Supplementary Materials for

Sporopollenin-inspired design and synthesis of robust polymeric materials

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Supplementary Methods

All reactions were performed under nitrogen unless otherwise noted. 1,8-octanediol (TCI, >99%), 1,10-decanediol (TCI, >95%), 1,12-dodecanediol (Acrōs, 99%), 1,14-tetradecanediol (Combi-Blocks, 97%), 1,16-hexadecanediol (TCI, >95%), Dess-Martin periodinane (Oakwood, 95%), polyvinyl alcohol ($M_{w,avg}$ = 31-50k, Sigma Aldrich, 98–99% hydrolyzed), polyvinyl alcohol ($M_{w,avg}$ = 85-124k, Sigma Aldrich, >99% hydrolyzed), polyvinyl alcohol ($M_{w,avg}$ = 89-98k, Sigma Aldrich, >99% hydrolyzed), polyvinyl alcohol ($M_{w,avg}$ = 146-186k, Sigma Aldrich >99% hydrolyzed), cyclohexanone (Acrōs, >99%), cyclohexylamine (TCI, >99%), *n*-butyllithium (Acrōs, 2.45 M), diisopropylamine (Spectrum, >99%), 11-bromo-1-undecene (Oakwood, 95%), sodium (meta)periodate (BTC, 98%), potassium permanganate (J.T. Baker, 99.4%), methyl iodide (Alfa Aesar, >98%), potassium carbonate (Sigma Aldrich, 99%), *meta*-chloroperbenzoic acid (Sigma Aldrich, <77%), sodium methoxide (Acrōs, >99%), 4-dimethylaminopyridine (Acrōs, 99%), *N*,*N'*-dicyclohexylcarbodiimide (TCI, >98%), lithium borohydride (Strem, 95%), tetrabutylammonium fluoride (Oakwood, 1 M in THF), triethylamine (Acrōs, 99%), sulfur trioxide pyridine complex (TCI, >95%), coumaric acid (TCI, >98%), *tert*-butyldimethylsilyl chloride (Chem-Impex, 99%), imidazole (Sigma Aldrich, 99%), ethane thiol (Sigma Aldrich, 97%), boron trifluoride diethyl etherate (Sigma Aldrich, >46.5% BF_3 basis), acetic acid (Spectrum, >99.7%), concentrated sulfuric acid (EMD Millipore, 95%), 4 Å molecular sieves (Sigma Aldrich), ammonium chloride (Mallinckrodt, 99.5%), sodium sulfate (Sigma Aldrich, >99%), Celite (Fisher), sodium bicarbonate (Mallinckrodt, >99.7%), conc. hydrochloric acid (Macron, 36.5–38.0%), sodium hydroxide (AmericanBio, 97%), sodium chloride (EMD Millipore, 99.5%), dicholoromethane (Fisher, >99.5%), dimethylsulfoxide (Fisher, >99.9%), diethyl ether (Fisher, >99.9%), tetrahydrofuran (Acrōs, >99.5%, extra dry, stabilized with BHT), acetone (Fisher, >99.5%), water (distilled), petroleum ether (Fisher, 36–60 °C Fraction), hexanes (Fisher, 98.5%), ethyl acetate (Fisher, 99.5%), dimethylformamide (Acrōs, 99.8%), chloroform (EMD Millipore, >99.8%), methanol (EMD Millipore, 99.9%), and dioxane (Acrōs, 99.8%) were used as received without further purification unless otherwise noted. Column chromatography was conducted using Silicycle SiliaFlash P60 SiO_2 (40–63 μm). Preparative TLC was conducted using Millipore SiO_2 60 F_{254} PTLC (0.5 mm). Analytical TLC was conducting using Millipore SiO_2 60 F_{254} TLC (0.250 mm) plates. Silicone molds for polymer curing were obtained from MiniatureSweet (“Small Geometry Silicone Mold”).

Melting points were obtained using a Mel-Temp II apparatus in open capillaries and are uncorrected. Solution state ^1H and ^{13}C NMR spectra were obtained using either a Bruker Avance Neo 400 MHz spectrometer equipped with a 5 mm BBFO SmartProbe or a Bruker Avance Neo 500 MHz spectrometer equipped with a 5 mm liquid nitrogen cooled Prodigy BBO cryoprobe using either $CDCl_3$ (Cambridge Isotope Laboratories, 99.8%D) or DMSO-d_6 (Cambridge Isotope Laboratories, 99.9%D) as solvents. ^{13}C MAS ssNMR spectra were obtained on a Bruker Avance Neo 500 MHz spectrometer equipped with a 3.2 mm HX solids probe set to a MAS speed of 20 kHz. IR spectra were obtained using a Bruker Alpha 2 with a Platinum ATR accessory. High resolution mass spectrometric analysis was performed on either a JEOL AccuTOF-DART or a Thermo Fisher Scientific Q-Exactive benchtop Orbitrap. Durometer hardness testing was performed by Element Materials Technology with a Durometer Type D from Pacific Transducer Corporation. Thermogravimetric analysis was performed by Element Materials Technology with a TGA Q500 from TA Instruments. Differential scanning calorimetry was performed by Element Materials Technology with a DSC Q2000 from TA Instruments. Mechanical characterization was performed with a mechanical testing apparatus from Zwick/Roell company.

Supplementary Note 1: Sample Degree of Crosslinking (DOC) Calculation

Formula:

$$\frac{mass\ PVA}{1} \times \frac{mol\ PVA}{44\ g\ PVA} \times \frac{mol - OH}{mol\ PVA} \times \frac{mol\ crosslinker}{4\ mol - OH} \times \frac{g}{mo} \quad \begin{matrix} g\ crosslinker\ to\ achieve \\ 100\%\ theoretical\ DOC \end{matrix}$$

Sample Calculation:

If 1 mL of 5 wt% PVA in DMSO is to be 20% crosslinked by dialdehyde **15:**

$$0.05\ g\ PVA \times \frac{mol\ PVA}{44\ g} \times \frac{mol\ crosslinker}{4\ mol - OH} \times \frac{254.41\ g\ crosslinker}{mol\ crosslinker} \times 0.2 = 14.5\ mg\ crosslinker$$

Supplementary Tables

Table S1. DOC results for 50 mg PVA crosslinked by dialdehyde **15**

Theoretical DOC (%)	Mass of Linker (mg)
0	0.000
1	0.723
2	1.45
5	3.63
10	7.25
20	14.5
30	21.7
40	28.9
50	36.1

Table S2. Synthetic Sporopollenin Analogue Numbering Key

Sporopollenin Analogue #	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Linker Carbon Count (#C)	16	16	16	8	10	12	14
Linker Density (%)	20	20	20	20	20	20	20
PVA MW_{avg} (g/mol)	166000	104500	40500	93500	93500	93500	93500
Sporopollenin Analogue #	**13**	**14**	**15**	**16**	**17**	**18**	**26**
Linker Carbon Count (#C)	16	16	16	16	16	16	16*
Linker Density (%)	5	10	20	30	40	50	20
PVA MW_{avg} (g/mol)	93500	93500	93500	93500	93500	93500	93500

* Indicates synthetic substituted crosslinker

Table S3. Chemical stability of synthetic sporopollenin polymer **15**

Solvent	Initial Mass (mg)	Final Mass (mg)	Mass Loss (%)	Notes:
CH_2Cl_2	29.28	26.84	8.334	N/A
Hexanes	28.75	26.86	6.574	N/A
Ethyl Acetate	27.34	25.63	6.255	N/A
Acetone	27.51	26.08	5.198	N/A
DMF	27.61	30.00	–8.656	48 h dry time
DMSO	27.10	32.02	–18.155	48 h dry time
H_2O	24.81	22.57	9.029	N/A
THF	26.46	25.13	5.026	N/A
$CHCl_3$	27.27	25.84	5.140	N/A
conc. H_2SO_4	27.11	N/A	N/A	Blackened and crumbling
5 N NaOH	27.39	29.03	–5.988	48 h dry time, add'l mass likely due to retained NaOH in sample

Table S4. Durometer hardness (Shore D) of synthetic sporopollenin analogues

Sporopollenin Analogue #	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Sample 1 (Shore D)	67	76	67	70	69	85	77
Sample 2 (Shore D)	69	77	69	68	69	84	75
Sample 3 (Shore D)	69	78	68	66	69	83	75
Sample 4 (Shore D)	70	77	---	62	71	84	---
Average (Shore D)	**69**	**77**	**68**	**67**	**70**	**84**	**76**
SD (Shore D)	**1**	**1**	**1**	**3**	**1**	**1**	**1**
Sporopollenin Analogue #	**13**	**14**	**15**	**16**	**17**	**18**	**26**
Sample 1 (Shore D)	77	68	67	71	65	66	70
Sample 2 (Shore D)	77	68	69	73	70	66	69
Sample 3 (Shore D)	73	67	70	72	65	65	75
Sample 4 (Shore D)	---	---	68	73	70	63	70
Average (Shore D)	**76**	**68**	**69**	**72**	**68**	**65**	**71**
SD (Shore D)	**2**	**1**	**1**	**1**	**3**	**1**	**3**

Overall:

Average (Shore D): 71
SD (Shore D): 5

Table S5. Moduli (MPa) of synthetic sporopollenin analogues

Sporopollenin Analogue #	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Sample 1 (MPa)	120	143	112	95	115	200	210
Sample 2 (MPa)	100	184	103	90	136	270	188
Sample 3 (MPa)	134	170	92	105	148	220	192
Average	**118**	**166**	**102**	**97**	**133**	**230**	**197**
SD	**17**	**21**	**10**	**8**	**17**	**36**	**12**

Sporopollenin Analogue #	**13**	**14**	**15**	**16**	**17**	**18**	**26**
Sample 1 (MPa)	158	105	156	157	120	86	90
Sample 2 (MPa)	111	107	160	135	106	100	86
Sample 3 (MPa)	131	87	175	116	118	95	116
Average	**133**	**100**	**164**	**136**	**115**	**94**	**97**
SD	**24**	**11**	**10**	**21**	**8**	**7**	**16**

Overall:

Average (MPa): 134
SD (MPa): 41

Table S6. Hysteresis ratio (dimensionless) of synthetic sporopollenin analogues

Sporopollenin Analogue #	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Sample 1	0.54	0.62	0.53	0.48	0.53	0.62	0.58
Sample 2	0.54	0.62	0.55	0.49	0.53	0.60	0.60
Sample 3	0.59	0.63	0.54	0.47	0.52	0.59	0.59
Average	**0.56**	**0.63**	**0.54**	**0.48**	**0.52**	**0.60**	**0.59**
SD	**0.03**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**

Sporopollenin Analogue #	**13**	**14**	**15**	**16**	**17**	**18**	**26**
Sample 1	0.58	0.56	0.63	0.55	0.55	0.55	0.57
Sample 2	0.58	0.57	0.63	0.55	0.54	0.56	0.56
Sample 3	0.60	0.55	0.64	0.57	0.55	0.56	0.58
Average	**0.59**	**0.56**	**0.63**	**0.56**	**0.55**	**0.56**	**0.57**
SD	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**

Overall:

Average (dimensionless): 0.53
SD (dimensionless): 0.15

Table S7. Volume swelling ratios (dimensionless) of synthetic sporopollenin analogues

Sporopollenin Analogue #	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Sample 1	1.24	1.47	1.38	1.51	1.44	1.62	1.53
Sample 2	1.28	1.41	1.35	1.56	1.40	1.57	1.50
Sample 3	1.27	1.39	1.39	1.54	1.41	1.70	1.51
Average	**1.26**	**1.43**	**1.37**	**1.54**	**1.42**	**1.63**	**1.51**
SD	**0.02**	**0.04**	**0.02**	**0.02**	**0.02**	**0.07**	**0.02**
Sporopollenin Analogue #	**13**	**14**	**15**	**16**	**17**	**18**	**26**
Sample 1	2.11	1.78	1.69	1.18	1.15	1.21	1.42
Sample 2	1.97	1.66	1.73	1.17	1.10	1.16	1.28
Sample 3	1.93	1.76	1.66	1.12	1.28	1.18	1.48
Average	**2.00**	**1.74**	**1.69**	**1.16**	**1.18**	**1.19**	**1.39**
SD	**0.10**	**0.06**	**0.03**	**0.03**	**0.09**	**0.03**	**0.10**

Table S8. Weight swelling ratios (dimensionless) of synthetic sporopollenin analogues

Sporopollenin Analogue #	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Sample 1	1.24	1.43	1.24	1.61	1.33	1.55	1.41
Sample 2	1.21	1.34	1.27	1.43	1.30	1.49	1.33
Sample 3	1.26	1.32	1.25	1.47	1.26	1.56	1.35
Average	**1.23**	**1.37**	**1.25**	**1.50**	**1.30**	**1.54**	**1.37**
SD	**0.03**	**0.06**	**0.02**	**0.09**	**0.03**	**0.04**	**0.04**
Sporopollenin Analogue #	**13**	**14**	**15**	**16**	**17**	**18**	**26**
Sample 1	1.74	1.57	1.59	1.09	1.06	1.09	1.34
Sample 2	1.76	1.57	1.58	1.11	0.95	1.08	1.26
Sample 3	1.65	1.57	1.53	1.09	1.04	1.13	1.28
Average	**1.71**	**1.57**	**1.57**	**1.10**	**1.02**	**1.10**	**1.30**
SD	**0.06**	**0.00**	**0.03**	**0.01**	**0.06**	**0.02**	**0.04**

Table S9. Thermogravimetric analysis of synthetic sporopollenin analogues

Sporopollenin Analogue #	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Loss 1 (%,°C)	33.4, 208	33.3, 217	34.4, 210	38.1, 211	37.2, 215	35.0, 218	34.9, 226
Loss 2 (%,°C)	55.6, 454	55.7, 455	53.8, 455	49.3, 446	50.1, 451	50.8, 452	51.8, 451
Loss 3 (%,°C)	9.7, 540	9.6, 535	10.4, 542	11.0, 532	11.1, 530	11.4, 534	10.8, 519
Residue (%)	1.3	1.5	1.3	1.6	1.6	2.7	2.5

Sporopollenin Analogue #	**13**	**14**	**15**	**16**	**17**	**18**	**26**
Loss 1 (%,°C)	37.9, 205	37.0, 210	35.6, 203	32.5, 220	30.6, 226	31.6, 218	32.3, 189
Loss 2 (%,°C)	50.1, 446	50.6, 450	53.2, 444	56.8, 457	60.8, 464	61.7, 463	56.5, 450
Loss 3 (%,°C)	10.6, 535	10.7, 535	9.0, 522	9.6, 540	7.9, 544	6.0, 548	9.8, 530
Residue (%)	1.4	1.6	2.2	1.1	0.7	0.7	1.3

Overall:

