Comparative Study of Titanium Complexes Bearing 2-(Arylideneamino)phenolates and 2-((Arylimino)methyl)phenolates as Catalysts for Ring-Opening Polymerization of ε-Caprolactone and L-Lactide

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Supporting Information

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Table S1. Crystallographic parameters of **F^{H}-Ti**, **S^{H}-Ti**, and **F^{OMe}-Ti**.

	F^{H}-Ti	**F^{OMe}-Ti**
CCDC number	2264712	2264713
Identification code	K11004-HYC-D	K11007-HYC-L
Empirical formula	$C_{64}H_{68}N_4O_8Ti_2$	$C_{9.71}H_{10.86}N_{0.57}O_{1.71}Ti_{0.29}$
Formula weight	1117.02	176.73
Temperature/K	113(2)	113(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$

a/Å	12.1742(3)	11.8926(2)
b/Å	16.9814(4)	14.8890(3)
c/Å	27.9303(5)	18.5751(3)
α/°	90	90
β/°	101.516(2)	104.270(2)
γ/°	90	90
Volume/$Å^3$	5657.9(2)	3187.59(10)
Z	4	14
$\rho_{calc}g/cm^3$	1.311	1.289
μ/mm^{-1}	0.342	0.315
F(000)	2352.0	1304.0
Crystal size/mm^3	0.4 × 0.1 × 0.1	0.2 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.822 to 49.998	4.47 to 49.996
Index ranges	$-14 \le h \le 14$, $-19 \le k \le 20$, $-33 \le l \le 32$	$-14 \le h \le 14$, $-17 \le k \le 17$, $-21 \le l \le 22$
Reflections collected	60053	79538
Independent reflections	9916 [R_{int} = 0.0568, R_{sigma} = 0.0451]	5595 [R_{int} = 0.1077, R_{sigma} = 0.0354]
Data/restraints/parameters	9916/2364/741	5595/1488/454
Goodness-of-fit on F^2	1.068	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0549, wR_2 = 0.1368	R_1 = 0.0419, wR_2 = 0.1150
Final R indexes [all data]	R_1 = 0.0710, wR_2 = 0.1436	R_1 = 0.0508, wR_2 = 0.1206
Largest diff. peak/hole / e $Å^{-3}$	0.61/-0.55	0.43/-0.38

Table S2. Kinetic study of CL polymerization with various five-membered ring Ti complexes[a]

	[CL]:[Ti]= 100:1			
Time (min)	**F^{OMe}-Ti**	**F^{H}-Ti**	**F^{Cl}-Ti**	**F^{Bu}-Ti**
	PCL conversion [b]			
90		0.10	0.10	
150			0.26	
180	0.16			0.20
200		0.30		
240			0.45	
270				0.31
300				0.36
325		0.50		
350			0.66	
360	0.33			
420			0.74	0.51
455		0.69		
540	0.53		0.86	
600		0.80		
670	0.64			
1080				0.90
1190		0.96		
1315	0.92			
$k_{obs}\times 10^3$/ min (error)	2.12(1)	2.88(6)	4.10(2)	2.35(4)

I.P min (error)	154(38)	61(13)	79(14)	104(11)
R^2	0.991	0.998	0.993	0.998

[a] In general, the reaction was carried out in toluene with [**CL**] = 2.0 M at 60°C.
[b] The data were determined from ^{1}H NMR analysis.

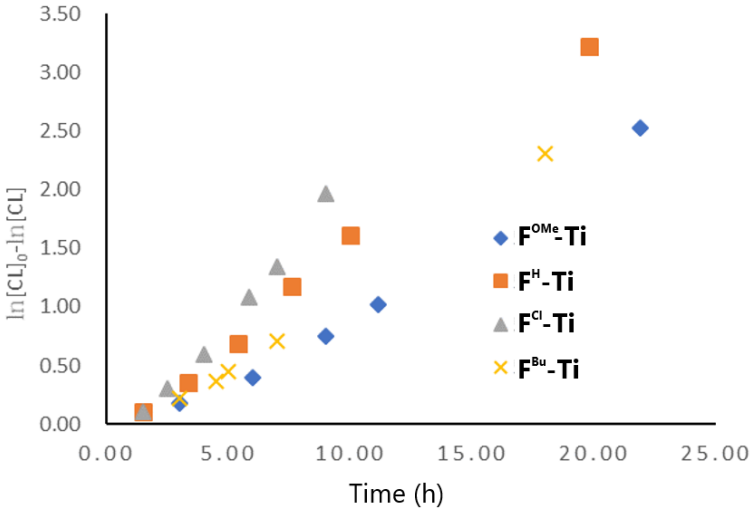


Figure S1. First-order kinetic plots of CL polymerization with various five membered ring Ti complexes plotted against time with [CL] = 2.0 M in toluene 5 mL (**Table S3**).

Table S3. Kinetic study of CL polymerization with various six-membered ring Ti complexes[a]

	[CL]:[Ti]= 100:1		
Time/ hour	**S^{OMe}-Ti**	**S^{H}-Ti**	**S^{Cl}-Ti**
	PCL conversion [b]		
1102			0.15
1200		0.19	
1290	0.22		
1410			0.22
1510	0.26		
1520		0.26	
1580			0.25
2495		0.42	
2900			0.49
3055	0.54		
3100			0.52

3115		0.51	
3725			0.60
4110		0.63	
4425			0.69
4500	0.73		
4505		0.67	
5795	0.83		
5820			0.80
7100			0.88
7260	0.90		
8425		0.90	
$k_{obs}\times 10^4$/ min (error)	3.5(1)	2.9(1)	3.2(1)
I.P min (error)	666(80)	576(76)	725(90)
R^2	0.998	0.998	0.996

[a] In general, the reaction was carried out in toluene with [CL] = 2.0 M at 60°C.
[b] The data were determined from ^{1}H NMR analysis.

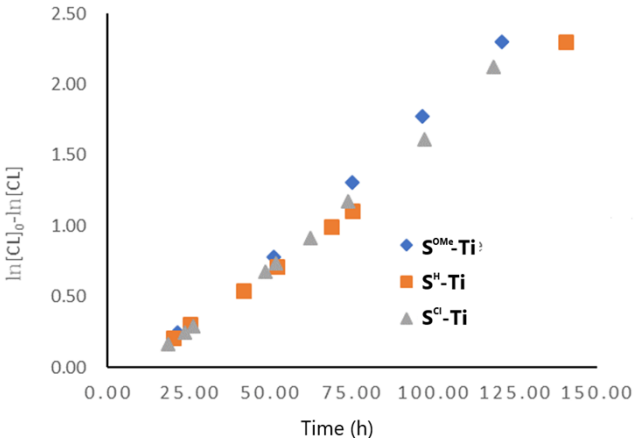


Figure S2. First-order kinetic plots of CL polymerization with various six membered ring Ti complexes plotted against time with [CL] = 2.0 M in toluene 5 mL

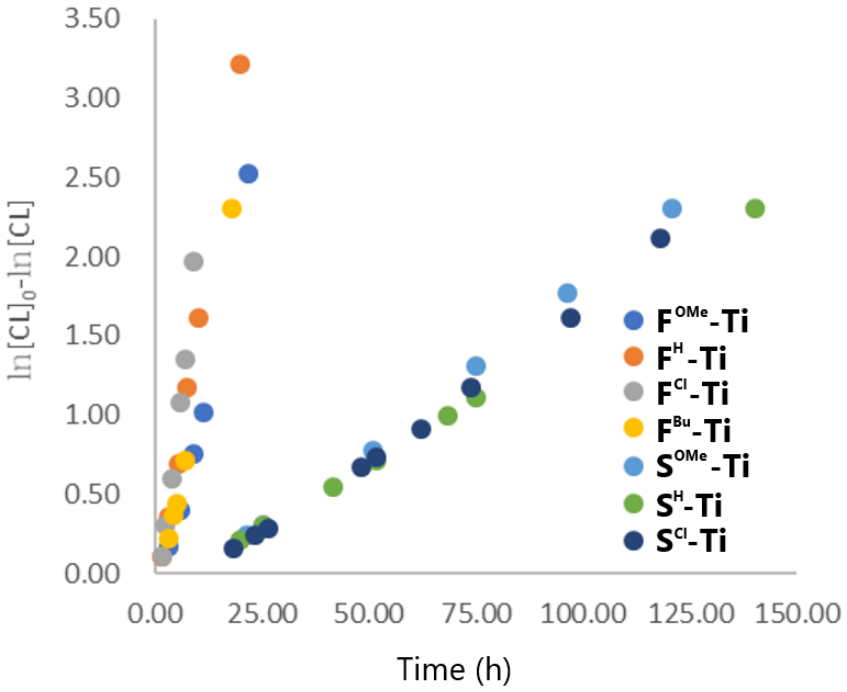


Figure S3. First-order kinetic plots of CL polymerization by various five and six membered ring Ti complexes plotted against time with [CL] = 2.0 M in toluene 5 mL

Table S4. Kinetic study of CL polymerization with various concentration of **F^{Cl}-Ti** in toluene 5 mL, [CL] = 2.0 M at 60°C[a]

	[CL]:[**F^{Cl}-Ti**]			
time	100:1	100:2	100:4	100:6
min	PCL conversion[b]			
10			0.10	
15			0.17	0.22
20				0.34
25				0.47
30			0.42	0.59
40		0.21		
50			0.72	
55				0.85
65			0.83	
70		0.40		
90	0.10	0.54		
115		0.67		
140		0.75		

150	0.26			
200		0.89		
240	0.45			
350	0.66			
420	0.74			
540	0.86			
$k_{obs}\times 10^4$/ min^{-1} (error)	41(2)	125(4)	309(20)	417(9)
I.P/ min (error)	79(14)	26(3)	9(2)	9(1)
R^2	0.993	0.998	0.996	0.999

[a] In general, the reaction was carried out in toluene with [CL] = 2.0 M at 60°C.
[b] The data were determined from ^{1}H NMR analysis.

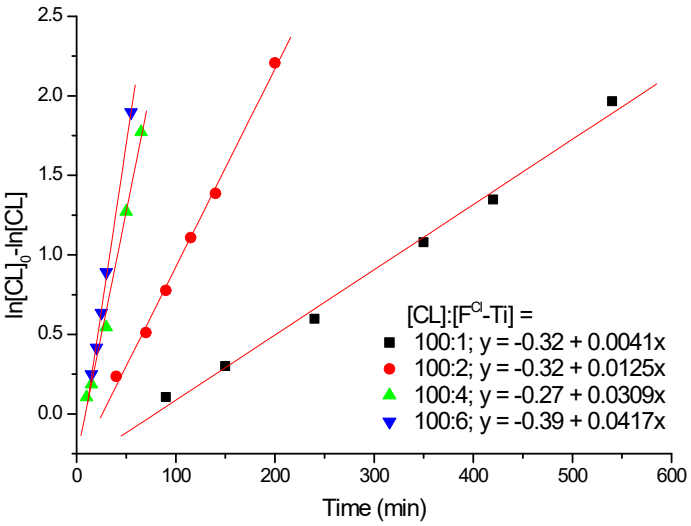


Figure S4. First-order kinetic plots of CL polymerization with various concentrations of [**F^{Cl}-Ti**] plotted against time with [CL] = 2.0 M in toluene 5 mL

Table S5. Kinetic study of LA polymerization with various five-membered ring Ti complexes[a]

	[LA]:[Ti]=25:1			
Time (min)	**F^{OMe}-Ti**	**F^{H}-Ti**	**F^{Cl}-Ti**	**F^{Bu}-Ti**
	PLA conversion[b]			
30		0.24	0.23	
60				0.34
70		0.38		
90		0.43	0.42	
110	0.33			
120			0.48	
135				0.46
150	0.38	0.53	0.55	
183			0.61	
222			0.65	
230	0.48			
240		0.68		
250			0.69	
270				0.61
280			0.72	
290	0.51			
300				0.63
350	0.55			
355			0.79	
410	0.60			
430			0.85	
450		0.87		
530	0.65			
540			0.91	
650	0.69			
1080				0.90
1250	0.85			
1510	0.90			
$k_{obs} \times 10^3$/ min (error)	1.30 (3)	4.14 (8)	4.08 (6)	1.79 (9)
R^2	0.995	0.998	0.997	0.992

[a] In general, the reaction was carried out in toluene with [LA] = 0.5 M at 60°C.
[b] The data were determined from ^{1}H NMR analysis.

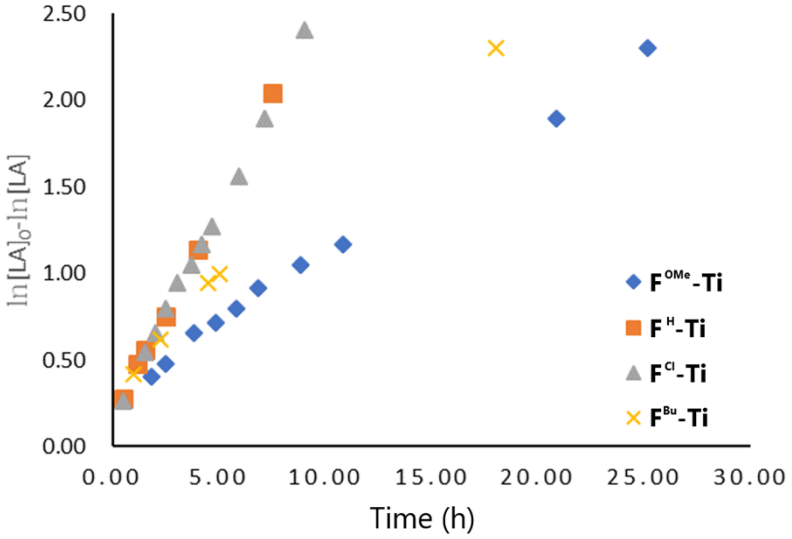


Figure S5. First-order kinetic plots of LA polymerization by various five membered ring Ti complexes plotted against time with [LA] = 0.5 M in toluene 5 mL **(Table S1)**

Table S6. Kinetic study of LA polymerization with various six-membered ring Ti complexes [a]

	[LA]:[Ti]= 25:1		
Time (h)	**S^{OMe}-Ti**	**S^{H}-Ti**	**S^{Cl}-Ti**
	PLA conversion [b]		
3.41		0.20	
4.00			0.19
8.41			0.24
10.58	0.25		
18.38			0.36
20.00		0.35	
21.50	0.34		
23.50			0.41
25.16	0.38		
26.33			0.43
41.58		0.49	
50.91	0.56		
51.66			0.59
68.50		0.62	
73.75			0.68
75.00	0.68		
75.08		0.65	
96.58	0.75		
97.00			0.76

118.33			0.82
121.00	0.82		
140.41		0.83	
142.33			0.87
144.50	0.86		
150.10		0.85	
156.36			0.90
$k_{obs}\times 10^4$/ min (error)	2.1 (0)	1.8 (0)	2.2 (1)
R^2	0.999	0.998	0.998

[a] In general, the reaction was carried out in toluene with [LA] = 0.5 M at 60°C.

