Electronic Supplementary Information

Group 4 permethylindenyl complexes for the polymerisation of *L*- and *rac*-lactide monomers

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General experimental details

Air- and moisture-sensitive compounds were handled under an inert N_2 atmosphere, using standard Schlenk line techniques and an MBraun Unilab glove box where required.

1.1 Solvent preparation

Pentane, hexane and benzene were dried using an MBraun SPS-800 solvent purification system, stored over a potassium mirror, and degassed under partial vacuum before use. THF was dried over and distilled from Na/Benzophenone and Et_2O was dried over and distilled from potassium metal, stored over 4 Å molecular sieves and degassed under partial vacuum before use.

Deuterated solvents were dried over NaK (toluene-d_8, benzene-d_6) or CaH_2 (pyridine-d_5, chloroform-d_1 and tetrahydrofuran-d_8), freeze-thaw degassed and stored over pre-activated 4 Å molecular sieves under N_2.

1.2 Solution phase NMR spectroscopy

NMR spectroscopy samples of air- and moisture-sensitive compounds were prepared in a glove box and sealed in 5 mm Young's tap NMR tubes. ^{1}H NMR spectra were recorded on a Bruker Avance III HD nanobay 400 MHz NMR spectrometer, $^{13}C\{^{1}H\}$ and $^{1}H\{^{1}H\}$ spectra were recorded on a Bruker Avance III NMR spectrometer. All spectra were recorded at 298 K and referenced internally to the residual *protio* solvent peak. All spectra are reported relative to tetramethylsilane (δ = 0 ppm). Two dimensional ^{1}H-^{1}H and ^{13}C-^{1}H correlation experiments were used, when necessary, to confirm ^{1}H and ^{13}C assignments.

1.3 Elemental analysis

Samples were prepared in a glove box and sealed in glass vials under nitrogen. CHN analyses were carried out in duplicate by Mr. Stephen Boyer, London Metropolitan University.

1.4 Infrared spectroscopy

Air-sensitive samples were prepared in the glove box and ground with anhydrous KBr before being pressed into discs using a specially designed press and airtight holder. IR spectra were recorded on a Nicolet iS5 ThermoScientific spectrometer (range = 4000–400 cm^{-1}, resolution = 1 cm^{-1}) in transmission mode. A background spectrum was run prior to the sample in each case and was subtracted from the spectrum.

1.5 Mass spectrometry

Samples were prepared in a glove box under a nitrogen atmosphere and sealed in glass tubes. Samples were run as electron impact (EI) and electrospray ionisation (ESI) mass spectra and the data collected by Dr James Wickens or Dr Victor Mikhailov, Chemistry Research Laboratory, University of Oxford.

MALDI-TOF-MS were collected Dr Victor Mikhailov using a Bruker MALDI Autoflex TOF MS. The DHB matrix was prepared by mixing the sample with DHB (10 mg mL^{-1} in 70:30 H_2O:CH_3CN) in a 1:1 volume ratio. The DCTB matrix was prepared by mixing 10 μL of sample with 10 μL DCTB (40 mg mL^{-1} in THF) and 2.5 μL KTFA (5 mg mL^{-1} in THF). 1.5 μL of the mixed solutions were spotted on the MALDI plate and dried.

1.6 Gel-permeation chromatography (GPC)

Gel permeation chromatography studies to determine polymer molecular weights were performed using a Shimadzu LC-20AD instrument at 40 °C. Two Mixed Bed PSS SDV linear S columns were used in series, with THF as the eluent and a flow rate of 1 mL min^{-1}. The instrument was calibrated using narrow M_n polystyrene standards (correction factor of 0.58) and polymer samples were dissolved in SEC grade THF and filtered prior to analysis.[1]

2. Representative NMR spectra

^{Me2}SB(Cp,I*)Li$_2$

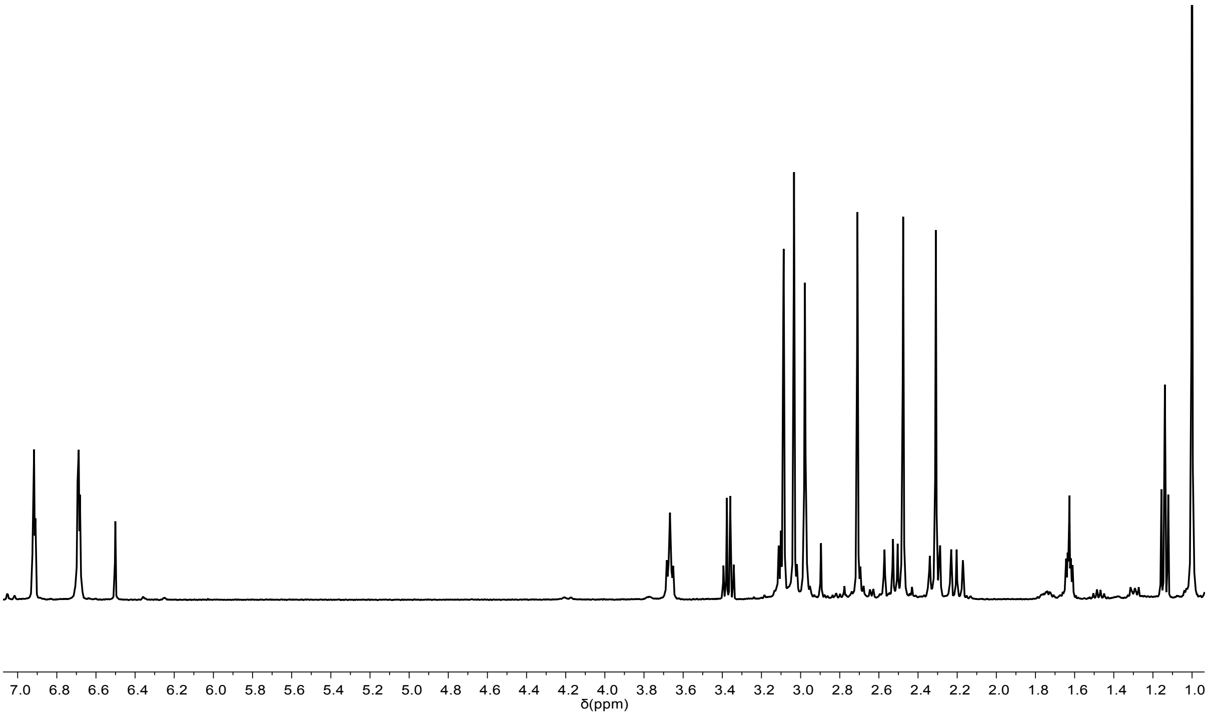


Fig. S1. ^{1}H NMR spectrum (C_5D_5N, 400 MHz, 298 K) of ^{Me2}SB(Cp,I*)Li$_2$.

^{Me2}SB(Cp^{Me},I*)Li$_2$

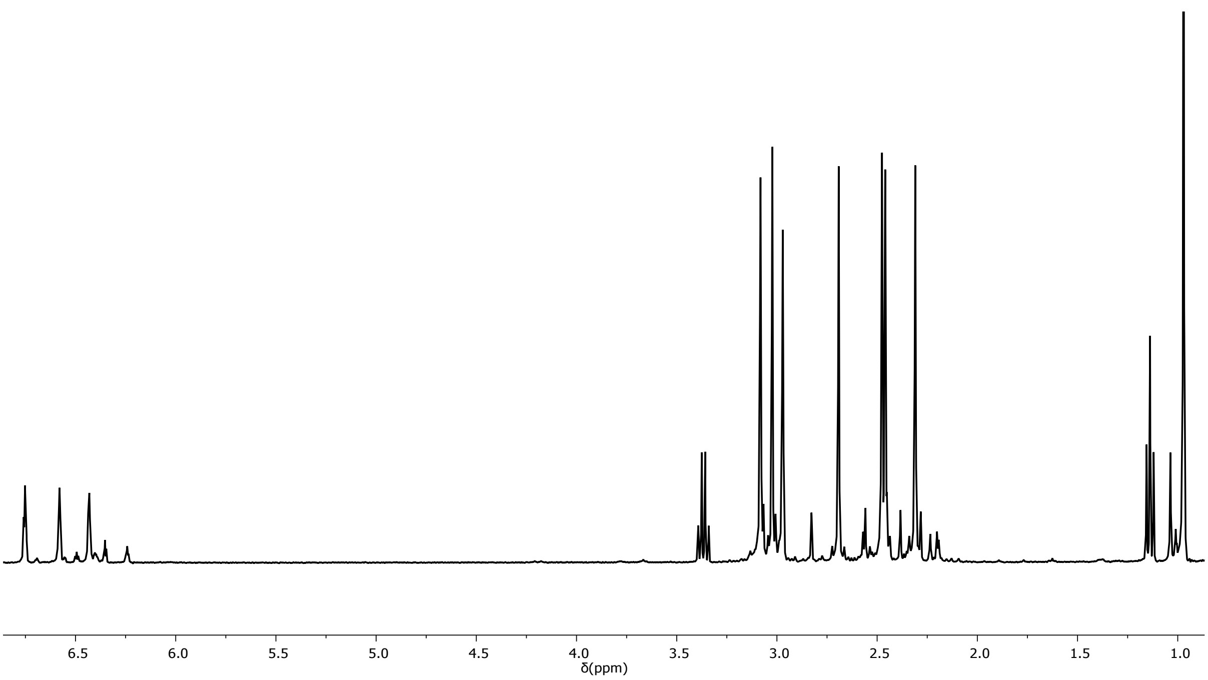


Fig. S2. ^{1}H NMR spectrum (C_5D_5N, 400 MHz, 298 K) of ^{Me2}SB(Cp^{Me},I*)Li$_2$.

^{Me2}SB(Cp,I*)ZrCl$_2$ (1)

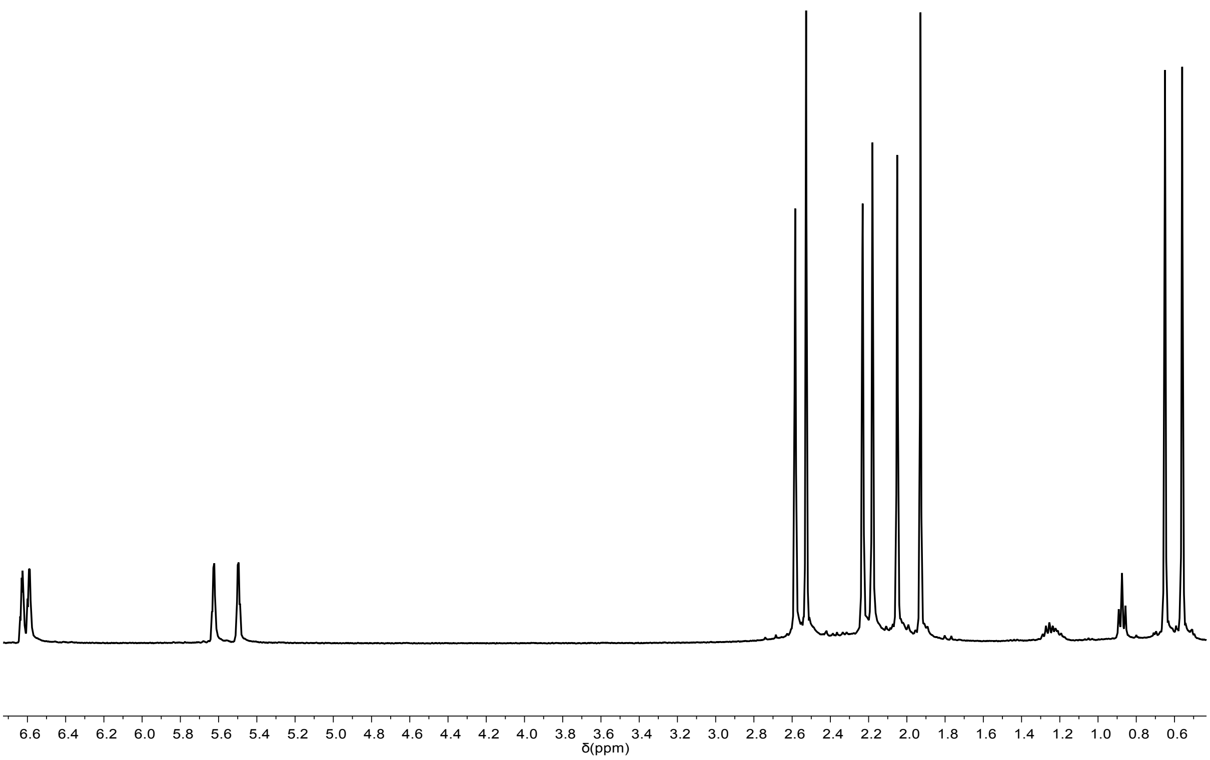


Fig. S3. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 298 K) of ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**).

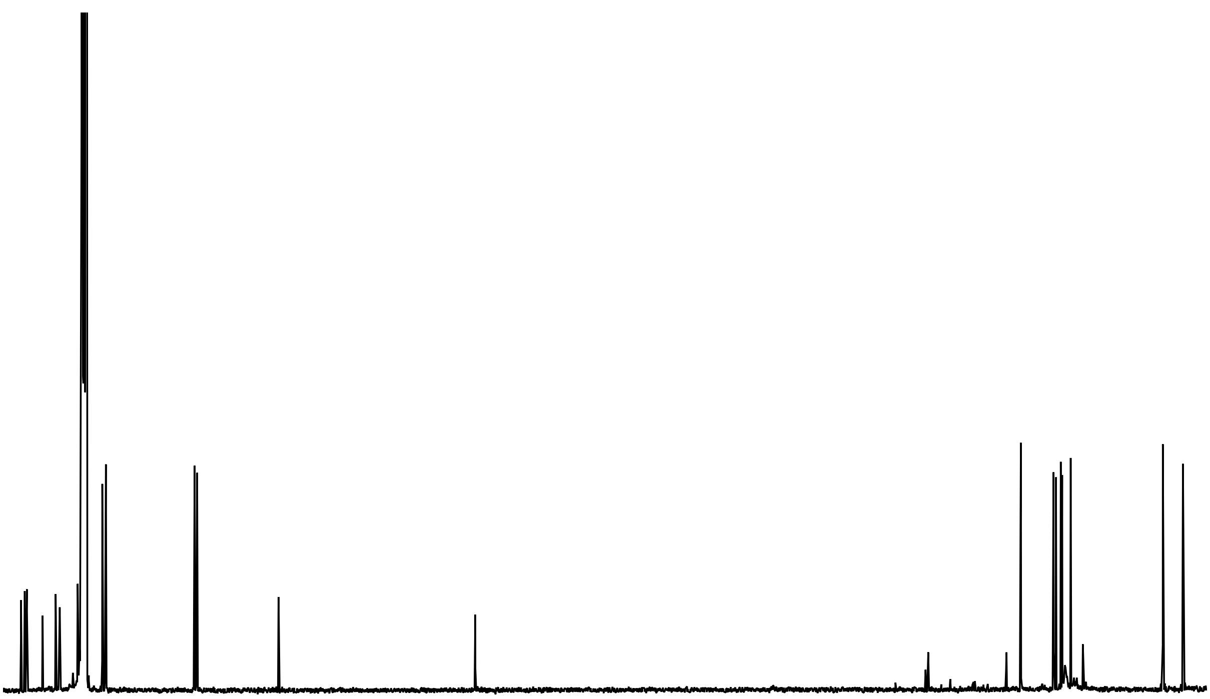


Fig. S4. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 125 MHz, 298 K) of ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**).

^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (2)

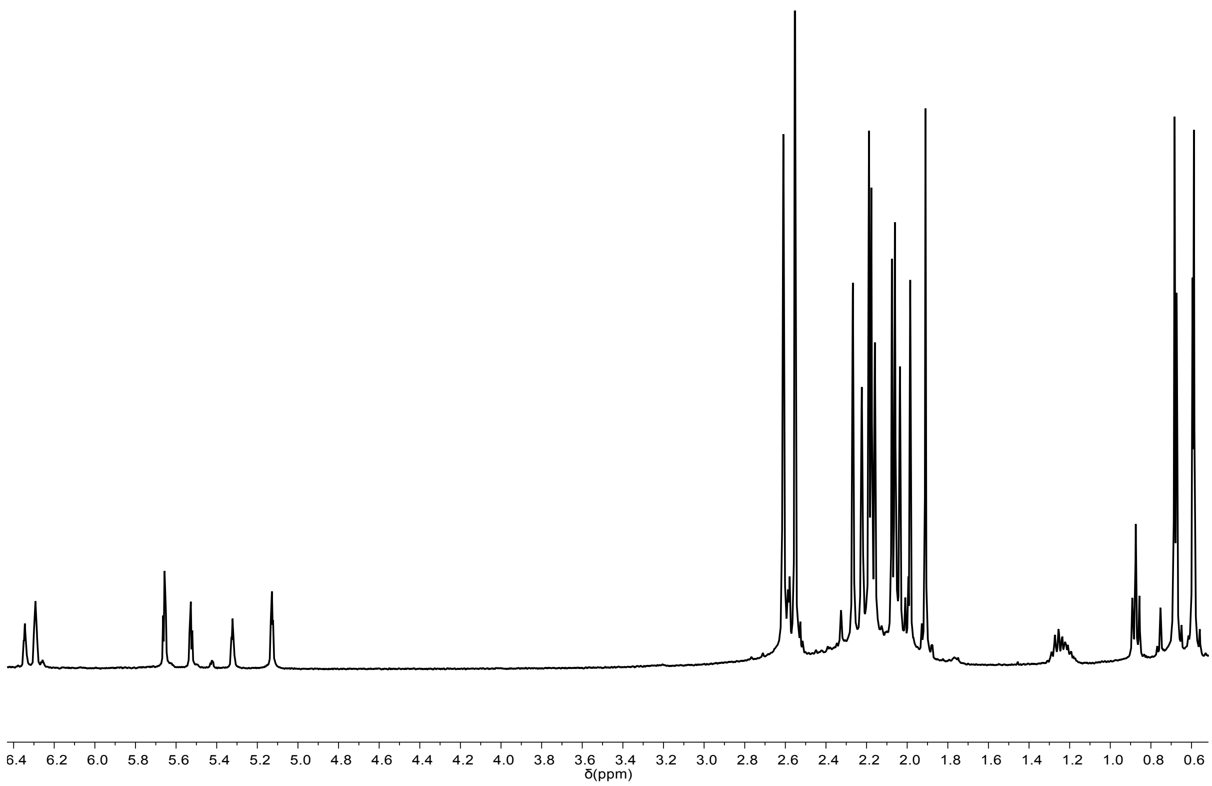


Fig. S5. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 298 K) of ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**). Isomers ***E*-2**:***Z*-2** in 60:40 ratio.

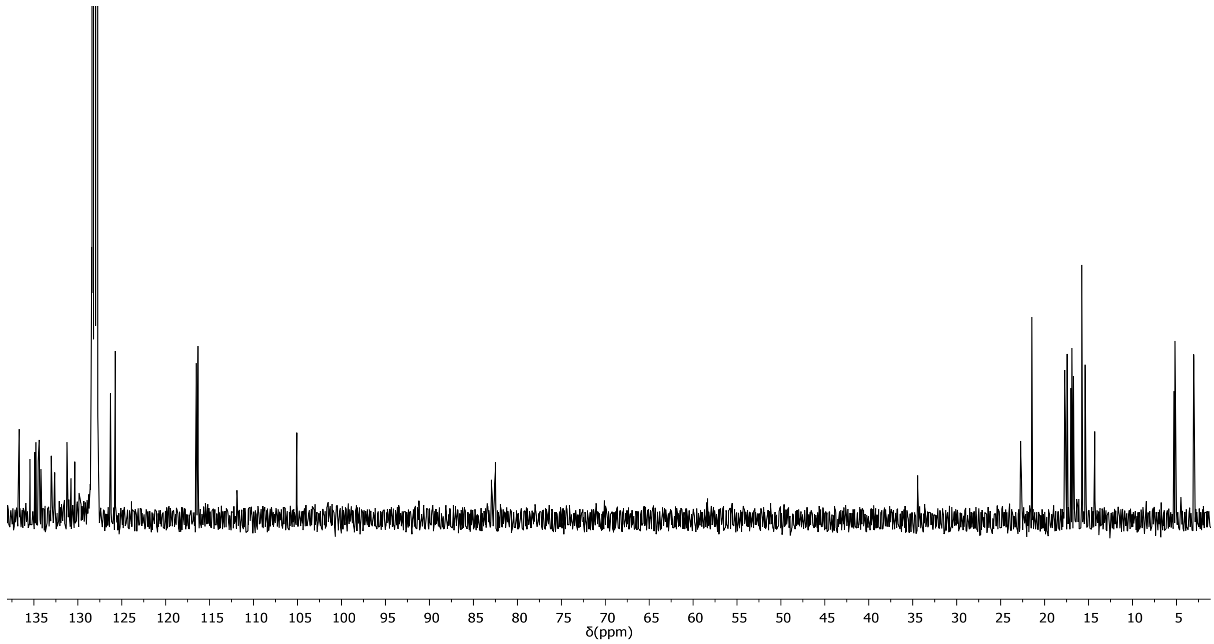


Fig. S6. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 125 MHz, 298 K) of ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**). Isomers ***E*-2**:***Z*-2** in 60:40 ratio.

