Simple and Efficient Process for Large Scale Glycerol Oligomerization by Microwave Irradiation

Rémi Nguyen, Nicolas Galy, Abhishek K. Singh, Florian Paulus, Daniel Stöbener, Cathleen Schlesener, Sunil K. Sharma, Rainer Haag and Christophe Len

1. Oligomerization process

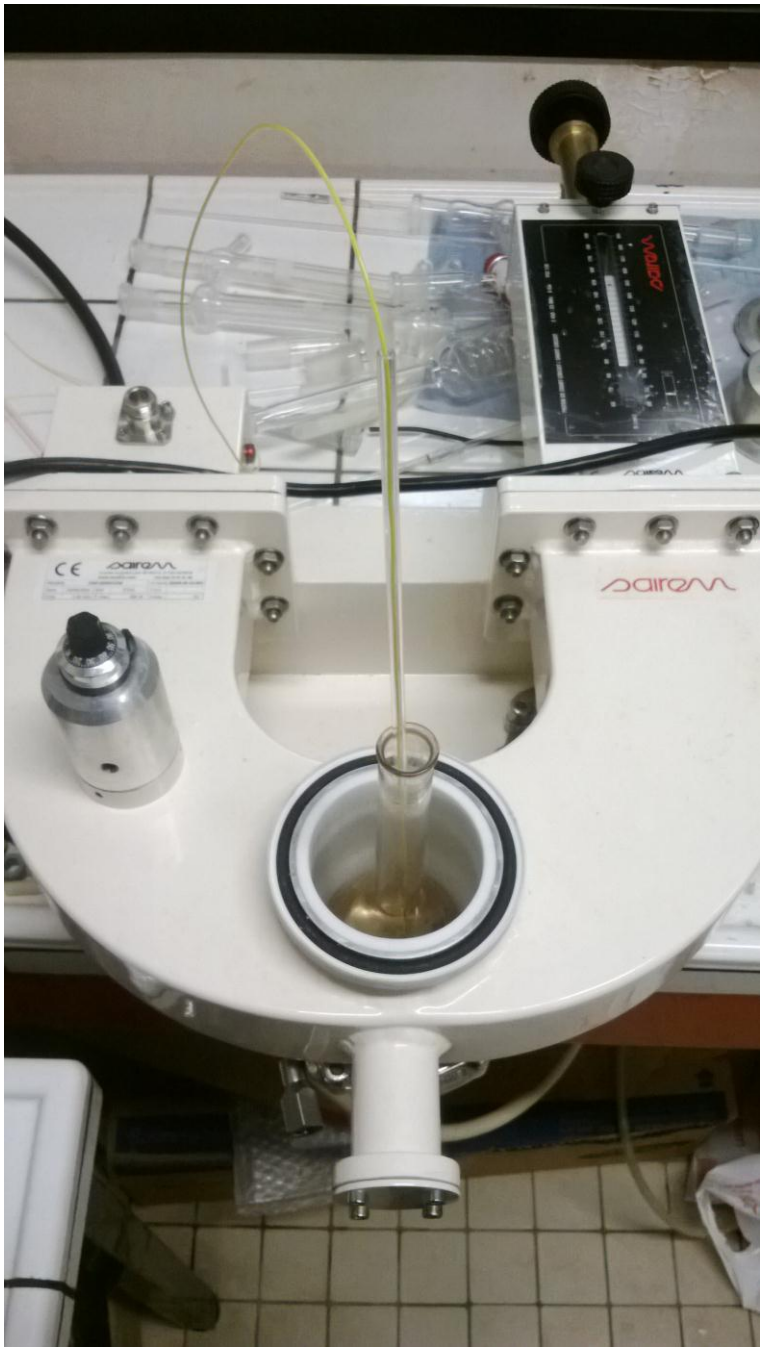


Figure SI 30: Monomodal MW process for oligomerization of glycerol.

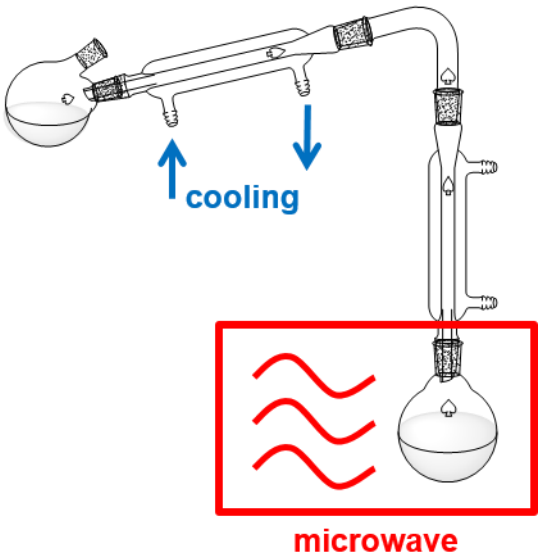


Figure SI 2. Multimode reactor with condensation system.

Figure SI 3: Multimodal MW process for olygomerization of glycerol.

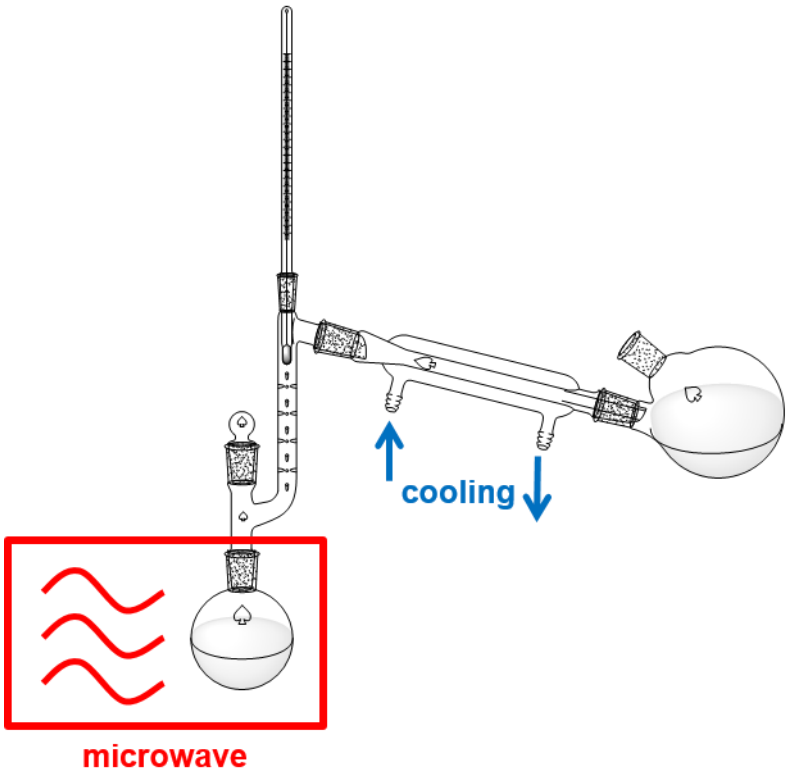


Figure SI 13. Optimized multimode reactor with distillation column and control of head temperature.

Figure SI 14: Optimized multimodal MW process for olygomerization of glycerol, with control of head temperature.

2. Mass spectrometry

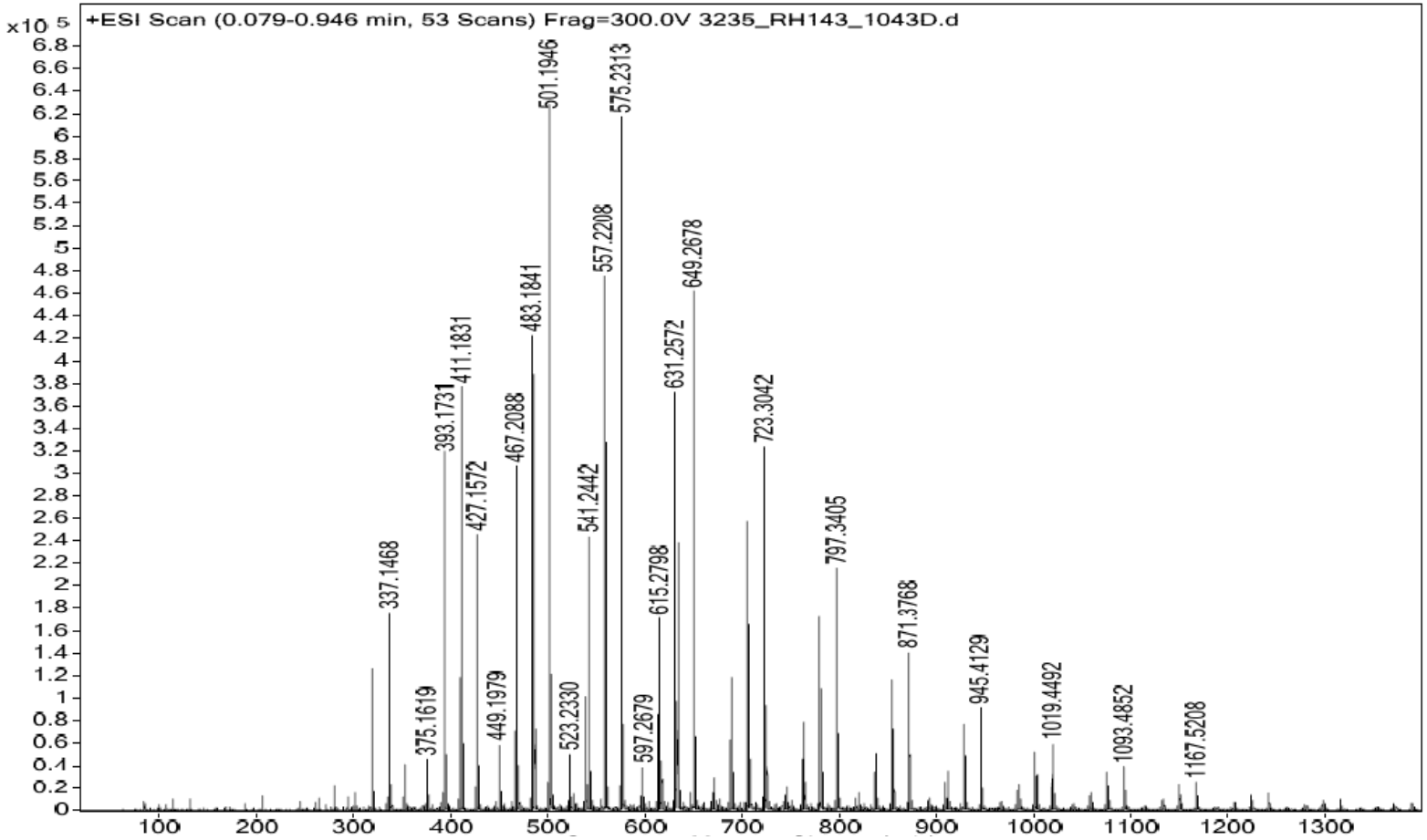


Figure SI 1: Mass spectrum of the reaction in SAIREM MW open reactor with K_2CO_3 (4 wt%) as catalyst, 16 h.

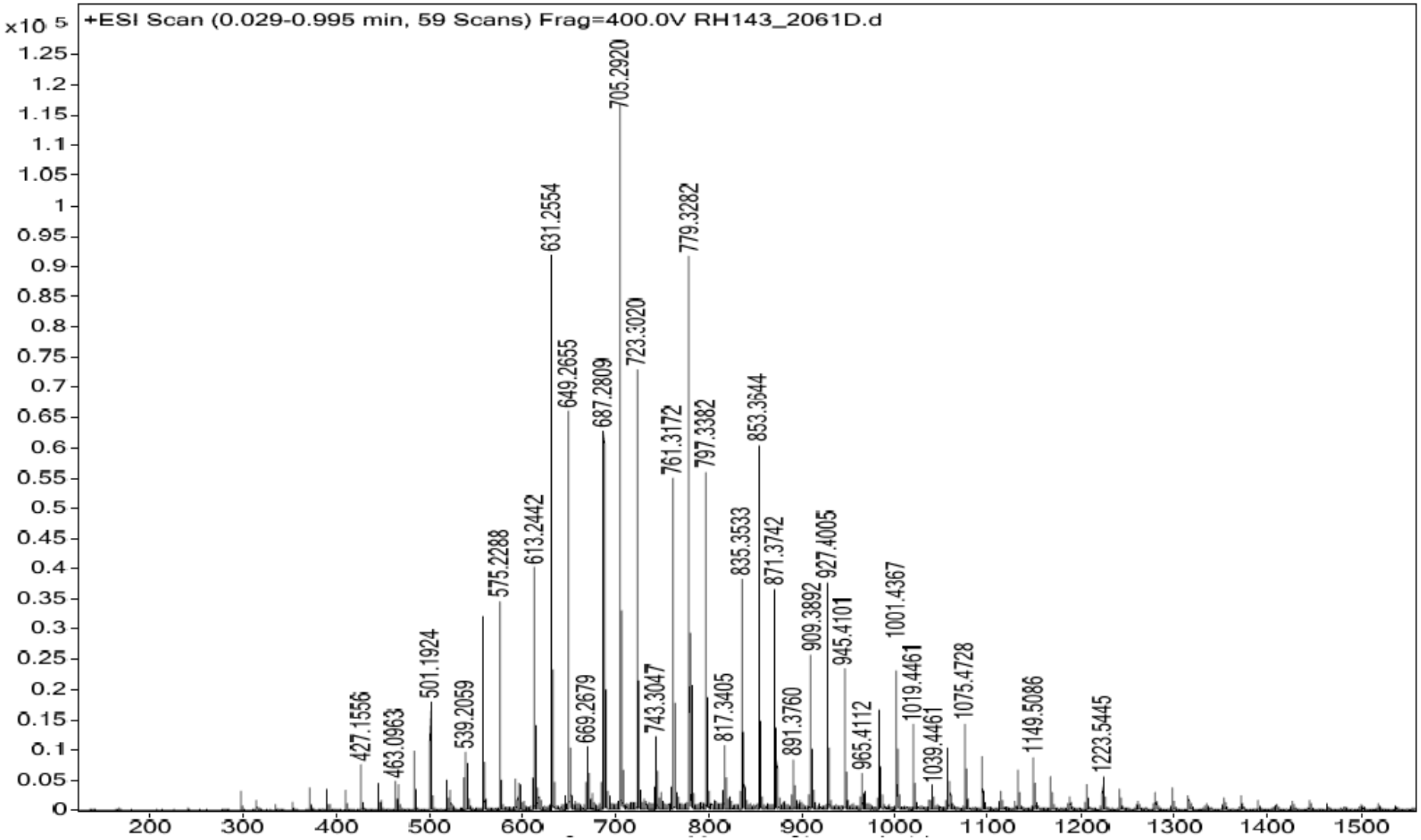


Figure SI 4: ESI analysis of the reaction with K_2CO_3 (4 wt%) as catalyst @300 W, 30 min.