[b] The data were determined from 1H NMR analysis.

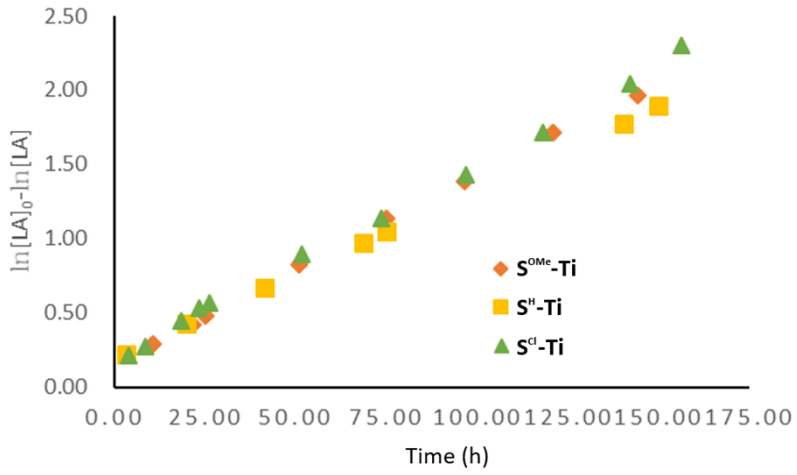


Figure S6. First-order kinetic plots of LA polymerization by various six membered ring Ti complexes plotted against time with [LA] = 0.5 M in toluene 5 mL (**Table S2**).

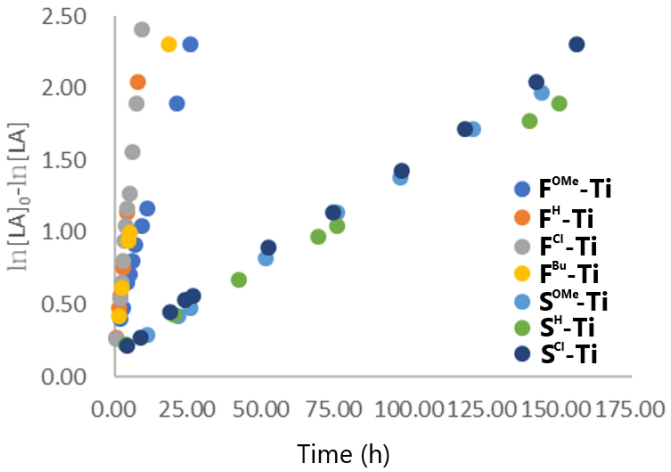


Figure S7. First-order kinetic plots of LA polymerization by various five and six membered ring Ti complexes plotted against time with [LA] = 0.5 M in toluene 5 mL

Table. S7 Kinetic study of LA polymerization with **F^{H}-Ti** [a] in various concentrations

	[LA]: [**F^{H}-Ti**]			
	25:0.25	25:0.5	25:1	25:2
Time/ min	PLA conversion [b]			
1				0.01
3				0.17
5			0.31	0.31
9				0.50
10		0.35		
15			0.46	
16				0.73
20		0.45	0.51	0.80
35			0.61	0.94
50		0.60		0.98
60	0.46		0.74	

70		0.69		
80	0.49			
110			0.88	
160	0.59			
180		0.89		
230	0.65			
360	0.73			
540	0.82			
710	0.87			
$k_{obs}\times 10^4$/ min^{-1} (error)	22(0)	103(4)	162(4)	799(3)
I.P/ min (error)	0(8)	0(3)	0(0)	0(0)
R^2	0.998	0.997	0.998	0.999

[a] In general, the reaction was carried out in toluene with [LA] = 0.5 M at 90°C.

[b] The data were determined from ^{1}H NMR analysis.

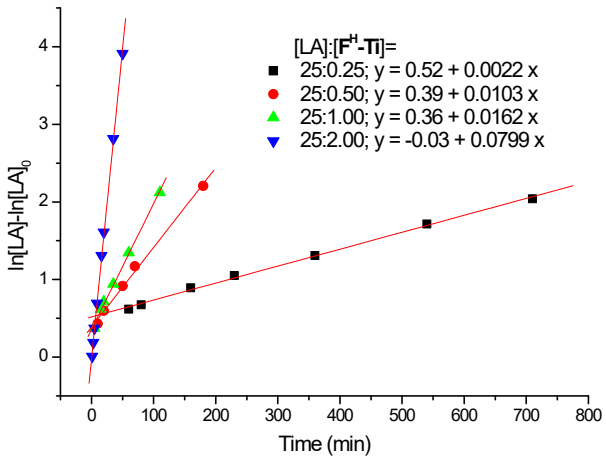


Figure S8. First-order kinetic plots of LA polymerization with various concentrations of [**F^H-Ti**] plotted against time with [LA] = 0.5 M in toluene 5 mL

Table. S8. Measuring polymer's molar masses at different times/conversions for CL polymerization using **F^{Cl}-Ti** as a catalyst

Entry	Time(min)	Conv. (%) [a]	$Mn_{cacld.}$ [b]	Mn_{GPC} [c]	$Đ$ [c]
1	10	5	1200	1735	1.08
2	20	18	4164	3696	1.07
3	30	29	6672	5639	1.11
4	40	36	8268	7461	1.15
5	50	57	13056	8320	1.20
6	60	64	14652	9379	1.24
7	75	78	17160	9221	1.30
8	90	87	19896	10028	1.40
9	105	91	20808	10851	1.35

The reaction was carried out in toluene with [CL] = 8 M, [CL]:[Cat]= 200:1, at 90°C

[a] Data were obtained through ^{1}H NMR analysis.

[b] Calculated from the molecular weight of Mw(CL) × $[CL]_0/2[Cat]_0$ × conversion yield + Mw(^{i}PrOH).

[c] Obtained through gel permeation chromatography (GPC). Values of Mn_{GPC} were obtained times 0.56 for PCL.

Table. S9. Measuring polymer's molar masses at different times/conversions for LA polymerization using **F^{H}-Ti** as a catalyst

Entry	Time(hr)	Conv. (%) [a]	$Mn_{cacld.}$ [b]	Mn_{GPC} [c]	$Đ$ [c]
1	1.50	15	2760	1040	1.13
2	4.37	34	6180	2201	1.10
3	7.83	51	9240	3212	1.07
4	10.25	54	9780	3657	1.10
5	23.50	76	13740	5231	1.16
6	30.50	86	15540	5591	1.20
7	48.87	94	16980	6309	1.29

The reaction was carried out in toluene with [LA] = 3.125 M, [LA]:[Cat]= 100:1, at 90°C

[a] Data were obtained through ^{1}H NMR analysis.

[b] Calculated from the molecular weight of Mw(LA) × $[LA]_0/2[Cat]_0$ × conversion yield + Mw(^{i}PrOH).

[c] Obtained through gel permeation chromatography (GPC). Values of Mn_{GPC} were obtained times 0.58 for PLA.

