Supporting information

The first facile stereoselectivity switch in the polymerization of *rac*-lactide - from heteroselective to isoselective dialkylgallium alkoxides with the help of N-heterocyclic carbenes

Paweł Horeglad,[a,*] Grzegorz Szczepaniak,[a] Maciej Dranka[b] and Janusz Zachara[b]

[a] *Faculty of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089, Warsaw, Poland*

[b] *Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664, Warsaw, Poland*

General Remarks

[1] All operations were carried out under dry nitrogen using standard Schlenk techniques. Solvents and reagents were purified and dried prior to use. Solvents were dried over potassium (toluene, hexane) or calcium hydride (CH_2Cl_2). L-Lactide and *rac*-Lactide were purchased from Aldrich and further purified by crystallization from anhydrous toluene. (*S*)-methyl lactate was purchased from Aldrich, dried over molecular sieves and distilled under argon. Me_3Ga was purchased from Strem Chemicals, Inc. and used as received. ^1H NMR spectra were recorded on a Varian UnityPlus – 200 MHz and for selected PLA samples on Varian INOVA 500 MHz spectrometers with shifts given in ppm according to deuterated solvent shift. GPC measurements were recorded on Spectra-Physics chromatograph equipped with two high performance Plgel 5 µm MIXED-C columns and detectors: RI (VE3580 Viscotek) and viscometer (270 Dual Detector Array Viscotek with universal calibration according to polystyrene standard. Measurement paremeters – THF, 35ºC, 1ml/min. FTIR spectra were recorded on FT-IR Perkin Elmer System 2000. (S,S)-$[Me_2Ga(\mu\text{-}(S)OCH(Me)CO_2Me)]_2$ (**1**) was synthesized according to the literature.[1] SIMes was synthesized by the modification of the method described in the literature.[2] $[Me_2GaOMe]_3$ was synthesized, analogously to **1**, in the reaction of methanol with trimethyl gallium – a generally used method for the synthesis of dialkylgallium alkoxides.[3]

Synthesis of SIMes (1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene)

2.3 g (6.71 mmol) of $(SIMesH)^+Cl^-$ was added to the suspension of KH (353 mg, 8.81 mmol) in toluene (80 mL) at room temperature followed by addition of catalytic amount of KO*t*Bu (~ 1%). The suspension was stirred for 4 hours until gas evolution essentially ceased. Then 65 mL of clear solution was collected from over precipitate and toluene removed under vacuum to give pale yellow solid. Obtained solid was dissolved in hexane (38 mL) and filtered through 45µm PTFE filter to give clear colourless solution which was subsequently cooled down to −18ºC. After 24 hours the solution was removed from over colourless crystals which were washed twice with 5 ml of cold hexane (−78ºC) and dried under vacuum to give 1.05g (51%) of SIMes. ^{1}HNMR(THF-d_8, 200MHz): 2.25 (s, 18H, CH_3), 3.66 (s, 4H, CH_2), 6.88 (s, 4H, CH_{Ar})

Synthesis of $[Me_2GaOMe]_3$

A stirred solution of Me_3Ga (0.35 g, 3.0 mmol) in methylene chloride (5 mL) was cooled to −78 C, and dry methanol (0.12 mL, 3.0 mmol) was added dropwise. After addition the reaction mixture was allowed to warm to a room temperature and stirred for 1 hour. Solvent and volatile residues were then removed under vacuum to give colorless liquid in essentially quantitative yield. ^{1}H NMR ($CDCl_3$, 200MHz): −0.33 (s, 6H, $GaCH_3$), 3.39 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, 200MHz): −7.42 ($GaCH_3$), 52.18 (OCH_3).

Synthesis of 2a in CH_2Cl_2. To the solution of **1** (64 mg, 0.16 mmol) in CH_2Cl_2 (3 mL) 0.35 mL of toluene solution of SIMes (97 mg, 0.32 mmol) was added dropwise and solution was subsequently stirred for 1 h. Then, toluene was removed under vacuum to give the colorless liquid of **2a** in essentially quantitative yield. ^{1}HNMR(CD_2Cl_2, 200MHz): −1.36 (s, 3H, $GaCH_3$), −1.30 (s, 3H, $GaCH_3$), 0.98 (d, 3H, ^3J(H,H)=6.8Hz, *CH*CH$_3$), 2.32 (s, 6H, CH_3), 2.34 (br., 12H, CH_3), 3.49 (s, 3H, OCH_3), 3.55 (q, 1H, ^3J(H,H)=6.8 Hz, CH*CH$_3$*), 3.93 (s, 4H, CH_2), 6.96 (s, 4H, CH_{Ar}).

^{1}H NMR and ^{13}C NMR of product obtained after dissolution of 2a in $CDCl_3$

^{1}H NMR ($CDCl_3$, 200MHz): −0.31 (s, 6H, $GaCH_3$), 1.39 (d, 3H, ^3J(H,H)=6.8 Hz, *CH*CH$_3$), 2.26 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 3.31 (m, 2H, CH_2), 3.77 (s, 3H, OCH_3), 3.92 (m, 2H, CH_2) 4.39 (q, 1H, ^3J(H,H)=6.8 Hz, CH*CH$_3$*), 6.85 (br, 2H, CH_{Ar}), 6.88 (br, 2H, CH_{Ar}).

