SUPPORTING INFORMATION

Mono- and Dimeric Zinc Complexes for PLA Production and Degradation into Methyl Lactate – A Chemical Recycling Method

Jack Payne[a], Paul McKeown[a], Mary F. Mahon[b], Emma A. C. Emanuelsson[c] and Matthew D. Jones[a]

[a] *Centre for Sustainable and Circular Technologies, University of Bath, Claverton Down, Bath, BA2 7AY, UK*
[b] *Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK*
[c] *Department of Chemical Engineering, University of Bath, Claverton Down, Bath, BA2 7AY, UK*

Contents

1. General experimental methods:

The synthesis and characterisation of all mono- and dimeric Zn(II)-complexes was performed under an inert atmosphere of argon using standard Schlenk or Glovebox techniques. All chemicals used were purchased from Sigma-Aldrich and used as received, with the exception of *rac*-lactide (*rac*-LA*)*, which was recrystallised once from anhydrous toluene prior to use. All dry solvents used in handling Zn(II) complexes were obtained *via* SPS (solvent purification system). ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were obtained on a Bruker 400 MHz spectrometer and referenced to residual solvent resonances.[1] Coupling constants (*J*) are provided in Hertz (Hz). $CDCl_3$ was dried over CaH_2 prior to use with Zn(II) complexes. C_6D_6 was degassed and stored over molecular sieves for use with Zn(II) complexes. All ligands were prepared according to standard literature procedures[2] and characterised *via* electron-spray ionisation-mass spectrometry (ESI-MS) in positive mode. CHN microanalysis was performed by Elemental Microanalysis. Diffusional ordered spectroscopy (DOSY) NMR analysis was carried out on a Bruker 500 MHz instrument.[3] The standard Bruker pulse sequence ledsp2s used was with 8 scans recorded per gradient level. A gradient strength between 1600 to 1750 μs was used with a diffusion time of 0.05 seconds. Ten gradient strengths were used between 10 to 90 %. Data was processed using DOSY methods.

All crystallographic data was obtained on either a SuperNova or Excalibur, EOS detector diffractometer using radiation Cu-Kα (λ = 1.54184 Å) or Mo-Kα (λ = 0.71073 Å) radiation all recorded at 150(2) K. All structures were solved by direct methods and refined on all F^2 data using the SHELXL-2014 suite of programs. All hydrogen atoms were included in idealised positions and refined using the riding model.

1.1 Polymerisation

Polymerisations were conducted in a Youngs ampoule under argon. All melt polymerisations were performed in the absence of solvent. Initial melt polymerisations were performed with *rac*-LA (1.0 g, 0.69 mmol) to which the required amount of Zn(II) initiator and benzyl alcohol (BnOH) co-initiator were loaded in a glovebox (2.5 μL, 0.023 mmol) ([*rac*-LA]:[Init]:[BnOH] = 300:1:1). The ampoule was then submerged in a preheated oil bath (130 °C) and the polymerisation start time commenced on melting of the monomer. The reaction was deemed finished once a polymer melt of sufficient viscosity stopped the stirrer bar. The reaction was then quenched in air and the product dissolved in DCM (20 mL) with stirring. The solvent was then removed *in vacuo* and a crude ^{1}H NMR spectrum of the polymer was obtained. The polymer was then washed with copious amounts of MeOH (100 mL) to remove initiator and any unreacted monomer, dried *in vacuo* and retained for materials characterisation. This procedure was repeated for melt polymerisations at 180 °C, which maintained a constant [*rac*-LA]:[BnOH] ratio ([*rac*-LA]:[Init]:[BnOH] = 3000:1:10). For solution polymerisations, *rac*-LA (1 g, 0.69 mmol) was dissolved in anhydrous toluene (10 mL) with the required amount of Zn(II) initiator and BnOH (7.5 μL, 0.069 mmol). The flask was then placed in a preheated oil bath (80 °C) and stirred for 2 h. The reaction was then quenched in air, the solvent removed *in vacuo* and a crude ^{1}H NMR spectrum of the polymer was obtained. The polymer was then purified as described for melt polymerisations. This method was repeated for solution polymerisations performed at room temperature (RT).

All polymer molecular weights were characterised by gel permeation chromatography (GPC), which was performed with a 1 mL min^{-1} flow rate at 35 °C with a THF eluent using a PLgel 5 μm MIXED-D 300 x 7.5 mm column. The system was referenced against 11 narrow molecular weight polystyrene standards with detection *via* refractive index response. Polymer tacticity

was determined *via* homonuclear decoupled ^{1}H NMR ($CDCl_3$) spectroscopy analysis of the methine region in accordance to relationships described by Coates *et al*.[3] MALDI-ToF mass spectra were determined on a Bruker Autoflex speed instrument using DCTB (trans-2- [3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix and ionised using NaTFA.

Materials characterisation (GPC, ESI-MS and MALDI-ToF) facilities were provided by the Material and Chemical Characterisation Facility (MC^2) at the University of Bath.

1.2 Degradation

Degradation reactions were performed in a Youngs ampoule under argon. The flask was loaded with Zn(II) catalyst (8 wt% - 1 mol% relative to PLA ester linkages, 0.02 g) in a Glovebox to which PLA (0.25 g, Vegware™, PLA cup, M_n = 45,510 g mol^{-1}) was added under a flow of argon. The polymer was then dissolved in THF (4 mL), with heating and stirring assisting dissolution. The flask was then submerged in a preheated oil bath (50 or 80 °C) to which MeOH (1 mL) was added. Aliquots were taken for ^{1}H NMR ($CDCl_3$) analysis of the methine region. After the reaction, the solvent was removed *in vacuo* and the residual methyl lactate (Me-La) was analysed further.

1.3 Reaction kinetics

1.3.1. Polymerisation

Kinetic analysis was performed as described for the solution polymerisation procedure in section 1.1 (toluene, 80 °C, [LA]:[I]:[BnOH] = 100:1:1). Aliquots were taken every 20 and 5 minutes for Zn(**1**)$_2$ and Zn(**2**)$_2$ respectively to acquire 6 data points. Plotting $\ln([LA]_o/[LA]_t)$ against time afforded a straight line fit with the gradient equivalent to the pseudo first-order rate constant.

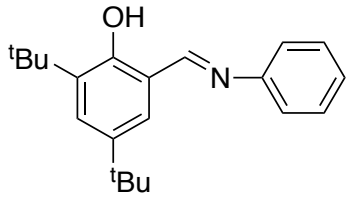
1.3.2. Degradation

Reaction kinetic analysis was performed as described for the degradation procedure at both 8 wt% (0.02 g) and 4 wt% (0.01 g) catalyst loading. Aliquots were taken hourly and the pseudo-first-order constants (k_{app}) were determined by plotting $\ln([PLA]_o/[PLA])$ against time, constraining the line of best fit to pass through the origin.

2. Synthesis and characterisation:

2.1 Ligands

1H:



To a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (4.68 g. 20 mmol) dissolved in MeOH (50 mL), aniline (1.86 g, 1.82 mL, 20 mmol) was added with stirring. The reaction mixture was then left to stir at RT for 18 h, affording a yellow solid product. The product was then separated by filtration, washed with MeOH (5 x 5 mL) and dried *in vacuo*. ^{1}H NMR (C_6D_6, 400 MHz):

δ = 14.09 (s, 1H; OH), 8.09 (s, 1H; ArCHN), 7.62 (d, *J* = 2.3 Hz, 1H; ArH), 7.10 (t, *J* = 7.6 Hz, 2H; ArH), 7.03 (d, *J* = 2.4 Hz, 1H; ArH), 7.00 (t, *J* = 7.4 Hz, 1H; ArH), 6.93 (d, *J* = 1.0 Hz, 1H; ArH), 6.91 (s, 1H; ArH), 1.68 (s, 9H; $C(CH_3)_3$), 1.34 (s, 9H; $C(CH_3)_3$). ESI-MS (+ve, MeOH): Calculated m/z = $[C_{21}H_{28}NO]^+$ = 310.2171, found m/z = 310.2197.
Yield = 4.74 g, 77%.

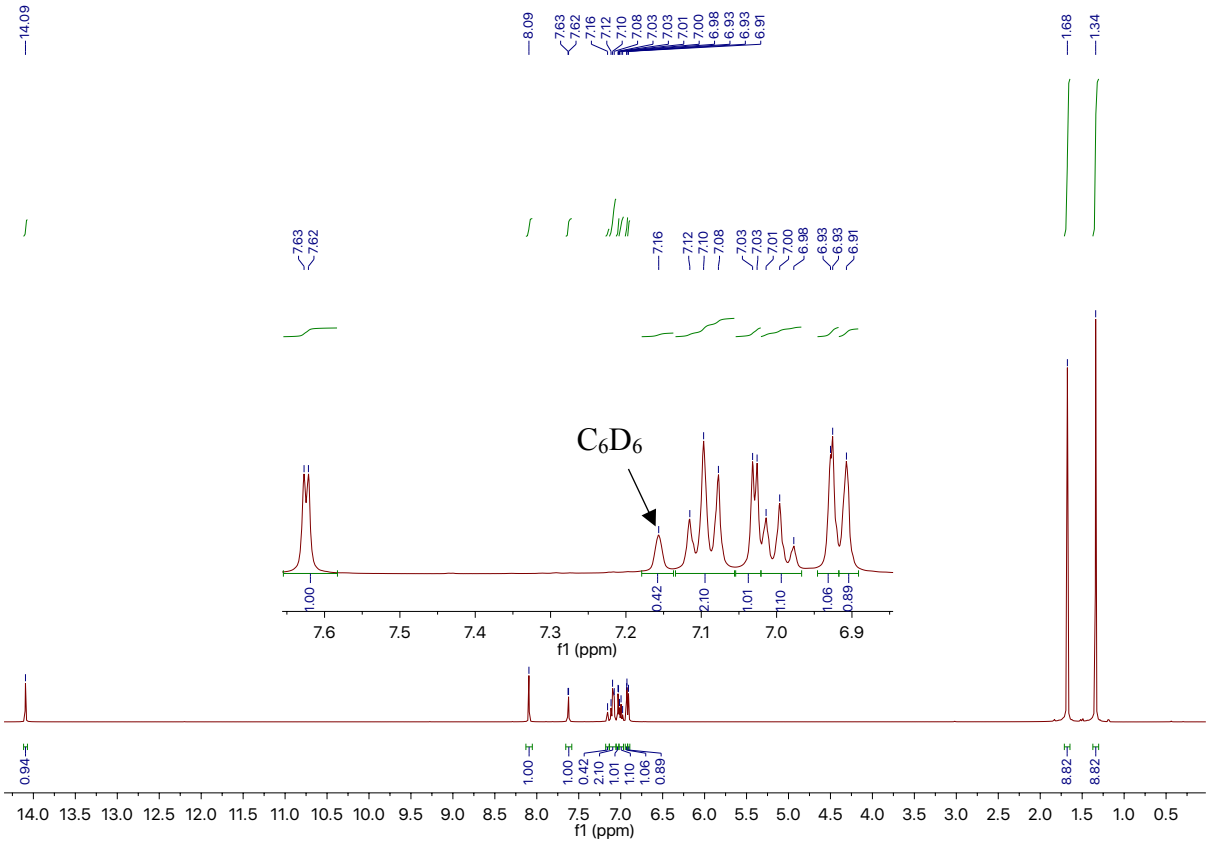
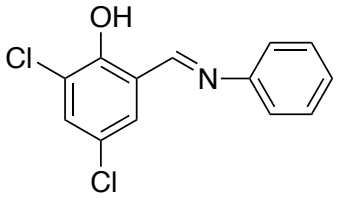


Figure 1. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of **1**H.

2H:



2H was prepared by the method described in **1**H, but instead using 3,5-dichloro-2-hydroxybenzaldehyde (3.82 g. 20 mmol). Rapid precipitation of an orange solid product was observed upon the addition of aniline. The product was then separated by filtration, washed with cold MeOH (50 mL) and dried *in vacuo*. ^{1}H NMR ($CDCl_3$, 400 MHz):

δ = 14.27 (s, 1H; OH), 8.57 (s, 1H; ArCHN), 7.47 (d, J = 2.5 Hz, 1H; ArH), 7.45 (d, J = 7.9 Hz, 2H; ArH), 7.35 (d, J = 7.3 Hz, 1H; ArH), 7.31 (d, J = 1.8 Hz, 2H; ArH), 7.29 (s, 1H; ArH). ESI-MS (+ve, MeOH): Calculated m/z = $[C_{13}H_{10}NOCl_2]^+$ = 266.0134, found m/z = 226.0135. Yield = 4.56 g, 86%.

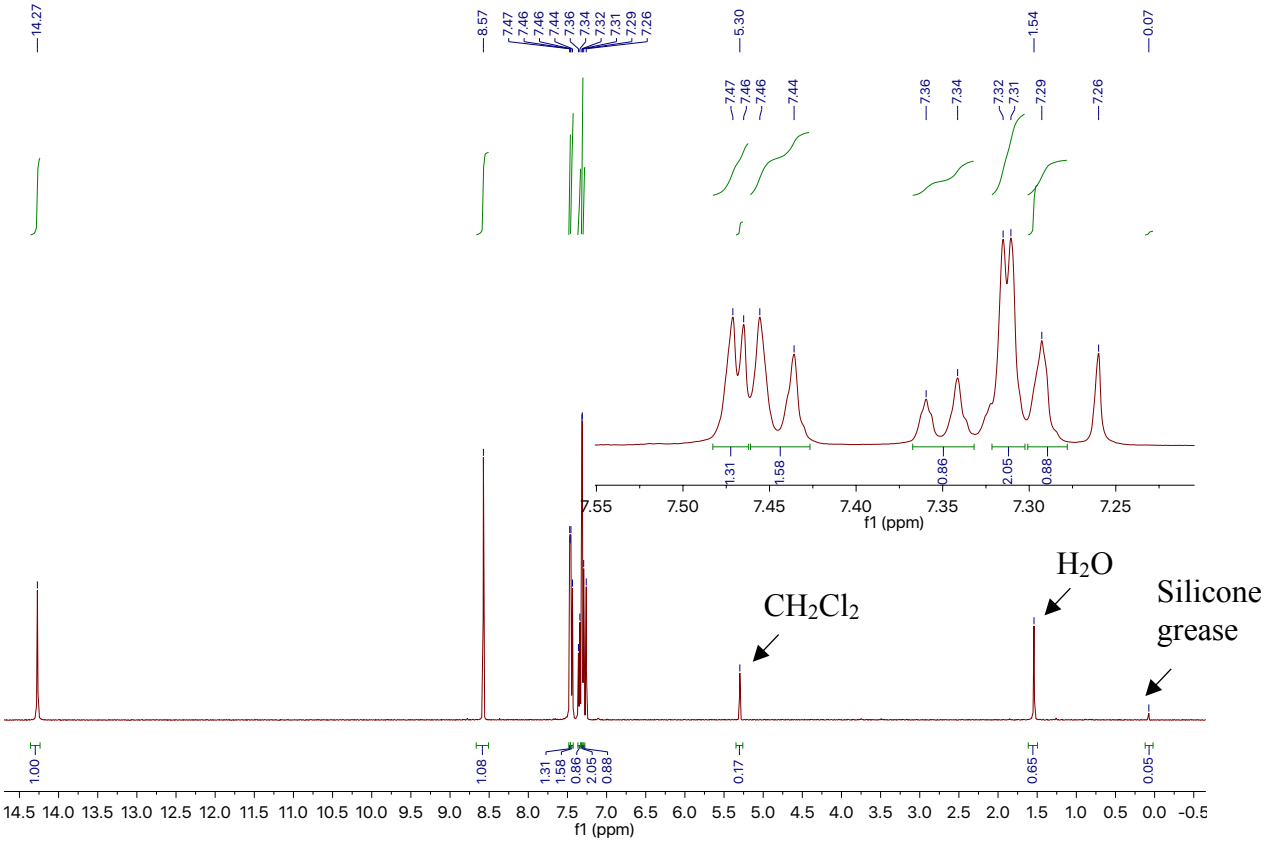
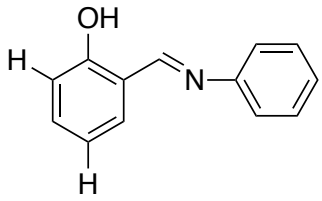


Figure 2. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2**H.

