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Supporting Information

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A Germanium Alkoxide Supported by a C_3-symmetric Ligand for the Stereoselective Synthesis of Highly Heterotactic Polylactide under Solvent-free Conditions

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General Experimental Details:

All reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk or glove-box techniques and all solvents were freshly distilled over suitable drying agents and degassed prior to use. Ligand H_3**L** was prepared according to a standard literature preparation.[1] Ge(O^{i}Pr)$_4$ was purchased from Aldrich and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz or 400 MHz spectrometer, referenced to residual solvent peaks. Coupling constants are given in Hertz. Elemental analysis was performed by Mr. A.K. Carver at the Department of Chemistry, University of Bath. X-ray data were collected at 150 K on a Nonius KappaCCD area detector diffractometer using Mo-Kα radiation (l = 0.71073 Å), and all structures were solved by direct methods and refined on all F^2 data using SHELXL-97 suite of programs, with hydrogen atoms included in idealised positions and refined using the riding mode, except H(1) which was located in the penultimate difference Fourier map and refined freely.[2] Gel Permeation Chromatography (GPC) analyses were performed on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 μm MIXED-D 300×7.5 mm column at 35 °C, THF solvent (flow rate, 1.0ml/min). The polydispersity index (PDI) was determined from M_w/M_n, where M_n is the number average molecular weight and M_w the weight average molecular weight. The polymers were referenced to 11 narrow molecular weight polystyrene standards with a range of M_w 615 – 5680000 Da. The probablitiy of heterotactic enchainment (P_r) was determined from the homonuclear decoupled ^{1}H spectra (Figs S5, 8, 11, 14, 17 and 20) using the following relationship: $[sis] = P_r^2/2$ (see ref [2] in the main text and references therein).

Synthesis and Characterization of 1. Tris(3,5-dimethyl-2-hydroxybenzyl) amine, H_3**L** (0.84 g, 2 mmol) was dissolved in toluene (20 ml) and Ge(O^{i}Pr)$_4$ (0.62 g, 2 mmol) was added under dry argon. The reaction mixture stirred at room temperature for 2 hr before the volatiles were removed under vacuum and the product recrystallised from the minimum amount of toluene at 0 °C. Yield 0.79 g, 65 %, m.p. 223-25 °C. Elemental analysis: Calc for $C_{36.5}H_{49}NO_5Ge$ C, 67.0; H, 7.55; N, 2.14. Found C, 66.7; H, 7.59; N, 2.31. ^{1}H NMR (400 MHz, $CDCl_3$) 1.21 (6H, d, J = 6 Hz O^{i}Pr, C$\underline{H}_3$). 1.41 (6H, d J = 6 Hz, O^{i}Pr, C$\underline{H}_3$), 1.60 (1H, br s, OH), 2.21 (9H, s, phenolate, C$\underline{H}_3$), 2.30 (9H, s, phenolate, C$\underline{H}_3$), 2.36 (1.5H, s, Tol, C$\underline{H}_3$), 3.64 (6H, br s, NCH_2) 3.95 (1H, sept, J = 6 Hz, HO^{i}Pr, C$\underline{H}$), 4.73 (1H, sept, J = 6 Hz, O^{i}Pr, C$\underline{H}$), 6.57 (3H, s, phenolate, ^{Ar}C$\underline{H}$), 6.93 (3H, s, phenolate, ^{Ar}C$\underline{H}$), 7.1-7.3 (2.5H, m, tol, C$\underline{H}$). ^{13}C NMR (300 MHz, $CDCl_3$) 16.5, 20.3 (Ar-CH_3), 25.3 (tol), 25.3 (HOCH($\underline{C}H_3)_2$), 26.4 (OCH($\underline{C}H_3)_2$), 59.3 (N-CH_2), 64.2 (HO$\underline{C}$H($CH_3)_2$), 65.7 (O$\underline{C}$H($CH_3)_2$), 119.1 (Ar), 125.2 (tol), 126.4 (Ar), 128.1 (tol), 128.6 (Ar), 129.0 (tol), 129.4, 131.9 (Ar), 137.8 (tol), 152.0 (O-Ar). HRMS (FAB, m/z) calc for $C_{30}H_{37}N_1O_4Ge$ (M^+) 549.1929; found 549.1931.

[1] M. Kol, M. Shamis, I. Goldberg, Z. Goldschmidt, S. Alfi, E. Hayut-Salant, *Inorg. Chem. Commun.,* **2001**, *4*, 177-179
[2] Sheldrick, G.M. SHELXL-97, University of Göttingen, Germany, 1997.

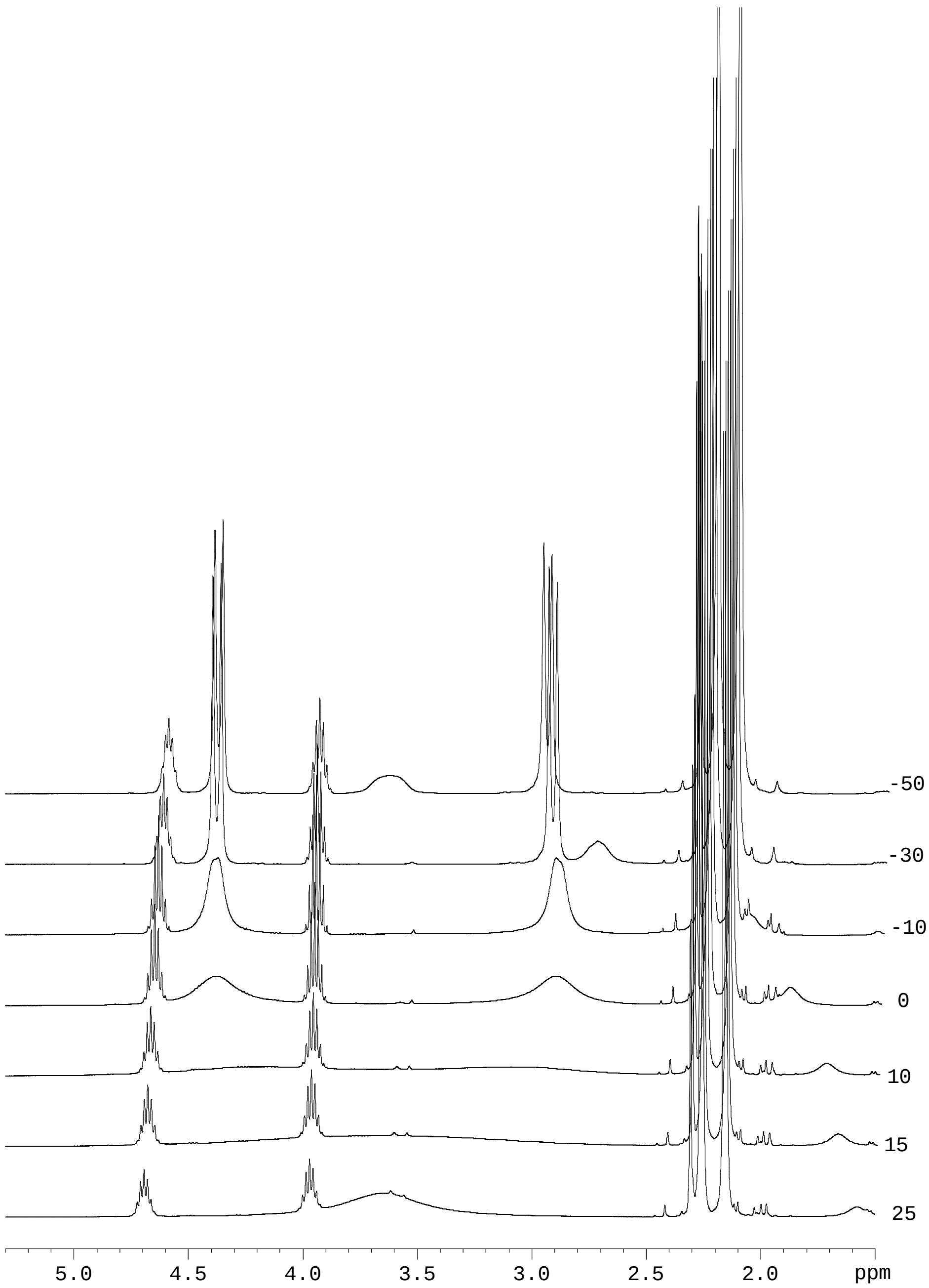

Figure S1: Variable temperature ^{1}H NMR ($CDCl_3$) of complex **1**.

