

Supporting information:

**Aluminium(III) and Zinc(II) complexes of azobenzene-containing ligands for ring opening polymerisation of  $\epsilon$ -caprolactone and *rac*-lactide**

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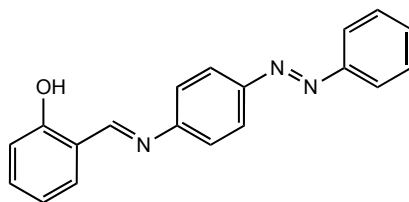
# 1. Synthesis and characterisation of the ligands and complexes

## 1.1 General

All manipulations were carried out under argon using Schlenk-line or glovebox techniques, unless otherwise stated. The chemicals were used as received from commercial sources. This was except for *rac*-lactide (LA) which was recrystallised once from dry toluene and stored under Ar.  $\epsilon$ -caprolactone (CL) was stirred over CaH<sub>2</sub> for 12h before distillation. All anhydrous solvents were collected under inert conditions from a solvent purification system (SPS) and stored over molecular sieves. Nuclear magnetic resonance spectra (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}) were recorded on a Bruker 400 MHz or 500 MHz instrument at room temperature and referenced according to residual solvent peaks. <sup>1</sup>H{<sup>1</sup>H} NMR spectra were recorded on a Bruker AV 400 MHz spectrometer. CDCl<sub>3</sub> was dried over CaH<sub>2</sub> and stored over sieves. C<sub>6</sub>D<sub>6</sub> was degassed and stored over sieves. The pro-ligands were characterised by electron-spray Ionisation Mass Spectrometry (ESI-MS) in positive mode. For the Zn(II) complexes the reaction solvent was removed, and single crystals were obtained by the addition of CH<sub>2</sub>Cl<sub>2</sub> layered with *n*-hexane. X-ray diffraction data was collected on either a SuperNova or Excalibur, EOS detector diffractometer using radiation Cu-K $\alpha$  ( $\lambda$  = 1.54184 Å) or Mo-K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation, all recorded at 150K. All structures were solved by direct methods and refined on all  $F^2$  data. All hydrogen atoms were included in ideal positions and refined using the riding model. UV-Vis absorption spectra were obtained using an Agilent Cary 60 UV-Vis spectrometer. CHN analysis was performed by Elemental Microanalysis.

## 1.2 Synthesis and characterisation of the ligands

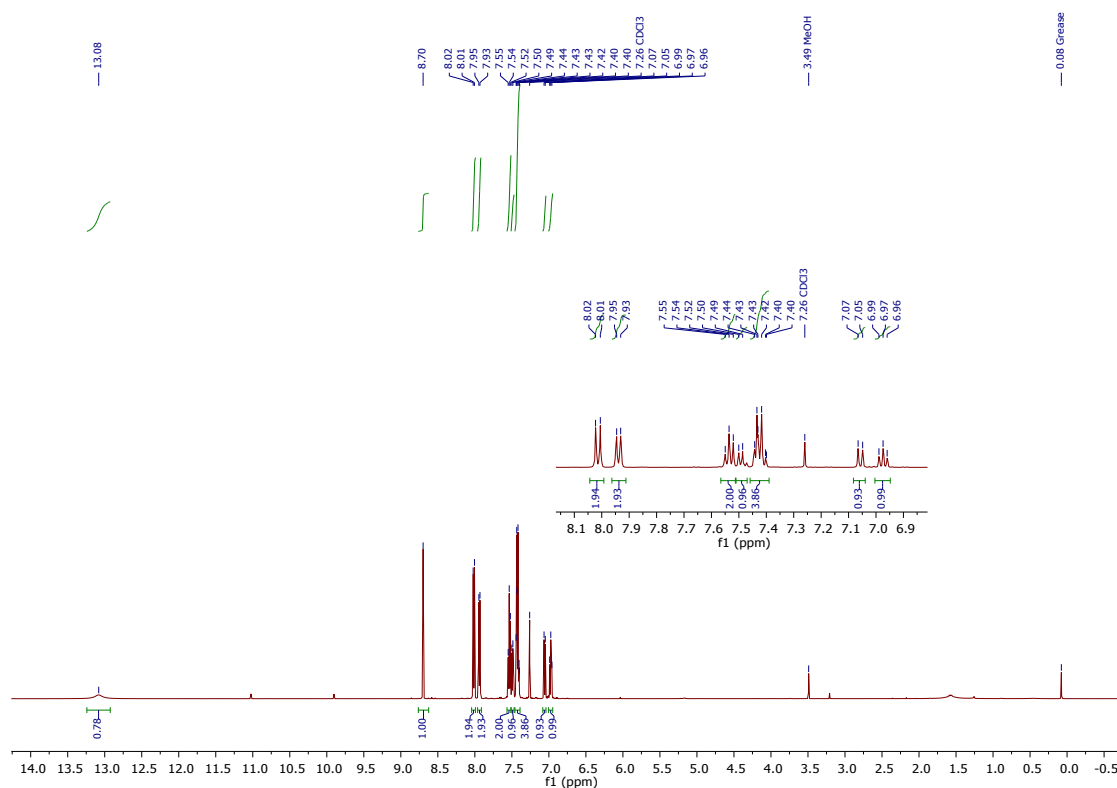
**1H**



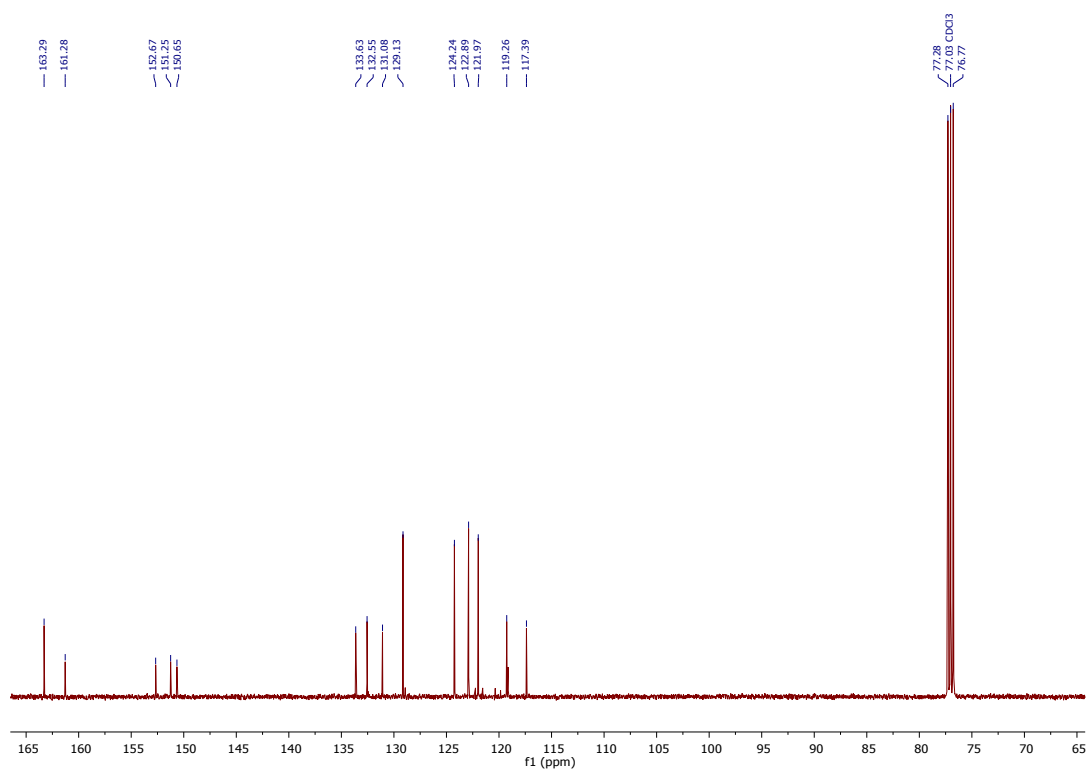
4-(phenyldiazenyl)aniline (1.97 g, 10 mmol) and salicylaldehyde (1.22 g, 10 mmol) were heated to reflux with continuous stirring in methanol (50 mL). After 2 hours, the solution was cooled, and the solvent was removed by filtration. The final product was washed with MeOH (20 mL) and dried *in vacuo*.

Isolated as an orange powder (2.53 g, 8.39 mmol, 84%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$  6.96 (1H, t,  $J = 7.5$  Hz; ArH), 7.05 (1H, d,  $J = 8.3$  Hz; ArH), 7.55-7.40 (7H, m; ArH), 7.94 (2H, d,  $J = 7.0$  Hz; ArH), 8.01 (2H, d,  $J = 9.0$  Hz; ArH), 8.70 (1H, s; HCN), 13.08 (1H, br s; OH).  $\delta$   $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3 (CHN), 161.3 (ArO), 152.7 (ArN), 151.3 (ArN), 150.7 (ArN), 133.63, 132.6, 131.1, 129.1, 124.2, 122.9, 122.0, 119.3, 117.4 (Ar).

ESI-MS (+ve,  $\text{CH}_3\text{CN}$ ): Calculated  $m/z = [\text{C}_{19}\text{H}_{16}\text{N}_3\text{O}]^+ = 302.1288$ , found  $m/z = 302.1300$

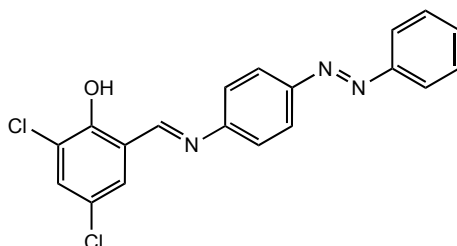


**Figure S1:**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **1H**



**Figure S2:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (126MHz,  $\text{CDCl}_3$ ) of **1H**

**2H**



Method same as used for **1H**, but 3,5-dichloro-2-hydroxybenzaldehyde (1.91 g, 10 mmol) used instead.

Isolated as a red powder (3.20 g, 8.64 mmol, 86%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$  7.34 (2H, d,  $J = 2.4$  Hz; ArH), 7.44 (2H, d,  $J = 8.6$  Hz; ArH), 7.48 - 7.56 (4H, m; ArH), 7.93 (2H, d,  $J = 7.2$  Hz; ArH), 8.02 (2H, d,  $J = 8.6$  Hz; ArH), 8.63 (1H, s; HCN), 14.05 (1H, s; OH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0 (CHN), 156.0 (ArO), 152.6 (ArN), 151.8 (ArN), 148.9 (ArN), 133.1, 131.3, 129.9, 129.2, 128.9, 124.4, 123.6, 123.0, 123.0, 122.1, 121.7, 120.2 (Ar). ESI-MS (+ve,  $\text{CH}_3\text{CN}$ ): Calculated  $m/z = [\text{C}_{19}\text{H}_{14}\text{Cl}_2\text{N}_3\text{O}]^+ = 370.0501$ , found  $m/z = 370.0508$

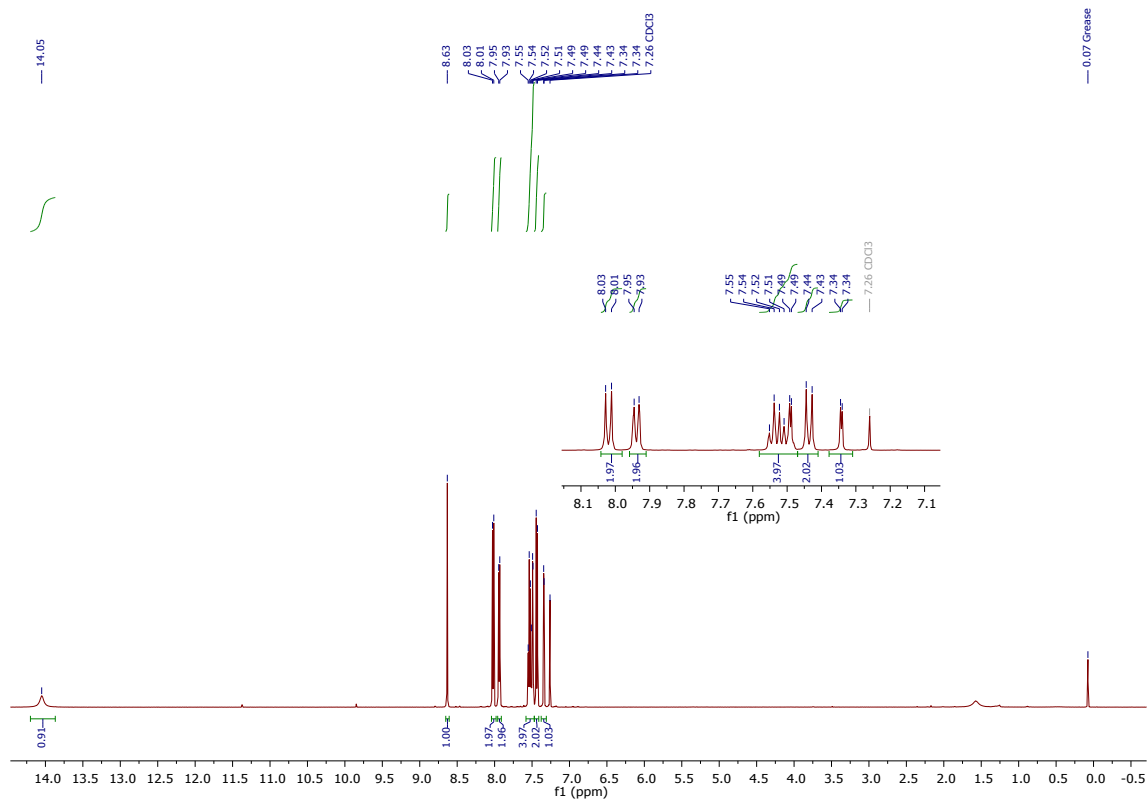


Figure S3: <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) of 2H

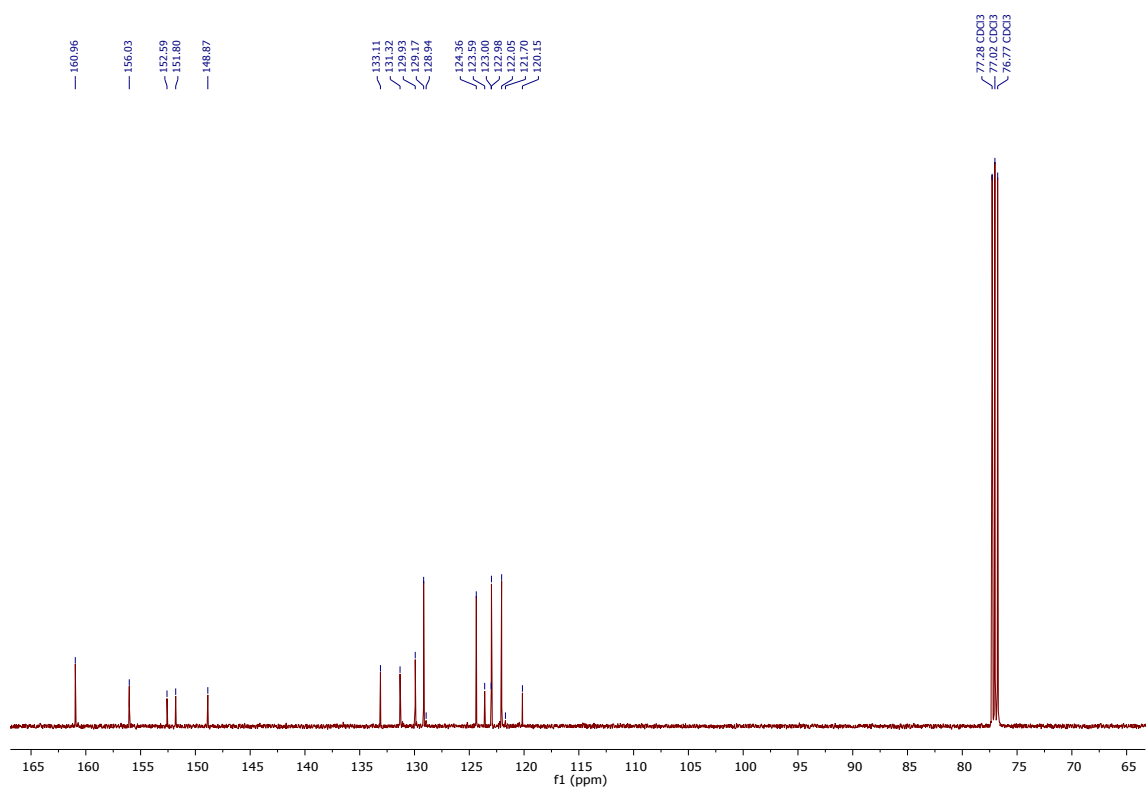
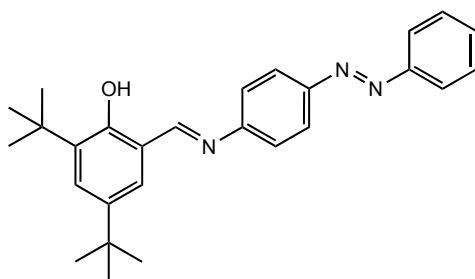