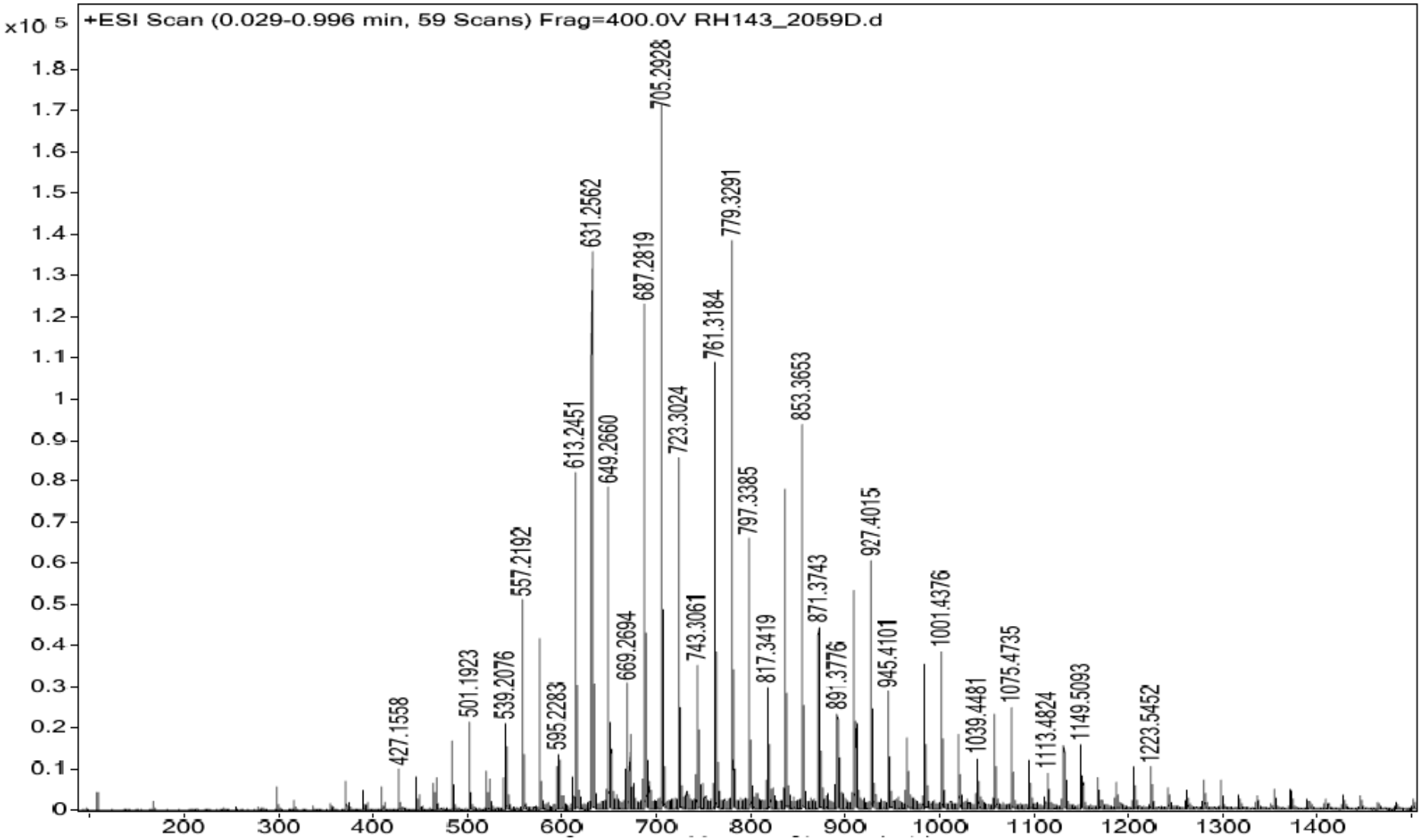


Figure SI 5: ESI analysis of the reaction with K_2CO_3 (4 wt%) as catalyst @600 W, 10 min 30 s.

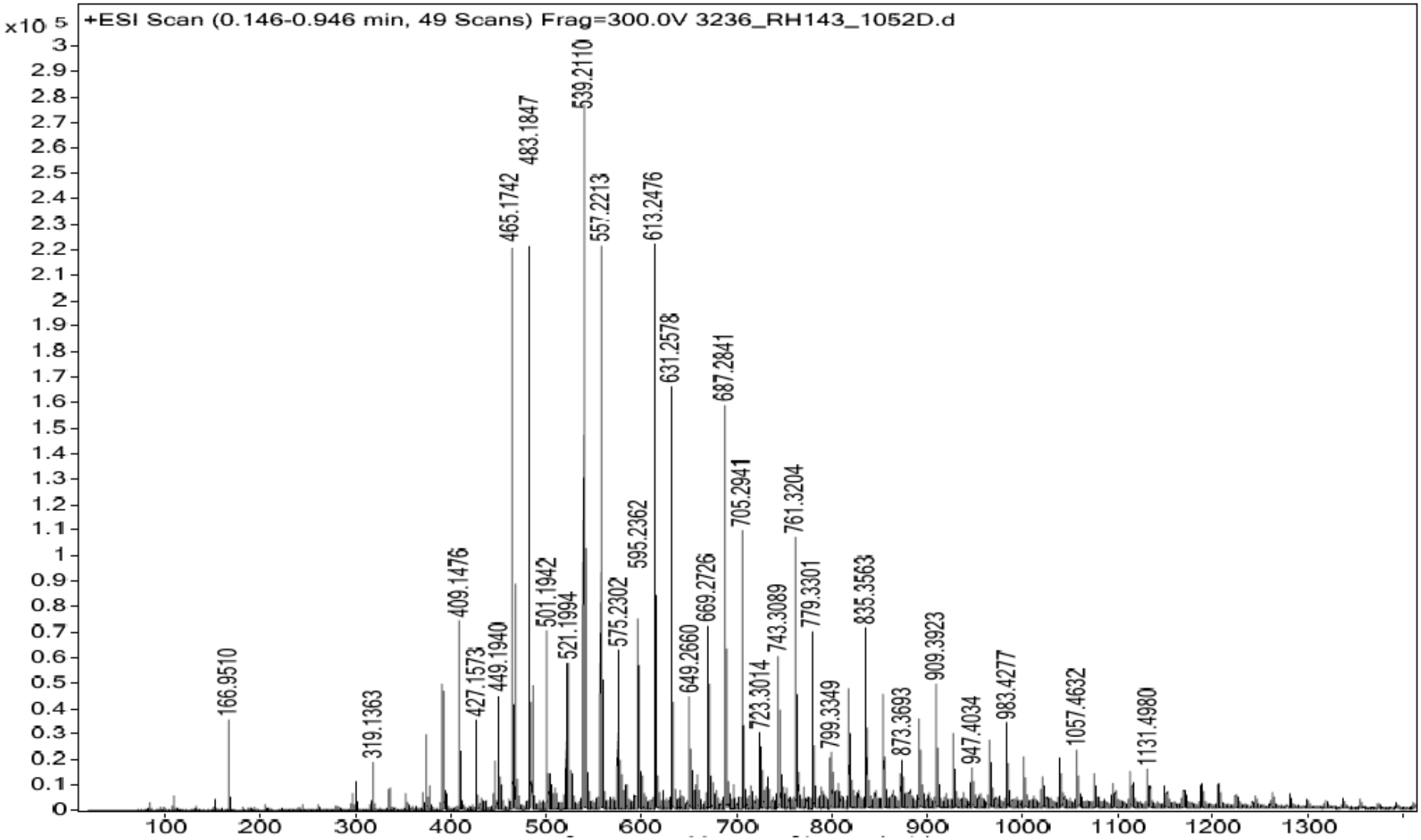


Figure SI 6: ESI analysis of the reaction with K_2CO_3 (4 wt%) as catalyst @800 W, 6 min 20 s.

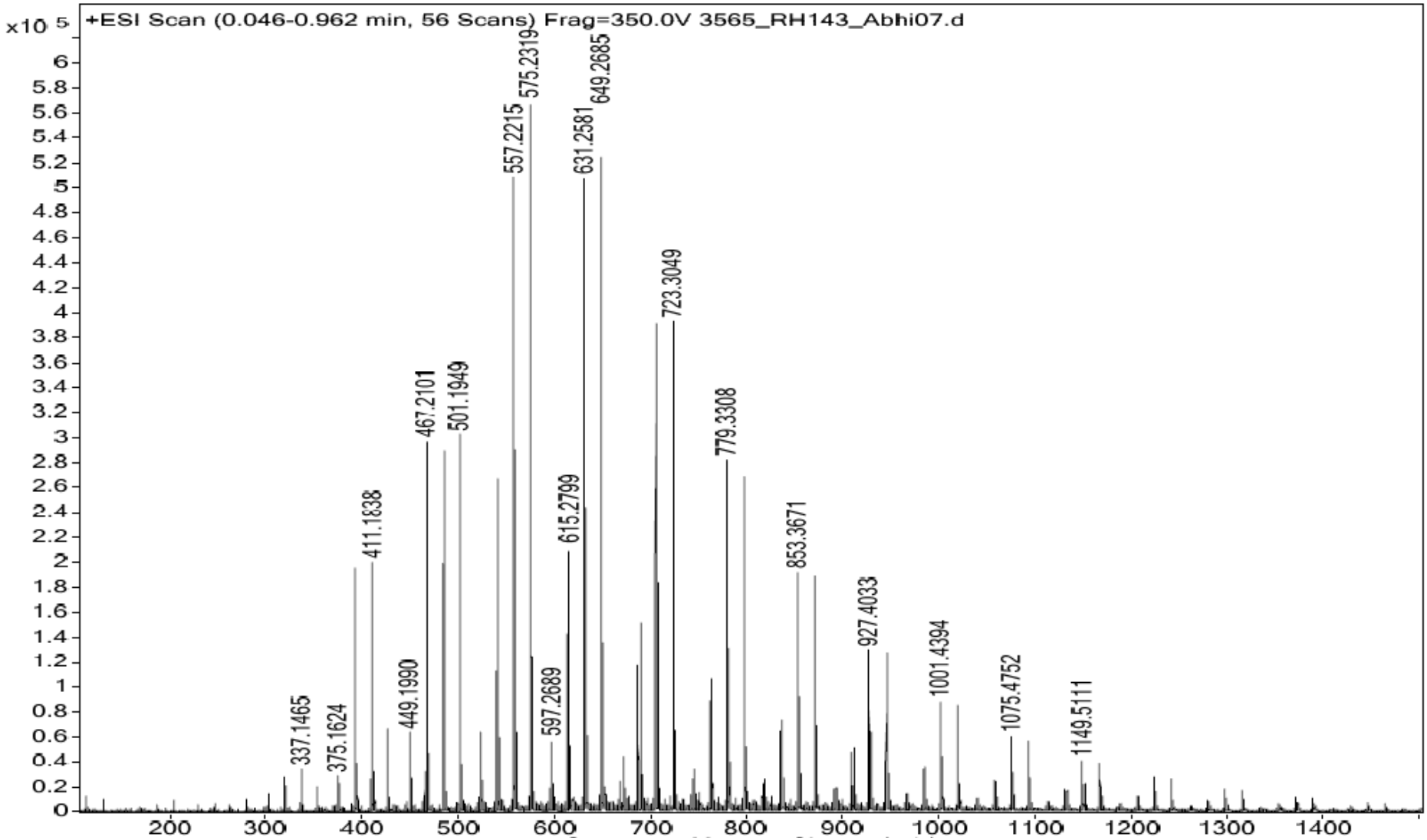


Figure SI 19: Crude oligomer from the optimized reaction protocol.

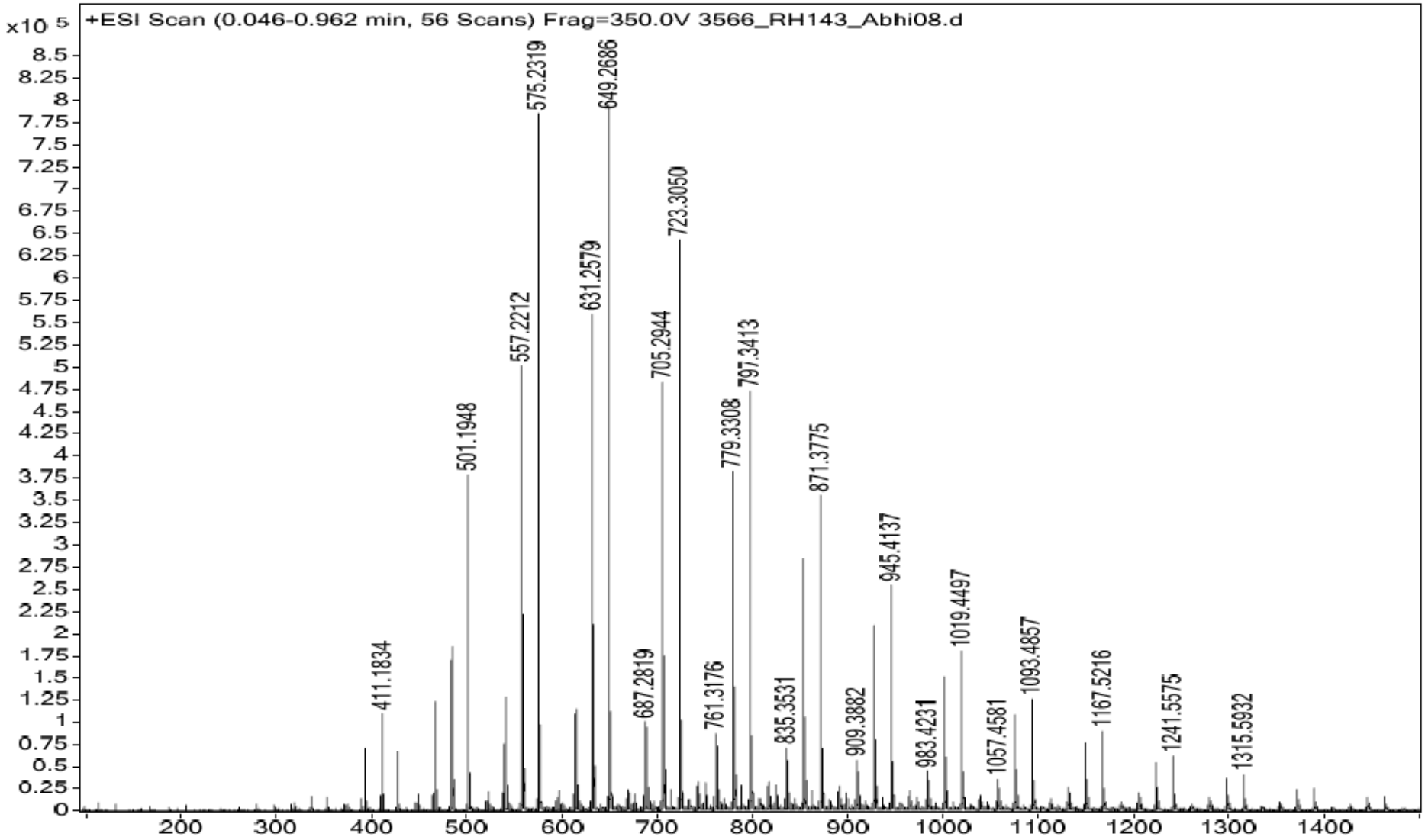


Figure SI 20: Purification cycle 1, precipitate 1.

