Stereoselective polymerization of *rac*- and *meso*-lactide catalyzed by a sterically encumbered *N*-heterocyclic carbene

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Experimental

General Methods and Materials. All reactions were performed under an inert atmosphere, using either standard Schlenk techniques or an MBraun glovebox. All solvents and reagents were obtained from commercial sources and used as received unless otherwise stated. Pentane, dichloromethane, tetrahydrofuran and toluene were passed through purification columns. Deuterated solvents (all 99 atom %D) were purchased from Cambridge Isotope Laboratories, dried over calcium hydride, distilled under vacuum, and stored under nitrogen. D,L-Lactide (*rac*-lactide) was purchased from Purac and purified by recrystallization from toluene. *meso*-Lactide was prepared based on a literature procedure.[1] 1,3-dimesitylimidazol-2-ylidene (IMes) was prepared as previously described.[2]

Characterization. ^{1}H NMR spectra were recorded in CDCl$_3$ with a Bruker Avance 400 (400 MHz) spectrometer with the solvent proton signal as an internal standard. ^{13}C NMR spectra were recorded at 100 MHz on a Bruker Avance 400 spectrometer with the solvent carbon signal as internal standard. Gel permeation chromatography (GPC) was carried out on a Waters chromatography instrument equipped with four 5 *í*m Waters columns (300 _ 7.7 mm) connected in series in order of increasing pore size (100, 1000, 105, 106) with THF as a solvent and a Waters 410 differential refractometer as detector. Polystyrene samples of known molecular weight were used as calibration standards.. Differential scanning calorimetry (DSC) was performed using a TA Differential Scanning

Calorimeter 1000 that was calibrated using high purity indium at a heating rate of 10 °C/min. Melting points were determined from the second scan following slow cooling (to remove the influence of thermal history) at a heating rate of 10 °C/min.

General Polymerization Procedure. Glassware used for polymerizations was oven or flame-dried, then oven dried for a minimum of 3 h. A reaction flask was charged in the glovebox with *rac*-lactide (100 mg, 0.7 mmol), 1-pyrenebutanol (2.06 mg, 7.0 μmol), 1.8mL of dry CH_2Cl_2 and a magnetic stirbar, then brought out of the glovebox and immersed in a temperature-controlled bath at the desired temperature. A solution of **1** (3.2mg, 7.0 μmol) in 0.2 mL CH_2Cl_2 was prepared in the glovebox and then removed from the glove box and quickly injected into the rapidly stirring flask using a gas-tight syringe equipped with a spraying needle. After an appropriate time, the reaction mixture was poured into pentane to precipitate the polymer. Excess pentane was removed by decantation and the polymer mixture was dried under vacuum prior to characterization by GPC and ^1H NMR spectroscopy.

Synthesis of 1.

1,4-Bis(2,4,6-trimethylphenyl)-2,3-diphenyl-1,4-diaza-1,3-butadiene. In a dry 1L round bottom flask, benzil (5g, 23.8 mmol) and 2,4,6-trimethylaniline (25.7g, 190 mmol) were dissolved in 700mL toluene. $TiCl_4$ (3.4 mL) was then added and the solution was stirred at 100 °C overnight. H_2O was added to quench the reaction, the toluene layer was next separated, dried over $MgSO_4$ and filtered. The solvent was removed under vacuum to yield yellow oil. The oil was then purified by column chromatography (silica/CH_2Cl_2) and recrystallization in ethanol (9.5g, 90% yield). ^1H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 2.247 (s, 12 H, *ortho*-CH_3, isomer 1), 2.288 (s, 12 H, *ortho*-CH_3, isomer 2), 2.598 (s, 6 H, *para*-CH_3, isomer 1), 2.648 (s, 6 H, *para*-CH_3, isomer 2), 7.091-7.986 (m, arom), ^{13}C NMR ($CDCl_3$, 23 °C, 100 MHz): δ 18.714 (*ortho*-CH_3), 19.089 (*ortho*-CH_3), 20.802 (*para*-CH_3), 20.932 (*para*-CH_3), 125.899, 126.780, 127.769, 128.243, 128.502, 128.858, 128.999, 129.148, 129.979, 131.252, 132.882, 135.405, 144.962, 145.398 (arom) 166.130, 167.144 (C=N)

