

Supporting information for:

A series of *bis*(phosphinic)diamido yttrium complexes as initiators for lactide polymerization.

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X-ray crystallography

With the exception of the disordered Si(31) unit in the structure of **13** (see below), all of the Si-H protons in the structures of compounds **13**, **14** and **16** were located from ΔF maps and refined subject to an Si-H distance constraint of 1.45 Å. The Si-H protons for both of the two identified orientations of the disordered Si(31) unit in **13** were placed in idealised positions and allowed to ride on their parent silicon atoms with an Si-H distance of 1.45 Å.

In the structure of **13**, disorder was found in the C(13) and C(19) isopropyl groups. In each case two orientations were identified, of *ca.* 57:43 and 71:29% partial occupancy respectively, with only the non-hydrogen atoms of the major occupancy orientations being refined anisotropically. In the same structure, disorder was also found in Si(31) SiMe₂H unit. In this case three partial orientations were identified of *ca.* 64, 19 and 17% occupancy, with only the non-hydrogen atoms of the major occupancy orientation being refined anisotropically. The included toluene solvent molecule in the structure of **13** was found to be disordered about a $\bar{4}$ position. One 25% occupancy orientation was identified (which was refined isotropically) and this generates three other overlapping orientations by operation of the $\bar{4}$ symmetry.

In the structure of **16**, disorder was found in the N(3)/N(6) cyclohexyl ring. Two orientations of *ca.* 52 and 48 % occupancy were identified for the C₆ ring (see Fig. S4), and only the non-hydrogen atoms for the major occupancy orientation were refined anisotropically.

