Zirconium vs Aluminum salalen initiators for the production of biopolymers

Sarah M. Kirk[a,b], Gabriele Kociok-Köhn[b] and Matthew D. Jones[b,*]

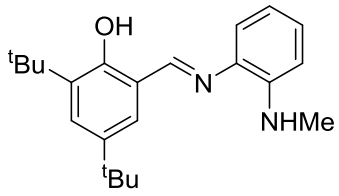
[a] Doctoral Training Centre in Sustainable Chemical Technologies, University of Bath, Bath BA2 7AY, UK

[b] Department of Chemistry, University of Bath, Bath BA2 7AY, UK.

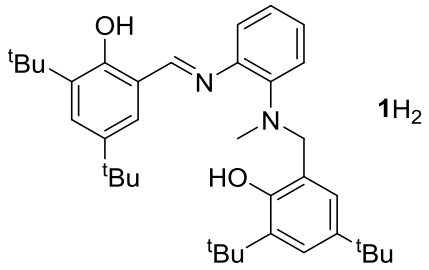
Ligand Preparation	2-3
Complex Preparation and representative NMRs	3-12
Selected GPC traces	12-15
Selected $^{1}H\{^{1}H\}$ NMR Spectra	15-19
Kinetic Plots	20
DSC Plots	21
Selected MALDI-ToF MS data	22-24
Crystallographic Parameters	25
DOSY Parameters of complexes	25

Ligand Preparation

1H_2 (Precursor)



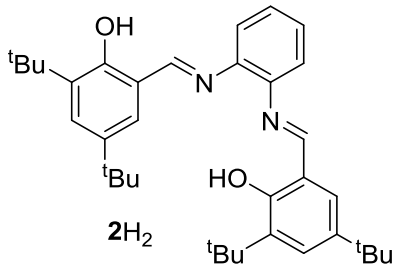
N-methyl-1,2-phenylenediamine (1.28 g, 10.5 mmol) was dissolved in methanol (10 ml) and 3,5-di-*tert*-butyl-2-hydroxbenzaldehyde (2.46 g, 10.5 mmol) dissolved in methanol (30 ml) was added. The solution was stirred for 16 hours, and the resulting precipitate isolated by vacuum filtration and washed with ice cold methanol (3 x 10 ml). The yellow solid was dried (2.51 g, 7.42 mmol, 71%). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 1.35 (s, 9 H, ^{t}Bu) 1.49 (s, 9 H, ^{t}Bu) 2.95 (s, 3 H, Me) 4.46 (br. S., 1 H, NH) 6.68 – 6.77 (m, 2 H, Ar-H) 7.01 (dd, *J*=7.8, 1.5 Hz, 1 H, Ar-H) 7.21 (td, *J*=7.8, 1.5 Hz, 1 H, Ar-H) 7.24 (d, *J*=2.3 Hz, 1 H, Ar-H) 7.47 (d, *J*=2.5 Hz, 1 H, Ar-H) 8.63 (s, 1 H, N=CH) 13.31 (s, 1 H, OH) ^{13}C NMR (400 MHz, CHLOROFORM-*d*) δ ppm 29.4 (C(**C**H_3)$_3$), 30.5 (N-CH_3), 31.5 (C(**C**H_3)$_3$), 34.2 (**C**(CH_3)$_3$), 35.1 (**C**(CH_3)$_3$), 110.0 (Ar), 116.8 (Ar), 117.9 (Ar), 118.7 (Ar), 126.8 (Ar), 127.9 (Ar), 128.0 (Ar), 135.6 (Ar), 136.9 (Ar), 140.8 (Ar), 143.1 (Ar), 157.7 (N=CH), 163.5 (Ar-OH) m/z [$C_{22}H_{30}N_2O$ + H]$^+$ Calc: 339.2436 gmol^{-1} Found: 339.2453 gmol^{-1}. Calculated for $C_{22}H_{30}N_2O$: C 78.06% H 8.93% N 8.27% Found: C 78.17% H 9.03% N 8.25%



1H_2

Precursor (2.075 g, 6.13 mmol) was dissolved in THF (20 ml) and 3,5-di-*tert*-butyl-2-hydroxy-benzyl bromide (1.834 g, 6.13 mmol) dissolved in THF (20 ml) was added. Triethylamine (0.85 ml, 6.13 mmol) was added to the solution which was then refluxed for 3 hours at 80°C. The precipitate was removed by vacuum filtration and the solvent of the filtrate removed by rotary evaporation. The oil was redissolved in dichloromethane (10 ml) and washed over silica. The solvent was removed by rotary evaporation and the yellow solid recrystallised in hexane (20 ml). Yellow crystals 1.25 g, 2.24 mmol, 37%. ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 1.32 (s, 9 H, ^{t}Bu) 1.36 (s, 9 H, ^{t}Bu) 1.39 (s, 9 H, ^{t}Bu) 1.49 (s, 9 H, ^{t}Bu) 2.71 (s, 3 H, N-CH_3) 4.32 (s, 2 H, CH_2) 6.96 (d, *J*=2.3 Hz, 1 H, Ar-H) 7.10 (dd, *J*=7.8, 1.3 Hz, 1 H, Ar-H) 7.19 – 7.23 (m, 1 H, Ar-H) 7.24 (d, *J*=2.5 Hz, 1 H, Ar-H) 7.26 (d, *J*=2.3 Hz, 1 H, Ar-H) 7.28 – 7.34 (m, 2 H, Ar-H) 7.50 (d, *J*=2.5 Hz, 1 H, Ar-H) 8.63 (s, 1 H, N=CH) 10.07 (s, 1 H, OH) 13.00 (s, 1 H, OH) ^{13}C{^{1}H} NMR (400 MHz, CHLOROFORM-*d*) δ ppm 29.5 (C(**C**H_3)$_3$), 29.7 (C(**C**H_3)$_3$), 31.5 (C(**C**H_3)$_3$), 31.7 (C(**C**H_3)$_3$), 34.2 (**C**(CH_3)$_3$), 34.2 (**C**(CH_3)$_3$), 34.9 (**C**(CH_3)$_3$), 35.2 (**C**(CH_3)$_3$), 42.8 (N-CH_3), 59.8 (CH_2), 118.5 (Ar), 120.4 (Ar-H), 120.8 (Ar-H), 121.0 (Ar), 123.1 (Ar-H), 123.7 (Ar-H), 125.5 (Ar-H), 127.0 (Ar-H), 128.3 (Ar-H), 135.9 (Ar), 137.2 (Ar), 140.5 (Ar), 140.5 (Ar), 145.1 (Ar), 145.4 (Ar), 154.2 (Ar-OH), 158.2 (Ar-OH), 165.3 (CH=N) m/z [$C_{37}H_{52}N_2O_2$ + Na]$^+$ Calc: 579.3926 gmol^{-1} Found: 579.3957 gmol^{-1}. Calculated for $C_{37}H_{52}N_2O_2$: C 79.81% H 9.41% N 5.03% Found: C 79.94% H 9.52% N 4.94%

2H_2



3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (4.55 g, 19.4 mmol) dissolved in methanol (25 ml) was added to o-phenylenediamine (1.05 g, 9.71 mmol) dissolved in methanol (25 ml) and the solution refluxed at 80 °C for 16 hours. The resulting yellow solid was filtered and washed with cold methanol (3 x 10 ml) and dried under vacuum (4.77 g, 8.82 mmol, 91 %) ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 1.34 (s, 18 H, ^{t}Bu) 1.46 (s, 18 H, ^{t}Bu) 7.23 (d, *J*=2.5 Hz, 2 H, Ar-H) 7.24 – 7.28 (m, 2H, Ar-H) 7.30 – 7.34 (m, 2 H, Ar-H), 7.46 (d, *J*=2.5 Hz, 2 H, Ar-H) 8.68 (s, 2 H, N=CH) 13.54 (br. S, 2 H, OH) ^{13}C NMR (400 MHz, CHLOROFORM-*d*) δ ppm 29.5 (C(**C**H_3)$_3$), 31.5 (**C**(CH_3)$_3$), 34.2 (**C**(CH_3)$_3$), 35.1 (**C**(CH_3)$_3$), 118.4 (Ar), 119.8 (Ar-H), 126.8 (Ar-H), 127.3 (Ar-H), 128.2 (Ar-H), 137.2 (Ar), 140.3 (Ar), 142.8 (Ar), 158.6 (Ar-OH), 164.7 (N=CH) m/z [$C_{36}H_{48}N_2O_2$ + Na]$^+$ (expected): Calc: 563.3613 gmol^{-1} Found: 563.3619 gmol^{-1}. Calculated for $C_{36}H_{48}N_2O_2$: C 79.95% H 8.94% N 5.18% Found: C 80.09% H 9.06% N 5.24%

Complex Preparation

Zr(**1**)(O^iPr)$_2$

1H_2 (0.83 g, 1.49 mmol) was dissolved in 40 ml hexane and 10 ml toluene with zirconium isoproxide isopropanol complex (0.578 g, 1.49 mmol). The solution was stirred at 60°C for 6 hours. The solution was concentrated by removal of solvent and the resulting crystals filtered (330.1 mg, 0.43 mmol, 29%). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.69 (d, *J*=5.8 Hz, 3 H, CH-C**H**$_3$) 0.87 (d, *J*=6.0 Hz, 3 H, CH-C**H**$_3$) 1.09 (s, 9 H, ^{t}Bu) 1.11 (s, 9 H, ^{t}Bu) 1.29 (br. S., 6 H, CH-C**H**$_3$) 1.32 (s, 9 H, ^{t}Bu) 1.55 (s, 9 H, ^{t}Bu) 3.32 (s, 3 H, N-CH_3) 3.78 (d, *J*=12.1 Hz, 1 H, CH_2) 3.92 (m, *J*=6.0 Hz, 1 H, C**H**-CH_3) 4.52 (m, *J*=6.0 Hz, 1 H, C**H**-CH_3) 4.69 (d, *J*=12.1 Hz, 1 H, CH_2) 6.51 (d, *J*=2.0 Hz, 1 H, Ar-H) 6.96 (d, *J*=2.3 Hz, 1 H, Ar-H) 7.11 (d, *J*=2.3 Hz, 1 H, Ar-H) 7.14 – 7.21 (m, 1 H, Ar-H) 7.27 (t, *J*=1.0 Hz, 1 H, Ar-H) 7.37 (d, *J*=8.0 Hz, 1 H, Ar-H) 7.47 (d, *J*=7.8 Hz, 1 H, Ar-H) 7.53 (d, *J*=2.3 Hz, 1 H, Ar-H) 8.52 (s, 1 H, N=CH) ^{13}C{^{1}H } NMR (400 MHz, CHLOROFORM-*d*) δ ppm 26.5 (CH-**C**H_3), 26.7 (CH-**C**H_3), 27.3 (CH-**C**H_3), 27.3 (CH-**C**H_3), 29.5 (C(**C**H_3)$_3$), 29.6 (C(**C**H_3)$_3$), 31.4 (C(**C**H_3)$_3$), 31.6 (C(**C**H_3)$_3$), 33.7 (**C**(CH_3)$_3$), 34.1 (**C**(CH_3)$_3$), 34.6 (**C**(CH_3)$_3$), 35.3 (**C**(CH_3)$_3$), 48.8 (N-CH_3), 67.1 (CH_2), 69.8 (**C**H-CH_3), 70.8 (**C**H-CH_3), 116.3 (Ar-H), 122.0 (Ar), 122.7 (Ar), 123.2 (Ar-H), 123.4 (Ar-H), 124.7 (Ar-H), 127.6 (Ar-H), 127.9 (Ar-H), 129.7 (Ar-H), 131.0 (Ar-H), 135.8 (Ar), 136.5 (Ar), 138.7 (Ar), 139.1 (Ar), 144.5 (Ar), 144.8 (Ar), 160.1 (Ar-O), 161.2 (Ar-O), 161.9 (N=CH) $C_{43}H_{64}N_2O_4Zr$ Calculated: C 67.58% H 8.44% N 3.67% Found: C 67.44% H 8.57% N 3.56%

Al(**1**)Me

1H_2 (0.5 g, 0.90 mmol) was dissolved in 20 ml toluene and 2 M trimethylaluminium solution (0.44 ml, 0.90 mmol) was added slowly. The solution was stirred for 2 hours, then solvent removed. The solid was redissolved in 20 ml hexane. The resulting crystals were filtered to yield a yellow solid (292.2 mg, 0.49 mmol, 54%). ^{1}H NMR (400 MHz, BENZENE-d_6) δ ppm -0.30 (s, 3 H, Al-CH_3) 1.37 (s, 9

H, ^{t}Bu) 1.45 (s, 9 H, ^{t}Bu) 1.76 (s, 9 H, ^{t}Bu) 1.81 (s, 9 H, ^{t}Bu) 2.26 (s, 3 H, N-CH_3) 3.00 (d, *J*=12.1 Hz, 1 H, CH) 4.13 (d, *J*=12.1 Hz, 1 H, CH) 6.36 (d, *J*=8.0 Hz, 1 H, Ar-H) 6.79 – 6.85 (m, 2 H, Ar-H) 6.94 (d, *J*=2.8 Hz, 3 H, Ar-H) 7.60 (d, *J*=2.5 Hz, 1 H, Ar-H) 7.81 (d, *J*=2.5 Hz, 1 H, Ar-H) 7.90 (s, 1 H, N=CH) $^{13}C\{^{1}H\}$ NMR (400 MHz, BENZENE-d_6) δ ppm 30.7 (C(**C**H_3)$_3$), 30.8 (C(**C**H_3)$_3$), 31.8 (C(**C**H_3)$_3$), 32.5 (C(**C**H_3)$_3$), 34.6 (**C**$(CH_3)_3$), 34.7 (**C**$(CH_3)_3$), 36.0 (**C**$(CH_3)_3$), 36.2 (**C**$(CH_3)_3$), 41.1 (N-CH_3), 66.1 (CH_2), 119.3 (Ar-H), 119.8 (Ar), 121.0 (Ar-H), 123.3 (Ar), 124.7 (Ar-H), 124.7 (Ar-H), 127.5(Ar-H), 128.3 (Ar-H), 128.8 (Ar-H), 133.7 (Ar-H), 138.4 (Ar), 139.0 (Ar), 139.1 (Ar) 141.4 (Ar), 142.2 (Ar), 145.9 (Ar), 157.8 (Ar-OH), 166.4 (N=CH), 168.3 (Ar-OH) $C_{38}H_{53}N_2O_2Al$ calculated: C 76.47% H 8.95% N 4.69% Found: C 76.25% H 9.08% N 4.60%

