Electronic Supplementary Information for Dalton Transactions

Supplementary Information for:

Tert-butylamidinate tin(II) complexes: single-site initiators for the controlled production of poly(lactic acid)

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1. X-ray Crystallography

Complex 1:

The two independent C_2-symmetric complexes present in the crystals of **1** have similar geometries, the biggest difference between them being a respective *ca.* 9° twist between their N(1)-bound 2,6-diisopropylphenyl rings.

Table 1. Selected bond lengths (Å) and angles (°) for **1**.

	Mol I	Mol II		Mol I	Mol II
Sn–N(1)	2.197(2)	2.215(3)	Sn–N(2)	2.444(2)	2.389(2)
N(1)–C(3)	1.343(3)	1.348(4)	N(2)–C(3)	1.314(3)	1.315(4)
N(1)–Sn–N(2)	57.13(8)	57.92(9)	N(1)–Sn–N(1A)	101.33(12)	102.89(13)
N(1)–Sn–N(2A)	97.98(8)	96.45(9)	N(2)–Sn–N(2A)	142.84(11)	140.74(12)
N(1)–C(3)–N(2)	114.1(2)	114.1(2)			

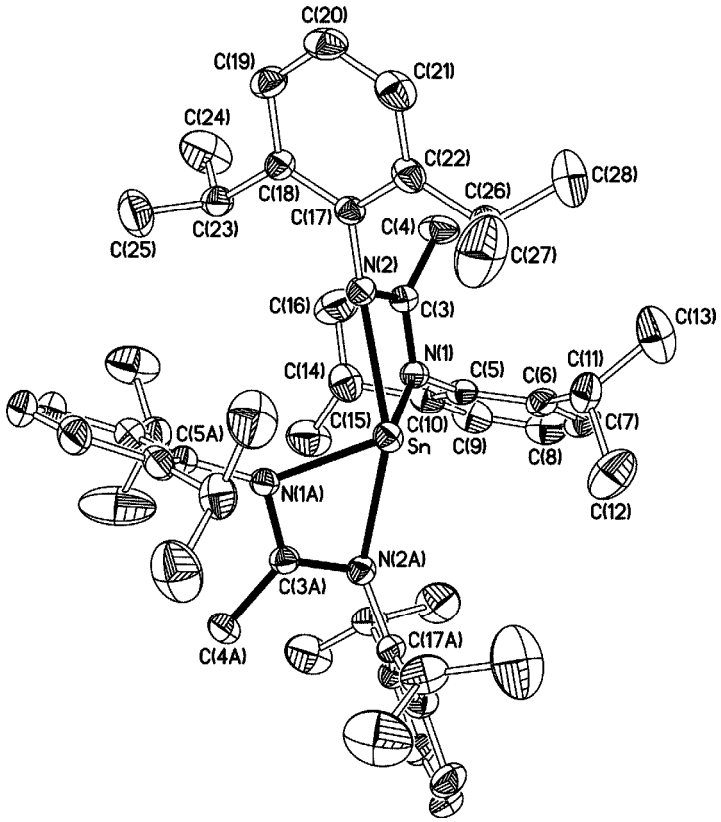

Figure S1. The molecular structure of one (**I**) of the two independent C_2-symmetric molecules present in the crystals of **1** (50% probability ellipsoids).