Average Loss 1 (%, °C): 34.6, 213
SD (%, °C): 2.4, 9.8

Average Loss 2 (%, °C): 54.1, 453
SD (%, °C): 4.0, 5.9

Average Loss 3 (%, °C): 9.8, 535
SD (%, °C): 1.4, 8.0

Average Residue (%): 1.5
SD (%): 0.6

Supplementary Figures

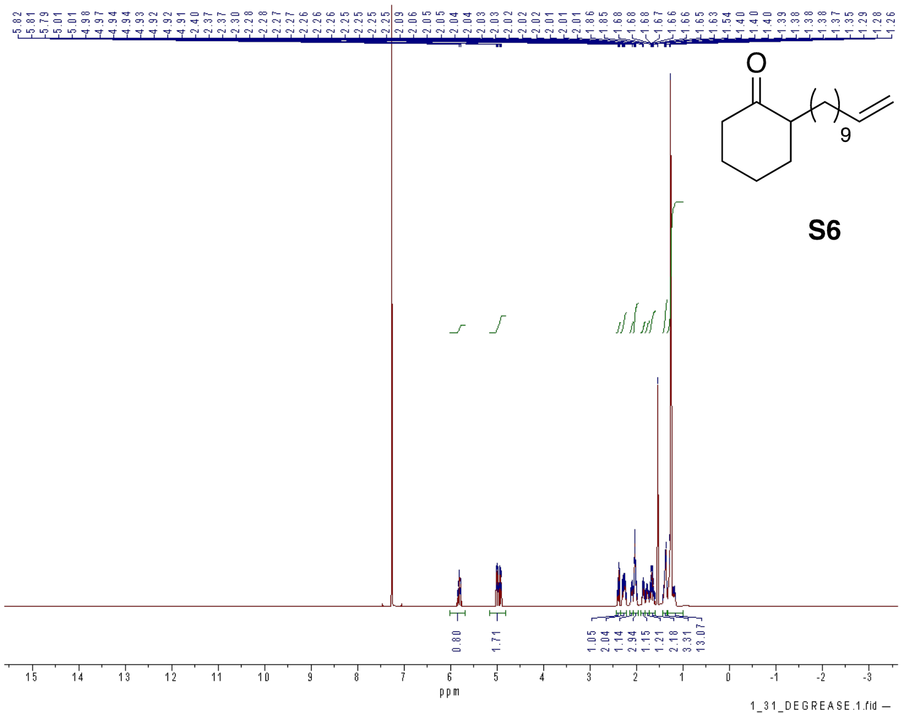

Figure S1. The ^{1}H NMR spectrum of compound **S6**

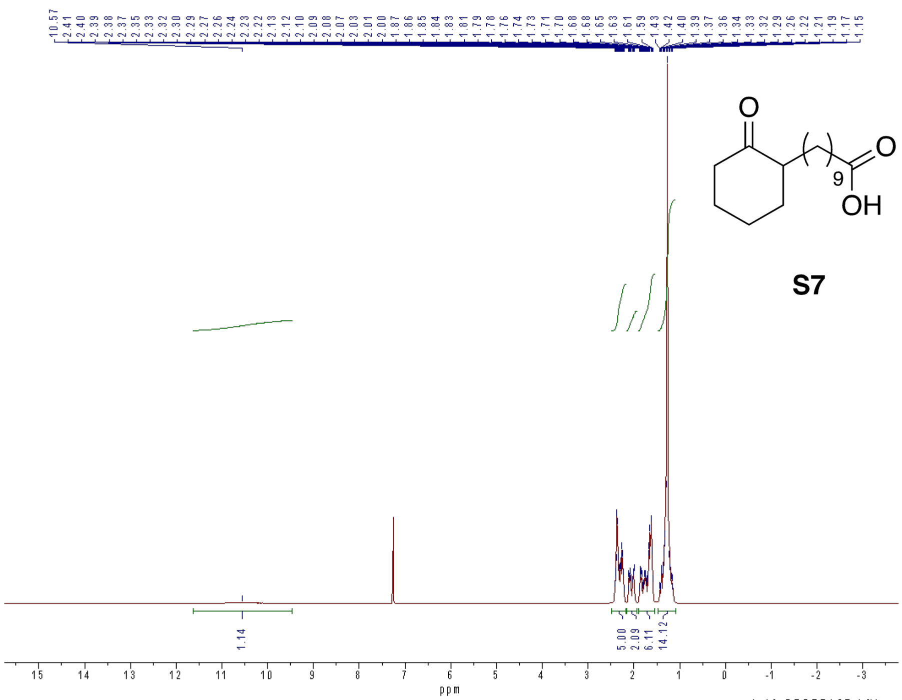

Figure S2. The ^{1}H NMR spectrum of compound **S7**

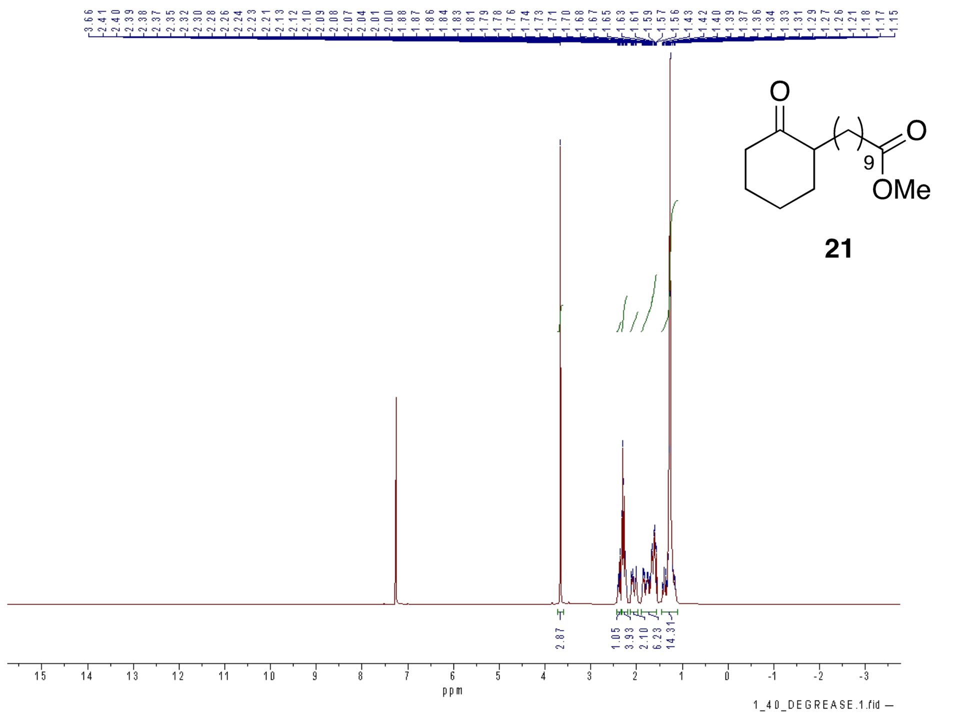

Figure S3. The ^{1}H NMR spectrum of compound **21**

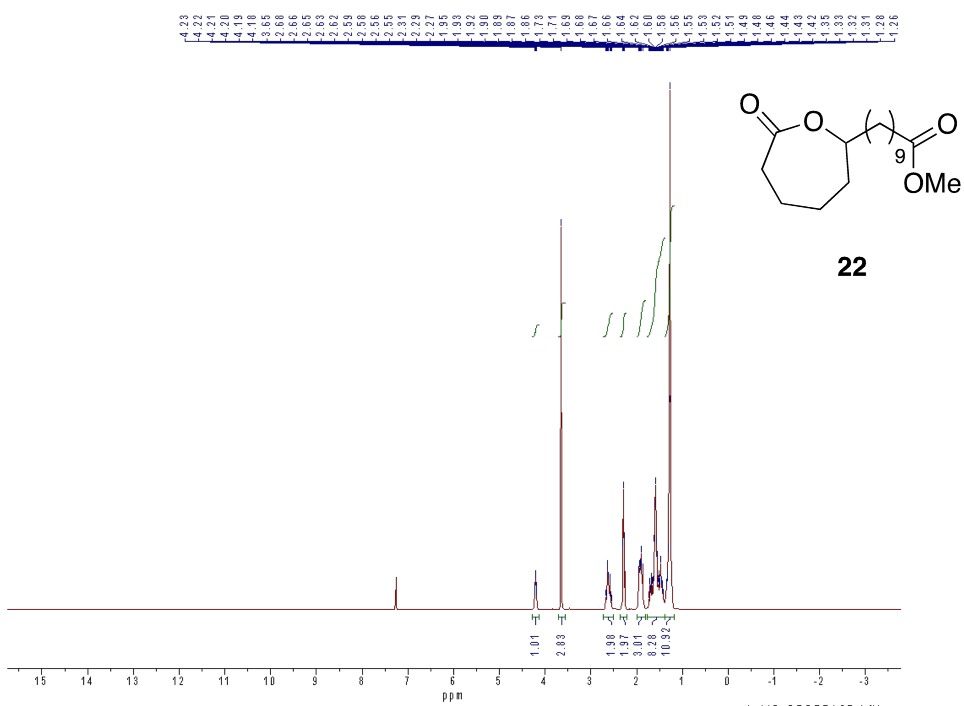

Figure S4. The ^{1}H NMR spectrum of compound **22**

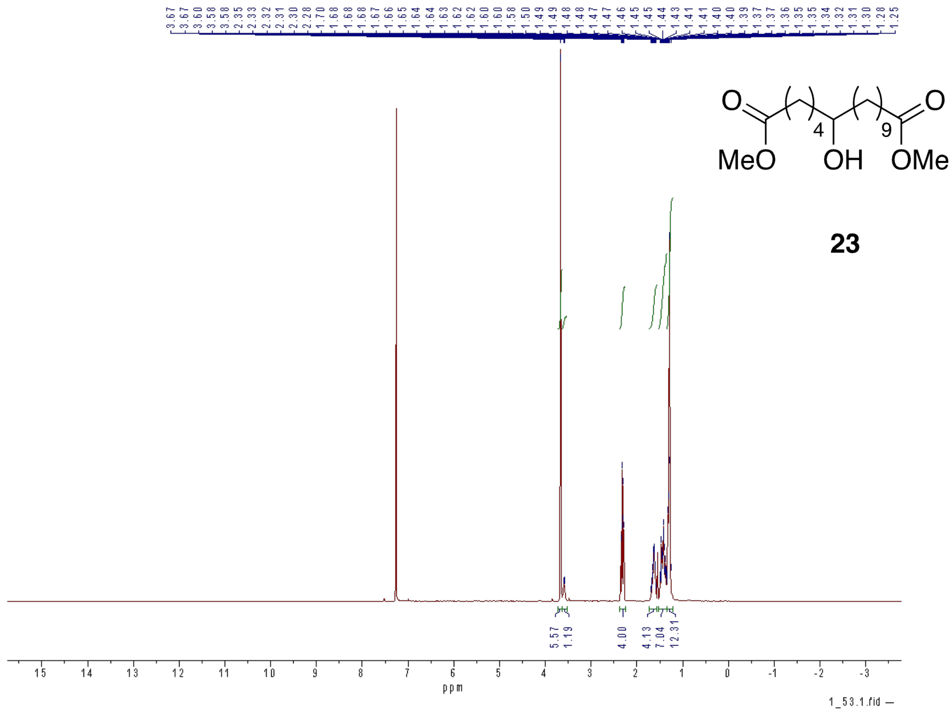

Figure S5. The ^{1}H NMR spectrum of compound **23**

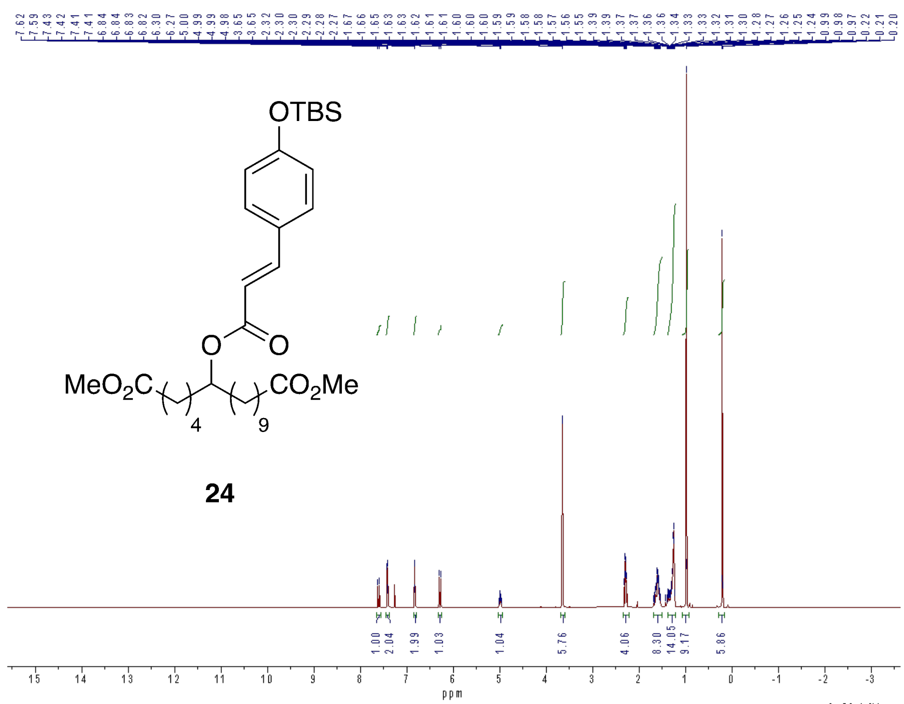

Figure S6. The ^{1}H NMR spectrum of compound **24**

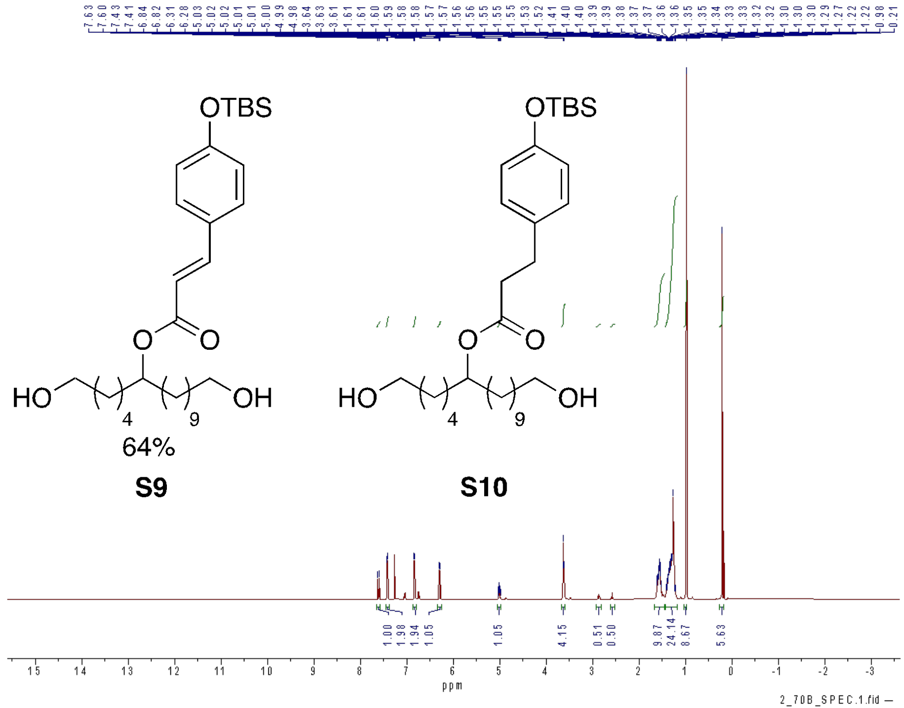

Figure S7. The ^{1}H NMR spectrum of compounds **S9** and **S10**

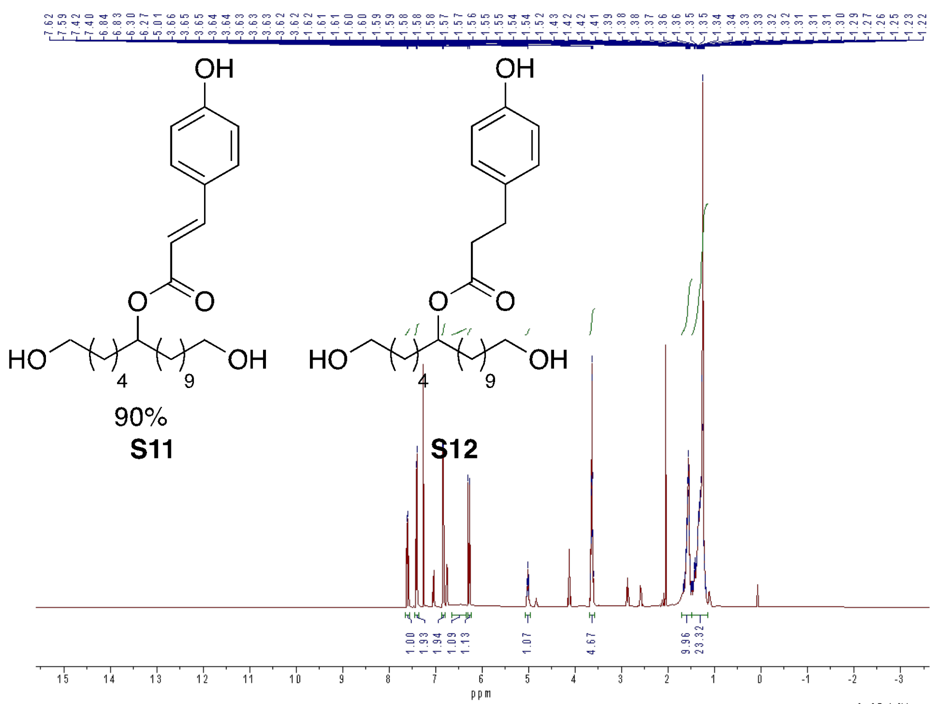

Figure S8. The ^{1}H NMR spectrum of compounds **S11** and **S12**

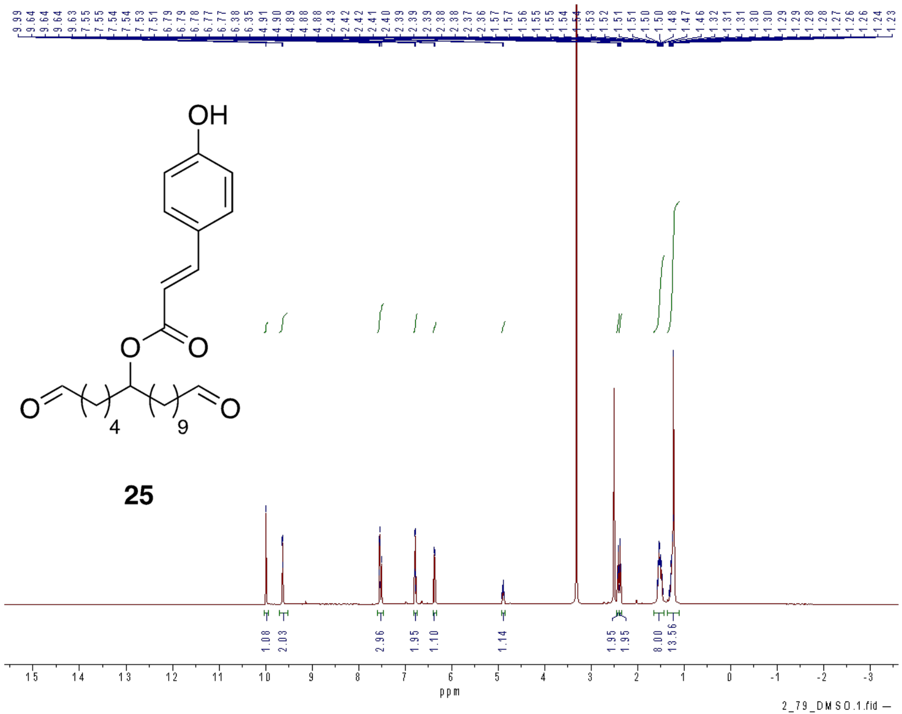

Figure S9. The ^{1}H NMR spectrum of compound **25**

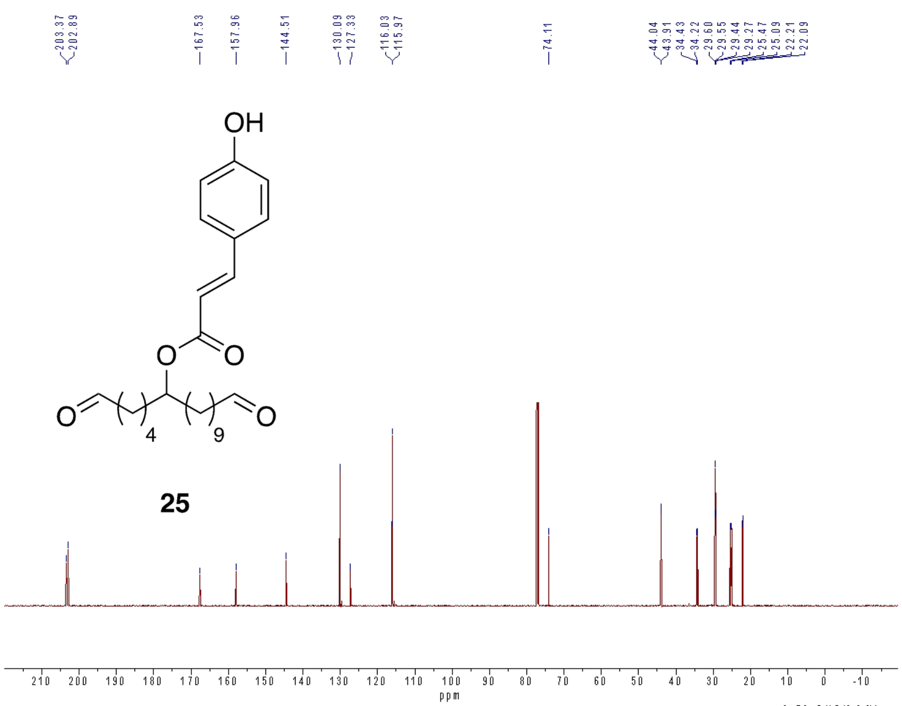

Figure S10. The ^{13}C NMR spectrum of compound **25**

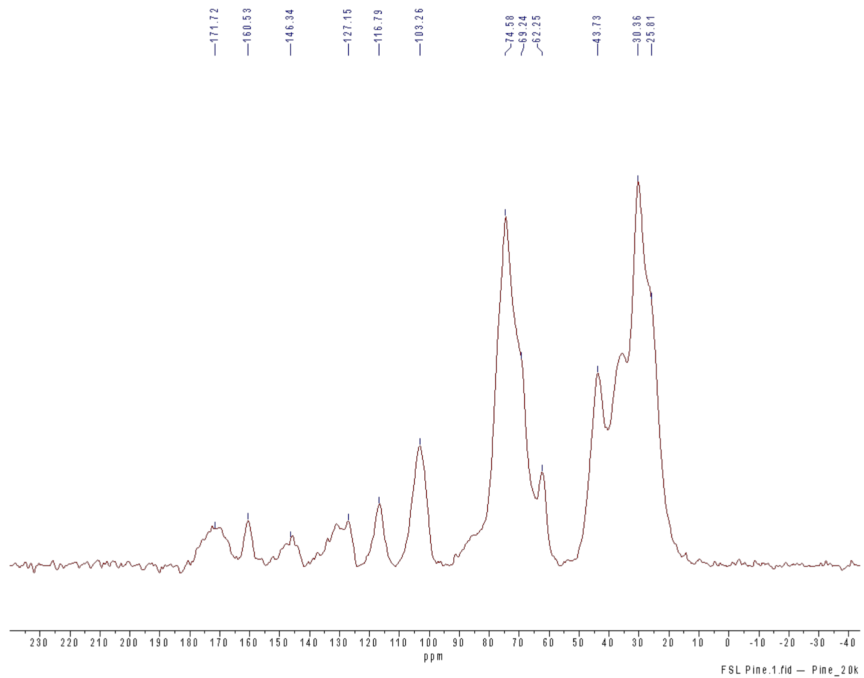

Figure S11. The ^{13}C MAS ssNMR spectrum of authentic *P. rigida* sporopollenin (*9*)

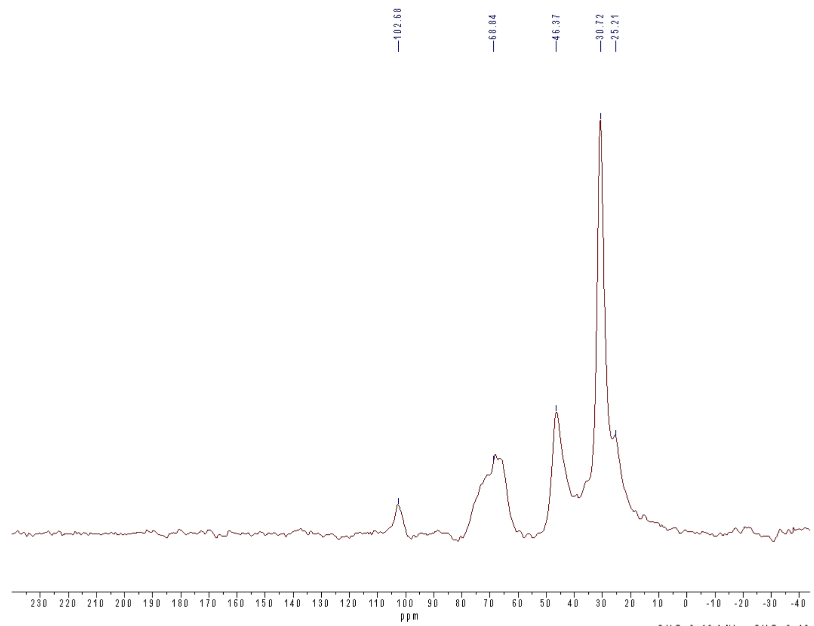

Figure S12. The ^{13}C MAS ssNMR spectrum of simplified sporopollenin analogue **15**

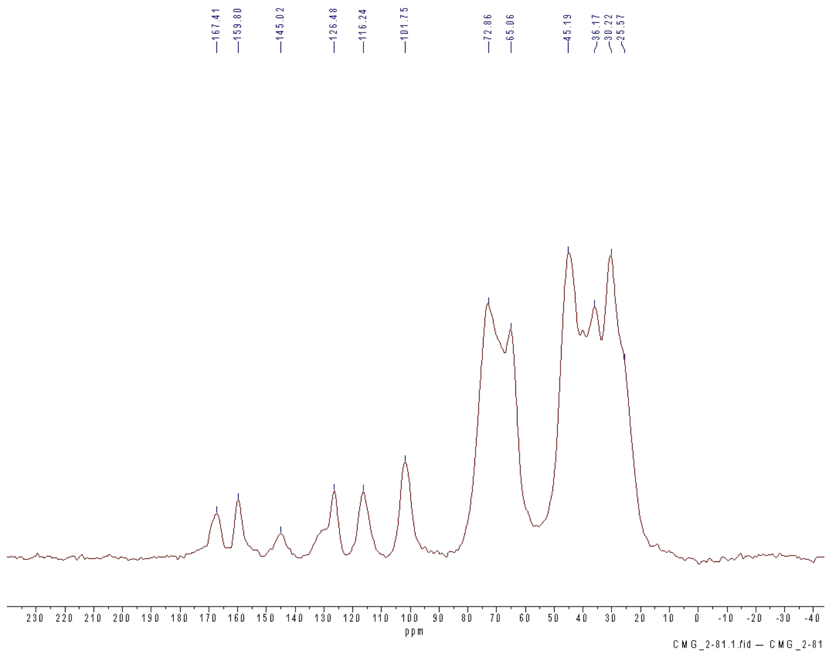

Figure S13. The ^{13}C MAS ssNMR spectrum of synthetic linker sporopollenin analogue **26**

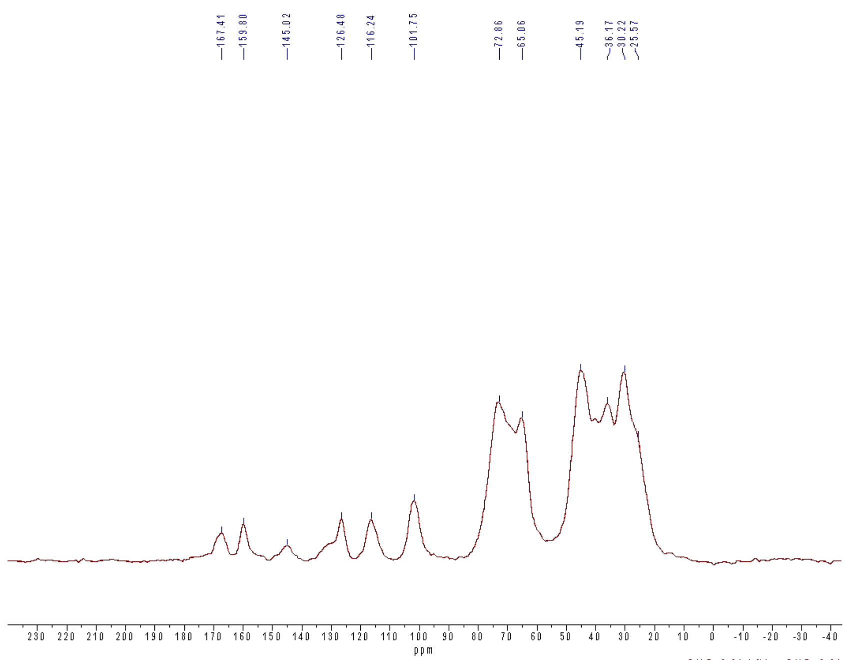

Figure S14. Overlaid ^{13}C MAS ssNMR spectra of authentic *P. rigida* sporopollenin (blue) (*9*), simplified sporopollenin analogue **15** (green), and synthetic linker sporopollenin analogue **26** (red)

