ELECTRONIC SUPPORTING INFORMATION

Synthesis of an Enantiopure Scorpionate Ligand by a Nucleophilic Addition to a Ketenimine and a Zinc Initiator for the Isoselective ROP of *rac*-Lactide.

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4) EXPERIMENTAL SECTION:

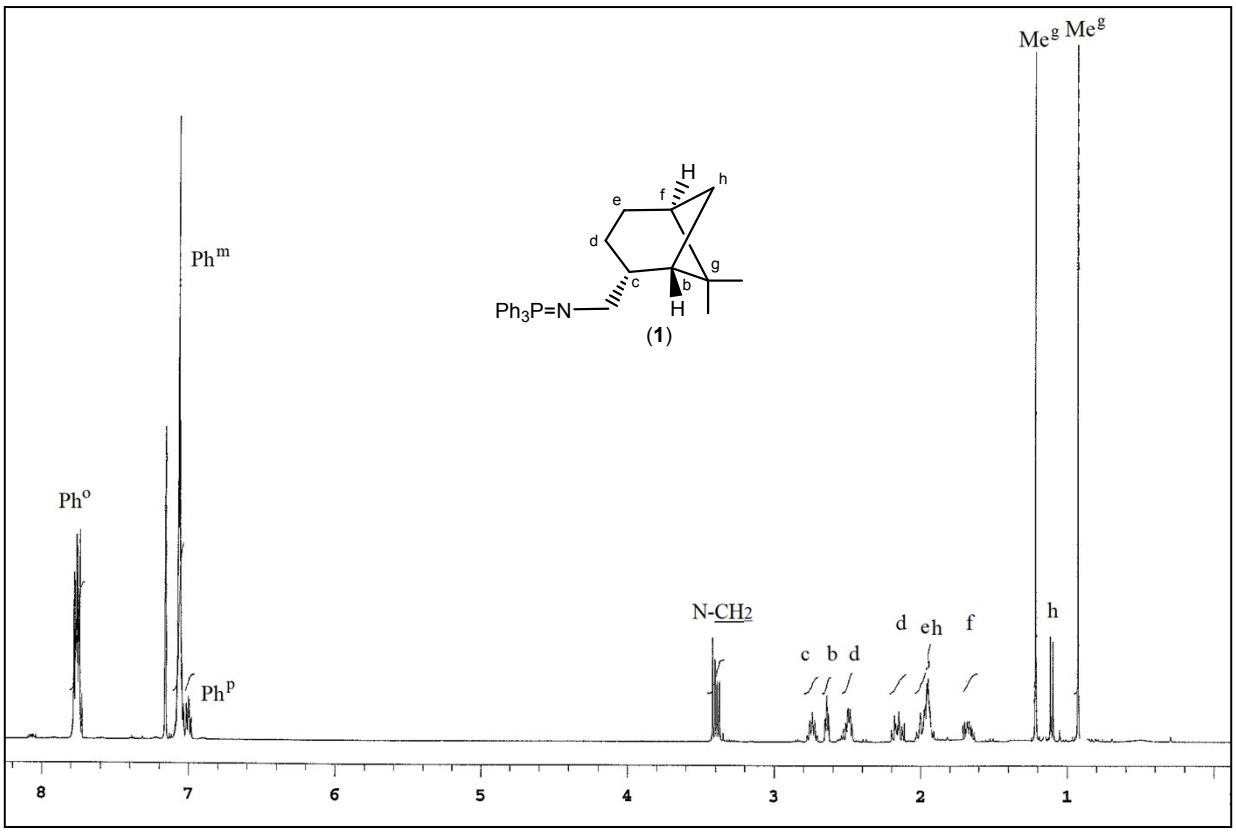


Figure S1a. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **1**.

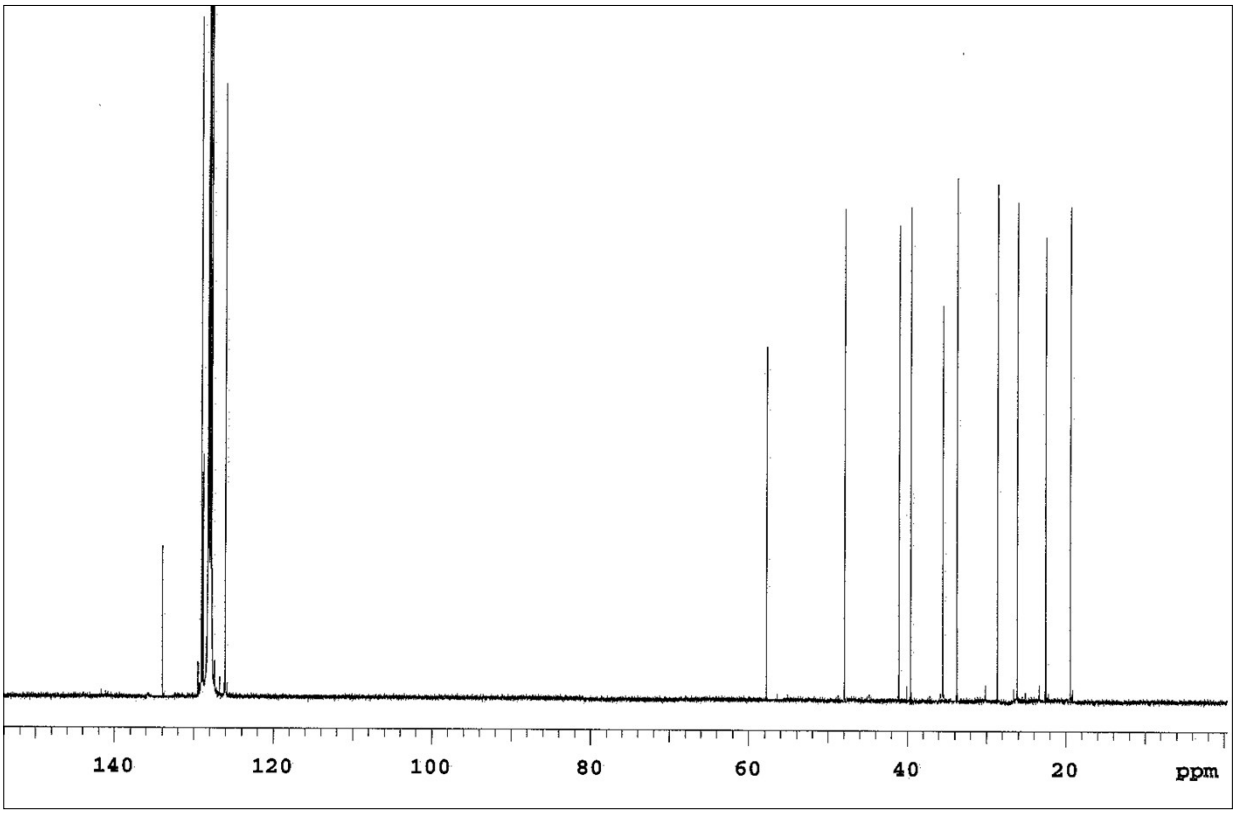


Figure S1b. ^{13}C-{^{1}H} NMR (125 MHz, 298 K, C_6D_6) spectrum of compound **1**.

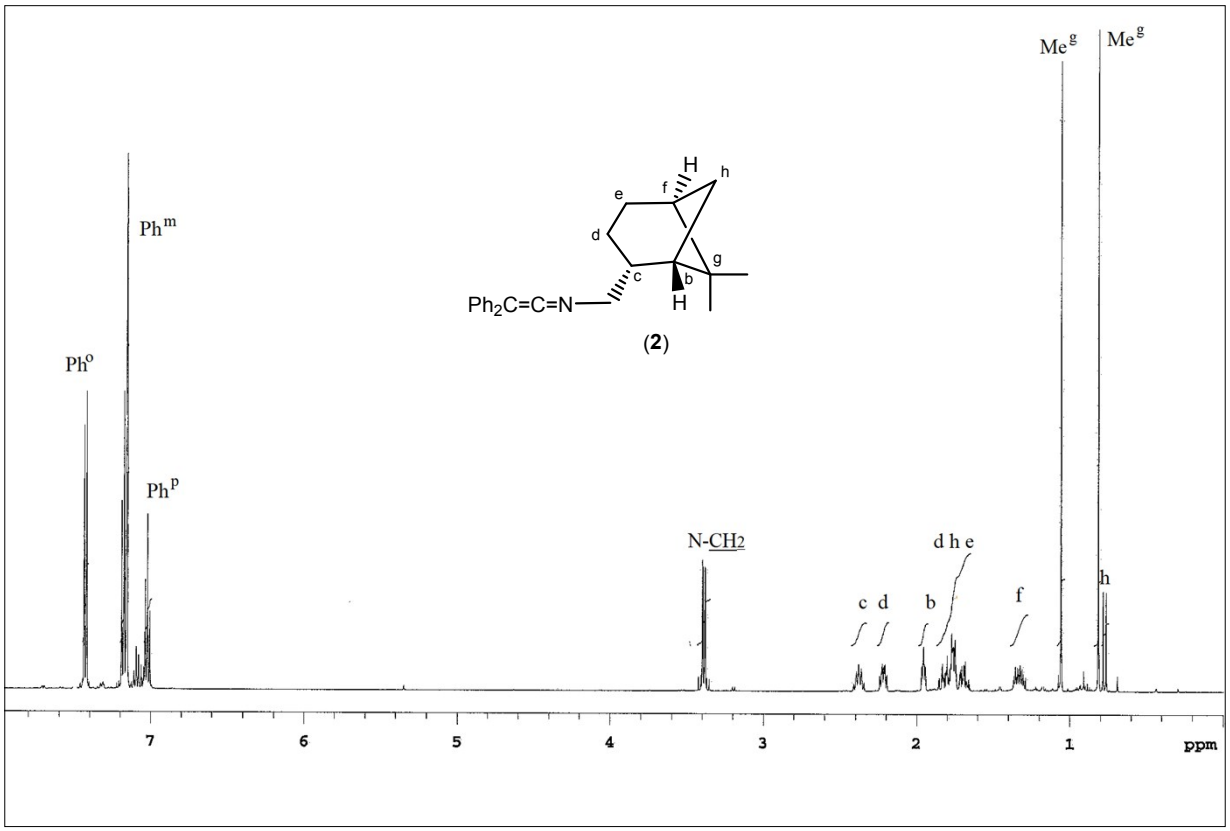


Figure S2a. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **2**.

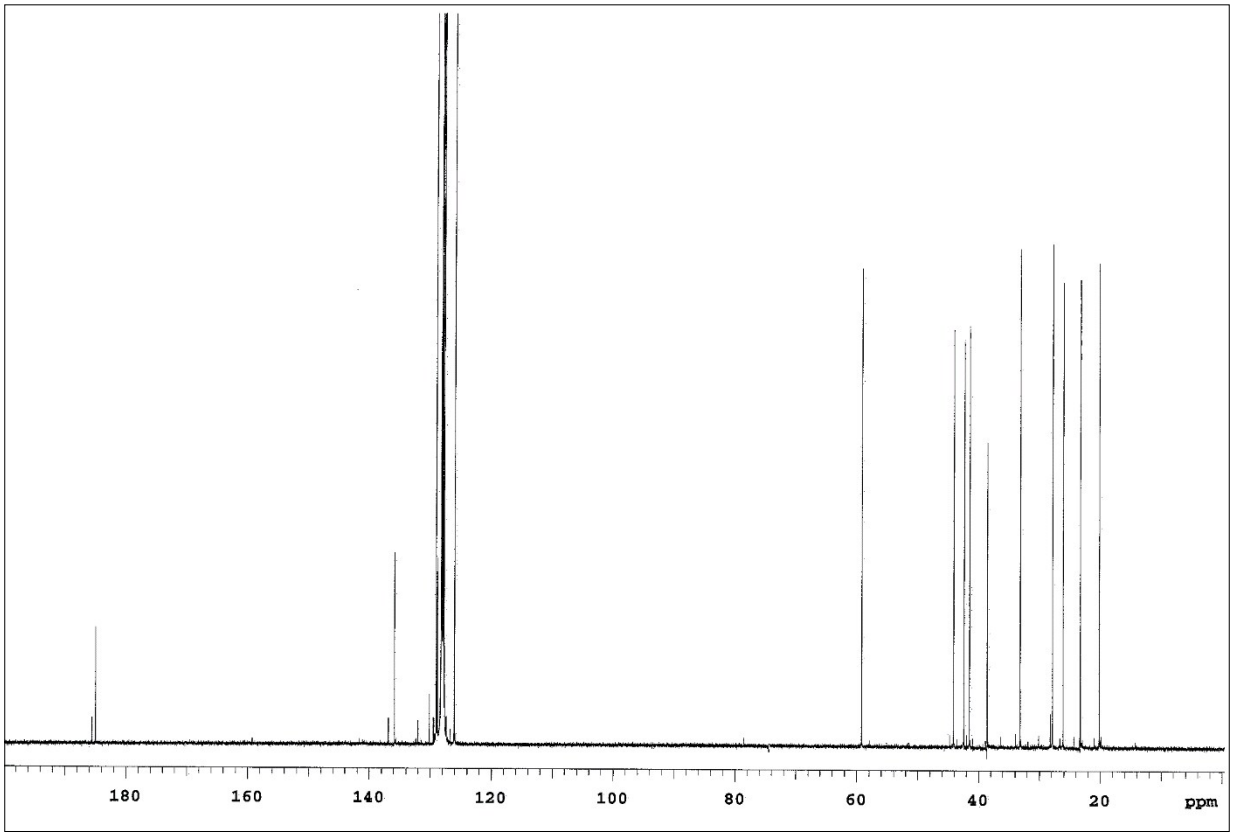


Figure S2b. ^{13}C-{^{1}H} NMR (125 MHz, 298 K, C_6D_6) spectrum of compound **2**.