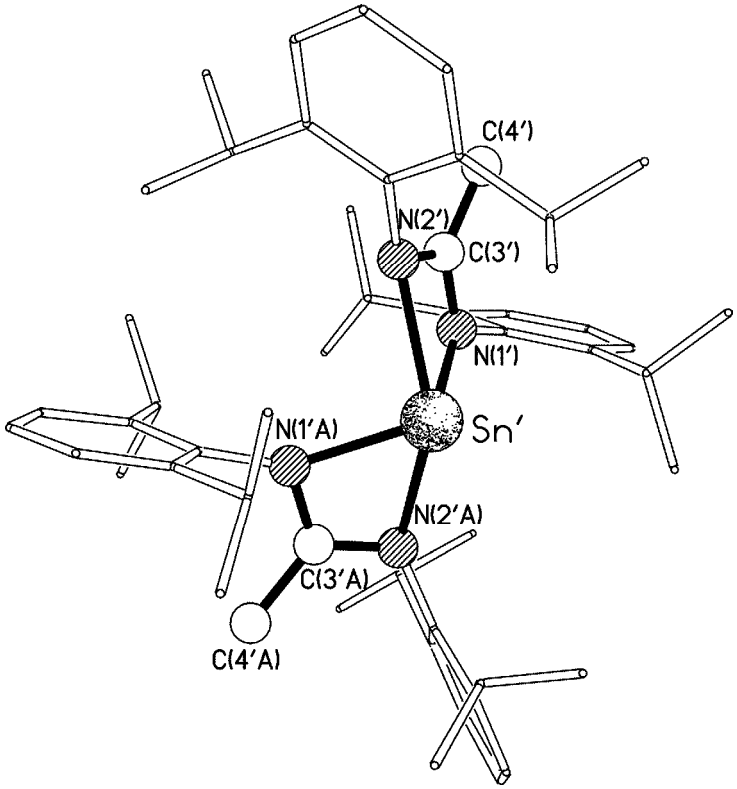

Figure S2. The molecular structure of one (**II**) of the two independent C_2-symmetric molecules present in the crystals of **1**.

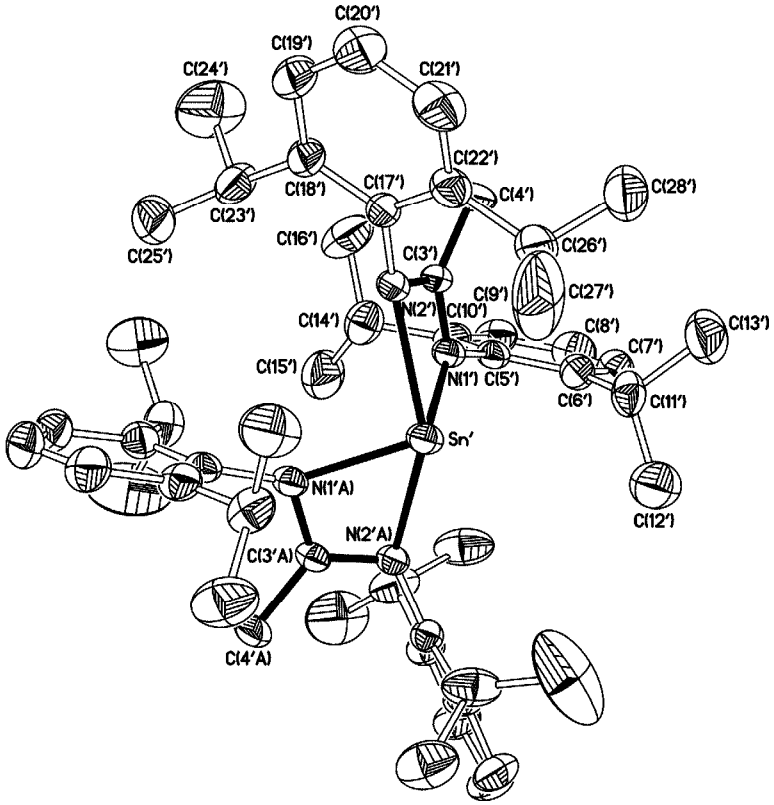

Figure S3. The molecular structure of one (**II**) of the two independent C_2-symmetric molecules present in the crystals of **1** (50% probability ellipsoids).

