

## Learning from the Trees: Biomimetic Crosslinking of Silicones by Phenolic Coupling

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### Supporting Information

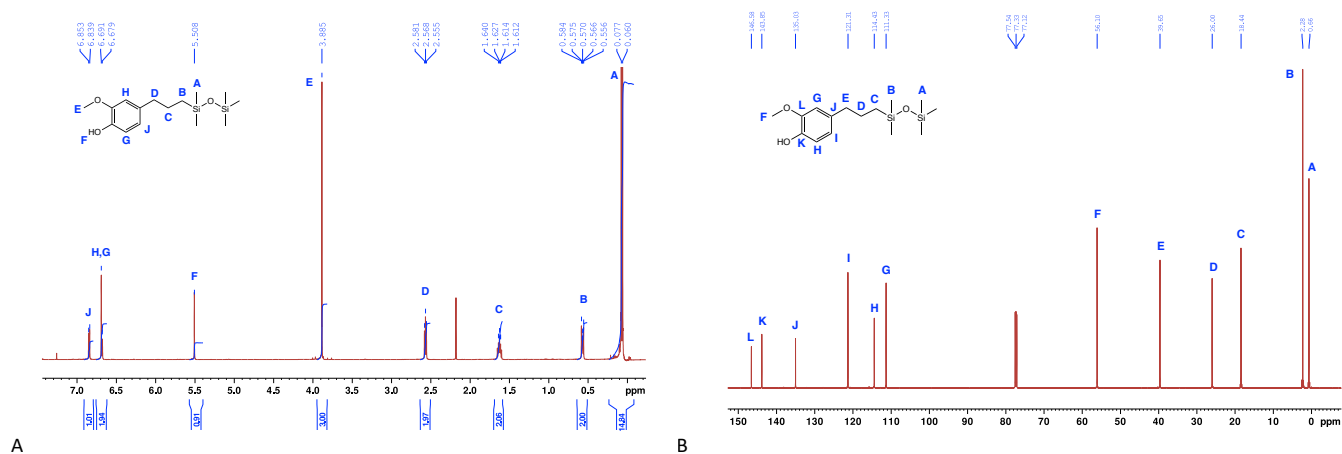


Figure S1 A) <sup>1</sup>H NMR and B) <sup>13</sup>C NMR of **1**.

