Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supplementary Information

Property Impact of Common Linker Segments in Sequence-Controlled Polyesters

Jordan H. Swisher[a], Jamie A. Nowalk[a], and Tara Y. Meyer *[,a, b]

a. Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

b. McGowan Institute for Regenerative Medicine, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

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1.0 SUPPLEMENTARY FIGURES AND PROCEDURES

1.1 OPTICAL PROFILES

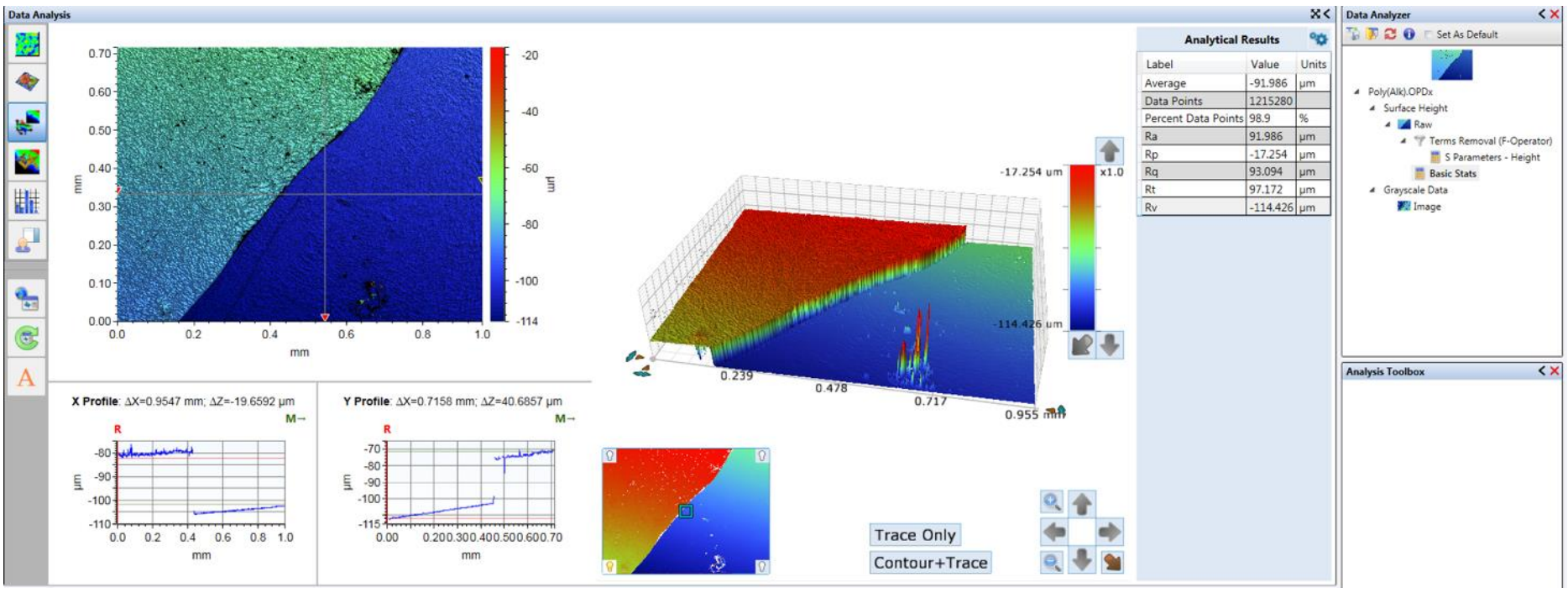


Figure S1. Optical profile of **poly(Alk).**

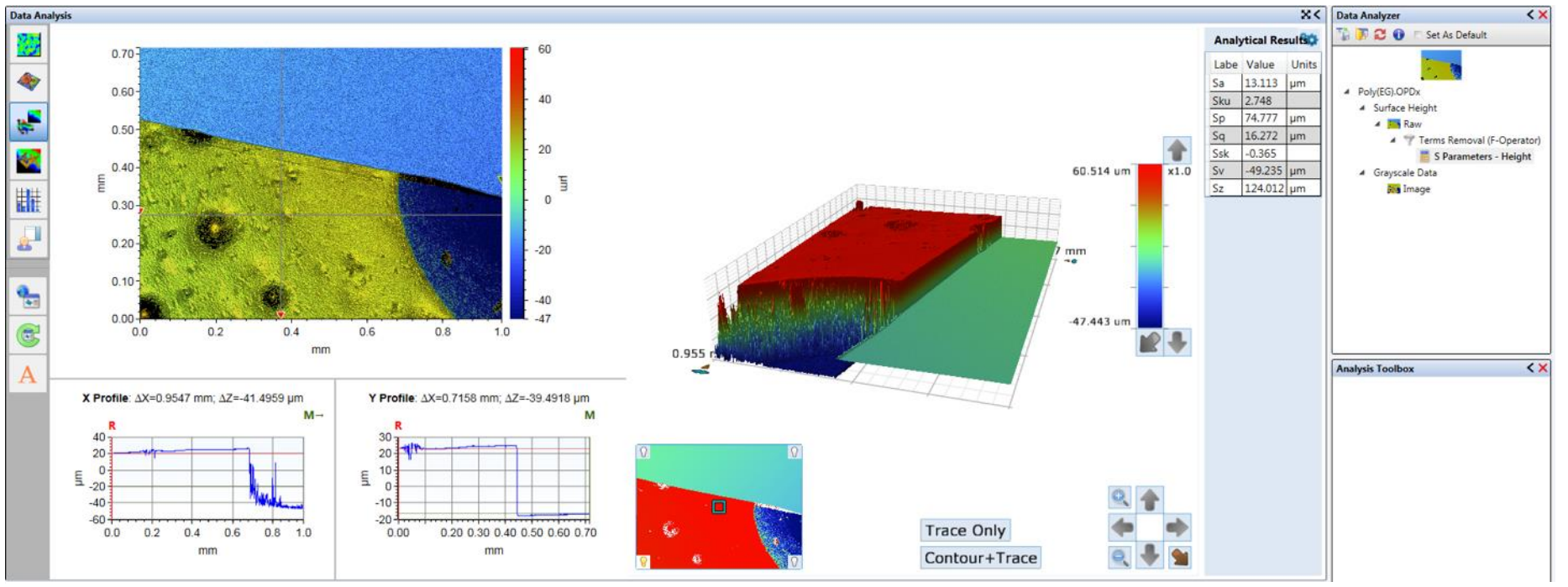


Figure S2. Optical profile of **poly(EG).**

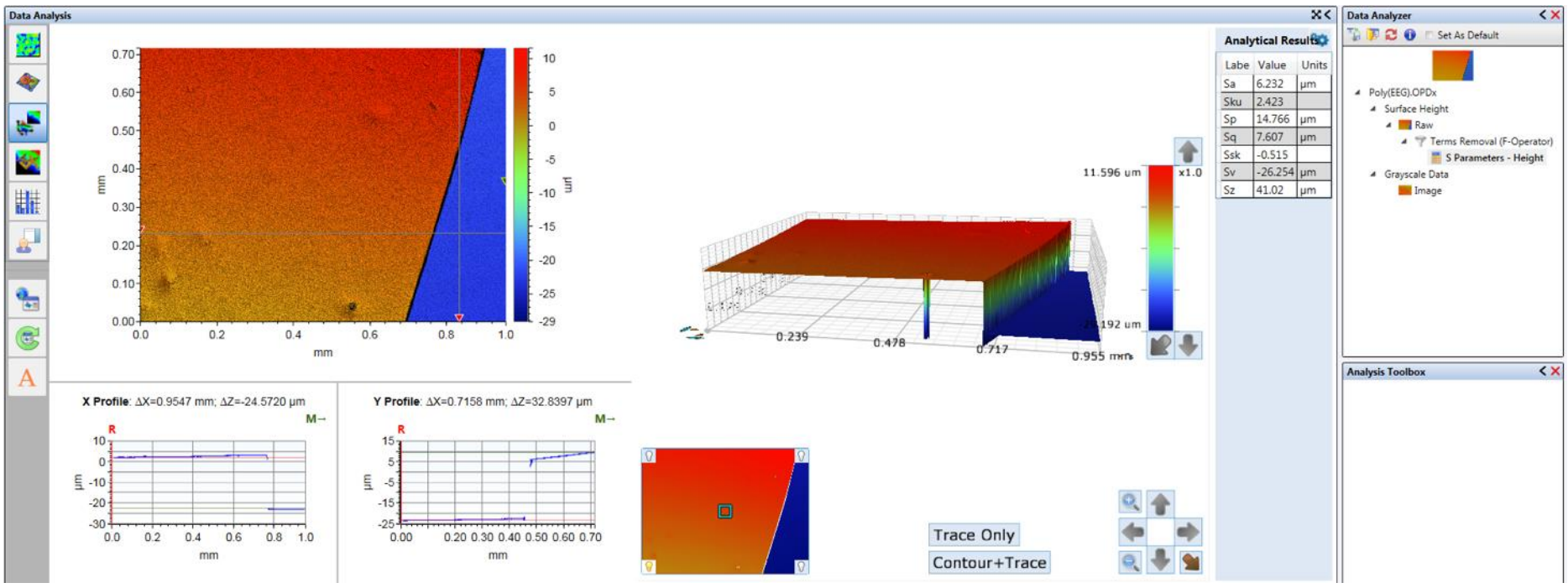


Figure S3. Optical profile of **poly(EEG).**

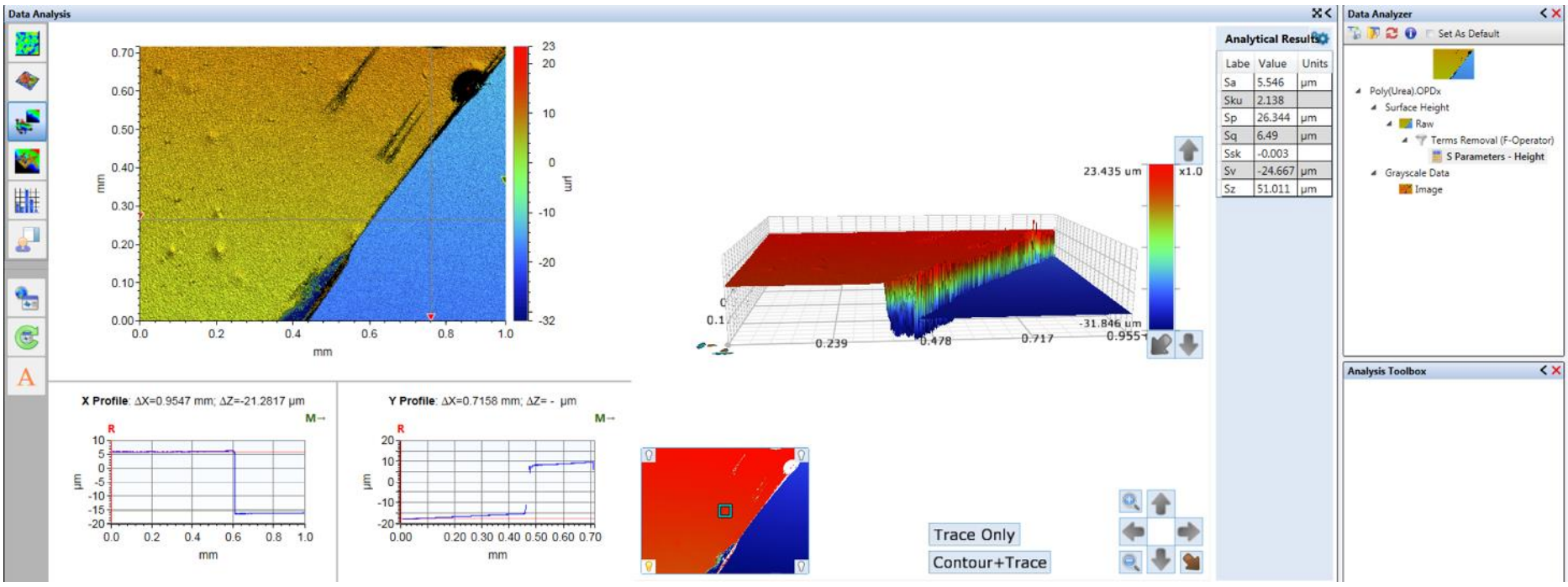


Figure S4. Optical profile of **poly(Urea).**

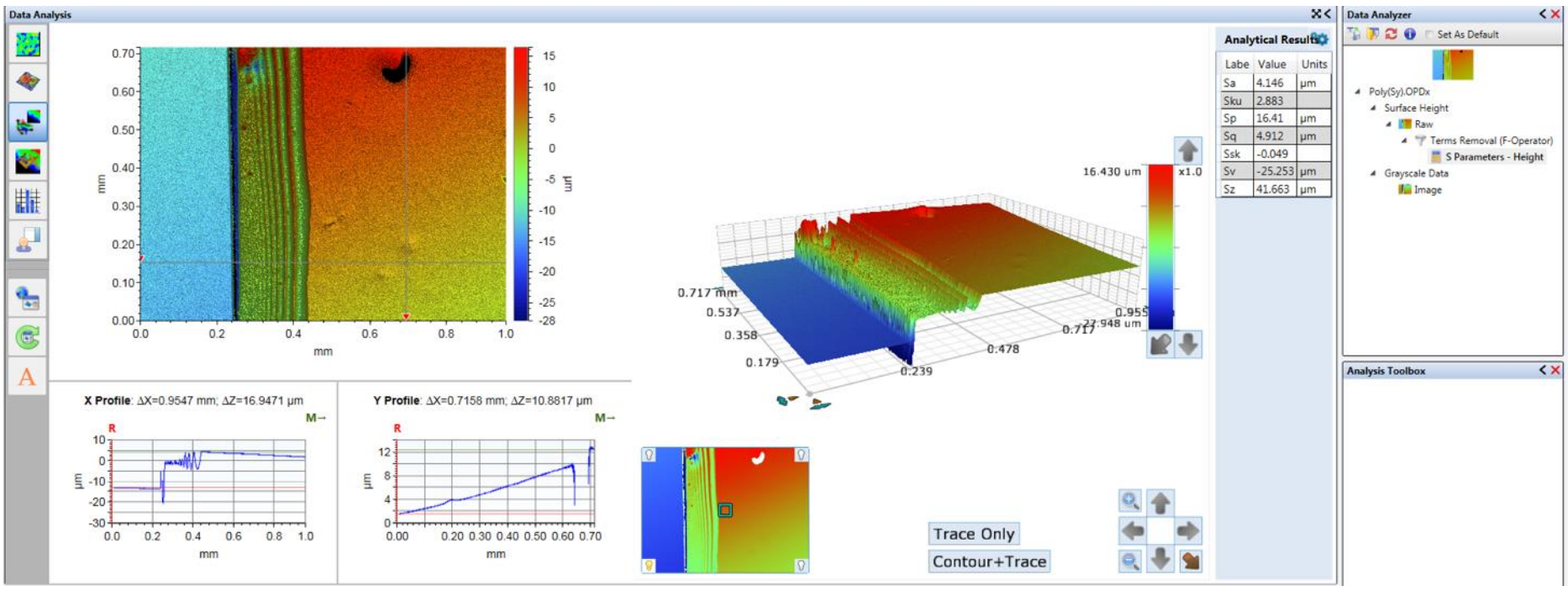


Figure S5. Optical profile of **poly(Sy).**

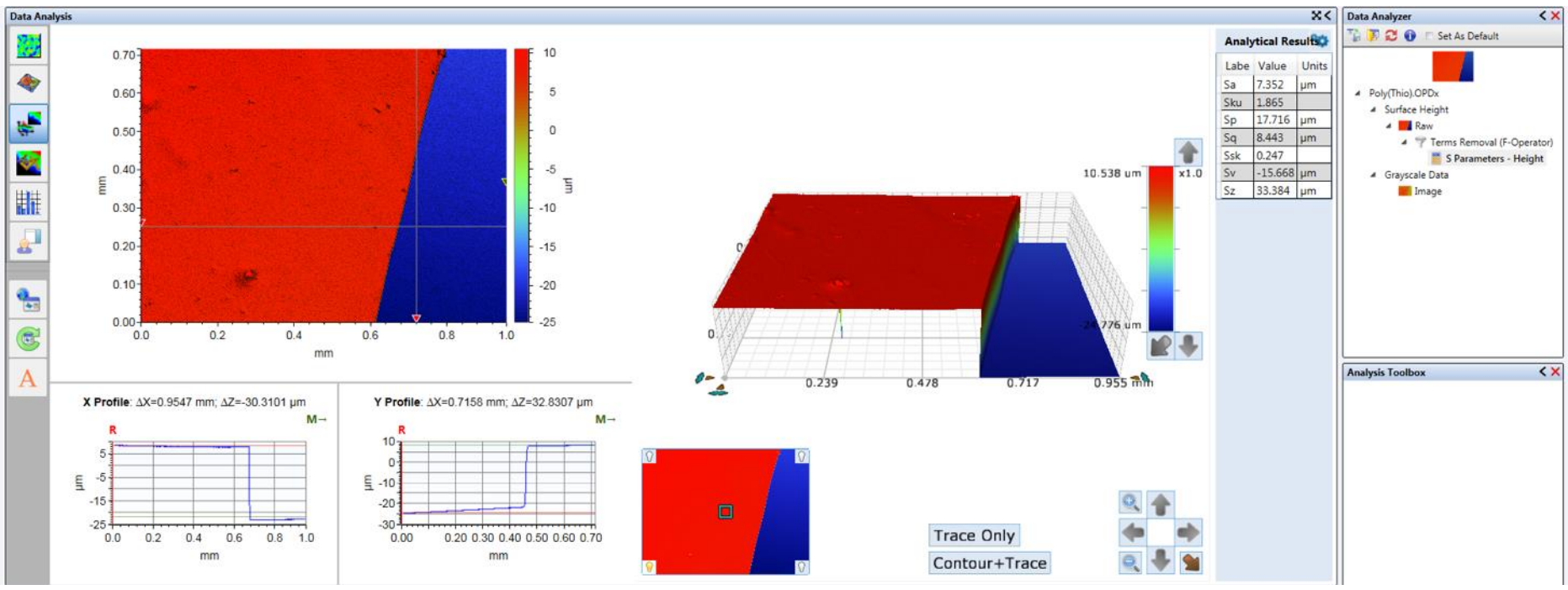


Figure S6. Optical profile of **poly(Thio).**

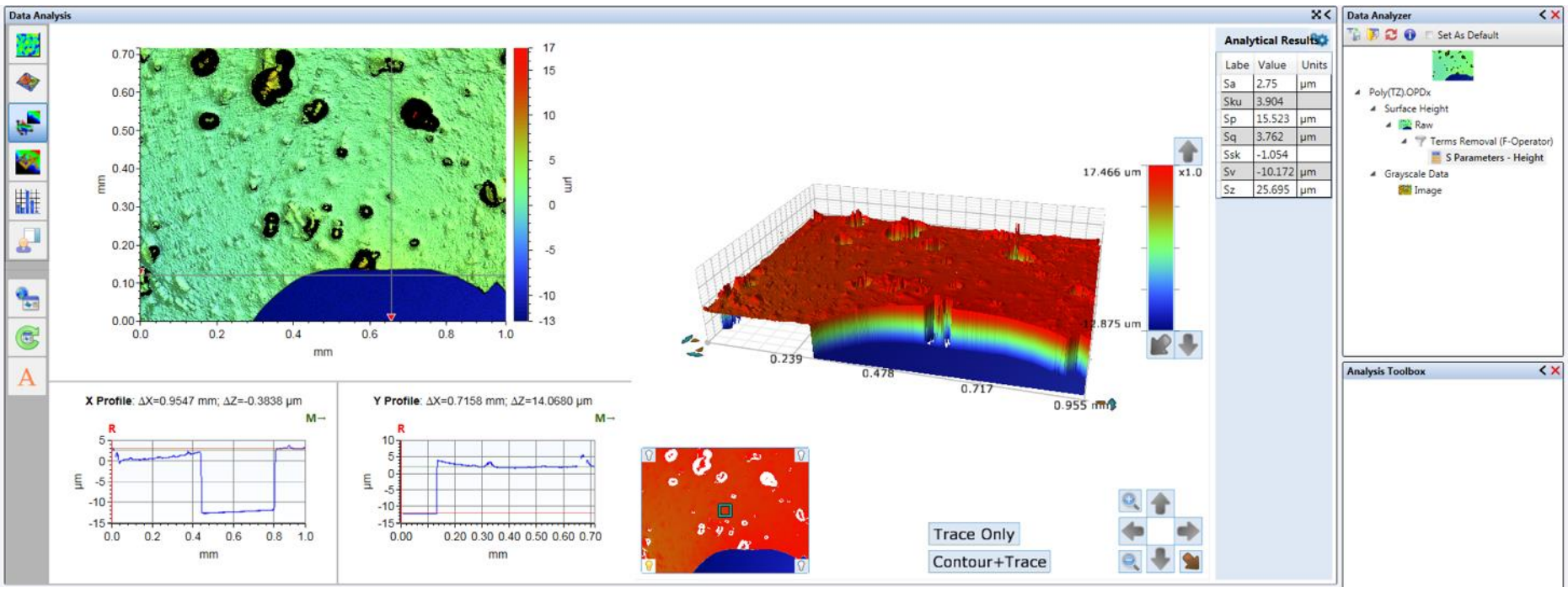


Figure S7. Optical profile of **poly(TZ).**

1.2 NANOINDENTATION

Nanoindentation was performed using a Hysitron TI 950 Triboindenter with a Berkovich diamond indenter tip. All indentations were performed at room temperature using a displacement-controlled method with a set displacement of 4,000 nm. Each indentation had a loading segment of 20 seconds, a holding segment of 10 s, and a deloading segment of 20 s. The loading segment had variable loading rates, depending on the material, to reach an indentation depth of 4,000 nm. The holding segment held the tip at 4,000 nm for 10 s to limit nosing. A 4 x 5 matrix of indentations was performed with 200 µm between indentations to avoid overlap and local bias on the film surface.

Load-displacement curves were provided by the instrument and all other values were obtained from analysis of the load-displacement curves using the Oliver-Pharr method.[1-5] A representative load-displacement curve with associated values is provided in Figure S8.

The maximum load, P_{Max}, is equal to the maximum force applied during the indentation. The stiffness of the films, S, is defined as the slope of the initial 30% of the deloading curve. The hardness value, H, is defined as:

$$H = \frac{P_{Max}}{A(h_c)} \quad \text{(S1)}$$

where $A(h_c)$ is the projected contact area at the contact depth, and is defined as:

$$A(h_c) = 24.5h_c^2 \quad \text{(S2)}$$

where 24.5 is a geometrical constant associated with the Berkovich tip. The contact depth, h_c, which is not equal to the maximum indentation depth, h_{max}, in elastic models, was estimated as:

$$h_c = h_{Max} - \varepsilon\frac{P_{Max}}{S} \quad \text{(S3)}$$

where ε is another geometrical constant related to the Berkovich tip equal to 0.75.

The reduced elastic modulus, E_r, was defined as:

$$E_r = S\frac{\sqrt{\pi}}{2\beta\sqrt{A(h_c)}} \quad \text{(S4)}$$

where β is a correction factor (β = 1.034 for a Berkovich tip). Finally, Young's Modulus, E, was calculated by Eq. S5:

$$\frac{1}{E_r} = \frac{1-v^2}{E} + \frac{1-v_i^2}{E_i} \quad \text{(S5)}$$

where v and E are the Poisson's ratio and modulus of the sample, (Poisson's ratio was defined as 0.3, a standard value for polymers[6]) and v_i and E_i are the Poisson's ratio and modulus of the diamond indenter (0.07 and 1141 GPa, respectively).

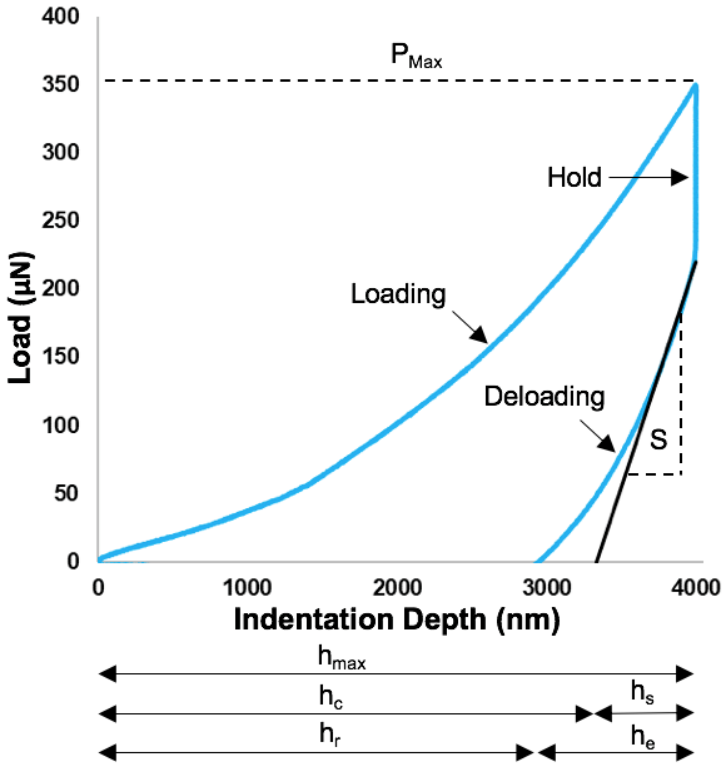


Figure S8. Representative load-displacement curve where h_s is the sink-in depth, h_r is the residual indent depth and h_e is the depth of elastic recovery.

From the 20 indentations performed on each polymer, at least 17 were averaged to determine E, P_{Max} E_r, H and S. The removed outliers were determined by using the Thompson-Tau method on E, E_r, H, S and P_{max} values of each indent, and if any of these five values for a particular indent were determined to be outliers, that indent was removed from the dataset.

Scanning probe microscopy (SPM) images were taken using the imaging mode of the Hysitron software with a scan rate of 1.00 Hz, tip velocity of 20 µm/sec, and scan size of 10 µm.

1.3 ICP-OES

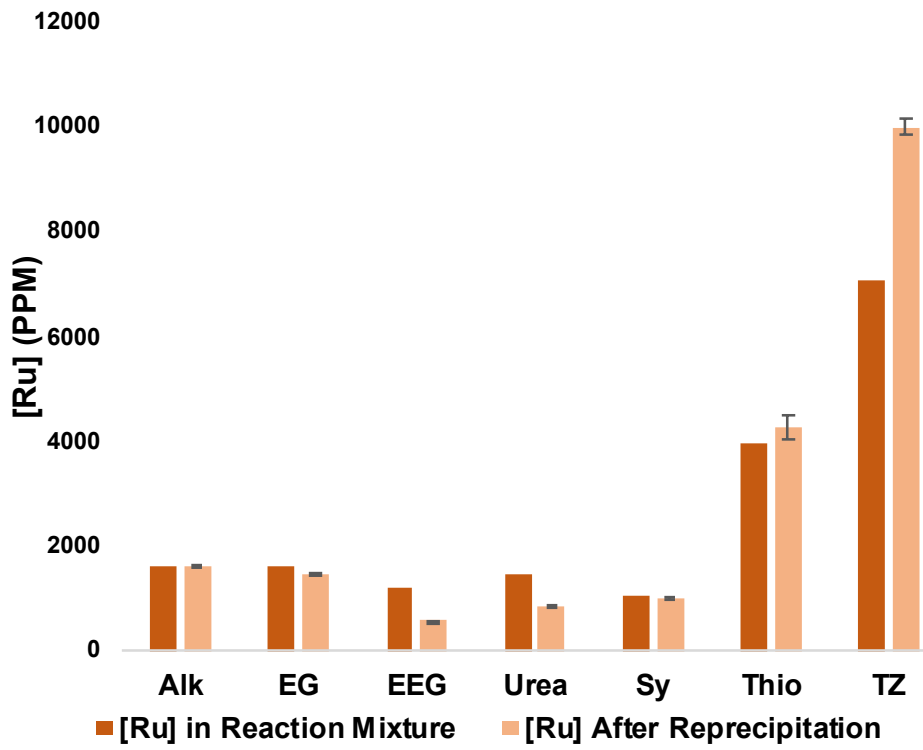


Figure S9. Calculated [Ru] in the polymerization reaction mixture, and the [Ru] after reprecipitation of the polymer samples determined by ICP-OES. Percent error determined by analysis of six duplicate samples.

1.4 FOX T_G PREDICTIONS

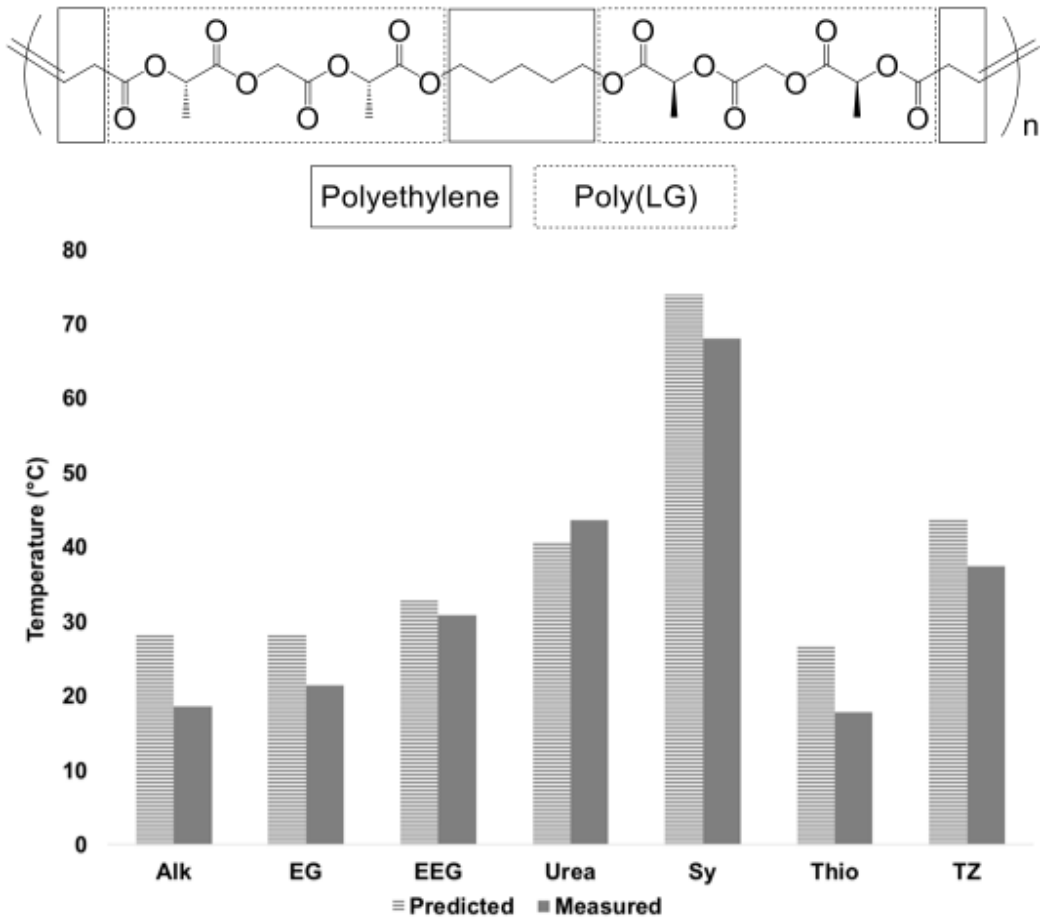


Figure S10. Method used to define segments for predicting T_g (top) and predicted and measured T_g (bottom).

1.5 THERMOGRAVIMETRIC ANALYSIS

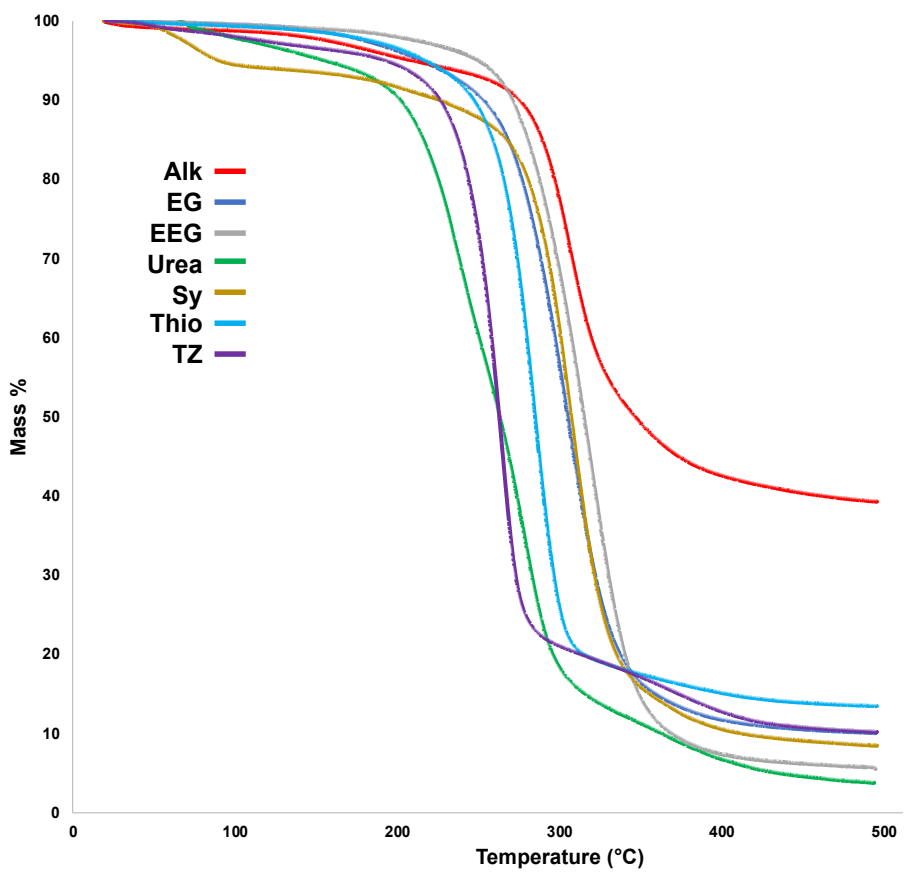


Figure S11. Thermogravimetric analysis.

1.6 SCANNING PROBE MICROSCOPY

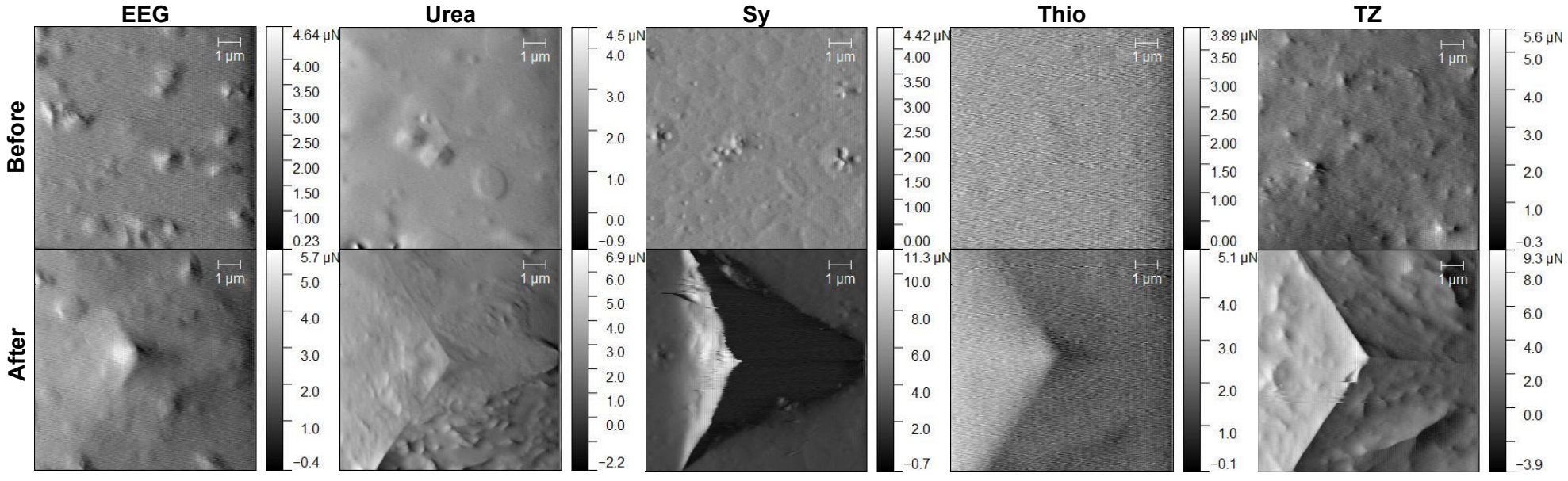


Figure S12. Scanning probe microscopy of selected polymers before and after indentation.

1.7 ADDITIONAL DEGRADATION STUDY DATA

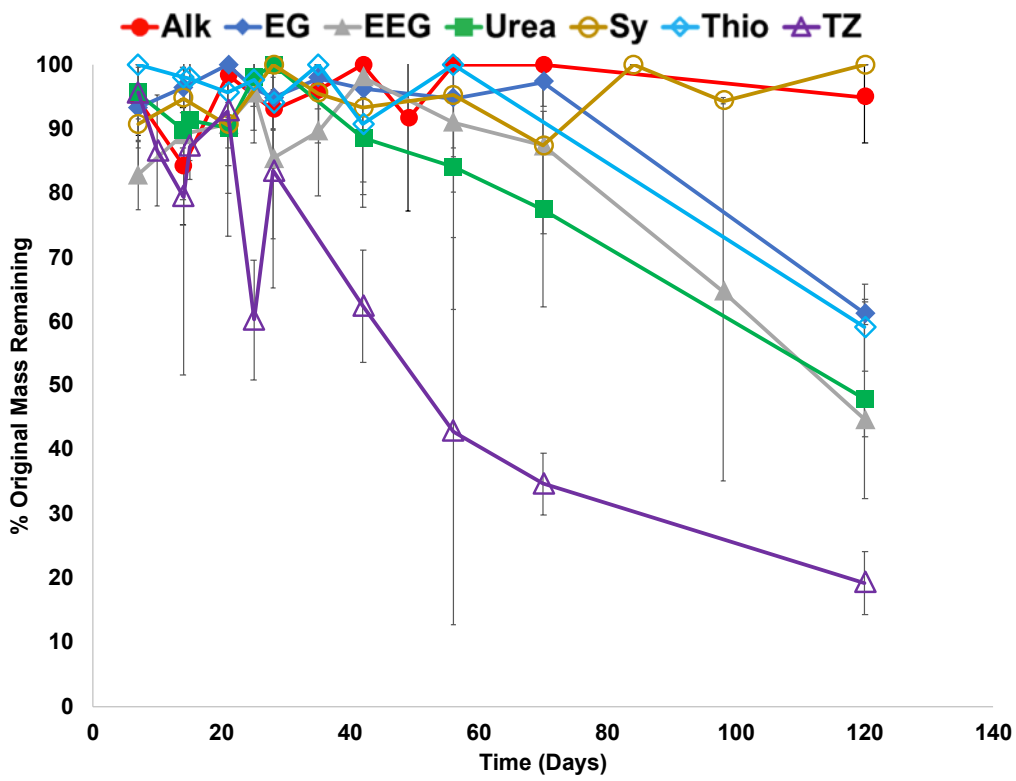


Figure S13. Film mass as a function of degradation time.

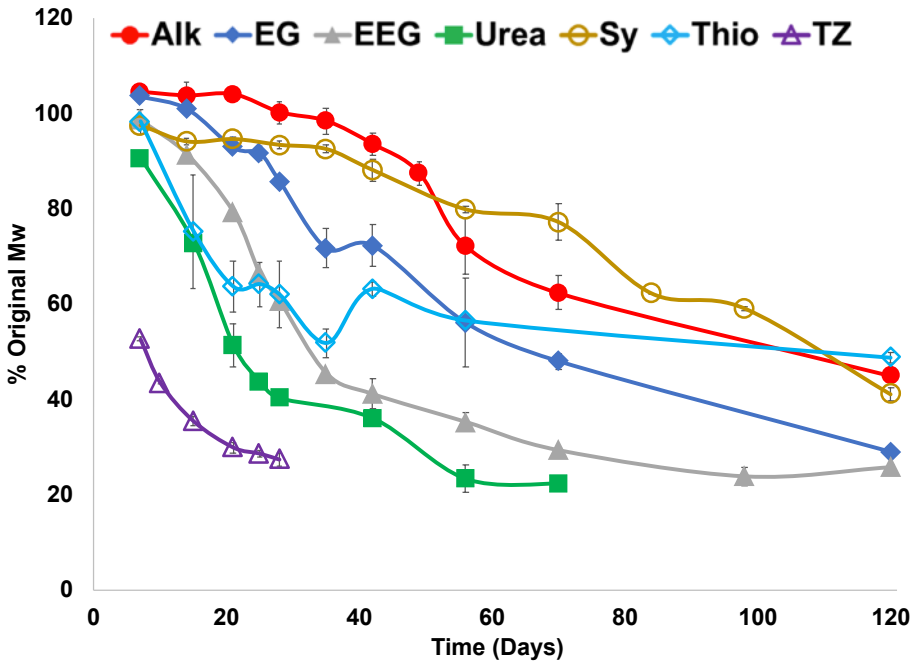


Figure S14. Molecular weight (M_W) as a function of degradation time.

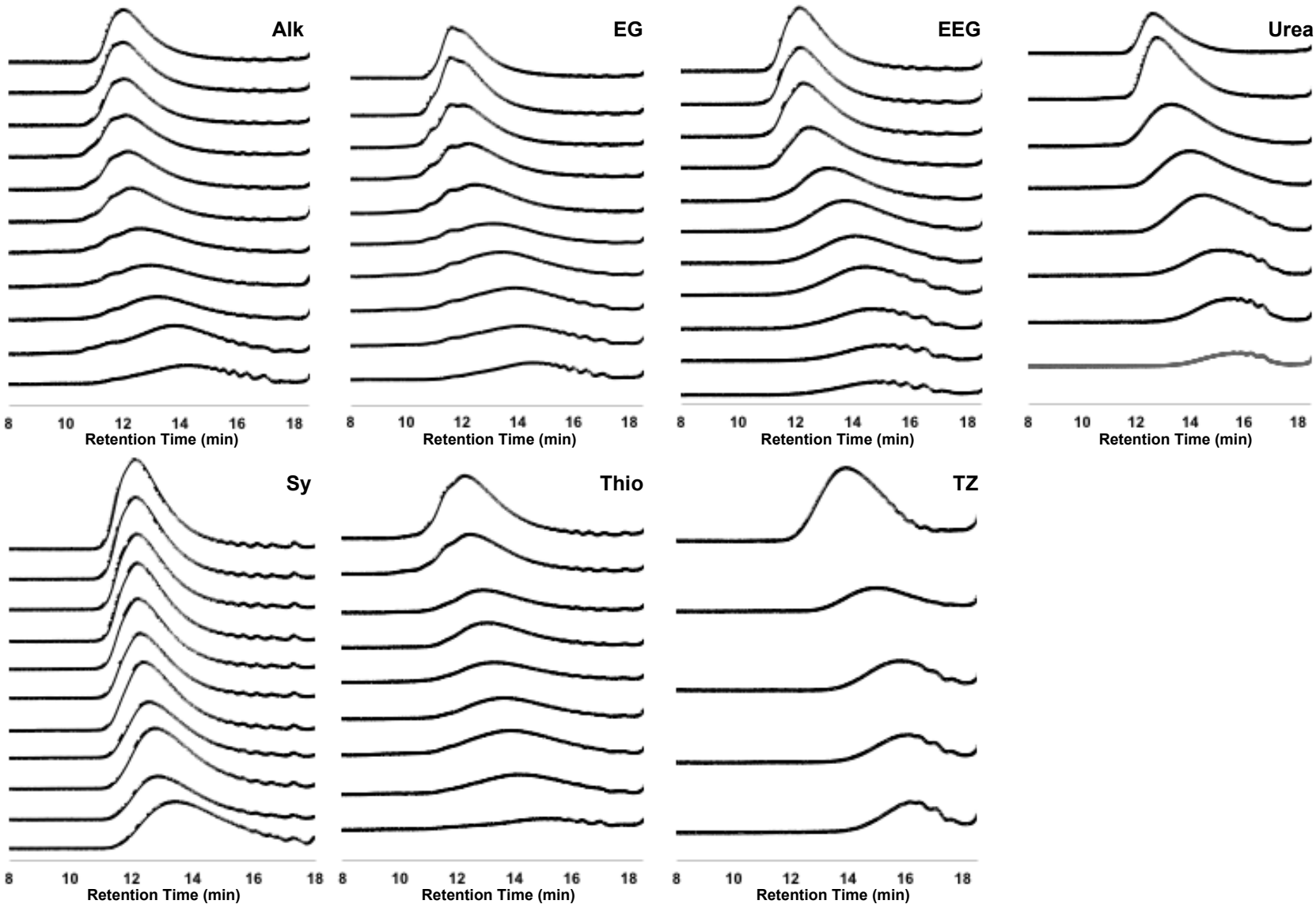


Figure S15. SEC traces of polymers at week 0 (top) and at each consecutive timepoint during degradation.

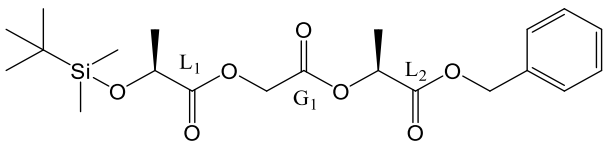
2.0 EXPERIMENTAL AND NMR DATA

2.1 MATERIALS

All chemicals were purchased from Sigma-Aldrich, Inc. and used without purification unless specified otherwise. Ethyl acetate, methylene chloride and tetrahydrofuran (Fisher Scientific, Inc.) were flowed through an aluminum oxide column. Column chromatography was done using Sorbent Tech. 60 Å, 40-63 µm standard grade silica. Dicyclohexylcarbodiimide (DCC) was purchased from Oakwood Products, Inc. 1,4-Dimethylpyidinium *p*-toluenesulfonate (DPTS) was prepared using a previously reported method.[7] Synthetic procedures were adapted from several previous references.[8-10]

2.2 STARTING MATERIALS

Bn-LGL-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.09	s	3	Si (CH_3)
0.11	s	3	Si (CH_3)
0.91	s	9	Si (t-Bu)
1.46	d (6.8)	3	L_1 (CH_3)
1.51	d (7.1)	3	L_2 (CH_3)
4.44	q (6.8)	1	L_1 (CH)
4.66	d (16)	1	G_1
4.80	d (16)	1	G_1
5.18	m	2	Bn (CH_2)
5.23	q (7.1)	1	L_2 (CH)
7.35	m	5	Bn (Aromatic)

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

δ (ppm)	Assignment
-5.20	Si
-4.81	Si
16.99	L (CH_3)
18.42	L (CH_3)
21.49	Si (C)
25.83	Si (t-Bu)
60.62	G (CH_2)
67.34	Bn (CH_2)
68.20	L (CH)
69.47	L (CH)
128.31	Bn (CH)
128.61	Bn (CH)
128.76	Bn (CH)
135.27	Bn (CH
167.06	CO
170.04	CO
173.56	CO

HRMS (ESI)

Calc. Mass
424.19 amu

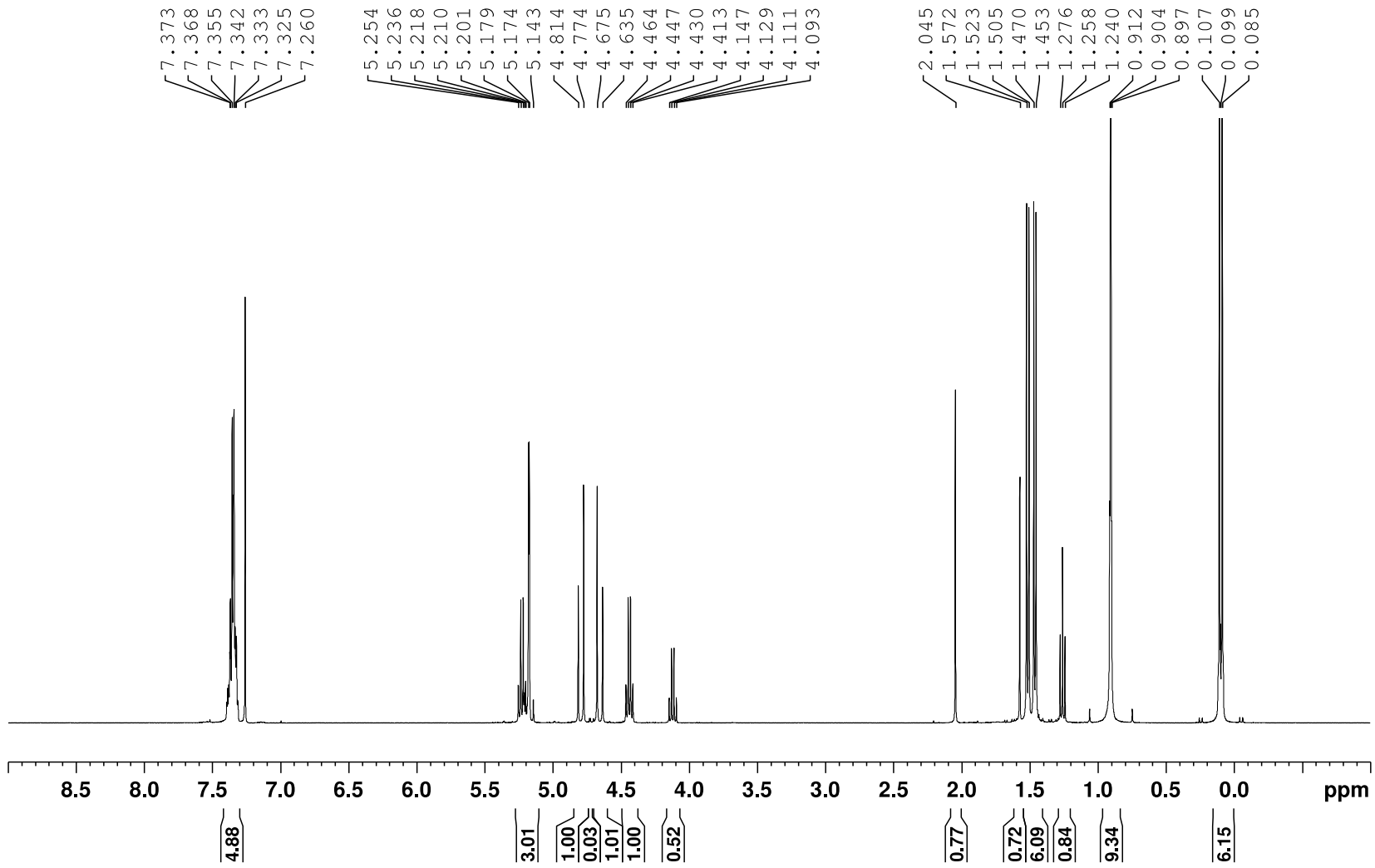
Calc.
$[M + H]^+$
425.19 amu

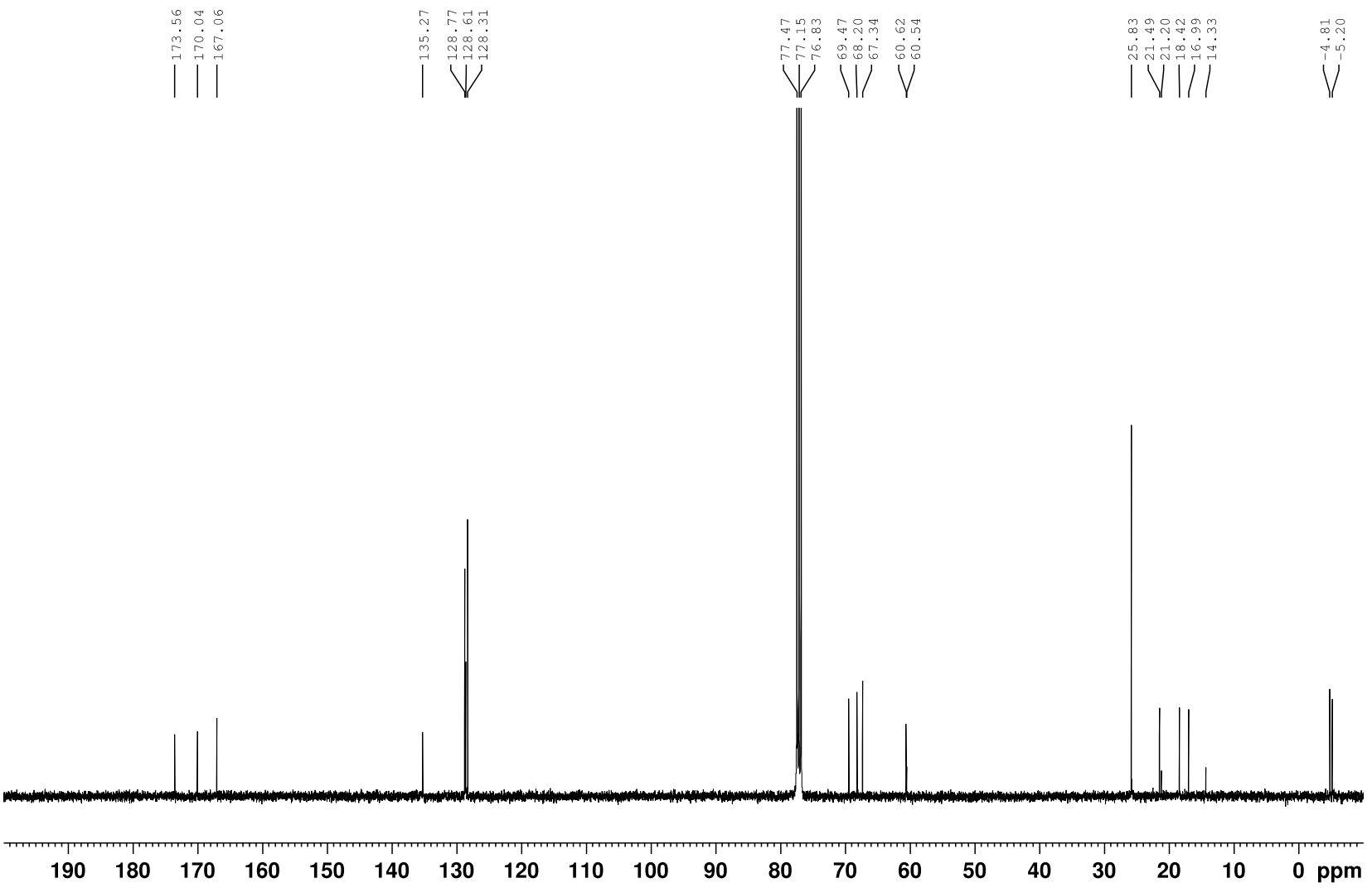
Found
$[M + H]^+$
425.20069 amu

Composition
$C_{21}H_{32}O_7Si$

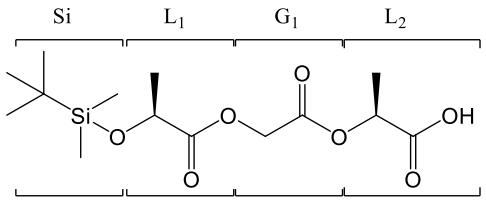
Bn-LG (4.17 g, 17.5 mmol, 1 eq) and **L-Si** (3.8 g, 18.4 mmol, 1.05 eq) were dissolved in dry DCM and added to a flame dried 100 mL Schlenk flask under nitrogen. DPTS (1.03 g, 3.5 mmol, 0.2 eq) and DCC (4.0 g, 19.3 mmol, 1.1 eq) were added to the reaction mixture sequentially and allowed to stir at RT overnight. The reaction mixture was diluted with hexanes, filtered to remove DCU, concentrated, and the crude oil was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (5.27 g, 71% yield).

JHS-3006; Bn-LGL-Si; CDCl3; 1H; 400a; 16 Scans;
9/13/16





LGL-Si



^{1}H-NMR (400 MHz, $CDCl_3$)			
dδ (ppm)	Mult. (J)	Int.	Assignment
0.086	s	3	Si (CH_3)
0.11	s	3	Si (CH_3)
0.90	s	9	Si (t-Bu)
1.46	d (6.8)	3	L_1 (CH_3)
1.56	d (7.1)	3	L_2 (CH_3)
4.44	q (6.8)	1	L_1 (CH)
4.66	d (16)	1	G_1
4.81	d (16)	1	G_1
5.22	q (7.1)	1	L_2 (CH)

^{13}C-NMR (400 MHz, $CDCl_3$)	
δ (ppm)	+ Assignment
-5.23	Si
-4.86	Si
16.99	L (CH_3)
18.39	L (CH_3)
21.45	Si (C)
25.79	Si (t-Bu)
60.55	G (CH_2)
68.17	L (CH)
68.89	L (CH)
167.02	CO
173.63	CO
175.34	CO

HRMS (ESI)

Calc. Mass
334.14 amu

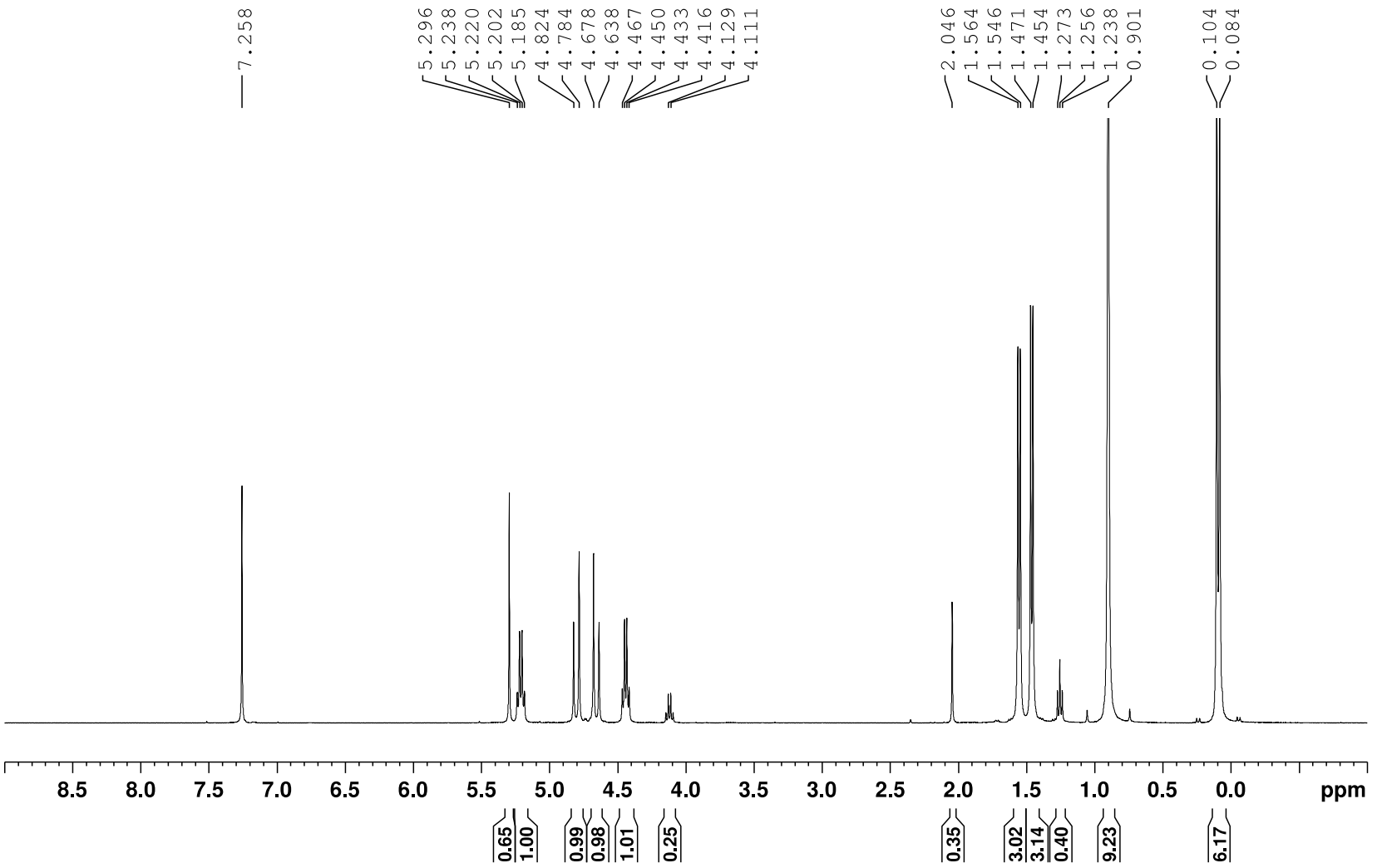
Calc.
$[M + H]^+$
335.14 amu

Found
$[M + H]^+$
335.15421 amu

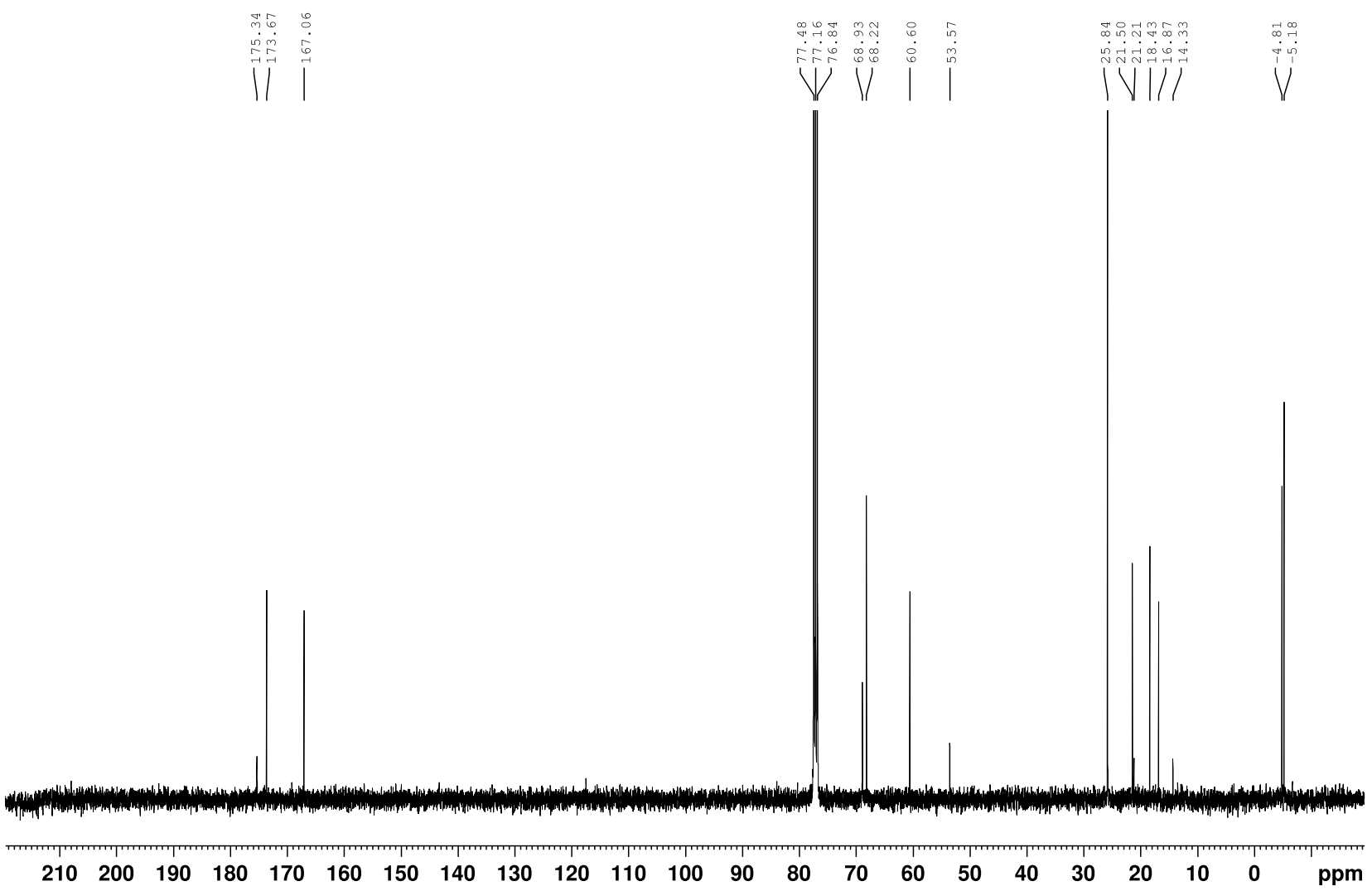
Composition
$C_{14}H_{26}O_7Si$

Bn-LGL-Si (4.20 g, 9.9 mmol) and Pd/C (0.42 g, 10 wt%) were dissolved in EtOAc (100 mL, 0.1 M) in a flame dried Schlenk flask and allowed to stir overnight at RT under 1 atm H_2. Upon consumption of starting material by TLC, the reaction mixture was filtered over celite and concentrated *in vacuo* to yield a colorless oil (3.31 g, 99% yield).