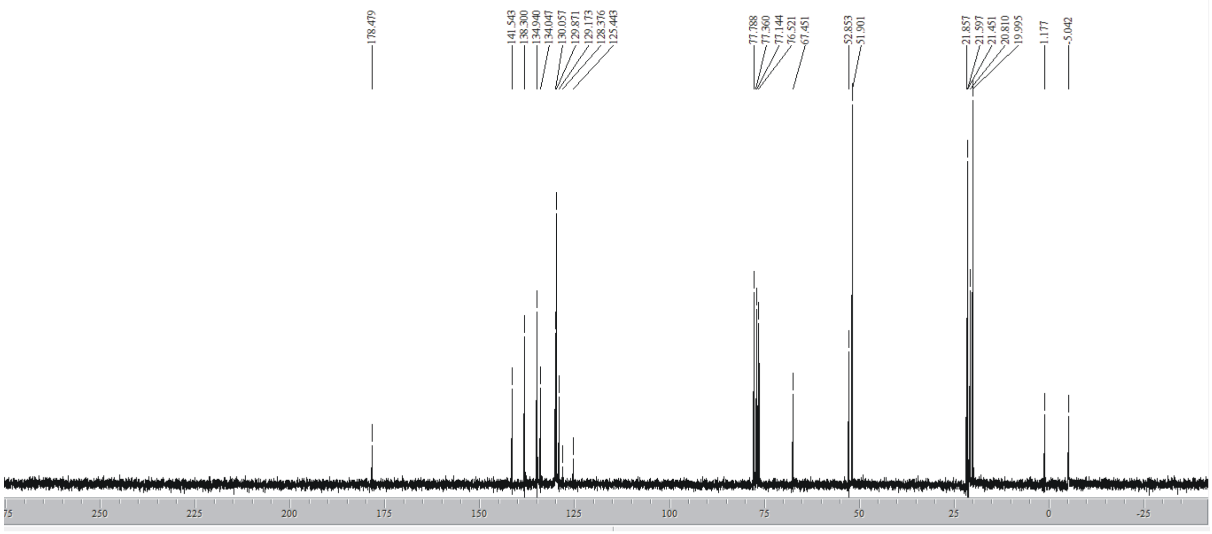


Figure S1. ^{13}C NMR spectrum of **2a** in $CDCl_3$

^{1}H NMR and ^{13}C NMR of 2a and 2b

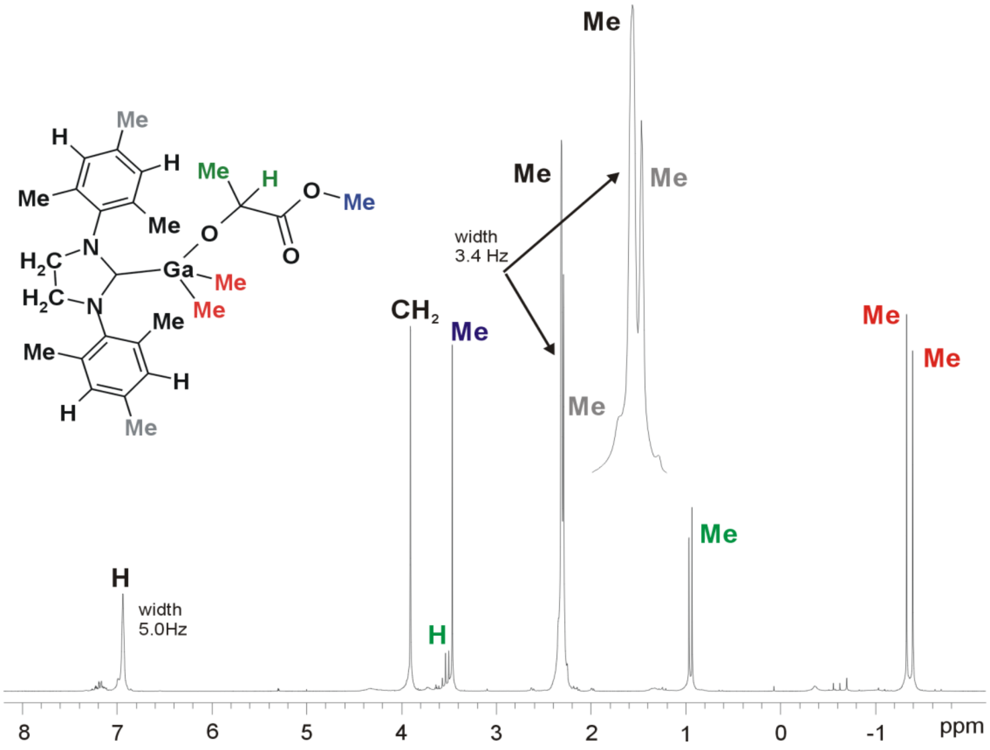


Figure S2. ^{1}H NMR spectrum of **2a** in CD_2Cl_2 ^{1}HNMR(CD_2Cl_2, 200MHz): −1.36 (s, 3H, $GaCH_3$), −1.30 (s, 3H, $GaCH_3$), 0.98 (d, 3H, ^{3}J(H,H)=6.8Hz, C*H*CH_3), 2.32 (s, 6H, CH_3), 2.34 (br., 12H, CH_3), 3.49 (s, 3H, OCH_3), 3.55 (q, 1H, ^{3}J(H,H)=6.8 Hz, CHCH_3), 3.93 (s, 4H, CH_2), 6.97 (br., 4H, CH_{Ar}).