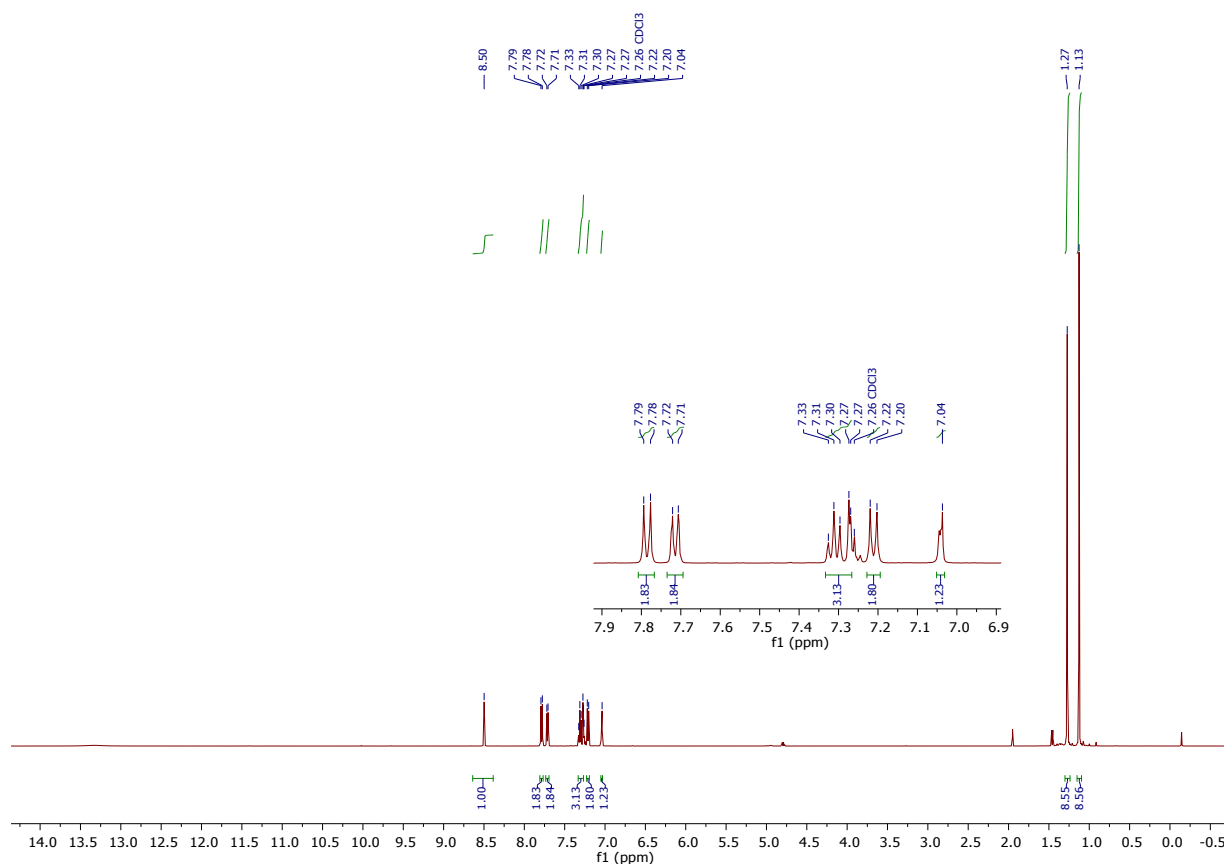
Figure S4: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (126 MHz, CDCl<sub>3</sub>) of 2H

3H

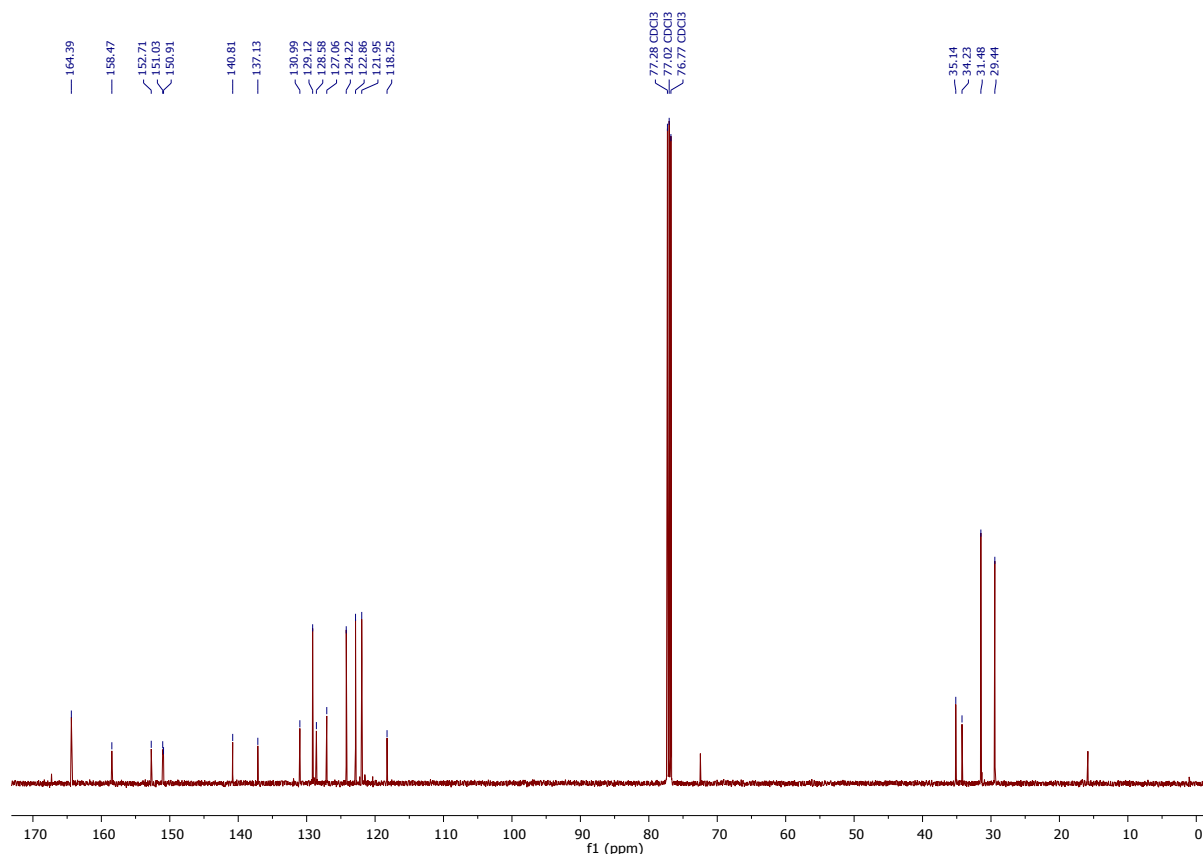


Method same as used for **1H**, but 3,5-ditertbutyl-2-hydroxybenzaldehyde used instead (2.34 g, 10 mmol)

Isolated as an orange powder (2.43 g, 5.87 mmol, 59 %). Recrystallised by the slow evaporation of MeOH at room temperature.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$  1.13 (9H, s;  $\text{CH}_3$ ), 1.27 (9H, s;  $\text{CH}_3$ ), 7.04 (1H, m; ArH), 7.20 (1H, d,  $J = 8.4$  Hz; ArH), 7.27-7.33 (3H, m; ArH), 7.71 (2H, d,  $J = 7.2$  Hz; ArH), 7.78 (2H, d,  $J = 8.6$  Hz; ArH), 8.50 (1H, s; HCN) Note: OH peak not visible.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4 (CHN), 158.5 (ArN), 152.7 (ArN), 151.0 (ArN), 140.8, 137.1, 131.0, 129.1, 128.6, 127.1, 124.2, 122.9, 122.0, 118.3 (Ar), 35.1 ( $\text{C}(\text{CH}_3)_3$ ), 34.2 ( $\text{C}(\text{CH}_3)_3$ ), 31.5 ( $\text{CH}_3$ ), 29.4 ( $\text{CH}_3$ ). ESI-MS (+ve,  $\text{CH}_3\text{CN}$ ): Calculated  $m/z = [\text{C}_{27}\text{H}_{32}\text{N}_3\text{O}]^+ = 414.2540$ , found  $m/z = 414.2503$



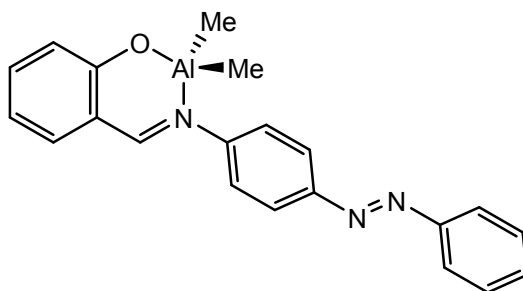
**Figure S5:**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **3H**



**Figure S6:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ ) of **3H**

### 1.3 Synthesis and characterisation of the Al(III) complexes

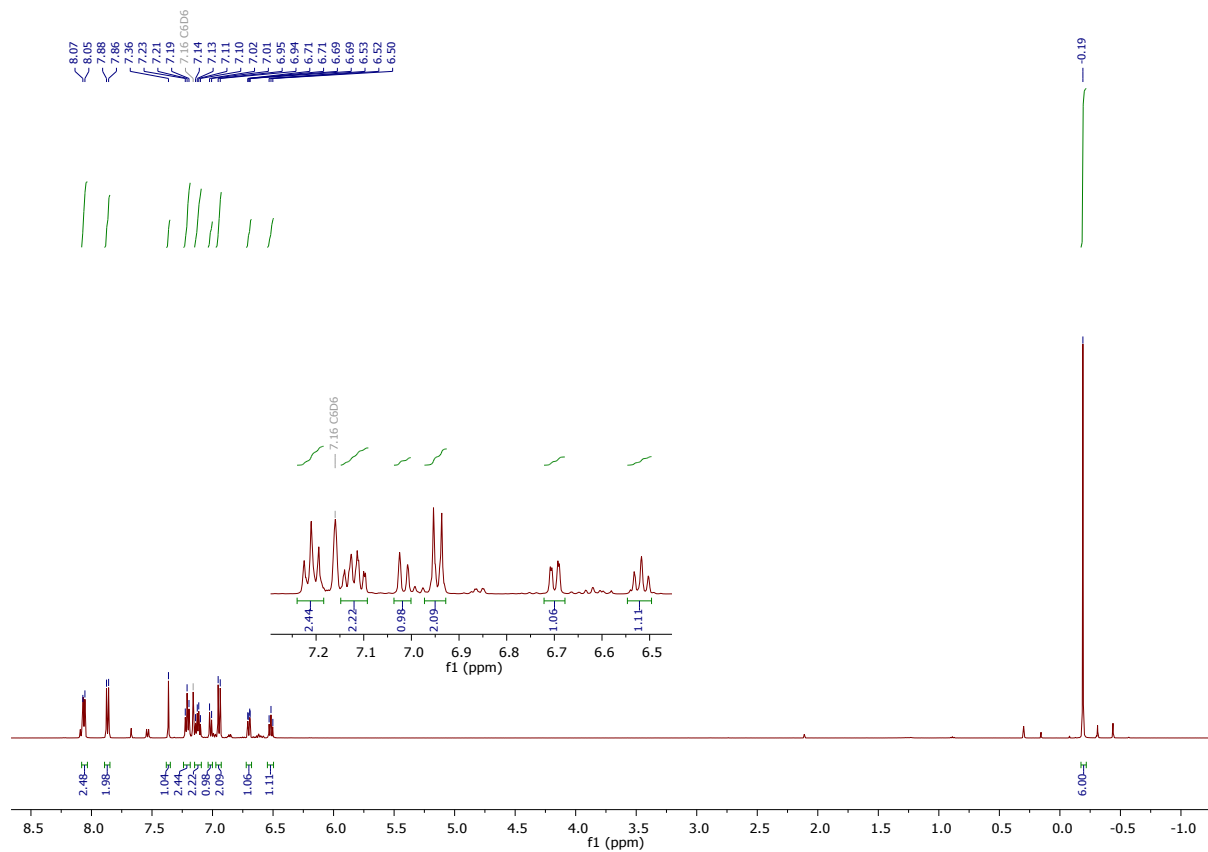
Al(1)Me<sub>2</sub>



**1H** (0.602 g, 2 mmol) was dissolved in toluene (10 mL) followed by the dropwise addition of  $\text{AlMe}_3$  (1 mL, 2M, 2 mmol). After complete addition, the solution was stirred for 2 hours at room temperature to allow complexation. The product was recrystallised by the addition of anhydrous *n*-hexane.

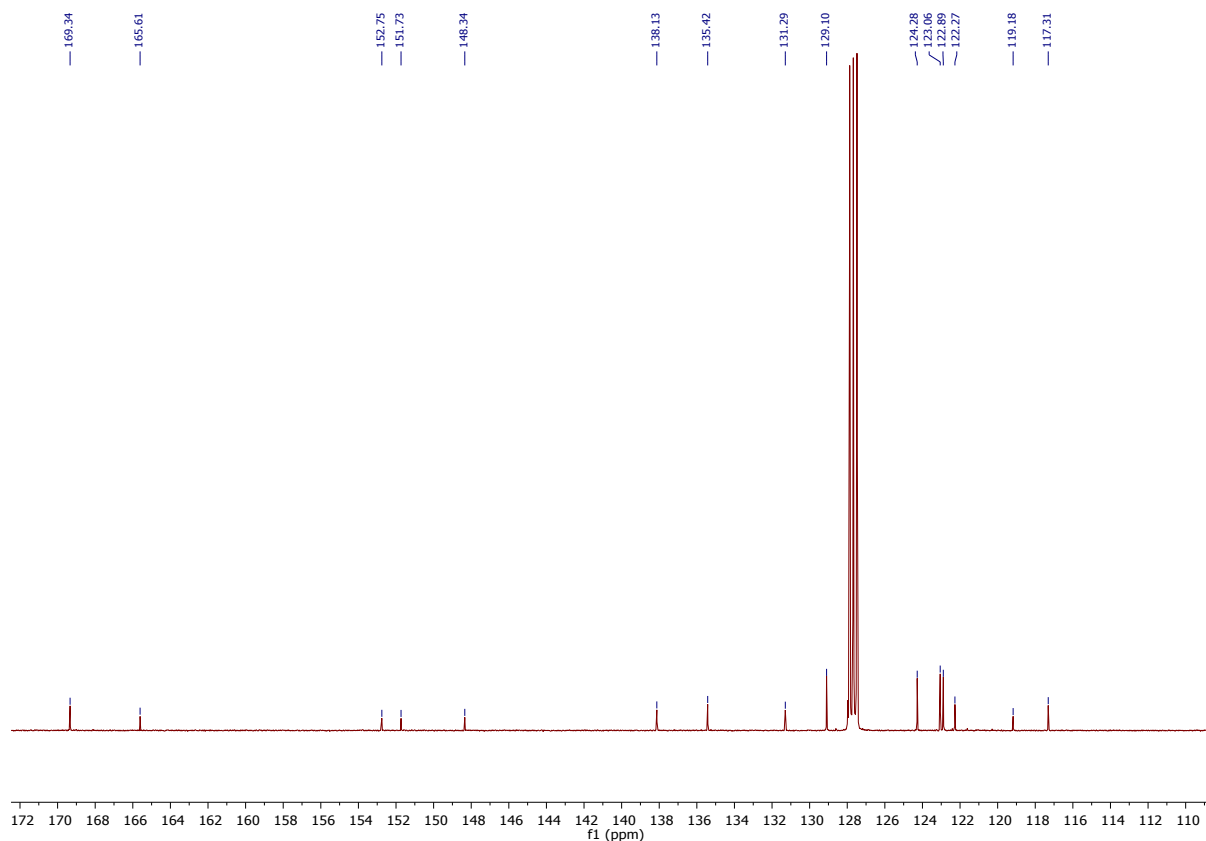
Isolated as orange crystals (0.31g, 0.87 mmol, 43%)  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  -0.19 (6H, s;  $\text{CH}_3$ ) 6.52 (1H, t,  $J = 7.8$  Hz; ArH), 6.69 (1H, dd,  $J = 7.8, 1.6$  Hz; ArH), 6.94 (2H, d,  $J = 8.6$  Hz; ArH), 7.01 (1H, d,  $J = 8.4$  Hz; ArH), 7.10-7.14 (2H, m; ArH), 7.19 (2H, t,  $J = 7.7$  Hz; ArH), 7.36 (1H, s; HCN), 7.87 (2H, d,  $J = 8.7$  Hz; ArH), 8.06 (2H, d,  $J = 8.5$  Hz; ArH).

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  169.3 (CHN), 165.6 (ArO), 152.8 (ArN), 151.7 (ArN), 148.3 (ArN), 138.1, 135.4, 131.3, 129.1, 124.3, 123.1, 122.9, 122.3, 119.2, 117.3, -8.9 ( $\text{CH}_3$ ) (assigned using HSQC). Elemental analysis: Calcd for  $\text{C}_{21}\text{H}_{20}\text{AlN}_3\text{O}$ : C, 70.58; H, 5.64; N, 11.76. Found: C, 67.48; H, 5.24; N, 11.19.



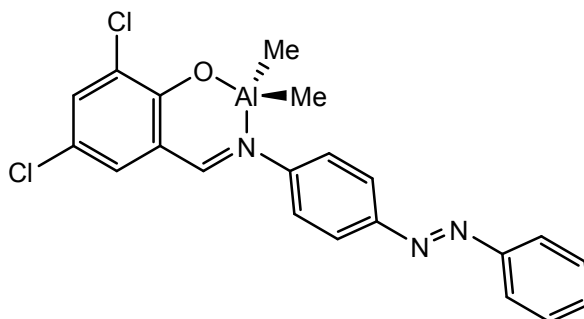
**Figure S7:**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{C}_6\text{D}_6$ ) of  $\text{Al}(\mathbf{1})\text{Me}_2$





**Figure S8:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{C}_6\text{D}_6$ ) of Al(1)Me<sub>2</sub>

Al(2)Me<sub>2</sub>



Method same as used for Al(1)Me<sub>2</sub> but 2H used instead (0.74 g, 2 mmol). Recrystallised from anhydrous *n*-hexane.

