SUPPORTING INFORMATION

Zirconium complexes of bipyrrolidine derived Salan ligands for the isoselective polymerisation of rac-lactide

Matthew D. Jones, Stuart L. Hancock, Paul McKeown, Pascal M. Schäfer, Antoine Buchard, Lynne H. Thomas, Mary F. Mahon and John P. Lowe

General Experimental:

For the preparation and characterisation of metal complexes, all reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk or glovebox techniques. *rac*-LA (Aldrich) was recrystallised from toluene prior to use. All other chemicals were purchased from Aldrich, except the pyrrolidines which were purchased from Orbiter. All solvents used in the preparation of metal complexes and polymerisation reactions were dry and obtained *via* SPS (solvent purification system). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 250, 300 or 400 or 500 MHz instrument and referenced to residual solvent peaks. Coupling constants are given in Hertz. CHN microanalysis was performed by Mr Stephen Boyer of London Metropolitan University.

Polymerisations:

For solvent-free polymerizations the monomer:initiator ratio employed was 300:1 at a temperature of 130 °C, in all cases 1.0 g of *rac*-lactide were used. After the reaction time methanol (20 ml) was added to quench the reaction and the resulting solid was dissolved in dichloromethane. For *rac*-BBL a ratio of 300:1 of monomer to inititator was utilised with 1.0 ml of monomer at 80 ºC. The solvents were removed in vacuo and the resulting solid was washed with copious amounts of methanol to remove any unreacted lactide monomer. ^{1}H NMR spectroscopy ($CDCl_3$) and GPC (THF) were used to determine tacticity and molecular weights (M_n and M_w) of the polymers produced; P_m (the probability of isotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ^{1}H NMR spectra, the equations used to calculate P_r and P_m are given by Coates *et al*. [1]

1. 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.

For solution polymerisations the monomer:initiator ratio employed was 100:1 at a temperature of 25 or 70 °C, in all cases 0.72 g of *rac*-LA was used. After the reaction time the reaction was quenched with methanol. The solvents were removed in vacuo and the resulting solid was washed with copious amounts of methanol to remove any unreacted monomer. GPC (THF) was used to determine molecular weights (M_n and M_w) of the polymers produced.

DSC

The DSC analyses were recorded on a TA Instruments DSC Q20. The sample was held at 40 ºC for 1 minute, heated to 250 ºC at 5 ºC/min held at this temperature for 1

minute, cooled to 40 ºC at 5 ºC/min held at this temperature for 1 minute and finally heated to 250 ºC at 5 ºC/min - the T_m values are quoted for the second heating cycle.

MALDI-ToF

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 NaOAc.

Crystallography:

All data were collected on a Xcalibur, Atlas diffractometer using Cu-Kα radiation (λ = 1.54184 Å) at 150(2) K. All structures were solved by direct methods and refined on all F^2 data using the SHELXL-97 suite of programs. All hydrogen atoms were included in idealised positions and refined using the riding model. Refinements were generally straightforward with the following exceptions and points of note. **3**H_2 – none. Zr(**1**)(O^iPr)$_2$ - Refined as a 2-component twin with pseudo merhedral twinning about the 1 1 0 direction (56:44). Zr(**2**)(O^iPr)$_2$ - Refined as a 2-component twin with pseudo merhedral twinning about the 1 1 0 direction (57:43). Zr(**3**)(O^iPr)$_2$ – Two coordinated isopropoxide moieties C1 C2 C3 and C4 C5 C6 are disordered over two positions (C1a C2a C3a and C4a C5a C6a). Anisotropic refinement of these atoms results in unreasonable displacement parameters due to large thermal motions of the atoms. The ISOR restraint was therefore applied to these atoms in the refinement. The relative occupancies of these two positions were allowed to freely refine to 52:48 and 60:40, respectively

Synthesis of ligands:

The general procedure is as follows: 2,2'-bipyrrolidine (1.0 g, 7.14 mmol) was dissolved in methanol (50 ml) to which 2,4-dimethyl phenol (1.8 ml, 14.8 mmol) was added together with paraformaldehyde (2.0 g) and heated to reflux for 4 hrs. Upon cooling a white precipitate was observed which was collected by filtration and washed with cold methanol and dried. Yields were approximately 40 % in all cases.

Ligand **1**H_2

^{1}H ($CDCl_3$) 1.60 (m, br, 2H), 1.83 (m, br 6H), 2.06 (m, br, 2H), 2.20 (s, 6H), 2.22 (s, 6H), 2.95 (m, br, 2H), 3.07 (m, br, 2H) 3.29 (d J = 13.5 Hz, 2H), 4.24 (d J = 13.5 Hz 2H), 6.64 (s, 2H), 6.86 (s, 2H), 10.69 (s, br 2H).

^{13}C{^{1}H} ($CDCl_3$) 15.7 (CH_3), 20.4 (CH_3), 23.6 (CH_2), 25.4 (CH_2), 54.8 (CH_2), 58.1 (CH_2), 64.8 (CH), 121.4 (Ar), 124.3 (Ar), 126.0 (Ar-H) 127.6 (Ar) 130.4 (Ar-H), 153.1 (Ar-O).

HR-MS $C_{26}H_{36}N_2O_2$+Na Theo. 431.2674 found 431.2688.

Ligand **2**H_2

^{1}H ($CDCl_3$) 1.60 (m, br, 2H), 1.84 (m, br 6H), 2.05 (m, br, 2H), 2.20 (s, 6H), 2.21 (s, 6H), 2.95 (m, br, 2H), 3.06 (m, br, 2H) 3.29 (d J = 13.5 Hz, 2H), 4.23 (d J = 13.5 Hz 2H), 6.64 (s, 2H), 6.86 (s, 2H), 10.68 (s, br 2H).

^{13}C{^{1}H} ($CDCl_3$) 15.7 (CH_3), 20.4 (CH_3), 23.6 (CH_2), 25.3 (CH_2), 54.8 (CH_2), 58.0 (CH_2), 64.8 (CH), 121.3 (Ar), 124.3 (Ar), 126.0 (Ar-H) 127.6 (Ar) 130.4 (Ar-H), 153.0 (Ar-O)

HR-MS $C_{26}H_{36}N_2O_2$+Na Theo. 431.2674 found 431.2692.

Ligand **3**H_2

^{1}H ($CDCl_3$) 1.83 (m, br, 4H), 1.93 (m, br 2H), 2.06 (m, br, 2H), 2.20 (s, 6H), 2.22 (s, 6H), 2.36 (m, br, 2H), 2.95 (m, br, 2H), 3.07 (m, br, 2H) 3.40 (d J = 13.5 Hz, 2H), 4.35 (d J = 13.5 Hz 2H), 6.64 (s, 2H), 6.86 (s, 2H), 10.69 (s, br 2H).

^{13}C{^{1}H} ($CDCl_3$) 15.7 (CH_3), 20.4 (CH_3), 23.0 (CH_2), 28.4 (CH_2), 54.2 (CH_2), 60.4 (CH_2), 68.2 (CH), 121.6 (Ar), 124.4 (Ar), 126.3 (Ar-H) 127.4 (Ar) 130.4 (Ar-H), 153.3 (Ar-O).

HR-MS $C_{26}H_{36}N_2O_2$+Na Theo. 431.2674 found 431.2702.

Synthesis of Complexes:

$Zr(O^iPr)_4OH^iPr$ (0.50 g, 1.29 mmol) was dissolved in toluene (20 ml) to which the salan-bipyrrolidine (0.528 g, 1.39 mmol) was added and the solution stirred for 1 hour. For the chiral complexes with ligands **1**H_2 and **2**H_2 a precipitate formed during this time and the solution was heated to re-dissolve this. After standing for 24 hours a crop of crystals was isolate. Yield: Zr(**1**)$(O^iPr)_2$ = 37%, Zr(**2**)$(O^iPr)_2$ = 25%. For the meso complex, Zr(**3**)$(O^iPr)_2$ no such precipitate was observed. For Zr(**3**)$(O^iPr)_2$ after 1 hour the toluene was removed *in-vacuo* and the resulting white solid recrystallised in hexane and left to stand at room temperature for 24 hours after which time a crop of crystals was isolated yield = 23%.

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

^{1}H ($CDCl_3$) 1.21 (m, br, 2H), 1.26 (d J = 6.0 Hz, 6H, CH_3), 1.29 (d J = 6.0 Hz, 6H, CH_3), 1.58-1.62 (m, 2H), 1.67-1.77 (m, 2H), 1.91-2.03 (m, 2H), 2.19 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 2.75 (m, 2H), 2.86-2.95 (m, 2H), 3.08 (d J = 13.0 Hz, 2H CH_2), 3.18-3.30 (m, 2H), 4.46-4.54 (m, 4H, CH_2 + OC<u>H</u>(CH_3)$_2$), 6.54 (s, 2H, Ar-H), 6.90 (s, 2H, Ar-H).

^{13}C{^{1}H} ($CDCl_3$) 16.7 (CH_3), 20.5 (CH_3), 20.7 (CH_2), 24.2 (CH_2), 27.1 (CH_3), 27.2 (CH_3), 52.6 (CH_2), 58.8 (CH_2), 62.7 (CH), 70.7 (CH), 123.4 (Ar), 124.9 (Ar), 126.0(Ar), 127.6 (Ar-H), 131.4 (Ar-H), 157.3 (Ar-O).

Calcd $C_{32}H_{48}N_2O_4Zr_1$ Cald: C, 62.34%; H, 7.79%; N, 4.55. Found: C, 62.25%; H, 7.87%; N, 4.61.

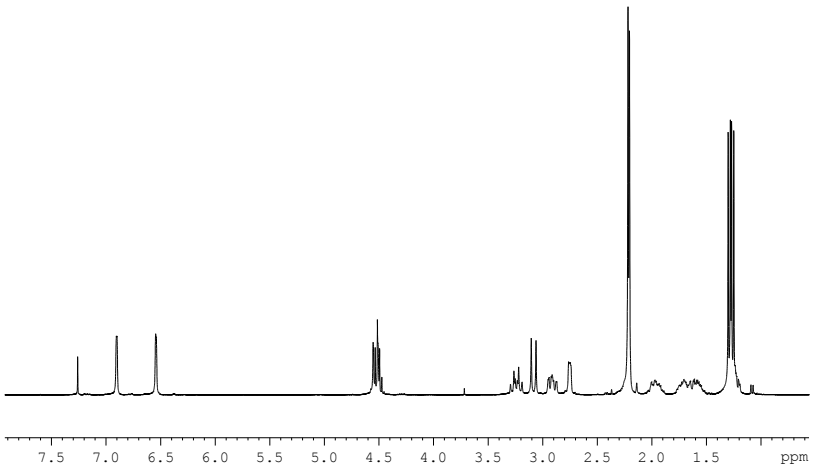


Figure S1: ^{1}H NMR spectrum of Zr(**1**)$O^iPr)_2$

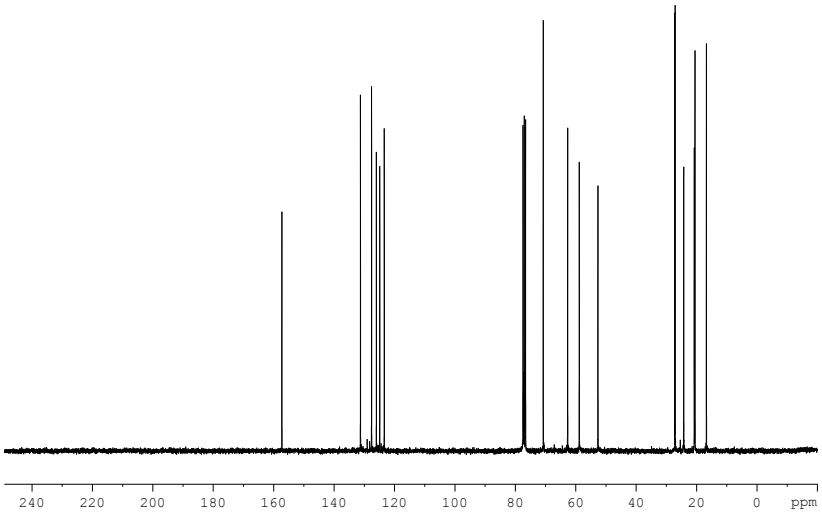


Figure S2: ^{13}C{^{1}H} NMR spectrum of Zr(**1**)$O^iPr)_2$

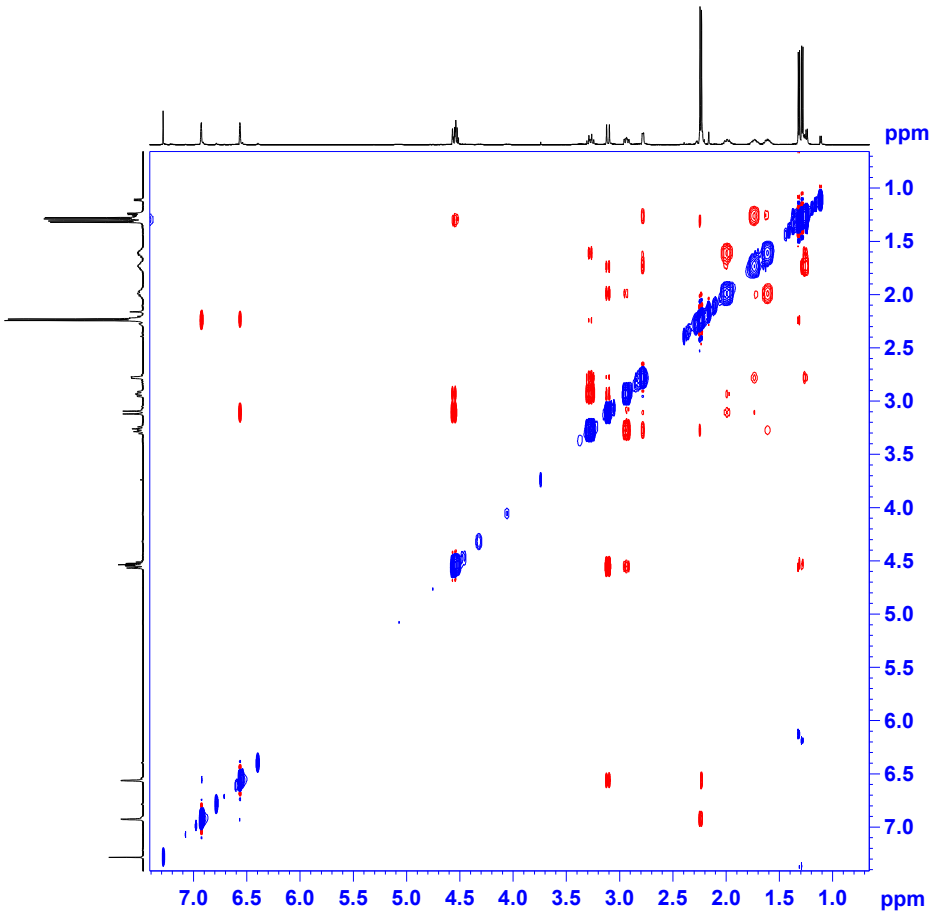


Figure S3: NOESY Spectrum of Zr(**1**)O^{i}Pr)$_2$ indicating no exchange

Zr(**2**)(O^{i}Pr)$_2$

^{1}H ($CDCl_3$) 1.20 (m, br, 2H), 1.25 (d J = 6.0 Hz, 6H, CH_3), 1.28 (d J = 6.0 Hz, 6H, CH_3), 1.52-1.62 (m, 2H), 1.67-1.77 (m, 2H), 1.90-2.03 (m, 2H), 2.19 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 2.74 (m, 2H), 2.86-2.95 (m, 2H), 3.07 (d J = 13.0 Hz, 2H CH_2), 3.18-3.30 (m, 2H), 4.46-4.54 (m, 4H, CH_2 + OC<u>H</u>$(CH_3)_2$), 6.52 (s, 2H, Ar-H), 6.89 (s, 2H, Ar-H).

