Supporting Information

Consequences of Isolated Critical Monomer Sequence Errors on the Hydrolysis Behaviors of Sequenced Degradable Polyesters

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1. Optical Profilometry Measurements

Figure S1

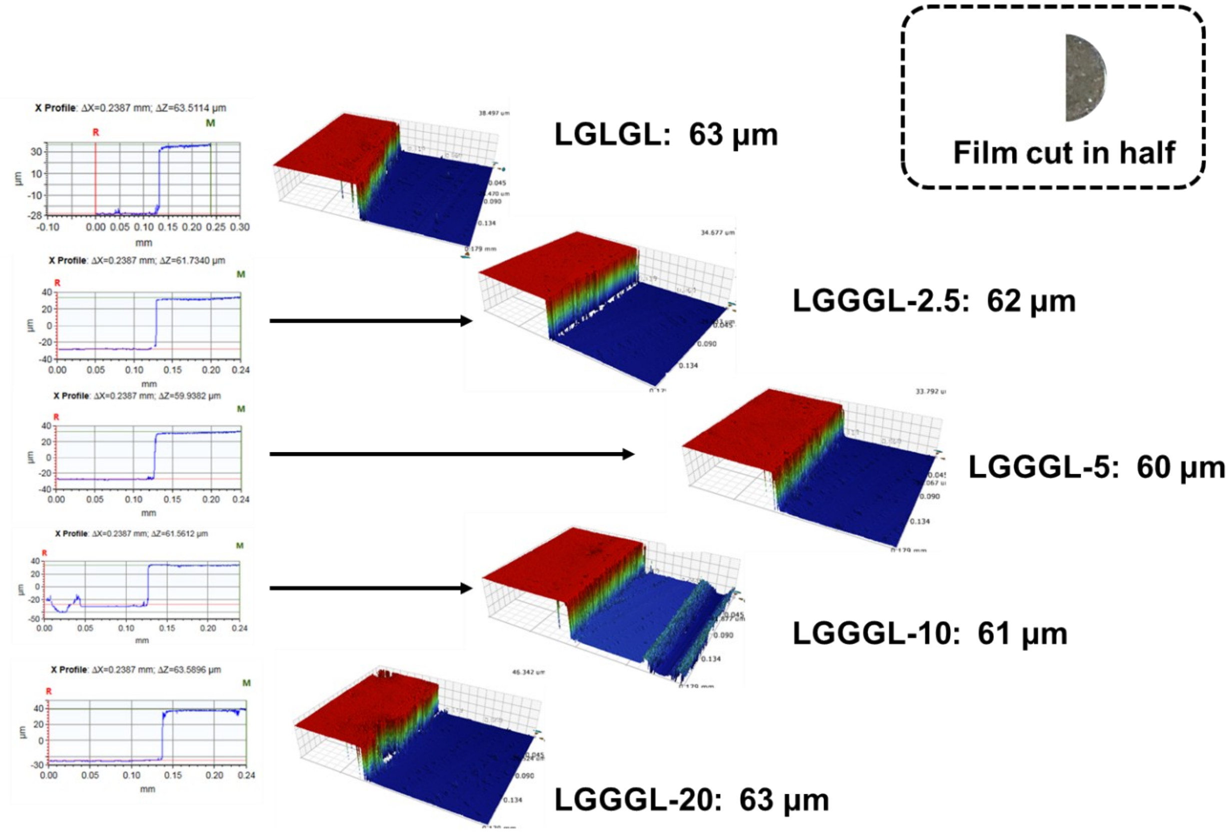


Figure S 1. Optical profilometry film thickness measurements.

2. Scanning Electron Microscopy Imaging

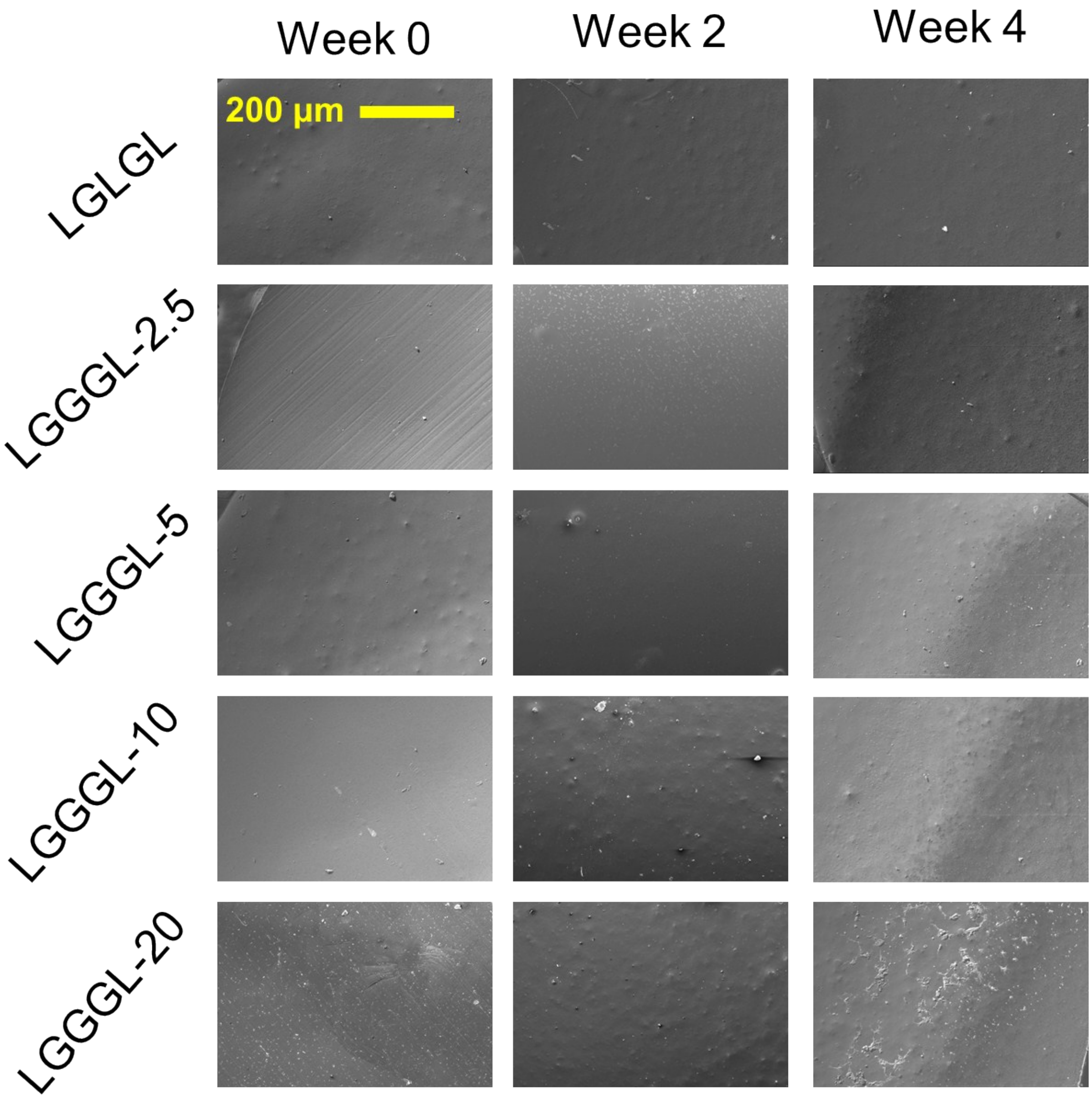


Figure S2. Scanning electron microscopy images (100x) of lyophilized films during hydrolysis.

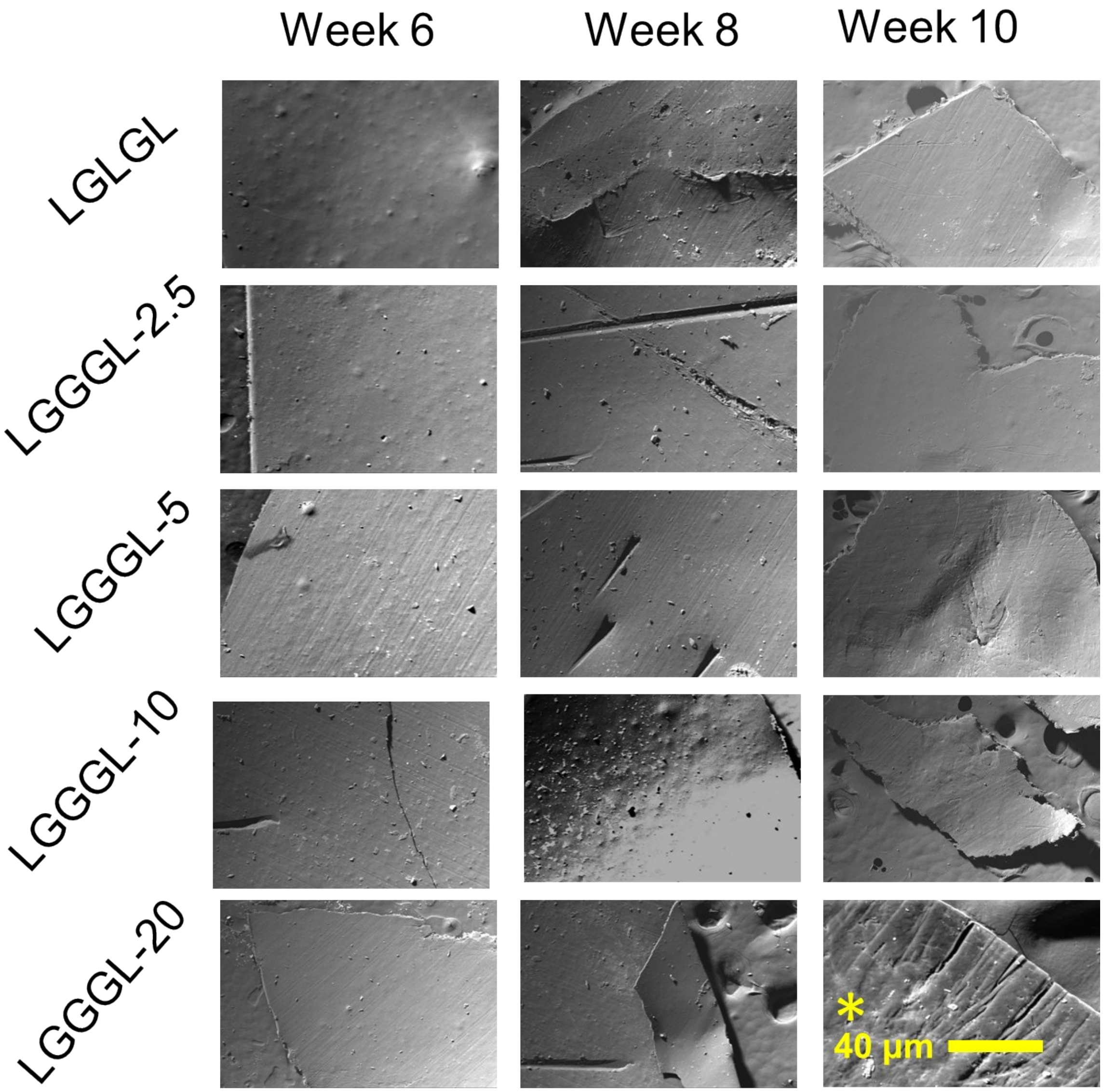


Figure S3. Scanning electron microscopy images (100x) of lyophilized films during hydrolysis.

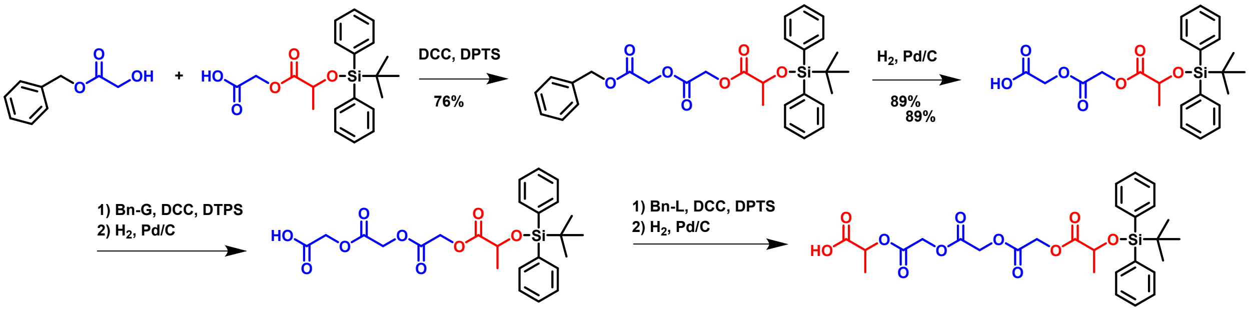
3 Experimental

3.1 General Information

All reactions were performed in an inert atmosphere under N_2 unless otherwise stated. Methylene chloride and ethyl acetate were purchased from Fisher Scientific, stored in a solvent system, and passed through an activated alumina column prior to use. DCC was purchased from Oakwood Chemicals and used without further purification. Nucleophilic catalyst DPTS was prepared by neutralization of p-toluene sulfonic acid with pyridine and purified by recrystallization in dichloroethane. Silica gel for column chromatography was purchased from Sorbent Technologies.

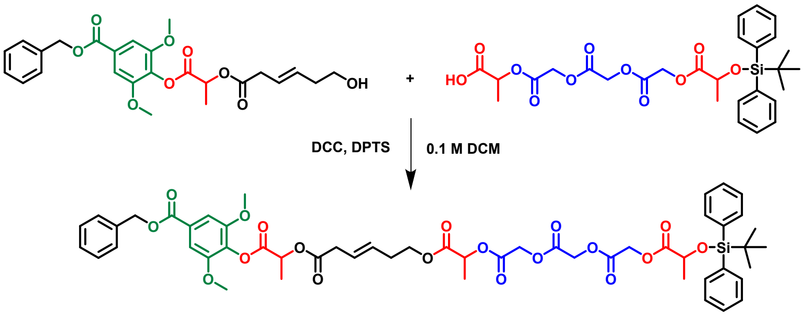
The detailed synthesis of **Cyc-SyLMLGLGL** was previously reported.[1]

Scheme S1



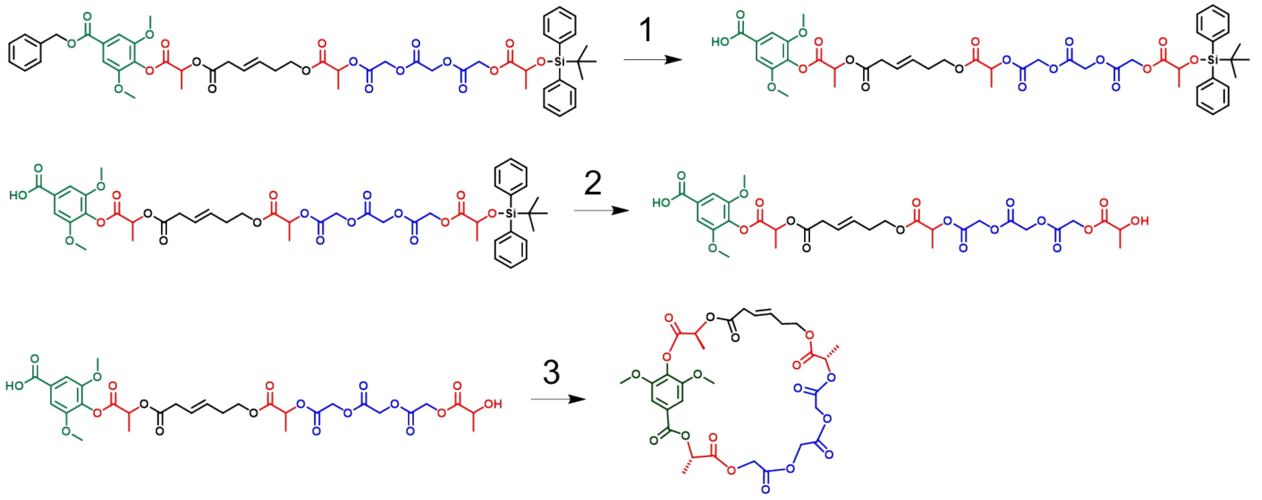
Scheme S1. Synthetic steps toward LGGGL-Si.

Scheme S2



Scheme S2. Steglich esterification to Bn-SyLMLGGGL-Si.

Scheme S3

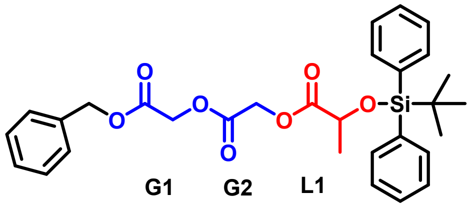


1:	$SiEt_3H$, NEt_3, PdOAc, 0.3 M DCM	70%
2:	TBAF, AcOH, 0.1 M THF	50%
3:	DCC, DPTS, 0.03 M, 16 hr. addition of SM, 60°C	65%

Scheme S3. Benzyl and silyl deprotections to yield SyLMLGGGL and subsequent macrolactonization reaction to prepare Cyc-SyLMLGGGL.

Spectra for all compounds/polymers begin on page S19.

Bn-GGL-Si



^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm)	Mult. (J)	Int.	Assignment
1.11	s	9	TBDPS - tBu
1.42	d (6.5)	3	L1 (CH_3)
4.40	q (6.5)	1	L1 (CH)
4.53	d (16)	1	G
4.73	d (16)	1	G
4.71	s	2	G
5.20	s	2	Bn (CH_2)
7.37	m	11	TBDPS – o, p + Bn
7.65	m	4	TBDPS - m

^{13}C-NMR (400 MHz, $CDCl_3$)

δ (ppm)	+ Assignment
19.90	TBDPS (C)
21.92	L1 (CH_3)
27.47	TBDPS (CH_3)
60.89	G (CH_2)
61.71	G (CH_2)
67.94	Bn (CH_2)
69.34	L1 (CH)
127.79	Arene
127.82	Arene
128.29	Arene
128.34	Arene
129.99	Arene
133.58	Arene
133.61	Arene
135.28	Arene
136.07	Arene
167.59	G1, G2 (CO)
173.62	L (CO)

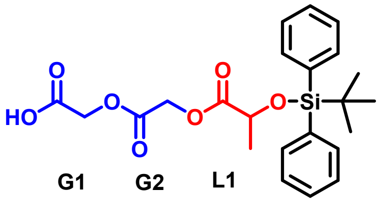
HRMS (ESI)

Calc. Mass	534.21 amu
Calc. $[M+Na^+]^+$	557.20 amu
Found $[M+Na^+]^+$	557.19766 amu
Composition	$C_{30}H_{34}O_7Si$

Bn-GGL-Si

Bn-G (5.12 g, 30.8 mmol) and **GL-Si** (11.35 g, 31.9 mmol) were dissolved in 290 mL DCM. DPTS (1.71 g, 5.8 mmol) was added and allowed to dissolve before the addition of DCC (6.58 g, 31.9 mmol). The reaction vessel was capped and the reaction was allowed to stir at RT overnight. The solution was filtered, concentrated *in vacuo*, and purified by column chromatography using 5% ethyl acetate in hexanes. Product eluted in fractions 5-11 (250 mL fractions). 10.3 g (66%).

GGL-Si



^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm)	Mult. (J)	Int.	Assignment
1.09	s	9	TBDPS - tBu
1.42	d (6.5)	3	L1 (CH_3)
4.40	q (6.5)	1	L1 (CH)
4.53	d (16)	1	G
4.73	d (16)	1	G
4.71	s	2	G
7.37	m	6	TBDPS – o, p
7.65	m	4	TBDPS - m

^{13}C-NMR (400 MHz, $CDCl_3$)

δ (ppm)	+ Assignment
19.38	TBDPS (C)
21.40	TBDPS (CH_3)
21.93	L1 (CH_3)
60.32	G (CH_2)
61.34	G (CH_2)
68.81	L (CH)
127.79	Arene
127.82	Arene
129.99	Arene
133.58	Arene
133.61	Arene
135.28	Arene
136.07	Arene
167.00	G (CO)
171.65	G (CO)
173.23	L (CO)

HRMS (ESI)

Calc. Mass
444.16 amu

Calc. $[M+Na^+]^+$
467.15 amu

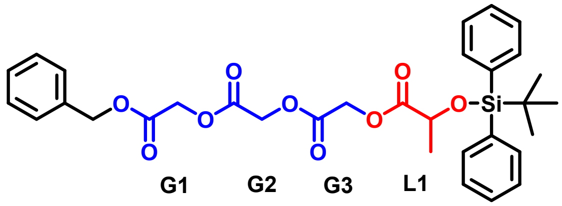
Found $[M+Na^+]^+$
467.14973 amu

Composition
$C_{23}H_{28}O_7Si$

GGL-Si

Bn-GGL-Si (10.3 g, 19.3 mmol) was dissolved in 190 mL ethyl acetate in a Schlenk flask to prepare a 0.1 M solution. Pd/C (1.03 g, 10% by mass) was added, and two balloons of H_2 (g) were passed through the flask. A third balloon was attached to serve as a source of excess H_2 (g). The reaction was stirred at RT overnight. The solution was then filtered through a thick pad of celite and concentrated to provide the pure product, 7.3 g yield (85%).

