Electronic Supplementary Information for A Dual Organic/Organometallic Approach for Catalytic Ring-Opening Polymerization.

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Materials and methods

All manipulations were carried out using either standard Schlenk line or drybox techniques under an inert atmosphere of argon. Solvents were dried and degassed before use, toluene (>99.9%) and dichloromethane (>99.95%) issued from purification columns (MBraun MB SPS-800) were distilled over NaK alloy for toluene and over CaH_2 for dichloromethane. Deuterated solvents were dried over P_2O_5 ($CDCl_3$), NaK alloy (C_6D_6) or molecular sieves 4Å (CD_2Cl_2) and distilled under reduced pressure. D,L-Lactide and L-Lactide were purchased from Purac and purified prior to use by recrystallization from toluene followed by repeated (2x) vacuum sublimation. All *neo*-pentanol was purchased from Aldrich and dried over Na for 1h or over molecular sieves (4Å) for 24h, and distilled under reduced pressure before use. All amines were dried over CaH_2 and distilled under reduced pressure before use. All solvents and reagents were stored in a drybox. Complex {ONN}ZnEt (**1**) was synthesized following the literature procedure.[1] $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$ was obtained from Boulder Chemicals and used as received.

Instrumentation and characterization

NMR analysis. ^{1}H (500 and 300 MHz), ^{13}C (125 MHz), ^{11}B (128 MHz), ^{19}F (188 MHz) NMR spectra were recorded in $CDCl_3$ on Bruker Avance AM 500 and AM 300 spectrometers at 20 °C. Chemical shifts (δ) are reported in ppm and were referenced internally relative to tetramethylsilane (δ 0 ppm) using the residual ^{1}H and ^{13}C solvent resonances.

Elemental analysis. Elemental analyses were performed on a Carlo Erba 1108 Elemental Analyser instrument at the London Metropolitan University by Stephen Boyer and are the average of a minimum of two independent measurements.

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[1] C. K. Williams, L. E Breyfogle, S. K. Choi, W. Nam, V. G. Young Jr., M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.* 2003, **125**, 11350.

SEC analysis. The number-average and weight-average molar masses (M_n and M_w, respectively) and molar mass distributions (M_w/M_n) of the PLA samples were determined by size exclusion chromatography (SEC) at 35ºC with a triple detection system, equipped with an Alliance Waters e2695, a multiangle light scattering detector (Wyatt Technology miniDAWN), a viscometer (Wyatt Technology Viscostar-II), and a refractive index detector (Waters 2414). THF (HPLC grade) was used as an eluent with a flow rate of 1 mL min^{-1}. The SEC system was equipped with a Styragel (WAT054405) pre-column, and two Shodex (KF-802.5 and KF-804) columns. Calibrations were performed using polystyrene standards (400 – 100 000 g/mol). Samples were prepared by dissolving the product (10 – 20 mg) in 1 mL of THF, and toluene was used as a marker. The solutions were then filtered with a 0.45µm filter.