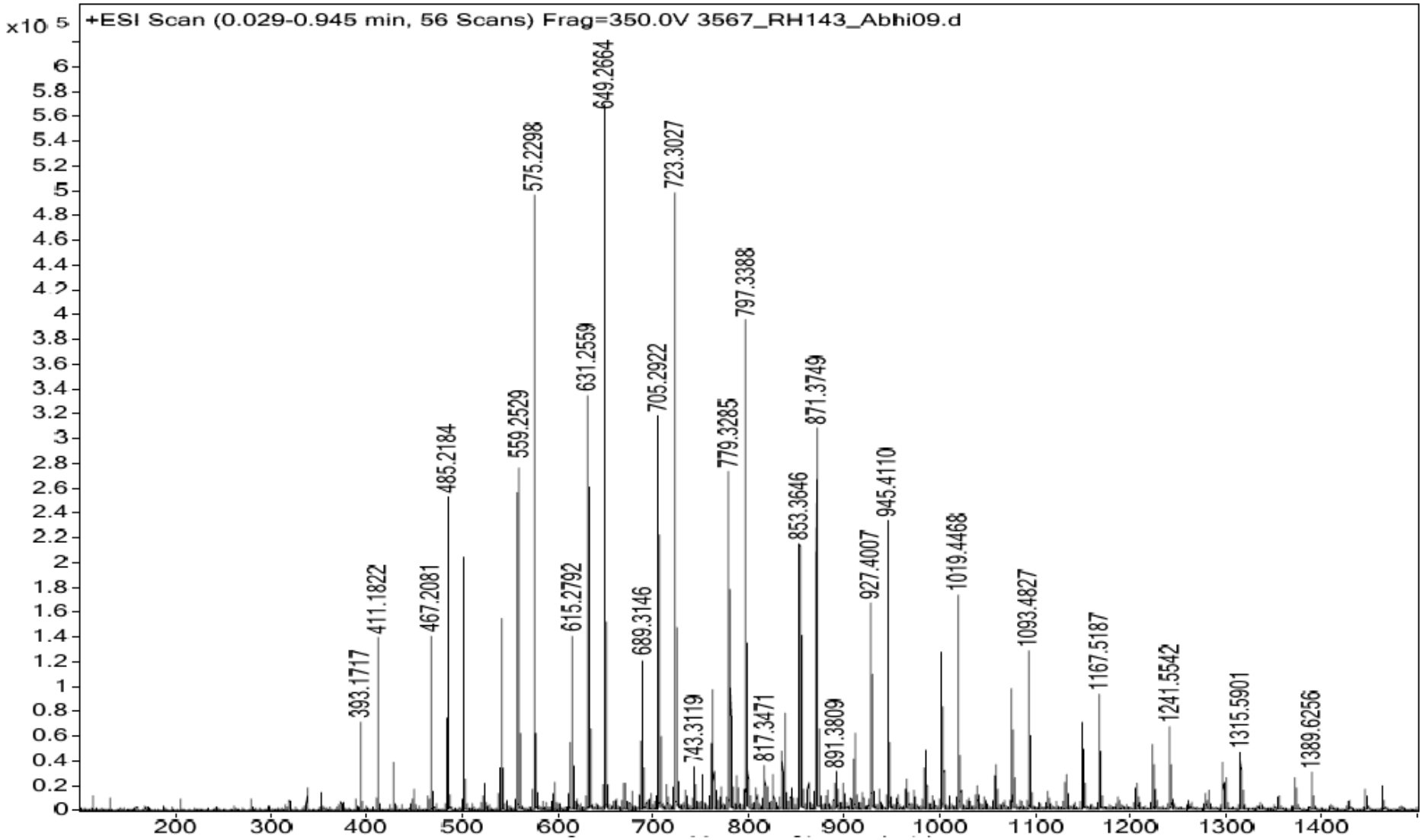


Figure SI 21: Purification cycle 1, precipitate 2.

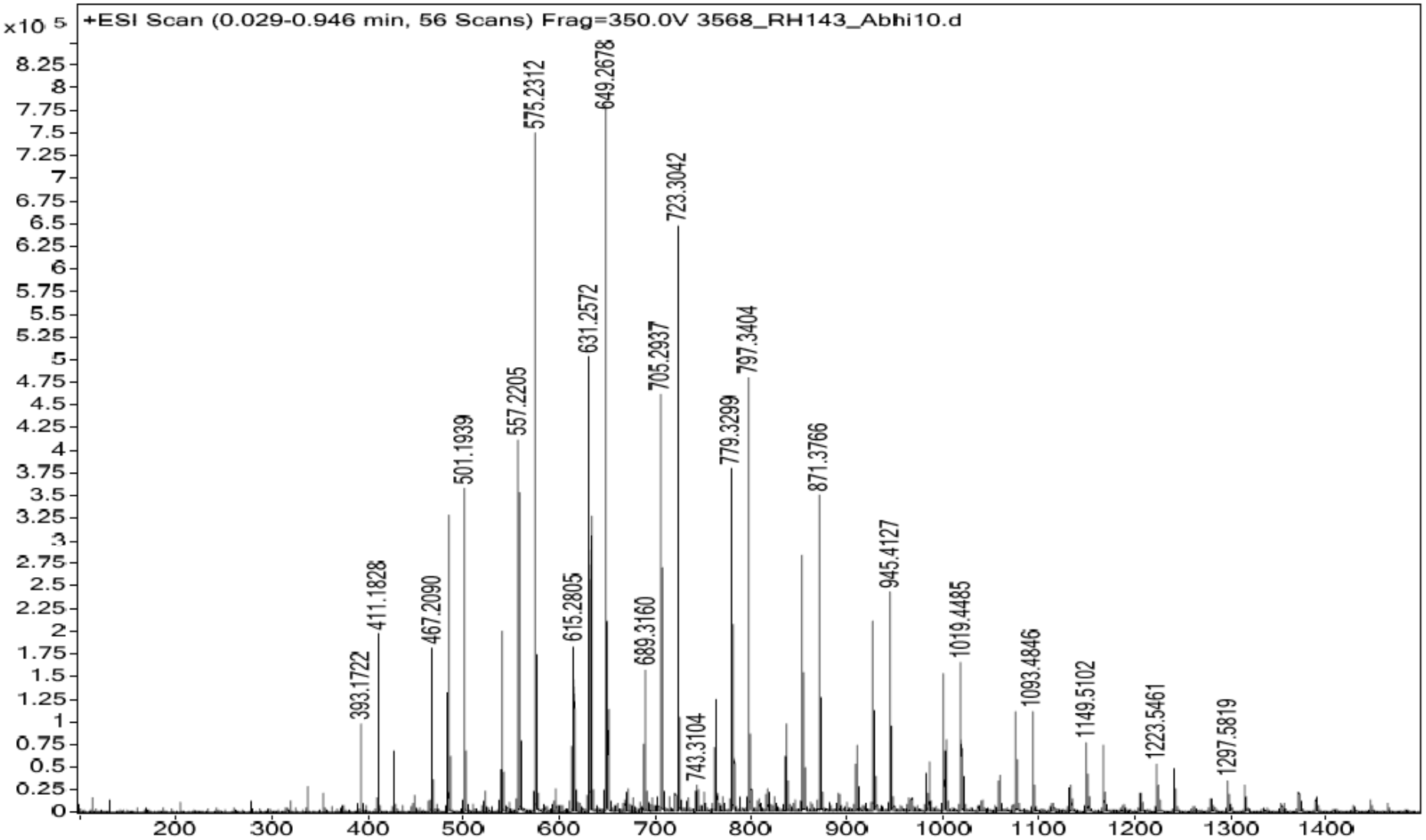


Figure SI 22: Purification cycle 1, precipitate 3.

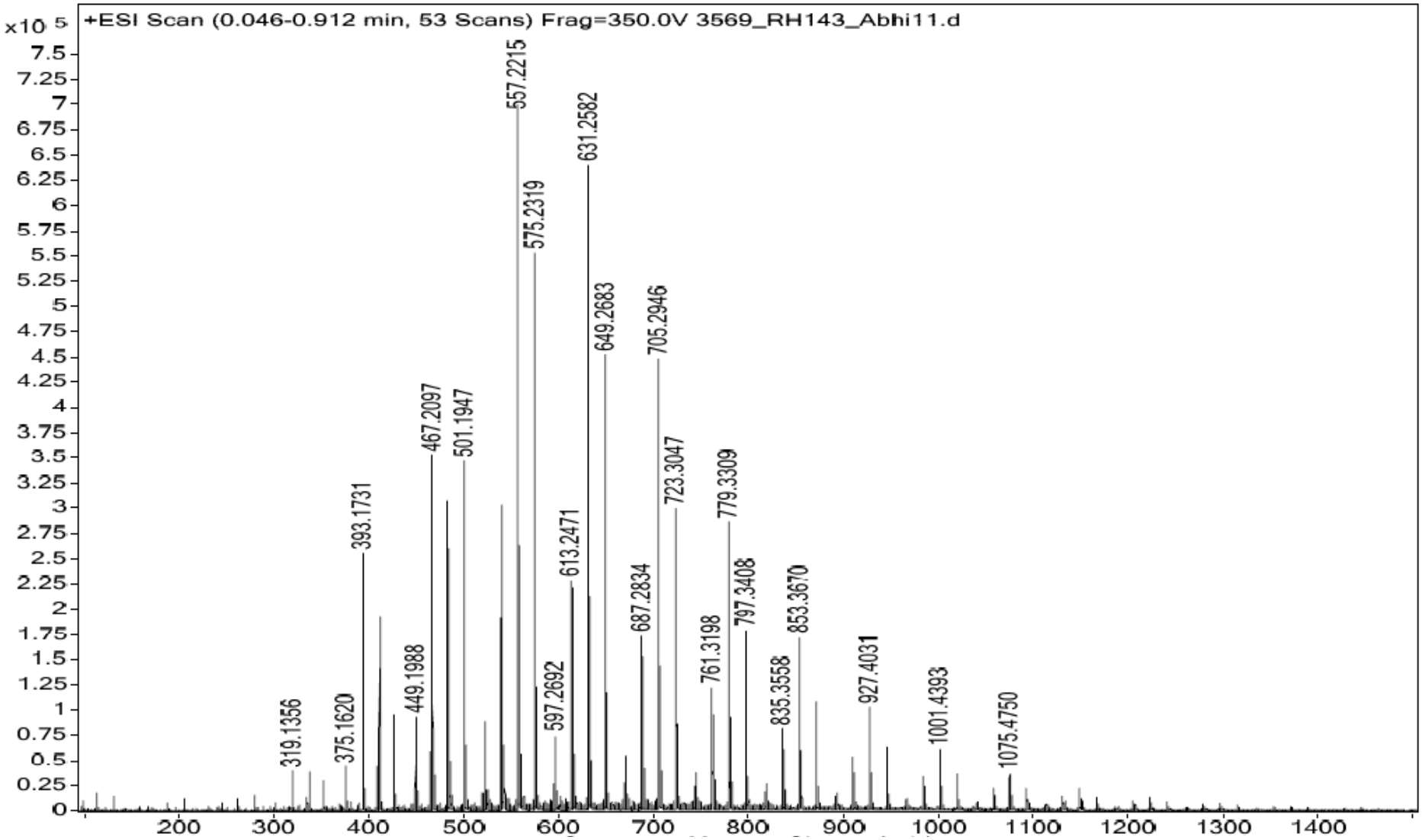


Figure SI 23: Purification cycle 1, solution 3.

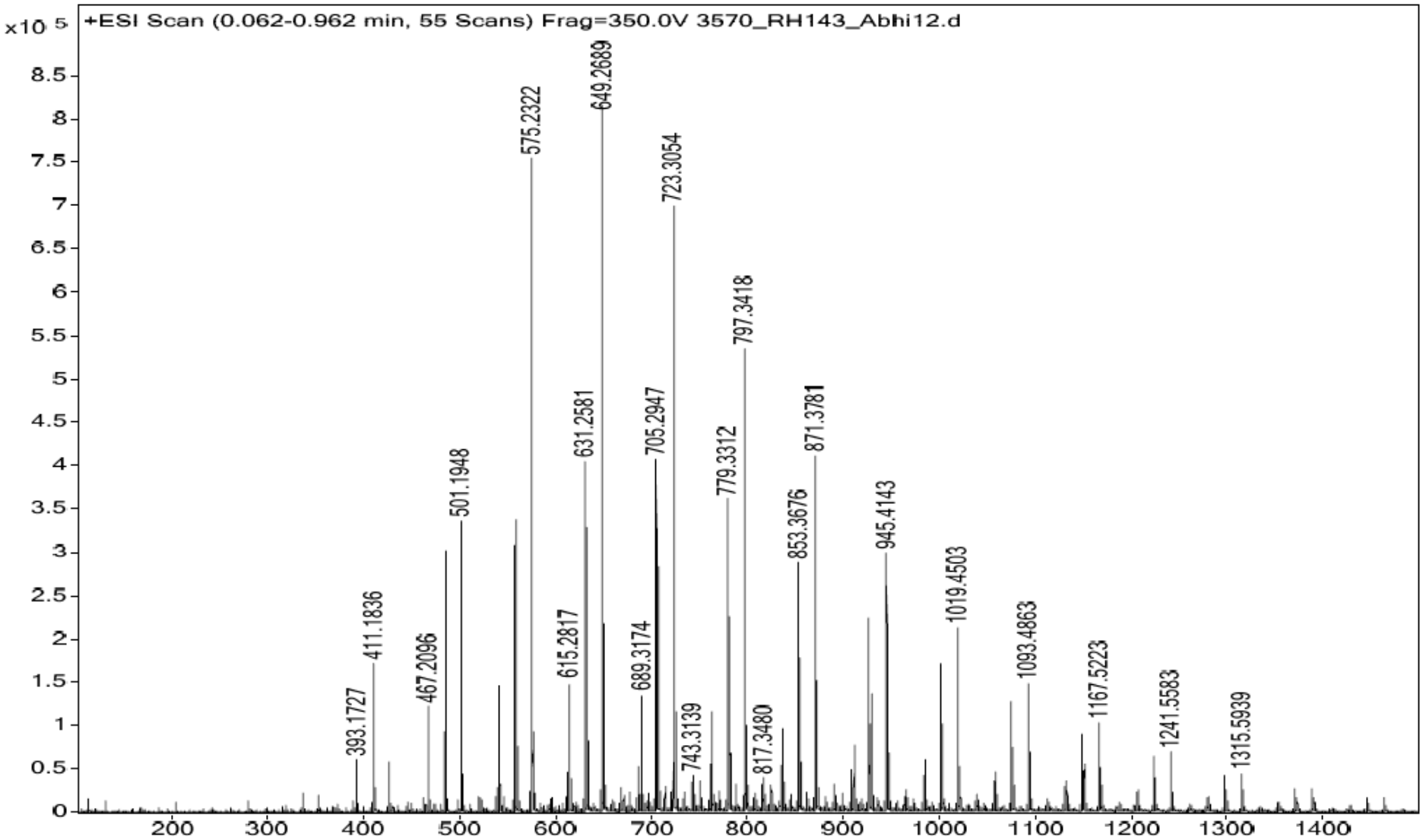


Figure SI 24: Purification cycle 2, precipitate 4.