1,3-(2,4,6-trimethylphenyl)-4,5-diphenyl-imidazolium chloride. To a suspension of AgOTf (1.90g, 7.4mmol) in 50 mL CH_2Cl_2 was added chloromethyl

pivalate (1.11g, 7.4mmol) and the resulting suspension was stirred for 45 min. The supernatant was transferred via syringe to vial containing a solution of 1,4-bis(2,4,6-trimethylphenyl)-2,3-diphenyl-1,4-diaza-1,3-butadiene (2.26g, 5.1mmol) in CH_2Cl_2, and the resulting solution was stirred in a sealed tube in the dark at 40 $^{\circ}$C for 20 h. After the solution was cooled to room temperature, the reaction was quenched with methanol and the solvent evaporated *in vacuo*. The resulting oil was chromatographed on silica gel (CH_2Cl_2/MeOH) to give 1,3-(2,4,6-trimethylphenyl)-4,5-diphenyl-imidazolium trifluoromethanesulfonate as a yellow oil. The oil was then dissolved in 50 mL CH_2Cl_2, 10 g IRA-900 resin was added and the suspension was stirred overnight. After filtration, the solvent was pumped off under vacuum. The product was washed with pentane at room temperature to give a yellow solid (1.9g, 78% yield). ^{1}H NMR (CDCl_3, 23 $^{\circ}$C, 400 MHz): δ 2.183 (s, 12 H, *ortho*-CH_3), 2.325 (s, 6 H, *para*-CH_3), 6.983 (s, 4H, *meta*-CH on IMes), 7.026 (d, 4H, *ortho*- CH on Ph), 7.308 (m, 6H, *meta-, para*- CH on Ph), 10.518 (s, 1H, im-^{2}H) ^{13}C NMR (CDCl_3, 23 $^{\circ}$C, 100 MHz): δ 18.414 (*ortho*-CH_3), 21.586 (*para*-CH_3), 125.355, 129.376, 129.444, 130.034, 130.308, 130.568, 132.525, 134.869, 141.619 (arom C)) MS FAB $\{(CH_3)_3C_6H_2)_2(C_6H_5)_2C_3N_2H\}^{+1}$ m/e 457.2 (M+, 100), 458.3 (M+1, 30) HRMS: Cald for $C_{33}H_{33}N_2H$ M[+], 457.2644; found: 457.2633.

1,3-dimethylimidazol-4,5-diphenyl-2-ylidene (1). KO[t]Bu (0.1g, 0.89mmol) and 1,3-(2,4,6-trimethylphenyl)-4,5-diphenyl-imidazolium chloride (0.44g, 0.89mmol) were added to 20 mL THF. The solution was stirred for 30 min then filtered, and all volatiles were removed under vacuum. The products were washed with pentane at room temperature to leave a yellow solid (0.30g, 75% yield). ^{1}H NMR (CDCl_3, 23 $^{\circ}$C, 400 MHz): δ 2.177 (s, 12 H, *ortho*-CH_3), 2.347 (s, 6 H, *para*-CH_3), 6.823 (s, 4H, *meta*-CH on IMes), 6.983 (m, 6H, *meta-, para*- CH on Ph), 7.206 (d, 4H, *ortho*- CH on Ph), ^{13}C NMR (CDCl_3, 23 $^{\circ}$C, 100 MHz): δ 18.369 (*ortho*-CH_3), 21.579 (*para*-CH_3), 125.359, 129.367, 129.417, 130.033, 130.301, 130.555, 132.446, 134.865, 141.611 (arom C), 242.132 (s, im-[2]C) MS, HRMS: Cald for $C_{33}H_{33}N_2$ M+1[+], 457.2644; found: 457.2641.

