

Supporting Information

Bis(imino)phenoxide complexes of zirconium: synthesis, structural characterization and solvent-free ring-opening polymerization of cyclic esters and lactide

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1. General Experimental Details:

All reactions were performed under dry argon atmosphere using standard Schlenk techniques or in a glove box with rigorous exclusion of moisture and air. Toluene was dried by heating under reflux over sodium and benzophenone and distilled fresh prior to use. CDCl_3 used for NMR spectral measurements was dried over calcium hydride, distilled and stored in a glove box. ^1H and ^{13}C spectra were recorded with a Bruker Avance 400 instrument. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to residual solvent resonances and are reported as parts per million relative to SiMe_4 . ESI-MS spectra of the samples were obtained from Waters Q-ToF micro mass spectrometer. Elemental analyses were done with a Perkin Elmer Series 11 analyzer. $[\text{Zr}(\text{O}^i\text{Pr})_4 \cdot i\text{PrOH}]_2$ were purchased from Aldrich and used without subsequent purification. CL VL and BL were purchased from Aldrich, dried over CaH_2 overnight and distilled fresh prior to use. *rac*-LA and *L*-LA were purchased from Aldrich and purified by sublimation and stored in a glove box. Compounds **1** and **2** were prepared using the literature procedure.

2. Synthesis and Characterization:

2.1 Preparation and characterization of complexes **3**· C_7H_8 and **4**· $i\text{PrOH}$

Synthesis of **3**· C_7H_8 : In an argon filled glove box, to a stirred solution of $[\text{Zr}(\text{O}^i\text{Pr})_4 \cdot i\text{PrOH}]_2$ (0.05 g, 0.13 mmol) in 5 mL toluene at $-24\text{ }^\circ\text{C}$ was added a solution of **1** (0.12 g, 0.26 mmol) in 5 mL toluene. The reaction mixture was brought to ambient temperature and stirred for an additional period of 24 h. Subsequently, the reaction mixture was evaporated to dryness to afford a yellow residue. The residue was crystallized from concentrated toluene solution at $-24\text{ }^\circ\text{C}$ overnight (Yield 0.13 g, 85%). Mp: $162\text{ }^\circ\text{C}$. Anal. Calc. for $\text{C}_{79}\text{H}_{104}\text{N}_4\text{O}_4\text{Zr}$: C, 75.01; H, 8.29; N, 4.43. Found: C, 75.31; H, 8.39, N, 4.58. ^1H NMR (400 MHz, CDCl_3): δ = 0.38–0.46 (m, O- $\text{CH}(\text{CH}_3)_2$, 12H), 1.02–1.27 (m, $\text{CH}(\text{CH}_3)_2$, 48H), 2.29 (s, Ar- CH_3 , 9H), 2.80–2.95 (s, $\text{CH}(\text{CH}_3)_2$, 8H), 3.67 (s, O- $\text{CH}(\text{CH}_3)_2$, 2H), 7.05–7.24 (m, Ar-*H*, 21H), 7.98 (s, $\text{CH}=\text{N}$, 1H), 8.21 (s, $\text{CH}=\text{N}$, 1H), 8.57 (s, $\text{CH}=\text{N}$, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 20.29 (Ar- CH_3), 22.29 (O- $\text{CH}(\text{CH}_3)_2$), 22.81 (O-Ar- CH_3), 23.35 ($\text{CH}(\text{CH}_3)_2$), 23.99 ($\text{CH}(\text{CH}_3)_2$), 25.54 ($\text{CH}(\text{CH}_3)_2$), 26.27 ($\text{CH}(\text{CH}_3)_2$), 27.33 ($\text{CH}(\text{CH}_3)_2$), 28.23 ($\text{CH}(\text{CH}_3)_2$), 70.18 (O- $\text{CH}(\text{CH}_3)_2$), 121.71(Ar-C), 123.19 (O-Ar- CH_3), 123.48 (Ar-C), 123.93 (Ar- CH_3), 124.19

(Ar-C), 125.33 (O-Ar-CH₃), 125.4 (Ar-CH₃), 126.59 (Ar-CH₃), 135.15 (Ar-CH₃), 138.53 (Ar-CH₃), 139.44 (Ar-C), 141.10 (Ar-C), 141.3 (Ar-C), 150.45 (Ar-C), 151.06 (Ar-C), 159.44 (Ar-O), 164.37 (CH=N), 172.09 (CH=N). ESI-MS: 1173 [M-C₇H₈ + H]⁺.