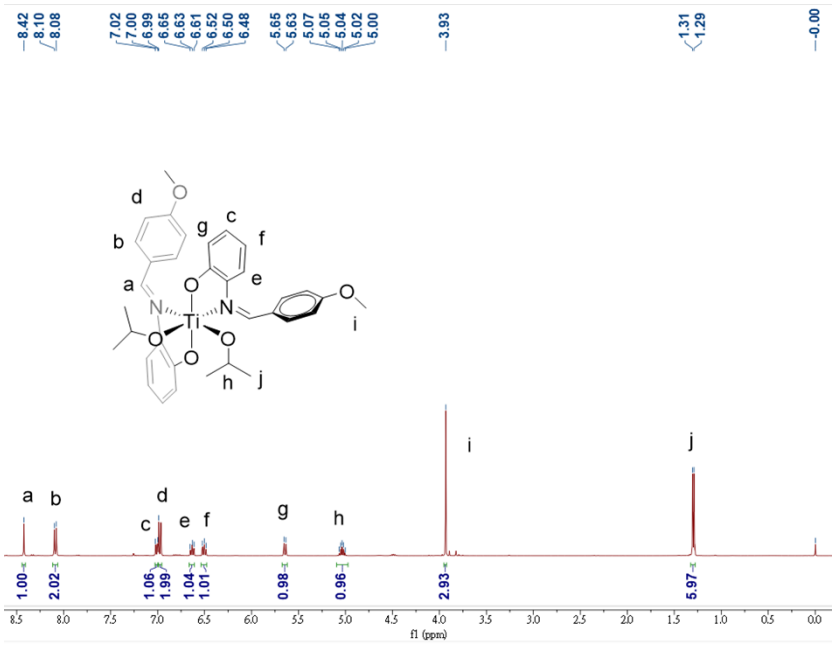


Figure S9. ^{1}H NMR spectrum of **F^{OMe}-Ti** in $CDCl_3$

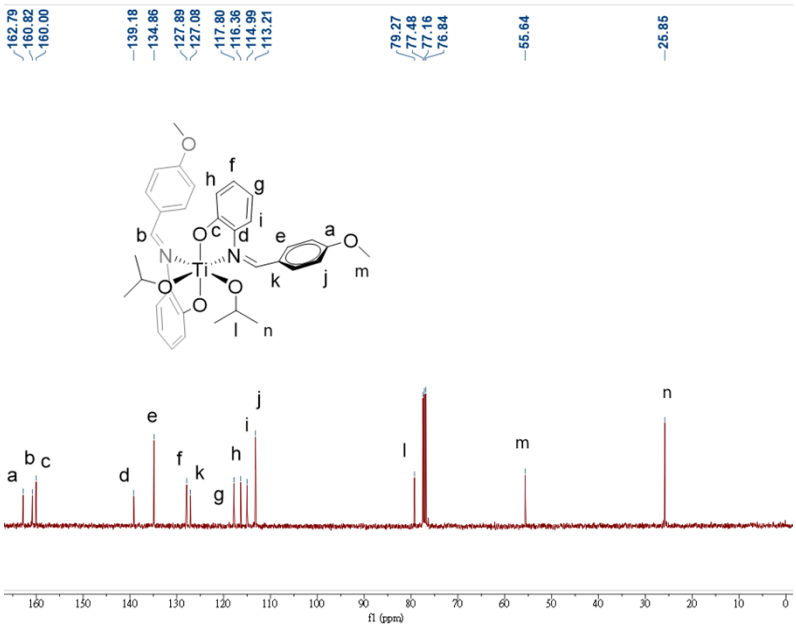


Figure S10. ^{13}C NMR spectrum of **F^{OMe}-Ti** in $CDCl_3$

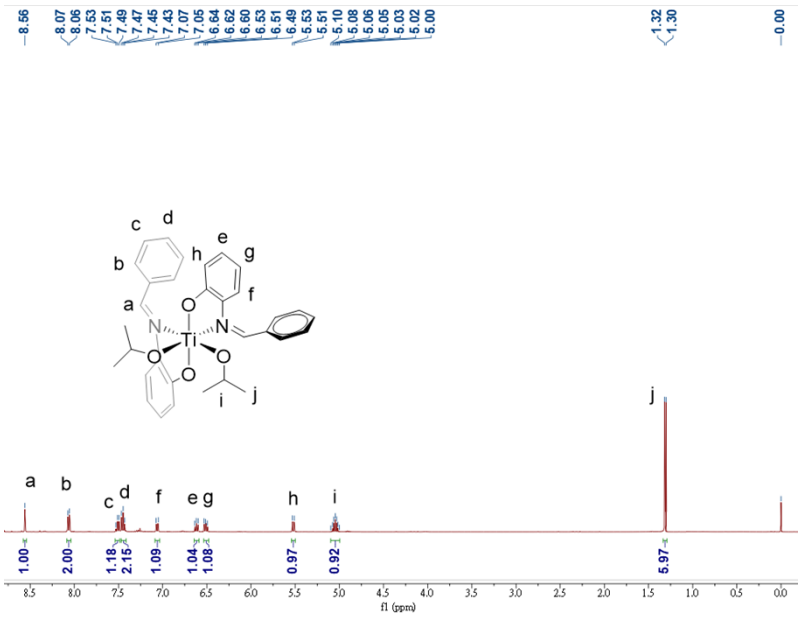


Figure S11. ^{1}H NMR spectrum of **F^{H}-Ti** in $CDCl_3$

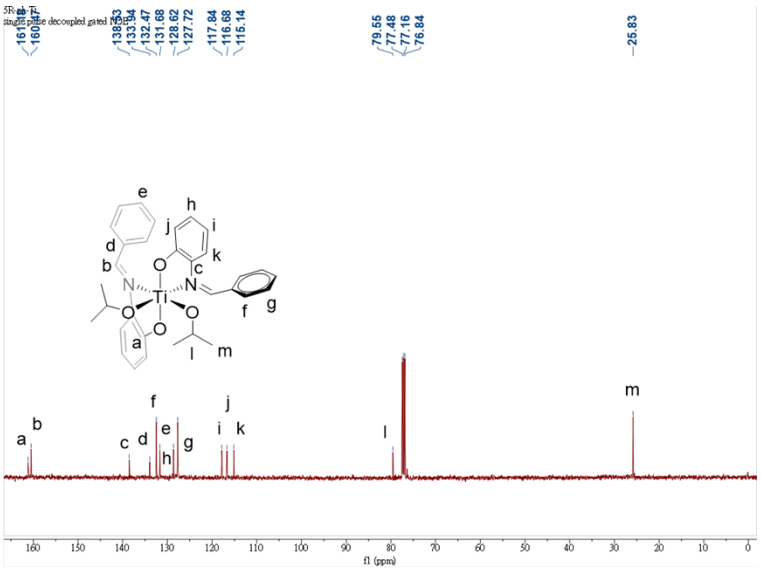


Figure S12. ^{13}C NMR spectrum of **F^{H}-Ti** in $CDCl_3$

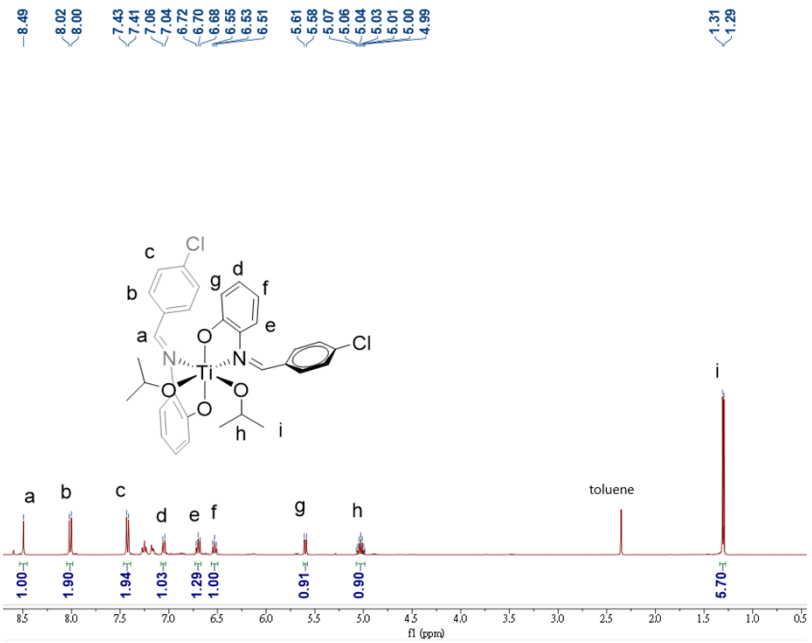


Figure S13. ^{1}H NMR spectrum of **F^{Cl}-Ti** in $CDCl_3$

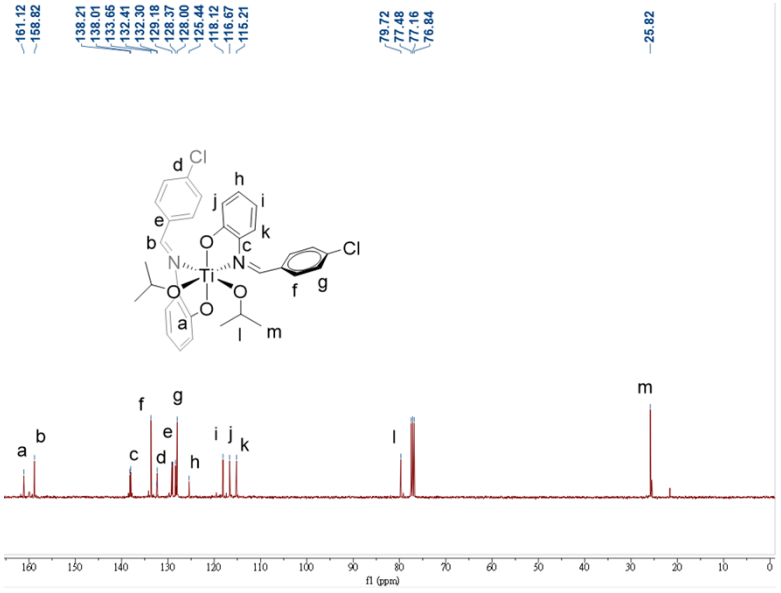


Figure S14. ^{13}C NMR spectrum of **F^{Cl}-Ti** in $CDCl_3$

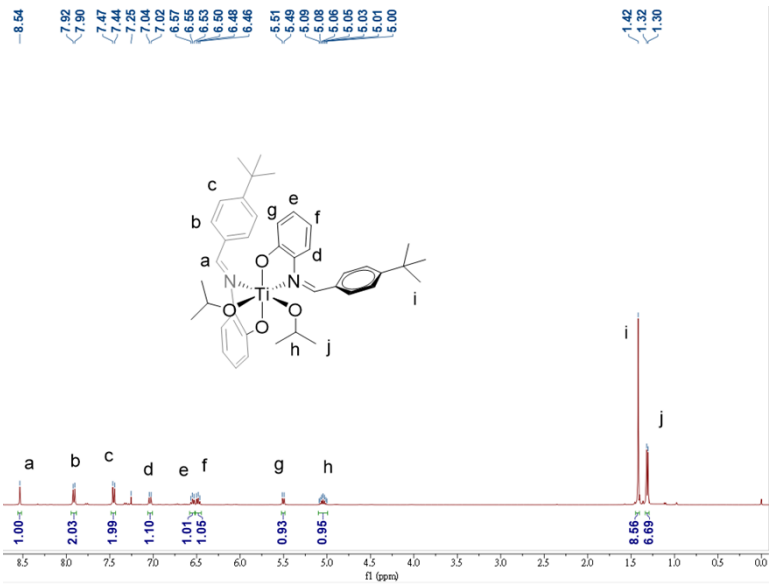


Figure S15. ^{1}H NMR spectrum of **F^{Bu}-Ti** in $CDCl_3$

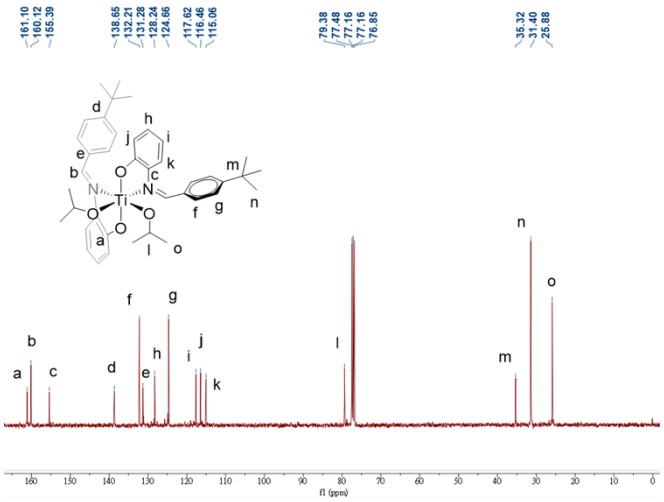


Figure S16. ^{13}C NMR spectrum of **F^{Bu}-Ti** in $CDCl_3$

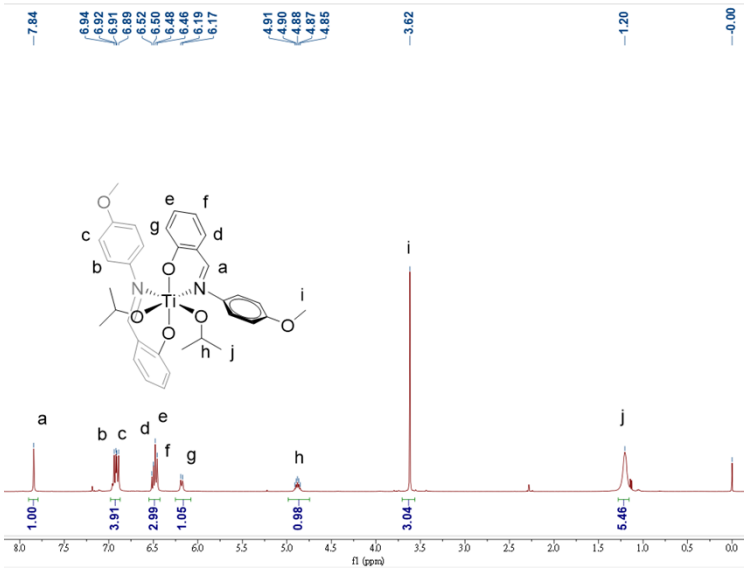


Figure S17. ^{1}H NMR spectrum of **S^{OMe}-Ti** in $CDCl_3$

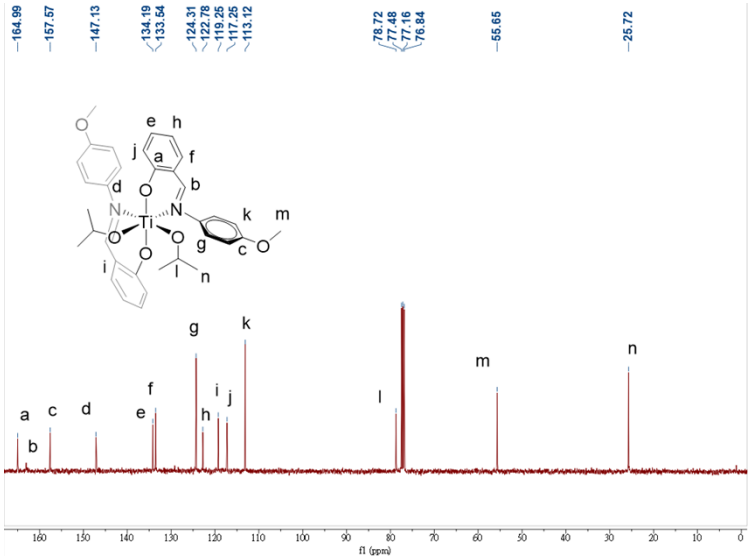


Figure S18. ^{13}C NMR spectrum of **S^{OMe}-Ti** in $CDCl_3$

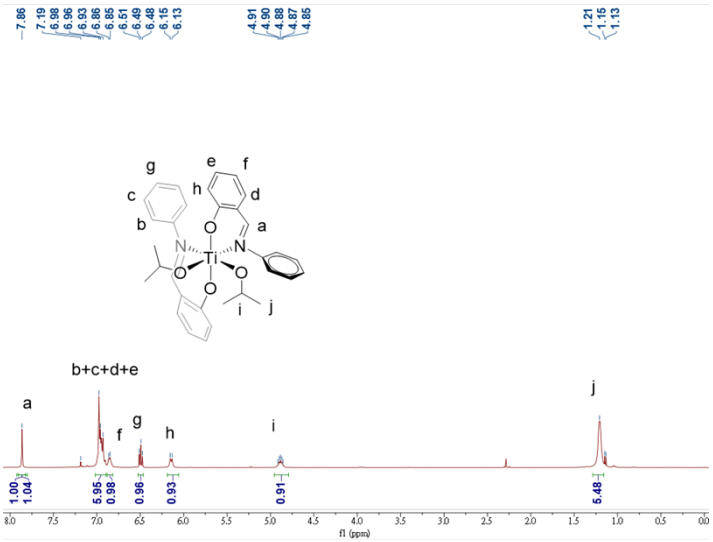


Figure S19. ^{1}H NMR spectrum of **S^{H}-Ti** in $CDCl_3$

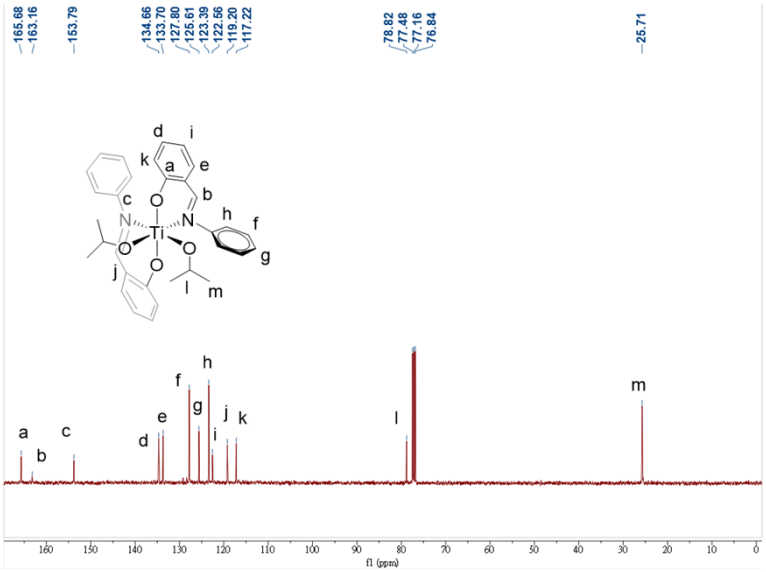


Figure S20. ^{13}C NMR spectrum of **S^{H}-Ti** in $CDCl_3$

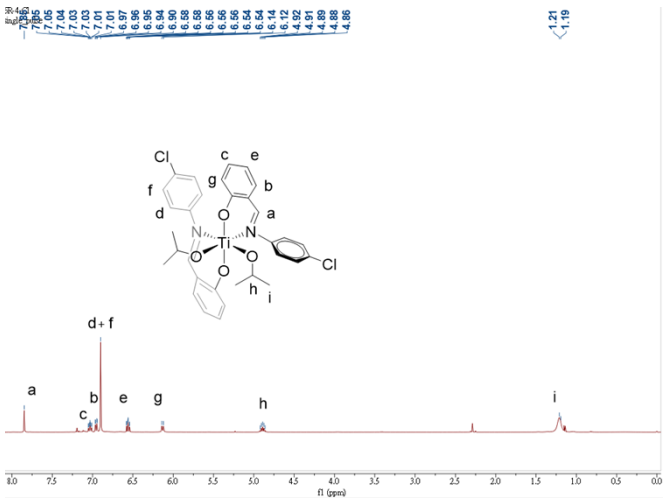


Figure S21. ^{1}H NMR spectrum of **S^{Cl}-Ti** in $CDCl_3$

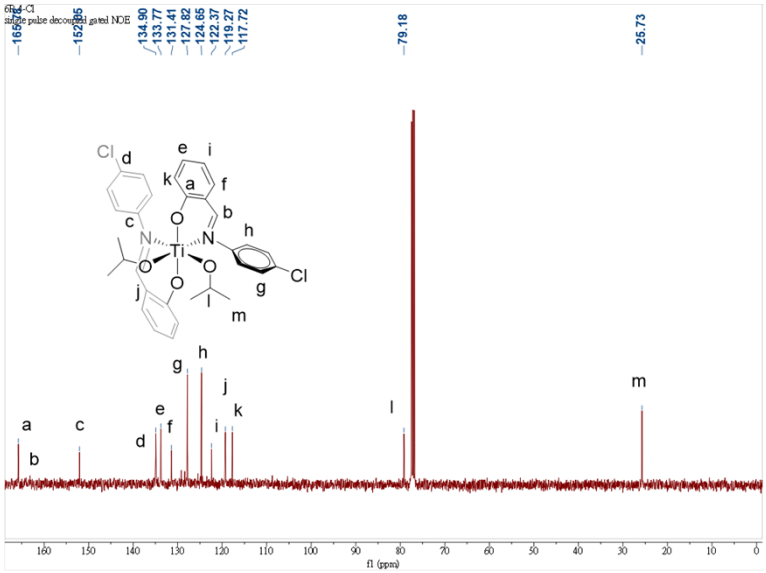


Figure S22. ^{13}C NMR spectrum of **S^{Cl}-Ti** in $CDCl_3$

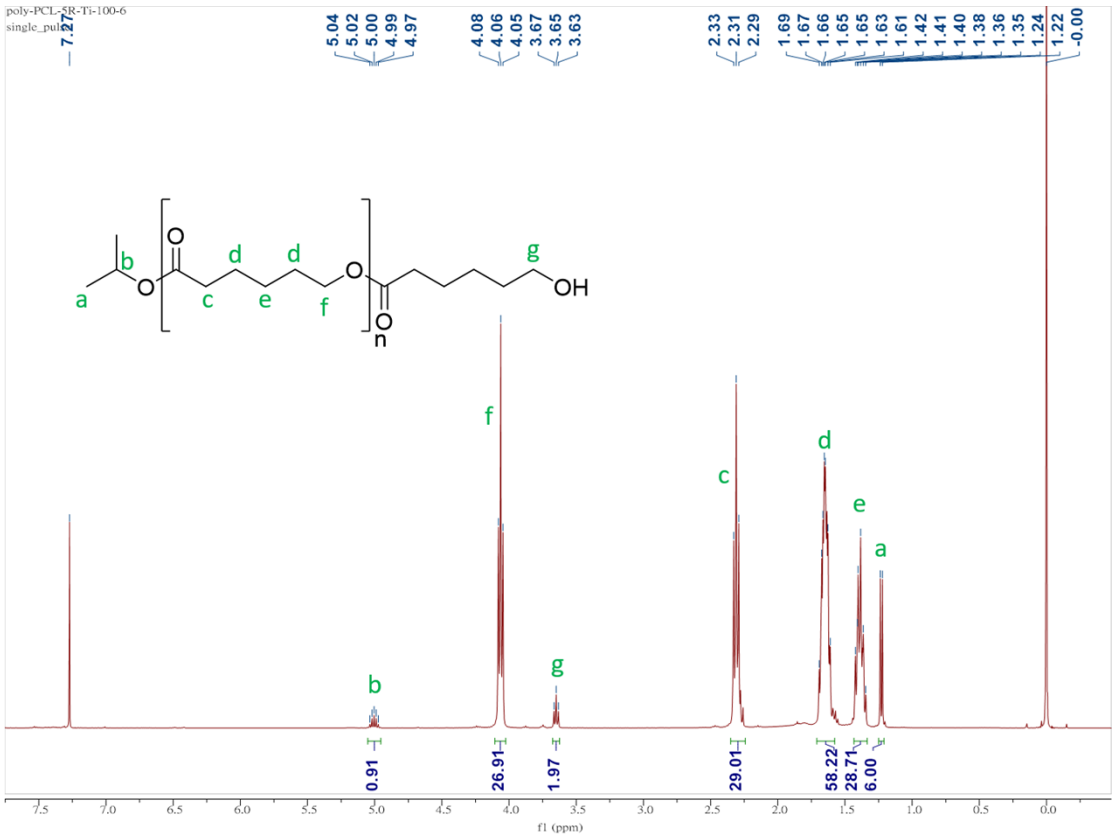


Figure S23. ^{1}H NMR spectrum of PCL in $CDCl_3$ (entry 8 of **Table 2**)

