

# Synthesis, Structures, and Ring Opening Polymerization of *rac*-Lactide with Tridentate vs Bidentate Cobalt(II), Zinc(II) and Cadmium(II) Complexes Containing *N*-Substituted *N,N*-Bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amines

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## Electronic Supporting Information

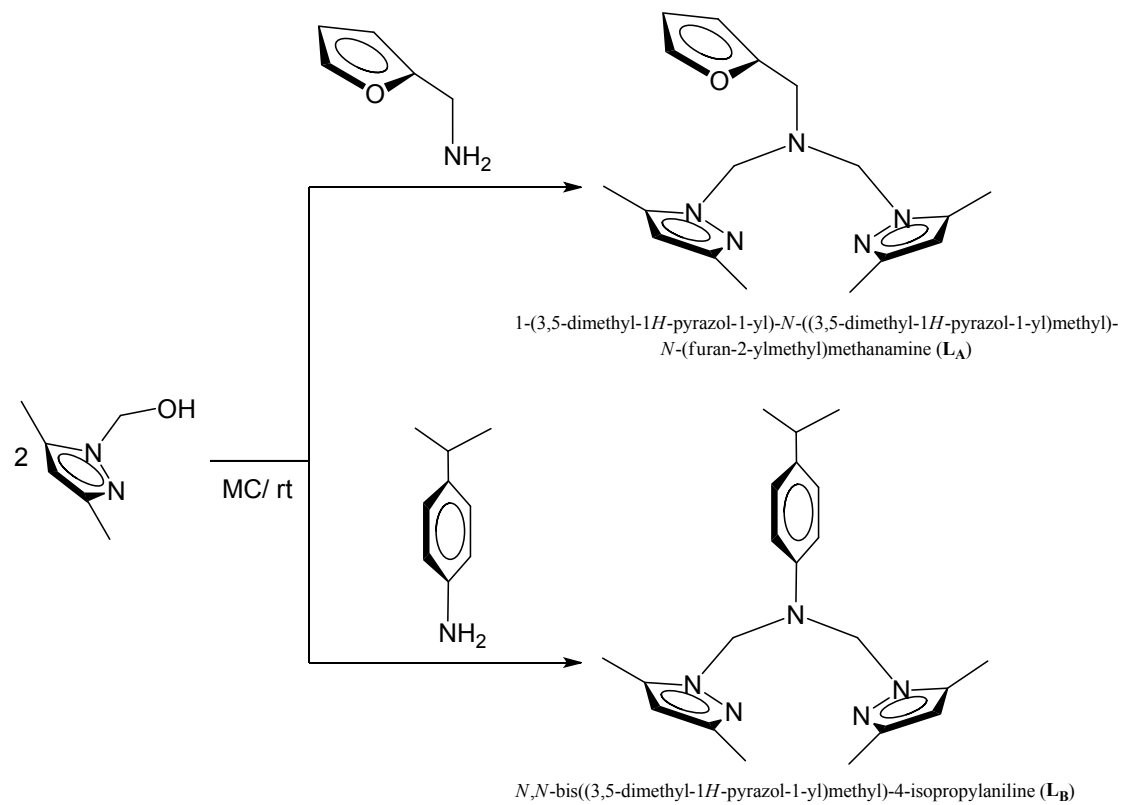
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**Scheme S1.** Synthetic route of Co(II), Zn(II), and Cd(II) complexes supported with *N'*-Substituted *N,N*-Bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amines derivatives.



**Figure S1.**  $^1\text{H}$  NMR of  $\text{L}_A$

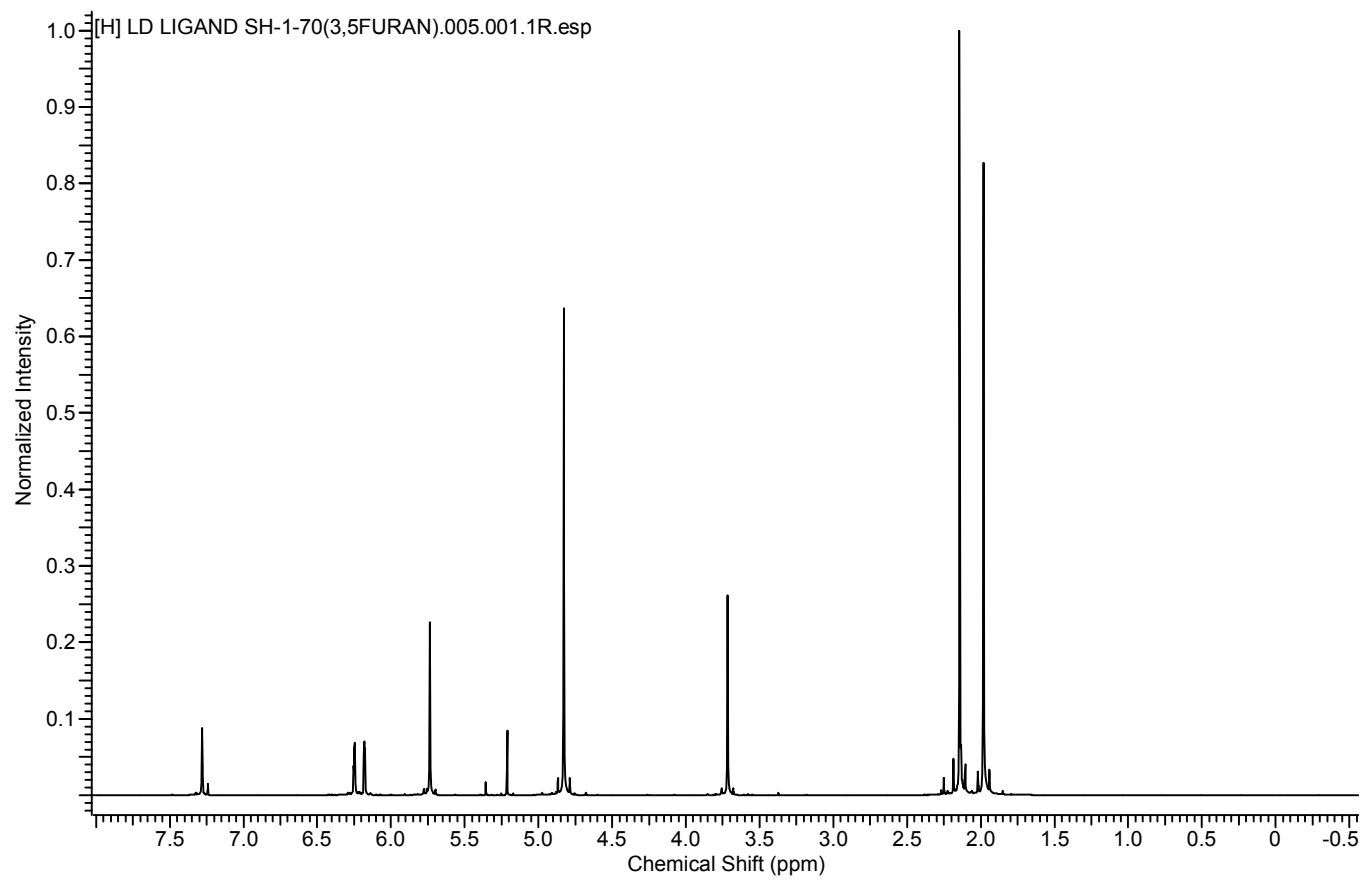


Figure S2.  $^1\text{H}$  NMR of  $\text{L}_\text{B}$

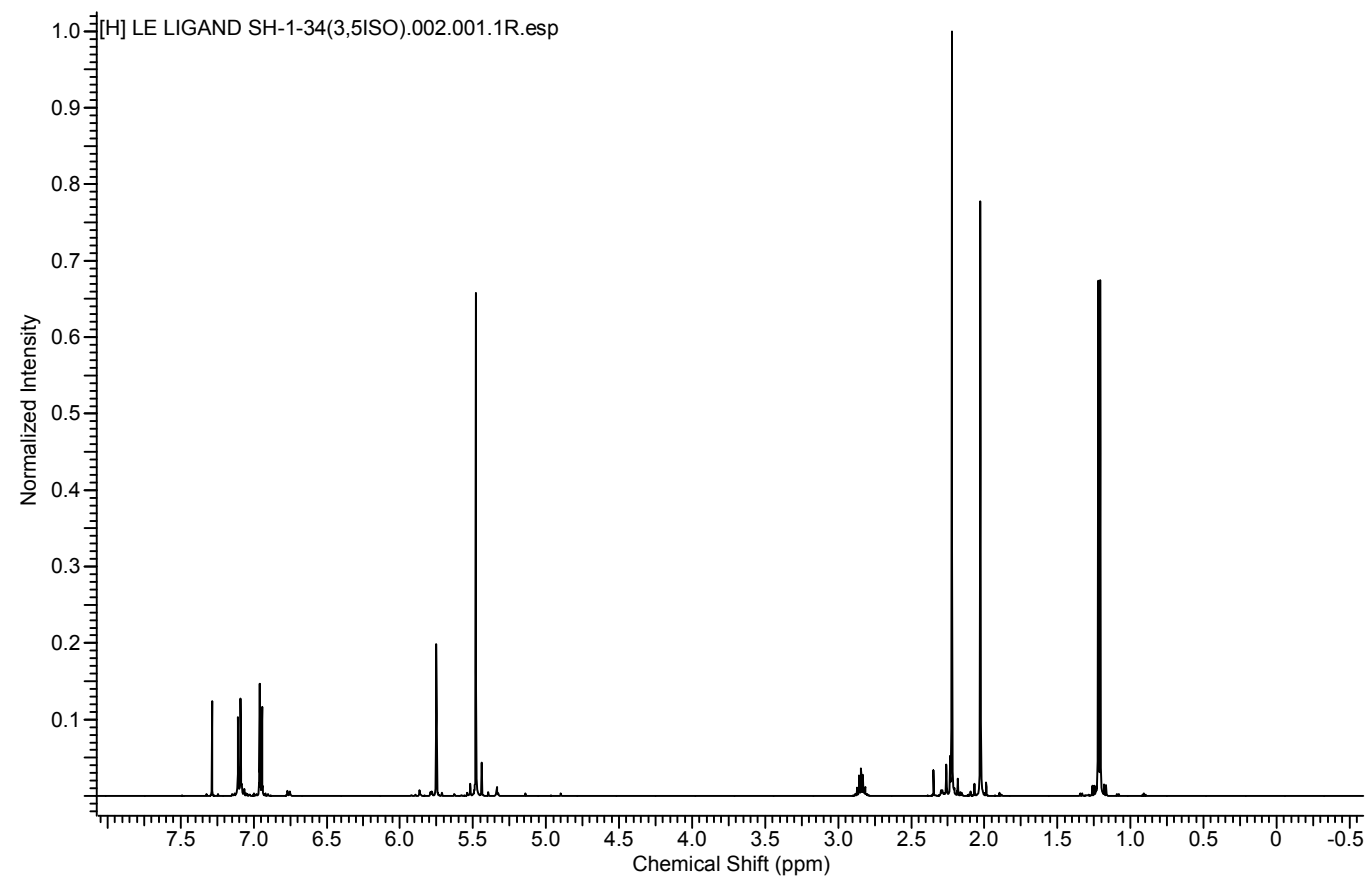


Figure S3.  $^1\text{H}$  NMR of  $[\text{L}_A\text{ZnCl}_2]$

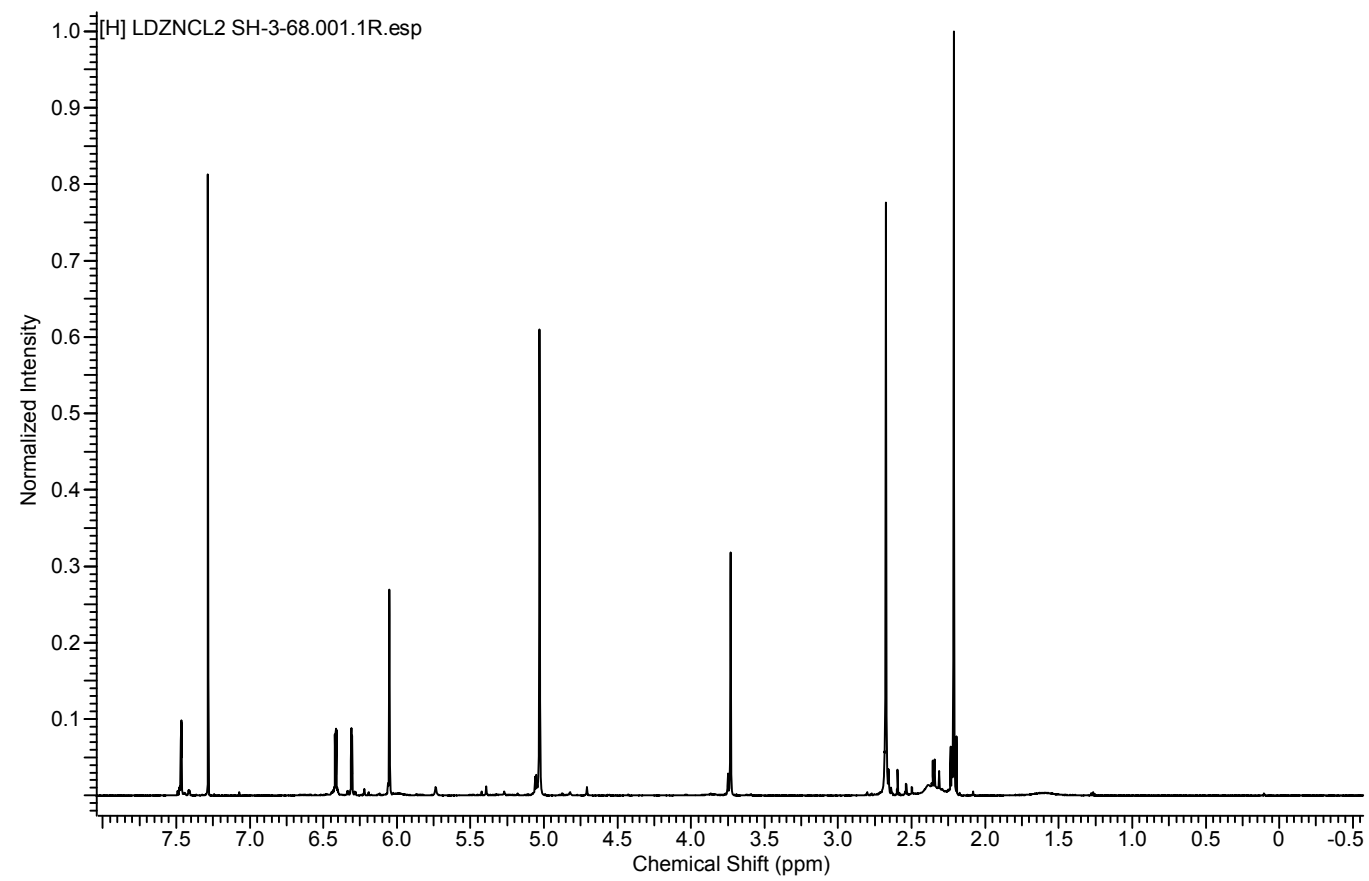




Figure S4.  $^1\text{H}$  NMR of  $[\text{L}_A\text{CdBr}_2]$

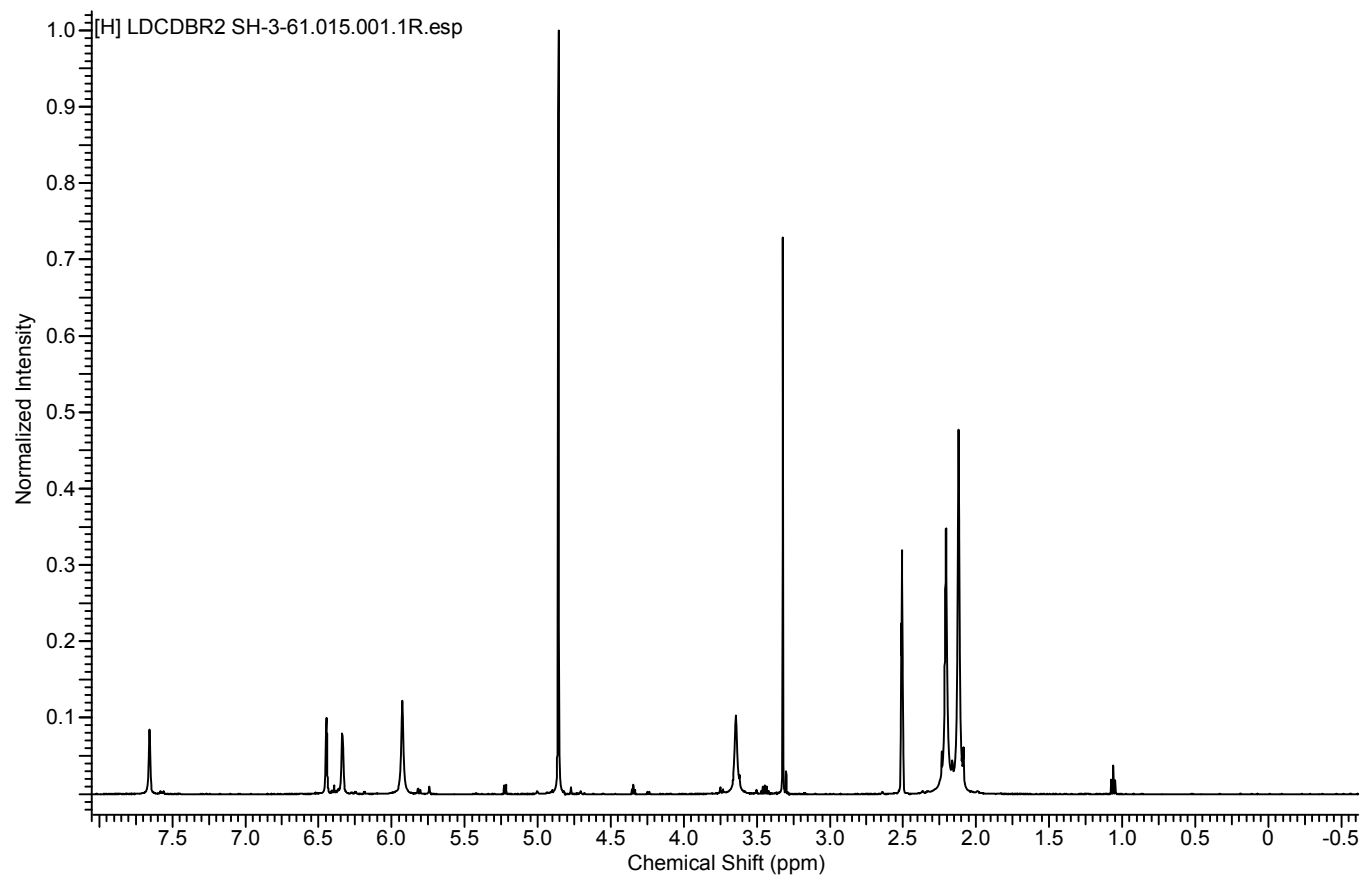
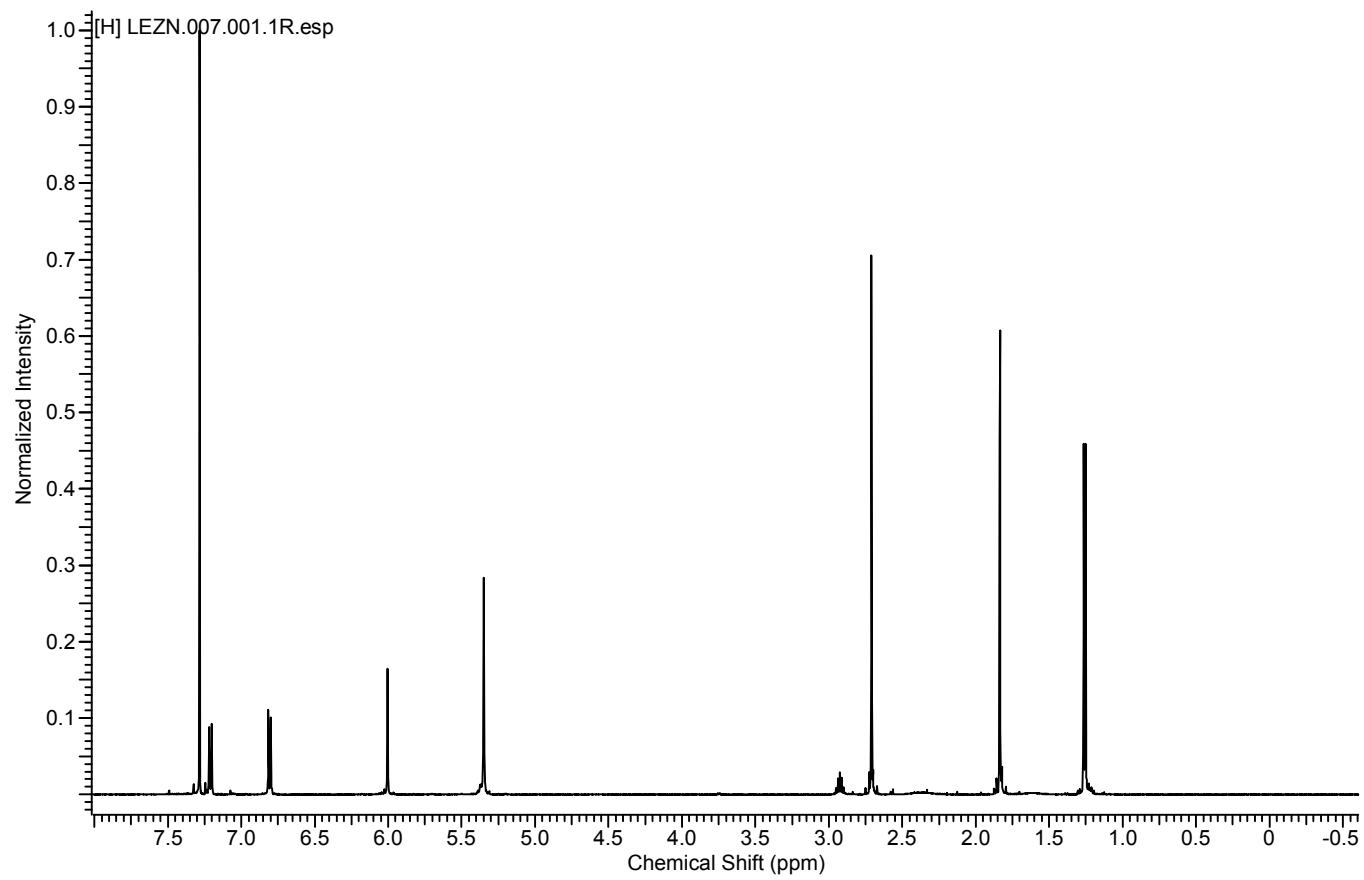
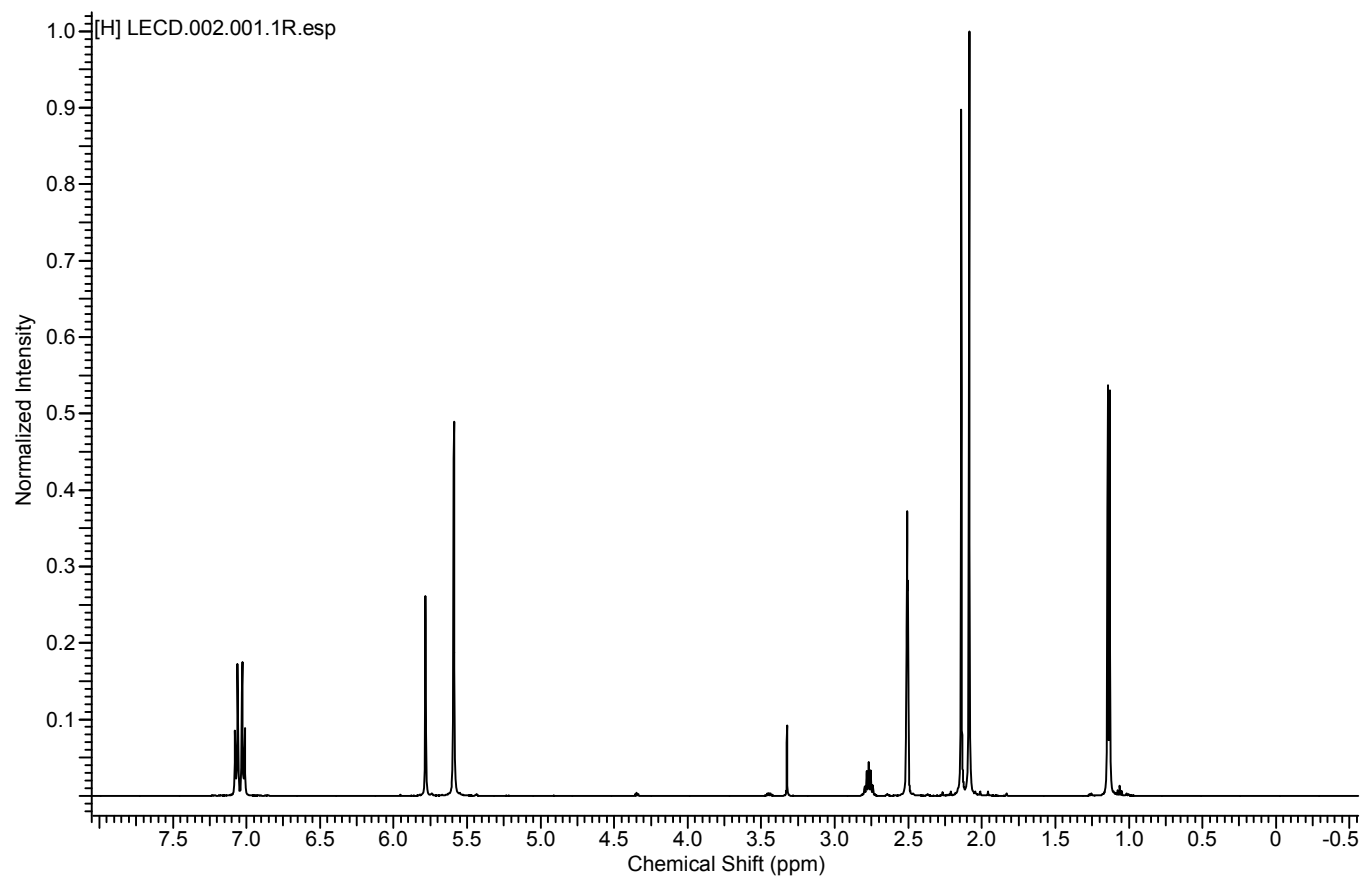


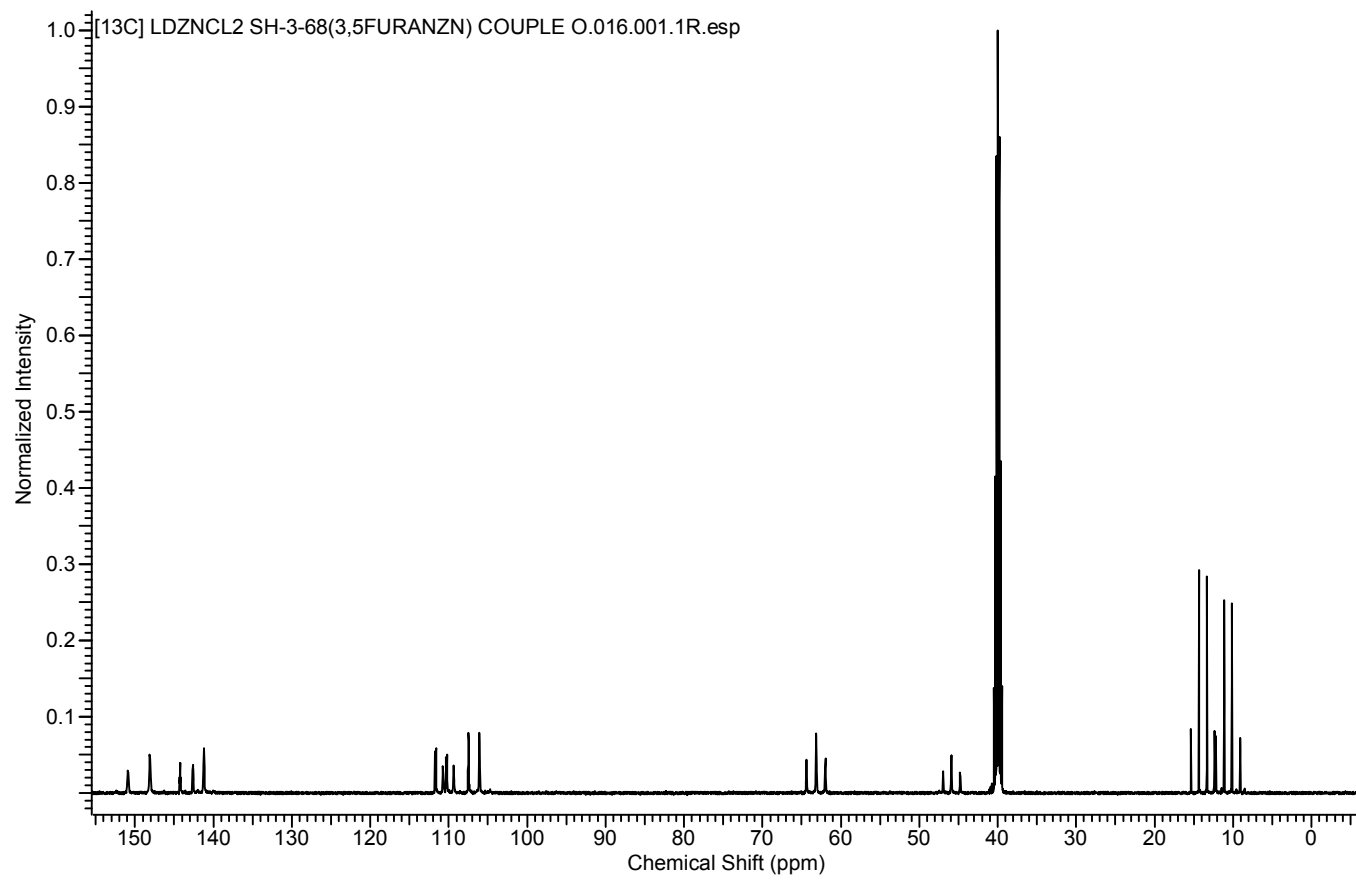
Figure S5.  $^1\text{H}$  NMR of  $[\text{L}_B\text{ZnCl}_2]$



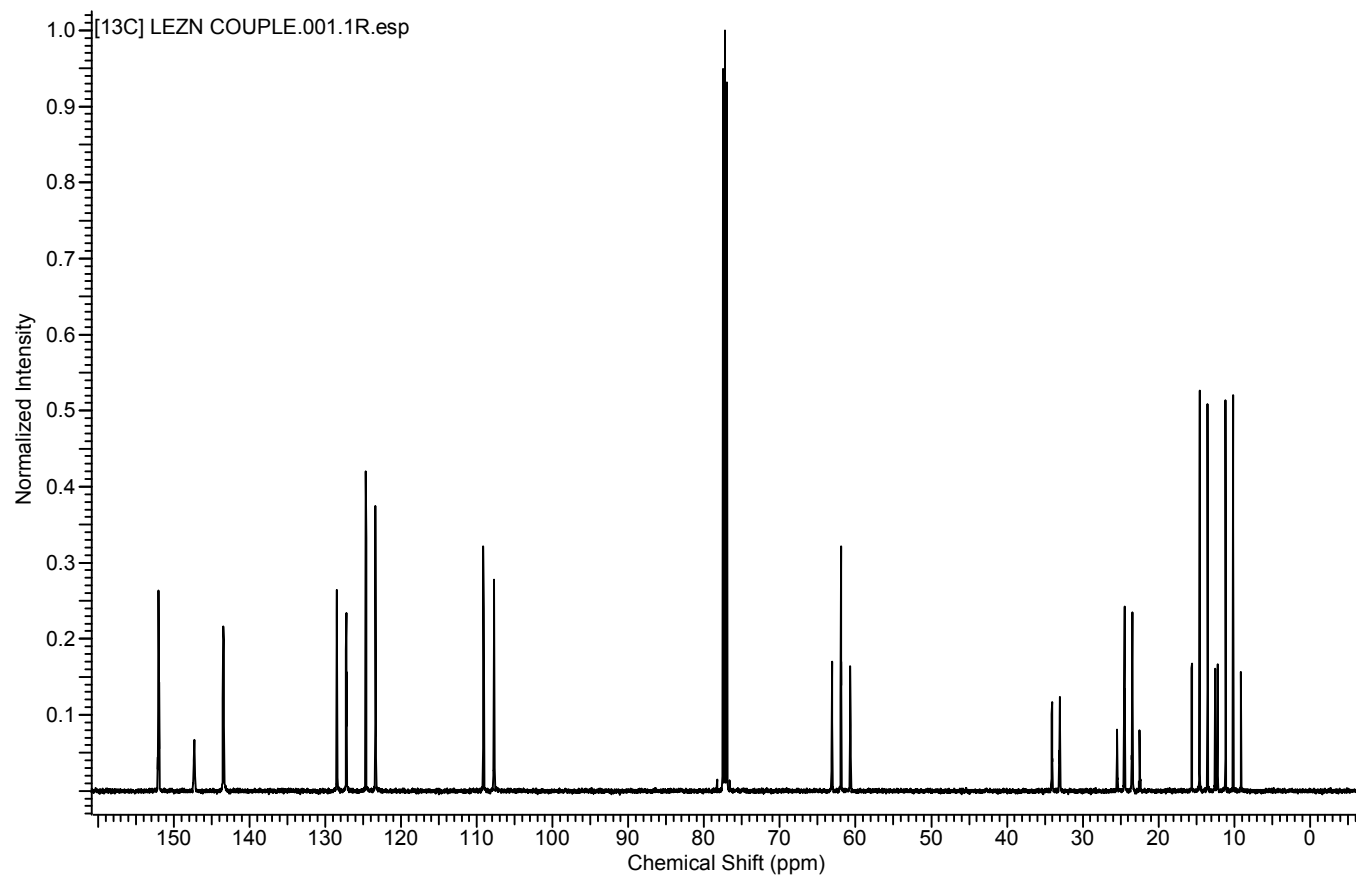
**Figure S6.**  $^1\text{H}$  NMR of  $[\text{L}_\text{B}\text{CdBr}_2]$



