**Supplementary Information** 

# **Property Impact of Common Linker Segments in Sequence-Controlled Polyesters**

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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.<sup>1-5</sup> A representative load-displacement curve with associated values is provided in Figure S8.

The maximum load, P<sub>Max</sub>, 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:

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

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

(S2) 
$$A(h_c) = 24.5h_c^2$$

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:

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

where  $\varepsilon$  is another geometrical constant related to the Berkovich tip equal to 0.75.

The reduced elastic modulus, E<sub>r</sub>, was defined as:

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

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

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

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<sup>6</sup>) and v<sub>i</sub> and

E<sub>i</sub> 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  $20 \,\mu$ m/sec, and scan size of  $10 \,\mu$ m.

#### 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<sub>G</sub> 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 S14. Molecular weight (M<sub>W</sub>) 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  $\mu$ m standard grade silica. Dicyclohexylcarbodiimide (DCC) was purchased from Oakwood Products, Inc. 1,4-Dimethylpyidinium *p*-toluenesulfonate (DPTS) was prepared using a previously reported method.<sup>7</sup> Synthetic procedures were adapted from several previous references.<sup>8-10</sup>

#### 2.2 STARTING MATERIALS

			Bn-LGL-Si			
				<sup>13</sup> C-NM C	<b>R</b> (400 MHz, DCl <sub>3</sub> )	HRMS (ESI)
	• 0			ة Ass	δ (ppm) + ignment	<u>Calc. Mass</u> 424.19 amu
Si				-5.20	Si	
0	$\int G_1$	$\circ$		-4.81	Si	Calc.
	Ö	Ö		16.99	L (CH <sub>3</sub> )	$[M + H]^+$
				18.42	L (CH <sub>3</sub> )	425.19 amu
1]	H-NMR (400 N	MHz, CE	DCl <sub>3</sub> )	21.49	Si (C)	
dδ (ppm)	Mult. (J)	Int.	Assignment	25.83	Si (t-Bu)	Found
0.09	S	3	Si (CH <sub>3</sub> )	60.62	$G(CH_2)$	$[M + H]^+$
0.11	S	3	Si (CH <sub>3</sub> )	67.34	Bn (CH <sub>2</sub> )	425.20069
0.91	S	9	Si (t-Bu)	68.20	L (CH)	amu
1.46	d (6.8)	3	L <sub>1</sub> (CH <sub>3</sub> )	69.47	L (CH)	
1.51	d (7.1)	3	L <sub>2</sub> (CH <sub>3</sub> )	128.31	Bn (CH)	<u>Composition</u>
4.44	q (6.8)	1	$L_1$ (CH)	128.61	Bn (CH)	$C_{21}H_{32}O_7Si$
4.66	d (16)	1	$G_1$	128.76	Bn (CH)	
4.80	d (16)	1	$G_1$	135.27	Bn (CH	
5.18	m	2	Bn (CH <sub>2</sub> )	167.06	CO	
5.23	q (7.1)	1	$L_2$ (CH)	170.04	CO	
7.05	1 /	-		1/3.56	CO	
7.35	m	5	Bn			
			(Aromatic)			

**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).





			LGL-Si			
				<sup>13</sup> C-NM	R (400 MHz, DCl <sub>3</sub> )	HRMS (ESI)
				δ (ppm) -	+ Assignment	Calc. Mass
Si	$L_1$	G <sub>1</sub>	L <sub>2</sub>	-5.23	Si	334.14 amu
		0	-	-4.86	Si	
		Ĭ		16.99	L (CH <sub>3</sub> )	Calc.
		<u> </u>		18.39	L (CH <sub>3</sub> )	$[M + H]^+$
	Ů		0 I	21.45	Si (C)	335.14 amu
				25.79	Si (t-Bu)	
				60.55	$G(CH_2)$	Found
				68.17	L (CH)	$[M + H]^{+}$
$^{1}\mathrm{H}$	-NMR (400 M	IHz, CI	DCl <sub>3</sub> )	68.89	L (CH)	335.15421
dð (ppm)	Mult. (J)	Int.	Assignment	107.02	C0 C0	amu
0.086	S	3	Si (CH <sub>3</sub> )	175.03	C0	Composition
0.11	S	3	Si (CH <sub>3</sub> )	175.54	co	$\frac{\text{composition}}{C_{14}H_{26}O_7S_i}$
0.90	S	9	Si (t-Bu)			01411200701
1.46	d (6.8)	3	$L_1$ (CH <sub>3</sub> )			
1.56	d (7.1)	3	$L_2$ (CH <sub>3</sub> )			
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 <sub>2</sub> (CH)			

**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<sub>2</sub>. 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; 13C; 400a; 2048 Scans; 11/12/16

	77.48 76.84 68.93 68.22 68.22 60.60	25.84 21.50 21.21 16.87 14.33	-5.18

				•																		
210	200	100	120	170	160	150	1/10	120	120	110	100	an	20	70	60	50	10	20	20	10	Ω	nnm
210	200	130	100	170	100	130	140	130	120	110	100	30	00	10	00	30	40	30	20	10	U	ppiii

#### 2.3 ALKYL LINKER CONTAINING COMPOUNDS

			Si-LGL-Alk-LGI	2-Si		
	_	_	_	<sup>13</sup> C-NM	IR (400 MHz,	HRMS (ESI)
				(	CDCl <sub>3</sub> )	
Si L <sub>1</sub>	L <sub>2</sub> Linker	<u></u>		δ (ppm)	+ Assignment	Calc. Mass
= O	=		• 0 • 1	-5.35	$CH_3$ (Si)	736.35 amu
				-5.32	$CH_3$ (Si)	
1F	I-NMR (400 N	Hz C	$DCl_3$	16.86	CH <sub>3</sub> (L)	Calc.
dδ (nnm)	1100000000000000000000000000000000000	Int	Assignment	18.24	C (Si)	$[M + H]^+$
0.09	s	6	CH <sub>2</sub> (Si)	20.98	$CH_{3}(L)$	737.35 amu
0.11	S	6	$CH_2$ (Si)	21.33	CH <sub>2</sub> (Linker)	
0.90	S	18	$t_{\rm -Bu}$ (Si)	25.67	t-Bu (Si)	Found
1 46	m	8	$CH_2$ (Linker) $CH_2$	28.00	CH <sub>2</sub> (Linker)	$[M + H]^+$
1.40	111	0	$(L_1)$	60.32	$CH_2(G_1)$	737.36003
1 50	d(70)	6	$(\mathbf{L}_1)$ $\mathbf{L}_2(\mathbf{C}\mathbf{H}_2)$	65.17	CH (L)	amu
1.50	u (7.0)	0 Л	$L_2$ (CH <sub>2</sub> )	68.03	CH (L)	~
1.00	m	т Л	Linker $(CH_2)$	69.33	CH <sub>2</sub> (Linker)	<u>Composition</u>
4.14	a(7.0)	- -	$L_{1}(CH)$	166.87	CO	$C_{33}H_{60}O_{14}Si_2$
4.42	q(7.0)	2	$L_{\Gamma}(C\Pi)$	170.02	CO	
4.00	d(10)	2	$G_1$	173.32	CO	
4.79	a (16)	2				
5.16	q (7.1)	2	$L_2$ (CH)			

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).



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

M N F			
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	000 0 000	N N N N H H	1 1
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190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0 ppm

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$\begin{array}{c c c c c c c c c c c c c c c c c c c $	)
$\frac{\delta (ppm) + Assignment}{16.92 CH_3 (L)} = \frac{\delta (ppm) + Assignment}{16.92 CH_3 (L)} = \frac{\delta (ppm) + Assignment}{16.92 CH_3 (L)} = \frac{\delta (ppm) + Assignment}{20.38 CH_3 (L)} = \frac{\delta (ppm) + Assignment}{20.3$	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	
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$\begin{array}{c c c c c c c c c c c c c c c c c c c $	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	
1.41 m 2 Linker (CH <sub>2</sub> ) 66.80 CH $(I)$ Found	
1.50 d (7.0) 6 $L_2$ (CH <sub>3</sub> ) 69.65 $CH_2$ (Linker) $[M + H]^+$	
1.52 d (7.1) 6 $L_1$ (CH <sub>3</sub> ) $166.76$ CO 509.18637 am	m
1.68 m 4 Linker (CH <sub>2</sub> ) $170.11$ CO	
2.85 m 2 $L_1$ (OH) 174.98 CO Composition	L
4.17 t (3.8) 4 Linker (CH <sub>2</sub> ) $C_{21}H_{32}O_{14}$	
4.42 m 2 L <sub>2</sub> (CH)	
4.74 d (16) 2 G <sub>1</sub>	
4.84 d (16) 2 G <sub>1</sub>	
5.16 q (7.08) 2 L <sub>1</sub> (CH)	

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<sub>4</sub> and concentrated. The crude oil was then purified via column chromatography (silica, EtOAc/hexanes) to yield a white solid (155 mg, 58% yield).

2074; LGL-Alk-LGL; CDCl3; 1H; 400a; 16 Scans; 8/1



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

 65. 39 65. 39 60. 93 60. 93	$\begin{array}{c c} & & & & & & & & & & & & & & & & & & &$

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	ul land han ha		hen hendeligt	Yoling good as	an en literation de la compañía de l Compañía de la compañía	errier and half after		( Prodite de la constante	ll a dhi dahalan (		4.000	ali la anti	hedrid a stip		la phylia		a hhere are the second s	lik kirkeriya		
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		.																		

			BLGL-Alk-LGLB	6		
0	0	C		<sup>13</sup> C-NN	/IR (400 MHz,	HRMS (ESI)
$\mathbb{A}$ $\mathbb{A}$ $\mathbb{A}$ $\mathbb{A}$ $\mathbb{A}$	$G_1 \circ \downarrow $				CDCl <sub>3</sub> )	
	Linke	δ (ppm)	+ Assignment	Calc. Mass		
-	-			16.92	CH <sub>3</sub> (L)	644.23 amu
				16.96	CH <sub>3</sub> (L)	
				25.03	CH <sub>2</sub> (Linker)	Calc.
				28.11	CH <sub>2</sub> (Linker)	$[M + H]^+$
1				38.68	$CH_{2}(B)$	645.23 amu
1	H-NMR (400 N	ИНz, (	CDCl <sub>3</sub> )	60.83	$CH_2(G_1)$	
dð (ppm)	Mult. (J)	Int.	Assignment	65.34	CH (L)	Found
1.41	m	2	Linker (CH <sub>2</sub> )	68.53	CH (L)	$[M + H]^+$
1.51	d (7.0)	6	$L_2$ (CH <sub>3</sub> )	69.56	CH <sub>2</sub> (Linker)	645.23982 amu
1.57	d (7.1)	6	$L_1$ (CH <sub>3</sub> )	119.09	$CH_{2}(B)$	
1.68	m	4	Linker (CH <sub>2</sub> )	129.71	CH (B)	<u>Composition</u>
3.18	m	4	$B(CH_2)$	166.72	CO	$C_{29}H_{40}O_{16}$
4.15	t (3.8)	4	Linker (CH <sub>2</sub> )	170.13	CO	
4.63	d (16)	2	$G_1$	170.23	CO	
4.87	d (16)	2	$G_1$	170.98	CO	
5.18	m	8	L <sub>1</sub> (CH), L <sub>2</sub> (CH), B			
			$(CH_2)$			
5.93	m	2	B (CH)			

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<sub>4</sub>, 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

# 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

			onomer					
	0 	O G1	<sup>13</sup> C-NN	<b>AR</b> (400 MHz, CDCl <sub>3</sub> )	HRMS (ESI)			
	Linker	-	δ (ppm)	) + Assignment	Calc. Mass			
	$\langle$			16.82	$CH_{3}(L)$	616.20 amu		
			Ó	16.85	$CH_{3}(L)$			
			в	22.31	CH <sub>2</sub> (Linker)	Calc.		
				28.06	CH <sub>2</sub> (Linker)	$[M + H]^+$		
	$\sim - \langle$	в		37.49	CH <sub>2</sub> (Linker)	617.20 amu		
	G1/O I	ہے ہے	60.80	CH (L)				
	Ţ		65.32	CH (L)	Found			
	<sup>1</sup> H-NMR (40)	0 MHz	68.49	$CH_2(G)$	$[M + H]^+$			
dð (ppm)	Mult (I)	Int	Assignment	69.45	$CH_{2}(B)$	617.20615 amu		
<u> </u>	$\frac{1}{2} \frac{1}{2} \frac{1}$	2	Linker (CH2)	125.78	CH (B)			
1.12	d(72)	6	$L_1 (CH_2)$	166.53	CO	<u>Composition</u>		
1.50	d(7.2)	6	$L_1$ (CH <sub>2</sub> )	169.93	CO	$C_{27}H_{36}O_{16}$		
1.54	u(7.2)	4	$L_2$ (CH <sub>3</sub> ) Linker (CH <sub>3</sub> $\beta$ L <sub>4</sub> )	170.11	CO			
2.17	quiii. (20)	т 1	$\frac{D}{D} \left( CH_{2} p - L_{1} \right)$	170.68	CO			
3.17 4.17	III	4	$\mathbf{D}$ (CH <sub>2</sub> )					
4.17		4	Linker (CH <sub>2</sub> $\alpha$ -L <sub>1</sub> )					
4.6/	d (16)	2	G <sub>1</sub>					
4.80	d (16)	2	$\mathbf{G}_1$					
5.14	q (20.8)	2	$L_1(CH)$					
5.20	q (21.2)	2	$L_2$ (CH)					
5.79	m	2	B (CH)					