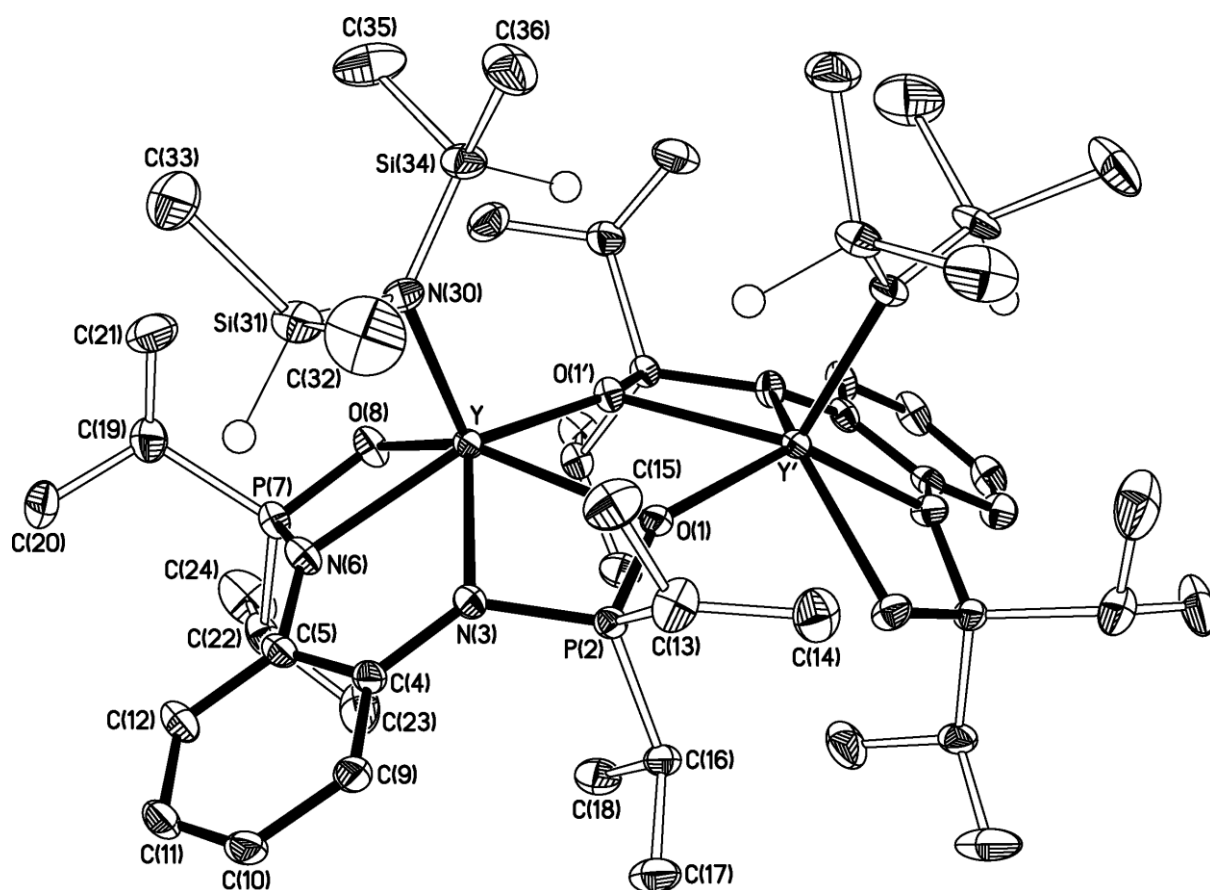


Fig. S1 The molecular structure of the C_2 symmetric complex **13** (30% probability ellipsoids).