JHS-3031; LGL-Si; CDCl3; 1H; 400a; 16 Scans;
11/12/16

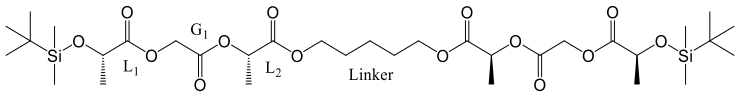


JHS-3031; LGL-Si; CDCl3; 13C; 400a; 2048 Scans;
11/12/16



2.3 ALKYL LINKER CONTAINING COMPOUNDS

Si-LGL-Alk-LGL-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.09	s	6	CH_3 (Si)
0.11	s	6	CH_3 (Si)
0.90	s	18	t-Bu (Si)
1.46	m	8	CH_2 (Linker), CH_3 (L_1)
1.50	d (7.0)	6	L_2 (CH_3)
1.68	m	4	Linker (CH_2)
4.14	m	4	Linker (CH_2)
4.42	q (7.0)	2	L_1 (CH)
4.66	d (16)	2	G_1
4.79	d (16)	2	G_1
5.16	q (7.1)	2	L_2 (CH)

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

δ (ppm)	Assignment
-5.35	CH_3 (Si)
-5.32	CH_3 (Si)
16.86	CH_3 (L)
18.24	C (Si)
20.98	CH_3 (L)
21.33	CH_2 (Linker)
25.67	t-Bu (Si)
28.00	CH_2 (Linker)
60.32	CH_2 (G_1)
65.17	CH (L)
68.03	CH (L)
69.33	CH_2 (Linker)
166.87	CO
170.02	CO
173.32	CO

HRMS (ESI)

Calc. Mass
736.35 amu

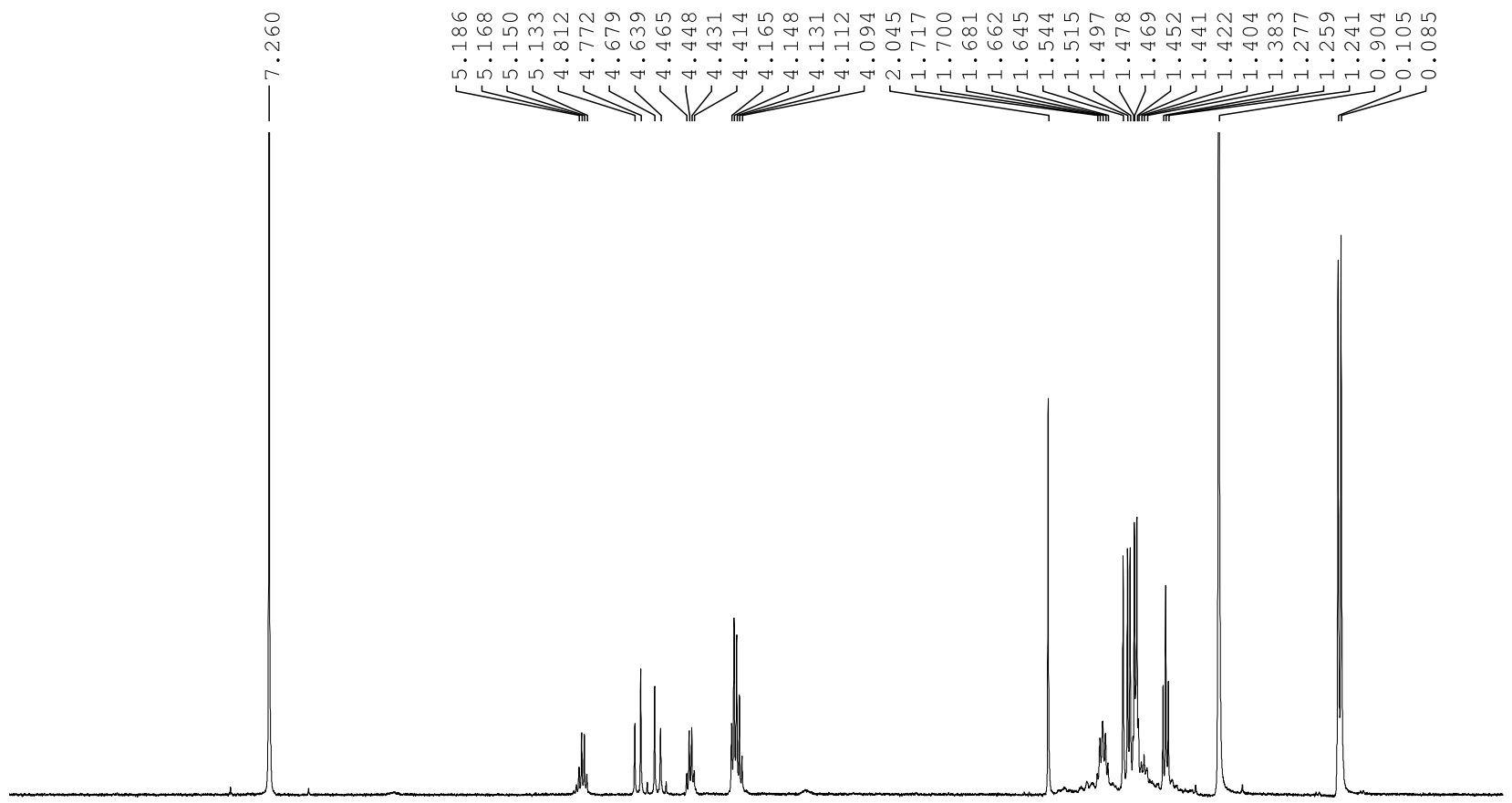
Calc.
$[M + H]^+$
737.35 amu

Found
$[M + H]^+$
737.36003 amu

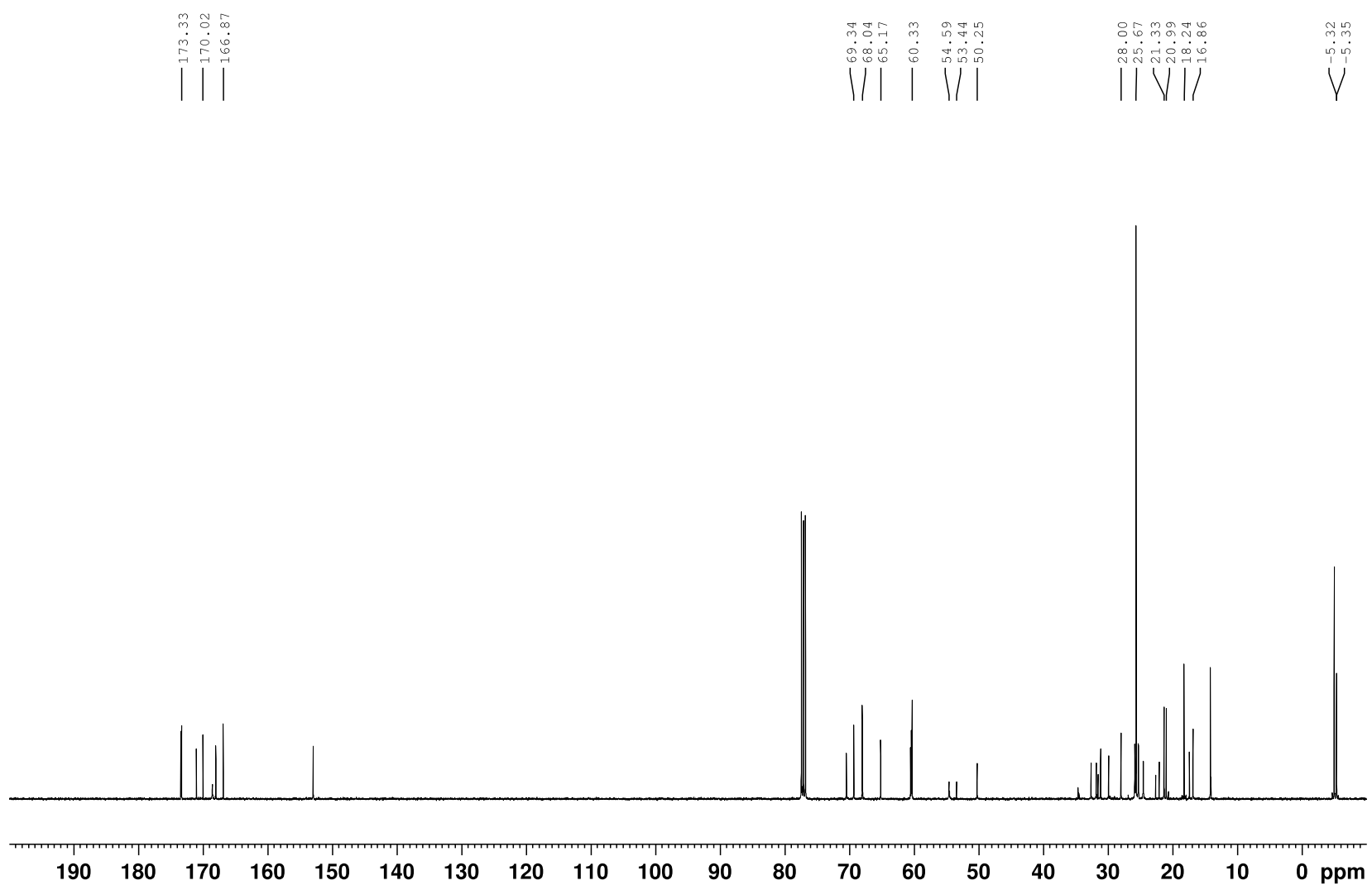
Composition
$C_{33}H_{60}O_{14}Si_2$

Pentamethylene glycol was dried over sieves for two h. **LGL-Si** (1.00 g, 2.99 mmol, 2.3 eq) and dry pentamethylene glycol (0.135 g, 1.30 mmol, 1 eq) were dissolved in dry DCM (8 mL, 0.4 M) in a flame dried 100 mL Schlenk flask under nitrogen. DPTS (0.17 g, 0.59 mmol, 0.45 eq) and DCC (0.62 g, 3.0 mmol, 2.3 eq) were added and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes, filtered to remove DCU, concentrated, and crude oil was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (5.27 g, 71% yield).

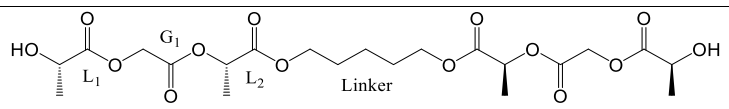
33-39; Si-LGL-Alk-LGL-Si; CDCl3; 1H; 400a; 16 Sca



JHS-2043-Mixture; Si-LGL-Alk-LGL-Si; CDCl3; 13C; 400a;
1024 Scans; 10/24/17



LGL-Alk-LGL



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.41	m	2	Linker (CH_2)
1.50	d (7.0)	6	L_2 (CH_3)
1.52	d (7.1)	6	L_1 (CH_3)
1.68	m	4	Linker (CH_2)
2.85	m	2	L_1 (OH)
4.17	t (3.8)	4	Linker (CH_2)
4.42	m	2	L_2 (CH)
4.74	d (16)	2	G_1
4.84	d (16)	2	G_1
5.16	q (7.08)	2	L_1 (CH)

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

δ (ppm)	Assignment
16.92	CH_3 (L)
20.38	CH_3 (L)
22.16	CH_2 (Linker)
28.05	CH_2 (Linker)
60.93	CH_2 (G_1)
65.39	CH (L)
66.80	CH (L)
69.65	CH_2 (Linker)
166.76	CO
170.11	CO
174.98	CO

HRMS (ESI)

Calc. Mass
508.18 amu

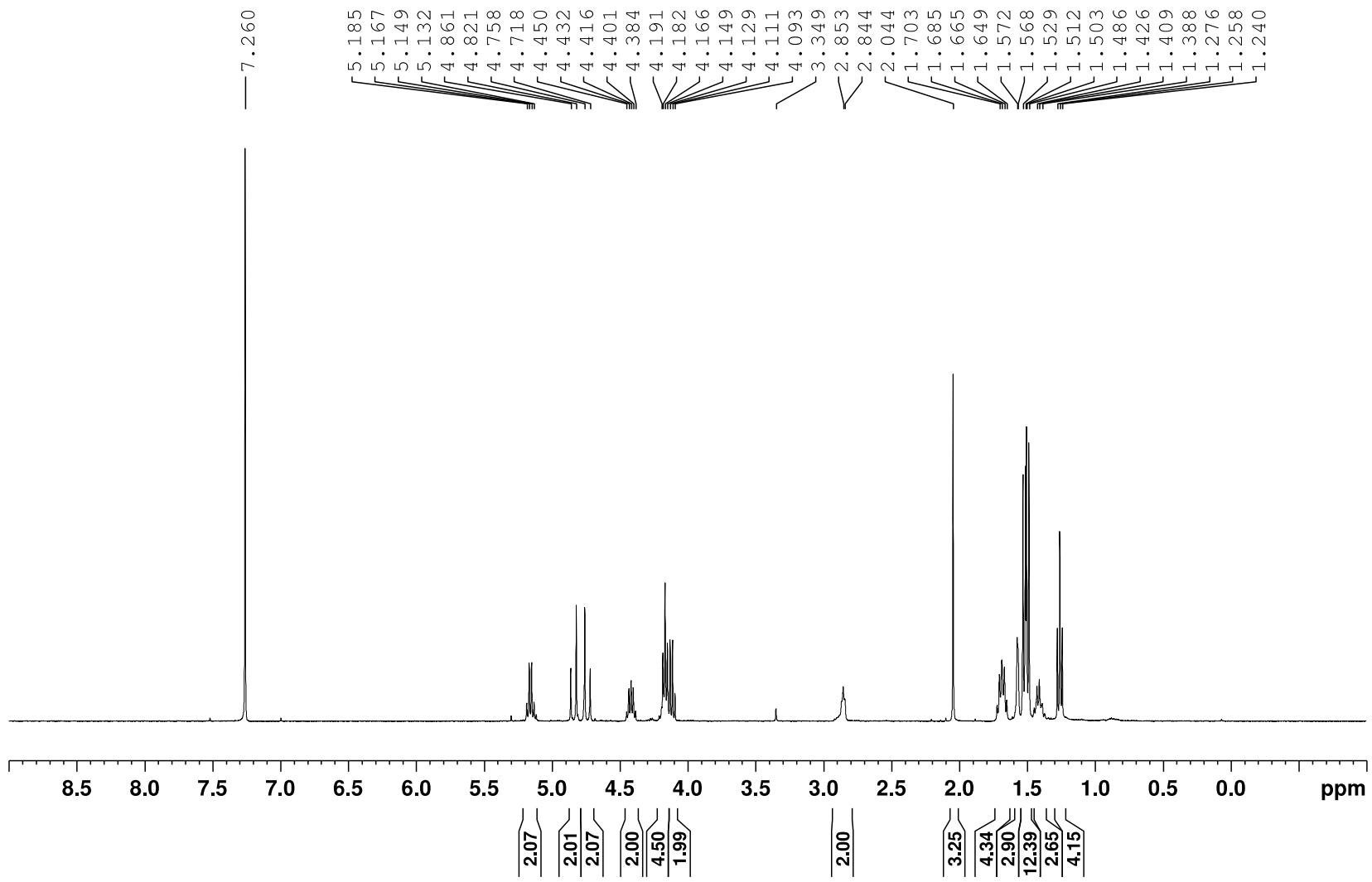
Calc.
$[M + H]^+$
509.18 amu

Found
$[M + H]^+$
509.18637 amu

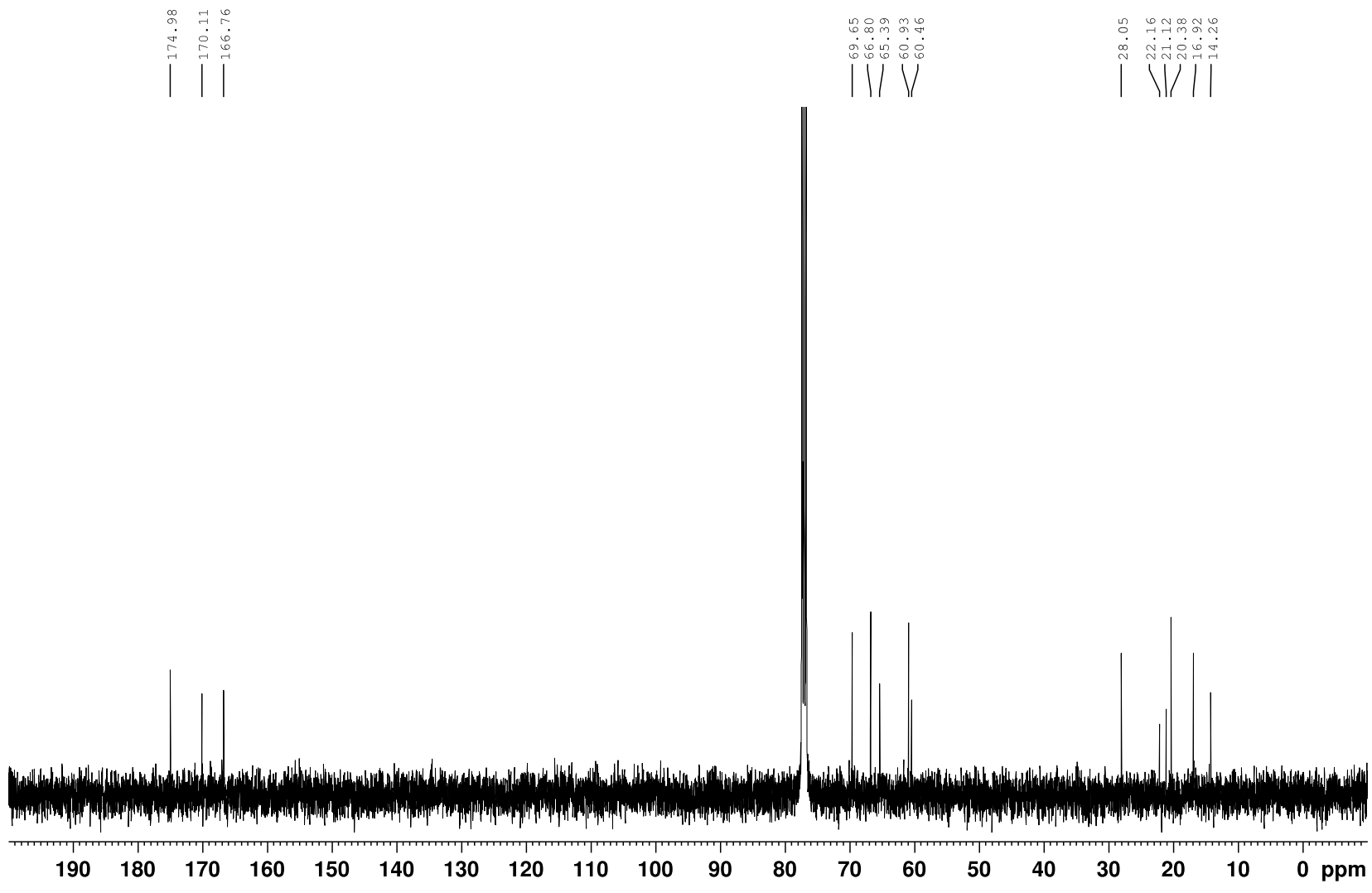
Composition
$C_{21}H_{32}O_{14}$

AcOH (0.48 mL, 8.32 mmol, 16 eq) and TBAF (1 M in THF) (1.6 mL, 1.6 mmol, 3 eq) were dried over activated sieves for 2 h. **Si-LGL-Alk-LGL-Si** (0.386 g, 0.52 mmol, 1 eq) was dissolved in dry THF (13 mL, 0.04 M) in a flame dried Schlenk flask under nitrogen. AcOH and TBAF were added dropwise at 0°C, allowed to warm to RT and stir for 24 h. An additional equivalent of TBAF was added and allowed to stir for 2 more h. The reaction mixture was then diluted with brine and extracted with EtOAc 3x, the combined organic layers were washed with brine 3x, dried over $MgSO_4$ and concentrated. The crude oil was then purified via column chromatography (silica, EtOAc/hexanes) to yield a white solid (155 mg, 58% yield).

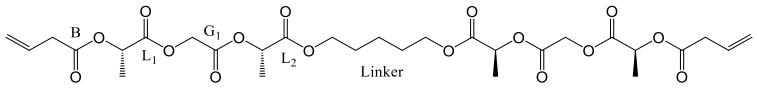
:074; LGL-Alk-LGL; CDCl3; 1H; 400a; 16 Scans; 8/1



JHS-2074; LGL-Alk-LGL; CDCl3; 13C; 400a; 2048 Scans; 8/10/16



BLGL-Alk-LGLB



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.41	m	2	Linker (CH_2)
1.51	d (7.0)	6	L_2 (CH_3)
1.57	d (7.1)	6	L_1 (CH_3)
1.68	m	4	Linker (CH_2)
3.18	m	4	B (CH_2)
4.15	t (3.8)	4	Linker (CH_2)
4.63	d (16)	2	G_1
4.87	d (16)	2	G_1
5.18	m	8	L_1 (CH), L_2 (CH), B (CH_2)
5.93	m	2	B (CH)

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

δ (ppm)	+ Assignment
16.92	CH_3 (L)
16.96	CH_3 (L)
25.03	CH_2 (Linker)
28.11	CH_2 (Linker)
38.68	CH_2 (B)
60.83	CH_2 (G_1)
65.34	CH (L)
68.53	CH (L)
69.56	CH_2 (Linker)
119.09	CH_2 (B)
129.71	CH (B)
166.72	CO
170.13	CO
170.23	CO
170.98	CO

HRMS (ESI)

Calc. Mass
644.23 amu

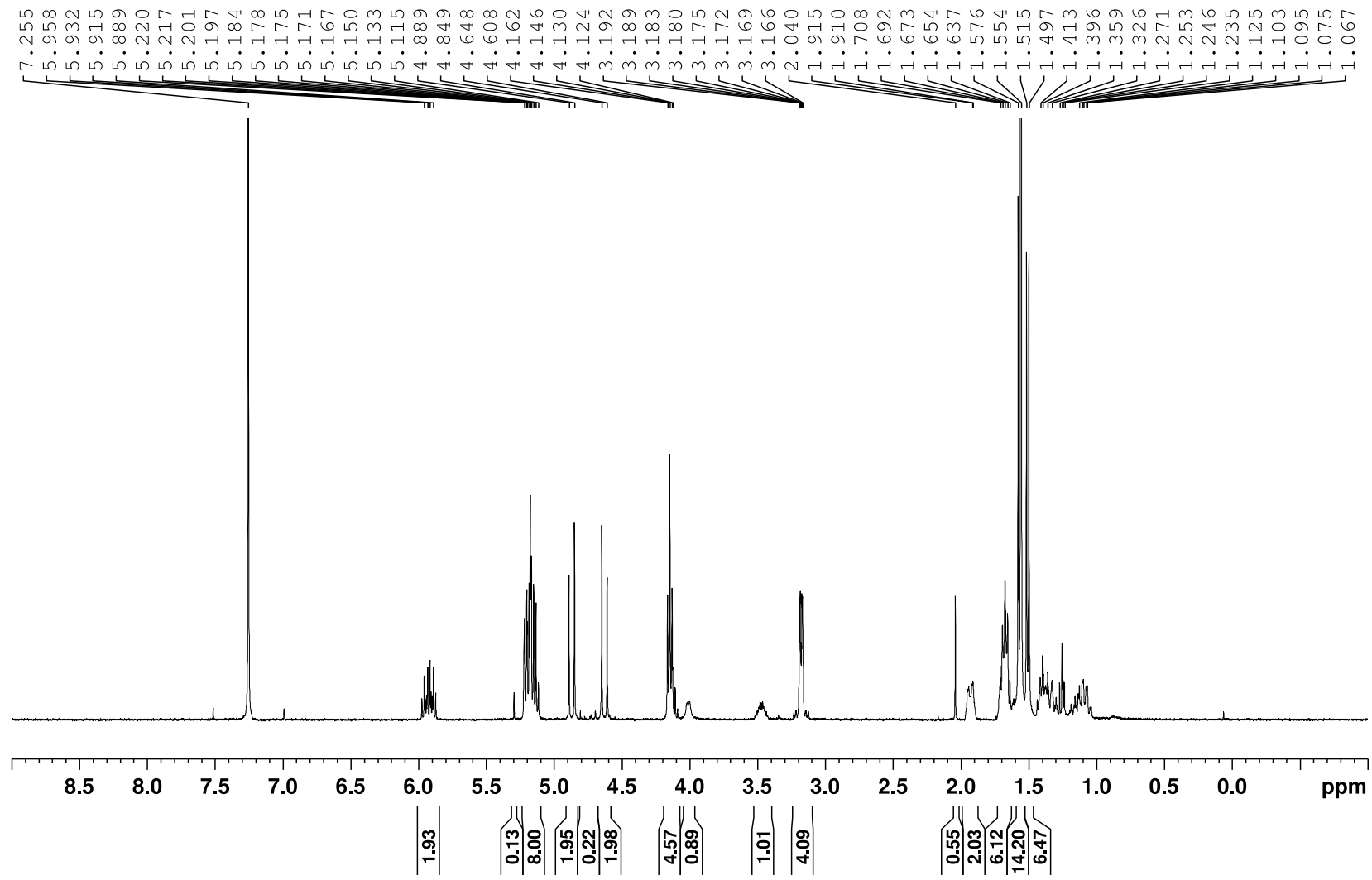
Calc.
$[M + H]^+$
645.23 amu

Found
$[M + H]^+$
645.23982 amu

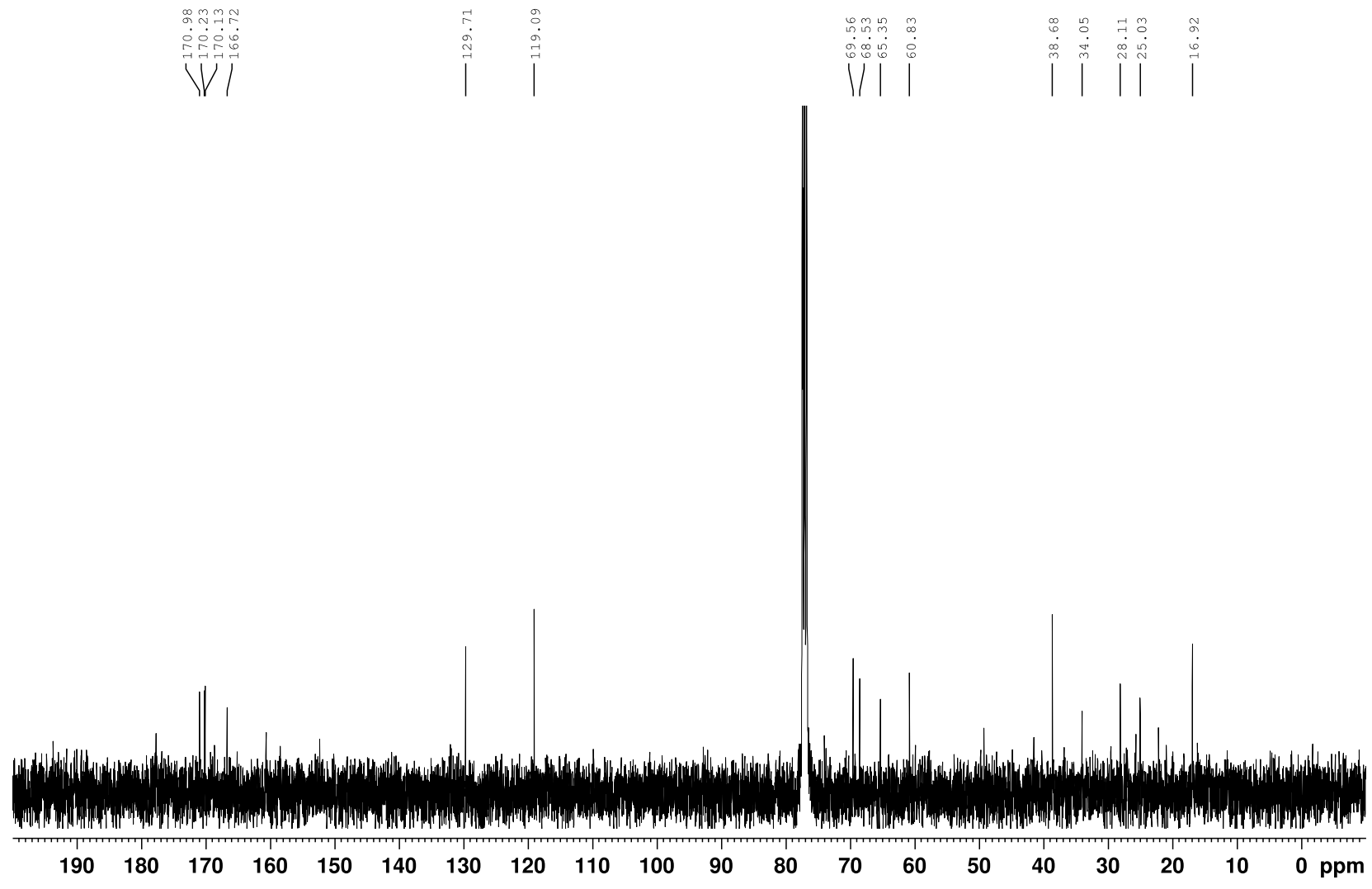
Composition
$C_{29}H_{40}O_{16}$

LGL-Alk-LGL (150 mg, 0.30 mmol, 1 eq) was dissolved in dry DCM (3 mL, 0.05 M) in an oven dried 20 mL vial under nitrogen. DPTS (39 mg, 0.13 mmol, 0.45 eq) and DCC (0.184 g, 0.89 mmol, 3 eq) were added sequentially. Butenoic acid (77 mg, 0.89 mmol, 3 eq) was then added dropwise and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes, washed with sodium bicarbonate 3x, dried over $MgSO_4$, filtered to remove DCU and drying agent, concentrated, and crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a thick brown oil (120 mg, 63% yield).

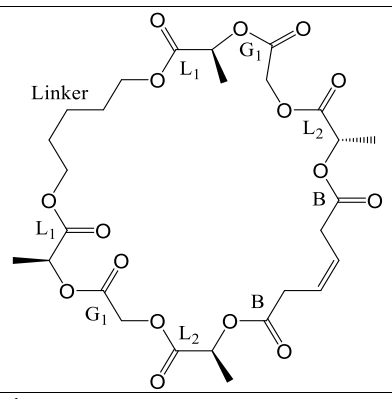
JHS-2076; BLGL-Alk-LGLB; CDCl3; 1H; 400a;
16 Scans; 8/16/16



JHS-2076; BLGL-Alk-LGLB; CDCl3; 13C; 400a;
2048 Scans; 8/16/16



Cyclic Alkyl Monomer



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.42	quin. (31.2)	2	Linker (CH_2)
1.50	d (7.2)	6	L_1 (CH_3)
1.54	d (7.2)	6	L_2 (CH_3)
1.68	quin. (28)	4	Linker (CH_2 β-L_1)
3.17	m	4	B (CH_2)
4.17	m	4	Linker (CH_2 α-L_1)
4.67	d (16)	2	G_1
4.80	d (16)	2	G_1
5.14	q (20.8)	2	L_1 (CH)
5.20	q (21.2)	2	L_2 (CH)
5.79	m	2	B (CH)

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

δ (ppm)	+ Assignment
16.82	CH_3 (L)
16.85	CH_3 (L)
22.31	CH_2 (Linker)
28.06	CH_2 (Linker)
37.49	CH_2 (Linker)
60.80	CH (L)
65.32	CH (L)
68.49	CH_2 (G)
69.45	CH_2 (B)
125.78	CH (B)
166.53	CO
169.93	CO
170.11	CO
170.68	CO

HRMS (ESI)

Calc. Mass
616.20 amu

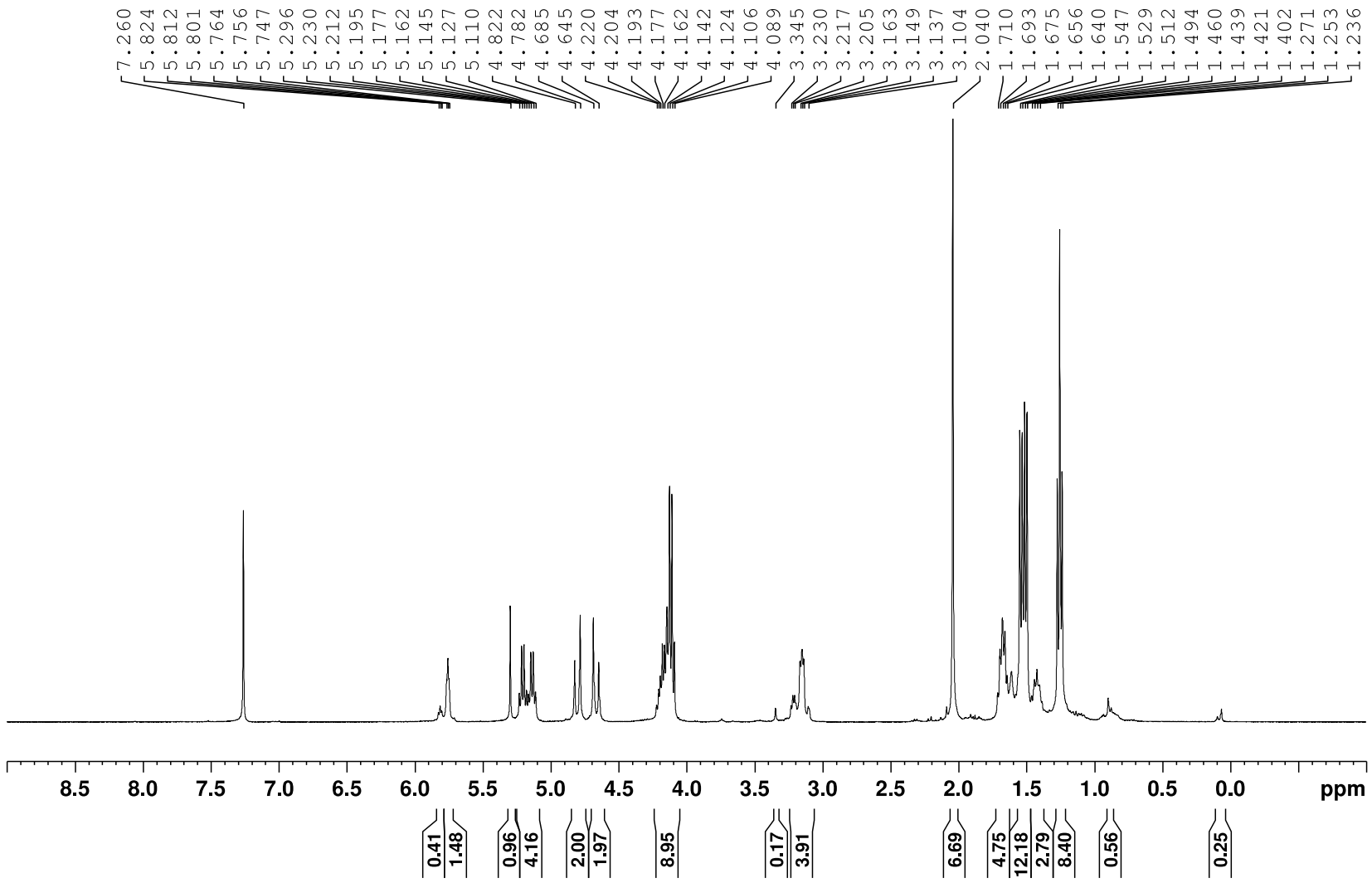
Calc.
$[M + H]^+$
617.20 amu

Found
$[M + H]^+$
617.20615 amu

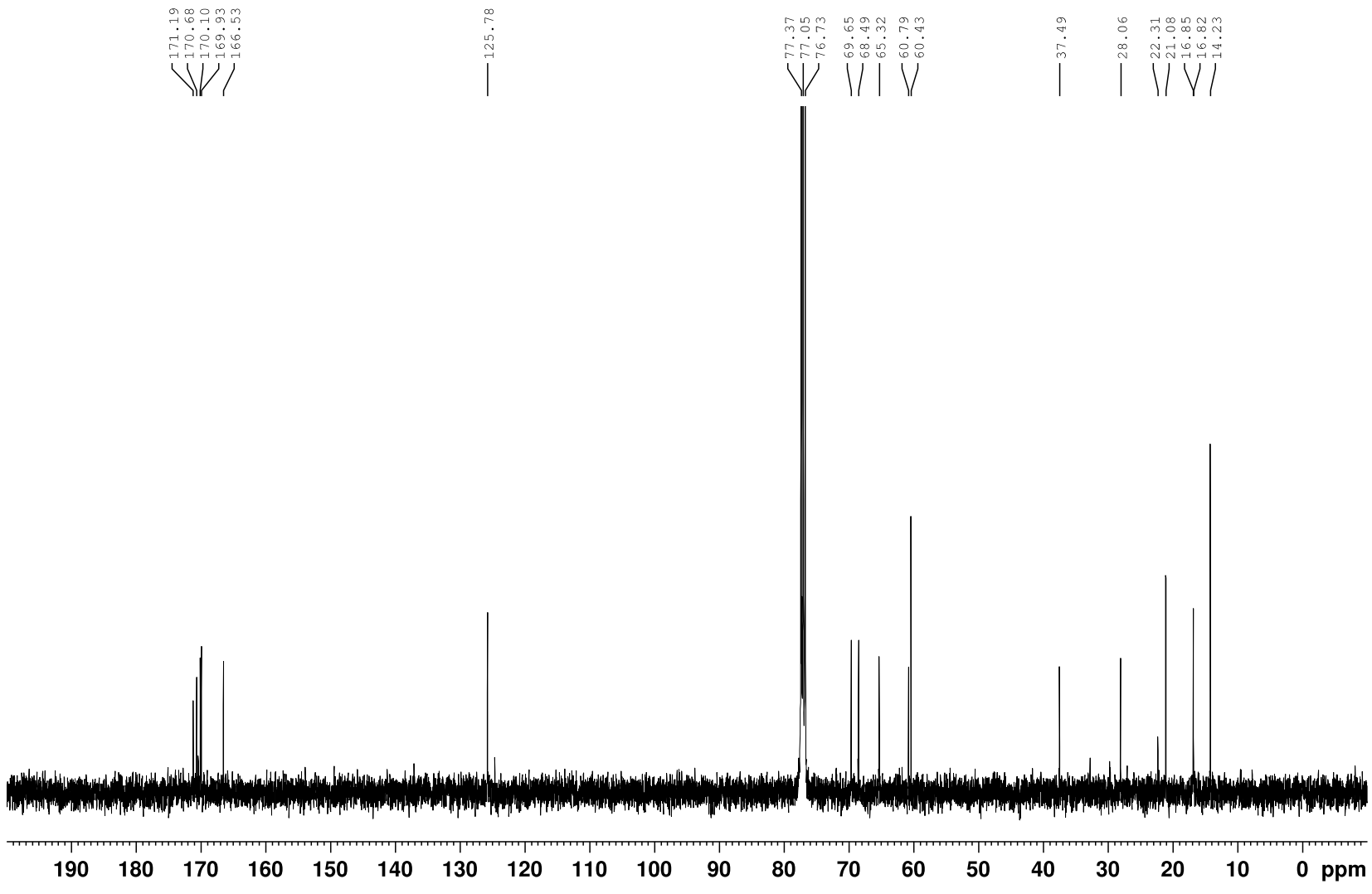
Composition
$C_{27}H_{36}O_{16}$

BLGL-Alk-LGLB (640 mg, 0.92 mmol, 1 eq) was dissolved in dry DCM (185 mL, 0.001M) in a flame-dried Schlenk flask under nitrogen. A stock solution of Grubbs 2 (16 mg, 0.019 mmol, 10 mol%) in dry DCM was added and allowed to stir at RT overnight. Upon consumption of starting material by TLC, reaction mixture was quenched by addition of excess ethyl vinyl ether and stirring for 10 additional min. The reaction mixture was then concentrated and the crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a thick brown oil (112 mg, 96% yield).

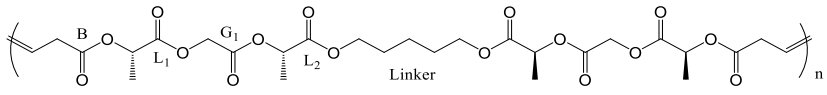
-Pure; LGLBLGL-AlkCyc; CDCl3; 1H; 400a; 16 Scans;



JHS-2061-Pure; LGLBLGL-AlkCyc; CDCl3; 13C; 400a; 1024 Scans; 7/27/16



Poly(Alk)



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.40	m	2	Linker (CH_2)
1.51	d (7.0)	6	L_2 (CH_3)
1.57	d (7.1)	6	L_1 (CH_3)
1.68	m	4	Linker (CH_2)
3.19	m	4	B (CH_2)
4.15	t (6.6)	4	Linker (CH_2)
4.63	d (16)	2	G_1
4.87	d (16)	2	G_1
5.16	m	4	L_1 (CH), L_2 (CH)
5.72	m	1.6	B (CH) Trans
5.81	m	0.4	B (CH) Cis

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

δ (ppm)	+ Assignment
16.92	CH_3 (L)
16.95	CH_3 (L)
22.21	CH_2 (Linker)
28.13	CH_2 (Linker)
37.39	CH_2 (Linker)
60.83	CH_2 (G_1)
65.33	CH_2 (B)
68.59	CH (L)
69.55	CH (L)
124.39	CH (B Cis)
125.82	CH (B Trans)
166.70	CO
170.09	CO
170.17	CO
170.87	CO

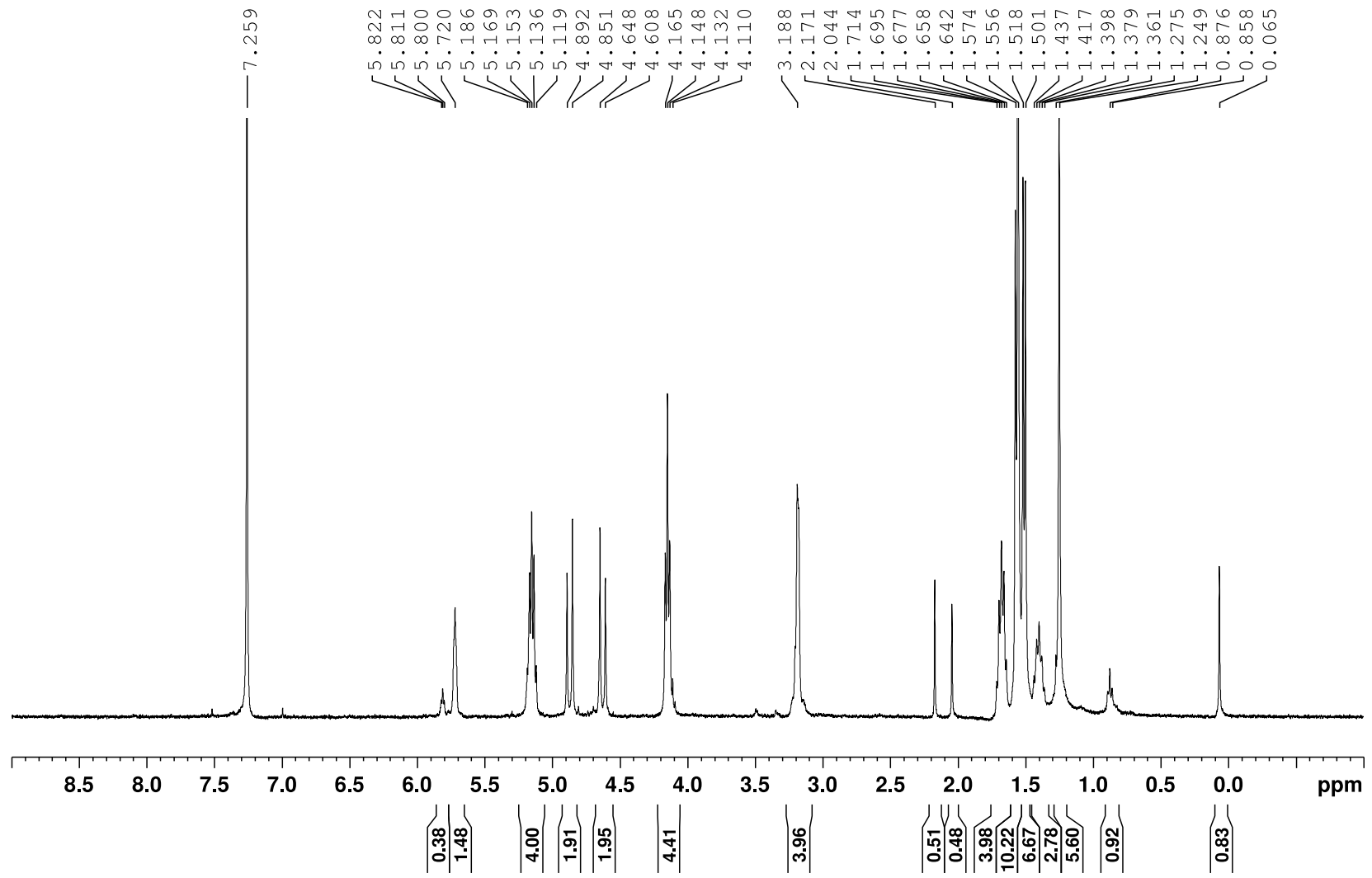
GPC

M_n
26,868

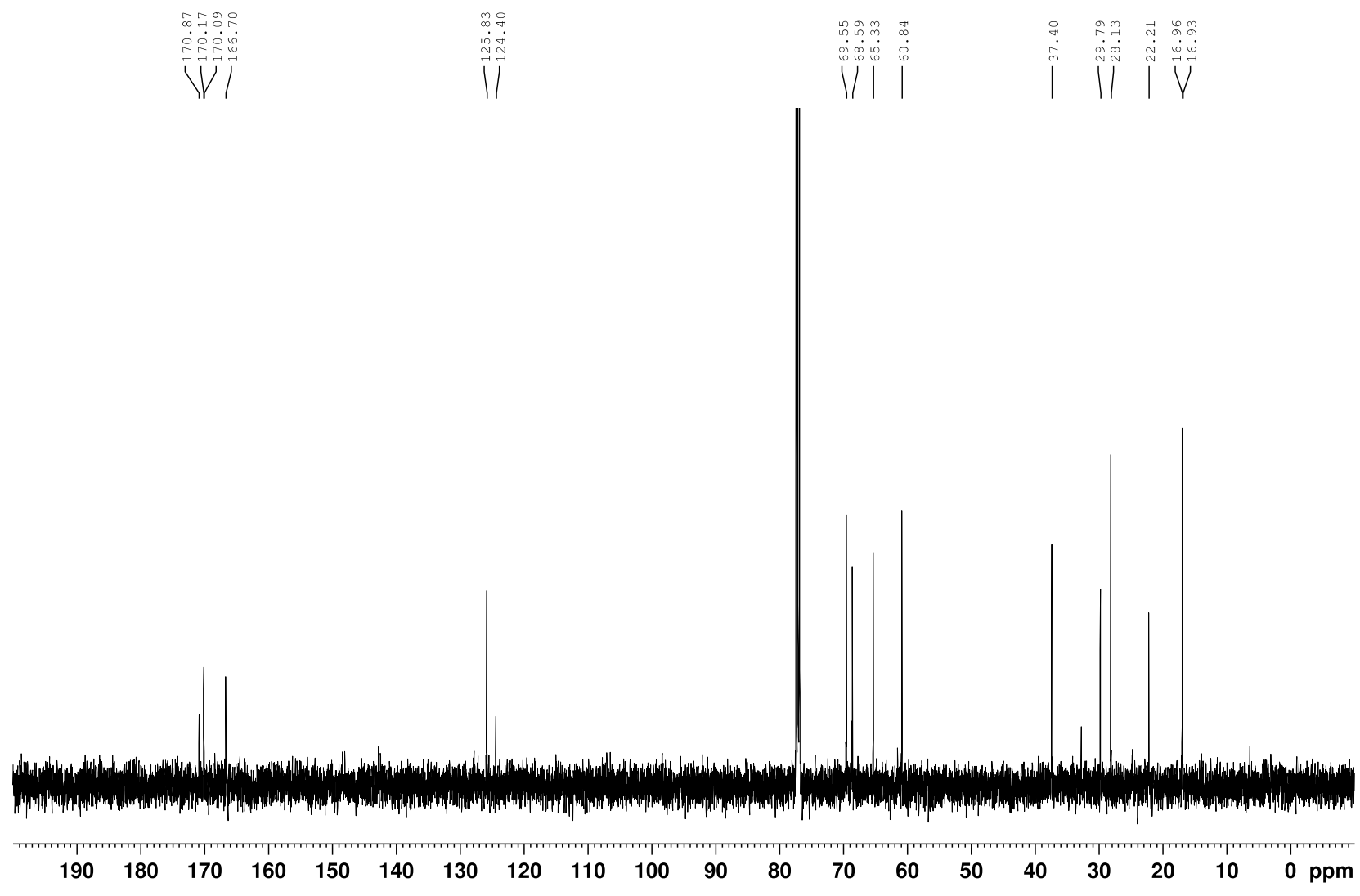
Đ
1.40

Cyclic Alkyl Monomer (73 mg, 0.118 mmol, 1 eq.) was weighed in a flame dried 1 mL vial under nitrogen. A stock solution of Grubbs II (1 mg, 0.0012 mmol, 1 mol%) in dry DCM (5.8 mg/mL, 0.17 mL, 0.7M) was added to the vial, and the vial was shaken for four hours. The reaction mixture was quenched by the addition of excess ethyl vinyl ether and vortexing. Solution was concentrated to yield a crude solid polymer which was reprecipitated into a stirring solution of MeOH, and filtered to collect pure polymer as a brown solid (50 mg, 70% yield).

JHS-3041-Pure; Poly(Alk; CDCl3; 1H; 400a;
16 Scans; 2/23/17

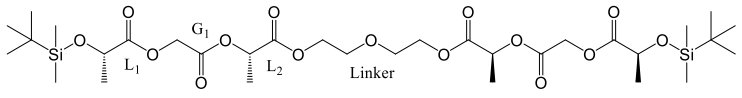


JHS-3041-500; Poly(Alk); CDCl3; 13C; 500;
128 Scans; 10/27/17



2.4 EG LINKER CONTATINING COMPOUNDS

Si-LGL-EG-LGL-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.10	s	6	CH_3 (Si)
0.12	s	6	CH_3 (Si)
0.92	s	18	t-Bu (Si)
1.47	d (6.8)	6	CH_3 (L_1)
1.54	d (7.1)	6	L_2 (CH_3)
3.71	t (4.7)	4	Linker (CH_2)
4.31	m	4	Linker (CH_2)
4.46	q (6.8)	2	L_1 (CH)
4.68	d (16)	2	G_1
4.81	d (16)	2	G_1
5.20	q (7.1)	2	L_2 (CH)

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

δ (ppm)	+ Assignment
-5.40	CH_3 (Si)
-5.02	CH_3 (Si)
16.74	CH_3 (L)
18.17	C (Si)
21.26	CH_3 (L)
25.62	t-Bu (Si)
60.36	CH_2 (G_1)
64.26	CH (L)
67.94	CH_2 (Linker)
68.64	CH (L)
69.23	CH_2 (Linker)
166.81	CO
169.85	CO
173.23	CO

HRMS (ESI)

Calc. Mass
738.33 amu

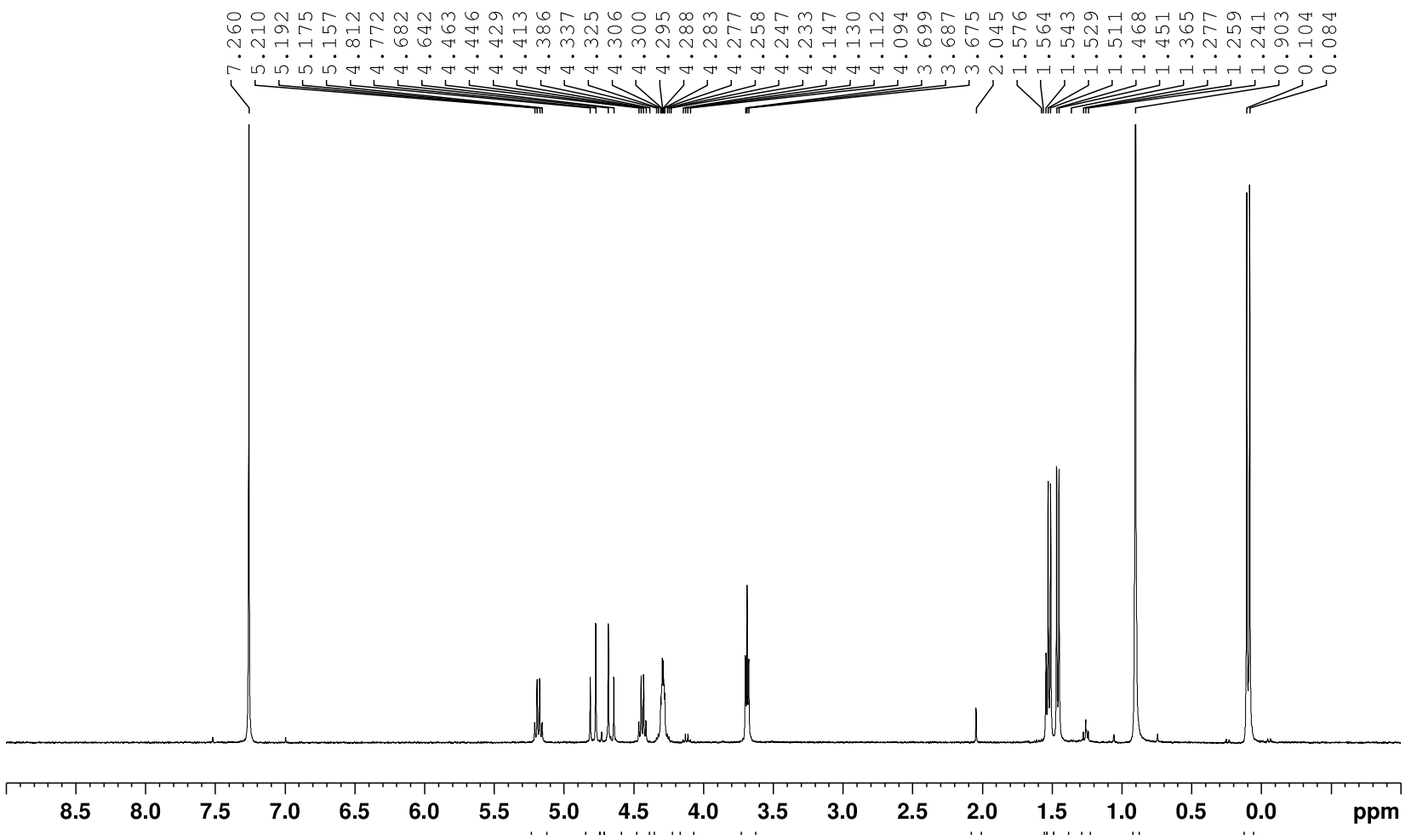
Calc.
$[M + H]^+$
739.33 amu

Found
$[M + H]^+$
739.33935 amu

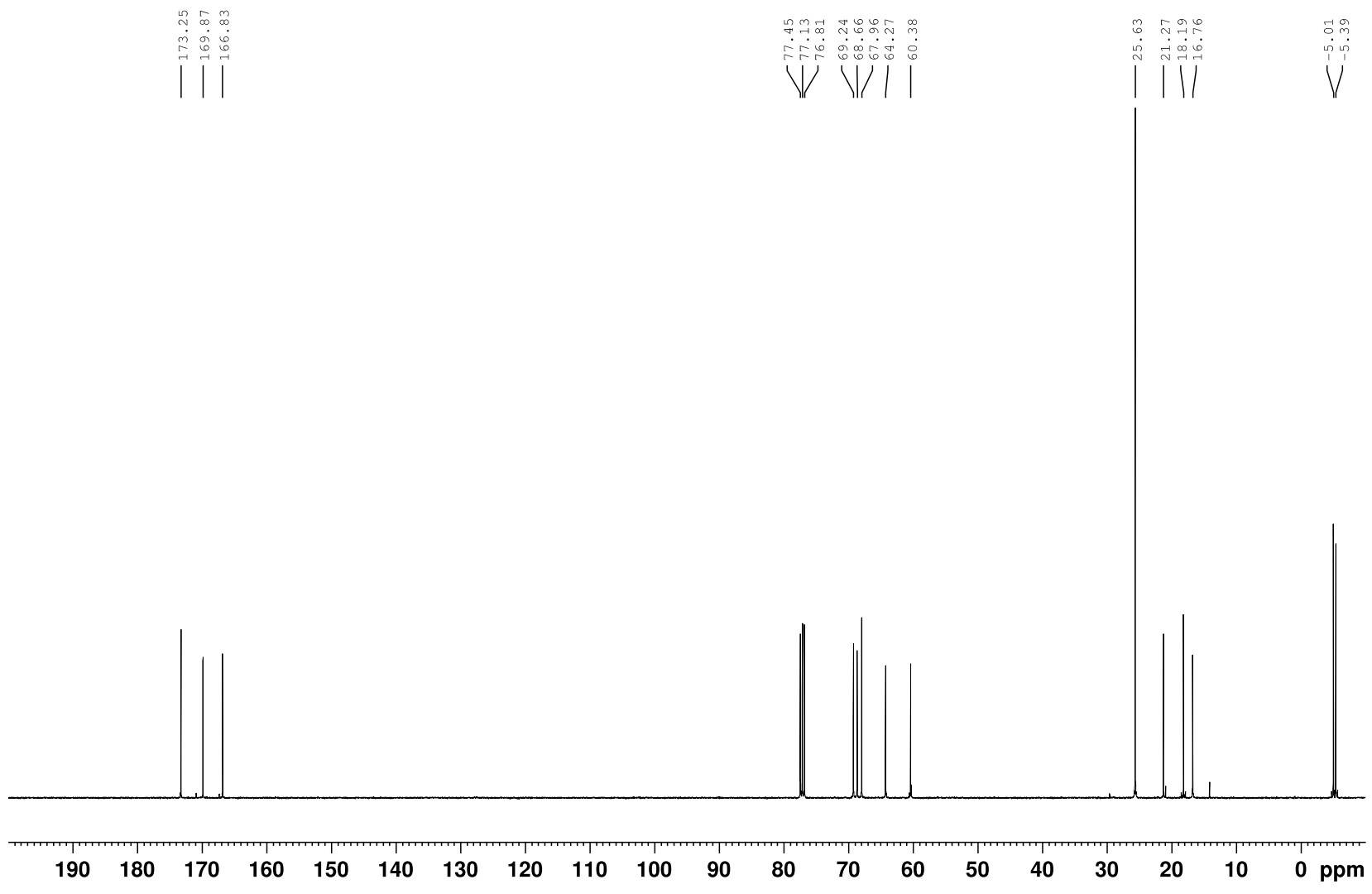
Composition
$C_{32}H_{58}O_{15}Si_2$

Diethylene glycol was dried over sieves for two h. **LGL-Si** (1.1 g, 3.3 mmol, 2.3 eq) was dissolved in dry DCM (10 mL, 0.4 M), and added to a flame-dried vial under nitrogen. Dry diethylene glycol (0.151 g, 1.43 mmol, 1 eq), DPTS (0.19 g, 0.65 mmol, 0.45 eq) and DCC (0.68 g, 3.3 mmol, 2.3 eq) were then added to the reaction mixture sequentially and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes and filtered to remove DCU, concentrated and crude oil was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (0.755 g, 71% yield).