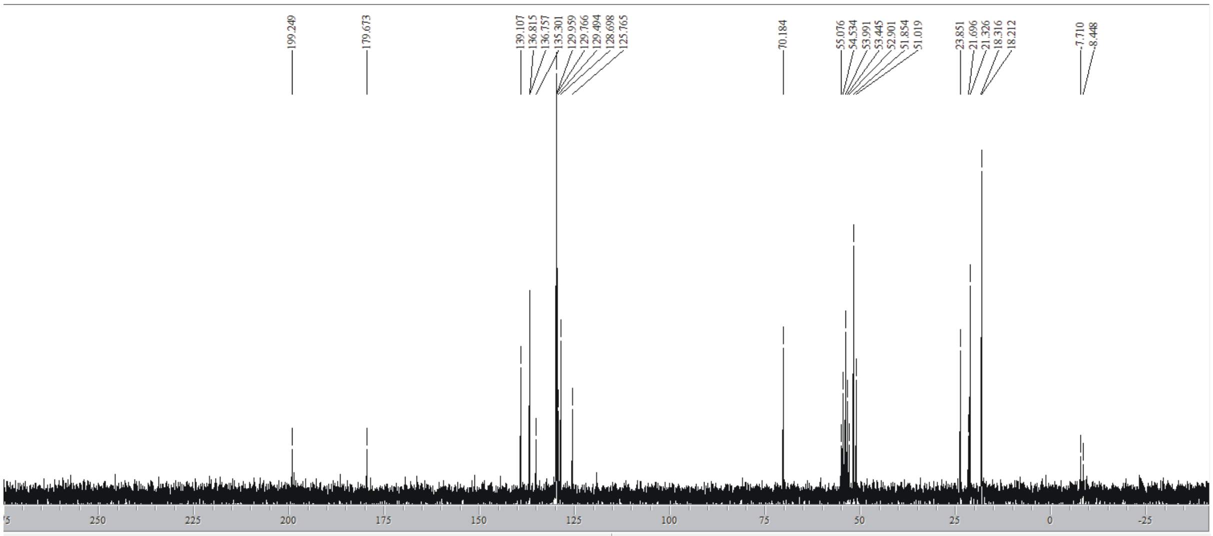


Figure S3. ^{13}C NMR spectrum of **2a** in CD_2Cl_2

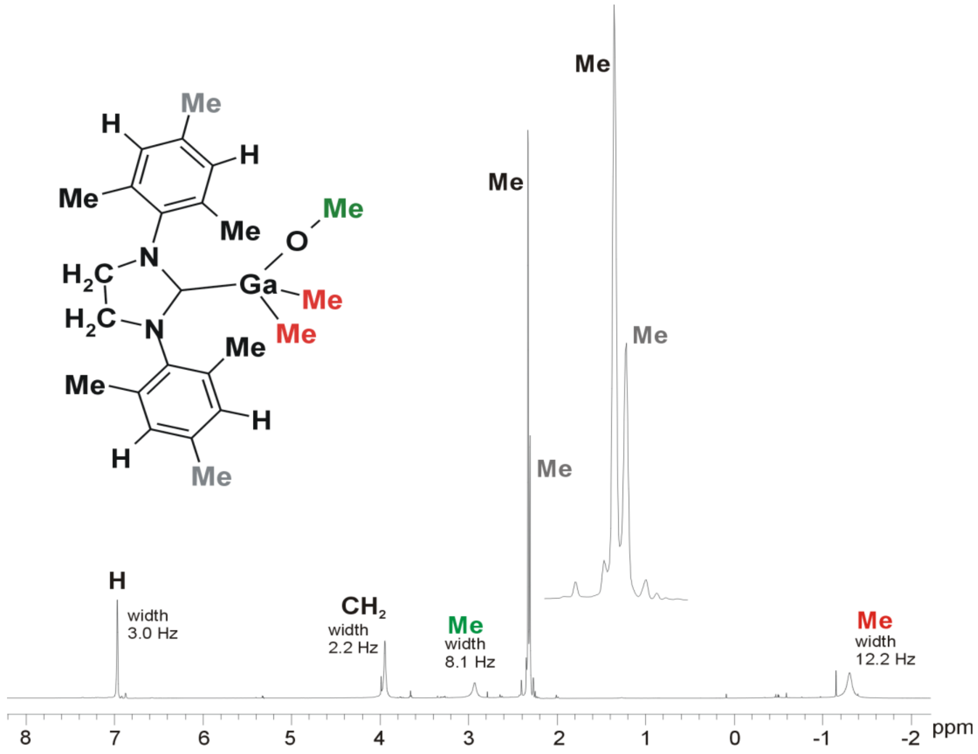


Figure S4. ^{1}H NMR spectrum of **2b** in CD_2Cl_2

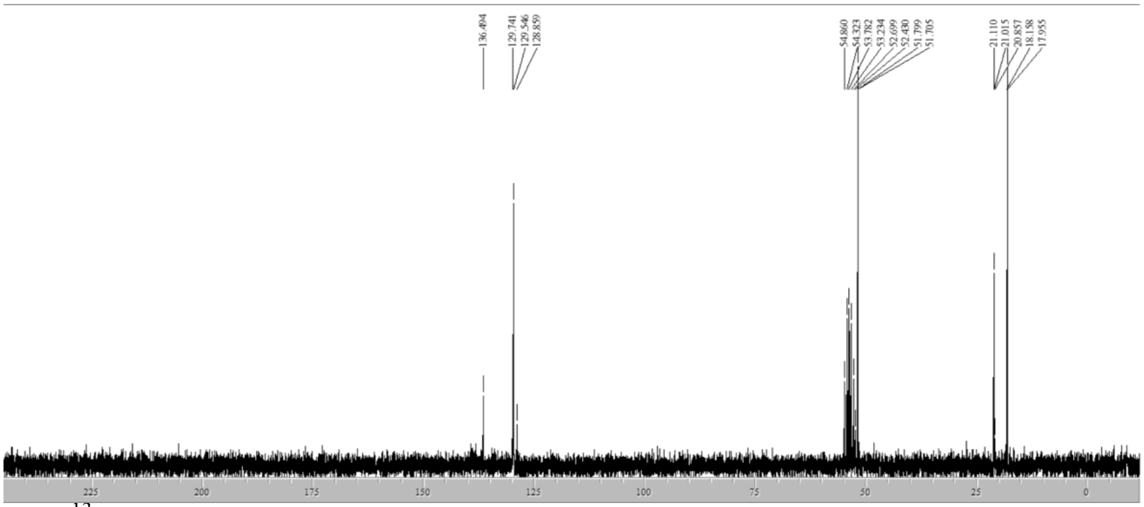
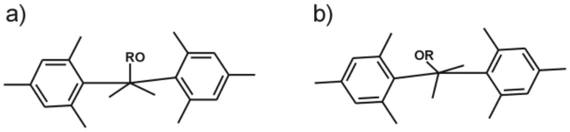


Figure S5. ^{13}C NMR spectrum of **2b** in CD_2Cl_2

Possible arrangement of NHC ligand for 2



Scheme S1. Top view of conformers of **2** with Ga atom in the centre and NHC ligand located above

The synthesis of *R*R**-[$Me_2Ga(\mu\text{-}OCH(Me)CO_2Me)]_2$ and raction of *R*R**-[$Me_2Ga(\mu\text{-}OCH(Me)CO_2Me)]_2$ with SIMes

*R*R**-[$Me_2Ga(\mu$-OCH(Me)$CO_2Me)]_2$ was synthesized analoguesly to **1** with the use of (*rac*)-methyl lactate instead of (*S*)-methyl lactate.[1] The ^{1}H NMR of *R*R**-[$Me_2Ga(\mu$-(*rac)*OCH(Me)$CO_2Me)]_2$ revealed the formation of homo- and heterochiral dimers. Homo- and heterochiral dimers were found by the analysis of the ^{1}H NMR spectrum in the region of Ga-Me, which revealed three singlets in 1:2:1 ratio. The reaction of *R*R**-[$Me_2Ga(\mu$-OCH(Me)$CO_2Me)]_2$ with SIMes resulted in the ^{1}H NMR spectrum essentially the same as for **2a** with a loss of initial character of Ga-Me signals, which indicates breaking of the dimeric gallium species.

*R*R**-[$Me_2Ga(\mu$-OCH(Me)$CO_2Me)]_2$: ^{1}HNMR($CDCl_3$, 200 MHz): -0.43, -0.35 -0.26 (s, 6H, $GaCH_3$), 1.35 (d, 3H, ^3J(H,H)=6.7Hz, $CHCH_3$), 3.73 (s, 3H, OCH_3), 4.38 (q, 1H, ^3J(H,H) = 6.7 Hz, $CHCH_3$).

Me_2Ga((R*)-OCH(Me)CO_2Me)(SIMes): ^{1}HNMR(CD_2Cl_2, 200MHz): −1.36 (s, 3H, $GaCH_3$), −1.29 (s, 3H, $GaCH_3$), 0.98 (d, 3H, ^3J(H,H)=6.8Hz, *CH*CH_3), 2.32 (s, 6H, CH_3), 2.35 (br., 12H, CH_3), 3.49 (s, 3H, OCH_3), 3.55 (q, 1H, ^3J(H,H)=6.8 Hz, CHCH_3), 3.93 (s, 4H, CH_2), 6.97 (br., 4H, CH_{Ar}).

Temperature studies for 2a

^{1}HNMR(toluene-d_8, 200MHz, -20ºC): −0.82 (s, 3H, $\mathrm{GaCH_3}$), −0.80 (s, 3H, $\mathrm{GaCH_3}$), 1.48 (d, 3H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$), 2.09 (s, 6H, $\mathrm{CH_3}$), 2.32, 2.33 (br., 12H, $\mathrm{CH_3}$, 3.0Hz), 3.05 (s, 4H, $\mathrm{CH_2}$), 3.41 (s, 3H, $\mathrm{OCH_3}$), 4.23 (q, 1H, $\mathrm{CHC}\mathit{H_3}$), 6.73 (br, 4H, $\mathrm{CH_{Ar}}$, 2.6Hz)

^{1}HNMR(toluene-d_8, 200MHz, 25ºC): −0.89 (s, 3H, $\mathrm{GaCH_3}$), −0.87 (s, 3H, $\mathrm{GaCH_3}$), 1.38 (d, 3H $\mathrm{C}\mathit{H}\mathrm{CH_3}$), 2.10 (s, 6H, $\mathrm{CH_3}$), 2.32, 2.33 (br., 12H, $\mathrm{CH_3}$, 2.8Hz), 3.18 (s, 4H, $\mathrm{CH_2}$), 3.42 (s, 3H, $\mathrm{OCH_3}$), 4.21 (q, 1H, $\mathrm{CHC}\mathit{H_3}$), 6.76 (br., 4H, $\mathrm{CH_{Ar}}$, 2.8Hz)

^{1}HNMR(toluene-d_8, 200MHz, 60ºC): −0.92, −0.89 (br., 6H, $\mathrm{GaCH_3}$, 2.6Hz), 1.32 (d, 3H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$), 2.12 (br., 6H, $\mathrm{CH_3}$, 2.1Hz), 2.32 (br., 12H, $\mathrm{CH_3}$, 3.7Hz), 3.25 (br., 4H, $\mathrm{CH_2}$, 2.3Hz), 3.44 (s, 3H, $\mathrm{OCH_3}$), 4.20 (q, 1H, $\mathrm{CHC}\mathit{H_3}$), 6.78 (br, 4H, $\mathrm{CH_{Ar}}$, 2.8Hz);

^{1}HNMR(toluene-d_8, 200MHz, 70ºC): −0.92, −0.90 (br., 6H, $\mathrm{GaCH_3}$, 6.0 Hz), 1.30 (br., 3H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$, 3.1 Hz), 2.13 (br. D, 6H, $\mathrm{CH_3}$, 2.3 Hz), 2.32 (br., 12H, $\mathrm{CH_3}$, 3.2 Hz), 3.27 (br., 4H, $\mathrm{CH_2}$, 3.0 Hz), 3.44 (br., 3H, $\mathrm{OCH_3}$, 3.2 Hz), 4.20 (br. Q, 1H, $\mathrm{CHC}\mathit{H_3}$, 3.7 Hz), 6.79 (br., 4H, $\mathrm{CH_{Ar}}$, 3.3 Hz);

