Supporting Information

Ring opening polymerisation of lactide with uranium(IV) and cerium(IV) phosphinoaryloxide complexes

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Experimental

General considerations

All polymerization reactions were performed under a dinitrogen atmosphere using a Vigor glovebox system equipped with a −35 °C freezer and [H_2O] and [O_2] analysers. Toluene, hexane, and THF was obtained from an Innovative Technologies solvent purification system incorporating columns of alumina and copper catalysts and were de-gassed by three freeze-pump-thaw cycles prior to use. *L*- and *rac*- lactide were purified via vacuum sublimation. Benzyl alcohol, $CDCl_3$, and toluene-d_8 were dried over calcium hydride for 24 h heated to reflux, distilled under dinitrogen and degassed by three freeze-pump-thaw cycles. Benzene-d_8 was dried over potassium at 80 °C for 24 h and degassed by three freeze-pump-thaw cycles after vacuum transfer. The compounds $Ce[N(SiMe_3)_2]_3$,[1] and $IU(OAr^P)_3$, $Me_3SiOU(OAr^P)_3Ni$, and $HOAr^P$[2] were prepared according to published procedures.

Characterization

Gel permeation chromatography (GPC) was performed using a Malvern Instruments Viscotek 270 GPC Max triple detection system with 2 × mixed bed styrene/DVB columns (300 × 7.5 mm) in THF at a flow rate of 1 mL min^{-1} and an injection volume of 200 µl. Samples for analysis were pre-dissolved in chloroform at a concentration of ~8-12 mg/ml. Analysis was carried out using OmniSEC 5.0 software with an inputted *dn/dc* value of 0.05. ^1H, ^{13}C, ^{31}P NMR spectra and 2D analysis (COSY, HSQC and HMBC) were recorded on Bruker AVA500, AVA600 or PRO500 spectrometers at 300 K and variable temperature (VT) experiments were conducted on a Bruker AVA400 spectrometer. End group analysis was performed on Bruker AVA spectrometer with 1024 scans for ^{13}C (151 MHz) and 128 scans for ^1H (600 MHz). ^1H homodecoupled NMR was recorded using Bruker AVA600 spectrometer, using a standard pulse program: zghd.2 irradiating at 1.59 ppm (949.18 H_z). Chemical shifts are reported in parts per million, δ, referenced to residual proton resonances, and calibrated against external TMS. Elemental analyses were carried out at London Metropolitan University, London, UK, and Pascher Labor, Remagen, Germany. Mass spectrometry samples were run on an AB Voyager MALDI at the EPSRC UK National Mass Spectrometry Facility at Swansea University. The sample was analysed in positive-linear and reflectron modes, with dithranol matrix and NaOAc additive.

Syntheses

$Me_3SiOU(OAr^P)_3$ (**1**). A Schlenk flask was charged with $IU(OAr^P)_3$ (705 mg, 0.500 mmol, 1.00 eq.) and $NaOSiMe_3$ (56 mg, 0.50 mmol, 1.0 eq.) and dissolved in THF (12 ml). The green mixture was stirred at ambient temperature for 18 h during which time a colourless precipitate formed. Volatiles were removed under reduced pressure to afford a green residue. The solids were extracted with toluene (3 × 5 ml). The solvent was again evaporated and the green residue taken up in a minimal amount of THF (ca. 4 ml) and the green solution layered with hexane

(ca. 5 ml) and stored at -20 °C for 3 d. The green precipitate was isolated, washed with hexane (3 × 5 ml), and dried under reduced pressure. **1** was isolated as a bright green microcrystalline solid (432 mg, 63 %). ^{1}H NMR (δ in ppm, toluene-*d8*, 370 K): -3.33 (vbr s), -1.84 (vbr s), -0.01 (br s), 4.57 (br s), 5.02 (br s), 6.46 (vbr s). Analysis calculated for $C_{72}H_{81}O_4P_3SiU$: C 63.15. H 5.95. Found: C 63.03. H 6.05.

$Me_3SiOCe(OAr^P)_3$ (**2**). A Schlenk flask was charged with $HOAr^P$ (523 mg, 1.500 mmol, 3.00 eq.), $Ce[N(SiMe_3)_2]_3$ (310 mg, 0.500 mmol, 1.00 eq.), and toluene (10 ml) and the clear yellow solution stirred at ambient temperature for 2 h. Then all volatiles were removed under reduced pressure and the yellow residue taken up again in toluene (10 ml) and a toluene solution of $NaOSiMe_3$ (48 mg, 0.500 mmol, 1.0 eq., 2 ml) added. After stirring the clear yellow solution at ambient temperature for 16 h a solution of Ph_3CCl (140 mg, 0.500 mmol, 1.0 eq.) in toluene (2 ml) was added causing an immediate colour change to dark brown. The dark brown mixture was allowed to stir for another 5 h, then all volatiles evaporated and the dark brown residue extracted with hexane (3 × 3 ml). The dark brown solution was then concentrated and allowed to stand at ambient temperature to give large dark brown crystals of **2** over 2 d (611 mg, 96 %). ^{1}H NMR (δ in ppm, C_6D_6, 300 K): -0.30 (s, 9H, Si*Me*$_3$), 1.55 (s, 19H, ^{t}*Bu*), 2.13 (s, 9H, *Me*), 6.72-7.12 (m, 17H, Ar*H*). ^{1}H NMR (δ in ppm, C_6D_6, 340 K): -0.31 (s, 9H, Si*Me*$_3$), 1.54 (s, 27H, ^{t}*Bu*), 2.15 (s, 9H, *Me*), 6.85 (d, *J* = 4 Hz, 3H, Ar*H*), 6.96 (s, 18H, Ph*H*), 7.21 (s, 3H, Ar*H*), 7.38 (s, 12H, Ph*H*). ^{29}Si NMR (δ in ppm, C_6D_6, 300 K): 6.1. ^{31}P NMR (δ in ppm, C_6D_6, 300 K): 8.8, 12.2, 16.2, 23.6. Analysis calculated for $C_{72}H_{81}CeO_4P_4$: C 68.01. H 6.42. Found: C 68.36. H 6.81.