**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



# 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

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			Poly(Alk)			
$\oint \circ B \circ \int \circ \circ$		<sup>13</sup> C-NN	GPC			
	L <sub>2</sub> L <sub>2</sub> Linker			δ (ppm)	+ Assignment	<u>M</u> <sub>n</sub>
0 0		· · · · ·	0	16.92	CH <sub>3</sub> (L)	26,868
				16.95	$CH_{3}(L)$	
				22.21	CH <sub>2</sub> (Linker)	Ð
				28.13	CH <sub>2</sub> (Linker)	1.40
<sup>1</sup> H-	NMR (400 MHz	CDCl	2)	37.39	CH <sub>2</sub> (Linker)	
dð (ppm)	1000000000000000000000000000000000000	<u>, CDCI</u> Int	Assignment	60.83	$CH_2(G_1)$	
<u> </u>	m	2	Linker (CH <sub>2</sub> )	65.33	$CH_{2}(B)$	
1.40	d(70)	6	$L_{1}(CH_{2})$	68.59	CH (L)	
1.51	d(7.0)	6	$L_2$ (CH <sub>3</sub> )	69.55	CH (L)	
1.57	u (7.1)	4	Linker (CH2)	124.39	CH (B Cis)	
2.10	III m	4	$\mathbf{P}(\mathbf{CH}_2)$	125.82	CH (B Trans)	
5.19		4	$\mathbf{D}(\mathbf{CH}_2)$	166.70	CO	
4.15	t(0.0)	4	Linker ( $CH_2$ )	170.09	CO	
4.63	d (16)	2	$G_1$	170.17	CO	
4.87	d (16)	2	$G_1$	170.87	CO	
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			

**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).



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high at the burden defendence.	4147 (m 1941) 						 Maluanthunth			Munuhirikani		r[1]						1		110,,,/man,00,00,00,00
190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	2	20	10	0 ppm

#### 2.4 EG LINKER CONTATINING COMPOUNDS

	Si-LGL-EG-LGL-Si													
			<sup>13</sup> C-NM	IR (400 MHz,	HRMS (ESI)									
G G G			(	CDCl <sub>3</sub> )										
Si L <sub>1</sub>	L <sub>2</sub> Linker			δ (ppm)	+ Assignment	Calc. Mass								
' - C	) -		-5.40	CH <sub>3</sub> (Si)	738.33 amu									
				-5.02	CH <sub>3</sub> (Si)									
1			16.74	CH <sub>3</sub> (L)	Calc.									
18 ( )	$\frac{1-1}{1} \frac{1}{1} $	$\frac{1}{1}$		18.17	C (Si)	$[M + H]^+$								
do (ppm)	Mult. (J)	Int.	Assignment	21.26	CH <sub>3</sub> (L)	739.33 amu								
0.10	S	6	$CH_3$ (S1)	25.62	t-Bu (Si)									
0.12	S	6	CH <sub>3</sub> (Si)	60.36	$CH_2(G_1)$	Found								
0.92	S	18	t-Bu (Si)	64.26	CH(L)	$[\overline{M + H}]^+$								
1.47	d (6.8)	6	$CH_3(L_1)$	67.94	CH <sub>2</sub> (Linker)	739.33935 amu								
1.54	d (7.1)	6	$L_2$ (CH <sub>3</sub> )	68.64	CH (L)									
3.71	t (4.7)	4	Linker (CH <sub>2</sub> )	69.23	CH <sub>2</sub> (Linker)	<b>Composition</b>								
4.31	m	4	Linker (CH <sub>2</sub> )	166.81	CO	C <sub>32</sub> H <sub>58</sub> O <sub>15</sub> Si <sub>2</sub>								
4.46	q (6.8)	2	$L_1$ (CH)	169.85	CO									
4.68	d (16)	2	$G_1$	173.23	CO									
4.81	d (16)	2	$G_1$											
5.20	q (7.1)	2	$L_2$ (CH)											

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

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190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20	10 0 ppm

	LGL-EG-LGL														
	0	0	<sup>13</sup> C-NN	AR (400 MHz,	HRMS (ESI)										
		$\sim$	V OH		CDCl <sub>3</sub> )										
Ŭ O	≣ <sup>2</sup> Linke	r	δ (ppm)	) + Assignment	Calc. Mass										
		16.93	$CH_{3}(L)$	510.16 amu											
		20.49	CH <sub>3</sub> (L)												
1	11 NIMD (200 N		60.98	CH <sub>2</sub> (Linker)	Calc.										
18 ( )	$\frac{\text{H-INMR}(500 \text{ N})}{\text{M-I}}$	<u>лнz, Сі</u>		64.55	CH <sub>2</sub> (Linker)	$[M + H]^+$									
do (ppm)	Mult. (J)	Int.	Assignment	66.86	$CH_{2}(G_{1})$	511.16 amu									
1.49	d (7.0)	6	$L_1$ (CH <sub>3</sub> )	68.82	CH (L)										
1.53	d (7.0)	6	$L_2$ (CH <sub>3</sub> )	69.64	CH (L)	Found									
2.86	d (5.6)	2	$L_1$ (OH)	166.86	CO	$[M + H]^+$									
3.69	t (5.0)	4	Linker (CH <sub>2</sub> )	170.09	CO	amu									
4.31	t (5.0)	4	Linker (CH <sub>2</sub> )	175.02	CO										
4.41	m	2	$L_1$ (CH)			<b>Composition</b>									
4.74	d (16)	2	$G_1$			$C_{20}H_{30}O_{15}$									
4.84	d (16)	2	$G_1$												
5.19	q (7.0)	2	L <sub>2</sub> (CH)												

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<sub>4</sub> 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





				BLGL-EG-LGLB			
			<sup>13</sup> C-N	MR (400	HRMS (ESI)		
			C	0 	MHz	, CDCl <sub>3</sub> )	
1			δ (1	opm) +	Calc. Mass		
L	=		Assi	gnment	646.21 amu		
	в L <sub>1</sub>	$G_1$ $L_2$ Linker	14.35	CH <sub>3</sub> (L)			
					16.96	$CH_{3}(L)$	Calc.
		111 312 62 (400 3			38.73	$CH_2$	$[M + H]^+$
		<sup>1</sup> H-NMR (400 N	ЛНz, (	CDCl <sub>3</sub> )	60.88	$CH_2$	647.21 amu
	dð (ppm)	Mult. (J)	Int.	Assignment	64.50	$CH_2$	
	1.52	d (7.0)	6	$L_2$ (CH <sub>3</sub> )	68.57	$CH_2$	Found
	1.57	d (7.0)	6	$L_1$ (CH <sub>3</sub> )	68.89	CH (L)	$[M + H]^+$
	3.18	m	4	$B(CH_2)$	69.56	CH (L)	647.21917 amu
	3.68	t (4.8)	4	Linker (CH <sub>2</sub> )	119.13	$CH_{2}(B)$	
	4.29	m	4	Linker (CH <sub>2</sub> )	129.76	CH (B)	Composition
	4.63	d (16)	2	G1	166.77	CO	$C_{28}H_{38}O_{17}$
	4.87	d (16)	2	$G_1$	170.09	CO	
	5.18	m	8	L <sub>1</sub> (CH), L <sub>2</sub> (CH), B	170.27	CO	
				$(CH_2)$	171.01	CO	
	5.93	m	2	B (CH)			

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<sub>4</sub> 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;





	Cyclic EG Monomer													
	L <sub>2</sub>	2	<sup>13</sup> C-NN	<b>AR</b> (400 MHz,	HRMS (ESI)									
	U intern O	0	h		CDCl <sub>3</sub> )									
		$\langle \cdot \rangle$	δ (ppm)	+ Assignment	Calc. Mass									
	о́ — ́	$\mathbf{V}$	14.33	$CH_{3}(L)$	618.18 amu									
	0	0-		16.92	$CH_{3}(L)$									
	$\mathbf{h}$		0	37.59	$CH_{2}(B)$	Calc.								
	0	;	) ) ) 0	60.94	CH <sub>2</sub> (Linker)	$[M + Na]^{+}$								
	∕=o		$\langle$	64.66	CH <sub>2</sub> (Linker)	641.17 amu								
	$- \langle \rho \rangle$		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	68.61	$CH_{2}(G)$									
	0			68.88	CH (L)	Found								
				69.65	CH (L)	$[M + Na]^{+}$								
	0		125.85	CH (B)	641.16984 amu									
	<sup>1</sup> H-NMR (400	MHz. 0	CDCl <sub>3</sub> )	166.68	CO									
dδ (ppm)	Mult. (J)	Int.	Assignment	170.08	CO	Composition								
1.52	d (7.0)	6	L <sub>1</sub> (CH <sub>3</sub> )	170.14	CO	$C_{26}H_{34}O_{17}$								
1.54	d (7.0)	6	$L_2$ (CH <sub>3</sub> )	170.76	CO									
3.17	m	4	B (CH <sub>2</sub> )											
3.69	m	4	Linker (CH <sub>2</sub> )											
4.30	m	4	Linker (CH <sub>2</sub> )											
4.67	d (16)	2	$G_1$											
4.80	d (16)	2	$G_1$											
5.19	5.19 m 2 $L_1$ (CH), $L_2$		L1 (CH), L2											
	(CH)		(CH)											
5.79	m	2	B (CH)											

**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

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210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	ppm

Poly(EG)													
Q	Q	Q	Q	<sup>13</sup> C-NN	AR (400 MHz,	HRMS							
B O L O		$\sim$		S (mmm)	$CDCI_3$	(ESI) M							
	O Linker			o (ppm)	+ Assignment	$\underline{NI_n}$							
				16.93	$CH_3$ (L)	32,608							
				37.41	CH <sub>2</sub> (Linker)	Da							
				60.85	$CH_2(G_1)$	Ð							
				64.46	$CH_{2}(B)$	1.23							
	<sup>1</sup> H-NMR (400 N		$\mathbf{C}_{1_2}$	68.60	CH (L)								
då (nnm)	$\frac{\mathbf{M}_{\mathrm{ult}}}{\mathbf{M}_{\mathrm{ult}}}$	Int $Int$	Assignment	68.87	CH (L)								
<u> </u>	$\frac{1}{d(7.0)}$	<u> </u>		69.53	CH <sub>2</sub> (Linker)								
1.52	d (7.0)	0	$L_2$ (CH <sub>3</sub> )	124.42	CH <sub>2</sub> (B Cis)								
1.57	a (7.0)	0	$L_1$ (CH <sub>3</sub> )	125.84	CH (B Trans)								
3.18	m	4	B (CH <sub>2</sub> )	166.71	CO								
3.68	t (4.7)	4	Linker (CH <sub>2</sub> )	170.02	СО								
4.29	m	4	Linker (CH <sub>2</sub> )	170.17	CO								
4.63	d (16)	2	$G_1$	170.87	CO								
4.87	d (16)	2	$G_1$										
5.17	m	4	L <sub>1</sub> (CH), L <sub>2</sub> (CH)										
5.72	m	1.6	B (CH) Trans										
5.81	m	0.4	B (CH) Cis										
				Į.		I							

**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

190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0 ppm

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#### 2.5 THIO LINKER CONTAINING COMPOUNDS

	Si-LGL-Thio-LGL-Si													
		$\sim$		<sup>13</sup> C-NM	R (400 MHz,	HRMS (ESI)								
	L <sub>2</sub> Linker	< ````````````````````````````````````	0	CDCl <sub>3</sub> )										
' - C	-	-	δ (ppm)	+ Assignment	Calc. Mass									
				-5.41	CH <sub>3</sub> (Si)	754.31 amu								
				-5.03	CH <sub>3</sub> (Si)									
11			C(1)	16.74	CH <sub>3</sub> (L)	Calc.								
	$\frac{1-NMR}{M} (400 M)$	IHZ, CD		18.16	C (Si)	$[M + H]^+$								
do (ppm)	Mult. (J)	Int.	Assignment	21.25	$CH_3(L)$	755.31 amu								
0.09	S	6	$CH_3$ (Si)	25.60	t-Bu (Si)									
0.11	S	6	CH <sub>3</sub> (Si)	30.25	CH <sub>2</sub> (Linker)	Found								
0.90	S	18	t-Bu (Si)	60.36	$CH_2(G_1)$	$[M + H]^+$								
1.46	d (6.8)	6	$CH_3(L_1)$	64.04	CH (L)	755.31684 amu								
1.52	d (7.1)	6	$L_2$ (CH <sub>3</sub> )	67.93	CH (L)									
2.80	t (6.9)	4	Linker (CH <sub>2</sub> )	69.21	CH <sub>2</sub> (Linker)	<b>Composition</b>								
4.30	m	4	Linker (CH <sub>2</sub> )	166.82	CO	C <sub>32</sub> H <sub>58</sub> O <sub>14</sub> SSi <sub>2</sub>								
4.44	q (6.8)	2	$L_1$ (CH)	169.70	CO									
4.67	d (16)	2	$G_1$	173.23	CO									
4.79	d (16)	2	$G_1$											
5.17	q (7.1)	2	L <sub>2</sub> (CH)											

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).