3H:



3H was prepared by the method described in **1**H, but instead using 2-hydroxybenzaldehyde (2.44 g. 20 mmol). After stirring at RT for 18 h, the reaction mixture was placed in a freezer. After 3 days at – 20 °C a yellow solid product was obtained, which was isolated and dried using the procedure described in **2**H. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 13.31 (s, 1H; OH), 8.62 (s, 1H; CHN), 7.44 (m, 4H; ArH), 7.31 (m, 3H; ArH), 7.07 (d, *J* = 8.9 Hz, 1H; ArH), 6.96 (td, *J* = 7.5, 1.2 Hz, 1H; ArH).
ESI-MS (+ve, MeOH): Calculated m/z = $[C_{13}H_{12}NO]^+$ = 198.0919, found m/z = 198.0923.
Yield = 3.07 g, 78%.

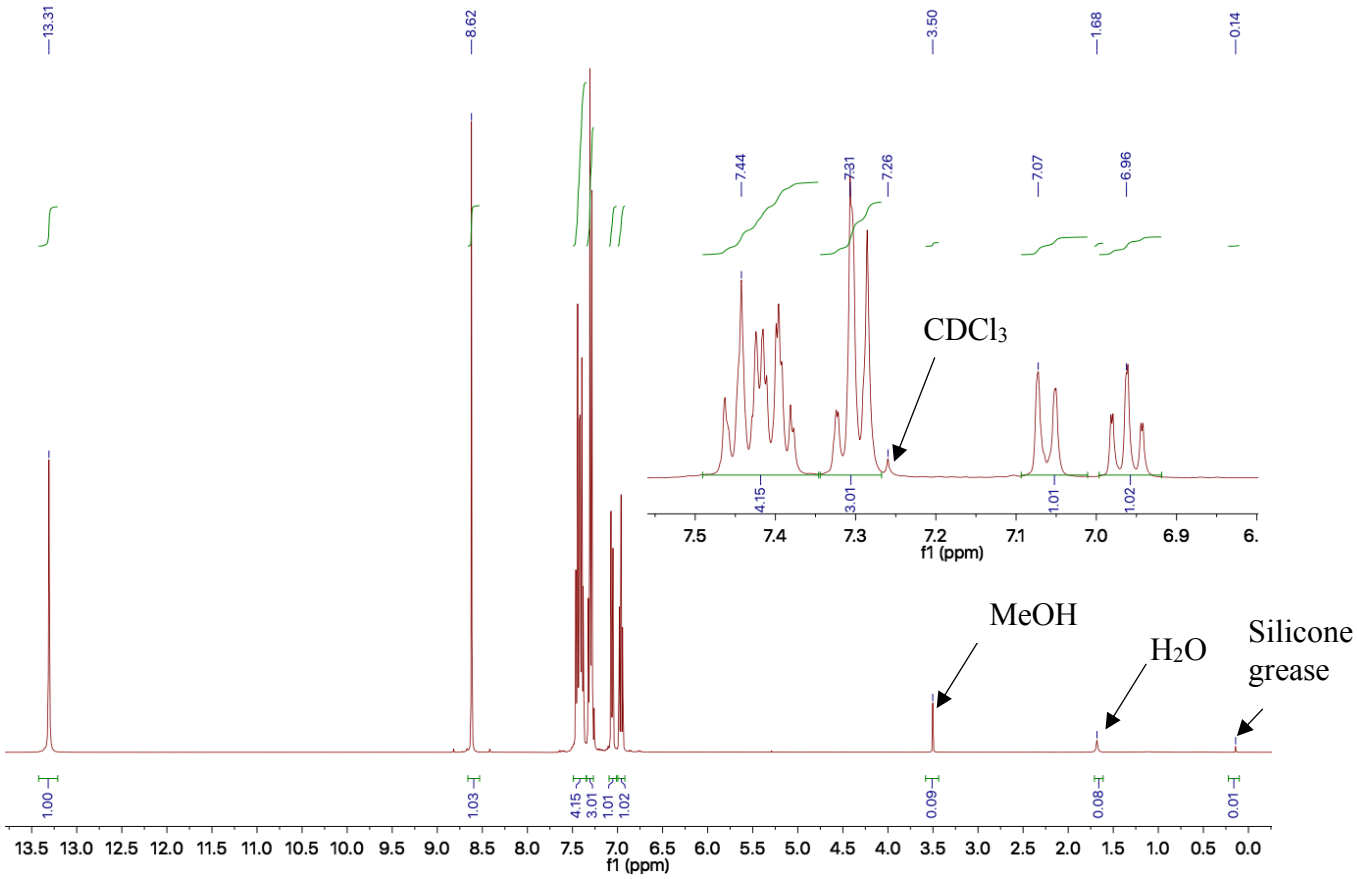


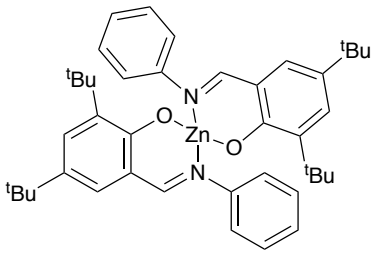
Figure 3. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3**H.

2.2 Zn(II) complexes

Synthesis of monomeric Zn(1-3)$_2$ complexes:

To a solution of ligand (**1-3**H, 2 mmol) dissolved in anhydrous toluene (10 mL), $ZnEt_2$ (1 M, 1 mmol) was added dropwise with stirring. After complete addition, the solution was stirred at RT for 15 minutes before being left to stand for 1 h. The solvent was then removed *via* cannula filtration and the desired Zn(II) complex was purified *via* washing or recrystallisation from hexane. Note $ZnMe_2$ was used as an alternative source of Zn(II) in the preparation of Zn(**3**)$_2$.

Zn(**1**)$_2$: recrystallised from hexane. Isolated as pale-yellow crystals.
Yield = 0.50 g, 73%.



^{1}H NMR (C_6D_6, 400 MHz): δ 7.86 (s, 1H; CHN), 7.73 (d, J = 2.5 Hz, 1H; ArH), 6.95 (d, J = 7.7 Hz, 2H; ArH), 6.86 (t, J = 7.7 Hz, 2H; ArH), 6.81 (d, J = 2.6 Hz, 1H; ArH), 6.78 (t, J = 7.4, 1H; ArH), 1.74, 1.36 (s, 9H; C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 170.4, 169.8 (ArCHN) 149.7, 142.3, 135.9, 131.1, 130.2, 129.6 (Ar), 129.2, 128.4, 126.3, 125.5, 121.6, 117.7 (Ar), 35.8, 34.1 (C(CH)$_3$), 31.5, 29.5 (CH$_3$).
Elemental analysis: Calculated for $C_{42}H_{52}N_2O_2Zn$: C; 73.94 %; H; 7.68 %; N; 4.11 %. Found: C; 74.39 %; H, 7.66 %; N, 3.97 %.

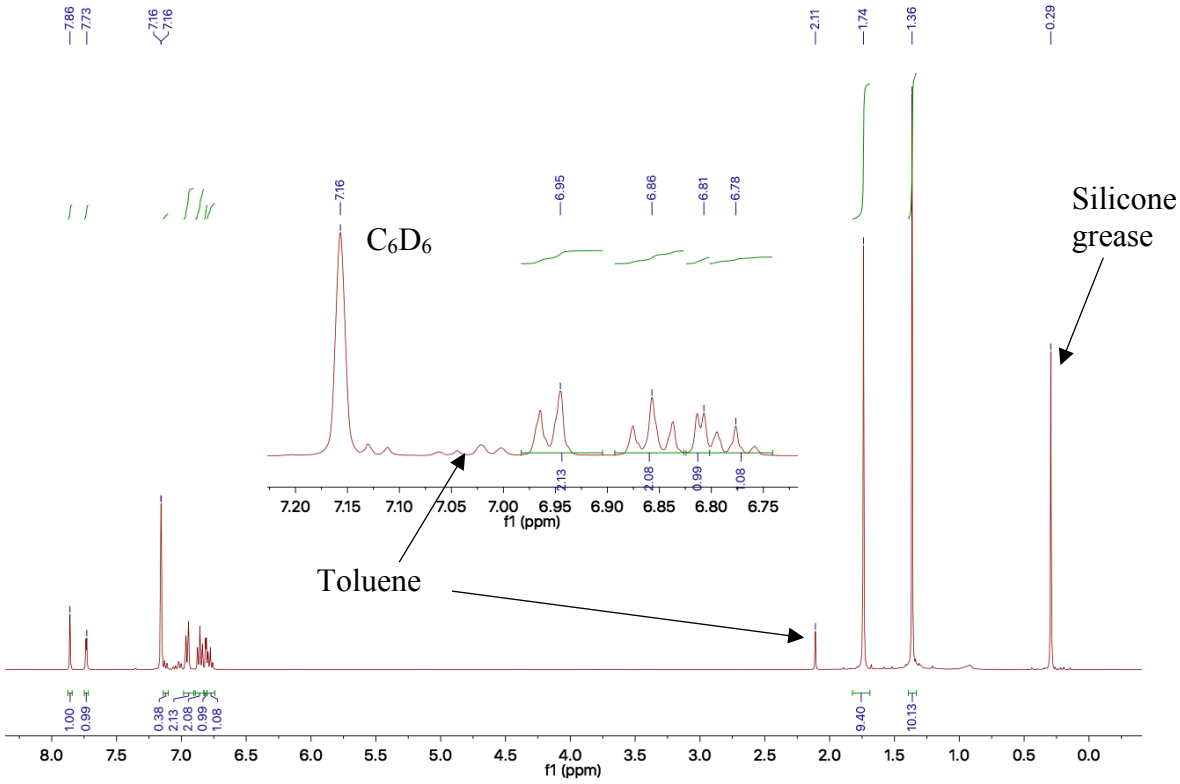


Figure 4a. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of Zn(**1**)$_2$.

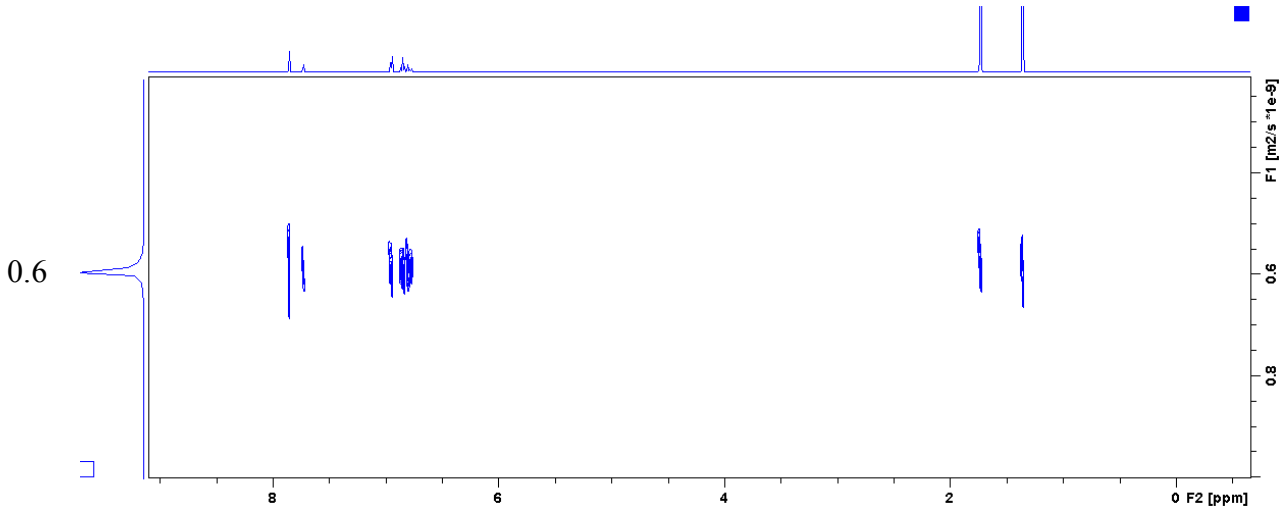


Figure 4b. DOSY NMR spectrum (C_6D_6, 500 MHz) of Zn(**1**)$_2$, indicating only the homoleptic species present in solution, with a diffusion constant of 0.6 x 10^{-9} m^2 s^{-1}.

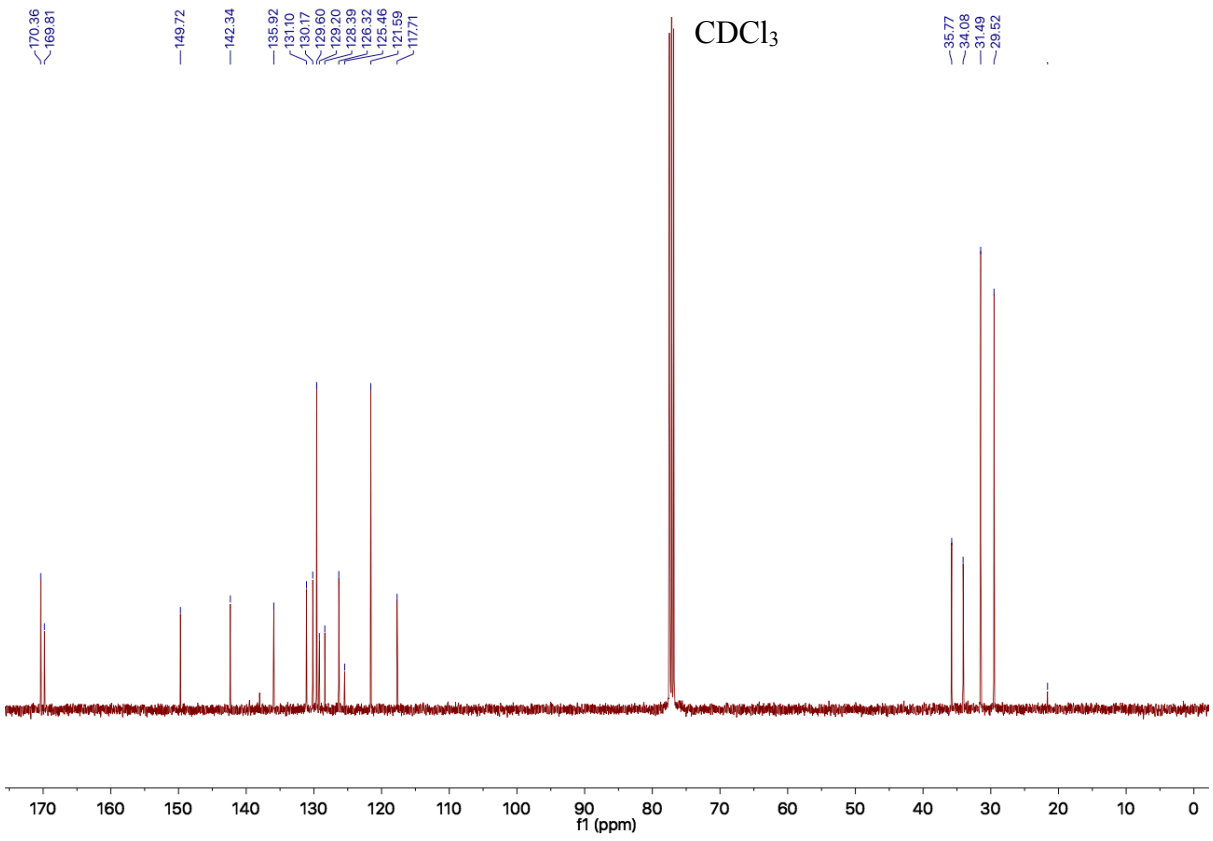
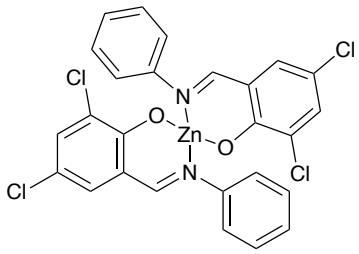


Figure 5. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 400 MHz) of Zn(**1**)$_2$.

Zn(**2**)$_2$: recrystallised from anhydrous toluene. Isolated as yellow crystals.
Yield = 0.42 g, 70%.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (s, 1H; CHN), 7.54 (d, J = 2.9 Hz, 1H; ArH), 7.24 (s, 1H; ArH), 7.18 (m, 1H; ArH), 7.12, (d, J = 2.1 Hz, 1H; ArH), 7.00 (d, J = 6.3 Hz, 2H; ArH). Σ(ArH) ≠ 7 as expected due to poor peak resolution, presumably due to fluxionality, consistent with observations on the ^{13}C{^{1}H} NMR. ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 168.5 (ArCHN), 135.1, 133.5, 129.9, 128.5, 127.9 (Ar), 121.7.
Elemental analysis: Calculated for $C_{26}H_{16}N_2O_2ZnCl_4$: C; 52.43 %; H; 2.71 %; N; 4.70 %. Found: C; 50.43 %; H, 3.11 %; N, 4.43 %.