$U(OAr^P)_4$ (**3**). An ampoule was charged with $UI_4(Et_2O)_2$ (89 mg, 0.10 mmol, 1.00 eq.), $KOAr^P$ (155 mg, 0.400 mmol, 4.0 eq.), and THF (10 ml) and heated to 80 °C for 2h. Then all volatiles were removed under reduced pressure and the green residue extracted with hot toluene. The extract was concentrated and allowed to stand to yield dark green crystals of **3** (117 mg, 72 %). ^{1}H NMR (δ in ppm, C_6D_6, 300 K): 1.38 (d, 16H, *J* = 7 Hz, *Ph*), 1.74 (s, 12H, *Me*), 2.01 (s, 4H, Ar*H*), 5.10 (t, 16H, *J* = 7 Hz, *Ph*), 5.53 (t, 8H, *J* = 8 Hz, *Ph*), 10.16 (s, 4H, Ar*H*), 11.73 (s, 36H, ^{t}*Bu*). 13C{1H} NMR (δ in ppm, C_6D_6, 300 K): 19.8, 41.1, 44.1, 86.8, 92.3, 125.4, 125.6, 126.3, 127.6, 130.3, 131.3, 132.4, 171.7. Analysis calculated for $C_{92}H_{96}O_4P_4U$: C 67.89. H 5.95. Found: C 68.03. H 6.02.

Ring opening polymerisation of lactide

Representative reaction procedure In a glove box to an oven-dried ampoule lactide, catalyst and BnOH (if required) were dissolved in the choice of solvent. The mixture was heated to the desired temperature and left for 19 hr. The reaction was quenched and precipitated in methanol with a small amount of dilute HCl.

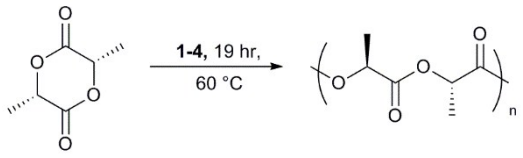
Example ROP (Table S1 entry 1): *l*-lactide (0.086 g, 0.6 mmol) and **1** (0.0041 g, 0.003 mmol) were dissolved in toluene (0.6 mL) and added to an oven dried ampoule to give a 1.0 M solution of lactide. The reaction mixture was heated to 60 °C for 19 hr. The product was quenched and precipitated in cold methanol with a small amount of of dilute hydrochloric acid. The polymer was collected via filtration to yield a white solid.

Example of immortal ROP (Table S2 entry 1): *l*-lactide (0.086 g, 0.6 mmol), **1** (0.0041 g, 0.003 mmol) and benzyl alcohol (1.6 µl, 0.015 mmol) were dissolved in toluene (0.6 mL) and added to an oven dried ampoule to give a

1.0 M solution of lactide. The reaction mixture was heated to 60 °C for 19 hr. The product was quenched and precipitated in cold methanol with a few drops of dilute hydrochloric acid. The polymer was collected via filtration to yield a white solid.

Example of in-situ monitoring of LA polymerisation: Ring-opening polymerisations were monitored using ^{1}H NMR spectroscopy. In a glove box to a Youngs NMR tube, lactide, catalyst and BnOH (if required) were dissolved in toluene-d_8 to make a 1M solution. The tube was sealed and placed in the spectrometer probe which was pre-heated to 333K. **End-group analysis (Figure S4):** ^{1}H NMR ($CDCl_3$, ppm): **end group 1**, $HOCHCH_3C{=}OO$-polymer: δ4.37 (m, 1H, $HOCHCH_3C{=}OO$-), δ2.67 (br, 1H, *H*$OCHCH_3C{=}OO$-), δ1.51 (br, 3H, $HOCHCH_3C{=}OO$-). **End group 2**, $PhCH_2O$-polymer: δ7.34-7.38 (m, 5H, *Ph*CH_2O-), δ5.18 (m, 2H, $PhCH_2O$-). ^{13}C NMR {^{1}H} ($CDCl_3$, ppm): **end group 1,** $HOCHCH_3C{=}OO$-polymer: δ 175.1, δ66.69, 20.54. **End group 2,** $PhCH_2O$-polymer: δ135.1, 128.6-128.3, 67.2. 2D analysis (COSY, HSQC and HMBC) was used to aid with end group identification.

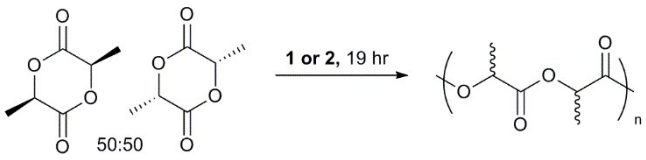
Table S1. Ring opening polymerisation of *l*-lactide



Entry	Catalyst	Solvent	Conversion (%)[a]	$M_{n,th}$[b]	$M_{n,GPC}$[c]	Đ[c]
1	1	Toluene	98	28,342	26,475	1.043
2	1	Benzene- d_6	98	28,342	22,445	1.111
3	1	Dichloroethane	94	27,188	20,668	1.108
4[d]	1	Toluene	99	14,225[e]	15,688	1.074
5[f]	1	Toluene	99	4,856[g]	4,896	1.096
6	3	Toluene	99	28,540[h]	56,593	1.270
7[f]	3	Toluene	99	5,880[i]	5,134	1.257
8	4	Toluene	2	N/A	N/A	N/A
9[f]	4	Toluene	25	N/A	N/A	N/A
10	2	Toluene	94	27,188	25,877	1.241
11	2	Benzene- d_6	98	28,342	39,800	1.473
12	2	Dichloroethane	80	23,152	35,857	1.641
13[d]	2	Toluene	98	14,225[e]	9,106	1.184
14[f]	2	Toluene	99	4,856[g]	7,257	1.179

