⁵⁻⁷

6.6 Characterising Data for Chapter 2

6.6.1 Synthesis of Ligand (LH_2)

The synthesis of the *ortho*-vanillin and diamine ligand followed general literature procedures.^{8,9} Formation of a Schiff base LH_2 was used to produce the ligand by addition of the desired diamine and 2 equiv *ortho*-vanillin in MeOH, at room temperature and pressure. ^1H NMRs of LH_2 were in agreement with previously reported literature.⁹⁻¹¹

Crude yields: $L_{C_2Me_2H_2} = 50 \%$, $L_{CycH_2} = 82 \%$, $L_{C_2Ph_2H_2} = 98 \%$, $L_{ProH_2} = 78 \%$, $L_{EtH_2} = 79 \%$.

Synthesis of L_{PhenH_2} was achieved by addition of *o*-phenylene diamine to *ortho*-vanillin in EtOH with reflux at 80 °C for 4h.¹²

For associated spectra see appendix.

6.6.2 Synthesis of Complex 1, $[L_{C_2Me_2AlK}(OAc)_2]$

The synthesis of complex **1** was achieved through a two-step procedure, following previous literature work.¹³ $AlEt_3$ (0.12 g, 0.9 mmol) was added to a solution of $L_{C_2Me_2H_2}$ (0.32 g, 0.9 mmol), in toluene (10 mL), under N_2 atmosphere, with stirring for 16 h, yielding $[L_{C_2Me_2AlEt}]$ as a yellow precipitate (crude yield = 50 %). Acetic acid (0.02 g, 0.3 mmol) was added, under N_2 flow, to a stirring mixture of $[L_{C_2Me_2AlEt}]$ (0.12 g, 0.3 mmol), in toluene (10 mL) and heated at 100 °C, for 12 h. $[L_{C_2Me_2AlOAc}]$ was isolated as a light yellow precipitate (crude yield = 75 %) and was washed 2x with Toluene and 1x with hexane. KOAc (13 mg, 0.13 mmol) was then added to $[L_{C_2Me_2AlOAc}]$ (57 mg, 0.13 mmol), in chloroform (10 mL), with stirring under N_2 atmosphere for 16 h at room temperature. The solvent was removed under vacuum leaving $[L_{C_2Me_2AlK}(OAc)_2]$ (**1**), a pale yellow powder (yield = 99 %). **¹H NMR** ($CDCl_3$, 400 MHz, 298 K): 8.16 (s, 1H, **HC=N**), 8.08 (s, 1H, **HC=N**), 6.81 (d, $^3J = 8.00$ Hz, 2H, *o/p*-PhH), 6.69 (d, $^3J = 8.00$ Hz, 2H, *o/p*-PhH), 6.57 (br. m, 2H, *m*-PhH), 3.88 (br. s, 2H, **HC-N**), 3.37 (br. 2s, 6H, , -OMeH), 1.60 (s, 6H, -C((CH₃*)₂/OAcH), 1.56 (s, 6H, -C((CH₃*)₂/OAcH). **¹³C NMR** (151 MHz, $CDCl_3$, 298 K): δ 174.19, 156.13, 155.29, 151.72, 151.50, 125.59, 124.85, 119.07, 118.95, 114.62, 114.11, 113.94, 66.27, 60.48, 55.00, 27.88, 24.66. **IR**: 349, 353, 357, 360, 372, 380, 453, 465, 490, 505, 538, 568, 612, 632, 658, 731, 779, 806, 859, 935, 969, 985, 1011, 1075, 1099, 1165,

1185, 1218, 1234, 1310, 1371, 1387, 1444, 1467, 1475, 1545, 1595, 1608, 1627, 1650, 2819, 2911, 2948, 3042 cm⁻¹. **MALDI-ToF:** 479 m/z [L_{C2Me2}AlK(OAc)]⁺

For associated spectra see appendix.

6.6.3 Synthesis of Complex 2, [L_{Cyc}AlK(OAc)₂]

This followed an analogous procedure to that outlined above for complex **1**. Firstly, the monometallic [L_{Cyc}AlOAc] was targeted. AlEt₃ (0.16 g, 1.4 mmol) was added to a solution of L_{Cyc}H₂ (0.50 g, 1.3 mmol), in toluene (10 mL), under N₂ atmosphere, with stirring and heated for 2 h at 100 °C, producing [L_{Cyc}AlEt] *in situ* as a light brown solution. Acetic acid (0.08 g, 1.3 mmol) was added, under N₂ flow, and stirring, with the reaction mixture heated for a further 1.5 h at 100 °C and before being left stirring at room temperature for 2 days. [L_{Cyc}AlOAc] was isolated as a yellow precipitate (crude yield = 80 %) and was washed 2x with Toluene and 1x with hexane. KOAc (13 mg, 0.13 mmol) was then added to [L_{Cyc}AlOAc] (60 mg, 0.13 mmol), in chloroform (10 mL), with stirring under N₂ atmosphere for 24 h at room temperature. The solvent was removed under vacuum leaving [L_{Cyc}AlK(OAc)₂] (**2**), a cream/yellow powder (72 mg, 0.13 mmol, 99 %).

¹H NMR (CDCl₃, 400 MHz, 298 K): 7.99 (s, 2H, **HC=N**), 6.80 (dd, ³J = 4.00 Hz ³J = 4.00 Hz, 2H, *m*-PhH), 6.56 (m, 4H, *o/p*-PhH), 3.97 (s, 2H, **HC-N**), 3.11 (s, 6H, -OMeH), 2.51 (s (d?), 2H, -CH₂*), 2.06 (s, 2H, -CH₂*), 1.63 (s, 6H, OAcH), 1.50 (s, 4H, -CH₂). **¹³C NMR** (151 MHz, CDCl₃, 298 K): δ 174.21, 160.08, 154.96, 151.27, 125.45, 118.92, 114.26, 113.39, 63.22, 54.45, 27.11, 24.68, 24.15. **IR:** 349, 356, 360, 367, 386, 392, 455, 598, 612, 658, 731, 779, 808, 859, 969, 1011, 1076, 1099, 1164, 1185, 1218, 1234, 1312, 1371, 1387, 1448, 1468, 1477, 1545, 1608, 1627, 1644, 2821, 2915, 2949, 3042 cm⁻¹. **MALDI-ToF:** 505 m/z [L_{Cyc}AlK(OAc)]⁺ For associated spectra see appendix.

6.6.4 Synthesis of Complex 3, [L_{C2Ph2}AlK(OAc)₂]

This followed an analogous procedure to that outlined above for complex **1**. AlEt₃ (0.13 g, 1.1 mmol) was added to a solution of L_{C2Ph2}H₂ (0.50 g, 1.0 mmol), in toluene (10 mL), under N₂ atmosphere, with stirring for 24 h. [L_{C2Ph2}AlEt] was isolated from solution by removal of solvent under vacuum, giving a yellow powder (crude yield = 98 %). Acetic acid (0.04 g, 0.6 mmol) was added, under N₂ flow, to a stirring mixture of [L_{C2Ph2}AlEt] (0.32 g, 0.6 mmol), in toluene (10 mL). This was left for 24 h at room temperature before being heated at 65 °C for 3 h. [L_{C2Ph2}AlOAc] was isolated as a yellow gel that had precipitated out of solution. This was then washed 2x with toluene and 1x with hexane before being dried, yielding a yellow powder (crude yield = 65 %). KOAc (21 mg, 0.22 mmol) was then added to [L_{C2Ph2}AlOAc] (121 mg, 0.22 mmol), in chloroform (10 mL), with stirring under N₂ atmosphere for 24 h at room temperature. The solvent was removed under vacuum leaving [L_{C2Ph2}AlK(OAc)₂] (**3**), a yellow powder (151 mg, 0.23 mmol, crude yield = 99 %). **¹H NMR** (CDCl₃, 400 MHz, 298 K): 7.61 (s, 2H, HC=N), 7.28 (s, 10H, -PhH), 6.55 (d, ³J = 8.00 Hz, 4H, *o/p*-PhH), 6.48 (t/dd, ³J = 6.00 Hz, 2H, *m*-PhH), 5.61 (s, 2H, HC-N), 3.12 (s, 6H, -OMeH), 1.84 (s, 6H, OAcH). **¹³C NMR** (151 MHz, CDCl₃, 298 K): δ 174.12, 164.08, 155.24, 151.31, 136.83, 130.34, 129.10, 128.60, 125.83, 118.90, 114.40, 113.76, 72.31, 54.59, 25.25. **IR**: 347, 355, 359, 372, 397, 465, 523, 545, 598, 609, 643, 698, 731, 779, 806, 859, 925, 981, 1001, 1038, 1075, 1101, 1164, 1188, 1215, 1235, 1312, 1378, 1444, 1467, 1545, 1593, 1615, 1644, 1675, 1691, 1708, 1724, 2819, 2914, 2945, 2986, 3011, 3042 cm⁻¹. **MALDI-ToF**: 603 m/z [L_{C2Ph2}AlK(OAc)]⁺

For associated spectra see appendix.

6.6.5 Synthesis of Complex 4, [L_{Phen}AlK(OAc)₂]

This followed an analogous procedure to that outlined above for complex **1**. AlEt₃ (0.13 g, 1.3 mmol) was added to a solution of L_{Phen}H₂ (0.50 g, 1.3 mmol) in THF (10 mL), under N₂ atmosphere, with stirring for 2 h, yielding [L_{Phen}AlEt] as a precipitate (crude yield = 68 %). Acetic acid (0.04 g, 0.6 mmol) was added, under N₂ flow, to a stirring mixture of [L_{Phen}AlEt] (0.27 g, 0.6 mmol) in THF (10 mL). This was left, for 20 h, at room temperature before heating at 65 °C, for 1.5 h. [L_{Phen}AlOAc] was then washed 2x with toluene and 1x with hexane before being dried, yielding a yellow precipitate (crude yield = 68 %). KOAc (13 mg, 0.13 mmol) was then added to [L_{Phen}AlOAc] (60 mg, 0.13 mmol), in acetonitrile (10 mL), with stirring and under N₂ atmosphere. This was left stirring at room temperature, for 3 day, before the solvent was removed under vacuum leaving [L_{Phen}AlK(OAc)₂] (**4**), a yellow powder (53 mg, 0.09 mmol, crude yield = 93 %). **¹H NMR** (DMSO, 400 MHz, 298 K): 9.01 (s, 2H, HC=N), 8.05 (m, 2H, *o/p*-PhH), 7.45 (br. s, 2H, *o/p*-PhH), 7.15 (d, ³*J* = 8.00 Hz, 2H, PhH), 7.02 (d, ³*J* = 8.00 Hz, 2H, PhH), 6.63 (br. s, 2H, *m*-PhH), 3.84 (s, 6H, -OMeH), 1.29 (s, 6H, OAcH). **¹³C NMR** (151 MHz, DMSO, 298 K): δ 171.36, 158.51, 156.13, 150.74, 138.29, 127.69, 126.44, 118.79, 116.47, 114.51, 113.84, 55.18, 24.54. **IR**: 349, 360, 369, 383, 403, 415, 440, 459, 495, 515, 545, 578, 586, 598, 613, 632, 649, 735, 741, 763, 781, 806, 842, 859, 896, 911, 934, 972, 982, 1008, 1041, 1075, 1101, 1164, 1174, 1189, 1234, 1315, 1324, 1368, 1440, 1474, 1498, 1541, 1573, 1607, 1624, 1675, 1691, 1708, 1724, 2825, 2919, 2951, 3044 cm⁻¹. **Anal. Calc.** C₂₆H₂₄AlKN₂O₈: C, 55.90; H, 4.33; N, 5.02 %. Found: C, 55.58; H, 4.04; N, 5.00 %. **MALDI-ToF**: 499 m/z [L_{Phen}AlK(OAc)]⁺

For associated spectra see appendix.

6.6.6 Synthesis of Complex 5, [L_{Pro}AlK(OAc)₂]

This followed an analogous procedure to that outlined above for complex **1**. Firstly, the monometallic [L_{Pro}AlOAc] was targeted. 1.05 equiv. of AlEt₃ (188 mg, 1.53 mmol) was added to a solution of L_{Pro}H₂ (500 mg, 1.46 mmol), in THF (10 mL), under N₂ atmosphere with stirring, for 48 h, producing [L_{Pro}AlEt] as an orange solution. The solvent was removed under vacuum and was isolated as an orange-yellow solid (crude yield = 99 %) and used without further purification. Acetic acid (38 mg, 0.63 mmol) was added, under N₂ flow, to a stirring solution of [L_{Pro}AlEt] (250 mg, 0.63 mmol), in THF (10 mL), with the reaction mixture heated to 100 °C for 3.5 h before being left stirring at room temperature for 3 days. [L_{Pro}AlOAc] was isolated from the yellow solution by removing the solvent under vacuum, giving a yellow powder (crude yield = 81 %) and used without further purification. KOAc (20 mg, 0.21 mmol) was then added to [L_{Pro}AlOAc] (88 mg, 0.21 mmol), in chloroform (10 mL), with stirring and under N₂ atmosphere. This was left at room temperature, for 48 h, before the solvent was removed under vacuum leaving [L_{Pro}AlK(OAc)₂] (**5**), a pale yellow powder (96 mg, 0.18 mmol, 88 %). ¹H NMR (CDCl₃, 400 MHz, 298 K): 7.96 (s, 2H, HC=N), 6.75 (dd, ³J = 8.00 Hz, ⁴J = 4.00 Hz, 2H, PhH), 6.60 (dd, ³J = 8.00 Hz, ⁴J = 4.00 Hz, 2H, PhH), 6.50 (t/dd, ³J = 8.00 Hz, 2H, PhH), 3.76 (t, ³J = 6.00 Hz, 4H, HC-N), 3.35 (s, 6H, -OCH₃), 2.26 (br. s, 2H, -CH₂), 1.56 (s, 6H, -OC(=O)CH₃). ¹³C NMR (151 MHz, CD₂Cl₂, 298 K): δ 173.62, 166.08, 156.42, 151.50, 125.38, 119.90, 114.46, 113.97, 63.07, 55.34, 29.15, 24.74. IR: 343, 349, 372, 390, 396, 417, 445, 492, 532, 568, 609, 631, 649, 729, 781, 805, 858, 936, 952, 968, 985, 1011, 1038, 1069, 1098, 1164, 1219, 1235, 1312, 1380, 1448, 1467, 1480, 1550, 1608, 1675, 1691, 1708, 1724, 282, 2908, 2942, 2982, 3042 cm⁻¹. Anal. Calc. C₂₃H₂₆AlKN₂O₈: C, 52.66; H, 5.00; N, 5.34 %. Found: C, 52.53; H, 5.22; N, 5.48 %. MALDI-ToF: 465 m/z [L_{Pro}AlK(OAc)]⁺ For associated spectra see appendix.

6.6.7 Synthesis of Complex 6, [L_{Et}AlK(OAc)₂]

This followed an analogous procedure to that outlined above for complex **1**. AlEt₃ (0.20 g, 1.6 mmol) was added to a solution of L_{Et}H₂ (0.50 g, 1.5 mmol) in toluene (10 mL), under N₂ atmosphere, with stirring at room temperature for 24 h, yielding [L_{Et}AlEt] as a yellow precipitate (crude yield = 29 %). Acetic acid (0.01 g, 0.2 mmol) was added, under N₂ flow, to a stirring mixture of [L_{Et}AlEt] (0.08 g, 0.2 mmol) in toluene (10 mL). This was heated to 100 °C for 1.5 h, before being left stirring at room temperature for 48 h. [L_{Et}AlOAc] was then washed 2x with toluene and 1x with hexane before being dried, yielding a yellow precipitate (yield = 98 %). KOAc (15 mg, 0.16 mmol) was then added to [L_{Et}AlOAc] (65 mg, 0.16 mmol), in chloroform (10 mL), with stirring and under N₂ atmosphere. This was left stirring at room temperature for 20 h, before the solvent was removed under vacuum leaving [L_{Et}AlK(OAc)₂] (**6**), a yellow powder that was then purified by 3x toluene and 2x hexane washes (75 mg, 0.15 mmol, crude yield = 93 %). **¹H NMR** (CDCl₃, 400 MHz, 298 K): 8.47 (s, 2H, HC=N), 7.09 (dd, ³J = 8.00 Hz, ⁴J = 4.00 Hz, 2H, *o/p*-PhH), 7.01 ((dd, ³J = 8.00 Hz, ⁴J = 4.00 Hz, 2H, *o/p*-PhH), 6.74 (t, ³J = 8.00 Hz, 2H, *m*-PhH), 4.03 (s, 2H, HC-N), 3.91 (s, 6H, -OMeH), 1.79 (s, 6H, -OAcH). **¹³C NMR** (151 MHz, CDCl₃, 298 K): 178.34, 169.06, 156.00, 152.36, 126.61, 120.42, 116.79, 116.08, 55.89, 54.56, 23.67. **IR**: 350, 355, 360, 366, 373, 380, 386, 390, 398, 405, 416, 473, 496, 515, 539, 576, 600, 613, 625, 639, 733, 746, 783, 861, 911, 939, 962, 982, 1014, 1042, 1076, 1101, 1159, 1215, 1232, 1311, 1325, 1384, 1445, 1467, 1545, 1593, 1607, 1633, 1650, 2818, 2914, 2981, 3042 cm⁻¹. **MALDI-ToF**: 451 m/z [L_{Et}AlK(OAc)]⁺

For associated spectra see appendix.

6.7 COPASI Modelling Parameters

6.7.1 CO₂ Insertion Equilibria

Table 6.1 Parameters and rate equations used for COPASI models on CHO/CO₂ ROCOP catalysed by **2**. All modelling was performed using COPASI v4.42.

Model	Reaction	Rate Law	Parameters
Experimental Rate Law 12.5 bar CO ₂ (Fig. 3.6a)	Catalyst + CHO + CO ₂ → PCHC + Catalyst	$k^*[\text{cat}]^*[\text{CHO}][\text{CO}_2]$	$k = 0.0246 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$, fixed; [cat] ₀ = $2.47 \times 10^{-3} \text{ mol L}^{-1}$, fixed; [CHO] ₀ = 9.88 mol L^{-1} , reactions; [CO ₂] ₀ = 0.741 mol L^{-1} , reactions; [PCHC] ₀ = 0 mol L^{-1} , reactions.
Experimental Rate Law 25 bar CO ₂ (Fig. 3.6b)	Catalyst + CHO + CO ₂ → PCHC + Catalyst	$k_p^*[\text{cat}]^*[\text{CHO}]$	$k_p = 0.0315 \text{ L mol}^{-1} \text{ s}^{-1}$, fixed; [cat] ₀ = $2.47 \times 10^{-3} \text{ mol L}^{-1}$, fixed; [CHO] ₀ = 9.88 mol L^{-1} , reactions; [PCHC] ₀ = 0 mol L^{-1} , reactions.
Unified Rate Law 12.5 bar CO ₂ (Fig. 3.7a)	(1) Alkoxide + CO ₂ = Carbonate + PCHC (2) Carbonate + CHO → Alkoxide	(1) $K_{\text{eq}}^*[\text{alkoxide}]^*[\text{CO}_2]$ (2) $k_p^*[\text{carbonate}]^*[\text{CHO}]$	$K_{\text{eq}} = 2.73 \text{ L mol}^{-1} \text{ s}^{-1}$, fixed; [alkoxide] ₀ = 0 mol L^{-1} , reactions; [CO ₂] ₀ = 0.741 mol L^{-1} , reactions; $k_p = 0.0246 \text{ L mol}^{-1} \text{ s}^{-1}$, fixed; [carbonate] ₀ = $2.47 \times 10^{-3} \text{ mol L}^{-1}$, reactions; [CHO] ₀ = 9.88 mol L^{-1} , reactions; [PCHC] ₀ = 0 mol L^{-1} , reactions.
Unified Rate Law 25 bar CO ₂ (Fig. 3.7b)	(1) Carbonate + CHO → Alkoxide (2) Alkoxide + CO ₂ = Carbonate + PCHC	$k_p^*[\text{carbonate}]^*[\text{CHO}]$	$k_p = 0.0315 \text{ L mol}^{-1} \text{ s}^{-1}$, fixed; [carbonate] ₀ = $2.47 \times 10^{-3} \text{ mol L}^{-1}$, fixed; [CHO] ₀ = 9.88 mol L^{-1} , reactions; [PCHC] ₀ = 0 mol L^{-1} , reactions.

6.7.2 CTA Rate Enhancement Tests

Table 6.2 Parameters and rate equations used for COPASI models on CHO/PA ROCOP with BnOH catalysed by **1**. All modelling was performed using COPASI v4.42.

Model	Reaction	Rate Law	Parameters
Pathway 1 without CTA	Catalyst + CHO + PA → PCHPE + Catalyst	$k_1[\text{cat}][\text{CHO}]$	$k_1 = 8.91 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$, fixed; $[\text{cat}]_0 = 4.94 \times 10^{-3} \text{ mol L}^{-1}$, fixed; $[\text{CHO}]_0 = 9.88 \text{ mol L}^{-1}$, reactions; $[\text{PCHPE}]_0 = 0 \text{ mol L}^{-1}$, reactions.
Pathway 2 with CTA	Catalyst + BnOH + CHO + PA → PCHPE + Catalyst	$k_2[\text{cat}][\text{CHO}][\text{BnOH}]$	$k_2 = 0.0409 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$, fixed; $[\text{cat}]_0 = 4.94 \times 10^{-3} \text{ mol L}^{-1}$, fixed; $[\text{CHO}]_0 = 9.88 \text{ mol L}^{-1}$, reactions; $[\text{BnOH}]_0 = 0.186 \text{ mol L}^{-1}$, fixed; $[\text{PCHPE}]_0 = 0 \text{ mol L}^{-1}$, reactions.

6.8 References

- (1) Dakshinamoorthy, D.; Weinstock, A. K.; Damodaran, K.; Iwig, D. F.; Mathers, R. T. Diglycerol-Based Polyesters: Melt Polymerization with Hydrophobic Anhydrides. *ChemSusChem* **2014**, 7 (10), 2923-2929. DOI: 10.1002/cssc.201402249.
- (2) Cosier, J.; Glazer, A. M. A nitrogen-gas-stream cryostat for general X-ray diffraction studies. *J. Appl. Crystallogr.* **1986**, 19 (2), 105-107. DOI: 10.1107/s0021889886089835.
- (3) *CrysAlisPRO*; Oxford Diffraction / Agilent Technologies UK Ltd, Yarnton, England.
- (4) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, 42 (2), 339-341. DOI: 10.1107/s0021889808042726.
- (5) *Bindfit*. <http://supramolecular.org> (accessed December 2024).
- (6) Thordarson, P. Determining association constants from titration experiments in supramolecular chemistry. *Chem. Soc. Rev.* **2011**, 40 (3), 1305-1323. DOI: 10.1039/c0cs00062k.

- (7) Brynn Hibbert, D.; Thordarson, P. The death of the Job plot, transparency, open science and online tools, uncertainty estimation methods and other developments in supramolecular chemistry data analysis. *Chemical Communications* **2016**, 52 (87), 12792-12805. DOI: 10.1039/c6cc03888c.
- (8) Aguiari, A.; Bullita, E.; Casellato, U.; Guerriero, P.; Tamburini, S.; Vigato, P. A. Macrocyclic and macroacyclic compartmental Schiff bases: synthesis, characterization, X-ray structure and interaction with metal ions. *Inorg. Chim. Acta* **1992**, 202 (2), 157-171. DOI: 10.1016/s0020-1693(00)86831-0.
- (9) Thevenon, A.; Garden, J. A.; White, A. J.; Williams, C. K. Dinuclear Zinc Salen Catalysts for the Ring Opening Copolymerization of Epoxides and Carbon Dioxide or Anhydrides. *Inorg. Chem.* **2015**, 54 (24), 11906-11915. DOI: 10.1021/acs.inorgchem.5b02233.
- (10) Bermejo, M. R.; Fernández, M. I.; Gómez-Fórneas, E.; González-Noya, A.; Maneiro, M.; Pedrido, R.; Rodríguez, M. J. Self-Assembly of Dimeric MnIII-Schiff-Base Complexes Tuned by Perchlorate Anions. *Eur. J. Inorg. Chem.* **2007**, 2007 (24), 3789-3797. DOI: 10.1002/ejic.200700199.
- (11) Jiang, Y.; Gong, L.; Feng, X.; Hu, W.; Pan, W.; Li, Z.; Mi, A. Salen-Ti(OR)₄ complex catalysed trimethylsilylcyanation of aldehydes. *Tetrahedron* **1997**, 53 (42), 14327-14338. DOI: 10.1016/s0040-4020(97)00984-8.
- (12) Routaray, A.; Nath, N.; Mantri, S.; Maharana, T.; Sutar, A. K. Synthesis and structural studies of copper(II) complex supported by –ONNO– tetradentate ligand: Efficient catalyst for the ring-opening polymerization of lactide. *Chin. J. Catal.* **2015**, 36 (5), 764-770. DOI: 10.1016/s1872-2067(14)60293-x.
- (13) Diment, W. T.; Gregory, G. L.; Kerr, R. W. F.; Phanopoulos, A.; Buchard, A.; Williams, C. K. Catalytic Synergy Using Al(III) and Group 1 Metals to Accelerate Epoxide and Anhydride Ring-Opening Copolymerizations. *ACS Catal.* **2021**, 11 (20), 12532-12542. DOI: 10.1021/acscatal.1c04020.

Appendix

Table of Figures

Figure S2.1. ^1H NMR Spectrum of $\text{LC}_2\text{Me}_2\text{H}_2$ ($\text{CDCl}_3(\#)$, 298 K, 400 MHz).	198
Figure S2.2. ^1H NMR Spectra of synthesis route for complex 1 .	198
Figure S2.3. ^{13}C NMR Spectrum of complex 1 ($\text{CDCl}_3(\#)$, 298 K, 151 MHz).	199
Figure S2.4. ^{27}Al NMR Spectrum of complex 1 (CDCl_3 , 298 K, 104 MHz).	199
Figure S2.5. ^1H COSY NMR Spectrum of complex 1 (CDCl_3 , 298 K, 400 MHz).	200
Figure S2.6. ^1H - ^{13}C HSQC NMR Spectrum of complex 1 (CDCl_3 , 298 K).	200
Figure S2.7. ^1H - ^{13}C HMBC NMR Spectrum of complex 1 (CDCl_3 , 298 K).	201
Figure S2.8. ^1H NMR Spectrum of complex 2 ($\text{CDCl}_3(\#)$, 298 K, 400 MHz).	201
Figure S2.9. ^{13}C NMR Spectrum of complex 2 ($\text{CDCl}_3(\#)$, 298 K, 151 MHz).	202
Figure S2.10. ^{27}Al NMR spectrum of complex 2 (CDCl_3 , 298 K, 104 MHz).	202
Figure S2.11. ^1H COSY NMR Spectrum of complex 2 (CDCl_3 , 298 K, 400 MHz).	203
Figure S2.12. ^1H - ^{13}C HSQC NMR Spectrum of complex 2 (CDCl_3 , 298 K).	203
Figure S2.13. ^1H - ^{13}C HMBC NMR Spectrum of complex 2 (CDCl_3 , 298 K).	204
Figure S2.14. ^1H NMR Spectrum of $\text{LC}_{\text{C}2\text{Ph}2}\text{H}_2$ ($\text{CDCl}_3(\#)$, 298 K, 400 MHz).	204
Figure S2.15. ^1H NMR spectrum of complex 3 ($\text{CDCl}_3(\#)$, 298 K, 400 MHz).	205
Figure S2.16. ^{13}C NMR Spectrum of complex 3 ($\text{CDCl}_3(\#)$, 298 K, 151 MHz).	205
Figure S2.17. ^{27}Al NMR spectrum of complex 3 (CDCl_3 , 298 K, 104 MHz).	206
Figure S2.18. ^1H COSY NMR Spectrum of complex 3 (CDCl_3 , 298 K, 400 MHz).	206
Figure S2.19. ^1H - ^{13}C HSQC NMR Spectrum of complex 3 (CDCl_3 , 298 K).	207
Figure S2.20. ^1H - ^{13}C HMBC NMR Spectrum of complex 3 (CDCl_3 , 298 K).	207
Figure S2.21. ^1H NMR Spectrum of $\text{L}_{\text{Phen}}\text{H}_2$ ($\text{CDCl}_3(\#)$, 298 K, 400 MHz).	208
Figure S2.22. ^1H NMR spectrum of complex 4 (DMSO ($\#$), 298 K, 400 MHz).	208
Figure S2.23. ^{13}C NMR Spectrum of complex 4 (DMSO($\#$), 298 K, 151 MHz).	209
Figure S2.24. ^{27}Al NMR spectrum of complex 4 (DMSO, 298 K, 104 MHz).	209
Figure S2.25. ^1H COSY NMR Spectrum of complex 4 (DMSO, 298 K, 400 MHz).	210
Figure S2.26. ^1H - ^{13}C HSQC NMR Spectrum of complex 4 (DMSO, 298 K).	210
Figure S2.27. ^1H - ^{13}C HMBC NMR Spectrum of complex 4 (DMSO, 298 K).	211
Figure S2.28. ^1H NMR Spectrum of $\text{L}_{\text{Pro}}\text{H}_2$ ($\text{CDCl}_3(\#)$, 298 K, 400 MHz).	211
Figure S2.29. ^1H NMR spectrum of complex 5 ($\text{CDCl}_3(\#)$, 298 K, 400 MHz).	212
Figure S2.30. ^{13}C NMR Spectrum of complex 5 (CD_2Cl_2 ($\#$), 298 K, 151 MHz).	212
Figure S2.31. ^{27}Al NMR spectrum of complex 5 (CDCl_3 , 298 K, 104 MHz).	213
Figure S2.32. ^1H COSY NMR Spectrum of complex 5 (CD_2Cl_2 , 298 K, 400 MHz).	213
Figure S2.33. ^1H - ^{13}C HSQC NMR Spectrum of complex 5 (CD_2Cl_2 , 298 K).	214
Figure S2.34. ^1H - ^{13}C HMBC NMR Spectrum of complex 5 (CD_2Cl_2 , 298 K).	214
Figure S2.35. ^1H NMR Spectrum of $\text{L}_{\text{Et}}\text{H}_2$ ($\text{CD}_3\text{CN}(\#)$, 298 K, 400 MHz).	215
Figure S2.36. ^1H NMR spectrum of complex 6 ($\text{MeOD-d}_4(\#)$, 298 K, 400 MHz).	215
Figure S2.37. ^{13}C NMR Spectrum of complex 6 ($\text{MeOD-d}_4(\#)$, 298 K, 151 MHz).	216

Figure S2.38. ^{27}Al NMR spectrum of complex 6 (MeOD- d_4 , 298 K, 104 MHz).	216
Figure S2.39. ^1H COSY NMR Spectrum of complex 6 (MeOD- d_4 , 298 K, 400 MHz).	217
Figure S2.40. ^1H - ^{13}C HSQC NMR Spectrum of complex 6 (MeOD- d_4 , 298 K).	217
Figure S2.41. ^1H - ^{13}C HMBC NMR Spectrum of complex 6 (MeOD- d_4 , 298 K).	218
Figure S2.42. IR spectrum of complex 1 .	220
Figure S2.43. MALDI-TOF spectrum of complex 1 .	220
Figure S2.44. IR spectrum of complex 2 .	221
Figure S2.45. MALDI-ToF spectrum of complex 2 .	221
Figure S2.46. IR spectrum of complex 3 .	222
Figure S2.47. MALDI-ToF spectrum of complex 3 .	222
Figure S2.48. IR spectrum of complex 4 .	223
Figure S2.49. MALDI-ToF spectrum of complex 4 .	223
Figure S2.50. IR spectrum of complex 5 .	224
Figure S2.51. MALDI-ToF spectrum of complex 5 .	224
Figure S2.52. IR spectrum of complex 6 .	225
Figure S2.53. MALDI-ToF spectrum of complex 6 .	225
Figure S2.54. DOSY NMR spectrum (500 MHz, MeOD- d_4 , 298 K) of complex 1 .	226
Figure S2.55. Excerpt of ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of reactant and products of CHO/PA copolymerization.	227
Figure S2.56. DOSY ^1H NMR spectrum (CDCl_3) of polymer formed by PA/CHO ROCOP using catalyst 4 .	228
Figure S2.57. VT ^1H NMR spectra (400 MHz, CD_2Cl_2) of 1.32 .	228
Figure S2.58. VT ^1H NMR spectra (400 MHz, CD_2Cl_2) of 5 .	228
Figure S2.59. Graph of [PA] against time for CHO/PA ROCOP catalysed by complex 3 .	229
Figure S2.60. Plot of change in polymer molar mass and dispersity with increasing PA conversion for complex 2 .	229
Figure S2.61. Plot of change in polymer molar mass and dispersity with increasing PA conversion for complex 3 .	230
Figure S2.62. Diagrams of the two key transition states being studied by DFT.	232
Figure S2.63. Computed Reaction Profile for epoxide ring-opening using 1 .	232
Figure S2.64. Computed Reaction Profile for epoxide ring-opening using 4 .	233
Figure S2.65. Graph showing the linear correlation between [PA] (mol dm^{-3}) and time (s).	234
Figure S2.66. TGA of 100 °C isotherm of 1 .	235
Figure S2.67. TGA of 100 °C isotherm of 1 + GEO.	235
Figure S2.68. TGA of 100 °C isotherm of 1.32 .	236
Figure S2.69. TGA of 100 °C isotherm of 1.32 + GEO.	236
Figure S2.70. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of isolated polymer from the polymerisation of CHO/PA.	237
Figure S2.71. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of isolated polymer from the polymerisation of vCHO/PA.	237
Figure S2.72. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of PO/PA polymerisation reaction mixture.	238
Figure S2.73. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of isolated polymer from the polymerisation of AGE/PA.	238

Figure S2.74. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of isolated polymer from the polymerisation of CHO/NBA.	239
Figure S2.75. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of isolated polymer from the polymerisation of CHO/TGA.	239
Figure S2.76. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of isolated polymer from the polymerisation of CHO/DGA.	240
Figure S2.77. GPC plot of CHO/PA polymerisation at full conversion.	240
Figure S2.78. GPC plot of vCHO/PA polymerisation at full conversion.	241
Figure S2.79. GPC plot of PO/PA polymerisation at full conversion.	241
Figure S2.80. GPC plot of AGE/PA polymerisation at full conversion.	241
Figure S2.81. GPC plot of CHO/NBA polymerisation at full conversion.	242
Figure S2.82. GPC plot of CHO/TGA polymerisation at full conversion.	242
Figure S2.83. GPC plot of CHO/DGA polymerisation at full conversion.	242
Figure S2.84. Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3 , 298 K) of isolated PO/PA polymer.	243
Figure S3.1 Excerpt of ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of CHO/ CO_2 copolymerization mixture.	244
Figure S3.2 GPC trace of CHO/ CO_2 polymerisation catalysed by 1	245
Figure S3.3 GPC trace of CHO/ CO_2 polymerisation catalysed by 2	245
Figure S3.4 GPC trace of CHO/ CO_2 polymerisation catalysed by 3	245
Figure S3.5 GPC trace of CHO/ CO_2 polymerisation catalysed by 4	246
Figure S3.6 GPC trace of CHO/ CO_2 polymerisation catalysed by 6	246
Figure S3.7 Graph of conversion (%) vs. time (s) for a typical high pressure CO_2 polymerisation.	247
Figure S3.8 Graph of $\ln([\text{CHO}]_t/[\text{CHO}]_0)$ against time (s) for the data presented in Figure S3.7.	247
Figure S3.9 ^1H NMR spectra of 2 before and after DSC thermal stability test.	248
Figure S3.10 ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of aliquot of vCHO/ CO_2 copolymerization.	248
Figure S3.11 Graph of $[\text{CO}_2]$ vs. $p(\text{CO}_2)$ taken from (DOI:) 10.1016/j.supflu.2011.12.015 at 100 °C for CHO with linear fit necessarily passing through origin.	249
Figure S3.12 Graph of $1/k_{\text{obs}}$ vs. $1/[\text{CO}_2]$ for the polymerisation data from 2	251
Figure S3.13 Graph of k_{obs} vs. $[\text{CO}_2]$ for CHO/ CO_2 copolymerisation catalysed by 2 . Blue squares are the data collected. Orange circles are the values obtained by the Michaelis-Menten model.	251
Figure S3.14 Graph of k_{obs} vs. $[\text{CO}_2]$ for PO/ CO_2 copolymerisation catalysed by a Co(III)/K(I) catalyst. Blue squares are the data collected. Orange circles are the values obtained by the Michaelis-Menten model.	252
Figure S3.15 Graph of k_{obs} vs. $[\text{CO}_2]$ for CHO/ CO_2 copolymerisation catalysed by a monometallic Zn BDI catalyst. Blue squares are the data collected. Orange circles are the values obtained using the Michaelis-Menten model.	252
Figure S3.16 Graph of k_{obs} vs. $[\text{CO}_2]$ for CHO/ CO_2 copolymerisation catalysed by a di-Zn BDI catalyst. Blue squares are the data collected. Orange circles are the values obtained by the Michaelis-Menten model.	253
Figure S3.17 ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of backbiting reaction mixture at completion.	254
Figure S4.1 Plot of $[\text{PCHPE}]$ (mol dm^{-3}) vs. time (s) for $[1]:[\text{PA}]:[\text{CHO}] = 1:400:2000$,	255
Figure S4.2 Plot of $[\text{PCHPE}]$ (mol dm^{-3}) vs. time (s) for $[1]:[\text{BnOH}]:[\text{PA}]:[\text{CHO}] = 1:50:400:2000$	255
Figure S4.3 GPC trace of polymer at full conversion for the Toluene control reaction of partway addition.	256

Figure S4.4 Graph of the offset in [PA] between [PA] ₀ and the intercept from the linear fitting of aliquots against equivalents of BnOH added.....	256
Figure S4.5 Plot of Concentration (mol L ⁻¹) against Time (s) for the reaction [1]:[BnOH]:[PA]:[CHO] = 1:25:400:2000, [PA] experimental (blue square), [PA] COPASI model (blue circle), [PCHPE] experimental (orange square), [PCHPE] COPASI model (orange circle).....	257
Figure S4.6 ¹ H NMR spectra (CDCl ₃ (#), 298 K, 400 MHz) of 1 with increasing equiv of BnOH (0 – 400).....	258

Table of Tables

Table S2.1. Selected bond lengths for L _{Cyc} AlK(OAc) ₂ (2).....	218
Table S2.2. Selected bond lengths for L _{Pro} AlK(OAc) ₂ (5).....	218
Table S2.3. Summary of crystallographic refinement data for complexes 1 , 2 & 5	219
Table S2.4. ¹ H Chemical Shifts for the reactant and products of CHO/PA copolymerization in CDCl ₃	227
Table S2.5. Summary of computed values for catalyst 1	231
Table S2.6. Summary of computed values for catalyst 4	231
Table S2.7. Rates for the ROCOP of CHO/PA using complex 1 with different CHD loadings.....	233
Table S2.8. Rates for the ROCOP of CHO/PA using complex 1.32 with different CHD loadings.....	234
Table S2.9. Rates for the ROCOP of epoxide/PA using complex 1 with different CHD loadings.....	243
Table S3.1. ¹ H Chemical Shifts for the reactant and products of CHO/CO ₂ copolymerization in CDCl ₃	244
Table S3.2. Rate data for CHO/CO ₂ ROCOP catalysed at different [2].	249
Table S3.3. Conversions from <i>p</i> (CO ₂) to [CO ₂] and associated rate data for CHO/CO ₂ ROCOP.	250
Table S3.4. Rate data for forward reaction of Eyring analysis.....	253
Table S3.5. Data from aliquot of backbiting test.	254
Table S3.6. Rate data for backbiting Eyring analysis	254
Table S4.1. Table showing rate of reaction, <i>k</i> _{obs} (x 10 ⁻⁴ mol dm ⁻³ s ⁻¹), both experimental and modelled by COPASI, for different [BnOH] (mol dm ⁻³).....	257
Table S4.2. Table showing [cat] and [BnOH] for the NMR binding studies along with the ¹ H NMR shift associated with the methoxy protons in 1	259
Table S4.3. Crystallographic refinement data for [1 •H ₂ O]	260

2 Supplementary Figures and Tables for Chapter 2

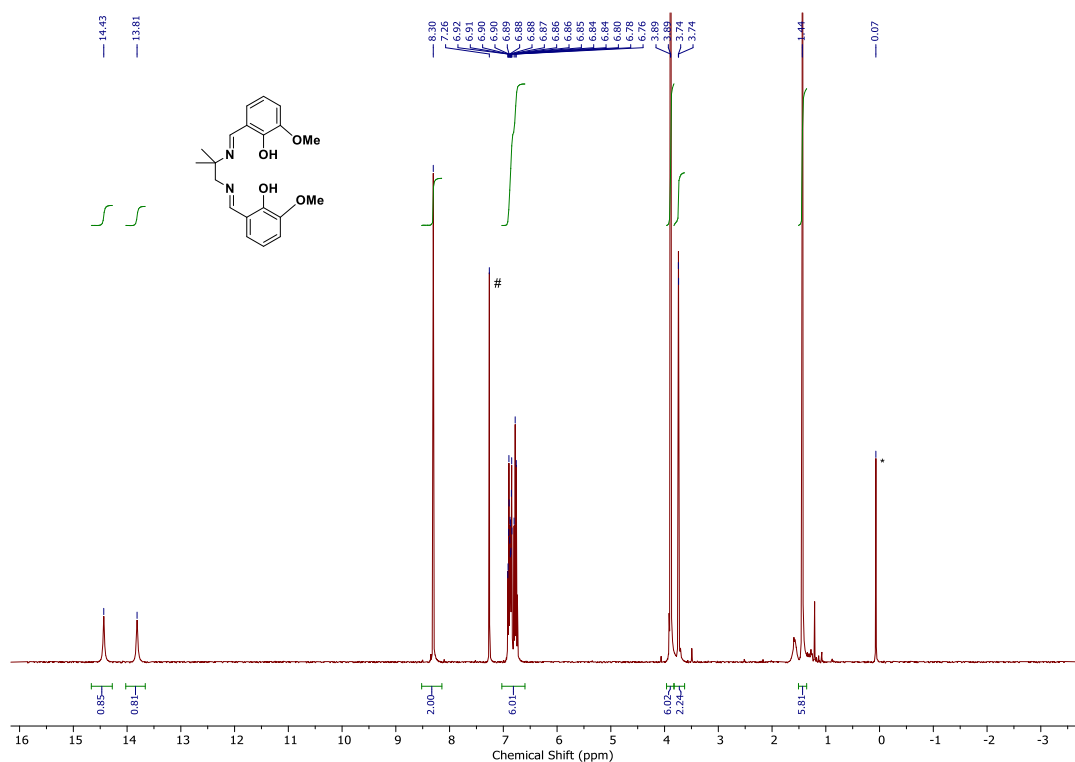


Figure S2.1. 1H NMR Spectrum of $Lc2Me2H2$ ($CDCl_3$ (#), 298 K, 400 MHz) *: impurity from grease.