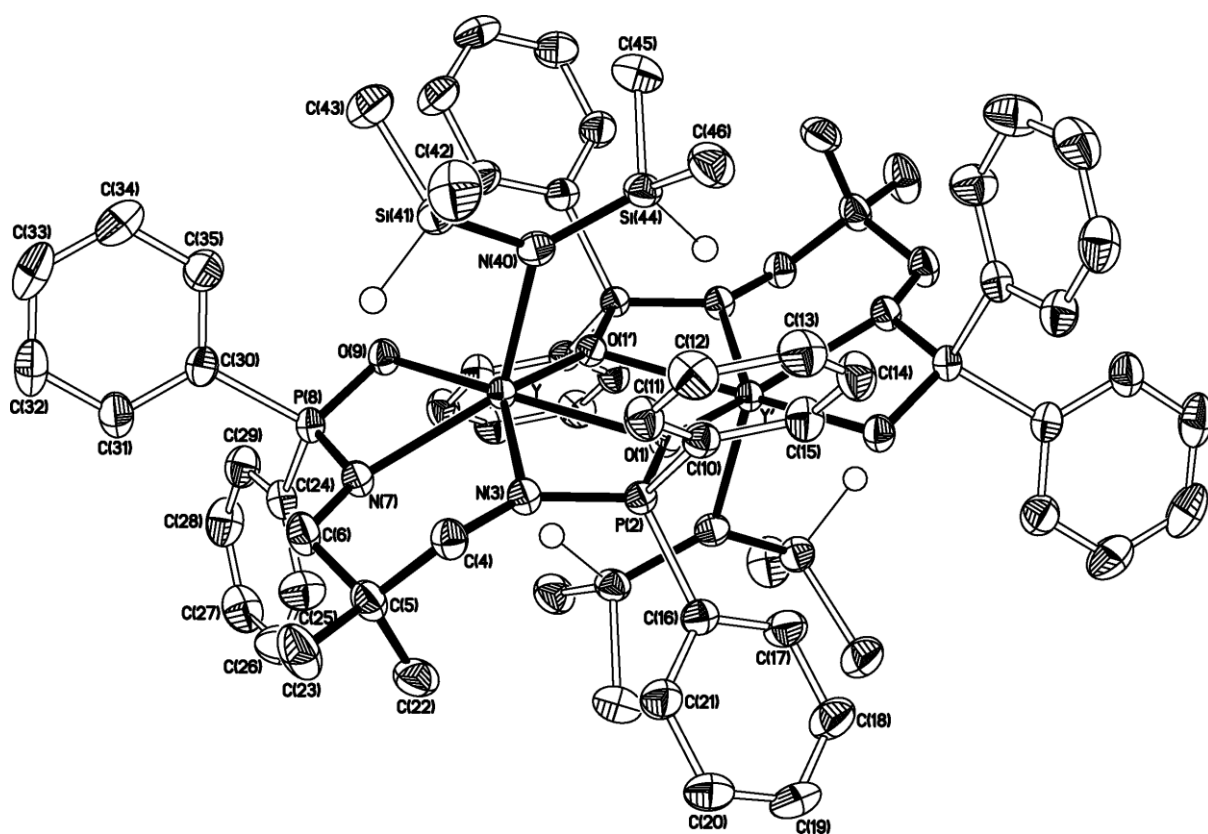


Fig. S2 The molecular structure of the C_i symmetric complex **14** (50% probability ellipsoids).

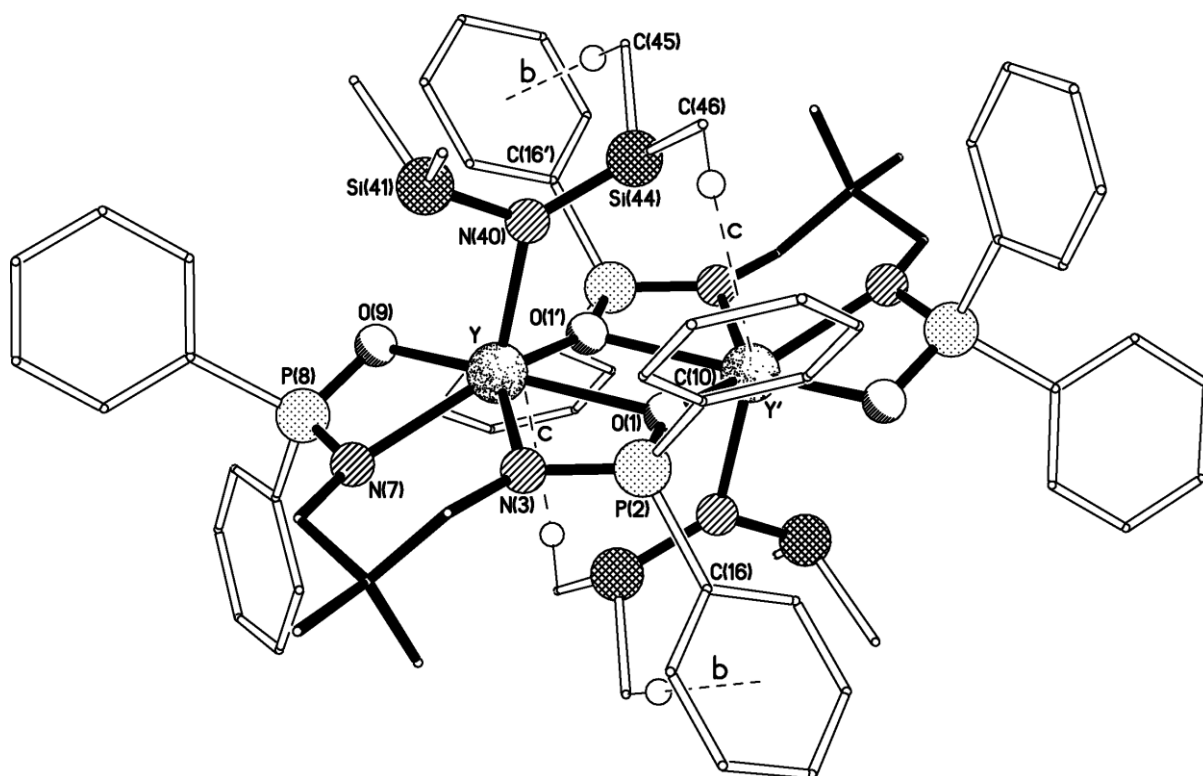


Fig. S3 The molecular structure of the C_i symmetric complex **14** showing the pairs of C–H $\cdots\pi$ contacts from the $N(\text{SiMe}_2\text{H})_2$ units “above” and “below” the Y_2O_2 ring plane. The geometries of the C–H $\cdots\pi$ contacts [$\text{H}\cdots\pi$] (\AA), [$\text{C–H}\cdots\pi$] ($^\circ$) are (**b**) 2.80, 179; (**c**) 2.69, 175 (C–H distances fixed at 0.96 \AA).