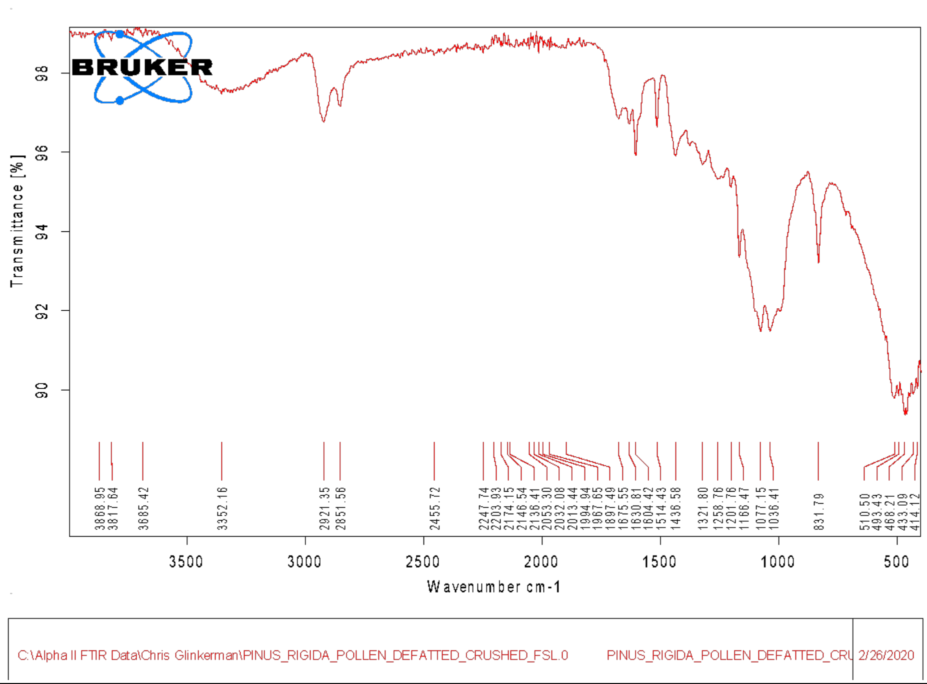

Figure S15. The IR spectrum of authentic *P. rigida* sporopollenin

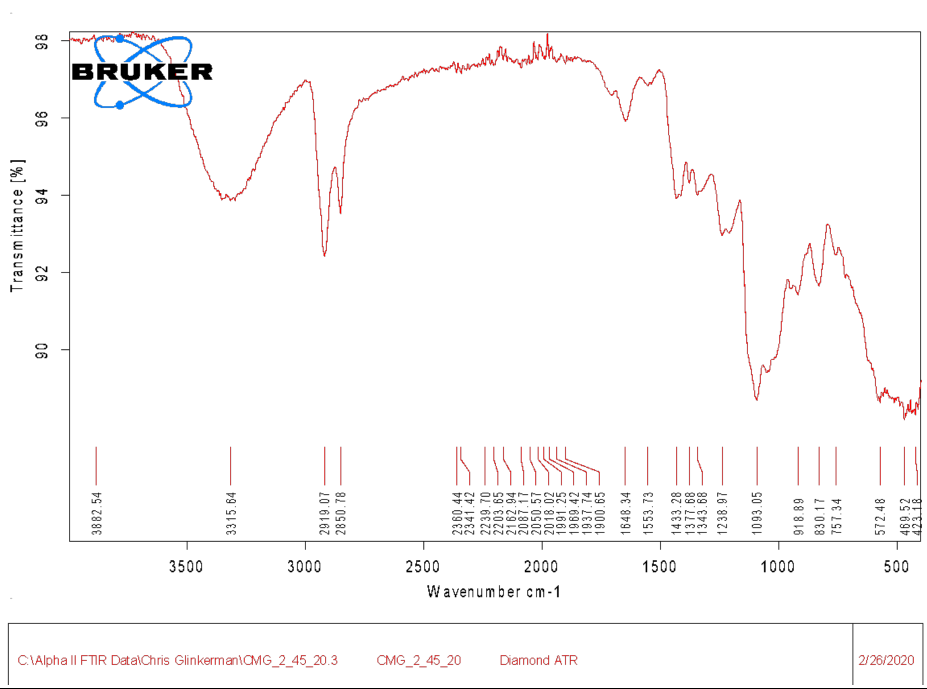

Figure S16. The IR spectrum of simplified sporopollenin analogue **15**

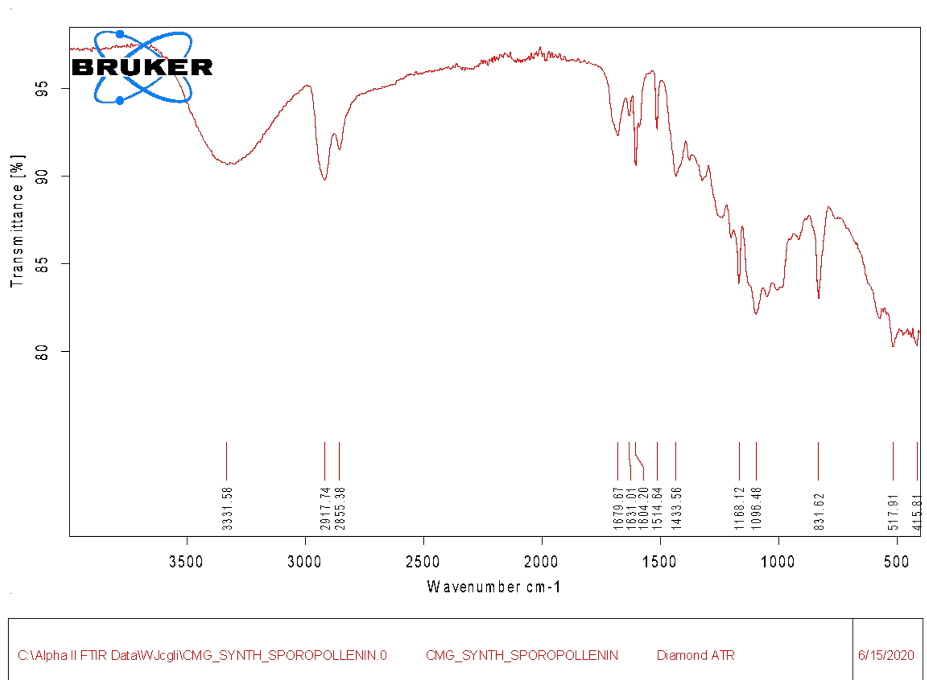

Figure S17. The IR spectrum of synthetic linker sporopollenin analogue **26**

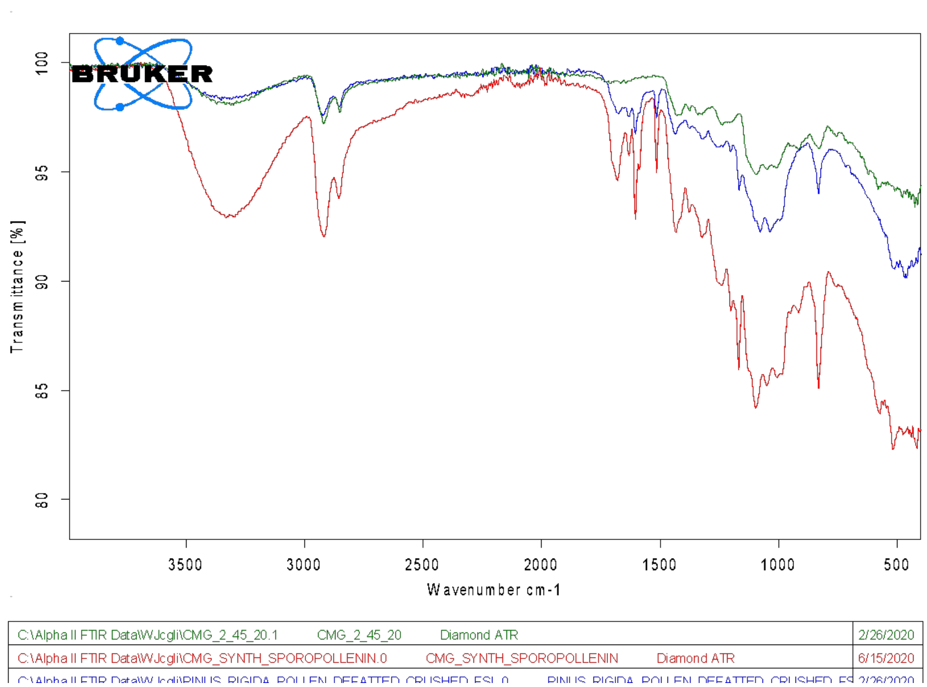

Figure S18. Overlaid IR spectra of authentic *P. rigida* sporopollenin (blue), simplified sporopollenin analogue **15** (green), and synthetic linker sporopollenin analogue **26** (red)

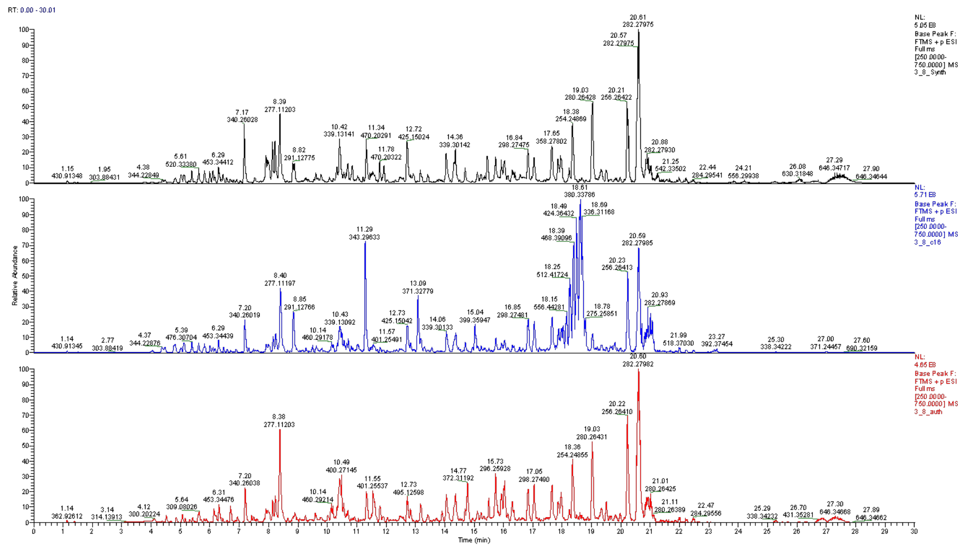

Figure S19. The base peak chromatograms of thioacidolyzed authentic *P. rigida* sporopollenin (red), simplified sporopollenin analogue **15** (blue), and synthetic linker sporopollenin analogue **26** (black)

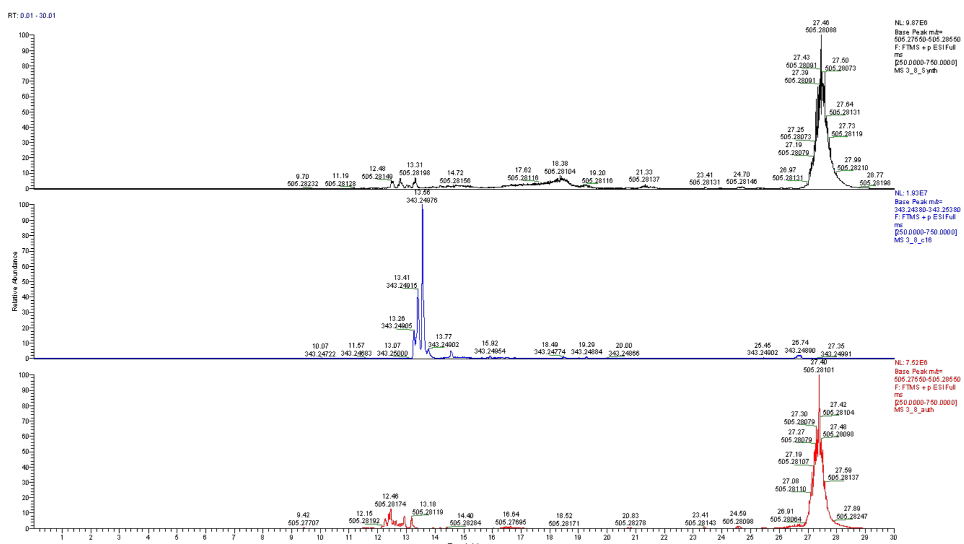

Figure S20. The extracted-ion chromatograms of thioacidolyzed authentic *P. rigida* sporopollenin (red), simplified sporopollenin analogue **15** (blue), and synthetic linker sporopollenin analogue **26** (black)

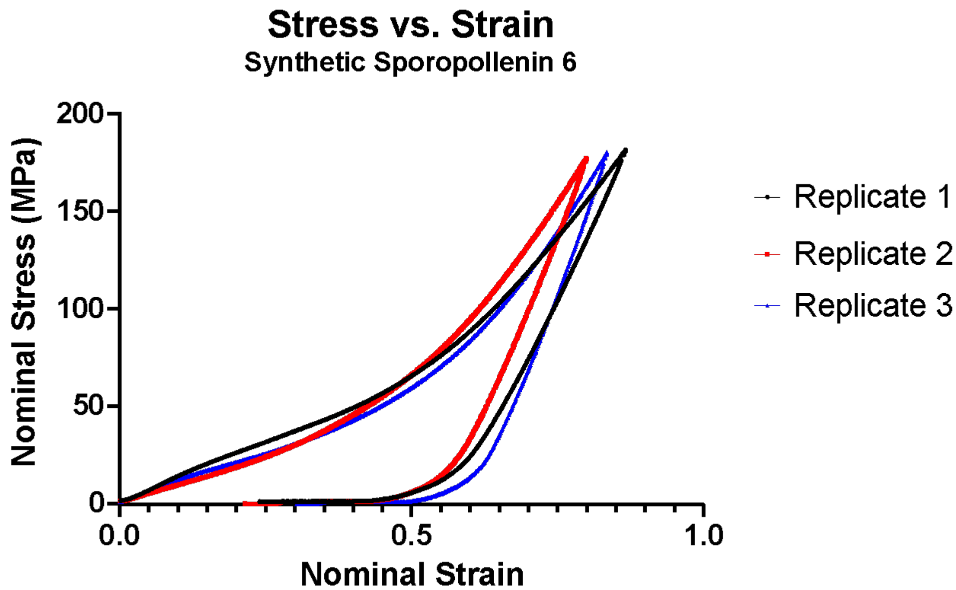

Figure S21. Compressive stress-strain curve for synthetic sporopollenin analogue **6**

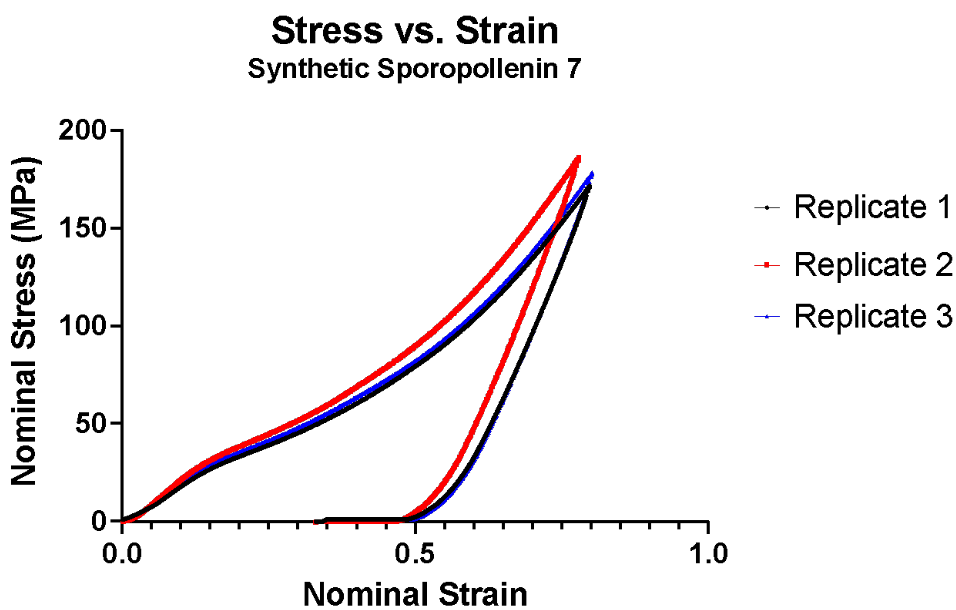

Figure S22. Compressive stress-strain curve for synthetic sporopollenin analogue **7**

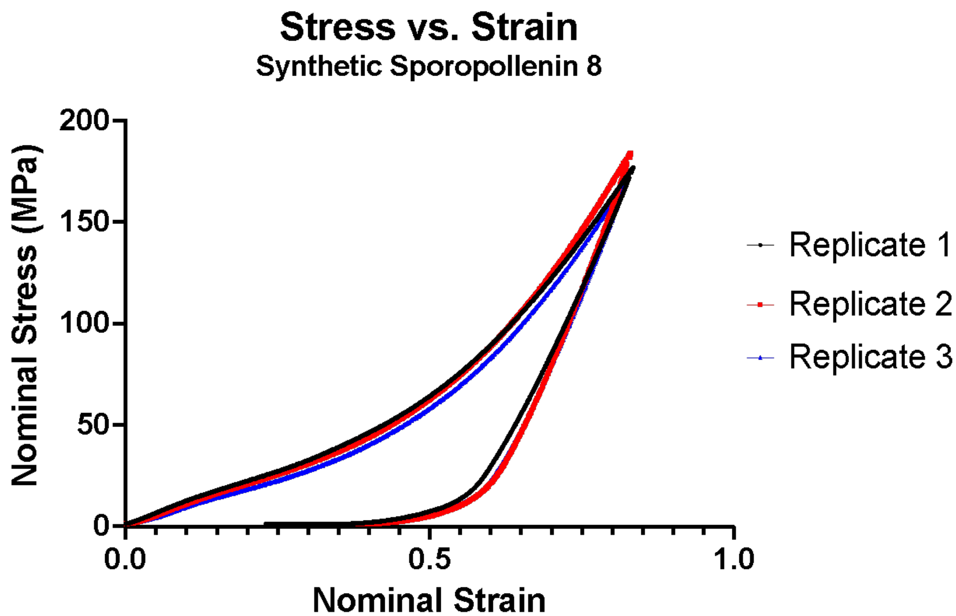

Figure S23. Compressive stress-strain curve for synthetic sporopollenin analogue **8**

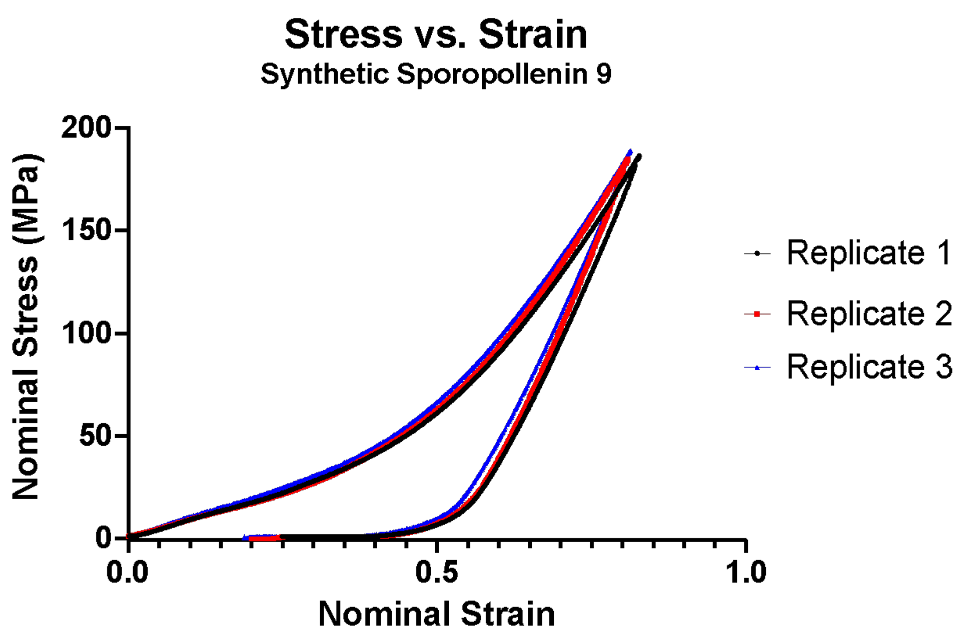

Figure S24. Compressive stress-strain curve for synthetic sporopollenin analogue **9**

