Yttrium Phosphasalen Initiators for *rac*-Lactide Polymerization

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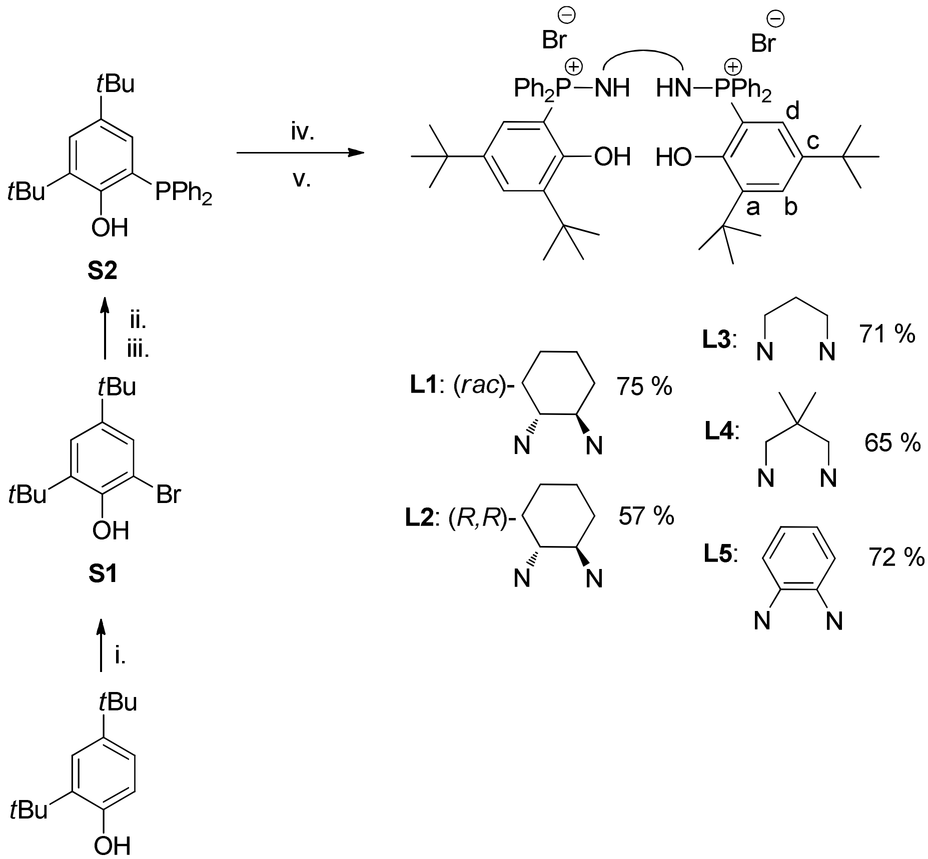
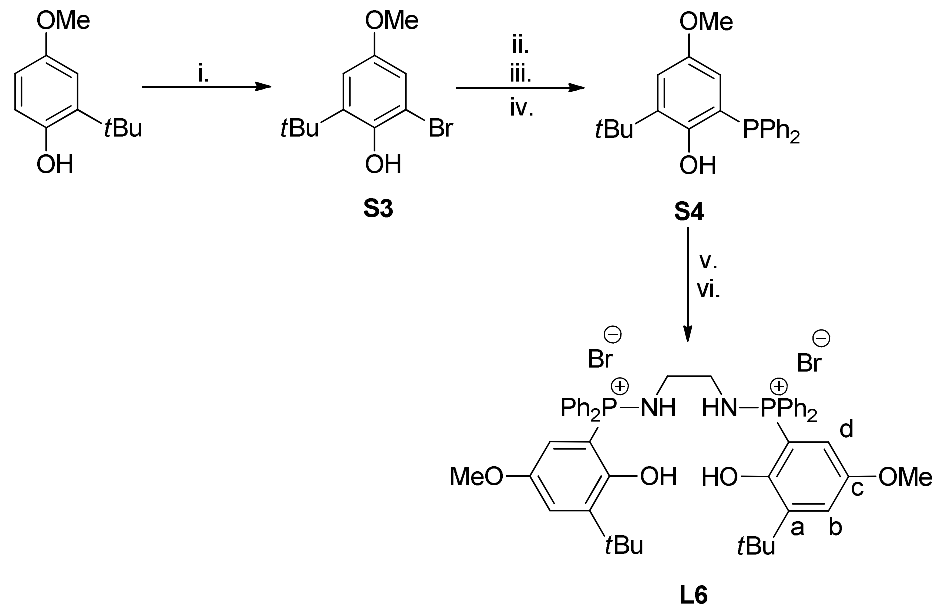


Scheme S1: Synthetic route for compounds $\mathbf{L^1}$-$\mathbf{L^5}$. Reagents and conditions: i. NBS, acetonitrile ii. n-BuLi (2 equiv.), petroleum ether iii. $ClPPh_2$ iv. Br_2 (1 equiv.), DCM v DABCO (0.5 equiv.), diamine (0.5 equiv.)