^{13}C{^{1}H} ($CDCl_3$) 16.7 (CH_3), 20.5 (CH_3), 20.7 (CH_2), 24.2 (CH_2) 27.1 (CH_3), 27.2 (CH_3), 52.6 (CH_2), 58.8 (CH_2), 62.7 (CH), 70.7 (CH), 123.4 (Ar), 124.9 (Ar), 126.0(Ar), 127.6 (Ar-H), 131.3 (Ar-H), 157.3 (Ar-O).

Calcd $C_{32}H_{48}N_2O_4Zr_1$ Cald: C, 62.34%; H, 7.79%; N, 4.55. Found: C, 62.22%; H, 7.85%; N, 4.62.

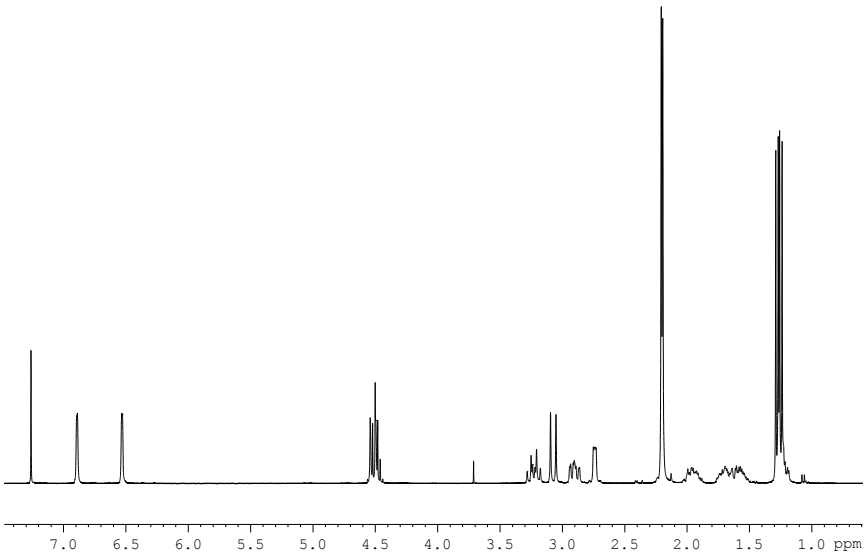


Figure S4: ^{1}H NMR spectrum of Zr(**2**)O^{i}Pr)$_2$

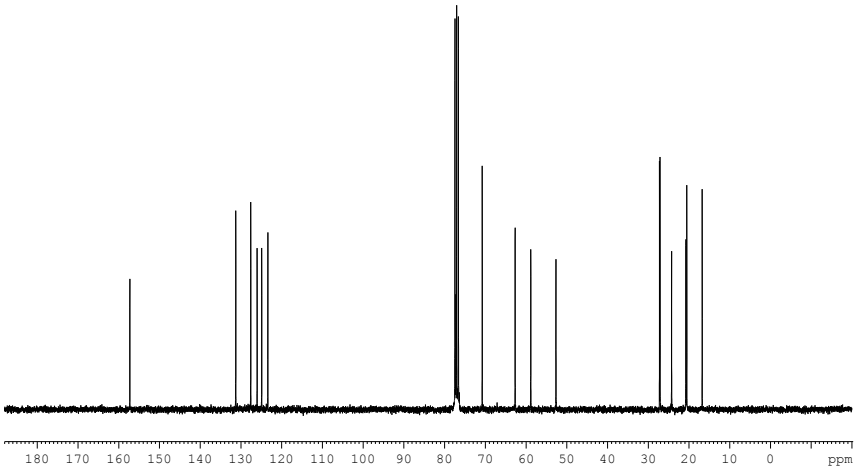


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum of Zr(**2**)O^{i}Pr)$_2$

Zr(**3**)(O^{i}Pr)$_2$

^{1}H ($CDCl_3$) 1.03 (d J= 6.0 Hz, 3H, CH_3), 1.13 (d J= 6.0 Hz, 3H, CH_3), 1.25 (d J= 6.0 Hz, 6H, CH_3), 1.50-1.54 (m, 1H), 1.63-1.69 (m, 1H), 1.78-1.92 (m, 4H), 1.96-2.03 (m, 2H), 2.07 (s, 3H, CH_3), 2.20 (s, 6H, CH_3), 2.24 (s, 3H, CH_3), 2.74-2.98 (m, 4H), 2.99-3.05 (m, 1H), 3.09-3.19 (m, 1H), 3,32 (d J = 12.5 Hz, 1H), 4.21 (sept J = 6.0 Hz, 1H CH), 4.29 (d J = 12.5 Hz, 1H), 4.34-4.41 (m, 1H), 4.46 (sept J = 6.0 Hz, 1H CH), 4.61 (d J = 12.5 Hz, 1H), 6.51 (s, Ar-H, 1H), 6.67 (s, Ar-H, 1H), 6.90 (s, Ar-H, 2H).

$^{13}C\{^{1}H\}$ ($CDCl_3$) 16.3 (CH_3), 20.5 (CH_3), 21.5 (CH_2), 23.5 (CH_2), 25.3 (CH_2), 27.1 (CH_3), 29.7 (CH_2), 51.9 (CH_2), 58.8 (CH_2), 60.4 (CH_2), 65.8 (CH_2), 68.1 (CH), 69.6 (CH), 71.0 (CH), 71.6 (CH), 123.2 (C), 123.6 (C), 124.0 (C), 125.1 (C), 125.4 (C), 126.0 (C), 127.8 (Ar-H), 128.4 (Ar-H), 131.2 (Ar-H), 131.8 (Ar-H), 158.1 (Ar-O), 159.0 (Ar-O).

Calcd $C_{32}H_{48}N_2O_4Zr_1$ Cald: C, 62.34%; H, 7.79%; N, 4.55. Found: C, 62.18%; H, 7.65%; N, 4.63.

^{1}H NMR ($CDCl_3$ 298K Zr(**3**)(O^iPr)$_2$

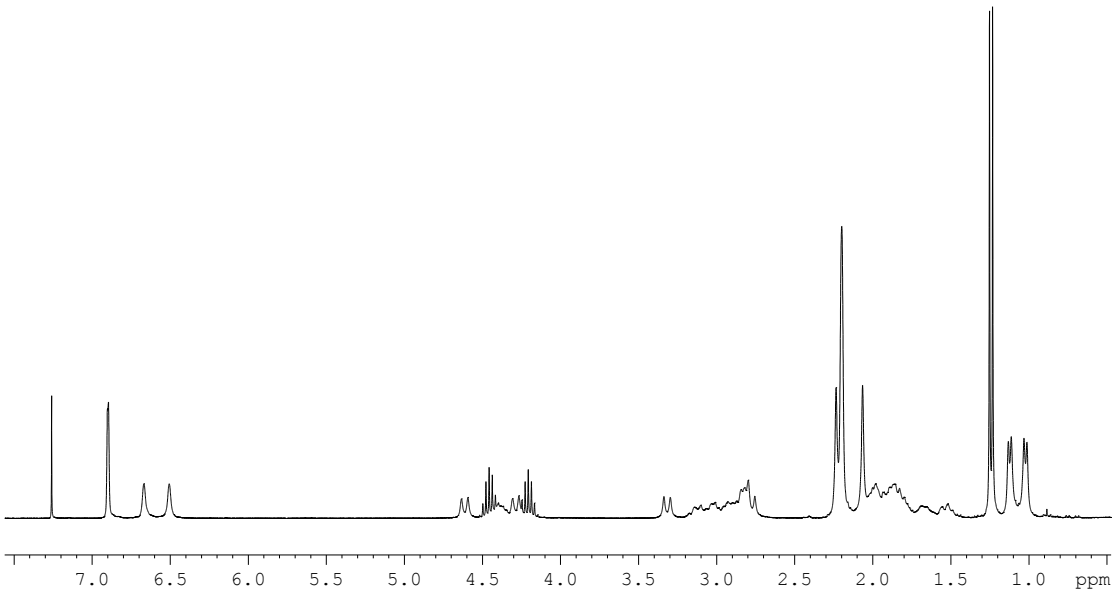


Figure S6: ^{1}H NMR ($CDCl_3$ 298K Zr(**3**)(O^iPr)$_2$) recrystallised in hexane

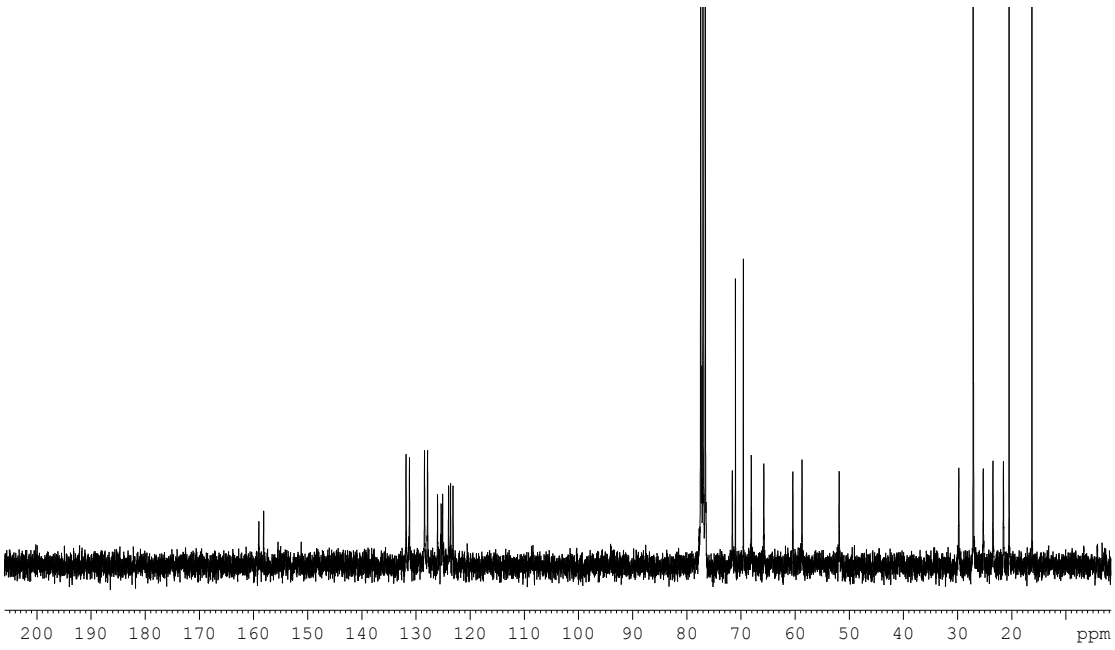


Figure S7: $^{13}C\{^1H\}$ NMR ($CDCl_3$ 298K Zr(**3**)(O^iPr)$_2$) recrystallised in hexane

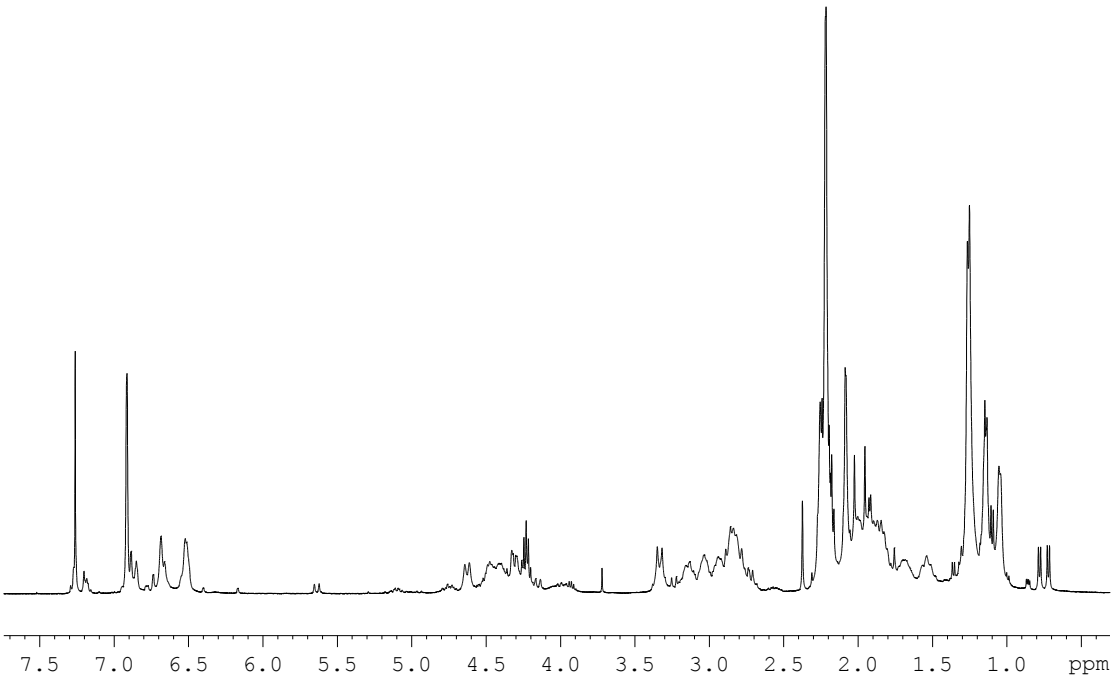


Figure S8: ^{1}H NMR ($CDCl_3$ 298K Zr(**3**)(O^iPr)$_2$) recrystallised in toluene

