Electronic Supporting Information (ESI) for

Synthesis and Characterisation of an Enantiomerically Pure Scandium Pentadienyl Complex and its Application in the Polymerisation of *rac*-Lactide

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1. Crystallographic details for complex 2

Table S1. Crystallographic details of scandium complex **2**.

	2
Chemical formula	$C_{27}H_{52}ONSi_2Sc$
Formula mass	507.83
Crystal system	orthorhombic
***a*/Å**	10.2101(2)
***b*/Å**	13.2214(2)
***c*/Å**	22.7451(4)
***α*/°**	90
***β*/°**	90
***γ*/°**	90
Unit cell volume/Å^3	3070.40(9)
Temperature/K	100(2)
Space group	$P2_12_12_1$
No. of formula units per unit cell, *Z*	4
Radiation type	Cu Kα
Absorption coefficient, μ/mm^{-1}	2.915
No. of reflections measured	35213
No. of independent reflections	6316
R_{int}	0.0575
Final R_1 value ($I > 2\sigma(I)$)	0.0368
Final $wR(F^2)$ value ($I > 2\sigma(I)$)	0.0945
Final R_1 value (all data)	0.0401
Final $wR(F^2)$ value (all data)	0.0963
Goodness of fit on F^2	1.066
Flack parameter	-0.006(4)
Δρ / e Å^{-3}	0.48 / -0.42

2. NMR spectroscopy

2.1. [Sc-pdl*SiMe$_2$N^{t}Bu-(thf)(CH$_2$SiMe$_3$)] (2)

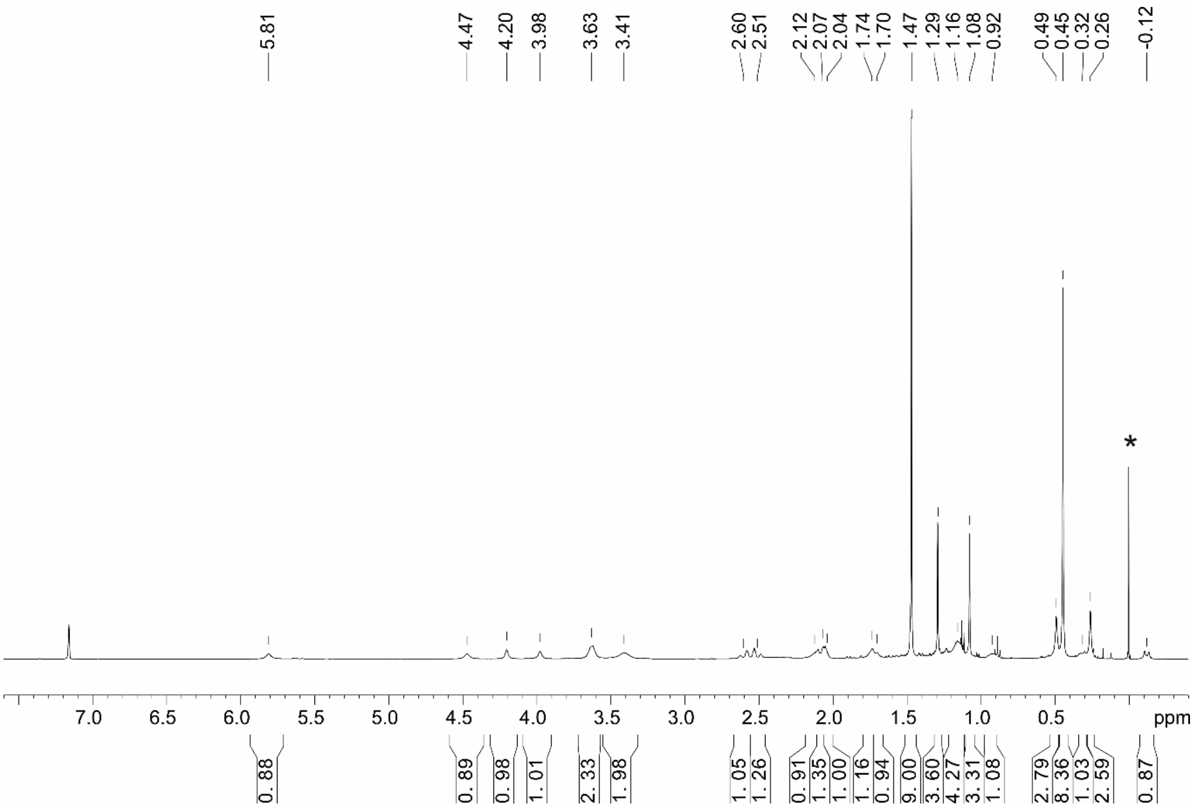

Figure S1. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) for **2**. The * demarks $SiMe_4$ formed during decomposition of the metal complex.

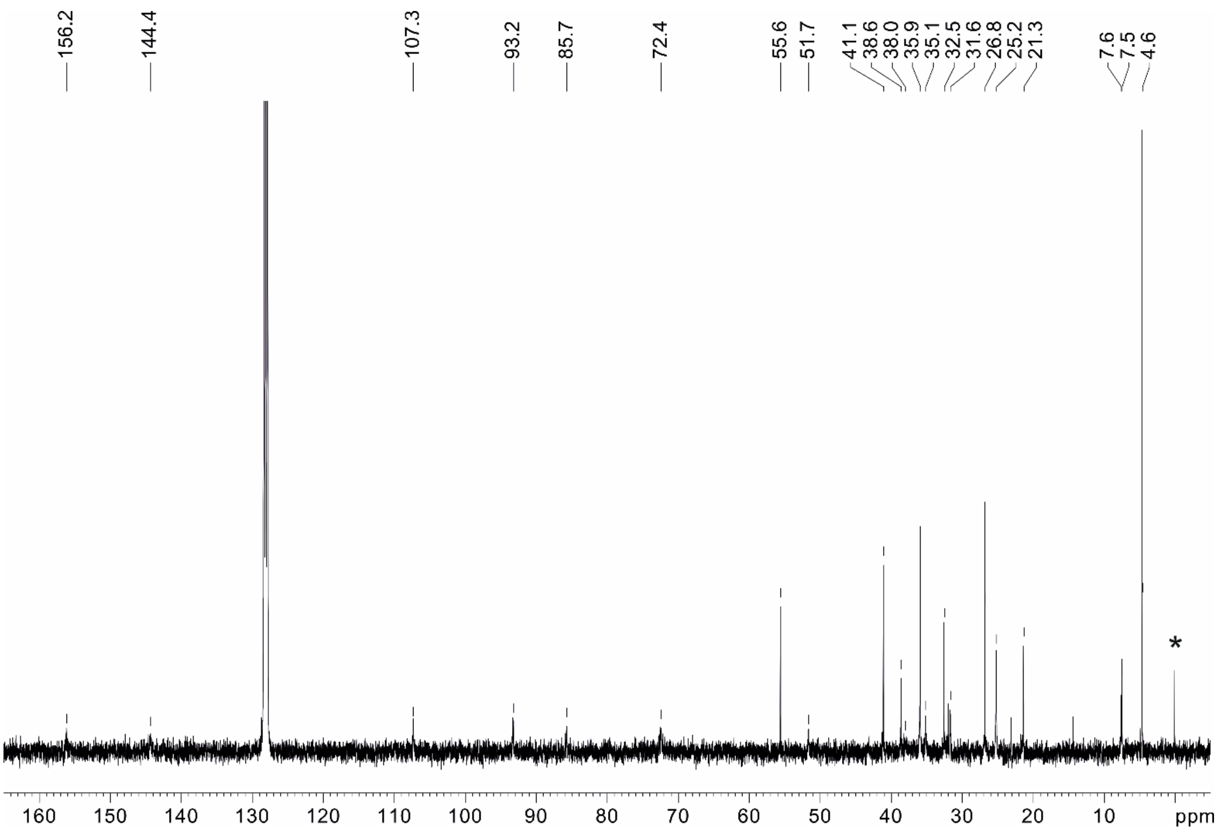

Figure S2. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6, 298 K) for **2**. * Hydrolized ligand.

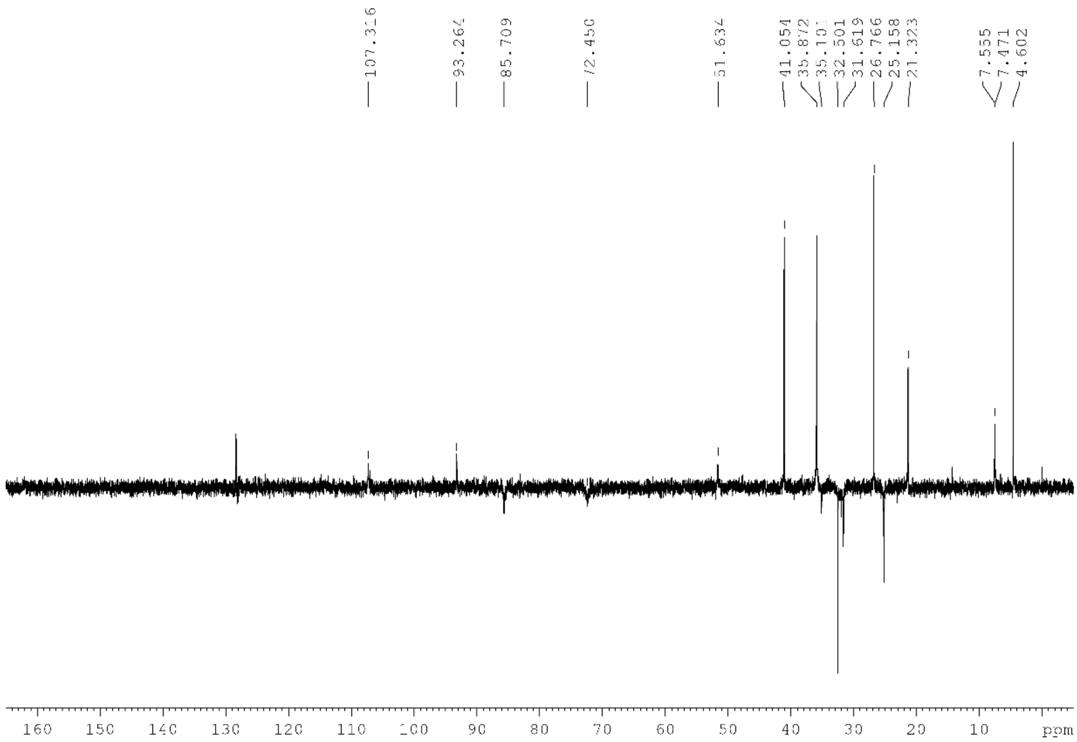

Figure S3. $^{13}C\{^{1}H\}$ dept NMR spectrum (101 MHz, C_6D_6, 298 K) for **2**.

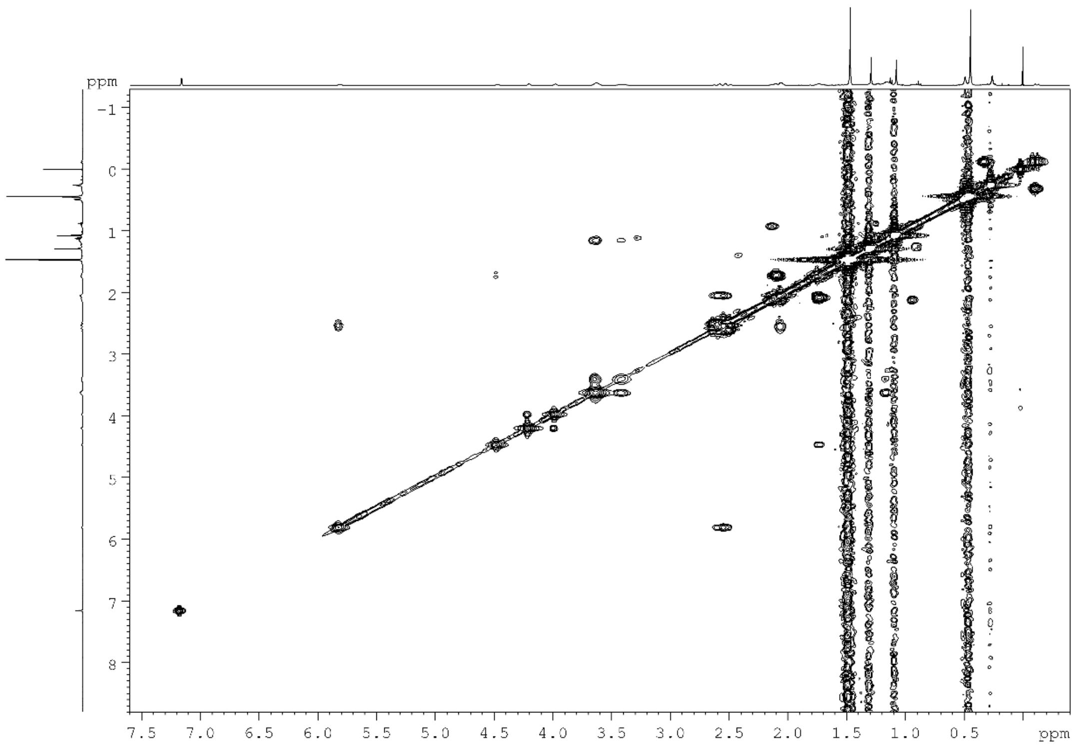

Figure S4. $^{1}H,^{1}H$ COSY NMR spectrum for **2**.

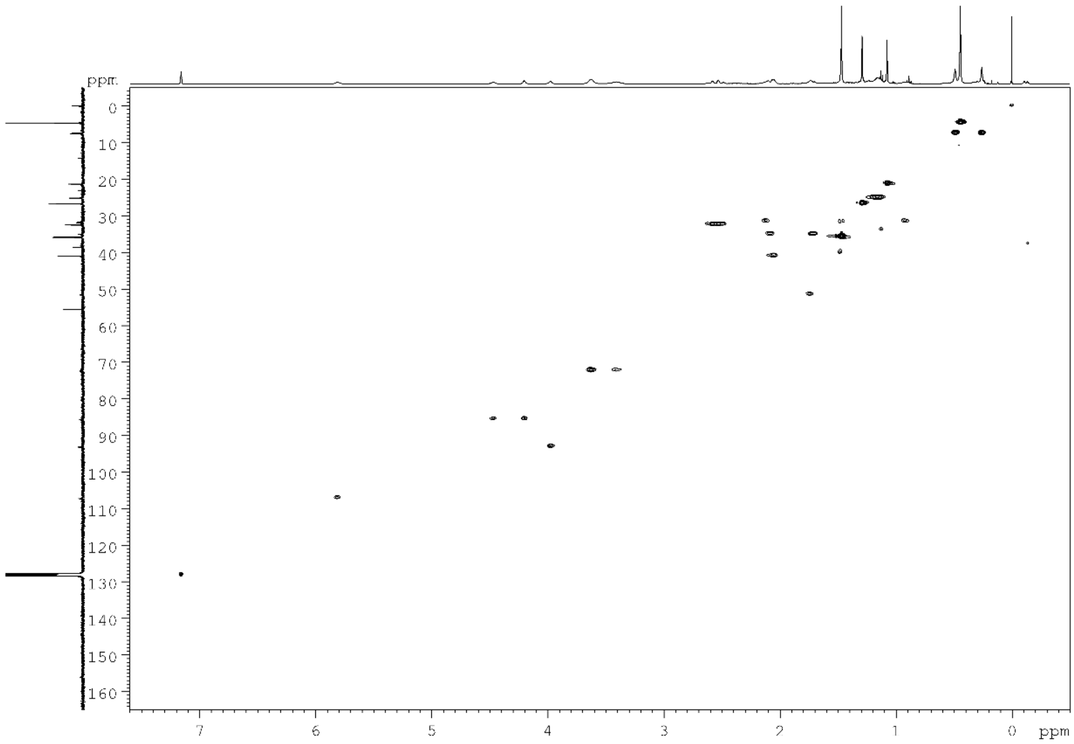

Figure S5. $^{1}H,^{13}C\{^{1}H\}$ HSQC NMR spectrum for **2**.

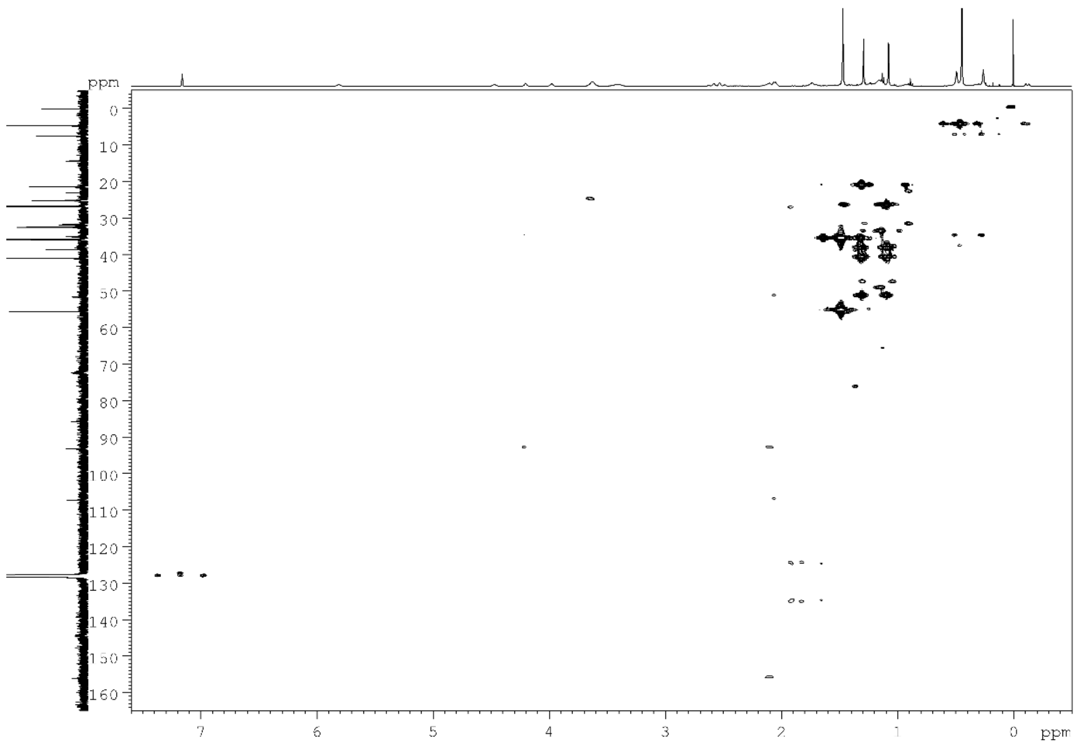

Figure S6. $^{1}H,^{13}C\{^{1}H\}$ HMBC NMR spectrum for **2**.

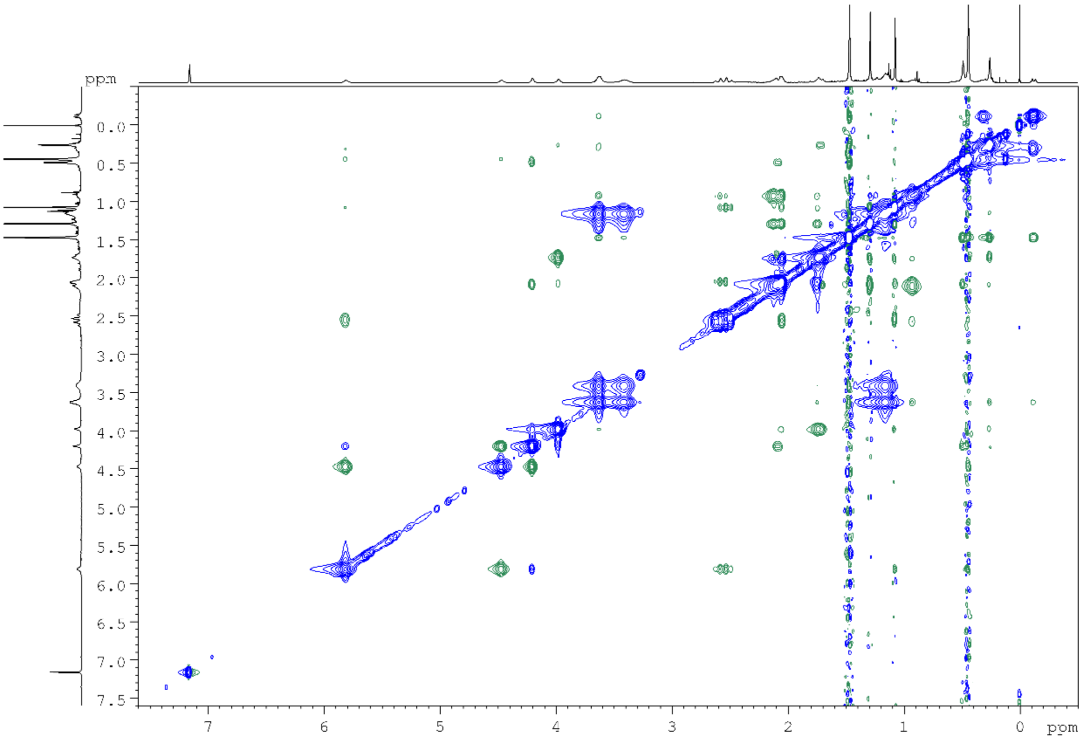

Figure S7. $^{1}H,^{1}H$ NOESY NMR spectrum for **2**.

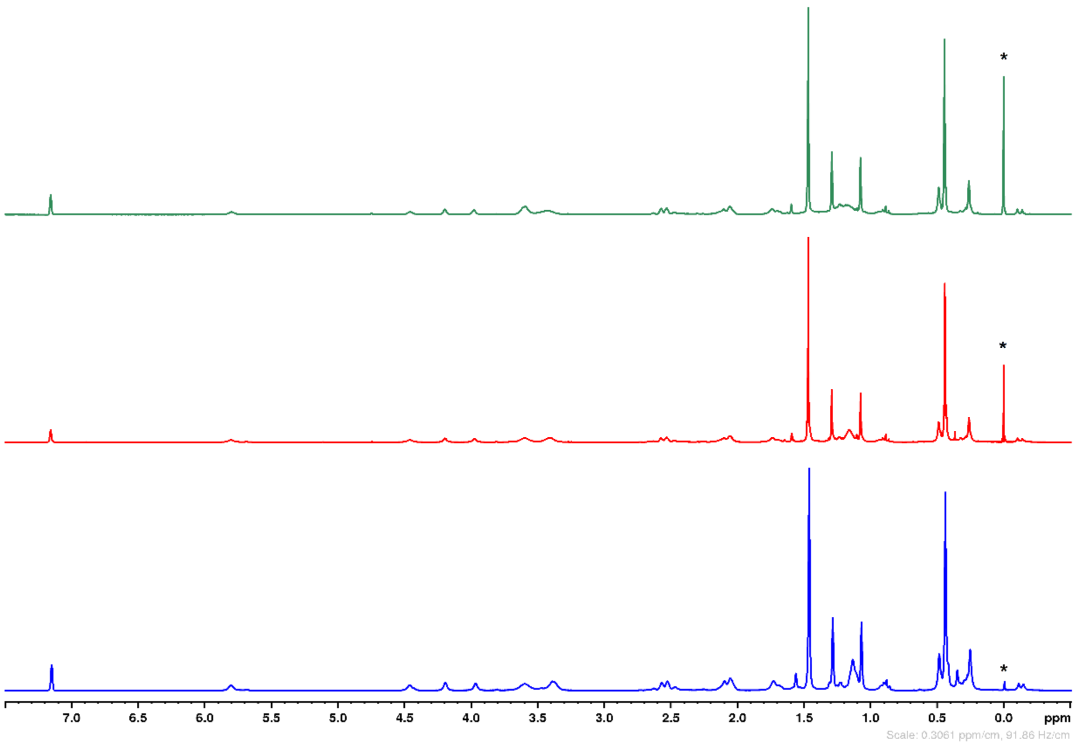

Figure S8. ^{1}H NMR spectra (300 MHz, C_6D_6) for **2** (blue) after heating to 60 °C for 1 h (red) and 24 h (green). The * demarks $SiMe_4$ formed during decomposition of the metal complex.

2.2. End-group analysis

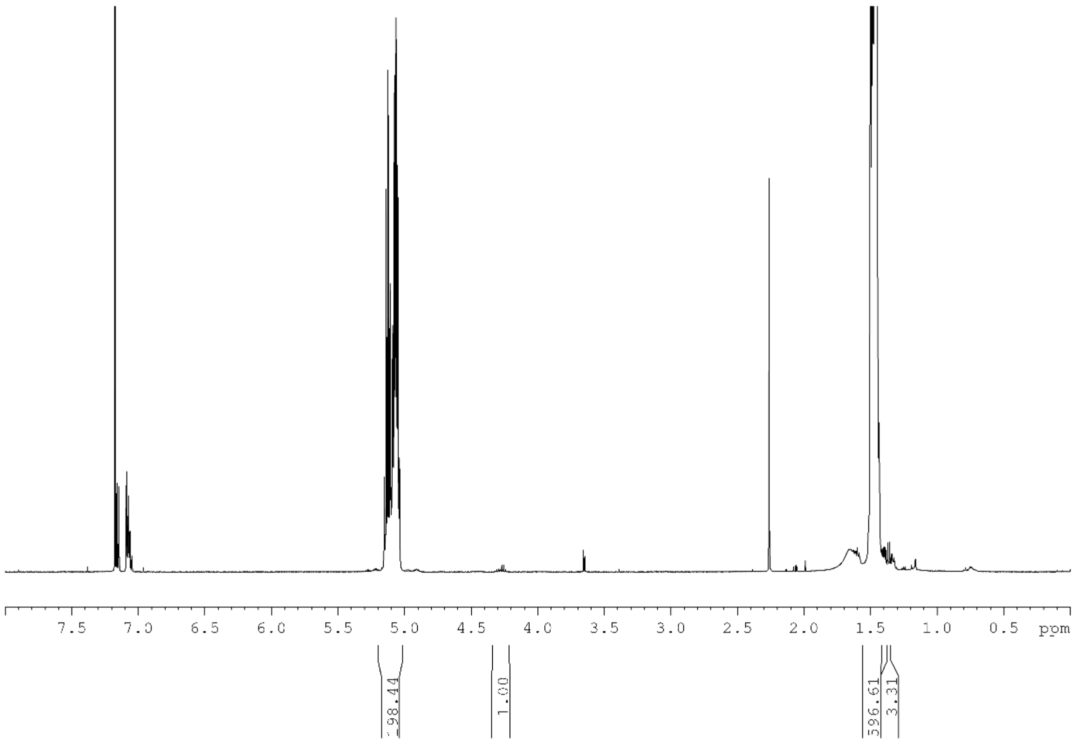

Figure S9. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 50 °C.

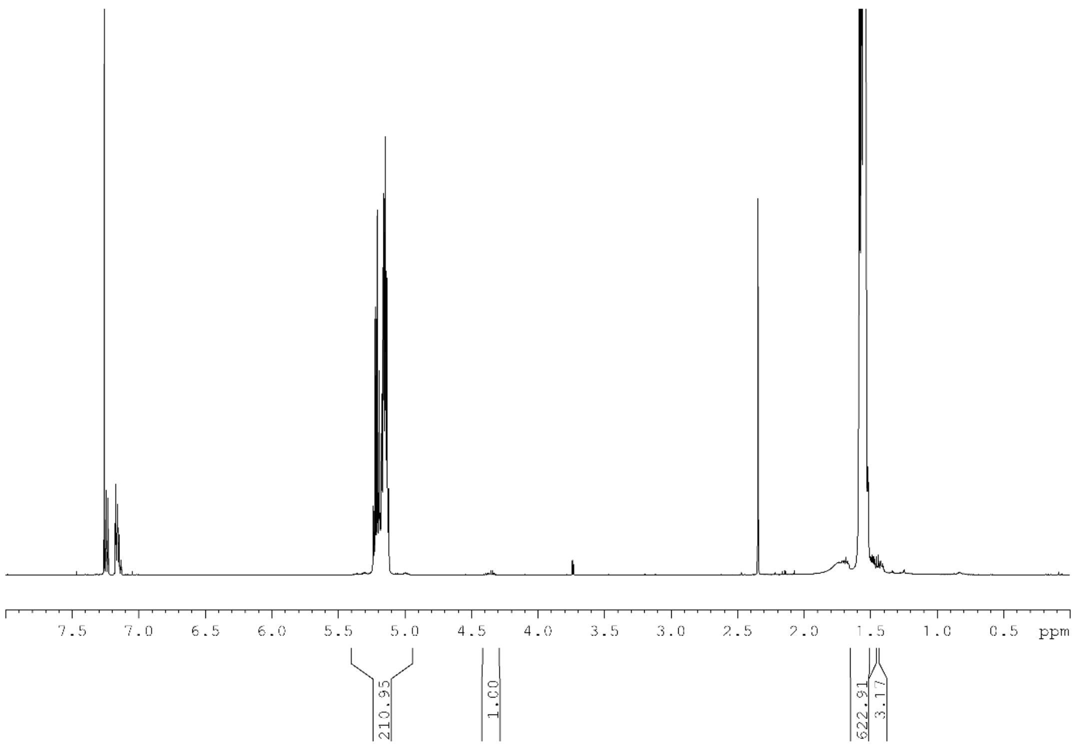

Figure S10. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 30 °C.