[a]Determined by ^{1}H NMR spectroscopy. [b]$M_{n,th}$ = (% conv. X ($MW_{(monomer)}$ x2)) + $MW_{(HOSi(Me)3)}$. [c]Determined by triple detection GPC using *dn/dc* value of 0.05. [d]Monomer: catalyst: BnOH (200:1:1). [e]$M_{n,th}$ = (% conv. X ($MW_{(monomer)}$ x2))/2 + $MW_{((HOSi(Me)3 + BnOH)/2)}$. [f]Monomer: catalyst: BnOH (200:1:5). [g]$M_{n,th}$ = (% conv. X ($MW_{(monomer)}$ x2))/6 + $MW_{((HOSi(Me)3 + BnOH)/2)}$. [h]$M_{n,th}$ = % conv. X ($MW_{(monomer)}$ x2). [i]$M_{n,th}$ (% conv. X ($MW_{(monomer)}$ x2))/5 + $MW_{(BnOH)}$.

Table S2. Ring opening polymerisation of *rac*-lactide



Entry	Catalyst	Solvent	Temperature (°C)	P_r[a]	Conversion (%)[b]	$M_{n,th}$[c]	$M_{n,GPC}$[d]	Đ[d]
1	1	Toluene	60	0.68	98	28,342	23,118	1.351
2	1	Dichloroethane	60	0.79	96	27,765	24,633	1.310
3	1	Dichloroethane	45	0.75	95	27,477	28,037	1.188
4	1	Benzene-d_6	90	0.62	99	28,630	23,654	1.469
5	1	Benzene- d_6	60	0.71	99	28,630	25,746	1.279
6	1	Benzene- d_6	50	0.73	74	21,423	28,998	1.155
7[e]	1	Benzene- d_6	60	0.58	99	4,903[f]	6,641	1.316
8	2	Toluene	60	0.37	95	27,477	22,405	1.642
9	2	Dichloroethane	60	0.45	70	20,270	32,811	1.832
10	2	Dichloroethane	45	0.51	71	20,558	31,478	1.656
11	2	Benzene- d_6	90	0.32	99	28,630	23,220	2.610
12	2	Benzene- d_6	60	0.4	92	28,612	28,480	1.565
13	2	Benzene- d_6	50	0.58	83	24,017	23,389	1.928
14[e]	2	Toluene	60	0.42	99	4,856[f]	7,925	1.232

[a]Determined by homodecoupled ^{1}H NMR spectroscopy [b]Determined by ^{1}H NMR spectroscopy. [c]$M_{n,th}$ = (% conv. X ($MW_{(monomer)}$ x2)) + $MW_{(HOSi(Me)3)}$. [d]Determined by triple detection GPC using *dn/dc* of 0.05. [e]Monomer: catalyst: BnOH (200:1:5). [f]$M_{n,th}$ = (% conv. X ($MW_{(monomer)}$ x2))/6 + $MW_{((HOSi(Me)3 + BnOH)/2)}$.