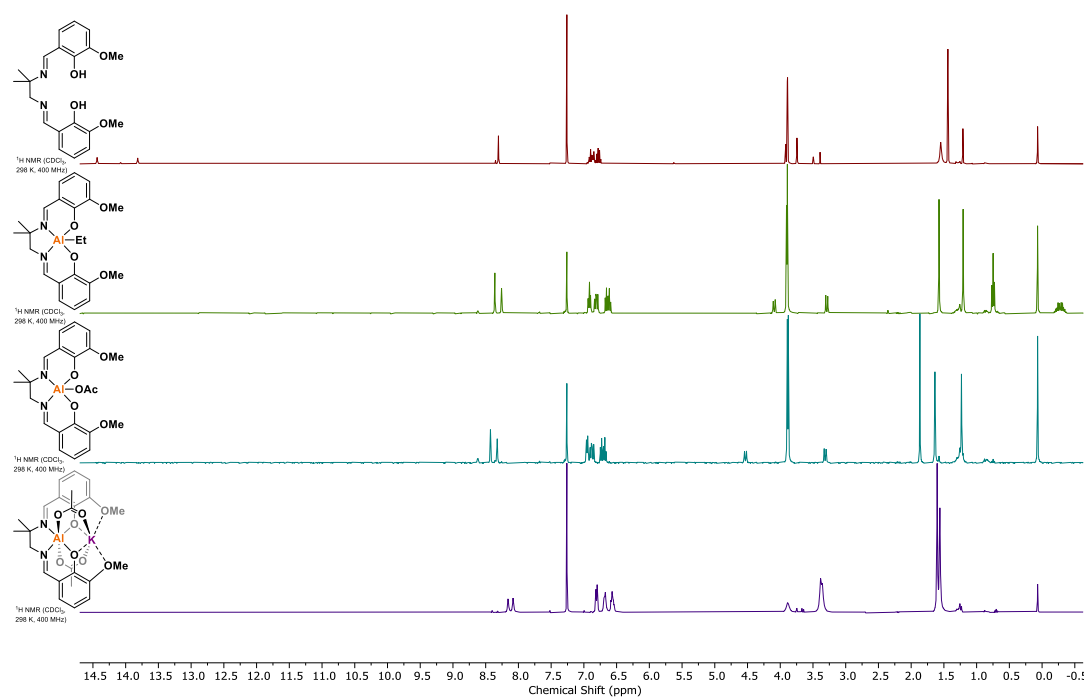


Figure S2.2. 1H NMR Spectra of synthesis route for complex **1**.

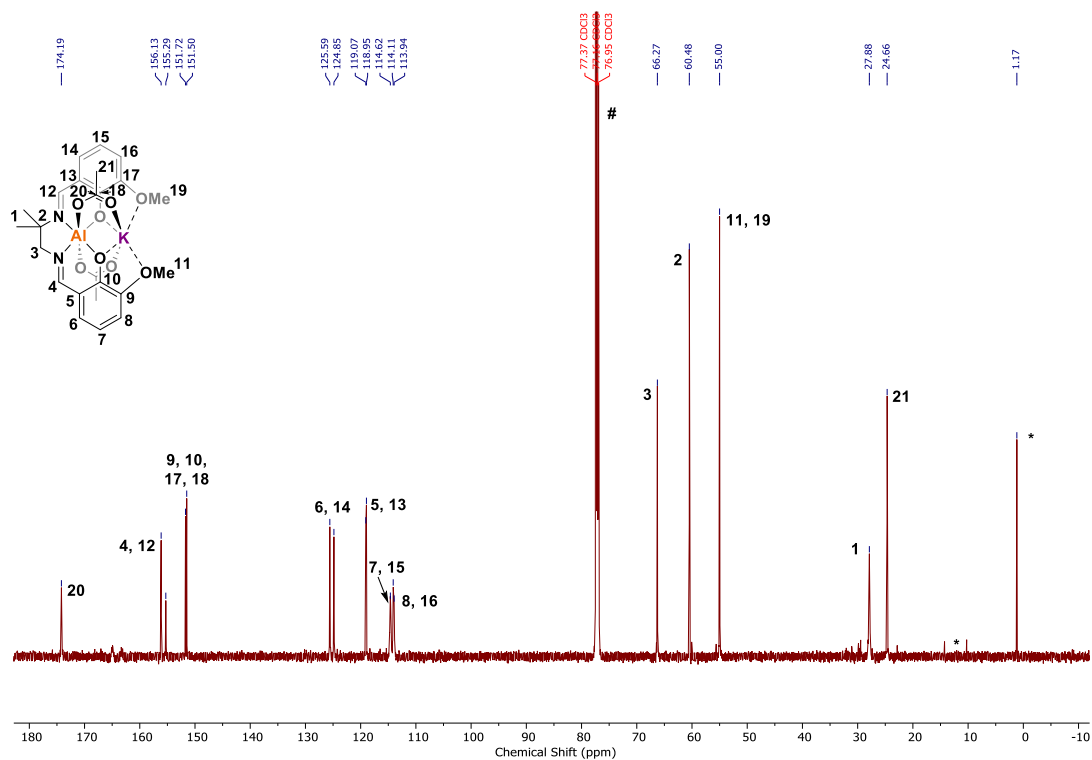


Figure S2.3. ¹³C NMR Spectrum of complex **1** (CDCl₃(#), 298 K, 151 MHz) *: impurities from grease and hexane (in glovebox atmosphere).

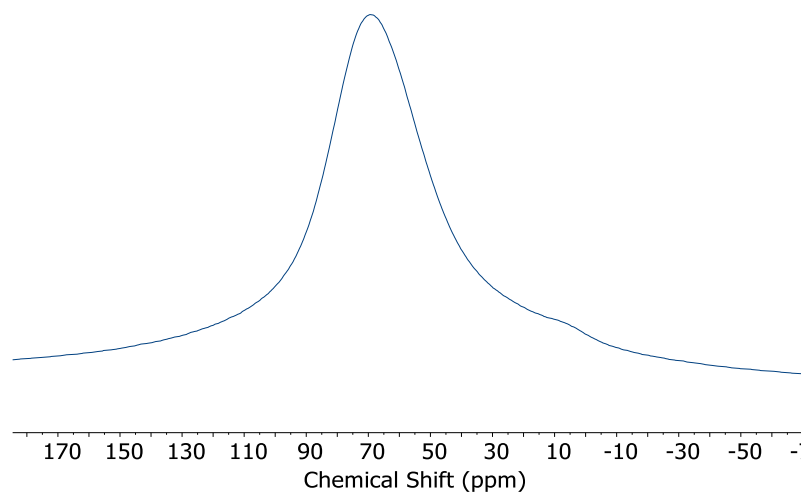


Figure S2.4. ²⁷Al NMR Spectrum of complex **1** (CDCl₃, 298 K, 104 MHz).

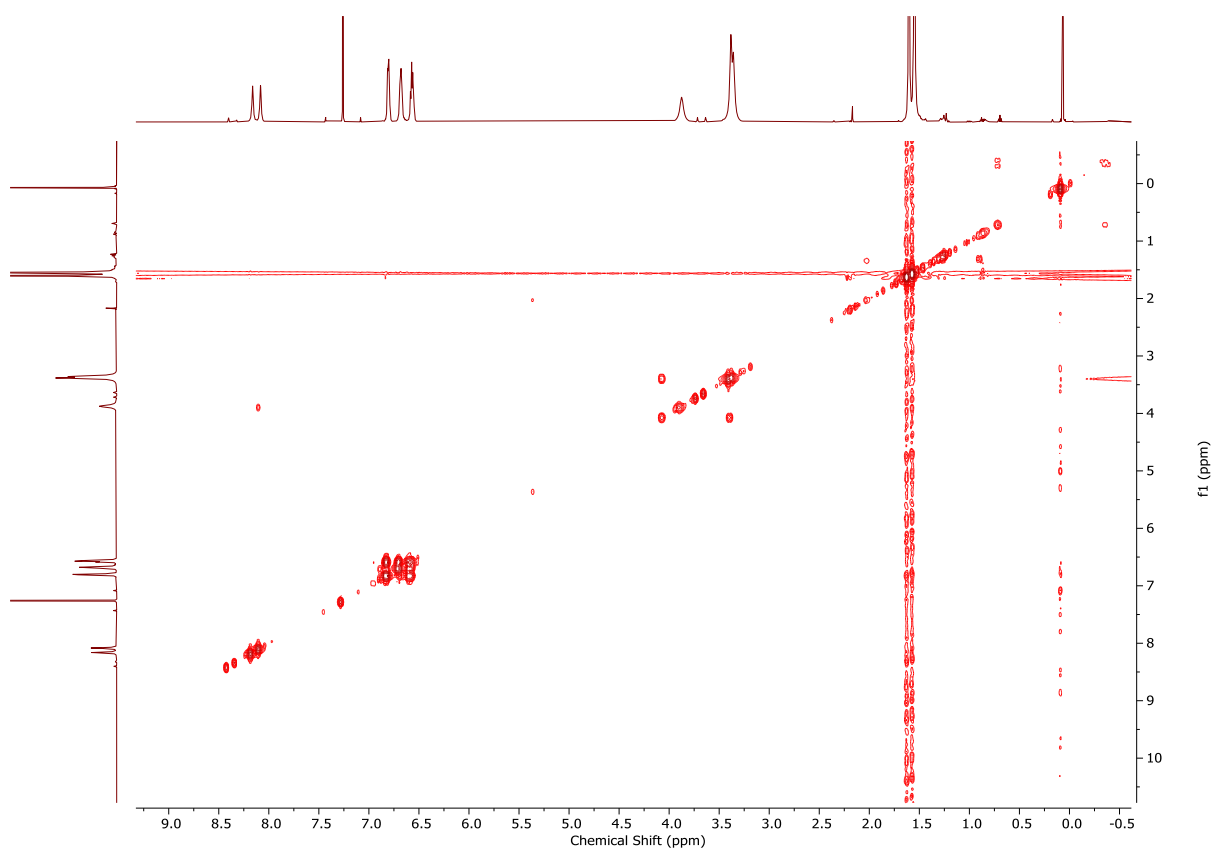


Figure S2.5. ^1H COSY NMR Spectrum of complex **1** (CDCl_3 , 298 K, 400 MHz).

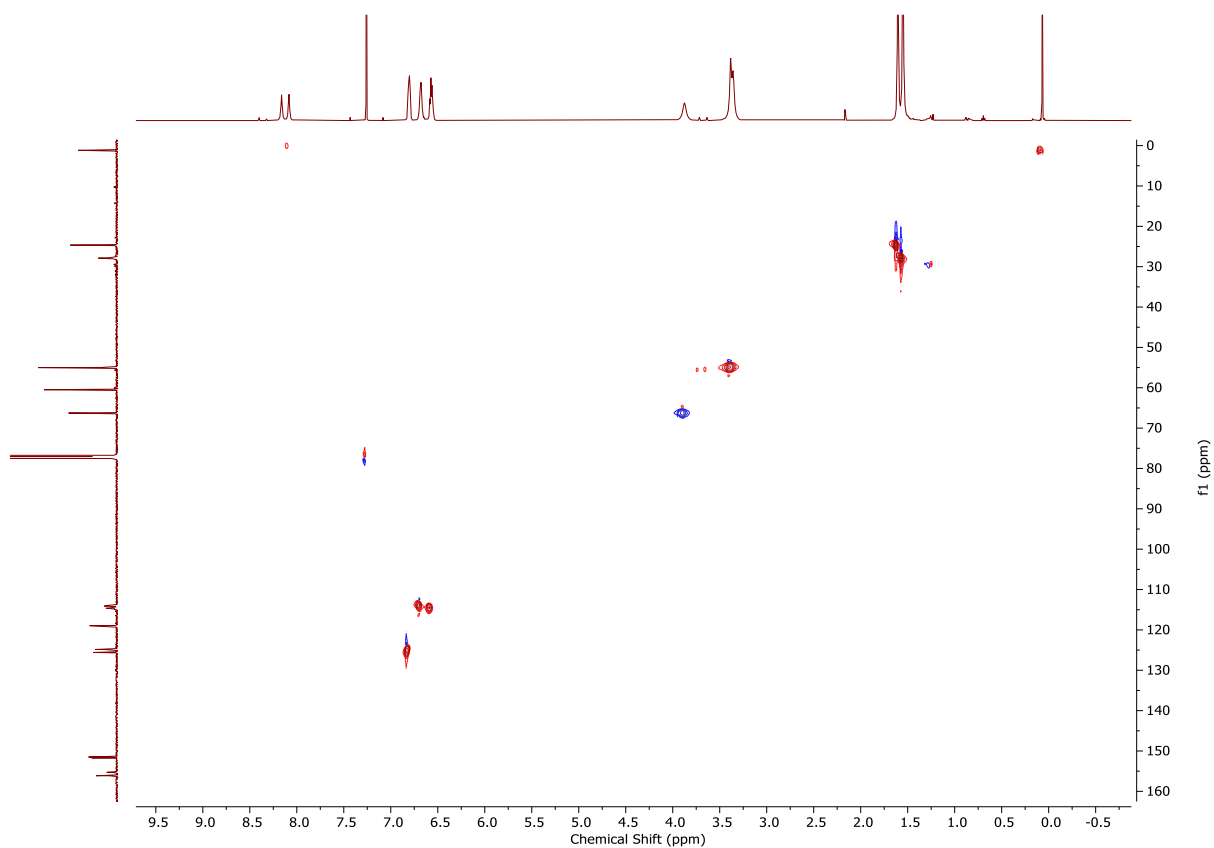


Figure S2.6. ^1H - ^{13}C HSQC NMR Spectrum of complex **1** (CDCl_3 , 298 K).

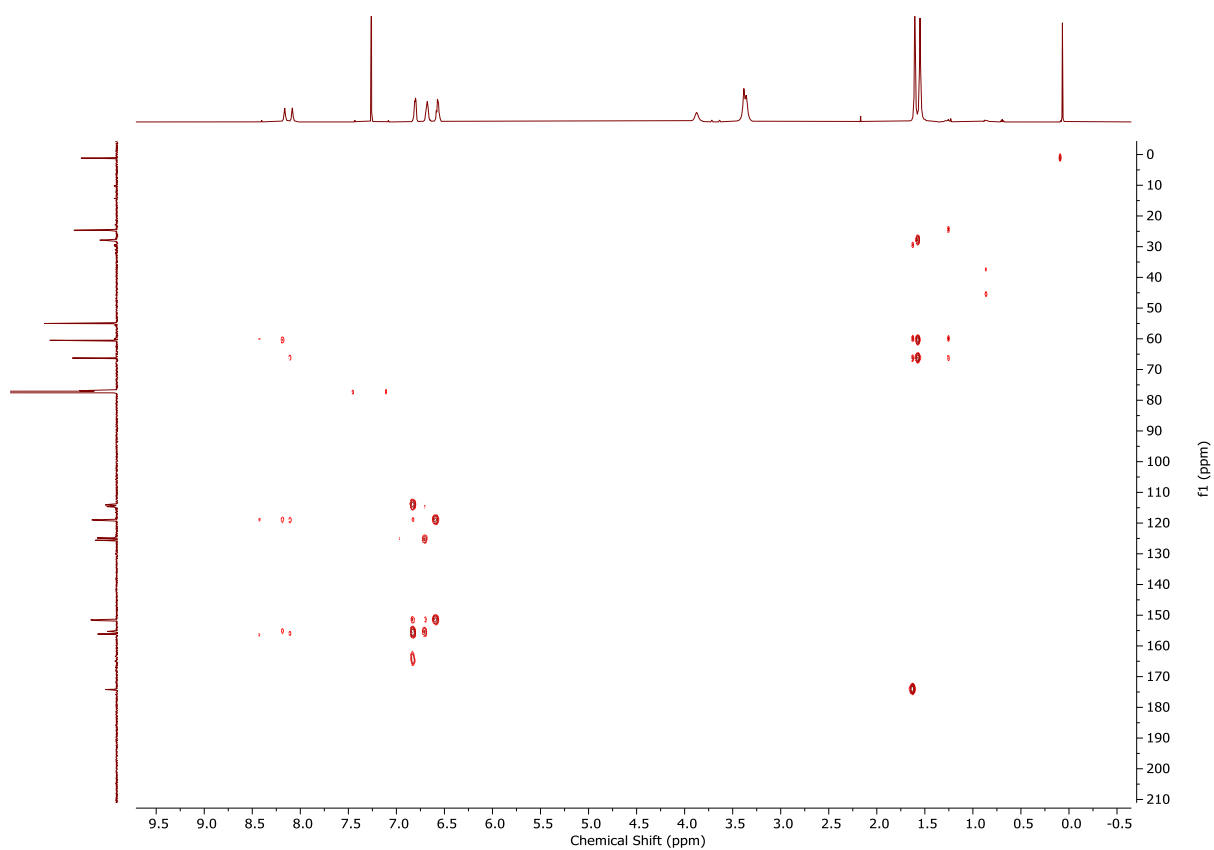


Figure S2.7. ^1H - ^{13}C HMBC NMR Spectrum of complex **1** (CDCl_3 , 298 K).

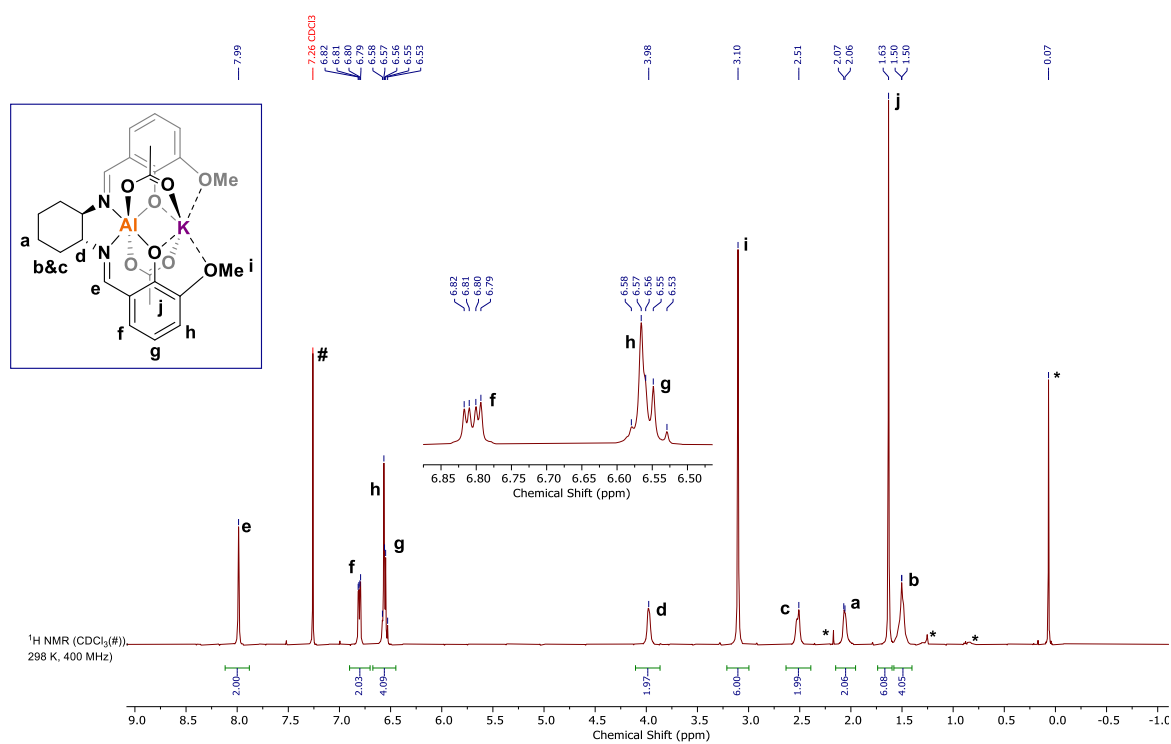


Figure S2.8. ^1H NMR Spectrum of complex **2** ($\text{CDCl}_3(\#)$, 298 K, 400 MHz) *: impurities from grease and hexane (in glovebox atmosphere).

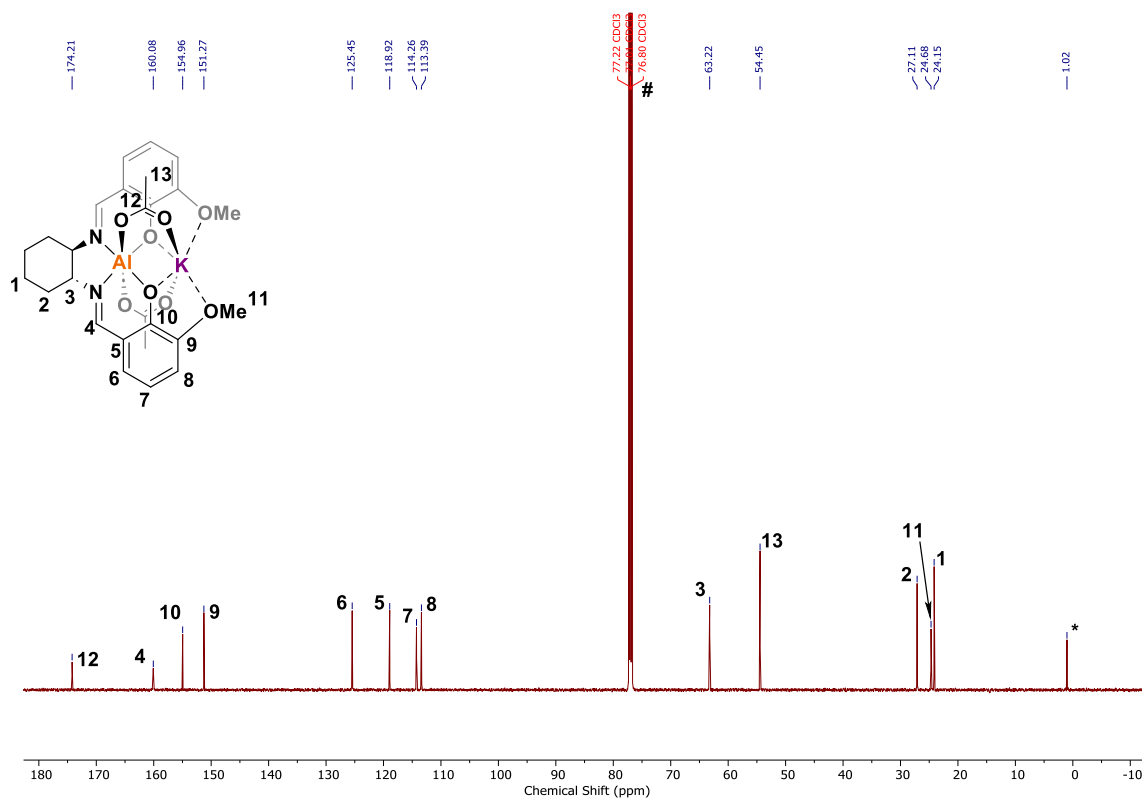


Figure S2.9. ^{13}C NMR Spectrum of complex **2** ($\text{CDCl}_3(\#)$, 298 K, 151 MHz) *: impurity from grease.

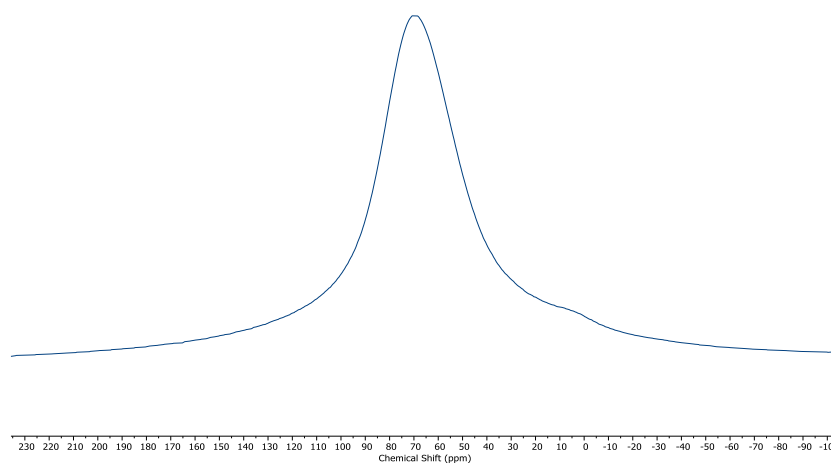


Figure S2.10. ^{27}Al NMR spectrum of complex **2** (CDCl_3 , 298 K, 104 MHz).

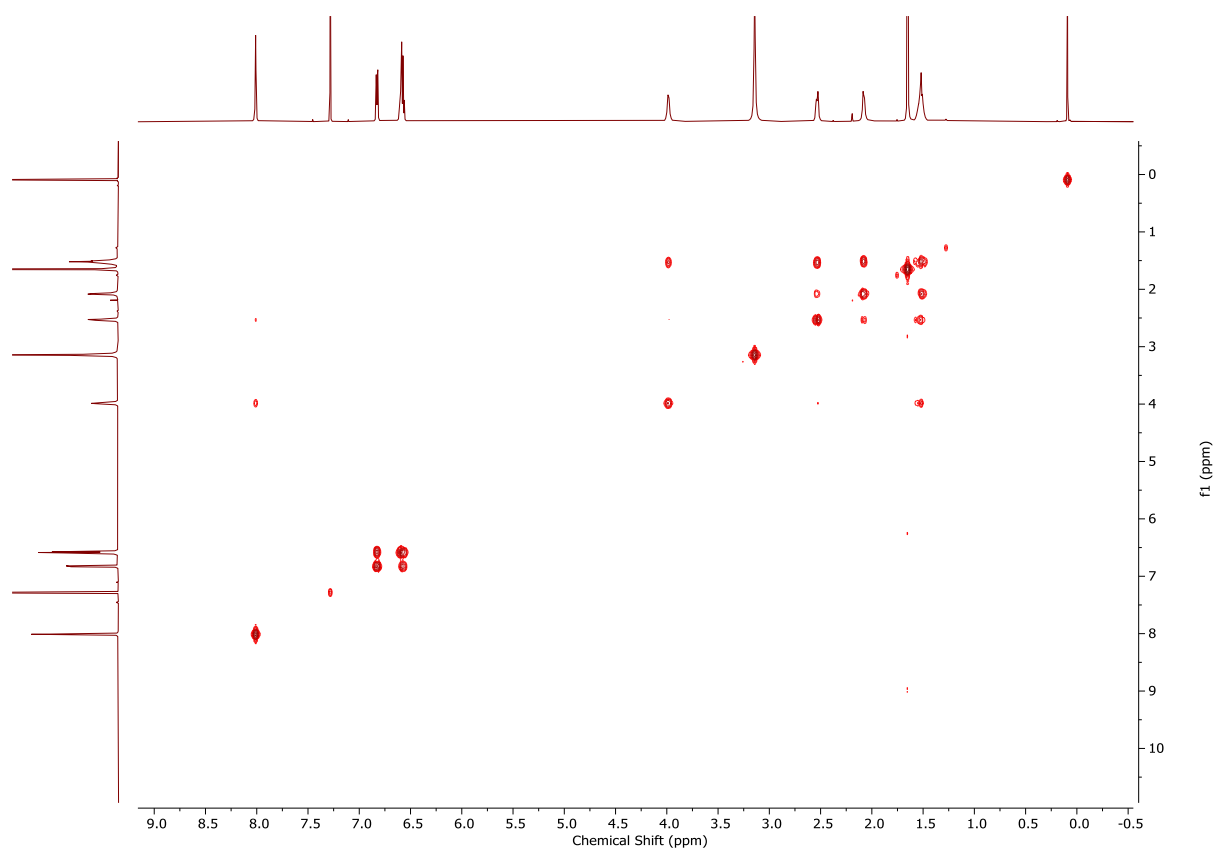


Figure S2.11. ^1H COSY NMR Spectrum of complex **2** (CDCl_3 , 298 K, 400 MHz).

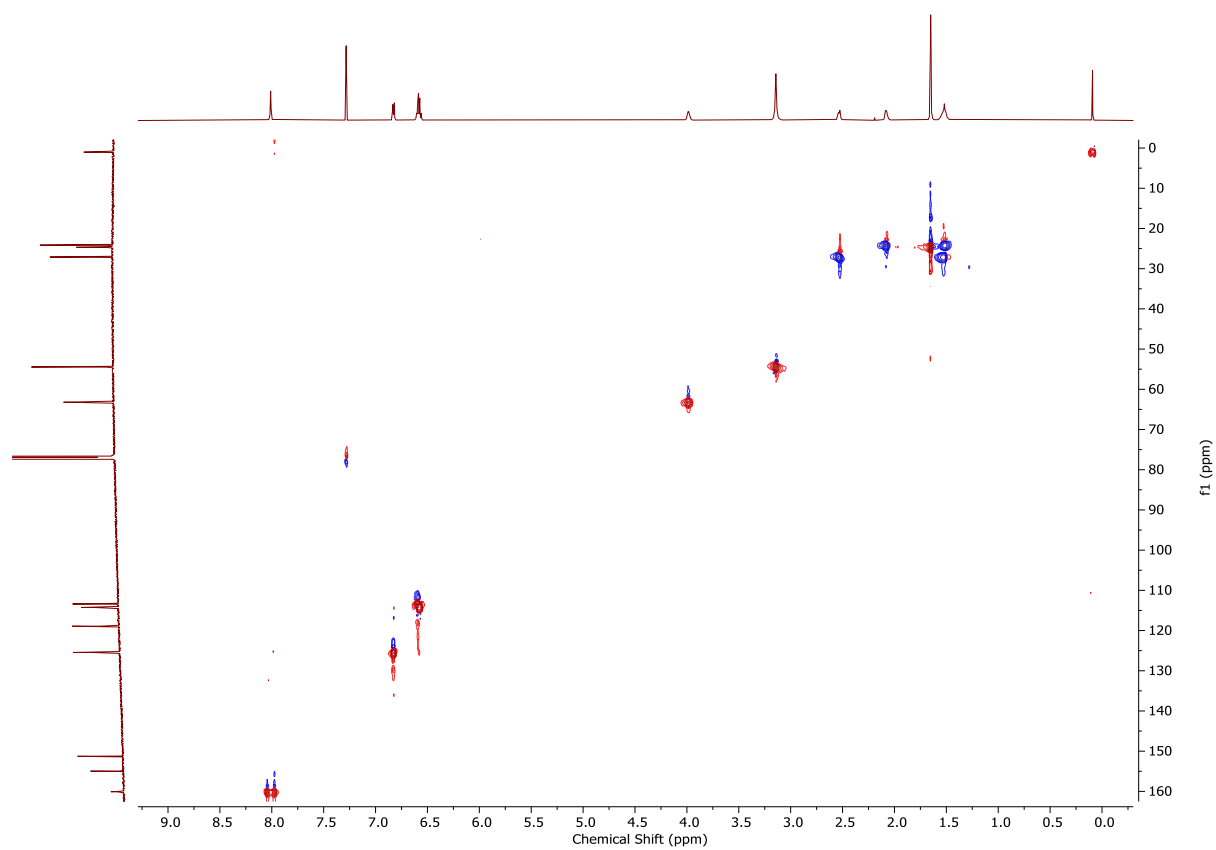


Figure S2.12. ^1H - ^{13}C HSQC NMR Spectrum of complex **2** (CDCl_3 , 298 K).

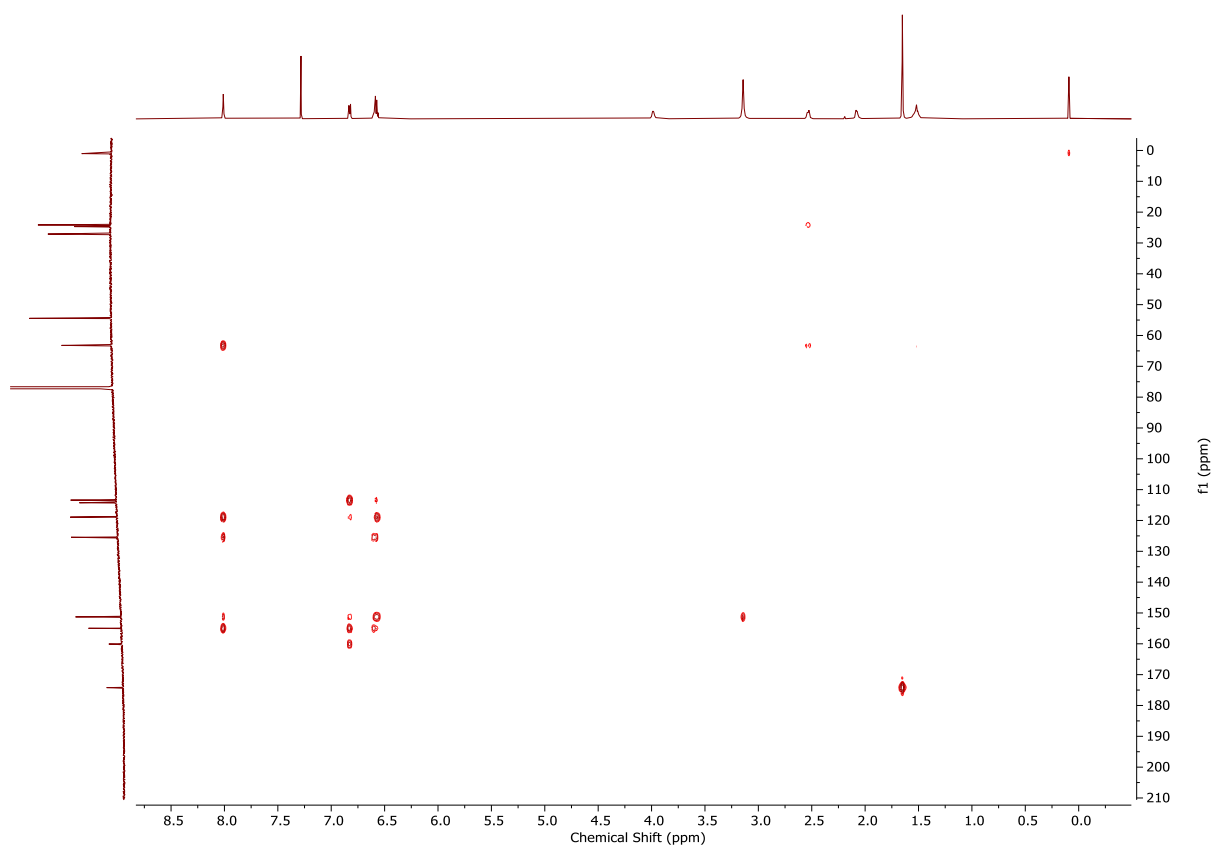


Figure S2.13. ^1H - ^{13}C HMBC NMR Spectrum of complex **2** (CDCl_3 , 298 K).