Synthesis of 4-ⁱPrOH: In an argon filled glove box, to a stirred solution of [Zr(OⁱPr)₄·ⁱPrOH]₂ (0.05 g, 0.13 mmol) in 5 mL toluene at -24 °C was added a solution of **2** (0.10 g, 0.26 mmol) in 5 mL toluene. The reaction mixture was brought to ambient temperature and stirred for an additional period of 24 h. Subsequently, the reaction mixture was evaporated to dryness to afford a yellow residue. The residue was crystallized from concentrated toluene solution at -24 °C overnight (Yield 0.12 g, 86%). Mp: 154 °C. Anal. Calc. for C₆₄H₈₂N₄O₅Zr: C, 71.27; H, 7.66; N, 5.19. Found: C, 71.57; H, 7.84; N, 5.34. ¹H NMR (400 MHz, CDCl₃): δ = 0.32 (s, O-CH(CH₃)₂, 6H), 0.52 (s, O-CH(CH₃)₂, 6H), 1.18 (s, H-O-CH(CH₃)₂, 6H), 1.89 (s, Ar-CH₃, 18H), 2.23 (s, Ar-CH₃, 24H), 3.12 (s, O-CH(CH₃)₂, 2H), 4.18 (s, HO-CH(CH₃)₂, 1H), 6.55–7.23 (m, Ar-H, 12H), 7.82 (s, CH=N, 1H), 8.00 (s, CH=N, 1H), 8.32 (s, CH=N, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 17.67 (Ar-CH₃), 18.50 (Ar-CH₃), 19.29 (Ar-CH₃), 20.25 (Ar-CH₃), 20.45 (O-Ar-CH₃), 20.89 (O-CH(CH₃)₂), 21.57 (O-CH(CH₃)₂), 25.50 (H-O-CH(CH₃)₂), 64.52 (HO-CH(CH₃)₂), 70.71 (O-CH(CH₃)₂), 125.44 (Ar-C), 127.20 (Ar-C), 127.76 (Ar-C), 128.36 (Ar-C), 128.55 (Ar-C), 129.0 (Ar-C), 129.17 (Ar-C), 130.39 (Ar-C), 134.48 (Ar-C), 138.0 (Ar-C), 138.57 (Ar-C), 159.71 (O-Ar-CH₃), 160.30 (CH=N), 171.84 (CH=N). ESI-MS: 1062 [M-ⁱPrOH + K]⁺.