Synthesis of [{NNO}Zn]$^+$[B(C_6F_5)$_4$)]$^-$ (2). An equimolar amount of [HNMe$_2$Ph]$^+$[B(C_6F_5)$_4$]$^-$ (1.94 g, 2.40 mmol) and of the neutral precursor {ONN}ZnEt (**1**) (1.00 g, 2.40 mmol) was dissolved in dry THF (20 mL) at room temperature. The resulting mixture was stirred for 1 h and then concentrated to *ca*. 10 mL. Dropwise addition of pentane (*ca*. 20 mL) allowed the precipitation of [{NNO}Zn]$^+$[B(C_6F_5)$_4$)]$^-$ (**2**) as a white powder, which was filtered, washed with benzene (3 × 5 mL) and dried under vacuum (2.50 g, 86%). Compound **2** is insoluble in benzene, poorly soluble in toluene and readily soluble in THF, in which it remains stable at room temperature for at least several days. ^{1}H NMR (THF-d_8, 500 MHz, 25 °C) (see figure S1-S3 for labeling of H and C atoms): δ 7.37 (d, $^4J_{H\text{-}H}$= 2.7 Hz, 1H, H^3 ArH), 7.01 (d, $^4J_{H\text{-}H}$= 2.4 Hz, 1H, H^4 ArH), 4.41 (d, $^2J_{H\text{-}H}$= 12.0 Hz, 1H, H^5 NC*H*HAr), 3.40 (t, $^2J_{H\text{-}H}$= 10.1 Hz , 1H, H^8 NCH$_2$C*H*HNMe$_2$), 3.28 (d, $^2J_{H\text{-}H}$= 12.0 Hz, 1H, H^5 NCH*H*Ar), 3.14 (m, 1H, H^7 NC*H*HCH$_2$NMe$_2$), 2.94 (m, 2H, H^{7,8} NCH*H*CH*H*NMe$_2$), 2.81 (s, 6H, H^9 NC*H*$_3$), 2.51 (s, 3H, H^6 NC*H*$_3$), 1.58 (s, 9H, H^2, C(C*H*$_3$)$_3$), 1.40 (s, 9H, H^1, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz, 25 C): δ 163.0 (C$_{13}$), 149.0 (d, $^1J_{C\text{-}F}$ = 242 Hz, *o*-C, C_6F_5), 139.3 (d, $^1J_{C\text{-}F}$ = 257 Hz, *p*-C, C_6F_5), 138.0 (C$_{12}$), 137.3 (d, $^1J_{C\text{-}F}$ = 222 Hz, *m*-C, C_6F_5), 137.2 (C$_{11}$), 126.8 (C$_4$), 124.9 (C$_3$), 124.8 (C-B), 121.9 (C$_{10}$), 62.1 (C$_5$), 57.9 (C$_8$), 54.7 (C$_7$), 48.2 (C$_9$), 46.9 (C$_9$), 43.9 (C$_6$), 35.9 (C$_2$'), 34.4 (C$_1$'), 32.1 (C$_1$), 30.2 (C$_2$). ^{19}F{^{1}H} NMR (188 MHz, THF-d_8, 25 °C) δ −135.1 (d, $^3J_{F\text{-}F}$= 9.4 Hz, 2F, *o*-F, C_6F_5), −167.3 (t, $^3J_{F\text{-}F}$= 20.7 Hz, 1F, *p*-F, C_6F_5), −170.8 (t, $^3J_{F\text{-}F}$= 18.8 Hz, 1F, *m*-F, C_6F_5). ^{11}B NMR (128 MHz, THF-d_8, 25 °C): δ −18.4. Elem. Anal. ($C_{44}H_{35}BF_{20}N_2OZn$): Calcd. C 49.67, H 3.32, N 2.63, Found C 49.58, H 3.37, N 2.53.

Typical polymerization procedure. All glassware used for polymerizations was oven-dried. Three stock solutions of zinc complex, *neo*pentanol and pentamethylpiperidine (PMP) were prepared in 0.2M, 1.0M and 0.2M concentration respectively, immediately prior to use. A representative procedure is given below. In the glovebox, a Schlenk tube was charged with LA (0.130 g, 0.902 mmol, 100 equiv) and CH_2Cl_2 (1.8 mL). A solution of zinc complex **1** (22.5µL, 4.5 x 10^{-3} mmol, 0.5 equiv) in CH_2Cl_2 was added to the monomer solution and stirred for few seconds at room temperature. A solution of *neo*pentanol (9µL, 9.0 x 10^{-3} mmol, 1 equiv) was added to the mixture and then, the PMP solution was added (22.5µL, 4.5 x 10^{-3} mmol, 0.5 equiv). After stirring for an appropriate time, an aliquot was withdrawn from the reaction and quenched with a MeOH/HCl (1%) solution. The solvent was evaporated under vacuum, and the crude material was analyzed by ^{1}H NMR spectroscopy in $CDCl_3$. ^{1}H NMR measurements were used to determine the monomer conversion, the NMR degree of polymerization (DP_{NMR}) and the end-group fidelity. Monomer conversion was determined from the relative intensities of the CH signals for the monomer (q, 5.05 ppm, J = 6.9Hz) and polymer (m, 5.09 ppm- 5.21 ppm). DP_{NMR} was determined from the relative intensities of the CH signals for the polymer (m, 5.09 ppm- 5.21 ppm) and the terminal ^{t}Bu signal of the *neo*-pentyl end group (s, 0.92 ppm). Complete consumption of LA is reached after 3h. The polymer was isolated in 90% yield after precipitation in cold methanol or ether, filtration and drying under vacuum. ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C): 0.92 ppm (s, 9H, $CH_2C(C\mathbf{H}_3)_3$), 1.60 – 1.40 ppm (m, 600H, $OCHC\mathbf{H}_3$), 3.80 ppm (dd, J = 0.9 Hz, J = 10.5 Hz, 1H, $C\mathbf{H}_2C(CH_3)_3$), 3.88 ppm (dd, J = 2.1 Hz, J = 10.5 Hz, 1H, $C\mathbf{H}_2C(CH_3)_3$), 4.20 ppm (q, J = 7.2 Hz, 1H, $HOC\mathbf{H}CH_3$), 5.10 – 5.20 ppm (m, 200H, $OC\mathbf{H}CH_3$). SEC (THF): $M_n \approx$ 22 000 g/mol and $M_w/M_n \approx$ 1.10 – 1.30.