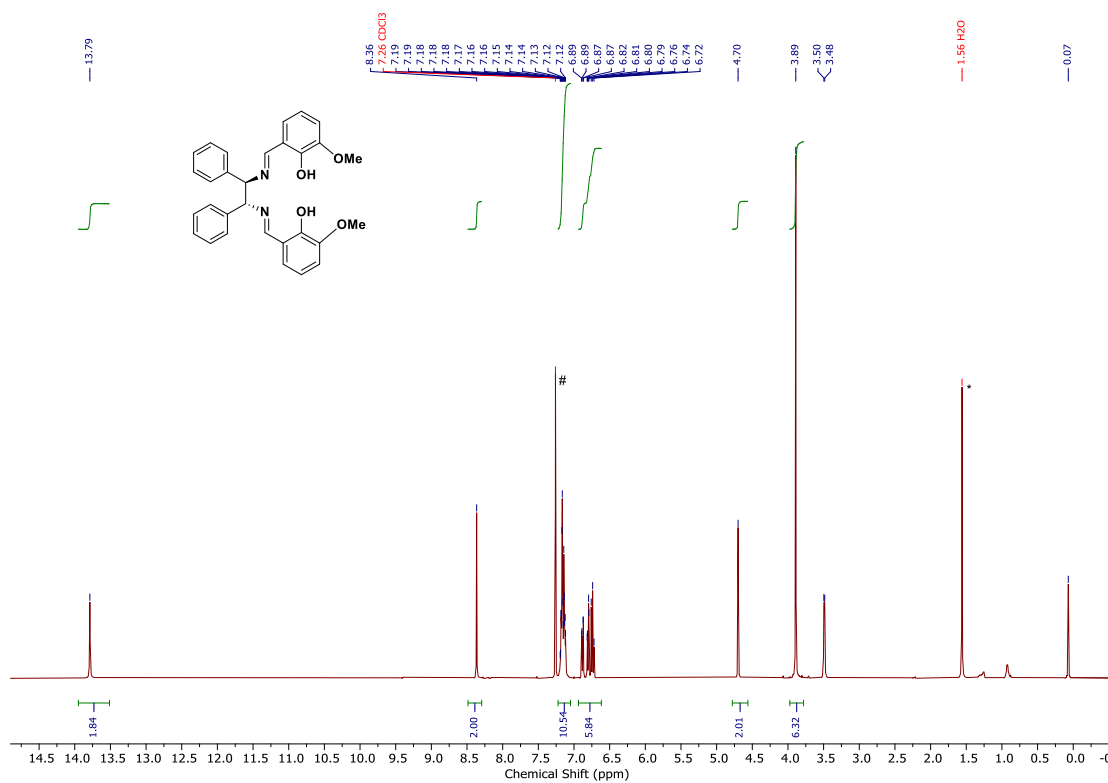


Figure S2.14. ^1H NMR Spectrum of $\text{LCc}_2\text{Ph}_2\text{H}_2$ (CDCl_3 (#), 298 K, 400 MHz) *: impurities from water and grease.

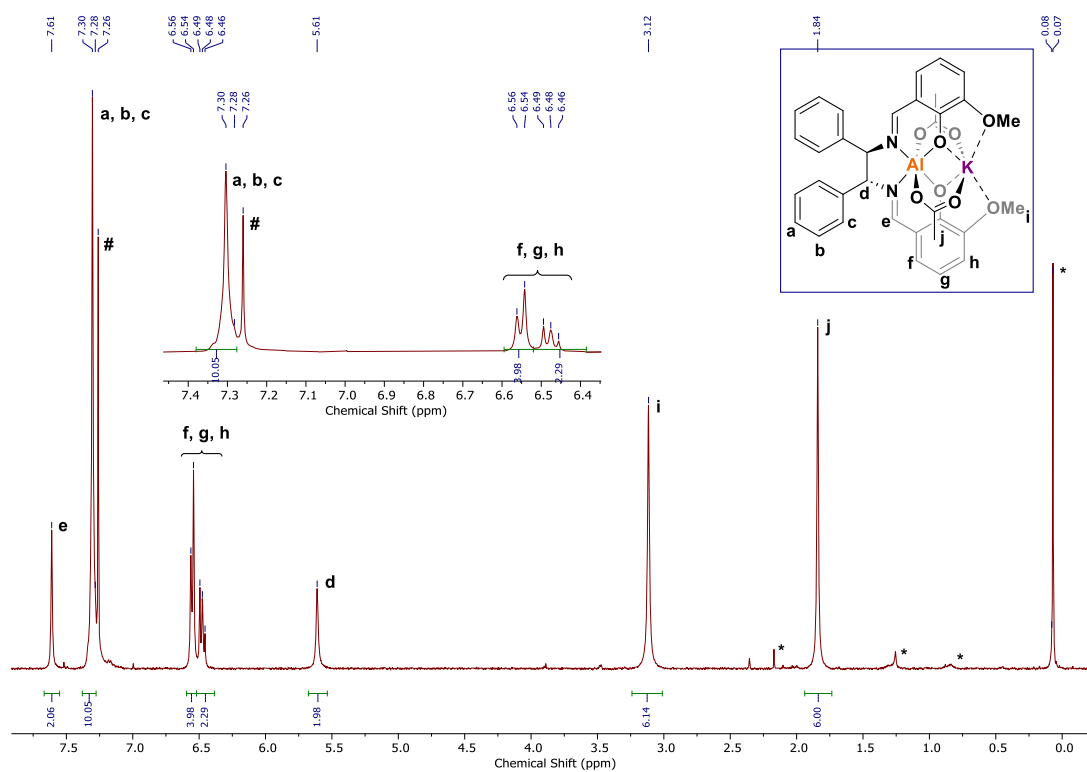


Figure S2.15. ^1H NMR spectrum of complex **3** (CDCl_3 (#), 298 K, 400 MHz) *: impurities from grease, hexane (glovebox atmosphere) and acetone (from NMR tube).

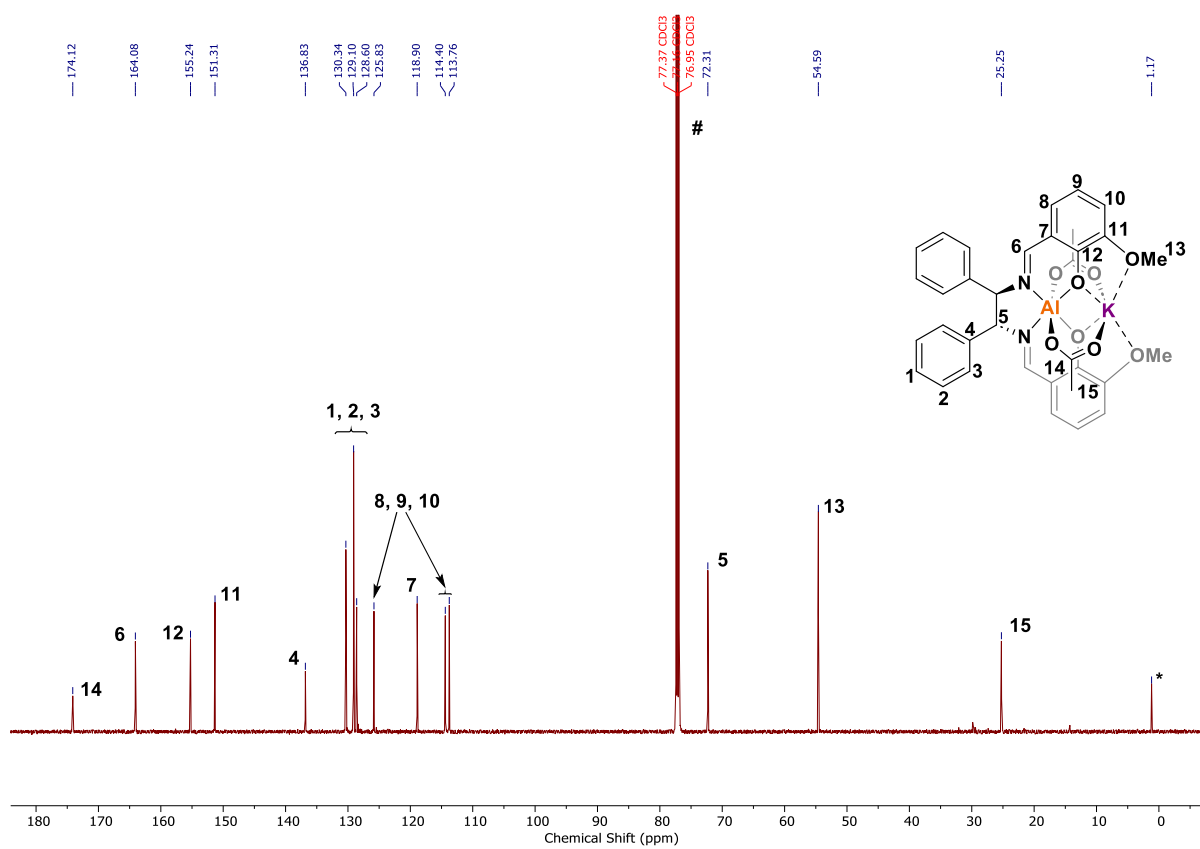


Figure S2.16. ^{13}C NMR Spectrum of complex **3** (CDCl_3 (#), 298 K, 151 MHz) *: impurity from grease.

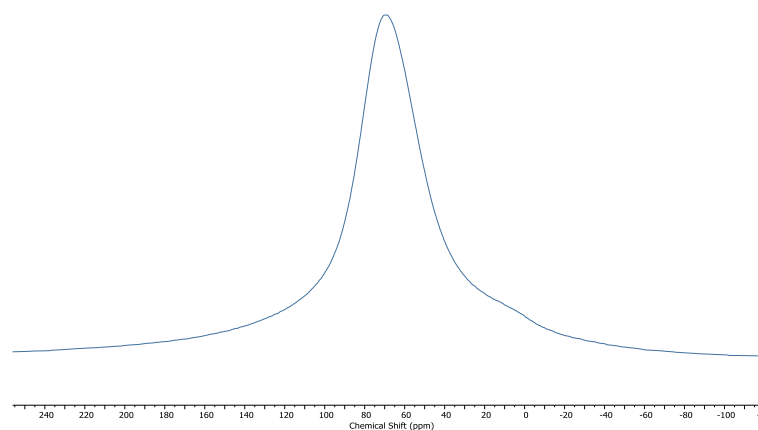


Figure S2.17. ^{27}Al NMR spectrum of complex **3** (CDCl_3 , 298 K, 104 MHz).

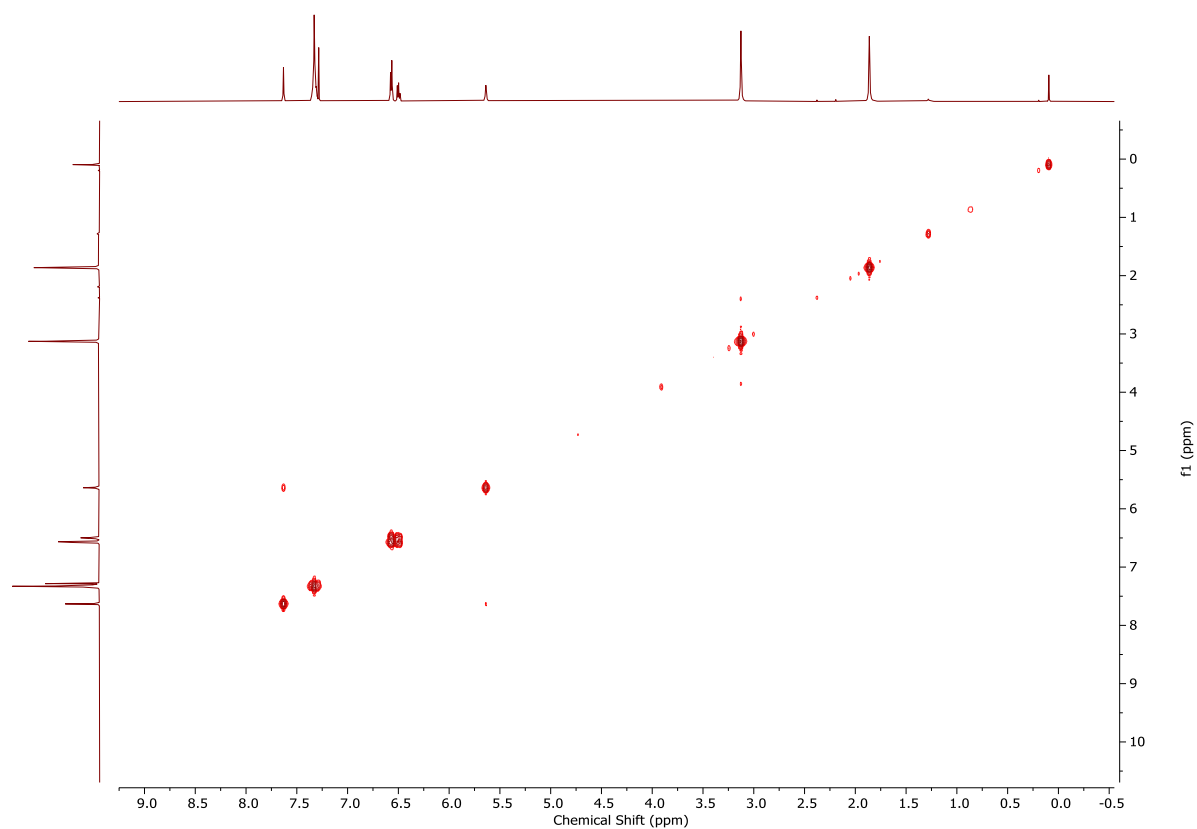


Figure S2.18. ^1H COSY NMR Spectrum of complex **3** (CDCl_3 , 298 K, 400 MHz).

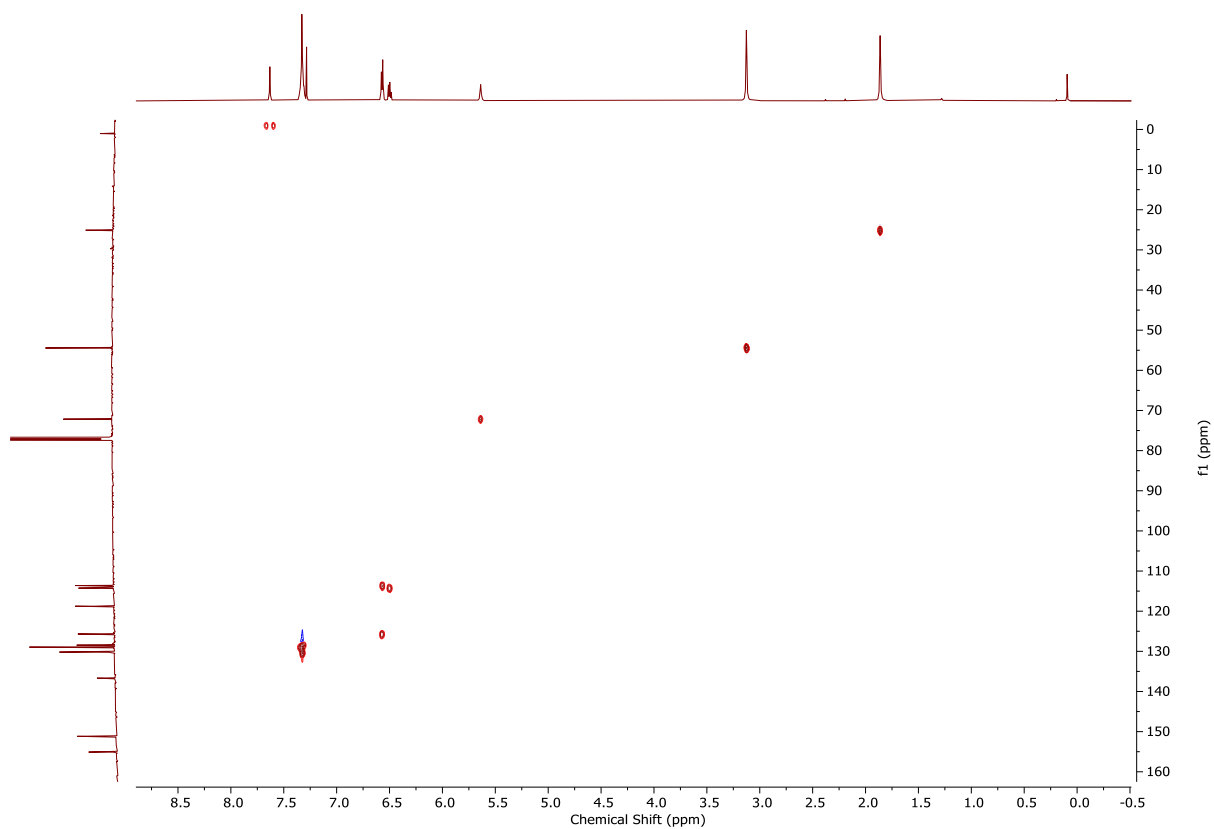


Figure S2.19. ^1H - ^{13}C HSQC NMR Spectrum of complex **3** (CDCl_3 , 298 K).

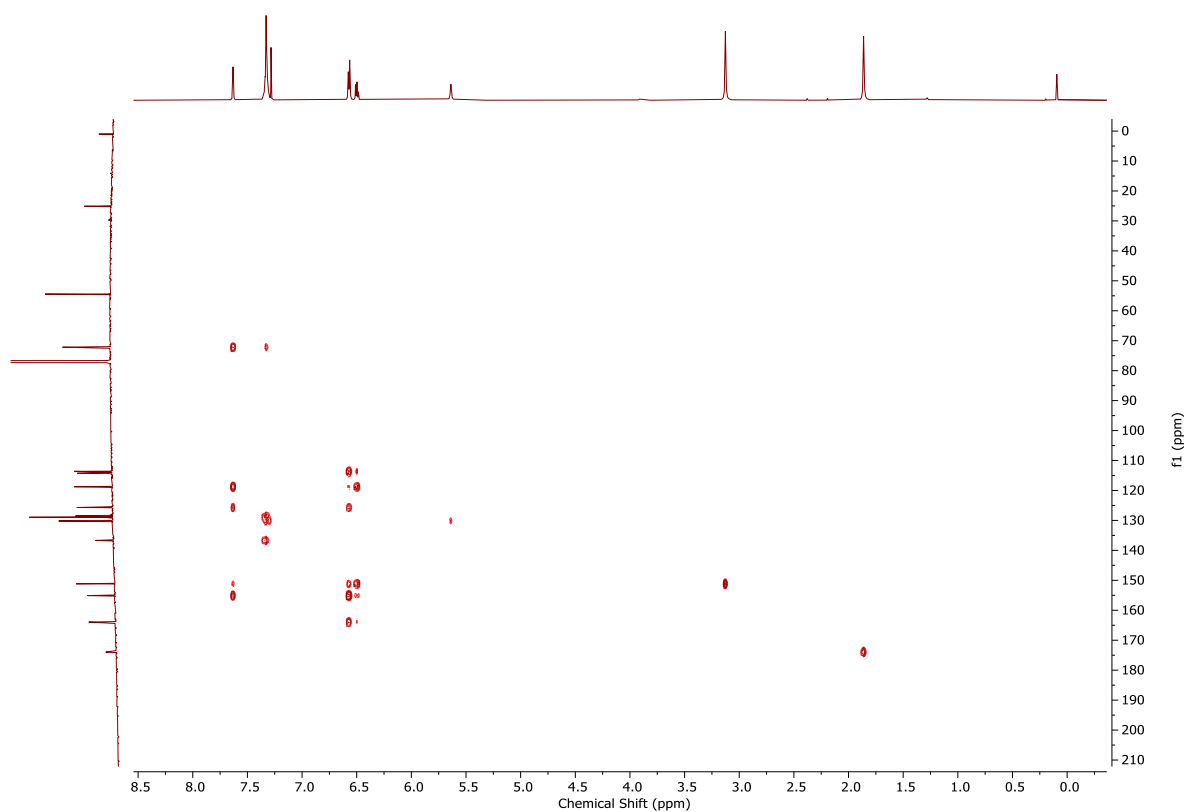


Figure S2.20. ^1H - ^{13}C HMBC NMR Spectrum of complex **3** (CDCl_3 , 298 K).

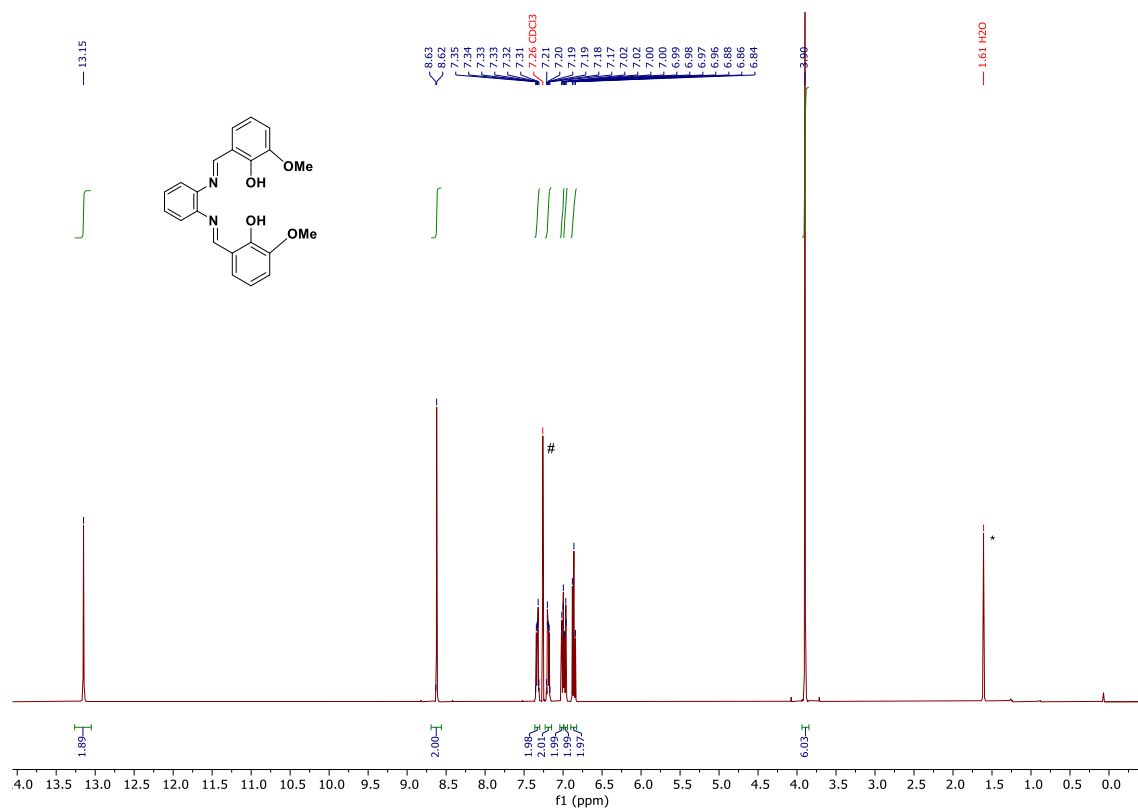


Figure S2.21. 1H NMR Spectrum of $L_{Phen}H_2$ ($CDCl_3$ (#), 298 K, 400 MHz) *: impurity from grease.

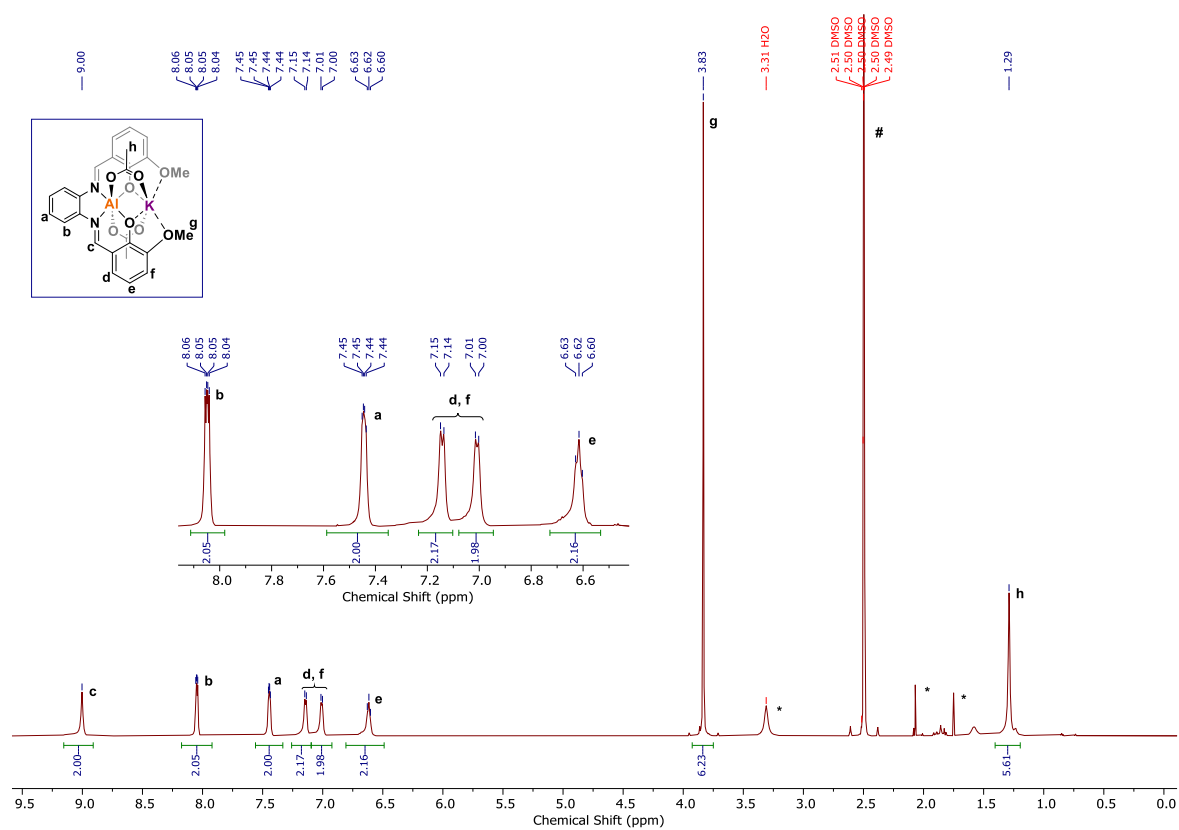


Figure S2.22. 1H NMR spectrum of complex 4 ($DMSO$ (#), 298 K, 400 MHz) *: impurities from hexane (in glovebox atmosphere) and water (from $DMSO$).

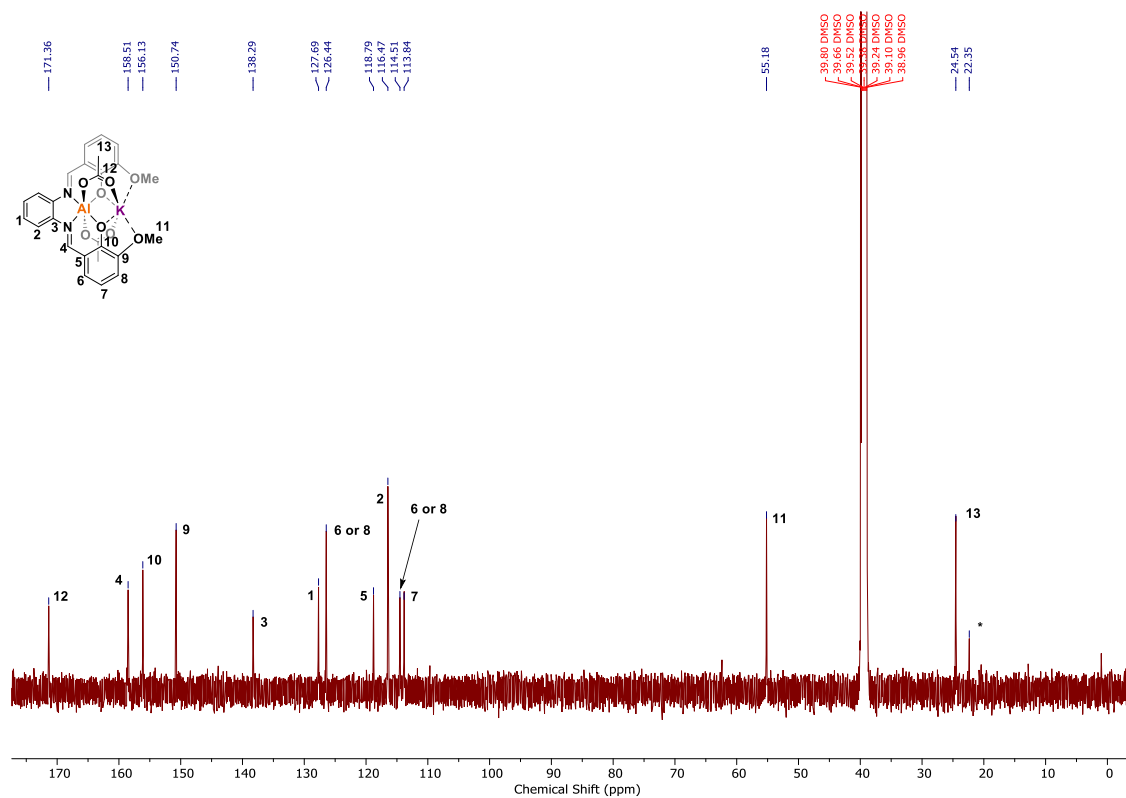


Figure S2.23. ¹³C NMR Spectrum of complex 4 (DMSO(#), 298 K, 151 MHz) *: impurity from hexane.

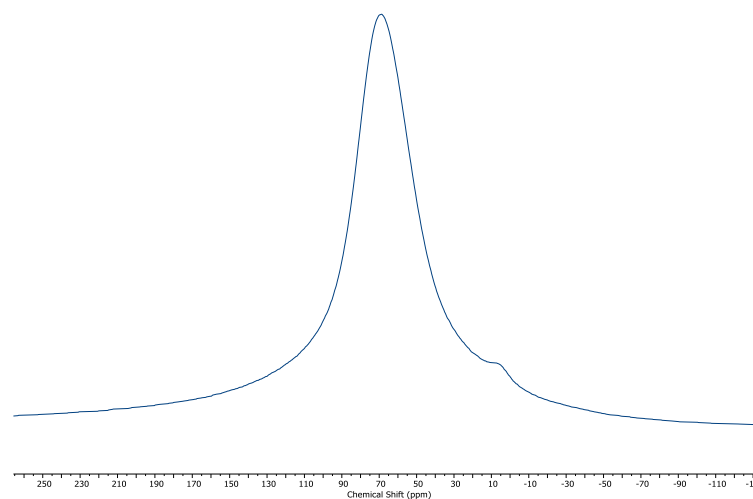


Figure S2.24. ²⁷Al NMR spectrum of complex 4 (DMSO, 298 K, 104 MHz).

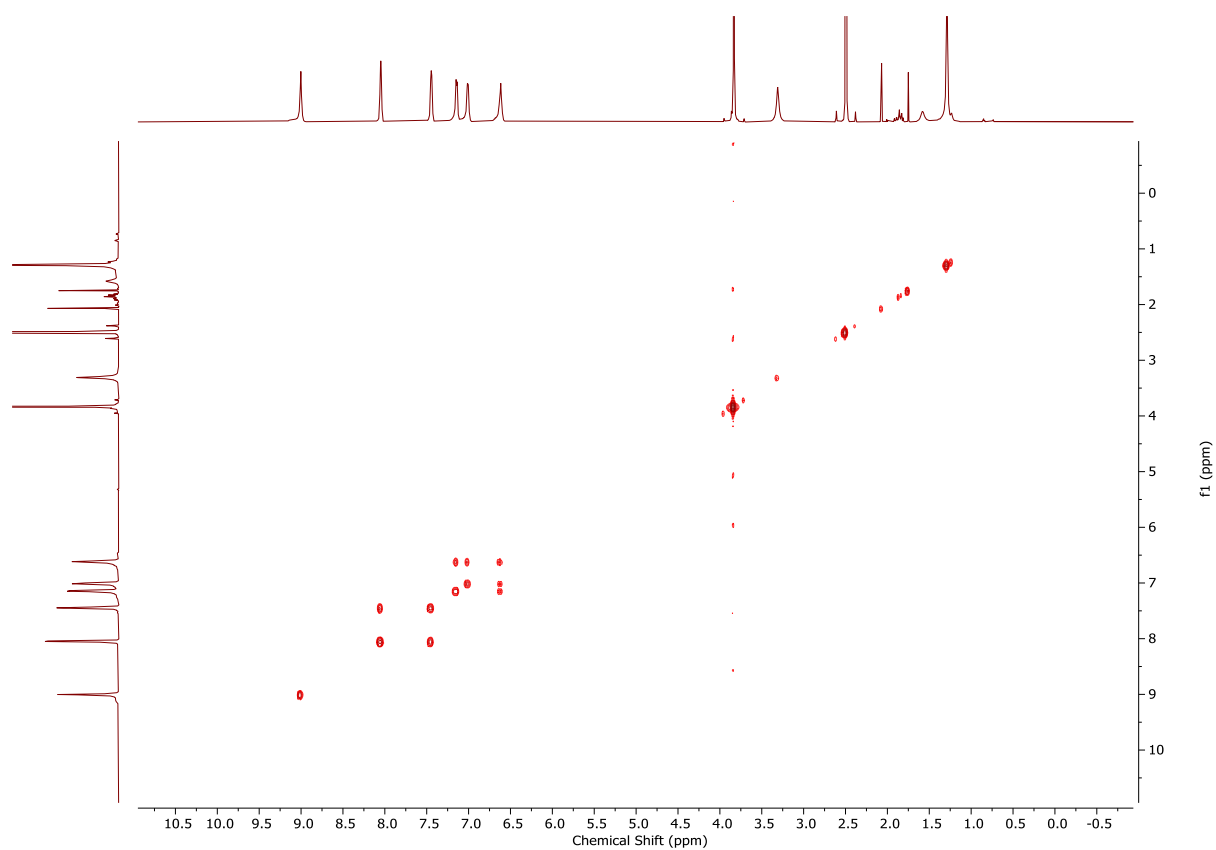


Figure S2.25. ^1H COSY NMR Spectrum of complex **4** (DMSO, 298 K, 400 MHz).

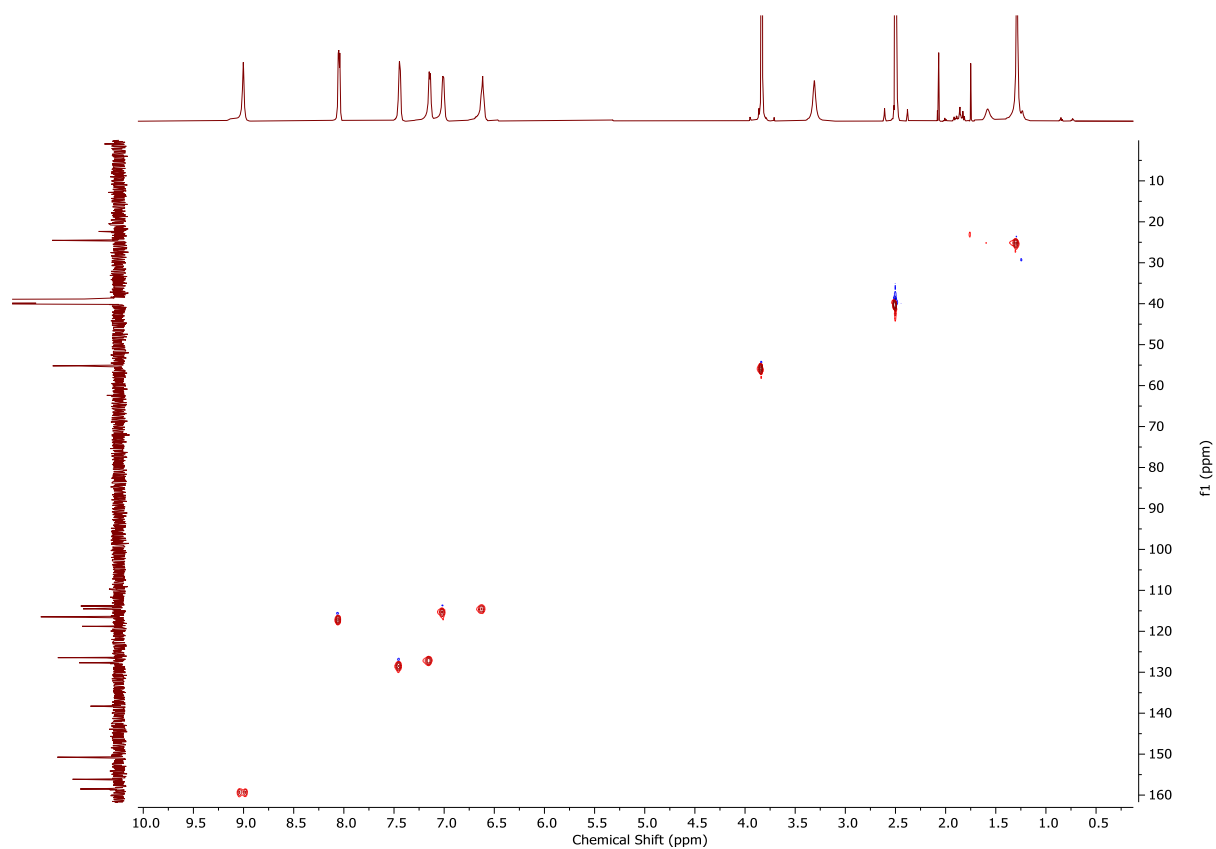


Figure S2.26. ^1H - ^{13}C HSQC NMR Spectrum of complex **4** (DMSO, 298 K).

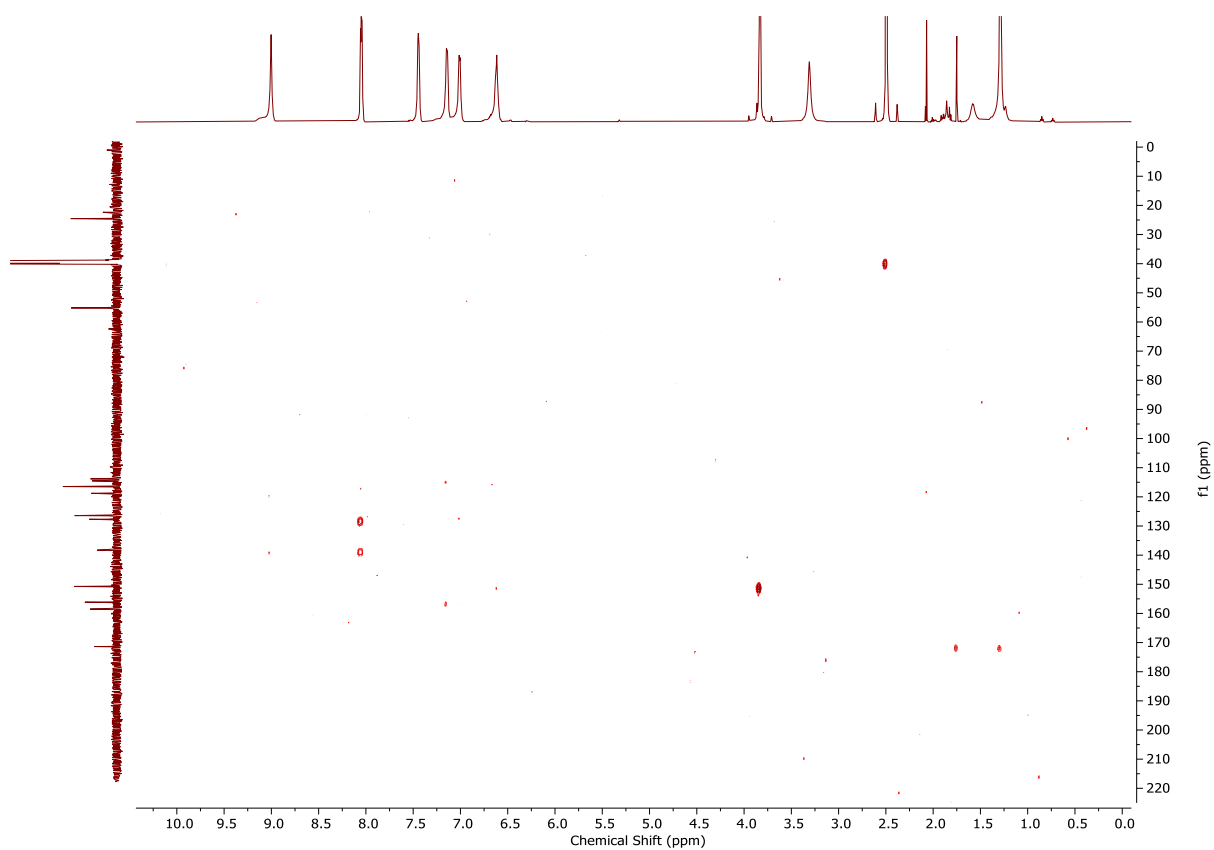


Figure S2.27. ^1H - ^{13}C HMBC NMR Spectrum of complex **4** (DMSO, 298 K).