Hf(**1**)($O^{i}Pr$)$_2$

1 (0.3 g, 0.54 mmol) was dissolved in 20 ml toluene with Hf($O^{i}Pr$)$_4$.^{i}PrOH (256 mg, 0.54 mmol) and stirred for 16 hours. The solvent was removed under vacuum and the orange powder recrystallised in hexane. Crystals were isolated and dried under vacuum (133 mg, 0.16 mmol, 29 %). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.70 (d, *J*=6.0 Hz, 3 H, CH-C**H**$_3$) 0.85 (d, *J*=6.0 Hz, 3 H, CH-C**H**$_3$) 1.07 (s, 9 H, ^{t}Bu) 1.09 (s, 9 H, ^{t}Bu) 1.29 (d, *J*=6.0 Hz, 6 H, CH-C**H**$_3$) 1.32 (s, 9 H, ^{t}Bu) 1.55 (s, 9 H, ^{t}Bu) 3.35 (s, 3 H, N-CH_3) 3.77 (d, *J*=12.3 Hz, 1 H, CH_2) 3.99 (spt, *J*=6.0 Hz, 1 H, C**H**-CH_3) 4.62 (spt, *J*=6.0 Hz, 1 H, C**H**-CH_3) 4.78 (d, *J*=12.1 Hz, 1 H, CH_2) 6.48 (d, *J*=2.5 Hz, 1 H, Ar-H) 6.97 (d, *J*=2.5 Hz, 1 H, Ar-H) 7.11 (d, *J*=2.5 Hz, 1 H, Ar-H) 7.14 – 7.21 (m, 1 H, Ar-H) 7.24 – 7.30 (m, 1 H, Ar-H) 7.38 (d, *J*=7.8 Hz, 1 H, Ar-H) 7.47 (dd, *J*=8.0, 1.25 Hz, 1 H, Ar-H) 7.57 (d, *J*=2.5 Hz, 1 H, Ar-H) 8.52 (s, 1 H, N=CH) $^{13}C\{^{1}H$ } NMR (400 MHz, CHLOROFORM-*d*) δ ppm 26.7 (CH-**C**H_3), 26.9 (CH-**C**H_3), 27.5 (CH-**C**H_3), 27.5 (CH-**C**H_3), 29.5 (C(**C**H_3)$_3$), 29.6 (C(**C**H_3)$_3$), 31.4 (C(**C**H_3)$_3$), 31.6 (C(**C**H_3)$_3$), 33.7 (**C**$(CH_3)_3$), 34.0 (**C**$(CH_3)_3$), 34.6 (**C**$(CH_3)_3$), 35.3 (**C**$(CH_3)_3$), 49.4 (N-CH_3), 67.1 (CH_2), 69.5 (**C**H-CH_3), 70.5 (**C**H-CH_3), 116.2 (Ar-H), 121.9 (Ar), 122.9 (Ar), 123.5 (Ar-H), 123.5 (Ar-H), 124.7 (Ar-H), 127.9 (Ar-H), 128.0 (Ar-H), 129.7 (Ar-H), 131.3 (Ar-H), 136.3 (Ar), 136.4 (Ar), 139.2 (Ar), 139.3 (Ar), 144.4 (Ar), 144.6 (Ar), 160.4 (Ar-O), 161.6 (Ar-O), 161.9 (N=CH) $C_{43}H_{64}N_2O_4Hf$ Calculated: C 60.66% H 7.58% N 3.29% Found: C 60.79% H 7.72% N 3.42%

Zr_2(**2**)($O^{i}Pr$)$_6$

2 (1 g, 1.8 mmol) was dissolved in 30 ml toluene with Zr($O^{i}Pr$)$_4$.^{i}PrOH (1.43 g, 3.70 mmol) and stirred for 16 hours. The toluene was removed and the orange solid dissolved in hexane (20 ml). This was concentrated to produce a precipitate which was filtered and dried under vacuum (0.6 g, 0.56 mmol, 31 %). ^{1}H NMR (400 MHz, BENZENE-d_6) δ ppm 1.15 (d, *J*=6.3 Hz, 6 H, CH-C**H**$_3$) 1.17 (s, 18 H,^{t}Bu) 1.18 (d, *J*=5.5 Hz, 6 H, CH-C**H**$_3$) 1.24 (d, *J*=6.5 Hz, 6 H, CH-C**H**$_3$) 1.27 (d, *J*=6.0 Hz, 6 H, CH-C**H**$_3$) 1.55 (dd, *J*=6.0, 0.5 Hz, 12 H, CH-C**H**$_3$) 1.74 (s, 18 H, ^{t}Bu) 4.42 (spt, *J*=6.1 Hz, 2 H, C**H**-CH_3) 4.79 (spt, *J*=6.1 Hz, 2 H, C**H**-CH_3) 4.93 (m, *J*=6.5 Hz, 1 H, C**H**-CH_3) 4.99 (m, *J*=6.3 Hz, 1 H, C**H**-CH_3) 6.96 – 7.00 (m, 3H, Ar-H) 7.03 – 7.06 (m, 2 H, Ar-H) 7.12 (d, *J*=7.5 Hz, 1 H, Ar-H) 7.69 (d, *J*=2.8 Hz, 2H, Ar-H) 8.02 (s, 2 H, N=CH) $^{13}C\{^{1}H\}$ NMR (400 MHz, BENZENE-d_6) δ ppm 24.1 (CH-**C**H_3), 25.7 (CH-**C**H_3), 27.6 (CH-**C**H_3), 27.8 (CH-**C**H_3), 27.8 (CH-**C**H_3), 28.0 (CH-**C**H_3), 30.7 (C(**C**H_3)$_3$), 31.8 (C(**C**H_3)$_3$), 34.4 (**C**$(CH_3)_3$), 36.0 (**C**$(CH_3)_3$), 70.2 (**C**H-CH_3), 71.5 (**C**H-CH_3), 72.3 (**C**H-CH_3), 72.8 (**C**H-CH_3), 123.0 (Ar-H), 125.4 (Ar-H), 127.4 (Ar), 128.3 (Ar-H), 128.5 (Ar), 130.3 (Ar-H), 131.4 (Ar), 139.2 (Ar), 139.7 (Ar), 148.7 (Ar), 161.9 (Ar-O), 170.6 (N=CH) $C_{54}H_{88}N_2O_8Zr_2$ calculated: C 60.29% H 8.25% N 2.60% Found: C 58.59% H 8.53% N 2.69%

Hf_2(**2**)($O^{i}Pr$)$_6$

2 (0.5 g, 0.92 mmol) was dissolved in toluene (20 ml) with Hf($O^{i}Pr$)$_4$.^{i}PrOH (0.77 g, 1.85 mmol) and stirred at 60°C for 16 hours. The solvent was removed under vacuum and the orange solid redissolved in hexane (10 ml). The solution was concentrated to produce a precipitate which was

filtered and dried under vacuum (293 mg, 0.23 mmol, 25 %). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.91 (d, *J*=6.8 Hz, 6 H, CH-C**H**$_3$) 0.98 (d, *J*=6.0 Hz, 6 H, CH-C**H**$_3$) 1.06 (d, *J*=6.0 Hz, 6 H, CH-C**H**$_3$) 1.27 (br. S., 9 H CH-C**H**$_3$) 1.28 (s, 18 H, ^{t}Bu) 1.29 (br. S., 9 H, CH-C**H**$_3$) 1.51 (s, 18 H, ^{t}Bu) 4.31 (spt, *J*=6.0 Hz, 2 H, C**H**-CH$_3$) 4.59 (spt, *J*=6.0 Hz, 2 H, C**H**-CH$_3$) 4.72 (m, *J*=6.5 Hz, 1 H, C**H**-CH$_3$) 4.83 (m, *J*=6.5 Hz, 1 H, C**H**-CH$_3$) 6.97 – 7.02 (m, 4 H, Ar-H) 7.26 – 7.29 (m, 2 H, Ar-H) 7.52 (d, *J*=2.5 Hz, 2 H, Ar-H) 7.98 (s, 2 H, N=CH) ^{13}C{^{1}H } NMR (400 MHz, CHLOROFORM-*d*) δ ppm 23.0 (CH-**C**H$_3$), 24.7 (CH-**C**H$_3$), 27.2 (CH-**C**H$_3$), 27.2 (CH-**C**H$_3$), 27.3 (CH-**C**H$_3$), 27.5 (CH-**C**H$_3$), 30.0 (C(**C**H$_3$)$_3$), 31.4 (C(**C**H$_3$)$_3$), 34.0 (**C**(CH$_3$)$_3$), 35.2 (**C**(CH$_3$)$_3$), 69.1 (**C**H-CH$_3$), 70.3 (**C**H-CH$_3$), 70.9 (**C**H-CH$_3$), 71.9 (**C**H-CH$_3$), 122.3 (Ar), 124.9 (Ar-H), 126.7 (Ar-H), 129.3 (Ar-H), 130.8 (Ar-H), 138.3 (Ar), 139.3 (Ar), 147.8 (Ar), 161.3 (Ar-O), 170.1 (N=CH) $C_{54}H_{88}N_2O_8Hf_2$ calculated: C 51.88% H 7.09% N 2.24% Found: C 50.17% H 7.22% N 2.49%

It should be noted that the elemental analysis (of the dried crystals) for Zr_2(**2**)($O^{i}Pr$)$_6$ and Hf_2(**2**)($O^{i}Pr$)$_6$ are less than desirable. This, we believe, is due to high reactivity of the bridging alkoxides to trace water during the elemental analysis sample preparation. If the elemental is calculated for one OiPr being replaced by an OH much more satisfactory results are obtained: $C_{51}H_{82}N_2O_8Hf_2$ calculated: C 50.70% H 6.84% N 2.32% Found: C 50.17% H 7.22% N 2.49%. $C_{51}H_{82}N_2O_8Hf_2$ calculated: C 59.26% H 8.00% N 2.71% Found: C 58.59% H 8.53% N 2.69%. The NMR spectra are clean and are in agreement with the bimetallic structure and do not show the presence of any impurities. The complexes with terminal OiPr's afford good elemental analysis.

Al_2(**2**)Me_4

2 (0.3 g, 0.55 mmol) was dissolved in hexane (20 ml) and 2M trimethylaluminium (0.55 ml, 1.1 mmol) solution added slowly. The resulting crystals were isolated and dried under vacuum (183 mg, 0.28 mmol, 51 %). ^{1}H NMR (400 MHz, BENZENE-d_6) δ ppm -0.26 (d, *J*=1.0 Hz, 12 H, Al-CH$_3$) 1.16 (s, 18 H, ^{t}Bu) 1.47 (s, 18 H, ^{t}Bu) 6.81 – 6.89 (m, 2 H, Ar-H) 6.95 (s, 2 H, Ar-H) 7.28 – 7.34 (m, 2 H, Ar-H) 7.54 (s, 2 H, Ar-H) 7.99 (s, 2 H, N=CH) ^{13}C NMR (400 MHz, BENZENE-d_6) δ ppm -8.1 (Al-CH$_3$), 29.9 (C(**C**H$_3$)$_3$), 31.5 (C(**C**H$_3$)$_3$), 34.4 (**C**(CH$_3$)$_3$), 35.8 (**C**(CH$_3$)$_3$), 119.2 (Ar), 127.0 (Ar-H), 130.3 (Ar-H), 134.4 (Ar-H), 140.1 (Ar), 141.0 (Ar), 141.2 (Ar), 163.5 (Ar-OH), 176.4 (N=CH) $C_{40}H_{58}N_2O_2Al_2$ calculated: C 73.59% H 8.95% N 4.29% Found: C 73.39% H 9.11% N 4.33%

NMR spectra of Complexes

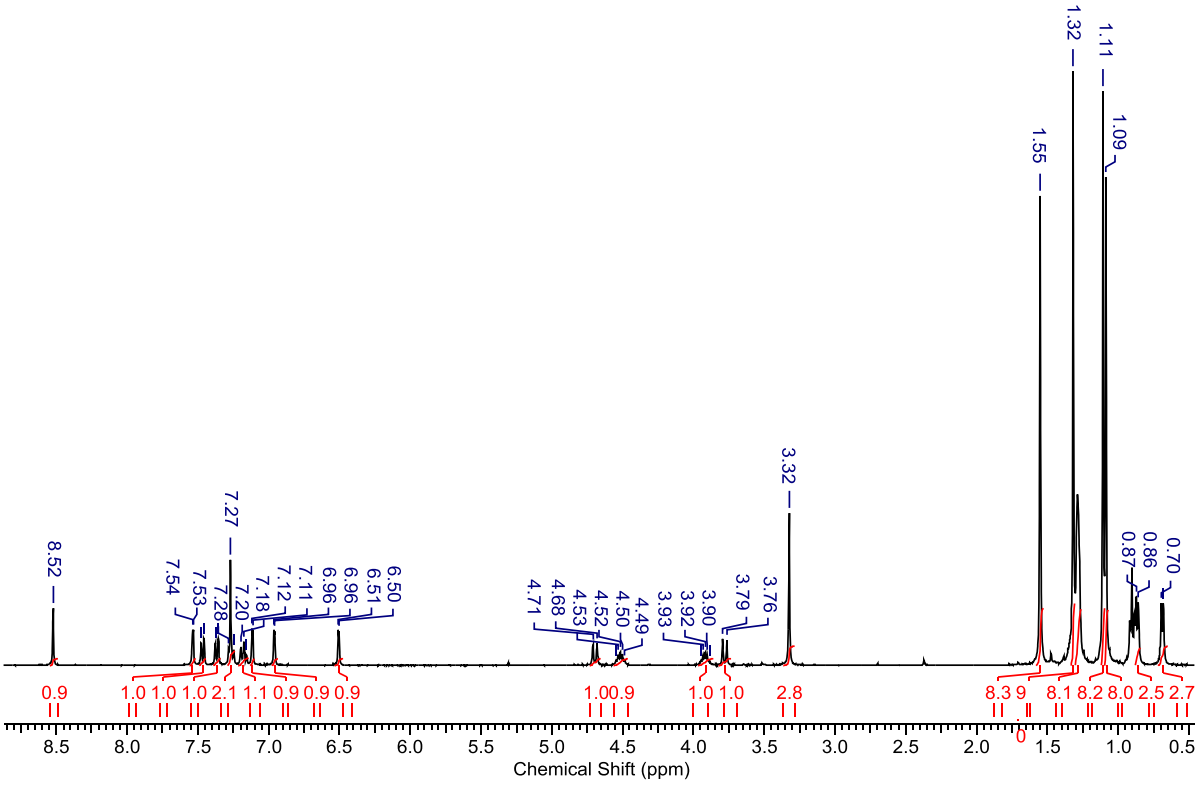


Figure SI1: ^{1}H NMR spectrum of Zr(**1**)($O^{i}Pr$)$_2$ ($CDCl_3$)