^{1}HNMR(toluene-d_8, 200MHz, 80ºC): −0.91 (br., 6H, $\mathrm{GaCH_3}$, 10.0 Hz), 1.30 (br., 3H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$, 3.4 Hz), 2.13 (br. D, 6H, $\mathrm{CH_3}$, 2.4 Hz), 2.33 (br., 12H, $\mathrm{CH_3}$, 2.7 Hz), 3.30 (br., 4H, $\mathrm{CH_2}$, 2.3 Hz), 3.44 (br., 3H, $\mathrm{OCH_3}$, 4.1 Hz), 4.20 (br. Q, 1H, $\mathrm{CHC}\mathit{H_3}$, 6.0 Hz), 6.80 (br., 4H, $\mathrm{CH_{Ar}}$, 3.1 Hz);

Temperature studies for 2b

^{1}HNMR($\mathrm{CD_2Cl_2}$, 200MHz, 25ºC): −1.29 (s, 6H, $\mathrm{GaCH_3}$, 12.6 Hz), 2.31 (s, 6H, $\mathrm{CH_3}$), 2.33 (s, 6H, $\mathrm{CH_3}$), 2.94 (s, 3H, $\mathrm{OCH_3}$, 8.1 Hz), 3.94 (br., 4H, $\mathrm{CH_2}$, 2.2 Hz), 6.97 (br., 4H, $\mathrm{CH_{Ar}}$, 3.0 Hz).

^{1}HNMR($\mathrm{CD_2Cl_2}$, 200MHz, -30ºC): −1.38 (s, 6H, $\mathrm{GaCH_3}$), 2.28, 2.29 (s, 18H, $\mathrm{CH_3}$), 2.85 (s, 3H, $\mathrm{OCH_3}$), 3.93 (s, 4H, $\mathrm{CH_2}$), 6.96 (br., 4H, $\mathrm{CH_{Ar}}$, 2.7 Hz).

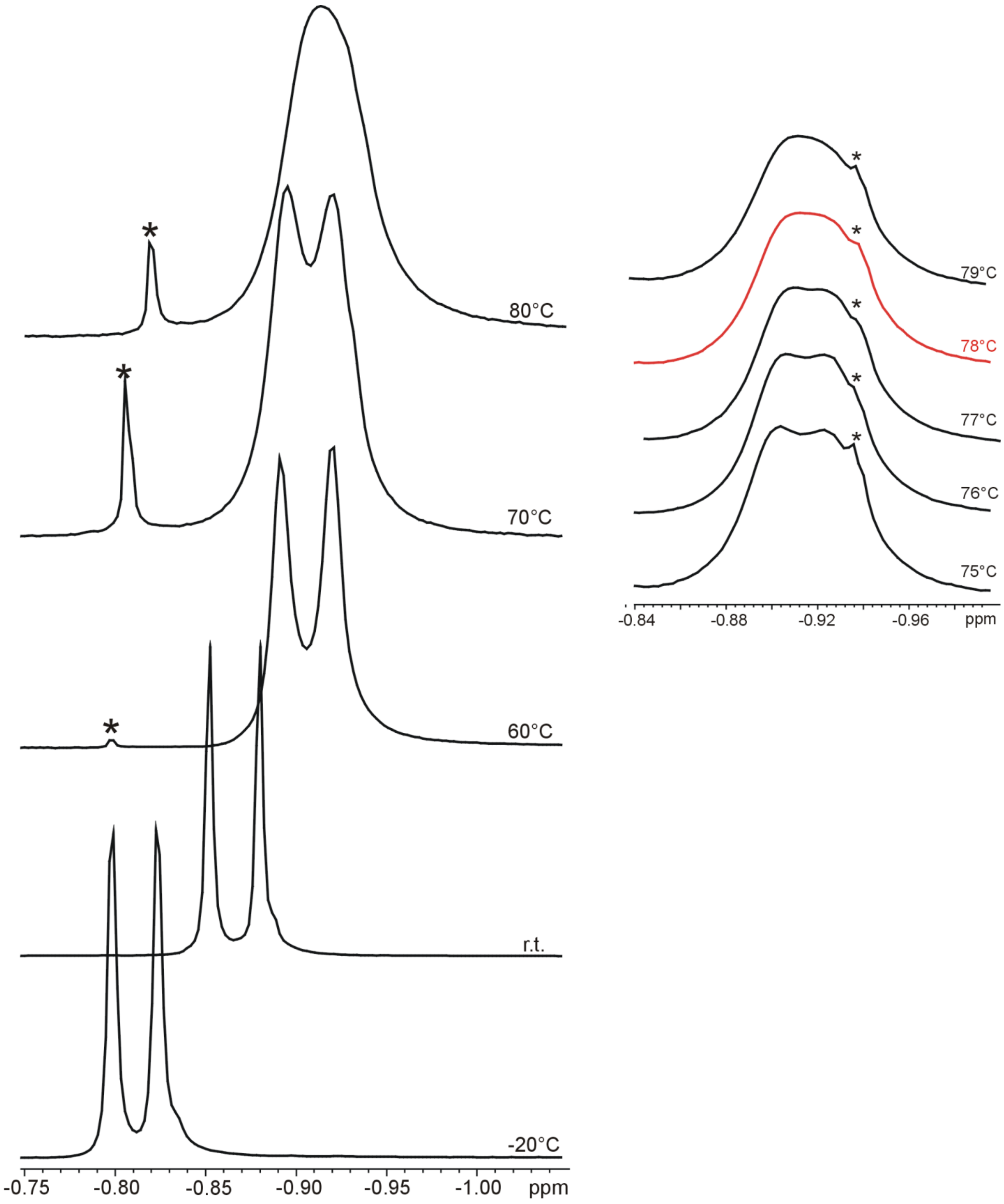


Figure S6. VT ^1H NMR spectrum of **2a** (Ga-CH_3 region) in toluene-d_8 (* - products of the decomposition of **2a** at elevated temperature)

IR data for 2a

3032 (m), 2954 (m), 1737 (s), 1634 (s), 1604 (w), 1559 (w), 1482 (s), 1458 (m), 1380 (w), 1246 (m), 1234 (s), 1193 (m), 1140 (m), 1098 (w), 1061 (s), 981 (w), 918 (w), 856 (w), 628 (w), 570 (w), 534 (w)