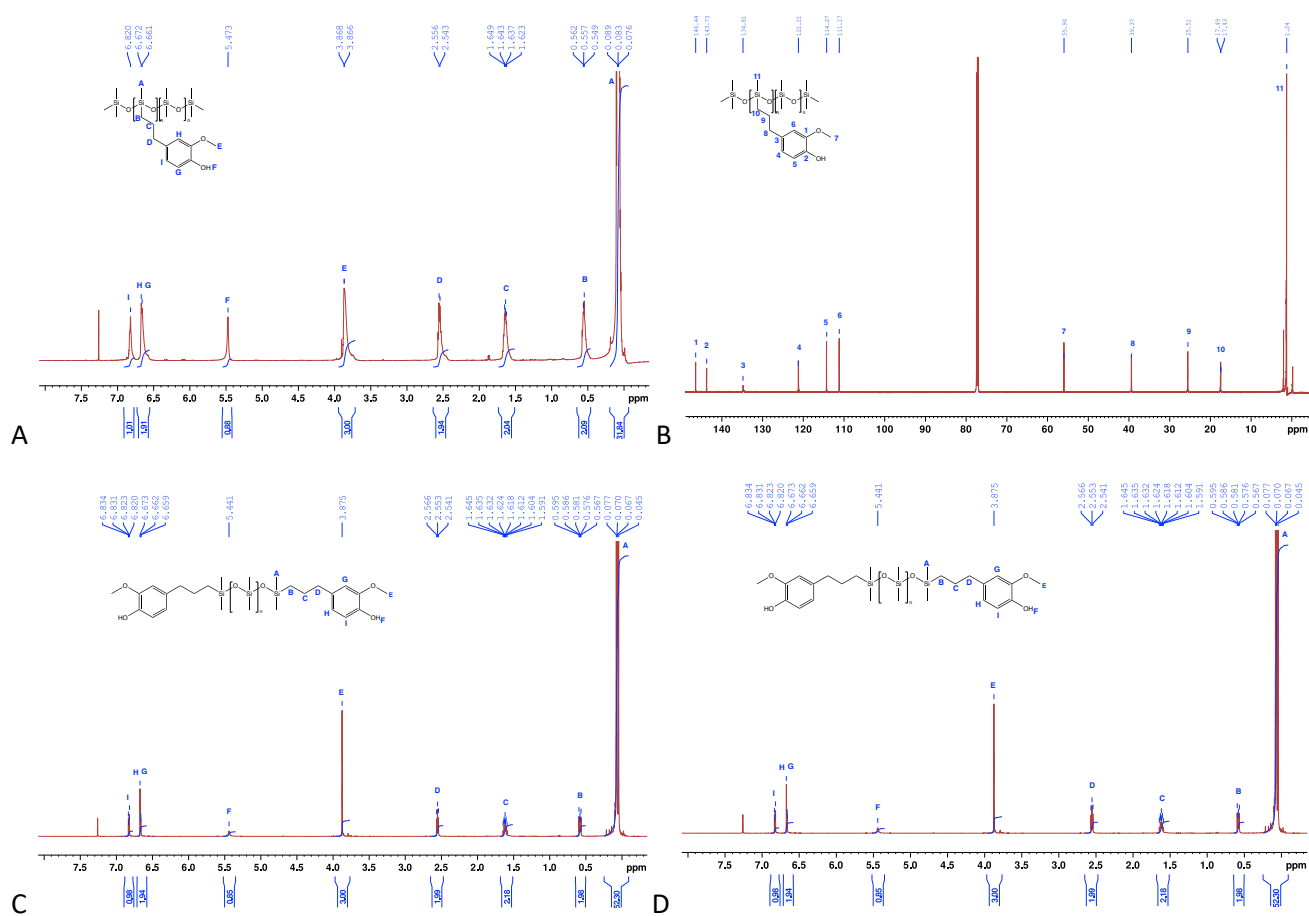


Figure S2. A,C) <sup>1</sup>H NMR and B,D) <sup>13</sup>C NMR of **P15-Eu** and **T12-Eu**, respectively.

## GC/MS

The GC/MS trace of the oxidation of **1** with BPO shows 6 principal compounds, labelled 1-6. Compounds 1/2; 3/4; and 5/6 are each related, with the latter being 2 amu less (missing the constituents of H<sub>2</sub>) than the earlier peak: 312 vs 310 (starting material **1**); 432 vs 430 and 622 vs 620 (dimeric product **3**). The compounds responsible for 432/430 are proposed to be compound **6** formed through equilibration from dimer **3**. Note that this compound was not seen in the starting materials. An alternative is the presence of small amounts of M<sup>H</sup>M<sup>H</sup> in the original formation of compound **1**. With these assumptions, the product mixture is 55% product. A more conservative value shows the peak at 312 **1** and its dimer **3** in a 5:1 ratio, or 20%. Sensitivity factors have been assumed to be identical for all compounds.