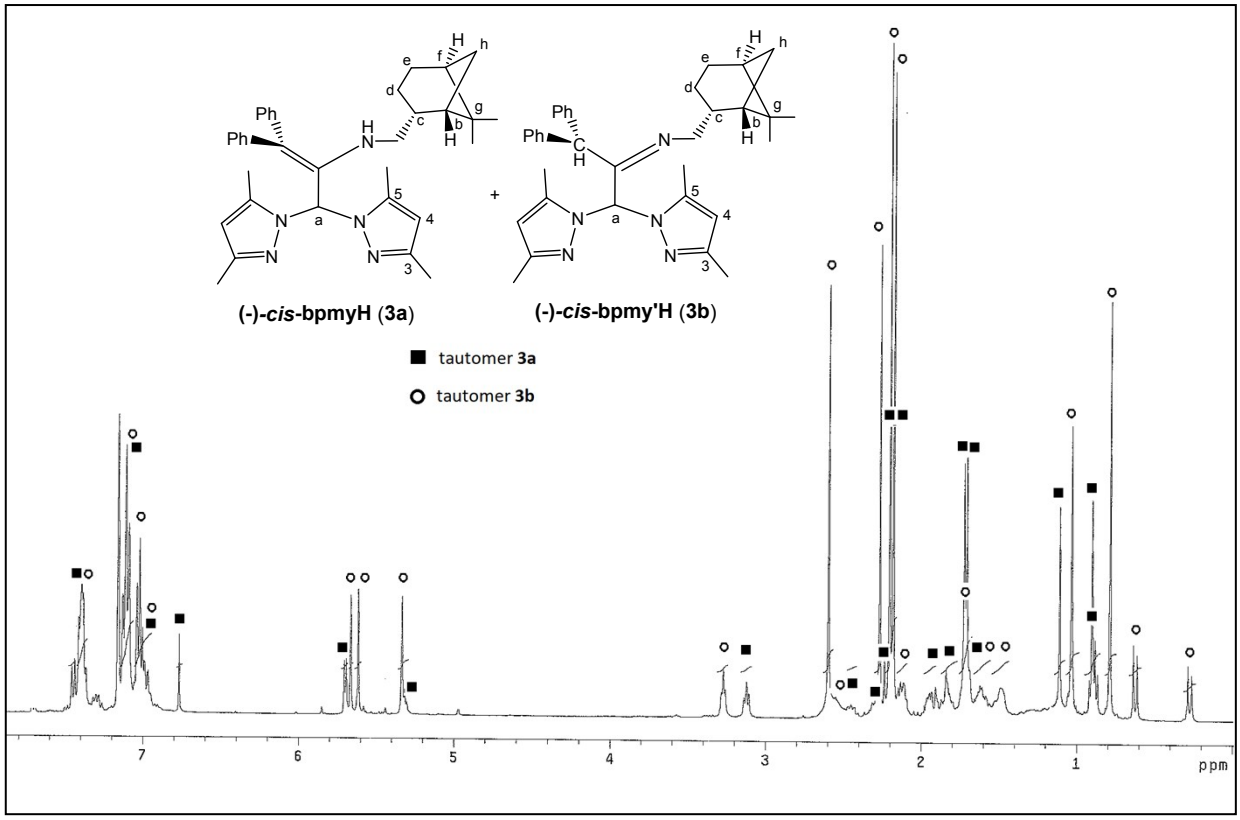


Figure S3a. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **3**.

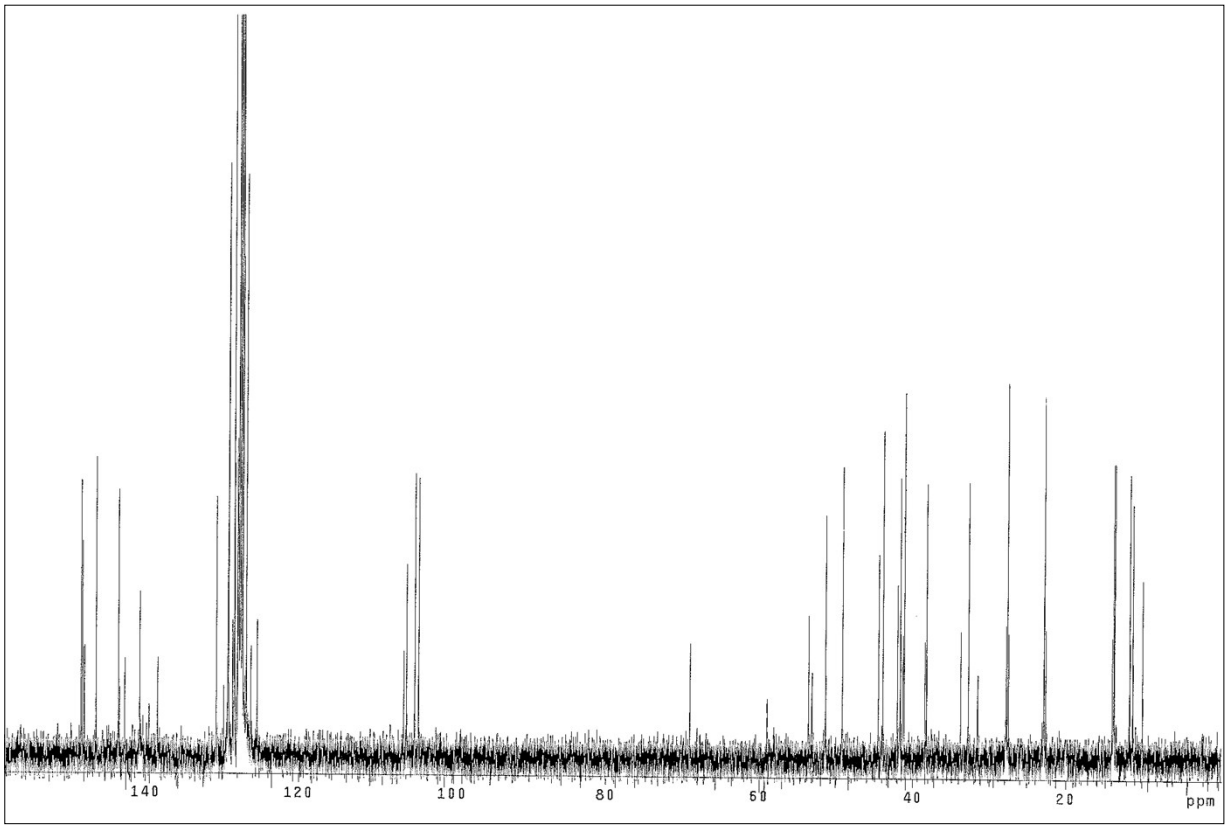


Figure S3b. ^{13}C-{^{1}H} NMR (125 MHz, 298 K, C_6D_6) spectrum of compound **3**.

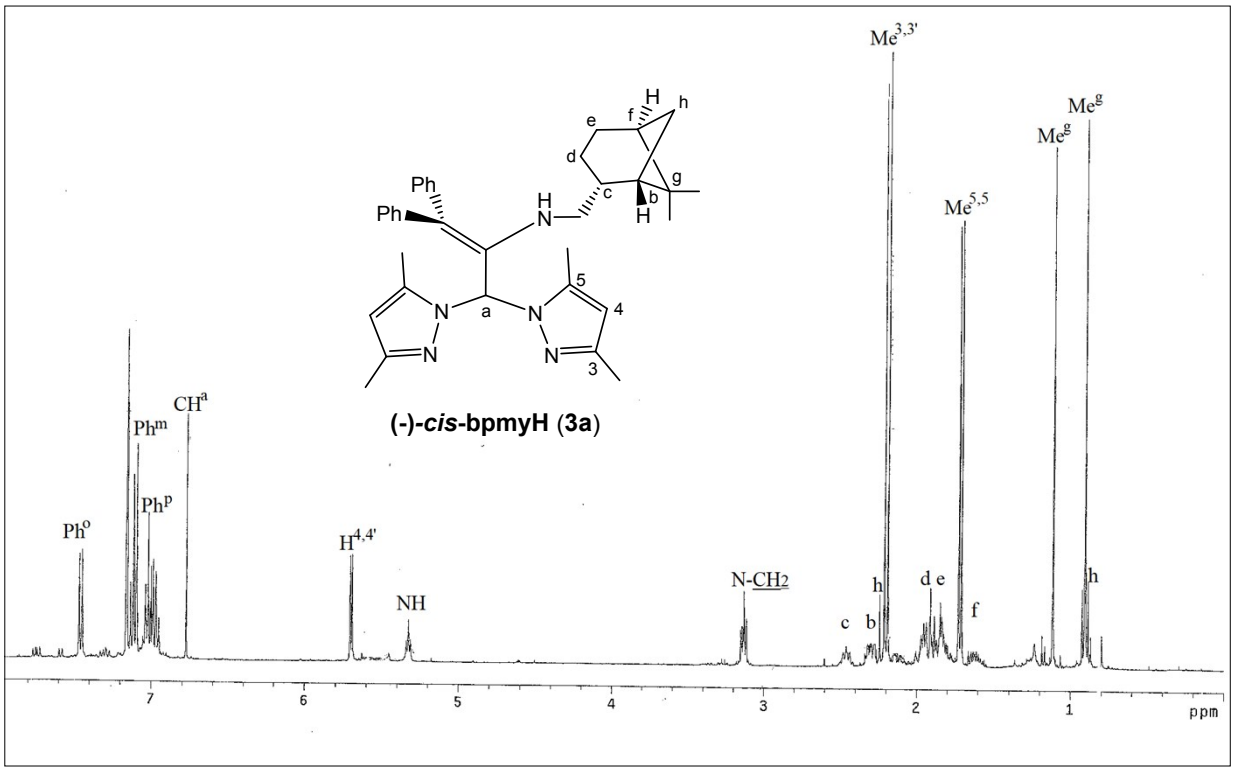


Figure S3c. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **3a**.

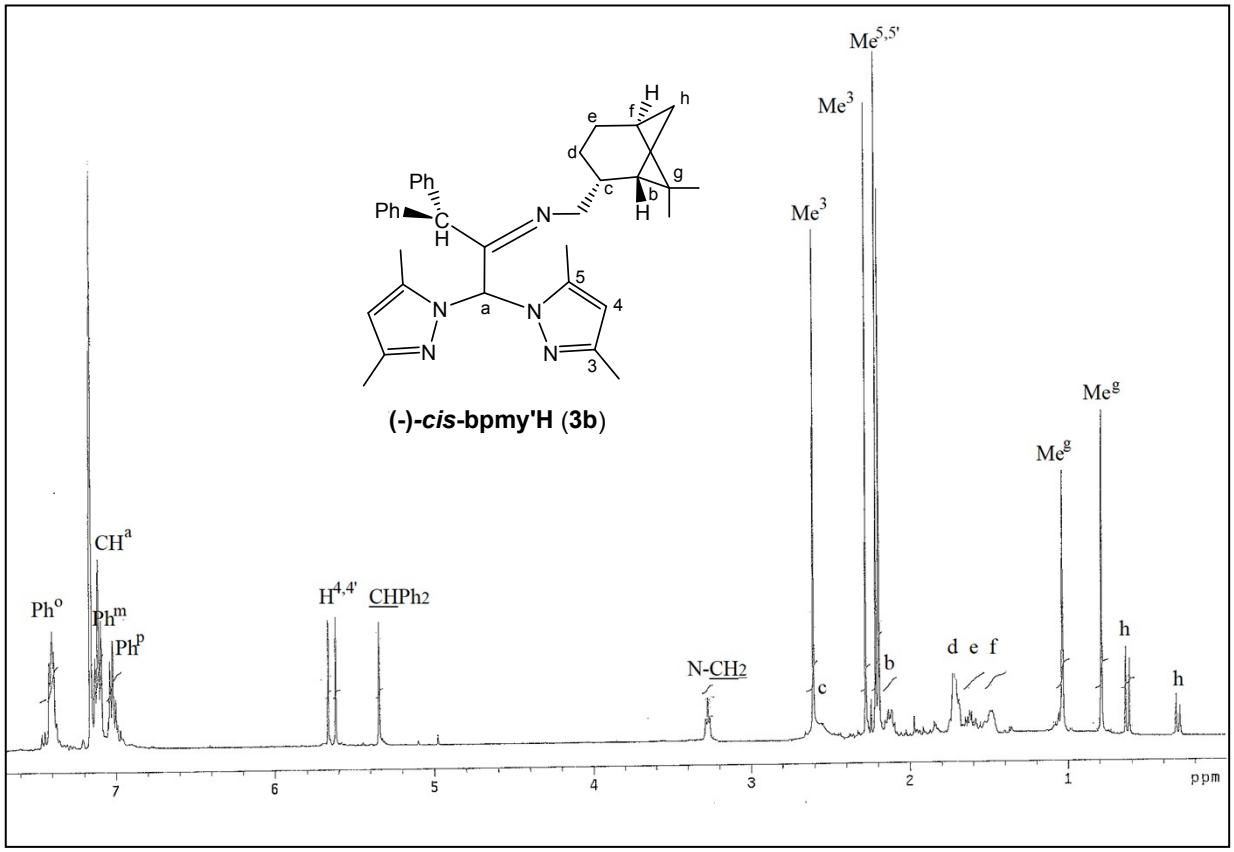


Figure S3d. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **3b**.

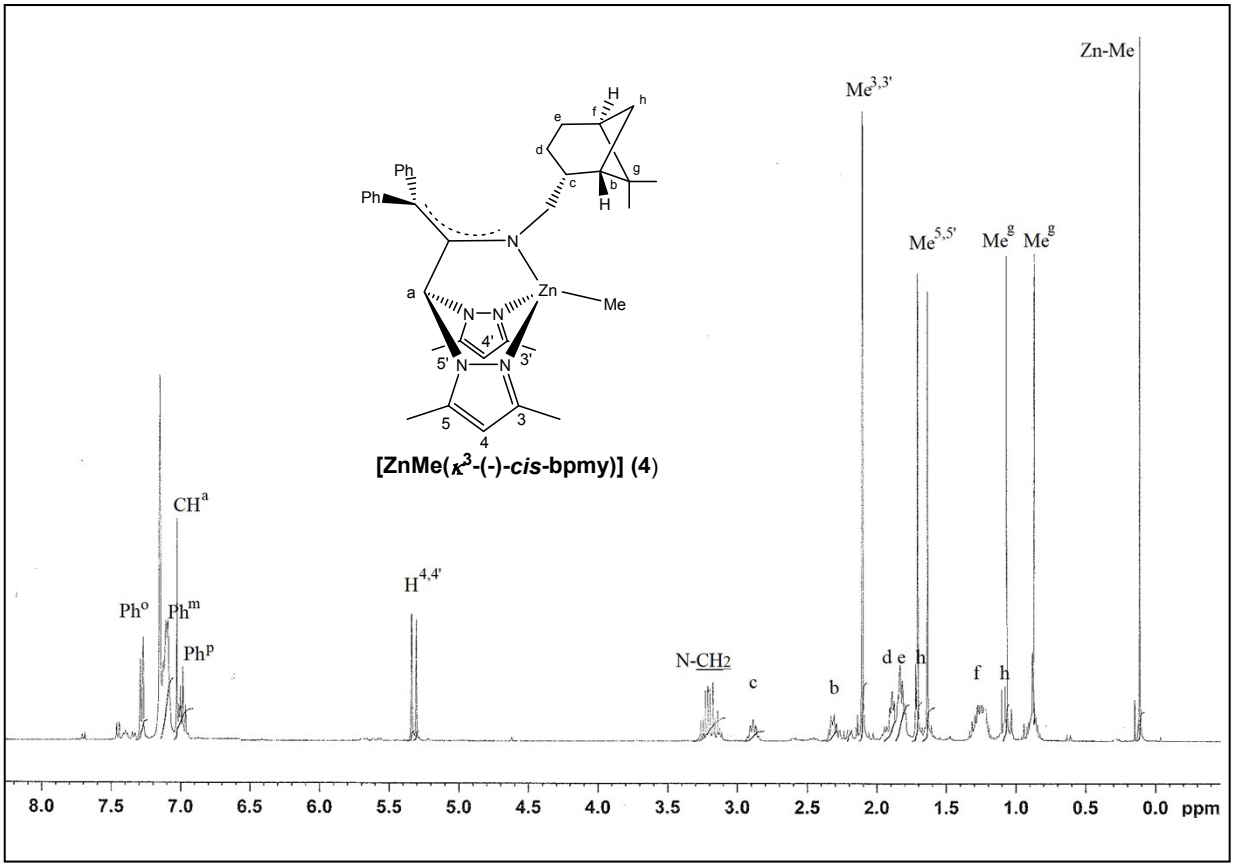


Figure S4a. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **4**.