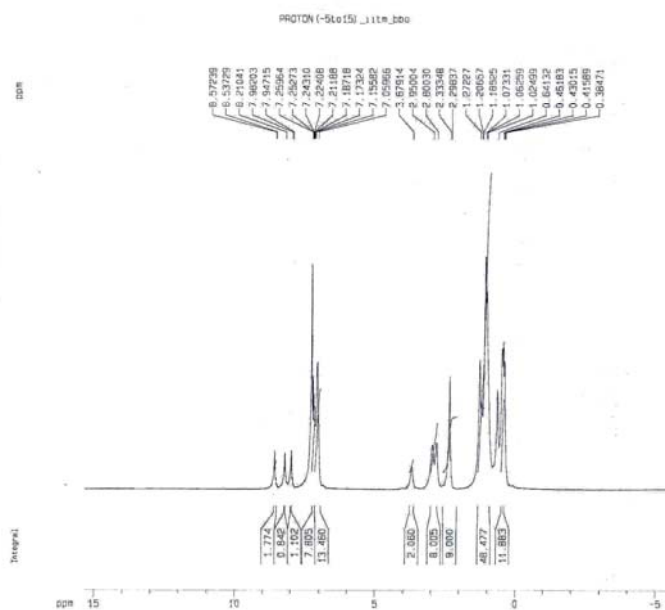


Figure S1: ^1H NMR (400 MHz, CDCl_3) of $3\text{-C}_7\text{H}_8$

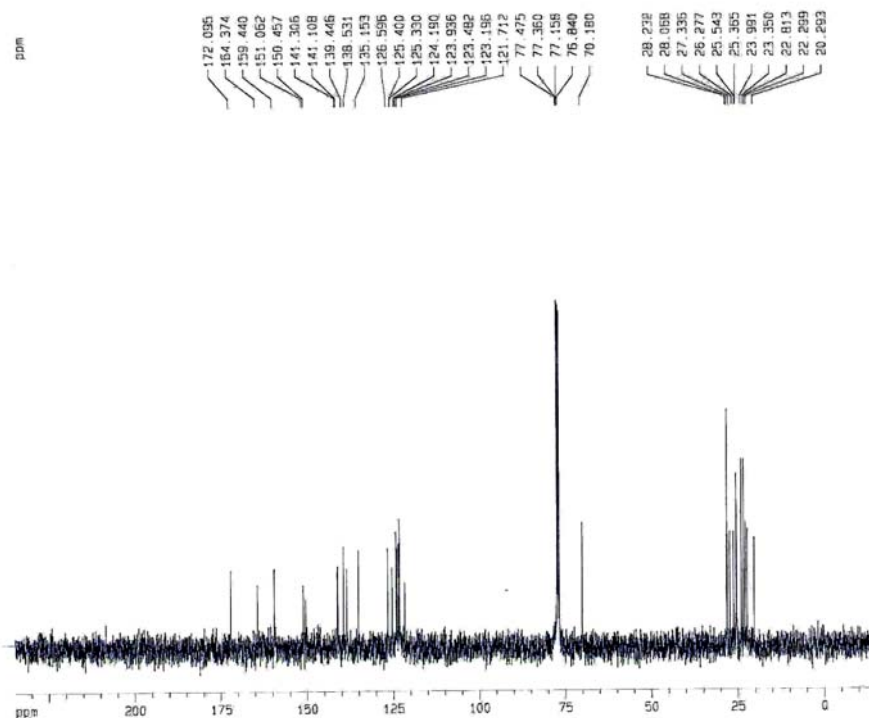


Figure S2: ^{13}C NMR (100 MHz, CDCl_3) of $3\text{-C}_7\text{H}_8$

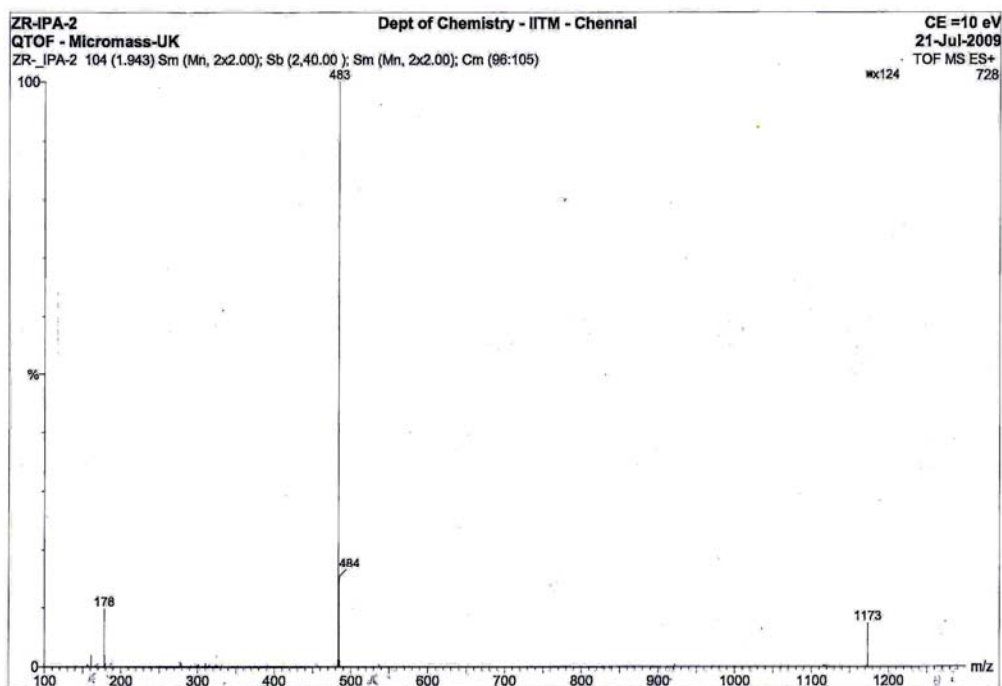


Figure S3: ESI-MS of 3-C₇H₈

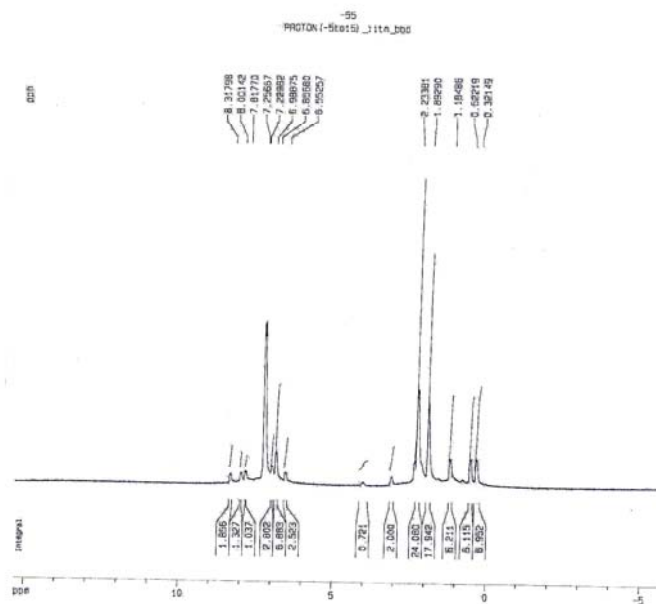