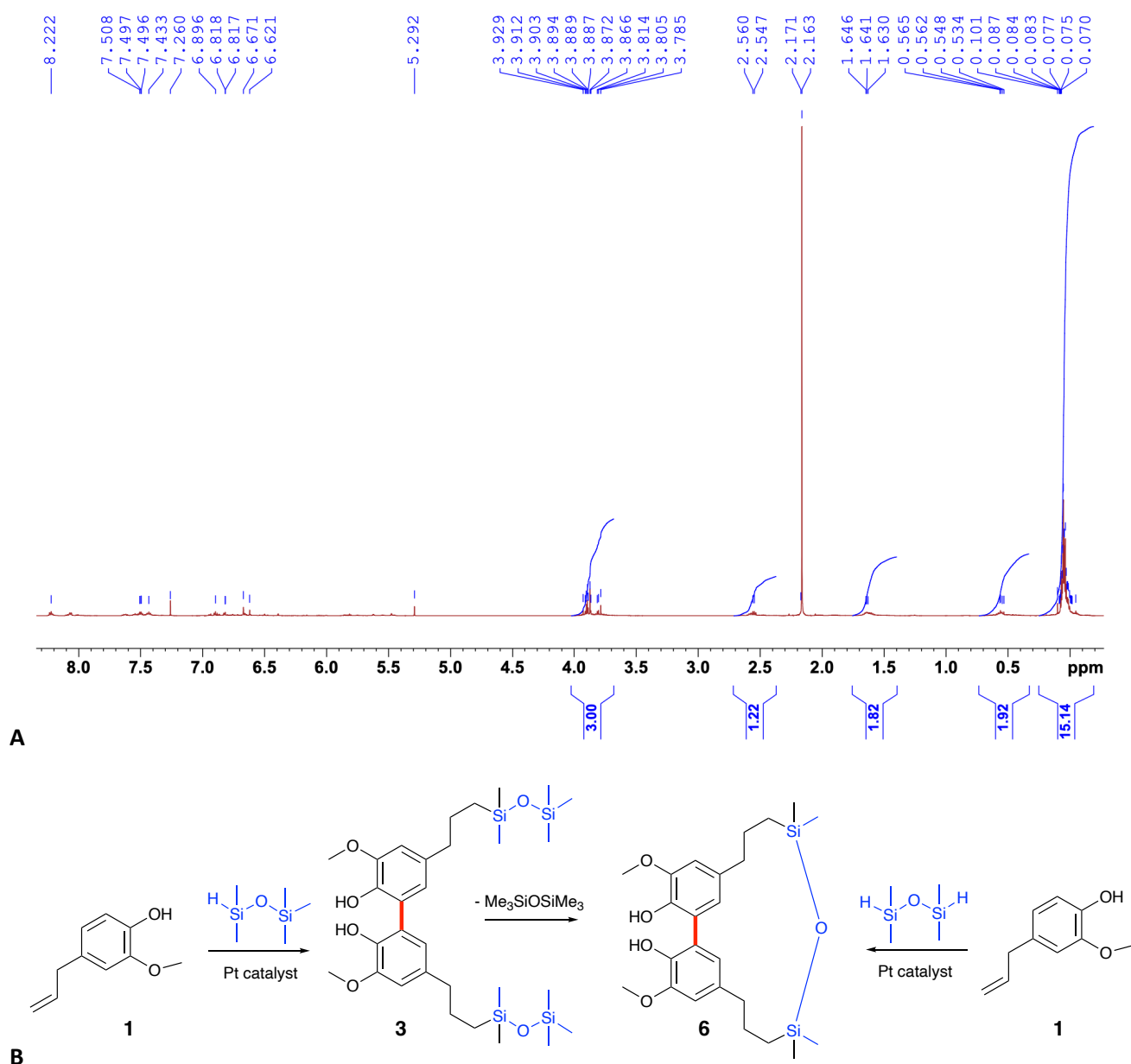
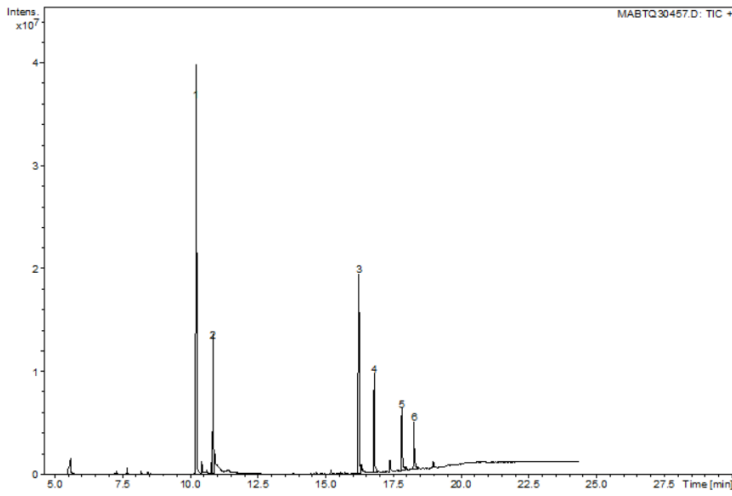