Scheme S2: Synthetic route for compound **L**[6]. Reagents and conditions: i. Br_2 (1 equiv.), CH_2Cl_2, 71 % ii. BuLi, Et_2O, iii. $ClPPh_2$ iv. H_2O, 84 % v. Br_2, CH_2Cl_2 vi. Ethylenediamine, Bu_3N, 69 %

Experimental

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 for the polymerization experiments, toluene, pentane, hexane and petroleum ether were distilled from sodium/benzophenone, under dry nitrogen. Tetrahydrofurane and petroleum ether for ligand and complex synthesis were directly taken from a MBraun MB-SPS 800 Solvent Purification Machine. Dichloromethane was distilled from CaH_2, under dry nitrogen. *Rac*-lactide was re-crystallised from anhydrous toluene and sublimed three times prior to use. $[YCl_3(THF)_{3.5}]$ was prepared following literature procedure.[1]

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Av300. Solvent peaks were used as internal references for ^{1}H NMR and ^{13}C NMR chemical shifts (ppm). ^{31}P NMR 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. ^{1}H 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. 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}.[2]

Compound S1[3] 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 with petroleum ether (4 x 70 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated, giving the product as a yellow solid (24.9 g, 90 %).

^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 7.33 (d, $^{4}J_{H,H}$ = 2.5 Hz, 1H, tBu-C^{IV}-C*H*-C^{IV}-tBu), 7.25 (d, $^{4}J_{H,H}$ = 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[4] *n*-Butyllithium (1.6 M in hexanes, 108 mL, 173 mmol) was added into a solution of **S1** (23.0 g, 80.6 mmol) in diethyl ether (170 mL) at -78 °C, giving immediately a white suspension. The cold bath was removed and stirring was continued at room temperature for 30 min, giving a pale yellow solution. Chlorodiphenylphosphine (14.5 mL, 80.6 mmol) was added into this solution at -78 °C. After overnight stirring, a white suspension was formed. The mixture was extracted quickly twice with aqueous solutions of NaH_2PO_4 (0.1 M, 2 x 100 mL). The organic layer was filtered to remove inorganic salts. Methanol (30 mL) was added and the solution was evaporated under vacuum until the volume of the remaining solvent was about 30 mL. A white solid precipitated out from the green solution. This solid was separated by filtration, washed with methanol (2 x 5 mL) and dried in vacuum (28 g, 90 %).

^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 7.26-7.25 (m, 11H, CH(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, OH), 1.34 (s, 9H, C_a-C(CH_3)$_3$), 1.08 (s, 9H, C_c-C(CH_3)$_3$); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, δ (ppm)): -30.8 (s, P); ^{13}C{^{1}H} 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*-CH(PPh_2)), 129.5 (d, $^2J_{P,C}$ = 3.5 Hz, C_dH), 129.1 (s, *p*-CH(PPh_2)), 128.8 (d, $^{2/3}J_{P,C}$ = 7.5 Hz, *o*-or *m*-CH(PPh_2)), 126.6 (s, C_bH), 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(CH$_3$)$_3$), 29.2 (s, C_a-C(CH$_3$)$_3$),

Compound S3[5] 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 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 was evaporated, the residue was taken in diethyl ether (200 mL), washed with an aqueous solution of Na_2CO_3 (1 M, 200 mL) and dried over Na_2SO_4. The solvent was evaporated again. The product was purified by chromatography (eluent diethyl ether/petroleum ether 2.5/97.5) (7.15 g, 71 %).

^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): δ 6.88 (d, $^4J_{H,H}$ = 3.0 Hz, 1H, $C_{phenyl}H$), 6.84 (d, $^4J_{H,H}$ = 3.0 Hz, 1H, $C_{phenyl}H$), 5.42 (s, 1H, OH), 3.74 (s, 3H, O-CH_3), 1.38 (s, 9H, C^{IV}(CH_3)$_3$).

Compound S4 n-Butyllithium (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 and a yellowish solution was obtained, stirring was continued at room temperature for 2 h. Chlorodiphenylphosphine (4.95 mL, 27.6 mmol) was added giving immediately a white suspension.

After overnight stirring at room temperature, the solid was isolated by filtration under inert atmosphere and was then put into 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) and dried over $MgSO_4$. 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-CH_3), 1.41 (s, 9H, $C^{IV}(CH_3)_3$); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, δ (ppm)): -28.3 (s, P^{III}); $^{13}C\{^1H\}$ 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-*C*H_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

General procedure for the synthesis of proligands L^1-L^6

At -78 °C bromine (200 µL, 3.88 mmol) was added dropwise to a solution of the phenolphosphine **S2** (1.52 g, 3.88 mmol) in methylene chloride (45 mL). The cold bath was removed and stirring was continued for 1 h at room temperature. Then the solution was cooled to -78 °C. 1,4-Diazabicyclo[2.2.2]octane (DABCO) (218 mg, 1.94 mmol) was added, followed by the diamine. The cold bath was removed. After 16 h a white slurry had formed. The methylene chloride was evaporated and THF (50 mL) was added. The insoluble diazabicyclo[2.2.2]octane salt was removed by centrifugation. The THF was evaporated, the white solid was washed with diethyl ether (7 mL) and dried *in vacuo*.