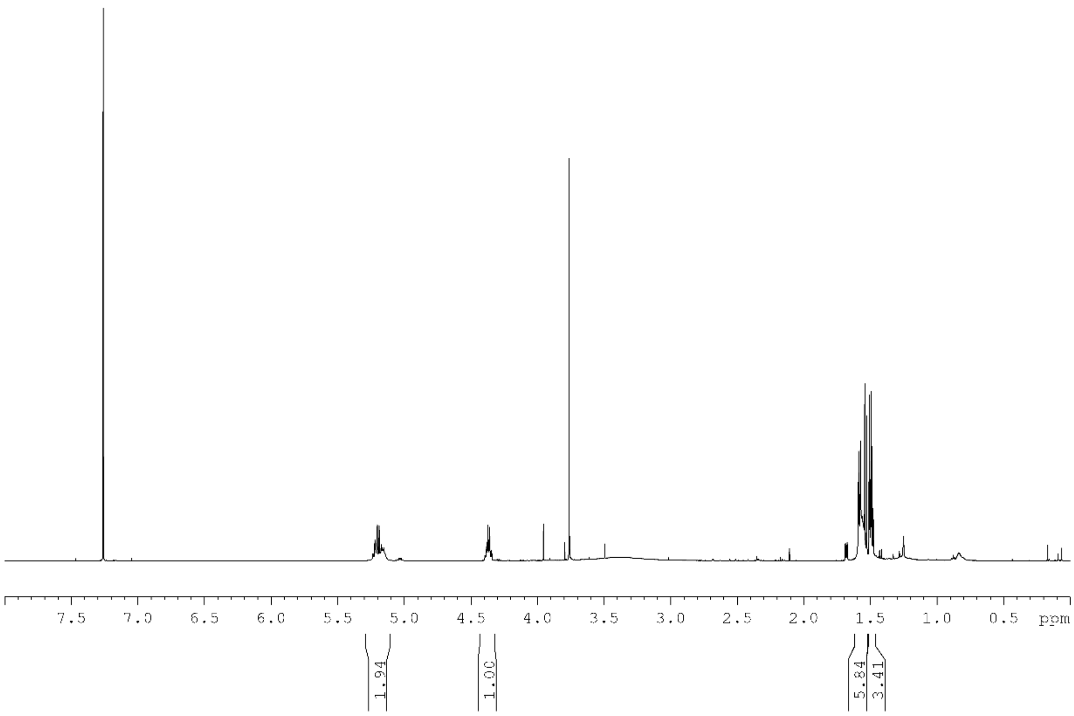

Figure S11. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 0 °C.

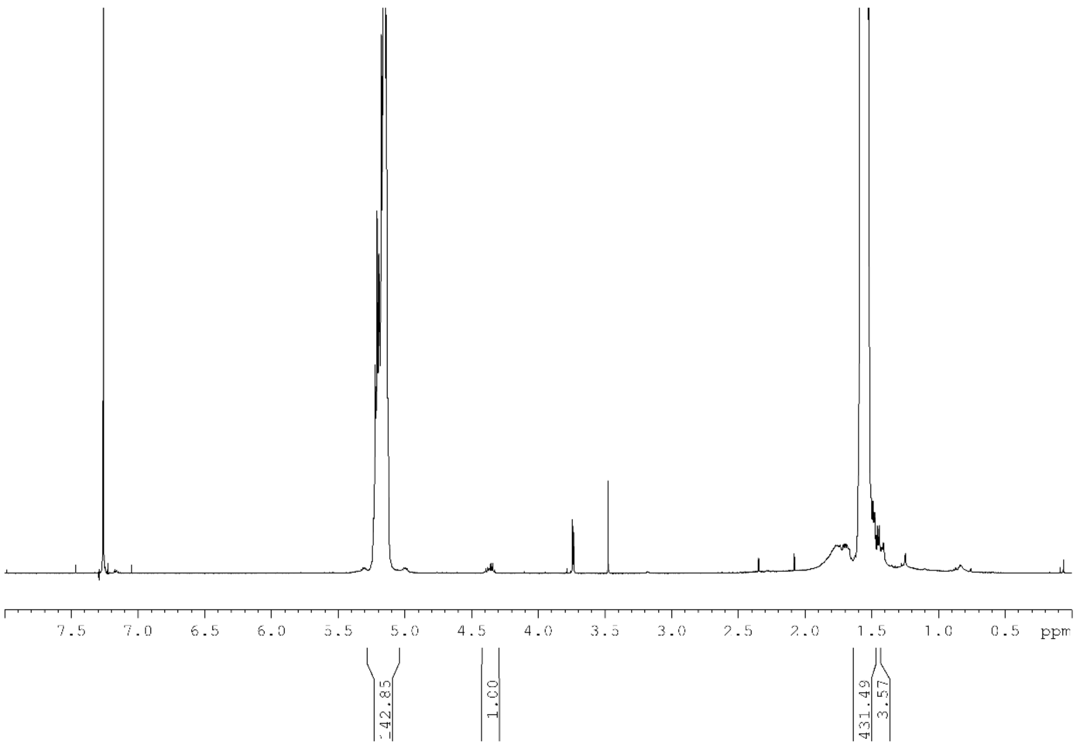

Figure S12. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **3**.

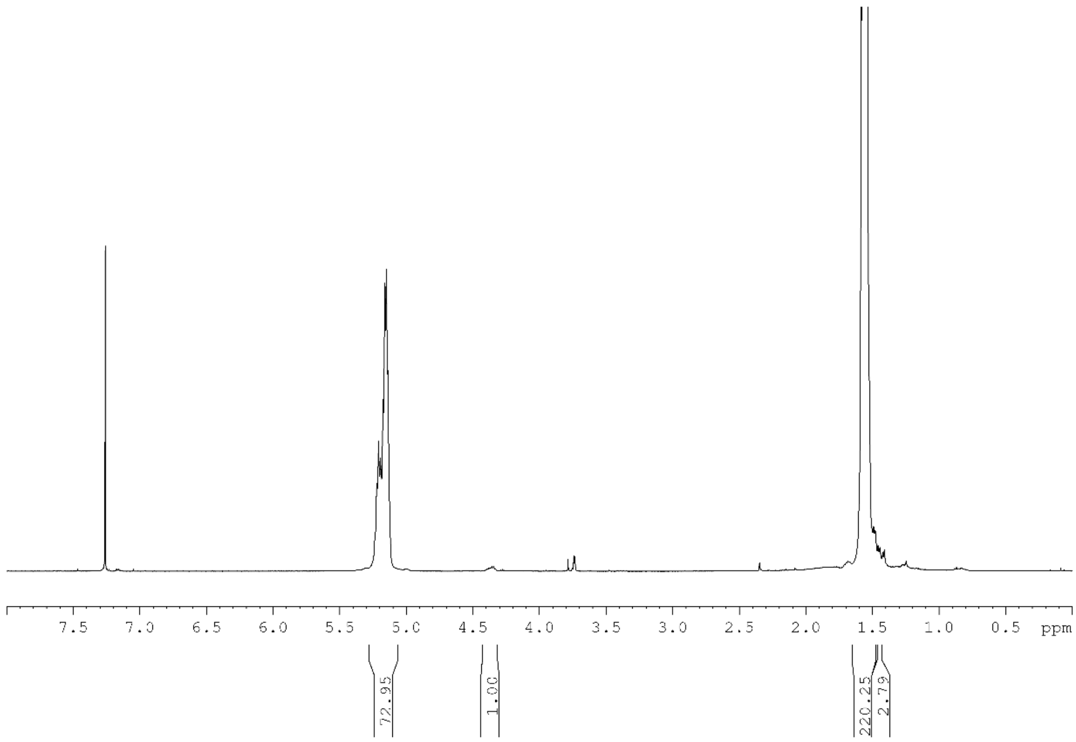

Figure S13. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **4**.

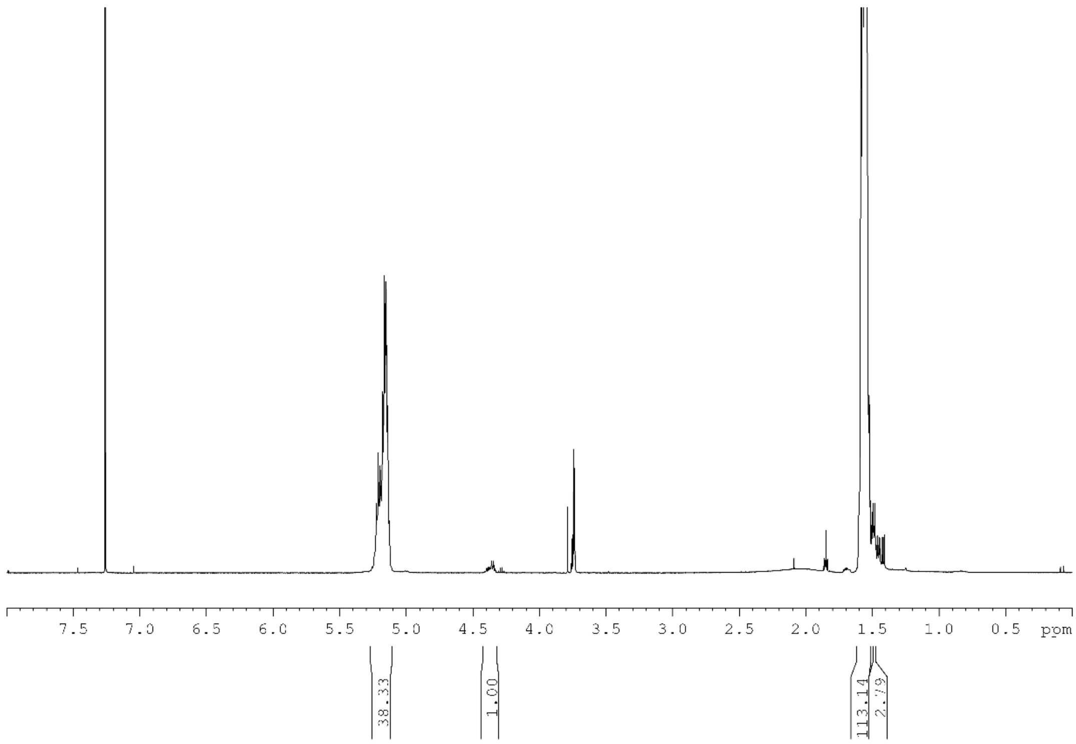

Figure S14. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **5**.

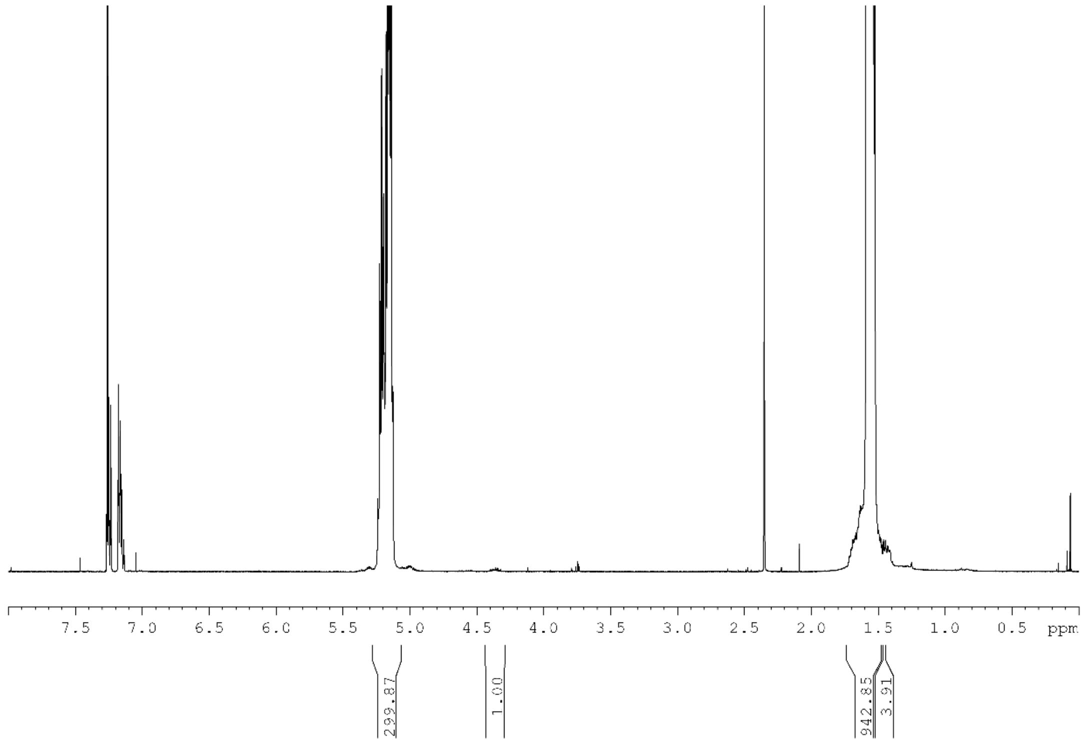

Figure S15. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **6**.

2.3. Calculation of P_m values

For the polymerisation of *rac*-lactide, only five possible tetrad sequences relevant for NMR analysis arise: *mmm*, *mmr*, *rmm*, *rmr* and *mrm*. As long as no epimerization takes place, it is not possible to find tetrads with two adjacent *r* diads, because the ring opening of (*R*,*R*)- or (*S*,*S*)-lactide always yields a *m* diad; consequently, every (*R*,*S*) or (*S*,*R*) combination must be enclosed by (*R*,*R*) or (*S*,*S*) stereoblocks, or in other words, by an *m* diad. The opposite situation arises for PLA obtained from *meso*-lactide, as the ring opening generates an *r* diad with (*S*,*R*) or (*R*,*S*) configuration. As a result, a tetrad can never contain two adjacent *m* diads. The five tetrad sequences causing distinguishable NMR resonances consequently are *rrr*, *mrr*, *rrm*, *rmr* and *mrm*.

Application of Bernoullian statistics to the polymerisation of *rac*-lactide yields the values P_m and P_r referring to the probabilities of forming *m* or *r* diads, respectively. [1,2]

$$P_{mmm} = \frac{P_m(P_m + 1)}{2} \tag{1a}$$

$$P_{mrm} = \frac{(1 - P_m)}{2} \tag{2a}$$

$$P_{mmr} = \frac{P_m(1 - P_m)}{2} \tag{3}$$

$$P_{rmm} = \frac{P_m(1 - P_m)}{2} \tag{4}$$

$$P_{rmr} = \frac{(1 - P_m)^2}{2} \tag{5}$$

$$P_m + P_r = 1 \tag{6}$$

P_{mmm}, P_{mrm}, P_{mmr}, P_{rmm} and P_{rmr} are obtained from the homodecoupled $^1H\{^1H\}$ NMR spectra of the PLA samples as the relative peak areas determined by deconvolution of the multiplets observed in the methine region. P_m values are calculated according to the equations (1d) and (2b) resulting from the Bernoullian statistics[1] based on the P_{mmm} and P_{mrm} tetrads:

$$P_{mmm} = \frac{P_m(P_m + 1)}{2} = \frac{P_m^2 + P_m}{2} \tag{1b}$$

$$0 = P_m^2 + P_m - 2P_{mmm} \tag{1c}$$

$$P_{m_{1,2}} = -\frac{1}{2} \pm \sqrt{\left(\frac{1}{2}\right)^2 + 2P_{mmm}} \tag{1d}$$

$$P_m = 1 - 2P_{mrm} \tag{2b}$$

The tetrad probabilities for a completely random polymerisation of *rac*-lactide in the absence of racemization and transesterification processes:

P_{mmm} = 0.375 P_{mrm} = 0.250 P_{mmr} = 0.125 P_{rmm} = 0.125 P_{rmr} = 0.125

The following pages show the methine regions of the $^{1}H\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra together with the deconvolution results. The Tables S2, S3, S4, S5, S6, S7 and S8 display the relative areas from the deconvolution of the $^{1}H\{^{1}H\}$ NMR spectra for the tetrads *rmr*, *rmm*/*mmr*, *mmr*/*rmm*, *mmm*, *mrm* and a signal at 5.19 ppm which was sometimes observed at 5.19 ppm, but could not be assigned to a tetrad (first row of the tables). However, the resonance was occasionally reported in literature without any further explanation or assignment.[3] The signal was included into the deconvolution of the multiplet in the methine region for the determination of the P_m values; however, due to its low intensity, incorporating it or not into the calculation has negligible impact on the resulting P_m value. The resonances for the *rmm* and *mmr* tetrads cannot be distinguished, but display identical values based on the Bernoullian statistics.

To detect transesterification in *rac*-lactide polymerisation, the three tetrads missing in the case of polylactide without any transesterification reactions are *rrr*, *rrm* and *mrr*. They are most conveniently identified in the $^{13}C\{^{1}H\}$ NMR spectra. The NMR resonances were assigned according to literature.[3,4] As the *mrm* tetrad can be assigned in both ^{1}H and $^{13}C\{^{1}H\}$ NMR, the relative intensities normalized to one for all tetrads were calculated by setting the values for the *mrm* tetrad equal (second and third row of the tables). The P_m values were calculated from the *mmm* and *mrm* tetrads and averaged (fourth row of the tables and below).

2.4. $^1H\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra and deconvolution results

2.4.1. Polymerisation of *rac*-lactide with compound 2 at 50 °C

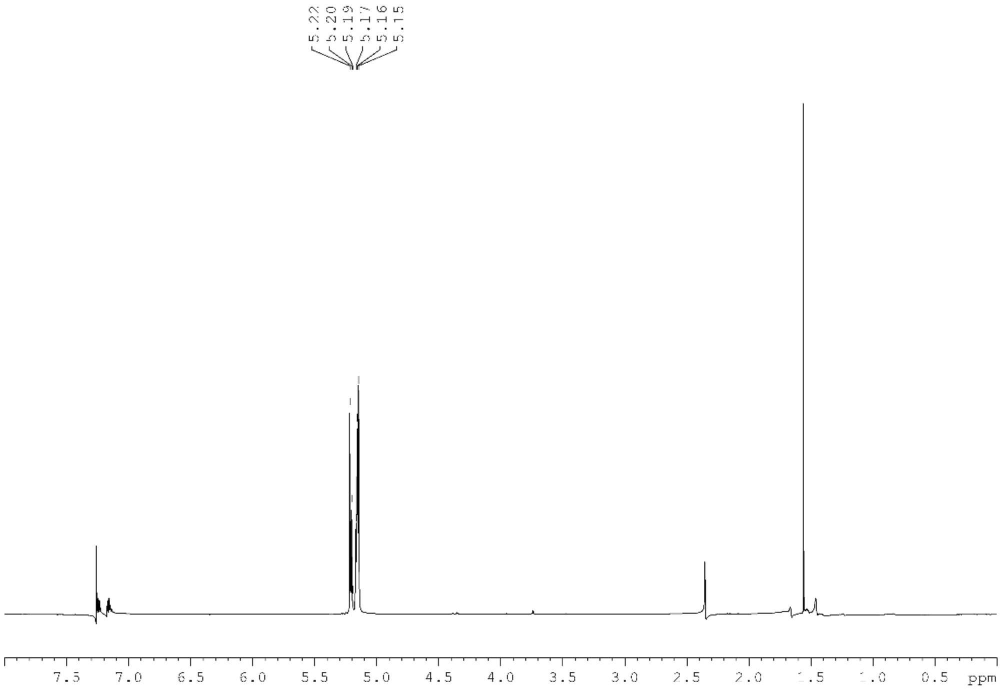

Figure S16. Homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 50 °C.

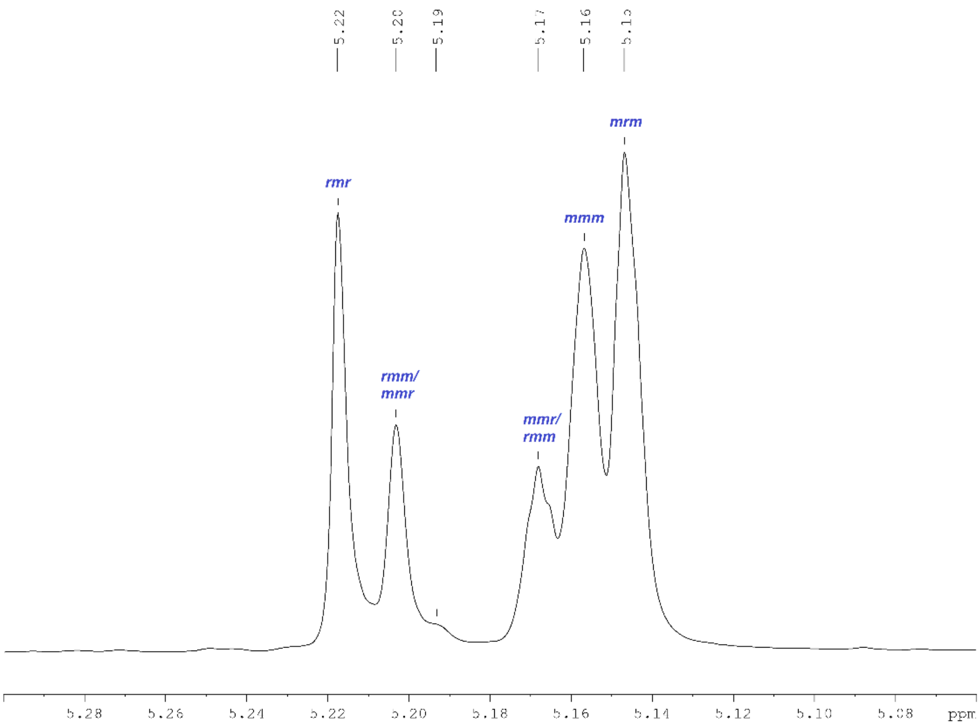

Figure S17. Methine region of the homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 50 °C.

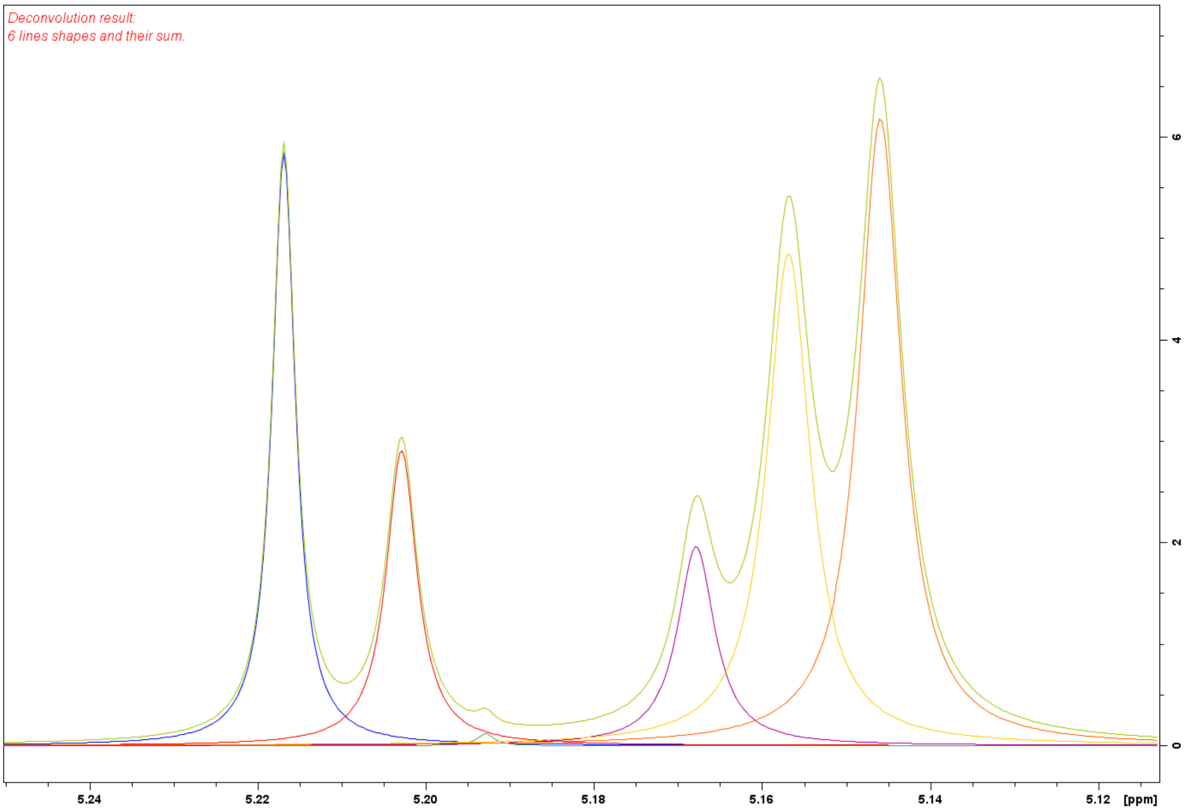

Figure S18. Deconvolution of the homodecoupled $^{1}H\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 50 °C.

Fit	Frequency		Width		Intensity	Area	%Lor.
	ppm	Hz	ppm	Hz			chisq
1							9.1e+15
	5.217	3131.11	0.00333	2.000	5.835	99.944	100.00
STD:	0.000	0.02	0.00009	0.055	0.111		
	5.203	3122.60	0.00443	2.660	2.911	66.305	100.00
STD:	0.000	0.04	0.00022	0.133	0.097		
	5.193	3116.50	0.00242	1.449	0.119	1.476	100.00
STD:	0.001	0.80	0.00390	2.342	0.130		
	5.168	3101.71	0.00537	3.224	1.962	54.177	100.00
STD:	0.000	0.07	0.00039	0.236	0.088		
	5.157	3094.92	0.00625	3.752	4.854	155.983	100.00
STD:	0.000	0.03	0.00021	0.124	0.082		
	5.146	3088.48	0.00614	3.683	6.183	195.012	100.00
STD:	0.000	0.03	0.00014	0.084	0.083		

Figure S19. $^{1}H\{^{1}H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

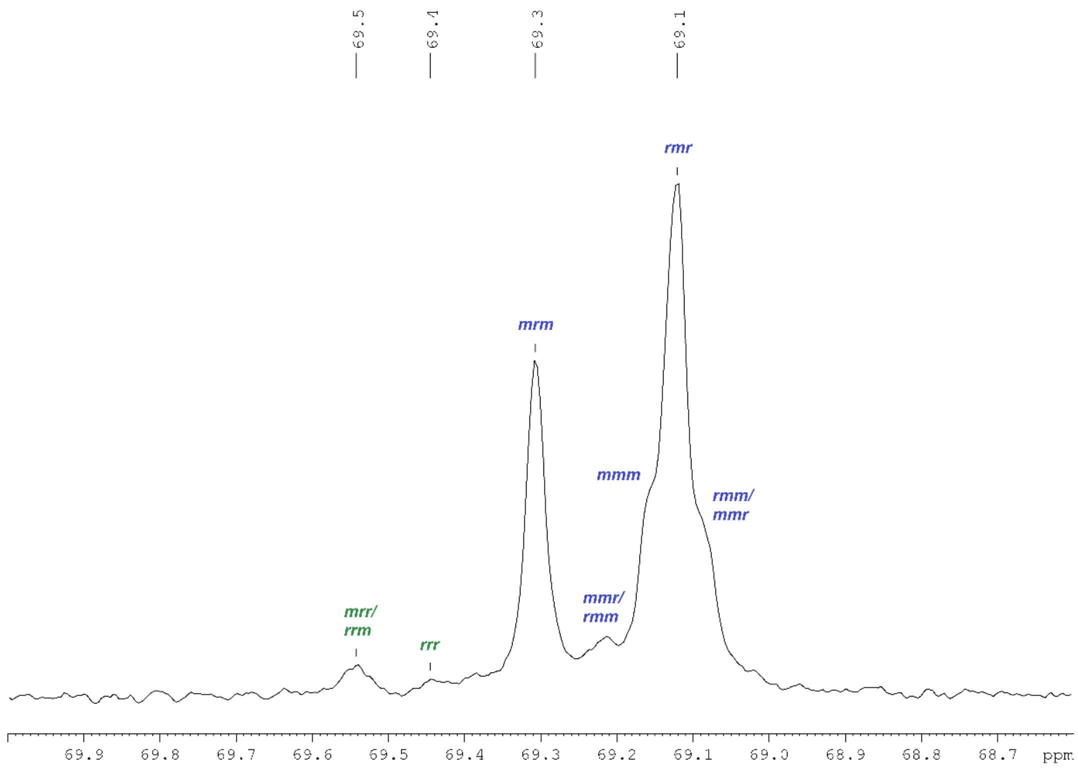

Figure S20. Methine region of the $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 50 °C.