Bn-GGGL-Si



^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm)	Mult. (J)	Int.	Assignment
1.10	s	9	TBDPS - tBu
1.43	d (6.5)	3	L1 (CH_3)
4.38	q (6.5)	1	L1 (CH)
4.53	d (16)	1	G
4.73	d (16)	1	G
4.77	dd (16)	4	G
4.79	s	2	G1
4.81	dd	2	G
5.20	dd	2	Bn
7.37	m	11	TBDPS – o, p + Bn
7.65	m	4	TBDPS - m

^{13}C-NMR (400 MHz, $CDCl_3$)

δ (ppm) + Assignment	
19.38	TBDPS (C)
21.40	TBDPS (CH_3)
60.32	G (CH_2)
60.81	G (CH_2)
61.34	G (CH_2)
67.49	Bn (CH_2)
68.81	L (CH)
127.79	Arene
127.82	Arene
128.59	Arene
128.79	Arene
128.83	Arene
130.00	Arene
133.58	Arene
133.61	Arene
135.28	Arene
136.07	Arene
166.70	G (CO)
166.96	G (CO)
166.97	G (CO)
173.11	L (CO)

HRMS (ESI)

Calc. Mass
938.30 amu

Calc. $[M+Na^+]^+$
961.30 amu

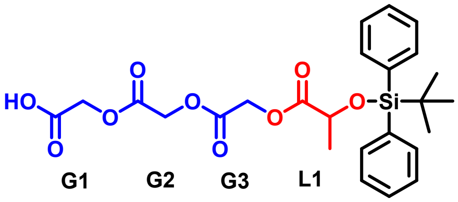
Found
961.2988 amu

Composition
$C_{46}H_{54}O_{19}Si$

Bn-GGGL-Si

Bn-G (1.91 g, 11.5 mmol and **GGL-Si** (4.64 g, 10.4 mmol) were dissolved in 104 mL DCM. DPTS (0.612 g, 2.1 mmol) was added and allowed to dissolved before the addition of DCC (2.37 g, 11.5 mmol). The reaction vessel was capped and the reaction was allowed to stir at RT overnight. The solution was filtered, concentrated *in vacuo*, and purified by column chromatography using 5-10% ethyl acetate in hexanes. Product eluted in fractions 4-9 (250 mL fractions). 3.31 g, 59%.

GGGL-Si



^{1}H-NMR (400 MHz, $CDCl_3$)

δ (ppm)	Mult. (J)	Int.	Assignment
1.09	s	9	TBDPS - tBu
1.41	d (6.5)	3	L1 (CH_3)
4.38	q (6.5)	1	L1 (CH)
4.53	d (16)	1	G
4.73	d (16)	1	G
4.77	dd (16)	4	G
4.79	s	2	G1
4.81	dd	2	G
7.37	m	6	TBDPS – o, p
7.65	m	4	TBDPS - m

^{13}C-NMR (400 MHz, $CDCl_3$)

δ (ppm)	Assignment
19.38	TBDPS (C)
26.95	TBDPS (CH_3)
60.63	G (CH_2)
60.72	G (CH_2)
60.76	G (CH_2)
68.82	L (CH)
127.79	Arene
130.00	Arene
133.58	Arene
133.61	Arene
135.28	Arene
136.07	Arene
166.63	G (CO)
167.03	G (CO)
171.24	G (CO)
173.12	L (CO)

HRMS (ESI)

Calc. Mass
502.17 amu

Calc. $[M-H]^-$
501.16 amu

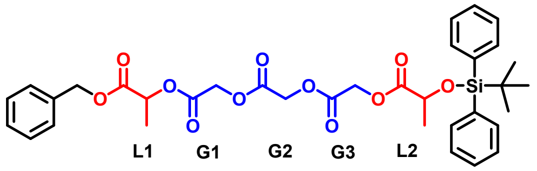
Found
$[M-H]^-$
501.15657 amu

Composition
$C_{25}H_{30}O_9Si$

GGGL-Si

Bn-GGGL-Si (3.31 g, 5.59 mmol) was dissolved in 55 mL ethyl acetate in a Schlenk flask to prepare a 0.1 M solution. Pd/C (0.330 g, 10% by mass) was added, and two balloons of H_2 (g) were passed through the flask. A third balloon was attached to serve as a source of excess H_2 (g). The reaction was stirred at RT overnight. The solution was then filtered through a thick pad of celite and concentrated to provide the pure product, 2.60 g yield (93%).

Bn-LGGGL-Si



^{1}H-NMR (400 MHz, CDCl$_3$)

δ (ppm)	Mult. (J)	Int.	Assignment
1.09	s	9	TBDPS - tBu
1.41	d (6.5)	3	L2 (CH$_3$)
1.56	d (6.5)	3	L1 (CH$_3$)
4.38	q (6.5)	1	L2 (CH)
4.63	d (16)	1	G3
4.70	dd (16)	1	G3
4.79	dd (16)	4	G1, G2
5.18	d	2	Bn
5.26	m	2	L1 , L2 (CH)
7.37	m	11	TBDPS – o, p + Bn
7.65	m	4	TBDPS - m

^{13}C-NMR (400 MHz, CDCl$_3$)

δ (ppm)	+ Assignment
16.94	L (CH$_3$)
19.38	TBDPS (C)
21.40	L (CH$_3$)
26.95	TBDPS (CH$_3$)
60.33	G (CH$_2$)
60.77	G (CH$_2$)
61.09	G (CH$_2$)
67.43	L (CH)
68.82	L (CH)
69.75	Bn (CH$_2$)
127.78	Arene
127.83	Arene
128.34	Arene
128.67	Arene
129.99	Arene
133.14	Arene
133.61	Arene
135.28	Arene
135.90	Arene
166.53	G (CO)
166.62	G (CO)
166.96	G (CO)
169.89	L (CO)
173.12	L (CO)

HRMS (ESI)

Calc. Mass
664.23 amu

Calc. [M+NH$_4$]$^+$
682.26 amu

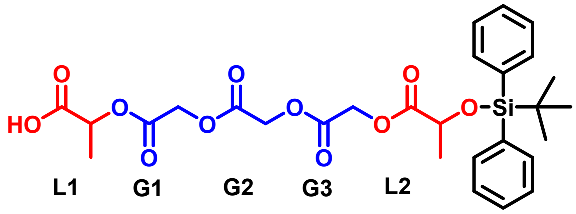
Found
[M+NH$_4$]$^+$
682.26891 amu

Composition
C$_{35}$H$_{40}$O$_{11}$Si

Bn-LGGGL-Si

Bn-L (1.02 g, 5.69 mmol) and **GGGL-Si** (2.367 g, 4.01 mmol) were dissolved in 50 mL DCM. DPTS (0.305 g, 1.04 mmol) was added and allowed to dissolved before the addition of DCC (1.17 g, 5.17 mmol). The reaction vessel was capped and the reaction was allowed to stir at RT overnight. The solution was filtered, concentrated *in vacuo*, and purified by column chromatography using 10% ethyl acetate in hexanes. Product eluted in fractions 10-18 (250 mL fractions). 2.90 g yield (84%).

LGGGL-Si



^{1}H-NMR (400 MHz, $CDCl_3$)

δ (ppm)	Mult. (J)	Int.	Assignment
1.09	s	9	TBDPS - tBu
1.41	d (6.5)	3	L2 (CH_3)
1.56	d (6.5)	3	L1 (CH_3)
4.38	q (6.5)	1	L2 (CH)
4.63	d (16)	1	G3
4.70	dd (16)	1	G3
4.79	dd (16)	4	G1, G2
5.26	m	2	L1 , L2 (CH)
7.37	m	6	TBDPS – o, p
7.65	m	4	TBDPS - m

^{13}C-NMR (400 MHz, $CDCl_3$)

δ (ppm) + Assignment	
16.94	L (CH_3)
19.38	TBDPS (C)
21.40	L (CH_3)
26.95	TBDPS (CH_3)
60.33	G (CH_2)
60.77	G (CH_2)
61.09	G (CH_2)
67.43	L (CH)
68.82	L (CH)
127.78	Arene
129.99	Arene
133.61	Arene
135.28	Arene
166.53	G (CO)
166.62	G (CO)
166.96	G (CO)
169.89	L (CO)
173.12	L (CO)

HRMS (ESI)

Calc. Mass
574.19 amu

Calc. $[M+NH_4]^+$
592.22 amu

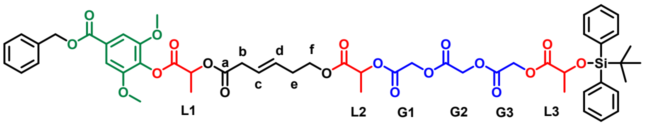
Found
$[M+NH_4]^+$
592.21976 amu

Composition
$C_{28}H_{34}O_{11}Si$

LGGGL-Si

Bn-LGGGL-Si (2.90 g, 4.36 mmol) was dissolved in 45 mL ethyl acetate in a Schlenk flask to prepare a 0.1 M solution. Pd/C (0.290 g, 10% by mass) was added, and two balloons of H_2 (g) were passed through the flask. A third balloon was attached to serve as a source of excess H_2 (g). The reaction was stirred at RT overnight. The solution was then filtered through a thick pad of celite and concentrated to provide the pure product, 2.33 g yield (Quantitative Yield).

Bn-SyLMLGGGL-Si



^{1}H-NMR (400 MHz, $CDCl_3$)

δ (ppm)	Mult. (J)	Int.	Assignment
1.09	s	9	TBDPS (tBu)
1.41	d (6.4)	3	L3 (CH_3)
1.48	d (6.4)	3	L2
1.68	d (6.4)	3	L1 (CH_3)
2.38	q (6.8)	2	**e**
3.13	m	2	**b**
3.85	s	6	Sy (CH_3)
4.15	m	2	**f**
4.37	q (6.4)	1	L3 (CH)
4.50	d (16)	1	G3
4.63	d (16)	1	G3
4.70	m	4	G1, G2
5.12	q (6.4)	1	L2 (CH)
5.37	s	2	Bn (CH_2)
5.45	q (6.4)	1	L1 (CH)
5.60	m	2	**d** , **e**
7.40	m	13	Sy + TBDPS o,p + Bn
7.65	m	4	TBDPS meta

^{13}C-NMR (400 MHz, $CDCl_3$)

δ (ppm) + Assignment			
16.80	L (CH_3)	127.69	Arene
17.16	L (CH_3)	128.36	Arene
19.23	TBDPS (C)	128.66	Arene
21.30	L (CH_3)	129.46	Arene
26.80	TBDPS (CH_3)	129.85	Arene
31.90	**e**	132.13	**d**
37.67	**b**	132.96	Arene
56.44	Sy (CH_3)	133.40	Arene
60.33	G (CH_2)	135.75	Arene
60.78	G (CH_2)	135.92	Arene
61.08	G (CH_2)	152.05	Arene
64.52	L (CH)	165.91	Sy (CO)
67.06	**b**	166.52	G (CO)
68.39	L (CH)	166.63	G (CO)
68.60	L (CH)	166.97	G (CO)
69.48	**f**	168.12	M (CO)
106.48	Arene	169.90	L (CO)
124.53	**c**	170.86	L (CO)
127.63	Arene	173.12	L (CO)

HRMS (ESI)

Calc. Mass
1028.35 amu

Calc Mass $[M+H^+]^+$
1029.2379 amu

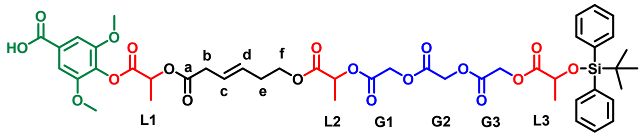
Found
1029.35679 amu

Composition
$C_{53}H_{60}O_{19}Si$

Bn-SyLMLGGGL-Si

Bn-SyLM (0.725 g, 1.53 mmol) and **LGGGL-Si** (0.966 g, 1.68 mmol) were dissolved in 16 mL DCM. DPTS (0.090 g, 0.31 mmol) was added and allowed to dissolved before the addition of DCC (0.378 g, 1.68 mmol). The reaction vessel was capped and the reaction was allowed to stir at RT overnight. The solution was filtered, concentrated *in vacuo*, and purified by column chromatography using 10% ethyl acetate in hexanes. Product eluted in fractions 10-18 (250 mL fractions). 0.947 g yield (60%).

SyLMLGGGL-Si



^{1}H-NMR (400 MHz, $CDCl_3$)

δ (ppm)	Mult. (J)	Int.	Assignment
1.09	s	9	TBDPS (tBu)
1.41	d (6.4)	3	L3 (CH_3)
1.48	d (6.4)	3	L2
1.68	d (6.4)	3	L1 (CH_3)
2.38	q (6.8)	2	**e**
3.13	m	2	**b**
3.85	s	6	Sy (CH_3)
4.15	m	2	**f**
4.37	q (6.4)	1	L3 (CH)
4.50	d (16)	1	G3
4.63	d (16)	1	G3
4.70	m	4	G1, G2
5.12	q (6.4)	1	L2 (CH)
5.45	q (6.4)	1	L1 (CH)
5.60	m	2	**d** , **e**
7.40	m	8	Sy + TBDPS o,p
7.65	m	4	TBDPS meta

^{13}C-NMR (400 MHz, $CDCl_3$)

δ (ppm) + Assignment

16.80	L (CH_3)	127.69	Arene
17.16	L (CH_3)	129.46	Arene
19.23	TBDPS (C)	129.85	Arene
21.30	L (CH_3)	132.13	**d**
26.80	TBDPS (CH_3)	132.96	Arene
31.90	**e**	133.40	Arene
37.67	**b**	135.75	Arene
56.44	Sy (CH_3)	135.92	Arene
60.33	G (CH_2)	152.05	Arene
60.78	G (CH_2)	165.91	Sy (CO)
61.08	G (CH_2)	166.52	G (CO)
64.52	L (CH)	166.63	G (CO)
67.06	**b**	166.97	G (CO)
68.39	L (CH)	168.12	M (CO)
68.60	L (CH)	169.90	L (CO)
69.48	**f**	170.86	L (CO)
106.48	Arene	173.12	L (CO)
124.53	**c**		
127.63	Arene		

HRMS (ESI)

Calc. Mass
938.30 amu

Calc Mass $[M+H^+]^+$
939.31 amu

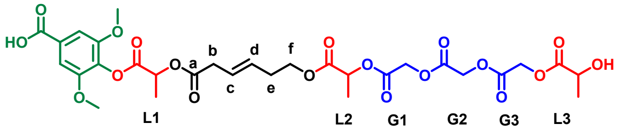
Found
939.31042 amu

Composition
$C_{46}H_{54}O_{19}Si$

SyLMLGGGL-Si

A 0.60 M solution of **Bn-SyLMLGGGL-Si** (0.947 g, 0.92 mmol) was prepared in DCM. A 0.60 M solution of palladium (II) acetate (0.0093 g, 0.041 mmol), triethylamine (16 µL, 0.0124 mmol), and triethylsilane (205 µL, 1.29 mmol) was prepared and allowed to stir for 30 min. The solution of **Bn-SyLMLGGGL-Si** was then added dropwise over the course of five minutes. The reaction was allowed to stir at RT overnight. The solution was quenched with 10 mL saturated aqueous ammonium chloride solution and the organic layer was extracted 3x with DCM. The organic phase was dried with magnesium sulfate, filtered, and concentrated *in vacuo* to yield the crude product as a yellow oil. The product was purified by column chromatography using 10% ethyl acetate in hexanes to yield pure product as a white solid (0.332 g, 38%).

SyLMLGGGL



^{1}H-NMR (400 MHz, $CDCl_3$)

δ (ppm)	Mult. (J)	Int.	Assignment
1.41	m	6	L2, L3 (CH_3)
1.68	d (6.4)	3	L1 (CH_3)
2.38	q (6.8)	2	**e**
3.17	m	2	**b**
3.88	s	6	Sy (CH_3)
4.15	m	2	**f**
4.41	q (6.4)	1	L3 (CH)
4.80	m	6	G1, G2, G3
5.12	q (6.4)	1	L2 (CH)
5.45	q (6.4)	1	L1 (CH)
5.60	m	2	**d** , **e**
7.37	s	2	Sy

^{13}C-NMR (400 MHz, $CDCl_3$)

δ (ppm) + Assignment

δ (ppm)	Assignment	δ (ppm)	Assignment
16.80	L (CH_3)	129.46	Arene
17.16	L (CH_3)	132.13	**d**
19.23	TBDPS (C)	152.33	Arene
21.30	L (CH_3)	165.91	Sy (CO)
26.80	TBDPS (CH_3)	166.52	G (CO)
31.90	**e**	166.54	G (CO)
37.67	**b**	166.76	G (CO)
56.44	Sy (CH_3)	168.21	M (CO)
60.33	G (CH_2)	169.90	L (CO)
60.78	G (CH_2)	170.90	L (CO)
61.08	G (CH_2)	175.11	L (CO)
64.52	L (CH)		
67.06	**b**		
68.39	L (CH)		
68.60	L (CH)		
69.48	**f**		
107.12	Arene		
124.53	**c**		
127.63	Arene		

HRMS (ESI)

Calc. Mass
700.19 amu

Calc Mass
$[M+H^+]^+$
701.197 amu

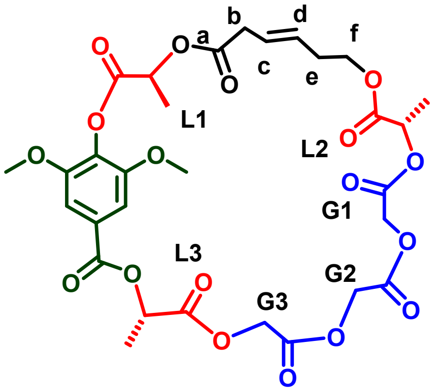
Found
701.19355amu

Composition
$C_{30}H_{36}O_{19}$

SyLMLGGGL

SyLMLGGGL-Si (0.332 g, 0.331 mmol) was dissolved in 3.3 mL THF to prepare a 0.1 M solution. The flask was cooled to 0 °C. TBAF (0.50 mL as a 1.0 M solution in THF, 0.50 mmol) was added to a vial and acetic acid (35 µL, 0.60 mmol) was added. The vial was vortexed briefly and this solution was added steadily to the solution of starting material. The reaction was warmed to RT over the course of 1 h and the reaction was quenched with 5 mL brine. The organics were extracted 3x with ethyl acetate, were dried with magnesium sulfate, filtered, and concentrated *in vacuo* to provide the crude product as a yellow oil. The product was purified by column chromatography (25% ethyl acetate in hexanes increased gradually to 90% ethyl acetate in hexanes). The product was a white solid (0.151 g, 65%).

Cyc-SyLMLGGGL



^{1}H-NMR (400 MHz, $CDCl_3$)

δ (ppm)	Mult. (J)	Int.	Assignment
1.39	d (6.4)	3	L (CH_3)
1.68	m	6	L (CH_3)
2.35	q (6.8)	2	**e**
3.17	m	2	**b**
3.86	s	6	Sy (CH_3)
4.15	m	2	**f**
4.80	m	6	G1, G2, G3
5.10	q (6.4)	1	L2 (CH)
5.45	q (6.4)	1	L1 (CH)
5.50	q (6.4)	1	L3 (CH)
5.60	m	2	**d** , **e**
7.36	s	2	Sy

^{13}C-NMR (400 MHz, $CDCl_3$)

δ (ppm) + Assignment

16.80	L (CH_3)	129.46	Arene
17.16	L (CH_3)	132.13	**d**
19.23	TBDPS (C)	152.33	Arene
21.30	L (CH_3)	165.91	Sy (CO)
26.80	TBDPS (CH_3)	166.52	G (CO)
31.90	**e**	166.54	G (CO)
37.67	**b**	166.76	G (CO)
56.44	Sy (CH_3)	168.21	M (CO)
60.33	G (CH_2)	169.90	L (CO)
60.78	G (CH_2)	170.90	L (CO)
61.08	G (CH_2)	175.11	L (CO)
64.52	L (CH)		
67.06	**b**		
68.39	L (CH)		
68.60	L (CH)		
69.48	**f**		
107.12	Arene		
124.53	**c**		
127.63	Arene		

HRMS (ESI)

Calc. Mass
682.17 amu

Calc Mass
[M+H$^+$]$^+$
683.18 amu

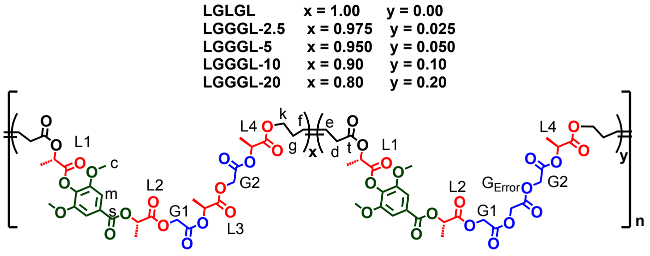
Found
683.18207 amu

Composition
$C_{30}H_{34}O_{18}$

Cyc-SyLMLGGGL

SyLM(L$_3$G$_2$) (0.113 g, 0.16 mmol) was dissolved in 2.5 mL dichloroethane and injected to a solution of DCC (0.066 g, 0.32 mmol) and DPTS (0.023 g, 0.08mmol) in 2.5 mL dichloroethane at 60°C over a span of 16 hours. The solution was allowed to stir for an additional 24 hours before being filtered and concentrated to obtain the crude product. A column loaded with 15% ethyl acetate in hexanes was used to purify the product (0.070 g, 64%), a white solid.