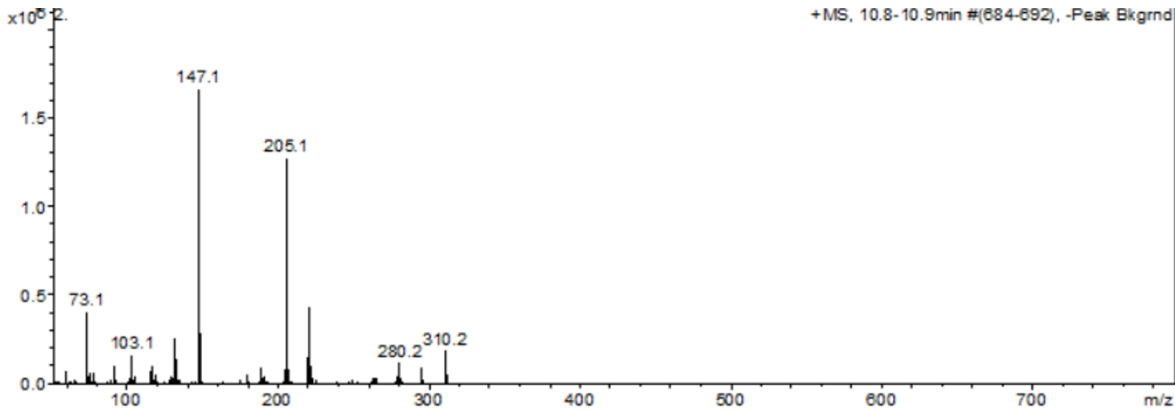
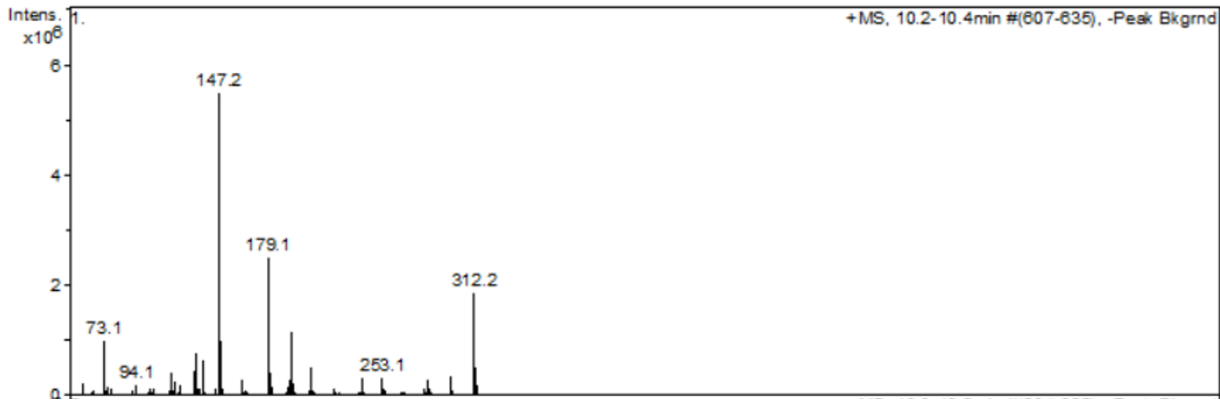
Figure S3 A) <sup>1</sup>H NMR and B) proposed structures of products **3** with m/z 2 less than expected.

Analysis Name: MABTQ30457.D  
Method: FSTFS\_340  
Sample Name: Mmeu 1 BPO

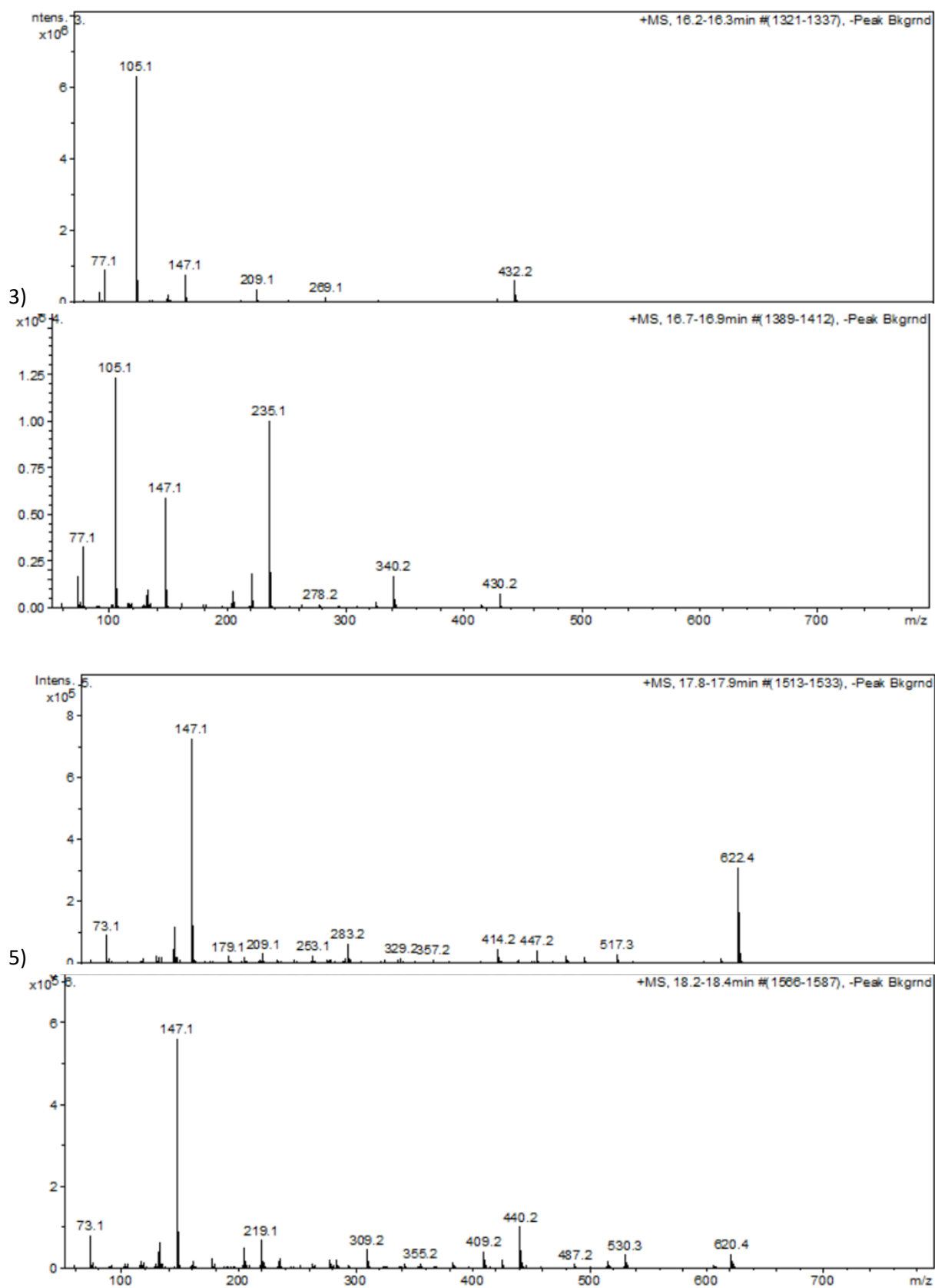
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Peak	Comp- ound	Retention time	Area	Area%
1	1	15.5	61698478	26.9
2	1	11.0	18331738	8.0
3	6	16.5	68418186	29.8
4	6	17.0	34854476	15.2
5	3	18.1	11761055	5.1
6	3	18.5	13802773	6.0



