Supporting Material For:

Cationic Zinc Complexes: A New Class of Catalyst for Living Polymerization of Lactide at Ambient Temperature

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General Experimental Considerations

All manipulations of air-sensitive materials and reagents were conducted using high-vacuum techniques under a purified argon atmosphere or in a glove box (MBraun Labmaster 130). All solvents were purified using an MBraun solvent purification system (MB-SPS), stored in teflon-sealed glass vessels over sodium benzophenone ketyl (THF and ether), CaH_2 (DCM, bromobenzene) or "titanocene" (pentane, benzene and toluene), and distilled prior to use. Deuterated solvents (Cambridge Isotopes) were dried over sodium benzophenone ketyl (benzene-d_6, toluene-d_8, and bromobenzene-d_5) or CaH_2 ($CDCl_3$, CD_2Cl_2), degassed *via* three freeze-pump-thaw cycles, distilled under vacuum and stored in glass bombs under argon. *Rac*-lactide was purchased from Alfa Aesar and was recrystallized from toluene and sublimed twice prior to use. $EtZn(OCH(CH_3)CO_2CH_3)$[1], $[H(OEt_2)_2][B((CF_3)_2C_6H_3)_4]$[2], 4,6-$(PPh_2)_2$dibenzofuran[3], and 4-*iso*propylphenyl-azide[4] were prepared according to the literature methods. All other materials were obtained from commercial sources in high purity (Sigma-Aldrich, Acros Organics) and used without additional purification. NMR spectra (^{1}H (300.13 MHz), $^{13}C\{^1H\}$ (75.47 MHz), $^{31}P\{^1H\}$ (121.48 MHz), ^{19}F (282.42 MHz), and ^{11}B (96.29 MHz)) were collected using a Bruker Avance II NMR spectrometer equipped with a variable-temperature unit. Spectra were collected at ambient temperature unless otherwise noted and referenced to either $SiMe_4$ through the residual solvent resonance(s) (^{1}H and $^{13}C\{^1H\}$), or an external standard (85% H_3PO_4 ($^{31}P\{^1H\}$), trifluorotoluene (^{19}F), or boron trifluoride diethyl etherate (^{11}B)). ^{1}H and $^{13}C\{^1H\}$ NMR peak assignments were facilitated by COSY, DEPT-90, and HSQC experiments. X-ray crystal structures were collected using a Bruker AXS

(1) F. Drouin, P. O. Oguadinma, T. J. J. Whitehorne, R. E. Prud'homme and F. Schaper, *Organometallics*, 2010, **29**, 2139–2147.
(2) M. Brookhart, B. Grant, and A. F. Volpe, *Organometallics*, 1992, **11**, 3920–3922.
(3) M. W. Haenel, D. Jakubik, E. Rothenberger and G Schroth, *Chem. Ber.*, 1991, **124**, 1705–1710.
(4) K. R. D. Johnson and Paul G. Hayes, *Organometallics*, 2009, **21**, 6352–6361.

SMART APEX II single crystal X-ray diffractometer (Mo Kα = 0.71073 Å). Elemental analyses were performed using an Elementar Vario Microcube instrument.

Synthesis

4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran, L.

In a 100 mL r.b. flask, 4,6-(PPh$_2$)$_2$dibenzofuran (1.30 g, 2.42 mmol) was dissolved in 40 mL of benzene. To this solution 2.1 equiv of 4-*iso*propylphenyl-azide (0.820 g, 5.09 mmol) was added. The reaction mixture was heated to 70 ºC for 18 h. After cooling to ambient temperature, the volume was reduced *in vacuo* to 5 mL, and 10 mL of pentane was added. Vigorous stirring over a period of 1 h produced the compound as a light yellow precipitate. This was collected by filtration, washed with pentane (3 x 5 mL), and dried *in vacuo*, yielding the compound as a light yellow powder. Yield: 1.65 g, 84.6%. ^{1}H NMR (C_6D_6): δ 8.28 (dd, 2H, $^{3}J_{PH}$ = 13.7 Hz, $^{3}J_{HH}$ = 7.6 Hz, 3,7-dbf), 7.70 (dd, 8H, $^{3}J_{PH}$ = 12.7 Hz, $^{3}J_{HH}$ = 7.7 Hz, *o*-Ph), 7.49 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.02 (ov m, 8H, *o*+*m*-Pipp), 6.97–6.88 (ov m, 6H, 2,8-dbf + *p*-Ph), 6.86–6.77 (td, 8H, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{PH}$ = 3.0 Hz, *m*-Ph), 2.73 (sp, 2H, $^{3}J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.16 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ –5.10. ^{13}C{^{1}H} NMR (C_6D_6): δ 156.86 (d, J_{CP} = 2.2 Hz), 149.77 (d, J_{CP} = 1.9 Hz), 138.20 (s), 135.02 (d, $^{2}J_{CP}$ = 7.1 Hz, 3,7-dbf), 132.92 (d, $^{2}J_{CP}$ = 10.2 Hz, *o*-Ph), 131.92 (d, $^{1}J_{CP}$ = 104.2 Hz, ipso-Ph), 131.79 (d, $^{4}J_{CP}$ = 2.8 Hz, *p*-Ph), 129.04 (d, $^{3}J_{CP}$ = 12.4 Hz, *m*-Ph), 127.43 (s, *m*-Pipp), 125.14 (dd, J_{CP} = 5.9 Hz, J_{CP} = 0.9 Hz), 124.90 (d, $^{4}J_{CP}$ = 2.4 Hz, 1,9-dbf), 124.14 (d, $^{3}J_{CP}$ = 10.5 Hz, 2,8-dbf), 124.12 (d, $^{3}J_{CP}$ = 17.7 Hz, *o*-Pipp), 117.20 (d, $^{1}J_{CP}$ = 91.1 Hz, 4,6-dbf), 34.13 (s, *C*H(CH$_3$)$_2$), 24.99 (s, CH(*C*H$_3$)$_2$). Anal. Calcd. (%) for $C_{54}H_{48}N_2OP_2$: C: 80.78; H: 6.03; N: 3.49; found: C: 80.52; H: 6.26; N: 3.29.

[4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·H]$^+$[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$, 1a.