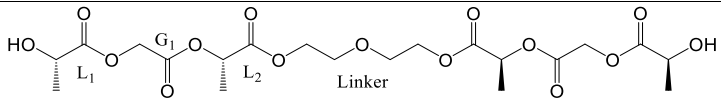
pot3; Si-LGL-EG-LGL-Si; CDCl3; 1H; 400a; 16 Scan



JHS-2055; Si-LGL-EG-LGL-Si; CDCl3; 13C; 400a;
1024 Scans; 10/24/17



LGL-EG-LGL



^{1}H-NMR (300 MHz, $CDCl_3$)

dδ (ppm)	Mult. (J)	Int.	Assignment
1.49	d (7.0)	6	L_1 (CH_3)
1.53	d (7.0)	6	L_2 (CH_3)
2.86	d (5.6)	2	L_1 (OH)
3.69	t (5.0)	4	Linker (CH_2)
4.31	t (5.0)	4	Linker (CH_2)
4.41	m	2	L_1 (CH)
4.74	d (16)	2	G_1
4.84	d (16)	2	G_1
5.19	q (7.0)	2	L_2 (CH)

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

δ (ppm)	+ Assignment
16.93	CH_3 (L)
20.49	CH_3 (L)
60.98	CH_2 (Linker)
64.55	CH_2 (Linker)
66.86	CH_2 (G_1)
68.82	CH (L)
69.64	CH (L)
166.86	CO
170.09	CO
175.02	CO

HRMS (ESI)

Calc. Mass
510.16 amu

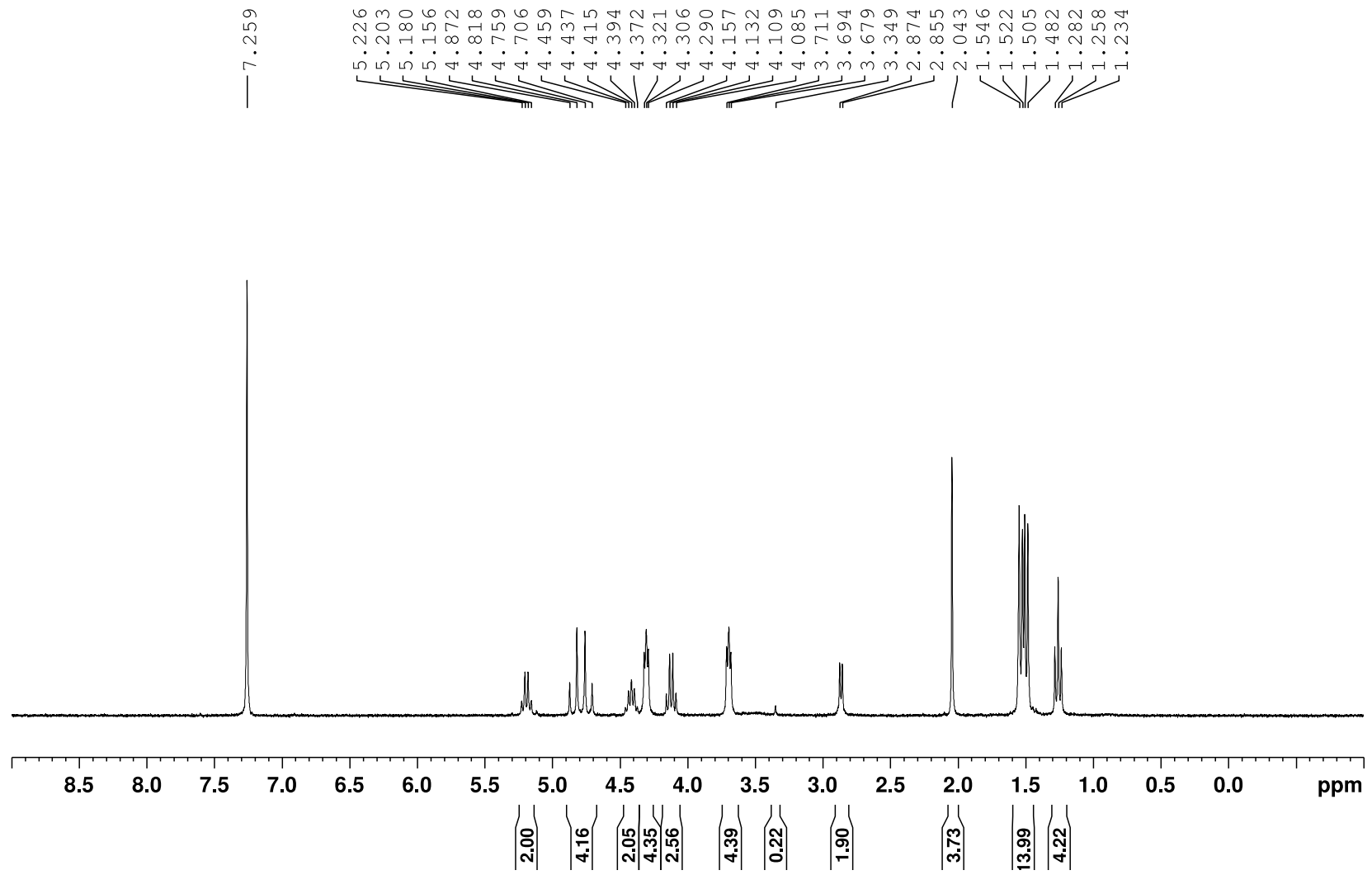
Calc.
$[M + H]^+$
511.16 amu

Found
$[M + H]^+$
amu

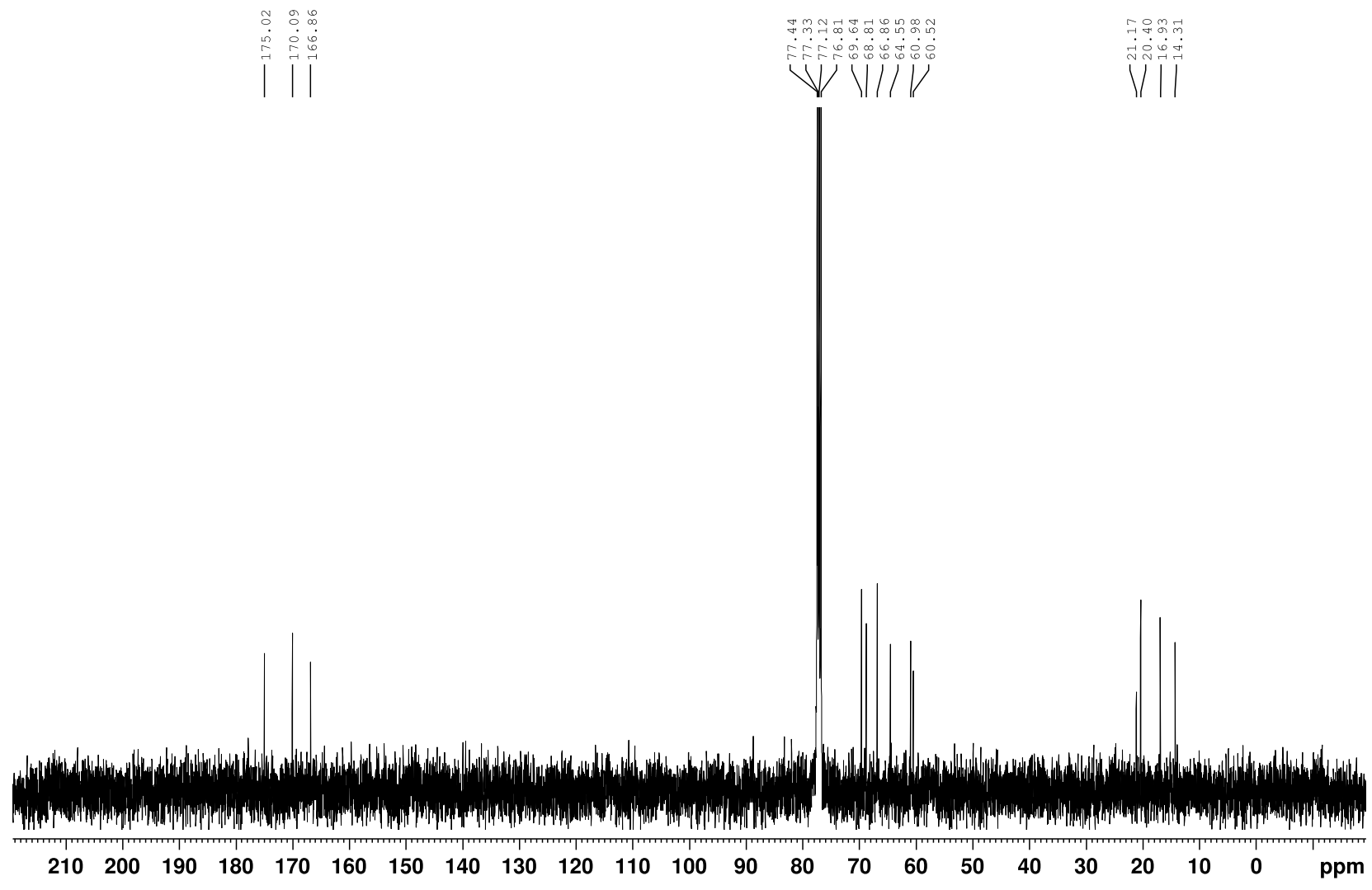
Composition
$C_{20}H_{30}O_{15}$

AcOH (0.62 mL, 10.8 mmol, 16 eq) and TBAF (1 M in THF) (2.03 mL, 2.03 mmol, 3 eq) were dried over activated sieves for 2 h. **Si-LGL-EG-LGL-Si** (0.498 g, 0.52 mmol, 1 eq) was dissolved in dry THF (17 mL, 0.04 M) in a flame dried Schlenk flask under nitrogen. AcOH and TBAF were added dropwise at 0°C, allowed to warm to RT and stir for 24 h. An additional equivalent of TBAF was added and allowed to stir for 2 more h. The reaction mixture was then diluted with brine and extracted with EtOAc 3x, the combined organic layers were washed with brine 3x, dried over $MgSO_4$ and concentrated. The crude oil was then purified via column chromatography (silica, EtOAc/hexanes) to yield a white solid (250 mg, 73% yield).

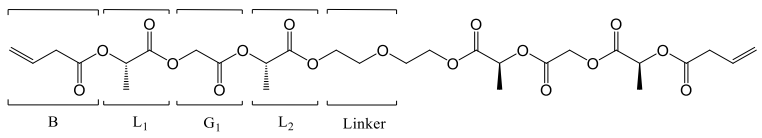
-2071; LGL-EG-LGL; CDCl3; 1H; 300; 16 Scans; 8/4



JHS-2071; LGL-EG-LGL; CDCl3; 13C; 400a; 1024 Scans; 8/8/16



BLGL-EG-LGLB



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.52	d (7.0)	6	L_2 (CH_3)
1.57	d (7.0)	6	L_1 (CH_3)
3.18	m	4	B (CH_2)
3.68	t (4.8)	4	Linker (CH_2)
4.29	m	4	Linker (CH_2)
4.63	d (16)	2	G_1
4.87	d (16)	2	G_1
5.18	m	8	L_1 (CH), L_2 (CH), B (CH_2)
5.93	m	2	B (CH)

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

δ (ppm) + Assignment	
14.35	CH_3 (L)
16.96	CH_3 (L)
38.73	CH_2
60.88	CH_2
64.50	CH_2
68.57	CH_2
68.89	CH (L)
69.56	CH (L)
119.13	CH_2 (B)
129.76	CH (B)
166.77	CO
170.09	CO
170.27	CO
171.01	CO

HRMS (ESI)

Calc. Mass
646.21 amu

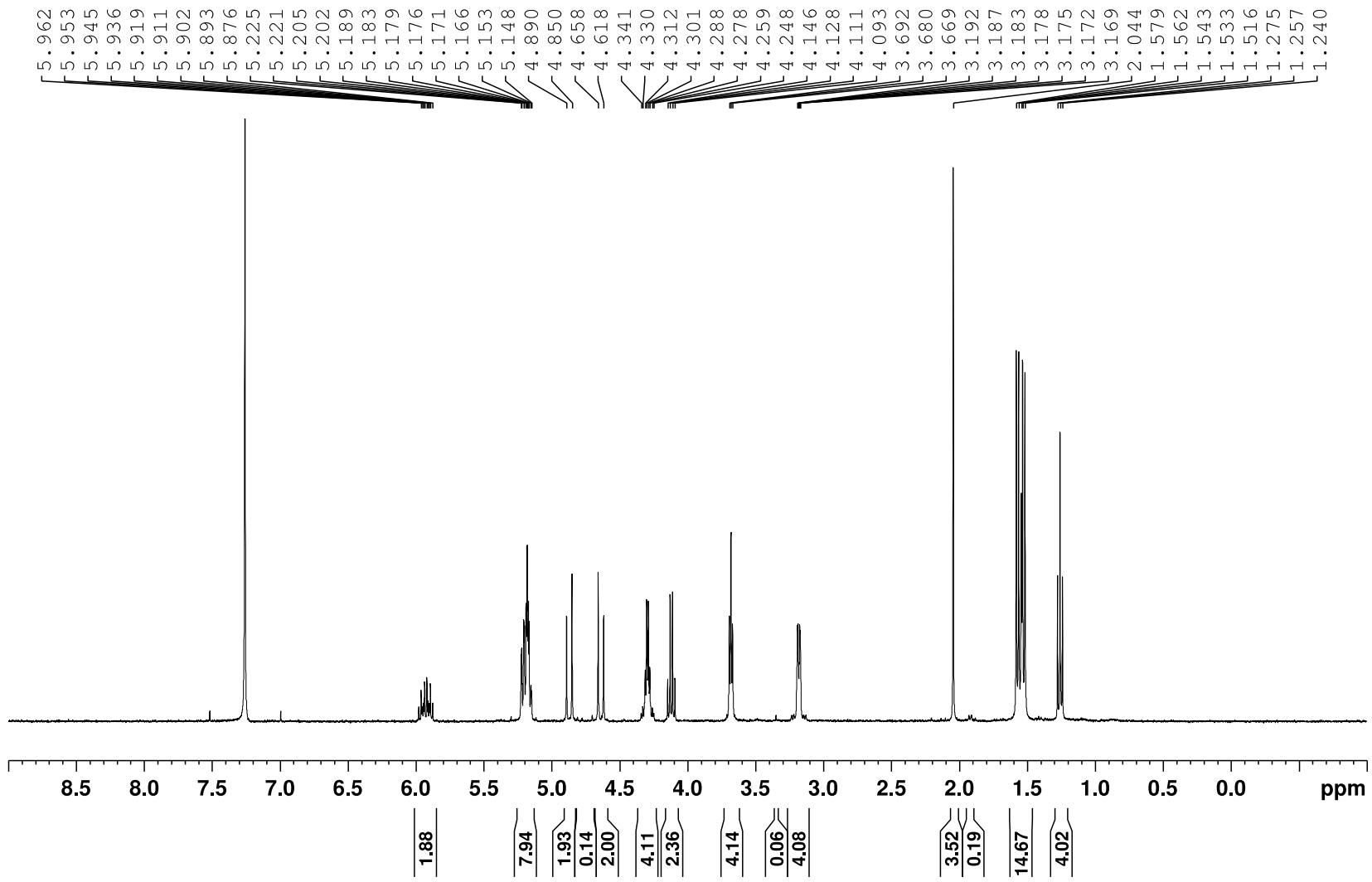
Calc.
$[M + H]^+$
647.21 amu

Found
$[M + H]^+$
647.21917 amu

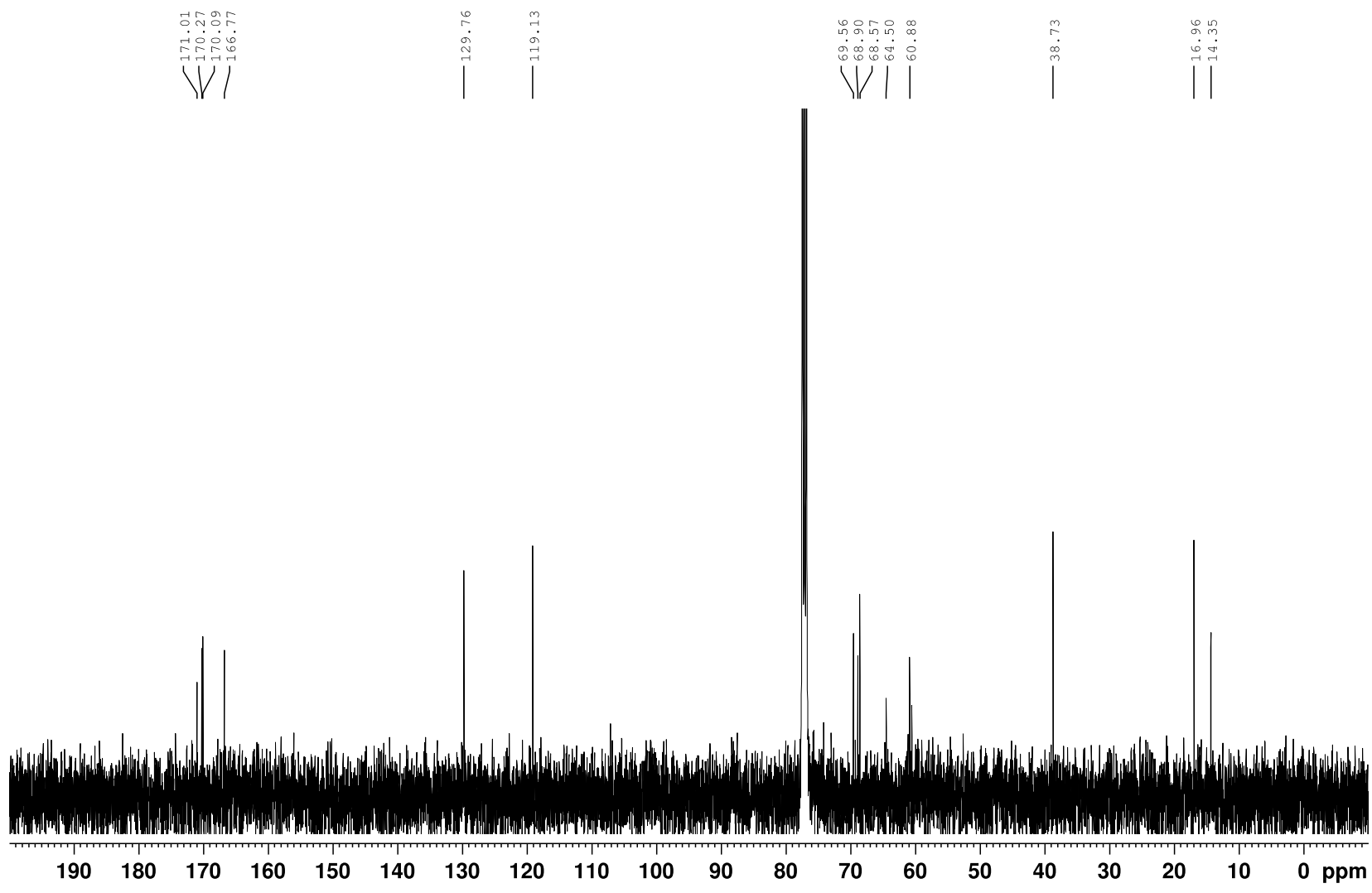
Composition
$C_{28}H_{38}O_{17}$

LGL-EG-LGL (246 mg, 0.52 mmol, 1 eq) was dissolved in dry DCM (10 mL, 0.05 M) in an oven dried 20 mL vial under nitrogen. DPTS (0.07 g, 0.23 mmol, 0.45 eq) and DCC (0.32 g, 1.55 mmol, 3 eq) were added sequentially. Butenoic acid (0.133 g, 1.55 mmol, 3 eq) was then added dropwise through and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes, washed with sodium bicarbonate 3x, dried over $MgSO_4$ and filtered to remove DCU and drying agent, concentrated, and crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (220 mg, 66% yield).

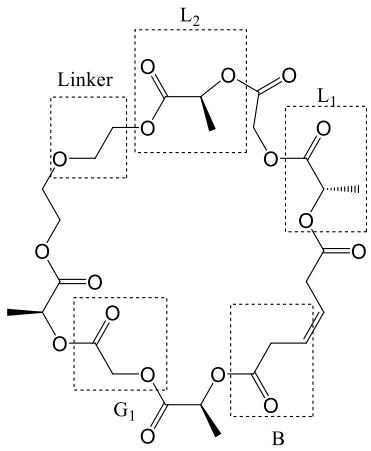
3-Spot2; BLGL-EG-LGLB; CDCl3; 1H; 400a; 16 Scans;



JHS-2073: BLGL-EG-LGLB; CDCl3; 13C; 400a; 2048 Scans; 8/10/16



Cyclic EG Monomer



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.52	d (7.0)	6	L_1 (CH_3)
1.54	d (7.0)	6	L_2 (CH_3)
3.17	m	4	B (CH_2)
3.69	m	4	Linker (CH_2)
4.30	m	4	Linker (CH_2)
4.67	d (16)	2	G_1
4.80	d (16)	2	G_1
5.19	m	2	L_1 (CH), L_2 (CH)
5.79	m	2	B (CH)

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

δ (ppm)	+ Assignment
14.33	CH_3 (L)
16.92	CH_3 (L)
37.59	CH_2 (B)
60.94	CH_2 (Linker)
64.66	CH_2 (Linker)
68.61	CH_2 (G)
68.88	CH (L)
69.65	CH (L)
125.85	CH (B)
166.68	CO
170.08	CO
170.14	CO
170.76	CO

HRMS (ESI)

Calc. Mass
618.18 amu

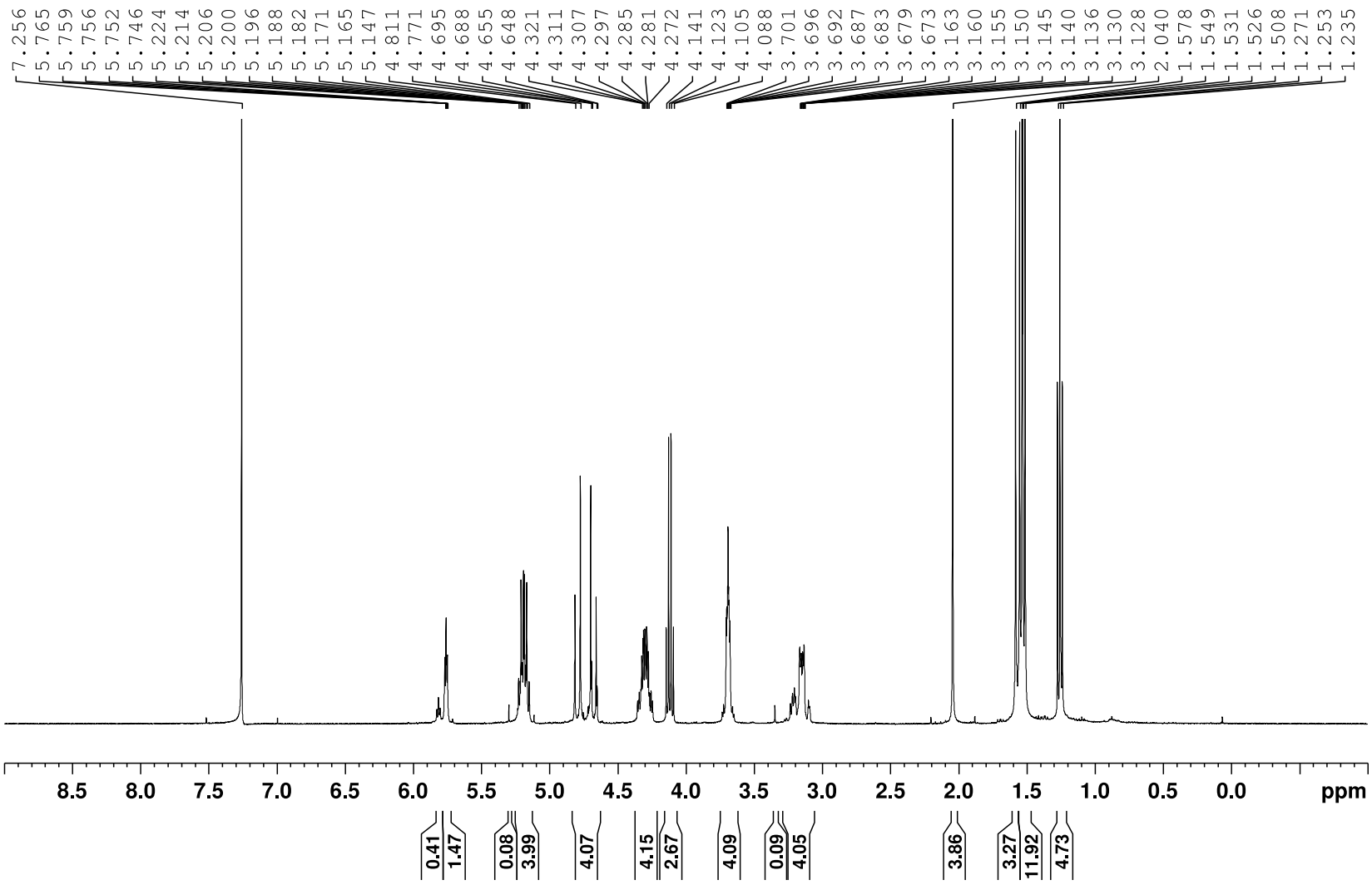
Calc.
$[M + Na]^+$
641.17 amu

Found
$[M + Na]^+$
641.16984 amu

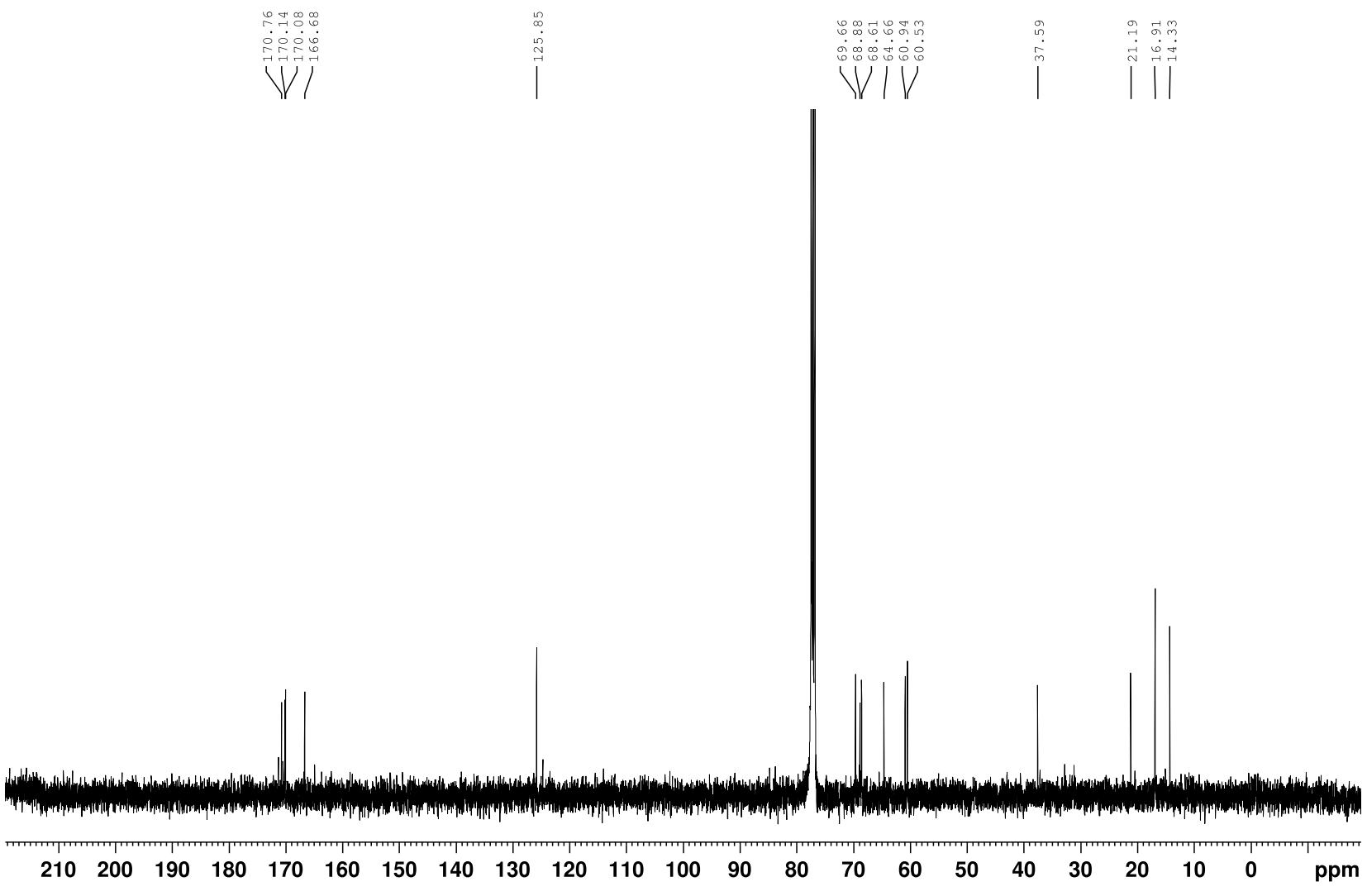
Composition
$C_{26}H_{34}O_{17}$

BLGL-EG-LGLB (215 mg, 0.33 mmol, 1 eq) was dissolved in dry DCM (330 mL, 0.001M) in a flame-dried Schlenk flask under nitrogen. A stock solution of Grubbs 2 (28 mg, 0.033 mmol, 10 mol%) in dry DCM was added and allowed to stir at RT overnight. Upon consumption of starting material by TLC, reaction mixture was quenched by addition of excess ethyl vinyl ether and stirring for 10 additional min. The reaction mixture was then concentrated and the crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a thick brown oil (189 mg, 93% yield).

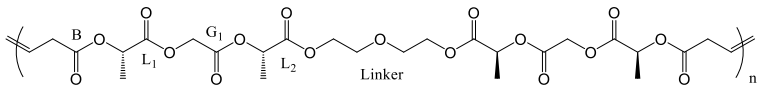
JHS-2075-Prod; EG Monomer; CDCl3; 1H; 400a;
16 Scans; 8/16/16



JHS-2075-Prod; EG Monomer; CDCl3; 13C; 400a;
2048 Scans; 8/16/16



Poly(EG)



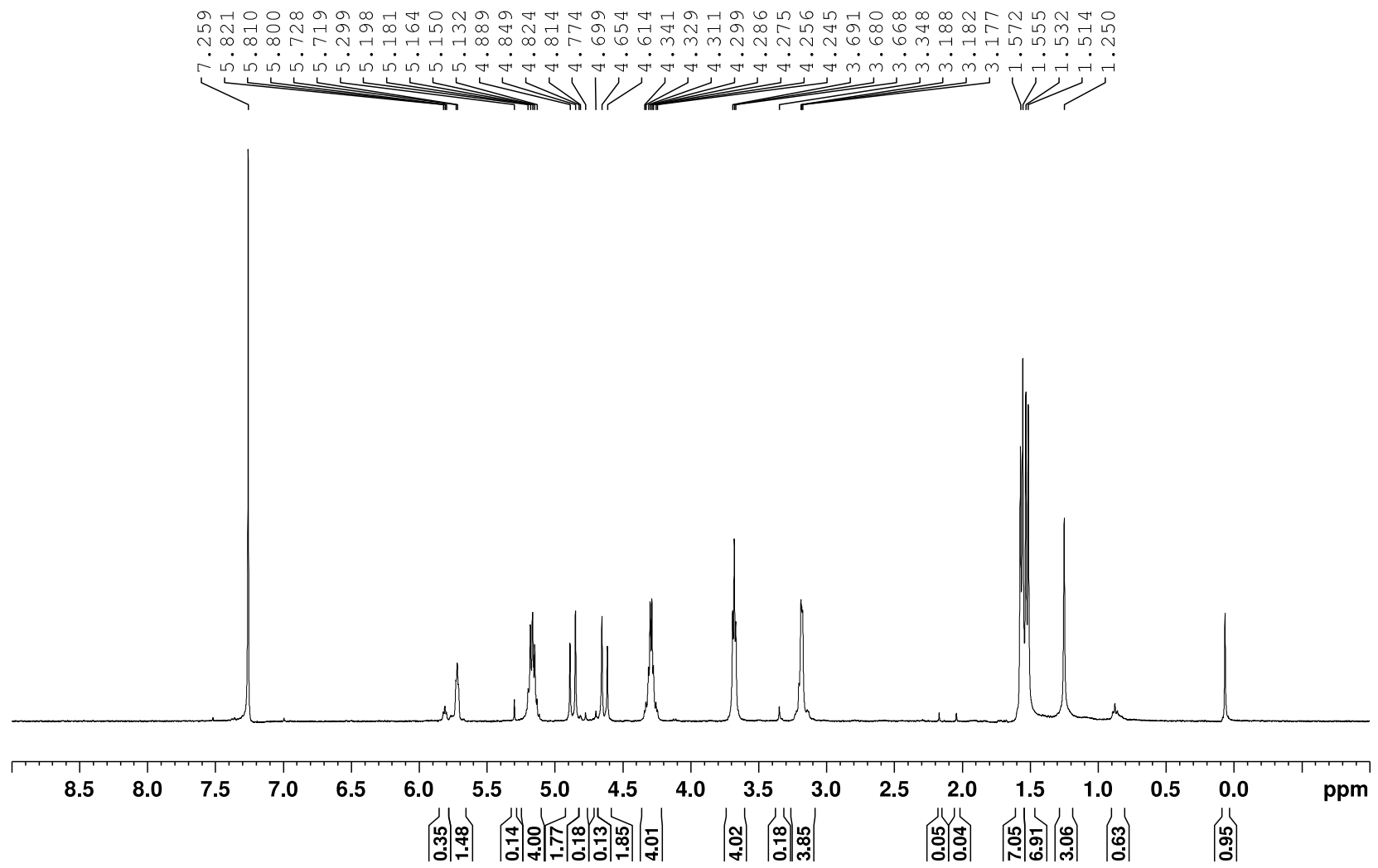
^{1}H-NMR (400 MHz, $CDCl_3$)			
dδ (ppm)	Mult. (J)	Int.	Assignment
1.52	d (7.0)	6	L_2 (CH_3)
1.57	d (7.0)	6	L_1 (CH_3)
3.18	m	4	B (CH_2)
3.68	t (4.7)	4	Linker (CH_2)
4.29	m	4	Linker (CH_2)
4.63	d (16)	2	G_1
4.87	d (16)	2	G_1
5.17	m	4	L_1 (CH), L_2 (CH)
5.72	m	1.6	B (CH) Trans
5.81	m	0.4	B (CH) Cis

^{13}C-NMR (400 MHz, $CDCl_3$)	
δ (ppm)	+ Assignment
16.93	CH_3 (L)
37.41	CH_2 (Linker)
60.85	CH_2 (G_1)
64.46	CH_2 (B)
68.60	CH (L)
68.87	CH (L)
69.53	CH_2 (Linker)
124.42	CH_2 (B Cis)
125.84	CH (B Trans)
166.71	CO
170.02	CO
170.17	CO
170.87	CO

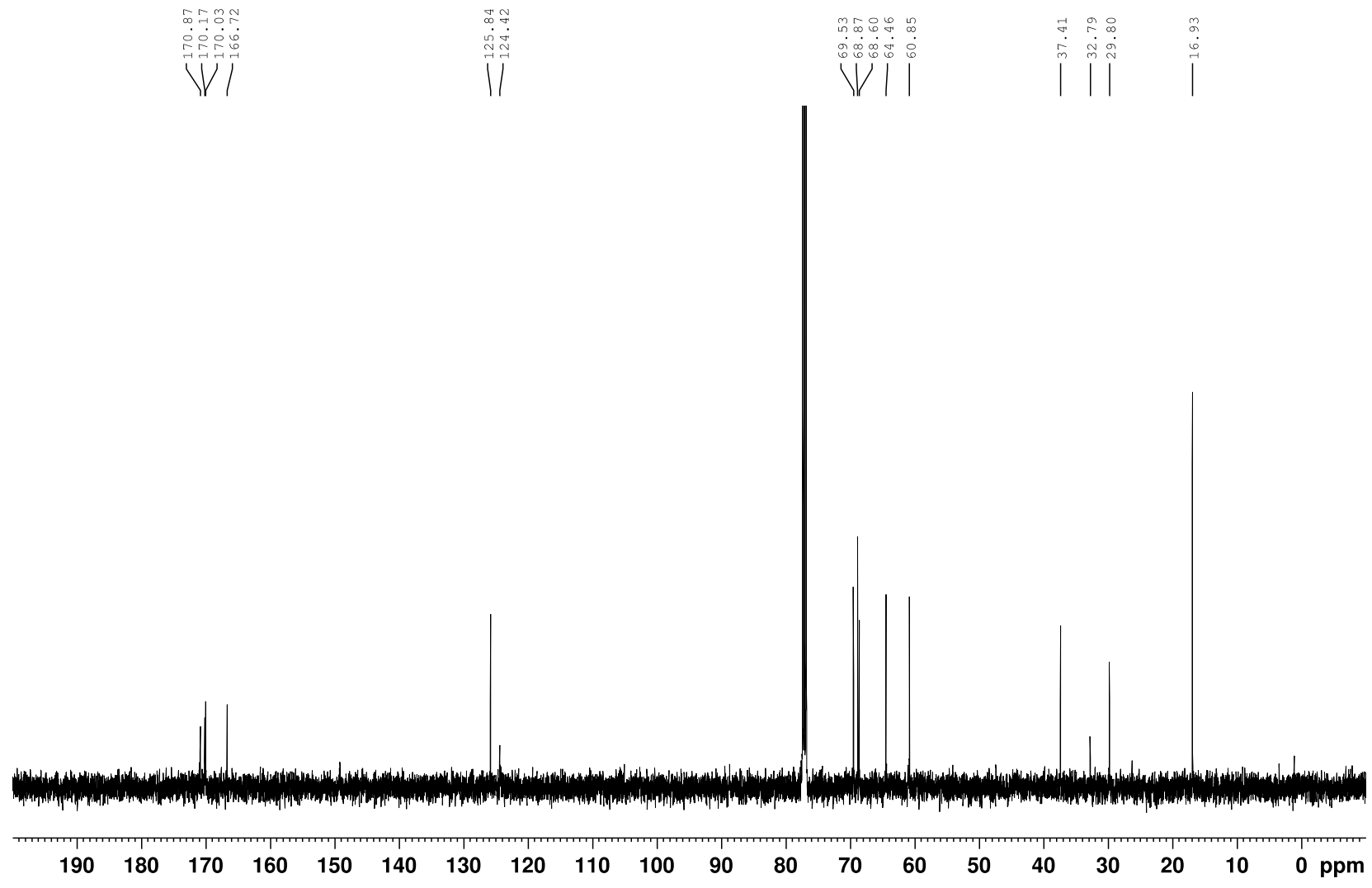
HRMS (ESI)
$\underline{M_n}$
32,608
Da
$\underline{Đ}$
1.23

Cyclic EG Monomer (73 mg, 0.118 mmol, 1 eq.) was weighed in a flame dried 1 mL vial under nitrogen. A stock solution of Grubbs II (1 mg, 0.0012 mmol, 1 mol%) in dry DCM (5.8 mg/mL, 0.17 mL, 0.7M) was added to the vial, and the vial was shaken for four hours. The reaction mixture was quenched by the addition of excess ethyl vinyl ether and vortexing. Solution was concentrated to yield a crude solid polymer, which was reprecipitated into a stirring solution of MeOH and filtered to collect pure polymer as a brown solid (41 mg, 56% yield).

JHS-3042-Pure; Poly(EG); CDCl3; 1H; 400a;
16 Scans; 2/23/17

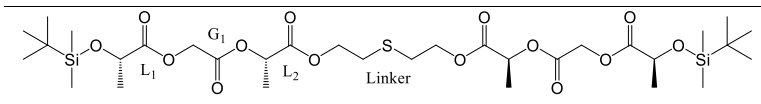


JHS-3042-500; Poly(EG); CDCl3; 1H; 500;
256 Scans; 10/27/17



2.5 THIO LINKER CONTAINING COMPOUNDS

Si-LGL-Thio-LGL-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.09	s	6	CH_3 (Si)
0.11	s	6	CH_3 (Si)
0.90	s	18	t-Bu (Si)
1.46	d (6.8)	6	CH_3 (L_1)
1.52	d (7.1)	6	L_2 (CH_3)
2.80	t (6.9)	4	Linker (CH_2)
4.30	m	4	Linker (CH_2)
4.44	q (6.8)	2	L_1 (CH)
4.67	d (16)	2	G_1
4.79	d (16)	2	G_1
5.17	q (7.1)	2	L_2 (CH)

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

δ (ppm)	Assignment
-5.41	CH_3 (Si)
-5.03	CH_3 (Si)
16.74	CH_3 (L)
18.16	C (Si)
21.25	CH_3 (L)
25.60	t-Bu (Si)
30.25	CH_2 (Linker)
60.36	CH_2 (G_1)
64.04	CH (L)
67.93	CH (L)
69.21	CH_2 (Linker)
166.82	CO
169.70	CO
173.23	CO

HRMS (ESI)

Calc. Mass
754.31 amu

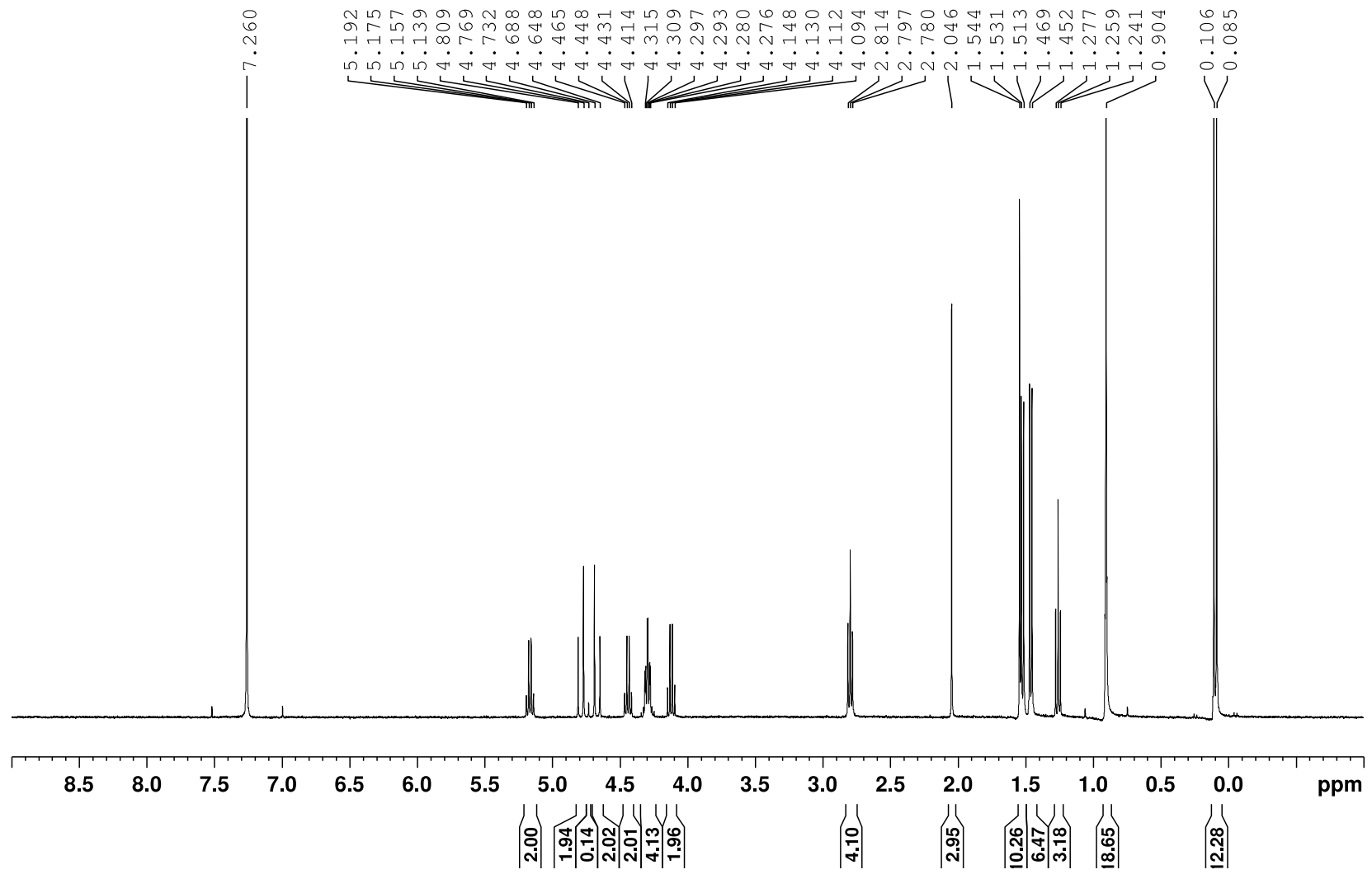
Calc.
$[M + H]^+$
755.31 amu

Found
$[M + H]^+$
755.31684 amu

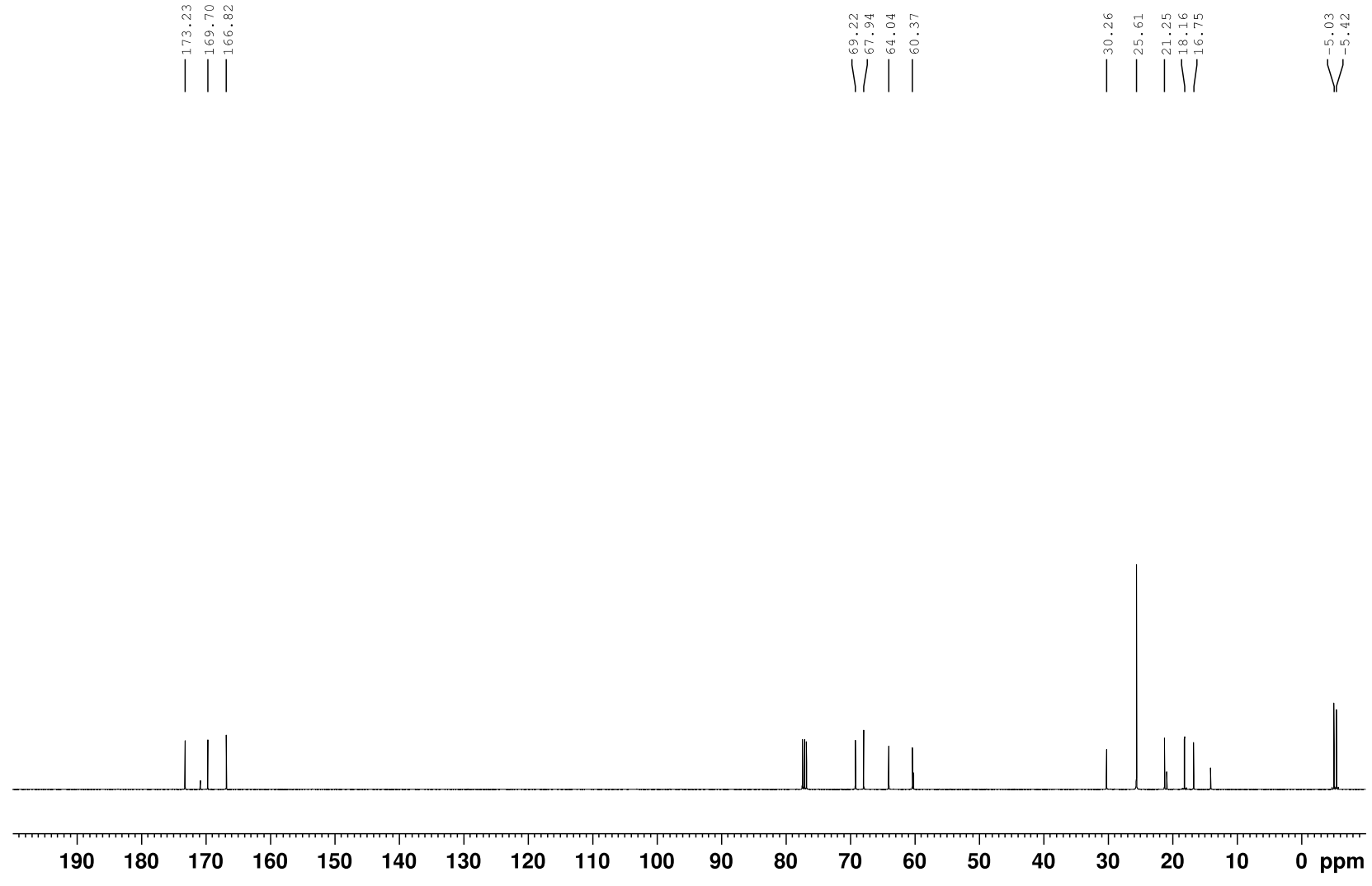
Composition
$C_{32}H_{58}O_{14}SSi_2$

2,2'-Thiodiethanol was dried over sieves for two h. **LGL-Si** (1.27 g, 3.8 mmol, 2.3 eq) was dissolved in dry DCM (12 mL, 0.4 M), and added to a flame-dried vial under nitrogen. Dry 2,2'-thiodiethanol (0.20 g, 1.63 mmol, 1 eq), DPTS (0.224 g, 0.76 mmol, 0.45 eq) and DCC (0.8 g, 3.8 mmol, 2.3 eq) were then added to the vial sequentially and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes and filtered to remove DCU, concentrated and crude oil was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (0.80 g, 65% yield).

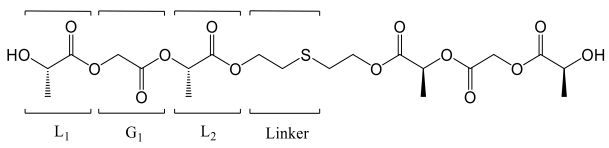
23-33; Si-LGL-Thio-LGL-Si; CDCl3; 1H; 400a; 16 Sc



JHS-2051; Si-LGL-Thio-LGL-Si; CDCl3; 13C; 400a
1024 Scans; 10/24/17



LGL-Thio-LGL



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.49	d (7.0)	6	L_1 (CH_3)
1.54	d (7.0)	6	L_2 (CH_3)
2.80	t (6.8)	4	Linker (CH_2)
2.86	d (5.6)	2	L_1 (OH)
4.31	t (6.8)	4	Linker (CH_2)
4.42	m	2	L_1 (CH)
4.74	d (16)	2	G_1
4.84	d (16)	2	G_1
5.17	q (7.0)	2	L_2 (CH)

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

δ (ppm)	+ Assignment
16.95	CH_3 (L)
20.45	CH_3 (L)
30.47	CH_2 (Linker)
61.01	CH_2 (Linker)
64.32	CH_2 (G_1)
66.87	CH (L)
69.65	CH (L)
166.86	CO
169.93	CO
175.04	CO

HRMS (ESI)

Calc. Mass
526.14 amu

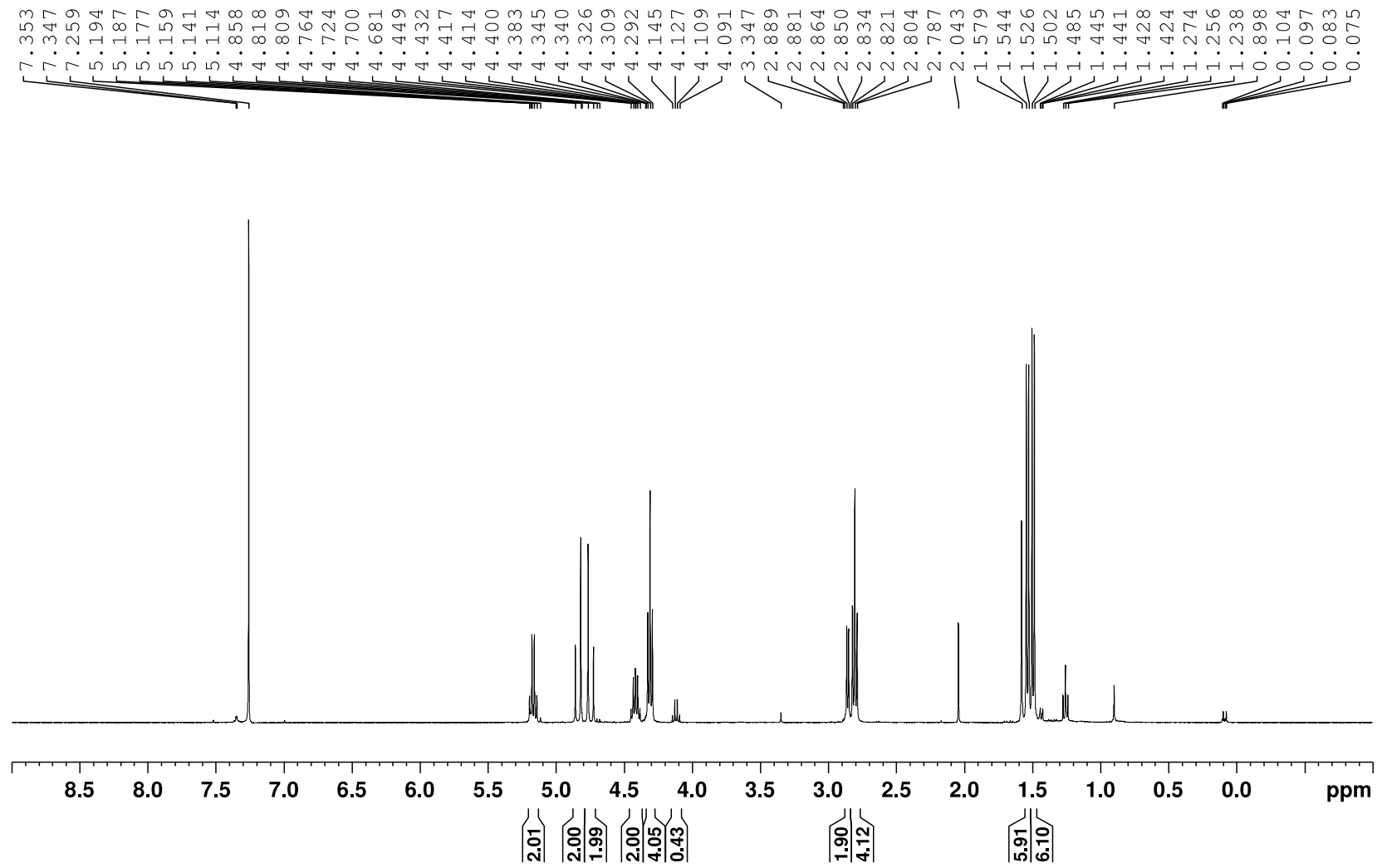
Calc.
$[M + H]^+$
527.14 amu

Found
$[M + H]^+$
527.14184 amu

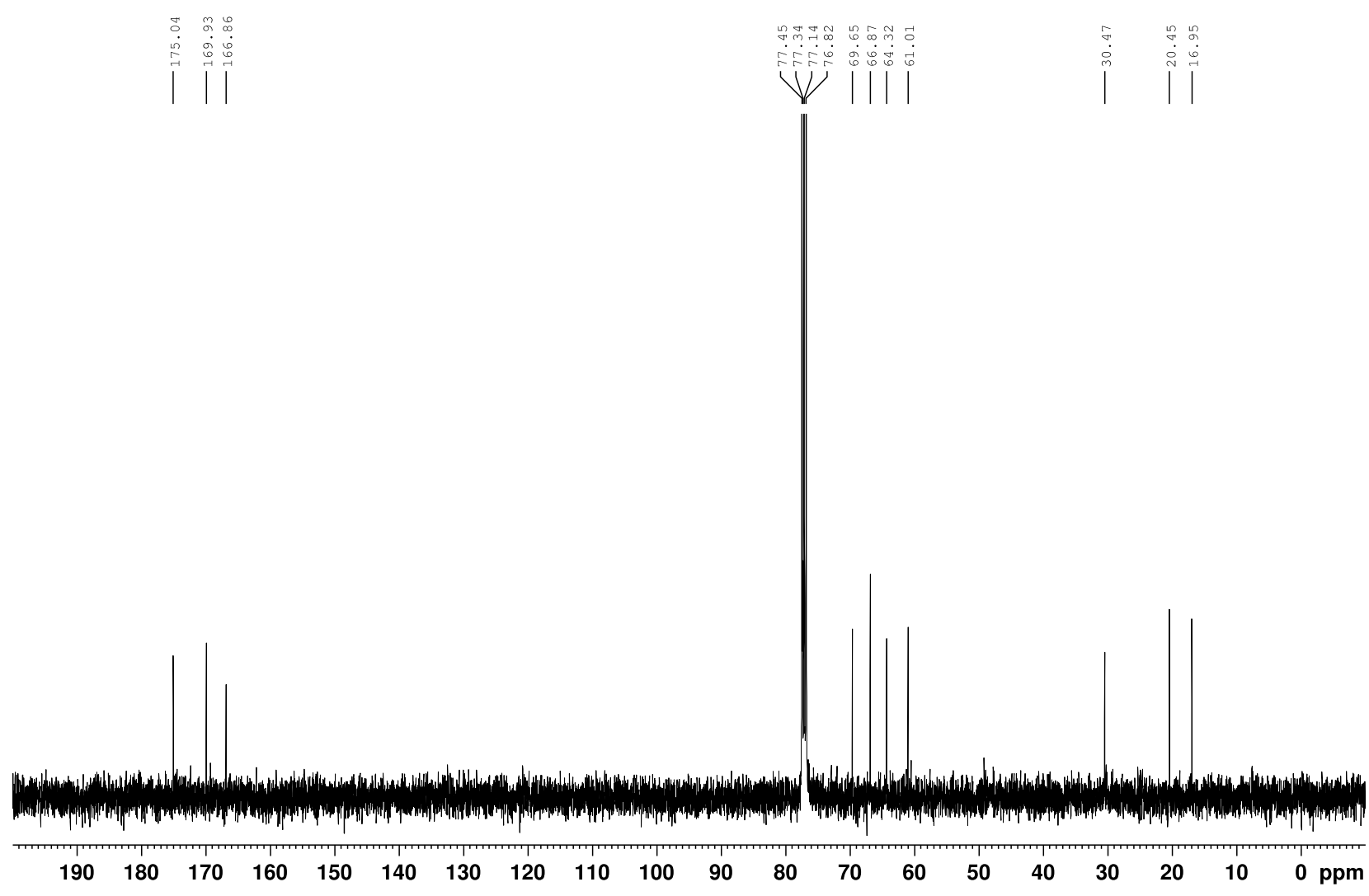
Composition
$C_{20}H_{30}O_{14}S$

AcOH (0.61 mL, 10.6 mmol, 16 eq) and TBAF (1 M in THF) (2.0 mL, 2.0 mmol, 3 eq) were dried over activated sieves for 2 h. **Si-LGL-Thio-LGL-Si** (500 mg, 0.663 mmol, 1 eq) was dissolved in dry THF (17 mL, 0.04 M) in a flame dried Schlenk flask under nitrogen. AcOH and TBAF were added dropwise at 0°C, allowed to warm to RT and stir for 30 h. The reaction mixture was then diluted with brine and extracted with EtOAc 3x, combined organic layers were washed with brine 3x, dried over $MgSO_4$, concentrated and the crude oil was then purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (221 mg, 63% yield).

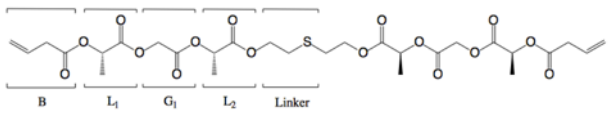
2063; LGL-THio-LGL; CDCl3; 1H; 400a; 16 scans; 8/



JHS-2063; LGL-THio-LGL; CDCl3; 13c; 400a; 1024 scans; 8/1/16



BLGL-Thio-LGLB



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

δ (ppm)	Mult. (J)	Int.	Assignment
1.52	d (6.8)	6	**L_1** CH_3
1.57	d (6.8)	6	**L_2** CH_3
2.79	t (13.6)	4	**Linker** CH_2 α to S
3.10-3.25	m	4	**B** Terminal CH_2
4.30	t (13.6)	4	**Linker** CH_2 β to S
4.64	d (16)	2	**G_1**
4.87	d (16)	2	**G_1**
5.13-5.30	m	8	**L_1** & **L_2** Methyne, **B** Methylene
5.88-5.98	m	2	**B** CH

^{13}C-NMR (500 MHz, $CDCl_3$)

δ (ppm)	+ Assignment
16.95	CH
30.52	CH
34.08	CH
38.71	CH
60.87	CH
64.22	CH
68.56	CH
69.53	CH
119.12	Olefin
129.73	Olefin
166.76	CO
169.92	CO
170.26	CO
171.00	CO

HRMS (ESI)

Calc. Mass
662.19 g/mol

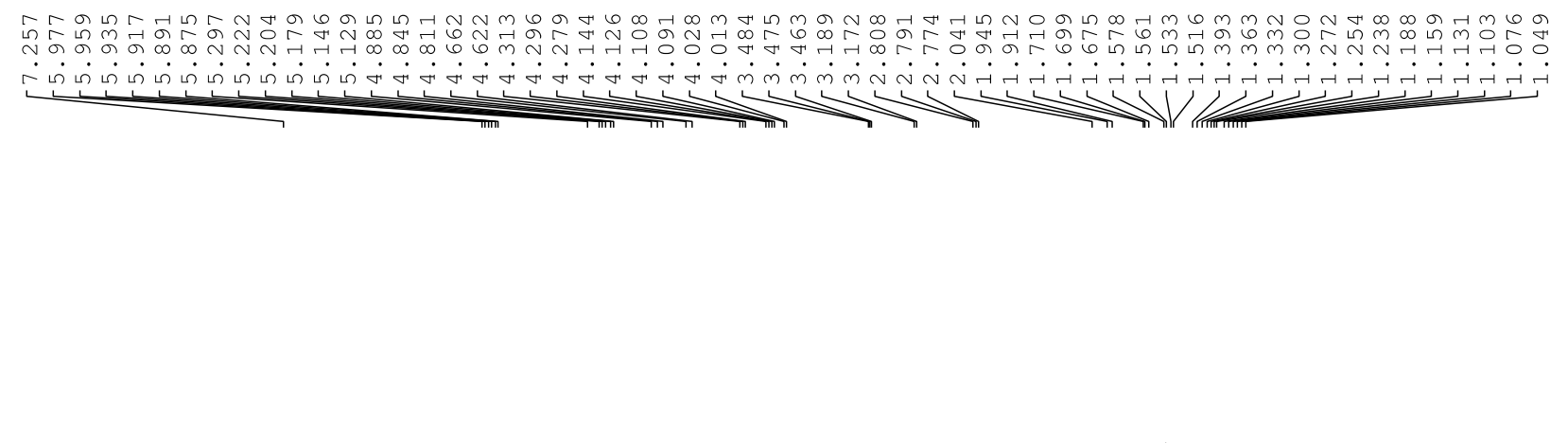
Calc.
$[M + H]^+$
663.19 amu

Found
$[M + H]^+$
663.19379 amu

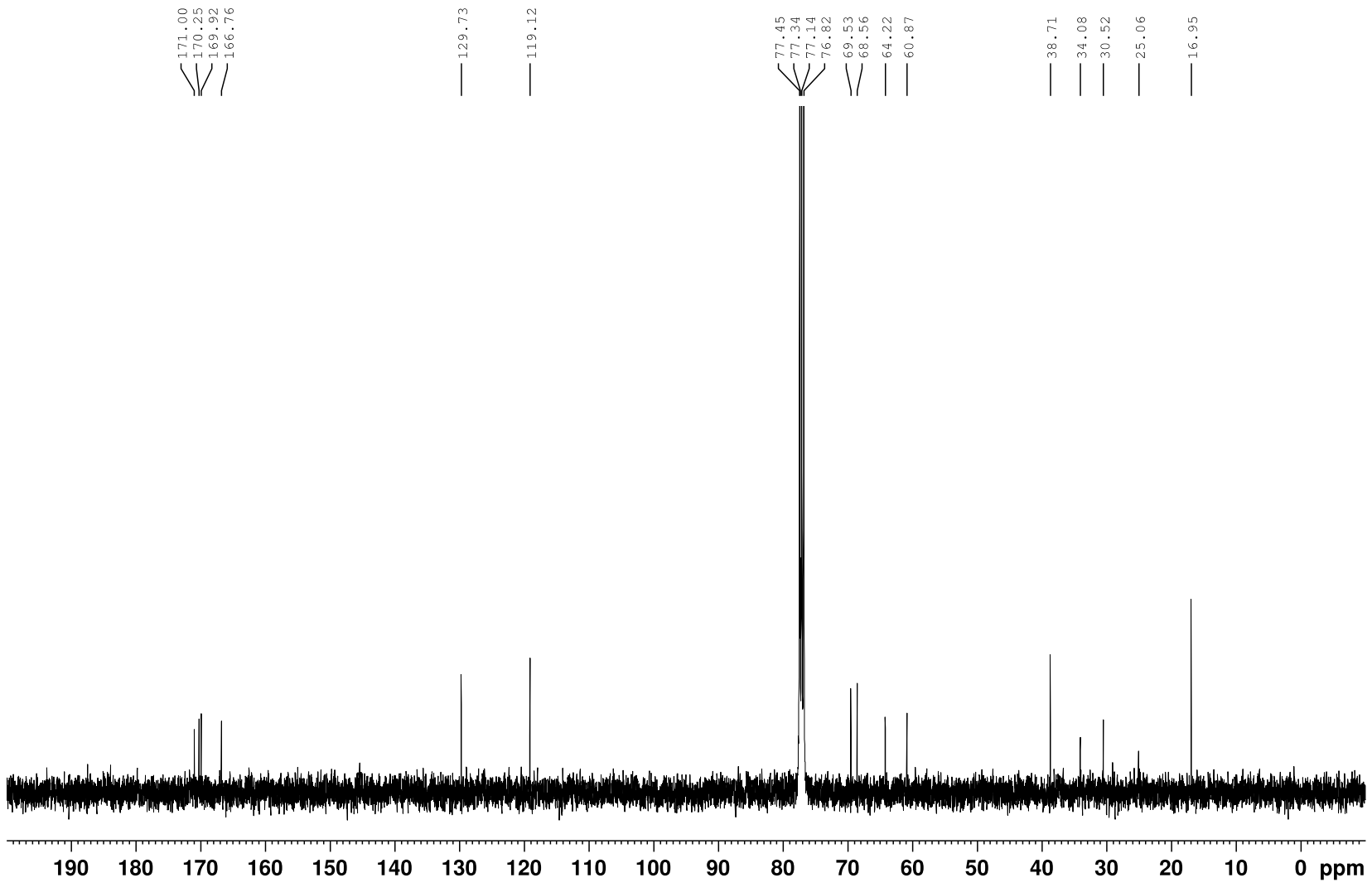
Composition
$C_{28}H_{38}O_{16}S$

LGL-Thio-LGL (221 mg, 0.42 mmol, 1 eq) was dissolved in dry DCM (8 mL, 0.05 M) in an oven dried vial under nitrogen. DPTS (56 mg, 0.19 mmol, 0.45 eq) and DCC (0.26 g, 1.3 mmol, 3 eq) were added sequentially. Butenoic acid (0.11 g, 1.3 mmol, 3 eq) was then added dropwise and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes, washed with sodium bicarbonate 3x, dried over $MgSO_4$ and filtered to remove DCU and drying agent, concentrated, and crude oil was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (203 mg, 73% yield).