2)



4)

6)

Figure S4 GC trace, intensity table of the 6 GC peaks seen, and their mass spectra Figure 1 A→C showing conversion of about 20% of **3** from **1**.

Table S1. Chain extension parameters of **T0-Eu** and **T12-Eu**

<b>T0-Eu</b>			
<b>T0-Eu (g)</b>	<b>Molar equivalents of DTBP</b>	<b>mmol DTBP</b>	<b>Volume (<math>\mu</math>L)</b>
0.4	1	0.86	159
0.4	2	1.73	318
0.4	5	4.32	794
<b>T0-Eu (g)</b>	<b>Molar equivalents of BPO</b>	<b>mmol BPO</b>	<b>weight (mg)</b>
0.4	1	0.86	209.4
0.4	2	1.73	418.8
0.4	5	4.32	1047
<b>T12-Eu</b>			
<b>T12-Eu (g)</b>	<b>Molar equivalents of DTBP</b>	<b>mmol DTBP</b>	<b>Volume (<math>\mu</math>L)</b>
0.4	1	0.27	49
0.4	2	0.53	98
0.4	5	1.33	245
<b>T12-Eu (g)</b>	<b>Molar equivalents of BPO</b>	<b>mmol BPO</b>	<b>weight (mg)</b>
0.4	1	0.27	64.6
0.4	2	0.53	129.1
0.4	5	1.33	322.8

Table S2. GPC data from chain extension studies using varying equivalents of BPO and DTBP

<b>Eugenol-modified M<sup>H</sup>M<sup>H</sup></b>				
<b>Peroxide</b>	<b>Equiv. peroxide</b>	<b>M<sub>n</sub></b>	<b>M<sub>w</sub></b>	<b><math>\bar{D}_M</math></b>
No peroxide DTBP	0	285	300	1.0478
	1	330	395	1.1953
	2	615	685	1.1135
	5	850	1255	1.4826
BPO	1	340	400	1.1812
	2	380	500	1.3102
	5	1240	2100	1.695
<b>Eugenol-modified T12</b>				
No peroxide DTBP	0	1555	2150	1.38
	1	1720	2290	1.3329
	2	1840	2650	1.4381
	5	2465	5445	2.2104
BPO	1	2655	5045	1.8994
	2	2630	6200	2.3608
	5	4830	12120	2.5102

Table S3. Oxidative coupling to create elastomers with DTBP

<b>Oxidative coupling of eugenol-modified P50-Eu (0.5 g, 1.51 mmol EUG)</b>		
Molar equiv. DTBP	mmol DTBP	vol ( $\mu$ L)
0	0	0
0.2	0.30	56
0.4	0.60	111
0.6	0.90	167
0.8	1.21	222
1	1.51	278
1.5	2.27	417
<b>Oxidative coupling of eugenol-modified P30-Eu (0.8 g 1.95 mmol EUG)</b>		
0	0	0
0.2	0.39	72
0.4	0.78	143
0.6	1.17	215
0.8	1.56	287
1	1.95	359
1.5	2.93	538
<b>Oxidative coupling of eugenol-modified P15-Eu (0.8 g 2.46 mmol EUG)</b>		
0	0	0
0.2	0.49	49
0.4	0.98	98
0.6	1.48	147
0.8	1.97	196
1	2.46	245
1.5	3.69	367