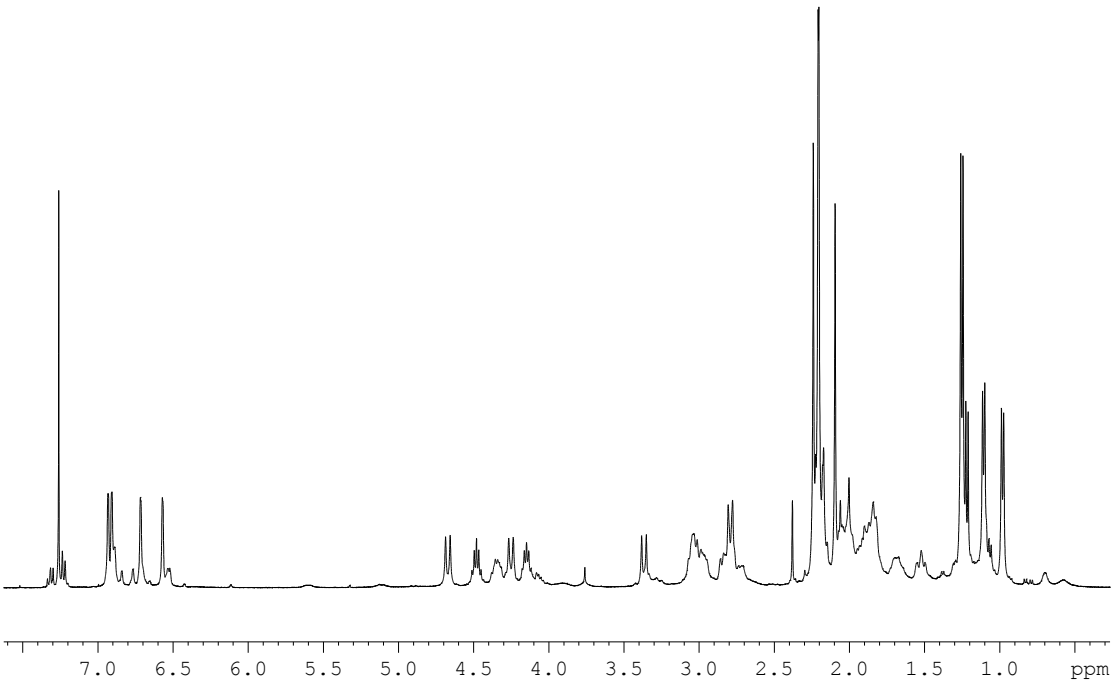


Figure S9: ^{1}H NMR ($CDCl_3$ 238K Zr(**3**)(O^iPr)$_2$) recrystallised in toluene

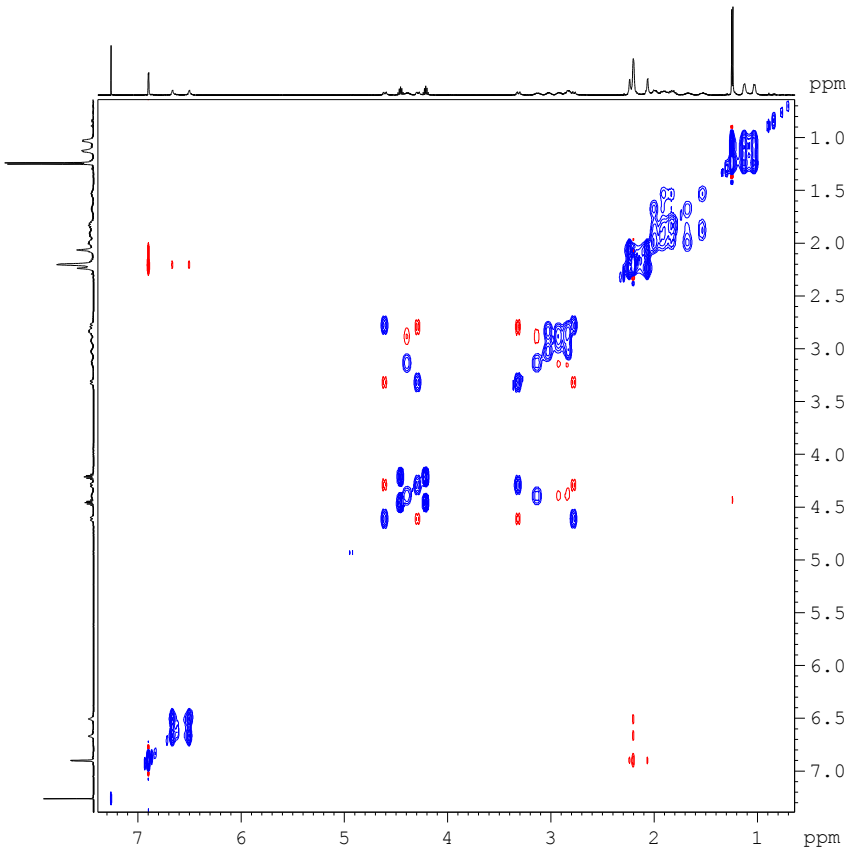


Figure S10: NOESY Spectrum of Zr(**3**)O^{i}Pr)$_2$ indicating exchange

Selected Homonuclear decouple NMR spectra:

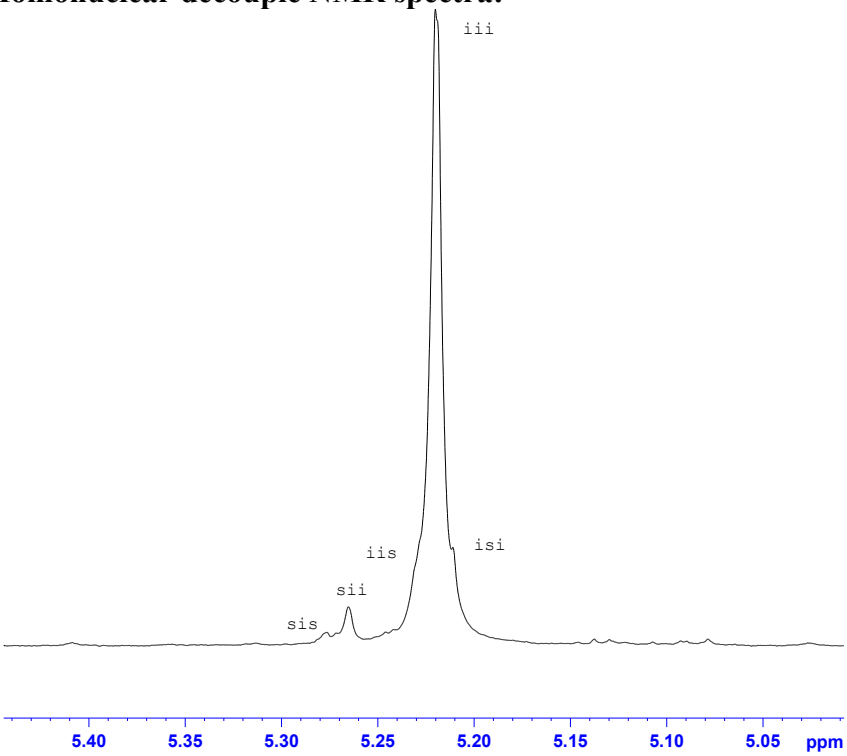


Figure S11: Homonuclear decoupled ^{1}H spectrum from Zr(**3**)(O^{i}Pr)$_2$ – entry 8 Table 1. Relative integrals sis = 1, sii = 4.1, iis = 5.1, isi = 4.3

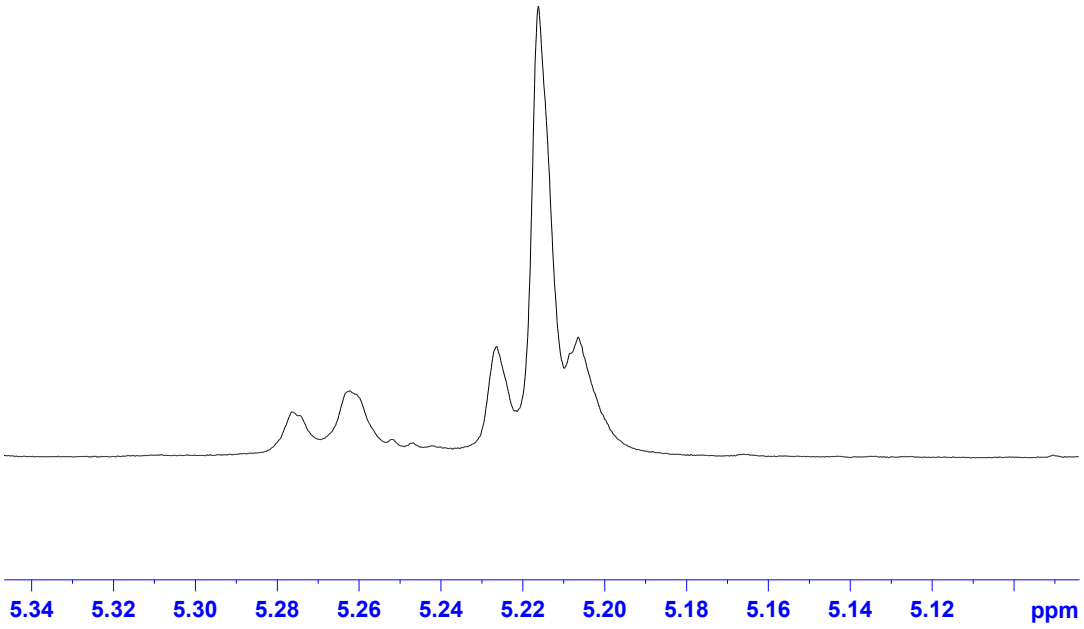


Figure S12: Homonuclear decoupled ^{1}H spectrum from Zr(**3**)($O^{i}Pr$)$_2$ – entry 3 Table 1.

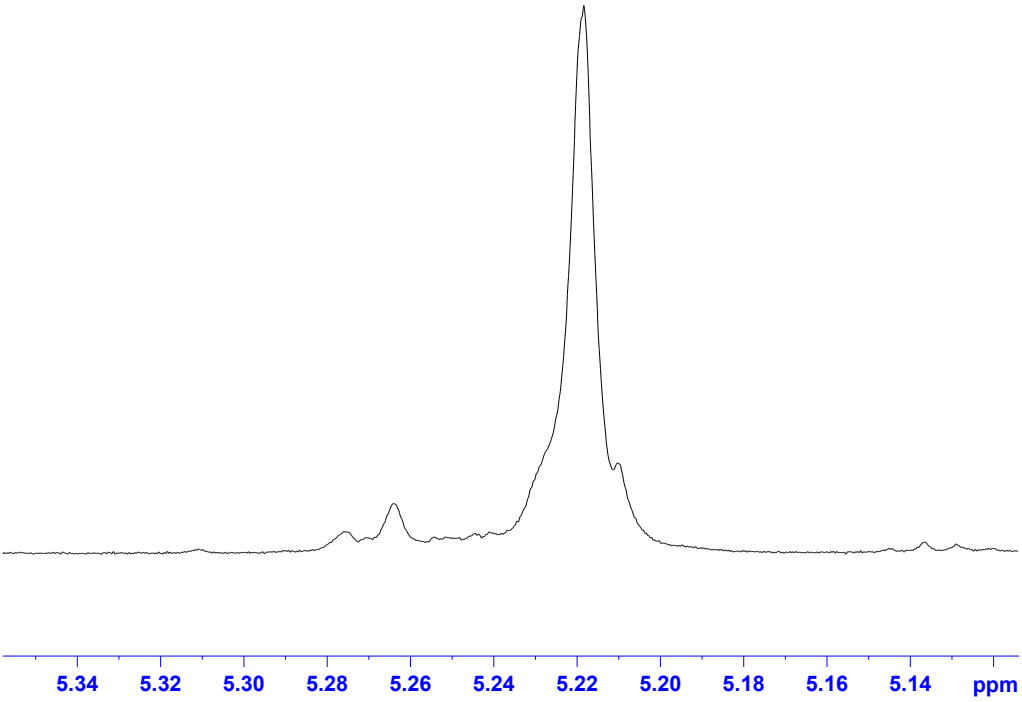


Figure S13: Homonuclear decoupled ^{1}H spectrum from Zr(**1**)($O^{i}Pr$)$_2$ – entry 3 Table 6.

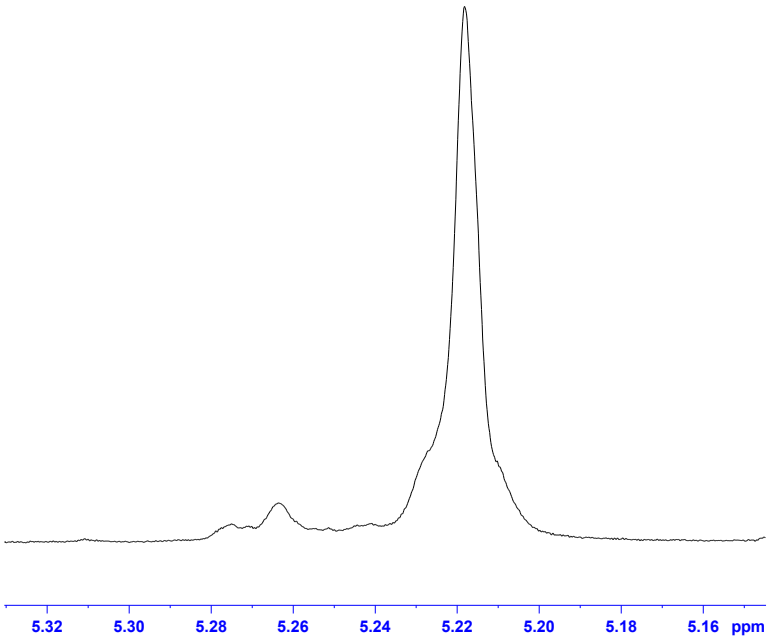


Figure S14: Homonuclear decoupled ^{1}H spectrum from Zr(**2**)($O^{i}Pr$)$_2$ – entry 3 Table 7.

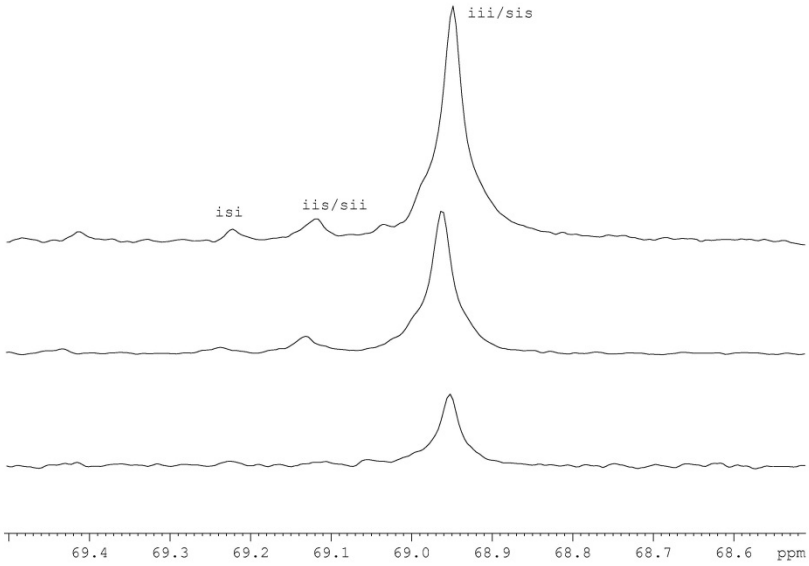


Figure S15: Methine region of the $^{13}C\{^{1}H\}$ NMR of the polymers formed in solution with Zr(**1-3**)($O^{i}Pr$)$_2$ Table 1 entries 6 (top), 7 (middle) 8 (bottom). Using the equation *[isi]* = $[P_i(1-P_i) + P_i(1-P_i)^2]/2$, then P_i = 0.89 (top), 0.9 (middle) not determinable (bottom) indicating a strong isotactic bias as eluded from the ^{1}H homonuclear decoupled spectra. Assignments taken from Dove *et al*.[2]

[2] M.J. Stanford, A.P. Dove, *Chem. Soc. Rev*., 2010, **39**, 486.