Polymers – LGLGL, LGGGL-2.5, LGGGL-5, LGGGL-10, LGGGL-20



^{1}H-NMR (400 MHz, $CDCl_3$)

δ (ppm)	Mult. (J)	Int.	Assignment
1.36	d (7.1)	3	L (CH_3)
1.49	d (7.1)	3	L (CH_3)
1.67	m	6	L (CH_3)
2.35	q (6.8)	2	**g**
3.16	m	2	**d**
3.85	s	6	**c**
4.11	t (6.8)	2	**k**
4.63	d (16)	1	G1, G2
4.68	d (16)	1	G1, G2
4.72	d (16)	1	G1, G2
4.85	d (16)	1	G1, G2
4.6 – 4.9	m	~0 – 0.3	G_{Error}
5.03	q (7.1)	1	L (CH)
5.22	q (7.1)	1	L (CH)
5.46	q (7.1)	1	L (CH)
5.50	q (7.1)	1	L (CH)
7.36	s	2	**m**

^{13}C-NMR (400 MHz, $CDCl_3$)

δ (ppm) + Assignment

δ (ppm)	Assignment	δ (ppm)	Assignment
16.58	L (CH_3)	127.73	Arene
16.66	L1(CH_3)	129.44	Arene
16.91	L (CH_3)	132.38	**f**
17.02	L (CH_3)	152.09	Arene
31.69	**g**	165.08	**s**
37.77	**d**	166.19	G (CO)
56.43	**c**	166.30	G (CO)
60.42	G (CH_2)	167.90	**t**
60.97	G (CH_2)	169.25	L (CO)
64.32	L (CH)	169.82	L (CO)
68.50	L (CH)	170.06	L (CO)
69.07	L (CH)	175.65	L (CO)
69.33	L (CH)		
69.57	**k**		
106.65	Arene		
124.51	**e**		

SEC (Relative to PS Standards)
LGLGL Mn = 54 kDa, Đ = 1.22
LGGGL-2.5 Mn = 54 kDa, Đ = 1.22
LGGGL-5 Mn = 50 kDa, Đ = 1.23
LGGGL-10 Mn = 50 kDa, Đ = 1.24
LGGGL-20 Mn = 49 kDa, Đ = 1.24

Polymerizations to prepare LGLGL, LGGGL-2.5, LGGGL-5, LGGGL-10, and LGGGL-20

Each monomer was dissolved in chloroform to prepare a 100 mg/mL solution. Each solution was pipetted using a micropipettor into a dram vial to prepare five 1,500 µL solution mixtures (Base sequence : Erromer = 1,500 µL : 0 µL, 1462 µL : 37 µL, 1425 µL : 75 µL, 1350 µL : 150 µL, and 1200 µL : 300 µL). The solutions were concentrated *in vacuo* to produce the solid mixtures ready for polymerization.

The polymerizations were performed with dry DCM obtained from a solvent system. A stock solution of Grubbs II was prepared and the appropriate volume was pipetted into each vial such that the reaction concentration was 0.7 M and 1.50 mol% catalyst was used. The vials were purged with nitrogen and sealed. Within 20 minutes, both solutions became very viscous. The reactions were left to react for 2 hours before quenching with 0.05 mL of ethyl vinyl ether. The vials were then concentrated *in vacuo* and placed in a vacuum chamber overnight. NMR spectra and SEC traces were collected on the following day. The polymers were reprecipitated in 500 mL cold methanol and allowed to stir for a half hour before filtering.

Solution Casting of Thick Polymer Films

The polymers were dissolved in methylene chloride to make 100 mg/mL solutions. On the bottom of flat differential scanning calorimetry pans, 28 uL of this solution was cast onto each (with a 10-200 uL micropipettor), very carefully to create a convex droplet that covered the entire surface. The best films were prepared by first coating the perimeter of the slide and then filling in the middle. The solution was allowed to dry on the slides for 3 hours before being placed in a vacuum chamber. After 2 days, those films that contained bubbles were removed from the glass slides using a razor blade and re-dissolved to prepare a 100 mg/mL solution. Films used for the hydrolysis study contained no bubbles, tears, or noticeable defects. The films were tan and transparent.

Film thicknesses were measured on representative films cut through the center using optical profilometry. A Bruker Contour Elite I optical profilometer was used. Samples were sliced to create a step indicative of film thickness and then analyzed.

Hydrolysis Study

Polymer films, removed from glass slides, were placed in dram vials followed by the addition of 2 mL 10x phosphate buffer solution, pH = 7.4 The vials were capped and placed in an incubator set at 37 ℃. The films were placed on a rotating platform with a slow speed of 8 rpm to promote gentle mixing and to prevent localized concentration of acidic monomer around the films. The pH of the buffer solution was monitored over time and showed no distinguishable change. When timepoints were collected, the appropriate films were removed from the incubator, removed from the buffer solution, and blotted dry with a paper towel. Photographs were taken of each film at this point. The films were then rinsed with deionized water, blotted dry again and placed in new vials. Liquid N_2 was poured over the films and the films were placed in a lyophilizer for several hours. A full film was used for SEC analysis (~3 mg) and DSC analysis on weeks 2, 4, 6, 8, and 10.

3. Experimental Spectra

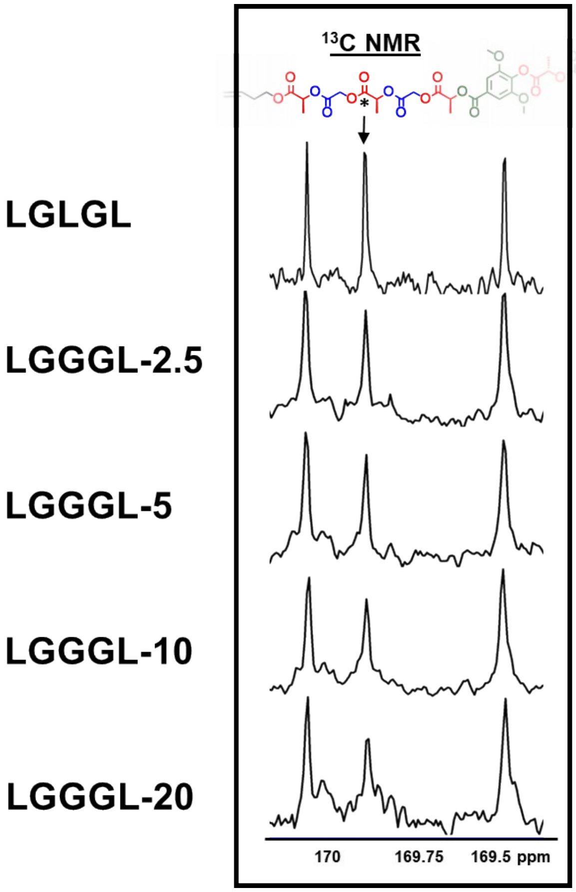


Figure S4. ^{13}C NMR spectra of the L-carbonyl region.

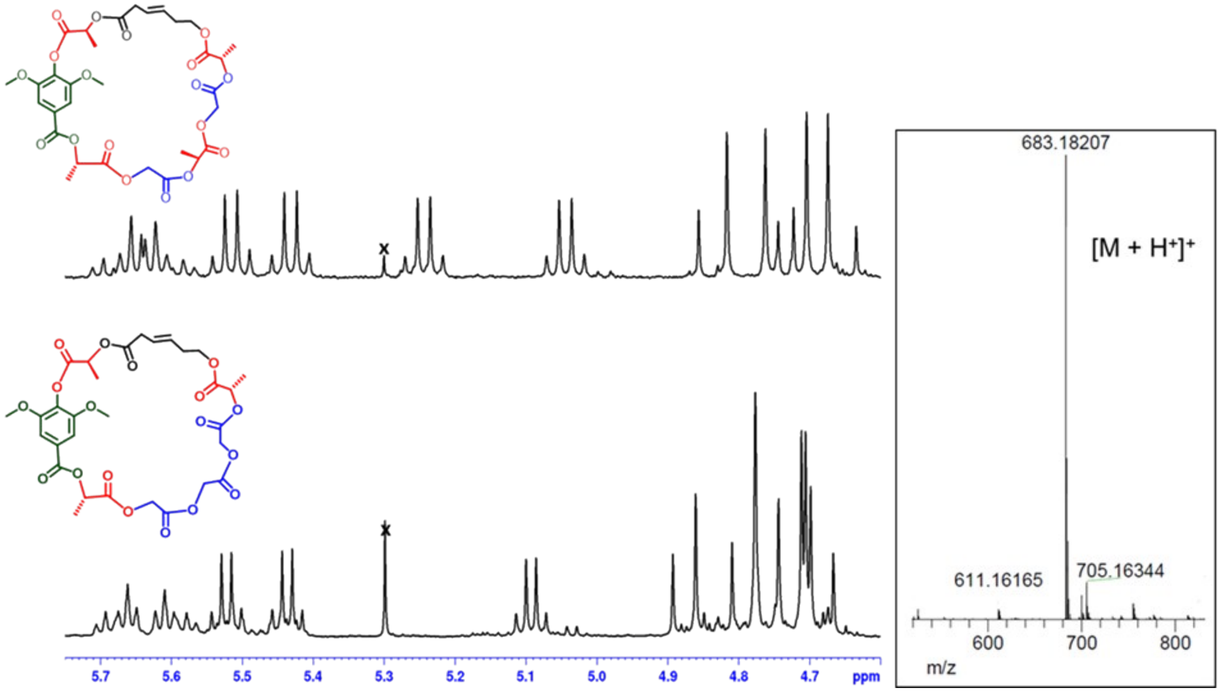
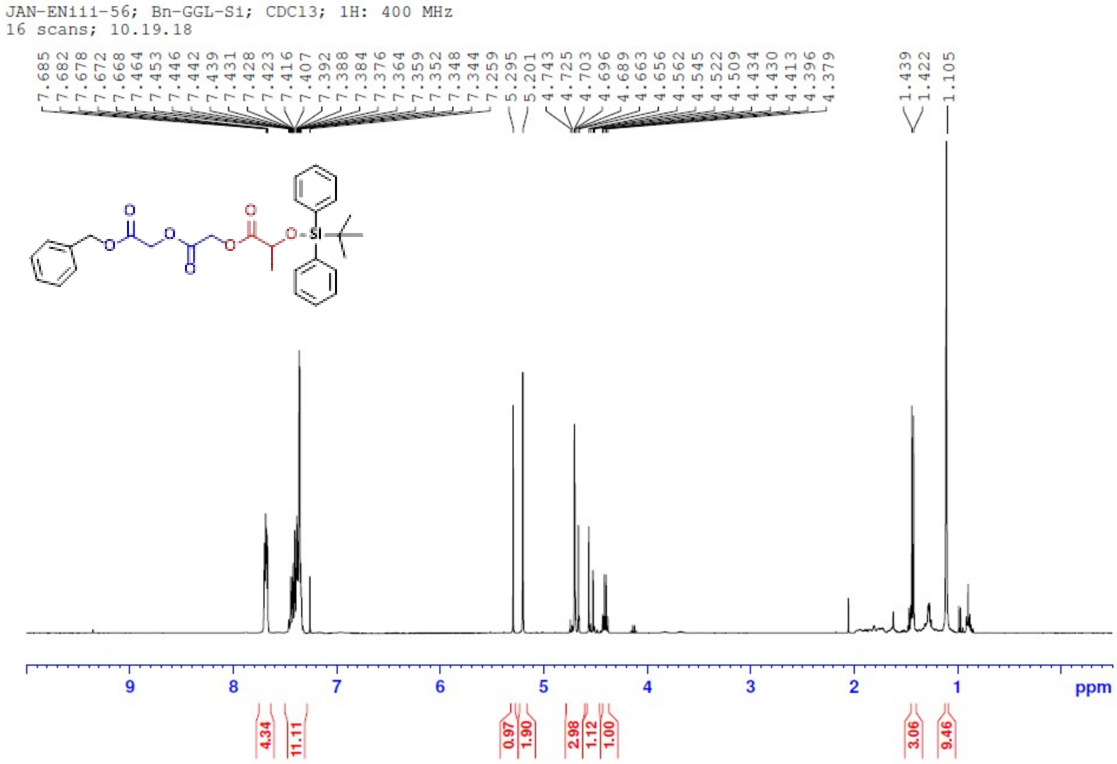
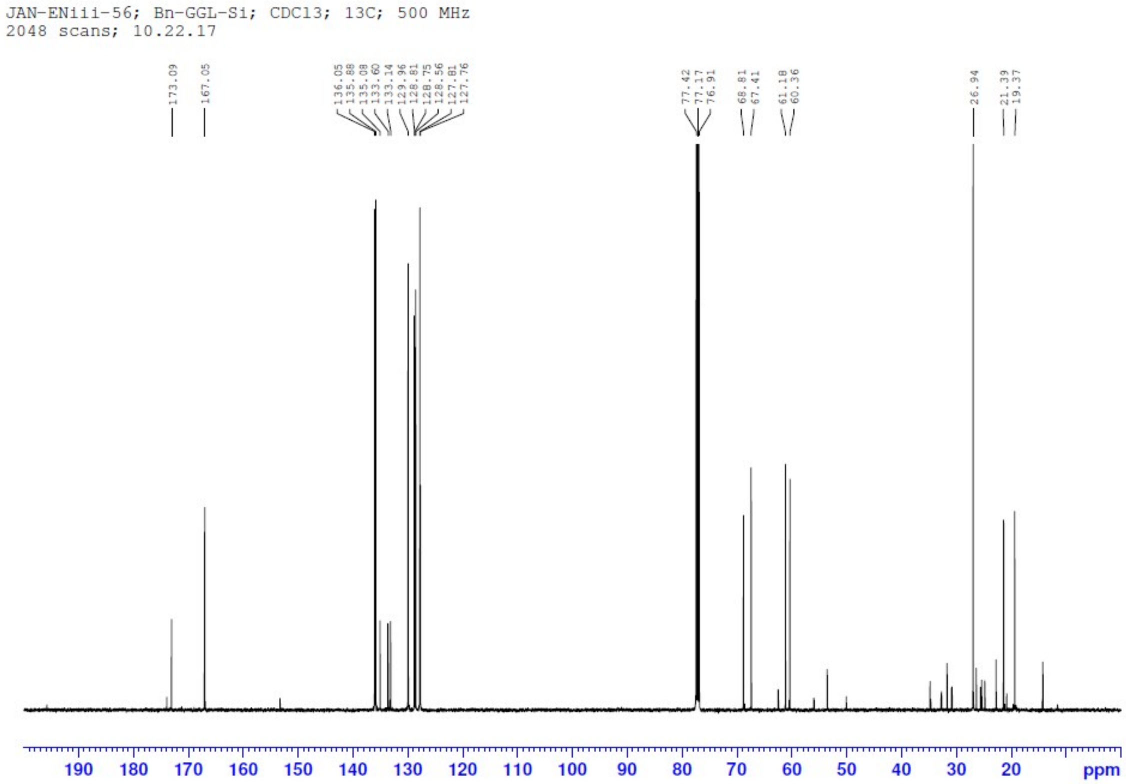
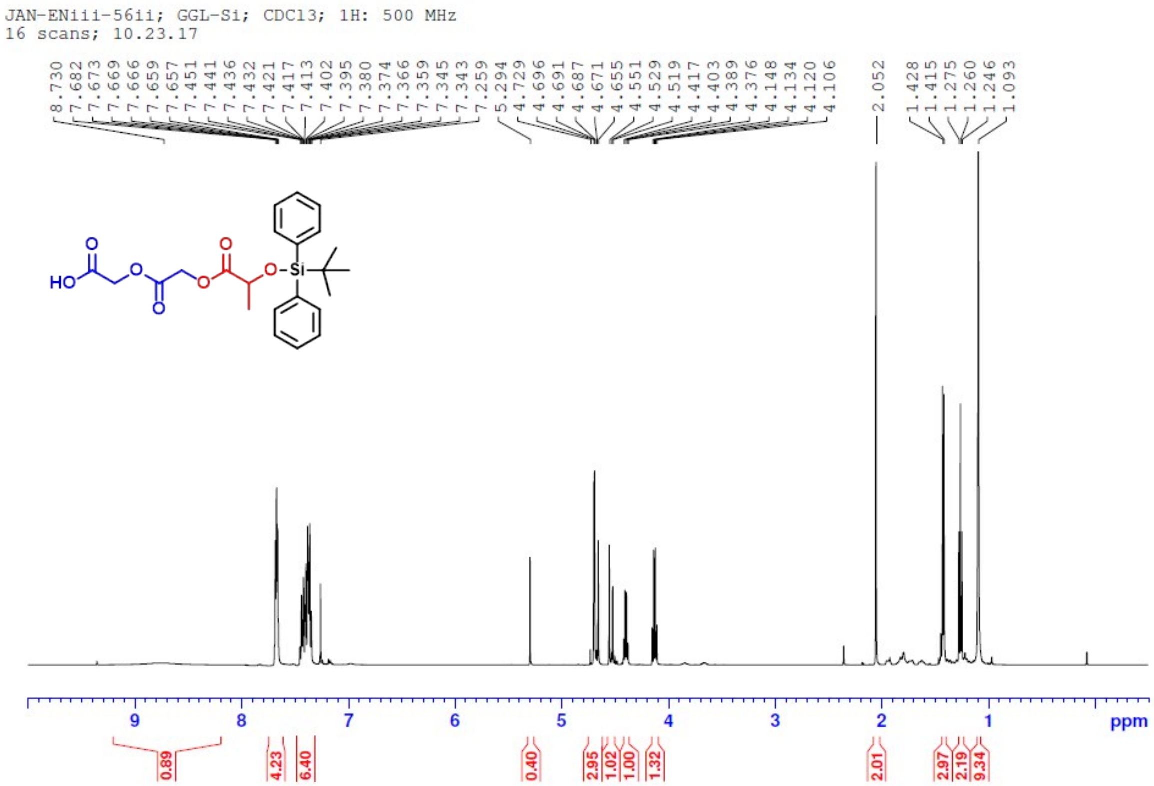
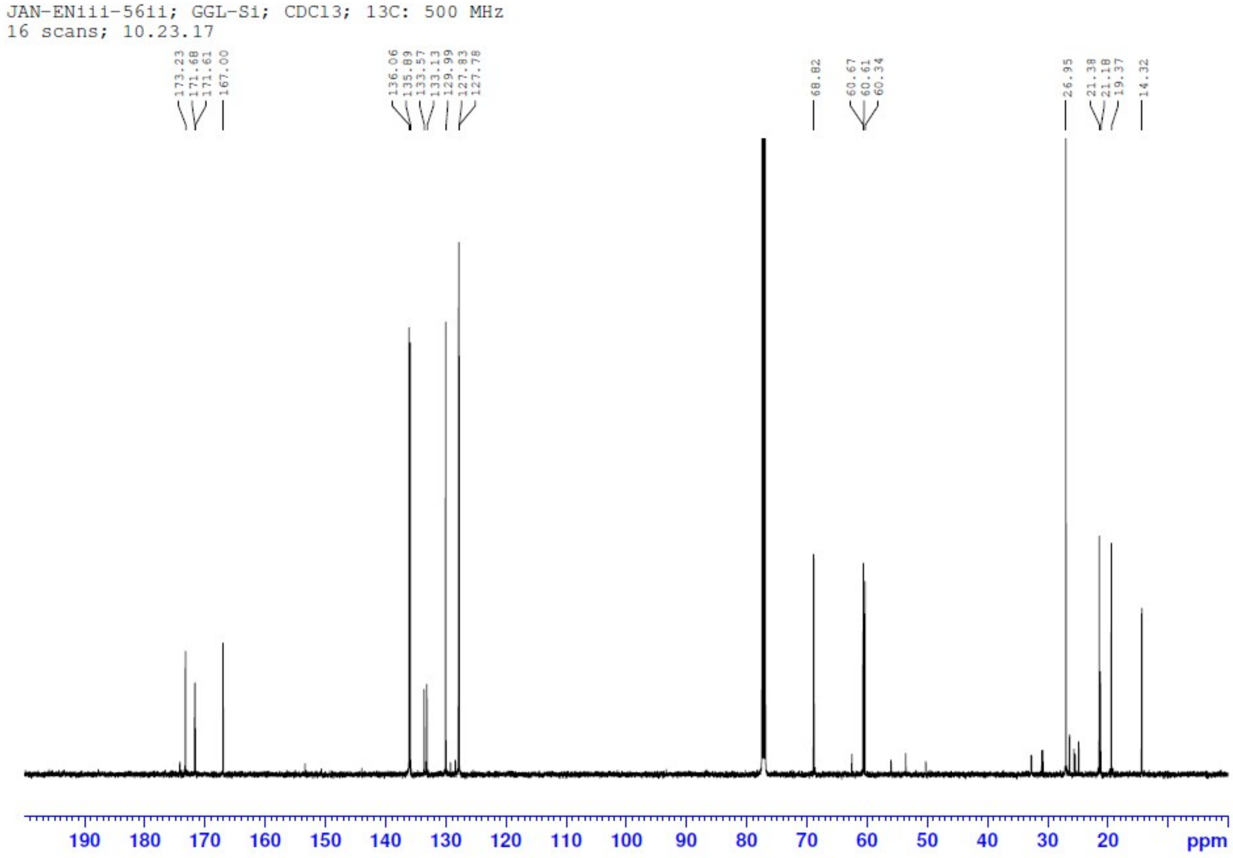