Figure S4: ¹H NMR (400 MHz, CDCl₃) of 4-*i*PrOH

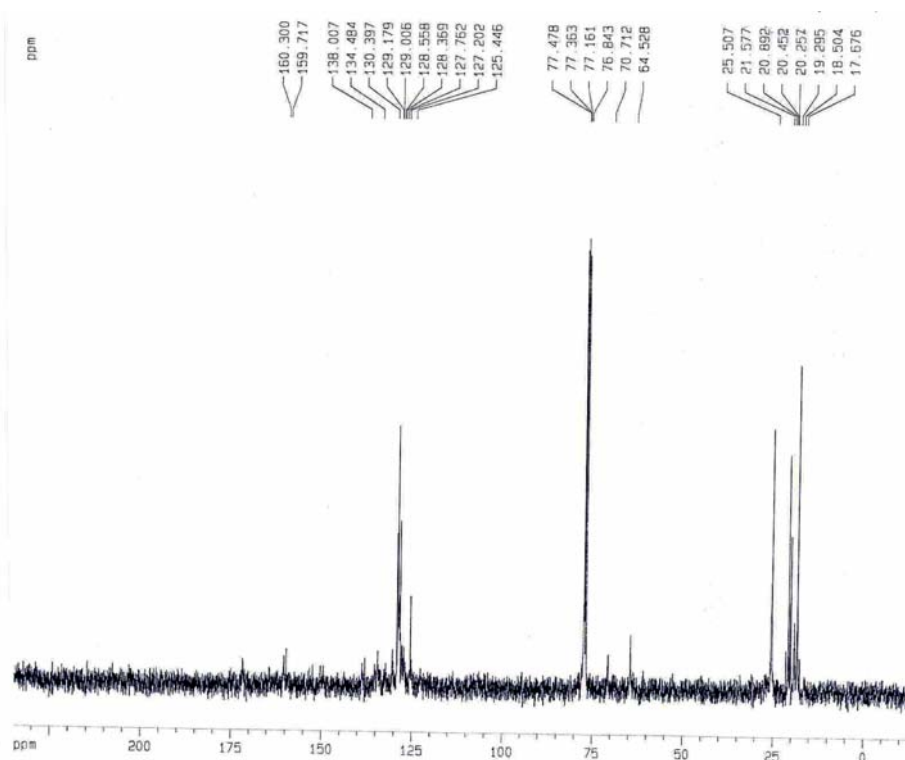


Figure S5: ^{13}C NMR (100 MHz, CDCl_3) of $4\text{-}^i\text{PrOH}$

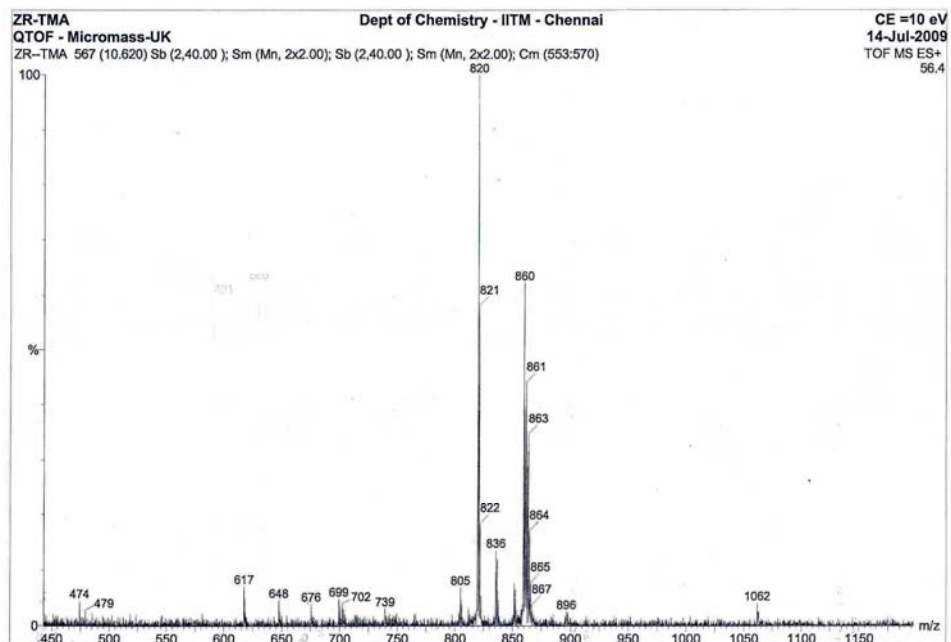


Figure S6: ESI-MS of $4\text{-}^i\text{PrOH}$

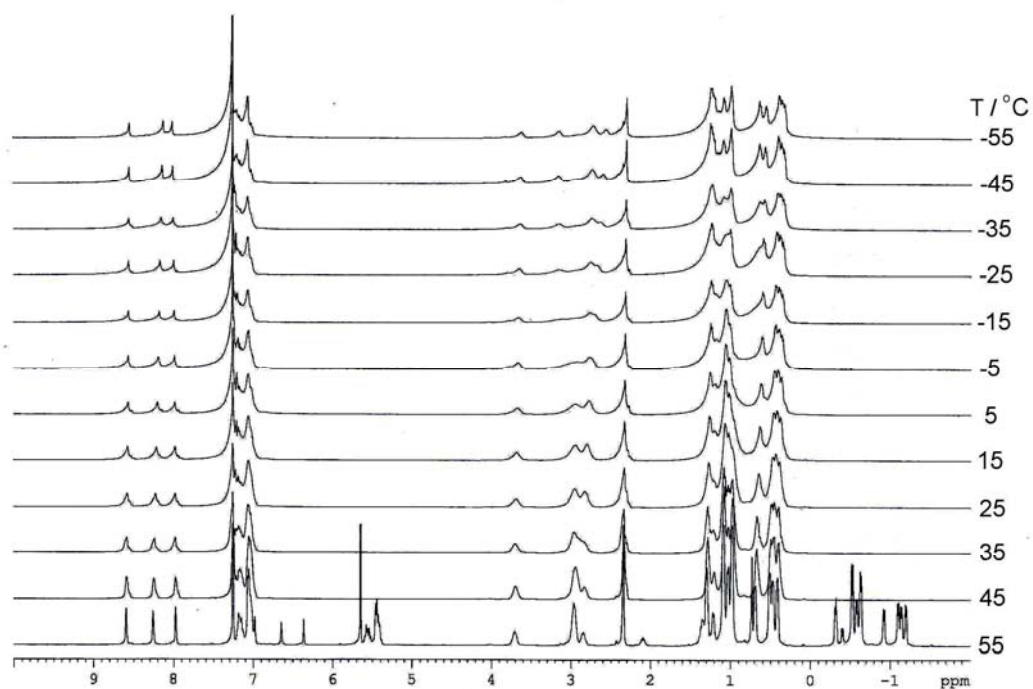


Figure S7: Variable temperature ^1H NMR (400 MHz, CDCl_3) of $3\text{-C}_7\text{H}_8$