Compound L^1: (*rac*)-1,2-diaminocyclohexane (232 µg, 1.94 mmol), 1.52 g, 75 % **:** ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 8.59 (s, 2H, N*H*), 7.77 (dd, $^3J_{H,H}$=7.5 Hz, $^3J_{P,H}$=12.8 Hz, 4H, *o*-C*H*(PPh_2)), 7.69 (dd, $^3J_{H,H}$=7.5 Hz, $^3J_{P,H}$=14.2 Hz, 4H, *o*-C*H*(PPh_2)), 7.70 (s, 1H, OH), 7.69 (s, 1H, OH), 7.50 (vtd, $^3J_{H,H}$=$^3J_{H,H}$=7.5 Hz, $^4J_{P,H}$ = 3.0 Hz, 2H, *m*-C*H*(PPh_2)), 7.63 (vt, $^3J_{H,H}$=$^3J'_{H,H}$=7.5 Hz, 2H, *p*-C*H*(PPh_2)), 7.40 (vt, $^{3}J_{H,H}$=$^{3}J'_{H,H}$=7.5 Hz, 4H, *p*-C*H*(PPh_2)), 7.13 (vtd, $^{3}J_{H,H}$=$^{3}J_{H,H}$=7.5 Hz, $^{4}J_{P,H}$ = 3.3 Hz, 4H, *m*-C*H*(PPh_2)), 6.56 (dd, $^{4}J_{H,H}$=2.2 Hz, $^{5}J_{P,H}$ = 8.0 Hz, 1H, C_b*H*), 6.53 (dd, $^{4}J_{H,H}$=2.2 Hz, $^{5}J_{P,H}$ = 8.0 Hz, 1H, C_b*H*), 6.37 (dd, $^{4}J_{H,H}$=2.2 Hz, $^{3}J_{P,H}$ = 15.6 Hz, 2H, C_b*H*), 3.82 (m, 2H, N-C*H*-C*H*-N), 2.05 (m, 2H, CH_2(cyclohexane)), 1.59 (m, 2H, CH_2(cyclohexane)), 1.53 (s, 18H, C_a- C(CH_3)$_3$), 1.30 (m, 2H, CH_2(cyclohexane)), 1.03 (s, 18H, C_c- C(CH_3)$_3$), 0.93 (m, 2H, CH_2(cyclohexane)); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, δ (ppm)): 38.5 (s, P^{V}); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, δ(ppm)): 155.9 (d, $^{3}J_{P,C}$= 0.9 Hz, C^{IV}-O), 145.7 (d, $^{3}J_{P,C}$=8.2 Hz, $C_{c,a}^{IV}$); 144.5 (d, $^{3}J_{P,C}$ =7.0 Hz, $C_{a,c}^{IV}$), 135.0-133.0 (m, *C*H(PPh_2)), 131.8 (d, $^{4}J_{P,C}$= 0.9 Hz, *p*-*C*H(PPh_2)), 131.5 (d, $^{4}J_{P,C}$= 0.9 Hz, *p*-*C*H(PPh_2)), 129.7-128.9 (m, *C*H(PPh_2) + C_bH), 128.6 (d, $^{2}J_{P,C}$=12.2 Hz, C_dH), 123.0 (d, $^{1}J_{P,C}$=109.7 Hz, C^{IV}(PPh_2)), 121.7 (d, $^{1}J_{P,C}$=97.5 Hz, C^{IV}-PPh_2), 116.0 (d, $^{1}J_{P,C}$=106.2 Hz, C^{IV}(PPh_2)), 59.0 (m, N-*C*H-*C*H-N), 35.6 (s, C_a^{IV}-*C*(CH_3)$_3$), 34.7 (s, C_c^{IV}- *C*(CH_3)$_3$), 30.2 (s, *C*H_2(cyclohexane)), 30.0 (s, *C*H_2(cyclohexane)), 29.8 (s, $C_{c,a}^{IV}$- C(*C*H_3)$_3$), 29.7 (s, $C_{a,c}^{IV}$- C(*C*H_3)$_3$), 29.5 (s, $C_{a,c}^{IV}$- C(*C*H_3)$_3$), 29.4(s, *C*H_2(cyclohexane)), 28.8 (s, *C*H_2(cyclohexane)). Anal. Calcd for $C_{58}H_{74}Br_2N_2O_2P_2$: C, 66.16; H, 7.08; N, 2.66. Found: C, 66.29; H, 7.15; N, 2.67.