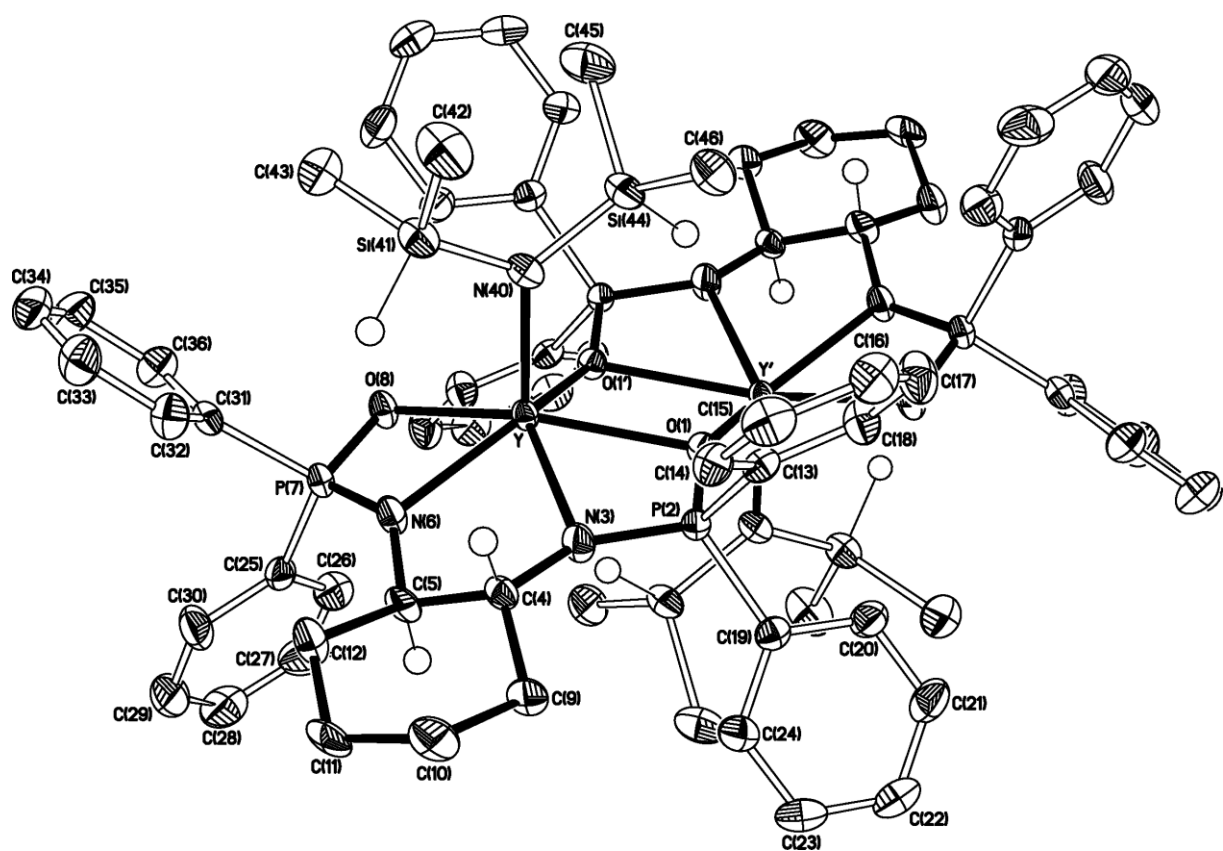


Fig. S4 The molecular structure of the C_i symmetric complex **16** (50% probability ellipsoids).