^{Me2}SB(Cp,I*)HfCl$_2$ (3)

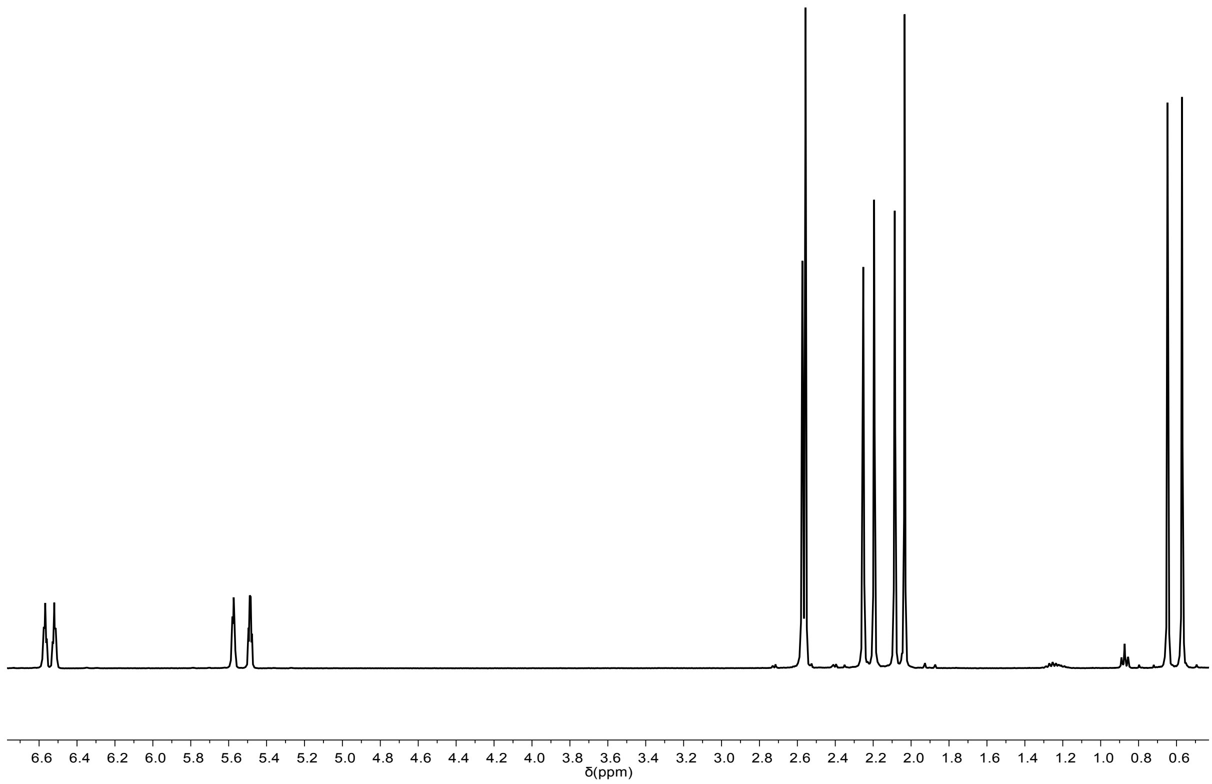


Fig. S7. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 298 K) of ^{Me2}SB(Cp,I*)HfCl$_2$ (**3**).

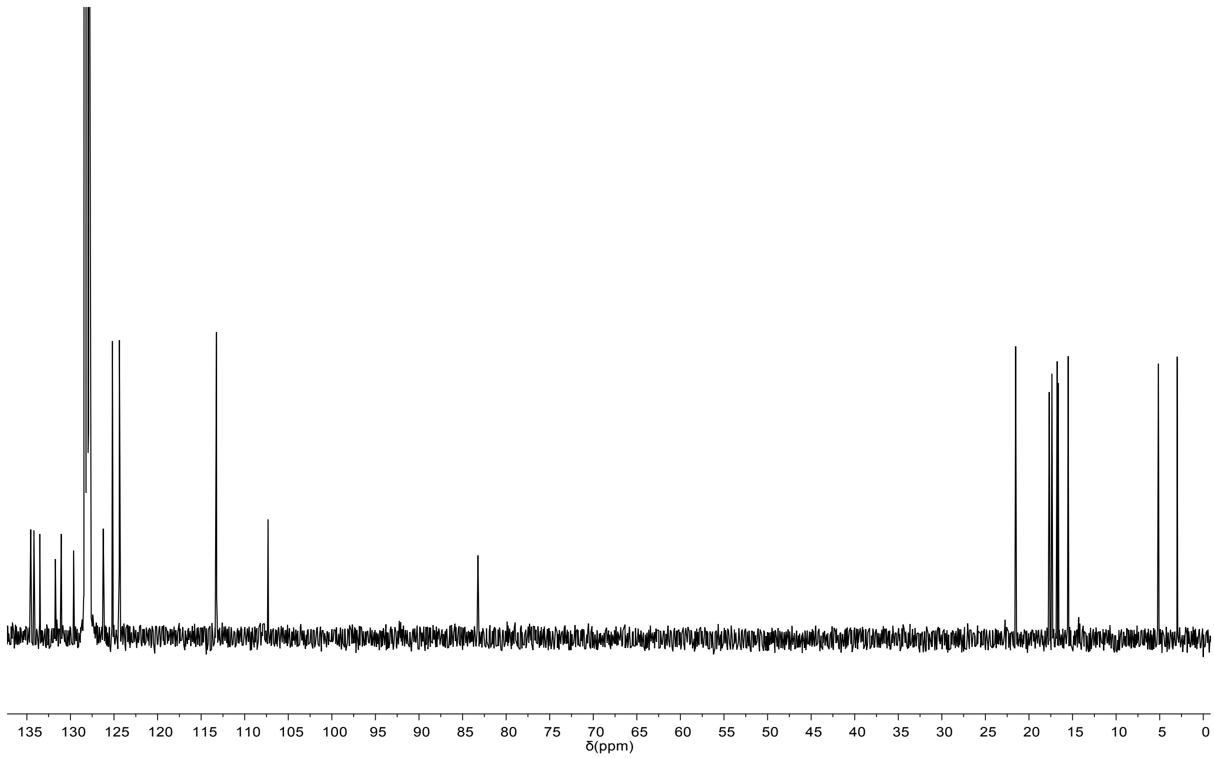


Fig. S8. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 125 MHz, 298 K) of ^{Me2}SB(Cp,I*)HfCl$_2$ (**3**).

^{Me_2}SB(Cp,I*)ZrCl,(O-2,4-Me-C_6H_3) (4)

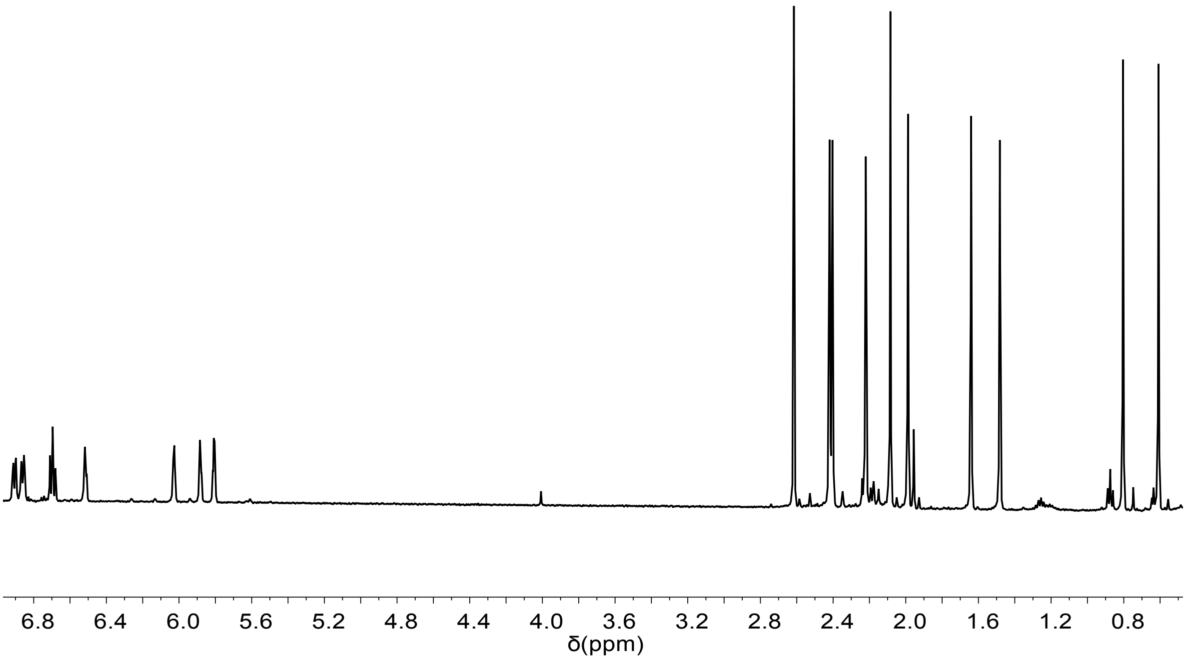


Fig. S9. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 298 K) of *Z*-^{Me_2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (**4**).

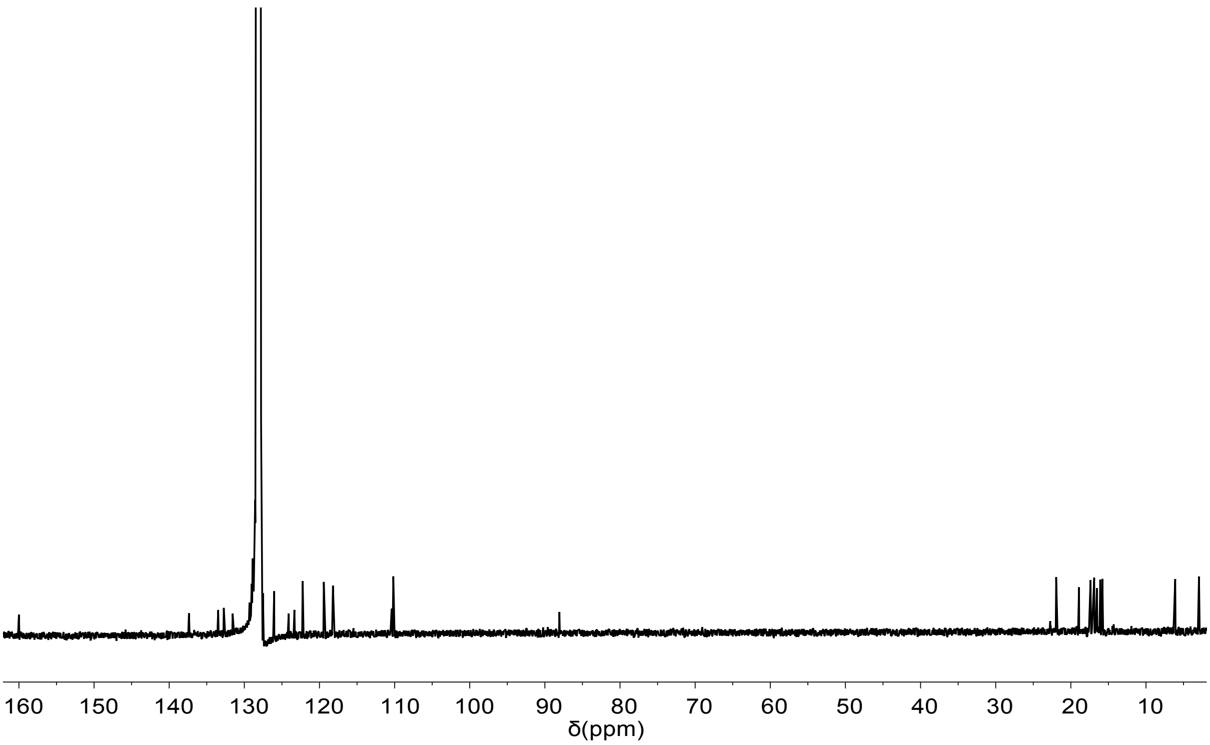


Fig. S10. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 125 MHz, 298 K) of *Z*-^{Me_2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (**4**).

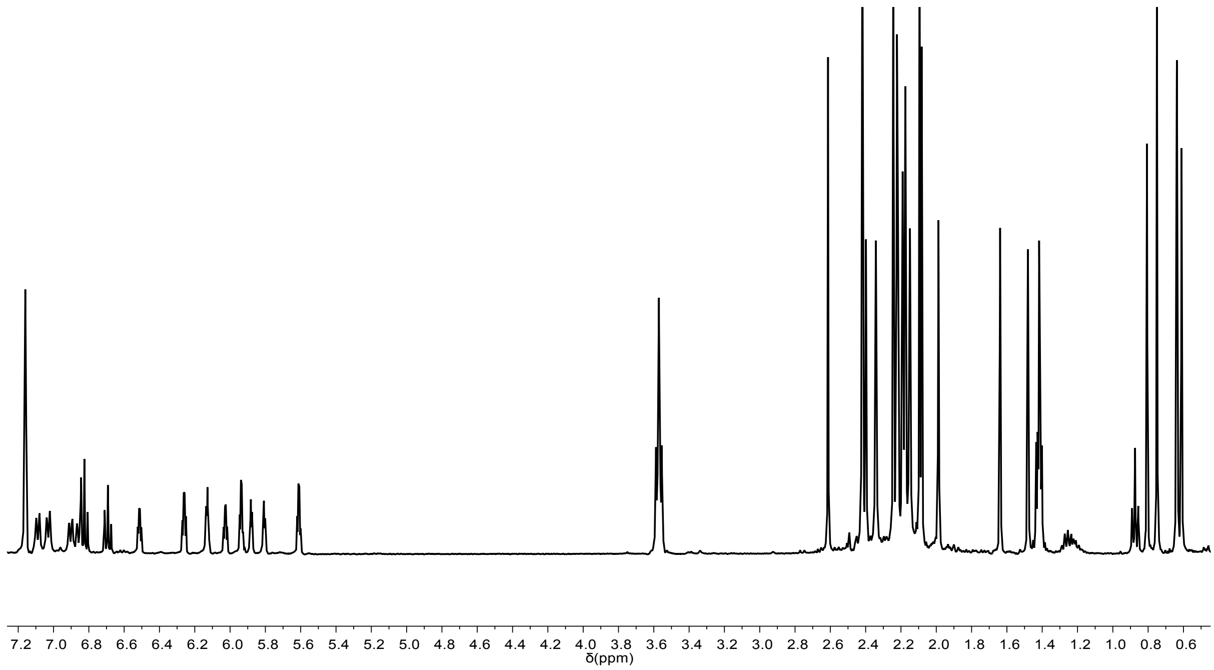


Fig. S11. Crude [1]H NMR spectrum (C_6D_6, 400 MHz, 298 K) of ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (**4**). Isomers ***E*-4**:***Z*-4** in 15:85 ratio.

PLA from $^{Me2}SB(Cp,I^*)ZrCl_2$ (1)

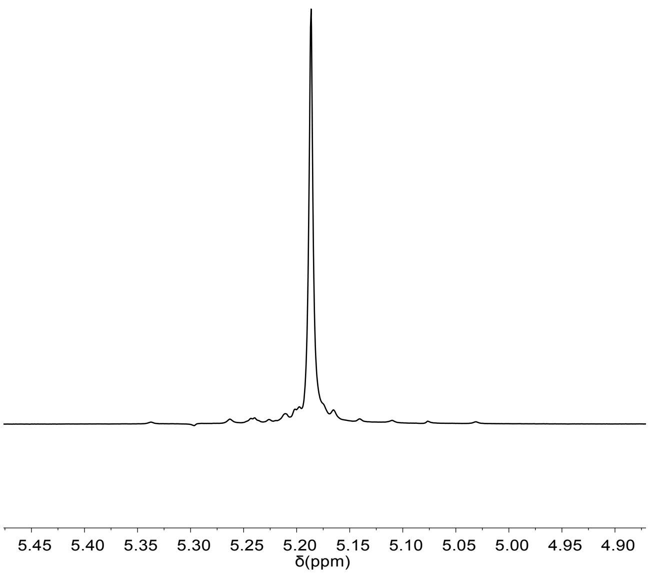


Fig. S12. $^1H\{^1H\}$ NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of the poly-*L*-lactide produced using $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**). Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M and $CDCl_3$.

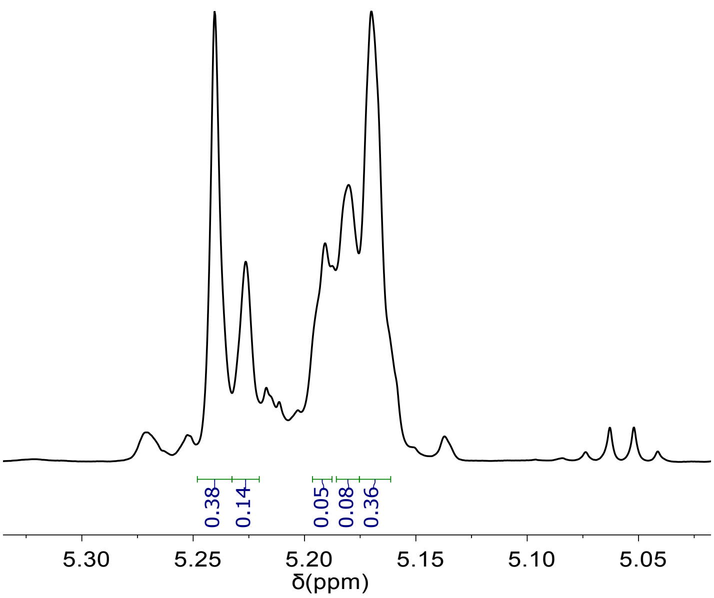


Fig. S13. $^1H\{^1H\}$ NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of the poly-*rac*-lactide produced using $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**). Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M and $CDCl_3$. $P_r = 0.79$ (calculated from the probability of tetra sequences in PLA based on Bernouillan statistics: $[rrr] = P_r^2 + (P_rP_m)/2$, $[rmr] = (P_m^2 + P_mP_r)/2$, $[rrm] = [mrr] = (P_rP_m)/2$ and $[mrm] = P_m^2/2$).

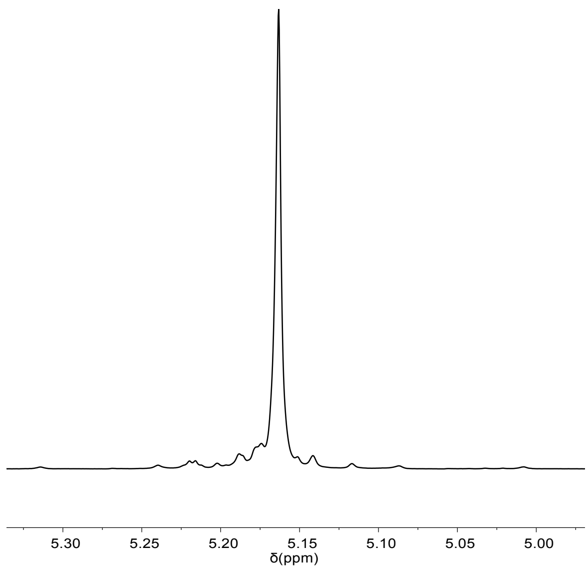


Fig. S14. $^1H\{^1H\}$ NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of the poly-*D*-lactide produced using $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**). Polymerisation conditions: 80 °C, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M and $CDCl_3$.

PLA from $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (2)

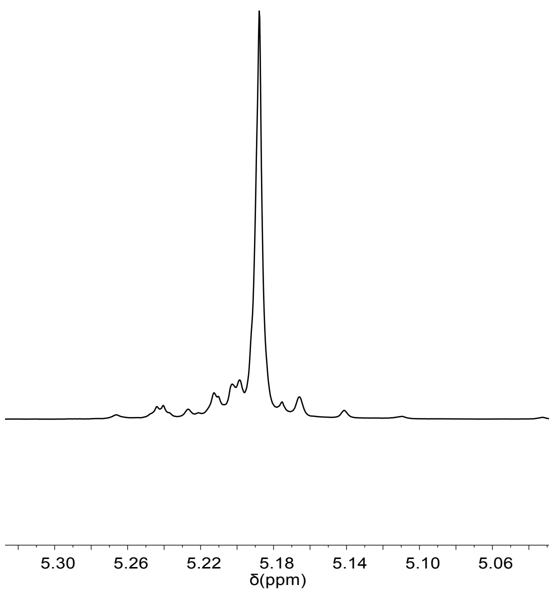


Fig. S15. $^1H\{^1H\}$ NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of the poly-*L*-lactide produced using $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**). Polymerisation conditions: 80 °C, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M and $CDCl_3$.

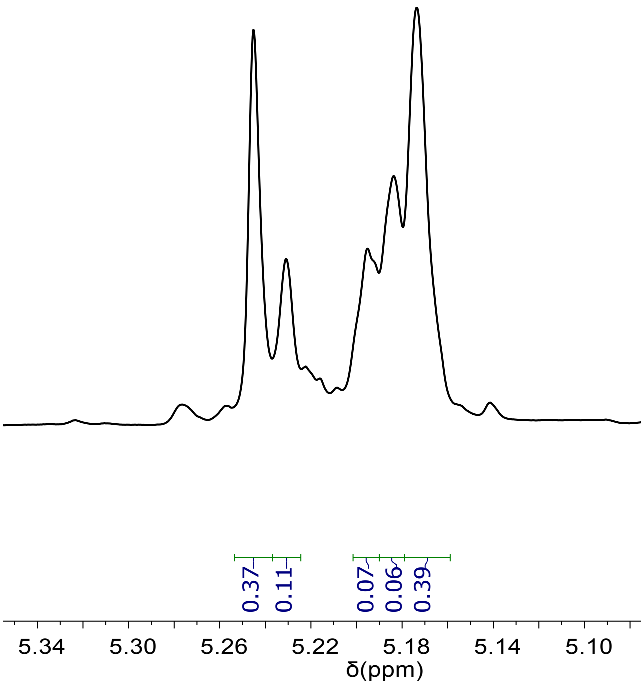


Fig. S16. $^{1}H\{^{1}H\}$ NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of the poly-*rac*-lactide produced using ^{Me_2}SB(Cp^{Me},I*)$ZrCl_2$ (**2**). Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M and $CDCl_3$. $P_r = 0.81$ (calculated from the probability of tetra sequences in PLA based on Bernouillan statistics: $[rrr] = P_r^2 + (P_rP_m)/2$, $[rmr] = (P_m^2 + P_mP_r)/2$, $[rrm] = [mrr] = (P_rP_m)/2$ and $[mrm] = P_m^2/2$).

PLA from ^{Me_2}SB(Cp,I*)$HfCl_2$ (3)

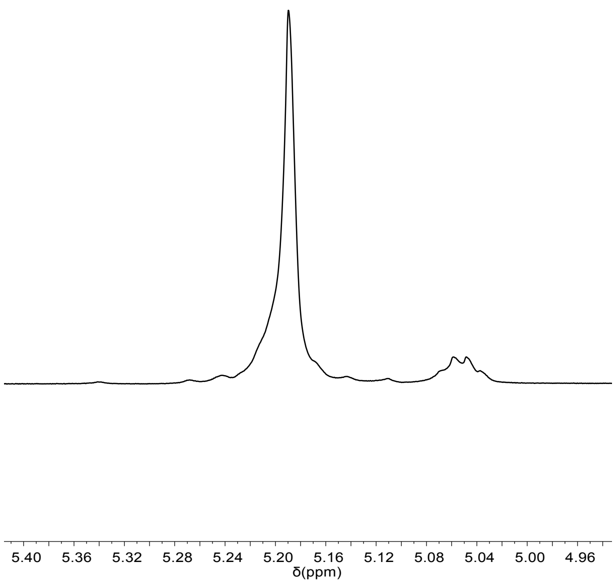


Fig. S17. $^{1}H\{^{1}H\}$ NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of the poly-*L*-lactide produced using ^{Me_2}SB(Cp,I*)$HfCl_2$ (**3**). Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, $CDCl_3$.