Compound L^2: (R,R)-1,2-diaminocyclohexane (222 mg, 1.94 mmol), 1.04 g, 57 % **:** ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 8.59 (s, 2H, N*H*), 7.77 (dd, $^{3}J_{H,H}$=7.5 Hz, $^{3}J_{P,H}$=12.8 Hz, 4H, *o*-C*H*(PPh_2)), 7.69 (dd, $^{3}J_{H,H}$=7.5 Hz, $^{3}J_{P,H}$=14.2 Hz, 4H, *o*-C*H*(PPh_2)), 7.70 (s, 1H, OH), 7.69 (s, 1H, OH), 7.50 (vtd, $^{3}J_{H,H}$=$^{3}J_{H,H}$=7.5 Hz, $^{4}J_{P,H}$ = 3.0 Hz, 2H, *m*-C*H*(PPh_2)), 7.63 (vt, $^{3}J_{H,H}$=$^{3}J'_{H,H}$=7.5 Hz, 2H, *p*-C*H*(PPh_2)), 7.40 (vt, $^{3}J_{H,H}$=$^{3}J'_{H,H}$=7.5 Hz, 4H, *p*-C*H*(PPh_2)), 7.13 (vtd, $^{3}J_{H,H}$=$^{3}J_{H,H}$=7.5 Hz, $^{4}J_{P,H}$ = 3.3 Hz, 4H, *m*-C*H*(PPh_2)), 6.56 (dd, $^{4}J_{H,H}$=2.2 Hz, $^{5}J_{P,H}$ = 8.0 Hz, 1H, C_b*H*), 6.53 (dd, $^{4}J_{H,H}$=2.2 Hz, $^{5}J_{P,H}$ = 8.0 Hz, 1H, C_b*H*), 6.37 (dd, $^{4}J_{H,H}$=2.2 Hz, $^{3}J_{P,H}$ = 15.6 Hz, 2H, C_b*H*), 3.82 (m, 2H, N-C*H*-C*H*-N), 2.05 (m, 2H, CH_2(cyclohexane)), 1.59 (m, 2H, CH_2(cyclohexane)), 1.53 (s, 18H, C_a- C(CH_3)$_3$), 1.30 (m, 2H, CH_2(cyclohexane)), 1.03 (s, 18H, C_c- C(CH_3)$_3$), 0.93 (m, 2H, CH_2(cyclohexane)); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, δ (ppm)): 38.5 (s, P^{V}); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, δ (ppm)): 155.9 (d, $^{3}J_{P,C}$= 0.9 Hz, C^{IV}-O), 145.7 (d, $^{3}J_{P,C}$=8.2 Hz, $C_{c,a}^{IV}$); 144.5 (d, $^{3}J_{P,C}$ =7.0 Hz, $C_{a,c}^{IV}$), 135.0-133.0 (m, *C*H(PPh_2)), 131.8 (d, $^{4}J_{P,C}$= 0.9 Hz, *p*-*C*H(PPh_2)), 131.5 (d, $^{4}J_{P,C}$= 0.9 Hz, *p*-*C*H(PPh_2)), 129.7-128.9 (m, *C*H(PPh_2) + C_bH), 128.6 (d, $^{2}J_{P,C}$=12.2 Hz, C_dH), 123.0 (d, $^{1}J_{P,C}$=109.7 Hz, C^{IV}(PPh_2)), 121.7 (d,

${}^1J_{P,C}$=97.5 Hz, C^{IV}-PPh$_2$), 116.0 (d, ${}^1J_{P,C}$=106.2 Hz, C^{IV}(PPh$_2$)), 59.0 (m, N-*C*H-*C*H-N), 35.6 (s, C_a^{IV}-*C*(CH$_3$)$_3$), 34.7 (s, C_c^{IV}- *C*(CH$_3$)$_3$), 30.2 (s, *C*H$_2$(cyclohexane)), 30.0 (s, *C*H$_2$(cyclohexane)), 29.8 (s, $C_{c,a}^{IV}$- C(*C*H$_3$)$_3$), 29.7 (s, $C_{a,c}^{IV}$- C(*C*H$_3$)$_3$), 29.5 (s, $C_{a,c}^{IV}$- C(*C*H$_3$)$_3$), 29.4(s, *C*H$_2$(cyclohexane)), 28.8 (s, *C*H$_2$(cyclohexane)). Anal. Calcd for $C_{58}H_{74}Br_2N_2O_2P_2$: C, 66.16; H, 7.08; N, 2.66. Found: C, 66.25; H, 6.96; N, 2.56.