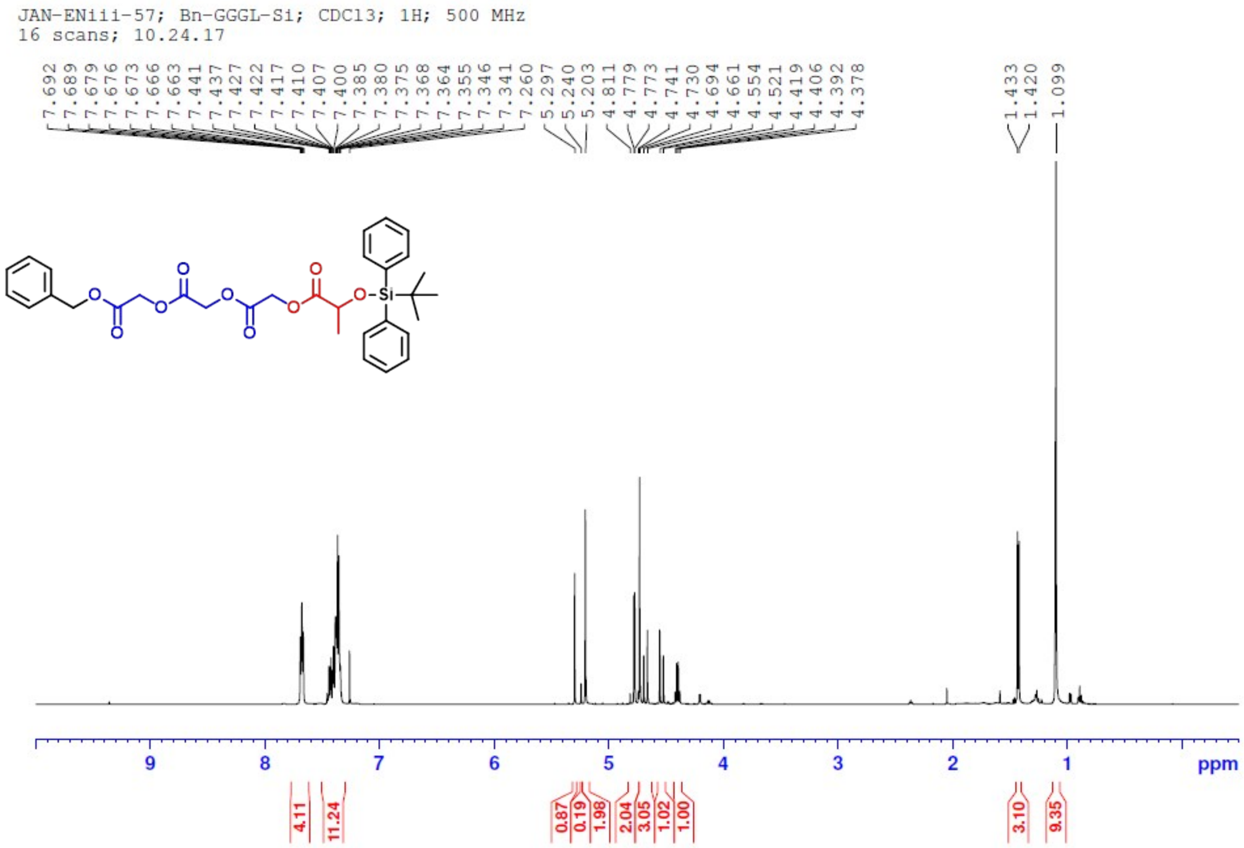
Figure S5. ^{1}H NMR spectral comparisons of the L/G/M region for Cyc-SyLMLGLGL and Cyc-SyLMLGGGL, in addition to the HRMS spectra of Cyc-SyLMLGGGL.

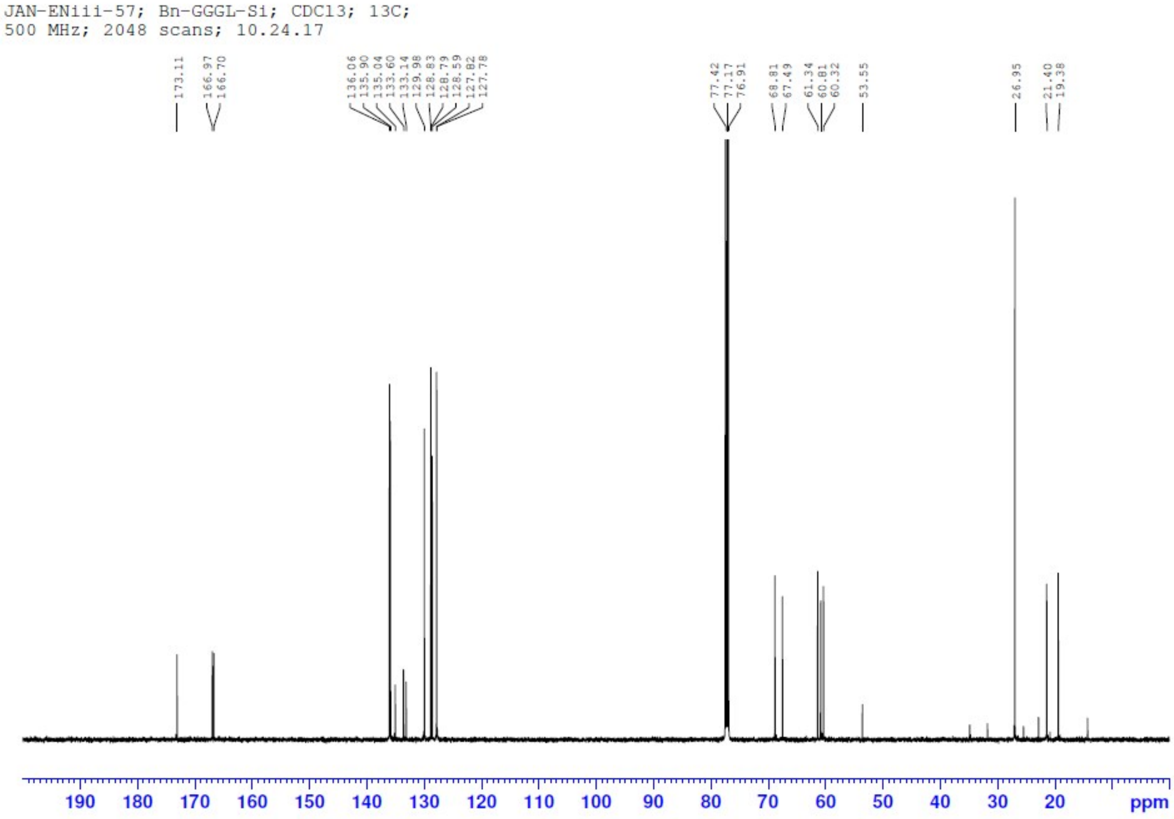

JAN-ENiii-56; Bn-GGL-Si; CDCl3; 1H: 400 MHz
16 scans; 10.19.18
7.685
7.682
7.678
7.672
7.668
7.464
7.453
7.446
7.442
7.439
7.431
7.428
7.423
7.416
7.407
7.392
7.388
7.384
7.376
7.364
7.359
7.352
7.348
7.344
7.259
5.295
5.201
4.743
4.725
4.703
4.696
4.689
4.663
4.656
4.562
4.545
4.522
4.509
4.434
4.430
4.413
4.396
4.379
1.439
1.422
1.105
O
O
O
O
O
O
O
Si
9
8
7
6
5
4
3
2
1
ppm
4.34
11.11
0.97
1.90
2.98
1.12
1.00
3.06
9.46


JAN-ENiii-56; Bn-GGL-Si; CDCl3; 13C; 500 MHz
2048 scans; 10.22.17
173.09
167.05
136.05
135.88
135.08
133.60
133.14
129.96
128.81
128.75
128.56
127.81
127.76
77.42
77.17
76.91
68.81
67.41
61.18
60.36
26.94
21.39
19.37
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

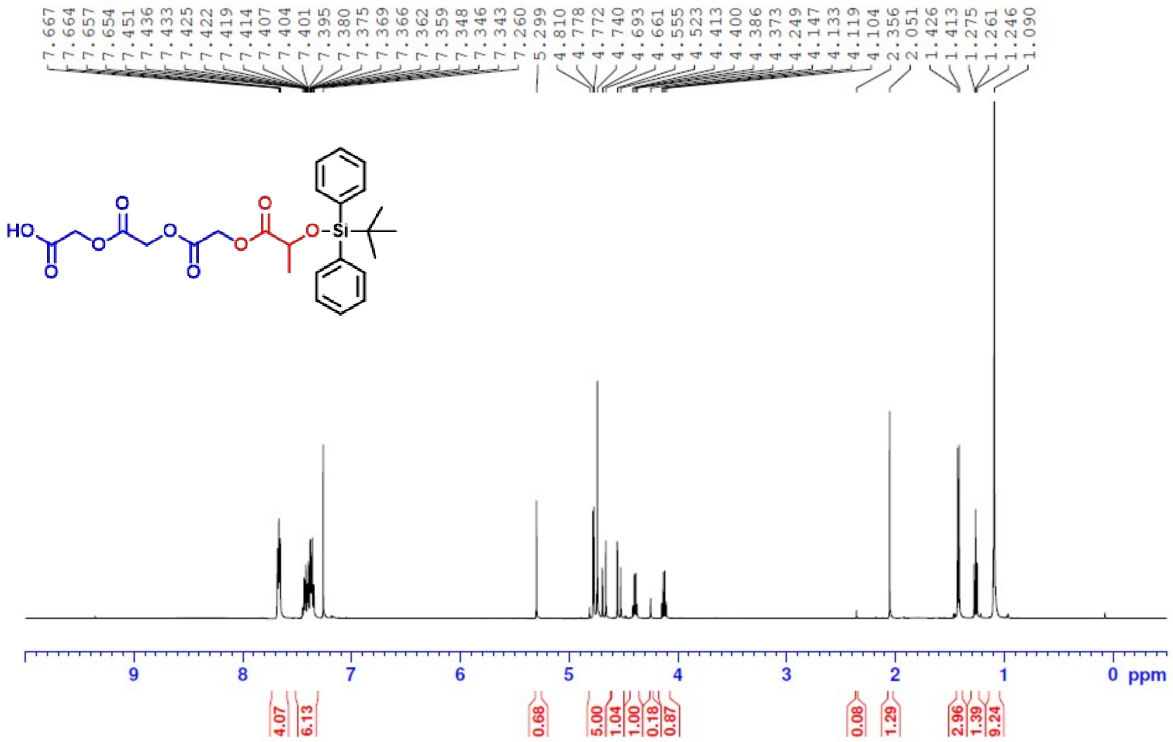

JAN-ENiii-56ii; GGL-Si; CDCl3; 1H: 500 MHz
16 scans; 10.23.17
8.730
7.682
7.673
7.669
7.666
7.659
7.657
7.451
7.441
7.436
7.432
7.421
7.417
7.413
7.402
7.395
7.380
7.374
7.366
7.359
7.345
7.343
7.259
5.294
4.729
4.696
4.691
4.687
4.671
4.655
4.551
4.529
4.519
4.417
4.403
4.389
4.376
4.148
4.134
4.120
4.106
2.052
1.428
1.415
1.275
1.260
1.246
1.093
HO
O
O
O
O
O
Si
9
8
7
6
5
4
3
2
1
ppm
0.89
4.23
6.40
0.40
2.95
1.02
1.00
1.32
2.01
2.97
2.19
9.34


JAN-ENiii-56ii; GGL-Si; CDCl3; 13C: 500 MHz
16 scans; 10.23.17
173.23
171.68
171.61
167.00
136.06
135.89
133.57
133.13
129.99
127.83
127.78
68.82
60.67
60.61
60.34
26.95
21.38
21.18
19.37
14.32
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

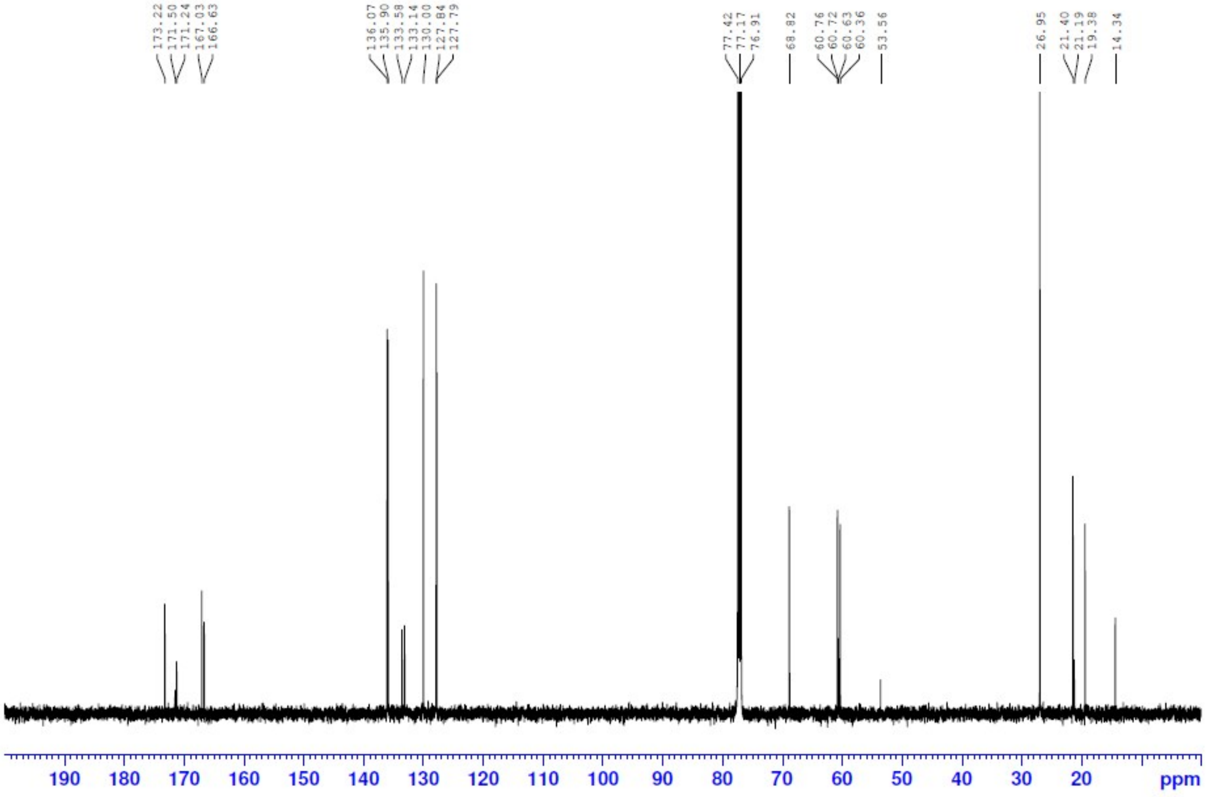

JAN-ENiii-57; Bn-GGGL-Si; CDCl3; 1H; 500 MHz
16 scans; 10.24.17
7.692
7.689
7.679
7.676
7.673
7.666
7.663
7.441
7.437
7.427
7.422
7.417
7.410
7.407
7.400
7.385
7.380
7.375
7.368
7.364
7.355
7.346
7.341
7.260
5.297
5.240
5.203
4.811
4.779
4.773
4.741
4.730
4.694
4.661
4.554
4.521
4.419
4.406
4.392
4.378
1.433
1.420
1.099
Si
O
9
8
7
6
5
4
3
2
1
ppm
4.11
11.24
0.87
0.19
1.98
2.04
3.05
1.02
1.00
3.10
9.35


JAN-ENiii-57; Bn-GGGL-Si; CDCl3; 13C;
500 MHz; 2048 scans; 10.24.17
173.11
166.97
166.70
136.06
135.90
135.04
133.60
133.14
129.98
128.83
128.79
128.59
127.82
127.78
77.42
77.17
76.91
68.81
67.49
61.34
60.81
60.32
53.55
26.95
21.40
19.38
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

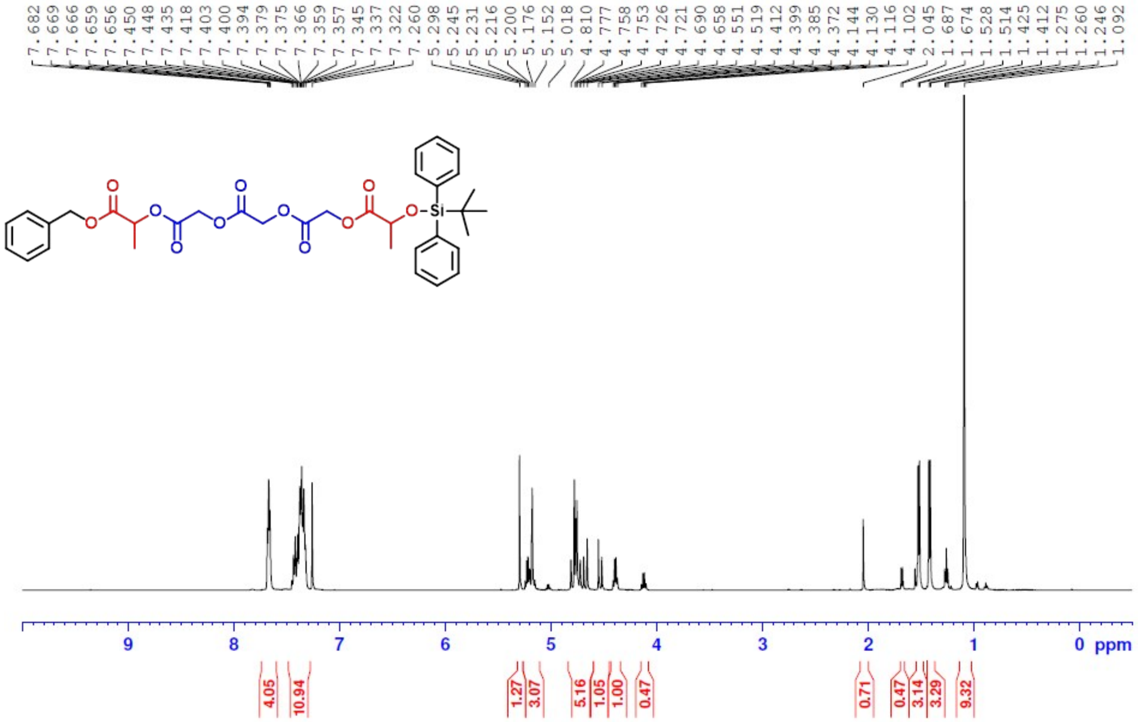
JAN-ENiii-58; GGGL-Si; CDCl3; 1H; 500 MHz
16 scans; 10.25.17



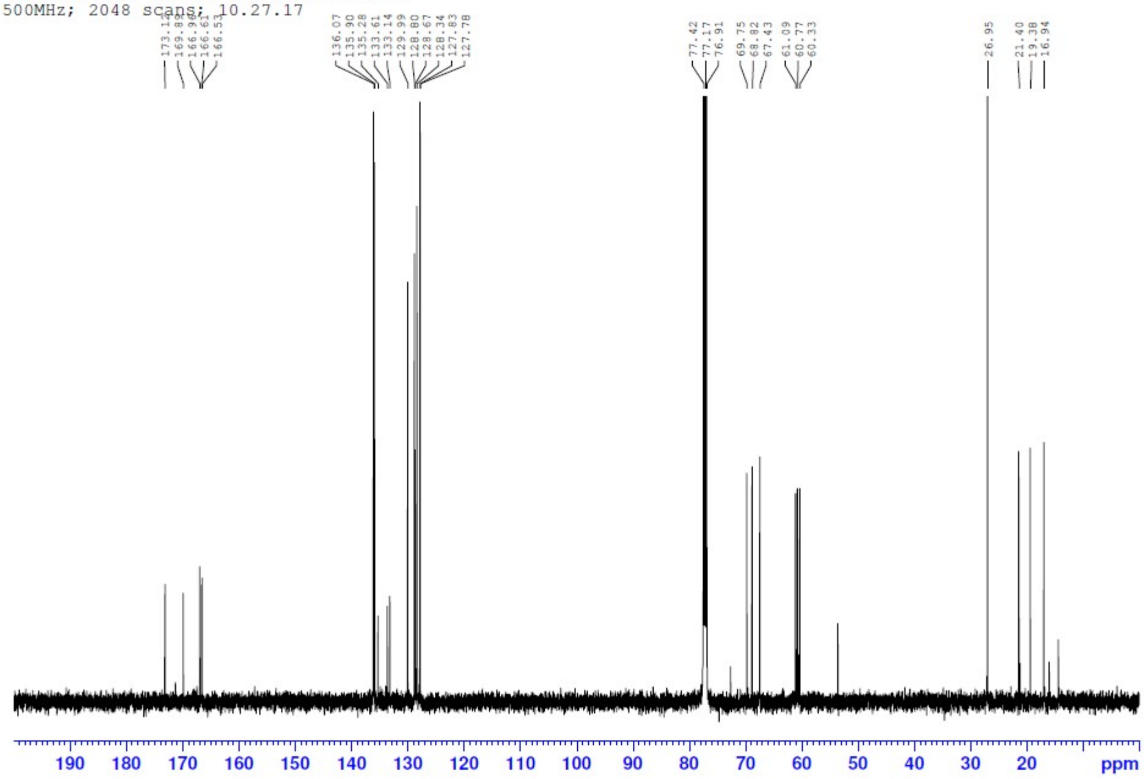
JAN-ENiii-58; GGGL-Si; CDCl3; 13C; 500 MHz
2048 scans; 10.25.17