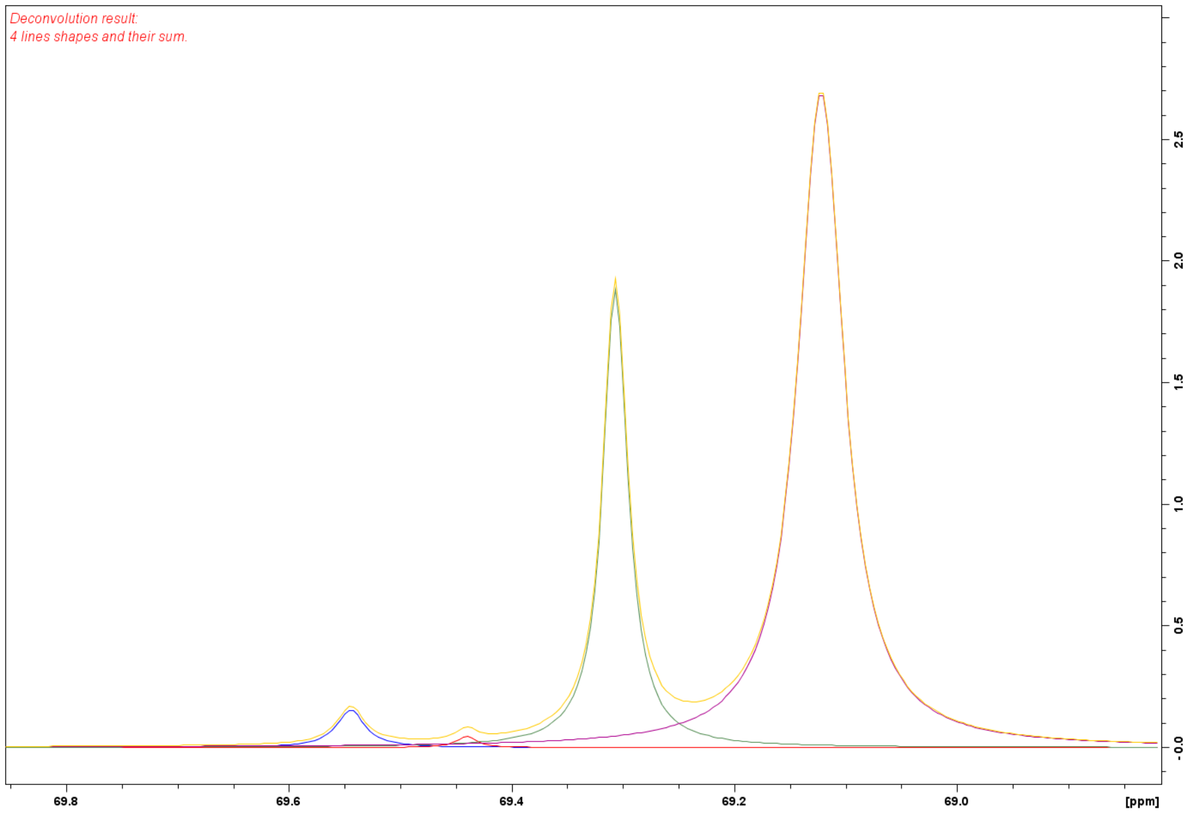

Figure S21. Deconvolution of the methine region of the $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 50 °C.

Fit	Frequency		Width		Intensity	Area	%Lor.
	ppm	Hz	ppm	Hz			chisq
1							6.4e+14
	69.546	8749.23	0.03086	3.883	0.154	1.966	100.00
STD:	0.005	0.63	0.01487	1.871	0.050		
	69.442	8736.13	0.02157	2.713	0.047	0.418	100.00
STD:	0.014	1.71	0.03933	4.948	0.059		
	69.309	8719.42	0.02697	3.393	1.881	21.032	100.00
STD:	0.000	0.05	0.00108	0.136	0.053		
	69.125	8696.37	0.04926	6.197	2.695	55.020	100.00
STD:	0.000	0.04	0.00105	0.132	0.039		

Figure S22. $^{13}C\{^{1}H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

Table S2. Tetrad intensities derived from the $^{1}H\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra.

	P_{rmr}	$P_{rmm/mmr}$	δ = 5.19 ppm	$P_{mmr/rmm}$	P_{mmm}	P_{mrm}	P_{rrr}	P_{rrm}	P_{mrm}
Area from deconvolution (^{1}H or $^{13}C\{^{1}H\}$ NMR)	99.944 [a]	66.305 [a]	1.476 [a]	54.177 [a]	155.983 [a]	195.012 [a]	0.418 [b]	1.996 [b]	21.032 [b]
Intensity in ^{1}H NMR (normalized) and relative intensity in $^{13}C\{^{1}H\}$ NMR (by equating P_{mrm} values from ^{1}H and $^{13}C\{^{1}H\}$ NMR)	0.1745	0.1157	0.0026	0.0946	0.2723	0.3404	0.0068	0.0323	0.3404
Relative intensities (normalized)	0.16791763	0.11133564	0.00250192	0.09103156	0.26202848	0.32755966	0.00654349	0.0310816	
P_m					0.3914	0.3192			

[a] from ^{1}H NMR. [b] from $^{13}C\{^{1}H\}$ NMR.

Average: P_m = 0.3553

2.4.2. Polymerisation of *rac*-lactide with compound 2 at 30 °C

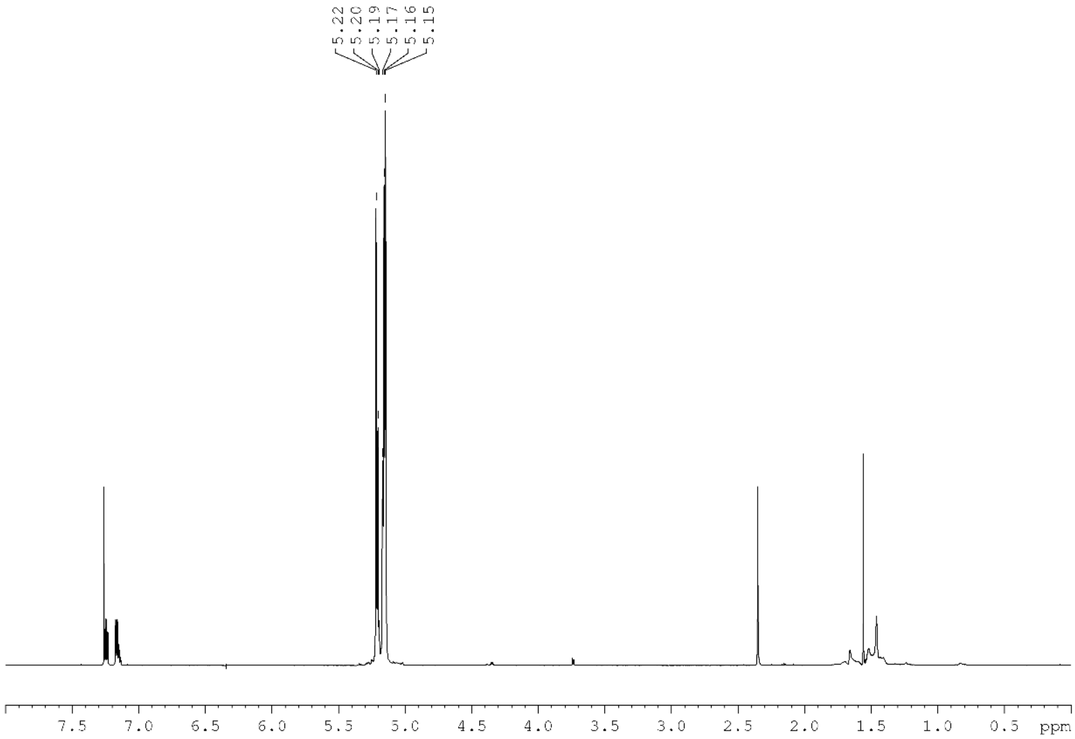

Figure S23. Homodecoupled $^{1}H\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 30 °C.

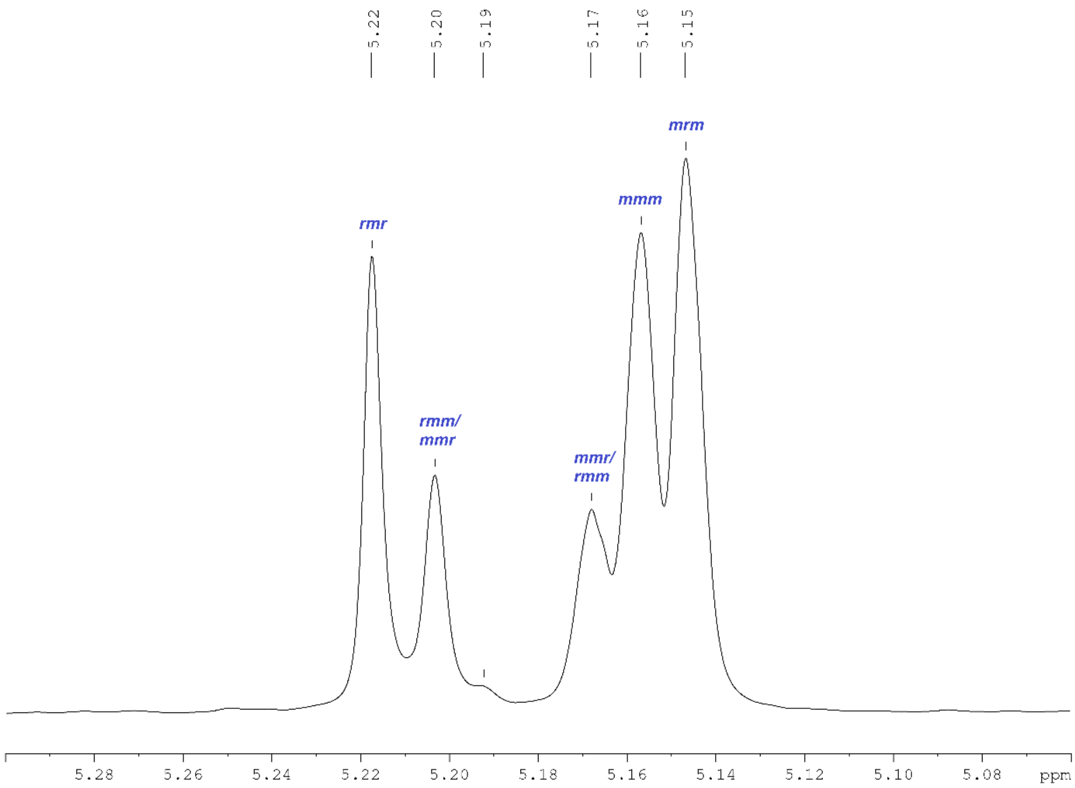

Figure S24. Methine region of the homodecoupled $^{1}H\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 30 °C.

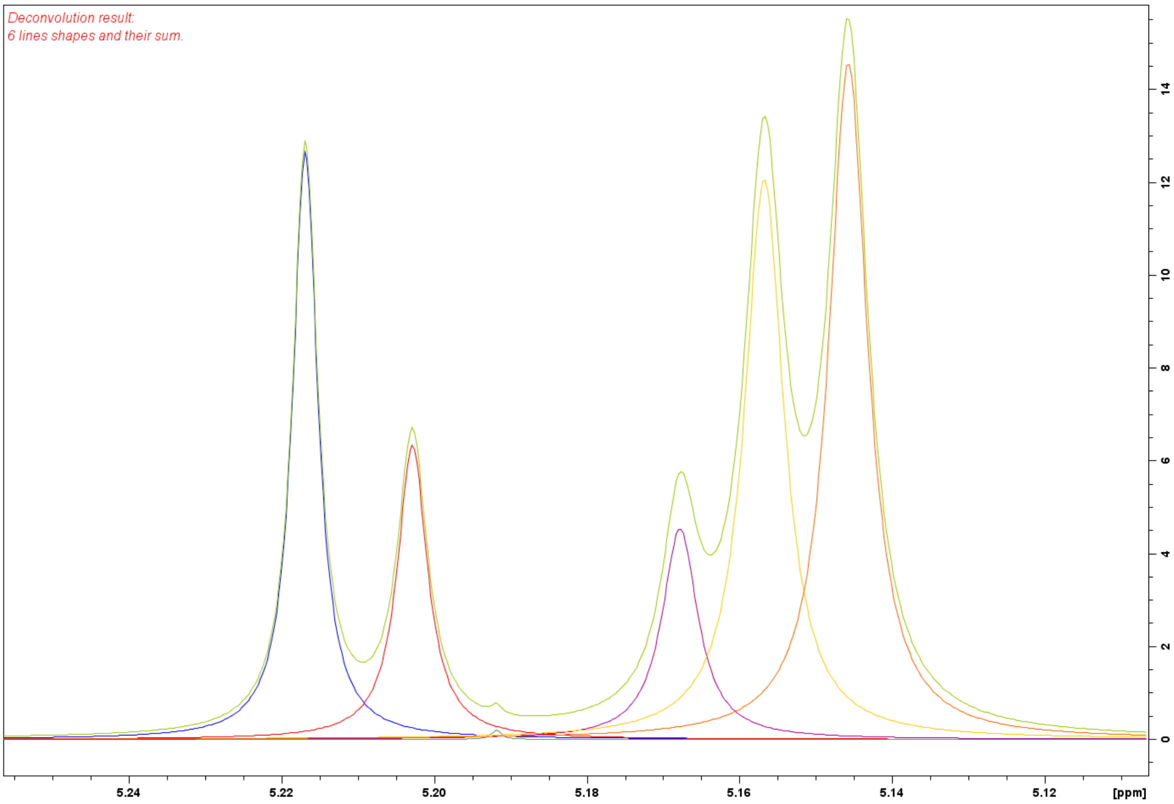

Figure S25. Deconvolution of the homodecoupled $^{1}H\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 30 °C.

Fit type: Mixed Lorentzian and Gaussian

Fit	Frequency ppm	Frequency Hz	Width ppm	Width Hz	Intensity	Area	%Lor. chisq
1							3.2e+16
	5.217	3131.16	0.00395	2.373	12.661	257.293	100.00
STD:	0.000	0.02	0.00010	0.058	0.210		
	5.203	3122.71	0.00474	2.847	6.338	154.563	100.00
STD:	0.000	0.04	0.00022	0.129	0.192		
	5.192	3116.12	0.00163	0.980	0.199	1.673	100.00
STD:	0.001	0.80	0.00385	2.310	0.325		
	5.168	3101.70	0.00568	3.407	4.538	132.405	100.00
STD:	0.000	0.07	0.00036	0.218	0.176		
	5.157	3095.03	0.00623	3.739	12.057	386.134	100.00
STD:	0.000	0.03	0.00017	0.104	0.169		
	5.146	3088.56	0.00615	3.690	14.562	460.288	100.00
STD:	0.000	0.02	0.00012	0.073	0.170		

Figure S26. $^{1}H\{^{1}H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

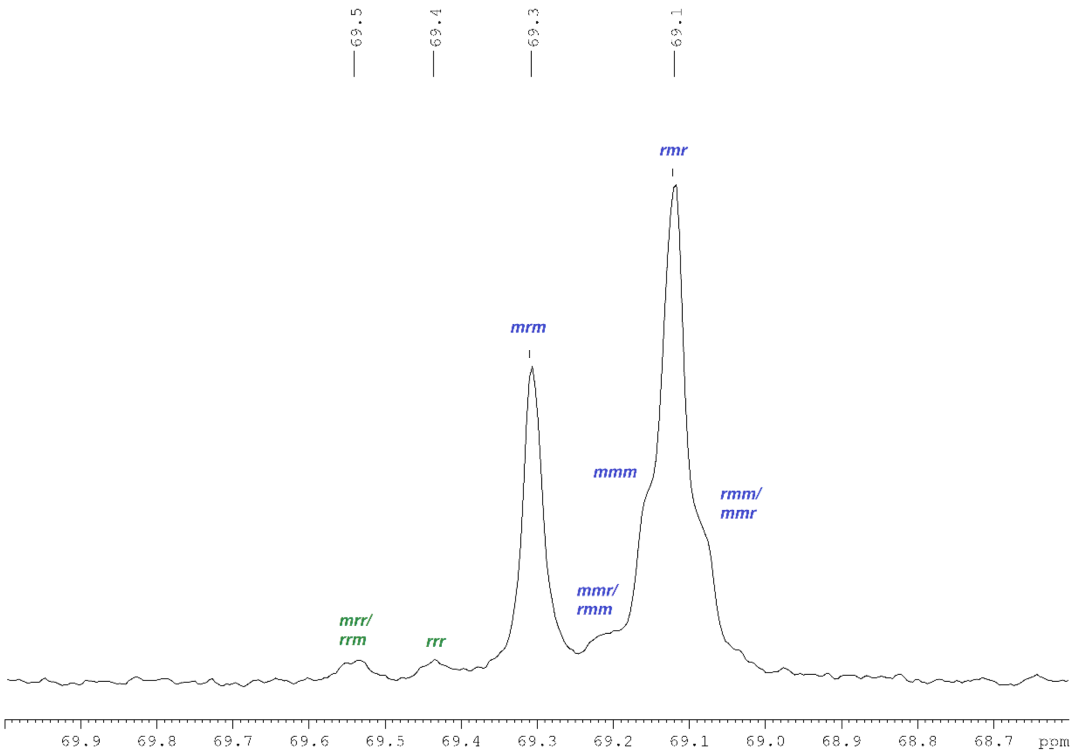

Figure S27. Methine region of the $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 30 °C.

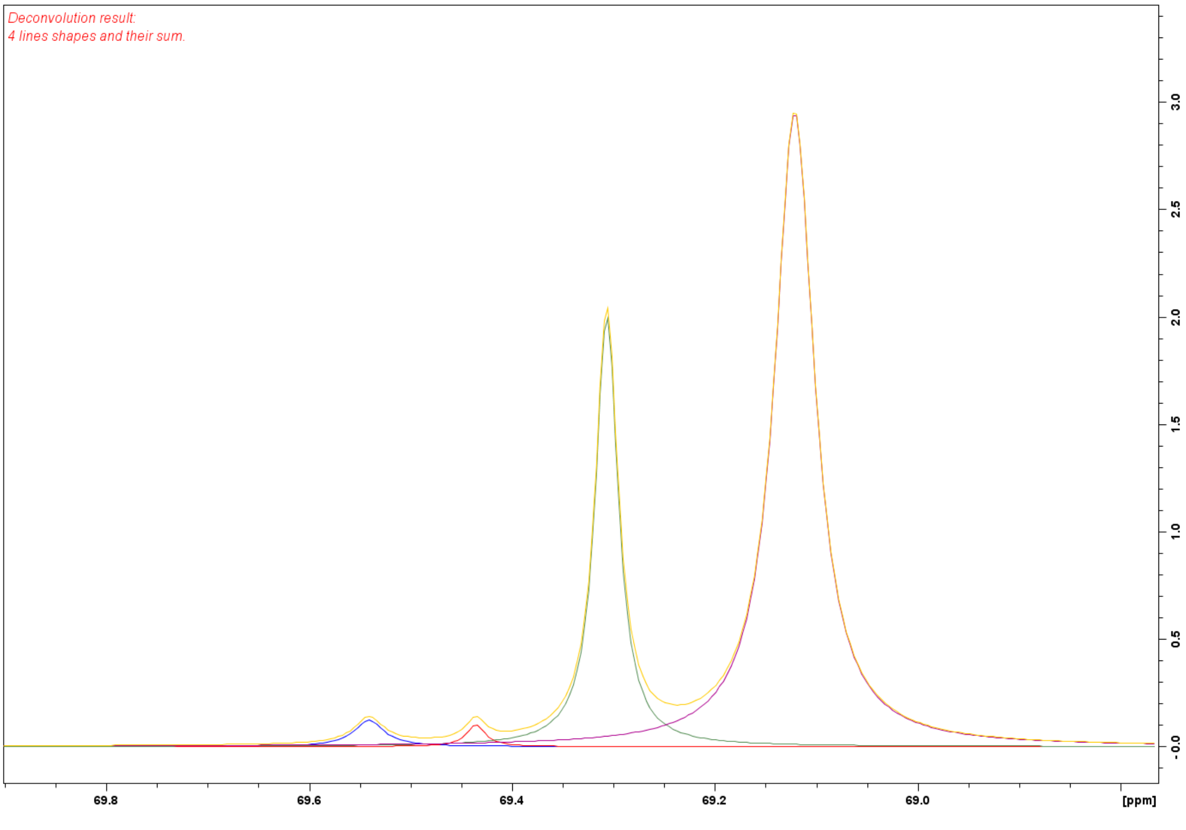

Figure S28. Deconvolution of the methine region of the $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 30 °C.

Fit	Frequency		Width		Intensity	Area	%Lor.
	ppm	Hz	ppm	Hz			chisq
1							7.8e+14
	69.542	8748.83	0.03599	4.528	0.122	1.817	100.00
STD:	0.008	1.01	0.02641	3.323	0.053		
	69.437	8735.56	0.02285	2.875	0.100	0.945	100.00
STD:	0.007	0.92	0.02133	2.684	0.064		
	69.308	8719.32	0.02687	3.381	2.009	22.371	100.00
STD:	0.000	0.05	0.00113	0.142	0.059		
	69.123	8696.10	0.04763	5.992	2.955	58.326	100.00
STD:	0.000	0.04	0.00104	0.131	0.044		

Figure S29. $^{13}C\{^1H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

Table S3. Tetrad intensities derived from the $^1H\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra.

	P_{rmr}	$P_{rmm/mmr}$	δ = 5.19 ppm	$P_{mmr/rmm}$	P_{mmm}	P_{mrm}	P_{rrr}	P_{rrm}	P_{mrm}
Area from deconvolution (^1H or $^{13}C\{^1H\}$ NMR)	257.293 [a]	154.563 [a]	1.673 [a]	132.405 [a]	386.134 [a]	460.288 [a]	0.945 [b]	1.817 [b]	22.371 [b]
Intensity in ^1H NMR (normalized) and relative intensity in $^{13}C\{^1H\}$ NMR (by equating P_{mrm} values from ^1H and $^{13}C\{^1H\}$ NMR)	0.1848	0.1110	0.0012	0.0951	0.2773	0.3306	0.0140	0.0269	0.3306
Relative intensities (normalized)	0.17753867	0.10663849	0.00115285	0.09136324	0.26640407	0.31760976	0.0134499	0.02584302	
P_m					0.3970	0.3388			

[a] from ^1H NMR. [b] from $^{13}C\{^1H\}$ NMR.

Average: P_m = 0.3679

2.4.3. Polymerisation of *rac*-lactide with compound **2** at 0 °C

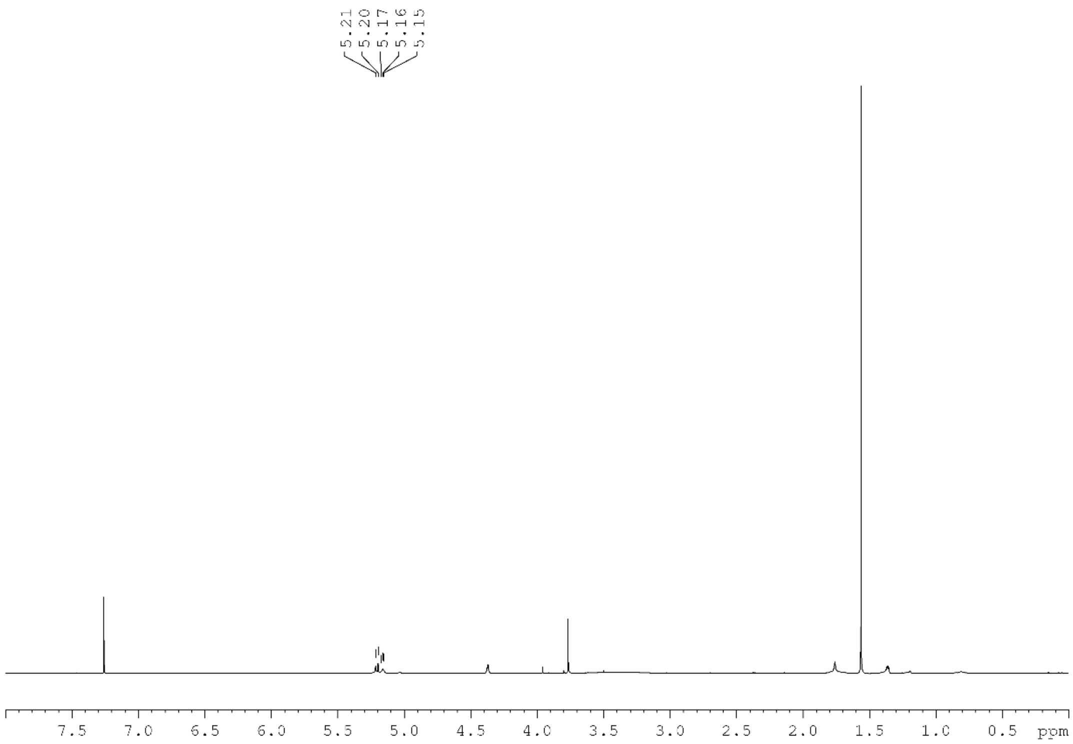

Figure S30. Homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 0 °C.

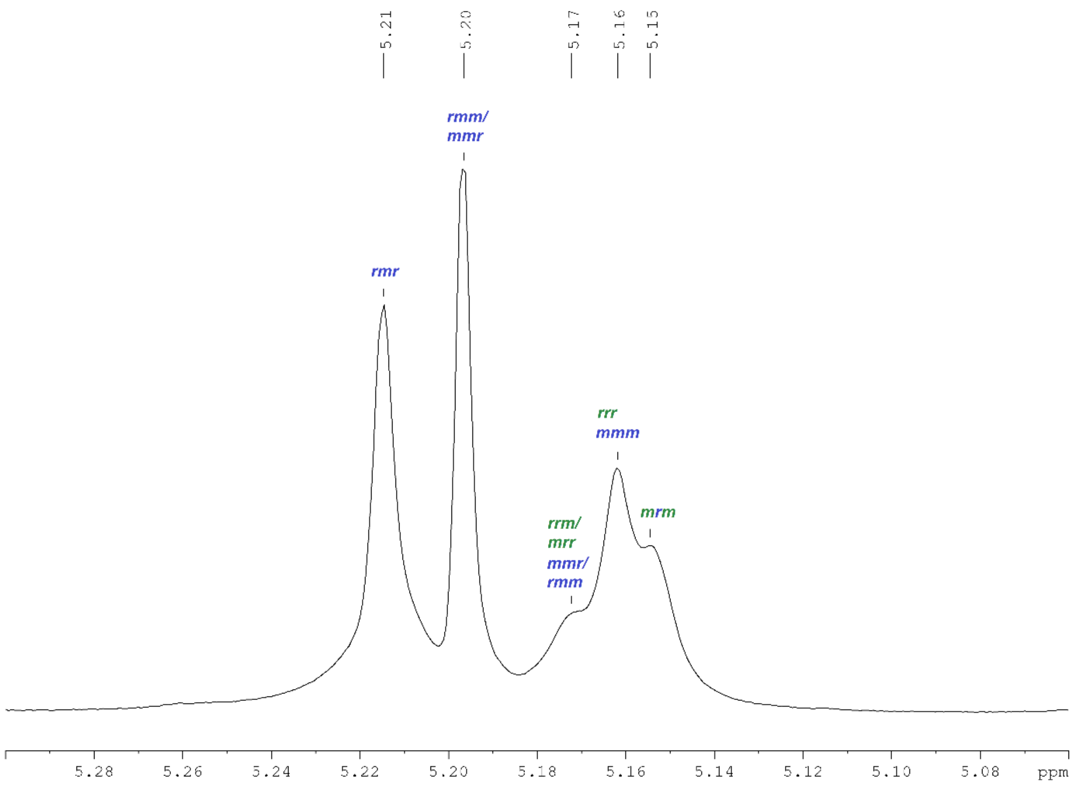

Figure S31. Methine region of the homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 0 °C.