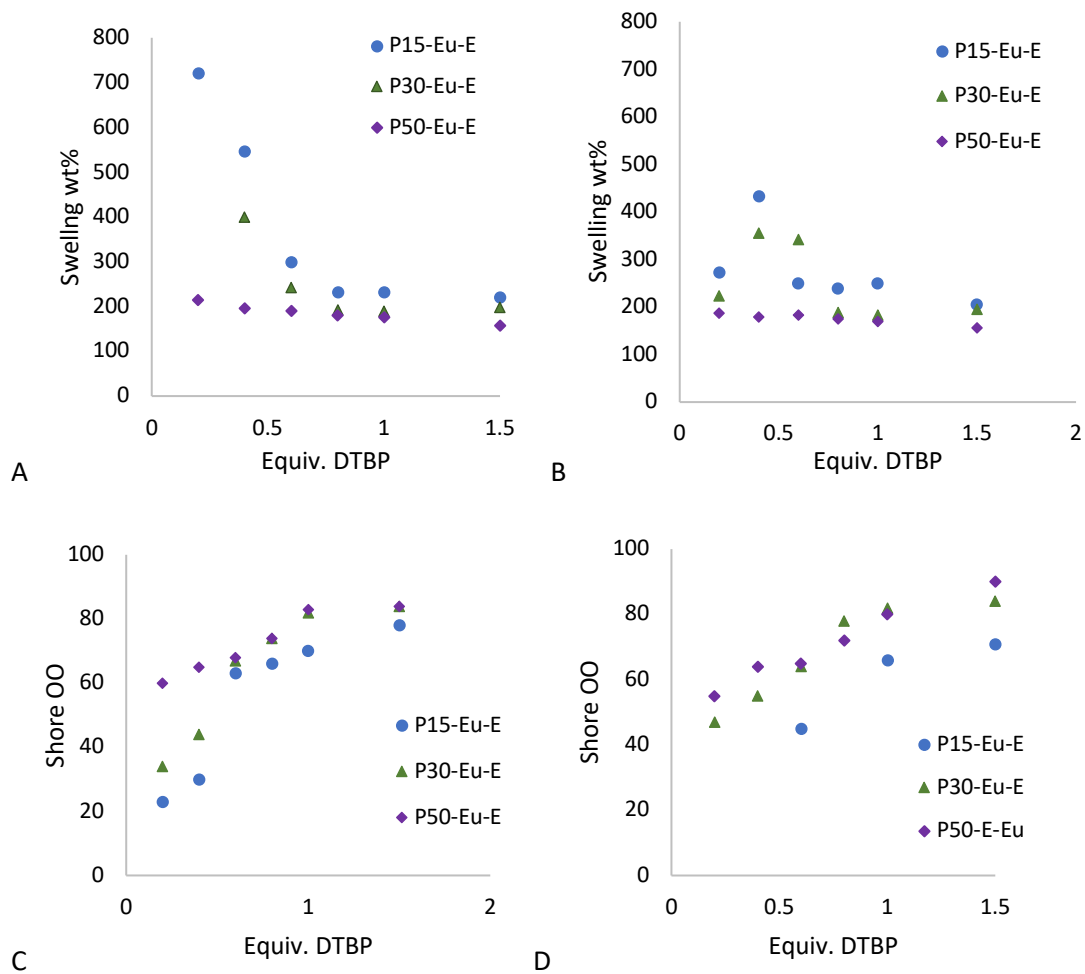


Figure S5. Swelling (wt% increase) of A) first prepared elastomers and B) after extraction with toluene. Shore OO hardness of C) first prepared elastomers and D) after extraction with toluene.