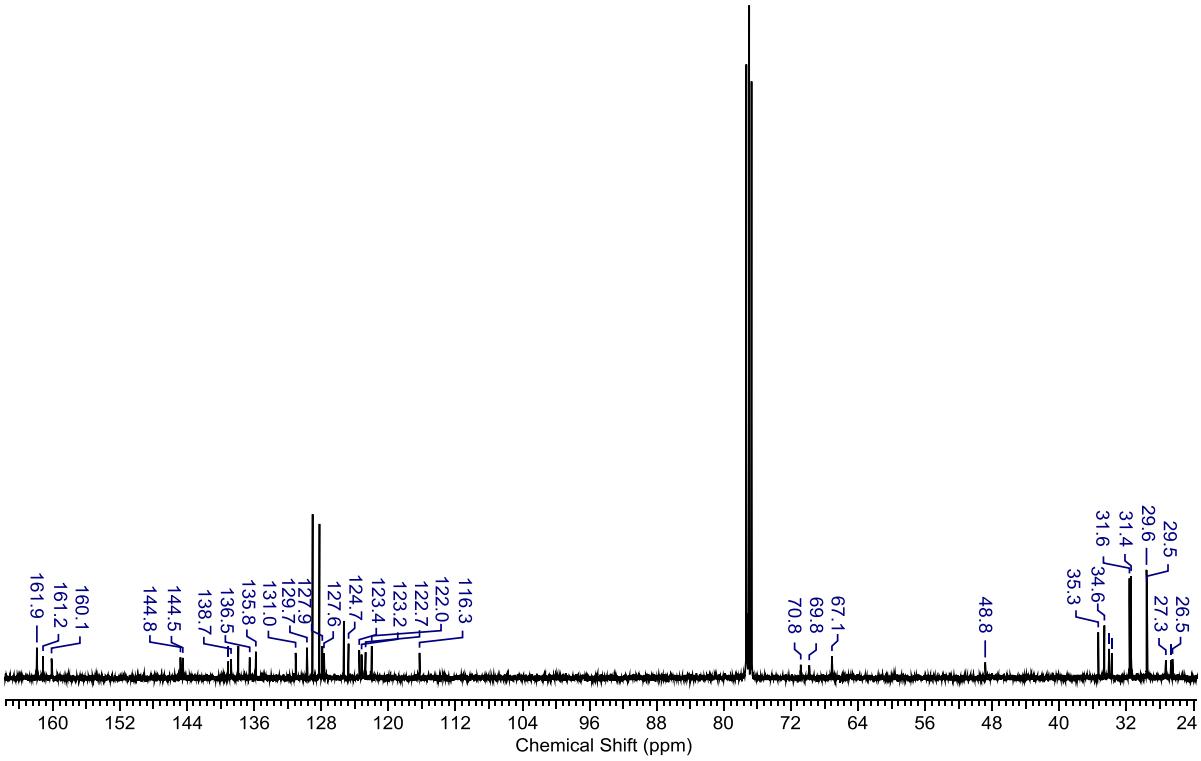


Figure SI2: $^{13}C\{^{1}H\}$ NMR spectrum of Zr(**1**)($O^{i}Pr$)$_2$ ($CDCl_3$)

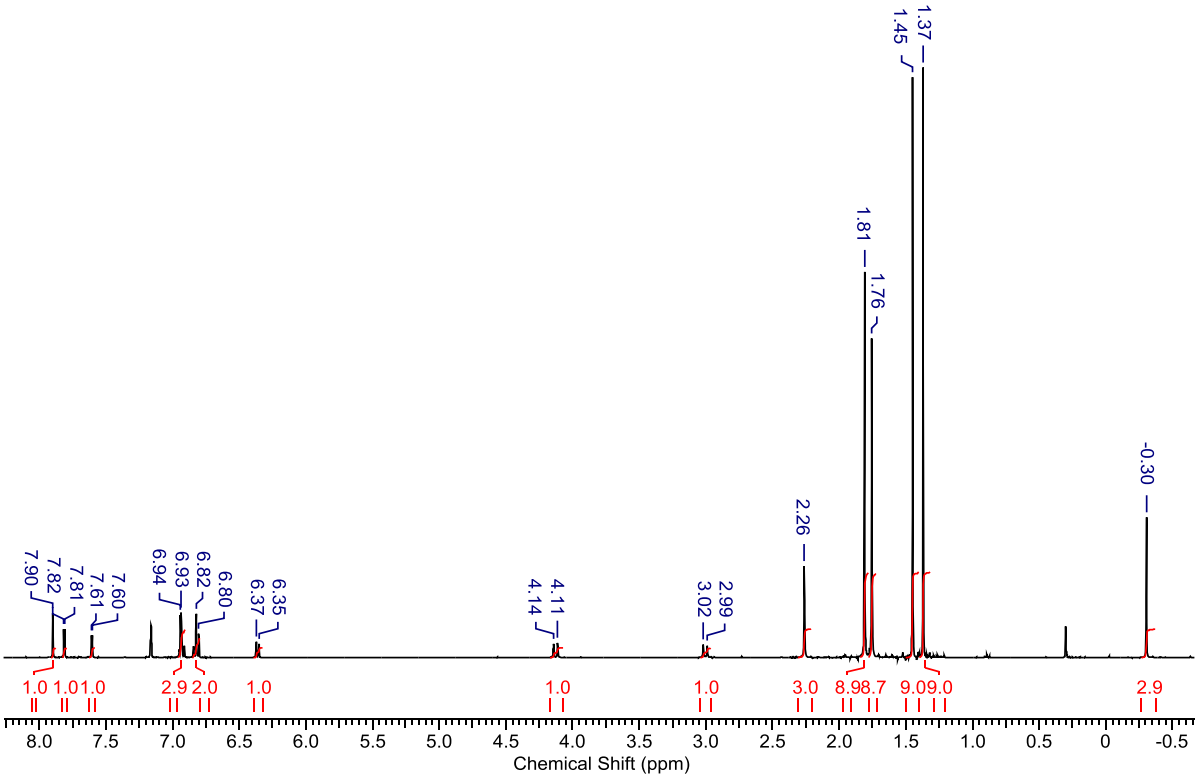


Figure SI3: ^{1}H NMR spectrum of Al(**1**)Me (C_6D_6)

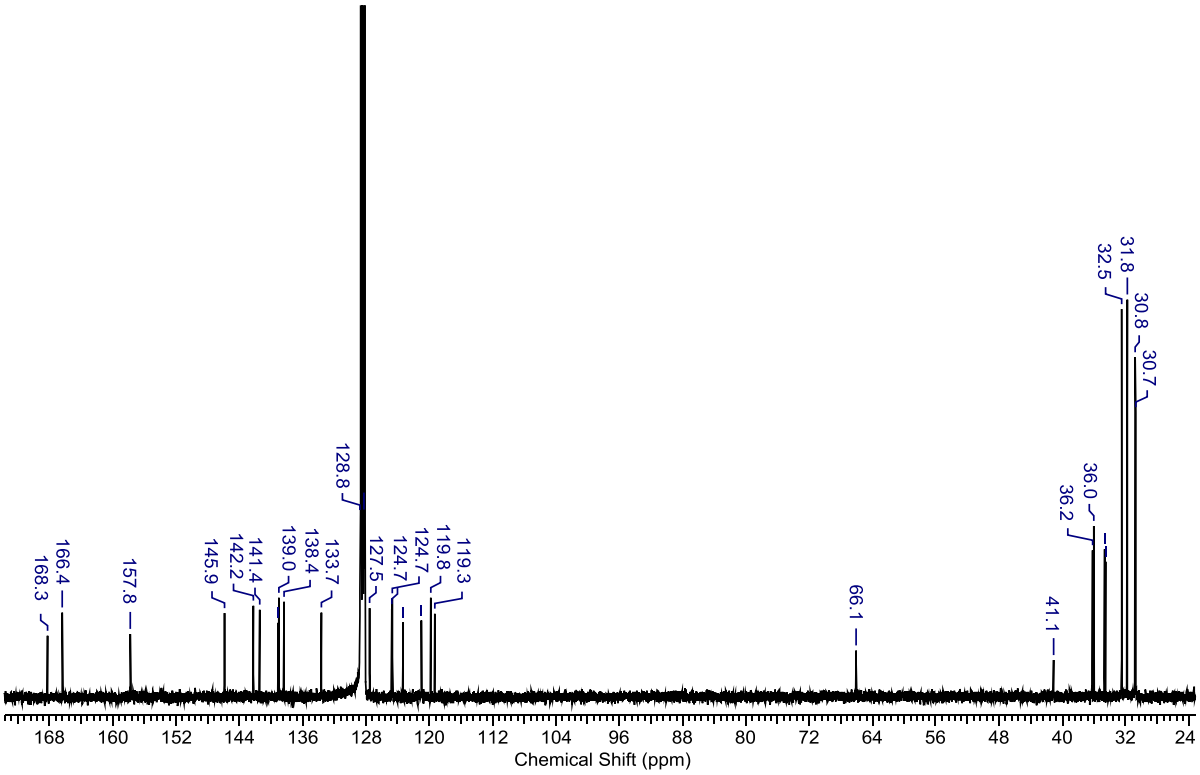


Figure SI4: ^{13}C{^{1}H} NMR spectrum of Al(**1**)Me (C_6D_6)

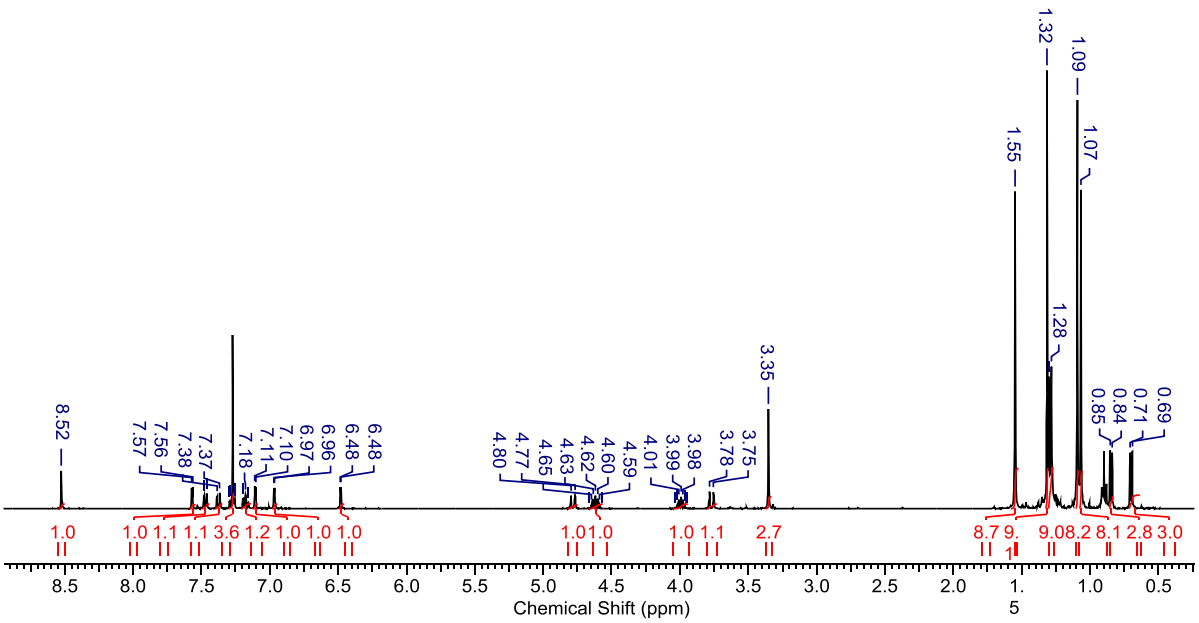


Figure SI5: ^{1}H NMR spectrum of Hf(**1**)(O^{i}Pr)$_2$ (CDCl$_3$)

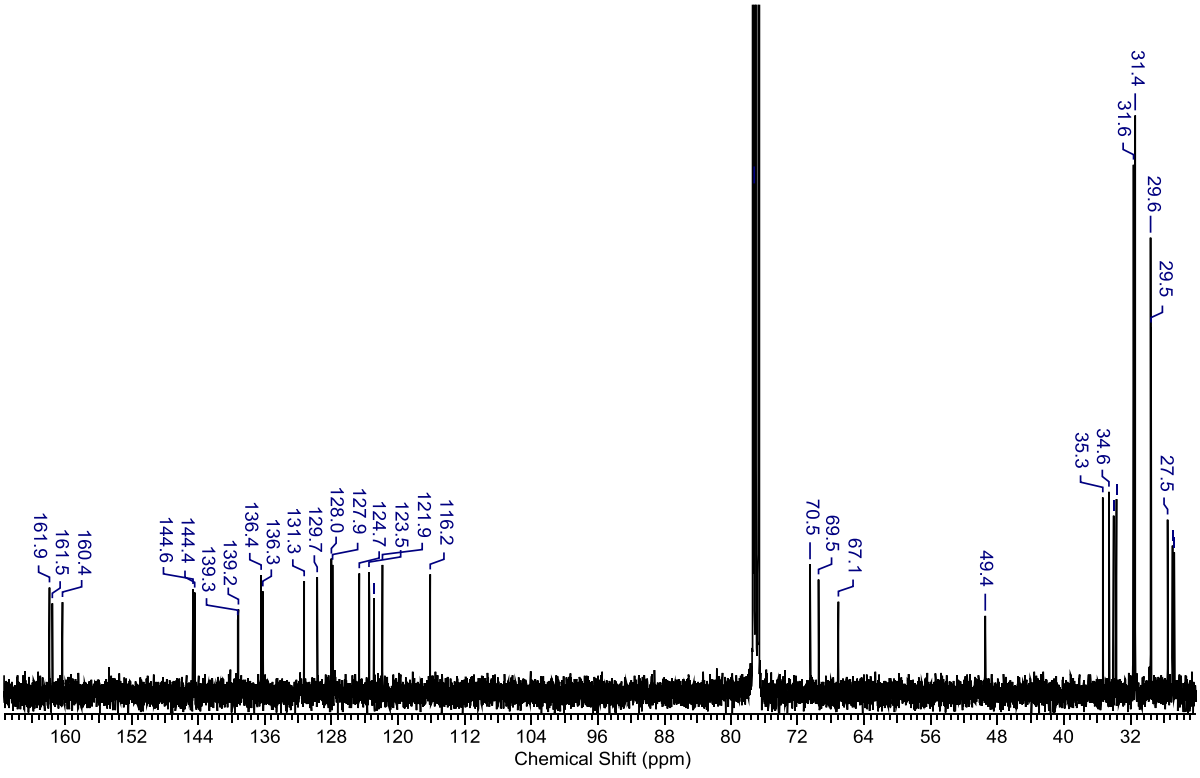


Figure SI6: ^{13}C{^{1}H} NMR spectrum of Hf(**1**)(O^{i}Pr)$_2$ (CDCl$_3$)