Isolated as orange crystals (0.51 g, 1.20 mmol, 60%).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  - 0.27 (6H, s; CH<sub>3</sub>), 6.39 (1H, d,  $J$  = 2.6 Hz; ArH), 6.92 (2H, d,  $J$  = 8.7 Hz; ArH), 6.97 (1H, s; HCN), 7.14 (1H, m; ArH), 7.20 (2H, t,  $J$  = 7.6 Hz; ArH), 7.26 (1H, d,  $J$  = 2.7 Hz; ArH), 7.86 (2H, d,  $J$  = 8.7 Hz; ArH), 8.07 (2H, d,  $J$  = 7.2 Hz; ArH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  167.9 (CHN), 158.9 (ArO), 152.7 (ArN), 152.1 (ArN), 147.5 (ArN), 136.7, 132.4, 132.3, 131.5, 129.2, 124.3, 123.1, 122.8, 121.1, 119.7 (Ar), -9.0 (CH<sub>3</sub>). Calcd for: C<sub>21</sub>H<sub>18</sub>AlCl<sub>2</sub>N<sub>3</sub>O, C, 59.17; H, 4.26; N, 9.86. Found: C, 58.25; H, 3.84; N, 10.02.

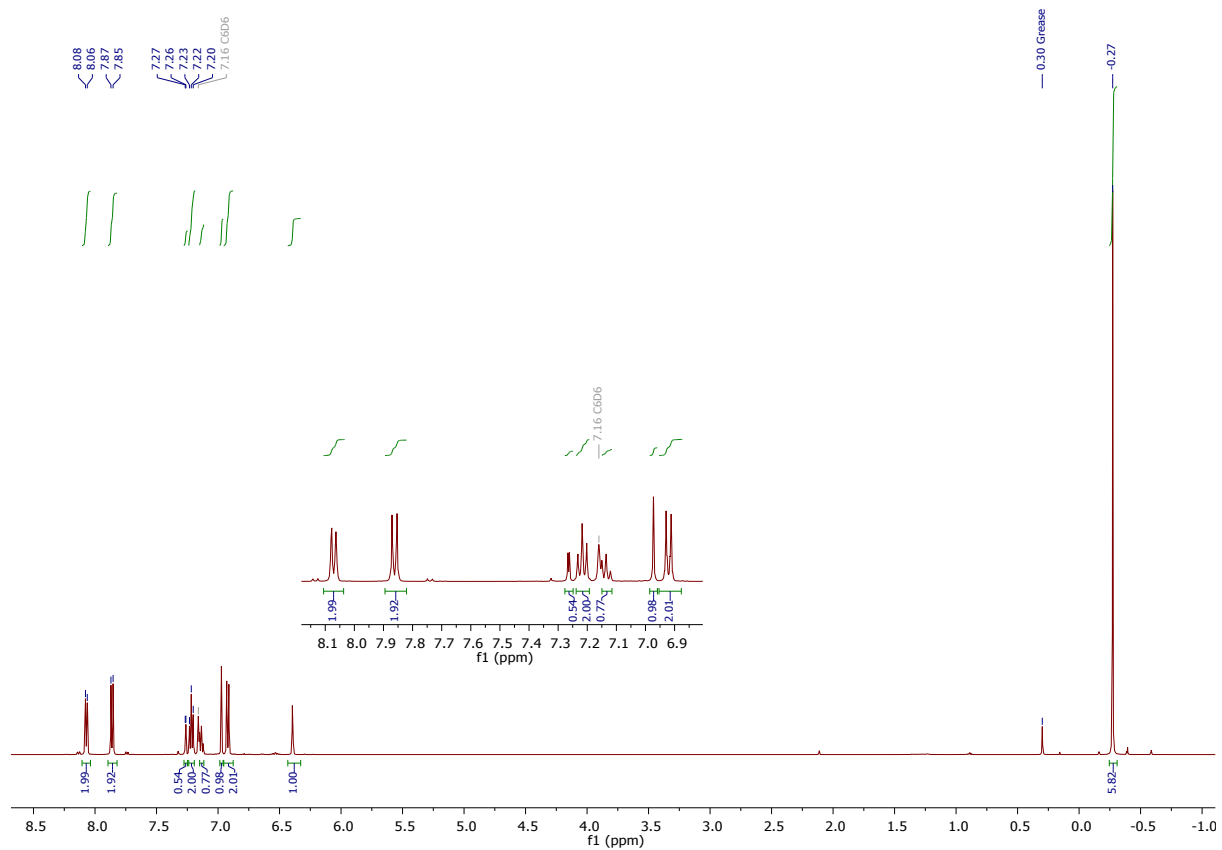
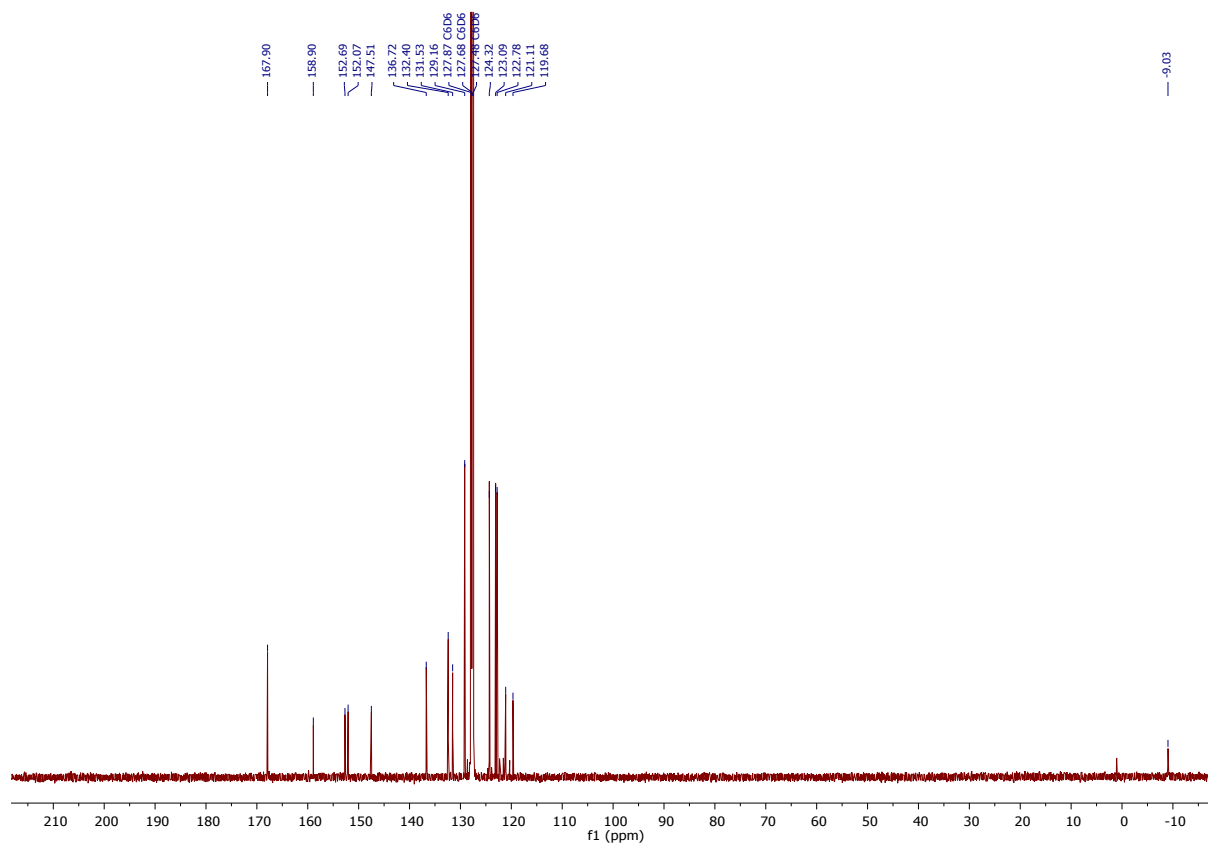
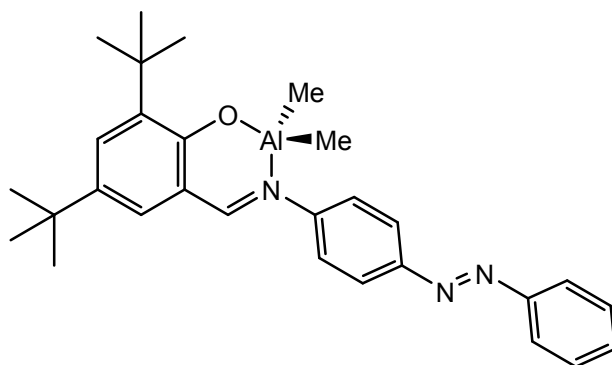


Figure S9:  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{C}_6\text{D}_6$ ) of  $\text{Al}(2)\text{Me}_2$



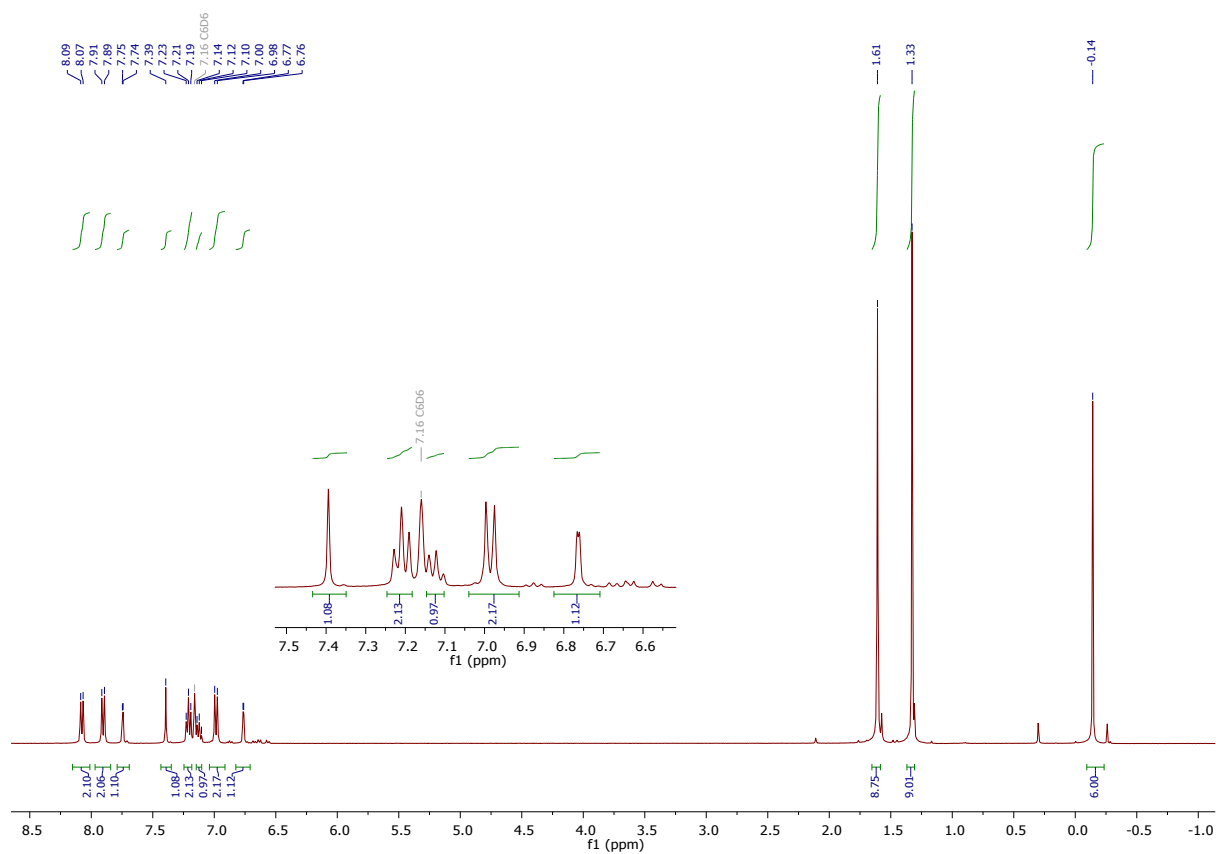
**Figure S10:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{C}_6\text{D}_6$ ) of  $\text{Al}(\mathbf{2})\text{Me}$

$\text{Al}(\mathbf{3})\text{Me}_2$

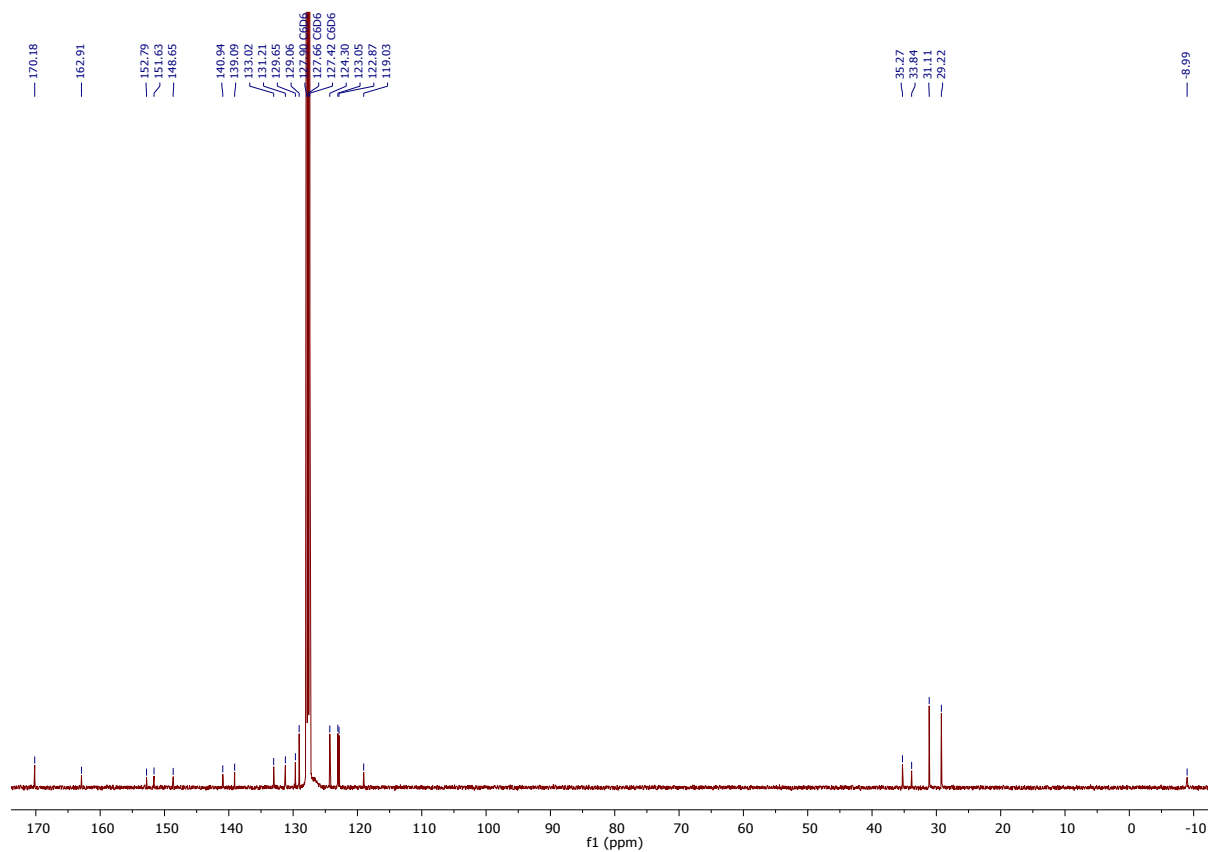


Method same as used for  $\text{Al}(\mathbf{1})\text{Me}_2$  but  $\mathbf{3H}$  used instead (0.83 g, 2 mmol). Recrystallised from anhydrous *n*-hexane.

Isolated as orange crystals (0.38g, 0.82 mmol, 41%).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  - 0.15 (6H, s;  $\text{CH}_3$ ), 1.33 (9H, s;  $\text{CH}_3$ ), 1.61 (9H, s;  $\text{CH}_3$ ), 6.77 (1H, d,  $J = 2.5$  Hz; ArH), 7.00 (2H, d,  $J = 8.7$  Hz; ArH), 7.13 (1H, t,  $J = 7.3$  Hz; ArH), 7.21 (2H, t,  $J = 7.4$  Hz; ArH), 7.42 (1H, s; HCN), 7.74 (1H, d,  $J = 2.5$  Hz; ArH), 7.90 (2H, d,  $J = 8.8$  Hz, ArH), 8.07 (2H, d,  $J = 7.4$  Hz, ArH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  170.2 (CHN), 162.9 (ArO), 152.8 (ArN), 151.6 (ArN), 148.7 (ArN), 140.9, 139.1, 133.0, 131.2, 129.7, 129.1, 124.3, 123.1, 122.9, 119.0 (Ar), 35.2 ( $\underline{\text{C}}(\text{CH}_3)$ ), 33.9 ( $\underline{\text{C}}(\text{CH}_3)$ ), 31.1 ( $\text{CH}_3$ ), 29.2 ( $\text{CH}_3$ ), -9.0 (Al- $\text{CH}_3$ ). Calcd for:  $\text{C}_{29}\text{H}_{36}\text{AlN}_3\text{O}$ , C, 74.17; H 7.37; N, 8.95. Found: C, 74.08; H, 7.62; N, 9.11.