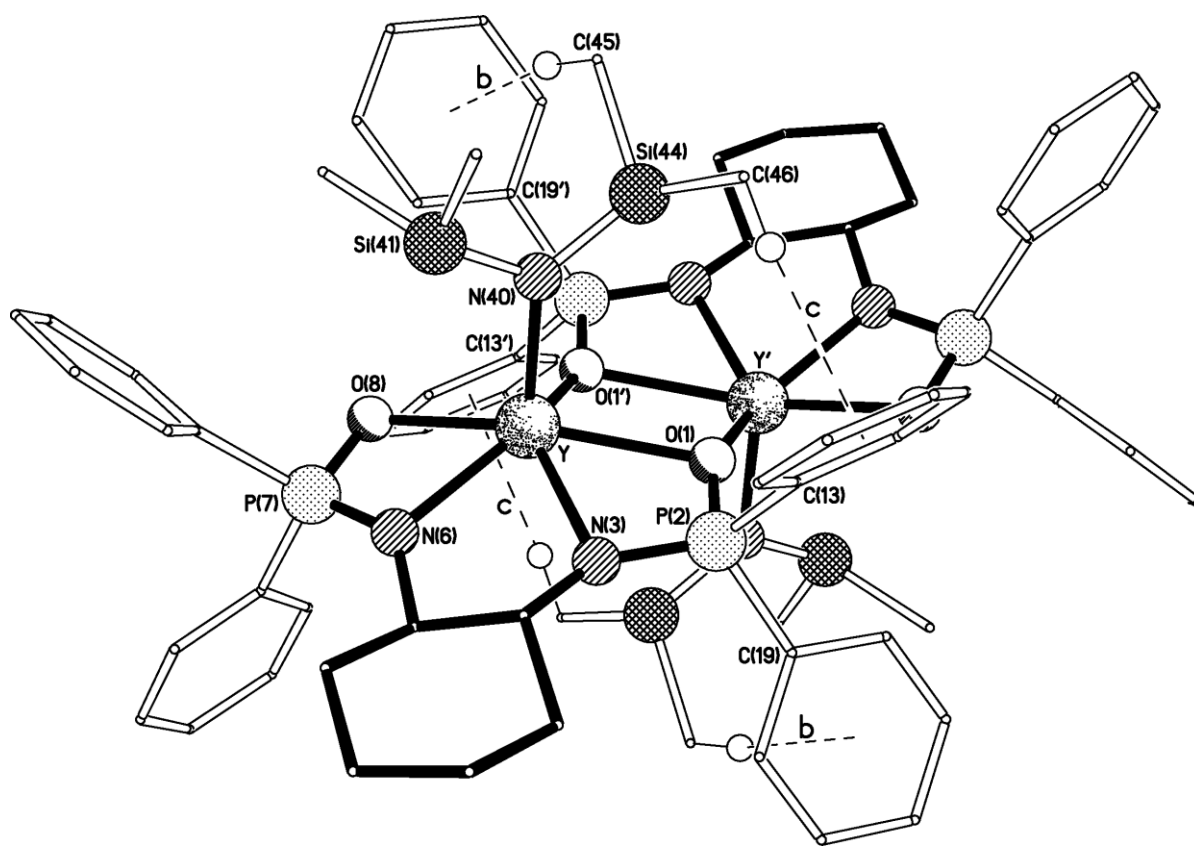


Fig. S5 The molecular structure of the C_i symmetric complex **16** showing the pairs of C–H $\cdots\pi$ contacts from the $N(\text{SiMe}_2\text{H})_2$ units “above” and “below” the Y_2O_2 ring plane. The geometries of the C–H $\cdots\pi$ contacts [$\text{H}\cdots\pi$] (\AA), [$\text{C–H}\cdots\pi$] ($^\circ$) are (b) 2.75, 165; (c) 2.75, 171 (C–H distances fixed at 0.96 \AA).