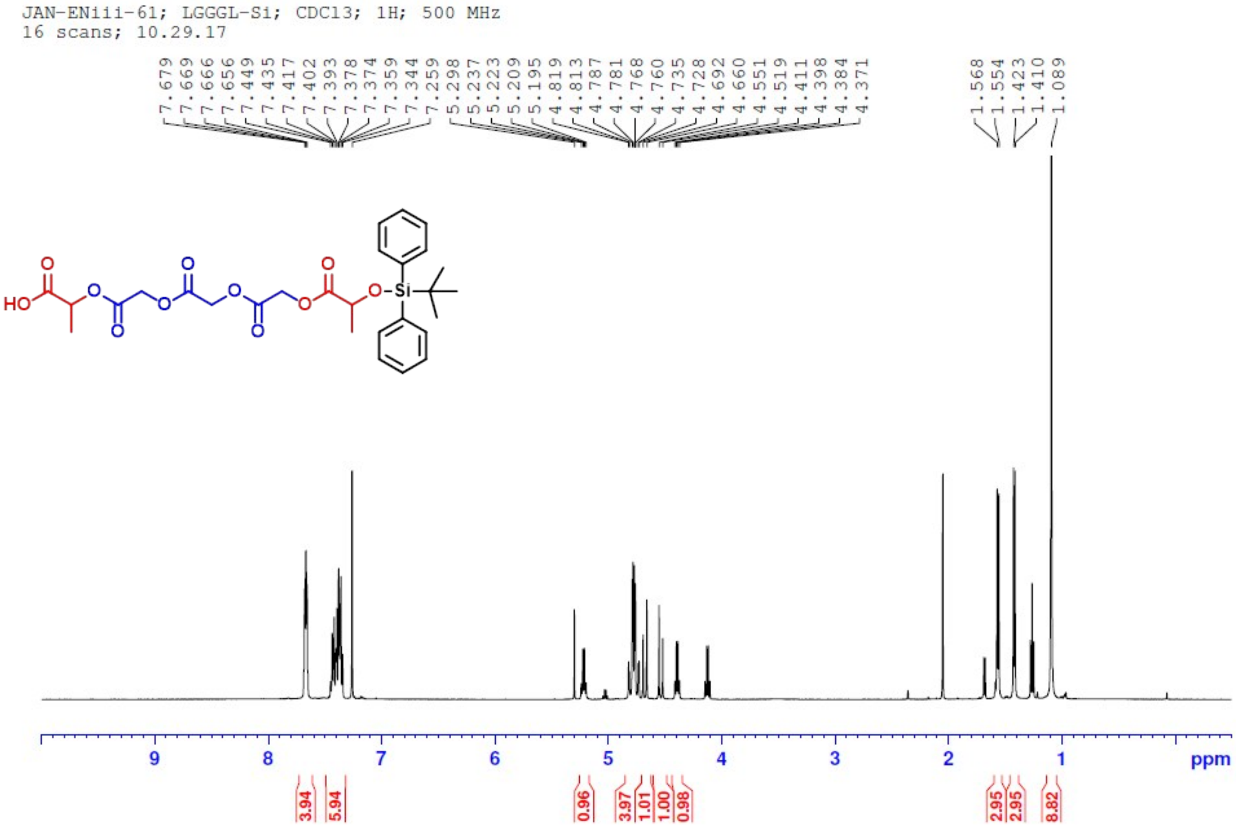


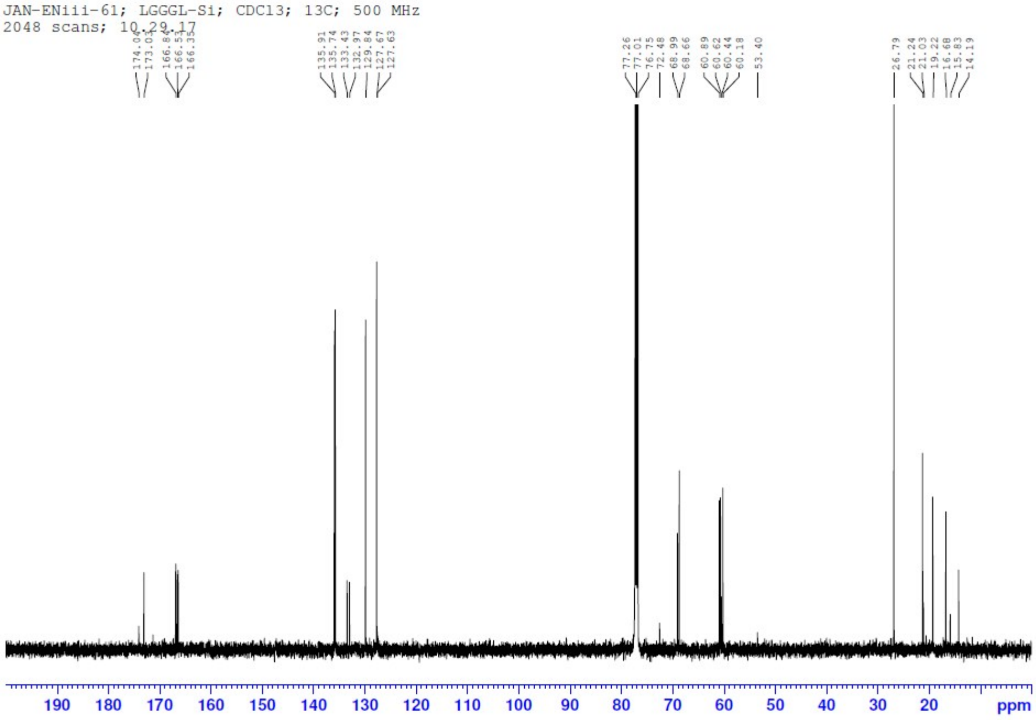
JAN-ENiii-59; Bn-LGGGL-Si; CDCl3; 1H; 500MHz
16 scans; 10.27.17

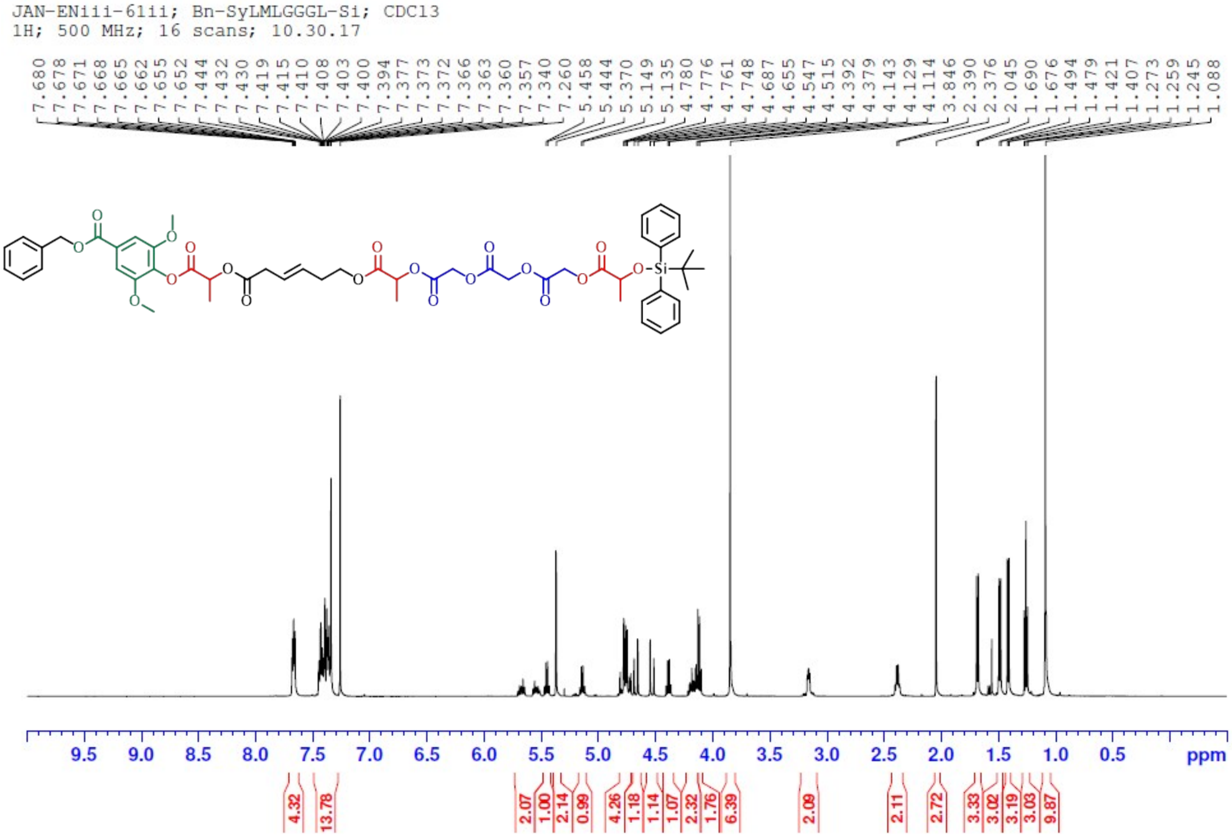


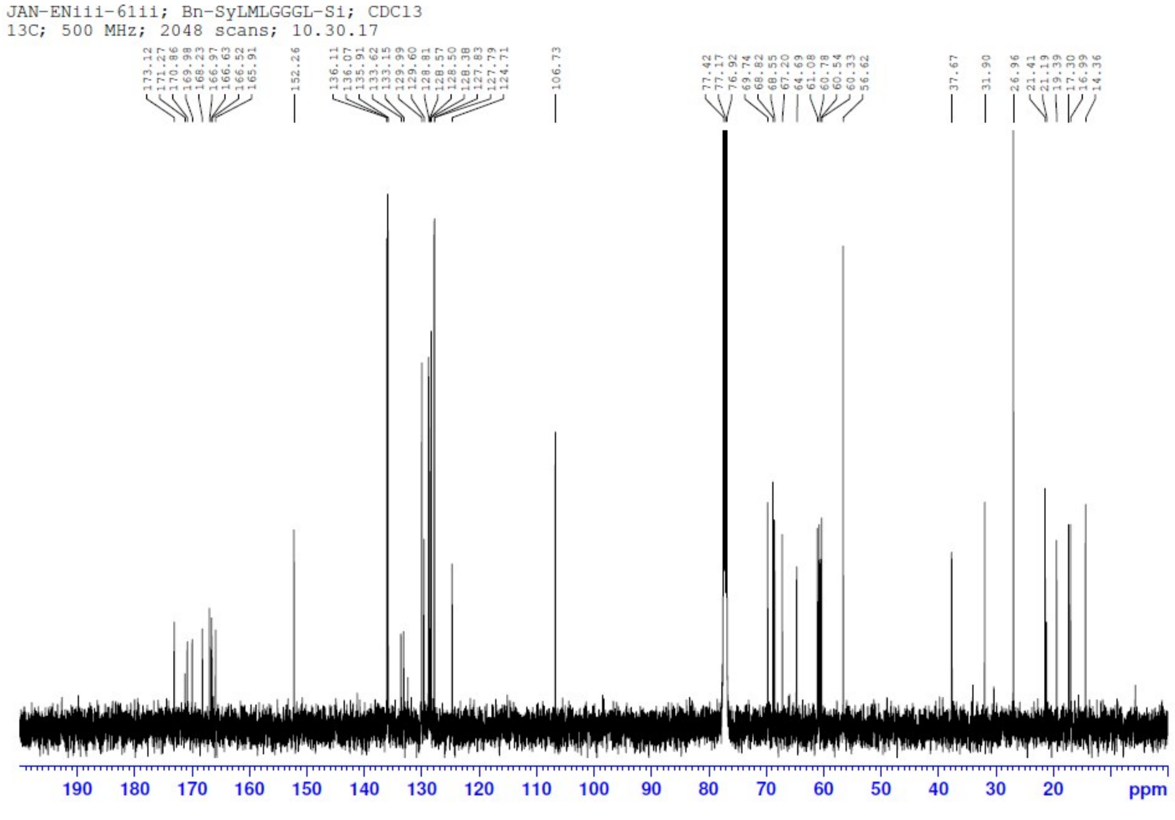
JAN-ENiii-59; Bn-LGGGL-Si; CDCl3; 13C;
500MHz; 2048 scans; 10.27.17



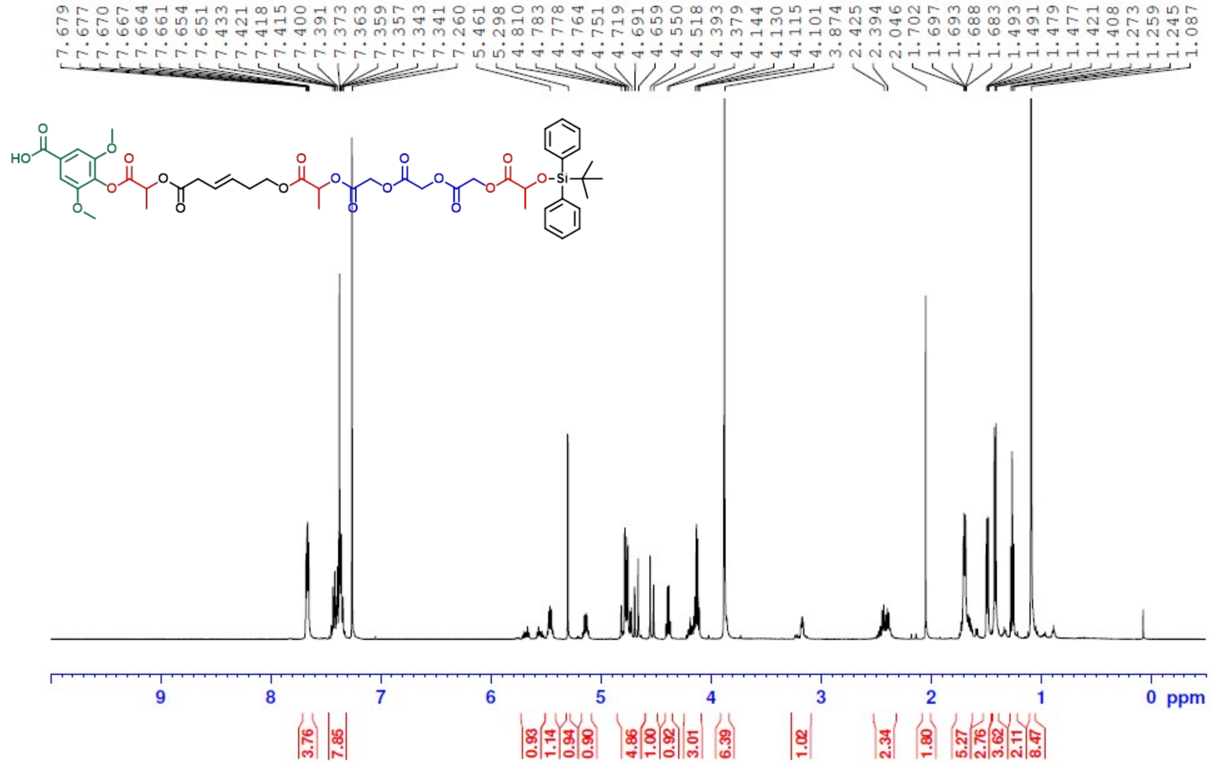

JAN-ENiii-61; LGGGL-Si; CDCl3; 1H; 500 MHz
16 scans; 10.29.17
7.679
7.669
7.666
7.656
7.449
7.435
7.417
7.402
7.393
7.378
7.374
7.359
7.344
7.259
5.298
5.237
5.223
5.209
5.195
4.819
4.813
4.787
4.781
4.768
4.760
4.735
4.728
4.692
4.660
4.551
4.519
4.411
4.398
4.384
4.371
1.568
1.554
1.423
1.410
1.089
HO
O
O
O
O
O
O
O
O
O
O
Si
9
8
7
6
5
4
3
2
1
ppm
3.94
5.94
0.96
3.97
1.01
1.00
0.98
2.95
2.95
8.82


JAN-ENiii-61; LGGGL-Si; CDCl3; 13C; 500 MHz
2048 scans; 10.29.17
174.04
173.03
166.84
166.53
166.35
135.91
135.74
133.43
132.97
129.84
127.67
127.63
77.26
77.01
76.75
72.48
68.99
68.66
60.89
60.62
60.44
60.18
53.40
26.79
21.24
21.03
19.22
16.68
15.83
14.19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