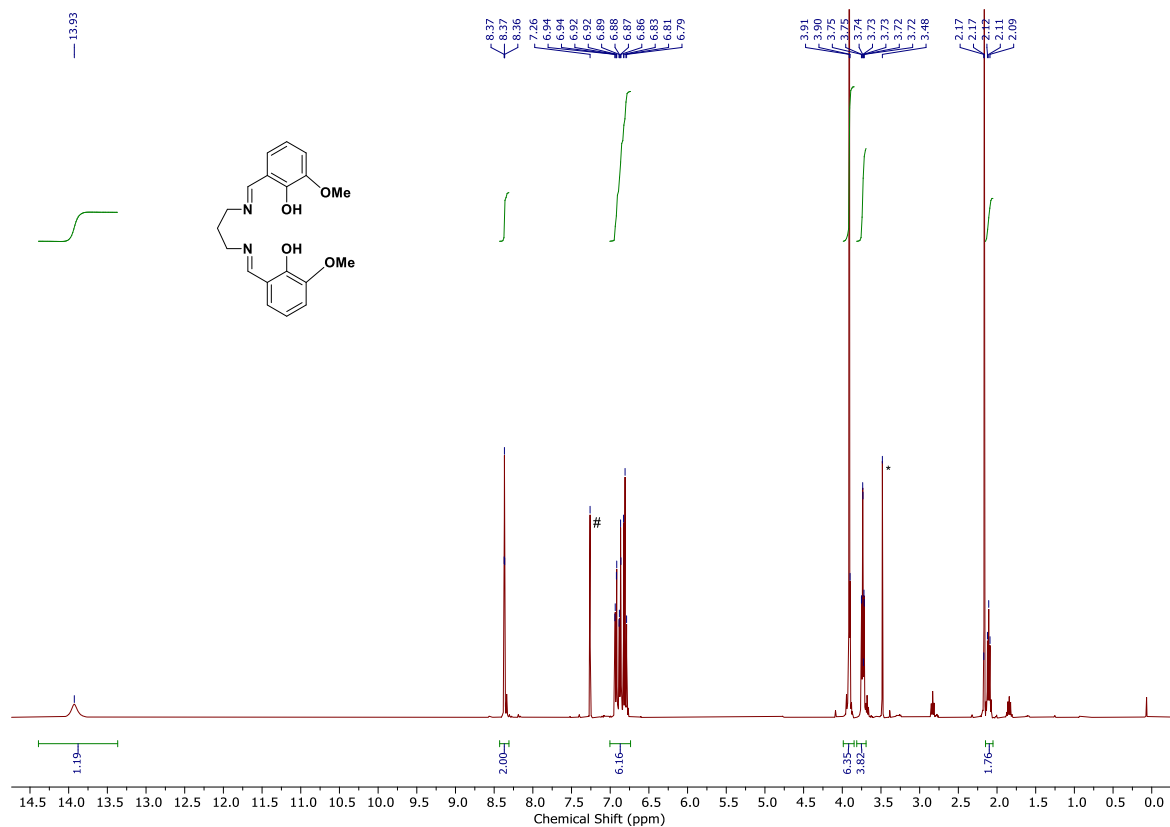
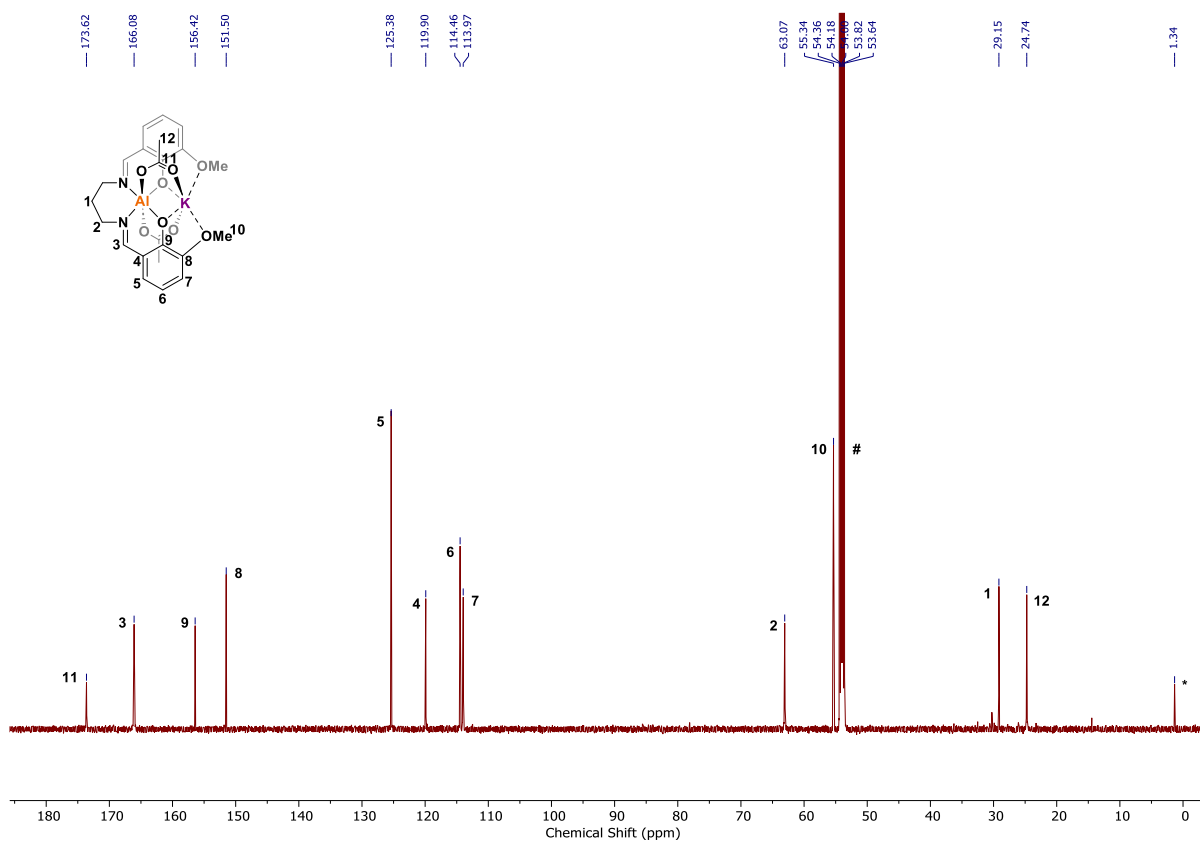
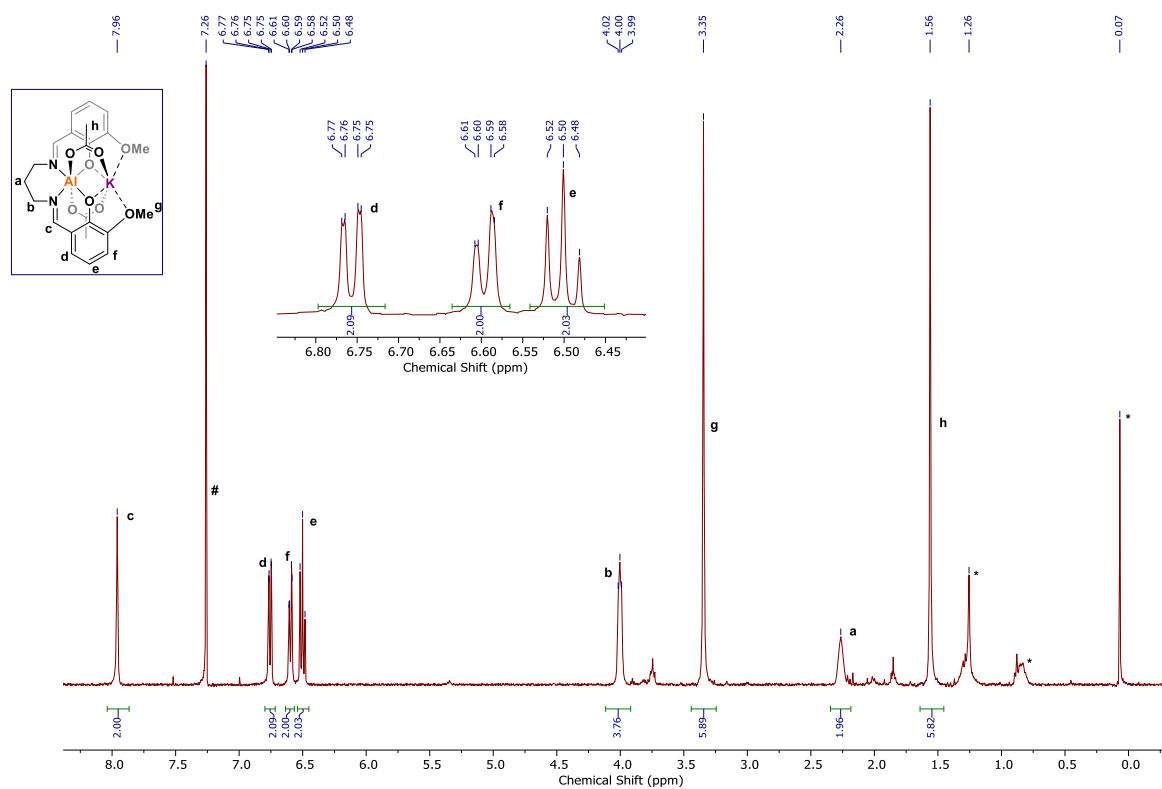


Figure S2.28. ^1H NMR Spectrum of LProH_2 ($\text{CDCl}_3(\#)$, 298 K, 400 MHz) *: impurity from methanol.



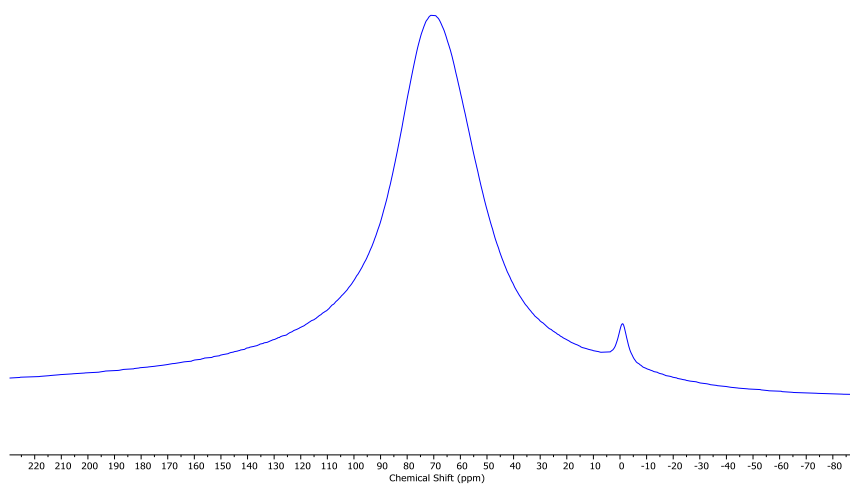


Figure S2.31. ^{27}Al NMR spectrum of complex **5** (CDCl_3 , 298 K, 104 MHz).

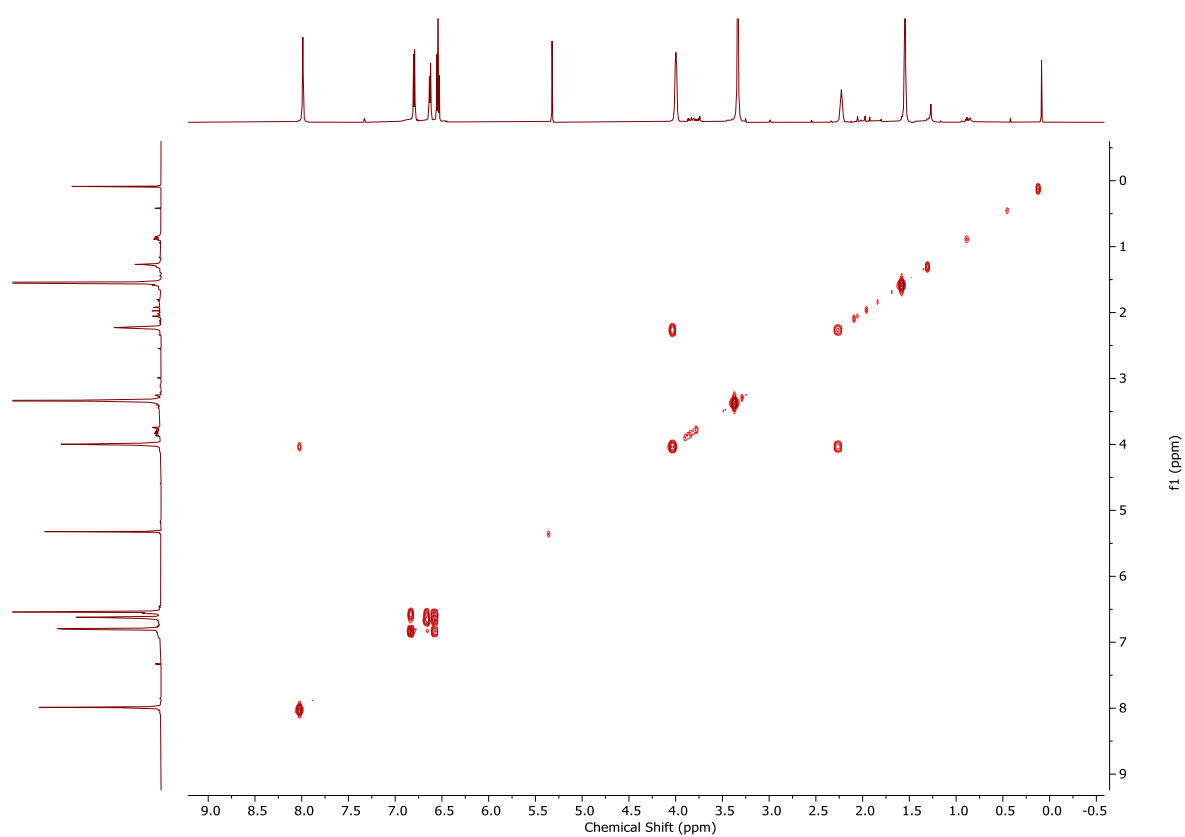


Figure S2.32. ^1H COSY NMR Spectrum of complex **5** (CD_2Cl_2 , 298 K, 400 MHz).

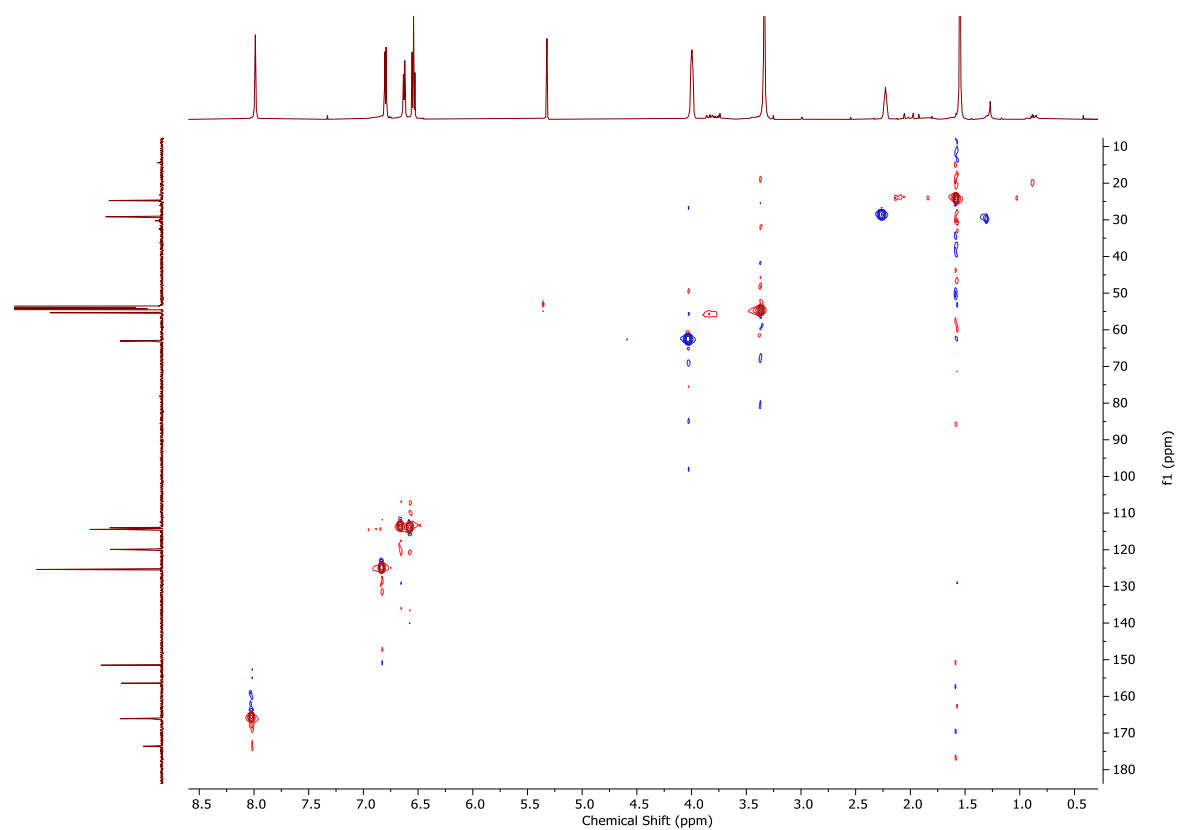


Figure S2.33. ^1H - ^{13}C HSQC NMR Spectrum of complex **5** (CD_2Cl_2 , 298 K).

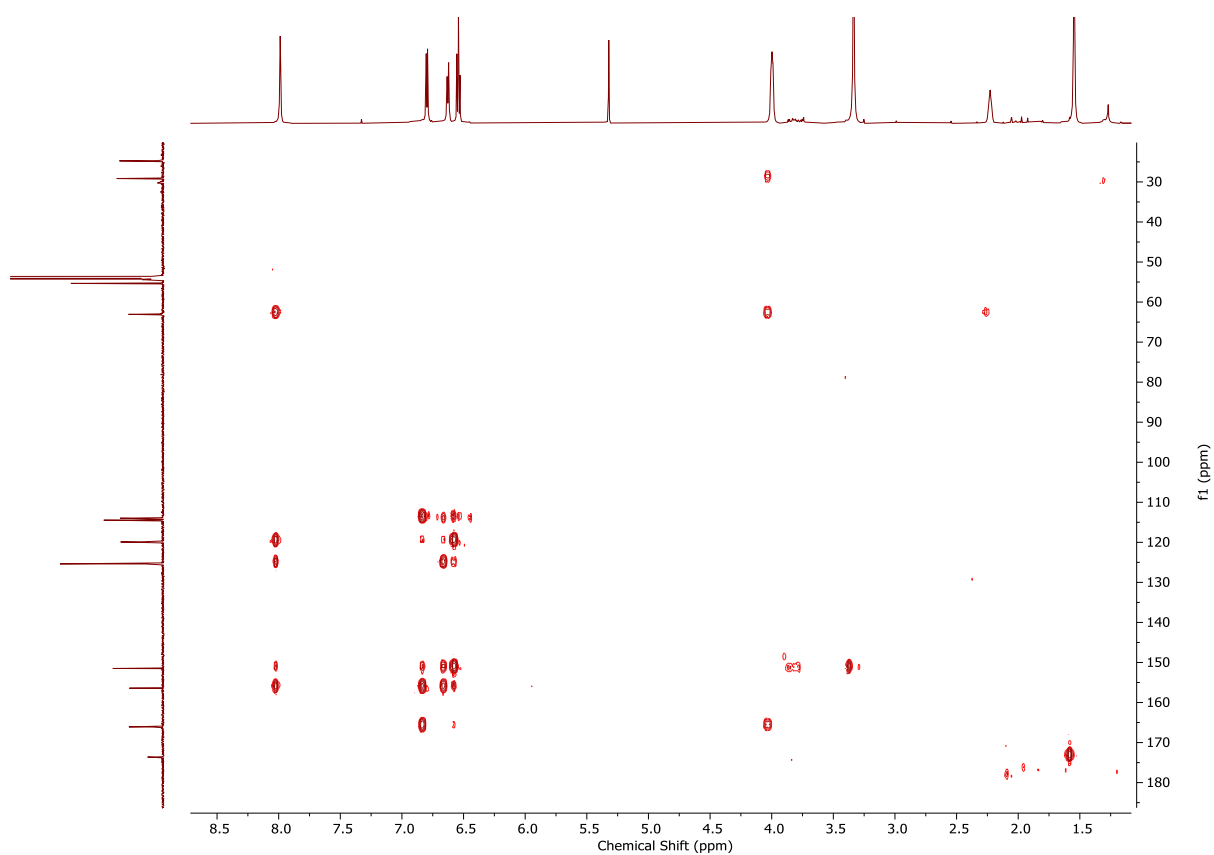


Figure S2.34. ^1H - ^{13}C HMBC NMR Spectrum of complex **5** (CD_2Cl_2 , 298 K).

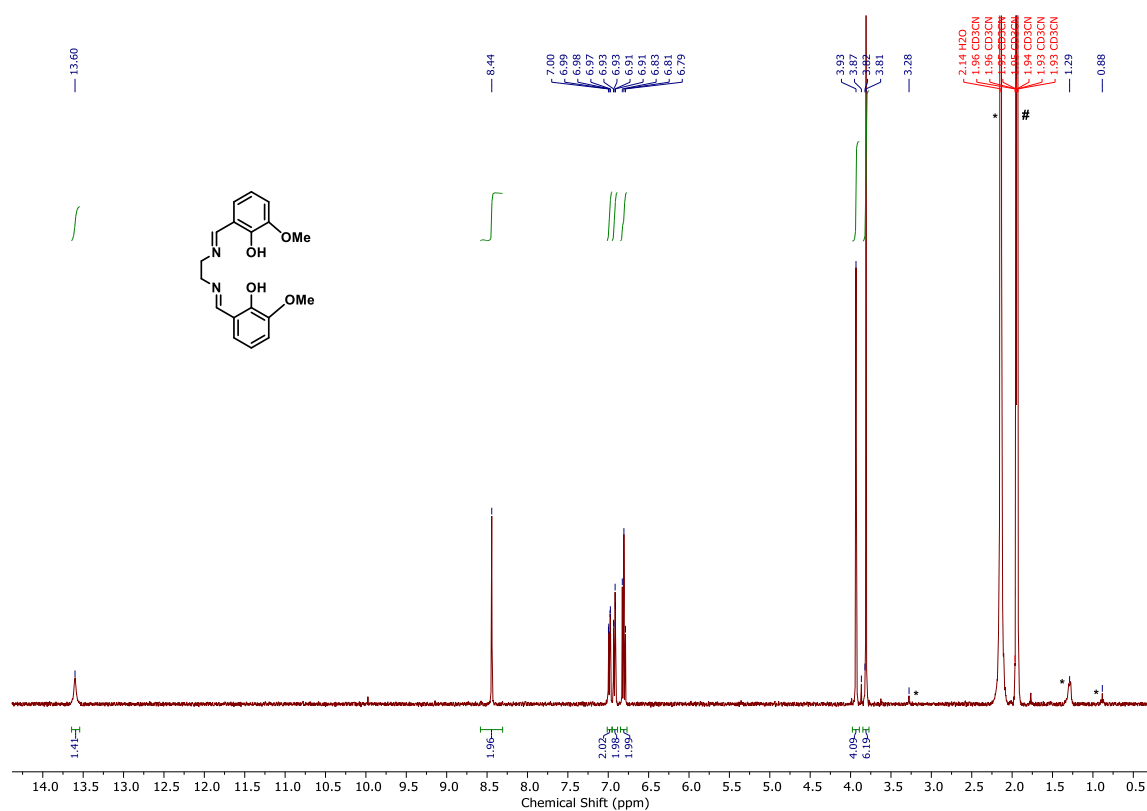
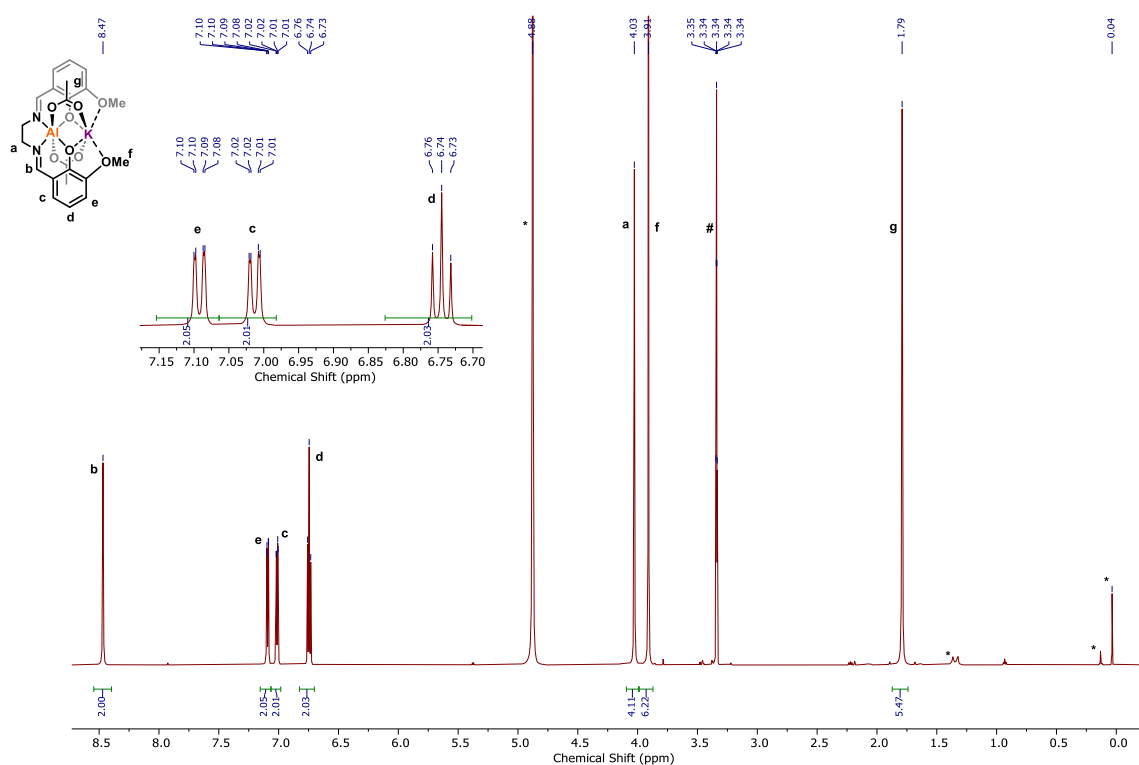


Figure S2.35. ¹H NMR Spectrum of **1** (CD₃CN(#), 298 K, 400 MHz) *: impurity from water.



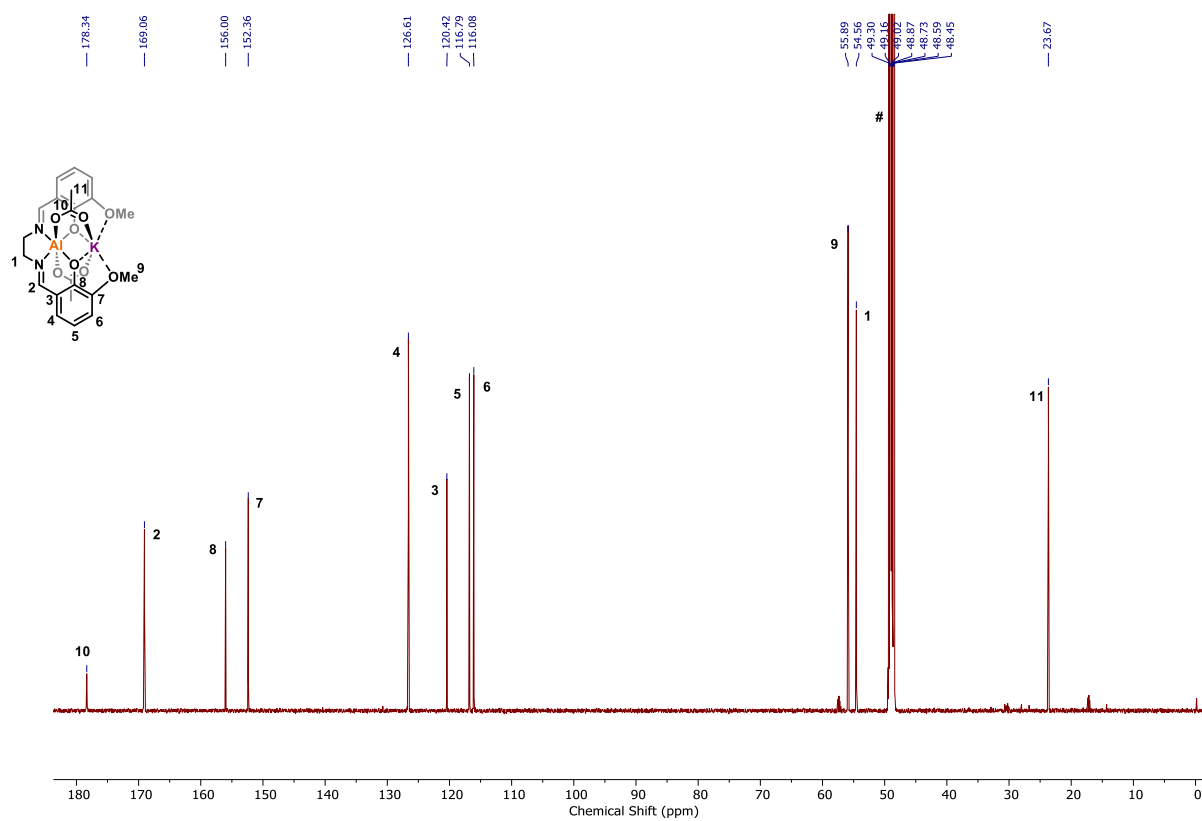


Figure S2.37. ¹³C NMR Spectrum of complex **6** (MeOD-d₄(#), 298 K, 151 MHz).

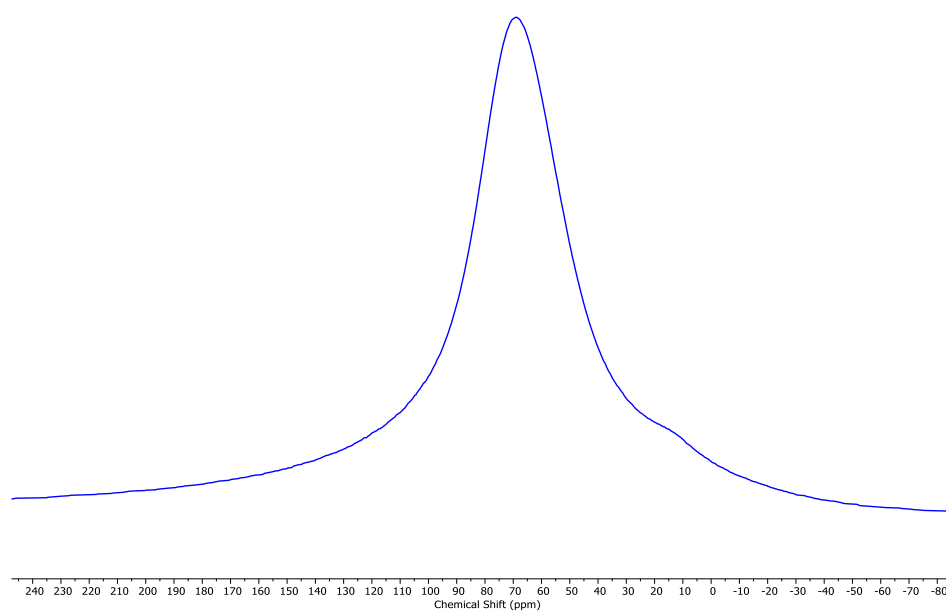


Figure S2.38. ²⁷Al NMR spectrum of complex **6** (MeOD-d₄, 298 K, 104 MHz).

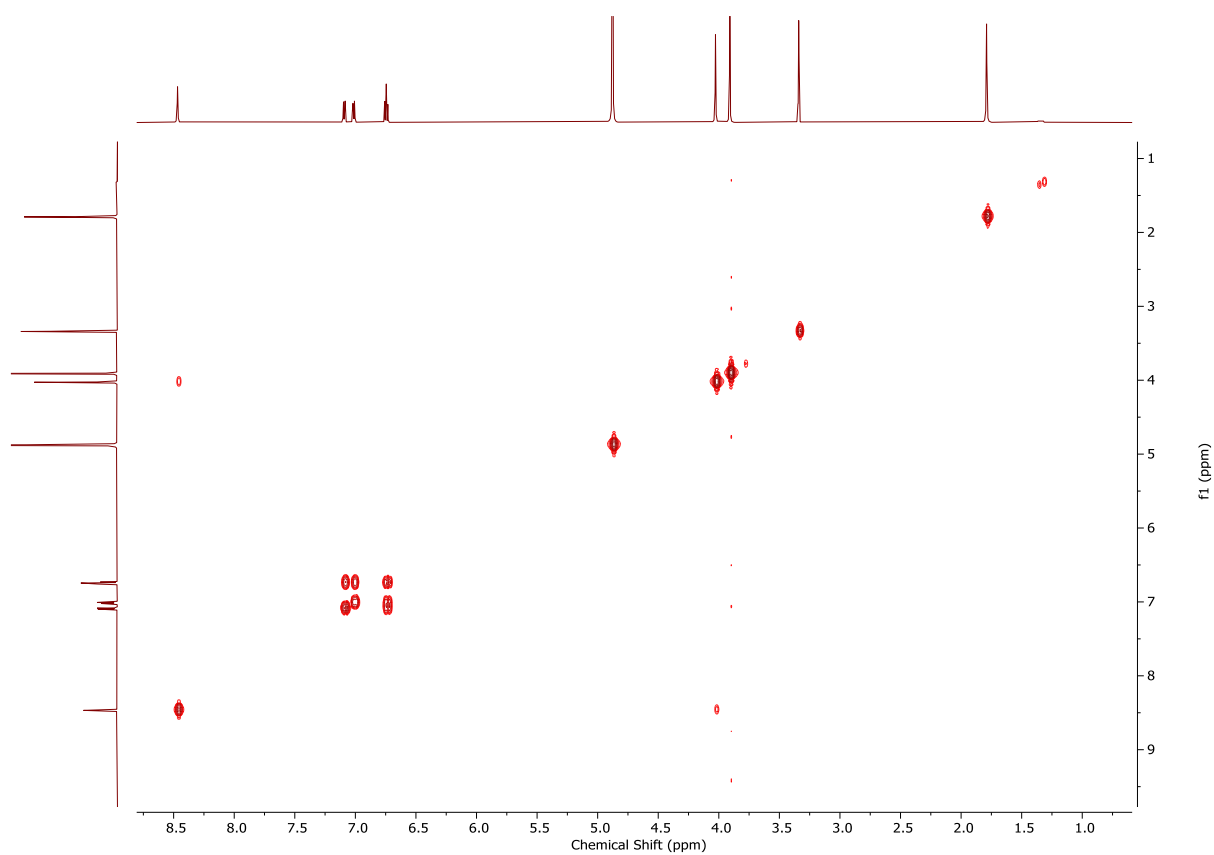


Figure S2.39. ^1H COSY NMR Spectrum of complex **6** (MeOD- d_4 , 298 K, 400 MHz).

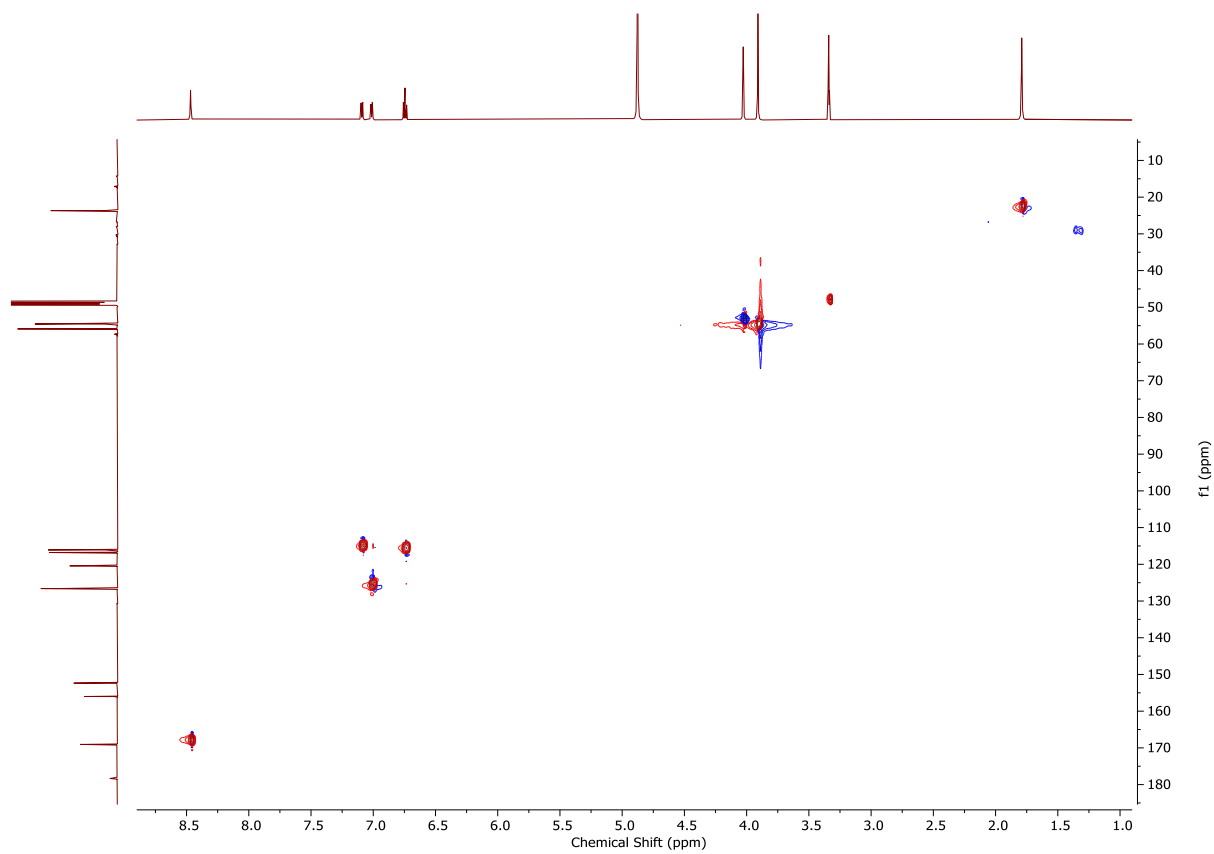


Figure S2.40. ^1H - ^{13}C HSQC NMR Spectrum of complex **6** (MeOD- d_4 , 298 K).