Procedure for *in situ* observation of D,L-LA Polymerization: Polymerization was carried out in an NMR tube (CD_2Cl_2 solution) by adding 4.8 mg of the cationic zinc complex (0.5 equiv.) and 130 mg of D,L-Lactide (100 equiv.). The reaction was monitored by ^{1}H NMR (300 MHz) at 25°C. At t = 0, a CD_2Cl_2 solution of *neo*-Pentanol (9 µL of 1M, 1 equiv.) and PMP (22,5 µL of 0,2M, 0,5 equiv.) was added. NMR spectra were recorded every 30 minutes over 3h until complete monomer conversion.

Second-feed polymerization procedure: 50 equiv. of *D,L*-Lactide were polymerized with $[Zn(NNO)][B(C_6F_5)_4]$/*n*-Pentanol/PMP (0,5 equiv./1 equiv./0.5 equiv.) in dichloromethane at 25 °C. After 3h, SEC analysis indicated the formation of a PLA (98% conversion) with M_n = 8 000 g/mol and M_w/M_n = 1.29. Polymerization was then restarted with 100 equiv. of *D,L*-Lactide to afford, after additional 3h, a PLA (96% conversion) with M_n = 22 000 g/mol and M_w/M_n = 1.27.

Figure S1. ^{1}H NMR spectrum (500 MHz, THF-d_8, 25 °C) of $[\{ONN\}Zn]^+[B(C_6F_5)_4]^-$ (**2**) (* stands for residual THF).