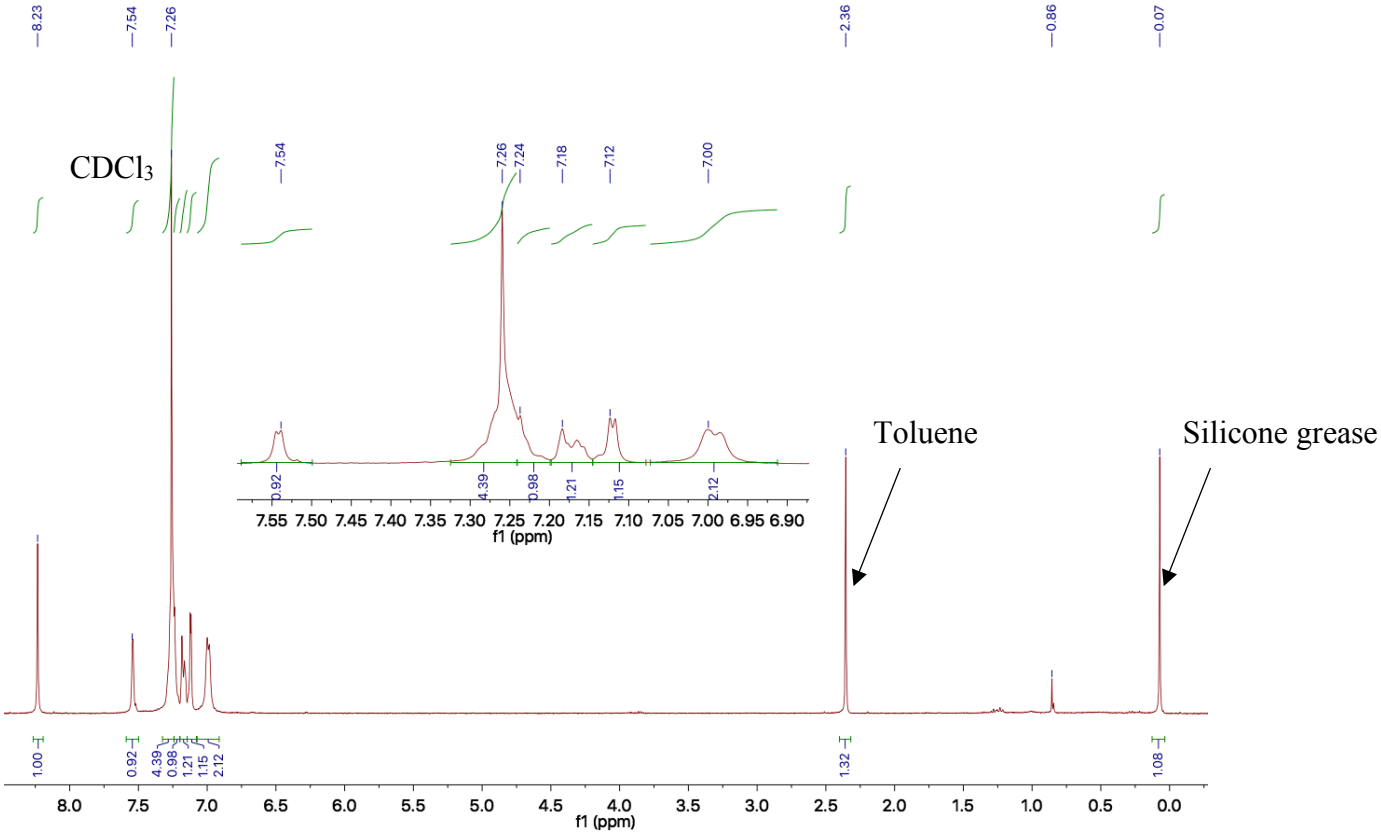


Figure 6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of Zn(**2**)$_2$.

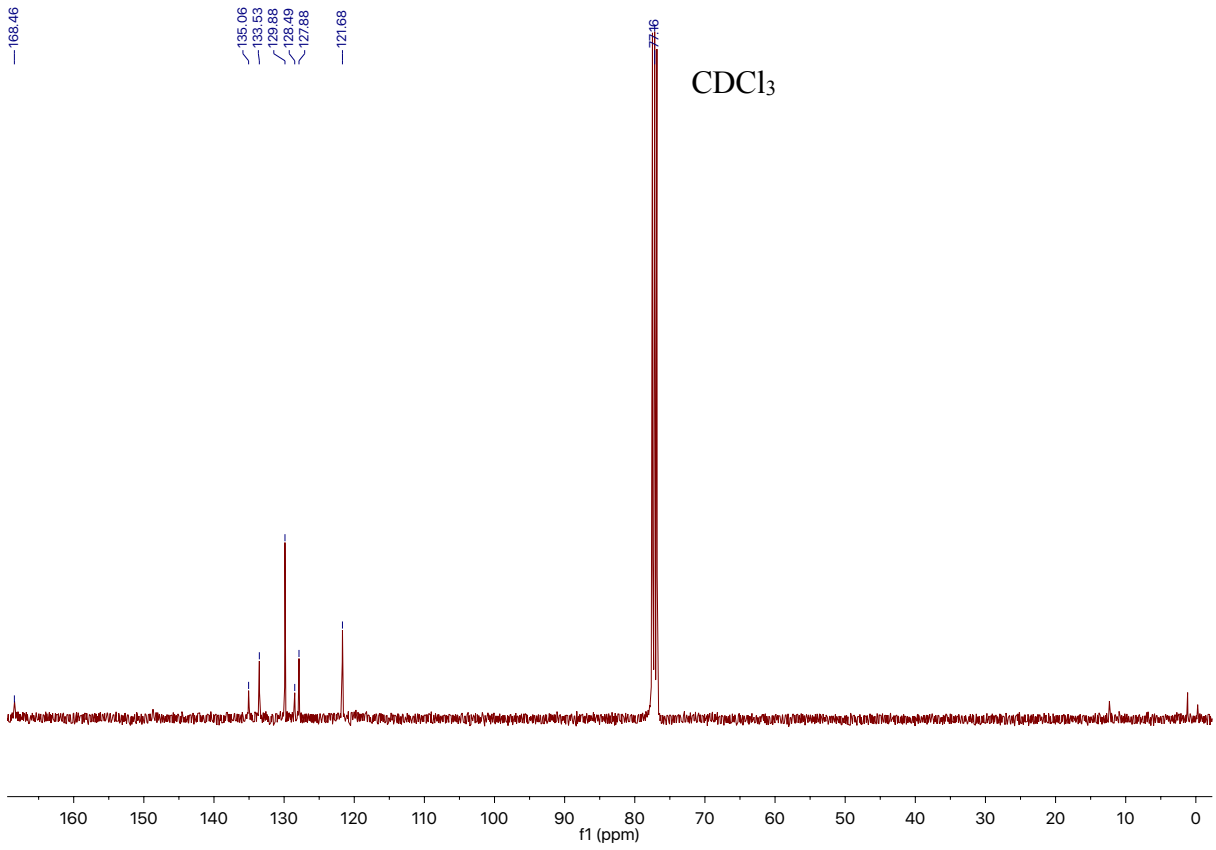


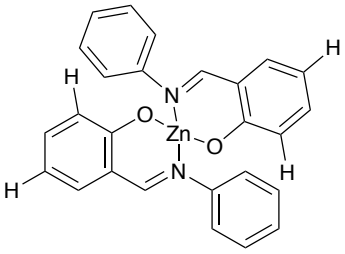
Figure 7. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 400 MHz) of Zn(**2**)$_2$.

Large scale synthesis of Zn(2)$_2$:

2H (15 g, 0.056 mol) was dissolved in anhydrous toluene (150 mL) and allowed to stir at RT for 15 minutes. The solvent was then degassed *in vacuo* over 5 minutes with stirring before being returned to a dynamic argon atmosphere. The reactor vessel was then submerged in an ice bath (- 78 °C) and $ZnEt_2$ (1M, 28 mL) was added dropwise. The reaction was then left to slowly proceed over 4 h, with stirring providing agitation. The reactor vessel was then removed from the ice bath and allowed to gradually warm to RT. The solution was then allowed to stir for a further 18 h. The orange product was isolated by cannula filtration and dried *in vacuo* at 80 °C for 2 days.

Yield = 14.6 g, 87%.

Zn(**3**)$_2$: recrystallised from anhydrous toluene. Isolated as pale-yellow crystals.
Yield = 0.31 g, 67%.



^{1}H NMR (C_6D_6, 400 MHz): δ 7.69 (s, 1H; CHN), 7.26 (d, *J* = 8.1 Hz, 1H; ArH), 7.21 (td, *J* = 1.6, 1.8, 7.5 Hz, 1H; ArH), 6.87 (d, *J* = 7.4 Hz, 2H; ArH), 6.82 (m, 4H; ArH), 6.52 (t, *J* = 6.5 Hz, 1H; ArH). ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 171.5, 169.8 (ArCHN), 148.9 (Ar), 136.7, 136.3, 129.7, 127.0, 123.9, 121.5, 118.7, 115.3 (Ar).
Elemental analysis: Calculated for $C_{26}H_{20}N_2O_2Zn$: C; 68.21 %; H; 4.40 %; N; 6.12 %. Found: C; 66.87 %; H, 4.30 %; N, 6.17 %.

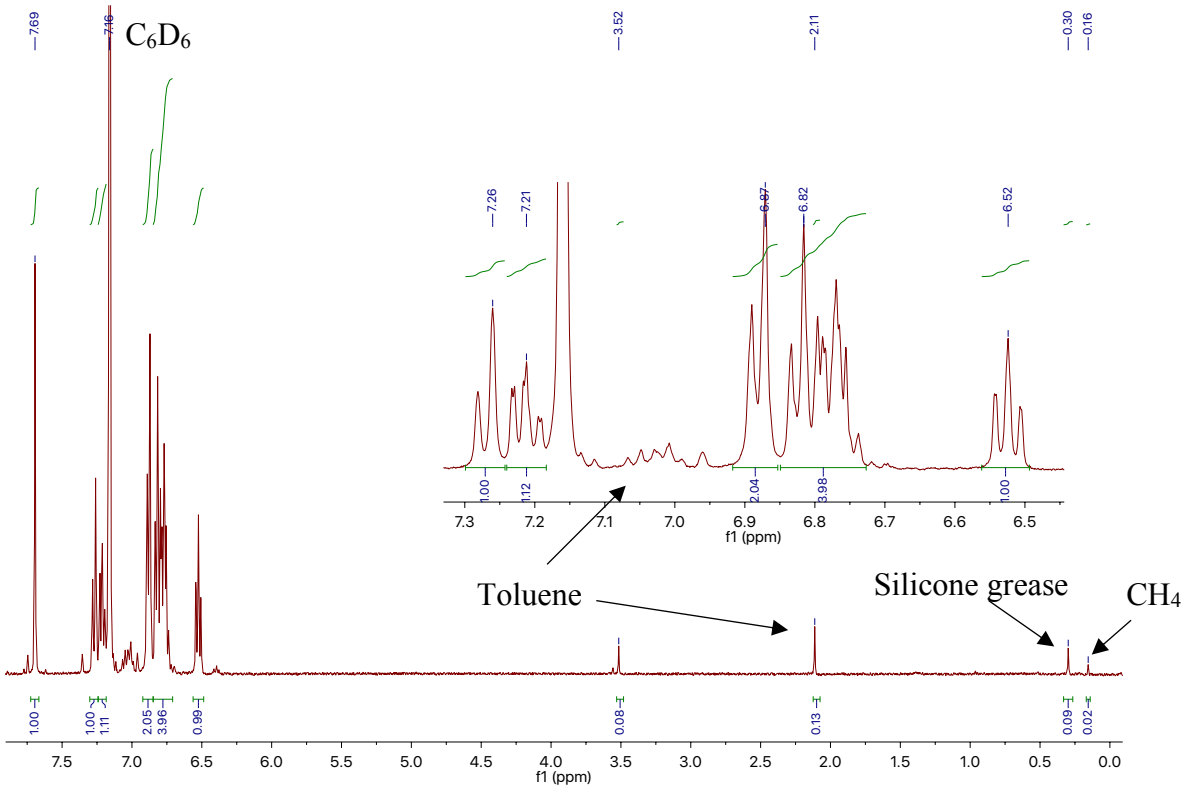


Figure 8. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of Zn(**3**)$_2$.

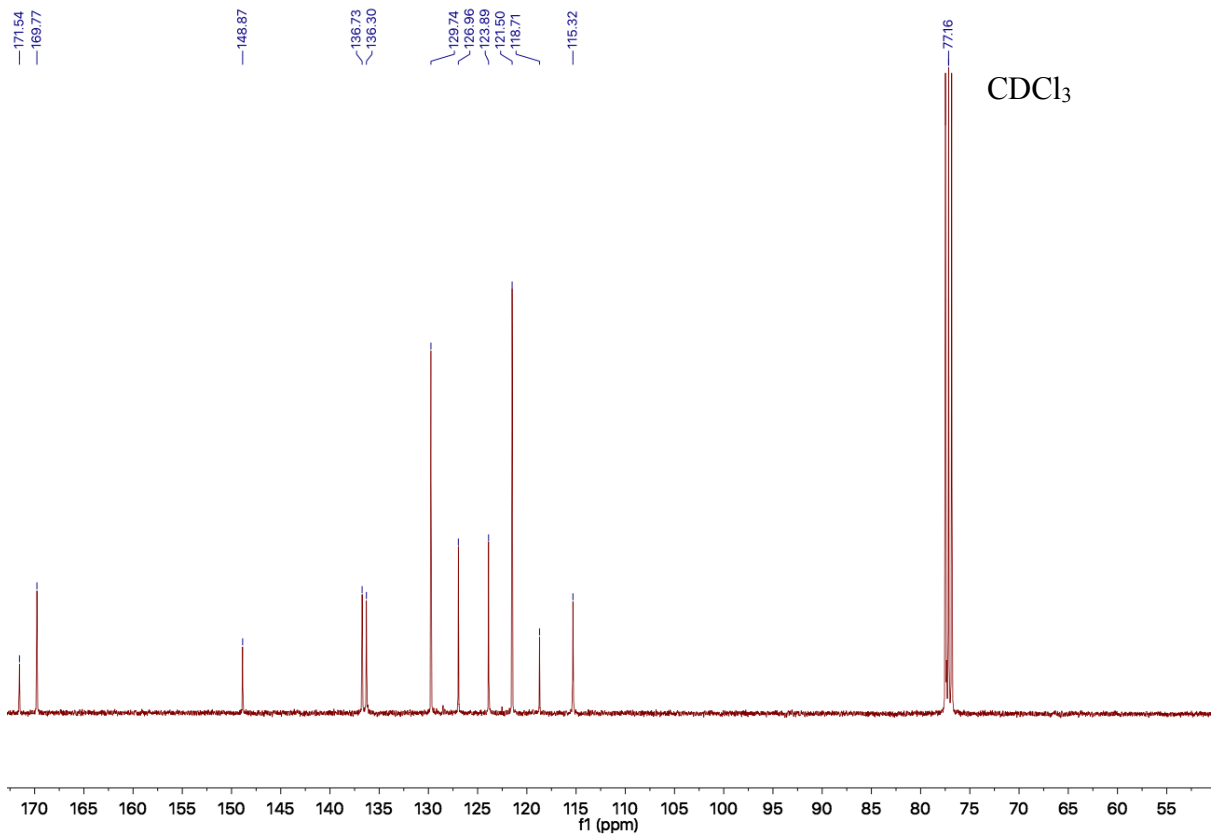
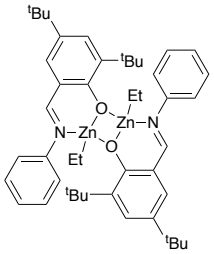


Figure 9. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 400 MHz) of Zn(**3**)$_2$

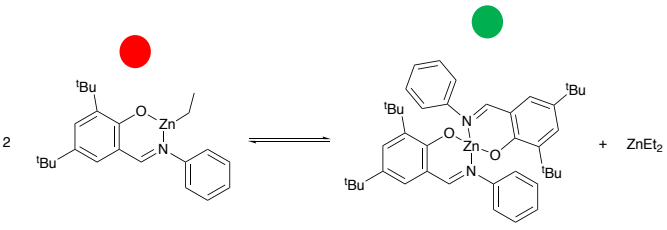
Synthesis of dimeric Zn$_2$(1-3)$_2$(Et)$_2$ complexes:
The method described for Zn(**1-3**)$_2$ was repeated, but instead a 1:1 ratio of ligand:Zn was employed at a 2 mmol scale. All $^{1}H/^{13}C\{^{1}H\}$ NMR spectra were obtained in C_6D_6 exclusively due to the suspected instability of Zn$_2$(**1-3**)$_2$(Et)$_2$ to acidic impurities present in $CDCl_3$.