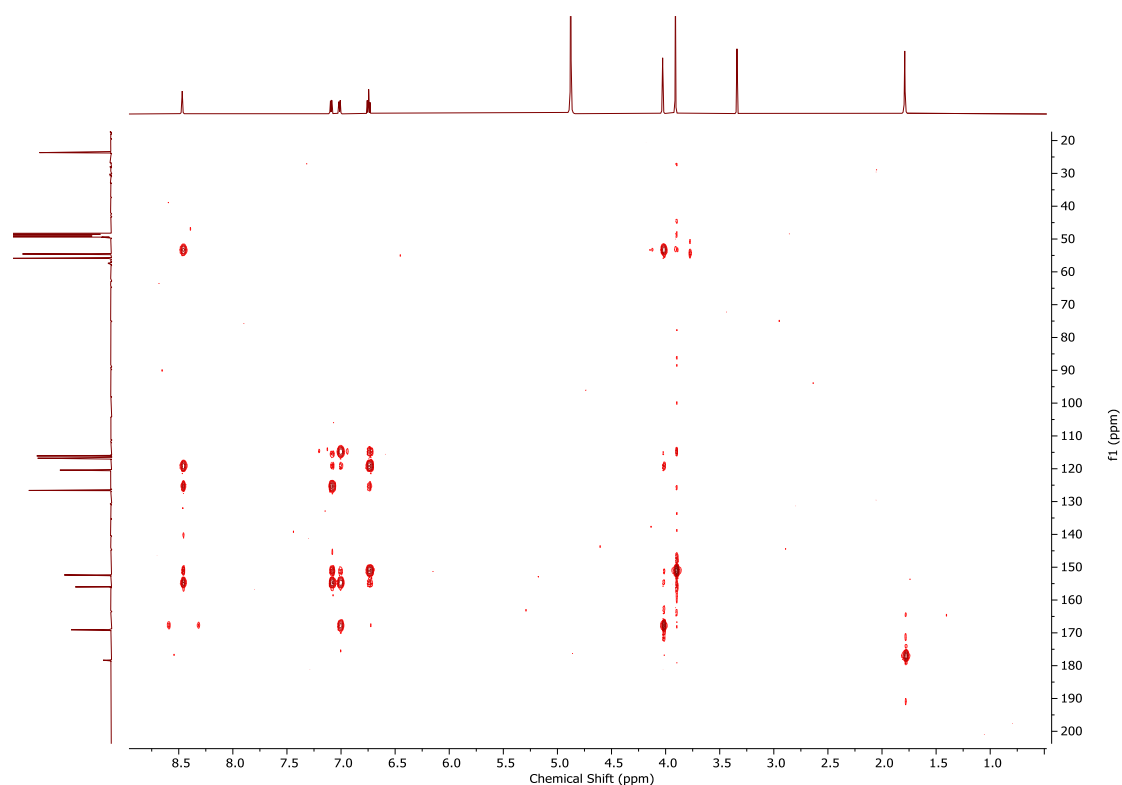


Figure S2.41. ^1H - ^{13}C HMBC NMR Spectrum of complex **6** (MeOD- d_4 , 298 K).

Table S2.1. Selected bond lengths for $\text{L}_{\text{Cyc}}\text{AlK}(\text{OAc})_2$ (**2**)

Bond	Bond Length (Å)
K(1)-Al(1)	3.603(2)
K(1)-O(2)	2.761(5)
K(2)-O(4)	2.582(6)
Al(1)-O(1)	1.912(4)
Al(1)-O(3)	1.917(4)
O(1)-C(1)	1.274(7)
O(2)-C(1)	1.240(7)
O(3)-C(3)	1.266(7)
O(4)-C(3)	1.228(9)

Table S2.2. Selected bond lengths for $\text{L}_{\text{Pro}}\text{AlK}(\text{OAc})_2$ (**5**)

Bond	Bond Length (Å)
K(1)-Al(1)	3.744(2)
K(1)-O(2)	2.713(5)
K(2)-O(4)	2.649(5)
Al(1)-O(1)	1.894(4)
Al(1)-O(3)	1.877(4)
O(1)-C(1)	1.275(7)
O(2)-C(1)	1.216(7)
O(3)-C(3)	1.268(7)
O(4)-C(3)	1.234(8)

Table S2.3. Summary of crystallographic refinement data for complexes **1**, **2** & **5**

	$\text{LC}_{2\text{Me}_2}\text{AlK}(\text{OAc})_2$ (1)	$\text{LC}_{\text{Cyc}}\text{AlK}(\text{OAc})_2$ (2)	$\text{L}_{\text{Pro}}\text{AlK}(\text{OAc})_2$ (5)
Local Code	008ff22	024nicj24	031nicj24
CCDC Deposition Number	2280611		
Crystal Data			
Chemical formula	$\text{C}_{24}\text{H}_{28}\text{AlKN}_2\text{O}_8$	$\text{C}_{26}\text{H}_{30}\text{AlKN}_2\text{O}_8 \cdot 0.5 \text{C}_3\text{H}_8\text{O}$	$\text{C}_{23}\text{H}_{26}\text{AlKN}_2\text{O}_8$
M_r	538.56	592.53	524.55
Crystal system, space group	Triclinic, $P-1$	Triclinic, $P1$	Triclinic, $P-1$
a, b, c (Å)	9.8713(4) 11.2080(4) 11.8060(4)	11.7126(4) 12.6180(4) 20.0180(6)	10.0807(4) 11.2145(5) 46.3187(13)
α, β, γ (°)	84.516(3) 78.103(3) 81.516(3)	99.494(2) 102.443(3) 99.896(3)	87.325(3) 84.348(3) 85.726(3)
V (Å ³)	1261.28(8)	2782.54(16)	5192.3(3)
Z	2	4	8
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ (mm ⁻¹)	1.54184	2.446	2.815
Crystal size (mm)	0.14 x 0.12 x 0.10	0.15 x 0.08 x 0.03	0.17 x 0.07 x 0.03
Data collection			
Absorption correction	CrysAlisPro 1.171.41.117a (Rigaku Oxford Diffraction, 2021) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.		
$T_{\min}, T_{\max}$	0.94043, 1.00000	0.94352, 1.00000	0.71045, 1.00000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18706, 5199, 4292	48433, 19725, 16221	123014, 21545, 13793
R_{int}	0.0264	0.0528	0.1480
$(\sin\theta/\lambda)_{\max}$ (Å ⁻¹)	0.630	0.442	0.431
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.044, 0.124, 1.04	0.055, 0.149, 1.01	0.097, 0.2584, 1.06
No of reflections	18706	19725	21545
No. of parameters	370	1485	1352
No. of restraints	0	3	0
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.44, -0.36	1.11, -0.40	1.19/-0.68

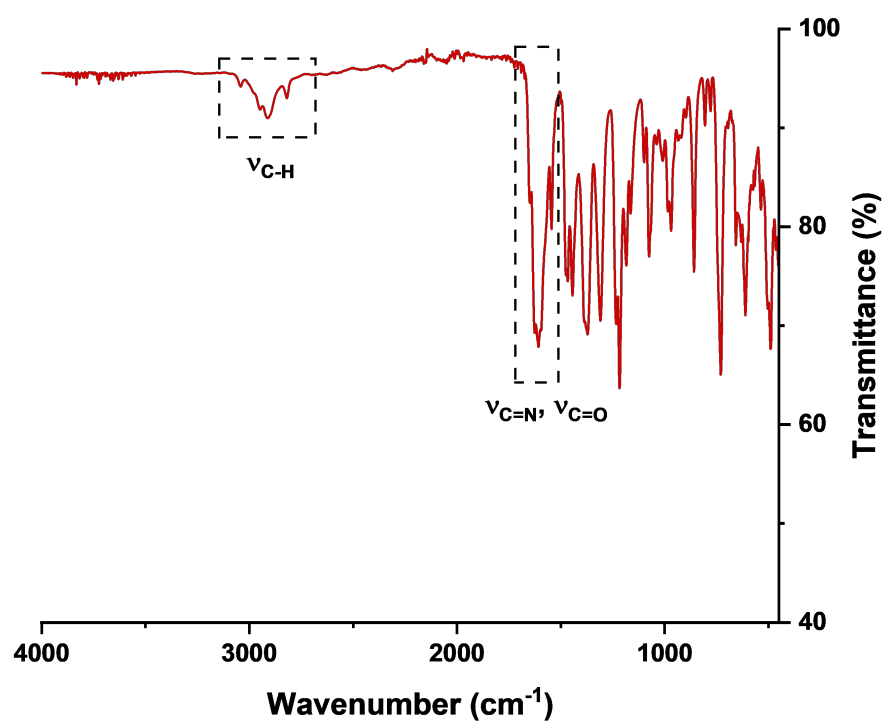


Figure S2.42. IR spectrum of complex **1**.

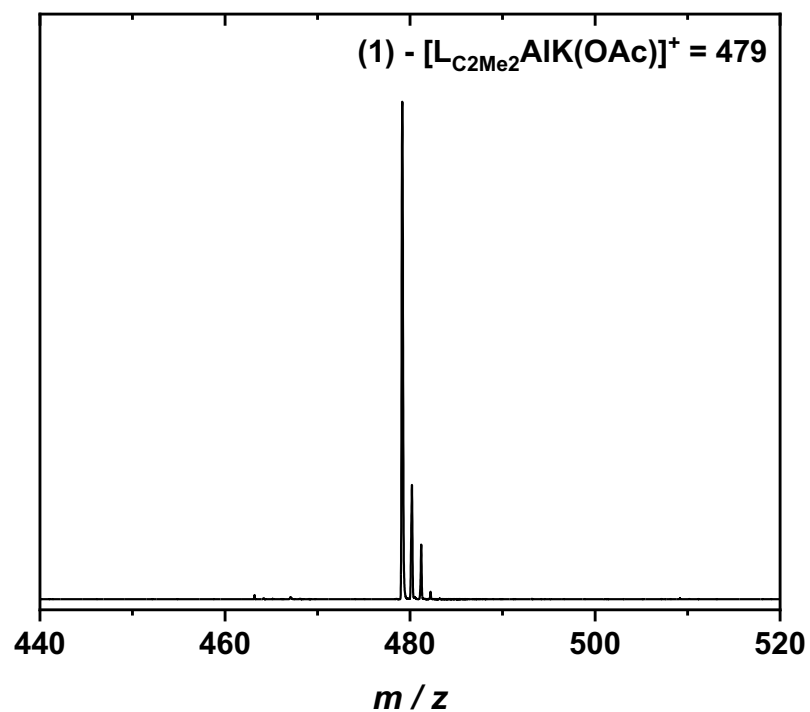


Figure S2.43. MALDI-TOF spectrum of complex **1**.

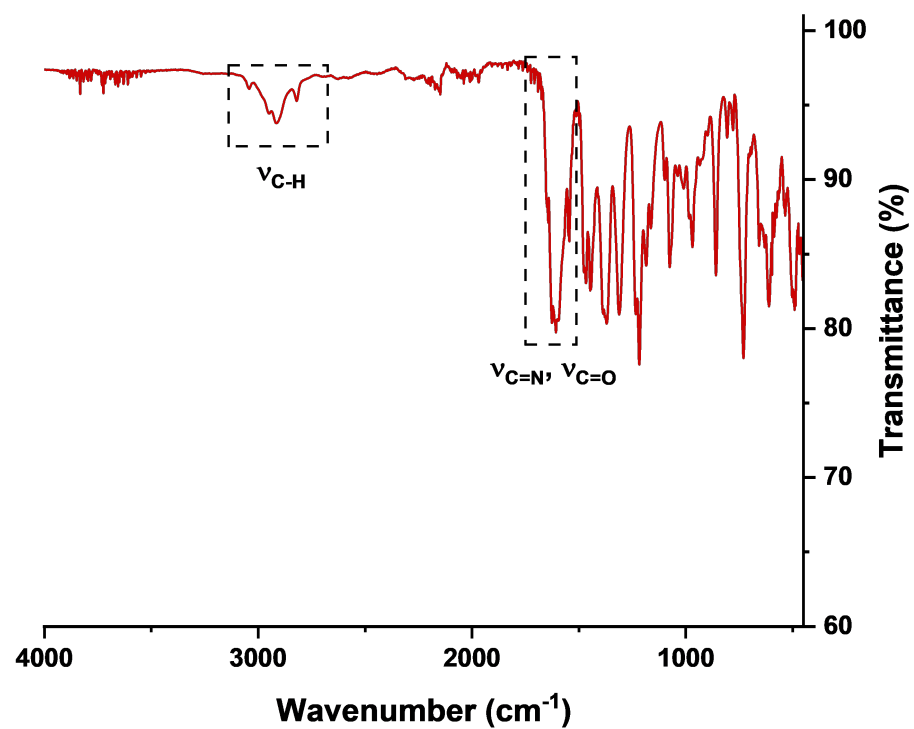


Figure S2.44. IR spectrum of complex 2.

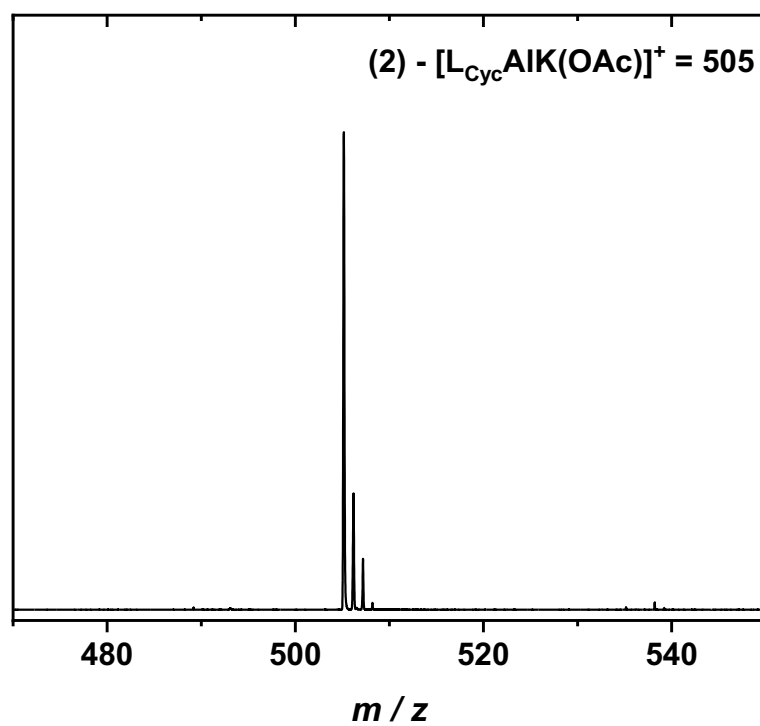


Figure S2.45. MALDI-ToF spectrum of complex 2.

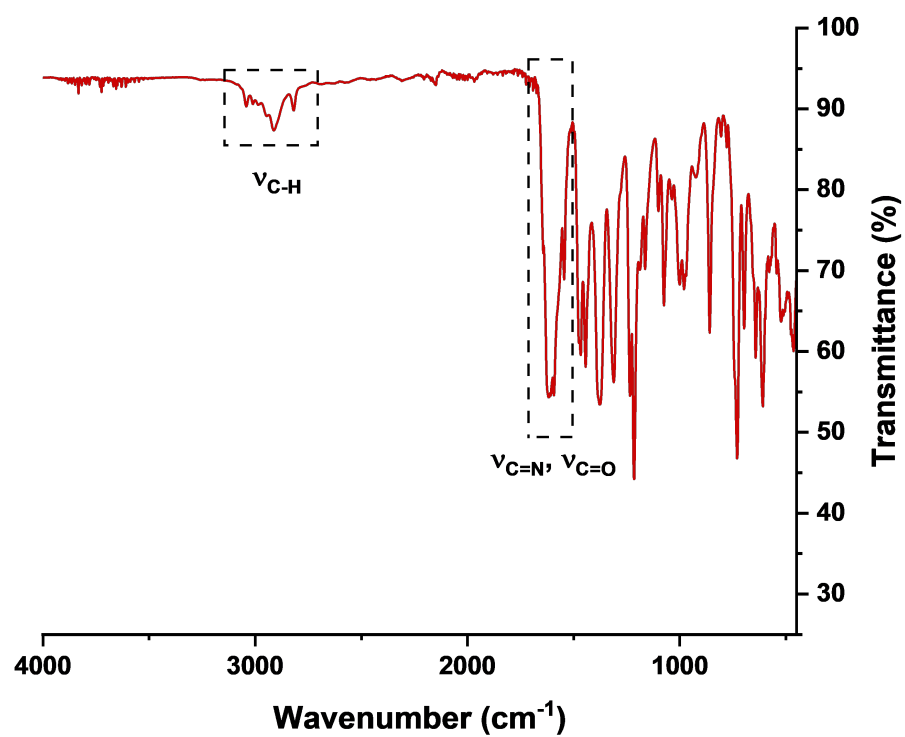


Figure S2.46. IR spectrum of complex 3.

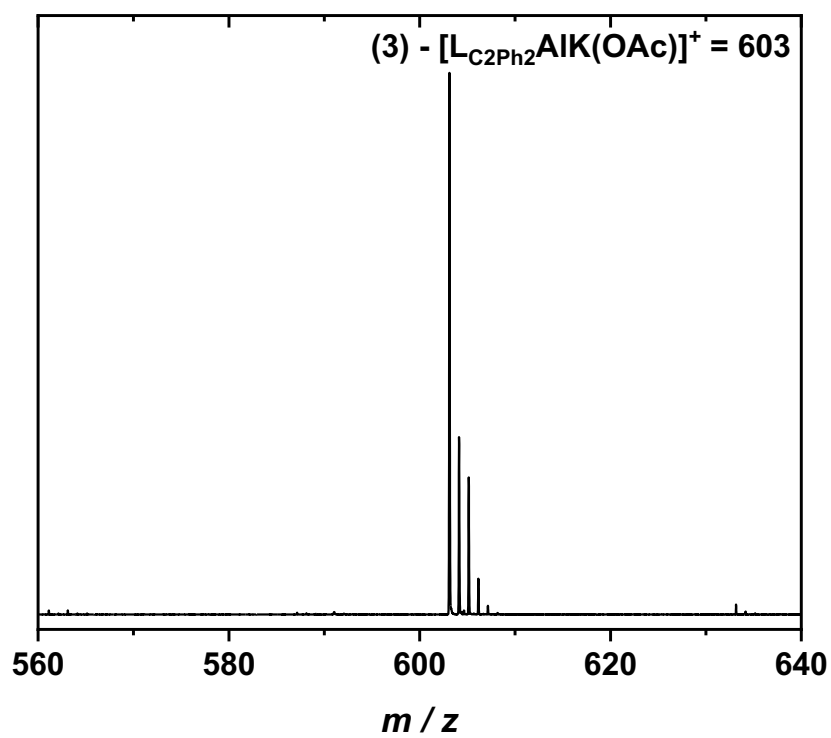


Figure S2.47. MALDI-ToF spectrum of complex 3.

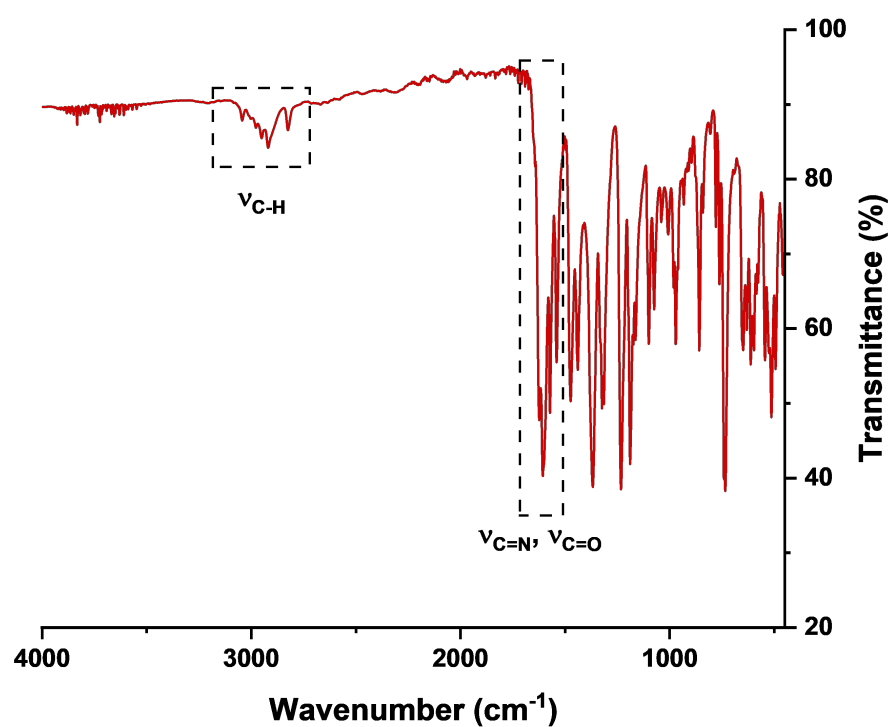


Figure S2.48. IR spectrum of complex 4.

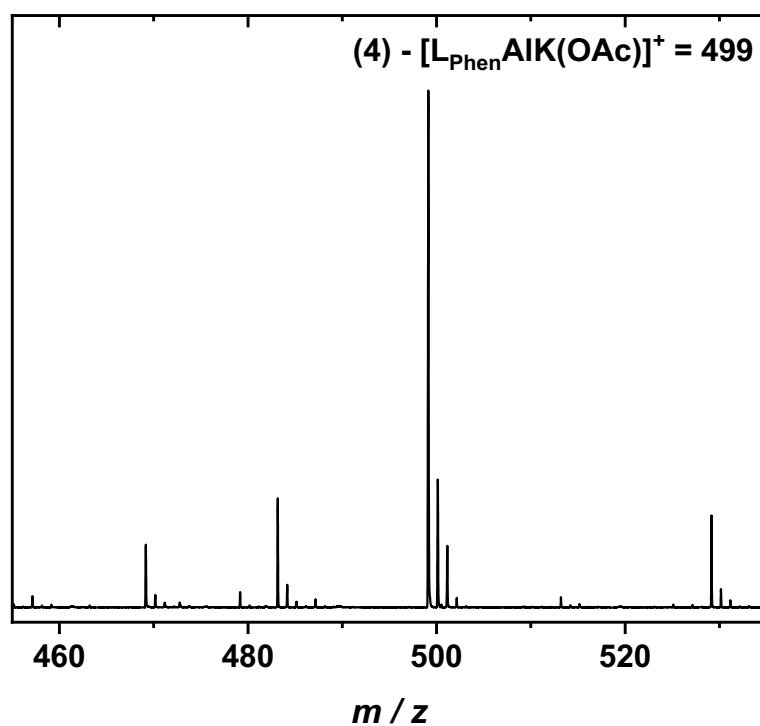


Figure S2.49. MALDI-ToF spectrum of complex 4. Sample did not fly well possibly due to low sample loading as a consequence of poor solubility.

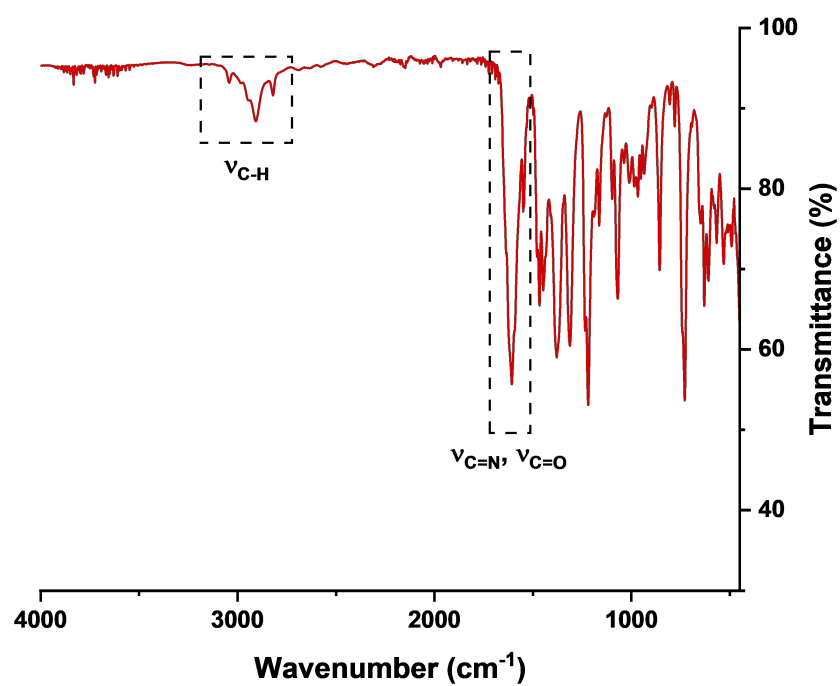


Figure S2.50. IR spectrum of complex 5.

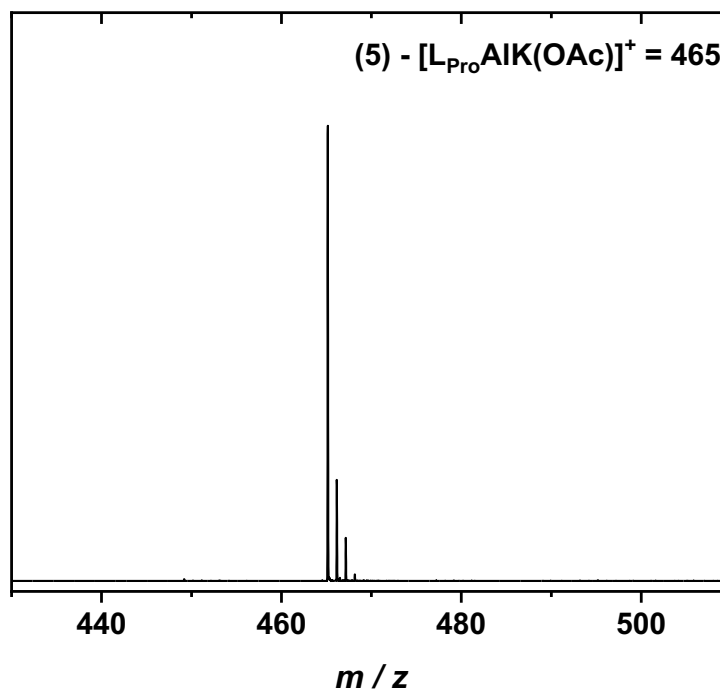


Figure S2.51. MALDI-ToF spectrum of complex 5.

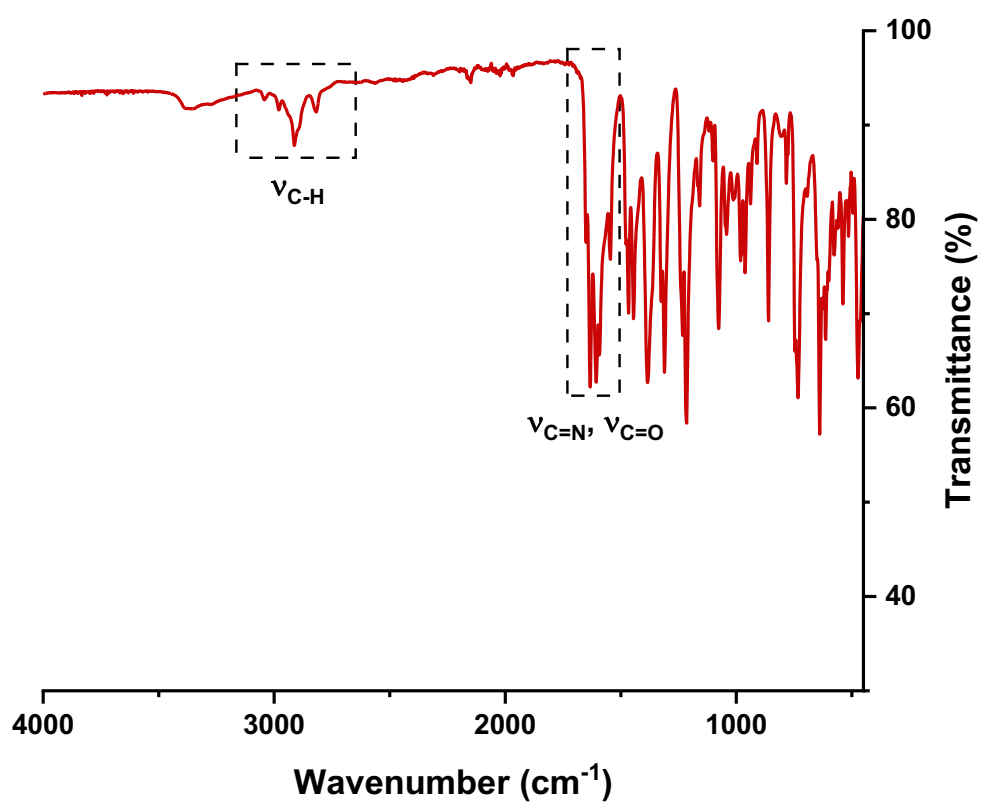


Figure S2.52. IR spectrum of complex 6.

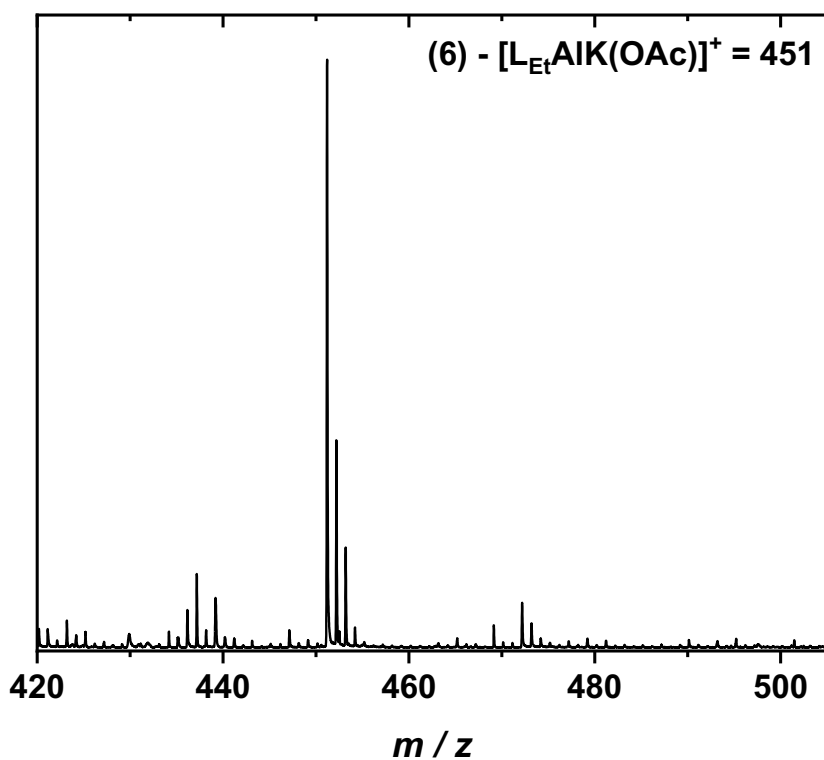


Figure S2.53. MALDI-ToF spectrum of complex 6.

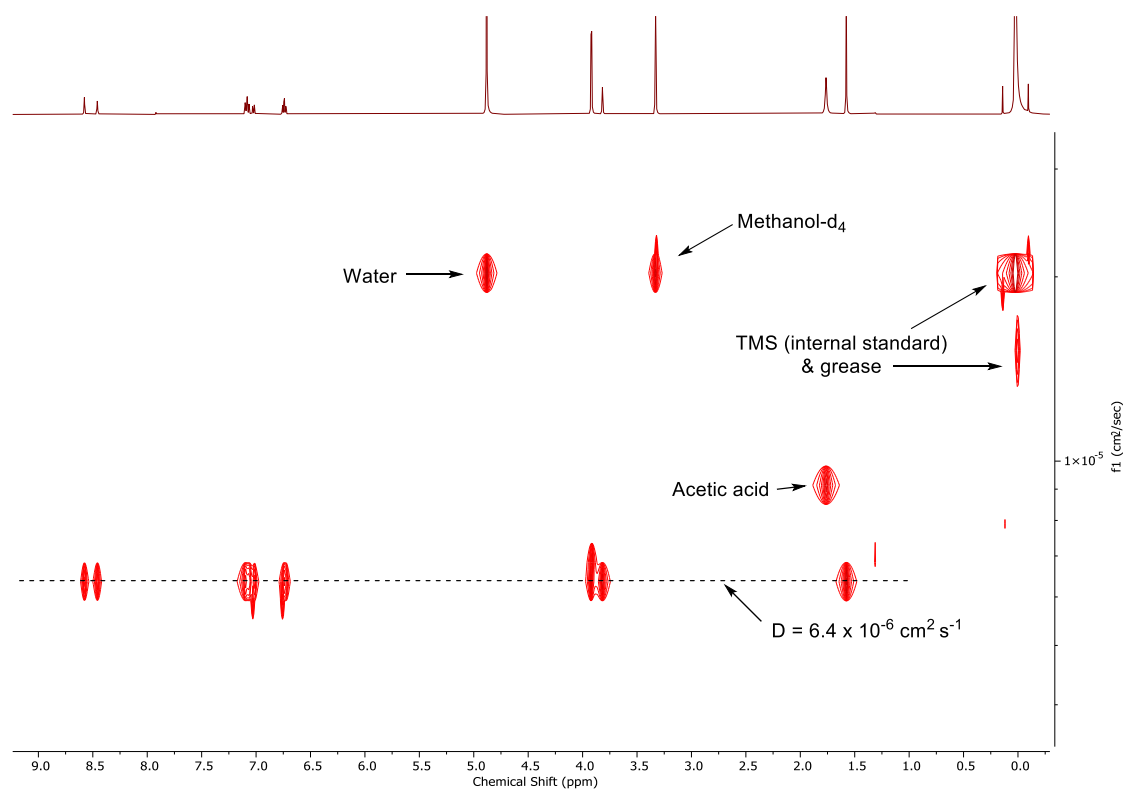


Figure S2.54. DOSY NMR spectrum (500 MHz, MeOD-d₄, 298 K) of complex **1**. The diffusion coefficient, D , obtained from this experiment and the Stokes-Einstein equation yields a solvation radius of 6.2 Å. This is close to the radius of the dimeric unit cell 6.7 Å.

Table S2.4. ^1H Chemical Shifts for the reactant and products of CHO/PA copolymerization in CDCl_3 .

Component	PA	PA in PCHPE	MES internal standard	CHO in ester linkage	CHO in ether linkage
Chemical shift (ppm)	8.06-8.00 7.94-7.88	7.63-7.52 7.44-7.34	6.78-6.81	5.22-5.04	3.80-3.20

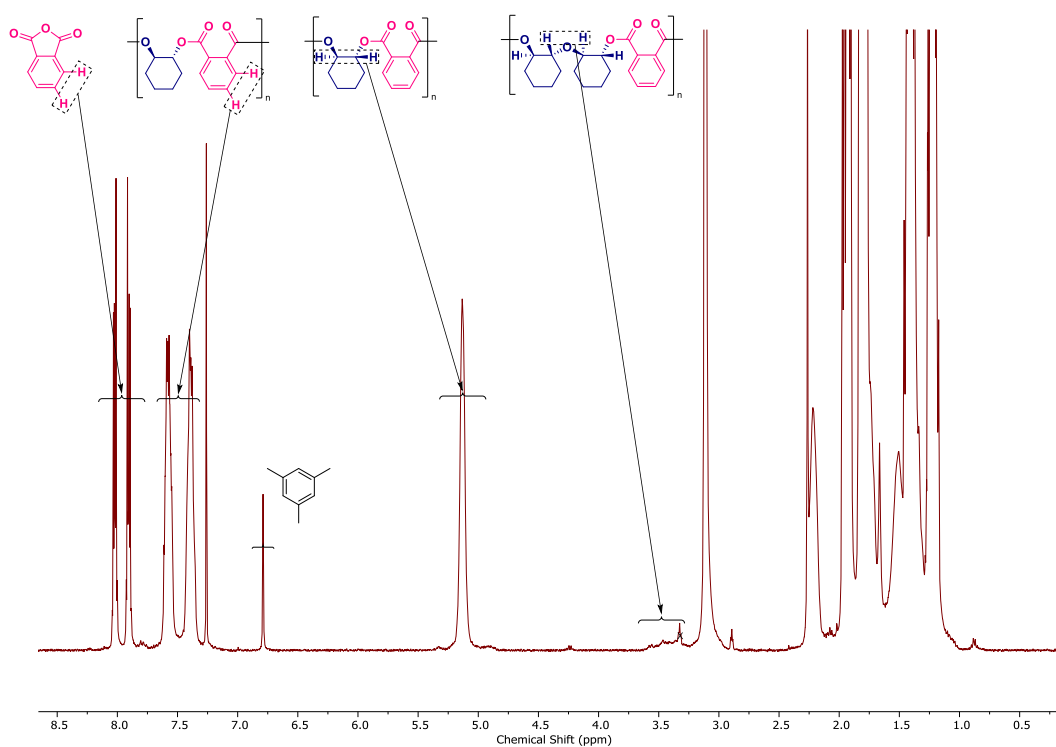
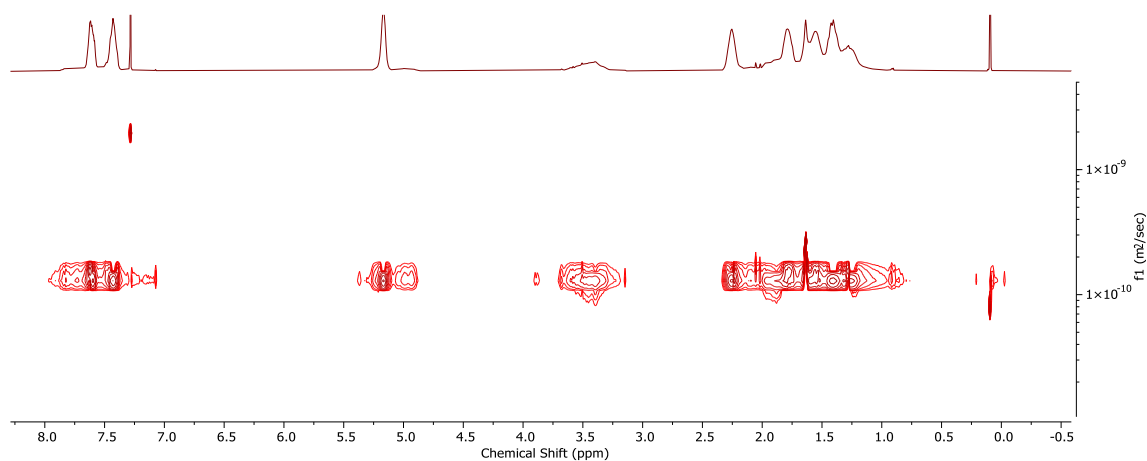
**Figure S2.55.** Excerpt of ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of reactant and products of CHO/PA copolymerization.

Figure S2.56. DOSY ^1H NMR spectrum (CDCl_3) of polymer formed by PA/CHO ROCOP using catalyst 4. A single diffusion coefficient is observed for the polymer indicating that the ether and ester linkages are both within the same polymer.

