Supporting information

Enhancing the stereoselectivity of $Me_2GaOR(NHC)$ species in the ring-opening polymerization of *rac*-lactide, with the help of the chelation effect

Paweł Horeglad,[a,*] Anna Rola-Noworyta,[a] Dawid Tuszyński,[a] Iga Fabianowska,[a] Natalia Agnieszka Marek,[a] Patrycja Gładysz,[a] Ireneusz Wielgus,[a] and Anna Maria Dąbrowska[a]

[a] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664, Warsaw, Poland.

1) **VT ^{1}H NMR data for complexes 3 and 4 (Figures S1 – S26)**
2) **FTIR data for complexes 3 and 4 (Figures S27 – S42)**
3) **^{13}C NMR spectra of PLA obtained with 1 and 2 (Figures S43 – S45)**
4) **MALDI-TOF and GPC of PLA obtained with complexes 1 and 3 (Figures S46 – S89)**

1) VT ^{1}H NMR Data

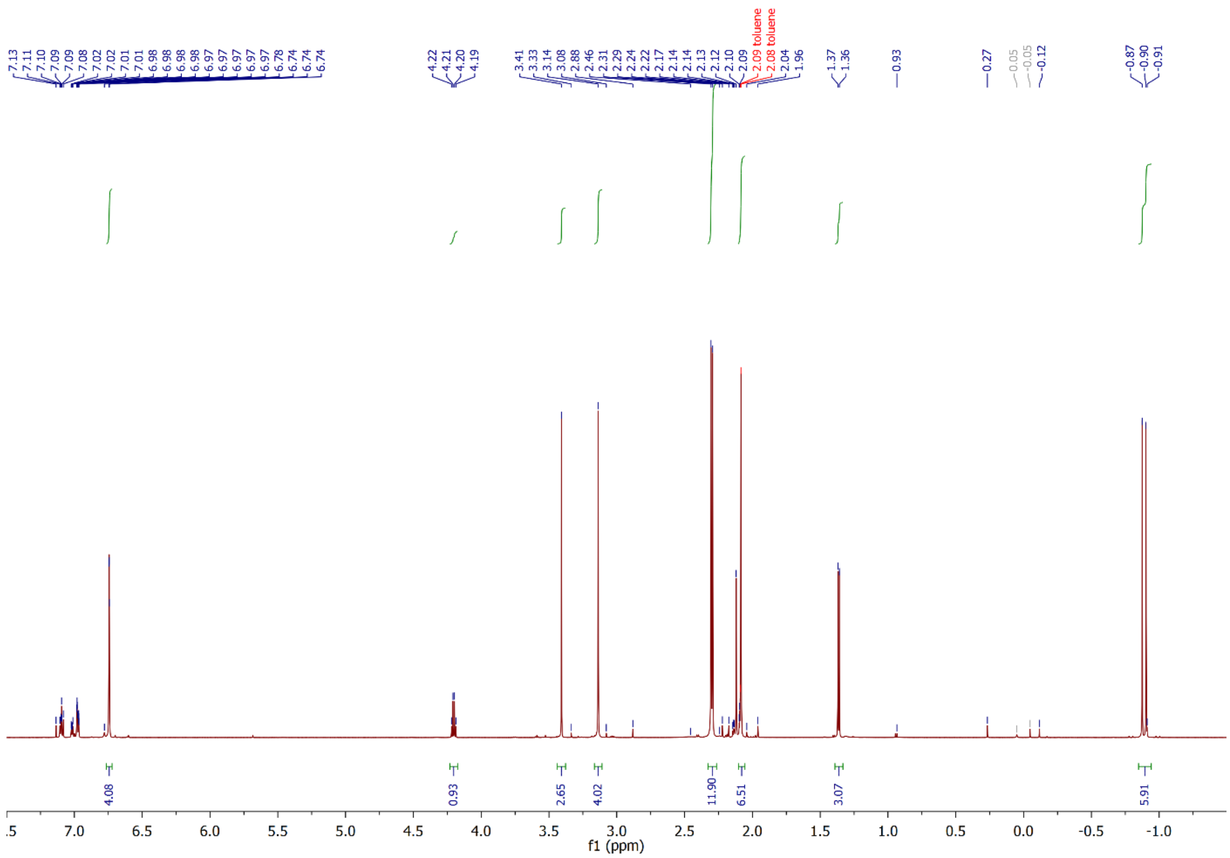


Figure S1. ^{1}H NMR (toluene-d_8, 400 MHz) spectrum of **3** at r.t.

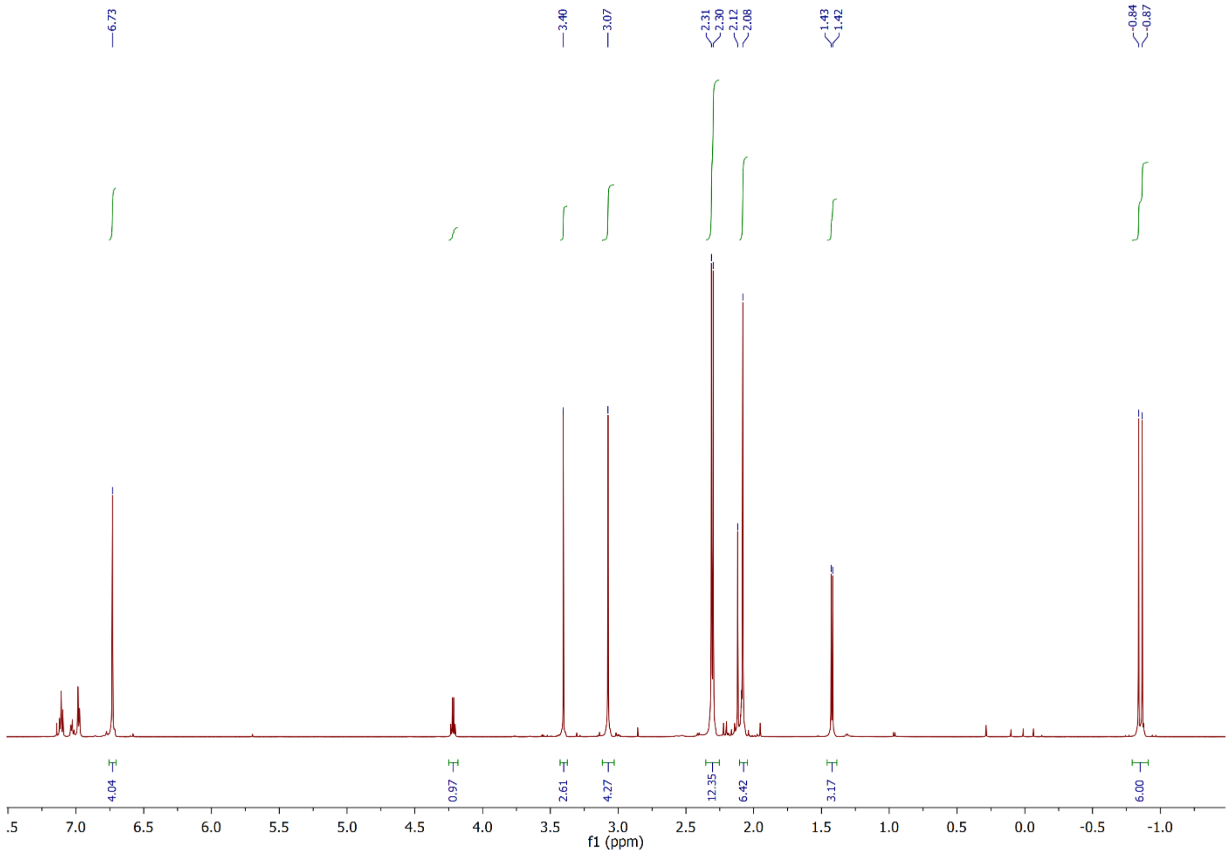


Figure S2. ^{1}H NMR (toluene-d_8, 400 MHz) spectrum of **3** at 0°C

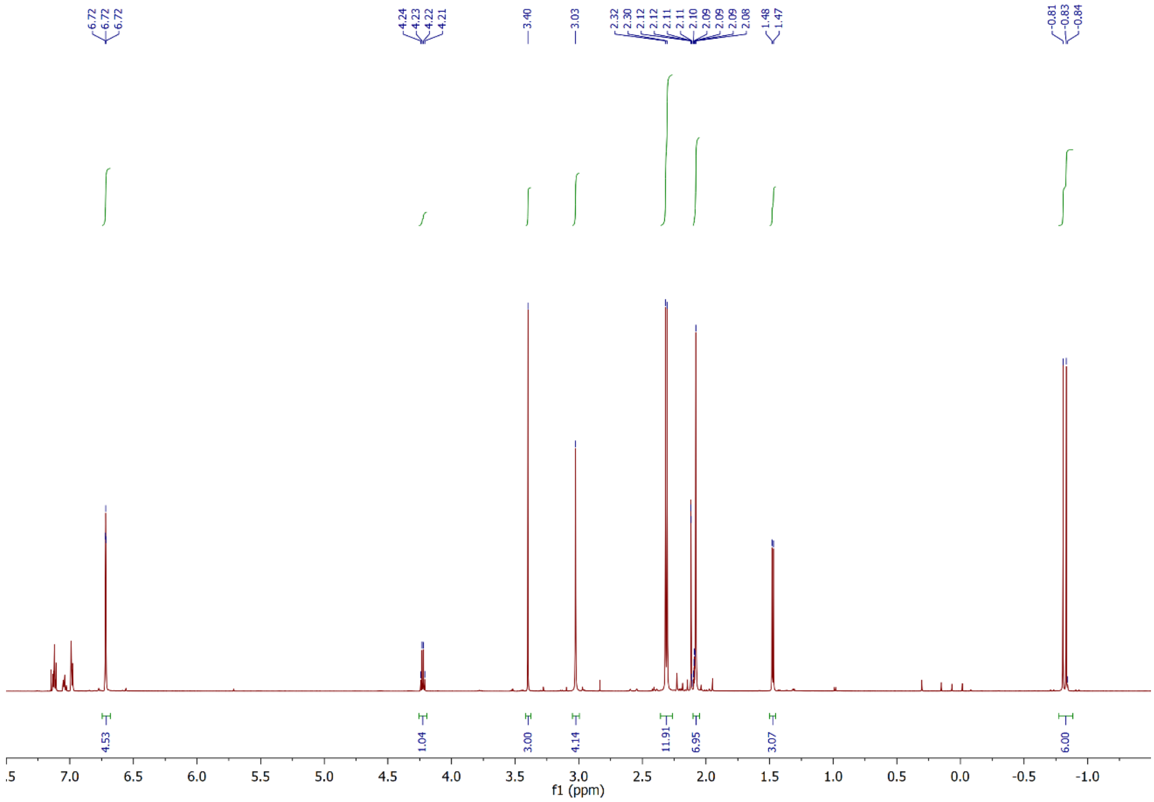


Figure S3. ^{1}H NMR (toluene-d_8, 400 MHz) spectrum of **3** at –20°C

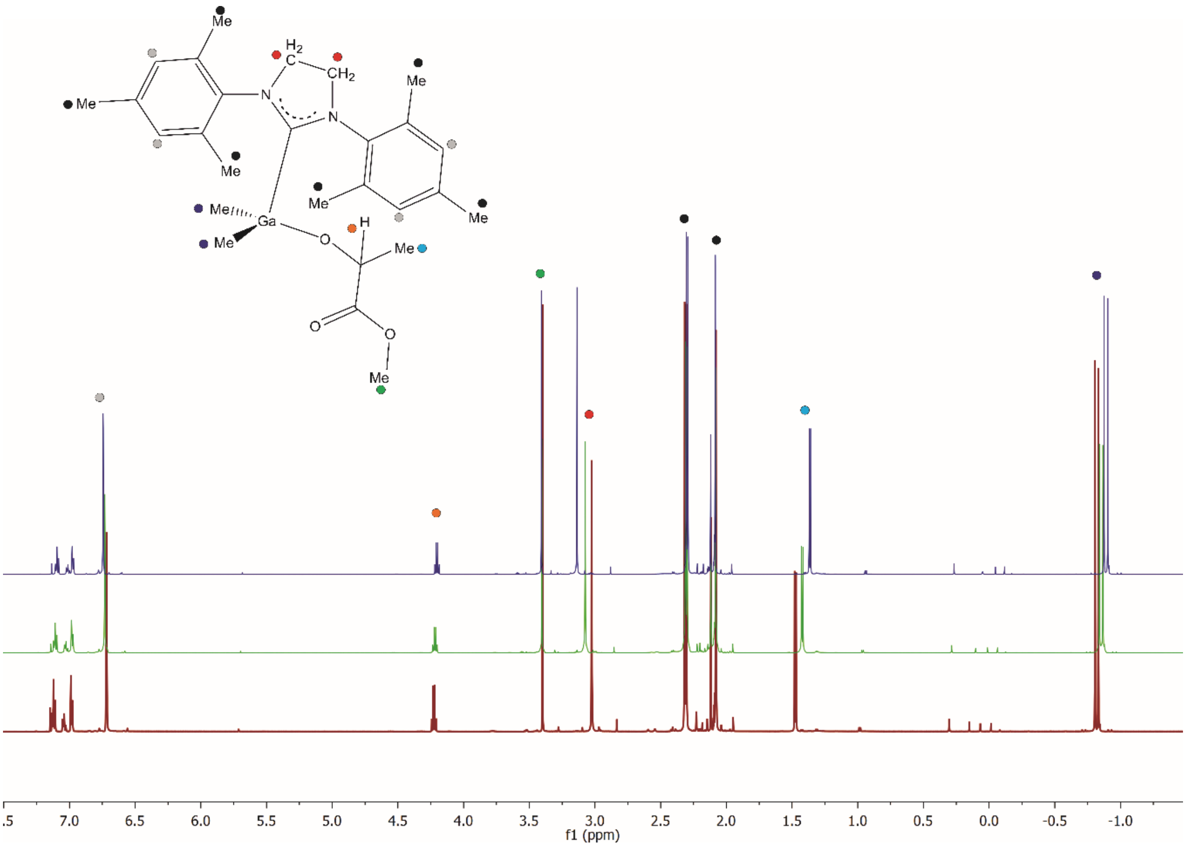


Figure S4. VT ^{1}H NMR (toluene-d_8, 400 MHz) spectra of **3** at r.t. (blue), 0°C (green) and –20°C (red)

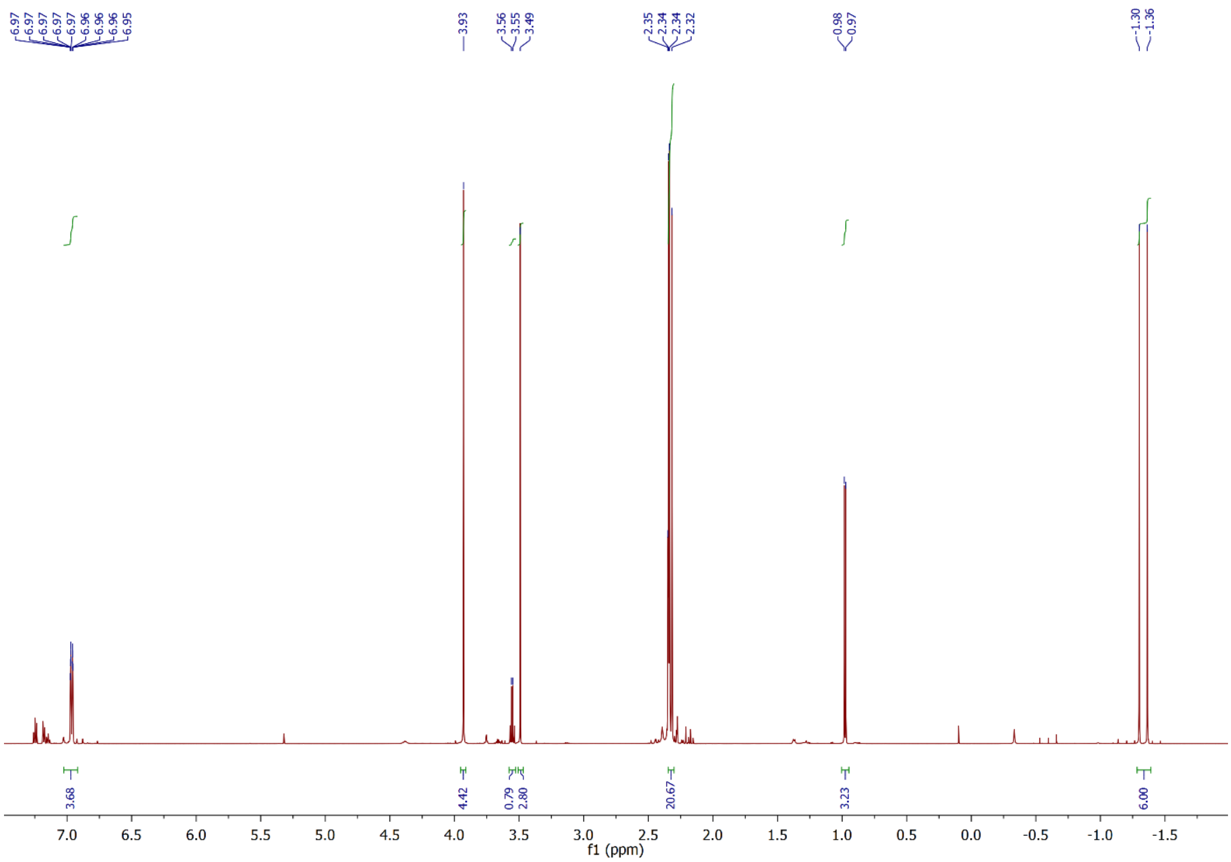


Figure S5. [1]H NMR (CD_2Cl_2, 400 MHz) spectrum of **3** at r.t.

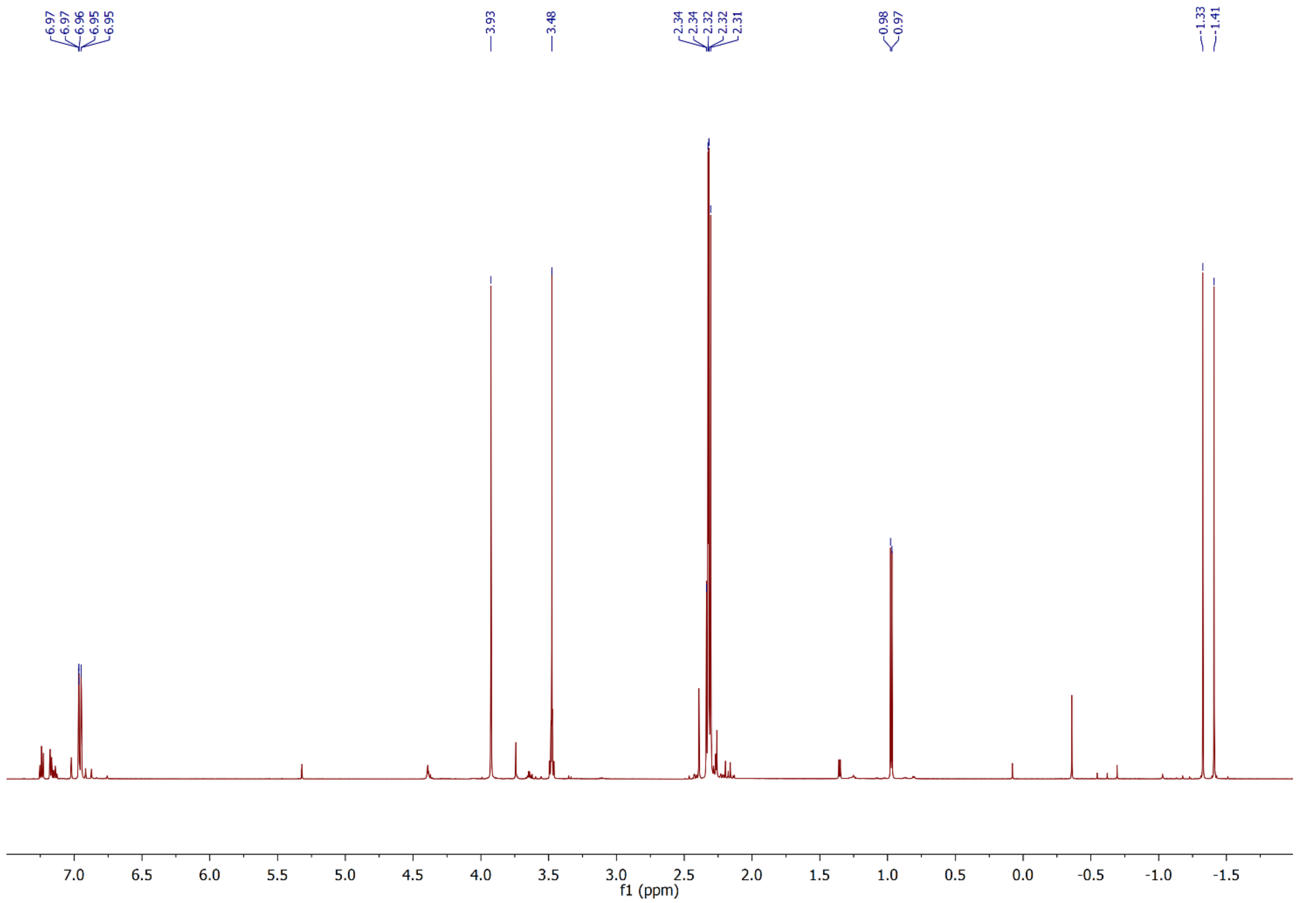


Figure S6. [1]H NMR (CD_2Cl_2, 400 MHz) spectrum of **3** at 0°C

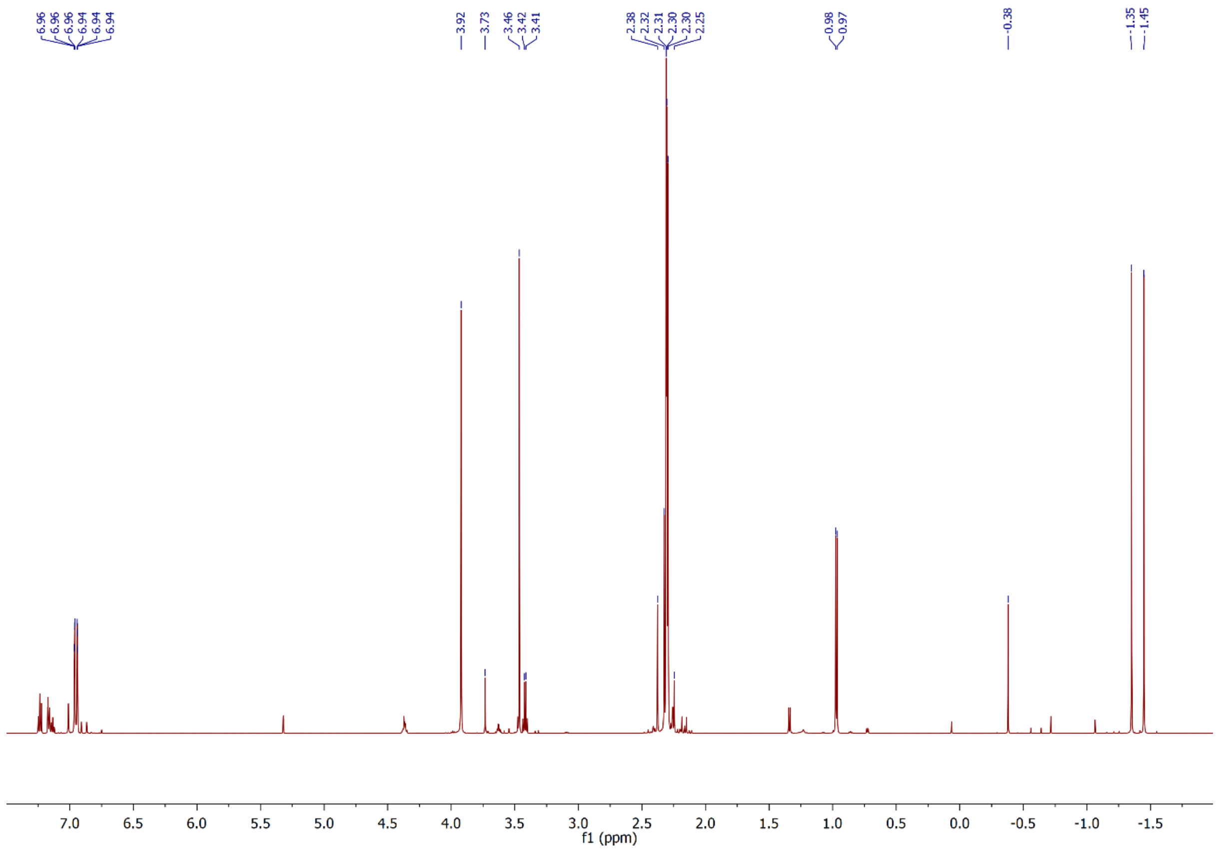


Figure S7. ^{1}H NMR (CD_2Cl_2, 400 MHz) spectrum of **3** at –20°C

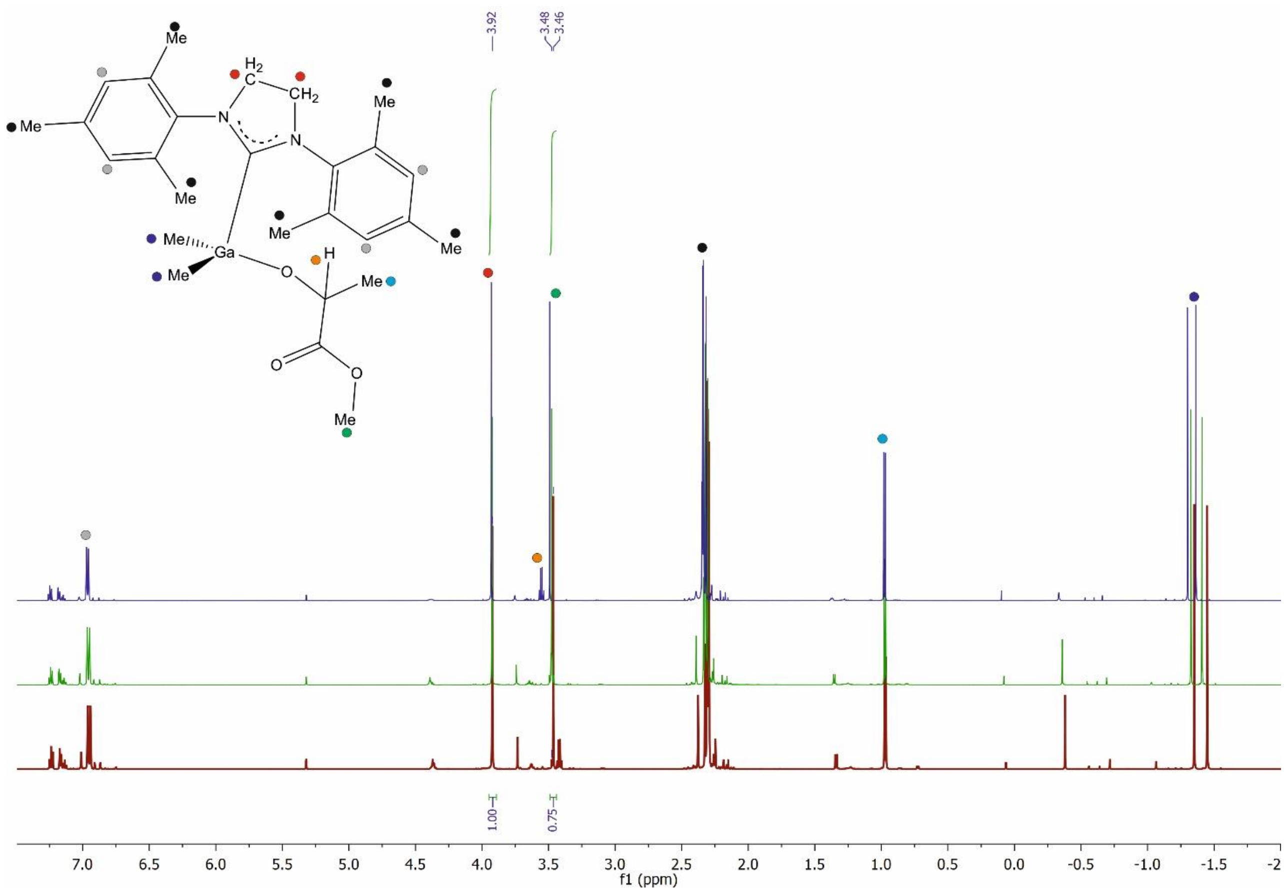


Figure S8. VT ^{1}H NMR (CD_2Cl_2, 400 MHz) spectra of **3** at r.t. (blue), 0°C (green) and –20°C (red)

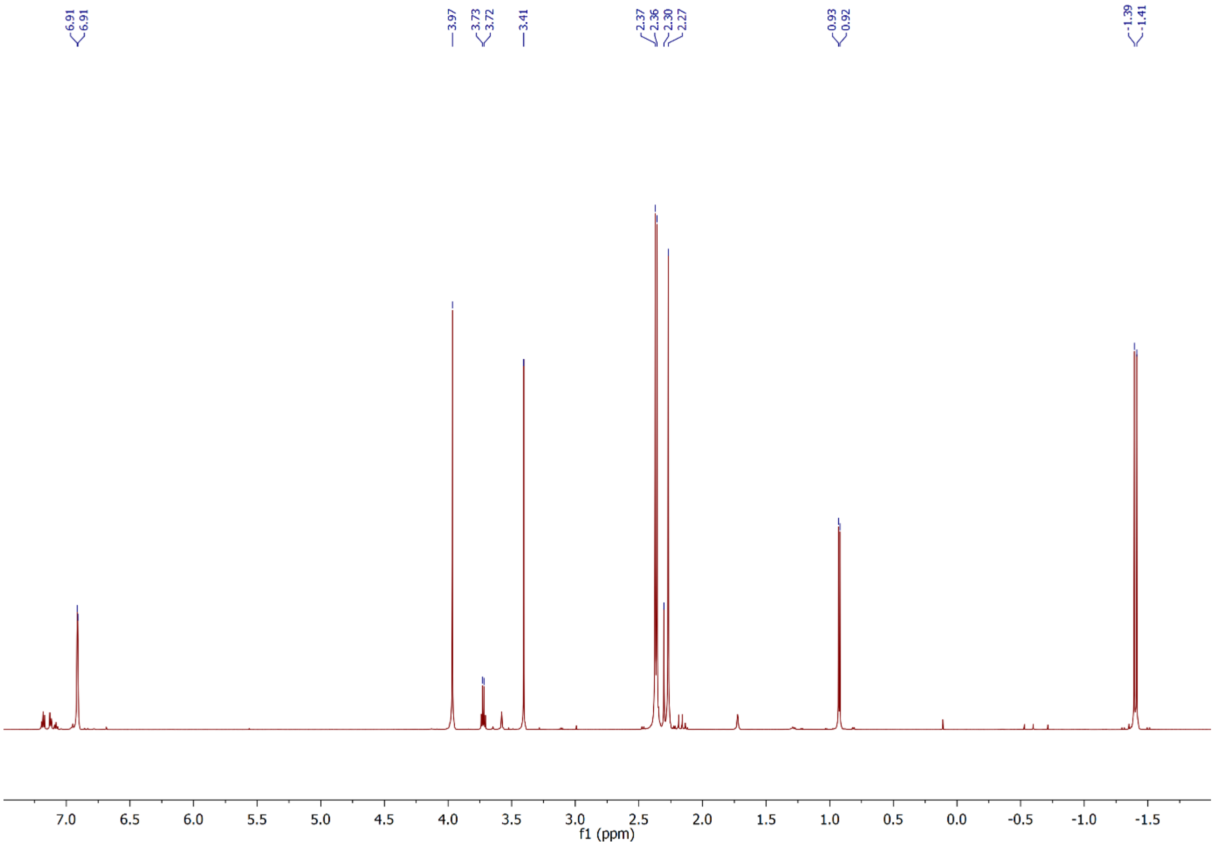


Figure S9. ¹H NMR (THF-*d*₈, 400 MHz) spectrum of **3** at r.t.

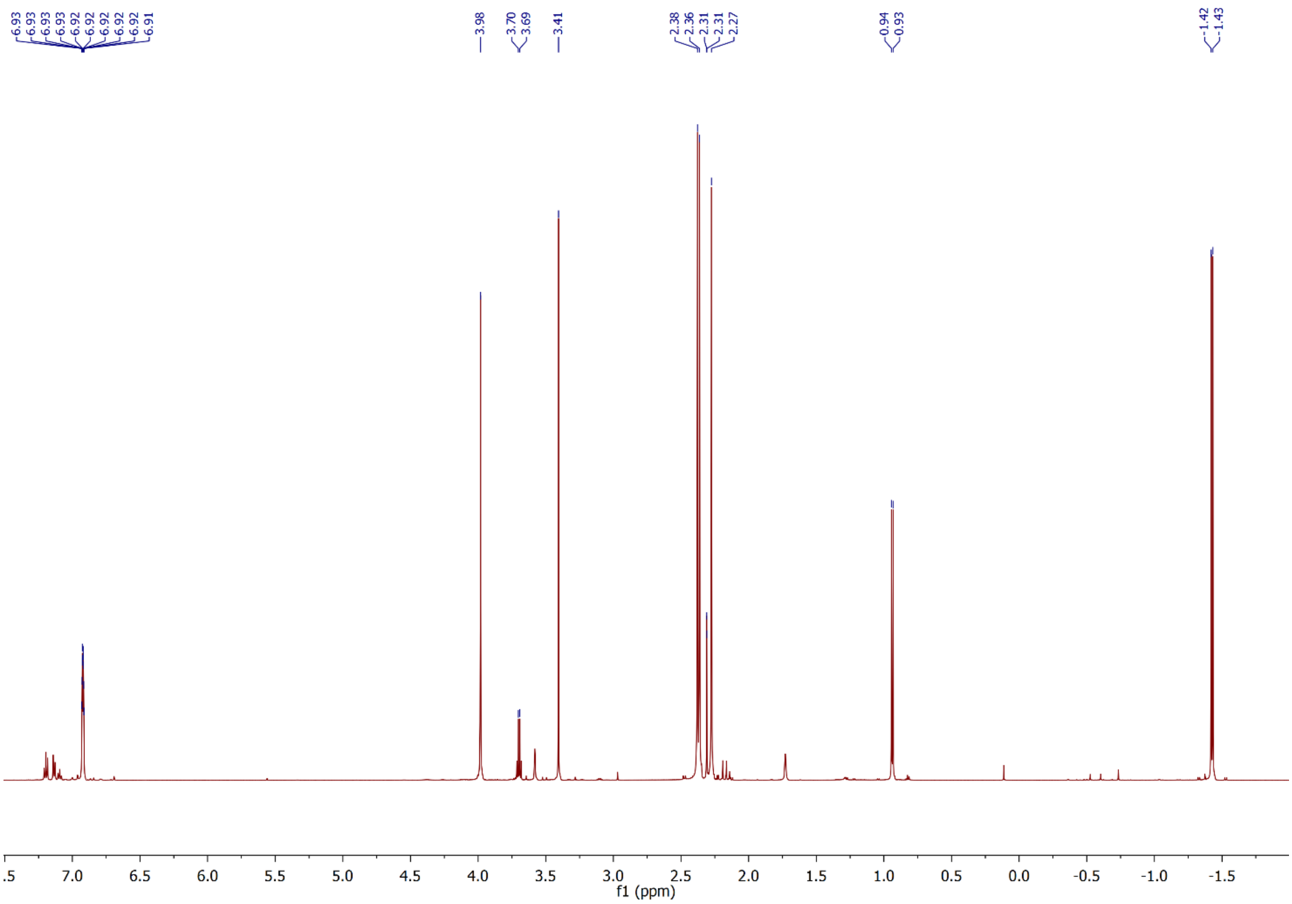


Figure S10. ¹H NMR (THF-*d*₈, 400 MHz) spectrum of **3** at 0°C

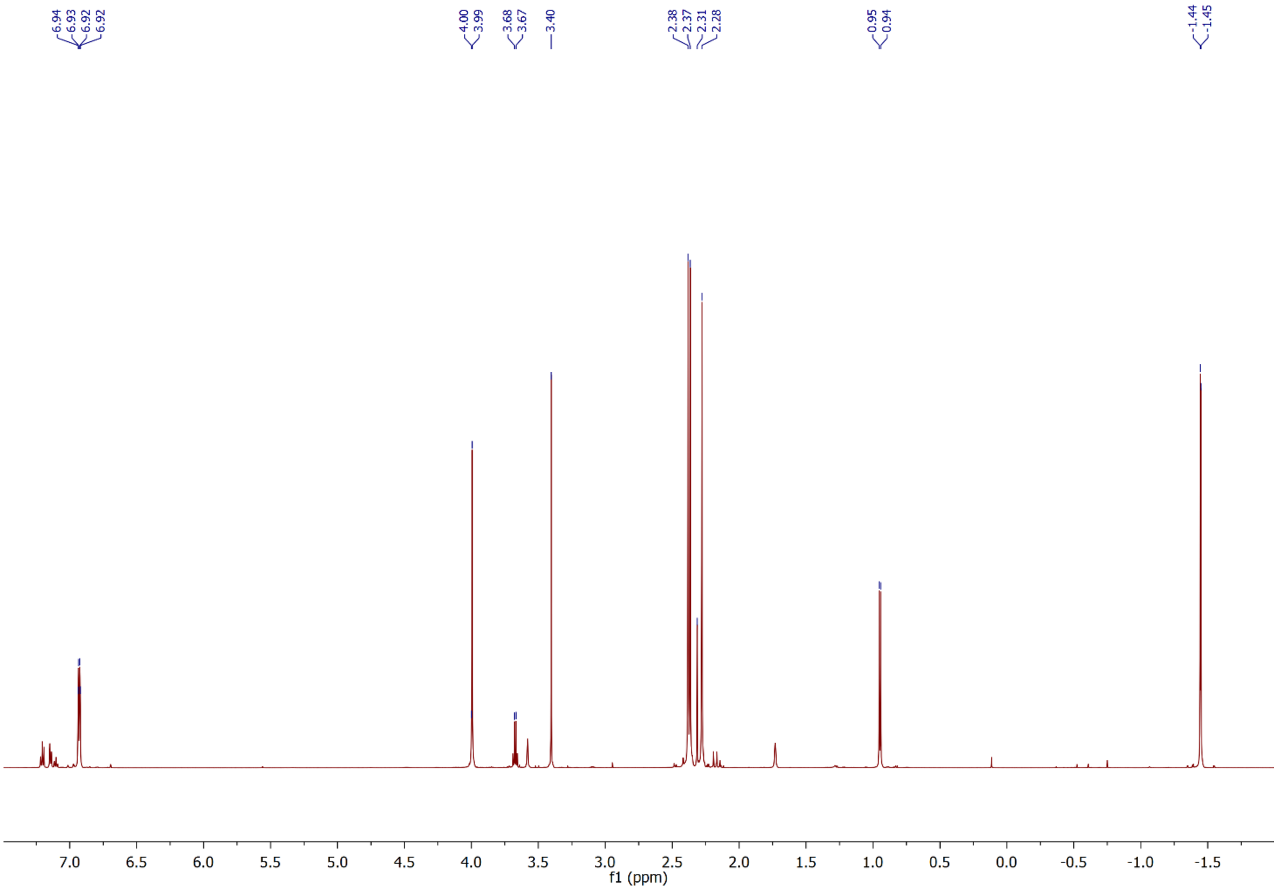


Figure S11. ^{1}H NMR (THF-d_8, 400 MHz) spectrum of **3** at –20°C

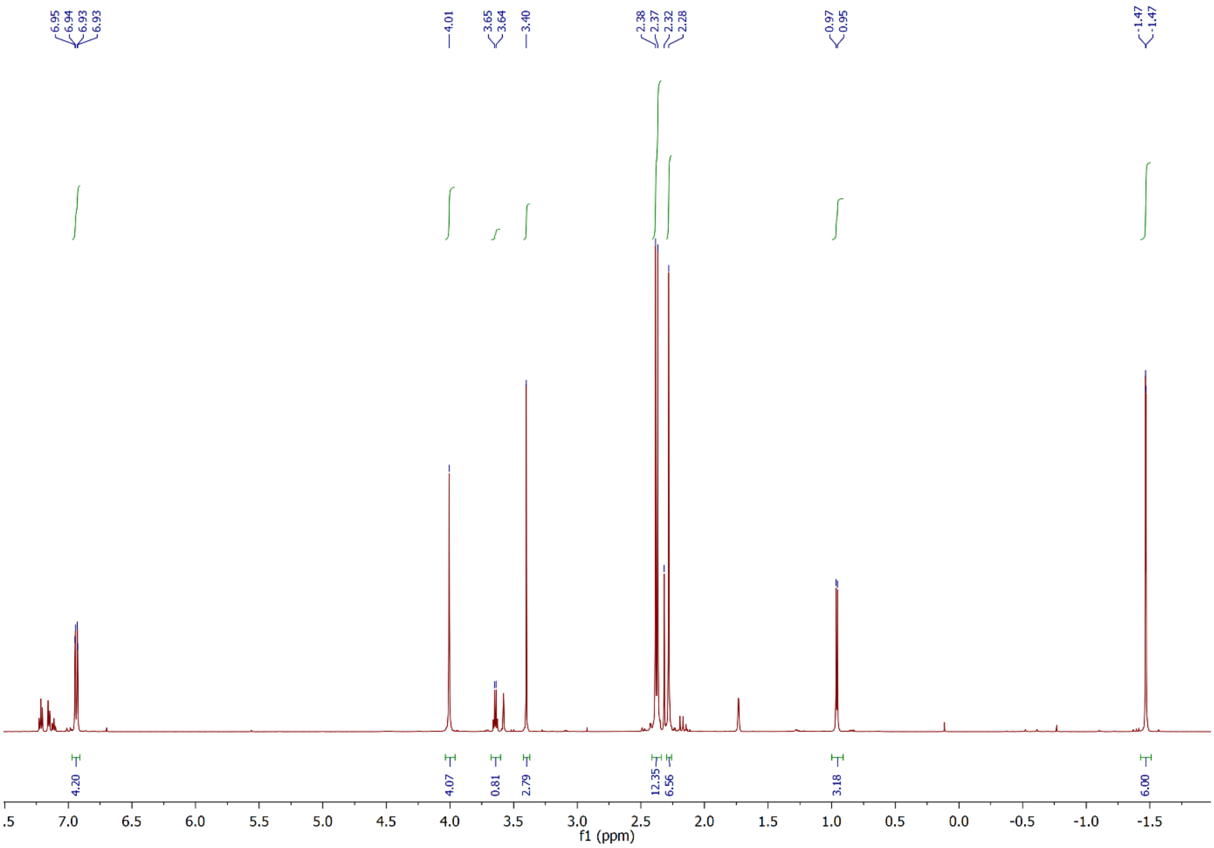


Figure S12. ^{1}H NMR (THF-d_8, 400 MHz) spectrum of **3** at –40°C

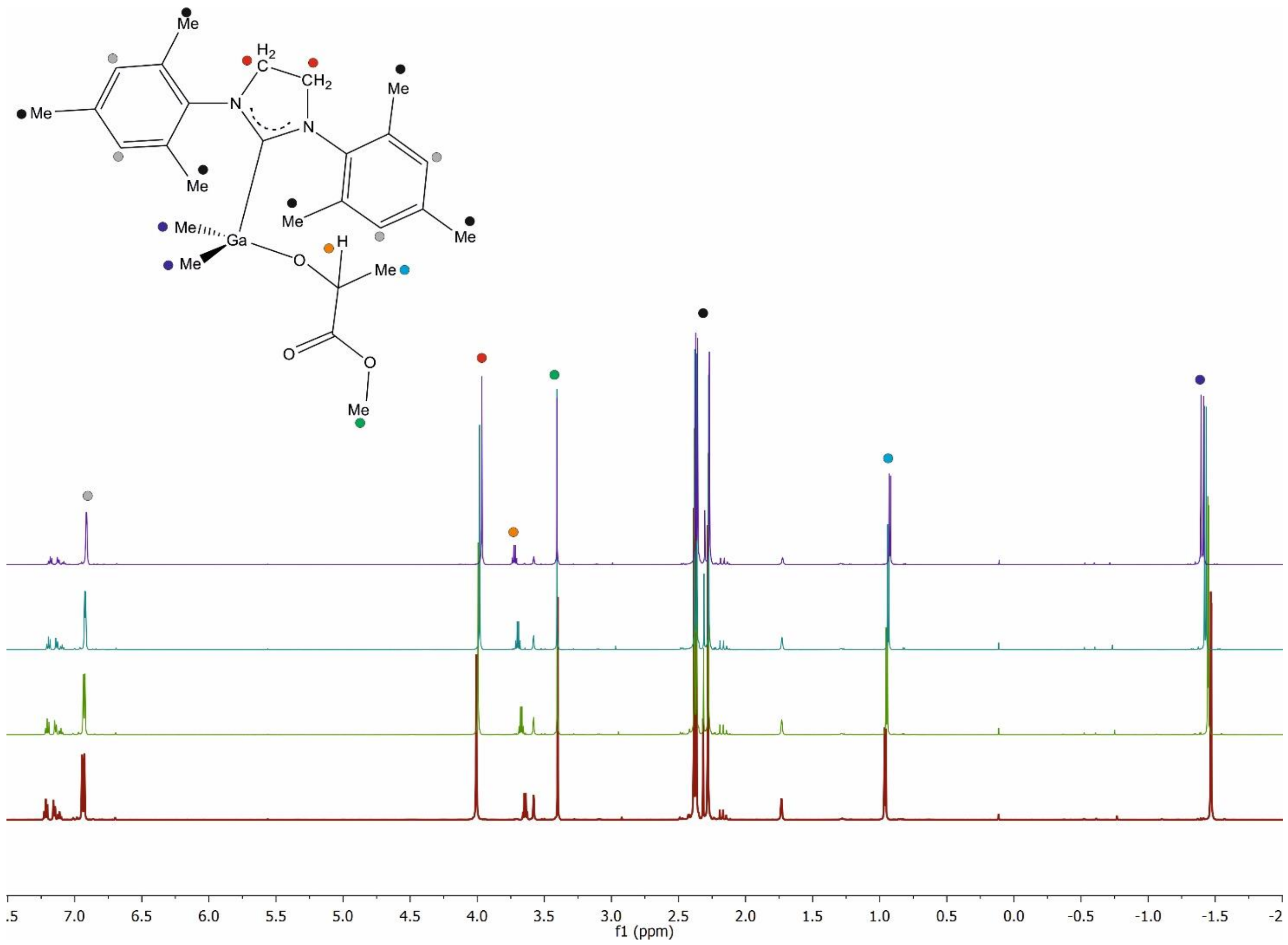


Figure S13. VT [1]H NMR (THF-d_8, 400 MHz) spectra of **3** at r.t. (purple), 0°C (blue), –20°C (green) and –40°C (red)

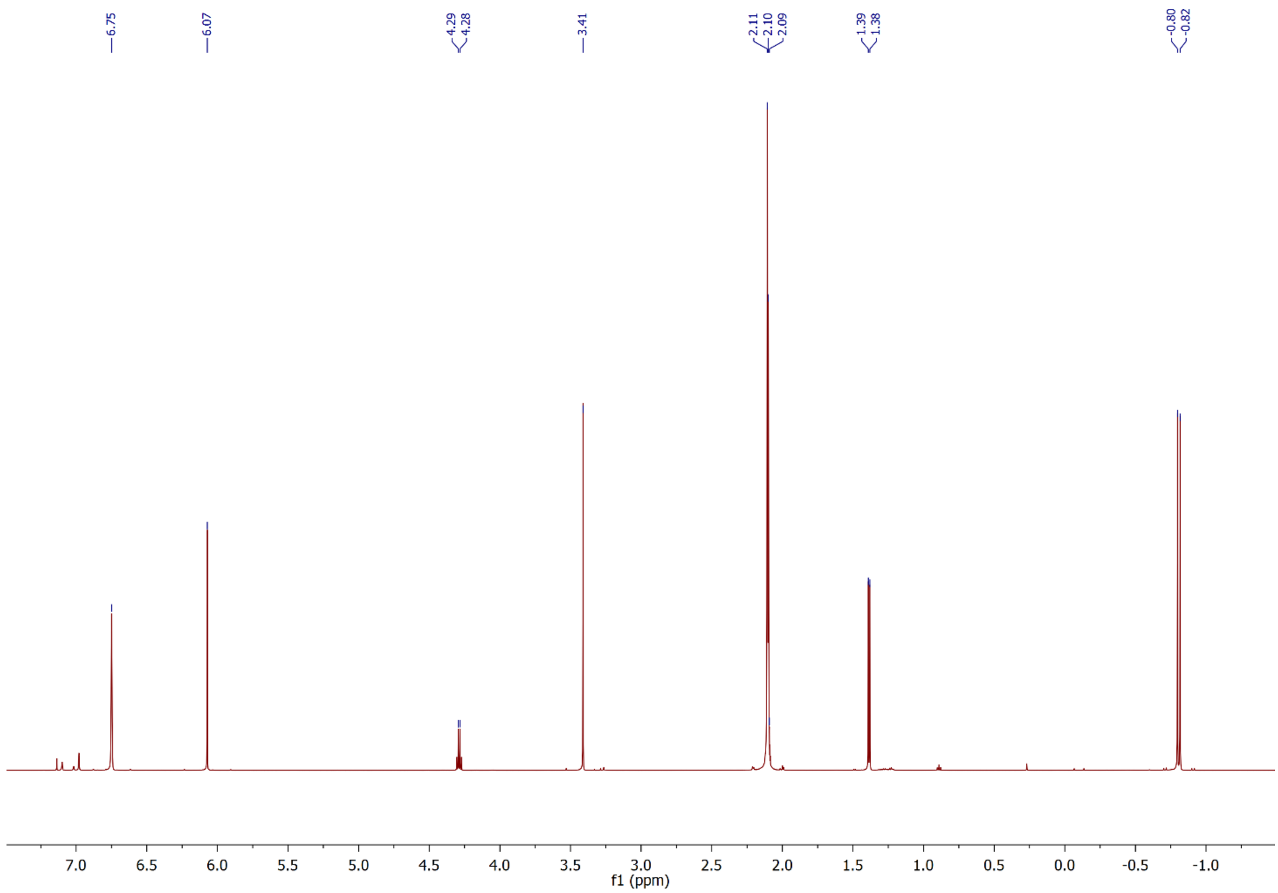


Figure S14. [1]H NMR (toluene-d_8, 400 MHz) spectrum of **4** at r.t.