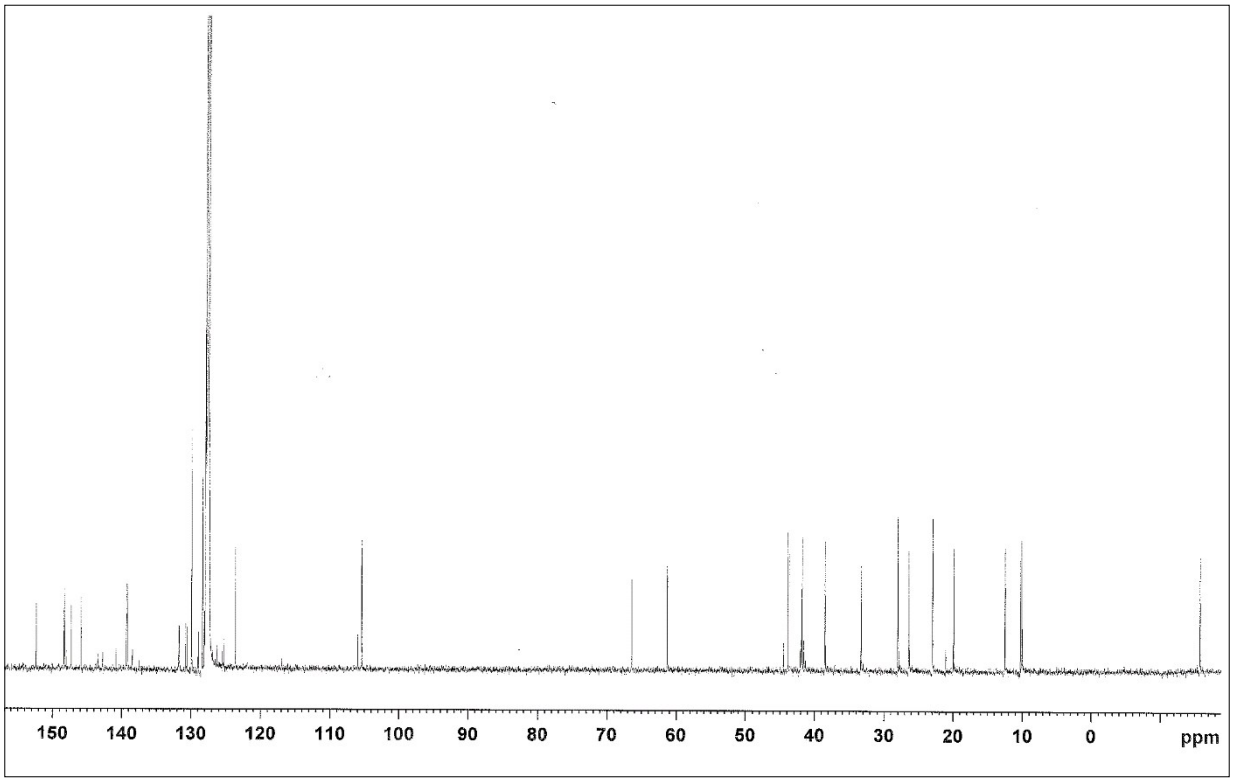


Figure S4b. ^{13}C-{^{1}H} NMR (125 MHz, 298 K, C_6D_6) spectrum of compound **4**.

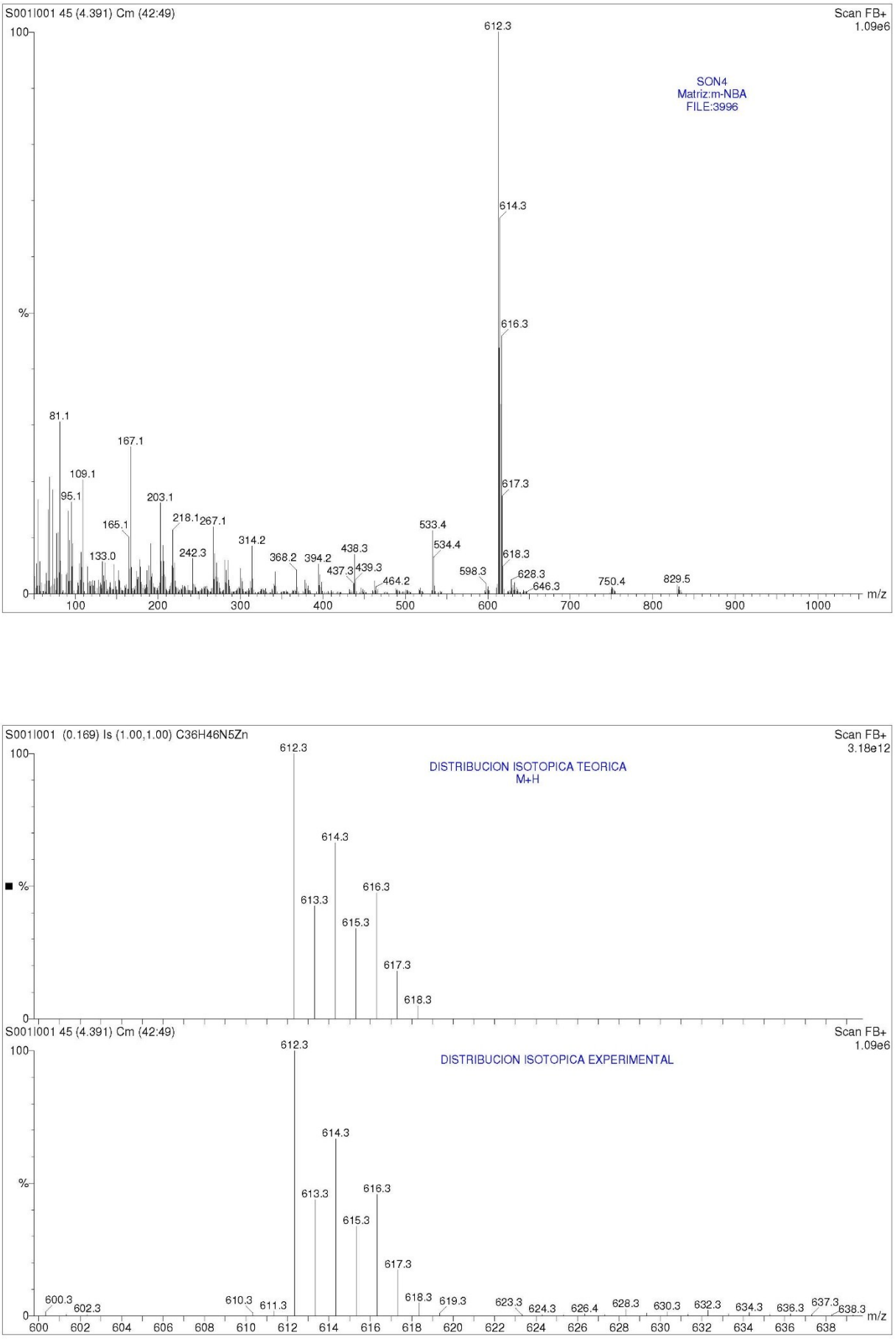


Figure S5. Mass spectra for compound **4**.

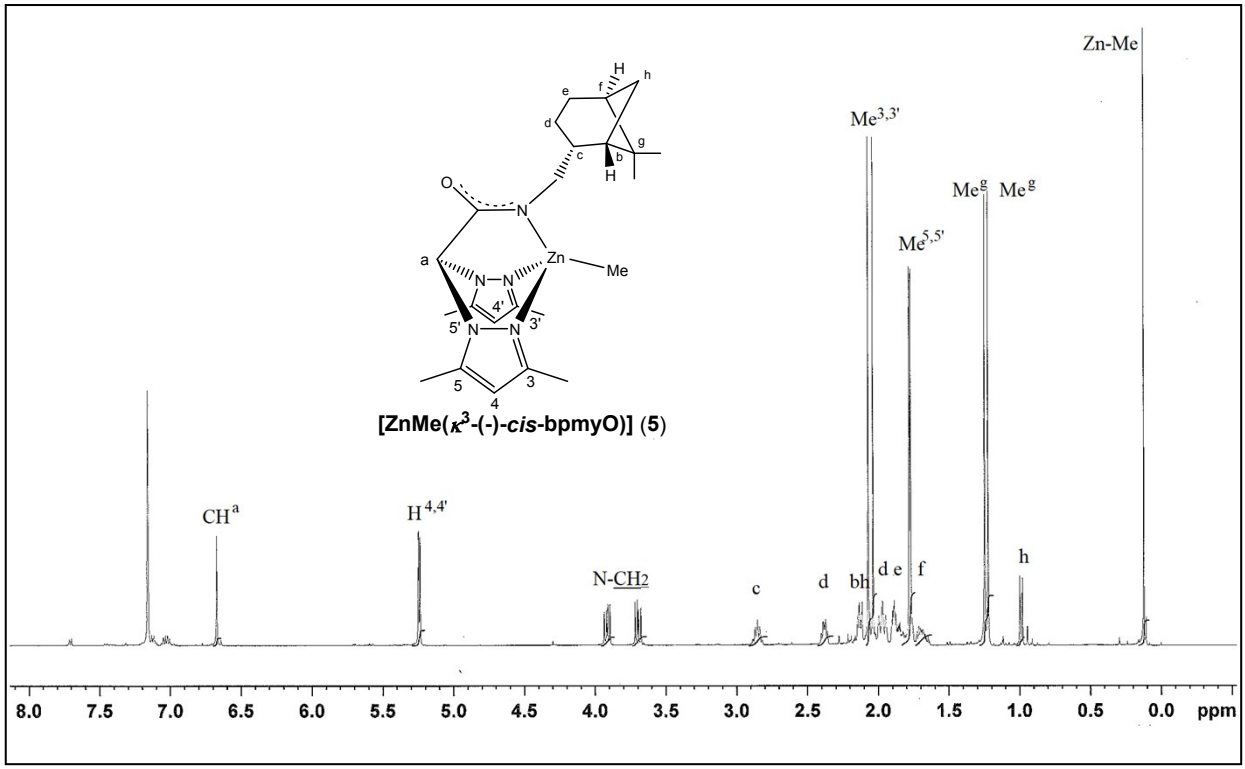


Figure S6a. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **5**.

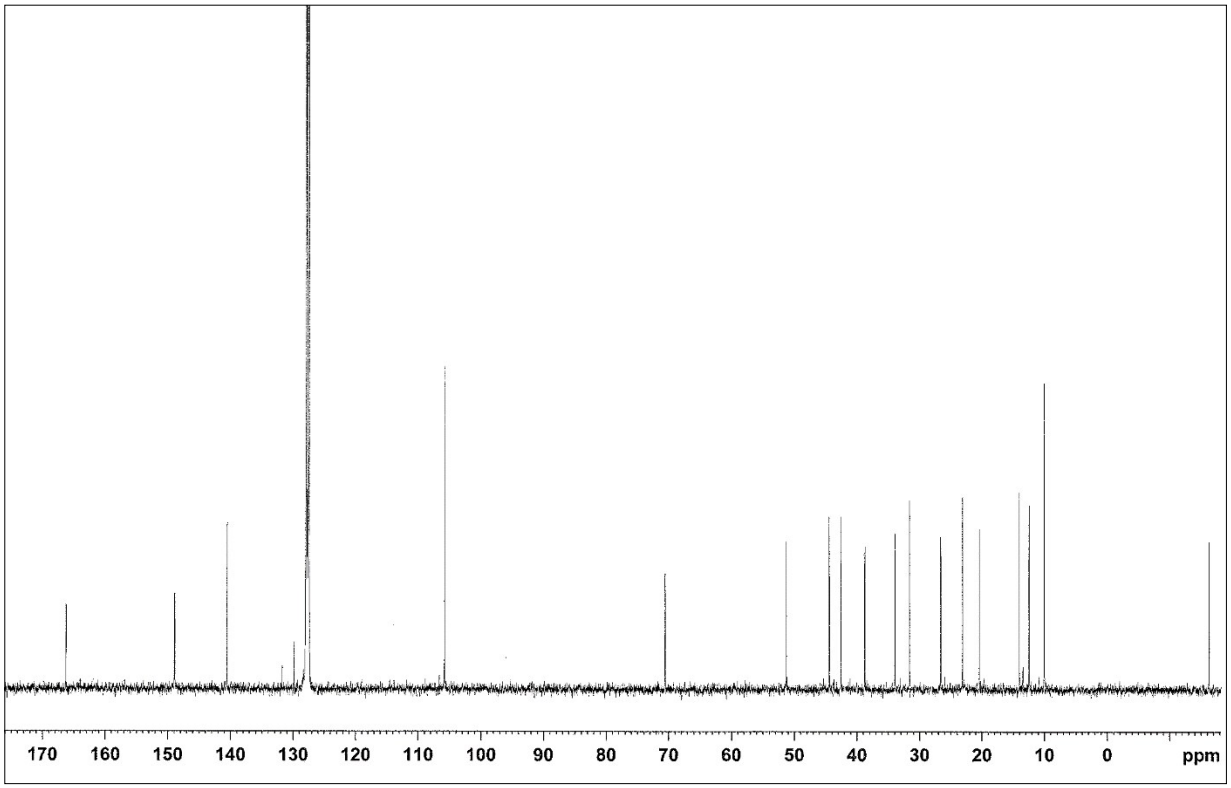
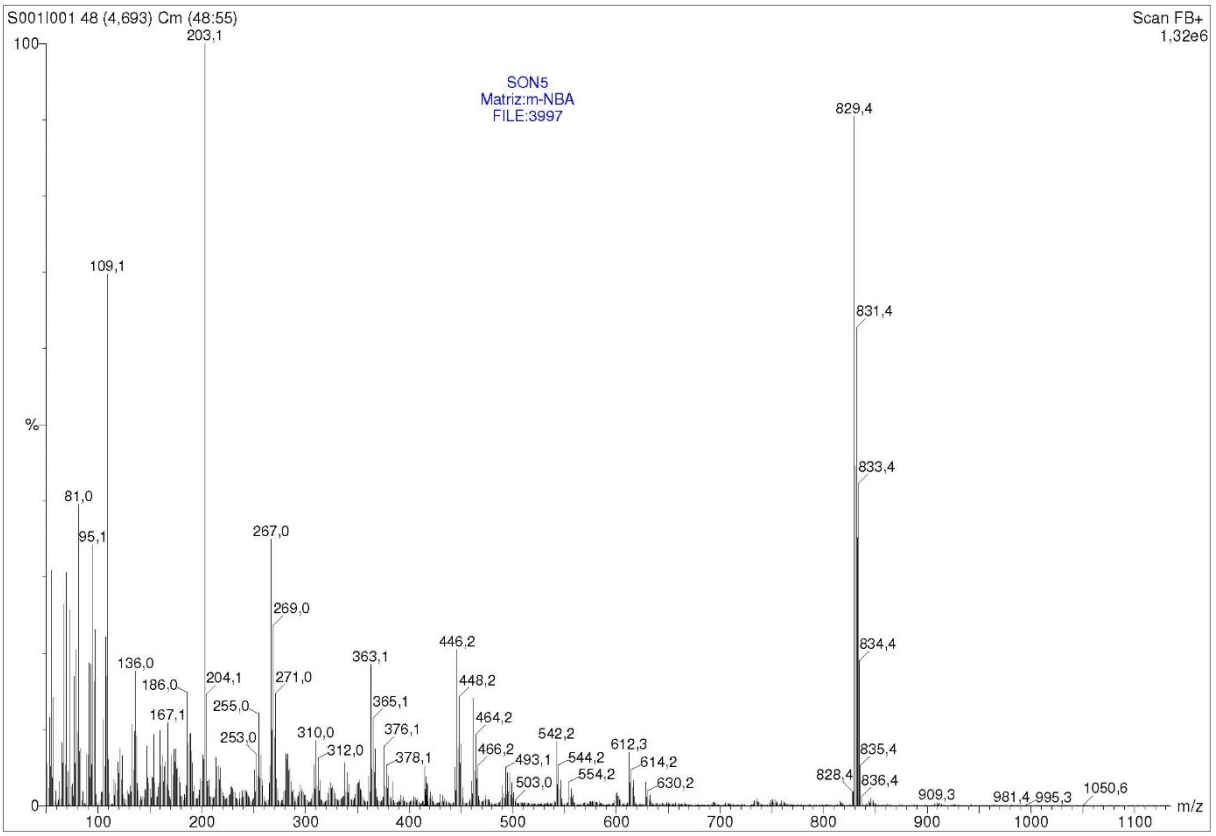