Solvent-free Polymerization of *rac*-LA. The appropriate amount of *rac*-lactide was weighed out in an Ar filled glove box. The catalyst was added to the reaction vessel and then the vessel was place in a pre-heated oil bath at 130 °C. After the appropriate time the polymerization was quenched with MeOH, the resulting solid was dissolved in CH_2Cl_2. The solvent was removed under vacuum and the solid washed with copious amounts of methanol. The GPC (THF, referenced to polystyrene standards) and NMR (CH_2Cl_2) were then performed.

For example for 300:1. Ge(O^{i}Pr)**1** the initiator (30 mg, 0.046 mmol) was added to the reaction vessel together with *rac*-lactide (2.0 g, 14 mmol) and heated at 130 °C for 24 hours, during which time the viscosity significantly increased. Methanol (20 ml) was then added and dichloromethane (50 ml) was added to dissolve the mixture. The volatiles were removed in-vacuo and the white solid was washed with methanol (3 × 100 ml) and dried, to afford polylactide as a white solid.

Crystal Data for 1·0.5(C_7H_8): $C_{36.5}H_{49}GeNO_5$, *M* = 654.36, 0.15 x 0.12 x 0.10 mm^3, orthorhombic, space group *Pbcn* (No. 60), *a* = 11.666(1), *b* = 16.581(1), *c* = 34.551(3) Å, *V* = 6683.34(9) $Å^3$, *Z* = 8, D_c = 1.301 g/cm^3, F_{000} = 2776, MoKa radiation,? = 0.71073 Å, *μ* = 0.959 mm^{-1}, *T* = 150(2)K, $2ß_{max}$ = 55.0º, 56003 reflections collected, 7620 unique (R_{int} = 0.0575). Final *GooF* = 1.040, *R1* = 0.0458, *wR2* = 0.1105, *R* indices based on 6527 reflections with I >2sigma(I) (refinement on F^2), 427 parameters, 0 restraints.

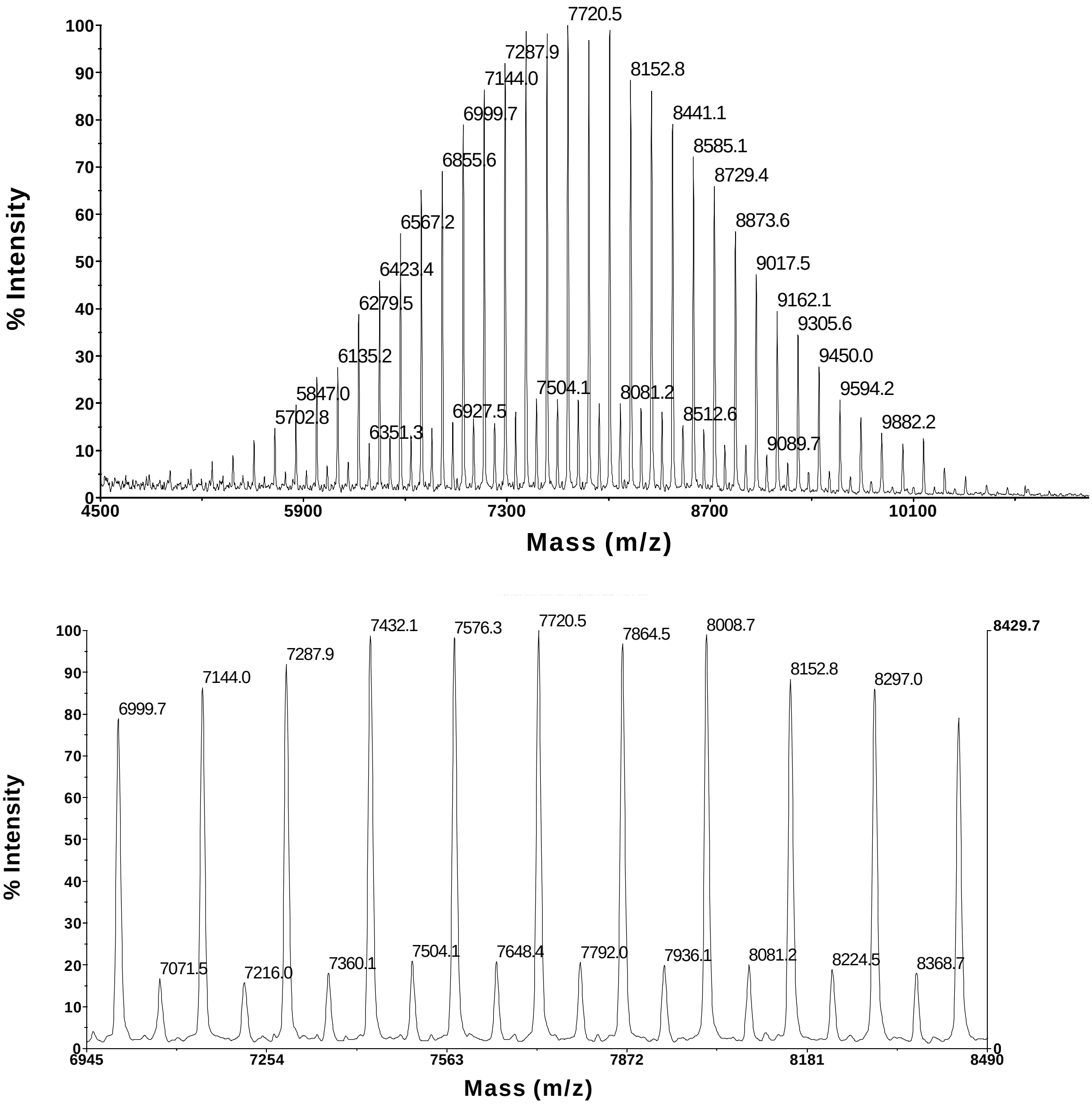

Figure S2: MALDI-TOF mass spectrum of PLA (polymerization conditions given in Table 1, entry 2). NaI used to ionise the polymer, spectrum run in PosLin mode.