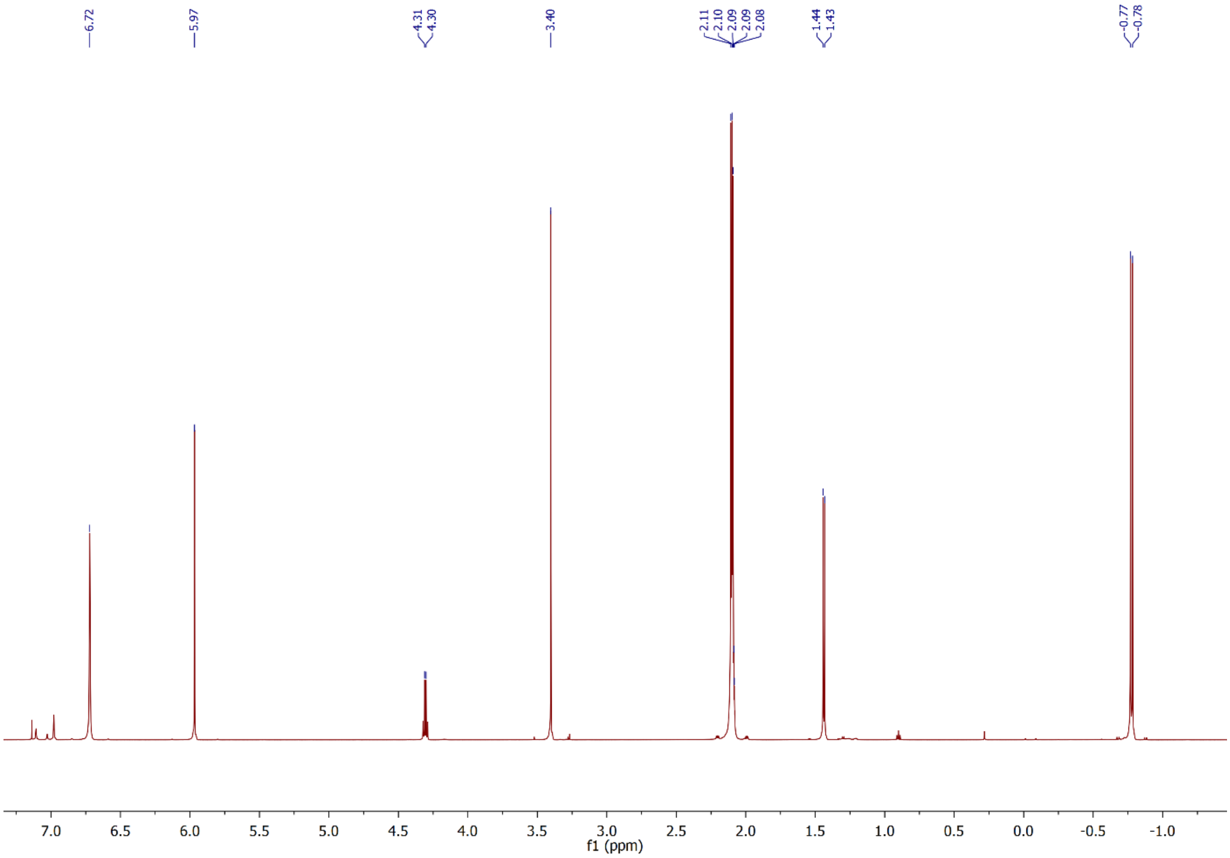


Figure S15. ^{1}H NMR (toluene-d_8, 400 MHz) spectrum of **4** at 0°C

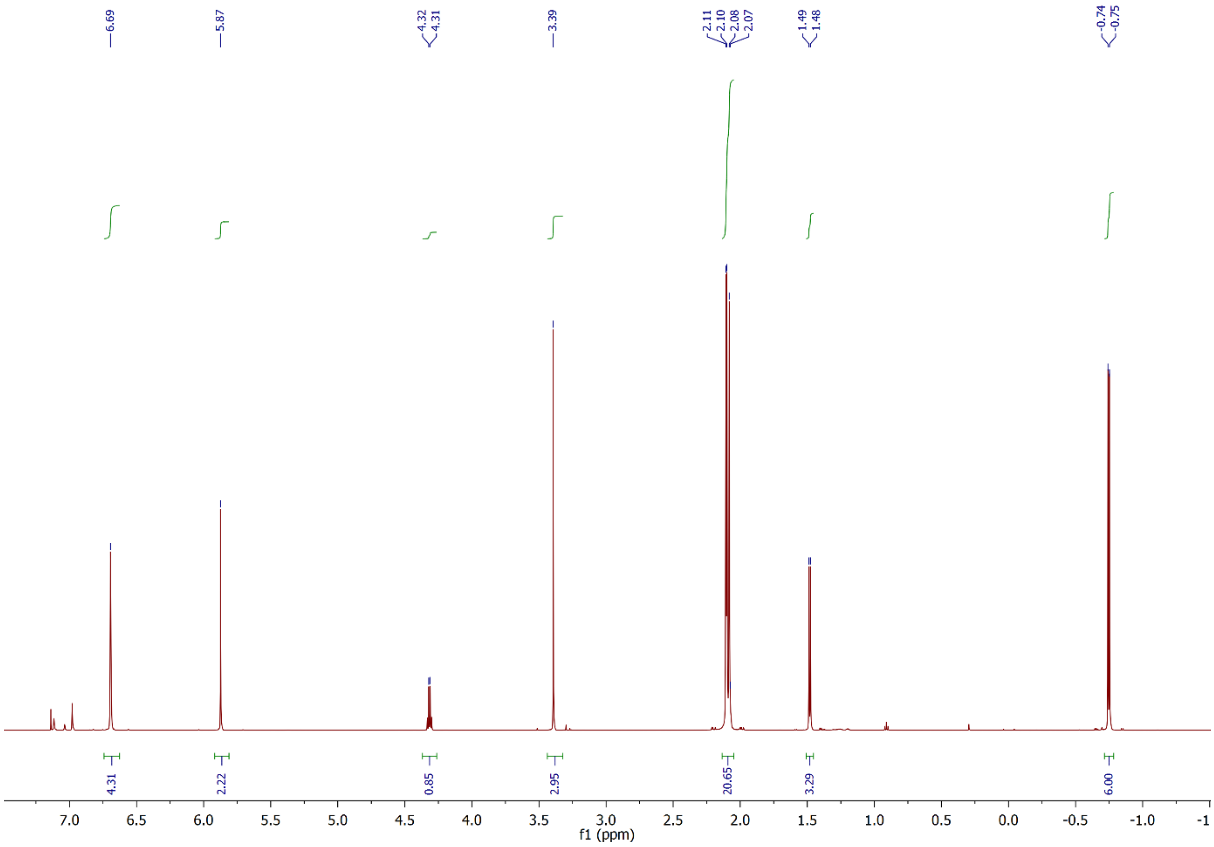


Figure S16. ^{1}H NMR (toluene-d_8, 400 MHz) spectrum of **4** at –20°C

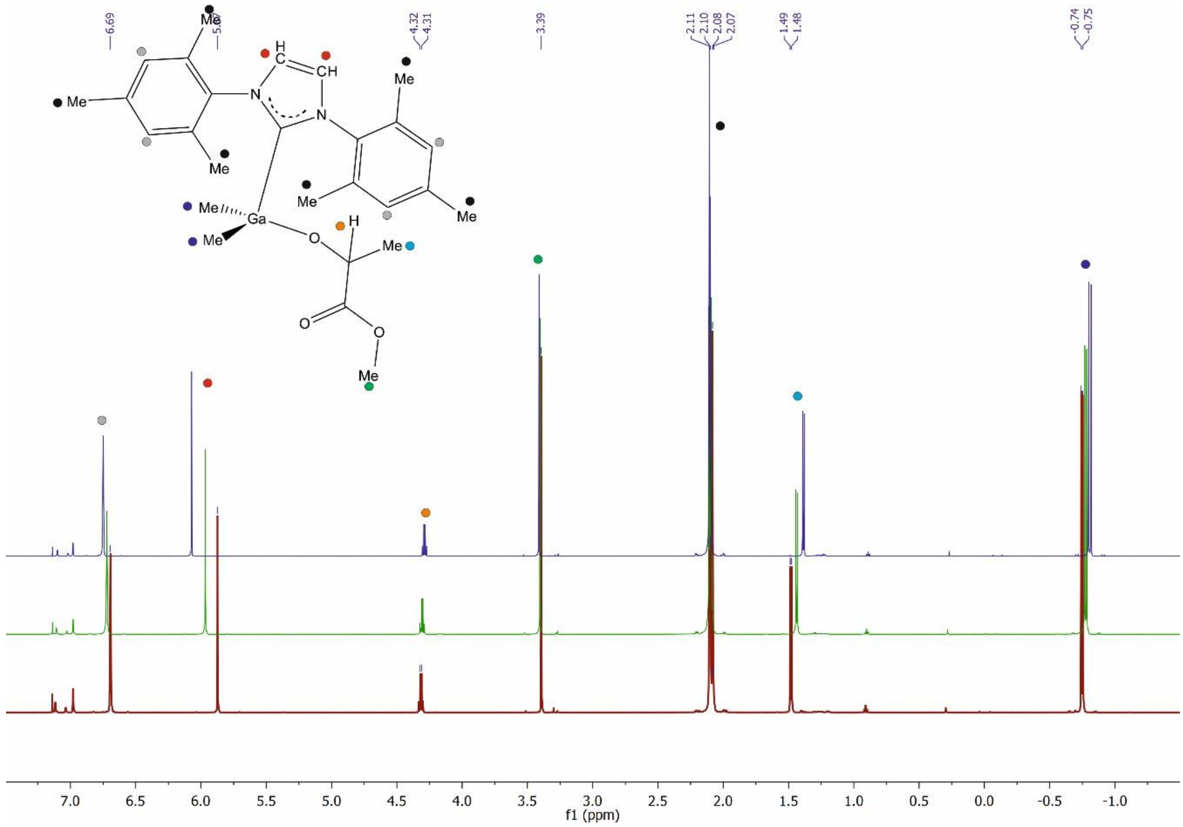


Figure S17. VT ^{1}H NMR (toluene-d_8, 400 MHz) spectra of **4** at r.t. (blue), 0°C (green) and –20°C (red)

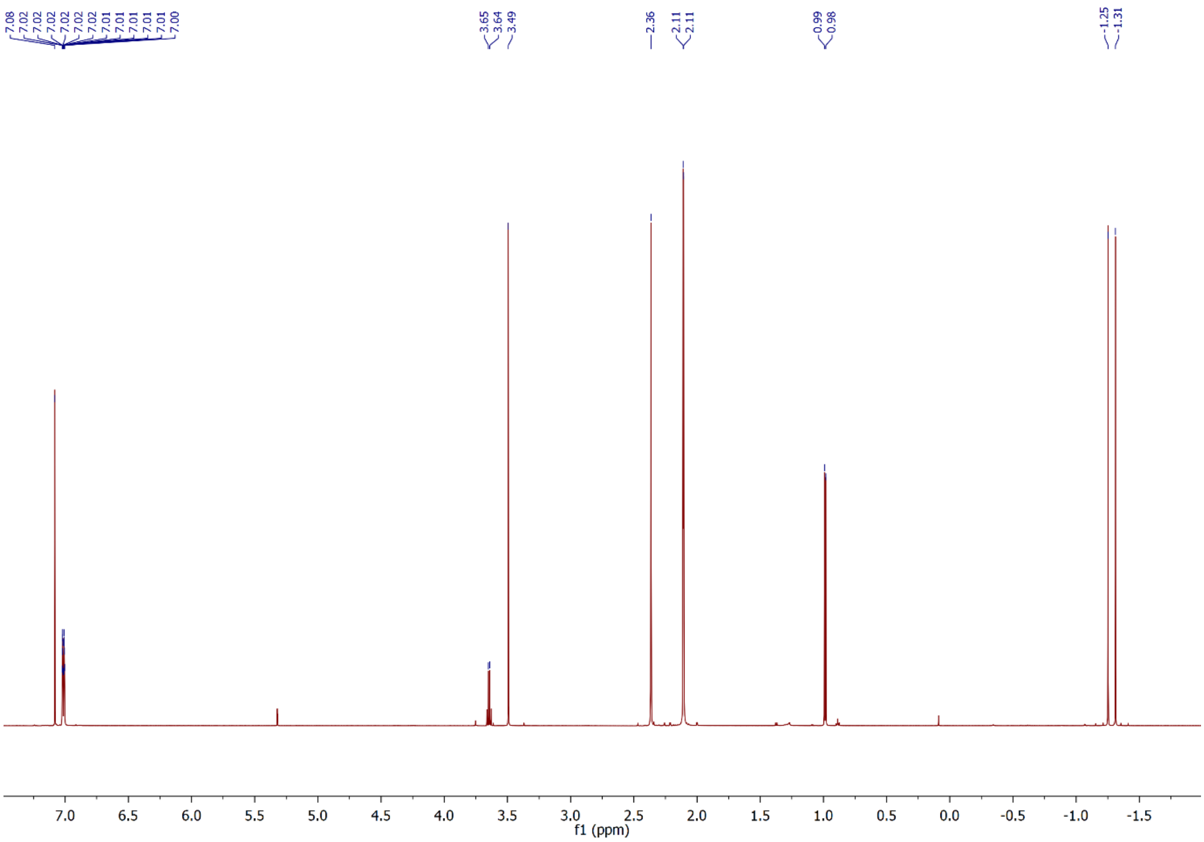


Figure S18. ^{1}H NMR (CD_2Cl_2, 400 MHz) spectrum of **4** at r.t.

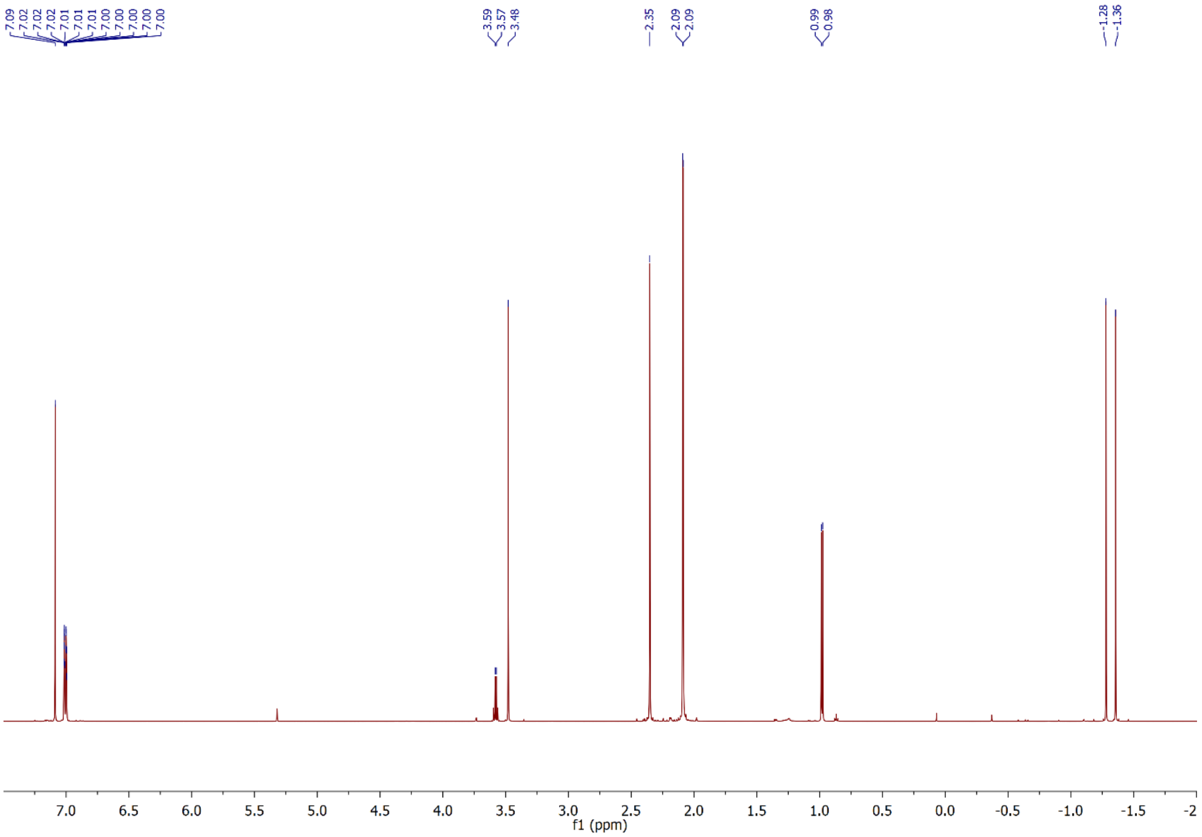


Figure S19. ^{1}H NMR (CD_2Cl_2, 400 MHz) spectrum of **4** at 0°C

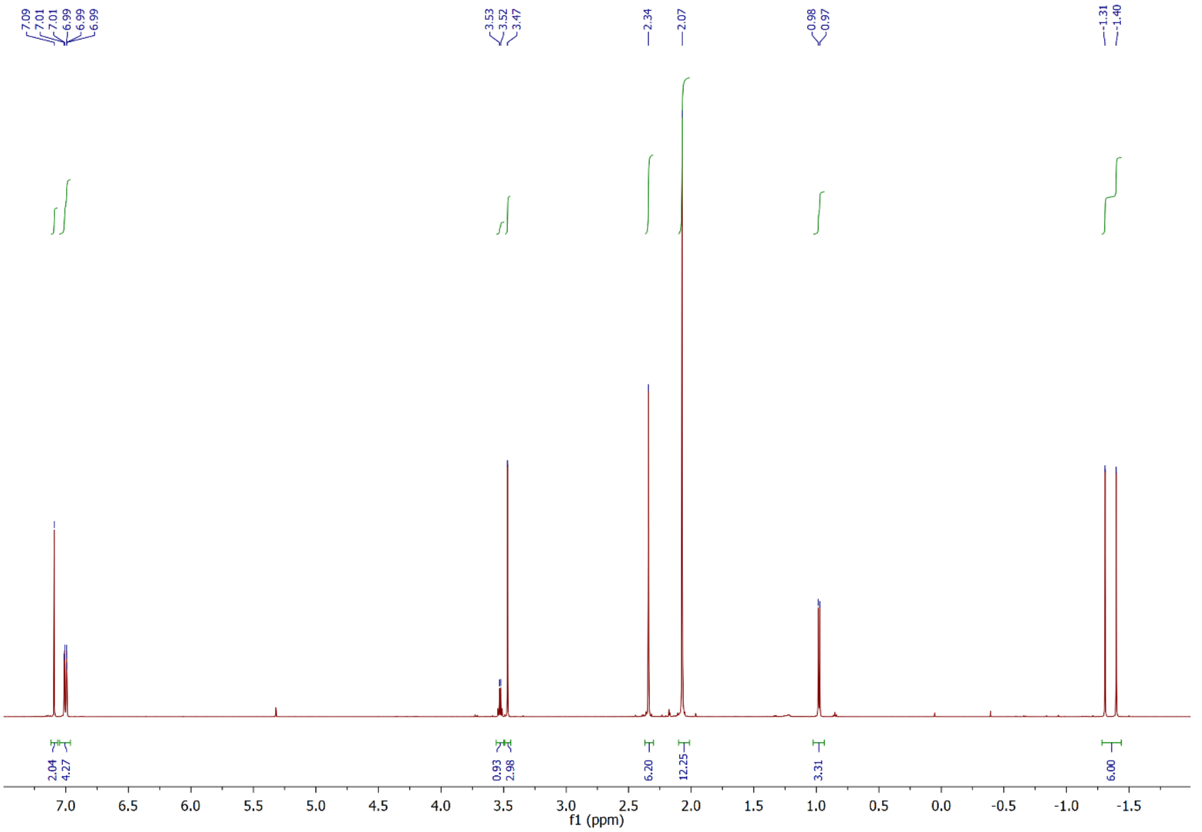


Figure S20. ^{1}H NMR (CD_2Cl_2, 400 MHz) spectrum of **4** at –20°C

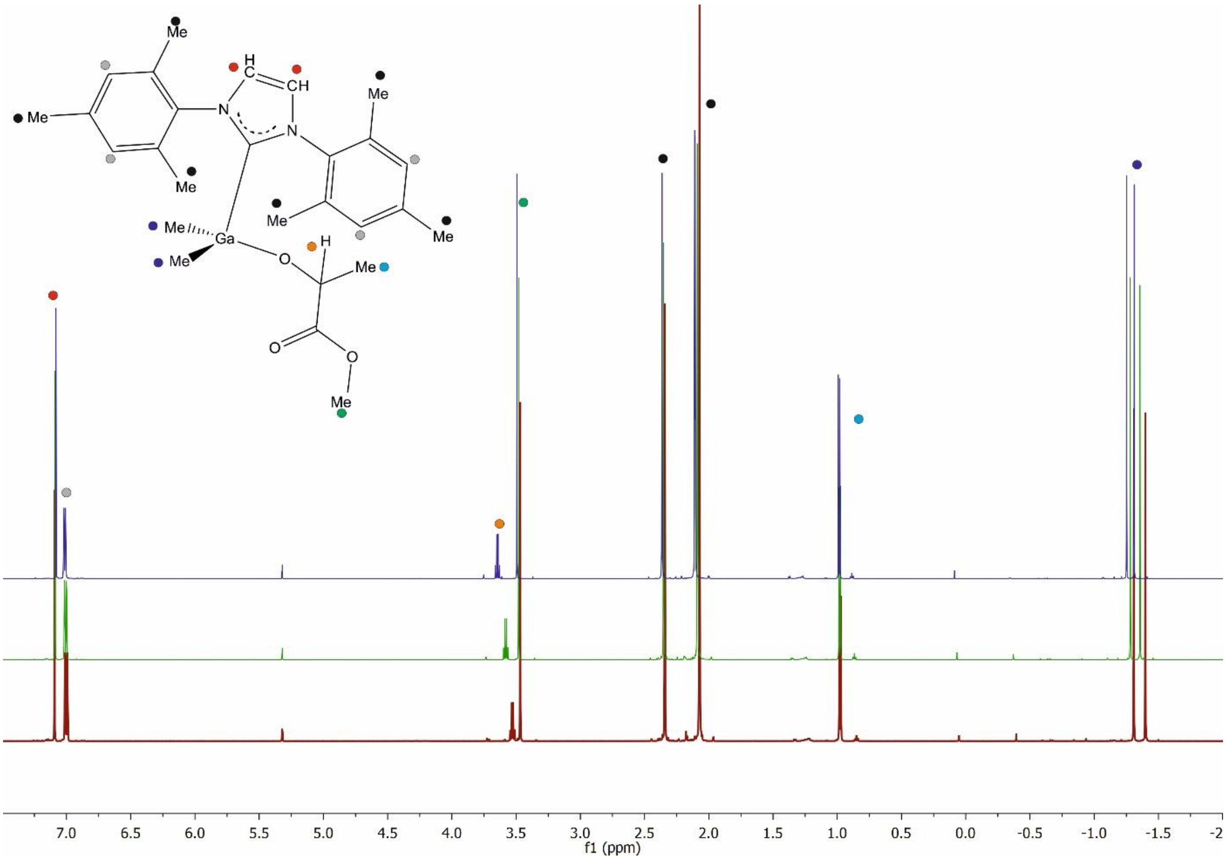


Figure S21. VT ^{1}H NMR (CD_2Cl_2, 400 MHz) spectra of **4** at r.t. (blue), 0°C (green) and –20°C (red)

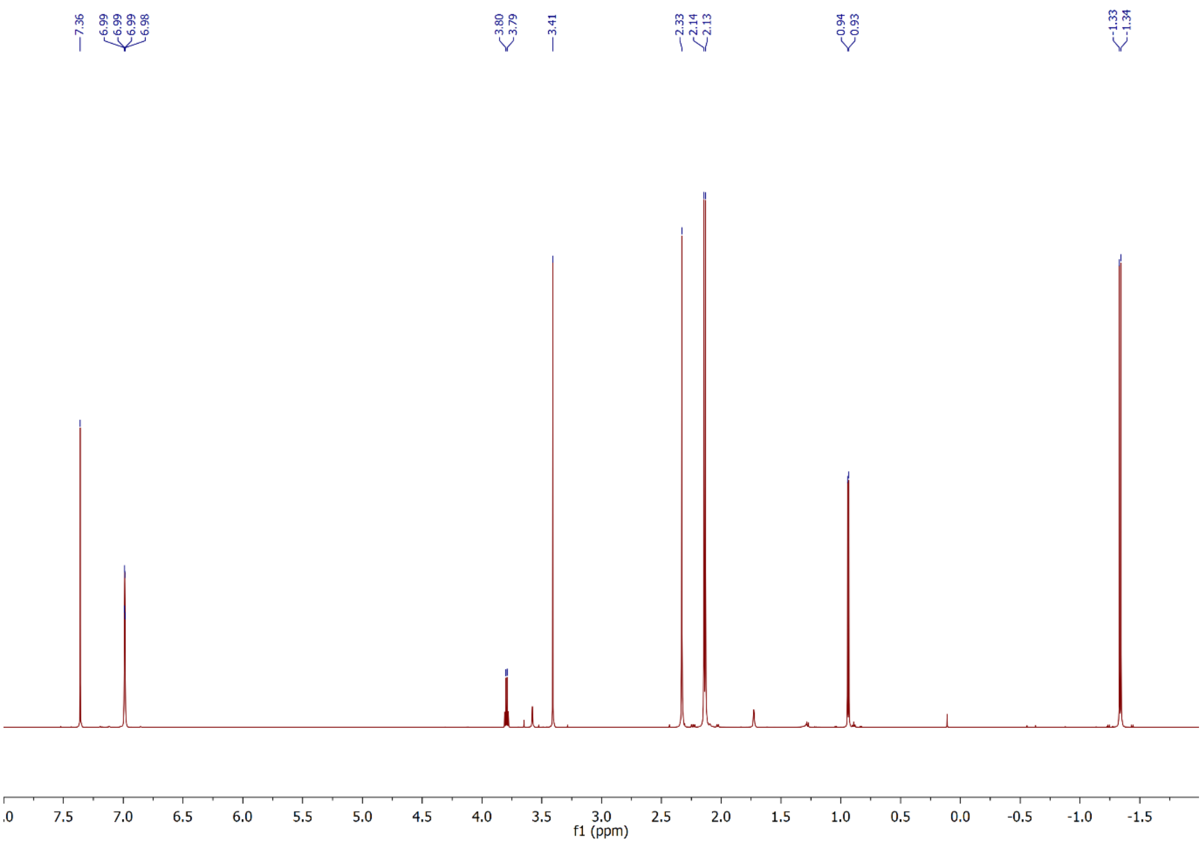


Figure S22. ^{1}H NMR (THF-d_8, 400 MHz) spectrum of **4** at r.t.

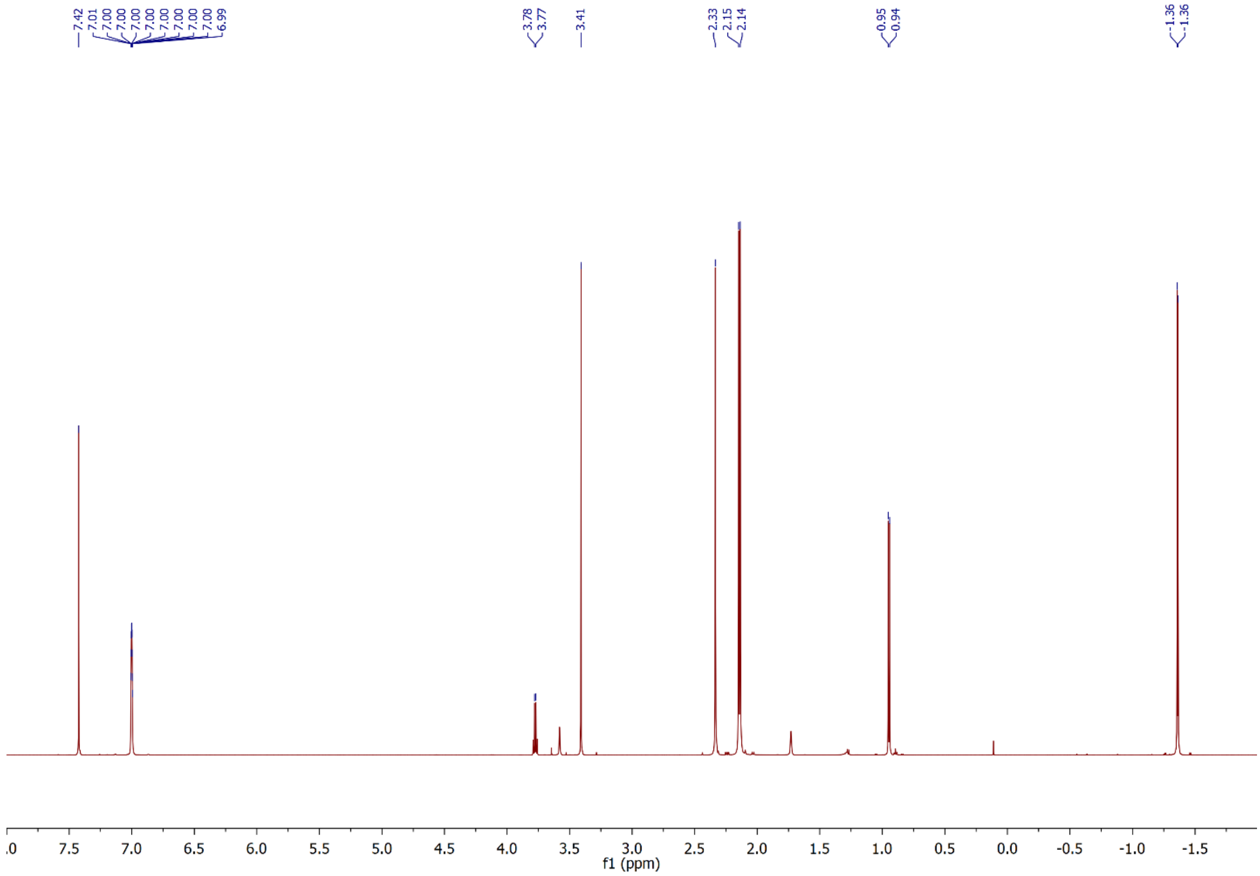


Figure S23. ^{1}H NMR (THF-d_8, 400 MHz) spectrum of **4** at 0°C

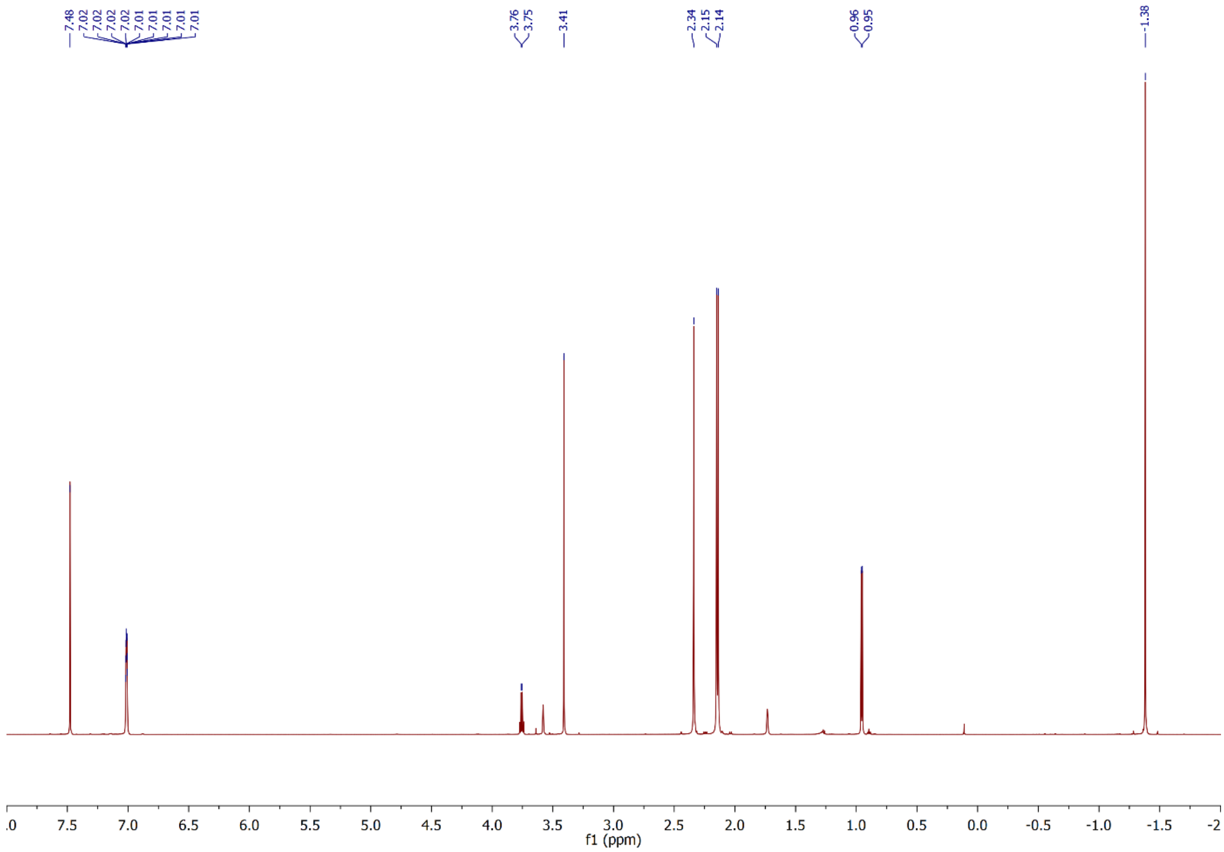


Figure S24. ^{1}H NMR (THF-d_8, 400 MHz) spectrum of **4** at –20°C

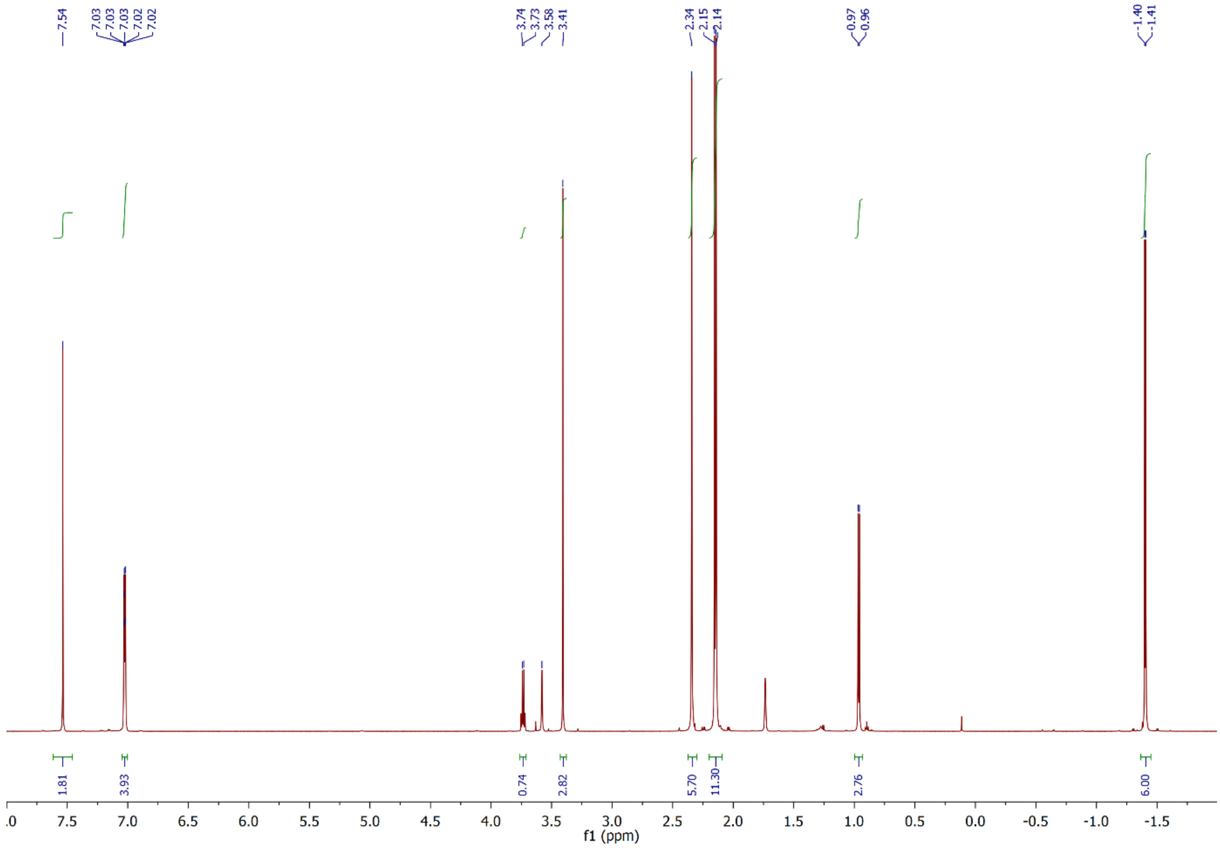


Figure S25. ^{1}H NMR (THF-d_8, 400 MHz) spectrum of **4** at –40°C

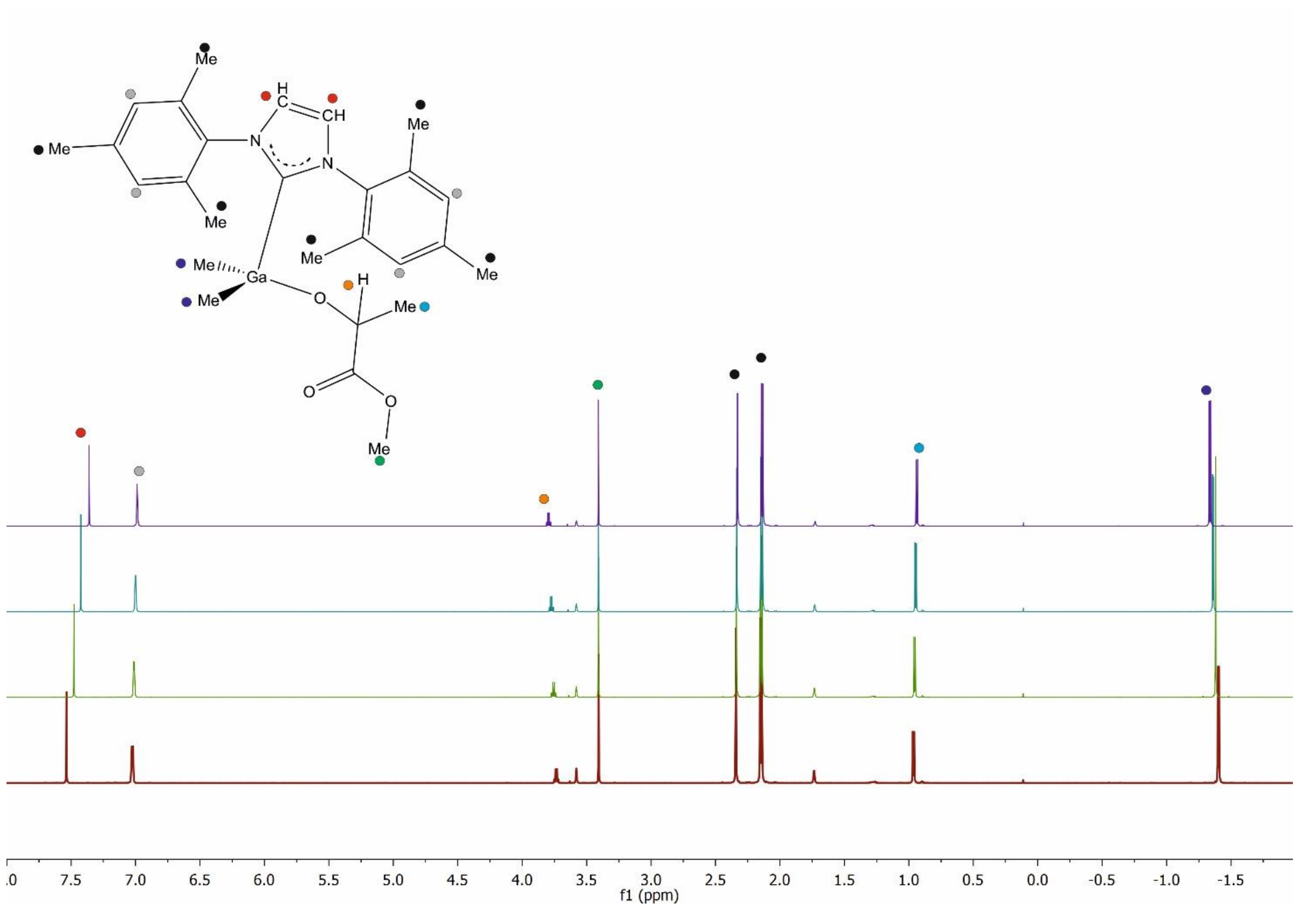


Figure S26. VT ^{1}H NMR (THF-d_8, 400 MHz) spectra of **4** at r.t. (purple), 0°C (blue), –20°C (green) and –40°C (red)

2) FTIR

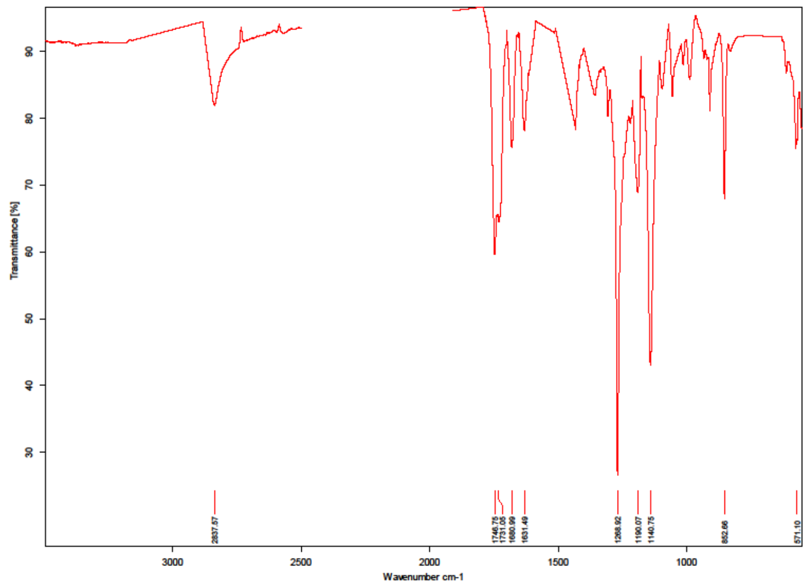


Figure S27. FTIR spectrum of 3% solution of complex **3** in toluene.