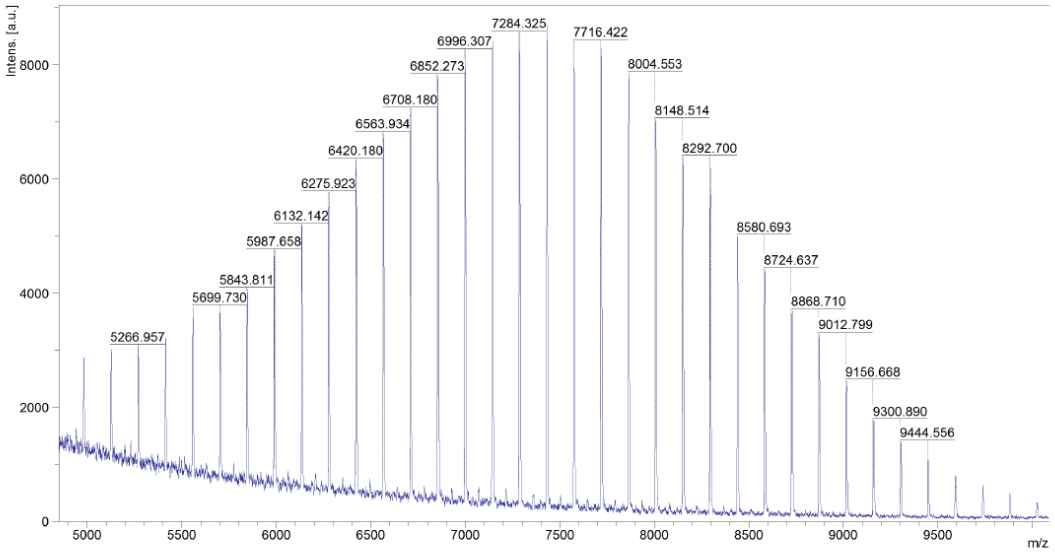


Figure S16: MALDI-ToF MS for solution polymerisation with Zr(**3**)(O^iPr)$_2$ – entry 8 Table 1.

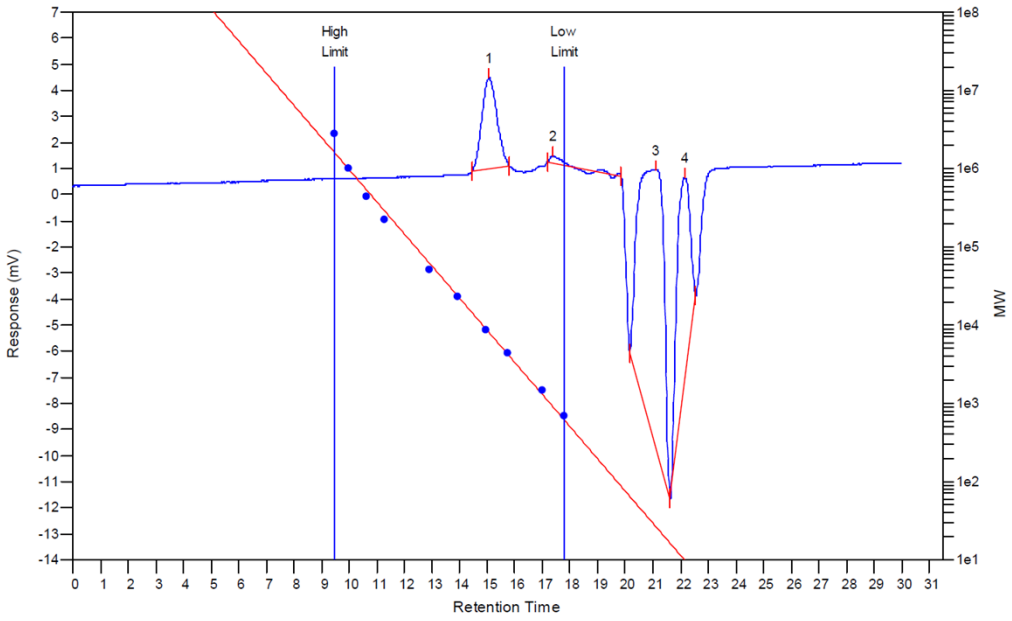


Figure S17: GPC for melt polymerisation with Zr(**2**)(O^iPr)$_2$ – entry 5 Table 1.

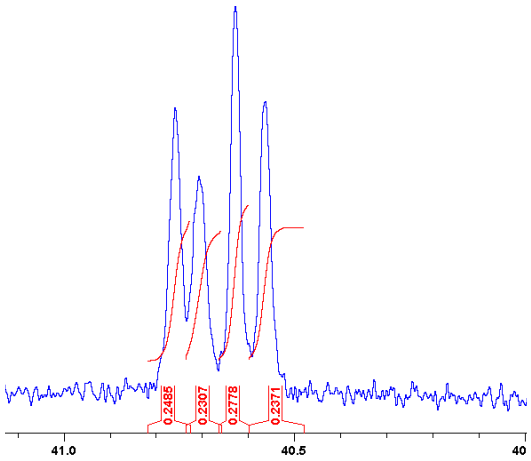


Figure S18: Methine region of the inverse gate $^{13}C\{1H\}$ indicating the atactic nature of the polymerisation of *rac*-butyrolactone.

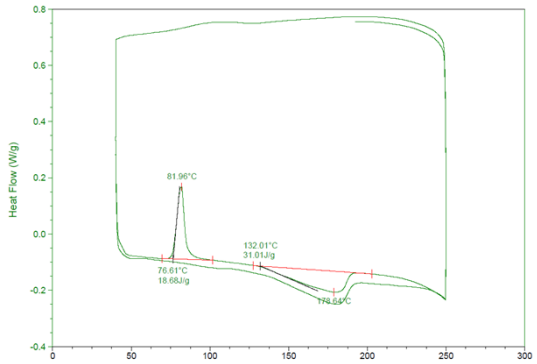


Figure S19: DSC of PLA from Table 1 entry 7/

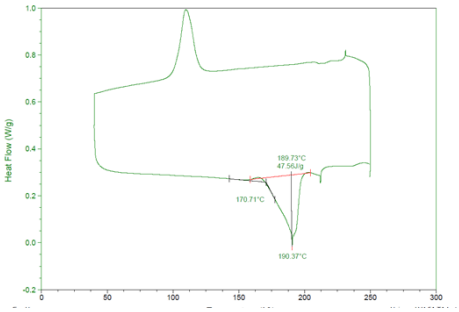


Figure S20: DSC of PLA from Table 1 entry 9.

DFT computational details

All calculations were performed using the Gaussian09 suite of codes (revision C.01).[3] Geometries were fully optimised without any symmetry or geometry constraints. The nature of all the stationary points as minima was verified by calculations of the vibrational frequency spectrum, and characterised by no imaginary mode. Free energies were calculated within the harmonic approximation for vibrational frequencies.

[3] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Frucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A.;, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

*A) Preliminary optimisations of Zr(**3**)(O^{i}Pr)$_2$ isomers*

Preliminary geometries of potential isomers of Zr(**3**)(O^{i}Pr)$_2$ were first obtained by full optimisation using the PBE0 hybrid functional[4] (which had been found to generate good geometries for transition metal complexes),[5] the 6-31g(d) basis set on the main group elements (H, C, N, O), and the LANL2DZ basis set and associated effective core potential on Zr, with no solvation model.

[4]. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158-6170.
[5] M. P. Waller, H. Braun, N. Hojdis and M. Bühl, *J. Chem. Theory Comput.*, 2007, **3**, 2234-2242.

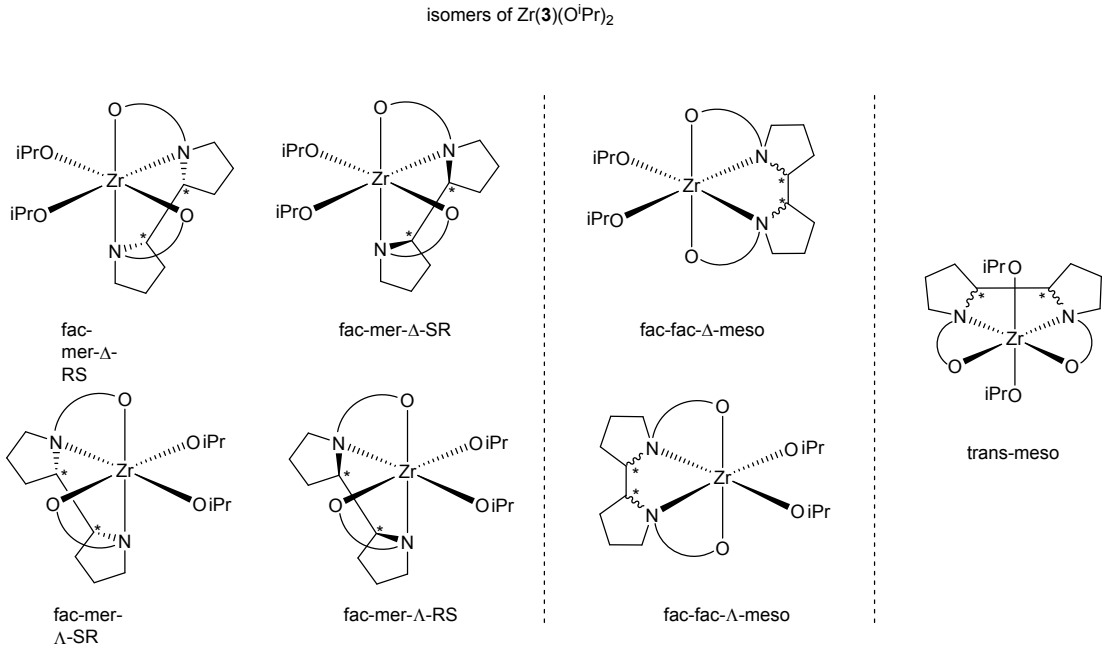


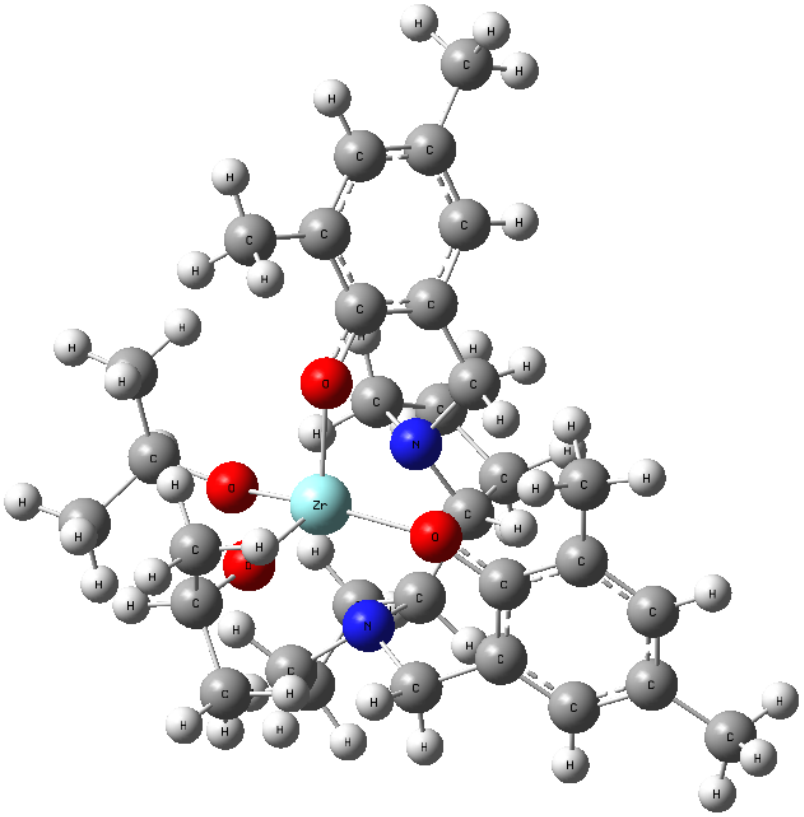
Figure S21: *Zr(3)(O^{i}Pr)$_2$ isomers.*

Isomer of Zr(**3**)(O^{i}Pr)$_2$	*G (Hartree)*	*ΔG (kcal mol^{-1})*
fac-mer-Δ-RS	-1702.937272	0.0 (reference)
fac-mer-Λ-SR	-1702.937242	0.0
fac-mer-Δ-SR	-1702.886165	+32.1
fac-mer-Λ-RS	-1702.886106	+32.1
fac-fac-Δ-meso	-1702.918240	+11.9
fac-fac-Λ-meso	-1702.918238	+11.9
trans-meso	-1702.925384	+7.5

Table S1: Computed Free Gibbs Energies of Zr(**3**)(O^{i}Pr)$_2$ isomers at the PBE0/6-31g(d)/LANL2DZ level of theory

Full coordinates for all calculated complexes, together with their 3 lowest calculated vibrations and their computed Free Gibbs Energy are reported below. They are also available via the corresponding Gaussian 09 output files, stored in the digital repository (DOI: http://dx.doi.org/10.6084/m9.figshare.1189338

fac-mer-Δ-RS



0 1

Zr	0.12963000	0.95914200	0.35480400
O	-0.29217500	2.44066300	1.55982400
N	0.40370700	-0.88177900	-1.28443200
O	0.96162100	2.04964600	-1.10337000
N	-1.90120500	0.98968500	-1.02486100
O	1.82661200	0.13097100	1.07220200
O	-1.08396400	-0.43836000	1.32389900
C	2.67899400	-0.85507900	0.79831400
C	3.98369400	-0.79990400	1.33119300
C	4.87410400	-1.82636000	1.03522800
H	5.87983800	-1.77597500	1.45156800
C	4.52629700	-2.91392500	0.22708300
C	3.23092600	-2.94776300	-0.28228500
H	2.92664700	-3.78580900	-0.90908600
C	2.29822000	-1.94513200	-0.00476600
C	4.36576300	0.35526000	2.20798300
H	4.28543500	1.30641200	1.66896900
H	5.39226900	0.25026800	2.57293100
C	-0.92697100	-1.20599200	-1.86346000
C	-1.81259400	0.01503400	-2.16370600
H	3.69524600	0.43137100	3.07217300
C	5.51801500	-4.00500600	-0.07091500
H	5.83077300	-4.52737100	0.84203600
H	6.42703500	-3.60887500	-0.54039800
H	5.09462900	-4.75307500	-0.74920700