2. Relationship between M_n and $[LA]_0/[3]$

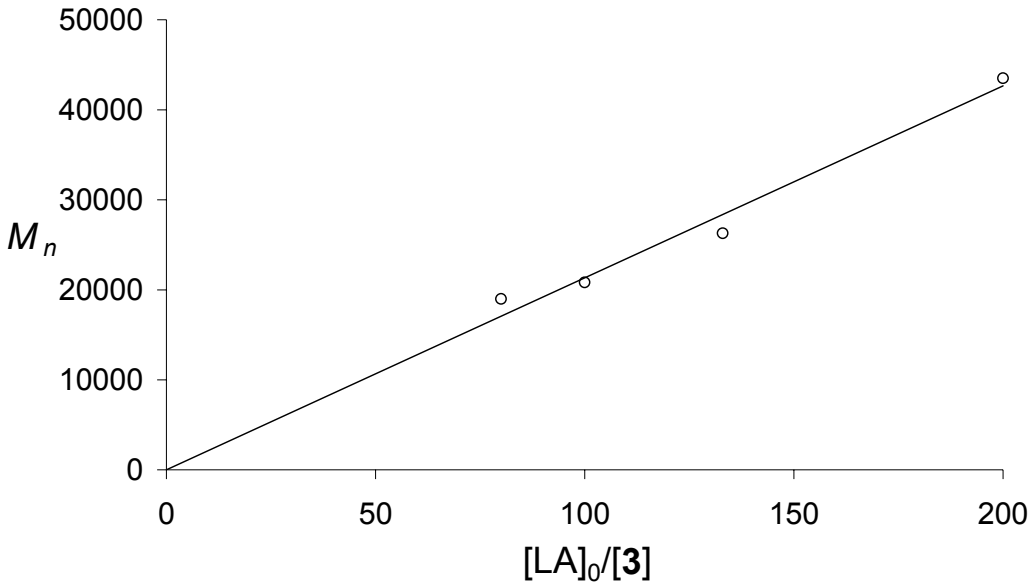

Figure S4. A plot of M_n *vs.* $[LA]_0/[3]$ for the polymerisation of *rac*-LA at 60 °C in toluene (M_n determined by GPC).

3. Determination of the rate law order dependence upon the concentration of 3.

Kinetic studies using **3** were carried out by performing polymerisations at different concentrations of the tin(II) initiator (1.4 - 3.5 x 10^{-2} mol l^{-1}) and at constant initial lactide concentration (0.28 mol l^{-1}; 200 – 80 equivalents). The monomer conversion (toluene, 60 °C) was then monitored with respect to time. In every case the semilogarithmic plot of LA conversion with time was linear, indicating a first order dependence on the concentration of lactide (Figure S5). Thus, the polymerisation proceeds according to the rate law:

$$-\frac{d[LA]}{dt} = k_{app}[LA] \qquad \text{(equation S1)}$$

where $k_{app} = k_p[\mathbf{3}]^x$ (k_p is the rate constant of propagation).

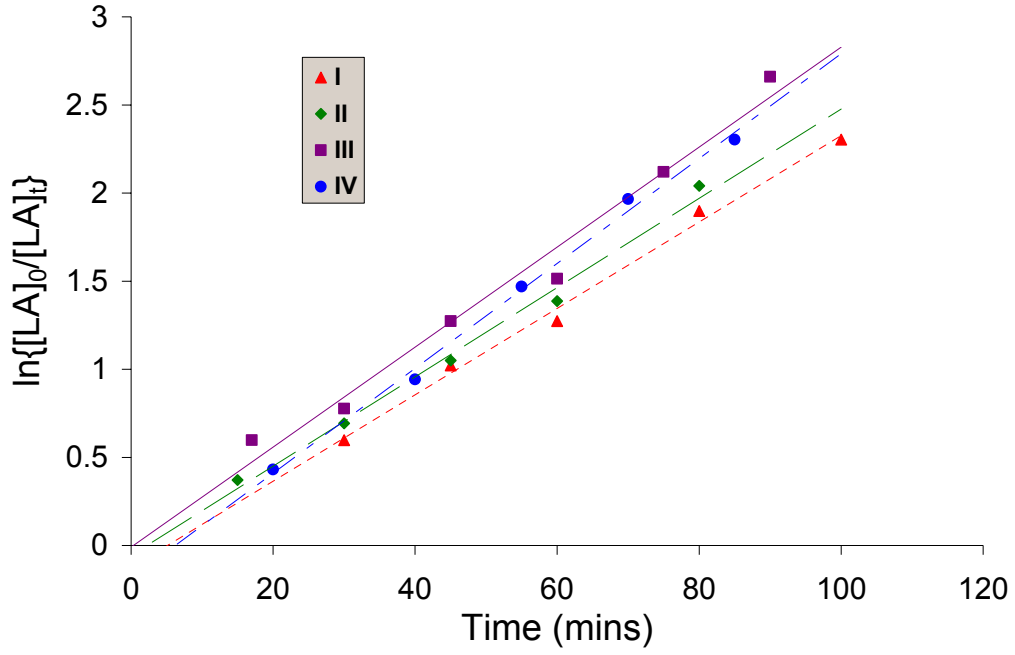

Figure S5. Plots of $\ln\{[LA]_0/[LA]_t\}$ *vs.* time for the polymerisation of *rac*-LA using complex **3** in toluene at 60 °C ($[LA]_0$ = 0.28 M; I: [**3**] = 0.0035 M; II: [**3**] = 0.0021 M; III: [**3**] = 0.0028 M; IV: [**3**] = 0.0014 M).