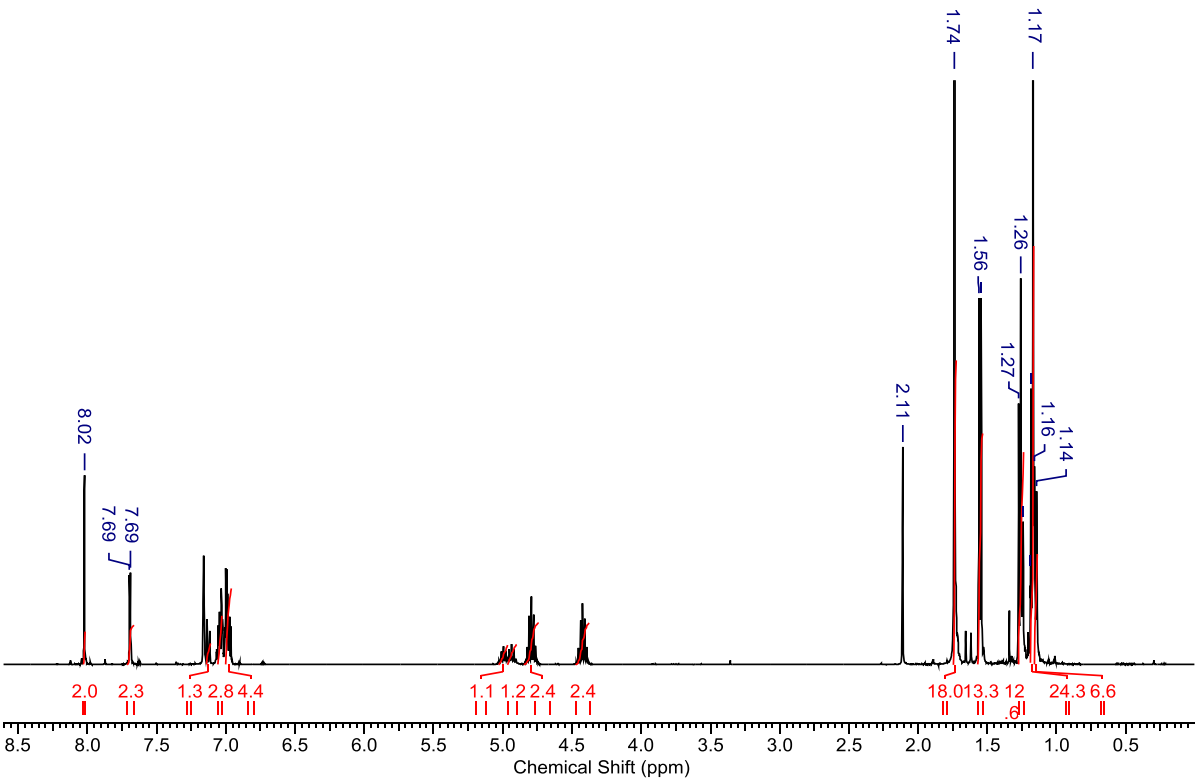


Figure SI7: ^{1}H NMR spectrum of Zr_2(**2**)$(OiPr)_6$ ($CDCl_3$)

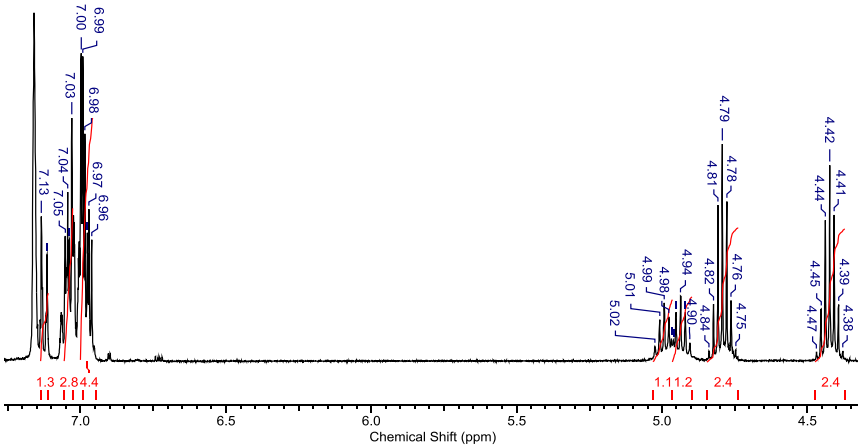


Figure SI8: Zoomed region of ^{1}H NMR spectrum of Zr_2(**2**)$(OiPr)_6$

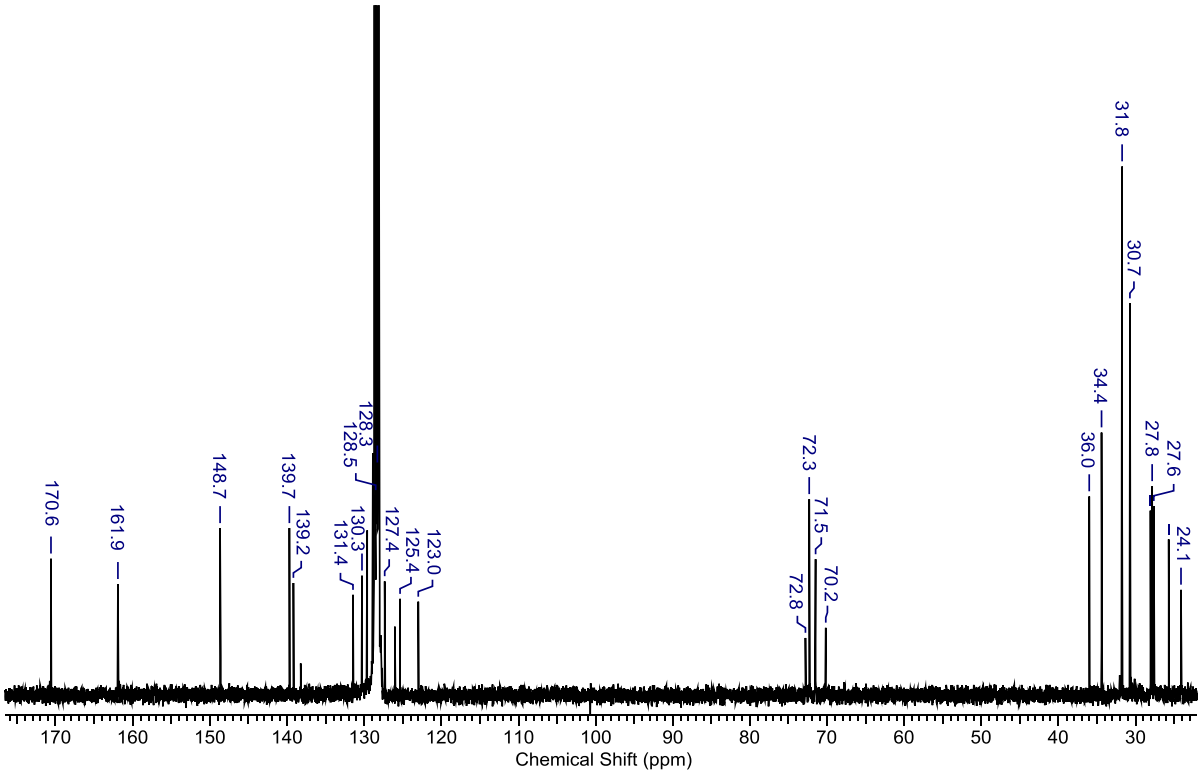


Figure SI9: $^{13}C\{^{1}H\}$ NMR spectrum of Zr_2(**2**)$(OiPr)_6$ ($CDCl_3$)

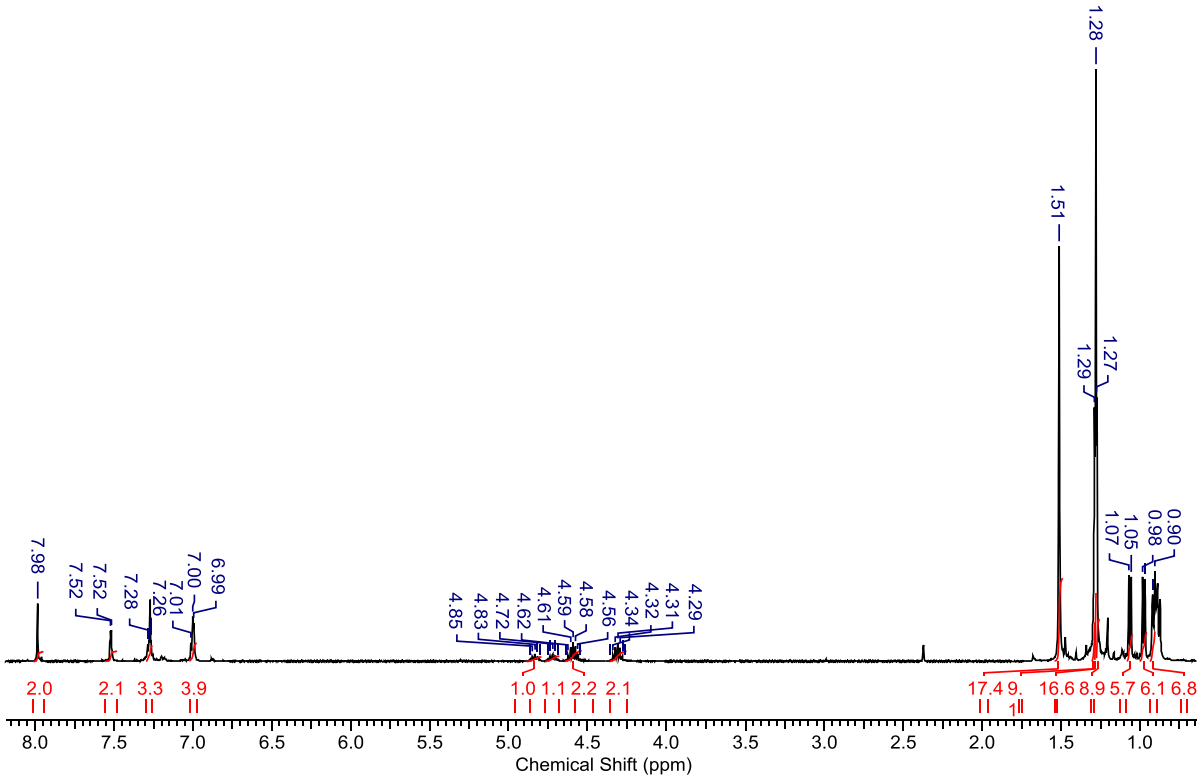


Figure SI10: ^{1}H NMR spectrum of Hf_2(**2**)$(OiPr)_6$ ($CDCl_3$)

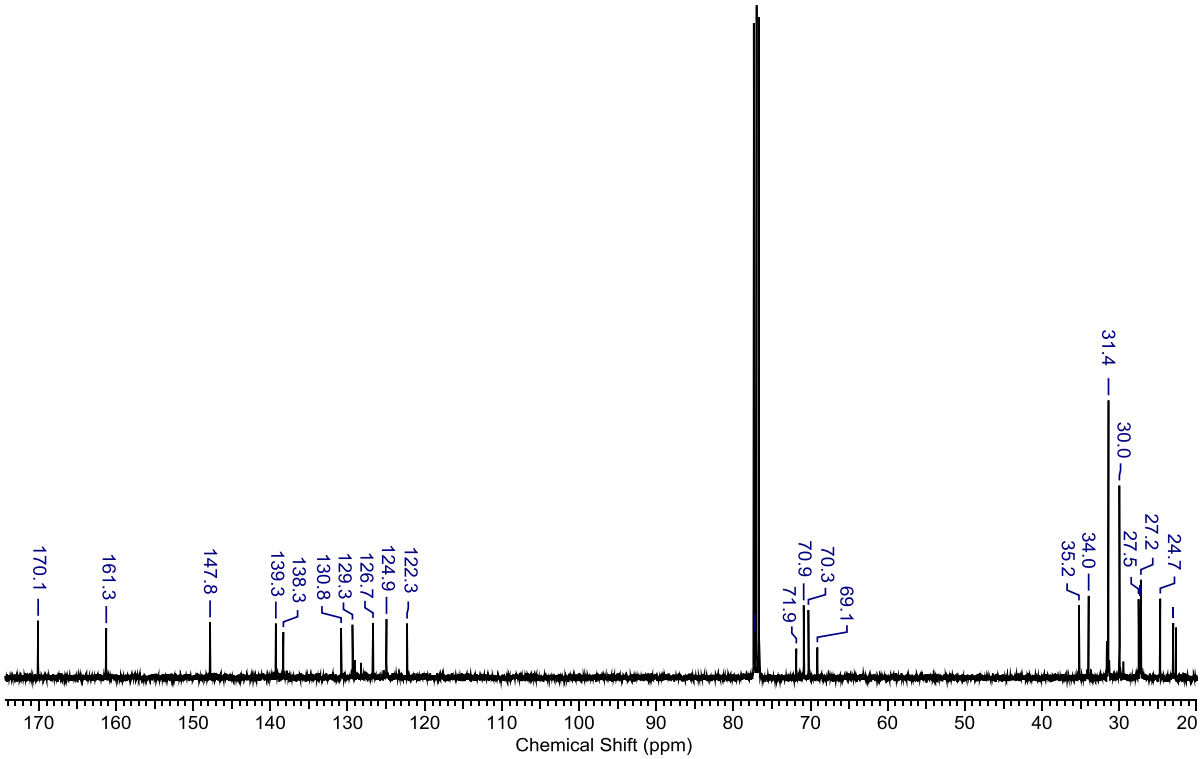


Figure SI11: $^{13}C\{^{1}H\}$ NMR spectrum of Hf_2(**2**)$(OiPr)_6$ ($CDCl_3$)

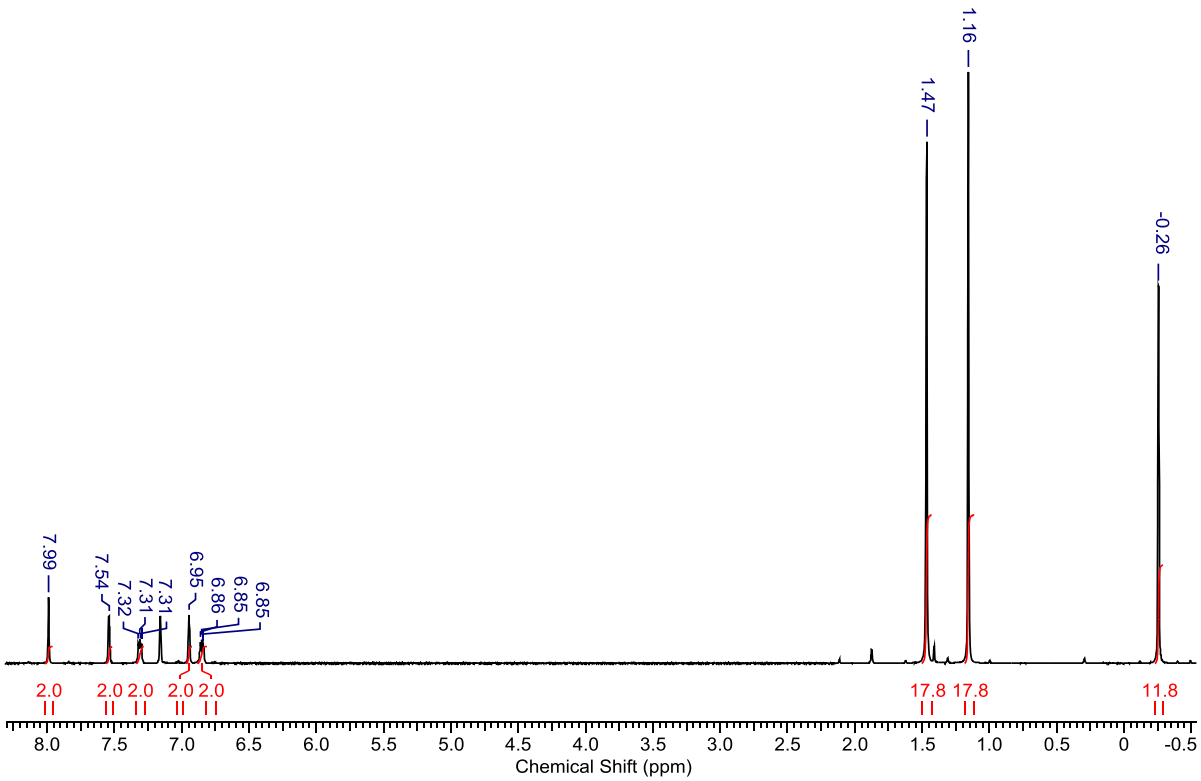


Figure SI12: ^{1}H NMR spectrum of Al_2(**2**)Me_4 (C_6D_6)