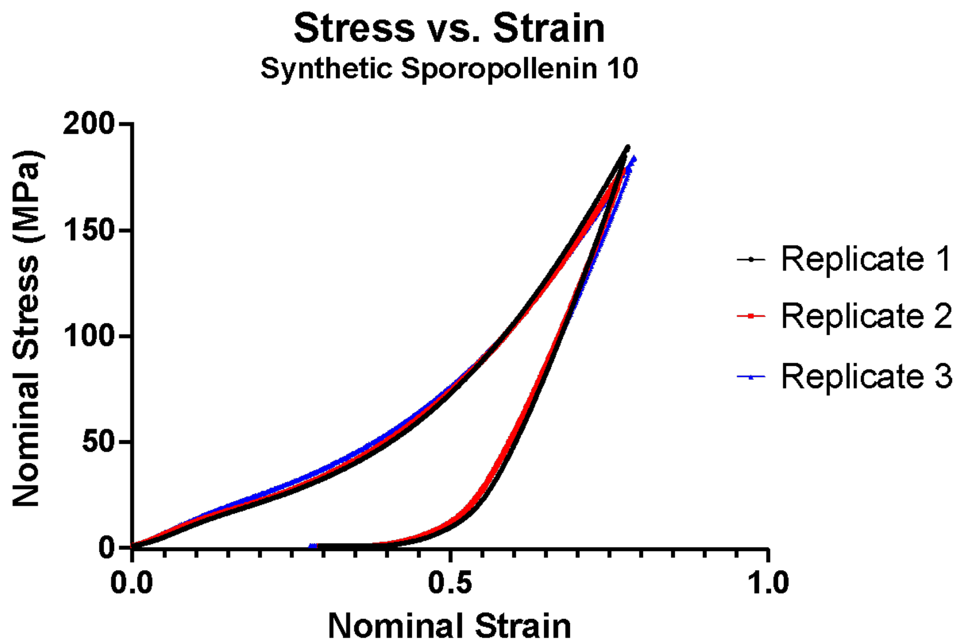

Figure S25. Compressive stress-strain curve for synthetic sporopollenin analogue **10**

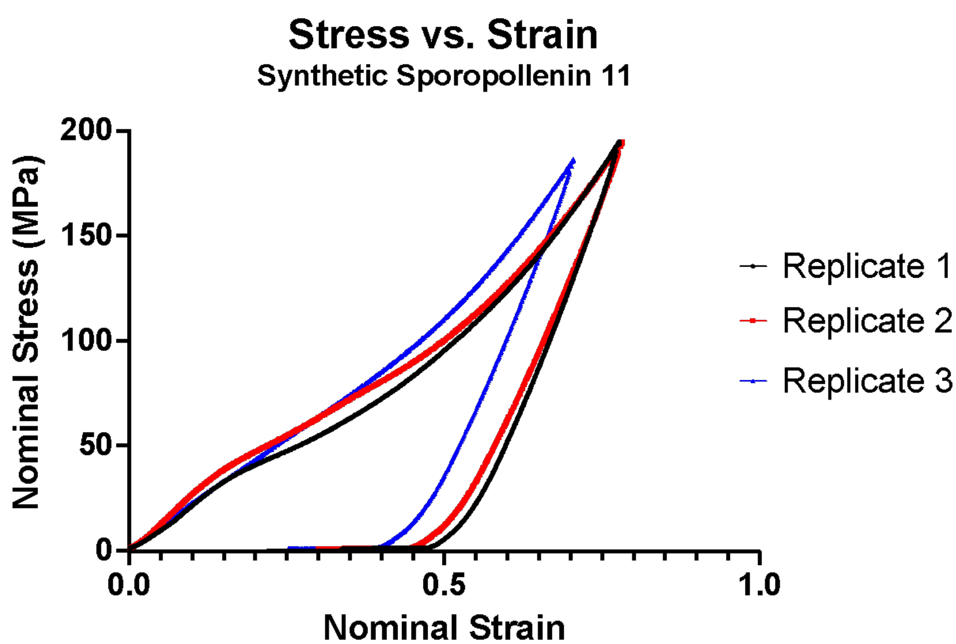

Figure S26. Compressive stress-strain curve for synthetic sporopollenin analogue **11**

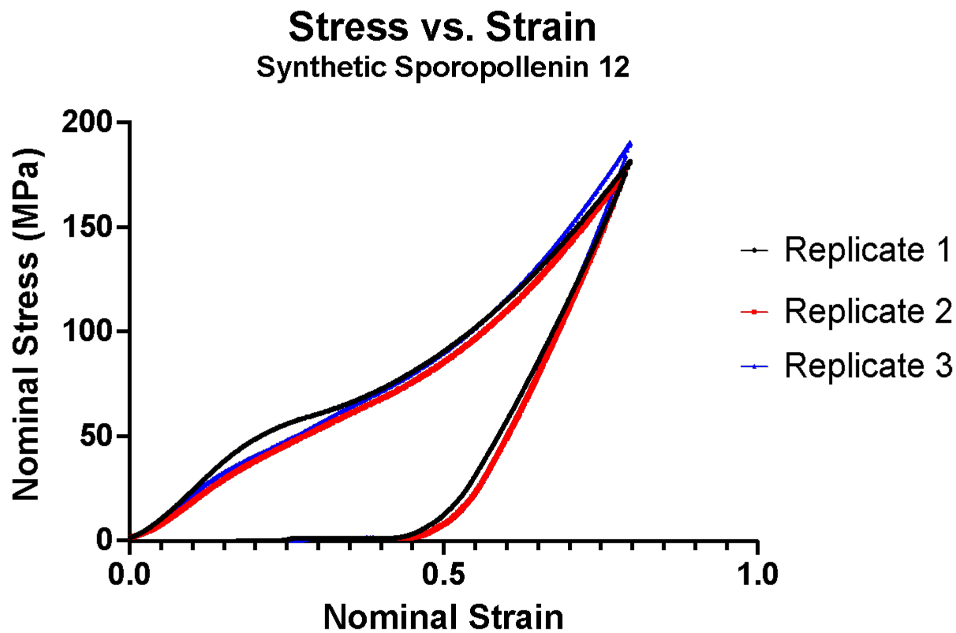

Figure S27. Compressive stress-strain curve for synthetic sporopollenin analogue **12**

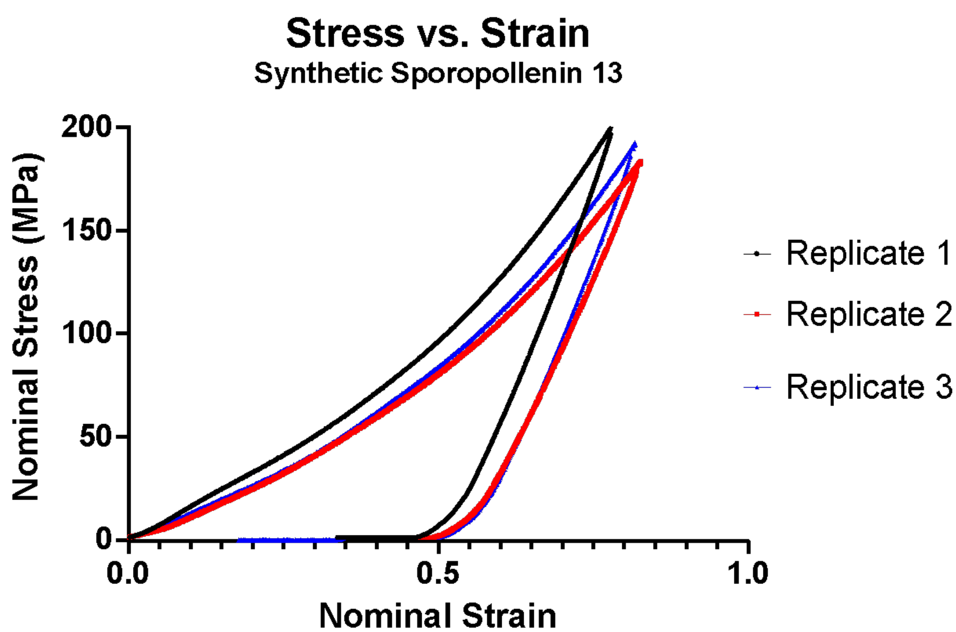

Figure S28. Compressive stress-strain curve for synthetic sporopollenin analogue **13**

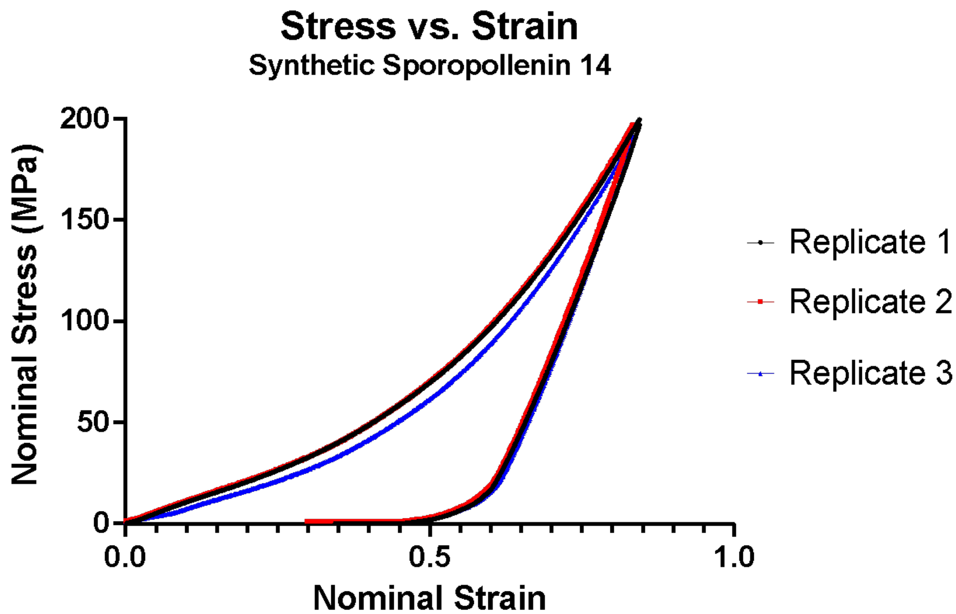

Figure S29. Compressive stress-strain curve for synthetic sporopollenin analogue **14**

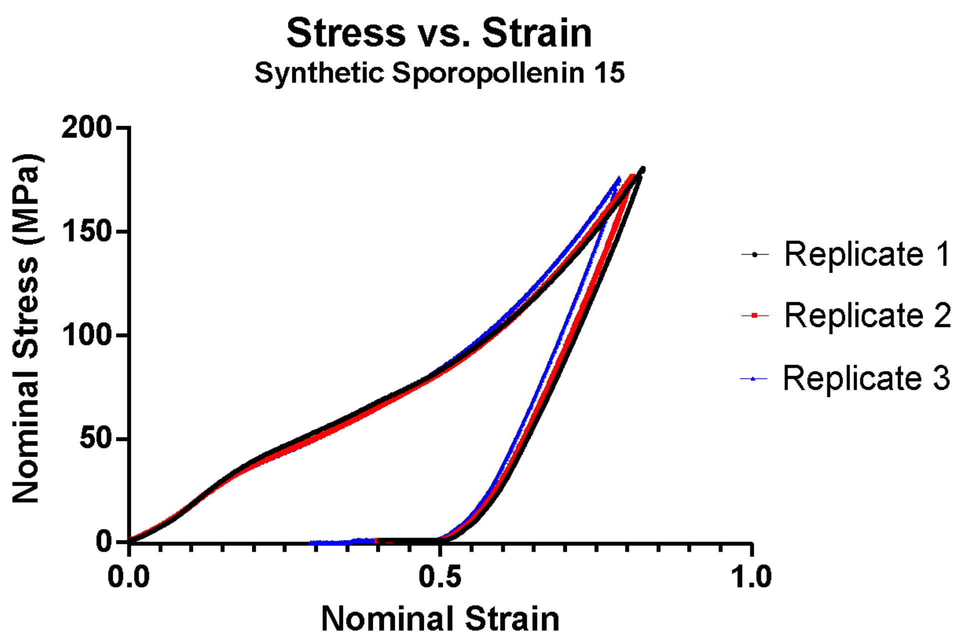

Figure S30. Compressive stress-strain curve for synthetic sporopollenin analogue **15**

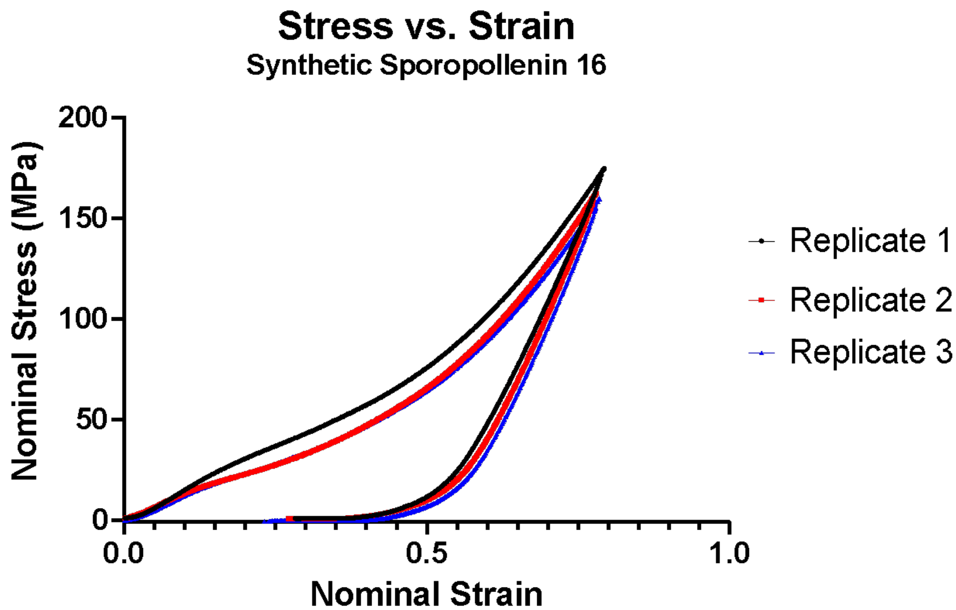

Figure S31. Compressive stress-strain curve for synthetic sporopollenin analogue **16**

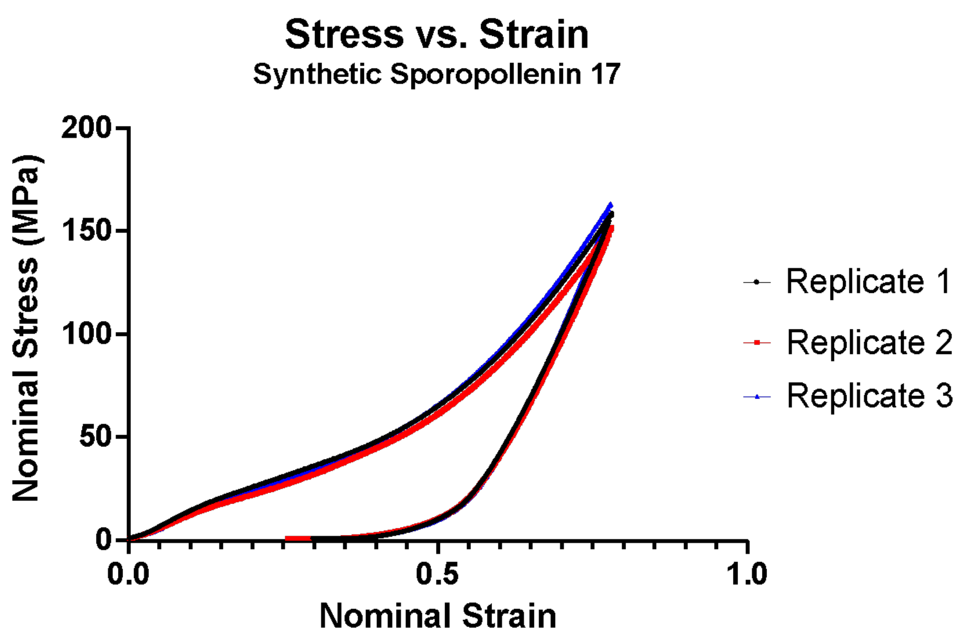

Figure S32. Compressive stress-strain curve for synthetic sporopollenin analogue **17**