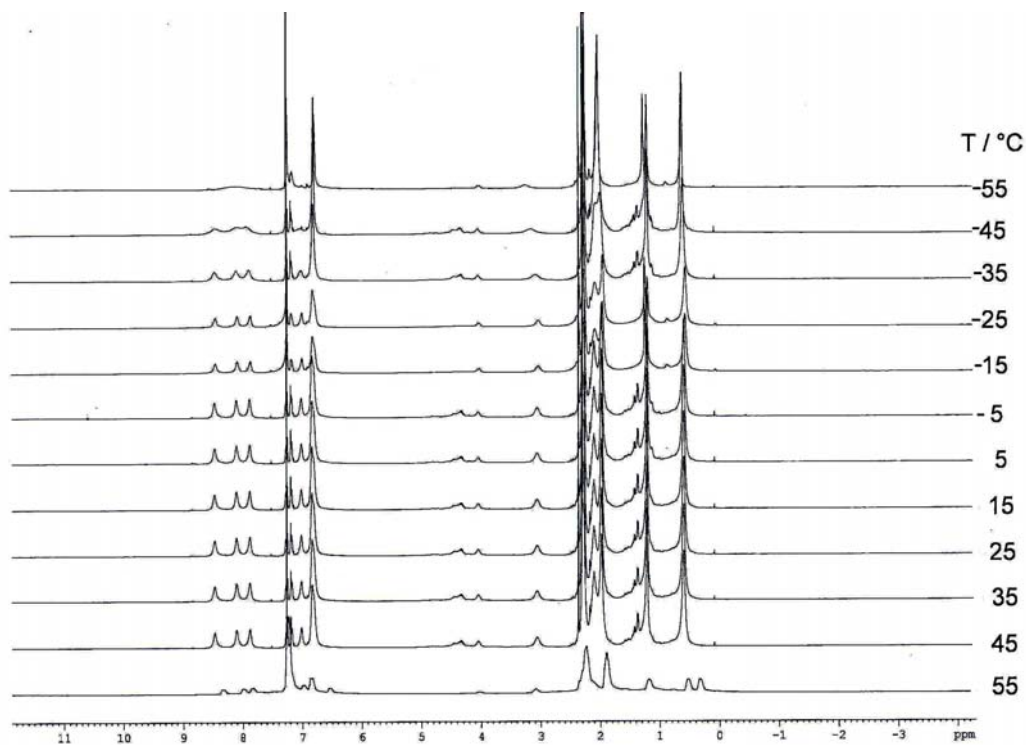


Figure S8: Variable temperature ^1H NMR (400 MHz, CDCl_3) of 4-iPrOH

2.2 Crystallographic data

Single crystals of $3 \cdot 2C_7H_8$ suitable for structural studies were obtained by crystallization from toluene at room temperature. X-ray data collection was performed with Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with graphite monochromated Mo (K_α) ($\lambda = 0.7107 \text{ \AA}$) radiation source. The data were collected with 100% completeness for θ up to 25° . ω and ϕ scans was employed to collect the data. The frame width for ω was set to 0.5° for data collection. The frames were integrated and data were reduced for Lorentz and polarization corrections using SAINT-NT. The multi-scan absorption correction was applied to the data set. All structures were solved using SIR-92 and refined using SHELXL-97. The non-hydrogen atoms were refined with anisotropic displacement parameter. All the hydrogen atoms could be located in the difference Fourier map. The hydrogen atoms bonded to carbon atoms were fixed at chemically meaningful positions and were allowed to ride with the parent atom during refinement.

$C_{72}H_{96}N_4O_4Zr \cdot 2C_7H_8$, $M = 1361.05$, yellow plates, $0.32 \times 0.25 \times 0.19 \text{ mm}^3$, monoclinic, space group $P2(1)/n$, $a = 16.3135(4)$, $b = 27.1846(7)$ $c = 19.8699(6) \text{ \AA}$, $V = 8152.8(4) \text{ \AA}^3$, $Z = 4$, $D_c = 1.109 \text{ g/cm}^3$, $F_{000} = 2928$, $T = 173(2) \text{ K}$, $2\theta_{\max} = 55.0^\circ$, 61149 reflections collected, 19211 unique ($R_{\text{int}} = 0.1263$). Final $GoF = 1.039$, $RI = 0.0875$, $wR2 = 0.2495$, $I > 2\sigma(I)$ (refinement on F^2), 880 parameters, 0 restraint. R indices (all data), $RI = 0.2114$, $wR2 = 0.3182$.

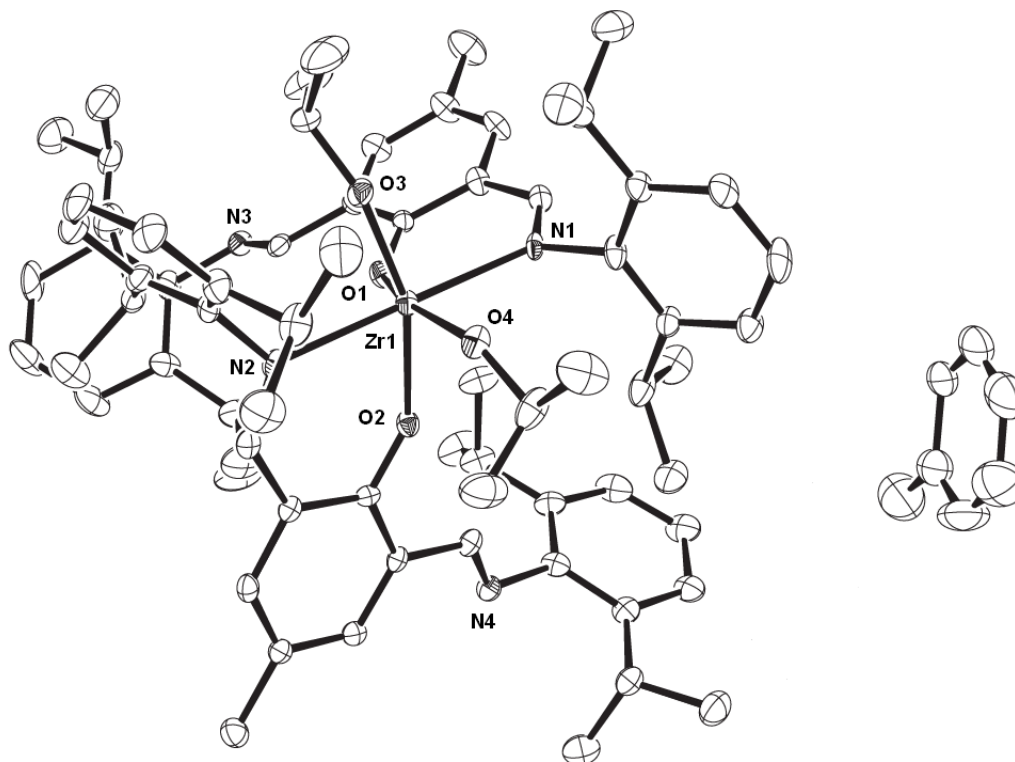


Figure S9: Molecular structure of $3\text{-C}_7\text{H}_8$ showing thermal ellipsoids at 30% probability level