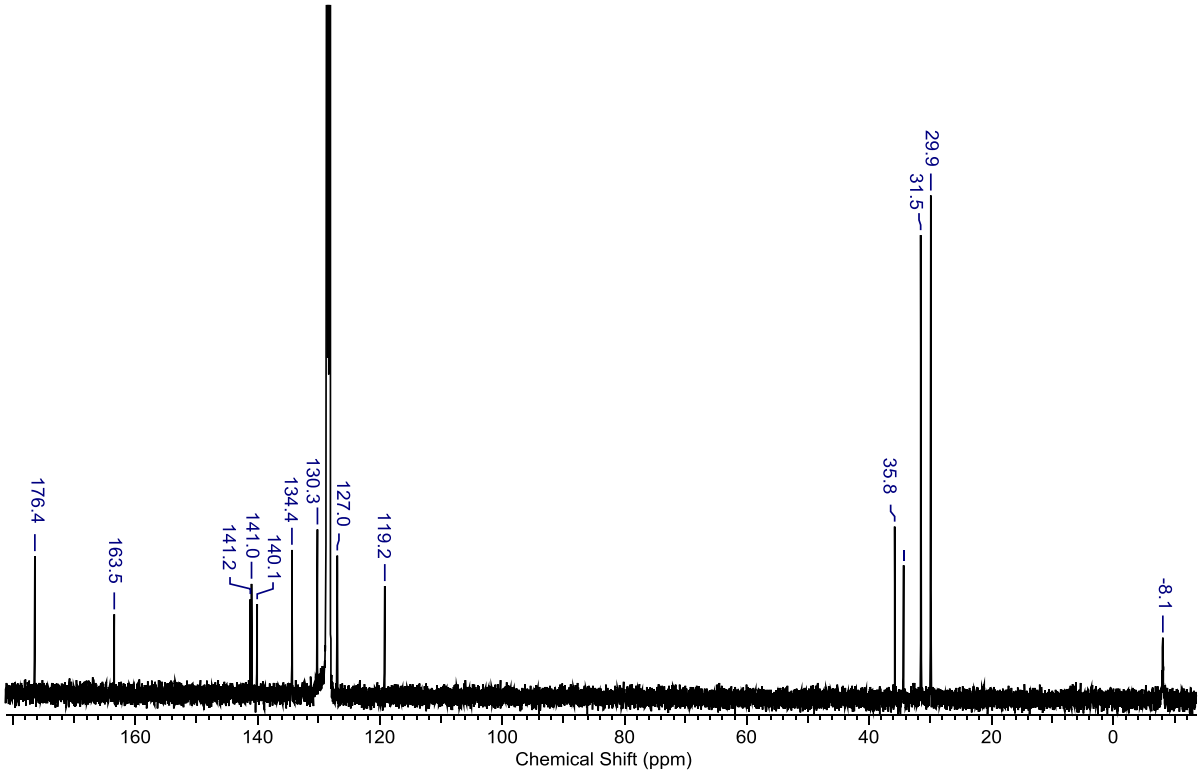


Figure SI13: $^{13}C\{^{1}H\}$ NMR spectrum of Al_2(**2**)Me_4 (C_6D_6)

Selected GPC Traces:

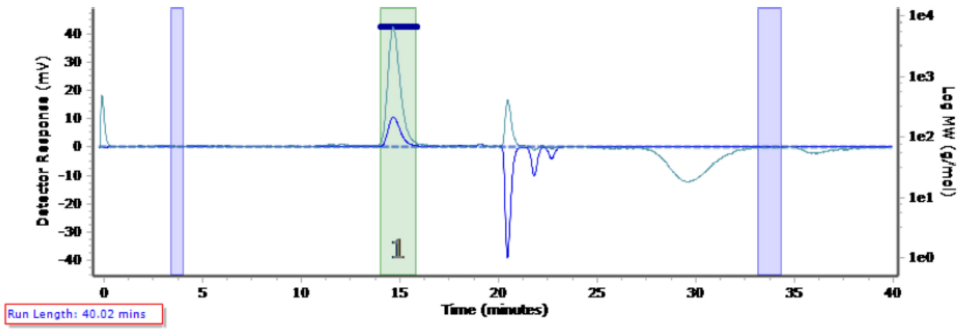


Figure SI14: GPC trace of polylactide produced using 100:1 Zr(**1**)($O^{i}Pr$)$_2$ at 50°C in toluene (Table 1 entry 4)

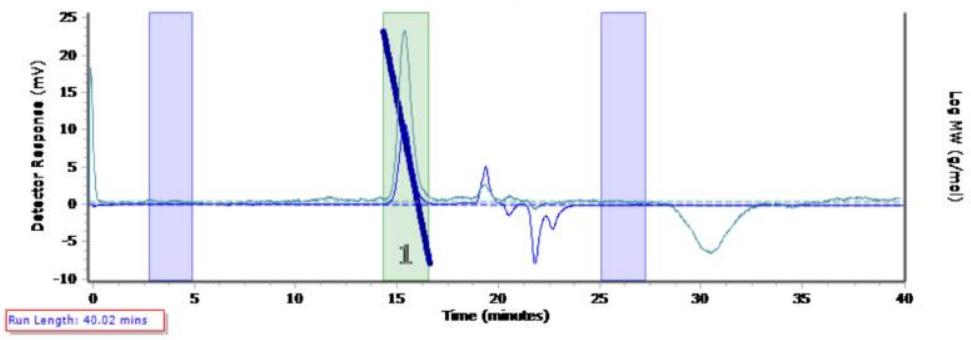


Figure SI15: GPC trace of polylactide produced using 100:1:2 Al_2(**2**)Me_2 at 80°C in toluene (Table 1 entry 13)

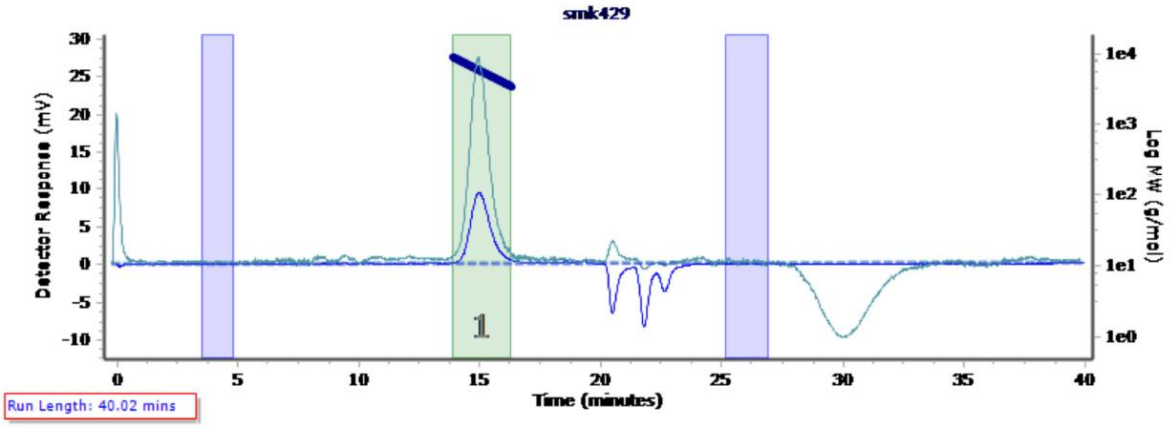


Figure SI16 GPC of the copolymer prepared with Zr(**1**)(O^iPr)$_2$. Table 2 entry 2

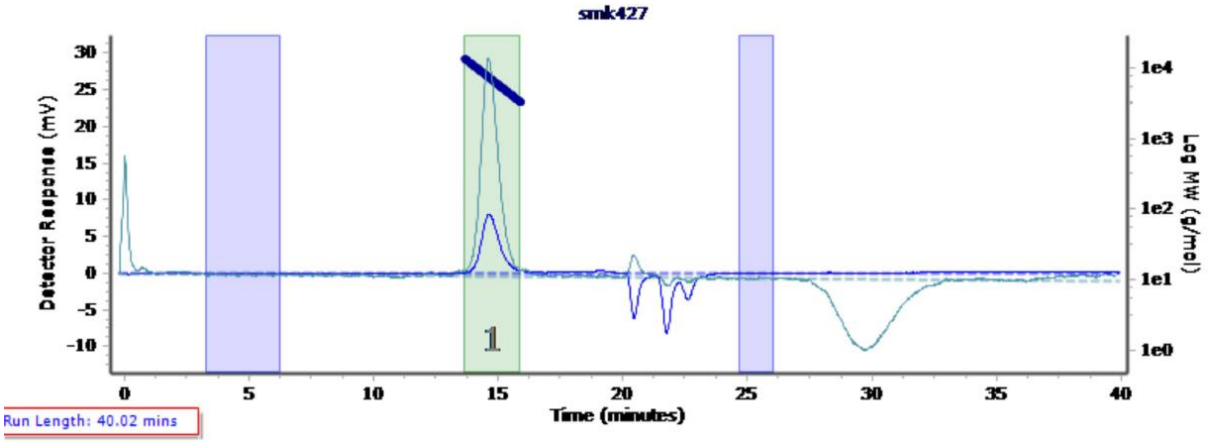


Figure SI17 GPC of the copolymer prepared with Zr(**1**)(O^iPr)$_2$. Table 2 entry 3

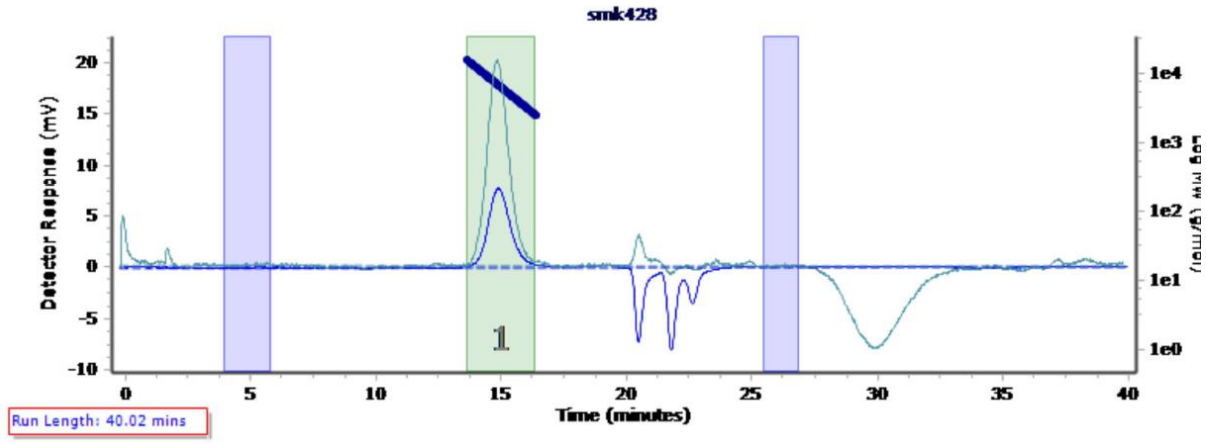


Figure SI18GPC of the copolymer prepared with Zr(**1**)(O^iPr)$_2$. Table 2 entry 4

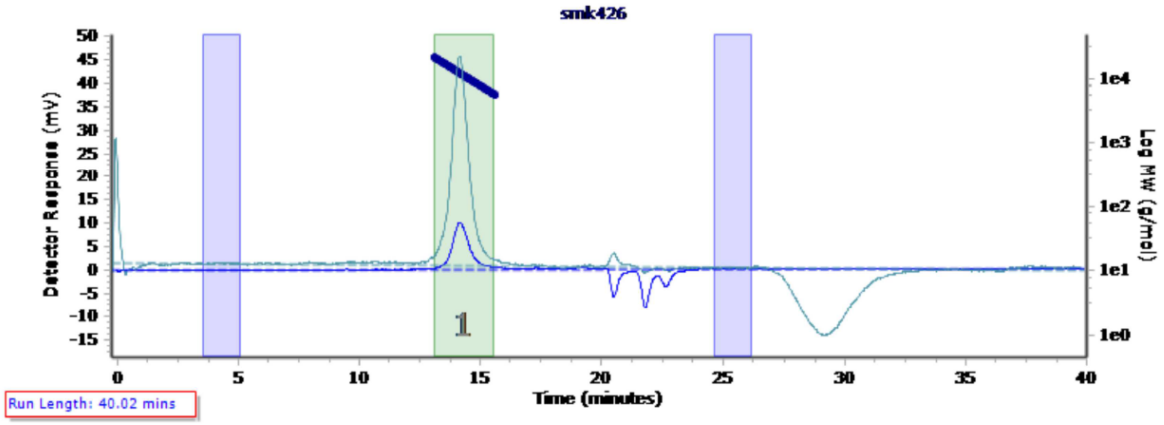


Figure SI19 GPC of the copolymer prepared with Zr(**1**)(O^iPr)$_2$. Table 2 entry 5