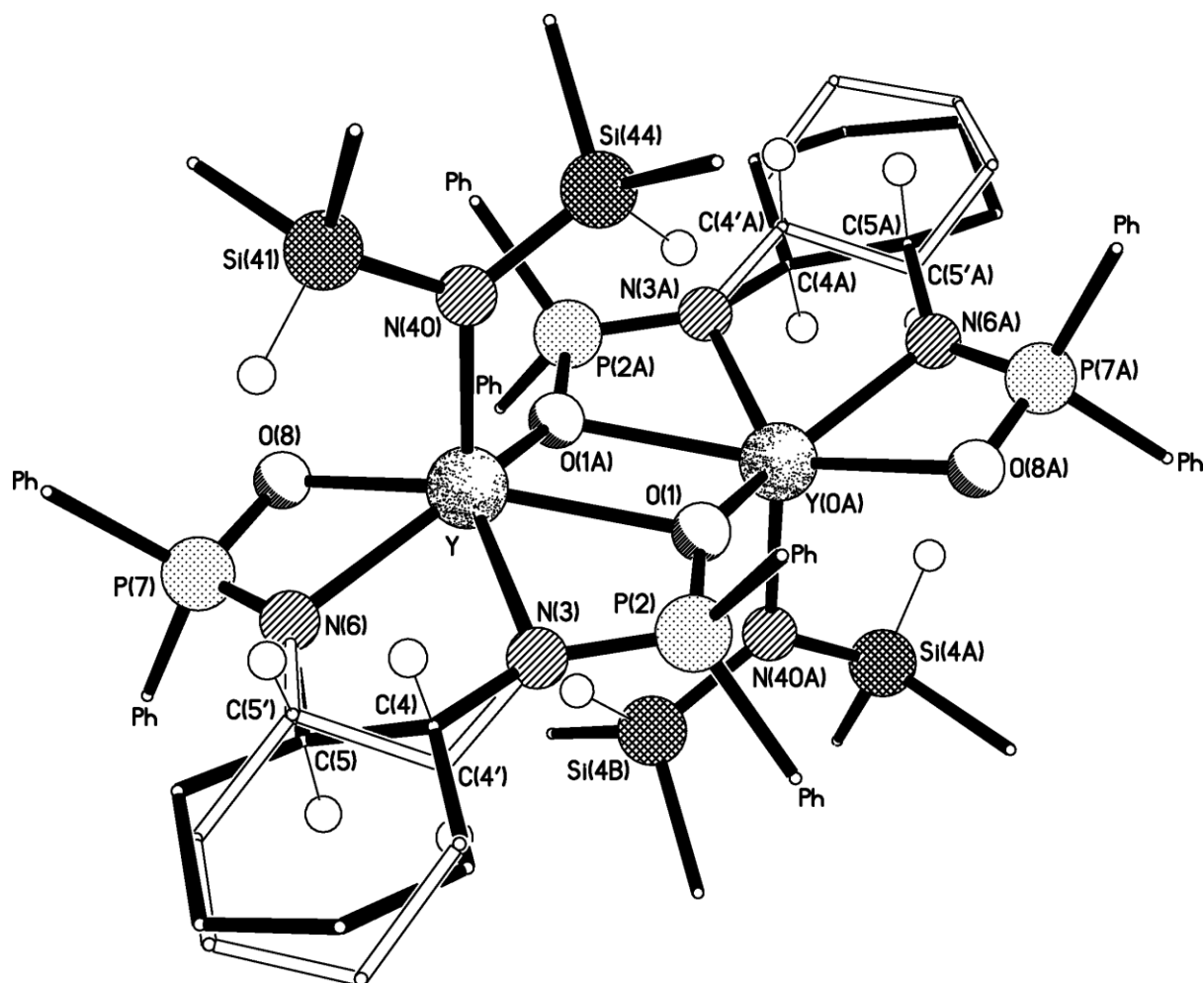


Fig. S6 The disorder in the N(3)/N(6) cyclohexyl ring in the structure of the C_i symmetric complex **16** showing the two partial occupancy orientations. The major occupancy orientation (*ca.* 52%) has been drawn with dark bonds, and the minor occupancy orientation (*ca.* 48%) with open bonds.