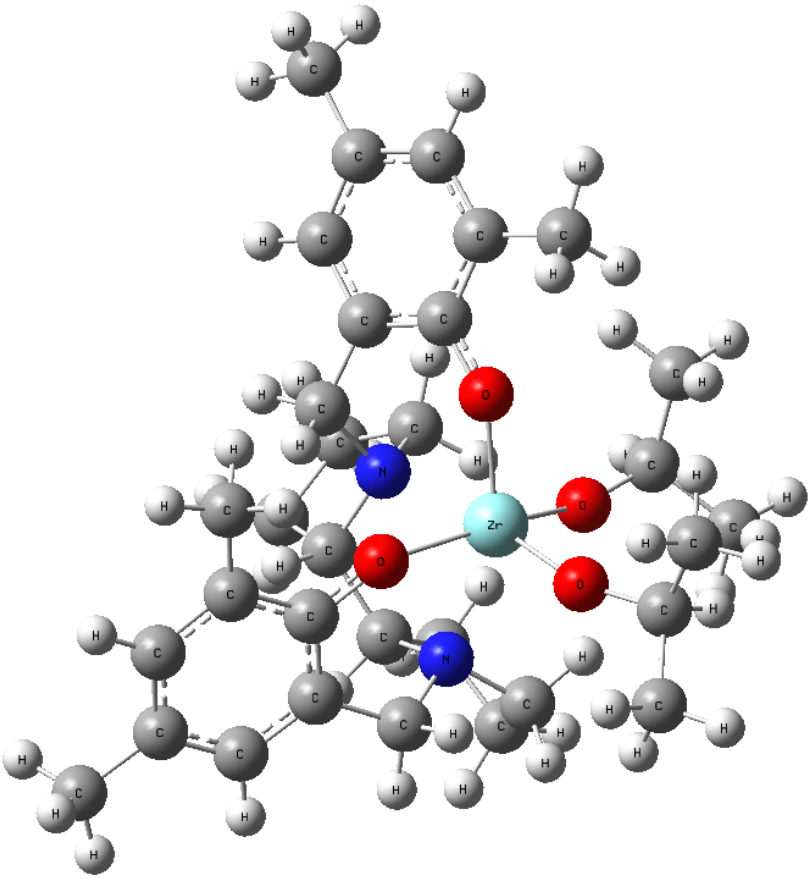
C	0.88849500	-2.06662800	-0.51144500
H	0.19371200	-2.18131800	0.32571200
H	0.81640100	-2.97264800	-1.13073400
C	1.28262200	-0.65254600	-2.45616400
H	2.31750200	-0.84814500	-2.16554400
H	1.21848900	0.40183900	-2.72264400
C	0.77765800	-1.57927600	-3.57882200
H	1.43822500	-2.44222300	-3.70881500
H	0.75541800	-1.05007600	-4.53688500
C	-0.62950100	-2.02789700	-3.13402000
H	-0.64262900	-3.09686600	-2.90069300
H	-1.38927800	-1.87129200	-3.90577000
H	-1.46535200	-1.80201800	-1.12243400
H	-2.82046600	-0.40647100	-2.31161700
C	-1.51450300	0.87633600	-3.39512500
H	-0.45731000	1.14800600	-3.45159200
H	-1.79240200	0.36999600	-4.32419900
C	-2.34300800	2.12231800	-3.11206800
H	-2.06750600	2.98050000	-3.73255900
H	-3.40971700	1.91856800	-3.27237200
C	-2.04213500	2.35596100	-1.63826700
H	-2.82020100	2.91402100	-1.11001000
H	-1.09458900	2.88466400	-1.52388600
C	-3.10665300	0.74123000	-0.17817400
H	-3.05289000	1.47455600	0.63674400
H	-4.00286800	0.97403200	-0.77461200
C	-3.24599700	-0.63324800	0.39851900
C	-4.41196400	-1.37945200	0.22456500
H	-5.20445500	-0.98210600	-0.40972200
C	-4.59248400	-2.60639700	0.85968800
C	-3.56364800	-3.05994500	1.69383500
H	-3.69081000	-4.00637600	2.21919500
C	-2.38079700	-2.35236500	1.88799000
C	-2.20821500	-1.12427500	1.21092300
C	-5.84754600	-3.41403500	0.67048700
H	-5.64103400	-4.38079600	0.19362800
H	-6.56950000	-2.88407500	0.04049300
H	-6.33890500	-3.62829900	1.62761200
C	-1.30568800	-2.84195900	2.81334900
H	-1.05691200	-2.07988300	3.56078500
H	-0.37142100	-3.06190000	2.28238900
H	-1.62033600	-3.75164200	3.33430100
C	1.89265300	2.95701300	-1.61160400
H	2.01268100	2.76361800	-2.69372500
C	3.25129200	2.76479600	-0.94764200
H	3.58604000	1.72728400	-1.04824100
H	4.00682100	3.42123600	-1.39585800
H	3.18079400	2.99549000	0.12204000
C	1.39464500	4.38976800	-1.44334800
H	2.11694800	5.10934500	-1.84673200
H	0.44180300	4.53893600	-1.96342300
H	1.24140000	4.60716700	-0.37978100
C	-0.50868600	3.48252800	2.46000900
H	-0.11441300	4.41189900	2.01381700
C	0.24604900	3.21025600	3.75532800
H	-0.13136400	2.29361200	4.22255900

H	1.31330800	3.07530300	3.55210100
H	0.12762400	4.03932400	4.46279000
C	-2.00289800	3.66110900	2.70082600
H	-2.19572200	4.49675500	3.38354600
H	-2.52165700	3.86327800	1.75699100
H	-2.42359700	2.74883100	3.13957300

Sum of electronic and thermal Free Energies= -1702.937272

Frequencies -- 5.4444 19.1863 24.6846

fac-mer-Λ-SR



0 1

Zr	0.13562000	0.91559100	-0.41592200
O	-0.26219800	2.40900100	-1.62800000
N	0.31864100	-0.91091300	1.26008700
O	1.03377600	2.01610800	0.99109900
N	-1.89071800	1.05492400	0.94559700
O	1.80288000	0.00667300	-1.10904400
O	-1.11937300	-0.44499300	-1.37573400
C	2.61312800	-1.00569100	-0.80513500
C	3.92596300	-1.01055500	-1.32108000
C	4.77337800	-2.06315400	-0.99177600
H	5.78565500	-2.05895900	-1.39509200
C	4.37454300	-3.12016000	-0.16686800
C	3.07210800	-3.09543700	0.32464000
H	2.72834900	-3.90900400	0.96326600
C	2.18139600	-2.06459200	0.01424400
C	4.36171800	0.11084700	-2.21651500
H	4.30520500	1.07632200	-1.70022900
H	3.70802000	0.19003100	-3.09316200
C	-1.03131400	-1.16992000	1.82676700
C	-1.86563300	0.09388300	2.09862300
H	5.38972500	-0.03740400	-2.56164400
C	5.32067800	-4.24092100	0.16707700
H	5.62988400	-4.79007500	-0.73120600

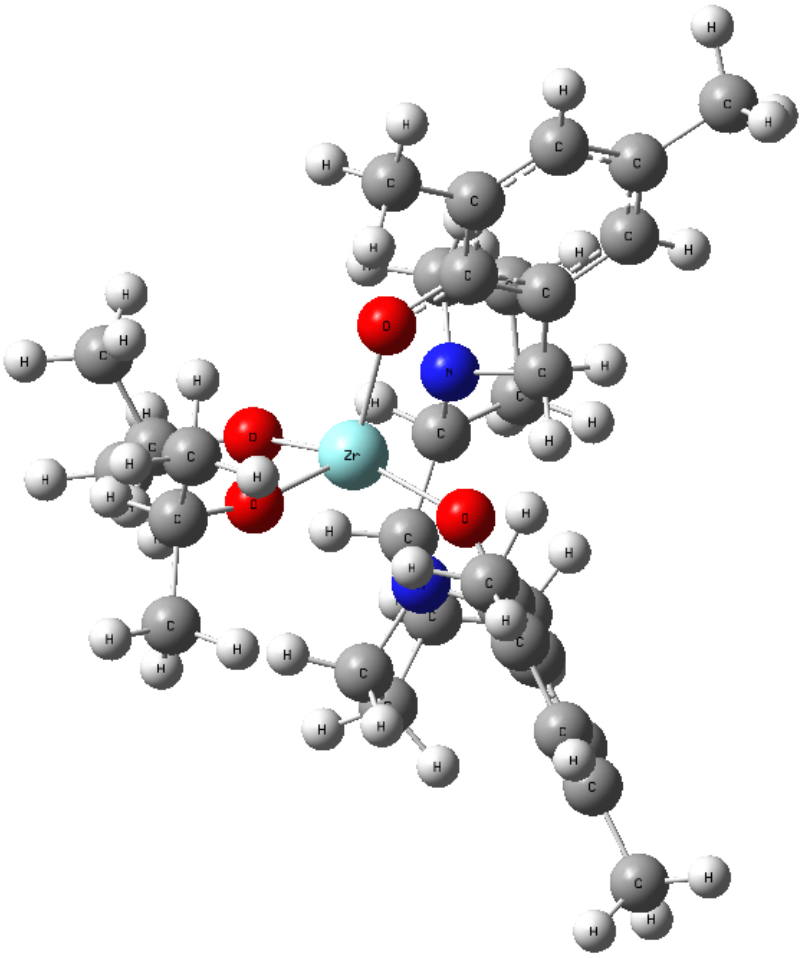
H	4.85863600	-4.96121700	0.85016900
H	6.23530400	-3.86972500	0.64598000
C	0.76178600	-2.12270100	0.50412100
H	0.64367300	-3.01910000	1.13029700
H	0.07313800	-2.21530900	-0.34082100
C	1.18988800	-0.70941500	2.44050500
H	1.14878300	0.34291600	2.71774100
H	2.22312000	-0.93018800	2.16250800
C	0.64428400	-1.62340000	3.55370100
H	0.65812800	-1.10947900	4.52016900
H	1.25926400	-2.52204000	3.66430000
C	-0.78737000	-1.98985600	3.11079500
H	-1.53711900	-1.77298600	3.87760200
H	-0.86762800	-3.05934400	2.89456800
H	-1.58679000	-1.75034500	1.08594000
H	-2.89373500	-0.27955300	2.23526100
C	-1.55003400	0.95849500	3.32379100
H	-1.86883500	0.48003100	4.25447400
H	-0.48237000	1.18107000	3.39881900
C	-2.31111300	2.23916800	3.00739300
H	-3.38941400	2.09044300	3.14948900
H	-2.00554800	3.09190500	3.62132300
C	-1.97091700	2.43562400	1.53669600
H	-0.99573500	2.91487400	1.43337100
H	-2.70835700	3.02533400	0.98525700
C	-3.09543200	0.85491300	0.08334600
H	-3.98659800	1.14556200	0.66142400
H	-2.98813900	1.56826600	-0.74401100
C	-3.29676400	-0.52139400	-0.47015100
C	-4.49787700	-1.20878000	-0.29357800
H	-5.27660600	-0.76303600	0.32534400
C	-4.72971100	-2.43739000	-0.90852300
C	-3.71624400	-2.95338400	-1.72500200
H	-3.88343300	-3.90210900	-2.23475800
C	-2.49973400	-2.30566500	-1.92062500
C	-2.27607300	-1.07544500	-1.26335300
C	-6.02256500	-3.18241200	-0.71660800
H	-5.86586700	-4.14683600	-0.21656200
H	-6.51288700	-3.39508200	-1.67457900
H	-6.72626500	-2.60636800	-0.10667100
C	-1.44069300	-2.86133100	-2.82691500
H	-1.14113200	-2.12017200	-3.57653400
H	-1.79748200	-3.75738600	-3.34438700
H	-0.52710200	-3.12744100	-2.28110300
C	2.03919600	2.72678800	1.64520700
H	2.12397500	2.34821400	2.68106800
C	-0.15391400	3.69438700	-2.16099200
H	0.22094600	4.37224800	-1.37403200
C	3.38279000	2.51290200	0.95820400
H	4.18831700	3.02740800	1.49576600
H	3.62319200	1.44615800	0.90559100
H	3.34382500	2.90235900	-0.06615600
C	1.68321600	4.20847100	1.72343500
H	0.72681500	4.35396000	2.23792300
H	2.45146700	4.77053500	2.26745900
H	1.59605500	4.62765500	0.71417100

C	0.84654500	3.68903500	-3.31028700
H	1.82129200	3.32908000	-2.96460500
H	0.49871500	3.01959900	-4.10519200
H	0.97358600	4.69436200	-3.72890600
C	-1.52676200	4.18283000	-2.60668800
H	-2.22642300	4.18357600	-1.76336200
H	-1.47335300	5.20087100	-3.00970900
H	-1.92597900	3.51990700	-3.38270900

Sum of electronic and thermal Free Energies= -1702.937242

Frequencies -- 16.2895 19.0157 21.3842

fac-mer-Δ-SR



0 1

Zr	0.01721500	0.61901000	0.70299400
O	0.10733300	2.64140200	0.59487500
O	1.84170400	-0.10350800	1.18360500
O	-0.88778500	0.74013300	2.42159500
O	-0.65151400	-1.31028900	0.32481300
N	1.40061600	0.96186600	-1.37511100
N	-1.57288500	0.81350000	-1.26241200
C	-0.57923700	4.93771000	0.62955000
C	-1.92736100	2.25788700	-3.14412300
C	1.28002600	1.68703700	-3.65412000
C	2.76123300	1.75742900	-3.19161900
C	-3.26787100	2.13231300	-2.37722300
C	0.58343500	1.81175900	-2.30061700
C	-0.22934900	3.69962200	1.44926400
C	0.92085000	3.97901100	2.41025600
C	-0.93077200	1.89958500	-2.04281700
C	2.71342000	1.59954400	-1.64201300
C	-2.90397600	1.43312600	-1.03651600
C	1.56450600	-0.49254000	-1.68729700
C	-1.80289500	-0.42540500	-2.06199200
C	2.64068900	-1.12845000	-0.83798800
C	3.58348400	-1.96635600	-1.43847400