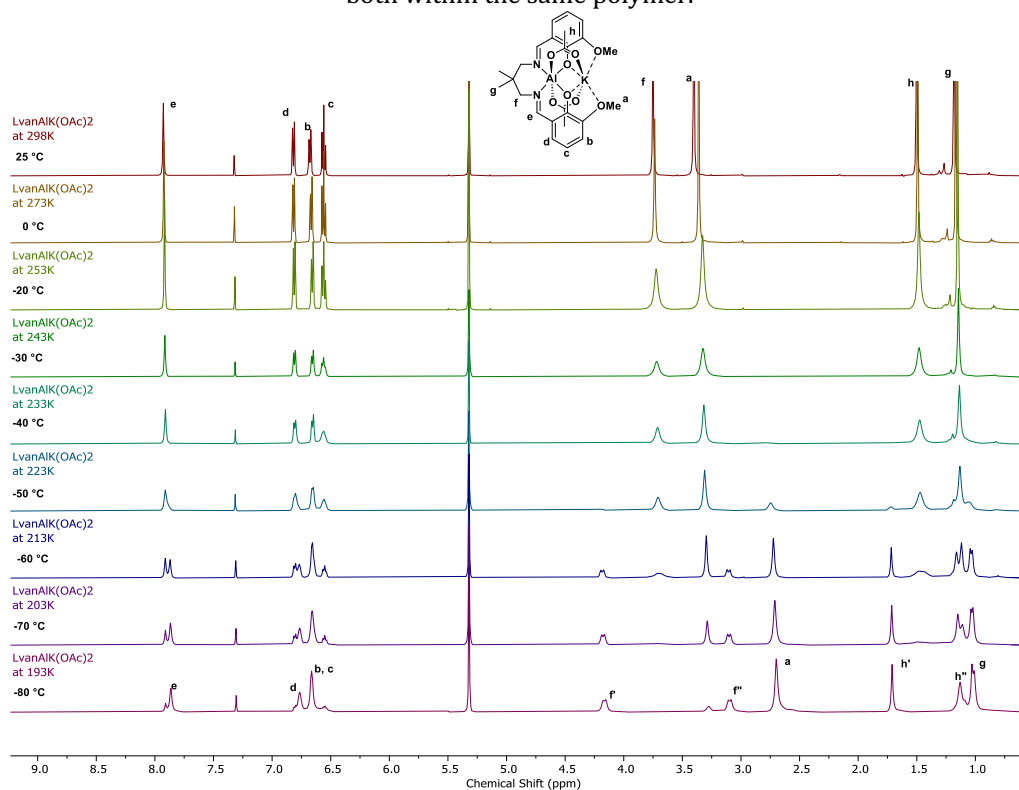


Figure S2.57. VT ^1H NMR spectra (400 MHz, CD_2Cl_2) of **1.32**. This shows a possible phase transition beginning at -40 °C but no indication of freezing out of fluxionality of the 6m metallocycle even at -80 °C.

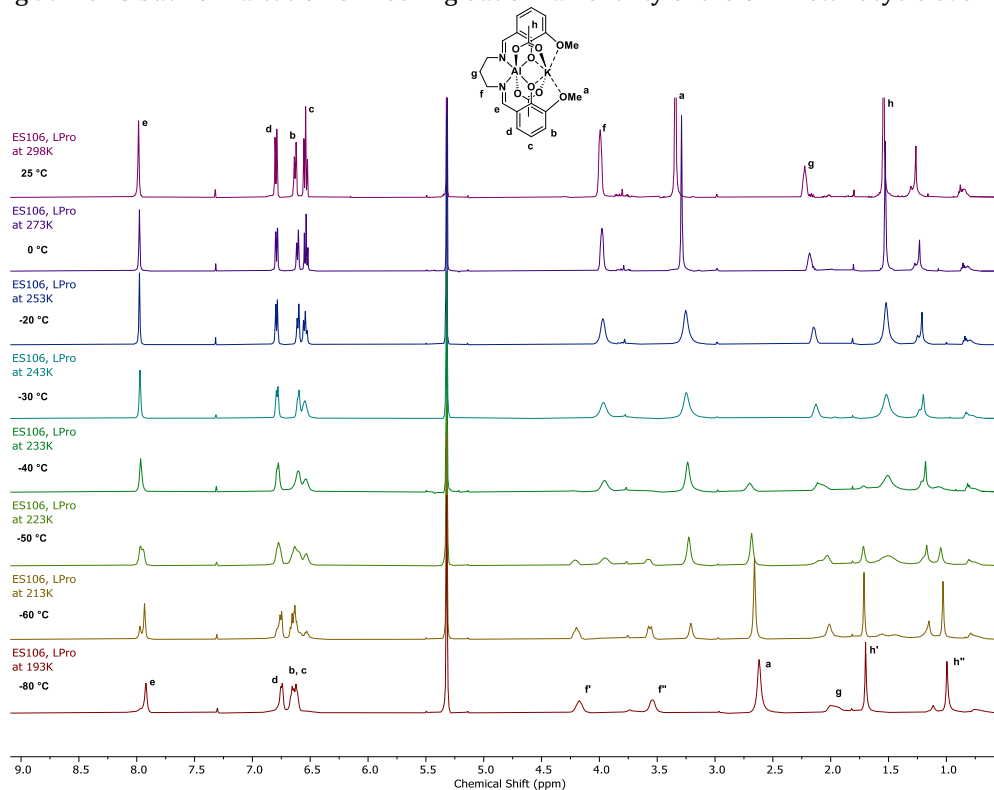


Figure S2.58. VT ^1H NMR spectra (400 MHz, CD_2Cl_2) of **5**. This shows a possible phase transition beginning at -40 °C but no indication of freezing out of fluxionality of the 6m metallocycle even at -80 °C.

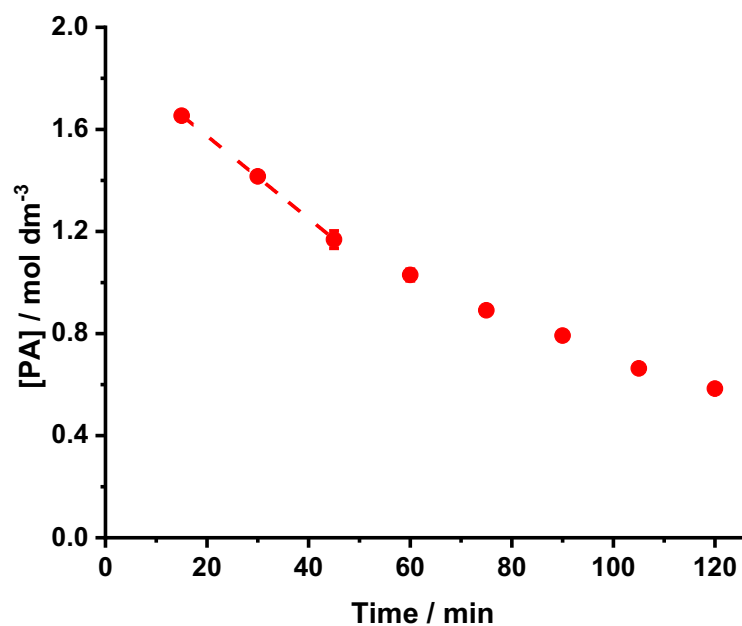


Figure S2.59. Graph of [PA] against time for CHO/PA ROCOP catalysed by complex 3.

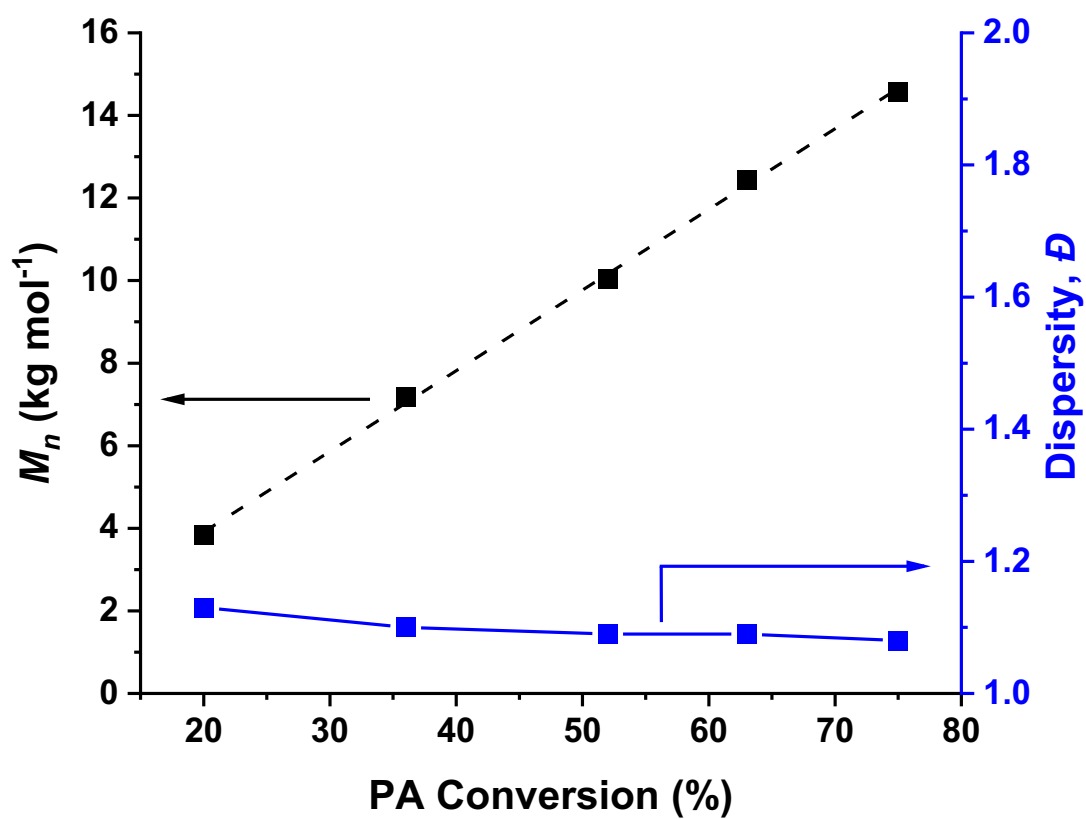


Figure S2.60. Plot of change in polymer molar mass and dispersity with increasing PA conversion for complex 2.

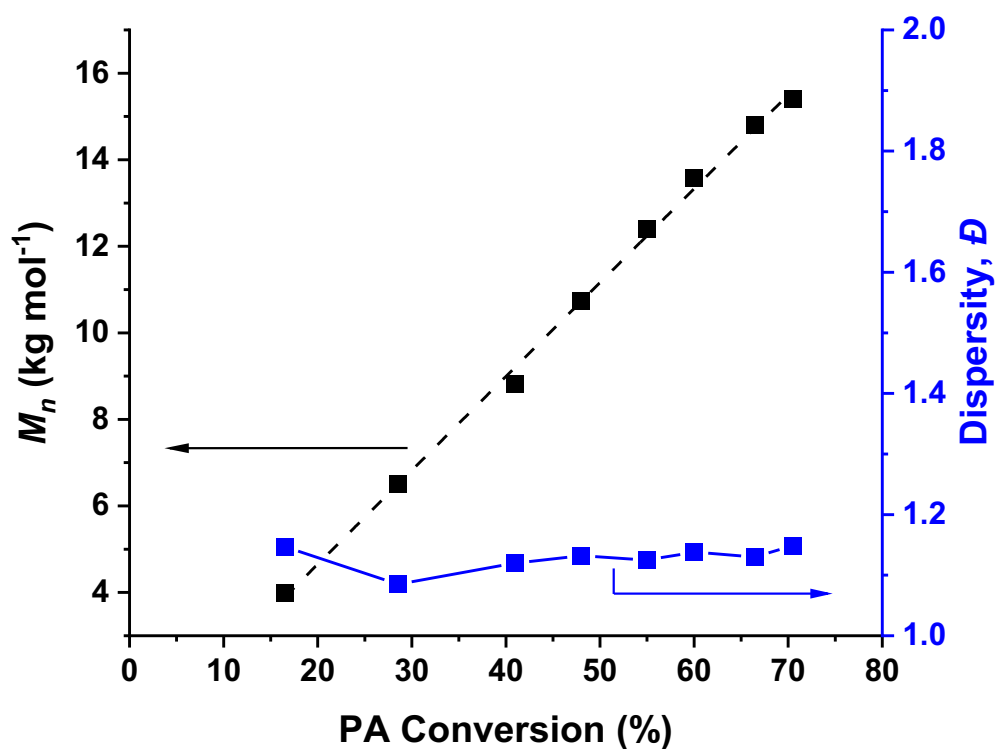


Figure S2.61. Plot of change in polymer molar mass and dispersity with increasing PA conversion for complex **3**.

Computational Details for Chapter 2

Density Functional theory (DFT) calculations were performed using Gaussian16 suite of codes (revision A.03). Geometries were fully optimised without any symmetry or geometry constraints. The nature of all the stationary points as minima or transition states (first-order saddle points) on the potential energy surface was verified by calculations of the vibrational frequency spectrum. All transition states were characterised by precisely one negative frequency corresponding to the intended reaction.

Free enthalpies were calculated at 298.15 K and a standard-state concentration in solution of 1 M within the harmonic approximation for vibrational frequencies.

Geometry optimisations were carried out using ω b97xD functional. The 6-31+G(d,p) basis set was used for C and H atoms, 6-311+G(d) for Al, K, O and N atoms. Solvent effects in cyclohexene oxide were computed using the cpcm continuum model, using modified parameters for THF ($\epsilon=16$, $\epsilon_{\text{inf}}=1.867$).¹

Full coordinates for all structures, together with computed energies and vibrational frequency data, are available via the corresponding Gaussian 09 output files, stored in the following open-access repository:

[GeorgeLGregory/DFT-for-Al-III-K-I-Heterodinuclear-ROCOP-Catalysts: DFT for Al-K ROCOP catalysts](#)

Table S2.5. Summary of computed values for catalyst **1**.^a

Structure	G (Hartrees)	ΔG (kcal mol ⁻¹)
CHO	-309.679573	-
I ₁	-2676.447496	-
Referece (CHO + I ₁)	-2986.127069	0.0
I _{Al1}	-2986.121265	+3.6
TS _{I-IIAl1}	-2986.091347	+22.4
II _{Al1}	-2986.136855	-6.1
I _{K1}	-2986.129389	-1.5
TS _{I-IIK1}	-2986.077815	+30.9
II _{K1}	-2986.091132	+22.6

^a ω b97xD/C H = 6-31+g(d,p)/K Al O N = 6-311+g(d)/solvent = modified THF $\epsilon=16$ $\epsilon_{\text{inf}}=1.867$ (cpcm)

Table S2.6. Summary of computed values for catalyst **4**.^a

Structure	G (Hartrees)	ΔG (kcal mol ⁻¹)
CHO	-309.679573	-
I ₄	-2750.243310	-
Referece (CHO + I ₄)	-3059.922883	0.0
I _{Al4}	-3059.924052	+5.8
TS _{I-IIAl4}	-3059.884832	+23.5
II _{Al4}	-3059.922868	-0.4
I _{K4}	-3059.912943	-0.7
TS _{I-IIK4}	-3059.872913	+31
II _{K4}	-3059.888235	+21.3

^a ω b97xD/C H = 6-31+g(d,p)/K Al O N = 6-311+g(d)/solvent = modified THF $\epsilon=16$ $\epsilon_{\text{inf}}=1.867$ (cpcm)

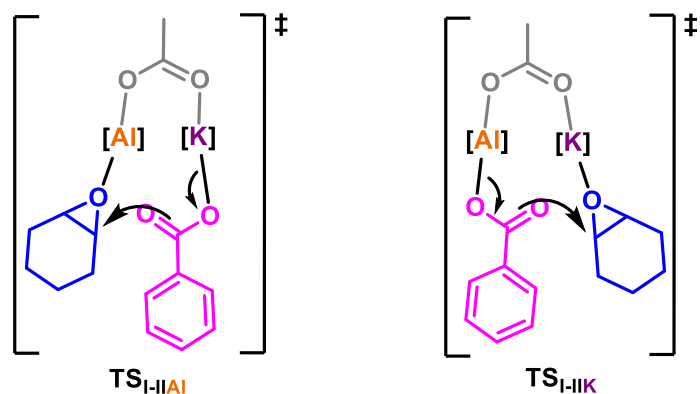


Figure S2.62. Diagrams of the two key transition states being studied.

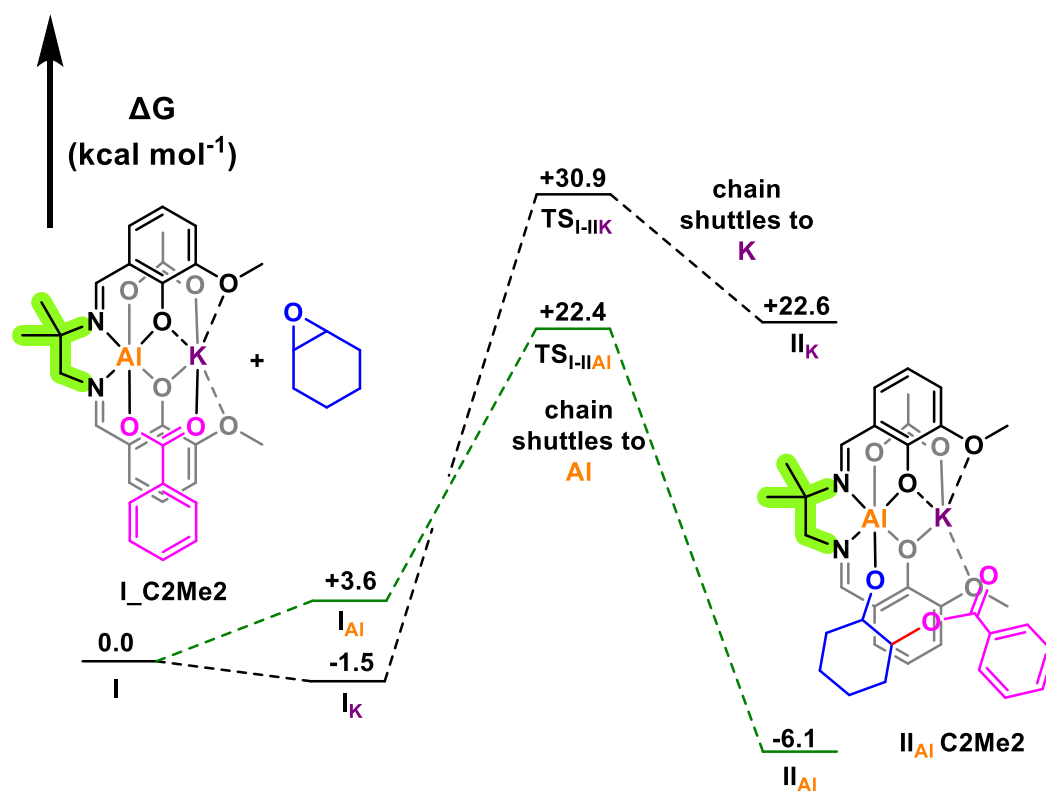


Figure S2.63. Computed Reaction Profile for epoxide ring-opening using **1**. rwb97xD/C H O= 6-31+g(d,p)/K Al= 6-311+g(d)/solvent = modified THF eps=16 epsinf=1.867 (cpcm).

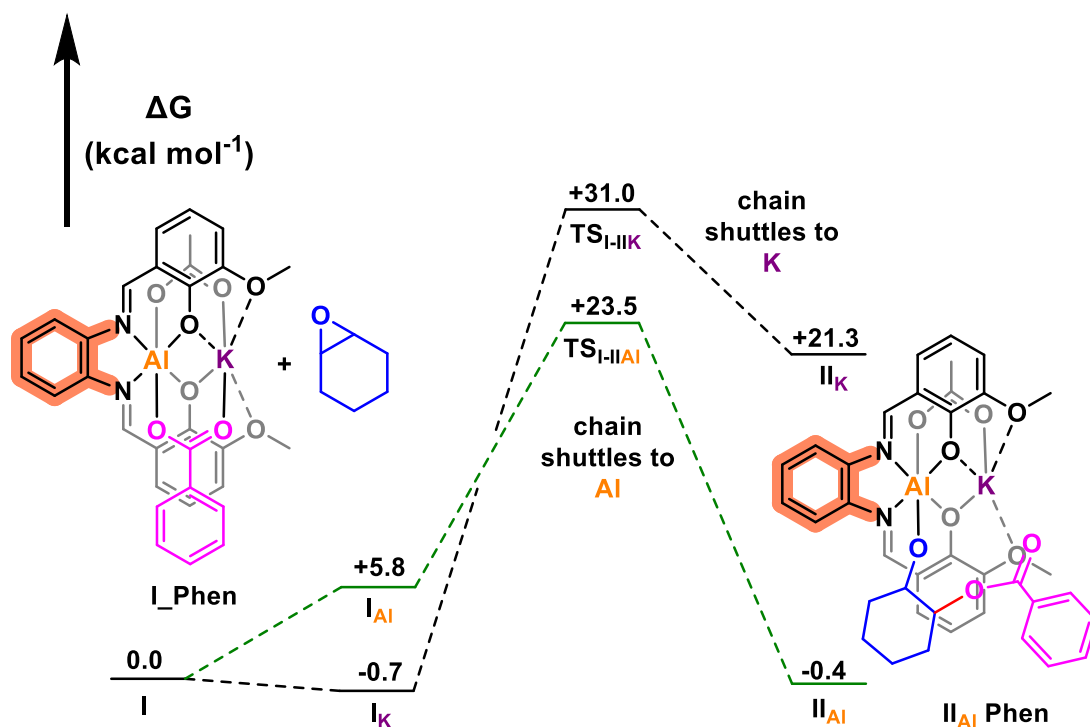


Figure S2.64. Computed Reaction Profile for epoxide ring-opening using **4**. rw97xD/C H O= 6-31+g(d,p)/K Al= 6-311+g(d)/solvent = modified THF eps=16 epsinf=1.867 (cpcm).

Table S2.7. Rates for the ROCOP of CHO/PA using complex **1** with different CHD loadings.

Entry	Conditions		Polymerisation Data			
	CHD equiv. (#)	[CHD] / mol dm ⁻³	TOF (h ⁻¹) ^a	<i>k</i> _{obs} (mol dm ⁻³ s ⁻¹ × 10 ⁻³) ^b	Relative Rate	PE select. (%) ^c
a	0	0	309	0.425 (± 0.009)	1	> 99
b	10	0.0494	510	0.70 (± 0.07)	1.7	> 99
c	20	0.0988	714	0.98 (± 0.07)	2.3	> 99
d	50	0.247	814	1.12 (± 0.04)	2.6	> 99
e	100	0.494	1020	1.41 (± 0.08)	3.3	> 99
f	200	0.988	1330	1.83 (± 0.07)	4.3	> 99
g	400	1.98	1330	1.83 (± 0.07)	4.3	> 99

[**1**]: [CHD]: [anhydride]: = 1#:400, 1 mL CHO such that [**1**] = 4.9 mmol, 100 °C ^a Turnover frequency from the gradient of TON vs time (h). TON = (conversion (%) / 100 (%)) * ([anhydride] / [**1**]). Conversion determined by ¹H NMR spectroscopy (298 K, 400 MHz, CDCl₃) by comparison of the normalised integrals of PA peaks, at 8.06-8.00 and 7.94- 7.88 ppm, vs. equivalent polymer peaks, 7.63-7.52 and 7.44-7.34 ppm. ^b Determined as the gradient of fits to plots of [PA] (mol dm⁻³) vs time (s). Errors from the error in fit of the linear gradient of [PA] (mol dm⁻³) vs t (s). ^c Selectivity for polyester over ether linkage formation. Determined by ¹H NMR spectroscopy (298 K, 400 MHz, CDCl₃) by comparison of polyester peaks (5.22-5.04 ppm) vs. any ether linkages (3.8-3.2 ppm).

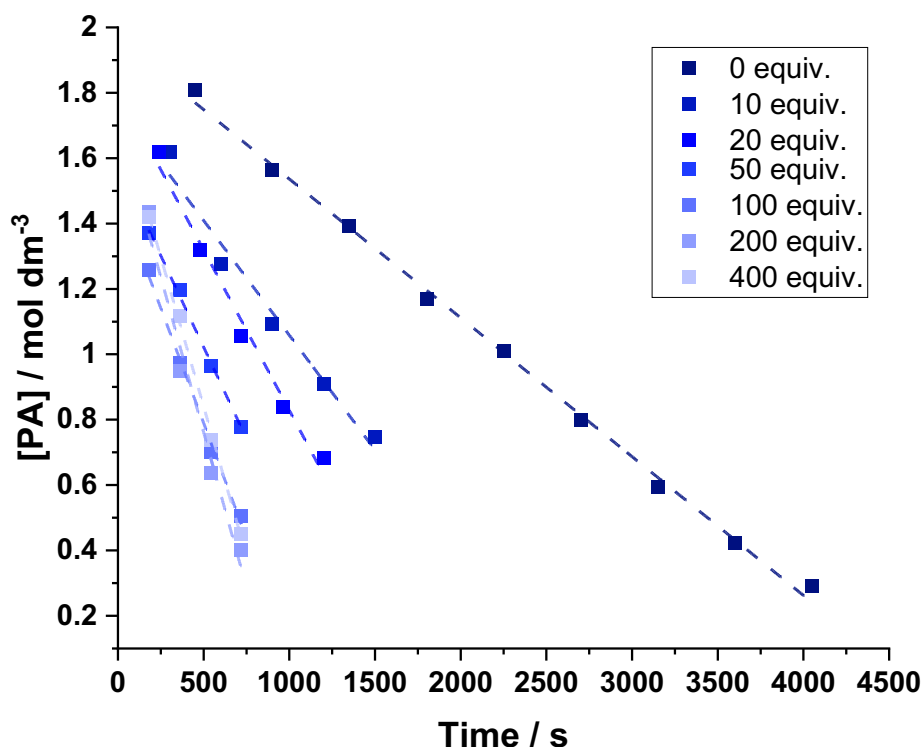


Figure S2.65. Graph showing the linear correlation between [PA] (mol dm^{-3}) and time (s) for all different [CTA]. [1]: [CHD] : [anhydride] = 1:#:400, 1 mL CHO such that [1] = 4.9 mmol, 100 °C.

Table S2.8. Rates for the ROCOP of CHO/PA using complex **1.32** with different CHD loadings.

Entry	CHD equiv. (#)	Time (min)	TON ^a	TOF (h^{-1}) ^b	Rel. Rate	PE Select. (%) ^c	$M_{n, \text{GPC}}$ (g mol^{-1}) ¹ [D_M] at full conversion ^d	$M_{n, \text{Theory}}$ (g mol^{-1}) ^e
a ²	0	15	268	1072	1	>99	-	49,000
b	20	5	111	1336	1.25	>99	3,500 [1.14]	4,600
c	100	5	145	1744	1.63	>99	900 [1.14]	1,100
d	200	5	155	1860	1.74	>99	540 [1.00]	600
e	400	5	103	1239	1.16	>99	-	360

[**1.32**]: [CHD] : [anhydride] = 1:#:400, 1 mL CHO such that [**1.32**] = 4.9 mmol, 100 °C ^a TON = (conversion (%) / 100 (%)) * ([anhydride] / [**1.32**]). Conversion (%) determined by ¹H NMR (298 K, 400 MHz, CDCl₃) spectroscopy; comparison of PA monomer peaks at 8.06-8.00 and 7.94- 7.88 ppm to polymer peaks at 7.63-7.52 and 7.44-7.34 ppm. ^b Turnover frequency = TON/time(h). TON determined *via* Conversion*[Anhydride]. ^c Selectivity for polyester linkages by analysis of the ¹H NMR spectrum (298 K, 400 MHz, CDCl₃); polyester 5.22-5.04 ppm vs. ether linkages 3.8-3.2 ppm. ^d Determined by GPC in THF, 30 °C, calibrated using PS standards. ^e Determined using $(\text{TON} \cdot M_{n, \text{repeatunit}}) / ([\text{Catalyst}] + [\text{CHD}]) + M_{n, \text{CHD}}$.

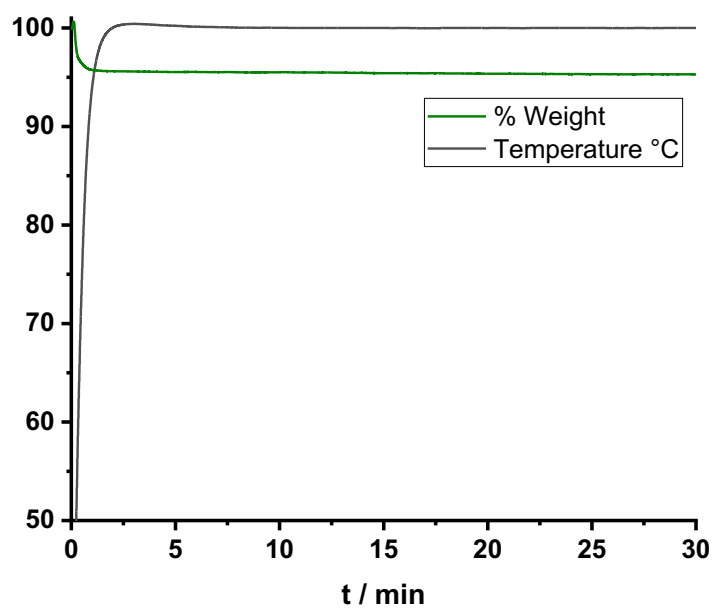


Figure S2.66. TGA of 100 °C isotherm of **1**. Initial mass drop upon heating attributed to solvent.

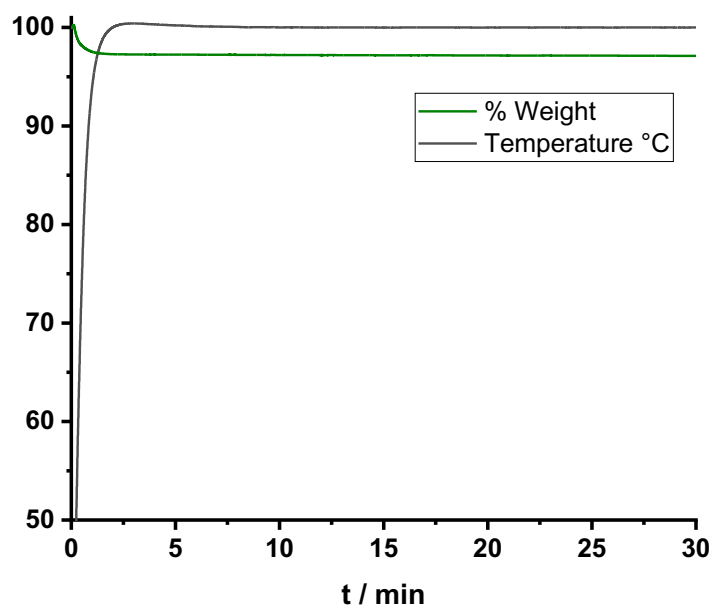


Figure S2.67. TGA of 100 °C isotherm of **1** + GEO.

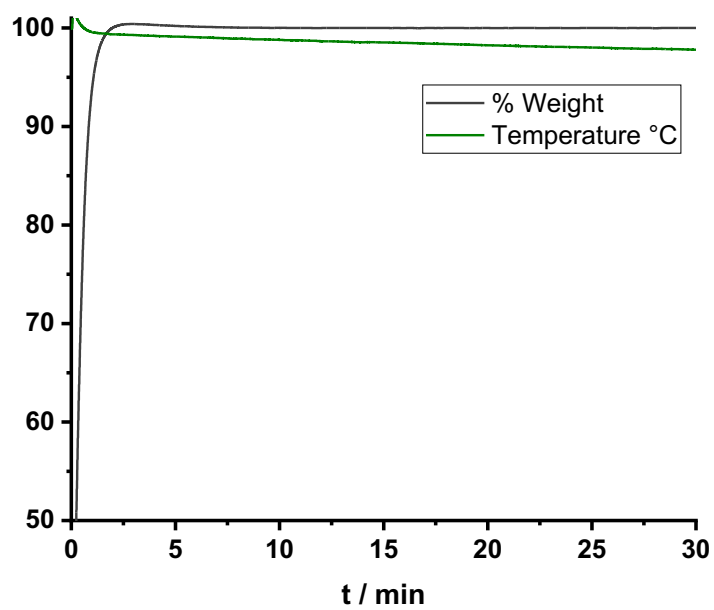


Figure S2.68. TGA of 100 °C isotherm of **1.32**.

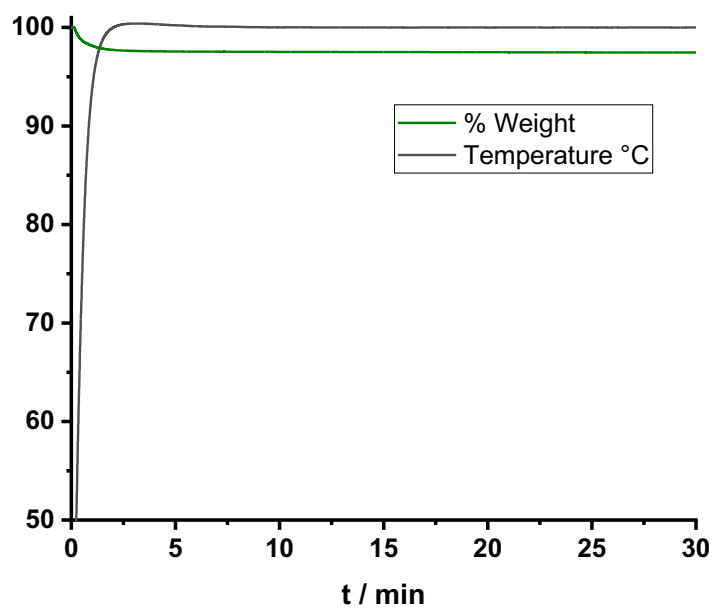


Figure S2.69. TGA of 100 °C isotherm of **1.32 + GEO**.

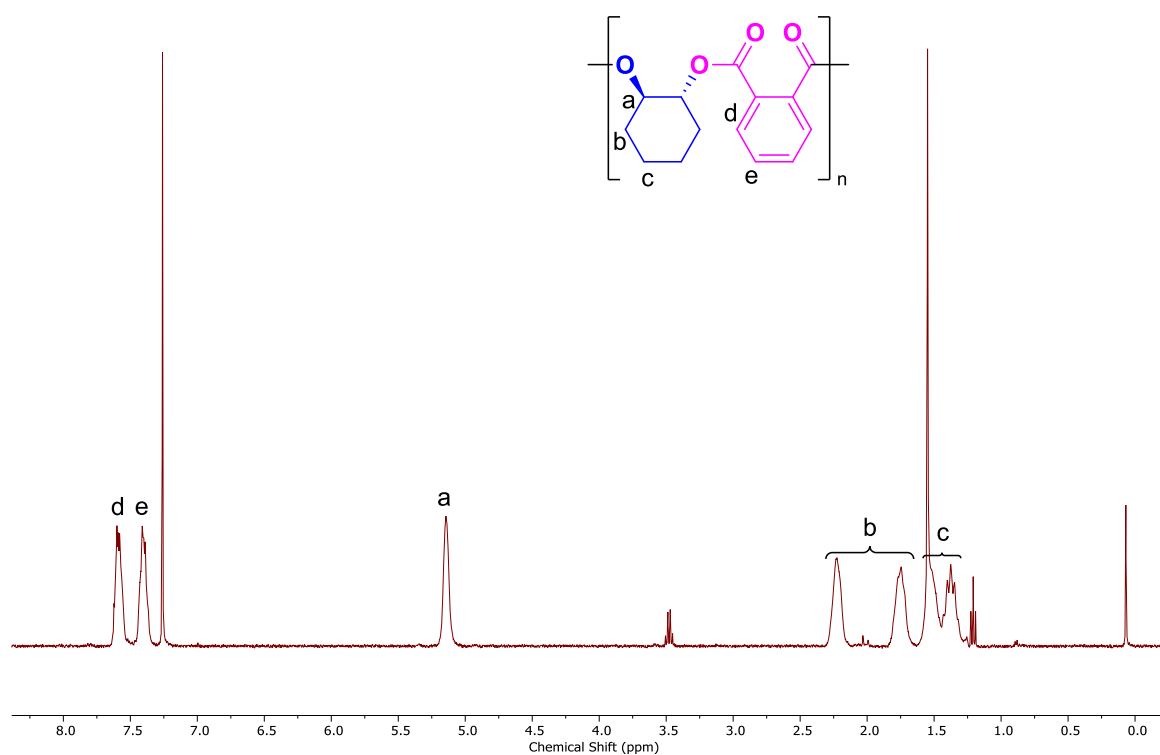


Figure S2.70. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of isolated polymer from the polymerisation of CHO/PA.

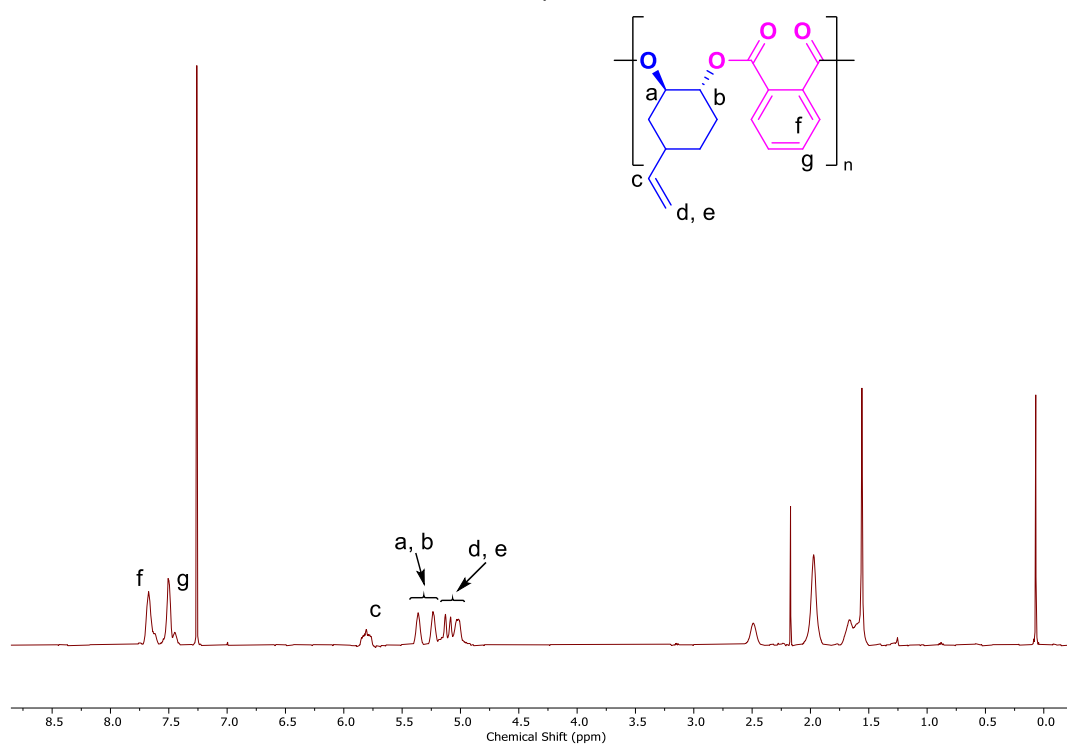


Figure S2.71. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of isolated polymer from the polymerisation of vCHO/PA.