Figure S6b. ^{13}C-{^{1}H} NMR (125 MHz, 298 K, C_6D_6) spectrum of compound **5**.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493,1
544,2
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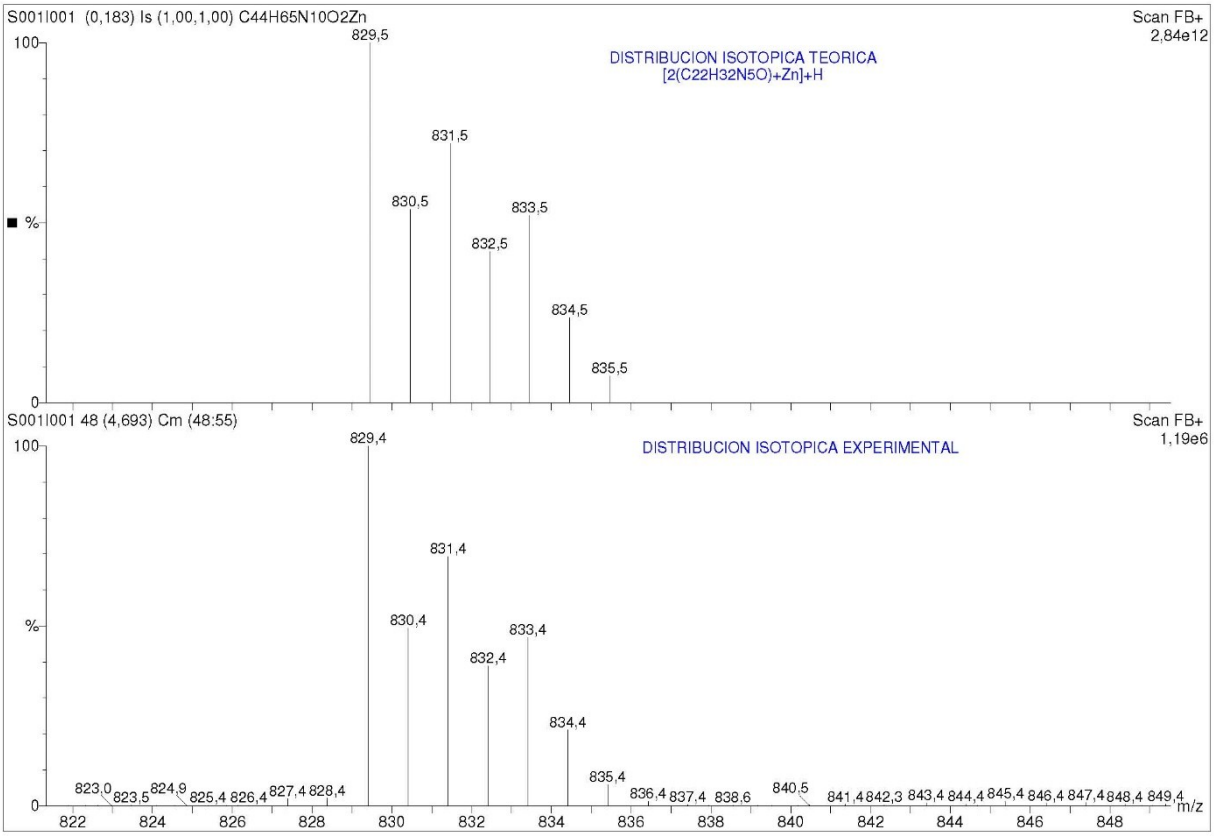
%
m/z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831,5
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%
S001l001 48 (4,693) Cm (48:55)
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838,6
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m/z

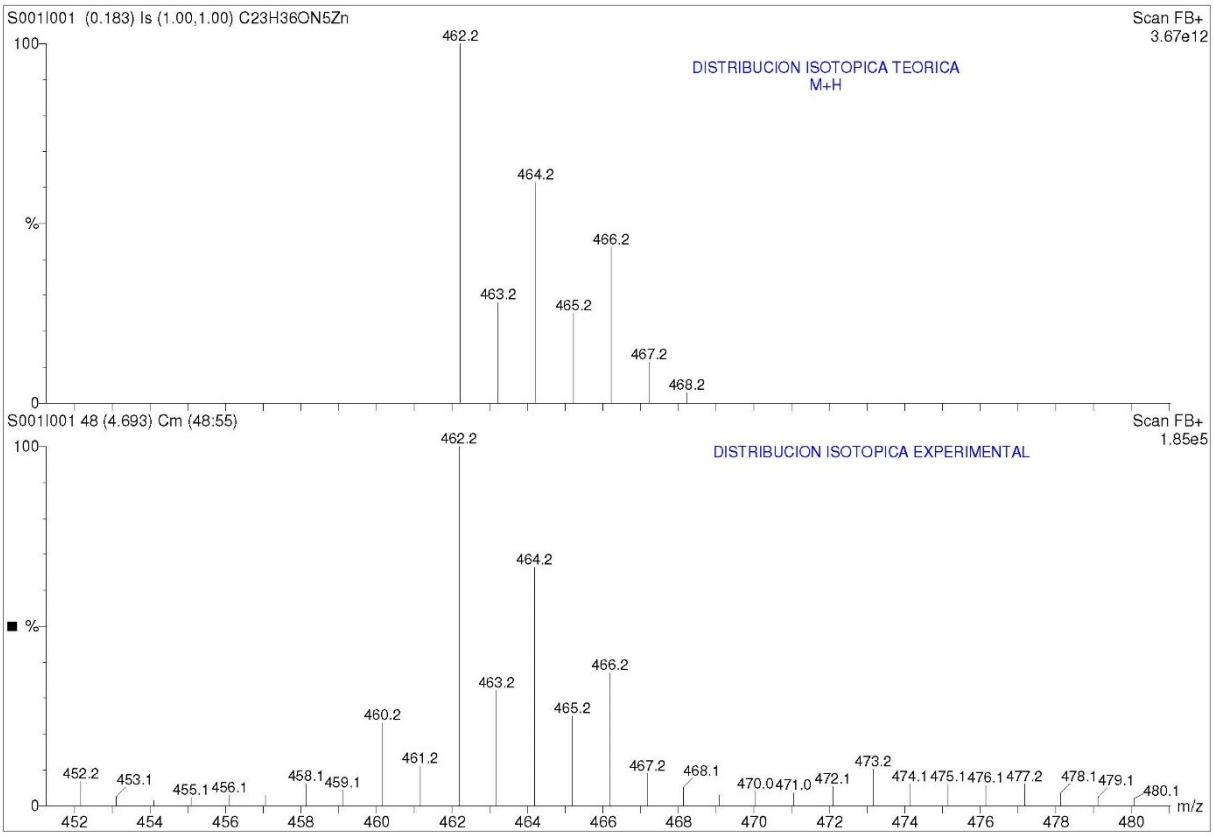

Figure S7. Mass spectra of compound **5**.

Table S1. Polymerization of *rac*-Lactide Catalyzed by 4 and 5.[a]

entry	catalyst	time (h)	yield (g)	conv (%)[b]	$M_{n\ (theor.)}$ (Da)[c]	M_n (Da)[d]	M_w/M_n[d]	P_i[e]
1	**4**	2.5	0.48	37	5 300	4 900	1.07	0.88
2	**4**[f]	5	traces	-	-	-	-	-
3	**4**[g]	5	traces	-	-	-	-	-
4	**4**	6	0.84	65	9 400	9 700	1.07	-
5	**4**	10	1.19	92	13 200	13 500	1.09	-
6	**5**	2.5	0.44	34	4 900	4 700	1.22	0.87
7	**5**	10	1.10	85	12 200	12 000	1.18	-
8	**5**[g]	5	traces	-	-	-	-	-

[a] Polymerization conditions: $[initiator]_0$ = 90 μmol of catalyst, 10 mL of tetrahydrofuran as solvent, $[rac\text{-lactide}]_0/[initiator]_0$ = 100, at 50 ºC. [b] Percentage conversion of the monomer [(weight of polymer recovered/weight of monomer) × 100]. [c] Theoretical M_n = (monomer/catalyst) × (% conversion) × (M_w of lactide). [d] Determined by size exclusion chromatography relative to polystyrene standards in tetrahydrofuran. Experimental M_n was calculated considering Mark–Houwink's corrections[1] for M_n [M_n(obsd) = 0.58 × M_n(GPC)]. [e] The parameter P_i (i = isotactic) is the probability of forming a new *i*-dyad. The P_i and the P_s (s = syndiotactic) values were calculated from the following tetrads probabilities based on enantiomophic site control statistics[2] in the polymerization of *rac*-lactide: *sis, sii, iis* = $[P_i^2(1\text{-}P_i)+P_i(1\text{-}P_i)^2]/2$; *iii* = $[P_i^2(1\text{-}P_i)^2+P_i^3+(1\text{-}P_i)^3]/2$; *isi* = $[P_i(1\text{-}P_i)+P_i(1\text{-}P_i)]/2$. [f] 20 mL of toluene as solvent. [g] Experiment at 35 ºC.

.

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\gpcresultados\2017\Sonia\PLA5.lcd

Acquired by	: Admin
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Sample ID	: PLA5
Vail #	:
Injection Volume	: 20 uL
Data File Name	: PLA5.lcd
Method File Name	: metodo_2017_Alberto.lcm
Batch File Name	: SingleRun120170425171458.lcb
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Data Acquired	: 25/04/2017 16:15:34
Data Processed	: 06/03/2019 19:05:28

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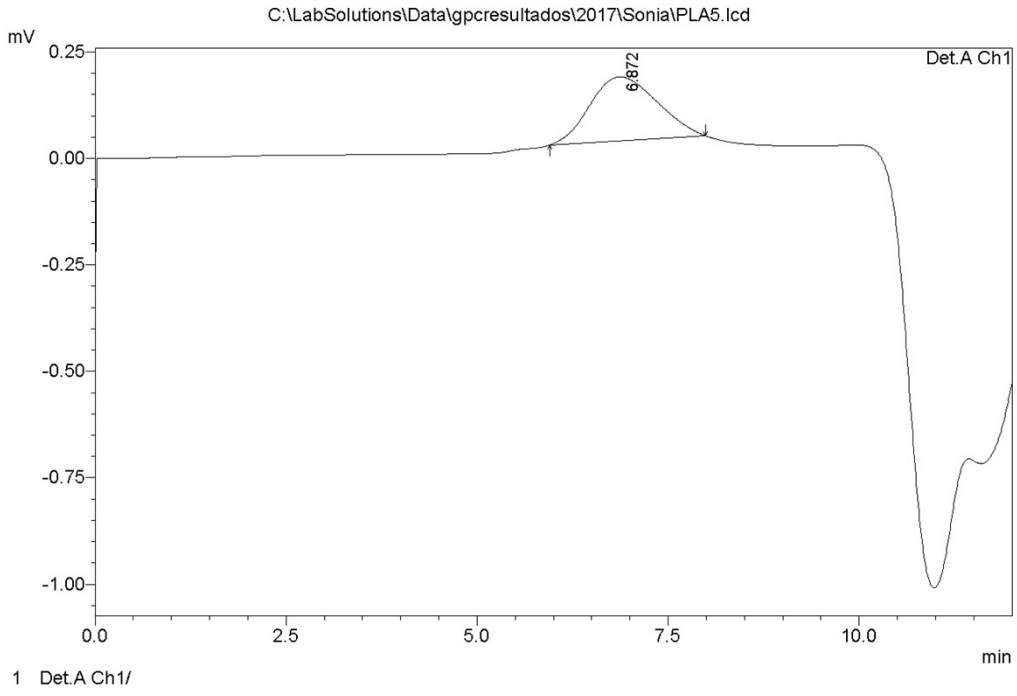

GPC Summary

Chromatogram Det.A Ch1

#	Title	Mn	Mw	Mw/Mn	Intrinsic Viscosity
1	PLA5.lcd	8187	10029	1.22501	1.00000
	Average	8187	10029	1.22501	1.00000
	%RSD	0.000	0.000	0.000	0.000
	Maximum	8187	10029	1.22501	1.00000
	Minimum	8187	10029	1.22501	1.00000
	SD	0	0	0.00000	0.00000

Figure S8. GPC trace corresponding to a poly(*rac*-lactide) (Table S1, entry 6) prepared with catalyst **5**.