**Figure S7.**  $^{13}\text{C}$  NMR of  $[\text{L}_A\text{ZnCl}_2]$



**Figure S8.**  $^{13}\text{C}$  NMR of  $[\text{L}_B\text{ZnCl}_2]$



**Figure S9.**  $^{13}\text{C}$  NMR of  $[\text{L}_\text{B}\text{CdBr}_2]$

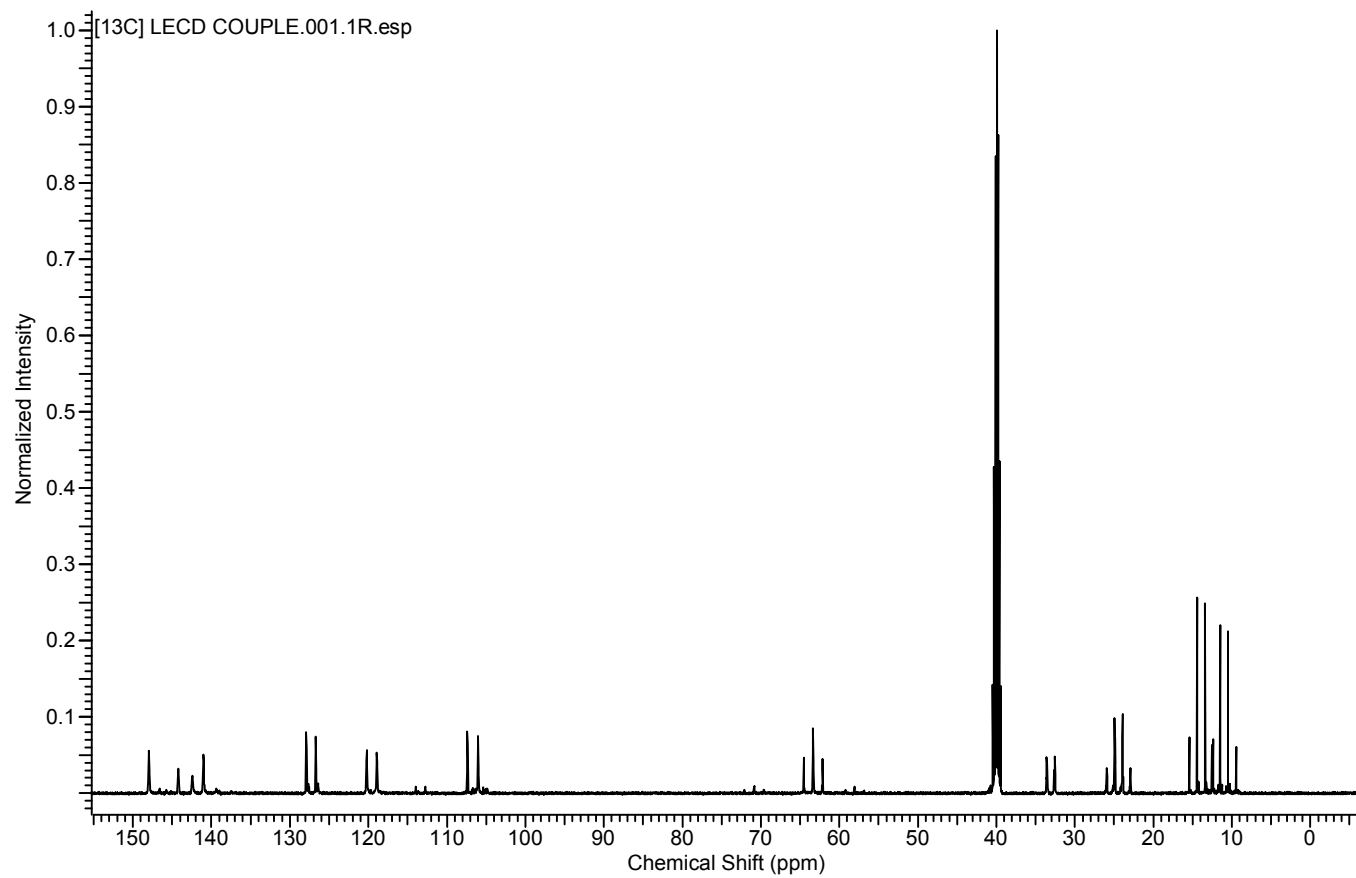
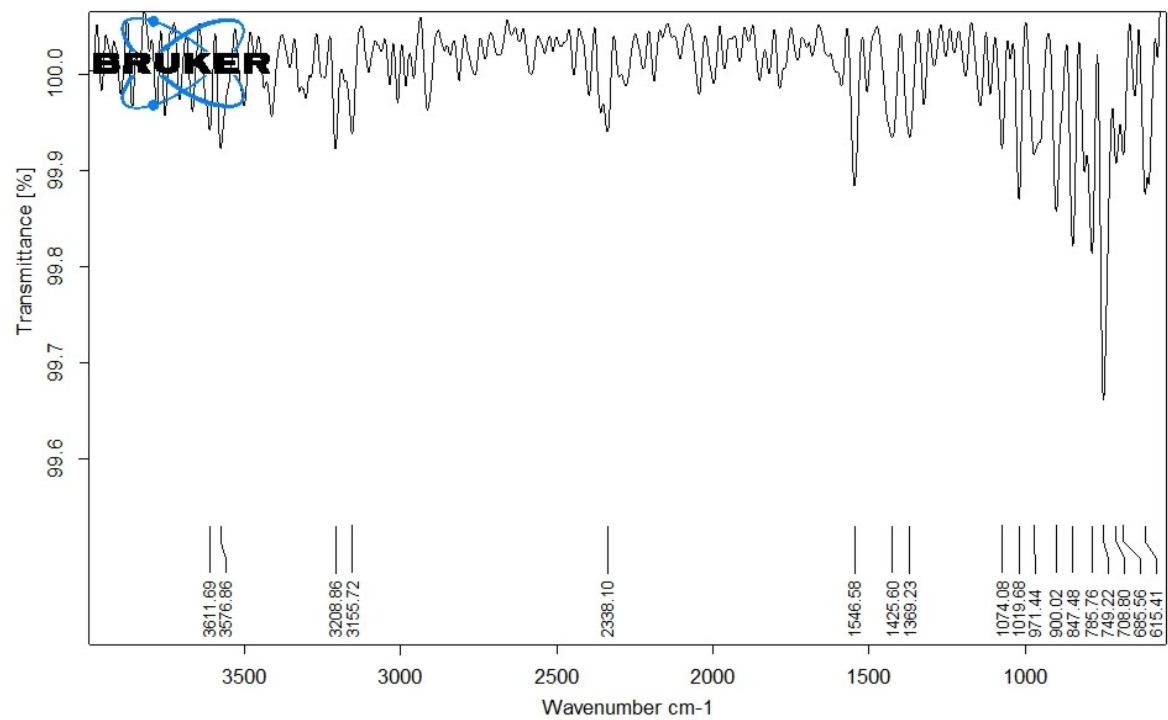
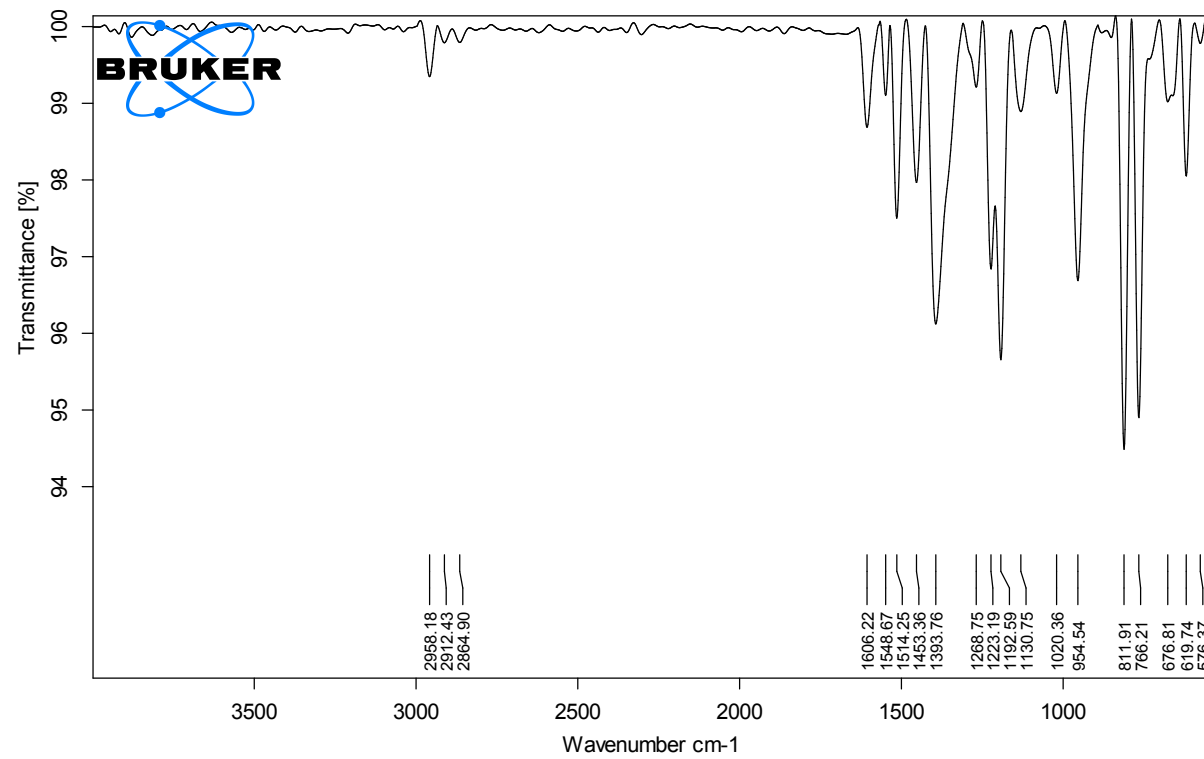


Figure S10. FTIR spectrum of L<sub>A</sub>



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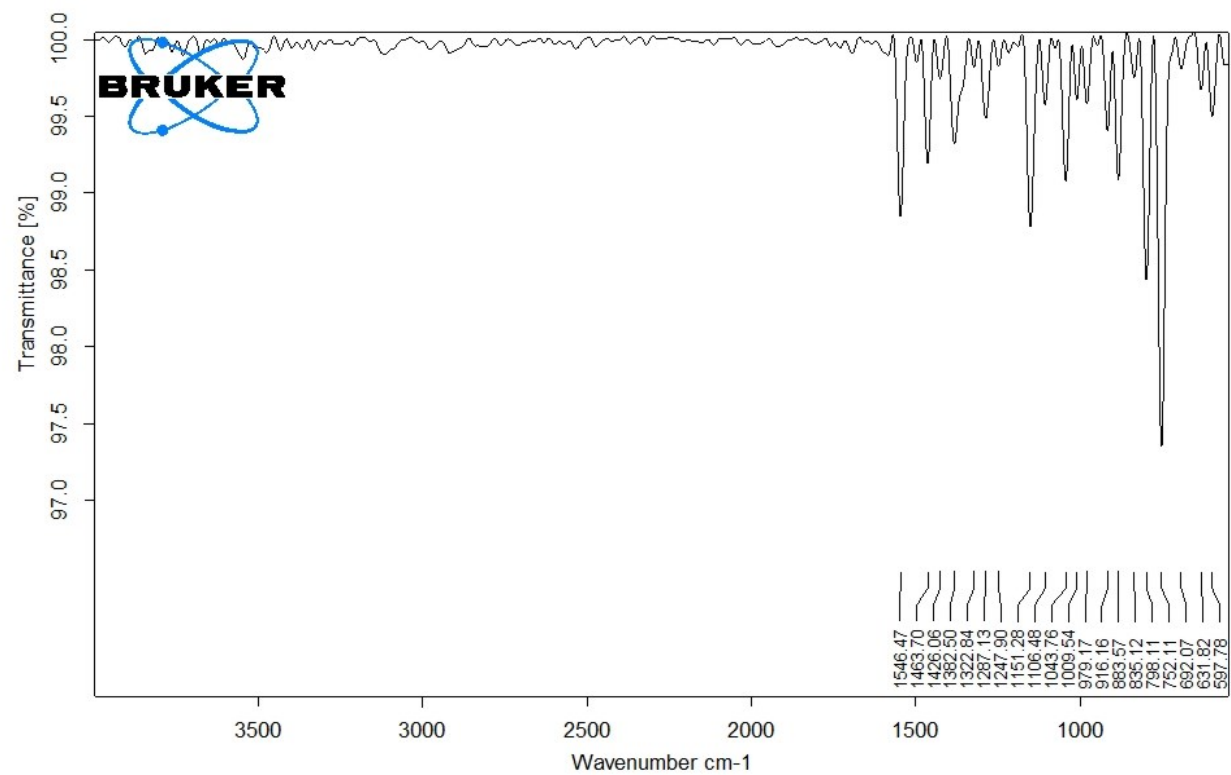
Figure S11. FTIR spectrum of **L<sub>B</sub>**



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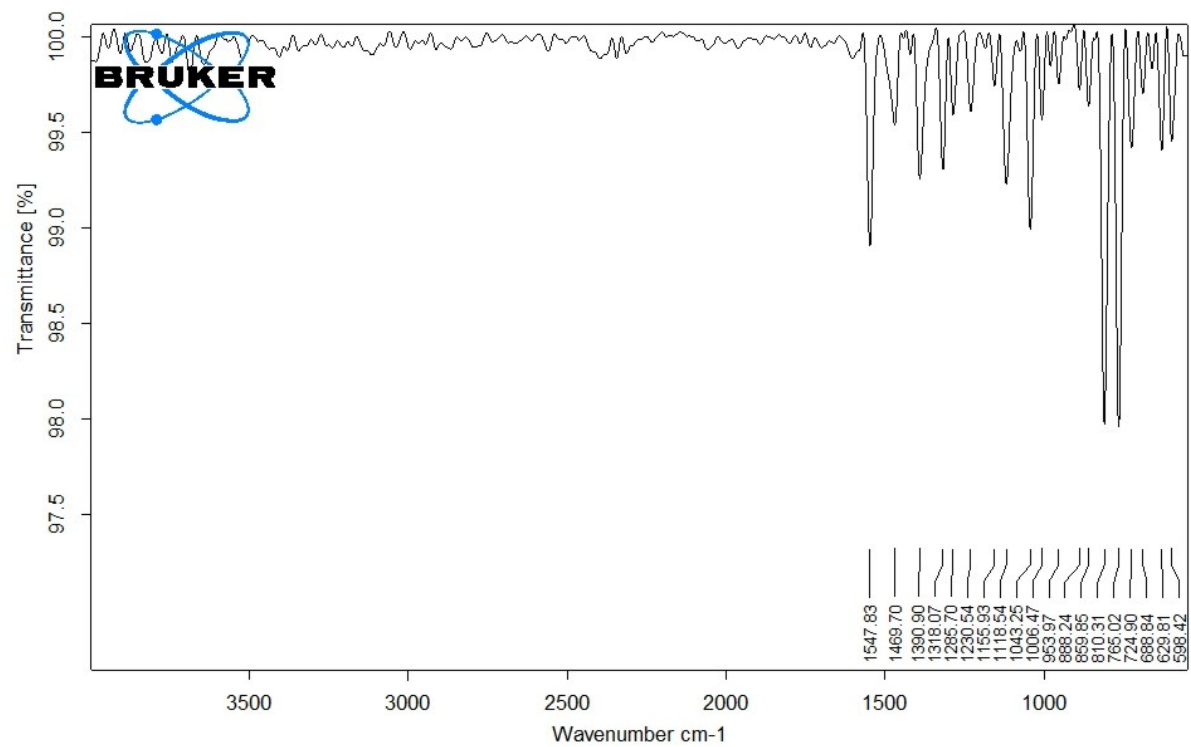


Figure S12. FTIR spectrum of [L<sub>A</sub>CoCl<sub>2</sub>]



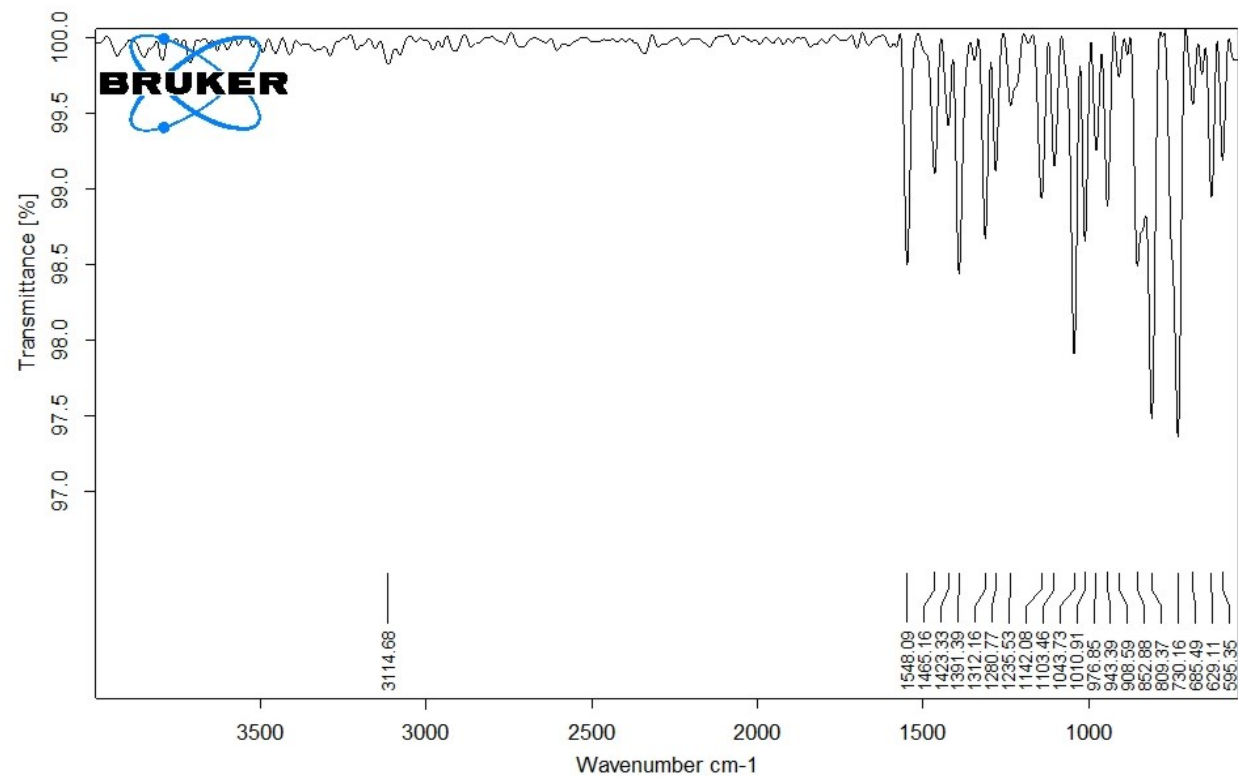
D:\실험\결과\FTIR\3,5 furan\3,5furanCo2.0	3,5furanCo2	ATR eco ZnSe	2020-06-26
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Figure S13. FTIR spectrum of [L<sub>A</sub>ZnCl<sub>2</sub>]



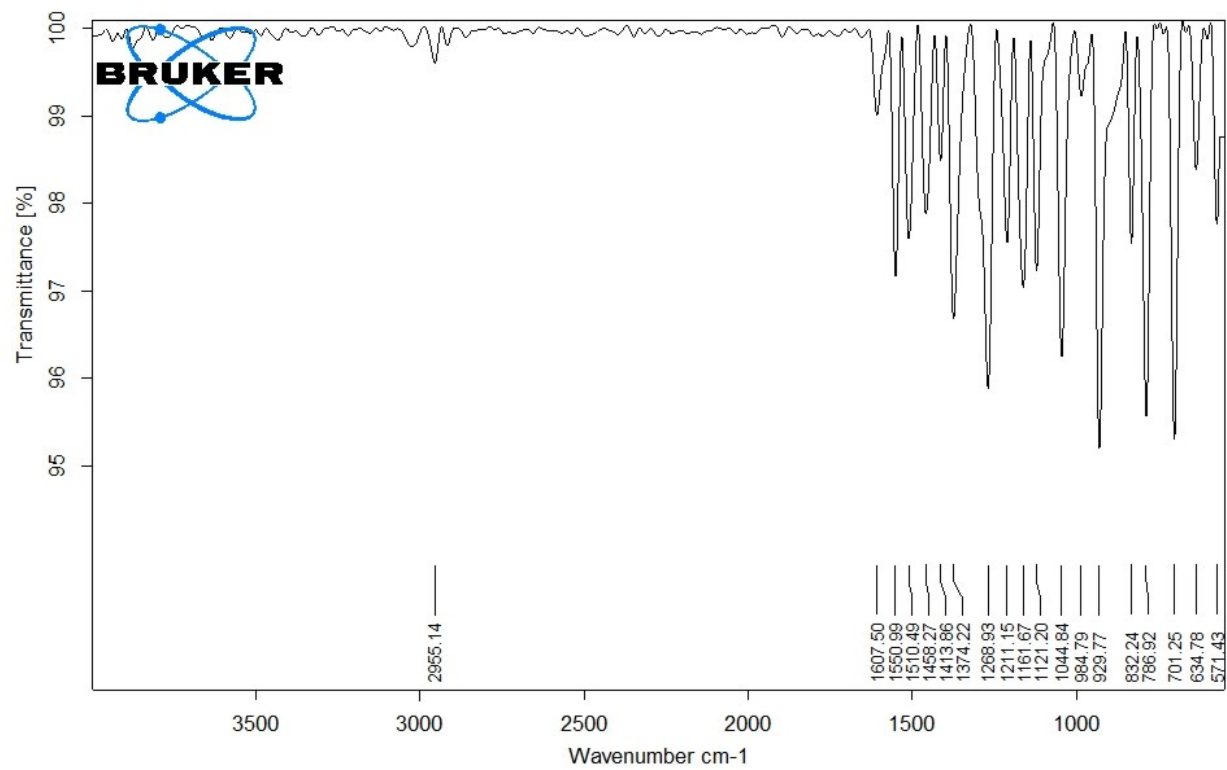
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Figure S14. FTIR spectrum of [L<sub>A</sub>CdBr<sub>2</sub>]



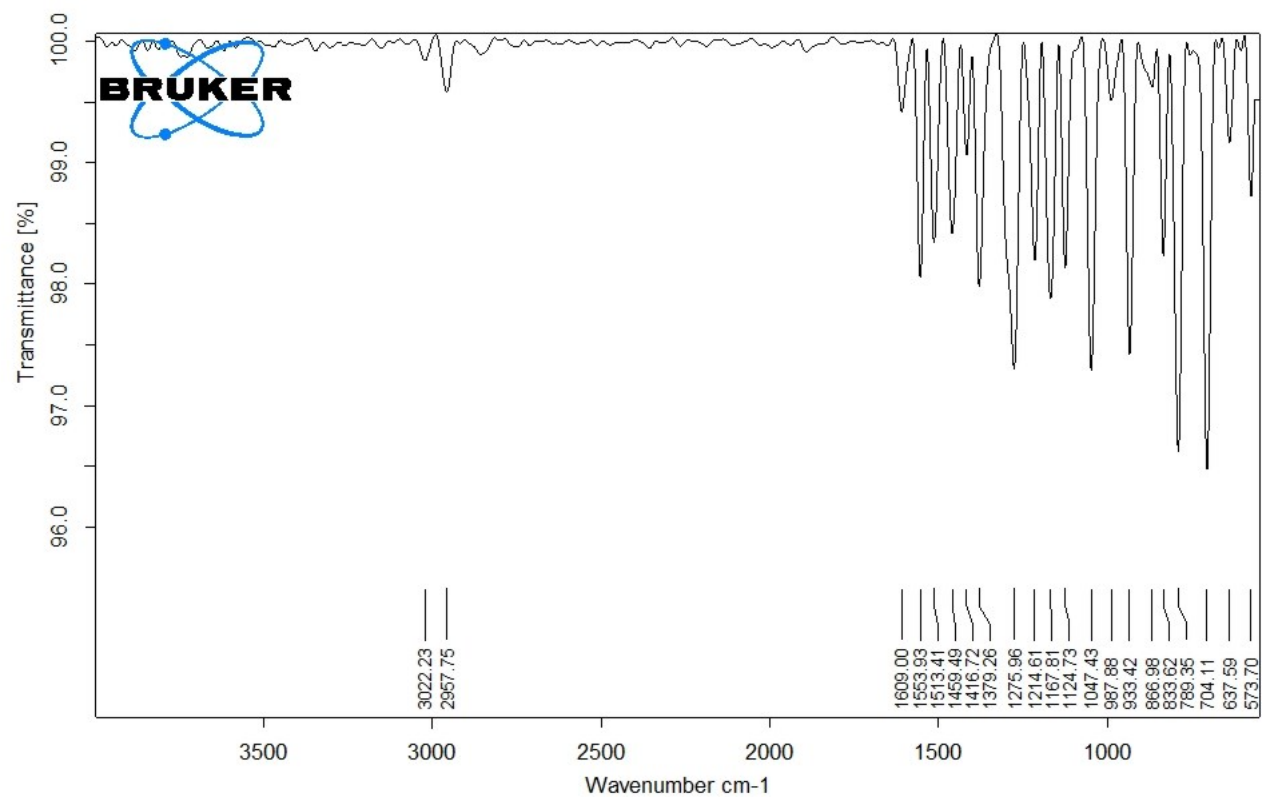
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Figure S15. FTIR spectrum of [L<sub>B</sub>CoCl<sub>2</sub>]



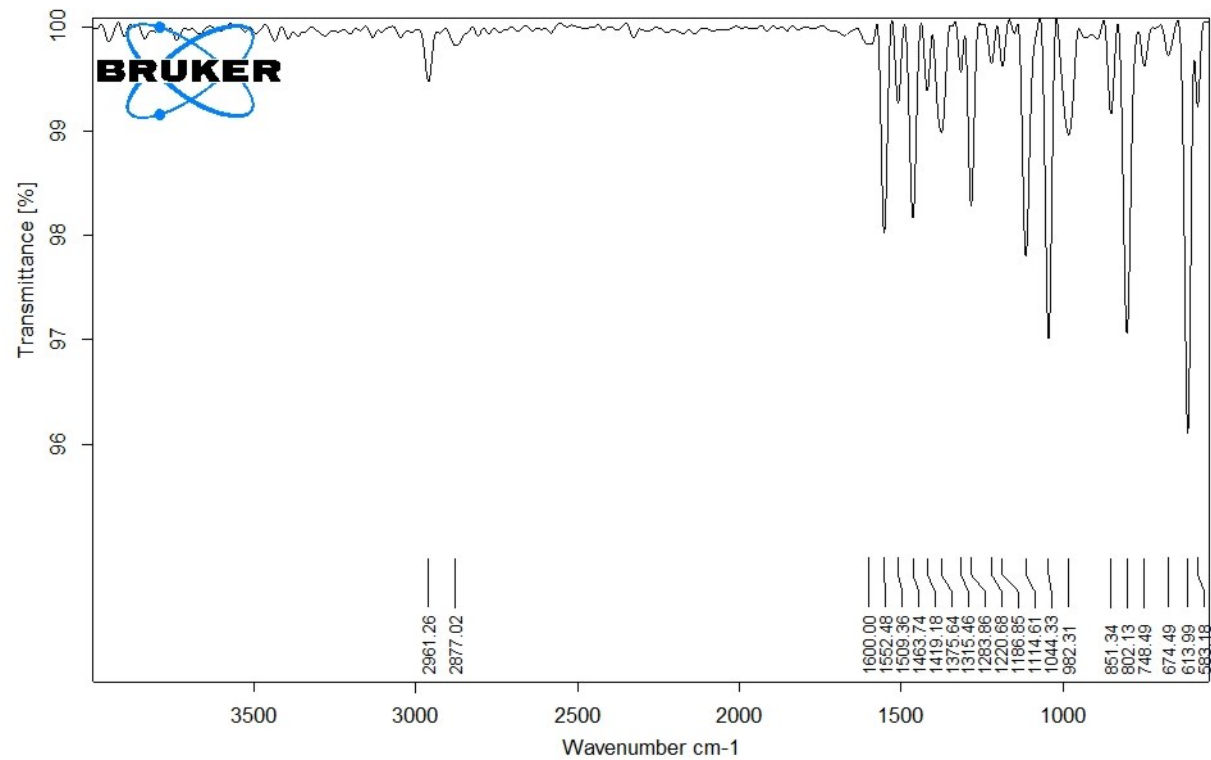
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Figure S16. FTIR spectrum of  $[L_BZnCl_2]$



D:\chem\IR\IR4-isopropyl serise\SH-1-40(35+ISO+Zn).0	SH-1-40(35+ISO+Zn)	ATR eco ZnSe	2019-01-16
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Figure S17. FTIR spectrum of [L<sub>B</sub>CdBr<sub>2</sub>]



D:\msd\msd\ip\VR4-isopropyl serise\SH-1-39(35+ISO+Cd).0	SH-1-39(35+ISO+Cd)	ATR eco ZnSe	2019-01-16
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Figure S18. Elemental analysis data for the synthesized complexes

Group No : 1 Sample Name	Element % Nitrogen%	Carbon%	Hydrogen%	Sulphur%
SH-3-60	15.80086517	46.29833984	5.292660713	0
SH-3-60	15.86852264	46.39331436	5.292596817	0

2 Sample(s) in Group No : 1

Component Name	Average
Nitrogen%	15.83469391
Carbon%	46.3458271
Hydrogen%	5.292628765
Sulphur%	0

[L<sub>A</sub>CoCl<sub>2</sub>] revised

[L<sub>A</sub>ZnCl<sub>2</sub>] revised

Group No : 1 Sample Name	Element % Nitrogen	Carbon	Hydrogen	Sulphur
SH-3-68-2	15.91970539	45.6293335	5.23718214	0
SH-3-68-2	15.93205547	45.74524689	5.237337589	0

2 Sample(s) in Group No : 1

Component Name	Average
Nitrogen	15.92588043
Carbon	45.68729019
Hydrogen	5.237259865
Sulphur	0

[L<sub>B</sub>CoCl<sub>2</sub>] revised

Group No : 1 Sample Name	Element % Nitrogen%	Carbon%	Hydrogen%	Sulphur%
SH-1-38	14.3549614	52.89284897	6.078319073	0
SH-1-38	14.23541451	52.61333084	6.064629078	0

2 Sample(s) in Group No : 1

Component Name	Average
Nitrogen%	14.29518795
Carbon%	52.7530899
Hydrogen%	6.071474075
Sulphur%	0

[L<sub>B</sub>ZnCl<sub>2</sub>] revised

Group No : 4	Element %			
Sample Name	Nitrogen	Carbon	Hydrogen	Sulphur
SH-1-40	14.80307961	51.76090622	6.033392429	0
SH-1-40	14.78108215	51.72053528	6.003000259	0

2 Sample(s) in Group No : 4

Component Name	Average
Nitrogen	14.79208088
Carbon	51.74072075
Hydrogen	6.018196344
Sulphur	0

[L<sub>B</sub>CdBr<sub>2</sub>] revised

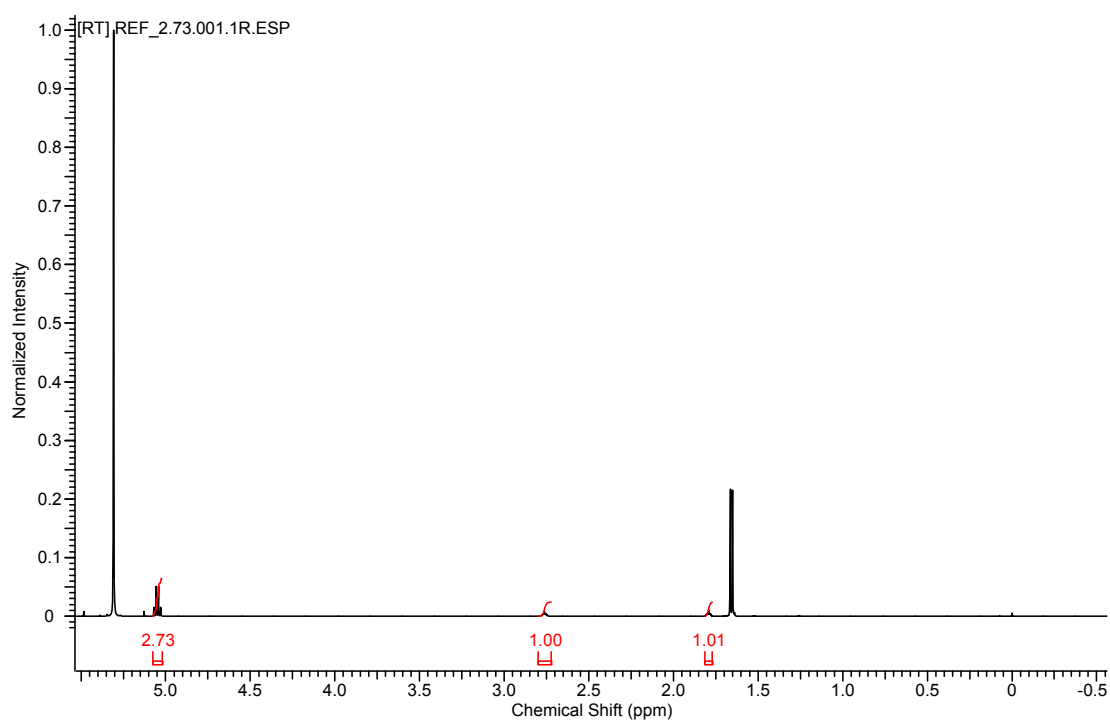
Group No : 5	Element %			
Sample Name	Nitrogen	Carbon	Hydrogen	Sulphur
SH-1-39	11.15274048	40.37996674	4.666033745	0
SH-1-39	11.19203472	40.45752716	4.664896011	0

2 Sample(s) in Group No : 5

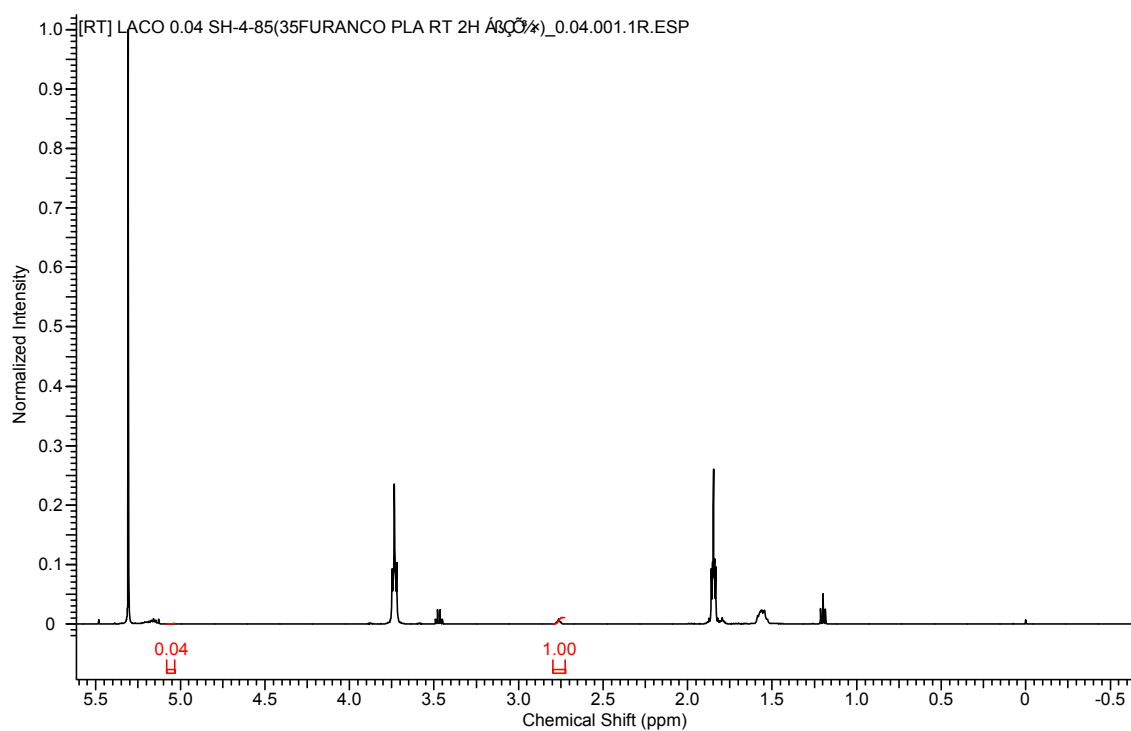
Component Name	Average
Nitrogen	11.1723876
Carbon	40.41874695
Hydrogen	4.665464878
Sulphur	0



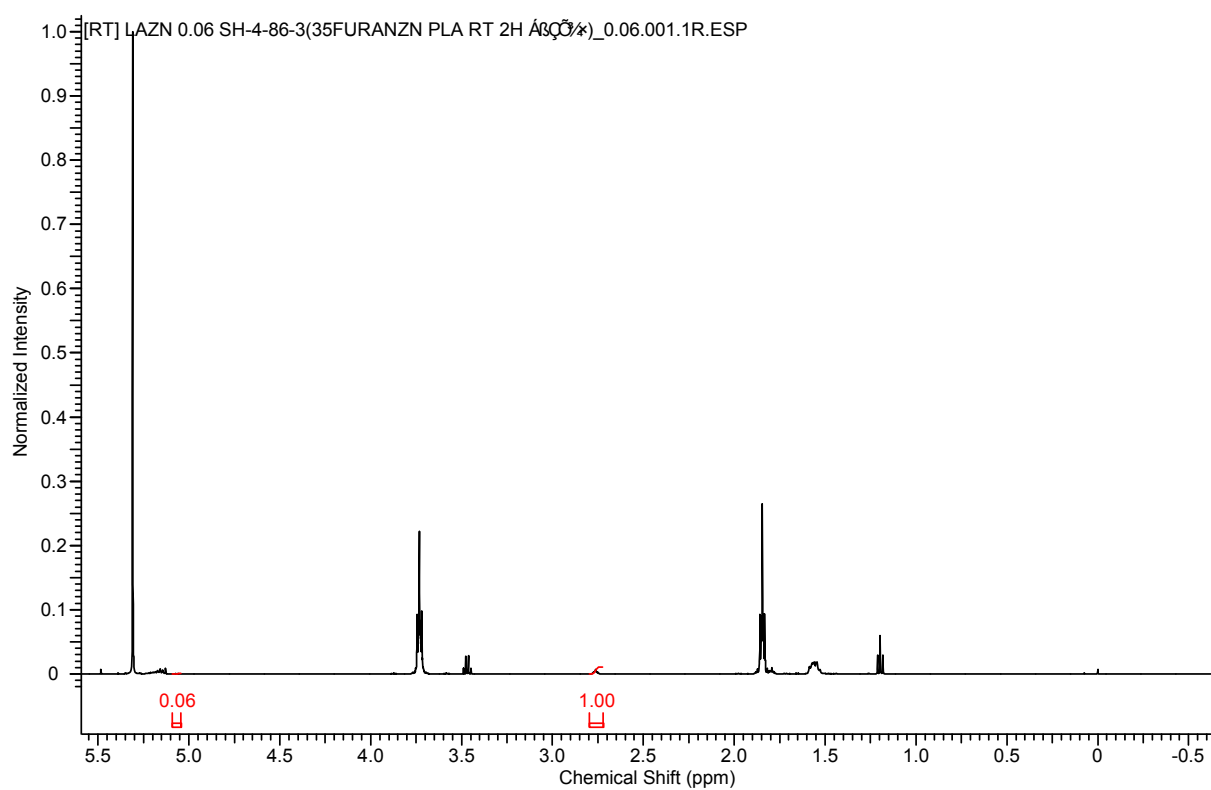
**Figure S19(a).**  $^1\text{H}$  NMR spectrum of reference at 25 °C



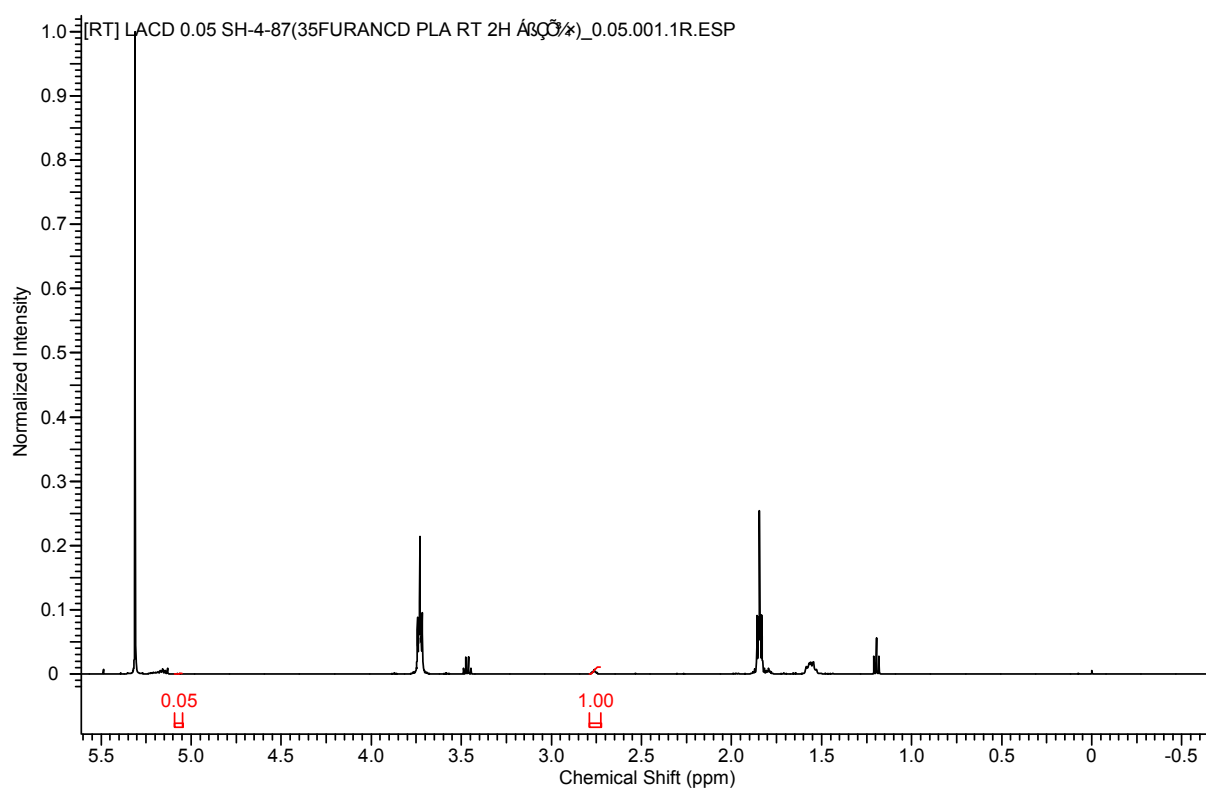
**Figure S19(b).**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_A\text{CoCl}_2]/\text{MeLi}$  system at 25 °C.