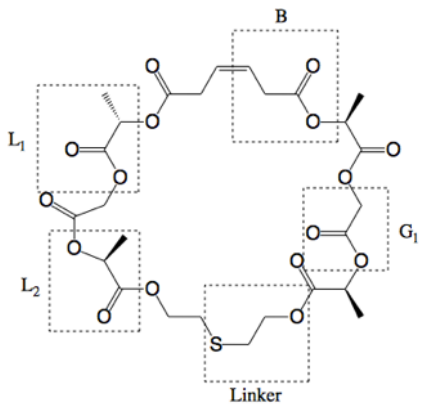
)66; BLGL-Thio-LGLB; CDCl3; 1H; 400a; 16 scans; 8



JHS-2066; BLGL-Thio-LGLB; CDCl3; 13c; 400a; 1024 scans; 8/1/16



Cyclic Thio Monomer



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

δ (ppm)	Mult. (J)	Int.	Assignment
1.52	d (6.8)	6	L_1 CH_3
1.54	d (6.8)	6	L_2 CH_3
2.82	t (13.6)	2	Linker CH_2 α to S
3.19	m	4	B CH_2
4.31	m	4	Linker CH_2 β to S
4.69	d (16)	2	G_1
4.79	d (16)	2	G_1
5.18	m	4	L_1 & L_2 Methyne, B Methylene
5.76	t (7.6)	1.5	B trans olefin
5.82	t (10)	0.4	B cis olefin

^{13}C-NMR (500 MHz, $CDCl_3$)

δ (ppm) + Assignment	
16.96	L (CH_3)
16.98	L (CH_3)
30.70	CH_2
37.66	CH_2
61.05	CH_2
64.86	CH_2
68.68	CH
69.79	CH
125.96	B (CH)
166.75	CO
169.99	CO
170.12	CO
170.80	CO

HRMS (ESI)

Calc. Mass
634.16 g/mol

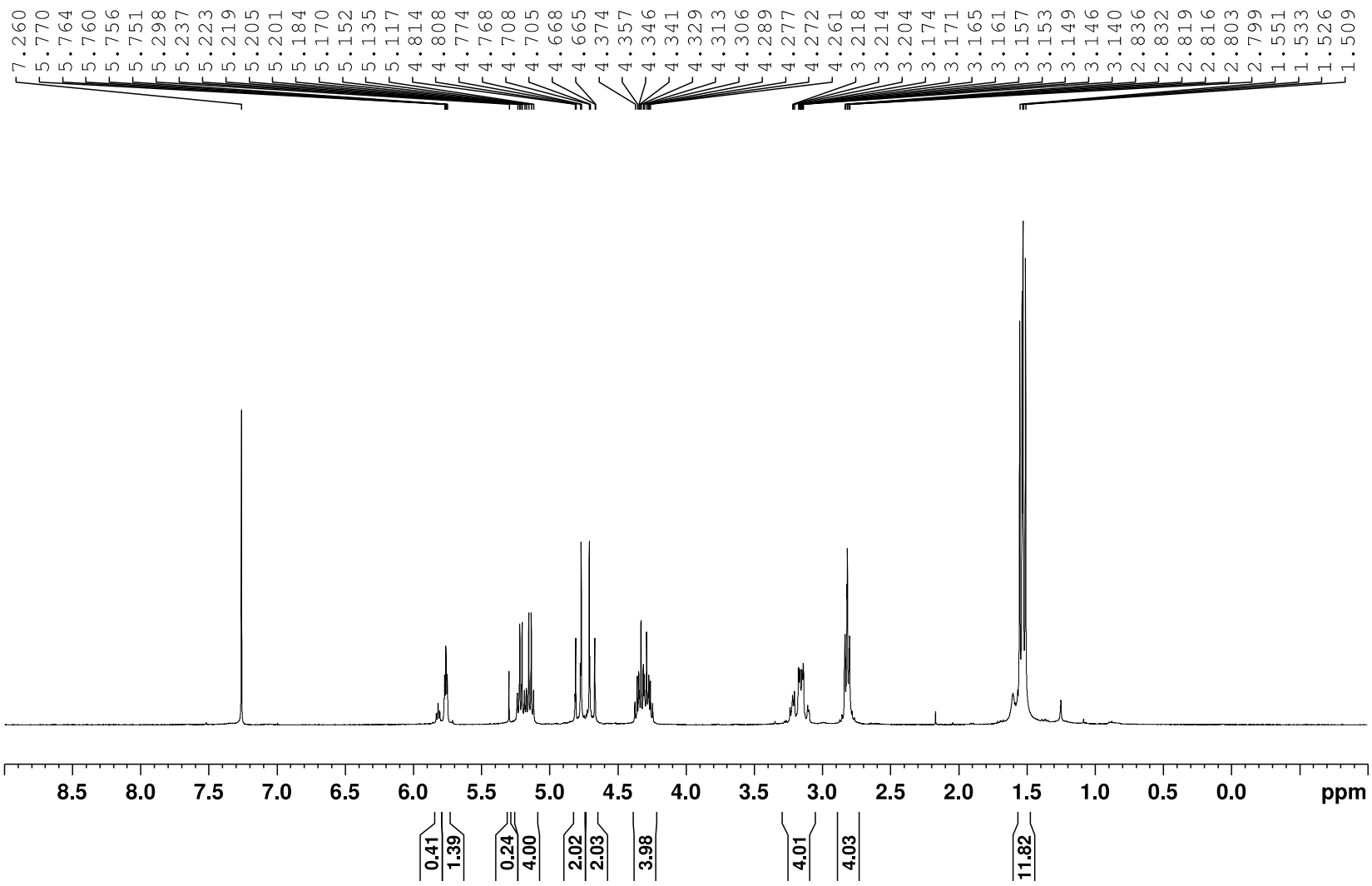
Calc.
635.16 [M + H]$^+$

Found
635.16390 [M + H]$^+$

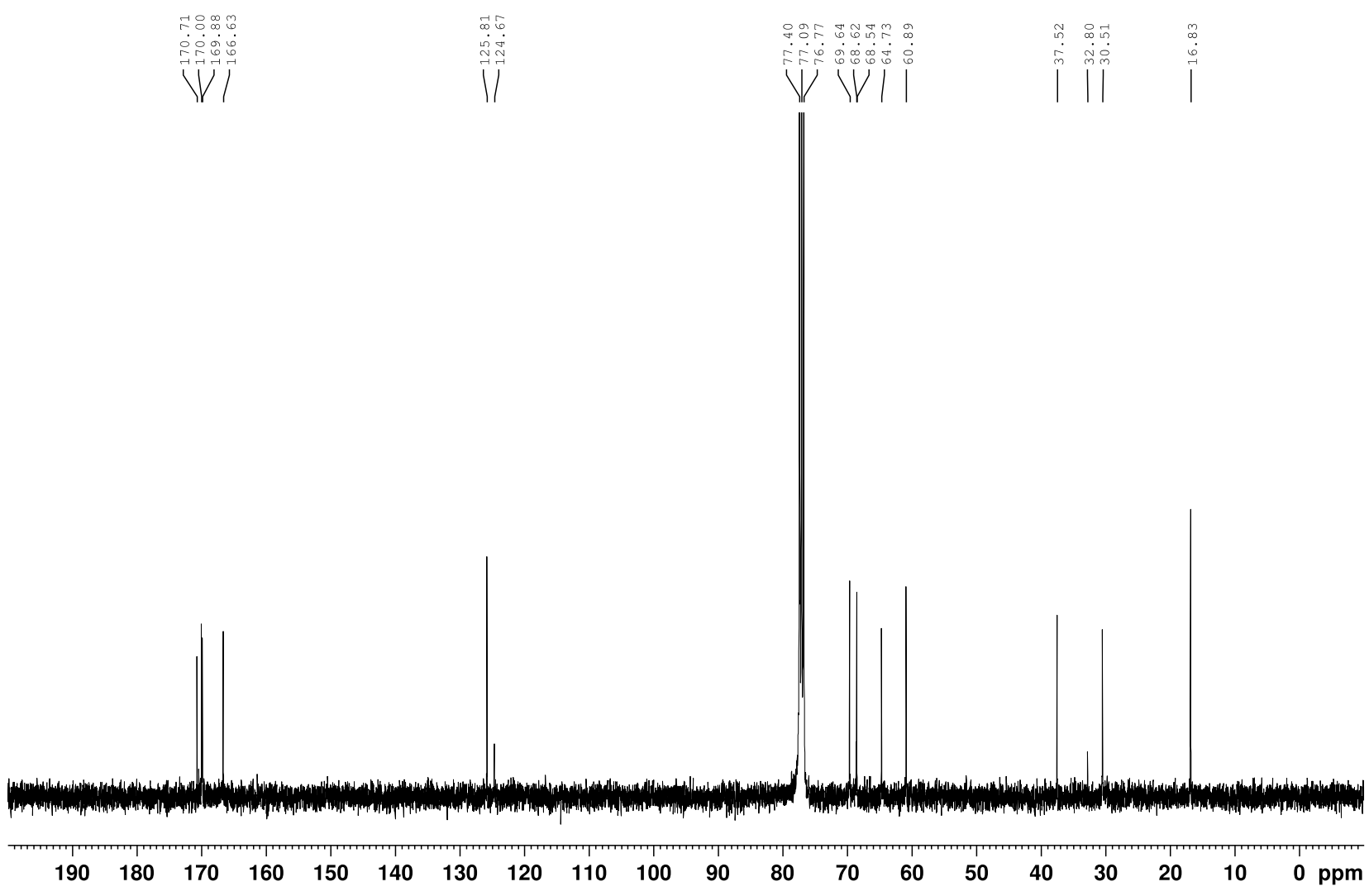
Composition
$C_{26}H_{34}O_{16}S$

BLGL-Thio-LGLB (185 mg, 0.28 mmol, 1 eq) was dissolved in dry DCM (300 mL, 0.001M) in a flame-dried Schlenk flask under nitrogen. A stock solution of Grubbs 2 (32 mg, 0.042 mmol, 15 mol%) in dry DCM was added and allowed to stir at RT overnight. Upon consumption of starting material by TLC, reaction mixture was quenched by addition of excess ethyl vinyl ether and stirring for 10 additional min. The reaction mixture was then concentrated and the crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a thick brown oil (112 mg, 63% yield).

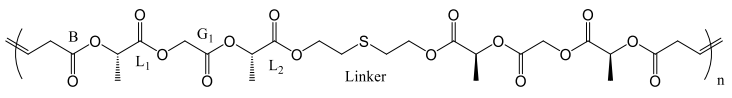
Thio Monomer; CDCl3; 1H; 400a; 16 Scans;
12/2/16



Thio Monomer; CDCl3; 13C; 400a; 2048 Scans;
12/2/16



Poly(Thio)



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

δ (ppm)	Mult. (J)	Int.	Assignment
1.53	d (6.8)	6	L_1 CH_3
1.57	d (6.8)	6	L_2 CH_3
2.79	t (6.8)	4	Linker CH_2 α to S
3.19	m	4	B Terminal CH_2
4.29	m	4	Linker CH_2 β to S
4.64	d (16)	2	G_1
4.87	d (16)	2	G_1
5.16	m	4	L_1 & L_2 CH
5.72	m	1.6	B CH Trans
5.81	m	0.4	B CH Cis

^{13}C-NMR (500 MHz, $CDCl_3$)

δ (ppm)	Assignment
16.93	CH_3 (L)
30.53	CH_2 (Linker)
37.40	CH_2 (Linker)
60.85	CH_2 (G_1)
64.20	CH_2 (B)
68.60	CH (L)
69.51	CH (L)
124.42	CH (B Cis)
125.83	CH (B Trans)
166.72	CO
169.87	CO
170.17	CO
170.87	CO

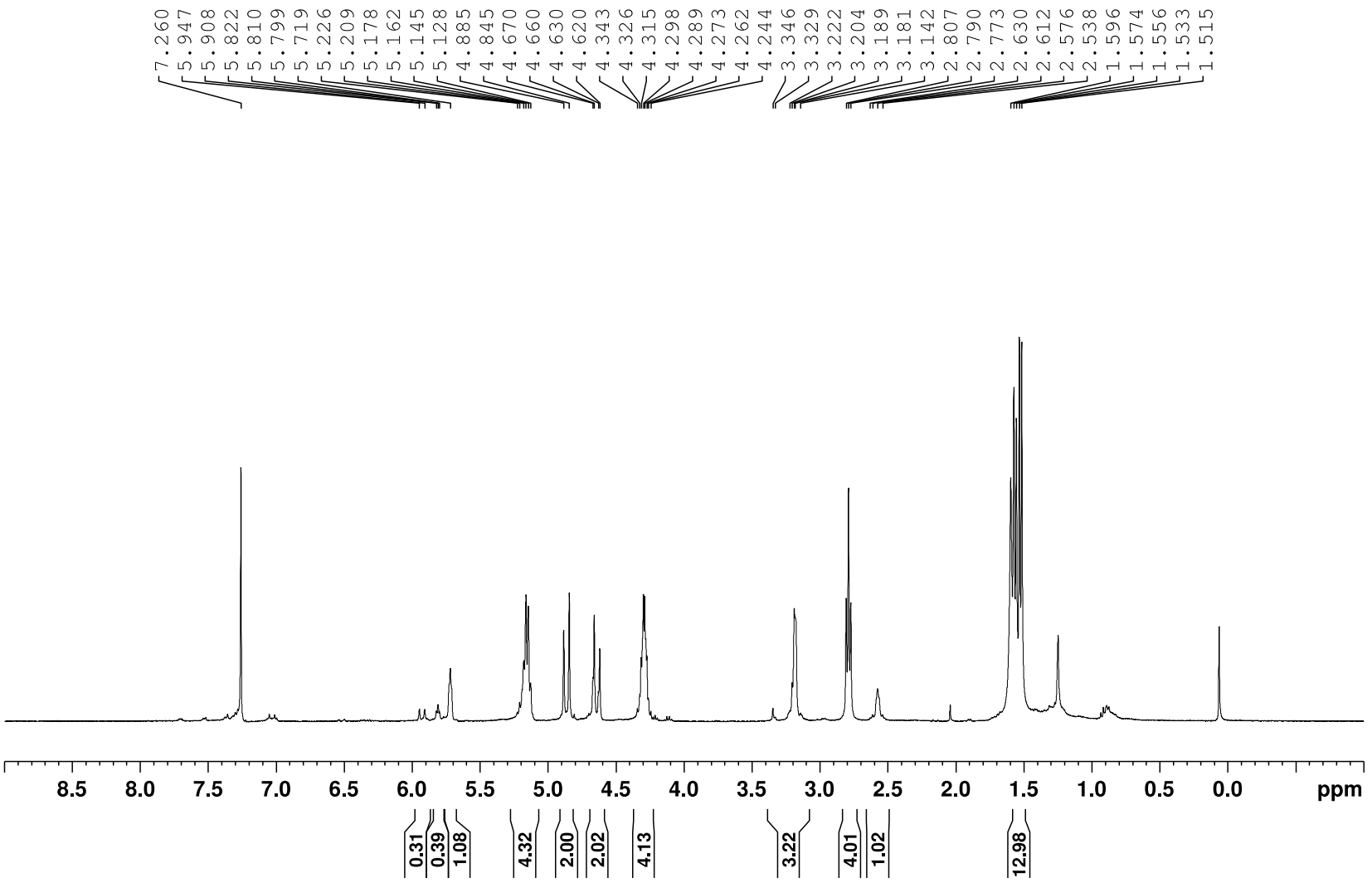
HRMS (ESI)

$\underline{M_n}$
22,452 Da

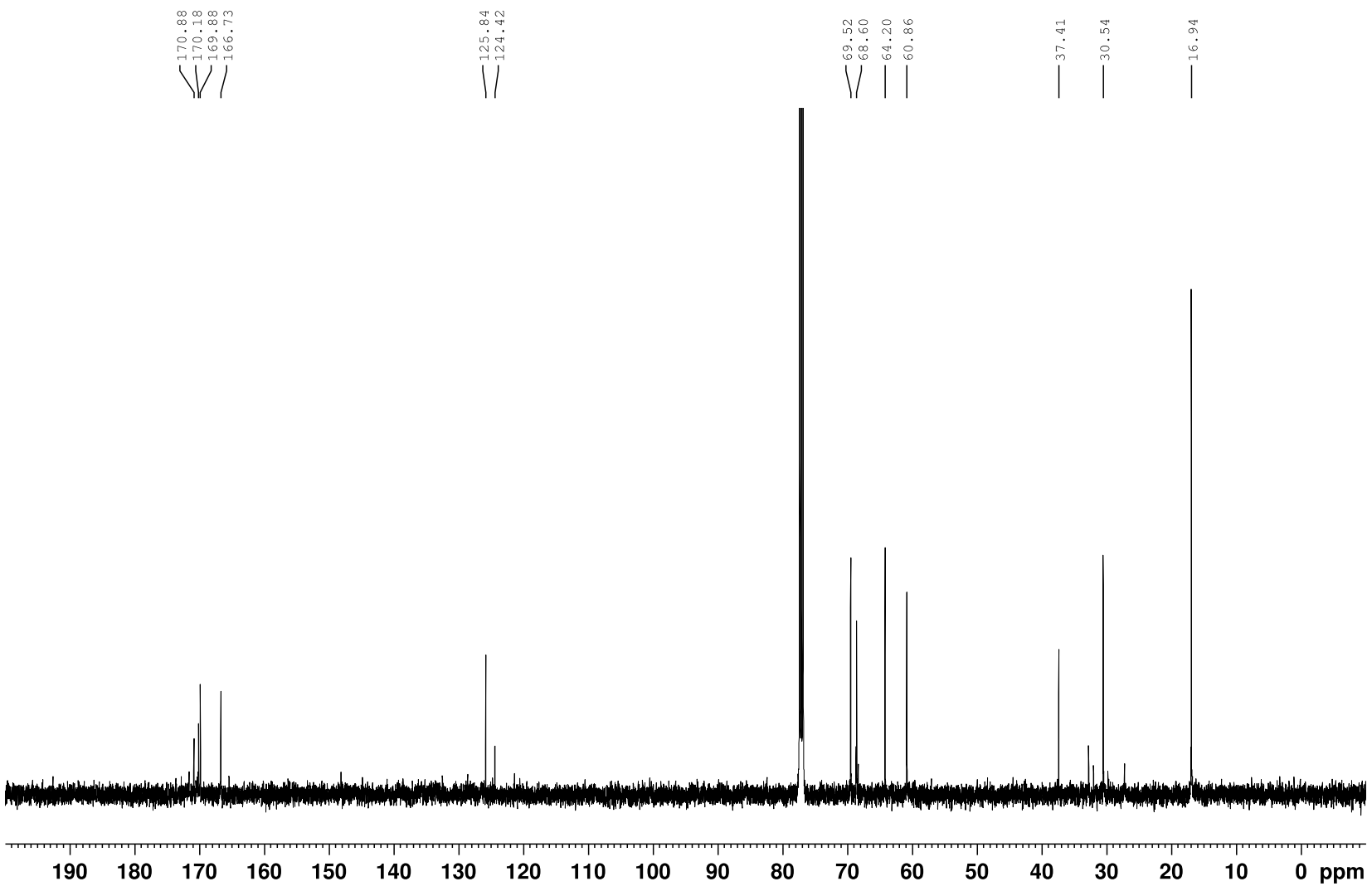
$\underline{Đ}$
1.54

Cyclic Thio Monomer (55 mg, 0.087 mmol, 1 eq.) was weighed in a flame dried 1 mL vial under nitrogen. A stock solution of Grubbs II (2.2 mg, 0.0026 mmol, 3 mol%) in dry THF (17.8 mg/mL, 0.124 mL, 0.7M) was added and stirred at 60°C for 4 h. The reaction mixture was quenched by the addition of excess ethyl vinyl ether and vortexing. Solution was concentrated to yield a crude solid polymer, which was reprecipitated into a stirring solution of MeOH and filtered to collect pure polymer as a brown solid (46 mg, 83% yield).

JHS-4047; Poly(Thio) Pure; CDCl3; 1H; 400a;
16 Scans; 7/11/17

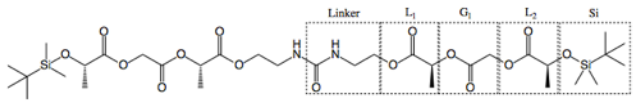


JHS-4047; Poly(Thio); CDCl3; 13C; 500; 256 Scan
10/27/17



2.6 UREA LINKER CONTAINING COMPOUNDS

Si-LGL-Urea-LGL-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.102	d (3.2)	12	Si (Me)
0.903	s	18	Si (t-Bu)
1.46	d (6.8)	6	L_2 (CH_3)
1.51	d (7.2)	6	L_1 (CH_3)
3.42	m	4	Linker (CH_2 α-amide)
4.20	m	4	Linker (CH_2 β-amide)
4.46	q (20.4)	2	L_2 (CH)
4.73	s	4	G_1
5.13	q (20.8)	4	L_1 (CH)
5.37	t (11.6)	2	Linker (amide)

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

δ (ppm)	+ Assignment
-4.85	CH_3 (Si)
16.99	CH_3 (L)
18.45	CH_3 (L)
21.55	t-Bu (Si)
25.82	t-Bu (Si
39.08	CH_2 (Linker)
60.88	CH_2 (G)
65.51	CH_2 (Linker)
68.19	CH (L)
69.89	CH (L)
158.09	CO (Linker)
167.05	CO
169.99	CO
174.61	CO

HRMS (ESI)

Calc. Mass
780.35 amu

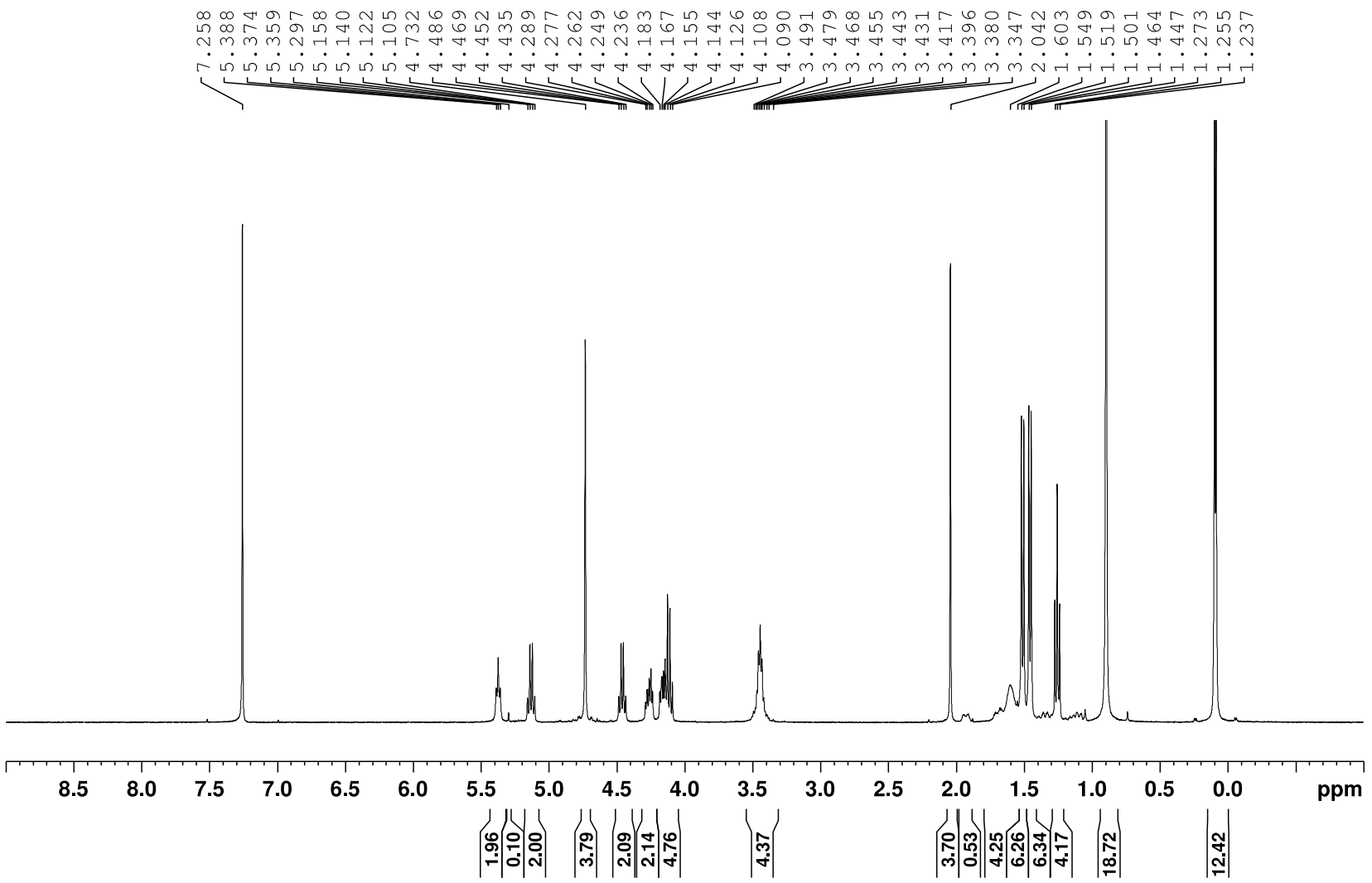
Calc.
$[M + H]^+$
781.35 amu

Found
$[M + H]^+$
781.35900 amu

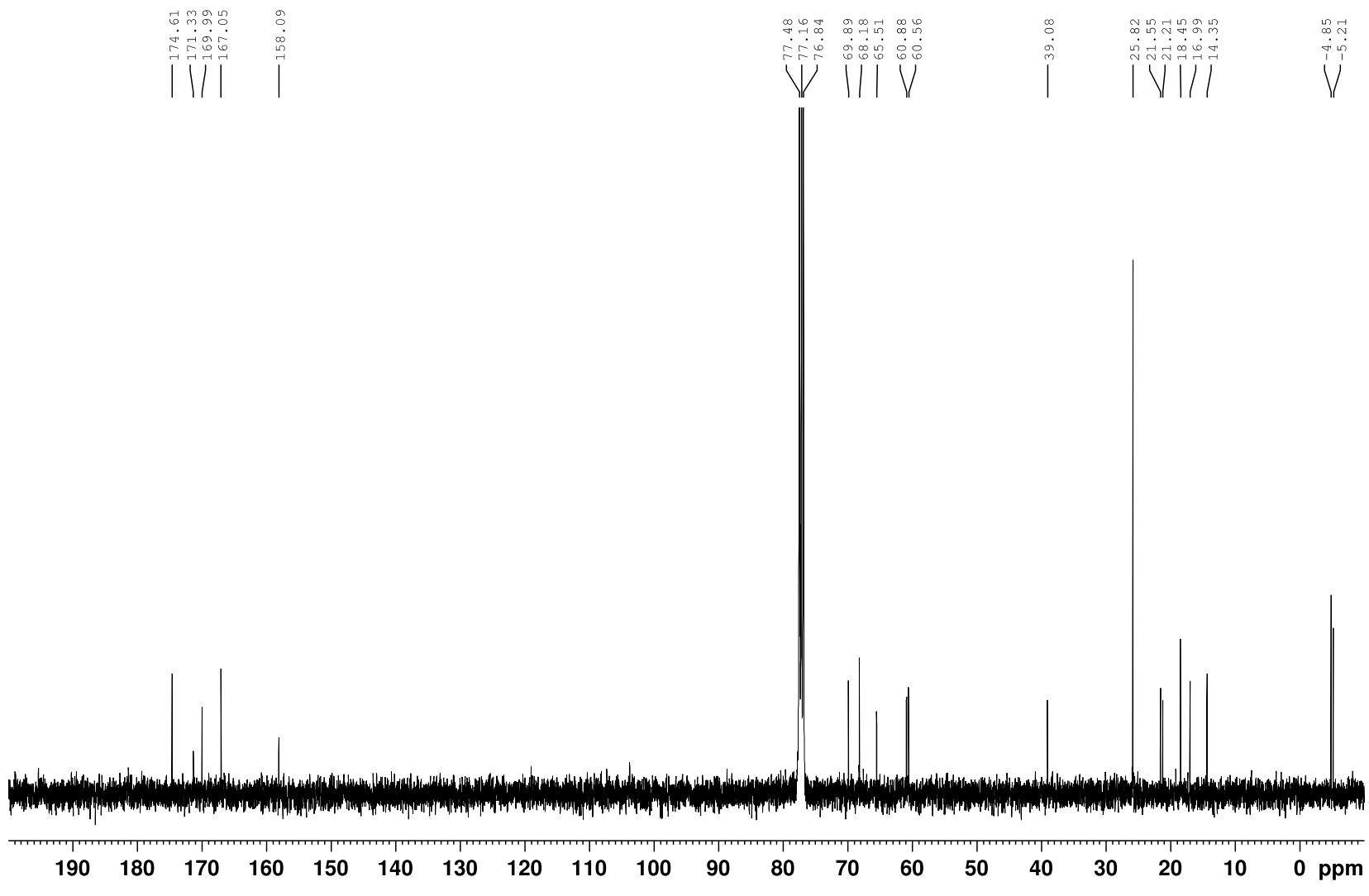
Composition
$C_{33}H_{60}O_{15}N_2Si_2$

LGL-Si (1.1 g, 3.3 mmol, 2.3 eq) and bis(hydroxyethyl)urea (0.218 g, 1.47 mmoles, 1 eq) were dissolved in dry DCM (35 mL, 0.1 M) and added to a flame-dried vial under nitrogen. DPTS (0.195 g, 0.66 mmol, 0.45 eq) and DCC (0.697 g, 3.4 mmol, 2.3 eq) were then added to the reaction mixture sequentially and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was filtered to remove DCU, concentrated and crude oil was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (1.04 g, 91% yield).

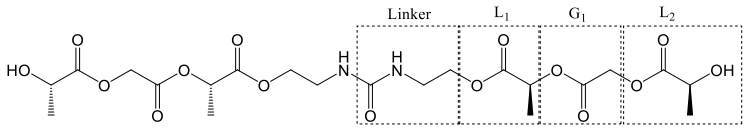
JHS-2058; Si-LGL-Urea-LGL-Si; CDCl3; 1H; 400a;
16 Scans; 8/17/16



JHS-2058; Si-LGL-Urea-LGL-Si; CDCl3; 13C; 400a
2048 Scans; 8/17/16



LGL-Urea-LGL



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.49	d (6.8)	6	L_2 (CH_3)
1.53	d (7.2)	6	L_1 (CH_3)
3.48	m	6	Linker (CH_2 α-amide), L_2 (OH)
4.23	m	4	Linker (CH_2 β-amide)
4.47	q (26.4)	2	L_2 (CH)
4.71	d (16)	2	G_1
4.81	d (16)	2	G_1
5.13	q (21.2)	4	L_1 (CH)
5.57	t (11.6)	2	Linker (amide)

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

δ (ppm)	Assignment
16.93	CH_3 (L)
20.35	CH_3 (L)
39.14	CH_2 (Linker)
61.20	CH_2 (G)
65.91	CH_2 (Linker)
66.90	CH (L)
70.25	CH (L)
158.00	CO (Linker)
167.42	CO
170.18	CO
175.76	CO

HRMS (ESI)

Calc. Mass
552.18 amu

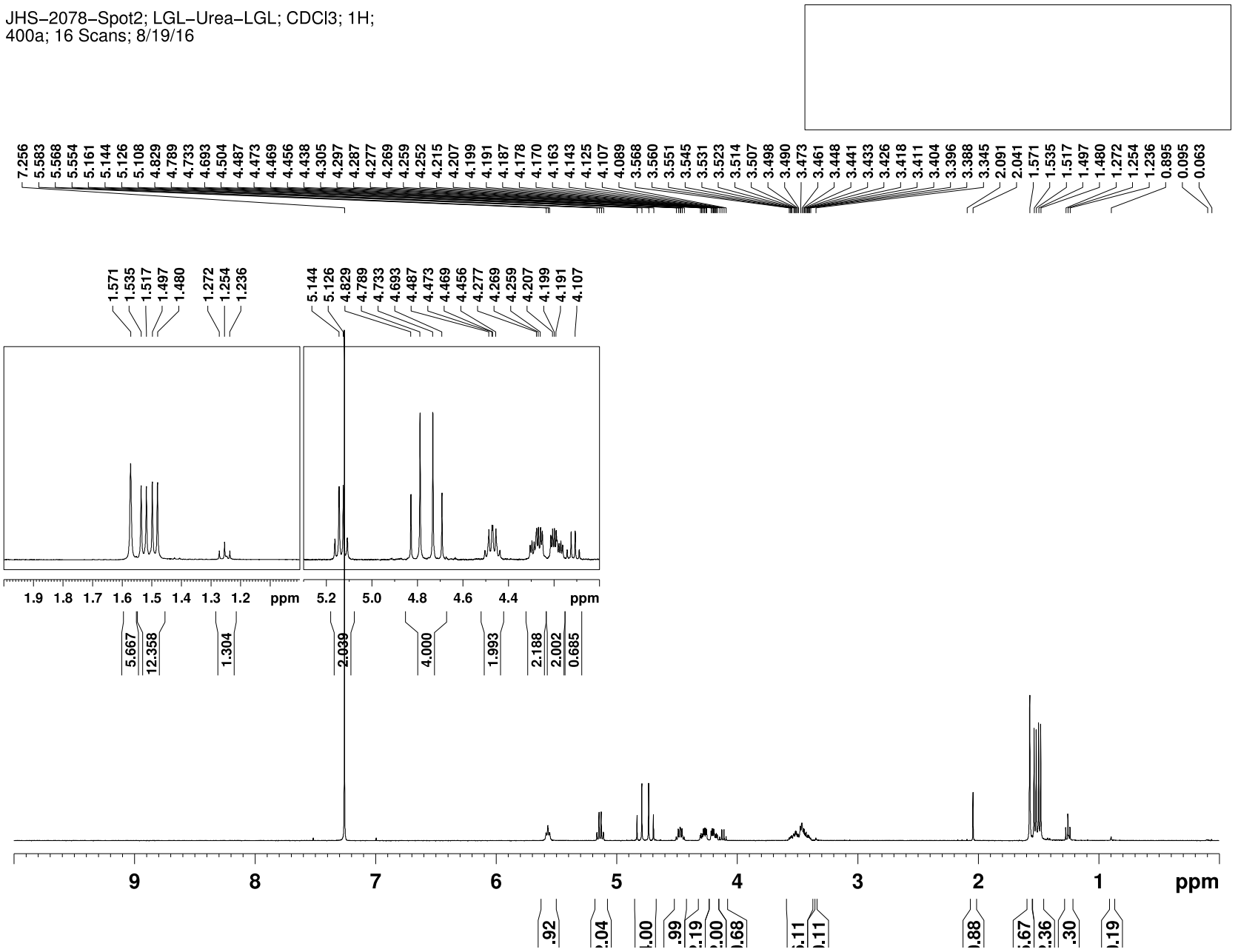
Calc.
$[M + H]^+$
553.19 amu

Found
$[M + H]^+$
553.18710 amu

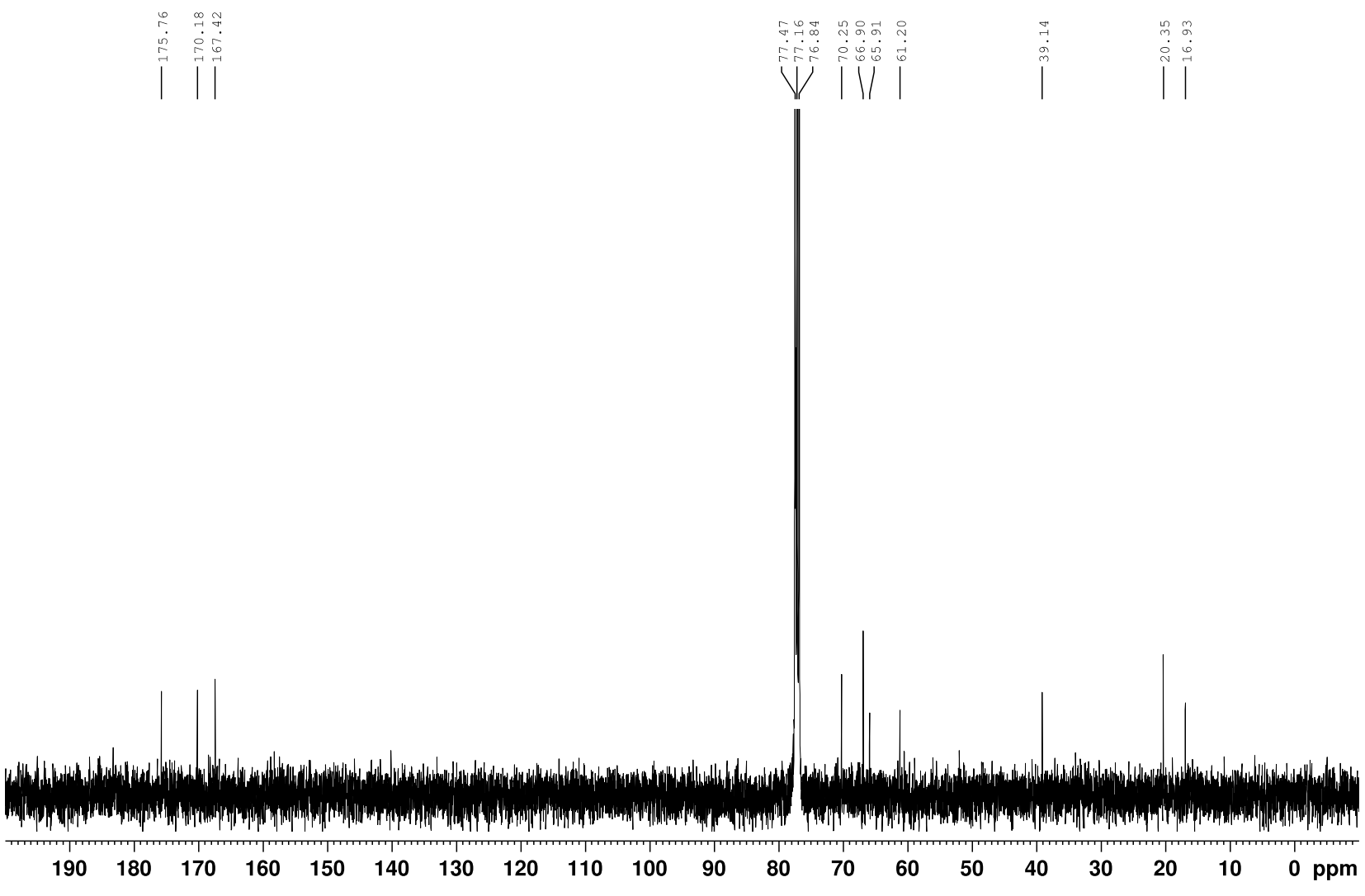
Composition
$C_{21}H_{32}O_{15}N_2$

AcOH (1.2 mL, 21 mmol, 16 eq) and TBAF (1 M in THF) (4.0 mL, 4.0 mmol, 3 eq) were dried over activated sieves for 2 h. **Si-LGL-Urea-LGL-Si** (1.038 mg, 1.33 mmol, 1 eq) was dissolved in dry THF (33 mL, 0.04 M) in a flame dried Schlenk flask under nitrogen. AcOH and TBAF were added dropwise at 0°C, allowed to warm to RT and stir for 30 h. The reaction mixture was then diluted with brine and extracted with EtOAc 3x, combined organic layers were washed with brine 3x, dried over $MgSO_4$, concentrated and the crude oil was then purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (360 mg, 49% yield).

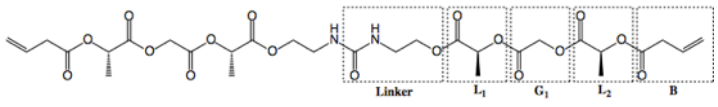
JHS–2078–Spot2; LGL–Urea–LGL; CDCl3; 1H;
400a; 16 Scans; 8/19/16



JHS-2078; LGL-Urea-LGL; CDCl3; 13C; 400a; \
2048 Scans; 8/20/16



BLGL-Urea-LGLB



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.51	d (6.8)	6	L_1 (CH_3)
1.57	d (7.2)	6	L_2 (CH_3)
3.17	m	4	B (Terminal Olefin)
3.44	m	4	Linker (CH_2 α-amide)
4.22	m	4	Linker (CH_2 β-amide)
4.73	d (16)	2	G1
4.78	d (16)	2	G1
5.14	m	10	L_1 (CH), L_2 (CH), B (CH_2), Linker (amide)
5.90	m	2	B (CH)

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

δ (ppm)	+ Assignment
16.82	L (CH_3)
16.87	L (CH_3)
38.60	CH_2 (Linker)
39.08	CH_2 (Linker
60.47	CH_2
65.33	CH_2
68.65	CH
69.98	CH
119.20	B
129.48	B
157.87	CO (Linker)
166.78	CO
169.89	CO
170.96	CO
171.09	CO

HRMS (ESI)

Calc. Mass
688.23 amu

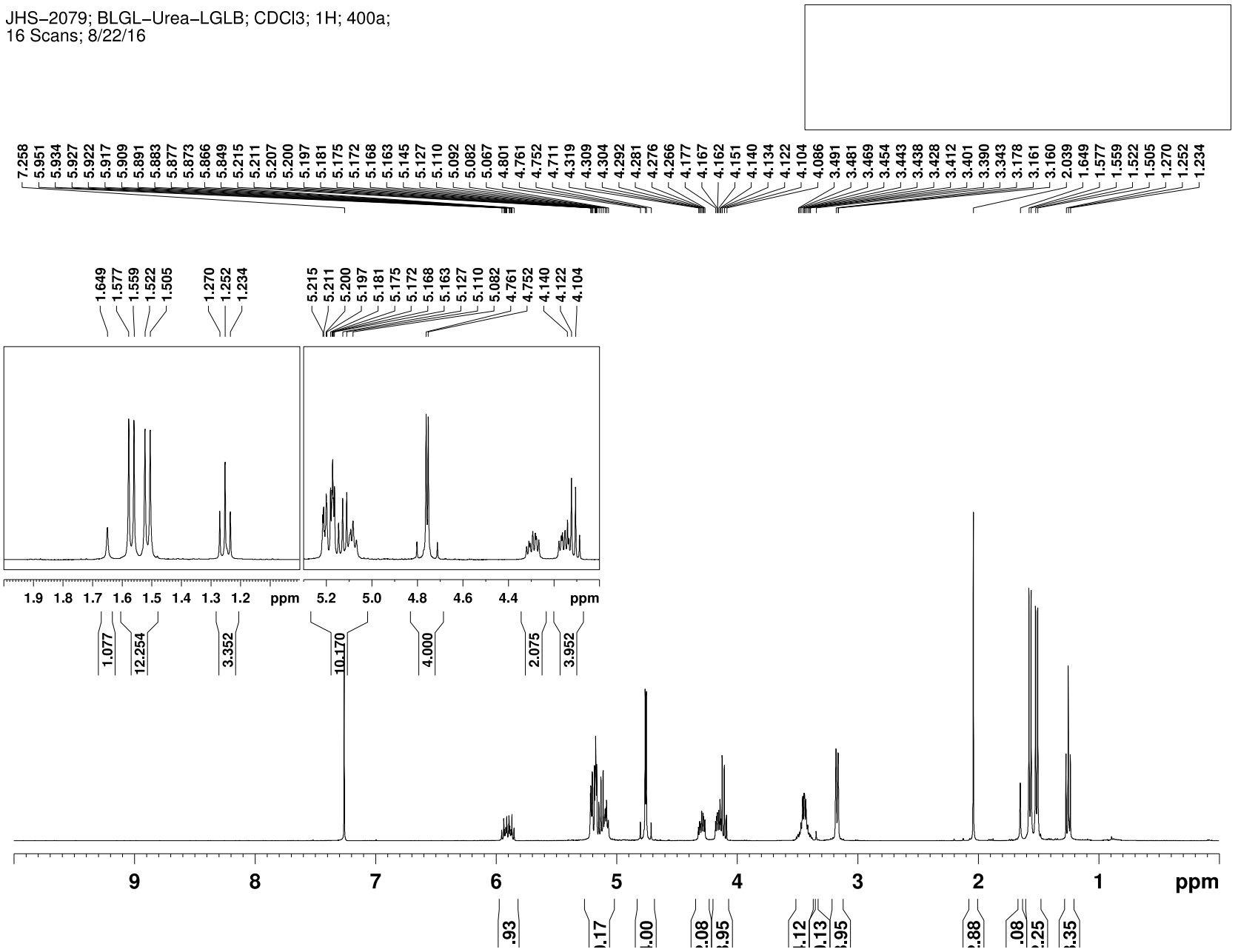
Calc.
$[M + H]^+$
689.23 amu

Found
$[M + H]^+$
689.23884 amu

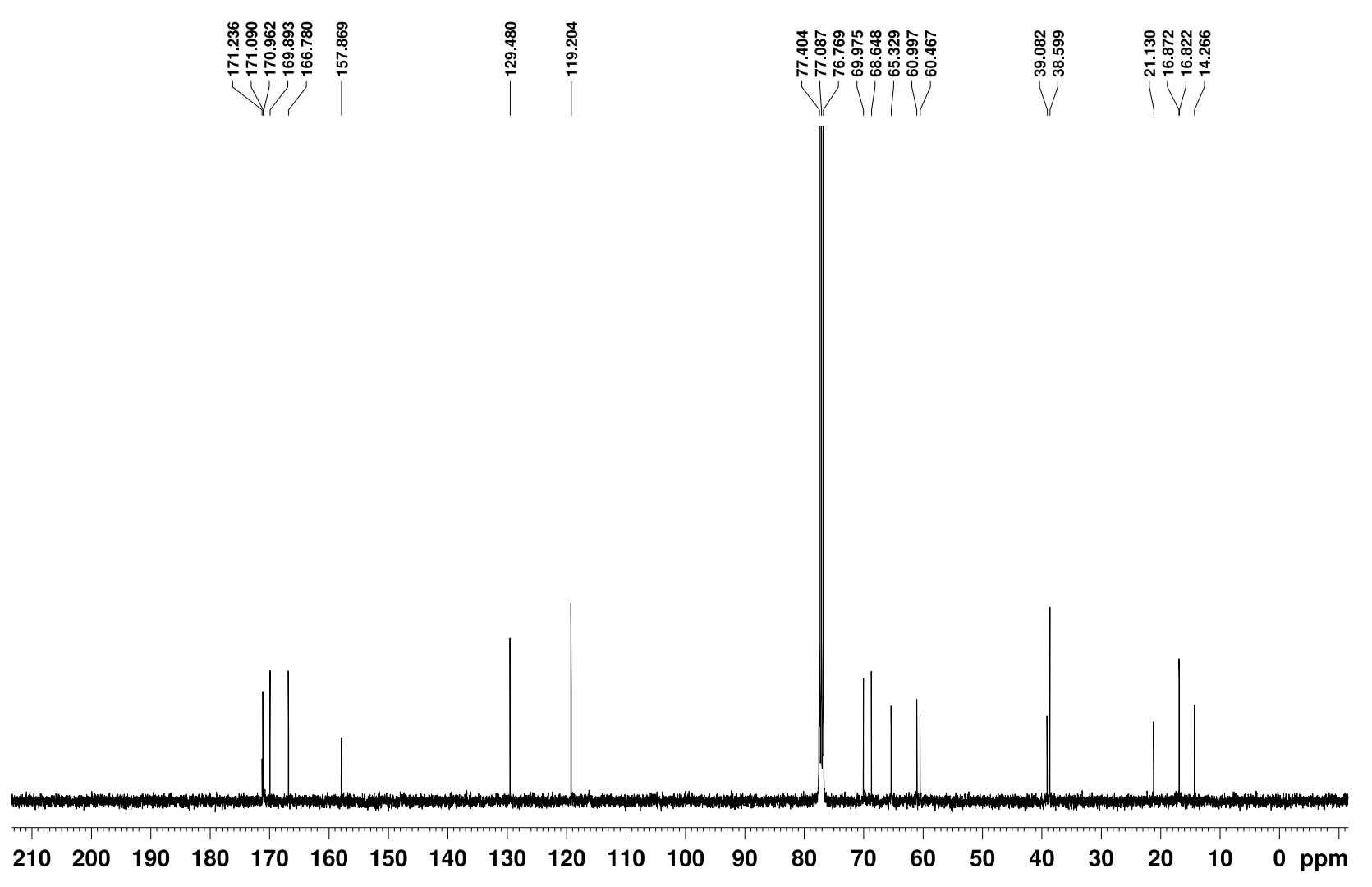
Composition
$C_{29}H_{41}O_{17}N_2$

LGL-Urea-LGL (350 mg, 0.633 mmol, 1 eq) was dissolved in a 2:1 mixture of dry EtOAc:DCM (15 mL, 0.04 M) in an oven dried vial under nitrogen. DPTS (84 mg, 0.29 mmol, 0.45 eq) and DCC (0.39 g, 1.9 mmol, 3 eq) were added sequentially. Butenoic acid (0.167 g, 1.9 mmol, 3 eq) was then added dropwise and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes, washed with sodium bicarbonate 3x, dried over $MgSO_4$ and filtered to remove DCU and drying agent, concentrated, and crude oil was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (307 mg, 70% yield).

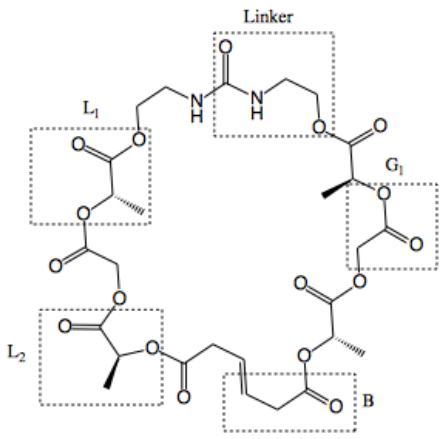
JHS–2079; BLGL–Urea–LGLB; CDCl3; 1H; 400a;
16 Scans; 8/22/16



JHS–2079; BLGL–Urea–LGLB; CDCl3; 13c; 400a;
2048 Scans; 8/22/16



Cyclic Urea Monomer



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.52	d (7.2)	6	L_1 (CH_3)
1.56	d (6.8)	6	L_2 (CH_3)
3.16	m	4	B (CH_2)
3.45	m	4	Linker (CH_2 α-amide)
4.23	m	4	Linker (CH_2 β-amide)
4.69	d (16)	2	G1
4.79	d (16)	2	G1
5.09	q (21)	2	L_1 (CH)
5.22	m	4	L_2 (CH), Linker (amide)
5.77	m	2	B (olefin)

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

δ (ppm)	Assignment
16.86	L (CH_3)
16.91	L (CH_3)
37.62	CH_2 (Linker)
39.14	CH_2 (Linker)
61.21	CH_2
65.54	CH_2
68.83	CH
70.19	CH
124.73	B (cis)
125.86	B (trans)
157.98	CO (Linker)
166.82	CO
170.60	CO
170.86	CO
171.54	CO

HRMS (ESI)

Calc. Mass
660.20 amu

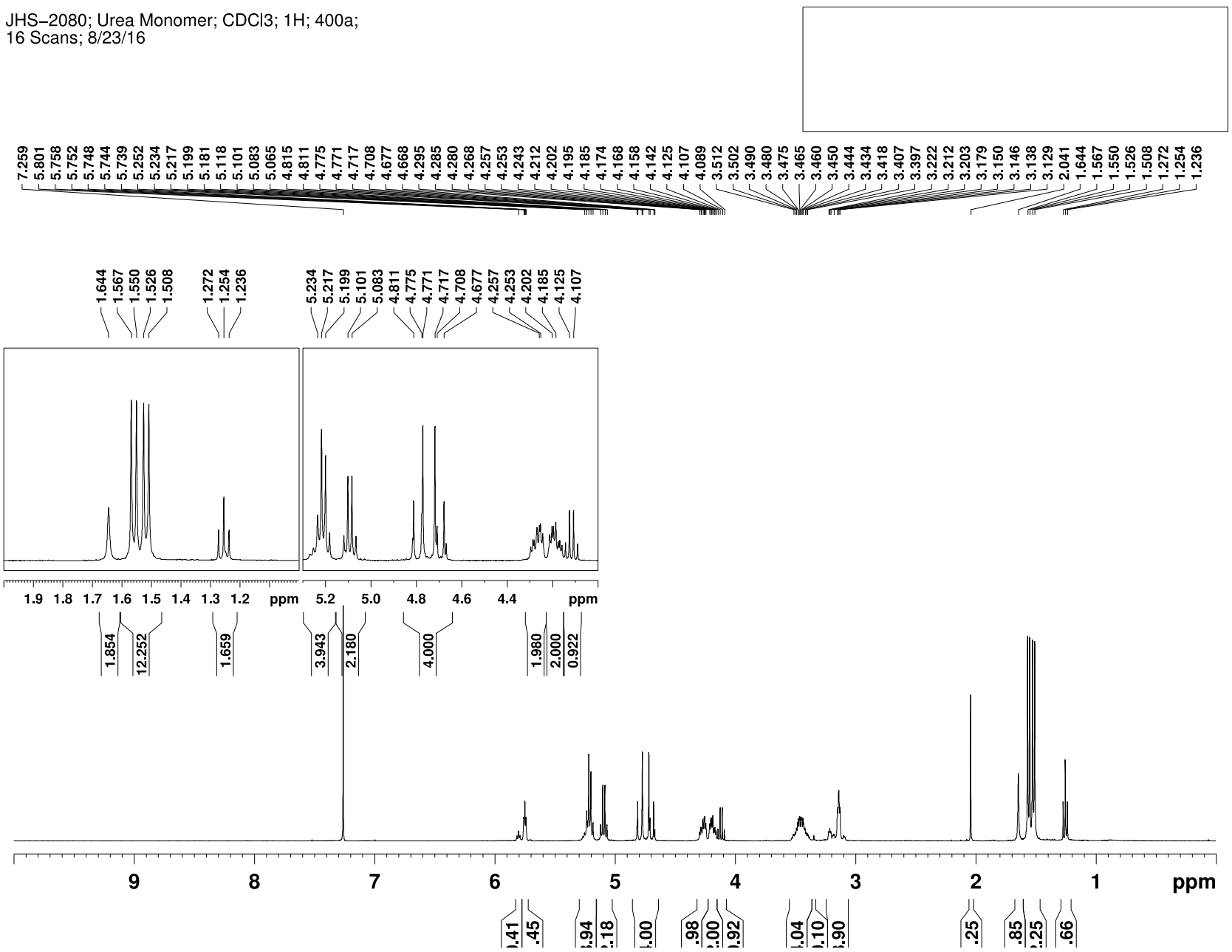
Calc.
$[M + H]^+$
661.20 amu

Found
$[M + H]^+$
661.20786 amu

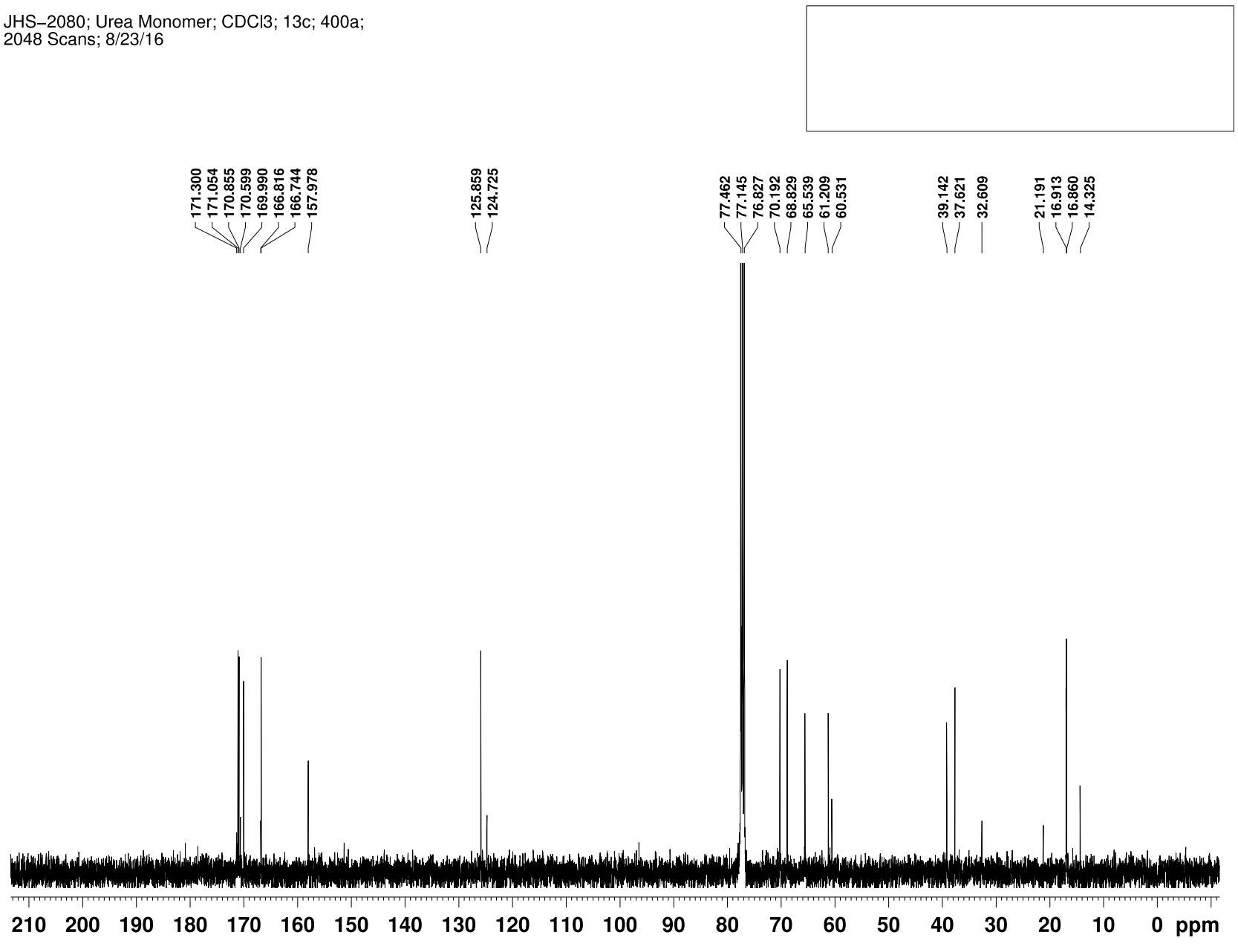
Composition
$C_{27}H_{36}O_{17}N_2$

BLGL-Urea-LGLB (300 mg, 0.44 mmol, 1 eq) was dissolved in dry DCM (435 mL, 0.001M) in a flame-dried Schlenk flask under nitrogen. A stock solution of Grubbs 2 (37 mg, 0.044 mmol, 10 mol%) in dry DCM was added and allowed to stir at RT overnight. Upon consumption of starting material by TLC, reaction mixture was quenched by addition of excess ethyl vinyl ether and stirring for 10 additional min. The reaction mixture was then concentrated and the crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a thick brown oil (252 mg, 87% yield).