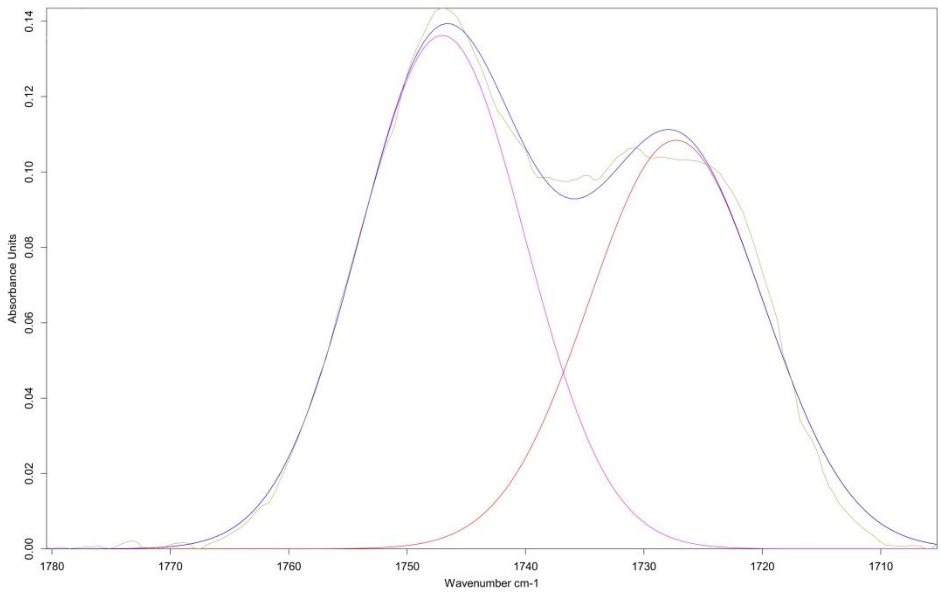


Figure S28. FTIR spectrum of 3% solution of complex **3** in toluene. Spectrum of C=O band deconvoluted for two bands **FWHM** – Full Width Half Maximum.

Peak Position	Absorbance	FWHM	Area	Peak Type
1726.340597	0.063908	18.316655	1.246039	0%Lorentz+Gauss
1748.195446	0.093912	16.482831	1.695958	6%Lorentz+Gauss

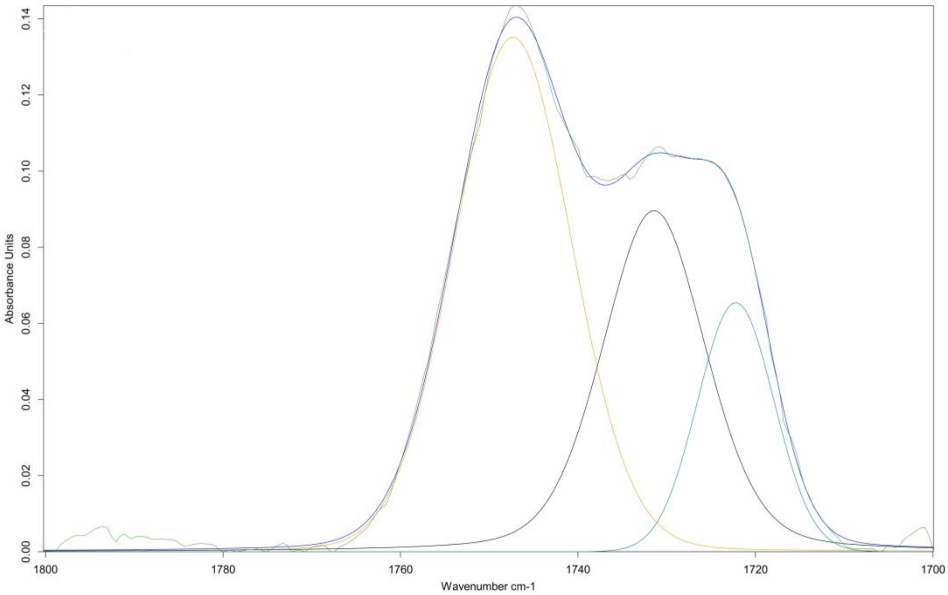


Figure S29. FTIR spectrum of 3% solution of complex **3** in toluene. Spectrum of C=O band deconvoluted for three bands.

Peak Position	**Absorbance**	**FWHM**	**Area**	**Peak Type**
1722.081993	0.062386	9.754557	0.695758	16%Lorentz+Gauss
1733.180318	0.049468	11.306937	0.595393	0%Lorentz+Gauss
1748.549451	0.096721	15.075776	1.655648	14%Lorentz+Gauss

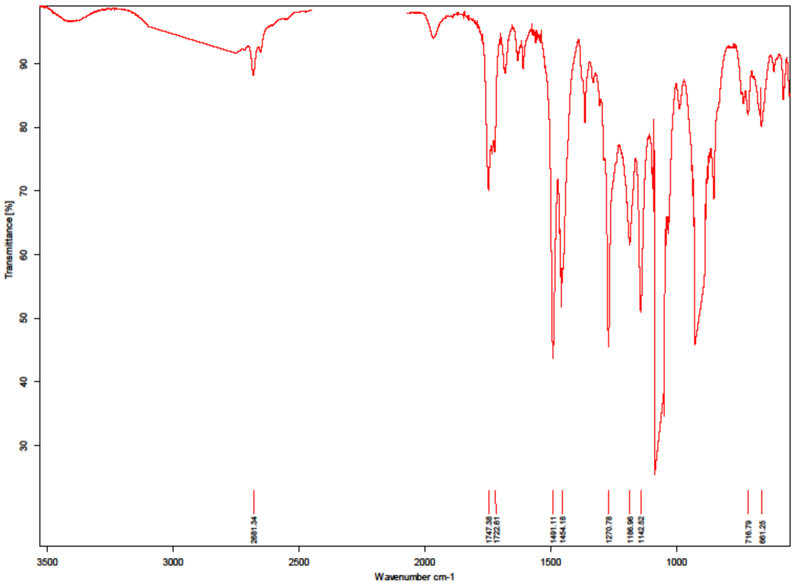


Figure S30. FTIR spectrum of 3% solution of complex **3** in THF.

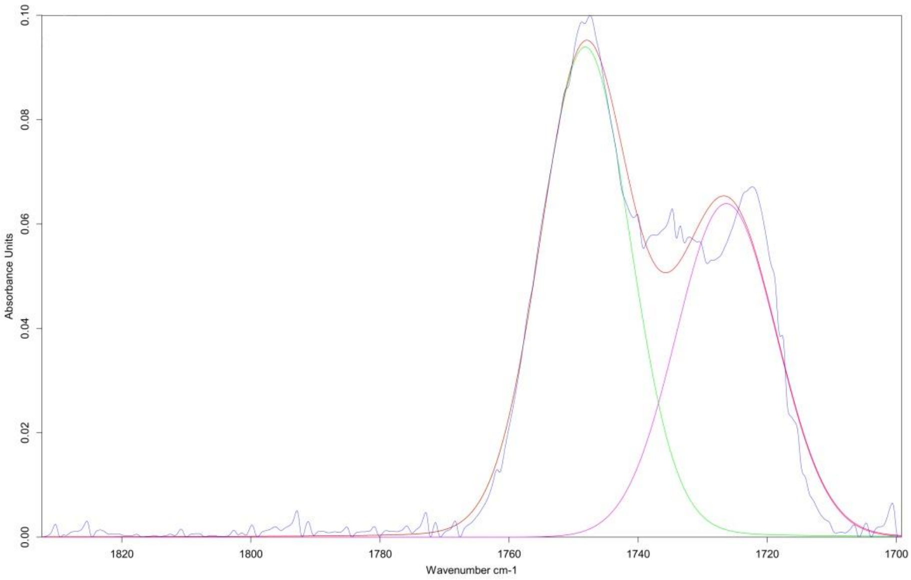


Figure S31. FTIR spectrum of 3% solution of complex **3** in THF. Spectrum of C=O band deconvoluted for two bands.

Peak Position	Absorbance	FWHM	Area	Peak Type
1726.340597	0.063908	18.316655	1.246039	0%Lorentz+Gauss
1748.195446	0.093912	16.482831	1.695958	6%Lorentz+Gauss

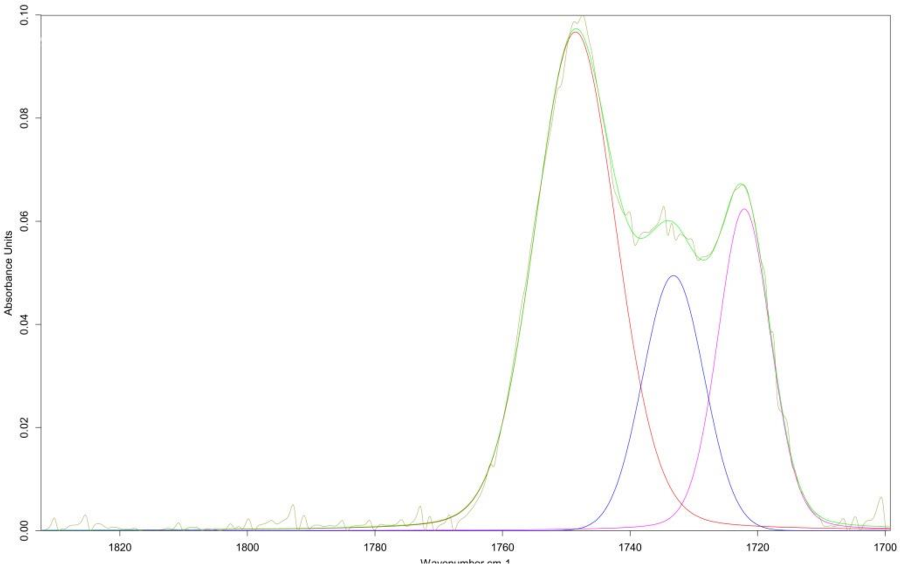


Figure S32. FTIR spectrum of 3% solution of complex **3** in THF. Spectrum of C=O band deconvoluted for three bands.

Peak Position	Absorbance	FWHM	Area	Peak Type
1722.081993	0.062386	9.754557	0.695758	16%Lorentz+Gauss
1733.180318	0.049468	11.306937	0.595393	0%Lorentz+Gauss

1748.549451	0.096721	15.075776	1.655648	14%Lorentz+Gauss

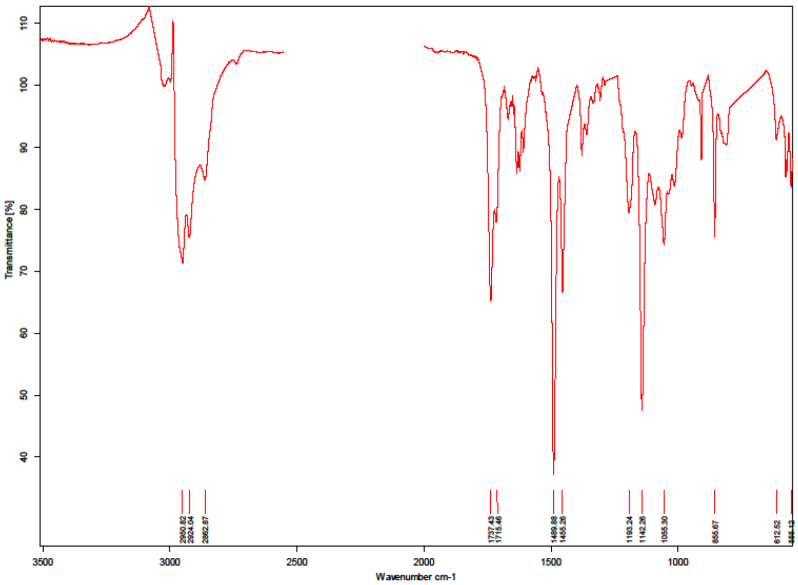


Figure S33. FTIR spectrum of 3% solution of complex **3** in CH_2Cl_2.

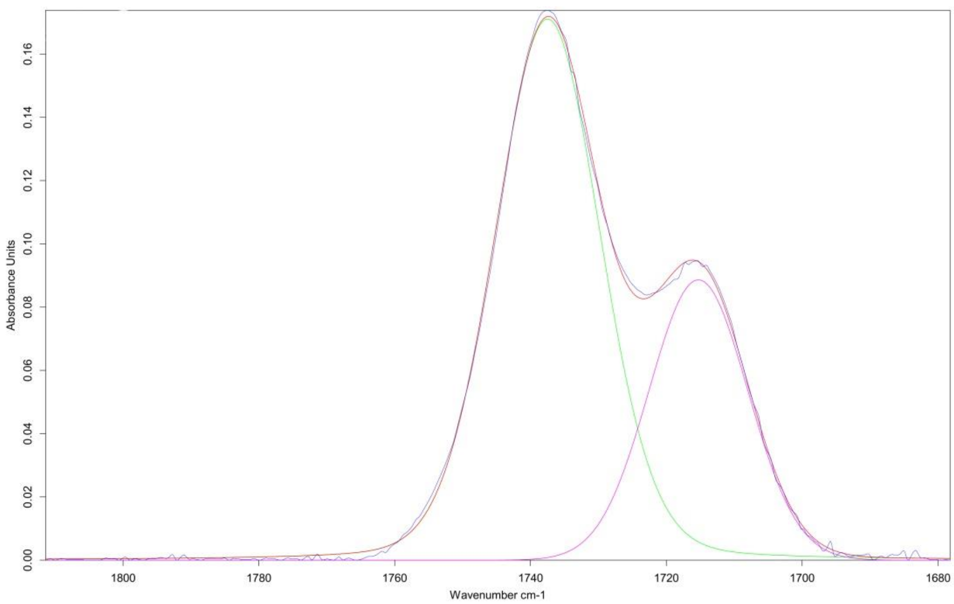


Figure S34. FTIR spectrum of 3% solution of complex **3** in CH_2Cl_2. Spectrum of C=O band deconvoluted for two bands.

Peak Position	Absorbance	FWHM	Area	Peak Type
1715.274664	0.088592	17.110649	1.613592	0%Lorentz+Gauss
1737.474323	0.171038	18.237052	3.533763	14%Lorentz+Gauss

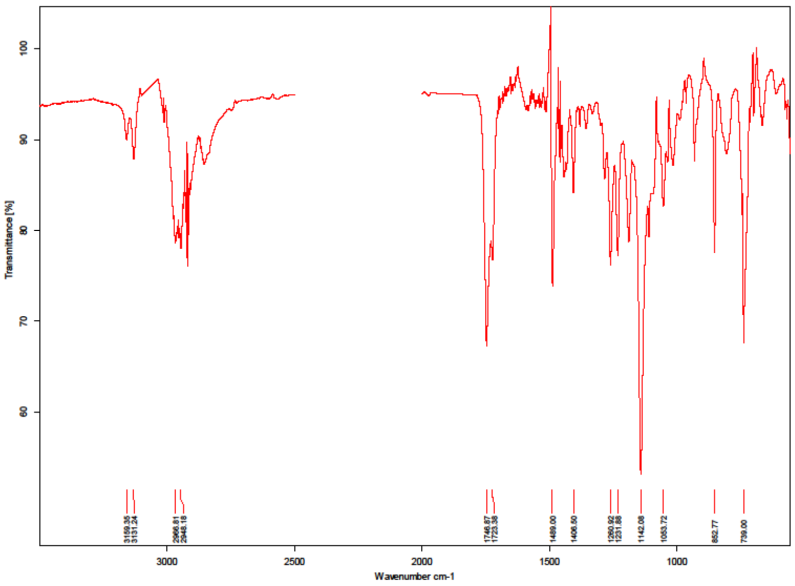


Figure S35. FTIR spectrum of 3% solution of complex **4** in toluene.

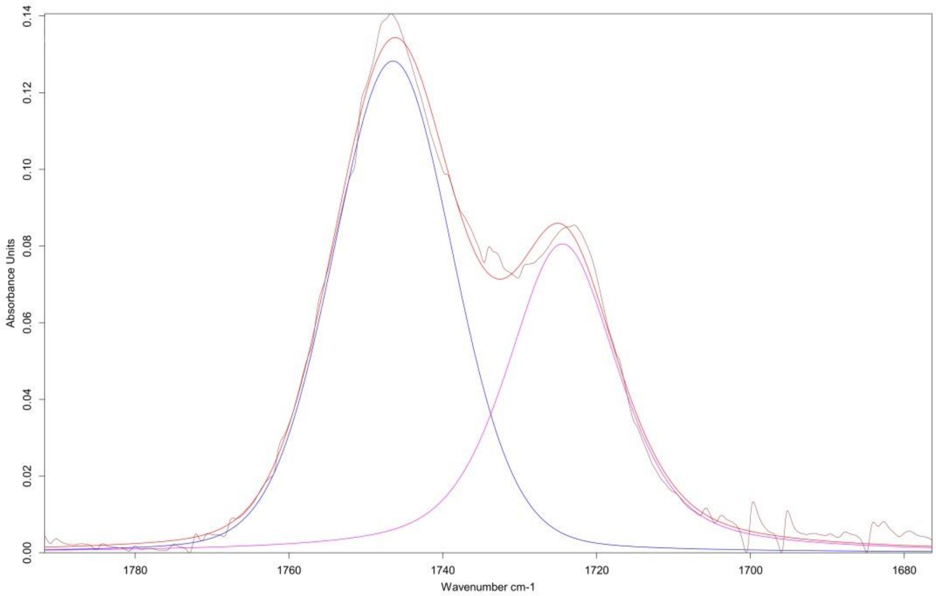


Figure S36. FTIR spectrum of 3% solution of complex **4** in toluene. Spectrum of C=O band deconvoluted for two bands.

Peak Position	**Absorbance**	**FWHM**	**Area**	**Peak Type**
1724.434753	0.080569	17.109827	1.842607	54%Lorentz+Gauss
1746.465898	0.128244	18.492731	2.708876	15%Lorentz+Gauss

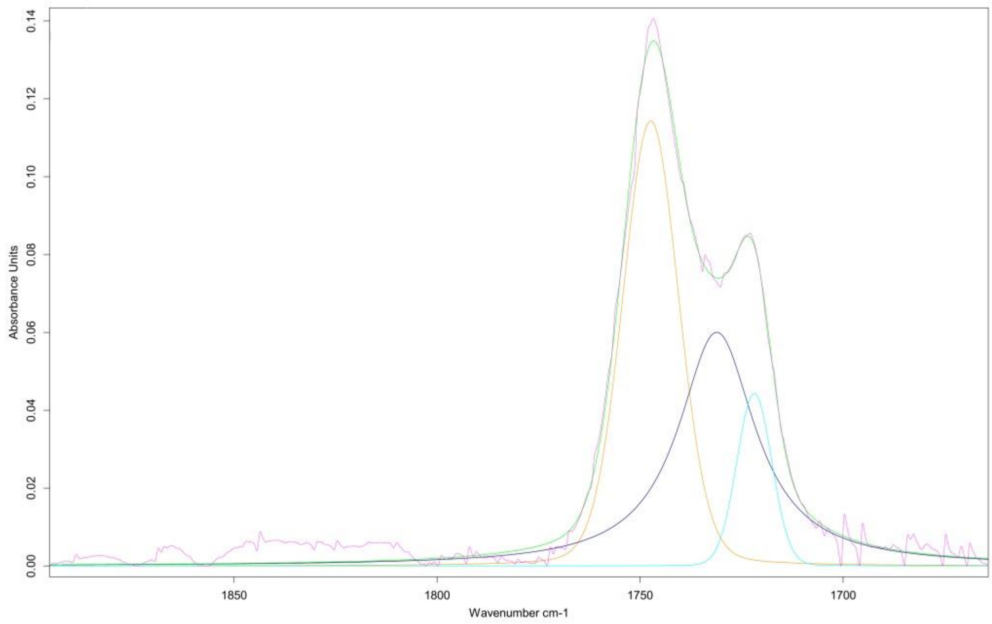


Figure S37. FTIR spectrum of 3% solution of complex **4** in toluene. Spectrum of C=O band deconvoluted for three bands.

Peak Position	Absorbance	FWHM	Area	Peak Type
1721.863847	0.044304	10.141491	0.487971	4%Lorentz+Gauss
1731.105339	0.060030	22.959413	2.164961	100%Lorentz+Gauss
1747.369518	0.114319	16.265737	2.105625	13%Lorentz+Gauss

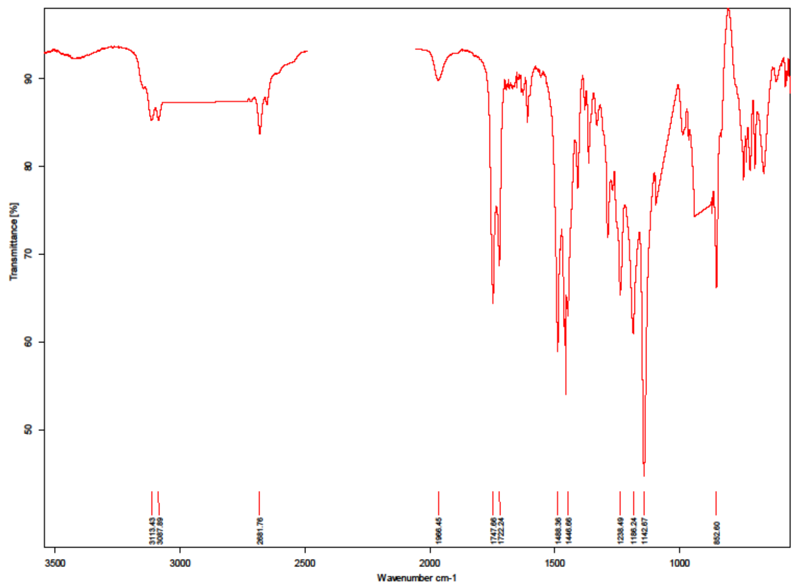


Figure S38. FTIR spectrum of 3% solution of complex **4** in THF.

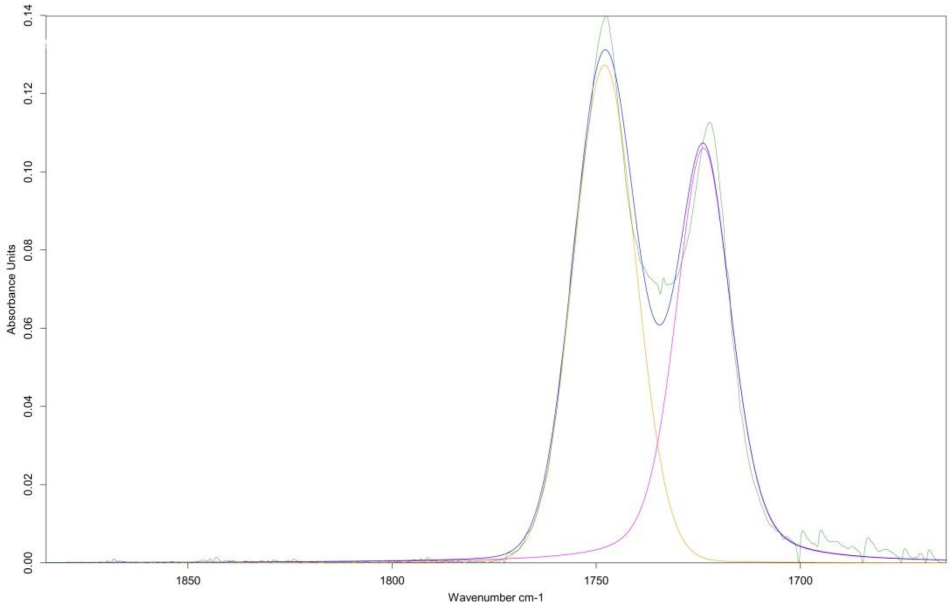


Figure S39. FTIR spectrum of 3% solution of complex **4** in THF. Spectrum of C=O band deconvoluted for two bands.

Peak Position	Absorbance	FWHM	Area	Peak Type
1723.709394	0.106060	16.120654	2.134105	36%Lorentz+Gauss
1747.924977	0.127205	17.978735	2.471268	3%Lorentz+Gauss

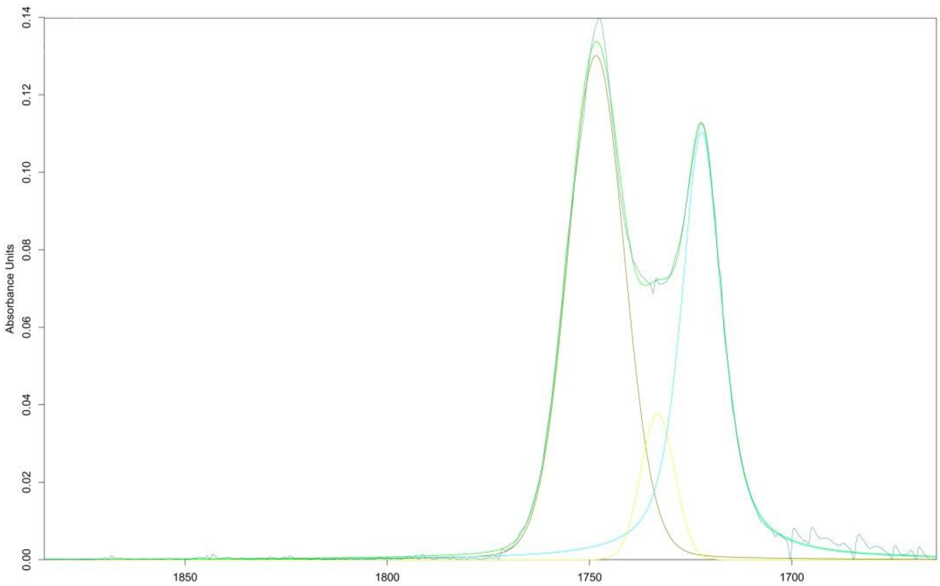


Figure S40. FTIR spectrum of 3% solution of complex **4** in THF. Spectrum of C=O band deconvoluted for three bands.

Peak Position	Absorbance	FWHM	Area	Peak Type
1722.285661	0.110339	12.014184	1.841557	64%Lorentz+Gauss
1733.142974	0.037659	9.835361	0.394268	0%Lorentz+Gauss
1748.379309	0.130130	16.522038	2.384595	9%Lorentz+Gauss

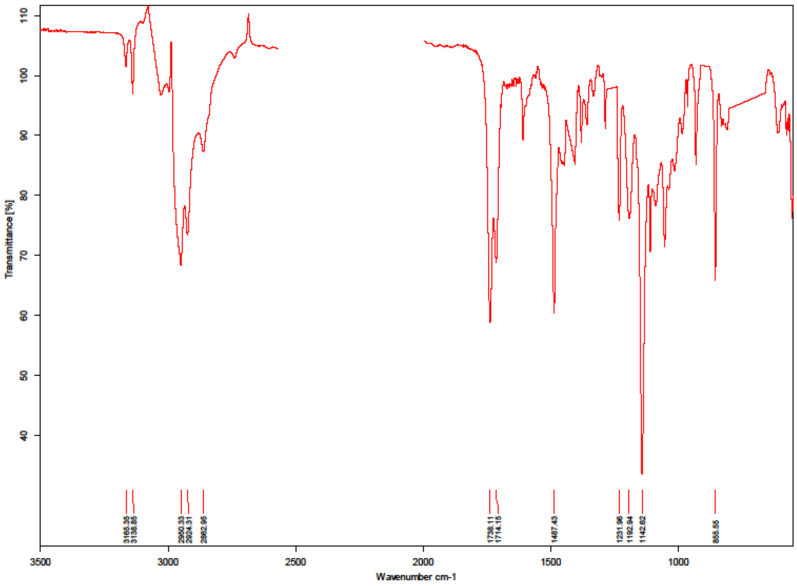


Figure S41. . FTIR spectrum of 3% solution of complex **4** in CH_2Cl_2.

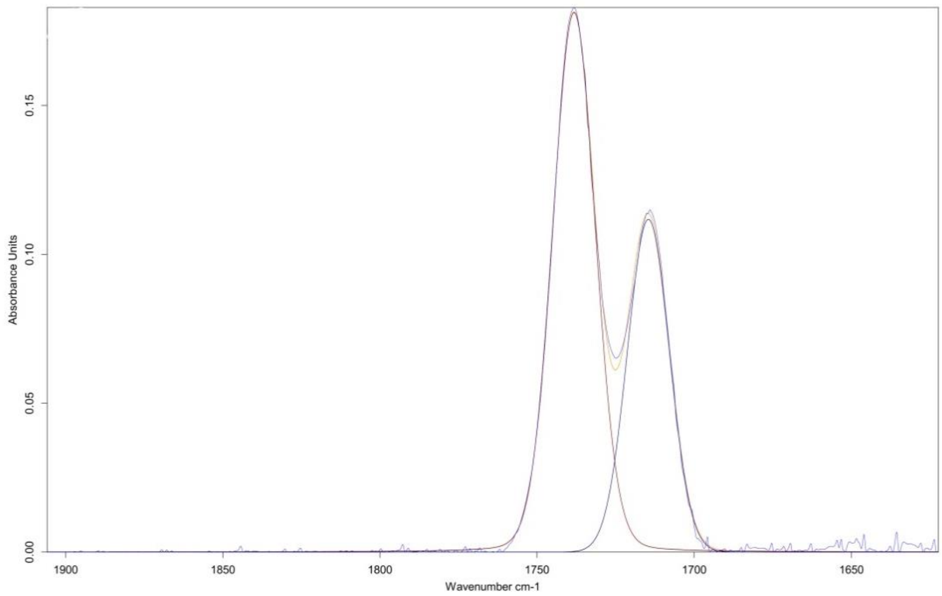


Figure S42. FTIR spectrum of 3% solution of complex **4** in CH_2Cl_2. Spectrum of C=O band deconvoluted for two bands.

Peak Position	**Absorbance**	**FWHM**	**Area**	**Peak Type**
1714.579417	0.111738	15.692485	1.866484	0%Lorentz+Gauss
1738.245088	0.181180	15.896046	3.190238	9%Lorentz+Gauss

3) Polymerization data

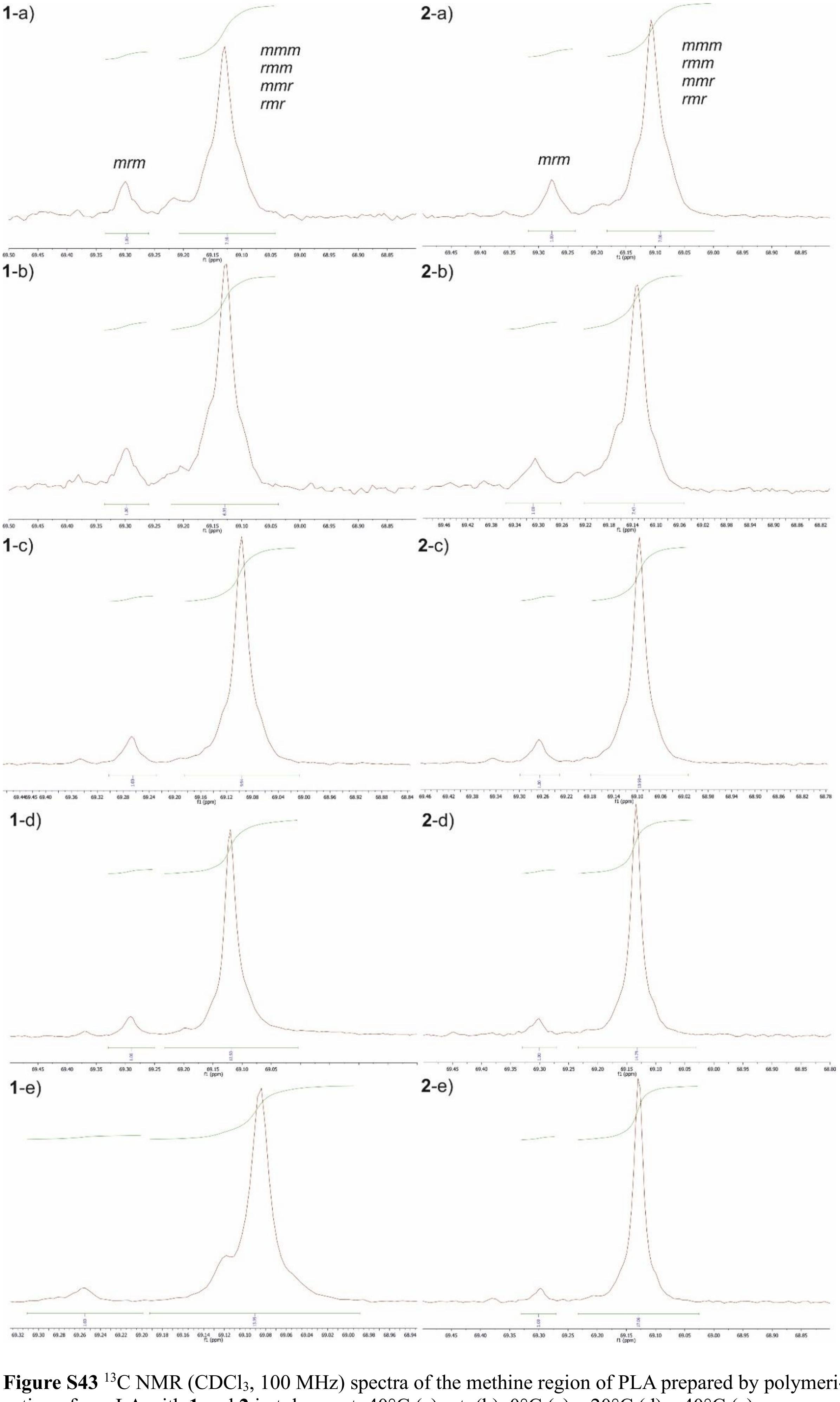
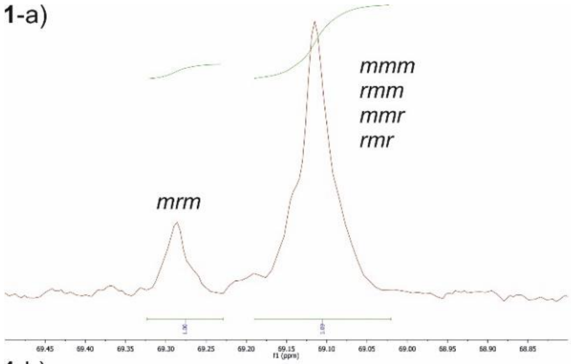


Figure S43 ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of the methine region of PLA prepared by polymerization of *rac*-LA with **1** and **2** in toluene at: 40°C (a), r.t. (b), 0°C (c), –20°C (d), –40°C (e)

1-a)

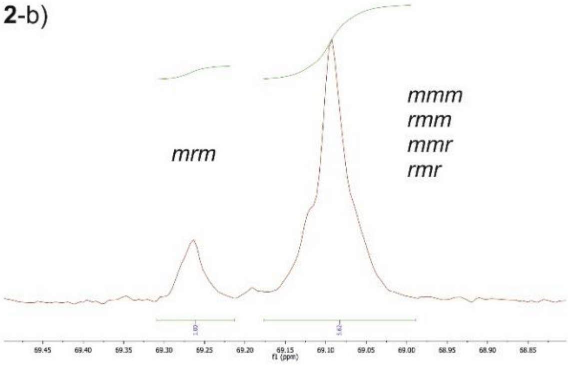


2-a)

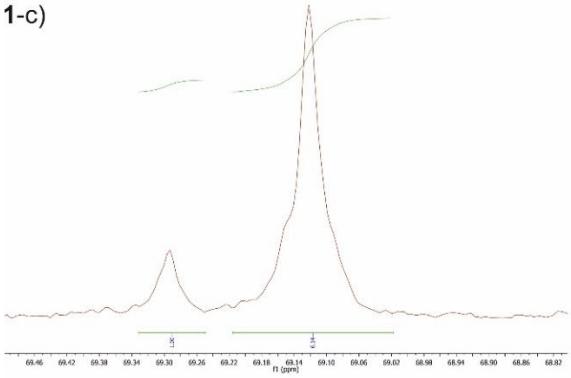
1-b)

In the cited reference

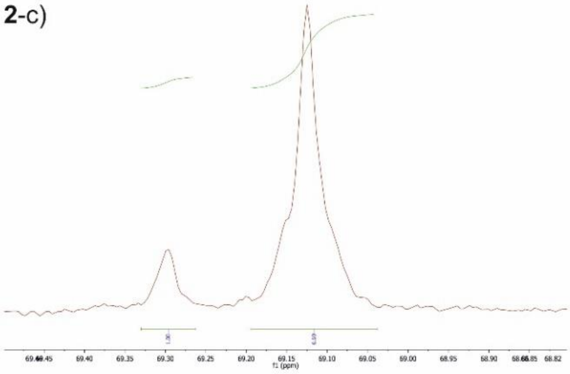
2-b)



1-c)



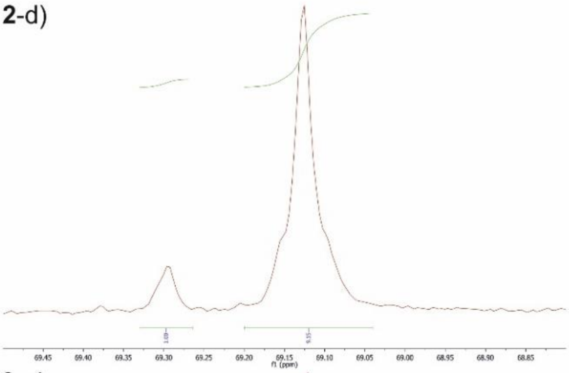
2-c)



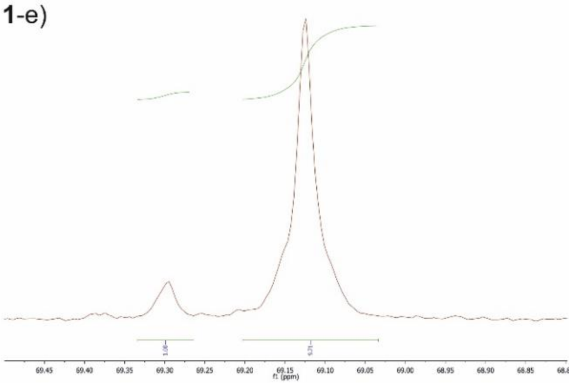
1-d)

In the cited reference

2-d)



1-e)



2-e)

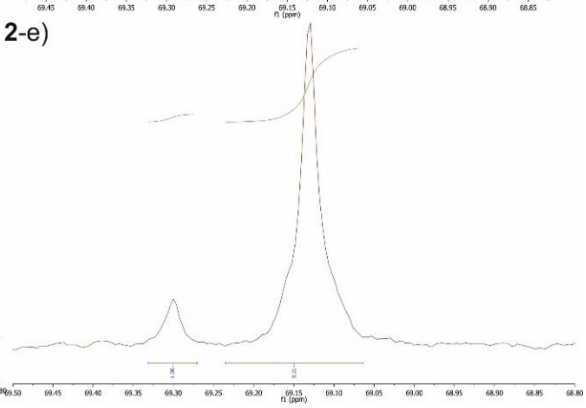


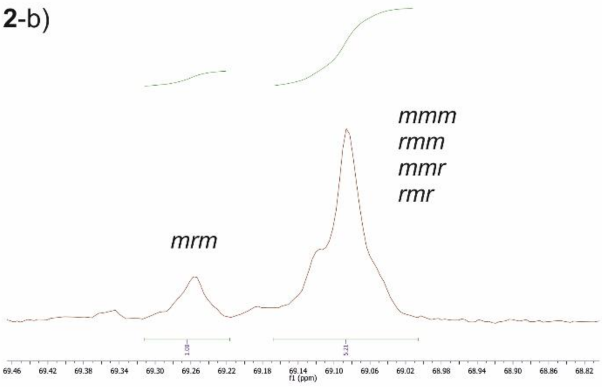
Figure S44 ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of the methine region of PLA prepared by polymerization of *rac*-LA with **1** and **2** in CH_2Cl_2 at: 40°C (a), r.t. (b), 0°C (c), –20°C (d), –40°C (e)

1-a)

2-a)

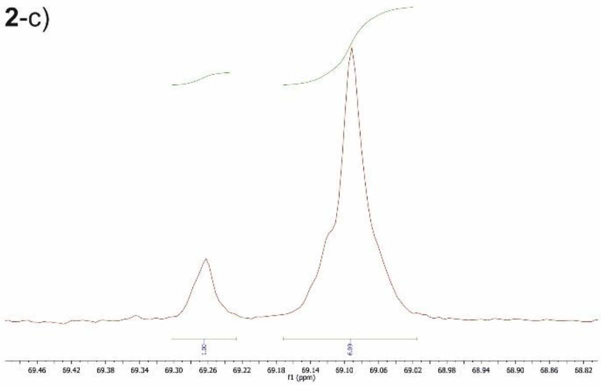
1-b)