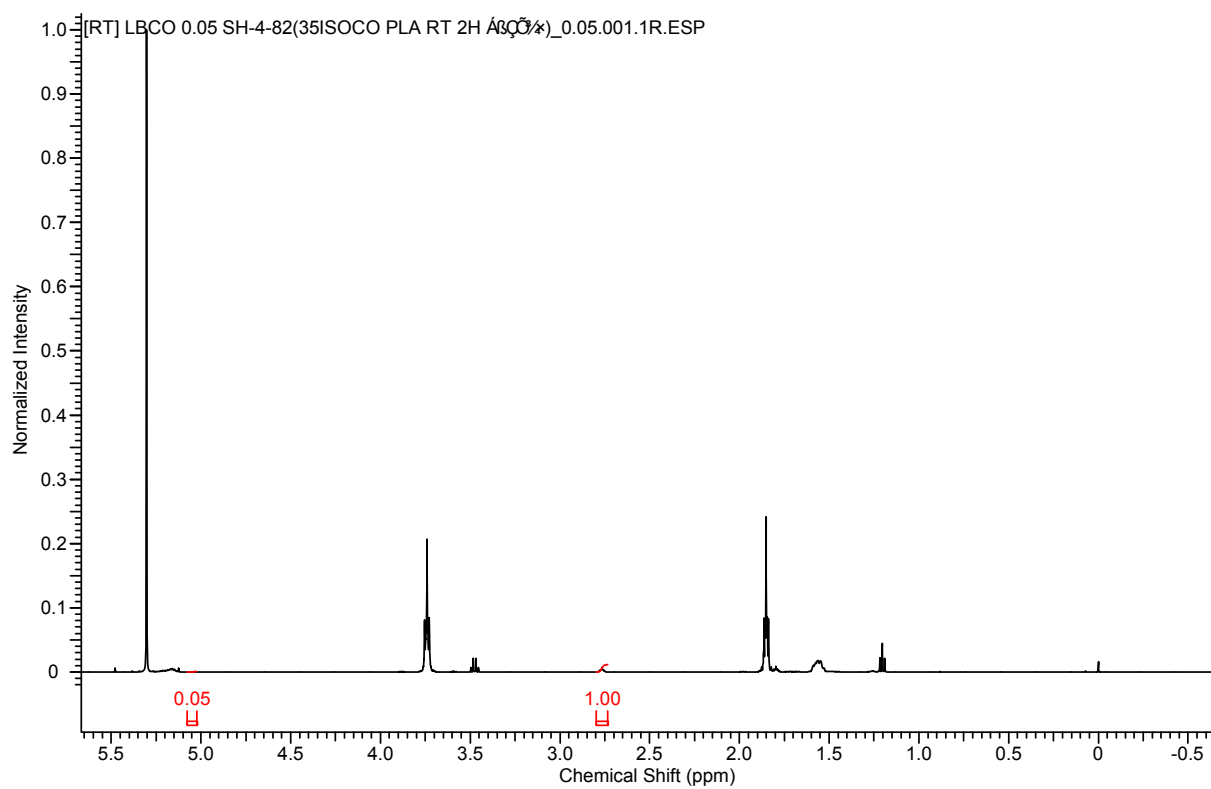
**Figure S20.**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_A\text{ZnCl}_2]/\text{MeLi}$  system at 25 °C



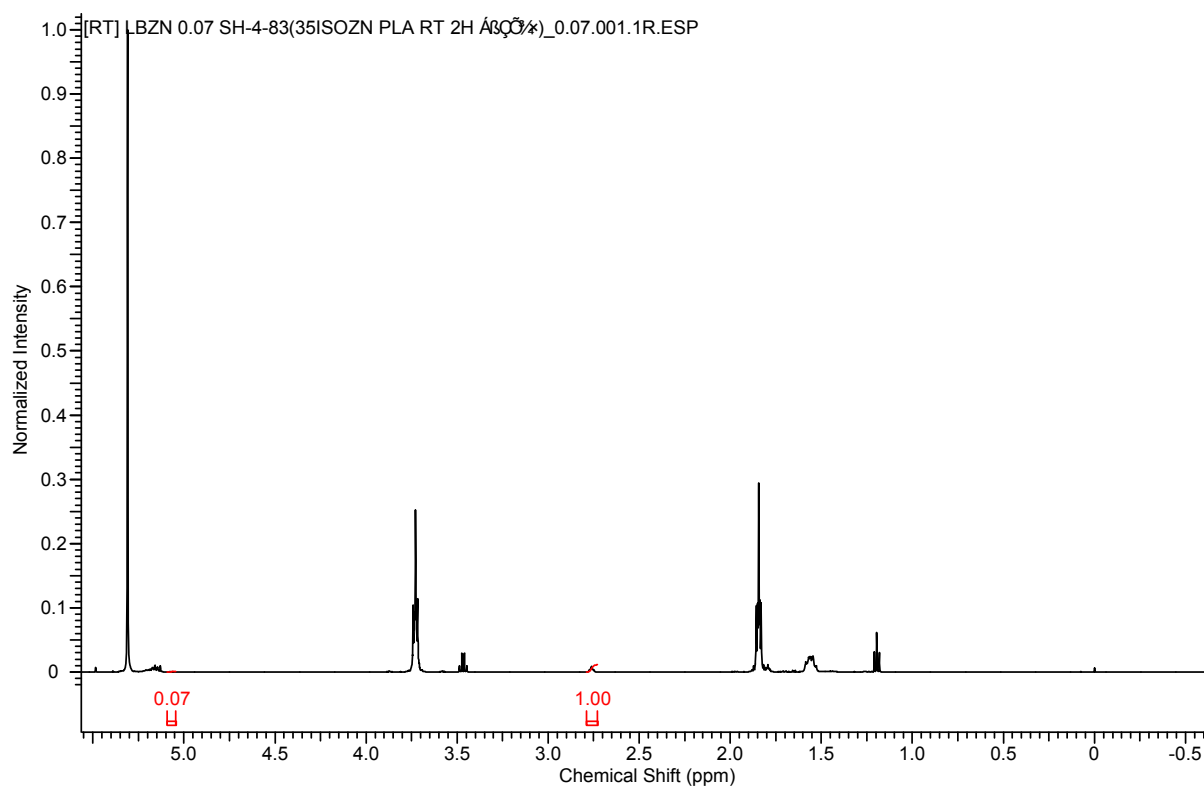
**Figure S21.**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_A\text{CdBr}_2]/\text{MeLi}$  system at 25 °C.



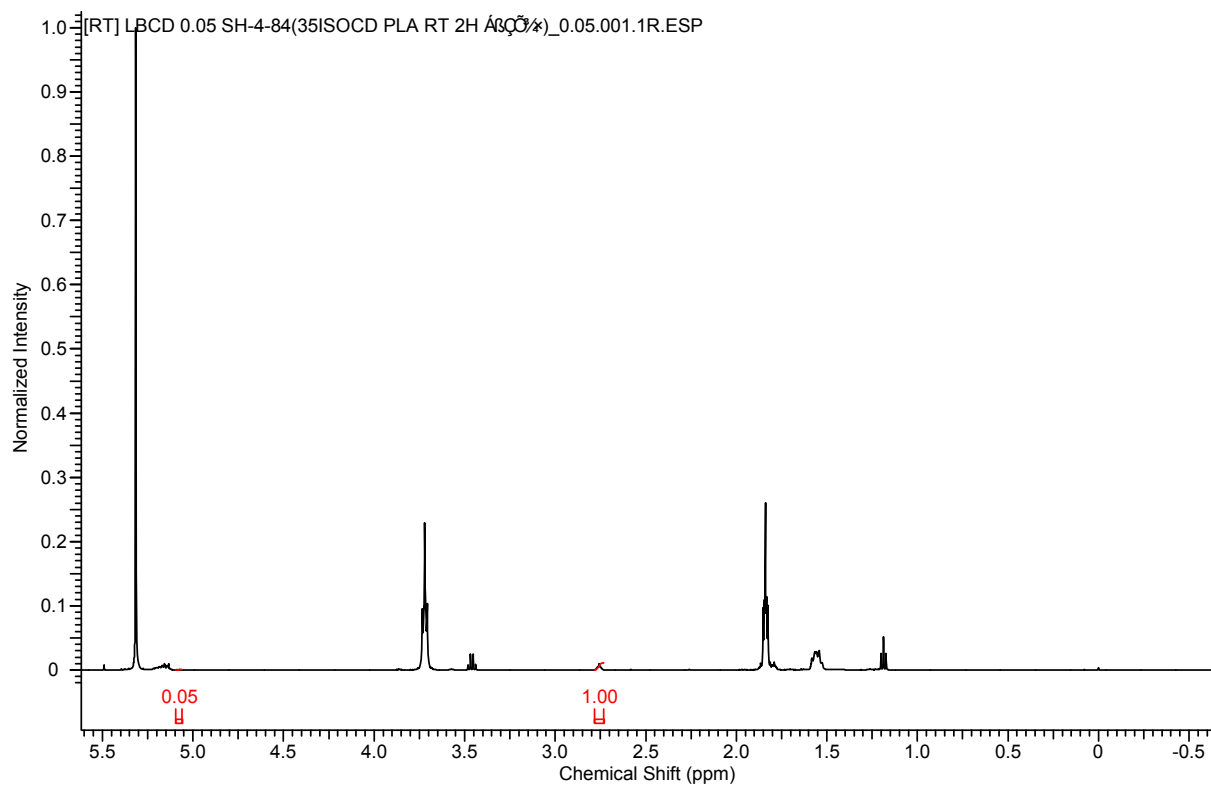
**Figure S22.**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_\text{B}\text{CoCl}_2]/\text{MeLi}$  system at 25 °C.



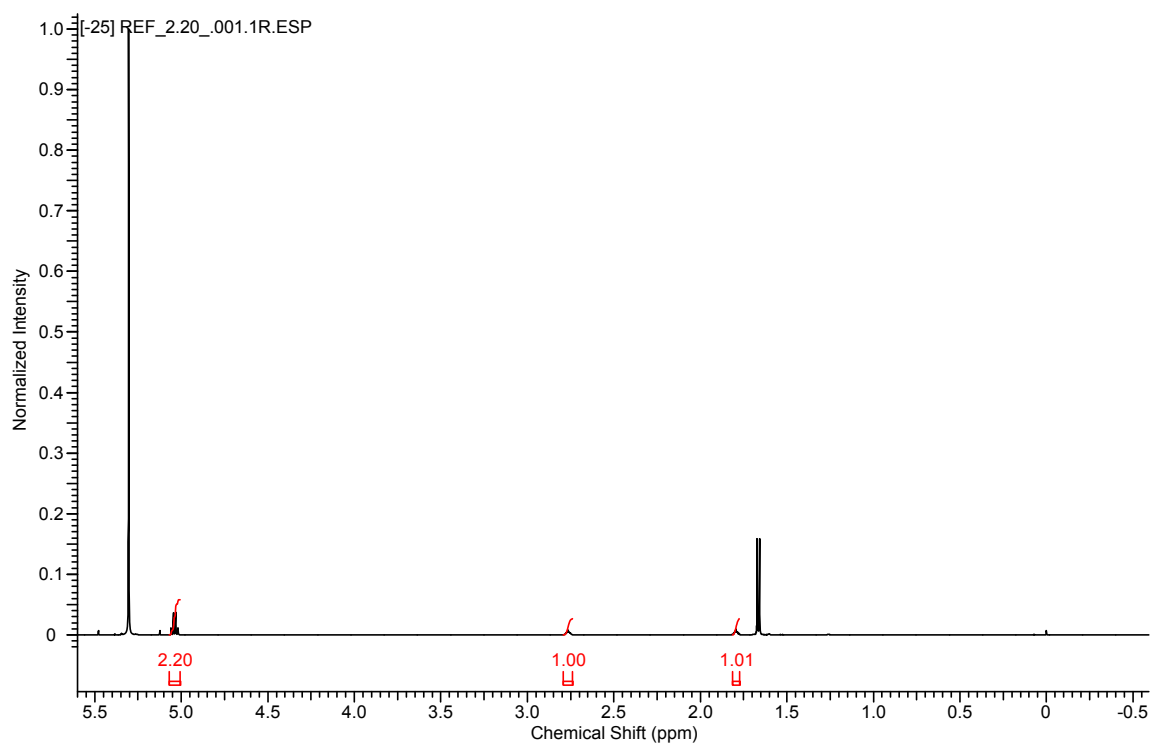
**Figure S23.**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_B\text{ZnCl}_2]/\text{MeLi}$  system at 25 °C.



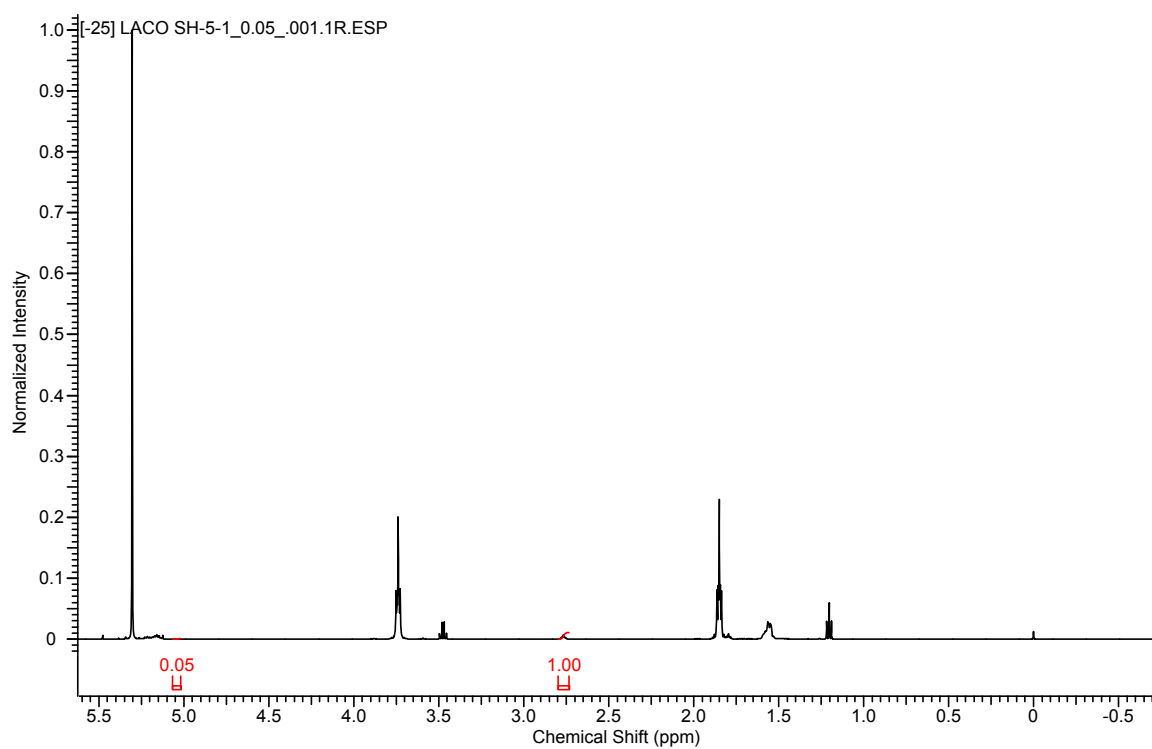
**Figure S24.**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_B\text{CdBr}_2]/\text{MeLi}$  system at 25 °C.



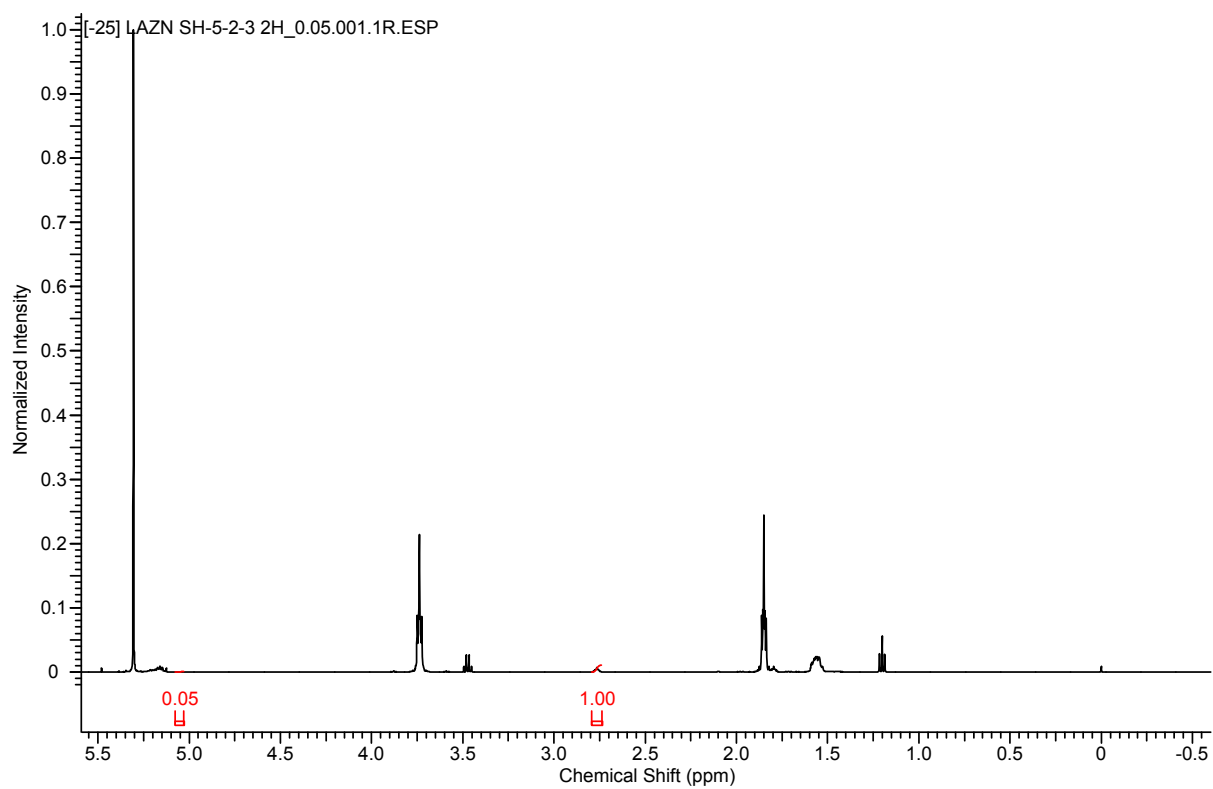
**Figure S25(a).**  $^1\text{H}$  NMR spectrum of reference at  $-25\text{ }^\circ\text{C}$ .



**Figure S25 (b).**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_A\text{CoCl}_2]/\text{MeLi}$  system at  $-25\text{ }^\circ\text{C}$

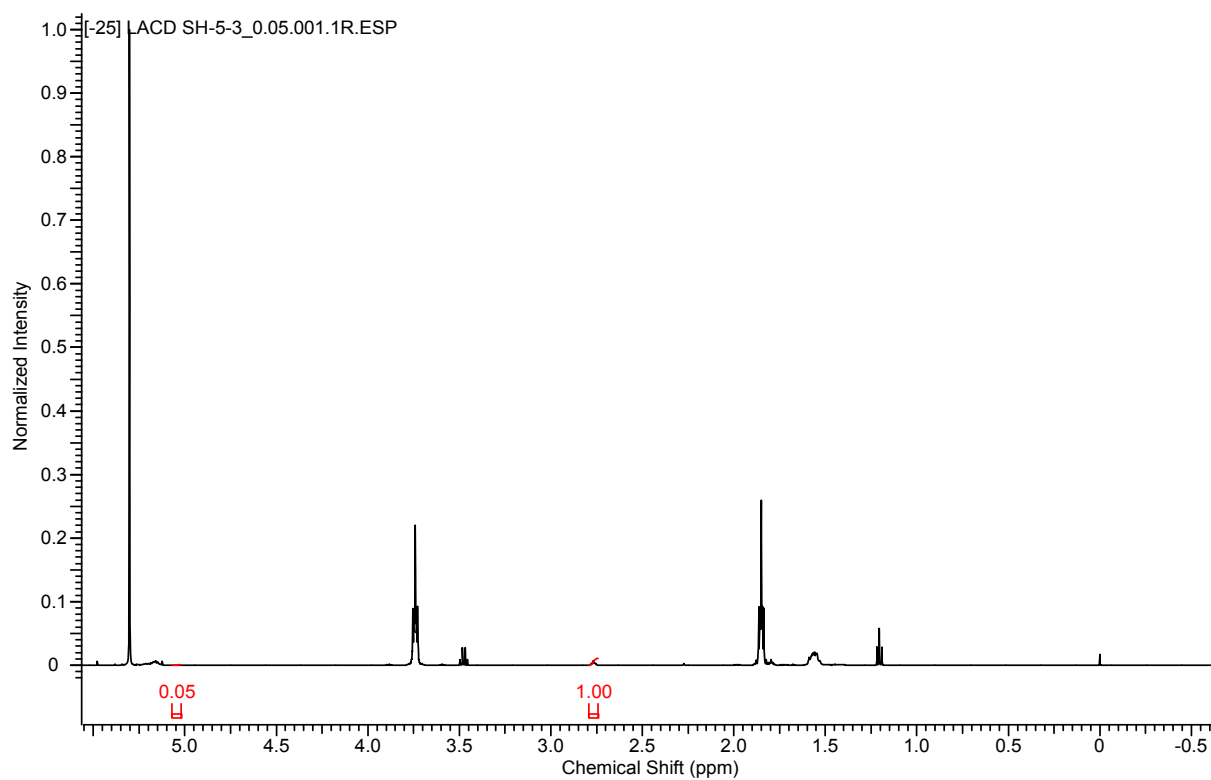


**Figure S26.**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_A\text{ZnCl}_2]/\text{MeLi}$  at  $-25\text{ }^\circ\text{C}$ .

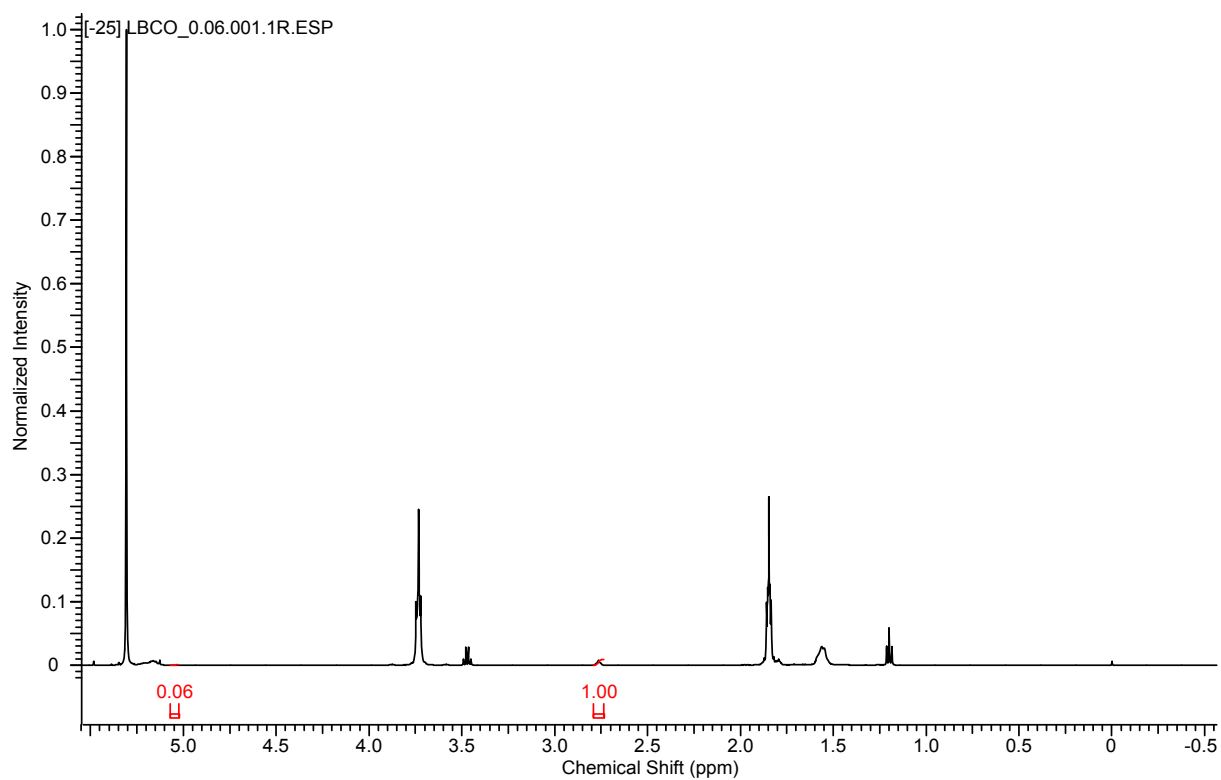




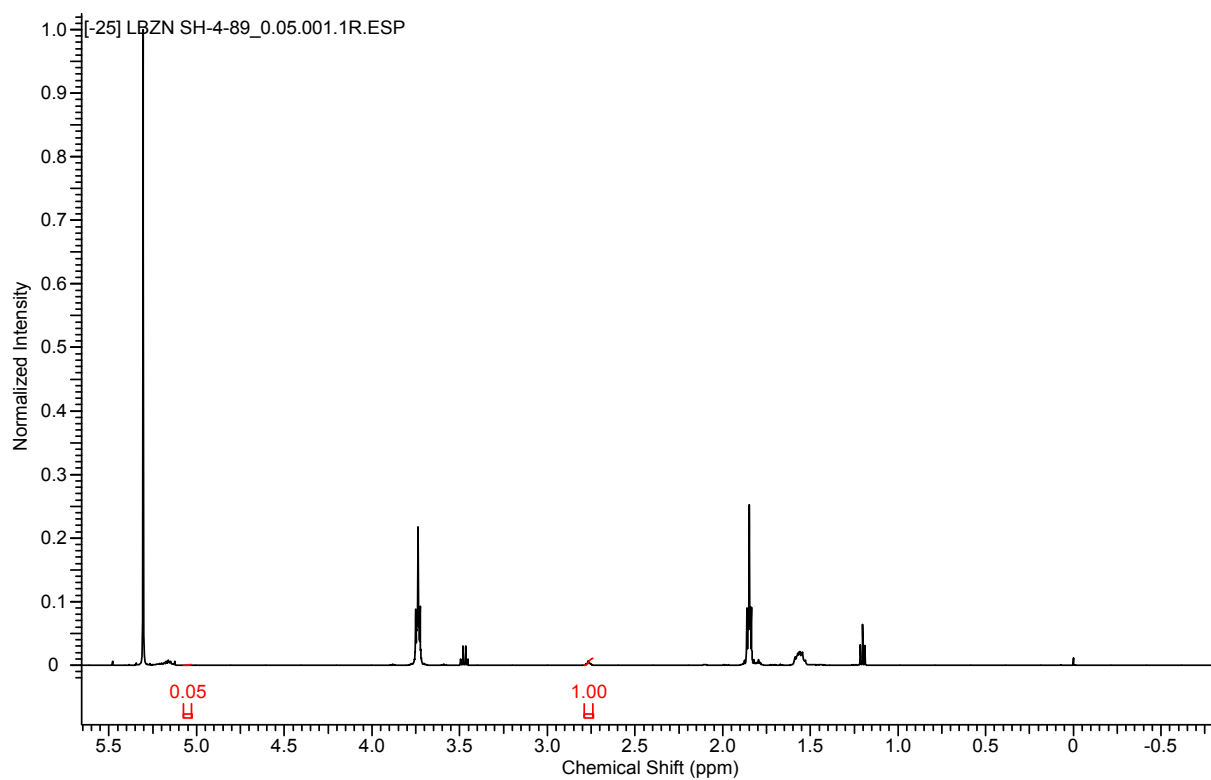
**Figure S27.**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_A\text{CdBr}_2]/\text{MeLi}$  system at  $-25\text{ }^\circ\text{C}$ .



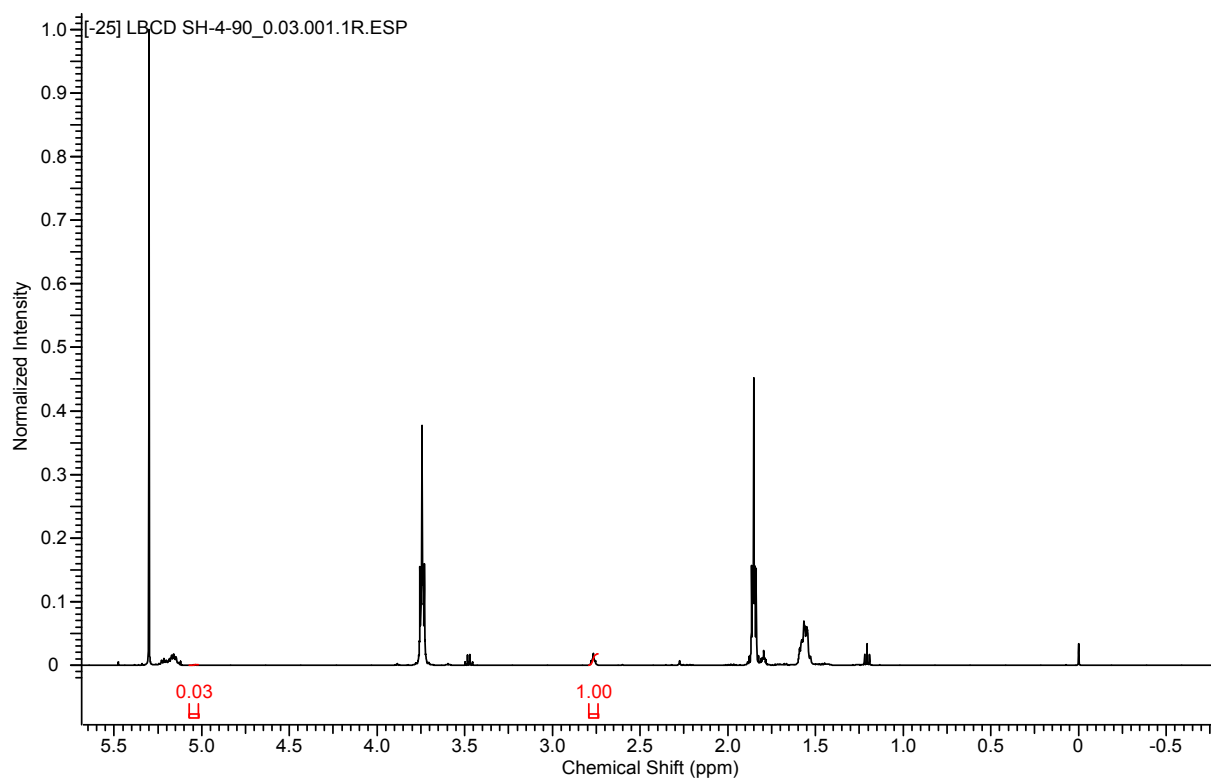
**Figure S28.**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_\text{B}\text{CoCl}_2]/\text{MeLi}$  system at  $-25\text{ }^\circ\text{C}$ .