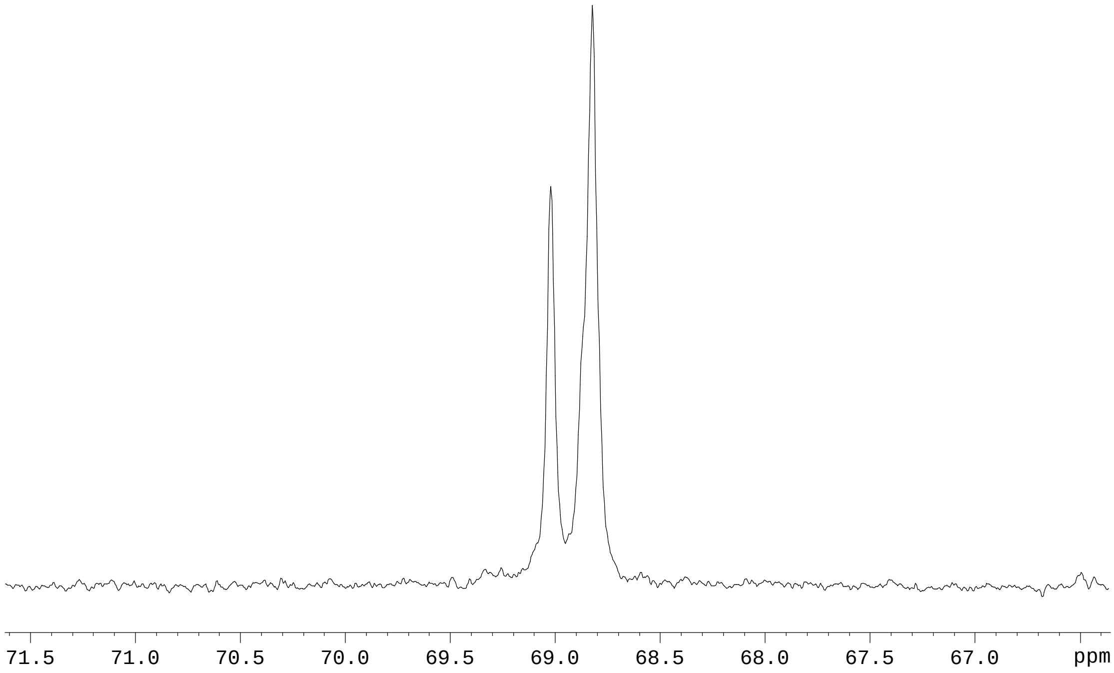

Figure S3: Methine region of the $^{13}C\{^1H\}$ NMR spectrum of PLA (Table 1, entry 1).

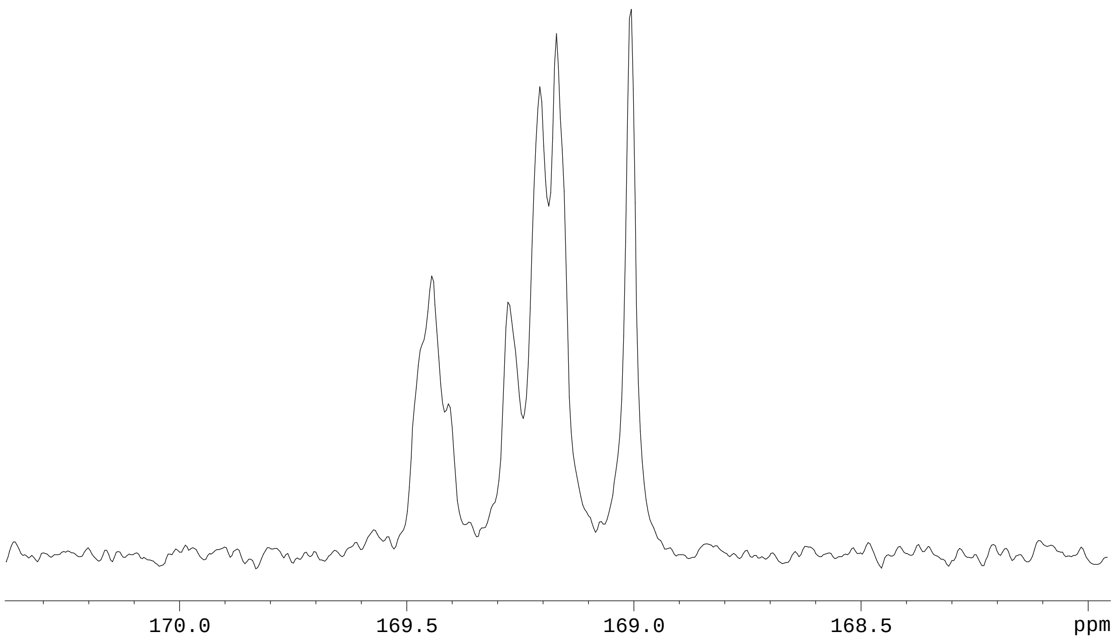

Figure S4: Carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum of PLA (Table 1, entry 1).

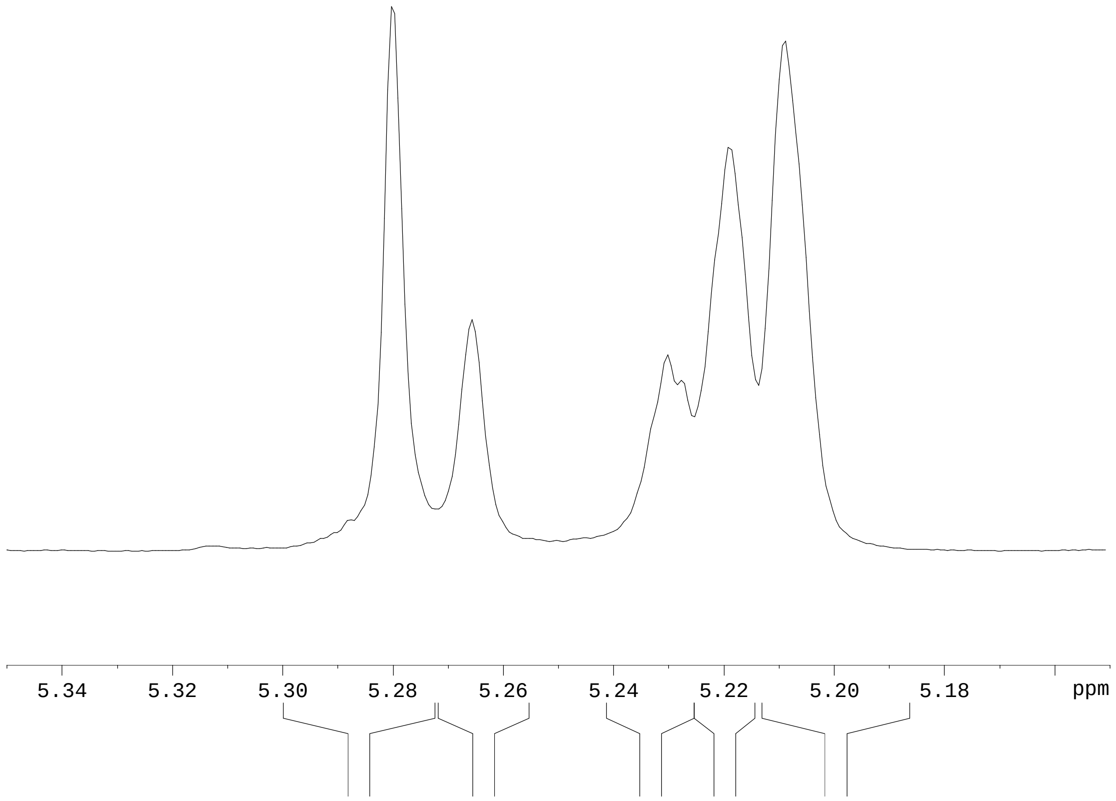

Figure S5: Methine region of the homonuclear decoupled ^{1}H NMR spectrum of PLA (Table 1, entry 1)