In a 20 mL scintillation vial, **L** (0.500 g, 0.623 mmol) and the oxonium acid [H(OEt$_2$)$_2$][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] (0.630 g, 0.622 mmol) were combined with 4 mL of benzene. The mixture was triturated until both components were dissolved, yielding a clear red solution. The product was then precipitated as a red oil by addition of 10 mL of pentane. After decanting the supernatant, the oily product was washed with pentane (4 x 2 mL), and dried *in vacuo* to yield a pale yellow powder. Yield: 0.955 g, 92.0%. ^{1}H NMR (CD_2Cl_2): δ 8.40 (d, 2H, $^3J_{HH}$ = 7.8 Hz, 1,9-dbf), 7.75 (s, 8H, *o*-Ph Anion), 7.66–7.48 (ov m, 18H, *p*-Ph Anion + *o*-Ph + *p*-Ph + 2,8-dbf), 7.48–7.35 (ov m, 10H, *m*-Ph + 3,7-dbf), 6.82 (ov m, 5H, $^3J_{HH}$ = 8.2 Hz, *m*-Pipp + N*H*), 6.56 (d, 4H, $^3J_{HH}$ = 8.2 Hz, *o*-Pipp), 2.75 (sp, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.15 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 16.2 (s). ^{19}F NMR (CD_2Cl_2): δ –62.82. ^{11}B{^{1}H} NMR (CD_2Cl_2): δ –6.59. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.33 (q, $^1J_{BC}$ = 49.7 Hz, *ipso*-BAr$_4$), 157.62 (s, aromatic C), 143.74 (s, aromatic C), 140.91 (s, aromatic C), 135.37 (br s, *o*-BAr$_4$), 134.59 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Ph), 133.47 (d, $^2J_{PC}$ = 10.6 Hz, *o*-Ph), 133.18 (d, $^2J_{CP}$ = 7.7 Hz, 3,7-dbf), 129.99 (d, $^3J_{CP}$ = 13.1 Hz, *m*-Ph), 129.44 (q of q, $^2J_{FC}$ = 31.5 Hz, $^3J_{BC}$ = 2.9 Hz, *m*-BAr$_4$), 127.78 (d, $^4J_{CP}$ = 1.9 Hz, 1,9-dbf), 127.60 (s, *m*-Pipp), 125.52 (q, $^1J_{CF}$ = 272.4 Hz, Anion *C*F$_3$), 125.49 (s, aromatic C), 125.42 (d, $^3J_{CP}$ = 11.4 Hz, 2,8-dbf), 125.00 (d, $^3J_{CP}$ = 10.8 Hz, *o*-Pipp), 124.56 (d, $^1J_{CP}$ = 70.4 Hz, *ipso*-Ph), 118.05 (m, *p*-BAr$_4$), 111.98 (d, $^1J_{CP}$ = 95.3 Hz, 4,6-dbf), 33.83 (s, *C*H(CH$_3$)$_2$), 24.30 (s, CH(*C*H$_3$)$_2$). Anal. Calcd. (%) for $C_{86}H_{61}BF_{24}N_2OP_2$: C: 61.96; H: 3.69; N: 1.68; found: C: 61.96; H: 3.65; N: 1.69.

[4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·H]$^+$[BPh$_4$]$^-$, 1b.

This synthesis was performed without exclusion of air and moisture. To a solution of **L** (0.50 g, 6.2 mmol) in methanol (5 mL) one equiv of aqueous 1M HCl (0.62 mL, 6.2 mmol) was added. To this solution a separately prepared solution of $NaBPh_4$ (0.23 g, 0.67 mmol) in methanol (2 mL) was added with rapid stirring, immediately generating a flocculent white precipitate. This precipitate was collected by filtration, washed with methanol and pentane, and dried *in vacuo*, yielding the compound as a white powder in 84% yield (0.58 g, 0.52 mmol). ^{1}H NMR (acetone-d^6): δ 8.66 (d, 2H, $^3J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.86 (dd, 2H, $^3J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.7 Hz, 3,7-dbf), 7.78–7.64 (ov m, 10H, *o*-Ph + 2,8-dbf), 7.60 (t, 4H, J_{HH} = 7.6 Hz, *p*-Ph), 7.43 (td, 8H, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 3.4 Hz, *m*-Ph), 7.34 (broad s, 8H *o*-BPh_4), 6.97–6.84 (ov m, 12H, *m*-BPh_4 + *m*-Pipp), 6.80–6.70 (ov m, 8H, *p*-BPh_4 + *o*-Pipp), 4.91 (br s, 1H, NH^+), 2.75 (sp, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH_3)$_2$), 1.13 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (acetone-d^6): δ 14.2 (broad singlet). ^{11}B NMR (acetone-d^6): δ –6.50. ^{13}C{^{1}H} NMR (acetone-d^6): δ 165.00 (q, $^1J_{CB}$ = 49.4 Hz, ipso-BPh_4), 157.54 (d, J = 2.2 Hz), 142.34 (s), 142.27 (s), 137.11 (q, $^2J_{CB}$ = 1.4 Hz, *o*-BPh_4), 134.85 (d, $^4J_{CP}$ = 2.8 Hz, *p*-Ph), 134.74 (d, $^2J_{CP}$ = 8.0 Hz, 3,7-dbf), 133.90 (d, $^2J_{CP}$ = 11.0 Hz, *o*-Ph), 130.48 (d, $^3J_{CP}$ = 13.2 Hz, *m*-Ph), 128.68 (d, $^4J_{CP}$ = 2.8 Hz, 1,9-dbf), 127.71 (s, *m*-Pipp), 126.06 (q, $^3J_{CB}$ = 2.8 Hz, *m*-BPh_4), 125.86 (d, $^3J_{CP}$ = 11.4 Hz, 2,8-dbf), 125.82 (dd, J_{PH} = 6.8 Hz, J_{CP} = 1.1 Hz), 124.54 (broad s), 123.34 (d, $^3J_{CP}$ = 11.6 Hz, *o*-Pipp), 122.31 (s, *p*-BPh_4), 111.34 (d, J_{CP} = 4.2 Hz), 34.03 (s, *C*H(CH_3)$_2$), 24.47 (s, CH(*C*H_3)$_2$). Anal. Calcd. (%) for $C_{78}H_{69}BN_2OP_2$: C: 83.41; H: 6.19; N: 2.49; found: C: 82.95; H: 5.93; N: 2.55.

[4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·ZnMe]$^+$[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$, 2a.