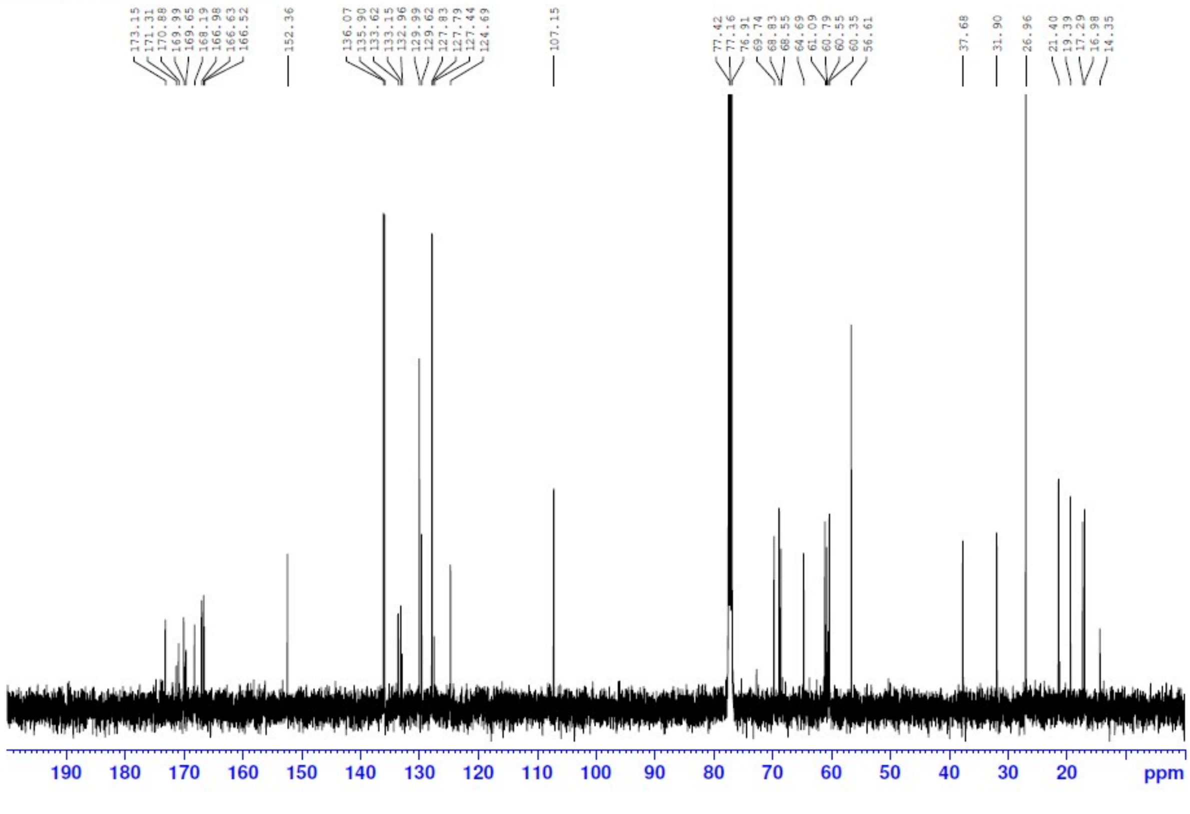

JAN-ENiii-61ii; Bn-SyLMLGGGL-Si; CDCl3
1H; 500 MHz; 16 scans; 10.30.17

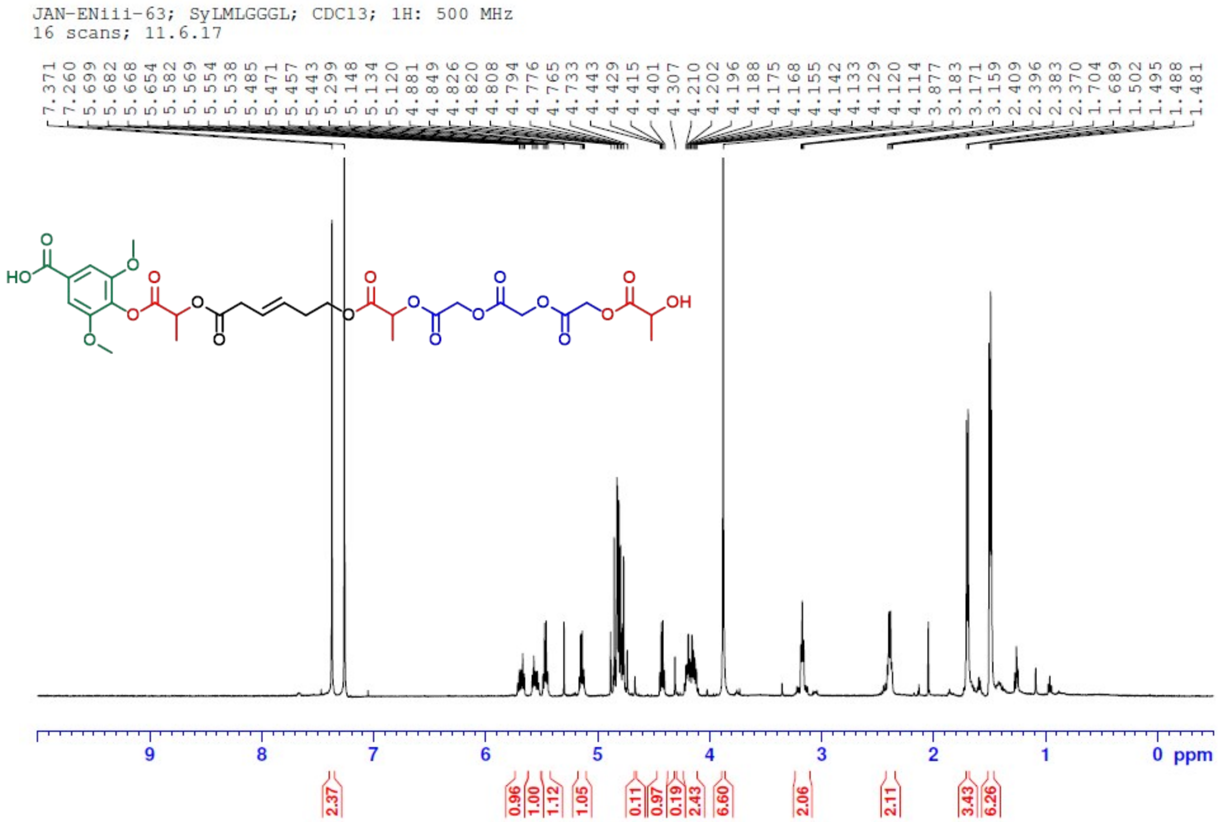

JAN-ENiii-61ii; Bn-SyLMLGGGL-Si; CDCl3
13C; 500 MHz; 2048 scans; 10.30.17

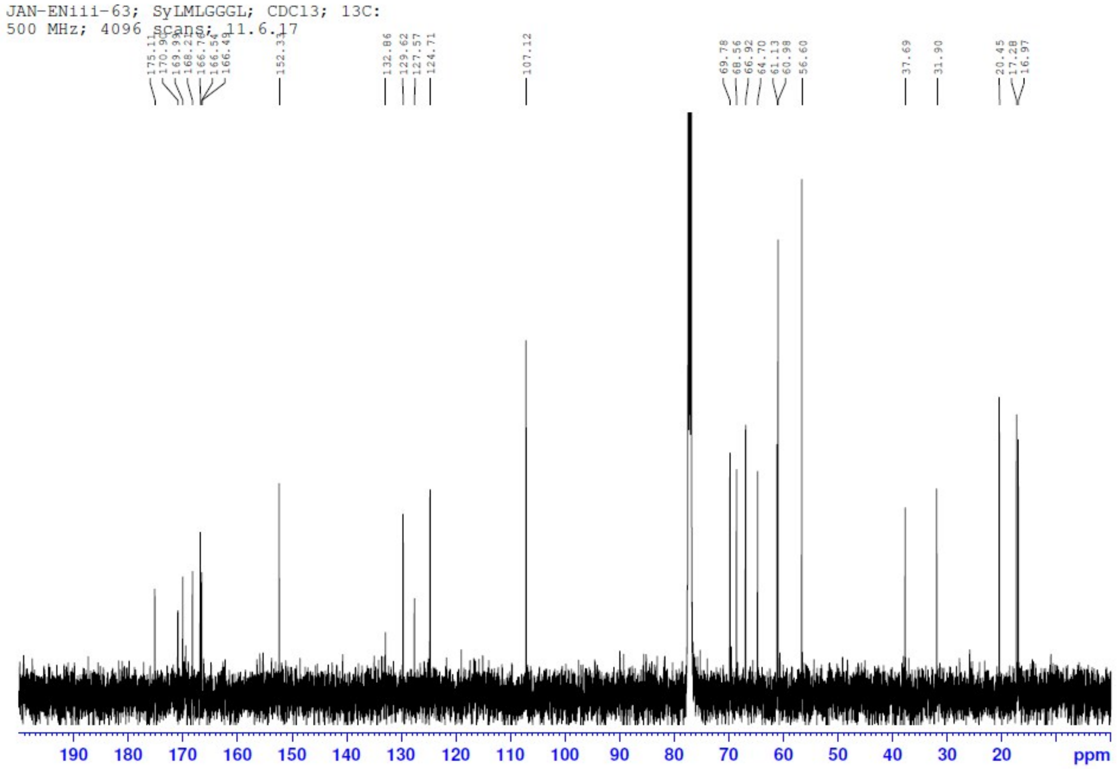
JAN-ENiii-62; SyLMLGGGL-Si; CDCl3; 1H;
500 MHz; 16 scans; 10.31.17

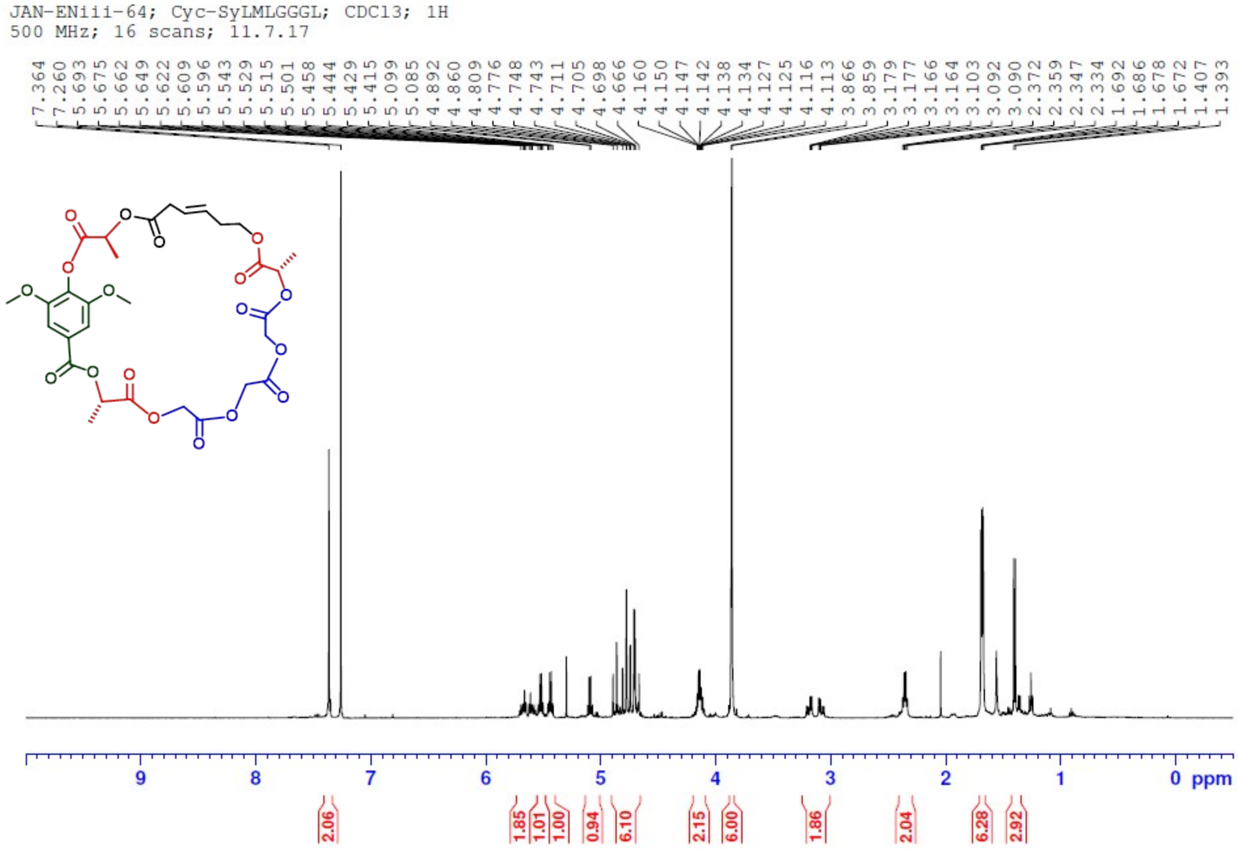


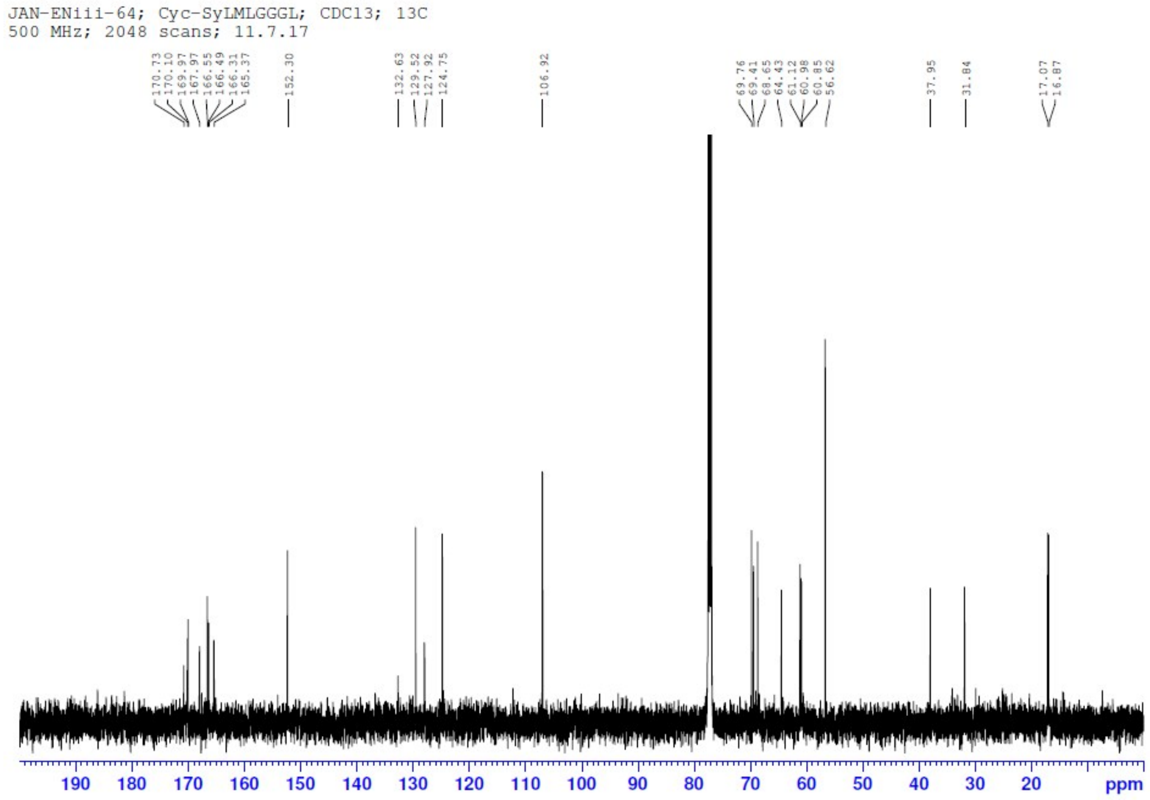
JAN-ENiii-62; SyLMLGGGL-Si; CDCl3; 13C:
500 MHz; 2048 scans; 11.3.17

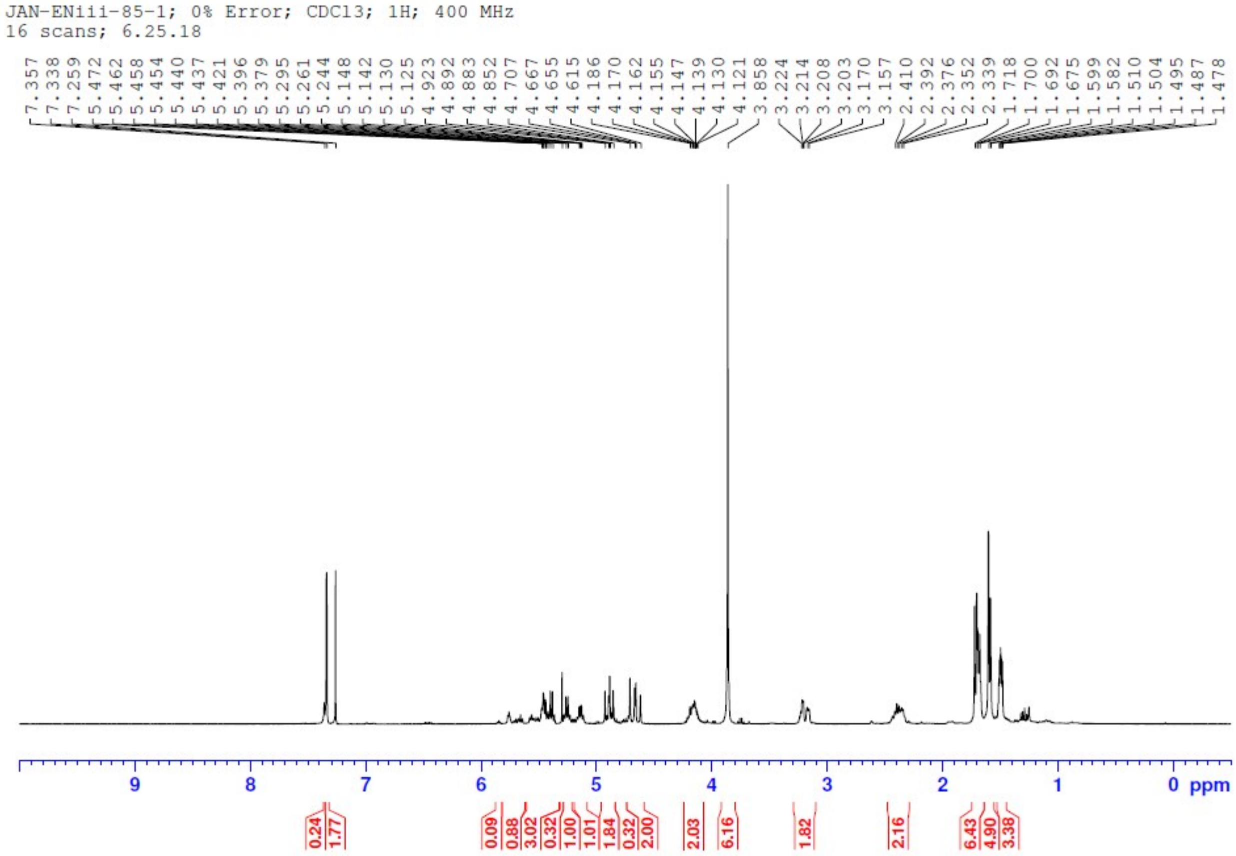


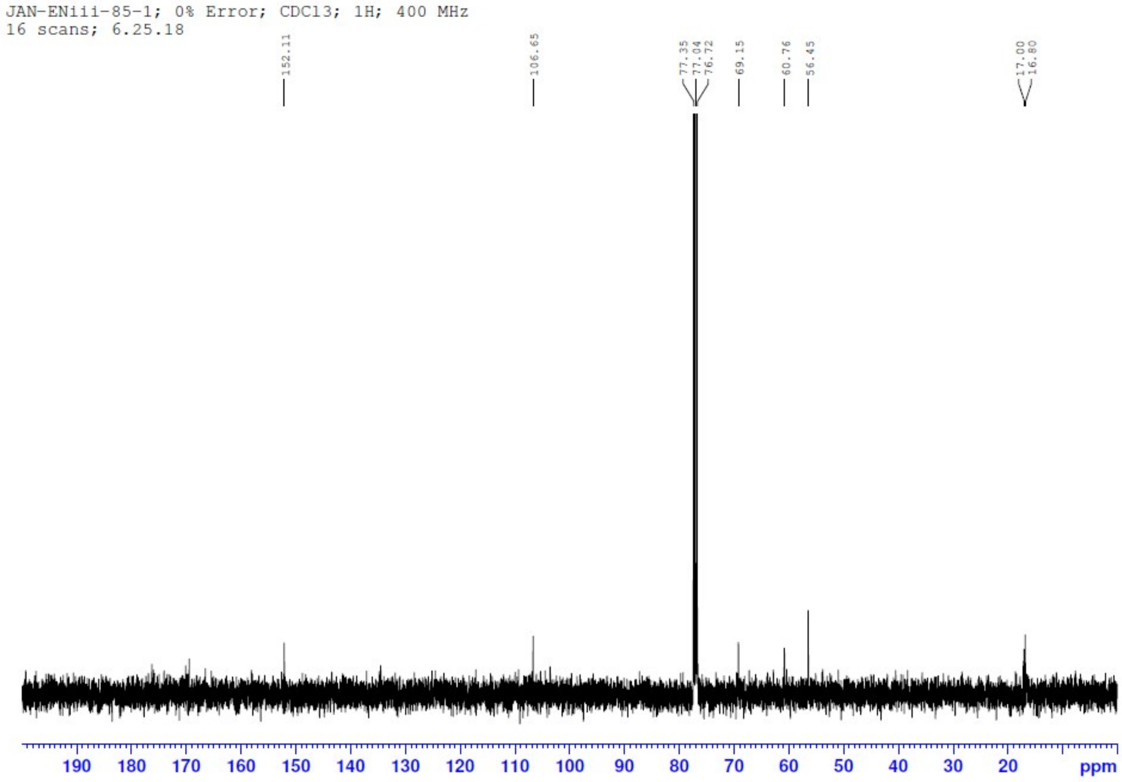

JAN-ENiii-63; SyLMLGGGL; CDCl3; 1H: 500 MHz
16 scans; 11.6.17
7.371
7.260
5.699
5.682
5.668
5.654
5.582
5.569
5.554
5.538
5.485
5.471
5.457
5.443
5.299
5.148
5.134
5.120
4.881
4.849
4.826
4.820
4.808
4.794
4.776
4.765
4.733
4.443
4.429
4.415
4.401
4.307
4.210
4.202
4.196
4.188
4.175
4.168
4.155
4.142
4.133
4.129
4.120
4.114
3.877
3.183
3.171
3.159
2.409
2.396
2.383
2.370
1.704
1.689
1.502
1.495
1.488
1.481
HO
O
OH
9
8
7
6
5
4
3
2
1
0 ppm
2.37
0.96
1.00
1.12
1.05
0.11
0.97
0.19
2.43
6.60
2.06
2.11
3.43
6.26


JAN-ENiii-63; SyLMLGGGL; CDCl3; 13C:
500 MHz; 4096 scans; 11.6.17
175.11
170.90
169.9
168.21
166.76
166.54
166.49
152.33
132.86
129.62
127.57
124.71
107.12
69.78
68.56
66.92
64.70
61.13
60.98
56.60
37.69
31.90
20.45
17.28
16.97
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

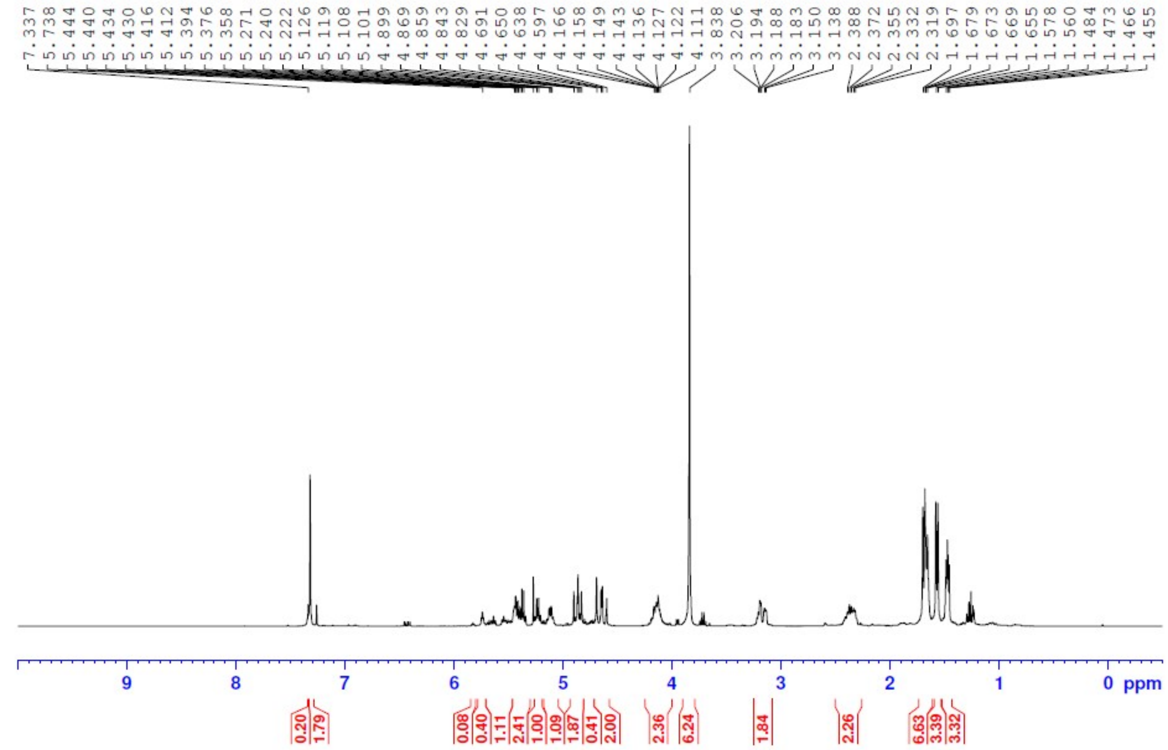

JAN-ENiii-64; Cyc-SyLMLGGGL; CDCl3; 1H
500 MHz; 16 scans; 11.7.17
7.364
7.260
5.693
5.675
5.662
5.649
5.622
5.609
5.596
5.543
5.529
5.515
5.501
5.458
5.444
5.429
5.415
5.099
5.085
4.892
4.860
4.809
4.776
4.748
4.743
4.711
4.705
4.698
4.666
4.160
4.150
4.147
4.142
4.138
4.134
4.127
4.125
4.116
4.113
3.866
3.859
3.179
3.177
3.166
3.164
3.103
3.092
3.090
2.372
2.359
2.347
2.334
1.692
1.686
1.678
1.672
1.407
1.393
9
8
7
6
5
4
3
2
1
0 ppm
2.06
1.85
1.01
1.00
0.94
6.10
2.15
6.00
1.86
2.04
6.28
2.92