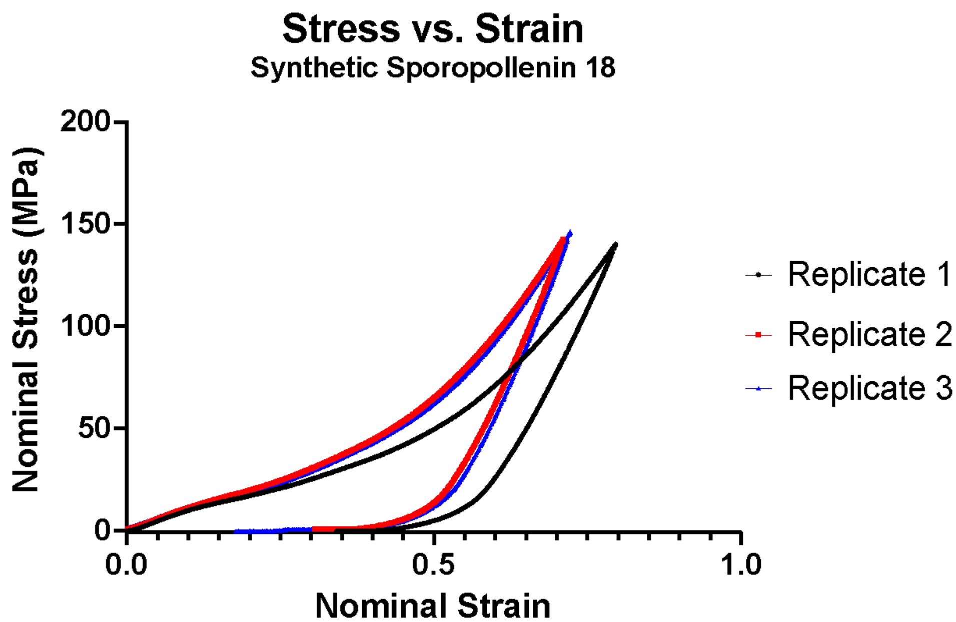

Figure S33. Compressive stress-strain curve for synthetic sporopollenin analogue **18**

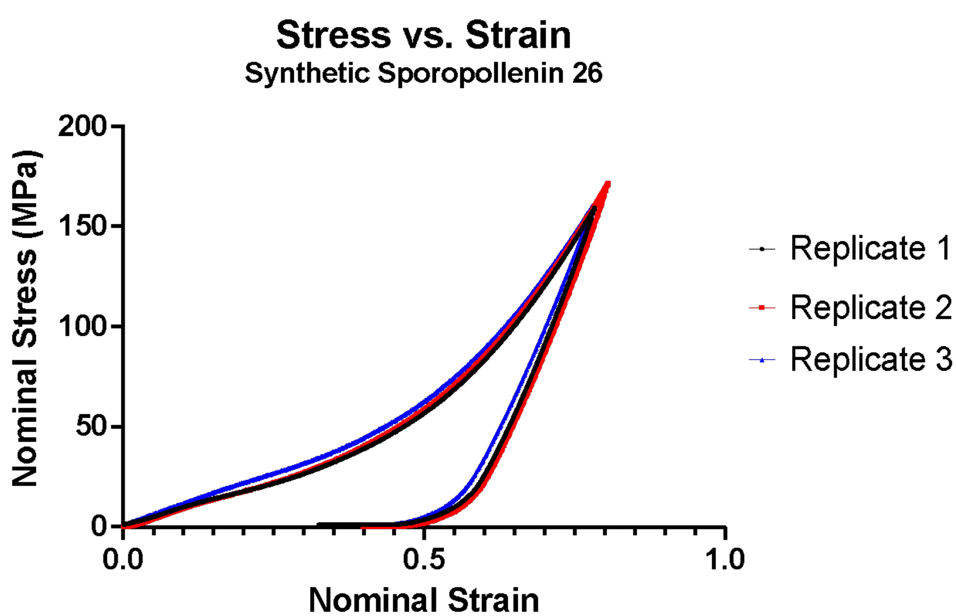

Figure S34. Compressive stress-strain curve for synthetic sporopollenin analogue **26**

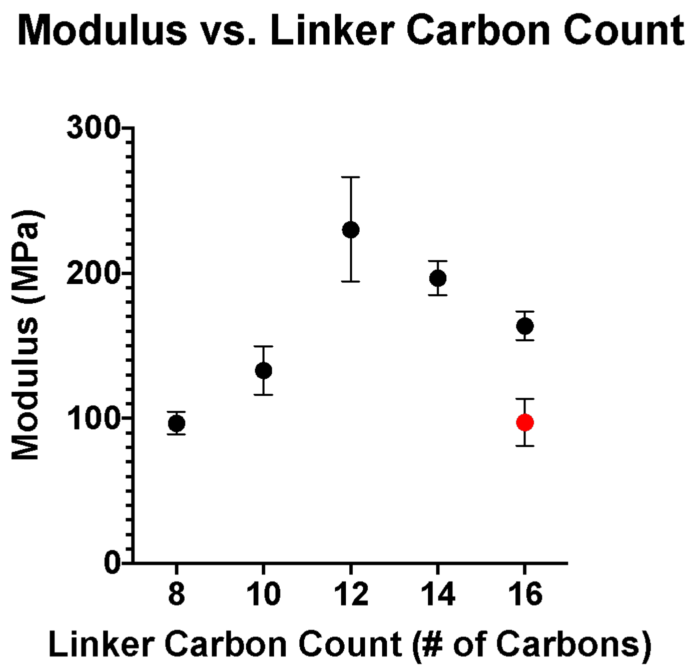

Figure S35. Relationship between compressive modulus and linker carbon count in simplified (black) and substituted (red) synthetic linker sporopollenin analogues (error bars = standard deviation)

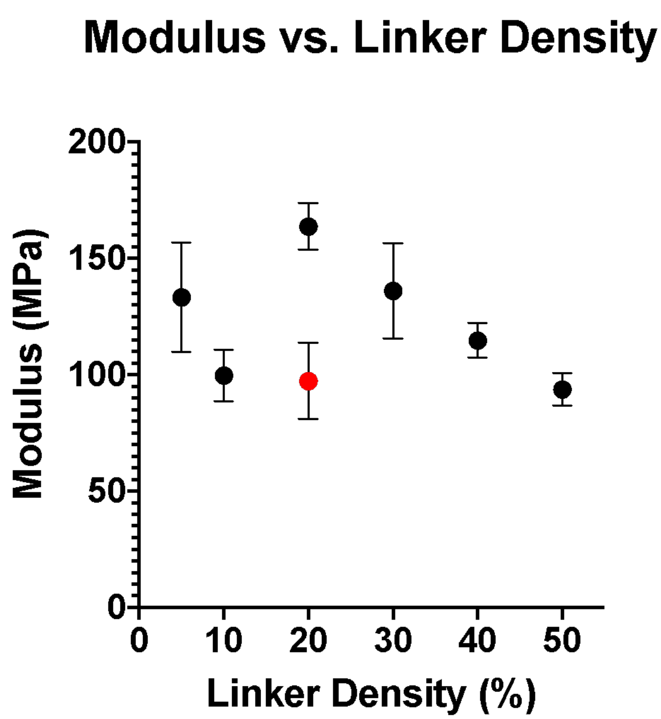

Figure S36. Relationship between compressive modulus and linker density in simplified (black) and substituted (red) synthetic linker sporopollenin analogues (error bars = standard deviation)

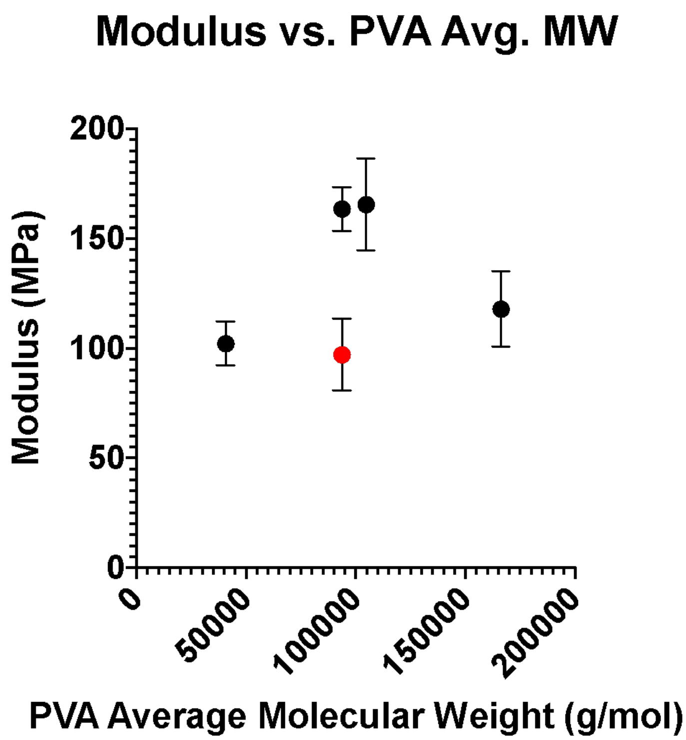

Figure S37. Relationship between compressive modulus and PVA MW_{avg} in simplified (black) and substituted (red) synthetic linker sporopollenin analogues (error bars = standard deviation)

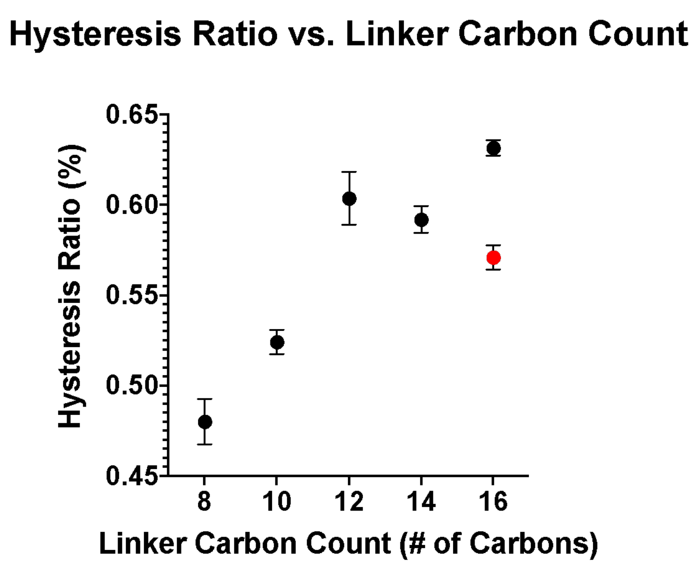

Figure S38. Relationship between compressive hysteresis ratio and linker carbon count in simplified (black) and substituted (red) synthetic linker sporopollenin analogues (error bars = standard deviation)

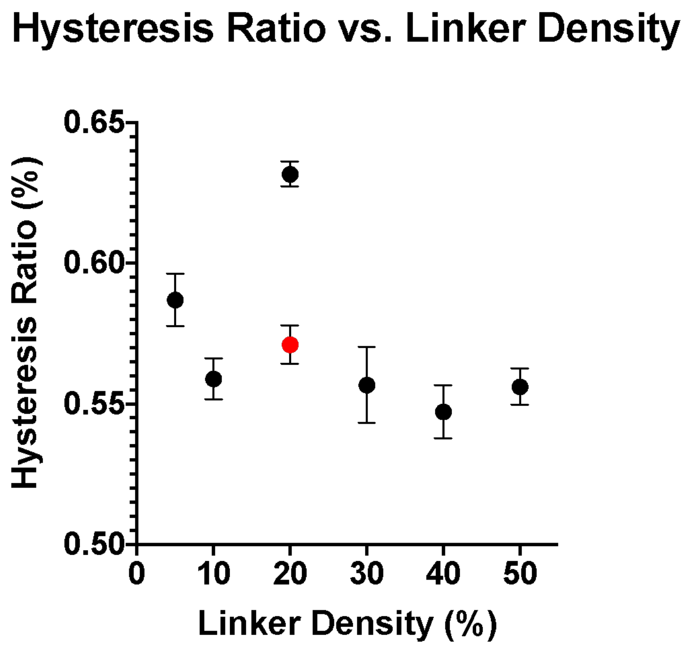

Figure S39. Relationship between compressive hysteresis ratio and linker density in simplified (black) and substituted (red) synthetic linker sporopollenin analogues (error bars = standard deviation)

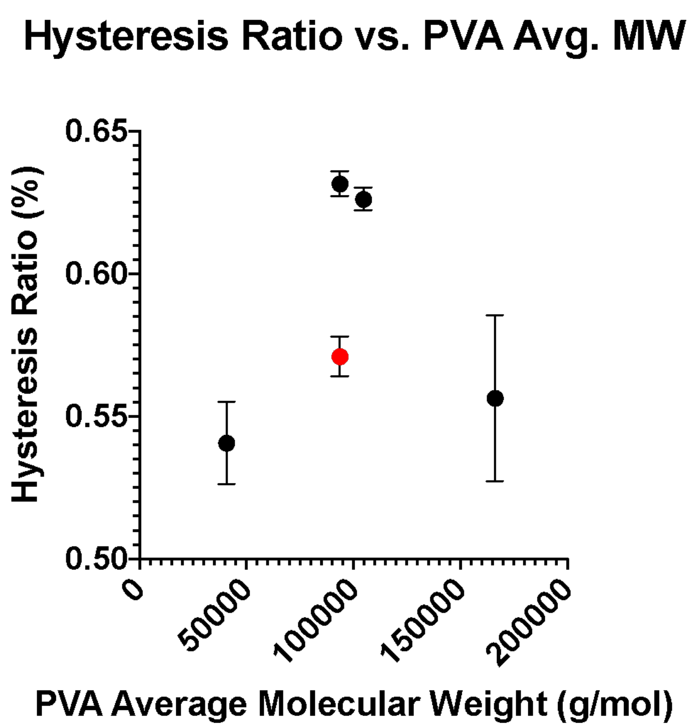

Figure S40. Relationship between compressive hysteresis ratio and PVA MW_{avg} in simplified (black) and substituted (red) synthetic linker sporopollenin analogues (error bars = standard deviation)

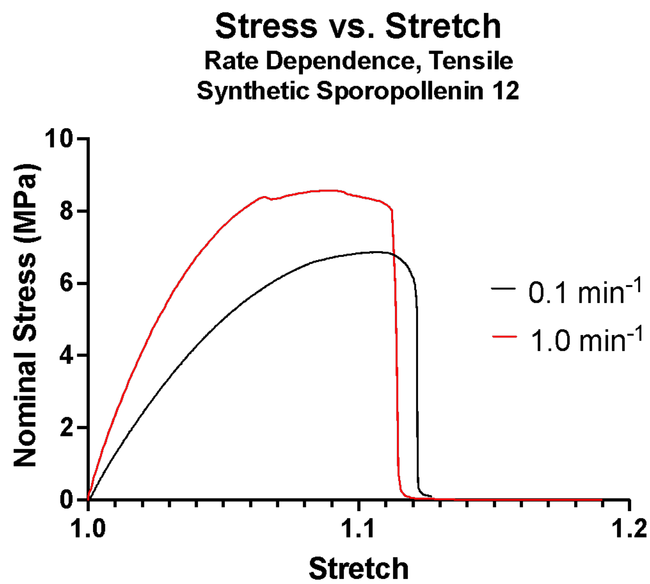

Figure S41. Tensile stress-strain curve for synthetic sporopollenin analogue **12** at 1.0 (red) and 0.1 min^{-1} (black) loading rates

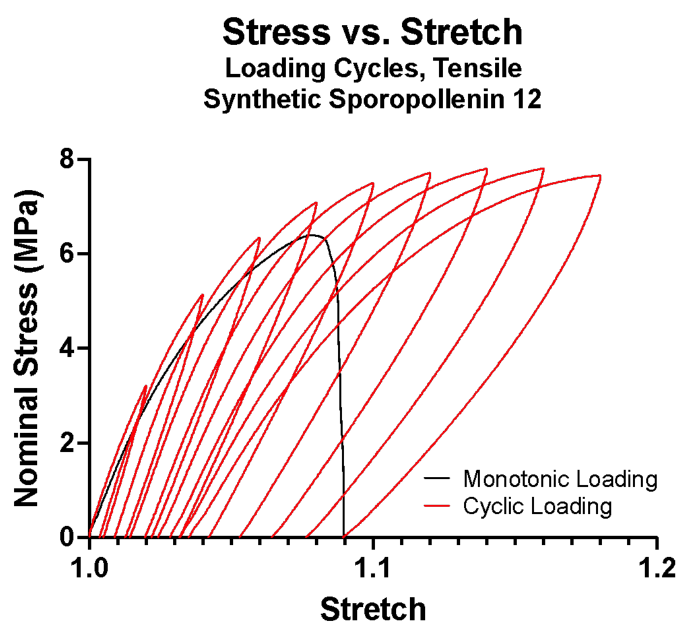

Figure S42. Tensile stress-strain curve for synthetic sporopollenin analogue **12** with cyclic (red) and monotonic (black) loading