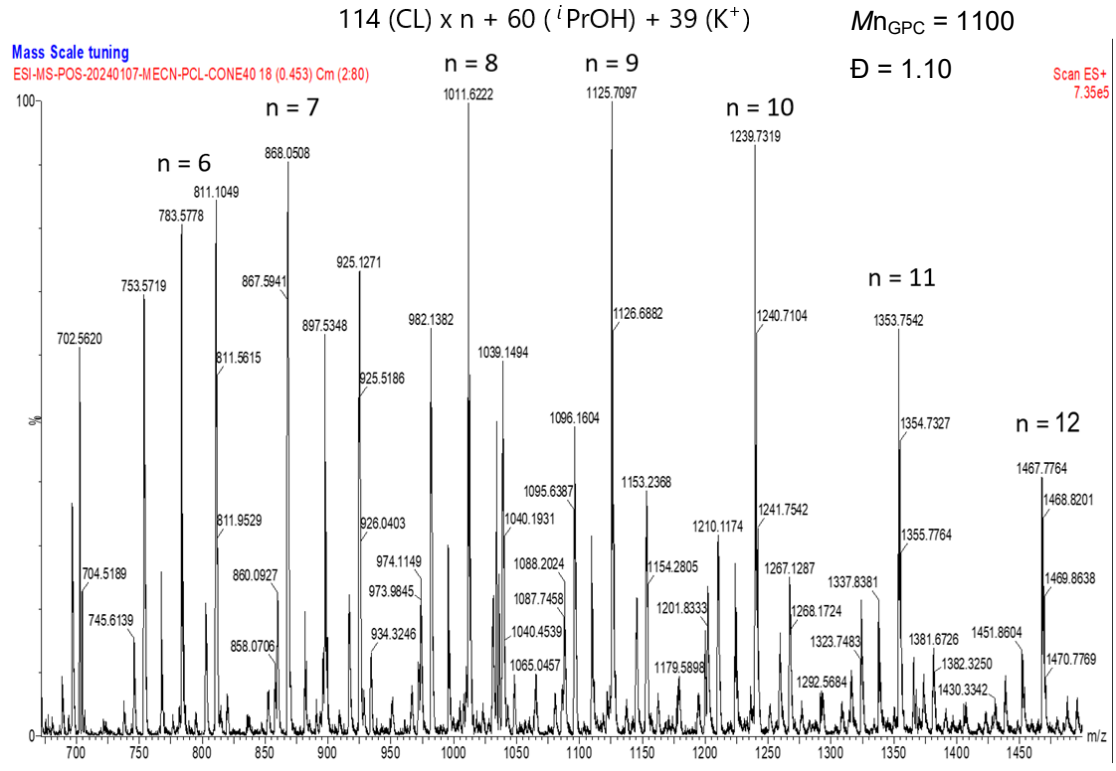


Figure S24. ESI-MS spectra of PCL synthesized by using $\mathbf{F^{Cl}}$**-Ti**

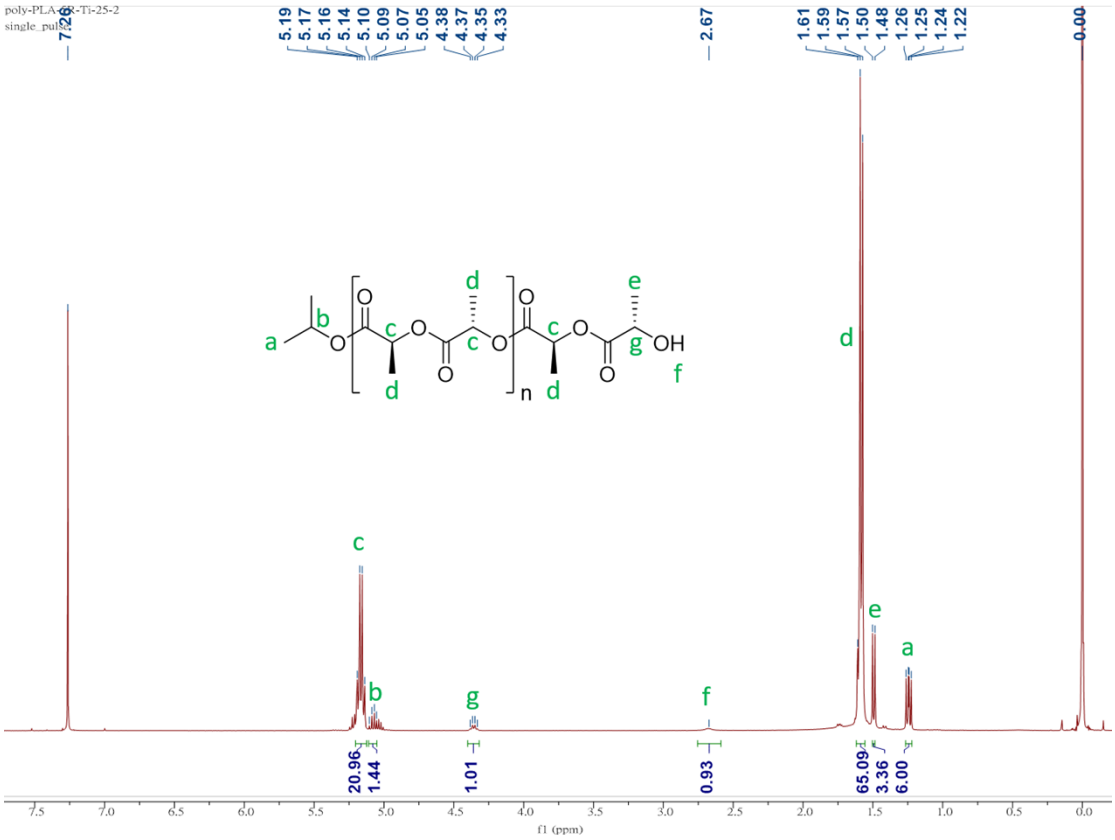


Figure S25. ^{1}H NMR spectrum of PLA in $CDCl_3$ (entry 9 of **Table 3**)

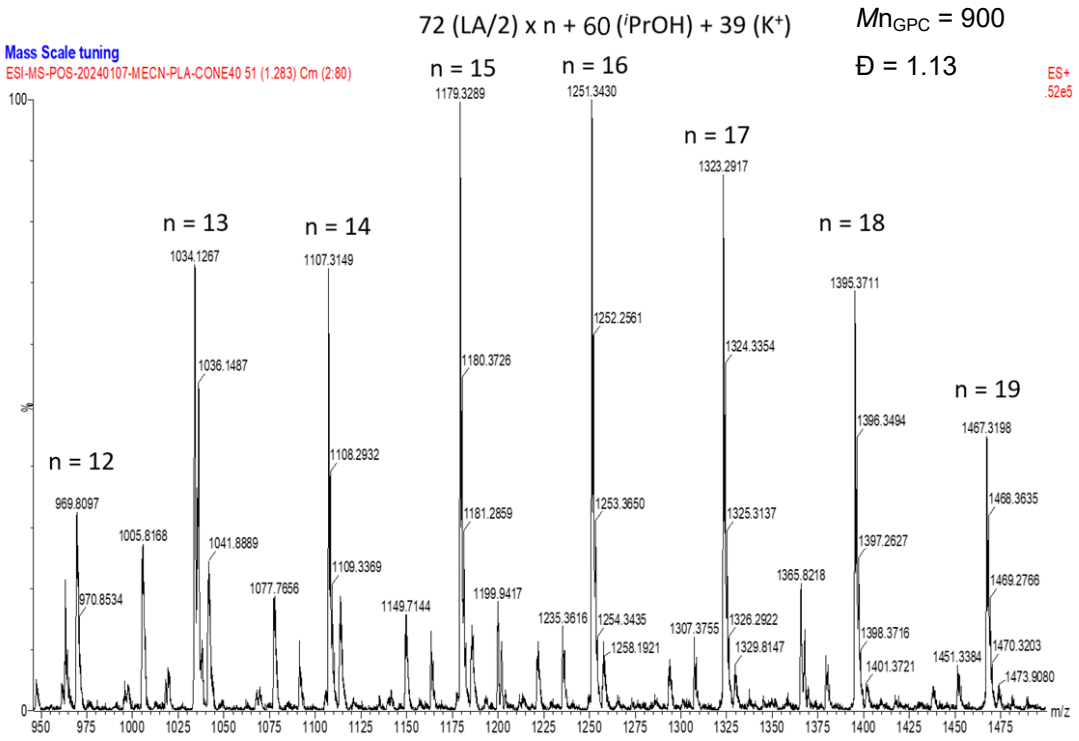


Figure S26. ESI-MS spectra of PCL synthesized by using **F^{H}-Ti**

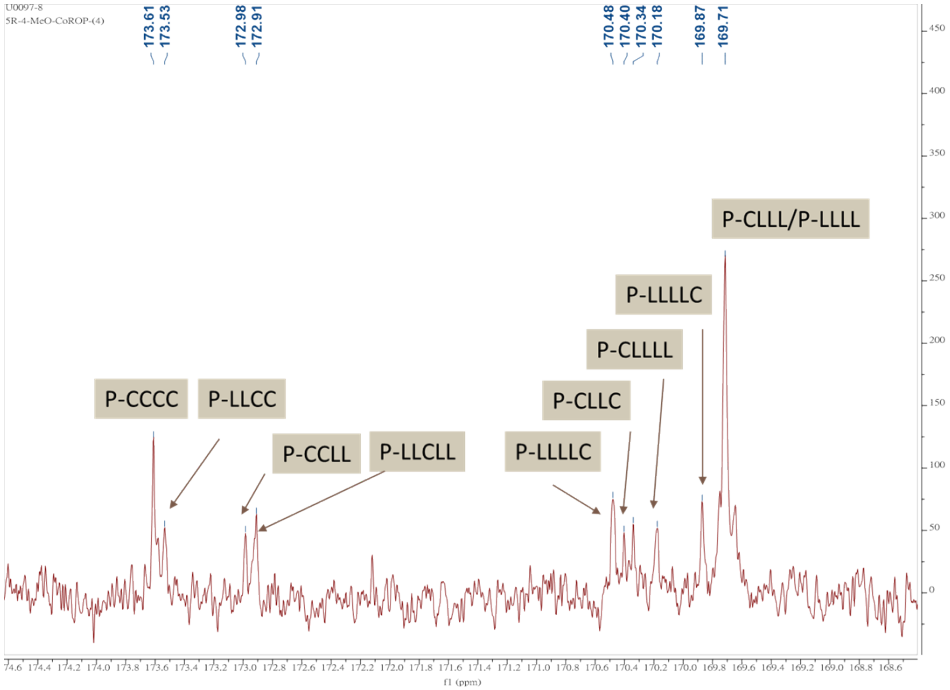
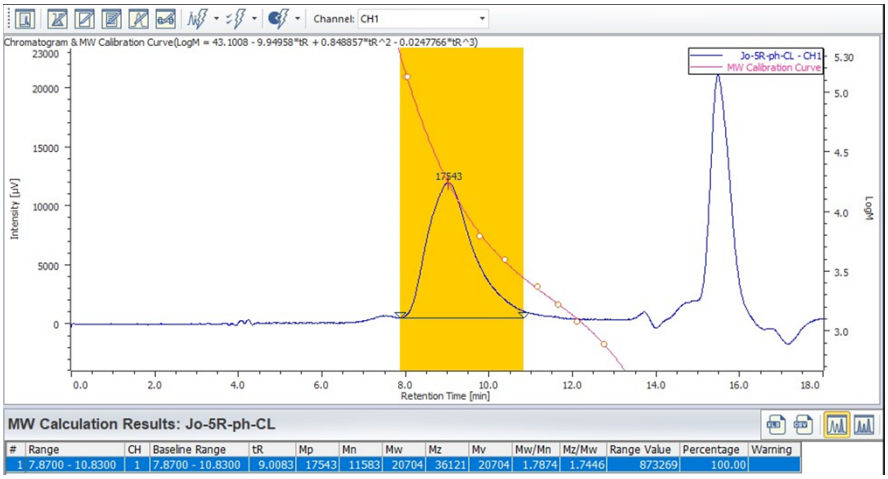


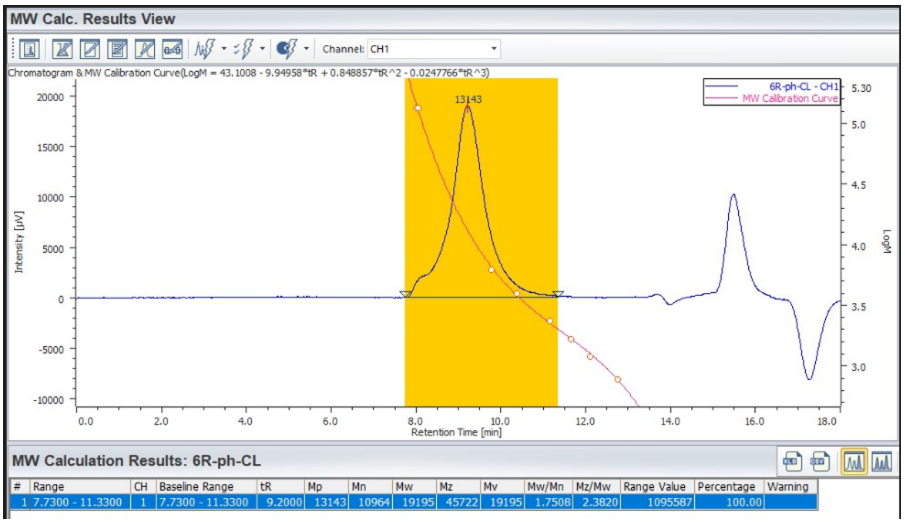
Figure S27. ^{13}C NMR of copolymer PLA-*grad*-PCL (entry 4 of **Table 4**) by **F^{OMe}-Ti**