Zn$_2$(**1**)$_2$(Et)$_2$: recrystallised from hexane. Isolated as pale-yellow crystals.
Yield = 0.77 g, 48%.

Solid state:



Solution:



^{1}H NMR (C_6D_6, 400 MHz): δ 7.86 (s, 1H; CHN), 7.78 (dd, *J* = 2.5, 17.1 Hz, 1H; ArH), 7.04 (d, *J* = 7.4 Hz, 1H; ArH), 6.95 (m, 2H; ArH), 6.86 (t, *J* = 7.4, 7.9 Hz, 1H; ArH), 6.80 (m, 1H, ArH), 6.75 (d, *J* = 7.9 Hz, 1H; ArH), 1.77, 1.74, 1.38, 1.37 (s, 9H; C(CH$_3$)$_3$), 1.34 (t, *J* = 8.2, 8.7 Hz, 3H; CH$_3$), 0.42 (q, *J* = 8.2, 8.7, 2H; CH$_2$). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 400 MHz): δ 170.5, 170.4, 169.4, 169.0 (ArCHN), 150.1, 149.9 142.4, 142.1, 136.9, 136.0, 131.3 (Ar), 131.0, 130.3, 129.6 (Ar), 129.6, 129.5, 126.3, 122.1, 121.7, 118.9, 118.4 (Ar), 36.1, 36.0, 34.2, 34.1 (C(CH)$_3$), 31.7, 30.0, 29.9 (C(CH)$_3$), 11.7 (CH$_3$), 2.5 (CH$_2$). Elemental analysis: Calculated for

$C_{46}H_{62}N_2O_2Zn_2$: C; 68.57 %; H; 7.76 %; N; 3.48 %. Found: C; 67.77 %; H, 7.73 %; N, 3.58 %.

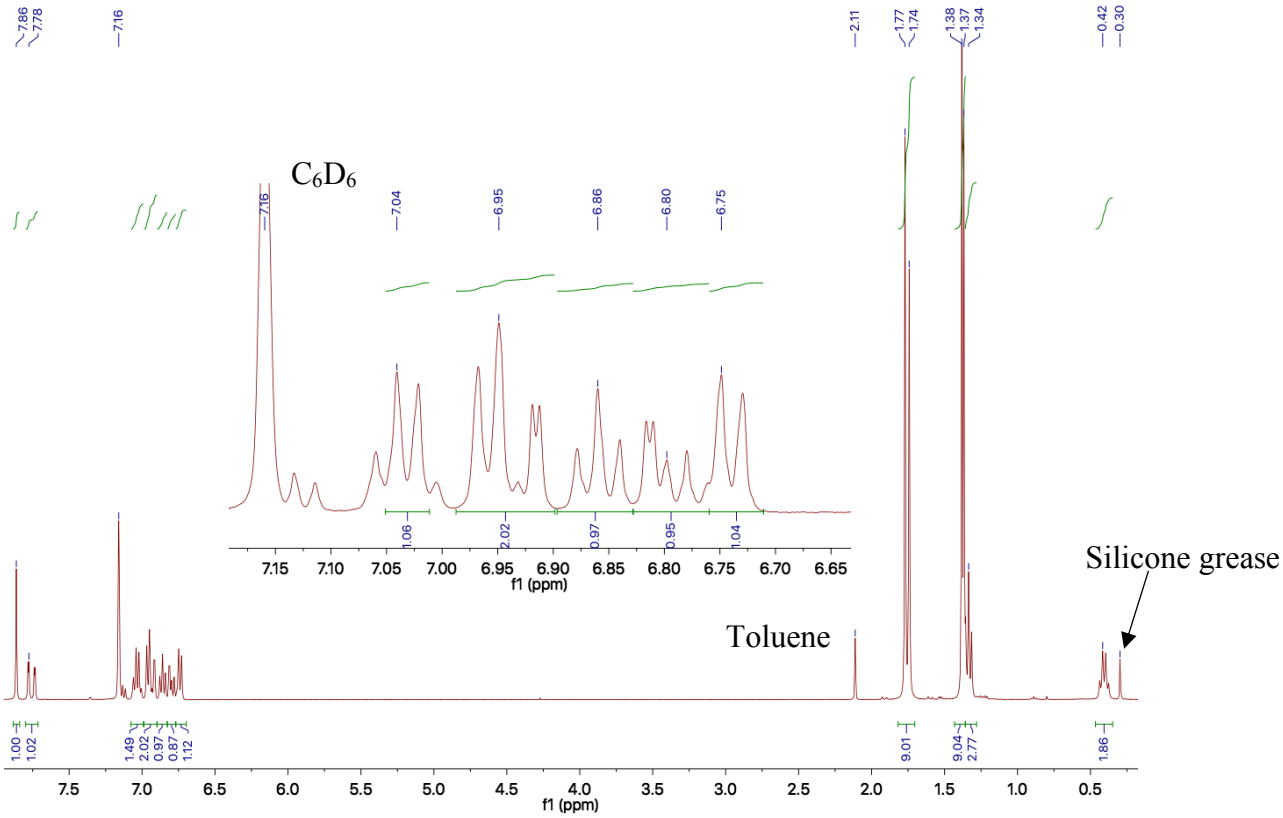
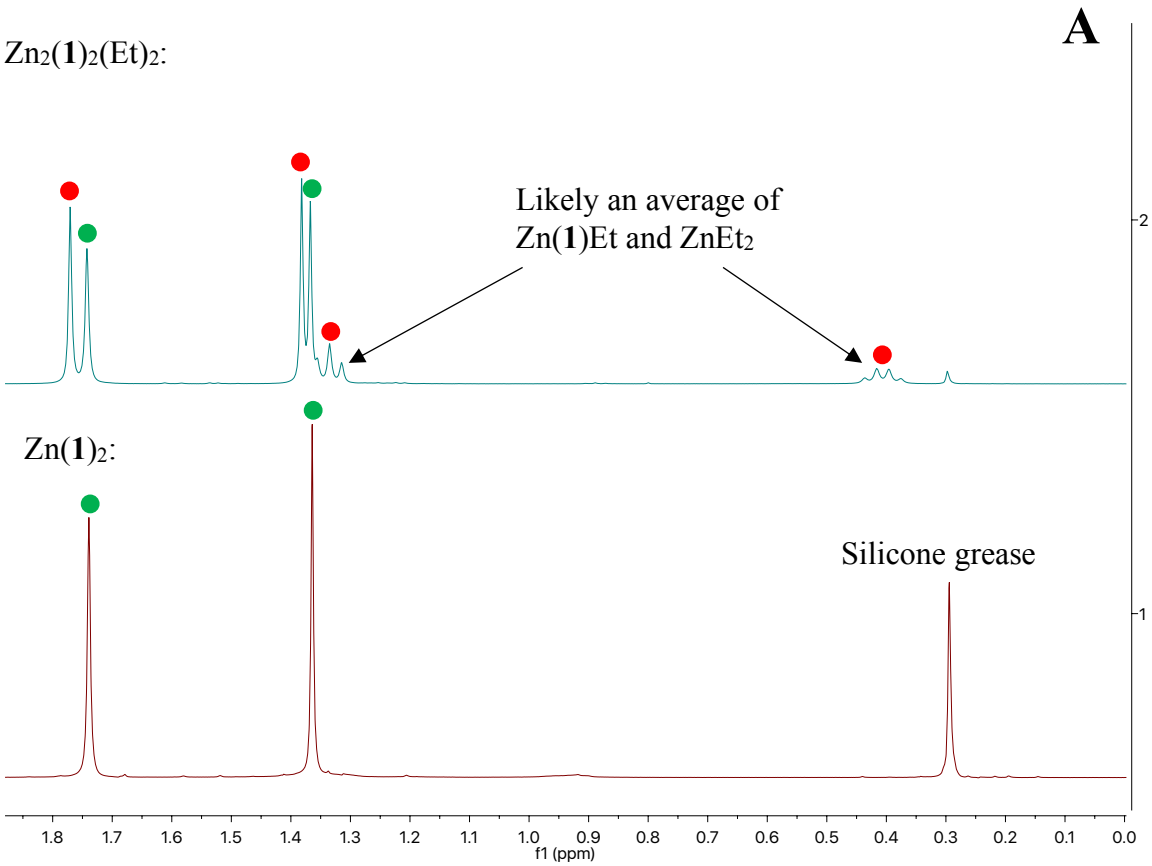


Figure 10a. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of $Zn_2(\mathbf{1})_2(Et)_2$.



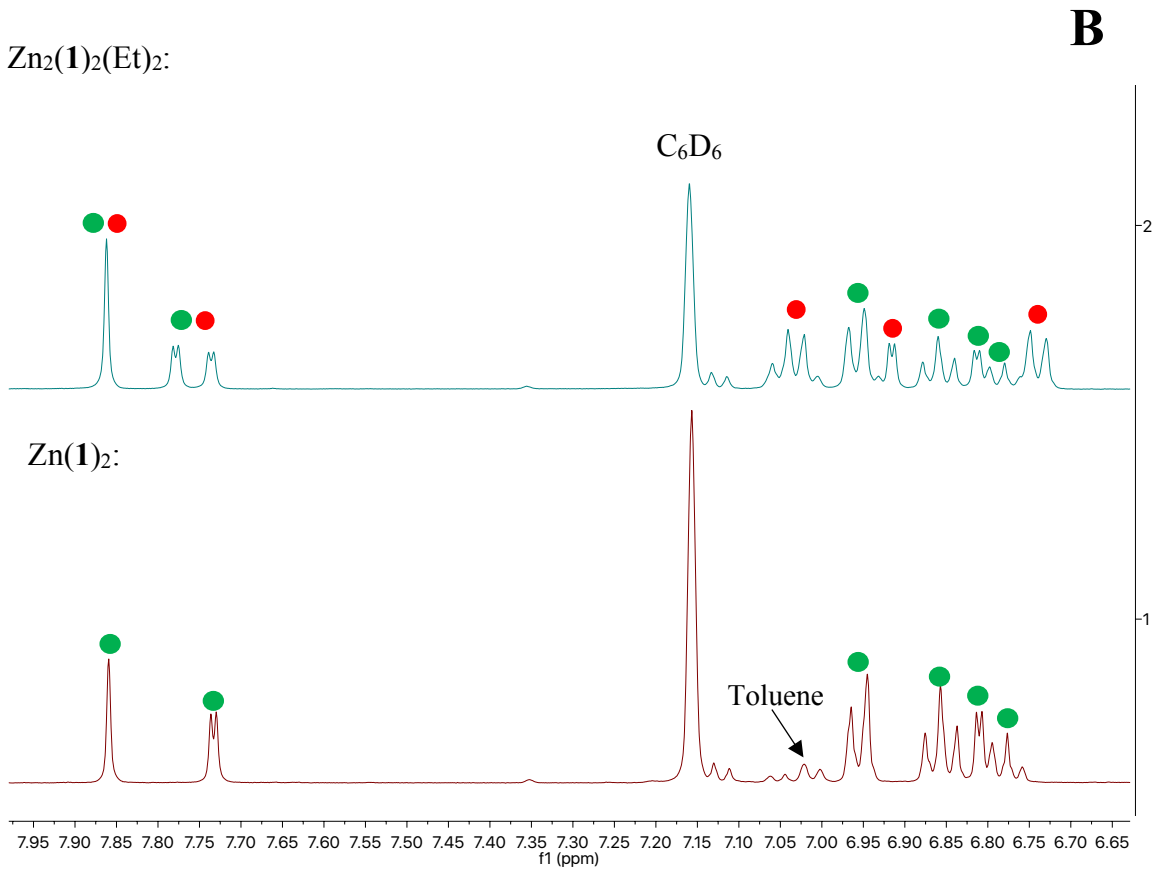


Figure 10b. ^{1}H NMR spectra (C_6D_6, 400 MHz) comparison between Zn(**1**)$_2$ and Zn_2(**1**)$_2$(Et)$_2$ in the alkyl (**A**) and aromatic (**B**) region highlighting the schlenk type equilibrium present, consistent with DOSY NMR (Figure 4b and 10d).

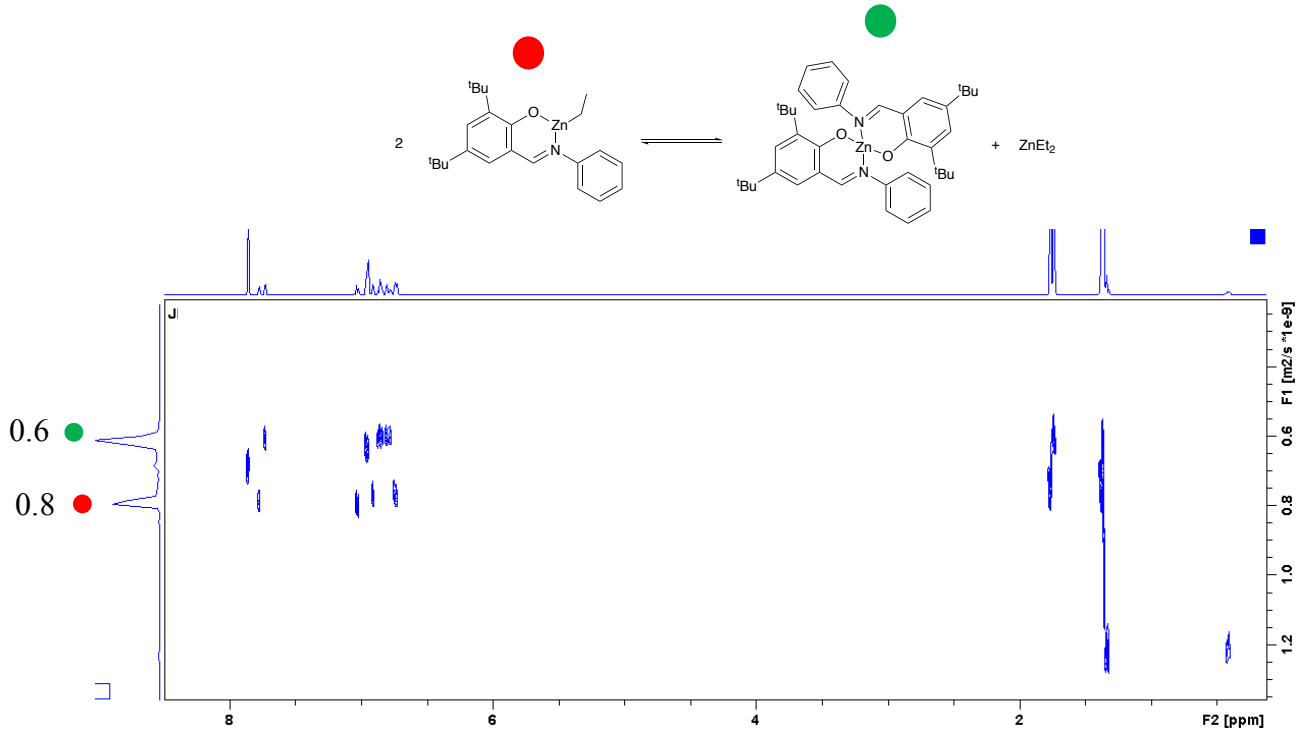


Figure 10c. DOSY NMR spectrum (C_6D_6, 500 MHz) of $Zn_2(\mathbf{1})_2Et_2$, indicating two species present in solution, with diffusion constants of 0.6 x 10^{-9} and 0.8 x 10^{-9} m^2 s^{-1} respectively.