1. G. Entenmann, D. Bendix German Patent Application **1988**, DE 382029.

2. A. J. Arduengo, III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron*, 1999, **55**, 14523.

Figure S1. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of the PLA methine resonances with selective decoupling of the PLA methyl resonances from the sample made in Table 1, entry 1. The experimental integration values shown were determined by deconvoluting the overlapping peaks using the line fitting procedure of the Nuts software application and then normalizing the total of the five peaks to be one. On the bottom is a table showing various predicted Bernoulian integration percentages for a given P_i (at left in table).
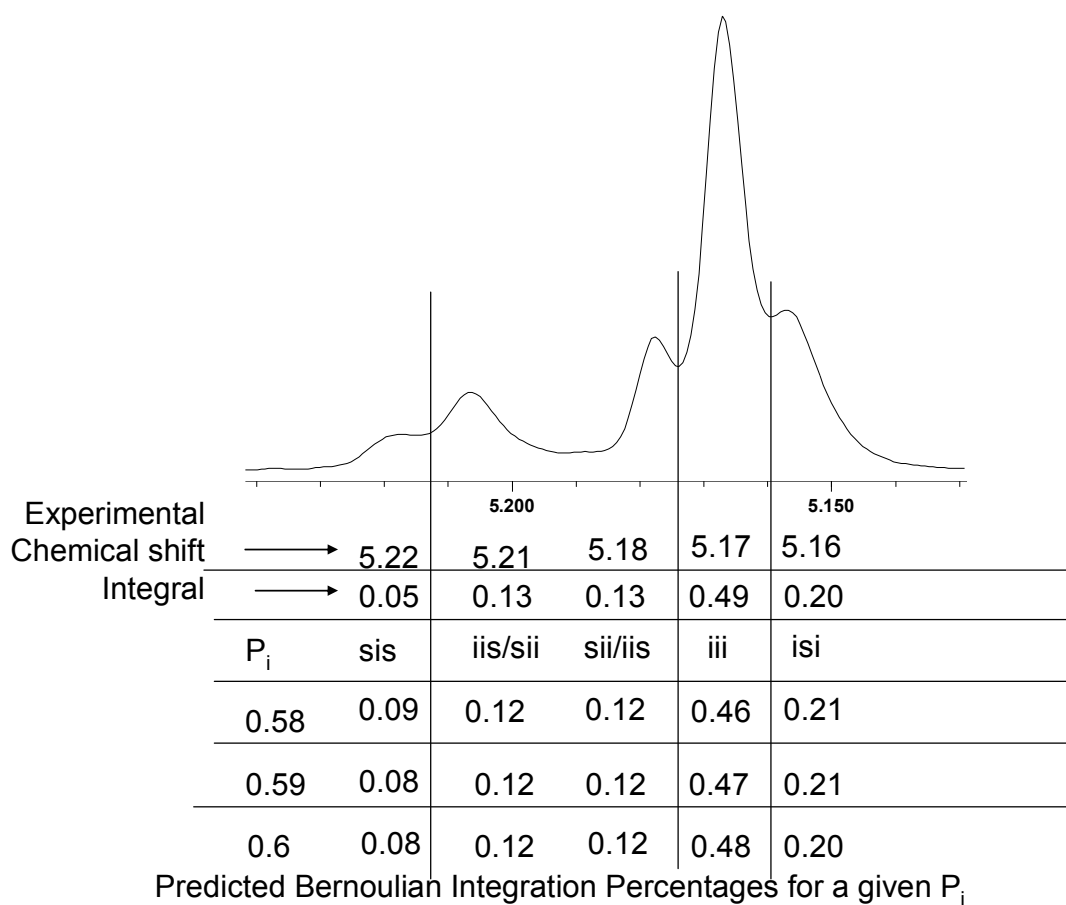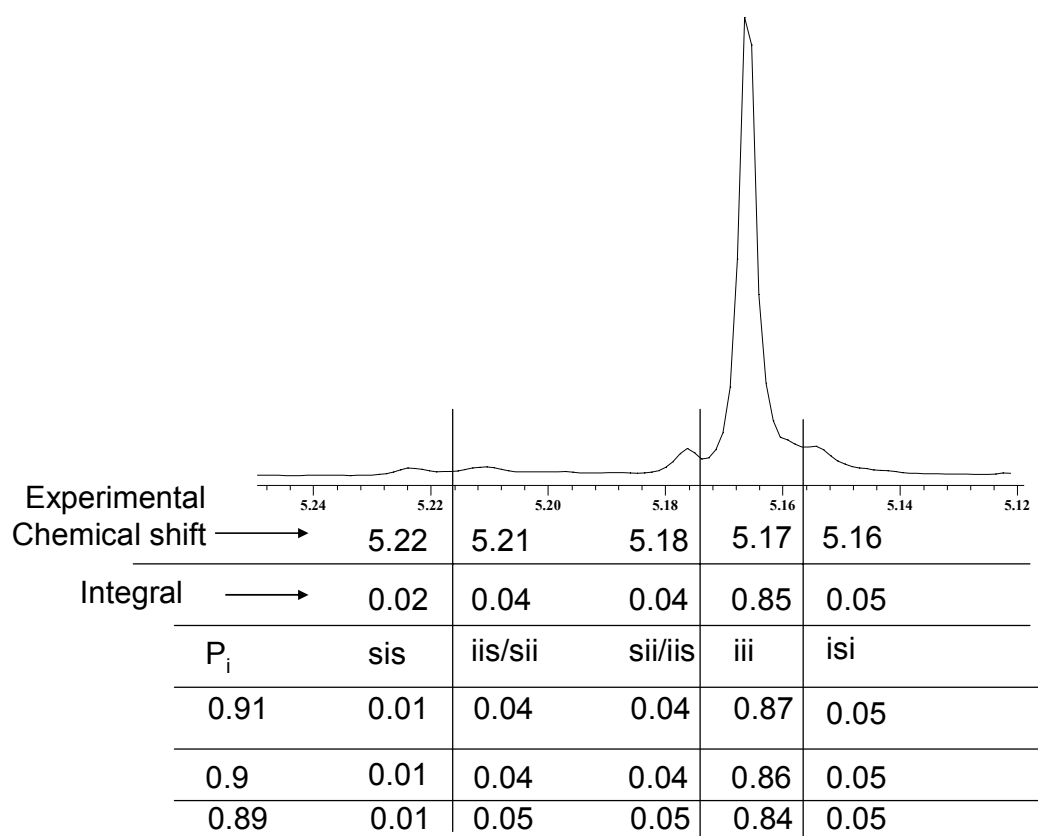
P_i =0.59