2-b)

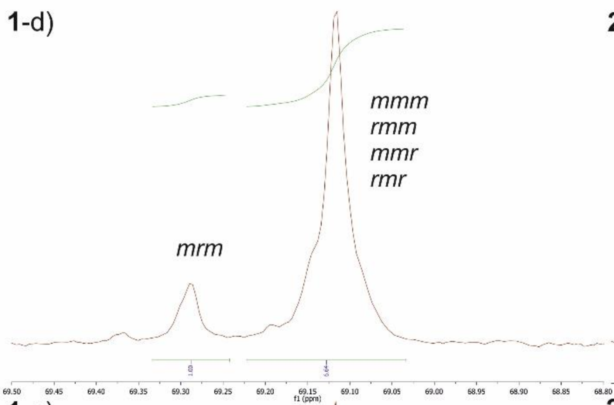


1-c)

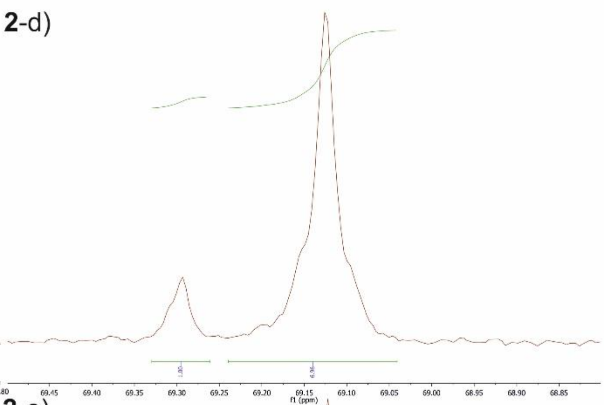
2-c)



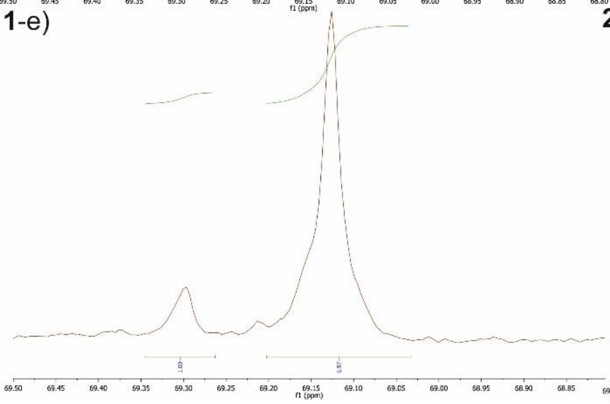
1-d)



2-d)



1-e)



2-e)

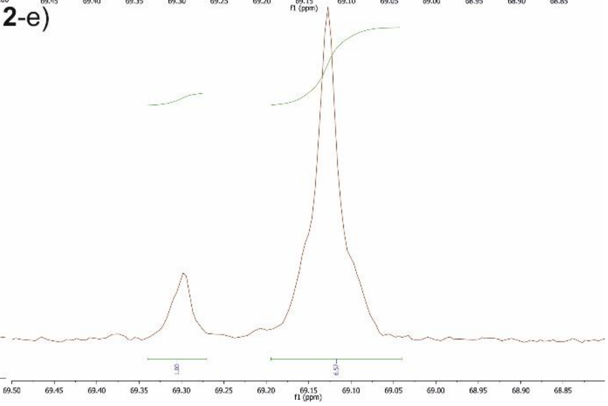


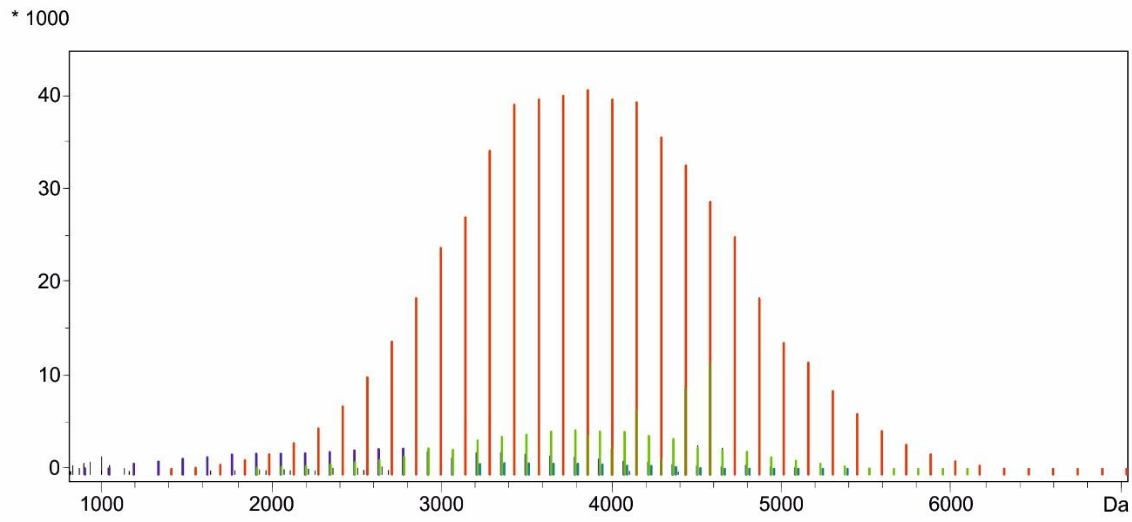
Figure S45 ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of the methine region of PLA prepared by polymerization of *rac*-LA with **1** and **2** in THF at: 40°C (a), r.t. (b), 0°C (c), –20°C (d), –40°C (e)

4) MALDI-TOF and GPC of PLA obtained with complexes 1 and 3

polytool

Date: 12/23/2021 Time: 16:42

FileName: ...M-1.0_DCTB_K_RP700-3500_P36_c5\0_K16\1\1SRef\pdata\1\peaklist.xml
peak integrals - NM 1.0 (CHCl3)
DCTB+K RP 700-3500 Da P=36% c=5

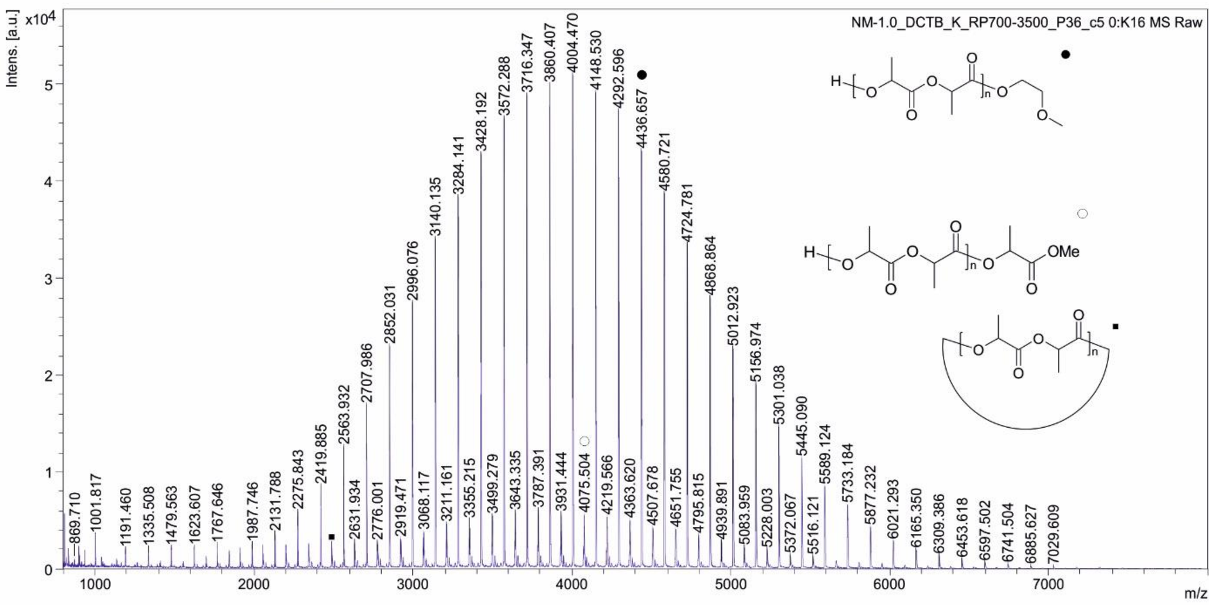


n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
1	1	144.054	76.0954			38.9637	3848.65	4014.98	1.04322	26.7168	74.7	40
2	2	144.054	-0.61353			38.9637	2640.04	3026.08	1.14622	18.3268	5.7	31
3	3	144.054	3.35827			38.9637	3831.29	3996.39	1.04309	26.5963	8.3	30
4	4	144.054	18.0490			38.9637	3964.42	4043.65	1.01999	27.5205	1.5	16
5	5	144.054	74.0545			38.9637	4144.76	4161.70	1.00409	28.7723	2.2	6

Traces

D:\Dane\Mass_Spectra\Rok_2021\Work\NM-1.0_DCTB_K_RP700-3500_P36_c5\0_K16\1\1SRef

Comment 1 NM 1.0 (CHCl3)
Comment 2 DCTB+K RP 700-3500 Da P=36% c=5

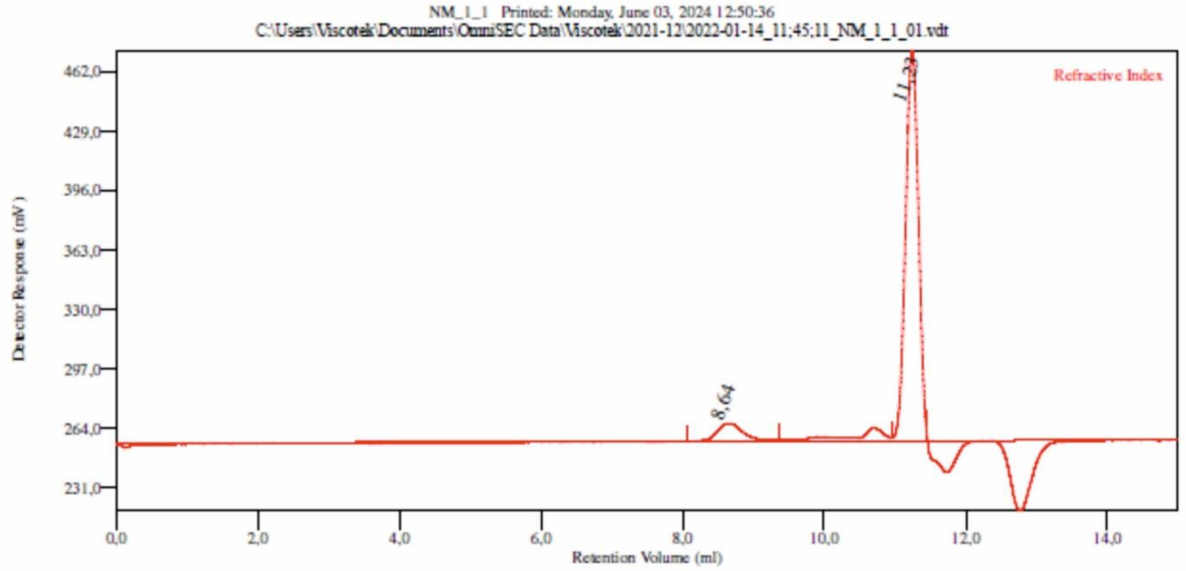


Bruker Daltonics flexAnalysis

page 1 of 1

printed: 12/23/2021 16:39:38

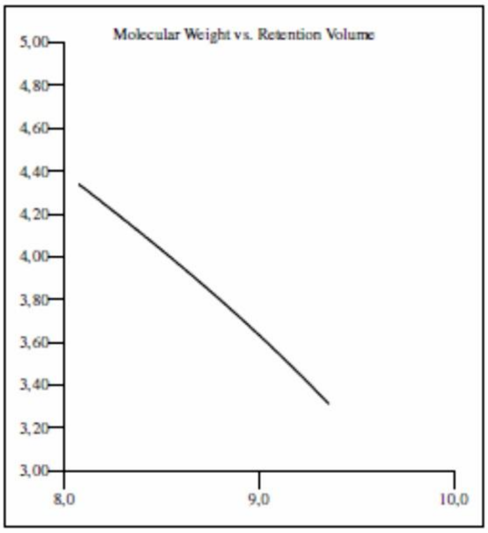
Figure S46. MALDI–TOF spectrum of PLA obtained with **1** in toluene at 40ºC, Table 1, entry 1. Figure 1 (—)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,643	11,233
Mn - (Daltons)	7 023	0
Mw - (Daltons)	8 051	0
Mz - (Daltons)	8 940	0
Mp - (Daltons)	8 349	0
Mw / Mn	1,146	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	3 553	0
Mw 10.0% High	13 319	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mv ml)	4,27	45,35
UV@240nm Area - (mv ml)	0,00	0,00

Annotation	
Method File	CC_RI_PS_2021-09_z_dnia_2022-01-05-0003.vcm
Limits File	
Date Acquired	Jan 14, 2022 - 11:45:11
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	70,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



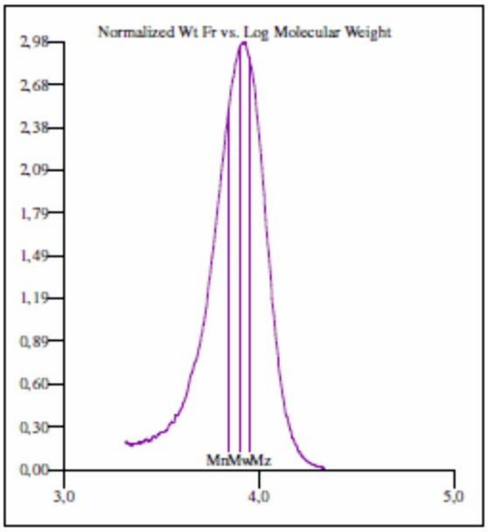
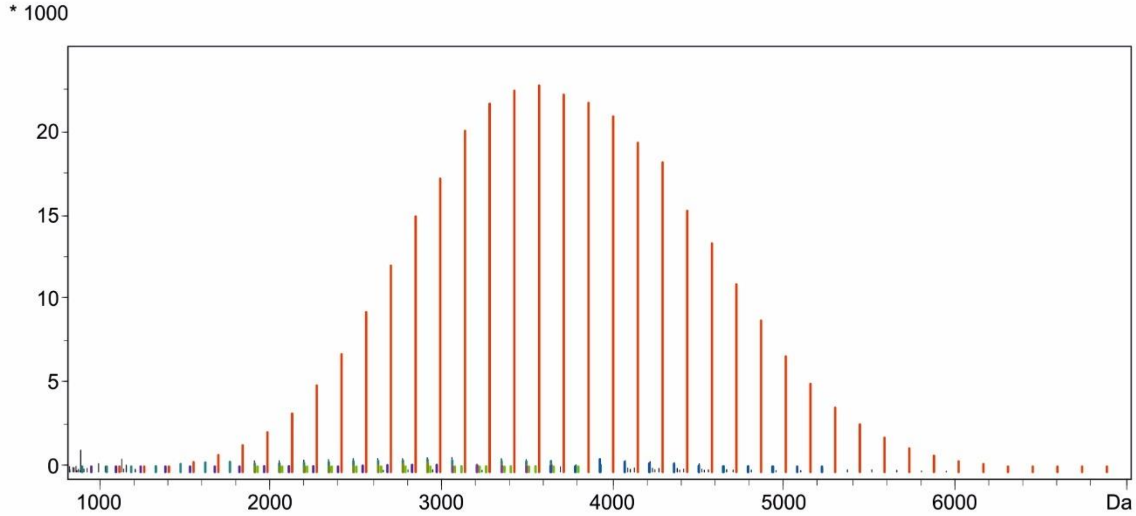


Figure S47. GPC eluogram of PLA obtained with **1** in toluene at 40ºC, Table 1, entry 1.

polytool Date: 12/23/2021 Time: 16:43

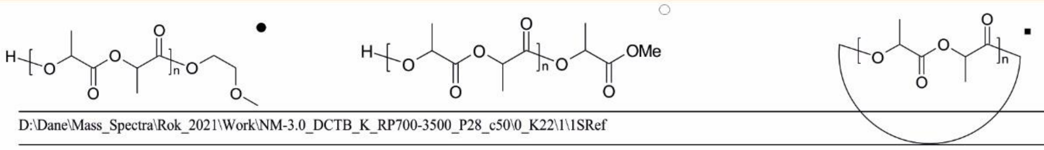
FileName: ...-3.0_DCTB_K_RP700-3500_P28_c50\0_K22\1\1SRef\pdata\1\peaklist.xml
peak integrals - NM 3.0 (CHCl3)
DCTB+K RP 700-3500 Da P=28% c=50



n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
1	1	144.050	76.0446			38.9637	3678.05	3866.73	1.05130	25.5331	86.3	43
2	2	144.050	55.6660			38.9637	2306.55	2524.42	1.09445	16.0121	1.3	20
3	3	144.050	55.9336			38.9637	3290.35	3298.05	1.00234	22.8417	0.2	4
4	4	144.050	1.25334			38.9637	2920.77	3281.72	1.12358	20.2761	4.1	30
5	5	144.050	3.53602			38.9637	2849.13	2923.13	1.02597	19.7787	0.9	13
6	6	144.050	3.99073			38.9637	3292.42	3303.86	1.00347	22.8561	0.3	5
7	7	144.050	17.9722			38.9637	2878.47	2980.12	1.03532	19.9824	0.5	14
8	8	144.050	142.470			38.9637	4222.53	4263.08	1.00961	29.3128	0.7	12

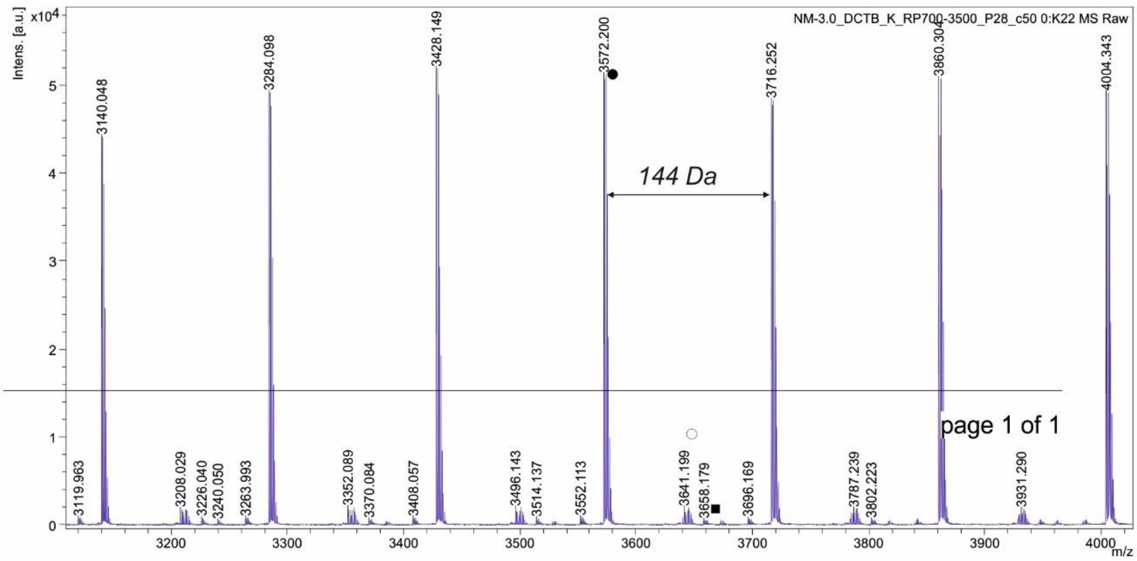
Traces

Traces



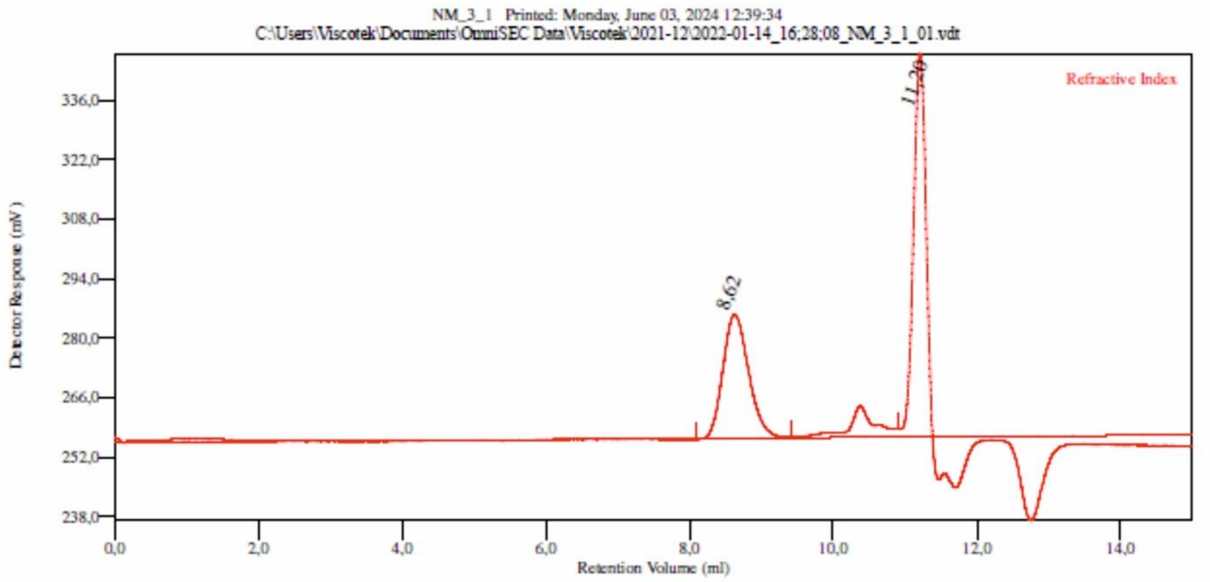
D:\Dane\Mass_Spectra\Rok_2021\Work\NM-3.0_DCTB_K_RP700-3500_P28_c50\0_K22\1\1SRef

Comment 1 NM 3.0 (CHCl3)
Comment 2 DCTB+K RP 700-3500 Da P=28% c=50



Bruker Daltonics flexAnalysis printed: 12/23/2021 16:41:22

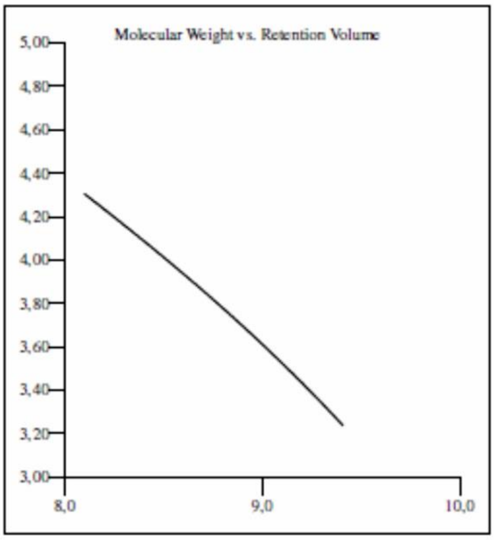
Figure S48. MALDI–TOF spectrum of PLA obtained with **1** in toluene at r.t., Table 1, entry 4. Figure 1 (—)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,623	11,200
Mn - (Daltons)	7 364	0
Mw - (Daltons)	8 121	0
Mz - (Daltons)	8 818	0
Mp - (Daltons)	8 283	0
Mw / Mn	1,103	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	4 267	0
Mw 10.0% High	12 388	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	12,02	17,71
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC_RI_PS_2021-09_z_dnia_2022-01-05-0003.vcm
Limits File	
Date Acquired	Jan 14, 2022 - 16:28:08
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



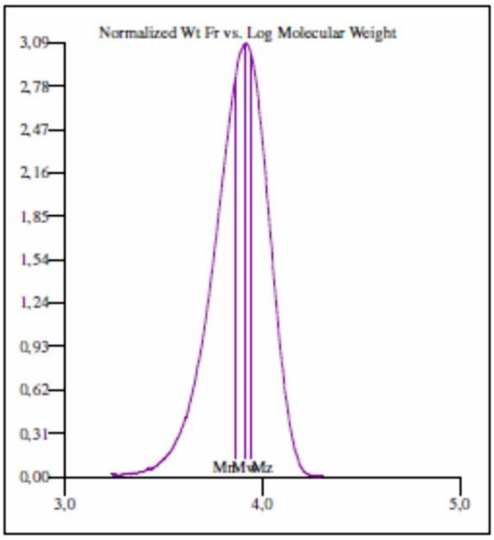
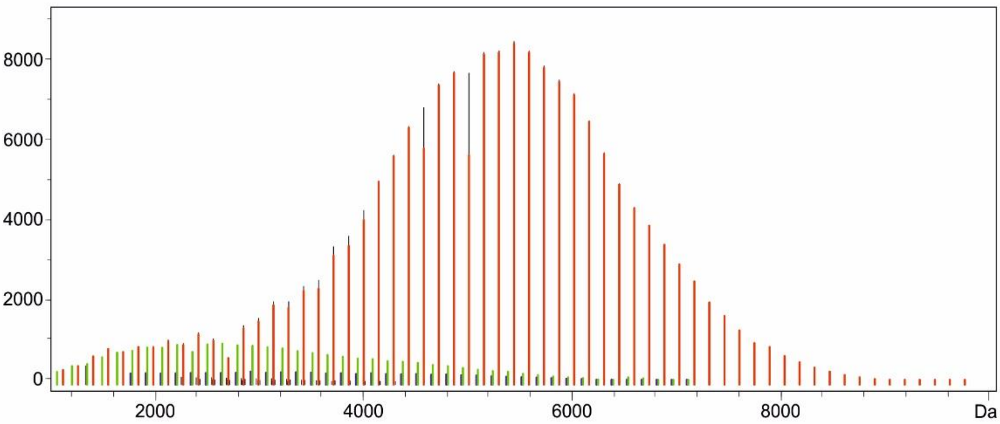


Figure S49. GPC eluogram of PLA obtained with **1** in toluene at r.t., Table 1, entry 4.

polytool Date: 08/01/2023 Time: 15:04

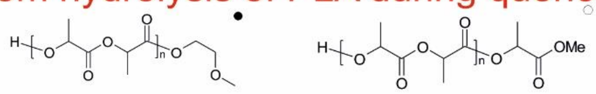
FileName: ...TB_K_RP700-3500_P34_c25_defl0640\0_B20\1\1SRef\pdata\1\peaklist.xml
peak integrals - DT-14,2 [CHCl3]
DCTB+K RP 700-3500 Da P=34% c=25 defl=640 Da



	n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
●	1	1	144.034	75.9145			38.9637	5136.56	5505.72	1.07187	35.6621	72.4	61
○	2	2	144.034	3.33406			38.9637	3902.54	4405.28	1.12882	27.0945	3.4	38
	3	3	144.034	18.0862			38.9637	3224.45	3786.04	1.17417	22.3867	9.2	43 *
	4	4	63.1228	36.3855			38.9637	801.534	804.615	1.00384	12.6980	1.2	3
	5	5	63.1228	56.3499			38.9637	779.269	785.009	1.00737	12.3453	1.1	4

Traces

* May originate from hydrolysis of PLA during quenching with H2O/H+



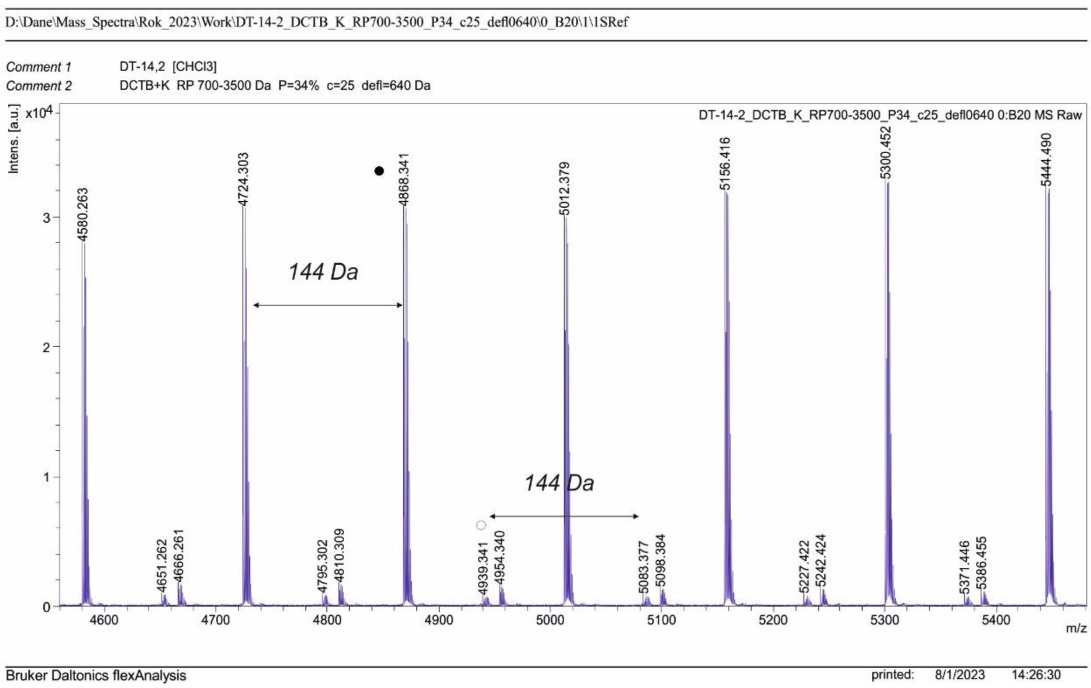
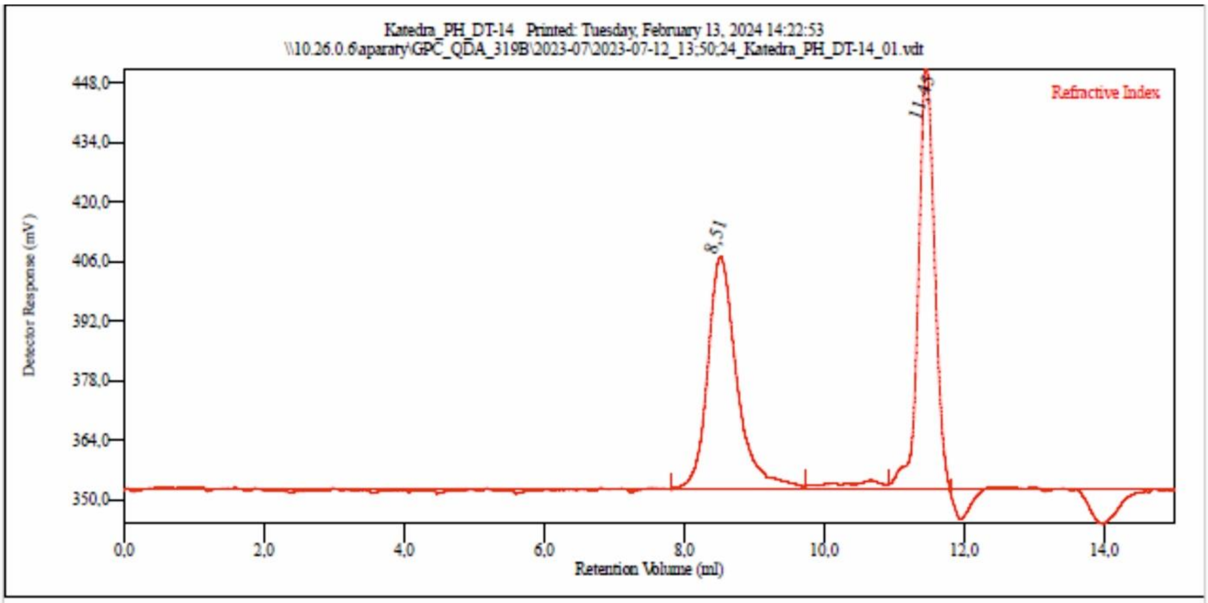


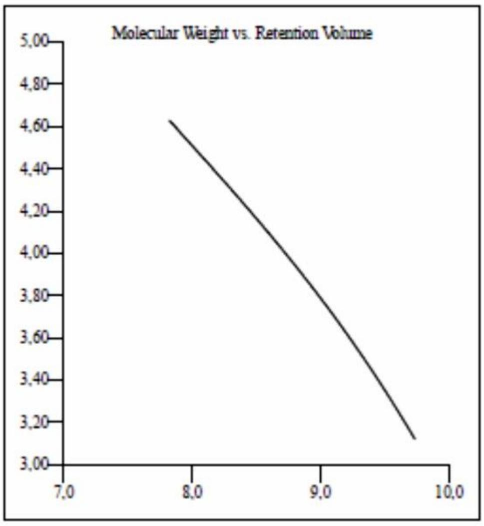
Figure S50. MALDI–TOF spectrum of PLA obtained with **1** in toluene at 0ºC, Table 1, entry 7. Figure 1 (▬)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,513	11,453
Mn - (Daltons)	10 853	0
Mw - (Daltons)	13 632	0
Mz - (Daltons)	15 627	0
Mp - (Daltons)	14 310	0
Mw / Mn	1,256	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	4 811	0
Mw 10.0% High	23 486	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	26,81	26,94
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC_PS_RI_2023-07-0012.vcm
Limits File	
Date Acquired	Jul 12, 2023 - 13:50:24
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



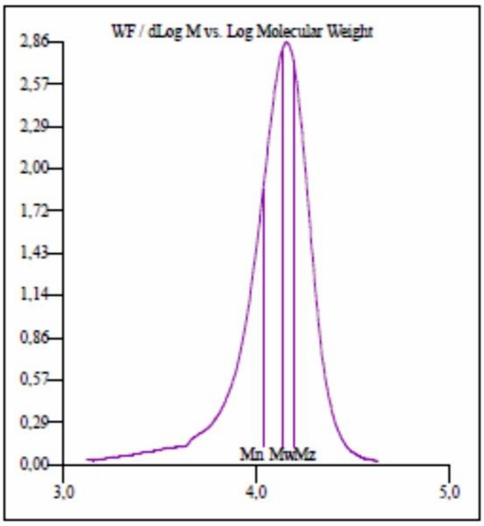
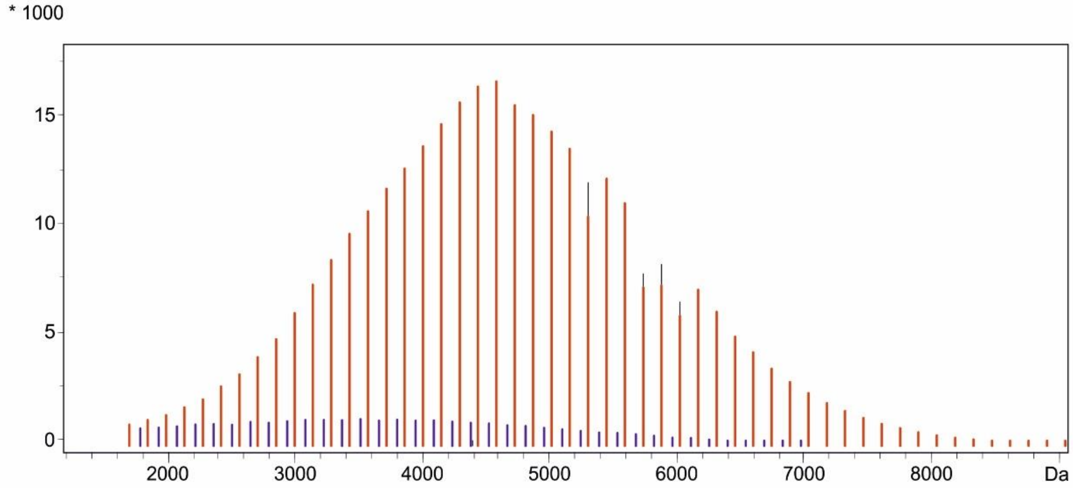


Figure S51. GPC eluogram of PLA obtained with **1** in toluene at 0ºC, Table 1, entry 7.

polytool Date: 12/23/2021 Time: 16:59

FileName: ...M-12.1_DCTB_K_RP700-3500_P38_c5\0_J5\1\1SRef\pdata\1\peaklist.xml
peak integrals - NM 12.1 (CHCl3)
DCTB+K RP 700-3500 Da P=38% c=5

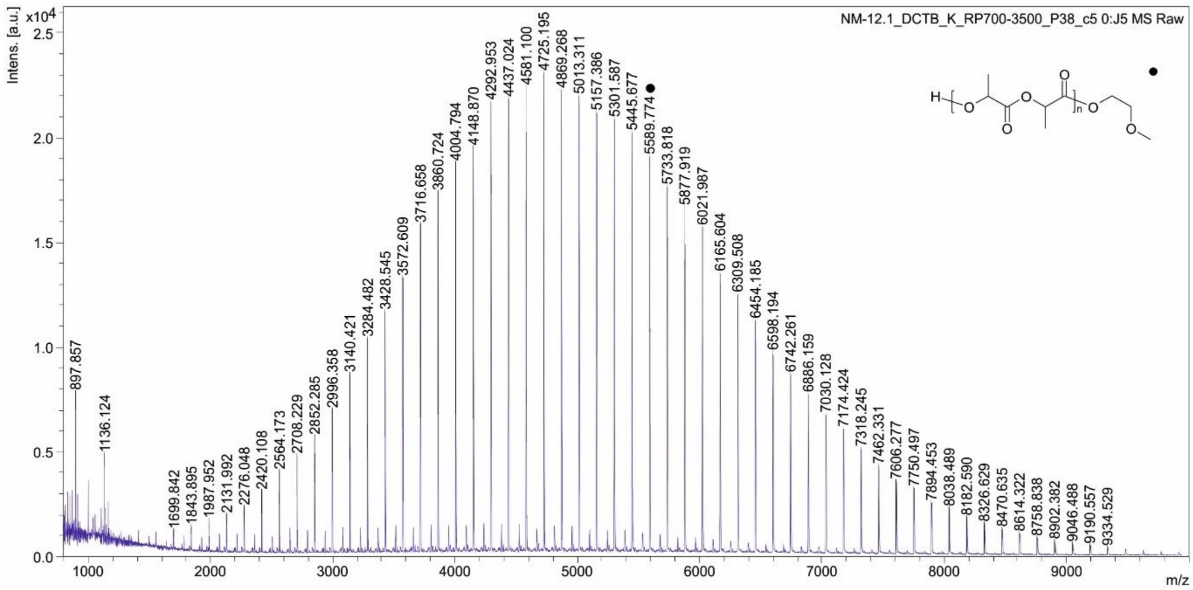


n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
1	1	144.052	76.5592			38.9637	4628.13	4944.80	1.06842	32.1283	81.1	54
2	2	144.052	18.4689			38.9637	3775.57	4181.42	1.10749	26.2098	7.2	37

May originate from hydrolysis of PLA during quenching with H2O/H+

D:\Dane\Mass_Spectra\Rok_2021\Work\NM-12.1_DCTB_K_RP700-3500_P38_c5\0_J5\1\1SRef

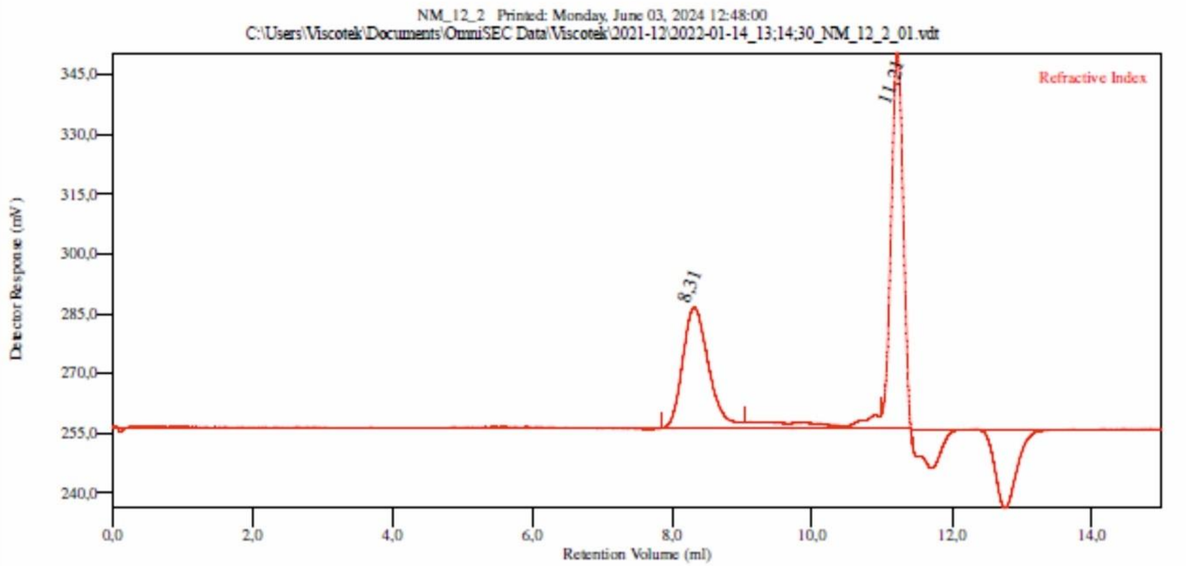
Comment 1 NM 12.1 (CHCl3)
Comment 2 DCTB+K RP 700-3500 Da P=38% c=5



Bruker Daltonics flexAnalysis printed: 12/23/2021 16:52:27

page 1 of 1

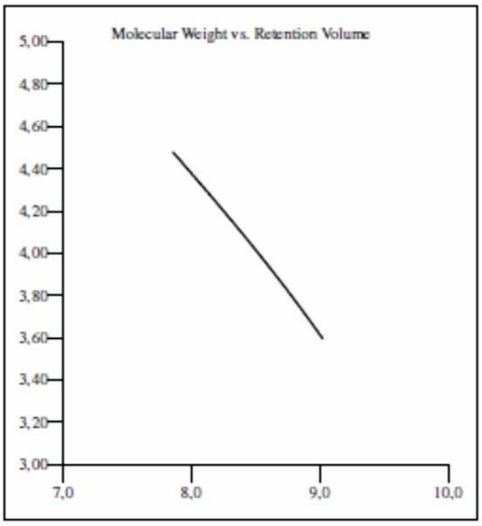
Figure S52. MALDI–TOF spectrum of PLA obtained with **1** in toluene at –20°C, Table 1, entry 9. Figure 1 (▬)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,310	11,207
Mn - (Daltons)	12 347	0
Mw - (Daltons)	13 774	0
Mz - (Daltons)	15 005	0
Mp - (Daltons)	14 331	0
Mw / Mn	1,116	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	6 744	0
Mw 10.0% High	21 261	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	13,14	18,52
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC_RI_PS_2021-09_z_dnia_2022-01-05-0003.vcm
Limits File	
Date Acquired	Jan 14, 2022 - 13:14:30
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



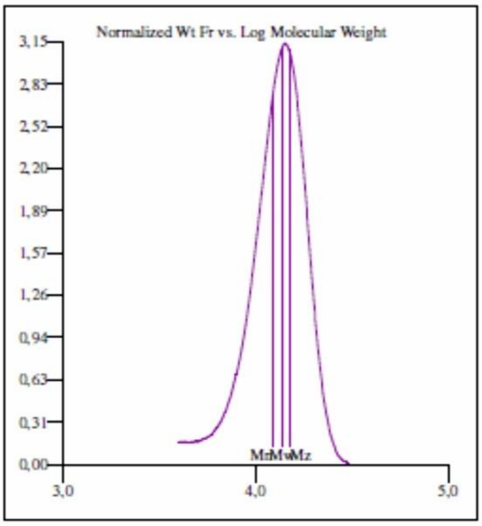
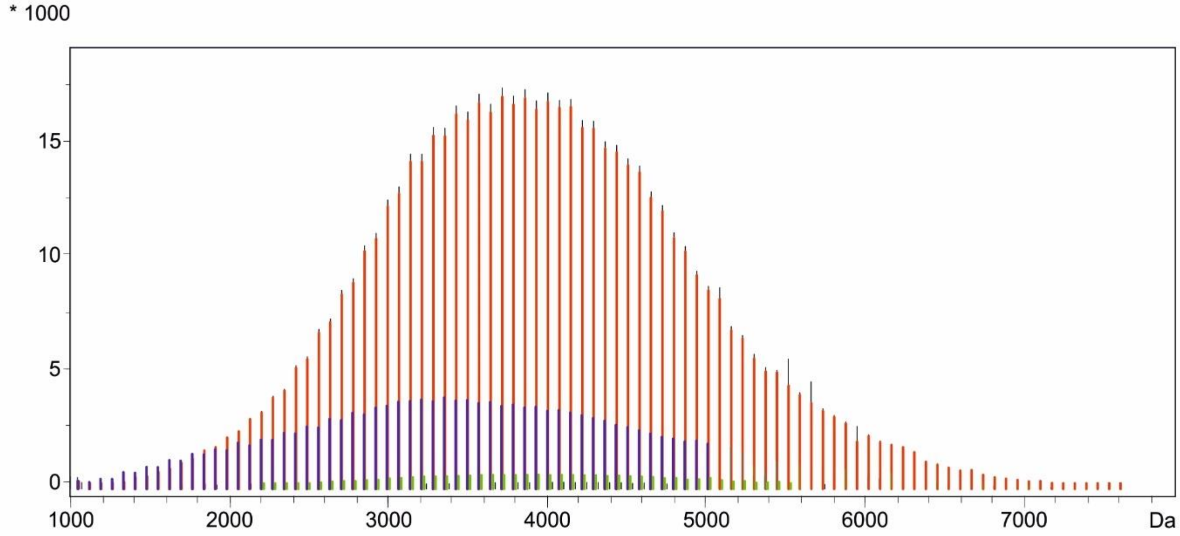


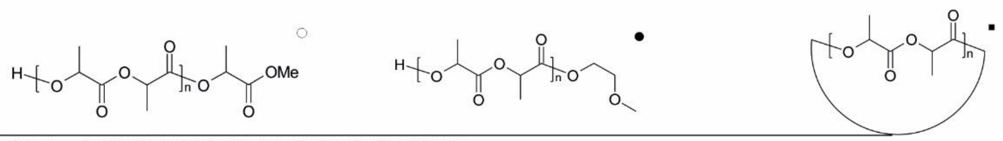
Figure S53. GPC eluogram of PLA obtained with **1** in toluene at –40°C, Table 1, entry 9.

