Supporting Information for:

Yttrium phosphasalen initiators for *rac*-lactide polymerization: Excellent rates and high *iso*-selectivities

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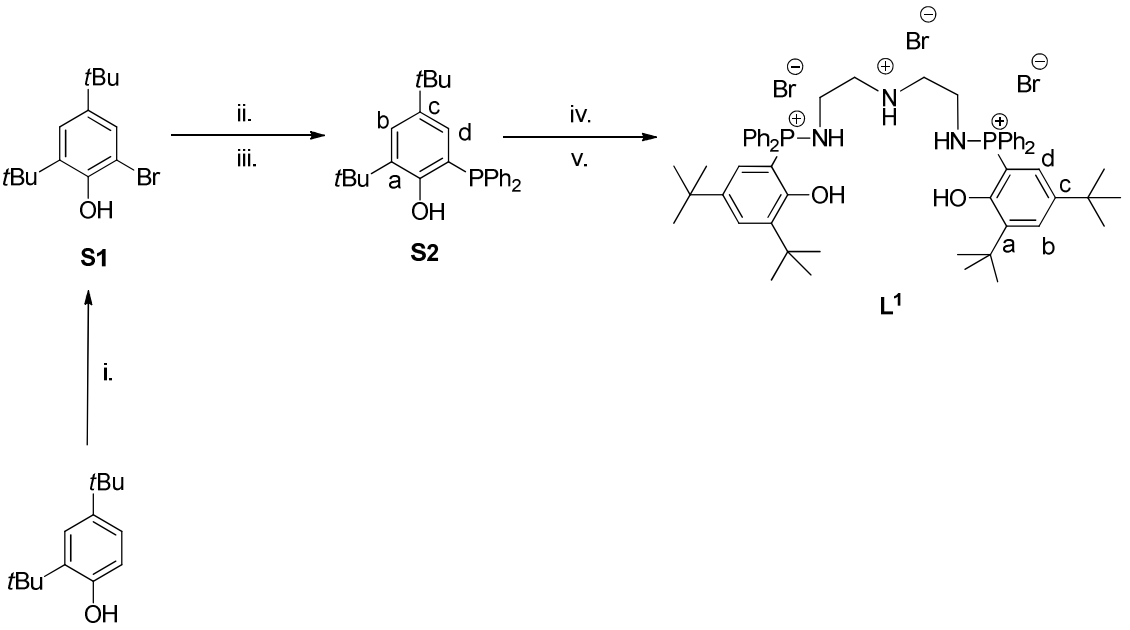
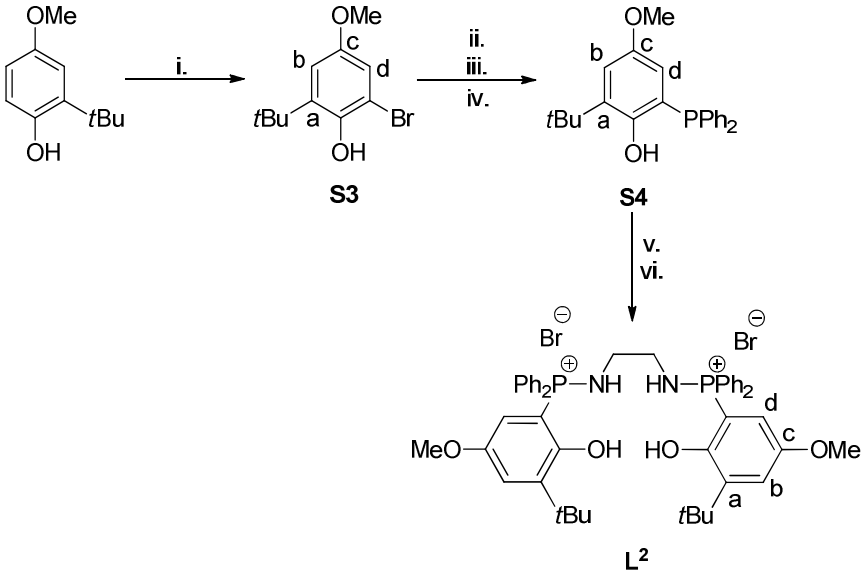


Scheme S1: i. NBS, acetonitrile ii. n-BuLi (2 equiv.), petroleum ether iii. $ClPPh_3$ iv. Br_2 (1 equiv.), CH_2Cl_2 v. diethylene triamine (0.5 equiv.), Bu_3N (1 equiv.), 78 %.



Scheme S2: i. Br_2 (1 equiv.), DCM, 71 % ii. BuLi, Et_2O, iii. $ClPPh_2$ iv. H_2O, 84 % v. Br_2, DCM vi. Ethylenediamine (0.5 equiv.), Bu_3N (1 equiv.), 69 %.

Experimental Section

Materials and Methods

All reactions were conducted under an atmosphere of dry nitrogen, or argon, using standard Schlenk line and glovebox techniques. Solvents and reagents were obtained from commercial sources. Tetrahydrofuran, toluene, pentane, hexane and petroleum ether were distilled from sodium/benzophenone, under dry nitrogen. Tetrahydrofuran and petroleum ether, used for the ligand and complex syntheses, were taken directly from a MBraun MB-SPS 800 Solvent Purification system. Dichloromethane was distilled from CaH_2, under dry nitrogen. *Rac*-lactide was recrystallised from anhydrous toluene and sublimed three times prior to use. $[YCl_3(THF)_{3.5}]$ was prepared following literature procedure.[1] Compound **4** was prepared as has been previously described in the literature.[2]

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Av300 instrument. Solvent peaks were used as internal references for ^1H and ^{13}C chemical shifts (ppm). ^{31}P peaks were referenced to external 85% H_3PO_4. When needed, higher resolution $^{31}P\{^1H\}$ NMR and $^1H\{^1H\}$ NMR (homo-decoupled spectroscopy) experiments were performed on a Bruker Av500 spectrometer, equipped with a z-gradient bbo/5 mm tuneable probe and a BSMS GAB 10 A gradient amplifier providing a maximum gradient output of 5.35 G/cmA. ^1H NMR spectra for all lactide polymerizations were performed on a Bruker Av500 instrument. The following abbreviations are used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiple; v, virtual.

Elemental analyses were determined by Mr. Stephen Boyer at London Metropolitan University. Electronic ionization mass spectra were recorded with a JEOL GCmate instrument. PLA number averaged molecular weight, M_n, and polydispersity index (M_w/M_n; PDI) were determined using gel permeation chromatography, equipped with multi-angle laser light scattering (GPC-MALLS). Two Polymer laboratories Mixed D columns were used in series, with THF as the eluent, at a flow rate of 1 mL min^{-1}, on a Polymer laboratories PL GPC-50 instrument at 35 °C. The light scattering detector was a triple-angle detector (Dawn 8, Wyatt Technology), and the data were analyzed using Astra V version 5.3.4.18. The refractive angle increment for polylactide (*dn/dc*) in THF was 0.042 mL g^{-1}.[3]

Compound S1[4]

At 0 °C, N-bromosuccinimide (18.2 g, 102 mmol) was added into a solution of 2,4-di-tert-butylphenol (20.1 g, 97.4 mmol) in acetonitrile (300 mL). Stirring was continued at room temperature overnight, giving an orange solution. A saturated aqueous solution of sodium bisulfide (10 mL) was added and induced the precipitation of a white solid. After filtration of this precipitate, the mixture was extracted four times with petroleum ether (4 x 70 mL). The total organic layer was dried over Na_2SO_4. The solvent was evaporated, giving the product as a slightly yellow solid (24.9 g, 90 %).