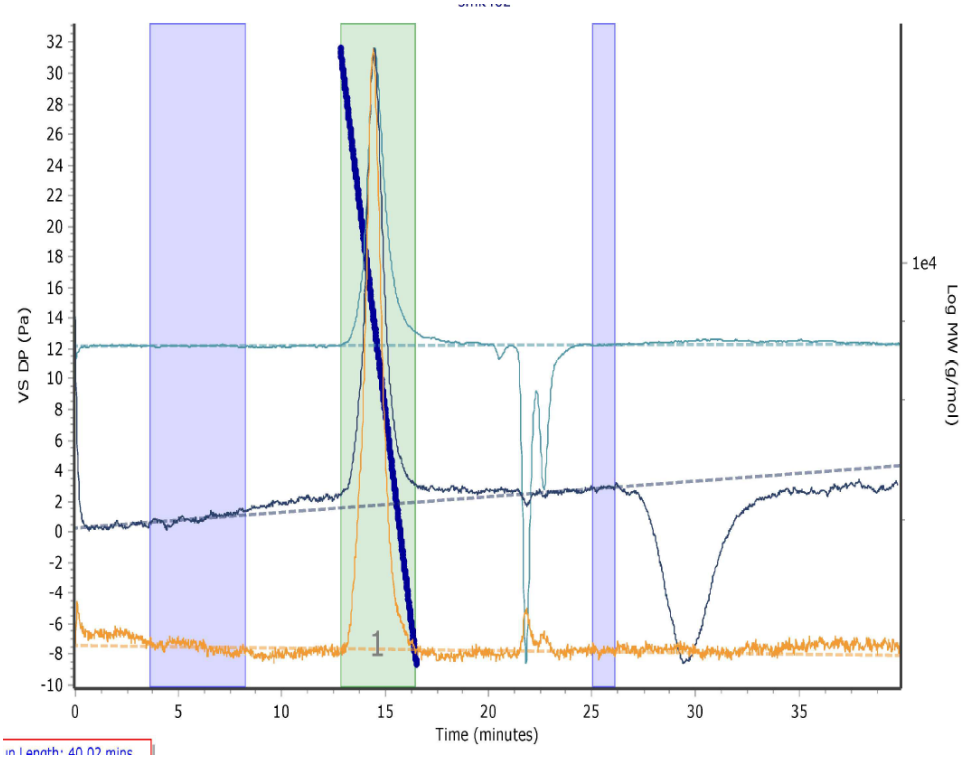


Figure SI20 GPC of the copolymer prepared with Zr(**1**)(O^iPr)$_2$. Table 2 entry 6

Selected Homonuclear NMR Spectra

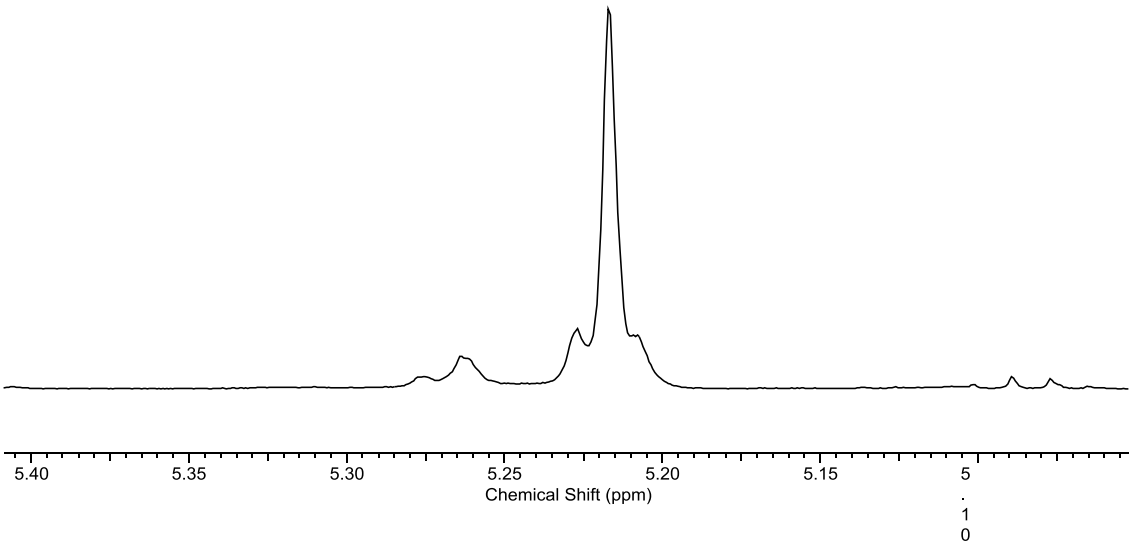
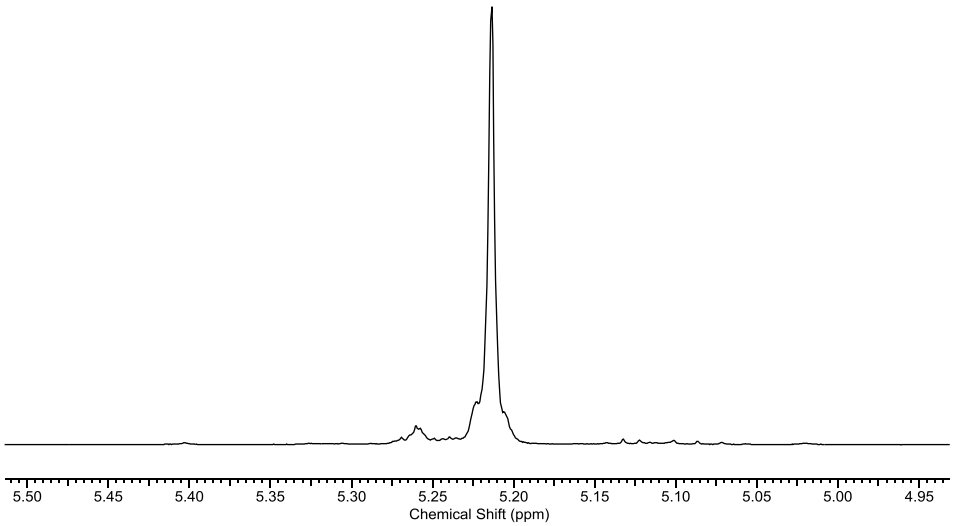
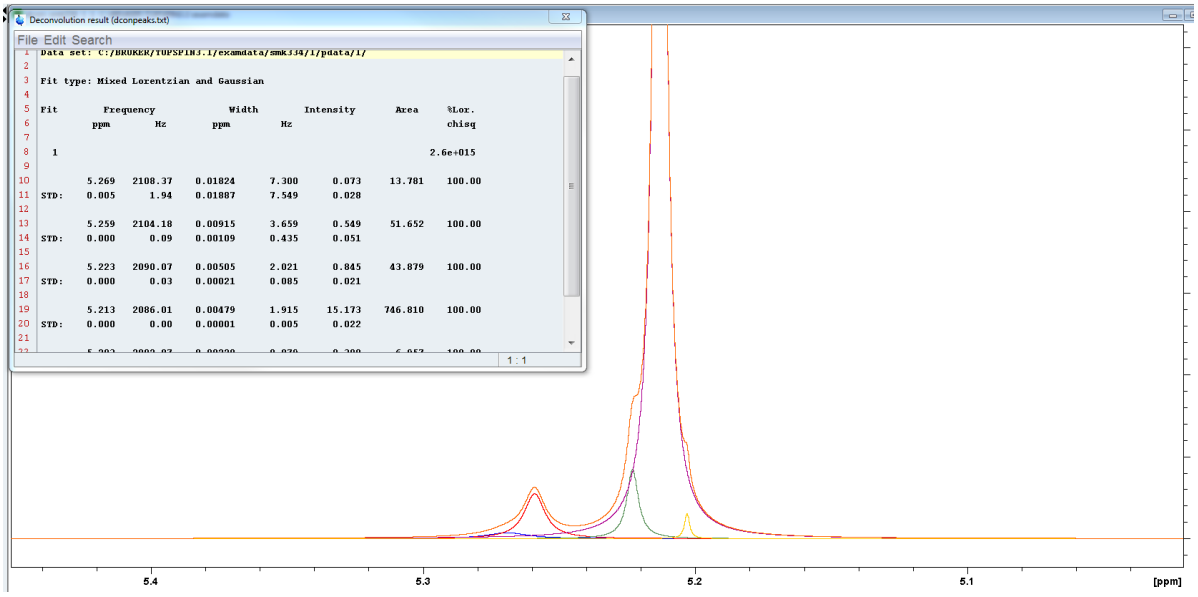


Figure SI21: $^1H\{^1H\}$ NMR spectrum of polylactide produced using 300:1 Zr(**1**)(O^iPr)$_2$ under melt conditions (Table 1 entry 17)


5.50
5.45
5.40
5.35
5.30
5.25
5.20
5.15
5.10
5.05
5.00
4.95
Chemical Shift (ppm)


Deconvolution result (dconpeaks.txt)
File Edit Search
Data set: C:/BRUKER/TOPSPIN3.1/examdata/smk334/1/pdata/1/
Fit type: Mixed Lorentzian and Gaussian
Fit Frequency Width Intensity Area %Lor.
ppm Hz ppm Hz chisq
1 2.6e+015
5.269 2108.37 0.01824 7.300 0.073 13.781 100.00
STD: 0.005 1.94 0.01887 7.549 0.028
5.259 2104.18 0.00915 3.659 0.549 51.652 100.00
STD: 0.000 0.09 0.00109 0.435 0.051
5.223 2090.07 0.00505 2.021 0.845 43.879 100.00
STD: 0.000 0.03 0.00021 0.085 0.021
5.213 2086.01 0.00479 1.915 15.173 746.810 100.00
STD: 0.000 0.00 0.00001 0.005 0.022
1 : 1
5.4
5.3
5.2
5.1
[ppm]

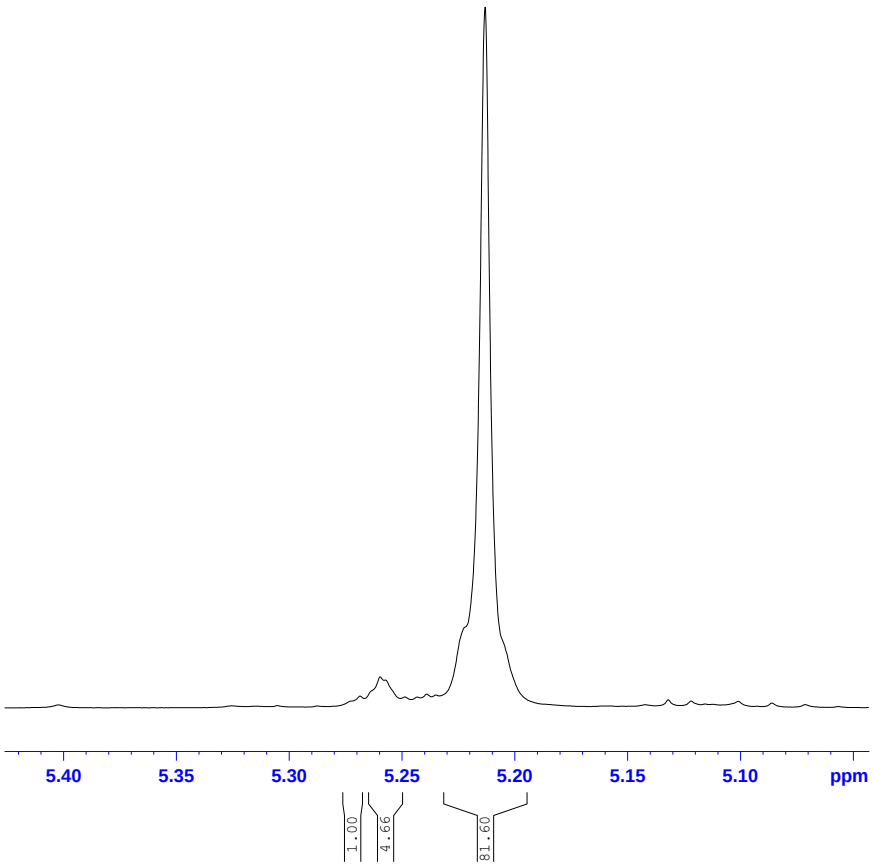


Figure SI22: $^{1}H\{^{1}H\}$ NMR spectrum of polylactide produced using 100:1 Zr(**1**)($O^{i}Pr$)$_2$ at 50°C in toluene (Table 1 entry 4). We determine the P_m values by deconvolution of the spectrum and then using the values and the 5 equations based on the isi, sis, iis, iii or ssi tetrads to determine P_m and then we take an average. We also integrate and use the equation [isi] = $[P_r]^2/2$. The value reported is the lower of these two methods.

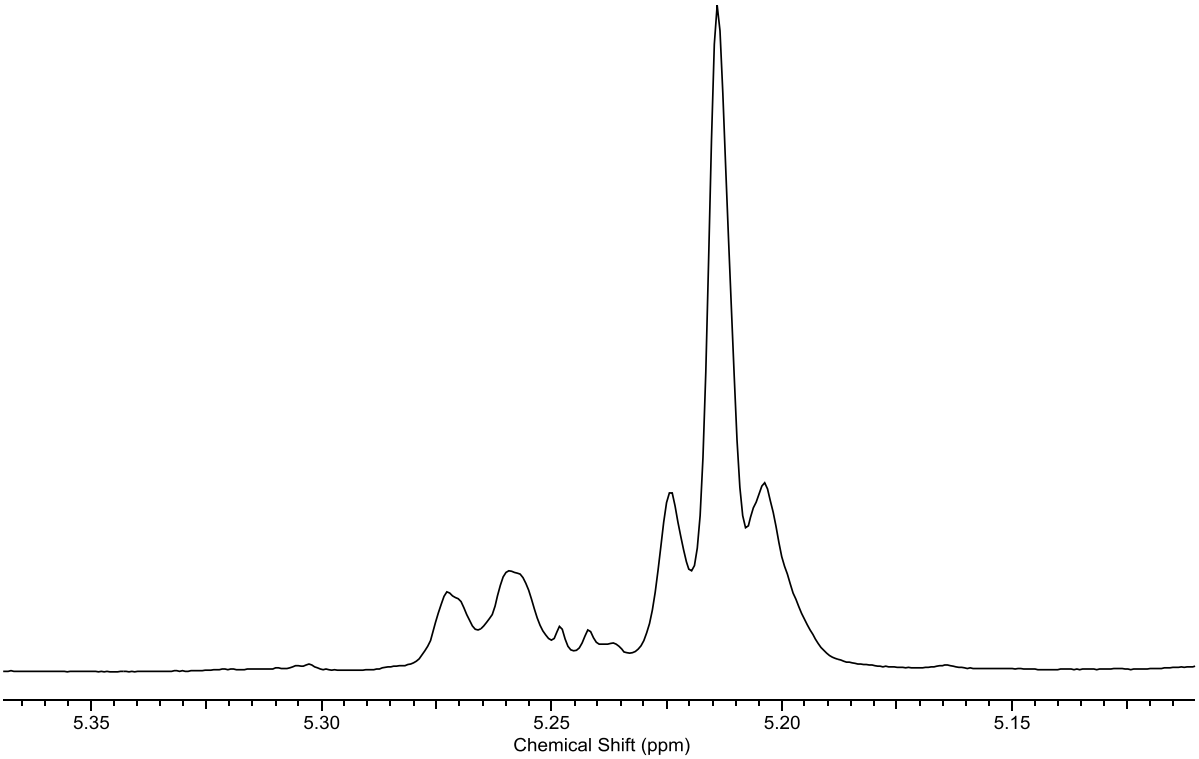


Figure SI23: $^{1}H\{^{1}H\}$ NMR spectrum of polylactide produced using 100:1:1 Al(**1**)Me at 80°C in toluene (Table 1 entry 9)