PLA from ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (4)

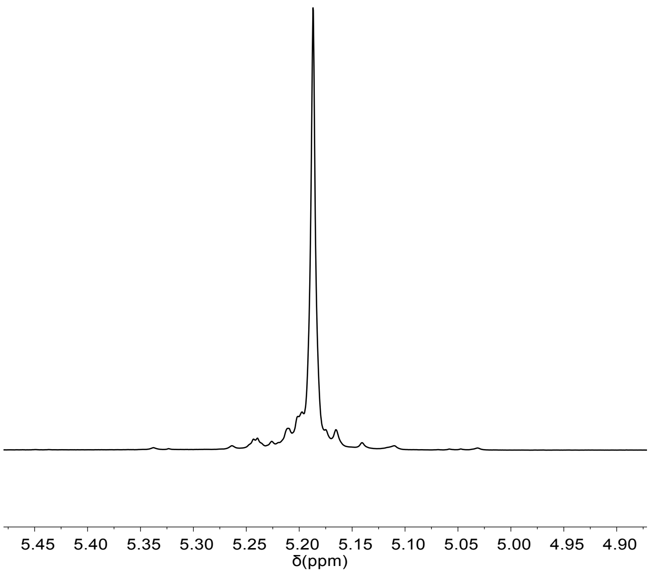


Fig. S18. $^{1}H\{^{1}H\}$ NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of the poly-*L*-lactide produced using ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (**4**). Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M and $CDCl_3$.

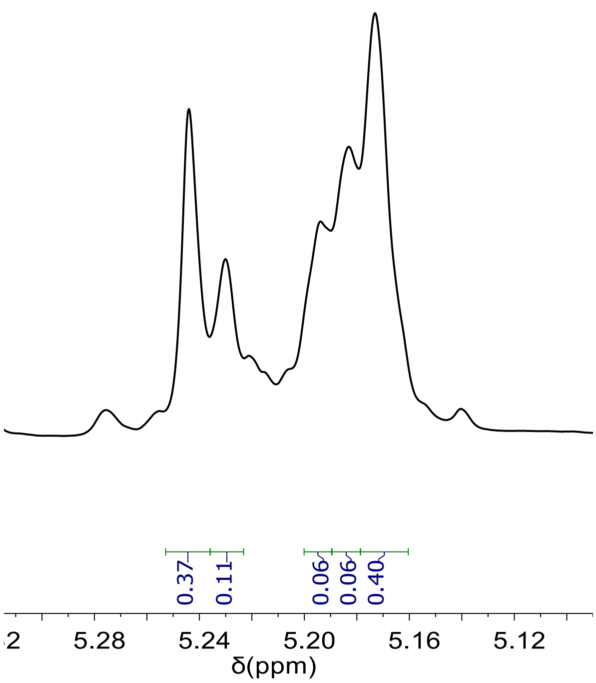
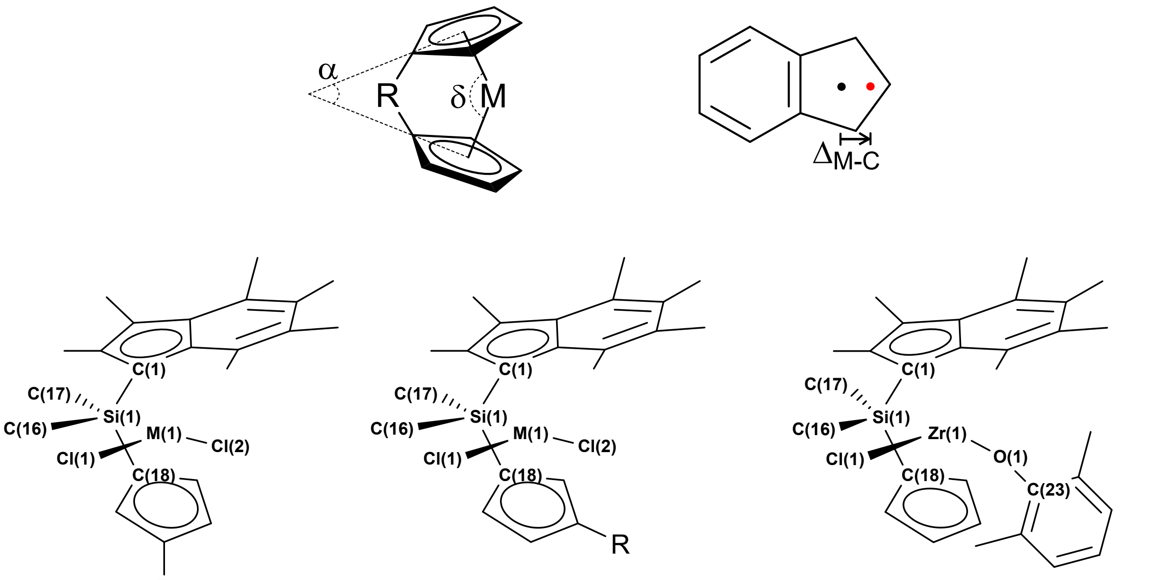


Fig. S19. $^{1}H\{^{1}H\}$ NMR spectrum ($CDCl_3$, 500 MHz, 298 K 00 MHz, $CDCl_3$, 25 °C) of the poly-*rac*-lactide produced using ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (**4**). Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M and $CDCl_3$. $P_r = 0.75$ (calculated from the probability of tetra sequences in PLA based on Bernouillan statistics: $[rrr] = P_r^2 + (P_rP_m)/2$, $[rmr] = (P_m^2 + P_mP_r)/2$, $[rrm] = [mrr] = (P_rP_m)/2$ and $[mrm] = P_m^2/2$).

3. Additional crystallographic data

3.1 Crystallographic details

Single crystal X-ray diffraction data collection and structure determinations were performed by Dr Zoë Turner (University of Oxford). Crystals were mounted on MiTeGen MicroMounts using perfluoropolyether oil and rapidly transferred to a goniometer head on a diffractometer fitted with an Oxford Cryosystems Cryostream open-flow nitrogen cooling device.[2] Data collections were carried out at 150 K using an Oxford Diffraction Supernova diffractometer using mirror-monochromated Cu Kα radiation (λ = 1.54178 Å) and the data was processed using CrysalisPro.[3] The structures were solved using direct methods (SIR-92)[4] or a charge flipping algorithm (SUPERFLIP)[5] and refined by full-matrix least-squares procedures using the Win-GX software suite.[6]



E-^{Me_2}SB(Cp^R,I*)MCl_2 (M = Zr, Hf)   *Z*-^{Me_2}SB(Cp^R,I*)MCl_2 (M = Zr, Hf) ^{Me_2}SB(Cp^{Me},I*)ZrCl(O-2,6-Me-C_6H_3)

Definition of geometric parameters α and β, and numbering scheme for complexes of the general formula ^{Me_2}SB(Cp^R,I*)ZrX_2.

3.2 Experimental crystallographic data

Table S1. Selected metrical data for ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**), ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) ^{Me2}SB(Cp,I*)ZrCl$_2$ (**3**), and ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C$_6$H$_3$) (**4**).

	1	**2***	**3**	**4**
M(1)-Ind$_{cent}$	2.2244(1)	2.2202(1)	2.2078(1)	2.2504(1)
M(1)-Cp$^{R}_{cent}$	2.2076(1)	*E*: 2.2194(1) *Z*: 2.1935(1)	2.1861(1)	2.2201(1)
M(1)-Cl(1)	2.4435(13)	2.4366(8)	2.4080(15)	2.4580(4)
M(1)-Cl(2)	2.4385(14)	2.4095(7)	2.4181(15)	-
M(1)-O(1)	-	-	-	1.9628(12)
Si(1)-C(1)	1.900(5)	1.901(6)	1.907(6)	1.9018(18)
Si(1)-C(18)	1.880(6)	*E*: 1.837(6) *Z*: 1.931(9)	1.877(6)	1.8680(18)
C(23)-O(1)	-	-	-	1.349(2)
Δ_{M-C}	0.0757	0.0503	0.0762	0.0243
α	60.11	*E*: 62.38 *Z*: 56.85	59.38	59.49
δ	126.37(1)	*E*: 126.12(1) *Z*: 130.60(1)	126.88	126.60
Cl(1)-M(1)-Cl(2)	97.73(5)	97.72(3)	96.59(5)	-
Zr(1)-O(1)-C(23)	-	-	-	173.09(12)
C(1)-Si(1)-C(16)	94.6(2)	*E*: 92.9(4) *Z*: 95.0(5)	94.3(3)	94.88(7)
C(16)-Si(1)-C(17)	105.1(4)	104.1(2)	105.9(4)	104.02(10)

* The crystallographic data shows two isomers, with crystallographic parameters differing only in the Cp^{R} ring substituent.

Table S2. Selected experimental crystallographic data for ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**), ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) ^{Me2}SB(Cp,I*)ZrCl$_2$ (**3**), and ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C$_6$H$_3$) (**4**)

Complex	**1**	**2**	**3**	**4**
		Crystal data		
Chemical formula	$C_{22}H_{28}Cl_2SiZr$	$C_{23}H_{30}Cl_2SiZr$	$C_{22}H_{28}Cl_2HfSi$	$C_{30}H_{37}ClOSiZr$
M_r	482.65	496.68	569.92	568.35
Crystal system, space group	Monoclinic, *I*2/*a*	Monoclinic, *P*2$_1$/*n*	Monoclinic, *I*2/*c*	Monoclinic, *P*2$_1$/*n*
Temperature (K)	150	150	150	
a, *b*, *c* (Å)	15.5105 (6), 10.3103 (3), 27.3957 (12)	11.6046 (2), 12.6961 (2), 15.1843 (2)	15.4820 (3), 10.3037 (2), 27.3060 (5)	14.7967 (1), 21.8481 (1), 16.9159 (1)
α, β, γ (°)	90, 104.496 (3), 90	90, 99.825 (2), 90	90, 104.261 (1), 90	90, 103.556 (1), 90
V (Å^3)	4241.6 (3)	2204.34 (6)	4221.67 (14)	5316.22 (6)
Z	8	4	8	8
Radiation type	Cu Kα	Cu Kα	Mo Kα	Cu Ka
μ (mm^{-1})	7.12	6.87	5.26	4.90
Crystal size (mm)	0.12 × 0.05 × 0.04	0.17 × 0.10 × 0.03	0.15 × 0.05 × 0.01	0.13 × 0.05 × 0.03
		Data Collection		
Diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer	KappaCCD	SuperNova, Dual, Cu at zero, Atlas diffractometer
Absorption correction	Gaussian. *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Numerical absorption correction based on gaussian	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical	Multi-scan Multi-scan from symmetry-related measurements using *SORTAV* (Blessing 1995).	Multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.21 (release 20-01-2012 CrysAlis171 .NET)

	integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	harmonics, implemented in SCALE3 ABSPACK scaling algorithm.		(compiled Jan 23 2012,18:06:46) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.956, 1.000	0.557, 1.000	0.792, 1.000	0.612, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17234, 4185, 3637	26231, 4501, 4090	9301, 4806, 4013	107247, 11070, 10264
R_{int}	0.036	0.039	0.035	0.037
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.184, 1.48	0.039, 0.106, 1.04	0.042, 0.110, 1.05	0.026, 0.068, 1.02
No. of reflections	4185	4501	4806	11070
No. of parameters	243	291	243	633
No. of restraints	0	1	0	0
$(\Delta/\sigma)_{max}$	0.002	0.004	0.001	0.002
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	5.79, -0.81	0.62, -0.50	6.25, -2.13	0.66, -0.56

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.21 (release 20-01-2012 CrysAlis171 .NET) (compiled Jan 23 2012, 18:06:46), *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), Collect (Nonius BV, 1997-2000), *HKL SCALEPACK* (Otwinowski & Minor 1997), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997), SUPERFLIP. Palatinus, L.; Chapuis, G. J. Appl. Cryst. 2007, 40, 786-790, Sir-92. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. J. Appl. Cryst. 1994, 27, 435., *SHELXL2014* (Sheldrick, 2014), *ORTEP-3 for Windows*. Farrugia, L. J. J. Appl. Cryst. 1997, 30, 565.

Exemplar enantiomers of ^{Me_2}SB(Cp,I*)ZrCl$_2$ (1)

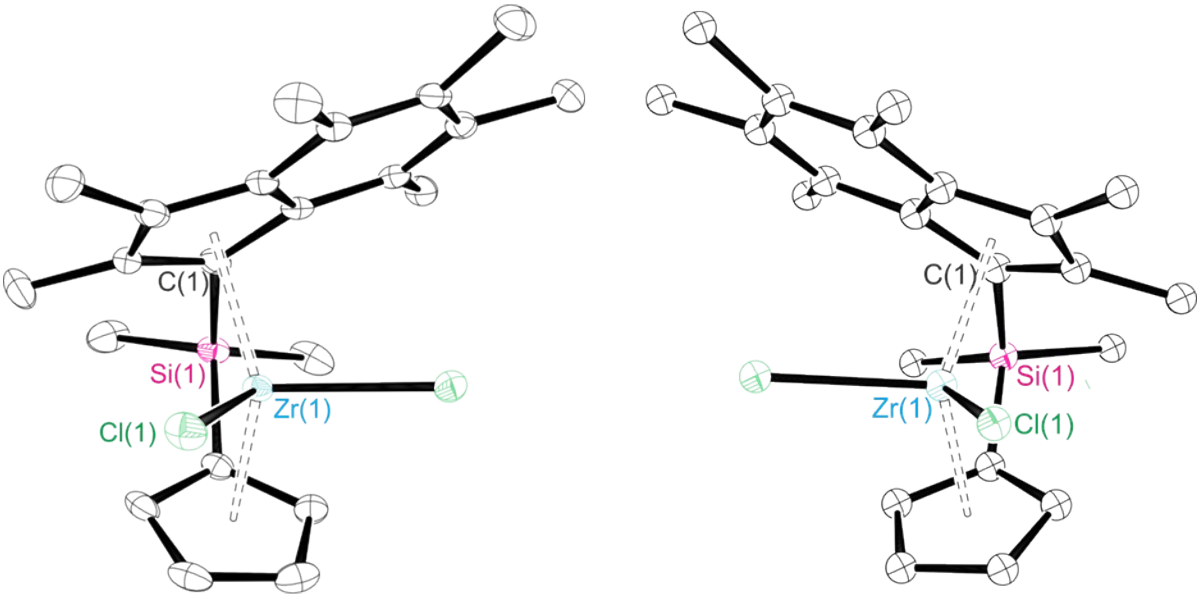


Fig. S20. Solid-state molecular structures of the two enantiomers of ^{Me_2}SB(Cp,I*)ZrCl$_2$ (**1**). Ellipsoids shown at 50% probability. H atoms omitted for clarity.

4. Additional polymerisation data

***D*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (1), ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (2) and ^{Me_2}SB(Cp,I*)ZrCl(O-2,6-Me-C$_6$H$_3$) (4).**

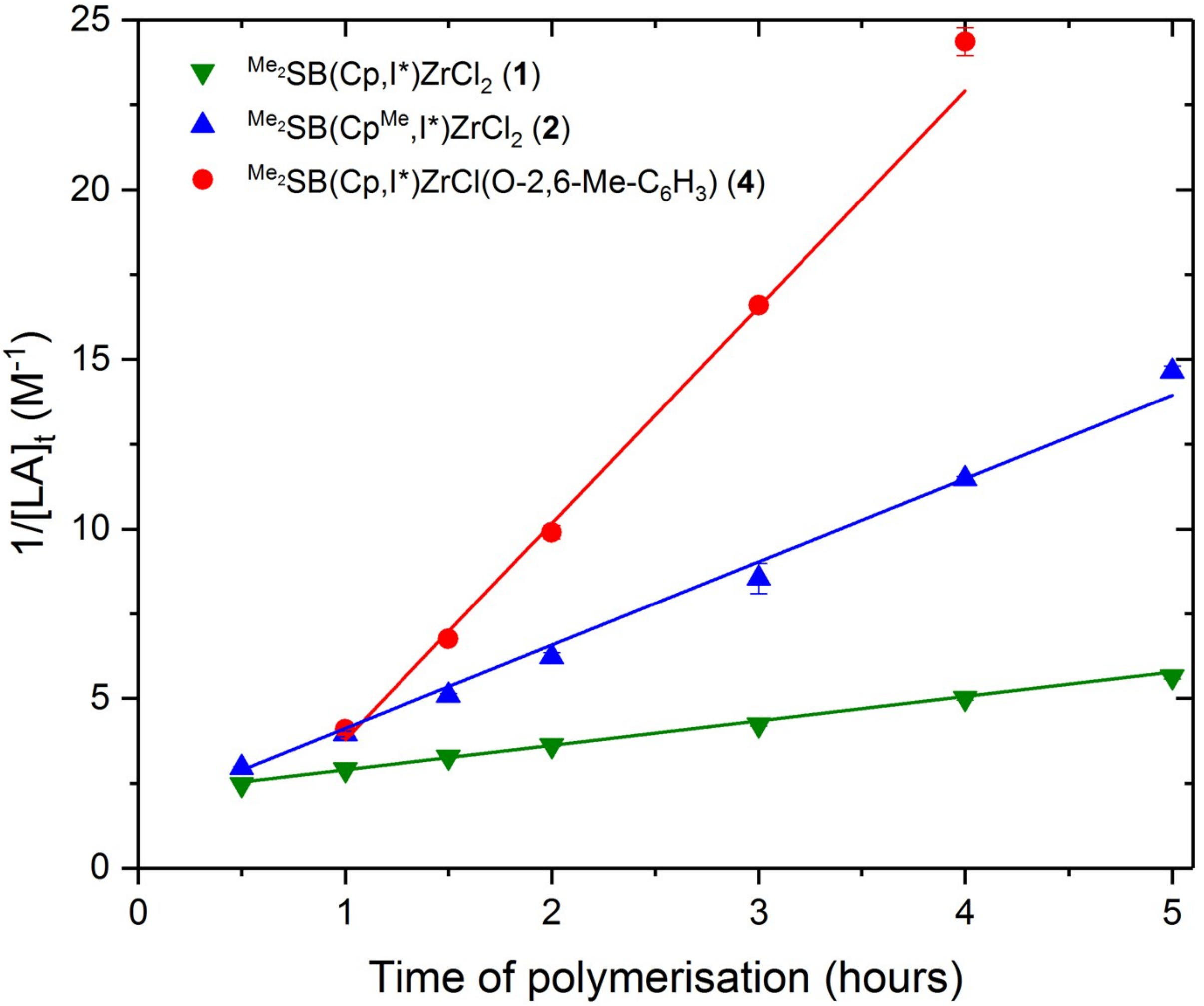


Fig. S21. *D*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (**1**) (green down triangle, $k_{obs} = 0.72 \pm 0.03$ M^{-1} h^{-1}), ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) (blue triangle, $k_{obs} = 2.46 \pm 0.07$ M^{-1} h^{-1}) and ^{Me_2}SB(Cp,I*)ZrCl(O-2,6-Me-C$_6$H$_3$) (**4**) (red circle, $k_{obs} = 6.38 \pm 0.30$ M^{-1} h^{-1}). Polymerisation conditions: 80 °C, CDCl$_3$, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents of benzyl alcohol as co-initiator. All polymerisations carried out in duplicate.

***L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (1) - scale variation**

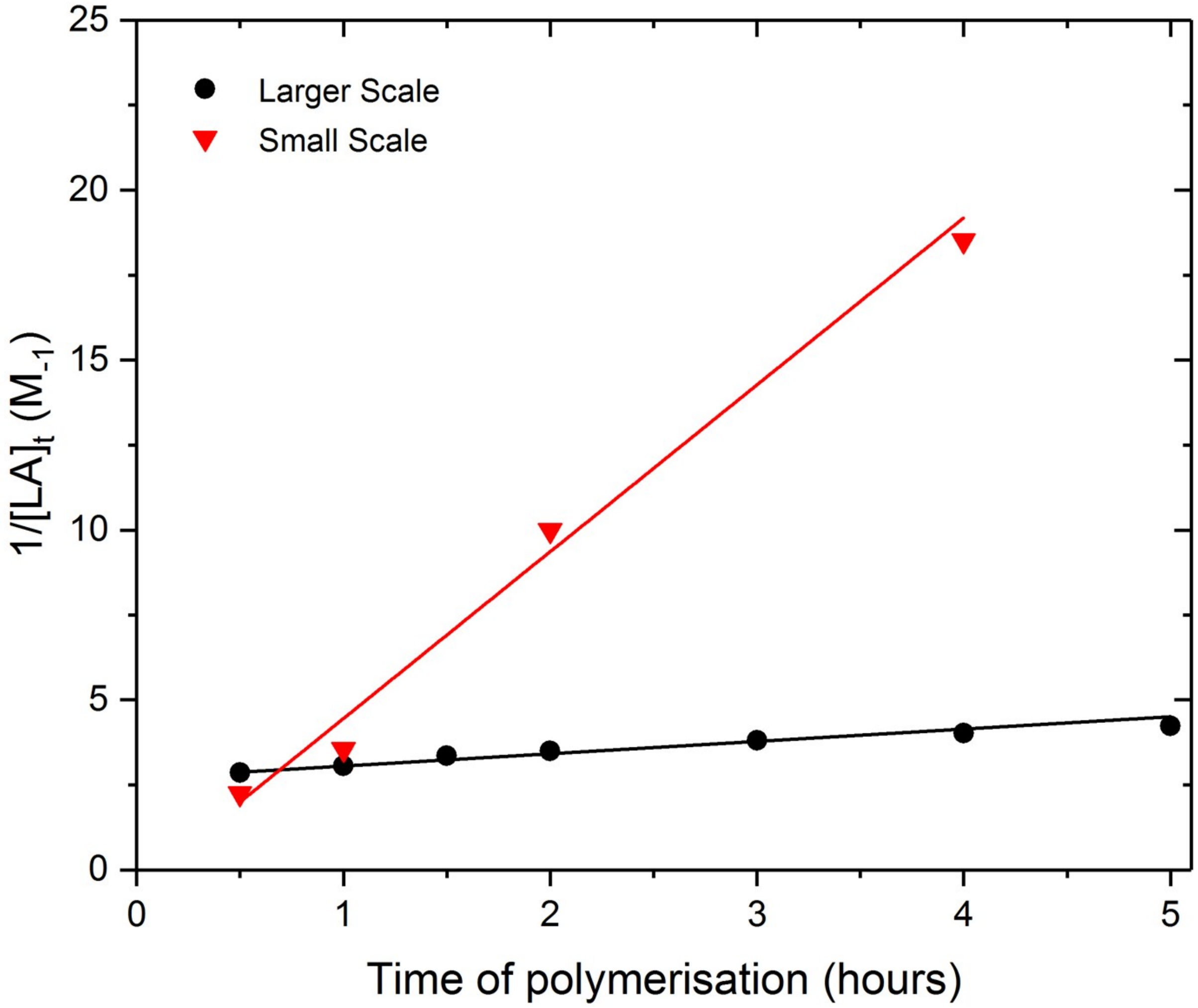


Fig. S22. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) on a small scale (black circle, k_{obs} = 2.69 ± 0.04 M^{-1} h^{-1}) and larger scale (red down triangle, k_{obs} = 4.91 ± 0.65 M^{-1} h^{-1}). Small scale polymerisation conditions: *L*-lactide (40 mg), toluene-d_8, 80 °C $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents of benzyl alcohol as co-initiator. Larger scale polymerisation conditions: *L*-lactide (200 mg), toluene, 80 °C $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents of benzyl alcohol as co-initiator.