Table S4. Mass loss after first swelling in solvent and Shore OO data before and after extraction in toluene.

raw elastomers						
P50						
equivalents DTBP	Shore OO	starting	swollen	final	% swelling	%sol <sup>a</sup>
0.2	60	0.1622	0.3472	0.1104	214.1	31.9
0.4	65	0.1604	0.3141	0.1275	195.8	20.5
0.6	68	0.163	0.3095	0.1291	189.9	20.8
0.8	74	0.1611	0.2903	0.1331	180.2	17.4
1	83	0.1608	0.2826	0.1341	175.7	16.6
1.5	84	0.1622	0.2564	0.1436	158.1	11.5
P30						
equivalents DTPB	Shore OO	starting	swollen	final	% swelling	%sol
0.2	34	0.1661	0.7204	0.1047	433.7	37.0
0.4	44	0.1579	0.6307	0.0999	399.4	36.7
0.6	67	0.1658	0.4014	0.1405	242.1	15.3
0.8	74	0.1615	0.3119	0.1471	193.1	8.9
1	82	0.1665	0.3159	0.154	189.7	7.5
1.5	84	0.1583	0.3148	0.1424	198.9	10.0
P15						
equivalents DTBP	Shore OO	starting	swollen	final	% swelling	%sol
0.2	23	0.1649	1.1899	0.0563	721.6	65.9
0.4	30	0.1637	0.8965	0.0803	547.6	50.9
0.6	63	0.1659	0.4963	0.1234	299.2	25.6
0.8	66	0.1658	0.3845	0.1345	231.9	18.9
1	70	0.1645	0.3832	0.141	232.9	14.3
1.5	78	0.1619	0.3576	0.1364	220.9	15.6

<sup>a</sup> Mass loss after 1 extraction with toluene.



extracted elastomers							
P50							
equivalents DTBP	Shore OO	starting	swollen	final	% swelling	% sol <sup>a</sup>	
0.2	60	49	91.7	45.5	187.2	7.1	
0.4	65	49.4	88.3	46.6	178.7	5.7	
0.6	68	46.3	85.1	44.1	183.8	4.8	
0.8	74	51.1	89.3	49.5	174.8	3.1	
1	83	50.4	85.5	47.9	169.6	5.0	
1.5	84	50	78	47.6	156.0	4.8	
P30							
equivalents DTPB	Shore OO	starting	swollen	final	% swelling	% sol	
0.2	34	52.8	117.8	47.7	223.1	9.7	
0.4	44	52.9	188.4	43.2	356.1	18.3	
0.6	67	50.1	171.6	47.1	342.5	6.0	
0.8	74	48.3	91.4	45.8	189.2	5.2	
1	82	54.3	99.5	51.4	183.2	5.3	
1.5	84	46.5	90.7	44.4	195.1	4.5	
P15							
equivalents DTBP	Shore OO	starting	swollen	final	% swelling	% sol	
0.2	23	40.9	111.6	31.3	272.9	23.5	
0.4	30	52.6	227.9	44.6	433.3	15.2	
0.6	63	53.1	132.5	48	249.5	9.6	
0.8	66	53.8	129	49.4	239.8	8.2	
1	70	48.8	121.7	45.8	249.4	6.2	
1.5	78	54.8	112.6	52.5	205.5	4.2	

<sup>a</sup> Mass loss after 3 extractions with toluene.

Table S5. Serial dilutions for DPPH assays

serial dilutions	[eugenol] (mM)	[DPPH] (mM)	total vol (mL)
100%	50	0.1	1
50%	25	0.1	1
10%	5	0.1	1
1%	0.5	0.1	1
0.10%	0.05	0.1	1
0.01%	0.005	0.1	1
0.001%	0.0005	0.1	1