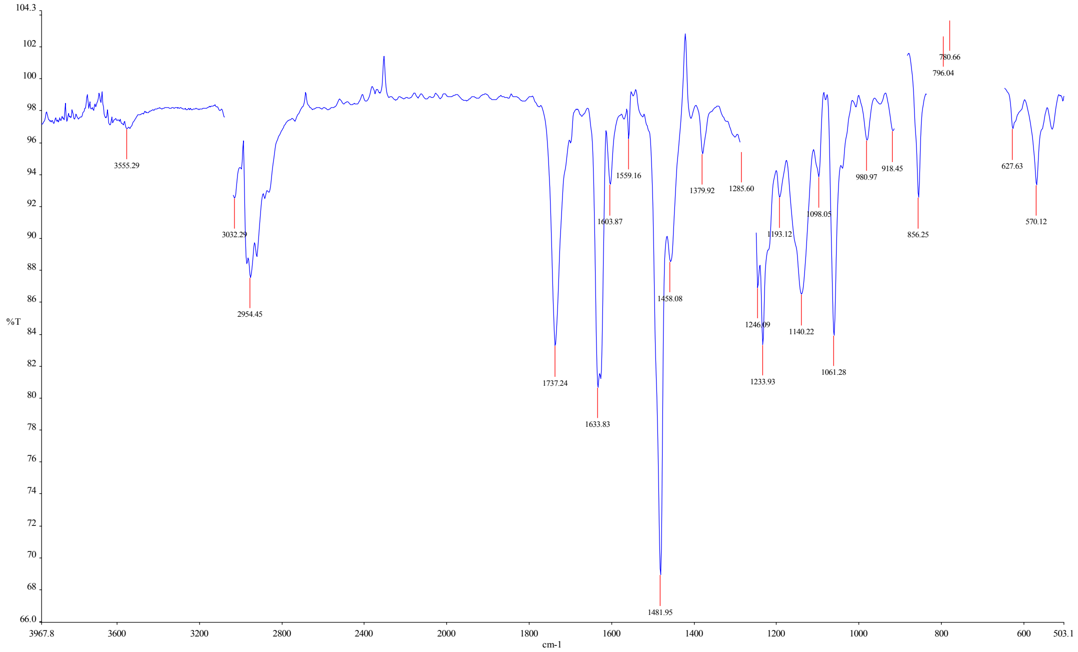


Figure S7. IR spectrum of **2a** in CH_2Cl_2 (3% solution)

Crystallographic Studies of 2b.

Single crystals of **2b** suitable for X-ray diffraction studies were selected under a polarizing microscope, mounted in inert oil and transferred to the cold gas stream of the diffractometer. Diffraction data were measured at 100(2) K with graphite-monochromated Mo-Kα radiation on the Oxford Diffraction κ-CCD Gemini A Ultra diffractometer. Cell refinement and data collection as well as data reduction and analysis were performed with the Oxford Diffraction software CrysAlis^{Pro}.[4] Absorption effects were corrected analytically from the crystal shape. The structure was solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares against F^2 with SHELXL-97[5]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at geometrically idealized coordinates and allowed to ride on their parent C-atoms. The final Fourier-difference maps have no significant chemical meaning. ORTEP drawing was made using Ortep3 for Windows.[6] Crystal data and structure refinement parameters are given in Table S1.

Table S1. Crystal data and structure refinement for compound **2b**.

Empirical formula	$C_{24}H_{35}GaN_2O$
Formula weight	437.26
Temperature / K	100.0
Crystal system	orthorhombic
Space group	*Pna*2$_1$
a , *b*, *c* / Å	22.5330(4), 7.78830(12), 12.96404(20)
Volume / Å^3	2275.11(6)
Z	4
ρ_{calc} / g cm^{-3}	1.277
Radiation	MoKα (0.71073 Å)
μ / mm^{-1}	1.225
F(000)	928
Crystal size / mm^3	0.42 × 0.36 × 0.25
2*Θ* range for data collection	7.1 to 65.68°
Index ranges	$-31 \leq h \leq 34$, $-11 \leq k \leq 11$, $-16 \leq l \leq 19$
Reflections collected	28944
Independent reflections	7072[*R*(int) = 0.0288]
Data/restraints/parameters	7072/1/262
Goodness-of-fit on F^2	1.051
Flack parameter	−0.005(6)
Final *R* indexes [I>2σ(I)]	*R*1 = 0.0260, *wR*2 = 0.0637
Final *R* indexes [all data]	*R*1 = 0.0289, *wR*2 = 0.0655
Largest diff. peak/hole / e Å^{-3}	0.624/−0.362

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}
Ga1	1779.37(6)	7147.41(17)	4169.30(17)	13.49(4)
O1	1398.0(5)	8263.1(15)	3069.6(9)	21.2(2)

N1	2567.0(5)	4177.6(16)	3395.4(9)	13.0(2)
N2	1643.0(5)	3730.0(15)	3019.4(9)	12.4(2)
C1	2016.0(6)	4787.9(17)	3500.7(10)	11.2(2)
C2	1940.4(7)	2240.4(18)	2533.1(12)	15.3(3)
C3	2590.8(7)	2550(2)	2812.3(13)	17.4(3)
C4	1243.7(8)	6754(2)	5356.5(13)	23.2(3)
C5	2505.4(7)	8497(2)	4472.2(14)	25.1(3)
C6	788.9(7)	8520(2)	3070.9(14)	24.6(3)
C7	3091.9(6)	4780.9(18)	3905.4(10)	11.5(2)
C8	3178.7(6)	4399.0(19)	4947.1(12)	13.0(2)
C9	3712.2(6)	4892.6(19)	5404.8(11)	15.9(3)
C10	4149.9(7)	5745(2)	4854.0(13)	17.5(3)
C11	4046.9(7)	6125(2)	3823.9(12)	18.2(3)
C12	3521.0(6)	5657.8(19)	3332.7(11)	14.9(2)
C13	1008.3(6)	3829.0(17)	3064.7(11)	12.1(2)
C14	693.0(6)	4523.7(17)	2240.0(11)	13.2(2)
C15	73.4(6)	4576.9(18)	2306.8(11)	15.4(2)
C16	−226.3(6)	3935.8(19)	3163.1(11)	15.4(3)
C17	102.7(6)	3202.5(19)	3957(1)	15.2(3)
C18	720.1(6)	3122.6(18)	3921.3(11)	13.9(2)
C19	2711.7(7)	3509(2)	5584.8(12)	18.4(3)
C20	4725.2(7)	6246(2)	5368.6(15)	27.1(4)
C21	3413.8(8)	6135(2)	2222.2(13)	24.9(3)
C22	1011.0(7)	5215(2)	1303.2(11)	18.8(3)
C23	−893.9(6)	4011(2)	3236.7(13)	22.1(3)
C24	1061.2(7)	2288(2)	4781.2(12)	19.5(3)

Table S3. Bond lengths for **2b**.

	Length/Å		Length/Å
Ga1-O1	1.8778(11)	C8-C19	1.507(2)
Ga1-C1	2.1007(13)	C9-C10	1.387(2)
Ga1-C4	1.9798(17)	C10-C11	1.387(2)
Ga1-C5	1.9838(16)	C10-C20	1.509(2)
O1-C6	1.387(2)	C11-C12	1.394(2)
N1-C1	1.3365(17)	C12-C21	1.506(2)
N1-C3	1.4771(19)	C13-C14	1.3930(19)
N1-C7	1.4342(17)	C13-C18	1.3991(19)
N2-C1	1.3322(17)	C14-C15	1.3995(19)
N2-C2	1.4807(18)	C14-C22	1.509(2)
N2-C13	1.4335(17)	C15-C16	1.392(2)
C2-C3	1.529(2)	C16-C17	1.391(2)

C7-C8	1.397(2)	C16-C23	1.508(2)
C7-C12	1.3972(19)	C17-C18	1.3934(19)
C8-C9	1.3946(19)	C18-C24	1.502(2)

Table S4. Bond angles for **2b**.