***L*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (1) - [LA]$_0$/[M]$_0$ variation**

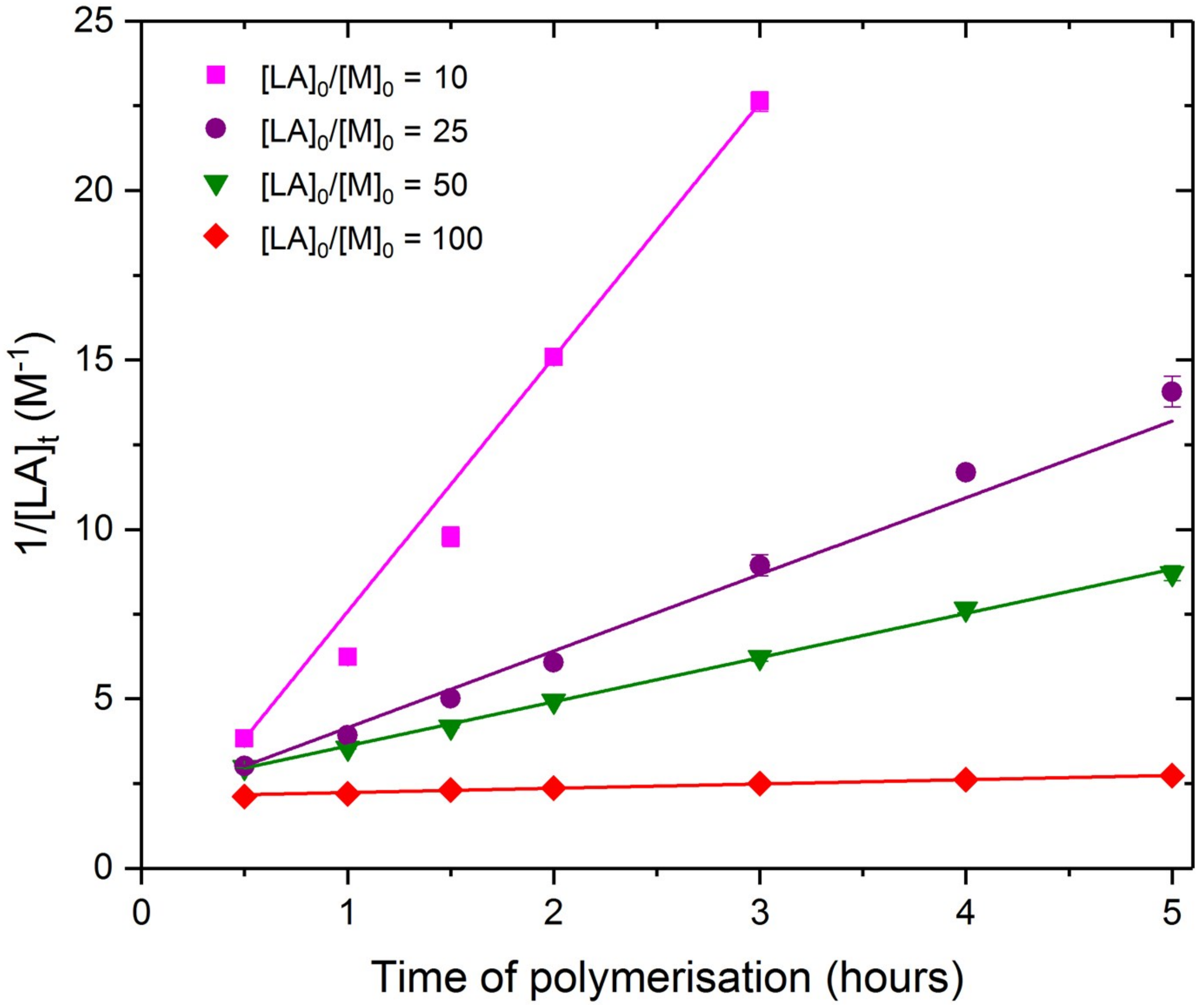


Fig. S23. *L*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (**1**) with [LA]$_0$/[M]$_0$ = 100 (red diamond, $k_{obs} = 0.13 \pm 0.01$ M^{-1} h^{-1}), [LA]$_0$/[M]$_0$ = 50 (green down triangle, $k_{obs} = 1.30 \pm 0.03$ M^{-1} h^{-1}), [LA]$_0$/[M]$_0$ = 25 (purple circle, $k_{obs} = 2.26 \pm 0.12$ M^{-1} h^{-1}) and [LA]$_0$/[M]$_0$ = 10 (pink square, $k_{obs} = 7.51 \pm 0.09$ M^{-1} h^{-1}). Polymerisation conditions: 80 °C, CDCl$_3$, [LA]$_0$ = 0.5 M, 2 equivalents of benzyl alcohol as co-initiator. All polymerisations carried out in duplicate.

***L*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (1) - [BnOH]$_0$ variation**

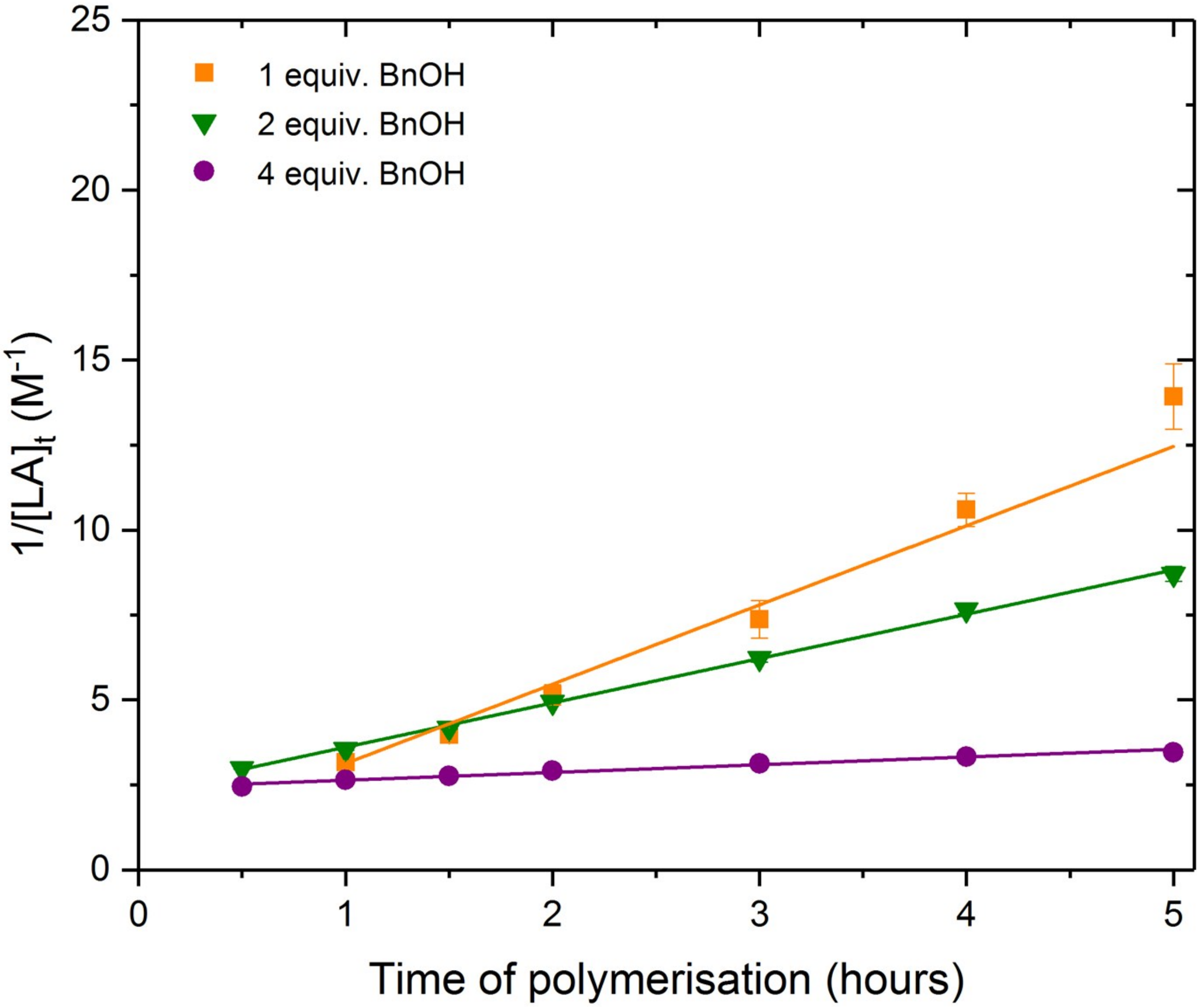


Fig. S24. *L*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (**1**) with 1 equivalent BnOH (orange square, $k_{obs} = 2.33 \pm 0.17$ M^{-1} h^{-1}), 2 equivalents BnOH (green down triangle, $k_{obs} = 1.30 \pm 0.03$ M^{-1} h^{-1}) and 4 equivalents BnOH (purple circle, $k_{obs} = 0.23 \pm 0.01$ M^{-1} h^{-1}). Polymerisation conditions: 80 °C, CDCl$_3$, [LA]$_0$ = 0.5 M, [LA]$_0$/[M]$_0$ = 50. All polymerisations carried out in duplicate.

***L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (1) - temperature variation**

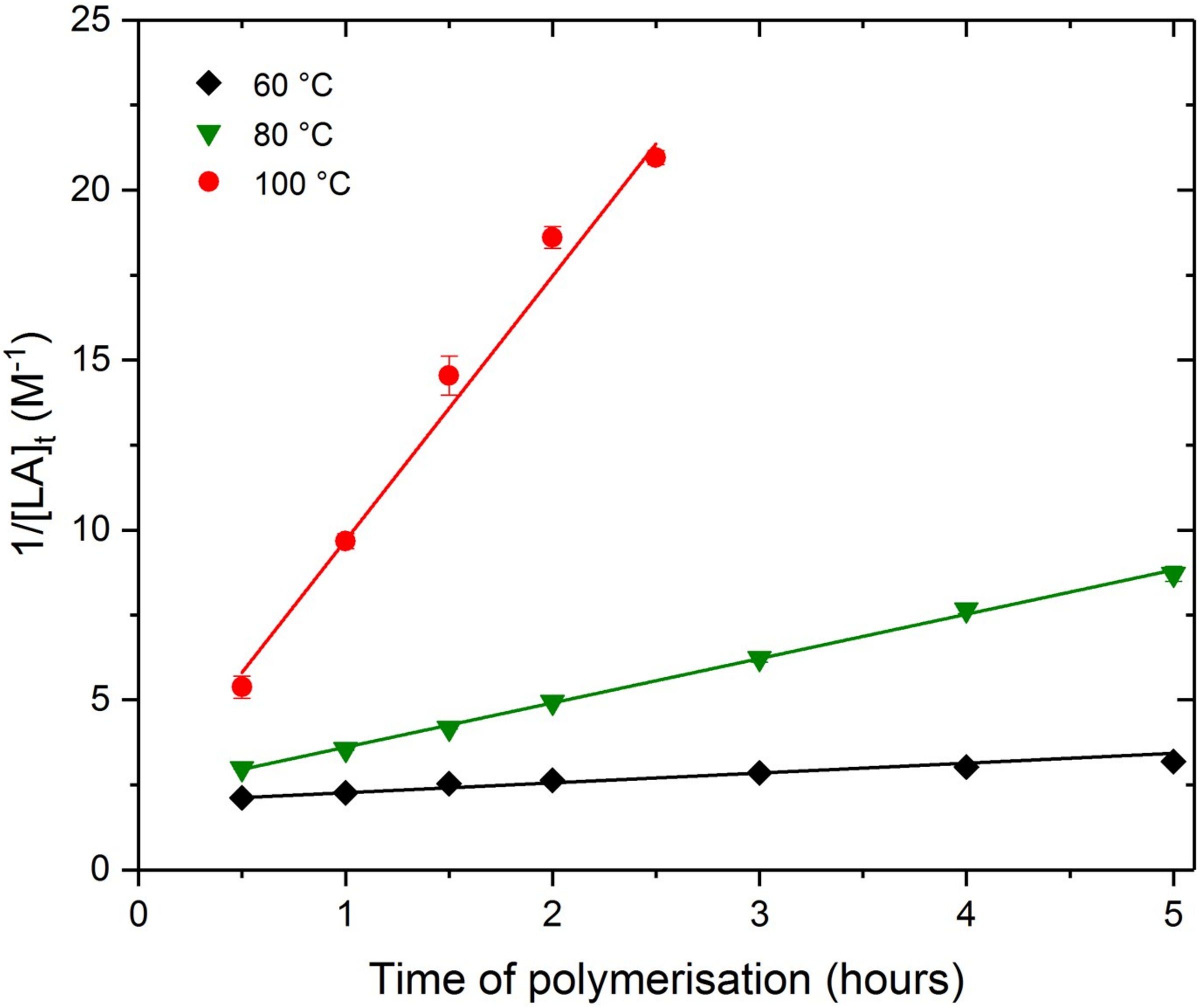


Fig. S25. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) at 60 °C (black diamond, k_{obs} = 0.29 ± 0.01 M^{-1} h^{-1}), 80 °C (green down triangle, k_{obs} = 1.30 ± 0.03 M^{-1} h^{-1}) and 100 °C (red circle, k_{obs} = 7.47 ± 0.40 M^{-1} h^{-1}). Polymerisation conditions: $CDCl_3$, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M, 2 equivalents of benzyl alcohol as co-initiator. All polymerisations carried out in duplicate.

***rac*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (1) - scale variation**

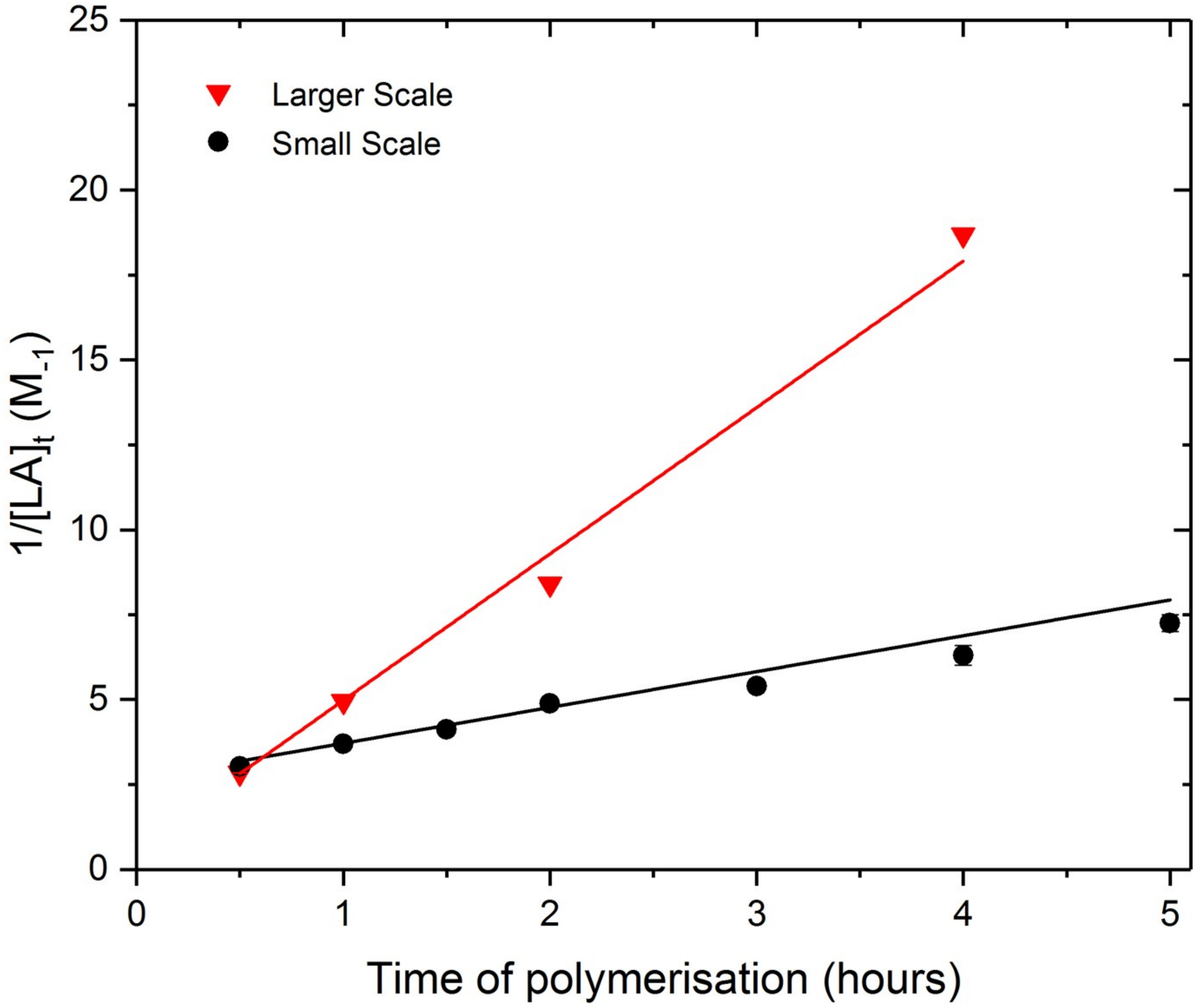


Fig. S26. *rac*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) on a small scale (black circle, k_{obs} = 1.05 ± 0.10 M^{-1} h^{-1}) and larger scale (red triangle, k_{obs} = 4.31 ± 0.16 M^{-1} h^{-1}). Small scale polymerisation conditions: *rac*-lactide (40 mg), toluene-d_8, 80 °C $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents of benzyl alcohol co-initiator. Larger scale polymerisation conditions: 200 mg *rac*-lactide (200 mg), toluene, 80 °C $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents of benzyl alcohol co-initiator.

rac-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (1) - [LA]$_0$/[M]$_0$ variation

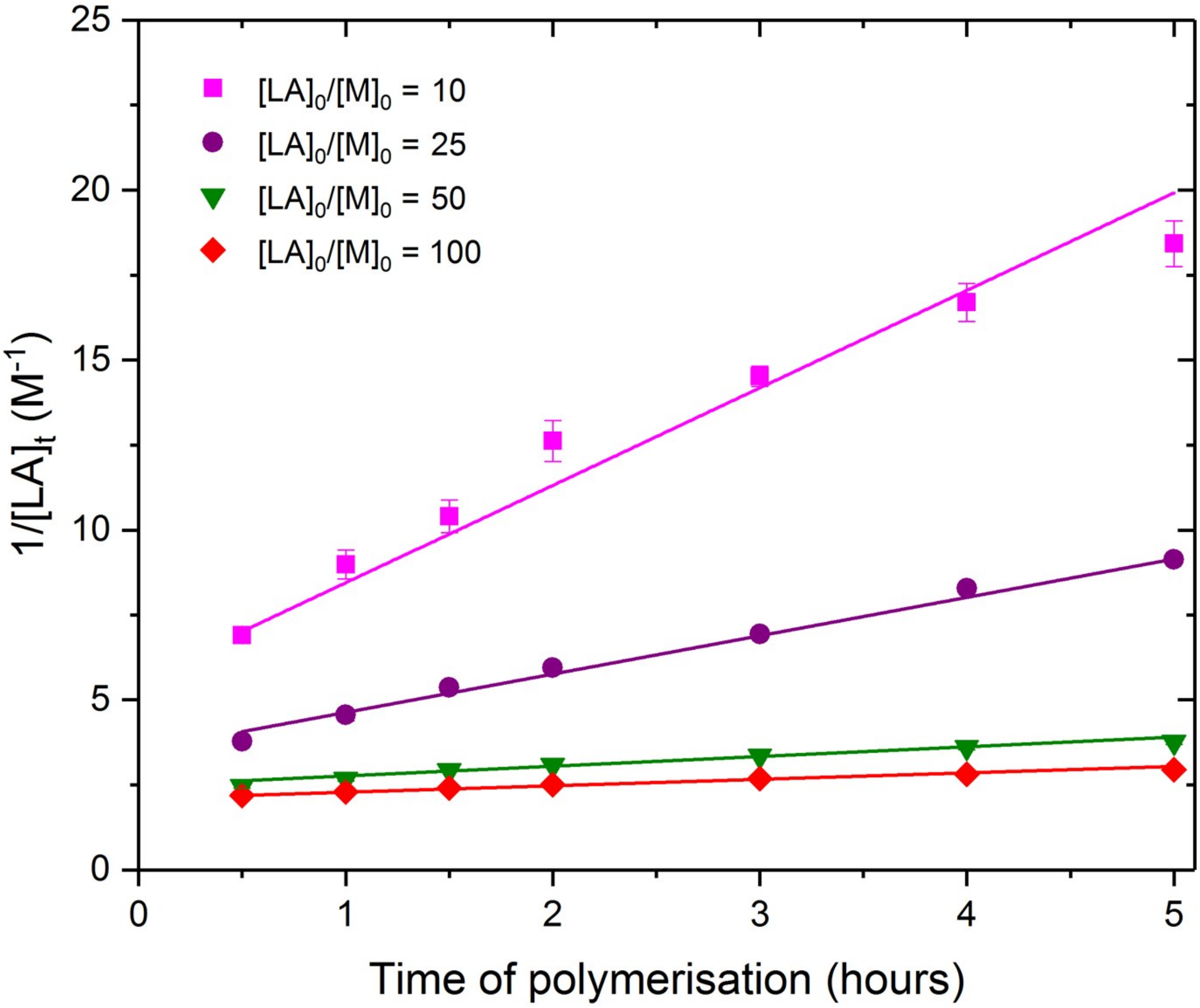


Fig. S27. *rac*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) with [LA]$_0$/[M]$_0$ = 100 (red diamond, $k_{obs} = 0.19 \pm 0.01$ M^{-1} h^{-1}), [LA]$_0$/[M]$_0$ = 50 (green down triangle, $k_{obs} = 0.29 \pm 0.03$ M^{-1} h^{-1}), [LA]$_0$/[M]$_0$ = 25 (purple circle, $k_{obs} = 1.13 \pm 0.03$ M^{-1} h^{-1}) and [LA]$_0$/[M]$_0$ = 10 (pink square, $k_{obs} = 2.87 \pm 0.15$ M^{-1} h^{-1}). Polymerisation conditions: 80 °C, $CDCl_3$, [LA]$_0$ = 0.5 M, 2 equivalents of benzyl alcohol as co-initiator. All polymerisations carried out in duplicate.