FileName: ...-10.1_DCTB_K_RP700-3500_P34_c50\0_K24\1\1SRef\pdata\1\peaklist.xml
peak integrals - NM 10.1 (CHCl3)
DCTB+K RP 700-3500 Da P=34% c=50



n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
1	1	72.0270	3.84128			38.9637	3918.61	4181.67	1.06713	54.4047	74.7	96
2	2	72.0270	-0.08261			38.9637	3295.57	3560.56	1.08041	45.7547	17.3	56
3	3	72.0270	17.8350			38.9637	3903.32	4089.18	1.04762	54.1924	2	47
4	4	71.9513	5.24635			38.9637	5228.53	5230.82	1.00044	72.6676	0.7	5
5	5	288.013	74.1501			38.9637	5679.03	5714.83	1.00630	19.7180	0.4	7

Traces



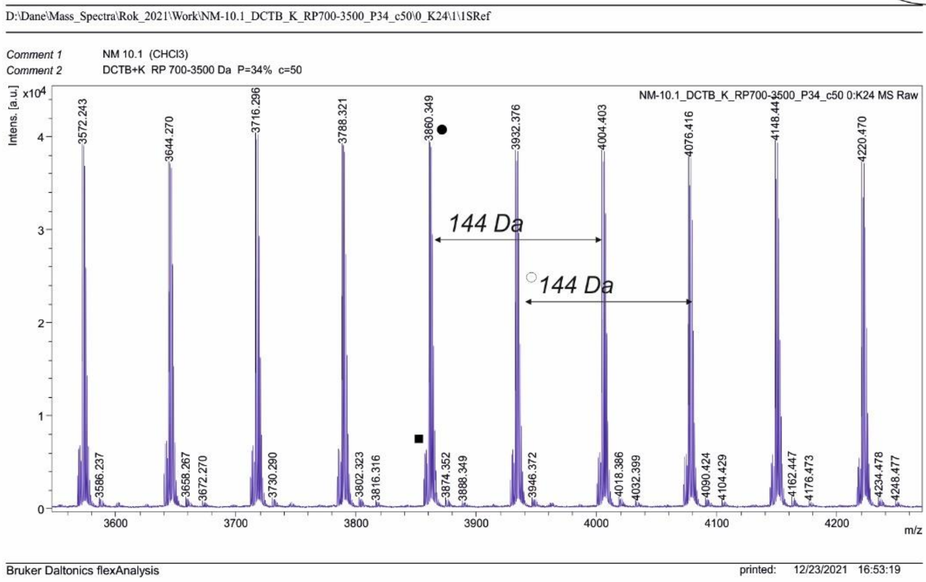
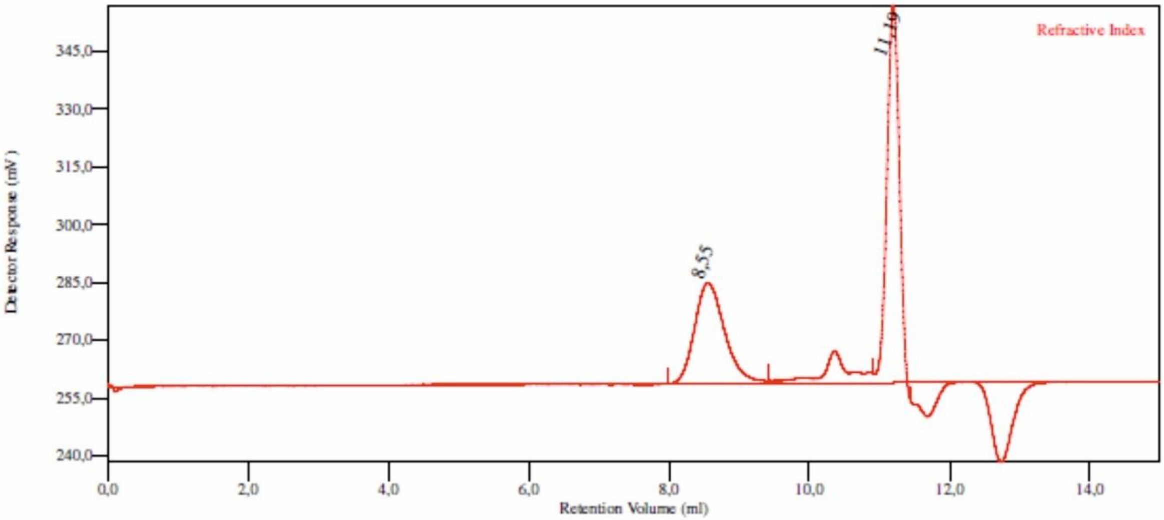


Figure S54. MALDI–TOF spectrum of PLA obtained with **1** in CH_2Cl_2 at 40°C, Table 1, entry 2. Figure 1 (▬)

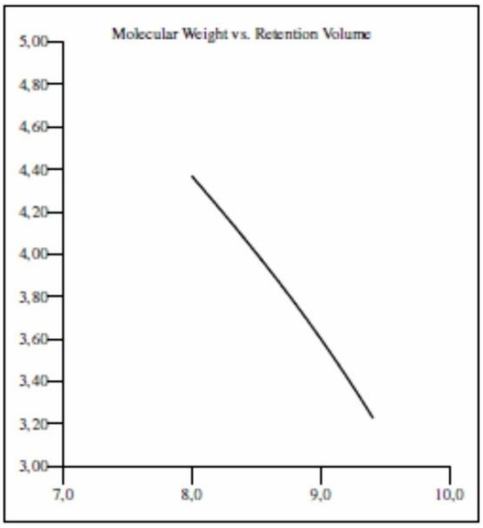
NM_10_2 Printed: Monday, June 03, 2024 12:49:42
C:\Users\Viscotek\Documents\OmniSEC Data\Viscotek\2021-12\2022-01-14_12;01;02_NM_10_2_01.vdt



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,550	11,187
Mn - (Daltons)	7 687	0
Mw - (Daltons)	8 987	0
Mz - (Daltons)	10 122	0
Mp - (Daltons)	9 264	0
Mw / Mn	1,169	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	3 863	0
Mw 10.0% High	15 034	0
Wt Fr (Peak)	1,000	0,000
RIArea - (mvml)	13,00	19,64
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC_RI_PS_2021-09_z_dnia_2022-01-05-0003.vcm
Limits File	
Date Acquired	Jan 14, 2022 - 12:01:02
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



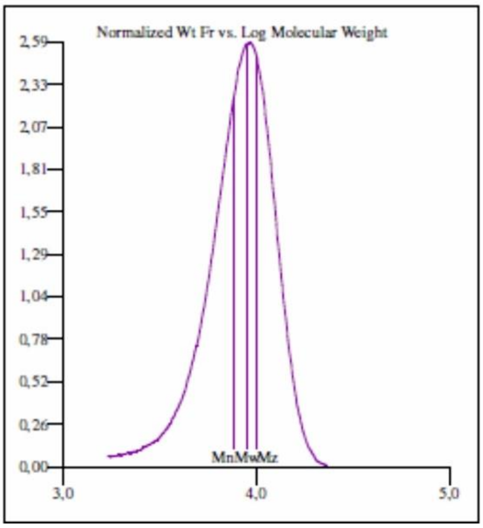
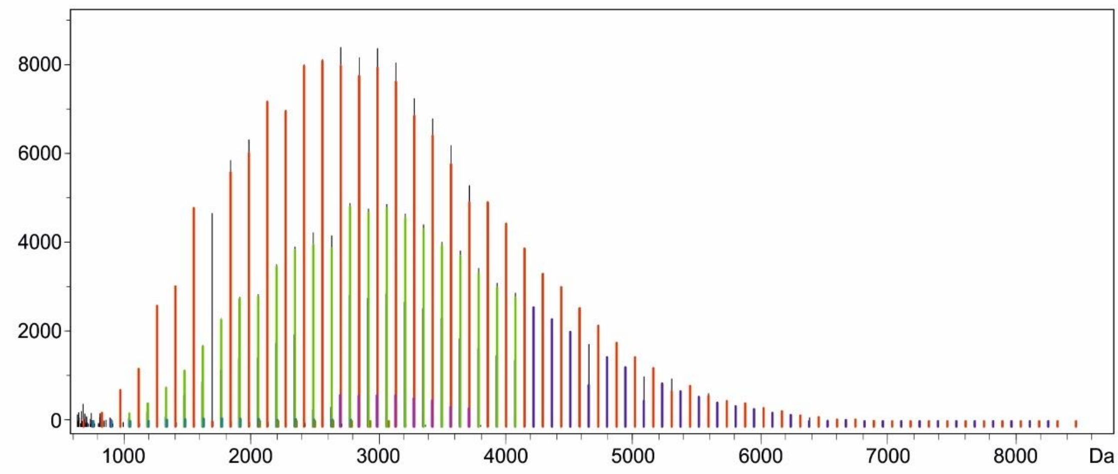


Figure S55. GPC eluogram of PLA obtained with **1** in CH_2Cl_2 at 40°C, Table 1, entry 2.

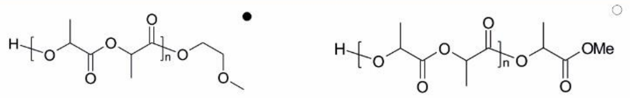
polytool Date: 08/01/2023 Time: 15:12

FileName: ...B_K_RP700-3500_P36_c05_defl0640\0_C22\1\1SRef\pdata\1\peaklist.xml
peak integrals - Ph-227,2 [CHCl3]
DCTB+K RP 700-3500 Da P=36% c=05 defl=640 Da



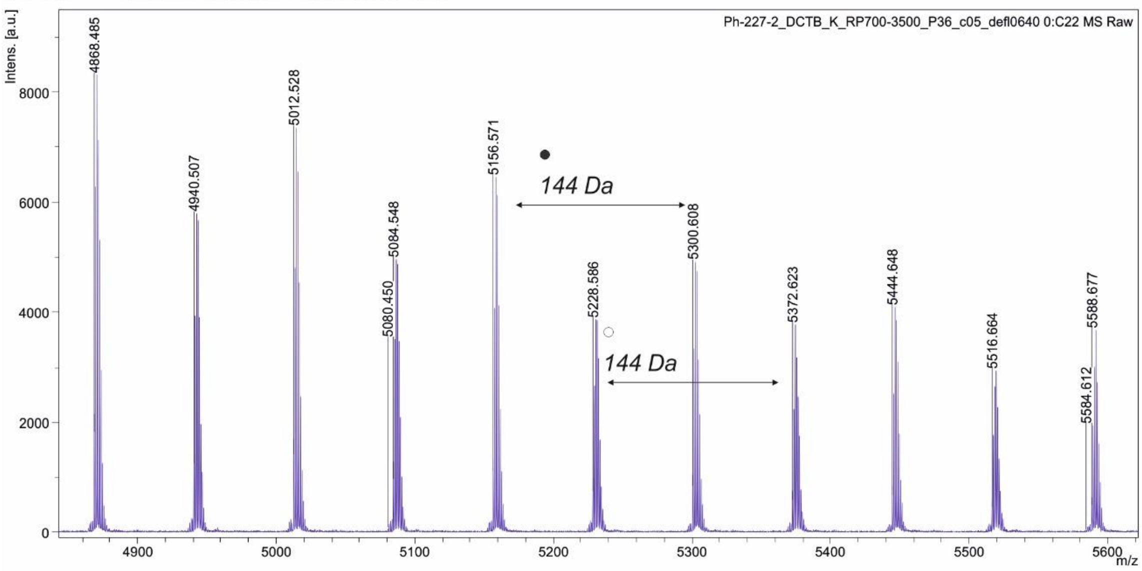
	n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
•	1	1	144.040	75.8543			38.9637	3042.05	3437.74	1.13008	21.1195	56.9	55
?○	2	2	144.040	1.88145			38.9637	4302.54	4683.92	1.08864	29.8705	9.2	53
	3	3	144.040	4.00462			38.9637	2848.86	3052.55	1.07150	19.7783	23.9	22
	4	4	144.040	10.1610			38.9637	1744.66	1926.36	1.10415	12.1124	0.7	15
	5	5	144.040	18.1885			38.9637	2536.95	2580.21	1.01705	17.6128	0.1	8
	6	6	144.040	71.3466			38.9637	3213.81	3248.70	1.01086	22.3120	0.8	8

Traces



D:\Dane\Mass_Spectra\Rok_2023\Work\Ph-227-2_DCTB_K_RP700-3500_P36_c05_defl0640\0_C22\1\1SRef

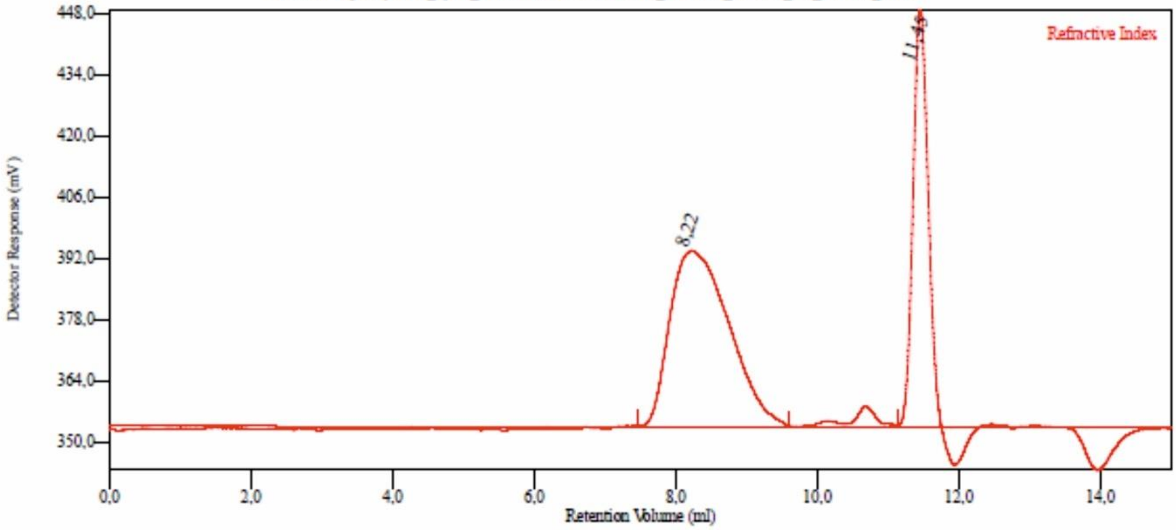
Comment 1 Ph-227,2 [CHCl3]
Comment 2 DCTB+K RP 700-3500 Da P=36% c=05 defl=640 Da



Bruker Daltonics flexAnalysis printed: 8/1/2023 14:37:57

Figure S56. MALDI–TOF spectrum of PLA obtained with **1** in CH_2Cl_2 at 0°C, Table 1, entry 8. Figure 1 (▬)

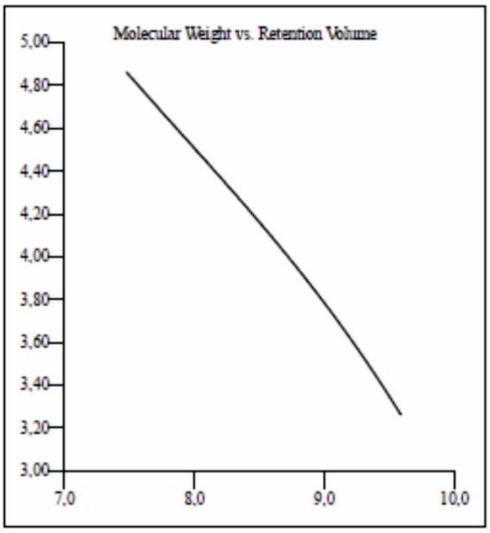
Katedra_PH_PH-227 Printed: Tuesday, February 13, 2024 13:54:54
\\10.26.0.6\aparaty\GPC_QDA_319B\2023-07\2023-07-12_14;22;06_Katedra_PH_PH-227_01.vdt



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,220	11,447
Mn - (Daltons)	13 732	0
Mw - (Daltons)	20 136	0
Mz - (Daltons)	26 165	0
Mp - (Daltons)	22 661	0
Mw / Mn	1,466	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	5 219	0
Mw 10.0% High	42 277	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	39,23	23,60
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC_PS_RI_2023-07-0012.vcm
Limits File	
Date Acquired	Jul 12, 2023 - 14:22:06
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



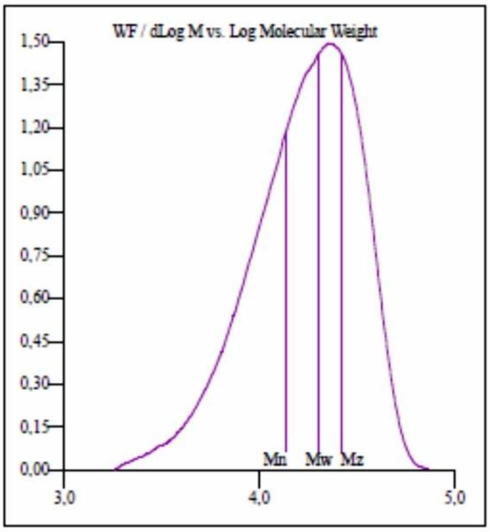
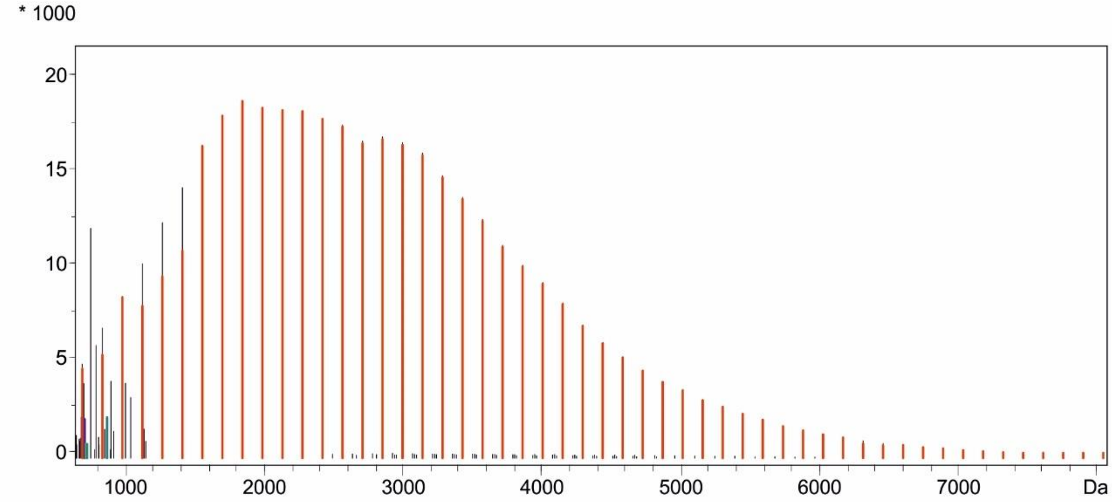


Figure S57. GPC eluogram of PLA obtained with **1** in CH_2Cl_2 at 0°C, Table 1, entry 8.

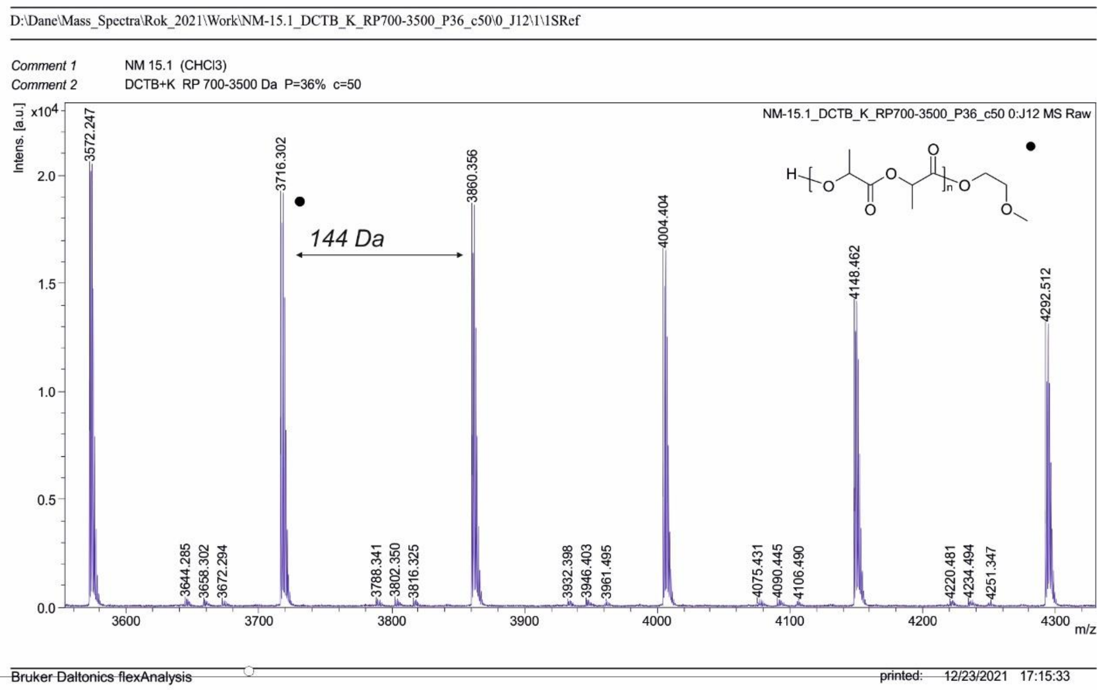
polytool Date: 12/23/2021 Time: 17:18

FileName: ...-15.1_DCTB_K_RP700-3500_P36_c50\0_J12\1\1SRef\pdata\1\peaklist.xml
peak integrals - NM 15.1 (CHCl3)
DCTB+K RP 700-3500 Da P=36% c=50



n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
• 1	1	144.053	75.7055			38.9637	2691.13	3350.40	1.24498	18.6816	67.6	65
2	2	144.053	92.2274			38.9637	523.592	546.025	1.04284	3.63473	2.1	3
3	3	144.053	101.951			38.9637	523.851	551.719	1.05320	3.63653	0.3	3
4	4	144.053	109.573			38.9637	661.046	700.150	1.05915	4.58893	0.8	4

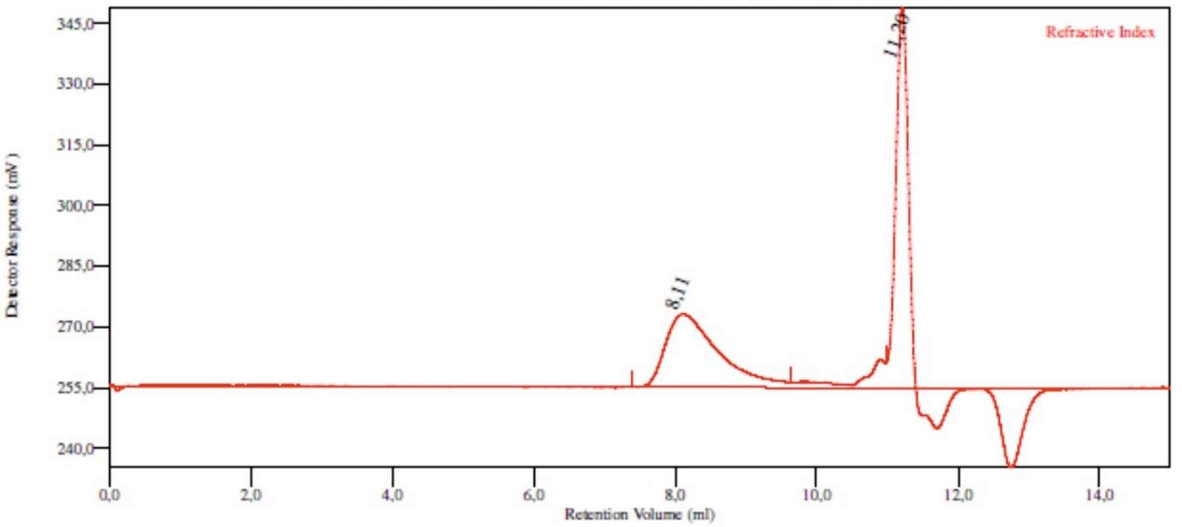
Traces



page 1 of 1

Figure S58. MALDI–TOF spectrum of PLA obtained with **1** in CH_2Cl_2 at –40°C, Table 1, entry 14. Figure 1 (▬)

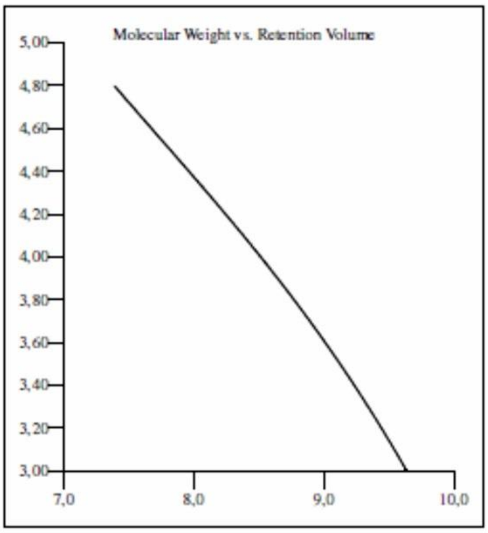
NM_15_2 Printed: Monday, June 03, 2024 12:42:15
C:\Users\Viscotek\Documents\OmniSEC Data\Viscotek\2021-12\2022-01-14_13;46;10_NM_15_2_01.vdt



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,107	11,197
Mn - (Daltons)	9 113	0
Mw - (Daltons)	16 069	0
Mz - (Daltons)	21 203	0
Mp - (Daltons)	19 817	0
Mw / Mn	1,763	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	2 739	0
Mw 10.0% High	33 368	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mv ml)	15,80	18,82
UV@240nm Area - (mv ml)	0,00	0,00

Annotation	
Method File	CC_RI_PS_2021-09_z_dnia_2022-01-05-0003.vcm
Limits File	
Date Acquired	Jan 14, 2022 - 13:46:10
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



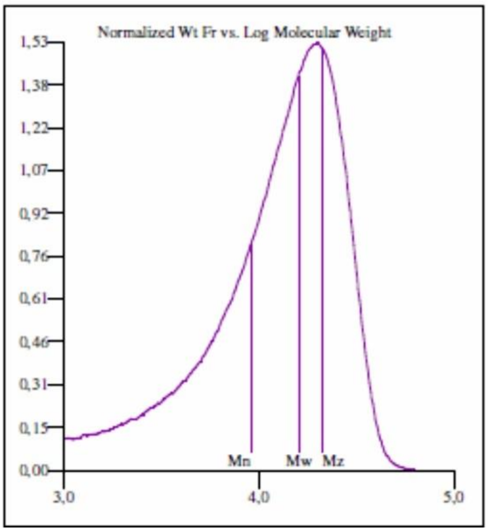
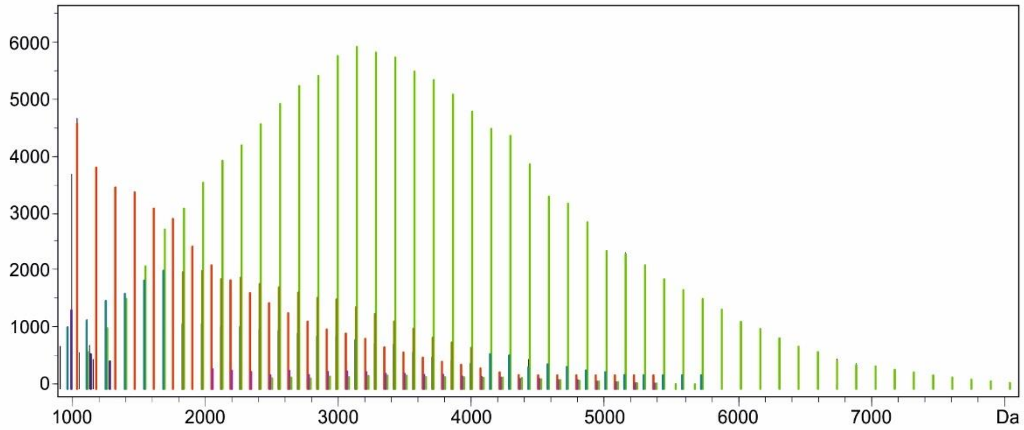


Figure S59. GPC eluogram of PLA obtained with **1** in CH_2Cl_2 at –40°C, Table 1, entry 14.

polytool Date: 12/23/2021 Time: 17:11

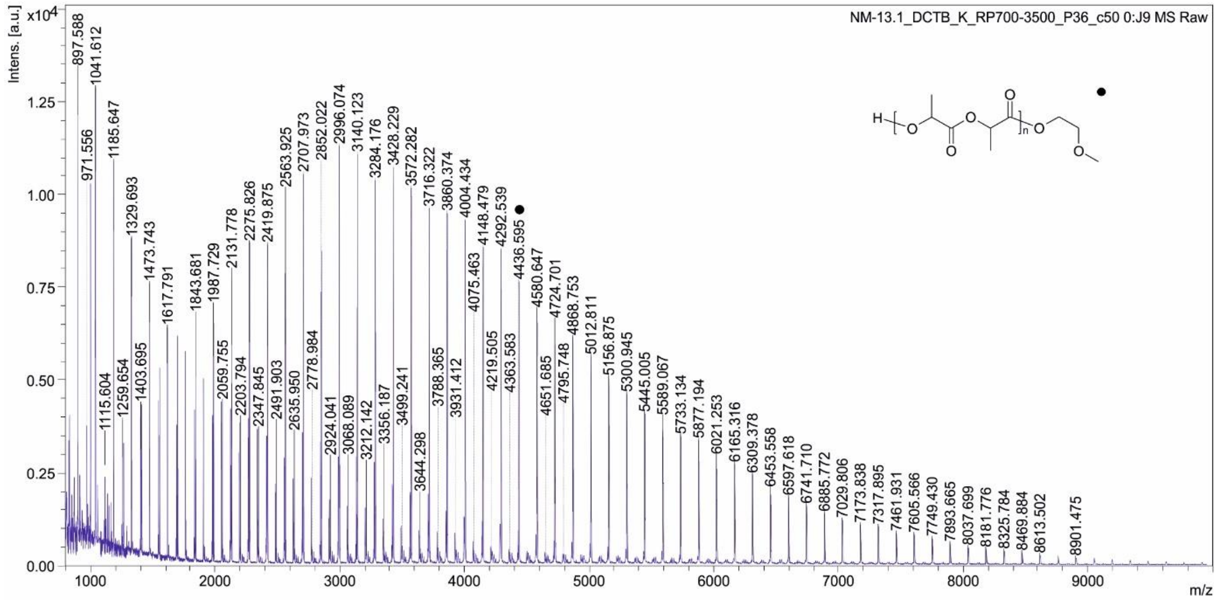
FileName: ...M-13.1_DCTB_K_RP700-3500_P36_c50\0_J9\1\1SRef\pdata\1\peaklist.xml
peak integrals - NM 13.1 (CHCl3)
DCTB+K RP 700-3500 Da P=36% c=50



n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
1	1	144.053	138.256			38.9637	1451.50	2128.77	1.46660	10.0761	16.2	35
2	2	144.053	96.9609			38.9637	637.907	717.109	1.12416	4.42827	2.4	7
● 3	3	144.053	76.0381			38.9637	3578.97	4075.26	1.13867	24.8447	31.5	53
4	4	144.053	65.9703			38.9637	1612.52	2835.01	1.75812	11.1939	8.2	37
5	5	144.053	68.2011			38.9637	2684.10	2828.29	1.05372	18.6327	5.7	16
6	6	144.053	3.47028			38.9637	3462.00	3702.98	1.06961	24.0328	1.1	24
7	7	144.053	18.0356			38.9637	3829.85	4026.20	1.05127	26.5863	0.9	23

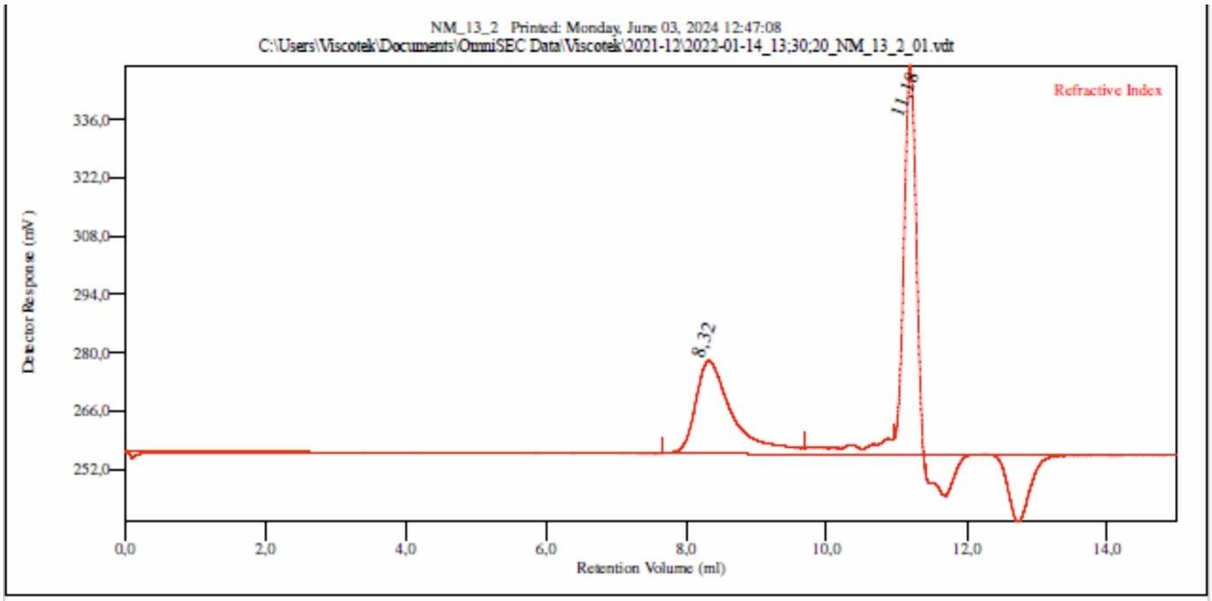
D:\Dane\Mass_Spectra\Rok_2021\Work\NM-13.1_DCTB_K_RP700-3500_P36_c50\0_J9\1\1SRef

Comment 1 NM 13.1 (CHCl3)
Comment 2 DCTB+K RP 700-3500 Da P=36% c=50



Bruker Daltonics flexAnalysis printed: 12/23/2021 17:03:05

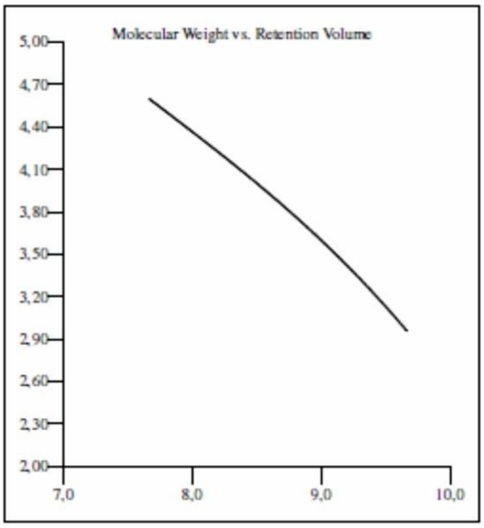
Figure S60. MALDI–TOF spectrum of PLA obtained with **1** in THF at –20°C, Table 1, entry 12. Figure 1 (**▬**)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,320	11,183
Mn - (Daltons)	7 378	0
Mw - (Daltons)	11 609	0
Mz - (Daltons)	14 233	0
Mp - (Daltons)	13 682	0
Mw / Mn	1,573	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	2 291	0
Mw 10.0% High	21 410	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	13,58	18,39
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC_RI_PS_2021-09_z_dnia_2022-01-05-0003.vcm
Limits File	
Date Acquired	Jan 14, 2022 - 13:30:20
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



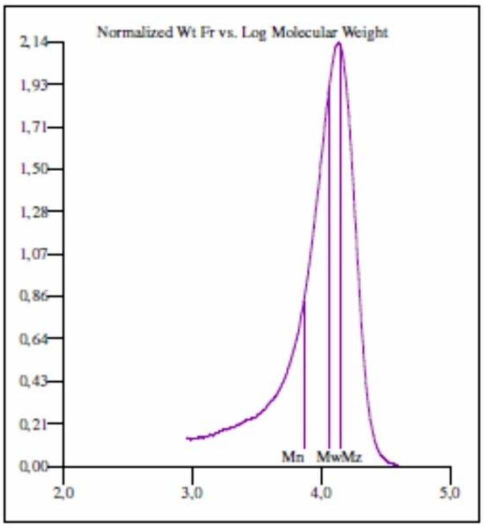
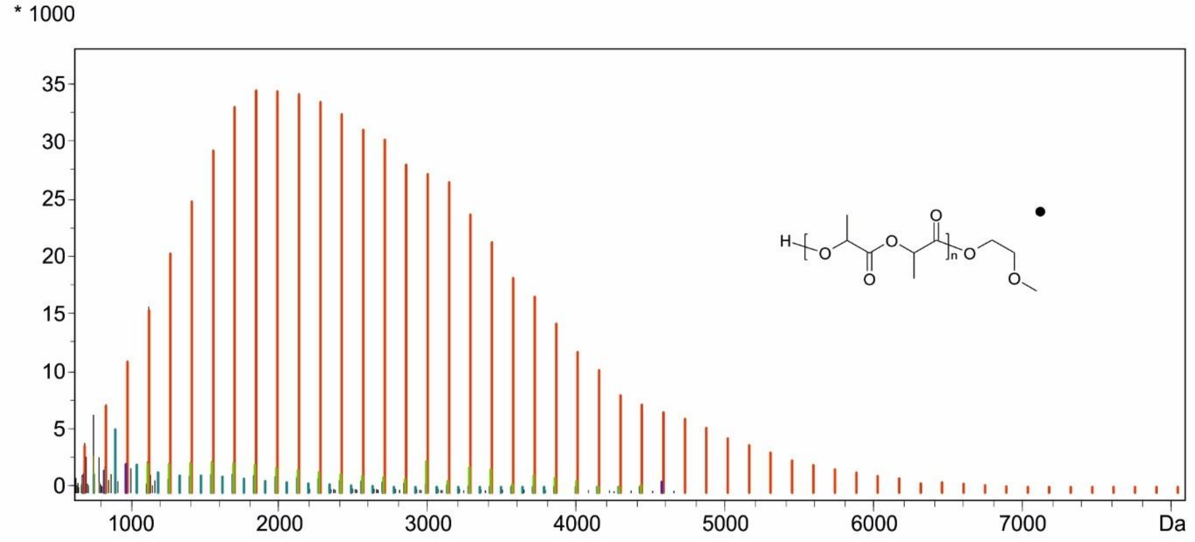


Figure S61. GPC eluogram of PLA obtained with **1** in THF at –20°C, Table 1, entry 12.

polytool Date: 12/23/2021 Time: 17:20

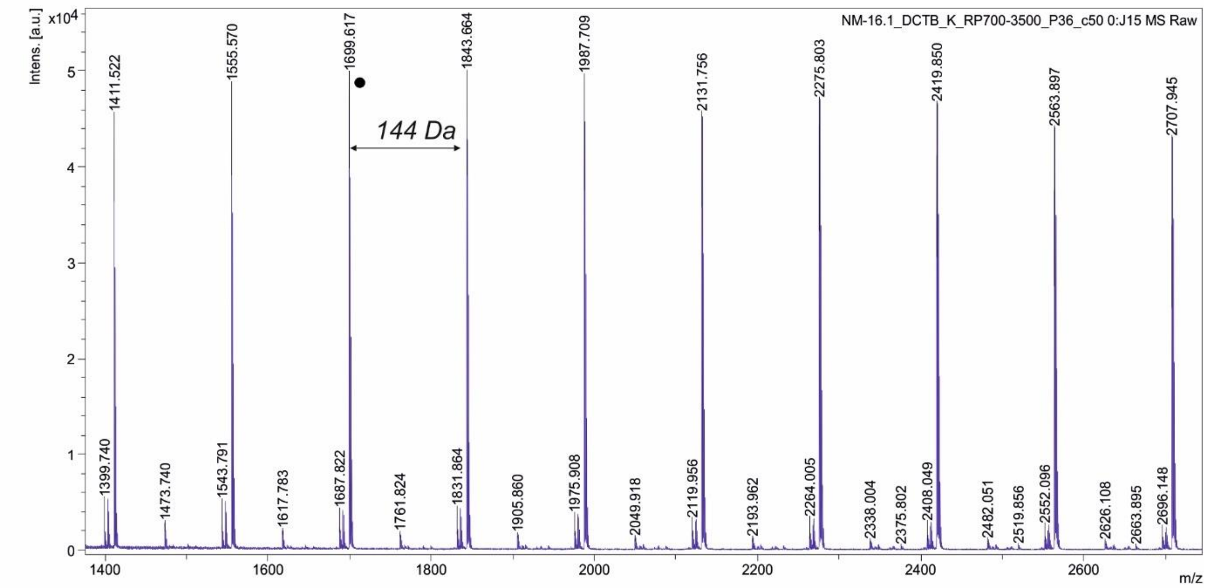
FileName: ...-16.1_DCTB_K_RP700-3500_P36_c50\0_J15\1\1SRef\pdata\1\peaklist.xml
peak integrals - NM 16.1 (CHCl3)
DCTB+K RP 700-3500 Da P=36% c=50



n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
• 1	1	144.039	76.4330			38.9637	2646.90	3172.81	1.19869	18.3763	73.7	67
2	2	144.039	64.2882			38.9637	1400.07	2081.71	1.48686	9.72007	4.2	29
3	3	144.039	67.9886			38.9637	2157.18	2483.63	1.15133	14.9763	3.9	24
4	4	144.039	138.463			38.9637	1339.16	1817.11	1.35690	9.29722	3.4	24
5	5	37.9089	31.5287			38.9637	589.187	618.076	1.04903	15.5422	4	12