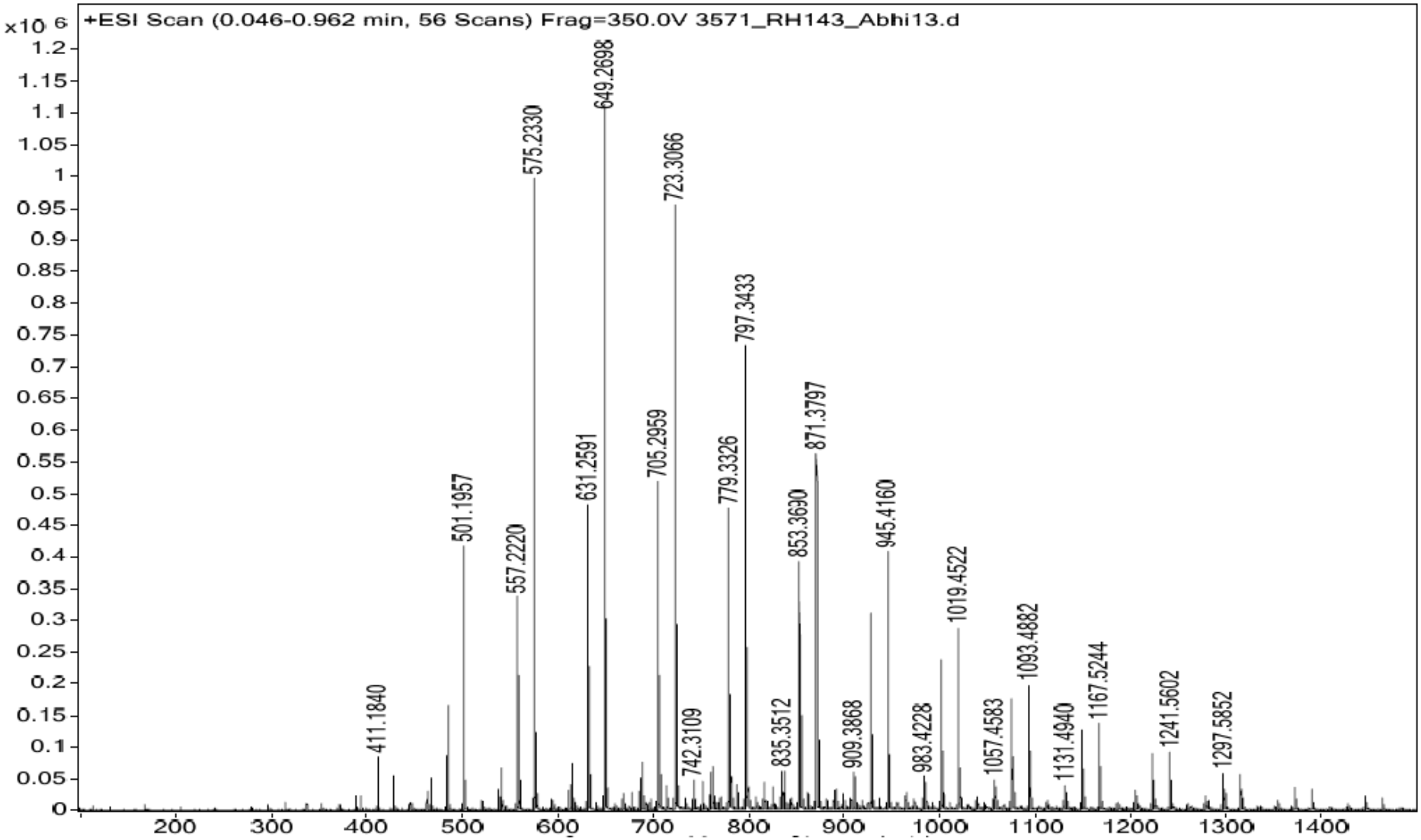


Figure SI 25: Purification cycle 2, precipitate 5.

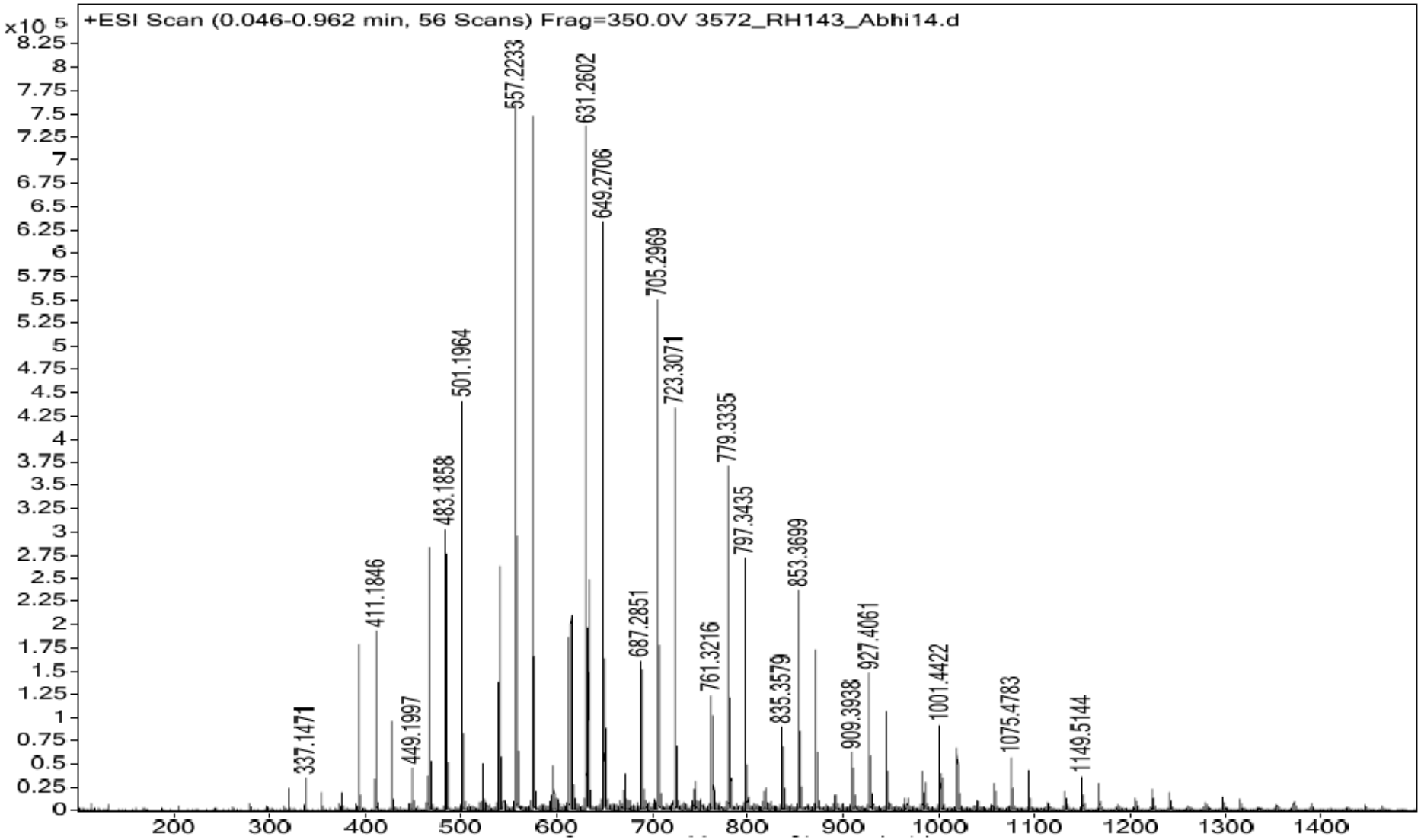


Figure SI 26: Purification cycle 2, solution 5.

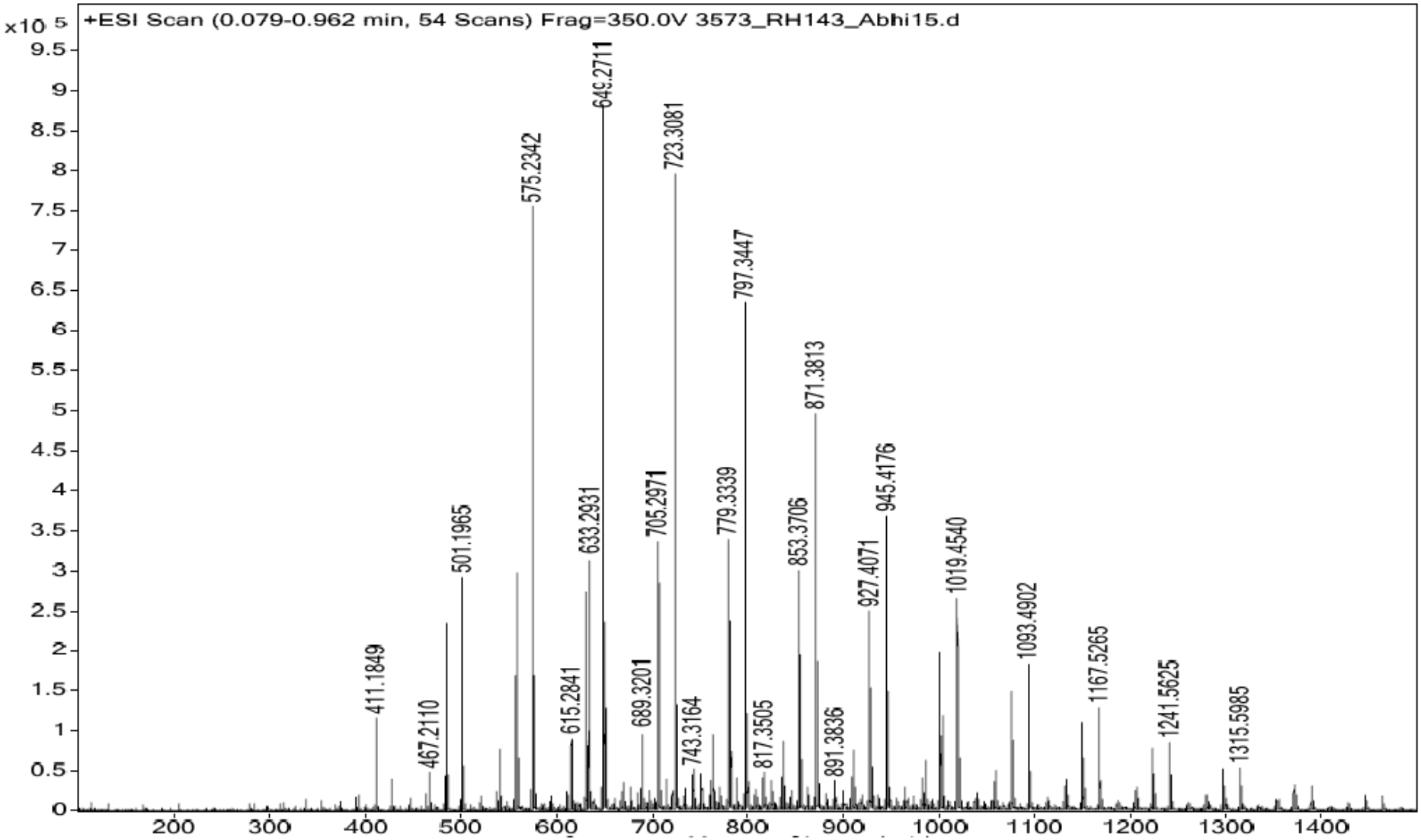


Figure SI 27: Purification cycle 3, precipitate 6.

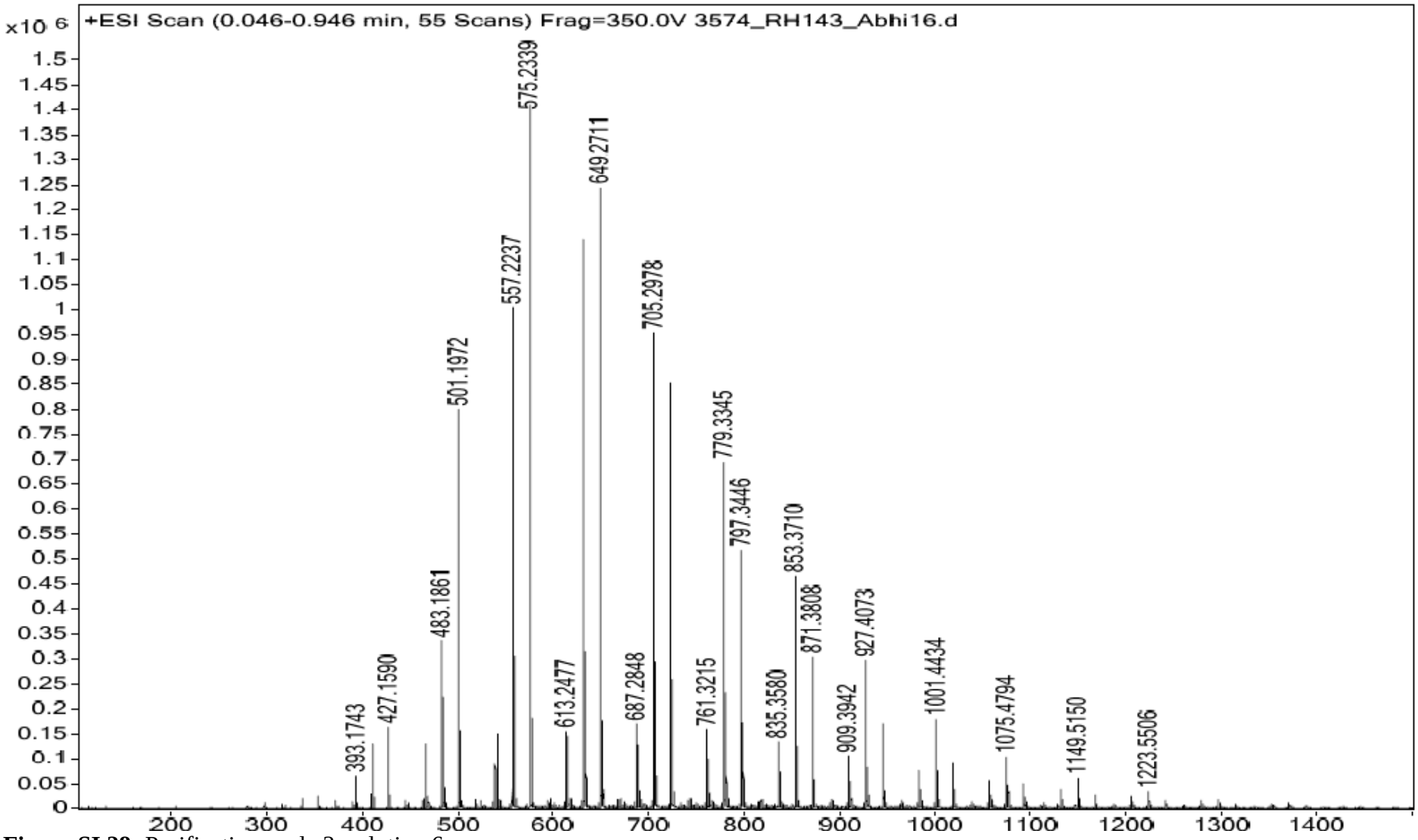


Figure SI 28: Purification cycle 3, solution 6.