Dimethylzinc (1.2 M in toluene, 50 μL, 0.0600 mmol) was added to a solution of **1a** (100 mg, 0.0600 mmol) in benzene (1 mL). The resulting mixture was triturated briefly and then left to stand for 30 min at ambient temperature. Pentane was added (~1 mL) to precipitate the product as a red/orange oil. The supernatant was decanted, and the oily product was washed thoroughly with pentane (3 x 1 mL). The resulting oil was dried *in vacuo*, yielding the product as an analytically pure white powder in 81.3% yield (85.2 mg, 0.0488 mmol). ^{1}H NMR (C_6D_5Br): δ 8.21 (s, 8H, *o*-$C_6H_3(CF_3)_2$), 7.78 (d, 2H, $^3J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.54 (s, 4H, *p*-$C_6H_3(CF_3)_2$), 7.40 (dd, 8H, $^3J_{PH}$ = 12.6 Hz, $^3J_{HH}$ = 7.5 Hz, *o*-Ph), 7.25 (t, 4H, $^3J_{HH}$ = 7.7 Hz, *p*-Ph), 7.20–7.00 (ov m, 12H, m-Ph + 2,8-dbf + 3,7-dbf), 6.60 (d, 4H, *m*-Pipp, $^3J_{HH}$ = 8.4 Hz), 6.52 (dd, 4H, $^3J_{HH}$ = 8.4 Hz, $^4J_{PH}$ = 1.5 Hz, *o*-Pipp), 2.53 (sp, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.00 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), –0.79 (s, 3H, ZnC*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_5Br): δ 25.4 (s). ^{19}F NMR (C_6D_5Br): δ –61.52 (s). ^{11}B{^{1}H} NMR (C_6D_5Br): δ –5.77 (s). ^{13}C NMR (C_6D_5Br): δ 162.3 (q, $^1J_{BH}$ = 49.9 Hz, *ipso*-$C_6H_3(CF_3)_2$), 156.06 (s), 143.58 (d, J_{PC} = 2.8 Hz), 142.31 (d, J_{PC} = 5.4 Hz), 135.07 (s, *o*-$C_6H_3(CF_3)_2$), 133.82 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Ph), 133.18 (d, $^2J_{PC}$ = 10.3 Hz, *o*-Ph), 131.74 (d, $^3J_{PC}$ = 8.4 Hz, 2,8-dbf), 129.28 (d, $^3J_{PC}$ = 12.7 Hz, *m*-Ph), 127.16 (s, *m*-Pipp), 126.96 (s, 1,9-dbf), 125.62 (d, $^3J_{PC}$ = 9.6 Hz, *o*-Pipp), 125.36 (d, $^2J_{PC}$ = 11.7 Hz, 3,7-dbf), 125.20 (s), 124.74 (q, $^1J_{FC}$ = 272.9 Hz, $C_6H_3(CF_3)_2$), 124.03 (d, J_{PC} = 5.8 Hz), 123.96 (d, J_{PC} = 8.7 Hz), 117.68 (sp, $^3J_{FC}$ = 3.7 Hz, *p*-$C_6H_3(CF_3)_2$), 112.62 (d, $^1J_{PC}$ = 107.5 Hz, 4,6-dbf), 33.23 (s, *C*H(CH$_3$)$_2$), 23.96 (s, CH(*C*H$_3$)$_2$), –11.30 (s, Zn-*C*H$_3$). Anal. Calcd. (%) for $C_{87}H_{63}BF_{24}N_2OP_2Zn$: C: 59.83; H: 3.64; N: 1.60; found: C: 59.66; H: 3.71; N: 1.65.

[4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·ZnMe]$^+$[BPh$_4$]$^-$, 2b.

Complex **2b** was prepared similarly to **2a** from **1b** (200 mg, 0.178 mmol) and dimethylzinc (1.2 M in toluene, 150 μL, 180 mmol), giving the compound in approximately 75% purity, as determined by ^{1}H and ^{31}P NMR spectroscopy. The impurity was identified to be the aryl analogue [4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·ZnPh]$^+$[BPh$_4$]$^-$, which was produced by transfer of a phenyl group from the BPh$_4$ anion. The material was isolated in an overall yield of 97.2% (208 mg, 0.173 mmol). ^{1}H NMR (C_6D_5Br): δ 7.87 (broad s, 8H, *o*-BPh$_4$), 7.68 (d, 2H, $^3J_{HH}$ = 7.6 Hz, 1,9-dbf), 7.39 (dd, 8H, $^3J_{PH}$ = 12.6 Hz, $^3J_{HH}$ = 7.6 Hz), 7.23 (t, 4H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph), 7.15–6.88 (ov m, 24H, *m*-BPh$_4$ + *p*-BPh$_4$ + *m*-Ph + 2,8-dbf + 3,7-dbf), 6.60 (d, 4H, $^3J_{HH}$ = 8.6 Hz, *m*-Pipp), 6.54 (dd, 4H, $^3J_{HH}$ = 8.6 Hz, $^4J_{PH}$ = 1.3 Hz, *o*-Pipp), 2.52 (sp, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.00 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), –0.79 (s, 3H, ZnC*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_5Br): δ 25.69 (**2b**), 27.29 ([4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·ZnPh]$^+$[BPh$_4$]$^-$). ^{11}B NMR (C_6D_5Br): δ –5.56 (BPh$_4$), –10.33 (CH$_3$BPh$_3$).

[4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·ZnOCH(Me)CO$_2$Me]$^+$[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$, 3.

In a glass bomb equipped with a magnetic stir bar **1a** (200 mg, 0.120 mmol) was mixed with a stoichiometric amount of EtZn(OCH(CH$_3$)CO$_2$CH$_3$) (23.7 mg, 0.120 mmol) dissolved in 3 mL of bromobenzene. The solution was then heated to 100 ºC with stirring. After cooling to ambient temperature, the solution was transferred to a 20 mL scintillation vial. The product was precipitated from solution as a red oil by addition of 5 mL of pentane. The resulting oil was twice redissolved in bromobenzene (1 mL) and reprecipitated by addition of pentane (2 mL). The product was washed twice with pentane and dried *in vacuo*, giving **3** in 56.8%