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<sup>−5</sup>.03
 <sup>−5</sup>.42

190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0 ppm

			LGL-Thio-L	<b>.GL</b>				
		0	0	<sup>13</sup> C-NM	<b>R</b> (400 MHz,	HRMS (ESI)		
			ОТОН	δ (ppm) 16.95	$\frac{1}{1} + \frac{1}{1} + \frac{1}$	<u>Calc. Mass</u> 526.14 amu		
	2 2			20.45	$CH_3 (L)$ $CH_2 (Linker)$	$\underline{Calc.}$		
<sup>1</sup> H-1	NMR (400 MH	z, CDC	Cl <sub>3</sub> )	61.01	$CH_2$ (Linker)	$[M + H]^{2}$		
dδ (ppm)	Mult. (J)	Int.	Assignment	64.32	$CH_2(G_1)$	527.14 amu		
1.49	d (7.0)	6	$L_1$ (CH <sub>3</sub> )	66.87	CH (L)			
1.54	d (7.0)	6	$L_2$ (CH <sub>3</sub> )	69.65	CH (L)	<u>Found</u>		
2.80	t (6.8)	4	Linker (CH <sub>2</sub> )	166.86	CO	$[M + H]^+$		
2.86	d (5.6)	2	$L_1$ (OH)	169.93	CO	527.14184 amu		
4.31	t (6.8)	4	Linker (CH <sub>2</sub> )	175.04	CO			
4.42	m	2	$L_1$ (CH)			<u>Composition</u>		
4.74	d (16)	2	G <sub>1</sub>			$C_{20}H_{30}O_{14}S$		
4.84	d (16)	2	$G_1$					
5.17	q (7.0)	2	L <sub>2</sub> (CH)					

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<sub>4</sub>, 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

 77.145 77.145 77.144 76.82 66.87 64.32 61.01	

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			BLGL-Thio-LGI	L <b>B</b>														
--	--------------------	-------------------	---	---------------------	------------	-----------------------												
				<sup>13</sup> C-NMR	(500 MHz,	HRMS												
		ö	Q		(13)	(ESI)												
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	yoylovs	$\sim$		o (ppm) + A	Assignment	Calc. Mass												
Ö	Ö	1		16.95	CH	662.19 g/mol												
B L <sub>i</sub> C	$B_1$ $L_2$ Linker			30.52	CH													
				34.08	CH													
				38.71	CH	Calc.												
				60.87	CH	$[M + H]^+$												
				64.22	CH	663.19 amu												
1	<b>H-NMR</b> (400	) MH <sub>7</sub>	$CDCl_2$	68.56	CH													
δ (nnm)	Mult (I)	Int	Assignment	69.53	CH	Found												
<u> </u>	d (6.8)	6	L1 CH2	119.12	Olefin	$[M + H]^+$												
1.52	d (6.8)	6		129.73	Olefin	663.19379												
2.70	t(0.6)	4		166.76	CO	amu												
2.19	t (13.0)	4	Linker $CH_2 \alpha$ to	169.92	CO													
0.10.0.05				170.26	CO	<b>Composition</b>												
3.10-3.25	m	4	<b>B</b> Terminal CH <sub>2</sub>	171.00	CO	$C_{28}H_{38}O_{16}S$												
4.30	t (13.6)	4	<b>Linker</b> $CH_2 \beta$ to S															
4.64	d (16)	2	G1															
4.87	d (16)	2	G1															
5.13-5.30	m	8	L <sub>1</sub> & L <sub>2</sub> Methyne, B Methylene															
5.88-5.98	m	2	<b>B</b> CH															

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<sub>4</sub> 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; {



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

171.00 170.25 169.92 166.76 77.45 77.34 77.14 76.82 68.55 64.22 64.22 60.87 -38.71 -34.08 -30.52 -25.06 .16.95

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 190	180	170	160	150	140	130	120	110	100	 			<b>50</b>	 40	  20	 10	0 ppm

400	400	470	460	450	440	400	400	440	400	~~	~~~	70	60	<b>EO</b>	40		~~~	40	
190	IAU	170	IDU	1.50	140	1.50	1/0		100	90	80	70	<u>nu</u>	<u></u>	40	.50	20	10	U DDM
										~~	00			00					

			Cyclic Thio Monome	er		
		В		<sup>13</sup> C-N	MR (500	HRMS (ESI)
	0		0	MHz,	CDCl <sub>3</sub> )	
		$\top \checkmark$	× ,	δ (p	pm) +	Calc. Mass
L	)—o		o_{	Assi	gnment	634.16 g/mol
				16.96	L (CH <sub>3</sub> )	
	0		$\rangle$	16.98	L (CH <sub>3</sub> )	Calc.
				30.70	$CH_2$	635.16 [M +
1		Q	0	37.66	$CH_2$	$H]^+$
		d	$\mathbf{N}$	61.05	$CH_2$	
		s—⁄		64.86	$CH_2$	
	1	Linker		68.68	СН	Found
	$^{1}$ H-NMR (4	00 MH	z, CDCl <sub>3</sub> )	69.79	CH	635.16390 [M
δ (ppm)	Mult. (J)	Int.	Assignment	125.96	B (CH)	$+ HJ^{+}$
1.52	d (6.8)	6	L <sub>1</sub> CH <sub>3</sub>	160.75		Composition
1.54	d (6.8)	6	L <sub>2</sub> CH <sub>3</sub>	109.99		
2.82	t (13.6)	2	Linker $CH_2 \alpha$ to S	170.12	C0	C261134O165
3.19	m	4	B CH <sub>2</sub>	170.80	CO	
4.31	m	4	Linker $CH_2 \beta$ to S			
4.69	d (16)	2	$G_1$			
4.79	d (16)	2	$G_1$			
5.18	m	4	L <sub>1</sub> & L <sub>2</sub> Methyne, B			
			Methylene			
5.76	t (7.6)	1.5	B trans olefin			
5.82	t (10)	0.4	B cis olefin			

**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).



#### -------..... 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

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			Poly(Thio)			
		\$		<sup>13</sup> C-NM	IR (500 MHz, CDCl <sub>3</sub> )	HRMS (ESI)
		Linker		δ (ppm)	+ Assignment	$\underline{\mathbf{M}}_{\underline{\mathbf{n}}}$
-				16.93	CH <sub>3</sub> (L)	22,452 Da
	1			30.53	CH <sub>2</sub> (Linker)	
	$^{1}\text{H-NMR}$ (4	-00 MH	z, CDCl <sub>3</sub> )	37.40	CH <sub>2</sub> (Linker)	
δ (ppm)	Mult. (J)	Int.	Assignment	60.85	$CH_2(G_1)$	$\underline{\mathbf{D}}$
1.53	d (6.8)	6	$L_1 CH_3$	64.20	$CH_2(B)$	1.54
1.57	d (6.8)	6	$L_2 CH_3$	68.60	CH (L)	
2.79	t (6.8)	4	Linker $CH_2 \alpha$ to S	69.51	CH (L)	
3.19	m	4	B Terminal CH <sub>2</sub>	124.42	CH (B Cis)	
4.29	m	4	Linker $CH_2 \beta$ to S	125.83	CH (B Trans)	
4.64	d (16)	2	$G_1$	166.72	CO	
4.87	d (16)	2	$G_1$	169.87	CO	
5.16	m	4	$L_1 \& L_2 CH$	170.17	CO	
5.72	m	1.6	B CH Trans	170.87	CO	
5.81	m	0.4	B CH Cis			

**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

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an de particular de la construction	an the second	alan anisi fanahan negara bilandan penyakan di kang dan bahar dan kana ang ana penyakan penyakan penyakan dan A Ana anisi bilan bahar ang	Hoursen Arganier	յուն, անդարան էլ էր որի հանդարան էն ու ներանույն էն ու ներանությունները է են ու ներան են հանդարան էն հանդարան է Դուս ու ներան ու ներան էլ էր ու ներան են հանդարան էլ էր ու ներան էլ էր ու ներան են հանդարան էլ էր ու ներան էլ է	terreti fi fajore de la constante de la constan	a a la a de contra de contra de atravée de la factor de la factor de la de La de la d

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190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0 ppm

### 2.6 UREA LINKER CONTAINING COMPOUNDS

			Si-LGL-Urea	n-LGL-Si		
				<sup>13</sup> C-NN	MR (400 MHz,	HRMS (ESI)
					CDCI <sub>3</sub> )	
				δ (ppm)	) + Assignment	Calc. Mass
. P				-4.85	$CH_3$ (Si)	780.35 amu
XSC 10	a lon N N	$\uparrow \circ \uparrow$		16.99	$CH_{3}(L)$	
~  * 0	= <u>0</u>		0 8 • 8	18.45	CH <sub>3</sub> (L)	Calc.
				21.55	t-Bu (Si)	$[M + H]^+$
				25.82	t-Bu (Si	781.35 amu
'H	-NMR (400 M	Hz, CI	DCl <sub>3</sub> )	39.08	CH <sub>2</sub> (Linker)	
dδ (ppm)	Mult. (J)	Int.	Assignment	60.88	$CH_2(G)$	Found
0.102	d (3.2)	12	Si (Me)	65.51	CH <sub>2</sub> (Linker)	$[M + H]^+$
0.903	S	18	Si (t-Bu)	68.19	CH (L)	781.35900 amu
1.46	d (6.8)	6	L <sub>2</sub> (CH <sub>3</sub> )	69.89	CH (L)	
1.51	d (7.2)	6	$L_1$ (CH <sub>3</sub> )	158.09	CO (Linker)	<b>Composition</b>
3.42	m	4	Linker (CH <sub>2</sub> α-	167.05	CO	$C_{33}H_{60}O_{15}N_2Si_2$
			amide)	169.99	CO	
4 20	m	4	Linker (CH <sub>2</sub> B <sub>-</sub>	174.61	CO	
1.20	111		amide)			
1 16	a(20.4)	2	L <sub>2</sub> (CH)			
4.40	q (20.4)	<u>∠</u> 4	$L_2$ (CII)			
4./3	S	4	U1			
5.13	q (20.8)	4	$L_1(CH)$			
5.37	t (11.6)	2	Linker (amide)			

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

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190	180	170	160	150	140	130	 120	110	100	••••• 90	••••• 80		 60	 50	 40		 10	0 ppm