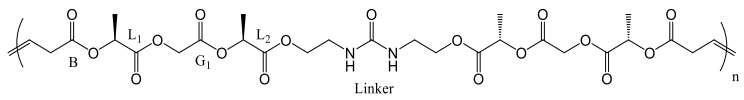
JHS–2080; Urea Monomer; CDCl3; 1H; 400a;
16 Scans; 8/23/16



JHS–2080; Urea Monomer; CDCl3; 13c; 400a;
2048 Scans; 8/23/16



Poly(Urea)



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

δ (ppm)	Mult. (J)	Int.	Assignment
1.51	d (6.8)	6	L_1 CH_3
1.56	d (6.8)	6	L_2 CH_3
3.17	m	4	B Terminal CH_2
3.43	m	4	Linker CH_2
4.16	m	2	Linker CH_2
4.27	m	2	Linker CH_2
4.29	m	4	Linker CH_2 β to S
4.73	d (16)	2	G_1
4.79	d (16)	2	G_1
5.15	m	6	L_1 & L_2 CH, Linker NH
5.75	m	2	B CH Trans

^{13}C-NMR (500 MHz, $CDCl_3$)

δ (ppm)	+ Assignment
16.86	CH_3 (L)
16.91	CH_3 (L)
37.34	CH_2 (Linker)
39.16	CH_2 (Linker)
61.05	CH_2 (G_1)
65.25	CH_2 (B)
68.74	CH (L)
69.97	CH (L)
124.41	CH (B Cis)
125.81	CH (B Trans)
158.04	CO
166.85	CO
169.95	CO
170.85	CO
170.96	CO

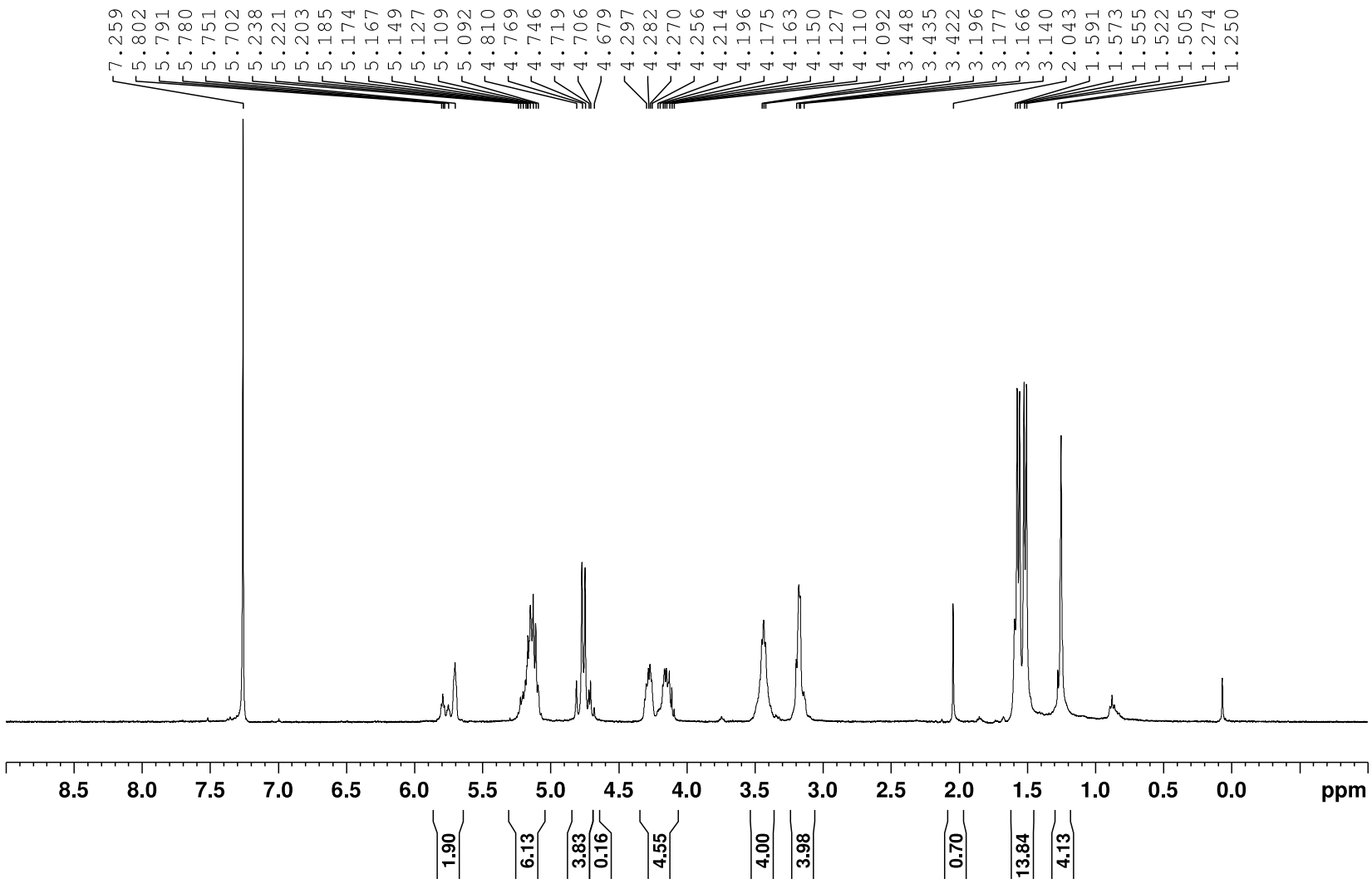
HRMS (ESI)

$\underline{M_n}$
26,596 Da

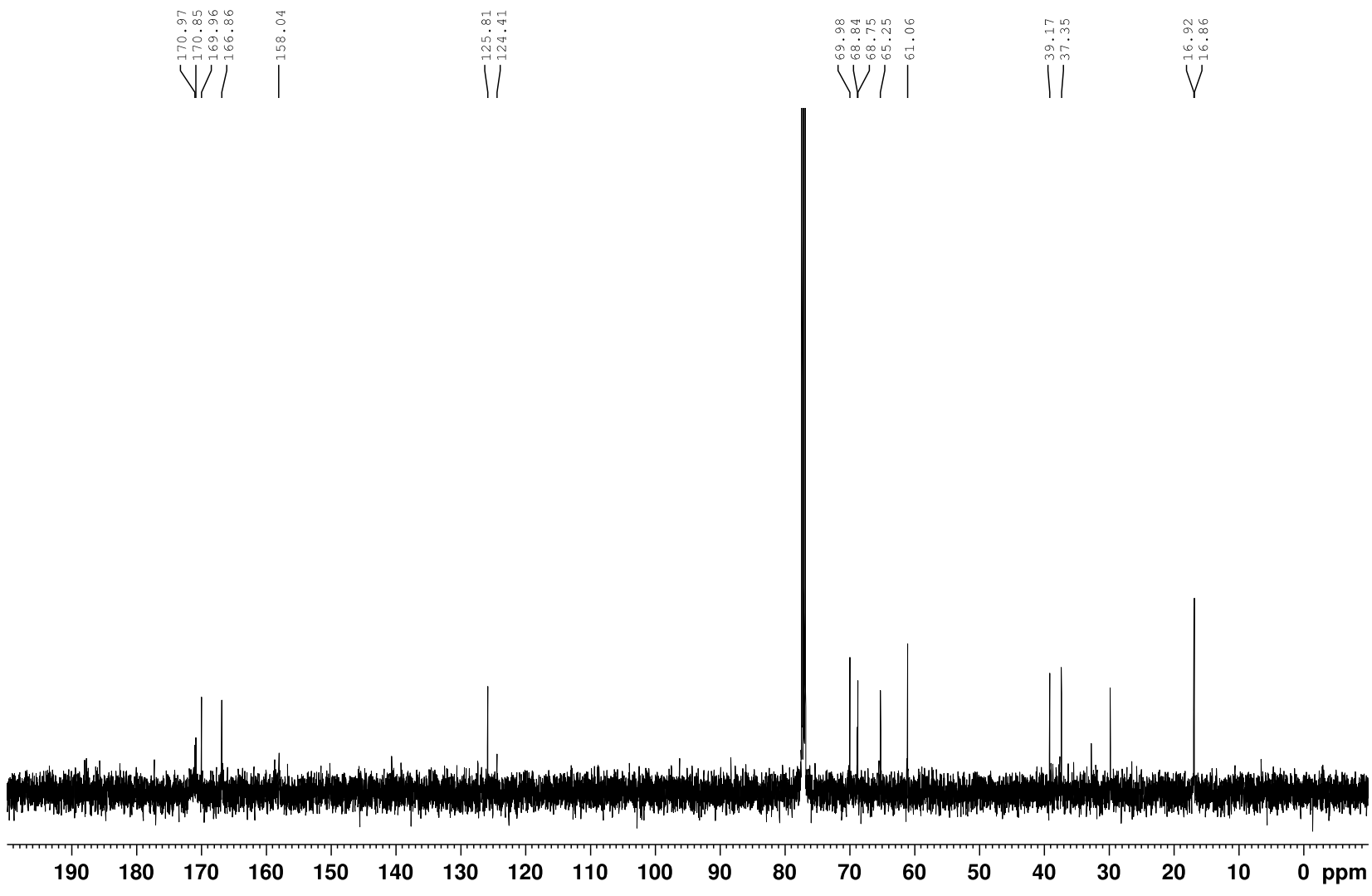
$\underline{Đ}$
1.38

Cyclic Urea Monomer (78 mg, 0.118 mmol, 1 eq.) was weighed in a flame dried 1 mL vial under nitrogen. A stock solution of Grubbs II (1 mg, 0.0012 mmol, 3 mol%) in dry DCM (5.8 mg/mL, 0.17 mL, 0.7M) was added and the vial was shaken for 4 h. The reaction mixture was quenched by the addition of excess ethyl vinyl ether and vortexing. Solution was concentrated to yield a crude solid polymer, which was reprecipitated into a stirring solution of MeOH and filtered to collect pure polymer as a brown solid (34 mg, 44% yield).

JHS-3043-Pure; Poly(Urea); CDCl3; 1H; 400a;
16 Scans; 2/28/17

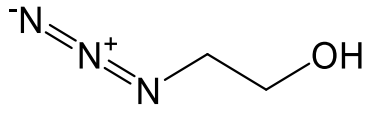


JHS-3043-500; Poly(Urea); CDCl3; 13C; 500;
256 Scans; 10/27/17



2.7 TRIAZOLE LINKER CONTAINING COMPOUNDS AND PRECURSORS

2-Azidoethanol



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

dδ (ppm)	Mult. (J Hz)	Int.	Assignment
1.90	t (5.75)	1	OH
3.45	t (4.9)	2	CH_2 (α to azide)
3.78	m (4.9, 5.75)	2	CH_2 (α to alcohol)

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

δ (ppm)	Assignment
53.66	CH_2
61.66	CH_2

HRMS (ESI)

Calc. Mass
87.04 amu

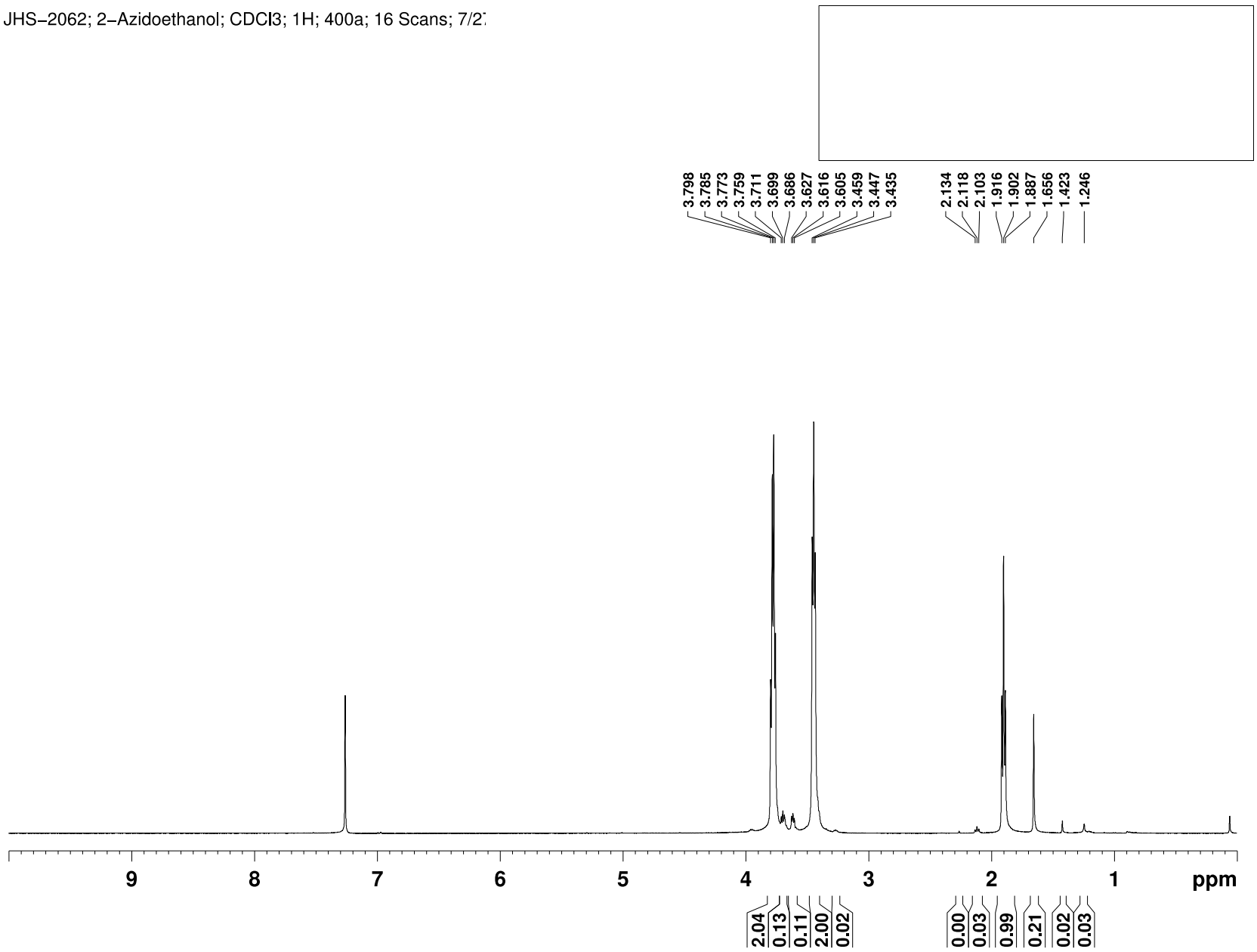
Calc.
$[M + H]^+$
88.04 amu

Found
$[M + H]^+$
88.04 amu

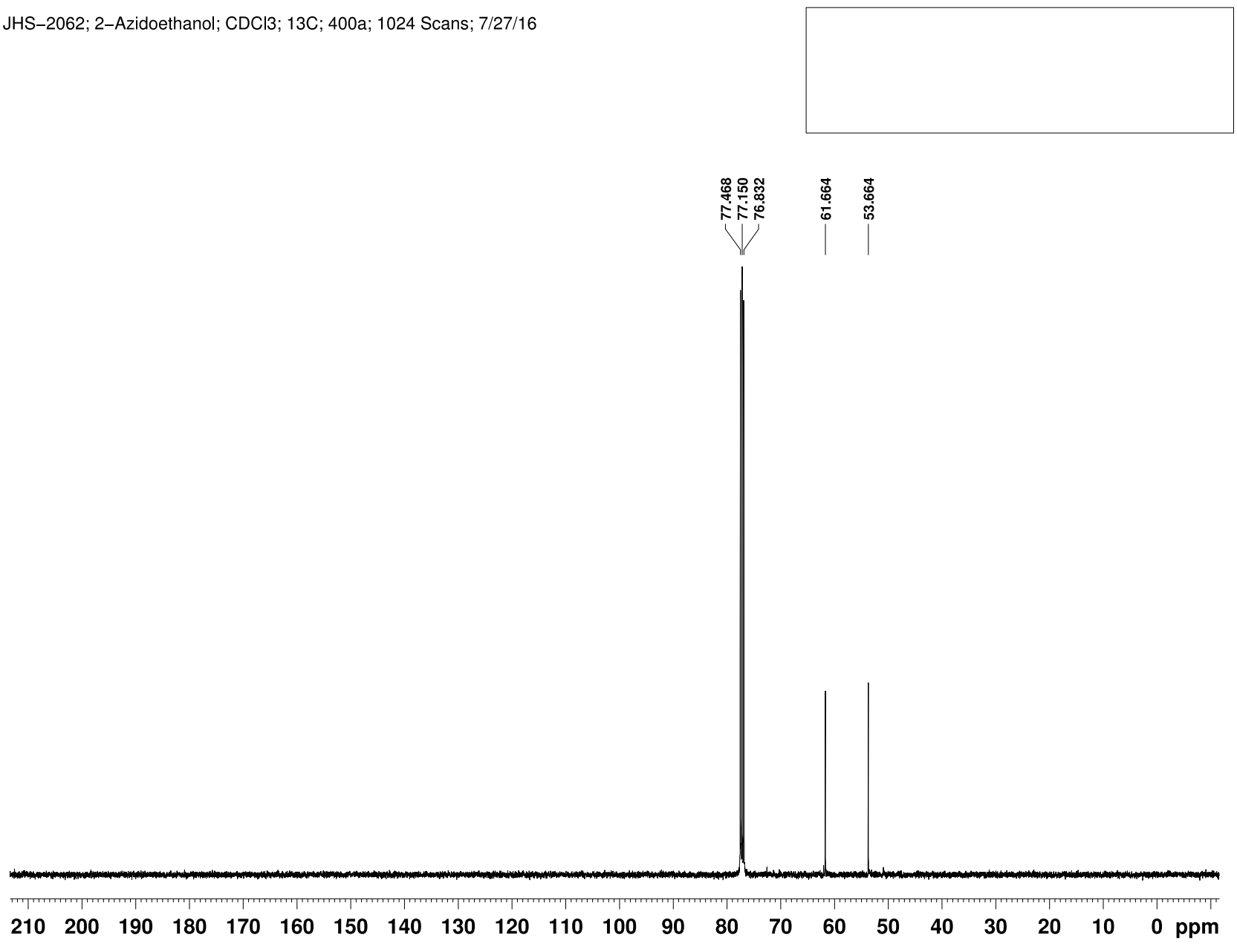
Composition
$C_2H_5N_3O$

Bromoethanol (3 g, 24 mmol, 1 eq) was dissolved in DI water (30 mL, 0.8 M) in a round bottom flask fitted with a condenser and heated to 80°C. Sodium azide (4.7 g, 72 mmol, 3 eq) was added and allowed to stir overnight at 80°C. After 20 h, reaction mixture was extracted with EtOAc 3x and the combined organic layers were dried over $MgSO_4$ and concentrated to yield an orange liquid (1.05 g, 50%).

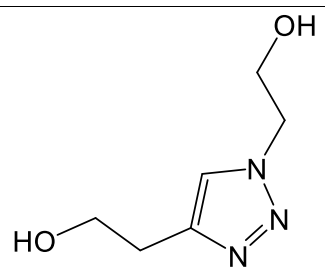
JHS–2062; 2–Azidoethanol; CDCl3; 1H; 400a; 16 Scans; 7/27



JHS–2062; 2–Azidoethanol; CDCl3; 13C; 400a; 1024 Scans; 7/27/16



Triazole Diol



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

dδ (ppm)	Mult. (J Hz)	Int.	Assignment
2.75	t (6.6)	2	CH_2 (α to alkene)
3.62	t (6.6)	2	CH_2 (α to alcohol)
3.74	t (5.2)	2	CH_2 (α to alcohol)
4.33	t (5.2)	2	CH_2 (α to N)
7.81	s	1	CH (Alkene)

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

δ (ppm) + Assignment	
28.93	CH_2
51.72	CH_2
59.66	CH_2
60.18	CH_2
122.54	Alkene
143.83	Alkene

HRMS (ESI)

Calc. Mass
157.09 amu

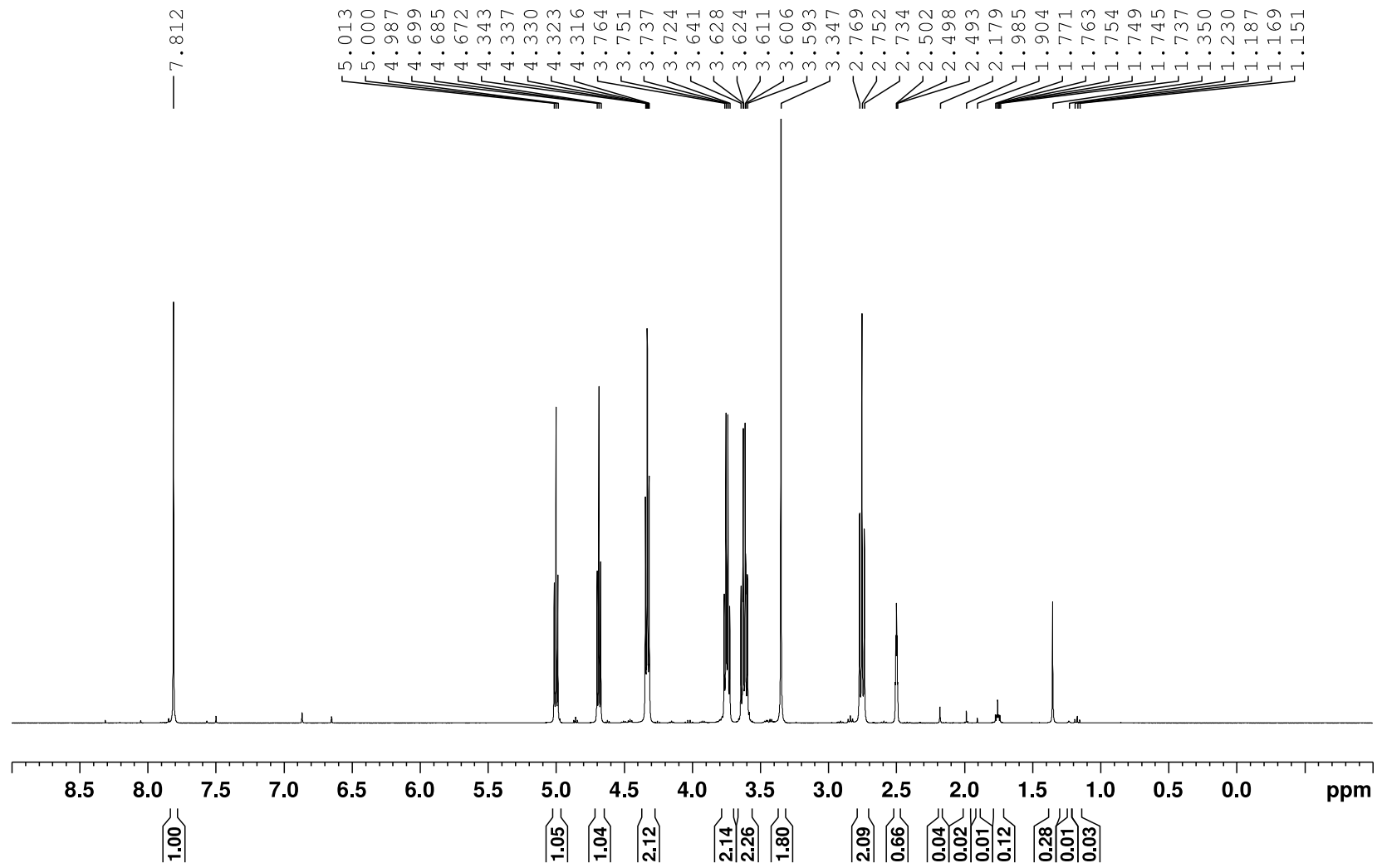
Calc.
$[M + H]^+$
158.09 amu

Found
$[M + H]^+$
158.09176 amu

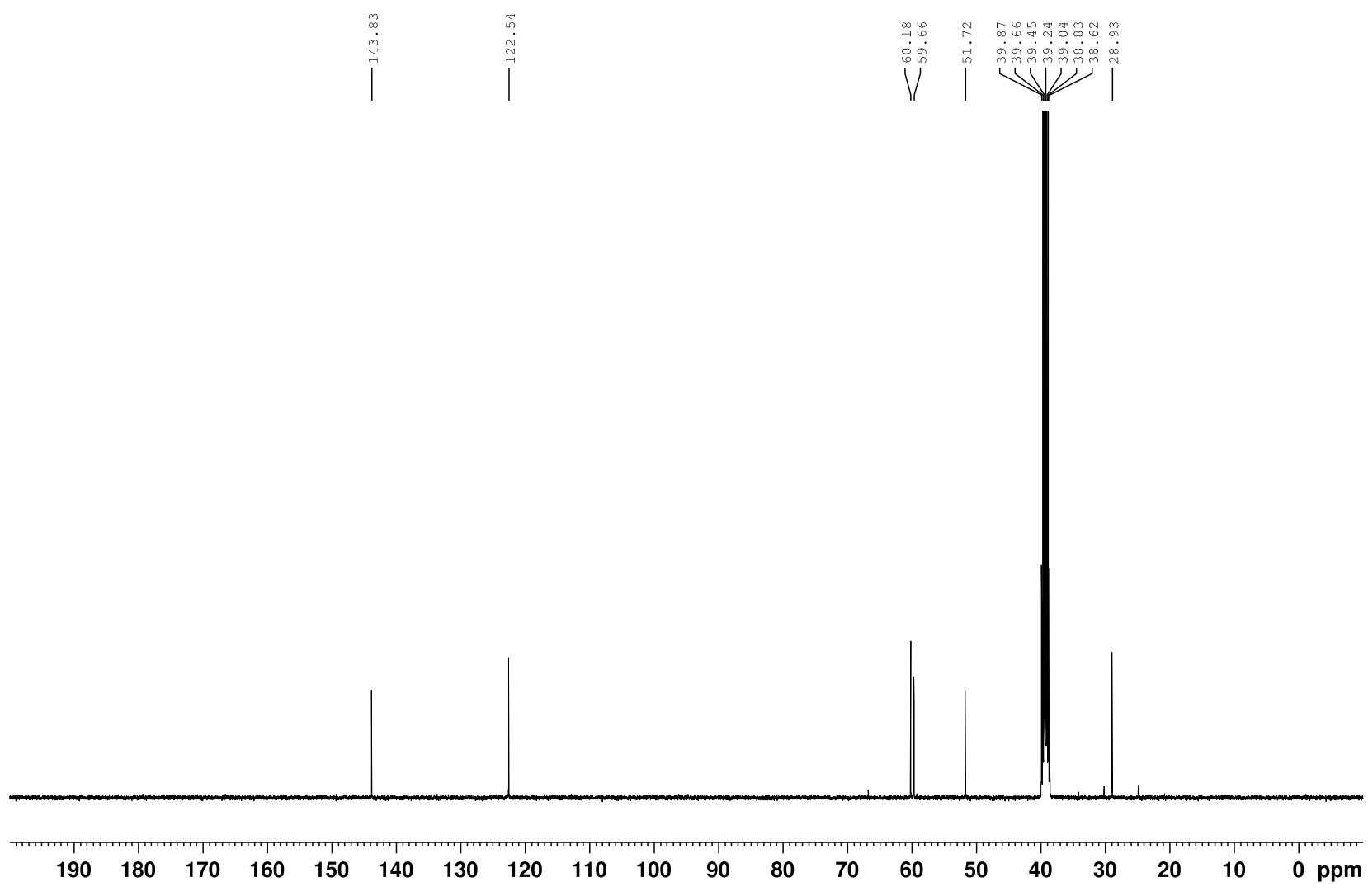
Composition
$C_6H_{11}N_3O_2$

Copper iodide (23 mg, 0.12 mmol, 0.01 eq), AcOH (14 µL, 0.24 mmol, 0.02 eq), diisopropylethylamine (42 µL, 0.24 mmol, 0.02 eq), 2-azidoethanol (1.08 g, 12.4 mmol, 1.05 eq) and 3-butyn-1-ol (0.826 g, 11.8 mmol, 1 eq) were added to a vial sequentially and allowed to stir for 10 min. Upon consumption of starting material by TLC, the reaction mixture turned dark brown and viscous, and was then run through a plug of silica with methanol and concentrated to yield a yellow oil (1.1 g, 60% yield).

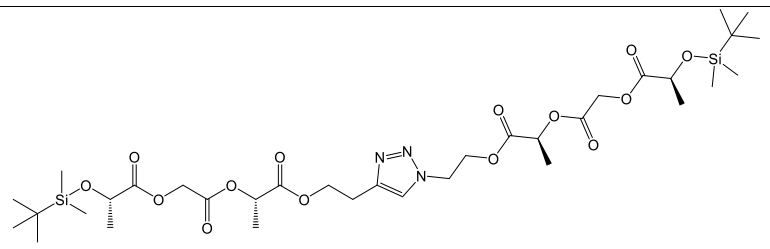
JHS-2082; TZ Diol; DMSO; 1H; 400a; 16 Scans;
8/24/16



JHS-2082; TZ Diol; DMSO; 13C; 400a; 2048 Scans
8/24/16



Si-LGL-TZ-LGL-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.09	m	12	Si (CH_3)
0.89	m	18	Si (t-Bu)
1.46	m	12	L_1 (CH_3), L_2 (CH_3)
3.09	m	2	Linker (CH_2 α-olefin)
4.44	m	4	L_1 (CH), Linker (CH_2 α-N)
4.53	m	2	Linker (CH_2 β-olefin)
4.71	m	6	G_1, Linker (CH_2 β-N)
5.10	m	2	L_2 (CH)
7.55	s	1	Linker (Olefin)

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

δ (ppm)	Assignment
-5.19	CH_3 (Si)
-4.83	CH_3 (Si)
16.79	CH_3
16.96	CH_3
18.40	CH_3
21.50	CH_3
25.46	CH_2 (Linker)
25.80	t-Bu (Si)
48.83	CH_2 (Linker)
60.62	CH_2
63.56	CH_2
64.34	CH_2
68.15	CH
69.44	CH
69.46	CH
122.74	CH (Linker)
144.07	C (Linker)
167.14	CO
167.28	CO
169.79	CO
170.06	CO
173.57	CO
173.64	CO

HRMS (ESI)

Calc. Mass
789.35 amu

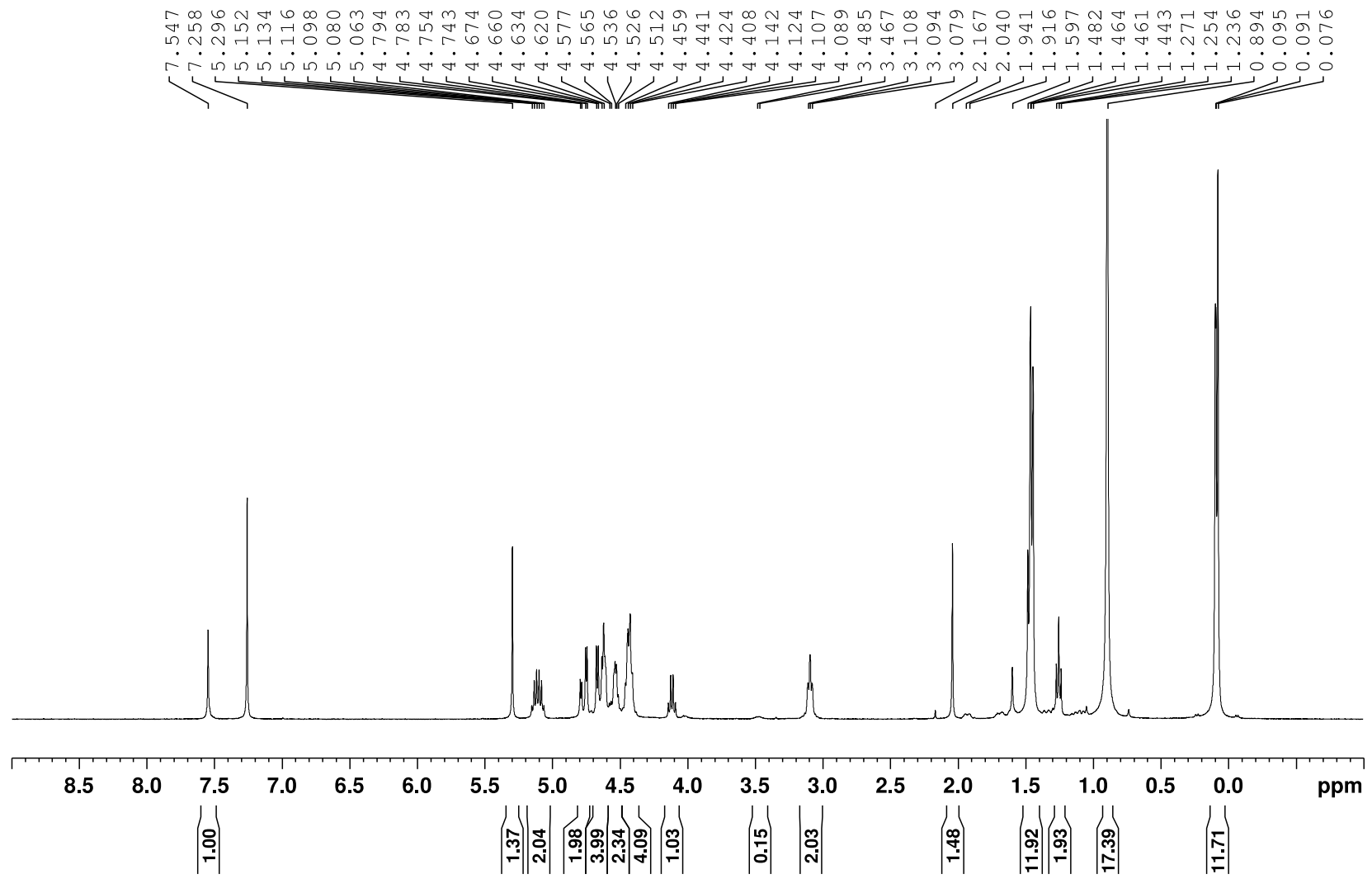
Calc.
$[M + H]^+$
790.35 amu

Found
$[M + H]^+$
790.35898 amu

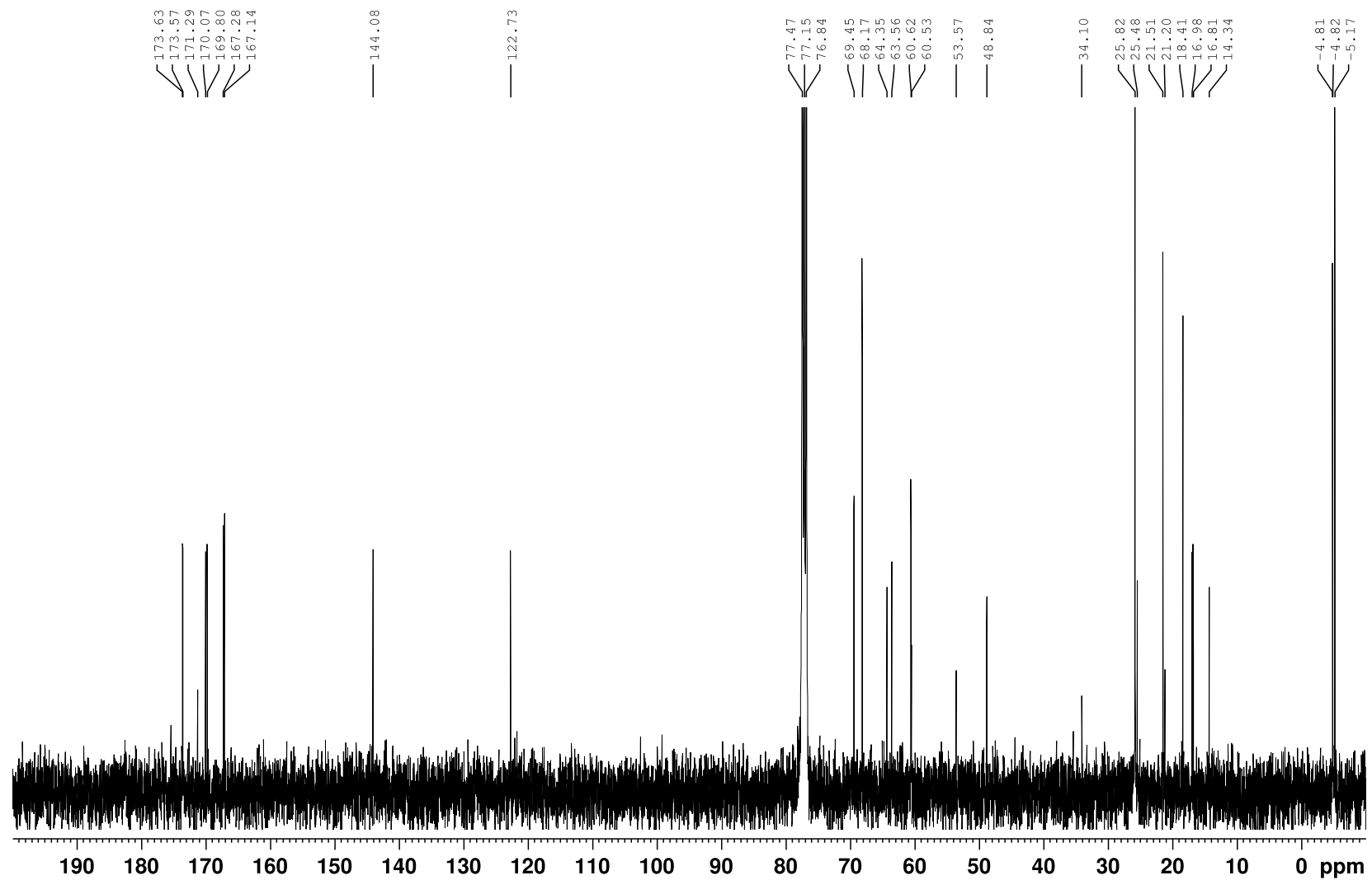
Composition
$C_{34}H_{59}N_3O_{14}Si_2$

LGL-Si (1.12 g, 3.34 mmol, 2.3 eq) and the triazole diol (0.238 g, 1.45 mmoles, 1 eq) were dissolved in dry THF (35 mL, 0.1 M) and added to a flame-dried Schlenk flask under nitrogen. DPTS (0.192 g, 0.65 mmol, 0.45 eq) and DCC (0.69 g, 3.34 mmol, 2.3 eq) were then added to the reaction mixture sequentially and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was filtered to remove DCU, concentrated and crude oil was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (0.928 g, 81% yield).

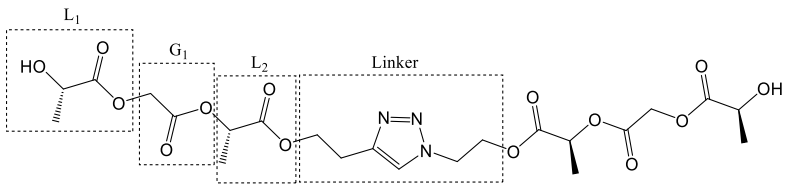
JHS-3032; Si-LGL-TZ-LGL-Si; CDCl3; 1H; 400a;
16 Scans; 11/16/16



JHS-3032; Si-LGL-TZ-LGL-Si; CDCl3; 13C; 400a;
2048 Scans; 11/16/16



LGL-TZ-LGL



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.49	m	12	L_1 (CH_3), L_2 (CH_3)
3.11	m	2	Linker (CH_2 α-olefin)
4.44	m	4	L_1 (CH), Linker (CH_2 α-N)
4.54	m	2	Linker (CH_2 β-olefin)
4.63	m	2	Linker (CH_2 β-N)
4.76	m	4	G_1
5.10	m	2	L_2 (CH)
7.53	s	1	Linker (Olefin)

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

δ (ppm)	Assignment
16.77	CH_3
16.90	CH_3
20.39	CH_3
20.41	CH_3
25.43	CH_2 (Linker)
48.84	CH_2 (Linker)
60.93	CH_2
60.98	CH_2
63.59	CH_2
64.34	CH_2
66.89	CH_2
69.59	CH
69.71	CH
122.69	CH (Linker)
144.12	C (Linker)
167.05	CO
167.09	CO
169.84	CO
170.14	CO
175.04	CO
175.05	CO

HRMS (ESI)

Calc. Mass
561.18 amu

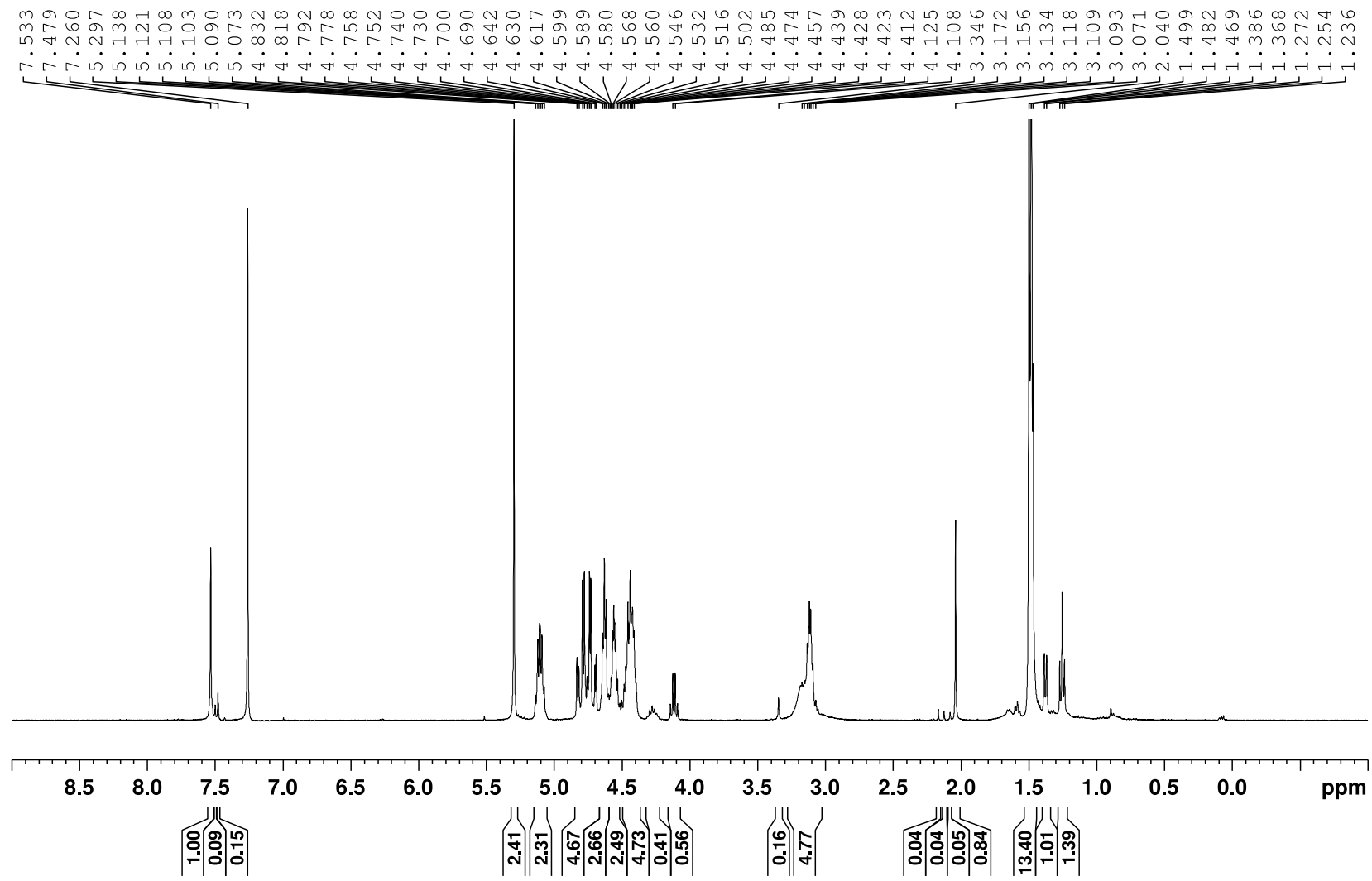
Calc.
$[M + H]^+$
562.18 amu

Found
$[M + H]^+$
562.18700 amu

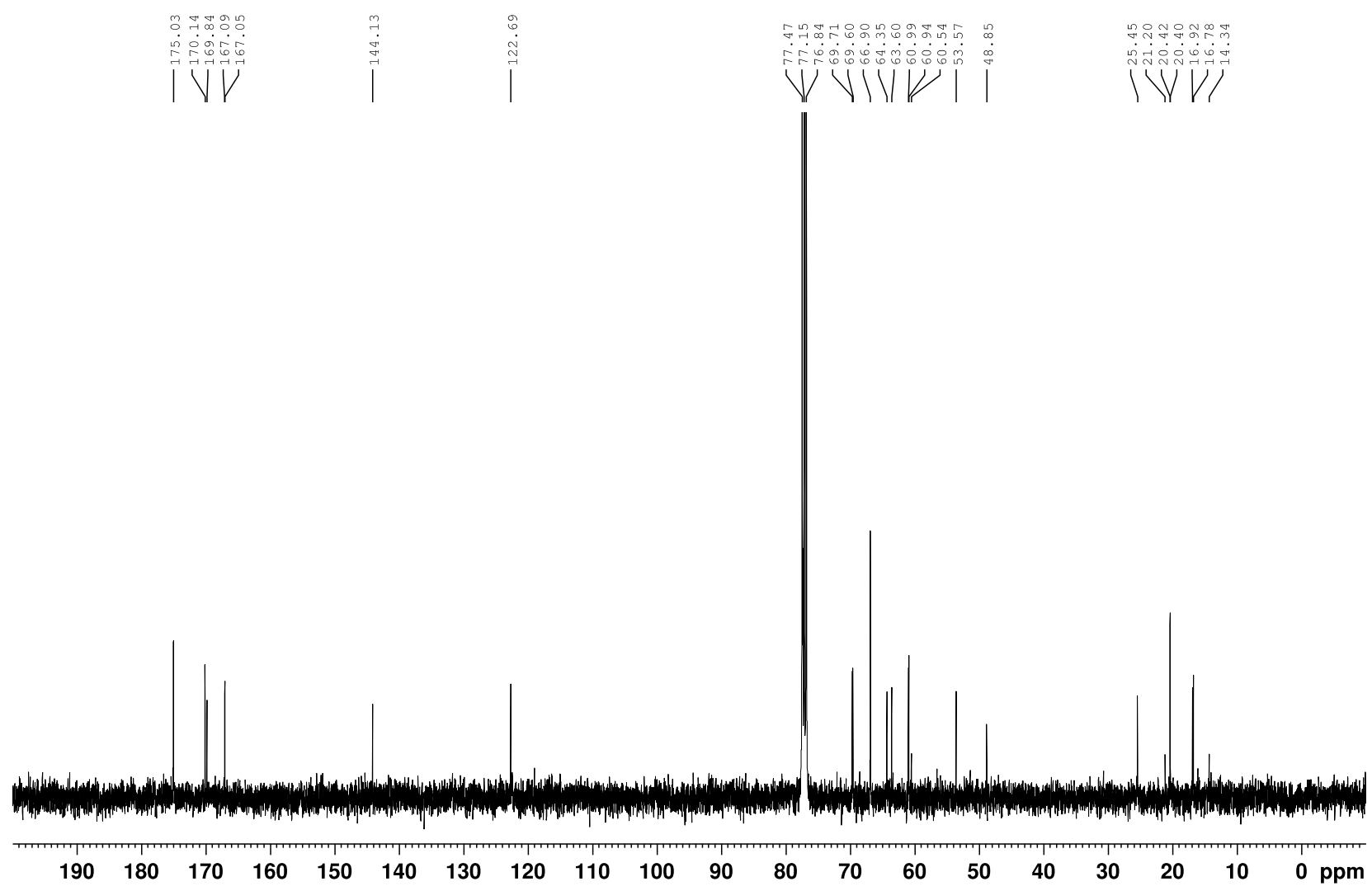
Composition
$C_{22}H_{31}O_{15}N_3$

AcOH (0.9 mL, 16 mmol, 12 eq) and TBAF (1 M in THF) (4 mL, 4 mmol, 3 eq) were dried over activated sieves for 2 h. **Si-LGL-TZ-LGL-Si** (1.04 g, 1.32 mmol, 1 eq) was dissolved in dry THF (33 mL, 0.04 M) in a flame dried Schlenk flask under nitrogen. AcOH and TBAF were added dropwise at 0°C, allowed to warm to RT and stir for 30 h. The reaction mixture was then diluted with brine and extracted with EtOAc 3x, combined organic layers were washed with brine 3x, dried over $MgSO_4$, concentrated and the crude oil was then purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (530 mg, 72% yield).

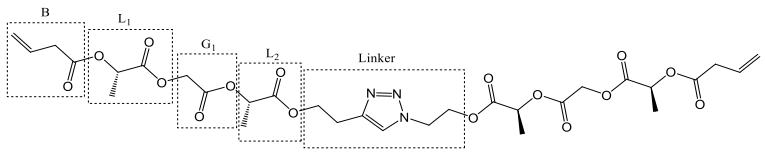
JHS-3033; LGL-TZ-LGL; CDCl3; 1H; 400a;
16 Scans; 11/18/16



JHS-3033; LGL-TZ-LGL; CDCl3; 13C; 400a;
2048 Scans; 11/18/16



BLGL-TZ-LGLB



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.47	m	6	L_1 (CH_3)
1.56	d (7.2)	6	L_2 (CH_3)
3.09	m	2	Linker (CH_2 α-olefin)
3.18	m	4	B (CH_2 α-carbonyl)
4.43	m	2	Linker (CH_2 α-N)
4.54	m	2	Linker (CH_2 β-olefin)
4.62	m	2	Linker (CH_2 β-N)
4.74	m	4	G_1
5.13	m	6	L_1 (CH), L_2 (CH), B (CH)
5.91	m	2	B (terminal olefin)
7.52	s	1	Linker (olefin)

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

δ (ppm)	+ Assignment
16.75	CH_3
16.90	CH_3
16.95	CH_3
25.45	CH_2 (Linker)
38.69	CH_2 (B)
48.85	CH_2 (Linker)
60.87	CH_2
63.56	CH_2
64.36	CH_2
68.52	CH_2
69.52	CH
69.57	CH
119.14	Olefin (B)
122.71	CH (Linker)
129.69	CH (B)
144.06	C (Linker)
166.83	CO
166.94	CO
169.74	CO
170.01	CO
170.27	CO
170.32	CO
170.96	CO
170.99	CO

HRMS (ESI)

Calc. Mass
697.23 amu

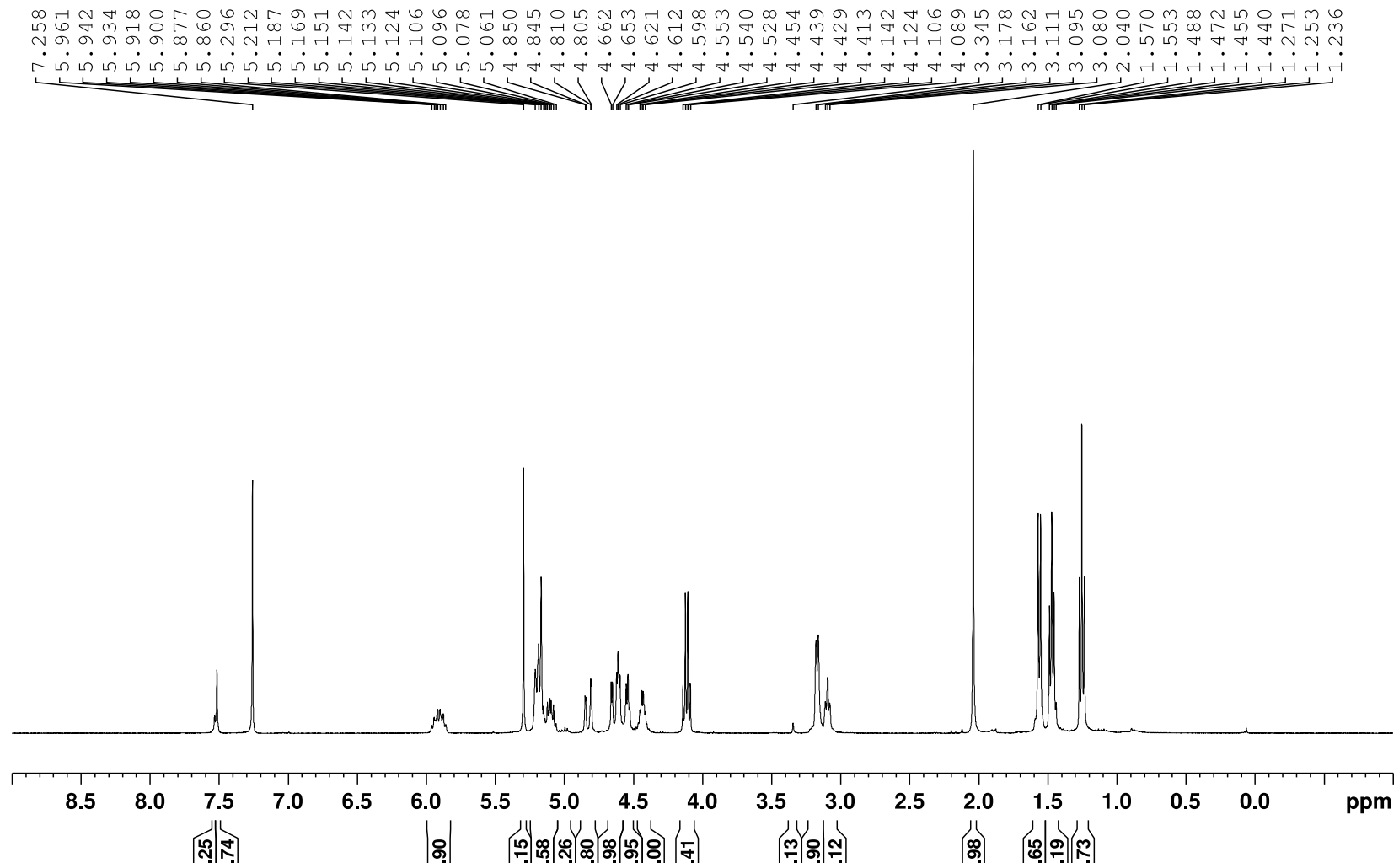
Calc.
$[M + H]^+$
698.23 amu

Found
$[M + H]^+$
698.23901 amu

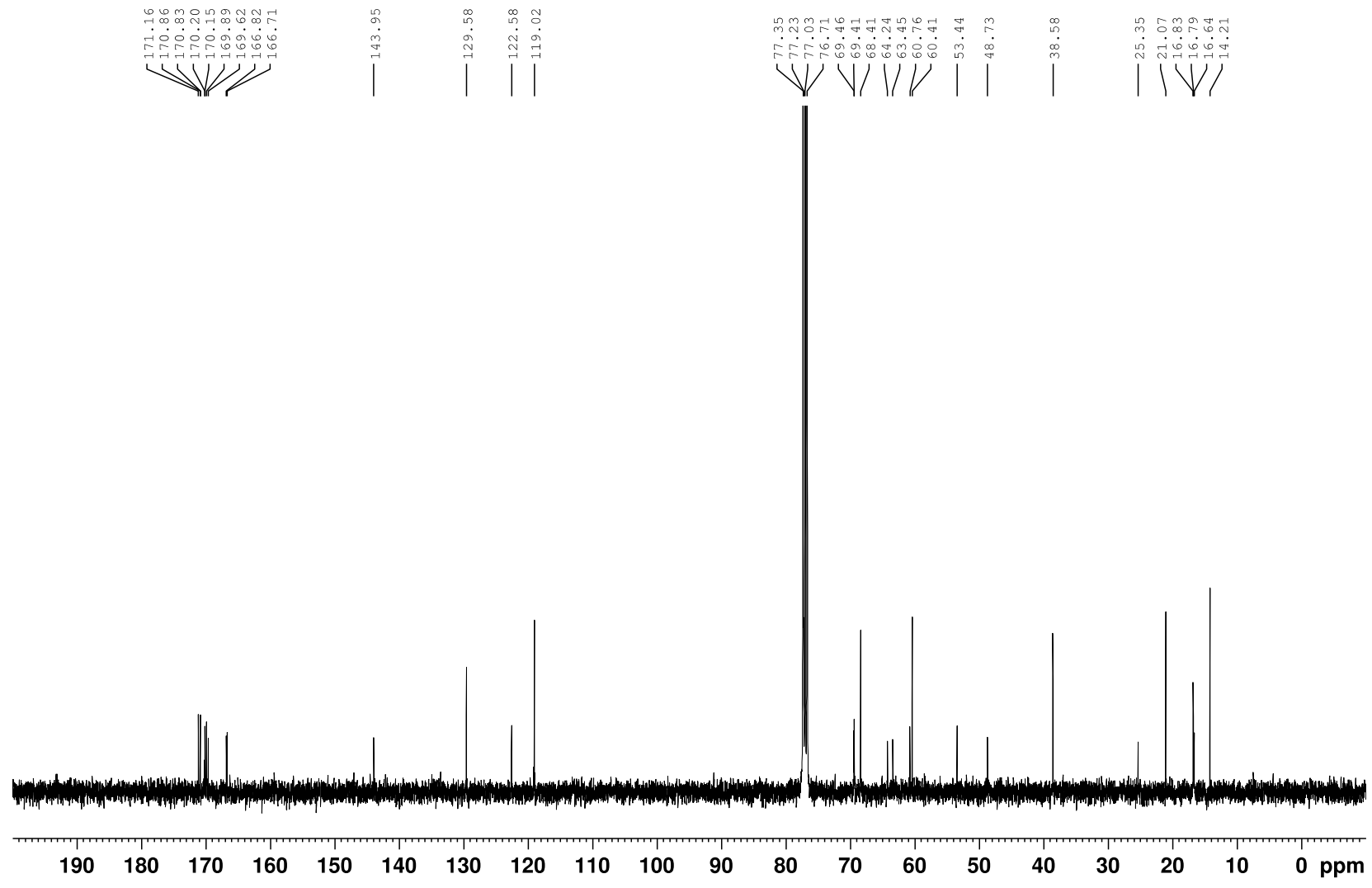
Composition
$C_{22}H_{31}O_{15}N_3$

LGL-TZ-LGL (530 mg, 0.94 mmol, 1 eq) was dissolved in dry THF (10 mL, 0.1 M) in an oven dried vial under nitrogen. DPTS (127 mg, 0.43 mmol, 0.45 eq) and DCC (0.59 g, 2.8 mmol, 3 eq) were added sequentially. Butenoic acid (0.244 g, 2.8 mmol, 3 eq) was then added dropwise and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes, washed with sodium bicarbonate 3x, dried over $MgSO_4$ and filtered to remove DCU and drying agent, concentrated, and crude oil was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (645 mg, 98% yield).