yield (125 mg, 0.0681 mmol). A single sharp resonance appears in the $^{31}P\{^{1}H\}$ NMR spectrum at δ 28.9 (C_6D_5Br), which at ambient temperature coexists with a very broad resonance between δ 33 and δ 30, with corresponding broad resonances occurring in the ^{1}H NMR spectrum. At elevated temperatures, these ^{31}P NMR signals coalesce to a single sharp peak. At all temperatures, two distinct structural isomers are apparent in the ^{1}H NMR spectrum, with a ratio of 3:1. ^{1}H NMR (C_6D_5Br, 80 ºC): δ 8.10 (s, 8H, *o*-$C_6H_3(CF_3)_2$), 7.86 (d, 2H, $^{3}J_{HH}$ = 6.9 Hz, 1,9-dbf), 7.57 (s, 4H, *p*-$C_6H_3(CF_3)_2$), 7.54–7.36 (m, 8H, *o*-Ph), 7.30–6.96 (ov m, 16H, *p*-Ph + *m*-Ph + 2,8-dbf + 2,7-dbf), 6.78 (d, 1H, $^{3}J_{HH}$ = 8.6 Hz, *o*-Pipp), 6.65 (d, 3H, $^{3}J_{HH}$ = 8.3 Hz, *o*-Pipp), 6.60 (d, 1H, $^{3}J_{HH}$ = 8.6 Hz, *m*-Pipp), 6.50 (dd, 3H, $^{3}J_{HH}$ = 8.3 Hz, $^{4}J_{PH}$ = 2.4 Hz, *m*-Pipp), 4.07 (q, 0.25H, $^{3}J_{HH}$ = 6.8 Hz, OC*H*$CH_3CO_2CH_3$), 3.78 (q, 0.75H, $^{3}J_{HH}$ = 6.8 Hz, OC*H*$CH_3CO_2CH_3$), 3.64 (s, 0.75H, $OCHCH_3CO_2CH_3$), 3.19 (s, 2.25H, $OCHCH_3CO_2CH_3$), 2.59 (sp, 2H, $^{3}J_{HH}$ = 6.9 Hz, C*H*$(CH_3)_2$), 1.34 (d, 0.75H, $^{3}J_{HH}$ = 6.8 Hz, $OCHCH_3CO_2CH_3$), 1.06 (d, 3H, $^{3}J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.02 (d, 9H, $^{3}J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 0.94 (d, 2.25H, $^{3}J_{HH}$ = 6.8 Hz, $OCHCH_3CO_2CH_3$). $^{31}P\{^{1}H\}$NMR (C_6D_5Br, 80 ºC): 29.17 (s). $^{19}F\{^{1}H\}$ NMR (C_6D_5Br, RT): δ –61.53 (s). $^{11}B\{^{1}H\}$ NMR (C_6D_5Br, RT): δ –5.78 (s). $^{13}C\{^{1}H\}$ NMR (C_6D_5Br, 80 ºC): (Note: Resonances are listed for both isomers, with the exception of quaternary carbons, which are too weak to be observed for the minor isomer. The ipso-Ph signal is not observed for either isomer due to obscuring solvent signals) δ 190.95 (s, $OCHCH_3CO_2CH_3$), 162.21 (q, $^{1}J_{BC}$ = 50.0 Hz, ipso-BAr_4), 157.49 (s, aromatic C), 144.74 (d, J_{PC} = 3.8 Hz,), 142.18 (d, J_{PC} = 6.8 Hz,), 135.08 (br s, *o*-BAr_4), 133.84 (d, J_{PC} = 2.9 Hz, *p*-Ph), 133.60 (d, J_{PC} = 9.9 Hz, *o*-Ph), 133.38 (d, J_{PC} = 3.1 Hz, *p*-Ph), 133.26 (d, J_{PC} = 9.9 Hz, *o*-Ph), 132.79 (d, J_{PC} = 10.5 Hz, 2,7-dbf), 132.42 (d, J_{PC} = 8.3 Hz, 2,7-dbf), 131.86 (s, aromatic C), 129.30 (d, J_{PC} = 13.3 Hz, *m*-Ph), 128.92 (d, J_{PC} = 12.5 Hz, *m*-Ph), 128.35 (d,

J_{PC} = 7.6 Hz, *o*-Pipp), 128.28 (s), 127.16 (s, *m*-Pipp), 126.58 (s, *m*-Pipp), 126.55 (s, 1,9-dbf), 125.45 (d, J_{PC} = 3.3 Hz, aromatic C), 125.03 (d, J_{PC} = 10.0 Hz, *o*-Pipp), 124.74 (q, $^{1}J_{FC}$ = 272.9 Hz, $C_6H_3(CF_3)_2$), 124.54 (d, J_{PC} = 11.8 Hz, 3,4-dbf), 117.60 (br s, *p*-$C_6H_3(CF_3)_2$), 111.64 (d, $^{1}J_{PC}$ = 106.1 Hz, 4,6-dbf), 69.89 (s, O*C*H$CH_3CO_2CH_3$), 67.33 (s, O*C*H$CH_3CO_2CH_3$), 53.68 (s, CHCH_3CO_2*C*H_3), 53.16 (s, CHCH_3CO_2*C*H_3), 33.30 (s, *C*H$(CH_3)_2$), 23.88 (s, CH(*C*$H_3)_2$), 23.77 (s, CH(*C*$H_3)_2$), 23.46 (s, CH*C*$H_3CO_2CH_3$), 23.31 (s, CH*C*$H_3CO_2CH_3$). Anal. Calcd. (%) for $C_{90}H_{67}BF_{24}N_2O_4P_2 \cdot C_6H_5Br$: C: 57.89; H: 3.64; N: 1.41; found: C: 58.02; H: 3.80; N: 1.43.

Polymerization Experiments - In-Situ Observation

In a glovebox, an NMR tube was loaded with an appropriate amount of catalyst (e.g. 4.6 mg for $[LA]_0/[\mathbf{3}]$ = 200) and 72.1 mg of *rac*-Lactide, to which 0.50 mL of CD_2Cl_2 was then added. The tube was immediately sealed with a rubber septum, removed from the glove box, and cooled to –78 ºC. The tube was then immediately transported to the temperature stabilised and pre-shimmed NMR instrument. The tube was then allowed to warm and was inserted into the probe after complete dissolution of the *rac*-Lactide. The polymerization was monitored to at least 3 half-lives (90–95%). For determination of activation parameters, temperatures were calibrated using Bruker calibration data, which gave the relation $T_{actual} = 1.111T_0 - 1.8505$.

Polymerization Experiments - Large Scale Preparation

General procedure: In a glove box with an ambient temperature of approximately 26 ºC, a scintillation vial was loaded with 144.1 mg of *rac*-lactide and an appropriate amount of catalyst (e.g. 9.2 mg for M:I = 200). To the vial 1 mL of CH_2Cl_2 was added and the resulting

solution was stirred for an appropriate period of time (Table S3). Following this, the vial was removed from the glove box and exposed to the atmosphere. To the solution 10 mL of cold (–35 ºC) wet methanol was added, causing the polymer to precipitate. The vial was centrifuged and the solvent decanted. The isolated polymer was redissolved in 1 mL of CH_2Cl_2 and reprecipitated and isolated by the same procedure. The polymer sample was then dried *in vacuo* for 24 hours.

Details of Crystal Refinement

4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran, L. Crystals of **L** were grown from a solution of the compound in a mixture of pentane and methylene chloride at –35 ºC. The reflection data were consistent with the orthorhombic space group $Pca2_1$, and the structure was determined at a resolution of 0.84 Å. The asymmetric unit contained a single molecule of the compound in addition to a single molecule of pentane. One of the *iso*propyl groups is disordered over two sites, at an approximate 60:40 ratio. The unit cell contains total solvent accessible voids of 396 Å^3, which have been accounted for using the SQUEEZE subroutine of the PLATON software suite. A total of only 24 electrons were removed (3 electrons per asymmetric unit), and have been left unassigned. The largest residual electron density peak (0.265 eÅ^{-3}) is associated with one of the P–C_{Ph} bonds. Full-matrix least squares refinement on F^2 gave R_1 = 0.0517 for 2σ data and wR_2 = 0.1238 for all data (GoF = 1.106). Crystal data are summarized in **Table S1**, and the structure is depicted in **Figure S1**.