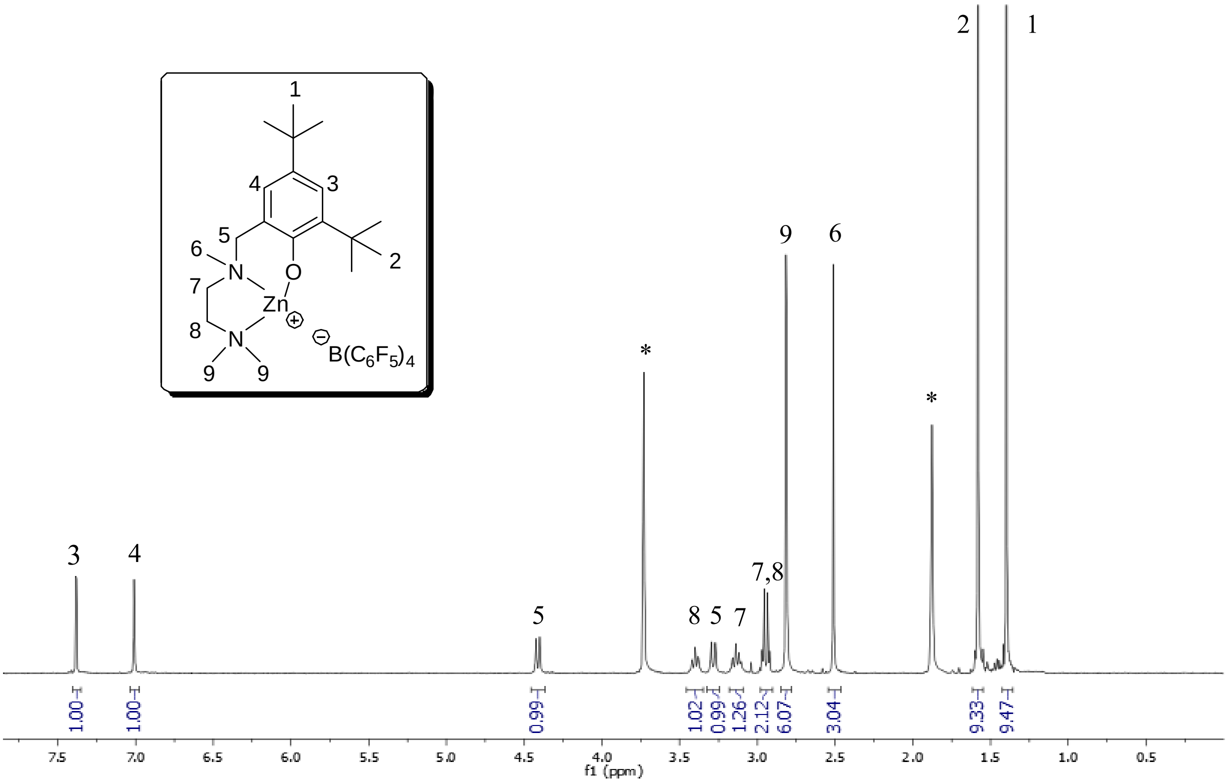

Figure S2. Detail of the ^{1}H-^{1}H COSY NMR spectrum (500 MHz, THF-d_8, 25 C) of [{ONN}Zn]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**2**) (* stands for residual THF).

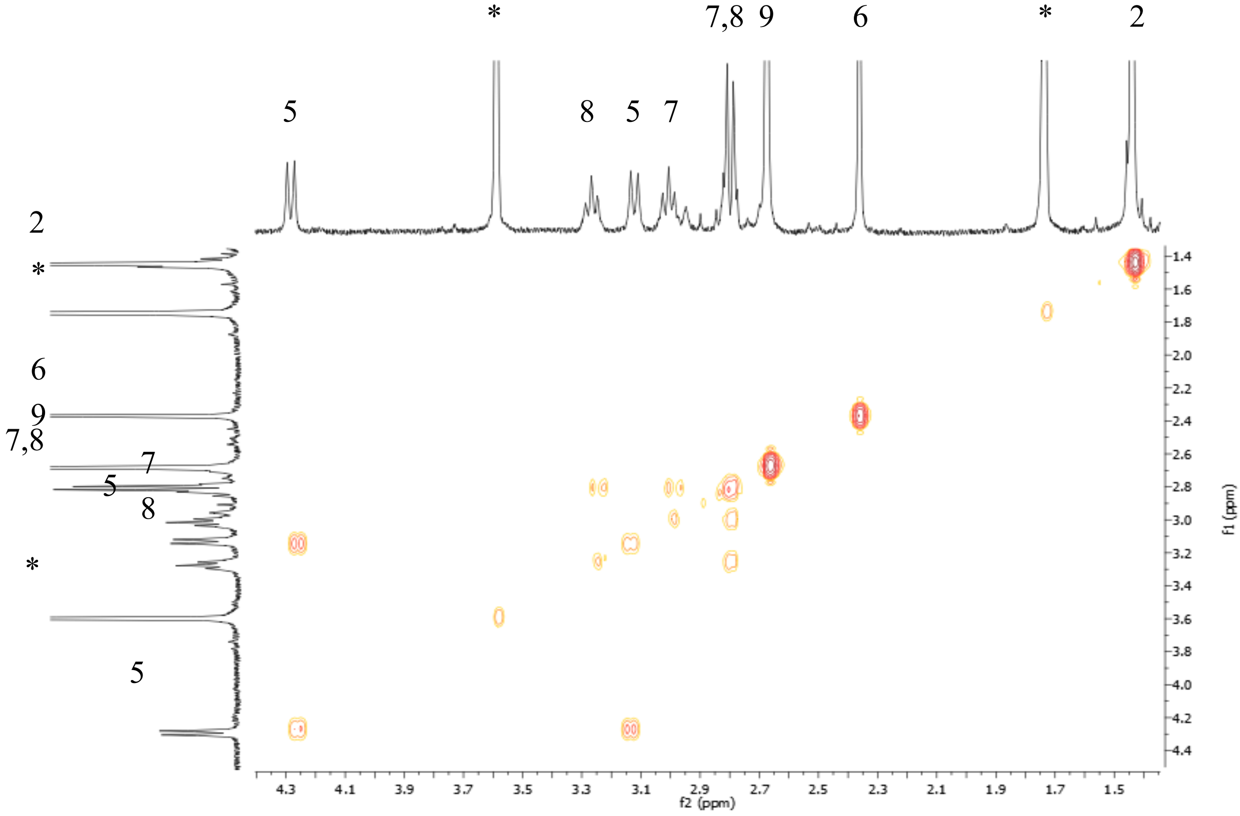

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, THF-d_8, 25 °C) of $[\{ONN\}Zn]^{+}[B(C_6F_5)_4]^{-}$ (**2**) (* stands for residual THF).