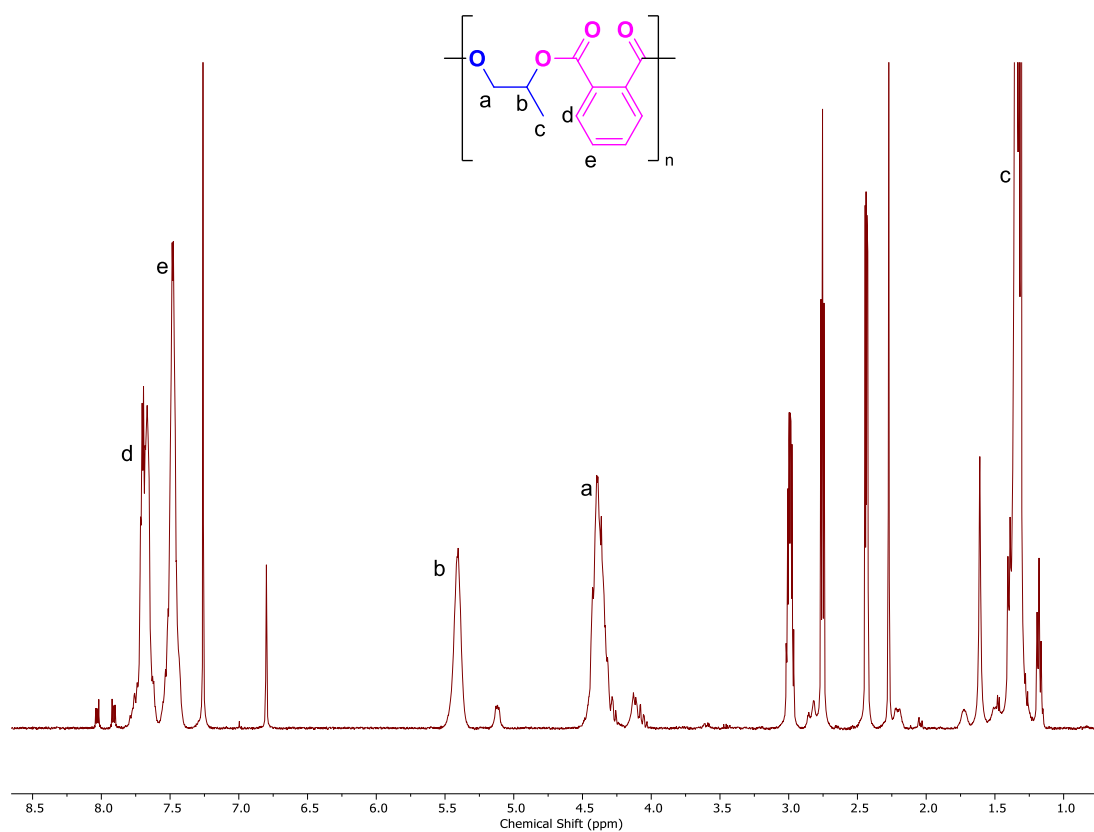


Figure S2.72. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of PO/PA polymerisation reaction mixture (at 99 % conversion).

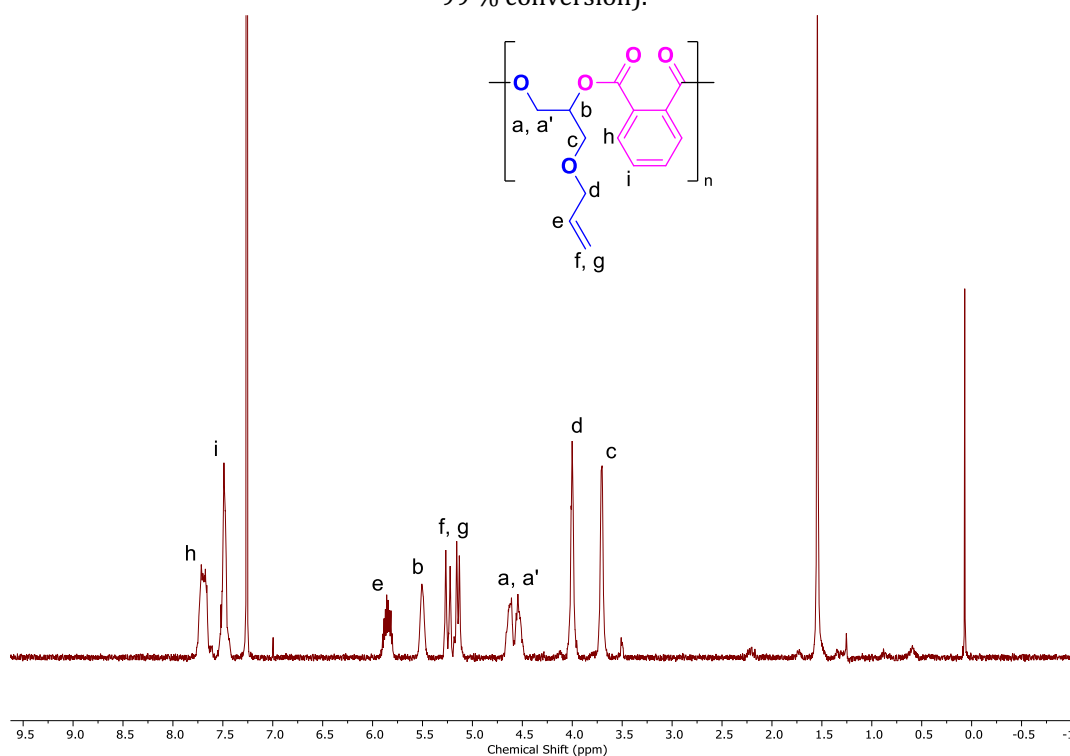


Figure S2.73. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of isolated polymer from the polymerisation of AGE/PA.

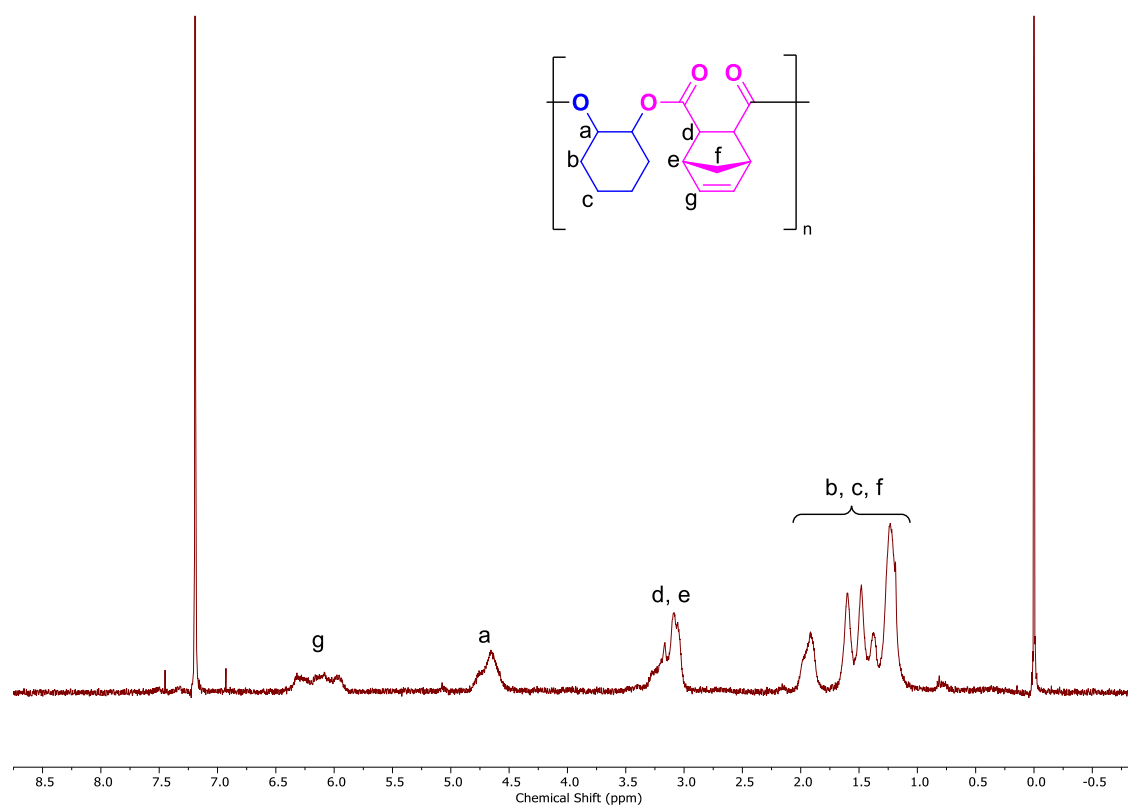


Figure S2.74. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of isolated polymer from the polymerisation of CHO/NBA.

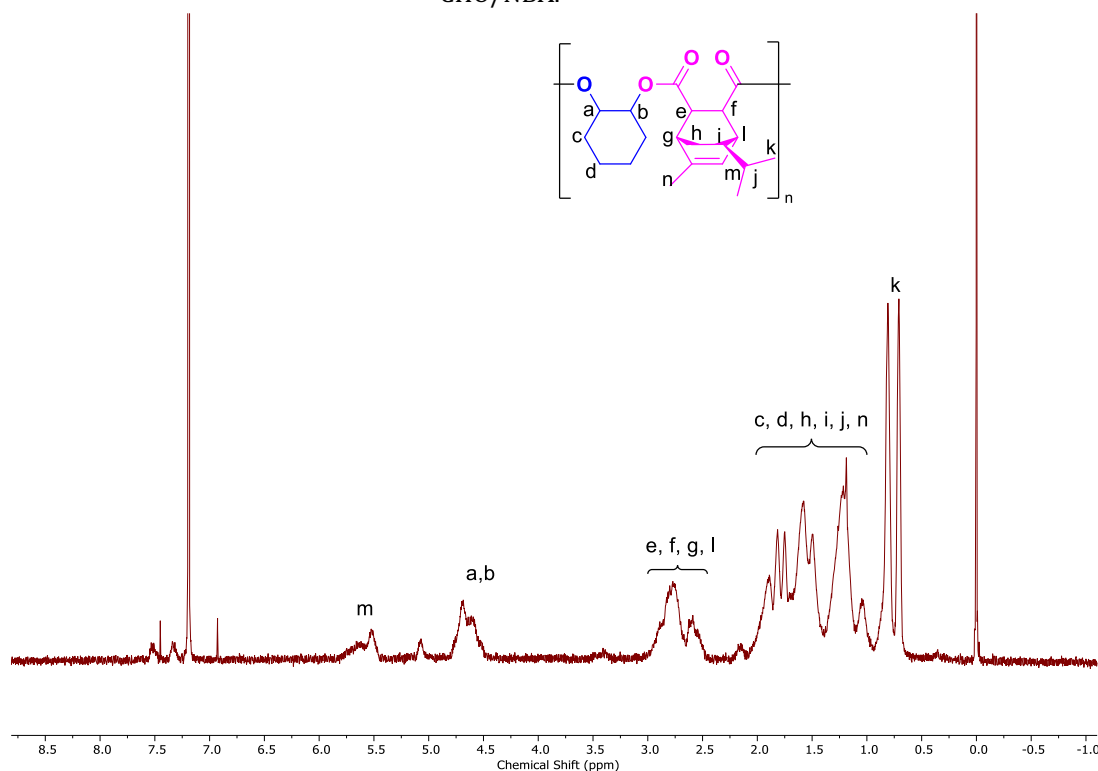


Figure S2.75. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of isolated polymer from the polymerisation of CHO/TGA.

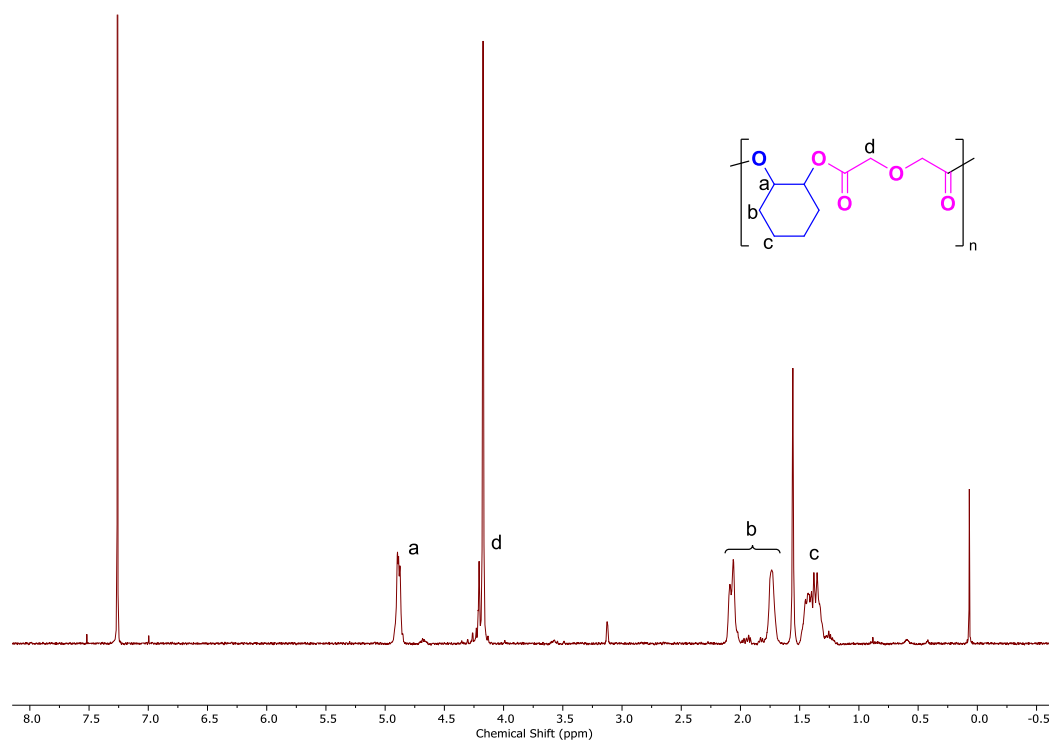


Figure S2.76. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of isolated polymer from the polymerisation of CHO/DGA.

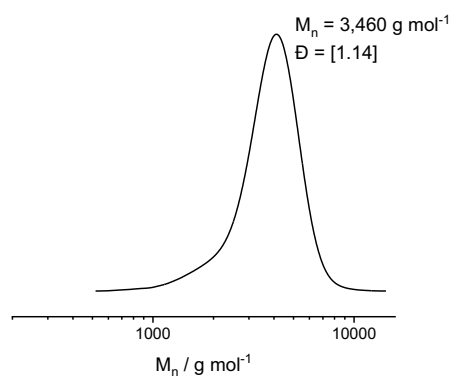


Figure S2.77. GPC plot of CHO/PA polymerisation at full conversion.

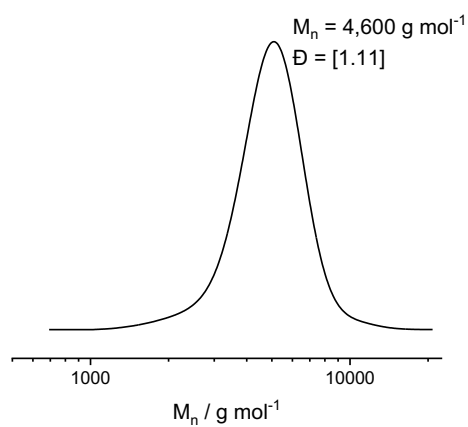


Figure S2.78. GPC plot of vCHO/PA polymerisation at full conversion.

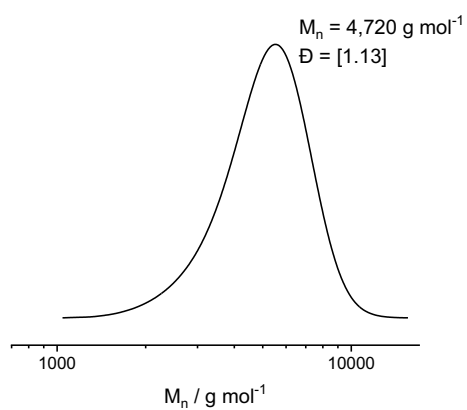


Figure S2.79. GPC plot of PO/PA polymerisation at full conversion.

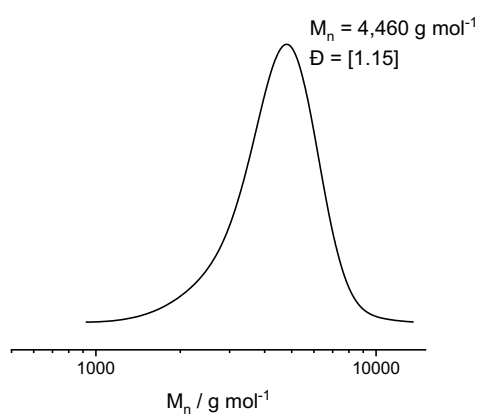


Figure S2.80. GPC plot of AGE/PA polymerisation at full conversion.

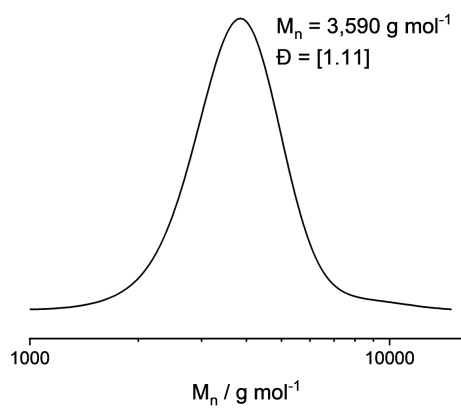


Figure S2.81. GPC plot of CHO/NBA polymerisation at full conversion.

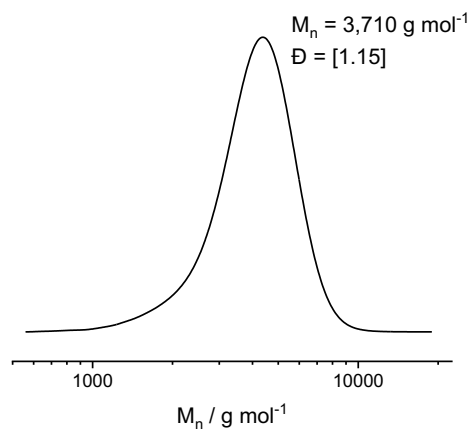


Figure S2.82. GPC plot of CHO/TCA polymerisation at full conversion.

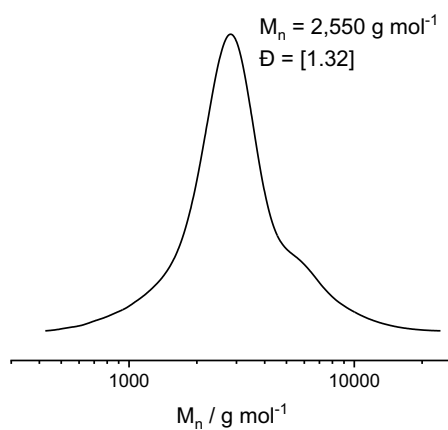


Figure S2.83. GPC plot of CHO/DGA polymerisation at full conversion.

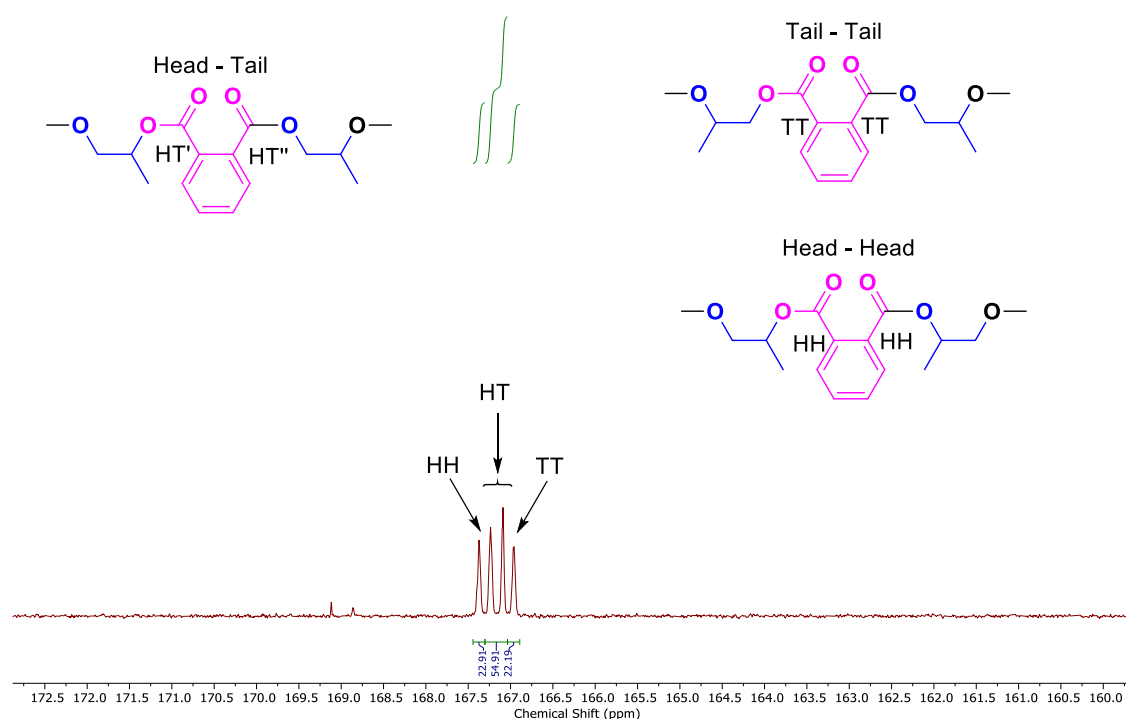


Figure S2.84. Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3 , 298 K) of isolated PO/PA polymer to find head-tail regioselectivity.

Table S2.9. Rates for the ROCOP of epoxide/PA using complex **1** with different CHD loadings.

Entry	Conditions		Polymerisation Data			
	Monomers	CHD equiv.	Time (min)	TON ^b	TOF (h ⁻¹) ^c	PE Select. (%) ^d
a	vCHO/PA	0	100	296	178	>99
b	vCHO/PA	20	15	225	901	>99
c ^a	PO/PA	0	1,020	336	20	>99
d ^a	PO/PA	20	420	198	28	>99
e ^a	PO/PA	100	300	200	40	>99

^a Reaction run at 60 °C. ^b Calculated using Conversion*[monomer] (where [] is the equivalence). Conversion determined by ^1H NMR (298 K, 400 MHz, CDCl_3) spectroscopy; comparison of PA monomer peaks at 8.06-8.00 and 7.94- 7.88 ppm to polymer peaks at 7.63-7.52 and 7.44-7.34 ppm. ^c Turnover frequency = TON/time(h). ^d Selectivity for polyester over polyether formation. Determined by ^1H NMR spectroscopy (298 K, 400 MHz, CDCl_3) by comparison of resonances from ester vs. ether linkages.

3 Supplementary Figures and Tables for Chapter 3

Table S3.1 ^1H Chemical Shifts for the reactant and products of CHO/ CO_2 copolymerization in CDCl_3 .

Component	CHO	PCHC Backbone	PCHC End Groups	<i>trans</i> -Cyclohexane carbonate	<i>cis</i> -Cyclohexane carbonate	Polyether
Chemical shift (ppm)	3.05	4.65	4.35, 3.50	4.00	4.68	3.45

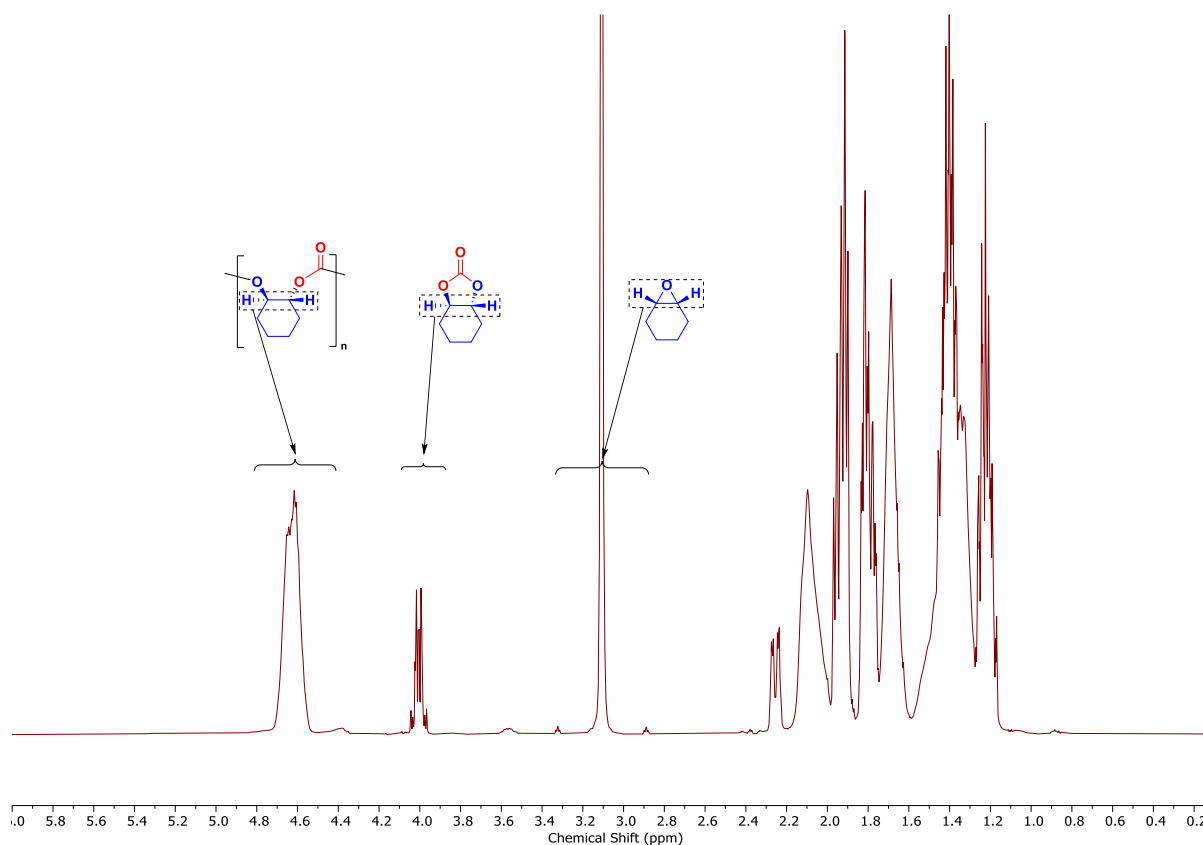


Figure S3.1 Excerpt of ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of CHO/ CO_2 copolymerization mixture.

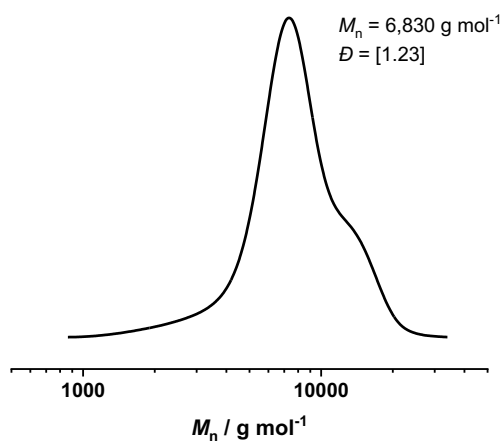


Figure S3.2 GPC trace of CHO/CO₂ polymerisation catalysed by **1**.

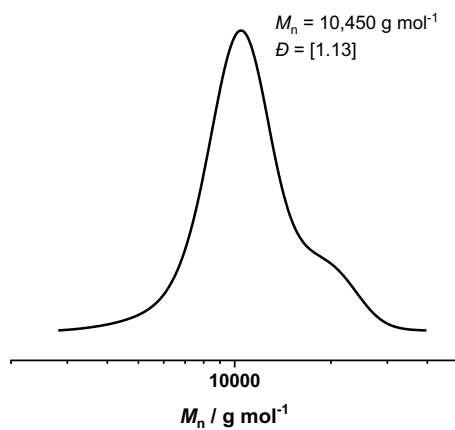


Figure S3.3 GPC trace of CHO/CO₂ polymerisation catalysed by **2**.

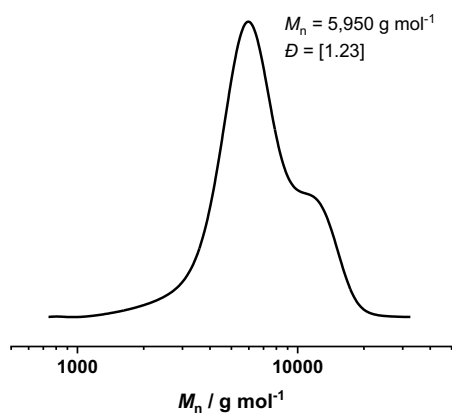


Figure S3.4 GPC trace of CHO/CO₂ polymerisation catalysed by **3**.

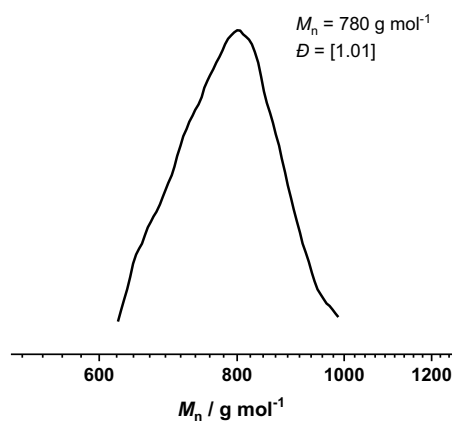


Figure S3.5 GPC trace of CHO/CO₂ polymerisation catalysed by **4**.

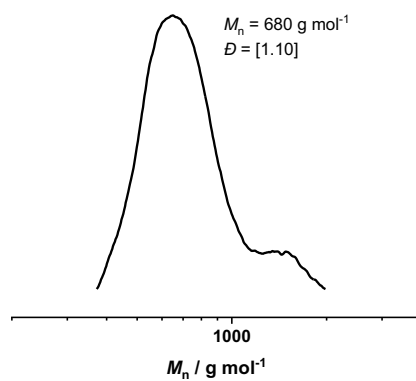


Figure S3.6 GPC trace of CHO/CO₂ polymerisation catalysed by **6**.

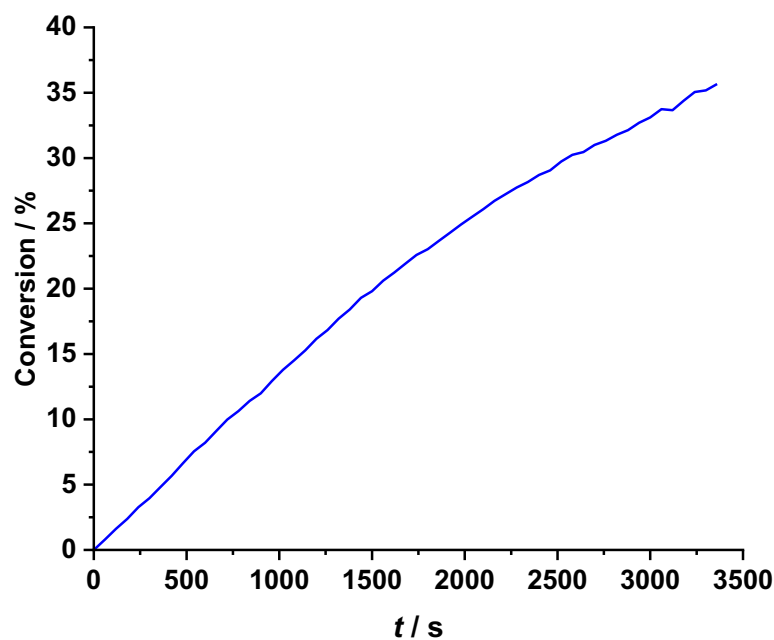


Figure S3.7 Graph of conversion (%) vs. time (s) for a typical high pressure CO₂ polymerisation ([2]:[CHD]:[CHO] = 1:20:2000, $p(\text{CO}_2)$ = 20bar, T = 100 °C). Peak at 1750 cm⁻¹ monitored.

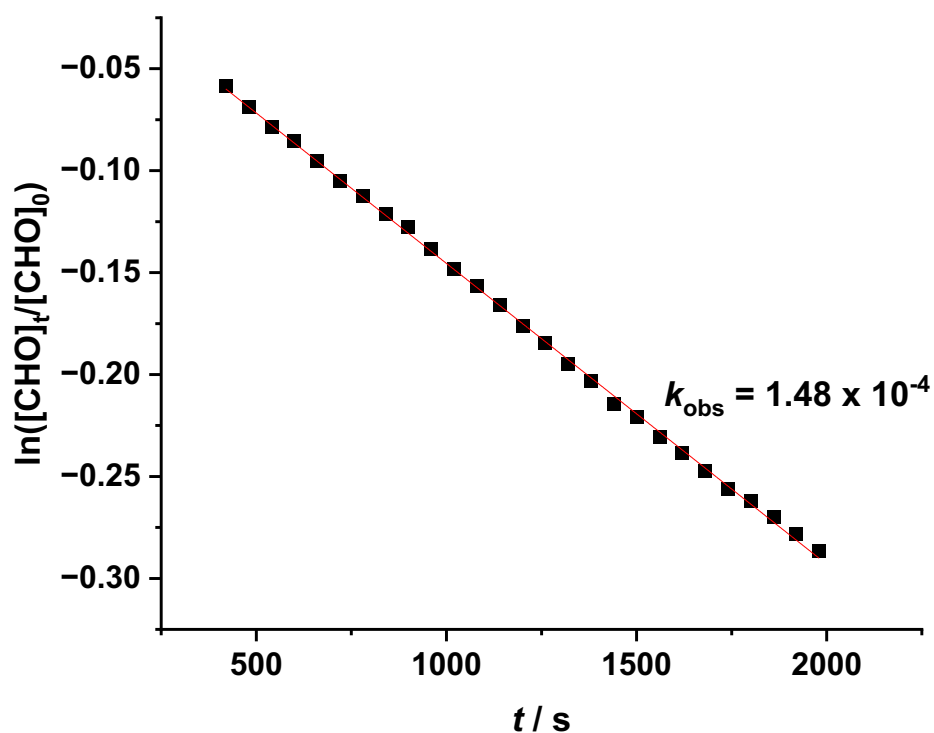


Figure S3.8 Graph of $\ln([\text{CHO}]_t/[\text{CHO}]_0)$ against time (s) for the data presented in Figure S3.7 between 5-25 % conversion ([2]:[CHD]:[CHO] = 1:20:2000, $p(\text{CO}_2)$ = 20bar, T = 100 °C). k_{obs} = -1 * gradient (linear fit).

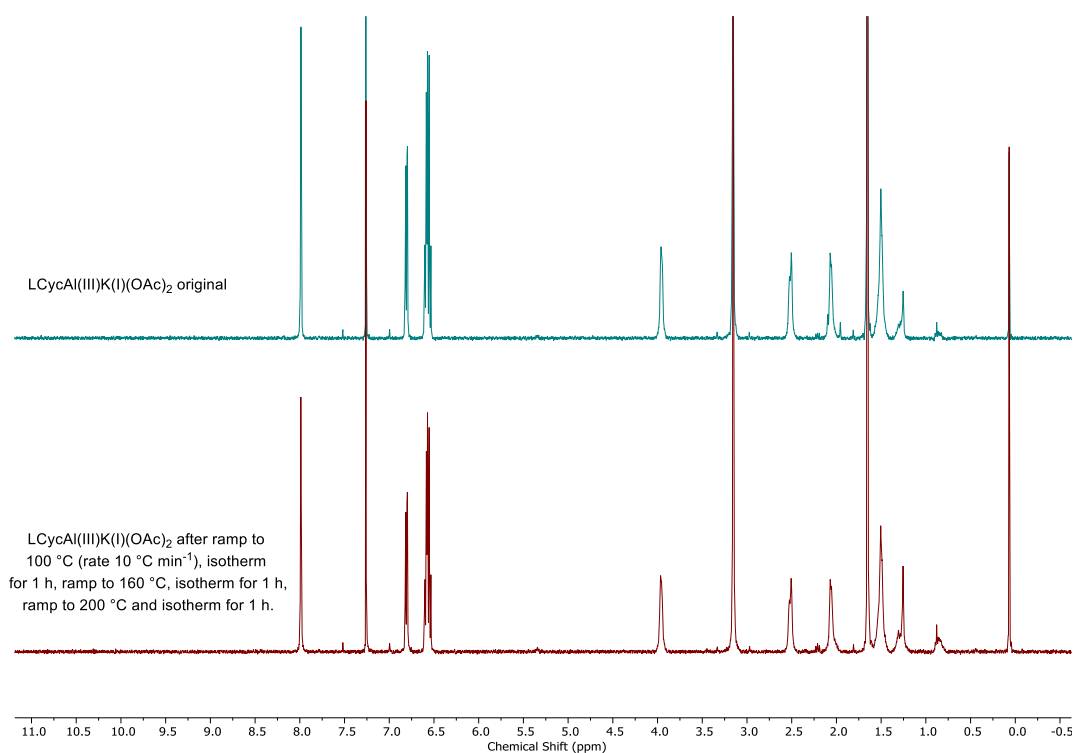


Figure S3.9 ¹H NMR spectra of **2** before and after DSC thermal stability test. Ramp to 100 °C (rate 10 °C min⁻¹), isotherm for 1 h, ramp to 160 °C, isotherm for 1 h, ramp to 200 °C and isotherm for 1 h. No change in spectra observed.

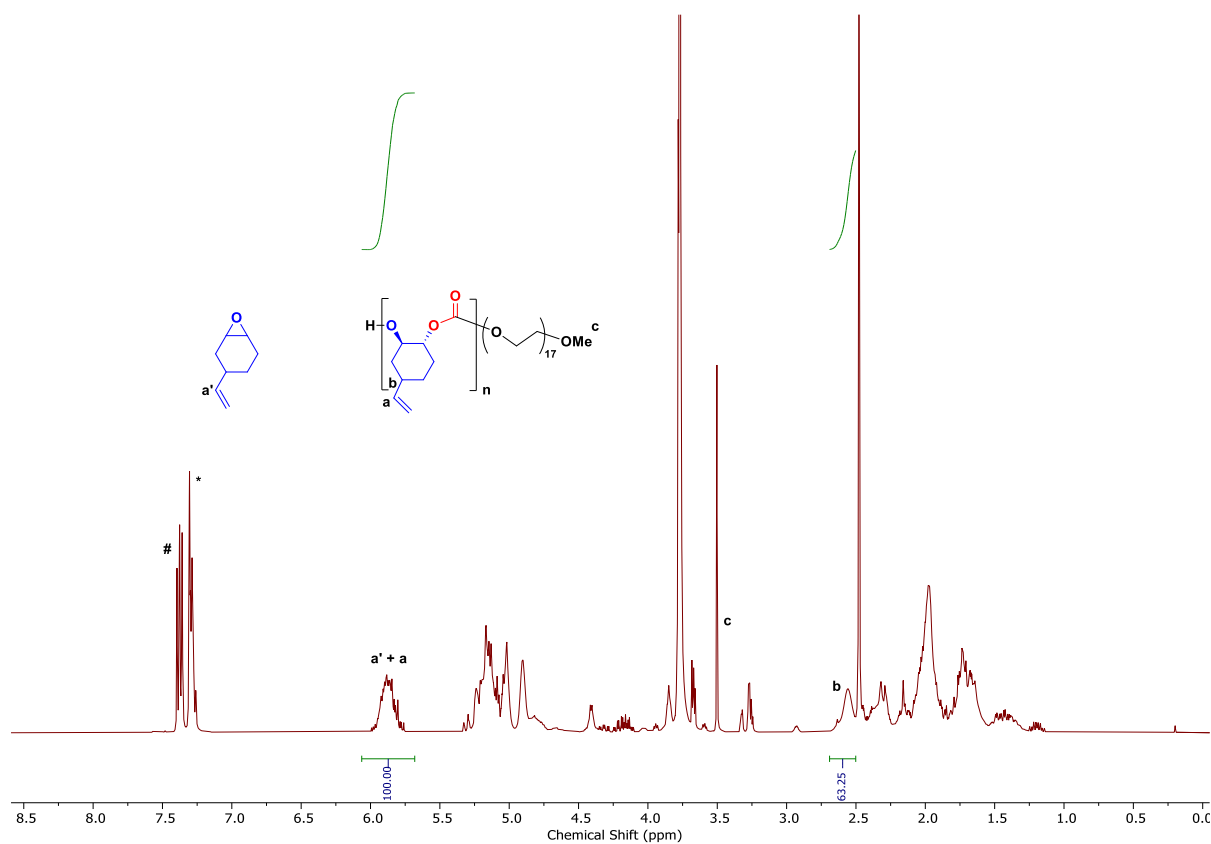


Figure S3.10 ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of aliquot of vCHO/CO₂ copolymerization mixture (Polymerisation conditions: [2]:[PEG-17]:[vCHO] = 1:98:1000, V(vCHO) = 4 mL, additional V(Toluene) = 2 mL, p(CO₂) = 20 bar, T = 100 °C, t = 44 h).