JAN-ENiii-64; Cyc-SyLMLGGGL; CDCl3; 13C
500 MHz; 2048 scans; 11.7.17
170.73
170.10
169.97
167.97
166.55
166.49
166.31
165.37
152.30
132.63
129.52
127.32
124.75
106.92
69.76
69.41
68.65
64.43
61.12
60.98
60.85
56.62
37.95
31.84
17.07
16.87
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

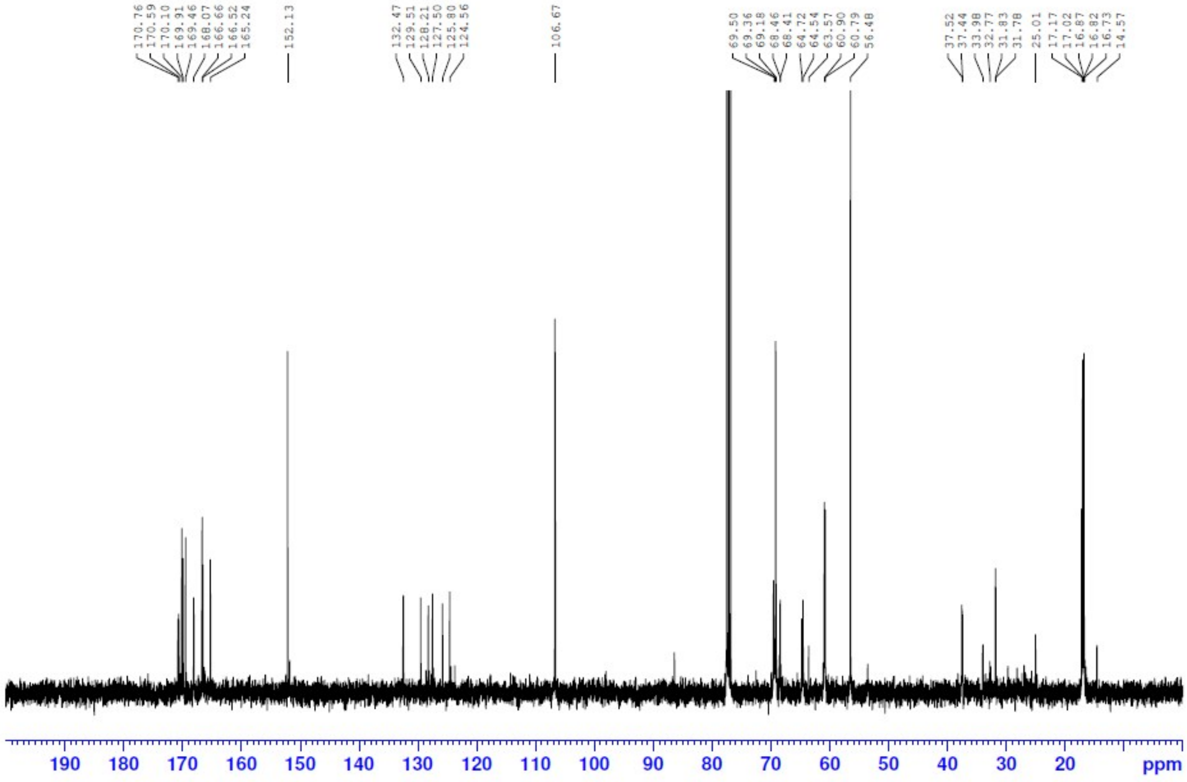

JAN-ENiii-85-1; 0% Error; CDCl3; 1H; 400 MHz
16 scans; 6.25.18
7.357
7.338
7.259
5.472
5.462
5.458
5.454
5.440
5.437
5.421
5.396
5.379
5.295
5.261
5.244
5.148
5.142
5.130
5.125
4.923
4.892
4.883
4.852
4.707
4.667
4.655
4.615
4.186
4.170
4.162
4.155
4.147
4.139
4.130
4.121
3.858
3.224
3.214
3.208
3.203
3.170
3.157
2.410
2.392
2.376
2.352
2.339
1.718
1.700
1.692
1.675
1.599
1.582
1.510
1.504
1.495
1.487
1.478
9
8
7
6
5
4
3
2
1
0 ppm
0.24
1.77
0.09
0.88
3.02
0.32
1.00
1.01
1.84
0.32
2.00
2.03
6.16
1.82
2.16
6.43
4.90
3.38


JAN-ENiii-85-1; 0% Error; CDCl3; 1H; 400 MHz
16 scans; 6.25.18
152.11
106.65
77.35
77.04
76.72
69.15
60.76
56.45
17.00
16.80
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

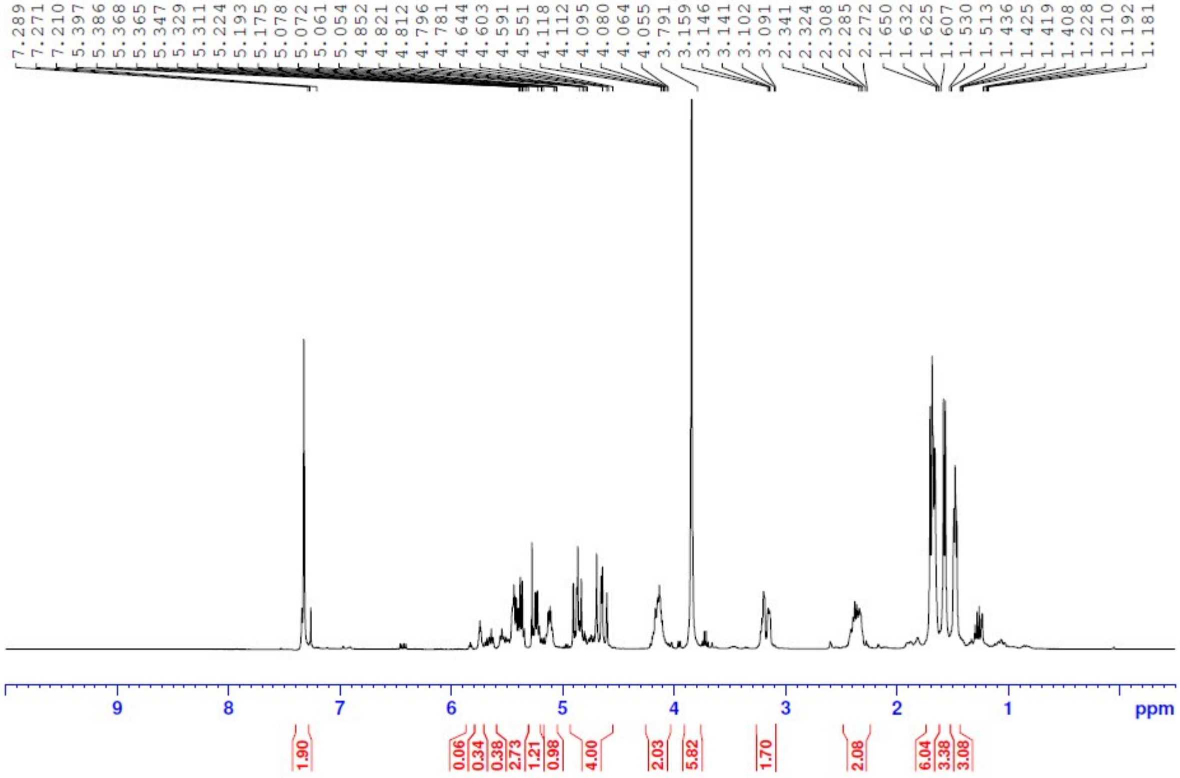
JAN-ENiii-85; 2.5% Error; CDCl3; 1H; 400 MHz
16 scans; 6.25.18



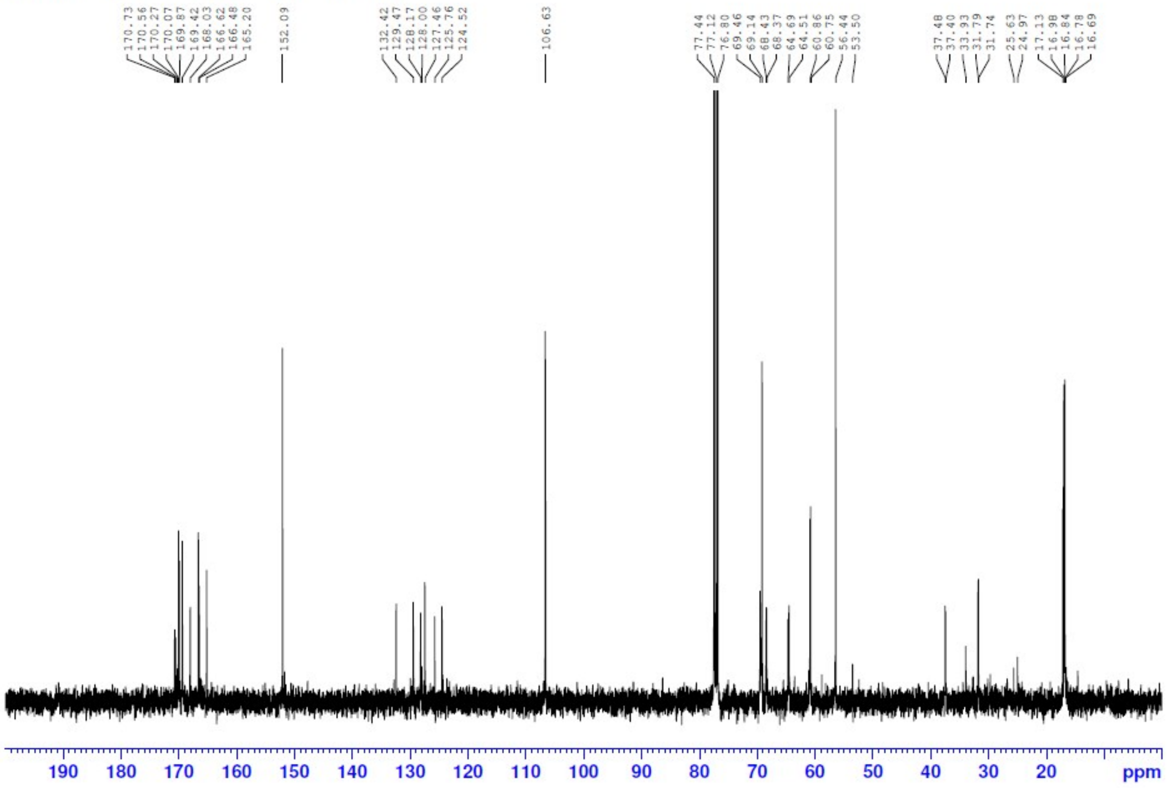
JAN-ENiii-85; 2.5% Error; CDCl3; 13C; 400 MHz
128 scans; 6.25.18