	Angle/°		Angle/°
O1-Ga1-C1	101.99(5)	C9-C8-C19	119.68(13)
O1-Ga1-C4	112.52(6)	C10-C9-C8	121.73(14)
O1-Ga1-C5	106.41(6)	C9-C10-C11	118.60(14)
C4-Ga1-C1	109.88(6)	C9-C10-C20	120.46(15)
C4-Ga1-C5	115.53(7)	C11-C10-C20	120.94(16)
C5-Ga1-C1	109.63(6)	C10-C11-C12	121.77(14)
C6-O1-Ga1	121.25(11)	C7-C12-C21	121.17(13)
C1-N1-C3	113.03(11)	C11-C12-C7	118.24(13)
C1-N1-C7	127.05(12)	C11-C12-C21	120.57(13)
C7-N1-C3	119.16(11)	C14-C13-N2	119.88(12)
C1-N2-C2	113.47(11)	C14-C13-C18	121.69(12)
C1-N2-C13	125.25(12)	C18-C13-N2	118.32(12)
C13-N2-C2	120.75(11)	C13-C14-C15	118.21(13)
N1-C1-Ga1	126.09(10)	C13-C14-C22	120.94(12)
N2-C1-Ga1	125.04(10)	C15-C14-C22	120.85(13)
N2-C1-N1	108.57(12)	C16-C15-C14	121.52(13)
N2-C2-C3	102.11(11)	C15-C16-C23	121.36(14)
N1-C3-C2	102.80(11)	C17-C16-C15	118.60(13)
C8-C7-N1	119.44(12)	C17-C16-C23	120.04(13)
C8-C7-C12	121.40(13)	C16-C17-C18	121.73(13)
C12-C7-N1	119.06(12)	C13-C18-C24	121.45(13)
C7-C8-C19	122.05(13)	C17-C18-C13	118.17(13)
C9-C8-C7	118.26(13)	C17-C18-C24	120.37(13)

Reaction of 2b with 5 equiv. of *rac*-lactide

To the solution of **2b** (70 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) cooled to −20°C the *rac*-lactide (115 mg, 0.80 mmol) was added and formed solution stirred for 15 minutes. Then 2.5 mL of solution was collected, CH_2Cl_2 was removed under vacuum and the resulting white solid dissolved in CD_2Cl_2. ^{1}H NMR ($CDCl_3$, 200 MHz): The conversion of *rac*-lactide – 100%. δ −1.32, −1.34 −1.35, −1.37 (s, 6H, $GaCH_3$), 0.98 (d, 3H, ^3J(H,H)=6.8Hz, *CH*CH_3), 1.35 (d, 3H, ^3J(H,H)=6.8Hz, *CH*CH_3), 1.51, 1.54 (d, 30H, ^3J(H,H)=6.8Hz, *CH*CH_3), 2.30 (s, 6H, CH_3), 2.32 (br., 12H, CH_3), 3.62, 3.69, 3.70 (s, 3H, OCH_3), 3.63 (q, 1H, ^3J(H,H)=6.8 Hz, CH*CH_3*) 3.92 (s, 4H, CH_2) 4.81 – 4.92 (m, 1H, CH*CH_3*), 5.10 – 5.21 (m, 10H, CH*CH_3*).

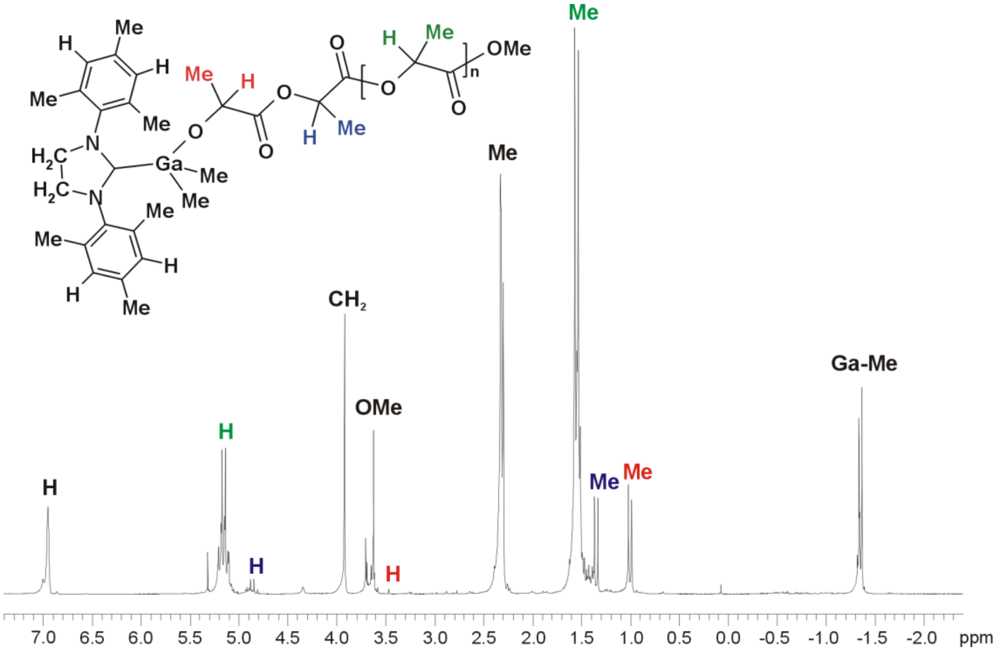


Figure S8. ^{1}HNMR spectrum of **2b/5 equiv. *rac*-LA** in CD_2Cl_2

Polymerization of *rac*-lactide

Polymerizations of rac-LA with **2a** and **2b**: To the *rac*-LA (0.9 g – 3.55 g depending on **rac**-LA/2 ratio) solution in methylene chloride (20mL) the toluene solution (0.5 mL) of an appropriate amount of catalyst was added at given temperaure. The polymerization was thermostated for the indicated time in the Schlenk vessel and quenched by addition of a HCl solution (5%, 50 mL). The organic phase was separated, washed twice with water (50 mL), and dried under vacuum to give PLA as a white solid. ^{1}H NMR ($CDCl_3$, 200 Mhz): (a) unreacted lactide 1.67 (d, 3H, ^3J(H,H)=6.7 Hz, C*H*CH_3), 5.03 (q, 1H, ^3J(H,H)=6.7 Hz, CHC*H_3*) (b) PLA signals: 1.50-1.60 (m, 3H, C*H*CH_3), 5.10 - 5.25 (m, 1H, CHC*H_3*) (c) end groups: 4.34 (m, CHC*H*$_3$), 3.73, 3.74 (s, OCH$_3$).

In each case PLA (0.5 g) was precipitated from methylene chloride solution (1 ml) with 20 mL of MeOH, filtered off and dried under vacuum to yield in each case PLA with approx 70% yield. Precipitated PLA was further analyzed by ^{1}H NMR, which confirmed the presence of exclusively -OH and -OCH(CH$_3$)C(O)OMe end groups. Probability of isotacic enchainment (P_m) were found in agreement with non-precipitates samples.

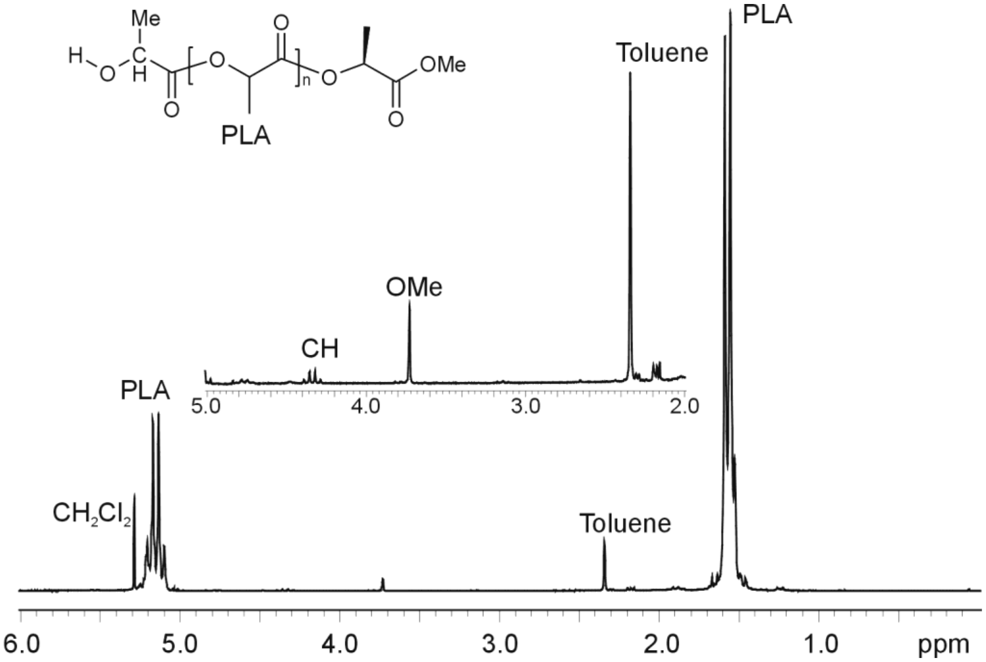


Figure S9. ^{1}H NMR (CDCl$_3$, 200MHz) spectra of polylactide prepared by polymerization of *rac*-LA with **2a** at −20ºC.