3. GPC chromatograms

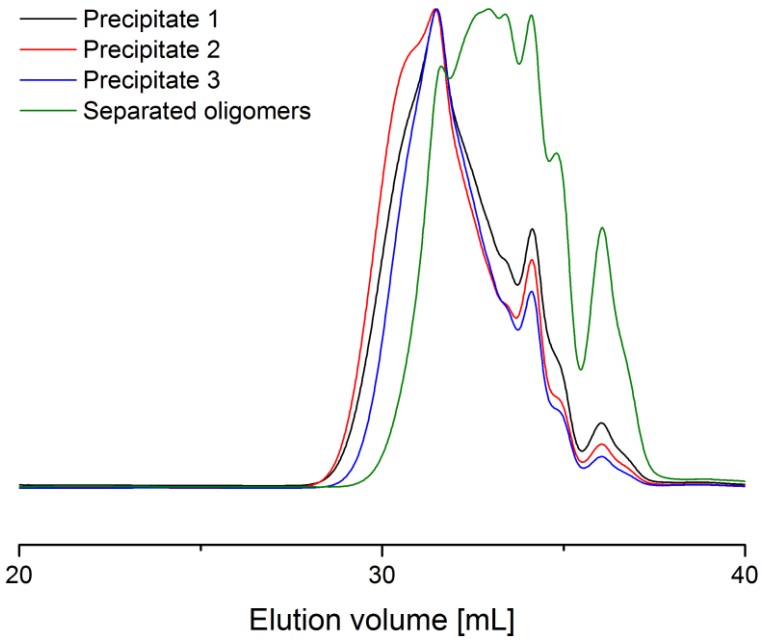


Figure SI 16: GPC eluogram of glycerol oligomers obtained from the 1st precipitation cycle.

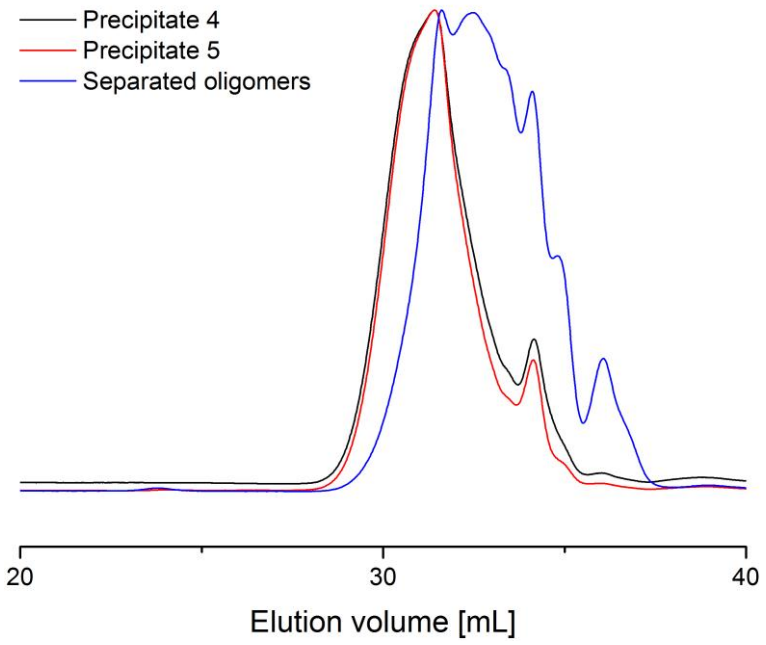


Figure SI 17: GPC eluogram of glycerol oligomers obtained from the 2nd precipitation cycle.

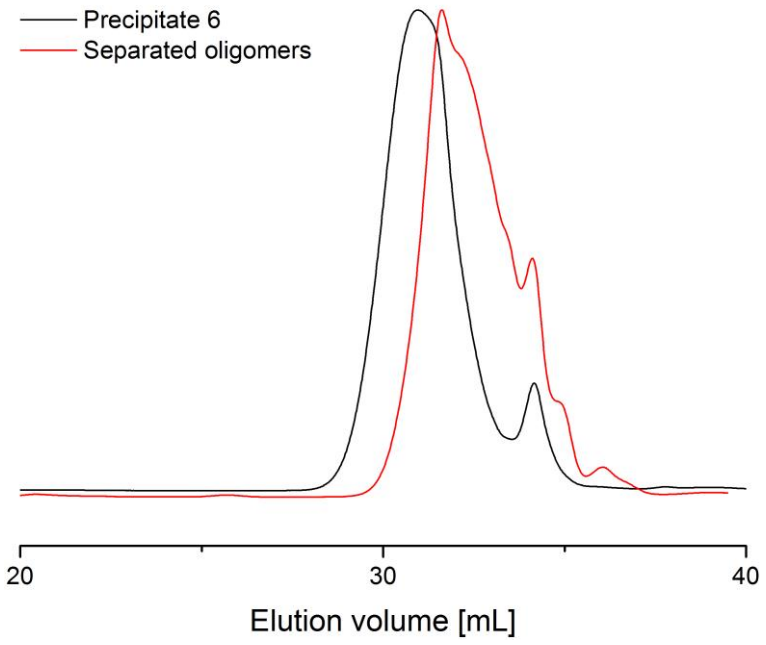
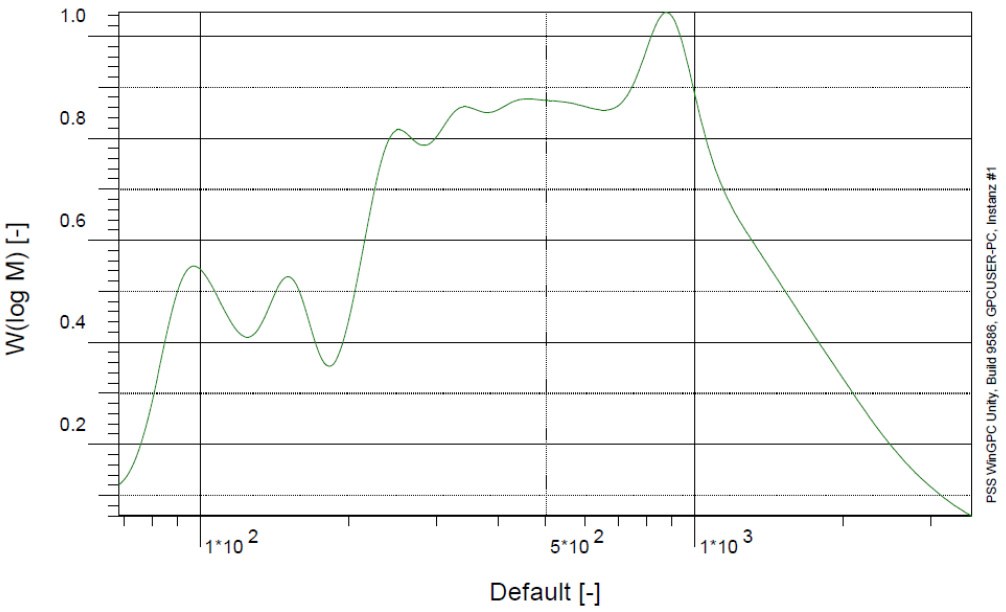
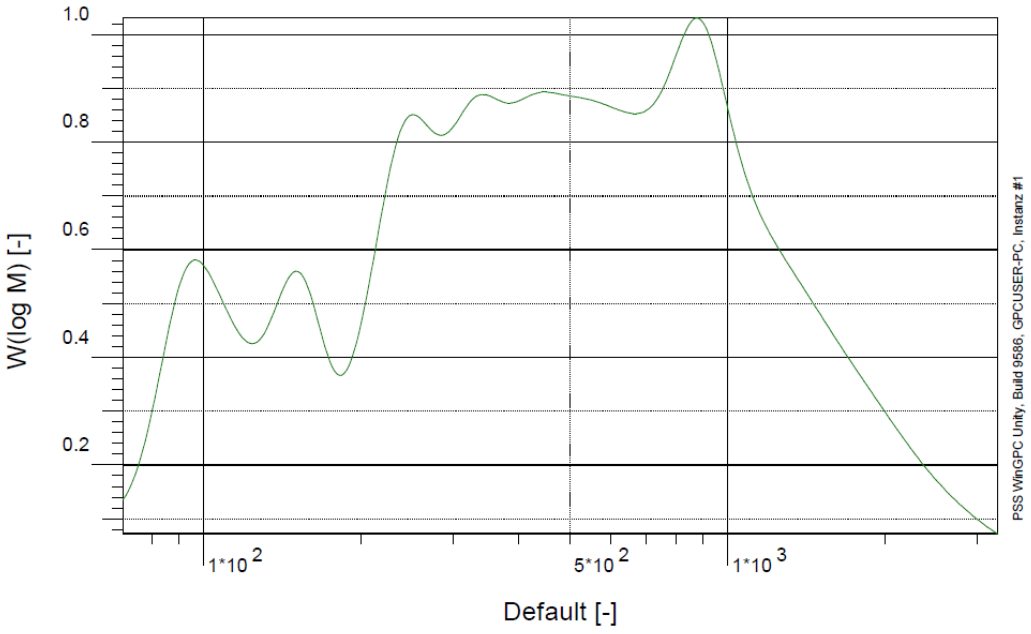


Figure SI 18: GPC eluogram of glycerol oligomers obtained from the 3rd precipitation cycle.

a.


1.0
0.8
0.6
0.4
0.2
W(log M) [-]
1*10 2
5*10 2
1*10 3
Default [-]
PSS WinGPC Unity, Build 9586, GPCUSER-PC, Instanz #1

b.


1.0
0.8
0.6
0.4
0.2
W(log M) [-]
1*10 2
5*10 2
1*10 3
Default [-]
PSS WinGPC Unity, Build 9586, GPCUSER-PC, Instanz #1

c.

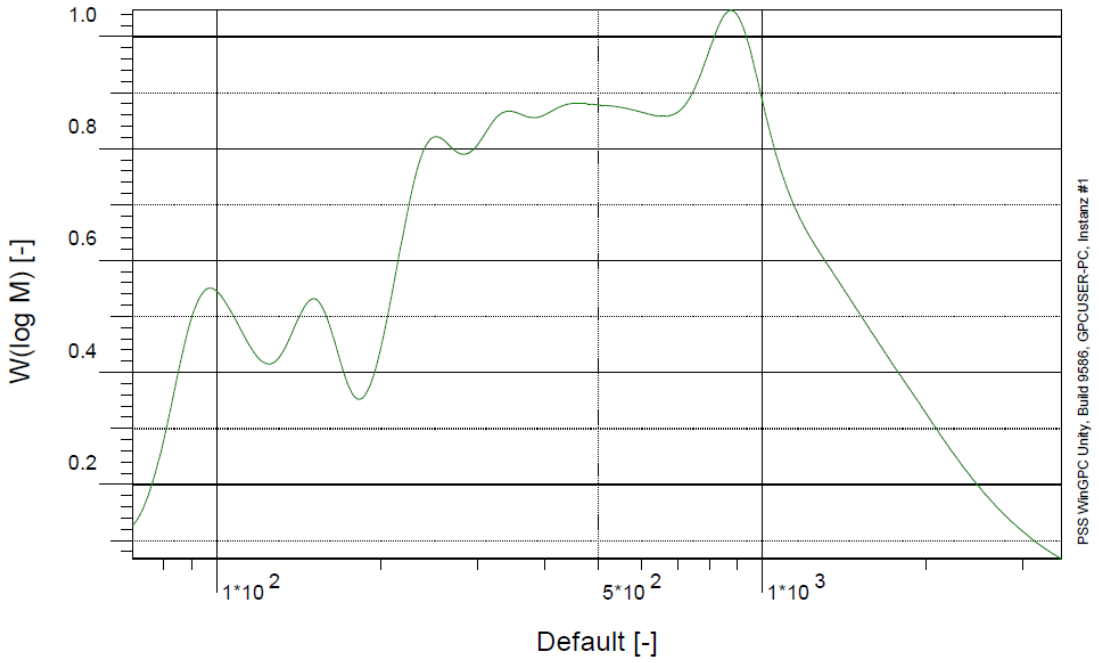


Figure SI 15: GPC eluogram of glycerol oligomers obtained (molecular weight in x axis) of crude olygomers of glycerol obtained from optimized multimodal MW process (repeated 3 times)