			LGL-Urea-LGL			
				<sup>13</sup> C-NN	IR (400 MHz, CDCl <sub>3</sub> )	HRMS (ESI)
				δ (ppm)	+ Assignment	Calc. Mass
0	O	ıker	$\begin{array}{ccc} L_1 & G_1 & L_2 \\ \hline O & O \end{array}$	16.93	CH <sub>3</sub> (L)	552.18 amu
но	H H		ОН	20.35	$CH_{3}(L)$	
		~ 0		39.14	CH <sub>2</sub> (Linker)	Calc.
-		·····	/	61.20	$CH_2(G)$	$[M + H]^+$
				65.91	CH <sub>2</sub> (Linker)	553.19 amu
				66.90	CH (L)	
1				70.25	CH (L)	Found
	<u>H-NMR (400 M</u>	1Hz, C	DCl <sub>3</sub> )	158.00	CO (Linker)	$[M + H]^+$
dð (ppm)	Mult. (J)	Int.	Assignment	167.42	CO	553.18710
1.49	d (6.8)	6	$L_2$ (CH <sub>3</sub> )	170.18	CO	amu
1.53	d (7.2)	6	$L_1$ (CH <sub>3</sub> )	175.76	CO	
3.48	m	6	Linker (CH <sub>2</sub> $\alpha$ -			Composition
			amide), L <sub>2</sub> (OH)			$C_{21}H_{32}O_{15}N_2$
4.23	m	4	Linker (CH <sub>2</sub> 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)			

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<sub>4</sub>, 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; LGL-Urea-LGL; CDCl3; 13C; 400a; \ 2048 Scans; 8/20/16

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~	$\sim$	9
-	-	$\leftarrow$

 $\begin{array}{c} \bullet & \overbrace{77,47}{77,16} \\ 76.84 \\ 76.84 \\ 65.99 \\ 65.99 \\ 65.91 \\ 65.29 \\ 61.20 \\ 99.14 \\ 99.14 \\ 99.14 \\ \hline 99.14 \\ 96.93 \\ \hline 99.16 \\ 99.35 \\ \hline 99.16 \\ \hline 99.16$ 

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and out have the state a second or a second state s	ulterinden langeden die het die		עריין איזיינעייינערער איז איזער אויזער און אין איז איז איזער איז איזער איז איזער איז איז איז איז איז איז איז א	Milmar (Milay Kawa) (Milay Milay),	Linkelland with a second second second	this to de the the second	hunder () to be determined a	ין איזעיער <mark>ון (</mark> עניון)א און)) געייאן ארא איזערע איז אין אין אין אין איזער איז איזער איז איז איז איז איז איז איז
190 180 170	160 150	140 130 1	20 110 10	0 90 80	70 6	0 50 4	0 30 2	20 10 0 ppm

BLGL-Urea-LGLB										
				<sup>13</sup> C-NN	AR (400 MHz,	HRMS (ESI)				
0	0				CDCI <sub>3</sub> )					
SAL	and have		K ~ L a ~ L a ~ /	<u>δ (ppm)</u>	+ Assignment	Calc. Mass				
V I V		~ Į	<u> </u>	16.82	L (CH <sub>3</sub> )	688.23 amu				
			Linker $L_1$ $G_1$ $L_2$ B	16.87	L (CH <sub>3</sub> )					
				38.60	CH <sub>2</sub> (Linker)	Calc.				
				39.08	CH <sub>2</sub> (Linker	$[M + H]^+$				
				60.47	$CH_2$	689.23 amu				
	<sup>1</sup> H-NMP	(400	MH <sub>2</sub> CDCl <sub>2</sub> )	65.33	$CH_2$					
ds (nnm)		. ( <del>4</del> 00 Int	Assignment	68.65	CH	Found				
<u>uo (ppiii)</u>	$\frac{1}{1}$	IIII.	Assignment	69.98	CH	$[M + H]^+$				
1.51	d (0.8)	0	$L_1$ (CH <sub>3</sub> )	119.20	В	689.23884				
1.57	d (7.2)	6	$L_2$ (CH <sub>3</sub> )	129.48	В	amu				
3.17	m	4	B (Terminal Olefin)	157.87	CO (Linker)					
3.44	m	4	Linker (CH <sub>2</sub> $\alpha$ -amide)	166.78	ĊO	Composition				
4.22	m	4	Linker (CH <sub>2</sub> $\beta$ -amide)	169.89	CO	$C_{29}H_{41}O_{17}N_2$				
4.73	d (16)	2	G1	170.96	CO					
4.78	d (16)	2	G1	171.09	CO					
5.14	m	10	L <sub>1</sub> (CH), L <sub>2</sub> (CH), B (CH <sub>2</sub> ),							
			Linker (amide)							
5.90	m	2	B (CH)							

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<sub>4</sub> 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).



210 200 190 180 170 160 150 140 130 120 110 100 90 80	70 60 50 40 30 20 10 0 ppm

			Cyclic Urea Monom	er		
	Linker			<sup>13</sup> C-NM	IR (400 MHz,	HRMS (ESI)
	O I			(	CDCl <sub>3</sub> )	
L			δ (ppm)	+ Assignment	Calc. Mass	
0		. <u> </u> 0		16.86	L (CH <sub>3</sub> )	660.20 amu
			G <sub>1</sub>	16.91	L (CH <sub>3</sub> )	
9				37.62	CH <sub>2</sub> (Linker)	Calc.
			™0	39.14	CH <sub>2</sub> (Linker)	$[M + H]^+$
0				61.21	CH <sub>2</sub>	661.20 amu
$\sim$		]		65.54	$CH_2$	
L <sub>2</sub>		Q		68.83	CH	Found
4	🖁 🔍	Ко в		70.19	СН	$[M + H]^+$
				124.73	B (cis)	661.20786 amu
	$^{1}$ H-NMR (40	0 MHz	, CDCl <sub>3</sub> )	125.86	B (trans)	~
dδ (ppm)	Mult. (J)	Int.	Assignment	157.98	CO (Linker)	<u>Composition</u>
1.52	d (7.2)	6	$L_1$ (CH <sub>3</sub> )	166.82	CO	$C_{27}H_{36}O_{17}N_2$
1.56	d (6.8)	6	$L_2$ (CH <sub>3</sub> )	170.60	CO	
3.16	m	4	B (CH <sub>2</sub> )	170.86	CO	
3.45	m	4	Linker (CH <sub>2</sub> a-amide)	171.54	CO	
4.23	m	4	Linker (CH <sub>2</sub> $\beta$ -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 <sub>2</sub> (CH), Linker (amide)			
5.77	m	2	B (olefin)			

**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).



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210 200 190 180 1	70 160	150 1	40 <b>130</b>	120 1	 	 <b>) 7</b> (		 50	 40	 20	 10	••••••••••••••••••••••••••••••••••••••

Poly(Urea)									
				<sup>13</sup> C-NM	HRMS				
	$\int_{L_2}^{0} \int_{L_2} L_2 = 0$	Î			(ESI)				
	$\sim_{G_1} \circ \uparrow \circ \circ \circ$	N N H H	$\sim$ $\gamma$ $\sim$ $\gamma$ $\sim$ $\gamma$ $\sim$ $\gamma$	δ (ppm)	$\underline{M}_{\underline{n}}$				
-	-	Linker		16.86	CH <sub>3</sub> (L)	26,596 Da			
				16.91	$CH_{3}(L)$				
	$^{1}$ H-NMR (40	00 MI	Hz, CDCl <sub>3</sub> )	37.34	CH <sub>2</sub> (Linker)				
δ (ppm)	Mult. (J)	Int.	Assignment	39.16	CH <sub>2</sub> (Linker)	Ð			
1.51	d (6.8)	6	$L_1 CH_3$	61.05	$CH_2(G_1)$	1.38			
1.56	d (6.8)	6	$L_2 CH_3$	65.25	$CH_{2}(B)$				
3.17	m	4	B Terminal CH <sub>2</sub>	68.74	CH (L)				
3.43	m	4	Linker CH <sub>2</sub>	69.97	CH (L)				
4.16	m	2	Linker CH <sub>2</sub>	124.41	CH (B Cis)				
4.27	m	2	Linker CH <sub>2</sub>	125.81	CH (B Trans)				
4.29	m	4	Linker $CH_2 \beta$ to S	158.04	CO				
4.73	d (16)	2	$G_1$	166.85	CO				
4.79	d (16)	2	$G_1$	169.95	CO				
5.15	m	6	L <sub>1</sub> & L <sub>2</sub> CH, Linker NH	170.85	CO				
5.75	m	2	B CH Trans	170.96	CO				

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

97 96 86	04	4 1	0 T D D 9	21.7	9 5
170. 169. 166.	158.	125.	69.9 68.1 65.2 61.0	39.1	10.0
$\mathbb{N}/\mathbb{N}$		$\backslash$ /	$\langle \vee \rangle$		V
	-				-

and descentrational of t	ill site blifte dage sloset 1949 ber 1947 ing til og	And	a de la casta d Na de la casta d	, bas 64/11, b <sup>1</sup> 194, 0, and 1649 J, 117 (1949), 117 (1	a fan an fan ar fan Fan ar fan ar	1980 - Alex I. Alex I. Alex 1997 - Alex I. Alex I. Alex 1997 - Alex I. Alex I. Alex	al you want di a you a y	lestef ma filme	Lata Jan and a		linda Laina da Lide Ante arganeta Lide	the fact the contract of the fact of the contract of the fact of t	In place with the	1). Li (n). J March, en Al (i (n). J March, e	toria (ana data data s programma (ana data s	1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.		a sali) sanka aya du Terpi aya farihiyan a	Andra bin ann bhand an ad ann An far bin ann bhand an ad ann
190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0 ppm

			2-Azidoethanol			
			ОН	<sup>13</sup> C-N MHz,	MR (400 CDCl <sub>3</sub> )	HRMS (ESI)
	Ň <sup>-</sup>	$\checkmark$		δ (p Assi 53.66 61.66	pm) + gnment CH <sub>2</sub> CH <sub>2</sub>	$\frac{Calc. Mass}{87.04 amu}$ $\frac{Calc.}{[M + H]^{+}}$
	<sup>1</sup> H-NMR (400 M)	Hz, CD	OCl <sub>3</sub> )			88.04 amu
dð (ppm)	Mult. (J Hz)	Int.	Assignment			Found
1.90 3.45 3.78	t (5.75) t (4.9) m (4.9, 5.75)	1 2 2	$\begin{array}{c} OH \\ CH_2  (\alpha \ to \ azide) \\ CH_2  (\alpha \ to \ alcohol) \end{array}$			$\frac{[M + H]}{88.04 \text{ amu}}$ $\frac{\text{Composition}}{C_2H_5N_3O}$

## 2.7 TRIAZOLE LINKER CONTAINING COMPOUNDS AND PRECURSORS

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<sub>4</sub> and concentrated to yield an orange liquid (1.05 g, 50%).



																1					
1 <b>1</b> - <b>1</b>																Luca					
210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0 ppm

OH <sup>13</sup> C-NMR (400 HRM	1S
	n
(ES MHz, DMSO)	l)
$\delta$ (ppm) + <u>Calc. N</u>	<u>lass</u>
Assignment 157.09	amu
$\overline{1}$ 28.93 CH <sub>2</sub>	
N 51.72 CH <sub>2</sub> <u>Cal</u>	<u>).</u>
HO <sup>2</sup> $N$ 59.66 CH <sub>2</sub> [M +	H]+
<sup>1</sup> H-NMR (400 MHz MeOD) 60.18 CH <sub>2</sub> 158.09	amu
$\frac{d\delta (\text{ppm})}{d\delta (\text{ppm})}$ Mult (I Hz) Int Assignment 122.54 Alkene	
$\frac{275}{275}$ t (6.6) 2 CH <sub>2</sub> (a to alkene) 143.83 Alkene <u>Fou</u>	<u>nd</u>
$\frac{1}{3.62}$ $\frac{1}{(6.6)}$ $\frac{1}{2}$ $\frac{1}{CH_2}$ ( $\alpha$ to alcohol) $\frac{1}{150}$ $\alpha$	H]⁺ 17<
3.74 t (5.2) 2 CH <sub>2</sub> (a to alcohol) 158.09	1/6
4.33 t (5.2) 2 $CH_2 (\alpha \text{ to } N)$	1
7.81 s 1 CH (Alkene)	sition
C <sub>6</sub> H <sub>11</sub> ]	$V_3O_2$

Copper iodide (23 mg, 0.12 mmol, 0.01 eq), AcOH (14  $\mu$ L, 0.24 mmol, 0.02 eq), diisopropylethylamine (42  $\mu$ L, 0.24 mmol, 0.02 eq), 2azidoethanol (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; 13C; 400a; 2048 Scans 8/24/16

59.66 59.66 51.72 39.66 39.466 39.466 33.43 38.73 38.87 38.83 38.83 38.83 38.63 38.63 58.93