Compound L^3: 1,3-diaminopropane (162 µL, 1.94 mmol), 1.5 g, 71 %. ^{1}H NMR (300 MHz, CDCl$_3$, δ (ppm)): 7.74-7.56 (m, 22H, C*H*(PPh$_2$) + C$_b$*H*), 6.54 (dd, ${}^4J_{H,H}$=2.0 Hz, ${}^3J_{P,H}$ = 15.5 Hz, 2H, C$_d$*H*), 3.37 (vq, ${}^3J_{H,H}$= ${}^3J_{P,H}$= 7.0 Hz, 4H, N-C*H$_2$*-CH$_2$-C*H$_2$*-N), 2.32 (qt, ${}^3J_{H,H}$= 7.0 Hz, 2H, N-CH$_2$-C*H$_2$*-CH$_2$-N), 1.49 (s, b, 18H, $C_{c,a}^{IV}$- C^{IV}(C*H*$_3$)$_3$), 1.11 (s, 18H, $C_{c,a}^{IV}$- C^{IV}(C*H*$_3$)$_3$); ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$, δ (ppm)): 40.4 (s, *P*^{V}); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, δ (ppm)): 156.0 (d, ${}^3J_{P,C}$= 1.0 Hz, C^{IV}-O), 145.4 (d, ${}^3J_{P,C}$=13.5 Hz, $C_{c,a}^{IV}$), 143.6 (d, ${}^3J_{P,C}$ =7.0 Hz, $C_{a,c}^{IV}$), 134.1 (m, *C*H(PPh$_2$)), 133.7 (d, ${}^{2/3}J_{P,C}$= 10.0 Hz, *o*-or *m*-*C*H(PPh$_2$)),133.4 (d, ${}^{2/3}J_{P,C}$= 10.0 Hz, *o*-or *m*-*C*H(PPh$_2$)), 131.9 (d, ${}^4J_{P,C}$= 0.9 Hz, *p*-*C*H(PPh$_2$)), 131.6 (d, ${}^4J_{P,C}$= 0.9 Hz, *p*-*C*H(PPh$_2$)), 129.7-128.9 (m, *C*H(PPh$_2$) + *C$_b$*H), 128.3 (d, ${}^2J_{P,C}$=12.2 Hz, *C$_d$*H), 122.8 (d, ${}^1J_{P,C}$=103.7 Hz, C^{IV}(PPh$_2$)), 114.9 (d, ${}^1J_{P,C}$=109.1 Hz, C^{IV}-PPh$_2$), 41.9 (m, N-*C*H$_2$), 35.3 (s, $C_{a/c}^{IV}$- *C*(CH$_3$)$_3$), 34.5 (s, $C_{c/a}^{IV}$- *C*(CH$_3$)$_3$), 31.0 (s, N-CH$_2$-*C*H$_2$-CH$_2$-N), 30.6 (s, $C_{c,a}^{IV}$- C(*C*H$_3$)$_3$), 29.7 (s, $C_{a,c}^{IV}$- C(*C*H$_3$)$_3$). Anal. Calcd for $C_{55}H_{70}Br_2N_2O_2P_2$: C, 65.22; H, 6.97; N, 2.77. Found: C, 65.19; H, 7.03; N, 2.70.

Compound L^4: 1,3-diamino-2,2-dimethylpropane (198 mg, 1.94 mmol), 1.32 g, 65 %. ^{1}H NMR (300 MHz, CDCl$_3$, δ (ppm)): 7.72 (dd, ${}^3J_{H,H}$=7.5 Hz, ${}^3J_{P,H}$=13.0 Hz, 8H, *o*-C*H*(PPh$_2$)), 7.65 (vt, ${}^3J_{H,H}$= ${}^3J'_{H,H}$ = 7.5 Hz, 4H, *p*-C*H*(PPh$_2$)), 7.56 (s, br, 2H, C$_b$*H*), 7.55 (vtd, ${}^4J_{P,H}$=3.0 Hz, ${}^3J_{H,H}$= ${}^3J'_{H,H}$ = 7.5 Hz, 8H, *m*-C*H*(PPh$_2$)), 6.73 (d, b, ${}^3J_{P,H}$ = 14.0 Hz, 2H, C$_d$*H*), 3.17 (s, 2H, N*H*), 3.14 (d, ${}^3J_{P,H}$= 9.0 Hz, 4H, N-C*H$_2$*), 1.29 (s, b, 18H, $C_{c,a}^{IV}$- C^{IV}(C*H*$_3$)$_3$), 1.10 (s, 18H, $C_{c,a}^{IV}$- C^{IV}(C*H*$_3$)$_3$), 0.74 (s, br, 6H, N-CH$_2$-C^{IV}(C*H*$_3$)$_2$); ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$, δ (ppm)): 41.7 (s, *P*^{V}); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, δ (ppm)): 141.9 (d, ${}^3J_{P,C}$= 2.5 Hz, $C_{c/a}^{IV}$), 133.9 (s, b, *p*-*C*H(PPh$_2$)), 133.7 (d, ${}^{2/3}J_{P,C}$= 10.5 Hz, *m*-or *o*-*C*H(PPh$_2$)), 131.6 (s, b, *C$_b$*H), 129.5 (d, ${}^{2/3}J_{P,C}$= 13.0 Hz, *m*-or *o*-*C*H(PPh$_2$)), 128.7 (d, ${}^2J_{P,C}$=12.0 Hz, *C$_d$*H), 50.6 (m,b, N-*C*H$_2$), 37.06 (t, ${}^3J_{P,C}$=8.0 Hz, N-CH$_2$-C^{IV}-CH$_2$-N), 35.2 (s, $C_{c,a}^{IV}$-

$C^{IV}(CH_3)_3$), 34.6 (s, $C_{c,a}^{IV}$-$C^{IV}(CH_3)_3$), 31.3 (s, $C_{c,a}^{IV}$-$C^{IV}(CH_3)_3$), 30.6 (s, N-CH_2-$C^{IV}(CH_3)_2$), (C^{IV}-OH, C^{IV}-PPh_2, $C^{IV}(PPh_2)$ and one of $C_{c/a}^{IV}$) were not observed at all, even in increasing the number of acquisitions). Anal. Calcd for $C_{57}H_{74}Br_2N_2O_2P_2$: C, 65.77; H, 7.17; N, 2.69. Found: C, 65.88; H, 7.08; N, 2.81.