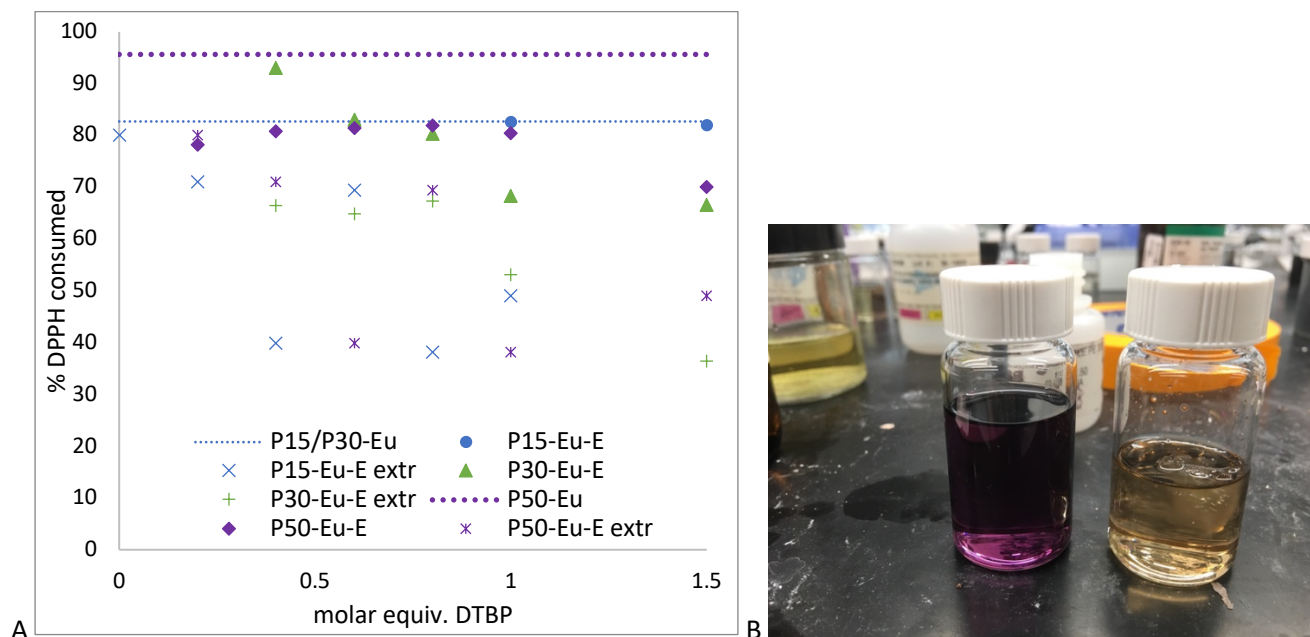


Figure S6 Antioxidant activity, by DPPH assay, of A) **P15-Eu-E**; **P30-Eu-E**; **P50-Eu-E** as prepared, and after extraction. B) Typical color change upon reaction of DPPH with phenols (left - before, right - after reaction).

The differences between Shore hardness (or Young's modulus<sup>1</sup>) for filled and unfilled silicones is rather significant. Note that Sylgard is typically filled with MQ resins, a related but distinct type of reinforcing agent.<sup>2</sup> Selected examples of elastomers cured using hydrosilylation, moisture cure (RTV) and phenolic coupling have comparable Shore hardness values (Table S6).

Table S6. A comparison of curing techniques for silicone elastomers (to prepare 0.8 g elastomer).

<b>Commercial Platinum-cure silicone rubber (Sylgard 184)<sup>a</sup></b>						
Crosslinker	Chain extender	Pt <sup>b</sup>	Filler	Cure temp.	Shore OO	
H-PDMS	vinyl-terminated PDMS	5-20 ppm	MQ resins	RT, 24 h	~ 83 (43 Shore A) <sup>1</sup>	
<b>Homemade Platinum cure silicone</b>						
H-PDMS	vinyl-terminated PDMS	5 ppm	none	RT, 24 h	40x	
<b>Commercial RTV (Dowsil 786)</b>						
Crosslinker	Chain extender	mol% of Sn <sup>c</sup>	Filler	Cure temp.	Shore OO	
Si(OAc) <sub>4</sub>	HO-terminated PDMS	<1%	silica	RT, 24h	(25 Shore A) <sup>d</sup>	
<b>Homemade RTV (moisture cure)</b>						
MeSi(OMe) <sub>3</sub>	HO-terminated PDMS	1%	none	RT, 24h	80 (25 Shore A)	
<b>P30-Eu-E</b>						
Crosslinker	Chain extender	DTBP	Filler	Cure temp.	Shore OO	
Pendent eugenol silicone	NA	195%	none	130 °C, 6 h	75-85	

<sup>a</sup> If higher temperatures are used, Sylgard will completely cure in about one hour at 100 °C, or 15 minutes at 150 °C ([www.dow.com/content/dam/dcc/documents/en-us/productdatasheet/11/11-31/11-3184-sylgard-184-elastomer.pdf](http://www.dow.com/content/dam/dcc/documents/en-us/productdatasheet/11/11-31/11-3184-sylgard-184-elastomer.pdf) accessed May 30, 2023.). <sup>b</sup> Karstedt's Pt catalyst. <sup>c</sup> Dibutyltin dilaurate. <sup>d</sup> [www.dow.com/content/dam/dcc/documents/en-us/productdatasheet/95/95-10/95-1047-01-dowsil-786-silicone-sealant.pdf?iframe=true](http://www.dow.com/content/dam/dcc/documents/en-us/productdatasheet/95/95-10/95-1047-01-dowsil-786-silicone-sealant.pdf?iframe=true), accessed May 30, 2023. Note: full cure is not noted on this sheet, but all data reported was 1 week after starting cure.

## References

1. A. W. Mix and A. J. Giacomini, *J. Testing Eval.*, 2011, **39**, 696-705.
2. D. H. Flagg and T. J. McCarthy, *Macromolecules*, 2016, **49**, 8581-8592.