			Si-LGL-TZ-LGL-	Si		
			0-si	<sup>13</sup> C-NI	MR (400 MHz, CDCl <sub>3</sub> )	HRMS (ESI)
		Ő		δ (ppm	) + Assignment	Calc. Mass
0	o N=N		$\langle \rangle$	-5.19	CH <sub>3</sub> (Si)	789.35 amu
			`	-4.83	CH <sub>3</sub> (Si)	
SÍ Ý Ý	ý or v v			16.79	CH <sub>3</sub>	Calc.
				16.96	CH <sub>3</sub>	$[M + H]^{+}$
				18.40	CH <sub>3</sub>	790.35 amu
				21.50	CH <sub>3</sub>	
				25.46	CH <sub>2</sub> (Linker)	Found
				25.80	t-Bu (Si)	$[M + H]^+$
<sup>1</sup> H	-NMR (400 MH	Iz, CD	OCl <sub>3</sub> )	48.83	CH <sub>2</sub> (Linker)	790.35898 amu
dδ (ppm)	Mult. (J)	Int.	Assignment	60.62	$CH_2$	
0.09	m	12	Si (CH <sub>3</sub> )	63.56	$CH_2$	<u>Composition</u>
0.89	m	18	Si (t-Bu)	64.34	$CH_2$	$C_{34}H_{59}N_3O_{14}Si_2$
1.46	m	12	L <sub>1</sub> (CH <sub>3</sub> ), L <sub>2</sub> (CH <sub>3</sub> )	68.15	CH	
3.09	m	2	Linker (CH <sub>2</sub> $\alpha$ -olefin)	69.44	CH	
4.44	m	4	$L_1$ (CH), Linker (CH <sub>2</sub>	69.46	СН	
			$\alpha$ -N)	122.74	CH (Linker)	
4 53	m	2	Linker (CH <sub>2</sub> B-olefin)	144.07	C (Linker)	
4 71	m	-	$G_1$ Linker (CH <sub>2</sub> $\beta$ -N)	167.14	CO	
7.71	111	0		167.28	CO	
5.10	m	2	$L_2$ (CH)	169.79	CO	
7.55	S	1	Linker (Olefin)	170.06	CO	
				173.57	CO	
				173.64	CO	

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).

2; Si-LGL-TZ-LGL-Si ans; 11/16/16	; CDC13; 1	13C; 400a;		
173.63 173.57 171.29 169.80 167.14 167.14	144.08	122.73	77.47 77.15 77.15 76.84 68.145 68.145 63.556 64.35 63.556 60.62 61.53 53.557 78.84	$ \begin{array}{c} & & & & & & & & & & & & & & & & & & &$
]				

JHS-3032 2048 Sca



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



			LGL-TZ-LGL			
			<sup>13</sup> C-NN	IR (400 MHz,	HRMS (ESI)	
					CDCl <sub>3</sub> )	
L <sub>1</sub>			δ (ppm)	+ Assignment	Calc. Mass	
НО G1	L <sub>2</sub> Li	16.77	CH <sub>3</sub>	561.18 amu		
0	0		OH OH	16.90	CH <sub>3</sub>	
·····				20.39	CH <sub>3</sub>	Calc.
			Ö	20.41	CH <sub>3</sub>	$[M + H]^+$
				25.43	CH <sub>2</sub> (Linker)	562.18 amu
				48.84	CH <sub>2</sub> (Linker)	
				60.93	$CH_2$	Found
				60.98	$CH_2$	$[M + H]^+$
	$^{1}$ H-NMR (400	) MHz	, CDCl <sub>3</sub> )	63.59	$CH_2$	562.18700
dδ (ppm)	Mult. (J)	Int.	Assignment	64.34	$CH_2$	amu
1.49	m	12	L <sub>1</sub> (CH <sub>3</sub> ), L <sub>2</sub> (CH <sub>3</sub> )	66.89	$CH_2$	
3.11	m	2	Linker (CH <sub>2</sub> α-olefin)	69.59	CH	<u>Composition</u>
4.44	m	4	$L_1$ (CH), Linker (CH <sub>2</sub>	69.71	CH	$C_{22}H_{31}O_{15}N_3$
			$\alpha$ -N)	122.69	CH (Linker)	
4.54	m	2	Linker (CH <sub>2</sub> β-olefin)	144.12	C (Linker)	
4.63	m	2	Linker ( $CH_2 \beta$ -N)	167.05	CO	
1.05	m	-	G	167.09	CO	
4.70	m	+	$\mathbf{U}_{\mathbf{I}}$	169.84	CO	
5.10	111	Z	$L_2(C\Pi)$	170.14	CO	
7.53	S	1	Linker (Olefin)	175.04	CO	
				175.05	CO	

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<sub>4</sub>, 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; 13C; 400a; 2048 Scans; 11/18/16

175.03 170.14 167.09 167.05	144.13	122.69	77.115 777.15 69.60 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 64.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.50 65.5	25.45 21.20 20.42 20.42 16.92 14.34
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ad dis historia di panado In pigna na pigna pi	sant alle antig uthe		tik lan sa ter we kin dia. In sa	unit de constituers Parine de constituers	lucion de la composition de la composit	a hallaida Mandaa I. Da		al weidet togener	and an a state of the state of	ara hay harana Ura Yana di ya ma ya ma	i di secilari Nationali di secilari		իննգ, ունեց եր լենց որվարգուղությունությունություն	եվիչում էրելը, շոցի Մեպե Դին Դեպես ու	bile sole (1) atten at			litere por molecular electric A por por en la conservação de la conservação
 190	180	170	160	150	140	130	<b>120</b>	110	100		80	<b>70</b>	  50	<b>40</b>	 30	20	 10	0 ppm

BLGL-TZ-LGLB												
				<sup>13</sup> C-NN	AR (400 MHz, CDCl <sub>3</sub> )	HRMS (ESI)						
	<i>.</i>			δ (ppm)	+ Assignment	Calc. Mass						
	C1 L2 Lin	16.75	CH <sub>3</sub>	697.23 amu								
Ö	P N	=N	Lorol	16.90	CH <sub>3</sub>							
i		~ <sup>N</sup> ~⁄	o b	16.95	CH <sub>3</sub>	Calc.						
				25.45	CH <sub>2</sub> (Linker)	$[M + H]^+$						
				38.69	$CH_{2}(B)$	698.23 amu						
	1			48.85	CH <sub>2</sub> (Linker)							
	<sup>1</sup> H-NMR (400	MHz,	CDCl <sub>3</sub> )	60.87	$CH_2$	Found						
dδ (ppm)	Mult. (J)	Int.	Assignment	63.56	$CH_2$	$[M + H]^+$						
1.47	m	6	$L_1$ (CH <sub>3</sub> )	64.36	$CH_2$	698.23901						
1.56	d (7.2)	6	$L_2$ (CH <sub>3</sub> )	68.52	$CH_2$	amu						
3.09	m	2	Linker (CH <sub>2</sub> α-olefin)	69.52	CH							
3.18	m	4	B (CH <sub>2</sub> $\alpha$ -carbonyl)	69.57	СН	Composition						
4.43	m	2	Linker (CH <sub>2</sub> $\alpha$ -N)	119.14	Olefin (B)	$C_{22}H_{31}O_{15}N_3$						
4.54	m	2	Linker (CH <sub>2</sub> β-olefin)	122.71	CH (Linker)							
4.62	m	2	Linker (CH <sub>2</sub> $\beta$ -N)	129.69	CH (B)							
4.74	m	4	$G_1$	144.06	C (Linker)							
5.13	m	6	L <sub>1</sub> (CH), L <sub>2</sub> (CH), B	166.83	CO							
			(CH)	166.94	CO							
5.91	m	2	B (terminal olefin)	169.74	CO							
7.52	S	1	Linker (olefin)	170.01	CO							
				170.27	CO							
				170.32	CO							
				170.96	CO							
				170.99	CO							

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<sub>4</sub> 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

h in mining a start for the big The physical starts for the	istorie and states		ling and the second	na da anima da ka pada a Na serie processione presidente presidente presidente presidente presidente presidente presidente presidente pr	ali kilua posta ta Solita segura segura de la	indes de la presidente	ng part to state of soundary	y casaliti (y diyanada) Ayrey (y giyana) * a	han bi chan thian bi chi Man ta dan ba ang ta f	- Marand I de plantes 110 per manyang man		adatulusi ana dia ay ay pinang si at		Unites states and states	alds a pill (k.) Pragy Departed		na ka mitawalik, (dan sa kita) 194 ppeng japo pengan kapata	li surren li, pila. Inggrada arguna	ale Lockson a sile	nada kasan na bir sa dik (kan La Dingener pang Yari kenergang M
 190	180	170	160	150	140	130	120	110	100	<b>90</b>	<b>80</b>	<b>70</b>	6	0	 50	<b>40</b>	<b>30</b>	<b>20</b>	10	0 ppm

			Cyclic TZ Monome	r		
				<sup>13</sup> C-NN	MR (400 MHz, CDCl <sub>3</sub> )	HRMS (ESI)
	Linker			δ (ppm	) + Assignment	Calc. Mass
	N			16.71	CH <sub>3</sub>	669.20 amu
			2	16.86	$CH_3, CH_3$	
۱	0			16.88	CH <sub>3</sub>	Calc.
$\rightarrow$		-	\ \	25.53	CH <sub>2</sub> (Linker)	$[M + H]^+$
Ó	Ő		Ò	37.57	$CH_{2}(B)$	670.20 amu
	=0	o≓	, \	48.88	CH <sub>2</sub> (Linker)	
G	<b>`</b>		<u>}</u> _1.	60.98	$CH_2$	Found
0=	<b>J</b> i	C		61.00	$CH_2$	$[M + H]^+$
	—о в	o—⁄		63.72	CH <sub>2</sub>	670.20783 amu
1				64.41	CH <sub>2</sub>	
	ď 🛁	ő		68.61	СН	Composition
	Li			68.65	СН	$C_{28}H_{35}O_{16}N_3$
				69.65	СН	
				69.68	СН	
				123.07	CH (Cis)	
				124.73	СН	
<sup>1</sup> H-N	MR (400 MF	z CDC	<b>1</b> <sub>2</sub> )	- 125.79	СН	
do (ppm)	Mult (I)	Int.	Assignment	- 125.80	CH	
1.47	m	6	L <sub>1</sub> (CH <sub>3</sub> )	- 144.17	C	
1.54	d (7.2)	6	$L_2$ (CH <sub>3</sub> )	166.74	C0 C0	
3.13	m	6	Linker (CH <sub>2</sub> ), B	166.94		
0110		0	(CH <sub>2</sub> )	109.79	C0 C0	
4.43	m	1	Linker (CH <sub>2</sub> )	170.02	C0 C0	
4.49	m	3	Linker (CH <sub>2</sub> , CH <sub>2</sub> )	170.10		
4.62	m	3	Linker (CH <sub>2</sub> , CH <sub>2</sub> )	170.20		
4.72	m	4	G	170.67	CO	
5.09	m	6	$L_1$ (CH)	1,0101	~~	
5.20	m	2	$L_2$ (CH)			
5.77	m	$\frac{1}{2}$	$\mathbf{B}$ (CH)			
5						

**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



	Poly(TZ)											
				<sup>13</sup> C-NM	IR (500 MHz,	HRMS (ESI)						
B O			o b	(	CDCl <sub>3</sub> )							
0 <u>L</u> 10-		N=N		δ (ppm)	+ Assignment	$\underline{\mathbf{M}}_{\underline{\mathbf{n}}}$						
		N_		16.64	CH <sub>3</sub> (L)	9,973 Da						
				16.78	$CH_{3}(L)$							
				16.82	$CH_{3}(L)$	_						
	<sup>1</sup> H-NMR	(400 MI	Hz. CDCl <sub>3</sub> )	25.34	CH <sub>2</sub> (Linker)	$\underline{\underline{\mathbf{D}}}$						
δ (ppm)	Mult. (J)	Int.	Assignment	32.64	CH <sub>2</sub> (Linker)	1.60						
1.47	m	6	CH <sub>3</sub> (L)	37.25	$CH_2$ (Linker)							
1.55	d (6.8)	6	$CH_3$ (L)	48.74	$CH_2$ (Linker)							
3.08	t (7.6)	2	$CH_2$ (Linker)	60.76	$CH_2(G_1)$							
3.17	m	4	CH <sub>2</sub> (B)	63.78	$CH_2(G_1)$							
4.43	t (6.3)	2	$CH_2$ (Linker)	64.2	$CH_2(B)$							
4.54	m	2	$CH_2$ (Linker)	68 <i>1</i> 7	$CH_2(D)$							
4.63	m	4	$CH_2$ (G <sub>1</sub> , Linker)	68 55	CH(L)							
4.83	m	2	$CH_2(G_1)$	69 38	CH(L)							
5.13	m	4	CH (L <sub>1/2</sub> )	69.46	CH (L)							
5.70	m	1.6	CH (B Trans)	122.54	CH (Linker)							
5.79	m	0.4	CH (B Cis)	124.29	CH (B Cis)							
7.52	S	1	CH (Linker)	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							

**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); CDC13; 13C; 500; 64 Scans; 10/27/17



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# 2.8 SY LINKER CONTAINING COMPOUNDS AND PRECURSORS

			Bn-Syringic Aci	d		
		Ö		<sup>13</sup> C-NM	R (400 MHz,	HRMS
			C	CDCl <sub>3</sub> )	(ESI)	
	$\sim$	$\frown$		δ (	ppm) +	Calc. Mass
				Ass	ignment	288.10 amu
l l		Ų		56.48	CH <sub>3</sub>	
~			↑ ОН	66.69	$CH_2$	Calc.
				106.78	Aromatic	$[M + H]^+$
		/		121.08	Aromatic	289.10 amu
				128.21	Aromatic	
				128.24	Aromatic	<u>Found</u>
				128.62	Aromatic	$[M + H]^+$
	H-NMR (40	J MHZ	, CDCl <sub>3</sub> )	_ 136.24	Aromatic	289.10803
dδ (ppm)	Mult. (J)	Int.	Assignment	139.32	Aromatic	amu
3.93	S	6	$CH_3$	146.63	Aromatic	
5.36	S	2	$CH_2$	166.27	CO	<u>Composition</u>
5.90	S	1	OH			$C_{16}H_{17}O_5$
7.39	m	7	Aromatic			

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<sub>4</sub> and concentrated to yield a white solid (9.89 g, 68% yield).