Experimental Chemical shift	5.22	5.21	5.18	5.17	5.16
Integral	0.05	0.13	0.13	0.49	0.20
P_i	sis	iis/sii	sii/iis	iii	isi
0.58	0.09	0.12	0.12	0.46	0.21
0.59	0.08	0.12	0.12	0.47	0.21
0.6	0.08	0.12	0.12	0.48	0.20

Predicted Bernoulian Integration Percentages for a given P_i

Figure S2. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of the PLA methine resonances with selective decoupling of the PLA methyl resonances from the sample made in Table 1, entry 4. The experimental integration values shown were determined by deconvoluting the overlapping peaks using the line fitting procedure of the Nuts software application and then normalizing the total of the five peaks to be one. On the bottom is a table showing various predicted Bernoulian integration percentages for a given P_i (at left in table).
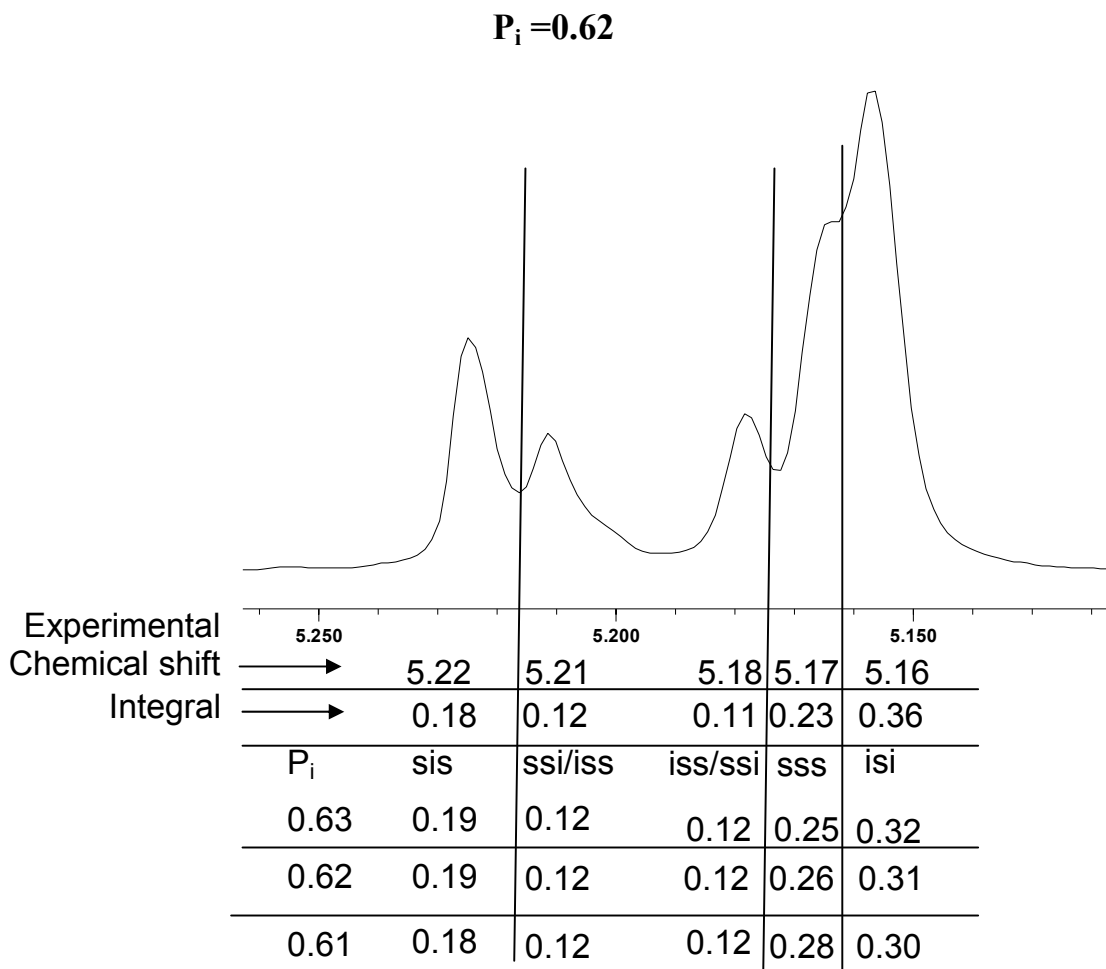
$P_i = 0.90$