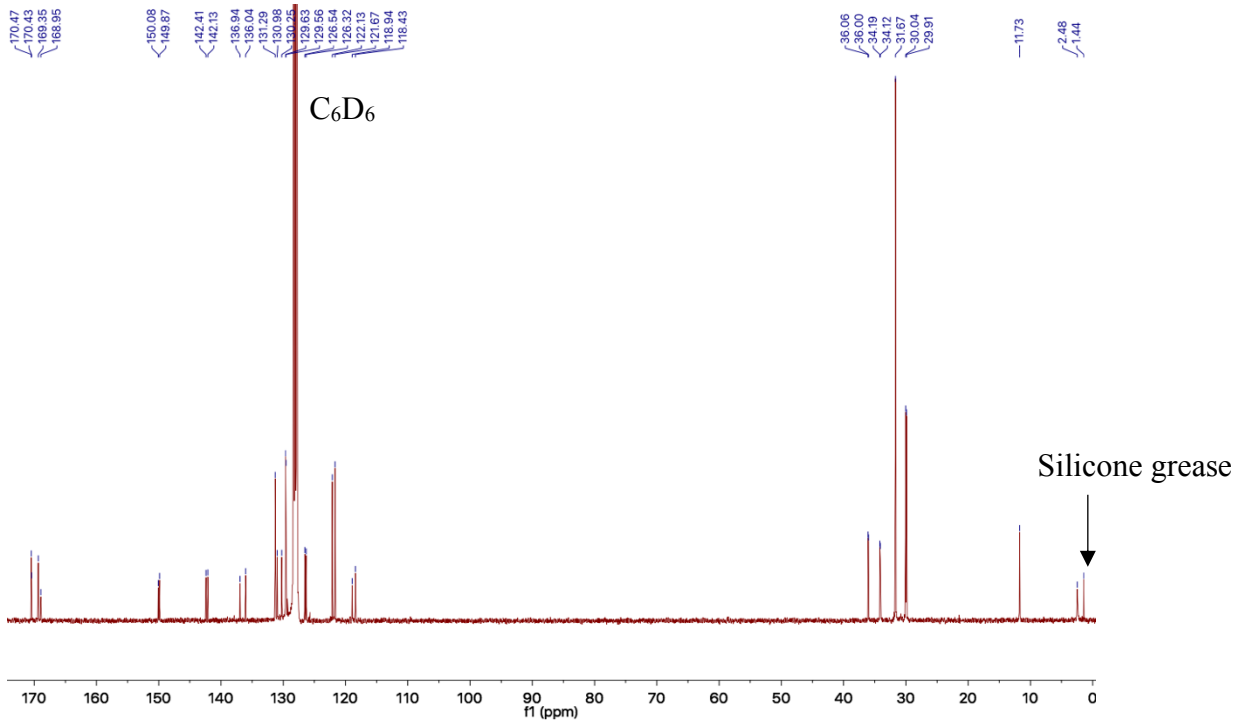
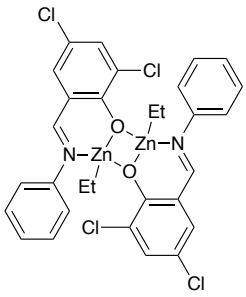


Figure 11. $^{13}C\{^1H\}$ NMR spectrum (C_6D_6, 400 MHz) of $Zn_2(\mathbf{1})_2(Et)_2$.

$Zn_2(\mathbf{2})_2(Et)_2$: recrystallised from anhydrous toluene. Isolated as yellow crystals.
Yield = 0.56 g, 39 %.



^{1}H NMR (C_6D_6, 400 MHz): δ 7.24 (s, 1H; CHN), 7.07 (s, 3H; ArH), 6.98 (s, 3H; ArH), 6.43 (d, J = 2.7 Hz, 1H; ArH), 1.48 (t, J = 1.5 Hz, 3H; CH_3), 0.68 (q, J = 7.9 Hz, 2H; CH_2). ^{13}C{^{1}H} NMR (C_6D_6, 400 MHz): δ 165.8 (ArCHN), 132.7, 131.9, 127.7 (Ar), 120.1, 11.1 (CH_3), -1.7 (CH_2).
Elemental analysis: Calculated for $C_{30}H_{26}N_2O_2Zn_2Cl_4$: C; 50.11 %; H; 3.64 %; N; 3.90 %. Found: C; 49.44 %; H, 3.59 %; N, 3.95 %.

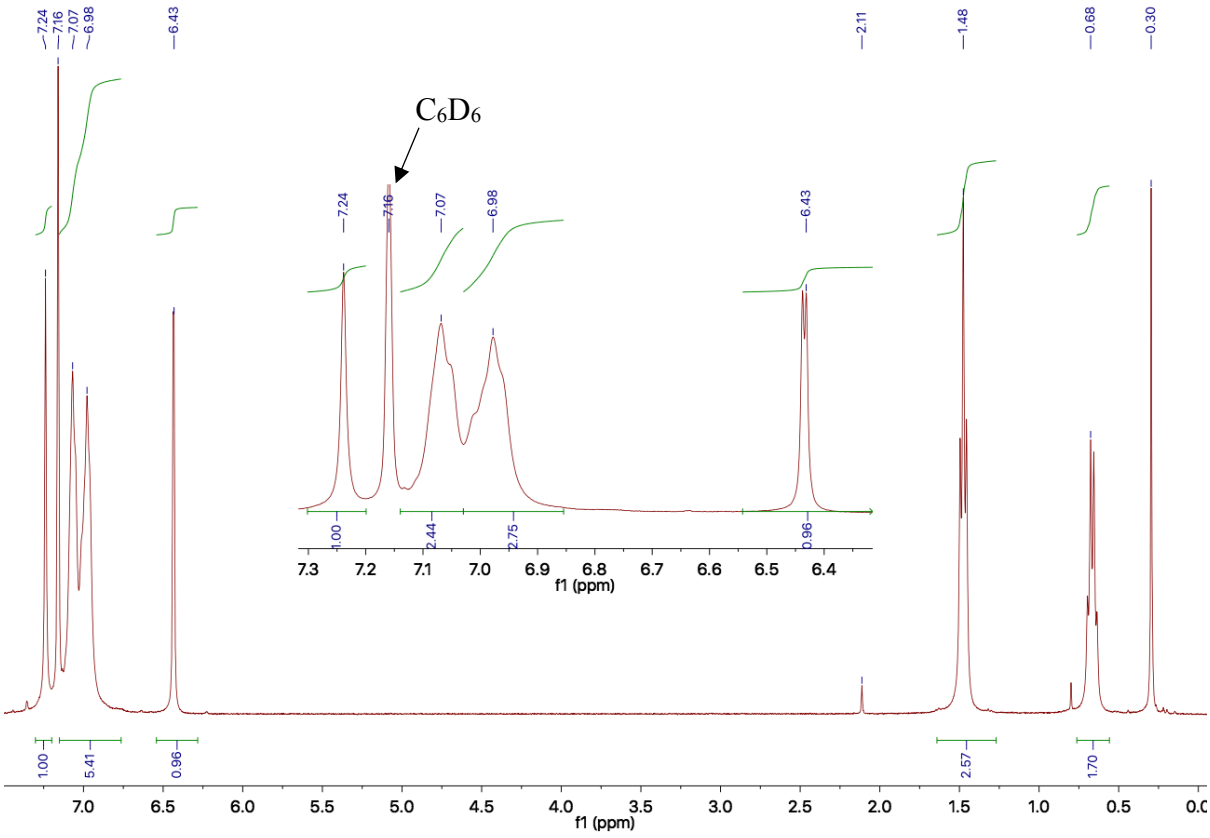


Figure 12a. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of $Zn_2(\mathbf{2})_2(Et)_2$.

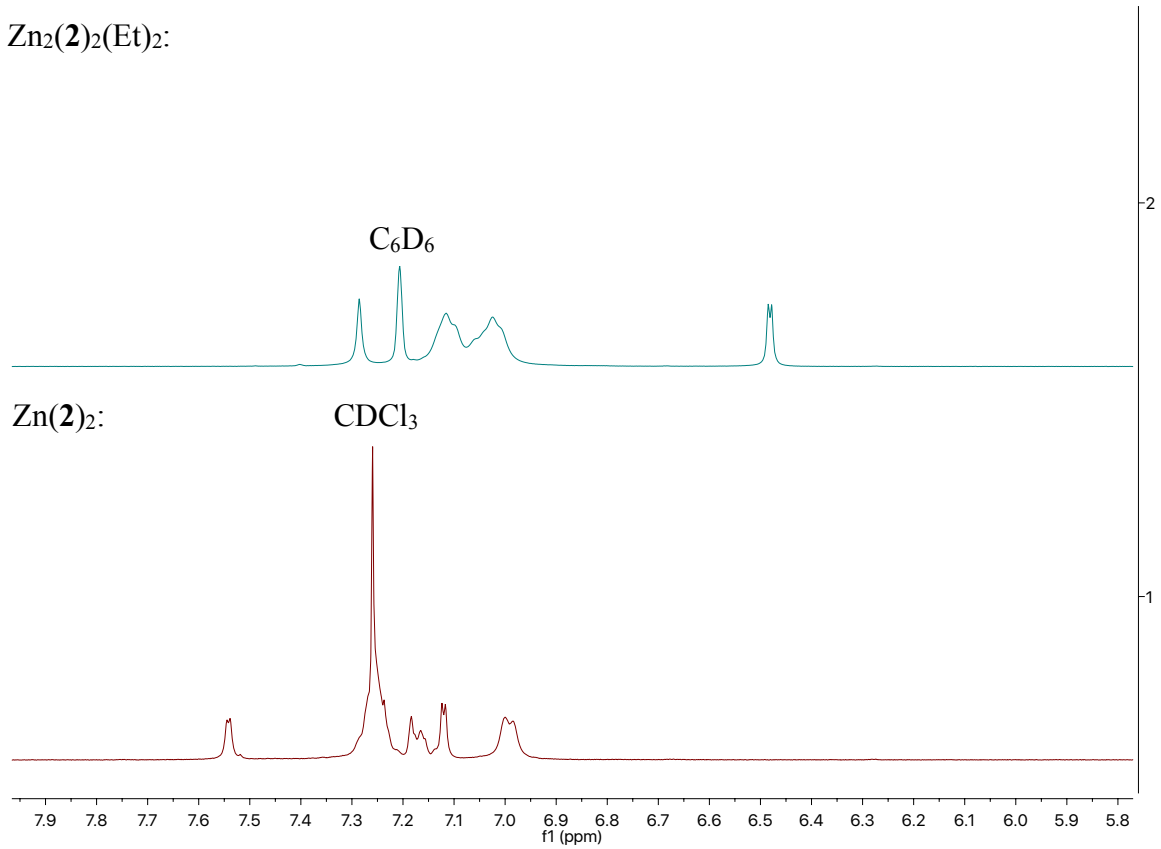


Figure 12b. ^{1}H NMR spectra (400 MHz) comparison between Zn(**2**)$_2$ and Zn$_2$(**2**)$_2$Et$_2$ indicating no evidence of Schlenk type equilibrium, suggesting dimeric structure present exclusively in solution, consistent with XRD analysis.

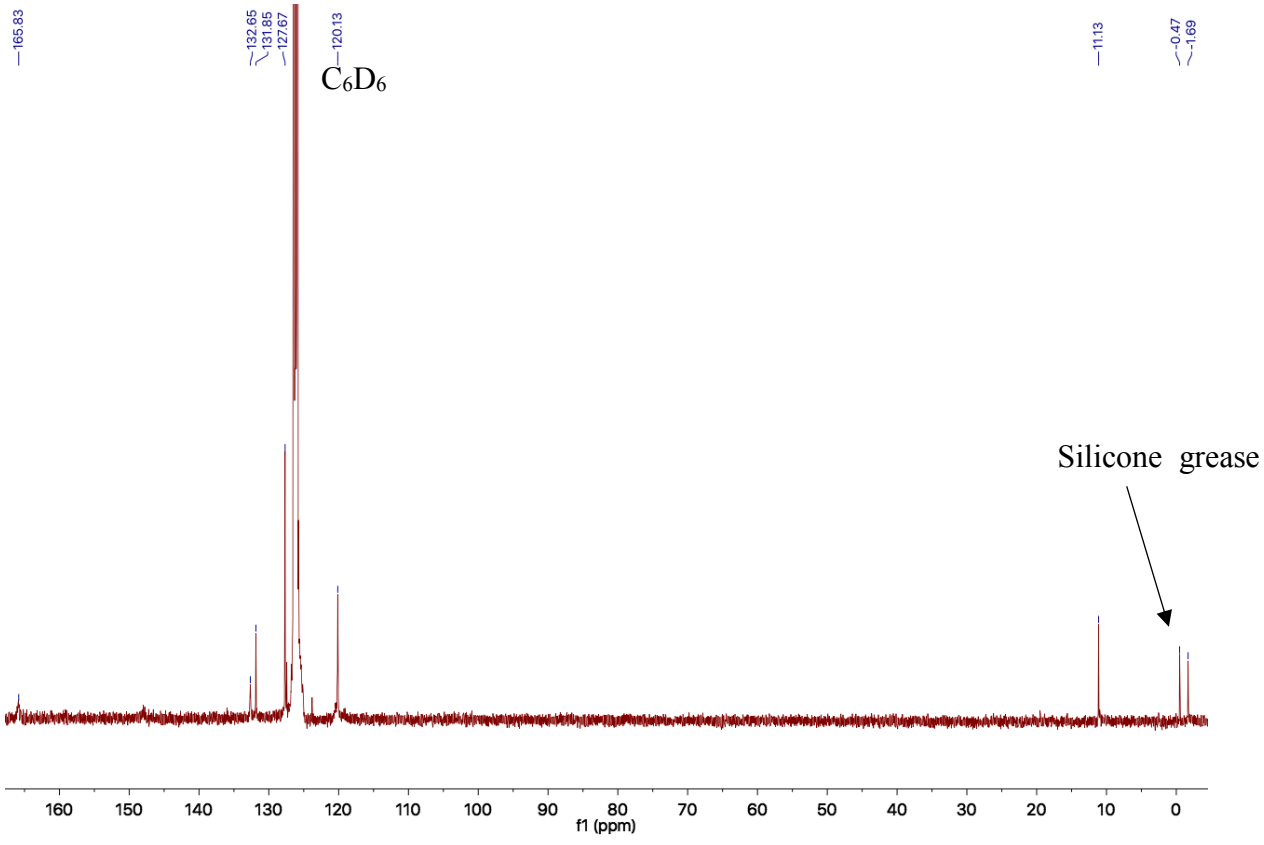
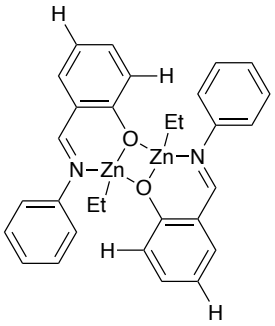


Figure 13. ^{13}C{^{1}H} NMR spectrum (C$_6$D$_6$, 400 MHz) of Zn$_2$(**2**)$_2$(Et)$_2$.

$Zn_2(\mathbf{3})_2(Et)_2$: recrystallised from anhydrous toluene. Isolated as pale-yellow crystals. Yield = 0.50 g, 43 %.



^{1}H NMR (C_6D_6, 400 MHz): δ 7.77 (s, 1H; CHN), 7.10 (t, *J* = 7.2 Hz, 2H; ArH), 7.00 (m, 3H; ArH), 6.79 (d, *J* = 7.9 Hz, 1H; ArH), 6.57 (t, *J* = 6.6 Hz, 1H; ArH), 1.38 (t, *J* = 8 Hz, 3H; CH_3), 0.60 (q, *J* = 8 Hz, 2H; CH_2). Σ(ArH) ≠ 9 as expected due to poor peak resolution in the aromatic region. $^{13}C\{^1H\}$ NMR (C_6D_6, 400 MHz): δ 167.9, 167.7 (ArCHN), 150.2 (Ar), 136.3, 135.5 (Ar), 129.7, 129.3, 127.2, 123.6, 122.0, 117.8 (Ar), 13.2 (CH_3), -1.3 (CH_2).
Elemental analysis: Calculated for $C_{30}H_{30}N_2O_2Zn_2$: C; 61.98 %; H; 5.20 %; N; 4.82 %. Found: C; 60.60 %; H, 5.14 %; N, 4.82 %.