***rac*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (1) - temperature variation**

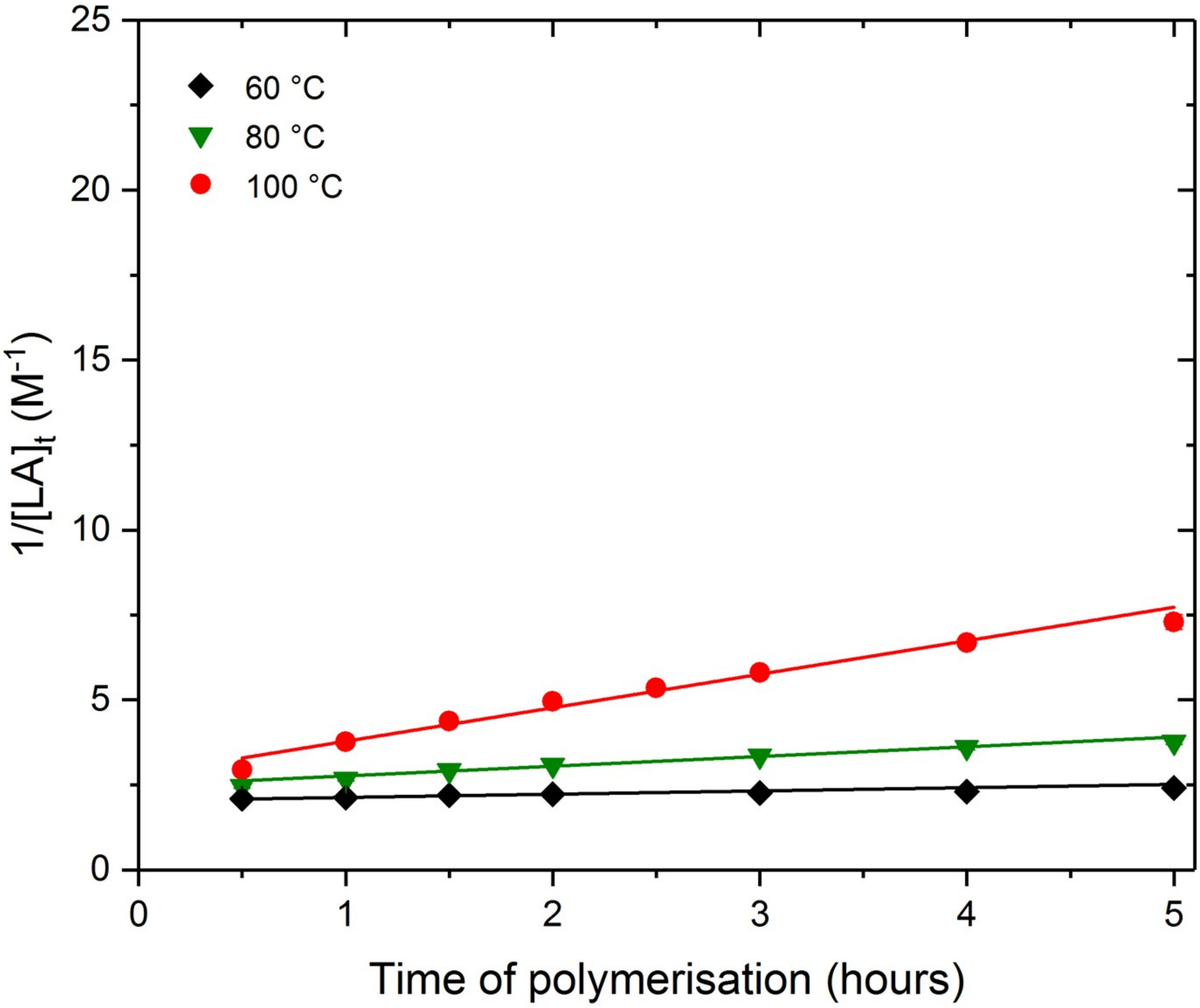


Fig. S28. *rac*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (**1**) at 60 °C (black diamond, k_{obs} = 0.10 ± 0.01 M^{-1} h^{-1}), 80 °C (green down triangle, k_{obs} = 0.29 ± 0.03 M^{-1} h^{-1}) and 100 °C (red circle, k_{obs} = 0.99 ± 0.05 M^{-1} h^{-1}). Polymerisation conditions: $CDCl_3$, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M, 2 equivalents of benzyl alcohol as co-initiator. All polymerisations carried out in duplicate.

***L*-Lactide polymerisation with ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (2) - [LA]$_0$/[M]$_0$ variation**

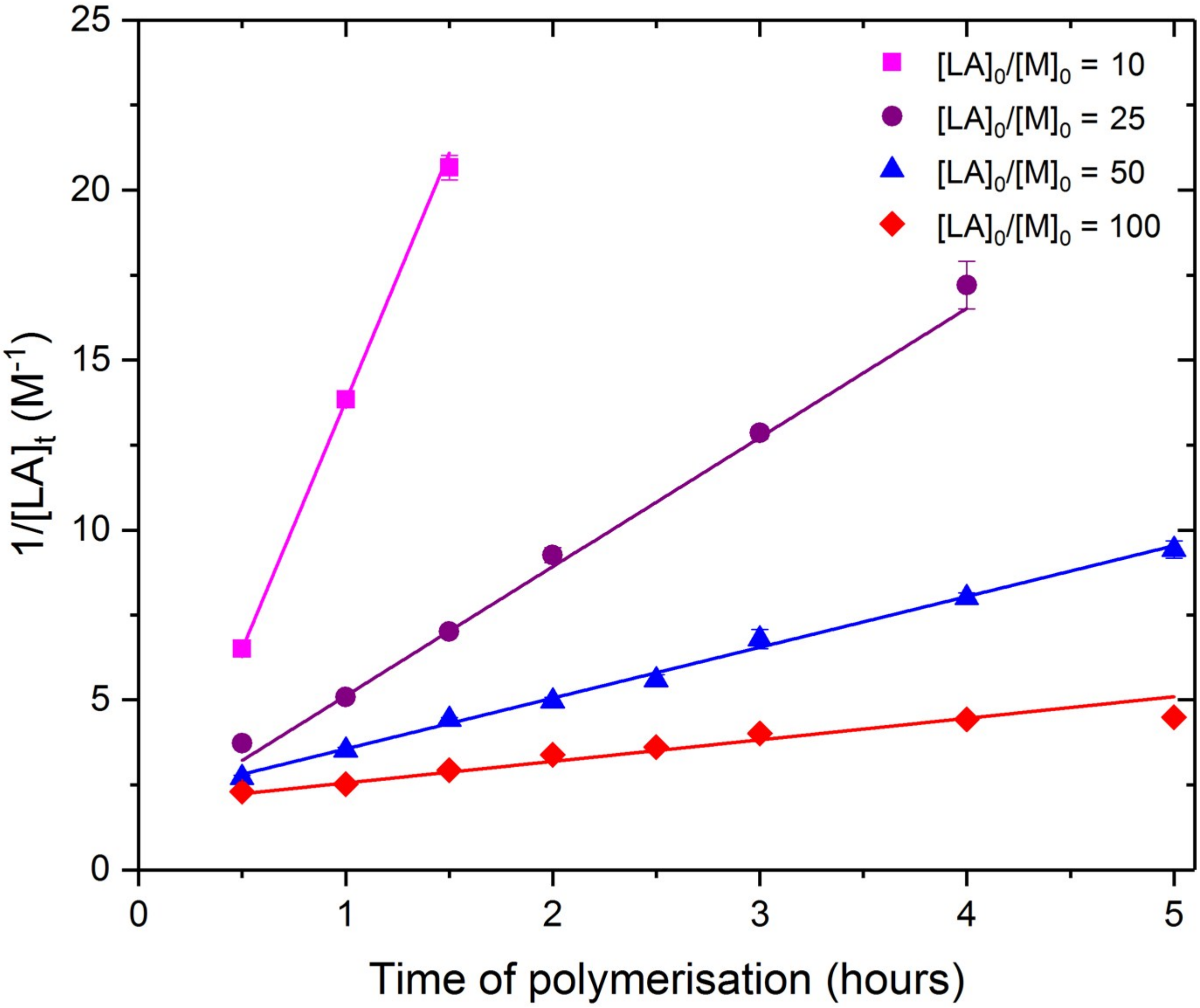


Fig. S29. *L*-Lactide polymerisation with ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) with [LA]$_0$/[M]$_0$ = 100 (red diamond, $k_{obs} = 0.63 \pm 0.05$ M^{-1} h^{-1}), [LA]$_0$/[M]$_0$ = 50 (blue triangle, $k_{obs} = 1.49 \pm 0.05$ M^{-1} h^{-1}), [LA]$_0$/[M]$_0$ = 25 (purple circle, $k_{obs} = 3.80 \pm 0.16$ M^{-1} h^{-1}) and [LA]$_0$/[M]$_0$ = 10 (pink square, $k_{obs} = 14.59 \pm 0.20$ M^{-1} h^{-1}). Polymerisation conditions: 80 °C, $CDCl_3$, [LA]$_0$ = 0.5 M, 2 equivalents of benzyl alcohol as co-initiator. All polymerisations carried out in duplicate.

***L*-Lactide polymerisation with ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (2) - [BnOH]$_0$ variation**

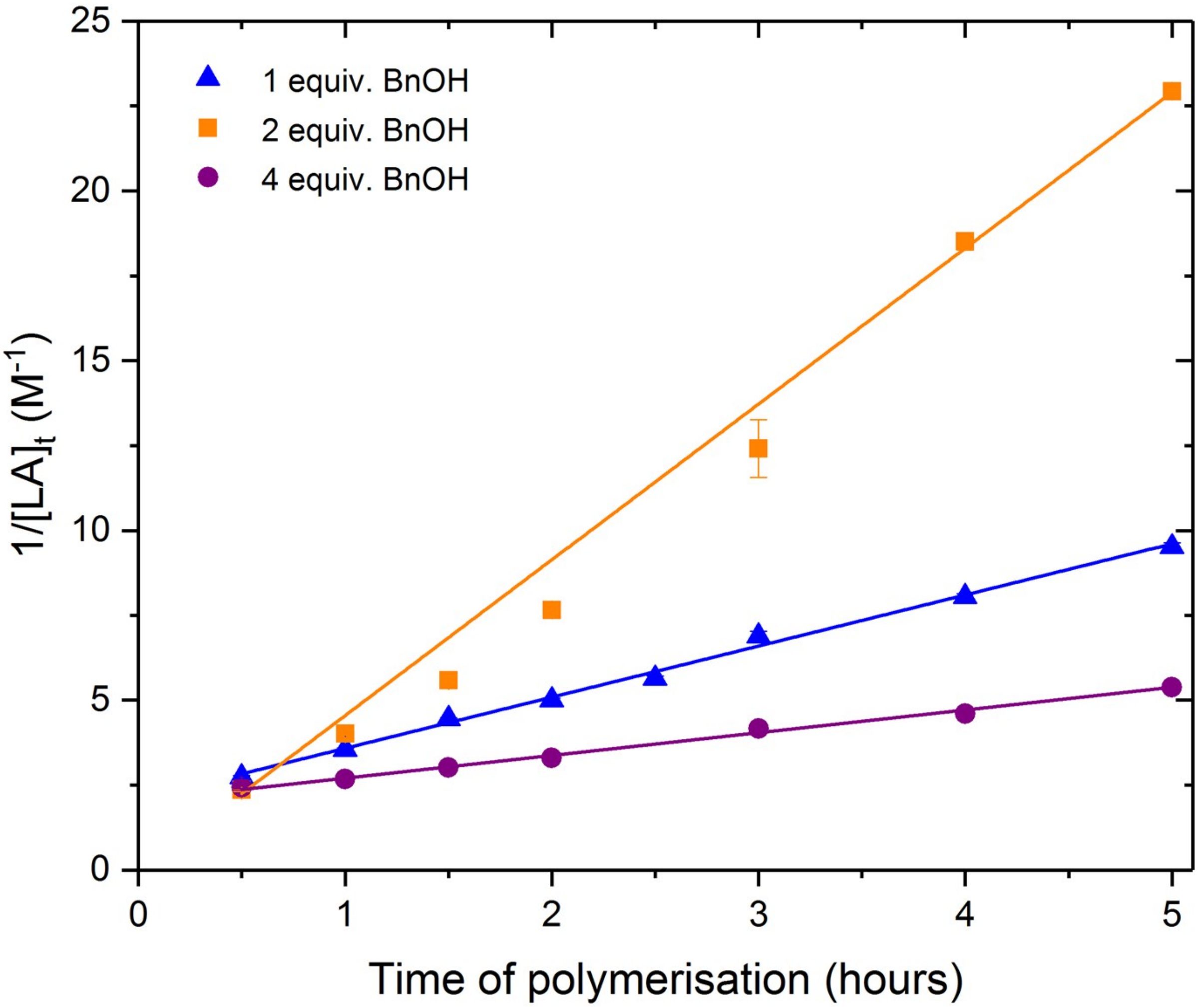


Fig. S30. *L*-Lactide polymerisation with ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) with 1 equivalent BnOH (oarange square, $k_{obs} = 4.59 \pm 0.06$ M^{-1} h^{-1}), 2 equivalents BnOH (green down triangle, $k_{obs} = 1.49 \pm 0.02$ M^{-1} h^{-1}) and 4 equivalents BnOH (purple circle, $k_{obs} = 0.67 \pm 0.01$ M^{-1} h^{-1}). Polymerisation conditions: 80 °C, $CDCl_3$, $[LA]_0 = 0.5$ M, $[LA]_0/[M]_0 = 50$. All polymerisations carried out in duplicate.

***L*-Lactide polymerisation with ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (2) - temperature variation**

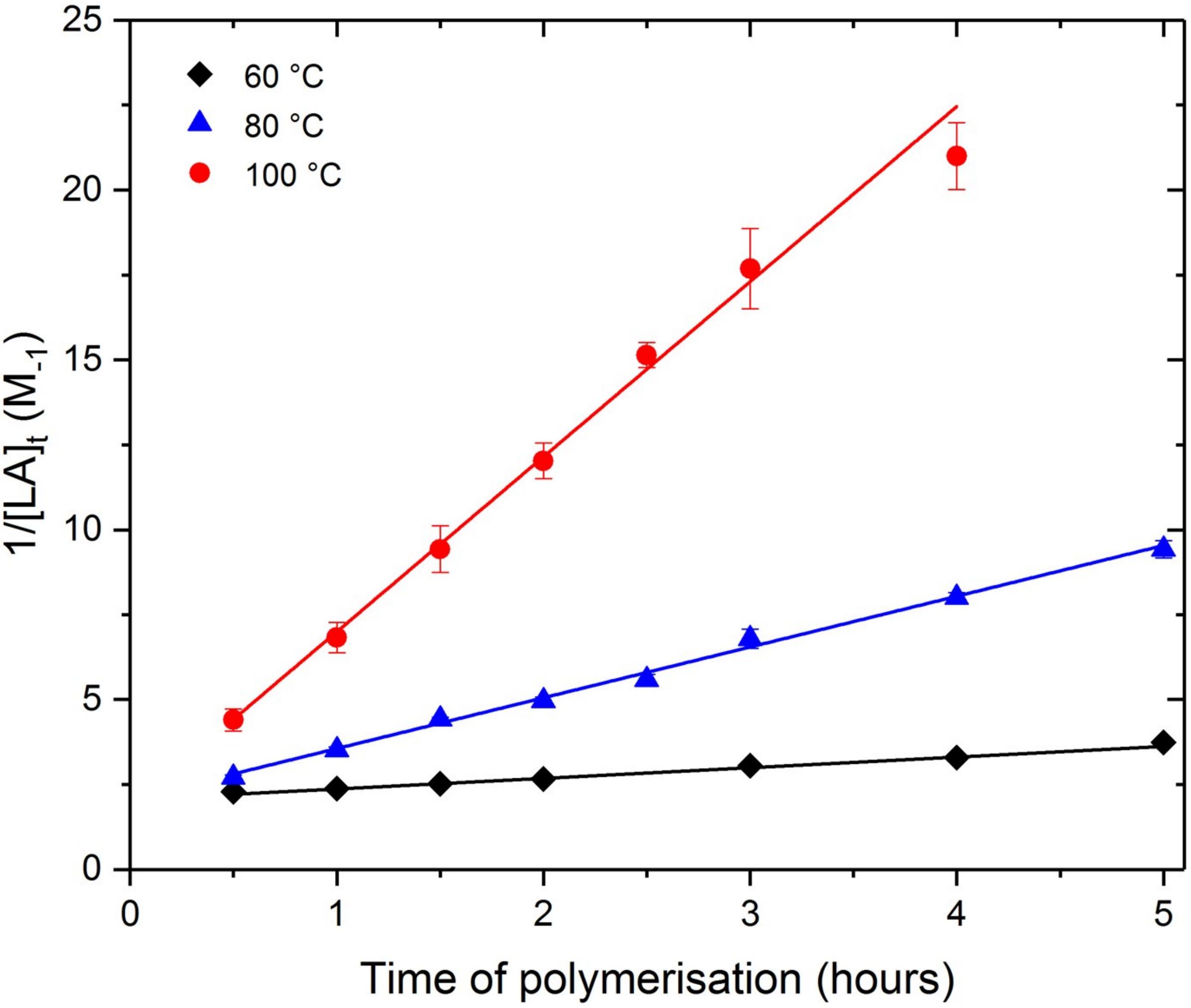


Fig. S31. *L*-Lactide polymerisation with ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) at 60 °C (black diamond, k_{obs} = 0.31 ± 0.01 M^{-1} h^{-1}), 80 °C (blue triangle, k_{obs} = 1.49 ± 0.05 M^{-1} h^{-1}) and 100 °C (red circle, k_{obs} = 5.15 ± 0.17 M^{-1} h^{-1}). Polymerisation conditions: $CDCl_3$, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M, 2 equivalents of benzyl alcohol as co-initiator. All polymerisations carried out in duplicate.

***rac*-Lactide polymerisation with ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (2) - [LA]$_0$/[M]$_0$ variation**

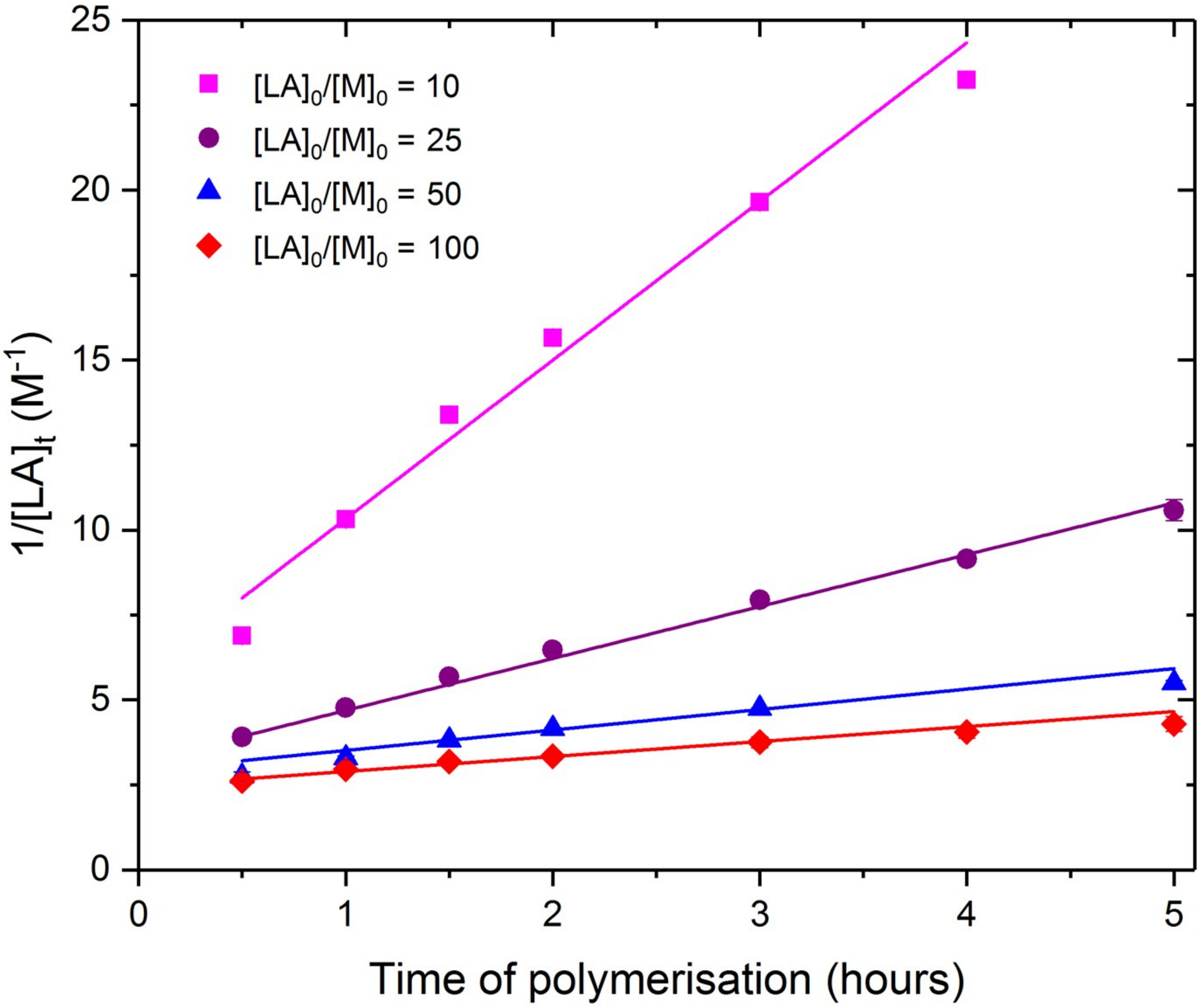


Fig. S32. *rac*-Lactide polymerisation with ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) with [LA]$_0$/[M]$_0$ = 100 (red diamond, $k_{obs} = 0.44 \pm 0.04$ M^{-1} h^{-1}), [LA]$_0$/[M]$_0$ = 50 (blue triangle, $k_{obs} = 0.60 \pm 0.06$ M^{-1} h^{-1}), [LA]$_0$/[M]$_0$ = 25 (purple circle, $k_{obs} = 1.53 \pm 0.04$ M^{-1} h^{-1}) and [LA]$_0$/[M]$_0$ = 10 (pink square, $k_{obs} = 4.67 \pm 0.24$ M^{-1} h^{-1}). Polymerisation conditions: 80 °C, CDCl$_3$, [LA]$_0$ = 0.5 M, 2 equivalents of benzyl alcohol as co-initiator. All polymerisations carried out in duplicate.