GC chromatograms

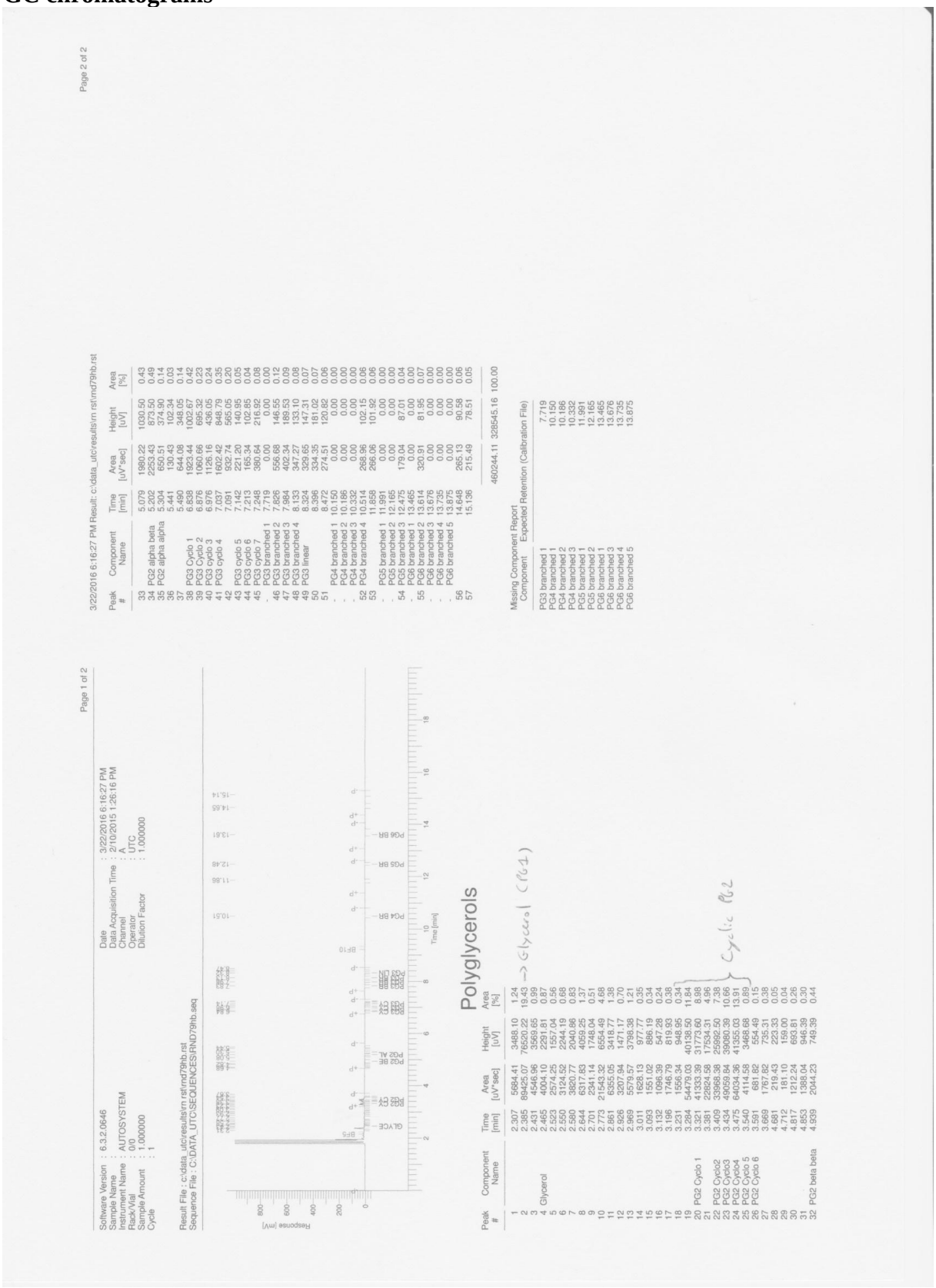
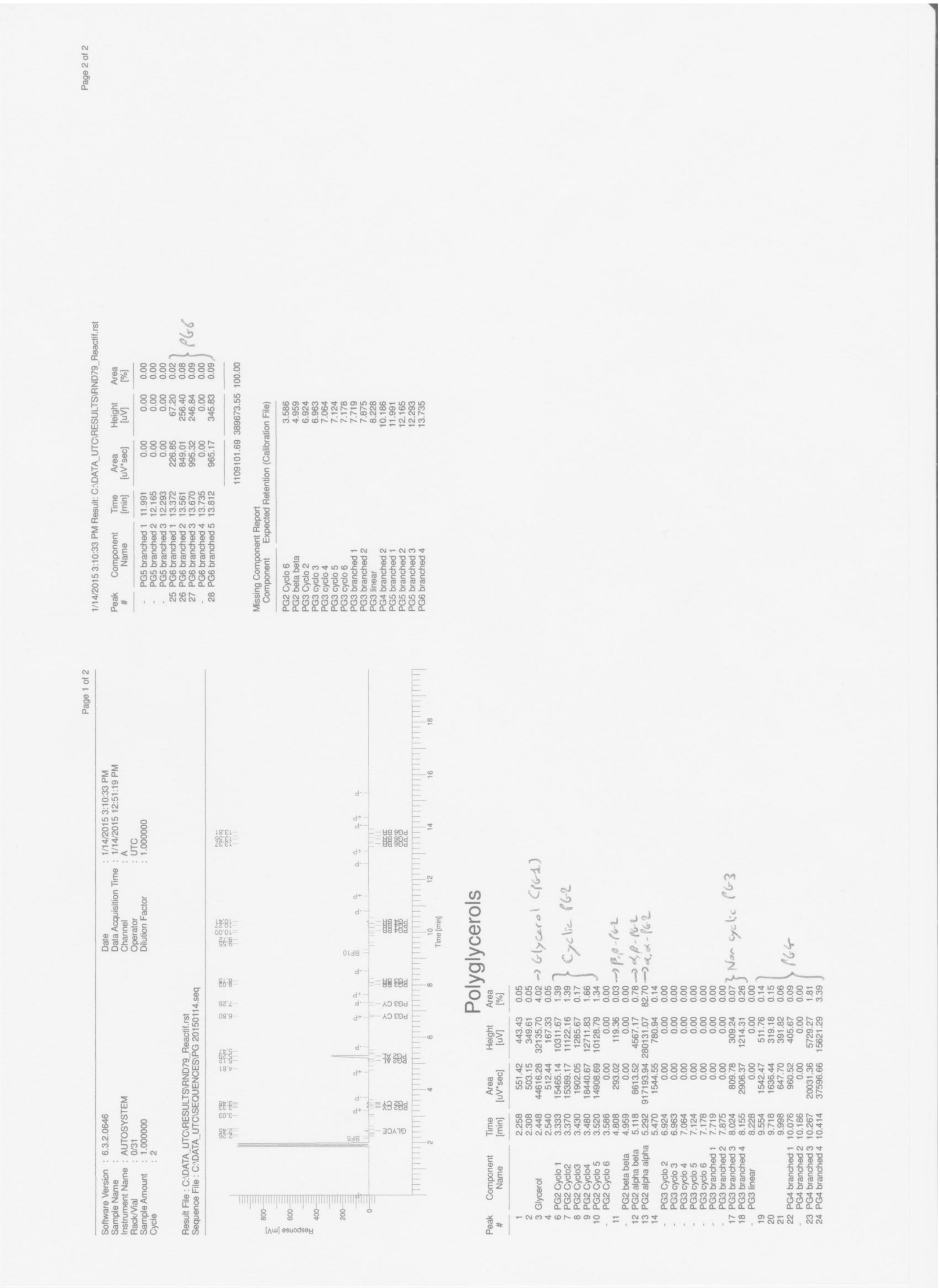


Figure SI 7: Identification of organic residue.



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Software Version : 6.3.2.0646
Sample Name :
Instrument Name : AUTOSYSTEM
Rack/Vial : 0/31
Sample Amount : 1.000000
Cycle : 2

Date : 1/14/2015 3:10:33 PM
Data Acquisition Time : 1/14/2015 12:51:19 PM
Channel : A
Operator : UTC
Dilution Factor : 1.000000

Result File : C:\DATA_UTC\RESULTS\RND79_Reactif.rst
Sequence File : C:\DATA_UTC\SEQUENCES\PG 20150114.seq

Polyglycerols

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	
1		2.258	551.42	443.43	0.05	
2		2.308	503.15	349.61	0.05	
3	Glycerol	2.448	44616.28	32135.70	4.02	→ Glycerol (PG1)
4		2.540	512.44	167.33	0.05	
6	PG2 Cyclo 1	3.333	15465.14	10311.67	1.39	Cyclic PG2
7	PG2 Cyclo2	3.370	15389.17	11122.16	1.39	
8	PG2 Cyclo3	3.430	1902.05	1285.67	0.17	
9	PG2 Cyclo4	3.480	18440.67	12711.83	1.66	
10	PG2 Cyclo 5	3.520	14908.69	10128.79	1.34	
-	PG2 Cyclo 6	3.586	0.00	0.00	0.00	
11		4.808	293.02	119.36	0.03	→ β,β-PG2
-	PG2 beta beta	4.959	0.00	0.00	0.00	
12	PG2 alpha beta	5.118	8613.52	4567.17	0.78	→ α,β-PG2
13	PG2 alpha alpha	5.292	917193.94	280131.07	82.70	→ α,α-PG2
14		5.470	1544.55	780.94	0.14	
-	PG3 Cyclo 2	6.924	0.00	0.00	0.00	
-	PG3 cyclo 3	6.963	0.00	0.00	0.00	
-	PG3 cyclo 4	7.064	0.00	0.00	0.00	
-	PG3 cyclo 5	7.124	0.00	0.00	0.00	
-	PG3 cyclo 6	7.178	0.00	0.00	0.00	
-	PG3 branched 1	7.719	0.00	0.00	0.00	
-	PG3 branched 2	7.875	0.00	0.00	0.00	
17	PG3 branched 3	8.024	809.78	309.24	0.07	Non cyclic PG3
18	PG3 branched 4	8.155	2906.37	1214.31	0.26	
-	PG3 linear	8.228	0.00	0.00	0.00	
19		9.554	1542.47	511.76	0.14	PG4
20		9.718	1636.44	319.18	0.15	
21		9.998	647.70	391.82	0.06	
22	PG4 branched 1	10.076	960.52	405.67	0.09	
-	PG4 branched 2	10.186	0.00	0.00	0.00	
23	PG4 branched 3	10.267	20031.36	5729.27	1.81	
24	PG4 branched 4	10.414	37596.66	15621.29	3.39	

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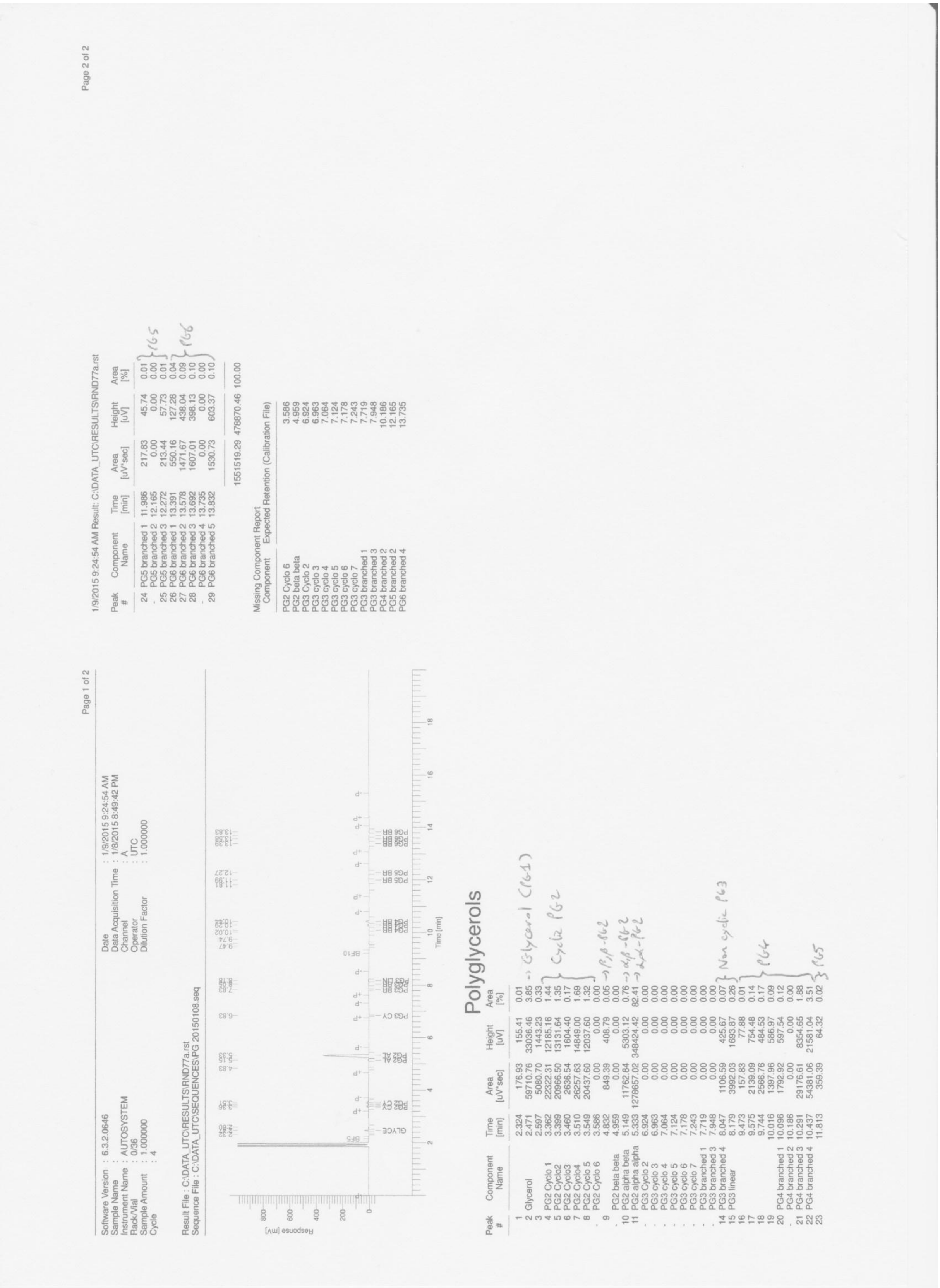
1/14/2015 3:10:33 PM Result: C:\DATA_UTC\RESULTS\RND79_Reactif.rst

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	
-	PG5 branched 1	11.991	0.00	0.00	0.00	
-	PG5 branched 2	12.165	0.00	0.00	0.00	
-	PG5 branched 3	12.293	0.00	0.00	0.00	
25	PG6 branched 1	13.372	226.85	67.20	0.02	PG6
26	PG6 branched 2	13.561	849.01	256.40	0.08	
27	PG6 branched 3	13.670	995.32	246.84	0.09	
-	PG6 branched 4	13.735	0.00	0.00	0.00	
28	PG6 branched 5	13.812	965.17	345.83	0.09	
			1109101.69	389673.55	100.00	

Missing Component Report

Component	Expected Retention (Calibration File)
PG2 Cyclo 6	3.586
PG2 beta beta	4.959
PG3 Cyclo 2	6.924
PG3 cyclo 3	6.963
PG3 cyclo 4	7.064
PG3 cyclo 5	7.124
PG3 cyclo 6	7.178
PG3 branched 1	7.719
PG3 branched 2	7.875
PG3 linear	8.228
PG4 branched 2	10.186
PG5 branched 1	11.991
PG5 branched 2	12.165
PG5 branched 3	12.293
PG6 branched 4	13.735

Figure SI 8: Reaction with diglycerol mixture (96 wt%) as reagent, and K_2CO_3 (4 wt%) as catalyst, at 300 W after 0 minutes.



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Software Version : 6.3.2.0646
Sample Name :
Instrument Name : AUTOSYSTEM
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Sample Amount : 1.000000
Cycle : 4

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Data Acquisition Time : 1/8/2015 8:49:42 PM
Channel : A
Operator : UTC
Dilution Factor : 1.000000

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Sequence File : C:\DATA_UTC\SEQUENCES\PG 20150108.seq

Polyglycerols

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1		2.324	176.93	155.41	0.01	
2	Glycerol	2.471	59710.76	33036.46	3.85	→ Glycerol (PG1)
3		2.597	5080.70	1443.23	0.33	
4	PG2 Cyclo 1	3.362	22322.31	12185.16	1.44	} Cyclic PG2
5	PG2 Cyclo2	3.399	20966.50	13131.64	1.35	
6	PG2 Cyclo3	3.460	2636.54	1604.40	0.17	
7	PG2 Cyclo4	3.510	26257.63	14849.00	1.69	
8	PG2 Cyclo 5	3.549	20437.60	12037.60	1.32	
-	PG2 Cyclo 6	3.586	0.00	0.00	0.00	
9		4.832	849.39	408.79	0.05	→ β,β-PG2
-	PG2 beta beta	4.959	0.00	0.00	0.00	
10	PG2 alpha beta	5.149	11762.84	5303.12	0.76	→ α,β-PG2
11	PG2 alpha alpha	5.333	1278657.02	348424.42	82.41	→ α,α-PG2
-	PG3 Cyclo 2	6.924	0.00	0.00	0.00	
-	PG3 cyclo 3	6.963	0.00	0.00	0.00	
-	PG3 cyclo 4	7.064	0.00	0.00	0.00	
-	PG3 cyclo 5	7.124	0.00	0.00	0.00	
-	PG3 cyclo 6	7.178	0.00	0.00	0.00	
-	PG3 cyclo 7	7.243	0.00	0.00	0.00	
-	PG3 branched 1	7.719	0.00	0.00	0.00	
-	PG3 branched 3	7.948	0.00	0.00	0.00	
14	PG3 branched 4	8.047	1106.59	425.67	0.07	} Non cyclic PG3
15	PG3 linear	8.179	3992.03	1693.87	0.26	
16		9.473	157.83	77.88	0.01	} PG4
17		9.575	2139.09	754.48	0.14	
18		9.744	2566.76	484.53	0.17	
19		10.016	1397.96	586.97	0.09	
20	PG4 branched 1	10.096	1792.92	597.54	0.12	
-	PG4 branched 2	10.186	0.00	0.00	0.00	
21	PG4 branched 3	10.291	29176.61	8354.65	1.88	
22	PG4 branched 4	10.437	54381.06	21581.04	3.51	
23		11.813	359.39	64.32	0.02	} PG5

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1/9/2015 9:24:54 AM Result: C:\DATA_UTC\RESULTS\RND77a.rst

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	
24	PG5 branched 1	11.986	217.83	45.74	0.01	} PG5
-	PG5 branched 2	12.165	0.00	0.00	0.00	
25	PG5 branched 3	12.272	213.44	57.73	0.01	
26	PG6 branched 1	13.391	550.16	127.28	0.04	} PG6
27	PG6 branched 2	13.578	1471.67	438.04	0.09	
28	PG6 branched 3	13.692	1607.01	398.13	0.10	
-	PG6 branched 4	13.735	0.00	0.00	0.00	
29	PG6 branched 5	13.832	1530.73	603.37	0.10	
			1551519.29	478870.46	100.00	

Missing Component Report

Component	Expected Retention (Calibration File)
PG2 Cyclo 6	3.586
PG2 beta beta	4.959
PG3 Cyclo 2	6.924
PG3 cyclo 3	6.963
PG3 cyclo 4	7.064
PG3 cyclo 5	7.124
PG3 cyclo 6	7.178
PG3 cyclo 7	7.243
PG3 branched 1	7.719
PG3 branched 3	7.948
PG4 branched 2	10.186
PG5 branched 2	12.165
PG6 branched 4	13.735

Figure SI 9: Reaction with diglycerol mixture (96 wt%) as reagent, and K_2CO_3 (4 wt%) as catalyst, at 300 W after 5 minutes.