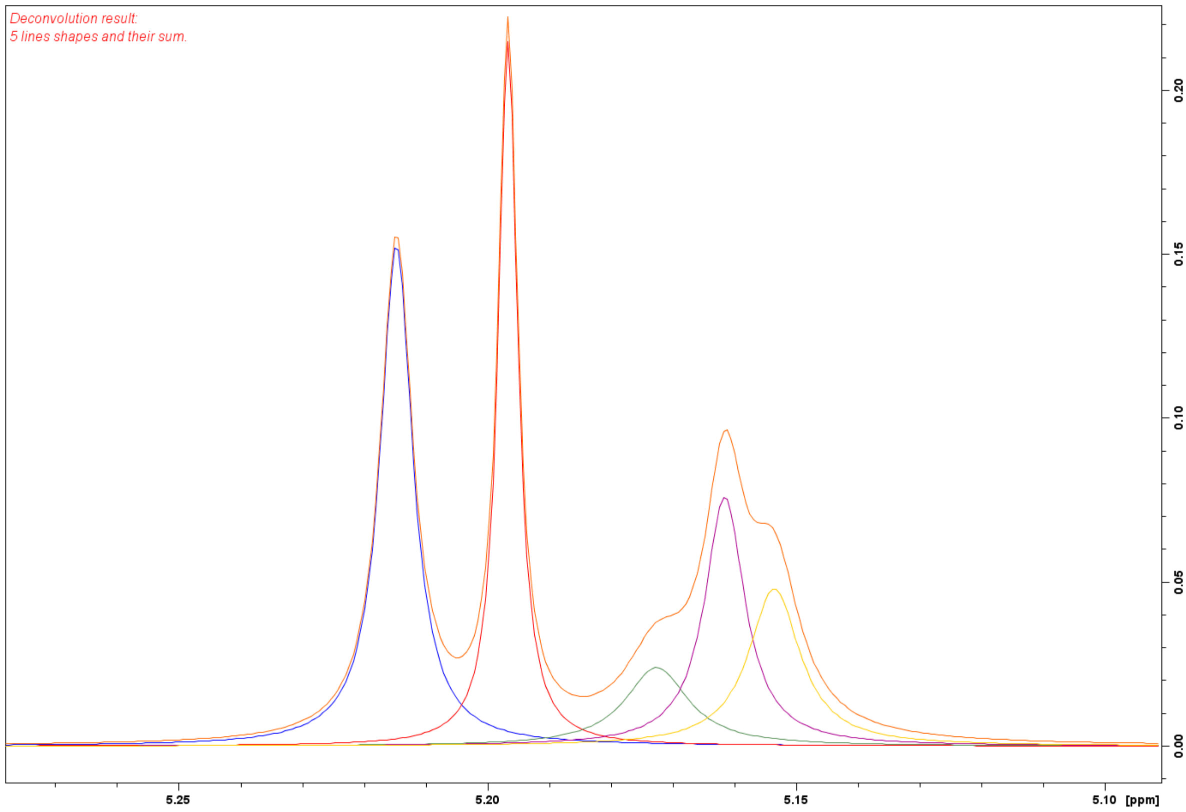

Figure S32. Deconvolution of the homodecoupled $^{1}H\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 0 °C.

Fit	Frequency ppm	Frequency Hz	Width ppm	Width Hz	Intensity	Area	%Lor. chisq
1							2.2e+12
	5.215	2609.15	0.00631	3.157	0.153	2.480	100.00
STD:	0.000	0.02	0.00013	0.065	0.002		
	5.197	2600.15	0.00373	1.865	0.215	2.068	100.00
STD:	0.000	0.01	0.00007	0.036	0.003		
	5.173	2588.32	0.01236	6.185	0.024	0.762	100.00
STD:	0.001	0.32	0.00184	0.923	0.002		
	5.162	2582.80	0.00786	3.933	0.076	1.530	100.00
STD:	0.000	0.08	0.00073	0.366	0.003		
	5.154	2578.47	0.01006	5.035	0.048	1.245	100.00
STD:	0.000	0.16	0.00088	0.441	0.003		

Figure S33. $^{1}H\{^{1}H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

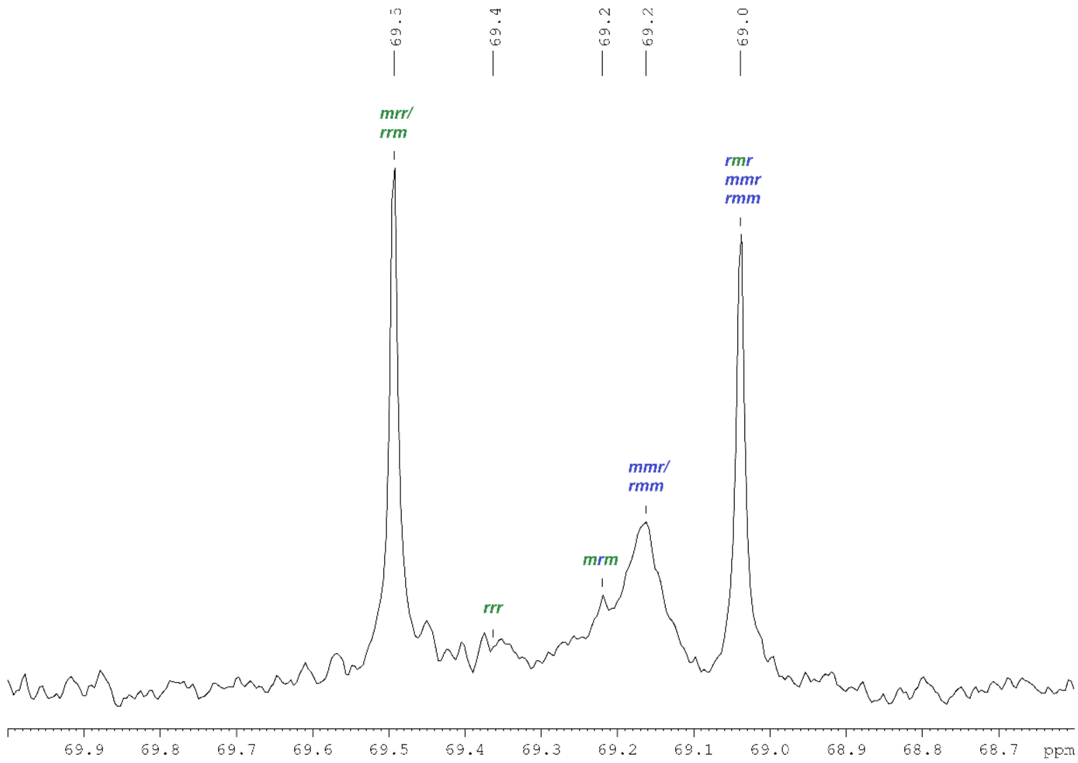

Figure S34. Methine region of the $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 0 °C.

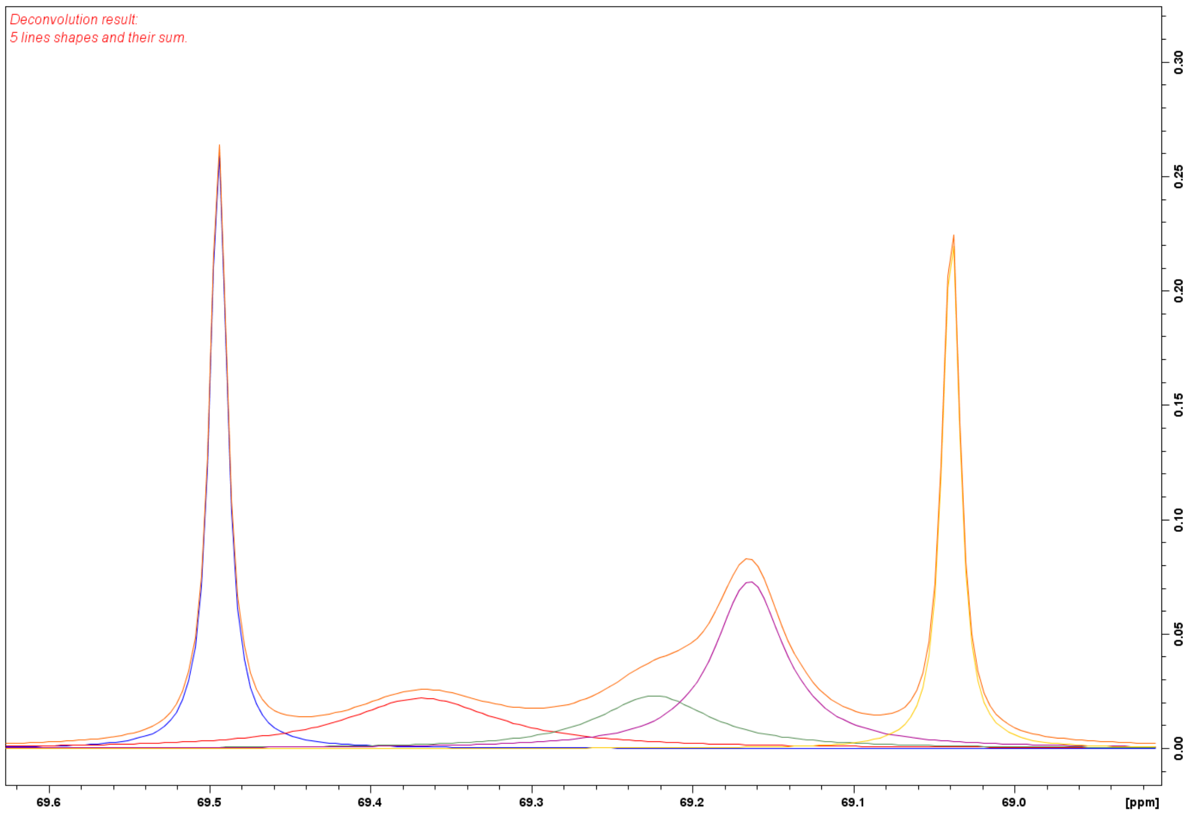

Figure S35. Deconvolution of the methine region of the $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **2** at 0 °C.

Fit	Frequency		Width		Intensity	Area	%Lor.
	ppm	Hz	ppm	Hz			chisq
1							5.5e+12
	69.495	8742.91	0.01321	1.661	0.261	1.430	100.00
STD:	0.000	0.02	0.00041	0.051	0.005		
	69.369	8726.97	0.11364	14.297	0.022	1.015	100.00
STD:	0.006	0.74	0.02145	2.699	0.002		
	69.225	8708.88	0.08426	10.600	0.023	0.795	100.00
STD:	0.009	1.14	0.02975	3.743	0.004		
	69.166	8701.52	0.05311	6.682	0.073	1.599	100.00
STD:	0.002	0.20	0.00553	0.696	0.006		
	69.041	8685.69	0.01271	1.599	0.230	1.210	100.00
STD:	0.000	0.02	0.00043	0.054	0.005		

Figure S36. $^{13}C\{^{1}H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

Table S4. Tetrad intensities derived from the $^{1}H\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra.

	P_{rmr}	$P_{rmm/mmr}$	**δ = 5.19 ppm**	$P_{mmr/rmm}$	P_{mmm}	P_{mrm}	P_{rrr}	P_{rrm}	P_{mrm}
Area from deconvolution (^{1}H or $^{13}C\{^{1}H\}$ NMR)	2.480 [a]	2.068 [a]	0.000 [a]	0.762 [a]	1.530 [a]	1.245 [a]	1.015 [b]	1.430 [b]	0.795 [b]
Intensity in ^{1}H NMR (normalized) and relative intensity in $^{13}C\{^{1}H\}$ NMR (by equating P_{mrm} values from ^{1}H and $^{13}C\{^{1}H\}$ NMR)	0.3067	0.2558	0.000	0.0942	0.1892	0.1540	0.1966	0.2770	0.1540
Relative intensities (normalized)	0.20814388	0.17360027	0	0.06392942	0.12840176	0.10451306	0.13342382	0.18798778	0.20814388
P_{m}					0.2928	0.6920			

[a] from ^{1}H NMR. [b] from $^{13}C\{^{1}H\}$ NMR.

Average: P_{m} = 0.4924

Due to insufficient resolution and strong line broadening, the value obtained from P_{mrm} is not reliable. Therefore, P_{m} obtained from P_{mmm} was selected, which is in good agreement with the values calculated for the previous samples.

2.4.4. Polymerisation of *rac*-lactide with compound 3

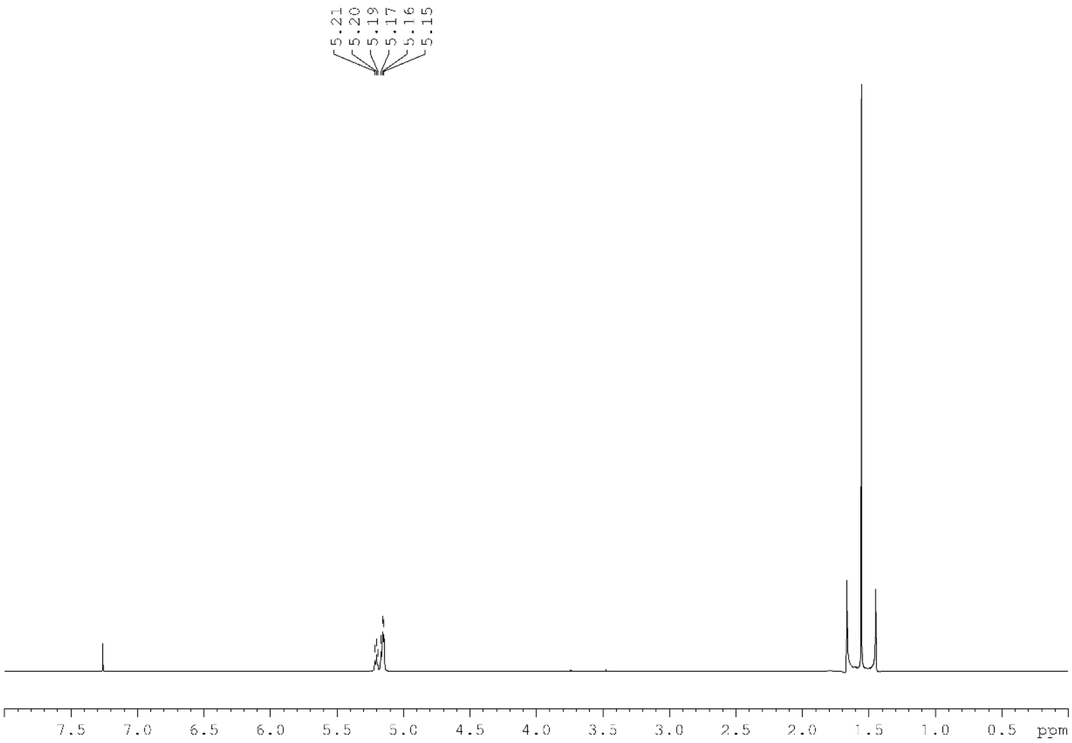

Figure S37. Homodecoupled $^{1}H\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **3**.

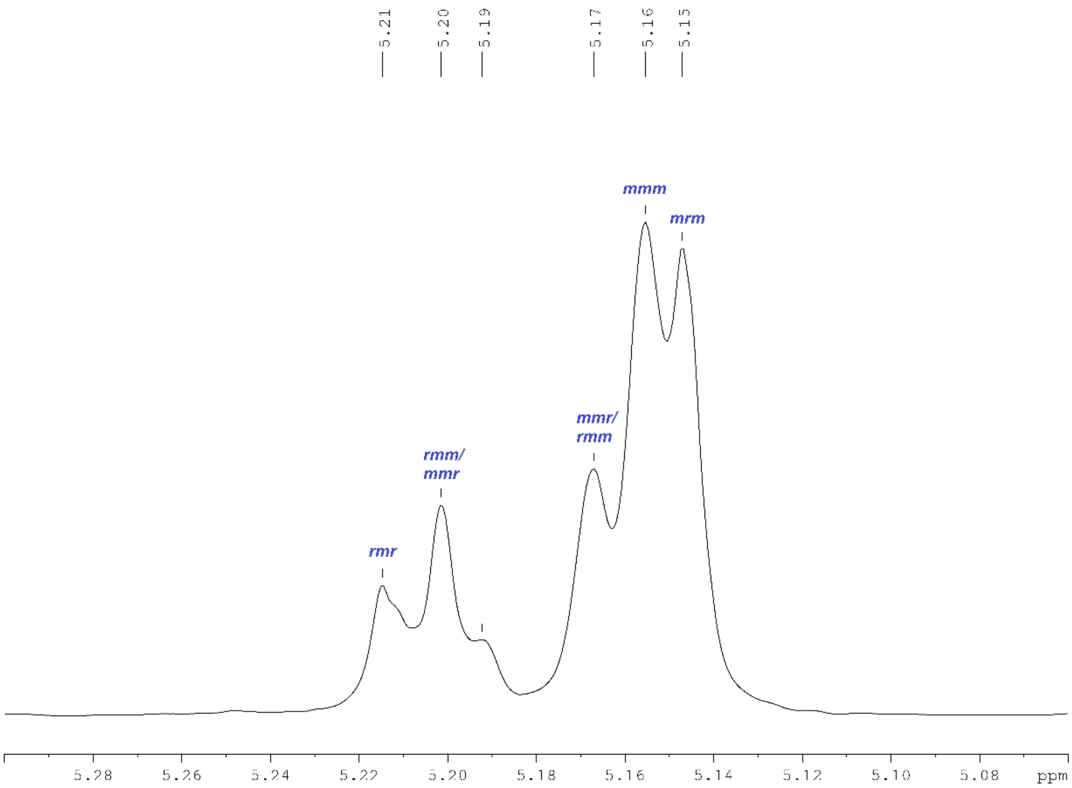

Figure S38. Methine region of the homodecoupled $^{1}H\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **3**.

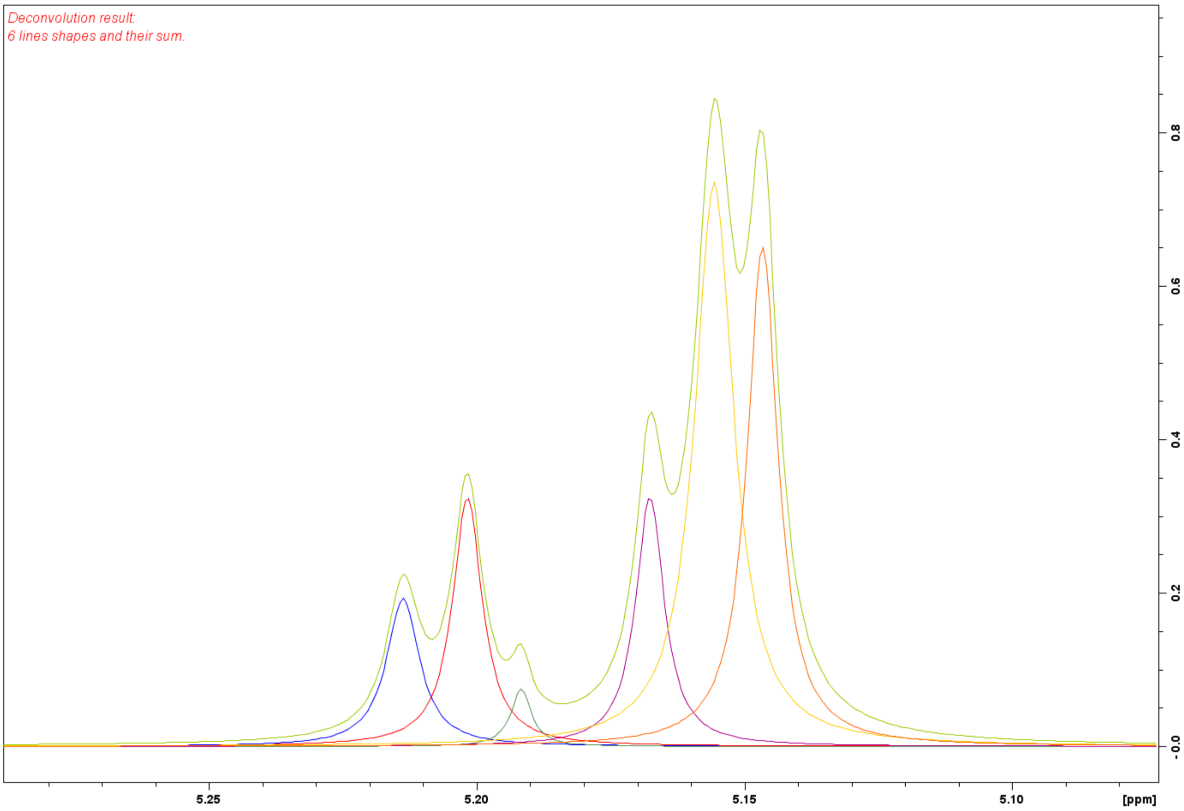

Figure S39. Deconvolution of the homodecoupled $^{1}H\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **3**.

Fit	Frequency ppm	Frequency Hz	Width ppm	Width Hz	Intensity	Area	%Lor. chisq
1							6e+13
	5.214	2608.77	0.00744	3.722	0.193	3.693	100.00
STD:	0.000	0.09	0.00057	0.284	0.009		
	5.202	2602.53	0.00673	3.367	0.324	5.619	100.00
STD:	0.000	0.05	0.00039	0.196	0.009		
	5.192	2597.73	0.00456	2.281	0.075	0.886	100.00
STD:	0.000	0.17	0.00114	0.571	0.011		
	5.168	2585.71	0.00640	3.200	0.325	5.353	100.00
STD:	0.000	0.05	0.00033	0.167	0.010		
	5.156	2579.57	0.00880	4.403	0.735	16.649	100.00
STD:	0.000	0.03	0.00027	0.138	0.009		
	5.147	2575.03	0.00701	3.505	0.651	11.750	100.00
STD:	0.000	0.03	0.00021	0.104	0.011		

Figure S40. $^{1}H\{^{1}H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

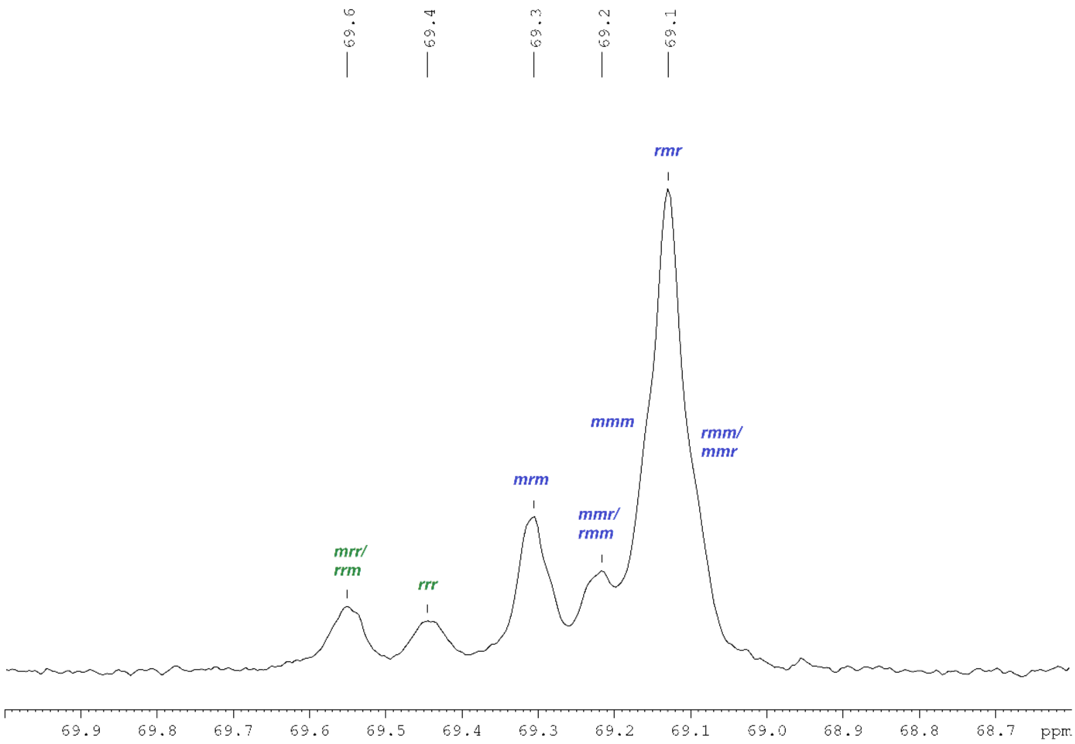

Figure S41. Methine region of the $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **3**.

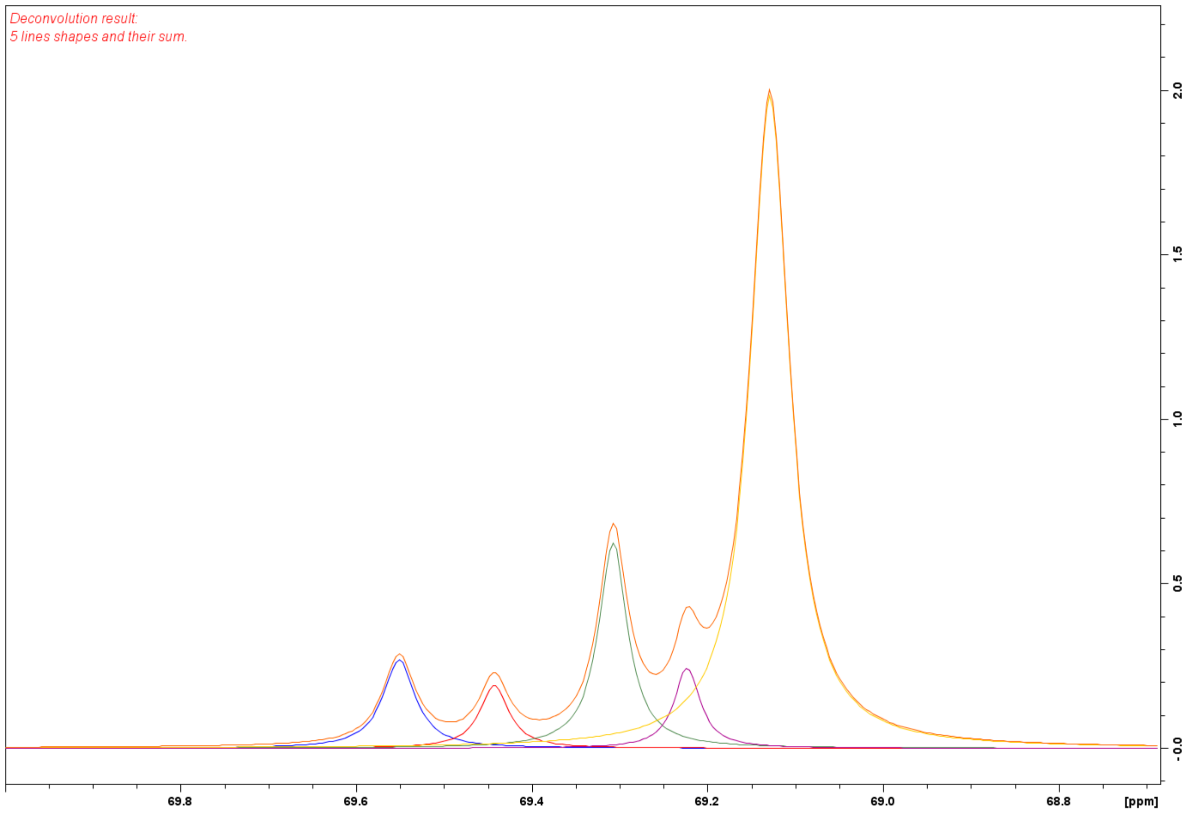

Figure S42. Deconvolution of the methine region of the $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **3**.

Fit	Frequency		Width		Intensity	Area	%Lor.
	ppm	Hz	ppm	Hz			chisq
1							1.3e+14
	69.553	8750.13	0.04471	5.625	0.268	4.973	100.00
STD:	0.001	0.19	0.00451	0.567	0.018		
	69.445	8736.60	0.03981	5.008	0.192	3.160	100.00
STD:	0.002	0.25	0.00606	0.762	0.019		
	69.310	8719.54	0.03978	5.004	0.624	10.294	100.00
STD:	0.001	0.08	0.00192	0.242	0.019		
	69.226	8708.99	0.03581	4.506	0.244	3.624	100.00
STD:	0.001	0.19	0.00500	0.630	0.020		
	69.132	8697.21	0.05385	6.774	1.984	44.266	100.00
STD:	0.000	0.03	0.00071	0.089	0.016		

Figure S43. $^{13}C\{^{1}H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

Table S5. Tetrad intensities derived from the $^1H\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra.