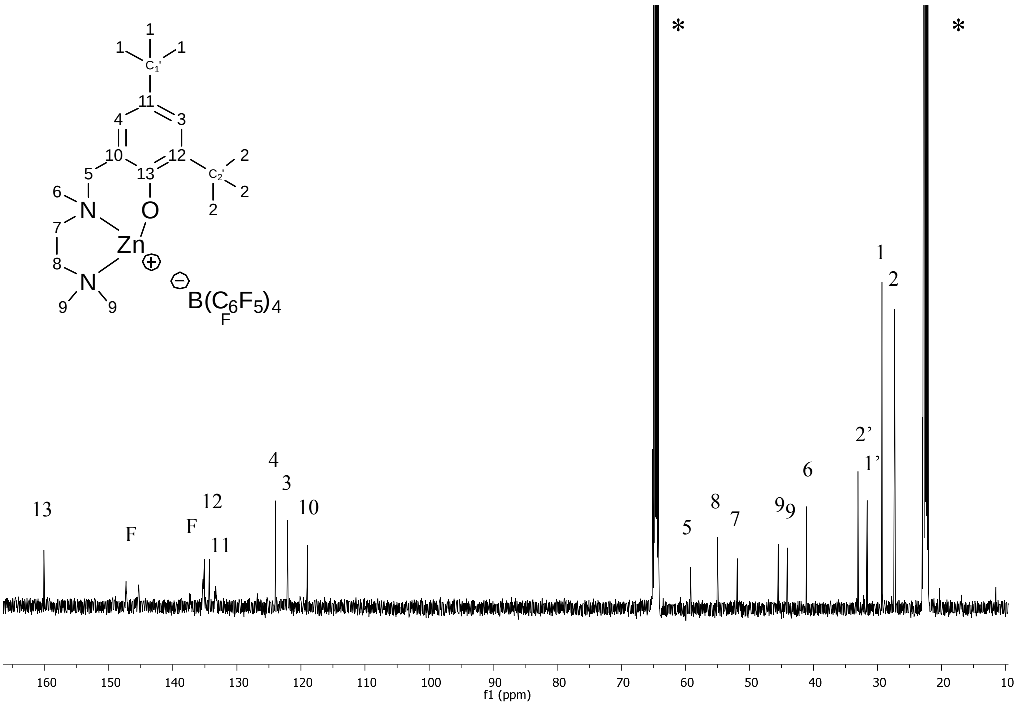

Figure S4. $^{19}F\{^{1}H\}$ NMR spectrum (188 MHz, THF-d_8, 25 °C) of $[\{ONN\}Zn]^{+}[B(C_6F_5)_4]^{-}$ (**2**).