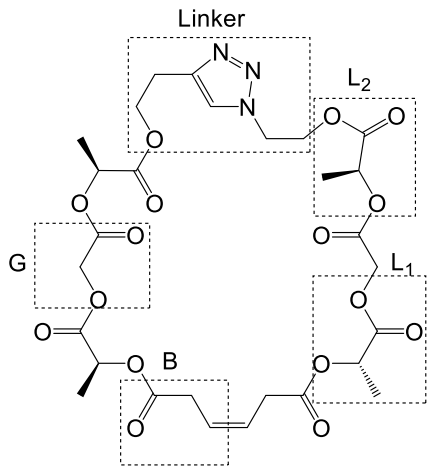
JHS-3034; BLGL-TZ-LGLB; CDCl3; 1H; 400a;
16 Scans; 11/21/16



JHS-3034; BLGL-TZ-LGLB; CDCl3; 13C; 400a;
2048 Scans; 11/21/16



Cyclic TZ Monomer



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.47	m	6	L_1 (CH_3)
1.54	d (7.2)	6	L_2 (CH_3)
3.13	m	6	Linker (CH_2), B (CH_2)
4.43	m	1	Linker (CH_2)
4.49	m	3	Linker (CH_2, CH_2)
4.62	m	3	Linker (CH_2, CH_2)
4.72	m	4	G
5.09	m	6	L_1 (CH)
5.20	m	2	L_2 (CH)
5.77	m	2	B (CH)
7.60	s	1	Linker (olefin)

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

δ (ppm)	+ Assignment
16.71	CH_3
16.86	CH_3, CH_3
16.88	CH_3
25.53	CH_2 (Linker)
37.57	CH_2 (B)
48.88	CH_2 (Linker)
60.98	CH_2
61.00	CH_2
63.72	CH_2
64.41	CH_2
68.61	CH
68.65	CH
69.65	CH
69.68	CH
123.07	CH (Cis)
124.73	CH
125.79	CH
125.80	CH
144.17	C
166.74	CO
166.94	CO
169.79	CO
170.02	CO
170.10	CO
170.20	CO
170.44	CO
170.67	CO

HRMS (ESI)

Calc. Mass
669.20 amu

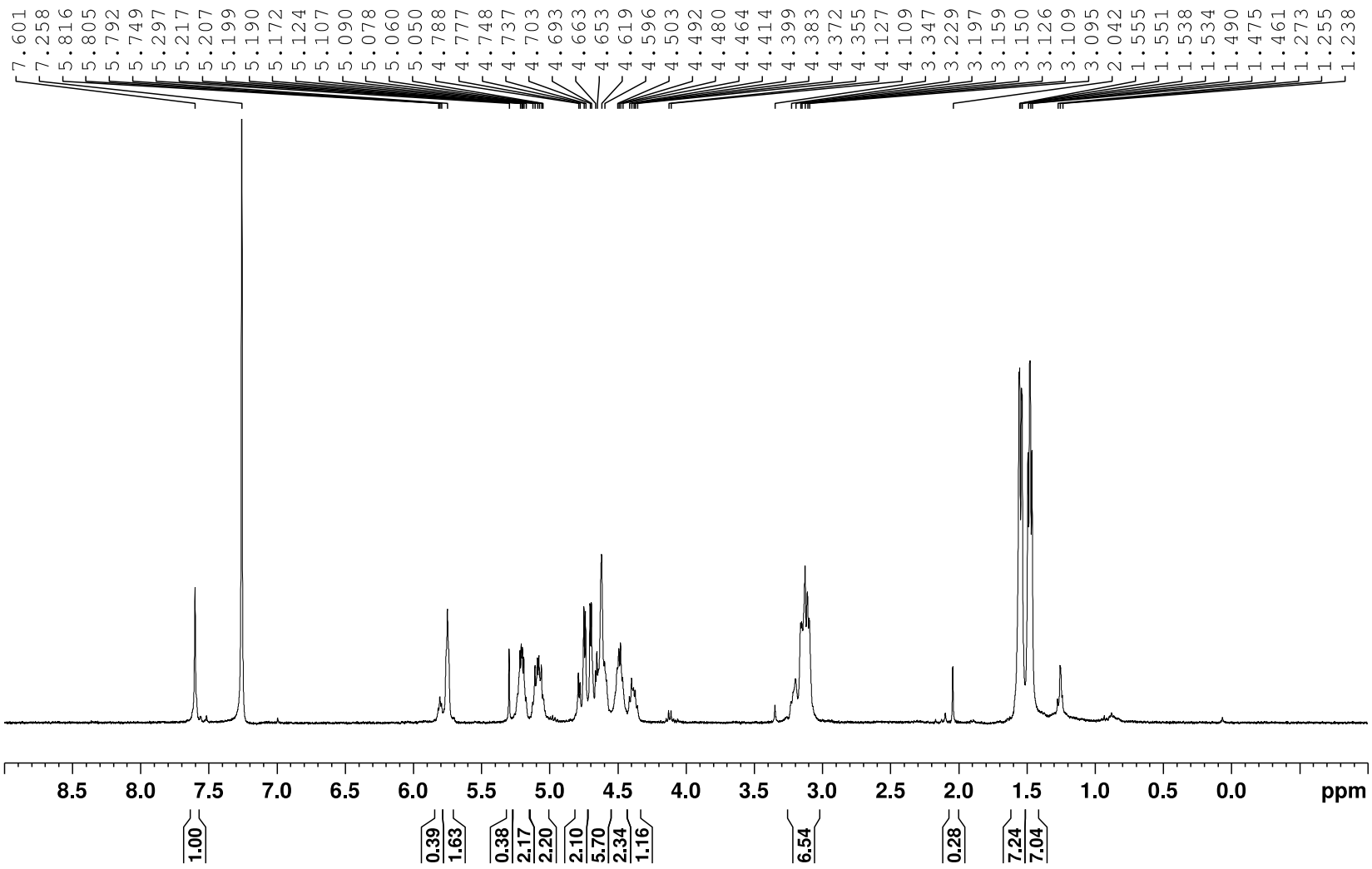
Calc.
$[M + H]^+$
670.20 amu

Found
$[M + H]^+$
670.20783 amu

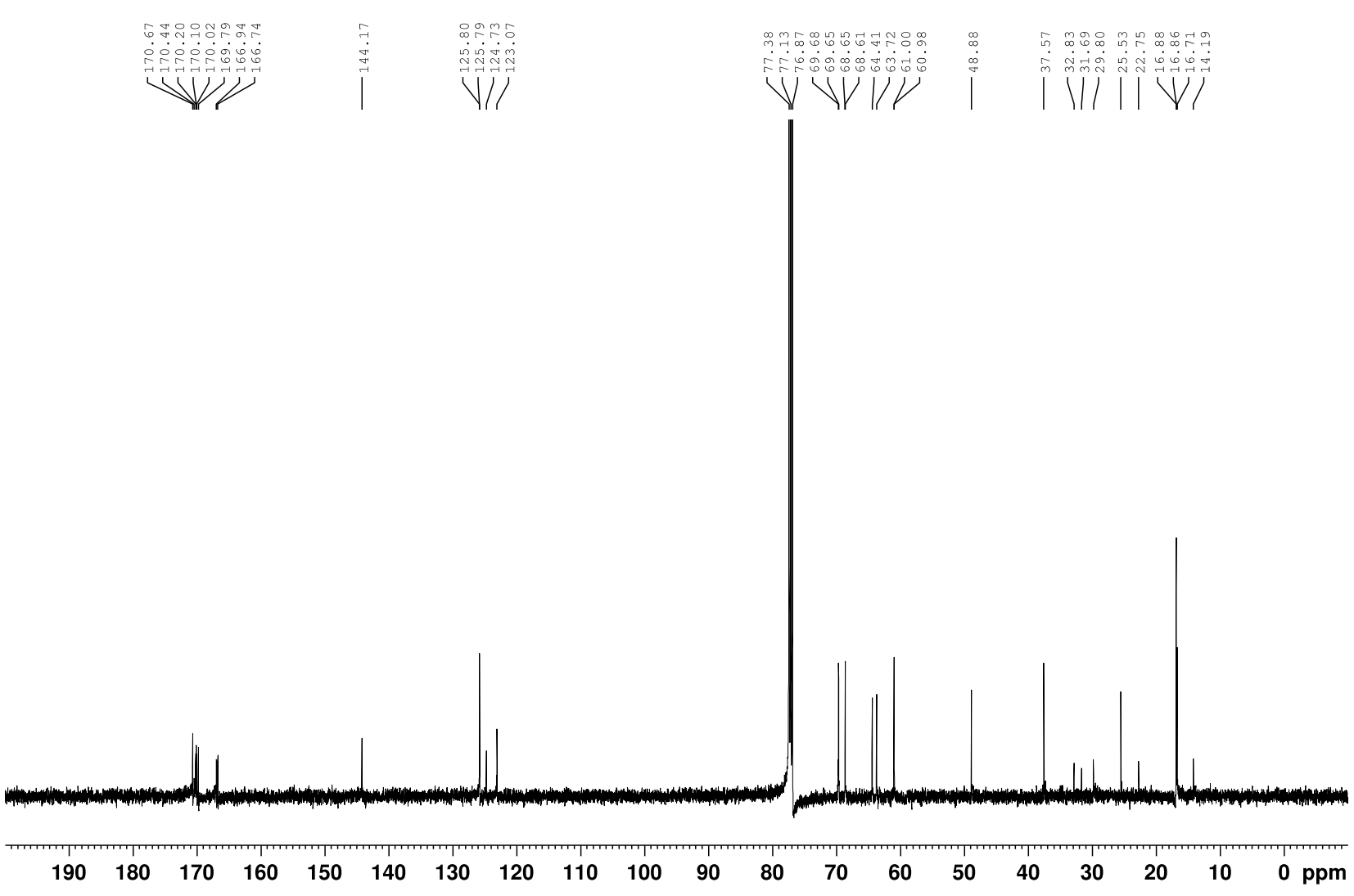
Composition
$C_{28}H_{35}O_{16}N_3$

BLGL-TZ-LGLB (640 mg, 0.92 mmol, 1 eq) was dissolved in dry DCM (920 mL, 0.001M) in a flame-dried Schlenk flask under nitrogen. A stock solution of Grubbs 2 (117 mg, 0.14 mmol, 15 mol%) in dry DCM was added and allowed to stir at RT overnight. Upon consumption of starting material by TLC, reaction mixture was quenched by addition of excess ethyl vinyl ether and stirring for 10 additional min. The reaction mixture was then concentrated and the crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a thick brown oil (376 mg, 61% yield).

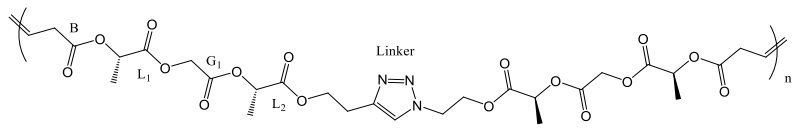
JHS-3035; TZ Monomer; CDCl3; 1H; 400a;
16 Scans; 12/2/16



JHS-3003; TZ Mon; CDCl3; 1H;
500; 16 Scans; 7/19/17



Poly(TZ)



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

δ (ppm)	Mult. (J)	Int.	Assignment
1.47	m	6	CH_3 (L)
1.55	d (6.8)	6	CH_3 (L)
3.08	t (7.6)	2	CH_2 (Linker)
3.17	m	4	CH_2 (B)
4.43	t (6.3)	2	CH_2 (Linker)
4.54	m	2	CH_2 (Linker)
4.63	m	4	CH_2 (G_1, Linker)
4.83	m	2	CH_2 (G_1)
5.13	m	4	CH ($L_{1/2}$)
5.70	m	1.6	CH (B Trans)
5.79	m	0.4	CH (B Cis)
7.52	s	1	CH (Linker)

^{13}C-NMR (500 MHz, $CDCl_3$)

δ (ppm)	+ Assignment
16.64	CH_3 (L)
16.78	CH_3 (L)
16.82	CH_3 (L)
25.34	CH_2 (Linker)
32.64	CH_2 (Linker)
37.25	CH_2 (Linker)
48.74	CH_2 (Linker)
60.76	CH_2 (G_1)
60.78	CH_2 (G_1)
63.43	CH_2 (B)
64.2	CH_2 (B)
68.47	CH (L)
68.55	CH (L)
69.38	CH (L)
69.46	CH (L)
122.54	CH (Linker)
124.29	CH (B Cis)
125.71	CH (B Trans)
143.91	C (Linker)
166.70	CO
166.79	CO
169.58	CO
169.86	CO
170.09	CO
170.14	CO
170.75	CO
170.76	CO

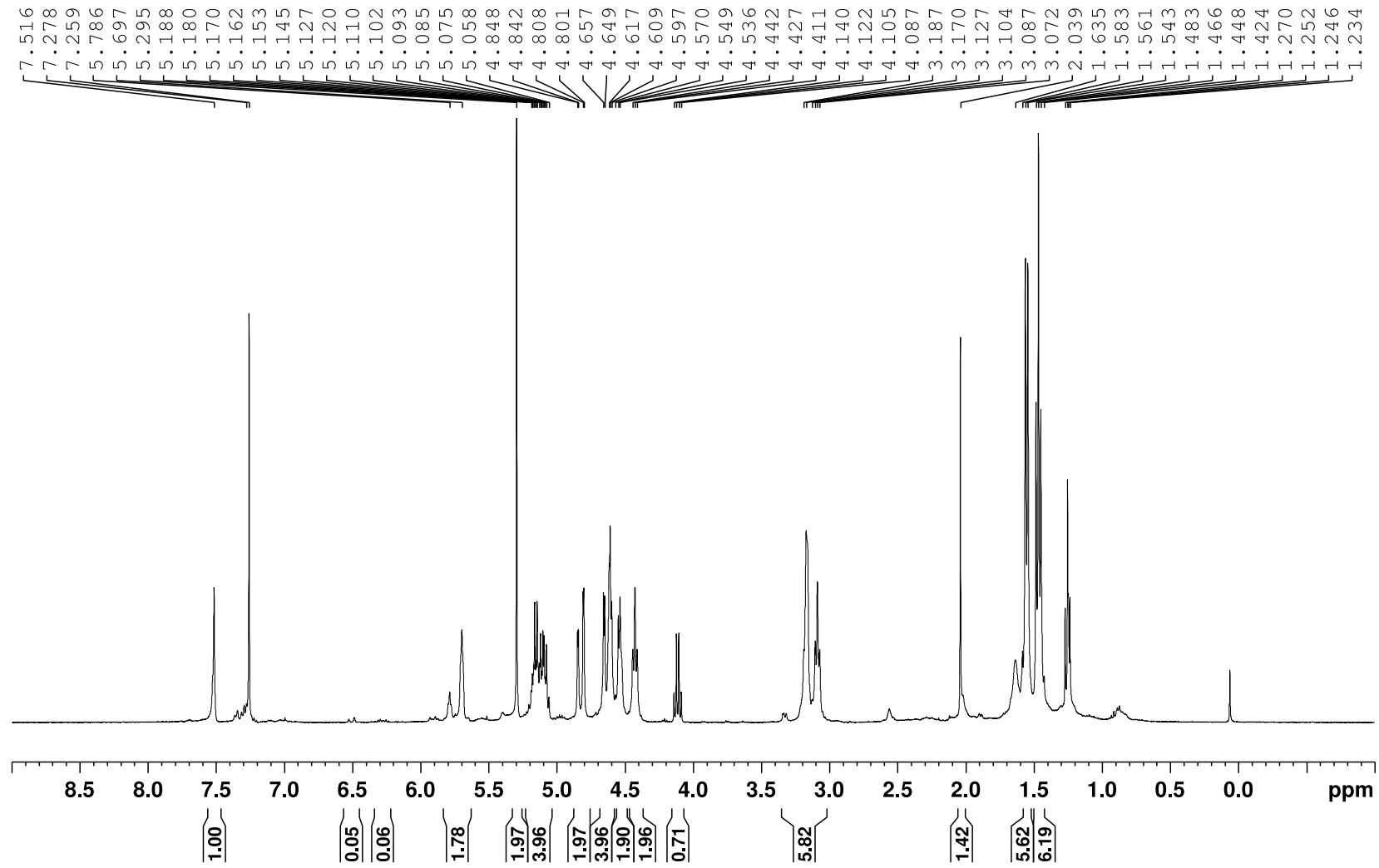
HRMS (ESI)

$\underline{M_n}$
9,973 Da

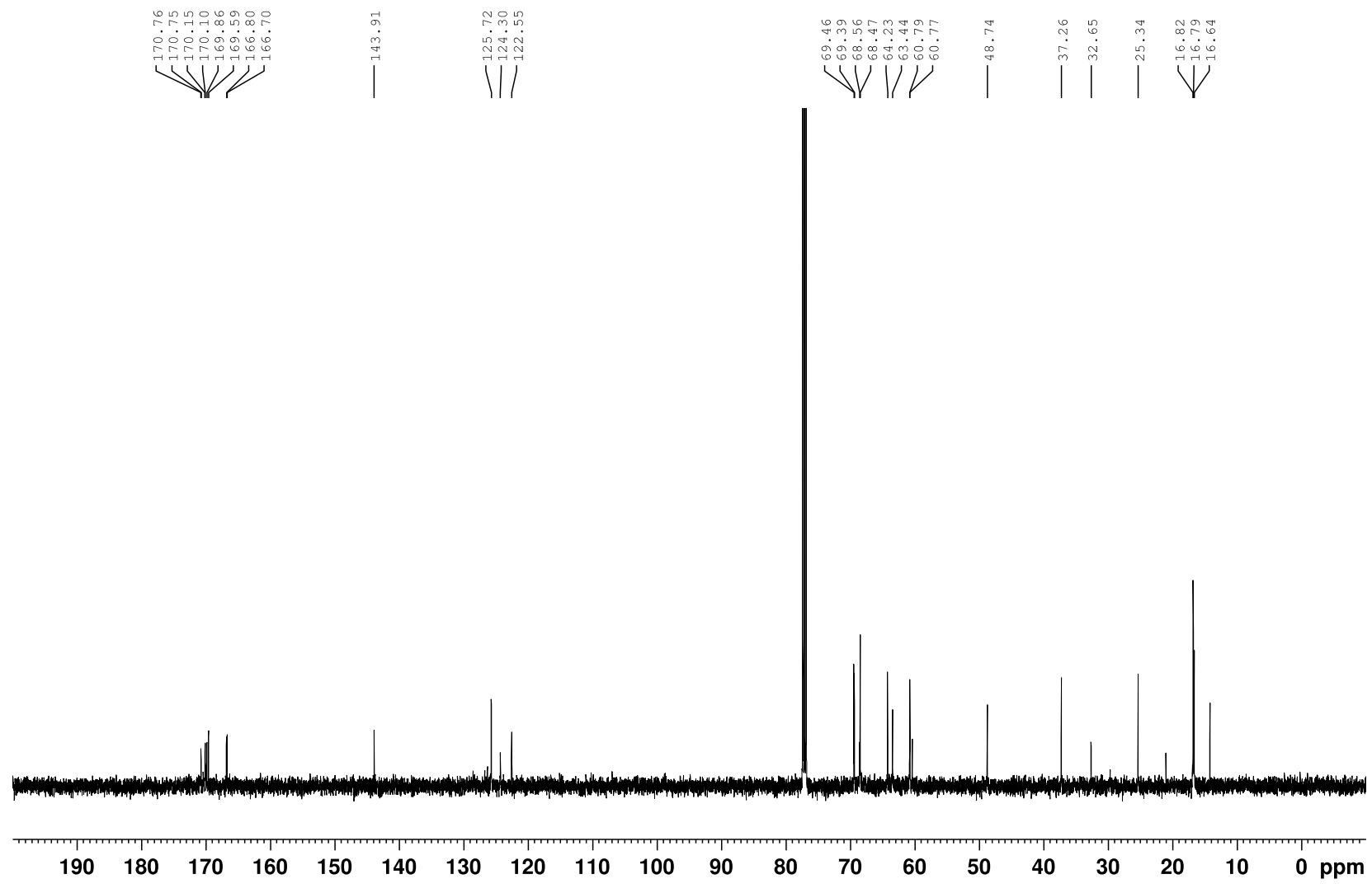
$\underline{Đ}$
1.60

Cyclic TZ Monomer (235 mg, 0.35 mmol, 1 eq.) was weighed in a flame dried 1 mL vial under nitrogen. A stock solution of Grubbs II (14.9 mg, 0.0185 mmol, 5 mol%) in dry THF (42.6 mg/mL, 0.35 mL, 1 M) was added and the vial was stirred at 60°C for 4 h. The reaction mixture was quenched by the addition of excess ethyl vinyl ether and vortexing. Solution was concentrated to yield a crude solid polymer, which was reprecipitated into a stirring solution of MeOH and filtered to collect pure polymer as a brown solid (160 mg, 68% yield).

JHS-4061; Poly(TZ) Pure; CDCl3; 1H; 400a;
16 Scans; 7/31/17

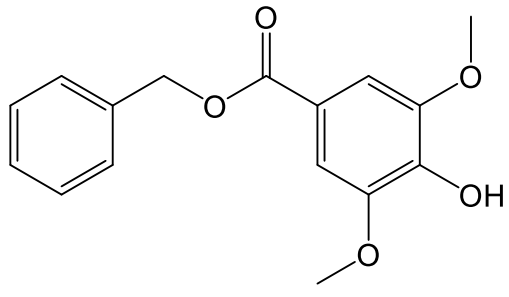


JHS-4061; Poly(TZ); CDCl3; 13C; 500; 64 Scans;
10/27/17



2.8 SY LINKER CONTAINING COMPOUNDS AND PRECURSORS

Bn-Syringic Acid



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

dδ (ppm)	Mult. (J)	Int.	Assignment
3.93	s	6	CH_3
5.36	s	2	CH_2
5.90	s	1	OH
7.39	m	7	Aromatic

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

δ (ppm) + Assignment	
56.48	CH_3
66.69	CH_2
106.78	Aromatic
121.08	Aromatic
128.21	Aromatic
128.24	Aromatic
128.62	Aromatic
136.24	Aromatic
139.32	Aromatic
146.63	Aromatic
166.27	CO

HRMS (ESI)

Calc. Mass
288.10 amu

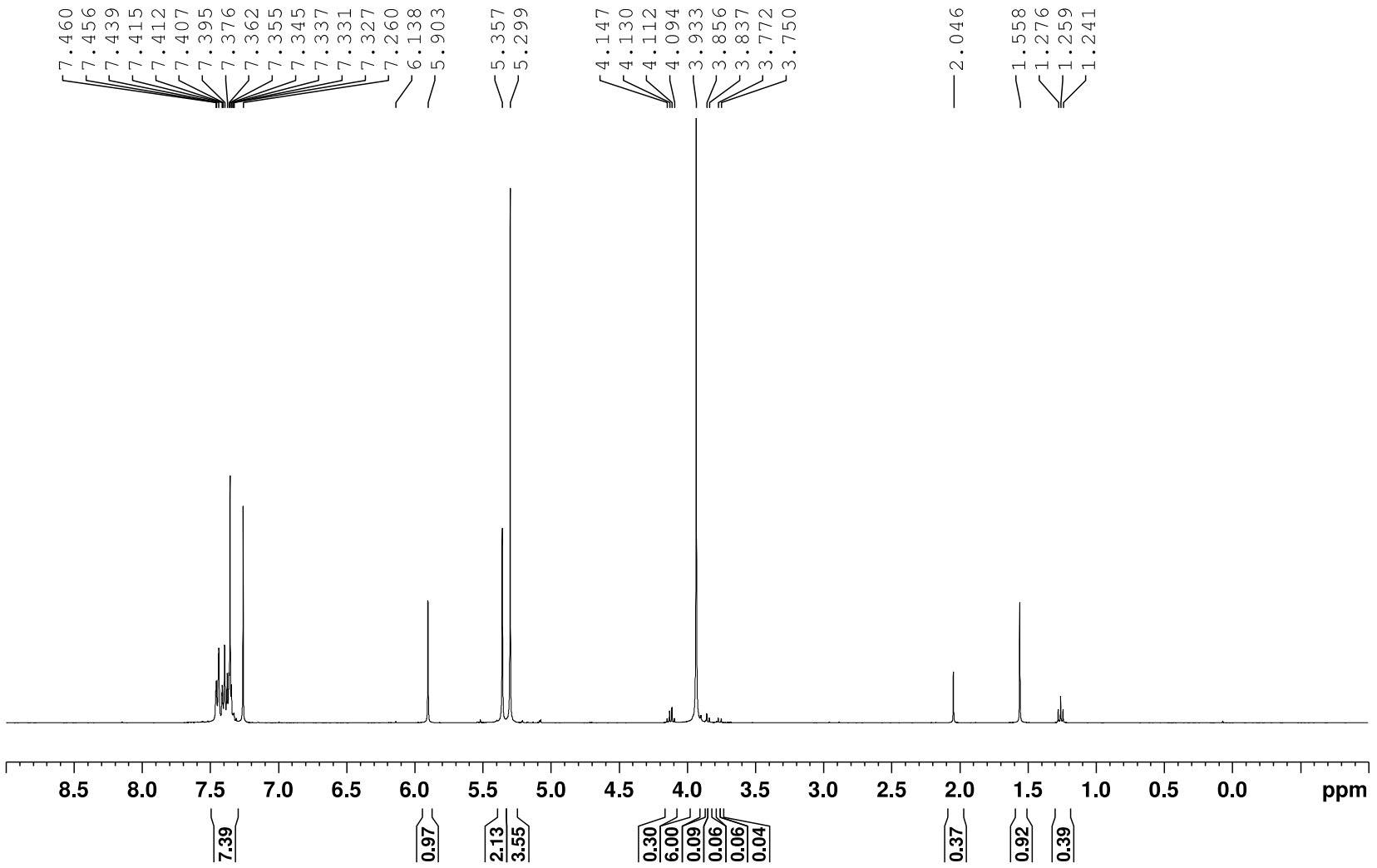
Calc.
$[M + H]^+$
289.10 amu

Found
$[M + H]^+$
289.10803 amu

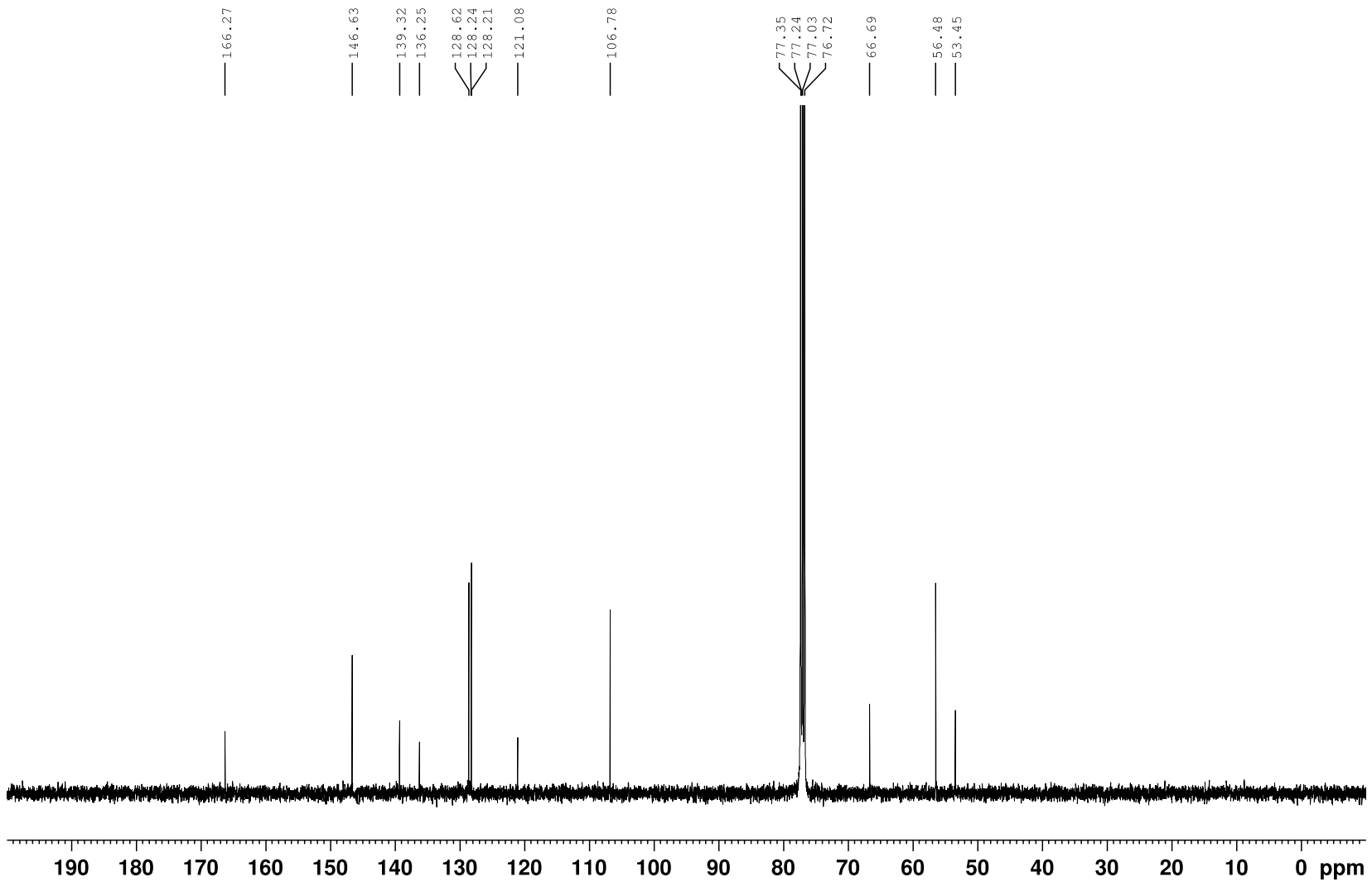
Composition
$C_{16}H_{17}O_5$

Syringic acid (10 g, 0.051 mol, 1.1 eq) and potassium carbonate (7.01 g, 0.051 mol, 1.1 eq) were dissolved in dry DMF (200 mL, 0.25 M) in a flame-dried Schlenk flask under nitrogen and allowed to stir at RT for 1 h. BnBr (7.885 g, 0.046 mol, 1 eq) was added to the flask and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with water, washed with EtOAc 3x, combined organic layer was washed with sodium bicarbonate 3x, dried over $MgSO_4$ and concentrated to yield a white solid (9.89 g, 68% yield).

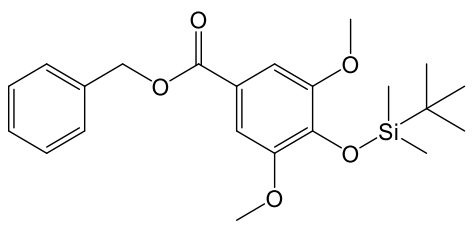
JHS-3013; Bn-Sy; CDCl3; 1H; 400a; 16 Scans;
10/5/16



JHS-3013; Bn-Sy; CDCl3; 13C; 400a; 2048 Scans;
10/5/16



Bn-Syringic Acid-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.14	s	6	CH_3
1.00	s	9	CH_3
3.83	s	6	CH_3
5.35	s	2	CH_2
7.39	m	7	Aromatic

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

δ (ppm) + Assignment	
-4.50	CH_3 (Si)
18.88	C (Si)
25.82	CH_3 (Si)
55.93	CH_3
66.71	CH_2
107.01	Aromatic
122.28	Aromatic
128.29	Aromatic
128.31	Aromatic
128.69	Aromatic
136.41	Aromatic
139.26	Aromatic
151.38	Aromatic
166.54	CO

HRMS (ESI)

Calc. Mass
402.19 amu

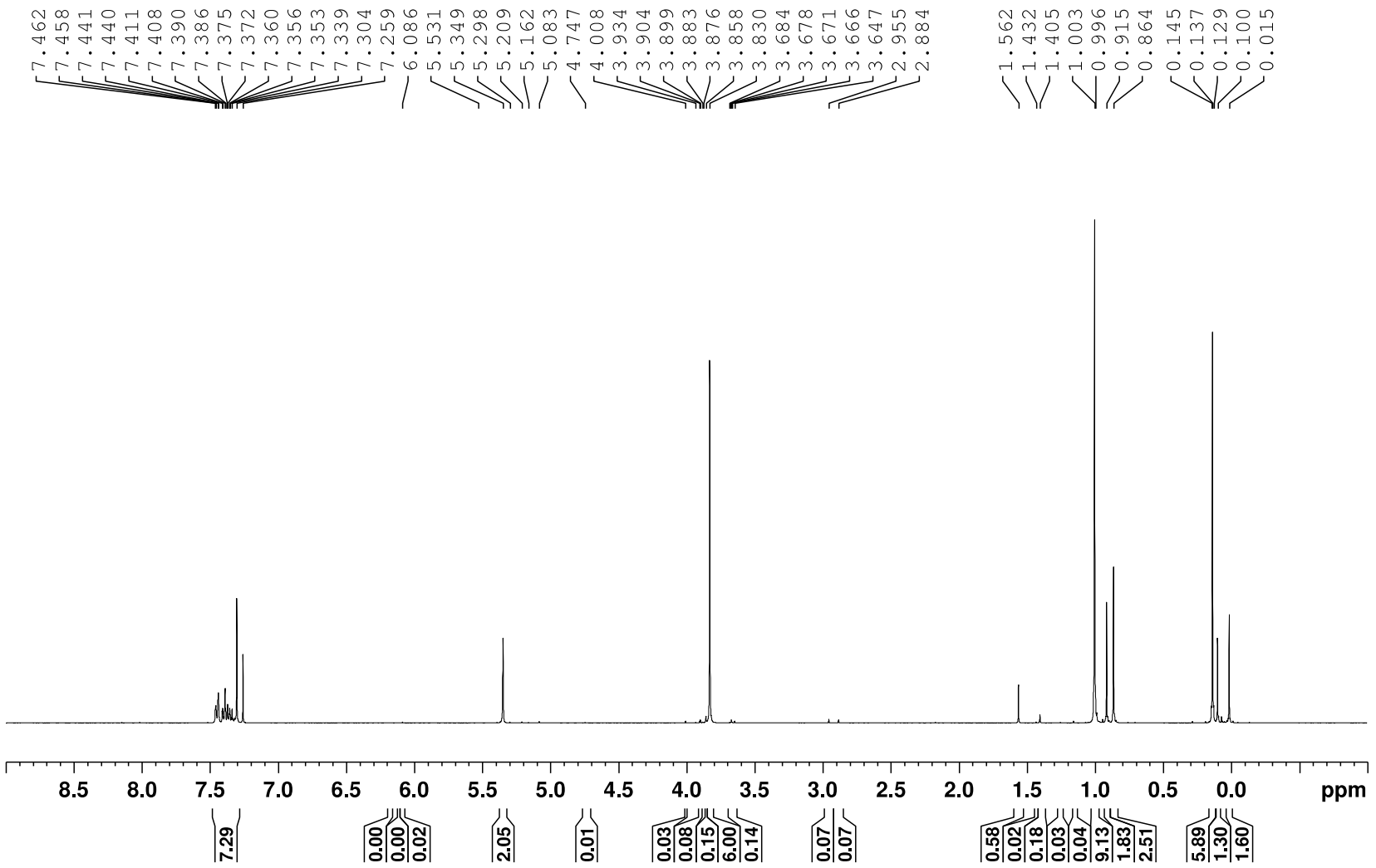
Calc.
$[M + H]^+$
403.19 amu

Found
$[M + H]^+$
403.19536 amu

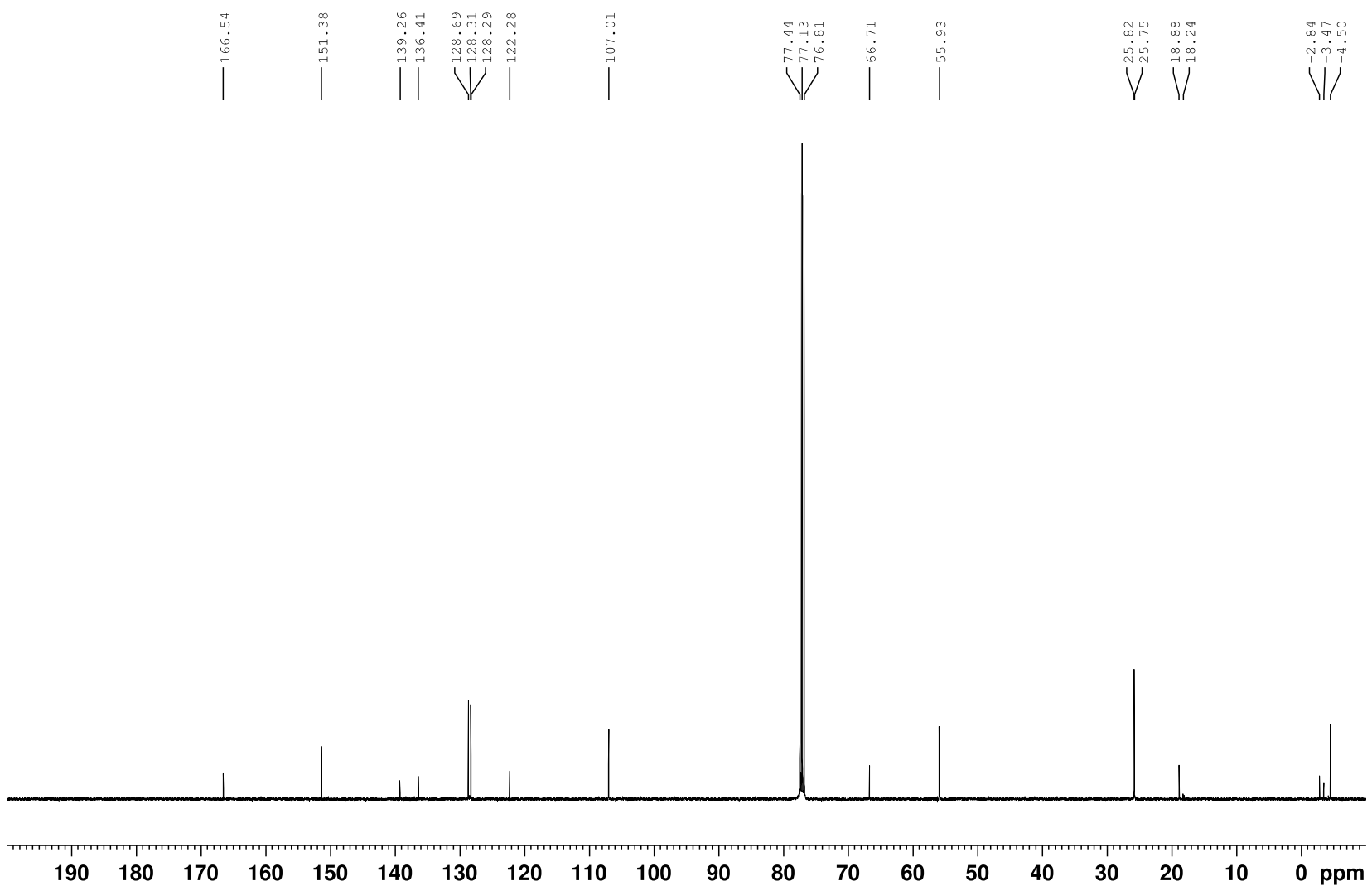
Composition
$C_{22}H_{31}O_5Si$

Bn-Syringic Acid (9.8 g, 34.3 mmol, 1 eq) and imidazole (2.34 g, 34.3 mmol, 1 eq) were dissolved in DMF (0.1 M, 300 mL) in a flame dried Schlenk flask under nitrogen and allowed to stir for 5 min. Tert-butyldimethylsilyl chloride (5.45 g, 36 mmol, 1.05 eq) was added and was allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with brine, washed with EtOAc 3x, and combined organic layers were dried over $MgSO_4$ and concentrated to yield a white solid (9.2 g, 67% yield).

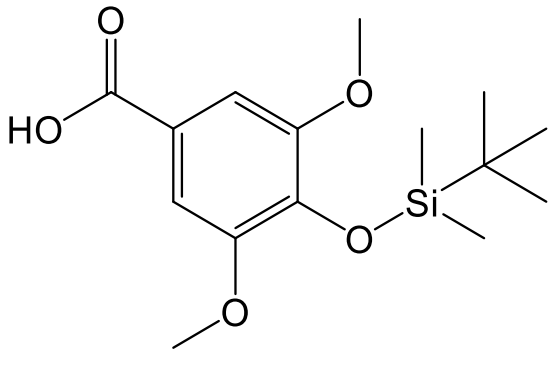
JHS-3014; Bn-Sy-Si; CDCl3; 1H; 400a; 16 Scans;
10/6/16



JHS-3014; Bn-Sy-Si; CDCl3; 13C; 400a; \
2048 Scans; 10/6/16



Syringic acid-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.16	s	6	CH_3 (Si)
1.01	s	9	CH_3 (Si)
3.86	s	6	CH_3
7.34	s	2	Aromatic

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

δ (ppm) + Assignment	
-4.44	CH_3 (Si)
18.92	C (Si)
25.84	CH_3 (Si)
55.93	CH_3
107.45	Aromatic
121.16	Aromatic
139.95	Aromatic
151.45	Aromatic
171.02	CO

HRMS (ESI)

Calc. Mass
312.14 amu

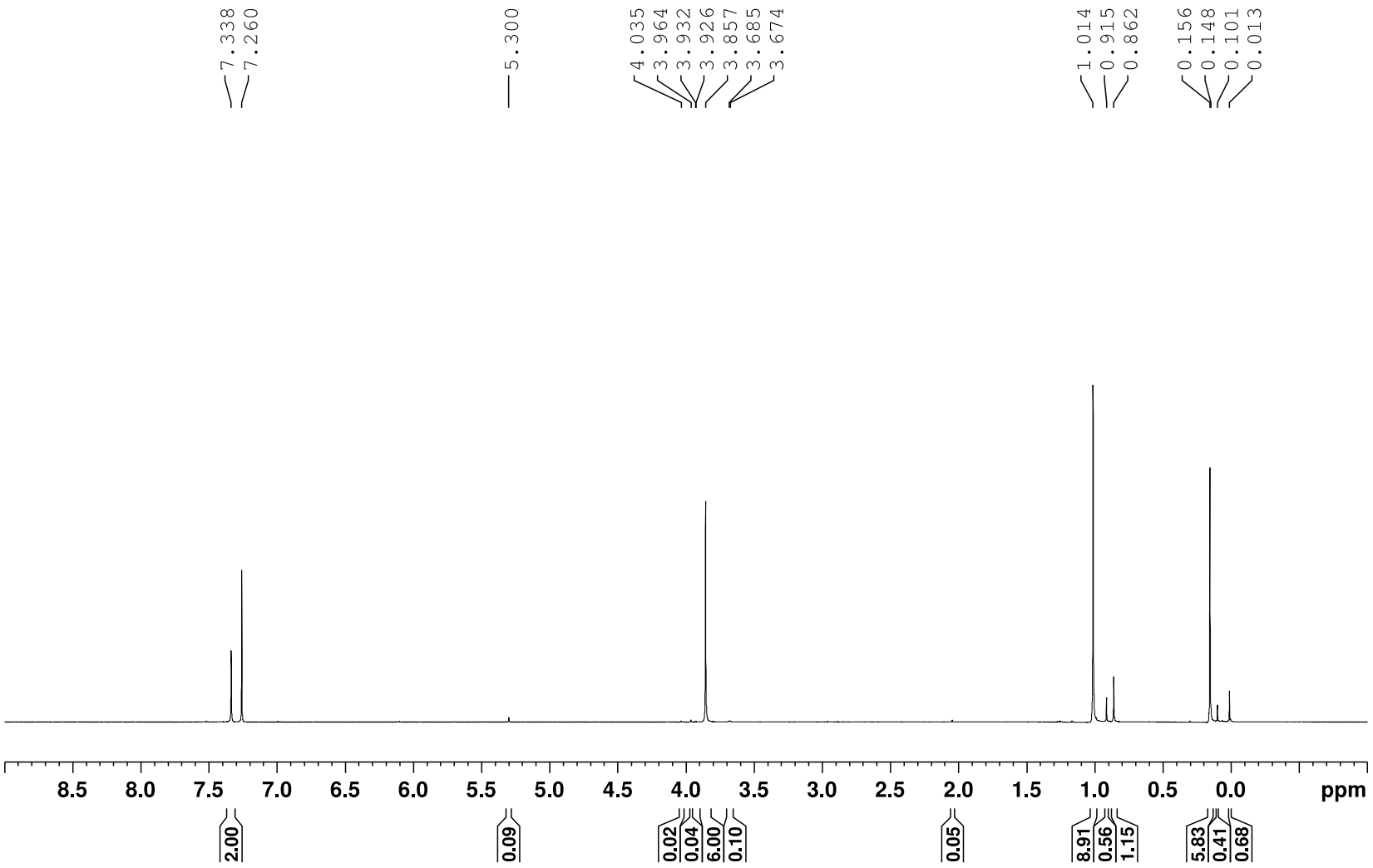
Calc.
$[M + H]^+$
313.14 amu

Found
$[M + H]^+$
313.14823 amu

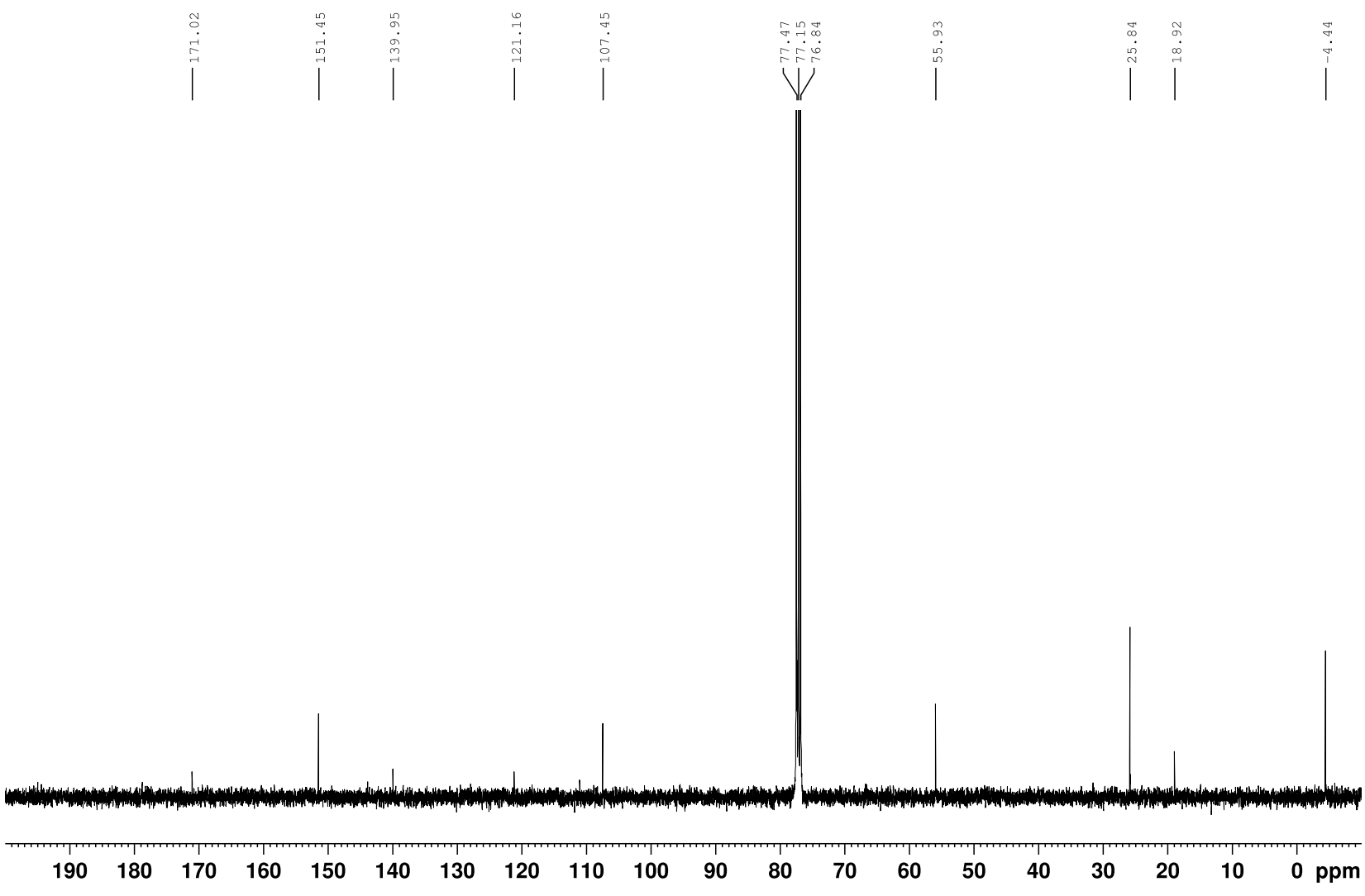
Composition
$C_{15}H_{25}O_5Si$

Bn-Syringic Acid-Si (2.55 g, 6.33 mmol) and Pd/C (0.26 g, 10 wt%) were dissolved in EtOAc (60 mL, 0.1 M) in a flame dried Schlenk flask and allowed to stir overnight at RT under 1 atm H_2. Upon consumption of starting material by TLC, the reaction mixture was filtered over celite and concentrated *in vacuo* to yield a white solid (1.92 g, 97% yield).

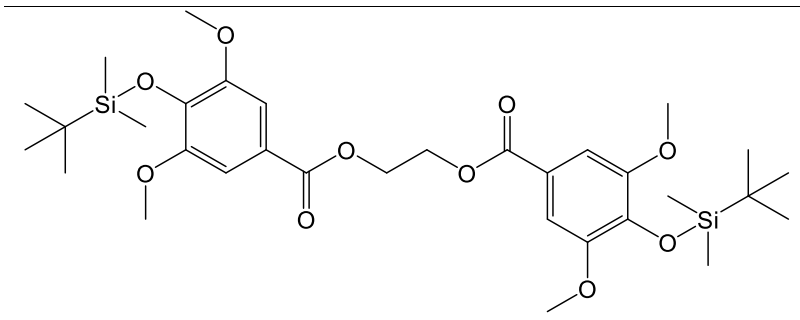
JHS-3015; Sy-Si; CDCl3; 1H; 400a; 16 Scans;
10/7/16



JHS-3015; Sy-Si; CDCl3; 13C; 400a; 2048 Scans;
10/7/16



Si-Sy-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.13	s	12	CH_3 (Si)
1.00	s	18	CH_3 (Si)
3.81	s	12	CH_3
4.63	s	4	CH_2
7.28	s	4	Aromatic

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

δ (ppm) + Assignment	
-4.47	CH_3 (Si)
18.91	C (Si)
25.84	CH_3 (Si)
55.90	CH_3
107.45	Aromatic
121.16	Aromatic
139.95	Aromatic
151.45	Aromatic
171.02	CO

HRMS (ESI)

Calc. Mass
650.29 amu

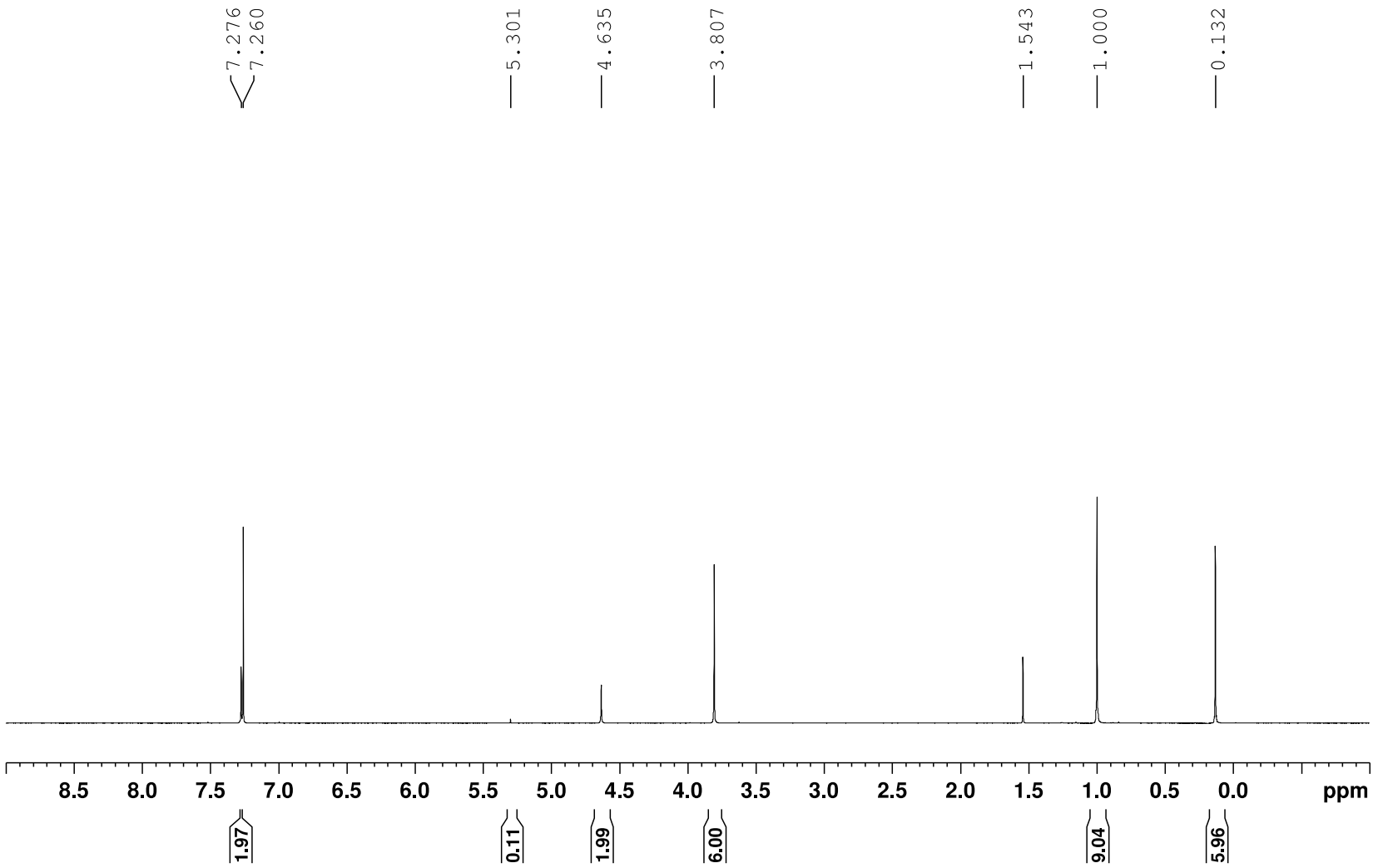
Calc.
$[M + H]^+$
651.29 amu

Found
$[M + H]^+$
651.30452 amu

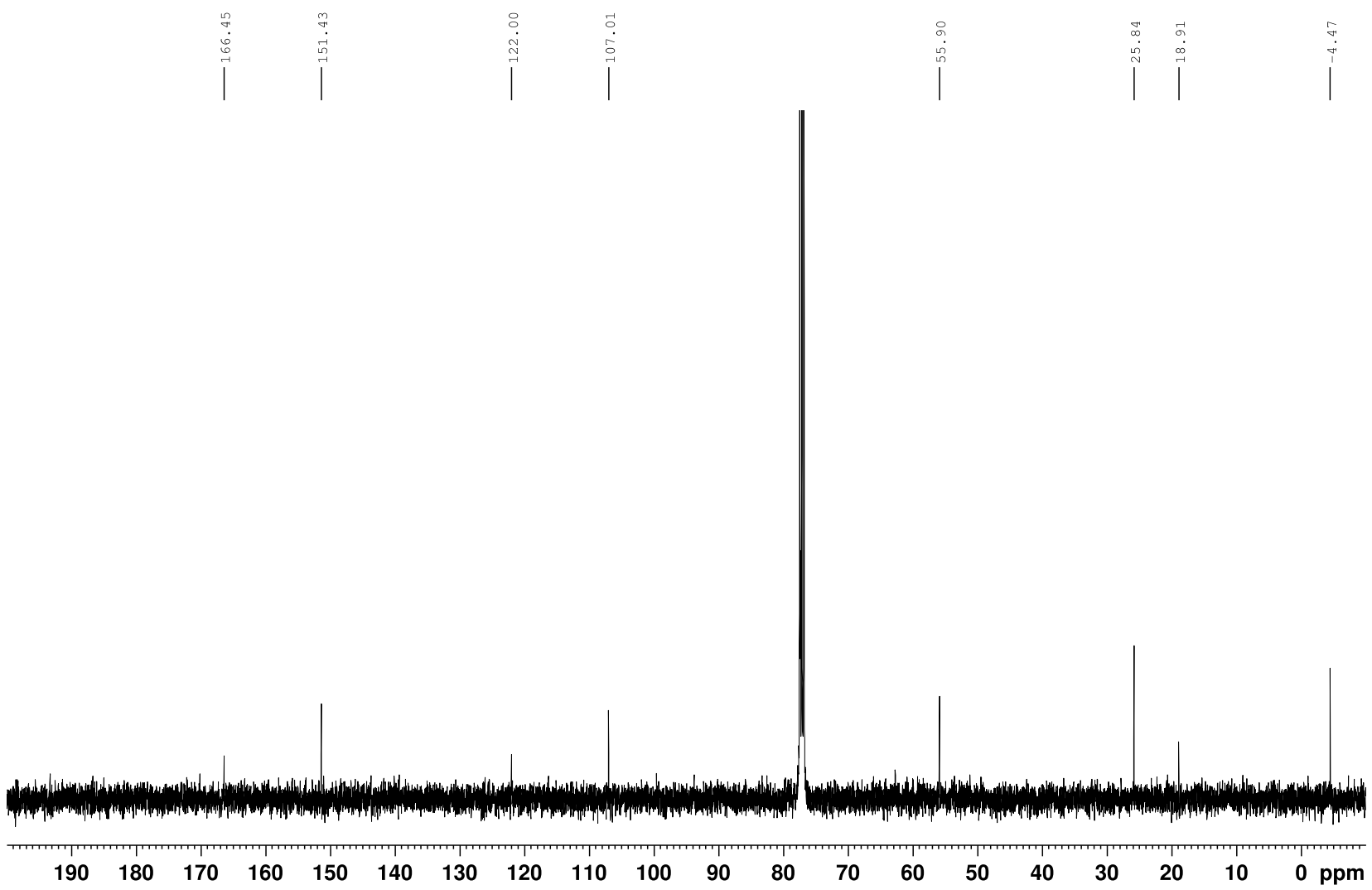
Composition
$C_{32}H_{50}O_{10}Si_2$

Sy-Si (1.9 g, 6.1 mmol, 2.2 eq) and ethylene glycol (0.172 g, 2.76 mmol, 1 eq) were dissolved in dry DCM (30 mL, 0.1 M) and added to a flame dried Schlenk under nitrogen. DPTS (0.37 g, 1.24 mmol, 0.45 eq) and DCC (1.31 g, 6.4 mmol, 2.3 eq) were added sequentially and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes and filtered to remove DCU and concentrated to yield a pure white solid (1.01 g, 56% yield).

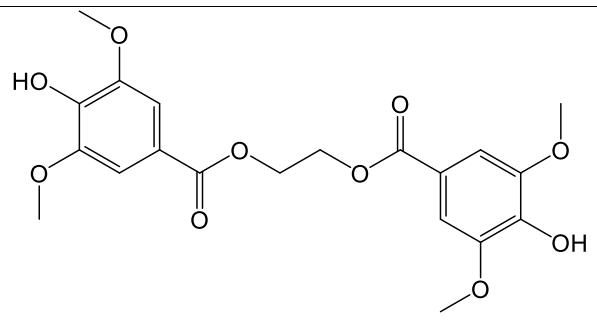
JHS-3016; Si-Sy-Si; CDCl3; 1H; 400a; 16 Scans;
10/11/16



JHS-3016; Si-Sy-Si; CDCl3; 13C; 400a; 2048 Scans
10/11/16



Sy Linker



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

dδ (ppm)	Mult. (J)	Int.	Assignment
3.91	s	12	CH_3
4.65	s	4	CH_2
5.91	s	2	OH
7.32	s	4	Aromatic

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

δ (ppm)	+ Assignment
56.52	CH_3
62.72	CH_2
106.87	Aromatic
120.84	Aromatic
139.54	Aromatic
146.75	Aromatic
166.23	CO

HRMS (ESI)

Calc. Mass
422.12 amu

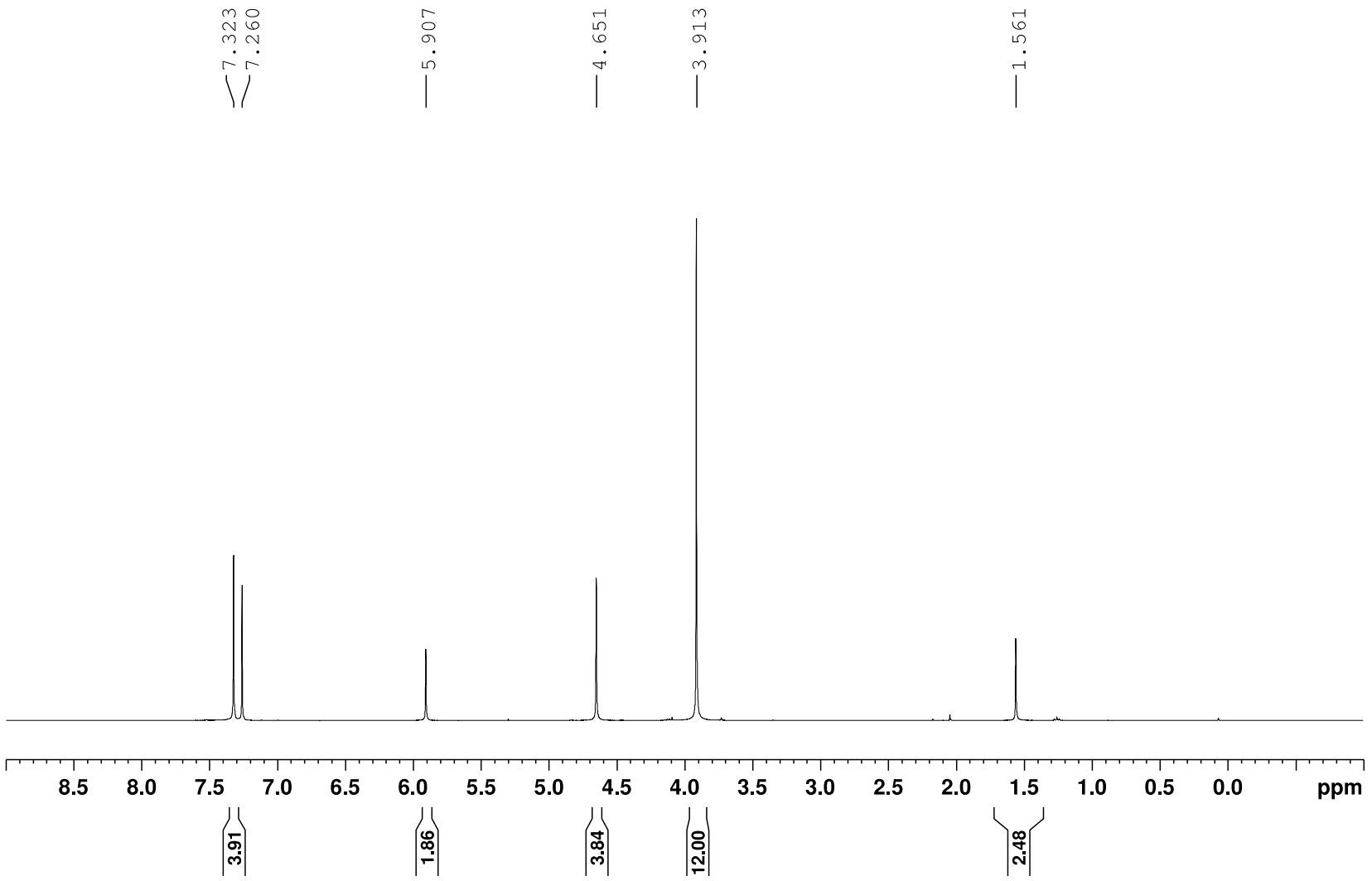
Calc.
$[M - H]^-$
421.12 amu

Found
$[M - H]^-$
421.11203 amu

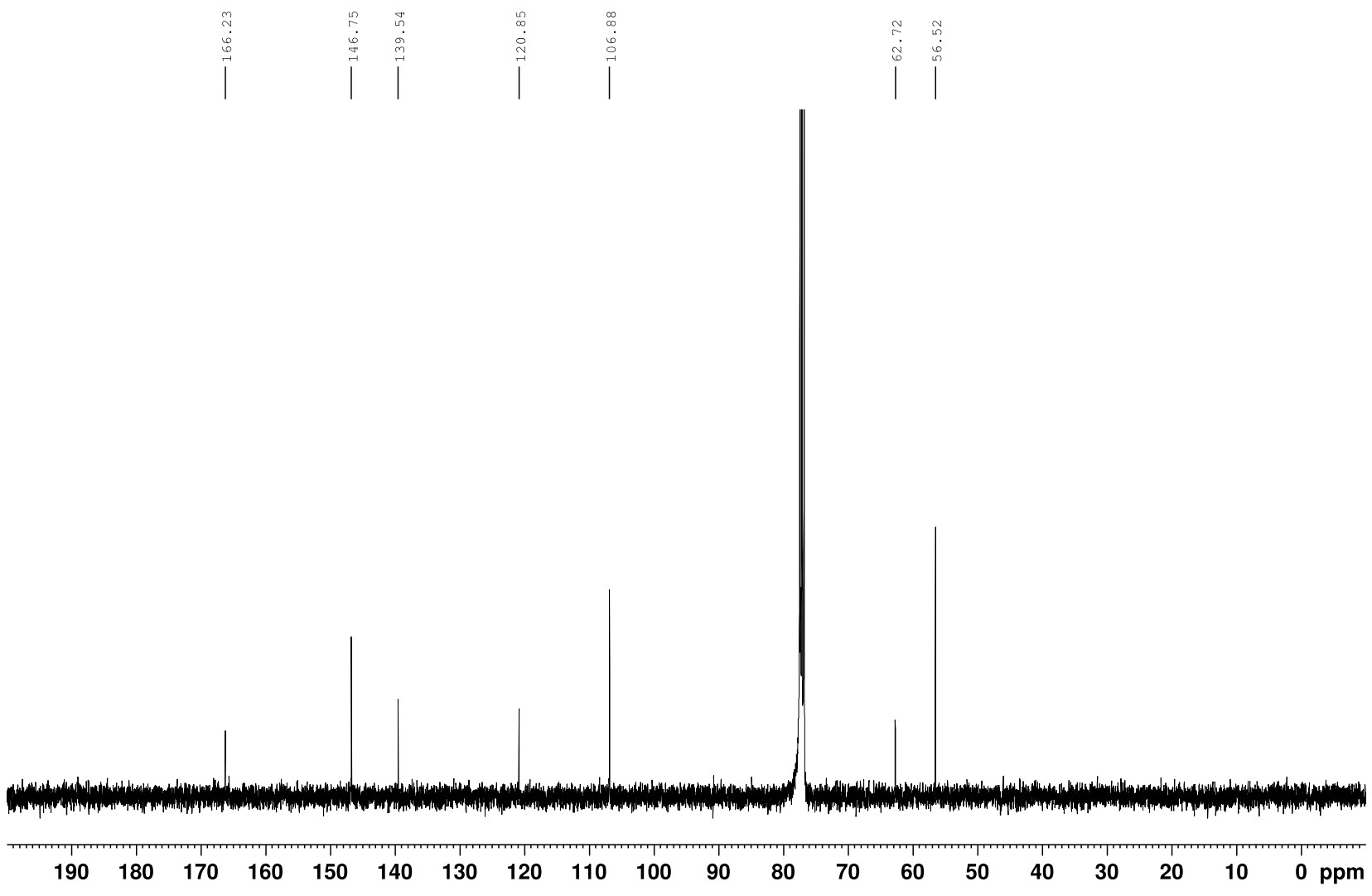
Composition
$C_{20}H_{22}O_{10}$

TBAF (1 M in THF) (4.66 mL, 4.66 mmol, 3 eq) and AcOH (1.06 mL, 18.6 mmol, 12 eq) were dried over sieves for two h. **Si-Sy-Si** (1.01 g, 1.55 mmol, 1 eq) was dissolved in dry THF (15 mL, 0.1 M) in a flame dried Schlenk flask under nitrogen. TBAF and AcOH were combined added dropwise at 0°C, allowed to warm to RT and stir overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with brine and washed with EtOAc 3x, the combined organic layers were dried over $MgSO_4$, concentrated, and crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a white solid (0.6 g, 76 %).