	P_{rmr}	$P_{rmm/mmr}$	δ = 5.19 ppm	$P_{mmr/rmm}$	P_{mmm}	P_{mrm}	P_{rrr}	P_{rrm}	P_{mrm}
Area from deconvolution (^{1}H or $^{13}C\{^1H\}$ NMR)	3.693 [a]	5.619 [a]	0.886 [a]	5.353 [a]	16.649 [a]	11.750 [a]	3.160 [b]	4.973 [b]	10.294 [b]
Intensity in ^{1}H NMR (normalized) and relative intensity in $^{13}C\{^1H\}$ NMR (by equating P_{mrm} values from ^{1}H and $^{13}C\{^1H\}$ NMR)	0.0840	0.1278	0.0202	0.1218	0.3788	0.2673	0.0821	0.1291	0.2673
Relative intensities (normalized)	0.06935843	0.1055239	0.01667905	0.10056973	0.31277351	0.22070845	0.06778961	0.10659731	0.06935843
P_m					0.5038	0.4653			

[a] from ^{1}H NMR. [b] from $^{13}C\{^1H\}$ NMR.

Average: P_m = 0.4846

2.4.5. Polymerisation of *rac*-lactide with compound 4

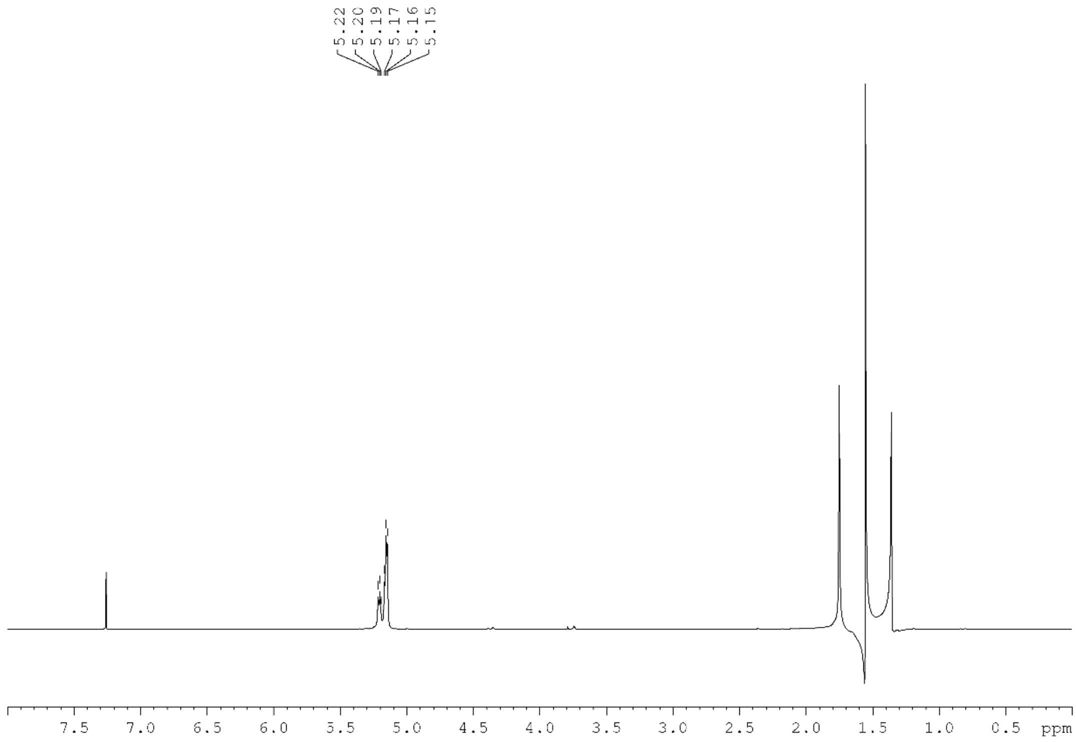

Figure S44. Homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **4**.

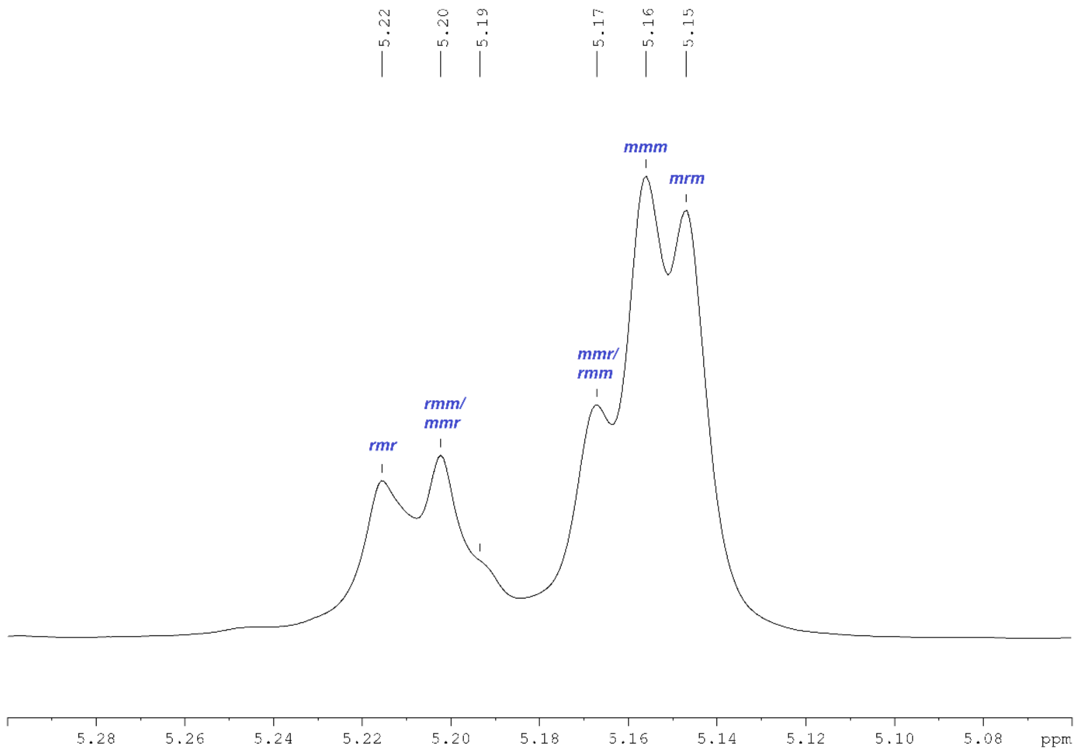

Figure S45. Methine region of the homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **4**.

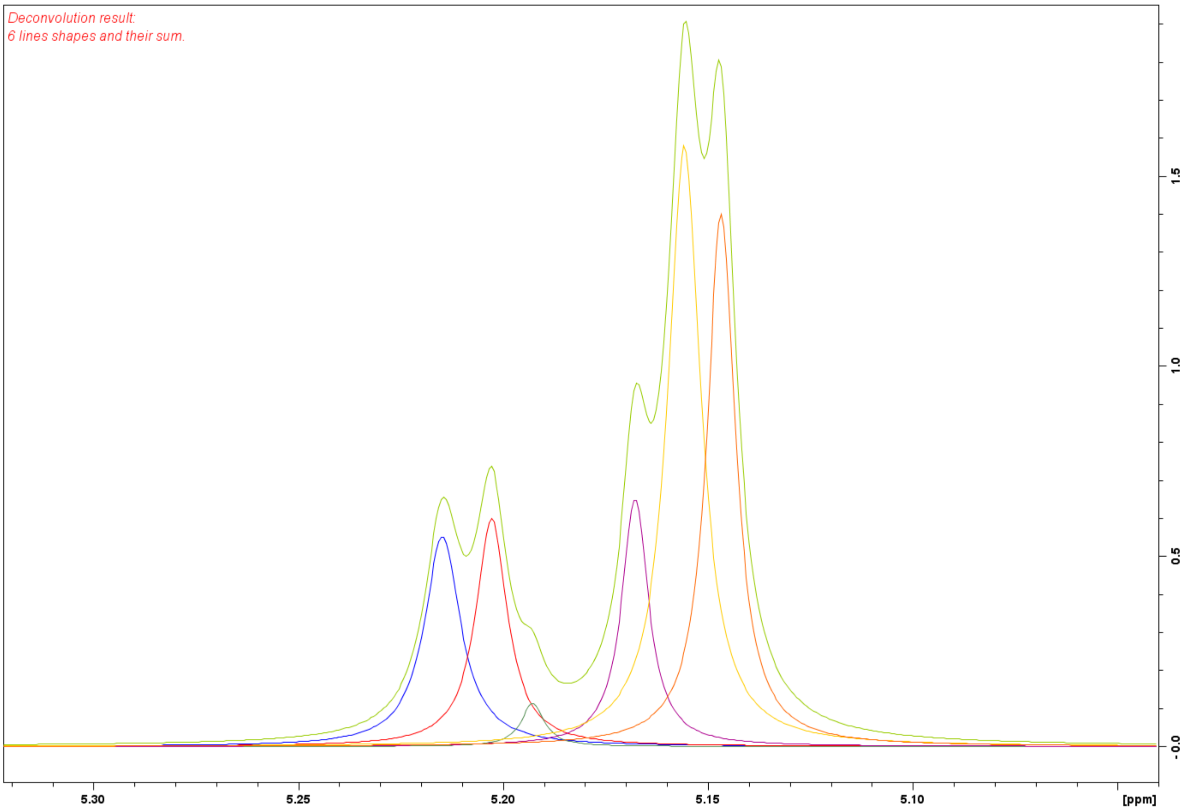

Figure S46. Deconvolution of the homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **4**.

Fit	Frequency ppm	Frequency Hz	Width ppm	Width Hz	Intensity	Area	%Lor. chisq
1							1e+14
	5.215	2609.34	0.01070	5.355	0.552	15.209	100.00
STD:	0.000	0.07	0.00042	0.212	0.012		
	5.203	2602.93	0.00932	4.662	0.600	14.387	100.00
STD:	0.000	0.06	0.00056	0.280	0.013		
	5.193	2598.06	0.00672	3.364	0.114	1.975	100.00
STD:	0.000	0.25	0.00171	0.853	0.016		
	5.168	2585.85	0.00795	3.978	0.651	13.335	100.00
STD:	0.000	0.05	0.00032	0.158	0.014		
	5.156	2579.89	0.00978	4.892	1.580	39.774	100.00
STD:	0.000	0.03	0.00024	0.122	0.014		
	5.147	2575.05	0.00838	4.192	1.401	30.222	100.00
STD:	0.000	0.03	0.00017	0.084	0.017		

Figure S47. $^1H\{^1H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

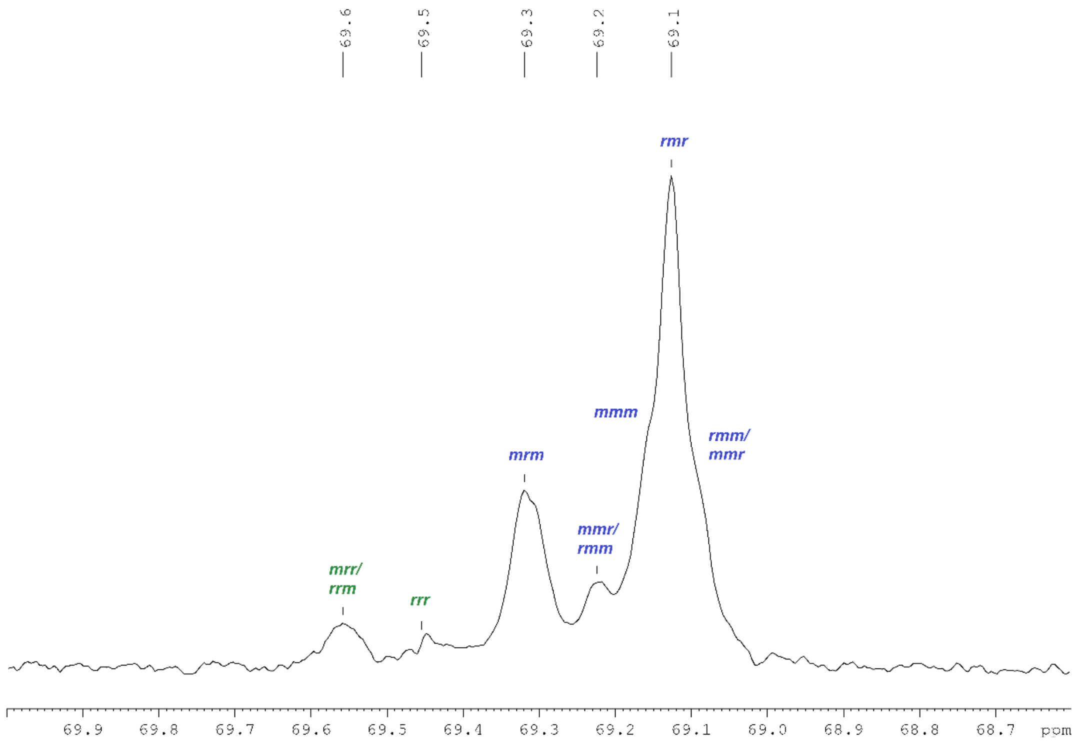

Figure S48. Methine region of the $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **4**.

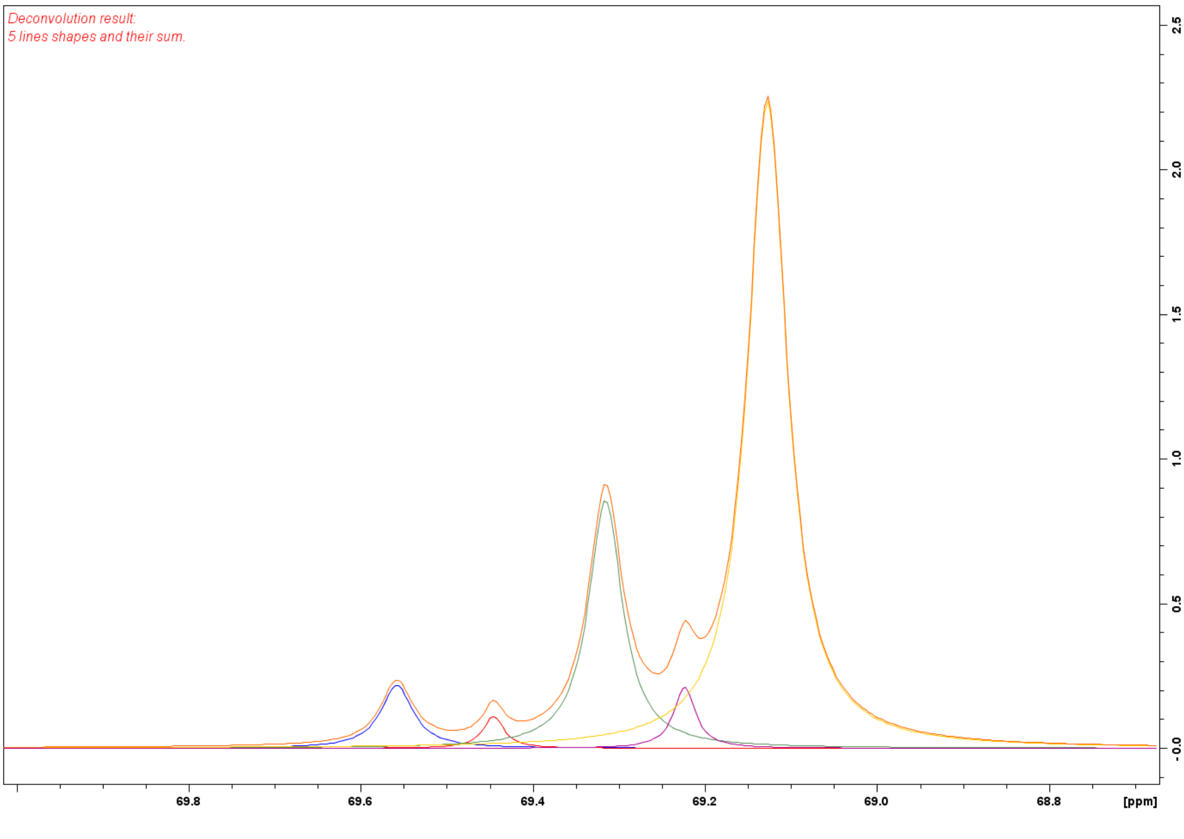

Figure S49. Deconvolution of the methine region of the $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **4**.

Fit	Frequency		Width		Intensity	Area	%Lor.
	ppm	Hz	ppm	Hz			chisq
1							2.5e+14
	69.559	8750.97	0.04567	5.746	0.217	4.116	100.00
STD:	0.003	0.34	0.00796	1.001	0.026		
	69.447	8736.81	0.02952	3.713	0.111	1.361	100.00
STD:	0.004	0.53	0.01263	1.588	0.032		
	69.317	8720.49	0.04748	5.973	0.859	16.901	100.00
STD:	0.001	0.09	0.00220	0.277	0.025		
	69.225	8708.95	0.03020	3.799	0.213	2.667	100.00
STD:	0.002	0.28	0.00729	0.917	0.031		
	69.129	8696.85	0.05562	6.998	2.235	51.511	100.00
STD:	0.000	0.04	0.00092	0.115	0.023		

Figure S50. $^{13}C\{^{1}H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

Table S6. Tetrad intensities derived from the $^{1}H\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra.

	P_{rmr}	$P_{rmm/mmr}$	δ = 5.19 ppm	$P_{mmr/rmm}$	P_{mmm}	P_{mrm}	P_{rrr}	P_{rrm}	P_{mrm}
Area from deconvolution (^{1}H or $^{13}C\{^{1}H\}$ NMR)	15.209 [a]	14.387 [a]	1.975 [a]	13.335 [a]	39.774 [a]	30.220 [a]	1.361 [b]	4.116 [b]	16.901 [b]
Intensity in ^{1}H NMR (normalized) and relative intensity in $^{13}C\{^{1}H\}$ NMR (by equating P_{mrm} values from ^{1}H and $^{13}C\{^{1}H\}$ NMR)	0.1324	0.1252	0.0172	0.1161	0.3462	0.2630	0.0212	0.0640	0.2630
Relative intensities (normalized)	0.12199392	0.11535981	0.01584815	0.10697503	0.31899014	0.24232931	0.01953377	0.05896987	
P_m					0.4707	0.4740			

[a] from ^{1}H NMR. [b] from $^{13}C\{^{1}H\}$ NMR.

Average: P_m = 0.4724

2.4.6. Polymerisation of *rac*-lactide with compound 5

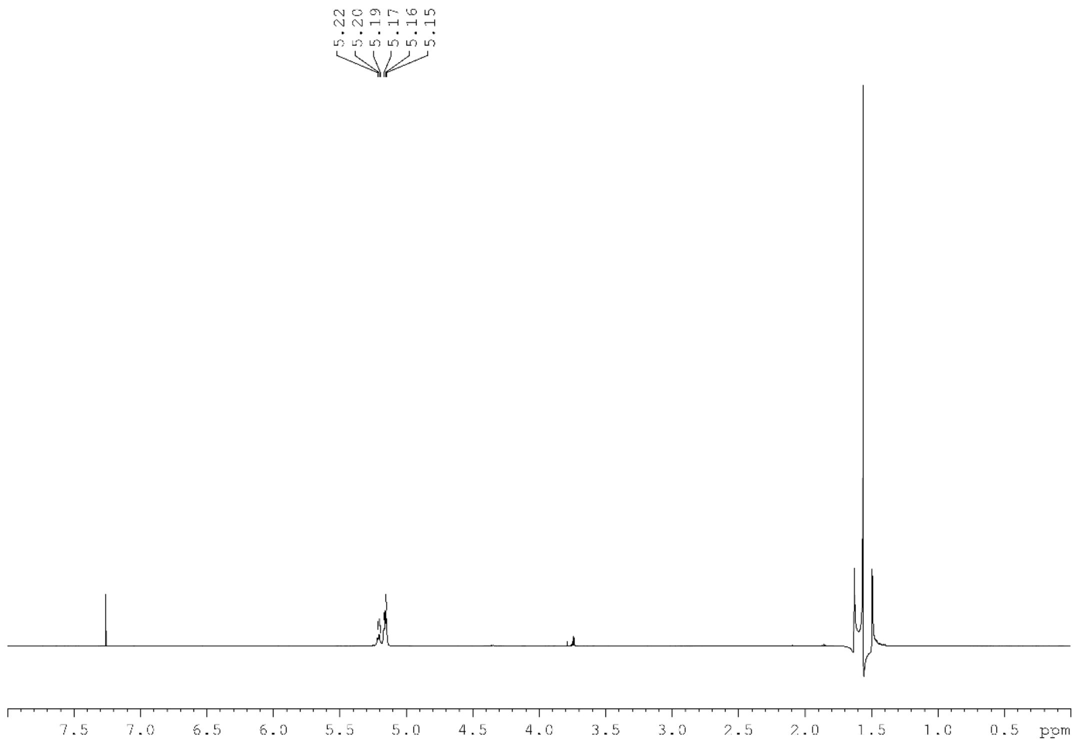

Figure S51. Homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **5**.

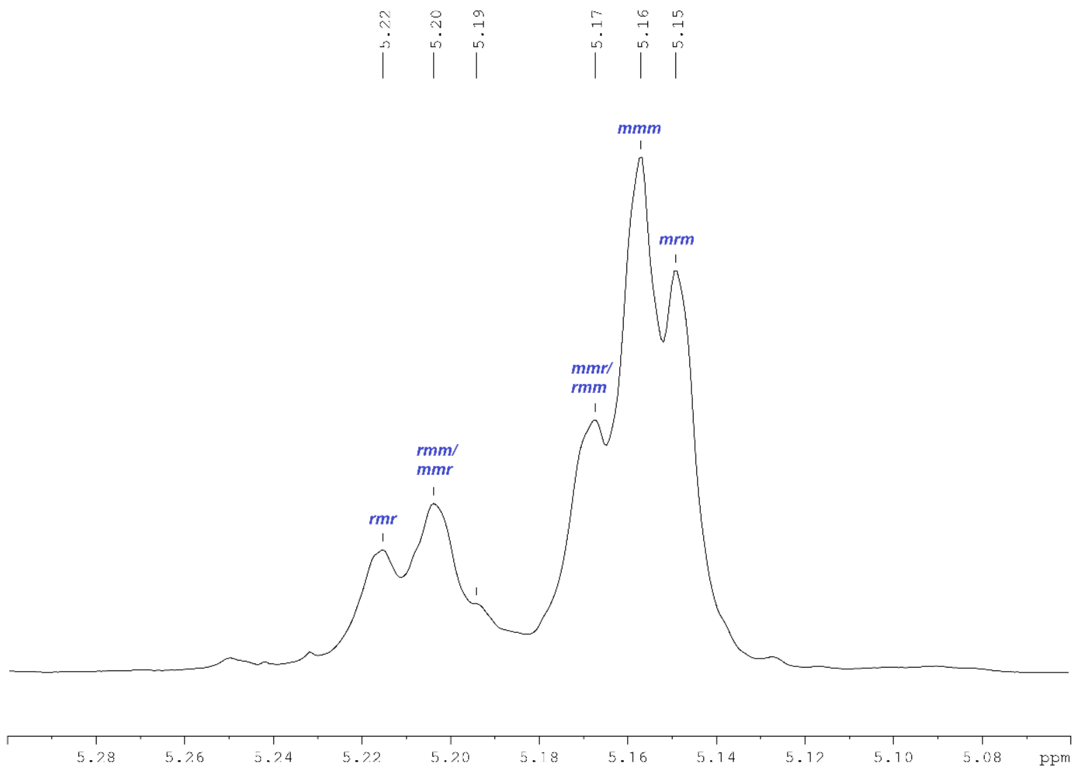

Figure S52. Methine region of the homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **5**.

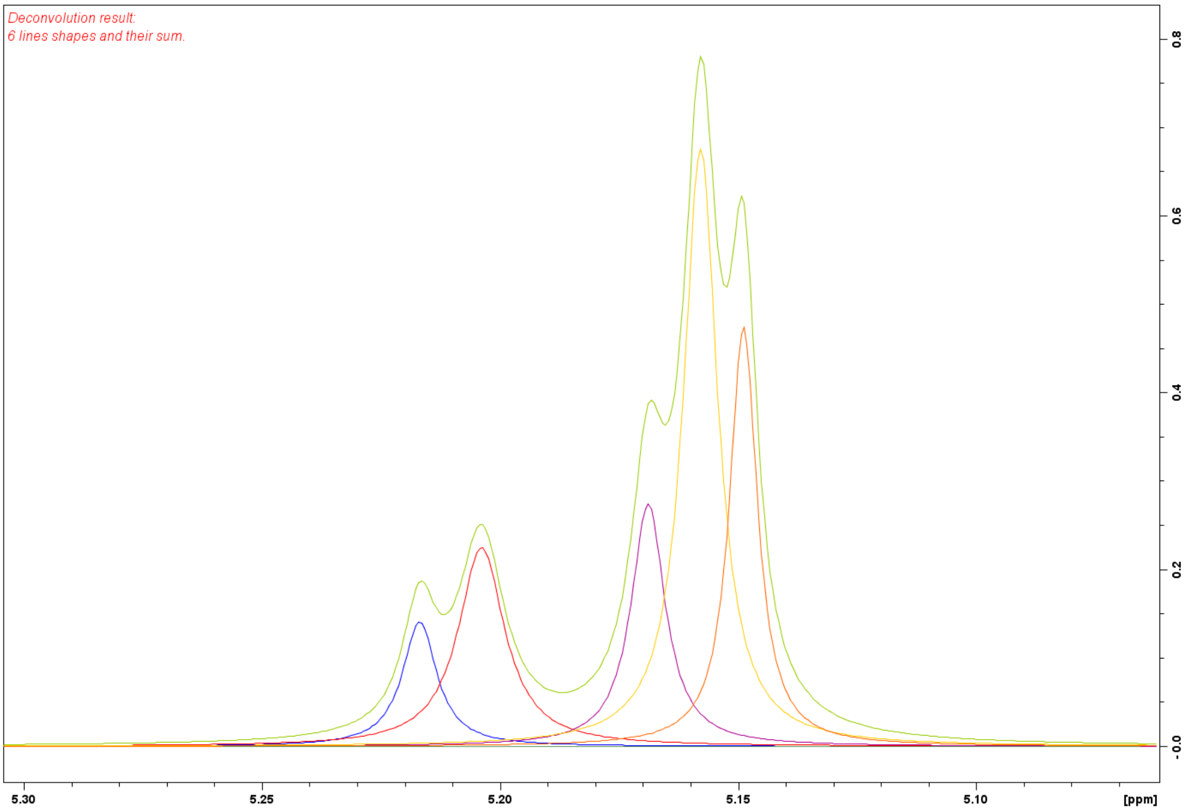

Figure S53. Deconvolution of the homodecoupled $^{1}H\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **5**.