CAS# 20834-61-1.[4] H NMR (300 MHz, $CDCl_3$, δ (ppm)): 7.33 (d, $^4J_{H,H}$ = 2.5 Hz, 1H, tBu-C^{IV}-C*H*-C^{IV}-tBu), 7.25 (d, $^4J_{H,H}$ = 2.5 Hz, 1H, tBu-C^{IV}-C*H*-CBr), 5.65 (s, 1H, O*H*), 1.41 (s, 9H, $C^{IV}(CH_3)_3$), 1.29 (s, 9H, $C^{IV}(CH_3)_3$).

Compound S2[5]

n-Butyl lithium (1.6 M in hexanes, 107 mL, 173 mmol) was added into a solution of **S1** (23.0 g, 80.6 mmol) in Et_2O (170 mL) at -78 °C, giving immediately a white suspension. The cold bath was removed and stirring was continued at room temperature for 30 mins, giving a pale yellow solution. Chlorodiphenylphosphine (14.5 mL, 80.6 mmol) was added into this solution at -78 °C. After stirring for 20 h, a white suspension was formed. The mixture was extracted with aqueous solutions of NaH_2PO_4 (0.1 M, 2 x 100 mL) and the organic layer was filtered to removed inorganic salts. Methanol (30 mL) was added and the solution reduced *in vacuo* until the volume of the remaining solvent was about 30 mL. A white solid precipitated from the green solution. This solid was separated by filtration, washed with MeOH (2 x 5 mL) and dried under vacuum (28 g, 90 %).

CAS# 185509-32-4.[5] ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 7.26-7.25 (m, 11H, C*H*(PPh_2) + C_bH), 6.81 (dd, $^4J_{H,H}$ = 1.5 Hz, $^3J_{P,H}$ = 5.5 Hz, 1H, C_dH), 6.60 (d, $^4J_{P,H}$ = 10.0 Hz, 1H, O*H*), 1.34 (s, 9H, C_a-C(CH_3)$_3$), 1.08 (s, 9H, C_c-C(CH_3)$_3$); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, δ (ppm)): -30.8 (s, *P*); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ (ppm)): 156.3 (d, $^2J_{P,C}$ = 19.2 Hz, OC^{IV}), 142.5 (d, $^3J_{P,C}$ = 3.0 Hz, C_c^{IV}), 135.6 (d, $^1J_{P,C}$ = 3.0 Hz, $C^{IV}(PPh_2)$), 135.5 (d, $^3J_{P,C}$ = 1.0 Hz, C_a^{IV}), 133.6 (d, $^{2/3}J_{P,C}$ = 18.5 Hz, *o*- or *m*-*C*H(PPh_2)), 129.5 (d, $^2J_{P,C}$ = 3.5 Hz, C_dH), 129.1 (s, *p*-*C*H(PPh_2)), 128.8 (d, $^{2/3}J_{P,C}$ = 7.5 Hz, *o*-or

m-*C*H(PPh$_2$)), 126.6 (s, *C*$_b$H), 120.1 (s, *C*^{IV}-PPh$_2$), 35.4 (d, $^4J_{P,C}$ = 2.0 Hz, C$_c$-*C*(CH$_3$)$_3$), 34.7 (s, C$_a$-*C*(CH$_3$)$_3$), 31.7 (s, C$_c$-C(*C*H$_3$)$_3$), 29.2 (s, C$_a$-C(*C*H$_3$)$_3$).

Compound S3[6]

At 0 °C, bromine (2.0 mL, 38.8 mmol) was added into a solution of 2-*tert*-butyl-4-methoxyphenol (7.00 g, 38.8 mmol) in methylene chloride (200 mL), leading to the immediate liberation of HBr (g) and the formation of a pale yellow solution. Stirring was continued at room temperature for 48 h. Dichloromethane and HBr were evaporated, the residue was taken into diethyl ether (200 mL), washed with an aqueous solution of Na_2CO_3 (1 M, 200 mL) and dried (Na_2SO_4). The solvent was removed in vacuo and the crude material was purified by chromatography (Et_2O/petroleum ether = 2.5/97.5) to yield the product (7.15 g, 71 %).

CAS# 21099-08-1.[6] NMR (300 MHz, $CDCl_3$, δ (ppm)): 6.88 (d, $^4J_{H,H}$ = 3.0 Hz, 1H, C*H*), 6.84 (d, $^4J_{H,H}$ = 3.0 Hz, 1H, C*H*), 5.42 (s, 1H, O*H*), 3.74 (s, 3H, O-C*H*$_3$), 1.38 (s, 9H, C^{IV}(C*H*$_3$)$_3$).

Compound S4

n-Buytllithium (1.6 M in hexanes, 34.5 mL, 55.2 mmol) was added into a solution of **S3** (7.15 g, 27.6 mmol) in diethyl ether (70 mL) at -78 °C. After the addition, the cold bath was removed, a yellowish solution was obtained, stirring was continued at room temperature for 2 h. Chlorodiphenylphosphine (4.95 mL, 27.6 mmol) was added forming a white suspension. After stirring for 20 h at room temperature, the solid was isolated by filtration under inert atmosphere and was then suspended in diethyl ether (80 mL). An aqueous solution of fluoroboric acid (1 M, 40 mL) was added, giving a biphasic system with the total disappearance of the solid. The organic phase was washed with water (40 mL), dried ($MgSO_4$). The solvent was isolated, giving the product as a yellow viscous oil (8.4 g, 84 %).

^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 7.36 (m, 10H, C*H*(PPh$_2$)), 6.94 (d, $^4J_{H,H}$ = 3.0 Hz, 1H, C$_b$*H*), 6.49 (d, $^2J_{P,H}$ =10.0 Hz, 1H, O*H*), 6.35 (dd, $^3J_{P,H}$ = 5.0 Hz, $^4J_{H,H}$= 3.0 Hz, 1H, C$_d$*H*), 3.58 (s, 3H, O-C*H*$_3$), 1.41 (s, 9H, C^{IV}(C*H*$_3$)$_3$); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, δ (ppm)): -28.3 (s, *P*^{III}); ^{13}C{^{1}H}

NMR (75 MHz, $CDCl_3$, δ (ppm)): 152.9 (d, $^2J_{P,C}$= 3.0 Hz, C^{IV}-OH), 152.6 (d, $^3J_{P,C}$= 19.0 Hz, C^{IV}-OMe), 137.9 (d, $J_{P,C}$= 1.5 Hz, C^{IV}), 135.0 (d, $J_{P,C}$= 1.5 Hz, C^{IV}), 133.5 (d, $^{2/3}J_{P,C}$= 19.0 Hz, *m*-or *o*-*C*H(PPh_2)), 129.1 (s, *p*-*C*H(PPh_2)), 128.8 (d, $^{2/3}J_{P,C}$= 7.5 Hz, *m*-or *o*-*C*H(PPh_2)), 121.3 (d, $J_{P,C}$= 1.0 Hz, C^{IV}), 116.7 (s, C_bH), 115.2 (d, $^2J_{P,C}$= 3.0 Hz, C_dH), 55.5 (s, O-CH_3), 35.2 (s, $C_{c,a}{}^{IV}$-$C^{IV}(CH_3)_3$), 29.6 (s, $C_{c,a}{}^{IV}$-$C^{IV}(CH_3)_3$). HRMS (EI+) ($C_{23}H_{25}O_2P$): calculated m/z: 364.1592, found: 364.1603