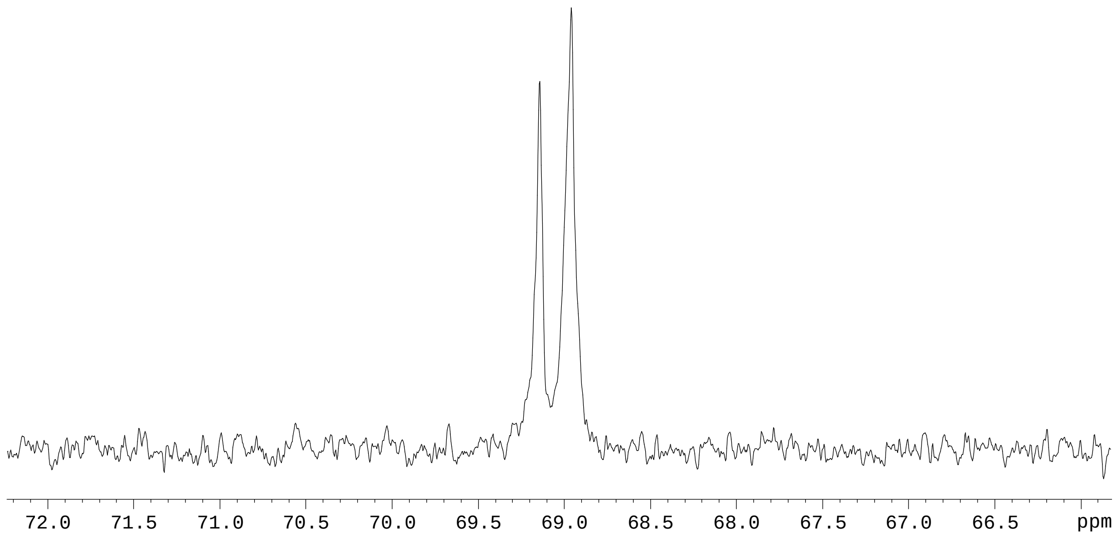

Figure S6: Methine region of the $^{13}C\{^{1}H\}$ NMR spectrum of PLA (Table 1, entry 2)

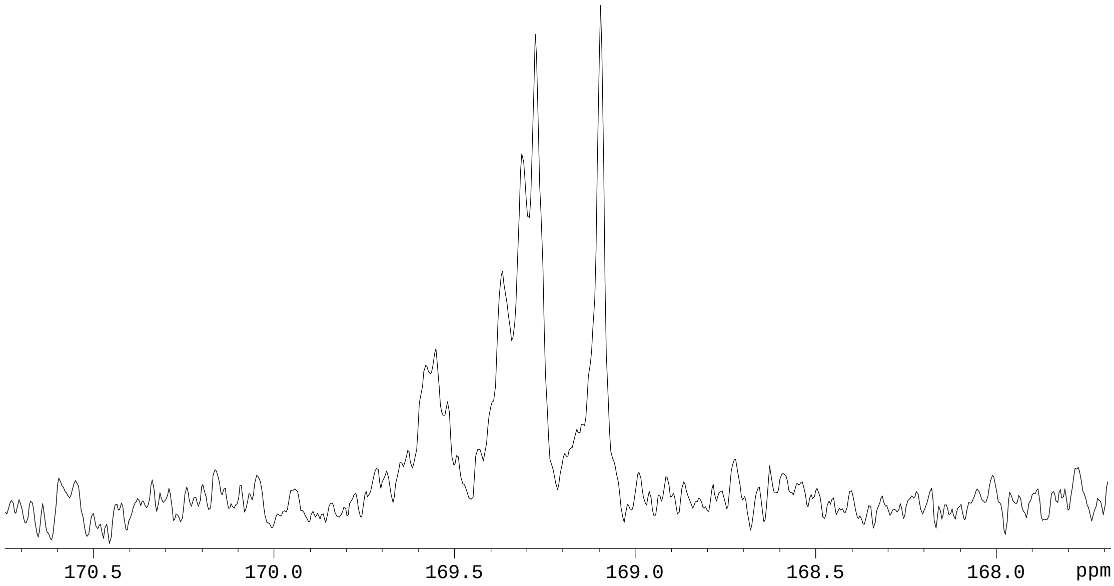

Figure S7: Carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum of PLA (Table 1, entry 2)

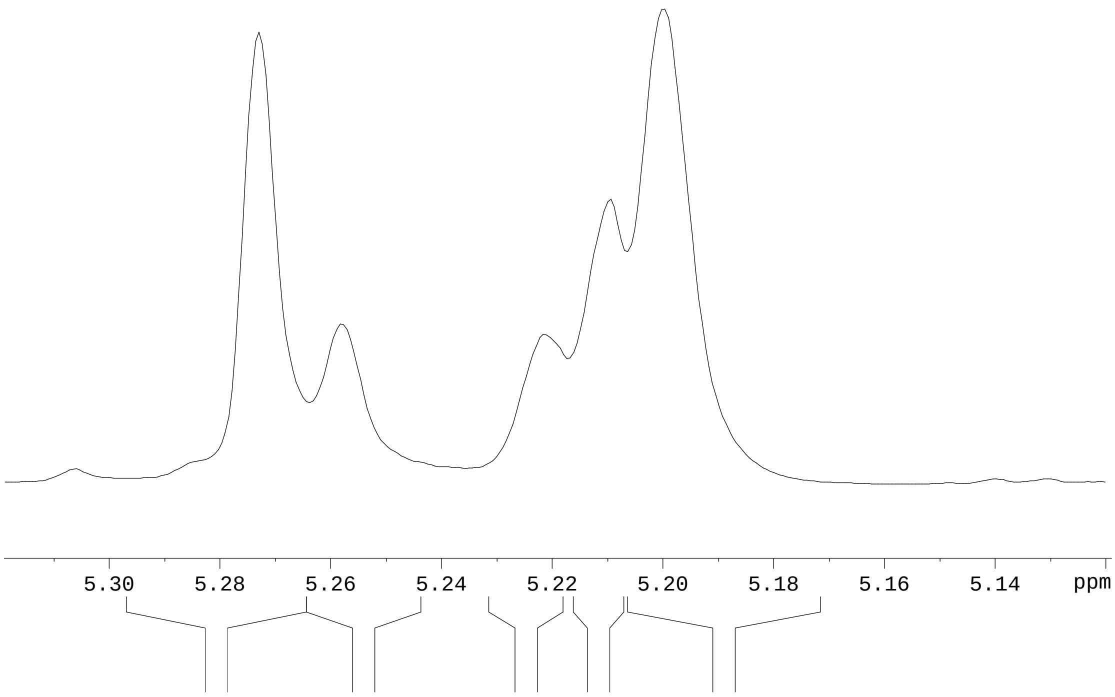

Figure S8: Methine region of the homonuclear decoupled ^1H NMR spectrum of PLA (Table 1, entry 2)