Compound L⁵: ortho-phenylenediamine (210 mg, 1.94 mmol), 1.47 g, 72 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 8.88 (d, $^2J_{P,H}$ =8.5 Hz, 2H, NH), 7.76 (d, 2H, $^4J_{H,H}$= 2.0 Hz, C_bH), 7.74 (vt, $^3J_{P,H}$ =$^3J_{H,H}$ =8.0 Hz, 4H, o-CH(PPh_2)), 7.73 (vt, $^3J_{P,H}$ =$^3J_{H,H}$ =8.0 Hz, 4H, o-CH(PPh_2)), 7.71 (vt, $^3J_{H,H}$ =$^3J'_{H,H}$ =8.0 Hz, 4H, p-CH(PPh_2)), 7.56 (vtd, $^3J_{H,H}$ =$^3J'_{H,H}$ =8.0 Hz, $^4J_{P,H}$ = 4.0 Hz, 8H, m-CH(PPh_2)), 7.48 (b, 2H, OH), 6.90 (dd, $^3J_{P,H}$ = 16.0 Hz, $^4J_{H,H}$= 2.0 Hz, C_dH), 6.65 (dd, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 3.5 Hz, 2H, C_fH), 6.53 (ddd, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 3.5 Hz, $^4J_{P,H}$ = 1.0 Hz, 2H, C_eH), 1.33 (s, 18H, $C_{c,a}^{IV}$-$C^{IV}(CH_3)_3$), 1.15 (s, 18H, $C_{c,a}^{IV}$- $C^{IV}(CH_3)_3$; $^{31}P\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ (ppm)): 38.9 (s, P^V); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ (ppm)): 155.8 (d, $^3J_{P,C}$= 2.0 Hz, C^{IV}-O), 145.8 (d, $^3J_{P,C}$= 13 Hz, $C_{c,a}^{IV}$), 141.6 (d, $^3J_{P,C}$=7.5 Hz, $C_{c,a}^{IV}$), 134.8 (d, $^4J_{P,C}$= 3.0 Hz, p-CH(PPh_2)), 133.7 (d, $^{2/3}J_{P,C}$= 11.0 Hz, m-or o-CH(PPh_2)), 132.9 (d, $^4J_{P,C}$= 2.0 Hz, C_bH), 132.5 (d, $^2J_{P,C}$= 6.5 Hz, C^{IV}-N), 129.9 (d, $^{2/3}J_{P,C}$= 13.5 Hz, m-or o-CH(PPh_2)), 129.1 (d, $^2J_{P,C}$= 11.5 Hz, C_dH), 125.3 (d, $^4J_{P,C}$= 1.0 Hz, C_fH), 125.0 (d, $^3J_{P,C}$= 3.0 Hz, C_eH), 121.5 (d, $^1J_{P,C}$=104.5 Hz, $C^{IV}(PPh_2)$), 111.0 (d, $^1J_{P,C}$=110.5 Hz, C^{IV}-PPh_2), 35.1 (s, $C_{c,a}^{IV}$-$C^{IV}(CH_3)_3$), 34.8 (s, $C_{c,a}^{IV}$-$C^{IV}(CH_3)_3$), 31.2 (s, $C_{c,a}^{IV}$-$C^{IV}(CH_3)_3$), 30.7 (s, $C_{c,a}^{IV}$-$C^{IV}(CH_3)_3$). Anal. Calcd for $C_{58}H_{68}Br_2N_2O_2P_2$: C, 66.54; H, 6.55; N, 2.68. Found: C, 66.68; H, 6.55; N, 2.58.

Compound L⁶ 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 methylene chloride (100 mL). The cold bath was removed and stirring was continued for 2 h at room temperature. The solution was cooled to -78 °C. Tributylamine (1.39 mL, 5.83 mmol) was added, followed by ethylenediamine (195 µL, 2.92 mmol). The cold bath was removed. After 16 h a cloudy solution was formed. The methylene chloride was evaporated and the residue was washed with THF (5 x 10 mL) to remove tributylamonium 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, $^{3}J_{H,H}$ =8.0 Hz, 4H, *p*-C*H*(PPh_2)), 7.63 (dd, $^{3}J_{P,H}$ =12.5 Hz, $^{3}J_{H,H}$ =8.0 Hz, 8H, *o*-C*H*(PPh_2)), 7.53 (vtd, $^{4}J_{P,H}$ =3.5 Hz, $^{3}J_{H,H}$ =$^{3}J'_{H,H}$ =8.0 Hz, 8H, *m*-C*H*(PPh_2)), 7.17 (d, $^{4}J_{H,H}$= 2.5 Hz, 2H, C_b*H*), 5.95 (dd, $^{3}J_{P,H}$ =16.5 Hz, $^{4}J_{H,H}$ =2.5 Hz, 2H, C_d*H*), 3.66 (dd, $^{3}J_{P,H}$ = 6.5 Hz, $^{4}J_{P,H}$ = 2.0 Hz, 4H, N-CH_2-CH_2-N), 3.50 (s, 6H, -OCH_3), 1.50 (s, 18H, C^{IV}(CH_3)$_3$); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, δ (ppm)): 40.1 (s, P^{V}); $^{13}C\{^{1}H\}$ 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, $^{2}J_{P,C}$= 9.0 Hz, *o*-*C*H(PPh_2)), 129.7 (d, $^{3}J_{P,C}$= 13.5 Hz, *m*-*C*H(PPh_2)), 122.1 (d, $^{1}J_{P,C}$=105 Hz, C^{IV}(PPh_2)), 121.2 (s, C_bH), 116.0 (d, $^{1}J_{P,C}$=120 Hz, C^{IV}-PPh_2), 115.0 (d, $^{2}J_{P,C}$= 13.5 Hz, C_dH), 55.6 (s, O-*C*H_3), 44.2 (dd, $^{2}J_{P,C}$ = 7.5 Hz, $^{3}J_{P,C}$ = 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}(*C*H_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.