Compound L[1]

At -78 °C, bromine (200 µL, 3.88 mmol) was added dropwise to a solution of the phenolphosphine (1.52 g, 3.88 mmol) in dichloromethane (45 mL). The cold bath was removed and stirring was continued for 2 h at room temperature. Then the solution was cooled to -78 °C. Tributylamine (463 µL, 1.94 mmol) was added, followed by diethylenetriamine (210 µL, 1.94 mmol). The cold bath was removed, and after 16 h a white slurry had formed. The dicholoromethane was evaporated and the residue was washed with THF (5 x 10 mL) to remove the tributylammonium salt. The product was isolated as a white solid and dried *in vacuo* (1.8 g, 78 %).

^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 7.74 (m, 2H, C*H*(PPh_2)), 7.65 (m, 20H, C*H*(PPh_2) + C_bH), 6.72 (m, b, 2H, O*H* or N*H*), 6.56 (dd, $^3J_{H,H}$= 2.0 Hz, $^3J_{P,H}$= 16.0 Hz, 2H, C_dH), 3.70 (s, b, 4H, CH_2-NH_2-CH_2), 3.52 (s, b, 4H, P^V-NH-CH_2), 2.02 (s, b, 4H, O*H* or N*H*), 1.47 (s, 18H, $C_{c,a}{}^{IV}$- $C^{IV}(CH_3)_3$), 1.10 (s, 18H, $C_{c,a}{}^{IV}$- $C^{IV}(CH_3)_3$); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, δ (ppm)): 41.8 (s, P^V); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ (ppm)): 155.7 (d, $^2J_{P,C}$= 1.0 Hz, C^{IV}-OH), 145.5 (d, $^3J_{P,C}$= 14.0 Hz, $C_{c/a}{}^{IV}$), 141.9 (d, $^3J_{P,C}$= 7.0 Hz, $C_{c/a}{}^{IV}$), 134.7 (d, $^4J_{P,C}$= 3.0 Hz, *p*-*C*H(PPh_2)), 133.5 (d, $^{2/3}J_{P,C}$= 11.5 Hz, *m*-or *o*-*C*H(PPh_2)), 132.3 (d, $^4J_{P,C}$= 1.5 Hz, C_bH), 130.0 (d, $^{2/3}J_{P,C}$= 13.0 Hz, *m*-or *o*-*C*H(PPh_2)), 128.6 (d, $^2J_{P,C}$=12.5 Hz, C_dH), 121.7 (d, $^1J_{P,C}$=105.0 Hz, C^{IV}(PPh_2)), 114.5 (d, $^1J_{P,C}$=98.0 Hz, C^{IV}-PPh_2), 113.1 (d, $^1J_{P,C}$=107.2 Hz, C^{IV}-PPh_2), 49.0 (d, $^2J_{P,C}$= 9.0 Hz, P^V-N-CH_2), 40.0 (s, P^V-N-CH_2-CH_2), 35.1 (d, $^4J_{P,C}$= 2.0 Hz, $C_{c,a}{}^{IV}$-$C^{IV}(CH_3)_3$), 34.7 (d, $^4J_{P,C}$= 1.0 Hz, $C_{c,a}{}^{IV}$-$C^{IV}(CH_3)_3$), 31.2 (s, $C_{c,a}{}^{IV}$-$C^{IV}(CH_3)_3$), 30.6 (s, N-CH_2-$C^{IV}(CH_3)_2$). Anal. Calcd for $C_{56}H_{74}Br_3N_3O_2P_2$: C, 59.90; H, 6.64; N, 3.74. Found: C, 59.78; H, 7.66.536; N, 3.74.

Compound L^2 At -78 °C, bromine (300 µL, 5.83 mmol) was added dropwise to a solution of the phenolphosphine **S4** (2.02 g, 5.83 mmol) in dichloromethane (100 mL). The cold bath was removed and stirring was continued for 2 h at room temperature. Then the solution was cooled down to -78 °C. Tributylamine (1.39 mL, 5.83 mmol) was added, followed by ethylenediamine (195 µL, 2.91 mmol). After 16 h, a cloudy solution was formed. The dichloromethane was evaporated and the residue was washed with THF (5 x 10 mL) to remove tributylammonium salt. The product was isolated as a white solid and dried under vacuum (1.9 g, 69 %).

^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 7.66 (t, $^3J_{H,H}$ =8.0 Hz, 4H, *p*-C*H*(PPh_2)), 7.63 (dd, $^3J_{P,H}$ =12.5 Hz, $^3J_{H,H}$ =8.0 Hz, 8H, *o*-C*H*(PPh_2)), 7.53 (vtd, $^4J_{P,H}$ =3.5 Hz, $^3J_{H,H}$ =$^3J'_{H,H}$ =8.0 Hz, 8H, *m*-C*H*(PPh_2)), 7.17 (d, $^4J_{H,H}$= 2.5 Hz, 2H, C_bH), 5.95 (dd, $^3J_{P,H}$ =16.5 Hz, $^4J_{H,H}$ =2.5 Hz, 2H, C_dH), 3.66 (dd, $^3J_{P,H}$ = 6.5 Hz, $^4J_{P,H}$ = 2.0 Hz, 4H, N-CH_2-CH_2-N), 3.50 (s, 6H, -OCH_3), 1.50 (s, 18H, $C^{IV}(CH_3)_3$); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, δ (ppm)): 40.1 (s, P^V); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ (ppm)): 154.4 (C^{IV}-O or $C_{c,a}{}^{IV}$), 151.8 (weak, C^{IV}-O or $C_{c,a}{}^{IV}$), 145.7 (C^{IV}-O or $C_{c,a}{}^{IV}$), 134.3 (s, *p*-*C*H(PPh_2)), 133.6 (d, $^2J_{P,C}$= 9.0 Hz, *o*-*C*H(PPh_2)), 129.7 (d, $^3J_{P,C}$= 13.5 Hz, *m*-*C*H(PPh_2)), 122.1 (d, $^1J_{P,C}$=105 Hz, $C^{IV}(PPh_2)$), 121.2 (s, C_bH), 116.0 (d, $^1J_{P,C}$=120 Hz, C^{IV}-PPh_2), 115.0 (d, $^2J_{P,C}$= 13.5 Hz, C_dH), 55.6 (s, O-*C*H_3), 44.2 (dd, $^2J_{P,C}$ = 7.5 Hz, $^3J_{P,C}$ = 1.0 Hz, N-*C*H_2-*C*H_2-N), 35.4 (s, $C_a{}^{IV}$-$C^{IV}(CH_3)_3$), 30.3 (s, b, $C_a{}^{IV}$-$C^{IV}(CH_3)_3$). Anal. Calcd for $C_{48}H_{56}Br_2N_2O_4P_2$: C, 60.90; H, 5.96; N, 2.96. Found: C, 60.71; H, 6.02; N, 3.02.