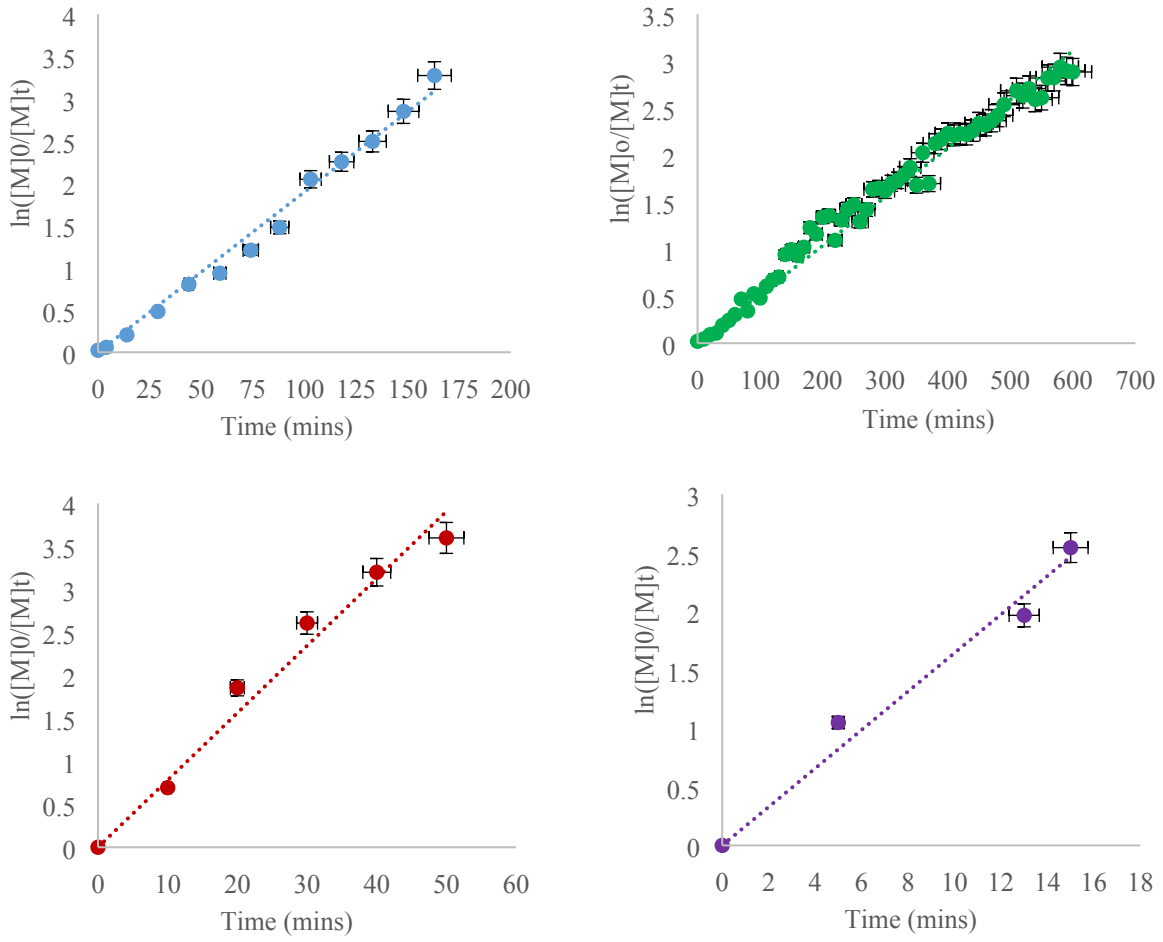


Figure S1. Kinetic plots of the ROP of *l*-lactide. Top left and top right: catalyst **1** and catalyst **2** respectively with a monomer: catalyst ratio of 200:1. Bottom left and right, immortal conditions using catalyst **1** and **2** respectively with a monomer: catalyst: BnOH ratio of 200:1:5. All kinetics were ran in toluene-d_8 at 333 K.

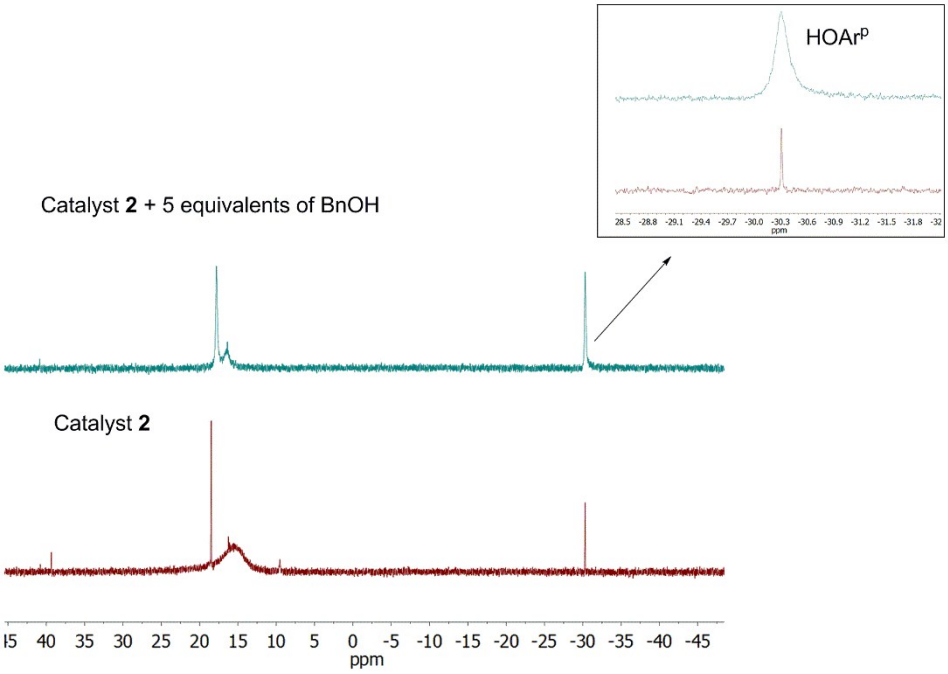
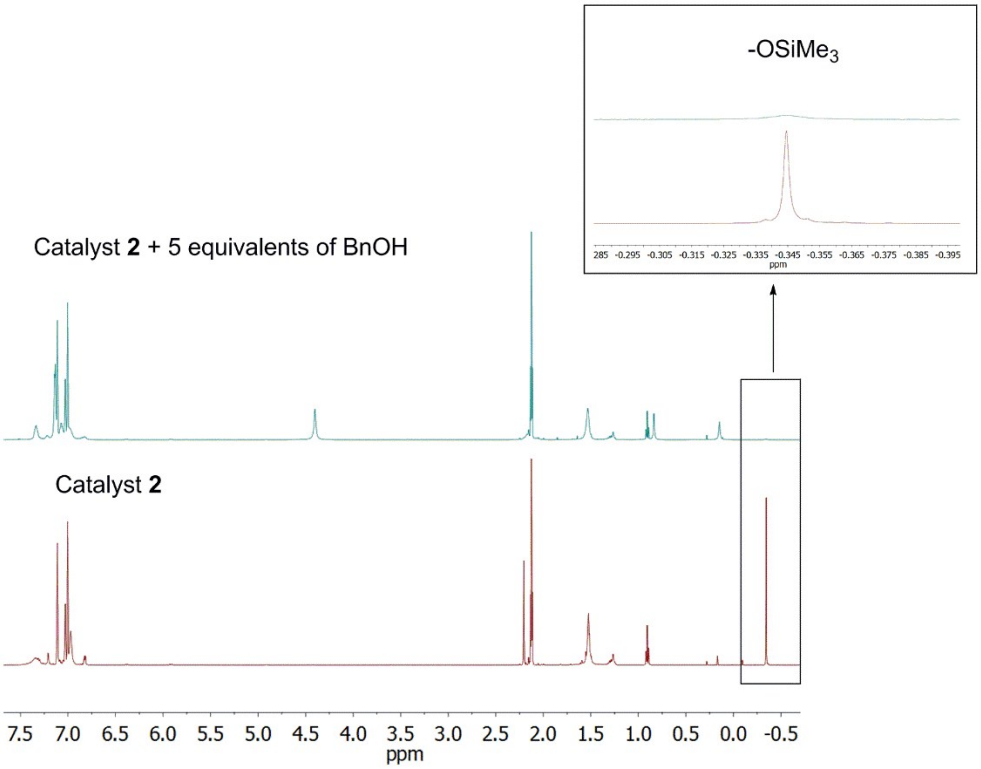


Figure S2. $^{31}P\{^{1}H\}$ NMR spectra of **2** in the presence (upper) and absence (lower) of BnOH (5 equivalents) in toluene-d_8 at 333 K.