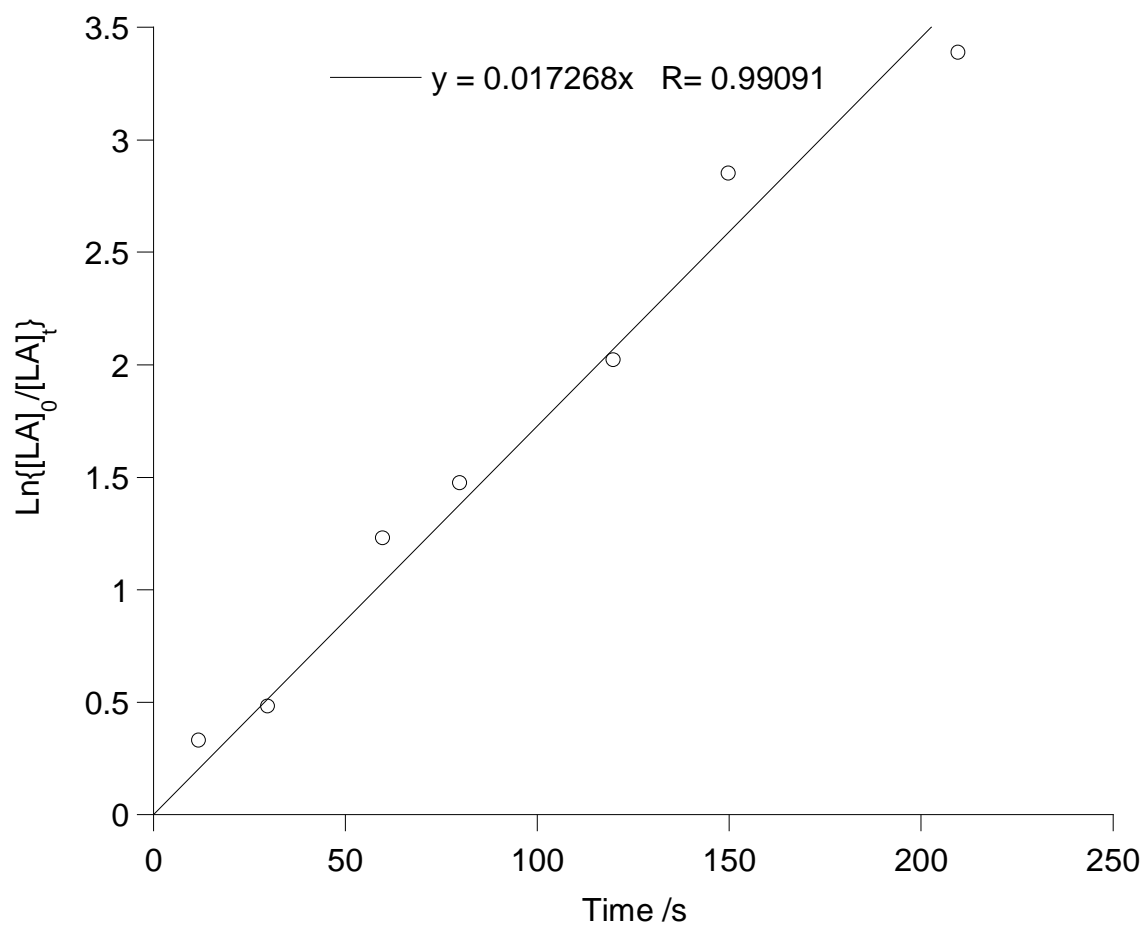


Fig. S7: Semilogarithmic plot of conversion vs. time using initiator **13** with 2 eq added $i\text{PrOH}$..