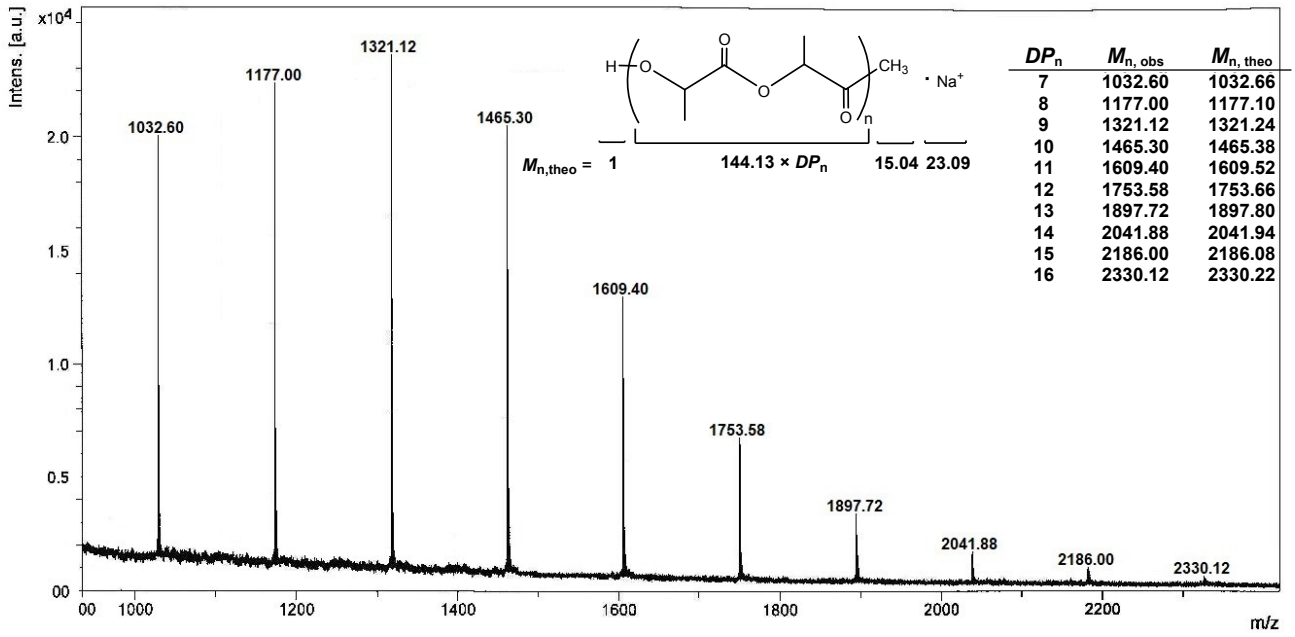

Figure S9. Selected area of MALDI-ToF mass spectrum of PLA sample obtained with $[rac\text{-LA}]_0/[\mathbf{4}]_0$ = 25, 64% conversion; theoretical molecular weights calculated according to the equation: $M_n = (DP_n \times M_{wLA}) + M_{wMeH} + M_{wNa}$, where DP_n is the degree of polymerization, M_{wLA} = 144.13, M_{wMeH} = 16.04 and M_{wNa} = 23.09 g·mol^{-1}.

The distribution in the spectrum indicates the existence of a single family of polymer chains capped by –CH(CH$_3$)OH and CH$_3$–OC–CH(CH$_3$)– *termini*, corresponding to oligomers of formula H(OCHMeCO)$_{2n}$(CH$_3$)·Na$^+$ (n = 7 to 16) with consecutive peaks separated by increments of 144 Da. Moreover, neither intermolecular ester-exchange (transesterification) reactions nor cyclic oligomers were detected.

Model	PsdVoigt1		
Equation	y = y0 + A * (mu * (2/PI) * (w / (4*(x-xc) ^2 + w^2)) + (1 - mu) * (sqrt(4*ln(2)) / (sqrt(PI) * w)) * exp(-(4*ln(2)/w^2)*(x-xc)^2))		
Reduced Chi-Sqr	23.94472		
Adj. R-Square	0.9941		
y0	0.61224	–	--
Tetrad		**Value**	**Standard Error**
isi	xc	5.14979	0.00159
	Area	**0.4179**	**0.05602**
	w	0.00537	5.40661E-4
	mu	1.14093	0.15362
iii	xc	5.16042	1.74116E-4
	Area	**3.12286**	**0.0827**
	w	0.00748	8.06226E-5
	mu	0.7948	0.0462
iis	xc	5.1716	0.00295
	Area	**0.17782**	**0.08649**
	w	0.0086	0.00147
	mu	0.19693	0.86038
sii	xc	5.20645	0.00199
	Area	**0.22867**	**0.07449**
	w	0.00789	5.93563E-4
	mu	0.18614	0.68595
sis	xc	5.22105	1,16108E-4
	Area	**0.23957**	**0.04633**
	w	0.00532	4.40167E-4
	mu	0.59822	0.36538

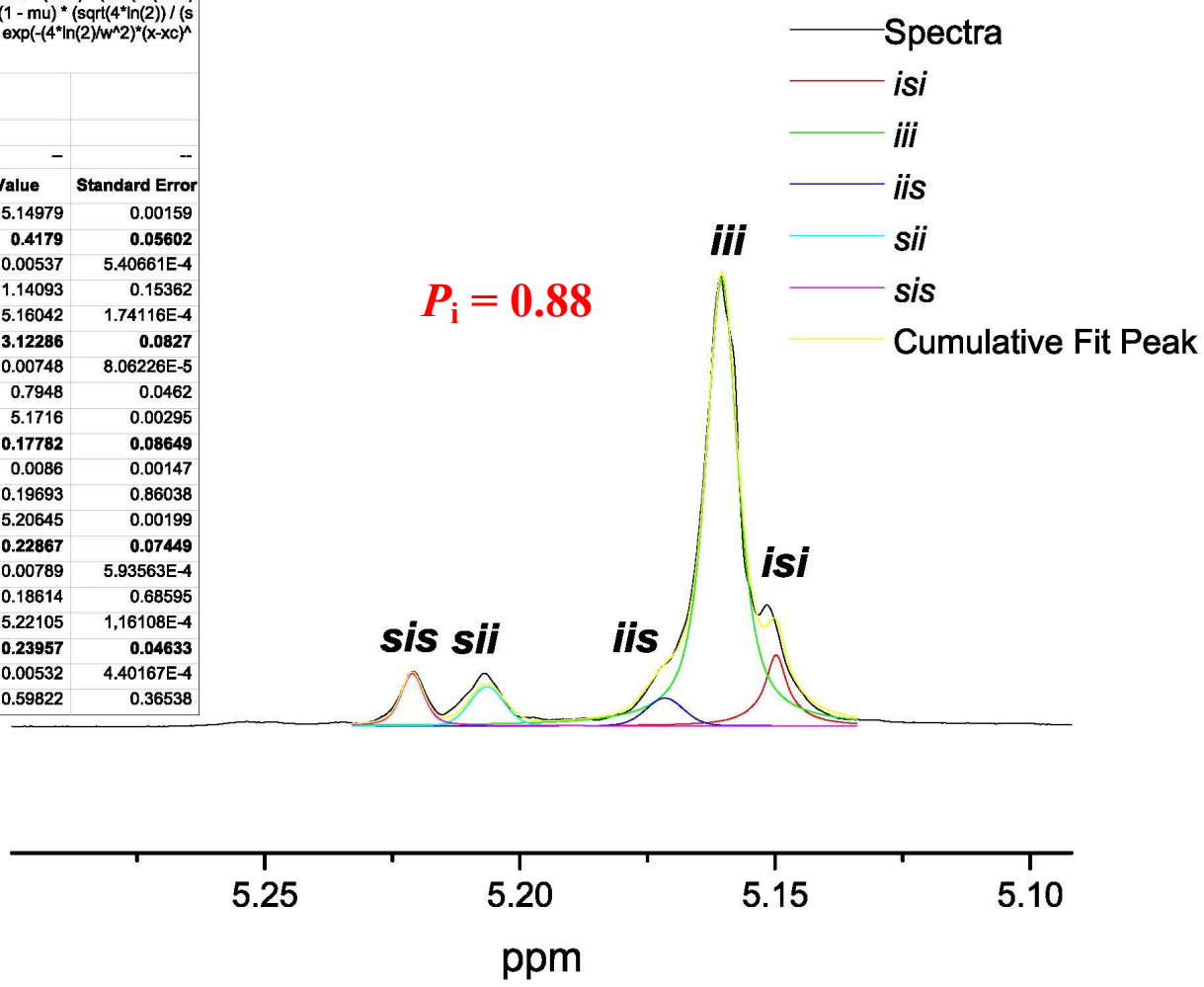

Figure S10. Deconvoluted ^{1}H NMR spectra (500 MHz, 298 K, $CDCl_3$) of the homodecoupled C*H* resonance of poly(*rac*-lactide) prepared employing [ZnMe(κ^3-(-)-*cis*-bpmy)] (**4**) as initiator in tetrahydrofuran at 50 ºC for 2.5 h. The tacticity of the polymer was assigned using the methine signals with homonuclear decoupling as described by Hillmyer and co-workers.[3]

Table S2: Tetrads Area Distribution and P_i Value Calculation.[a]

	sis	*sii*	*iis*	*iii*	*isi*	
	Experimental Normalized Values					
	0.057	0.055	0.042	0.746	0.100	
	Theoretical Values					**Differences of squares**
P_i	$[P_i^2(1-P_i)+P_i(1-P_i)^2]/2$			$[P_i^2(1-P_i)^2+P_i^3+(1-P_i)^3]/2$	$[P_i(1-P_i)+P_i(1-P_i)]/2$	
0.87	0.05655	0.05655	0.05655	0.71725	0.1131	0.046
0.88	0.0528	0.0528	0.0528	0.736	0.1056	0.030
0.89	0.0490	0.0490	0.0490	0.7553	0.0979	0.031

[a] The relative theoretical tetrad proportions are based on an enantiomorphic site control statistics as proposed by Ovitt and Coates.[2] The best experimental P_i value is estimated by minimizing the sum of absolute differences between experimental and predicted squared values.

Table S3. Crystal data and structure refinement for 5.

Identification code	5	
Empirical formula	C_{29} H_{49} N_5 O Zn	
Formula weight	549.12	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1	
Unit cell dimensions	a = 7.9364(9) Å	α= 90º.
	b = 21.825(2) Å	β= 93.640(6)º.
	c = 17.4095(17) Å	γ = 90º.
Volume	3009.4(5) $Å^3$	
Z	4	
Density (calculated)	1.212 Mg/m^3	
Absorption coefficient	0.845 mm^{-1}	
F(000)	1184	
Crystal size	0.360 x 0.200 x 0.180 mm^3	
Theta range for data collection	2.344 to 26.368°.	
Index ranges	-9≤h≤9, -27≤k≤24, -21≤l≤21	
Reflections collected	33635	
Independent reflections	11609 [R(int) = 0.0969]	
Completeness to theta = 25.242º	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.577	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11609 / 596 / 652	
Goodness-of-fit on F^2	0.862	
Final R indices [I>2sigma(I)]	R1 = 0.0612, wR2 = 0.1387	
R indices (all data)	R1 = 0.1380, wR2 = 0.1849	
Absolute structure parameter	0.031(16)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.389 and -0.656 $e.Å^{-3}$	

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 5. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	4802(2)	4053(1)	5920(1)	21(1)
N(1)	3188(12)	4454(4)	6702(6)	19(2)
N(2)	4026(12)	4762(5)	7294(5)	21(2)
N(3)	6289(12)	3768(5)	6912(6)	22(2)
N(4)	6611(12)	4217(5)	7457(6)	19(2)
N(5)	5994(12)	4852(4)	5902(5)	19(2)
O(1)	7390(12)	5579(4)	6657(5)	35(2)
C(1)	2935(16)	4950(6)	7820(7)	29(3)
C(2)	1370(17)	4772(6)	7539(8)	38(3)
C(3)	1533(15)	4460(6)	6839(8)	27(3)
C(4)	3537(19)	5266(7)	8549(8)	41(4)
C(5)	288(15)	4178(7)	6300(8)	39(4)
C(6)	7455(15)	3993(6)	8094(7)	23(3)
C(7)	7740(17)	3380(6)	7945(8)	29(3)
C(8)	6993(16)	3258(6)	7213(8)	24(3)
C(9)	7854(17)	4372(6)	8793(7)	33(3)
C(10)	6956(17)	2673(6)	6769(8)	33(3)
C(11)	5858(14)	4824(5)	7314(7)	18(2)
C(12)	6486(15)	5122(6)	6561(7)	20(2)
C(13)	6541(15)	5189(6)	5222(6)	25(3)
C(14)	5578(12)	5011(5)	4479(5)	27(2)
C(15)	6309(13)	5359(5)	3800(5)	32(2)
C(16)	4983(14)	5586(6)	3168(6)	44(3)
C(17)	3185(14)	5496(5)	3398(7)	41(3)
C(18)	2937(13)	4854(6)	3670(6)	38(3)
C(19)	3634(13)	5080(5)	4466(6)	32(2)
C(20)	2963(14)	5724(6)	4238(6)	37(2)
C(21)	3895(16)	6304(5)	4533(7)	42(3)
C(22)	1093(14)	5777(7)	4391(7)	51(3)
C(23)	4068(17)	3452(6)	5129(8)	31(3)
Zn(2)	10145(2)	7400(1)	9095(1)	22(1)
N(6)	8666(11)	7665(5)	8082(6)	19(2)
N(7)	8308(12)	7199(4)	7578(6)	19(2)
N(8)	11696(12)	6946(5)	8357(6)	23(2)
N(9)	10828(12)	6617(4)	7772(6)	20(2)
N(10)	8789(12)	6633(5)	9162(6)	22(2)
O(2)	7479(11)	5869(4)	8457(5)	29(2)