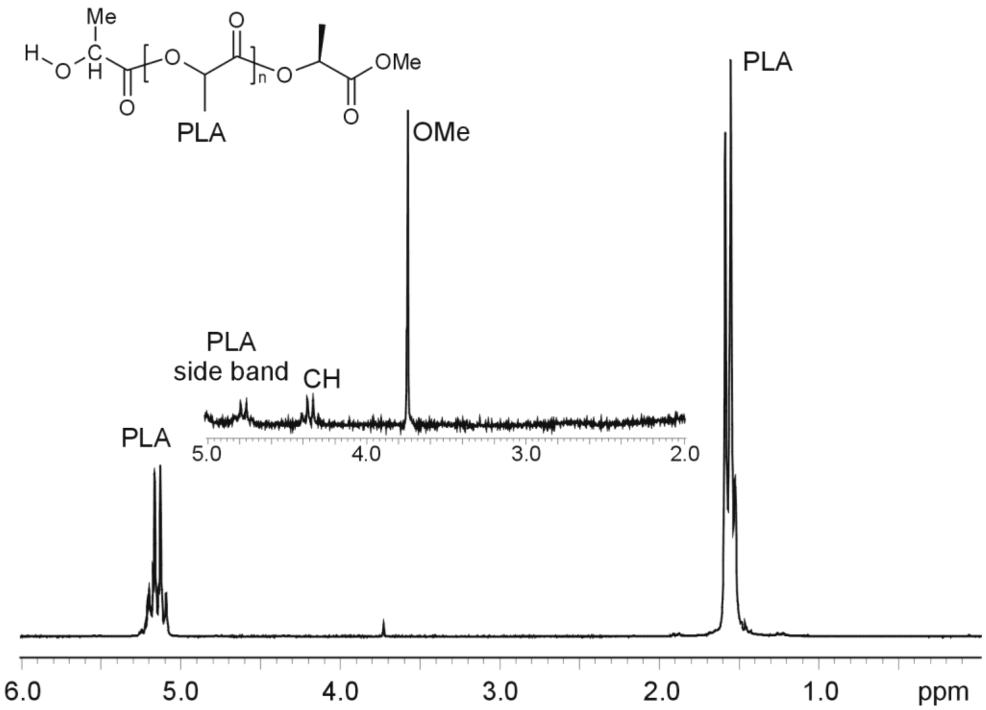


Figure S10. ^{1}H NMR (CDCl$_3$, 200MHz) spectra of polylactide (after precipitation with methanol) prepared by polymerization of *rac*-LA with **2a** at −20ºC.

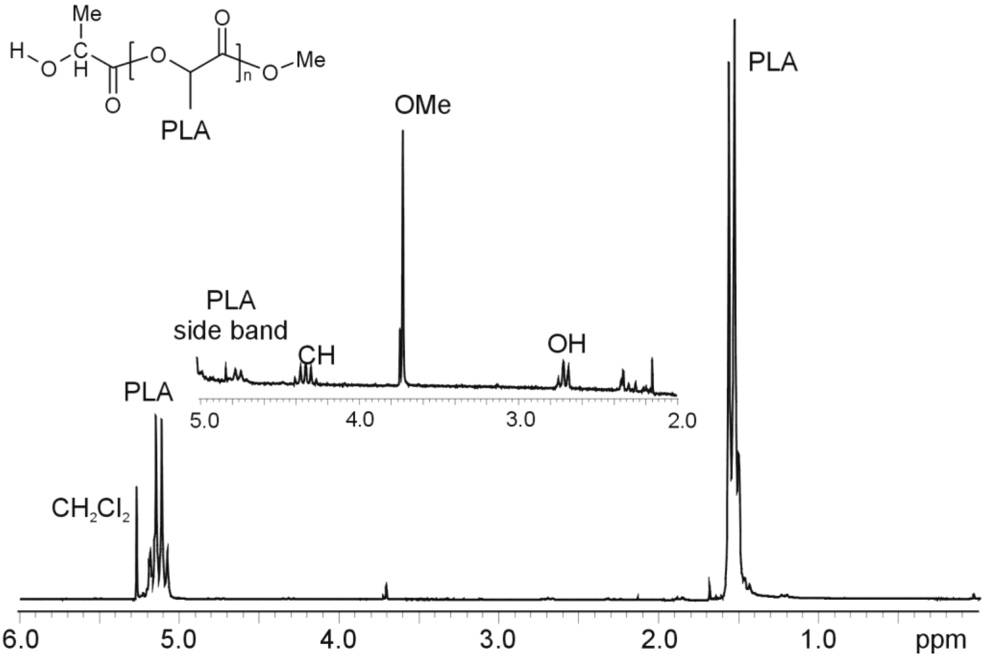


Figure S11. ^{1}H NMR (CDCl$_3$, 200MHz) spectra of polylactide prepared by polymerization of *rac*-LA with **2b** at −20ºC.

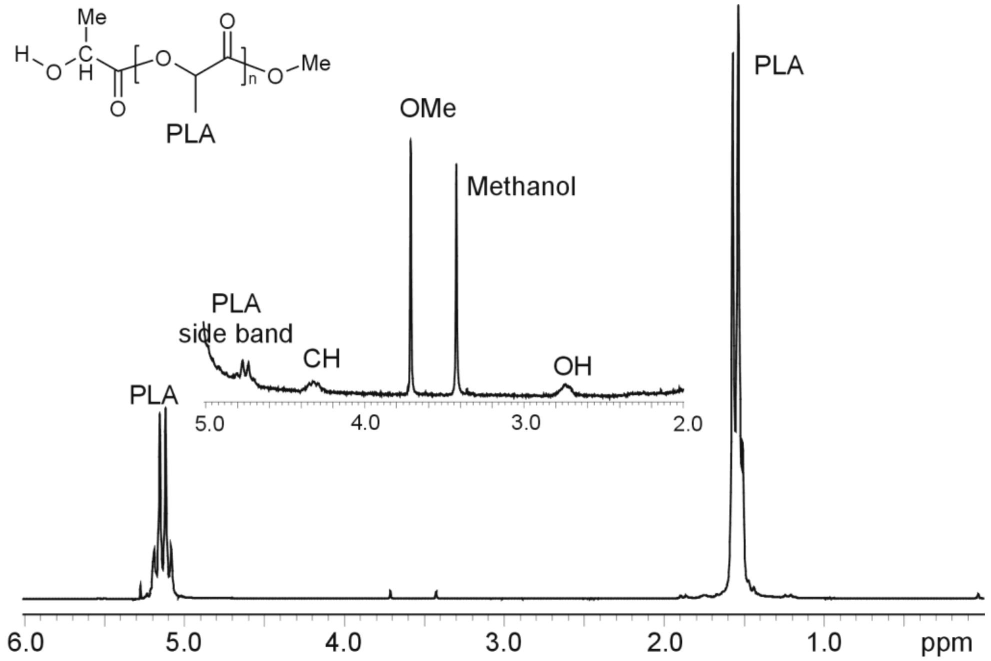


Figure S12. ^{1}H NMR ($CDCl_3$, 200MHz) spectra of polylactide (after precipitation with methanol) prepared by polymerization of *rac*-LA with **2b** at −20ºC.