Fit	Frequency		Width		Intensity	Area	%Lor.
	ppm	Hz	ppm	Hz			chisq
1							1e+13
	5.217	2610.07	0.00874	4.374	0.141	3.182	100.00
STD:	0.000	0.08	0.00056	0.283	0.005		
	5.204	2603.50	0.01179	5.899	0.225	6.840	100.00
STD:	0.000	0.09	0.00043	0.217	0.005		
	5.200	2601.63	0.00116	0.580	0.000	0.000	100.00
STD:	0.082	40.90	0.26454	132.355	0.013		
	5.169	2586.39	0.00870	4.351	0.274	6.147	100.00
STD:	0.000	0.05	0.00031	0.153	0.005		
	5.158	2580.60	0.00872	4.361	0.676	15.183	100.00
STD:	0.000	0.02	0.00019	0.095	0.005		
	5.149	2575.93	0.00700	3.503	0.475	8.574	100.00
STD:	0.000	0.02	0.00017	0.083	0.006		

Figure S54. $^{1}H\{^{1}H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

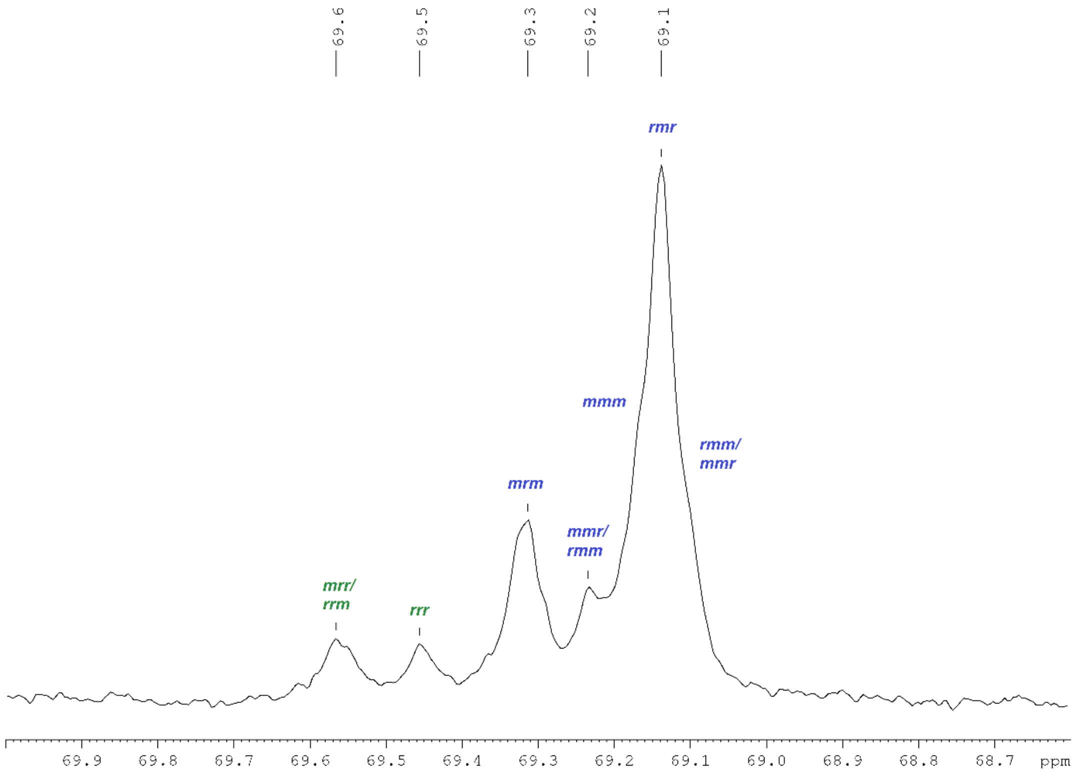

Figure S55. Methine region of the $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **5**.

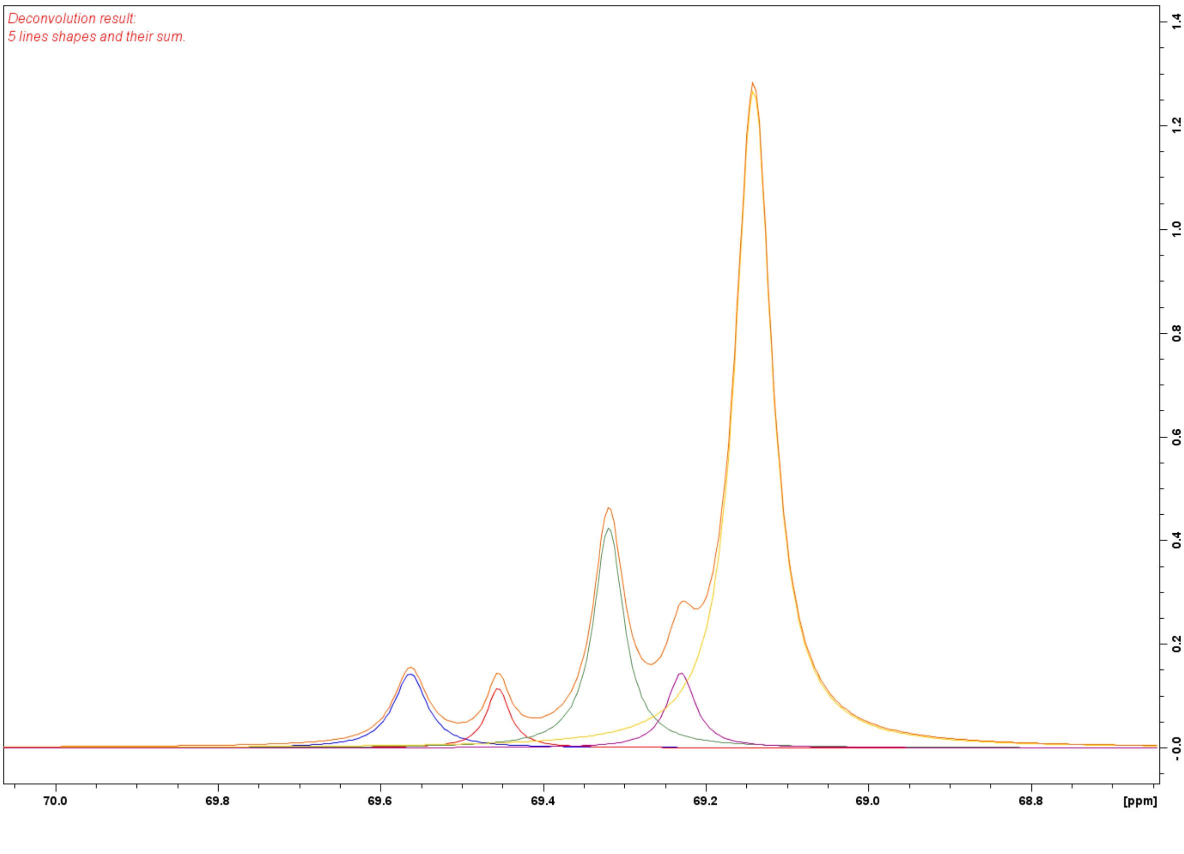

Figure S56. Deconvolution of the methine region of the $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **5**.

Fit	Frequency		Width		Intensity	Area	%Lor.
	ppm	Hz	ppm	Hz			chisq
1							1.5e+14
	69.564	8751.52	0.04998	6.287	0.143	2.963	100.00
STD:	0.002	0.26	0.00653	0.822	0.012		
	69.456	8737.89	0.03415	4.297	0.115	1.624	100.00
STD:	0.002	0.27	0.00659	0.828	0.014		
	69.320	8720.87	0.04476	5.632	0.425	7.882	100.00
STD:	0.001	0.09	0.00218	0.275	0.013		
	69.231	8709.69	0.04205	5.290	0.144	2.501	100.00
STD:	0.002	0.25	0.00702	0.884	0.013		
	69.142	8698.42	0.05493	6.911	1.268	28.862	100.00
STD:	0.000	0.03	0.00083	0.104	0.011		

Figure S57. $^{13}C\{^1H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

Table S7. Tetrad intensities derived from the $^1H\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra.

	P_{rmr}	$P_{rmm/mmr}$	δ = 5.19 ppm	$P_{mmr/rmm}$	P_{mmm}	P_{mrm}	P_{rrr}	P_{rrm}	P_{mrm}
Area from deconvolution (^{1}H or $^{13}C\{^1H\}$ NMR)	3.182 [a]	6.840 [a]	0.000 [a]	6.147 [a]	15.183 [a]	8.574 [a]	1.624 [b]	2.963 [b]	7.882 [b]
Intensity in ^{1}H NMR (normalized) and relative intensity in $^{13}C\{^1H\}$ NMR (by equating P_{mrm} values from ^{1}H and $^{13}C\{^1H\}$ NMR)	0.0797	0.1713	0.000	0.1540	0.3803	0.2147	0.0442	0.0807	0.2147
Relative intensities (normalized)	0.07085074	0.1522802	0	0.13690106	0.3380745	0.19086141	0.03929238	0.07173971	
P_m					0.5053	0.5705			

[a] from ^{1}H NMR. [b] from $^{13}C\{^1H\}$ NMR.

Average: P_m = 0.5379

2.4.7. Polymerisation of *rac*-lactide with compound 6

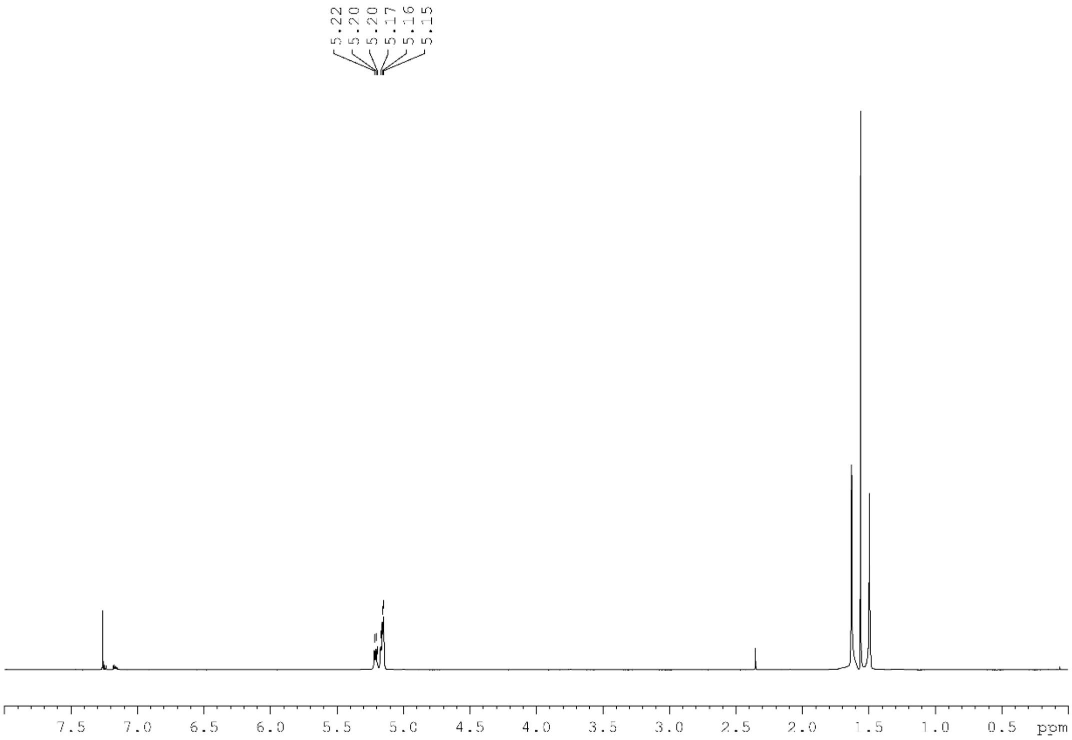

Figure S58. Homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **6**.

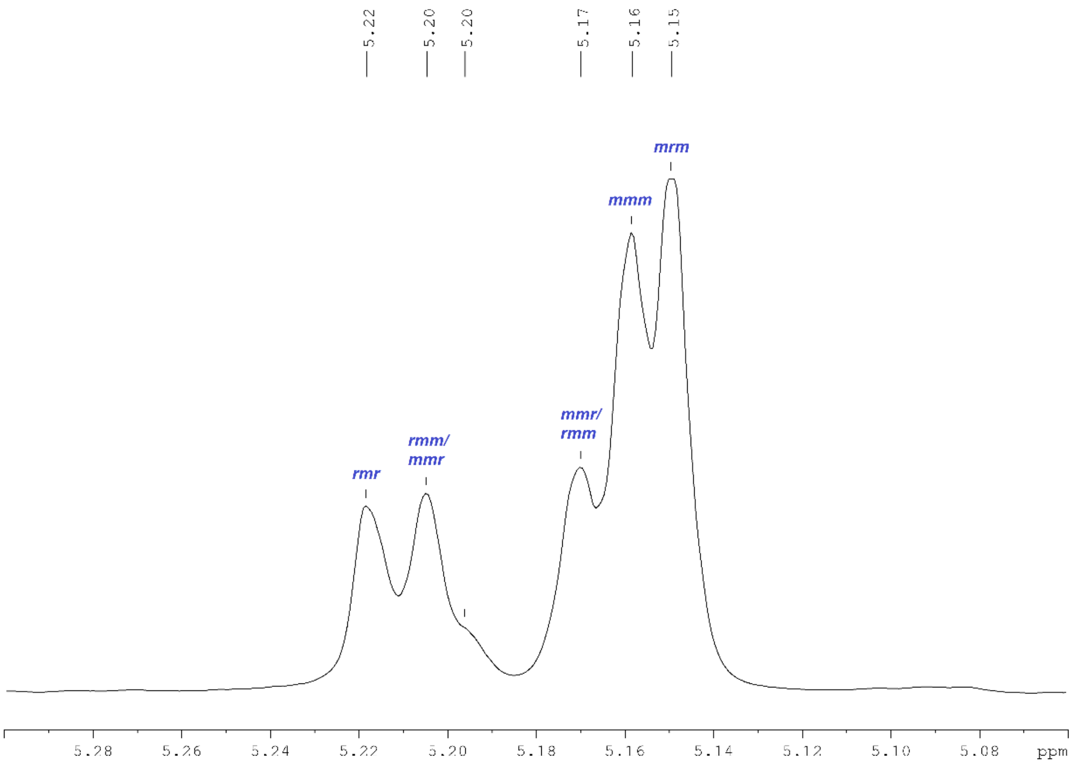

Figure S59. Methine region of the homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **6**.

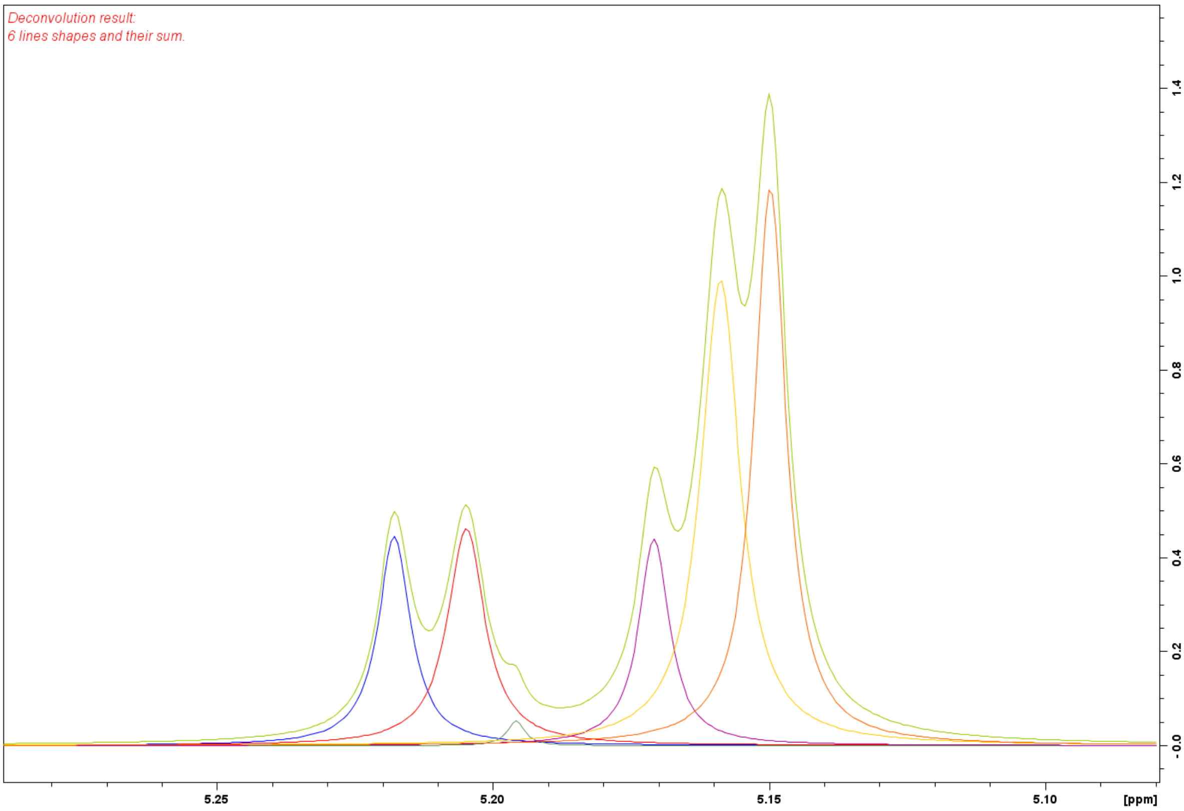

Figure S60. Deconvolution of the homodecoupled $^1H\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **6**.

Fit	Frequency		Width		Intensity	Area	%Lor.
	ppm	Hz	ppm	Hz			chisq
1							1.3e+14
	5.218	2610.71	0.00707	3.535	0.446	8.109	100.00
STD:	0.000	0.07	0.00043	0.216	0.016		
	5.205	2604.20	0.00809	4.047	0.463	9.636	100.00
STD:	0.000	0.07	0.00057	0.283	0.015		
	5.196	2599.43	0.00369	1.844	0.053	0.504	100.00
STD:	0.001	0.39	0.00262	1.312	0.022		
	5.171	2587.28	0.00669	3.346	0.440	7.587	100.00
STD:	0.000	0.07	0.00045	0.226	0.017		
	5.159	2581.30	0.00853	4.270	0.992	21.810	100.00
STD:	0.000	0.04	0.00034	0.169	0.015		
	5.150	2576.45	0.00698	3.491	1.188	21.350	100.00
STD:	0.000	0.03	0.00019	0.096	0.018		

Figure S61. $^1H\{^1H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

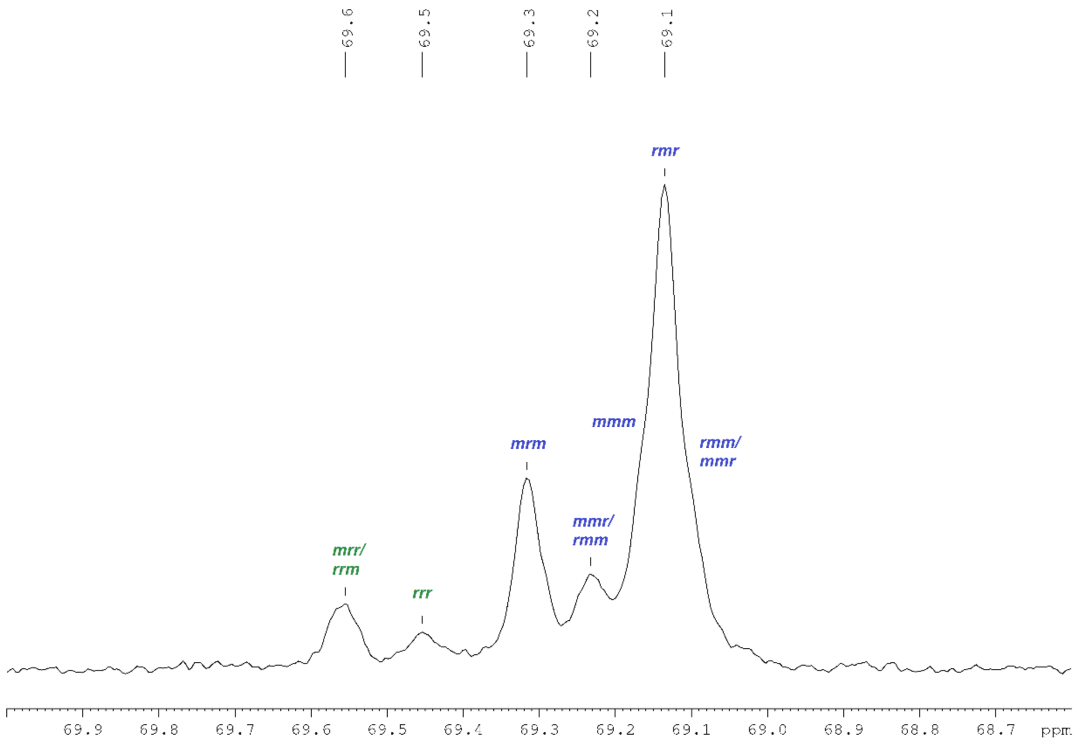

Figure S62. Methine region of the $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **6**.

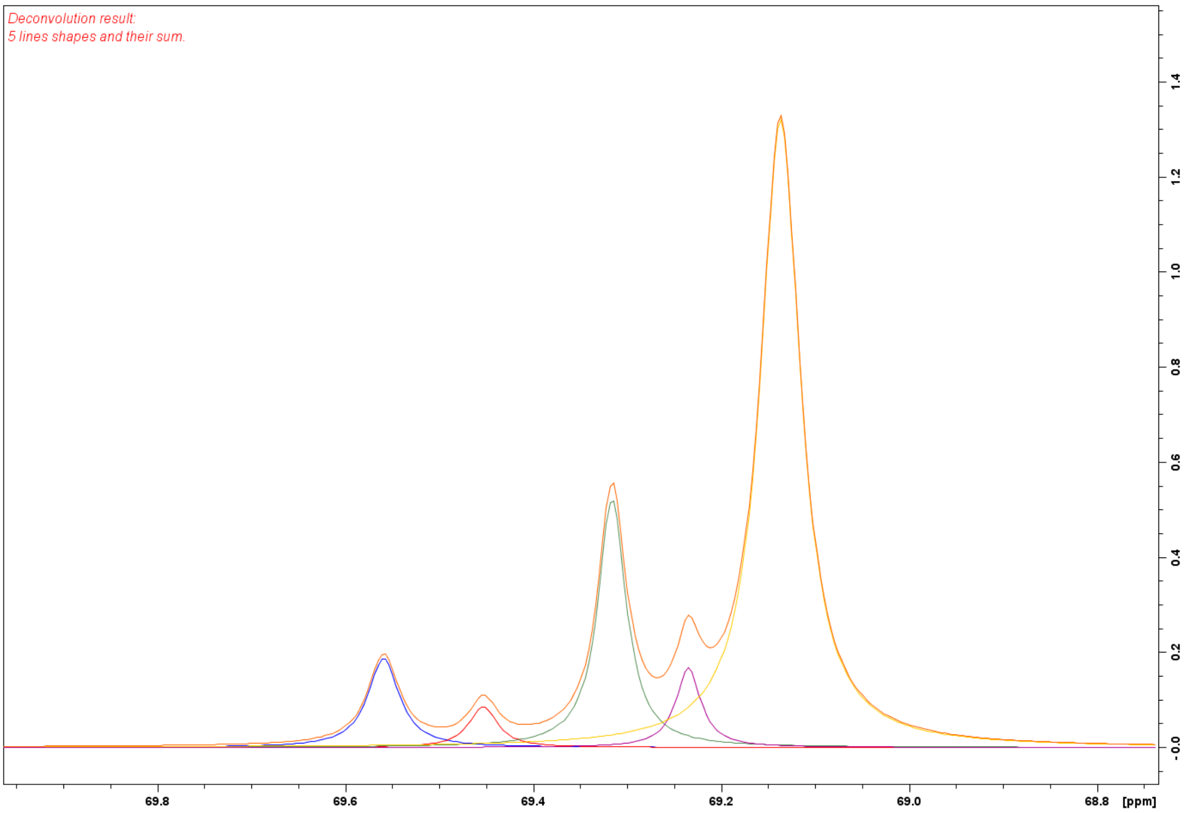

Figure S63. Deconvolution of the methine region of the $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of poly(lactide) obtained from the polymerisation of *rac*-lactide with **6**.

Fit	Frequency		Width		Intensity	Area	%Lor.
	ppm	Hz	ppm	Hz			chisq
1							9.2e+13
	69.560	8751.08	0.04036	5.077	0.187	3.132	100.00
STD:	0.001	0.14	0.00339	0.427	0.010		
	69.454	8737.72	0.03657	4.601	0.086	1.304	100.00
STD:	0.002	0.29	0.00709	0.892	0.011		
	69.317	8720.49	0.03598	4.526	0.523	7.803	100.00
STD:	0.000	0.05	0.00119	0.150	0.011		
	69.236	8710.22	0.03194	4.018	0.168	2.224	100.00
STD:	0.001	0.14	0.00366	0.461	0.012		
	69.138	8697.89	0.05127	6.450	1.321	28.074	100.00
STD:	0.000	0.02	0.00056	0.071	0.009		

Figure S64. $^{13}C\{^{1}H\}$ NMR deconvolution results. Fit type: Mixed Lorentzian and Gaussian.

Table S8. Tetrad intensities derived from the $^{1}H\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra.

	P_{rmr}	$P_{rmm/mmr}$	**δ = 5.19 ppm**	$P_{mmr/rmm}$	P_{mmm}	P_{mrm}	P_{rrr}	P_{rrm}	P_{mrm}
Area from deconvolution (^{1}H or $^{13}C\{^{1}H\}$ NMR)	8.109 [a]	9.636 [a]	0.504 [a]	7.587 [a]	21.810 [a]	21.350 [a]	1.304 [b]	3.132 [b]	7.803 [b]
Intensity in ^{1}H NMR (normalized) and relative intensity in $^{13}C\{^{1}H\}$ NMR (by equating P_{mrm} values from ^{1}H and $^{13}C\{^{1}H\}$ NMR)	0.1175	0.1397	0.0073	0.1100	0.3161	0.3094	0.0517	0.1242	0.3094
Relative intensities (normalized)	0.09992346	0.11880262	0.00620801	0.09354537	0.26881538	0.26311761	0.04396632	0.10562123	
P_m					0.4393	0.3811			

[a] from ^{1}H NMR. [b] from $^{13}C\{^{1}H\}$ NMR.

Average: P_m = 0.4102

3. Kinetic studies

The rate law for a second-order reaction is:

$$-\frac{dc_{LA}}{dt} = k \cdot c_{LA}^2 \cdot c_{cat0}^b = k_{obs} \cdot c_{LA}^2 \tag{3}$$

$$\frac{dc_{LA}}{c_{LA}^2} = -k_{obs} \cdot dt \tag{4}$$

$$\int_0^{c_{LA}} \frac{dc_{LA}}{c_{LA}^2} = \int_0^t -k_{obs}\, dt \tag{5}$$

$$\frac{1}{c_{LA}} = k_{obs} \cdot t \tag{6}$$

with: $k_{obs} = k \cdot c_{cat0}^b$

From the plot of $1/c_{LA}$ and the time, k_{obs} can be calculated.

The polymerisation progress was monitored by ^{1}H NMR spectroscopy using the methine resonances of *rac*-lactide and poly(lactide). HMDSO was used as an internal standard. To calculate the actual polymer and monomer concentrations, the values obtained by relative integration to the HMDSO resonance set to 1 (Tables S9-S14, columns 3 and 5) were multiplied with ($18 \cdot c_{HMDSO}$) (Tables S9-S14, columns 4 and 6).

Table S9. 1 mol%, 25 °C, c_{HMDSO} = 0.007 mol/l.

Time / min	Time / h	c(polymer) with HMDSO resonance set to 1	c(polymer) / mol·l^{-1}	c(monomer) with HMDSO resonance set to 1	c(monomer) / mol·l^{-1}	1/c(monomer) / l·mol^{-1}
0	0	0.0402	0.00507	1.9933	0.25116	3.98159
68	1.13333	0.3323	0.04187	1.7277	0.21769	4.59368
147	2.45	0.491	0.06187	1.5919	0.20058	4.98556
220	3.66667	0.5664	0.07137	1.5137	0.19073	5.24312
298	4.96667	0.6676	0.08412	1.4337	0.18065	5.53568
356	5.93333	0.7138	0.08994	1.4024	0.1767	5.65923
402	6.7	0.7369	0.09285	1.3728	0.17297	5.78126

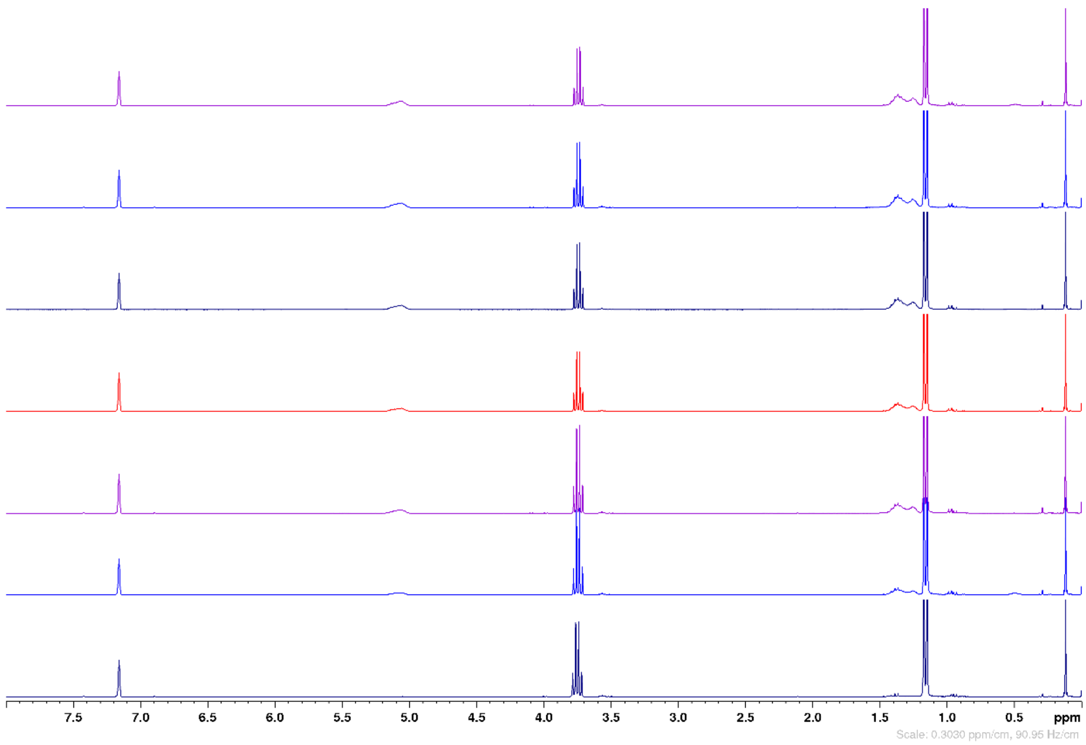

Figure S65. ^{1}H NMR spectra (300 MHz, $CDCl_3$) for the polymerisation of *rac*-lactide with complex **2** (1 mol%) at 25 °C between t = 0 min (bottom spectrum) and t = 402 min (top spectrum).