Compound 1

Potassium *bis*(trimethylsilyl)amide (300 mg, 1.5 mmol) was added into a slurry of ligand L^1 (350 mg, 0.3 mmol) in THF (20 mL). After 4 h, a cloudy solution was yielded and the insoluble potassium salt was removed by centrifugation. [$YCl_3(THF)_{3.5}$] (134 mg, 0.3 mmol) was added and stirred for 4 h at 298 K, the $^{31}P\{^1H\}$ NMR spectrum showed the clean formation of a complex with one singlet at 35.0 ppm. Potassium *tert*-butoxide (34 mg, 0.3 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents

was evaporated *in vacuo* and the residue was crystallised in cyclohexane (5 mL), giving the product as colorless crystals (260 mg, 0.24 mmol, 83 %).

^{1}H NMR (300 MHz, THF-d_8; δ (ppm)): 7.60 (ddd, $^{4}J_{H,H}$=1.5 Hz, $^{3}J_{H,H}$=7.0 Hz, $^{3}J_{P,H}$=11.5 Hz, 4H, *o*-C*H*(PPh$_2$)), 7.57 (ddd, $^{4}J_{H,H}$=1.5 Hz, $^{3}J_{H,H}$=7.0 Hz, $^{3}J_{P,H}$=11.5 Hz, 4H, *o*-C*H*(PPh$_2$)), 7.50 (tvq, $^{4}J_{H,H}$=1.5 Hz, $^{3}J_{H,H}$= 7.0 Hz, $^{5}J_{P,H}$=1.5 Hz, 2H, *p*-C*H*(PPh$_2$)), 7.42 (vtd, $^{4}J_{P,H}$=2.5 Hz, $^{3}J_{H,H}$= $^{3}J'_{H,H}$ = 7.0 Hz, 4H, *m*-C*H*(PPh$_2$)), 7.40 (tvq, $^{4}J_{H,H}$=1.5 Hz, $^{3}J_{H,H}$= 7.0 Hz, $^{5}J_{P,H}$=1.5 Hz, 2H, *p*-C*H*(PPh$_2$)), 7.24 (vtd, $^{4}J_{P,H}$=2.5 Hz, $^{3}J_{H,H}$= $^{3}J'_{H,H}$ = 7.0 Hz, 4H, *m*-C*H*(PPh$_2$)), 7.21 (d, $^{4}J_{H,H}$= 2.0 Hz, 2H, C$_b$*H*), 6.59 (dd, $^{4}J_{H,H}$=2.0 Hz, $^{3}J_{P,H}$ = 15.5 Hz, 2H, C$_d$*H*), 3.24 (m, 4H, P=N-C*H*$_2$), 2.93 (m, 2H, P=N-CH$_2$-C*H*$_2$), 2.58 (m, 2H, P=N-CH$_2$-C*H*$_2$), 1.15 (s, 18H, $C_{c,a}^{IV}$- C^{IV}(C*H*$_3$)$_3$), 1.10 0.80 (s, 9H, O-C^{IV}(C*H*$_3$)$_3$), 1.09 (s, 18H, $C_{c,a}^{IV}$- C^{IV}(C*H*$_3$)$_3$); ^{31}P{^{1}H} NMR (202.5 MHz, THF-d_8; δ (ppm)): 33.6 (d, $^{2}J_{P\text{-}Y}$=1.62 Hz); ^{13}C{^{1}H} NMR (75 MHz, THF-d_8; δ (ppm)): 169.1 (d, $^{3}J_{P,C}$= 3.0 Hz, *C*^{IV}-O), 169.0 (d, $^{3}J_{P,C}$= 3.0 Hz, *C*^{IV}-O), 139.9 (d, $^{3}J_{P,C}$=8.0 Hz, $C_{c,a}^{IV}$), 133.8 (d, $^{2/3}J_{P,C}$= 9.5 Hz, *m*-or *o*-*C*H(PPh$_2$)), 133.7 (d, $^{2/3}J_{P,C}$= 9.5 Hz, *m*-or *o*-*C*H(PPh$_2$)), 133.6 (d, $^{3}J_{P,C}$=8.0 Hz, $C_{c,a}^{IV}$), 133.3 (d, $^{1}J_{P,C}$=87.5 Hz, *C*^{IV}(PPh$_2$)), 132.1 (d, $^{1}J_{P,C}$=90.0 Hz, *C*^{IV}(PPh$_2$)), 131.8 (d, $^{4}J_{P,C}$= 2.5 Hz, *p*-*C*H(PPh$_2$)), 131.6 ($^{4}J_{P,C}$= 2.5 Hz, *p*-*C*H(PPh$_2$)), 128.9 (d, $^{2/3}J_{P,C}$= 11.0 Hz, *m*-or *o*-*C*H(PPh$_2$)), 128.8 (d, $^{2/3}J_{P,C}$= 11.0 Hz, *m*-or *o*-*C*H(PPh$_2$)), 128.2 (d, $^{4}J_{P,C}$= 2.5 Hz, *C*$_b$H), 127.5 (d, $^{2}J_{P,C}$=12.5 Hz, *C*$_d$H), 111.8 (d, $^{1}J_{P,C}$=118.0 Hz, *C*^{IV}-PPh$_2$), 69.7 (s, O-*C*^{IV}(CH$_3$)$_3$), 54.0 (d, $^{2}J_{P,C}$=16.0 Hz, P^{IV}-N-*C*H$_2$), 48.6 (d, $^{3}J_{P,C}$=5.0 Hz, P^{IV}-N-CH$_2$-*C*H$_2$), 35.8 (s, $C_{c,a}^{IV}$-*C*^{IV}(CH$_3$)$_3$), 35.2 (s, O-C^{IV}(*C*H$_3$)), 34.3 (s, $C_{c,a}^{IV}$-*C*^{IV}(CH$_3$)$_3$), 31.8 (s, $C_{c,a}^{IV}$-C^{IV}(*C*H$_3$)$_3$), 30.2 (s, $C_{c,a}^{IV}$-C^{IV}(*C*H$_3$)$_3$). Anal. Calcd for $C_{60}H_{78}N_3O_3P_2Y$: C, 69.28; H, 7.56; N, 4.04. Found: C, 69.16; H, 7.64; N, 3.95

Compound 2

Potassium *bis*(trimethylsilyl)amide (300 mg, 1.5 mmol) was added into a slurry of ligand **L^1** (350 mg, 0.3 mmol) in THF (20 mL). After 4 h, a cloudy solution was yielded and the insoluble potassium salt was removed by centrifugation. [YCl$_3$(THF)$_{3.5}$] (134 mg, 0.3 mmol) was added and stirred at 298 K for 4 h, by which time the ^{31}P{^{1}H} NMR spectrum showed the clean formation of a complex with one singlet at 35.0 ppm. Potassium ethoxide (25.2 mg, 0.3 mmol) was added into the mixture, giving a

cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents were evaporated in *vacuo* and the residue was crystallised in cyclohexane (5 mL), giving the product as colourless crystals (265 mg, 0.26 mmol, 87 %).