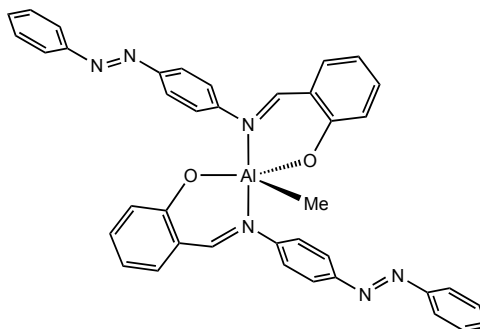


**Figure S11:**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{C}_6\text{D}_6$ ) of  $\text{Al}(\mathbf{3})\text{Me}_2$



**Figure S12:**  $^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{C}_6\text{D}_6$ ) of  $\text{Al}(\mathbf{3})\text{Me}_2$

Al(1)<sub>2</sub>Me



**1H** (0.60 g, 2 mmol) was dissolved in toluene (10 mL) followed by the dropwise addition of AlMe<sub>3</sub> (2M, 0.5 mL, 1 mmol). After complete addition, the solution was stirred for 2 hours at room temperature to allow complexation. The product was recrystallised by the addition of anhydrous hexane and isolated via cannula filtration.

Isolated as orange crystals (0.29 g, 0.46 mmol, 46%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ - 0.97 (3H, s; CH<sub>3</sub>), 6.84 (4H, t, *J* = 7.7 Hz; ArH), 7.33 (2H, d, *J* = 7.5 Hz; ArH), 7.41 (2H, t, *J* = 8.0 Hz; ArH), 7.49-7.56 (6H, m; ArH), 7.70 (4H, d, *J* = 8.4 Hz; ArH), 7.94 (4H, d, *J* = 7.2 Hz; ArH), 8.02 (4H, d, *J* = 8.0 Hz; ArH), 8.29 (1H, s; HCN). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ 167.2 (CHN), 163.8 (ArO), 153.3 (ArN), 152.3 (ArN), 151.0 (ArN), 135.9, 134.3, 131.1, 129.1, 124.5, 123.6, 122.9, 121.4, 120.0, 117.6 (Ar), -5.6 (CH<sub>3</sub>) (assigned using HSQC). Calcd for C<sub>39</sub>H<sub>31</sub>AlN<sub>6</sub>O<sub>2</sub>: C, 72.88; H, 4.86; N, 13.08. Found: C, 72.57; H, 4.91; N, 12.77.

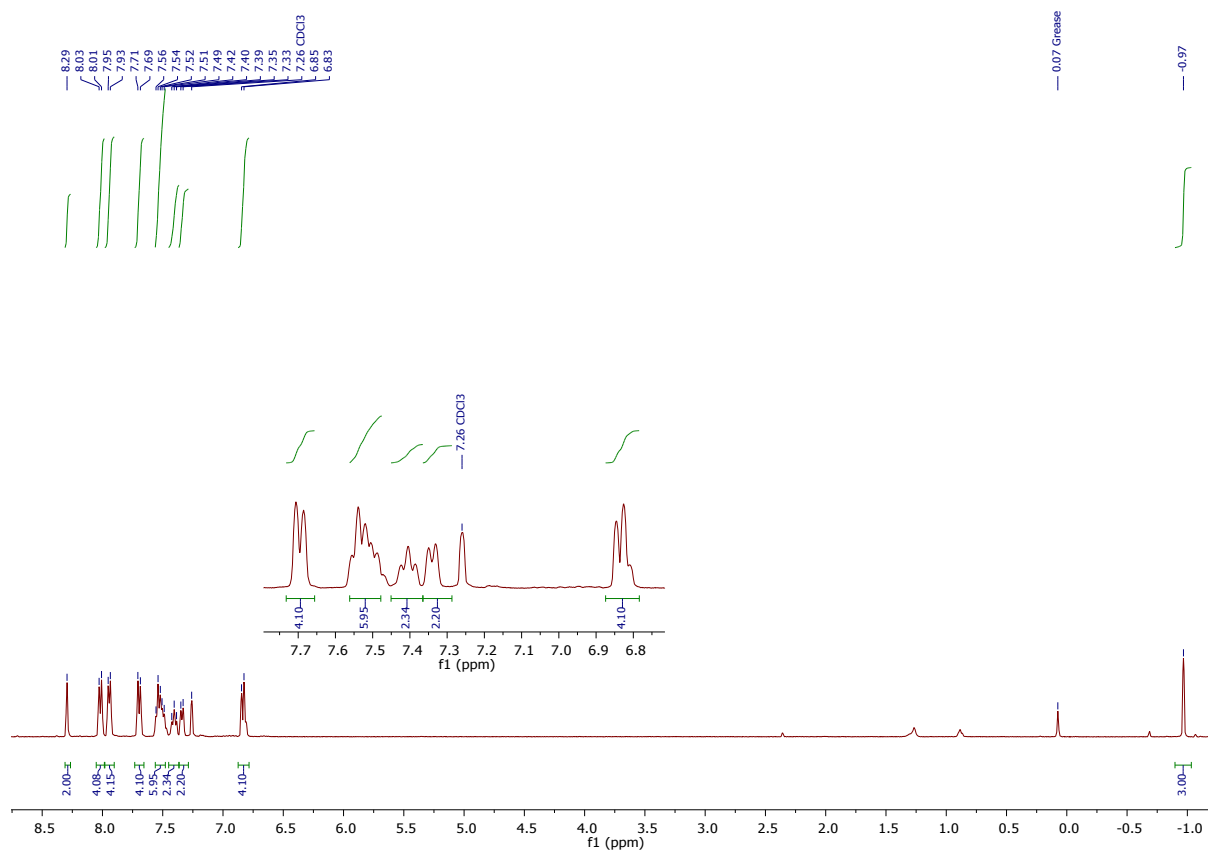


Figure S13:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of  $\text{Al}(\mathbf{1})_2\text{Me}$

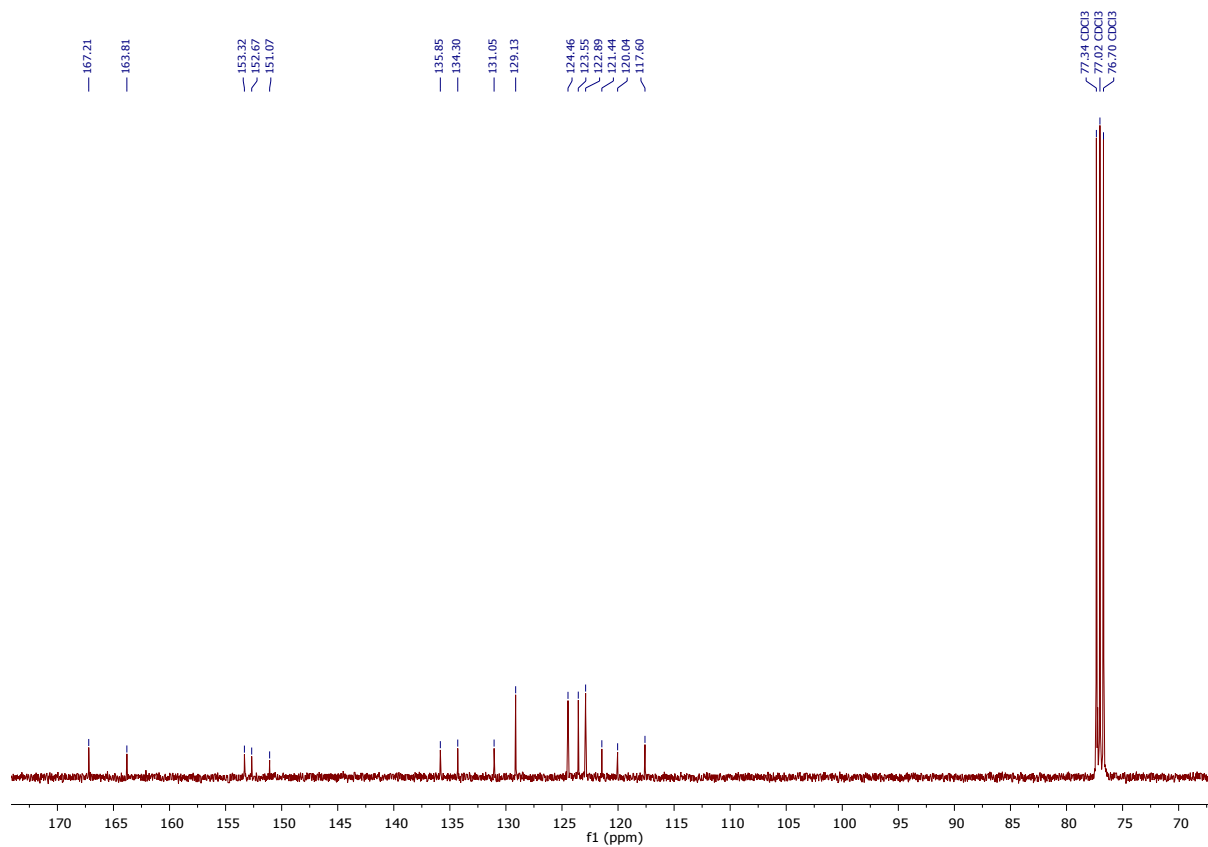
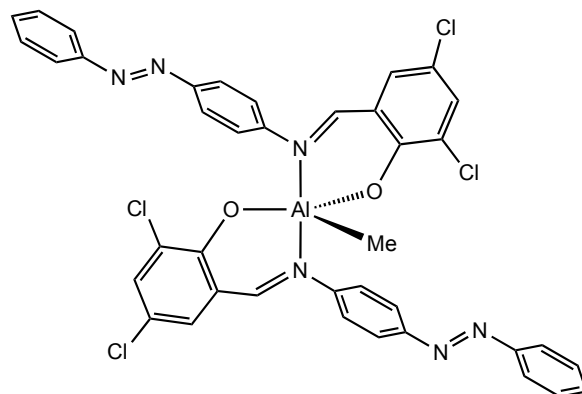


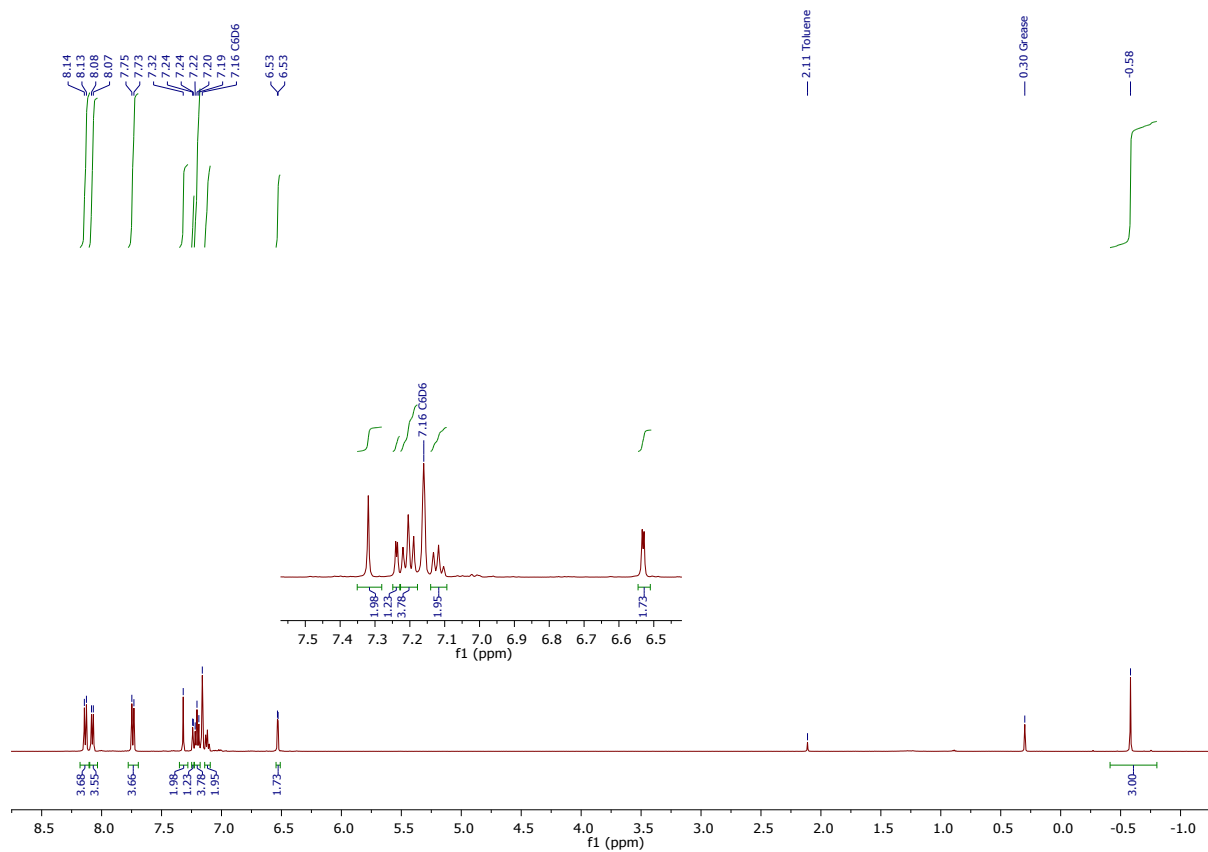
Figure S14:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of  $\text{Al}(\mathbf{1})_2\text{Me}$

Al(2)<sub>2</sub>Me



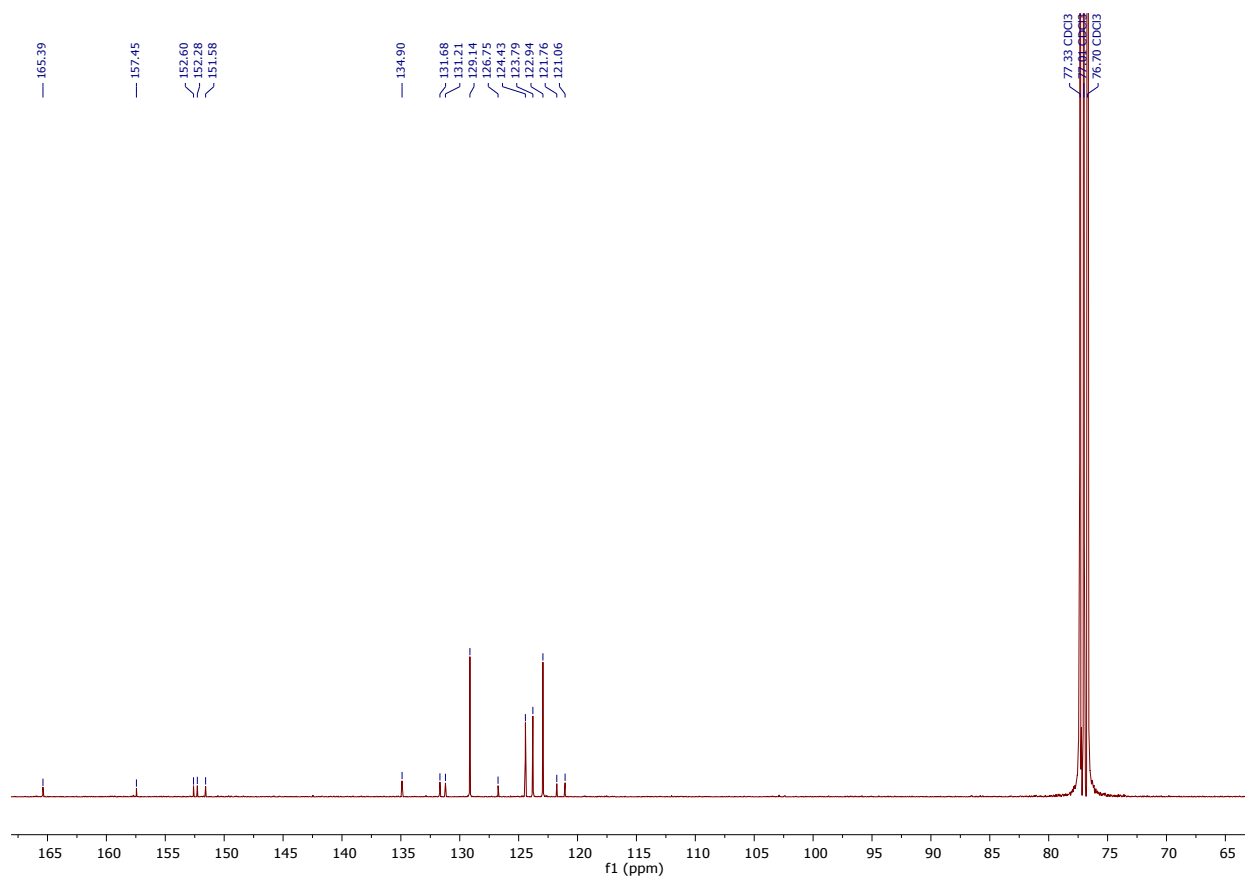
Method same as used for Al(1)<sub>2</sub>Me but 2H used instead (0.74 g, 2 mmol). Recrystallised from anhydrous *n*-hexane.

Isolated as orange crystals (0.47 g, 0.60 mmol, 60%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ - 0.58 (3H, s; CH<sub>3</sub>), 6.53 (2H, d, *J* = 2.6 Hz; ArH), 7.10 (2H, t, *J* = 7.3 Hz; ArH), 7.20 (4H, t, *J* = 7.7 Hz; ArH), 7.24 (2H, d, *J* = 2.6 Hz; ArH), 7.32 (2H, s; HCN), 7.73 (4H, d, *J* = 8.7 Hz; ArH), 8.08 (4H, d, *J* = 7.5 Hz; ArH), 8.14 (4H, d, *J* = 8.7 Hz, ArH). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ 165.4 (C=N), 157.5 (ArO), 152.6 (ArN), 152.3 (ArN), 151.6 (ArN), 134.9, 131.7, 131.2, 129.1, 126.8 (Ar), 124.4, 123.8, 122.9, 121.8, 121.1, -5.70 (CH<sub>3</sub>) (assigned using HSQC). Calcd for: C<sub>39</sub>H<sub>27</sub>AlCl<sub>4</sub>N<sub>6</sub>O<sub>2</sub>, C 60.02; N, 10.77; H, 3.49. Found: C, 60.02; N, 10.83; H, 3.41.