Table S1. Crystallographic data for compounds **2**.

	Compound **2**
Formula	$C_{66}H_{87}N_2O_4P_2Y$
M_r	1123.23
Space group	$P2_1$
T (°C)	-123
λ (Å)	0.71069
a(Å)	10.654(1)
b(Å)	26.055(1)
c(Å)	11.449(1)
α(°)	90.00
β(°)	107.091(1)
γ(°)	90.00
V($Å^3$)	3037.8(4)
Z	2
d(g cm^{-3})	1.228
μ(cm^{-1})	1.060
R1[a)]	0.0500
wR2[b)]	0.1178
CCDC Number	

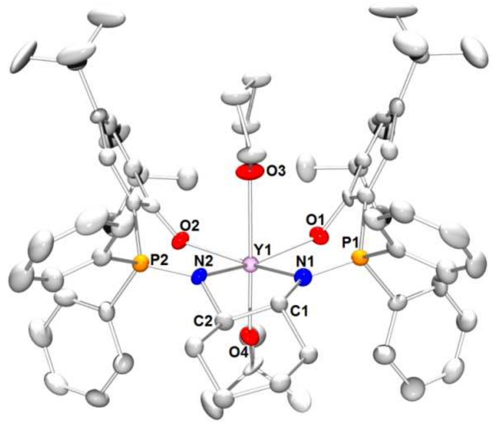


Figure S1: ORTEP view of the solid state structure of compound **2,** with thermal ellipsoids drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity

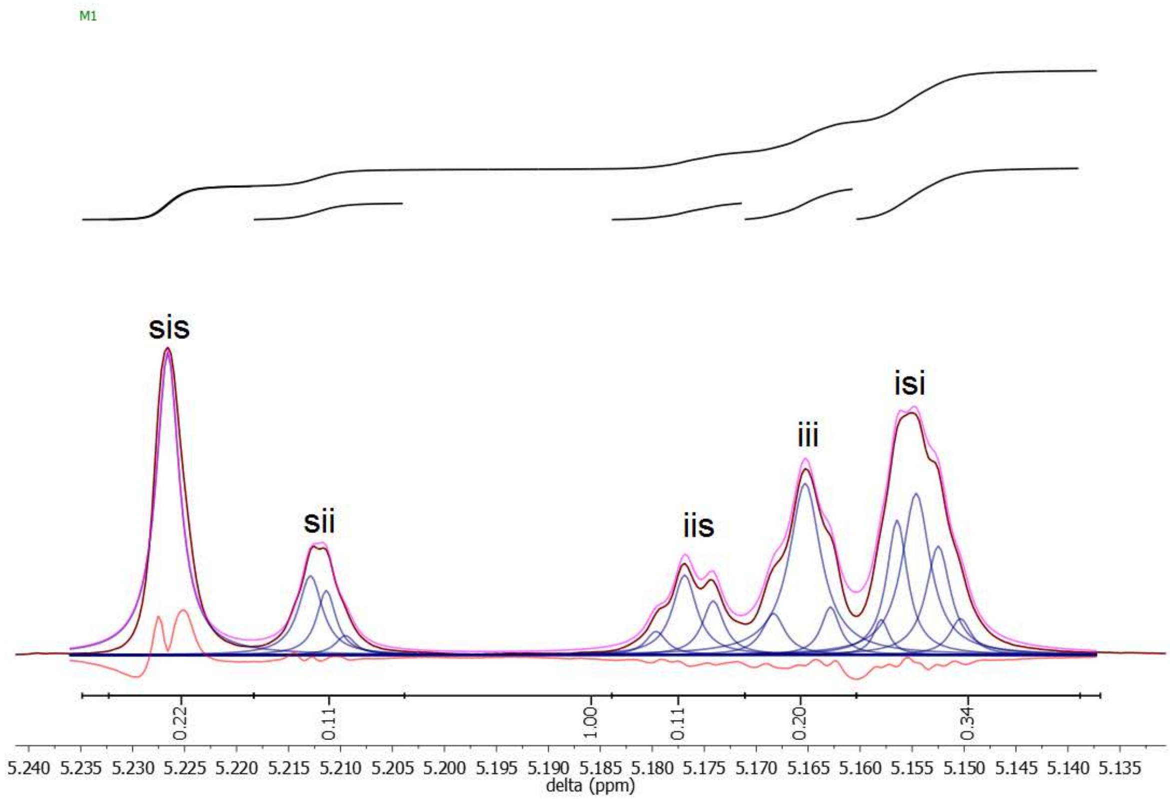


Fig. S2: Homonuclear decoupled ^{1}H {^{1}H} NMR spectrum of PLA ($CDCl_3$), polymerized using initiator **3**, P_s=0.67[6]

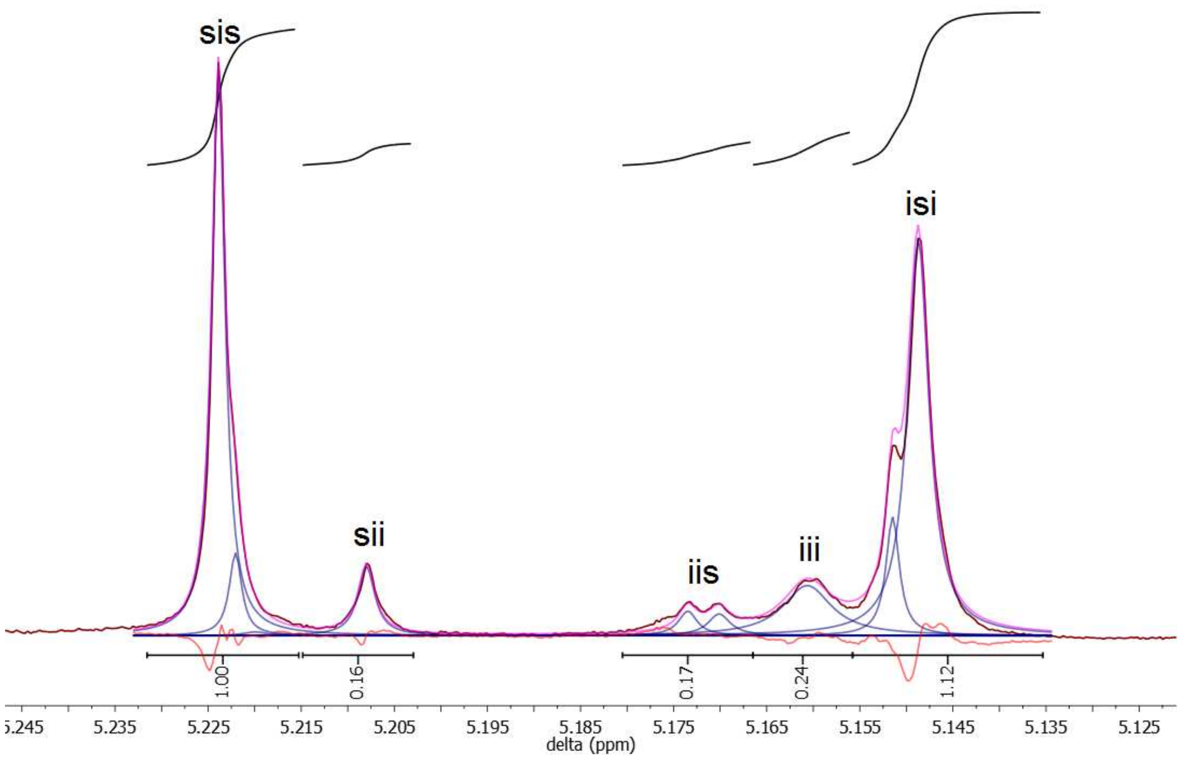


Fig. S3: Homonuclear decoupled ^{1}H $\{^{1}H\}$ NMR spectrum of PLA ($CDCl_3$), polymerized using initiator **6**, P_s=0.87[6]

References

1. Sobota, P.; Utko, J.; Szafert, S., *Inorg. Chem.* **1994,** *33*, 5203-5206.
2. Dorgan, J. R.; Janzen, J.; Knauss, D. M.; Hait, S. B.; Limoges, B. R.; Hutchinson, M. H., *J. Polym. Sci. Part B: Polym. Phys.* **2005,** *43*, 3100-3111.
3. Kavala, V.; Naik, S.; Patel, B. K., *J. Org. Chem.* **2005,** *70*, 4267-4271.
4. He, L.-P.; Mu, H.-L.; Li, B.-X.; Li, Y.-S., *J. Polym. Sci., Part A: Polym. Chem.* **2010,** *48*, 311 - 319.
5. Tashiro, M.; Yoshiya, H., *Heterocycles* **1983,** *20*, 653-660.
6. Coudane, J.; Ustariz-Peyret, C.; Schwach, G.; Vert, M., *J. Polym. Sci., Part A: Polym. Chem.* **1997,** *35*, 1651-1658.