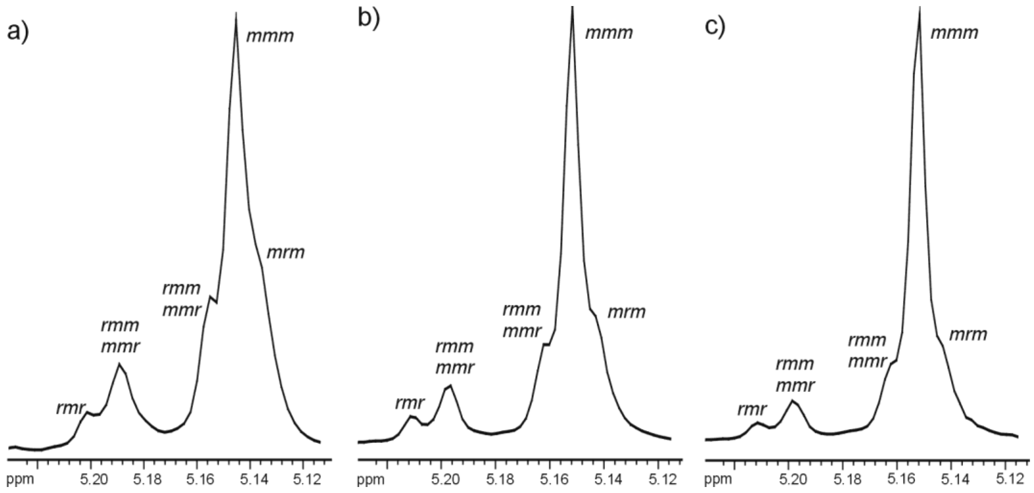


Figure S13. Homonuclear decoupled ^{1}H NMR ($CDCl_3$, 200MHz) spectra of the methine region of polylactide prepared by polymerization of *rac*-LA with **2a** at room temperature – P_m = 0.65 (a), 0ºC - P_m = 0.72 (b), and −20ºC - P_m = 0.78 (c).

^{13}C NMR spectra for PLA obtained with 2a and 2b

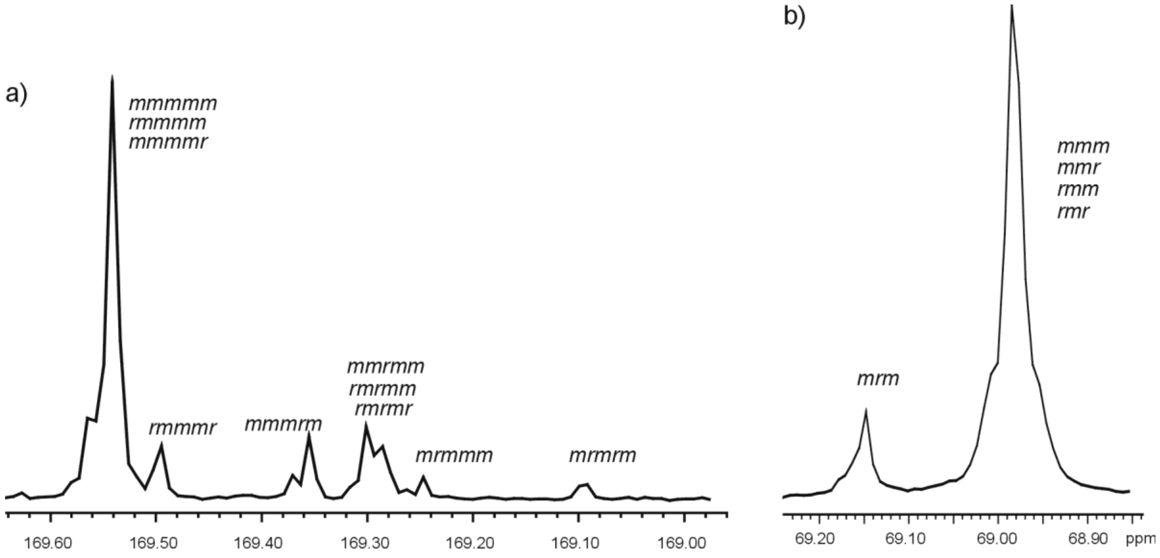


Figure S14. ^{13}C NMR ($CDCl_3$, 500MHz, 25ºC) proton decoupled spectrum of PLA prepared with **2a**: (a) carbonyl region, (b) methine region.

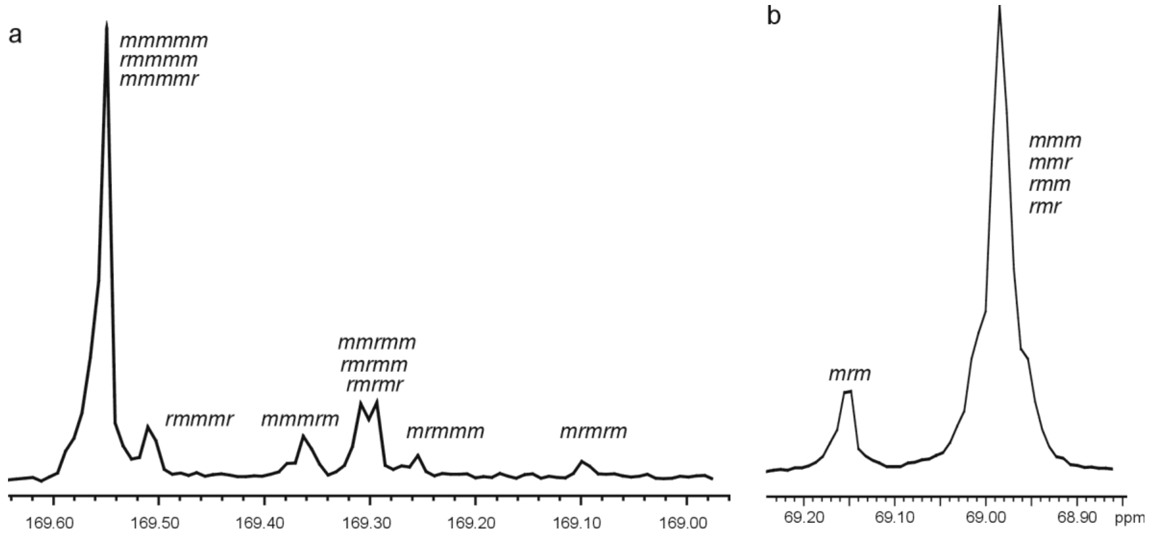


Figure S15. ^{13}C NMR ($CDCl_{3,}$ 500MHz, 25ºC) proton decoupled spectrum of PLA prepared with **2b**: (a) carbonyl region, (b) methine region.

---

1 P. Horeglad, P. Kruk, J. Pécaut, *Organometallics*, **2010**, *29*, 3729.
2 A. J. Arduengo, J. R. Goerlich, W.J.Marshall, *J.Am.Chem.Soc.* , **1995**, *117*, 11027.
3 C. J. Carmalt, S. J. King, *Coord. Chem. Rev.*, **2006**, *250*, 682.
4 *CrysAlis^{Pro} Software system (ver. 1.171.35)*, Agilent Technologies, Santa Clara, USA, 2010.
5 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, **2008**, *64*, 112–122.
6 L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.