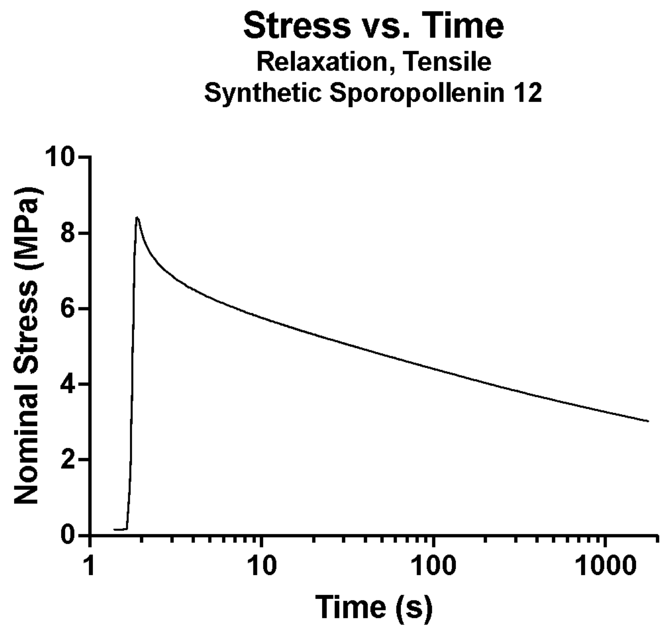

Figure S43. Tensile stress-time relaxation curve for synthetic sporopollenin analogue **12**