^{1}H NMR (300 MHz, THF-d_8; δ (ppm)): 7.61 (ddd, $^{4}J_{H,H}$=1.5 Hz, $^{3}J_{H,H}$=8.0 Hz, $^{3}J_{P,H}$=9.0 Hz, 4H, *o*-C*H*(PPh$_2$)), 7.55 (ddd, $^{4}J_{H,H}$=1.5 Hz, $^{3}J_{H,H}$=8.0 Hz, $^{3}J_{P,H}$=9.0 Hz, 4H, *o*-C*H*(PPh$_2$)), 7.49 (tt, $^{4}J_{H,H}$=1.5 Hz, $^{3}J_{H,H}$= 8.0 Hz, 2H, *p*-C*H*(PPh$_2$)), 7.39 (vtd, $^{4}J_{P,H}$=2.5 Hz, $^{3}J_{H,H}$= $^{3}J'_{H,H}$ = 8.0 Hz, 4H, *m*-C*H*(PPh$_2$)), 7.37 (tt, $^{4}J_{H,H}$=1.5 Hz, $^{3}J_{H,H}$= 8.0 Hz, 2H, *p*-C*H*(PPh$_2$)), 7.22 (vtd, $^{4}J_{P,H}$=2.5 Hz, $^{3}J_{H,H}$= $^{3}J'_{H,H}$ = 8.0 Hz, 4H, *m*-C*H*(PPh$_2$)), 7.21 (d, $^{4}J_{H,H}$= 2.0 Hz, 2H, C$_b$*H*), 6.65 (dd, $^{4}J_{H,H}$=2.0 Hz, $^{3}J_{P,H}$ = 15.5 Hz, 2H, C$_d$*H*), 3.96 (m, 1H, O-C*H*$_2$-CH$_3$), 3.32 (m, 1H, O-C*H*$_2$-CH$_3$), 3.27 (m, 4H, P=N-C*H*$_2$), 2.83 (m, 2H, P=N-CH$_2$-C*H*$_2$), 2.58 (m, 2H, P=N-CH$_2$-C*H*$_2$), 1.12 (s, 36H, $C_{c,a}^{IV}$- C^{IV}(C*H*$_3$)$_3$), 0.90 (m, 3H, O-CH$_2$-C*H*$_3$); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d_8; δ (ppm)): δ 34.2 (s); ^{13}C{^{1}H} NMR (75 MHz, THF-d_8; δ (ppm)): 168.9 (d, $^{3}J_{P,C}$= 3.0 Hz, *C*^{IV}-O), 168.8 (d, $^{3}J_{P,C}$= 3.0 Hz, *C*^{IV}-O), 139.9 (d, $^{3}J_{P,C}$=7.5 Hz, $C_{c,a}^{IV}$), 133.7 (d, $^{2/3}J_{P,C}$= 8.0 Hz, *m*-or *o*-*C*H(PPh$_2$)), 133.6 (d, $^{2/3}J_{P,C}$= 8.0 Hz, *m*-or *o*-*C*H(PPh$_2$)), 133.5 (d, $^{3}J_{P,C}$=8.0 Hz, $C_{c,a}^{IV}$), 133.3 (d, $^{1}J_{P,C}$=83.0 Hz, *C*^{IV}(PPh$_2$)), 131.8 ($^{4}J_{P,C}$= 2.5 Hz, *p*-*C*H(PPh$_2$)), 131.6 (d, $^{1}J_{P,C}$=88.0 Hz, *C*^{IV}(PPh$_2$)), 131.6 (d, $^{4}J_{P,C}$= 2.5 Hz, *p*-*C*H(PPh$_2$)), 128.9 (d, $^{2/3}J_{P,C}$= 11.0 Hz, *m*-or *o*-*C*H(PPh$_2$)), 128.8 (d, $^{2/3}J_{P,C}$= 11.0 Hz, *m*-or *o*-*C*H(PPh$_2$)), 128.3 (d, $^{4}J_{P,C}$= 2.0 Hz, *C*$_b$H), 127.2 (d, $^{2}J_{P,C}$=12.5 Hz, *C*$_d$H), 113.0 (d, $^{1}J_{P,C}$=119.0 Hz, *C*^{IV}-PPh$_2$), 62.5 (s, O-*C*H$_2$-CH$_3$), 53.7 (d, $^{2}J_{P,C}$=16.0 Hz, P^{IV}-N-*C*H$_2$), 48.8 (d, $^{3}J_{P,C}$=5.0 Hz, P^{IV}-N-CH$_2$-*C*H$_2$), 35.7 (s, C$_{c,a}^{IV}$-*C*^{IV}(CH$_3$)$_3$), 34.3 (s, C$_{c,a}^{IV}$-*C*^{IV}(CH$_3$)$_3$), 31.9 (s, C$_{c,a}^{IV}$-C^{IV}(*C*H$_3$)$_3$), 29.9 (s, C$_{c,a}^{IV}$-C^{IV}(*C*H$_3$)$_3$), 23.3 (s, O-CH$_2$-*C*H$_3$). Anal. Calcd for C$_{58}$H$_{74}$N$_3$O$_3$P$_2$Y: C, 68.83; H, 7.37; N, 4.74. Found: C, 68.14; H, 7.54; N, 4.27.

Compound 3

Potassium *bis*(trimethylsilyl)amide (240 mg, 1.2 mmol) was added into a slurry of ligand **L^2** (295 mg, 0.3 mmol) in THF (20 mL). After 4 h, a cloudy solution was yielded and the insoluble potassium salt was removed by centrifugation. [YCl$_3$(THF)$_{3.5}$] (134 mg, 0.3 mmol) was added and stirred for 4 h at 298 K, the ^{31}P{^{1}H} NMR spectrum showed the clean formation of a complex with one singlet at 31.5 ppm. Potassium *tert*-butoxide (33.7 mg, 0.3 mmol) was added into the mixture, giving a cloudy

solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents was evaporated in vacuum and the residue was crystallised in cyclohexane (5 mL), giving the product as colorless crystals (250 mg, 0.26 mmol, 88 %).