***rac*-Lactide polymerisation with ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (2) - temperature variation**

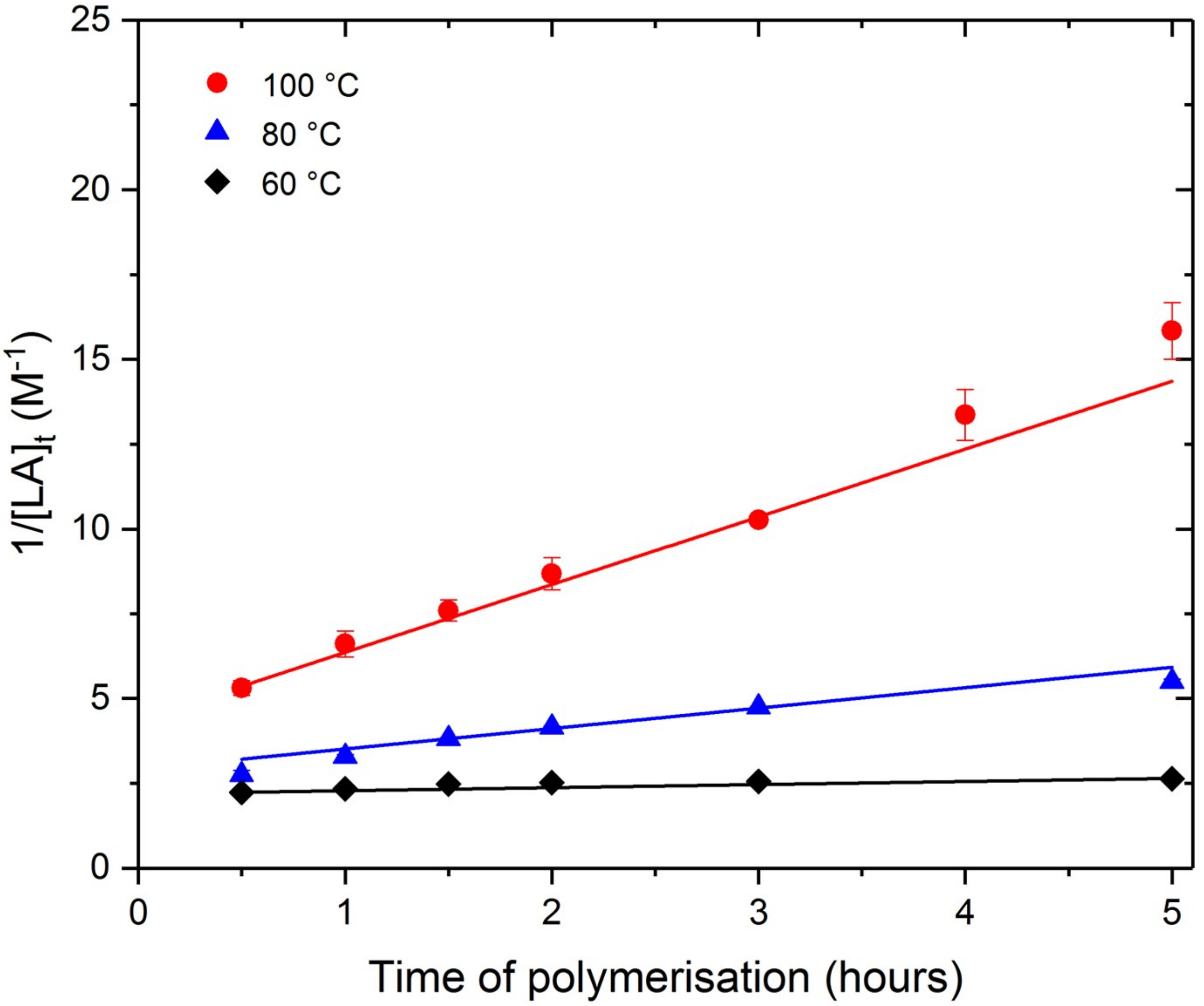


Fig. S33. *rac*-Lactide polymerisation with ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) at 60 °C (black diamond, k_{obs} = 0.09 ± 0.01 M^{-1} 1 h^{-1}), 80 °C (blue triangle, k_{obs} = 0.60 ± 0.06 M^{-1} h^{-1}) and 100 °C (red circle, k_{obs} = 2.00 ± 0.10 M^{-1} h^{-1}). Polymerisation conditions: CDCl$_3$, [LA]$_0$/[M]$_0$ = 50, [LA]$_0$ = 0.5 M, 2 equivalents of benzyl alcohol as co-initiator. All polymerisations carried out in duplicate.

***L*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (1), ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (2) and ^{Me_2}SB(Cp,I*)ZrCl(O-2,6-Me-C$_6$H$_3$) (4) without BnOH co-initiator.**

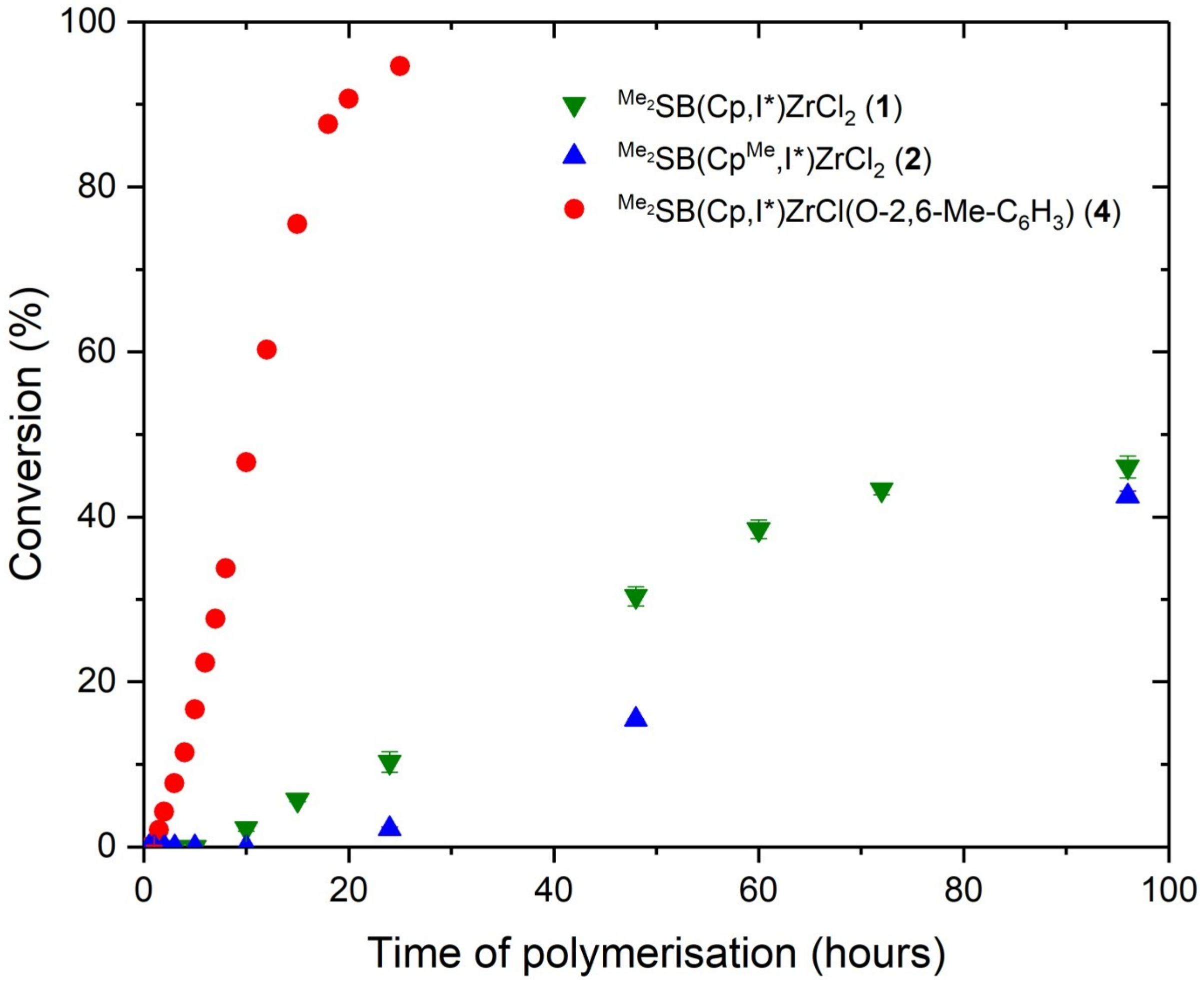


Fig. S34. *L*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (1) (green down triangle), ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (2) (blue triangle) and ^{Me_2}SB(Cp,I*)ZrCl(O-2,6-Me-C$_6$H$_3$) (**4**) (red circle). Polymerisation conditions: 80 °C, CDCl$_3$, $[LA]_0 = 0.5$ M, $[LA]_0/[M]_0 = 50$. All polymerisations carried out in duplicate.

–ln(k_{obs}) as a function of –ln($[BnOH]_0$) for the polymerisation of *L*-lactide with $^{Me2}SB(Cp,I^*)ZrCl_2$ (1) and $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (2).

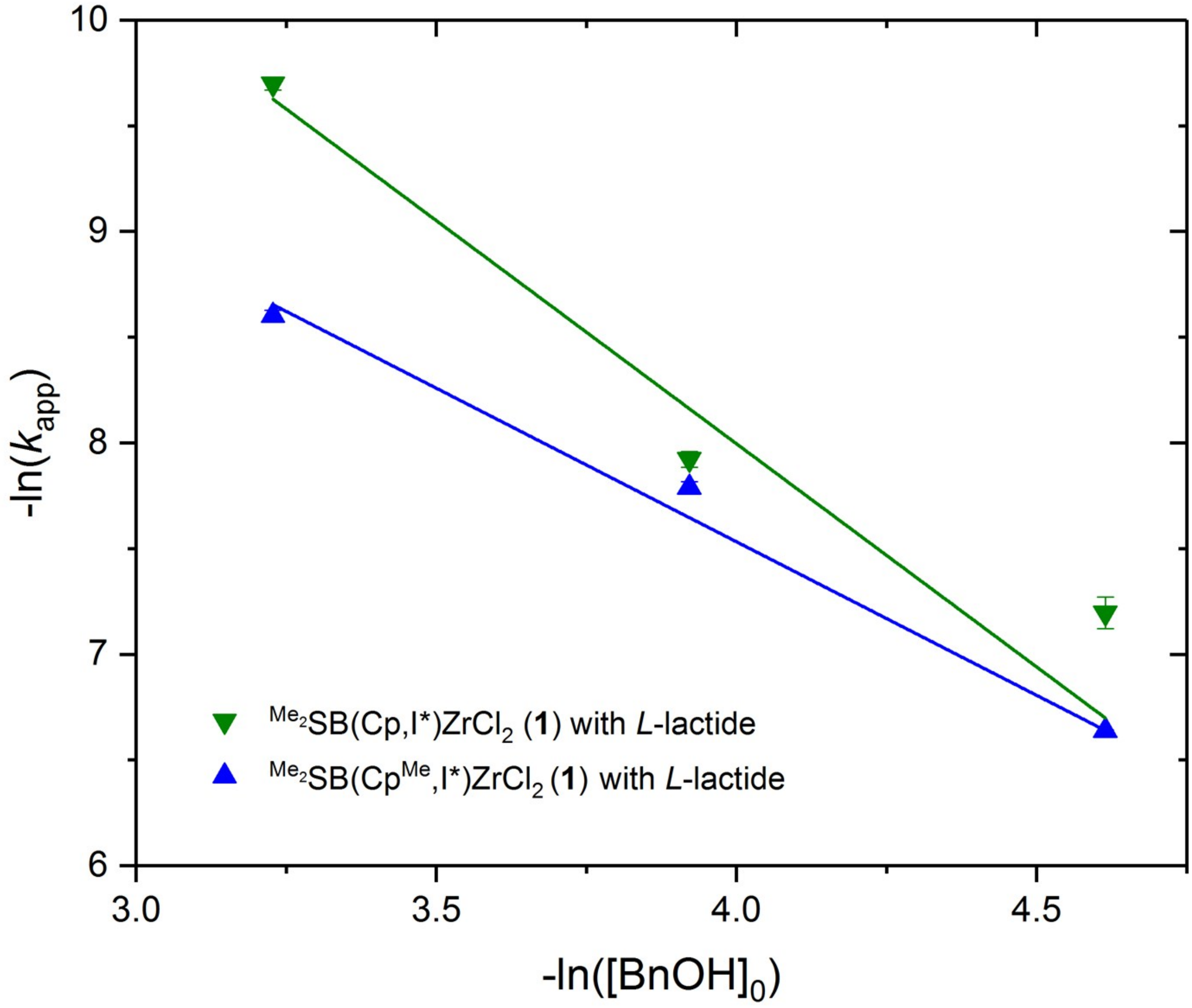


Fig. S35. –ln(k_{obs}) as a function of –ln($[BnOH]_0$) for the polymerisation of *L*-lactide with $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**) (green down triangle, slope = –2.11 ± 0.47 with R^2 = 0.954) and $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) (blue triangle, slope = –1.45 ± 0.09 with R^2 = 0.996). Polymerisation conditions: $CDCl_3$, $[LA]_0/[M]_0$ = 50, 80 °C and $[LA]_0$ = 0.5 M.

.

Table S3. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**), ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) ^{Me2}SB(Cp,I*)ZrCl$_2$ (**3**) and ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C$_6$H$_3$) (**4**).

Initiator	**Temp (°C)**	k_{obs}[a] (M^{-1} h^{-1})	**Time[b] (h)**	**Conversion[c] (%)**	$M_{n, theo}$[d] (g mol^{-1})	$M_{n, exp}$[e] (g mol^{-1})	M_w/M_n[e]
1	60	0.29 ± 0.01	70	88	6444	2156	1.11
1	80	1.30 ± 0.03	20	91	6660	2782	1.11
1	100	7.78 ± 0.42	3	92	6732	2031	1.13
2	60	0.31 ± 0.01	264	91	6660	1884	1.11
2	80	1.49 ± 0.02	24	93	6804	3183	1.12
2	100	5.15 ± 0.17	12	93	6804	3380	1.18
3	80	1.21 ± 0.10	6	81	5940	3826	1.11
4[f]	80	3.23 ± 0.06 6.39 ± 0.19	5	93	6840	1667	1.14

a) Polymerisation conditions: $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, $CDCl_3$, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

b) Time polymerisation quenched.

c) Average % conversion over two repeats.

d) $M_{n, theo} = (M_{LA}$ x $[LA]_0/[M]_0$ x conversion) + $M_{end\ group}$

e) Determined by GPC analysis, calibrated with polystyrene standards in THF.

f) Two linear fit regions in second order rate plot: first region 0.5-2 h, second region 2-4 h.

Table S4. *rac*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**), ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) ^{Me2}SB(Cp,I*)ZrCl$_2$ (**3**) and ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C$_6$H$_3$) (**4**).

Initiator	**Temp (°C)**	**k_{obs}[a] (h^{-1})**	**Time[b] (h)**	**Conversion[c] (%)**	**$M_{n, theo}$[d] ($g\ mol^{-1}$)**	**$M_{n, exp}$[e] ($g\ mol^{-1}$)**	**M_w/M_n[e]**
1	60	0.10 ± 0.01	175	76	5508	862	1.76
1	80	0.29 ± 0.03	100	89	6516	1060	1.07
1	100	0.99 ± 0.05	40	91	6588	1868	1.23
2	60	0.09 ± 0.01	96	56	4140	233	1.44
2	80	0.60 ± 0.06	60	94	6876	1983	1.14
2	100	2.00 ± 0.10	10	93	6732	840	1.69
3	80	0.06 ± 0.01	6	24	1836	-	-
4	80	5.89 ± 0.25	4	91	6588	1153	1.12

a) Polymerisation conditions: $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, $CDCl_3$, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

b) Time polymerisation quenched.

c) Average % conversion over two repeats.

d) $M_{n,\ theo} = (M_{LA}$ x $[LA]_0/[M]_0$ x conversion$) + M_{end\ group}$

e) Determined by GPC analysis, calibrated with polystyrene standards in THF.

Table S5. *D*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (**1**), ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) and ^{Me_2}SB(Cp,I*)ZrCl(O-2,6-Me-C$_6$H$_3$) (**4**).

Initiator	**Temp (°C)**	k_{obs}[a] (h^{-1})	**Time**[b] **(h)**	**Conversion**[c] **(%)**	$M_{n, theo}$[d] ($g\ mol^{-1}$)	$M_{n, exp}$[e] ($g\ mol^{-1}$)	M_w/M_n[e]
1	80	0.72 ± 0.03	30	90	6588	2086	1.12
2	80	2.46 ± 0.07	7	91	6660	2325	1.09
4	80	6.38 ± 0.30	4	92	6732	1828	1.13

a) Polymerisation conditions: $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, $CDCl_3$, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

b) Time polymerisation quenched.

c) Average % conversion over two repeats.

d) $M_{n, theo} = (M_{LA}$ x $[LA]_0/[M]_0$ x conversion) + $M_{end\ group}$

e) Determined by GPC analysis, calibrated with polystyrene standards in THF.

f) Bimodal molecular weight distribution 4706 g mol^{-1} (89%) and 11502 g mol^{-1} (11%).

Table S6. *L*- and *rac*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (**1**) on a larger scale.

Lactide	**Scale**	k_{obs}[a] ($M^{-1}\ h^{-1}$)	**Time**[b] **(h)**	**Conversion**[c] **(%)**
L	Small	2.69 ± 0.04	100	82
L	Larger	4.91 ± 0.65	4	89
rac	Small	1.05 ± 0.10	100	92
rac	Larger	4.31 ± 0.16	4	89

a) Small scale polymerisation conditions: Lactide (40 mg), 80 °C $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in toluene-d_8. Larger scale polymerisation conditions: Lactide (200 mg), 80 °C $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in toluene.

b) Time polymerisation quenched.

c) Average % conversion over 2 repeats

Table S7. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) and ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) at various catalyst loadings.

Initiator	**[LA]$_0$/[M]$_0$**	k_{obs}[a] (M^{-1} h^{-1})	**Time**[b] (h)	**Conversion**[c] (%)	$M_{n,\,theo}$[d] (g mol^{-1})	$M_{n,\,exp}$[e] (g mol^{-1})	M_w/M_n[e]
1	10	7.51 ± 0.09	3	91	1418	-	-
1	25	2.26 ± 0.12	9	91	3384		
1	50	1.30 ± 0.03	20	91	6660	3826	1.11
1	100	0.13 ± 0.01	216	72	10476	-	-
2	10	14.59 ± 0.20	1.5	91	1418	-	-
2	25	3.80 ± 0.16	8	96	3564	1204	1.21
2	50	1.49 ± 0.02	24	93	6804	2782	1.11
2[f]	100	0.63 ± 0.05	200	88	12780	4706 11502	1.08 1.02

a) Polymerisation conditions: 80 °C, [LA]$_0$ = 0.5 M, $CDCl_3$, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

b) Time polymerisation quenched.

c) Average % conversion over 2 repeats

d) $M_{n,\,theo} = (M_{LA} \times [LA]_0/[M]_0 \times \text{conversion}) + M_{\text{end group}}$

e) Determined by GPC analysis, calibrated with polystyrene standards in THF.

f) Bimodal molecular weight distribution 4706 g mol^{-1} (89%) and 11502 g mol^{-1} (11%).

Table S8. *rac*-Lactide polymerisation with ^{Me_2}SB(Cp,I*)ZrCl$_2$ (**1**) and ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) at various catalyst loadings.