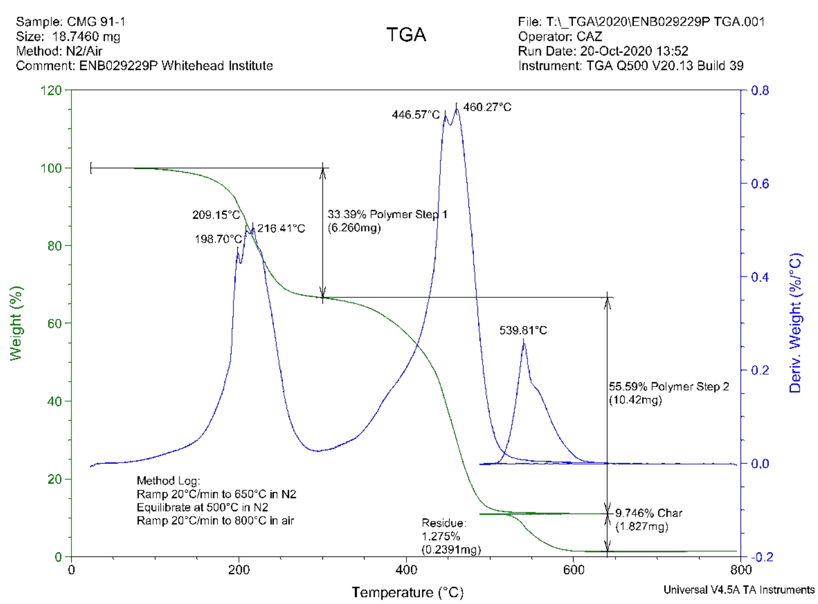

Figure S44. The TGA thermogram for synthetic sporopollenin analogue **6**

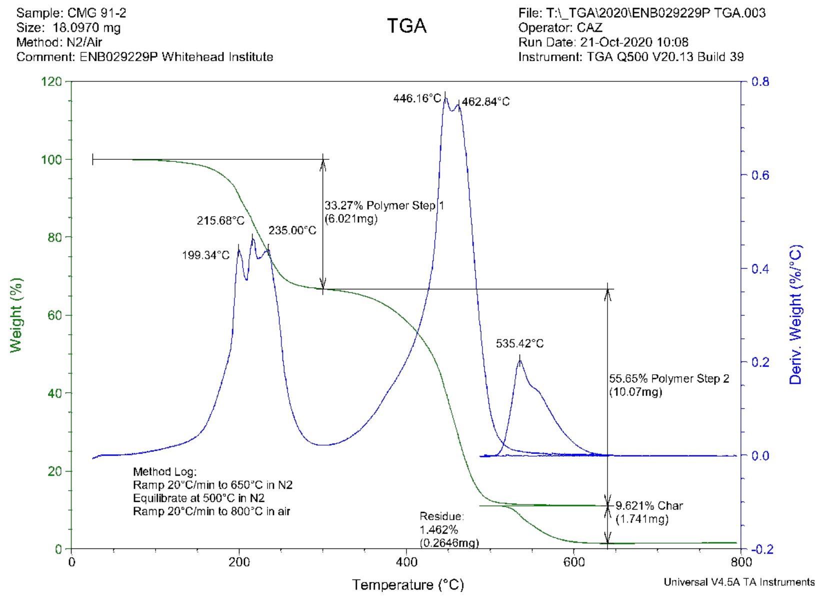

Figure S45. The TGA thermogram for synthetic sporopollenin analogue **7**

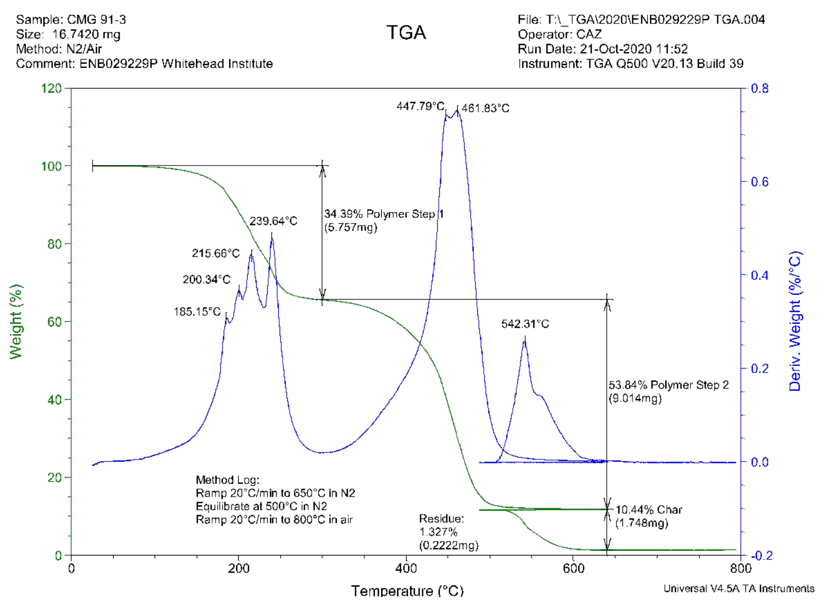

Figure S46. The TGA thermogram for synthetic sporopollenin analogue **8**

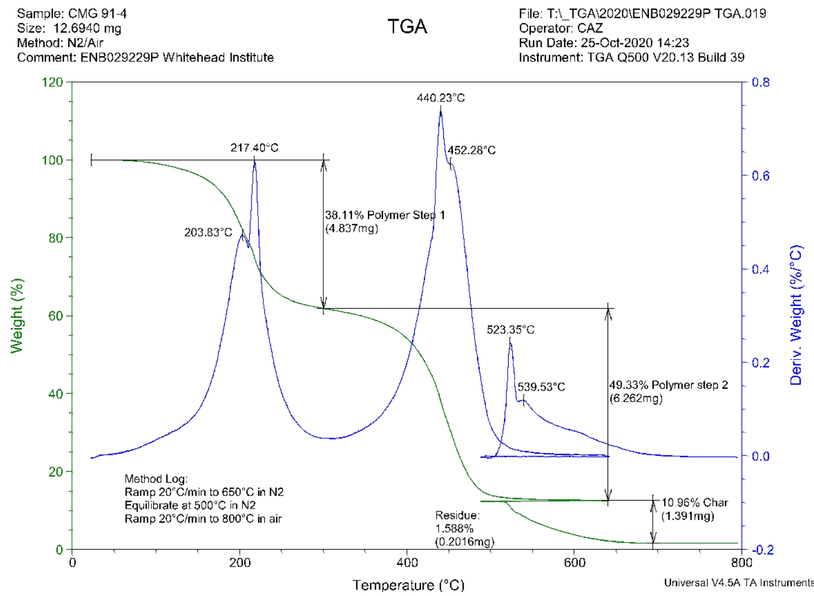

Figure S47. The TGA thermogram for synthetic sporopollenin analogue **9**

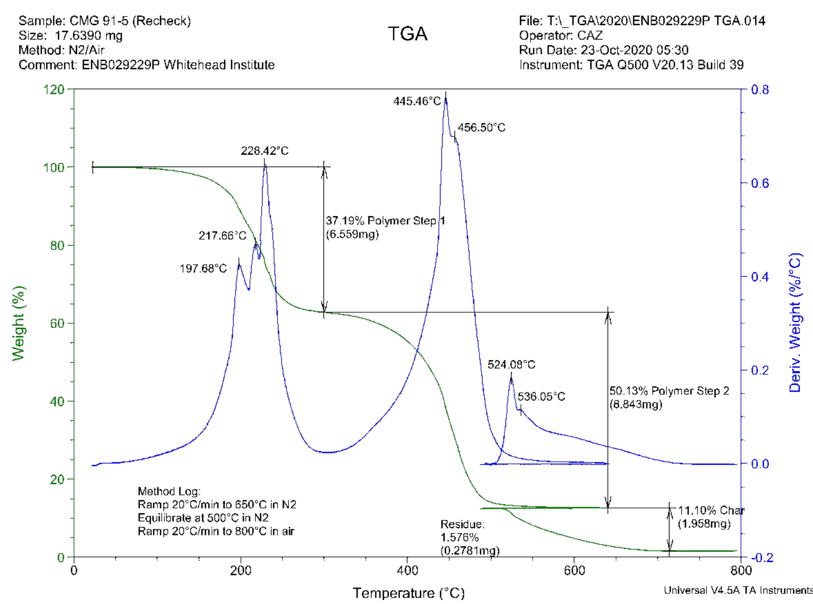

Figure S48. The TGA thermogram for synthetic sporopollenin analogue **10**

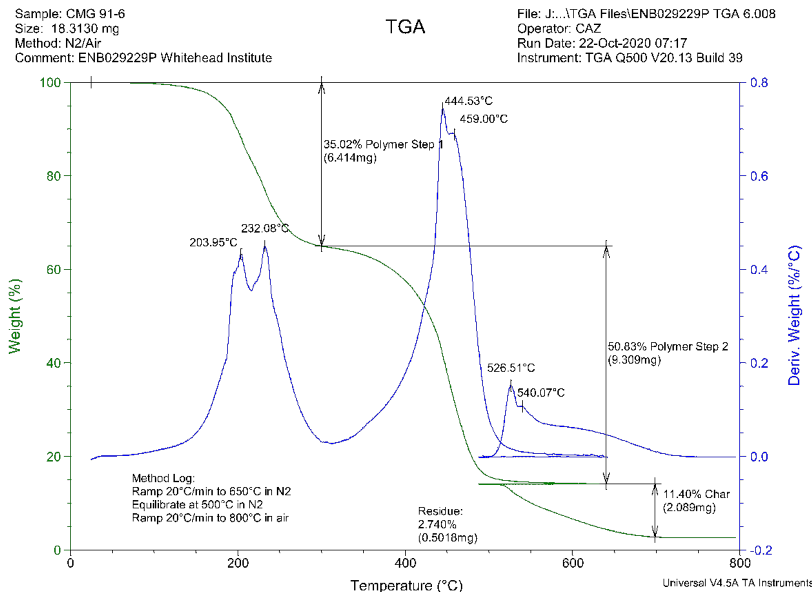

Figure S49. The TGA thermogram for synthetic sporopollenin analogue **11**

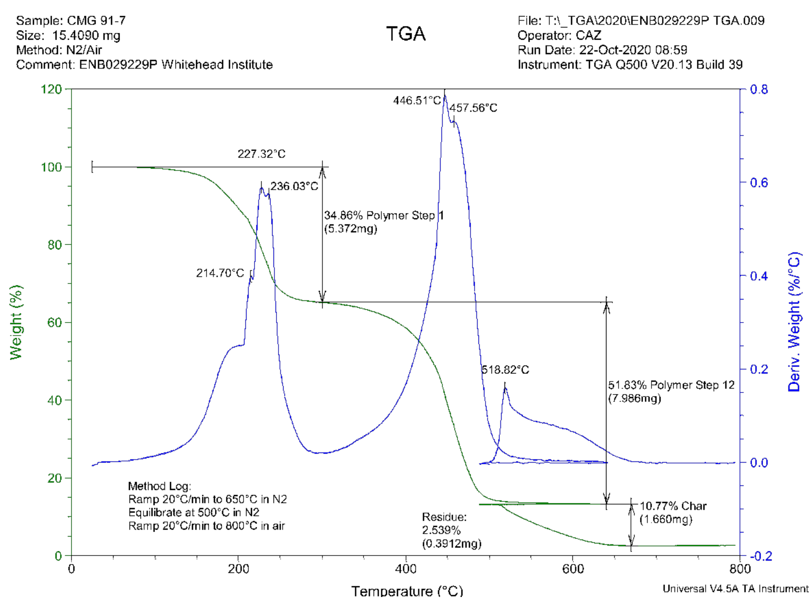

Figure S50. The TGA thermogram for synthetic sporopollenin analogue **12**

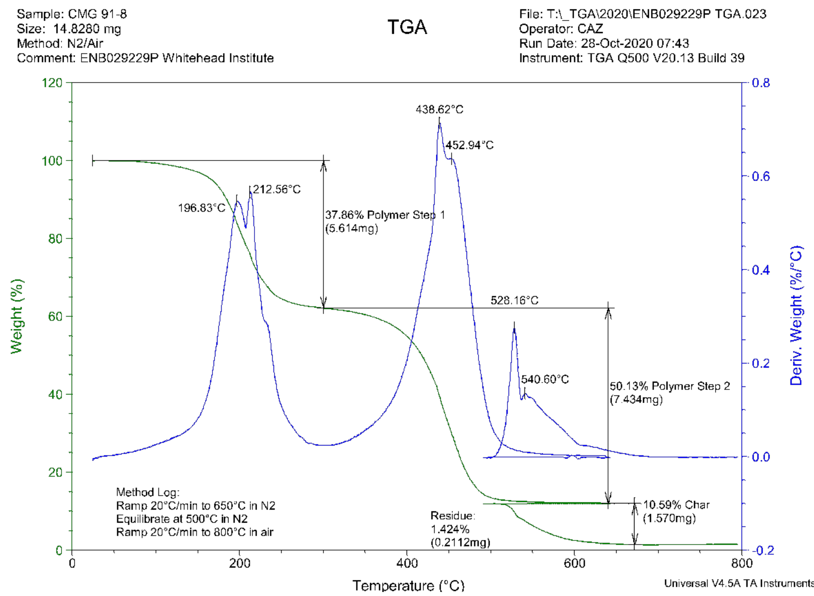

Figure S51. The TGA thermogram for synthetic sporopollenin analogue **13**

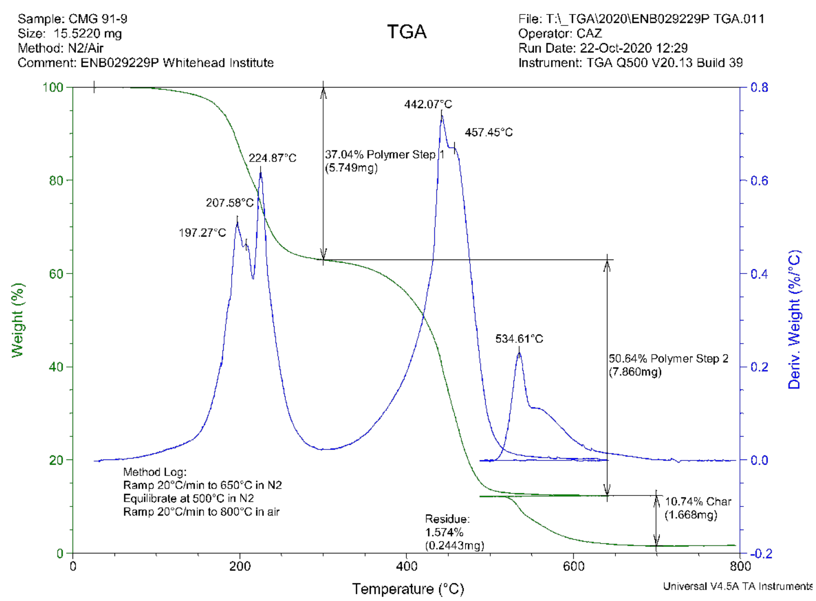

Figure S52. The TGA thermogram for synthetic sporopollenin analogue **14**

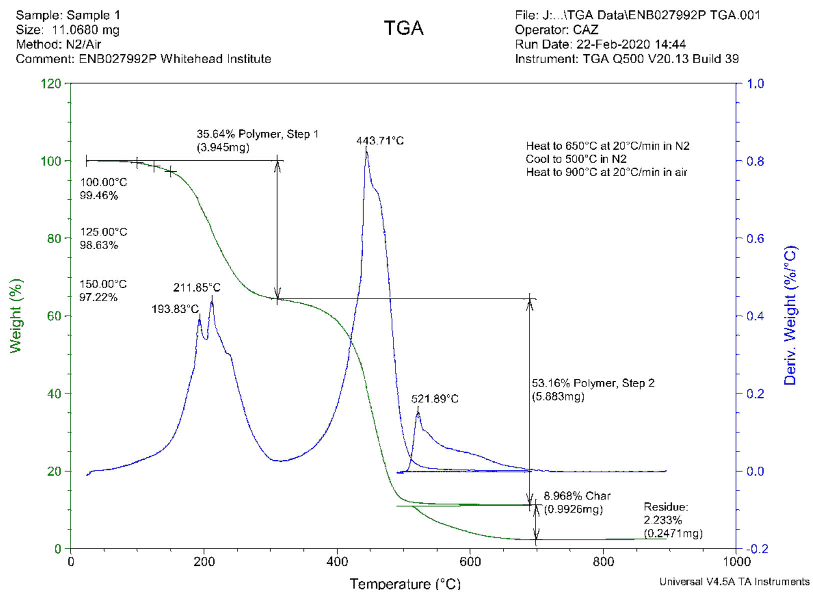

Figure S53. The TGA thermogram for synthetic sporopollenin analogue **15**