**Figure S15:**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{C}_6\text{D}_6$ ) of  $\text{Al}(\mathbf{2})_2\text{Me}$

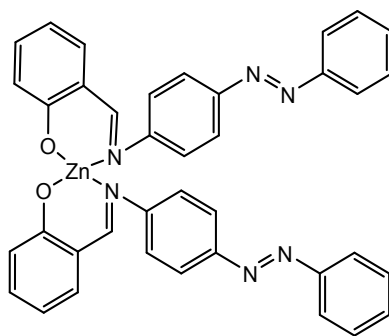




**Figure S16:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of  $\text{Al}(\mathbf{2})_2\text{Me}$

#### 1.4 Synthesis and characterisation of the Zn(II) complexes

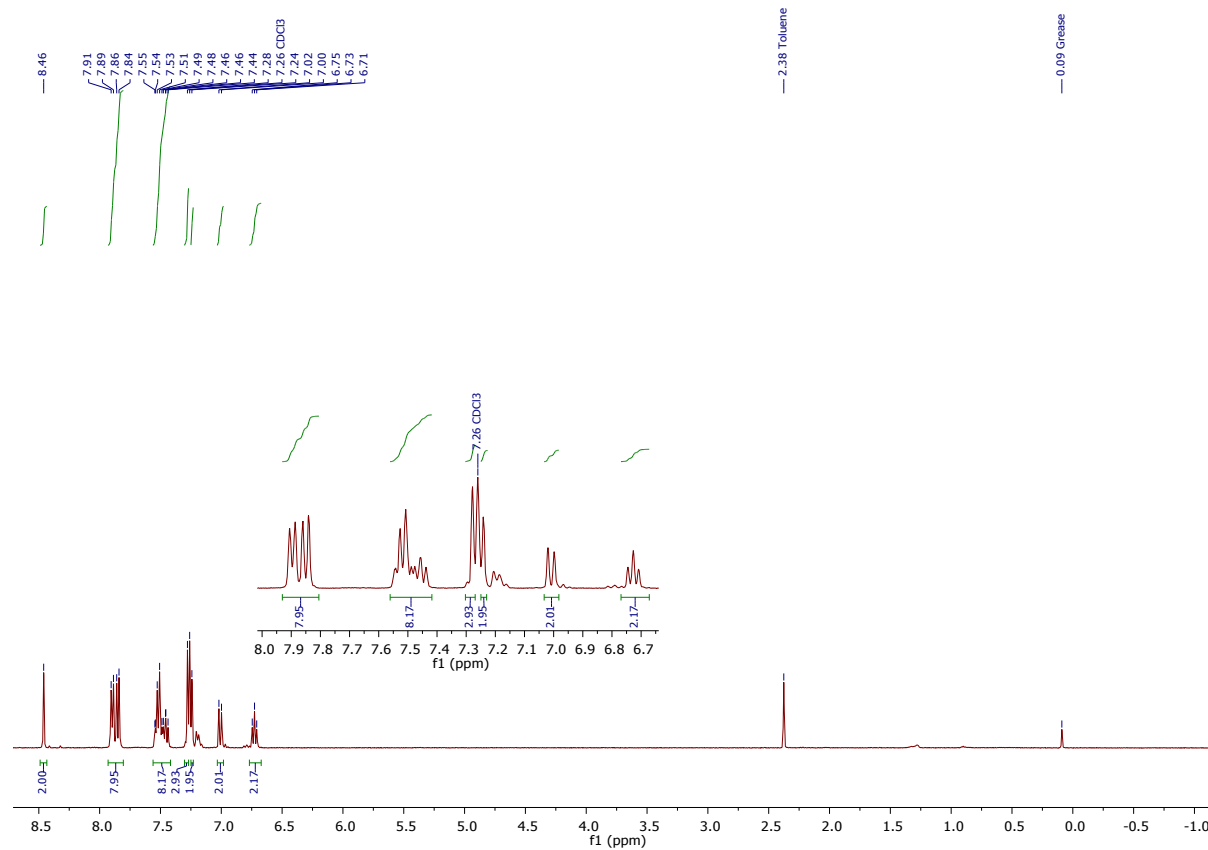
$\text{Zn}(\mathbf{1})_2$



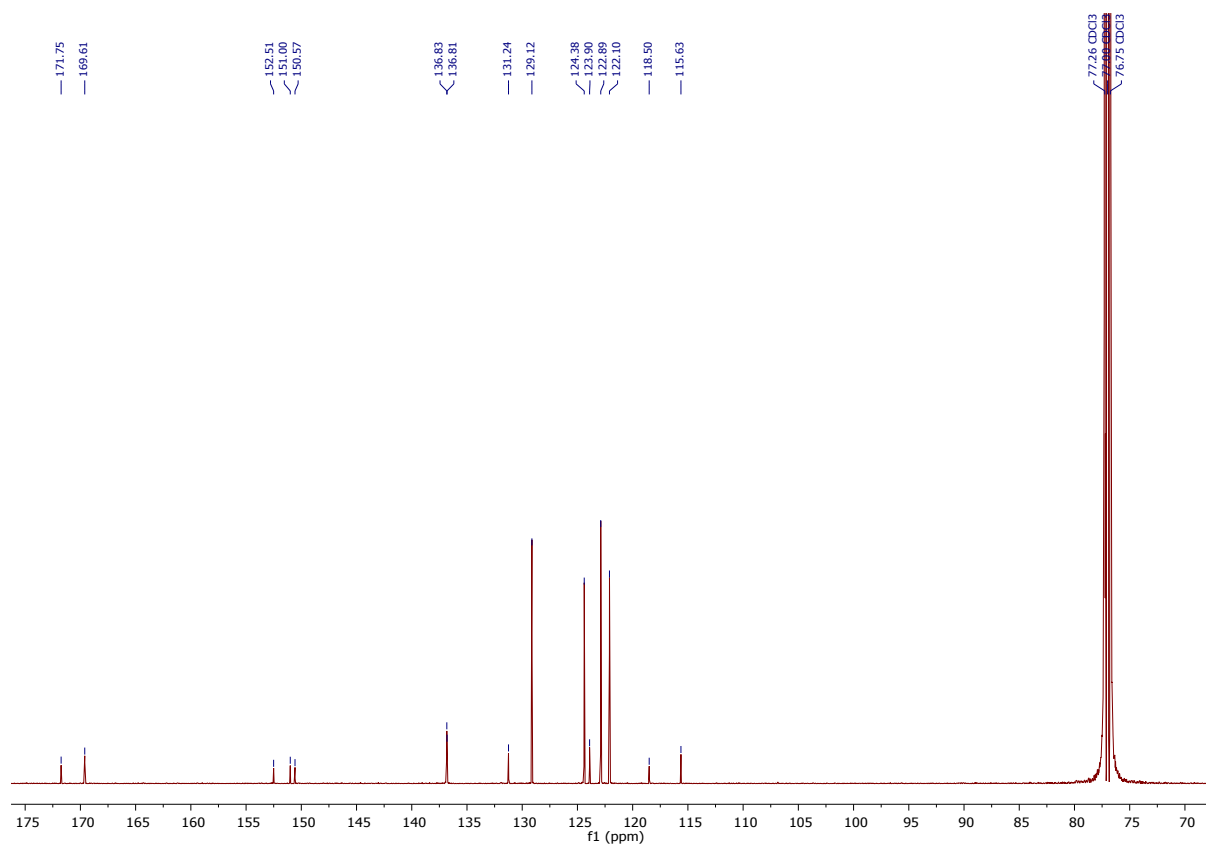
$\mathbf{1H}$  (0.60 g, 2 mmol) was dissolved in toluene (10 mL) followed by the dropwise addition of  $\text{Zn}(\text{Et})_2$  (1M, 1.0 mL, 1 mmol). After complete addition, the solution was stirred for 2 hours to allow complexation. Solvent was removed and the product dried *in vacuo*.

Isolated as an orange powder (0.57 g, 0.86 mmol, 86%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  6.73 (2H, t,  $J = 7.3$  Hz; ArH), 7.01 (2H, d,  $J = 8.6$  Hz; ArH), 7.24 (2H, s; ArH), 7.28 (3H, s; ArH), 7.44-7.55 (8H, m; ArH), 7.87 (8H, dd,  $J = 18.3, 7.6$  Hz; ArH), 8.46 (2H, s, HCN). .  $\delta$

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.75 (CHN), 169.6 (ArO), 152.5 (ArN), 151.0 (ArN), 150.6 (ArN), 136.8, 136.8, 131.2, 129.1, 124.4, 123.9, 122.9, 122.1, 118.5, 115.6 (Ar). Calcd. for:  $\text{C}_{38}\text{H}_{28}\text{N}_6\text{O}_2\text{Zn}$ , C, 68.52; H, 4.24; N, 12.62. Found: C, 68.58; N, 4.06; H, 12.66.

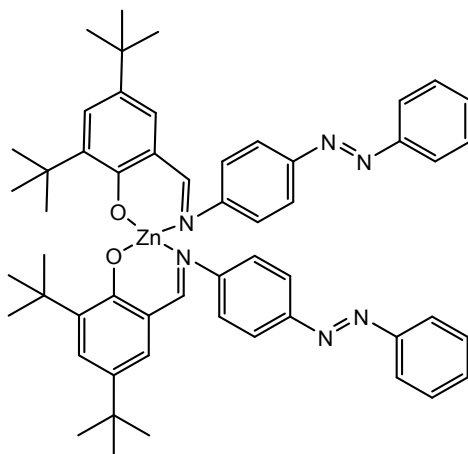


**Figure S17:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of  $\text{Zn}(\mathbf{1})_2$



**Figure S18:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (126MHz,  $\text{CDCl}_3$ ) of  $\text{Zn}(\mathbf{1})_2$

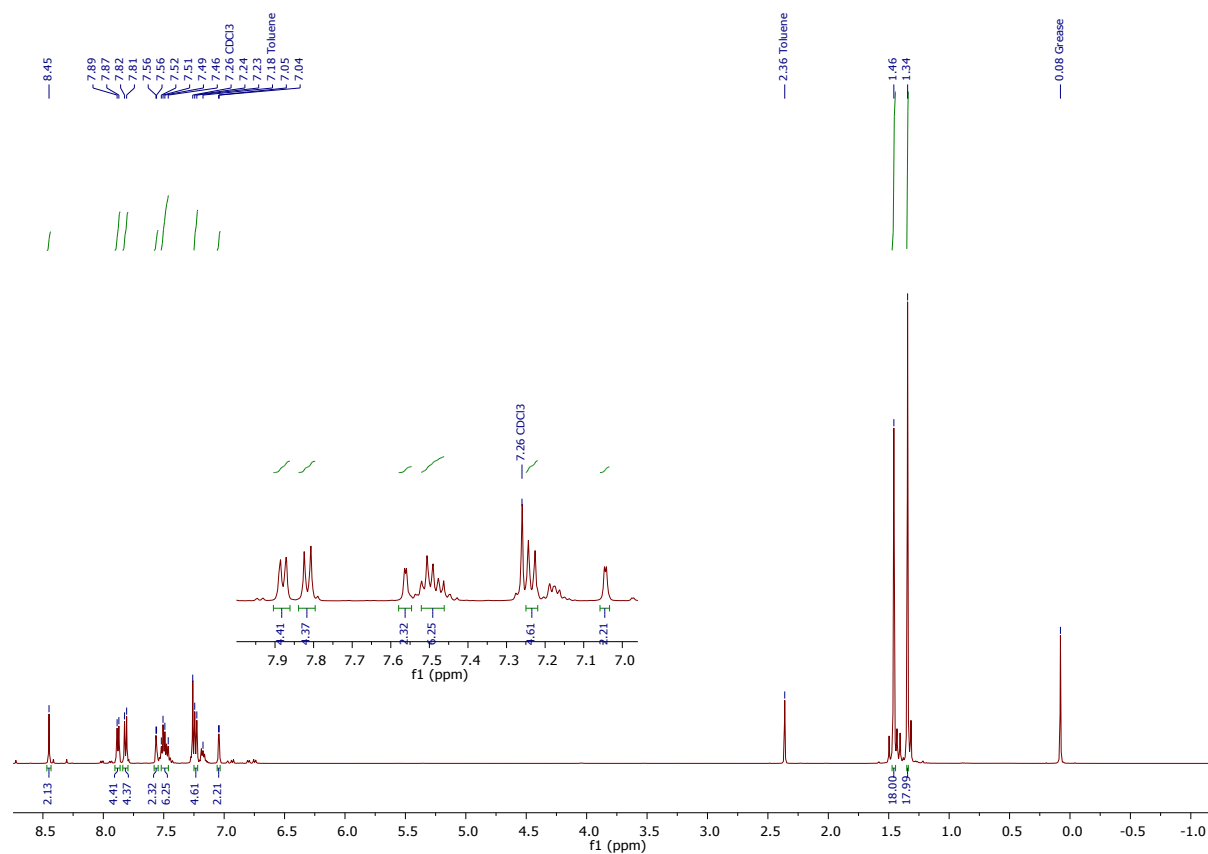
$\text{Zn}(\mathbf{3})_2$



Method same as used for  $\text{Zn}(\mathbf{1})_2$  but  $\mathbf{3H}$  used instead. Solvent removed *in vacuo* and the product recrystallised by the addition of  $\text{CH}_2\text{Cl}_2$  followed by layering with hexanes.

Isolated as orange crystals (0.34 g, 0.38 mmol, 38%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  1.34 (18H, s;  $\text{CH}_3$ ), 1.46 (18H, s;  $\text{CH}_3$ ), 7.04 (2H, d,  $J = 2.3$  Hz; ArH), 7.23 (4H, d,  $J = 8.7$  Hz; ArH), 7.46- 7.52 (6H, m, ArH), 7.56 (2H, d,  $J = 2.5$  Hz; ArH), 7.81 (4H, d,  $J = 8.7$  Hz; ArH), 7.88 (4H, d,  $J = 7.2$  Hz; ArH), 8.45 (2H, s, HCN).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 293K):  $\delta$  169.0 (CHN), 168.9 (ArO), 149.6 (ArN), 150.5 (ArN), 151.5 ArN), 141.3, 135.3, 130.0, 130.7,

128.1, 127.2, 124.3, 123.3, 121.1, 116.6 (Ar), 34.6 ( $\underline{\text{C}}(\text{CH}_3)_3$ ), 32.9 ( $\underline{\text{C}}(\text{CH}_3)_3$ ), 30.3 ( $(\text{CH}_3)_3$ ), 28.3 ( $(\text{CH}_3)_3$ ). Elemental analysis: Calcd. for  $\text{C}_{54}\text{H}_{60}\text{N}_6\text{O}_2\text{Zn}$ : C, 72.84; H, 6.79; N, 9.44. Found: C, 72.34; H, 6.90; N, 8.37.