Figure S28. ^{13}C NMR of copolymer PLA-*grad*-PCL polymerized by **F^{OMe}-Ti** (A) and **S^{OMe}-Ti** (B)



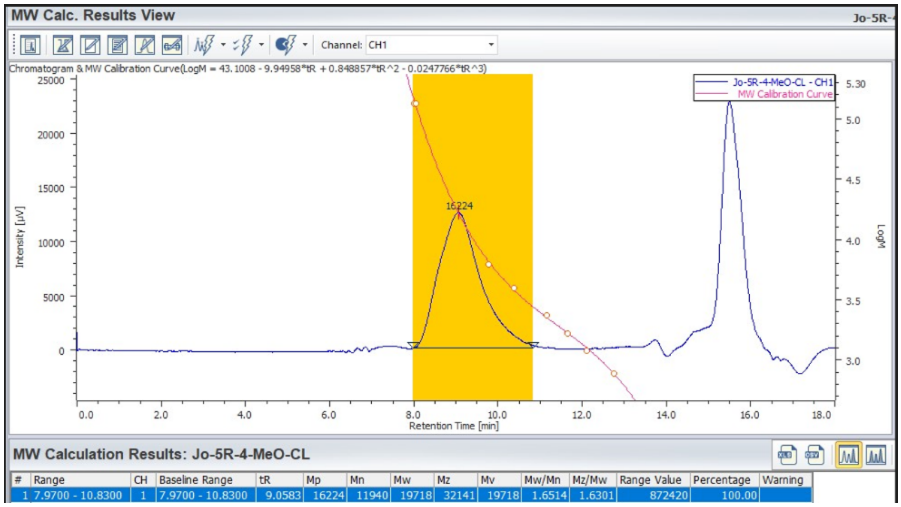
#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage	Warning
1	7.8700 - 10.8300	1	7.8700 - 10.8300	9.0083	17543	11583	20704	36121	20704	1.7874	1.7446	873269	100.00	

Figure S29. GPC spectrum of PCL (entry 1 of **Table 1**)



#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage	Warning
1	7.7300 - 11.3300	1	7.7300 - 11.3300	9.2000	13143	10964	19195	45722	19195	1.7508	2.3820	1095587	100.00	

Figure S30. GPC spectrum of PCL (entry 2 of **Table 1**)



#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage	Warning
1	7.9700 - 10.8300	1	7.9700 - 10.8300	9.0583	16224	11940	19718	32141	19718	1.6514	1.6301	872420	100.00	

Figure S31. GPC spectrum of PCL (entry 3 of **Table 1**)

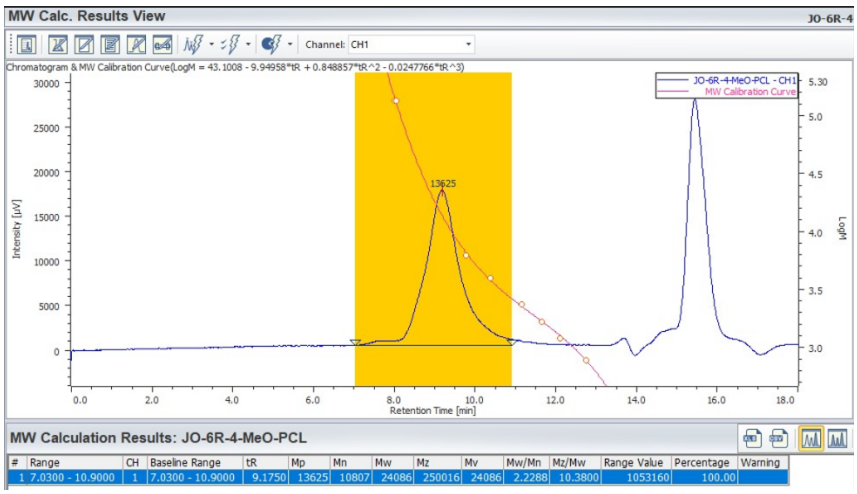


Figure S32. GPC spectrum of PCL (entry 4 of **Table 1**)

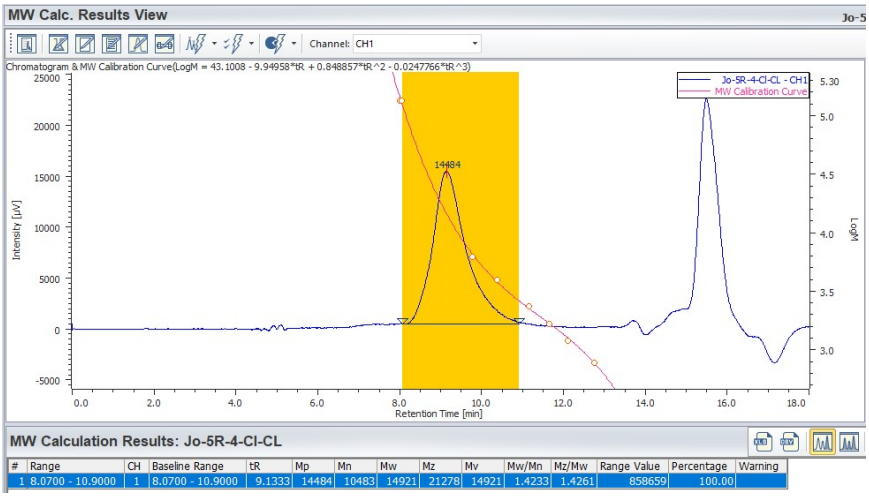


Figure S33. GPC spectrum of PCL (entry 5 of **Table 1**)

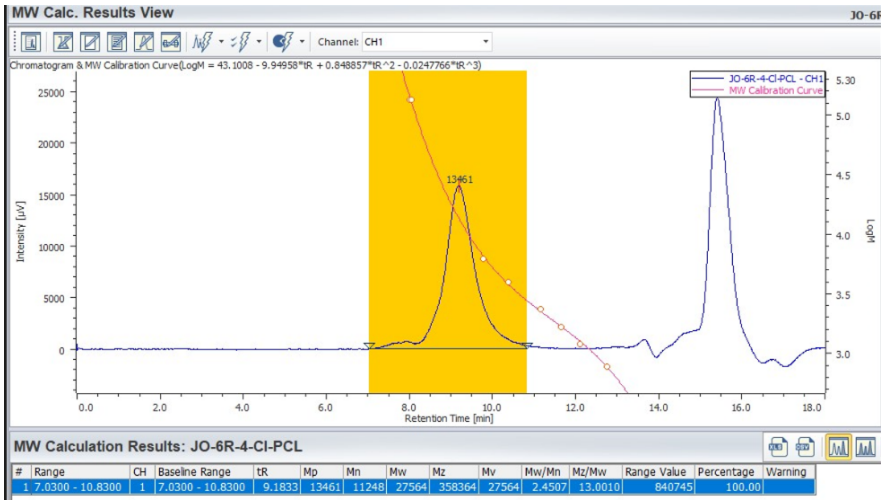


Figure S34. GPC spectrum of PCL (entry 6 of **Table 1**)

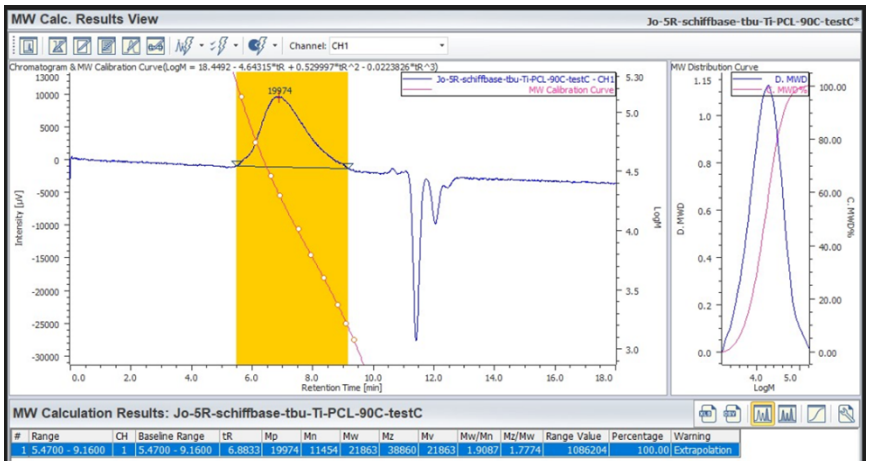


Figure S35. GPC spectrum of PCL (entry 7 of **Table 1**)

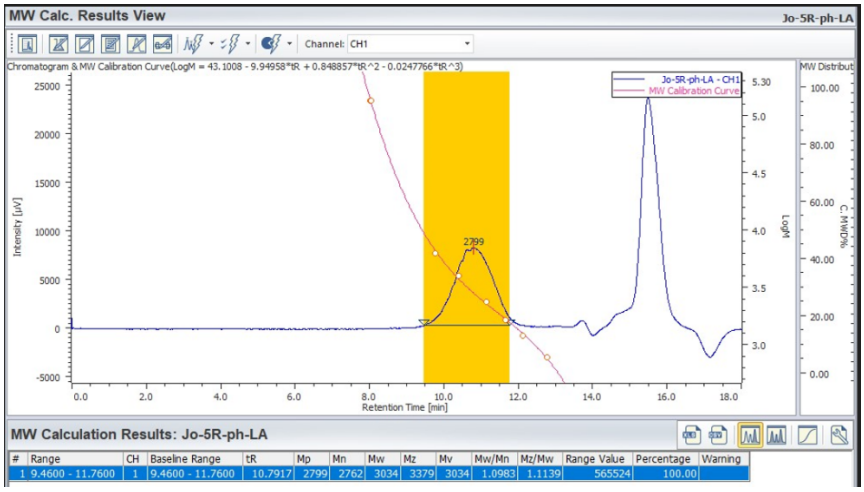


Figure S36. GPC spectrum of PLA (entry 1 of **Table 2**)

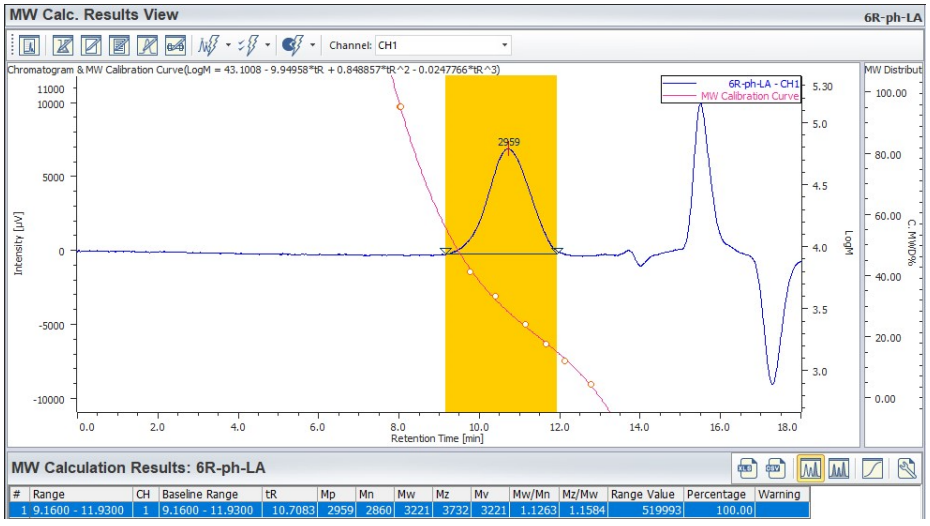


Figure S37. GPC spectrum of PLA (entry 2 of **Table 2**)

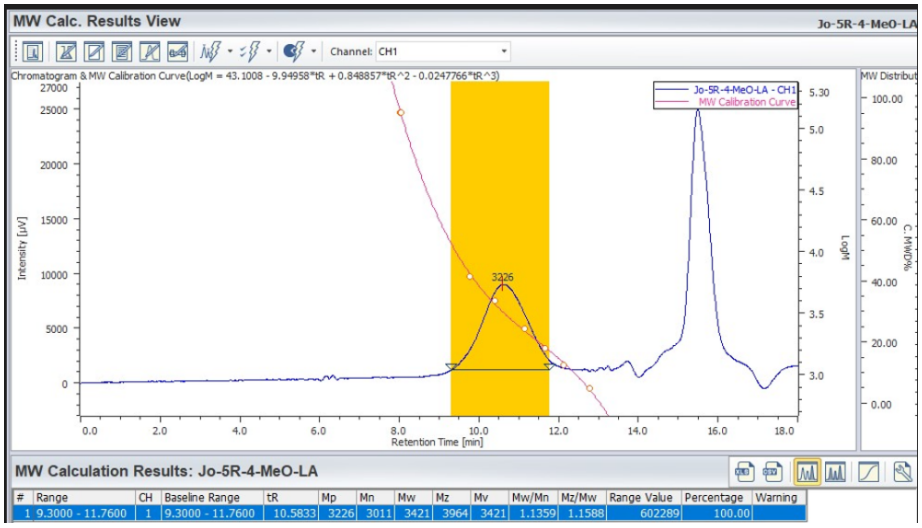


Figure S38. GPC spectrum of PLA (entry 3 of **Table 2**)

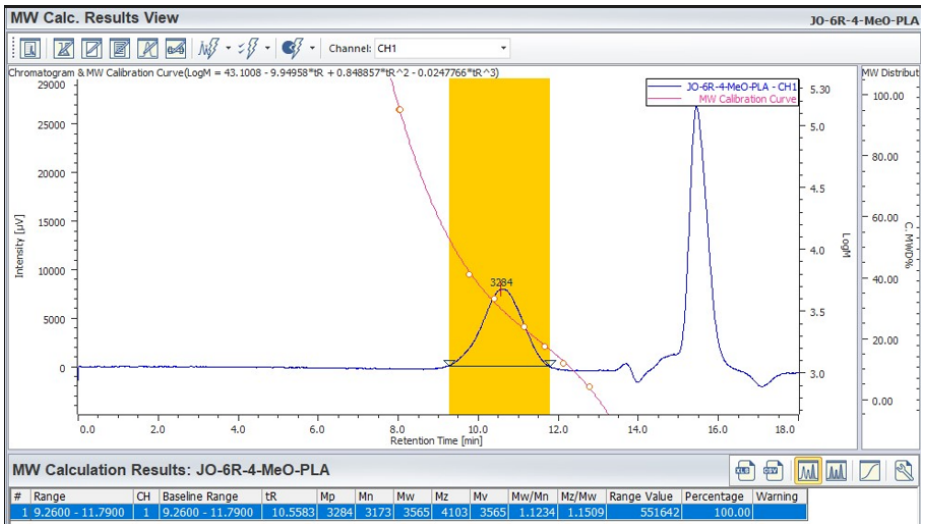


Figure S39. GPC spectrum of PLA (entry 4 of **Table 2**)