Initiator	**[LA]$_0$/[M]$_0$**	**k_{obs}[a] (M^{-1} h^{-1})**	**Time[b] (h)**	**Conversion[c] (%)**	**$M_{n, theo}$[d] (g mol^{-1})**
1	10	2.87 ± 0.15	7	91	1418
1	25	1.13 ± 0.03	18	89	3312
1	50	0.29 ± 0.03	100	89	6516
1	100	0.19 ± 0.01	175	82	11916
2	10	4.67 ± 0.24	4	91	1418
2	25	1.53 ± 0.04	12	90	3348
2	50	0.60 ± 0.06	60	94	6876
2	100	0.44 ± 0.04	48	86	12492

a) Polymerisation conditions: 80 °C, [LA]$_0$ = 0.5 M, $CDCl_3$, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

b) Time polymerisation quenched.

c) Average % conversion over 2 repeats

d) $M_{n, theo} = (M_{LA} \times [LA]_0/[M]_0 \times \text{conversion}) + M_{end\ group}$

e) Determined by GPC analysis, calibrated with polystyrene standards in THF.

Table S9. *L*-Lactide polymerisation with $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**) and $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at various BnOH concentrations.

Initiator	BnOH Equivalents	$[BnOH]_0$	k_{obs}[a] (M^{-1} h^{-1})	Time[b] (h)	Conversion[c] (%)
1	0	0	-	216	61
1	1	0.01	2.33 ± 0.17	10	93
1	2	0.02	1.30 ± 0.03	20	91
1	4	0.04	0.23 ± 0.01	170	83
2	0	0	-	168	88
2	1	0.01	4.59 ± 0.06	5	91
2	2	0.02	1.49 ± 0.05	24	93
2	4	0.04	0.67 ± 0.01	48	87

a) Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, in $CDCl_3$.

b) Time polymerisation quenched.

c) Average % conversion over 2 repeats

d) $M_{n,\ theo} = (M_{LA} \times [LA]_0/[M]_0 \times \text{conversion}) + M_{end\ group}$

e) Determined by GPC analysis, calibrated with polystyrene standards in THF.

Table S10. *L*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) in various deuterated solvents.

Initiator	Solvent	k_{obs}[a] (M^{-1} h^{-1})	Time[b] (h)	Conversion[c] (%)	$M_{n,\ theo}$[d] (g mol^{-1})	M_n[e] (g mol^{-1})	M_w/M_n[e]
2	C_6D_6	7.78 ± 0.70	3	92	7073	3061	1.12
2	C_7D_8	5.10 ± 0.32	4	91	6660	2438	1.13
2	$CDCl_3$	1.49 ± 0.05	24	93	6804	3183	1.12
2	C_4D_8O	-	-	-	-	-	-

a) Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M and 2 equivalents benzyl alcohol co-initiator.

b) Time polymerisation quenched.

c) Average % conversion over 2 repeats

d) $M_{n,\ theo} = (M_{LA}$ x $[LA]_0/[M]_0$ x conversion) + $M_{end\ group}$

e) Determined by GPC analysis, calibrated with polystyrene standards in THF.

Table S11. *L*-Lactide polymerisation with $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**) at 60 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	6	5	2.12
1	12	12	2.27
1.5	22	20	2.53
2	25	23	2.63
3	30	30	2.85
4	35	33	3.03
5	39	36	3.18
7	45	43	3.57
10	49	50	3.97
15	63	64	5.47
24	76	76	8.41
48	85	83	12.52
70	89	87	17.18

Polymerisation conditions: 60 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S12. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)$ZrCl_2$ (**1**) at 80 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	33	33	2.98
1	43	44	3.54
1.5	52	52	4.17
2	59	60	4.94
3	67	68	6.22
4	74	74	7.65
5	77	77	8.71
7	81	81	10.50
9	84	84	12.54
12	87	87	15.43
16	90	89	19.00
20	91	90	21.71

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S13. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)$ZrCl_2$ (**1**) at 100 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	64	61	5.38
1	80	79	9.67
1.5	87	86	14.55
2	89	89	18.61
2.5	91	90	20.95
3	92	92	23.78

Polymerisation conditions: 100 °C, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S14. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)$ZrCl_2$ (**1**) at 80 °C with $[LA]_0/[M]_0 = 10$.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	48	48	3.83
1	69	67	6.23
1.5	80	79	9.79
2	90	90	15.08
3	91	91	22.63

[a]Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 10$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S15. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)$ZrCl_2$ (**1**) at 80 °C with $[LA]_0/[M]_0 = 25$.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	34	34	3.02
1	49	49	3.93
1.5	59	61	5.01
2	67	67	6.07
3	77	78	8.94
4	83	83	11.69
5	85	86	14.07
7	89	90	18.80
9	91	92	23.44

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 25$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S16. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) at 80 °C with $[LA]_0/[M]_0 = 100$.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average 1/[LA]$_t$ (M^{-1})
0.5	6	5	2.11
1	9	9	2.20
1.5	13	13	2.31
2	15	16	2.36
3	20	20	2.50
4	23	24	2.62
5	27	27	2.74
7	31	32	2.91
10	35	36	3.10
15	38	40	3.26
24	43	46	3.61
48	51	53	4.18
120	61	63	5.27
216	70	74	7.12

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 100$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S17. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) at 80 °C without benzyl alcohol co-initiator.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**
0.5	0	0
1	0	0
2	0	0
3	0	0
5	0	0
10	2	2
15	6	6
24	11	9
48	31	30
60	39	38
72	43	44
96	45	47
216	60	62

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M in $CDCl_3$.

Table S18. *L*-Lactide polymerisation with $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**) at 80 °C with 1 equivalent benzyl alcohol co-initiator.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	19	20	2.49
1	37	36	3.16
1.5	51	48	3.97
2	63	59	5.14
3	74	71	7.38
4	82	80	10.60
5	86	85	13.93
7	91	90	21.07
10	93	92	27.84

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 1 equivalent benzyl alcohol co-initiator in $CDCl_3$.

Table S19. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) at 80 °C with 4 equivalents benzyl alcohol co-initiator.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	21	17	2.46
1	26	23	2.65
1.5	29	26	2.77
2	33	30	2.92
3	37	35	3.13
4	41	39	3.33
5	44	41	3.46
7	47	44	3.66
9	49	47	3.83
12	52	50	4.10
24	61	57	4.89
48	66	65	5.77
72	69	68	6.33
170	82	84	11.85

Polymerisation conditions: 80 °C, [LA]$_0$/[M]$_0$ = 50, [LA]$_0$ = 0.5 M, 4 equivalents benzyl alcohol co-initiator in CDCl$_3$.

Table S20. *L*-Lactide polymerisation with $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**) at 80 °C in C_7D_8.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	30	30	2.86
1	36	34	3.07
1.5	41	40	3.35
2	44	42	3.50
3	49	47	3.82
4	51	50	4.02
5	54	52	4.23
7	57	55	4.57
9	59	58	4.82
12	63	61	5.21
24	69	67	6.24
48	74	72	7.53
100	83	82	11.3952

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in C_7D_8.

Table S21. *L*-Lactide polymerisation with $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**) in toluene on a larger scale.

Time (h)	**Conversion (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	59	4.83
1	60	5.03
2	80	9.99
4	89	18.52

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M and 2 equivalents benzyl alcohol co-initiator in toluene.

Table S22. *rac*-Lactide polymerisation with $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**) at 60 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average $1/[LA]_t$ (M^{-1})**
0.5	5	4	2.10
1	6	6	2.13
1.5	9	9	2.20
2	10	10	2.22
3	10	12	2.26
4	11	14	2.30
5	15	18	2.41
7	17	19	2.46
9	23	25	2.64
12	26	30	2.81
24	42	43	3.47
48	59	62	5.13
100	68	69	6.45
175	75	76	8.15

Polymerisation conditions: 60 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S23. *rac*-Lactide polymerisation with ^{Me2}SB(Cp,I*)$ZrCl_2$ (**1**) at 80 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	20	17	2.46
1	28	24	2.67
1.5	33	31	2.93
2	36	35	3.08
3	42	40	3.35
4	47	44	3.61
5	49	46	3.76
7	53.	51	4.14
9	56	55	4.44
12	60	59	4.89
24	72	70	6.77
48	79	76	8.61
100	90	88	17.79

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S24. *rac*-Lactide polymerisation with $^{Me2}SB(Cp,I^{*})ZrCl_2$ (**1**) at 100 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average $1/[LA]_t$ (M^{-1})**
0.5	30	34	2.95
1	44	48	3.77
1.5	52	55	4.38
2	57	60	4.95
2.5	61	63	5.36
3	65	66	5.80
4	69	70	6.68
5	71	73	7.29
7	77	79	9.29
9	80	82	10.68
12	84	85	12.74
16	86	87	15.00
24	89	89	18.16
40	90	91	21.03

Polymerisation conditions: 100 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S25. *rac*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) at 80 °C with $[LA]_0/[M]_0 = 10$.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	71	71	6.91
1	78	77	8.98
1.5	81	80	10.41
2	84	85	12.62
3	86	86	14.53
4	88	88	16.70
5	89	89	18.43
7	91	91	21.77

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 10$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S26. *rac*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) at 80 °C with $[LA]_0/[M]_0 = 25$.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	46	48	3.78
1	55	57	4.56
1.5	62	63	5.37
2	66	67	5.95
3	72	71	6.94
4	76	76	8.28
5	78	78	9.14
7	81	81	10.64
9	835	84	12.03
12	86	86	14.66
18	89	89	18.00

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 25$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S27. *rac*-Lactide polymerisation with $^{Me2}SB(Cp,I^{*})ZrCl_2$ (**1**) at 80 °C with $[LA]_0/[M]_0 = 100$.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	9	8	2.19
1	14	12	2.30
1.5	18	16	2.41
2	22	18	2.50
3	27	25	2.69
4	31	27	2.82
5	34	30	2.94
7	37	34	3.10
10	41	39	3.34
15	47	44	3.67
24	54	51	4.20
48	66	67	5.95
120	76	78	8.76
175	81	83	11.11

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 100$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S28. *rac*-Lactide polymerisation with $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**) at 80 °C in C_7D_8.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average $1/[LA]_t$ (M^{-1})**
0.5	33	35	3.04
1	46	46	3.70
1.5	51	52	4.12
2	59	59	4.89
3	64	62	5.40
4	69	67	6.30
5	73	25	7.25
7	75	74	7.76
9	77	75	8.34
12	79	77	9.20
24	82	85	12.11
48	89	88	17.69
100	93	92	25.49

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in C_7D_8.

Table S29. *rac*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) in toluene on a larger scale.

Time (h)	**Conversion (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	30	2.84
1	60	4.96
2	76	8.40
4	89	18.69

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in toluene.

Table S30. *D*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) at 80 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	19	20	2.48
1	31	31	2.91
1.5	39	39	3.28
2	45	44	3.62
3	53	52	4.23
4	60	60	5.0
5	64	65	5.65
7	72	72	7.12
10	78	77	8.95
15	83	83	11.93
24	89	89	17.68
30	90	90	19.95

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S31. *L*-Lactide polymerisation with $^{Me_2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 60 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average $1/[LA]_t$ (M^{-1})**
0.5	12	13	2.29
1	17	15	2.38
1.5	21	20	2.52
2	25	25	2.66
3	34	35	3.06
4	39	39	3.29
5	46	47	3.75
6	50	50	4.01
8	54	55	4.39
10	57	57	4.66
12	59	59	4.89
16	64	64	5.56
20	68	67	6.08
24	71	70	6.74
32	77	75	8.29
48	79	77	9.21
72	81	80	10.42
120	86	84	13.52
192	89	88	17.20
264	91	90	21.10

Polymerisation conditions: 60 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S32. *L*-Lactide polymerisation with $^{Me_2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 80 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	25	28	2.71
1	42	44	3.51
1.5	54	55	4.43
2	59	60	4.97
2.5	63	65	5.59
3	70	71	6.79
4	75	75	8.00
5	78	79	9.42
7	83	84	12.14
9	86	87	15.09
12	89	91	19.72
16	90	92	23.13
20	91	93	25.92
24	92	94	29.11

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S33. *L*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 100 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	52	57	4.40
1	69	72	6.82
1.5	78	80	9.43
2	83	84	12.03
2.5	87	87	15.14
3	88	8	17.68
4	90	91	21.00
4	90	91	22.86
5	91	92	26.76
7	93	93	28.27
9	93	93	29.30

Polymerisation conditions: 100 °C, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S34. *L*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 80 °C with $[LA]_0/[M]_0 = 10$.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	69	69	6.50
1	83	84	13.84
1.5	91	91	20.66

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 10$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S35. *L*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 80 °C with $[LA]_0/[M]_0 = 25$.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	47	45	3.73
1	61	61	5.09
1.5	71	72	7.01
2	78	79	9.26
3	84	85	12.86
4	88	89	17.20

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 25$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S36. *L*-Lactide polymerisation with ^{Me_2}SB(Cp^{Me},I*)$ZrCl_2$ (**2**) at 80 °C with $[LA]_0/[M]_0 = 100$.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average $1/[LA]_t$ (M^{-1})**
0.5	13	13	2.03
1	21	21	2.52
1.5	31	32	2.93
2	40	41	3.38
2.5	44	45	3.61
3	51	50	4.01
4	56	54	4.43
5	56	55	4.49
8	59	57	4.75
12	60	58	4.91
20	65	63	5.55
36	70	68	6.42
60	75	74	7.97
125	83	83	11.52
200	88	89	17.38

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 100$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S37. *L*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^{*})ZrCl_2$ (**2**) at 80 °C without benzyl alcohol co-initiator.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average $1/[LA]_t$ (M^{-1})**
0.5	0	0	2.00
1	0	0	2.00
2	0	0	2.00
3	0	0	2.00
5	0	0	2.00
10	0	0	2.00
24	2	2	2.04
48	15	15	2.36
96	42	43	3.48
120	64	64	5.59
168	88	89	17.17

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M in $CDCl_3$.

Table S38. *L*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 80 °C with 1 equivalent benzyl alcohol co-initiator

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	16	14	2.36
1	51	49	4.01
1.5	65	63	5.58
2	74	73	7.66
3	85	83	12.41
4	89	89	18.51
5	91	91	22.94

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 1 equivalent benzyl alcohol co-initiator in $CDCl_3$.

Table S39. *L*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 80 °C with 4 equivalents of benzyl alcohol co-initiator.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	19	17	2.44
1	27	24	2.68
1.5	34	33	3.02
2	40	39	3.31
3	53	51	4.17
4	56	57	4.61
5	63	63	5.38
7	65	66	5.86
10	70	701	6.68
15	75	75	8.01
24	80	80	9.96
48	87	87	15.43

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 4 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S40. *L*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 80 °C in C_6D_6.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	49	55	4.19
1	71	71	6.93
1.5	83	84	11.93
2	86	88	15.36
2.5	89	90	19.59
3	91	92	23.80

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in C_6D_6.

Table S41. *L*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 80 °C in C_7D_8.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	39	41	3.33
1	59	62	5.09
1.5	75	76	8.24
2	81	83	11.20
2.5	85	86	13.77
3	88	89	17.84
4	91	91	23.41

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in C_7D_8.

Table S42. *rac*-Lactide polymerisation with $^{Me_2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 60 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average $1/[LA]_t$ (M^{-1})**
0.5	11	10	2.24
1	16	14	2.34
1.5	20	19	2.47
2	22	20	2.53
3	22	21	2.55
5	24	24	2.63
7	31	31	2.90
9	31	33	2.93
15	37	39	3.2447
24	42	44	3.52
48	49	49	3.94
96	57	56	4.59

Polymerisation conditions: 60 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S43. *rac*-Lactide polymerisation with ^{Me_2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) at 80 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	25	30	2.76
1	39	40	3.30
1.5	48	47	3.82
2	52	52	4.16
3	58	58	4.75
5	63	64	5.50
7	67	69	6.25
10	73	74	7.49
15	78	81	10.13
20	84	85	12.85
36	91	91	22.14
60	94	94	33.91

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S44. *rac*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 100 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average $1/[LA]_t$ (M^{-1})**
0.5	61	63	5.31
1	68	71	6.61
1.5	73	74	7.59
2	76	78	8.68
3	80	81	10.28
4	84	86	13.37
5	87	88	15.84
6	88	89	17.67
8	91	91	23.01
10	92	92	25.24

Polymerisation conditions: 100 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S45. *rac*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 80 °C with $[LA]_0/[M]_0 = 10$.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	72	70	6.89
1	81	81	10.32
1.5	85	85	13.40
2	87	87	15.66
3	90	90	19.65
4	91	91	23.24

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 10$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S46. *rac*-Lactide polymerisation with $^{Me2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 80 °C with $[LA]_0/[M]_0 = 25$.

Time (h)	Conversion 1 (%)	Conversion 2 (%)	Average $1/[LA]_t$ (M^{-1})
0.5	49	49	3.91
1	59	57	4.77
1.5	65	64	5.67
2	70	69	6.48
3	75	74	7.94
4	78	78	9.14
5	81	81	10.59
7	86	85	13.72
9	88	88	16.74
12	89	90	19.04

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 25$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S47. *rac*-Lactide polymerisation with ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) at 80 °C with $[LA]_0/[M]_0 = 100$.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	23	24	2.62
1	32	33	2.96
1.5	37	38	3.19
2	40	41	3.34
3	45	48	3.75
4	49	52	4.06
5	52	55	4.29
7	55	58	4.62
9	59	61	5.02
12	63	66	5.68
24	73	76	7.82
48	85	87	14.58

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 100$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S48. *D*-Lactide polymerisation with $^{Me_2}SB(Cp^{Me},I^*)ZrCl_2$ (**2**) at 80 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average $1/[LA]_t$ (M^{-1})**
0.5	32	33	2.96
1	49	50	3.96
1.5	60	61	5.09
2	67	68	6.22
3	76	77	8.54
4	83	83	11.48
5	86	86	14.65
7	91	91	21.42

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.5$ M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S49. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)HfCl$_2$ (**3**) at 80 °C.

Time (h)	**Conversion (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	29	2.82
1	44	3.57
2	59	4.88
3	64	5.56
4	71	6.90
5	77	8.70
6	81	10.53

Polymerisation conditions: 80 °C, [LA]$_0$/[M]$_0$ = 50, [LA]$_0$ = 0.5 M, 2 equivalents benzyl alcohol co-initiator in CDCl$_3$.

Table S50. *rac*-Lactide polymerisation with ^{Me2}SB(Cp,I*)HfCl$_2$ (**3**) at 80 °C.

Time (h)	**Conversion (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	11	2.35
1	15	2.38
2	16	2.44
3	18	2.50
4	20	2.56
5	22	2.63
6	24	2.35

Polymerisation conditions: 80 °C, [LA]$_0$/[M]$_0$ = 50, [LA]$_0$ = 0.5 M, 2 equivalents benzyl alcohol co-initiator in CDCl$_3$.

Table S51. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (**4**) at 80 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	18	16	2.42
1	52	51	4.12
1.5	65	65	5.65
2	74	73	7.53
3	85	85	13.17
4	91	90	20.23
5	93	93	29.22

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S52. *L*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (**4**) at 80 °C without benzyl alcohol co-initiator.

Time (h)	Conversion 1 (%)	Conversion 2 (%)
0.5	0	0
1	0	0
1.5	2	2
2	4	4
3	8	8
4	11	11
5	17	17
6	22	22
7	28	28
8	34	34
10	47	47
12	60	61
15	75	76
18	88	84
20	91	90
25	95	95

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M in $CDCl_3$.

Table S53. *rac*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (**4**) at 80 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	27	25	2.70
1	59	58	4.82
1.5	78	77	8.83
2	83	83	11.62
3	89	88	18.09
4	92	91	23.49

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

Table S54. *D*-Lactide polymerisation with ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (**4**) at 80 °C.

Time (h)	**Conversion 1 (%)**	**Conversion 2 (%)**	**Average 1/[LA]$_t$ (M^{-1})**
0.5	31	32	2.91
1	51	51	4.10
1.5	70	70	6.76
2	80	80	9.91
3	88	88	16.59
4	92	92	24.36

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0$ = 50, $[LA]_0$ = 0.5 M, 2 equivalents benzyl alcohol co-initiator in $CDCl_3$.

5. MALDI-TOF mass spectra

PLA from $^{Me_2}SB(Cp,I^*)ZrCl_2$ (1)

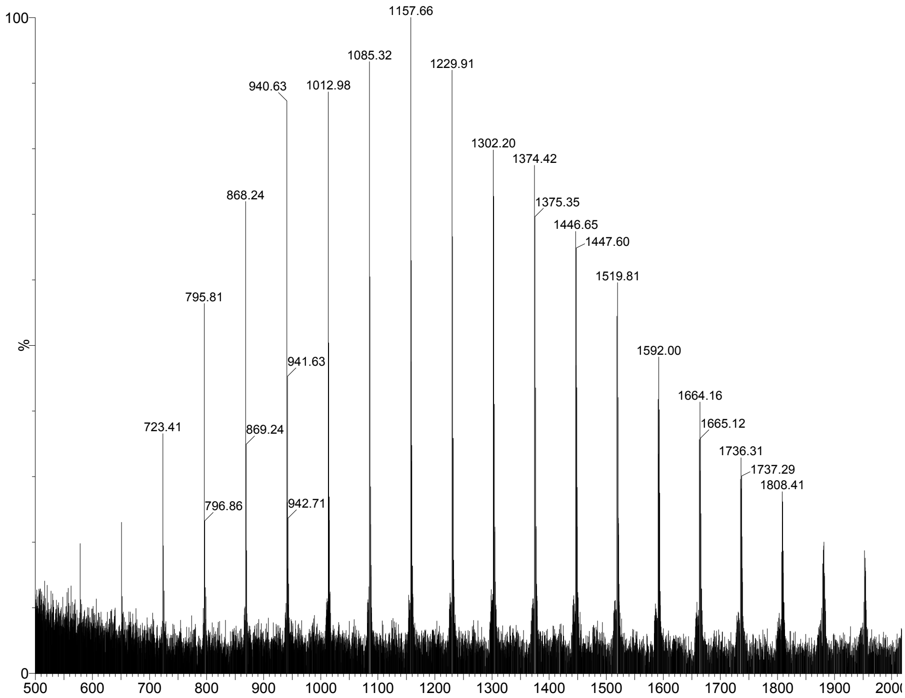


Fig. S36. MALDI-TOF mass spectrum recorded in a DCTB + KTFA matrix of the PLA produced from $^{Me_2}SB(Cp,I^*)ZrCl_2$ (**1**) and *L*-lactide. Polymerisation conditions: *L*-lactide (40 mg), 80 °C, $[LA]_0/[M]_0 = 10$, $[LA]_0 = 0.5$ M and $CDCl_3$ (0.56 mL).