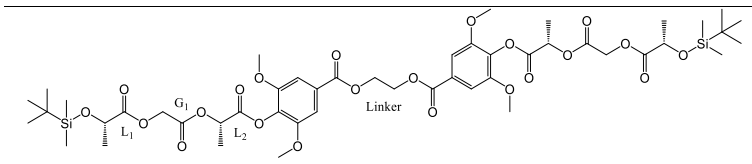
JHS-3017; Sy; CDCl3; 1H; 400a; 16 Scans;
10/12/16



JHS-3017; Sy; CDCl3; 13C; 400a; 2048 Scans;
10/12/16



Si-LGL-Sy-LGL-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.10	s	6	CH_3 (Si)
0.12	s	6	CH_3 (Si)
0.91	s	18	t-Bu (Si)
1.48	d (6.8)	6	CH_3 (L_1)
1.71	d (7.1)	6	L_2 (CH_3)
3.83	s	12	CH_3 (Linker)
4.46	q (6.8)	2	L_1 (CH)
4.70	m	6	CH_2 (G_1, Linker)
4.84	d (16)	2	G_1
5.54	q (7.1)	2	L_2 (CH)
7.31	s	4	Aromatic (Linker)

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

δ (ppm)	Assignment
-5.22	CH_3 (Si)
-4.84	CH_3 (Si)
17.25	CH_3 (L)
18.39	C (Si)
21.46	CH_3 (L)
25.80	t-Bu (Si)
56.47	CH_3 (MeO)
60.51	CH_2 (G_1)
62.99	CH (L)
68.18	CH_2 (Linker)
69.08	CH (L)
106.52	Aromatic
128.12	Aromatic
132.24	Aromatic
152.15	Aromatic
165.73	CO
166.73	CO
167.57	CO
173.54	CO

HRMS (ESI)

Calc. Mass
1,054.39 amu

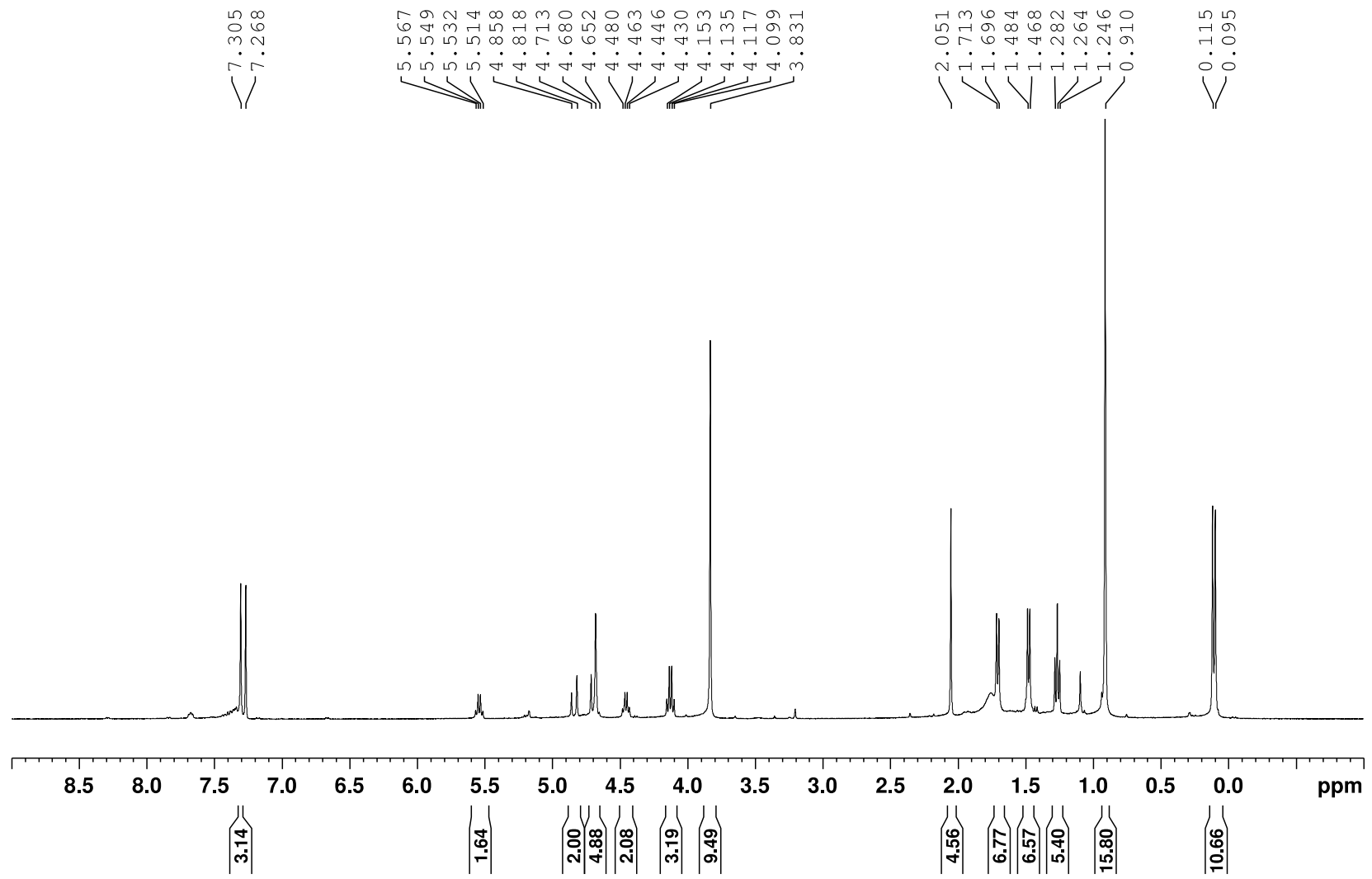
Calc.
$[M + H]^+$
1,055.39 amu

Found
$[M + H]^+$
1,055.40008 amu

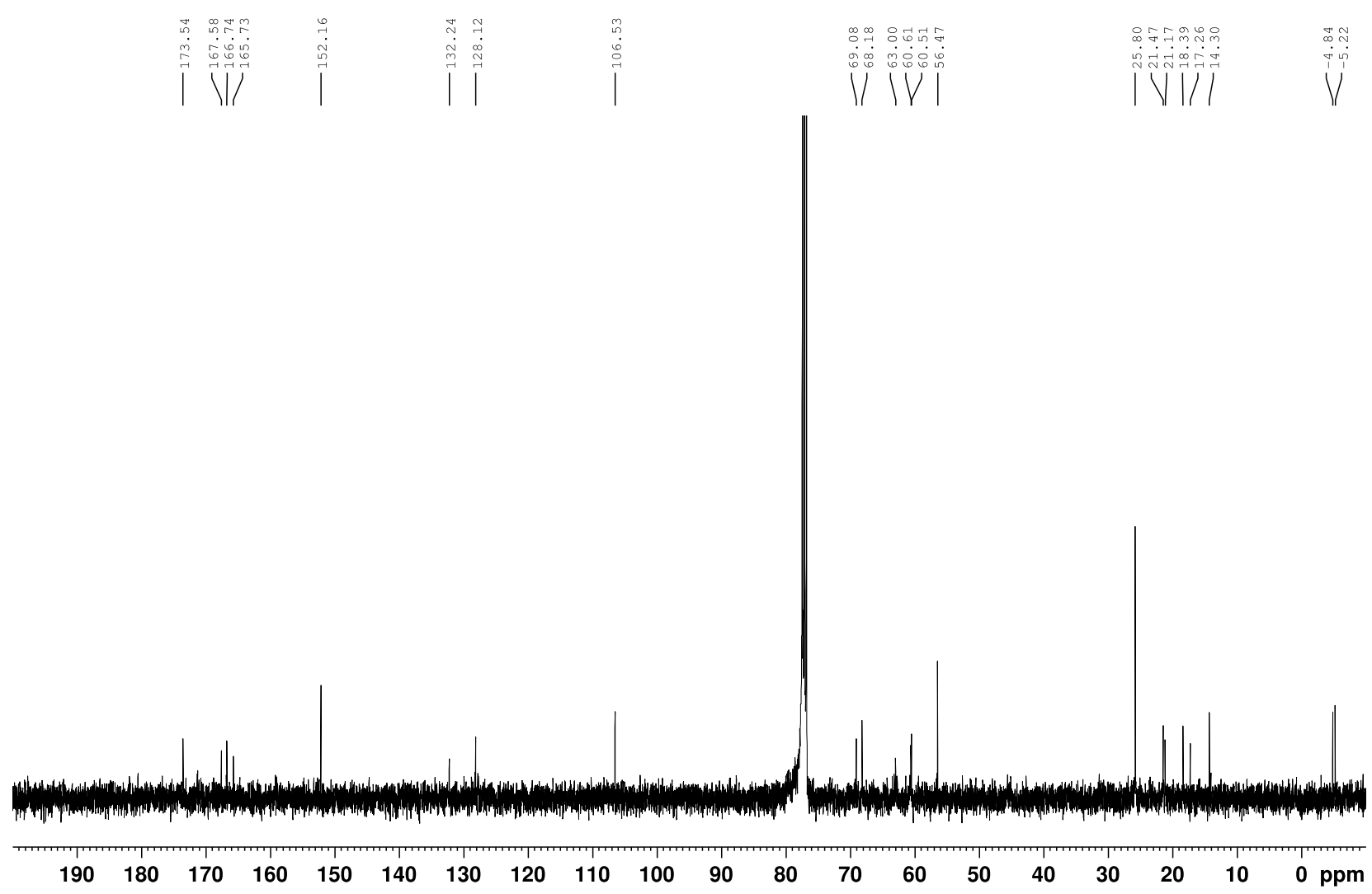
Composition
$C_{48}H_{70}O_{22}Si_2$

LGL-Si (1.085 g, 3.24 mmol, 2.3 eq) was dissolved in dry DCM (35 mL, 0.1 M), and added to a flame-dried vial under nitrogen. **Sy** linker (0.60 g, 1.41 mmol, 1 eq), DPTS (0.19 g, 0.65 mmol, 0.45 eq) and DCC (0.68 g, 3.3 mmol, 2.3 eq) were then added and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was filtered to remove DCU, washed with sodium bicarbonate 3x, dried over $MgSO_4$ and concentrated to yield a pure white solid (1.5 g, 99% yield).

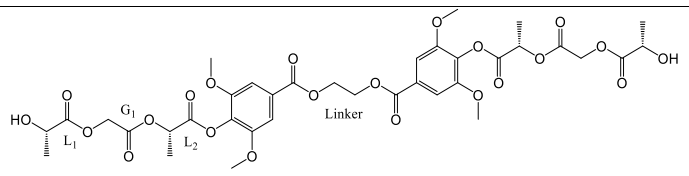
JHS-3019; Si-LGL-Sy-LGL-Si; CDCl3; 1H; 400a;
16 Scans; 10/20/16



JHS-3019; Si-LGL-Sy-LGL-Si; CDCl3; 13C; 400a;
2048 Scans; 10/20/16



LGL-Sy-LGL



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.51	d (6.8)	6	CH_3 (L_1)
1.71	d (7.1)	6	CH_3 (L_2)
2.73	d (4.5)	2	OH
3.82	s	12	CH_3 (Linker)
4.42	m	2	CH (L_1)
4.67	s	4	CH_2 (Linker)
4.75	d (16)	2	CH_2 (G_1)
4.84	d (16)	2	CH_2 (G_1)
5.53	q (7.1)	2	CH (L_2)
7.31	s	4	Aromatic (Linker)

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

δ (ppm)	+ Assignment
17.21	CH_3 (L)
20.48	CH_3 (L)
56.47	CH_3 (MeO)
61.04	CH_2 (G_1)
66.85	CH (L)
68.37	CH_2 (Linker)
69.30	CH (L)
106.50	Aromatic
128.17	Aromatic
132.17	Aromatic
152.13	Aromatic
165.70	CO
166.47	CO
167.47	CO
175.07	CO

HRMS (ESI)

Calc. Mass
826.22 amu

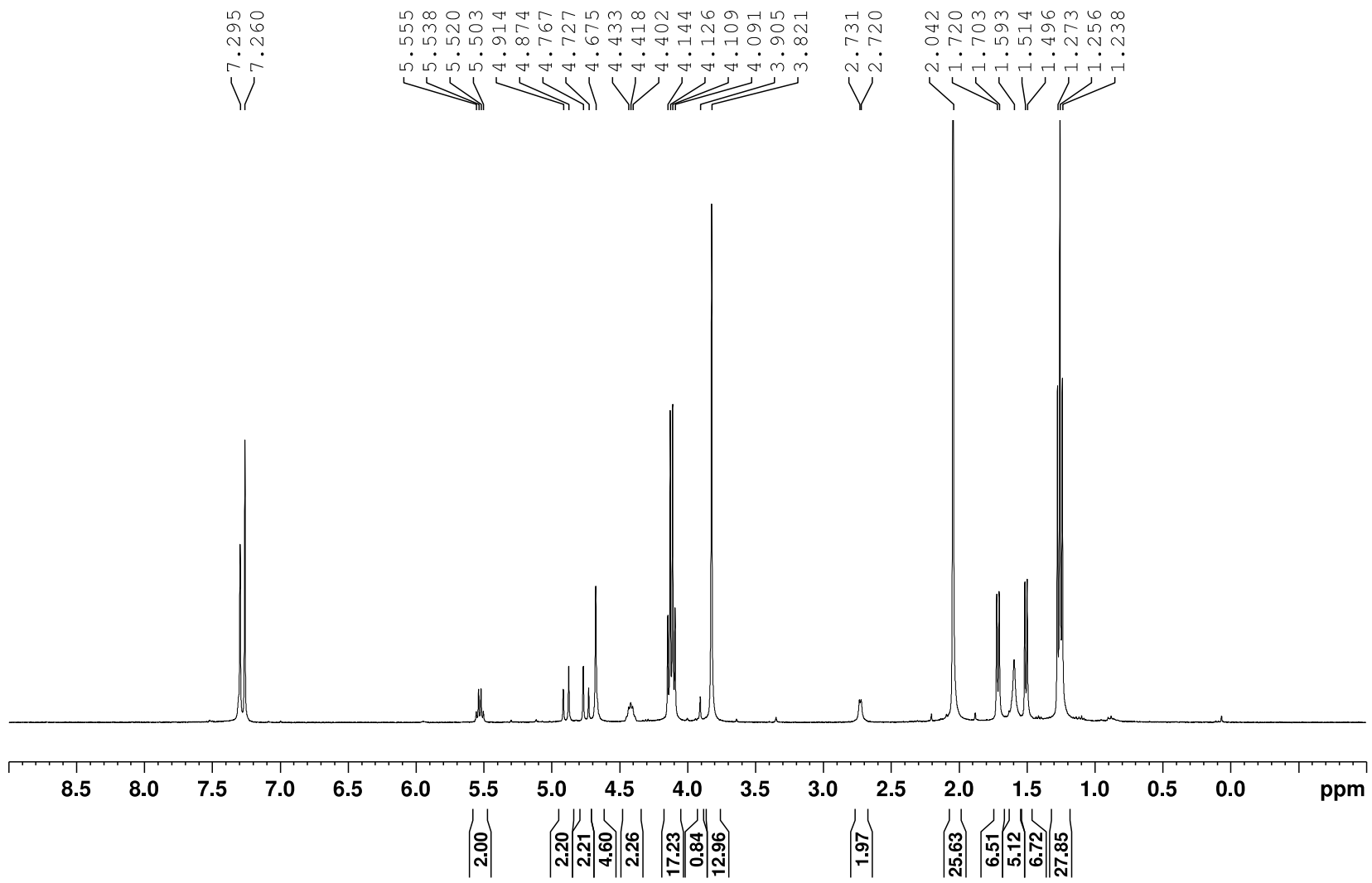
Calc.
$[M + H]^+$
827.22 amu

Found
$[M + H]^+$
827.22794 amu

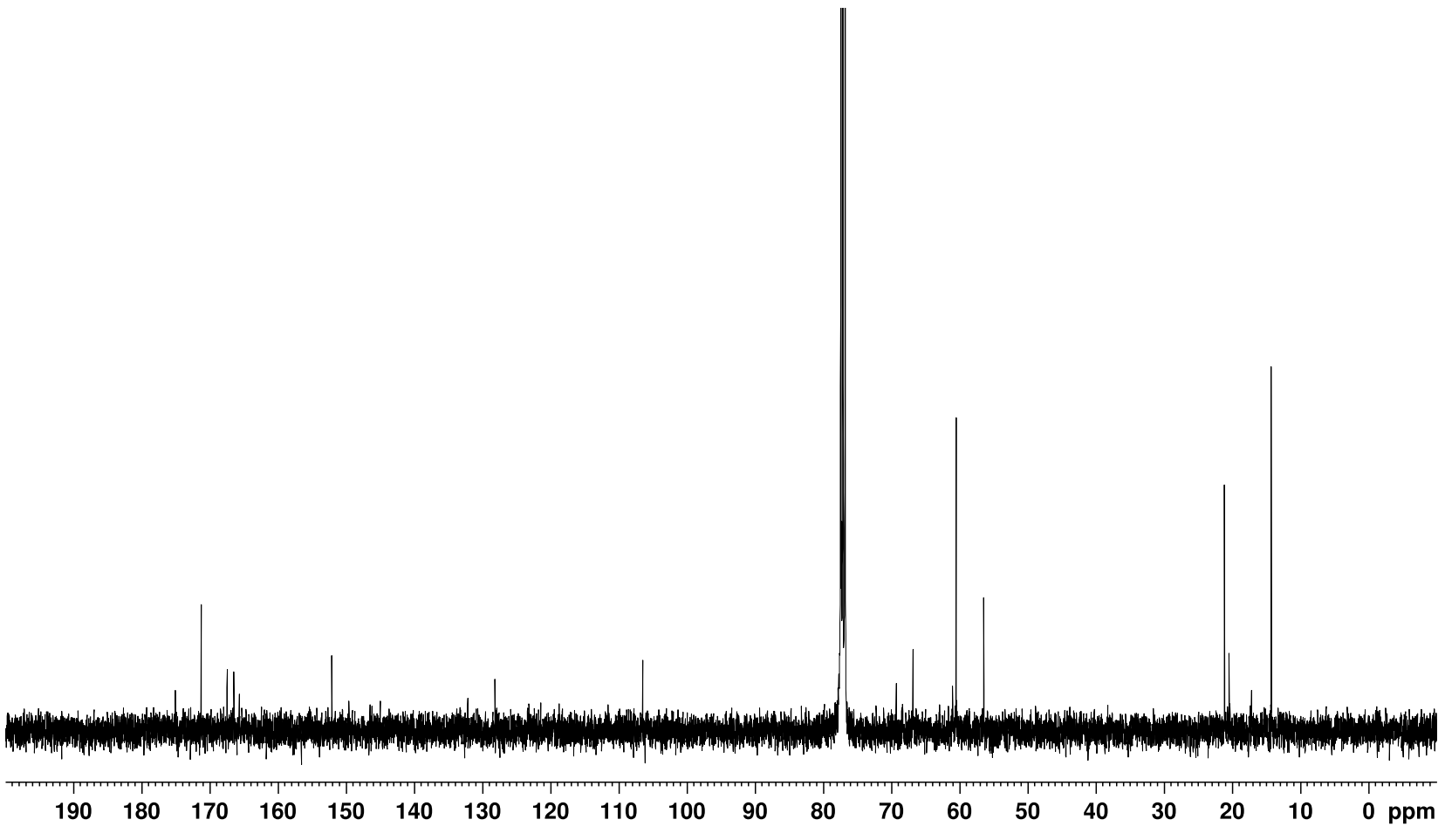
Composition
$C_{36}H_{42}O_{22}$

AcOH (1.29 mL, 22.7 mmol, 16 eq) and TBAF (1 M in THF) (4.3 mL, 4.3 mmol, 3 eq) dried over activated sieves for two h. **Si-LGL-Sy-LGL-Si** (1.5 g, 1.42 mmol, 1 eq) was dissolved in dry THF (25 mL, 0.04 M) in a flame dried Schlenk flask under nitrogen. AcOH and TBAF were added dropwise at 0°C, allowed to warm to RT and stir for 24 h. An additional equivalent of TBAF was added and allowed to stir for two more h. Upon consumption of starting material by TLC, the reaction mixture was then diluted with brine and extracted with EtOAc 3x, the combined organic layers were washed with brine 3x, dried over $MgSO_4$ and concentrated. The crude solid was then purified via column chromatography (silica, EtOAc/hexanes) to yield a white solid (0.747 g, 64% yield).

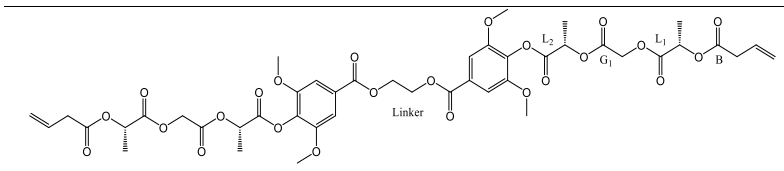
JHS-3020; LGL-Sy-LGL; CDCl3; 1H; 400a;
16 Scans; 10/20/16



JHS-3020; LGL-Sy-LGL; CDCl3; 13C; 400a;
2048 Scans; 10/20/16



BLGL-Sy-LGLB



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

dδ (ppm)	Mult. (J Hz)	Int.	Assignment
1.59	d (7)	6	L_1 (CH_3)
1.71	d (7)	6	L_2 (CH_3)
3.19	m	4	B (CH_2)
3.83	s	12	Linker (CH_3)
4.66	s + d	6	Linker (CH_2) + G_1 (CH_2)
4.92	d (16)	2	G_1 (CH_2)
5.21	m	6	L_1 (CH) + B (CH_2)
5.53	q (7)	2	L_2 (CH)
5.94	m	2	B (CH)
7.31	s	4	Linker (Aromatic)

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

δ (ppm)	+ Assignment
16.96	CH_3
17.23	CH_3
38.73	CH_2 (Linker)
56.51	CH_3 (Linker)
60.91	CH_2
63.02	CH_2
68.58	CH
69.25	CH
106.55	Aromatic
119.12	Aromatic
128.18	Aromatic
129.75	Aromatic
132.25	Alkene
152.18	Alkene
165.74	CO
166.48	CO
167.55	CO
170.26	CO
171.02	CO

HRMS (ESI)

Calc. Mass
962.27 amu

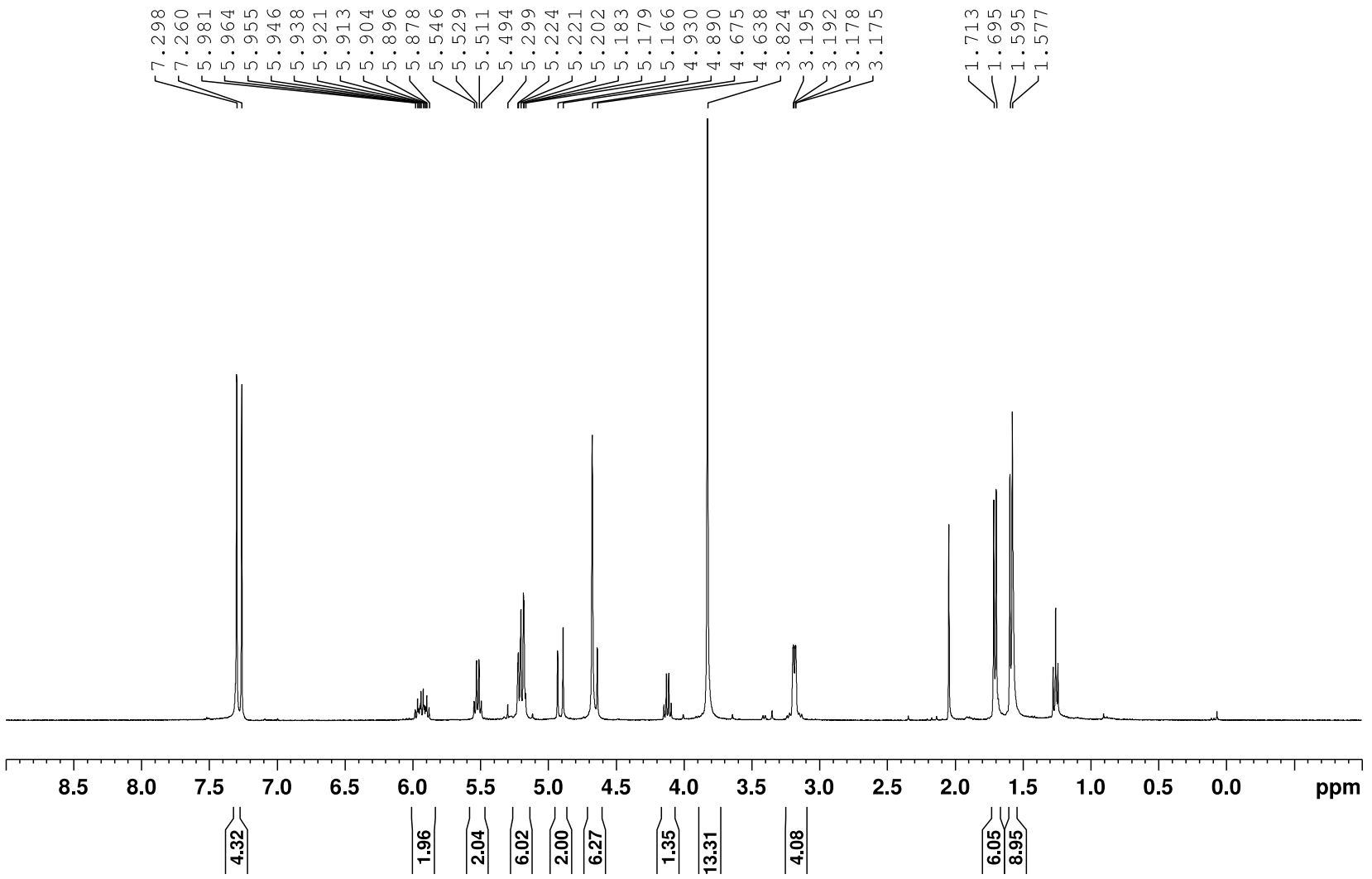
Calc.
$[M + H]^+$
963.27 amu

Found
$[M + H]^+$
963.28008 amu

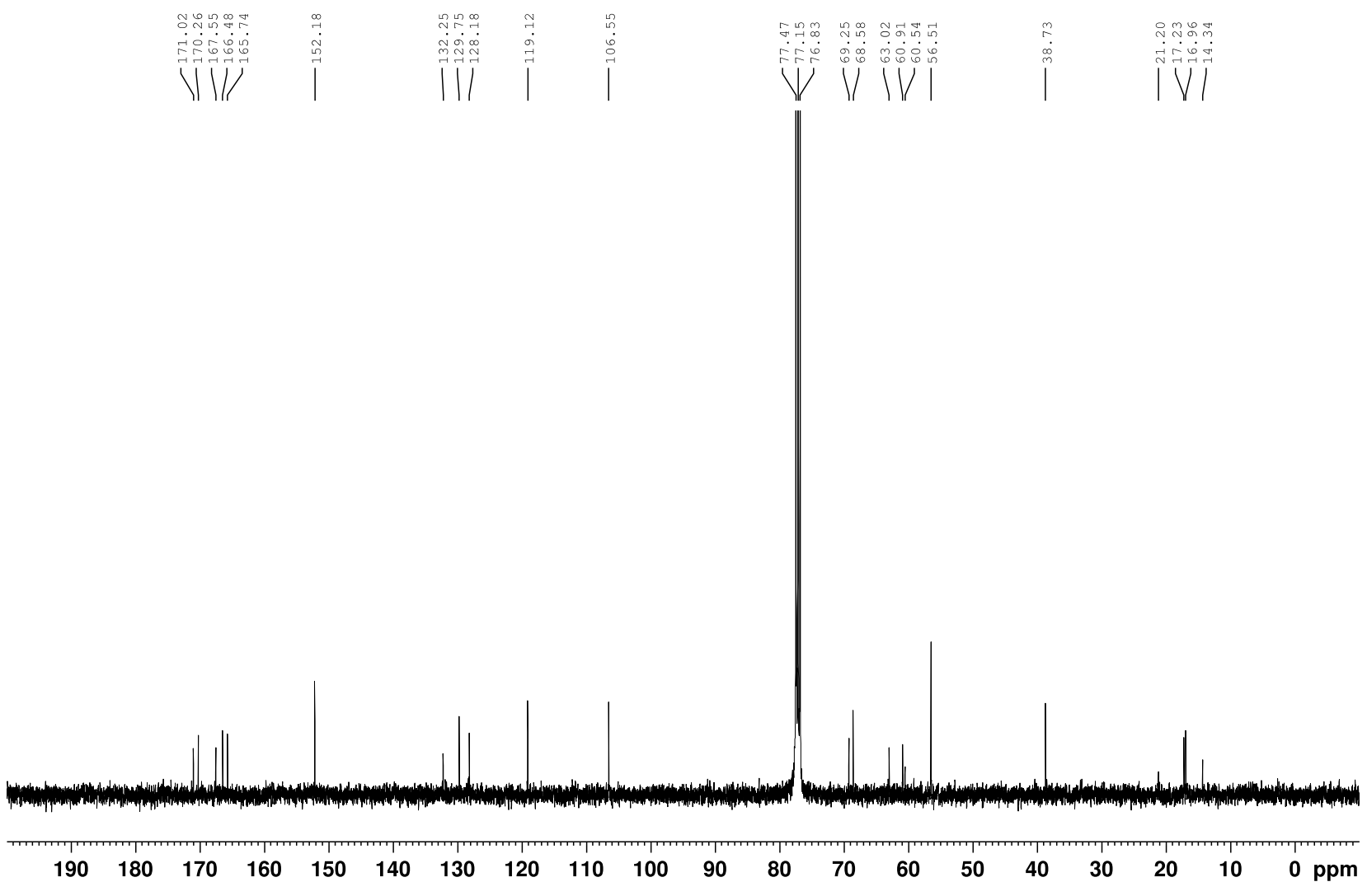
Composition
$C_{44}H_{50}O_{24}$

LGL-Sy-LGL (0.74 gg, 0.90 mmol, 1 eq) was dissolved in dry EtOAc (10 mL, 0.1 M) in an oven dried vial under nitrogen. DPTS (0.121 g, 0.41 mmol, 0.45 eq) and DCC (0.56 g, 2.7 mmol, 3 eq) were added sequentially. Butenoic acid (0.232 g, 2.7 mmol, 3 eq) was then added dropwise and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes, washed with sodium bicarbonate 3x, dried over $MgSO_4$ and filtered to remove DCU and drying agent, concentrated, and crude oil was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (612 mg, 71% yield).

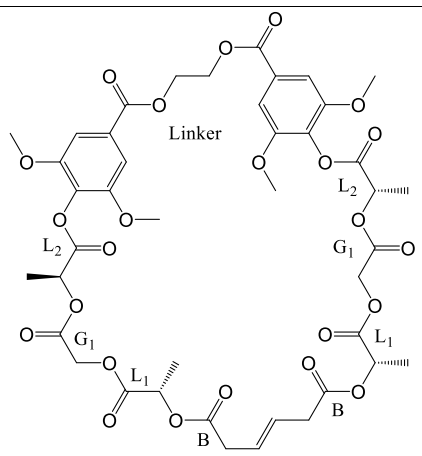
JHS-3021; BLGL-Sy-LGLB; CDCl3; 1H; 400a;
16 Scans; 10/21/16



JHS-3021; BLGL-Sy-LGLB; CDCl3; 13C; 400a;
2048 Scans; 10/21/16



Cyclic Sy Monomer



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

dδ (ppm)	Mult. (J Hz)	Int.	Assignment
1.57	d (7)	6	CH_3 (L_1)
1.71	d (7)	6	CH_3 (L_2)
3.19	m	4	CH_2 (B)
3.81	s	12	-OCH_3 (Linker)
4.69	s	6	CH_2 (Linker)
4.75	d (16)	2	CH_2 (G_1)
4.86	d (16)	2	CH_2 (G_1)
5.24	q (7)	2	CH (L_1)
5.52	q (7)	2	CH (L_2)
5.76	m	1.6	CH (B) Trans
5.83	m	0.4	CH (B) Cis
7.30	s	4	Aromatic

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

δ (ppm)	+ Assignment
16.68	CH_3 (L)
16.91	CH_3 (L)
32.63	CH_2 (Linker)
37.28	CH_2 (B)
56.27	CH_3 (Linker)
60.77	CH_2 (G)
62.66	CH (L)
68.42	CH (L)
69.08	CH_2 (Linker)
106.38	Aromatic
124.44	Alkene (Cis)
125.65	Alkene
128.04	Aromatic
132.13	Aromatic
152.02	Aromatic
165.43	CO
166.15	CO
167.14	CO
169.77	CO
170.49	CO

HRMS (ESI)

Calc. Mass
934.24 amu

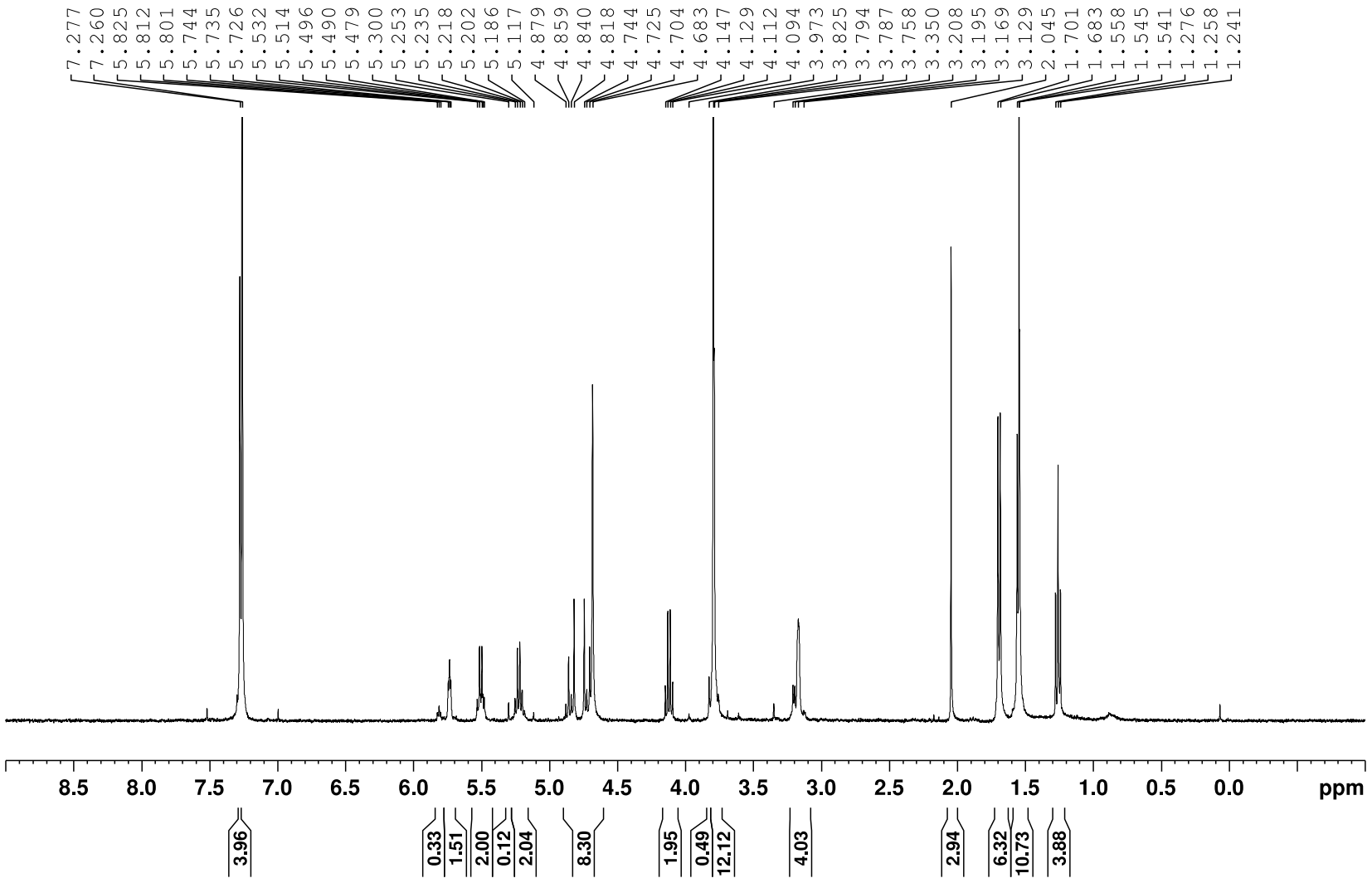
Calc.
$[M + H]^+$
935.24 amu

Found
$[M + H]^+$
935.25000 amu

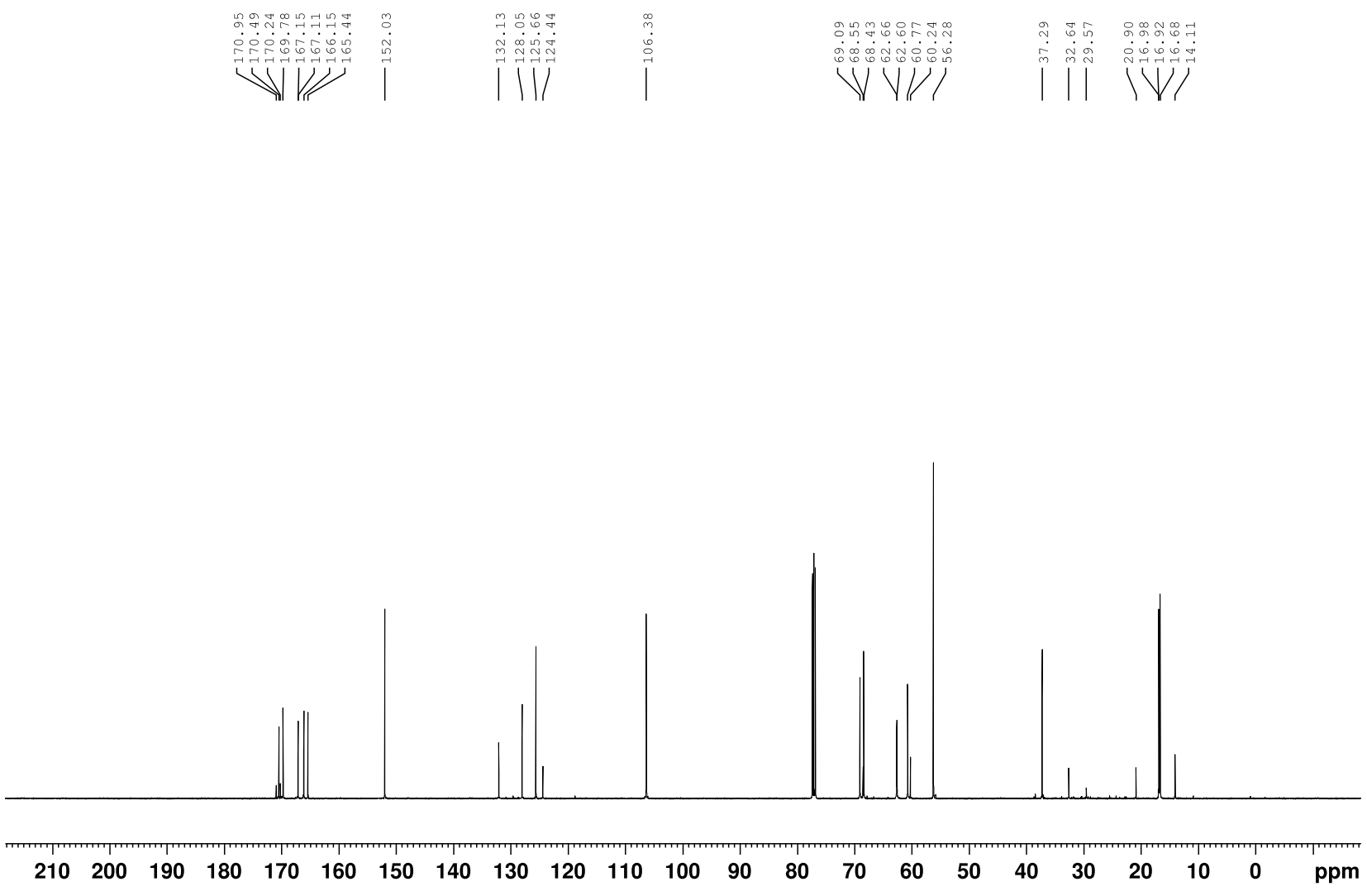
Composition
$C_{42}H_{46}O_{24}$

BLGL-Sy-LGLB (610 mg, 0.634 mmol, 1 eq) was dissolved in dry DCM (630 mL, 0.001M) in a flame-dried Schlenk flask under nitrogen. A stock solution of Grubbs 2 (54 mg, 0.063 mmol, 10 mol%) in dry DCM was added and allowed to stir at RT overnight. Upon consumption of starting material by TLC, reaction mixture was quenched by addition of excess ethyl vinyl ether and stirring for 10 additional min. The reaction mixture was then concentrated and the crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a brown solid (470 mg, 79% yield).

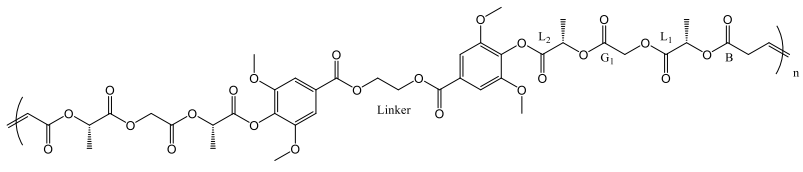
JHS-3022; Sy Monomer; CDCl3; 1H; 400a;
16 Scans; 10/26/16



JHS-3022-500; Sy Monomer; CDCl3; 13C; 500;
1024 Scans; 10/24/17



Poly(Sy)



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

δ (ppm)	Mult. (J)	Int.	Assignment
1.57	d (6.8)	6	CH_3 (L)
1.70	d (6.8)	6	CH_3 (L)
3.18	m	4	CH_2 (Linker)
3.82	s	12	MeO- (Linker)
4.65	m	6	CH_2 (G_1, Linker)
4.90	d (16)	2	CH_2 (G_1)
5.17	m	2	CH (L)
5.51	m	2	CH (L)
5.72	m	1.4	CH (B Trans)
5.81	m	0.6	CH (B Cis)
7.29	s	4	Aromatic

^{13}C-NMR (500 MHz, $CDCl_3$)

δ (ppm)	Assignment
16.91	CH_3 (L)
17.18	CH_3 (L)
37.40	CH_2 (B)
56.47	MeO- (Linker)
60.87	CH_2 (G_1)
62.97	CH_2 (Linker)
68.59	CH (L)
69.21	CH (L)
106.56	Aromatic
124.40	CH (B Cis)
125.82	CH (B Trans)
128.16	Aromatic
132.25	Aromatic
152.17	Aromatic
165.68	CO
166.43	CO
167.47	CO
170.16	CO

HRMS (ESI)

$\underline{M_n}$

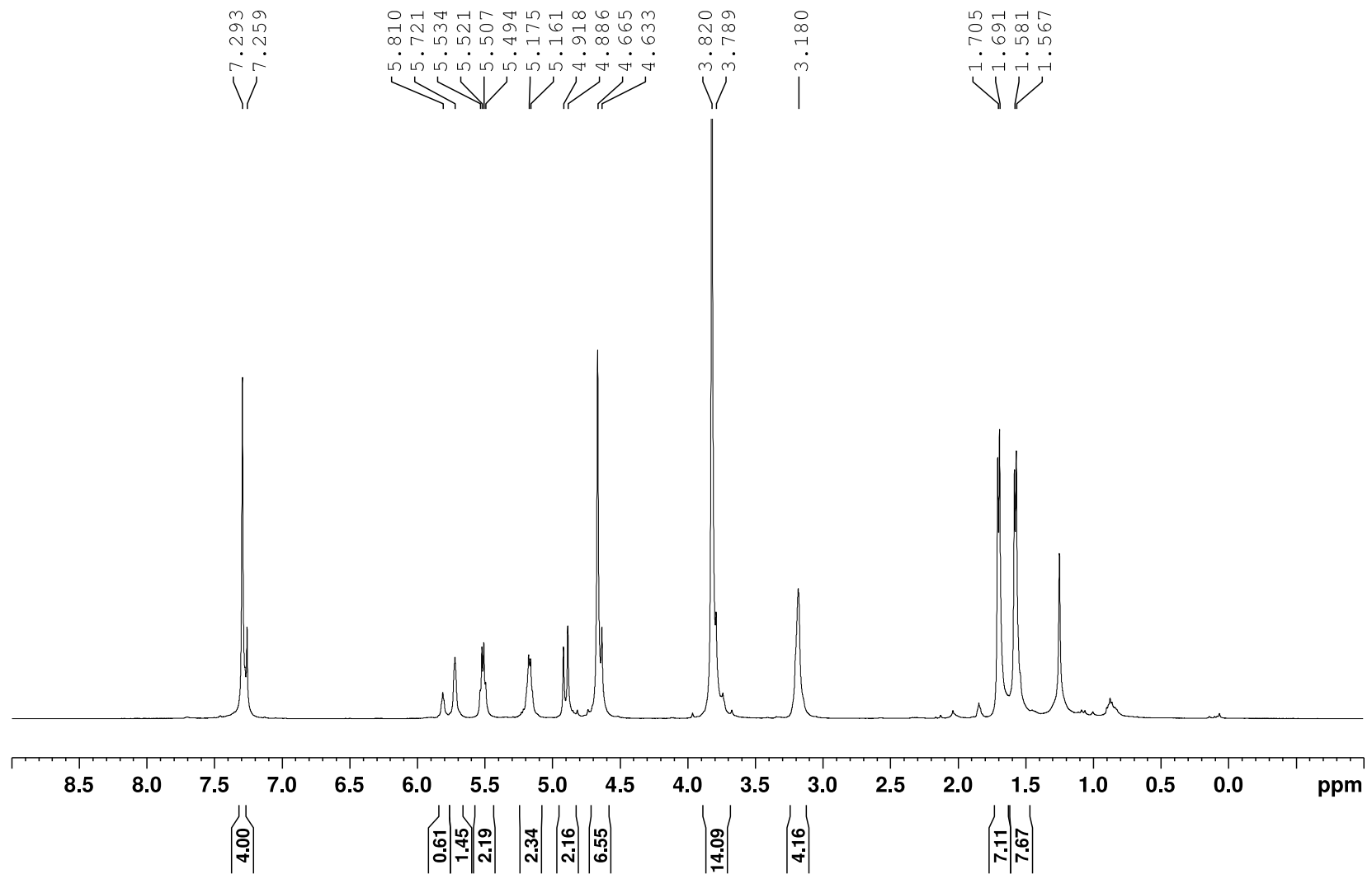
25,242 Da

$\underline{Đ}$

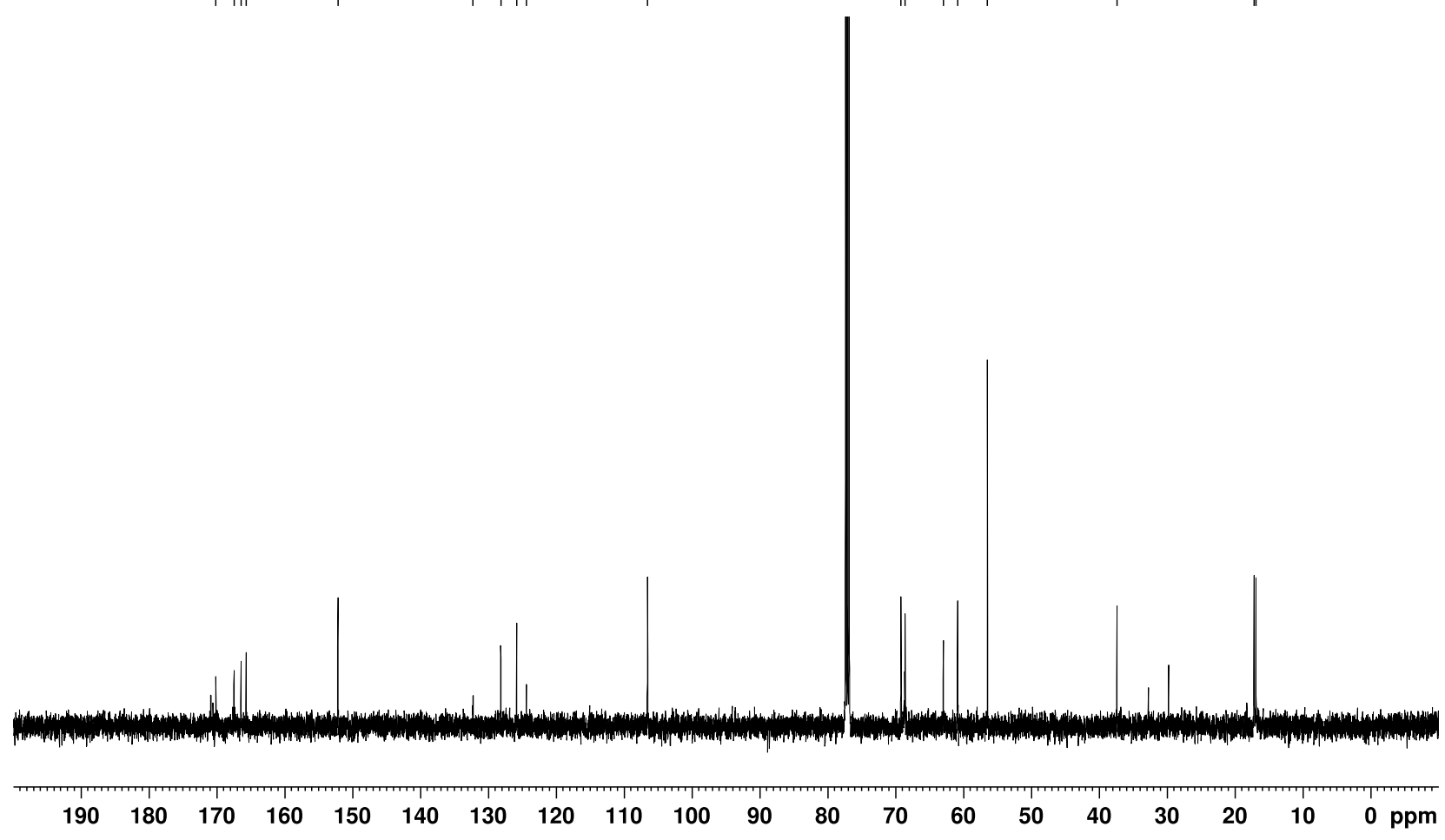
1.40

Cyclic Sy Monomer (110 mg, 0.118 mmol, 1 eq.) was weighed in a flame dried 1 mL vial under nitrogen. A stock solution of Grubbs II (1 mg, 0.0012 mmol, 1 mol%) in dry THF (5.8 mg/mL, 0.17 mL, 0.7 M) was added and the vial was shaken at RT for 4 h. The reaction mixture was quenched by the addition of excess ethyl vinyl ether and vortexing. Solution was concentrated to yield a crude solid polymer, which was reprecipitated into a stirring solution of MeOH and filtered to collect pure polymer as a brown solid (45 mg, 41% yield).

JHS-3047; Poly(Sy); CDCl3; 1H; 500; 16 Scans;
10/27/17

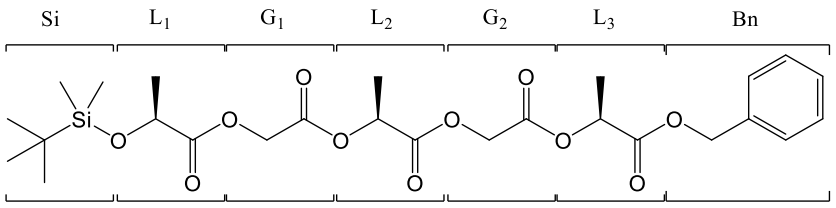


JHS-3047; Poly(Sy); CDCl3; 13C; 500; 128 Scans;
10/27/17



2.9 EEG LINKER CONTATINING COMPOUNDS AND PRECURSORS

Bn-LGLGL-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.08	s	3	Si (Me)
0.10	s	3	Si (Me)
0.90	s	9	Si (t-Bu)
1.46	d (6.8)	3	L_1 (CH_3)
1.52	d (7.2)	3	L_2 (CH_3)
1.58	d (7.2)	3	L_3 (CH_3)
4.44	q (6.8)	1	L_1 (CH)
4.75	m	4	G_1 (CH_3), G_2 (CH_2)
5.21	m	4	L_2 (CH_3), L_3 (CH), Bn (CH_2)
7.34	m	5	Bn (Aromatic)

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

δ (ppm) + Assignment	
-5.22	Si
-4.84	Si
16.91	L (CH_3)
18.40	L (CH_3)
21.47	L (CH_3)
25.80	Si (t-Bu)
60.56	G (CH_2)
60.95	G (CH_2)
67.37	Bn (CH_2)
68.16	L (CH)
69.11	L (CH)
69.61	L (CH)
128.29	Bn (CH)
128.62	Bn (CH)
128.75	Bn (CH)
135.20	Bn (CH
166.63	CO
167.01	CO
169.59	CO
169.93	CO
173.54	CO

HRMS (ESI)

Calc. Mass
554.22 amu

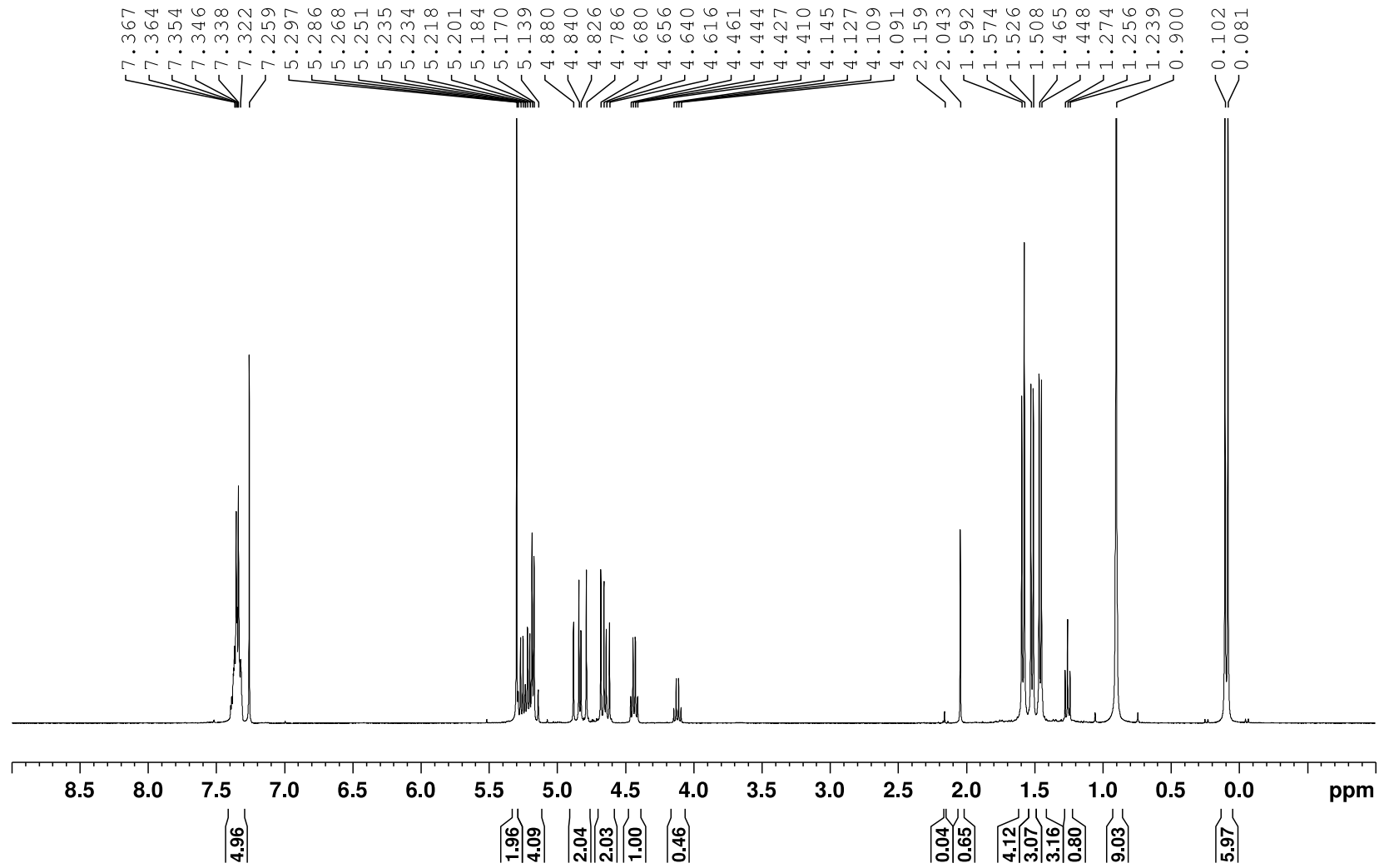
Calc.
$[M + H]^+$
555.22 amu

Found
$[M + H]^+$
555.22634 amu

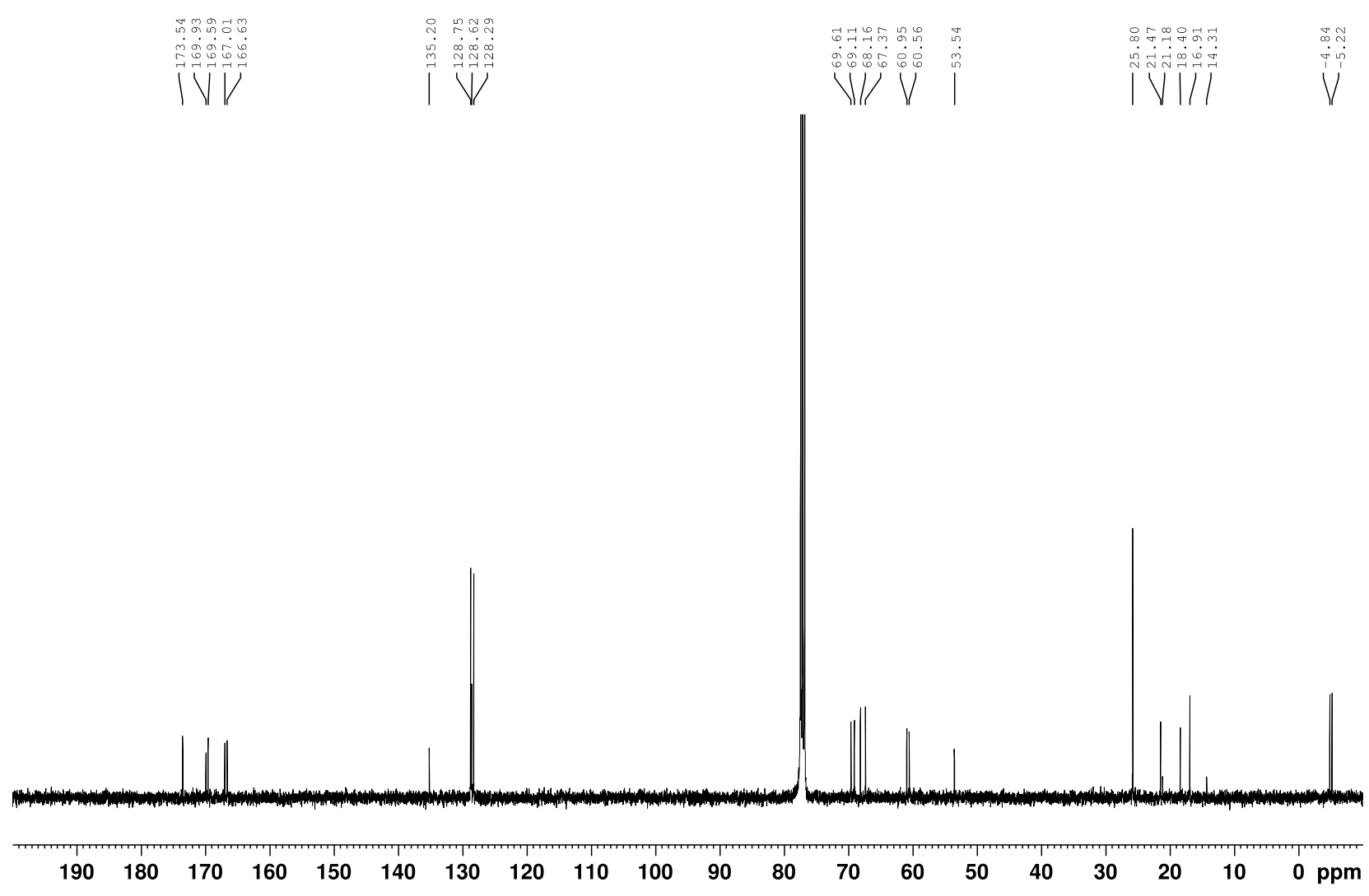
Composition
$C_{26}H_{38}O_{11}Si$

Bn-LG (0.86 g, 3.61 mmol) and **LGL-Si** (1.15 g, 3.44 mmol) were dissolved in dry DCM and added to a flame dried 100 mL Schlenk under nitrogen. DPTS (0.21 g, 0.7 mmol) and DCC (0.80 g, 3.8 mmol) were added to the reaction mixture sequentially through a funnel. The reaction mixture was allowed to stir overnight under nitrogen. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes and filtered to remove DCU. The filtrate was then concentrated *in vacuo* to yield a colorless oil (1.776 g, 93% yield).