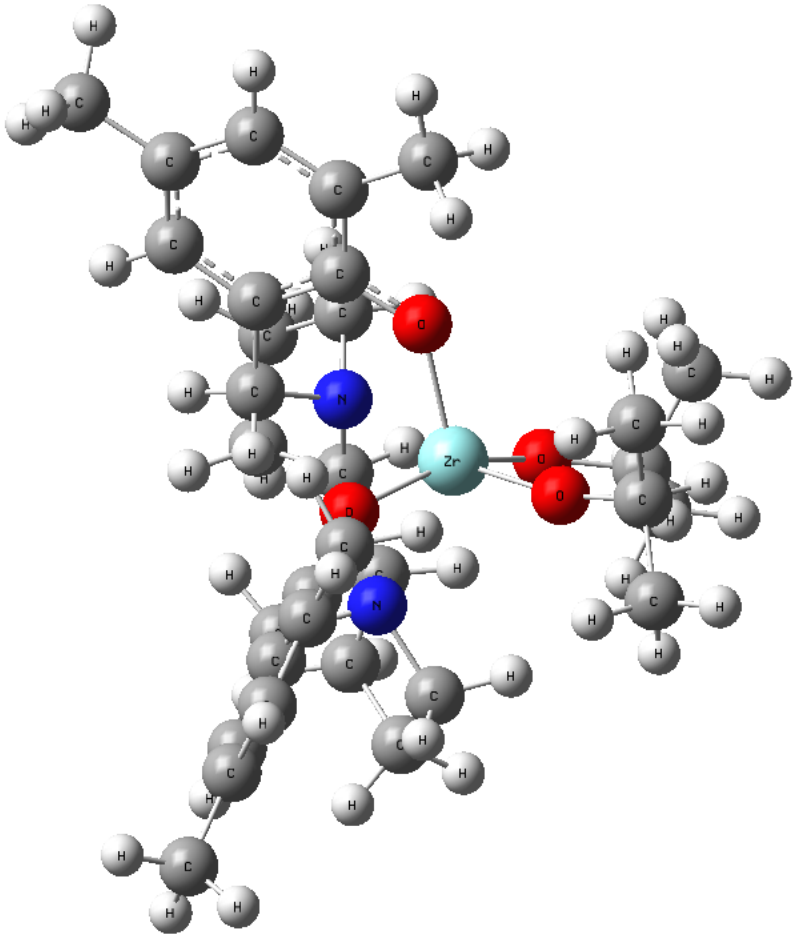
C	2.70059700	-0.91013000	0.55261800
C	-2.39900900	-1.53838700	-1.25377900
C	-1.26558100	0.88845600	3.75879800
C	-3.56071900	-2.19348300	-1.66747800
C	-2.75318900	0.59287500	3.90139500
C	4.57798000	-2.60817100	-0.70557100
C	3.70949000	-1.53723600	1.31222400
C	5.56666400	-3.53128400	-1.36336500
C	-1.75351400	-1.93368900	-0.07187900
C	4.61958100	-2.37085100	0.67192900
C	3.76289000	-1.28831800	2.79011600
C	-0.41309700	-0.01324300	4.64249700
C	-4.09693500	-3.25356100	-0.94127000
C	-5.33974500	-3.96975400	-1.39466100
C	-2.27693400	-3.00706900	0.68023000
C	-3.43093600	-3.63846200	0.22894200
C	-1.56643400	-3.43306400	1.92943800
H	0.27936600	5.23829000	0.01674600
H	-0.85332400	5.78042300	1.27513600
H	-1.75565300	3.27088100	-3.52094000
H	1.01033800	2.51034100	-4.32262500
H	3.22344100	2.70932400	-3.47032900
H	-1.42393300	4.73541400	-0.03974700
H	-3.71185700	3.11341400	-2.18453500
H	0.88324000	2.81246200	-1.96872600
H	-1.87307300	1.57927800	-4.00221500
H	1.82296000	4.24789500	1.84775400
H	0.68036600	4.80001900	3.09654800
H	2.72934200	2.56425500	-1.12702600
H	-0.99025800	2.72599700	-1.33003000
H	3.36312100	0.96471700	-3.64630400
H	1.05071500	0.75303800	-4.17910500
H	-4.00507000	1.55601700	-2.94411300
H	-1.11425200	3.42003100	2.04736900
H	-2.80916900	2.16162900	-0.22501900
H	3.52581700	0.98823600	-1.24990900
H	1.14473900	3.08531900	3.00286500
H	-2.47329500	-0.20430400	-2.90260100
H	1.80539400	-0.65715700	-2.74618800
H	-3.61718500	0.66503400	-0.72940600
H	-0.84959700	-0.71972300	-2.50709200
H	-1.08756900	1.93565100	4.05547900
H	0.62519700	-1.00602800	-1.47818900
H	3.53278100	-2.12287800	-2.51587900
H	-3.33818000	1.25717600	3.25648800
H	-4.05181800	-1.87058000	-2.58578500
H	5.52326500	-3.45019700	-2.45455900
H	3.90130300	-0.22231800	3.00730600
H	6.59477000	-3.30979300	-1.05306600
H	-3.08428600	0.73478700	4.93669100
H	0.64991300	0.20623300	4.49889800
H	-5.78203400	-3.48386100	-2.27065700
H	-2.96180000	-0.44152400	3.60590000
H	-0.65959600	0.12927100	5.70109400
H	5.39237200	-2.85225300	1.27023400
H	4.58208300	-1.84592100	3.25472500

H	2.82328600	-1.58260600	3.27232000
H	5.37225100	-4.58048200	-1.10524800
H	-0.58111000	-1.06484400	4.38381200
H	-6.10364600	-3.99313300	-0.60775400
H	-1.50972100	-2.60906000	2.65053000
H	-5.12995200	-5.01185300	-1.66814400
H	-0.53103900	-3.72217900	1.71324700
H	-3.83004700	-4.46694600	0.81375200
H	-2.07294400	-4.27874600	2.40534900

Sum of electronic and thermal Free Energies= -1702.886165

Frequencies -- 15.3641 20.5459 22.5567

fac-mer-Λ-RS



0 1

Zr	-0.01723400	0.61898400	0.70301100
O	0.88784000	0.74007000	2.42160100
N	-1.40062800	0.96185100	-1.37506700
O	-0.10734600	2.64135400	0.59486900
N	1.57285300	0.81345900	-1.26241900
O	-1.84165800	-0.10350200	1.18364800
O	0.65150100	-1.31026400	0.32476100
C	-2.70059700	-0.91007000	0.55259700
C	-3.70949500	-1.53722400	1.31222100
C	-4.61959300	-2.37077400	0.67188600
H	-5.39243400	-2.85222600	1.27022000
C	-4.57797500	-2.60812800	-0.70555100
C	-3.58347900	-1.96628200	-1.43848800
H	-3.53279900	-2.12279700	-2.51590100
C	-2.64070300	-1.12840300	-0.83799800
C	-3.76292300	-1.28831800	2.79006800
H	-3.90125000	-0.22228400	3.00726600
H	-2.82326500	-1.58256800	3.27226900
C	-0.58341400	1.81177800	-2.30056800
C	0.93082900	1.89955000	-2.04276300
H	-4.58209300	-1.84590800	3.25473700

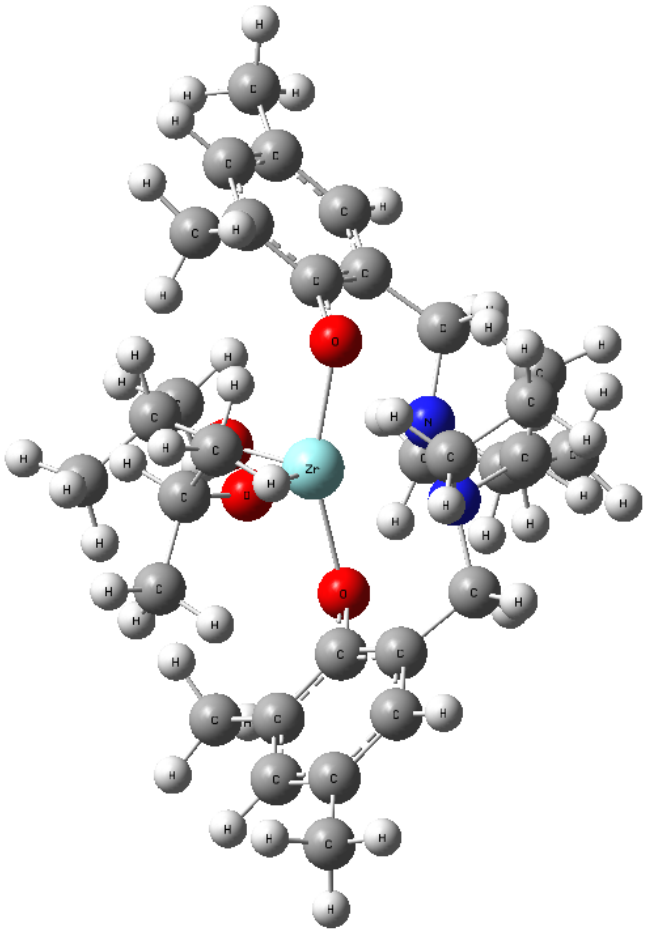
C	-5.56670200	-3.53119300	-1.36343100
H	-5.37234500	-4.58035900	-1.10526400
H	-5.52327100	-3.45011400	-2.45461800
H	-6.59479200	-3.30973100	-1.05311900
C	-1.56452900	-0.49251500	-1.68727600
H	-1.80543200	-0.65713000	-2.74624000
H	-0.62521800	-1.00598800	-1.47820700
C	-2.71338500	1.59957700	-1.64199300
H	-2.72931000	2.56434600	-1.12701500
H	-3.52579000	0.98829100	-1.24991200
C	-2.76116700	1.75749000	-3.19164300
H	-3.22344000	2.70940600	-3.47029700
H	-3.36306100	0.96475900	-3.64634200
C	-1.27998700	1.68710000	-3.65411300
H	-1.01032800	2.51043400	-4.32264400
H	-1.05073100	0.75311500	-4.17912400
H	-0.88315900	2.81245300	-1.96871500
H	0.99034200	2.72597600	-1.32999300
C	1.92735300	2.25794900	-3.14407800
H	1.87314500	1.57927200	-4.00223500
H	1.75566400	3.27089300	-3.52092200
C	3.26794200	2.13230500	-2.37721400
H	4.00510400	1.55595100	-2.94407300
H	3.71189900	3.11340700	-2.18451500
C	2.90401900	1.43312600	-1.03648100
H	2.80917700	2.16155800	-0.22504800
H	3.61720900	0.66499600	-0.72940400
C	1.80292400	-0.42536100	-2.06204500
H	0.84958700	-0.71966800	-2.50711800
H	2.47326500	-0.20430800	-2.90258400
C	2.39904800	-1.53835300	-1.25375800
C	3.56066900	-2.19347900	-1.66745400
H	4.05182800	-1.87064700	-2.58583400
C	4.09685800	-3.25360200	-0.94132300
C	3.43087300	-3.63852700	0.22887200
H	3.82995900	-4.46702900	0.81371400
C	2.27685600	-3.00706800	0.68016800
C	1.75346100	-1.93366800	-0.07189100
C	5.33966900	-3.96982200	-1.39466200
H	5.12985000	-5.01188100	-1.66821200
H	6.10356700	-3.99319400	-0.60777500
H	5.78198900	-3.48386200	-2.27071600
C	1.56637100	-3.43307200	1.92943600
H	1.50969600	-2.60912400	2.65050100
H	2.07285800	-4.27876800	2.40530000
H	0.53102900	-3.72217500	1.71323600
C	0.22942400	3.69964500	1.44925700
H	1.11433500	3.41999600	2.04744600
C	1.26561000	0.88838000	3.75878700
H	1.08755800	1.93559600	4.05545400
C	0.57931700	4.93770500	0.62959200
H	0.85341200	5.78035100	1.27516800
H	1.42400600	4.73541200	-0.03967700
H	-0.27934900	5.23832500	0.01682700
C	-0.92081600	3.97899900	2.41034200
H	-1.14466000	3.08526000	3.00285400

H	-0.68025300	4.80002900	3.09658200
H	-1.82288200	4.24785800	1.84775100
C	0.41309300	-0.01331700	4.64246400
H	-0.64992600	0.20623600	4.49892600
H	0.58114800	-1.06491300	4.38375800
H	0.65958000	0.12916400	5.70113400
C	2.75318500	0.59284700	3.90142300
H	3.33816000	1.25712400	3.25646900
H	3.08431000	0.73465600	4.93666500
H	2.96181000	-0.44164000	3.60588300

Sum of electronic and thermal Free Energies= -1702.886106

Frequencies -- 15.4814 20.5220 22.6673

fac-fac-Δ-meso



0 1

N	1.17287600	1.81884500	0.90474400
O	1.50419500	0.23573900	-1.47982100
C	2.79348300	0.10968600	-1.12872500
C	3.60802300	-0.86845300	-1.73133900
C	4.93148400	-0.98295900	-1.31515000
H	5.55759900	-1.74227600	-1.78352000
C	5.48362400	-0.17131200	-0.31736600
C	4.66306700	0.80174000	0.25027800
H	5.07026500	1.47142800	1.00794300
C	3.33550400	0.95594700	-0.14764400
C	3.02373800	-1.75697900	-2.78833000
H	2.20118100	-2.36149100	-2.38588300
H	3.77993400	-2.43294000	-3.20022500
C	0.26867400	2.98971500	0.63668500
C	-0.33985900	2.79829300	-0.75085400
H	2.59811800	-1.16842300	-3.60957500
C	6.91423700	-0.34469700	0.11560200
H	7.60436100	-0.28798900	-0.73517100
H	7.07737800	-1.31788100	0.59610000
H	7.20894300	0.42871900	0.83256900
C	2.50675200	2.11574900	0.31153000
H	2.32185000	2.74172000	-0.57001400

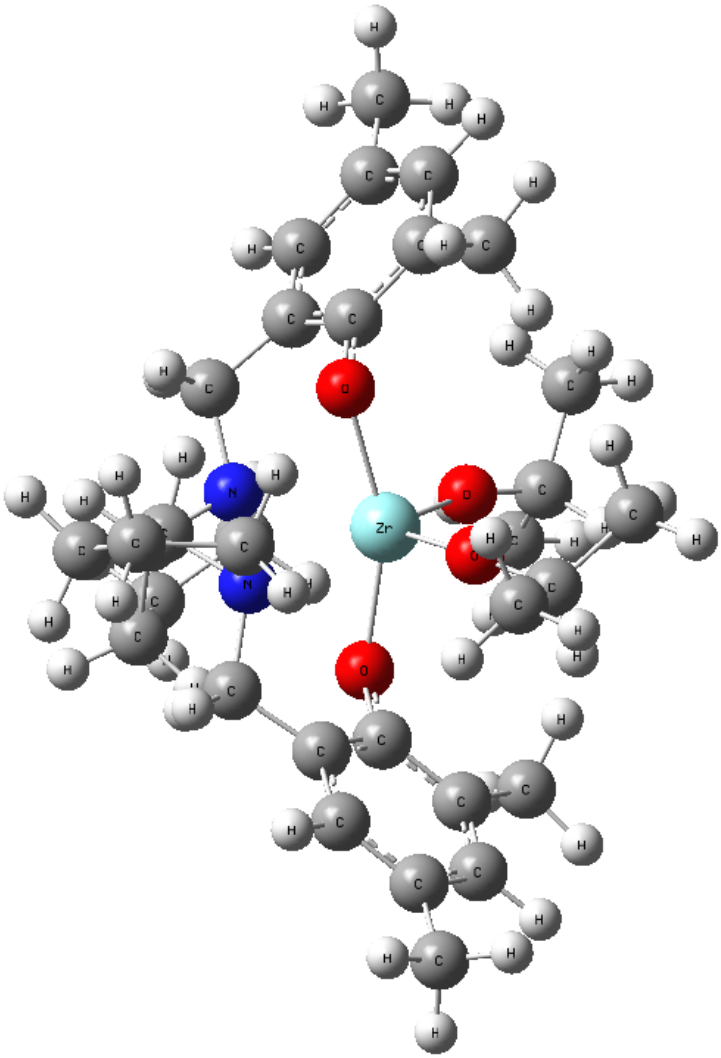
H	3.07773500	2.73779700	1.01797400
C	1.24442600	1.66398200	2.39099400
H	2.28486100	1.51780000	2.69526400
H	0.68108200	0.77568000	2.68871500
C	0.58577600	2.91421100	2.96707500
H	1.29007900	3.75593600	2.99960100
H	0.20105300	2.75423300	3.97858100
C	-0.51388000	3.16825400	1.93703700
H	-0.97741200	4.15724700	2.01105000
H	-1.27477600	2.39475500	2.06211700
H	0.90228100	3.88920700	0.54301200
H	0.52585600	2.50957000	-1.36287500
C	-0.99963600	3.94678200	-1.51726000
H	-1.79570800	4.42427500	-0.93516800
H	-0.27623000	4.72380200	-1.78312500
C	-1.56033600	3.20296500	-2.75369800
H	-2.59184500	3.49953000	-2.96676100
H	-0.97478100	3.42169800	-3.65171000
C	-1.45384500	1.69340500	-2.39522400
H	-0.57862500	1.23469200	-2.86585200
H	-2.33299300	1.10498900	-2.66688000
N	-1.26285700	1.64885100	-0.92602000
C	-2.58976200	1.89817400	-0.27735100
H	-2.42161300	2.55710500	0.57538900
H	-3.23377600	2.45660400	-0.96894300
C	-3.31808700	0.67370700	0.18645300
C	-2.67321400	-0.18298300	1.09207700
C	-4.64172500	0.43078100	-0.18172500
C	-3.37763900	-1.27560100	1.63753100
C	-5.35702000	-0.64610300	0.33849900
H	-5.12909700	1.10833400	-0.88313900
C	-4.69989500	-1.47880700	1.25152100
H	-5.23978800	-2.32474500	1.67684500
C	-6.78647700	-0.90473100	-0.05342800
H	-6.91424400	-1.90591100	-0.48357200
H	-7.46175100	-0.83822100	0.80908400
H	-7.13170200	-0.17969600	-0.79785000
C	-2.68109800	-2.18439900	2.60575000
H	-3.36462500	-2.94346600	2.99948000
H	-1.83494300	-2.69708300	2.13035600
H	-2.26509500	-1.61959500	3.44819100
O	-1.39377400	0.03654400	1.42197000
Zr	0.06156700	-0.28026800	-0.05645600
O	-0.98101200	-1.51462700	-1.13170000
O	1.15843900	-1.43900000	1.05548200
C	1.63097900	-2.49967900	1.83649500
H	0.94028000	-3.34935200	1.70457000
C	-1.76171900	-2.57514600	-1.60716200
H	-2.41436500	-2.90934200	-0.78547900
C	3.01376800	-2.91860300	1.35776600
H	3.71826200	-2.08549800	1.45634800
H	3.38537700	-3.76908200	1.94175100
H	2.98220400	-3.20580600	0.30243500
C	1.62819300	-2.10450400	3.30755900
H	2.32824300	-1.27812400	3.47785000
H	0.62743700	-1.78316700	3.61453200