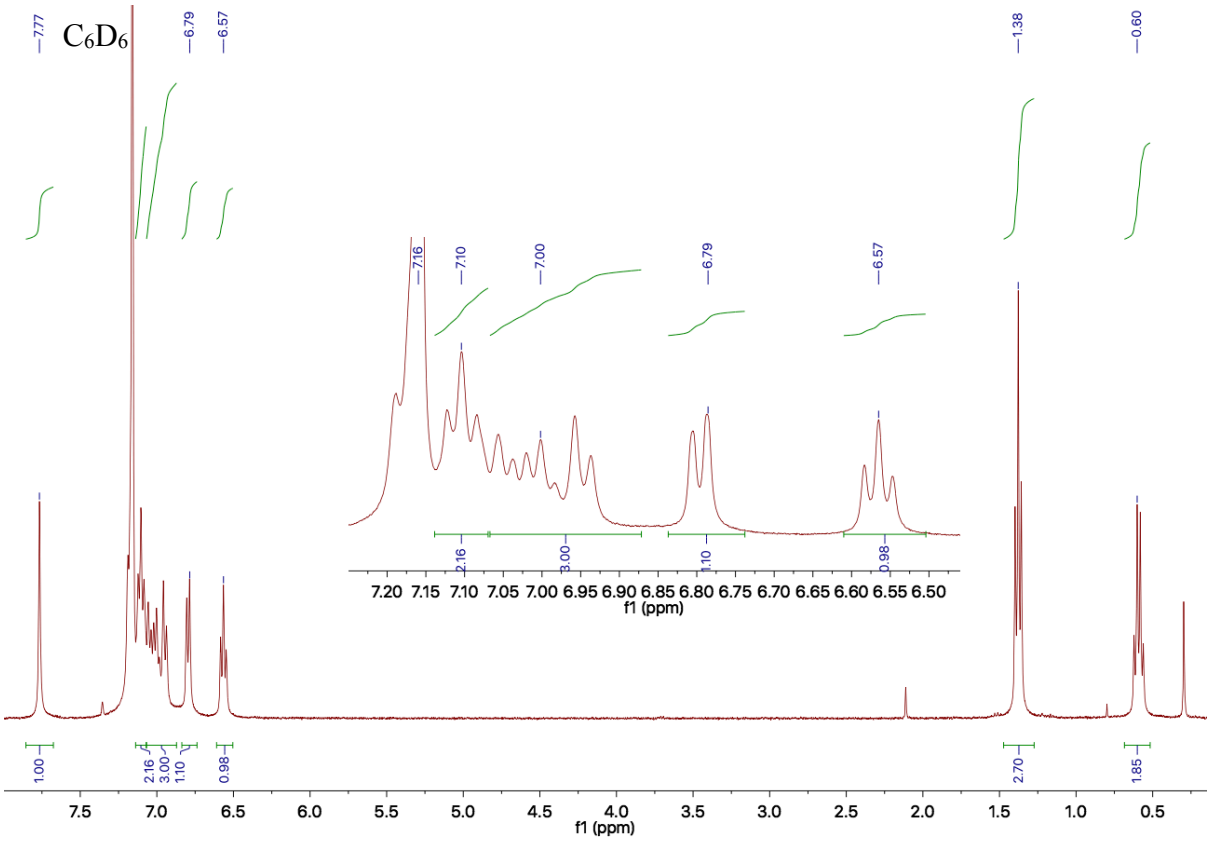


Figure 14a. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of $Zn_2(\mathbf{3})_2(Et)_2$.

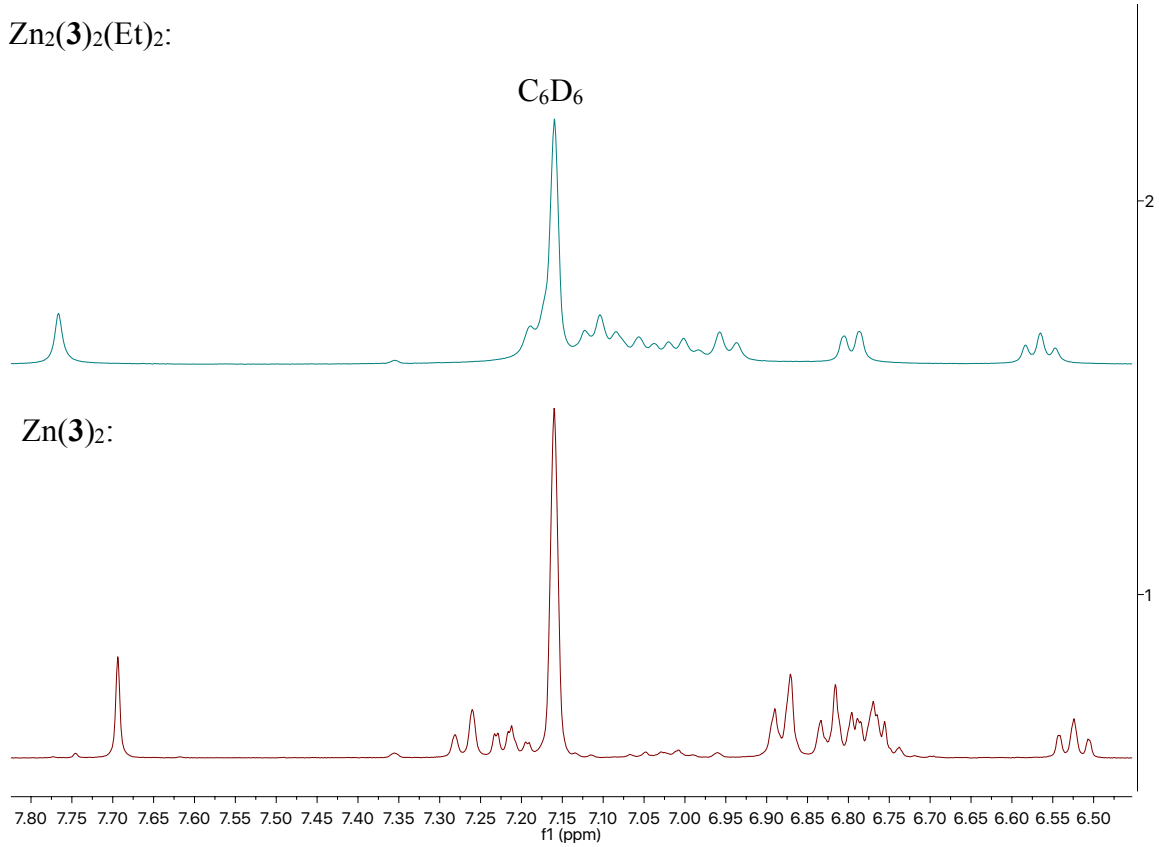


Figure 14b. ^{1}H NMR spectra (400 MHz) comparison between Zn(**3**)$_2$ and Zn$_2$(**3**)$_2$Et$_2$ indicating no evidence of Schlenk type equilibrium, suggesting dimeric structure present exclusively in solution, consistent with XRD analysis.

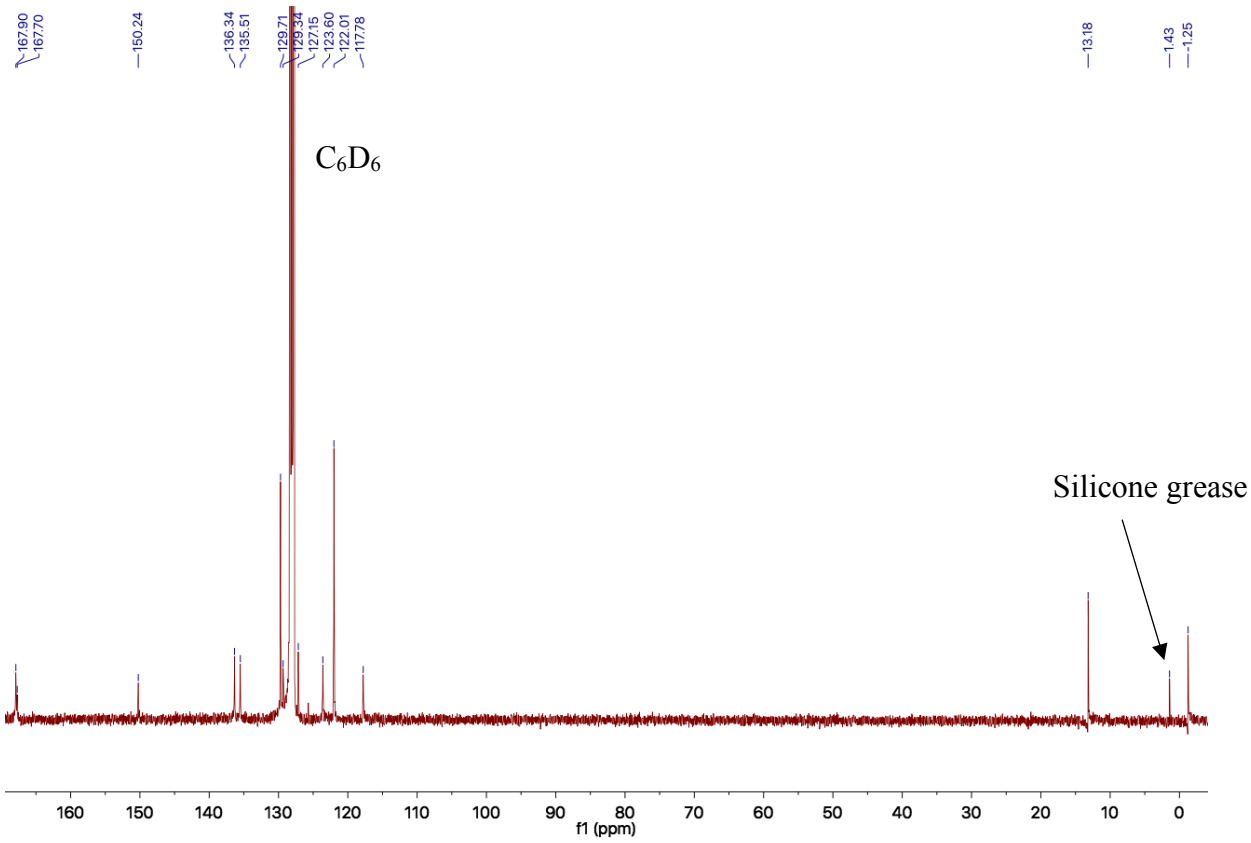


Figure 15. ^{13}C{^{1}H} NMR spectrum (C$_6$D$_6$, 400 MHz) of Zn$_2$(**3**)$_2$(Et)$_2$.

2.3 Catalyst stability testing:

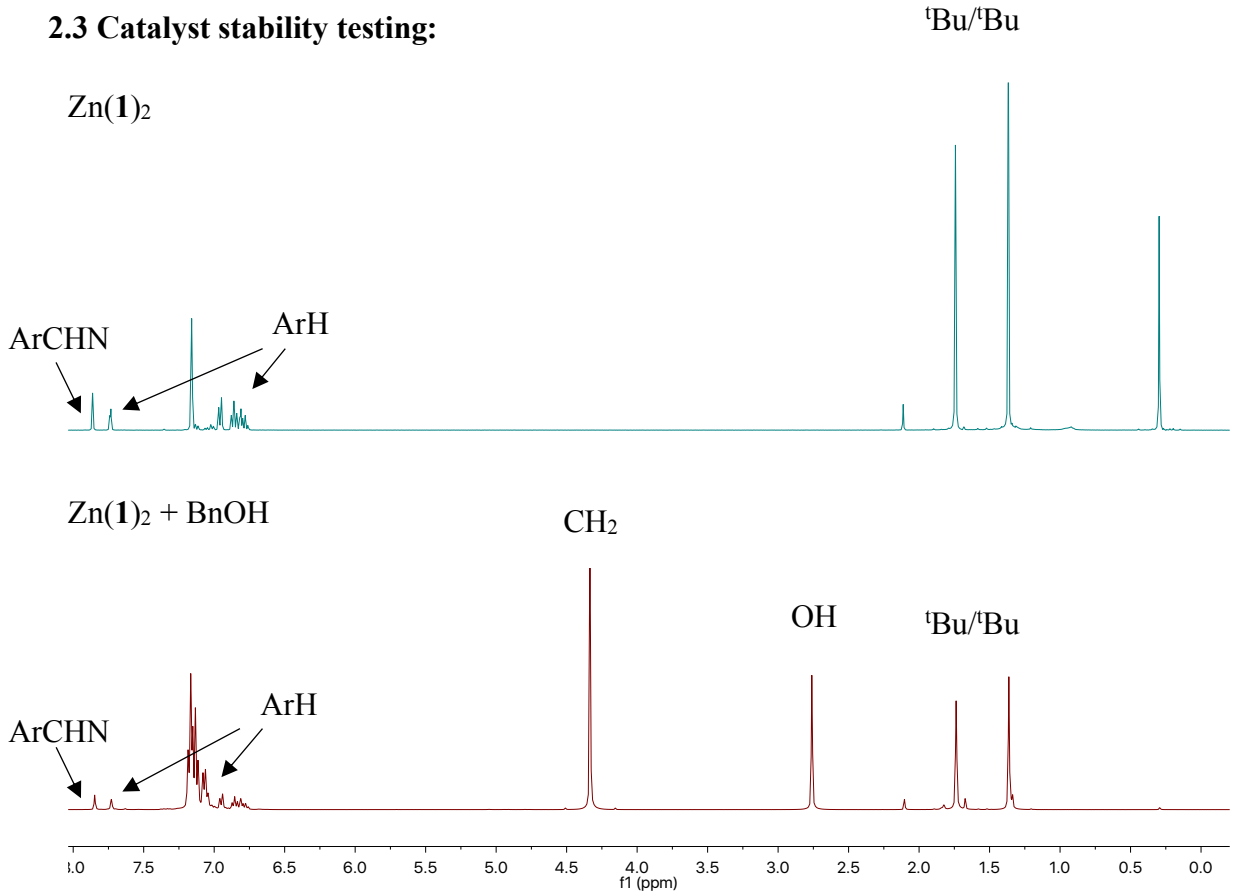


Figure 16. ^{1}H NMR (C_6D_6, 400 MHz) spectrum of Zn(**1**)$_2$ compared to Zn(**1**)$_2$ with BnOH.

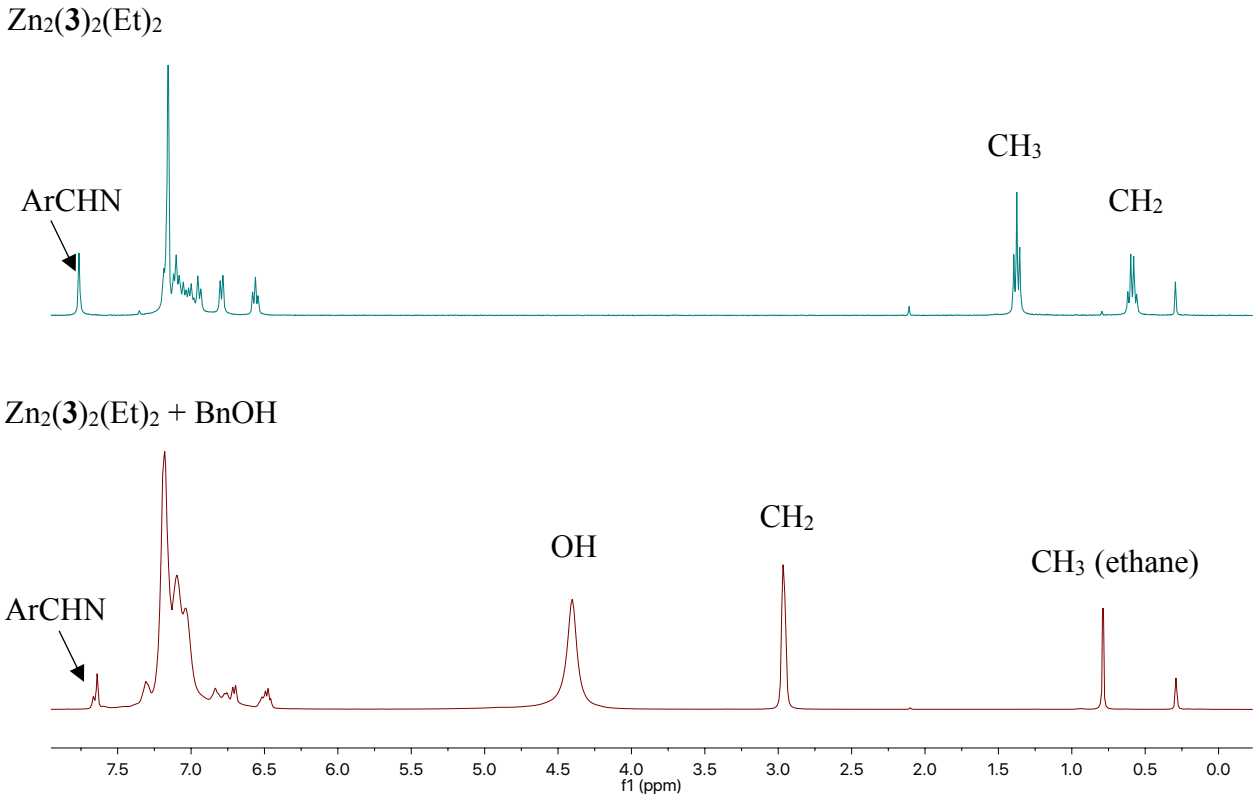


Figure 17. ^{1}H NMR (C_6D_6, 400 MHz) spectrum of Zn$_2$(**3**)$_2$(Et)$_2$ compared to Zn$_2$(**3**)$_2$(Et)$_2$ with BnOH.