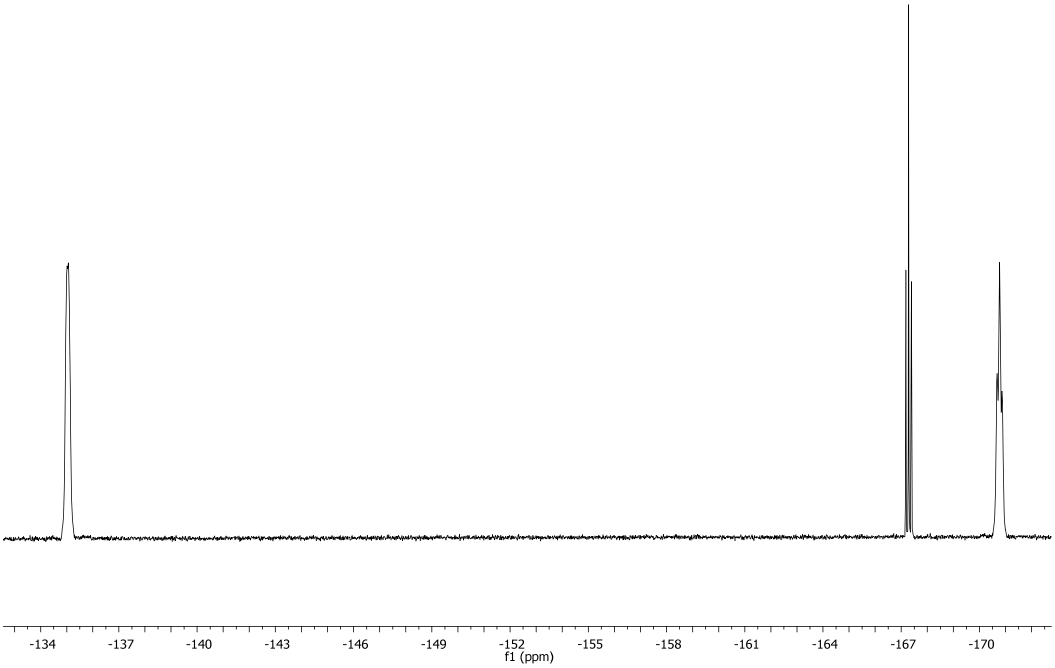

Figure S5. $^{11}B\{^1H\}$ NMR spectrum (128 MHz, THF-d_8, 25 °C) of $[\{ONN\}Zn]^+[B(C_6F_5)_4]^-$ (**2**).

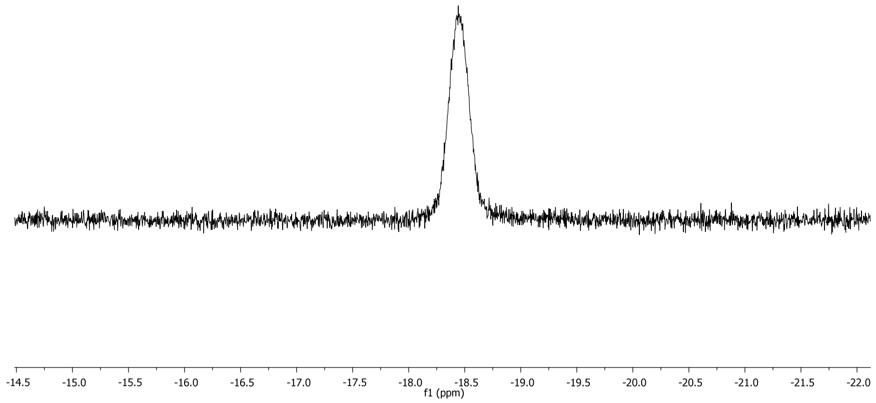

Figure S6. ^{1}H-^{13}C HMQC NMR spectrum (400 MHz, THF-d_8, 25 °C) of $[\{ONN\}Zn]^{+}[B(C_6F_5)_4]^{-}$ (**2**) (* stands for residual THF)