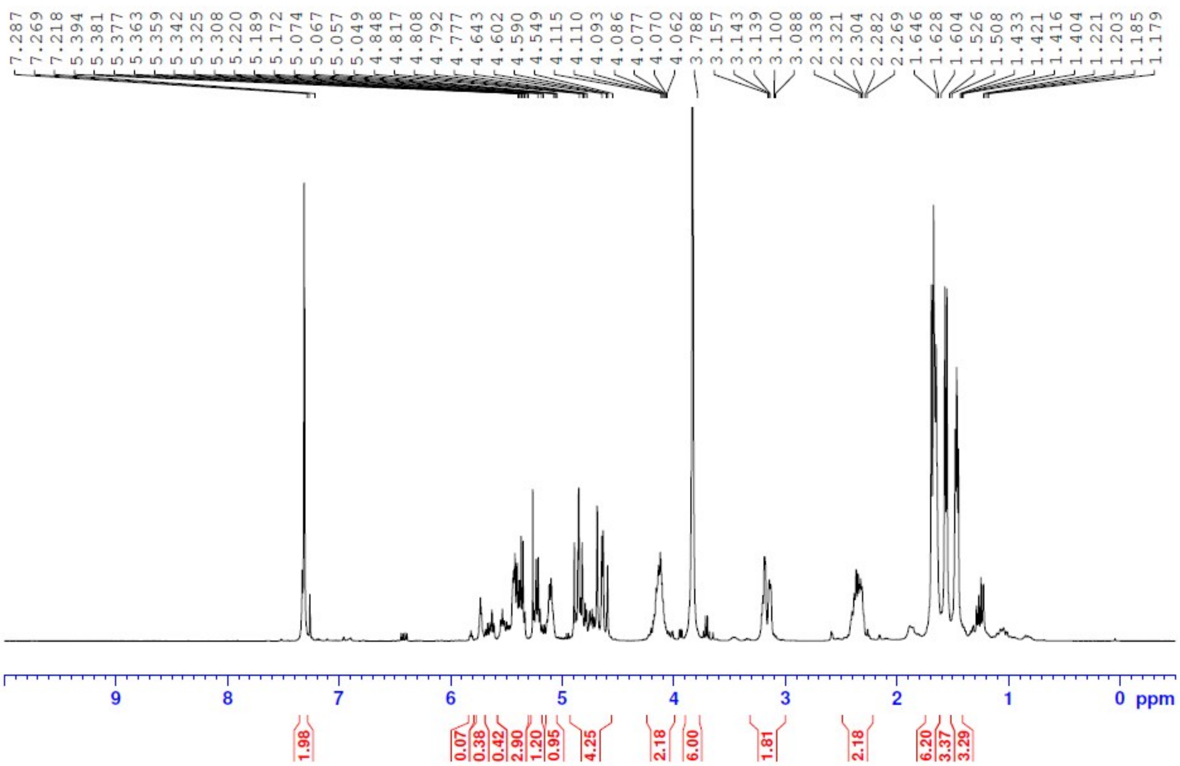
JAN-ENiii-85; 5% Error; 1H



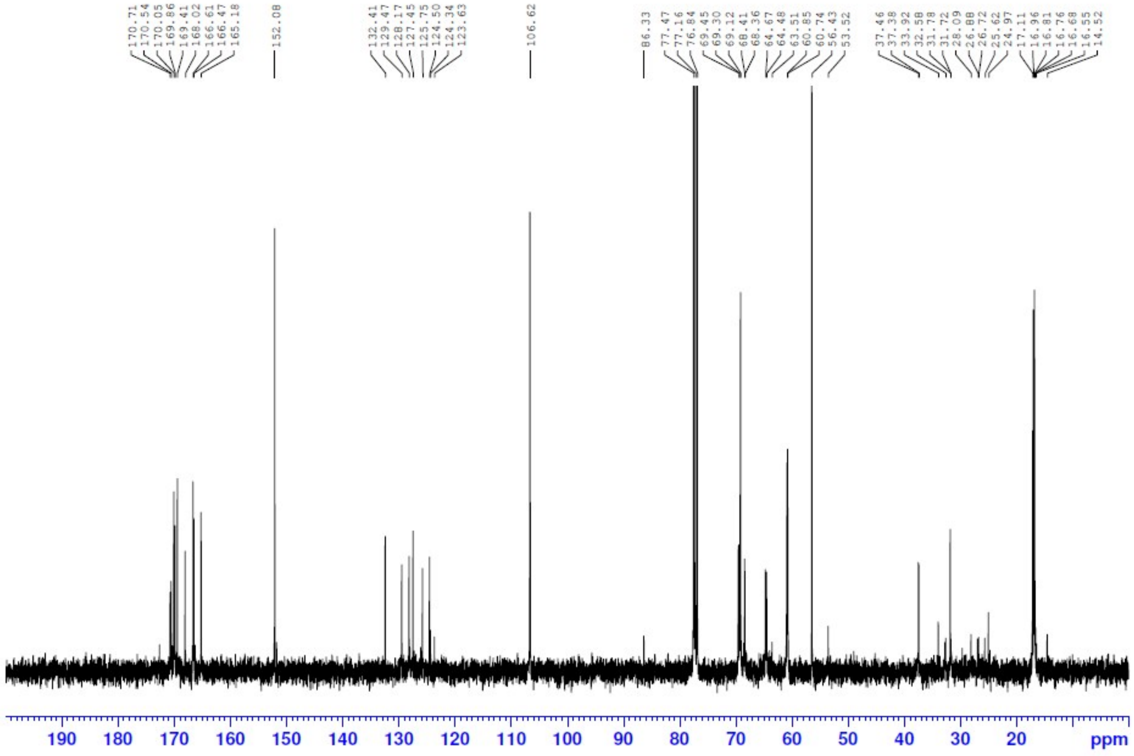
JAN-ENiii-85; 5% Error; 13C; 128 scans



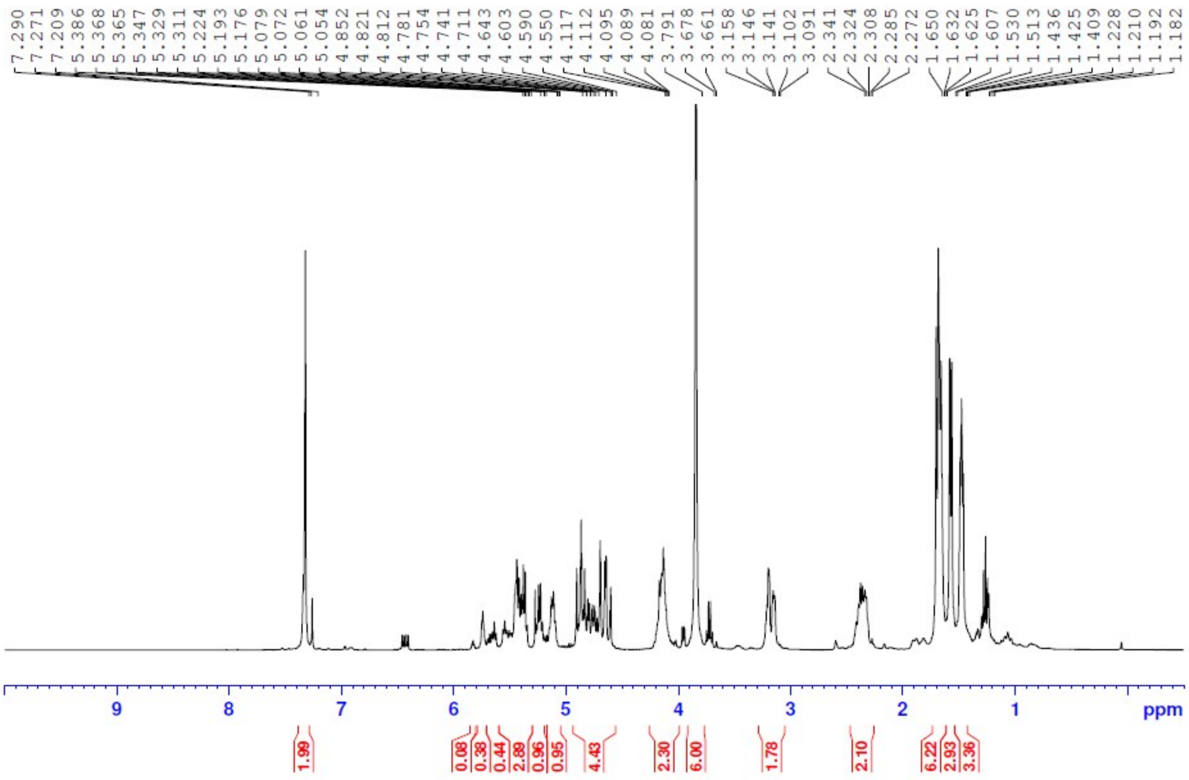
JAN-ENiii-85; 10% Error; 1H



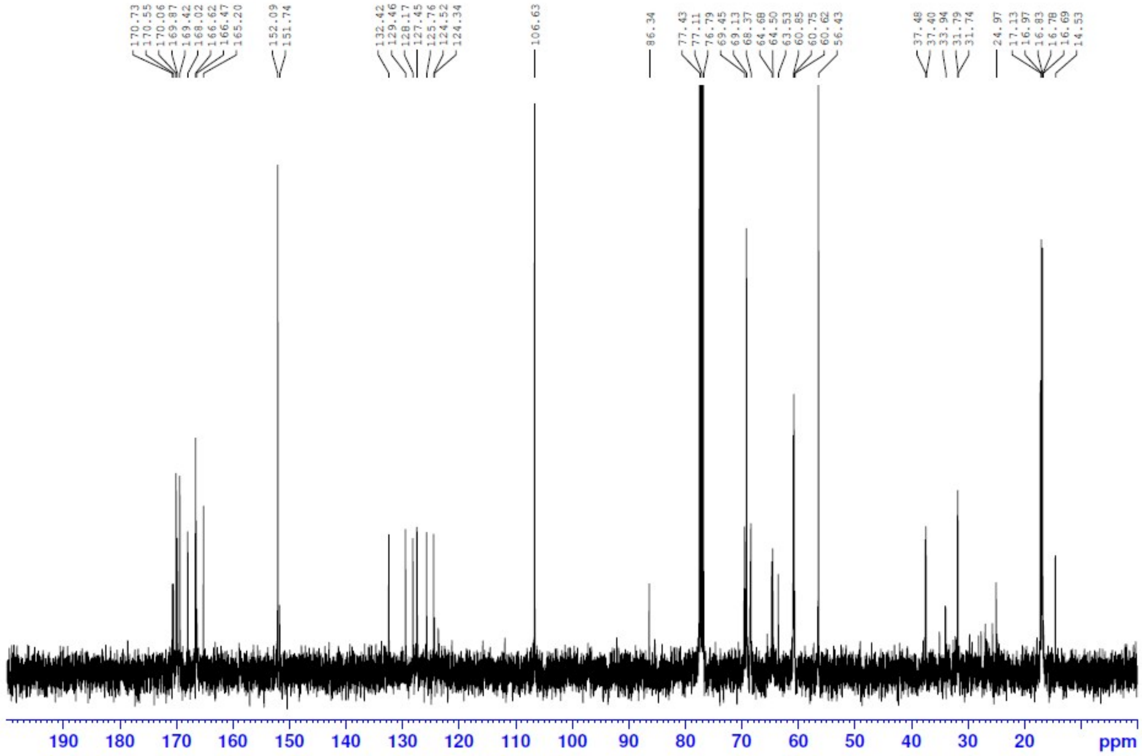
JAN-ENiii-85; 10% Error; 13C; 128 scans



JAN-ENiii-85; 20% Error; 1H



JAN-ENiii-85; 20% Error; 13C; 128 scans



SEC Plots

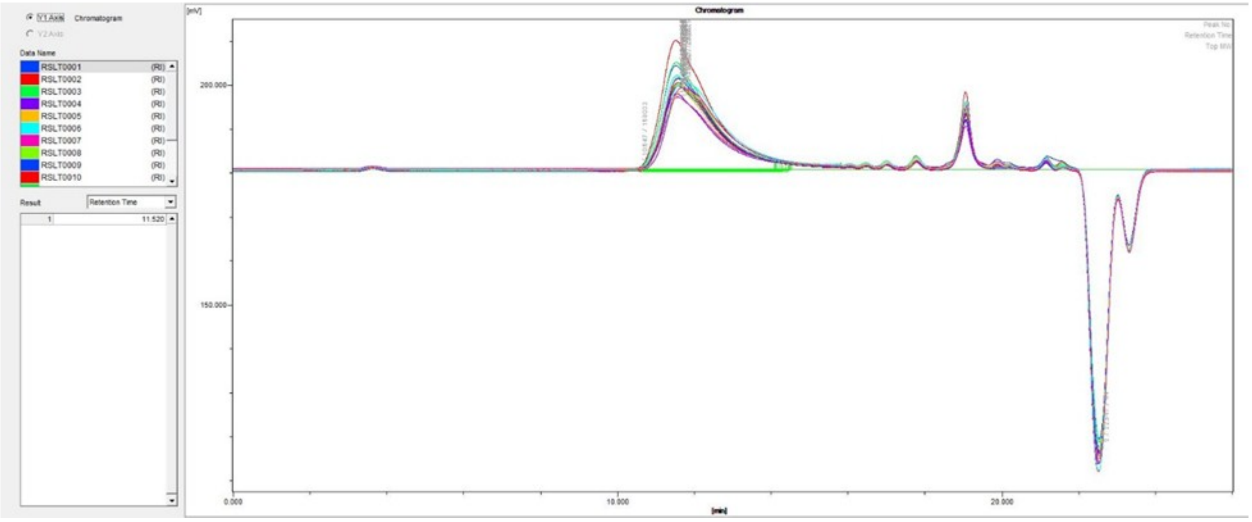


Figure S6. SEC plots of copolymers, Week 2 of hydrolysis.

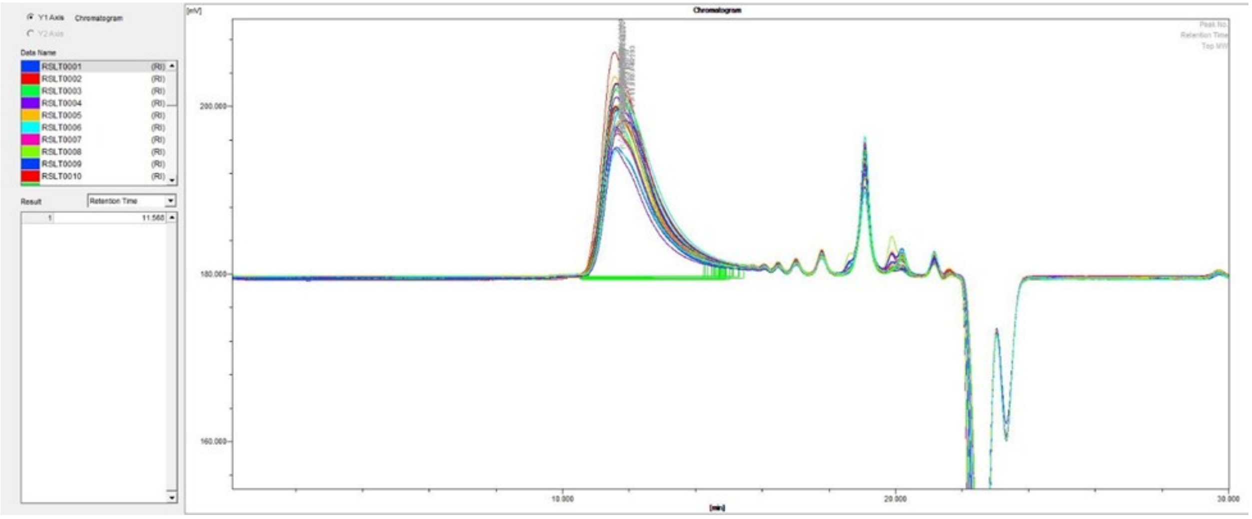


Figure S7. SEC plots of copolymers, Week 3 of hydrolysis.

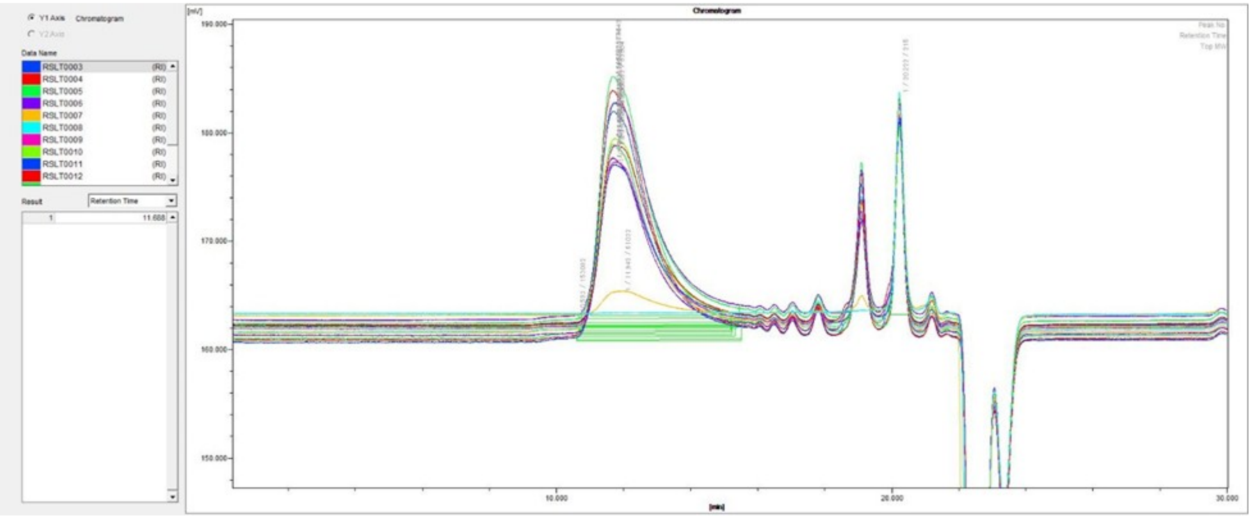


Figure S8. SEC plots of copolymers, Week 4 of hydrolysis.

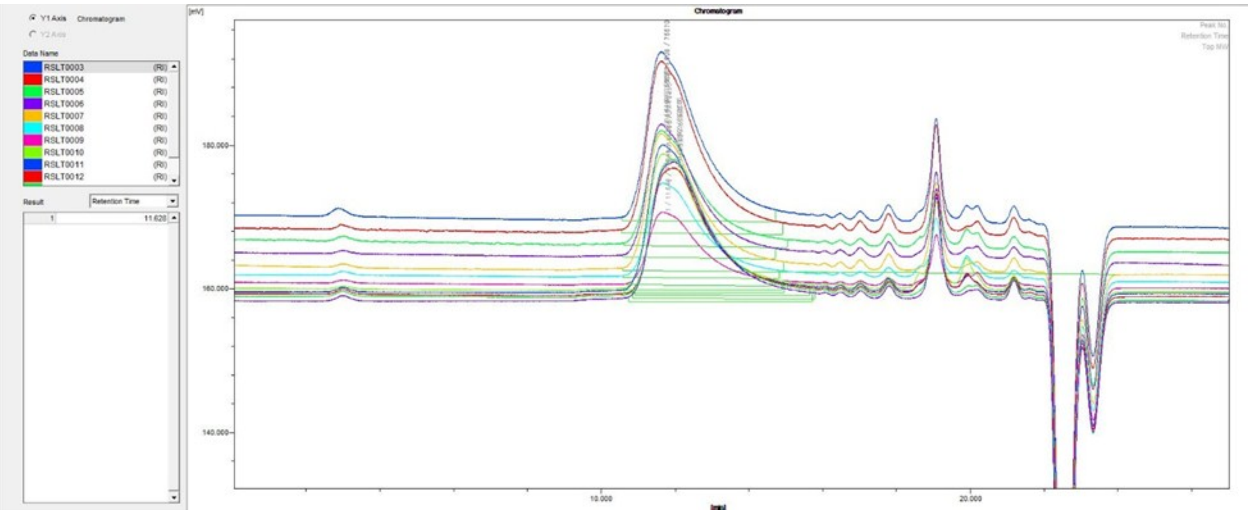


Figure S9. SEC plots of copolymers, Week 5 of hydrolysis.

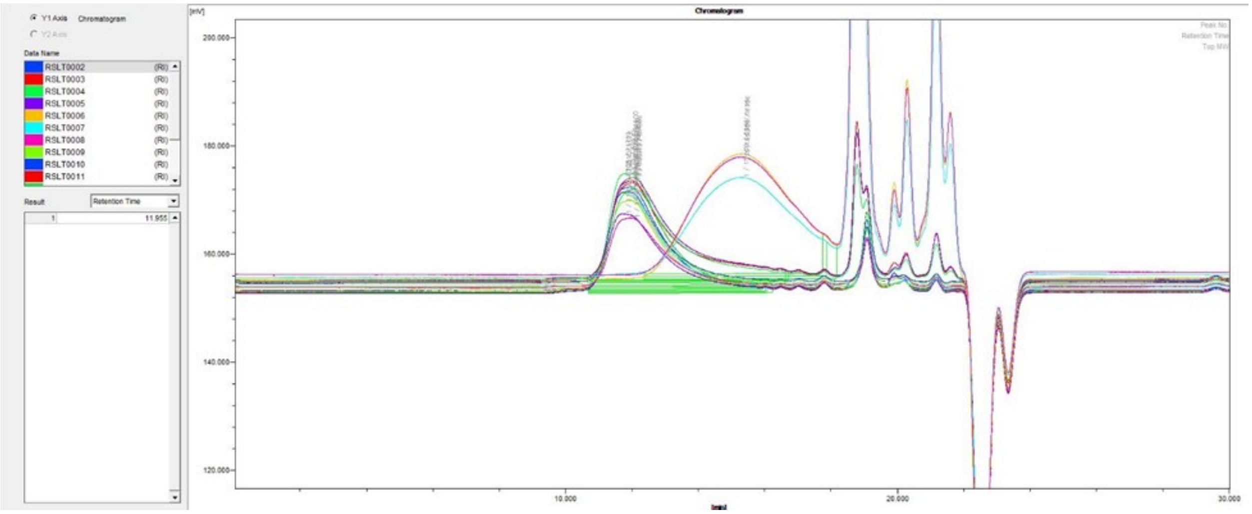


Figure S10. SEC plots of copolymers, Week 6 of hydrolysis.

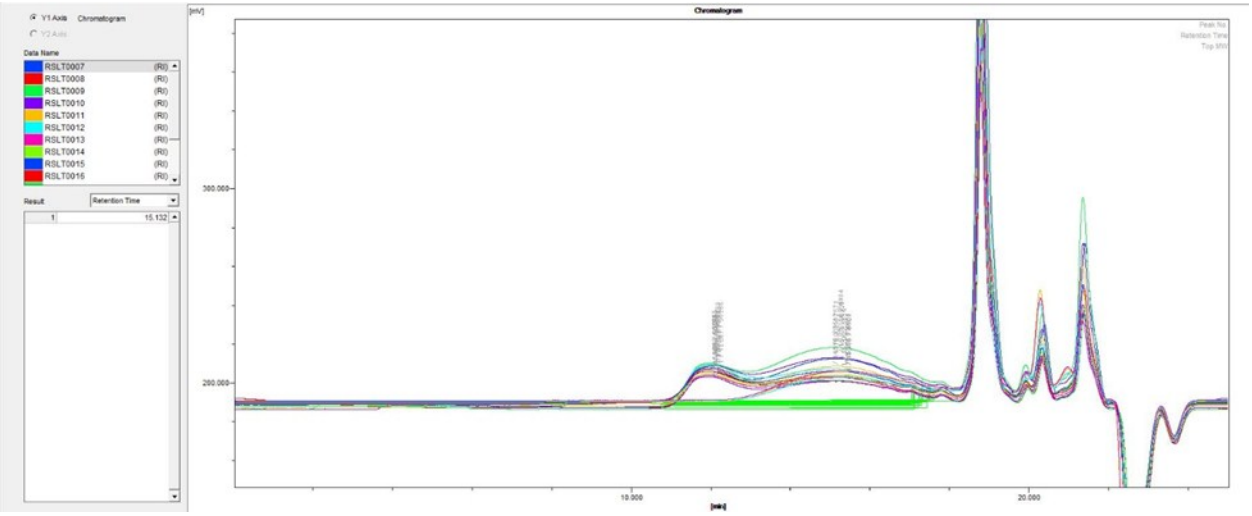


Figure S11. SEC plots of copolymers, Week 7 of hydrolysis.

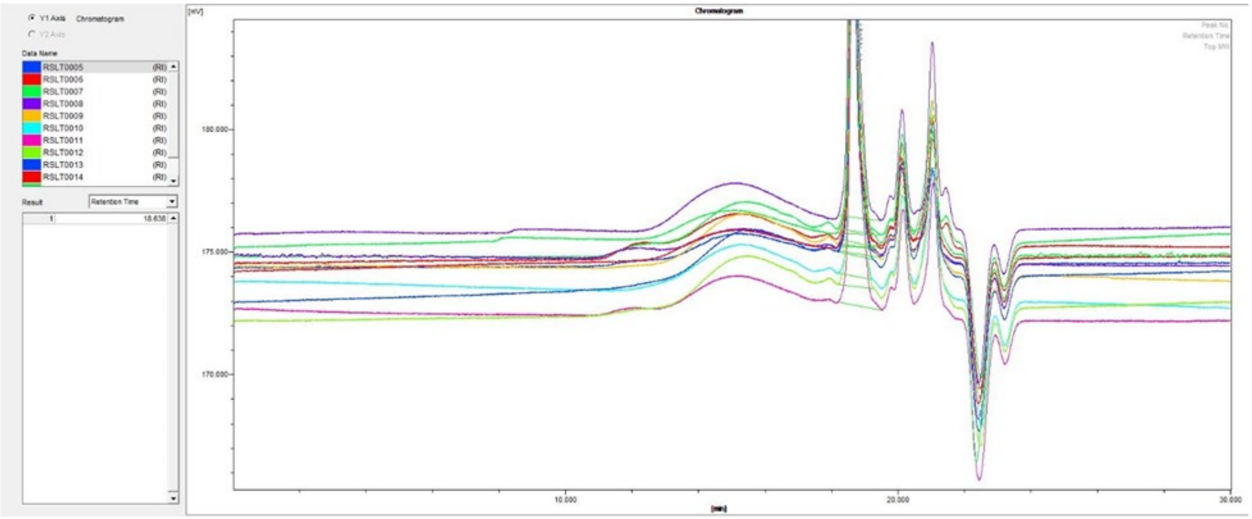


Figure S12. SEC plots of copolymers, Week 8 of hydrolysis.

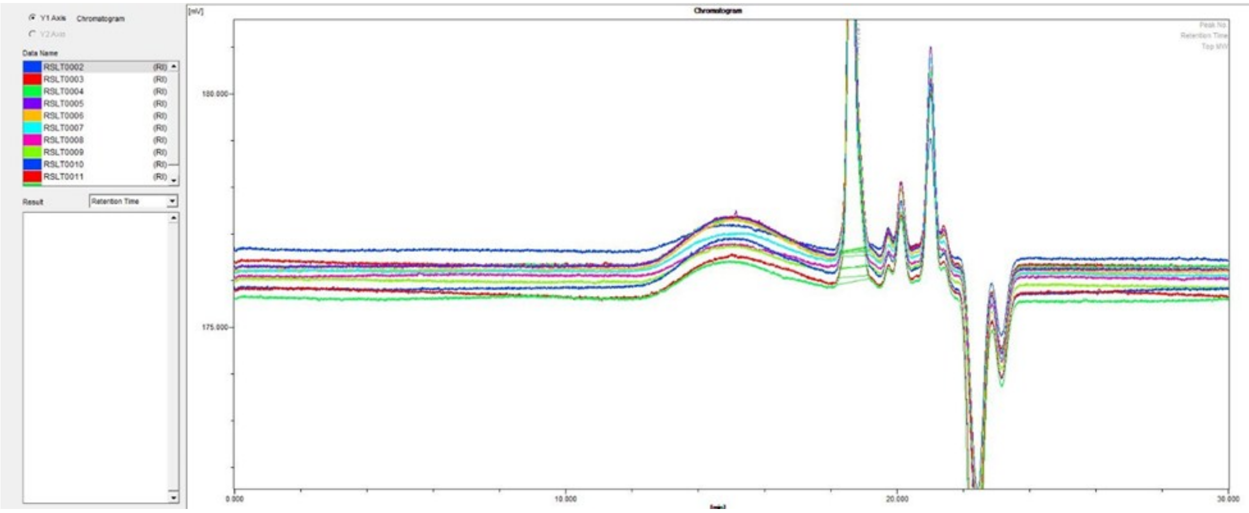
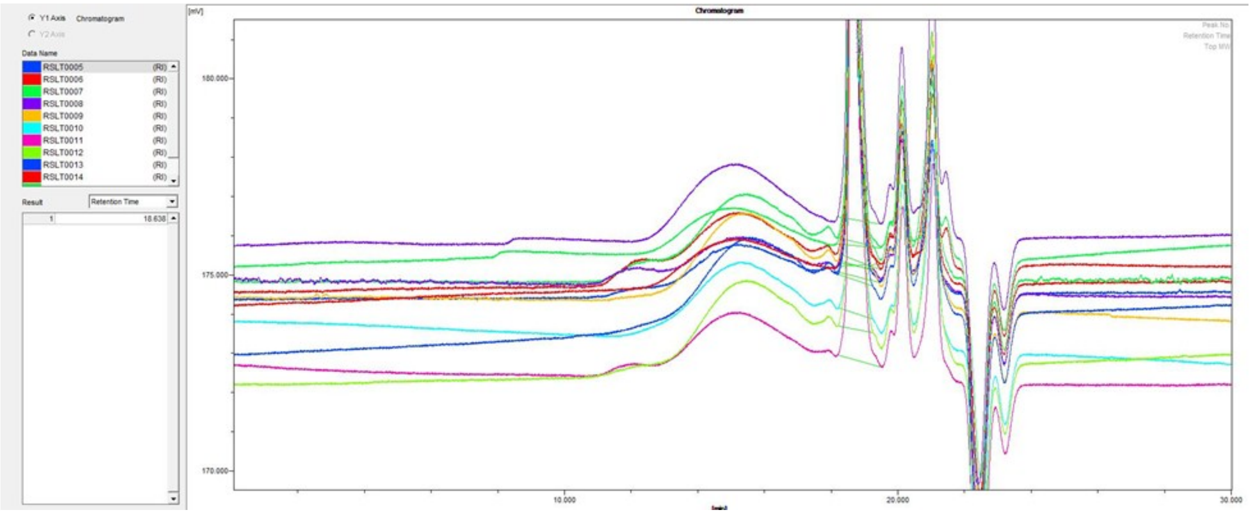


Figure S13. SEC plots of copolymers, Week 9 of hydrolysis.



● Y1 Axis Chromatogram
○ Y2 Axis

Data Name
🟦 RSLT0005 (RI)
🟥 RSLT0006 (RI)
🟩 RSLT0007 (RI)
🟪 RSLT0008 (RI)
🟧 RSLT0009 (RI)
🟦 RSLT0010 (RI)
🟪 RSLT0011 (RI)
🟩 RSLT0012 (RI)
🟦 RSLT0013 (RI)
🟥 RSLT0014 (RI)

Result: Retention Time
1 18.638

Figure S14. SEC plots of copolymers, Week 10 of hydrolysis.

References

1. Nowalk, J. A.; Fang, C.; Short, A. L.; Weiss, R. M.; Swisher, J. H.; Liu, P.; Meyer, T. Y., Sequence-Controlled Polymers Through Entropy-Driven Ring-Opening Metathesis Polymerization: Theory, Molecular Weight Control, and Monomer Design. *Journal of the American Chemical Society* **2019**.