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

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9	4	mm	000	$\sim$	0	9	9	ωm	
		-	$\neg$ $\neg$ $\neg$				9	വവ	
			$\forall$			$\bigvee$			

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190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0 ppn	1

Bn-Syringic Acid-Si											
				<sup>13</sup> C-NM	R (400 MHz,	HRMS					
	O II			C	CDCl <sub>3</sub> )	(ESI)					
	$\sim$			δ (	ppm) +	Calc. Mass					
Í		Ĭ	Ť I 📈	Ass	ignment	402.19 amu					
U V			Śi	-4.50	CH <sub>3</sub> (Si)						
			0	18.88	C(Si)	Calc.					
		_0		25.82	CH <sub>3</sub> (Si)	$[M + H]^+$					
				55.93	CH <sub>3</sub>	403.19 amu					
				66.71	$CH_2$						
1	$^{1}$ H-NMR (40	)0 MHz	z, CDCl <sub>3</sub> )	107.01	Aromatic	Found					
dδ (ppm)	Mult. (J)		Assignment	122.28	Aromatic	$[M + H]^+$					
		Int.		128.29	Aromatic	403.19536					
0.14	S	6	CH <sub>3</sub>	128.31	Aromatic	amu					
1.00	S	9	$CH_3$	128.69	Aromatic						
3.83	S	6	CH <sub>3</sub>	136.41	Aromatic	<u>Composition</u>					
5.35	S	2	$CH_2$	139.26	Aromatic	$C_{22}H_{31}O_5Si$					
7.39	m	7	Aromatic	151.38	Aromatic						
				166.54	CO						

**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<sub>4</sub> and concentrated to yield a white solid (9.2 g, 67% yield).



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

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			$\forall$		$\mathbb{V}$			Y	Y	N/

						l												
 190	180	170	160	150	140	130	<sub>1</sub> 20	110	100	90	80	<b>70</b>	<b>60</b>	 	<b>30</b>	20	 10	0 ppm

Syringic acid-Si												
	0		<sup>13</sup> C-NM	R (400 MHz,	HRMS							
	Ĩ		C	DCl <sub>3</sub> )	(ESI)							
	$ \land $		δ (	ppm) +	Calc. Mass							
HO	$\sim$	$\searrow$	Ass	ignment	312.14 amu							
				-4.44	CH <sub>3</sub> (Si)							
	ų į	$\triangleleft$	Ś	18.92	C(Si)	Calc.						
	Ý		0 \	25.84	CH <sub>3</sub> (Si)	$[M + H]^+$						
				55.93	CH <sub>3</sub>	313.14 amu						
	_0			107.45	Aromatic							
			121.16	Aromatic	<u>Found</u>							
		0.0.000		139.95	Aromatic	$[M + H]^+$						
	H-NMR (40	0 MHz	, CDCl <sub>3</sub> )	151.45	Aromatic	313.14823						
dδ (ppm)	Mult. (J)	Int.	Assignment	171.02	CO	amu						
0.16	S	6	CH <sub>3</sub> (Si)									
1.01	S	9	CH <sub>3</sub> (Si)			<b>Composition</b>						
3.86	S	6	CH <sub>3</sub>			$C_{15}H_{25}O_5Si$						
7.34	S	2	Aromatic									

**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<sub>2</sub>. 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).



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la ni bi bili bid hadan inda kada da	alitaa ki Diaan 19 yesta ya tayoo	ki anihan da ki ki ki sena si Ki anihan da ki ki ki sena si Ki anihan sena si ki sena s	a dahara da a bilanta ang Pinging ay ang pinangan Pinging ang pinangan	and a second	de digene a bille a bi A star a bille a	i tin da bahain Referensi		laisis shukuraki Pisisis shukuraki	k ditta stati saal Qaree taabii saal			e ( kali) sinta kale na papita ( na propia kale	a la anal ta dalar Perena	ala di perintika di langan da Manggan teran di taga pa	ili andarah matalan ang Manangan Panganan ang	an dah bilan tilan di Kanga pinangan sa sa	in Australia India Milatan Managementan Inggapang
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Si-Sy-Si																	
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	`O			<sup>13</sup> C-N	MR (400	HRMS (ESI)											
				MHz,	CDCl <sub>3</sub> )												
Si			0 I	δ (p	pm) +	Calc. Mass											
	$\sim$ $\downarrow$ $_{0}$	$\sim$		Assi	gnment	650.29 amu											
0 \	$\checkmark$ $\checkmark$ $\checkmark$	<u> </u>		-4.47	CH <sub>3</sub> (Si)												
	Ö		Si	18.91	C(Si)	Calc.											
			Ý 0	25.84	CH <sub>3</sub> (Si)	$[M + H]^+$											
			Ó	55.90	CH <sub>3</sub>	651.29 amu											
				107.45	Aromatic												
				121.16	Aromatic	Found											
				139.95	Aromatic	$[M + H]^+$											
	H-NMR (40	JU MHZ	, CDCI3)	151.45	Aromatic	651.30452											
dð (ppm)	Mult. (J)	Int.	Assignment	171.02	CO	amu											
0.13	S	12	CH <sub>3</sub> (Si)														
1.00	S	18	CH <sub>3</sub> (Si)			<b>Composition</b>											
3.81	S	12	CH <sub>3</sub>			$C_{32}H_{50}O_{10}Si_2$											
4.63	S	4	$CH_2$														
7.28	S	4	Aromatic														

**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).



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 190	180	170	160	150	140	130	120	 110	100	90		70	 60		 40		20	10	<b>0 b</b>	 

Sy Linker											
	Ω			<sup>13</sup> C-NMF	R (400 MHz,	HRMS					
НО				C	DCl <sub>3</sub> )	(ESI)					
			Q I	δ (ppm) +	- Assignment	Calc. Mass					
	.0.	$\sim$		56.52	CH <sub>3</sub>	422.12 amu					
o_ ~	$\sim$	$\sim$ $\sim$		62.72	$CH_2$						
	U O			106.87	Aromatic	Calc.					
			ОН	120.84	Aromatic	[M - H]⁻					
			_0	139.54	Aromatic	421.12 amu					
				146.75	Aromatic						
	1			166.23	CO	Found					
	$^{1}\text{H-NMR}$ (4	00 MH	z, CDCl <sub>3</sub> )	_		[M - H] <sup>-</sup>					
dδ (ppm)	Mult. (J)	Int.	Assignment	_		421.11203					
3.91	S	12	$CH_3$			amu					
4.65	S	4	$CH_2$								
5.91	S	2	OH			<b>Composition</b>					
7.32	S	4	Aromatic			$C_{20}H_{22}O_{10}$					

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<sub>4</sub>, concentrated, and crude solid was purified via column chromatography (silica, EtOAc/hexanes) to yield a white solid (0.6 g, 76 %).



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190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0 ppm

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Si-LGL-Sy-LGL-Si												
		-		<sup>13</sup> C-NM	IR (400 MHz,	HRMS (ESI)						
					CDCl <sub>3</sub> )							
	Linker	Į –		δ (ppm)	+ Assignment	Calc. Mass						
				-5.22	CH <sub>3</sub> (Si)	1,054.39 amu						
				-4.84	CH <sub>3</sub> (Si)							
1 <b>T</b>	I NINAD (400 N			17.25	CH <sub>3</sub> (L)	Calc.						
	1-100000000000000000000000000000000000	$\frac{1}{1}$		18.39	C (Si)	$[M + H]^+$						
dð (ppm)	Mult. (J)	Int.	Assignment	21.46	CH <sub>3</sub> (L)	1,055.39 amu						
0.10	S	6	$CH_3$ (S1)	25.80	t-Bu (Si)							
0.12	S	6	$CH_3$ (Si)	56.47	CH <sub>3</sub> (MeO)	Found						
0.91	S	18	t-Bu (Si)	60.51	$CH_2(G_1)$	$[M + H]^+$						
1.48	d (6.8)	6	$CH_3(L_1)$	62.99	CH (L)	1.055.40008 amu						
1.71	d (7.1)	6	$L_2$ (CH <sub>3</sub> )	68.18	CH <sub>2</sub> (Linker)	,						
3.83	S	12	CH <sub>3</sub> (Linker)	69.08	CH (L)	Composition						
4.46	q (6.8)	2	$L_1$ (CH)	106.52	Aromatic	$C_{48}H_{70}O_{22}Si_2$						
4.70	m	6	CH <sub>2</sub> (G <sub>1</sub> , Linker)	128.12	Aromatic							
4.84	d (16)	2	$G_1$	132.24	Aromatic							
5.54	q (7.1)	2	$L_2$ (CH)	152.15	Aromatic							
7.31	S	4	Aromatic (Linker)	165.73	CO							
				166.73	CO							
				167.57	CO							
				173.54	CO							

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<sub>4</sub> 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

•	•					•	•					•				•			
100	100	170	160	150	1/10	120	120	110	100	00	00	70	60	50	10	20	20	10	0 nnm
190	100	170	100	100	140	130	120	110	100	30	00	10	00	50	40	30	20	10	

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LGL-Sy-LGL												
		0		<sup>13</sup> C-NM	IR (400 MHz,	HRMS (ESI)						
			<u>Тото</u> он	(	CDCl <sub>3</sub> )							
				δ (ppm)	+ Assignment	Calc. Mass						
		0		17.21	CH <sub>3</sub> (L)	826.22 amu						
Ŭ				20.48	CH <sub>3</sub> (L)							
1 <b>1</b>				56.47	CH <sub>3</sub> (MeO)	Calc.						
1 15 (	1-100000000000000000000000000000000000			61.04	$CH_2(G_1)$	$[M + H]^+$						
do (ppm)	Mult. (J)	Int.	Assignment	66.85	CH (L)	827.22 amu						
1.51	d (6.8)	6	$CH_3(L_1)$	68.37	CH <sub>2</sub> (Linker)							
1.71	d (7.1)	6	$CH_3 (L_2)$	69.30	CH (L)	Found						
2.73	d (4.5)	2	OH	106.50	Aromatic	$[M + H]^+$						
3.82	S	12	CH <sub>3</sub> (Linker)	128.17	Aromatic	827.22794 amu						
4.42	m	2	$CH(L_1)$	132.17	Aromatic							
4.67	S	4	CH <sub>2</sub> (Linker)	152.13	Aromatic	<b>Composition</b>						
4.75	d (16)	2	$CH_2(G_1)$	165.70	CO	$C_{36}H_{42}O_{22}$						
4.84	d (16)	2	$CH_2(G_1)$	166.47	CO							
5.53	q (7.1)	2	$CH(L_2)$	167.47	CO							
7.31	S	4	Aromatic (Linker)	175.07	CO							

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<sub>4</sub> 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

#### haddaddonnaen olda ogalada sinda llin eftil. Mi yn gwynaed feiniaeth yn yn ffiging son still a sinda feidd y da ar yn ffiging a gwlanaeth yn y ffiging yn y الأرباطا فناسلون فأبان na na hina kana kana hina hina ka And the second state of th د الدارية الكرية الأن الدلال، المانية li su a cu du 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