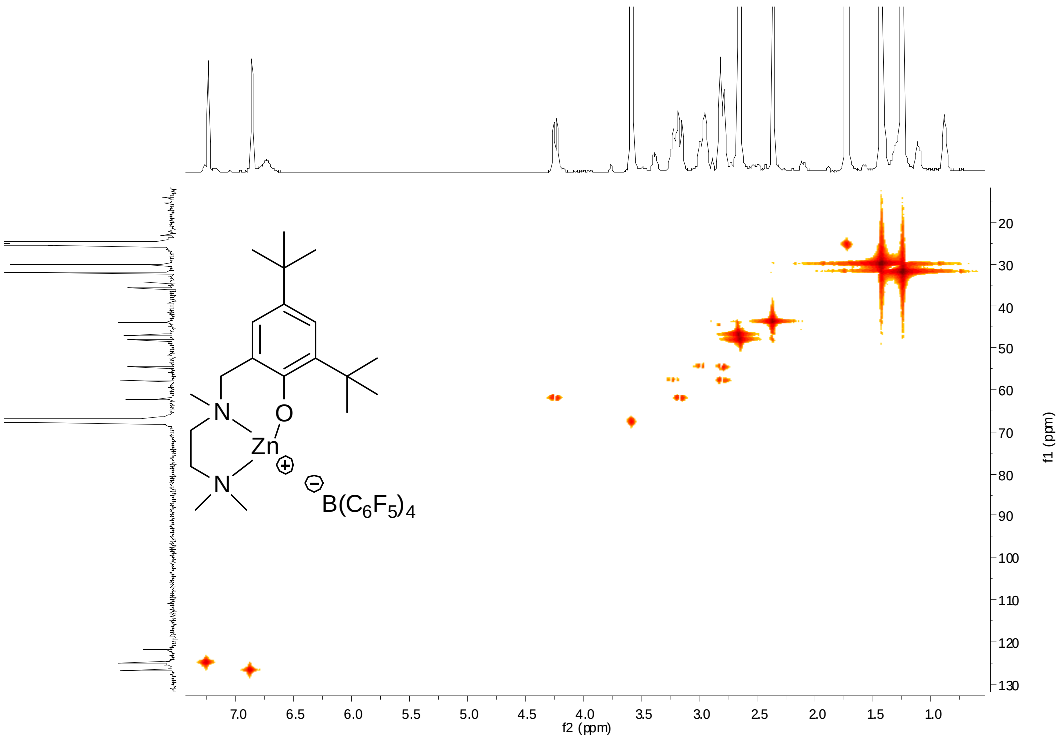

Figure S7. ^{1}H-^{13}C HMBC NMR spectrum (400 MHz, THF-d_8, 25 °C) of $[\{ONN\}Zn]^+[B(C_6F_5)_4]^-$ (**2**) (* stands for residual THF)

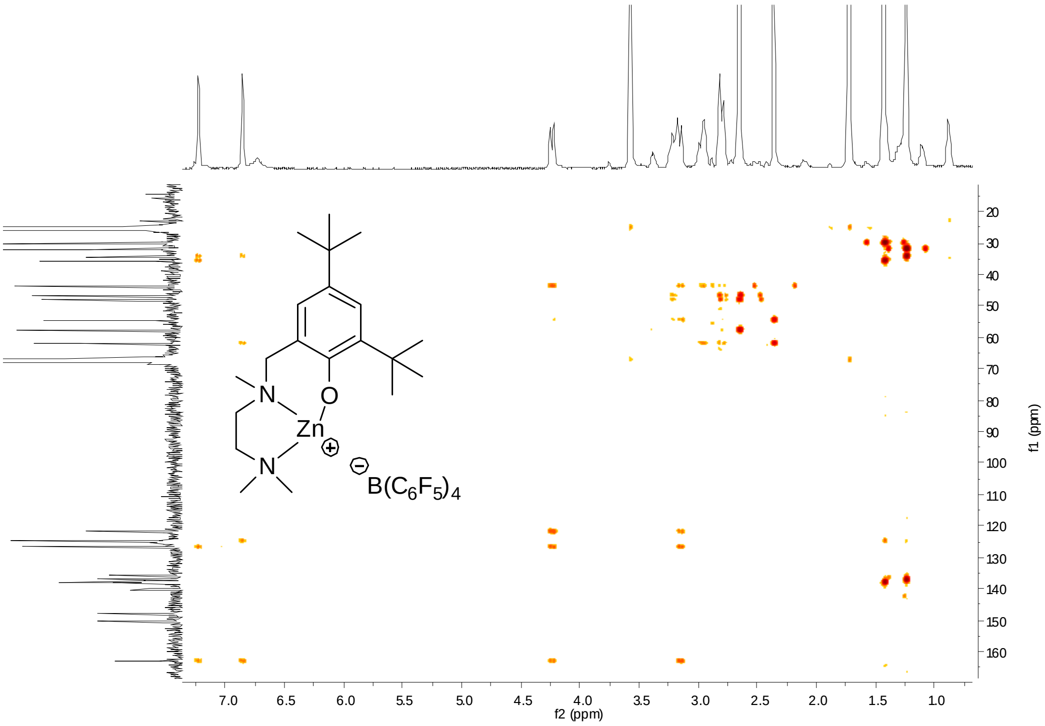

Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 25°C) of a polylactide sample obtained by polymerization of *rac*-Lactide (*rac*-LA) with *neo*-PentOH as initiator (CH_2Cl_2, 25°C, [*rac*-LA]$_0$/[*neo*-PentOH]$_0$ = 60:1, [LA]$_0$ = 0.5 M).