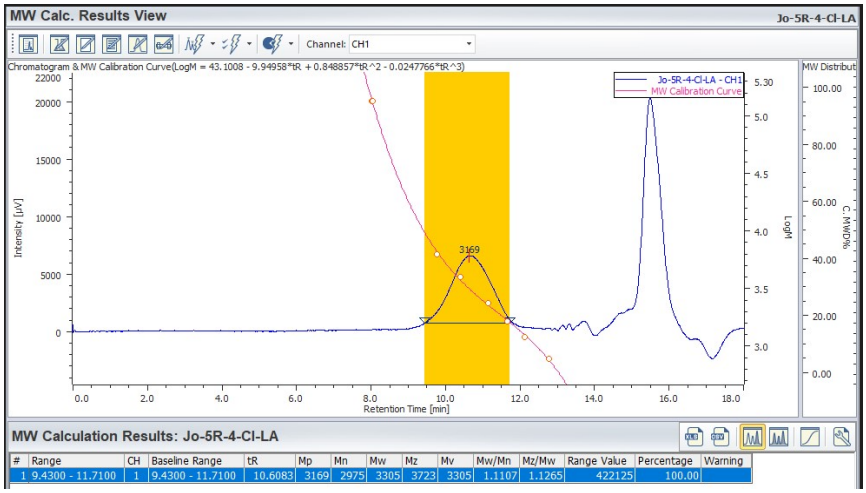


Figure S40. GPC spectrum of PLA (entry 5 of **Table 2**)

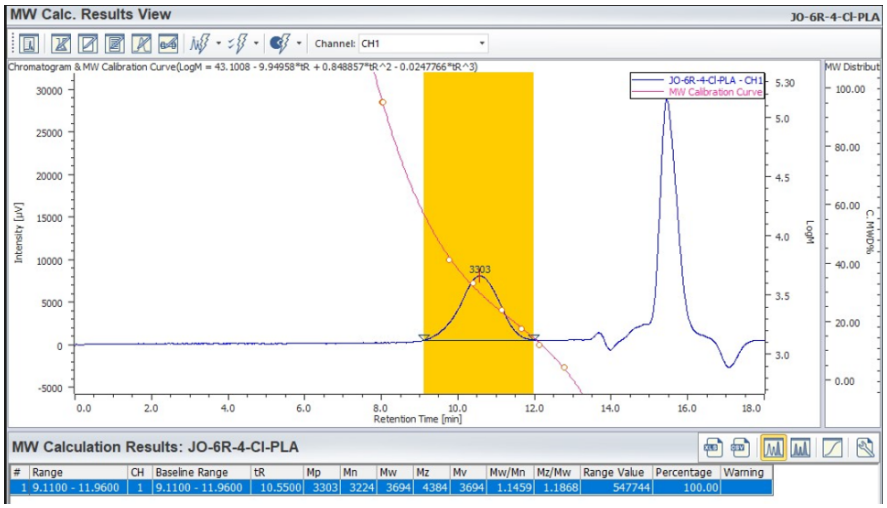


Figure S41. GPC spectrum of PLA (entry 6 of **Table 2**)

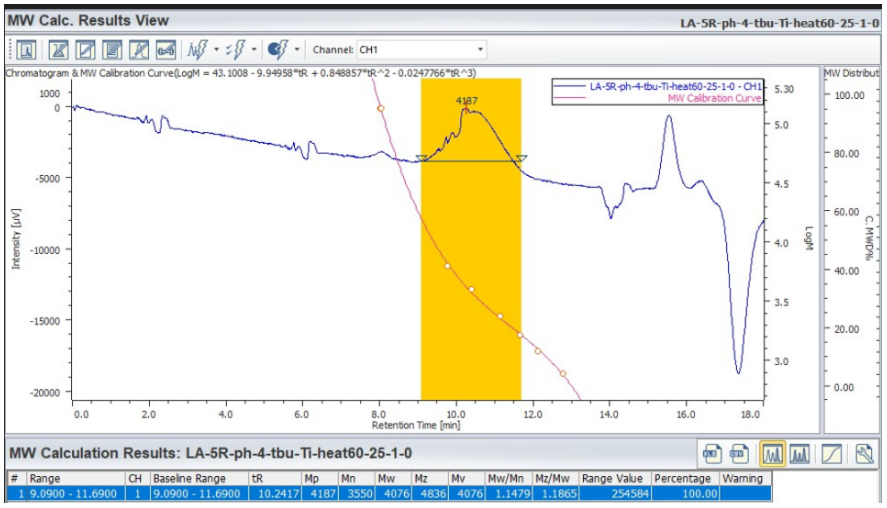


Figure S42. GPC spectrum of PLA (entry 7 of **Table 2**)

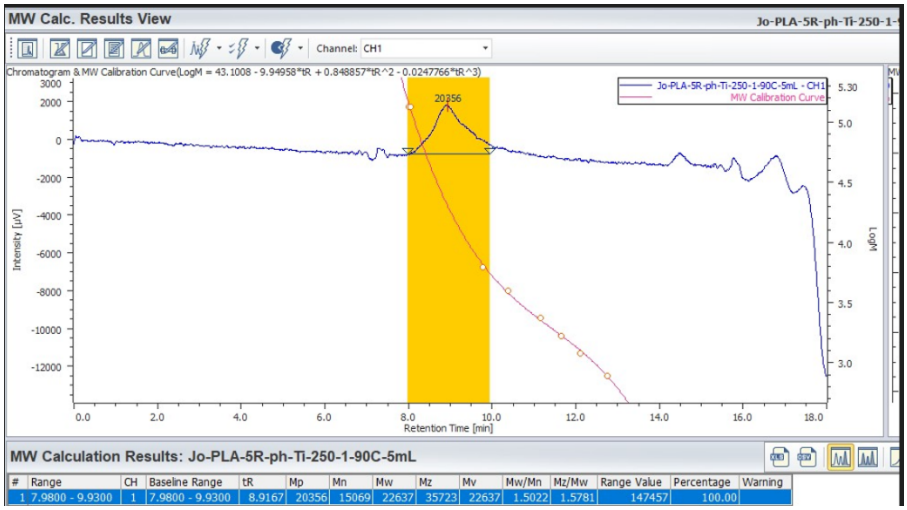


Figure S43. GPC spectrum of PLA (entry 8 of **Table 2**)

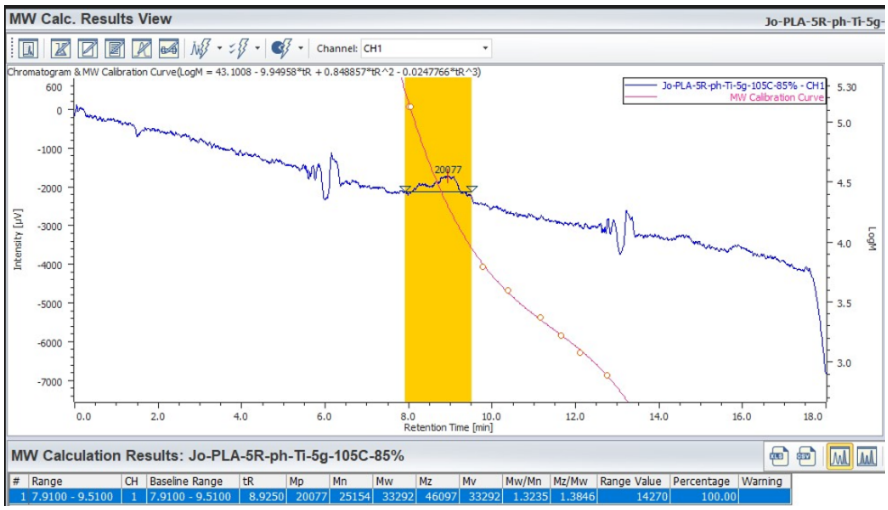


Figure S44. GPC spectrum of PLA (entry 9 of **Table 2**)

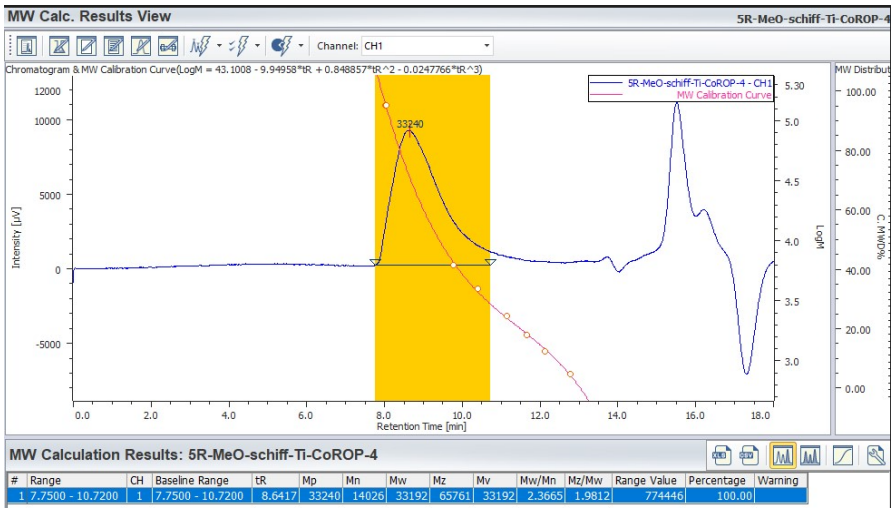


Figure S45. GPC spectrum of PLA (entry 4 of **Table 3**)

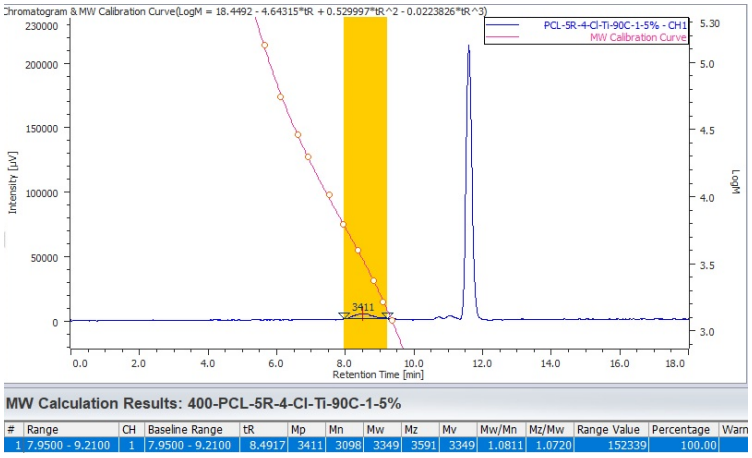
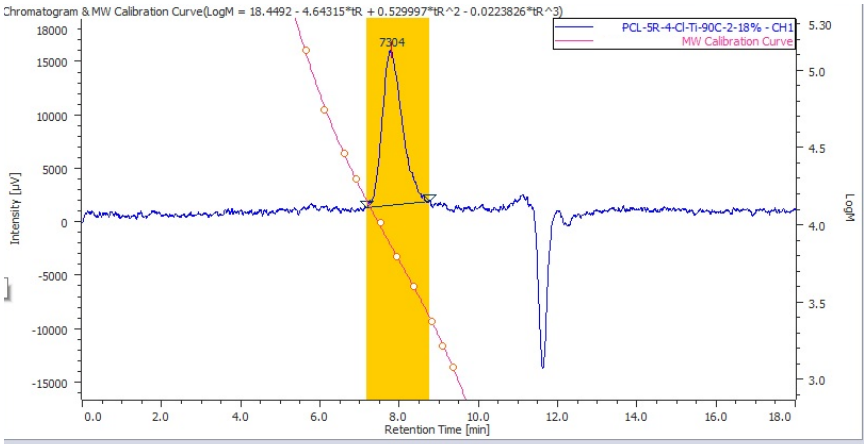


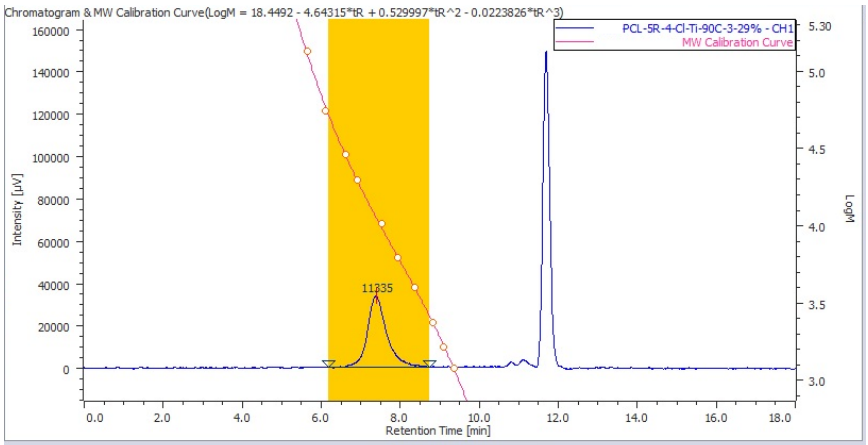
Figure S46. GPC spectrum of PCL (entry 1 of **Table S8**)



MW Calculation Results: 400-PCL-5R-4-Cl-Ti-90C-2-18%

#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage	Warn
1	7.1600 - 8.7600	1	7.1600 - 8.7600	7.7833	7304	6600	7092	7569	7092	1.0746	1.0672	507353	100.00	

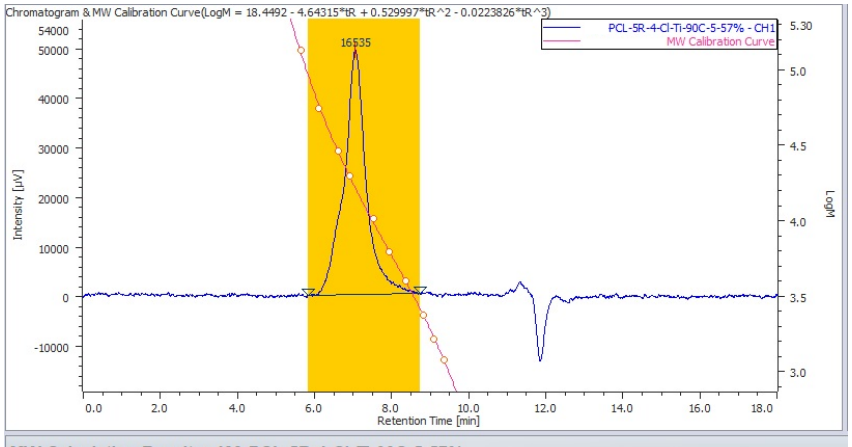
Figure S47. GPC spectrum of PCL (entry 2 of **Table S8**)



MW Calculation Results: 400-PCL-5R-4-Cl-Ti-90C-3-29%

#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage
1	6.1770 - 8.7200	1	6.1700 - 8.7200	7.3750	11335	10069	11128	12199	11128	1.1052	1.0962	1126596	100.00