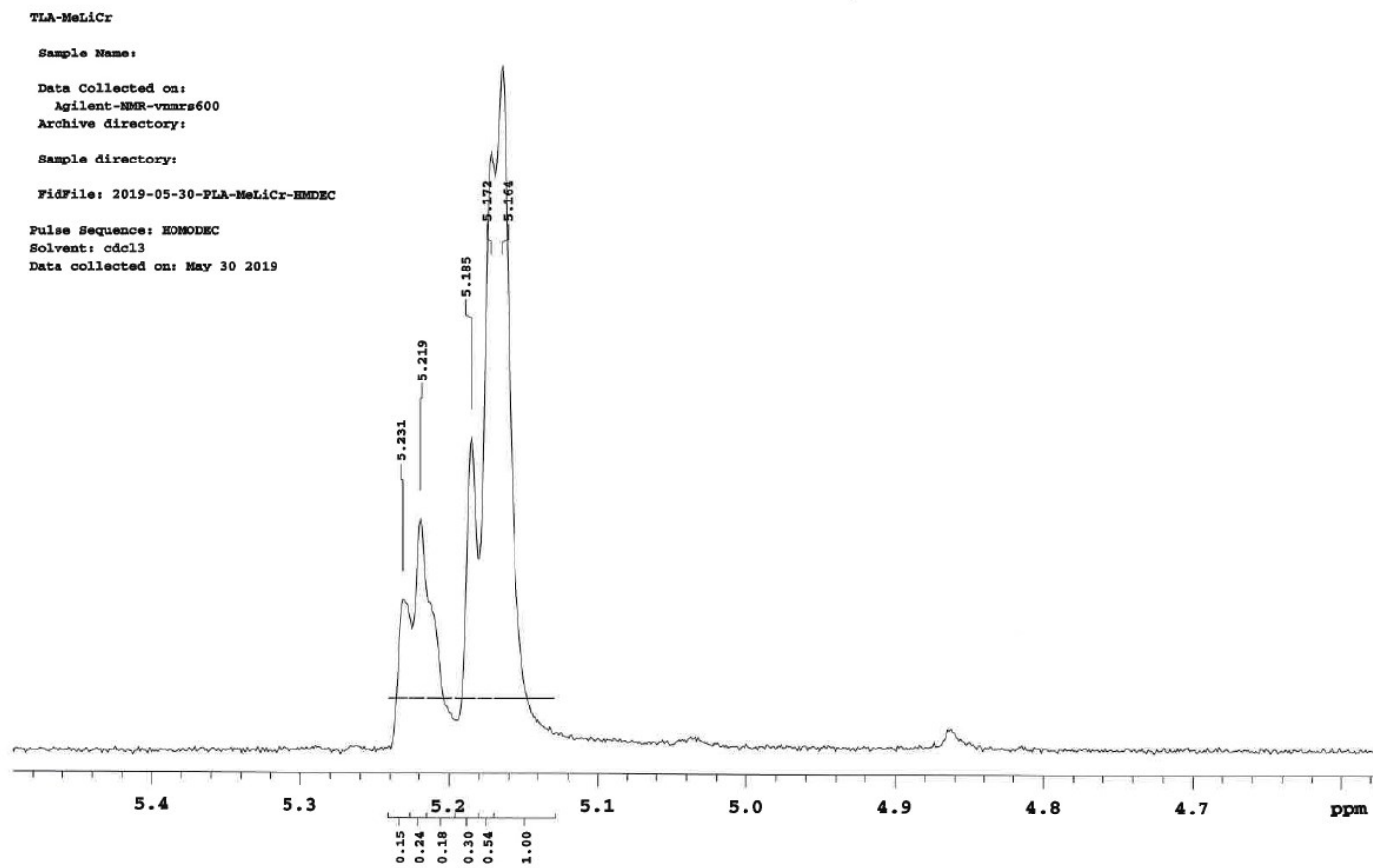
**Figure S29.**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_\text{B}\text{ZnCl}_2]/\text{MeLi}$  system at  $-25\text{ }^\circ\text{C}$ .



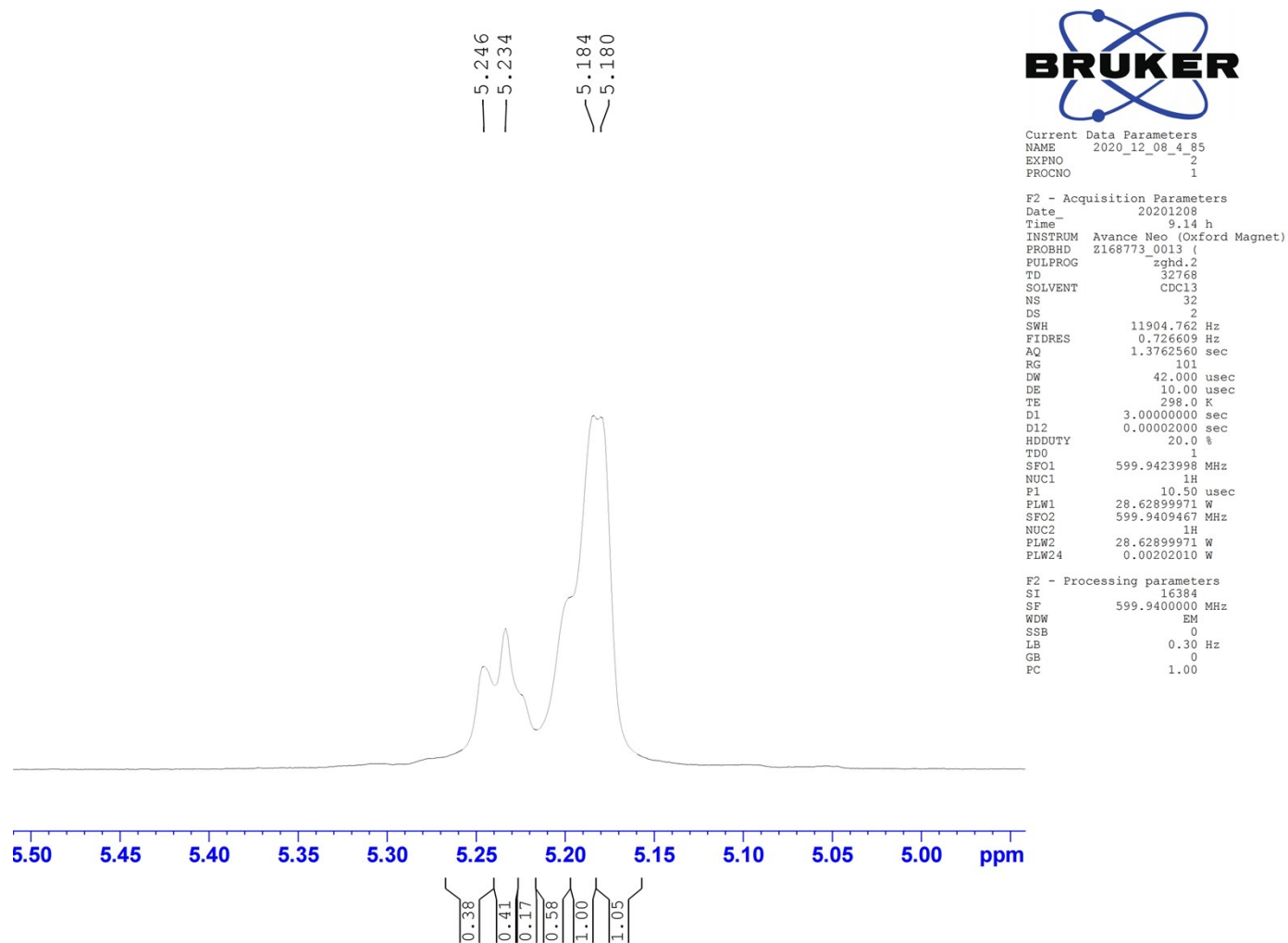
**Figure S30.**  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_\text{B}\text{CdBr}_2]/\text{MeLi}$  system at  $-25\text{ }^\circ\text{C}$ .



**Figure S31.** Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with **MeLi** at 25 °C.



**Figure S32.** Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_A\text{CoCl}_2]/\text{MeLi}$  system at 25 °C.



**Figure S33.** Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_A\text{ZnCl}_2]/\text{MeLi}$  system at 25 °C.

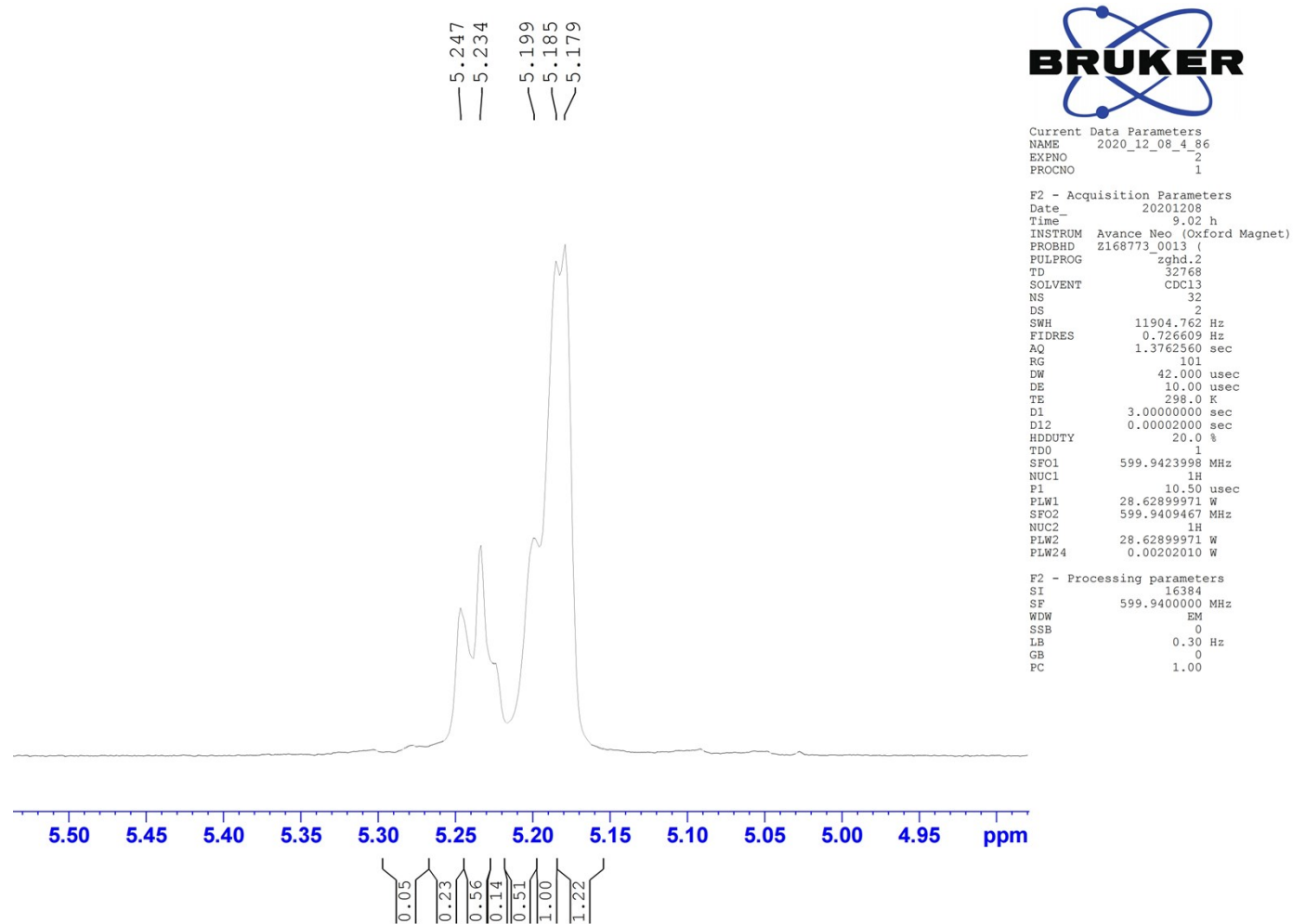


Figure S34. Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_A\text{CdBr}_2]/\text{MeLi}$  system at 25 °C.

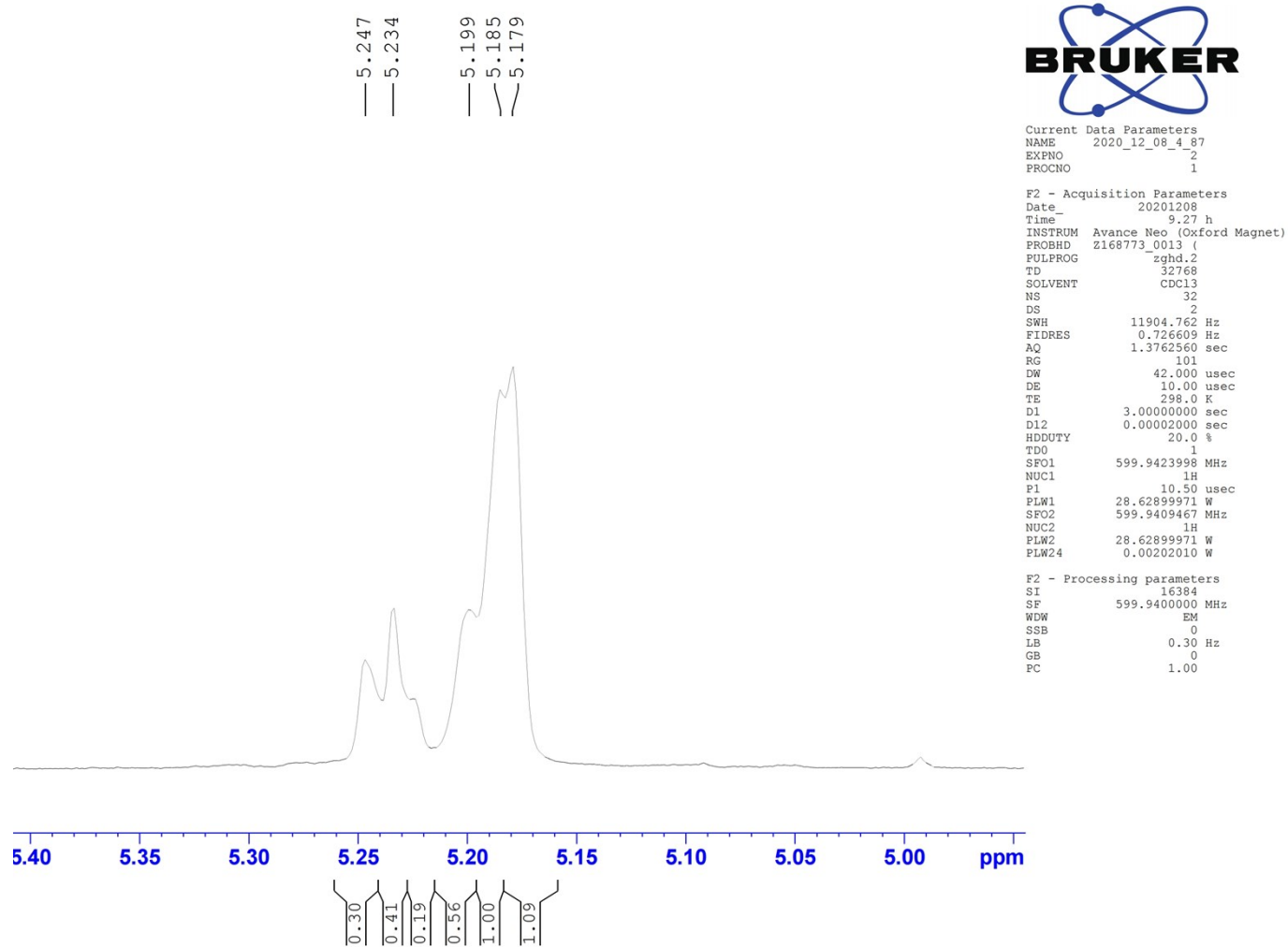
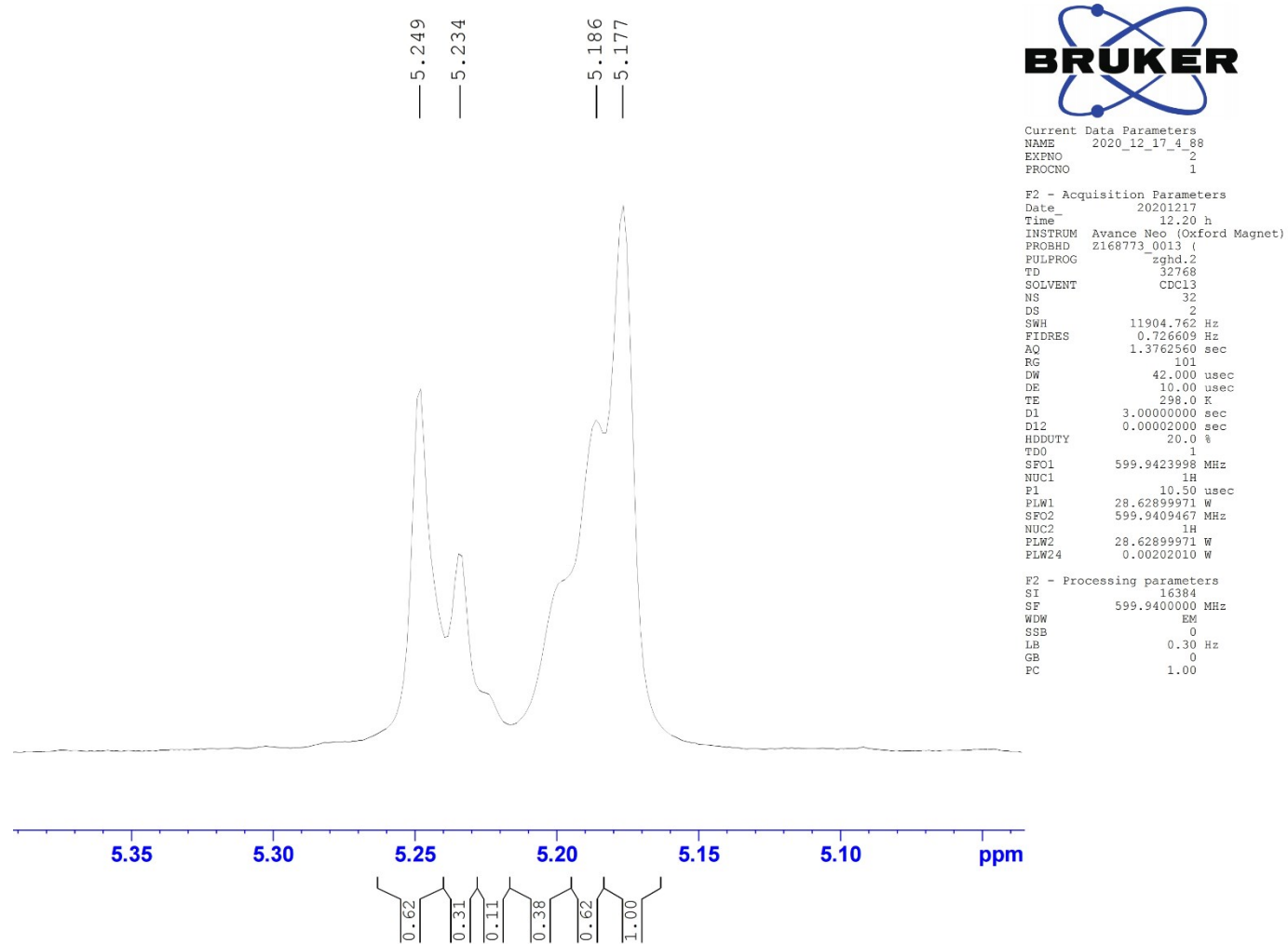




Figure S35. Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_B\text{CoCl}_2]/\text{MeLi}$  system at 25 °C.



**Figure S36.** Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_\text{B}\text{ZnCl}_2]/\text{MeLi}$  system at 25 °C.

3Zn

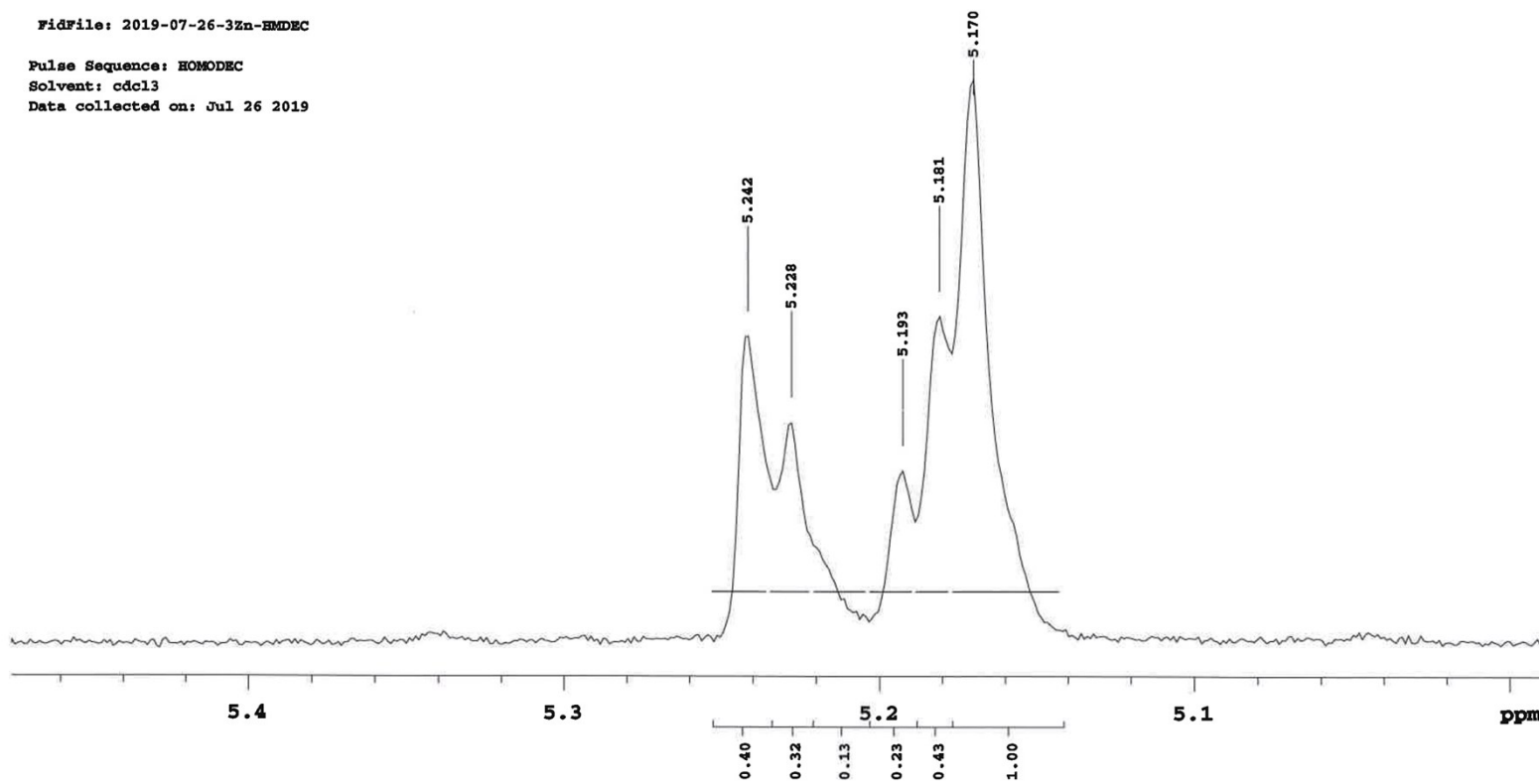
Sample Name:

Data Collected on:  
Agilent-NMR-vnmrs600  
Archive directory:

Sample directory:

Fidfile: 2019-07-26-3Zn-HMDEC

Pulse Sequence: HOMODEC  
Solvent:  $\text{cdCl}_3$   
Data collected on: Jul 26 2019



**Figure S37.** Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_\text{B}\text{CdBr}_2]/\text{MeLi}$  system at 25 °C.

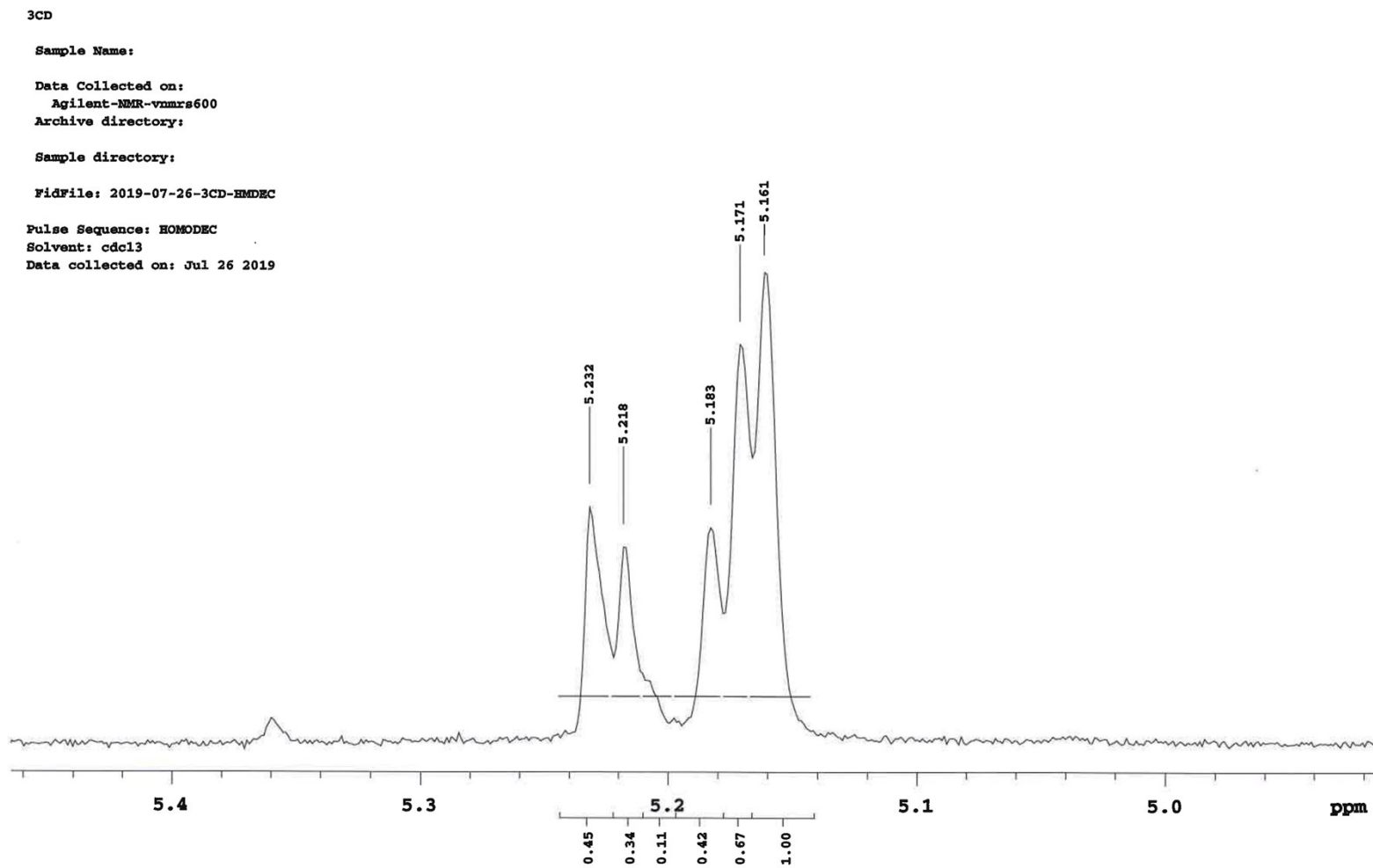


Figure S38. Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with MeLi at  $-25\text{ }^\circ\text{C}$ .

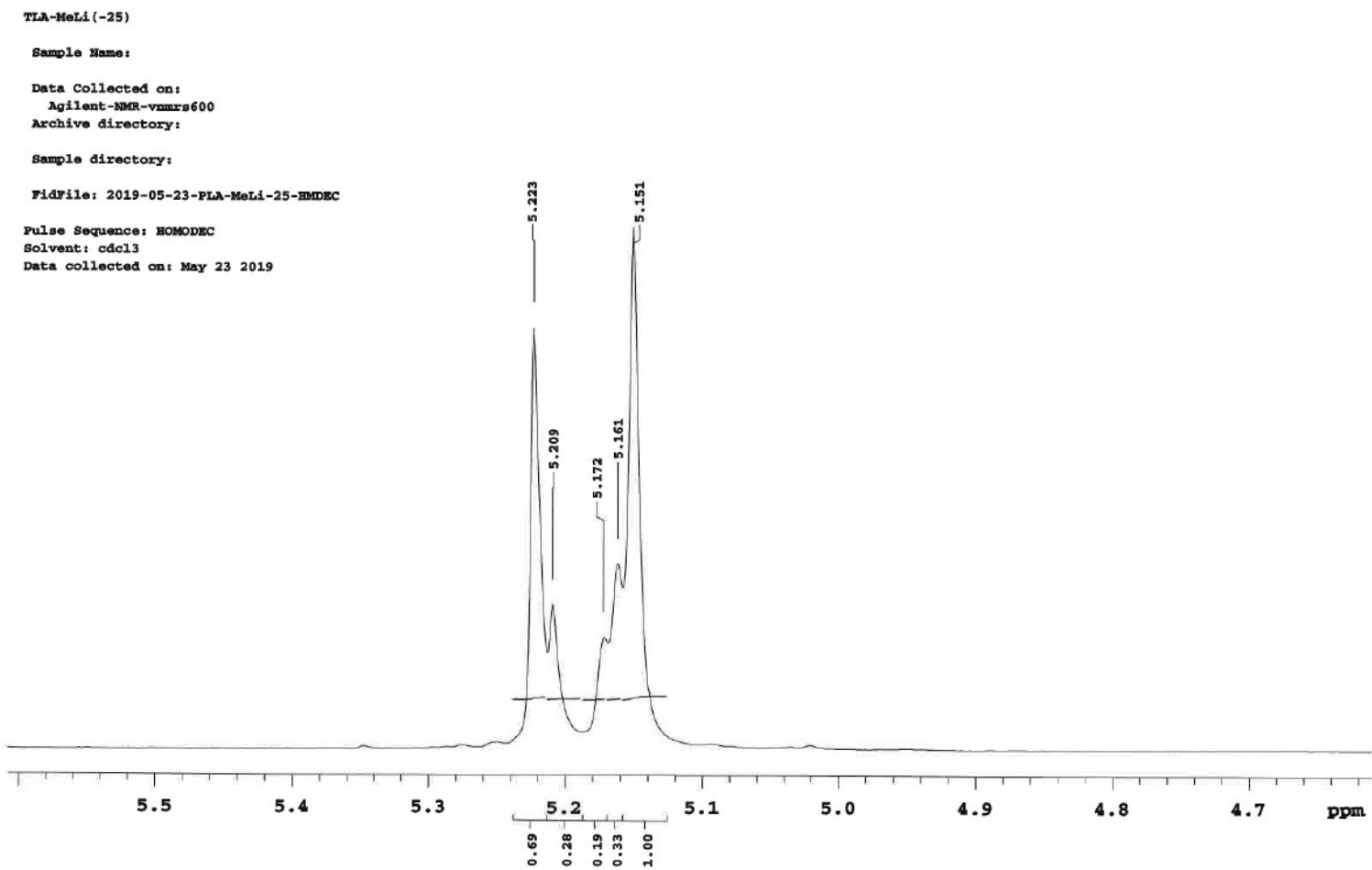
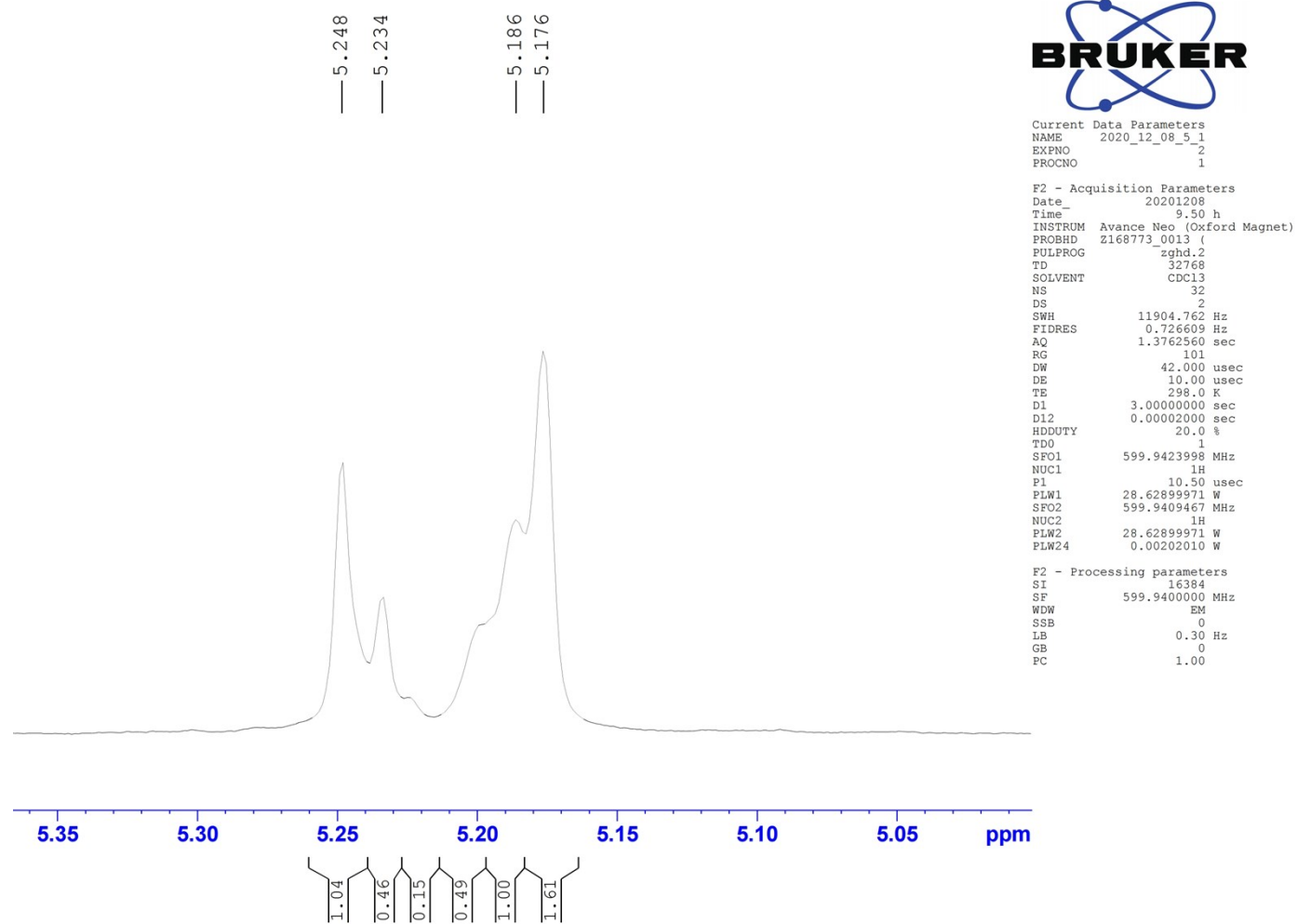
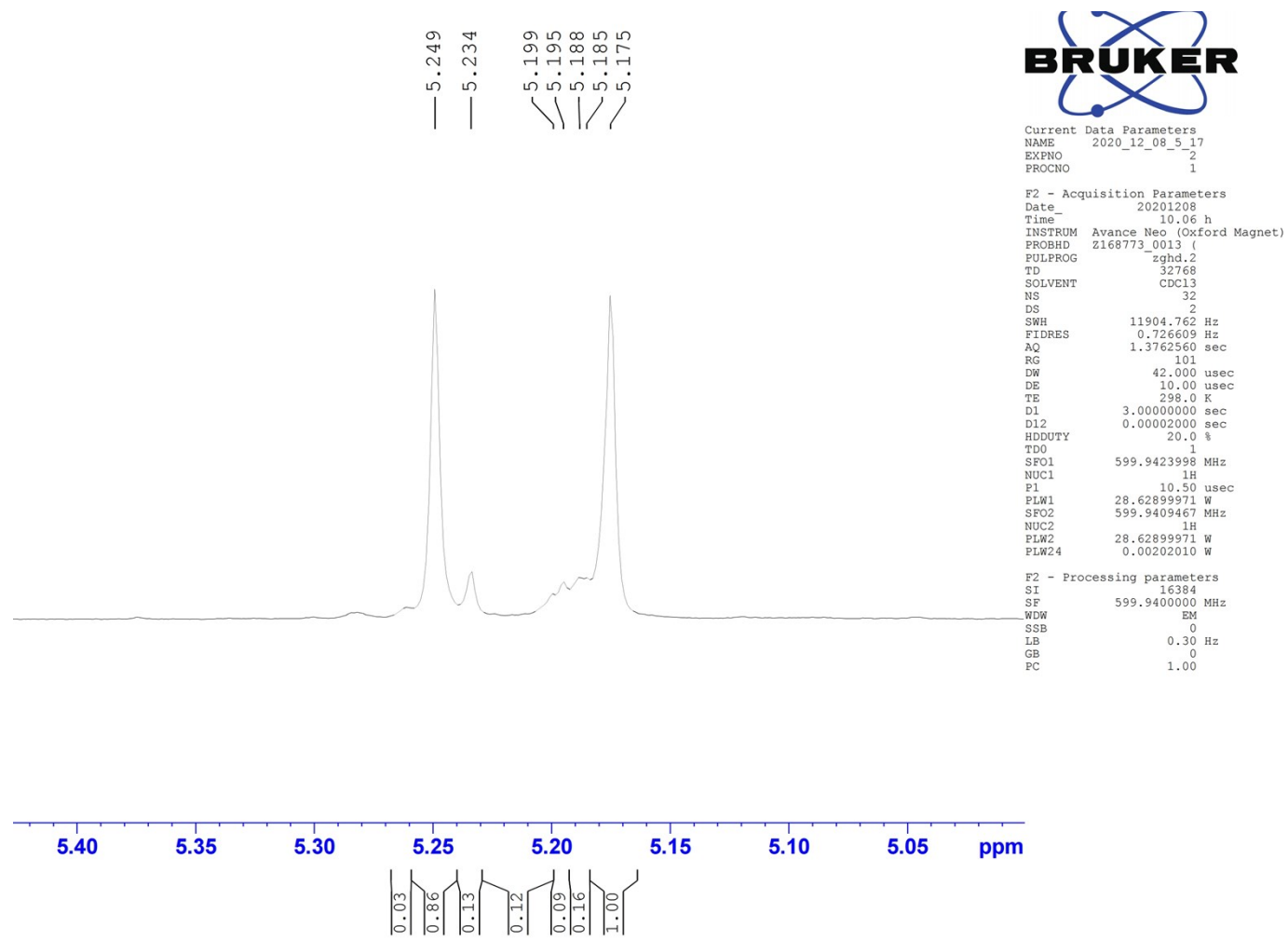


Figure S39. Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_A\text{CoCl}_2]/\text{MeLi}$  system at  $-25\text{ }^\circ\text{C}$ .