**Figure S19:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of  $\text{Zn}(\mathbf{3})_2$

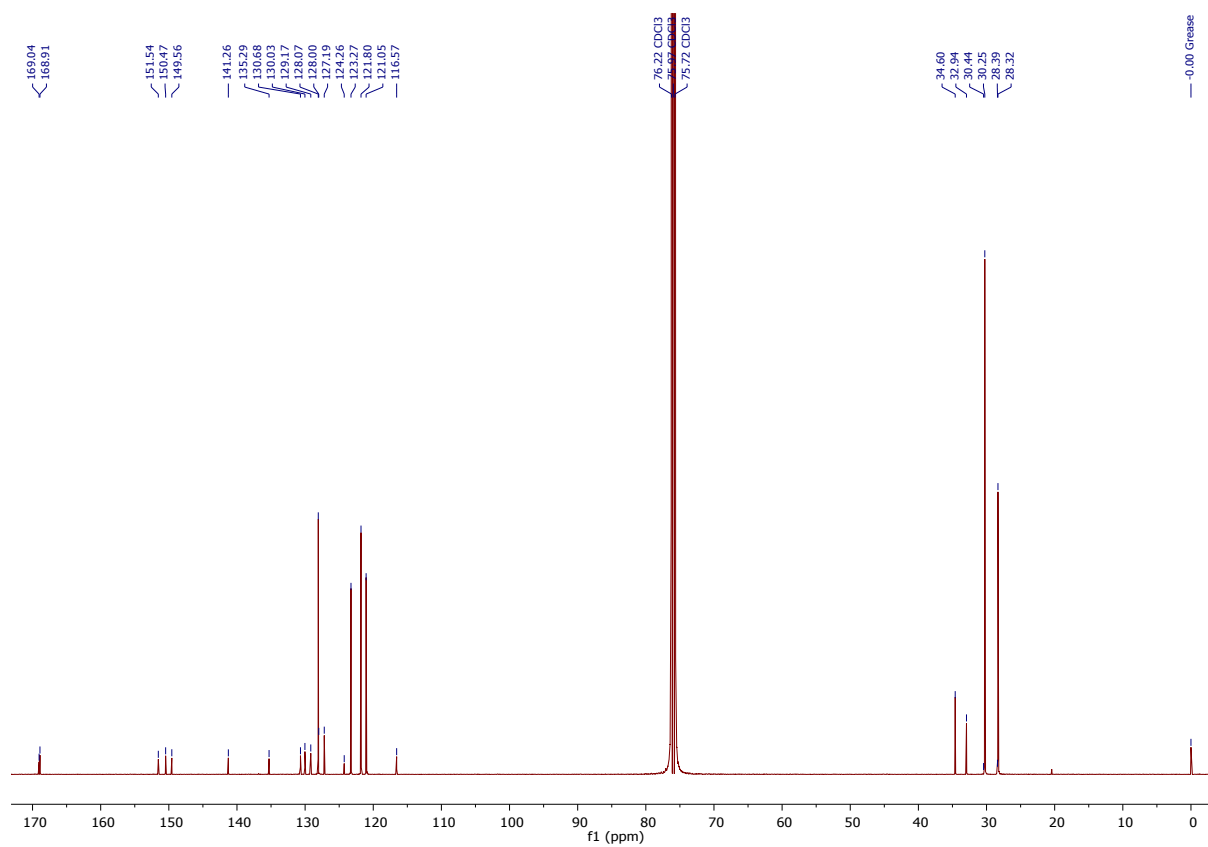
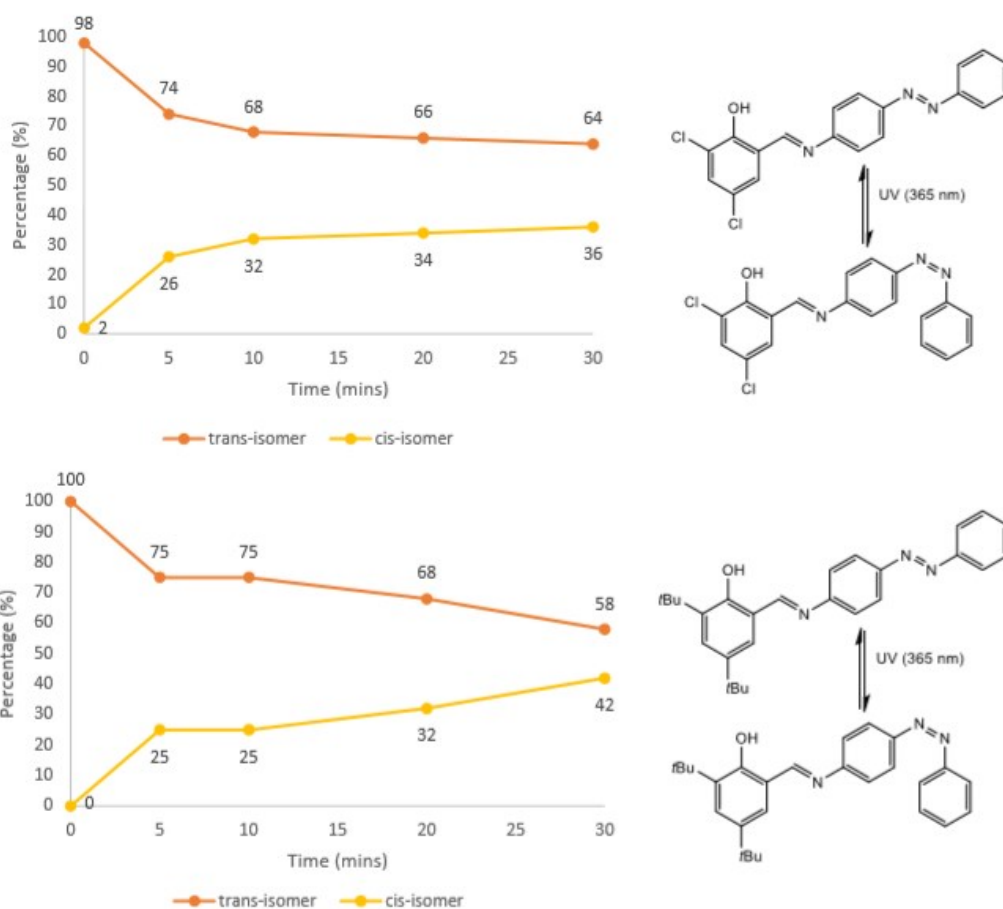


Figure S20:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ ) of  $\text{Zn}(\mathbf{3})_2$

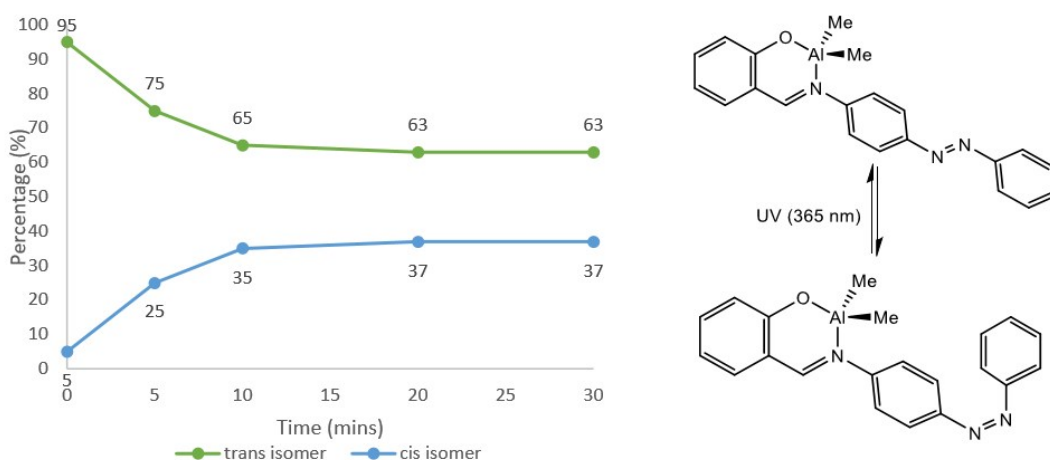
## 2. Photoisomerisation of the ligands and complexes

## 2.1 Photoisomerisation of the ligands

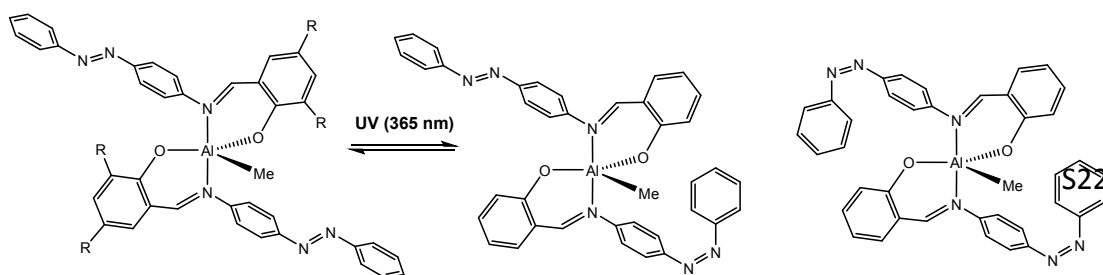


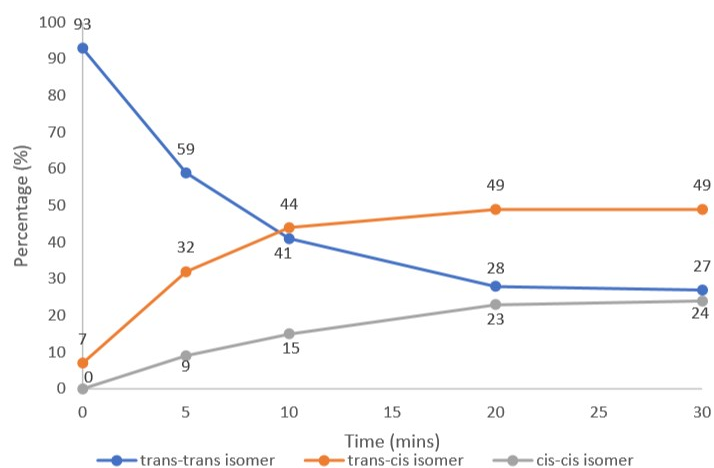
**Figure S21:** Changes in concentration of *cis* and *trans* isomers of **2H** (top) and **3H** (bottom) during irradiation obtained from  $^1\text{H}$  NMR spectroscopy.

## 2.2 Photoisomerisation of the complexes

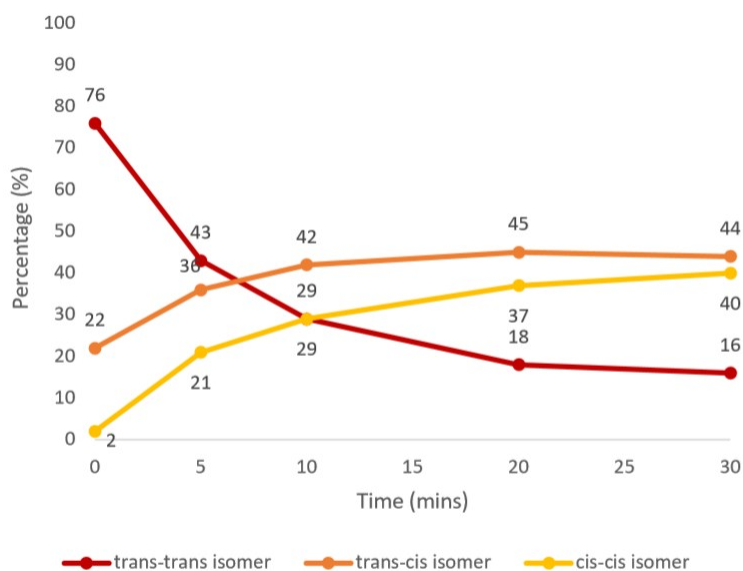
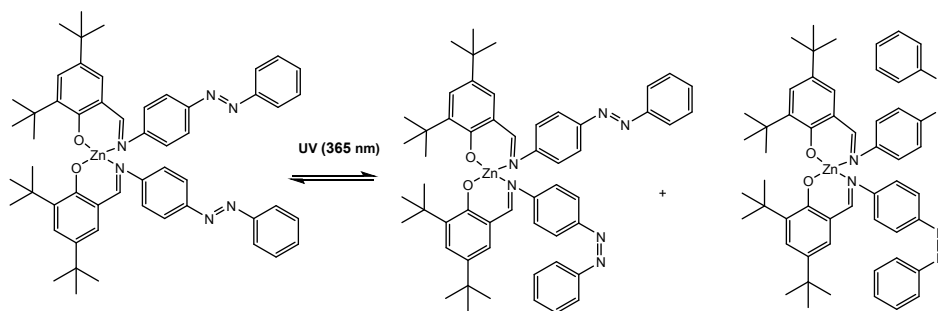


**Figure S22:** Changes in concentration of *cis* and *trans* isomers of  $\text{Al}(\mathbf{1})\text{Me}_2$  during irradiation obtained from  $^1\text{H}$  NMR spectroscopy.





**Figure S23:** Changes in concentration of *cis* and *trans* isomers of Al(1)<sub>2</sub>Me during irradiation obtained from <sup>1</sup>H NMR spectroscopy.



**Figure S24:** Changes in concentration of *cis* and *trans* isomers of Zn(3)<sub>2</sub> during irradiation obtained from <sup>1</sup>H NMR spectroscopy.

### 3. Polymerisations

#### 3.1 General procedure for polymerisations under ambient light

Polymerisations were prepared inside a glovebox by loading a J-Young's flask with *rac*-lactide (1.00 g, 6.94 mmol, 100 eq.), toluene (10 mL), BnOH initiator (7.2  $\mu$ L, 1 eq.) and catalyst (0.069 mmol, 1 eq.). For  $\epsilon$ -caprolactone polymerisations, a similar procedure was followed except the flask was loaded with  $\epsilon$ -caprolactone (1.11 mL, 10 mmol, 100 eq.), toluene (10 mL), BnOH (10.3  $\mu$ L, 1 eq.) and catalyst (0.1 mmol, 1 eq.). The polymerisation solution was heated using an oil-bath heated to 80 °C (unless stated otherwise) with continuous stirring for the required length of time. The reaction was quenched by exposure to air and the product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The solvent was removed using a rotary evaporator and conversion calculated by analysis of the methine region of the <sup>1</sup>H{<sup>1</sup>H} NMR spectra, recorded on a Bruker AV 400 MHz spectrometer. Molecular weights and molecular weight distributions of the polymers were determined by Gel Permeation Chromatography (GPC), employing a PLgel 5 $\mu$ m MIXED-D 300 x 7.5 mm column, with THF as an eluent (1.0 mL min<sup>-1</sup>). The instrument was calibrated against a series of 11 low molecular weight polystyrene standards. MALDI-ToF mass spectra were acquired on a Bruker Autoflex speed instrument using DCTB (trans-2-[3-(4tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix and ionised using NaTFA for PLA and NaI for PCL.

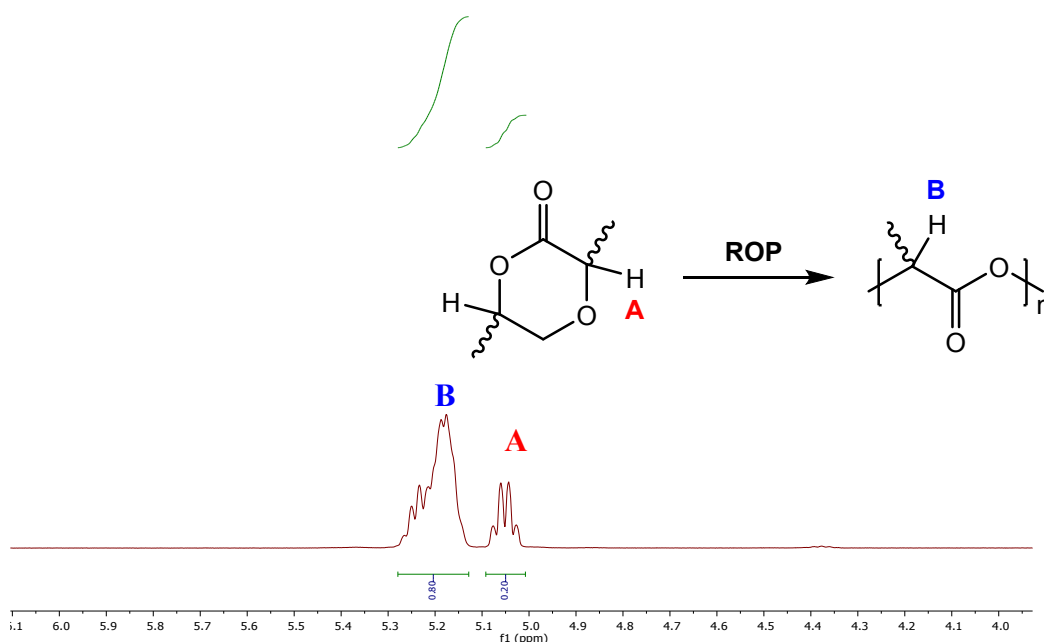
### 3.2 General procedure for polymerisations under UV light

The procedure for polymerisations under 365 nm light was the same as above, however the initiator in toluene (5 mL) was irradiated in a J-Young's flask using a HepatoChem PhotoRedox Ox Box for one hour before the addition of monomer, BnOH and toluene (5 mL). For *rac*-LA polymerisations, the reaction was heated to 80 °C by recirculation of a thermostatic fluid (1:1 water-ethylene glycol) through a HepatoChem temperature-controlled PhotoRedox Ox Box. A 365 nm 18W EvoluChem™ LED spotlight was used for irradiation.

### 3.3 <sup>1</sup>H NMR spectra

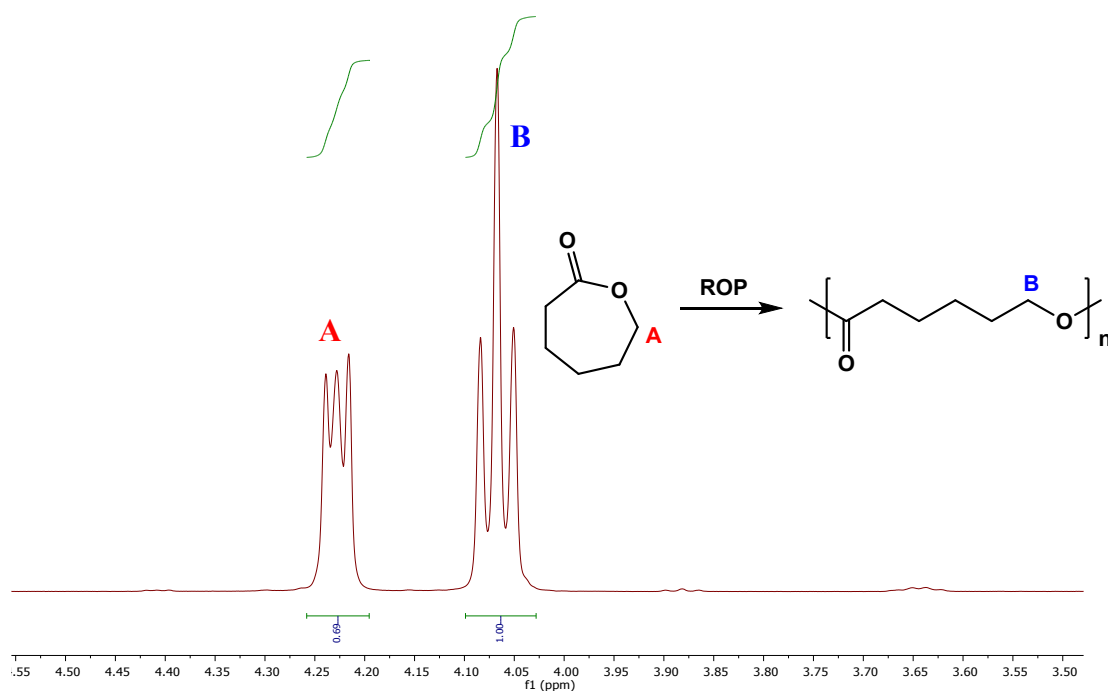
#### 3.3.1 Representative <sup>1</sup>H NMR spectrum for *rac*-LA polymerisation





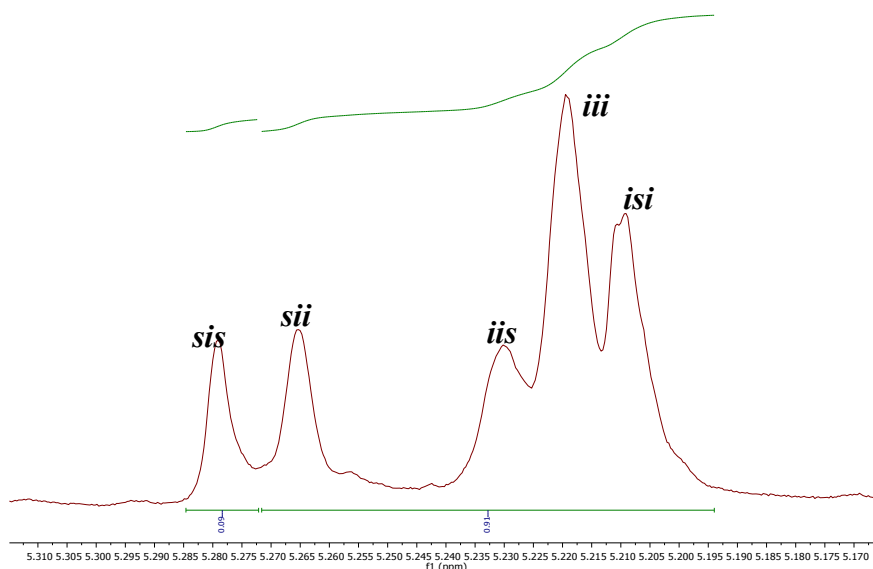
**Figure S25:**  $^1\text{H}$  NMR of PLA obtained from *rac*-LA ROP under ambient light with  $\text{Al}(\text{2})\text{Me}_2$  as an initiator at a ratio of 100:1:1 [LA]:[I]:[BnOH] at 80 °C/4h. Conv.(%) =  $(\text{B}/(\text{A}+\text{B})) \times 100$  (Table 2, Entry 5)

### 3.3.2 Representative $^1\text{H}$ NMR spectrum of $\epsilon$ -CL polymerisation



**Figure S26:**  $^1\text{H}$  NMR spectrum of PCL obtained from  $\epsilon$ -CL ROP under UV light with  $\text{Al}(\text{2})_2\text{Me}$  as an initiator at a ratio of 100:1:1 [ $\epsilon$ -CL]:[I]:[BnOH] at rt/12h. Conv.(%) =  $(\text{B}/(\text{A}+\text{B})) \times 100$  (Table 4, Entry 8).