Table S3.2 Rate data for CHO/CO₂ ROCOP catalysed at different [2].

Entry	[cat] ($\times 10^{-3}$ mol dm ⁻³)	ln[cat]	k_{obs} ($\times 10^{-5}$ s ⁻¹) ^a	ln(k_{obs})	TOF (h ⁻¹) ^b
a	4.93	-5.31	14.4 ± 0.4	-8.85 ± 0.02	880 ± 73
b	2.47	-6.00	7.6 ± 0.9	-9.49 ± 0.12	971 ± 100
c	1.65	-6.41	3.8 ± 0.3	-10.17 ± 0.08	812 ± 48
d	1.24	-6.70	3.4 ± 0.2	-10.55 ± 0.09	781 ± 53
e	0.99	-6.92	1.9 ± 0.1	-10.98 ± 0.01	753 ± 111

Reaction conditions [2]:[CHD]:[CHO] = 1:20:2000-10000 at 20 bar CO₂, $T = 100$ °C. ^a k_{obs} obtained from gradient of linear fit between $\ln([\text{CHO}]_t/[\text{CHO}]_0)$ vs. t (s) for conversions 5-25 %. CHO conversion determined by ¹H NMR (298 K, 400 MHz, CDCl₃) spectroscopy; comparison of CHO peak 3.05 ppm, PCHC backbone peak 4.65 ppm. ^bTOF at 20 % conversion. TOF = TON/time(h). TON calculated from conversion(of CHO)*equiv.(monomer).

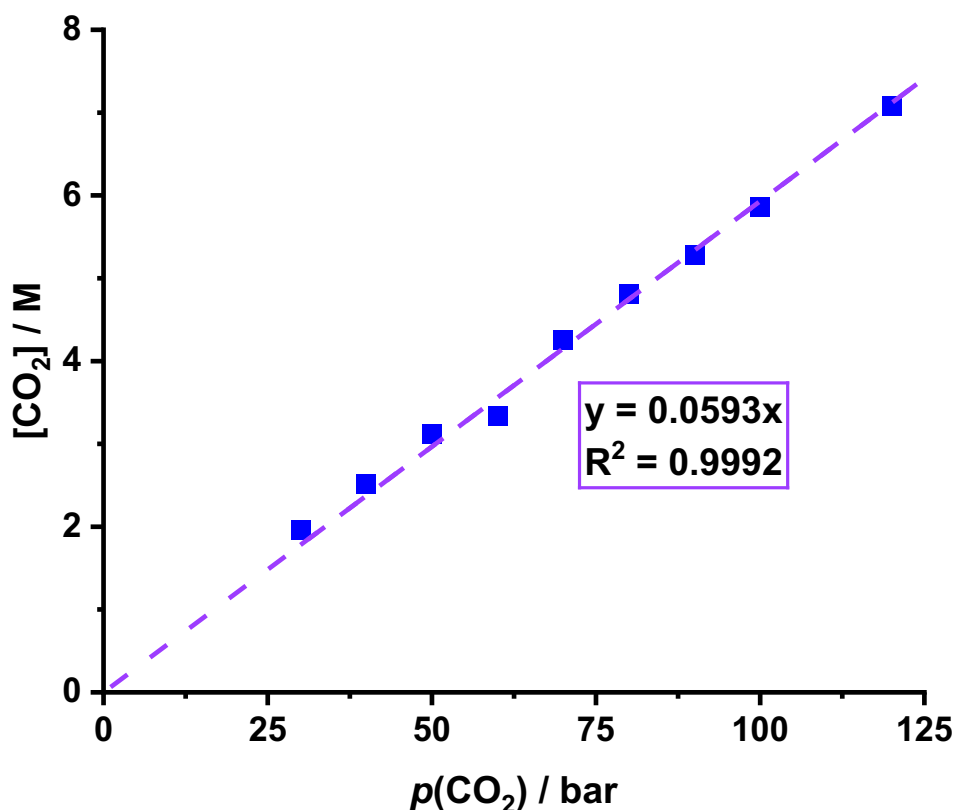
**Figure S3.11** Graph of $[\text{CO}_2]$ vs. $p(\text{CO}_2)$ taken from (DOI: 10.1016/j.supflu.2011.12.015 at 100 °C for CHO with linear fit necessarily passing through origin.³

Table S3.3 Conversions from $p(\text{CO}_2)$ to $[\text{CO}_2]$ and associated rate data for CHO/ CO_2 ROCOP.

$p(\text{CO}_2)$ (bar)	$[\text{CO}_2]$ (M) ^a	k_{obs} ($\times 10^{-5} \text{ s}^{-1}$) ^b
5	0.297	1.3 ± 0.3
7.5	0.445	3.0 ± 0.5
10	0.593	4.2 ± 0.5
12.5	0.741	6.1 ± 0.2
15	0.890	5.7 ± 0.3
17.5	1.038	6.4 ± 0.9
20	1.186	7.6 ± 1.3
25	1.483	8.0 ± 0.3
30	1.779	6.8 ± 0.2

Reaction conditions: $[\mathbf{2}]:[\text{CHD}]:[\text{CHO}] = 1:20:2000\text{-}10000$ at 20 bar CO_2 , $T = 100^\circ \text{C}$. ^aConversion between from $p(\text{CO}_2)$ to $[\text{CO}_2]$ from linear extrapolation of graph in Figure S3.11. ^b k_{obs} obtained from gradient of linear fit between $\ln([\text{CHO}]_t/[\text{CHO}]_0)$ vs. t (s) for conversions 5-25 %. CHO conversion determined by ^1H NMR (298 K, 400 MHz, CDCl_3) spectroscopy; comparison of CHO peak 3.05 ppm, PCHC backbone peak 4.65 ppm.

k_{max} calculated from the average of k_{obs} in the plateau region (≥ 20 bar).

K_{eq} calculated at each pressure in the linear tangent region (5-17.5 bar) and the average of these is calculated.

Firstly $[\text{carbonate}]$ is calculated from (1) using the rate of the polymerisation and assuming that this is proportional to $[\text{carbonate}]$ in the reaction mixture.

$$[\text{carbonate}]_p = [\text{cat}]_0 \times \frac{\text{rate}_p}{\text{rate}_{\text{max}}} \quad (1)$$

Then K_{eq} can be obtained from (2), by inputting $[\text{carbonate}]$ and also by noting that it is necessary for $[\text{alkoxide}] = [\text{cat}] - [\text{carbonate}]$.

$$K_{\text{eq}} = \frac{[\text{carbonate}]}{[\text{alkoxide}][\text{CO}_2]} \quad (2)$$

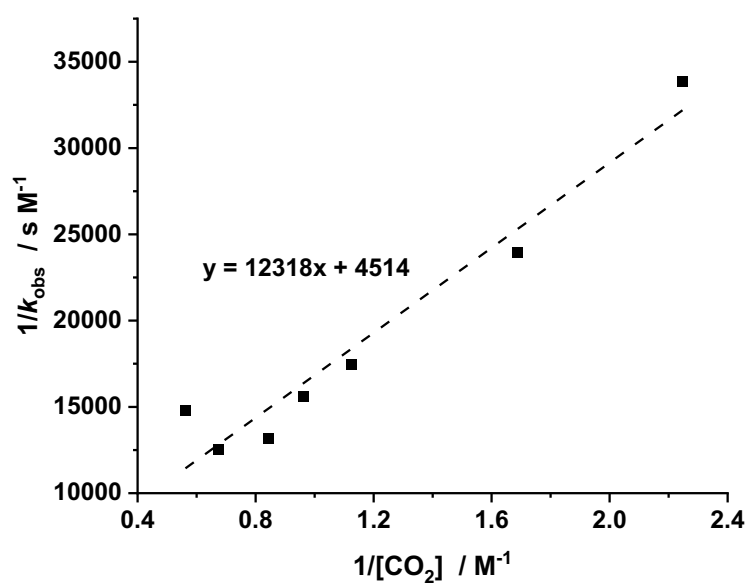


Figure S3.12 Graph of $1/k_{\text{obs}}$ vs. $1/[\text{CO}_2]$ for the polymerisation data from **2**. The gradient and intercept was used to calculate a new k_{max} and K_{eq} .

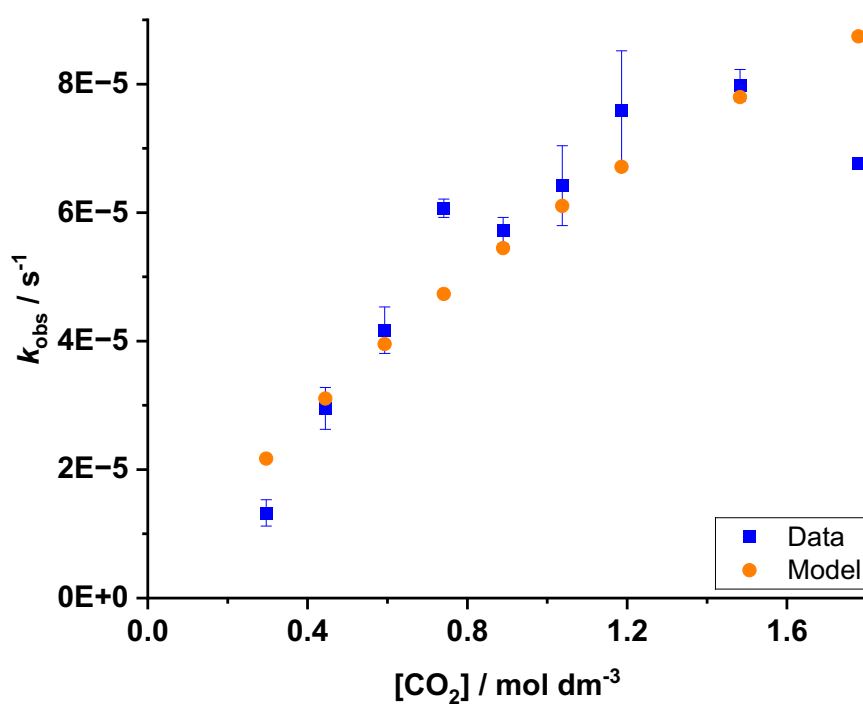


Figure S3.13 Graph of k_{obs} vs. $[\text{CO}_2]$ for CHO/ CO_2 copolymerisation catalysed by **2**. Blue squares are the data collected. Orange circles are the values obtained by the Michaelis-Menten model as discussed in Section 3.4, $k_{\text{max}} = 22.2 \pm 8.6 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$, $K_{\text{eq}} = 2.73 \pm 1.06 \text{ M}^{-1}$.

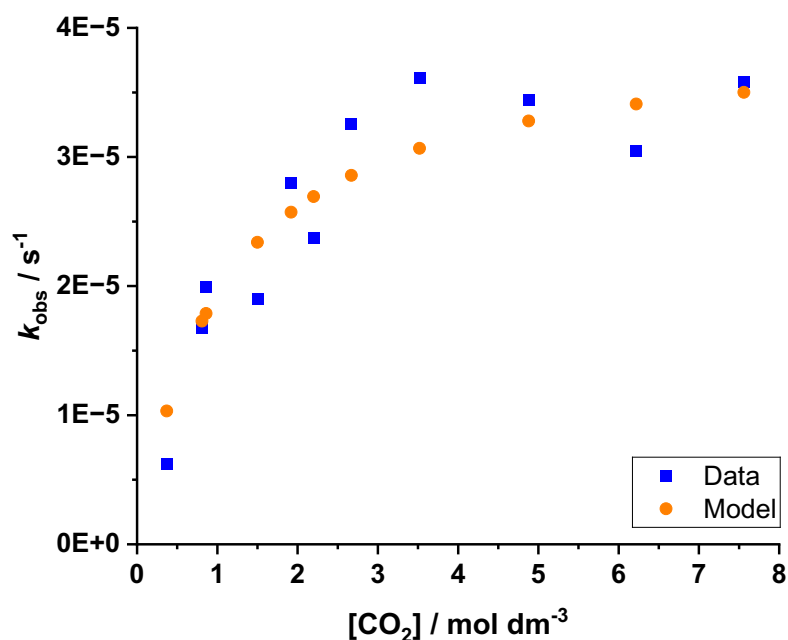


Figure S3.14 Graph of k_{obs} vs. $[\text{CO}_2]$ for PO/ CO_2 copolymerisation catalysed by a Co(III)/K(I) catalyst as described in (DOI:) 10.1021/jacs.3c13959.⁴ Blue squares are the data collected. Orange circles are the values obtained by the Michaelis-Menten model interpretation outlined in Section 3.4. $k_{\text{max}} = 4.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$, $K_{\text{eq}} = 1.06 \text{ M}^{-1}$.

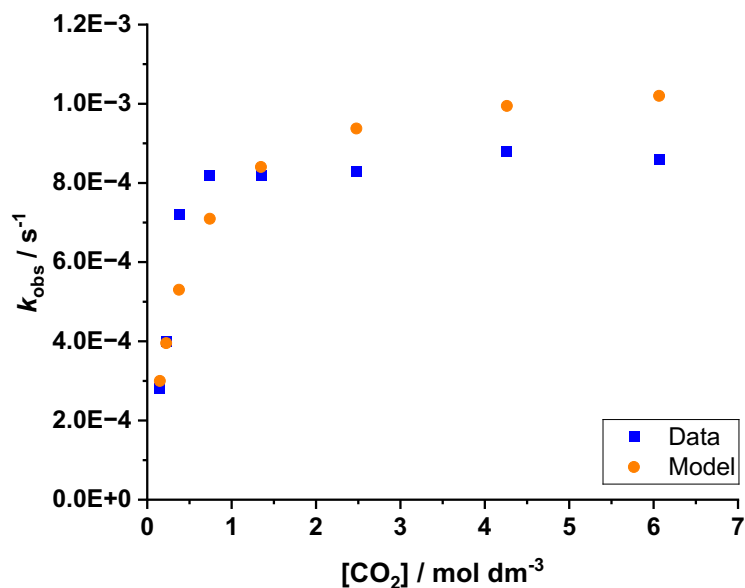


Figure S3.15 Graph of k_{obs} vs. $[\text{CO}_2]$ for CHO/ CO_2 copolymerisation catalysed by a monometallic Zn BDI catalyst as described in (DOI:) 10.1021/acs.macromol.9b01777.⁵ Blue squares are the data collected. Orange circles are the values obtained using the Michaelis-Menten model interpretation outlined in Section 3.4. $k_{\text{max}} = 1.1 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$, $K_{\text{eq}} = 0.39 \text{ M}^{-1}$.

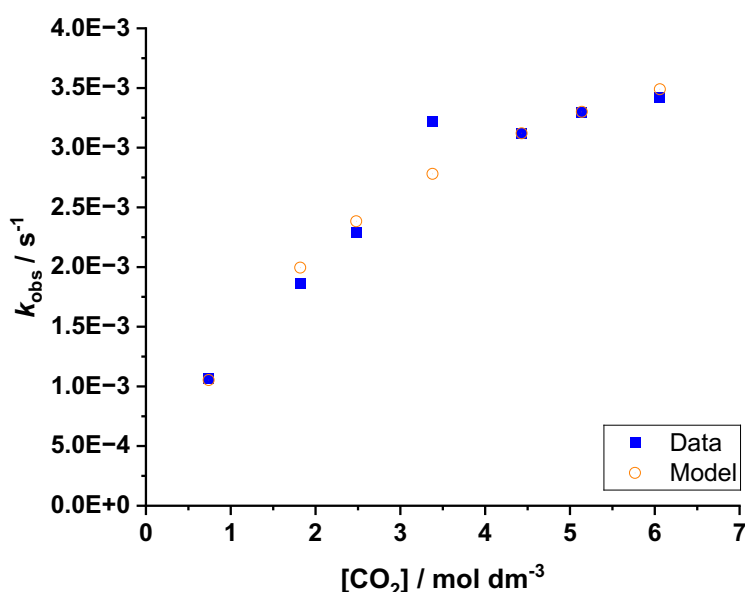


Figure S3.16 Graph of k_{obs} vs. $[\text{CO}_2]$ for CHO/ CO_2 copolymerisation catalysed by a di-Zn BDI catalyst as described in (DOI:) 10.1002/anie.201302157.⁶ Blue squares are the data collected. Orange circles are the values obtained by the Michaelis-Menten model outlined in Section 3.4. $k_{\text{max}} = 5.1 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$, $K_{\text{eq}} = 2.9 \text{ M}^{-1}$.

Table S3.4 Rate data for forward reaction of Eyring analysis

T (°C)	1/T (x 10 ⁻³ K ⁻¹)	$k_{\text{obs}} / (\text{x } 10^{-5} \text{ s}^{-1})^a$	$\ln(k_{\text{p}}/T)^b$
90	2.75	4.0 ± 0.2	-10.01 ± 0.05
100	2.68	8.0 ± 0.4	-9.35 ± 0.04
105	2.65	8.7 ± 1.1	-9.28 ± 0.12
110	2.61	10.6 ± 0.4	-9.10 ± 0.04

Reaction conditions: $[\text{2}]:[\text{CHD}]:[\text{CHO}] = 1:20:4000$ at 20 bar CO_2 , $V(\text{CHO}) = 6 \text{ mL}$, $T = 90\text{--}110^\circ\text{C}$. ^a k_{obs} obtained from gradient of linear fit between $\ln([\text{CHO}]_t/[\text{CHO}]_0)$ vs. t (s) for conversions 5–25 %. CHO conversion determined by ^1H NMR (298 K, 400 MHz, CDCl_3) spectroscopy; comparison of CHO peak 3.05 ppm, PCHC backbone peak 4.65 ppm. ^b $k_{\text{p}} = k_{\text{obs}} / [\text{cat}]$.

Backbiting discussion

Rates, given as k_{obs} , were calculated from a linear fit to the conversion time data at conversions between 5–40 %. This is because the rate of backbiting is given by:

$$\text{Rate} = k_{\text{obs}}[\text{endgroup}]$$

Until high conversion of polymer is reached, $[\text{endgroup}]$ shouldn't change. Then, once entire polymer chains have reacted to form cyclic carbonate, $[\text{endgroup}]$ will reduce and the rate would slow down, and behave in a more first order manner. Therefore, this conversion range has been selected with the linear fit analysis.

Table S3.5 Data from aliquot of backbiting test. $[2]:[\text{PCHC}] = 1:100$, $[2] = 2.47 \times 10^{-3} \text{ mol dm}^{-3}$, $V(\text{CHO}) = 6 \text{ mL}$, $T = 115^\circ\text{C}$.

Entry	t (min)	Conversion of PCHC (%) ^a	M_n (g mol ⁻¹) [$\mathcal{D}$] ^b
a	0	0	6,800 [1.13]
b	20	46	4,100 [1.14]

^a Conversion determined by NMR by comparing PCHC backbone peak 4.65 ppm with *trans*-cyclic carbonate peak 4.00 ppm. ^b Determined by GPC in THF, 30 °C, calibrated using PS standards.

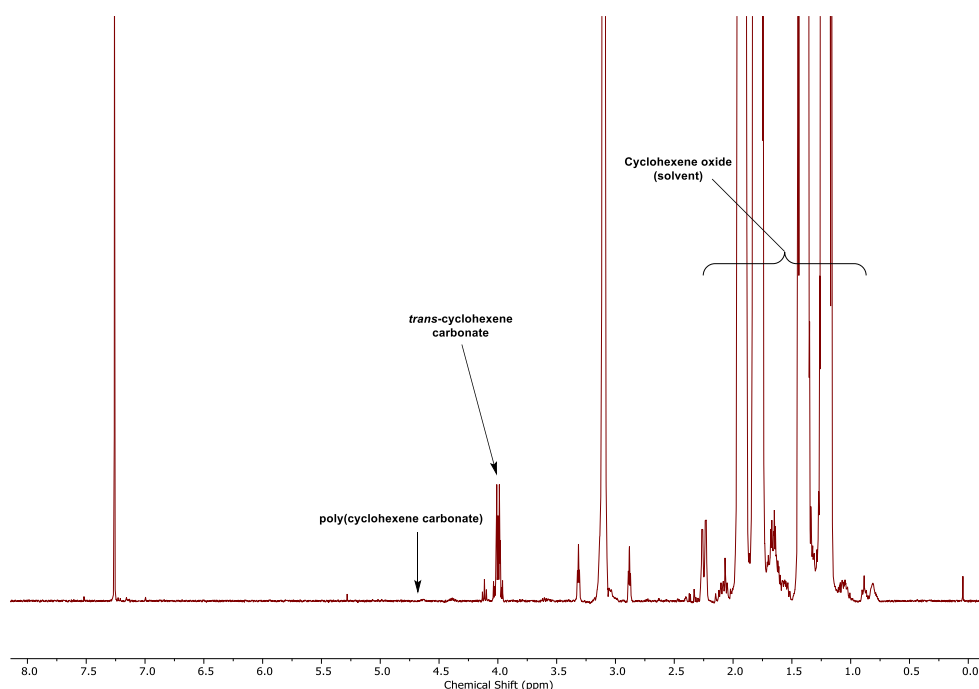


Figure S3.17 ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of backbiting reaction mixture at completion showing only *trans*-cyclohexene carbonate produced.

Table S3.6 Rate data for backbiting Eyring analysis

T ($^\circ\text{C}$)	$1/T$ ($\times 10^{-3} \text{ K}^{-1}$)	$k_{\text{obs}} / (\times 10^{-5} \text{ s}^{-1})^a$	$\ln(k_p/T)^b$
105	2.65	3.8 ± 0.4	-10.10 ± 0.05
110	2.61	4.3 ± 0.1	-10.00 ± 0.01
115	2.58	6.6 ± 0.1	-9.59 ± 0.02
120	2.54	10.6 ± 1.4	-9.12 ± 0.14

Reaction conditions: $[2]:[\text{PCHC}] = 1:100$, $V(\text{CHO}) = 6 \text{ mL}$, $[2] = 2.47 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 105\text{--}120^\circ\text{C}$. ^a k_{obs} from gradient of linear fit to conversion vs time between 5–40%. Conversion determined by NMR by comparing PCHC backbone peak 4.65 ppm with *trans*-cyclic carbonate peak 4.00 ppm. ^b $k_p = k_{\text{obs}} / [\text{cat}]$.

4 Supplementary Figures and Tables for Chapter 4

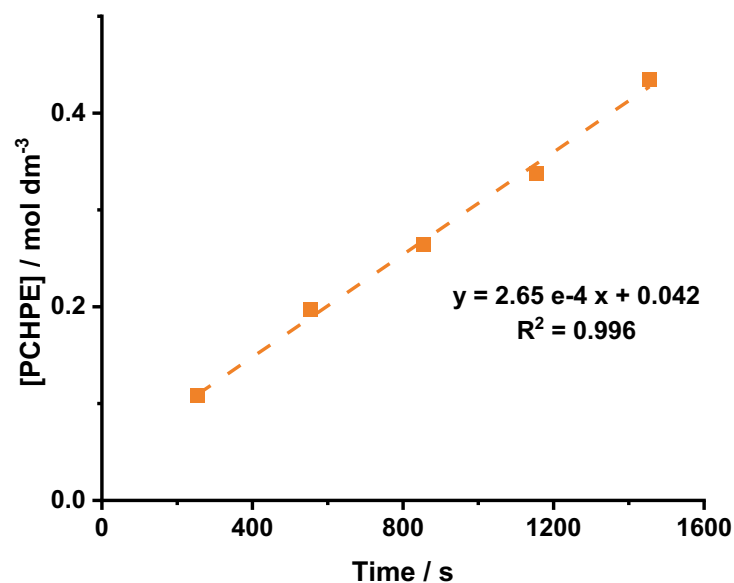


Figure S4.1 Plot of $[PCHPE]$ (mol dm^{-3}) vs. time (s) for $[1]:[PA]:[CHO] = 1:400:2000$, $V(\text{CHO}) = 1 \text{ mL}$, $[1] = 4.94 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 100^\circ \text{C}$. This was for the partway addition experiment. Values given here are from NMR aliquots but the reaction was also monitored by ReactIR.

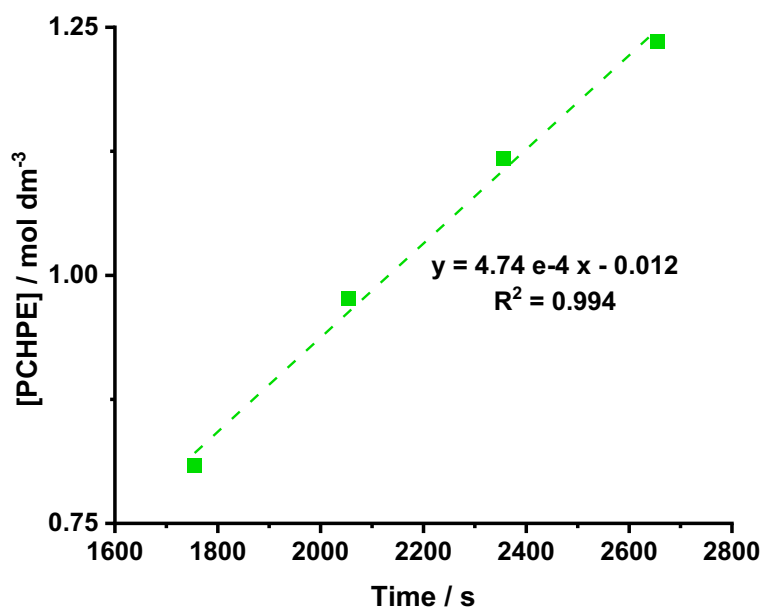


Figure S4.2 Plot of $[PCHPE]$ (mol dm^{-3}) vs. time (s) for $[1]:[\text{BnOH}]:[PA]:[CHO] = 1:50:400:2000$, $V(\text{CHO}) = 1 \text{ mL}$, $[1] = 4.94 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 100^\circ \text{C}$. This was from the partway addition experiment, after addition of the BnOH. Values given here are from NMR aliquots but the reaction was also monitored by ReactIR.

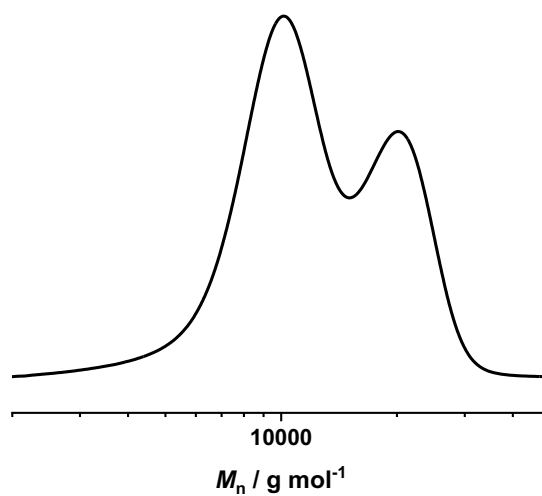


Figure S4.3 GPC trace of polymer at full conversion for the Toluene control reaction of partway addition. This shows a bimodal distribution from acetate initiation and residual diol, but no additional initiation from when Toluene added. $M_n = 11100$ [1.23] g mol^{-1} .

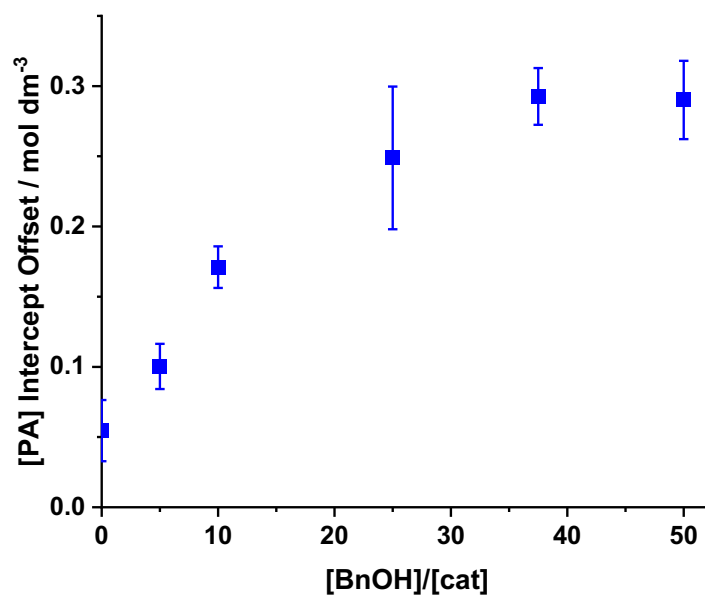


Figure S4.4 Graph of the offset in [PA] between $[\text{PA}]_0$ and the intercept from the linear fitting of aliquots against equivalents of BnOH added. $[\text{PA}] \text{ Intercept Offset} = [\text{PA}]_0 - [\text{PA}]_{\text{intercept}}$.

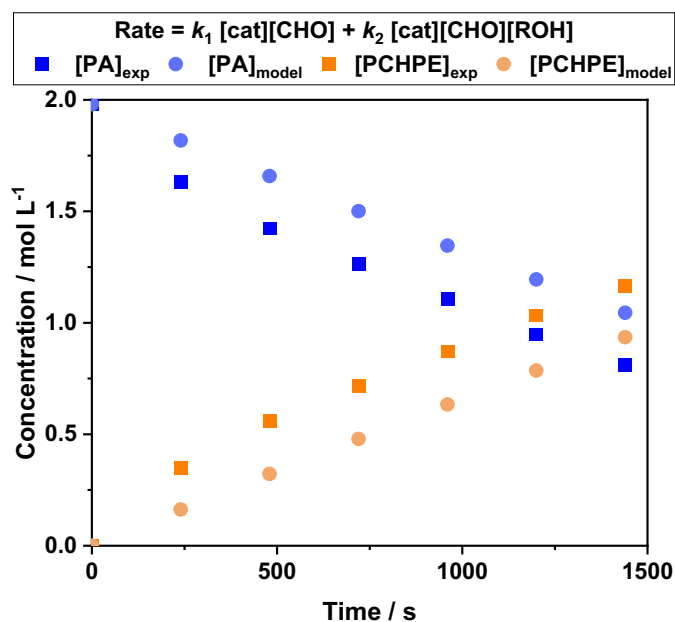


Figure S4.5 Plot of Concentration (mol L^{-1}) against Time (s) for the reaction $[\mathbf{1}]:[\text{BnOH}]:[\text{PA}]:[\text{CHO}] = 1:25:400:2000$, $V(\text{CHO}) = 1 \text{ mL}$, $[\mathbf{1}] = 4.94 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 100 \text{ }^{\circ}\text{C}$. $[\text{PA}]$ experimental (blue square), $[\text{PA}]$ COPASI model (blue circle), $[\text{PCHPE}]$ experimental (orange square), $[\text{PCHPE}]$ COPASI model (orange circle). Offset caused by rapid initiation clearly visible in experimental data, and this is not adequately accounted for in the COPASI model.

Table S4.1 Table showing rate of reaction, k_{obs} ($\times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$), both experimental and modelled by COPASI, for different $[\text{BnOH}]$ (mol dm^{-3}).

Entry	$[\text{BnOH}]$ $/ \text{mol dm}^{-3}$	$k_{\text{obs, expt}}$ $/ \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$	$k_{\text{obs, COPASI}}$ $/ \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
a	0	4.13 ± 0.58	4.10
b	0.0248	5.01 ± 0.41	4.64
c	0.0495	5.67 ± 0.26	5.14
d	0.1238	6.64 ± 0.17	6.49
e	0.1857	7.24 ± 0.10	7.6
f	0.2475	8.89 ± 0.74	8.83

Reaction conditions: $[\mathbf{1}]:[\text{BnOH}]:[\text{PA}]:[\text{CHO}] = 1:(0-50):400:2000$, $V(\text{CHO}) = 1 \text{ mL}$, $[\mathbf{1}] = 4.94 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 100 \text{ }^{\circ}\text{C}$. $k_{\text{obs, expt}}$ from gradient of linear fit of $[\text{PA}]$ (mol dm^{-3}) vs t (s) for experimental data. $k_{\text{obs, COPASI}}$ from gradient of linear fit of $[\text{PA}]$ (mol dm^{-3}) vs t (s) for the calculated values from COPASI.

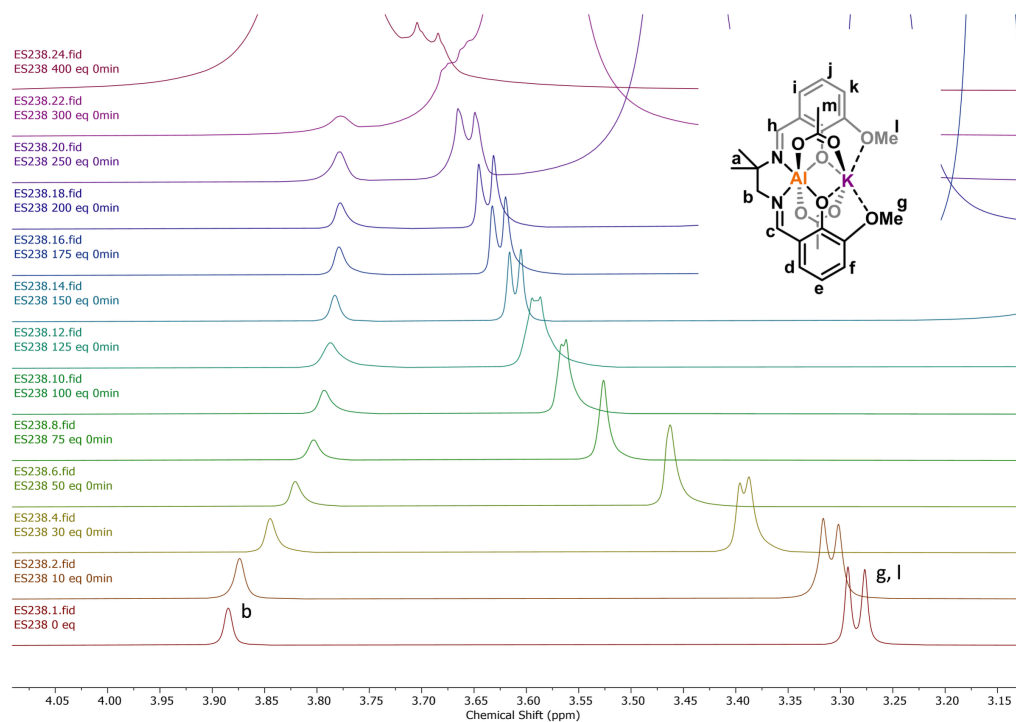


Figure S4.6 ^1H NMR spectra (CDCl_3 (#), 298 K, 400 MHz) of **1** with increasing equiv of BnOH (0 – 400).
Close up showing the movement of peaks relating to b, g & l.

Table S4.2 Table showing [cat] and [BnOH] for the NMR binding studies along with the ^1H NMR shift associated with the methoxy protons in **1**.

Entry	[cat] / mol dm ⁻³	[BnOH] / mol dm ⁻³	Equiv. (BnOH)	$\delta \approx 3.3$ (MeO -) / ppm
a	0.01000	0	0	3.2768
b	0.00980	0.098	10	3.3018
c	0.00943	0.283	30	3.3873
d	0.00909	0.455	50	3.4617
e	0.00870	0.652	75	3.5262
f	0.00833	0.833	100	3.5616
g	0.00800	1.000	125	3.5864
h	0.00769	1.154	150	3.6052
i	0.00741	1.296	175	3.6198
j	0.00714	1.429	200	3.6313
k	0.00667	1.667	250	3.6491
l	0.00625	1.875	300	3.6552
m	0.00556	2.222	400	3.6844

Table S4.3 Crystallographic refinement data for [**1**•H₂O]

Local Code	028nicj24
CCDC Deposition Number	
Crystal Data	
Chemical formula	C ₂₄ H ₃₀ AlKN ₂ O ₉
<i>M_r</i>	646.70
Crystal system, space group	Triclinic, <i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.2300(3) 11.6518(5) 12.7768(6)
α , β , γ , (°)	88.005(4) 89.318(3) 71.814(4)
<i>V</i> (Å ³)	1304.67(10)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	2.685
Crystal size (mm)	0.35 x 0.2 x 0.07
Data collection	
Absorption correction	CrysAlisPro 1.171.41.117a (Rigaku Oxford Diffraction, 2024) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
<i>T_{min}</i> , <i>T_{max}</i>	0.79443, 1.00000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	11877, 5365
<i>R_{int}</i>	0.0196
(sinθ/λ) _{max} (Å ⁻¹)	0.445
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.054, 0.152, 1.03
No of reflections	5365
No. of parameters	341
No. of restraints	0
Δ _{max} , Δ _{min} (e Å ⁻³)	1.26, -0.47

References for Appendix

- (1) Scalmani, G.; Frisch, M. J. Continuous surface charge polarizable continuum models of solvation. I. General formalism. *J. Chem. Phys.* **2010**, *132* (11). DOI: 10.1063/1.3359469.
- (2) Diment, W. T.; Gregory, G. L.; Kerr, R. W. F.; Phanopoulos, A.; Buchard, A.; Williams, C. K. Catalytic Synergy Using Al(III) and Group 1 Metals to Accelerate Epoxide and Anhydride Ring-Opening Copolymerizations. *ACS Catal.* **2021**, *11* (20), 12532-12542. DOI: 10.1021/acscatal.1c04020.
- (3) Foltran, S.; Cloutet, E.; Cramail, H.; Tassaing, T. In situ FTIR investigation of the solubility and swelling of model epoxides in supercritical CO₂. *J. Supercrit. Fluids.* **2012**, *63*, 52-58. DOI: 10.1016/j.supflu.2011.12.015.
- (4) Eisenhardt, K. H. S.; Fiorentini, F.; Lindeboom, W.; Williams, C. K. Quantifying CO₂ Insertion Equilibria for Low-Pressure Propene Oxide and Carbon Dioxide Ring Opening Copolymerization Catalysts. *J. Am. Chem. Soc.* **2024**, *146* (15), 10451-10464. DOI: 10.1021/jacs.3c13959.
- (5) Kernbichl, S.; Reiter, M.; Mock, J.; Rieger, B. Terpolymerization of β -Butyrolactone, Epoxides, and CO₂: Chemoselective CO₂-Switch and Its Impact on Kinetics and Material Properties. *Macromol.* **2019**, *52* (21), 8476-8483. DOI: 10.1021/acs.macromol.9b01777.
- (6) Lehenmeier, M. W.; Kissling, S.; Altenbuchner, P. T.; Bruckmeier, C.; Deglmann, P.; Brym, A. K.; Rieger, B. Flexibly Tethered Dinuclear Zinc Complexes: A Solution to the Entropy Problem in CO₂/Epoxide Copolymerization Catalysis? *Angew. Chem. Int. Ed.* **2013**, *52* (37), 9821-9826. DOI: 10.1002/anie.201302157.