**Figure S40.** Homodecoupled <sup>1</sup>H NMR spectrum of PLA obtained with [L<sub>A</sub>ZnCl<sub>2</sub>]/MeLi system at -25 °C.



**Figure S41.** Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_A\text{CdBr}_2]/\text{MeLi}$  system at  $-25\text{ }^\circ\text{C}$ .

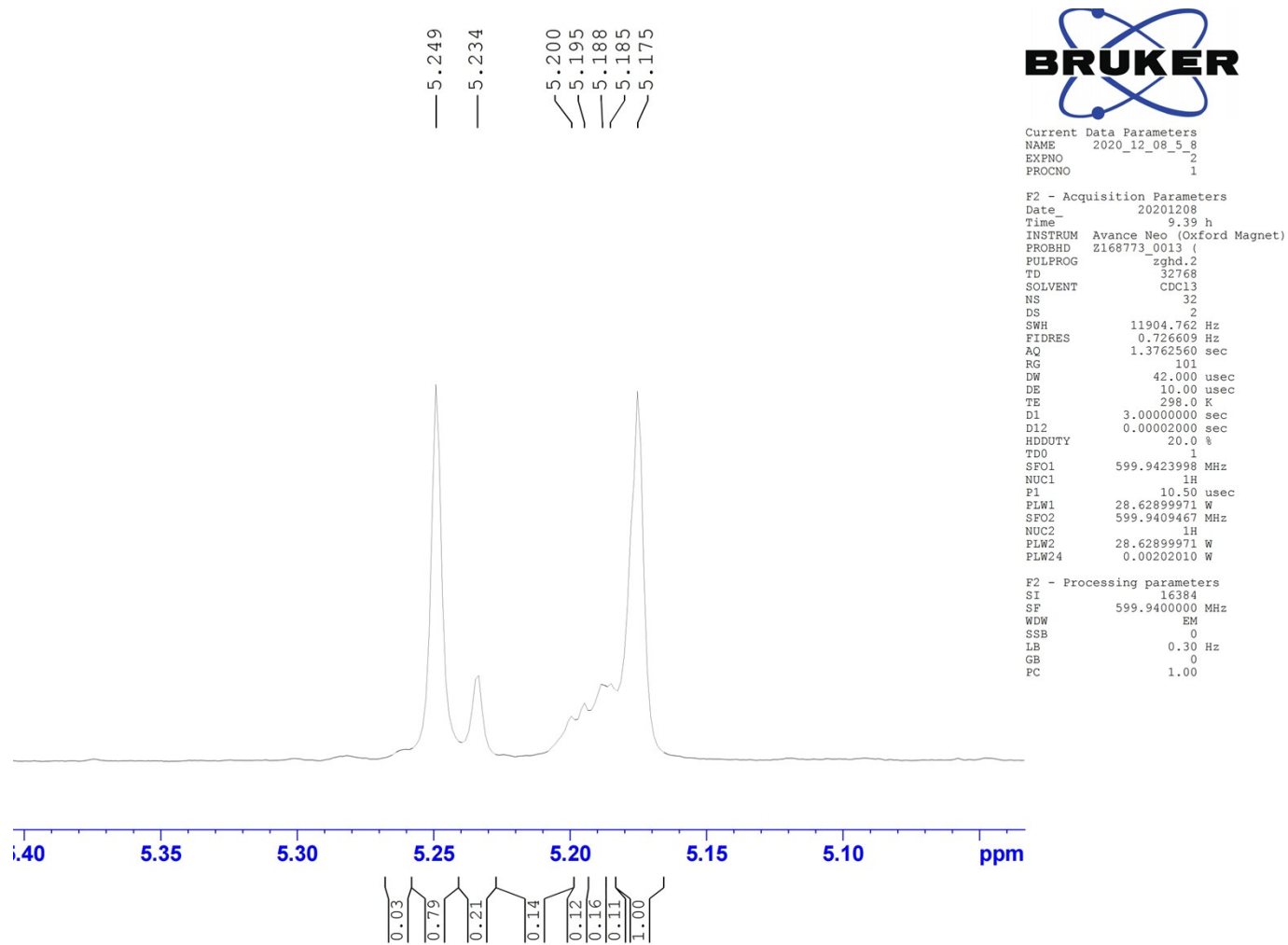
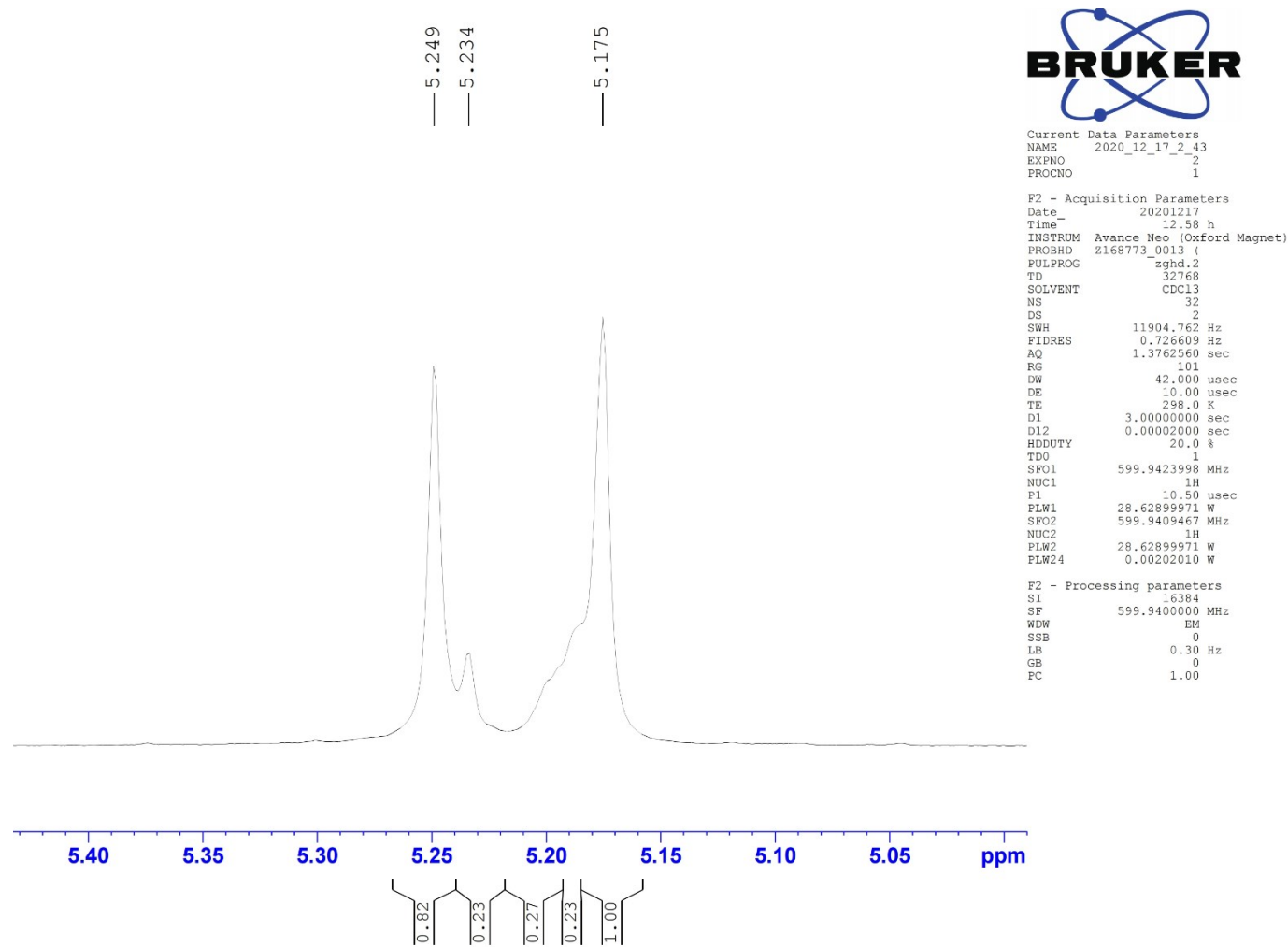


Figure S42. Homodecoupled <sup>1</sup>H NMR spectrum of PLA obtained with [L<sub>B</sub>CoCl<sub>2</sub>]/MeLi system at -25 °C.





**Figure S43.** Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_\text{B}\text{ZnCl}_2]/\text{MeLi}$  system at  $-25\text{ }^\circ\text{C}$ .

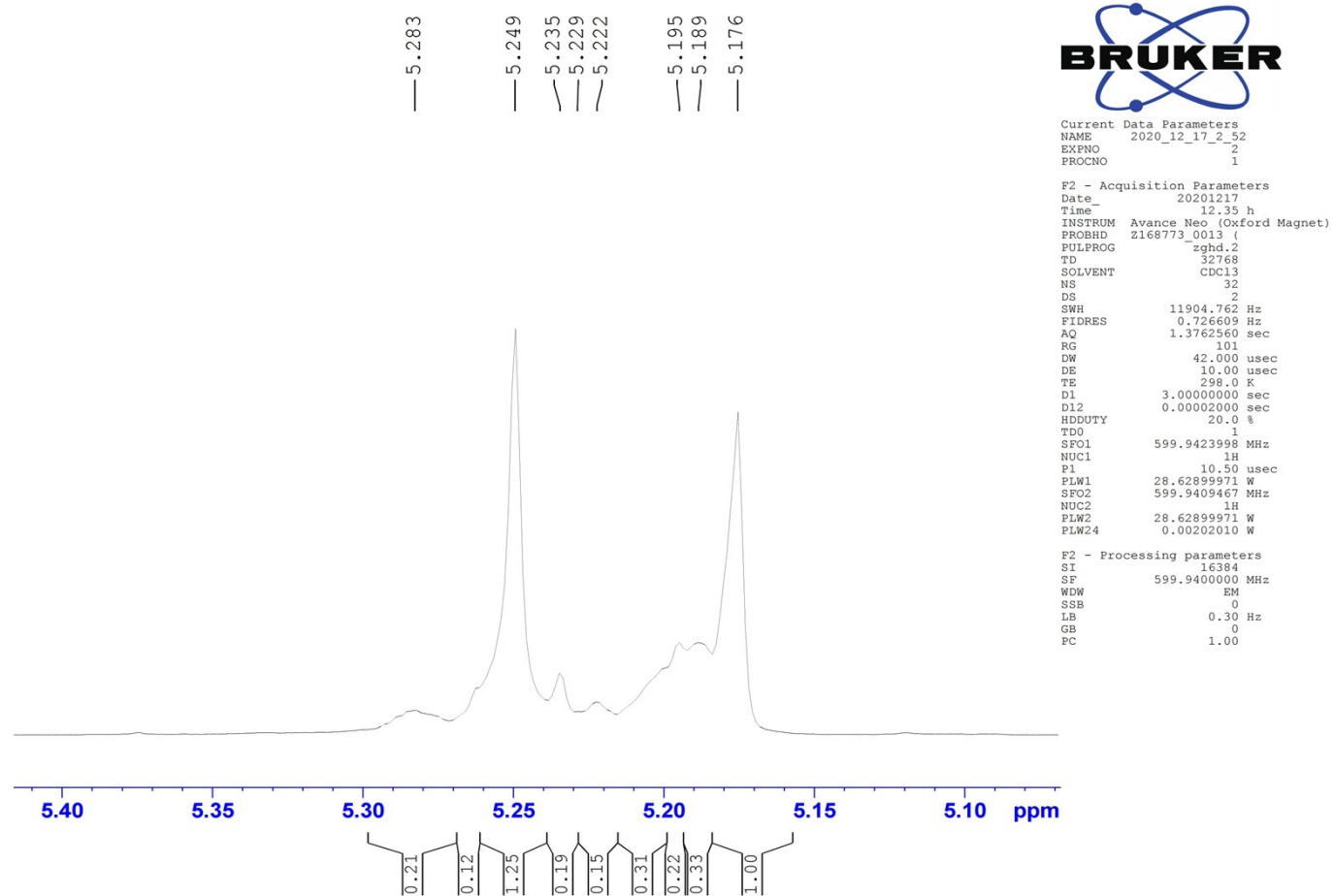
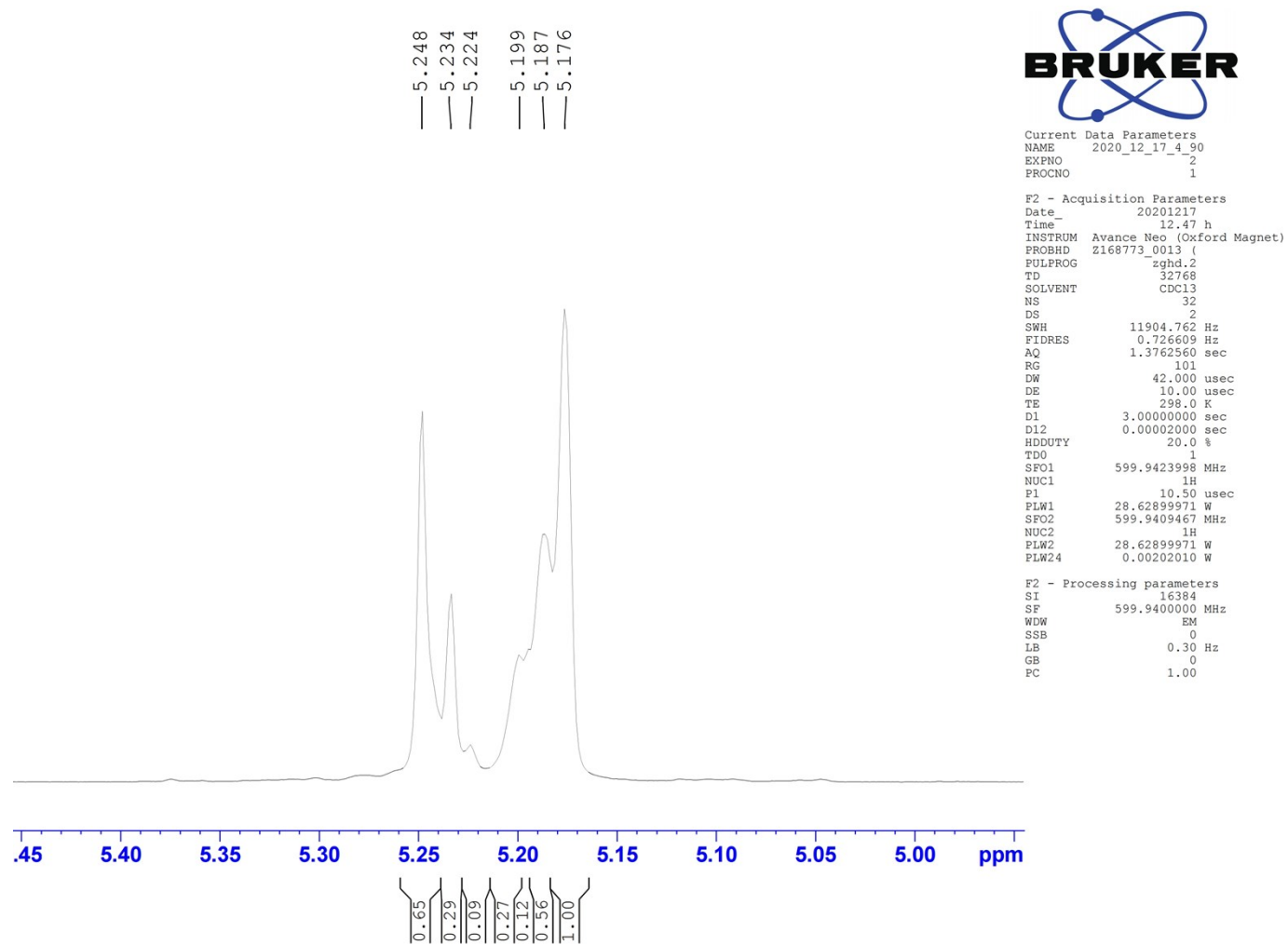
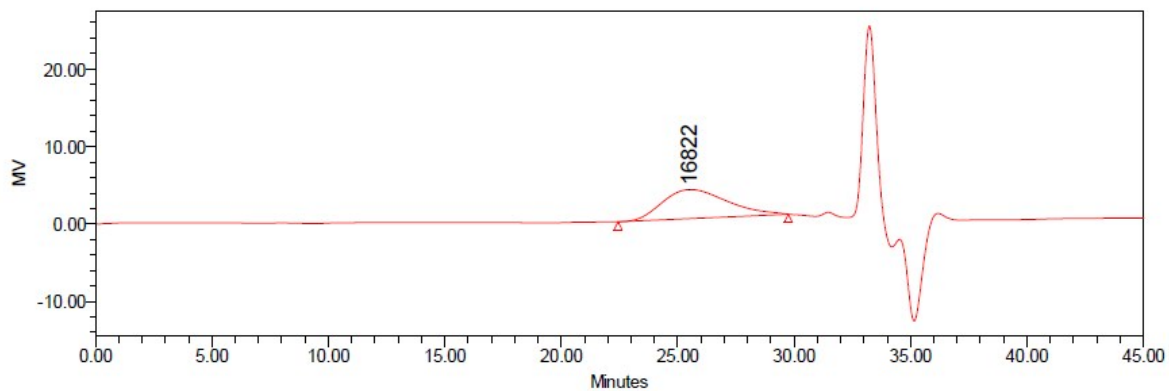


Figure S44. Homodecoupled  $^1\text{H}$  NMR spectrum of PLA obtained with  $[\text{L}_\text{B}\text{CdBr}_2]/\text{MeLi}$  system at  $-25\text{ }^\circ\text{C}$ .



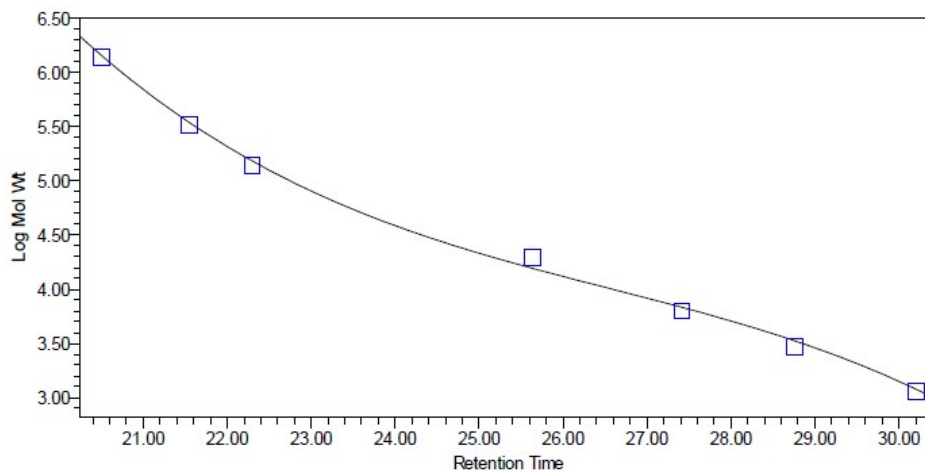
**Figure S45.** GPC data of PLA obtained with MeLi at 25 °C.

SAMPLE INFORMATION			
Sample Name:	PLA-MeLi(rt)	Sample Set Name:	190529
Sample Type:	Broad Unknown	Acq. Method Set:	THF_1x0ml
Vial:	8	Injection Volume:	100.00 ul
Injection #:	1	Acquired By:	System
Run Time:	45.0 Minutes		
Date Acquired:	2019-05-29 PM 9:35:46 KST		

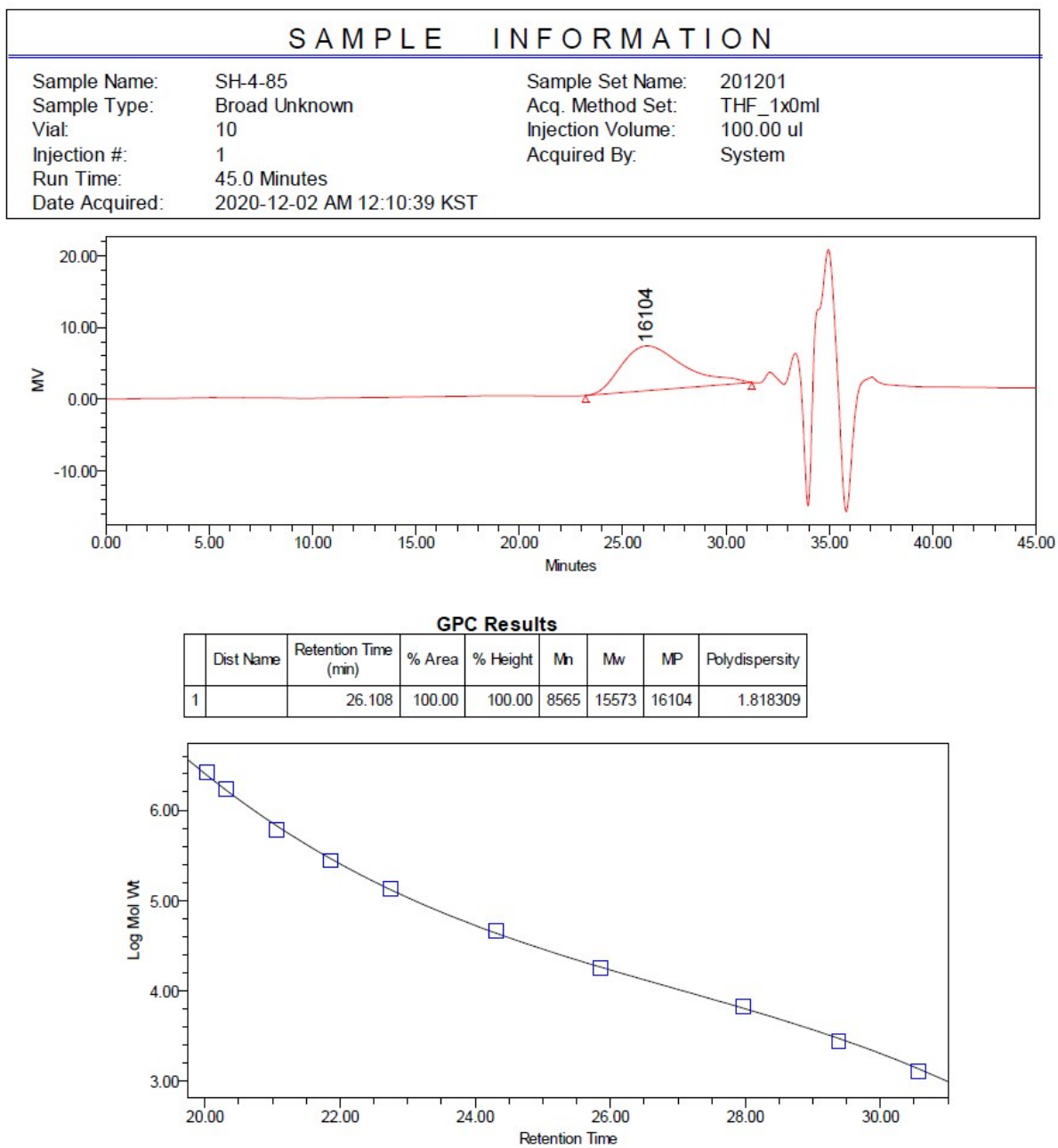


**GPC Results**

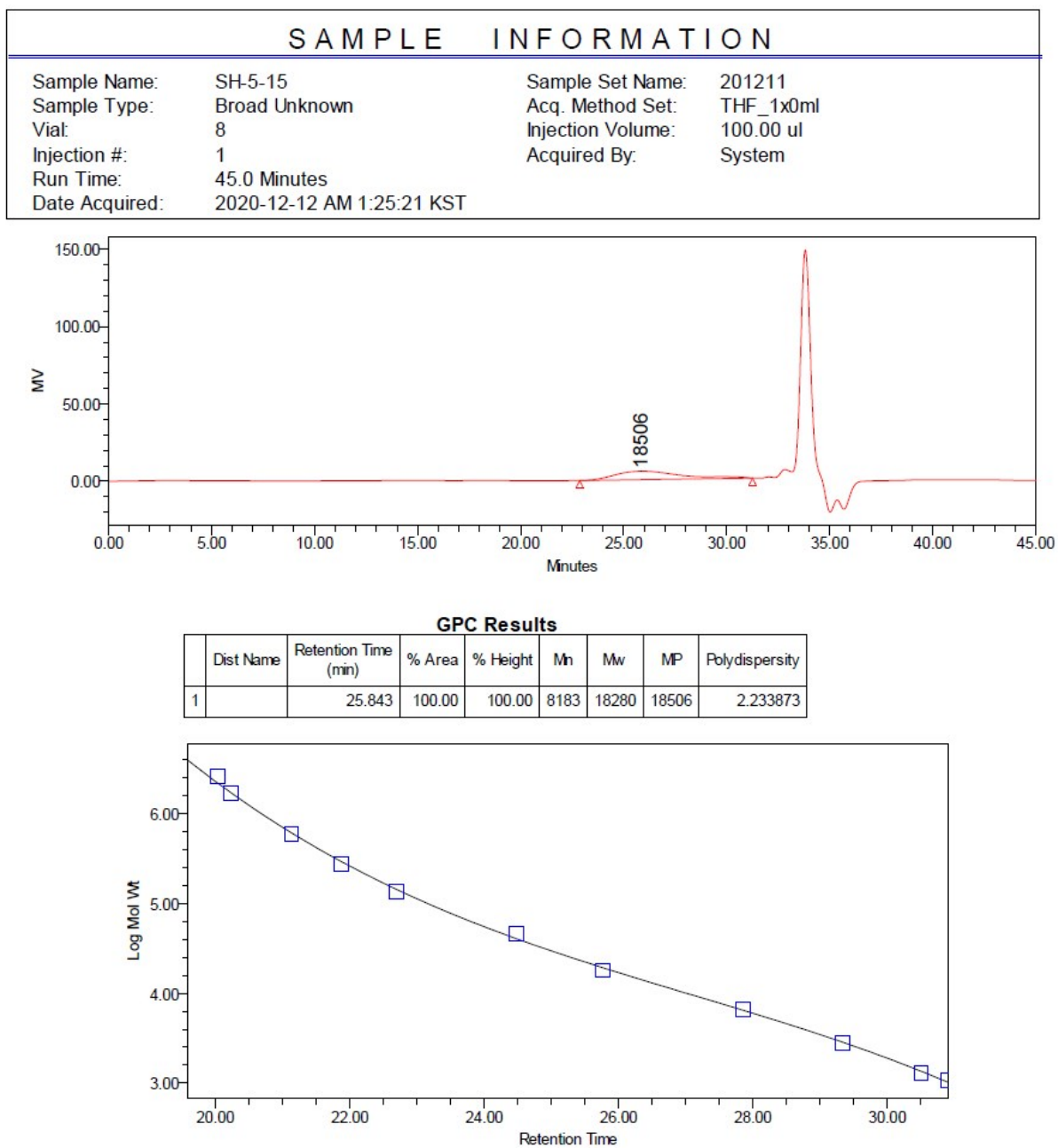
Dist Name	Retention Time (min)	% Area	% Height	Mn	Mw	MP	Polydispersity
1	25.483	100.00	100.00	11441	17214	16822	1.504505



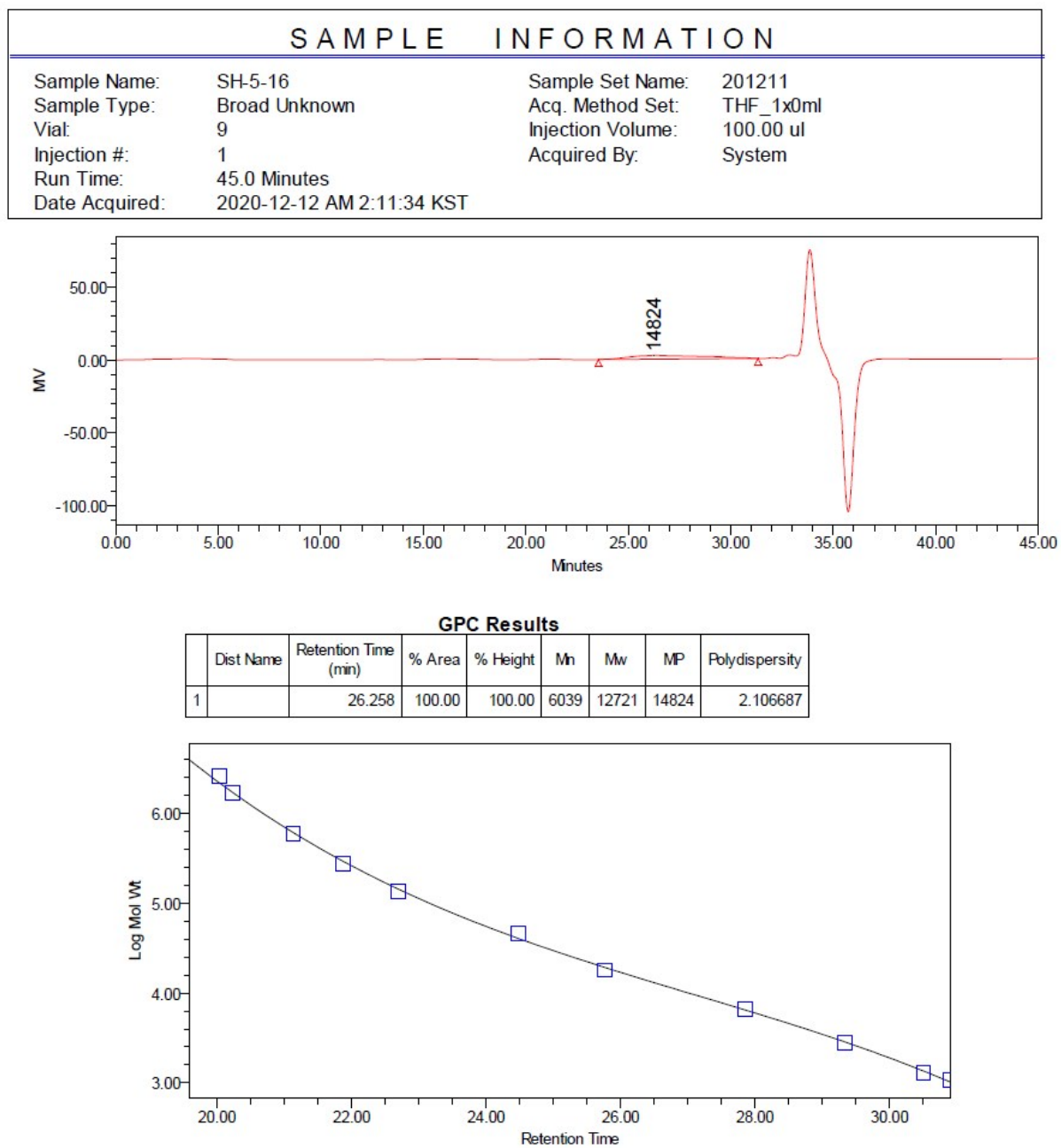
**Figure S46.** GPC data of PLA obtained with  $[L_ACoCl_2]/MeLi$  system at 25 °C.



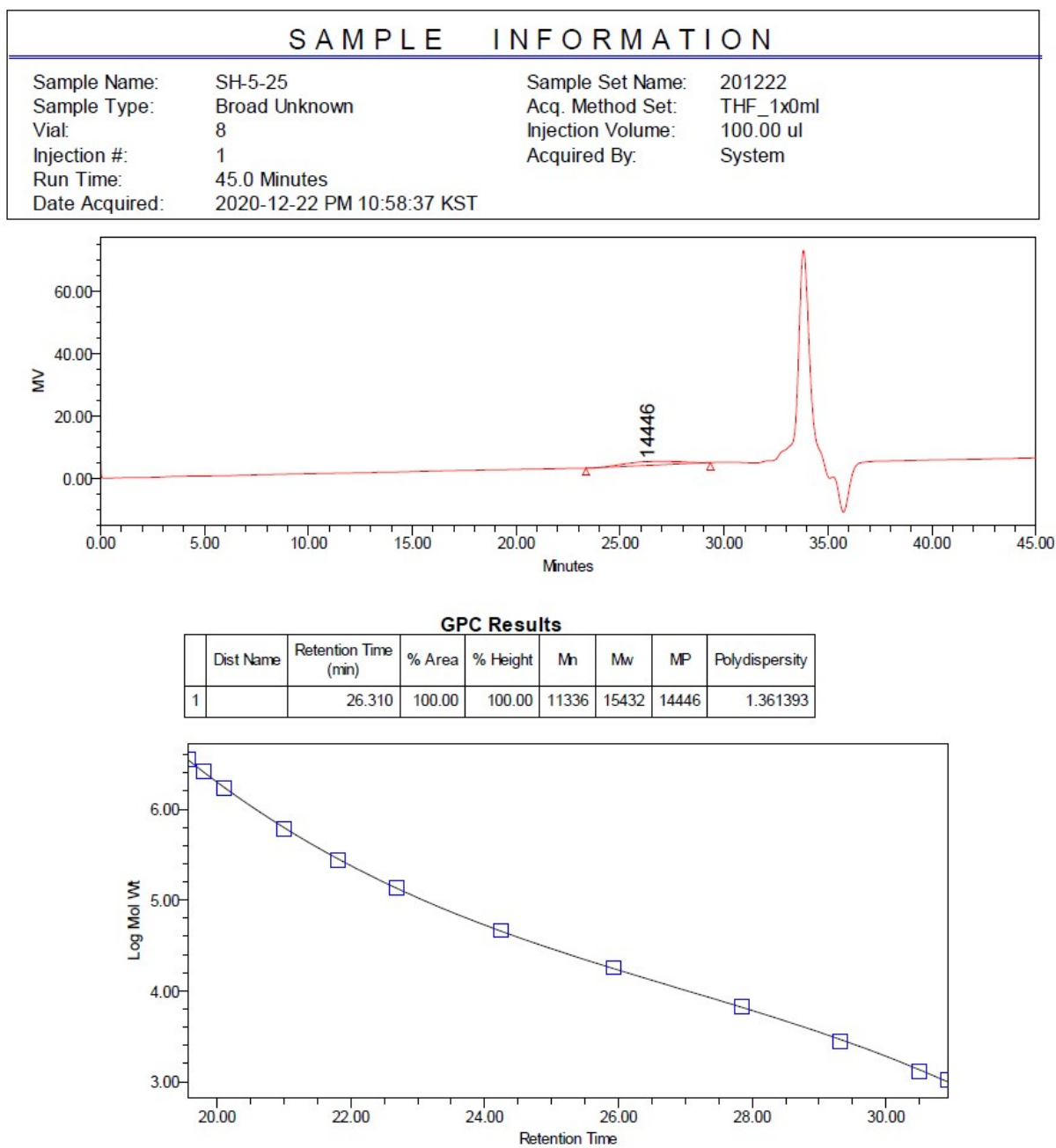
**Figure S47.** GPC data of PLA obtained with  $[L_AZnCl_2]/MeLi$  system at 25 °C.