Table S10. 2 mol%, 25 °C, c_{HMDSO} = 0.062 mol/l.

Time / min	Time / h	c(polymer) with HMDSO resonance set to 1	c(polymer) / mol·l^{-1}	c(monomer) with HMDSO resonance set to 1	c(monomer) / mol·l^{-1}	1/c(monomer) / l·mol^{-1}
16	0.26667	0.3021	0.03371	2.066	0.23057	4.33716
41	0.68333	0.8003	0.08931	1.6479	0.18391	5.43757
93	1.55	1.4673	0.16375	1.0629	0.11862	8.43031
151	2.51667	1.8368	0.20499	0.7632	0.08517	11.74079
199	3.31667	2.1548	0.24048	0.4853	0.05416	18.46399
289	4.81667	2.2938	0.25599	0.3704	0.04134	24.19161
353	5.88333	2.3403	0.26118	0.3137	0.03501	28.56415
409	6.81667	2.3839	0.26604	0.2827	0.03155	31.6964
465	7.75	2.4146	0.26947	0.2569	0.02867	34.87962

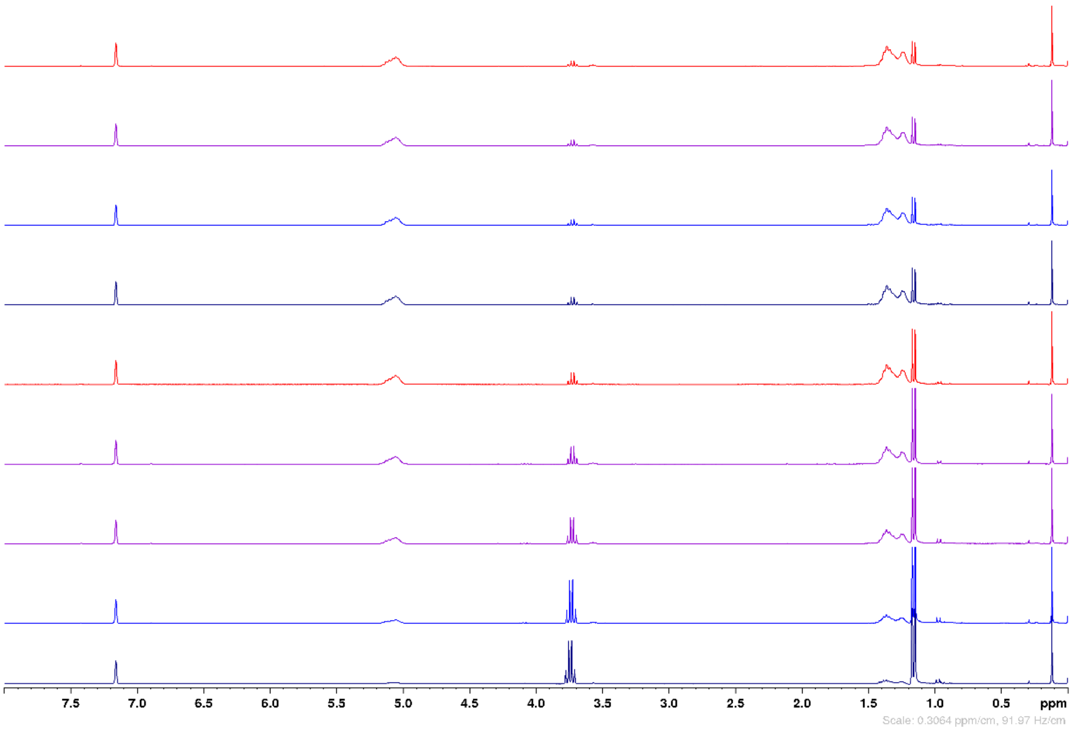

Figure S66. ^{1}H NMR spectra (300 MHz, $CDCl_3$) for the polymerisation of *rac*-lactide with complex **2** (2 mol%) at 25 °C between t = 16 min (bottom spectrum) and t = 465 min (top spectrum).

Table S11. 4 mol%, 25 °C, c_{HMDSO} = 0.047 mol/l.

Time / min	Time / h	c(polymer) with HMDSO resonance set to 1	c(polymer) / mol·l^{-1}	c(monomer) with HMDSO resonance set to 1	c(monomer) / mol·l^{-1}	1/c(monomer) / l·mol^{-1}
26	0.43333	0.97	0.08206	2.3436	0.19827	5.04366
47	0.78333	1.739	0.14712	1.699	0.14374	6.95723
102	1.7	2.5784	0.21813	1.0213	0.0864	11.57381
160	2.66667	2.9678	0.25108	0.6924	0.05858	17.07154
208	3.46667	3.2801	0.2775	0.4033	0.03412	29.30903
298	4.96667	3.3788	0.28585	0.2612	0.0221	45.25395
362	6.03333	3.4054	0.2881	0.2406	0.02035	49.12856
418	6.96667	3.3966	0.28735	0.2088	0.01766	56.61078
474	7.9	3.4587	0.29261	0.1857	0.01571	63.65283

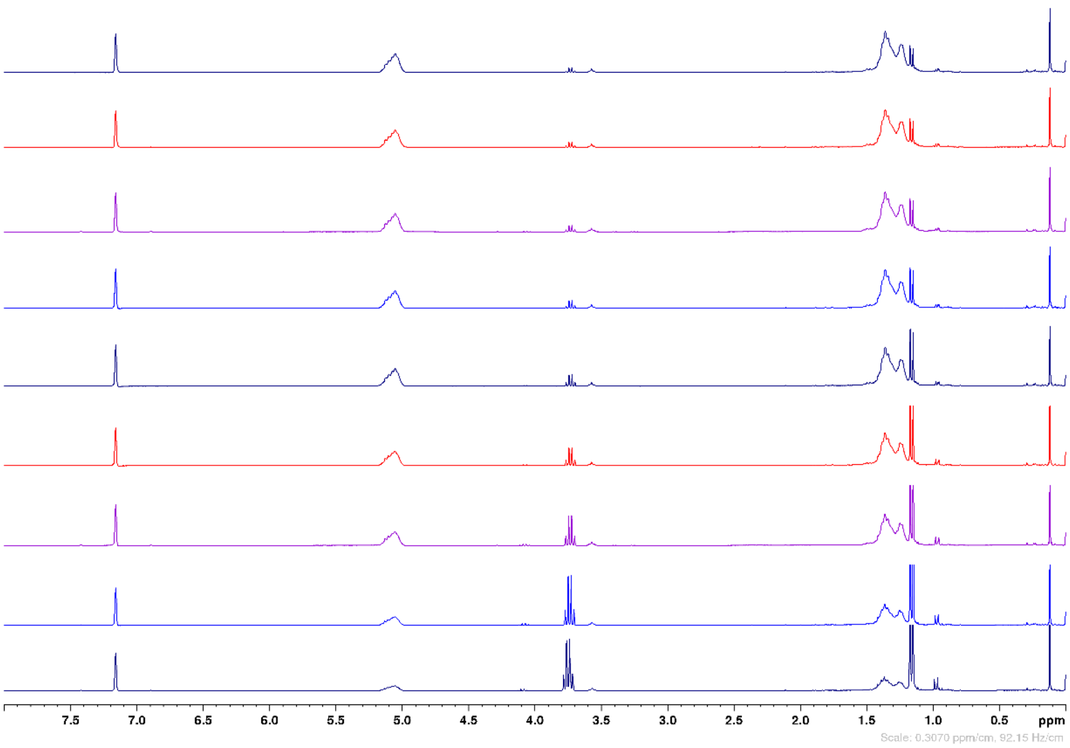

Figure S67. ^{1}H NMR spectra (300 MHz, $CDCl_3$) for the polymerisation of *rac*-lactide with complex **2** (4 mol%) at 25 °C between t = 26 min (bottom spectrum) and t = 474 min (top spectrum).

Table S12. 6 mol%, 25 °C, c_{HMDSO} = 0.007 mol/l.

Time / min	Time / h	c(polymer) with HMDSO resonance set to 1	c(polymer) / mol·l^{-1}	c(monomer) with HMDSO resonance set to 1	c(monomer) / mol·l^{-1}	1/c(monomer) / l·mol^{-1}
15	0.25	0.3696	0.04657	1.3553	0.17077	5.8559
87	1.45	1.4027	0.17674	0.525	0.06615	15.11716
207	3.45	1.8091	0.22795	0.2215	0.02791	35.83074
244	4.06667	1.6017	0.20181	0.1409	0.01775	56.32724
290	4.83333	1.69	0.21294	0.1378	0.01736	57.5944
371	6.18333	1.7753	0.22369	0.1011	0.01274	78.50156
429	7.15	1.8004	0.22685	0.0878	0.01106	90.39303
537	8.95	1.7863	0.22507	0.0615	0.00775	129.04891

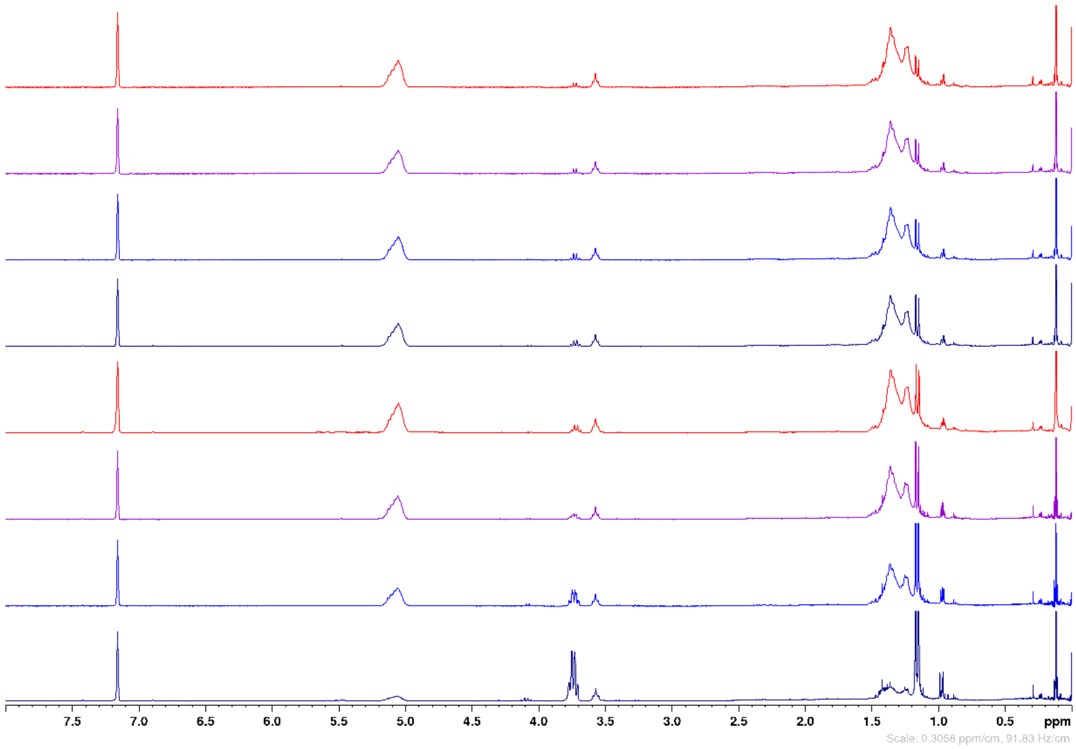

Figure S68. ^{1}H NMR spectra (300 MHz, $CDCl_3$) for the polymerisation of *rac*-lactide with complex **2** (6 mol%) at 25 °C between t = 15 min (bottom spectrum) and t = 537 min (top spectrum).

Table S13. 2 mol%, 40 °C, c_{HMDSO} = 0.0062 mol/l.

Time / min	Time / h	c(polymer) with HMDSO resonance set to 1	c(polymer) / mol·l^{-1}	c(monomer) with HMDSO resonance set to 1	c(monomer) / mol·l^{-1}	1/c(monomer) / l·mol^{-1}
19	0.31667	0.4234	0.04725	2.0959	0.2339	4.27529
131	2.18333	2.2001	0.24553	0.4998	0.05578	17.92832
192	3.2	2.4163	0.26966	0.317	0.03538	28.26679
297	4.95	2.5157	0.28075	0.191	0.02132	46.914
387	6.45	2.5648	0.28623	0.1534	0.01712	58.41313
441	7.35	2.5714	0.28697	0.1387	0.01548	64.60399

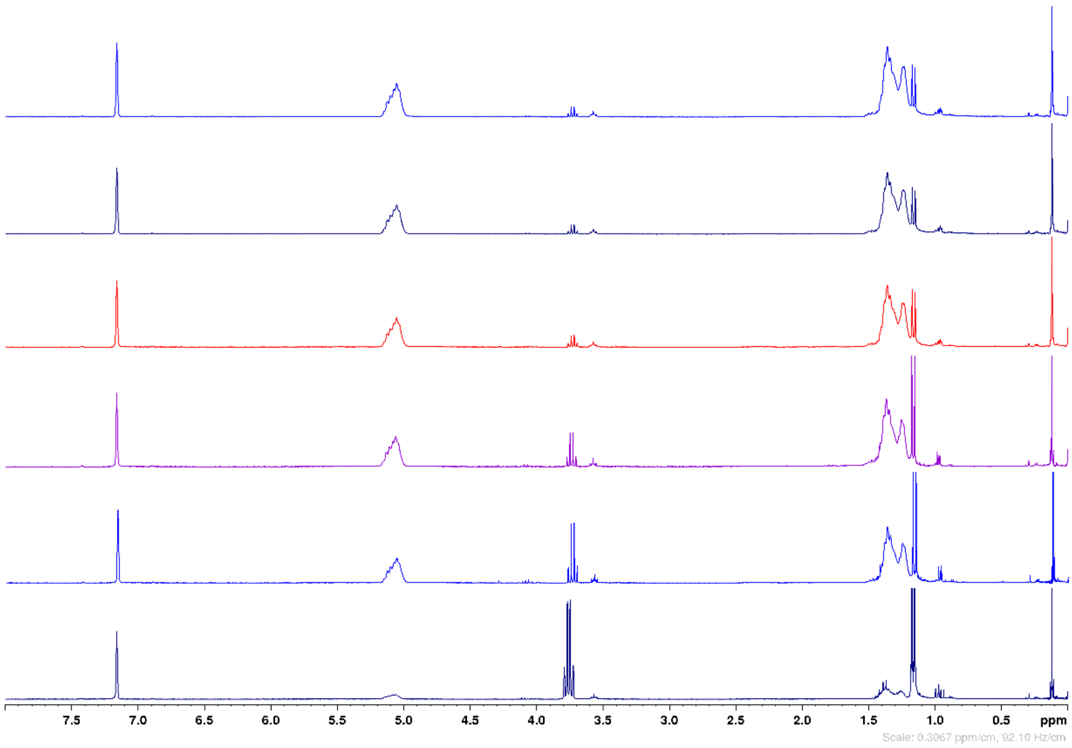

Figure S69. ^{1}H NMR spectra (300 MHz, $CDCl_3$) for the polymerisation of *rac*-lactide with complex **2** (2 mol%) at 40 °C between t = 19 min (bottom spectrum) and t = 441 min (top spectrum).

Table S14. 2 mol%, 60 °C, c_{HMDSO} = 0.0062 mol/l.

Time / min	Time / h	c(polymer) with HMDSO resonance set to 1	c(polymer) / mol·l⁻¹	c(monomer) with HMDSO resonance set to 1	c(monomer) / mol·l⁻¹	1/c(monomer) / l·mol⁻¹
24	0.4	0.5678	0.06337	1.7054	0.19032	5.25424
106	1.76667	2.0996	0.23432	0.4288	0.04785	20.89686
198	3.3	2.3161	0.25848	0.2472	0.02759	36.24827
306	5.1	2.3531	0.26261	0.1954	0.02181	45.85759
395	6.58333	2.3876	0.26646	0.1742	0.01944	51.43842
450	7.5	2.2762	0.25402	0.1556	0.01736	57.58723

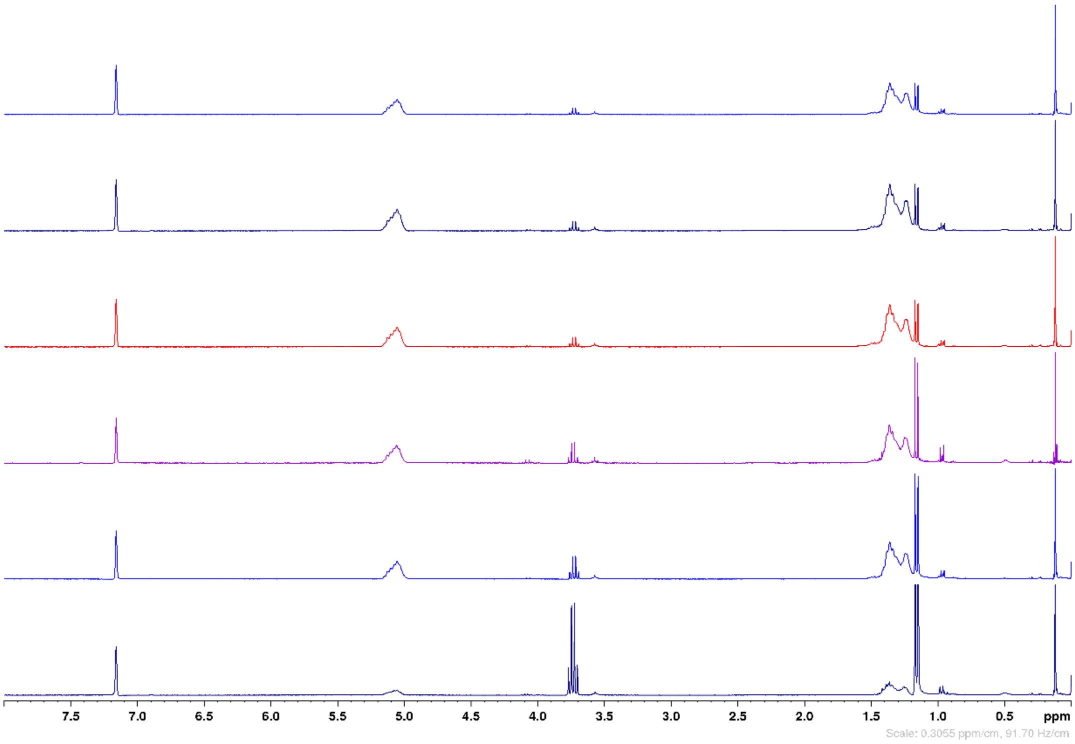

Figure S70. ¹H NMR spectra (300 MHz, $CDCl_3$) for the polymerisation of *rac*-lactide with complex **2** (2 mol%) at 60 °C between t = 24 min (bottom spectrum) and t = 450 min (top spectrum).

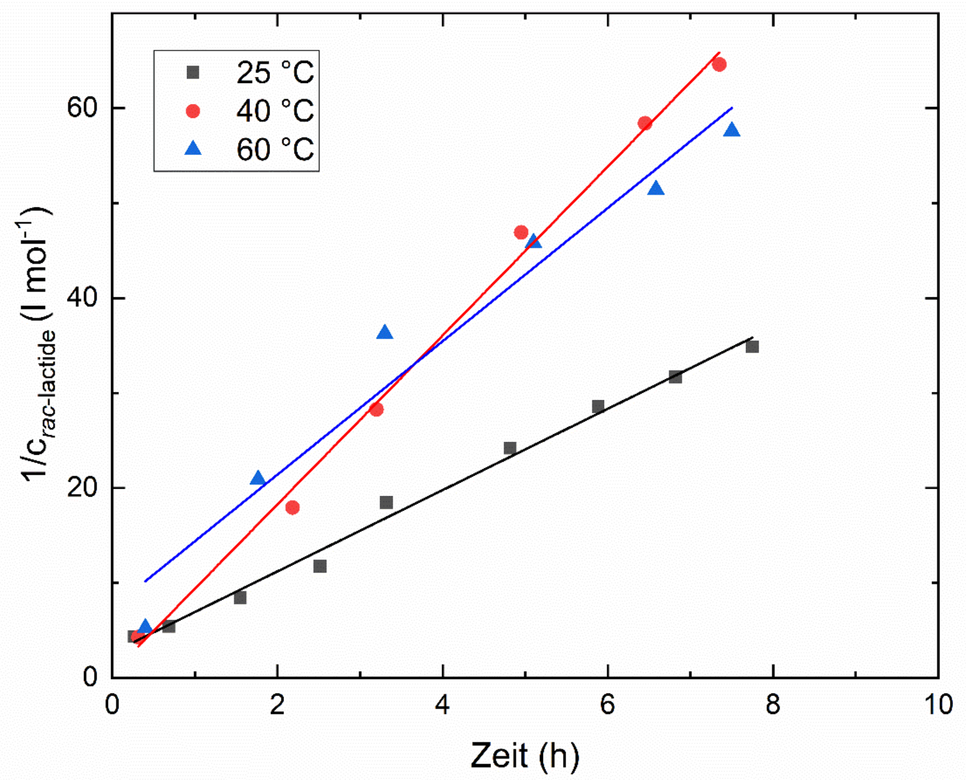

Figure S71. 2 mol% at 25 °C (k_{obs} = (4.2828 ± 0.14563) l·mol^{-1}·h^{-1}), 40 °C (k_{obs} = (8.89423 ± 0.30181) (l·mol^{-1}·h^{-1})) and 60 °C (k_{obs} = (7.02277 ± 0.70192) (l·mol^{-1}·h^{-1})).

4. Gel permeation chromatography

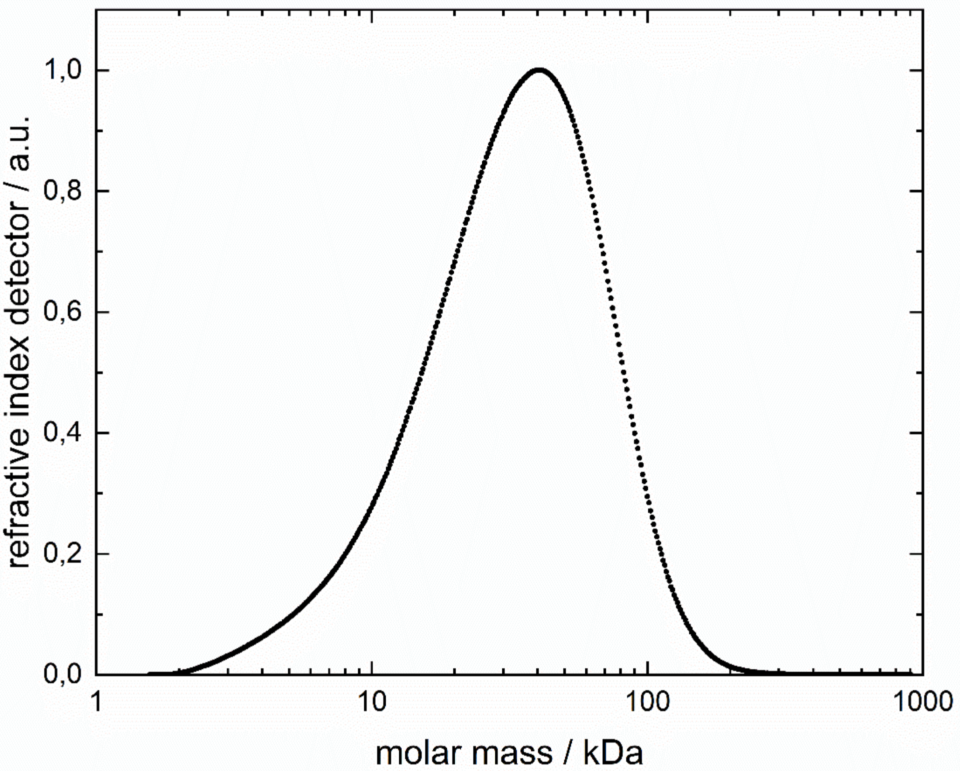

Figure S72. Elugram of poly(lactide) obtained from the polymerisation of *rac*-lactide with complex **2** at 50 °C.

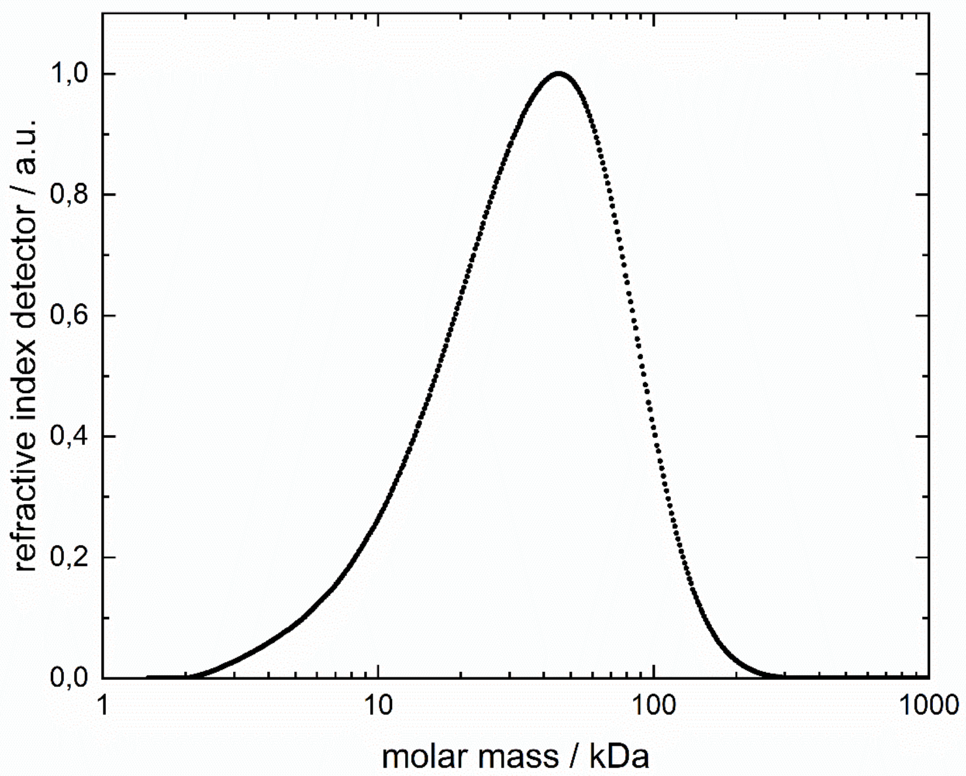

Figure S73. Elugram of poly(lactide) obtained from the polymerisation of *rac*-lactide with complex **2** at 30 °C.