C(31)	7501(15)	7417(7)	6915(7)	25(2)
C(32)	7287(15)	8022(6)	7013(8)	25(3)
C(33)	8024(16)	8169(5)	7744(8)	23(3)
C(34)	6996(16)	7018(6)	6235(7)	29(3)
C(35)	8225(17)	8767(6)	8133(8)	32(3)
C(36)	11903(14)	6411(5)	7254(7)	23(3)
C(37)	13495(15)	6585(6)	7521(7)	29(3)
C(38)	13295(15)	6919(6)	8191(8)	25(3)
C(39)	11330(17)	6088(6)	6532(8)	34(3)
C(40)	14625(14)	7206(6)	8725(8)	30(3)
C(41)	8998(14)	6596(6)	7770(7)	20(2)
C(42)	8361(15)	6342(6)	8519(7)	19(2)
C(43)	8263(15)	6380(6)	9883(7)	26(3)
C(44)	9279(14)	5818(5)	10149(6)	35(2)
C(45)	8528(15)	5557(6)	10888(7)	53(3)
C(46)	9905(16)	5313(7)	11499(8)	59(4)
C(47)	11651(14)	5461(5)	11292(6)	37(2)
C(48)	11940(20)	5266(7)	10468(7)	63(4)
C(49)	11139(14)	5887(5)	10239(6)	36(2)
C(50)	11877(14)	6124(6)	11029(6)	37(2)
C(51)	13680(18)	6313(8)	11015(9)	84(5)
C(52)	10916(18)	6606(6)	11454(7)	60(4)
C(53)	10942(18)	7998(6)	9863(8)	35(4)
C(61)	3780(20)	3624(8)	9788(10)	73(5)
C(62)	3750(20)	3100(8)	9272(10)	69(5)
C(63)	3013(17)	3194(8)	8478(9)	55(4)
C(64)	3000(20)	2636(7)	7969(10)	64(4)
C(65)	2149(18)	2724(8)	7205(9)	65(4)
C(66)	2060(20)	2128(7)	6688(10)	76(5)
C(71)	9090(20)	2789(8)	4787(9)	65(5)
C(76)	6520(20)	4078(8)	1661(9)	75(5)
C(72)	8370(30)	2813(10)	3971(11)	39(6)
C(73)	8130(40)	3434(12)	3597(13)	39(8)
C(74)	7460(30)	3405(10)	2783(12)	38(6)
C(75)	7030(30)	4036(11)	2483(12)	55(7)
C(74A)	7640(40)	3732(14)	3009(15)	46(8)
C(72A)	8910(50)	3349(14)	4286(17)	70(10)
C(75A)	6930(50)	3600(15)	2232(16)	76(11)
C(73A)	8020(60)	3197(18)	3530(19)	85(15)

Table S5. Bond lengths [Å] and angles [º] for 5.

Zn(1)-C(23)	1.962(13)
Zn(1)-N(5)	1.986(10)
Zn(1)-N(1)	2.117(9)
Zn(1)-N(3)	2.122(10)
N(1)-C(3)	1.350(14)
N(1)-N(2)	1.368(13)
N(2)-C(1)	1.363(14)
N(2)-C(11)	1.459(14)
N(3)-C(8)	1.339(16)
N(3)-N(4)	1.376(13)
N(4)-C(6)	1.350(15)
N(4)-C(11)	1.468(15)
N(5)-C(12)	1.325(15)
N(5)-C(13)	1.483(13)
O(1)-C(12)	1.235(14)
C(1)-C(2)	1.362(18)
C(1)-C(4)	1.496(18)
C(2)-C(3)	1.408(17)
C(3)-C(5)	1.455(18)
C(6)-C(7)	1.385(18)
C(6)-C(9)	1.488(17)
C(7)-C(8)	1.397(19)
C(8)-C(10)	1.492(16)
C(11)-C(12)	1.572(16)
C(13)-C(14)	1.512(14)
C(14)-C(19)	1.548(13)
C(14)-C(15)	1.549(13)
C(15)-C(16)	1.555(15)
C(16)-C(17)	1.520(15)
C(17)-C(18)	1.496(16)
C(17)-C(20)	1.565(15)
C(18)-C(19)	1.540(15)
C(19)-C(20)	1.547(15)
C(20)-C(21)	1.538(16)
C(20)-C(22)	1.528(15)
Zn(2)-C(53)	1.945(13)
Zn(2)-N(10)	1.998(10)
Zn(2)-N(8)	2.086(10)
Zn(2)-N(6)	2.136(10)
N(6)-C(33)	1.333(15)

N(6)-N(7)	1.361(13)
N(7)-C(31)	1.370(15)
N(7)-C(41)	1.457(15)
N(8)-C(38)	1.321(15)
N(8)-N(9)	1.391(14)
N(9)-C(36)	1.357(14)
N(9)-C(41)	1.453(14)
N(10)-C(42)	1.313(14)
N(10)-C(43)	1.457(13)
O(2)-C(42)	1.248(14)
C(31)-C(32)	1.343(18)
C(31)-C(34)	1.504(17)
C(32)-C(33)	1.403(19)
C(33)-C(35)	1.475(17)
C(36)-C(37)	1.371(16)
C(36)-C(39)	1.488(17)
C(37)-C(38)	1.393(16)
C(38)-C(40)	1.499(17)
C(41)-C(42)	1.531(16)
C(43)-C(44)	1.525(15)
C(44)-C(49)	1.482(15)
C(44)-C(45)	1.559(15)
C(45)-C(46)	1.569(16)
C(46)-C(47)	1.490(17)
C(47)-C(48)	1.527(16)
C(47)-C(50)	1.531(16)
C(48)-C(49)	1.538(16)
C(49)-C(50)	1.549(15)
C(50)-C(51)	1.491(17)
C(50)-C(52)	1.520(16)
C(61)-C(62)	1.45(2)
C(62)-C(63)	1.48(2)
C(63)-C(64)	1.51(2)
C(64)-C(65)	1.47(2)
C(65)-C(66)	1.58(2)
C(71)-C(72)	1.50(2)
C(71)-C(72A)	1.50(2)
C(76)-C(75)	1.47(2)
C(76)-C(75A)	1.46(2)
C(72)-C(73)	1.51(2)
C(73)-C(74)	1.49(2)
C(74)-C(75)	1.50(2)

C(74A)-C(75A)	1.46(2)
C(74A)-C(73A)	1.50(3)
C(72A)-C(73A)	1.49(3)

C(23)-Zn(1)-N(5)	134.1(5)
C(23)-Zn(1)-N(1)	124.3(5)
N(5)-Zn(1)-N(1)	87.4(4)
C(23)-Zn(1)-N(3)	120.0(5)
N(5)-Zn(1)-N(3)	91.6(4)
N(1)-Zn(1)-N(3)	85.7(4)
C(3)-N(1)-N(2)	107.1(10)
C(3)-N(1)-Zn(1)	138.9(9)
N(2)-N(1)-Zn(1)	113.8(7)
C(1)-N(2)-N(1)	110.8(10)
C(1)-N(2)-C(11)	129.2(10)
N(1)-N(2)-C(11)	120.0(9)
C(8)-N(3)-N(4)	105.5(9)
C(8)-N(3)-Zn(1)	139.4(9)
N(4)-N(3)-Zn(1)	115.0(7)
C(6)-N(4)-N(3)	111.7(10)
C(6)-N(4)-C(11)	129.9(11)
N(3)-N(4)-C(11)	118.0(9)
C(12)-N(5)-C(13)	112.7(10)
C(12)-N(5)-Zn(1)	119.4(8)
C(13)-N(5)-Zn(1)	127.8(8)
N(2)-C(1)-C(2)	106.1(11)
N(2)-C(1)-C(4)	121.7(12)
C(2)-C(1)-C(4)	132.2(11)
C(1)-C(2)-C(3)	108.5(11)
N(1)-C(3)-C(2)	107.6(11)
N(1)-C(3)-C(5)	120.7(11)
C(2)-C(3)-C(5)	131.8(11)
N(4)-C(6)-C(7)	106.0(12)
N(4)-C(6)-C(9)	122.7(12)
C(7)-C(6)-C(9)	131.3(12)
C(8)-C(7)-C(6)	106.8(13)
N(3)-C(8)-C(7)	109.9(11)
N(3)-C(8)-C(10)	121.0(12)
C(7)-C(8)-C(10)	129.0(13)
N(2)-C(11)-N(4)	108.3(9)
N(2)-C(11)-C(12)	112.8(9)
N(4)-C(11)-C(12)	111.5(9)

O(1)-C(12)-N(5)	127.9(12)
O(1)-C(12)-C(11)	115.6(11)
N(5)-C(12)-C(11)	116.5(10)
N(5)-C(13)-C(14)	113.4(9)
C(13)-C(14)-C(19)	115.9(8)
C(13)-C(14)-C(15)	109.4(8)
C(19)-C(14)-C(15)	111.3(8)
C(14)-C(15)-C(16)	115.3(9)
C(17)-C(16)-C(15)	112.1(9)
C(18)-C(17)-C(16)	110.5(10)
C(18)-C(17)-C(20)	88.7(9)
C(16)-C(17)-C(20)	111.7(9)
C(17)-C(18)-C(19)	86.4(9)
C(14)-C(19)-C(18)	106.4(8)
C(14)-C(19)-C(20)	114.8(9)
C(18)-C(19)-C(20)	87.8(8)
C(21)-C(20)-C(22)	109.3(10)
C(21)-C(20)-C(19)	120.9(9)
C(22)-C(20)-C(19)	110.3(10)
C(21)-C(20)-C(17)	119.5(10)
C(22)-C(20)-C(17)	110.8(9)
C(19)-C(20)-C(17)	83.8(8)
C(53)-Zn(2)-N(10)	132.5(5)
C(53)-Zn(2)-N(8)	124.3(5)
N(10)-Zn(2)-N(8)	88.7(4)
C(53)-Zn(2)-N(6)	121.6(5)
N(10)-Zn(2)-N(6)	90.3(4)
N(8)-Zn(2)-N(6)	86.3(4)
C(33)-N(6)-N(7)	105.8(9)
C(33)-N(6)-Zn(2)	139.7(9)
N(7)-N(6)-Zn(2)	114.3(7)
C(31)-N(7)-N(6)	110.6(10)
C(31)-N(7)-C(41)	131.0(11)
N(6)-N(7)-C(41)	117.9(9)
C(38)-N(8)-N(9)	104.8(10)
C(38)-N(8)-Zn(2)	140.2(9)
N(9)-N(8)-Zn(2)	114.3(7)
C(36)-N(9)-N(8)	110.7(9)
C(36)-N(9)-C(41)	131.1(10)
N(8)-N(9)-C(41)	117.8(9)
C(42)-N(10)-C(43)	118.7(10)
C(42)-N(10)-Zn(2)	117.8(8)

C(43)-N(10)-Zn(2)	123.5(8)
C(32)-C(31)-N(7)	106.9(12)
C(32)-C(31)-C(34)	129.7(13)
N(7)-C(31)-C(34)	123.3(12)
C(31)-C(32)-C(33)	106.9(12)
N(6)-C(33)-C(32)	109.8(11)
N(6)-C(33)-C(35)	120.0(12)
C(32)-C(33)-C(35)	130.2(12)
N(9)-C(36)-C(37)	106.7(10)
N(9)-C(36)-C(39)	123.2(11)
C(37)-C(36)-C(39)	130.0(11)
C(36)-C(37)-C(38)	106.1(10)
N(8)-C(38)-C(37)	111.6(11)
N(8)-C(38)-C(40)	119.6(12)
C(37)-C(38)-C(40)	128.7(10)
N(7)-C(41)-N(9)	109.4(9)
N(7)-C(41)-C(42)	112.5(9)
N(9)-C(41)-C(42)	113.2(10)
O(2)-C(42)-N(10)	125.9(11)
O(2)-C(42)-C(41)	116.1(11)
N(10)-C(42)-C(41)	118.0(10)
N(10)-C(43)-C(44)	113.0(9)
C(49)-C(44)-C(43)	117.0(9)
C(49)-C(44)-C(45)	112.3(8)
C(43)-C(44)-C(45)	108.8(10)
C(44)-C(45)-C(46)	113.4(10)
C(47)-C(46)-C(45)	112.3(10)
C(46)-C(47)-C(48)	111.2(11)
C(46)-C(47)-C(50)	114.0(10)
C(48)-C(47)-C(50)	87.4(9)
C(47)-C(48)-C(49)	85.1(9)
C(44)-C(49)-C(50)	116.5(9)
C(44)-C(49)-C(48)	109.1(11)
C(50)-C(49)-C(48)	86.4(9)
C(51)-C(50)-C(52)	109.1(12)
C(51)-C(50)-C(47)	113.4(11)
C(52)-C(50)-C(47)	115.9(10)
C(51)-C(50)-C(49)	112.8(11)
C(52)-C(50)-C(49)	119.3(9)
C(47)-C(50)-C(49)	84.6(9)
C(61)-C(62)-C(63)	117.3(16)
C(62)-C(63)-C(64)	115.2(15)

C(65)-C(64)-C(63)	114.3(14)
C(64)-C(65)-C(66)	114.2(13)
C(71)-C(72)-C(73)	117.9(18)
C(74)-C(73)-C(72)	114(2)
C(73)-C(74)-C(75)	111(2)
C(76)-C(75)-C(74)	116(2)
C(75A)-C(74A)-C(73A)	117(3)
C(73A)-C(72A)-C(71)	111(2)
C(76)-C(75A)-C(74A)	123(3)
C(72A)-C(73A)-C(74A)	115(3)