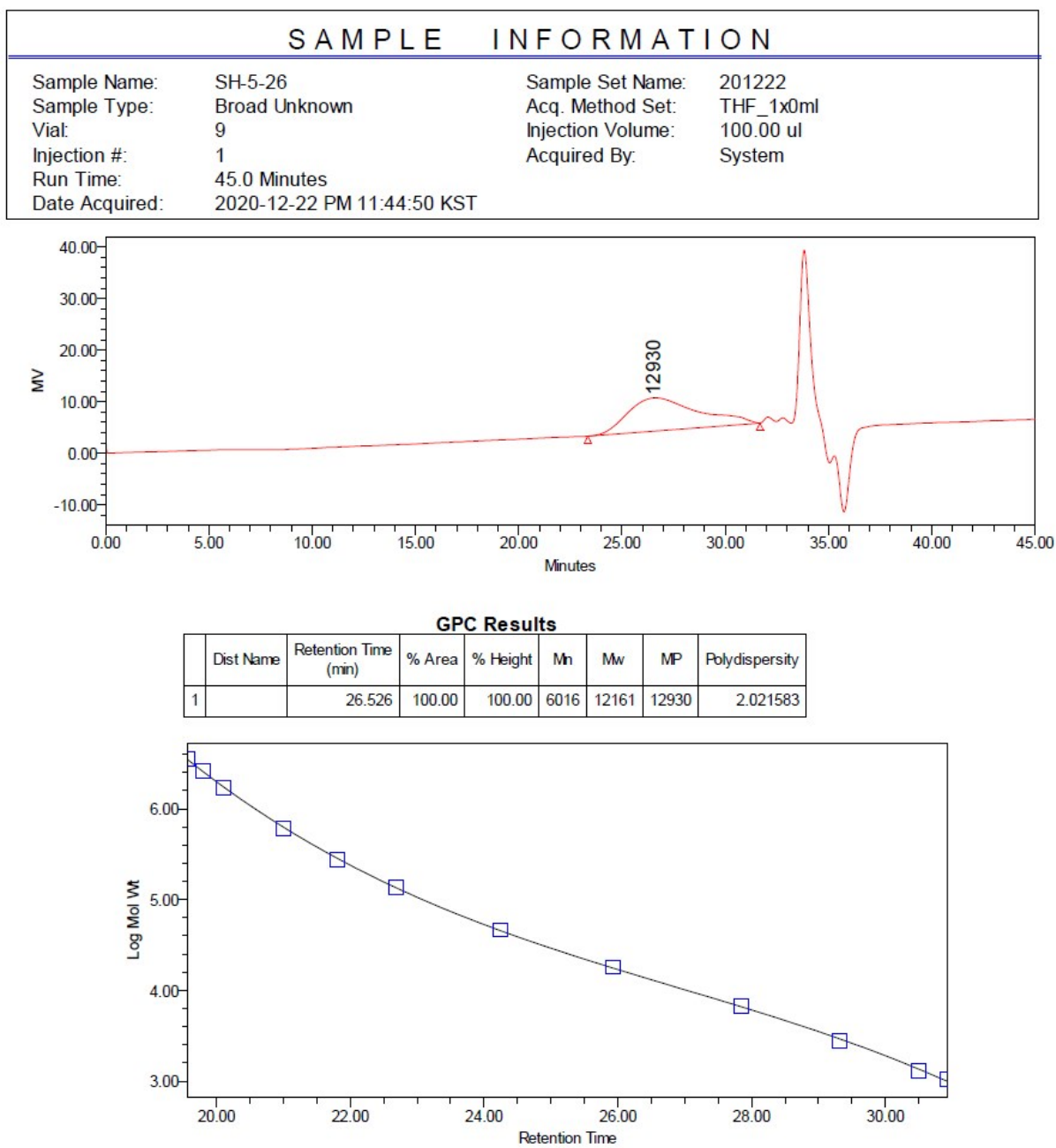
**Figure S48.** GPC data of PLA obtained with  $[L_A\text{CdBr}_2]/\text{MeLi}$  system at 25 °C.



**Figure S49.** GPC data of PLA obtained with  $[L_BCoCl_2]/MeLi$  system at 25 °C.

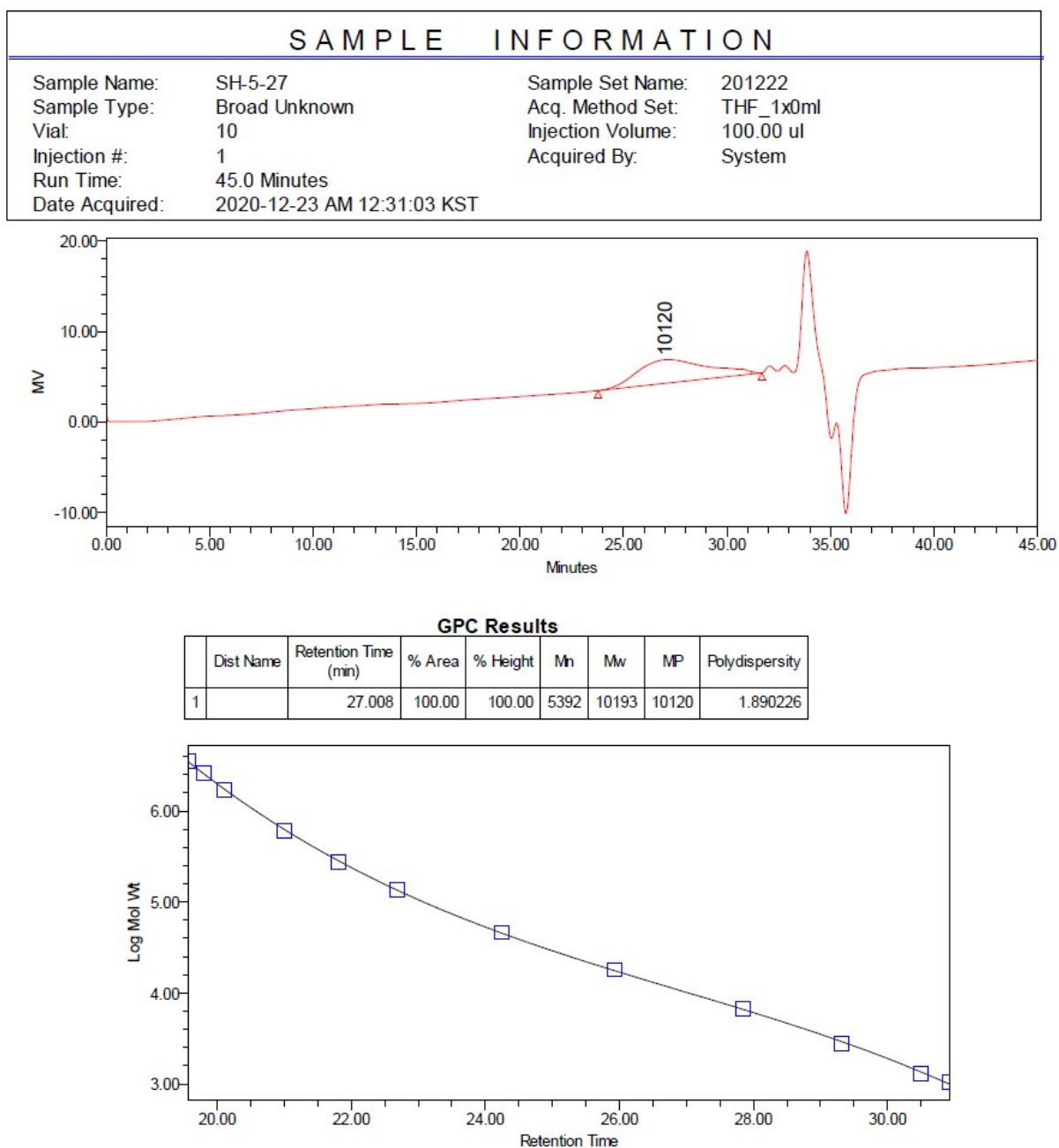


**Figure S50.** GPC data of PLA obtained with  $[L_BZnCl_2]/MeLi$  system at 25 °C.

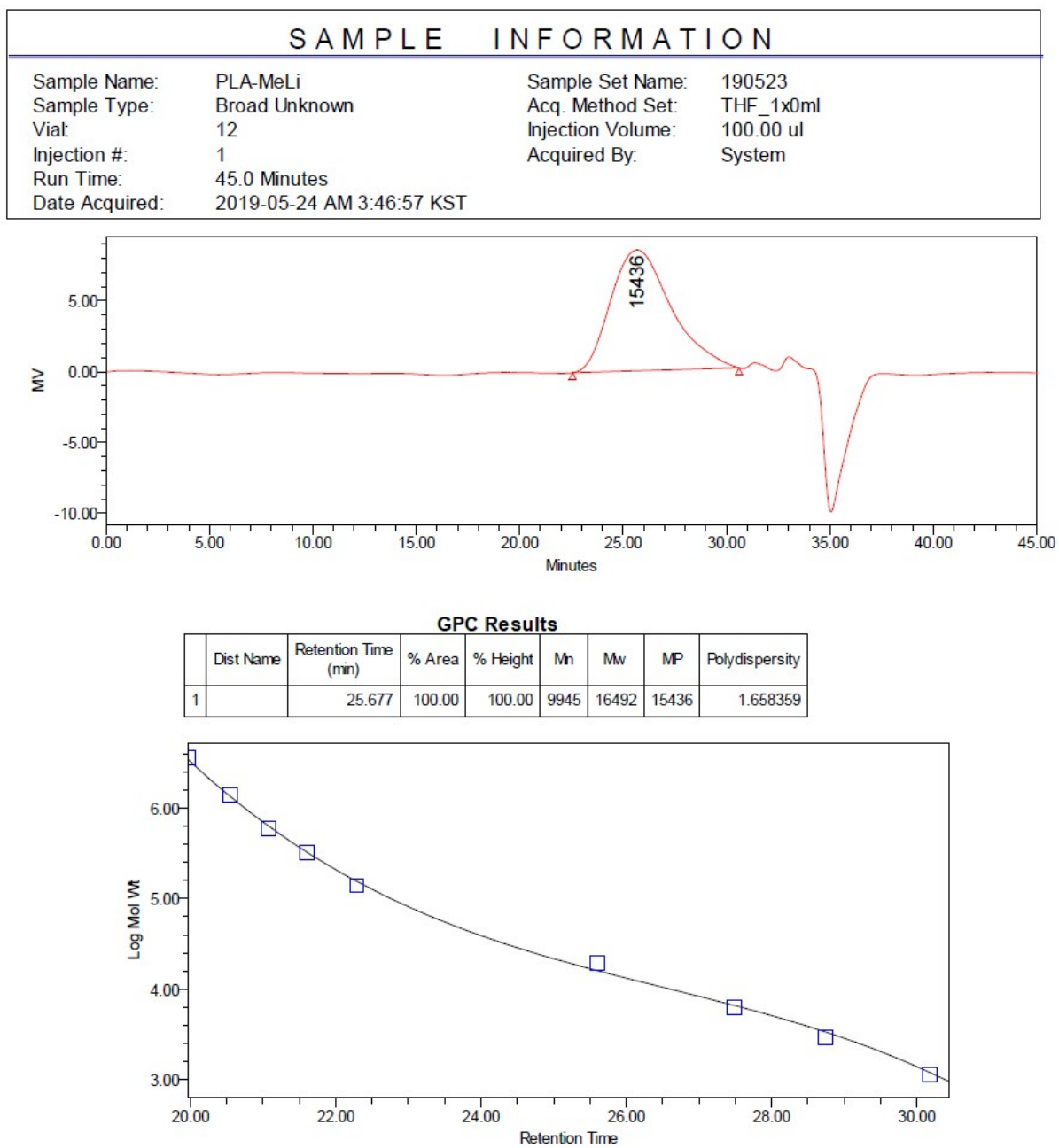




**Figure S51.** GPC data of PLA obtained with  $[L_B\text{CdBr}_2]/\text{MeLi}$  system at 25 °C.

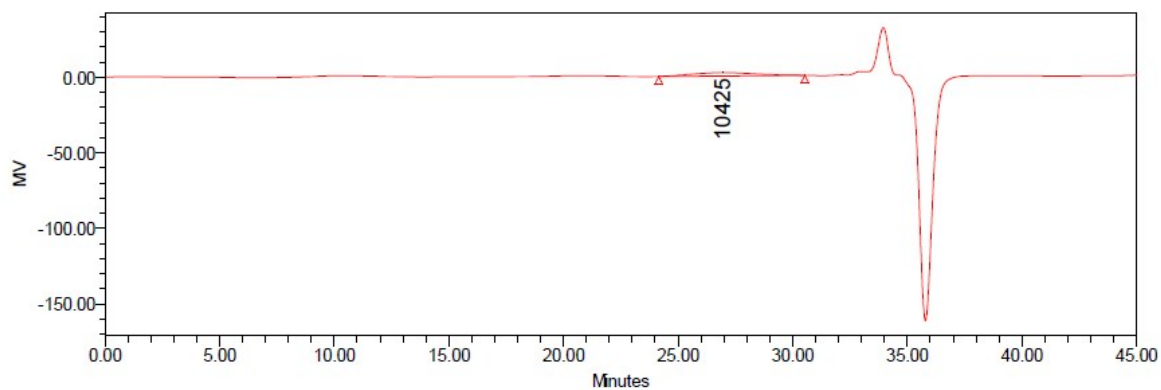


**Figure S52.** GPC data of PLA obtained with **MeLi** at -25 °C.



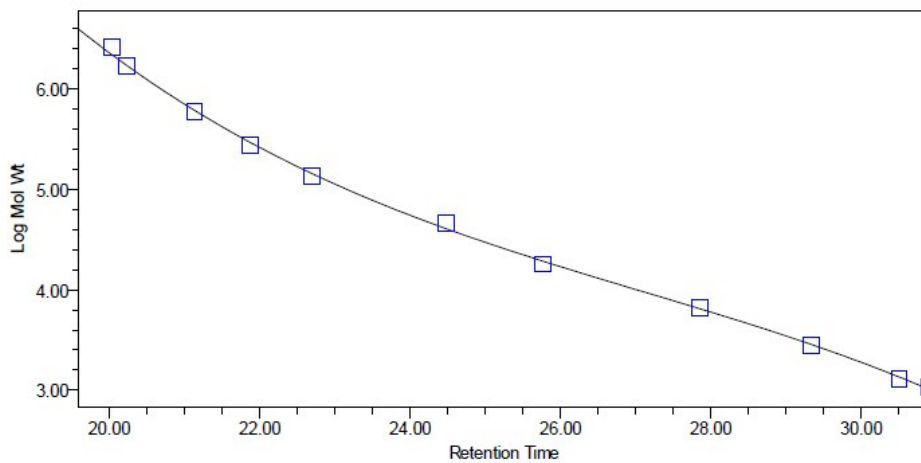
**Figure S53.** GPC data of PLA obtained with  $[L_ACoCl_2]/MeLi$  system at  $-25\text{ }^\circ\text{C}$ .

SAMPLE INFORMATION			
Sample Name:	SH-5-19	Sample Set Name:	201211
Sample Type:	Broad Unknown	Acq. Method Set:	THF_1x0ml
Vial:	12	Injection Volume:	100.00 ul
Injection #:	1	Acquired By:	System
Run Time:	45.0 Minutes		
Date Acquired:	2020-12-12 AM 4:30:14 KST		

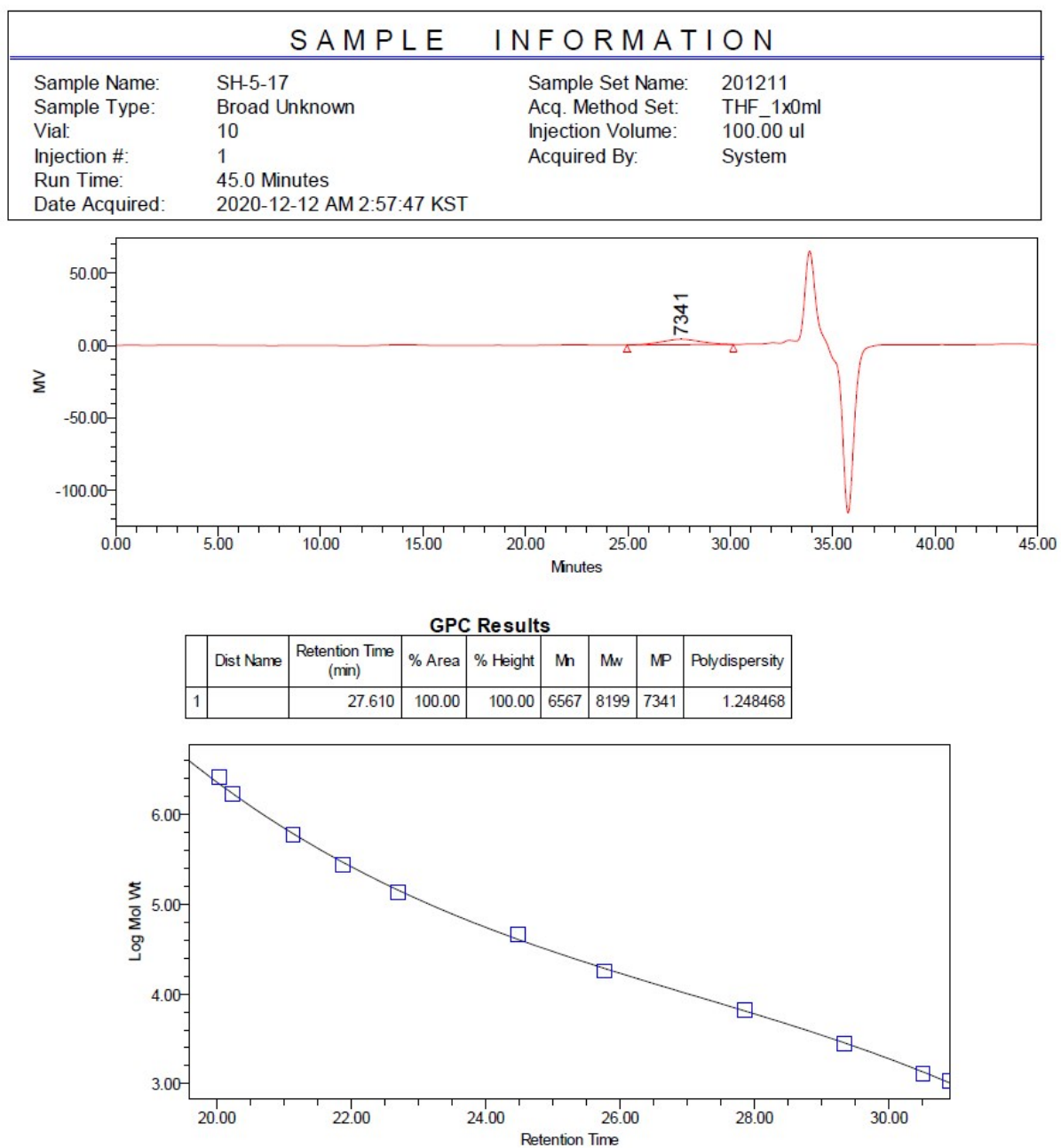


**GPC Results**

	Dist Name	Retention Time (min)	% Area	% Height	Mn	Mw	MP	Polydispersity
1		26.933	100.00	100.00	7769	11800	10425	1.518824



**Figure S54.** GPC data of PLA obtained with  $[L_AZnCl_2]/MeLi$  system at  $-25\text{ }^\circ\text{C}$ .



**Figure S55.** GPC data of PLA obtained with  $[L_A\text{CdBr}_2]/\text{MeLi}$  system at  $-25\text{ }^\circ\text{C}$ .

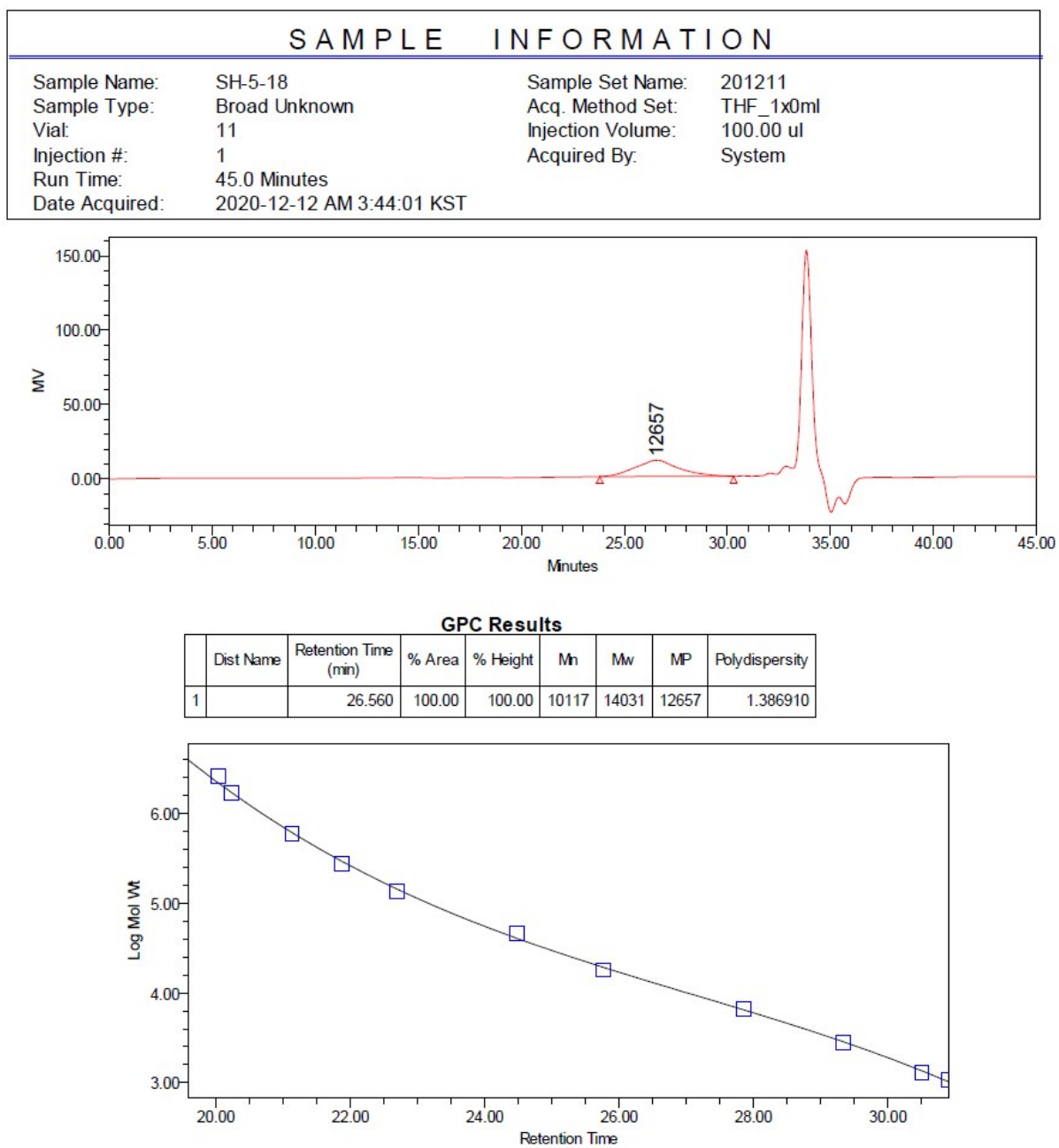
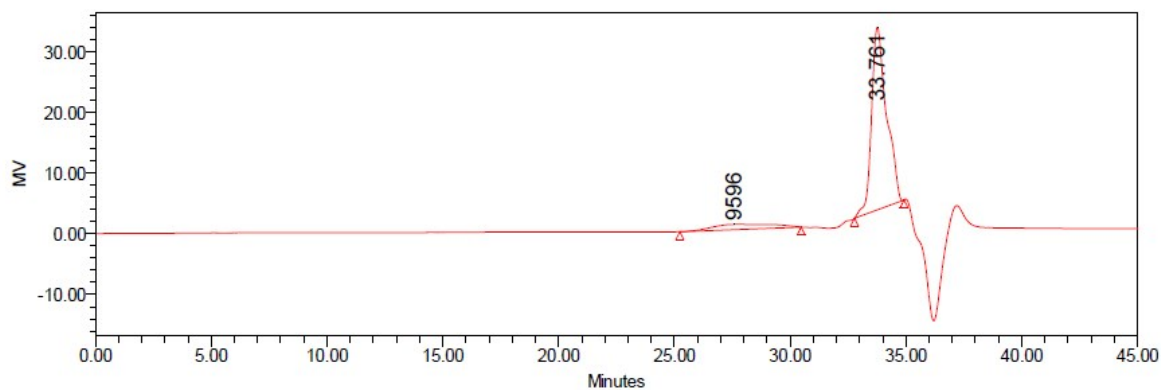


Figure S56. GPC data of PLA obtained with  $[L_BCoCl_2]/MeLi$  system at  $-25\text{ }^\circ\text{C}$ .

SAMPLE INFORMATION			
Sample Name:	35isoCo(-25)	Sample Set Name:	191021
Sample Type:	Broad Unknown	Acq. Method Set:	THF_1x0ml
Vial:	17	Injection Volume:	100.00 ul
Injection #:	1	Acquired By:	System
Run Time:	45.0 Minutes		
Date Acquired:	2019-10-26 AM 5:15:13 KST		



GPC Results

	Dist Name	Retention Time (min)	% Area	% Height	Mn	Mw	MP	Polydispersity
1		33.761	89.76	97.16				
2		27.558	10.24	2.84	6415	8635	9596	1.346101

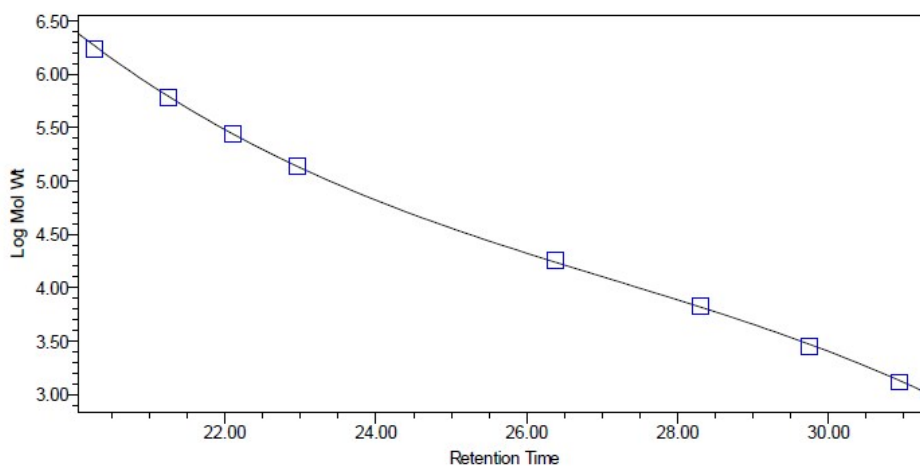
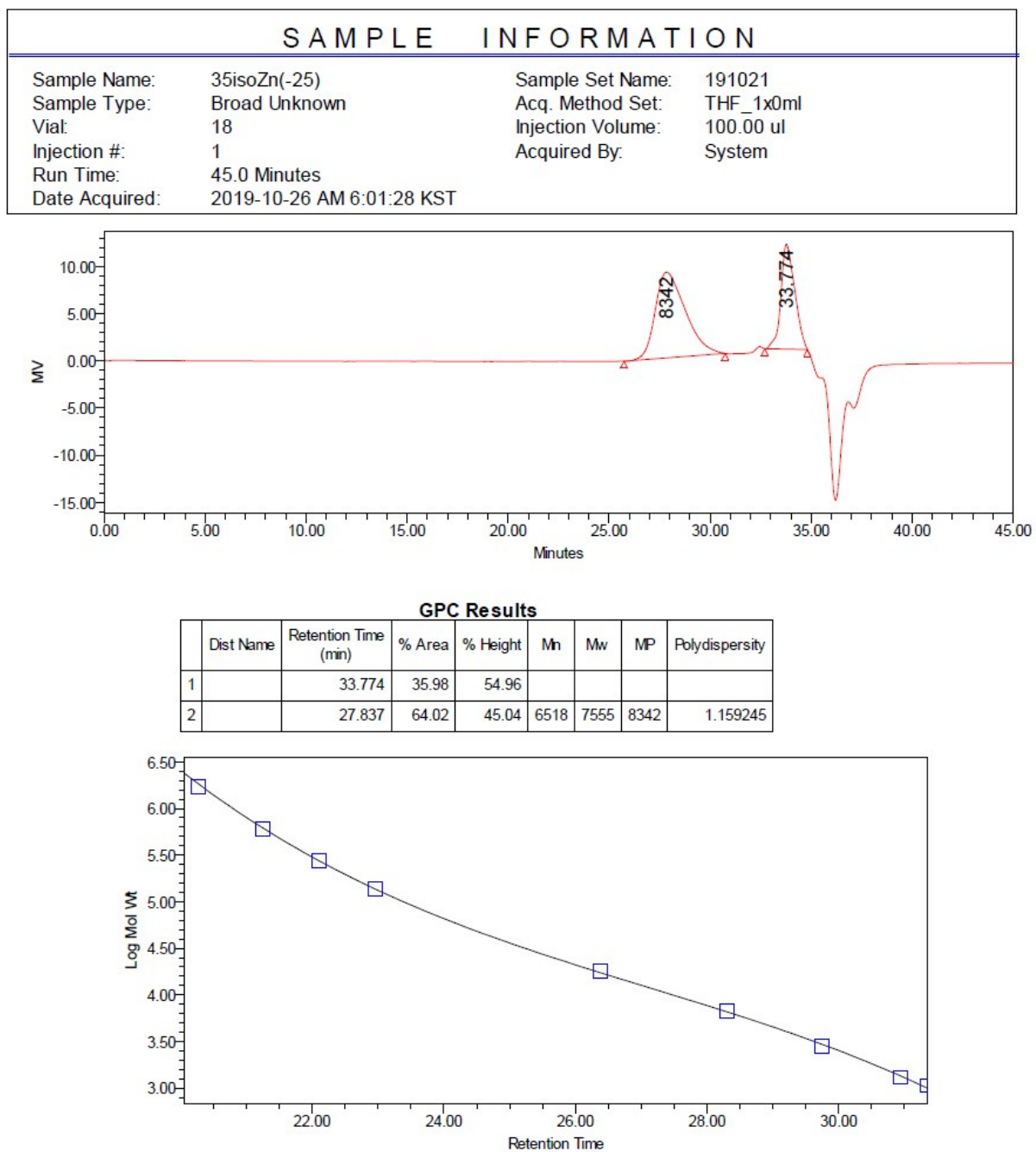
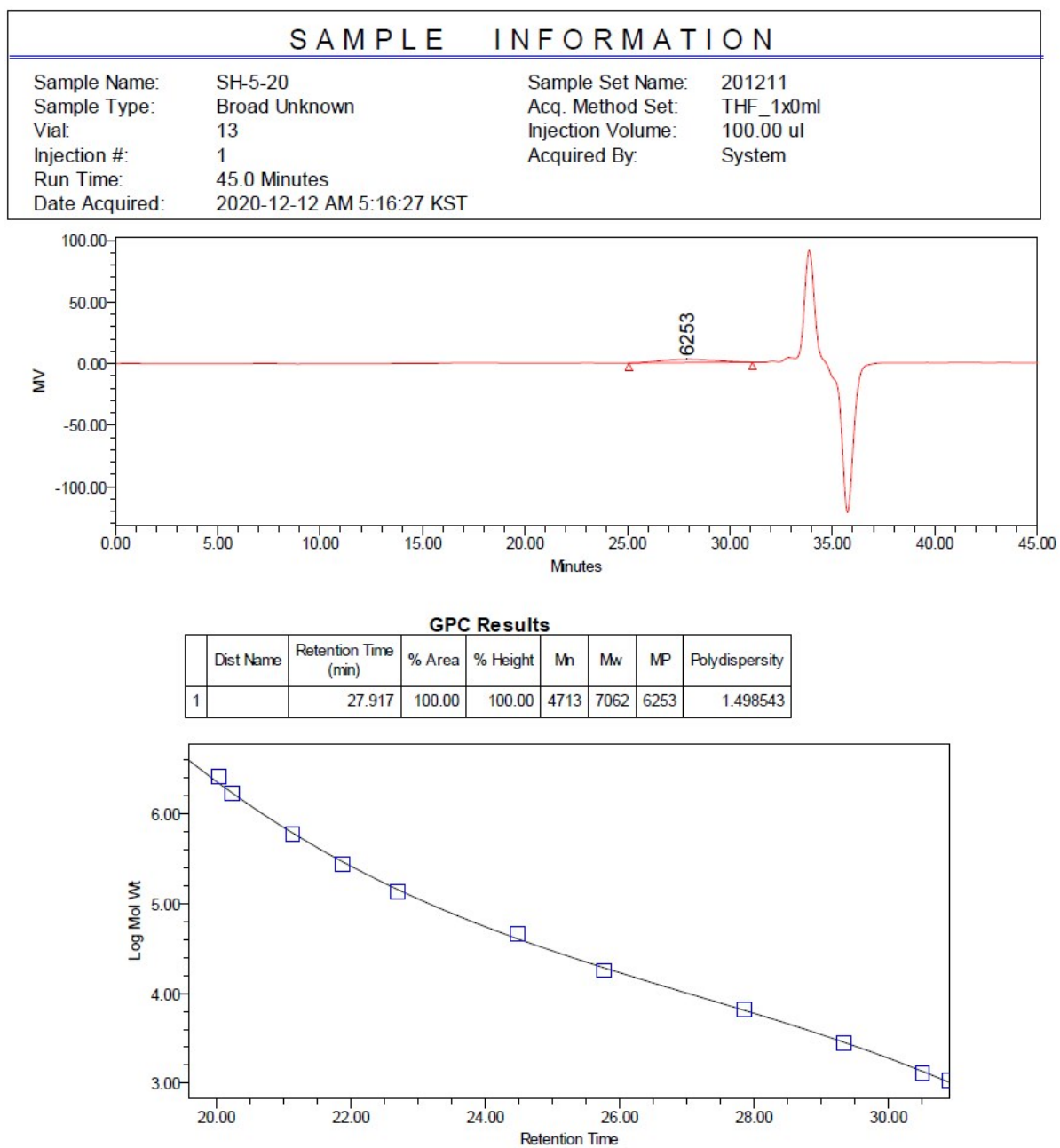


Figure S57. GPC data of PLA obtained with  $[L_BZnCl_2]/MeLi$  system at  $-25\text{ }^\circ\text{C}$ .