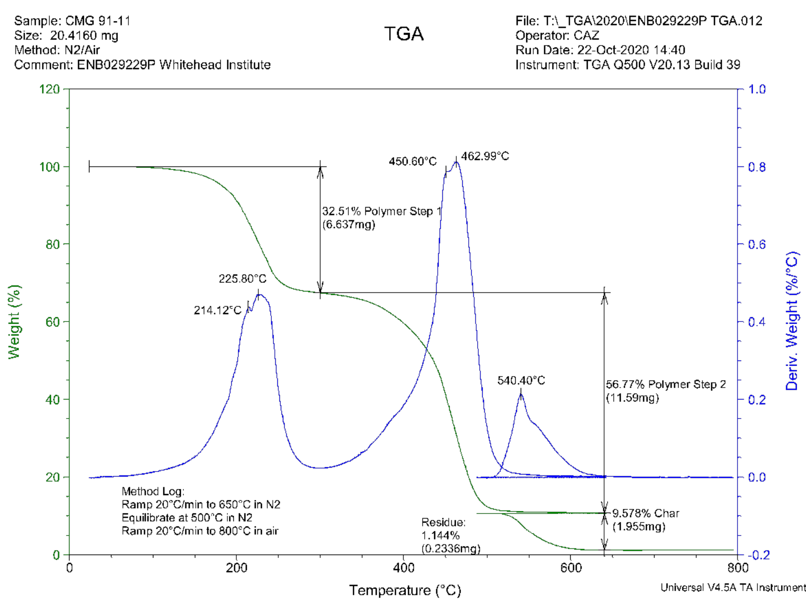

Figure S54. The TGA thermogram for synthetic sporopollenin analogue **16**

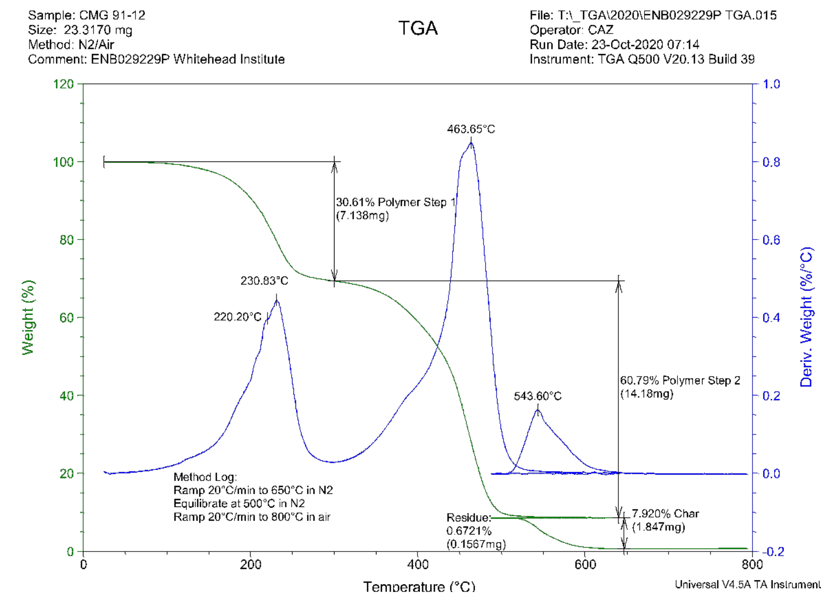

Figure S55. The TGA thermogram for synthetic sporopollenin analogue **17**

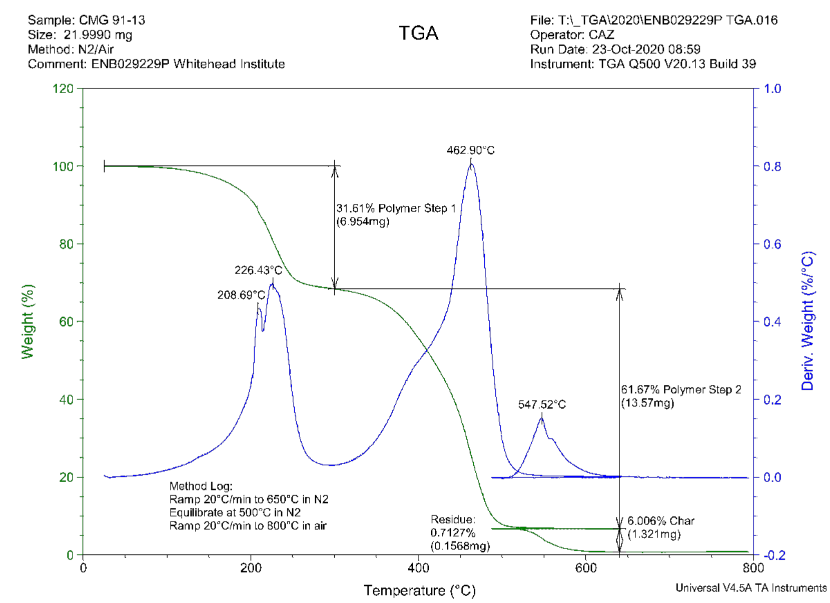

Figure S56. The TGA thermogram for synthetic sporopollenin analogue **18**

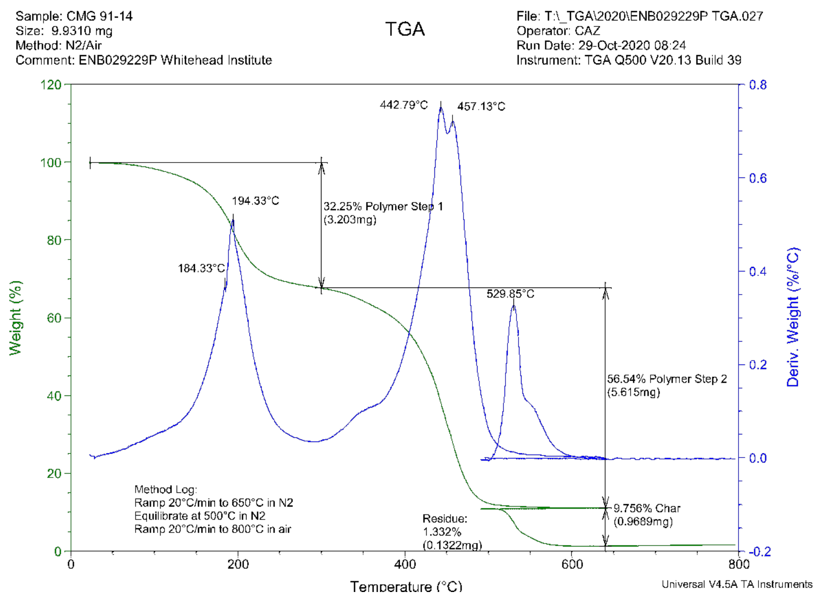

Figure S57. The TGA thermogram for synthetic sporopollenin analogue **26**

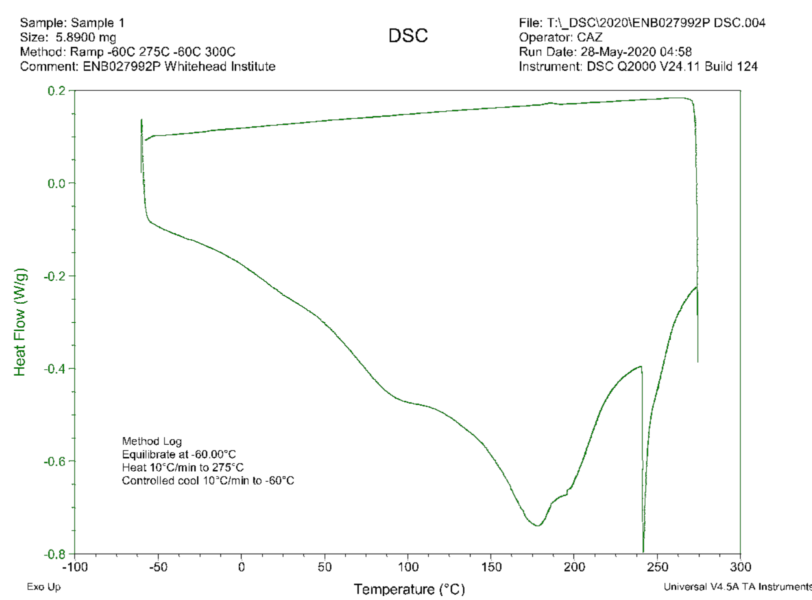

Figure S58. The DSC thermogram for synthetic sporopollenin analogue **15**, first replicate

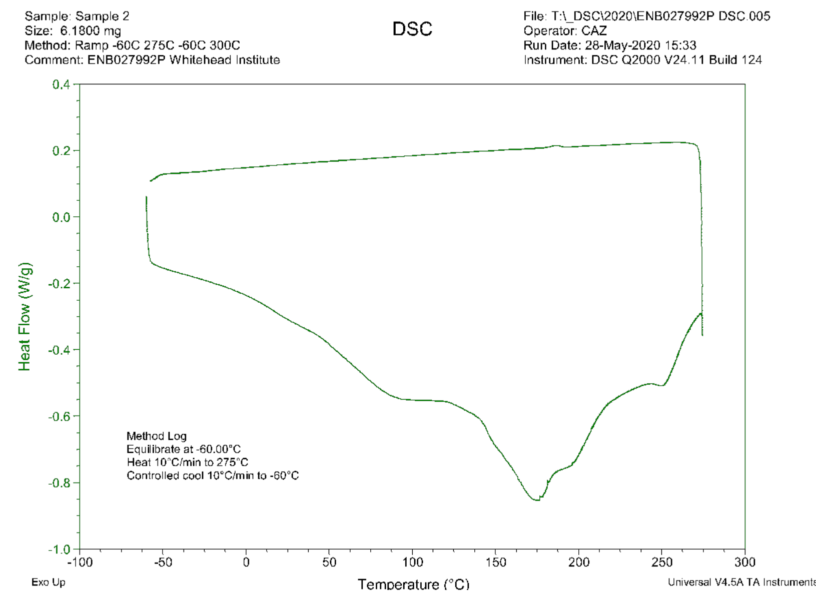

Figure S59. The DSC thermogram for synthetic sporopollenin analogue **15**, second replicate

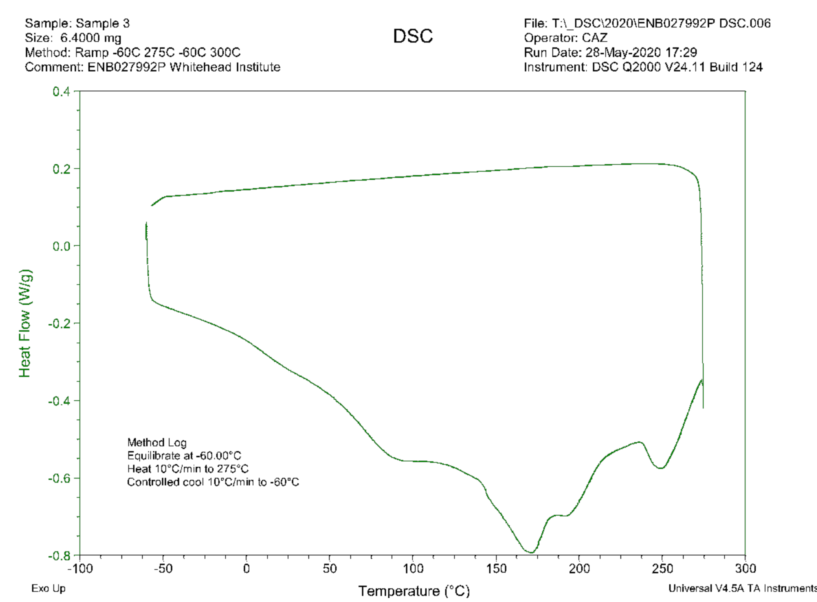

Figure S60. The DSC thermogram for synthetic sporopollenin analogue **15**, third replicate

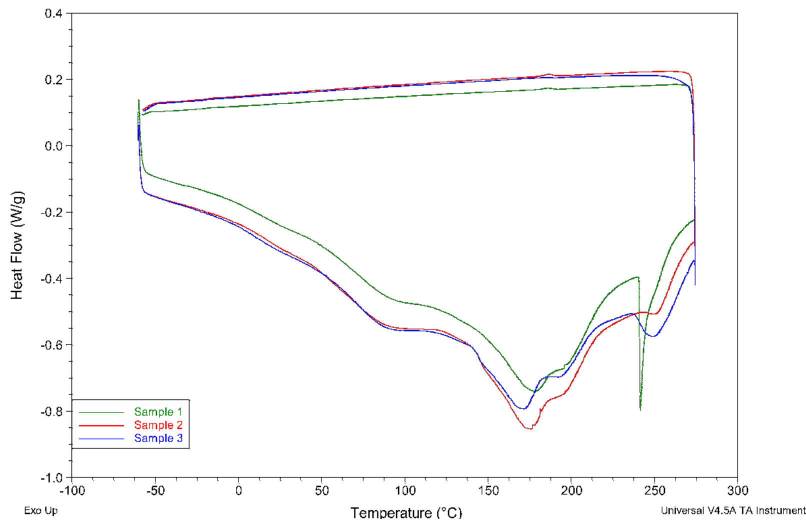

Figure S61. The DSC thermogram for synthetic sporopollenin analogue **15**, all replicates

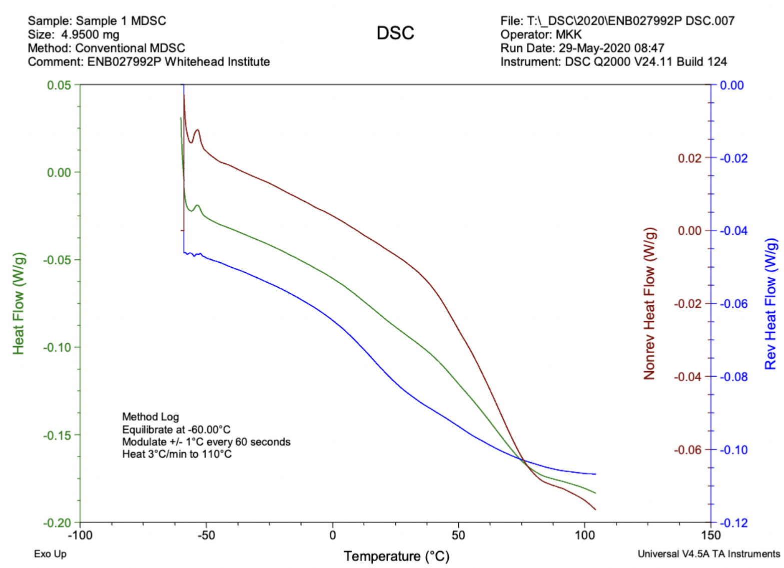

Figure S62. The modulated DSC thermogram for synthetic sporopollenin analogue **15**