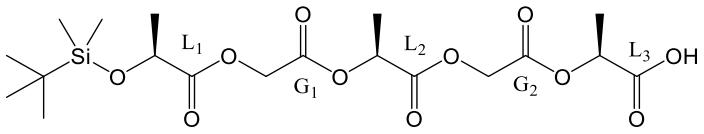
JHS-3007; Bn-LGLGL-Si; CDCl3; 1H; 400a; 16
Scans; 9/9/16



JHS-3007; Bn-LGLGL-Si; CDCl3; 13C; 400a; 2048
Scans; 9/9/16



LGLGL-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.08	s	3	Si (Me)
0.10	s	3	Si (Me)
0.90	s	9	Si (t-Bu)
1.46	d (6.8)	3	L_1 (CH_3)
1.56	d (7.2)	3	L_2 (CH_3)
1.59	d (7.2)	3	L_3 (CH_3)
4.44	q (6.8)	1	L_1 (CH)
4.65	d (16)	1	G_1 (CH_2)
4.66	d (16)	1	G_2 (CH_2)
4.81	d (16)	1	G_1 (CH_2)
4.87	d (16)	1	G_2 (CH_2)
5.20	q (7.2)	1	L_2 (CH_3)
5.26	q (7.2)	1	L_3 (CH_3)

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

δ (ppm) + Assignment	
-5.21	Si
-4.84	Si
16.81	L (CH_3)
16.91	L (CH_3)
18.41	L (CH_3)
21.47	SI
25.81	Si
60.94	G (CH_2)
68.19	L (CH)
69.11	L (CH)
69.14	L (CH)
166.63	CO
167.05	CO
169.66	CO
173.59	CO
174.46	CO

HRMS (ESI)

Calc. Mass
464.17 amu

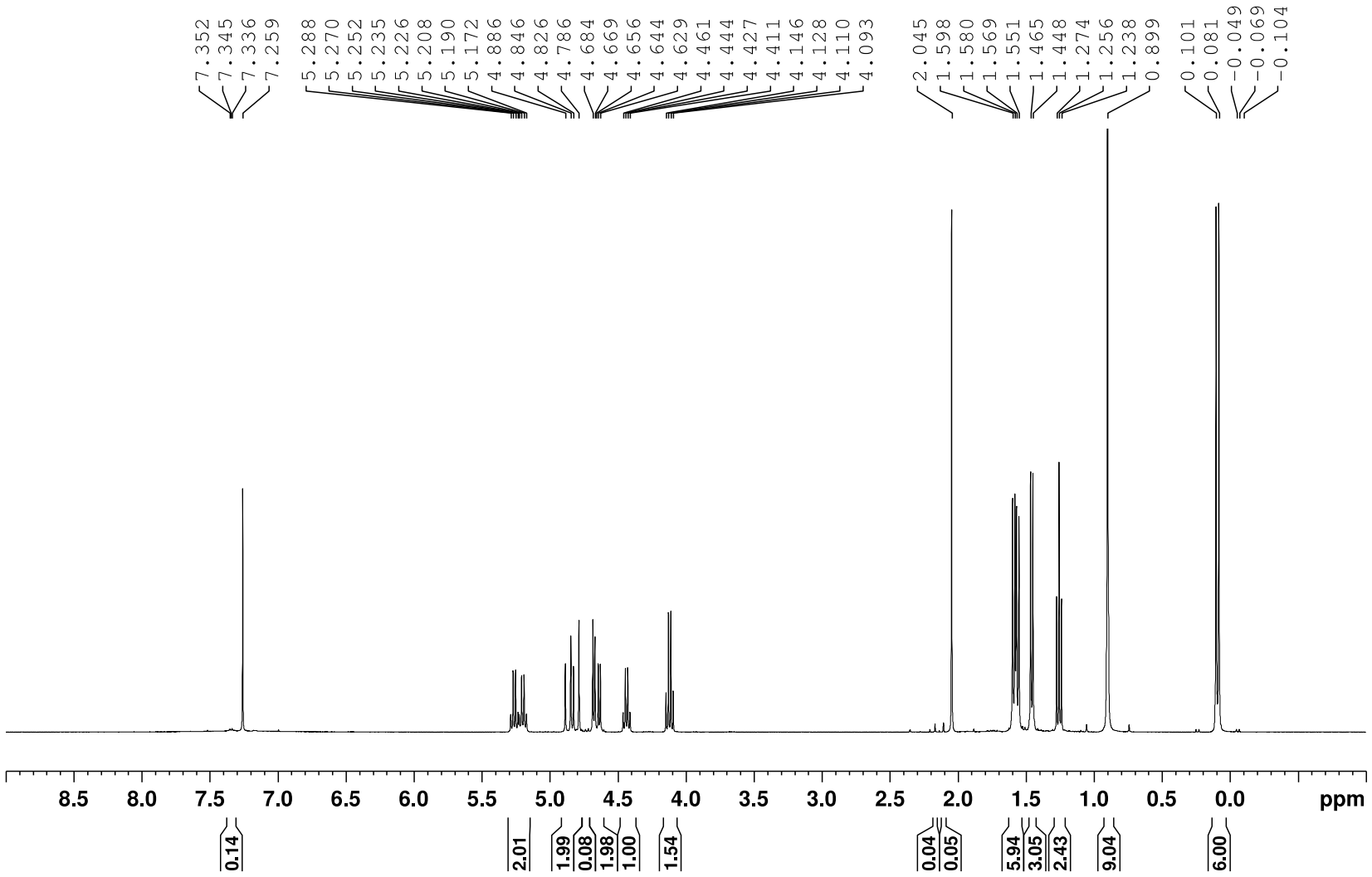
Calc.
$[M + H]^+$
465.17 amu

Found
$[M + H]^+$
349.07634 amu (minus Si)

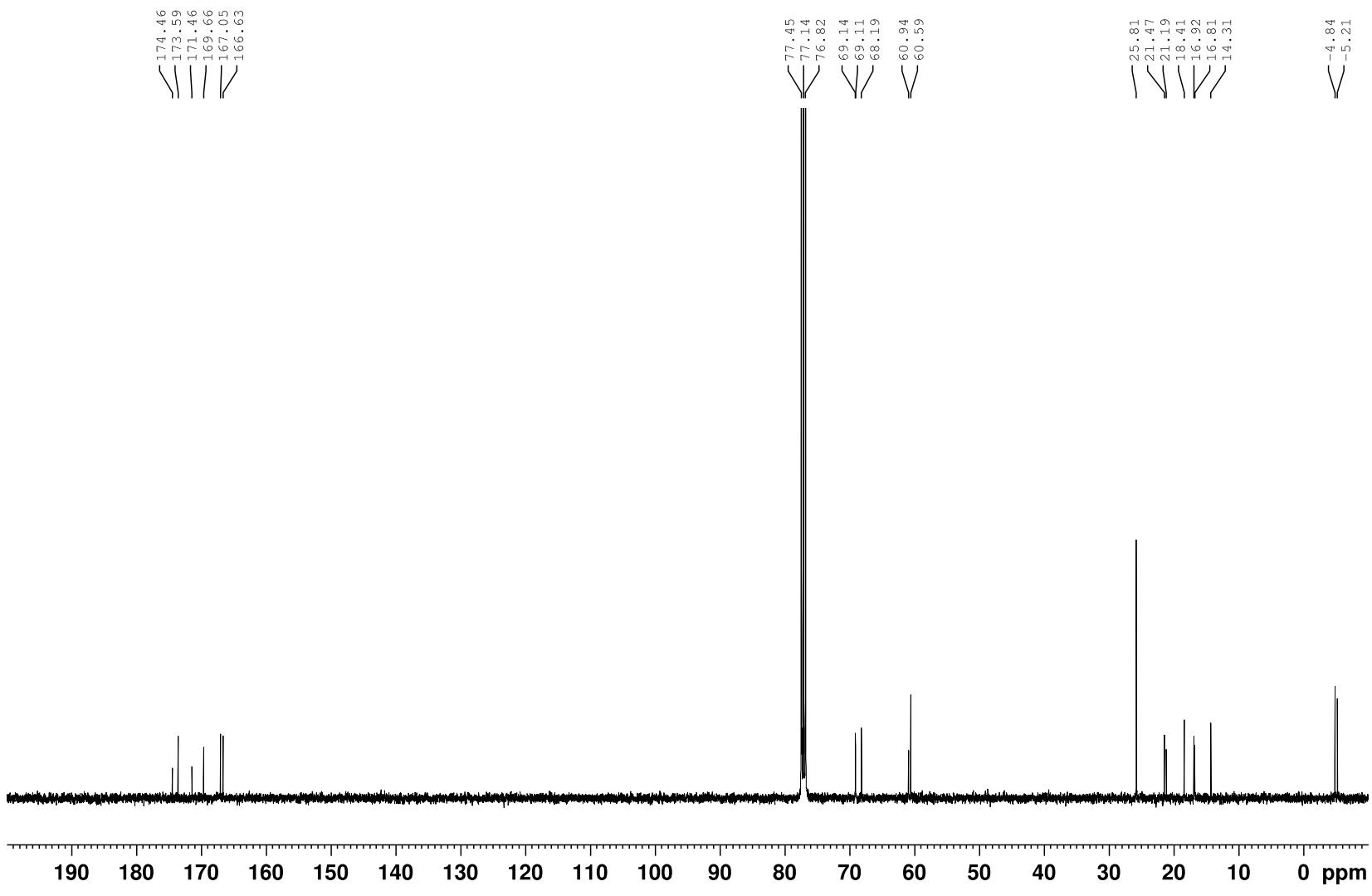
Composition
$C_{19}H_{32}O_{11}Si$

Bn-LGLGL-Si (1.7 g, 3.1 mmol) and Pd/C (0.17 g, 10 wt%) were dissolved in EtOAc (30 mL, 0.1 M) in a flame dried Schlenk flask and allowed to stir overnight at RT under 1 atm H_2. Upon consumption of starting material by TLC, the reaction mixture was filtered over celite and concentrated *in vacuo* to yield a colorless oil (1.43 g, 99% yield).

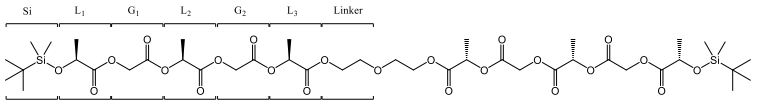
JHS-3008; LGLGL-Si; CDCl3; 1H; 400a; 16 Scans;
9/12/16



JHS-3008; LGLGL-Si; CDCl3; 13C; 400a;
2048 Scans; 9/12/16



Si-LGLGL-EG-LGLGL-Si



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

dδ (ppm)	Mult. (J)	Int.	Assignment
0.08	s	3	Si (Me)
0.10	s	3	Si (Me)
0.90	s	9	Si (t-Bu)
1.45	d (6.8)	3	L_1 (CH_3)
1.52	d (7.2)	3	L_2 (CH_3)
1.58	d (7.2)	3	L_3 (CH_3)
3.68	t (4.9)	4	Linker (CH_2)
4.29	m	4	Linker (CH_2)
4.44	q (6.8)	1	L_1 (CH)
4.65	d (16)	1	G_1 (CH_2)
4.66	d (16)	1	G_2 (CH_2)
4.80	d (16)	1	G_1 (CH_2)
4.86	d (16)	1	G_2 (CH_2)
5.17	q (7.2)	1	L_2 (CH_3)
5.26	q (7.2)	1	L_3 (CH_3)

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

δ (ppm)	Assignment
-5.18	Si
-4.81	Si
16.95	L (CH_3)
18.43	L (CH_3)
21.50	L (CH_3)
25.84	Si
60.59	G (CH_2)
60.97	G (CH_2)
64.50	Linker (CH_2)
68.19	Linker (CH_2)
68.88	L (CH)
69.13	L (CH)
69.159	L (CH)
166.66	CO
167.03	CO
169.63	CO
170.06	CO
173.56	CO

HRMS (ESI)

Calc. Mass
998.38 amu

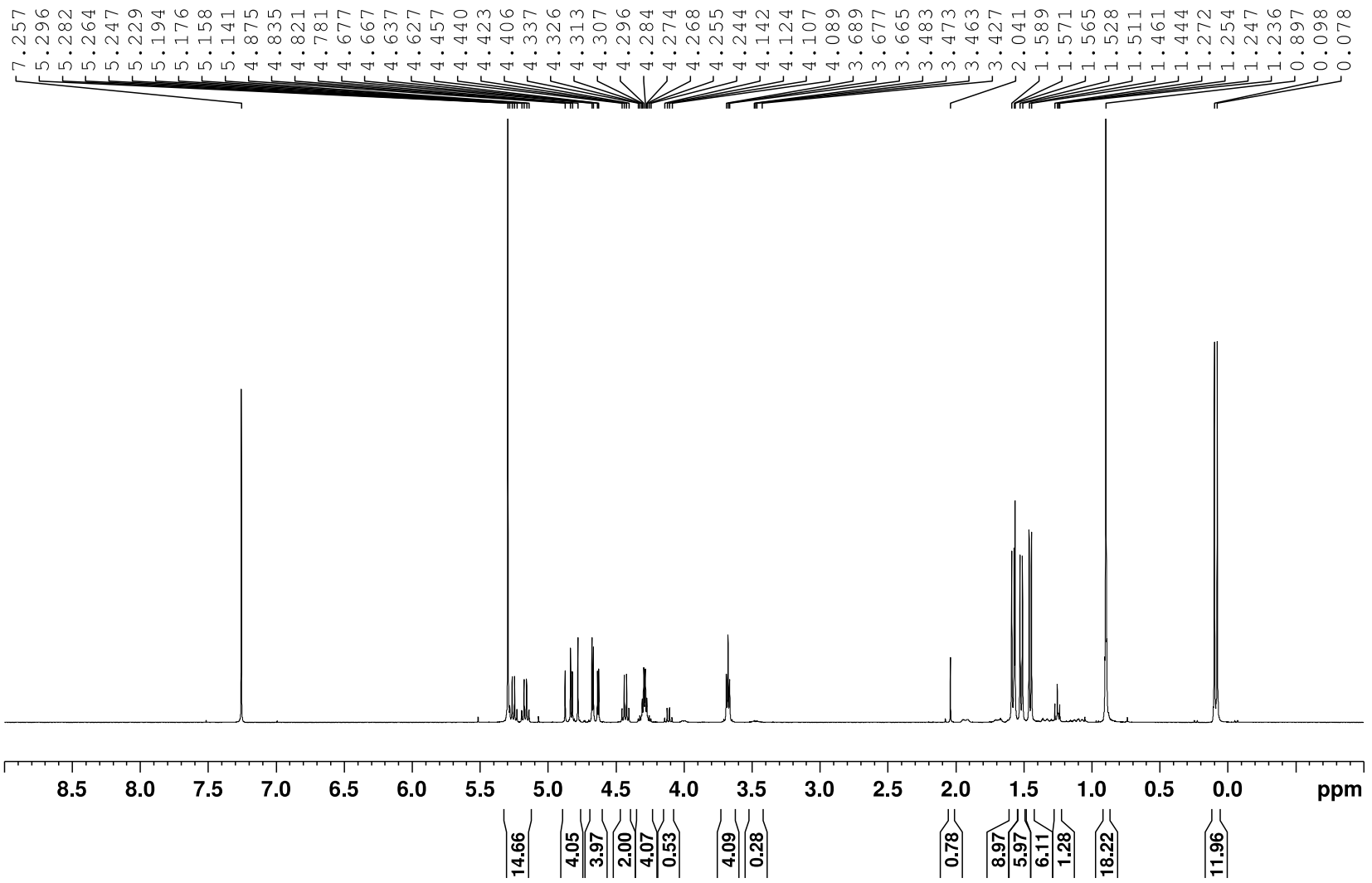
Calc.
$[M + H]^+$
999.39 amu

Found
$[M + H]^+$
999.38999 amu

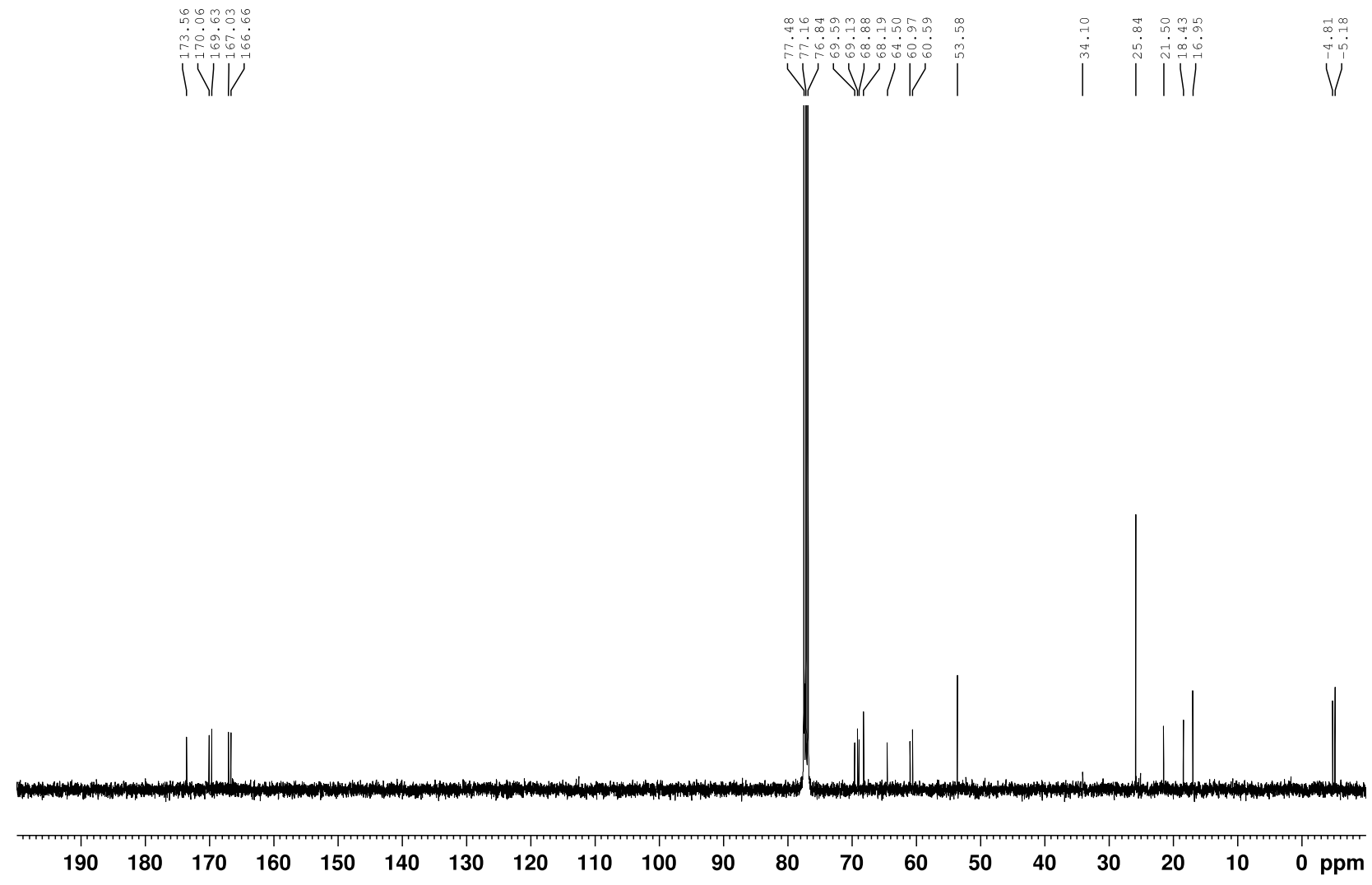
Composition
$C_{42}H_{70}O_{23}Si_2$

Diethylene glycol was dried over sieves for two h. **LGLGL-Si** (1.43 g, 3.07 mmol, 2.2 eq) was dissolved in dry DCM (8 mL, 0.4 M) in flame-dried vial under nitrogen. Dry diethylene glycol (0.149 g, 1.40 mmol, 1 eq), DPTS (0.185 g, 0.63 mmol, 0.45 eq) and DCC (0.664 g, 3.2 mmol, 2.3 eq) were then added sequentially and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes and filtered to remove DCU, concentrated and crude oil was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (1.022 g, 73% yield).

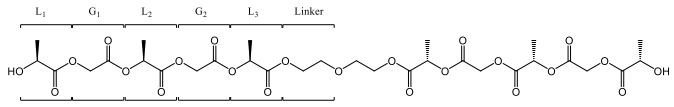
JHS-3009-Fr17-24; Si-LGLGL-EG-LGLGL-Si;
CDCl3; 1H; 400a; 16 Scans; 9/14/16



JHS-3009-Fr17-24; Si-LGLGL-EG-LGLGL-Si;
CDCl3; 13C; 400a; 2048 Scans; 9/14/16



LGLGL-EG-LGLGL



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.49	d (6.8)	3	L_1 (CH_3)
1.53	d (7.2)	3	L_2 (CH_3)
1.60	d (7.2)	3	L_3 (CH_3)
2.78	d (5.4)	2	L_1 (OH)
3.68	t (4.9)	4	Linker (CH_2)
4.29	m	4	Linker (CH_2)
4.41	qd (6.8, 5.4)	1	L_1 (CH)
4.67	d (16)	1	G_1 (CH_2)
4.73	d (16)	1	G_2 (CH_2)
4.86	m	1	G_1 (CH_2), G_2 (CH_2)
5.17	q (7.2)	1	L_2 (CH_3)
5.27	q (7.2)	1	L_3 (CH_3)

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

δ (ppm)	+ Assignment
16.92	L (CH_3)
16.94	L (CH_3)
20.48	L (CH_3)
61.01	G_1, G_2 (CH_2)
64.54	Linker (CH_2)
66.86	Linker (CH_2)
68.87	L (CH)
69.32	L (CH)
69.63	L (CH)
166.64	CO
166.78	CO
169.54	CO
170.08	CO
175.08	CO

HRMS (ESI)

Calc. Mass
770.21 amu

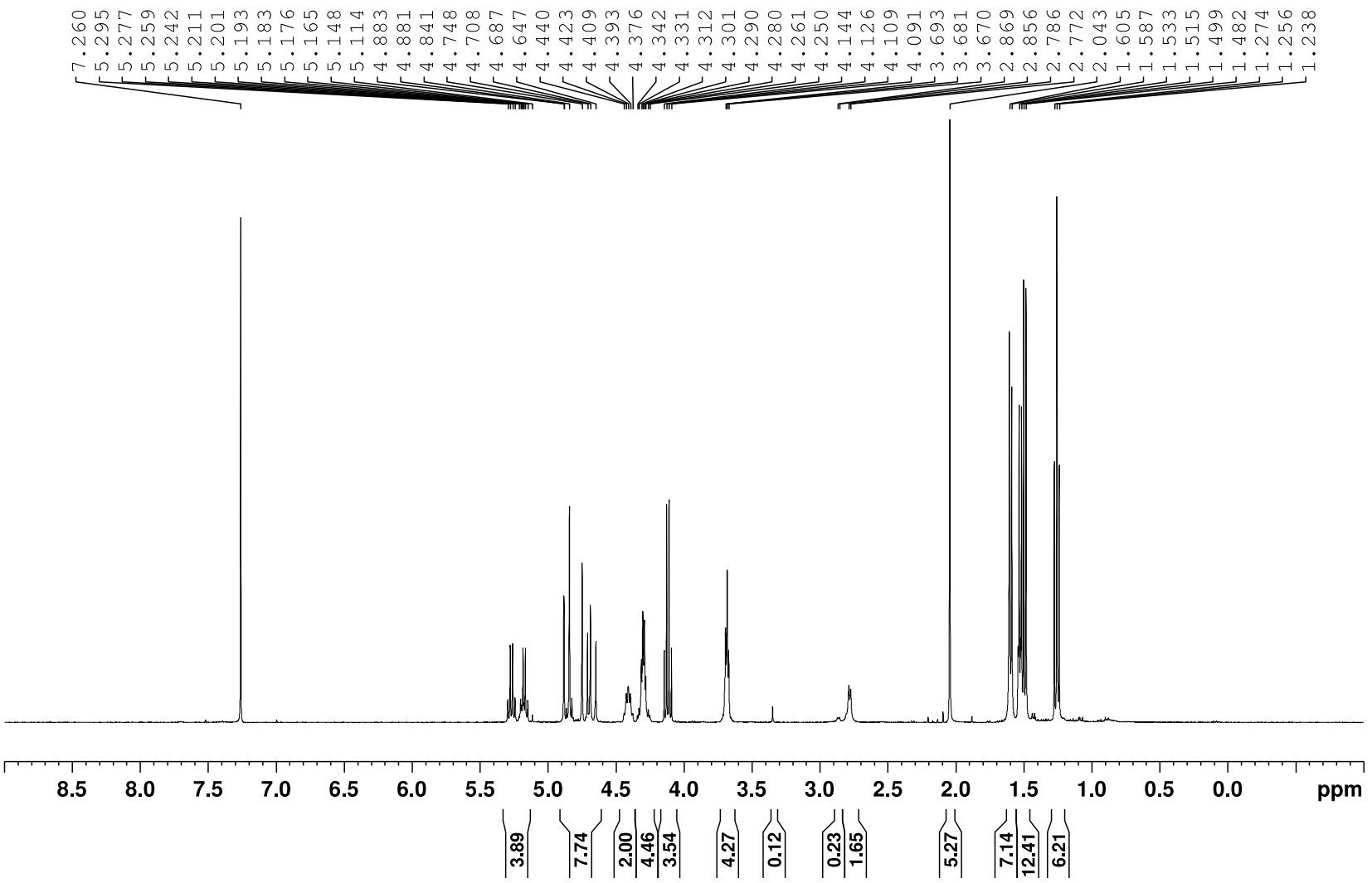
Calc.
$[M + H]^+$
771.21 amu

Found
$[M + H]^+$
771.21900 amu

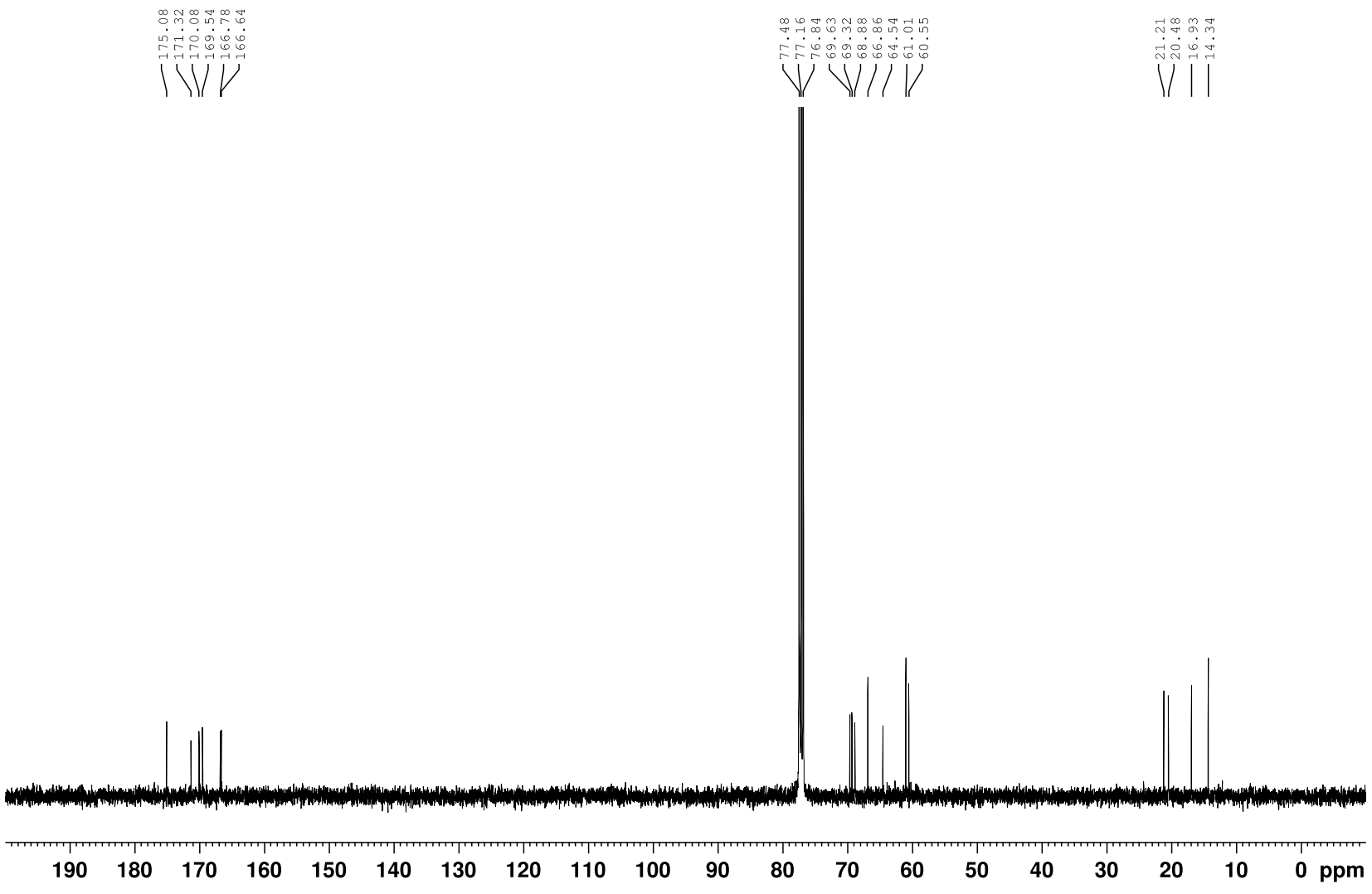
Composition
$C_{30}H_{42}O_{23}$

AcOH (0.93 mL, 16.3 mmol, 16 eq) and TBAF (1 M in THF) (3.06 mL, 3.06 mmol, 3 eq) were dried over activated sieves for 2 h. **Si-LGLGL-EG-LGLGL-Si** (1.02 g, 1.02 mmol, 1 eq) was dissolved in dry THF (25 mL, 0.04 M) in a flame dried Schlenk flask under nitrogen. AcOH and TBAF were added dropwise at 0°C, allowed to warm to RT and stir for 24 h. An additional equivalent of TBAF was added and allowed to stir for 2 more h. The reaction mixture was then diluted with brine and extracted with EtOAc 3x, the combined organic layers were washed with brine 3x, dried over $MgSO_4$ and concentrated. The crude oil was then purified via column chromatography (silica, EtOAc/hexanes) to yield a white solid (493 mg, 63% yield).

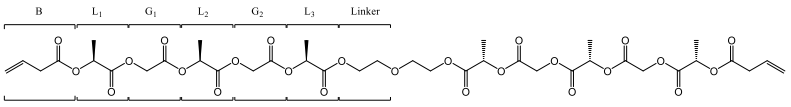
JHS-3010; LGLGL-EG-LGLGL; CDCl3; 1H; 400a;
16 Scans; 9/16/16



JHS-3010; LGLGL-EG-LGLGL; CDCl3; 13C; 400a;
2048 Scans; 9/16/16



BLGLGL-EG-LGLGLB



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.52	d (6.8)	3	L_1 (CH_3)
1.57	d (7.2)	3	L_2 (CH_3)
1.59	d (7.2)	3	L_3 (CH_3)
3.18	m	4	B (CH_2)
3.68	t (4.9)	4	Linker (CH_2)
4.29	m	4	Linker (CH_2)
4.63	d (16)	1	G_1 (CH_2)
4.64	d (16)	1	G_2 (CH_2)
4.86	d (16)	1	G_1 (CH_2)
4.88	d(16)	1	G_2 (CH_2)
5.21	m	10	L_1 (CH), L_2 (CH), L_3 (CH), B (CH_2)
5.92	m	2	B (CH)

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

δ (ppm)	+ Assignment
16.88	L (CH_3)
16.92	L (CH_3)
16.93	L (CH_3)
60.81	G (CH_2)
60.97	G (CH_2)
64.47	Linker (CH_2)
64.49	Linker (CH_2)
68.53	B (CH_2)
68.84	L (CH)
69.22	L (CH)
69.56	L (CH)
119.11	B (CH_2)
129.71	B (CH)
166.60	CO
166.70	CO
169.55	CO
170.24	CO
170.99	CO

HRMS (ESI)

Calc. Mass
906.26 amu

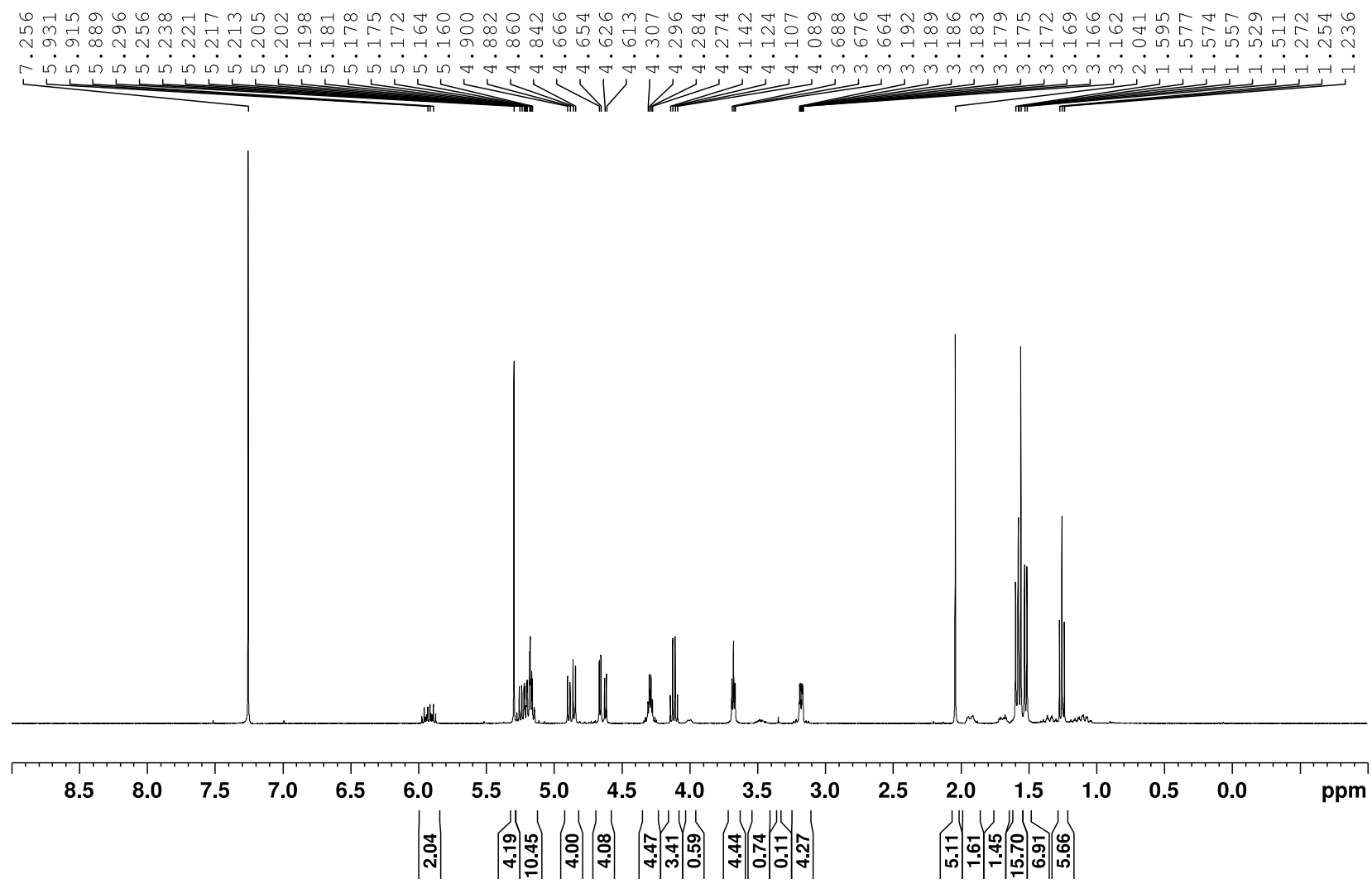
Calc.
$[M + H]^+$
907.27 amu

Found
$[M + H]^+$
907.27152 amu

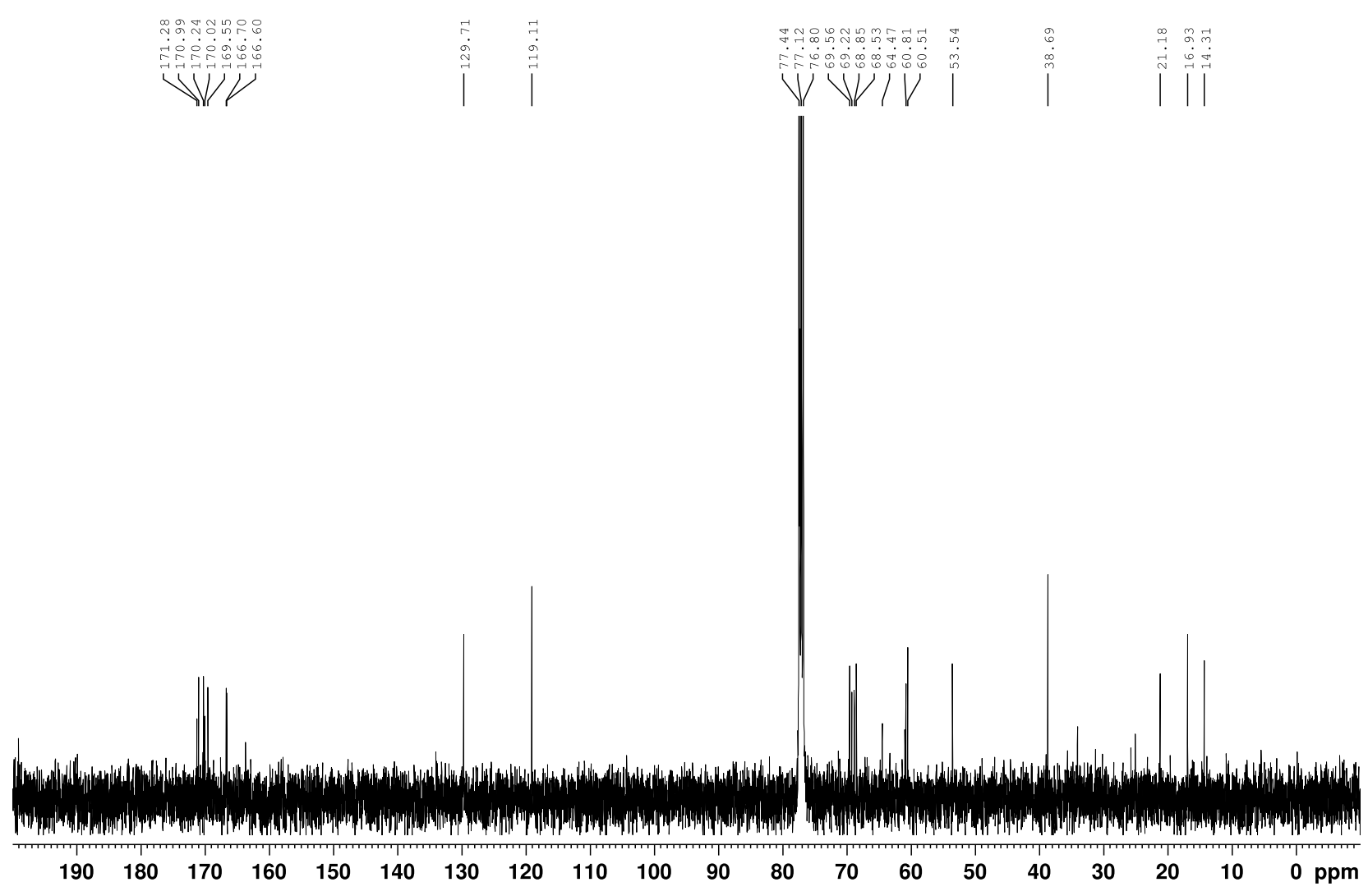
Composition
$C_{38}H_{50}O_{25}$

LGLGL-EG-LGLGL (485 mg, 0.63 mmol, 1 eq) was dissolved in dry DCM (10 mL, 0.05 M) in an oven dried vial under nitrogen. DPTS (84 mg, 0.28 mmol, 0.45 eq) and DCC (0.39 g, 1.89 mmol, 3 eq) were added sequentially. Butenoic acid (0.165 g, 1.89 mmol, 3 eq) was then added dropwise and allowed to stir at RT overnight. Upon consumption of starting material by TLC, the reaction mixture was diluted with hexanes, washed with sodium bicarbonate 3x, dried over $MgSO_4$ and filtered to remove DCU and drying agent and concentrated. Crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a colorless oil (549 mg, 96% yield).

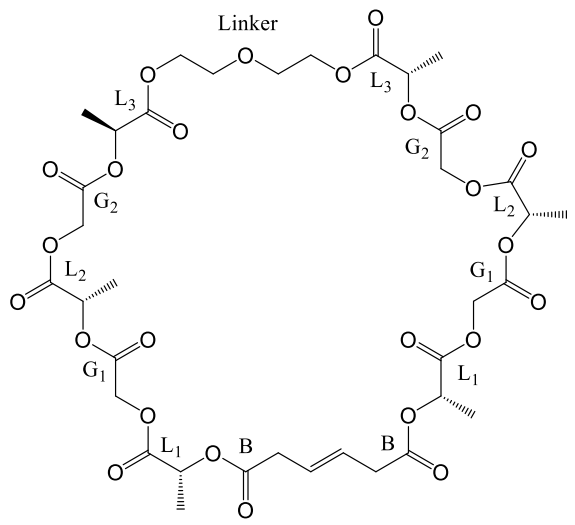
1; BLGLGL-EG-LGLGLB; CDCl3; 1H; 400a; 16 Scans;



JHS-3011; BLGLGL-EG-LGLGLB; CDCl3; 13C; 400 2048 Scans; 9/20/16



Cyclic EEG Monomer



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.52	d (6.8)	3	L_1 (CH_3)
1.54	d (7.2)	3	L_2 (CH_3)
1.57	d (7.2)	3	L_3 (CH_3)
3.16	m	4	B (CH_2)
3.68	m	4	Linker (CH_2)
4.30	m	4	Linker (CH_2)
4.70	m	4	G_1 (CH_2), G_1 (CH_2)
4.81	d (16)	2	G_1 (CH_2)
4.83	d(16)	2	G_2 (CH_2)
5.21	m	6	L_1 (CH), L_2 (CH), L_3 (CH)
5.78	m	2	B (CH)

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

δ (ppm)	+ Assignment
16.70	L (CH_3)
16.73	L (CH_3), L (CH_3)
37.35	B (CH_2)
60.79	G (CH_2)
60.86	G (CH_2)
64.39	Linker (CH_2)
68.44	Linker (CH_2)
68.70	L (CH)
69.09	L (CH)
69.50	L (CH)
125.67	B (CH)
166.50	CO
166.51	CO
169.36	CO
169.89	CO
169.92	CO
170.61	CO

HRMS (ESI)

Calc. Mass
878.23 amu

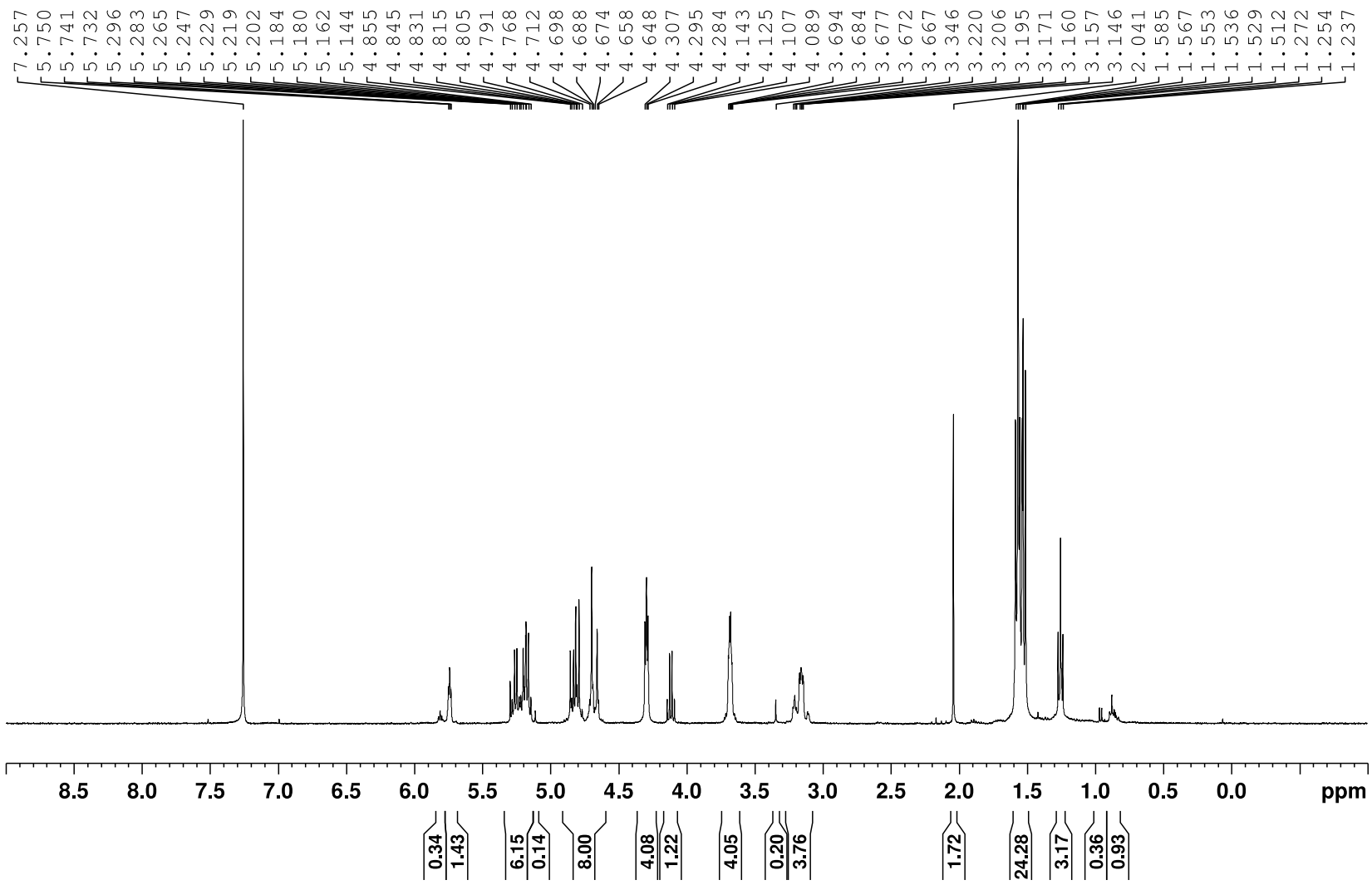
Calc.
$[M + H]^+$
879.23 amu

Found
$[M + H]^+$
879.23971 amu

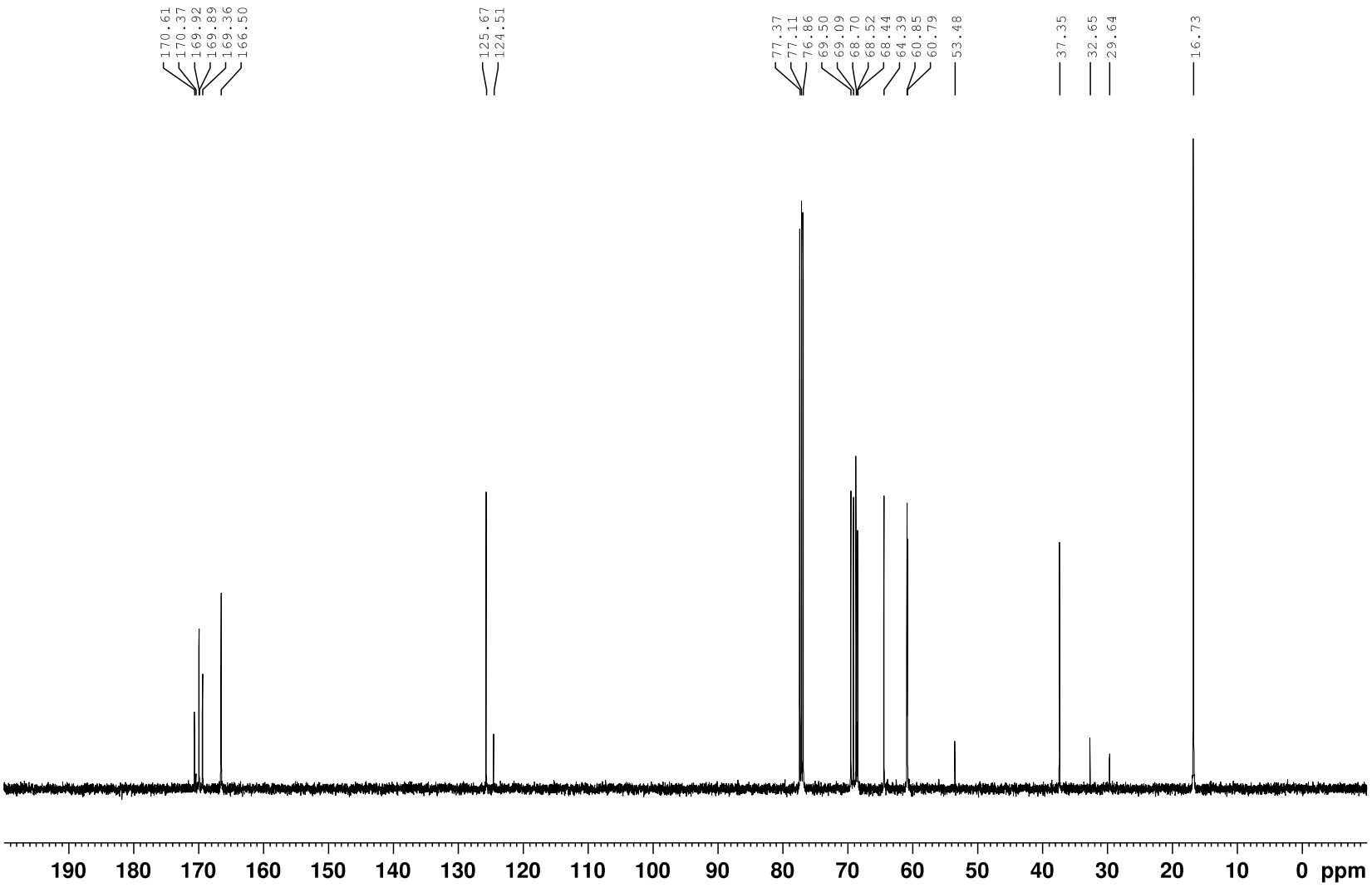
Composition
$C_{36}H_{46}O_{25}$

BLGLGL-EG-LGLGLB (500 mg, 0.55 mmol, 1 eq) was dissolved in dry DCM (550 mL, 0.001M) in a flame-dried Schlenk flask under nitrogen. A stock solution of Grubbs 2 (51 mg, 0.055 mmol, 10 mol%) in dry DCM was added and allowed to stir at RT overnight. Upon consumption of starting material by TLC, reaction mixture was quenched by addition of excess ethyl vinyl ether and stirring for 10 additional min. The reaction mixture was then concentrated and the crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a thick brown oil (400 mg, 83% yield).

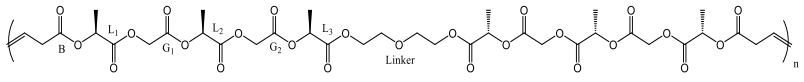
JHS-3012; Ext. EG Monomer; CDCl3; 1H; 400a;
16 Scans; 9/21/16



JHS-3012; EEG Monomer; CDCl3; 13C; 500;
128 Scans; 10/12/17



Poly(EEG)



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

dδ (ppm)	Mult. (J)	Int.	Assignment
1.53	m	12	CH_3 ($L_{1/2/3}$)
3.15	m	4	CH_2 (B)
3.65	m	4	CH_2 (Linker)
4.26	m	4	CH_2 (Linker)
4.61	d (16)	2	CH_2 (G)
4.62	d (16)	2	CH_2 (G)
4.84	d (16)	2	CH_2 (G)
4.86	d(16)	2	CH_2 (G)
5.17	m	10	CH ($L_{1/2/3}$)
5.69	m	1.5	CH (B Trans)
5.78	m	0.5	CH (B Cis)

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

δ (ppm)	Assignment
16.80	L (CH_3)
37.33	B (CH_2)
60.74	G (CH_2)
60.89	G (CH_2)
64.39	Linker (CH_2)
68.51	L (CH)
68.77	L (CH)
69.14	L (CH)
69.50	Linker (CH_2)
124.34	B (CH Cis)
125.76	B (CH Trans)
166.53	CO
166.62	CO
169.45	CO
169.92	CO
170.10	CO
170.81	CO

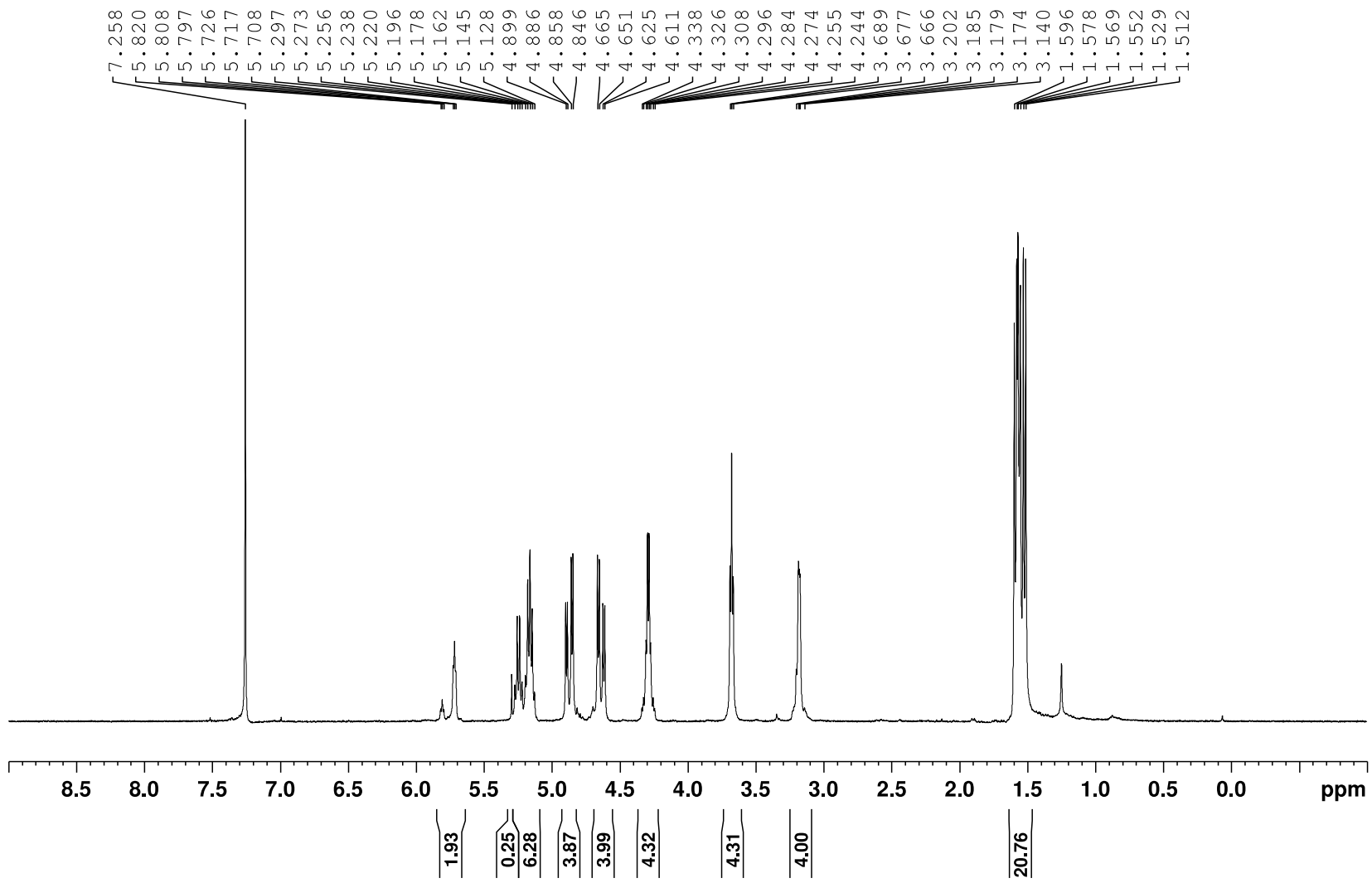
HRMS (ESI)

$\underline{M_n}$
27,178 Da

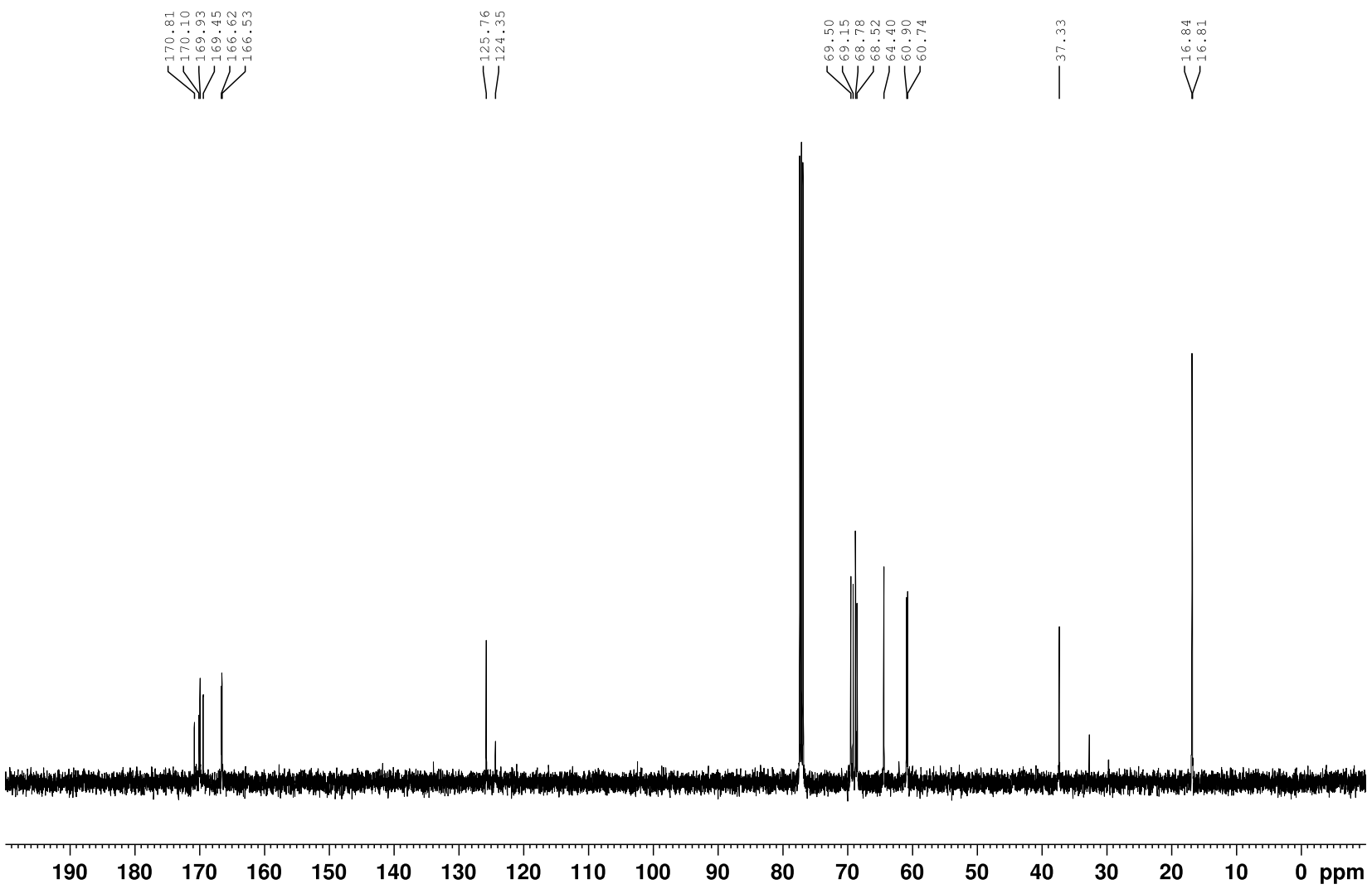
$\underline{Đ}$
1.25

Cyclic EEG Monomer (104 mg, 0.118 mmol, 1 eq.) was weighed in a flame dried 1 mL vial under nitrogen. A stock solution of Grubbs II (1 mg, 0.0012 mmol, 3 mol%) in dry DCM (5.8 mg/mL, 0.17 mL, 0.7M) was added and the vial was shaken for 4 h. The reaction mixture was quenched by the addition of excess ethyl vinyl ether and vortexing. Solution was concentrated to yield a crude solid polymer, which was reprecipitated into a stirring solution of MeOH and filtered to collect pure polymer as a brown solid (84 mg, 81% yield).

JHS-3044-Pure; Poly(EEG); CDCl3; 1H; 400a;
16 Scans; 2/28/17



JHS-3044; Poly(EEG); CDCl3; 13C; 500; 64 Scans;
10/27/17



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