^{1}H NMR (300 MHz, THF-d_8; δ (ppm)): 7.63 (dd, $^{3}J_{P,H}$ =11.5 Hz, $^{3}J_{H,H}$ =7.0 Hz, 4H, *o*-C*H*(PPh$_2$)), 7.54 (m, 2H, *p*-C*H*(PPh$_2$)), 7.48 (m, 5H, *p*-C*H*(PPh$_2$) + *m*-C*H*(PPh$_2$)), 7.40 (dd, $^{3}J_{P,H}$ =11.5 Hz, $^{3}J_{H,H}$ =7.0 Hz, 4H, *o*-C*H*(PPh$_2$)), 7.39 (vt, $^{3}J_{H,H}$ =$^{3}J'_{H,H}$ =7.0 Hz, 1H, *m*-C*H*(PPh$_2$)), 6.92 (d, $^{4}J_{H,H}$= 3.0 Hz, 2H, C$_b$*H*), 5.94 (dd, $^{3}J_{P,H}$ =15.5 Hz, $^{4}J_{H,H}$ =3.0 Hz, 2H, C$_d$*H*), 3.35 (s, 6H, -OC*H*$_3$), 3.31 (m,b, 2H, N-C*H*$_2$-C*H*$_2$-N), 3.18 (m,b, 2H, N-C*H*$_2$-C*H*$_2$-N), 1.39 (s, 18H, C$_a^{IV}$-C^{IV}(C*H*$_3$)$_3$), 0.84 (s, b, 9H, O-C^{IV}(C*H*$_3$)$_3$); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d_8; δ (ppm)): 31.6 (s); ^{13}C{^{1}H} NMR (75 MHz, THF-d_8; δ (ppm)): 166.8 (s, *C*^{IV}-O), 148.2 (d, $^{3}J_{P,C}$= 20.0 Hz, *C*$_c^{IV}$), 141.1 (d, $^{3}J_{P,C}$= 9.5 Hz, *C*$_a^{IV}$), 134.1 (d, $^{2}J_{P,C}$= 9.0 Hz, *o*-*C*H(PPh$_2$)), 133.6 (d, $^{2}J_{P,C}$= 9.0 Hz, *o*-*C*H(PPh$_2$)), 132.3 (d, $^{1}J_{P,C}$=88.0 Hz, *C*^{IV}(PPh$_2$)), 132.0 (d, $^{4}J_{P,C}$=1.5 Hz, *p*-*C*H(PPh$_2$)), 131.7 (d, $^{1}J_{P,C}$=90.0 Hz, *C*^{IV}(PPh$_2$)), 131.7 (d, $^{4}J_{P,C}$=1.5 Hz, *p*-*C*H(PPh$_2$)), 129.0 (d, $^{3}J_{P,C}$= 10.5 Hz, *m*-*C*H(PPh$_2$)), 128.9 (d, $^{3}J_{P,C}$= 10.5 Hz, *m*-*C*H(PPh$_2$)), 120.3 (d, $^{4}J_{P,C}$=1.0 Hz, *C*$_b$H), 114.2 (d, $^{2}J_{P,C}$= 14.5 Hz, *C*$_d$H), 111.6 (d, $^{1}J_{P,C}$=123.0 Hz, *C*^{IV}-PPh$_2$), 55.5 (s, O-*C*H$_3$), 52.1 (dd, $^{2/3}J_{P,C}$ = 6.5 Hz, $^{3/3}J_{P,C}$ = 18.0 Hz, N-*C*H$_2$-*C*H$_2$-N), 35.7 (s, C$_a^{IV}$-*C*^{IV}(CH$_3$)$_3$), 33.3 (s, O-C^{IV}(*C*H$_3$)$_3$), 30.2 (s, C$_a^{IV}$-C^{IV}(*C*H$_3$)$_3$), 26.0 (s, O-*C*^{IV}(CH$_3$)$_3$). Anal. Calcd for $C_{52}H_{61}N_2O_5P_2Y$: C, 66.10; H, 6.51; N, 2.96. Found: C, 65.89; H, 6.42; N, 2.85.

General Polymerization Procedure

In a glove box, a centrifuge tube was loaded with *rac*-lactide (288 mg, 2 mmol) and dissolved in THF (1.8 mL). A stock solution of initiator (0.2 mL, 0.02 M) was injected into the reaction, such that the overall concentration of lactide was 1 M and of initiator was 2 mM. Aliquots were taken from the reaction under a nitrogen atmosphere, quenched with wet hexane (1-2 mL) and the solvent was allowed to evaporate. The crude product was analysed by ^{1}H NMR and homonuclear decoupled ^{1}H NMR spectroscopy and GPC. The conversion of LA to PLA was determined by integration of the methyne proton peaks of the ^{1}H NMR spectra, δ 5.00 – 5.30. The P_s or P_i value was determined by integration of the methyne region of the homonuclear decoupled ^{1}H NMR spectrum, δ 5.1 – 5.24.[7]

The methyne proton regions were deconvoluted using MestReNova software. The PLA number-averaged molecular weight, M_n, and polydispersity index (M_w/M_n; PDI) were determined using gel permeation chromatography equipped with multiangle laser light scattering (SEC-MALLS).

General polymerization Procedure at Low Temperature

In a glove box, a Young's tap ampoule was loaded with *rac*-lactide (107 mg, 0.74 mmol) and dissolved in cold THF (1 mL). The initiator (**2**) (7.5 mg, 0.0074 mmol) was dissolved in cold THF (0.48 mL). The initiator solution was then injected into the reaction, such that the overall concentration of lactide was 0.5 M. The ampoule was then removed from the glovebox and placed in an ice or ice/salt bath, such that the temperature was maintained at 258 K or 273 K respectively. After an allotted period of time the reaction was quenched with hexane (5 mL) and the solvent was allowed to evaporate. The resultant polymer was analysed as described above.

X-ray crystallography

Data were collected at 150 K on a Kappa APEX II diffractometer using a Mo Kα (λ = 0.71069 Å) X-ray source and a graphite monochromator. The crystal structure was solved using SIR 97 and Shelxl-97. ORTEP drawings were made using ORTEP III for Windows.

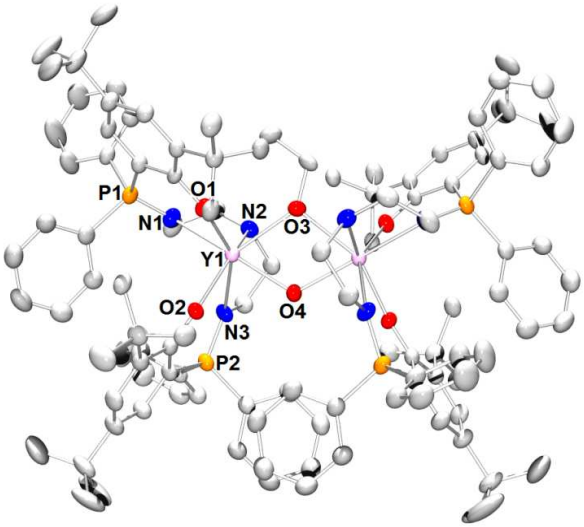


Figure S1: Partly hydrolysed X-ray crystal structure of compound **2**

Table S1: Selected bond lengths (Å) and angles (°) for the partly hydrolysed X-ray crystal structure of compound **2**

Bond Length		**Bond Length**	
Y(1) – O(2)	2.230 (2)	Y(1) – O(4)	2.248 (2)
Y(1) – O(1)	2.271 (2)	Y(1) – O(3)	2.411 (2)
Y(1) – N(1)	2.433 (3)	Y(1) – N(2)	2.511 (3)
Y(1) – N(3)	2.517 (3)		
Bond Angle		**Bond Angle**	
O(2) – Y(1) – O(4)	88.2(1)	O(2) – Y(1) – O(1)	86.26 (8)
O(4) – Y(1) – O(1)	120.01 (6)	O(2) – Y(1) – O(3)	142.48 (7)
O(4) – Y(1) – O(3)	64.8 (1)	O(1) – Y(1) – O(3)	86.17 (7)
O(2) – Y(1) – N(1)	98.2 (1)	O(4) – Y(1) – N(1)	162.89 (7)
O(1) – Y(1) – N(1)	75.7 (1)	O(3) – Y(1) – N(1)	115.3 (1)
O(2) – Y(1) – N(2)	138.4 (1)	O(4) – Y(1) – N(2)	96.66 (8)
O(1) – Y(1) – N(2)	124.3 (1)	O(3) – Y(1) – N(2)	73.59 (7)
N(1) – Y(1) – N(2)	68.1 (1)	O(2) – Y(1) – N(3)	74.5 (1)
O(4) – Y(1) – N(3)	80.1 (1)	O(1) – Y(1) – N(3)	151.5 (1)
O(3) – Y(1) – N(3)	121.84 (7)	N(1) – Y(1) – N(3)	86.3 (1)
N(2) – Y(1) – N(3)	65.9 (1)		