H	1.93185400	-2.94792000	3.93844800
C	-0.85811300	-3.72912300	-2.02120600
H	-0.20298300	-3.42002500	-2.84404900
H	-0.22920000	-4.04200700	-1.18097700
H	-1.44963100	-4.59061400	-2.35240900
C	-2.64342500	-2.09695000	-2.75263100
H	-3.26681700	-2.91506700	-3.13175300
H	-3.30250400	-1.29304700	-2.41003600
H	-2.02331400	-1.72291600	-3.57605900

Sum of electronic and thermal Free Energies= -1702.918240

Frequencies -- 15.0093 17.2195 22.2299

fac-fac-Λ-meso



0 1

N	-1.17272600	1.81903500	0.90458700
N	1.26294200	1.64863800	-0.92633100
O	-1.15846800	-1.43890600	1.05551500
O	1.39369200	0.03676000	1.42189200
O	-1.50429100	0.23540000	-1.47990500
O	0.98119700	-1.51483700	-1.13158000
C	-6.91422800	-0.34451900	0.11613500
C	-1.62951900	-2.10343900	3.30762000
C	-5.48365500	-0.17124200	-0.31700900
C	-4.66295700	0.80178400	0.25048700
C	-3.01334700	-2.91916400	1.35729100
C	-0.58560900	2.91502000	2.96659400
C	-1.24420100	1.66457600	2.39088100
C	-1.63107600	-2.49937900	1.83676500
C	-4.93167200	-0.98295200	-1.31482200
C	-3.33543100	0.95589300	-0.14758700
C	-2.50665600	2.11576900	0.31137000

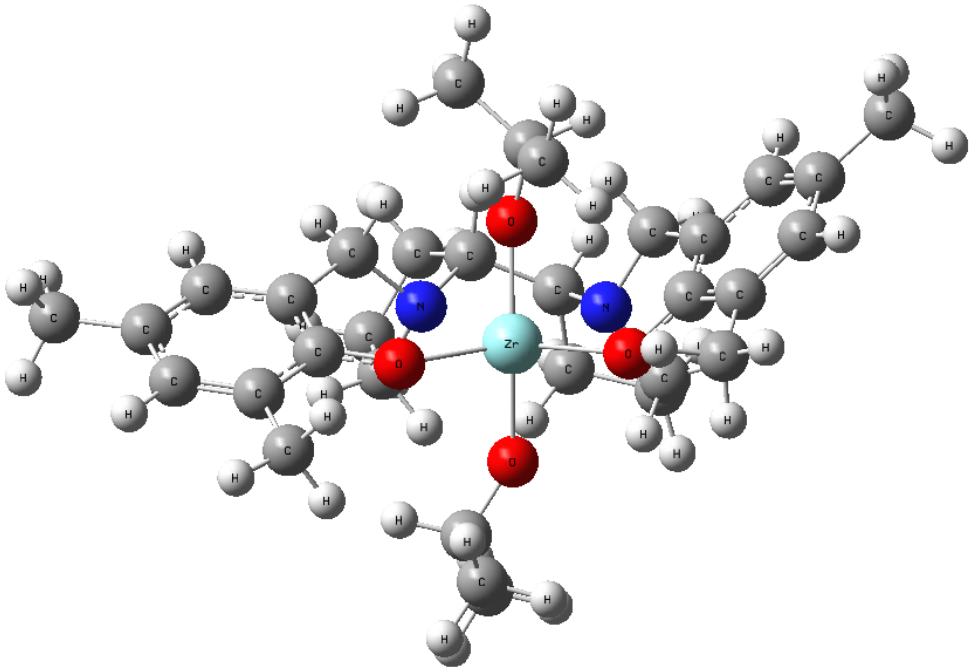
C	0.51400400	3.16885000	1.93647800
C	-0.26854600	2.98985200	0.63619400
C	0.33997000	2.79815200	-0.75130400
C	-3.60824900	-0.86855600	-1.73116200
C	-2.79355000	0.10951300	-1.12865900
C	2.68083000	-2.18393300	2.60634200
C	-3.02416500	-1.75714800	-2.78821200
C	3.37750400	-1.27538300	1.63798800
C	2.67315800	-0.18288300	1.09218600
C	0.99978600	3.94651700	-1.51788800
C	2.58987700	1.89797100	-0.27770400
C	4.69979400	-1.47869500	1.25216700
C	0.85828600	-3.72939000	-2.02097900
C	3.31812600	0.67358100	0.18642200
C	1.76188400	-2.57537800	-1.60701900
C	1.45389600	1.69302100	-2.39555000
C	1.56053600	3.20251700	-2.75419500
C	4.64180300	0.43054000	-0.18156200
C	5.35702700	-0.64622300	0.33900400
C	2.64355500	-2.09722700	-2.75254700
C	6.78652100	-0.90496300	-0.05270400
H	-7.20885600	0.42906300	0.83295400
H	-7.07731900	-1.31759300	0.59687400
H	-7.60442400	-0.28800000	-0.73458200
H	-1.93334600	-2.94663800	3.93872900
H	-5.07003100	1.47155300	1.00815400
H	-2.32999300	-1.27721900	3.47696000
H	-3.38497600	-3.76951800	1.94144400
H	-3.71828700	-2.08632900	1.45497700
H	-2.28460500	1.51845600	2.69525500
H	-0.20084900	2.75535700	3.97813800
H	-1.28997200	3.75670800	2.99890400
H	-0.62910800	-1.78159800	3.61518900
H	-3.07762500	2.73793600	1.01771600
H	-5.55788900	-1.74223900	-1.78311900
H	-0.68075200	0.77641800	2.68884100
H	-2.98092200	-3.20689600	0.30213500
H	-0.93991800	-3.34882200	1.70577300
H	2.26469800	-1.61891600	3.44858000
H	-2.32180900	2.74157300	-0.57030400
H	-0.90220600	3.88928300	0.54226900
H	0.97744400	4.15792300	2.01017800
H	1.27498100	2.39547200	2.06177200
H	1.83475300	-2.69674700	2.13095900
H	-3.78046300	-2.43308000	-3.19997400
H	3.36431000	-2.94289000	3.00037100
H	-2.20157900	-2.36170600	-2.38586800
H	-0.52575500	2.50940200	-1.36329500
H	-2.59862700	-1.16864900	-3.60953400
H	0.22939000	-4.04222700	-1.18071500
H	2.42179800	2.55712500	0.57486900
H	0.27637800	4.72349200	-1.78390400
H	1.79583600	4.42410800	-0.93585500
H	5.23963400	-2.32453500	1.67775800
H	2.41455900	-2.90952200	-0.78534500
H	0.20313400	-3.42034600	-2.84383400

H	0.57860400	1.23435000	-2.86609300
H	1.44980500	-4.59089500	-2.35214300
H	3.23395100	2.45618100	-0.96943500
H	0.97511000	3.42120500	-3.65230700
H	2.33296300	1.10447800	-2.66717500
H	2.59210300	3.49896800	-2.96715100
H	7.46170400	-0.83820700	0.80986200
H	5.12925200	1.10791700	-0.88309600
H	3.30258300	-1.29326200	-2.41002300
H	2.02340300	-1.72331500	-3.57598900
H	3.26699700	-2.91534200	-3.13159700
H	6.91434300	-1.90626100	-0.48254800
H	7.13182500	-0.18013200	-0.79729400
Zr	-0.06152400	-0.28039000	-0.05656900

Sum of electronic and thermal Free Energies= -1702.918238

Frequencies -- 15.1539 17.1844 22.2190

trans-meso



0 1

N	1.41997600	1.20004200	-0.89265000
N	-1.46891900	1.61421800	-0.38861100
O	1.62376200	-1.31923900	0.64753300
O	-1.88353800	-0.78402800	1.06565800
C	2.88020700	-1.30576800	0.21734200
C	3.84383400	-2.08943700	0.89021700
C	5.16303700	-2.06348900	0.45405300
H	5.89515500	-2.67369000	0.98248400
C	5.58273600	-1.28314300	-0.62903700
C	4.61796500	-0.51944900	-1.27848300
H	4.91167400	0.09366900	-2.13057800
C	3.27525600	-0.52304400	-0.88713100
C	3.41031300	-2.92683000	2.05602800
H	3.00303400	-2.30411300	2.86181200
H	4.24690900	-3.50673900	2.45816200
C	0.59171900	2.01388900	-1.82153700
C	-0.67406700	2.61016300	-1.17963500
H	2.61164200	-3.62103200	1.76910800
C	7.02066400	-1.27853200	-1.07047100
H	7.34642000	-2.27387300	-1.39813200
H	7.69316400	-0.97272600	-0.25925800
H	7.17741200	-0.58964100	-1.90712100
C	2.27154600	0.25482000	-1.69202900
H	1.56837900	-0.41991700	-2.18838800
H	2.81061500	0.81967200	-2.46515400

C	2.28827400	2.18063200	-0.19419200
H	3.19696000	1.66988300	0.13272900
H	1.77071000	2.52306900	0.70184800
C	2.55477300	3.32068200	-1.19834300
H	3.58110900	3.28567700	-1.57590600
H	2.42618000	4.29533600	-0.71739800
C	1.54040300	3.10925000	-2.34251000
H	2.04386100	2.77132100	-3.25327100
H	1.00083700	4.02379100	-2.60636400
H	0.26112900	1.33892100	-2.61754600
H	-1.29490200	2.92800300	-2.03373300
C	-0.55620200	3.83680700	-0.26685300
H	0.23282500	3.71865100	0.48053400
H	-0.35399300	4.74819800	-0.83757500
C	-1.91005500	3.83859000	0.43005400
H	-1.93637700	4.46926800	1.32369200
H	-2.69458300	4.18912500	-0.25301900
C	-2.08314500	2.36364200	0.76105700
H	-3.12258200	2.04974400	0.88001900
H	-1.53503700	2.10142900	1.66862100
C	-2.52503300	1.00747000	-1.23864600
H	-3.13145700	1.82211500	-1.66700800
H	-2.00885700	0.50838900	-2.06568100
C	-3.46488800	0.04304300	-0.55107200
C	-4.77402100	-0.02225200	-1.04450100
H	-5.05565500	0.64505600	-1.85931000
C	-5.72209000	-0.90506400	-0.54132200
C	-5.33191300	-1.73382600	0.51660100
H	-6.05449800	-2.42931000	0.94248000
C	-4.05253600	-1.69545000	1.05340900
C	-3.09605200	-0.80422200	0.51358800
C	-7.11788300	-0.96455500	-1.09838800
H	-7.34276400	-1.95295800	-1.51864600
H	-7.26014800	-0.22767300	-1.89575800
H	-7.87127600	-0.76662500	-0.32570000
C	-3.64677500	-2.57801700	2.19636500
H	-3.29000000	-1.98435000	3.04611200
H	-2.81758700	-3.23878400	1.91495400
H	-4.48391000	-3.19874500	2.53064700
Zr	-0.05869800	-0.18610400	0.38324800
O	0.38006800	0.89047100	2.01920500
O	-0.45891200	-1.07860500	-1.37735500
C	-1.00084800	-2.05672800	-2.21390100
C	-1.13015400	-3.38034900	-1.46846700
C	-0.15670000	-2.20862300	-3.47602400
H	-2.01510100	-1.73864100	-2.51646700
H	-1.76283900	-3.25454400	-0.58421800
H	-1.57743300	-4.15214200	-2.10626800
H	-0.14138000	-3.72462300	-1.14283600
H	-0.06938400	-1.25104100	-4.00330000
H	0.85196100	-2.55443500	-3.21920500
H	-0.60311600	-2.93522400	-4.16496100
C	1.09824300	1.11327700	3.19490100
C	0.81118500	0.00553100	4.20254900
C	0.75952100	2.48632500	3.76753300
H	2.17792800	1.09304800	2.96172300

H	1.07024500	-0.96851100	3.77500500
H	1.38819200	0.14597300	5.12446400
H	-0.25557100	-0.00404900	4.45538800
H	0.96143700	3.27551400	3.03351400
H	-0.30325300	2.53172500	4.03453500
H	1.34951400	2.69928800	4.66661800

Sum of electronic and thermal Free Energies= -1702.925384

Frequencies -- 13.4540 27.3520 30.4804

*B) Advanced optimisations of fac-mer-*Δ-RS *and trans-meso isomers of Zr(**3**)(O^{i}Pr)$_2$*

Based on the preliminary optimised geometries, refined optimisations of the and *fac-mer*-Δ-RS and *trans*-meso isomers of Zr(**3**)(O^{i}Pr)$_2$ were performed based on the recommendation of Sun and Chen benchmark article for Zr compounds.[6] These optimisations were carried out with functional M06-2X.[7] The ccpVTZ basis set was used on the main group elements (H, C, N, O, Cl),[8] and the cc-pVTZ-PP basis set in association with the Stuttgart new relativistic energy-consistent small-core pseudopotential ECP28MDF was used for Zr to account for the scalar relativistic effect.[9] Finally, a self-consistent-reaction-cavity continuum solvation model of chloroform was also implemented.[10]