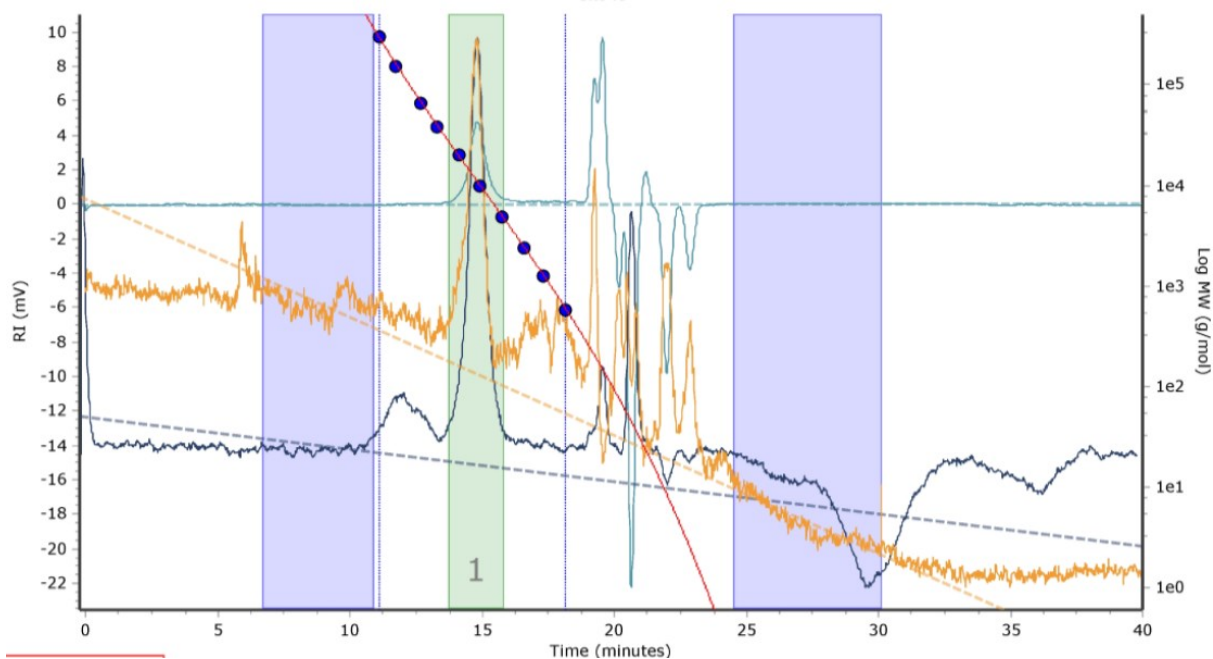
### 3.4 Homonuclear decoupled $^1\text{H}$ NMR spectra



**Figure S27:**  $^1\text{H}\{^1\text{H}\}$  NMR spectrum of PLA obtained from *rac*-LA ROP under ambient light with  $\text{Al}(\text{1})\text{Me}_2$  as an initiator at a ratio of 100:1:1 [LA]:[I]:[BnOH] at 80 °C/4h.  $\text{Pr} = \sqrt{2}[\text{sis}] = 0.42$ . (Table 2, Entry 1)

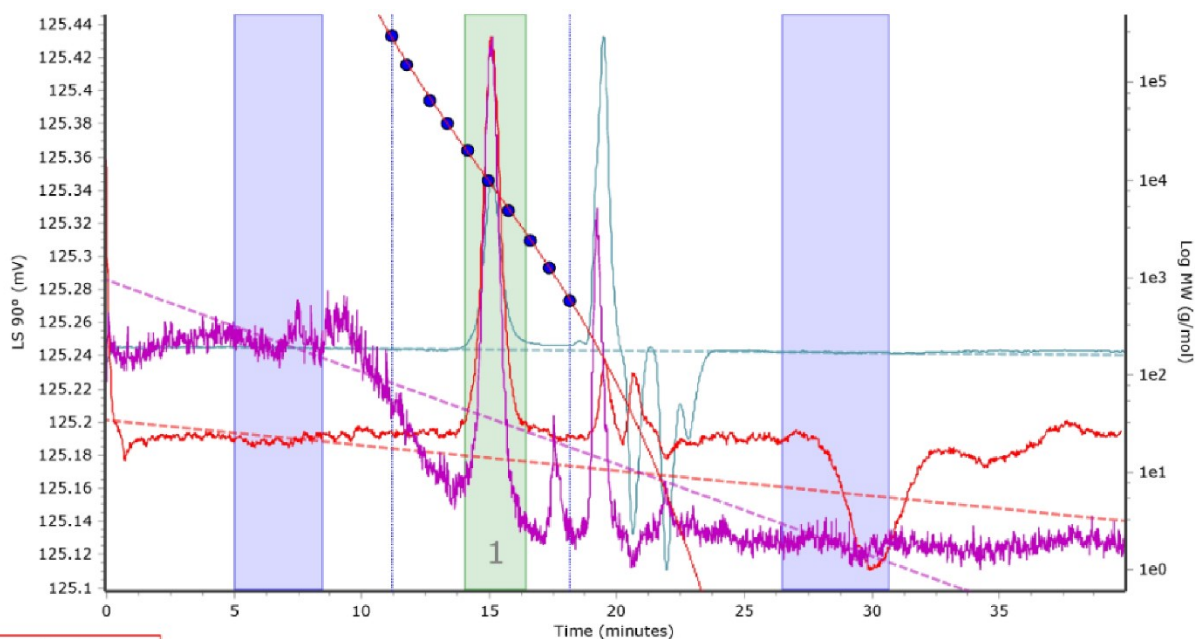
### 3.5 GPC Spectra

#### 3.5.1 Representative GPC spectra of PLA obtained from ambient light ROP



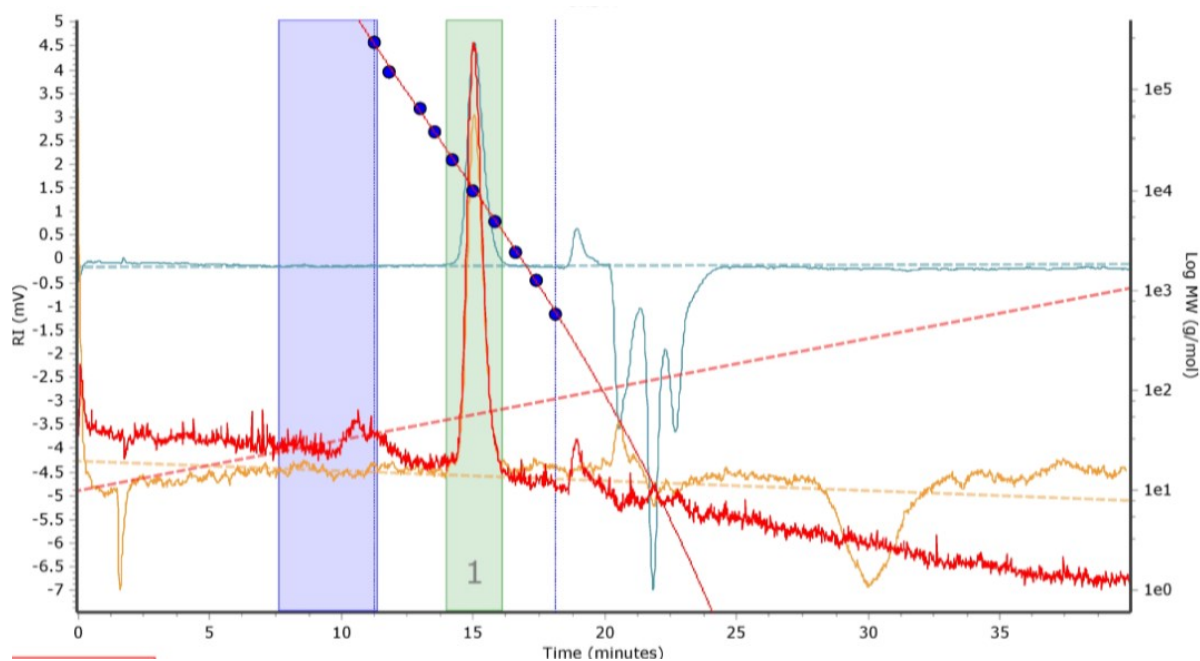
**Figure S28:** GPC spectra of PLA obtained from *rac*-LA ROP under ambient light with  $\text{Al}(\text{1})_2\text{Me}$  as an initiator at a ratio of 100:1:1 [LA]:[I]:[BnOH].  $M_n = 10090 \text{ g mol}^{-1}$ ,  $\text{Đ} = 1.10$  (Table 2, Entry 3)

#### 3.5.2 Representative GPC spectra of PLA obtained from UV light ROP



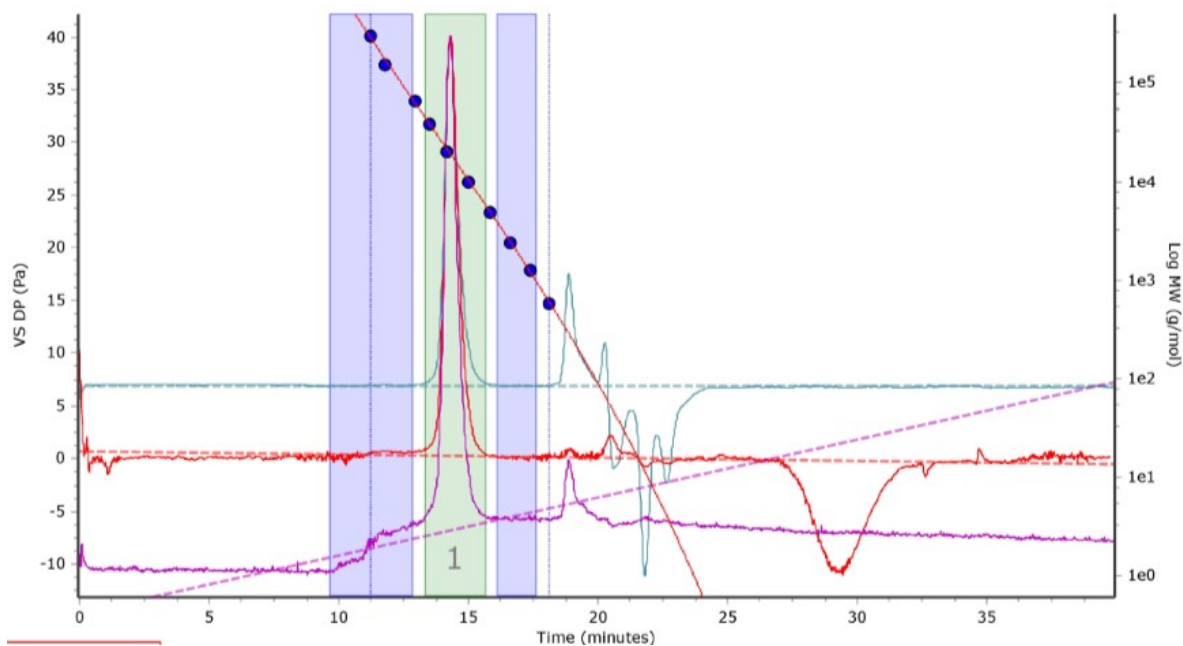
**Figure S29:** GPC spectra of PLA obtained from *rac*-LA ROP under UV light with  $\text{Al}(\mathbf{1})_2\text{Me}$  as an initiator at a ratio of 100:1:1 [LA]:[I]:[BnOH].  $M_n = 7676 \text{ g mol}^{-1}$ ,  $\bar{D} = 1.12$  (Table 2, Entry 4)

### 3.5.3 Representative GPC spectra of PCL obtained from ambient light ROP



**Figure S30:** GPC spectra of PCL obtained from  $\epsilon$ -CL ROP under ambient light with  $\text{Al}(\mathbf{2})_2\text{Me}$  as an initiator at a ratio of 100:1:1 [ $\epsilon$ -CL]:[I]:[BnOH].  $M_n = 8905 \text{ g mol}^{-1}$ ,  $\bar{D} = 1.10$  (Table 4, Entry 7)

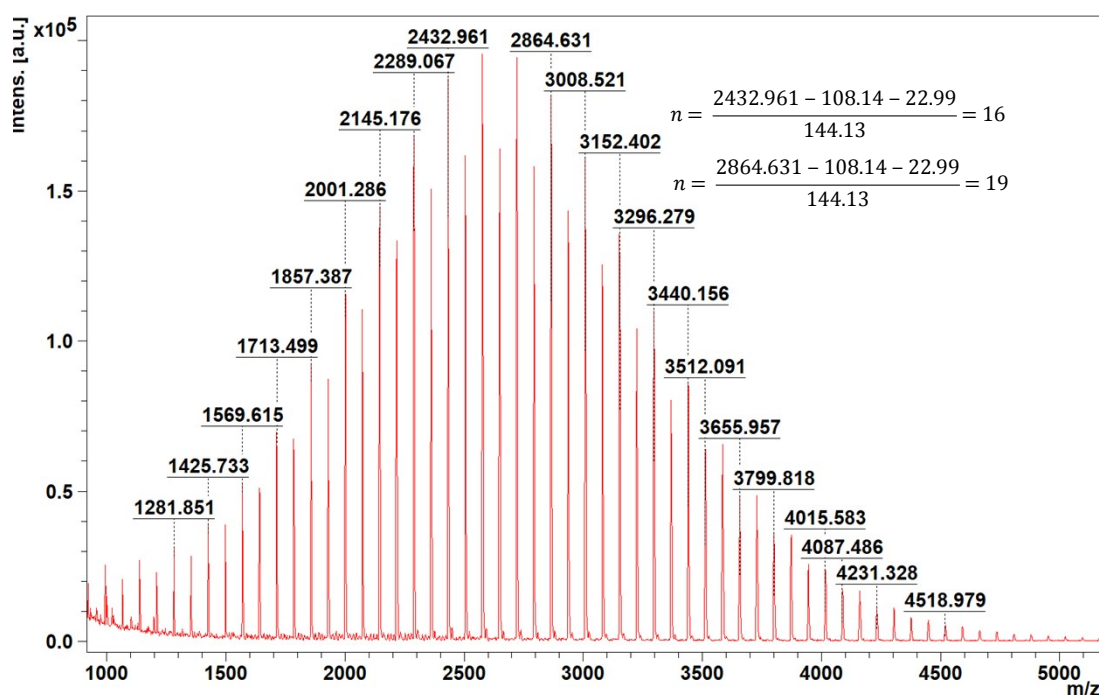
### 3.5.4 Representative GPC spectra of PCL obtained from UV light ROP



**Figure S31:** GPC spectra of  $\epsilon$ -CL ROP under UV light with  $\text{Al}(\text{C}_2\text{Me})_2$  as an initiator at a ratio of 100:1:1 [ $\epsilon$ -CL]:[I]:[BnOH].  $M_n = 16693 \text{ g mol}^{-1}$ ,  $\text{Đ} = 1.10$  (Table 4, Entry 8).