3. Polymerization Details

3.1. Typical procedure for the bulk polymerization of *L*-LA, *rac*-LA, CL, VL and *rac*-BL

All polymerizations were performed in 200:1 ratio between the respective monomers and $3\text{-C}_7\text{H}_8$ or $4\text{-}^i\text{PrOH}$.

For, CL polymerization, 11.78 μmol of $3\text{-C}_7\text{H}_8$ or 11.78 μmol of $4\text{-}^i\text{PrOH}$. was used for 0.25 mL of monomer. The polymerization was performed at 80 °C. Rise in viscosity of the polymerization reaction was observed and finally the stirring ceased. The contents were dissolved into minimum quantity of CH_2Cl_2 and poured into cold methanol. The polymer precipitated immediately and was isolated by filtration. The filtered product was dried in vacuum until a constant weight was attained. Similarly for, VL polymerization, 13.47 μmol of $3\text{-C}_7\text{H}_8$ or 13.47 μmol of $4\text{-}^i\text{PrOH}$. was used for 0.25 mL of monomer. The polymerization was performed at 80 °C and same procedure for work up was followed.

Again, for, *rac*-BL polymerization, 15.33 μmol of **3** $\cdot\text{C}_7\text{H}_8$ or 15.33 μmol of **4** $\cdot^i\text{PrOH}$. was used for 0.25 mL of monomer. The polymerization was performed at 80 $^\circ\text{C}$ and same procedure for work up was followed.

For *L*-LA or *rac*-LA, polymerization, 8.67 μmol of **3** $\cdot\text{C}_7\text{H}_8$ or 8.67 μmol of **4** $\cdot^i\text{PrOH}$. and 0.25 g *L*-LA or *rac*-LA were taken in a flask under an argon atmosphere. The contents were rapidly stirred at 130 $^\circ\text{C}$. Once the monomer melted completely, rise in viscosity of the polymerization reaction was observed and finally the stirring ceased. The contents were dissolved into minimum quantity of CH_2Cl_2 and poured into cold methanol. The polymer precipitated immediately and was isolated by filtration. The filtered product was dried in vacuum until a constant weight was attained.

3.2 Polymer Characterization

Molecular weights and the polydispersity indices of the polymers were determined by GPC instrument with Waters 510 pump and Waters 410 Differential Refractometer as the detector. Three columns namely WATERS STRYGEL-HR5, STRYGEL-HR4 and STRYGEL-HR3 each of dimensions (7.8 \times 300 mm) were connected in series. Measurements were done in THF at 27 $^\circ\text{C}$. Number average molecular weights (M_n) and polydispersity (M_w/M_n) of polymers were measured relative to polystyrene standards.

3.3 Polymerization Kinetics

Bulk polymerization using **3** $\cdot\text{C}_7\text{H}_8$ and **4** $\cdot^i\text{PrOH}$. were carried out at 140 $^\circ\text{C}$ under an argon atmosphere. At appropriate interval of time, 0.2 mL aliquots were removed from the reaction mixture and poured directly into CDCl_3 containing 250 ppm BHT. These quenched aliquots obtained at various time intervals were analyzed by ^1H NMR. The $[L\text{-LA}]_0/[L\text{-LA}]_t$ ratio was calculated by integration of the peak corresponding to the methine proton for the monomer and polymer. Apparent rate constant were obtained from the slopes of the best-fit lines.

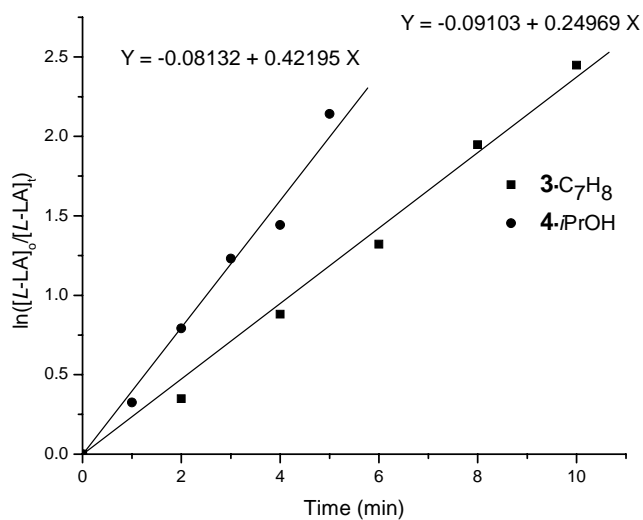


Figure S10: Semilogarithmic plots of *L*-LA conversion in time initiated by $3\text{-C}_7\text{H}_8$ and 4-iPrOH : $[L-LA]_0/[Zr]_0 = 200$ at $130\text{ }^\circ\text{C}$