Figures S3. ^{1}H NMR spectra of **2** in the presence (upper) and absence (lower) of BnOH (5 equivalents) in toluene-d_8 at 333 K.

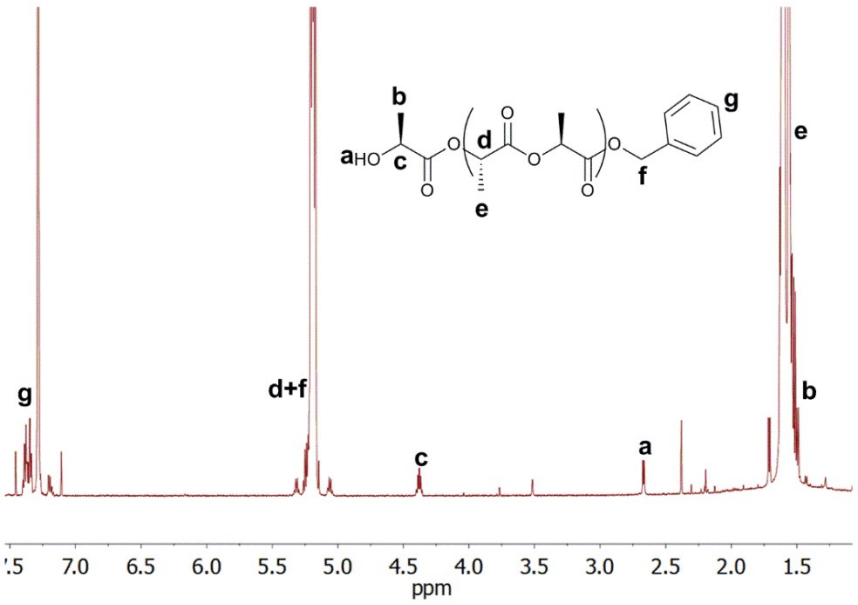


Figure S4. ^{1}H NMR spectrum of poly-*l*-lactide made for end-group analysis using **2** with a monomer: catalyst: BnOH ratio of 300:1:5 in $CDCl_3$ at 300 K.

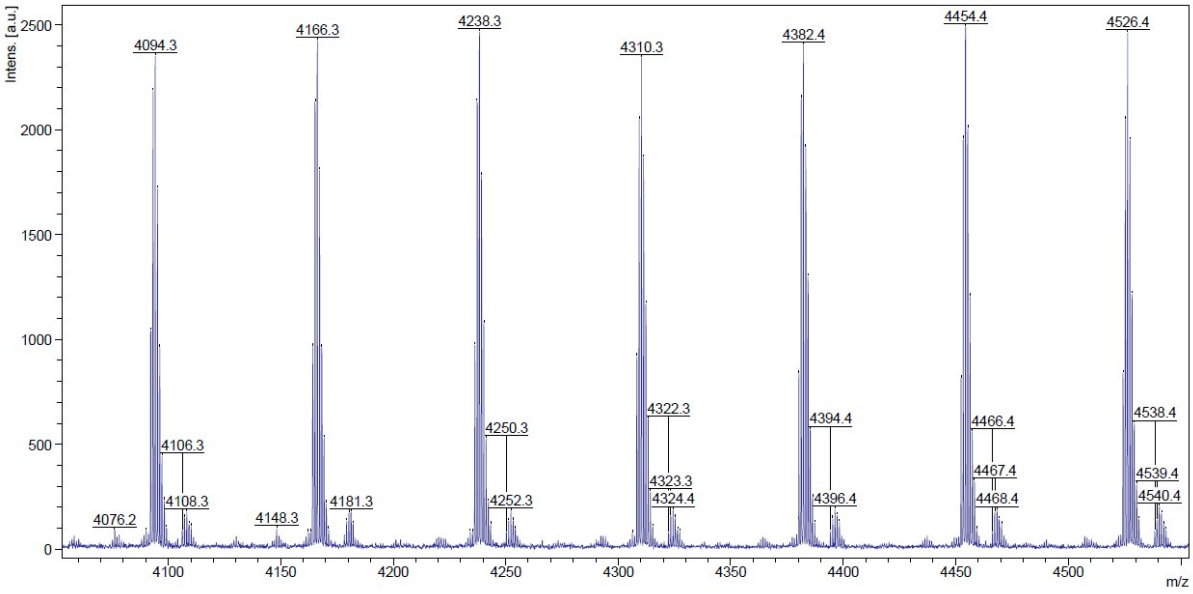


Figure S5 MALDI of PLA from ROP of l-lactide, catalyst **2** and BnOH with a ratio of 300:1:5. Theoretical $[M + Na]^+$ (for $C_7H_7O(C_6H_8O_4)_{30}H$)

Crystallography

X-ray diffration data for **2** and **3** were collected on an Excalibur Eos diffractometer at 170(2) K using Mo *K*α radiation. The structure of **2** and **3** were solved and least-squares refined using SHELX14 in Olex2 and SHELX97 in WinGX, respectively.[3-5] The latter was refined as an inversion twin. Two disordered *n*-hexane molecules per unit cell of **2**, which could not be satisfactory modelled, were masked using SQUEEZE.[6, 7] Similarly, in case of **3** two disorded molecules of THF had to be processed with SQUEEZE.