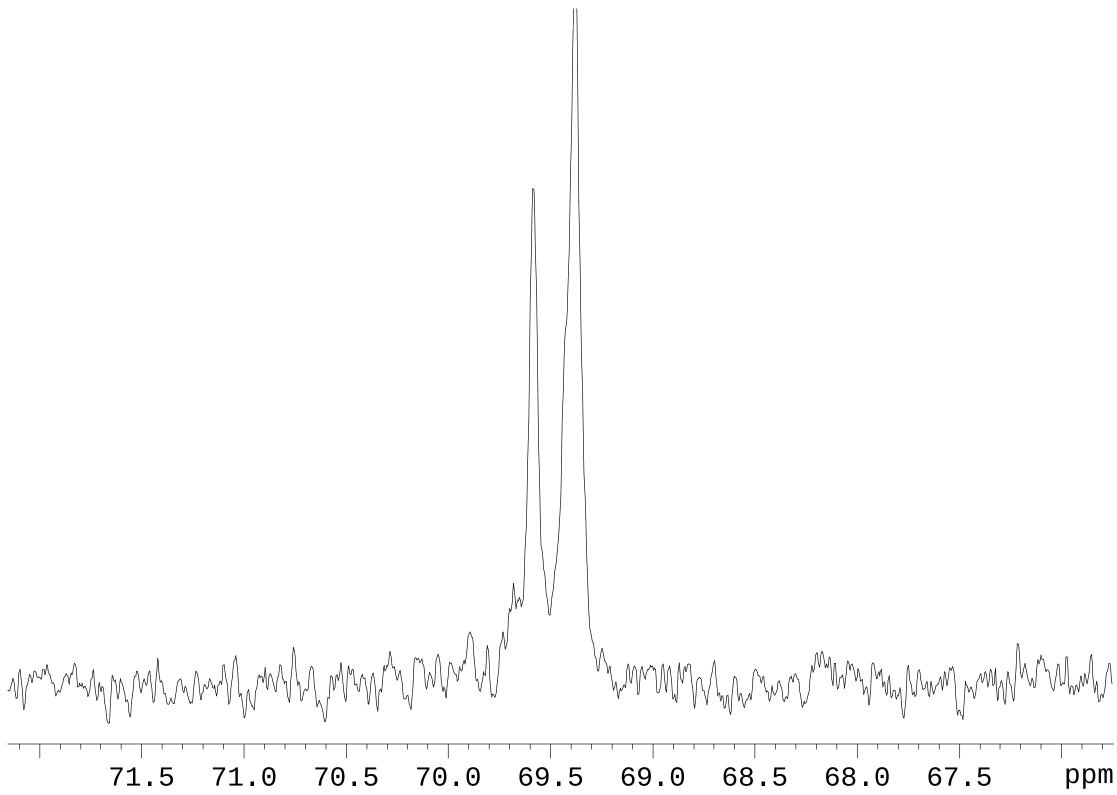

Figure S9: Methine region of the $^{13}C\{^{1}H\}$ NMR spectrum of PLA (Table 1, entry 3)

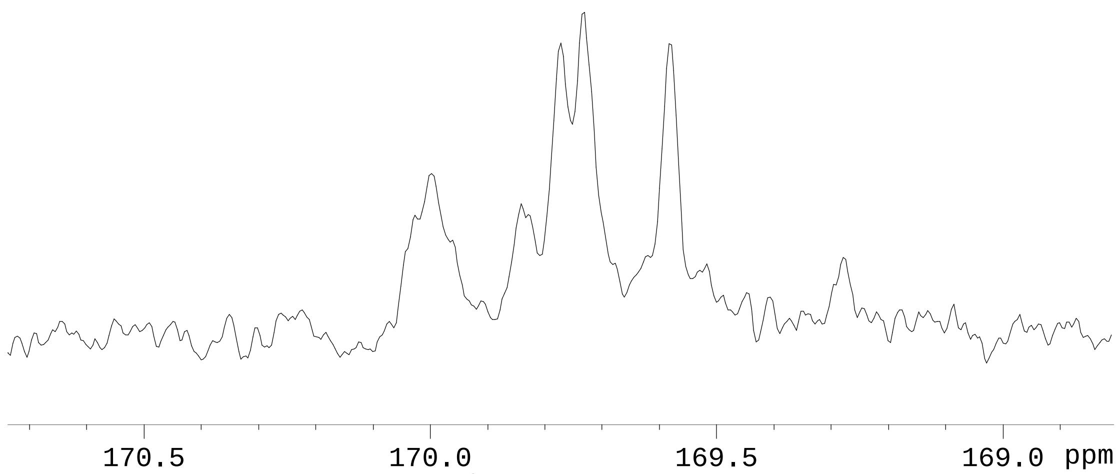

Figure S10: Carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectrum of PLA (Table 1, entry 3)

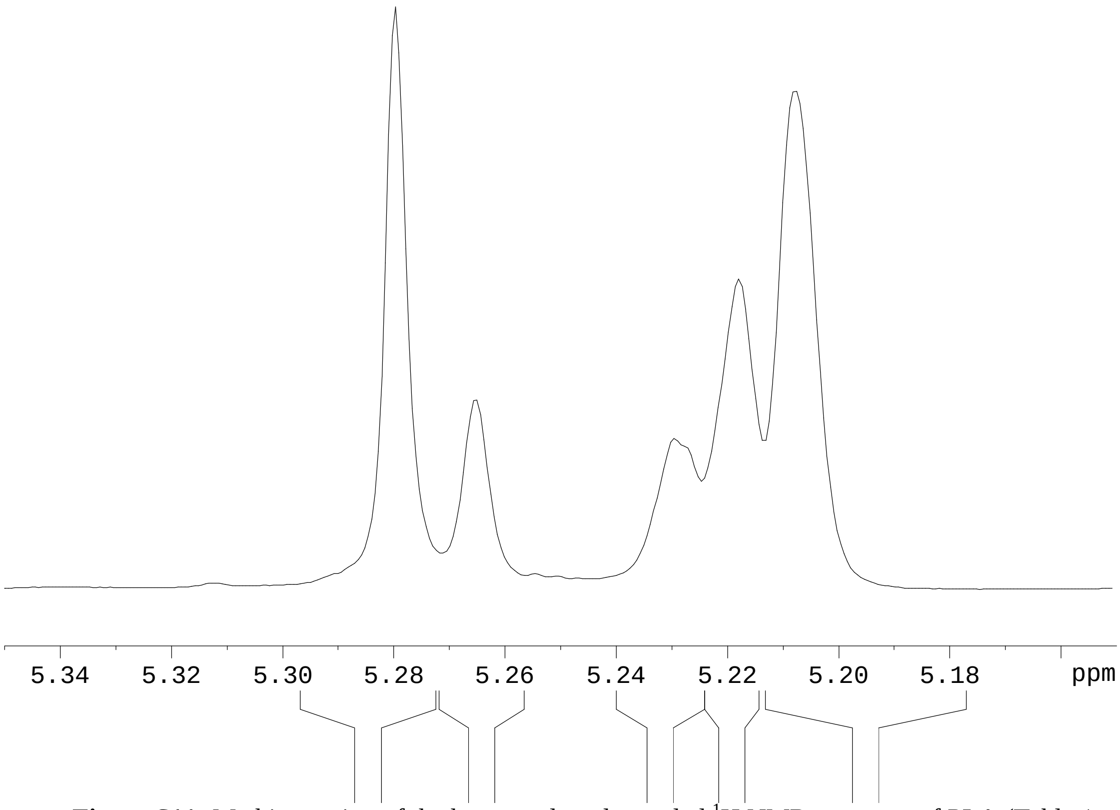

Figure S11: Methine region of the homonuclear decoupled ^{1}H NMR spectrum of PLA (Table 1, entry 3)