Experimental Chemical shift ⟶	5.22	5.21	5.18	5.17	5.16
Integral ⟶	0.02	0.04	0.04	0.85	0.05
P_i	sis	iis/sii	sii/iis	iii	isi
0.91	0.01	0.04	0.04	0.87	0.05
0.9	0.01	0.04	0.04	0.86	0.05
0.89	0.01	0.05	0.05	0.84	0.05

Predicted Bernoulian Integration Percentages for a given P_i

Figure S3. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of the PLA methine resonances with selective decoupling of the PLA methyl resonances from the sample made in Table 1, entry 7. The experimental integration values shown were determined by deconvoluting the overlapping peaks using the line fitting procedure of the Nuts software application and then normalizing the total of the five peaks to be one. On the bottom is a table showing various predicted Bernoulian integration percentages for a given P_i (at left in table).

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$P_i = 0.62$

Experimental Chemical shift ⟶	5.22	5.21	5.18	5.17	5.16
Integral ⟶	0.18	0.12	0.11	0.23	0.36
P_i	sis	ssi/iss	iss/ssi	sss	isi
0.63	0.19	0.12	0.12	0.25	0.32
0.62	0.19	0.12	0.12	0.26	0.31
0.61	0.18	0.12	0.12	0.28	0.30

Predicted Bernoulian Integration Percentages for a given P_i

Figure S4. ^{1}H NMR spectrum (400 MHz, CDCl3) of the PLA methine resonances with selective decoupling of the PLA methyl resonances from the sample made in Table 1, entry 9. The experimental integration values shown were determined by deconvoluting the overlapping peaks using the line fitting procedure of the Nuts software application and then normalizing the total of the five peaks to be one. On the bottom is a table showing various predicted Bernoulian integration percentages for a given P_i (at left in table).

$P_i = 0.83$

Experimental Chemical shift	5.23	5.22	5.17	5.165	5.16
Integral	0.41	0.02	0.08	0.14	0.35
P_i	sis	ssi/iss	iss/ssi	sss	isi
0.82	0.41	0.07	0.07	0.11	0.34
0.83	0.42	0.07	0.07	0.10	0.34
0.84	0.42	0.07	0.07	0.09	0.35