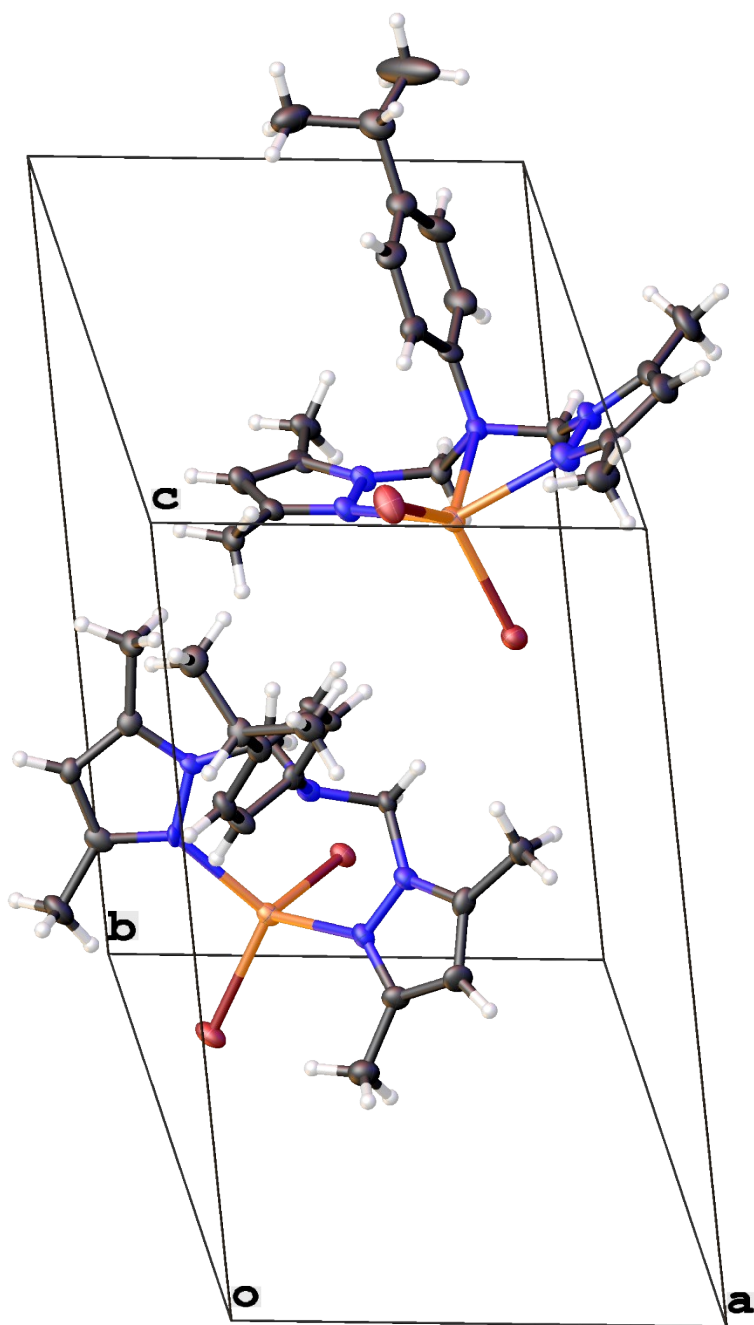


**Figure S58.** GPC data of PLA obtained with  $[L_B CdBr_2]/MeLi$  system at  $-25\text{ }^\circ\text{C}$ .

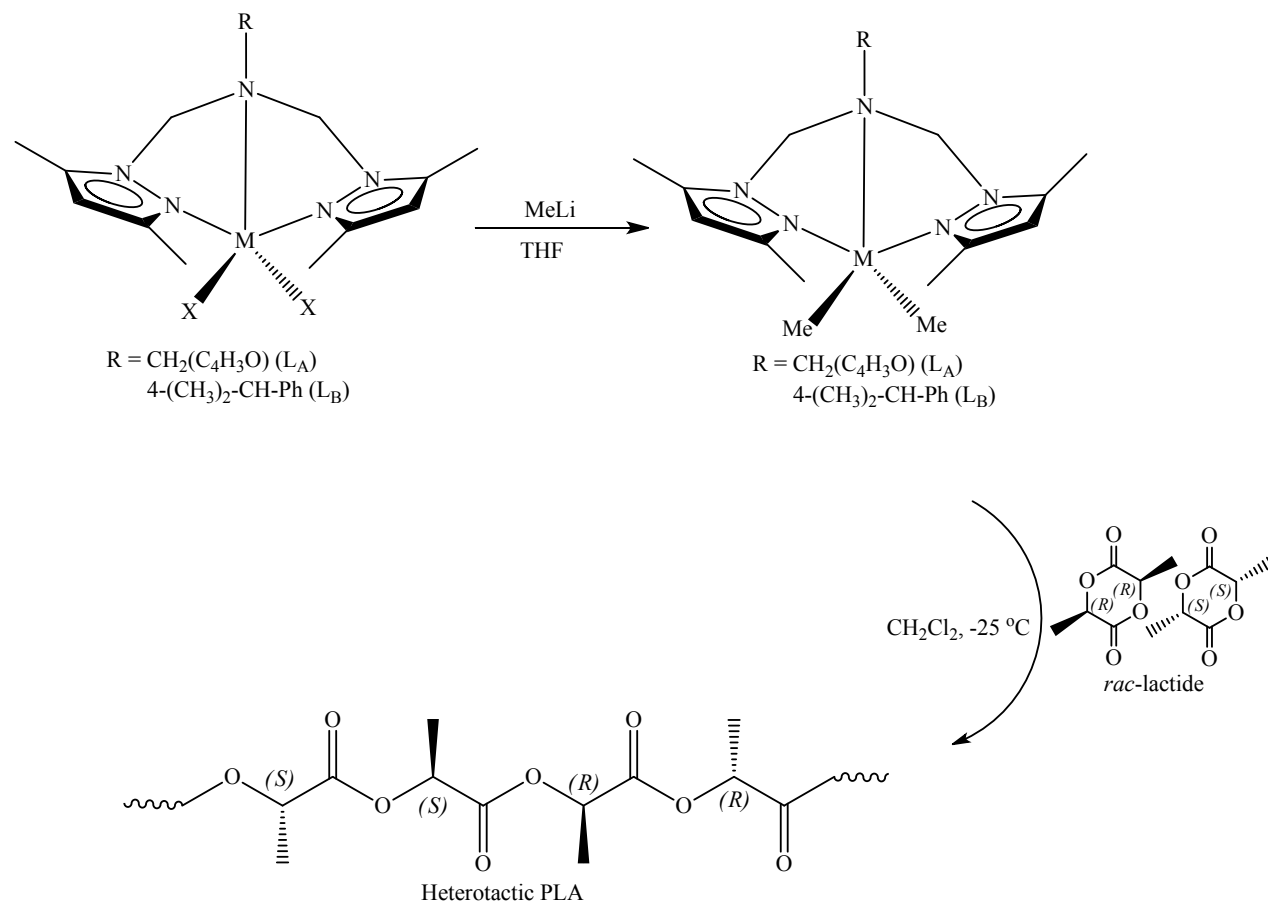




**Figure S59.** An Olex2 drawing of  $[L_B CdBr_2]$  unit cell.



**Scheme S2.** Preparation of dimethyl catalytic species for ROP of *rac*-LA.



**TABLE S1.** Crystal data and structure refinement.

	[L <sub>A</sub> CoCl <sub>2</sub> ]	[L <sub>A</sub> ZnCl <sub>2</sub> ]	[L <sub>A</sub> CdBr <sub>2</sub> ]	[L <sub>B</sub> CoCl <sub>2</sub> ]	[L <sub>B</sub> ZnCl <sub>2</sub> ]	[L <sub>B</sub> CdBr <sub>2</sub> ]
Empirical formula	C <sub>17</sub> H <sub>23</sub> Cl <sub>2</sub> N <sub>5</sub> OCo	C <sub>17</sub> H <sub>23</sub> Cl <sub>2</sub> N <sub>5</sub> OZn	C <sub>17</sub> H <sub>23</sub> Br <sub>2</sub> N <sub>5</sub> Ocd	C <sub>21</sub> H <sub>29</sub> Cl <sub>2</sub> CoN <sub>5</sub>	C <sub>21</sub> H <sub>29</sub> Cl <sub>2</sub> ZnN <sub>5</sub>	C <sub>21</sub> H <sub>29</sub> Br <sub>2</sub> CdN <sub>5</sub>
Formula weight	443.23	449.67	585.62	481.32	487.76	623.71
Temperature (K)	100(2)	98(2)	223(2)	100(2)	100(2)	293(2)
Wavelength (Å)	0.700	0.700	0.71073	0.630	0.610	0.700
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	P2 <sub>1</sub> /n	Cmc2 <sub>1</sub>	Pna2(1)	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n	p-1
a (Å)	13.536(3)	14.177(3)	11.5549(9)	12.775(3)	12.837(3)	8.9830(2)
b (Å)	10.185(2)	11.340(2)	14.9462(1)	12.623(3)	12.585(3)	13.250(3)
c (Å)	14.325(3)	12.075(2)	12.0964(9)	14.263(3)	14.222(3)	21.860(4)
α (°)	90	90	90	90	90	107.51(3)
β (°)	95.38(3)	90	90	92.00(3)	92.04(3)	99.64(3)
γ (°)	90	90	90	90	90	93.76(3)
Volume (Å <sup>3</sup> ), Z	1966.2(7), 4	1941.4(7), 4	2089.1(3), 4	2298.6(8), 4	2296.2(8), 4	2427.5(9), 4
Density (calculated) (Mg m <sup>-3</sup> )	1.497	1.538	1.862	1.391	1.411	1.707
Absorption coefficient (mm <sup>-1</sup> )	1.105	1.489	4.886	0.710	0.867	4.041
F(000)	916	928	1144	1004	1016	1232
Crystal size (mm <sup>3</sup> )	0.100 × 0.090 × 0.050	0.12 × 0.05 × 0.02	0.14 × 0.04 × 0.03	0.1 × 0.09 × 0.08	0.105 × 0.095 × 0.075	0.025 × 0.005 × 0.005
Theta range for data collection (°)	1.950 to 33.639	2.265 to 33.651	2.17 to 26.00	1.865 to 29.999	1.855 to 26.999	1.589 to 26.999

Index ranges	-17 ≤ h ≤ 17	-21 ≤ h ≤ 21	-11 ≤ h ≤ 14	-20 ≤ h ≤ 20	-19 ≤ h ≤ 19	-11 ≤ h ≤ 11
	-16 ≤ k ≤ 16	-16 ≤ k ≤ 16	-18 ≤ k ≤ 15	-20 ≤ k ≤ 20	-18 ≤ k ≤ 18	-17 ≤ k ≤ 17
	-22 ≤ l ≤ 22	-16 ≤ l ≤ 16	-14 ≤ l ≤ 14	-22 ≤ l ≤ 22	-21 ≤ l ≤ 21	-28 ≤ l ≤ 28
Reflections collected	22610	9446	12348	33425	27490	21781
Independent reflections	6909 [R(int) = 0.0889]	3323 [R(int) = 0.0680]	4046 [R(int) = 0.0344]	9553 [R(int) = 0.0931]	7909 [R(int) = 0.0792]	11032 [R(int) = 0.0720]
Completeness to theta	99.9 % (24.835°)	97.4 % (24.835°)	99.8 % (26.00°)	99.9 % (22.210°)	99.8 % (21.469°)	99.7 % (24.835°)
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6909 / 0 / 239	3323 / 1 / 135	4046 / 1 / 239	9553 / 0 / 268	7909 / 0 / 268	11032 / 0 / 535
Goodness-of-fit on F <sup>2</sup>	1.151	1.198	1.065	1.122	1.142	0.872
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0652 wR <sub>2</sub> = 0.11951	R <sub>1</sub> = 0.0526 wR <sub>2</sub> = 0.1597	R <sub>1</sub> = 0.0305 wR <sub>2</sub> = 0.0717	R <sub>1</sub> = 0.0502 wR <sub>2</sub> = 0.1310	R <sub>1</sub> = 0.0386 wR <sub>2</sub> = 0.1085	R <sub>1</sub> = 0.0554 wR <sub>2</sub> = 0.1380
R indices (all data)	R <sub>1</sub> = 0.0694 wR <sub>2</sub> = 0.1999	R <sub>1</sub> = 0.0534 wR <sub>2</sub> = 0.1601	R <sub>1</sub> = 0.0450 wR <sub>2</sub> = 0.0933	R <sub>1</sub> = 0.0686 wR <sub>2</sub> = 0.1393	R <sub>1</sub> = 0.0420 wR <sub>2</sub> = 0.1105	R <sub>1</sub> = 0.0799 wR <sub>2</sub> = 0.1479
Largest diff. peak and hole (e.Å <sup>-3</sup> )	2.599 and -2.214	1.278 and -1.362	0.520 and -1.027	0.848 and -2.025	1.207 and -1.154	2.588 and -1.783

**TABLE S2.** Five-coordinate geometry indices ( $\tau_5$ ) for  $[\text{L}_\text{A}\text{CoCl}_2]$ ,  $[\text{L}_\text{A}\text{ZnCl}_2]$ ,  $[\text{L}_\text{A}\text{CdBr}_2]$ ,  $[\text{L}_\text{B}\text{CdBr}_2]$  and representative examples from the literature.

Complexes	Geometry	$\tau_5$	References
Trigonal bipyramidal ( $D_{3h}$ ) <sup>a</sup>	Trigonal bipyramidal	1.000	37-40
$[\text{L}_\text{A}\text{CoCl}_2]$	Trigonal bipyramidal	0.777	This work
$[\text{L}_\text{A}\text{ZnCl}_2]$	Trigonal bipyramidal	0.533	This work
$[\text{L}_\text{A}\text{CdBr}_2]$	Square pyramidal	0.145	This work
$[\text{L}_\text{B}\text{CdBr}_2]$	Square pyramidal	0.089	This work
Square pyramidal ( $C_{4v}$ ) <sup>a</sup>	Square pyramidal	0.000	37-40

<sup>a</sup> See reference<sup>37-40</sup>

37 K. S. Kwon, S. Nayab and J. H. Jeong, *Polyhedron*, 2015, **85**, 615–620.

38 N. W. Attandoh, S. O. Ojwach and O. Q. Munro, *Eur. J. Inorg. Chem.*, 2014, 3053–3064.

39 S. O. Ojwach, T. T. Okemwa, N. W. Attandoh and B. Omondi, *Dalton Trans.*, 2013, **42**, 10735–10745.

40 M. Zikode, S. O. Ojwach and M. P. Akerman, *Appl. Organomet. Chem.*, 2017, **31**, e3556.

**Table S3.** Four-coordinate geometry indices ( $\tau_4$ ) for  $[\text{L}_\text{B}\text{CoCl}_2]$ ,  $[\text{L}_\text{B}\text{ZnCl}_2]$ ,  $[\text{L}_\text{B}\text{CdBr}_2]$  and representative example from the literature.

Complexes	Geometry	$\tau_4$	THC <sub>DA</sub> /100	FCGP/100	References
Square planar ( $D_{4h}$ ) <sup>a</sup>	Square planar	0.000	-1.43	-0.40	<sup>41</sup>
$[\text{L}_\text{B}\text{CoCl}_2]$	Tetrahedral	0.927	0.741	0.205	This work
$[\text{L}_\text{B}\text{ZnCl}_2]$	Tetrahedral	0.919	0.742	0.208	This work
$[\text{L}_\text{B}\text{CdBr}_2]$	Tetrahedral	0.899	0.670	0.258	This work
Tetrahedral ( $T_d$ ) <sup>a</sup>	Tetrahedral	1.000	1.00	0.00	<sup>41</sup>

<sup>a</sup> See reference <sup>41</sup>

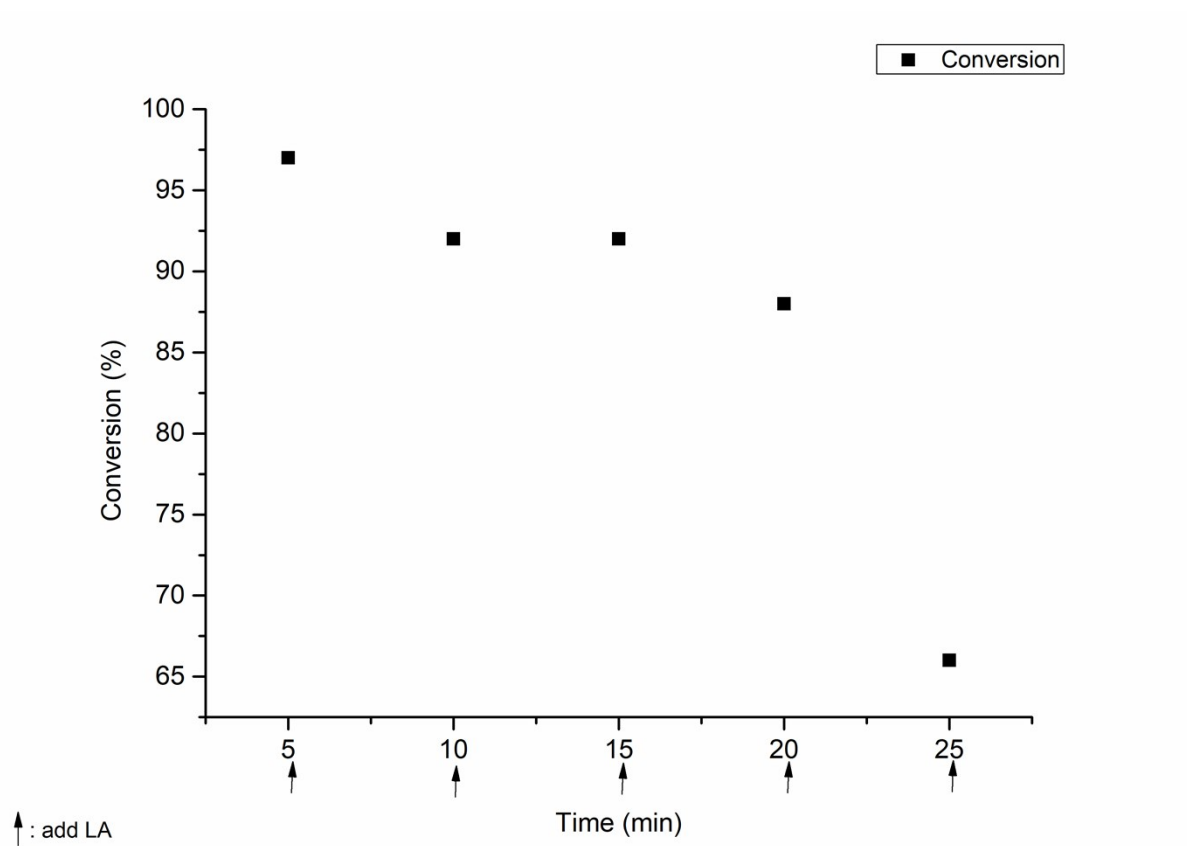
41 M. Zikode, S. O. Ojwach and M. P. Akerman, *J. Mol. Catal. A: Chem.*, 2016, **413**, 24–31.

**TABLE S4.** ROP of *rac*-LA using  $[\mathbf{L}_B\mathbf{ZnCl}_2]/\mathbf{MeLi}$  system to determine stability of catalytic species with an addition of 200-500 equivalent of monomer at the interval of 5 min without adding the initiator.

Entry	Initiator	Conversion (%)	Time (min)
1	$[\mathbf{L}_B\mathbf{ZnCl}_2]/\mathbf{MeLi}$ <sup>a</sup>	98	5
2	$[\mathbf{L}_B\mathbf{ZnCl}_2]/\mathbf{MeLi}$ <sup>b</sup>	93	10
3	$[\mathbf{L}_B\mathbf{ZnCl}_2]/\mathbf{MeLi}$ <sup>c</sup>	93	15
4	$[\mathbf{L}_B\mathbf{ZnCl}_2]/\mathbf{MeLi}$ <sup>d</sup>	88	20
5	$[\mathbf{L}_B\mathbf{ZnCl}_2]/\mathbf{MeLi}$ <sup>e</sup>	67	25

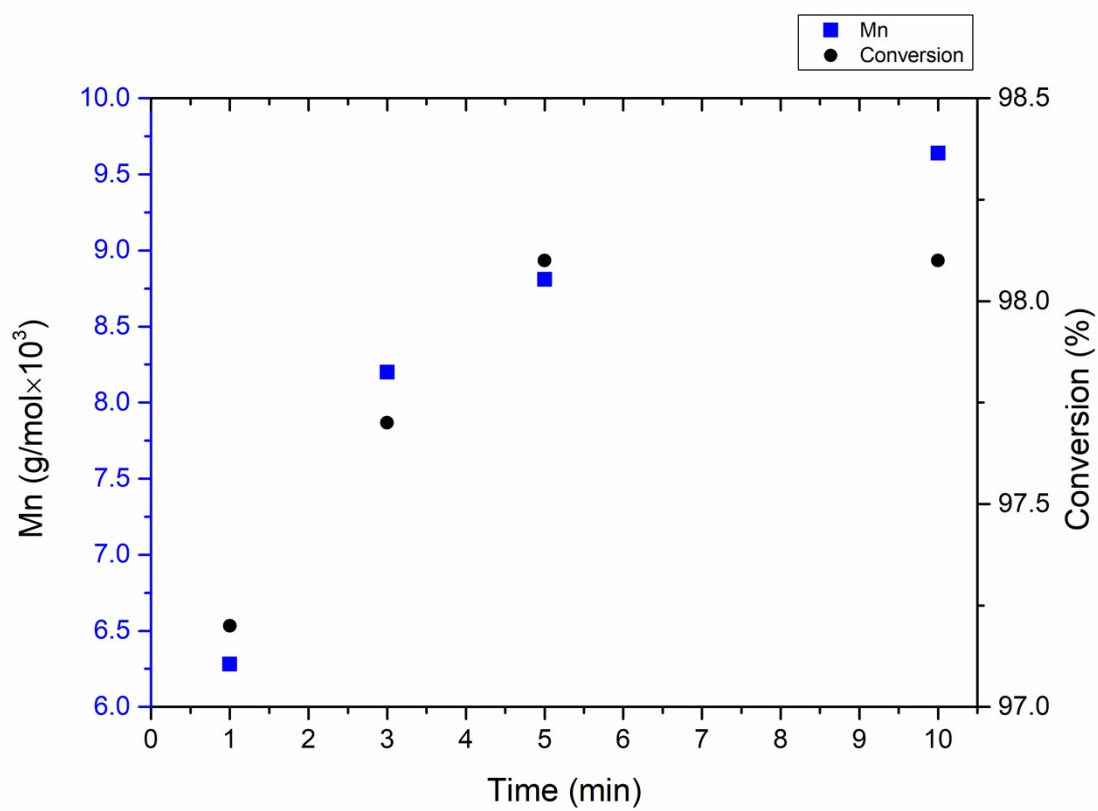
<sup>a</sup> Conditions: [Initiator] = (0.901 g; 0.0625 mmol), [*rac*-LA]/[Initiator] = 100:1; 5.00 mL of CH<sub>2</sub>Cl<sub>2</sub> as polymerisation solvent; polymerisation temperature 25 °C, polymerization time 5 min. <sup>b</sup> Addition of second equivalent of *rac*-LA without adding the initiator and the polymerization stopped after 5 min of addition of second batch of *rac*-LA (100 equivalent, 0.901 g). <sup>c</sup> Addition of third equivalent of *rac*-LA without adding the initiator and the polymerization stopped after 5 min of addition of third batch of *rac*-LA (100 equivalent, 0.901 g). <sup>d</sup> Addition of fourth equivalent of *rac*-LA without adding the initiator and the polymerization stopped after 5 min of addition of fourth batch of *rac*-LA (100 equivalent, 0.901 g). <sup>e</sup> Addition of fifth equivalent of *rac*-LA without adding the initiator and the polymerization stopped after 5 min of addition of fifth batch of *rac*-LA (100 equivalent, 0.901 g). Polymerization stopped at 5 min (total 25 min) after addition of 500 equivalents of *rac*-LA.

**Figure S60.** Plot of % conversion vs. time of the first to fifth cycle experiments for  $[L_BZnCl_2]/MeLi$  system at 25 °C; 1<sup>st</sup> cycle:  $[rac-LA]/[catalyst] = 100$ . Equivalent amount of *rac*-LA was added in the every cycle without adding the catalyst.





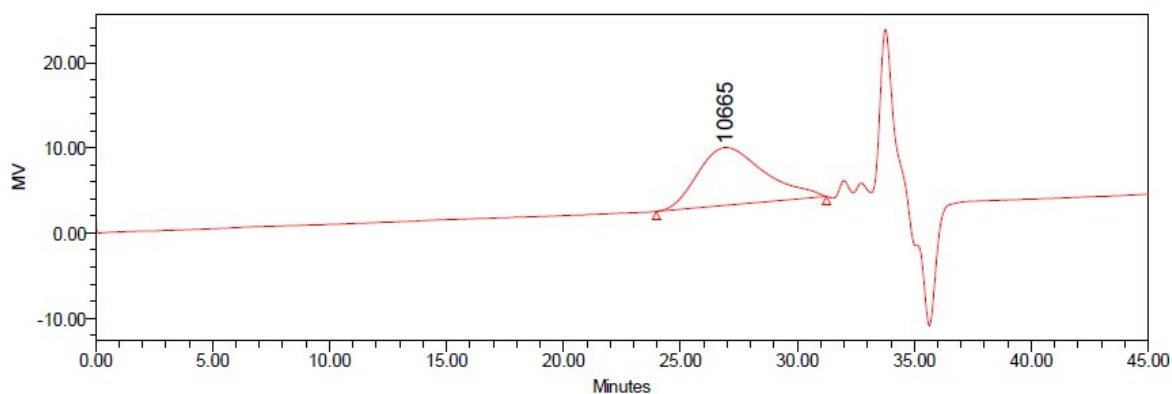
**Figure S61.** Plot of  $M_n$  and % conversion vs. time of experiments for  $[\text{L}_B\text{ZnCl}_2]/\text{MeLi}$  system at 25 °C.



Time (min)	$M_n$ (g/mol $\times 10^3$ )	Conversion (%)
1	6.28	97.2
3	8.20	97.7
5	8.81	98.1
10	9.64	98.1

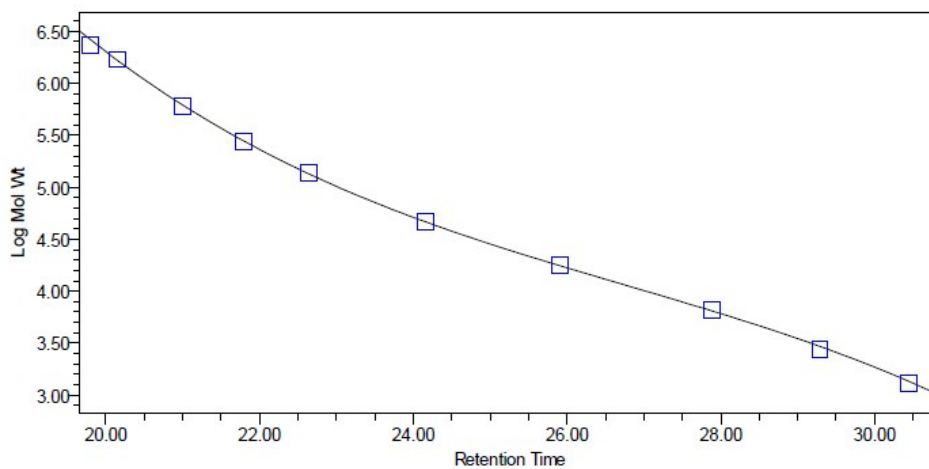
**Figure S62.** GPC data of PLA obtained with  $[L_BZnCl_2]/MeLi$  system at 25 °C (1 min).

SAMPLE INFORMATION			
Sample Name:	SH-5-43-1	Sample Set Name:	210204
Sample Type:	Broad Unknown	Acq. Method Set:	THF_1x0ml
Vial:	8	Injection Volume:	100.00 ul
Injection #:	1	Acquired By:	System
Run Time:	45.0 Minutes		
Date Acquired:	2021-02-04 PM 10:21:58 KST		



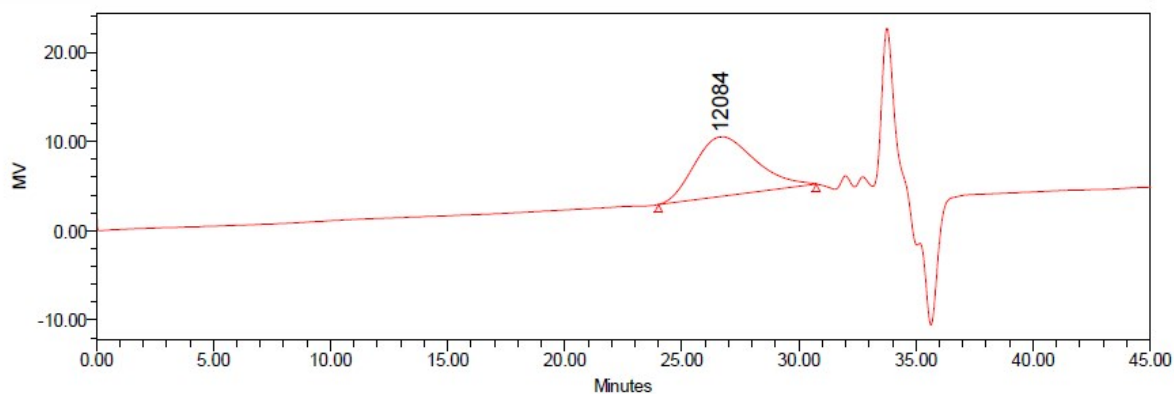
**GPC Results**

Dist Name	Retention Time (min)	% Area	% Height	Mn	Mw	MP	Polydispersity
1	26.900	100.00	100.00	6284	10428	10665	1.659374



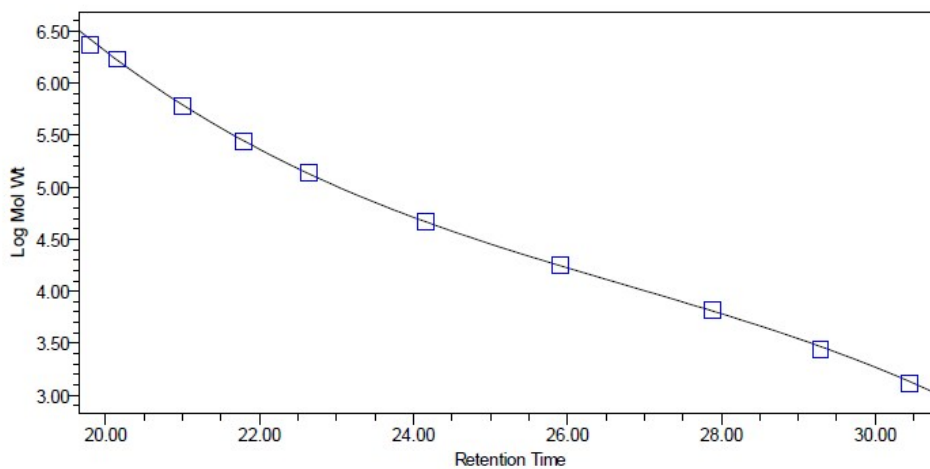
**Figure S63.** GPC data of PLA obtained with  $[L_BZnCl_2]/MeLi$  system at 25 °C (3 min).

SAMPLE INFORMATION			
Sample Name:	SH-5-43-2	Sample Set Name:	210204
Sample Type:	Broad Unknown	Acq. Method Set:	THF_1x0ml
Vial:	9	Injection Volume:	100.00 ul
Injection #:	1	Acquired By:	System
Run Time:	45.0 Minutes		
Date Acquired:	2021-02-04 PM 11:08:12 KST		

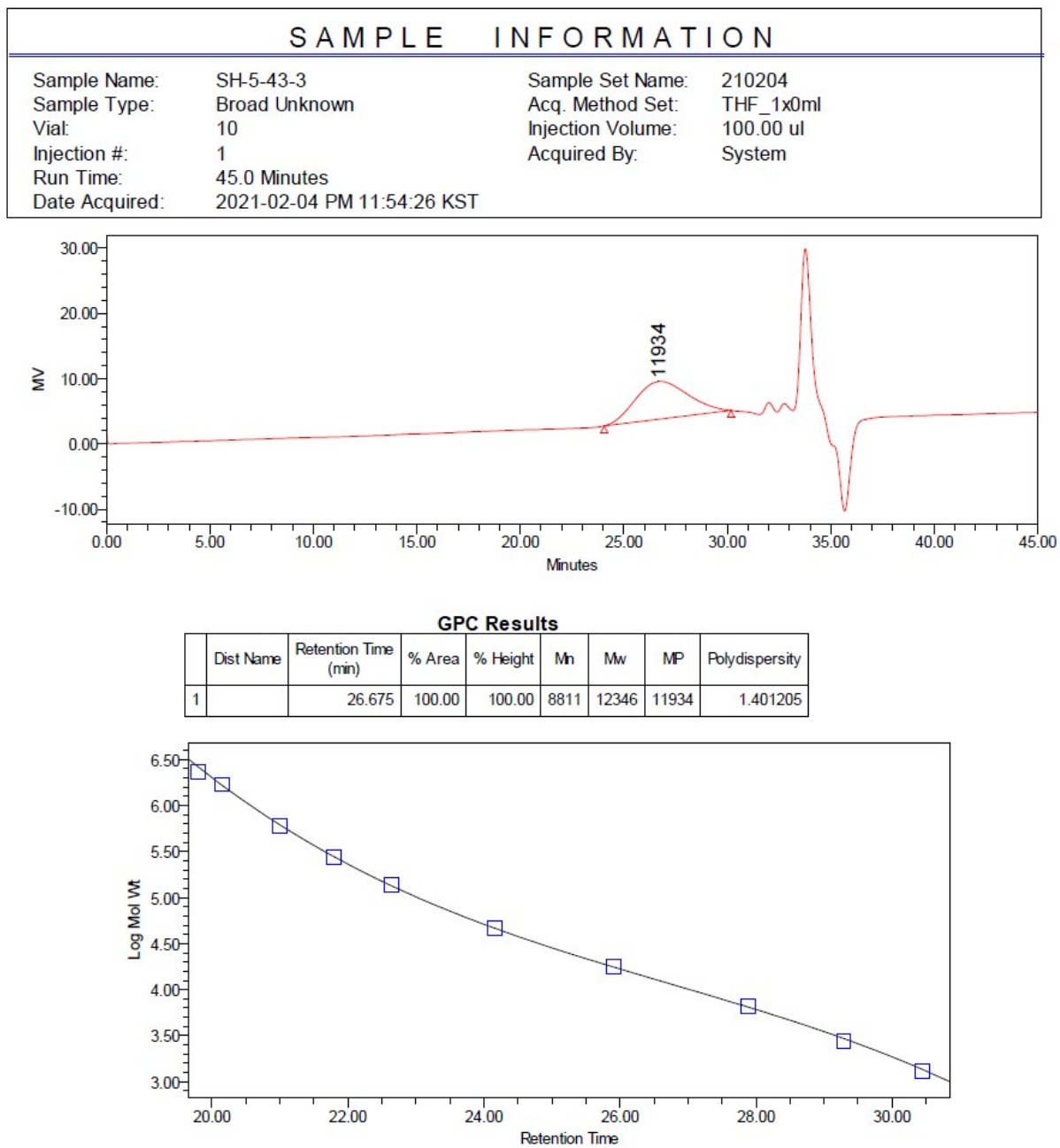


**GPC Results**

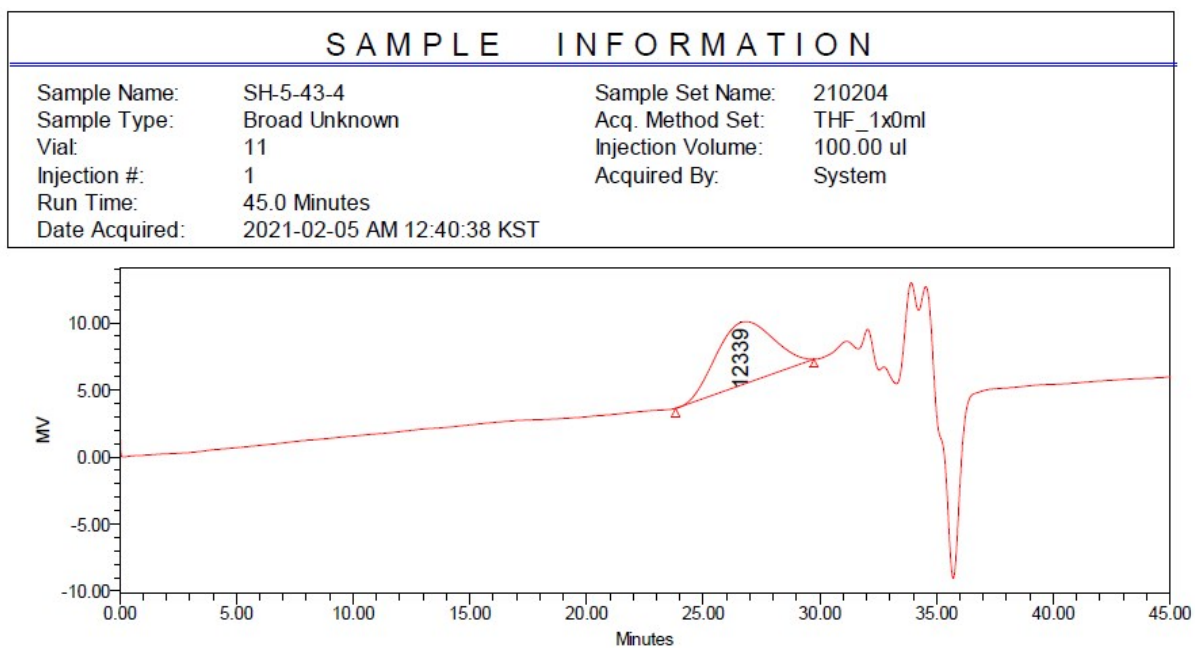
Dist Name	Retention Time (min)	% Area	% Height	Mn	Mw	MP	Polydispersity
1	26.650	100.00	100.00	8200	12165	12084	1.483574