BLGL-Sy-LGLB												
			<sup>13</sup> C-NN	AR (400 MHz, CDCl <sub>3</sub> )	HRMS (ESI)							
		inker		δ (ppm)	+ Assignment	Calc. Mass						
				16.96	CH <sub>3</sub>	962.27 amu						
				17.23	CH <sub>3</sub>							
				38.73	CH <sub>2</sub> (Linker)	Calc.						
	<sup>1</sup> H-NMR (400	MHz	$CDCl_2$	56.51	CH <sub>3</sub> (Linker)	$[M + H]^+$						
dð (ppm)	$\frac{111000}{11000}$	Int	Assignment	60.91	$CH_2$	963.27 amu						
<u> </u>	$\frac{d(7)}{d(7)}$	6 6	L <sub>1</sub> (CH <sub>2</sub> )	63.02	$CH_2$							
1.57	d (7)	6	$L_1$ (CH <sub>3</sub> )	68.58	CH	Found						
1.71	u (7)	4	$\mathbf{L}_2$ (CII <sub>3</sub> ) $\mathbf{P}$ (CII <sub>3</sub> )	69.25	CH	$[M + H]^+$						
2.02	III	4	$\mathbf{D}(\mathbf{CH}_2)$	106.55	Aromatic	963.28008 amu						
5.85	S	12	Linker (CH3) Linker (CH) $\downarrow$ C	119.12	Aromatic							
4.00	s + a	0	Linker $(CH_2) + G_1$	128.18	Aromatic	<u>Composition</u>						
			$(CH_2)$	129.75	Aromatic	$C_{44}H_{50}O_{24}$						
4.92	d (16)	2	G <sub>1</sub> (CH <sub>2</sub> )	132.25	Alkene							
5.21	m	6	$L_1$ (CH) + B (CH <sub>2</sub> )	152.18	Alkene							
5.53	q (7)	2	$L_2$ (CH)	165.74	CO							
5.94	m	2	B (CH)	166.48	CO							
7.31	S	4	Linker (Aromatic)	167.55	CO							
				170.26	CO							
				171.02	CO							

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<sub>4</sub> 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; 13C; 400a; 2048 Scans; 10/21/16

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Cyclic Sy Monomer													
	0 ~		2	<sup>13</sup> C-NM	IR (400 MHz, CDCl <sub>3</sub> )	HRMS (ESI)							
	)—ó		$\rightarrow - o$	δ (ppm)	+ Assignment	Calc. Mass							
	Link	er 🗡		16.68	$CH_{3}(L)$	934.24 amu							
		Q		16.91	$CH_{3}(L)$								
	o o—		Q	32.63	CH <sub>2</sub> (Linker)	Calc.							
			$G_1 \rightarrow 0$	37.28	$CH_{2}(B)$	$[M + H]^+$							
				56.27	CH <sub>3</sub> (Linker)	935.24 amu							
	$O = (G_1)$		$O = L_1$	60.77	$CH_2(G)$								
	<u> </u>			62.66	CH (L)	Found							
		°	B	68.42	CH (L)	$[M + H]^+$							
	в			69.08	CH <sub>2</sub> (Linker)	935.25000 amu							
	<sup>1</sup> LI NIMD (400	MUz		_ 106.38	Aromatic								
ds (nnm)	11-10000000000000000000000000000000000	Int	(DC13)	_ 124.44	Alkene (Cis)	<u>Composition</u>							
<u> </u>	$\frac{1}{d(7)}$	<u>пп.</u>	CH <sub>2</sub> (L <sub>2</sub> )	_ 125.65	Alkene	$C_{42}H_{46}O_{24}$							
1.37	d (7)	6	$CH_3(L_1)$	128.04	Aromatic								
1./1	u (7)	4	$CH_3(L_2)$	132.13	Aromatic								
5.19 2.91	111	4	$C\Pi_2(D)$	152.02	Aromatic								
5.81	S	12	-OCH <sub>3</sub> (Linker)	165.43	CO								
4.69	S L (1 C)	0	$CH_2$ (Linker)	166.15	CO								
4.75	d (16)	2	$CH_2(G_1)$	167.14	CO								
4.86	d (16)	2	$CH_2(G_1)$	169.77	CO								
5.24	q (7)	2	$CH(L_1)$	170.49	CO								
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										

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

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## 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Poly(Sy)										
				<sup>13</sup> C-NMR (	500 MHz, CDCl <sub>3</sub> )	HRMS				
						(ESI)				
				δ (ppm)	+ Assignment	$\underline{\mathbf{M}}_{\underline{\mathbf{n}}}$				
h a l a	. III	Linker		16.91	CH <sub>3</sub> (L)	25,242 Da				
				17.18	$CH_{3}(L)$					
				37.40	$CH_{2}(B)$					
	<sup>1</sup> H-NMR	(500 M	Hz CDCl <sub>3</sub> )	56.47	MeO- (Linker)	Ð				
δ (ppm)	Mult (I)	Int	Assignment	60.87	$CH_2(G_1)$	1.40				
<u> </u>	d (6.8)	6	CH <sub>2</sub> (L)	62.97	CH <sub>2</sub> (Linker)					
1.37	d (6.8)	6	$CH_2(L)$	68.59	CH(L)					
3.18	u (0.0) m	0 4	$CH_2$ (Linker)	69.21	CH (L)					
3.82	s	12	$MeO_{-}$ (Linker)	106.56	Aromatic					
5.62 4.65	m	6	$CH_2$ (G1 Linker)	124.40	CH (B C1s)					
4 90	d (16)	2	$CH_2(G_1, Linker)$	125.82	CH (B Trans)					
5 17	u (10)	$\frac{2}{2}$	CH(L)	128.16	Aromatic					
5 51	m	$\frac{2}{2}$	CH(L)	132.25	Aromatic					
5.72	m	$\frac{2}{1}$	CH(B)	152.17	Aromatic					
5.81	m	1. <del>4</del> 0.6	CH (B Cis)	165.68						
7 20	111 C	1	Aromatic	100.43						
1.29	3	+	Aiomatic	107.47						
				170.10						

**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

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190	100	170	100	150	140	130	120	110	100	30	00	10	00	30	40	30	20	10	o ppin

Bn-LGLGL-Si											
				<sup>13</sup> C-N	MR (400	HRMS (ESI)					
				MHz	, CDCl <sub>3</sub> )						
				δ (p	pm) +	Calc. Mass					
Si L <sub>1</sub>	G <sub>1</sub> L <sub>2</sub>	G <sub>2</sub>	L <sub>3</sub> Bn	Assi	gnment	554.22 amu					
· · · ·	"		o' <b>,</b> ' /	-5.22	Si						
si (		.0.		-4.84	Si	Calc.					
				16.91	$L(CH_3)$	$[M + H]^{+}$					
	, Ö		Ö	18.40	$L(CH_3)$	555.22 amu					
				21.47	$L(CH_3)$	<b>F</b> 1					
				25.80	$S_1$ (t-Bu)	$\frac{Found}{[M + 11]^+}$					
				60.56	$G(CH_2)$	$[M + \Pi]$					
				60.93 67.27	$G(CH_2)$	555.22054 amu					
				68 16	I (CH)	Composition					
	_			69.10	L (CH)	$\frac{\text{Composition}}{\text{C}_{24}\text{H}_{29}\text{O}_{11}\text{Si}}$					
	<sup>1</sup> H-NMR $(400)$	MHz, C	CDCl <sub>3</sub> )	69.61	L(CH)	C201158O1151					
dδ (ppm)	Mult. (J)	Int.	Assignment	128 29	Bn (CH)						
0.08	S	3	Si (Me)	128.62	Bn (CH)						
0.10	S	3	Si (Me)	128.75	Bn (CH)						
0.90	S	9	Si (t-Bu)	135.20	Bn (CH						
1.46	d (6.8)	3	$L_1$ (CH <sub>3</sub> )	166.63	ĊŎ						
1.52	d (7.2)	3	$L_2$ (CH <sub>3</sub> )	167.01	CO						
1.58	d (7.2)	3	$L_{3}(CH_{3})$	169.59	CO						
4.44	q (6.8)	1	$L_1$ (CH)	169.93	CO						
4.75	m	4	$G_1$ (CH <sub>3</sub> ), $G_2$ (CH <sub>2</sub> )	173.54	CO						
5.21	m	4	L <sub>2</sub> (CH <sub>3</sub> ), L <sub>3</sub> (CH), Bn								
			$(CH_2)$								
7.34	m	5	Bn (Aromatic)								

### 2.9 EEG LINKER CONTATINING COMPOUNDS AND PRECURSORS

**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; 13C; 400a; 2048 Scans; 9/9/16

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190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0 ppi	n

LGLGL-Si											
				<sup>13</sup> C-NMR CD	(400 MHz, Cl <sub>3</sub> )	HRMS (ESI)					
Sio				δ (pj Assig -5.21 -4.84 16.81 16.91 18.41 21.47 25.81	pm) + siment Si $L (CH_3)$ $L (CH_3)$ $L (CH_3)$ SI SI Si	$\frac{\text{Calc. Mass}}{464.17 \text{ amu}}$ $\frac{\text{Calc.}}{[M + H]^{+}}$ $465.17 \text{ amu}$ $\frac{\text{Found}}{[M + H]^{+}}$					
1				60.94	G (CH <sub>2</sub> )	349.07634					
dδ (ppm)	$\frac{11-1001}{Mult. (J)}$	Int.	Assignment	68.19	L (CH)	amu (minus					
0.08	s	3	Si (Me)	69.11	L (CH)	Si)					
0.10	S	3	Si (Me)	69.14	L (CH)	Commonition					
0.90	S	9	Si (t-Bu)	166.63		<u>Composition</u>					
1.46	d (6.8)	3	L <sub>1</sub> (CH <sub>3</sub> )	107.05	C0 C0	C19H32O11SI					
1.56	d (7.2)	3	L <sub>2</sub> (CH <sub>3</sub> )	109.00	C0						
1.59	d (7.2)	3	L <sub>3</sub> (CH <sub>3</sub> )	173.39							
4.44	q (6.8)	1	$L_1$ (CH)	174.40	0						
4.65	d (16)	1	G1 (CH2)								
4.66	d (16)	1	$G_2$ (CH <sub>2</sub> )								
4.81	d (16)	1	G1 (CH2)								
4.87	d (16)	1	G <sub>2</sub> (CH <sub>2</sub> )								
5.20	q (7.2)	1	L <sub>2</sub> (CH <sub>3</sub> )								
5.26	q (7.2)	1	L <sub>3</sub> (CH <sub>3</sub> )								

**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<sub>2</sub>. 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; 13C; 400a; 2048 Scans; 9/12/16

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



		Si-L	GLGL-EG-LGLG	L-Si		
				<sup>13</sup> C-N	MR (400 MHz, CDCl <sub>3</sub> )	HRMS (ESI)
Si L <sub>1</sub> G <sub>1</sub> L <sub>2</sub>	G <sub>2</sub> L <sub>3</sub> Linker			δ (ppm	) + Assignment	Calc. Mass
				-3.18	SI Si	998.38 annu
$\overline{\lambda \wedge \hat{\lambda} \wedge \lambda}$	$\sim$ $\sim$ $\gamma$ $\sim$ $\sim$ $\sim$	Ĵ~~	, l	16.95	$I (CH_2)$	Calc
				18.43	$L(CH_2)$	$[M + H]^+$
				21 50	$L(CH_3)$	999.39 amu
1-			~	25.84	Si	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
12 ( )	<u>I-NMR (400 M</u>	Hz, CDC	Cl <sub>3</sub> )	60.59	G (CH <sub>2</sub> )	Found
dð (ppm)	Mult. (J)	Int.	Assignment	60.97	$G(CH_2)$	$[M + H]^+$
0.08	S	3	Si (Me)	64.50	Linker (CH <sub>2</sub> )	999.38999
0.10	S	3	Si (Me)	68.19	Linker (CH <sub>2</sub> )	amu
0.90	S	9	Si (t-Bu)	68.88	L (CH)	
1.45	d (6.8)	3	$L_1$ (CH <sub>3</sub> )	69.13	L (CH)	Composition
1.52	d (7.2)	3	L <sub>2</sub> (CH <sub>3</sub> )	69 159	L (CH)	$C_{42}H_{70}O_{23}Si_2$
1.58	d (7.2)	3	L <sub>3</sub> (CH <sub>3</sub> )	166 66	CO	
3.68	t (4.9)	4	Linker (CH <sub>2</sub> )	167.03	CO	
4.29	m	4	Linker (CH <sub>2</sub> )	169.63	CO	
4.44	q (6.8)	1	$L_1$ (CH)	170.06	CO	
4.65	d (16)	1	G <sub>1</sub> (CH <sub>2</sub> )	173.56	CO	
4.66	d (16)	1	G <sub>2</sub> (CH <sub>2</sub> )			
4.80	d (16)	1	$G_1$ (CH <sub>2</sub> )		,	
4.86	d (16)	1	G <sub>2</sub> (CH <sub>2</sub> )			
5.17	q (7.2)	1	$L_2$ (CH <sub>3</sub> )			
5.26	q (7.2)	1	$L_3$ (CH <sub>3</sub> )			

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).