3. Polymer characterisation

3.1 Representative ^{1}H NMR spectra:

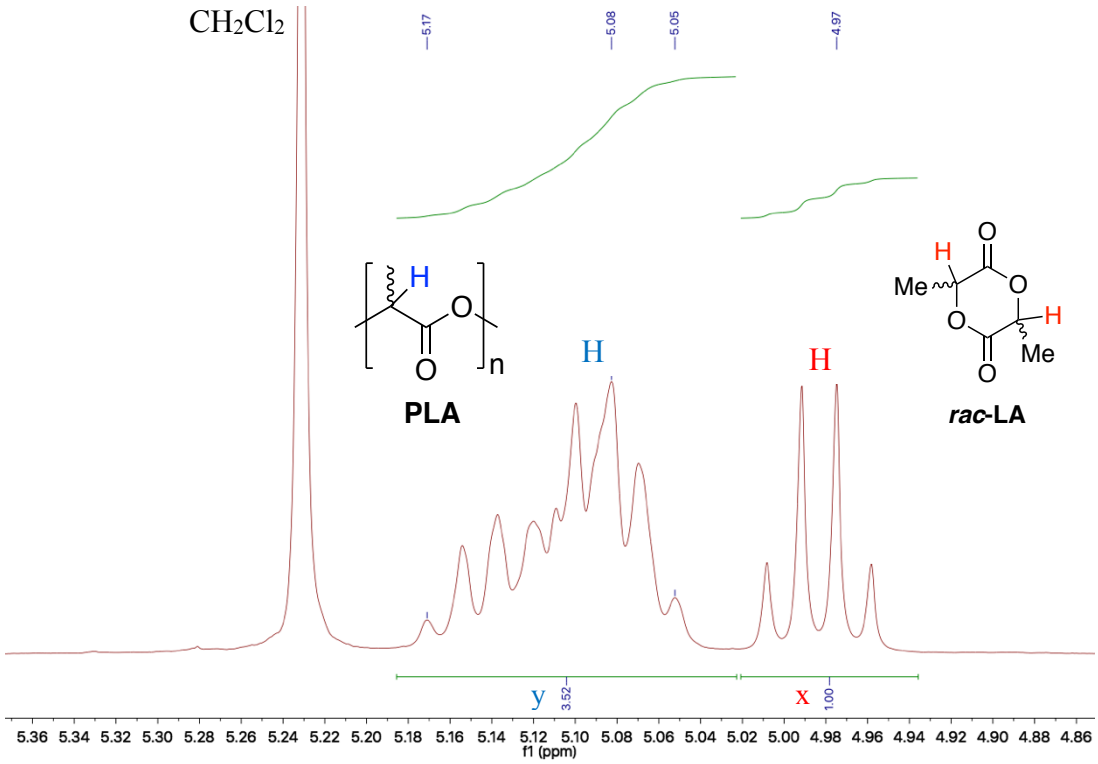


Figure 18. ^{1}H NMR ($CDCl_3$) spectrum of crude PLA product from the melt polymerisation of *rac*-LA at 130 °C using Zn(**2**)$_2$ ([*rac*-LA]:[Init]:[BnOH] = 300:1:1), akin to remaining melt/solution polymerisation spectra. PLA conversion = [y/(x+y)] x 100%. (Table 2, entry 2).

3.2 Representative GPC spectra:

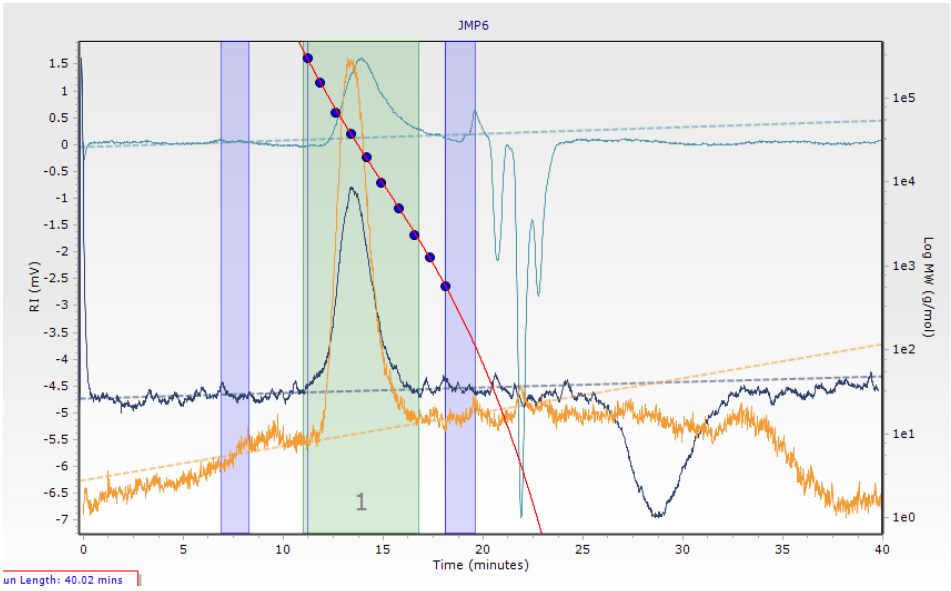


Figure 19. GPC spectrum of purified PLA product from the solution polymerisation of *rac*-LA at 80 °C for 2 h using Zn(**2**)$_2$ (Table 4, Entry 2).

3.3 Representative homonuclear decoupled ^{1}H NMR spectra:

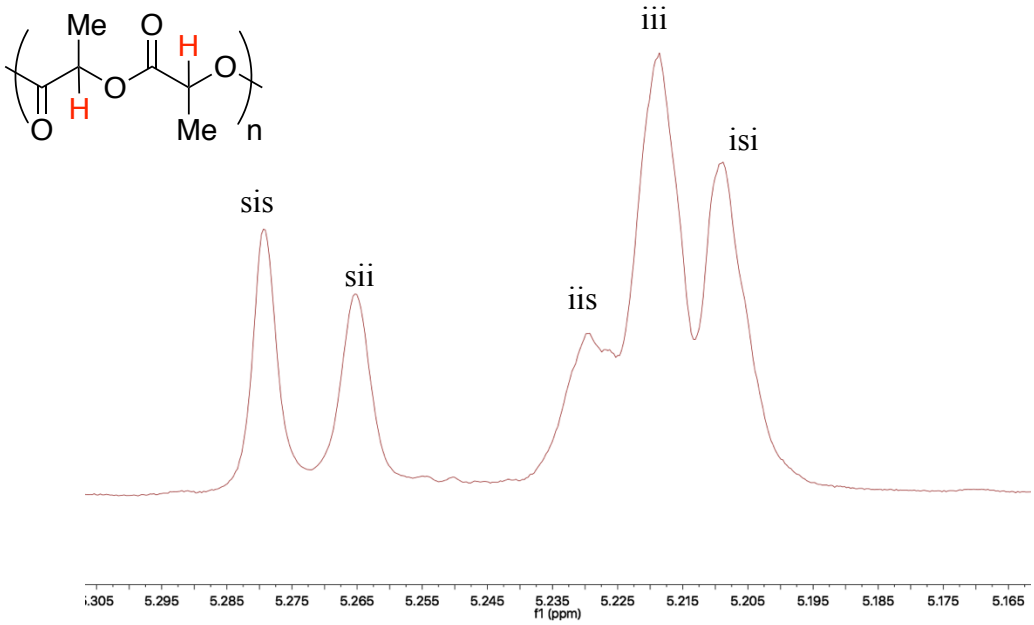


Figure 20. Homonuclear decoupled ^{1}H NMR ($CDCl_3$) spectra of purified atactic PLA (P_r = 0.50) product from the solution polymerisation of *rac*-LA at 80 °C for 2 h using Zn(**3**)$_2$, displaying the five tetrad possibilities in the methine region (red). [4]

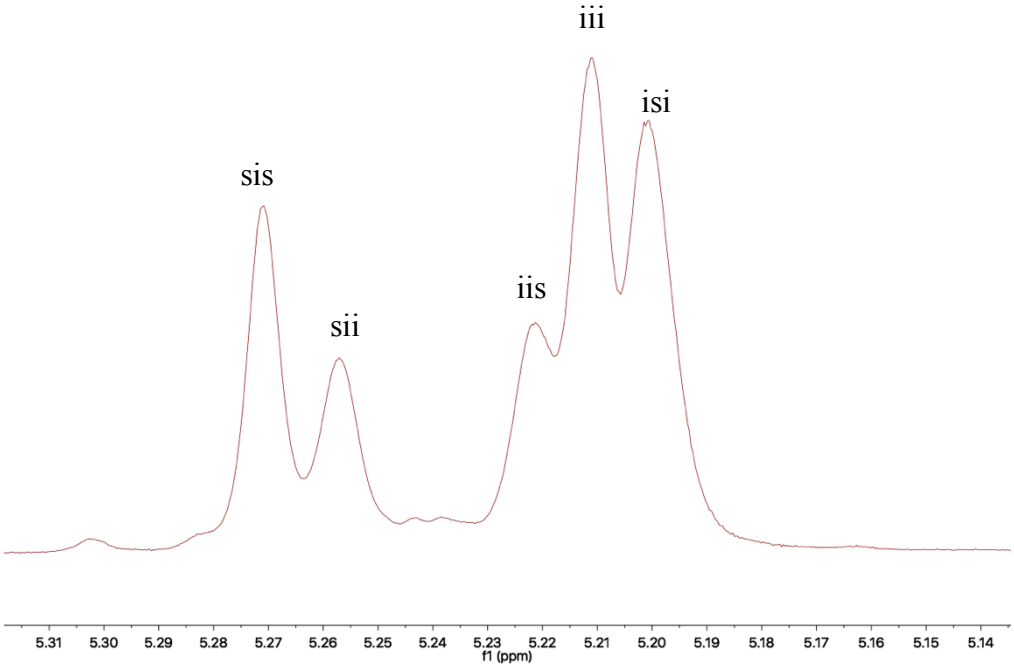


Figure 21. Homonuclear decoupled ^{1}H NMR ($CDCl_3$) spectra of purified slightly heterotactic PLA (P_r = 0.59) from the solution polymerisation of *rac*-LA at RT for 30 h using Zn_2(**2**)$_2$(Et)$_2$, displaying the five tetrad possibilities in the methine region (red). [4]

3.4 MALDI-ToF spectrum:

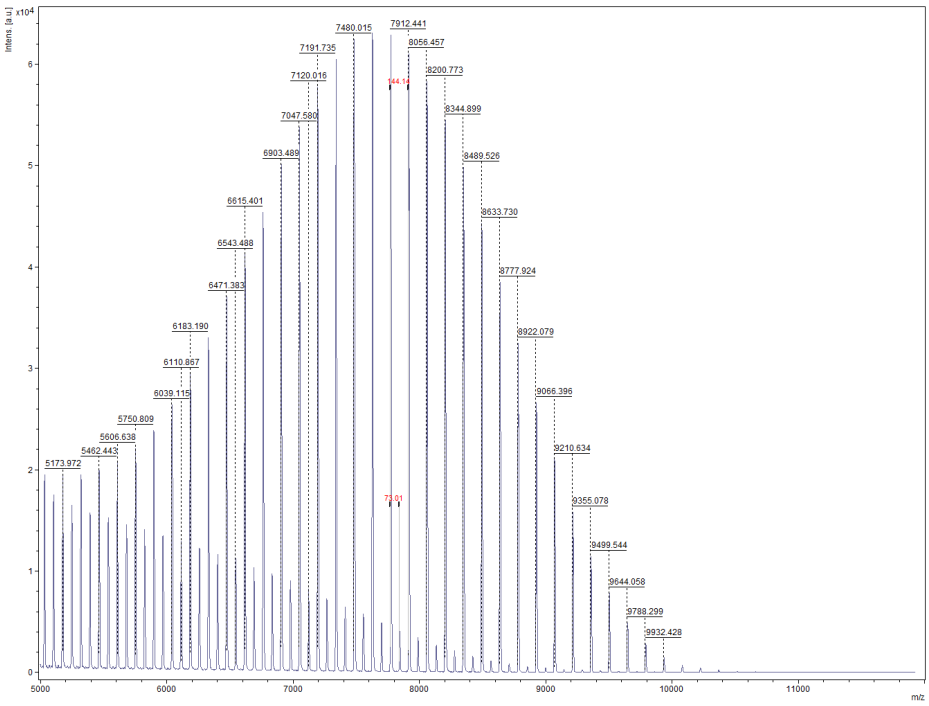


Figure 22. MALDI-ToF spectra of PLA produced using Zn(**1**)$_2$ (80 °C, 100:1:1) (Table 4, Entry 1).

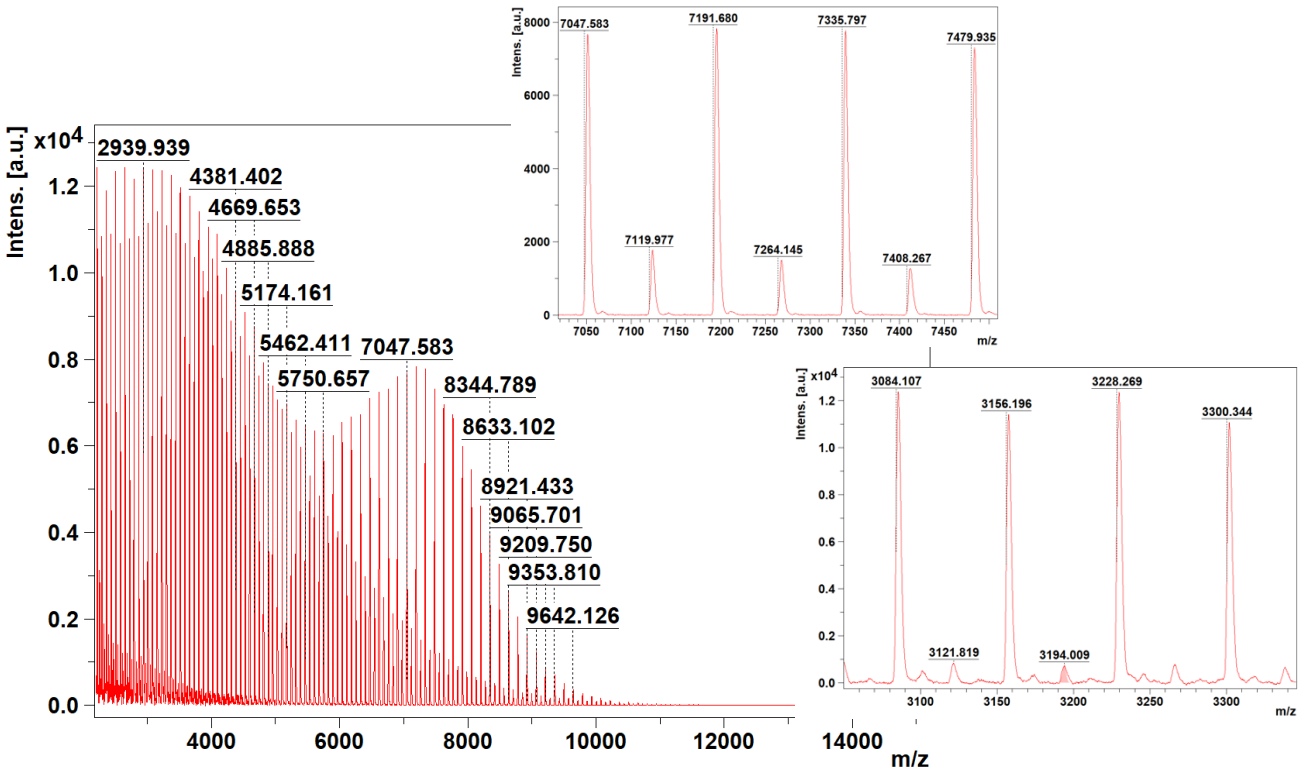


Figure 23. MALDI-ToF spectra of PLA produced using Zn(**1**)$_2$ (130 °C, 300:1:6) (Table 2, Entry 2). Magnified versions of smaller series are provided to assist in identifying the repeat unit.