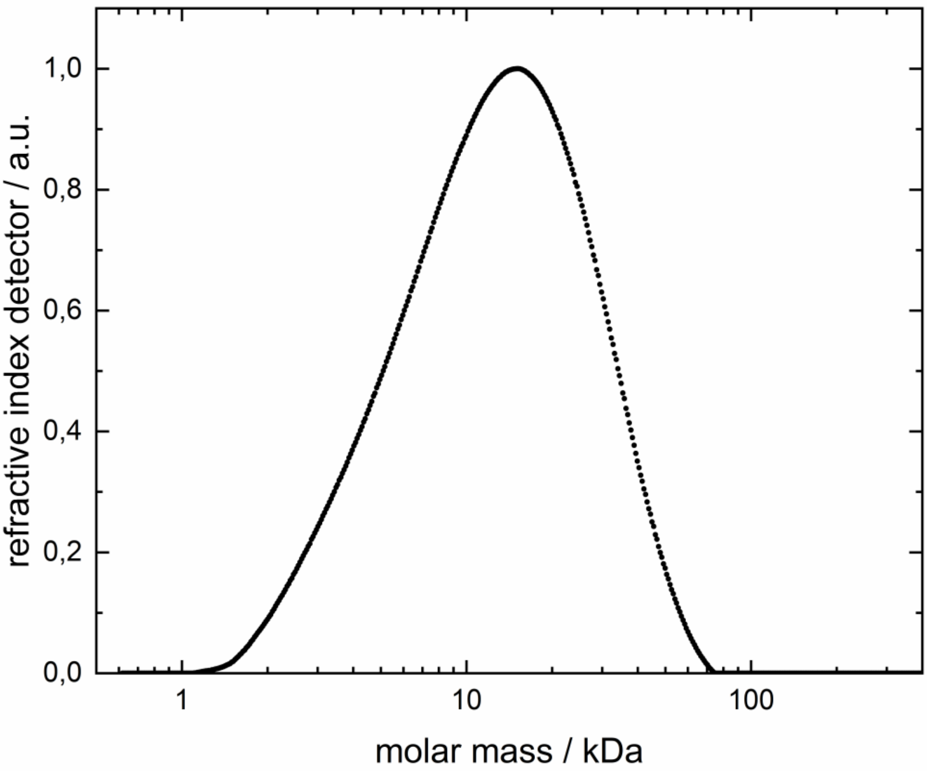

Figure S74. Elugram of poly(lactide) obtained from the polymerisation of *rac*-lactide with complex **3**.

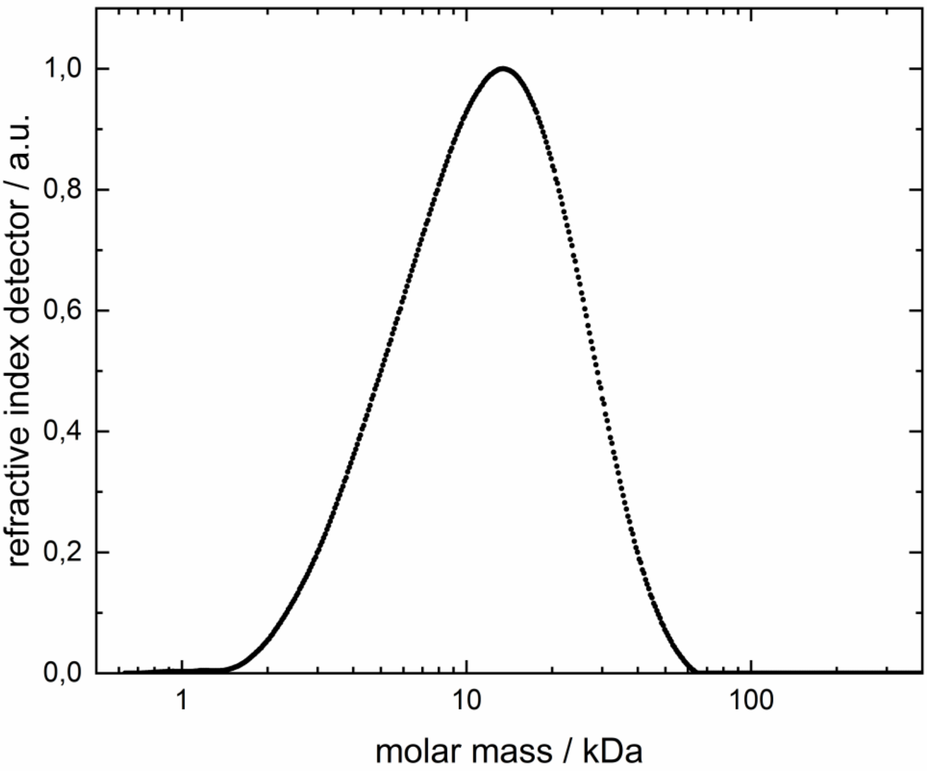

Figure S75. Elugram of poly(lactide) obtained from the polymerisation of *rac*-lactide with complex **4**.

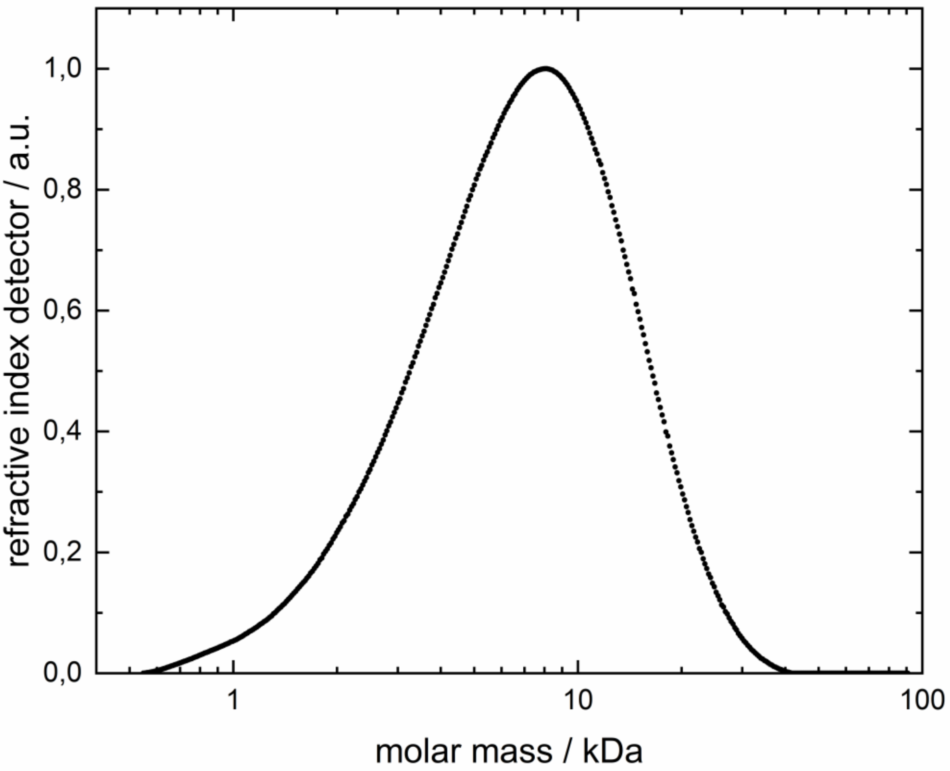

Figure S76. Elugram of poly(lactide) obtained from the polymerisation of *rac*-lactide with complex **5**.

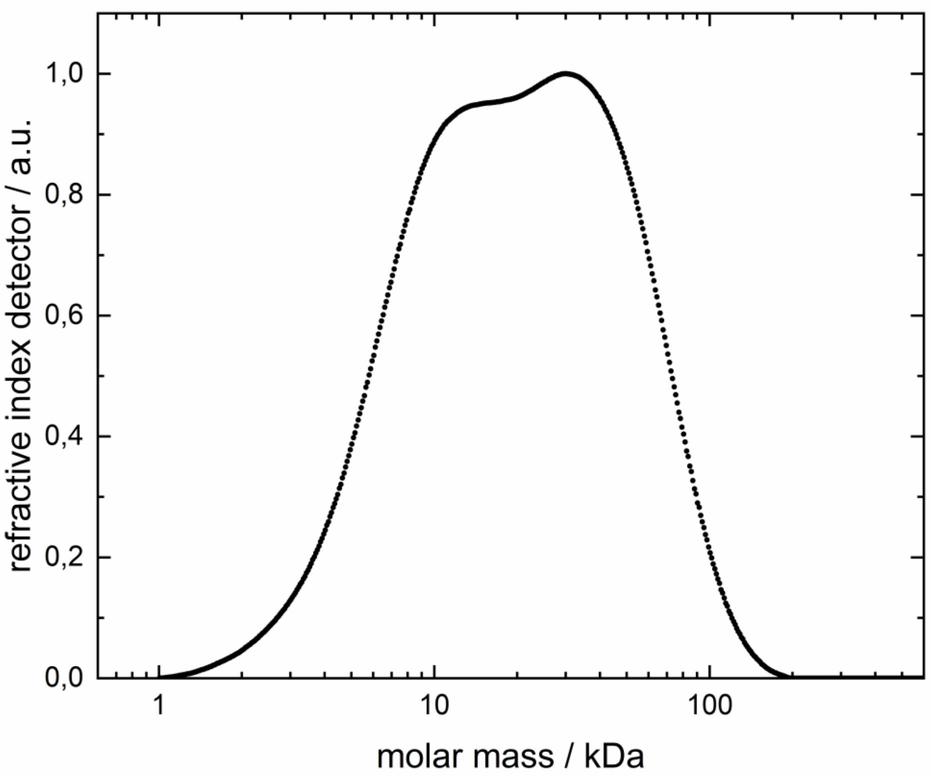

Figure S77. Elugram of poly(lactide) obtained from the polymerisation of *rac*-lactide with complex **6**.

5. Differential scanning calorimetry

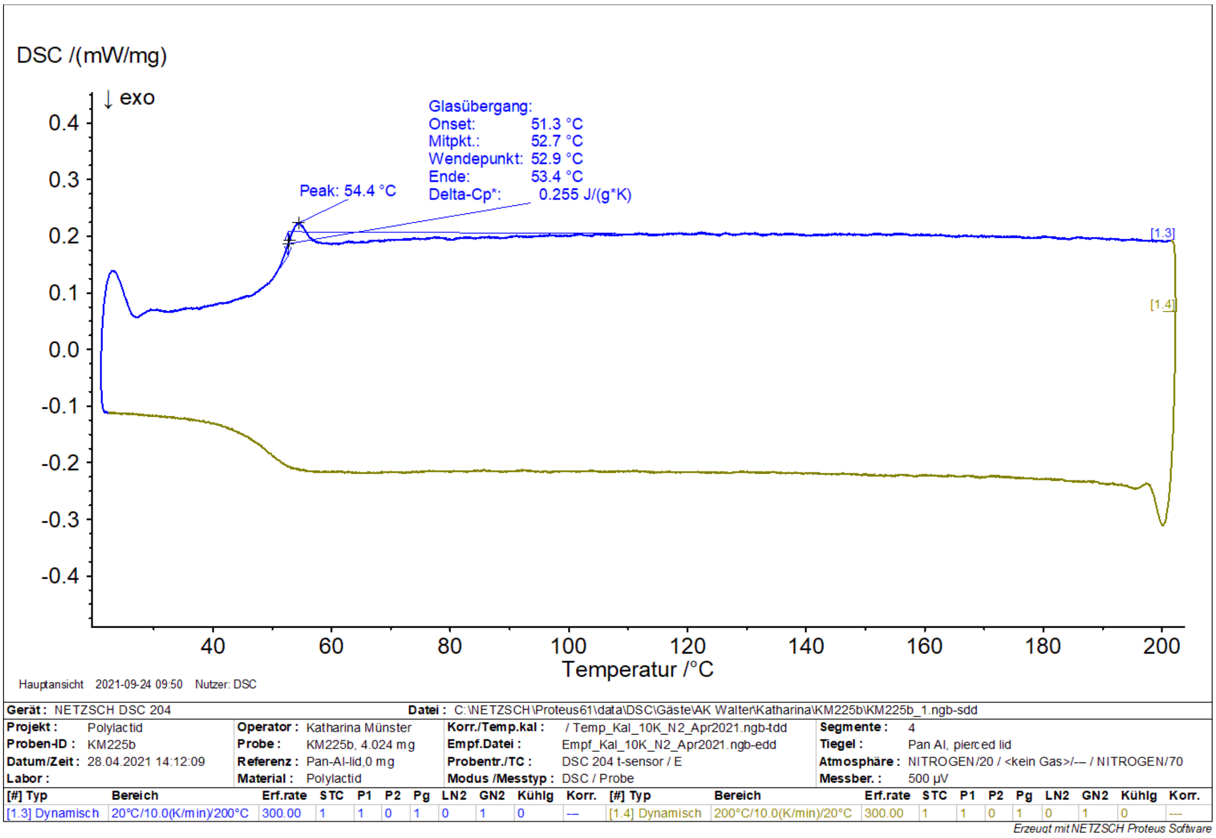

Figure S78. DSC thermogram of poly(lactide) obtained from the polymerisation of *rac*-lactide by complex **2** at 50 °C.

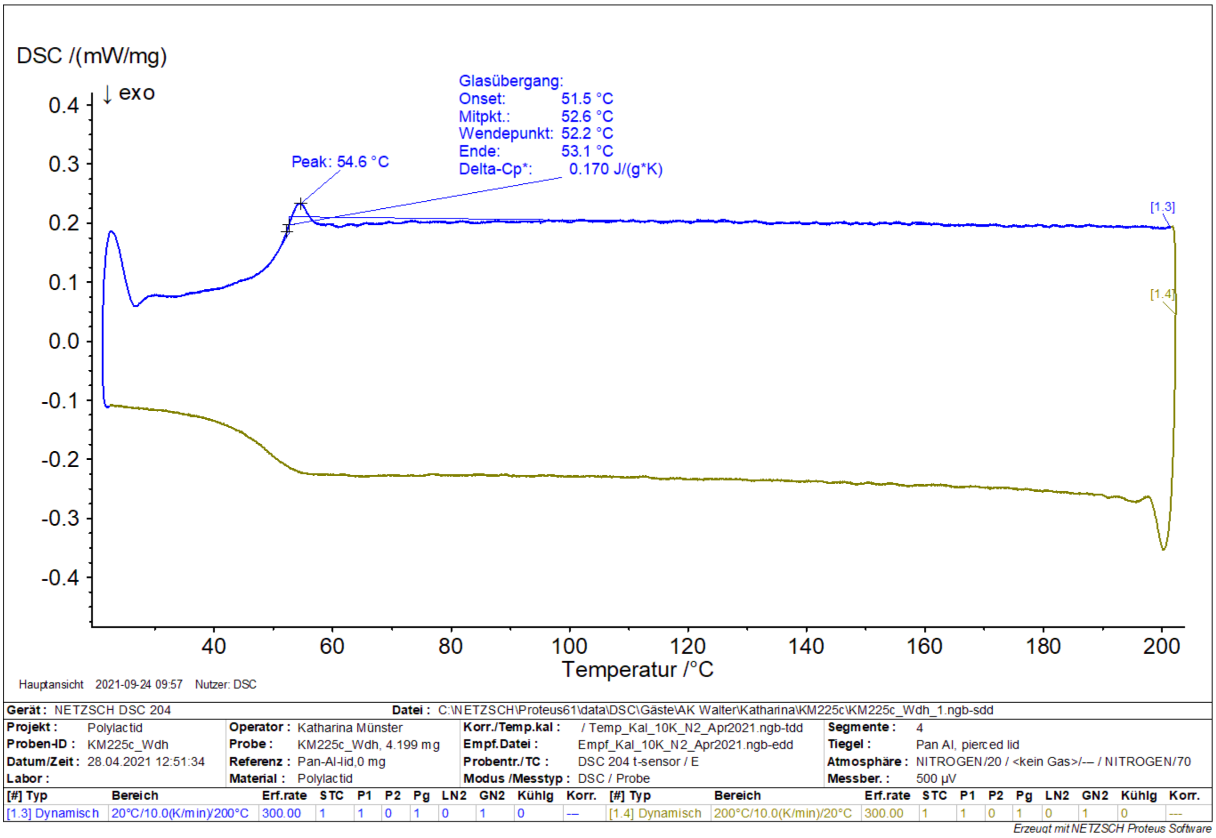

Figure S79. DSC thermogram of poly(lactide) obtained from the polymerisation of *rac*-lactide by complex **2** at 30 °C.

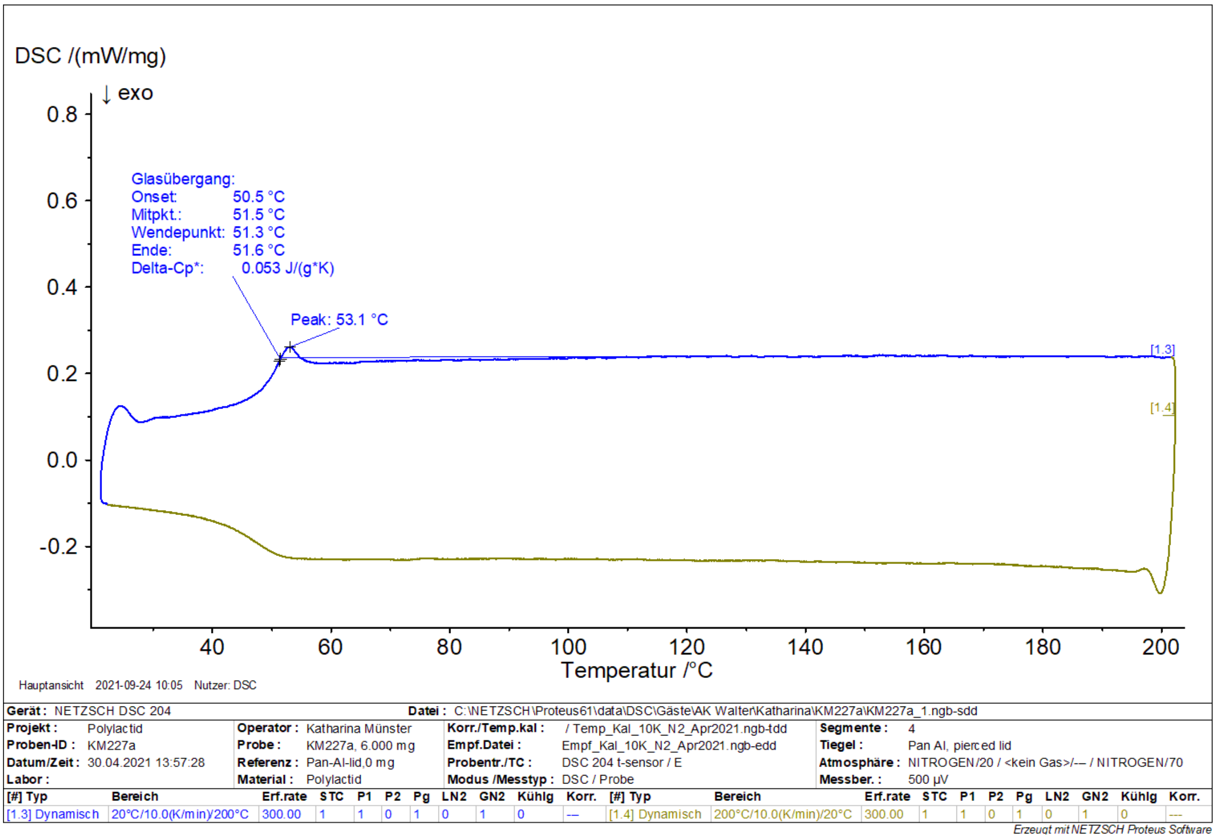

Figure S80. DSC thermogram of poly(lactide) obtained from the polymerisation of *rac*-lactide by complex **3**.

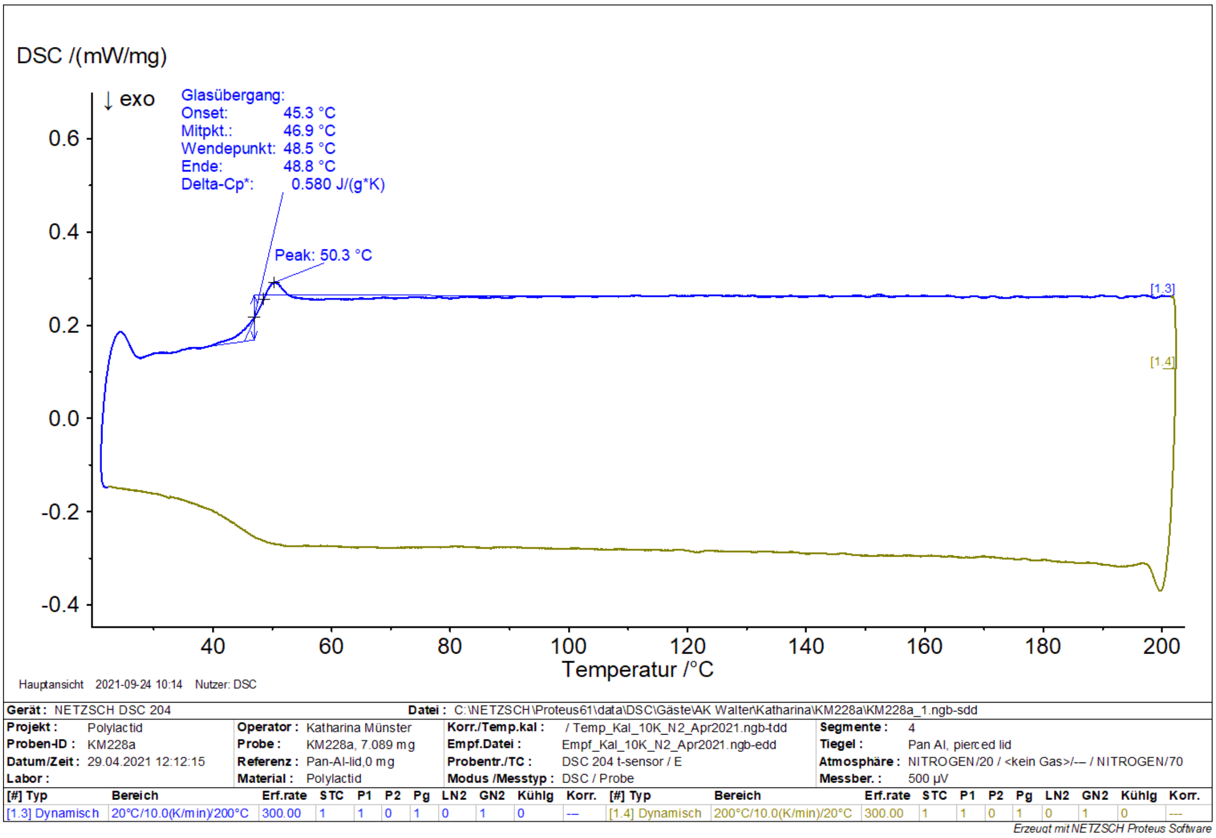

Figure S81. DSC thermogram of poly(lactide) obtained from the polymerisation of *rac*-lactide by complex **4**.

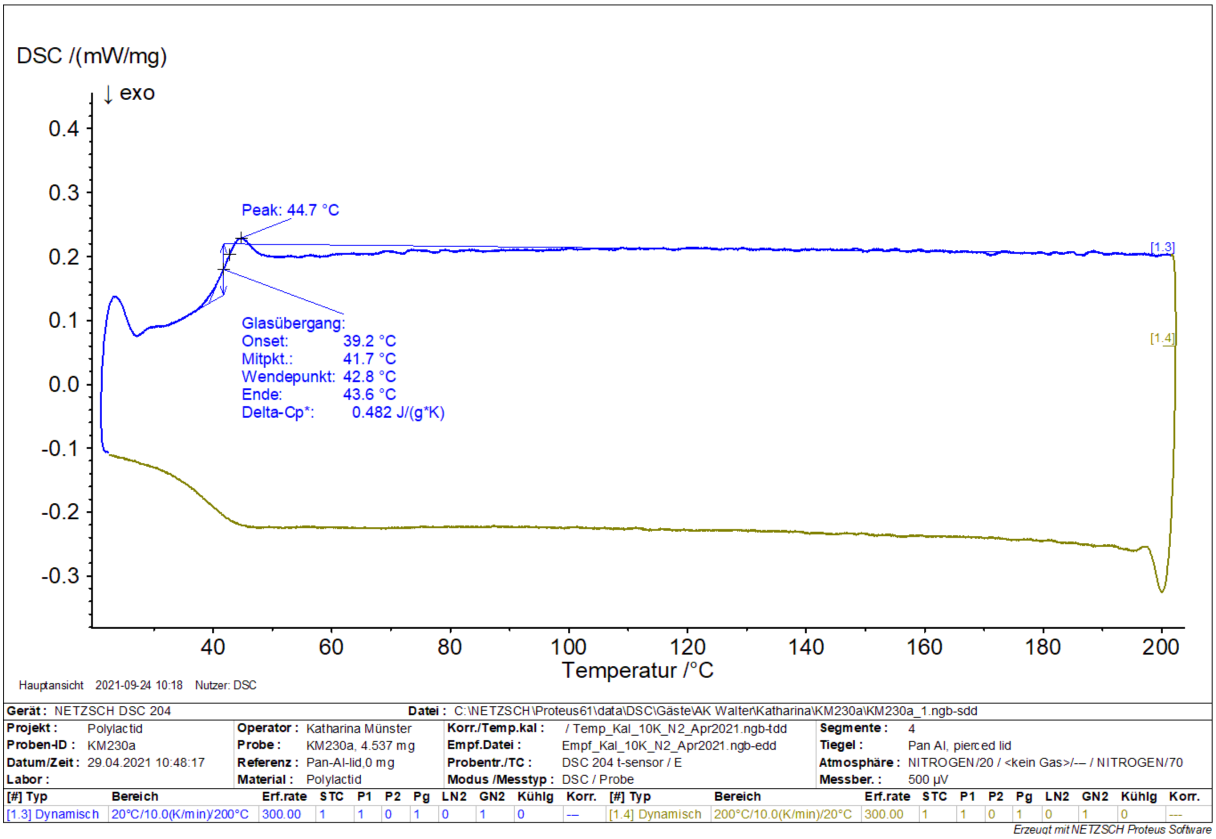

Figure S82. DSC thermogram of poly(lactide) obtained from the polymerisation of *rac*-lactide by complex **5**.

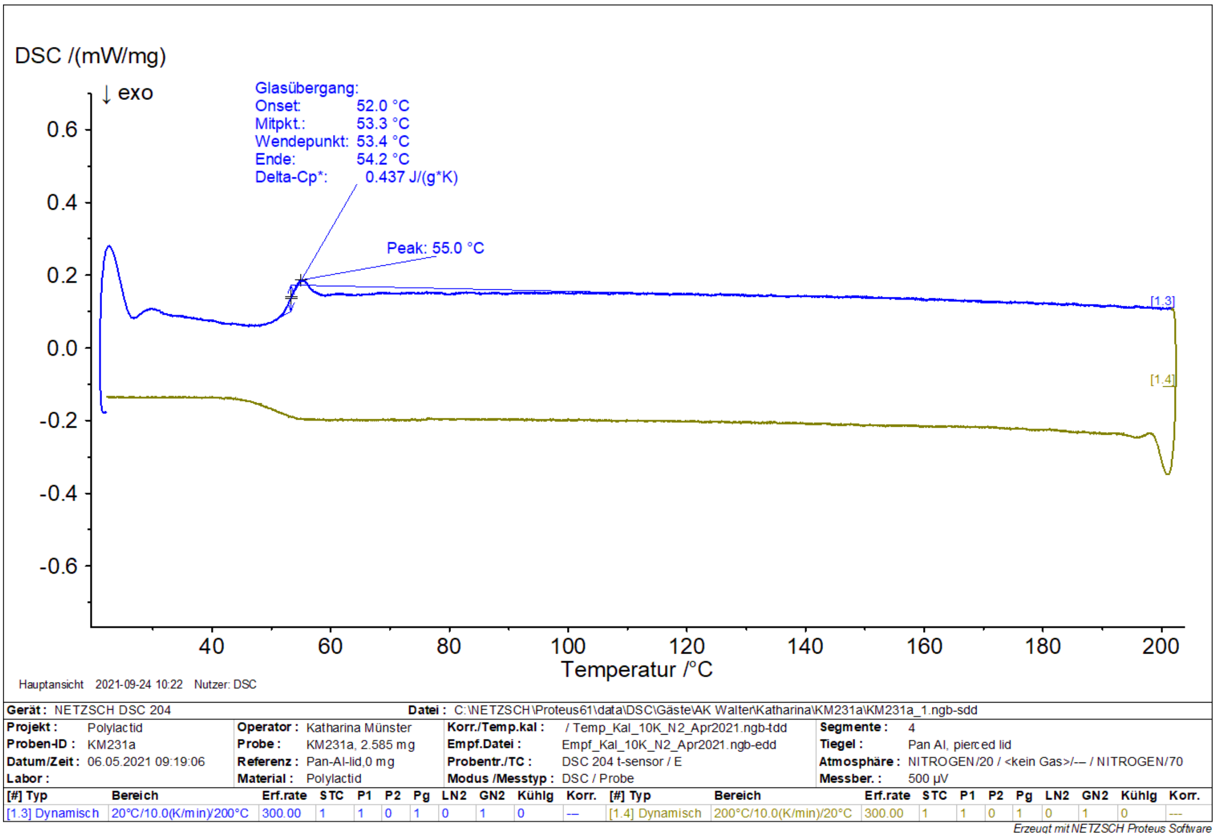

Figure S83. DSC thermogram of poly(lactide) obtained from the polymerisation of *rac*-lactide by complex **6**.

6. References

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