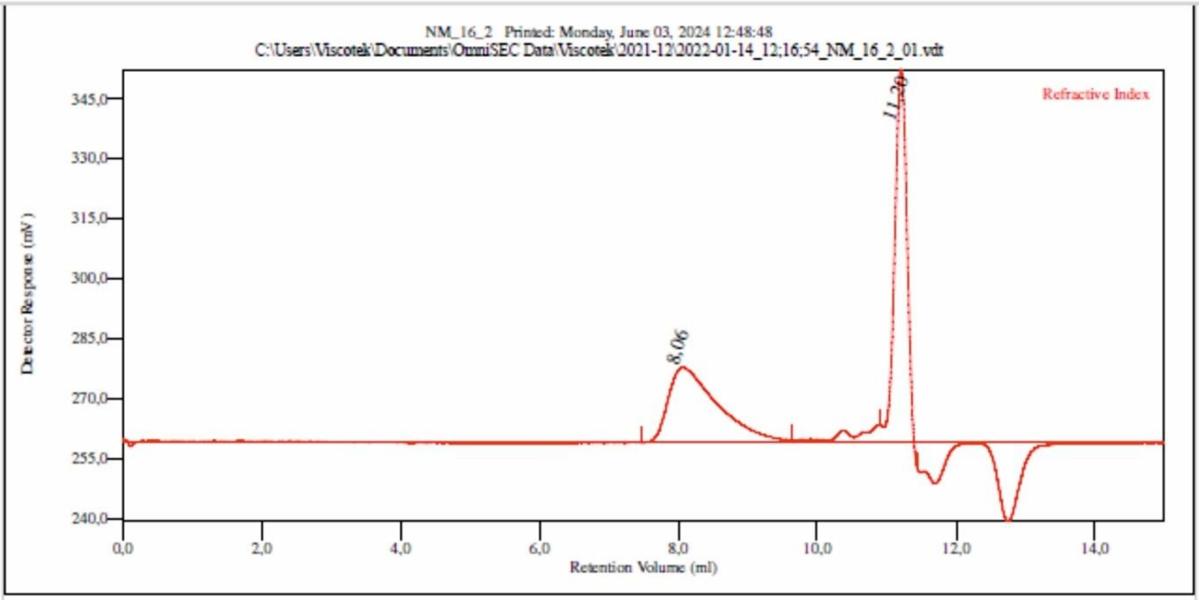
D:\Dane\Mass_Spectra\Rok_2021\Work\NM-16.1_DCTB_K_RP700-3500_P36_c50\0_J15\1\1SRef

Comment 1 NM 16.1 (CHCl3)
Comment 2 DCTB+K RP 700-3500 Da P=36% c=50



Bruker Daltonics flexAnalysis page 1 of 1 17:16:12

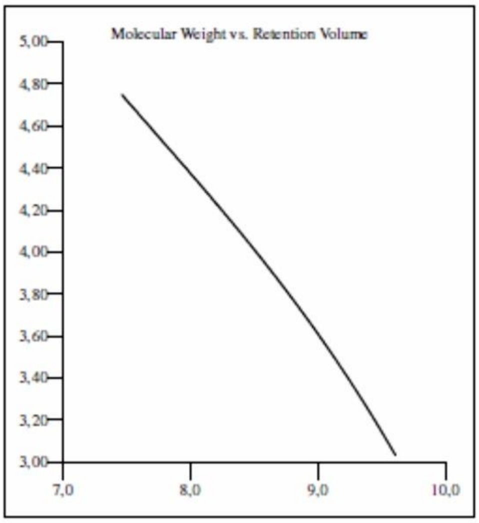
Figure S62. MALDI–TOF spectrum of PLA obtained with **1** in THF at –40°C, Table 1, entry 15. Figure 1 (—)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,060	11,200
Mn - (Daltons)	10 163	0
Mw - (Daltons)	16 413	0
Mz - (Daltons)	21 080	0
Mp - (Daltons)	21 463	0
Mw / Mn	1,615	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	3 354	0
Mw 10.0% High	32 497	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mv ml)	15,60	18,71
UV@240nm Area - (mv ml)	0,00	0,00

Annotation	
Method File	CC_RI_PS_2021-09_z_dnia_2022-01-05-0003.vcm
Limits File	
Date Acquired	Jan 14, 2022 - 12:16:54
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



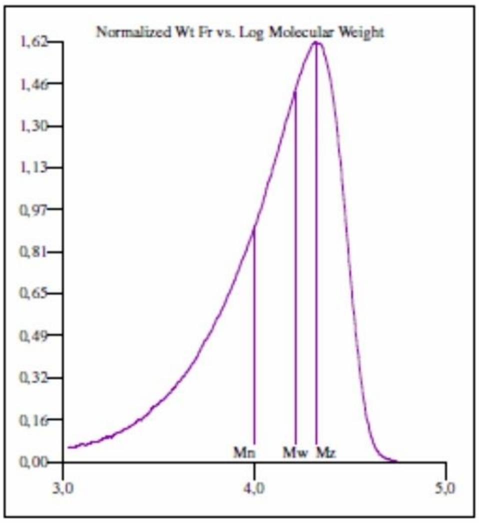
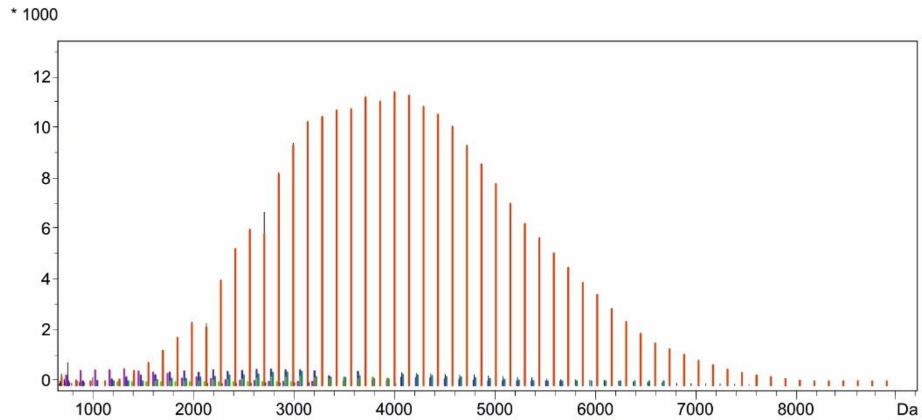


Figure S63. GPC eluogram of PLA obtained with **1** in THF at –40°C, Table 1, entry 15.

polytool Date: 08/01/2023 Time: 15:07

FileName: ...B_K_RP700-3500_P34_c25_defl0640\0_C17\1\1SRef\pdata\1\peaklist.xml
peak integrals - IG-1,1 [CHCl3]
DCTB+K RP 700-3500 Da P=34% c=25 defl=640 Da

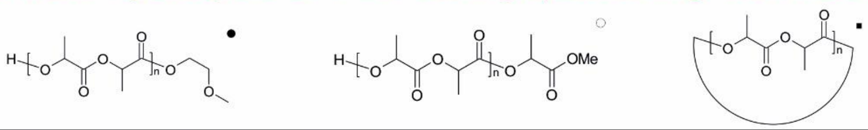


	n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
●	1	1	144.035	75.9395			38.9637	4082.78	4458.89	1.09212	28.3459	83.5	58
■	2	2	144.035	-0.37868			38.9637	2779.97	3206.80	1.15354	19.3007	3.7	35
○	3	3	144.035	3.46072			38.9637	2973.30	3104.11	1.04399	20.6430	1	17
*	4	4	144.035	18.0274			38.9637	3509.73	3966.43	1.13013	24.3673	3.4	39
	5	5	144.035	3.94192			38.9637	3577.39	3596.33	1.00529	24.8371	0.4	6
	6	6	144.035	122.220			38.9637	1548.93	1799.59	1.16183	10.7539	2	18
	7	7	144.035	56.0008			38.9637	2106.83	2239.85	1.06314	14.6272	0.4	13

Traces

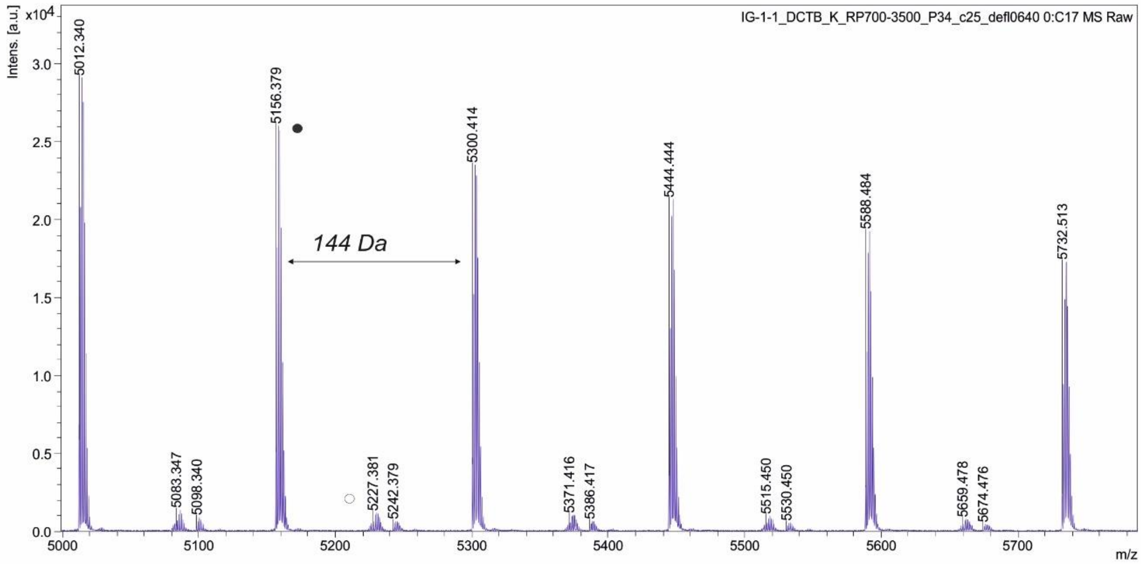
Traces

* May originate from hydrolysis of PLA during quenching with H2O/H+



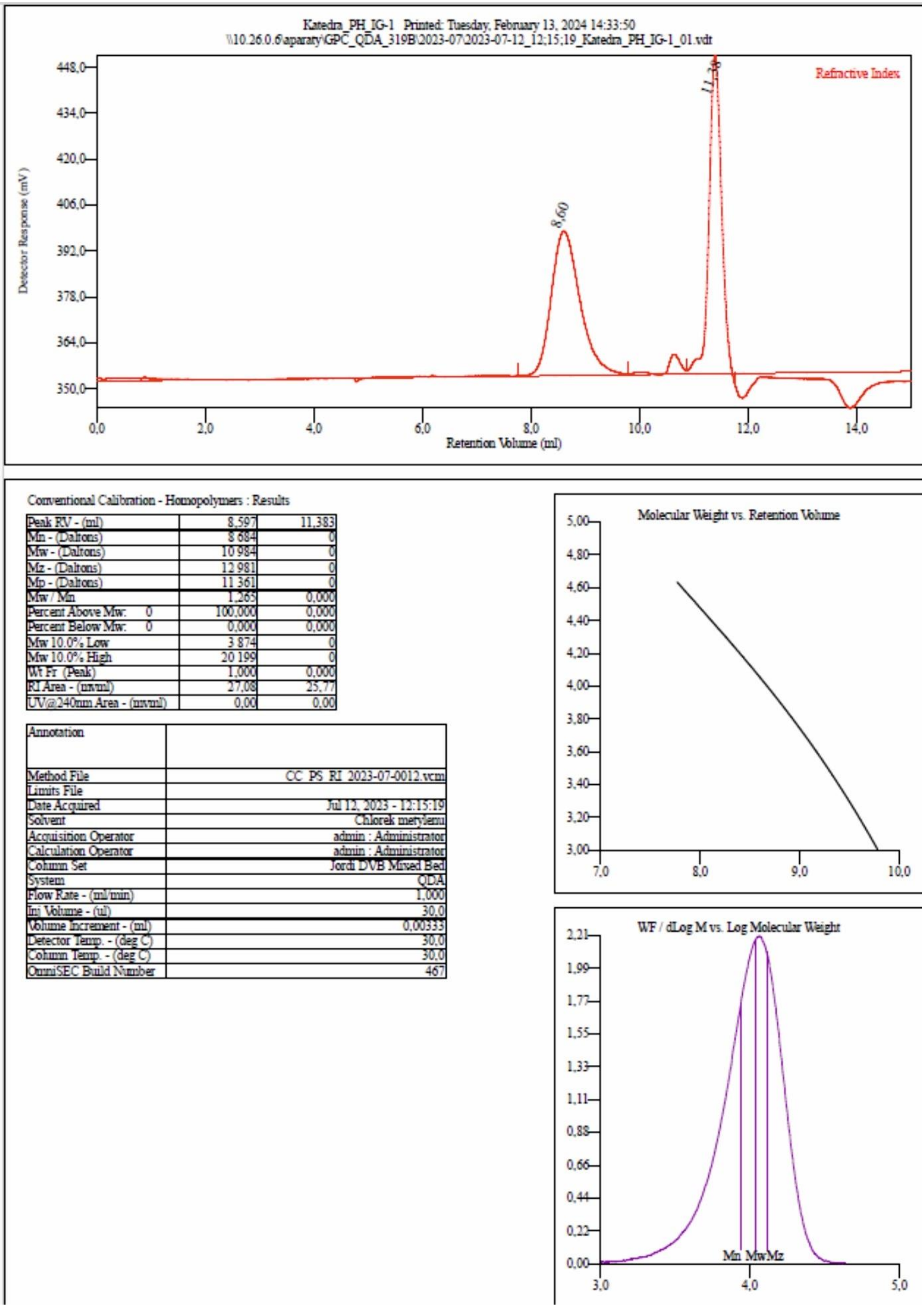
D:\Dane\Mass_Spectra\Rok_2023\Work\IG-1-1_DCTB_K_RP700-3500_P34_c25_defl0640\0_C17\1\1SRef

Comment 1 IG-1,1 [CHCl3]
Comment 2 DCTB+K RP 700-3500 Da P=34% c=25 defl=640 Da



Bruker Daltonics flexAnalysis printed: 8/1/2023 14:31:57

Figure S64. MALDI–TOF spectrum of PLA obtained with **2** in toluene at 40°C, Table 1, entry 16. Figure 2 (—)



Conventional Calibration - Homopolymers : Results

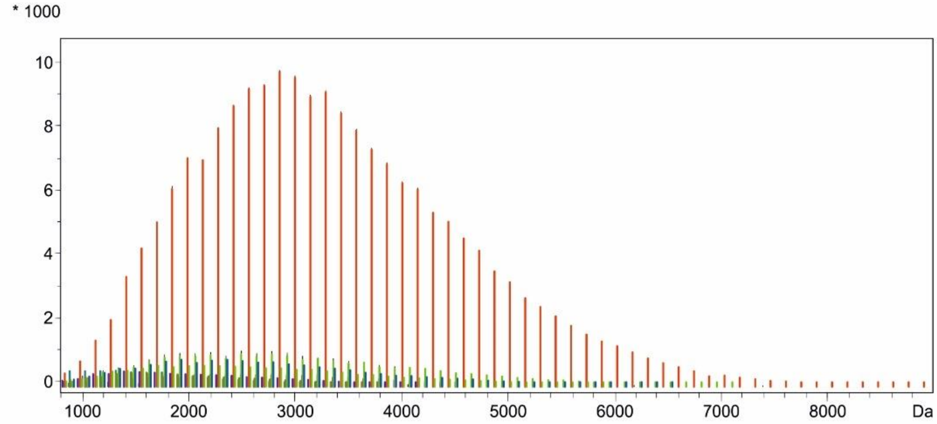
Peak RV - (ml)	8,597	11,383
Mn - (Daltons)	8 684	0
Mw - (Daltons)	10 984	0
Mz - (Daltons)	12 981	0
Mp - (Daltons)	11 361	0
Mw / Mn	1,265	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	3 874	0
Mw 10.0% High	20 199	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	27,08	25,77
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC_PS_RI_2023-07-0012.vcm
Limits File	
Date Acquired	Jul 12, 2023 - 12:15:19
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467

Figure S65. GPC eluogram of PLA obtained with **2** in toluene at 40°C, Table 1, entry 16.

polytool   Date: 08/01/2023   Time: 14:54

FileName: ...TB_K_RP700-3500_P26_c25_defl0640\0_A18\1\1SRef\pdata\1\peaklist.xml
peak integrals - DT-9,2 [CHCl3]
DCTB+K RP 700-3500 Da P=26% c=25 defl=640 Da

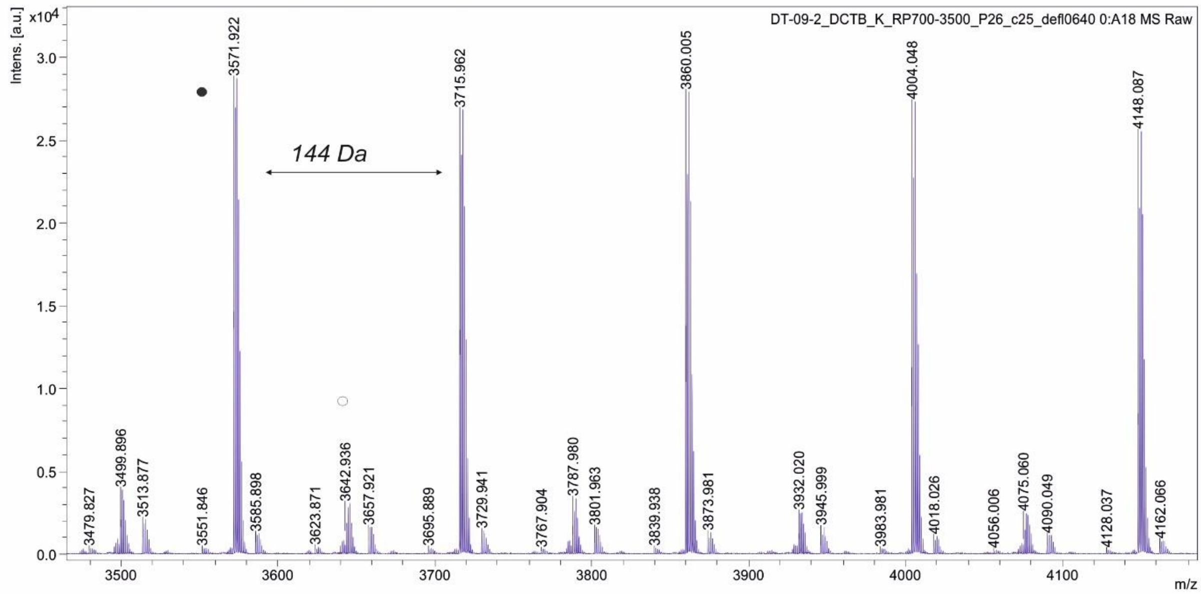


	n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt	
●	1	1	144.035	75.9827			38.9637	3304.38	3793.78	1.14811	22.9415	71.2	58	
	2	2	144.035	55.9977	Traces		38.9637	2068.46	2411.88	1.16603	14.3608	2.3	25	
	3	3	144.035	90.0547			38.9637	2693.72	3179.83	1.18046	18.7018	4.5	37	
	4	4	144.035	122.206			38.9637	1662.87	1955.05	1.17571	11.5449	2.1	20	
	5	5	144.035	128.007	Traces		38.9637	1983.68	2278.37	1.14856	13.7722	1.9	22	
	6	6	144.035	-0.28390			38.9637	2569.05	2846.84	1.10813	17.8363	2	25	
○	7	7	144.035	3.51679			38.9637	3019.85	3559.40	1.17867	20.9661	8.2	45	
	8	8	144.035	17.9662			38.9637	2773.79	3277.96	1.18176	19.2577	5.7	41	*

* May originate from hydrolysis of PLA during quenching with H2O/H+

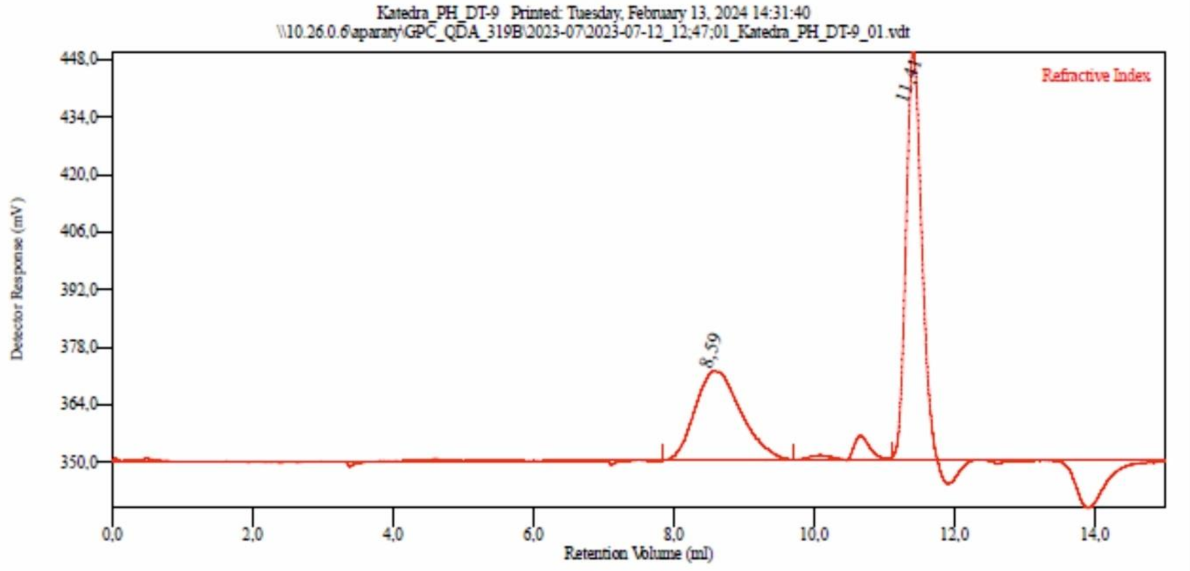
D:\Dane\Mass_Spectra\Rok_2023\Work\DT-09-2_DCTB_K_RP700-3500_P26_c25_defl0640\0_A18\1\1SRef

Comment 1   DT-9,2 [CHCl3]
Comment 2   DCTB+K RP 700-3500 Da P=26% c=25 defl=640 Da



Bruker Daltonics flexAnalysis   printed: 8/1/2023   14:20:41

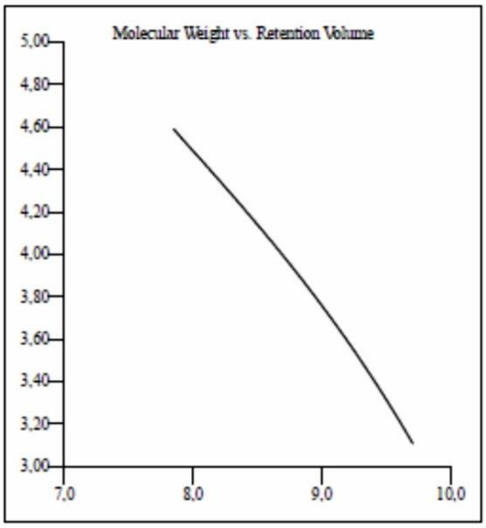
Figure S66. MALDI–TOF spectrum of PLA obtained with **2** in toluene at r.t., Table 1, entry 17. Figure 2 (—)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,590	11,407
Mn - (Daltons)	8 771	0
Mw - (Daltons)	11 717	0
Mz - (Daltons)	14 522	0
Mp - (Daltons)	11 878	0
Mw / Mn	1,336	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	3 655	0
Mw 10.0% High	23 265	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	16,52	25,61
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC_PS_RI_2023-07-0012.vcm
Limits File	
Date Acquired	Jul 12, 2023 - 12:47:01
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



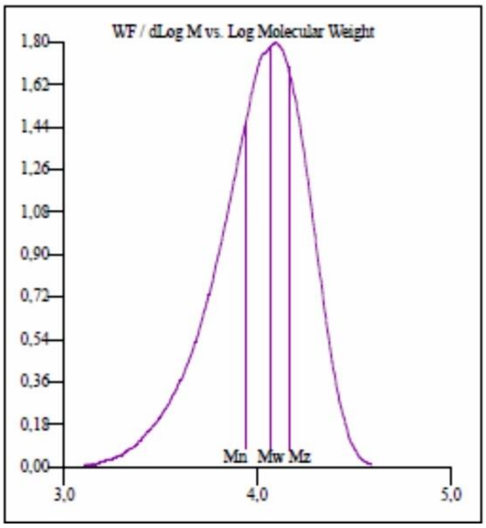
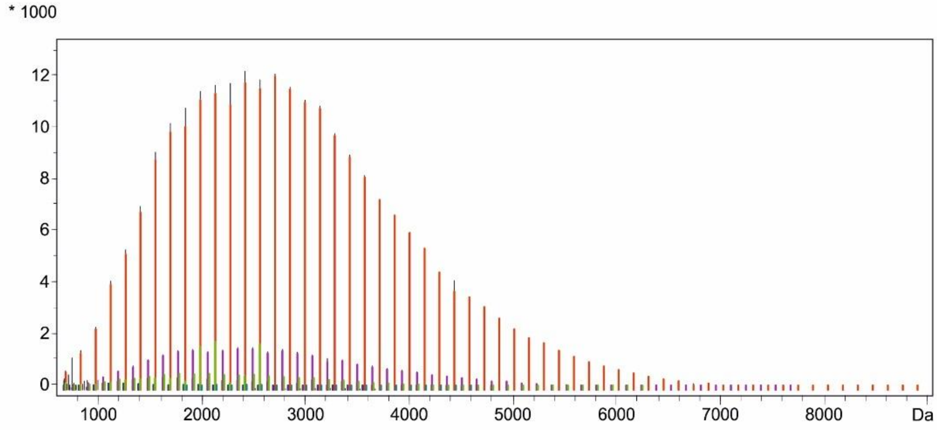


Figure S67. GPC eluogram of PLA obtained with **2** in toluene at r.t., Table 1, entry 17.

polytool Date: 08/01/2023 Time: 15:06

FileName: ...TB_K_RP700-3500_P34_c25_defl0640\0_B24\1\1SRef\pdata\1\peaklist.xml
peak integrals - DT-15,1 [CHCl3]
DCTB+K RP 700-3500 Da P=34% c=25



	n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
●	1	1	144.041	75.9214			38.9637	2882.58	3377.71	1.17177	20.0122	78	58
	2	2	144.041	55.9961			38.9637	1793.91	2106.40	1.17420	12.4542	0.9	21
■	3	3	144.041	71.6743			38.9637	1669.40	1838.30	1.10118	11.5898	1.3	14
	4	4	144.041	89.9821			38.9637	2914.65	3119.45	1.07026	20.2349	0.6	20
■	5	5	144.041	-0.10421			38.9637	2258.30	2676.31	1.18510	15.6782	2.1	29
○	6	6	144.041	3.84777			38.9637	2829.32	3344.32	1.18202	19.6425	10	49
	7	7	144.041	18.0425			38.9637	2596.87	3085.59	1.18819	18.0287	3.6	39

Traces

Traces may originate from hydrolysis of PLA during quenching with H2O/H+

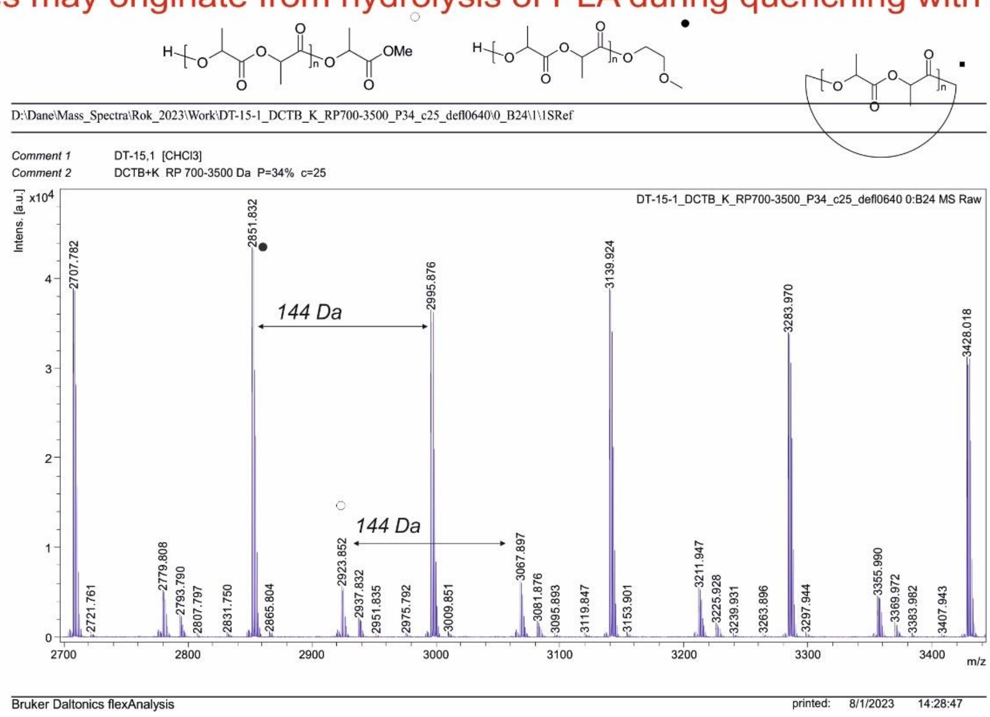
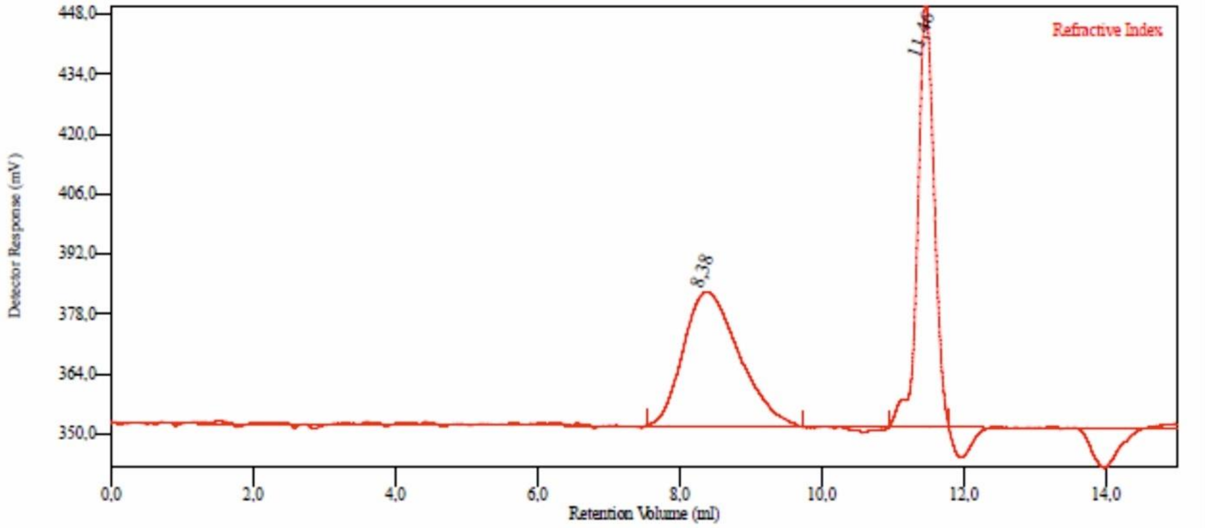


Figure S68. MALDI–TOF spectrum of PLA obtained with **2** in toluene at 0°C, Table 1, entry 20. Figure 2 (▬)

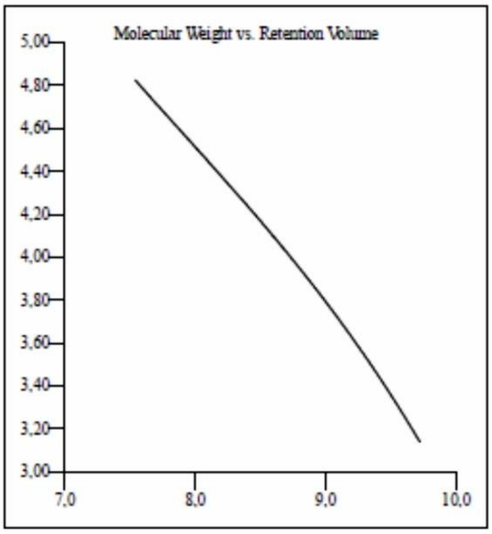
Katedra_PH_DT-15 Printed: Tuesday, February 13, 2024 13:57:34
\\10.26.0.6\aparaty\GPC_QDA_319B\2023-07\2023-07-12_14;06;15_Katedra_PH_DT-15_01.vdt



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,377	11,460
Mn - (Daltons)	11 860	0
Mw - (Daltons)	17 462	0
Mz - (Daltons)	22 973	0
Mp - (Daltons)	17 959	0
Mw / Mn	1,472	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	4 480	0
Mw 10.0% High	37 854	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	28,52	26,54
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC_PS_RI_2023-07-0012.vcm
Limits File	
Date Acquired	Jul 12, 2023 - 14:06:15
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



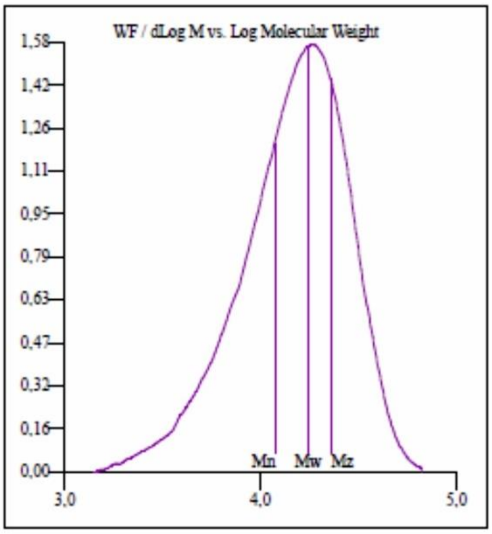
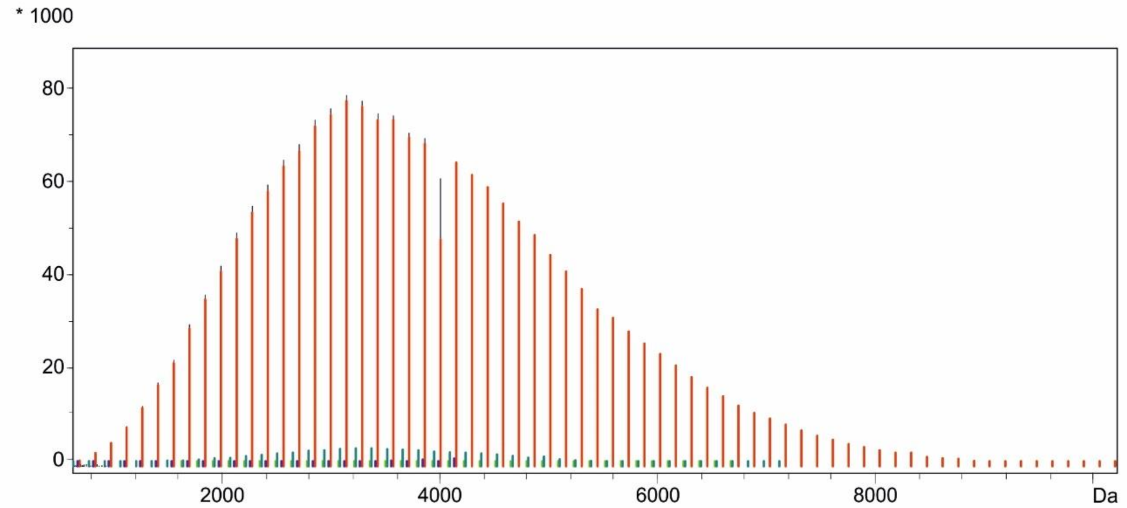


Figure S69. GPC eluogram of PLA obtained with **2** in toluene at 0°C, Table 1, entry 20.

polytool Date: 12/06/2022 Time: 20:07

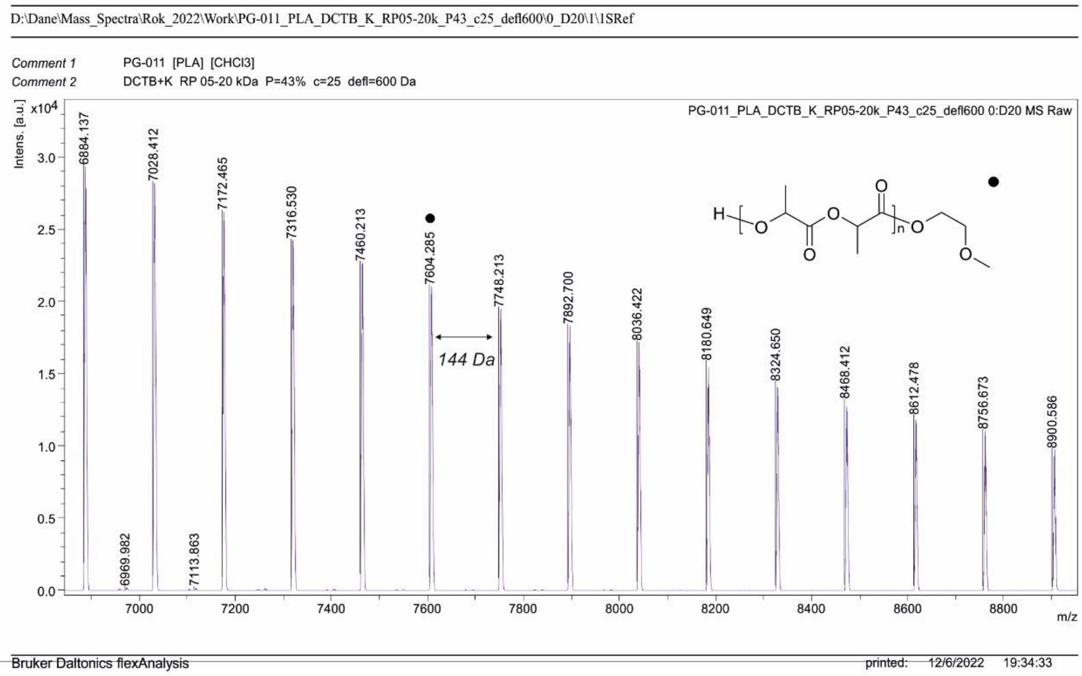
FileName: ...DCTB_K_RP05-20k_P43_c25_defl600\0_D20\1\1SRef\pdata\1\peaklist.xml
peak integrals - PG-011 [PLA] [CHCl3]
DCTB+K RP 05-20 kDa P=43% c=25 defl=600 Da



n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
• 1	1	144.042	75.5290			38.9637	3844.87	4436.29	1.15382	26.6927	94	73
2	2	144.042	55.7392			38.9637	2267.64	2661.64	1.17375	15.7429	0.2	25
3	3	144.042	2.65078			38.9637	3806.54	4109.31	1.07954	26.4265	0.6	36
4	4	144.042	17.5127			38.9637	3408.24	3797.83	1.11431	23.6614	3.7	46

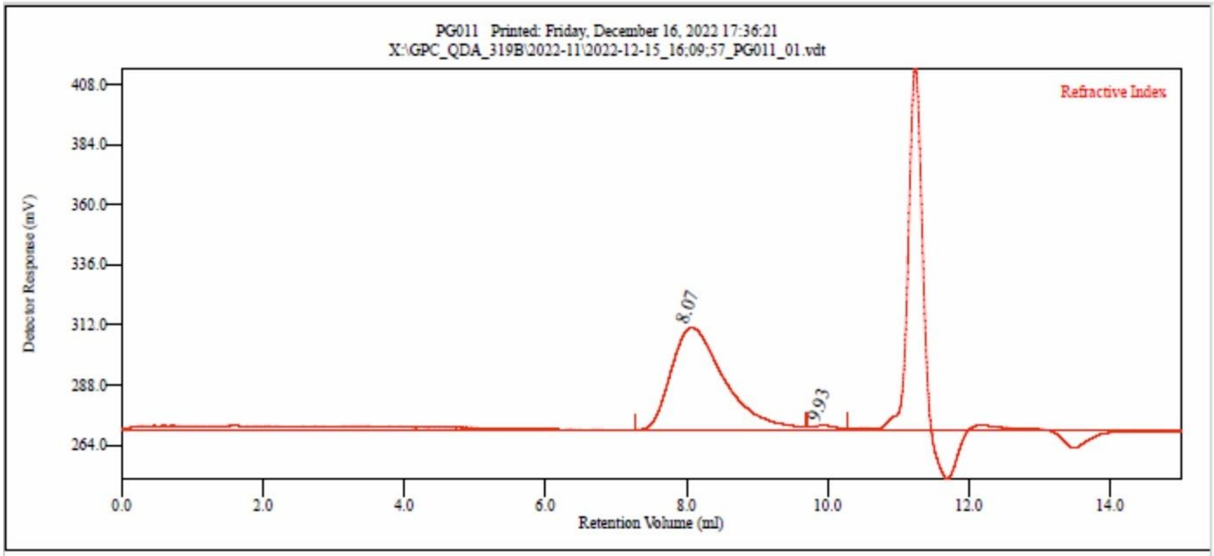
Traces

May originate from hydrolysis of PLA during quenching with H2O/H+



page 1 of 1

Figure S70. MALDI–TOF spectrum of PLA obtained with **2** in toluene at –20°C, Table 1, entry 23. Figure 2 (▬)

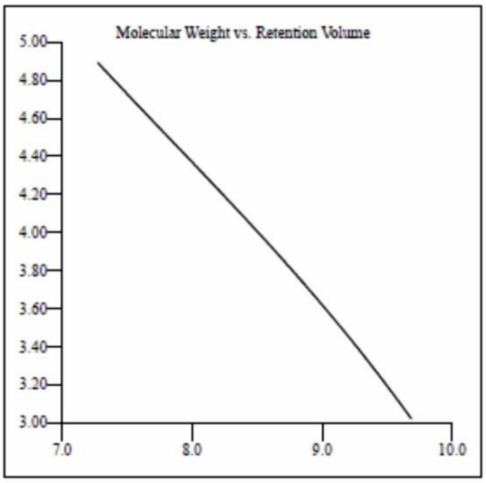


Warning: No flow rate marker was found.

Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8.067	9.930
Mn - (Daltons)	11,462	531
Mw - (Daltons)	18,907	598
Mz - (Daltons)	24,918	662
Mp - (Daltons)	20,910	606
Mw / Mn	1.649	1.125
Percent Above Mw: 0	100.000	100.000
Percent Below Mw: 0	0.000	0.000
Mw 10.0% Low	3,846	301
Mw 10.0% High	40,167	954
Wt Fr (Peak)	0.979	0.021
RI Area - (mvml)	35.86	0.79
UV@240nm Area - (mvml)	0.00	0.00

Annotation	
Method File	CC_RI_PS_11-2022-0003-MLtry-0001.vcm
Limits File	
Date Acquired	Dec 15, 2022 - 16:09:57
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	50.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	30.0
Column Temp. - (deg C)	30.0
OmniSEC Build Number	467



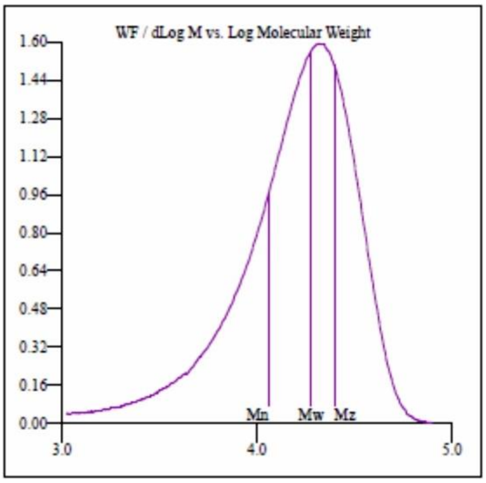
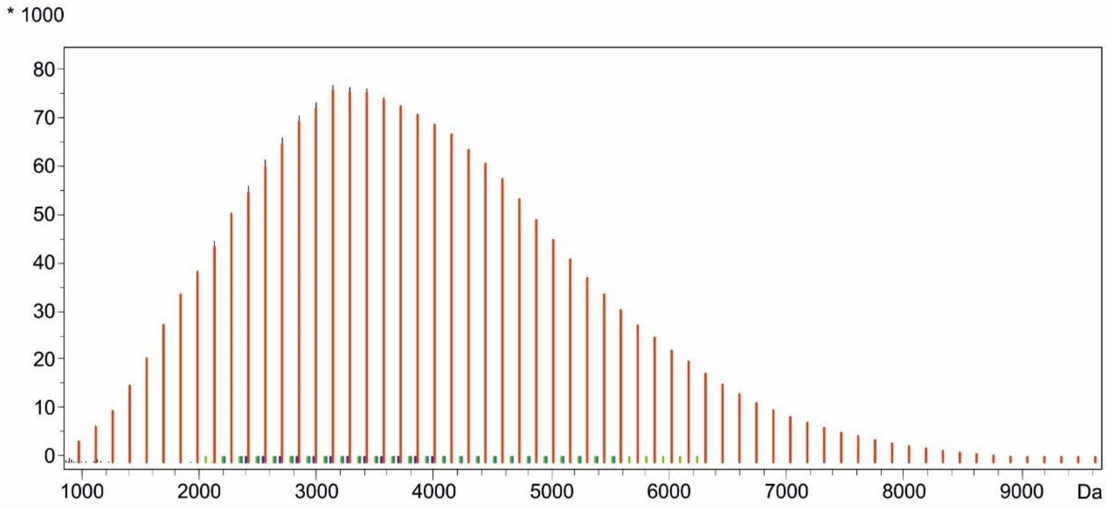


Figure S71. GPC eluogram of PLA obtained with **2** in toluene at –20°C, Table 1, entry 23.

polytool Date: 12/06/2022 Time: 20:08

FileName: ...DCTB_K_RP05-20k_P42_c25_defl600\0_E17\1\1SRef\pdata\1\peaklist.xml
peak integrals - PG-012 [PLA] [CHCl3]
DCTB+K RP 05-20 kDa P=42% c=25 defl=600 Da

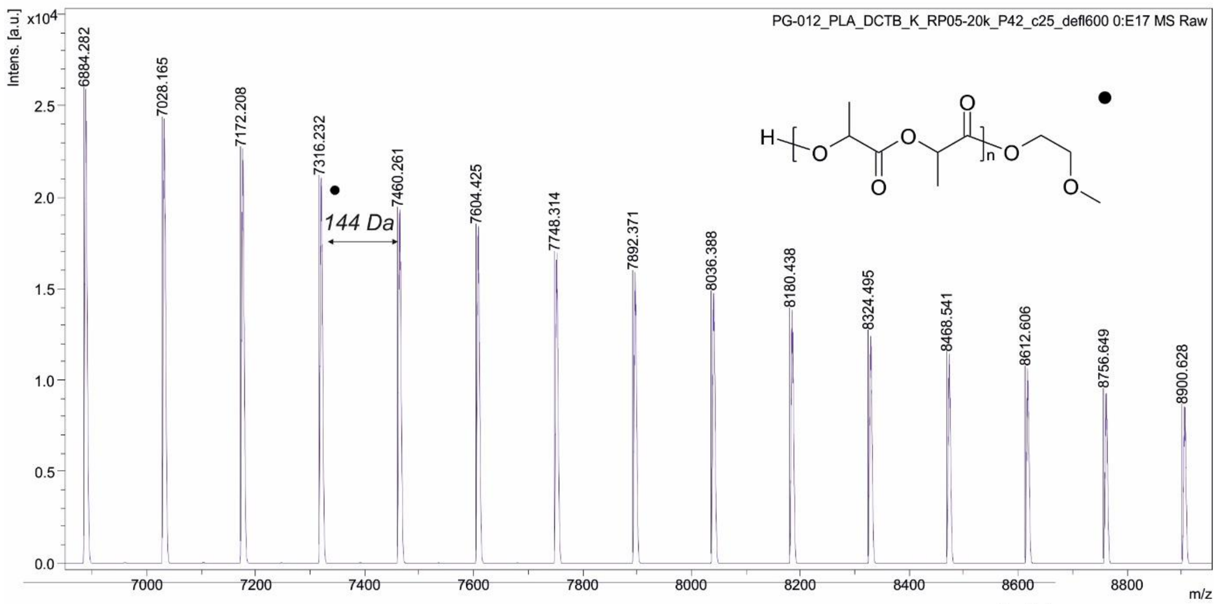


n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
• 1	1	144.042	75.4831			38.9637	3868.03	4436.31	1.14692	26.8535	98.8	73
2	2	144.042	55.4497			38.9637	3063.35	3133.94	1.02304	21.2670	0	12
3	3	144.042	2.88355			38.9637	3899.12	4142.38	1.06239	27.0692	0.3	30
4	4	144.042	17.4573			38.9637	3663.47	3874.31	1.05755	25.4333	0.1	24

Traces

D:\Dane\Mass_Spectra\Rok_2022\Work\PG-012_PLA_DCTB_K_RP05-20k_P42_c25_defl600\0_E17\1\1SRef

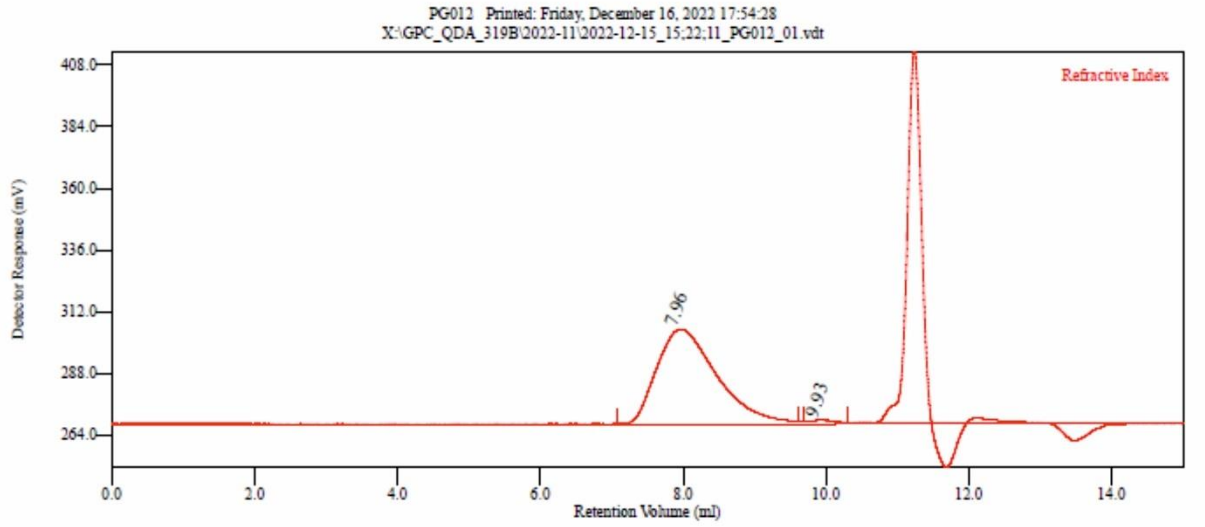
Comment 1 PG-012 [PLA] [CHCl3]
Comment 2 DCTB+K RP 05-20 kDa P=42% c=25 defl=600 Da



page 1 of 1

Bruker Daltonics flexAnalysis printed: 12/6/2022 19:25:43

Figure S72. MALDI–TOF spectrum of PLA obtained with **2** in toluene at –40°C, Table 1, entry 26. Figure 2 (▬)

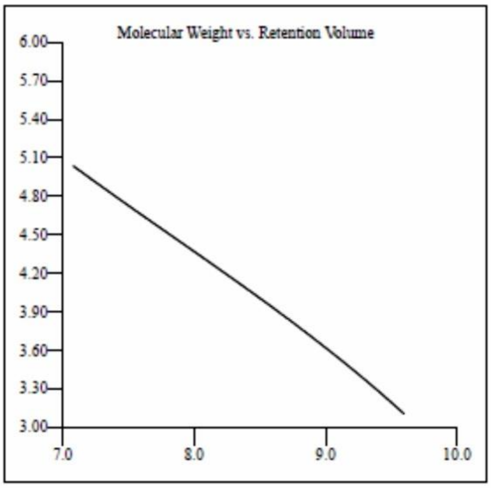


Warning: No flow rate marker was found.

Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	7.960	9.930
Mn - (Daltons)	13,877	524
Mw - (Daltons)	23,402	596
Mz - (Daltons)	31,934	666
Mp - (Daltons)	24,933	604
Mw / Mn	1.686	1.139
Percent Above Mw: 0	100.000	100.000
Percent Below Mw: 0	0.000	0.000
Mw 10.0% Low	4,650	286
Mw 10.0% High	52,682	970
Wt Fr (Peak)	0.983	0.017
RI Area - (mvml)	35.88	0.62
UV@240nm Area - (mvml)	0.00	0.00

Annotation	
Method File	CC_RI_PS_11-2022-0003-MLtry-0001.vcm
Limits File	
Date Acquired	Dec 15, 2022 - 15:22:11
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	50.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	30.0
Column Temp. - (deg C)	30.0
OmniSEC Build Number	467



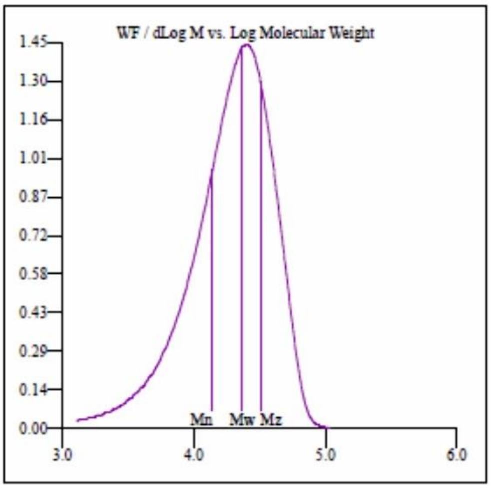
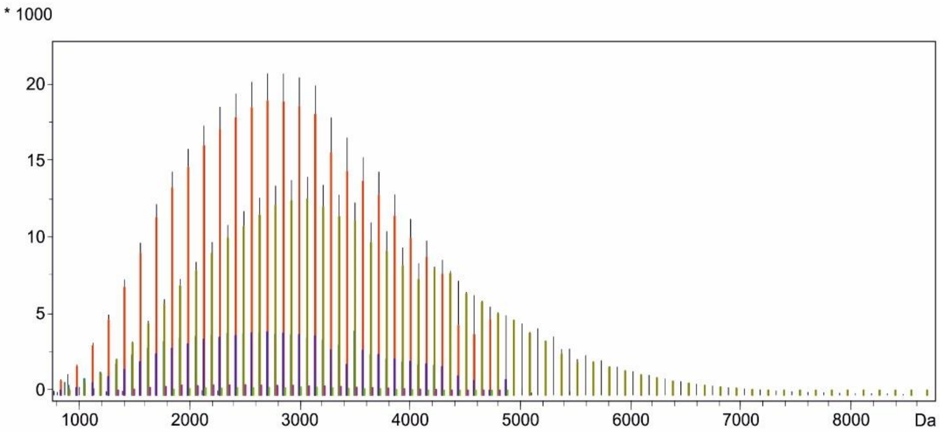


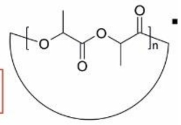
Figure S73. GPC eluogram of PLA obtained with **2** in toluene at –40°C, Table 1, entry 26.

polytool Date: 08/01/2023 Time: 15:02

FileName: ...TB_K_RP700-3500_P38_c25_defl0640\0_B16\1\1SRef\pdata\1\peaklist.xml
peak integrals - DT-13,2 [CHCl3]
DCTB+K RP 700-3500 Da P=38% c=25 defl=640 Da



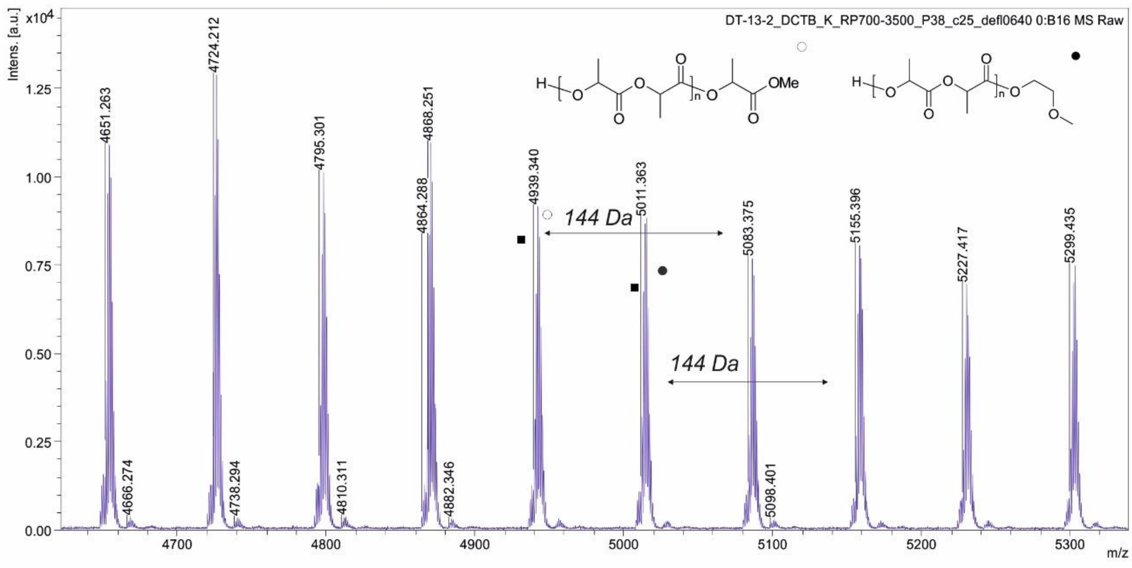
	n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
●	1	1	144.028	75.8146			38.9637	2834.07	3113.20	1.09849	19.6772	43.7	29
■	2	2	144.028	72.4182			38.9637	2869.62	3194.81	1.11332	19.9241	6.9	30
	3	3	144.028	90.2888	Traces		38.9637	3101.55	3316.81	1.06940	21.5343	0.9	22
■	4	4	144.028	0.08505			38.9637	2536.12	2798.01	1.10326	17.6085	8.3	25
○	5	5	144.028	3.68096			38.9637	3359.63	3778.97	1.12482	23.3262	32.6	55
	6	6	144.028	18.2493			38.9637	2824.67	3106.02	1.09960	19.6119	1.3	25 *



* May originate from hydrolysis of PLA during quenching with H2O/H+

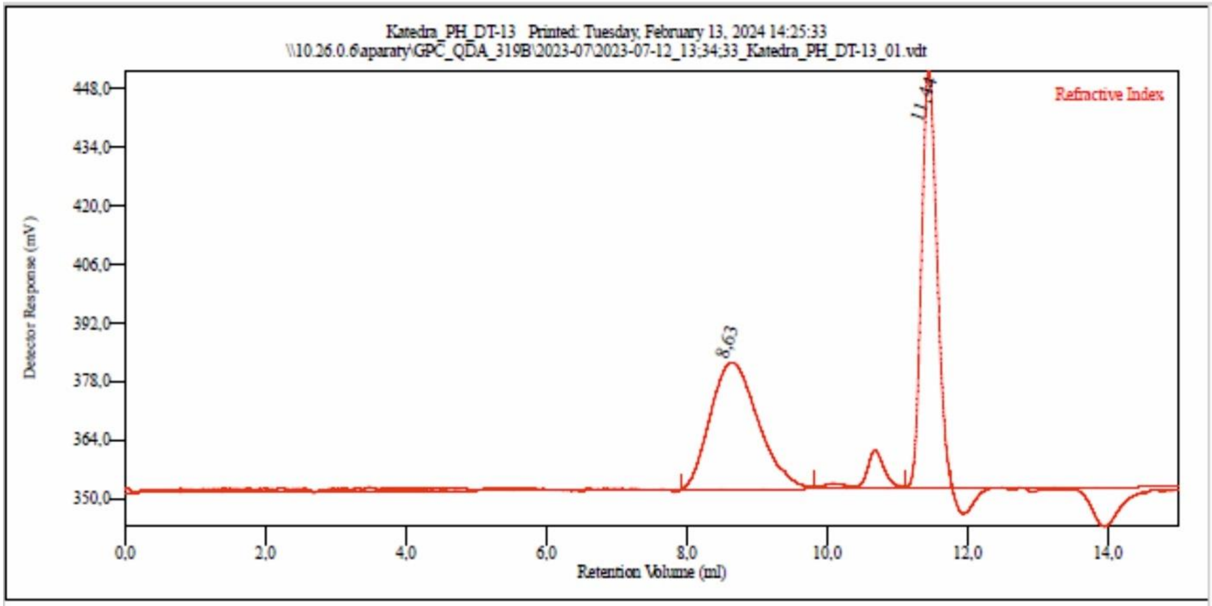
D:\Dane\Mass_Spectra\Rok_2023\Work\DT-13-2_DCTB_K_RP700-3500_P38_c25_defl0640\0_B16\1\1SRef

Comment 1 DT-13,2 [CHCl3]
Comment 2 DCTB+K RP 700-3500 Da P=38% c=25 defl=640 Da



Bruker Daltonics flexAnalysis printed: 8/1/2023 14:24:41

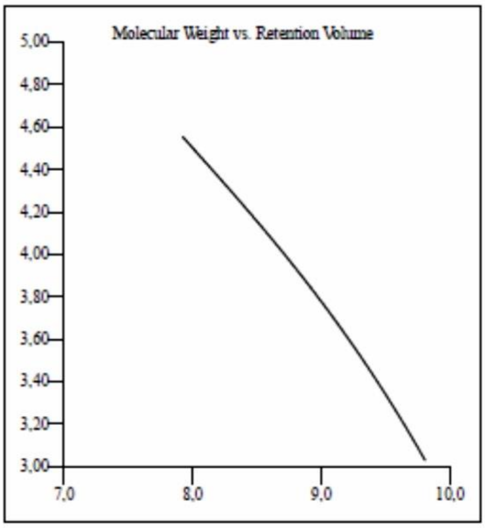
Figure S74. MALDI–TOF spectrum of PLA obtained with **2** in CH_2Cl_2 at r.t., Table 1, entry 18. Figure 2 (▬)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,633	11,437
Mn - (Daltons)	8 295	0
Mw - (Daltons)	11 439	0
Mz - (Daltons)	14 370	0
Mp - (Daltons)	11 428	0
Mw / Mn	1,379	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	3 351	0
Mw 10.0% High	23 174	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	23,97	25,57
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC PS RI 2023-07-0012.vcm
Limits File	
Date Acquired	Jul 12, 2023 - 13:34:33
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



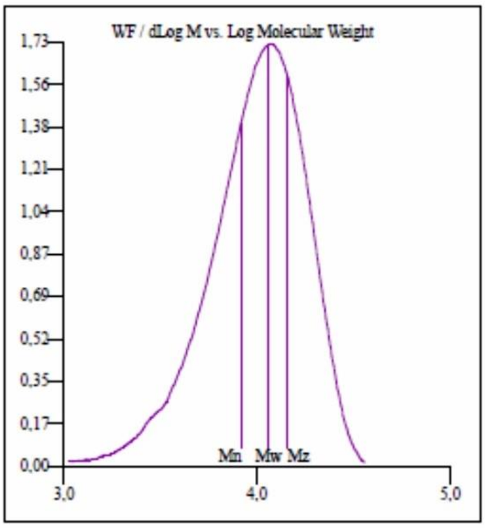
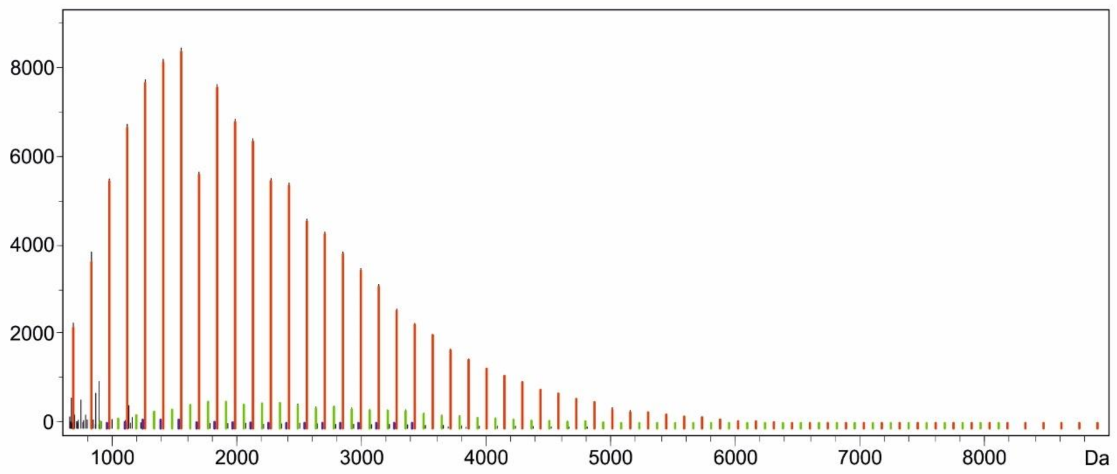


Figure S75. GPC eluogram of PLA obtained with **2** in CH_2Cl_2 at r.t., Table 1, entry 18.

polytool Date: 08/01/2023 Time: 14:56

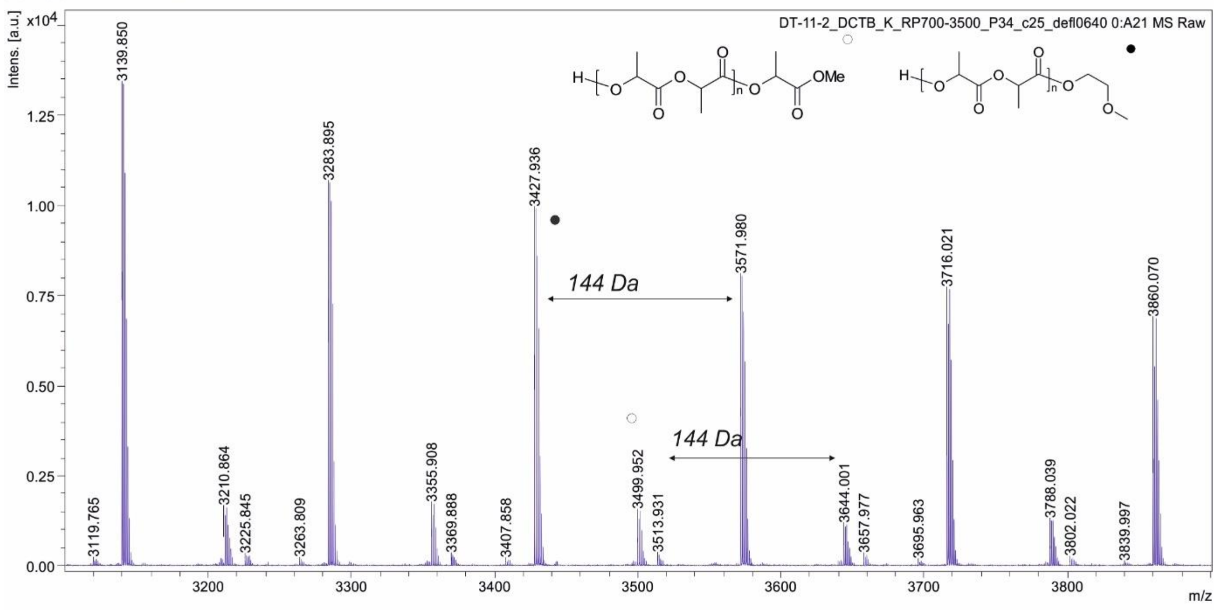
FileName: ...TB_K_RP700-3500_P34_c25_defl0640\0_A21\1\1SRef\pdata\1\peaklist.xml
peak integrals - DT-11,2 [CHCl3]
DCTB+K RP 700-3500 Da P=34% c=25 defl=640 Da



n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
● 1	1	144.033	75.9157			38.9637	2208.41	2802.67	1.26909	15.3327	81.8	58
2	2	144.033	56.0530	Traces		38.9637	1911.17	2157.42	1.12885	13.2690	1.3	18
○ 3	3	144.033	3.81902			38.9637	2956.59	3609.83	1.22095	20.5272	7.6	51

D:\Dane\Mass_Spectra\Rok_2023\Work\DT-11-2_DCTB_K_RP700-3500_P34_c25_defl0640\0_A21\1\1SRef

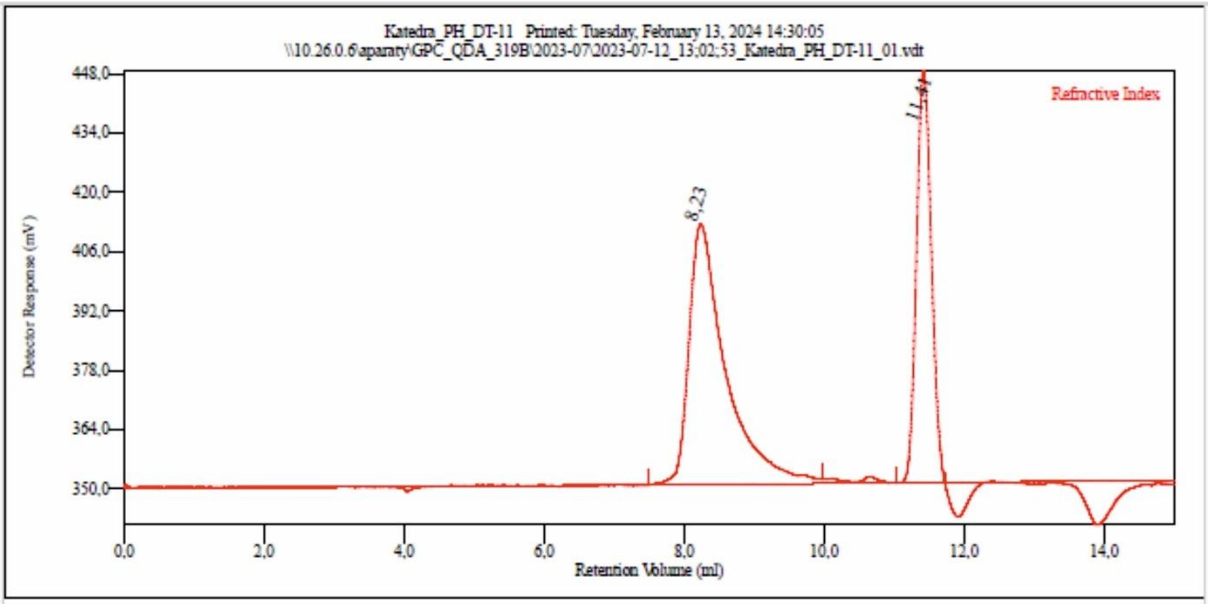
Comment 1 DT-11,2 [CHCl3]
Comment 2 DCTB+K RP 700-3500 Da P=34% c=25 defl=640 Da



Bruker Daltonics flexAnalysis printed: 8/1/2023 14:22:11

page 1 of 1

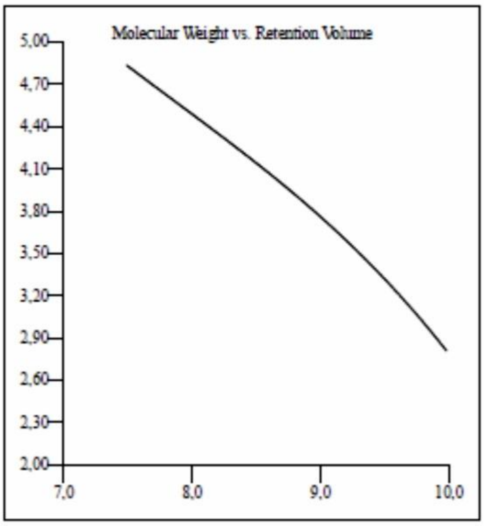
Figure S76. MALDI–TOF spectrum of PLA obtained with **2** in CH_2Cl_2 at 0ºC, Table 1, entry 21. Figure 2 (**—**)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,233	11,410
Mn - (Daltons)	10 702	0
Mw - (Daltons)	17 304	0
Mz - (Daltons)	20 995	0
Mp - (Daltons)	21 342	0
Mw / Mn	1,617	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	3 666	0
Mw 10.0% High	31 123	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	37,39	23,93
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC PS RI 2023-07-0012.vcm
Limits File	
Date Acquired	Jul 12, 2023 - 13:02:53
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



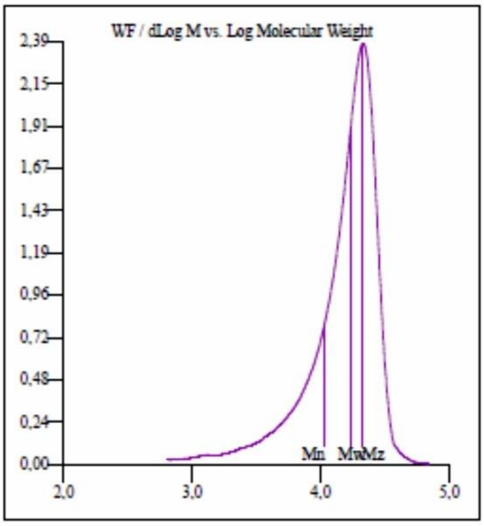
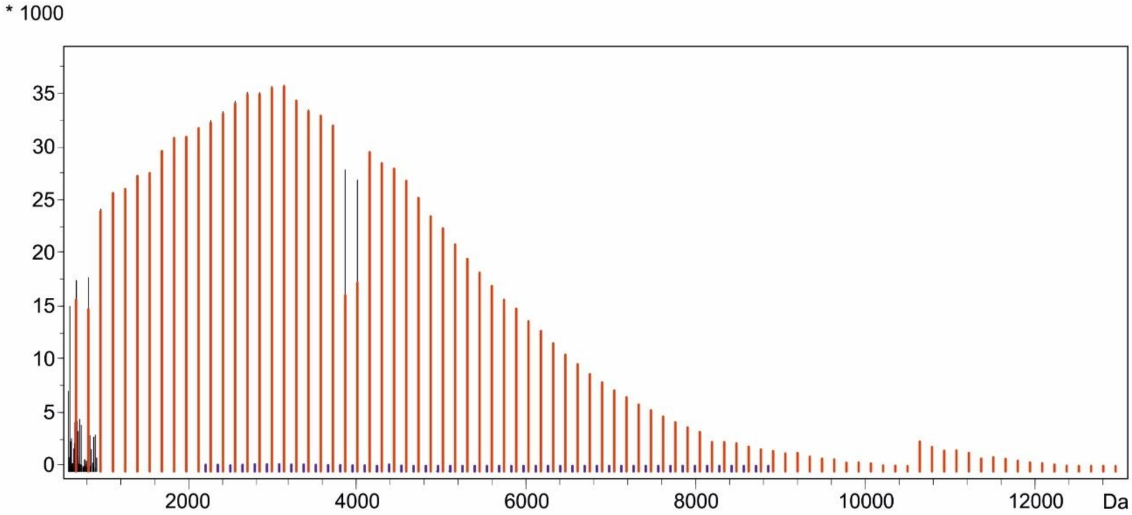


Figure S77. GPC eluogram of PLA obtained with **2** in CH_2Cl_2 at 0°C, Table 1, entry 21.

polytool Date: 12/06/2022 Time: 20:03

FileName: ...DCTB_K_RP05-20k_P45_c25_defl600\0_D14\1\1SRef\pdata\1\peaklist.xml
peak integrals - PG-009 [PLA] [CHCl3]
DCTB+K RP 05-20 kDa P=45% c=25 defl=600 Da

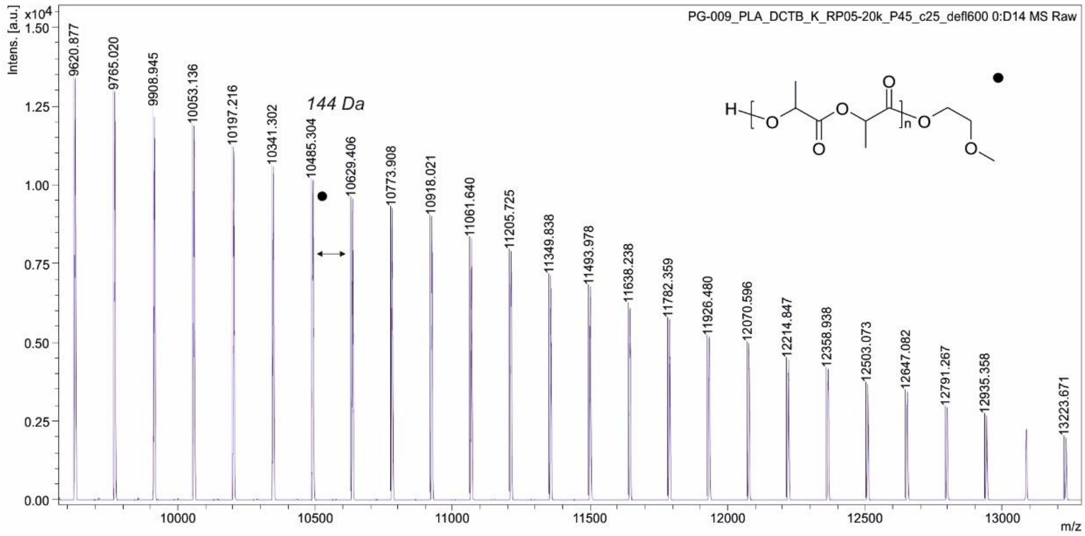


n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
• 1	1	144.042	75.6169			38.9637	3756.79	4953.89	1.31865	26.0812	90.2	86
2	2	144.042	17.1469			38.9637	4428.09	4860.22	1.09759	30.7416	1	47

May originate from hydrolysis of PLA during quenching with H2O/H+

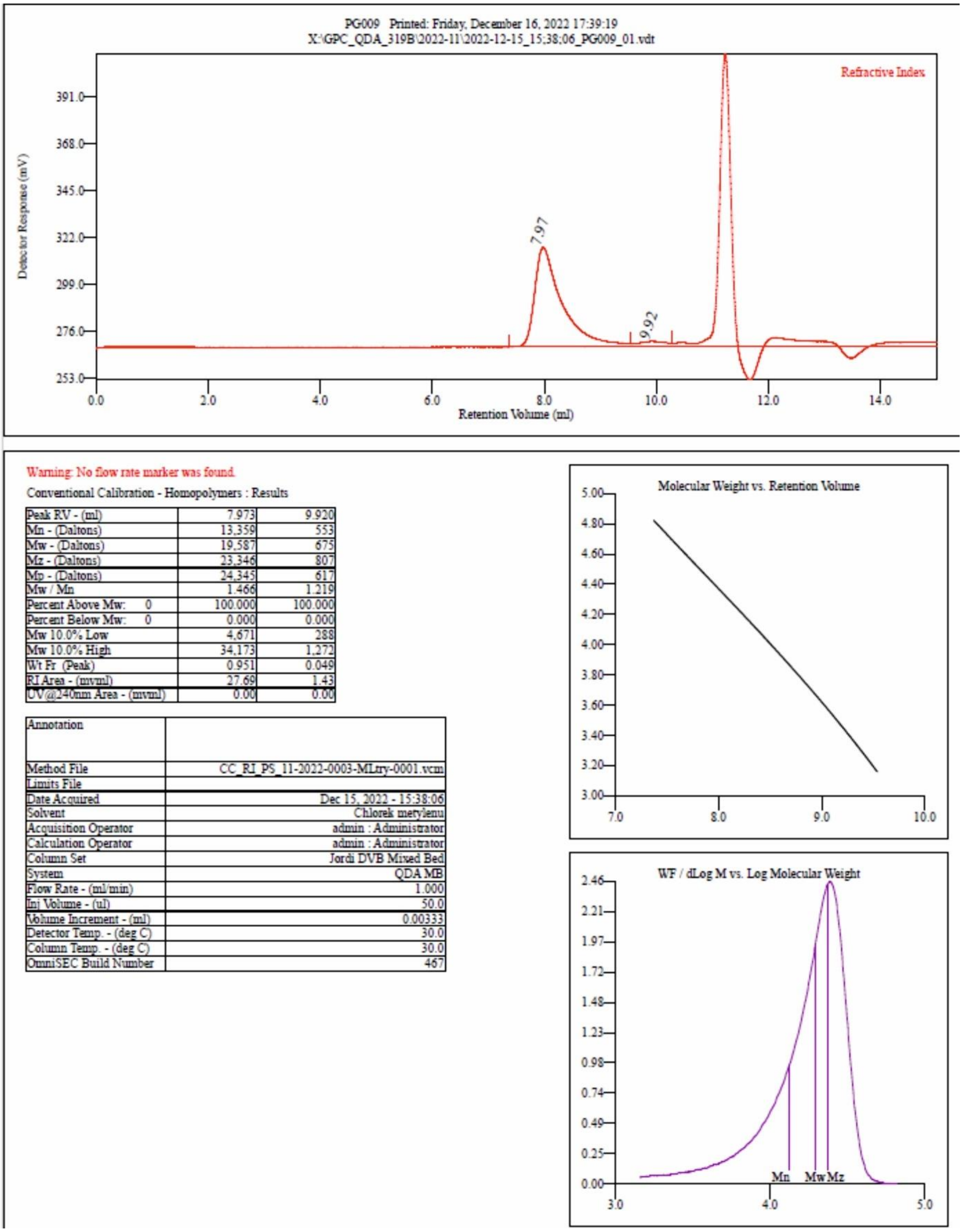
D:\Dane\Mass_Spectra\Rok_2022\Work\PG-009_PLA_DCTB_K_RP05-20k_P45_c25_defl600\0_D14\1\1SRef

Comment 1 PG-009 [PLA] [CHCl3]
Comment 2 DCTB+K RP 05-20 kDa P=45% c=25 defl=600 Da



Bruker Daltonics flexAnalysis printed: 12/6/2022 19:18:52

Figure S78. MALDI–TOF spectrum of PLA obtained with **2** in CH_2Cl_2 at –20°C, Table 1, entry 24. Figure 2 (▬)



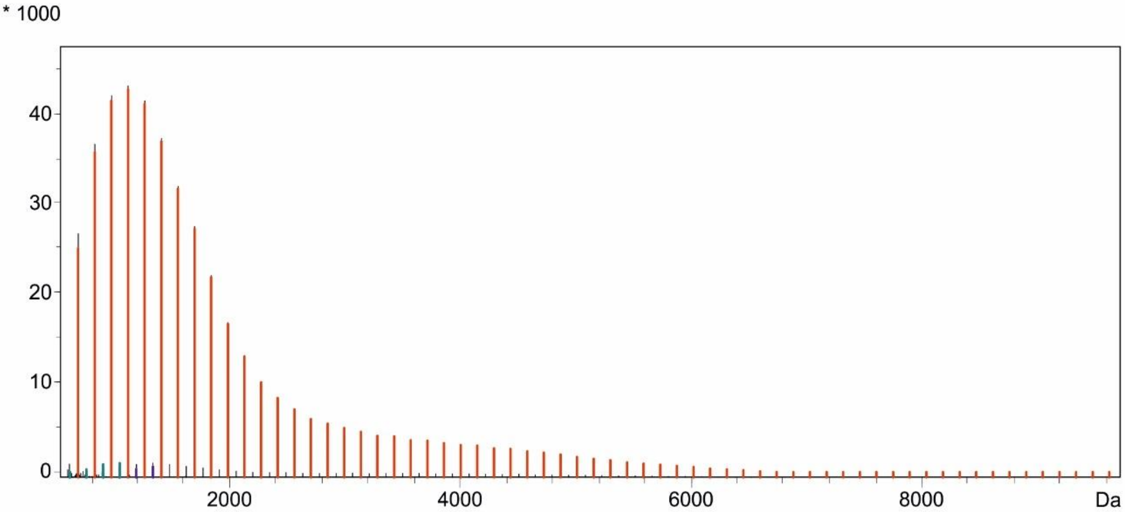
Peak RV - (ml)	7.973	9.920
Mn - (Daltons)	13,359	553
Mw - (Daltons)	19,587	675
Mz - (Daltons)	23,346	807
Mp - (Daltons)	24,345	617
Mw / Mn	1.466	1.219
Percent Above Mw: 0	100.000	100.000
Percent Below Mw: 0	0.000	0.000
Mw 10.0% Low	4,671	288
Mw 10.0% High	34,173	1,272
Wt Fr (Peak)	0.951	0.049
RI Area - (mvml)	27.69	1.43
UV@240nm Area - (mvml)	0.00	0.00

Annotation	
Method File	CC_RI_PS_11-2022-0003-MLtry-0001.vcm
Limits File	
Date Acquired	Dec 15, 2022 - 15:38:06
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	50.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	30.0
Column Temp. - (deg C)	30.0
OmniSEC Build Number	467

Figure S79. GPC eluogram of PLA obtained with **2** in CH_2Cl_2 at –20°C, Table 1, entry 24.

polytool Date: 12/06/2022 Time: 20:10

FileName: ...DCTB_K_RP05-20k_P43_c25_defl600\0_E20\1\1SRef\pdata\1\peaklist.xml
peak integrals - PG-013 [PLA] [CHCl3]
DCTB+K RP 05-20 kDa P=43% c=25 defl=600 Da



n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
• 1	1	144.042	75.5111			38.9637	1880.46	2770.85	1.47349	13.0549	92.8	63
2	2	144.042	3.29811			38.9637	1146.90	1172.95	1.02272	7.96226	0.8	6
3	2	144.042	2.75935			38.9637	712.087	723.536	1.01608	4.94360	0	3
4	2	144.042	3.97660			38.9637	865.401	887.775	1.02585	6.00796	0.9	4

Traces

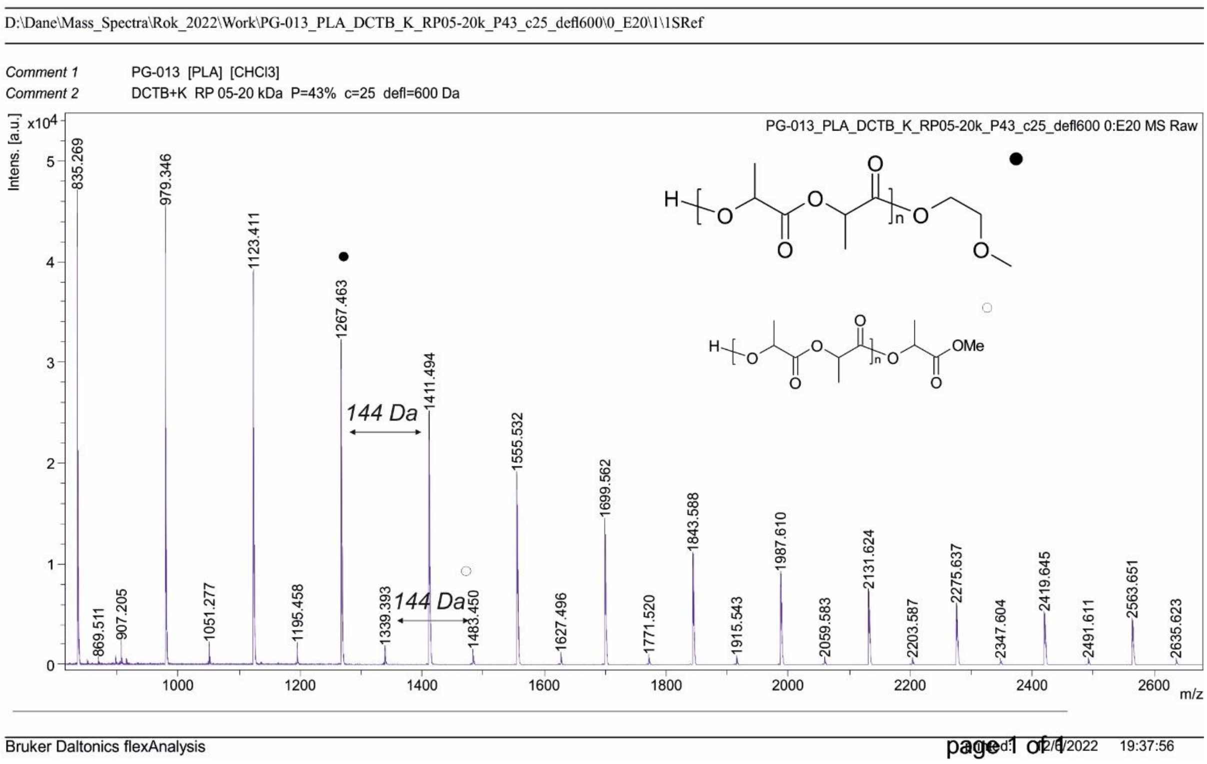
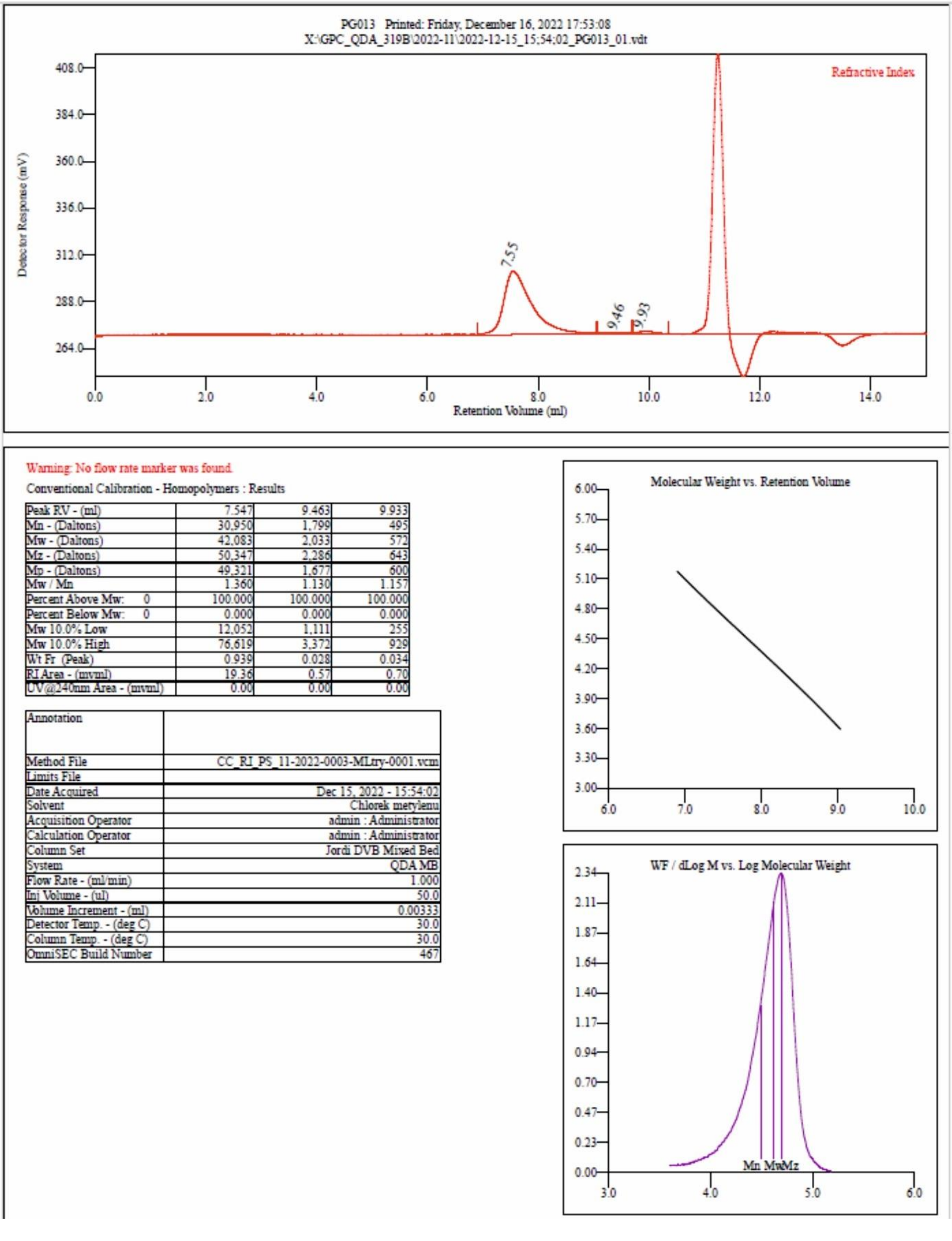