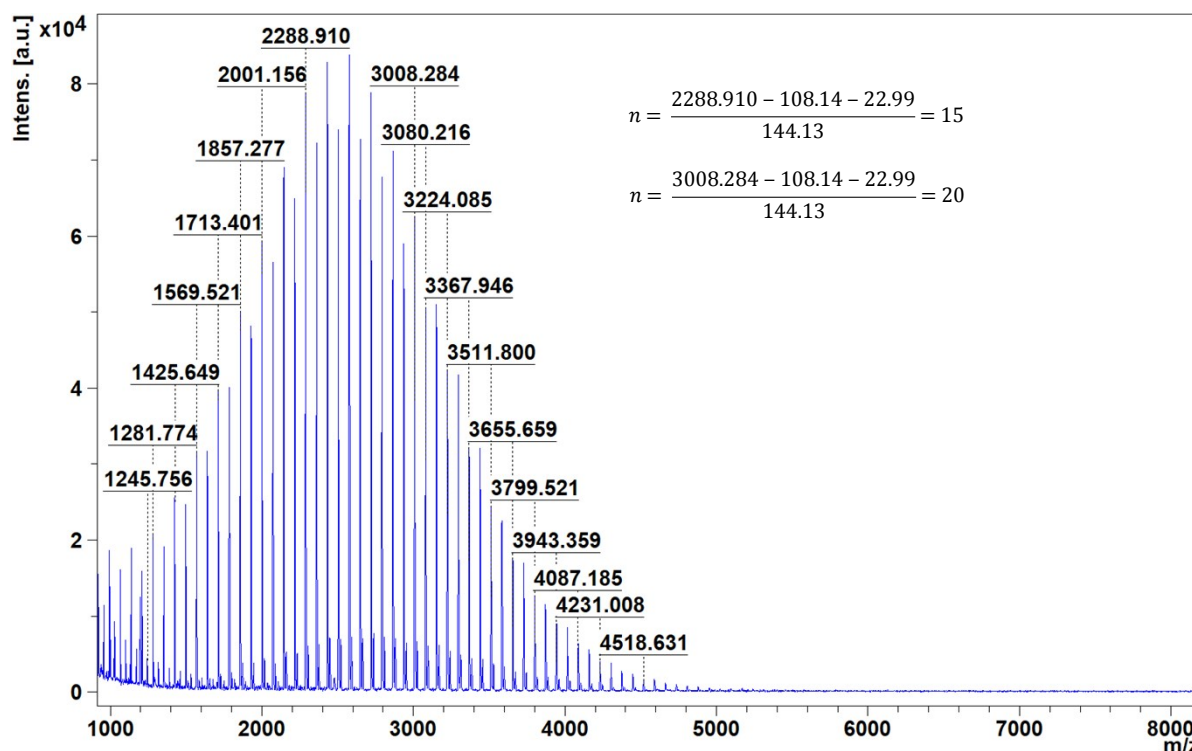
### 3.6 MALDI-ToF Spectra

#### 3.6.1 Representative MALDI-ToF spectrum of PLA obtained from ambient light ROP



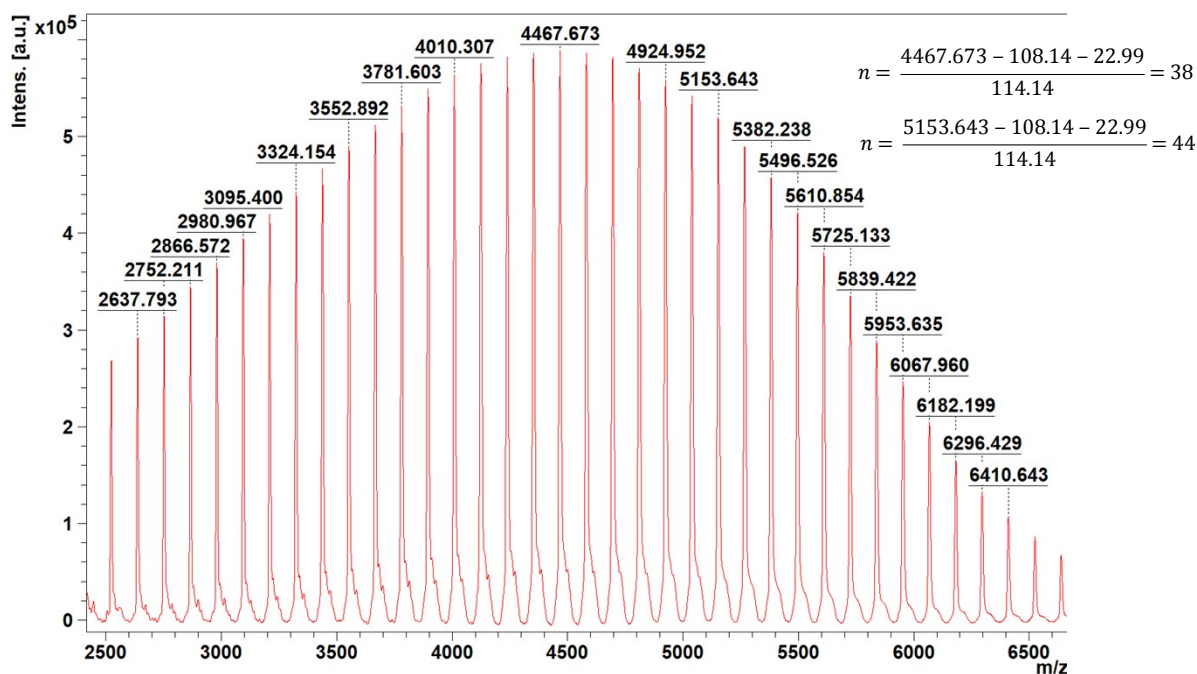
**Figure S32:** MALDI-ToF spectrum of PLA obtained from *rac*-LA ROP under ambient light with  $\text{Al}(\text{C}_2\text{Me})_2$  as an initiator (Table 2, Entry 5). Reflectron positive mode.

#### 3.6.2 Representative MALDI-ToF spectrum of PLA obtained from UV light ROP



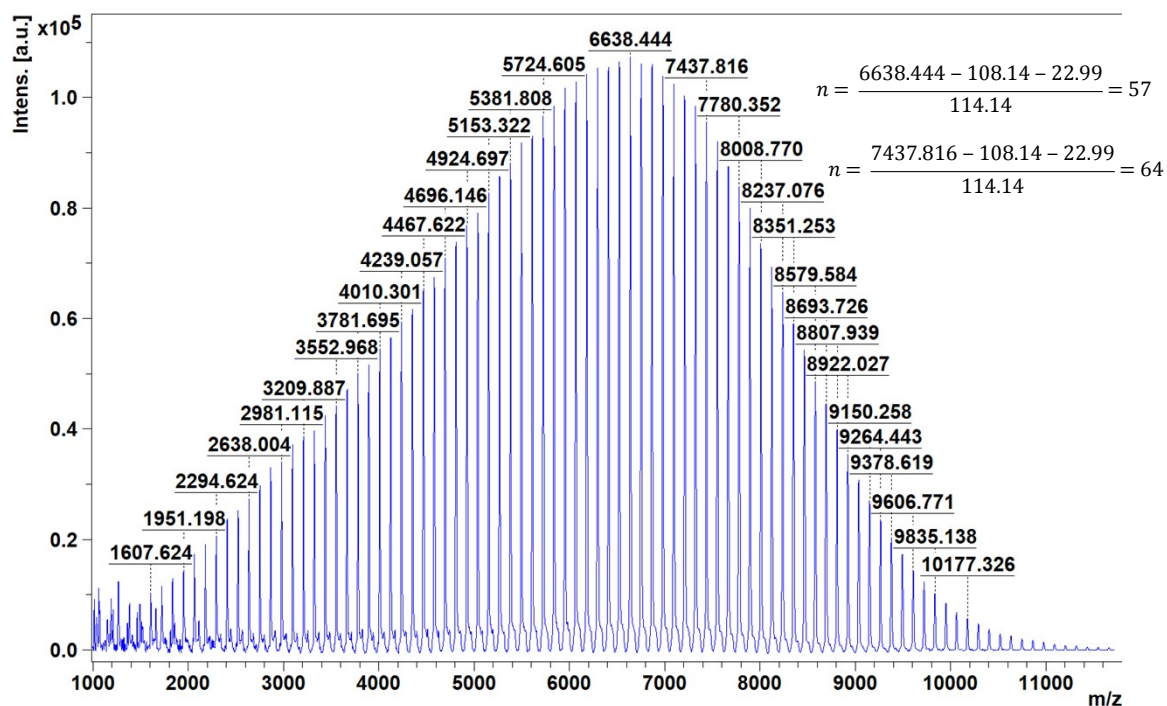
**Figure S33:** MALDI-ToF spectrum of PLA obtained from *rac*-LA ROP under UV light with Al(2)Me<sub>2</sub> as an initiator (Table 2, Entry 6). Reflectron positive mode.

### 3.6.3 Representative MALDI-ToF spectrum of PCL obtained from ambient light ROP



**Figure S34:** MALDI-ToF spectrum of PCL obtained from  $\epsilon$ -CL ROP under ambient light with Al(1)Me<sub>2</sub> as an initiator (Table 4, Entry 1). Linear positive mode.

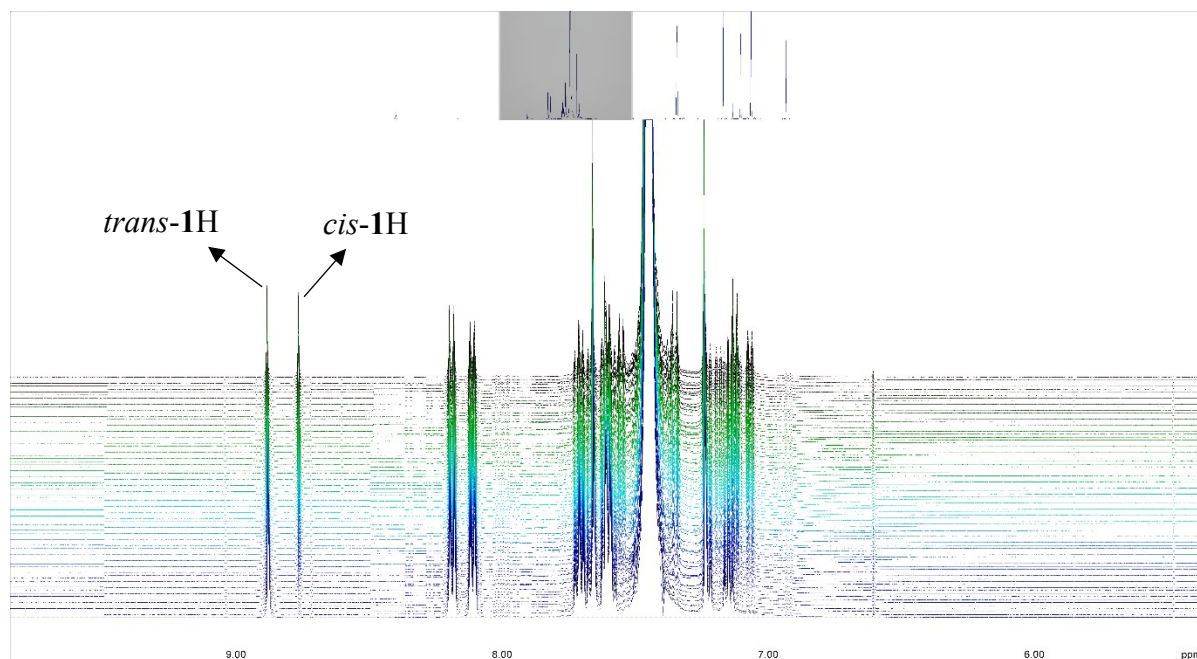
### 3.6.4 Representative MALDI-ToF spectrum of PCL obtained from UV light ROP



**Figure S35:** MALDI-ToF spectrum of PCL obtained  $\epsilon$ -CL ROP under UV light with  $\text{Al}(\text{I})\text{Me}_2$  as an initiator (Table 4, Entry 2). Linear positive mode.

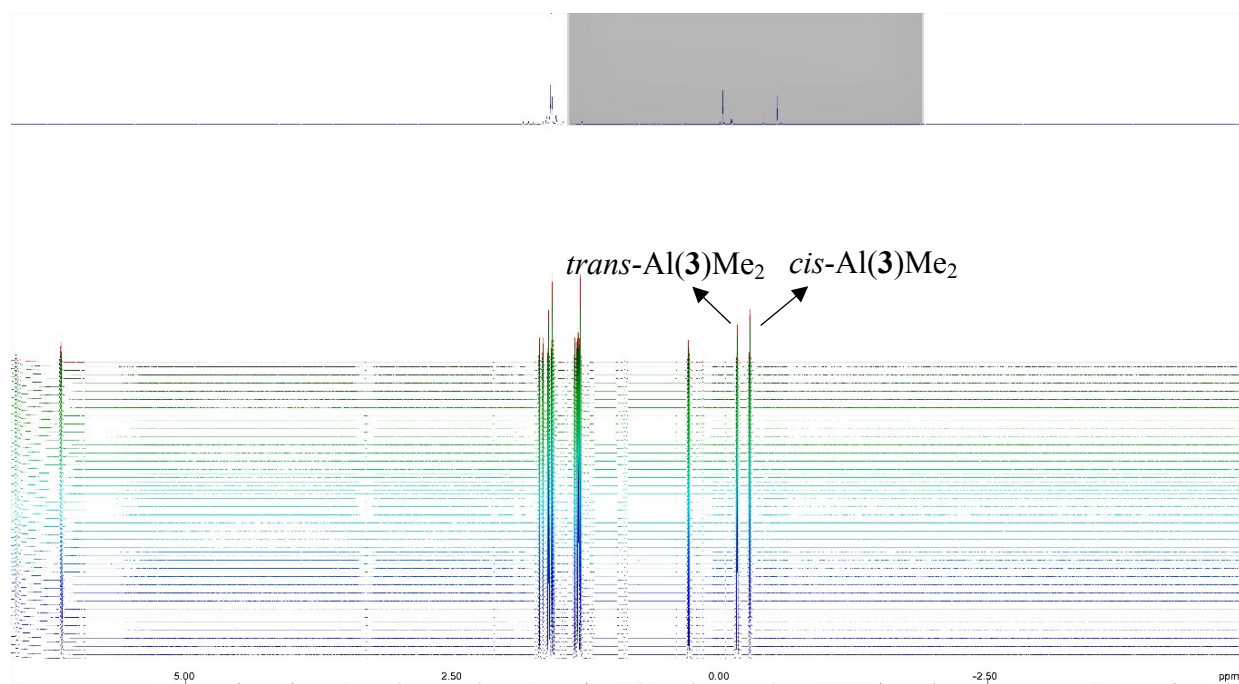
## 4. FlowNMR data

### 4.1 Representative FlowNMR spectrum of ligand photoisomerisation



**Figure S36:** Stacked FlowNMR spectrum of the aromatic region of  $1\text{H}$

### 4.2 Representative FlowNMR spectrum of $\text{Al}(\text{III})$ complex photoisomerisation



**Figure S37:** Stacked Flow NMR spectrum of metal-alkyl region of  $\text{Al}(\mathbf{3})\text{Me}_2$

## 5. Crystallographic data

**Table S1:** Crystallographic data for Al(III) and Zn(II) complexes

Compound Reference	Al(1)Me <sub>2</sub>	Al(2)Me <sub>2</sub>	Al(3)Me <sub>2</sub>	Al(1) <sub>2</sub> Me	Al(2) <sub>2</sub> Me	Zn(3) <sub>2</sub>
Chemical Formula	C <sub>21</sub> H <sub>20</sub> AlN <sub>3</sub> O <sub>1</sub>	C <sub>21</sub> H <sub>18</sub> AlCl <sub>2</sub> N <sub>3</sub> O	C <sub>58</sub> H <sub>72</sub> Al <sub>2</sub> N <sub>6</sub> O <sub>2</sub>	C <sub>39</sub> H <sub>31</sub> AlN <sub>6</sub> O <sub>2</sub>	C <sub>39</sub> H <sub>27</sub> AlC <sub>14</sub> N <sub>6</sub> O <sub>2</sub>	C <sub>54</sub> H <sub>60</sub> N <sub>6</sub> O <sub>2</sub> Zn
Crystal System	Orthorhombic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
A/Å	9.8983(6)	7.5892(7)	28.7883(9)	7.2924(6)	11.2845(3)	13.0316(5)
B/Å	9.0014(8)	7.6293(9)	6.7471(2)	14.1839(10)	22.8481(6)	18.68720(10)
C/Å	43.022(3)	18.1648(17)	28.8005(12)	16.6784(13)	14.3230(3)	23.2771(11)
A/°	90	86.424(9)	90	69.347(7)	90	90
B/°	90	79.662(8)	100.036(4)	87.386(6)	94.101(2)	96.619(4)
Γ/°	90	79.819(9)	90	84.995(6)	90	90
Unit Cell Volume/Å <sup>3</sup>	3833.2(5)	1017.87(18)	5508.5(3)	1607.9(2)	3683.43(16)	5630.8(3)
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Space Group	P b c a	P -1	P 2 <sub>1</sub> /n	P -1	P 2 <sub>1</sub> /c	P2 <sub>1</sub> /c
No. Of Formula Units Per Unit Cell, Z	8	2	4	2	4	4
ABSORPTION COEFFICIENT, μ/MM-1	1.032	0.379	0.824	0.920	3.513	0.476
No. Of Reflections Measured	21761	7985	16895	9351	22628	22281
No. Of Independent Reflections	3386	4127	16895	9351	7010	10309
R <sub>int</sub>	0.0567	0.0535	-	-	0.0551	0.0363
Final R <sub>1</sub> Values (I > 2σ(I))	0.0702	0.1130	0.1731	0.0607	0.0552	0.0667
Final WR <sub>2</sub> Values (I > 2σ(I))	0.2390	0.2790	0.4070	0.1546	0.1392	0.1368
Final R <sub>1</sub> Values (All Data)	0.0783	0.1441	0.2233	0.0830	0.0778	0.1186
Final WR <sub>2</sub> Values (All Data)	0.2452	0.3017	0.4281	0.1642	0.1533	0.1608
Goodness of fit on F <sup>2</sup>	1.800	1.195	1.104	0.927	1.018	1.014