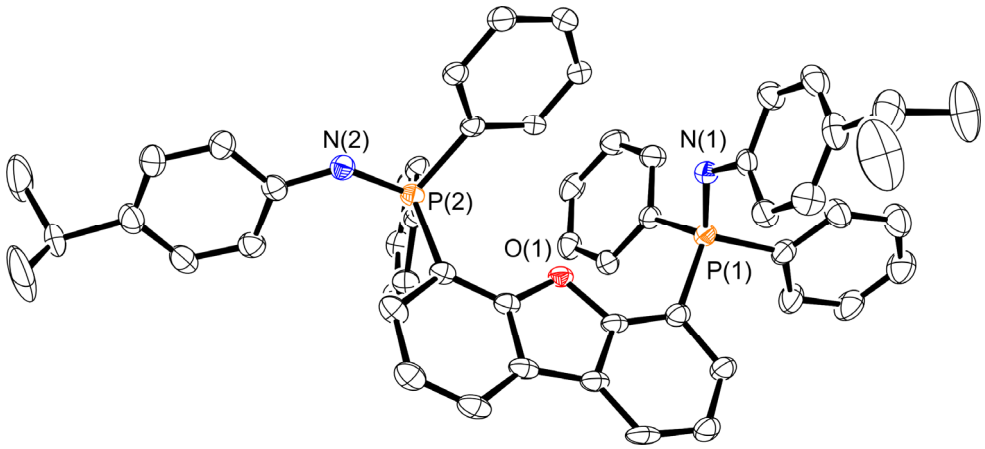

Figure S1 Solid-state structure of **L**, showing 30% thermal ellipsoids and with hydrogen atoms omitted for clarity.

[4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·ZnMe/Ph]$^+$[BPh$_4$]$^-$, 2b. Single crystals containing a mixture of **2b** and **[4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·ZnPh]$^+$[BPh$_4$]$^-$** were grown by slow diffusion of pentane into a solution containing both compounds in a benzene/bromobenzene mixture at ambient temperature. The reflection data were consistent with the space group P(-1), and the structure was determined at a resolution of 0.84 Å. A phenyl group of the ligand and a phenyl group of the anion were modelled as a disorder over two sites, while all other atoms are well ordered. The mixture of **2b** and **[4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·ZnPh]$^+$[BPh$_4$]$^-$** was modelled as a disorder, where a methyl group occupies the coordination site of zinc 84% of the time, while a phenyl ring exists in its place for the remaining 16%. The unit cell contains solvent accessible voids totalling 433 Å^3 (11.9% of the unit cell). These voids were accounted for using the SQUEEZE subroutine of the PLATON software suite, resulting in reduced residuals. 120 electrons were removed, and have been assigned to 1 molecule of benzene and 1 molecule of bromobenzene (0.5 molecules of benzene and 0.5 molecules of bromobenzene per asymmetric unit). The largest residual electron density peak (0.536 eÅ^{-3}) is associated with one of the P–C$_{Ph}$ bonds of the

ligand. Full-matrix least squares refinement on F^2 gave R_1 = 0.0507 for 2σ data and wR_2 = 0.1284 for all data (GoF = 1.035). Crystal data are summarized in **Table S1**.

[4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·ZnOCH(CH$_3$)CO$_2$CH$_3$]$^+$[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$, 3.

Single crystals of **3** were grown at ambient temperature from a dilute solution of the compound in a mixture of benzene and pentane. The reflection data were consistent with the space group P2(1)/c. Only small, weakly diffracting crystals could be obtained, and the structure was this determined at a resolution of 1 Å. Many CF_3 groups of the anion are poorly ordered, and four of these have been modelled as a disorder over two sites, with relative occupancies of the minor components ranging from 24 to 48%. Additionally, one of the *iso*propyl groups of the ligand is disordered over two sites in a 62:38 ratio. The lactate moiety is also disordered, apparently due to the presence of both enantiomers in a 50:50 mixture. Only the CH(CH_3) methyl group is explicitly modelled over two sites, though other atomic positions of the lactate moiety are poorly ordered as well, causing larger thermal parameters, especially for OCH_3. The asymmetric unit contains one molecule of benzene which is disordered over two sites. With the exception of disordered atoms already described, all atomic positions of the cationic component are very well ordered and display small thermal parameters. The largest residual electron density peak (0.486 eÅ^{-3}) is associated with a poorly ordered CF_3 group. Full-matrix least squares refinement on F^2 gave R_1 = 0.0761 for 2σ data and wR_2 = 0.1665 for all data (GoF = 1.106). Crystal data are summarized in **Table S1**.

Table S1. Details of the crystallographic data and refinements for **L**, **2b/[4,6-(4-^{i}PrPh-N=PPh$_2$)$_2$dibenzofuran·ZnPh]$^+$[BPh$_4$]$^-$**, and **3**.

Complex	**L · C_5H_{12}**	**2b · C_6H_6 · C_6H_5Br**	**3 · C_6H_6**
Empirical Formula	$C_{59}H_{60}N_2OP_2$	$C_{85}H_{76.5}BBr_{0.5}N_2OP_2Zn$	$C_{96}H_{73}BF_{24}N_2O_4P_2Zn$
Formula Weight	875.03	1320.09	1912.68
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal System	Orthorhombic	Triclinic	Monoclinic
Space Group	Pca2(1)	P(-1)	P2(1)/c
a / Å	26.938(3)	9.878(7)	19.087(2)
b / Å	18.828(2)	17.43(1)	26.603(2)
c / Å	10.274(1)	21.93(1)	19.538(2)
α / °	90	80.235(8)	90
β / °	90	82.751(8)	116.133(1)
γ / °	90	80.160(8)	90
V / Å^3	5211.1(9)	3647(4)	8907(1)
Z	4	2	4
ρ_{calc} / Mg m^{-3}	1.115	1.095	1.426
μ / mm^{-1}	0.123	0.423	0.415
Crystal Size / mm^3	0.49 x 0.15 x 0.14	0.58 x 0.40 x 0.14	0.27 x 0.15 x 0.09
Theta Range / °	2.16 to 25.03°	2.58 to 25.03	1.92 to 20.81
Reflections Collected	61302	44021	72717
Independent Reflections	9201 [R(int) = 0.0504]	12848 [R(int) = 0.0270]	9322 [R(int) = 0.0803]
Goodness-of-fit on F^2	1.106	1.035	1.275
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0517; $wR2$ = 0.1195	$R1$ = 0.0507; $wR2$ = 0.1231	$R1$ = 0.0761; $wR2$ = 0.1605
R indices (all data)	$R1$ = 0.0602; $wR2$ = 0.1238	$R1$ = 0.0621; $wR2$ = 0.1284	$R1$ = 0.0932; $wR2$ = 0.1665
Absolute structure parameter	-0.01(9)		
Largest diff. peak/hole (eÅ^{-3})	0.265 and -0.177	0.536 and -0.525	0.486 and -0.424

Kinetic Data for Polymerization of *rac*-Lactide with 3

Table S2. Rate constants measured for various concentrations of catalyst **3**.