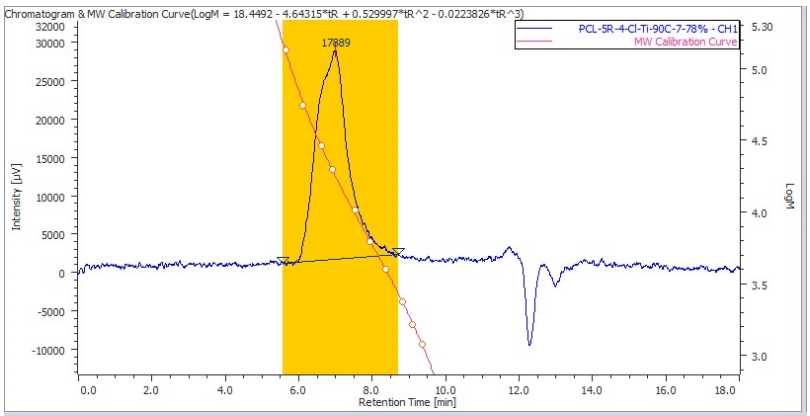
Figure S48. GPC spectrum of PCL (entry 3 of **Table S8**)



MW Calculation Results: 400-PCL-5R-4-Cl-Ti-90C-5-57%

#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage
1	5.8400 - 8.7200	1	5.8400 - 8.7200	7.0417	16535	14858	17879	21238	17879	1.2033	1.1879	1977044	100.00

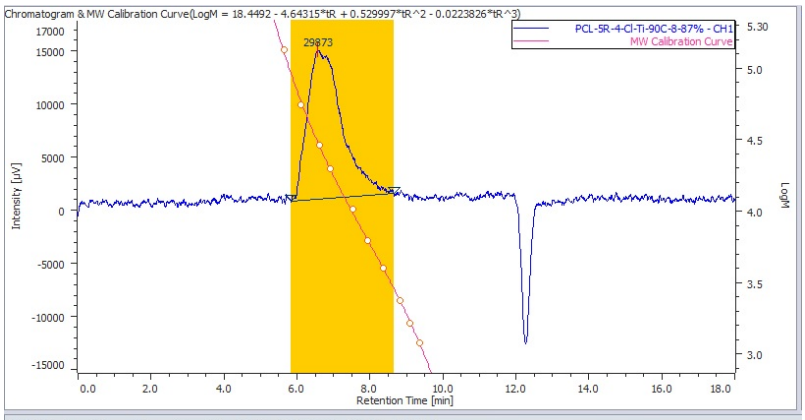
Figure S49. GPC spectrum of PCL (entry 4 of **Table S8**)



MW Calculation Results: 400-PCL-5R-4-Cl-Ti-90C-7-78%

#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage
1	5.5700 - 8.7100	1	5.5700 - 8.7100	6.9750	17889	16466	21437	26772	21437	1.3019	1.2489	1635784	100.00

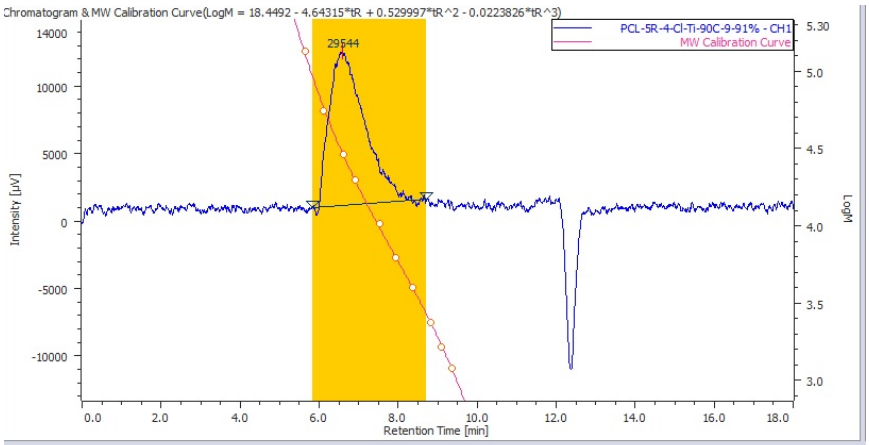
Figure S50. GPC spectrum of PCL (entry 5 of **Table S8**)



MW Calculation Results: 400-PCL-5R-4-Cl-Ti-90C-8-87%

#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage
1	5.8200 - 8.6400	1	5.8200 - 8.6400	6.5667	29873	17907	25143	32361	25143	1.4041	1.2871	914013	100.00

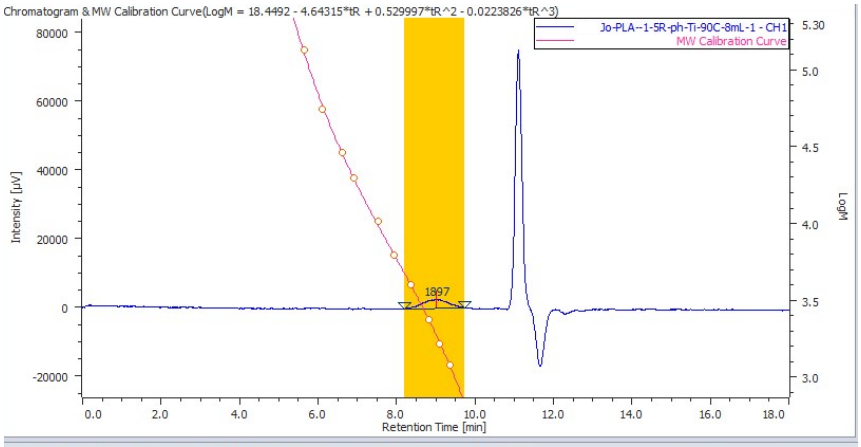
Figure S51. GPC spectrum of PCL (entry 6 of **Table S8**)



MW Calculation Results: 400-PCL-5R-4-Cl-Ti-90C-9-91%

#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage
1	5.8200 - 8.7100	1	5.8200 - 8.7100	6.5750	29544	19376	26189	32772	26189	1.3516	1.2514	711347	100.00

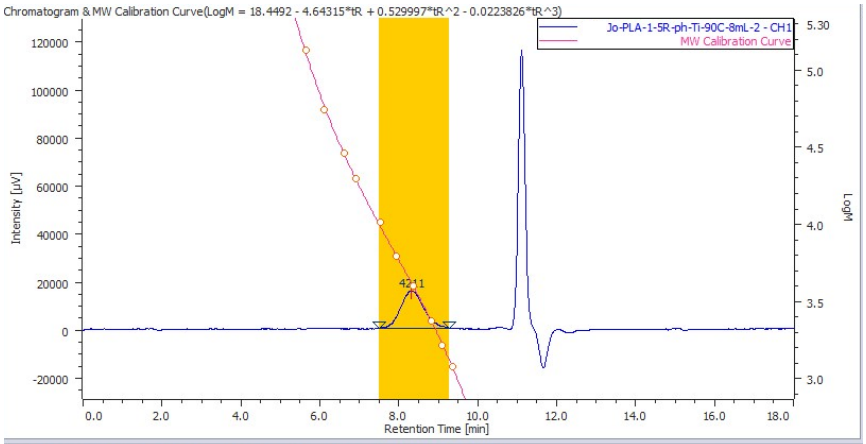
Figure S52. GPC spectrum of PCL (entry 7 of **Table S8**)



MW Calculation Results: Jo-PLA-250-1-5R-ph-Ti-90C-8mL-1

#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage	Warn
1	8.2000 - 9.7300	1	8.2000 - 9.7300	8.9917	1897	1793	2031	2279	2031	1.1325	1.1219	112305	100.00	Extra

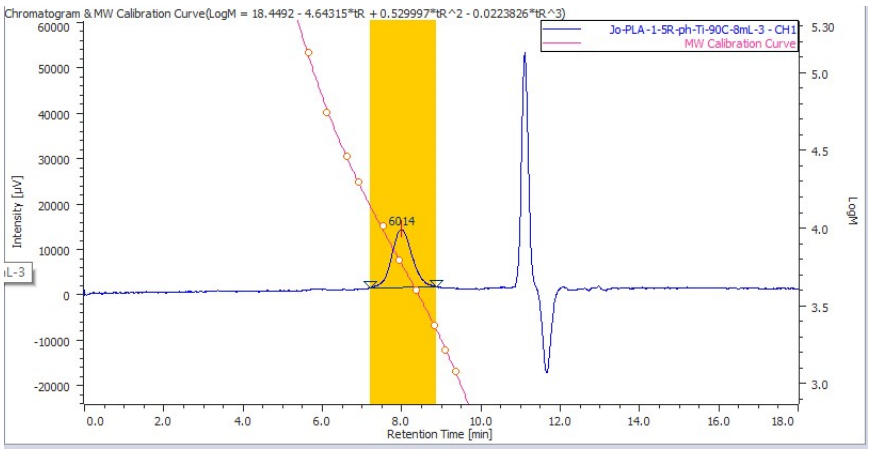
Figure S53. GPC spectrum of PLA (entry 1 of **Table S9**)



MW Calculation Results: Jo-PLA-250-1-5R-ph-Ti-90C-8mL-2

#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage	Warn
1	7.5000 - 9.2600	1	7.5000 - 9.2600	8.3000	4211	3795	4159	4521	4159	1.0961	1.0870	618522	100.00	

Figure S54. GPC spectrum of PLA (entry 2 of **Table S9**)



MW Calculation Results: Jo-PLA-250-1-5R-ph-Ti-90C-8mL-3

#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage	Warn
1	7.2000 - 8.8600	1	7.2000 - 8.8600	7.9667	6014	5538	5948	6372	5948	1.0741	1.0712	451322	100.00	

Figure S55. GPC spectrum of PLA (entry 3 of **Table S9**)

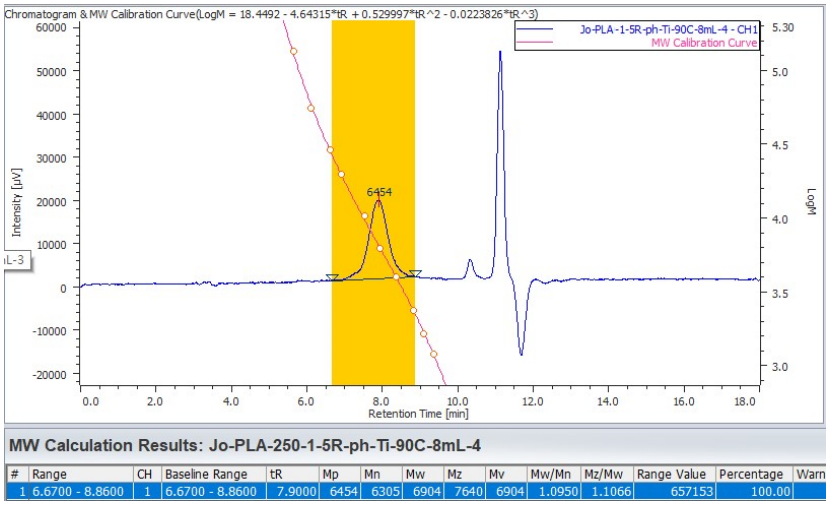


Figure S56. GPC spectrum of PLA (entry 4 of **Table S9**)

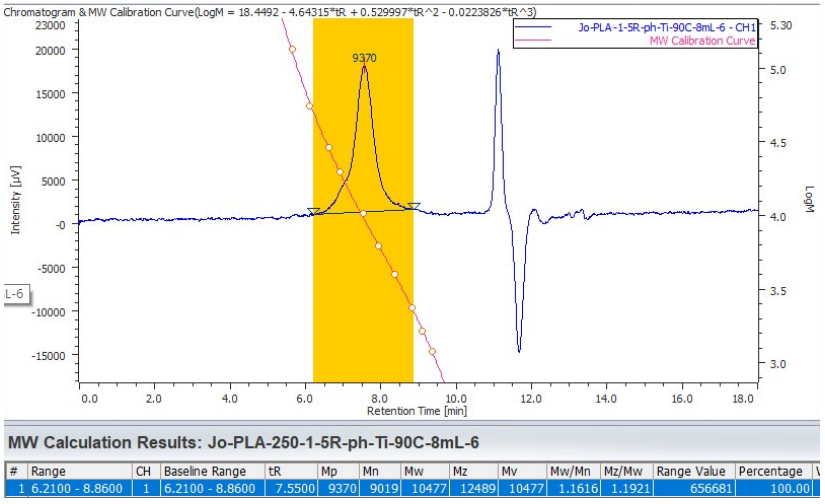


Figure S57. GPC spectrum of PLA (entry 5 of **Table S9**)

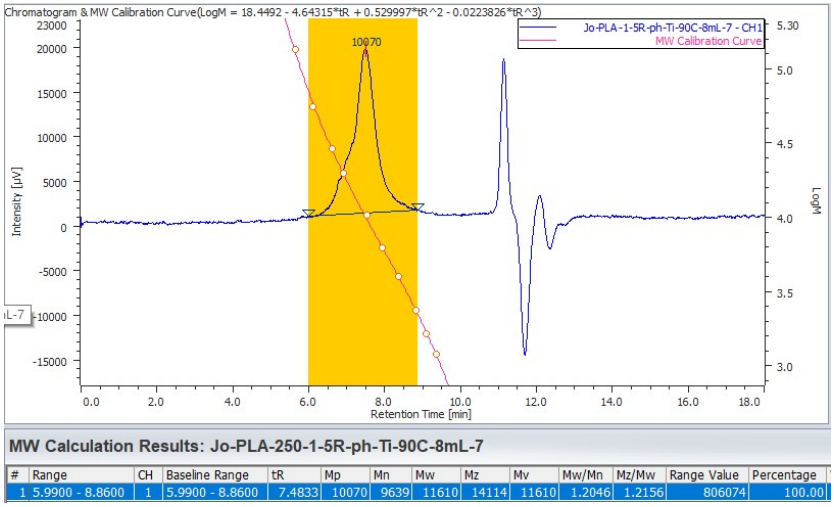
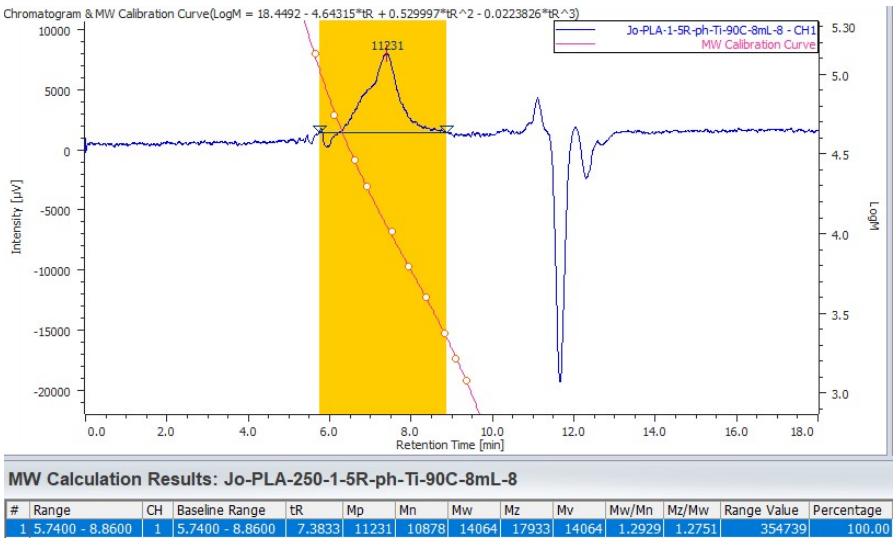