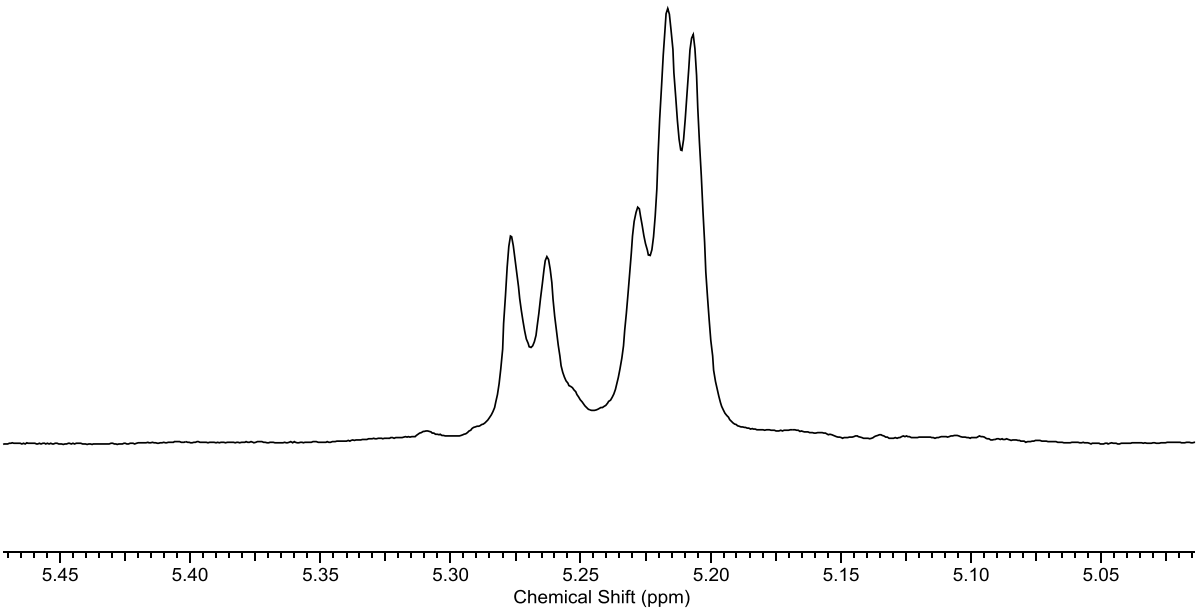


Figure SI24: $^{1}H\{^{1}H\}$ NMR spectrum of polylactide produced using 100:1 Zr_2(**2**)($O^{i}Pr$)$_6$ at 80°C in toluene (Table 1 entry 5)

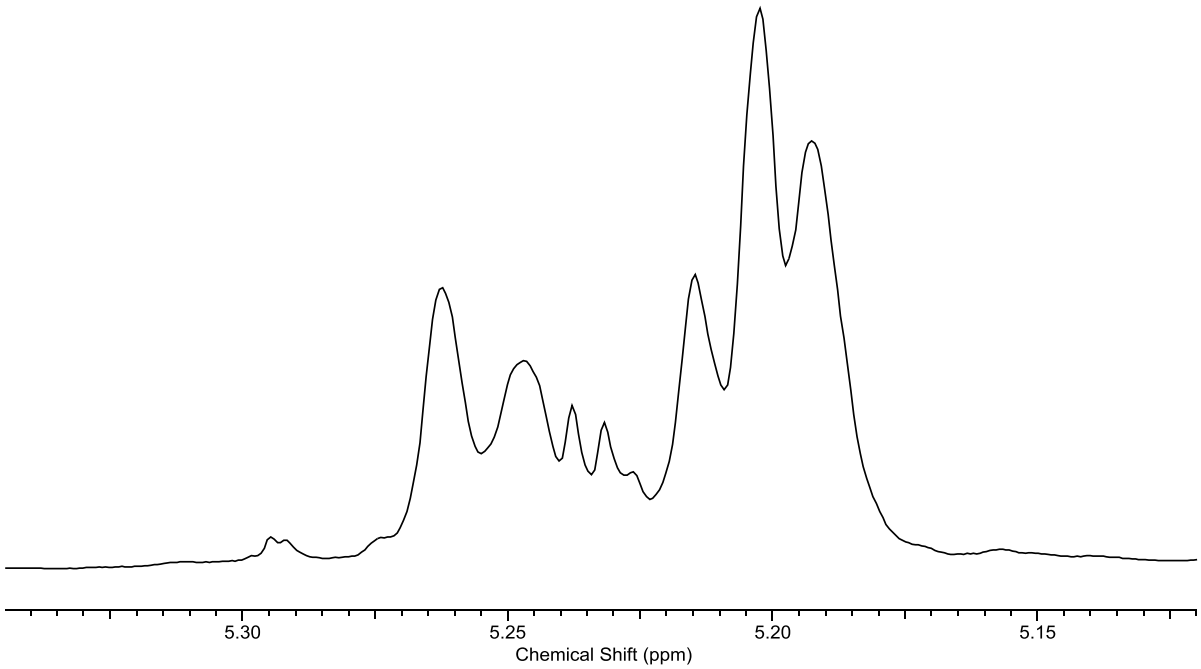


Figure SI25: $^{1}H\{^{1}H\}$ NMR spectrum of polylactide produced using 100:1:2 Al_2(**2**)Me_2 at 80°C in toluene (Table 1 entry 13)

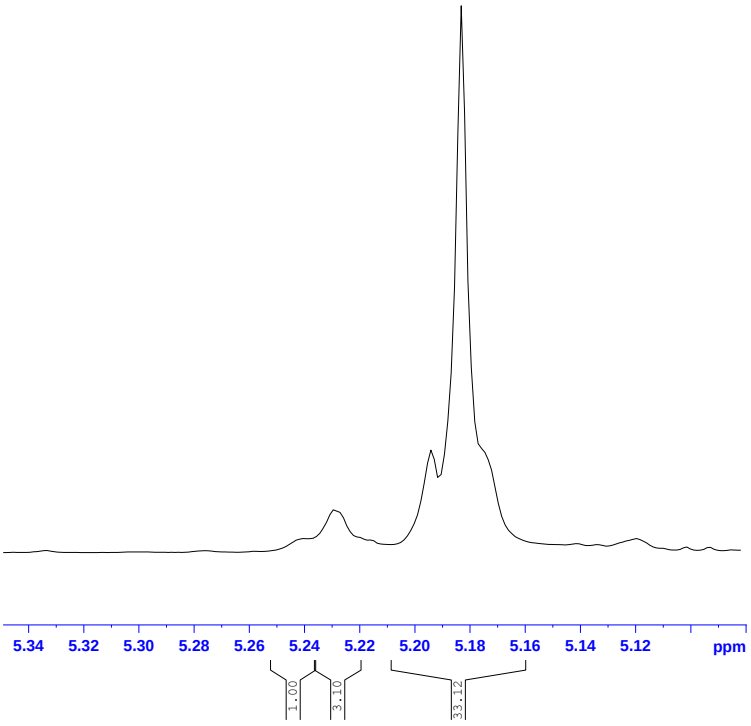


Figure SI26: $^{1}H\{^{1}H\}$ NMR spectrum of copolymer produced with Zr(**1**)($O^{i}Pr$)$_2$ Table 2 entry 3.

Kinetic Plots

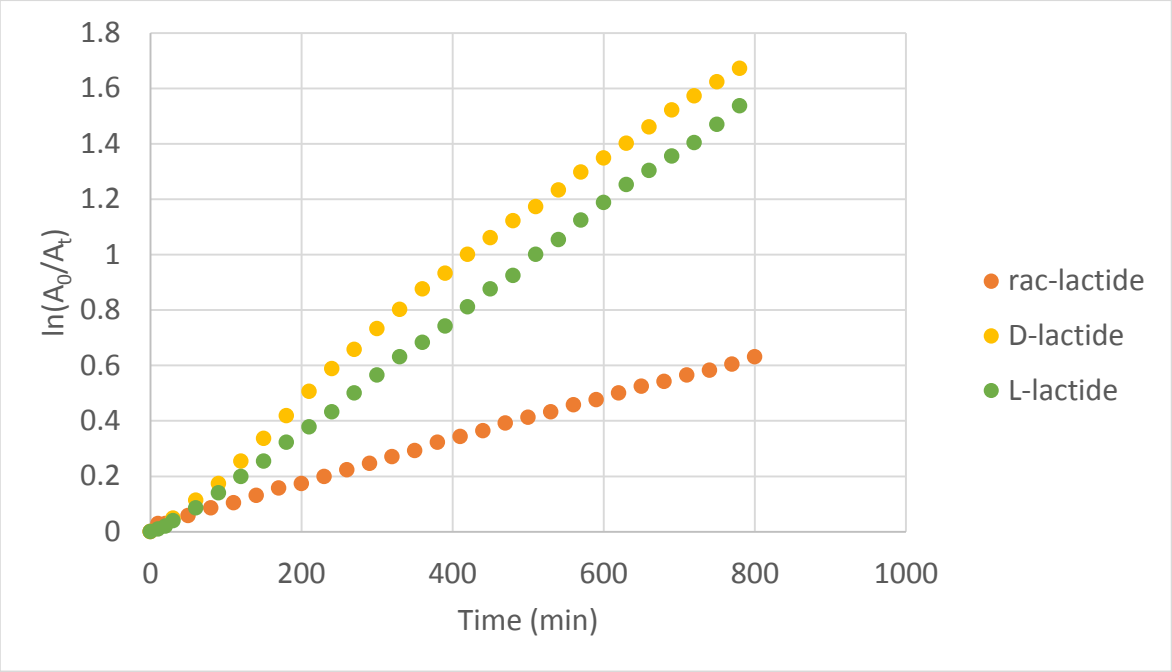


Figure SI27: Pseudo first-order rate plot for D-, L- and *rac*- lactide at 100:1 using Zr(**1**)(O^iPr)$_2$ at 80°C in toluene

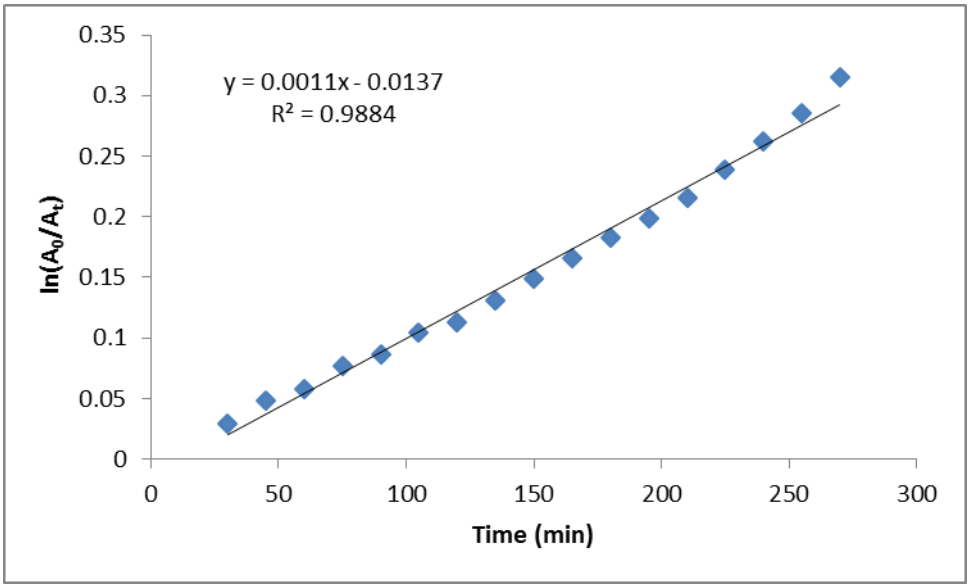


Figure SI28: Pseudo first-order rate plot for *rac*- lactide at 100:1 (LA:Zr) using Zr_2(**2**)(O^iPr)$_6$ at 80°C in toluene. Both kinetic complexes are comparing the same metal basis.

DSC Images:

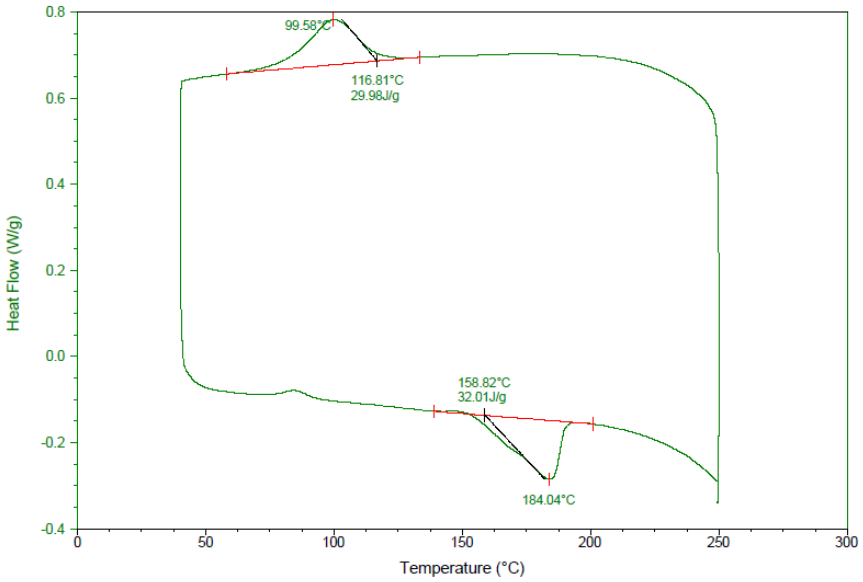


Figure SI29: DSC of polylactide produced using 100:1 Zr(**1**)(O^iPr)$_2$ at 50°C in toluene

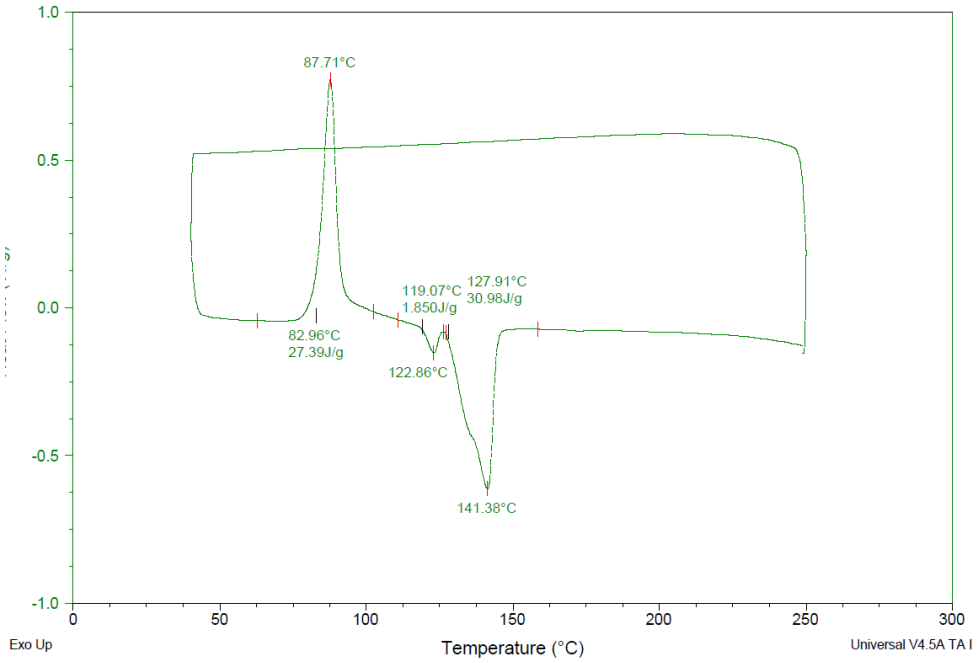


Figure SI30: DSC of PLLA-PCL produced using 75:25 with Zr(**1**)(O^iPr)$_2$ Table 2 entry 6