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Software Version : 6.3.2.0646
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Instrument Name : AUTOSYSTEM
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Cycle : 5

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Data Acquisition Time : 1/8/2015 9:19:49 PM
Channel : A
Operator : UTC
Dilution Factor : 1.000000

Result File : C:\DATA_UTC\RESULTS\RND77b.rst
Sequence File : C:\DATA_UTC\SEQUENCES\PG 20150108.seq

Response [mV]

Time [min]

Polyglycerols

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		2.277	353.31	237.99	0.02
2		2.327	386.47	260.77	0.02
3	Glycerol	2.469	67013.00	38448.31	4.04
4		2.575	4300.28	1325.02	0.26
5	PG2 Cyclo 1	3.361	22664.75	12852.37	1.36
6	PG2 Cyclo2	3.388	22597.53	14264.49	1.36
7	PG2 Cyclo3	3.459	2788.99	1709.50	0.17
8	PG2 Cyclo 4	3.509	2772.57	1653.88	1.67
9	PG2 Cyclo 5	3.549	21889.57	13161.20	1.32
10	PG2 Cyclo 6	3.586	0.00	0.00	0.00
		4.834	579.34	251.06	0.03
	PG2 beta beta	4.959	0.00	0.00	0.00
11	PG2 alpha beta	5.153	12565.26	5400.87	0.76
12	PG2 alpha alpha	5.331	1362170.54	356245.79	82.02
13	PG3 Cyclo 1	6.831	101.94	80.10	0.01
	PG3 Cyclo 2	6.924	0.00	0.00	0.00
	PG3 cyclo 3	6.963	0.00	0.00	0.00
	PG3 cyclo 4	7.064	0.00	0.00	0.00
	PG3 cyclo 5	7.124	0.00	0.00	0.00
	PG3 cyclo 6	7.178	0.00	0.00	0.00
	PG3 cyclo 7	7.243	0.00	0.00	0.00
	PG3 branched 1	7.719	0.00	0.00	0.00
14	PG3 branched 2	7.834	257.57	95.86	0.02
	PG3 branched 3	7.948	0.00	0.00	0.00
15	PG3 branched 4	8.056	2667.81	1120.15	0.16
16	PG3 linear	8.182	6469.64	2797.33	0.39
17		8.473	2241.85	1102.82	0.13
18		9.578	2464.19	855.92	0.15
19		9.744	2387.06	515.35	0.14
20		10.019	1115.64	601.47	0.07
21	PG4 branched 1	10.099	1416.21	598.09	0.09
	PG4 branched 2	10.186	0.00	0.00	0.00

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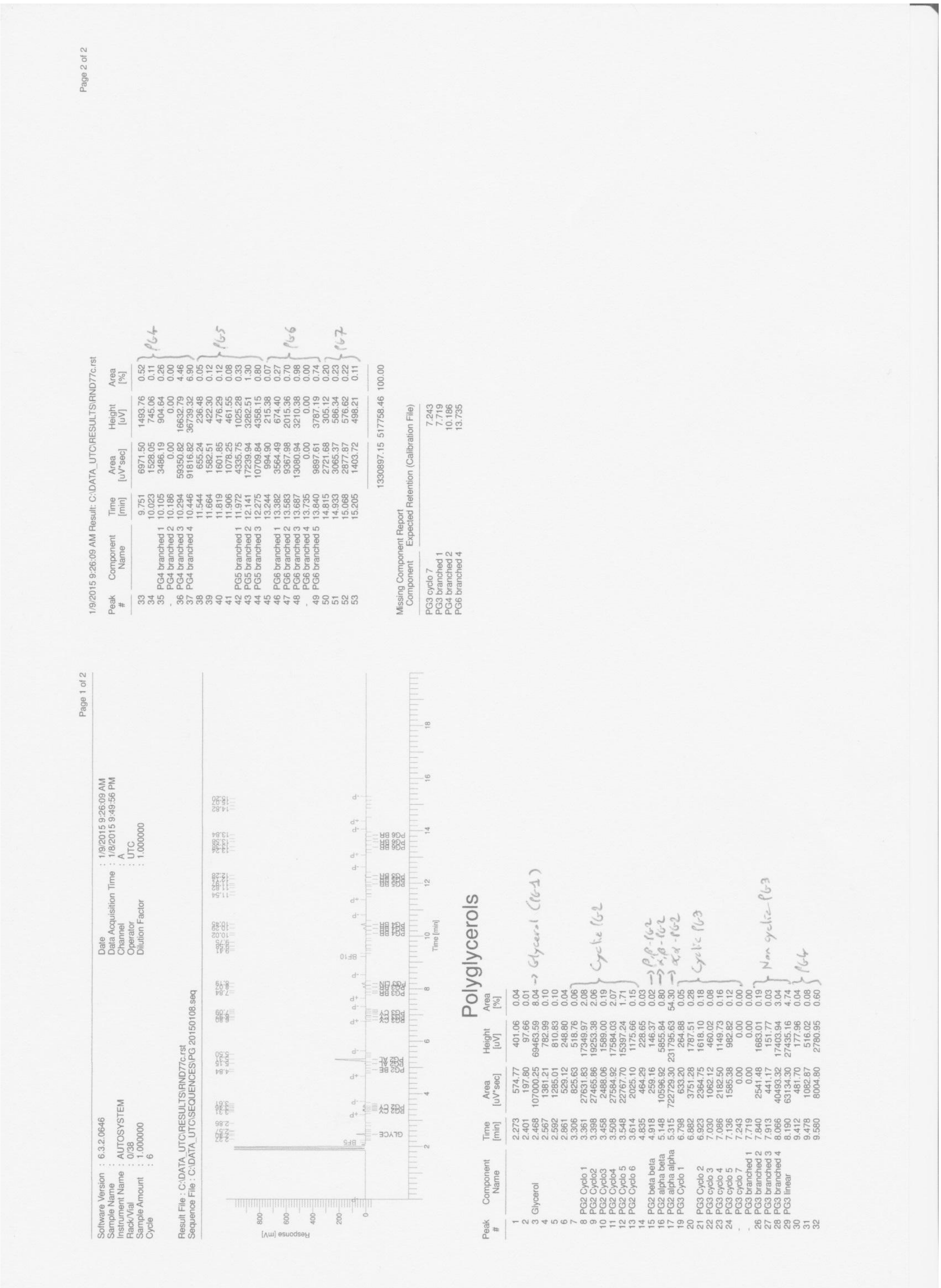
1/9/2015 9:25:24 AM Result: C:\DATA_UTC\RESULTS\RND77b.rst

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
22	PG4 branched 3	10.296	31849.89	9029.67	1.92
23	PG4 branched 4	10.438	5967.91	2375.08	0.36
24		11.383	161.78	58.12	0.01
25		11.538	204.12	97.84	0.01
	PG5 branched 1	11.991	0.00	0.00	0.00
26	PG5 branched 2	12.095	399.03	75.47	0.02
27	PG5 branched 3	12.266	308.72	114.61	0.02
28	PG6 branched 1	13.391	654.38	141.72	0.04
29	PG6 branched 2	13.578	1683.14	484.32	0.10
30	PG6 branched 3	13.693	1868.23	467.43	0.11
	PG6 branched 4	13.735	0.00	0.00	0.00
31	PG6 branched 5	13.835	1819.28	657.22	0.11
			1660765.77	501977.04	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PG2 Cyclo 6	3.586
PG2 beta beta	4.959
PG3 Cyclo 2	6.924
PG3 cyclo 3	6.963
PG3 cyclo 4	7.064
PG3 cyclo 5	7.124
PG3 cyclo 6	7.178
PG3 cyclo 7	7.243
PG3 branched 1	7.719
PG3 branched 3	7.948
PG4 branched 2	10.186
PG5 branched 1	11.991
PG6 branched 4	13.735

Figure SI 10: Reaction with diglycerol mixture (96 wt%) as reagent, and K_2CO_3 (4 wt%) as catalyst, at 300 W after 10 minutes.



Software Version : 6.3.2.0646
Sample Name :
Instrument Name : AUTOSYSTEM
Rack/Vial : 0/38
Sample Amount : 1.000000
Cycle : 6

Date : 1/9/2015 9:26:09 AM
Data Acquisition Time : 1/8/2015 9:49:56 PM
Channel : A
Operator : UTC
Dilution Factor : 1.000000

Result File : C:\DATA_UTC\RESULTS\RND77c.rst
Sequence File : C:\DATA_UTC\SEQUENCES\PG 20150108.seq

Polyglycerols

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		2.273	574.77	401.06	0.04
2		2.401	197.80	97.66	0.01
3	Glycerol	2.468	107000.25	69463.59	8.04
4		2.567	1381.21	782.99	0.10
5		2.592	1285.01	810.83	0.10
6		2.861	529.12	248.80	0.04
7		3.306	825.63	518.76	0.06
8	PG2 Cyclo 1	3.361	27631.83	17349.97	2.08
9	PG2 Cyclo2	3.398	27465.86	19253.38	2.06
10	PG2 Cyclo3	3.458	2488.06	1589.00	0.19
11	PG2 Cyclo4	3.508	27584.92	17584.03	2.07
12	PG2 Cyclo 5	3.548	22767.70	15397.24	1.71
13	PG2 Cyclo 6	3.614	2025.10	1175.66	0.15
14		4.835	464.29	228.65	0.03
15	PG2 beta beta	4.918	259.16	146.37	0.02
16	PG2 alpha beta	5.148	10596.92	5855.84	0.80
17	PG2 alpha alpha	5.315	722729.30	231795.63	54.30
19	PG3 Cyclo 1	6.798	633.20	264.88	0.05
20		6.882	3751.28	1787.51	0.28
21	PG3 Cyclo 2	6.923	2364.75	1618.10	0.18
22	PG3 cyclo 3	7.030	1062.12	460.02	0.08
23	PG3 cyclo 4	7.086	2182.50	1149.73	0.16
24	PG3 cyclo 5	7.136	1585.38	982.82	0.12
-	PG3 cyclo 7	7.243	0.00	0.00	0.00
-	PG3 branched 1	7.719	0.00	0.00	0.00
26	PG3 branched 2	7.840	2541.48	1683.01	0.19
27	PG3 branched 3	7.913	441.17	151.77	0.03
28	PG3 branched 4	8.066	40493.32	17403.94	3.04
29	PG3 linear	8.190	63134.30	27435.16	4.74
30		9.412	481.70	177.96	0.04
31		9.478	1082.87	516.02	0.08
32		9.580	8004.80	2780.95	0.60

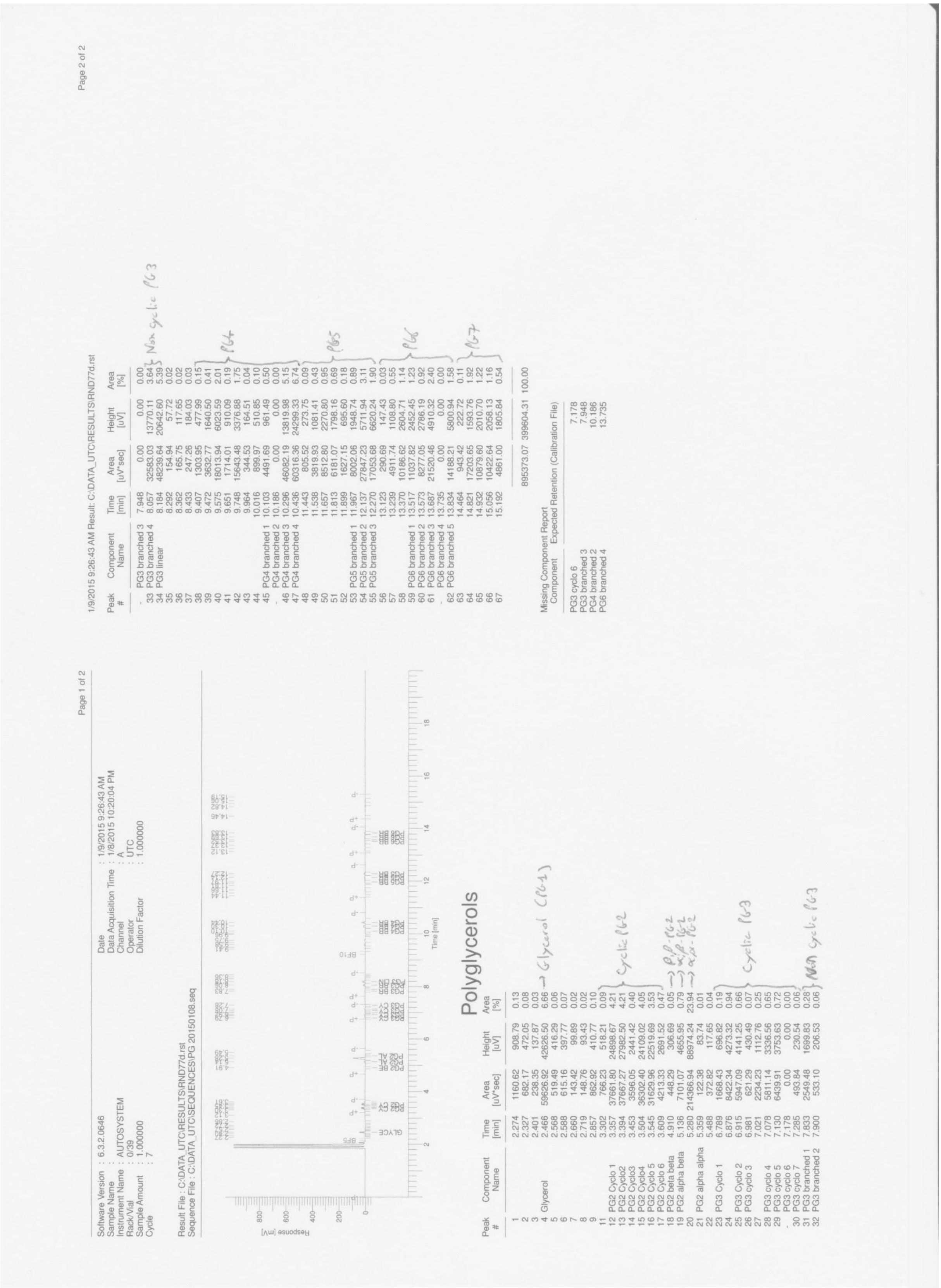
1/9/2015 9:26:09 AM Result: C:\DATA_UTC\RESULTS\RND77c.rst