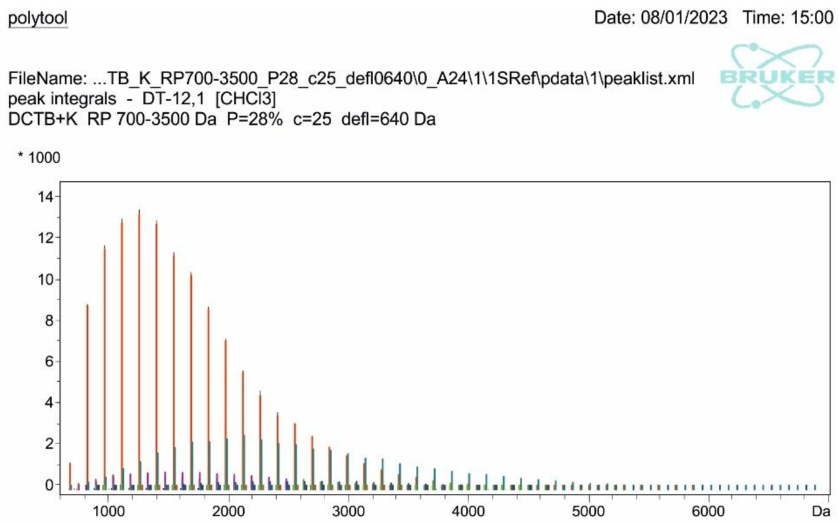
Figure S80. MALDI–TOF spectrum of PLA obtained with **2** in CH_2Cl_2 at –40°C, Table 1, entry 27. Figure 2 (—)



Peak RV - (ml)	7.547	9.463	9.933
Mn - (Daltons)	30,950	1,799	495
Mw - (Daltons)	42,083	2,033	572
Mz - (Daltons)	50,347	2,286	643
Mp - (Daltons)	49,321	1,677	600
Mw / Mn	1.360	1.130	1.157
Percent Above Mw: 0	100.000	100.000	100.000
Percent Below Mw: 0	0.000	0.000	0.000
Mw 10.0% Low	12,052	1,111	255
Mw 10.0% High	76,619	3,372	929
Wt Fr (Peak)	0.939	0.028	0.034
RI Area - (mvml)	19.36	0.57	0.70
UV@240nm Area - (mvml)	0.00	0.00	0.00

Annotation	
Method File	CC_RI_PS_11-2022-0003-MLtry-0001.vcm
Limits File	
Date Acquired	Dec 15, 2022 - 15:54:02
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	50.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	30.0
Column Temp. - (deg C)	30.0
OmniSEC Build Number	467

Figure S81. GPC eluogram of PLA obtained with **2** in CH_2Cl_2 at –40°C, Table 1, entry 27.



n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
1	1	144.040	66.1240			38.9637	1613.83	1900.26	1.17748	11.2041	63.5	37
2	2	144.040	55.9850	Traces		38.9637	1792.59	1971.94	1.10005	12.4451	0.5	16
3	3	144.040	59.8062			38.9637	2443.11	2772.69	1.13490	16.9614	0.7	25
4	4	144.040	76.0859			38.9637	2605.89	3064.70	1.17607	18.0914	20.6	47
5	5	144.040	136.846			38.9637	1973.39	2469.53	1.25141	13.7003	3.9	32
6	5	144.040	138.242			38.9637	1625.56	1761.85	1.08384	11.2855	4.1	13
7	6	144.040	-0.05486	Traces		38.9637	1950.22	2106.92	1.08035	13.5395	0.5	15
8	7	144.040	3.79145			38.9637	3047.74	3504.34	1.14982	21.1590	3.8	42
9	8	144.040	17.8703			38.9637	2417.31	2763.52	1.14322	16.7823	0.8	27 *
10	9	144.040	89.8719			38.9637	2225.74	2397.51	1.07717	15.4523	0.3	16

* Traces may originate from hydrolysis of PLA during quenching with H2O/H+

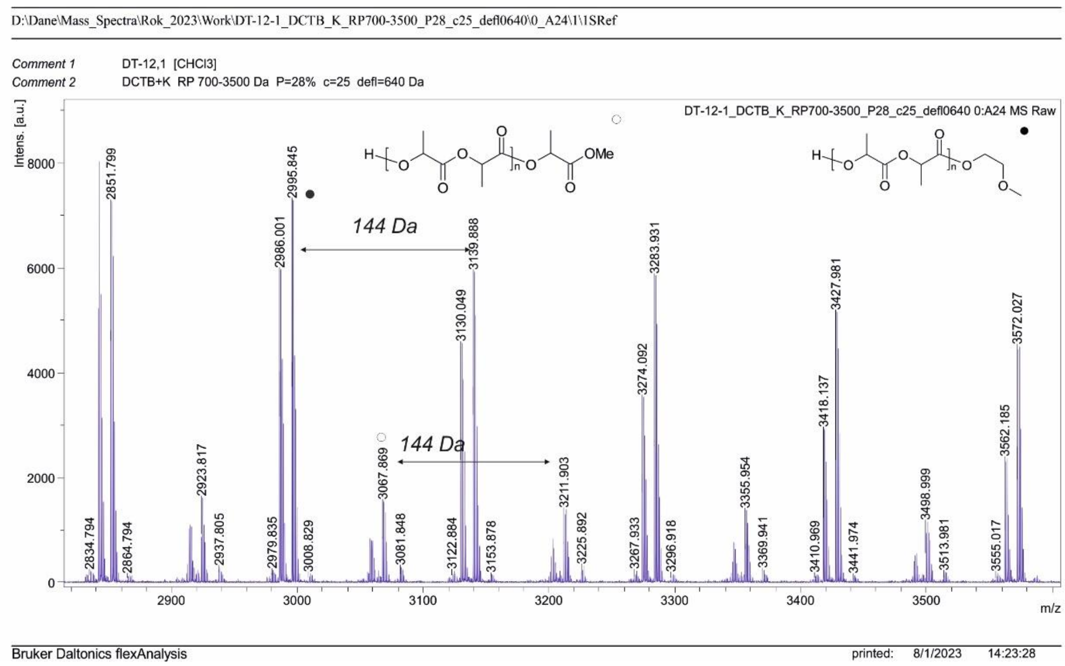
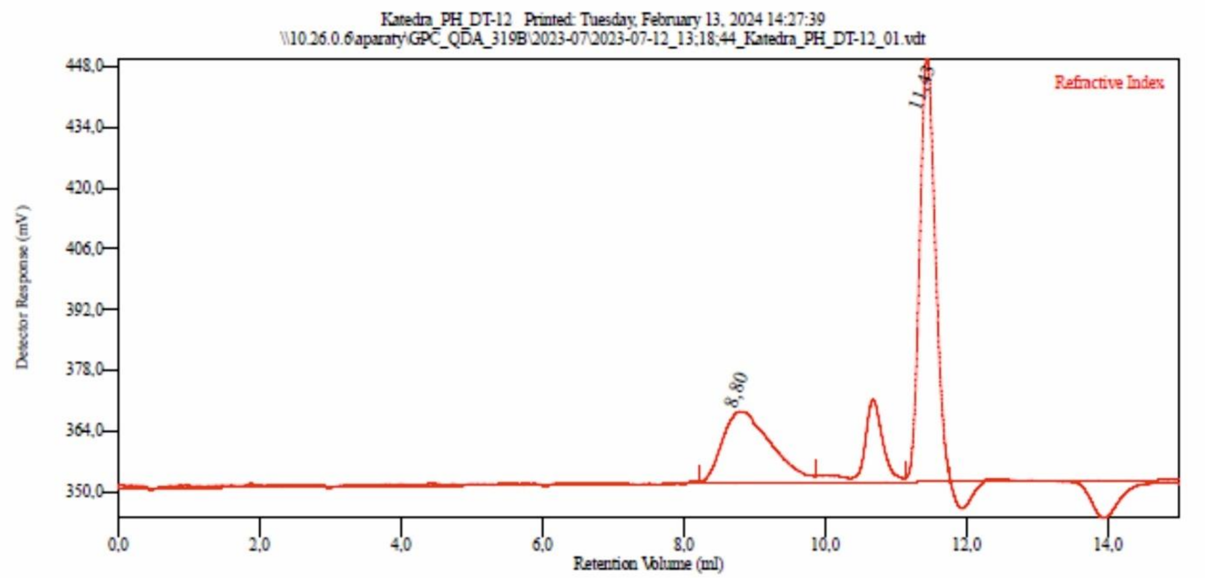


Figure S82. MALDI–TOF spectrum of PLA obtained with **2** in THF at r.t., Table 1, entry 19.

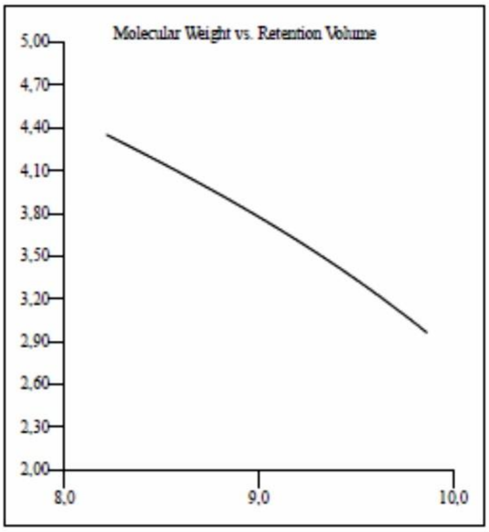
Figure 2 (—)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,803	11,433
Mn - (Daltons)	5 089	0
Mw - (Daltons)	7 505	0
Mz - (Daltons)	9 628	0
Mp - (Daltons)	8 478	0
Mw / Mn	1,475	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	1 840	0
Mw 10.0% High	15 309	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	13,32	25,04
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC_PS_RI_2023-07-0012.vcm
Limits File	
Date Acquired	Jul 12, 2023 - 13:18:44
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



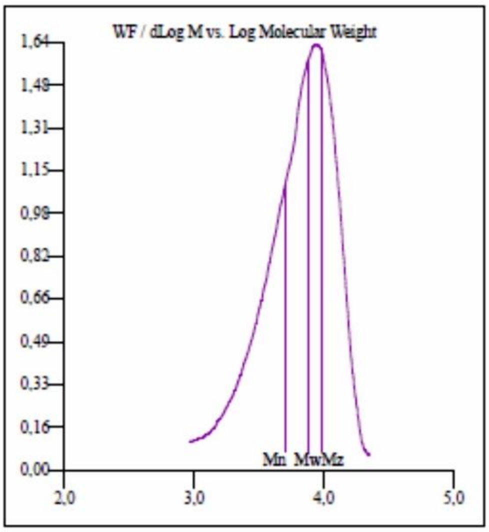
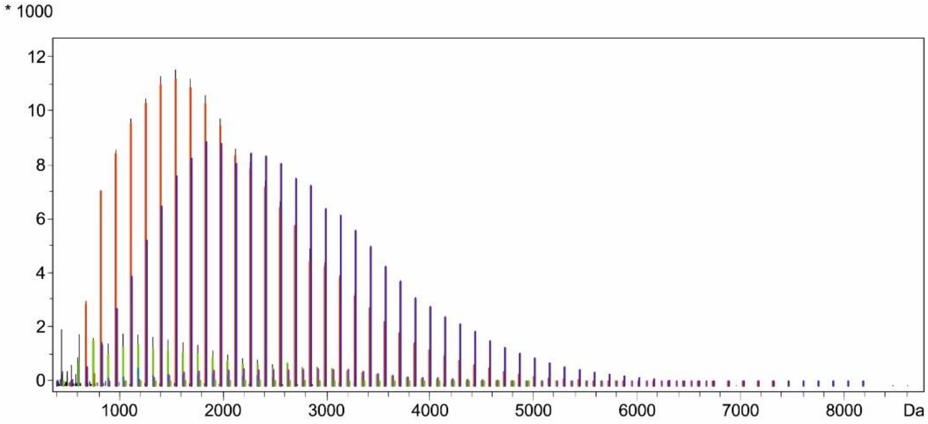


Figure S83. GPC eluogram of PLA obtained with **2** in THF at r.t., Table 1, entry 19.

polytool Date: 08/01/2023 Time: 15:09

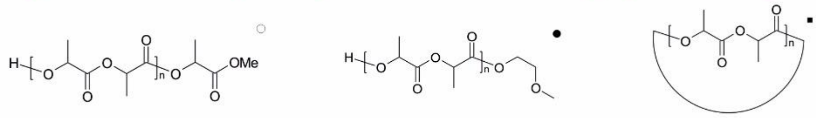
FileName: ...B_K_RP700-3500_P34_c25_defl0400\0_C20\1\1SRef\pdata\1\peaklist.xml
peak integrals - IG-2,1 [CHCl3]
DCTB+K RP 700-3500 Da P=34% c=25 defl=400 Da



	n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
	1	1	144.038	66.0510			38.9637	2022.63	2473.14	1.22273	14.0423	42.4	48
•	2	2	144.038	75.8817			38.9637	2606.34	3085.06	1.18368	18.0948	40.8	55
	3	3	144.038	136.880			38.9637	1882.72	2440.74	1.29639	13.0710	6.6	38
	4	4	144.038	138.406			38.9637	1647.44	1774.12	1.07689	11.4375	0.9	12
▪	5	5	144.038	0.18417			38.9637	1872.34	2036.65	1.08776	12.9989	0.5	15
○	6	6	144.038	3.68597			38.9637	2926.99	3394.22	1.15963	20.3209	3.2	41
*	7	7	144.038	17.8345			38.9637	2642.80	3003.72	1.13657	18.3479	0.8	28

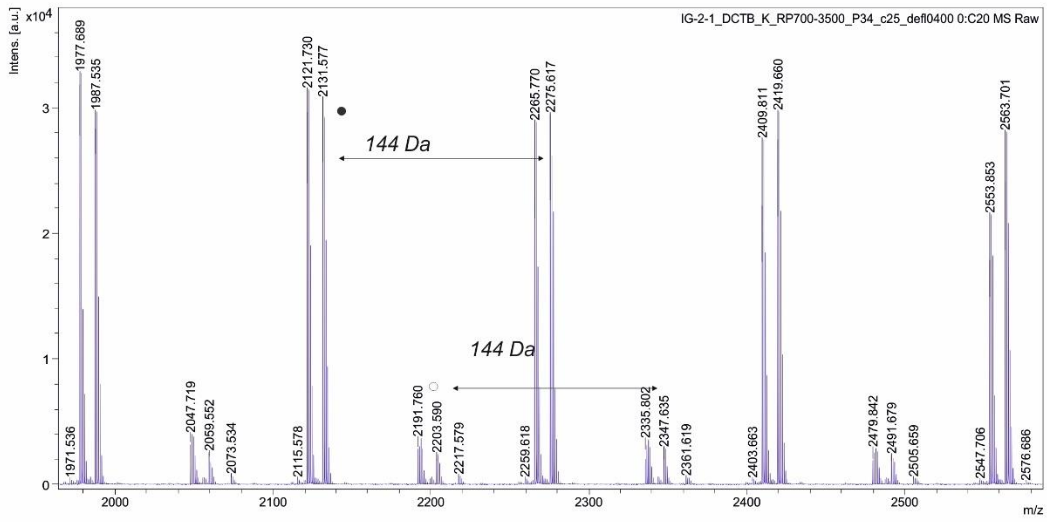
Traces

Traces may originate from hydrolysis of PLA during quenching with H2O/H+



D:\Dane\Mass_Spectra\Rok_2023\Work\IG-2-1_DCTB_K_RP700-3500_P34_c25_defl0400\0_C20\1\1SRef

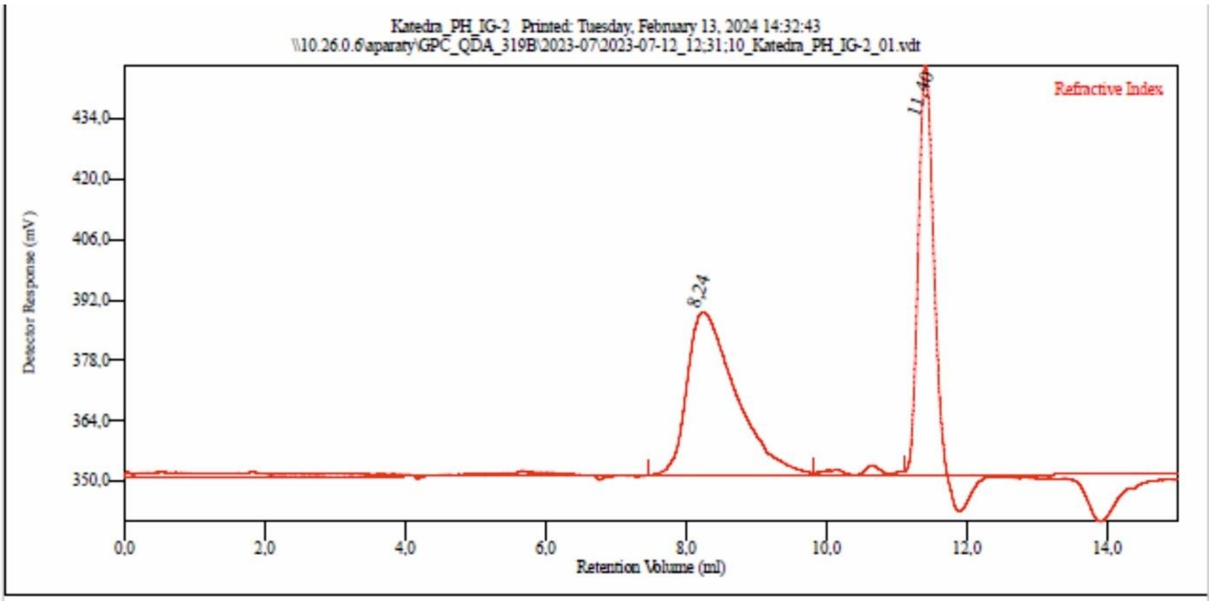
Comment 1 IG-2,1 [CHCl3]
Comment 2 DCTB+K RP 700-3500 Da P=34% c=25 defl=400 Da



Bruker Daltonics flexAnalysis printed: 8/1/2023 14:33:44

Figure S84. MALDI–TOF spectrum of PLA obtained with **2** in THF at 0°C, Table 1, entry 22.

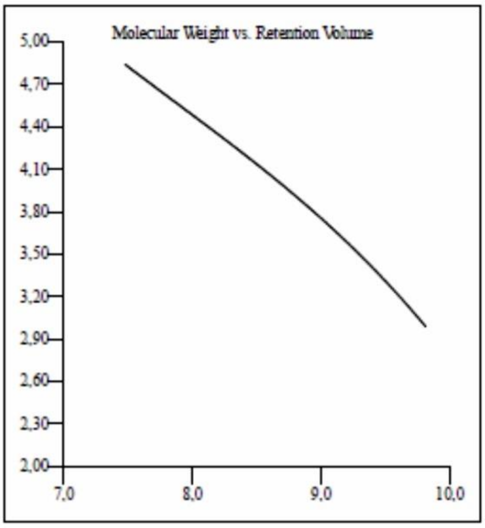
Figure 2 (▬)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8,243	11,400
Mn - (Daltons)	11 314	0
Mw - (Daltons)	17 348	0
Mz - (Daltons)	22 099	0
Mp - (Daltons)	20 807	0
Mw / Mn	1,533	0,000
Percent Above Mw: 0	100,000	0,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	4 003	0
Mw 10.0% High	34 700	0
Wt Fr (Peak)	1,000	0,000
RI Area - (mvml)	30,52	23,22
UV@240nm Area - (mvml)	0,00	0,00

Annotation	
Method File	CC_PS_RI_2023-07-0012.vcm
Limits File	
Date Acquired	Jul 12, 2023 - 12:31:10
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	30,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467



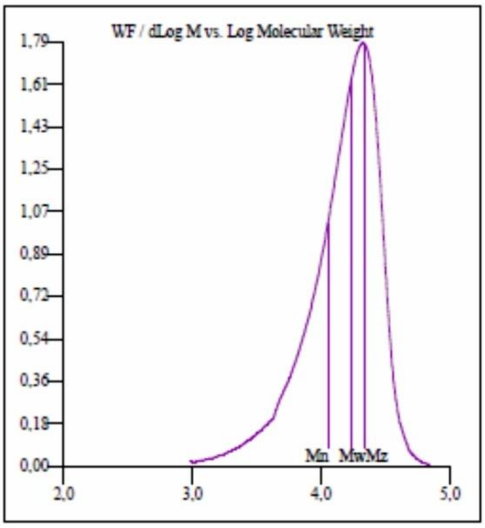
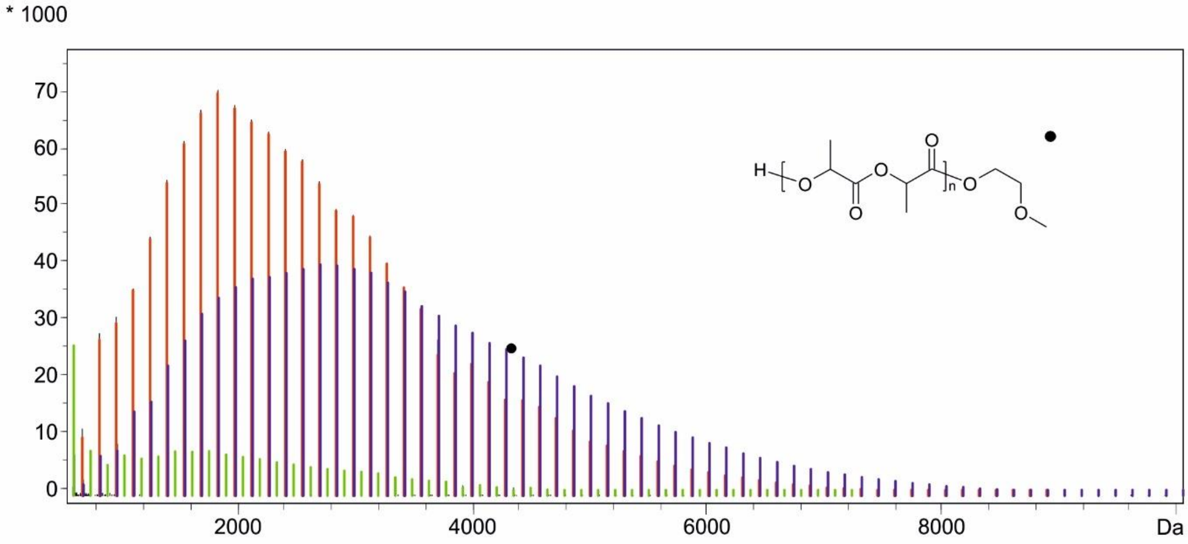


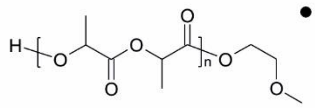
Figure S85. GPC eluogram of PLA obtained with **2** in THF at 0°C, Table 1, entry 22.

polytool Date: 12/06/2022 Time: 20:06

FileName: ...DCTB_K_RP05-20k_P43_c25_defl600\0_D17\1\1SRef\pdata\1\peaklist.xml
peak integrals - PG-010 [PLA] [CHCl3]
DCTB+K RP 05-20 kDa P=43% c=25 defl=600 Da

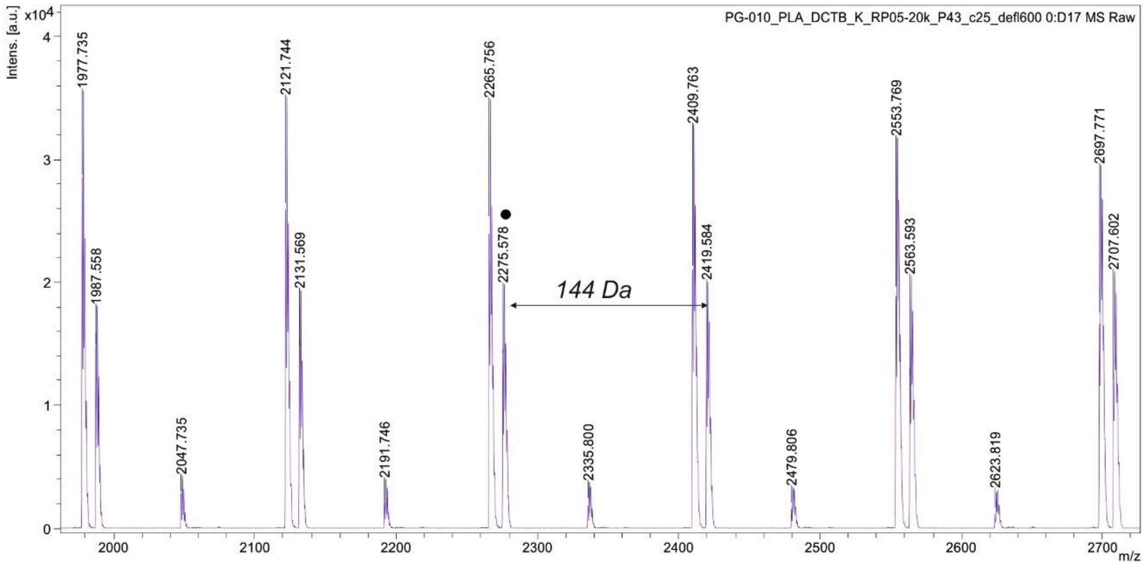


n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
1	1	144.042	65.6140			38.9637	2610.62	3229.86	1.23720	18.1240	51.6	58
• 2	2	144.042	75.3782			38.9637	3495.85	4273.79	1.22253	24.2696	40.7	80
3	3	144.042	136.174			38.9637	1973.39	2739.37	1.38815	13.7001	6.5	47



D:\Dane\Mass_Spectra\Rok_2022\Work\PG-010_PLA_DCTB_K_RP05-20k_P43_c25_defl600\0_D17\1\1SRef

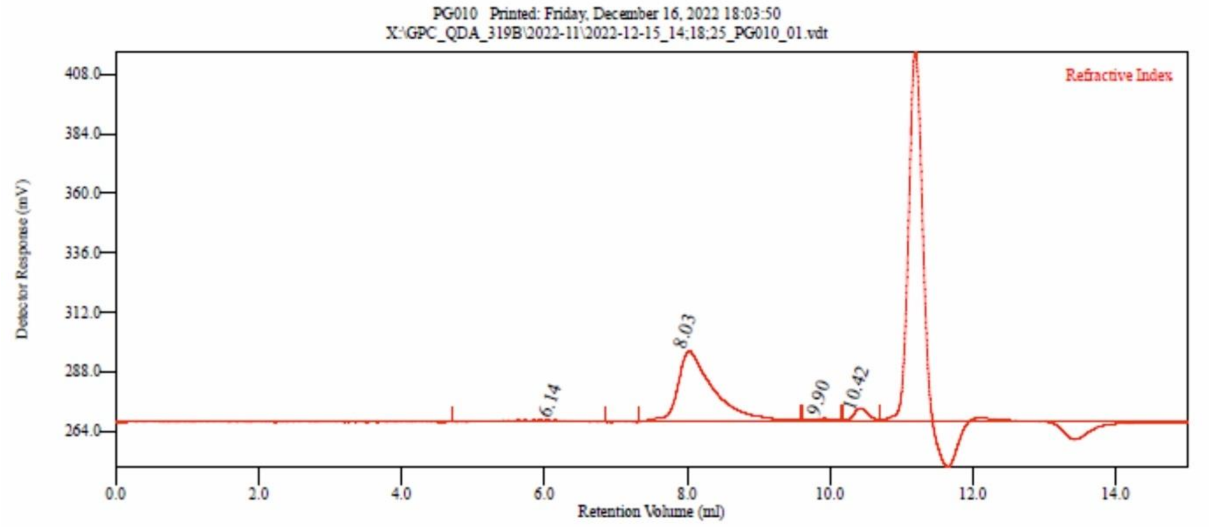
Comment 1 PG-010 [PLA] [CHCl3]
Comment 2 DCTB+K RP 05-20 kDa P=43% c=25 defl=600 Da



Bruker Daltonics flexAnalysis printed: 12/6/2022 19:20:27

page 1 of 1

Figure S86. MALDI–TOF spectrum of PLA obtained with **2** in THF at –20°C, Table 1, entry 25. Figure 2 (—)

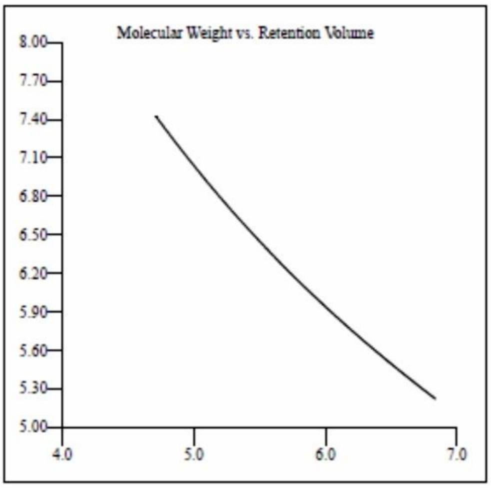


Warning: No flow rate marker was found.

Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	6.137	8.027	9.897	10.420
Mn - (Daltons)	1.094 e 6	12,745	643	162
Mw - (Daltons)	5.452 e 6	18,620	707	176
Mz - (Daltons)	1.386 e 7	22,875	776	190
Mp - (Daltons)	648,422	22,420	654	177
Mw / Mn	4.985	1.461	1.100	1.083
Percent Above Mw: 0	100.000	100.000	100.000	100.000
Percent Below Mw: 0	0.000	0.000	0.000	0.000
Mw 10.0% Low	276,962	4,572	400	100
Mw 10.0% High	1.042 e 7	35,083	1,134	273
Wt Fr (Peak)	0.037	0.867	0.025	0.071
RI Area - (mvml)	0.71	16.76	0.49	1.38
UV@240nm Area - (mvml)	0.00	0.00	0.00	0.00

Annotation	
Method File	CC_RI_PS_11-2022-0003-MLtry-0001.vcm
Limits File	
Date Acquired	Dec 15, 2022 - 14:18:25
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	50.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	30.0
Column Temp. - (deg C)	30.0
OmniSEC Build Number	467



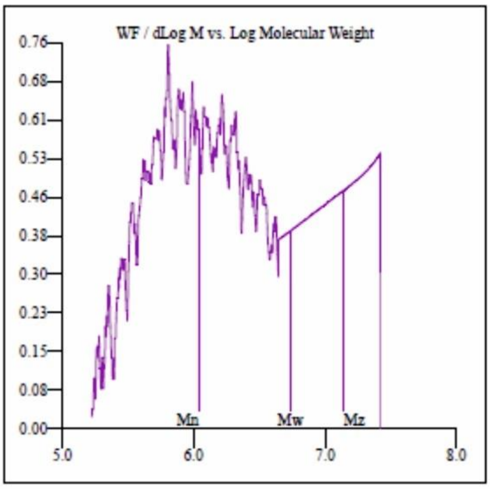
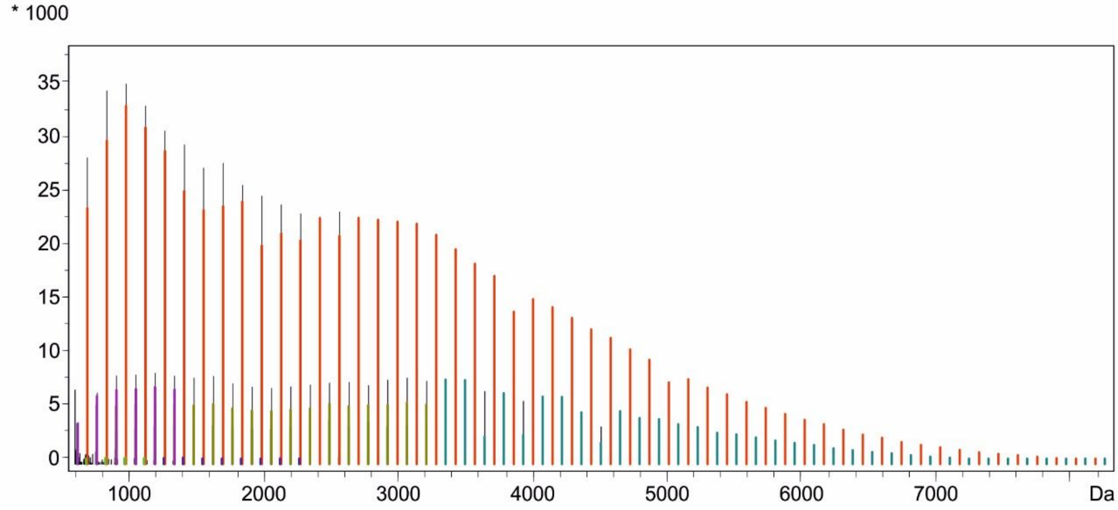


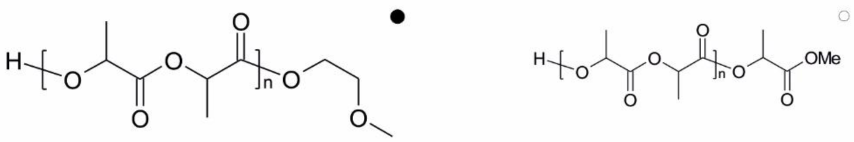
Figure S87. GPC eluogram of PLA obtained with **2** in THF at –20°C, Table 1, entry 25.

polytool Date: 12/06/2022 Time: 20:11

FileName: ...DCTB_K_RP05-20k_P40_c25_defl600\0_E24\1\1SRef\pdata\1\peaklist.xml
peak integrals - PG-014 [PLA] [CHCl3]
DCTB+K RP 05-20 kDa P=40% c=25 defl=600 Da



	n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
	1	1	144.042	75.5478			38.9637	2713.01	3622.50	1.33523	18.8348	71.1	66
Traces	2	2	144.042	65.530[illegible]			38.9637	1430.01	1540.63	1.07735	9.92774	0.2	12
Traces	3	2	144.042	66.2388			38.9637	899.477	922.065	1.02511	6.24454	0.1	4
? ○	4	3	144.042	1.45041			38.9637	4198.30	4655.64	1.10893	29.1463	10.8	59
? ○	5	3	144.042	2.62546			38.9637	2274.03	2420.19	1.06427	15.7873	9.7	17
○	6	3	144.042	3.38903			38.9637	1010.91	1069.56	1.05802	7.01818	3.4	6



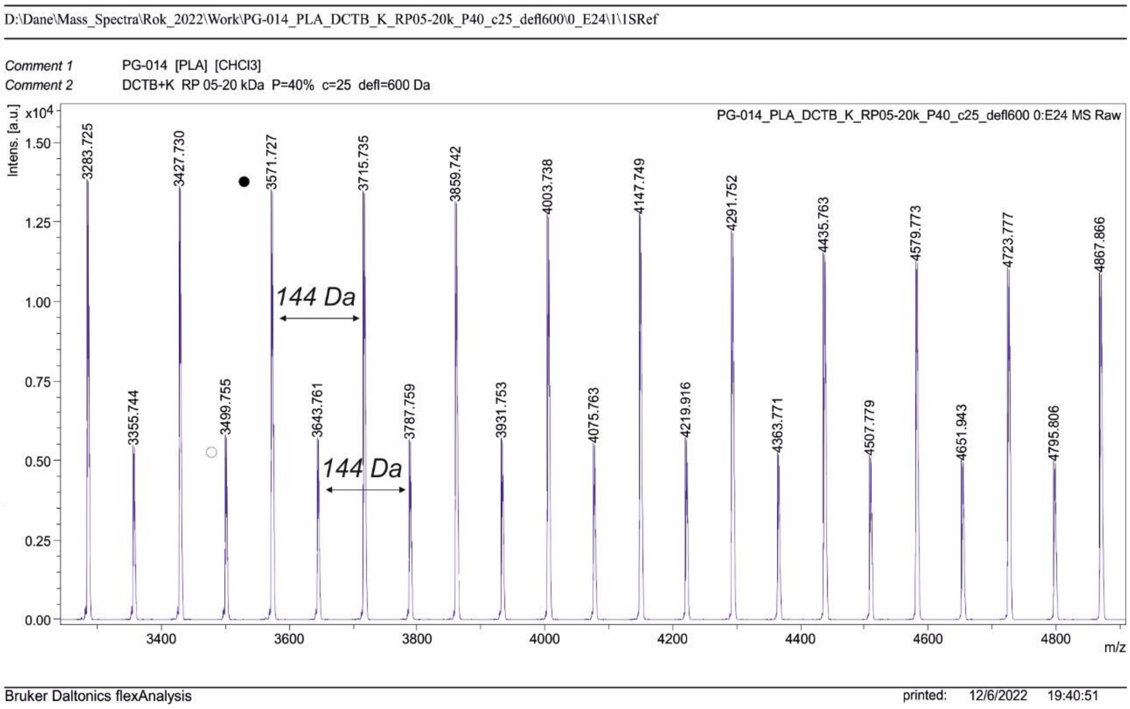
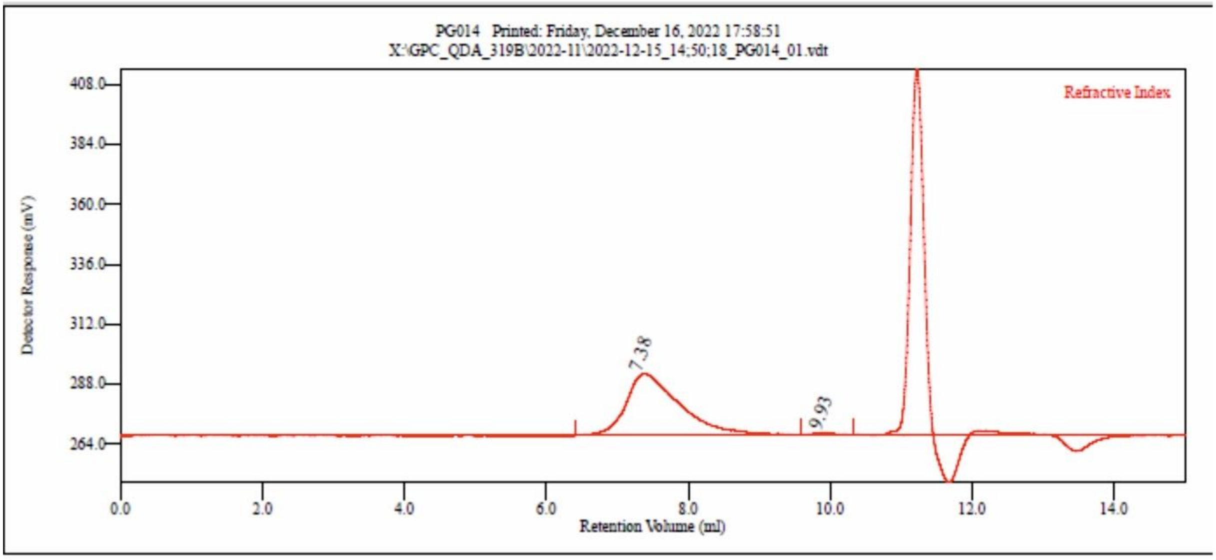


Figure S88. MALDI–TOF spectrum of PLA obtained with **2** in THF at –40°C, Table 1, entry 28. Figure 2 (—)

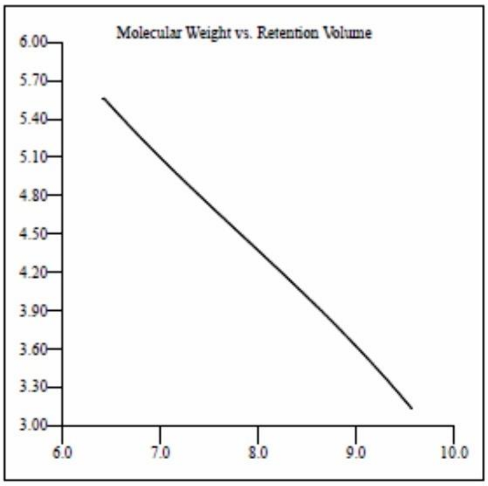


Warning: No flow rate marker was found.

Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	7.383	9.927
Mn - (Daltons)	30,060	557
Mw - (Daltons)	56,283	648
Mz - (Daltons)	79,831	740
Mp - (Daltons)	64,750	612
Mw / Mn	1.872	1.162
Percent Above Mw: 0	100.000	100.000
Percent Below Mw: 0	0.000	0.000
Mw 10.0% Low	10,045	288
Mw 10.0% High	133,794	1,163
Wt Fr (Peak)	0.980	0.020
RI Area - (mvml)	21.85	0.44
UV@240nm Area - (mvml)	0.00	0.00

Annotation	
Method File	CC_RI_PS_11-2022-0003-MLtry-0001.vcm
Limits File	
Date Acquired	Dec 15, 2022 - 14:50:18
Solvent	Chlorek metylenu
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	50.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	30.0
Column Temp. - (deg C)	30.0
OmniSEC Build Number	467



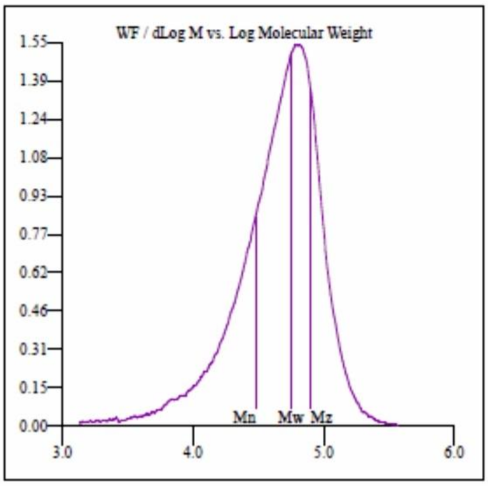


Figure S89. GPC eluogram of PLA obtained with **2** in THF at –40°C, Table 1, entry 28.