Concentration of 3 ($mol \cdot L^{-1}$)	k_{obs} (s^{-1})
0.01	$1.65(1) \times 10^{-3}$
0.008	$1.317(7) \times 10^{-3}$
0.006	$1.081(4) \times 10^{-3}$
0.005	$8.65(4) \times 10^{-4}$
0.004	$8.43(4) \times 10^{-4}$
0.002	$1.921(5) \times 10^{-4}$
0	0

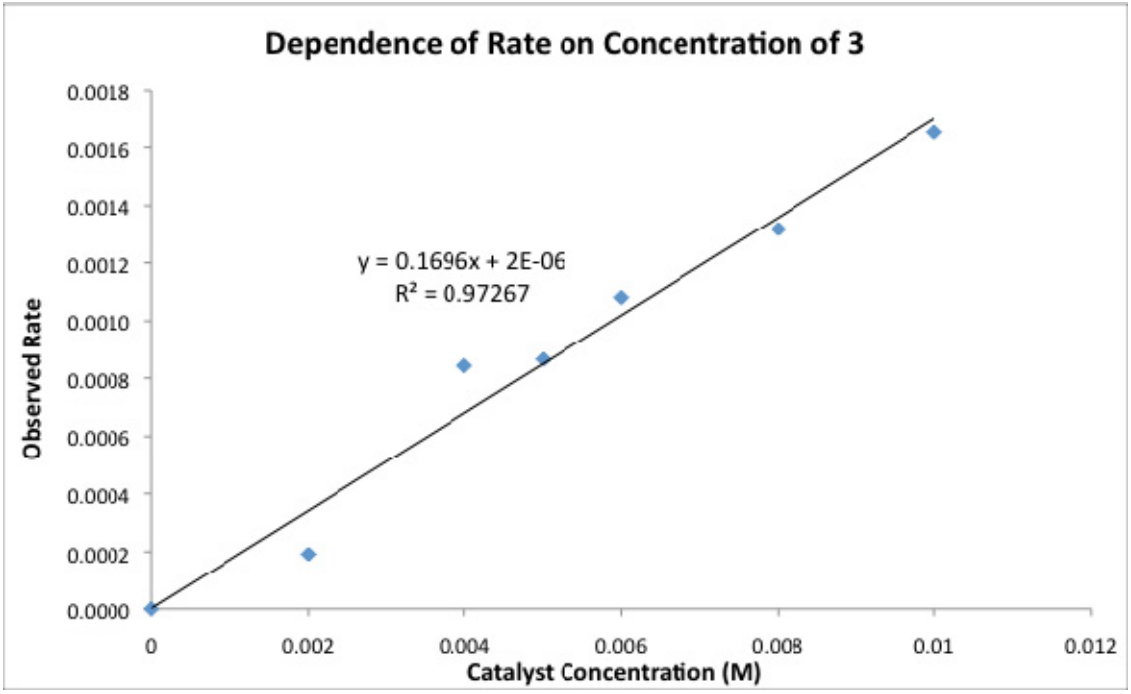

Figure S2. Plot depicting the linear dependence of rate on [**3**].

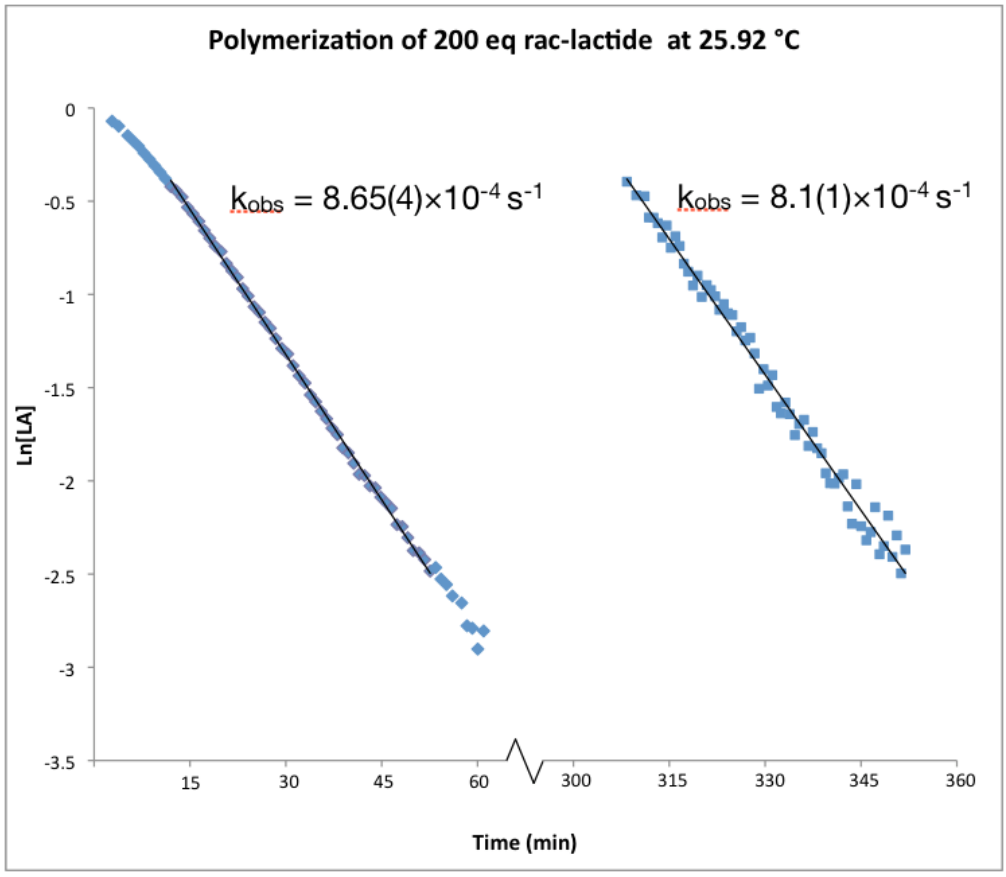

Figure S3. Living polymerization experiment showing the polymerization of 200 equiv of LA followed by another 200 equiv at virtually the same rate when added 4 hours later.

Activation Parameters

Table S2. Measured rates of polymerization of *rac*-lactide by **3** at various temperatures.

Temperature (°C)	k_{obs} (s^{-1})	Ln(k_{obs}/T) ($mol \cdot s^{-1} \cdot K^{-1}$)
37.03	$1.94(1) \times 10^{-3}$	–11.98
31.48	$1.265(5) \times 10^{-3}$	–12.39
25.92	$8.65(4) \times 10^{-4}$	–12.75
14.80	$3.90(2) \times 10^{-4}$	–13.51
3.70	$1.90(1) \times 10^{-4}$	–14.19
–7.41	$7.58(6) \times 10^{-5}$	–15.07