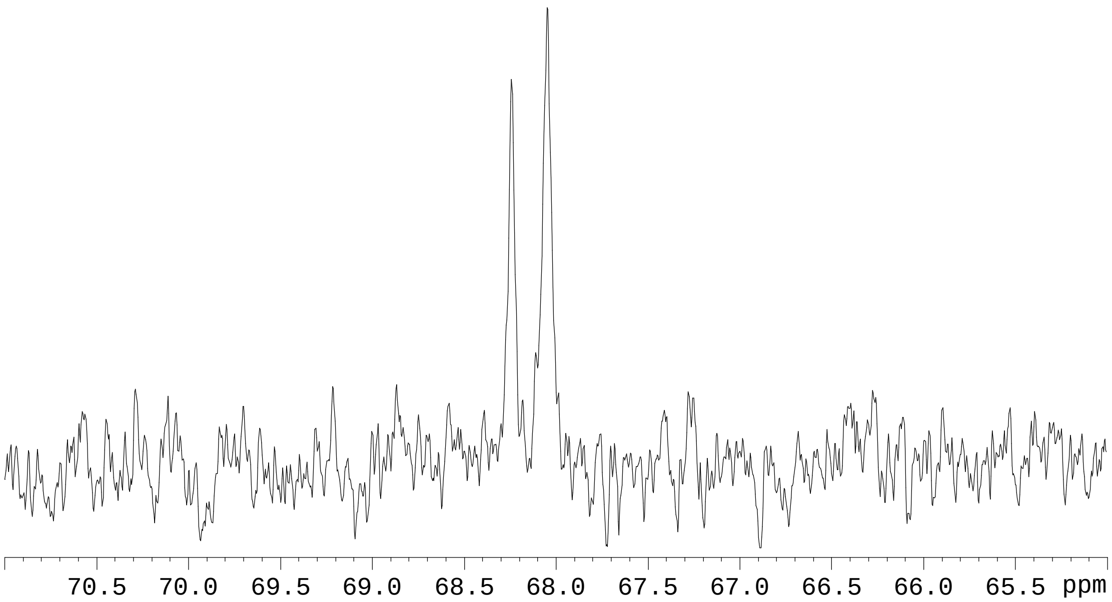

Figure S12: Methine region of the $^{13}C\{^{1}H\}$ NMR spectrum of PLA (Table 1, entry 4)

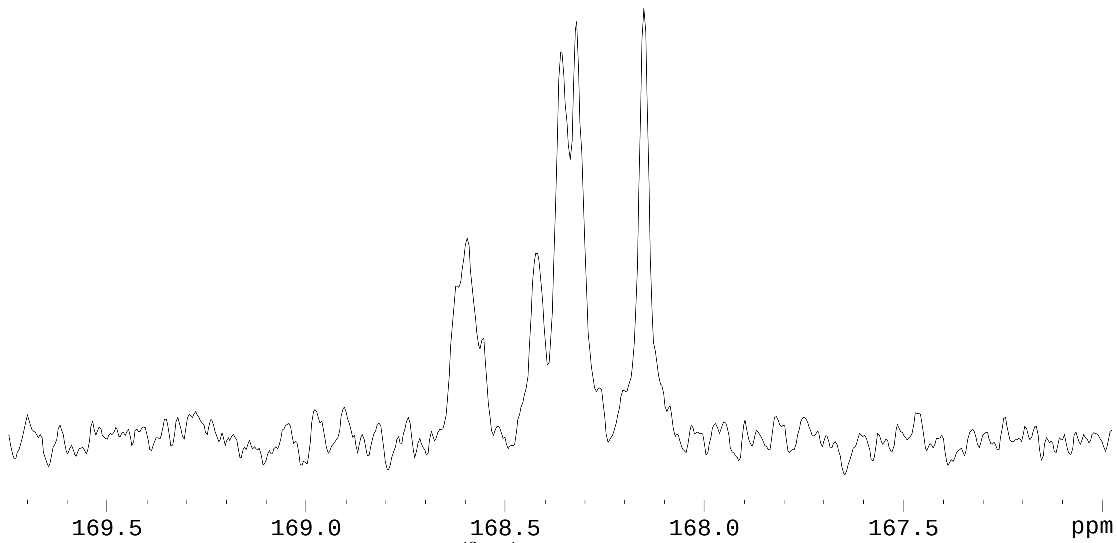

Figure S13: Carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectrum of PLA (Table 1, entry 4)

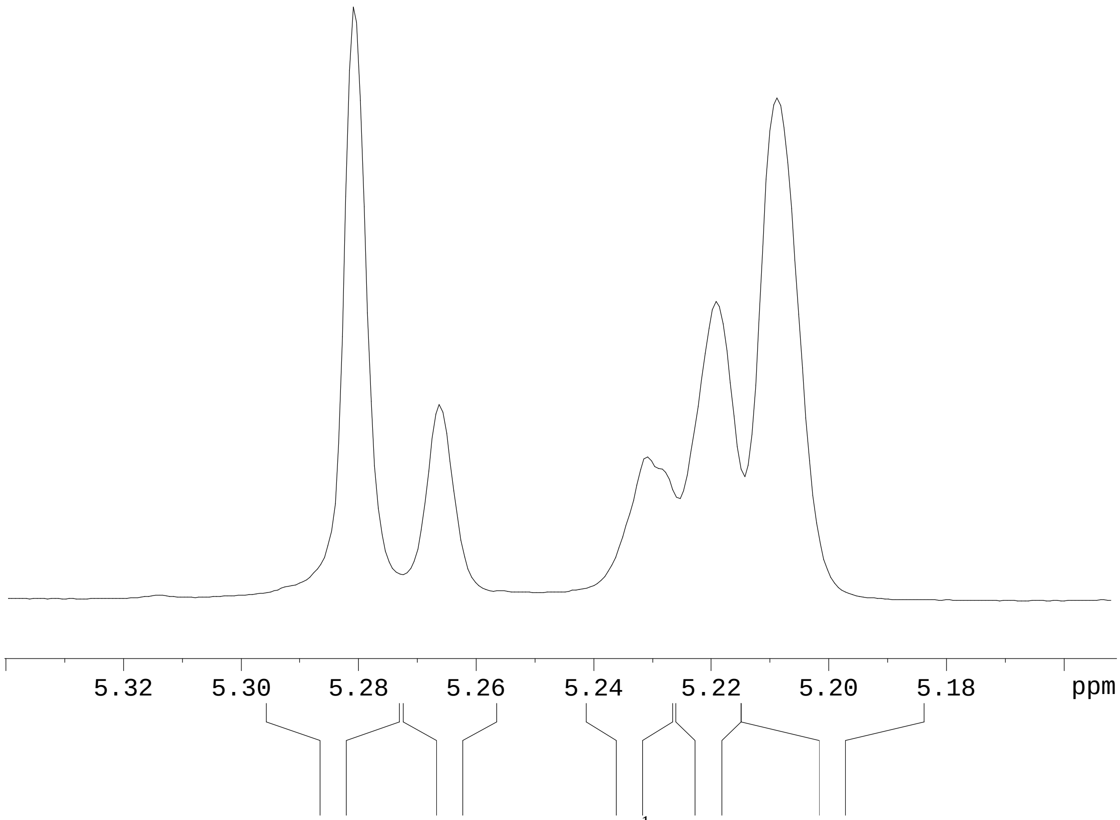

Figure S14: Methine region of the homonuclear decoupled ^{1}H NMR spectrum of PLA (Table 1, entry 4)