Figure S58. GPC spectrum of PLA (entry 6 of **Table S9**)



#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage
1	5.7400 - 8.8600	1	5.7400 - 8.8600	7.3833	11231	10878	14064	17933	14064	1.2929	1.2751	354739	100.00

Figure S59. GPC spectrum of PLA (entry 7 of **Table S9**)

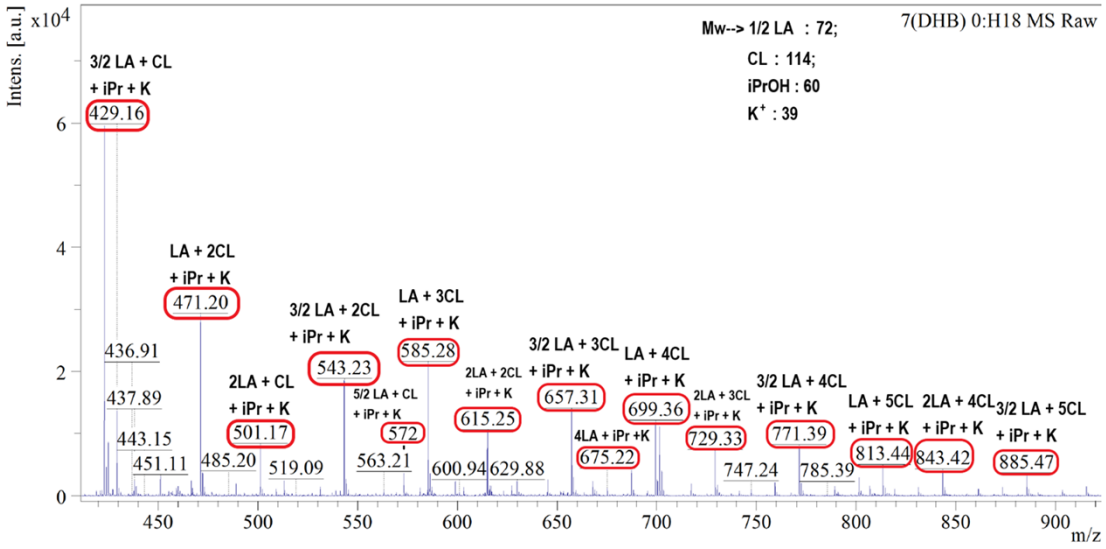


Figure S60. MALDI-TOF spectra of PLA-*grad*-PCL copolymer (50 CL + 50 LA) using **F^{OMe}-Ti** as a catalyst; PLA conversion = 19% and PCL conversion = 2% (matrix: DCTB; ionization salt: KI; solvent: CH_2Cl_2).

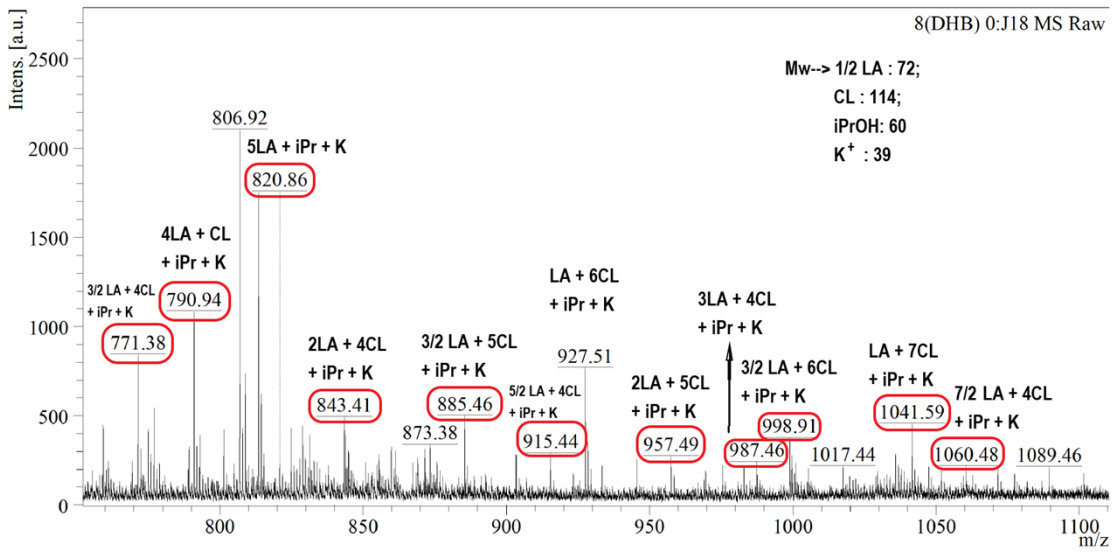


Figure S61. MALDI-TOF spectra of PLA-*grad*-PCL copolymer (50 CL + 50 LA) using **F^{OMe}-Ti** as a catalyst; PLA conversion = 37% and PCL conversion = 10% (matrix: DCTB; ionization salt: KI; solvent: CH_2Cl_2).

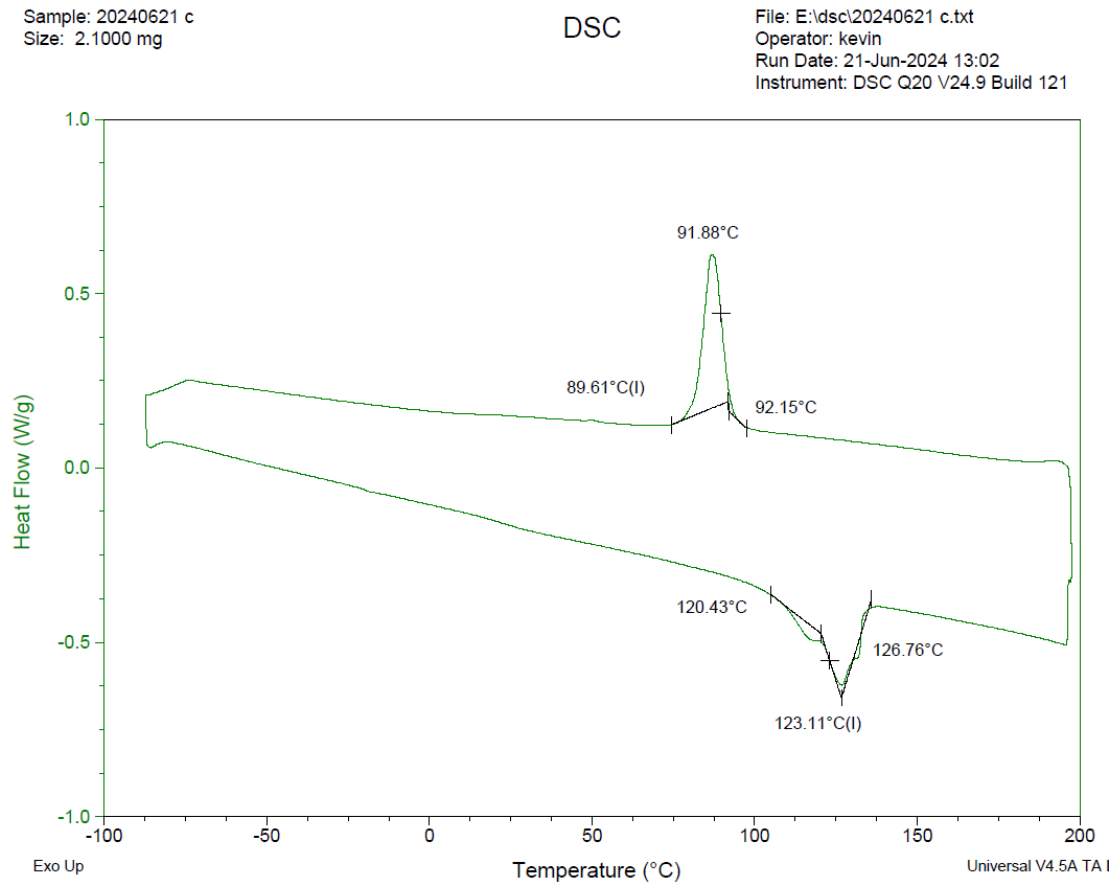


Figure S62. DSC curve of PLA (entry 3 of **Table 3**)

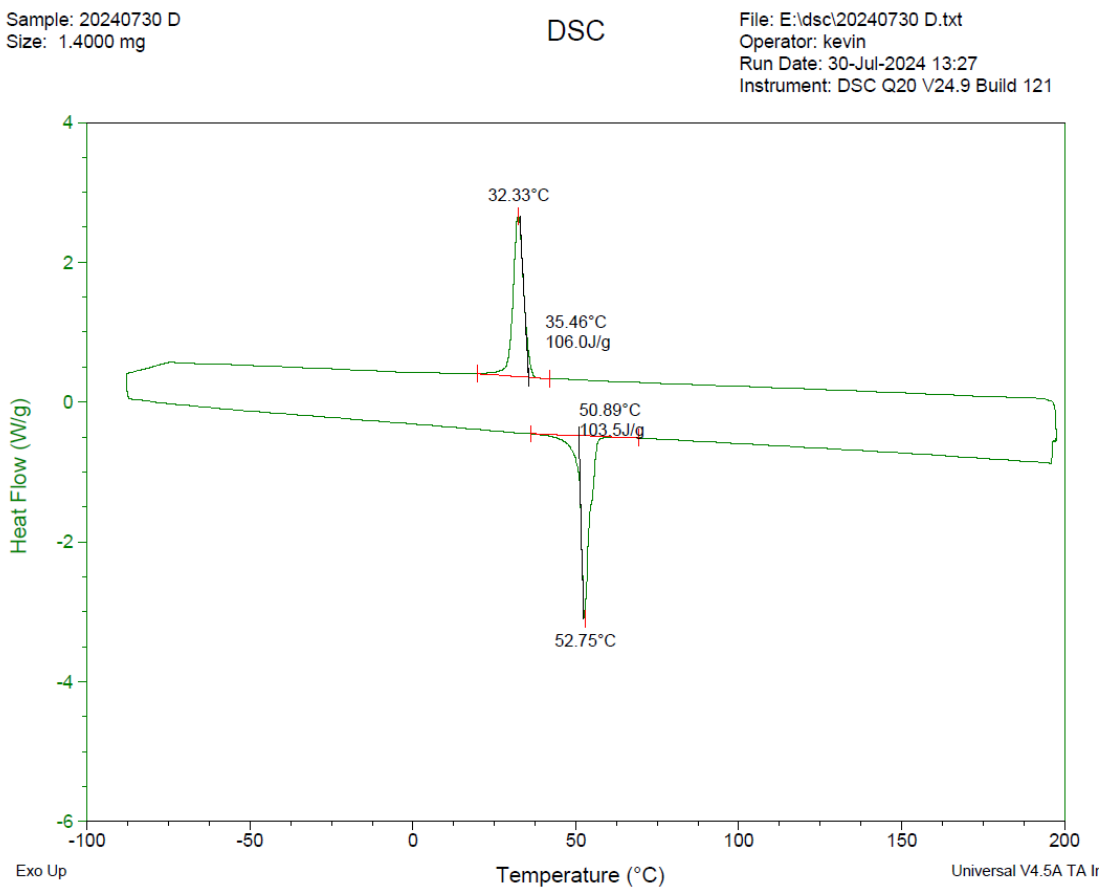


Figure S63. DSC curve of PCL (entry 3 of **Table 2**)

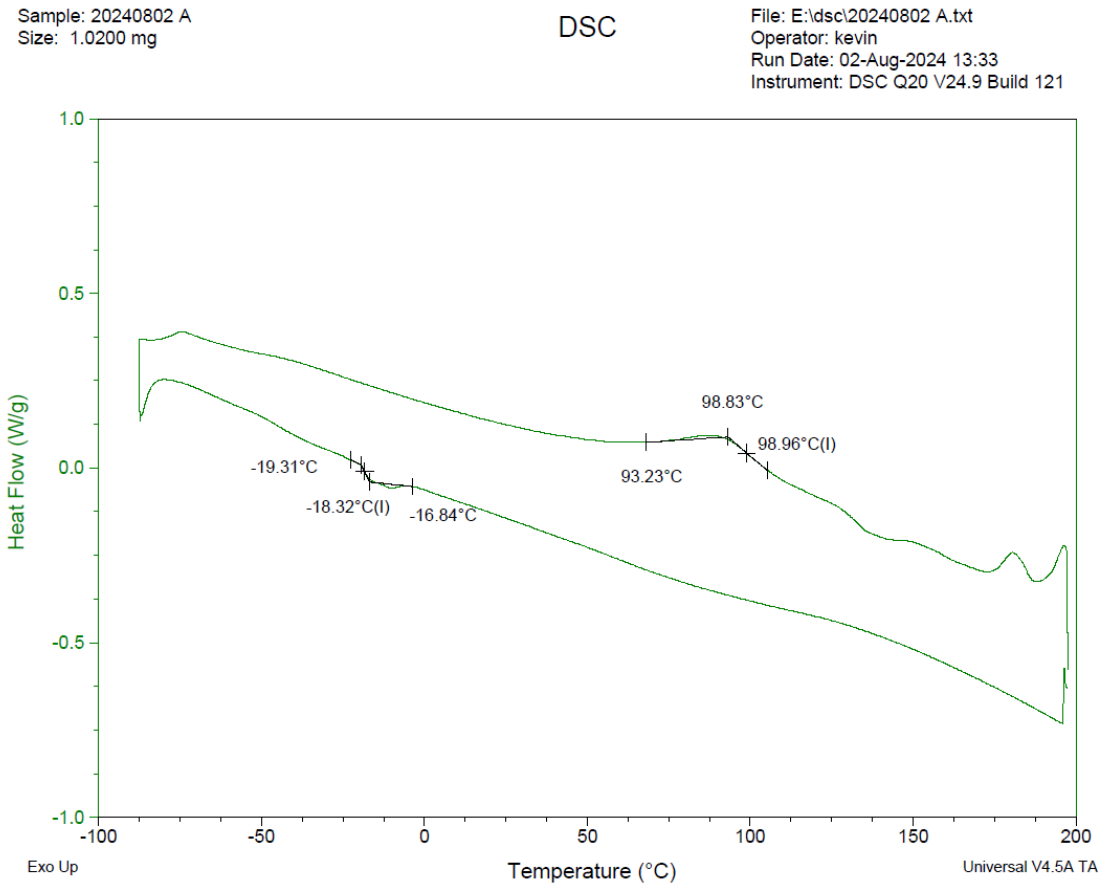


Figure S64. DSC curve of PLA-*grad*-PCL (entry 8 of **Table 4**)