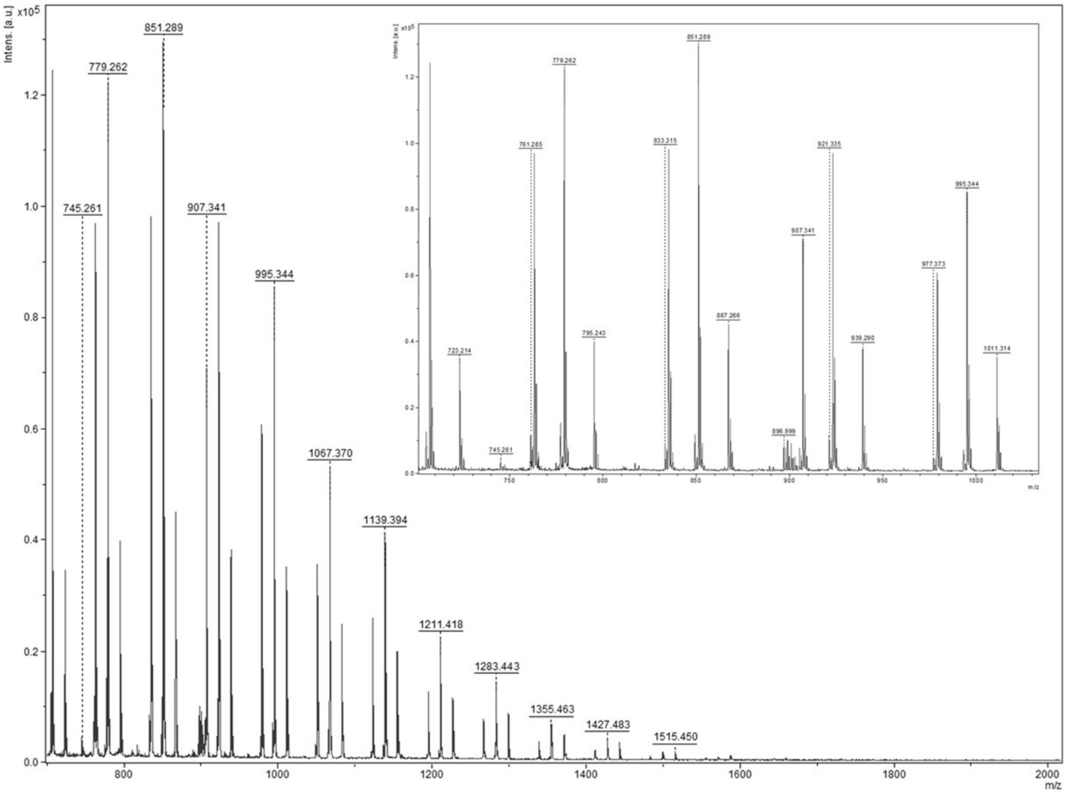


Fig. S37. MALDI-TOF mass spectrum recorded in a DCTB + KTFA matrix of the PLA produced from ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) and *L*-lactide on the larger scale. Polymerisation conditions: *L*-lactide (200 mg), 80 °C, $[LA]_0/[M]_0 = 10$, $[LA]_0 = 0.5$ M and toluene (2.8 mL).

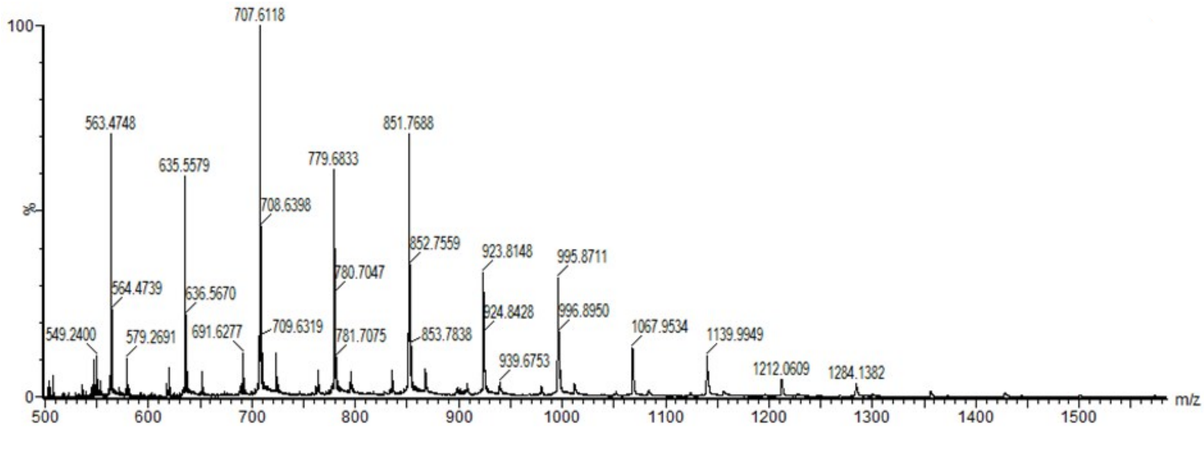


Fig. S38. MALDI-TOF mass spectrum recorded in a DHB matrix of the PLA produced from ^{Me2}SB(Cp,I*)ZrCl$_2$ (**1**) and *rac*-lactide. Polymerisation conditions: *rac*-lactide (40 mg), 80 °C, $[LA]_0/[M]_0 = 10$, $[LA]_0 = 0.5$ M and $CDCl_3$ (0.56 mL).

PLA from ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (2)

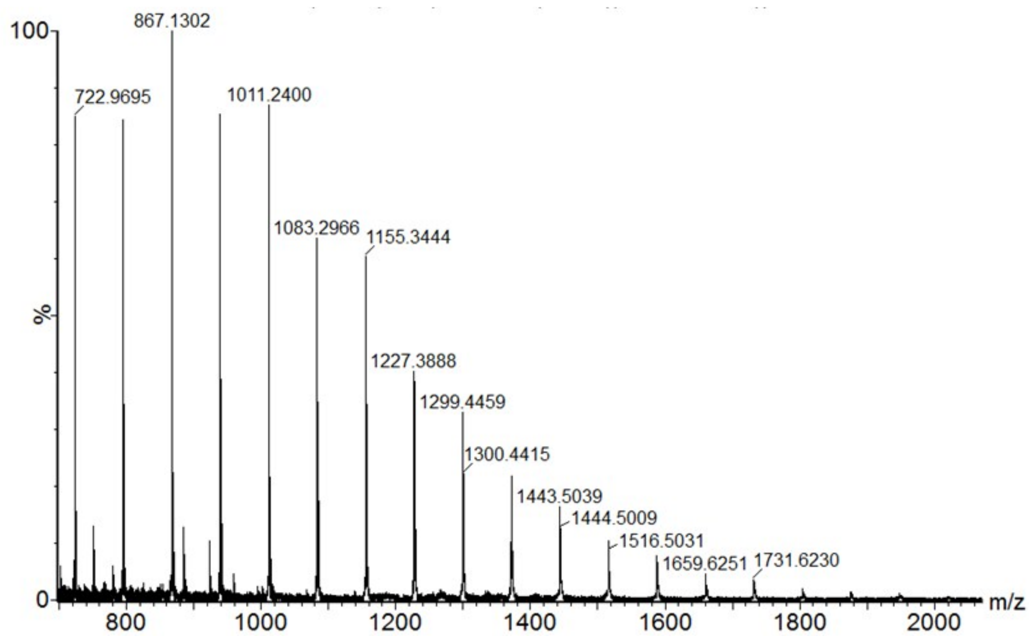


Fig. S39. MALDI-TOF mass spectrum recorded in a DCTB + KTFA matrix of the PLA produced from ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) and *L*-lactide. Polymerisation conditions: *L*-lactide (40 mg), 80 °C, $[LA]_0/[M]_0 = 10$, $[LA]_0 = 0.5$ M and $CDCl_3$ (0.56 mL).

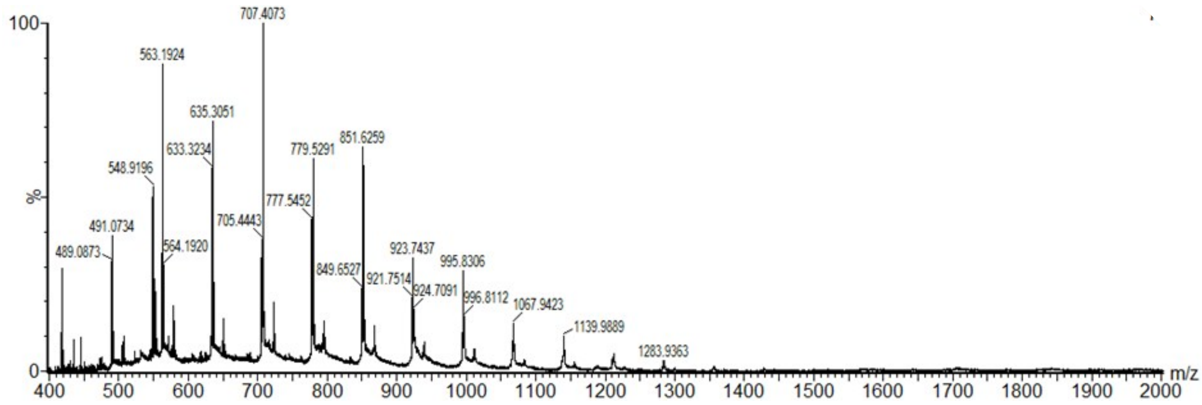


Fig. S40. MALDI-TOF mass spectrum recorded in a DHB matrix of PLA produced from ^{Me2}SB(Cp^{Me},I*)ZrCl$_2$ (**2**) and *rac*-lactide. Polymerisation conditions: *rac*-lactide (40 mg) 80 °C, $[LA]_0/[M]_0 = 10$, $[LA]_0 = 0.5$ M and $CDCl_3$ (0.56 mL).

PLA from ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (4)

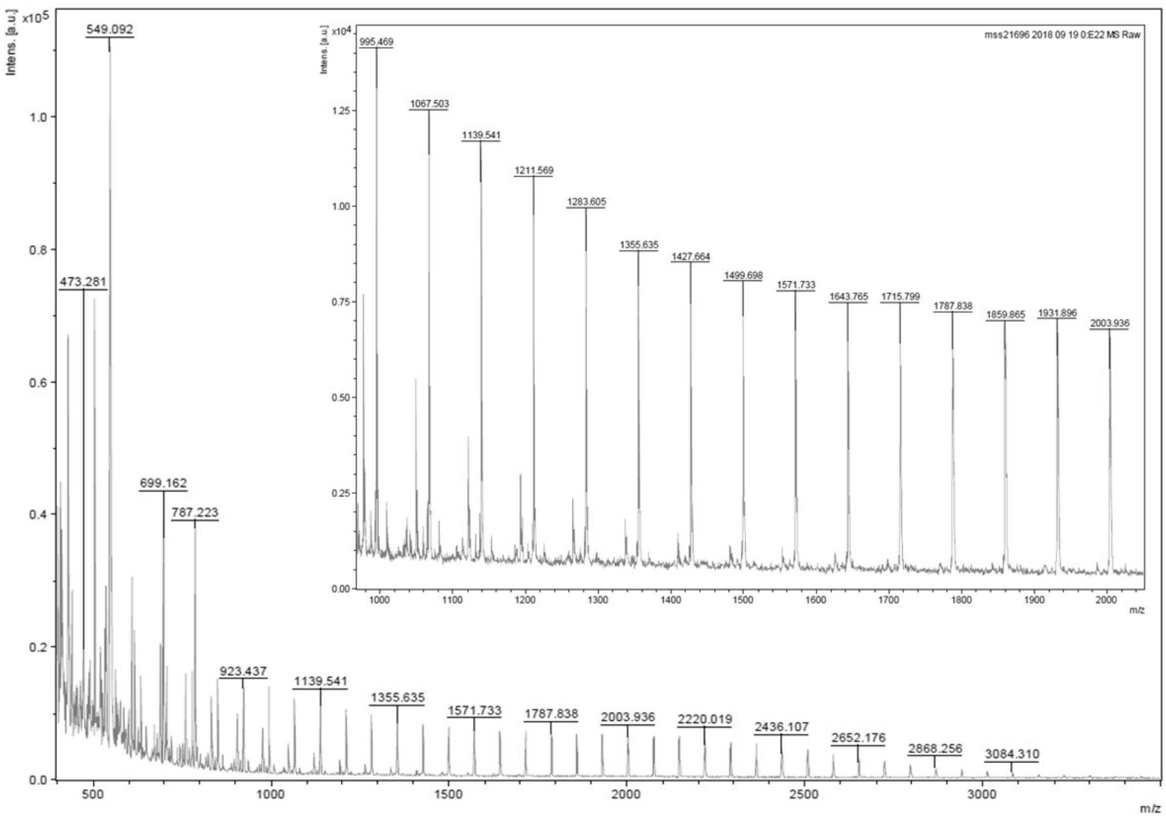


Fig. S41. MALDI-TOF mass spectrum recorded in a DHB matrix of the PLA produced from ^{Me2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (**4**) and *L*-lactide. Polymerisation conditions: *L*-lactide (40 mg), 80 °C, $[LA]_0/[M]_0 = 10$, $[LA]_0 = 0.5$ M and $CDCl_3$ (0.56 mL).

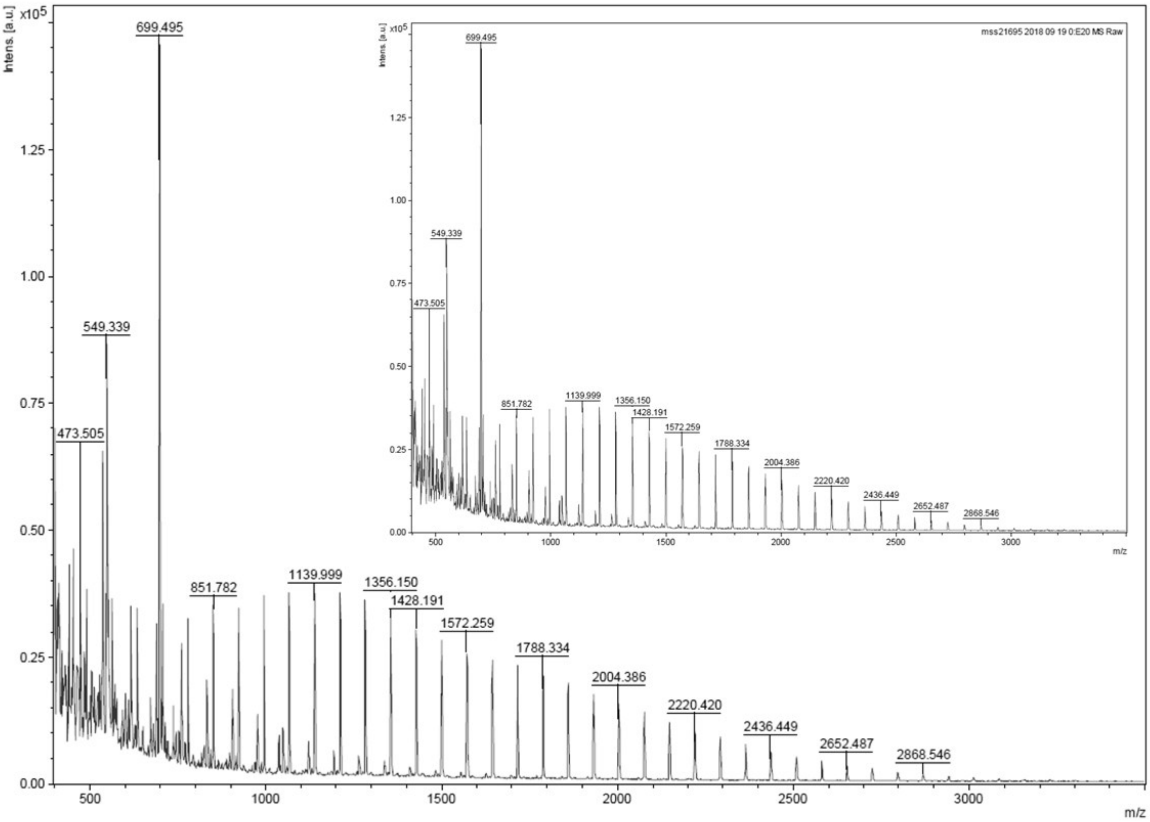


Fig. S42. MALDI-TOF mass spectrum recorded in a DHB matrix of PLA produced from ^{Me_2}SB(Cp,I*)ZrCl(O-2,6-Me-C_6H_3) (**4**) and *rac*-lactide. Polymerisation conditions: *rac*-lactide (40 mg), 80 °C, $[LA]_0/[M]_0 = 10$, $[LA]_0 = 0.5$ M and $CDCl_3$ (0.95 mL).

6. Dilute lactide polymerisation studies

L-lactide (40 mg, 0.278 mmol) was weighed into a 10 mL ampoule. A solution of $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**) ($[LA]_0/[M]_0 = 50$) and benzyl alcohol ($[BnOH]_0/[M]_0 = 2$) in an amount of toluene corresponding to an initial lactide concentration ($[LA]_0$) of 0.05 M (ca. 5.5 mL) was prepared and added to the ampoule. The polymerisation was run at 80 °C with stirring at 1000 rpm and was monitored by ^1H NMR spectroscopy.

Table S55. *L*-Lactide polymerisation with $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**) at 80 °C.

Time (h)	**Conversion 1 (%)**	**$1/[LA]_t$ (M^{-1})**
1	25	2.67
2	28	2.76
4	32	2.93
20	54	4.35

Polymerisation conditions: 80 °C, $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.05$ M, 2 equivalents benzyl alcohol co-initiator in toluene.

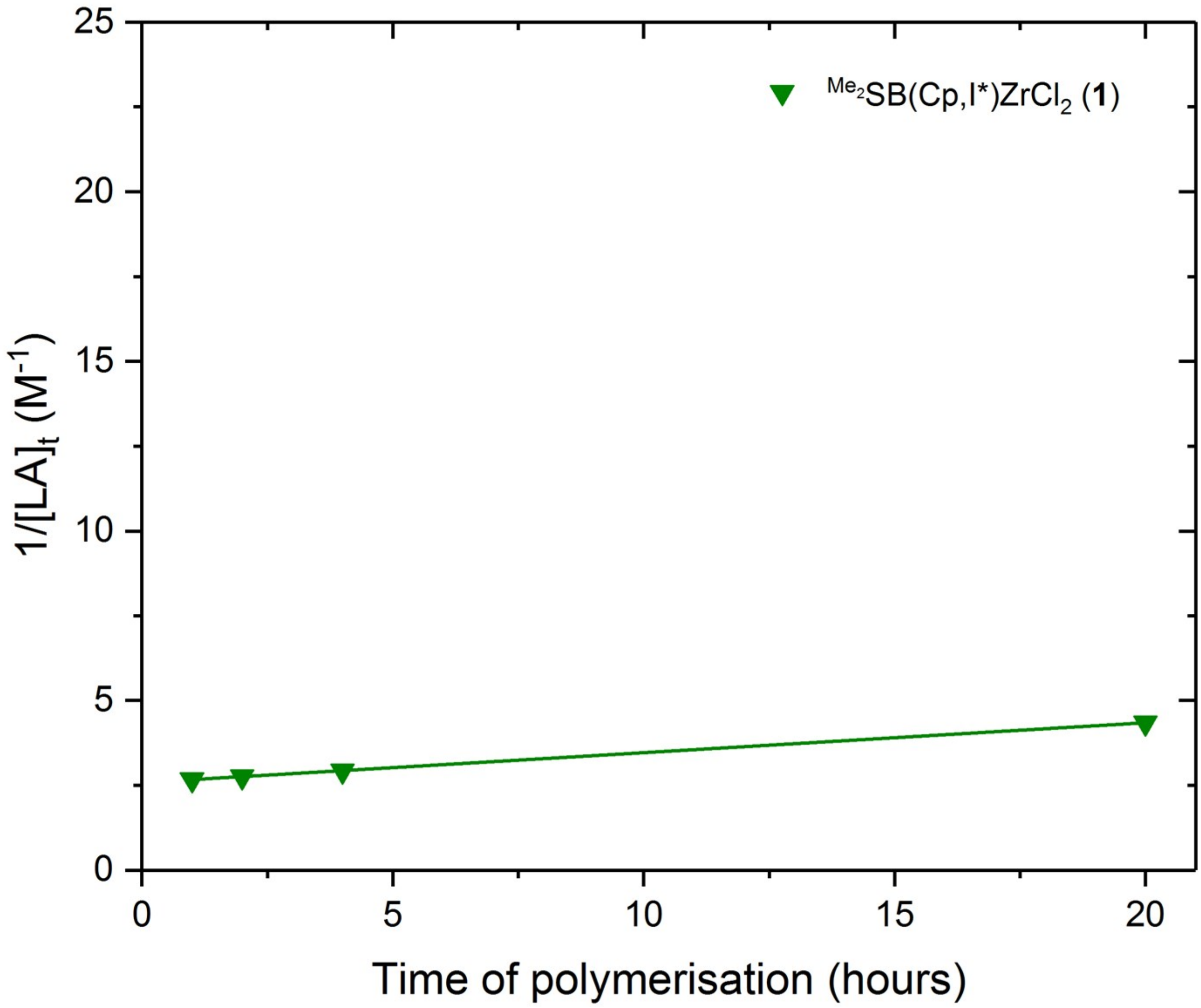


Fig. S43. *L*-Lactide polymerisation with $^{Me2}SB(Cp,I^*)ZrCl_2$ (**1**) (green down triangle, $k_{obs} = 0.08 \pm 0.01$ M^{-1} h^{-1}). Polymerisation conditions: *L*-lactide (40 mg), 80 °C, toluene (5.5 mL), $[LA]_0/[M]_0 = 50$, $[LA]_0 = 0.05$ M, 2 equivalents of benzyl alcohol as co-initiator.

7. References

1. M. Save, M. Schappacher and A. Soum, *Macromolecular Chemistry and Physics*, 2002, **203**, 889–899.
2. J. Cosier and A. M. Glazer, *Journal of Applied Crystallography*, 1986, **19**, 105–107.
3. CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.
4. A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *Journal of Applied Crystallography*, 1993, **26**, 343–350.
5. L. Palatinus and G. Chapuis, *Journal of Applied Crystallography*, 2007, **40**, 786–790.
6. L. Farrugia, *Journal of Applied Crystallography*, 1999, **32**, 837–838.