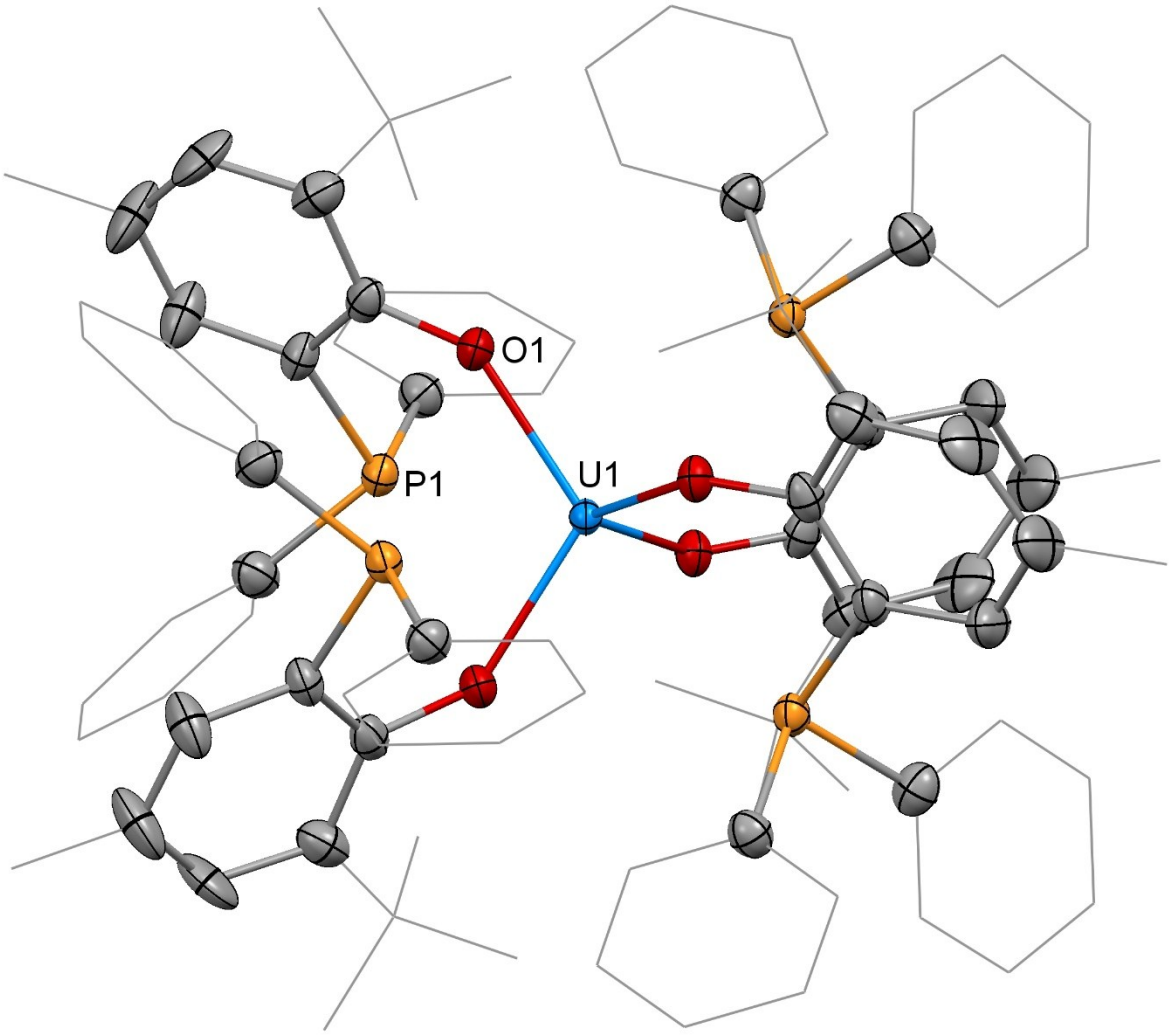


Figure S6. Molecular structure of **3**. Hydrogen atoms are omitted, and peripheral carbon atom are depicted as wireframe, for clarity. Thermal ellipsoids drawn at 50 % probability. Selected bond distances (Å) and angles (°): U1-O1: 2.193, U1-P1: 3.276, U1-P2: 3.275, O1-U1-O1': 98.6, O1-U1-O1": 116.4, O1-U1-P1: 60.03.

Table S3. Crystallographic data of **2** and **3** calculated without taking masked solvent molecules into account.

	2	**3**
Empirical formula	$C_{72}H_{81}CeO_4P_3Si$ $2(C_6H_{14})$	$C_{92}H_{96}O_4P_4U$ $2(C_4H_8O)$
Formula weight	1271.48	1627.59
Temperature/K	170(2)	170.15
Crystal system	triclinic	tetragonal
Space group	P-1	P-4n2
a/Å	11.9128(3)	14.0127(3)
b/Å	12.8140(4)	14.0127(3)
c/Å	25.3401(6)	21.3415(4)
α/°	102.706(2)	90
β/°	102.3247(19)	90
γ/°	93.444(2)	90
Volume/Å^3	3663.17(16)	4190.5(2)
Z	2	2
ρ_{calc}g/cm^3	1.153	1.290
μ/mm^{-1}	0.745	2.061
F(000)	1324.0	1664.0
Crystal size/mm^3	0.2134 × 0.0822 × 0.0493	1.0328 × 0.7638 × 0.455
2Θ range for data collection/°	5.836 to 52.744	6.422 to 54.964
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -31 ≤ l ≤ 31	-18 ≤ h ≤ 18, -18 ≤ k ≤ 17, -27 ≤ l ≤ 27
Reflections collected	59812	38298
Independent reflections	14943 [R_{int} = 0.0537, R_{sigma} = 0.0576]	4807 [R_{int} = 0.0494, R_{sigma} = 0.0269]
Data/restraints/parameters	14943/0/745	4807/0/228
Goodness-of-fit on F^2	1.018	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0382, wR_2 = 0.0749	R_1 = 0.0235, wR_2 = 0.0495
Final R indexes [all data]	R_1 = 0.0543, wR_2 = 0.0797	R_1 = 0.0357, wR_2 = 0.0544
Largest diff. peak/hole / e Å^{-3}	0.57/-0.45	0.65/-0.57
Flack parameter	-	0.149(7)

Table S4. SambVca 2 – generated topographic steric volumes calculated for the set of U^{IV} complexes $IU(OAr^P)_3$ **A** and $IU(OAr^P)_3Ni$ (the iodide analogue of **4**), and $Me_3SiOU(OAr^P)_3$ (a model made by replacement of Ce^{IV} by U^{IV} in the x-ray structure of **2**).