As the concentration of lactide remains constant throughout this study comparison of the k_{app} values obtained at each concentration of **3** (chosen to give monomer : initiator stoichiometries of 80, 100, 133 and 200) can be used to derive the order in the tin(II) complex (*i.e.* x). Rearrangement of equation S2 into equation S3 shows that the value of x can be obtained from the slope of the plot of $\ln k_{app}$ against ln[**3**] (Figure S6):

$$k_{app} = k_p[\mathbf{3}]^x \qquad \text{(equation S2)}$$

$$\therefore \ln k_{app} = \ln k_p + x\ln[\mathbf{3}] \qquad \text{(equation S3)}$$

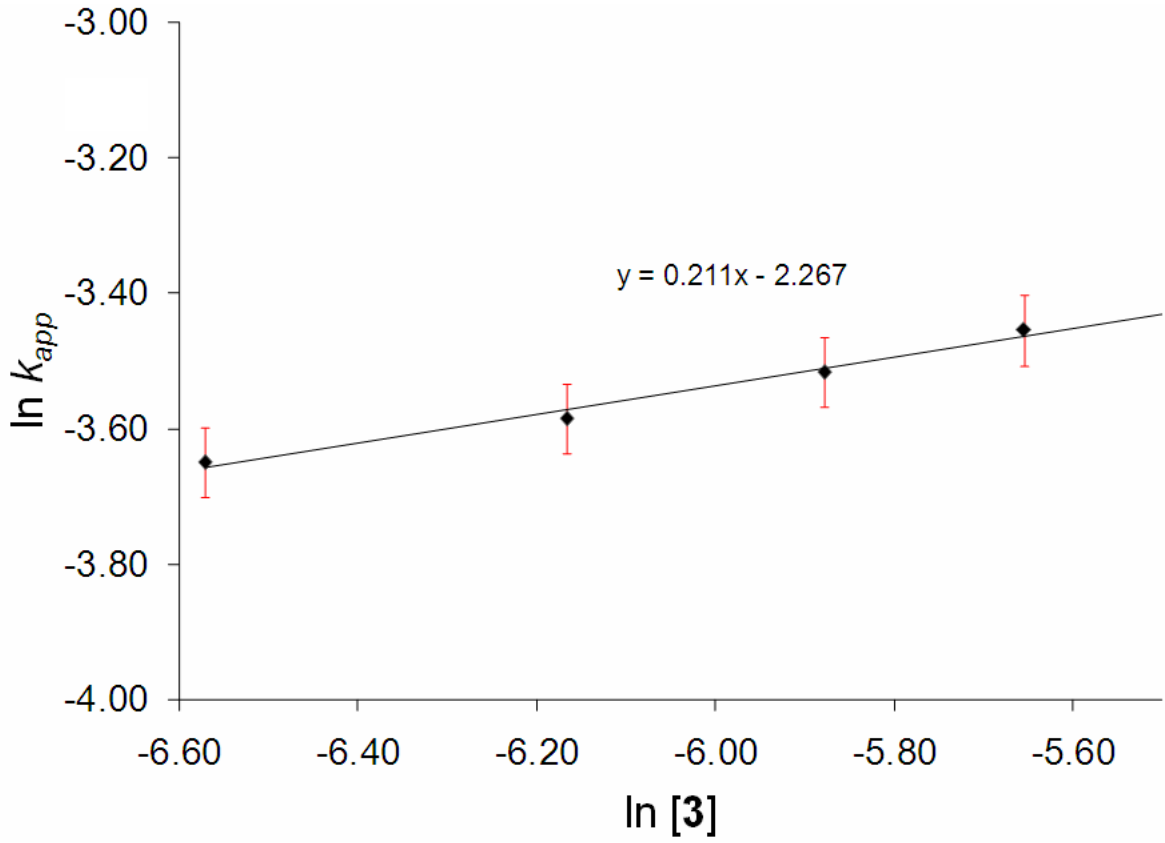

Figure S6. A plot of ln k_{app} *versus* ln [**3**] for the polymerisation of *rac*-LA in toluene at 60 °C.

The slope of the resulting plot (Figure S6) was found to be 0.21. The overall rate law for the polymerisation is therefore:

$$-\frac{d[LA]}{dt} = k_{app}[LA] = k_p[LA][\mathbf{3}]^{0.21}$$