Table S6. Anisotropic displacement parameters ($Å^2$x 10^3) for 5. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	17(1)	21(1)	25(1)	-2(1)	-2(1)	-1(1)
N(1)	15(4)	20(5)	23(4)	-3(4)	-1(3)	2(3)
N(2)	17(4)	23(5)	22(4)	0(4)	3(3)	-1(3)
N(3)	22(5)	22(4)	22(4)	-2(3)	-1(4)	-1(4)
N(4)	15(5)	24(4)	20(4)	-2(3)	0(3)	-1(3)
N(5)	16(4)	24(4)	17(4)	5(3)	-1(3)	2(3)
O(1)	44(5)	32(5)	27(5)	-2(4)	-2(4)	-16(4)
C(1)	32(5)	25(6)	32(5)	-3(5)	17(4)	-1(4)
C(2)	31(5)	37(7)	47(6)	-6(5)	15(5)	-5(5)
C(3)	16(5)	28(7)	36(6)	2(5)	3(4)	0(4)
C(4)	45(8)	41(8)	39(6)	-12(6)	20(5)	3(6)
C(5)	19(6)	36(9)	60(8)	-5(7)	-8(5)	1(6)
C(6)	21(6)	27(6)	21(5)	2(4)	-2(4)	2(4)
C(7)	32(7)	27(6)	28(6)	5(4)	-4(5)	2(5)
C(8)	22(6)	23(5)	28(5)	-1(4)	3(5)	2(4)
C(9)	34(7)	37(7)	27(6)	-1(5)	-8(5)	-4(6)
C(10)	34(7)	24(6)	41(7)	-9(5)	-4(6)	9(5)
C(11)	17(4)	22(5)	14(5)	1(4)	-2(4)	-1(3)
C(12)	17(5)	19(5)	25(5)	-3(4)	-2(4)	3(4)
C(13)	25(5)	33(6)	17(4)	2(4)	2(4)	-5(5)
C(14)	24(4)	31(6)	25(4)	-5(4)	1(3)	-1(4)
C(15)	31(5)	47(7)	19(5)	7(4)	6(4)	2(4)
C(16)	38(5)	57(8)	36(6)	7(5)	-1(4)	1(5)
C(17)	38(6)	50(6)	35(5)	-4(5)	-3(4)	1(4)
C(18)	24(5)	47(6)	42(6)	-7(5)	1(5)	-3(4)
C(19)	24(5)	38(5)	34(5)	0(4)	1(4)	-1(4)
C(20)	38(5)	39(5)	31(5)	0(4)	-4(4)	6(4)
C(21)	53(7)	36(6)	36(7)	4(5)	-6(6)	5(5)
C(22)	35(5)	73(9)	46(7)	0(6)	-3(5)	18(5)
C(23)	30(7)	32(7)	33(7)	-2(6)	3(6)	-7(6)
Zn(2)	18(1)	22(1)	24(1)	-2(1)	-2(1)	-2(1)
N(6)	10(4)	17(4)	29(5)	0(3)	-3(4)	-1(3)
N(7)	16(5)	15(4)	25(4)	-1(3)	-3(4)	-2(3)
N(8)	17(4)	20(5)	33(5)	0(4)	1(3)	-1(3)
N(9)	16(4)	16(5)	28(5)	-3(4)	4(3)	-1(3)
N(10)	18(4)	26(5)	23(4)	0(3)	-1(3)	0(4)
O(2)	37(5)	25(4)	25(4)	3(4)	-7(4)	-14(4)

C(31)	20(6)	29(5)	26(5)	5(4)	1(4)	-2(5)
C(32)	18(6)	28(5)	29(5)	11(4)	1(4)	0(4)
C(33)	17(6)	16(5)	37(6)	8(4)	0(5)	1(4)
C(34)	32(7)	34(7)	21(6)	6(5)	-5(5)	-5(6)
C(35)	33(7)	23(6)	39(7)	0(5)	4(6)	5(5)
C(36)	21(5)	18(6)	31(5)	3(4)	2(4)	6(4)
C(37)	22(5)	27(6)	40(6)	-3(5)	7(4)	6(4)
C(38)	13(4)	22(6)	41(6)	-2(5)	2(4)	0(4)
C(39)	33(7)	32(7)	38(6)	-4(5)	7(5)	6(5)
C(40)	14(5)	31(8)	47(7)	-2(6)	6(5)	-2(5)
C(41)	15(4)	19(5)	25(5)	0(4)	1(4)	0(3)
C(42)	16(5)	18(5)	22(5)	2(4)	-4(4)	2(4)
C(43)	23(5)	32(6)	24(5)	7(4)	0(4)	-2(4)
C(44)	52(5)	20(5)	31(5)	1(4)	-19(4)	2(4)
C(45)	38(6)	60(8)	59(7)	35(6)	-20(5)	-16(5)
C(46)	53(6)	62(8)	61(7)	27(6)	-13(5)	3(5)
C(47)	45(6)	45(6)	20(5)	3(4)	-12(4)	14(4)
C(48)	92(10)	67(8)	28(6)	-5(5)	-20(6)	48(7)
C(49)	37(5)	46(6)	26(5)	3(4)	-3(4)	21(4)
C(50)	35(5)	50(6)	25(5)	4(5)	-7(4)	8(4)
C(51)	56(7)	112(12)	81(10)	45(9)	-19(6)	-13(7)
C(52)	70(8)	57(8)	51(7)	-18(6)	-28(6)	12(6)
C(53)	37(8)	31(7)	37(7)	-10(6)	-2(6)	-5(6)
C(61)	50(9)	77(10)	93(11)	2(8)	20(8)	-4(8)
C(62)	50(9)	72(9)	88(9)	15(7)	16(6)	-3(7)
C(63)	18(6)	65(9)	84(8)	23(6)	24(5)	2(6)
C(64)	43(8)	55(8)	95(8)	21(6)	21(6)	-1(6)
C(65)	39(7)	66(9)	93(9)	11(7)	22(6)	15(6)
C(66)	58(10)	59(9)	113(12)	0(8)	13(8)	0(7)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 5.

	x	y	z	U(eq)
H(2)	364	4844	7770	45
H(4A)	3843	4966	8936	61
H(4B)	2653	5521	8722	61
H(4C)	4503	5514	8457	61
H(5A)	-572	4472	6151	59
H(5B)	-214	3834	6541	59
H(5C)	829	4043	5853	59
H(7)	8319	3102	8270	35
H(9A)	7676	4796	8670	50
H(9B)	9012	4309	8970	50
H(9C)	7132	4253	9189	50
H(10A)	6016	2677	6394	50
H(10B)	6841	2334	7114	50
H(10C)	7987	2630	6514	50
H(11)	6212	5090	7748	22
H(13A)	7734	5114	5172	30
H(13B)	6397	5625	5305	30
H(14)	5806	4575	4398	32
H(15A)	7101	5091	3561	39
H(15B)	6938	5710	4004	39
H(16A)	5171	6018	3071	53
H(16B)	5133	5365	2693	53
H(17)	2313	5641	3017	49
H(18A)	3642	4553	3436	45
H(18B)	1767	4723	3653	45
H(19)	3110	4893	4903	39
H(21A)	5040	6293	4386	63
H(21B)	3888	6322	5083	63
H(21C)	3339	6660	4313	63
H(22A)	592	6104	4086	77
H(22B)	982	5863	4926	77
H(22C)	531	5399	4257	77
H(23A)	3942	3058	5364	47
H(23B)	4897	3427	4752	47
H(23C)	3006	3578	4884	47
H(32)	6752	8292	6663	30

H(34A)	7990	6871	6007	44
H(34B)	6325	7252	5862	44
H(34C)	6350	6677	6401	44
H(35A)	8850	8714	8619	47
H(35B)	7133	8934	8216	47
H(35C)	8824	9042	7817	47
H(37)	14503	6498	7299	35
H(39A)	10413	5819	6631	51
H(39B)	12248	5855	6349	51
H(39C)	10958	6384	6149	51
H(40A)	15361	7452	8433	45
H(40B)	15269	6891	8992	45
H(40C)	14098	7461	9090	45
H(41)	8603	6317	7356	24
H(43A)	7078	6270	9820	32
H(43B)	8383	6693	10279	32
H(44)	9061	5507	9749	42
H(45A)	7759	5226	10742	64
H(45B)	7882	5876	11122	64
H(46A)	9716	5492	11997	71
H(46B)	9791	4872	11545	71
H(47)	12533	5321	11671	45
H(48A)	11279	4913	10290	76
H(48B)	13112	5225	10357	76
H(49)	11631	6081	9797	44
H(51A)	14171	6339	11533	126
H(51B)	13745	6706	10771	126
H(51C)	14286	6017	10733	126
H(52A)	9738	6503	11430	91
H(52B)	11059	6999	11218	91
H(52C)	11342	6622	11982	91
H(53A)	11526	8322	9617	53
H(53B)	11698	7803	10240	53
H(53C)	9997	8165	10110	53
H(61A)	4527	3930	9610	109
H(61B)	4162	3496	10297	109
H(61C)	2660	3791	9799	109
H(62A)	3128	2774	9504	83
H(62B)	4902	2959	9240	83
H(63A)	3640	3516	8239	66
H(63B)	1860	3336	8505	66
H(64A)	4161	2513	7906	77

H(64B)	2453	2303	8225	77
H(65A)	2735	3042	6938	78
H(65B)	1009	2867	7268	78
H(66A)	1634	2233	6176	115
H(66B)	1324	1834	6903	115
H(66C)	3171	1956	6670	115
H(71A)	9159	2371	4956	97
H(71B)	8380	3016	5111	97
H(71C)	10202	2966	4817	97
H(71D)	9659	2898	5272	97
H(71E)	9741	2486	4537	97
H(71F)	7996	2627	4873	97
H(76A)	6269	4497	1529	113
H(76B)	5532	3832	1549	113
H(76C)	7420	3934	1366	113
H(76D)	6063	3894	1192	113
H(76E)	7524	4302	1562	113
H(76F)	5701	4353	1854	113
H(72A)	7273	2613	3951	47
H(72B)	9089	2572	3659	47
H(73A)	7369	3675	3889	47
H(73B)	9214	3644	3620	47
H(74A)	6458	3150	2744	45
H(74B)	8295	3221	2471	45
H(75A)	6118	4197	2771	66
H(75B)	8001	4298	2588	66
H(74C)	6859	3998	3256	56
H(74D)	8677	3961	2965	56
H(72C)	8271	3659	4543	84
H(72D)	10014	3515	4203	84
H(75C)	7708	3322	2003	91
H(75D)	5897	3370	2290	91
H(73C)	6970	2993	3624	102
H(73D)	8713	2908	3265	102

EXPERIMENTAL SECTION

General Procedures

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or a glovebox. Solvents were predried over sodium wire and distilled under nitrogen from sodium (toluene and *n*-hexane) or sodium-benzophenone (THF and diethyl ether). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. The starting materials $ZnMe_2$, (-)-*cis*-myrtanylamine, diphenylacetyl chloride, Et_3N, ^nBuLi and KO^tBu were used as purchased, and the 3,5-dimethylpyrazole[4] and PPh_3Br_2[5] were prepared as described in the literature. *rac*-Lactide was sublimed twice, recrystallized from THF and finally sublimed again prior to use.

Instruments and Measurements

NMR spectra were recorded on a Bruker Avance Neo 500 (^1H NMR 500 MHz and ^{13}C NMR 125 MHz) spectrometer and were referenced to the residual deuterated solvent signal. Microanalyses were performed with a Perkin-Elmer 2400 CHN analyzer. Mass spectra were recorded on a VG Autospec instrument using the FAB technique and nitrobenzyl alcohol as matrix. The specific rotation $[\alpha]_D^{25}$ was measured at a concentration of 0.1% w/v in toluene at 22 ºC on a JASCO P2000 Polarimeter equipped with a sodium lamp operating at 589 nm with a light path length of 10 cm. The molecular weights (M_n) and the molecular mass distributions (M_w/M_n) of polymer samples were measured by Gel Permeation Chromatography (GPC) performed on a Shimadzu LC-20AD GPC equipped with a TSK-GEL G3000Hxl column and an ELSD-LTII light-scattering detector. The GPC column was eluted with THF at 40 ºC at 1 mL/min and was calibrated using eight monodisperse polystyrene standards in the range 580–483 000 Da. MALDI-ToF MS data were acquired with a Bruker Autoflex II ToF/ToF spectrometer, using a nitrogen laser source (337 nm, 3 ns) in linear mode with a positive acceleration voltage of 20 kV. Samples were prepared as follows: PLA (20 mg) was dissolved in HPLC quality THF with matrix and NaI in a 100:5:5 ratio. Before evaporation, 10 μL of the mixture solution was deposited on the sample plate. External calibration was performed by using Peptide

Calibration Standard II (covered mass range: 700–3 200 Da) and Protein Calibration Standard I (covered mass range: 5 000–17 500 Da). All values are the average of two independent measurements. The microstructures of PLA samples were determined by examination of the methine region in the homodecoupled ^{1}H NMR spectrum of the polymers recorded at room temperature in $CDCl_3$ on a Bruker Avance Neo 500 spectrometer with concentrations in the range 1.0 to 2.0 mg/mL.

Preparation of compounds 1–5.

Synthesis of phosphanimine (1). In a 250 cm^3 Schlenk tube, (-)-*cis*-myrtanylamine (5 cm^3, 4.58 g, 29.85 mmol) was dissolved in dry THF (30 cm^3). A solution of PPh_3Br_2[5] (12.60 g, 29.85 mmol) in THF (50 cm^3) was added. To the yellow-colored mixture was added Et_3N (4,16 mL, 29.85 mmol), leaving the reaction at room temperature during 4 h. After this time, a solution of KO^tBu (3.51 g, 31.29 mmol) in THF (30 cm^3) was added, the reaction mixture was stirred for overnight and the resulting yellow suspension was filtered. The solvent of the solution obtained was removed under reduced pressure to yield **1** as a yellow oil. Yield: 11.20 g, 91%. Anal. Calcd. for $C_{28}H_{32}NP$: C, 81.32; H, 7.80; N, 3.39. Found: C, 81.23; H, 7.82; N, 3.41. ^{1}H NMR (C_6D_6, 297 K), δ 7.8-7.7 (m, 6H, Ph^o), 7.08 (m, 6H, Ph^m), 7.00 (m, 3H, Ph^p), 3.40 (m, 2H, N-$\underline{CH_2}^{Myr}$), 2.75 (m, 1H, H^c), 2.63 (m, 1H, H^b), 2.50, 2.17 (m, 2H, H^d), 1.95 (m, 2H, H^e), 1.65 (m, 1H, H^f), 1.21, 0.94 (s, 6H, Me^g), 1.96, 1.11 (d, 2H, H^h). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K), δ 134.0 ($C^{Ph,i}$), 129.5 ($C^{Ph,o}$), 128.0 ($C^{Ph,m}$), 126.0 ($C^{Ph,p}$), 58.0 (N-$\underline{CH_2}^{Myr}$), 44.2 (C^b), 42.8 (C^c), 41.9 (C^e), 38.7 (C^h), 28.0, 23.9 (Me^g), 26.1 (C^d), 20.1 (C^f). $[\alpha]_D^{25}$ = -7.3 (*c* 1.00, EtOH).