	$\%V_{Free}$	$\%V_{Bur}$
$Me_3SiOU(OAr^P)_3$	25.3	74.7
$IU(OAr^P)_3$ **A**	22.9	77.1
$IU(OAr^P)_3Ni$	24.7	75.3

NMR spectra of complexes

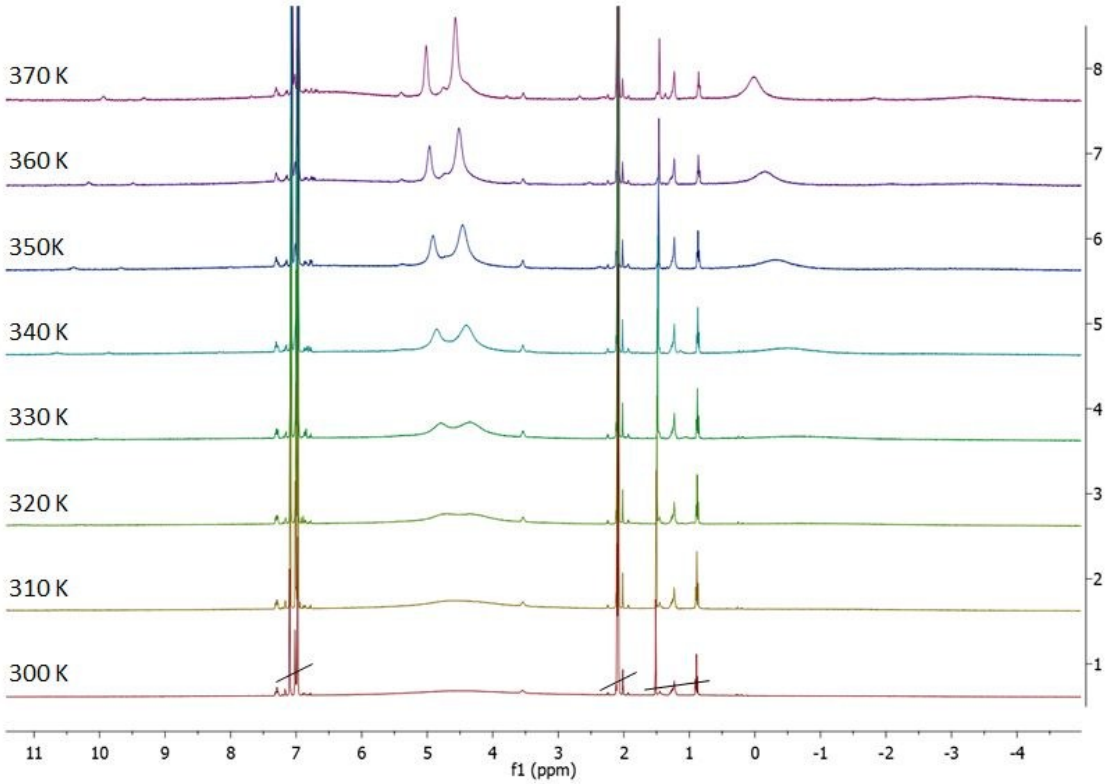


Figure S7. Stacked variable temperature ^{1}H NMR spectra of **1** in toluene-*d8* from -5 to 11 ppm over a temperature range of 300 to 370 K. Resonances corresponding to *protio*-toluene and impurities are scored through in the 300 K spectrum.