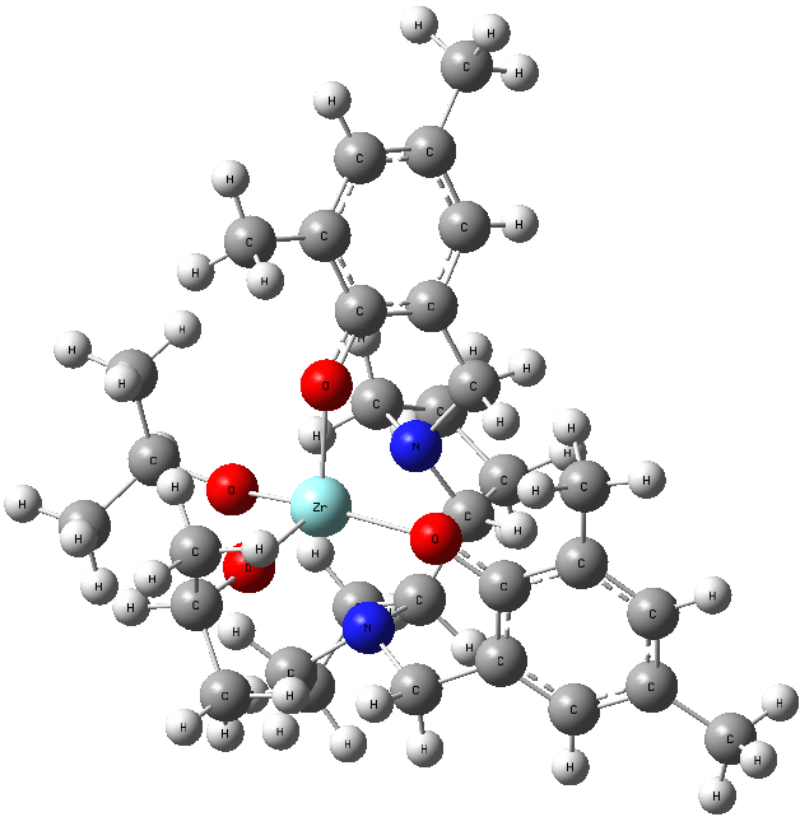
[6] Y. Sun and H. Chen, *J. Chem. Theory Comput.*, 2013, **9**, 4735-4743.
[7] Y. Zhao and D. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
[8] T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007-1023.
[9] K. A. Peterson, D. Figgen, M. Dolg and H. Stoll, *J. Chem. Phys.*, 2007, **126**, 124101-124112.
[10] G. Scalmani and M. J. Frisch, *J. Chem. Phys.*, 2010, **132**, 114110-1141

Isomer of Zr(**3**)(O^{i}Pr)$_2$	*G (Hartree)*	*ΔG (kcal mol^{-1})*
fac-mer-Δ-RS	-1705.087165	0.0 (reference)
trans-meso	-1705.073983	+8.3

Table S2: Computed Free Gibbs Energies of Zr(**3**)(O^{i}Pr)$_2$ *fac-mer*-Δ-RS and *trans*-meso isomers at the M06-2X /cc-pVTZ/ cc-pVTZ-PP/ ECP28MDF/ SCRF=(cpcm,solvent= chloroform) level of theory.

Full coordinates for both complexes, together with their 3 lowest calculated vibrations and their computed Free Gibbs Energy are reported below. They are also available via the corresponding Gaussian 09 output files, stored in the digital repository: http://dx.doi.org/10.6084/m9.figshare.1190538

fac-mer-Δ-RS (advanced level of theory)



0 1

Zr	-0.13923900	0.89658100	-0.55395100
O	0.28715500	2.36420300	-1.80906600
N	-0.20124000	-0.80949400	1.26140200
O	-1.02180500	2.08164500	0.75513000
N	1.91767800	1.20033900	0.68680400
O	-1.77442800	-0.14500200	-1.09786700
O	1.10191300	-0.46477700	-1.51652600
C	-2.50154700	-1.20163300	-0.73195300
C	-3.81898100	-1.31642900	-1.20679800
C	-4.58041300	-2.41039900	-0.82527400
H	-5.59693700	-2.49056600	-1.19651200
C	-4.08604800	-3.40214700	0.02013300
C	-2.78612800	-3.26126700	0.48459800
H	-2.37892000	-4.01066100	1.15533300
C	-1.98015200	-2.18518900	0.11877400
C	-4.35611800	-0.24866500	-2.11351100
H	-4.30775300	0.72920400	-1.63193000
H	-5.38910400	-0.45492600	-2.38728400
C	1.16992900	-0.93195400	1.83367100
C	1.91041600	0.40488400	1.95810400
H	-3.75991300	-0.17642200	-3.02455400
C	-4.93209200	-4.58759300	0.39923200
H	-5.00557100	-5.29875400	-0.42579100

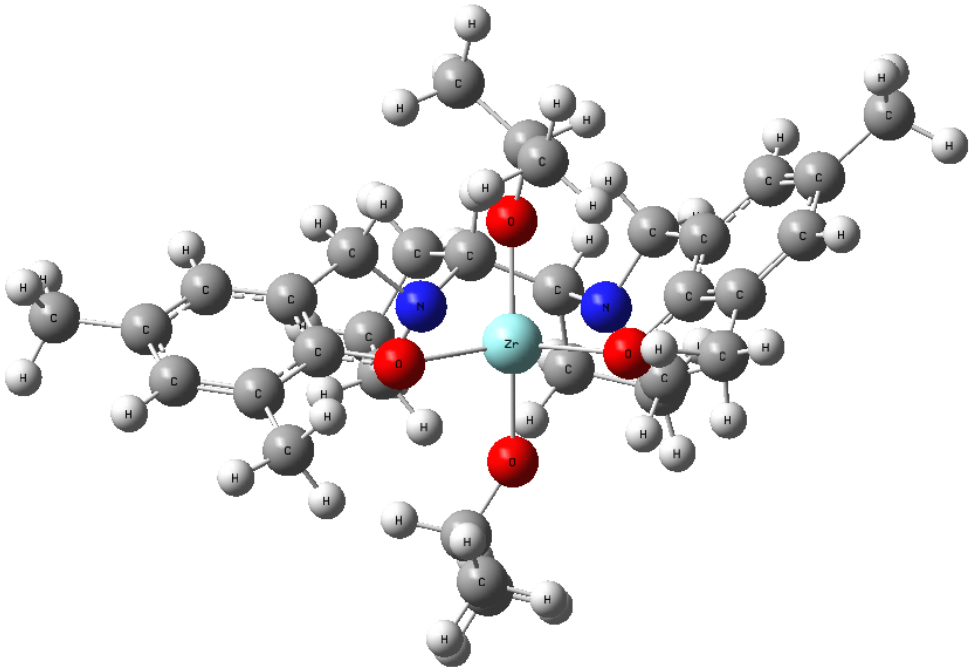
H	-5.94691200	-4.28273700	0.65529500
H	-4.50828200	-5.11372700	1.25338000
C	-0.56482100	-2.11374500	0.62999500
H	0.14493800	-2.27044500	-0.18128600
H	-0.42152800	-2.92172500	1.35401200
C	-1.09239300	-0.56484700	2.42850600
H	-2.07852600	-0.96842900	2.21132800
H	-1.20772400	0.50262100	2.56559600
C	-0.43009500	-1.22623700	3.65421700
H	-0.98663300	-2.10302000	3.97874800
H	-0.40544200	-0.52906900	4.48997600
C	0.98876200	-1.61504800	3.19776300
H	1.07498500	-2.69396500	3.08613200
H	1.75795900	-1.30705000	3.90378800
H	1.74905500	-1.55907600	1.15957000
H	2.94911200	0.14153700	2.19670100
C	1.44269400	1.40056200	3.01890100
H	0.36974000	1.57142900	2.95338500
H	1.68752200	1.06913300	4.02584200
C	2.17671700	2.66711300	2.59808800
H	1.77243200	3.57110800	3.04822900
H	3.23293500	2.59506700	2.86268000
C	1.99764700	2.65581100	1.08423600
H	2.81881000	3.13144300	0.55231800
H	1.07399000	3.15585000	0.80351900
C	3.10465200	0.89145500	-0.16587700
H	2.99891000	1.51397000	-1.05780100
H	4.00414300	1.21373400	0.36865100
C	3.25996100	-0.54165500	-0.57677100
C	4.41475900	-1.26107700	-0.29381500
H	5.20252000	-0.78737900	0.28288500
C	4.58233100	-2.56559400	-0.74258400
C	3.55667700	-3.12612500	-1.50306400
H	3.67593600	-4.13688900	-1.88018500
C	2.38613900	-2.44195900	-1.80323900
C	2.22795100	-1.13484900	-1.31264400
C	5.82441000	-3.35494800	-0.42612900
H	5.60774200	-4.17592500	0.25976000
H	6.58175900	-2.72447400	0.03728100
H	6.25358900	-3.79247400	-1.32807900
C	1.30740000	-3.04442400	-2.65619900
H	1.19634600	-2.48502700	-3.58693000
H	0.33472600	-3.01192700	-2.16265100
H	1.53914500	-4.07935900	-2.90123800
C	-1.95924500	2.73291500	1.55845400
H	-1.73832300	2.51678600	2.61452700
C	-3.35526000	2.21502300	1.24263200
H	-3.39047700	1.12887800	1.34410000
H	-4.10003100	2.65724800	1.90541700
H	-3.61076000	2.46786300	0.21116800
C	-1.86329700	4.23999800	1.36636000
H	-2.56228300	4.75993100	2.02267500
H	-0.85364500	4.58857800	1.58790800
H	-2.09842800	4.49644900	0.33152500
C	-0.01234000	3.73325800	-1.92101500
H	-0.04026500	4.17148700	-0.91390300

C	-1.38590900	3.91026300	-2.55073700
H	-1.38929600	3.48862000	-3.55759900
H	-2.13929500	3.39016700	-1.95560300
H	-1.65710600	4.96529300	-2.61212200
C	1.07412100	4.42886200	-2.72507900
H	0.87977400	5.49947900	-2.79951800
H	2.04615900	4.28327600	-2.25292100
H	1.11438200	4.01102100	-3.73247600

Sum of electronic and thermal Free Energies= -1705.087165

Frequencies -- 10.7352 17.8608 19.7236

trans-meso (advanced level of theory)



0 1

N	1.38111400	1.00522100	-1.03470100
N	-1.44843600	1.64973400	-0.45572800
O	1.59653800	-1.21205400	0.80996000
O	-1.95227800	-0.39860900	1.32909200
C	2.81578200	-1.34553200	0.29337200
C	3.80003800	-2.03582200	1.02574900
C	5.07233100	-2.16832700	0.49280100
H	5.82267100	-2.70343200	1.06612600
C	5.42201100	-1.63162100	-0.74569600
C	4.44206000	-0.94320400	-1.44434200
H	4.68697400	-0.50170800	-2.40490700
C	3.14518600	-0.79744400	-0.95427400
C	3.43961300	-2.59768600	2.36894900
H	3.11578700	-1.80391900	3.04449700
H	4.28834200	-3.11177700	2.81621700
C	0.53956900	1.76385100	-2.00400300
C	-0.62416000	2.51839200	-1.35340000
H	2.60684900	-3.29812500	2.29013100
C	6.81490800	-1.79550100	-1.29161100
H	7.04551500	-2.84616400	-1.47551800
H	7.56085700	-1.41906700	-0.59031700
H	6.93273400	-1.25805100	-2.23124800
C	2.12527900	-0.06156100	-1.78145000
H	1.37047600	-0.74548900	-2.16300500
H	2.63882800	0.38959700	-2.63432400

C	2.35565100	2.00449800	-0.51540500
H	3.26327500	1.48881000	-0.21291600
H	1.93875800	2.46616700	0.37106500
C	2.58859300	3.02491500	-1.64969000
H	3.58281800	2.91665600	-2.07806300
H	2.50933300	4.03958300	-1.26376400
C	1.50254900	2.73188700	-2.70475400
H	1.93442000	2.26614700	-3.58751800
H	0.98761400	3.63069700	-3.03861400
H	0.11197400	1.03459800	-2.69331200
H	-1.25524600	2.83667400	-2.19273400
C	-0.35401700	3.77612100	-0.52659500
H	0.40886200	3.60900300	0.23022900
H	-0.05697400	4.61630900	-1.15055800
C	-1.69897500	3.96882900	0.16380000
H	-1.65818700	4.65972200	1.00281100
H	-2.43976500	4.33617400	-0.54865000
C	-2.02161200	2.54821500	0.60924600
H	-3.08617700	2.34977900	0.71272800
H	-1.53225800	2.32356900	1.55279900
C	-2.54243200	1.02355100	-1.23353900
H	-3.15693700	1.82753400	-1.65616000
H	-2.08295800	0.49075000	-2.06783500
C	-3.45894500	0.08858500	-0.47611600
C	-4.71266200	-0.14095300	-1.04839300
H	-4.96344100	0.38164400	-1.96627600
C	-5.63848100	-1.00719700	-0.49404400
C	-5.28619400	-1.65151700	0.69289900
H	-5.99178300	-2.33527200	1.15379400
C	-4.06271600	-1.44496000	1.30357500
C	-3.12567500	-0.56930500	0.71478400
C	-6.98302300	-1.24138900	-1.12791900
H	-7.14835200	-2.30222400	-1.32116600
H	-7.06866500	-0.70869100	-2.07368800
H	-7.79074900	-0.90314100	-0.47670100
C	-3.68263800	-2.14901200	2.57262800
H	-3.45151900	-1.43321400	3.36275200
H	-2.78298500	-2.75052800	2.42715800
H	-4.48720400	-2.79880800	2.91178100
Zr	-0.09867200	-0.10932900	0.50242400
O	0.47249600	1.20338800	1.91352600
O	-0.65299500	-1.19085300	-1.08693800
C	-1.31611400	-2.14660600	-1.85754100
C	-1.65388100	-3.35826000	-0.99852600
C	-0.46915200	-2.53834500	-3.06136200
H	-2.25985900	-1.71714100	-2.22478100
H	-2.27320900	-3.05445300	-0.15347400
H	-2.19209300	-4.11310200	-1.57366500
H	-0.73175200	-3.80172200	-0.61594400
H	-0.24359200	-1.66303300	-3.67278700
H	0.47290800	-2.97728700	-2.72408600
H	-0.98873100	-3.26834100	-3.68300200
C	1.49110800	1.43172600	2.84627500
C	1.26377700	0.56676000	4.07896100
C	1.54134000	2.90817600	3.21620600
H	2.45644600	1.14642100	2.40023900

H	1.21062100	-0.48389000	3.79184600
H	2.06824400	0.69154500	4.80528300
H	0.31978600	0.84384500	4.55261000
H	1.72627900	3.52641500	2.33655600
H	0.58533800	3.20898800	3.64994000
H	2.33006600	3.10388000	3.94385400

Sum of electronic and thermal Free Energies= -1705.073983

Frequencies -- 21.0951 25.6720 33.4566