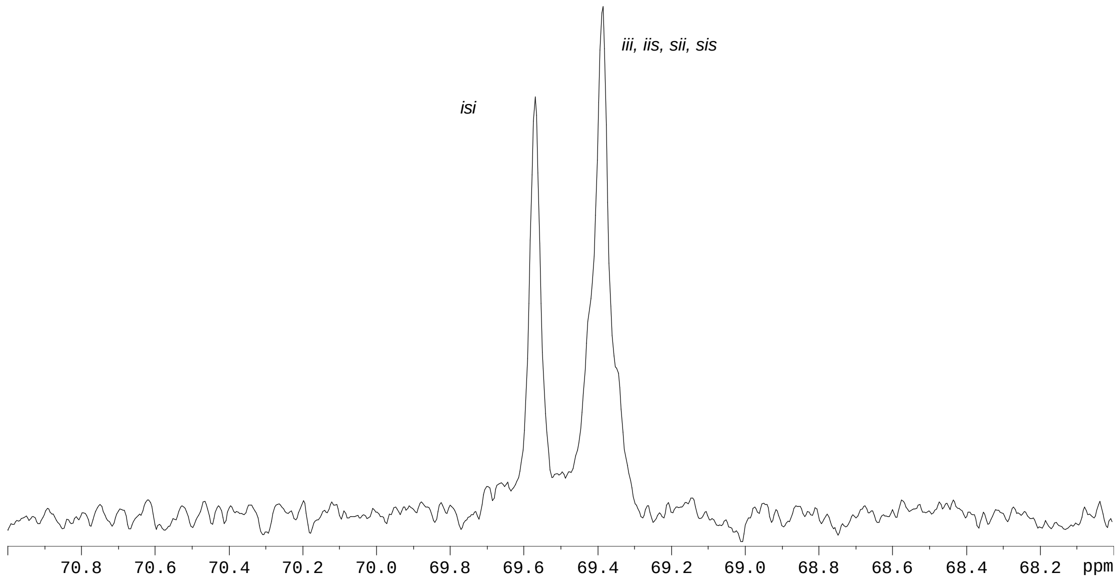

Figure S15: Methine region of the $^{13}C\{^1H\}$ NMR spectrum of PLA (Table 1, entry 5).

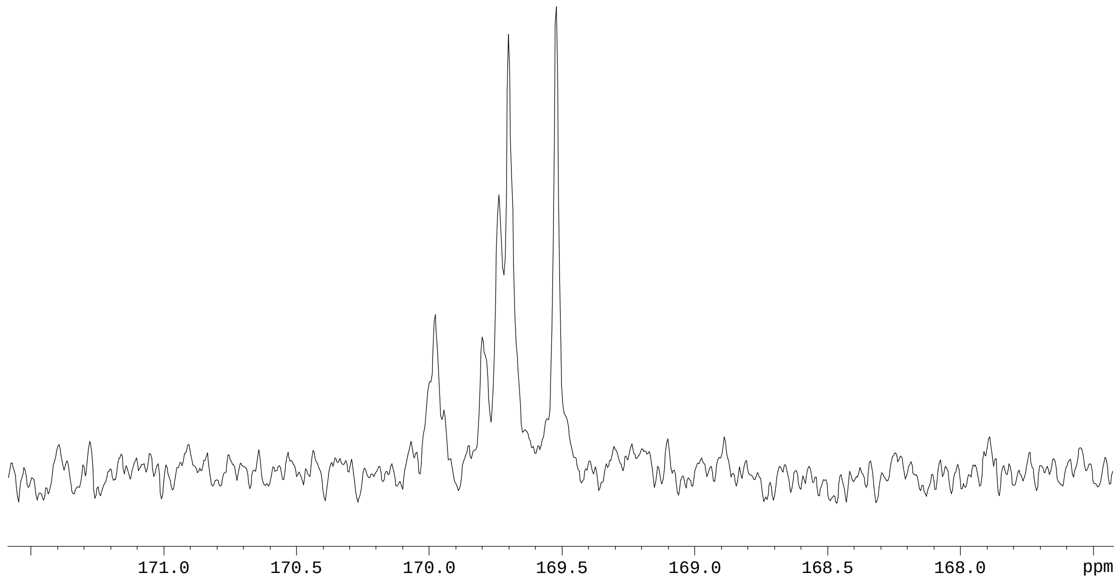

Figure S16: Carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum of PLA (Table 1, entry 5).

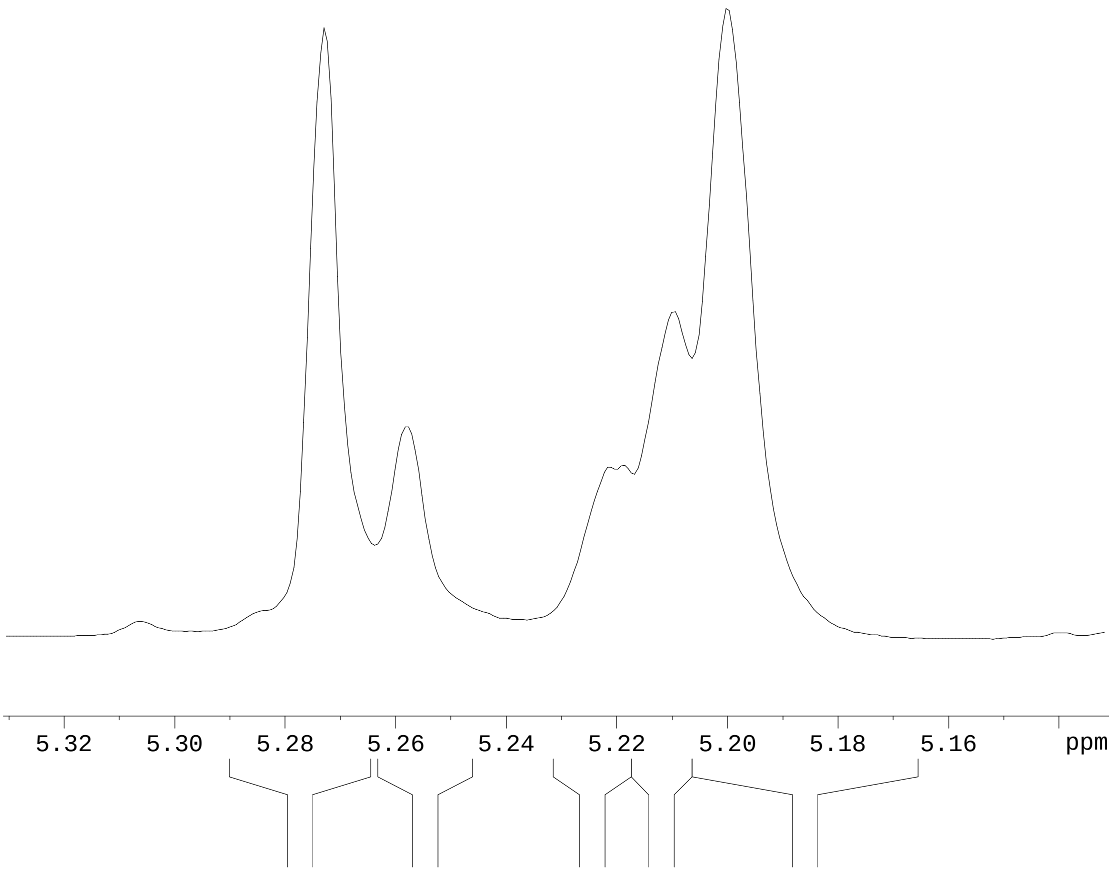

Figure S17: Methine region of the homonuclear decoupled ^{1}H NMR spectrum of PLA (Table 1, entry 5)