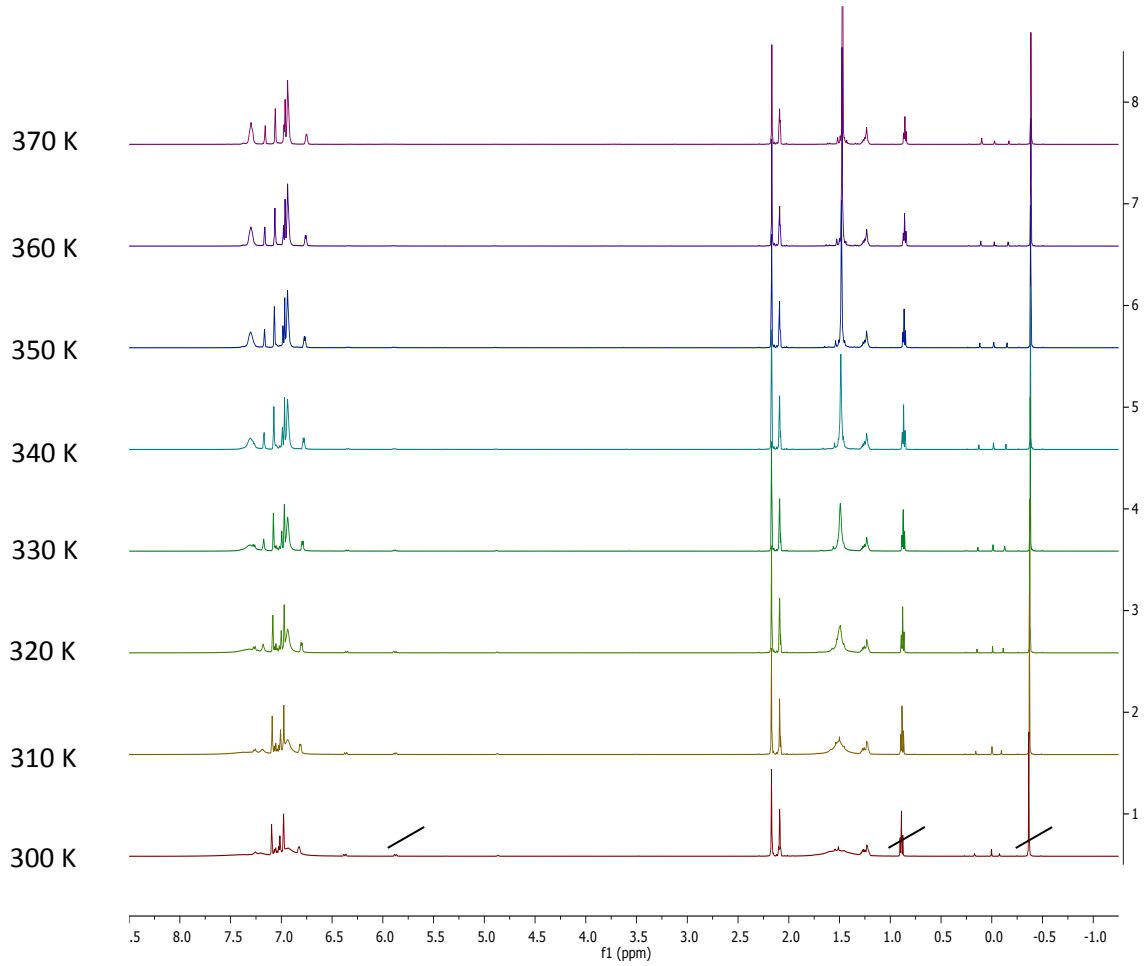


Figure S8. Stacked variable temperature ^{1}H NMR spectra of **2** in toluene-d_8 from 8.5 to -1.25ppm over a temperature range 300 to 370 K. Resonances corresponding to *protio*-toluene and impurities are scored through in the 300 K spectrum.

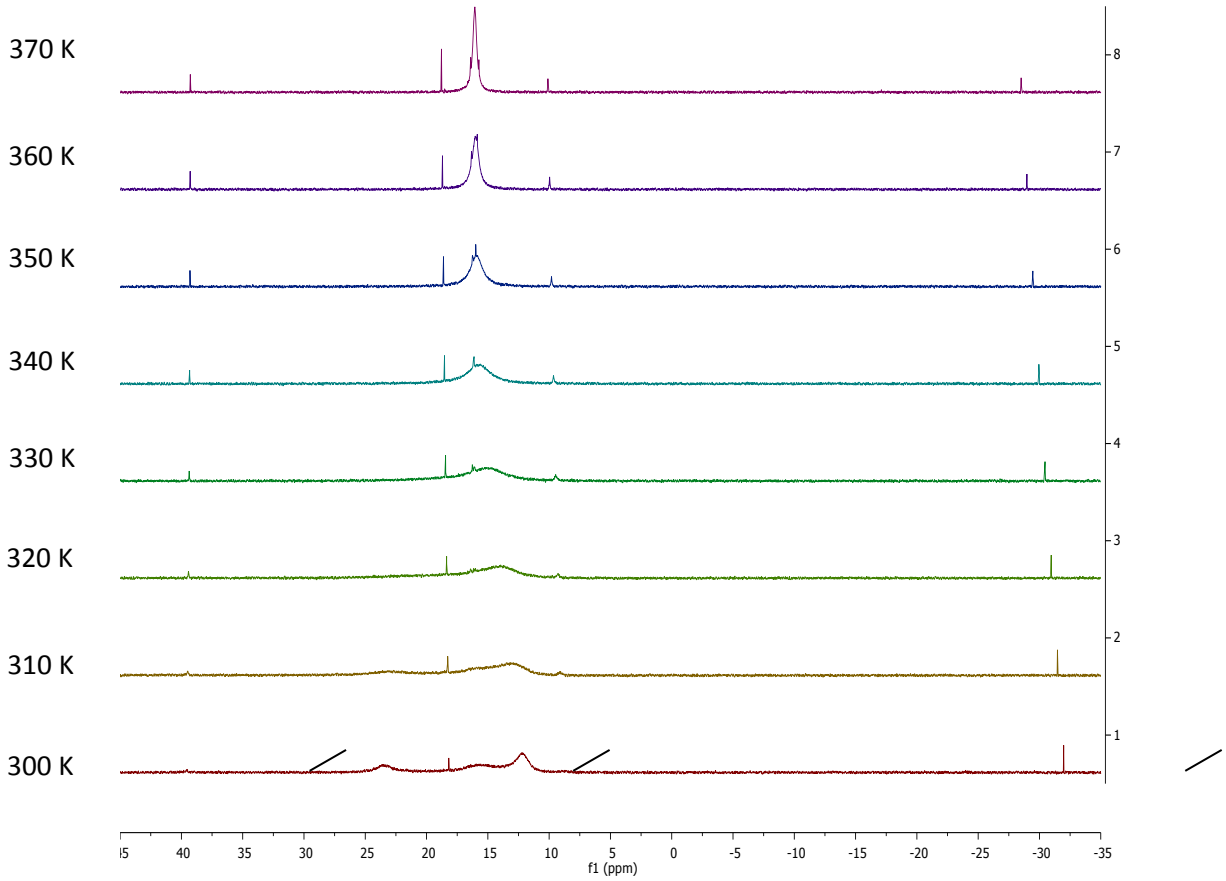


Figure S9. Stacked variable temperature $^{31}P\{^{1}H\}$ NMR spectra of **2** in toluene-d_8 from 45 to -35ppm over a temperature range 300 to 370 K. Resonances corresponding to impurities are scored through in the 300K spectrum. These have chemical shifts of +40, +17, +10 and -32 ppm. The resonance at +40 ppm is due to oxidised ligand $HOAr^{P=O}$ (OC_6H_2-6-^{t}Bu-4-Me-2-PPh_2); that at -32 ppm is $KOAr^{P}$.

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