MALDI-ToF Sepctra:

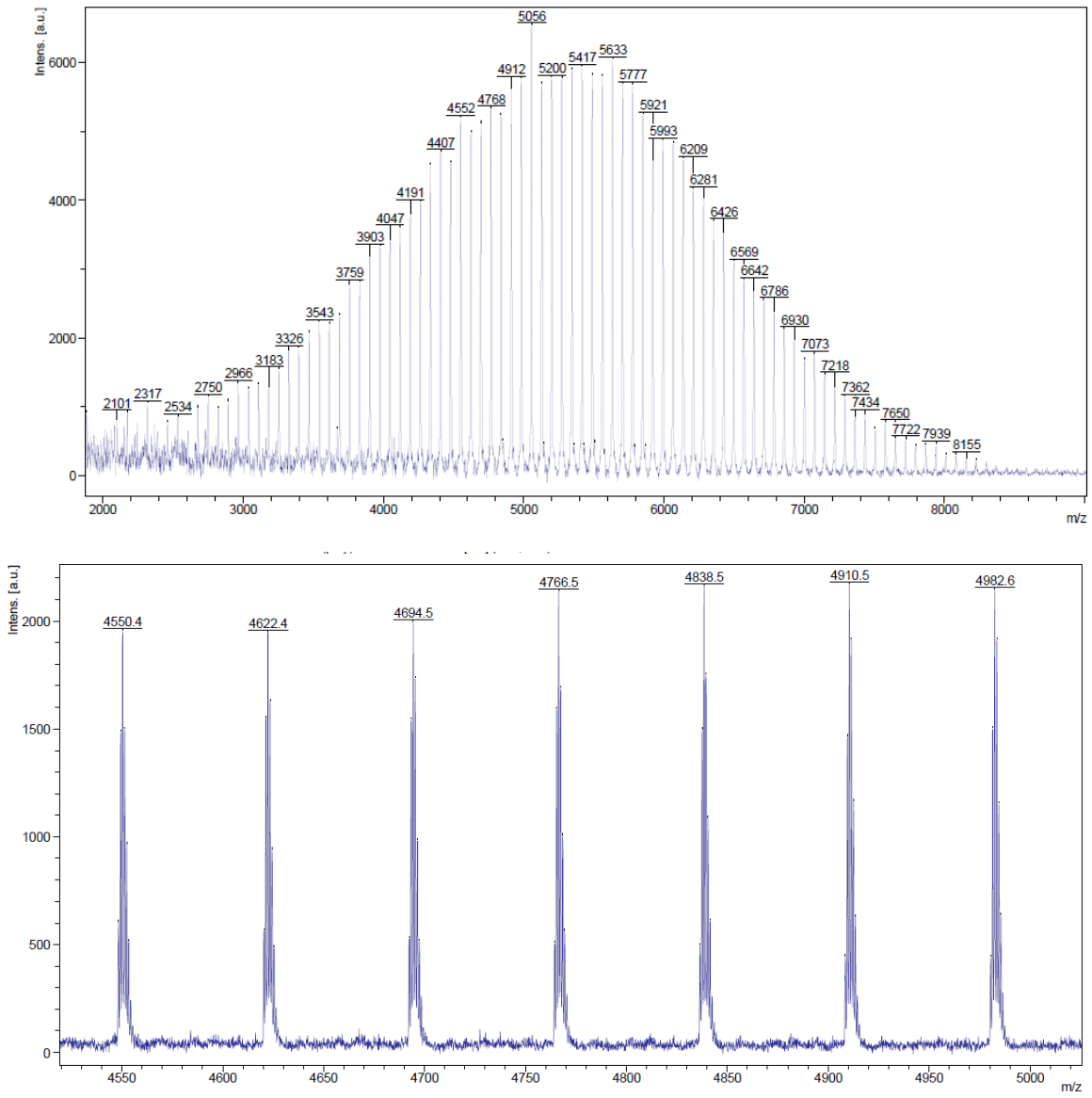


Figure SI31: MALDI-ToF for PLA produced using 100:1 Zr(**1**)(O^iPr)$_2$ at 50°C in toluene (Table 1 entry 4). Peak at 4838.5 g/mol $H(C_6H_8O_4)_{33}OC_3H_7$.Na

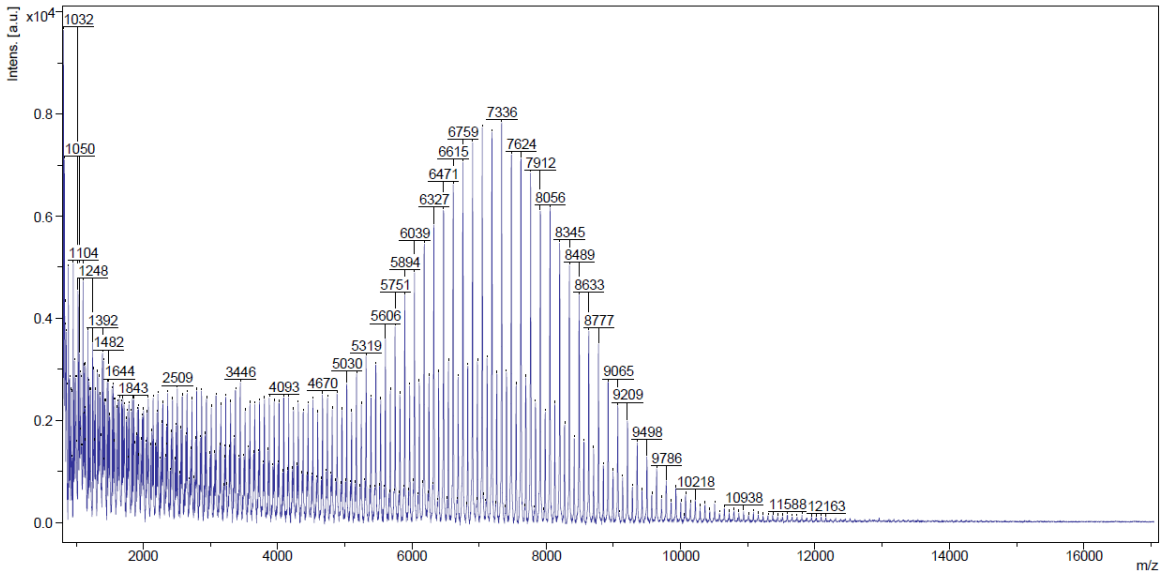


Figure SI32: MALDI-ToF for PLA produced using 100:1 Al(**1**)Me with 1 eq BnOH (Table 1 entry 9) peak at 7336 g/mol $H(C_6H_8O_4)_{50}OC_7H_7.Na$

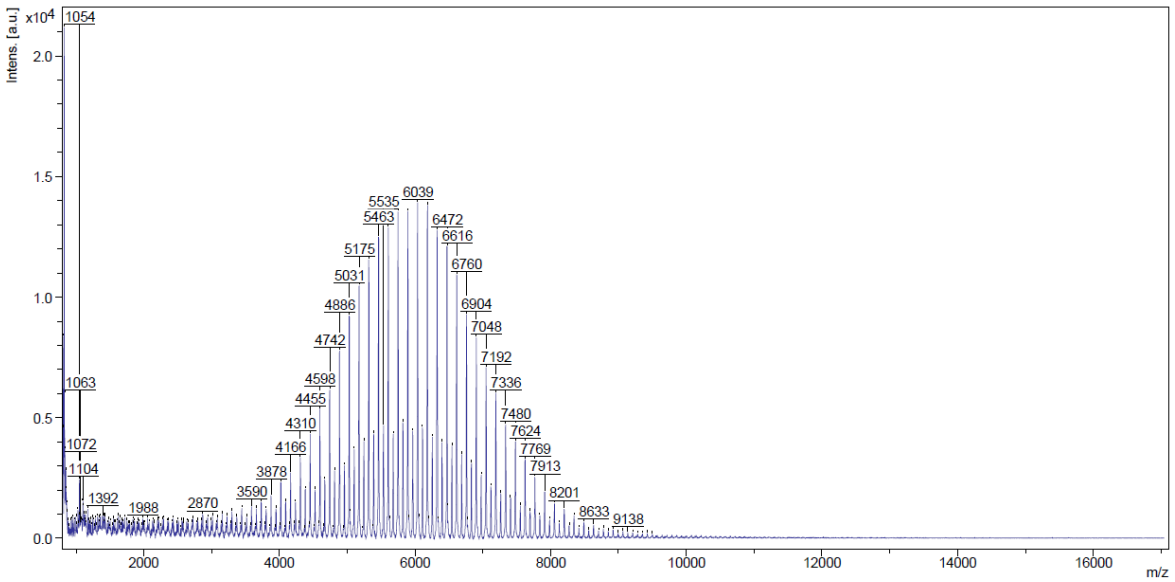


Figure SI33: MALDI-ToF for PLA produced using 100:1 Al(**1**)Me with 1 eq BnOH (Table 1 entry 12) peak at 6039 g/mol $H(C_6H_8O_4)_{41}OC_7H_7.Na$

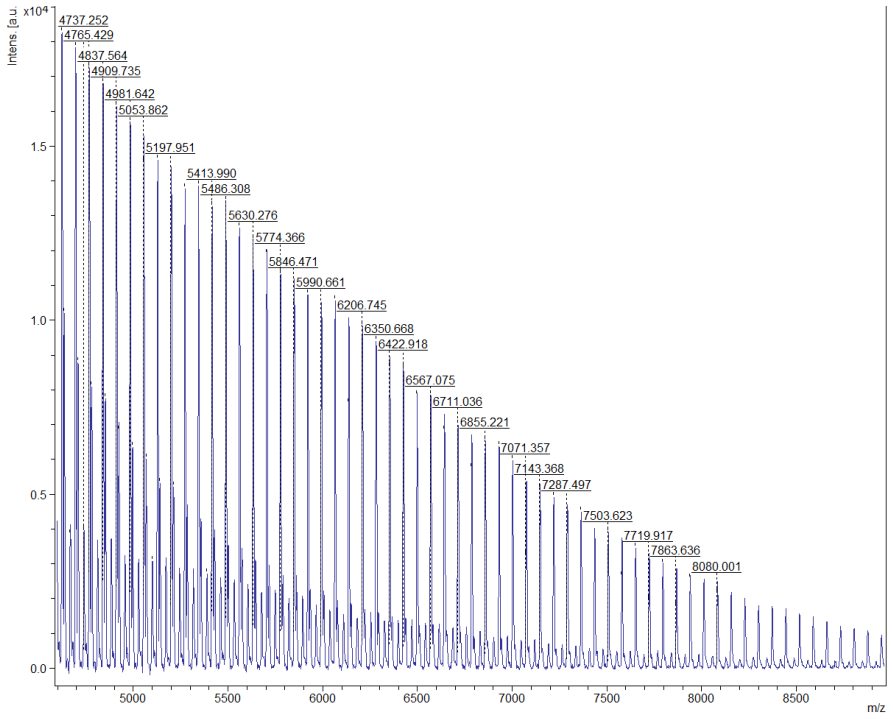


Figure SI34: MALDI-ToF for PLA produced using 100:1 $Zr_2(\mathbf{2})_2(O^iPr)_6$ at 80°C in toluene. (Table 1 entry 5) Peak at 4981.6 g/mol $H(C_6H_8O_4)_{34}OC_3H_7.Na$

Table SI 1 Crystallographic Parameters

Compound reference	Zr(**1**)$(OiPr)_2$	Zr_2(**2**)$(OiPr)_6$	Al(**1**)Me	Al_2(**2**)Me_4	Hf(**1**)$(OiPr)_2$	Hf_2(**2**)$(OiPr)_6$
Chemical formula	$C_{43}H_{64}N_2O_4Zr$	$2(C_{54}H_{88}N_2O_8Zr_2)$ $\bullet 5(C_7H_8)$	$C_{38}H_{53}AlN_2O_2$	$C_{40}H_{58}Al_2N_2O_2$	$C_{91}H_{140}Hf_2N_4O_8$	$C_{54}H_{88}Hf_2N_2O_8$ $\bullet 1.5(C_6H_{14})$
Formula Mass	764.18	2612.06	596.80	652.84	1775.04	1379.50
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
a/Å	14.9527(4)	10.6100(3)	9.36640(10)	39.9899(3)	14.665(4)	15.0674(3)
b/Å	20.9673(4)	13.4662(3)	29.9373(2)	21.8307(2)	22.490(3)	15.3066(3)
c/Å	15.1609(5)	27.2278(7)	13.10040(10)	9.34980(10)	15.545(3)	16.2254(4)
α/°	90	101.501(2)	90	90	90	89.944(2)
β/°	115.285(3)	90.510(2)	105.9740(10)	90	114.16(2)	65.437(2)
γ/°	90	107.840(2)	90	90	90	87.572(2)
Unit cell volume/Å^3	4297.8(2)	3618.57(17)	3531.57(5)	8162.45(13)	4677.8(17)	3399.81(14)
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$Fdd2$	$P2_1/n$	$P\bar{1}$
No. of formula units per unit cell, *Z*	4	1	4	8	2	2
No. of reflections measured	34194	37526	49141	33608	70175	26427
No. of independent reflections	11290	18460	6932	3849	10594	12915
R_{int}	0.0393	0.0204	0.0234	0.0275	0.0671	0.0231
Final R_1 values ($I > 2\sigma(I)$)	0.0422	0.0417	0.0337	0.0242	0.0625	0.0291
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0873	0.0876	0.0860	0.0660	0.1132	0.0698
Final R_1 values (all data)	0.0695	0.0577	0.0353	0.0242	0.1041	0.0351
Final $wR(F^2)$ values (all data)	0.0991	0.0962	0.0872	0.0660	0.1269	0.0741

Table SI 2 DOSY NMR Parameters for selected complexes

Sample	D/ m^2s^{-1}	r
Zr_2(**2**)$(O^iPr)_6$	6.9×10^{-10}	5.8 Å
Zr(**1**)$(O^iPr)_2$	6.9×10^{-10}	5.8 Å
Hf_2(**2**)$(O^iPr)_6$	6.3×10^{-10}	6.3 Å
Hf(**1**)$(O^iPr)_2$	6.9×10^{-10}	5.8 Å