Table S2: Selected bond lengths (Å) and angles (°) for the X-ray crystal structure of compound **1**

Bond Length		**Bond Length**	
Y(1) – O(2)	2.223(5)	Y(1) – N(3)	2.410(6)
Y(1) – O(1)	2.161(6)	Y(1) – O(3)	2.069(6)
Y(1) – N(1)	2.467(6)	Y(1) – N(2)	2.529(7)
Bond Angle		**Bond Angle**	
O(1) – Y(1) – N(1)	76.8 (2)	O(3) – Y(1) – N(1)	102.3(2)
O(1) – Y(1) – N(2)	145.2(2)	O(3) – Y(1) – N(2)	83.2 (2)
N(1) – Y(1) – N(2)	68.6 (2)	O(2) – Y(1) – N(3)	75.7 (2)
O(3) – Y(1) – N(3)	143.0 (2)	O(2)-Y(1)-N(2)	119.2(2)
N(2) – Y(1) – N(3)	68.1 (2)	N(3) – Y(1) – N(1)	88.7 (2)
O(1)-Y(1)-O(2)	92.0(2)	O(2)-Y(1)-N(1)	156.7 (2)
O(3)-Y(1)-O(1)	107.4(2)	O(3)-Y(1)-O(2)	100.5 (2)

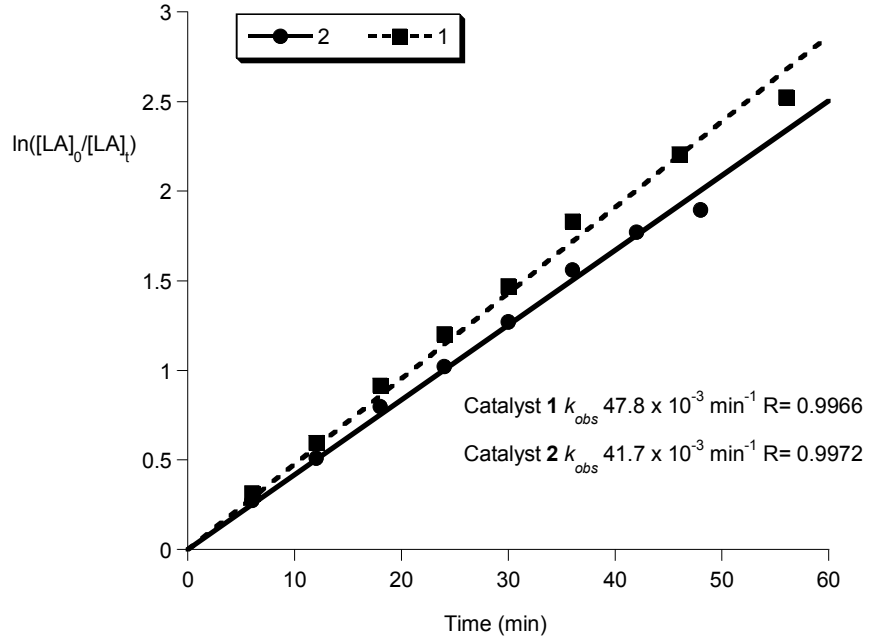


Figure S2: Plot of $\ln([LA]_0/[LA]_t)$ vs. time for initiators **1** and **2**. Conditions (**1**): $[LA]_0$ = 1 M, 1:1:500 [**1**]:[*i*PrOH]:[LA], THF, 298 K. (**2**): $[LA]_0$ = 1 M, 1:500 [**2**]:[LA], THF, 298 K.

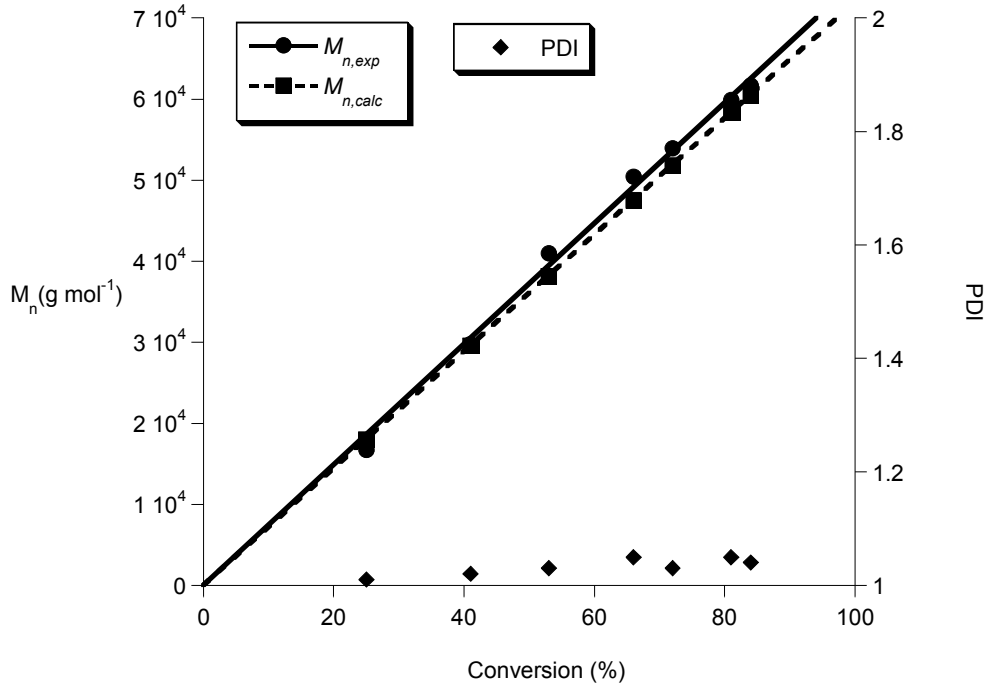


Figure S3: Evolution of $M_{n,exp}$ versus % conversion for the polymerization using initiator **1** (squares), evolution of $M_{n,calc}$ versus % conversion for the polymerization using initiator **2** (circles), PDI versus % conversion (squares). Conditions: (**1**): $[LA]_0$ = 1 M, 1:1:500 [**1**]:[*i*PrOH]:[LA], THF, 298 K. (**2**): $[LA]_0$ = 1 M, 1:500 [**2**]:[LA], THF, 298

ii.