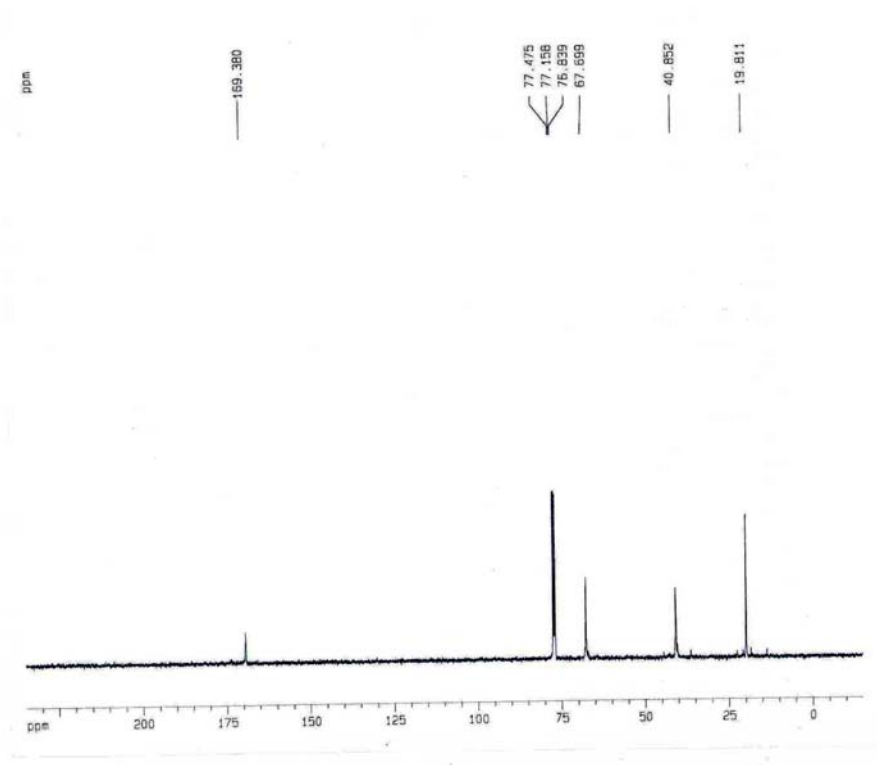


Figure S11: ^{13}C NMR (100 MHz, CDCl_3) of PHB prepared by polymerization of *rac*-BL with $3\text{-C}_7\text{H}_8$ (Table 1, Entry 3)

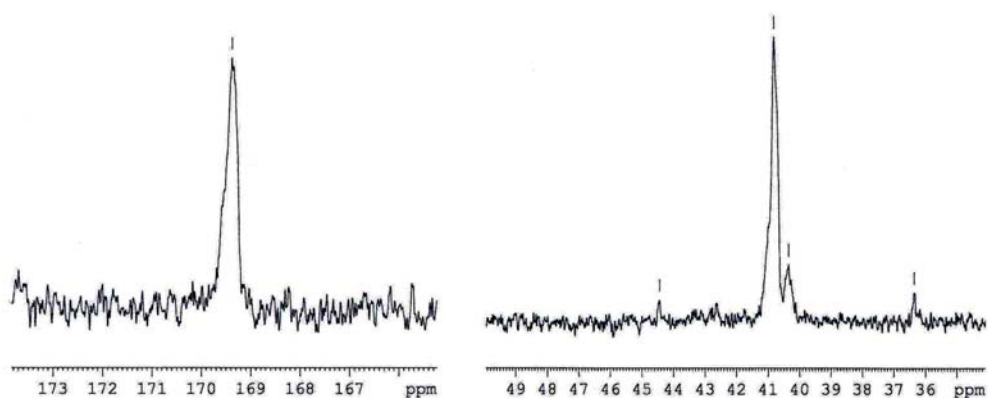


Figure S12: Methine region and methyl region of the ^{13}C NMR (100 MHz, CDCl_3) of PHB prepared by polymerization of *rac*-BL with **3**- C_7H_8 (Table 1, Entry 3)

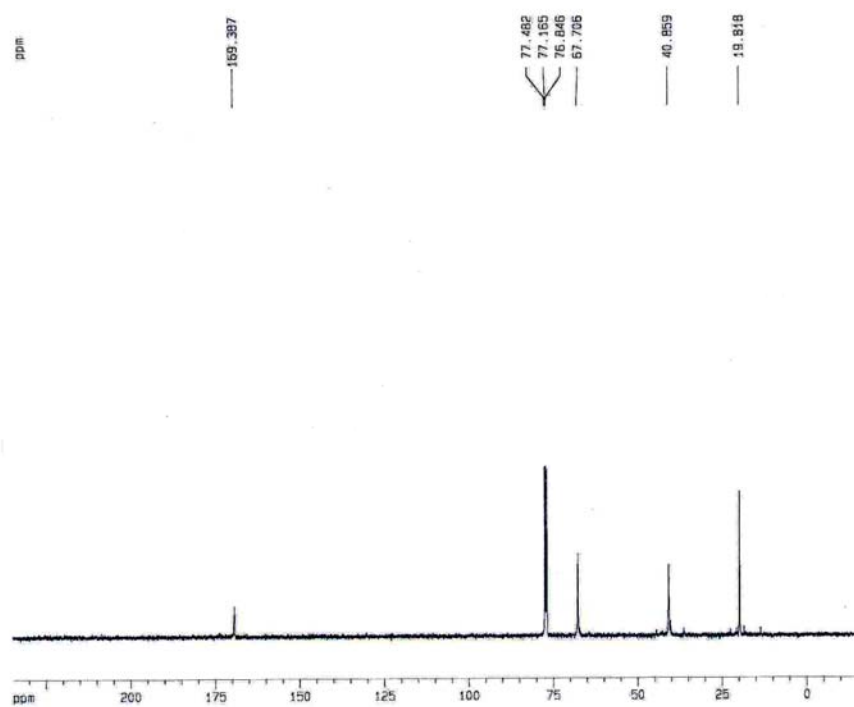


Figure S13: ^{13}C NMR (100 MHz, CDCl_3) of PHB prepared by polymerization of *rac*-BL with **4**- i -PrOH. (Table 1, Entry 8)