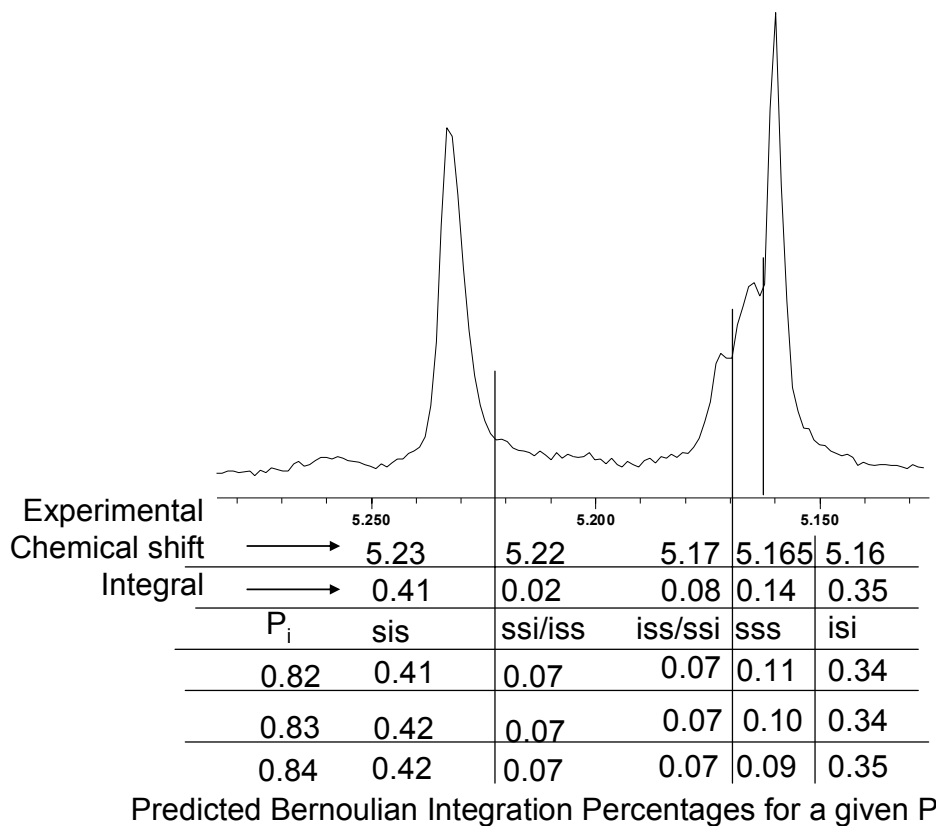Predicted Bernoulian Integration Percentages for a given P_i

Figure S5. An illustrative line fit of the spectra (Table 1, entry 2). The fits were done using the line fitting procedure of the Nuts software application. The blue line is the actual spectra. The red and green lines are the assigned peak fits. The areas of these peaks were then normalized, with the total of all five peaks set to one in order to obtain the relative integrations.
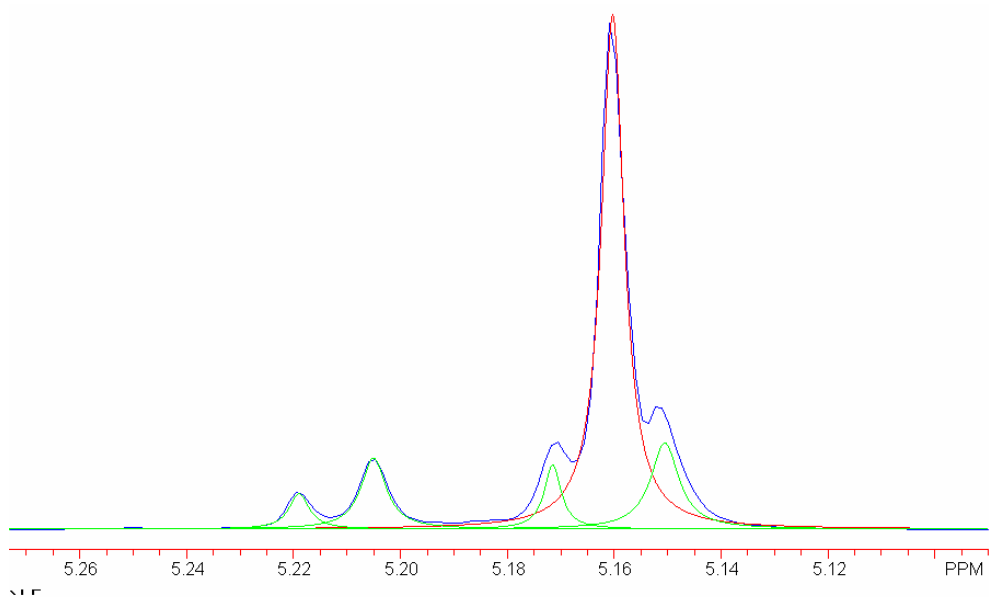