**Figure S64.** GPC data of PLA obtained with  $[L_BZnCl_2]/MeLi$  system at 25 °C (5 min).

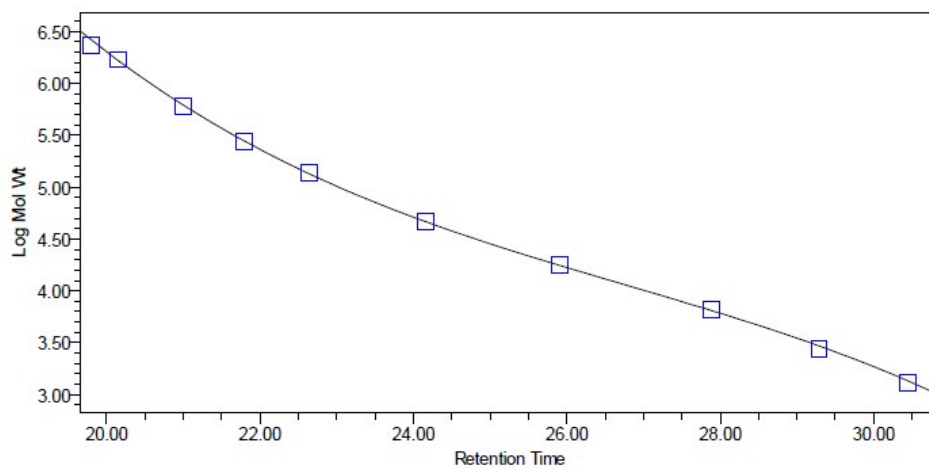


**Figure S65.** GPC data of PLA obtained with  $[L_BZnCl_2]/MeLi$  system at 25 °C (10 min).

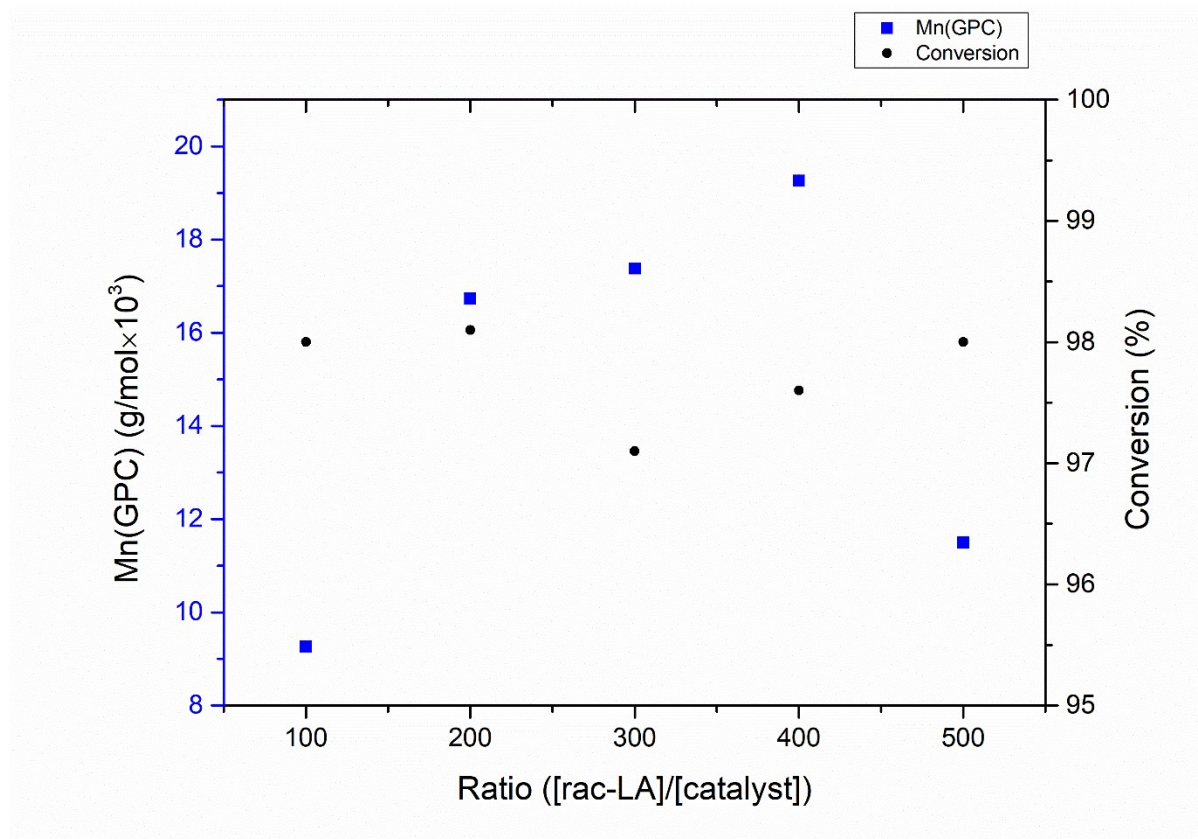


**GPC Results**

Dist Name	Retention Time (min)	% Area	% Height	Mn	Mw	MP	Polydispersity
1	26.608	100.00	100.00	9639	12815	12339	1.329478



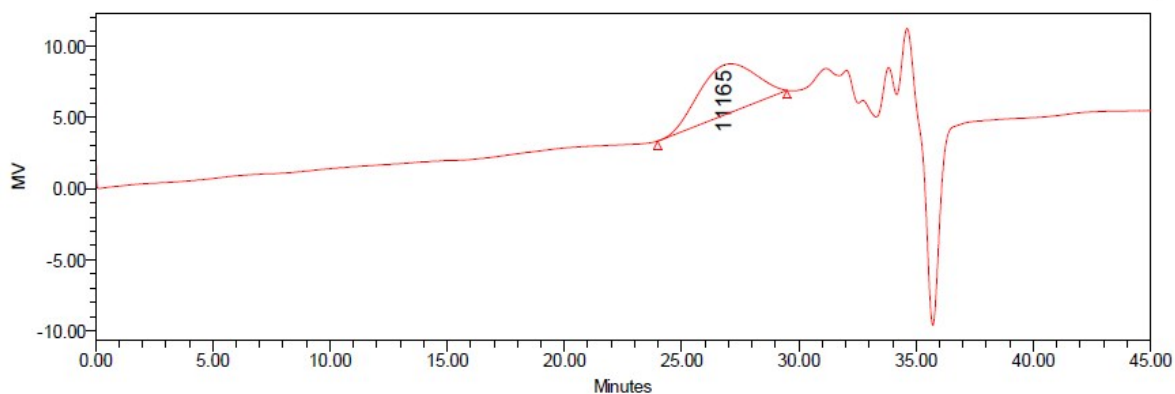
**Figure S66.** Plot of  $M_n$  and conversion vs  $[rac\text{-LA}]/[\text{catalyst}]$  in the ROP of  $rac\text{-LA}$  by  $[\text{L}_B\text{ZnCl}_2]/\text{MeLi}$  system at 25 °C; polymerization time 5 minutes.



Ratio ( $[rac\text{-LA}]/[\text{catalyst}]$ )	$M_n$ ( $\text{g/mol} \times 10^3$ )	Conversion (%)
100	9.27	98.0
200	16.73	98.1
300	17.38	97.1
400	19.26	97.6
500	11.5	98.0

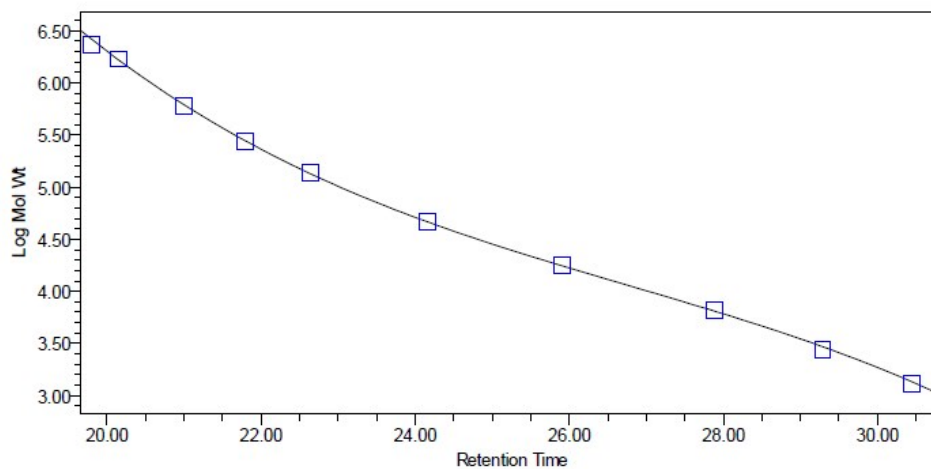
**Figure S67.** GPC data of PLA obtained with  $[L_BZnMe_2]$  at 25 °C ( $[rac-LA]/[catalyst] = 100$ ).

SAMPLE INFORMATION			
Sample Name:	SH-5-43-5	Sample Set Name:	210204
Sample Type:	Broad Unknown	Acq. Method Set:	THF_1x0ml
Vial:	12	Injection Volume:	100.00 ul
Injection #:	1	Acquired By:	System
Run Time:	45.0 Minutes		
Date Acquired:	2021-02-05 AM 1:26:50 KST		

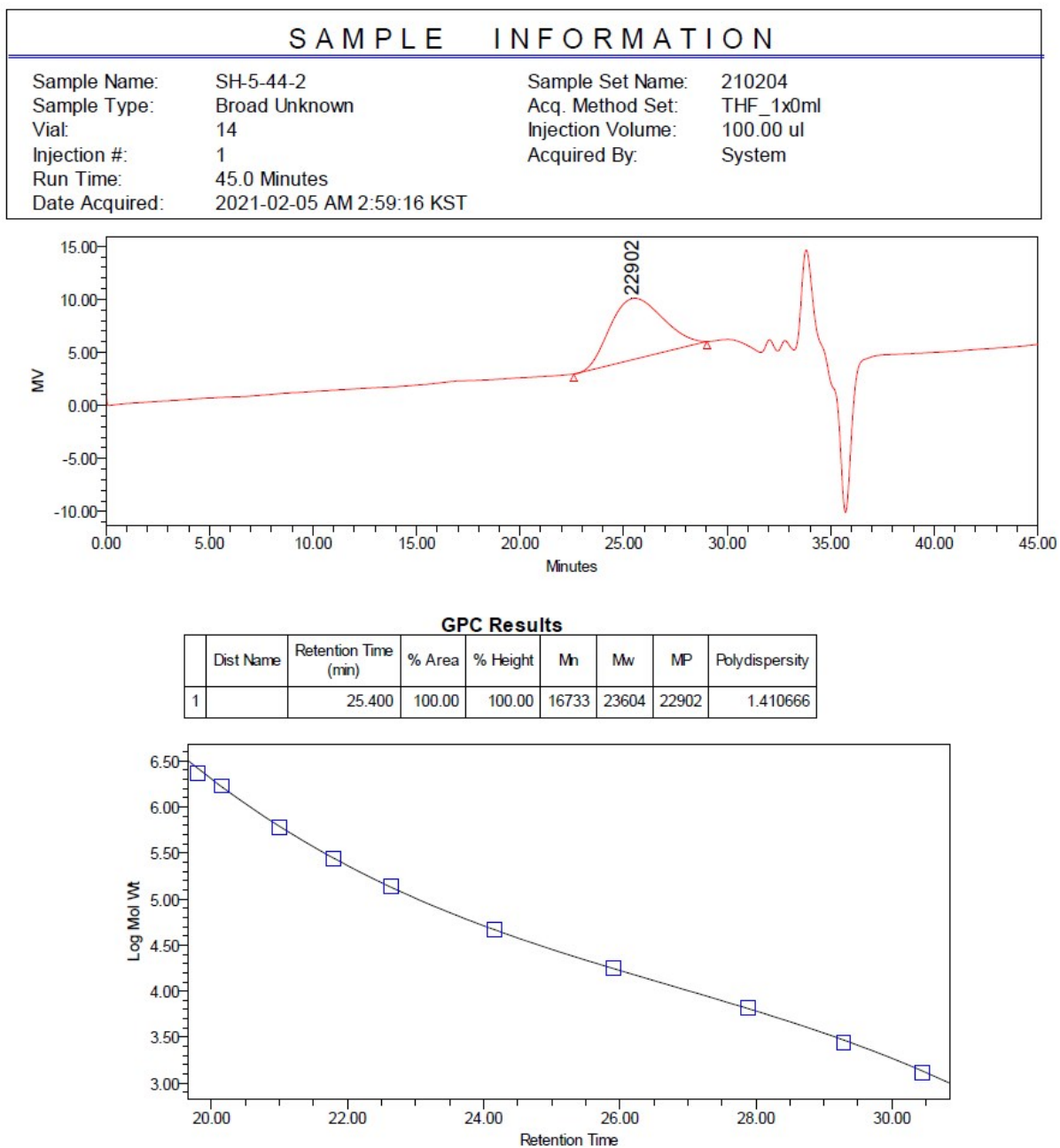


**GPC Results**

Dist Name	Retention Time (min)	% Area	% Height	Mn	Mw	MP	Polydispersity
1	26.808	100.00	100.00	9274	12039	11165	1.298039



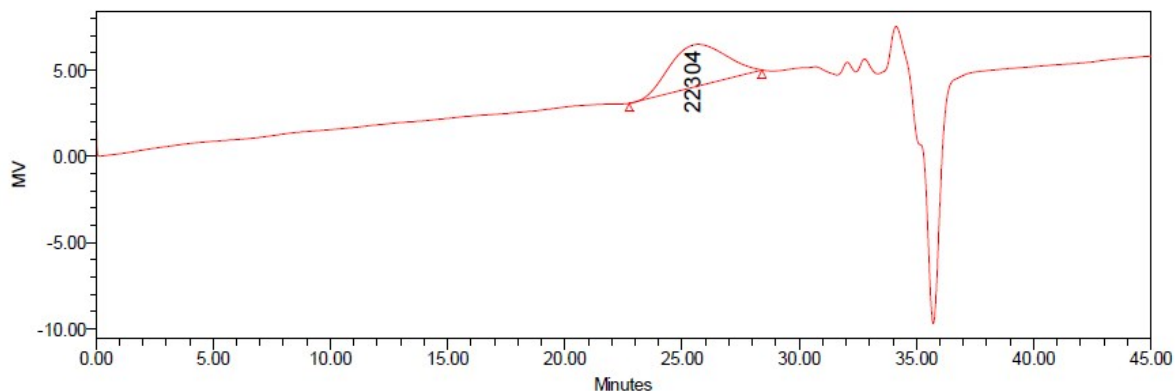
**Figure S68.** GPC data of PLA obtained with  $[L_BZnMe_2]$  at 25 °C ( $[rac-LA]/[catalyst] = 200$ ).





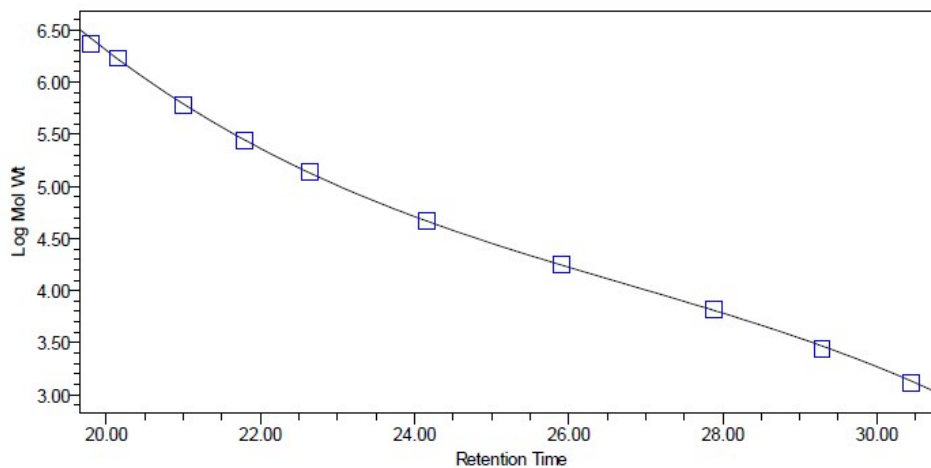
**Figure S69.** GPC data of PLA obtained with  $[L_BZnCl_2]/MeLi$  system at 25 °C ( $[rac-LA]/[catalyst] = 300$ ).

SAMPLE INFORMATION			
Sample Name:	SH-5-44-1	Sample Set Name:	210204
Sample Type:	Broad Unknown	Acq. Method Set:	THF_1x0ml
Vial:	13	Injection Volume:	100.00 ul
Injection #:	1	Acquired By:	System
Run Time:	45.0 Minutes		
Date Acquired:	2021-02-05 AM 2:13:03 KST		

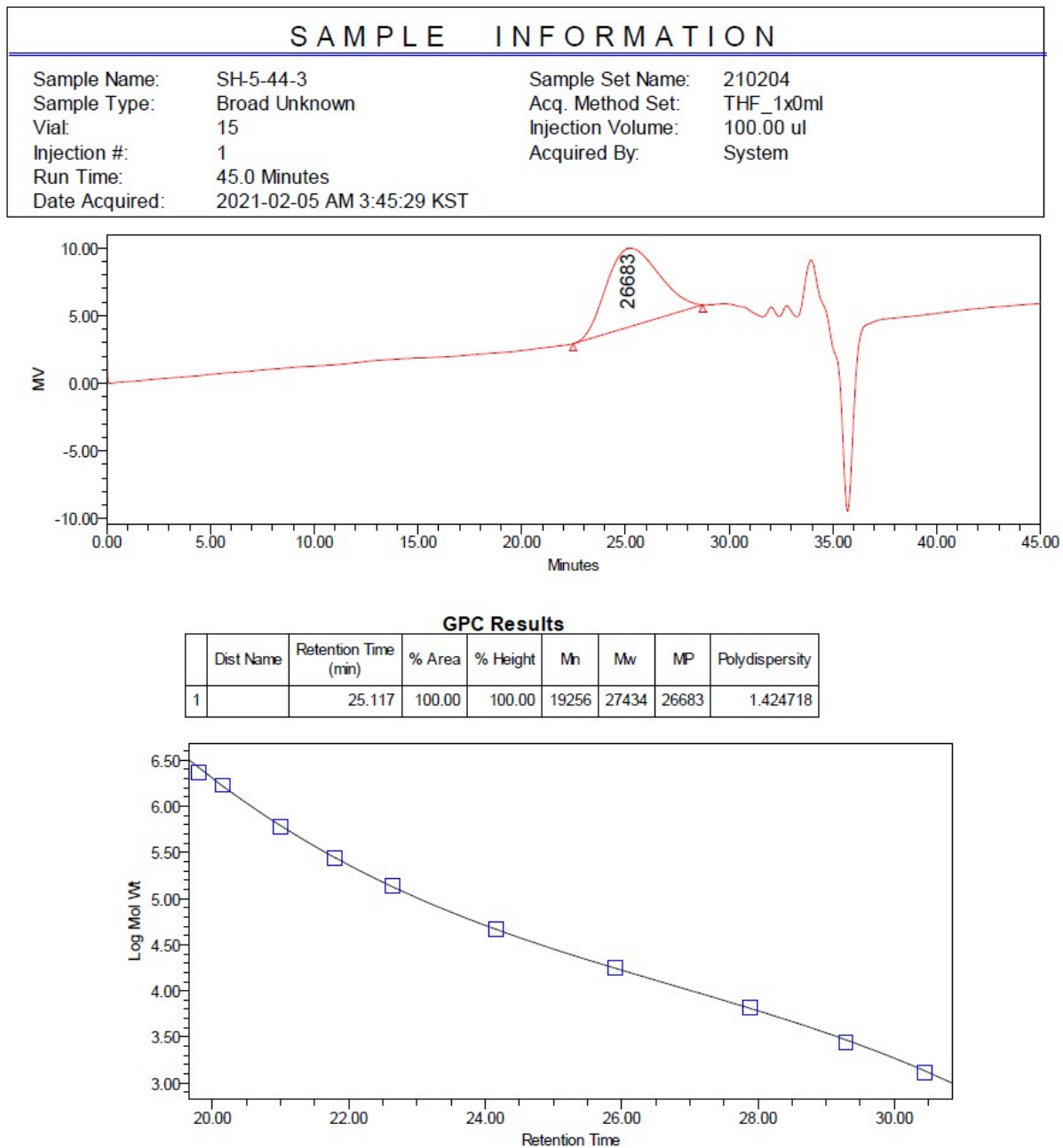


**GPC Results**

Dist Name	Retention Time (min)	% Area	% Height	Mn	Mw	MP	Polydispersity
1	25.450	100.00	100.00	17379	23094	22304	1.328847

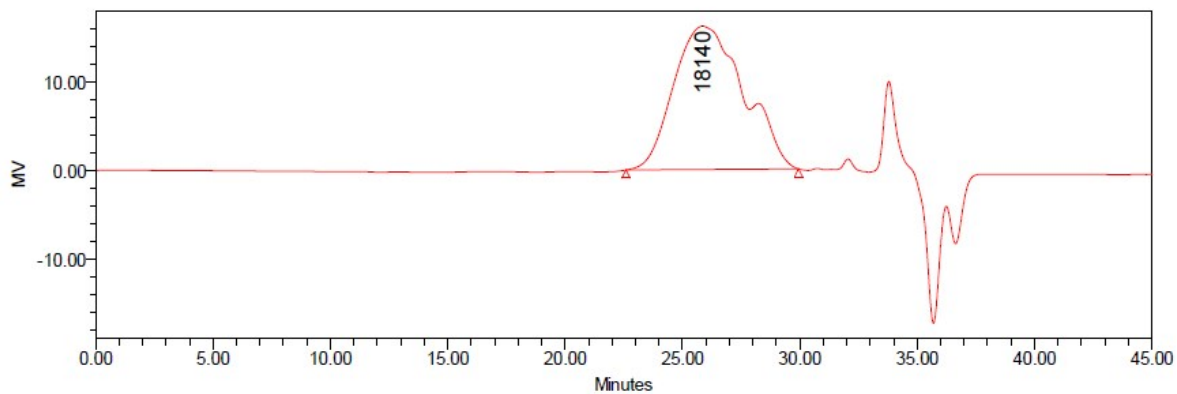


**Figure S70.** GPC data of PLA obtained with  $[L_BZnCl_2]/MeLi$  system at 25 °C ( $[rac-LA]/[catalyst] = 400$ ).



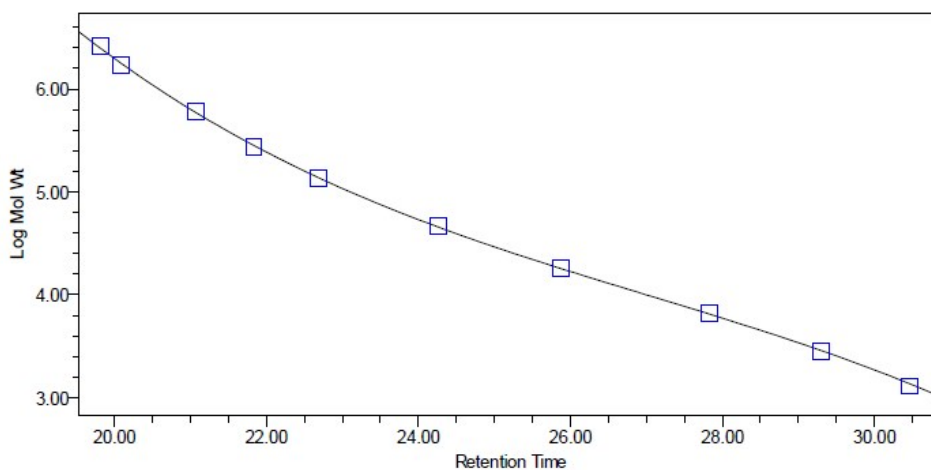
**Figure S71.** GPC data of PLA obtained with  $[L_BZnCl_2]/MeLi$  system at 25 °C ( $[rac-LA]/[catalyst] = 500$ ).

SAMPLE INFORMATION			
Sample Name:	SH-5-32	Sample Set Name:	210120
Sample Type:	Broad Unknown	Acq. Method Set:	THF_1x0ml
Vial:	12	Injection Volume:	100.00 ul
Injection #:	1	Acquired By:	System
Run Time:	45.0 Minutes		
Date Acquired:	2021-01-21 AM 2:24:49 KST		

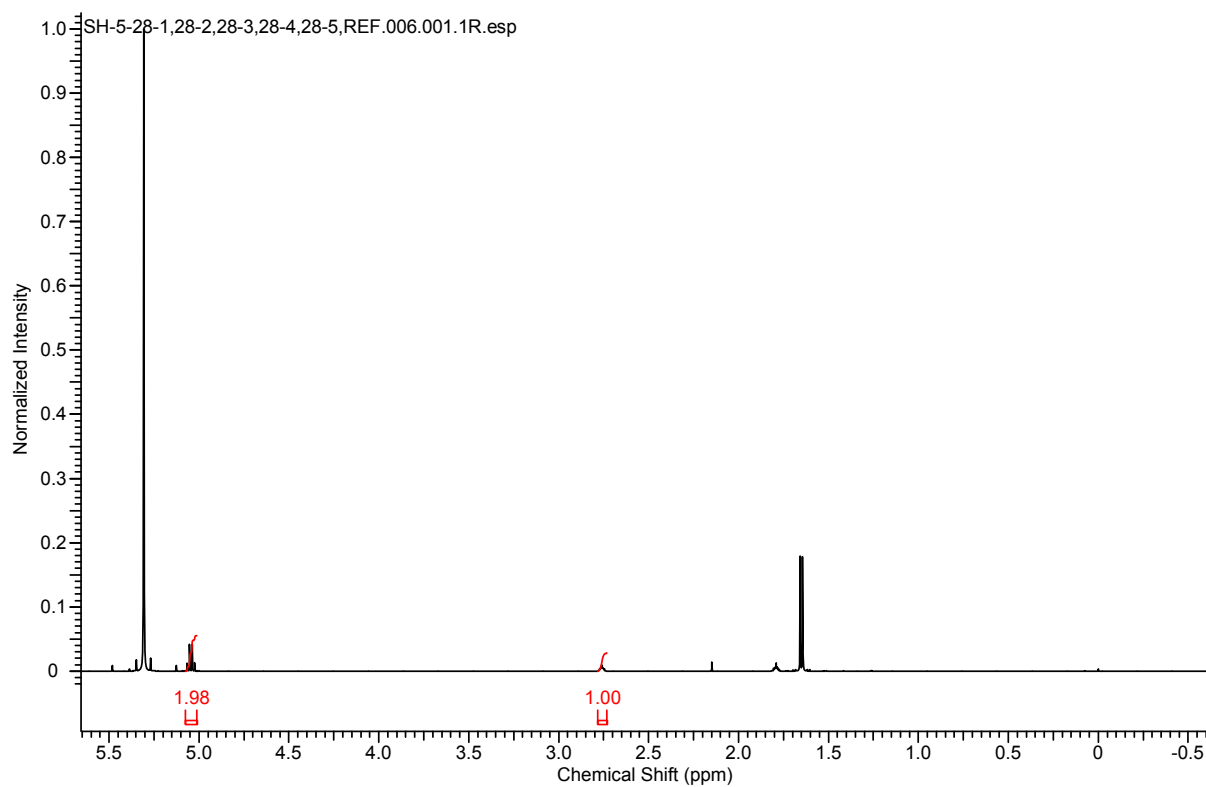


**GPC Results**

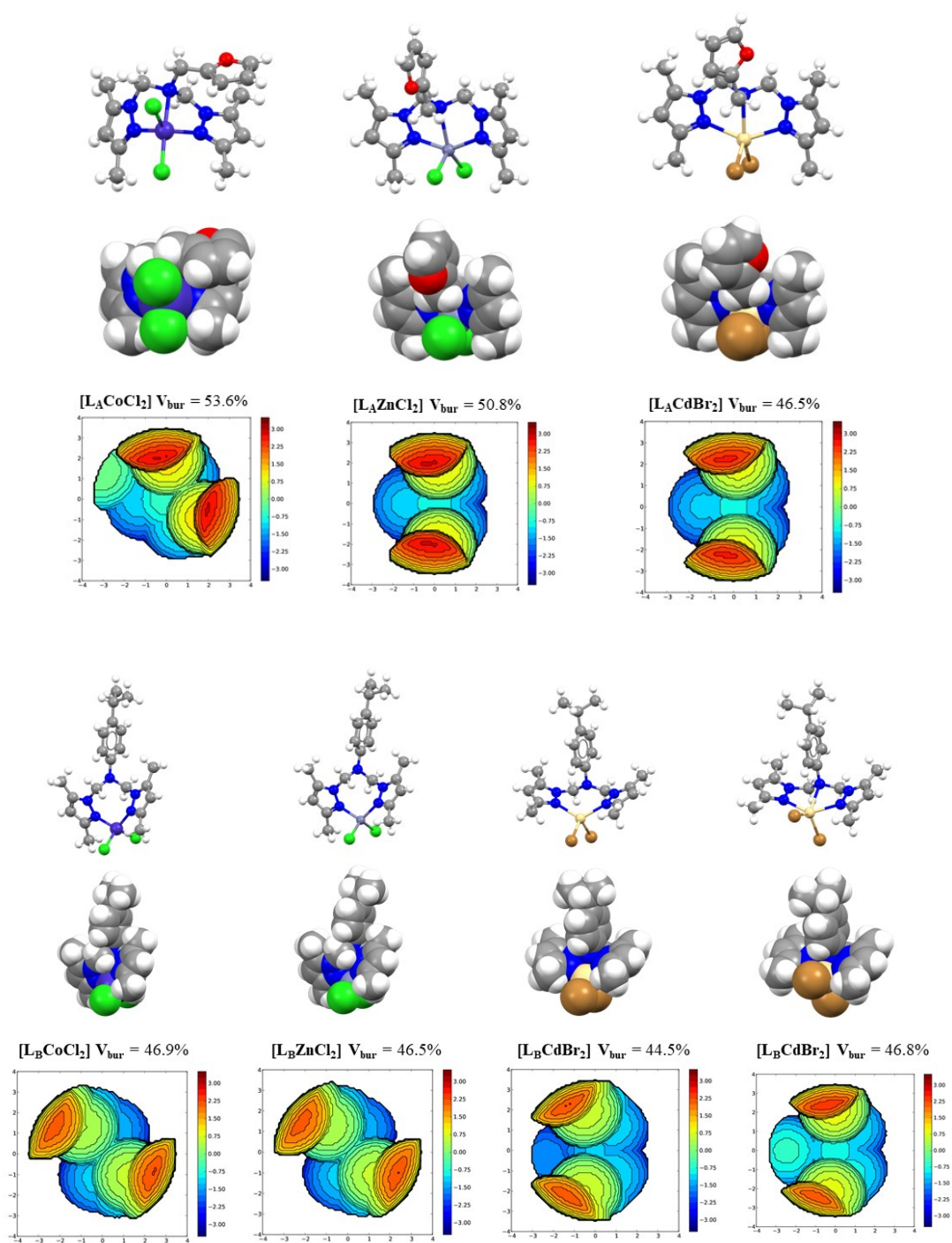
Dist Name	Retention Time (min)	% Area	% Height	Mn	Mw	MP	Polydispersity
1	25.860	100.00	100.00	11496	19003	18140	1.653033



**Figure S72.**  $^1\text{H}$  NMR spectrum of PLA obtained with **MeLi** at 25 °C, reaction time 5 min.



**Figure S73.** Ball and stick model, space-filling model, and topographic steric map of for presenting bulk of the attached ligands.



## General procedure for determining the stability of initiators

**Experiment 1;** The active catalytic species for *rac*-LA polymerization were prepared by dissolving 0.50 mmol of dichloro Zn(II) complex, i.e.,  $[\mathbf{L}_B\mathbf{ZnCl}_2]$  (0.244 g) in anhydrous THF (7.35 mL) in 100 mL Schlenk flask under inert atmosphere. The resultant mixture was stirred at 25 °C to dissolve the corresponding metal complex. To the above mentioned solution was then added MeLi (0.65 mL, 1.0 mmol of 1.6 M/in Et<sub>2</sub>O) dropwise and stirred at 25 °C for 2 h to get ROP initiator. For Polymerization reaction, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5.00 mL) was added to 100 mL five Schlenk flasks each containing *rac*-LA (0.901 g, 6.25 mmol) and stirred to make a homogenous solution. The catalyst solution (1.0 mL, 0.0625 mmol) was added slowly to one of the above-mentioned Schlenk flasks at 25 °C to initiate polymerization. Polymerization was continued for 5 minutes. Immediately at 5 minutes after, another LA solution (0.901 g *rac*-LA, 5.00 ml CH<sub>2</sub>Cl<sub>2</sub>) is added to polymerization solution Schlenk flask being polymerized without adding the catalyst. This process was repeated 4 times. (This experiment is carried out in one Schlenk flask. LA solution is added every 5 minutes in one Schlenk flask). Sampling was done at regular intervals (every 5 minutes) and percentage conversions of *rac*-LA to PLA determined by <sup>1</sup>H NMR (500 MHz) comparing the integral of the *rac*-LA signals at 4.0 ppm to that of the tetralin at 4.2 ppm (Fig. S). Polymerization reaction was quenched by adding H<sub>2</sub>O (5.00 mL), and polymer was precipitated by the adding *n*-hexane (10.00 mL). The solvent was removed directly to afford a crude polymer as sticky material. The precipitate obtained from the bulk mixture was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and successively precipitated by *n*-hexane. Decantation of solvent yielded white solids which were vacuum-dried for 12 h at 40 °C.

**Experiment 2;** The initiators were generated as described in experiment 1. The general procedure for monomer (*rac*-LA, 0.901 g, 6.25 mmol; 1.802 g, 12.50 mmol; 2.703 g, 18.75 mmol; and 3.604 g, 25.00 mmol; 4.505 g, 31.25 mmol) were each prepared in five Schlenk flasks (100 mL; 100 mL; 100 mL; 250 mL and 250 mL) to make the catalyst to monomer ratio of 1:100, 1:200, 1:300, 1:400 and 1:500, respectively. For the ROP reaction of *rac*-LA, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5.00, 10.00, 15.00, 20.00 and 25.00 mL) was added each to five monomer Schlenk flasks to form a homogenous solution. The THF solution of catalyst solution (1.0 mL, 0.0625 mmol) was added slowly to each of the four above-mentioned solution at 25 °C to initiate polymerization. The polymerization reaction was continued for 5 min at prescribed temperatures, i.e. 25 °C. Polymerization reaction was quenched by adding H<sub>2</sub>O (1.0 – 5.0 mL),

and polymer was precipitated by the adding *n*-hexane (2.0 – 10.0 mL). Subsequently, the solvent was removed directly to afford a crude polymer as sticky material. The precipitate obtained from the bulk mixture was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and successively precipitated by *n*-hexane. Decantation of solvent yielded white solids which were vacuum-dried for 12 h at 40 °C. The number average molecular weight ( $M_n$ ) and of the purified PLA samples were determined by a Waters Alliance e2695 instrument possessing differential refractive index detectors and calibrated against a polystyrene standard. THF was utilized as the eluting solvent at a flow rate of 1.0 mL/min at 35 °C. PDI and  $M_n$  of the polymer were reported regarding the polystyrene standard.