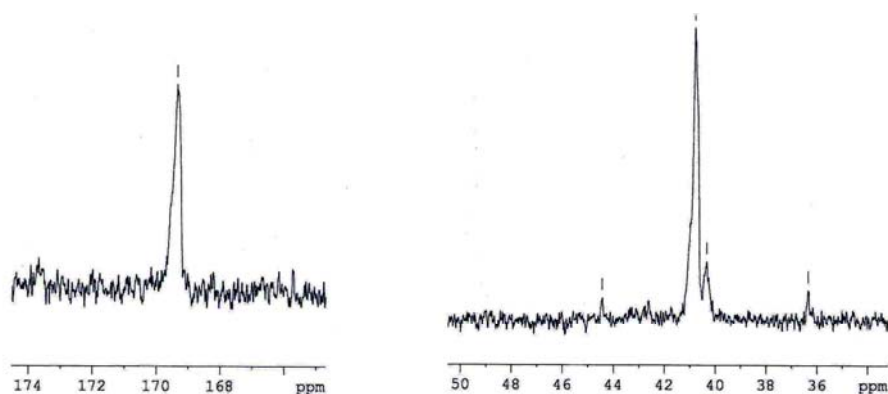


Figure S14: Methine region and methyl region of the ^{13}C NMR (100 MHz, CDCl_3) of PHB prepared by polymerization of *rac*-BL with $4\text{-}^i\text{PrOH}$. (Table 1, Entry 8)

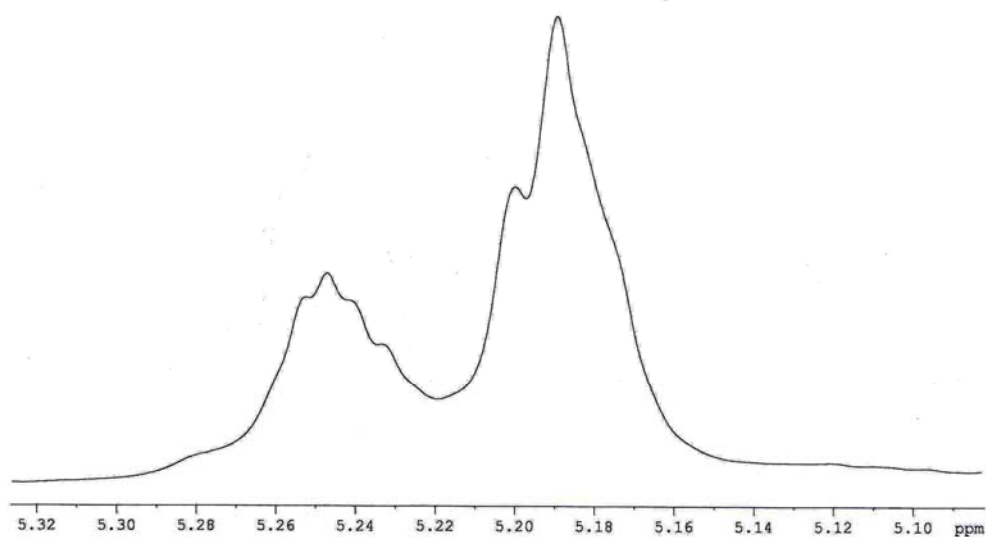


Figure S15: Homonuclear decoupled ^1H NMR (400 MHz, CDCl_3) spectrum of the methine region of heterotactic PLA obtained using $3\text{-C}_7\text{H}_8$ (Table 1, Entry 5)

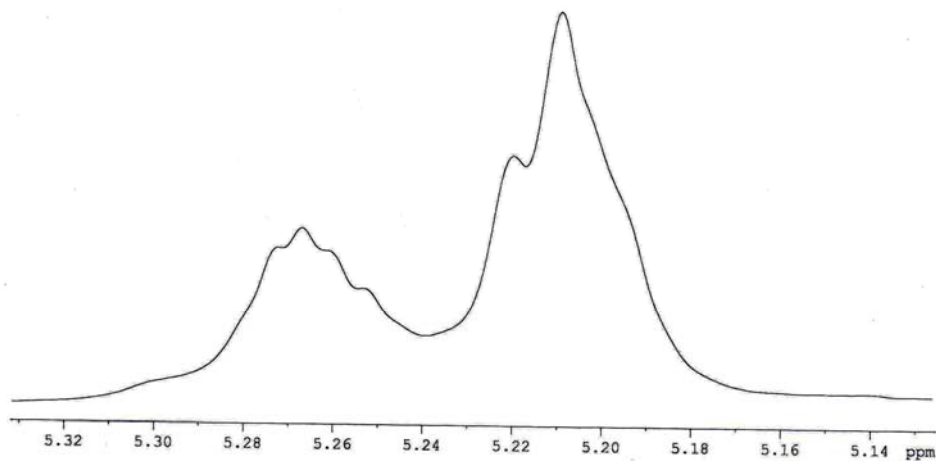


Figure S16: Homonuclear decoupled ^1H NMR (400 MHz, CDCl_3) spectrum of the methine region of heterotactic PLA obtained using $4\text{-}^i\text{PrOH}$. (Table 1, Entry 10)