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Figure S6. ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of the PLA methine resonances from the sample made in Table 1, entry 4
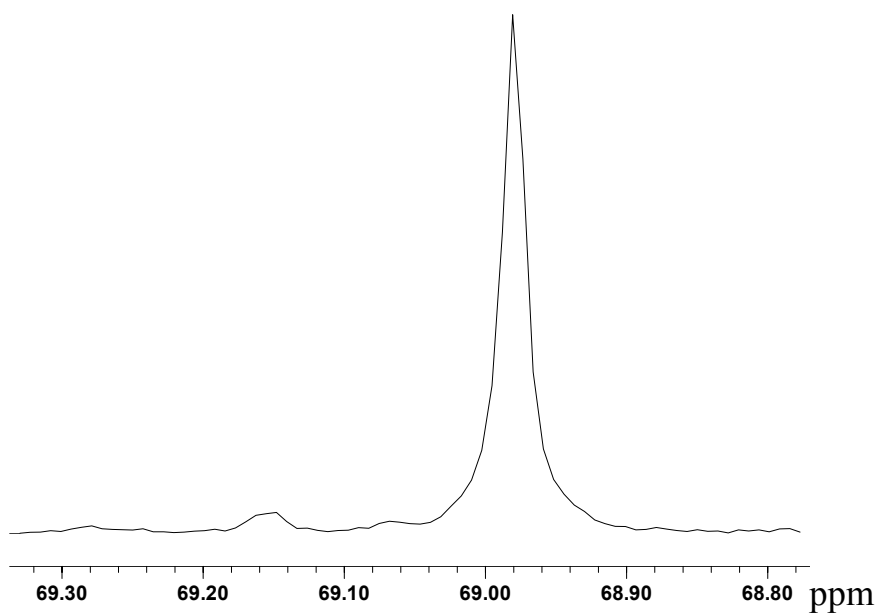

Figure S7. ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of the PLA methine resonances from the sample made in Table 1, entry 8.
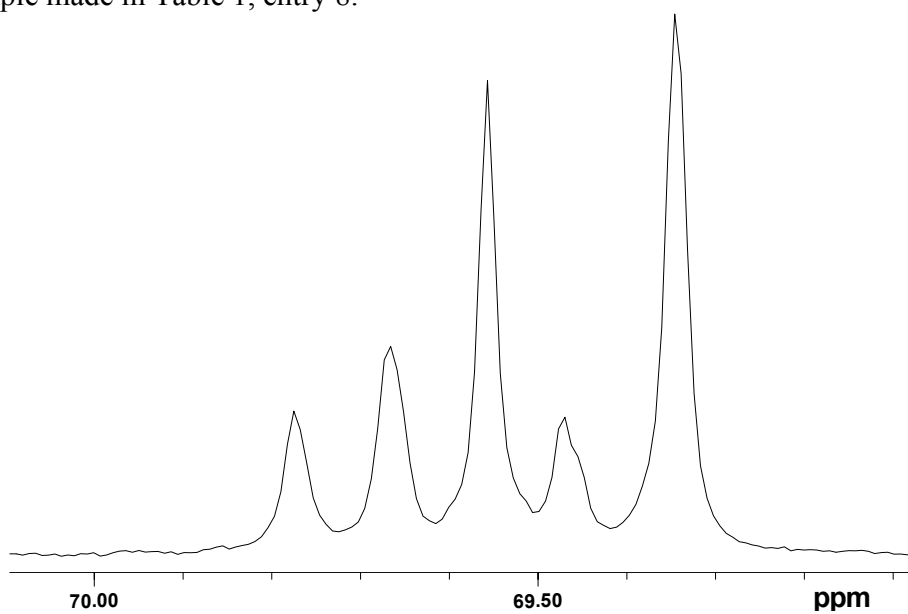
Figure S8. DSC of PLA made with **1** (Table 1, entry 4). This figure is from the second scan (ramp rate of 10 °C/min).