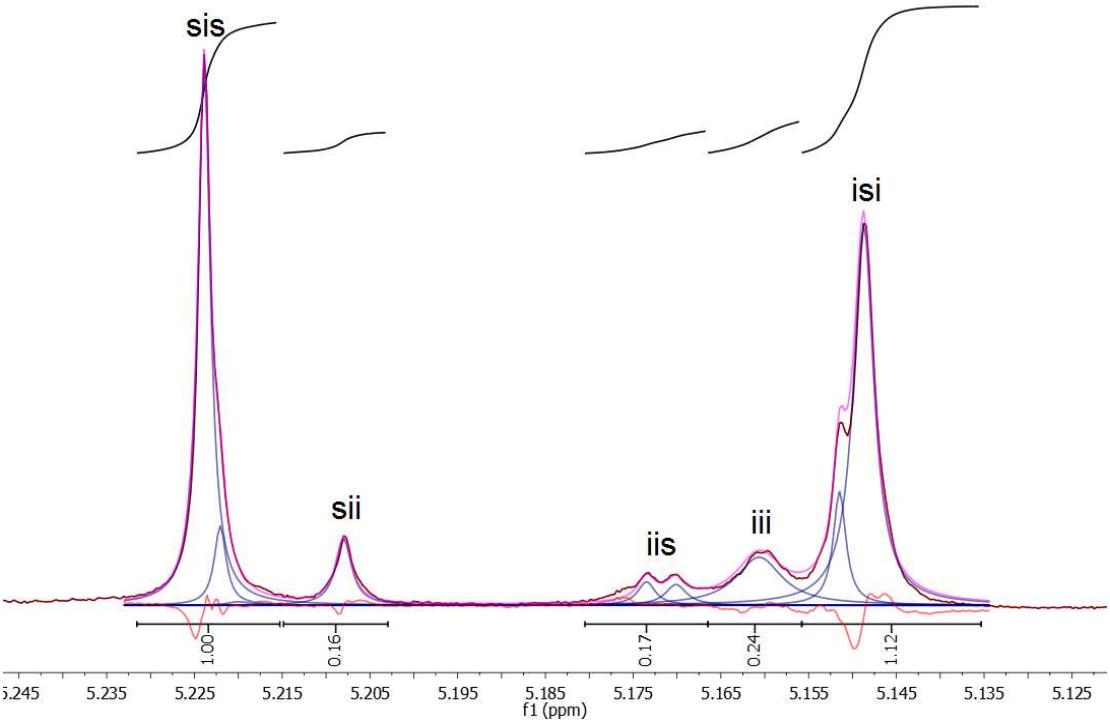


Figure S4: De-convoluted homonuclear decoupled $^{1}H\{^{1}H\}$ NMR of the methyne region of PLA ($CDCl_3$) polymerized using initiator 3, P_s=0.87.[7]

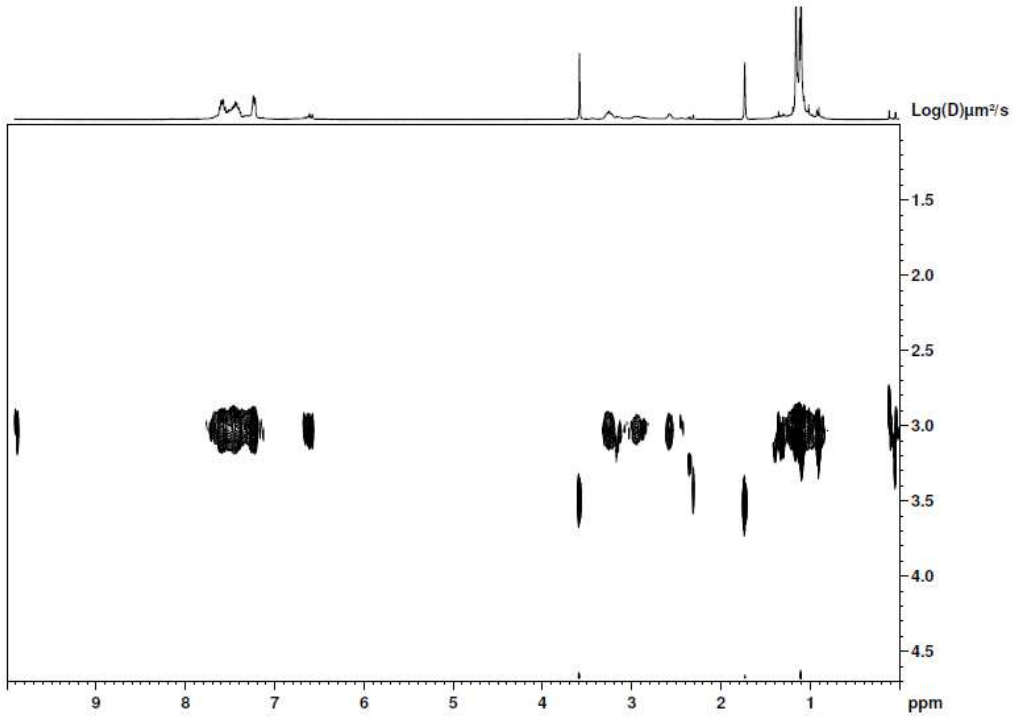


Figure S5: DOSY spectrum of compound **1** in THF-d_8

Diffusion NMR experiment calculations[8]

The ^{1}H PGSE (dosy) experiment was performed on a Bruker Av500 spectrometer running TopSpin 2.1 pl6, equipped with a z-gradient bbo/5 mm probe and a GAB 10 amp gradient amplifier providing a maximum gradient output of 5.35 G/cmA

The experiment was measured unlocked using the ledbpgp2s pulse program at a temperature of 298 K with a gas flow of 535 L h^{-1}. The spectrum was collected at a frequency of 500.13 MHz with a spectral width of 5000.0 Hz (centred on 5 ppm) and 32768 data points. A relaxation delay of 12 s was employed along with a diffusion time (big delta) of 50 ms and an eddy current delay of 5 ms. Bipolar gradient pulses (little delta/2) of 2.2 ms and homospoil gradient pulses of 1.1 ms were used . The gradient strength of the 2 homospoil pulses were -17.13 % and -13.17 % respectively. Sixteen experiments of twenty-four scans each were collected with the bipolar gradient strength, initially at 2 % (1st experiment), linearly increased to 95 % (16th experiment). All gradient pulses were sine shaped and after each application a recovery delay of 200 µs used.

The spectra were processed using 16384 data points and an exponential function with a line broadening of 1 Hz. Further processing was achieved using the DOSYm software (©NMRtec).

Calculation of the hydrodynamic radius of compound **1**.[9]

From the DOSY experiment the diffusion coefficient (D) was calculated:

$$D = \frac{10^{y}}{10^{-12}}$$

Where y = Log(D) value (from DOSY spectrum)

$$= \frac{10^{3}}{10^{12}}$$

$$= 1\,x\,10^{-9}$$

Next the hydrodynamic radius (r_s) was calculated:

$$D = \frac{kT}{6\pi\eta r_s}$$

Where r_s is the hydrodynamic radius, k is the Boltzmann constant, T is the temperature and η is the viscosity of the liquid.

Rearrange:

$$r_s = \frac{kT}{D6\pi\eta} = \frac{1.38\,x\,10^{-23}\,m^2\,kg\,s^{-2}K^{-1}\,x\,298\,K}{1\,x\,10^{-9}\,m^2\,s^{-1}\,x\,6\,x\,\pi\,x\,4.8\,x\,10^{-4}\,kg\,m^{-1}s^{-1}}$$

$$r_s = 4.5\,\text{Å}$$

The hydrodynamic radius (r_s) of compound **2** was determined from the X-ray crystal data, assuming a spherical shape:

$$V = \frac{4}{3}\pi r^3$$

Where V is the volume and r is the radius.

Rearrange:

$$r = \sqrt[3]{\frac{3V}{4\pi}}$$

$$= \sqrt[3]{\frac{3\,x\,2950\ \text{Å}^3}{4\,x\,\pi}}$$

$$= 8.9\ \text{Å}$$

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