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
33		9.751	6971.50	1493.76	0.52
34		10.023	1528.05	745.06	0.11
35	PG4 branched 1	10.105	3486.19	904.64	0.26
-	PG4 branched 2	10.186	0.00	0.00	0.00
36	PG4 branched 3	10.294	59350.82	16632.79	4.46
37	PG4 branched 4	10.446	91816.82	36739.32	6.90
38		11.544	655.24	236.48	0.05
39		11.664	1582.51	422.30	0.12
40		11.819	1601.85	476.29	0.12
41		11.906	1078.25	461.55	0.08
42	PG5 branched 1	11.972	4335.75	1025.28	0.33
43	PG5 branched 2	12.141	17239.94	3282.51	1.30
44	PG5 branched 3	12.275	10709.84	4358.15	0.80
45		13.244	994.90	215.38	0.07
46	PG6 branched 1	13.382	3564.49	674.40	0.27
47	PG6 branched 2	13.583	9367.98	2015.36	0.70
48	PG6 branched 3	13.687	13080.94	3210.38	0.98
-	PG6 branched 4	13.735	0.00	0.00	0.00
49	PG6 branched 5	13.840	9897.61	3787.19	0.74
50		14.815	2721.68	305.12	0.20
51		14.933	3065.37	586.34	0.23
52		15.068	2877.87	576.62	0.22
53		15.205	1403.72	498.21	0.11
			1330897.15	517758.46	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PG3 cyclo 7	7.243
PG3 branched 1	7.719
PG4 branched 2	10.186
PG6 branched 4	13.735

Figure SI 11: Reaction with diglycerol mixture (96 wt%) as reagent, and K_2CO_3 (4 wt%) as catalyst, at 300 W after 15 minutes.



Page 1 of 2

Software Version : 6.3.2.0646
Sample Name :
Instrument Name : AUTOSYSTEM
Rack/Vial : 0/39
Sample Amount : 1.000000
Cycle : 7

Date : 1/9/2015 9:26:43 AM
Data Acquisition Time : 1/8/2015 10:20:04 PM
Channel : A
Operator : UTC
Dilution Factor : 1.000000

Result File : C:\DATA_UTC\RESULTS\RND77d.rst
Sequence File : C:\DATA_UTC\SEQUENCES\PG 20150108.seq

Polyglycerols

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		2.274	1160.62	908.79	0.13
2		2.327	682.17	472.05	0.08
3		2.401	238.35	137.87	0.03
4	Glycerol	2.466	59626.92	42626.50	6.66
5		2.568	519.49	416.29	0.06
6		2.588	615.16	397.77	0.07
7		2.660	143.42	99.89	0.02
8		2.719	148.76	93.43	0.02
9		2.857	862.92	410.77	0.10
11		3.302	766.23	518.21	0.09
12	PG2 Cyclo 1	3.357	37661.80	24898.67	4.21
13	PG2 Cyclo2	3.394	37667.27	27982.50	4.21
14	PG2 Cyclo3	3.453	3596.05	2441.42	0.40
15	PG2 Cyclo4	3.504	36302.40	24109.02	4.05
16	PG2 Cyclo 5	3.545	31629.96	22519.69	3.53
17	PG2 Cyclo 6	3.609	4213.33	2691.52	0.47
18	PG2 beta beta	4.910	448.29	306.69	0.05
19	PG2 alpha beta	5.136	7101.07	4655.95	0.79
20		5.280	214366.94	88974.24	23.94
21	PG2 alpha alpha	5.359	122.38	83.74	0.01
22		5.488	372.82	117.65	0.04
23	PG3 Cyclo 1	6.789	1668.43	696.82	0.19
24		6.876	8422.34	4273.32	0.94
25	PG3 Cyclo 2	6.915	5947.09	4141.25	0.66
26	PG3 cyclo 3	6.981	621.29	430.49	0.07
27		7.021	2234.23	1112.76	0.25
28	PG3 cyclo 4	7.078	5811.14	3336.56	0.65
29	PG3 cyclo 5	7.130	6439.91	3753.63	0.72
-	PG3 cyclo 6	7.178	0.00	0.00	0.00
30	PG3 cyclo 7	7.285	493.84	230.54	0.06
31	PG3 branched 1	7.833	2549.48	1699.83	0.28
32	PG3 branched 2	7.900	533.10	206.53	0.06

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1/9/2015 9:26:43 AM Result: C:\DATA_UTC\RESULTS\RND77d.rst

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
-	PG3 branched 3	7.948	0.00	0.00	0.00
33	PG3 branched 4	8.057	32583.03	13770.11	3.64
34	PG3 linear	8.184	48239.64	20642.60	5.39
35		8.292	154.94	57.72	0.02
36		8.362	165.75	117.65	0.02
37		8.433	247.26	184.03	0.03
38		9.407	1303.95	477.99	0.15
39		9.472	3632.77	1640.50	0.41
40		9.575	18013.94	6023.59	2.01
41		9.651	1714.01	910.09	0.19
42		9.748	15643.48	3376.88	1.75
43		9.964	344.53	164.51	0.04
44		10.016	899.97	510.85	0.10
45	PG4 branched 1	10.103	4491.69	961.49	0.50
-	PG4 branched 2	10.186	0.00	0.00	0.00
46	PG4 branched 3	10.296	46082.19	13819.98	5.15
47	PG4 branched 4	10.436	60316.36	24299.33	6.74
48		11.443	805.52	273.75	0.09
49		11.538	3819.93	1081.41	0.43
50		11.657	8512.80	2270.80	0.95
51		11.813	6181.07	1798.16	0.69
52		11.899	1627.15	695.60	0.18
53	PG5 branched 1	11.967	8002.06	1948.74	0.89
54	PG5 branched 2	12.137	27847.23	5711.94	3.11
55	PG5 branched 3	12.270	17053.68	6620.24	1.90
56		13.123	290.69	147.43	0.03
57		13.239	4911.74	1108.80	0.55
58		13.370	10186.62	2604.71	1.14
59	PG6 branched 1	13.517	11037.82	2452.45	1.23
60	PG6 branched 2	13.573	8277.05	2786.19	0.92
61	PG6 branched 3	13.687	21520.46	4910.32	2.40
-	PG6 branched 4	13.735	0.00	0.00	0.00
62	PG6 branched 5	13.834	14188.21	5800.94	1.58
63		14.464	943.42	222.72	0.11
64		14.821	17203.65	1593.76	1.92
65		14.932	10879.60	2010.70	1.22
66		15.056	10422.64	2058.13	1.16
67		15.192	4861.00	1805.84	0.54
			895373.07	399604.31	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PG3 cyclo 6	7.178
PG3 branched 3	7.948
PG4 branched 2	10.186
PG6 branched 4	13.735

Figure SI 12: Reaction with diglycerol mixture (96 wt%) as reagent, and K_2CO_3 (4 wt%) as catalyst, at 300 W after 20 minutes.

4. Aspect of the glycerol oligomers

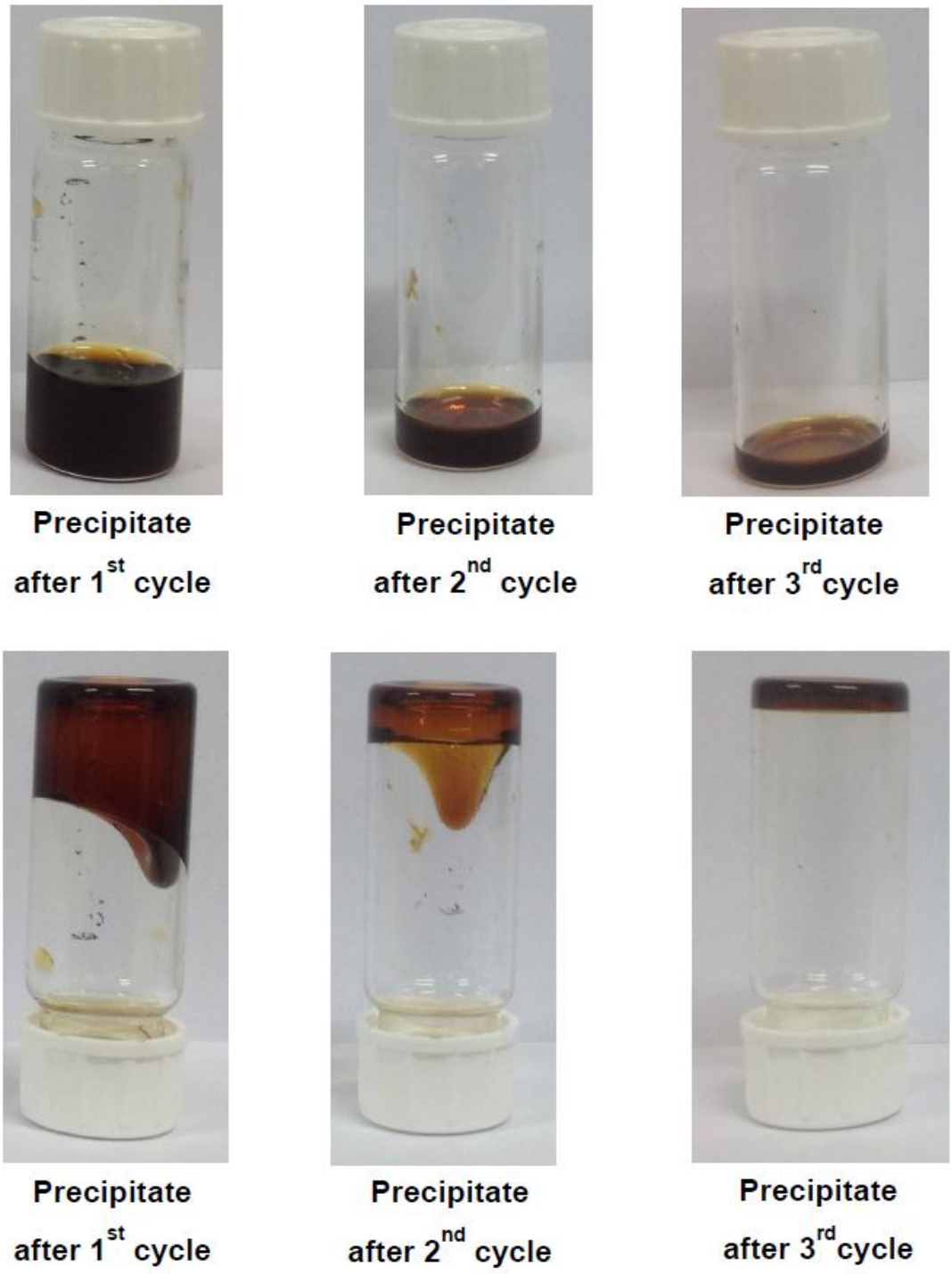

Figure SI 29: Aspect of glycerol oligomers after various purification cycles.

5. Preparation of α,α'-Diglycerol

5.1. Materials and Methods

All reagents from commercially available source. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker 400 MHz hold apparatus.

5.2. Synthesis of solketal glycidyl ether

To 110 g (0.81 mol) of solketal and 1.83 g (4.96 mmol) of TBAI, 96 g of an aqueous solution of NaOH (50 wt%, 1.2 mol) is added. The mixture is stirred for 30 minutes at room temperature, then cooled at < 0 ℃ and 150 g (1.62 mol) of epichlorohydrin are slowly added. Then, the mixture is allowed to warm slowly up to room temperature and stirred for 20 hours. It is finally hydrolyzed with 500 mL of water, and the aqueous layer is removed by decantation. The organic layer is dried over $MgSO_4$ and concentrated under reduced pressure, and purified by distillation under reduced pressure (105 ℃, 10 mmHg) to give 105.7 g (0.56 mol, 69% yield) of product.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.24 (m, 1H; CH), 4.01 (ddd, *J* = 1.4, 6.4, 8.1 Hz, 1H; CH_2), 3.77 (dt, *J* = 2.9, 12.0 Hz, 1H; CH_2), 3.68 (ddd, *J* = 6.4, 7.5, 8.3 Hz, 1H; CH_2), 3.58 ($^{1}/_{2}$ AB, *J* = 5.8, 10.0 Hz, 1H; CH_2, *diastereoisomer **1***), 3.52 (d, *J* = 5.0 Hz, 1H; CH_2, *diastereoisomer 2*), 3.52 (d, *J* = 6.1 Hz, 1H; CH_2, *diastereoisomer **2***), 3.46 ($^{1}/_{2}$ AB, *J* = 5.3, 10.0 Hz, 1H; CH_2, *diastereoisomer **1***), 3.37 (ddd, *J* = 6.0, 11.7, 15.8 Hz, 1H; CH_2), 3.13–3.08 (m, 1H; CH (Epoxide)), 2.74 (dd, *J* = 4 Hz, 5 Hz, 1H; CH_2 (Epoxide)), 2.55 (dt, *J* = 3 Hz, 5 Hz, 1H; CH_2 (Epoxide)), 1.37 (s, 3H; CH_3), 1.31 (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 109.4 (C4), 74.7 (CH_2), 72.4 (CH_2, *diastereoisomer **1***), 72.3 (2C, CH_2, *diastereoisomer **2***), 72.2 (CH_2, *diastereoisomer **1***), 66.6 (CH_2), 50.7 (CH), 44.1 (CH_2), 26.7 (CH_3), 25.4 (CH_3).

5.3. Deprotection

100 g of solketal glycidyl ether are dissolved in 200 mL of water in an autoclave and heated at 200 ℃ under saturated vapor pressure for 30 minutes. The solution is then lyophilized to afford the glycerol dimer (PG2).

^{1}H NMR (400 MHz, DMSO-d_6, δ): 3.56 (q, J = 4.0 Hz, 2H; CH), 3.27–3.42 (m, 8H; CH_2); ^{13}C NMR (100 MHz, DMSO-d_6, δ): 72.8 (CH_2)(2 C), 70.5 (CH)(2 C), 63.0 (CH_2)(2 C).