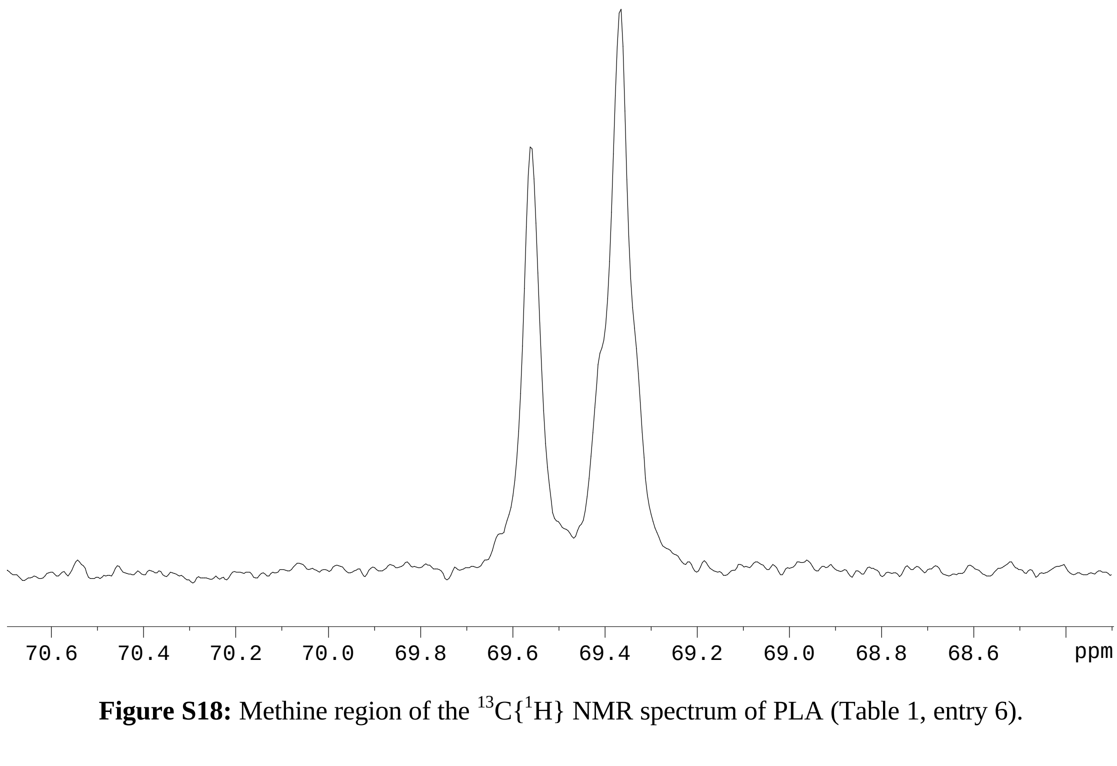

Figure S18: Methine region of the $^{13}C\{^{1}H\}$ NMR spectrum of PLA (Table 1, entry 6).

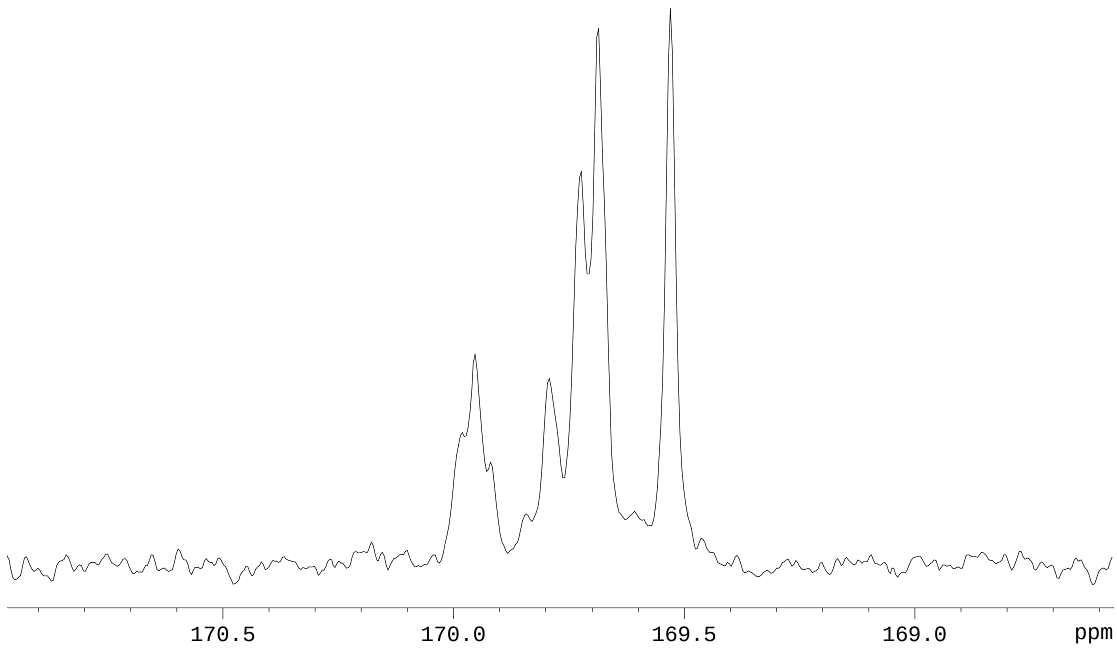

Figure S19: Carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum of PLA (Table 1, entry 6).

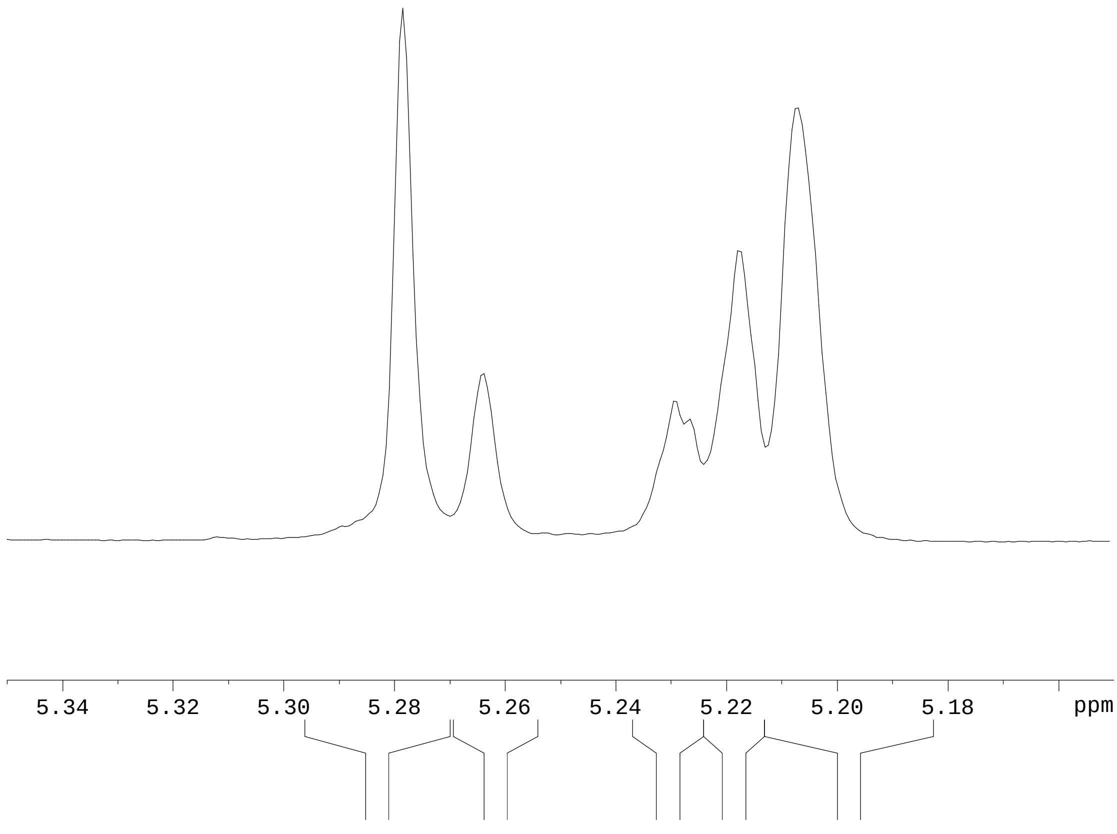

Figure S20: Methine region of the homonuclear decoupled ^1H NMR spectrum of PLA (Table 1, entry 6)