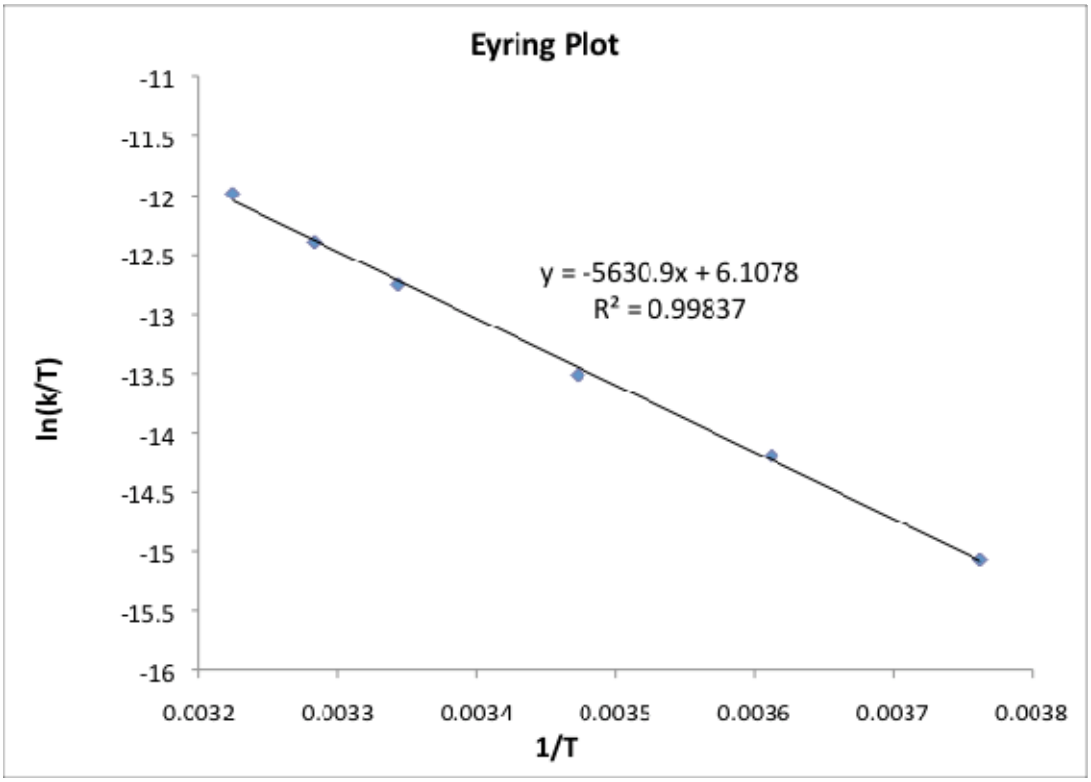

Figure S4. Eyring plot for determination of the activation parameters of polymerization of *rac*-lactide with **3**.

Polymer Characterization

MALDI mass spectra were performed on an ultraflexXtreme™ MALDI-TOF/TOF (Bruker Daltonics, Billerica, MA, USA) mass spectrometer in positive MS mode. MALDI-ToF mass spectra were obtained using 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix compound. The solution of the matrix compound was prepared in CH_2Cl_2 with a final concentration of 15 mg/mL. The sample was dissolved in CH_2Cl_2 with a concentration of approximately 0.1–1 mg/mL and mixed with an equal volume of the matrix solution. A MALDI plate was then loaded with 0.5–1 µL of the sample/matrix solution and allowed to dry.

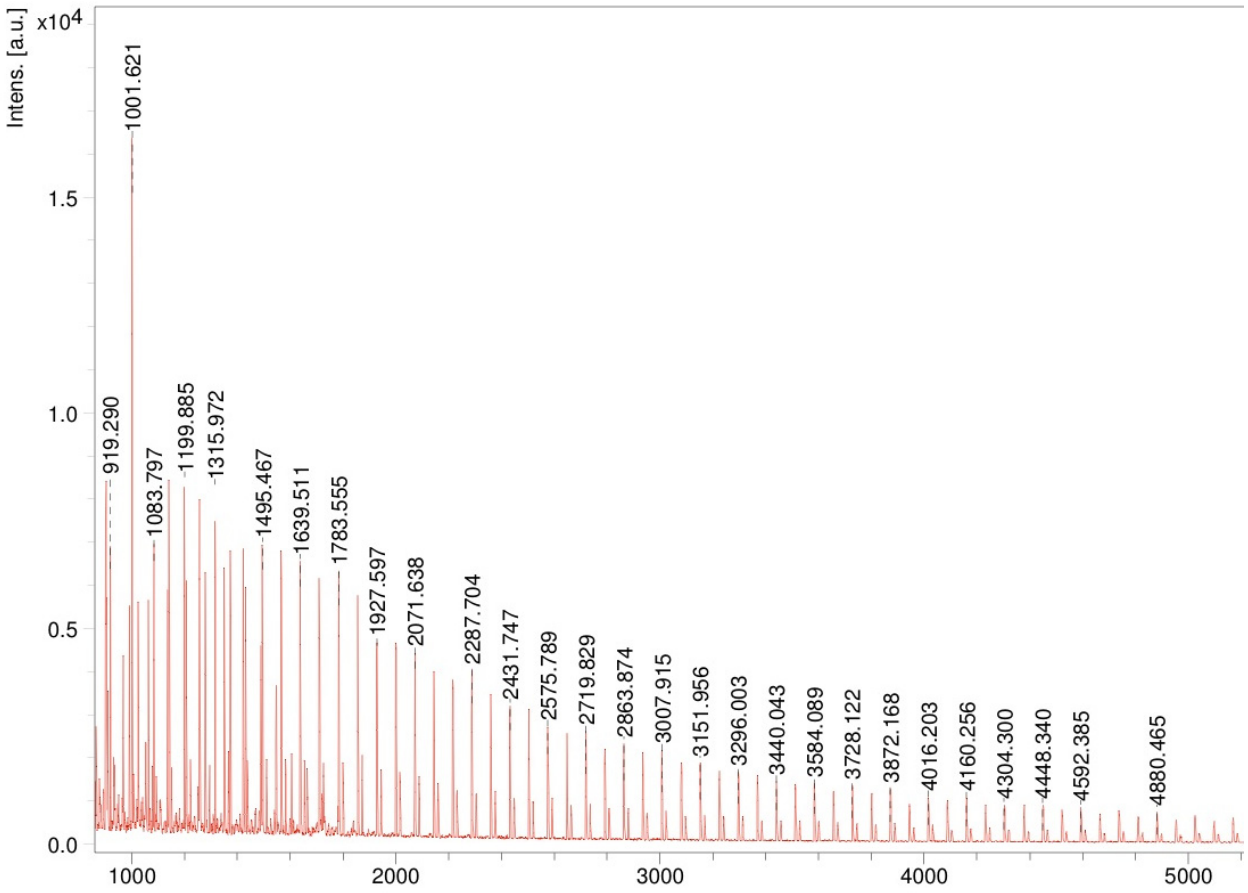

Figure S5. MALDI-TOF mass spectrum of a PLA sample prepared with catalyst **3** using a monomer to initiator ratio of 50.

GPC

Instrument Details

GPC analyses were performed on a Waters 2695 equipped with a Waters 410 refractive index detector and a Wyatt light scattering detector. Solutions of the polymer samples were prepared in THF to a concentration of approximately 5 mg/mL, except for the samples with M:I = 100, which were prepared at higher concentration to improve signal strength. All samples were filtered (0.2 μm) prior to performing the analysis, and were run at a temperature of 40 ºC. Light scattering data were processed using dn/dc = 0.049.