Synthesis of ketenimine (2). In a 250 cm^3 Schlenk tube, phosphanimine **(1) (**10 g, 24.18 mmol) was dissolved in dry THF (50 cm^3). A solution of diphenylketene[6] (4.7 g, 24.18 mmol) in THF (30 cm^3) was added, the reaction mixture was stirred for 4 h at room termperature and a orange suspension was obtained. The solvent was removed under reduced pressure to yield an orange oil. 100 cm^3 of n-hexane was added and the new suspension was leaved to -26ºC overnight to favor the precipitation of triphenylphosfine oxide. The mixture of reaction was filtered and the solution dried under reduced pressure to yield **2** as a orange oil. Yield: 7.49 g, 94%. Anal. Calcd. for $C_{24}H_{27}N$: C, 87.49; H, 8.26; N, 4.25. Found: C, 87.63; H, 8.09; N, 4.28. ^{1}H NMR (C_6D_6, 297 K), δ 7.42 (m, 4H, Ph^o), 7.17 (m, 4H, Ph^m),

7.01 (m, 2H, Ph^p), 3.40 (m, 2H, N-$\underline{CH_2}^{Myr}$), 2.39 (m, 1H, H^c), 2.22, 1.80 (m, 2H, H^d), 1.96 (m, 1H, H^b), 1.70 (m, 2H, H^e), 1.37 (m, 1H, H^f), 1.05, 0,81 (s, 6H, Me^g), 1.78, 0.79 (d, 2H, H^h). ^{13}C-{^1H} NMR (C_6D_6, 297 K), δ 185.9, 185.0 (C=C), 136.0 ($C^{Ph,i}$), 129.0 ($C^{Ph,o}$), 128.0 ($C^{Ph,m}$), 126.0 ($C^{Ph,p}$), 59.2 (N-$\underline{CH_2}^{Myr}$), 44.0 (C^b), 42.3 (C^c), 41.8 (C^g), 38.8 (C^e), 33.2 (C^h), 28.0, 23,8 (Me^g), 26.0 (C^d), 20.0 (C^f). $[\alpha]_D^{25}$ = -22.0 (*c* 1.00, EtOH).

Synthesis of (-)-*cis*-bpmyH (3a) and (-)-*cis*-bpmy'H (3b). In a 250 cm^3 Schlenk tube bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm)[4] (1 g, 4.89 mmol) was dissolved in dry THF (50 mL) and cooled to around –70 º C (acetone/liquid nitrogen). ^{n}BuLi (2.5 M in n-hexane) (1.95 cm^3, 4.89 mmol) was added dropwise, maintaining the reaction temperature at –70 ºC for 1 h to give a yellow suspension. A pre-cooled solution (salt/ice at 0 ºC) of ketenimine **2** (1.61 g, 4.89 mmol) in THF (20 mL) was added dropwise to the suspension. The resulting mixture was allowed to reach 0 ºC and was maintained at this temperature for one hour. After this time a saturated solution of NH_4Cl in water (40 mL) was added to the mixture and the organic layer is decanted into a 250 mL separatory funnel. The resulting organic phase was dried over $MgSO_4$ and solvent was removed under vacuum to give a yellow oil. The product were purified using a plug of silica, eluting with a mixture of AcOEt/*n*-hexane (1:9) to give compound **3** yellow oil as two tautomers mixture (**3a**, **3b**) (1:1). Tautomer **3a** was separated by crystallization at -26 ° C in a hexane solution, while from mother liquor after several recrystallizations, tautomer **3b** was obtained as the majority product. Yield of mixture: 1.77 g, 68%. Anal. Calcd. for $C_{35}H_{43}N_5$: C, 78.76; H, 8.12; N, 13.12. Found: C, 78.45; H, 8.17; N, 13.42. **(-)-*cis*-bpmyH** (**3a**): ^1H NMR (C_6D_6, 297 K), δ 7.42 (m, 4H, Ph^o), 7.15 (m, 4H, Ph^m), 7.01 (m, 2H, Ph^p), 6.78 (s, 1H, CH^a), 5.70, 5.69 (s, 1H, $H^{4,4'}$), 5.36 (t,1H, -$\underline{NH}$-CH_2^{Myr}), 3.17 (m, 2H, NH-$\underline{CH_2}^{Myr}$), 2.5-2.4 (m, 1H, H^c), 2.3 (m, 1H, H^b), 2.21, 1.19 (s, 6H, $Me^{3,3'}$), 1.90 (m, 2H, H^d), 1.80 (m, 2H, H^e), 1.73, 1.70 (s, 6H, $Me^{5,5'}$), 1.60 (m, 1H, H^f), 1.17, 0.91 (s, 6H, Me^g), 2.22, 0.90 (d, 2H, H^h). ^{13}C-{^1H} NMR (C_6D_6, 297 K), δ 148.5, 146.4 (C=C), 148.4 ($C^{Ph,i}$), 148.1, 142.7, 139.7, 139.5 ($C^{3,3',5,5'}$), 129.2 ($C^{Ph,o}$), 128.5 ($C^{Ph,m}$), 126.9 ($C^{Ph,p}$), 126.3 (C^g), 106.5, 106.0 ($C^{4,4'}$), 59.4 (CH^a), 54.1 (N-$\underline{CH_2}^{Myr}$), 44.5 (C^f), 42.0 (C^d), 41.8 (C^e), 41.7 (C^c), 38.2 (C^h), 31.8 (C^b), 27.8, 23.1 (Me^g), 13.8, 11.7 ($Me^{3,3'}$), 10.0, 9.9 ($Me^{5,5'}$). **(-)-*cis*-bpmy'H** (**3b**): ^1H NMR (C_6D_6, 297 K), δ 7.40 (m, 4H, Ph^o), 7.17 (m, 4H, Ph^m), 7.03 (m, 2H, Ph^p), 7.00 (s, 1H, CH^a),

5.65, 5.60 (s, 2H, $H^{4,4'}$), 5.38 (s, 1H, $\underline{CH}Ph_2$), 3.28 (m, 2H, N-$\underline{CH_2}^{Myr}$), 2.60 (m, 1H, H^c), 2.60, 2,28 (s, 6H, $Me^{3,3'}$), 2.20 (m, 1H, H^b), 2.21, 1.19 (s, 6H, $Me^{5,5'}$), 1.80, 1.70 (m, 2H, H^d), 1.65 (m, 2H, H^e), 1.50 (m, 1H, H^f), 1.05, 0.80 (s, 6H, Me^g), 0.61, 0.29 (d, 2H, H^h). ^{13}C-{^1H} NMR (C_6D_6, 297 K), δ 143.4, 143.3 (C=C), 148.4 ($C^{Ph,i}$), 148.0, 140.8, 133.5, 133.4 ($C^{3,3',5,5'}$), 129.3 ($C^{Ph,o}$), 128.6 ($C^{Ph,m}$), 126.9 ($C^{Ph,p}$), 125.4 (C^g), 105.0, 104.5 ($C^{4,4'}$), 69.1 (CH^a), 54.7 (N-$\underline{CH_2}^{Myr}$), 52.5 ($\underline{CH}Ph_2$), 49.1 (C^c), 44.0 (C^f), 41.6 (C^d), 38.1 (C^e), 33.7 (C^b), 33.0 (C^h), 27.9, 23.0 (Me^g), 13.9, 11.9 ($Me^{3,3'}$), 13.8, 11.7 ($Me^{5,5'}$). $[\alpha]_D^{25}$ of **3** = -5.1 (*c* 1.00, EtOH).

Synthesis of [ZnMe(κ³-(-)-*cis*-bpmy)] (4). In a 250 cm^3 Schlenk tube the scorpionate ligand **3** (1.0 g, 1.87 mmol) was dissolved in dry toluene. $ZnMe_2$ (0.94 mL, 1.87 mmol, 2.0 M in toluene) was added and the mixture was heated at 80 ºC for 72 h. The crude reaction mixture was dried under reduced pressure, resulting a sticky orange solid. Yield: 1.07 g, 93%. Anal. Calcd. for $C_{36}H_{45}N_5Zn$: C, 70.52; H, 7.40; N, 11.42; Found: C, 70.53; H, 7.27; N, 11.38. mp 134-136 ºC. ^1H NMR (C_6D_6, 297 K), δ 7.30 (m, 4H, Ph^o), 7.10 (m, 4H, Ph^m), 7.02 (s, 1H, CH^a), 7.00 (m, 2H, Ph^p), 5.32, 5.29 (s, 2H, $H^{4,4'}$), A 3.23, B 3.18, X 2.89 [ABX, J_{AB} = 13.4, J_{AX} = 7.4, J_{BX} = 8.3 Hz (N-$\underline{CH_2}^{Myr}$, H^c)] 2.30 (m, 1H, H^b), 2.10 (s, 6H, $Me^{3,3'}$), 1.90 (m, 2H, H^d), 1.80 (m, 2H, H^e), 1.70, 1.62 (s, 6H, $Me^{5,5'}$), 1.25 (m, 1H, H^f), 1.70, 1.11 (d, 2H, H^h), 1.09, 0.89 (s, 6H, Me^g), 0.11 (s, 1H, Zn-Me). ^{13}C-{^1H} NMR (C_6D_6, 297 K), δ 152.0, 148.0 (C=C), 148.0, 140.0, 132.0, 131.0 ($C^{3,3',5,5'}$), 139.1 ($C^{Ph,i}$), 130.0 ($C^{Ph,o}$), 129.0 ($C^{Ph,m}$), 124.2 ($C^{Ph,p}$), 105.5 ($C^{4,4'}$), 66.5 (CH^a), 61.0 (N-$\underline{CH_2}^{Myr}$), 44.0 (C^b), 42.0 (C^c), 38.5 (C^e), 33.5 (C^h), 28.1, 23.0 (Me^g), 26.0 (C^d), 20.1 (C^f), 12.5 ($Me^{3,3'}$), 10.2, 9.8 ($Me^{5,5'}$), -16.0 (ZnMe). $[\alpha]_D^{25}$ = -9.1 (*c* 1.00, EtOH). Mass spectrum (FAB): (*m*/*z* assignment, % intensity): 612,3 $[ZnMe(bpmy) + H]^+$, 100.

Synthesis of [ZnMe(κ³-(-)-*cis*-bpmyO)] (5). In a 250 cm^3 Schlenk tube the complex **4** (1.5 g, 2.45 mmol) was dissolved in dry *n*-hexane (25 cm^3). After 72 hours at room temperature in an air atmosphere were obtained complex **5** as pale orange crystals suitable for X-ray diffraction. Yield: 0.42 g, 37%. Anal. Calcd. for $C_{23}H_{35}ON_5Zn$: C, 59.67; H, 7.62; N, 15.13. Found: C, 59.75; H, 7.48; N, 15.22. mp 177-179 ºC**.** ^1H NMR (C_6D_6, 297 K), δ 6.67 (s, 1H, CH^a), 5.24, 5.23 (s, 2H, $H^{4,4'}$), A 3.89, B 3.67, X 2,83 [ABX, J_{AB} = 12.2, J_{AX} = 7.8, J_{BX} = 8.2 Hz (N-$\underline{CH_2}^{Myr}$, H^c)], 2.39, 2.00 (m, 2H, H^d), 2.24 (m, 1H, H^b), 2.08, 2.04

(s, 6H, $Me^{3,3'}$), 1.80 (m, 2H, H^e), 1.78, 1.77 (s, 6H, $Me^{5,5'}$), 1.70 (m, 1H, H^f), 1.25, 1.22 (s, 6H, Me^g), 2.10, 1.00 (d, 2H, H^h), 0.12 (s, 1H, Zn-Me). ^{13}C-{^1H} NMR (C_6D_6, 297 K), δ 166.0 (C=O), 149.0, 141.0, 132.0, 130.0 ($C^{3,3'5,5'}$), 71.0 (CH^a), 51.0 (N-$\underline{CH_2}$), 44.5 (C^b), 43.0 (C^c), 39.0 (C^e), 34.0 (C^h), 31.0, 24.0 (Me^g), 27.0 (C^d), 20.5 (C^f), 14.0, 12.5 ($Me^{3,3'}$), 10.0, 9.9 ($Me^{5,5'}$), -16.0 (ZnMe). $[\alpha]_D^{25}$ = -3.3 (*c* 1.00, EtOH). Mass spectrum (FAB): (*m*/*z* assignment, % intensity): 829,4 $[Zn(bpmyO)_2 + H]^+$, 100; 462,2 $[ZnMe(bpmyO) + H]^+$, 23.

Typical Polymerization Procedures.

Polymerizations of *rac*-lactide (LA) were performed on a Schlenk line in a flame-dried Schlenk tube equipped with a magnetic stirrer. The Schlenk tubes were charged in a glovebox with the required amount of LA and initiator, separately, and then attached to the vacuum line. The initiator and LA were dissolved in the appropriate amount of solvent and temperature equilibration was ensured in both Schlenk tubes by stirring the solutions for 15 min in a bath. Next, the appropriate amount of initiator was added by using a syringe and polymerization times were measured from that point. Polymerizations were stopped by injecting a solution of acetic acid in water (0.35 M). Polymers were precipitated in methanol, filtered off, redissolved and reprecipitated in methanol, and dried in vacuo to a constant weight.

X-ray Crystallographic Structure Determination for Complex 5.

The single crystal for **5** was mounted on a glass fibber and transferred to a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite monochromated MoKα radiation source (λ= 0.71073 Å). The highly redundant datasets were integrated using SAINT[7] and corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements with the program SADABS.[8]

The software package WINGX[9] was used for structure solution and refinement by full-matrix least-squares methods based on F^2. A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating

series of least-squares cycles and difference Fourier maps. The compound crystallise with one molecule of hexane in the asymmetric unit disordered over two positions. DFIX restrain and isotropic refinement were necessary for this molecule. The remaining non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

References

[1] (a) J. Baran, A. Duda, A. Kowalski, R. Szymanski and S. Penczek, *Macromol. Rapid Commun.* 1997, **18**, 325–333; (b) I. Barakat, P. Dubois, R. Jérôme and P. Teyssié, *J. Polym. Sci., Part A: Polym. Chem.* 1993, **31**, 505–514.

[2] T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc*. 2002, **124**, 1316–1326.

[3] M. T. Zell, B. E. Padden, A. J. Paterick, K. A. M. Thakur, R. T. Kean, M. A. Hillmyer and E. J. Munson, *Macromolecules* 2002, **35**, 7700–7707.

[4] (a) J. Sebastian, P. Sala, J. Del Mazo, M. Sancho, C. Ochoa, J. Elguero, J. P. Fayet and M. C. Vertut, *J. Heterocyclic Chem.* 1982, **19**, 1141–1145. (b) E. Díez-Barra, A. de la Hoz, A. Sánchez-Migallon and J. Tejeda, *J. Chem. Soc., Perkin Trans.* 1993, **1**, 1079–1083.

[5] K. W. Lee and L. A. Singer, *J. Org. Chem.* 1974, **39**, 3780–3781.

[6] E. C. Taylor, A. Mckillop and G. H. Hawks, *Org. Syn.*, 1973, **52**, 36–37.

[7] SAINT v8.37, Bruker-AXS (2016), APEX3 v2016.1.0. Madison, Wisconsin, USA.

[8] SADABS, L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, Comparison of Silver and Molybdenum Microfocus X-Ray Sources for Single-Crystal Structure Determination. *J. Appl. Crystallogr.* 2015, **48**, 3–10.

[9] (a) L. J. Farrugia, WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* 2012, **45**, 849–854; (*b*). G. M. Sheldrick, SHELX-2014, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 2014.