4. Degradation characterisation

4.1 Representative ^{1}H NMR spectra:

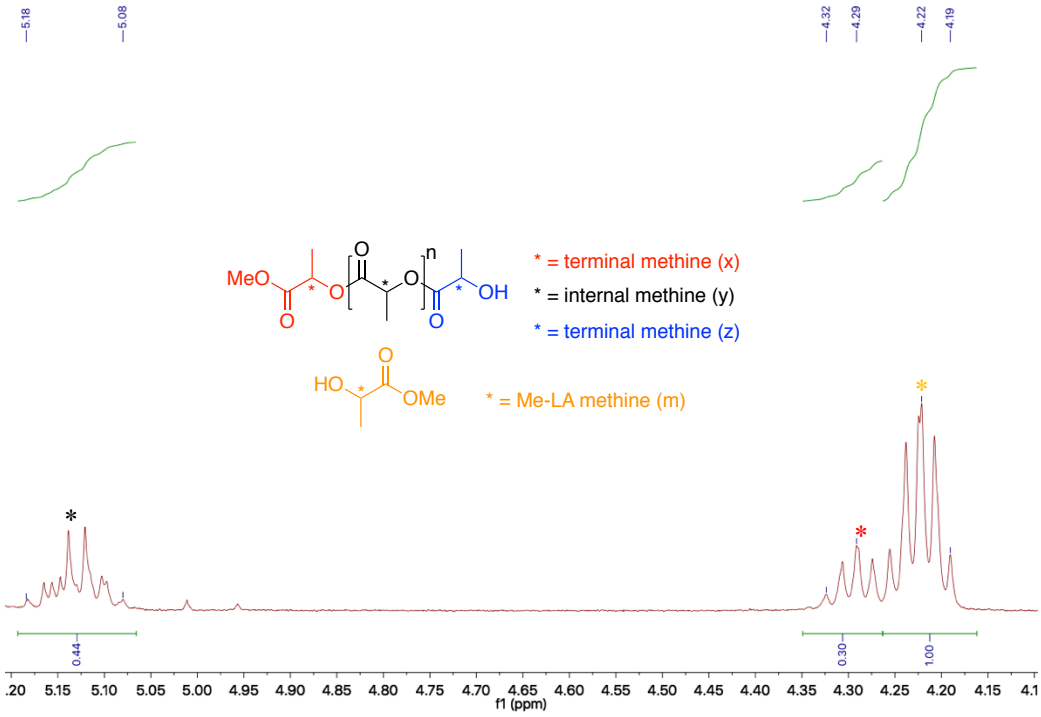


Figure 24. ^{1}H NMR ($CDCl_3$) spectrum of PLA Vegware cup degradation into methyl lactate (Me-LA) using $Zn_2(\mathbf{1})_2(Et)_2$ (8 wt% - corresponding to 1 mol% relative to PLA ester linkages) at 50 °C for 18 h. Me-LA conversion (x_1) = (m/Σ(m, x, y-z) x 100%. Oligomer conversion (x_2) = (x/Σ(m, x, y-z) x 100%. PLA conversion = 100 – (x_1+x_2).

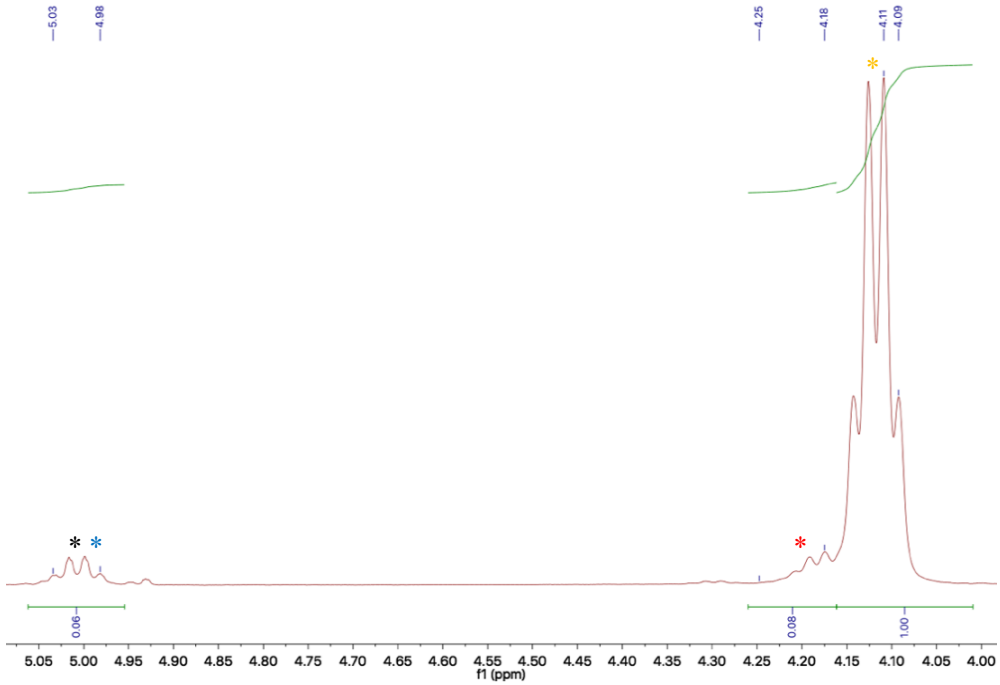


Figure 25. ^{1}H NMR ($CDCl_3$) spectrum of PLA Vegware cup degradation into methyl lactate (Me-LA) using $Zn_2(\mathbf{2})_2(Et)_2$ (8 wt% - corresponding to 1 mol% relative to PLA ester linkages) at 80 °C for 8 h. Superior peak resolution is observed at higher Me-LA conversion.

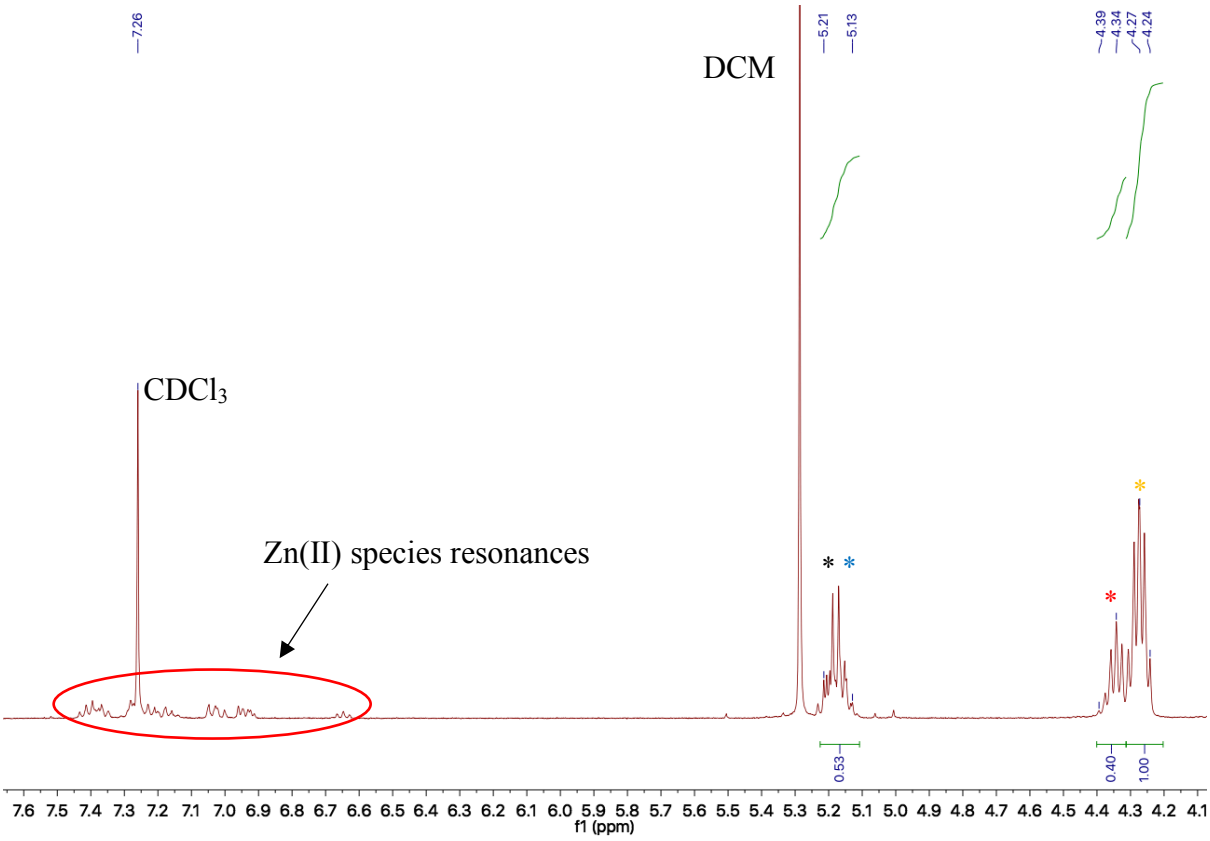


Figure 26. ^{1}H NMR ($CDCl_3$) spectrum of PLA Vegware cup degradation into methyl lactate (Me-LA) using Zn_2(**3**)$_2$(Et)$_2$ (8 wt% - corresponding to 1 mol% relative to PLA ester linkages) at 50 °C for 18 h. Appearance of aromatic resonances attributed to the presence of catalyst in sample.

4.2 Reaction kinetics:

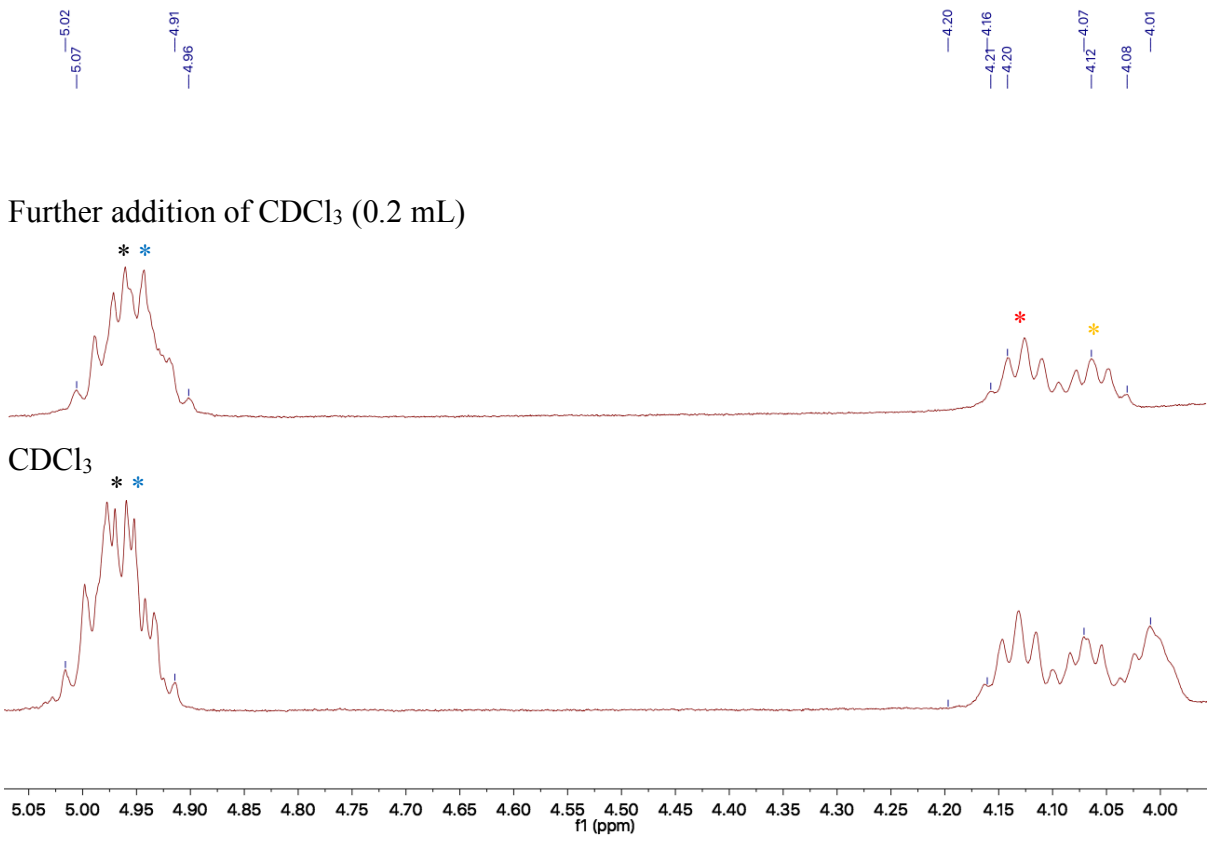


Figure 27. ^{1}H NMR ($CDCl_3$) spectrum of PLA Vegware cup degradation into methyl lactate (Me-LA) using Zn(**2**)$_2$ (4 wt%) at 80 °C after 1 h. Initially, unusual peak multiplicity was observed in the methyl lactate/oligomer methine region, which was resolved upon the addition of further $CDCl_3$ (0.2 mL), suggesting the presence of a Me-adduct in the concentrate.

5. Crystallographic data

All refinements were straight forward except for Zn(**1**)$_2$ and Zn$_2$(**1**)$_2$(Et)$_2$. Zn(**1**)$_2$: the bond lengths of toluene, the solvent of recrystallisation, have be constrained. Zn$_2$(**1**)$_2$(Et)$_2$: the crystal was twinned, component 2 was 50% by a rotation of 180 ° about the 0,0,1 reciprocal axis

Table 1. Crystallographic data of Zn(**1-3**)$_2$ and Zn$_2$(**1-3**)$_2$(Et)$_2$

Compound reference	[Zn(**1**)$_2$]	[Zn(**2**)$_2$]	[Zn(**3**)$_2$]	[Zn(**1**)Et]$_2$	[Zn(**2**)Et]$_2$	[Zn(**3**)Et]$_2$
Chemical formula	$C_{45.50}H_{56}N_2O_2Zn$	$C_{33}H_{24}Cl_4N_2O_2Zn$	$C_{26}H_{20}N_2O_2Zn$	$C_{46}H_{62}N_2O_2Zn_2$	$C_{30}H_{26}Cl_4N_2O_2Zn_2$	$C_{30}H_{30}N_2O_2Zn_2$
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	9.7165(4)	11.4229(6)	9.4398(7)	25.1264(8)	8.3728(4)	9.4634(2)
b/Å	13.0789(8)	11.7375(6)	10.7434(8)	18.5514(5)	13.2623(5)	12.7656(2)
c/Å	16.8043(8)	13.3309(6)	12.1939(10)	18.1043(5)	13.5714(7)	11.4410(2)
α/°	76.357(5)	65.684(5)	67.141(7)	90	90	90
β/°	79.830(4)	83.729(4)	68.745(7)	90.301(3)	97.625(5)	105.049(2)
γ/°	85.530(4)	66.409(5)	77.707(7)	90	90	90
Unit cell volume/Å^3	2041.18(19)	1489.37(15)	1058.27(16)	8438.8(4)	1493.68(12)	1334.74(4)
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$
No. of formula units per unit cell, *Z*	2	2	2	8	2	2
Radiation type	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Mo Kα	Cu Kα
Absorption coefficient, μ/mm^{-1}	1.119	4.725	1.813	1.679	1.995	2.435
No. of reflections measured	20807	9666	7050	16863	10691	9129
No. of independent reflections	7214	5450	3859	16863	2834	2534
R_{int}	0.0474	0.0239	0.0198	-	0.0420	0.0364
Final R_1 values ($I > 2\sigma(I)$)	0.0547	0.0268	0.0298	0.0468	0.0327	0.0365
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1517	0.0679	0.0800	0.1285	0.0685	0.0968
Final R_1 values (all data)	0.0608	0.0289	0.0323	0.0533	0.0445	0.0388
Final $wR(F^2)$ values (all data)	0.1589	0.0699	0.0822	0.1338	0.0733	0.0996
Goodness of fit on F^2	1.056	1.031	1.000	1.101	1.034	1.070

Selected bond lengths:

Table 2. Zn-N bond lengths in Zn(**1-3**)$_2$ and Zn$_2$(**1-3**)$_2$(Et)$_2$.

Init.	**Bond**	**Bond length / Å**
Zn(**1**)$_2$	Zn(1)-N(1), Zn(1)-N(2)	2.005(2), 1.9937(18)
Zn(**2**)$_2$		1.9908(13), 2.0056(13)
Zn(**3**)$_2$		2.0050(15), 2.0063(15)
Zn$_2$(**1**)$_2$(Et)$_2$	Zn(1)-N(2), Zn(2)-N(1)	2.017(3), 2.014(3)
Zn$_2$(**2**)$_2$(Et)$_2$	Zn(1)-N(2)[a]	2.060(2)
Zn$_2$(**3**)$_2$(Et)$_2$		2.0521(15)

[a]Bond length equivalent to Zn(2)-N(1) due to Zn(II)-complex possessing a centre of inversion (C_2-symmetry operation).

References:

1. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, **9**, 2010, 2176-2179.
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4. B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229-3238.