Data

Table S3. GPC data for polymer samples prepared at various catalyst loadings of **3**.

Entry	*M:I*	*Isolated Yield (%)*	*Time (h)*	*Calc. M_n ($\times 10^3$)*	*M_n ($\times 10^3$)*	*M_w($\times 10^3$)*	*PDI*
1	100	99	1	14.3	12.9	17.3	1.34
2	200	98	1	28.3	28.7	33.0	1.15
3	300	92	1.5	39.8	35.0	37.8	1.08
4	400	90	2.5	51.9	33.4	36.5	1.09
5	500	98	2.5	70.6	41.9	50.7	1.21
6	1000	99	5	142.7	49.9	63.4	1.30
7	400[a]	98	3[a]	56.5	31.5	38.2	1.21

[a] Sample prepared by sequentially polymerizing two batches of 200 equiv of *rac*-Lactide for 90 min at each stage.

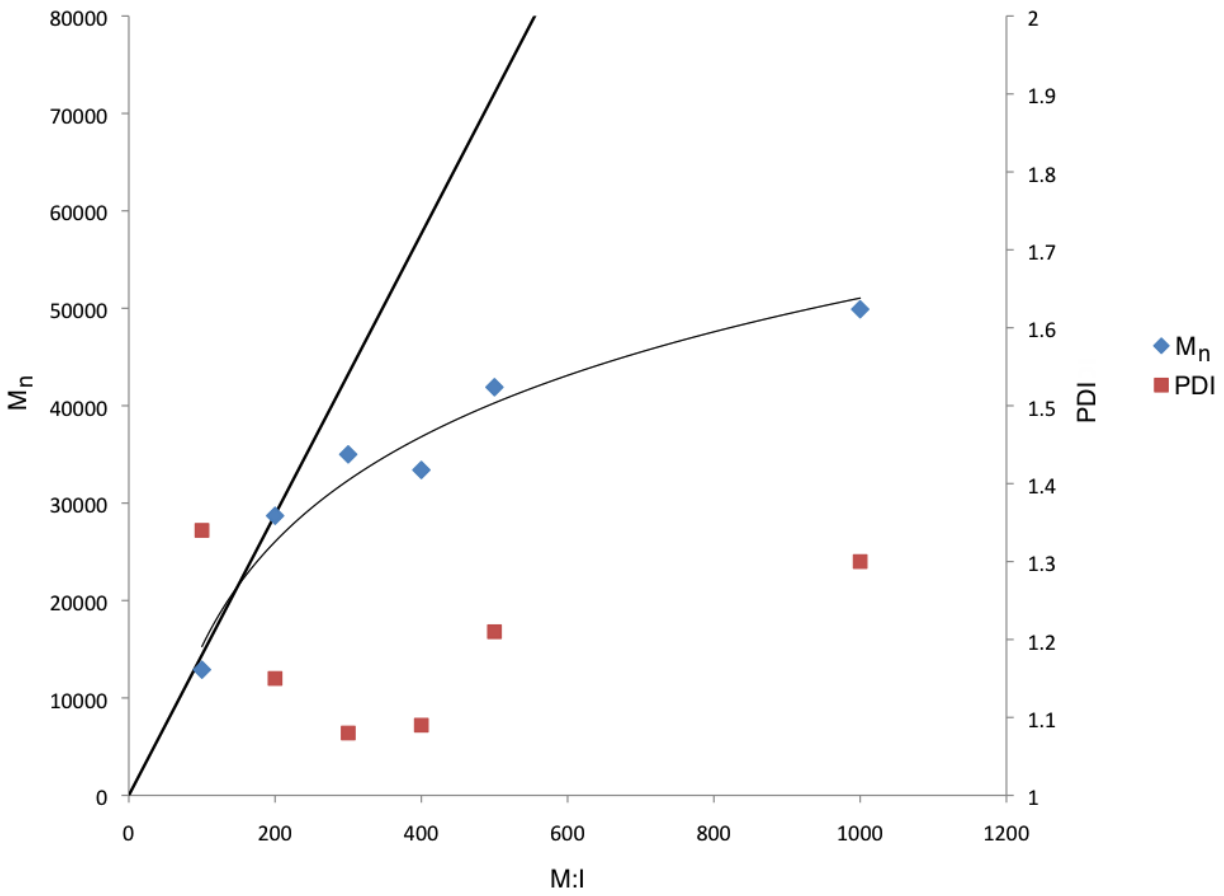

Figure S6. Plot of M_n and PDI versus catalyst loading.

Polymer Microstructure Analysis

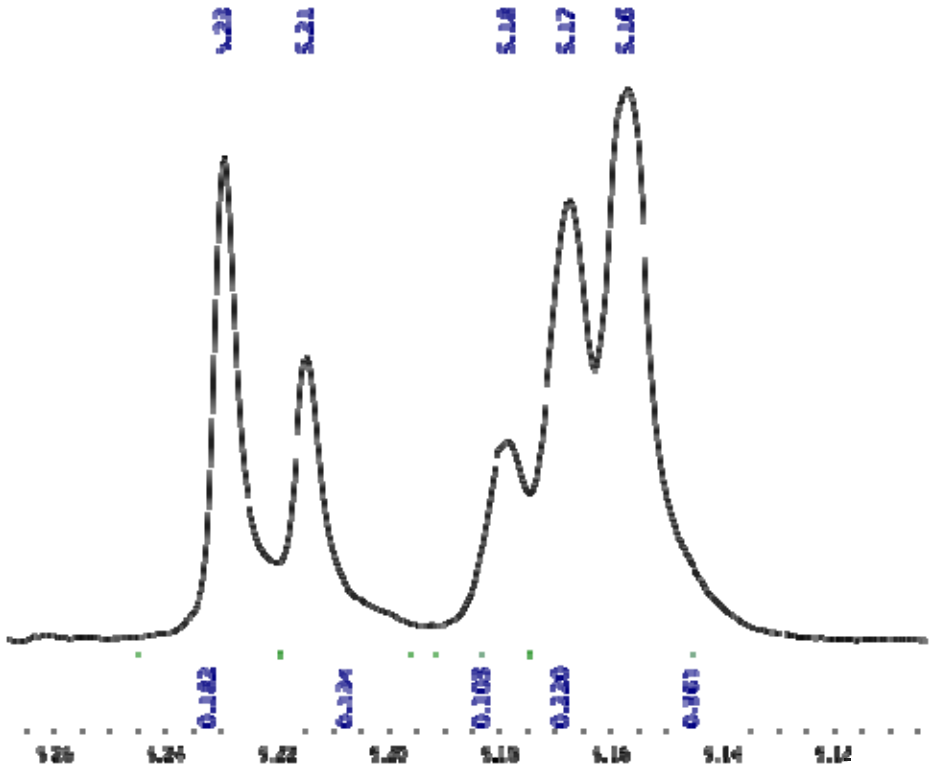

Figure S7. Homodecoupled ^{1}H NMR spectrum of the methine region of PLA produced using **3** as the catalyst.