<ul> <li>7.257</li> <li>5.2596</li> <li>5.2596</li> <li>5.2596</li> <li>5.2596</li> <li>5.2596</li> <li>5.2596</li> <li>5.1794</li> <li>4.2835</li> <li>4.450</li> <li>4.45</li></ul>	4.307 4.296 4.284 4.284 4.274 4.258 4.255 4.142	4.124 4.107 4.089 3.689 3.665 3.665	.3.473 .3.463 .3.463 .2.041 .1.571 .1.571	1.528 1.511 1.511 1.511 1.228 1.254 1.254	1.236 0.897 0.098 0.078
	1 1				
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0	4.5 4.0 3.5	3.0 2.5	2.0 1.5 1.0	0.5 0.0	ppm
4.05 4.05	3.97 2.00 0.53 0.28 0.28	ĺ	0.78 8.97 5.97 6.11 1.28	11.96	
JHS-3009-Fr17-24; Si-LGLGL-EG-LGLGL-Si; CDCl3; 13C; 400a; 2048 Scans; 9/14/16					
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JHS-3009-Fr17-24; Si-LGLGL-EG-LGLGL-Si; CDCl3; 1H; 400a; 16 Scans; 9/14/16

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#### 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LGLGL-EG-LGLGL											
				<sup>13</sup> C-NN	/IR (400 MHz,	HRMS (ESI)					
					CDCl <sub>3</sub> )						
	G I Linka			δ (ppm)	+ Assignment	Calc. Mass					
		≡ 0	= 0 =	16.92	L (CH <sub>3</sub> )	770.21 amu					
HOLOCA	$\sim \sim \sim \sim \sim \sim$	16.94	L (CH <sub>3</sub> )								
<u>ö, ö</u>		20.48	L (CH <sub>3</sub> )	Calc.							
				61.01	$G_1, G_2 (CH_2)$	$[M + H]^{+}$					
11.			71.)	- 64.54	Linker (CH <sub>2</sub> )	771.21 amu					
15 ( )	<u>1-NMR (400 MF</u>	$\frac{1Z, CDC}{I}$	_13)	66.86	Linker (CH <sub>2</sub> )						
do (ppm)	Mult. (J)	Int.	Assignment	68.87	L (CH)	<u>Found</u>					
1.49	d (6.8)	3	$L_1$ (CH <sub>3</sub> )	69.32	L (CH)	$[M + H]^+$					
1.53	d (7.2)	3	$L_2$ (CH <sub>3</sub> )	69.63	L (CH)	771.21900					
1.60	d (7.2)	3	$L_3$ (CH <sub>3</sub> )	166.64	CO	amu					
2.78	d (5.4)	2	$L_1$ (OH)	166.78	CO						
3.68	t (4.9)	4	Linker (CH <sub>2</sub> )	169.54	CO	Composition					
4.29	m	4	Linker (CH <sub>2</sub> )	170.08	CO	$C_{30}H_{42}O_{23}$					
4.41	qd (6.8, 5.4)	1	$L_1$ (CH)	175.08	CO						
4.67	d (16)	1	G1 (CH2)								
4.73	d (16)	1	G <sub>2</sub> (CH <sub>2</sub> )								
4.86	m	1	G1 (CH2), G2								
			$(CH_2)$								
5.17	q (7.2)	1	L <sub>2</sub> (CH <sub>3</sub> )								
5.27	q (7.2)	1	L <sub>3</sub> (CH <sub>3</sub> )								

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<sub>4</sub> 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

175.08 171.22 166.64 166.64	77.48 77.46 69.33 69.32 66.88 66.88 66.88 61.01 61.01 60.55	21.21 20.48 20.48 16.93

94

a a geodetica de la construcción de Teneral de la construcción de la con	er forseren jelen forst. In stranseren jelen forseren f		na fina Mada sakilan sakan sa 19 manganan genara (jara ma	ga kata je kali na od jeli ka 11 go kata je kana na pri jeli ka	nakahila jeruka kutoka kutoka k	ti sil dir. 2 ku adala Kara pografi si si dala	When the strength	ne i la statu an cal ange	nad Vilay a solad da a Garca - periodori garc	Loren K. 284 Mars have Providency of Property		Minter of the Maria		na fir an an fillion in A tha an an fillion in	dhàd al nha airi 1 k daoi ga Pagaga ya na ang	Alex I align a score align by a score align by the		n let si de mar si de la de Let el fes mar per de la de	
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190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	u ppm

BLGLGL-EG-LGLGLB											
				<sup>13</sup> C-NN	AR (400 MHz,	HRMS (ESI)					
			CDCl <sub>3</sub> )								
		δ (ppm)	+ Assignment	Calc. Mass							
	L <sub>2</sub> G <sub>2</sub> L <sub>3</sub> Linker	16.88	L (CH <sub>3</sub> )	906.26 amu							
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	16.92	L (CH <sub>3</sub> )								
	<u> </u>	ő	Ö Ö	16.93	L (CH <sub>3</sub> )	Calc.					
		60.81	G (CH <sub>2</sub> )	$[M + H]^+$							
	111 NIMD (400 M	60.97	$G(CH_2)$	907.27 amu							
18 (		HZ, CDCI	<u>3)</u>	64.47	Linker (CH <sub>2</sub> )						
<u>do (ppm)</u>	Mult. (J)	Int.	Assignment	64.49	Linker (CH <sub>2</sub> )	<u>Found</u>					
1.52	d (6.8)	3	$L_1$ (CH <sub>3</sub> )	68.53	B (CH <sub>2</sub> )	$[M + H]^+$					
1.57	d (7.2)	3	$L_2$ (CH <sub>3</sub> )	68.84	L (CH)	907.27152					
1.59	d (7.2)	3	$L_3$ (CH <sub>3</sub> )	69.22	L (CH)	amu					
3.18	m	4	$B(CH_2)$	69.56	L (CH)						
3.68	t (4.9)	4	Linker (CH <sub>2</sub> )	119.11	B (CH <sub>2</sub> )	Composition					
4.29	m	4	Linker (CH <sub>2</sub> )	129.71	B (CH)	$C_{38}H_{50}O_{25}$					
4.63	d (16)	1	G1 (CH2)	166.60	CO						
4.64	d (16)	1	$G_2(CH_2)$	166.70	CO						
4.86	d (16)	1	G1 (CH2)	169.55	CO						
4.88	d(16)	1	$G_2(CH_2)$	170.24	CO						
5.21	m	10	L <sub>1</sub> (CH), L <sub>2</sub>	170.99	CO						
			(CH), L <sub>3</sub> (CH), B	l							
			$(CH_2)$	1							
5.92	m	2	B (CH)								

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<sub>4</sub> 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

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77.44 77.12 69.56 69.56 68.85 68.85 68.43 69.22 60.61 53.54 

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han dhu ya dhu ya hu		ւ <sub>ննան</sub> կներին։	<b>PRAN</b>			allinkin Anada	al the subscript of the	<b>I I I I I I I I I I I I I I I I I I I </b>	a (fil bardina)	a an			ala nin ilan	<sub>p</sub> xlld <sup>*</sup> pd <sup>*</sup> lxtd <sup>*r</sup>			, <sup>V</sup> irvia IV.	nahit, Palitica (	li de la constante de la const
190	180	170	160	150	140	130	120	110	100	90	80	<b>70</b>	60	50	40	30	20	10	0 ppm

Cyclic EEG Monomer											
				<sup>13</sup> C-l	NMR (400 MHz,	HRMS (ESI)					
	Linke	er (		CDCl <sub>3</sub> )							
	0,0,	$\sim$	L - Journal	δ (pp	m) + Assignment	Calc. Mass					
	L <sub>3</sub>		0, 0	16.70	L (CH <sub>3</sub> )	878.23 amu					
	$\checkmark$ $^{\circ}$ 0		G <sub>2</sub> O	16.73	L (CH <sub>3</sub> ), L (CH <sub>3</sub> )						
O <sub>≷</sub>	Ó			37.35	B (CH <sub>2</sub> )	Calc.					
	$\int G_2$			60.79	G (CH <sub>2</sub> )	$[M + H]^+$					
0			Ó	60.86	$G(CH_2)$	879.23 amu					
0				64.39	Linker (CH <sub>2</sub> )						
	0, 20		0, 0	68.44	Linker (CH <sub>2</sub> )	Found					
	G <sub>1</sub>			68.70	L (CH)	$[M + H]^+$					
	<u>`</u> 0		0	69.09	L (CH)	879.23971					
	$L_1 O B$	$\sim$	В	69.50	L (CH)	amu					
	0* 1		~ ~0	125.67	B (CH)	C					
	≡ O			166.50		<u>C U O</u>					
				100.31		C36H46O25					
				169.30	C0						
				169.69	C0						
	<sup>1</sup> H-NMR (40	JU MHZ,	CDCI <sub>3</sub> )	170.61	CO						
dδ (ppm)	Mult. (J)	Int.	Assignment								
1.52	d (6.8)	3	L <sub>1</sub> (CH <sub>3</sub> )								
1.54	d (7.2)	3	$L_2$ (CH <sub>3</sub> )								
1.57	d (7.2)	3	$L_{3}$ (CH <sub>3</sub> )								
3.16	m	4	B (CH <sub>2</sub> )								
3.68	m	4	Linker (CH <sub>2</sub> )								
4.30	m	4	Linker (CH <sub>2</sub> )								
4.70	m	4	G1 (CH2), G1 (CH2)								
4.81	d (16)	2	G <sub>1</sub> (CH <sub>2</sub> )								
4.83	d(16)	2	$G_2$ (CH <sub>2</sub> )								
5.21	m	6	L <sub>1</sub> (CH), L <sub>2</sub> (CH), L <sub>3</sub>								
			(CH)								
5.78	m	2	B (CH)								

**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





			Poly(EEG)					
		<sup>13</sup> C-NN	<sup>13</sup> C-NMR (400 MHz, CDCl <sub>3</sub> )					
		δ (ppm)	$\delta$ (ppm) + Assignment					
		16.80	L (CH <sub>3</sub> )	27,178 Da				
	G <sub>2</sub> O Linker			37.33	B (CH <sub>2</sub> )			
				60.74	$G(CH_2)$	Ð		
				60.89	$G(CH_2)$	1.25		
1	II NIMD (500 MI	64.39	Linker (CH <sub>2</sub> )					
18 (	$\frac{\Pi - \text{INMR} (300 \text{ IM})}{M - 14}$		(3)	- 68.51	L (CH)			
do (ppm)	Mult. (J)	Int.	Assignment	68.77	L (CH)			
1.53	m	12	$CH_3 (L_{1/2/3})$	69.14	L(CH)			
3.15	m	4	$CH_{2}(B)$	69.50	Linker (CH <sub>2</sub> )			
3.65	m	4	CH <sub>2</sub> (Linker)	124.34	B (CHCis)			
4.26	m	4	CH <sub>2</sub> (Linker)	125.76	B (CH Trans)			
4.61	d (16)	2	$CH_{2}(G)$	166.53	CO			
4.62	d (16)	2	$CH_{2}(G)$	166.62	CO			
4.84	d (16)	2	$CH_2(G)$	169.45	CO			
4.86	d(16)	2	$CH_2(G)$	169.92	CO			
5.17	m	10	CH (L <sub>1/2/3</sub> )	170.10	CO			
5.69	m	1.5	CH (B Trans)	170.81	CO			
5.78	m	0.5	CH (B Cis)					

**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; Poly(EEG); CDCl3; 13C; 500; 64 Scans; 10/27/17

125.76 170.81 170.10 169.93 169.45 166.62 166.53

69.50 68.78 68.78 68.78 68.78 68.78 66.90 60.90  $\bigwedge^{16.84}_{16.81}$ 

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

## 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

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