Reaction conditions: $[\text{LA}]_0 = 0.5 \text{ M}$ in CH_2Cl_2 ; $[\text{LA}]:[i\text{PrOH}]:[\mathbf{13}] = 400:2:1$.

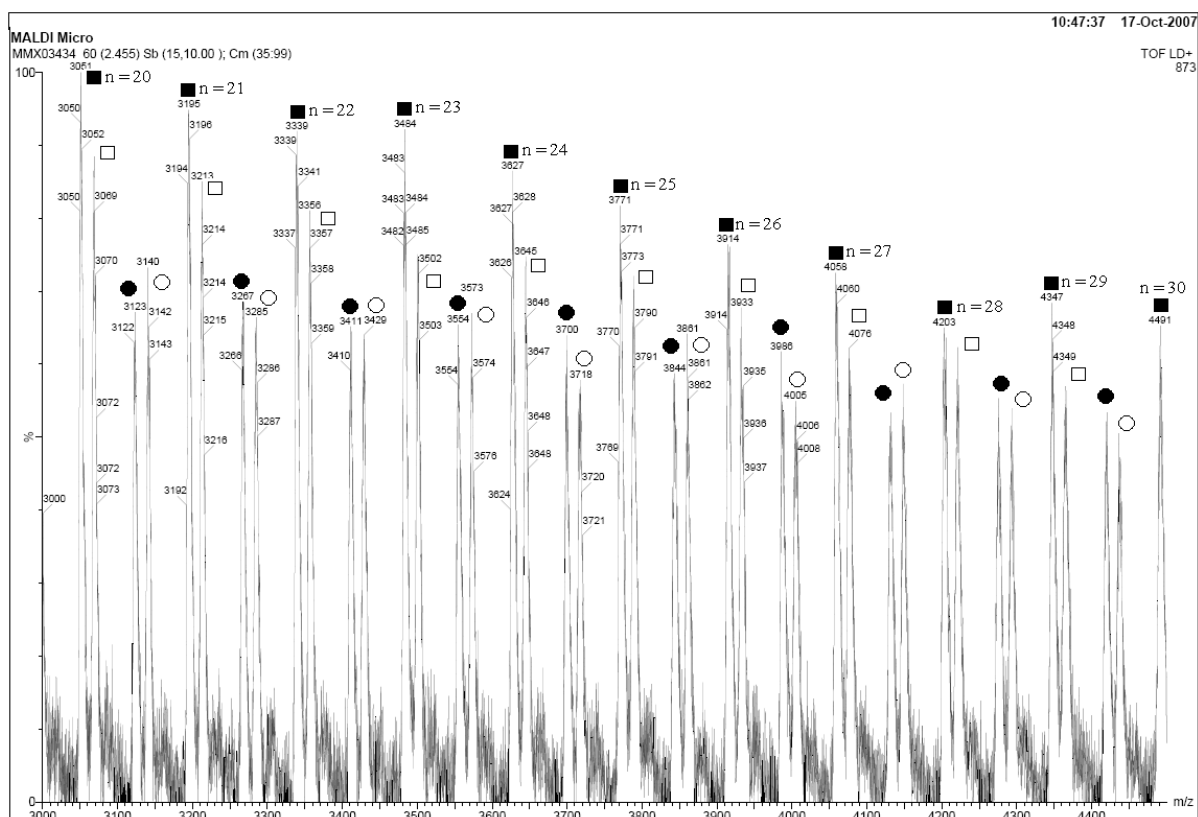


Fig. S8: Selected area of a MALDI-TOF mass spectrum of PLA using complex **16** as an initiator. Reaction conditions: $[LA]_0 = 1.0 \text{ M}$ in CH_2Cl_2 ; $[LA]_0/[N(\text{SiHMe}_2)_2] = 200$. Percentage conversion = 15 %. Key:

