

Functionalizing natural polymers with alkoxysilane coupling agents: Reacting 3- glycidoxypipropyl trimethoxysilane with poly(γ -glutamic acid) and gelatin

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Supporting Information

1. Additional ^1H and ^{13}C NMR experiments.

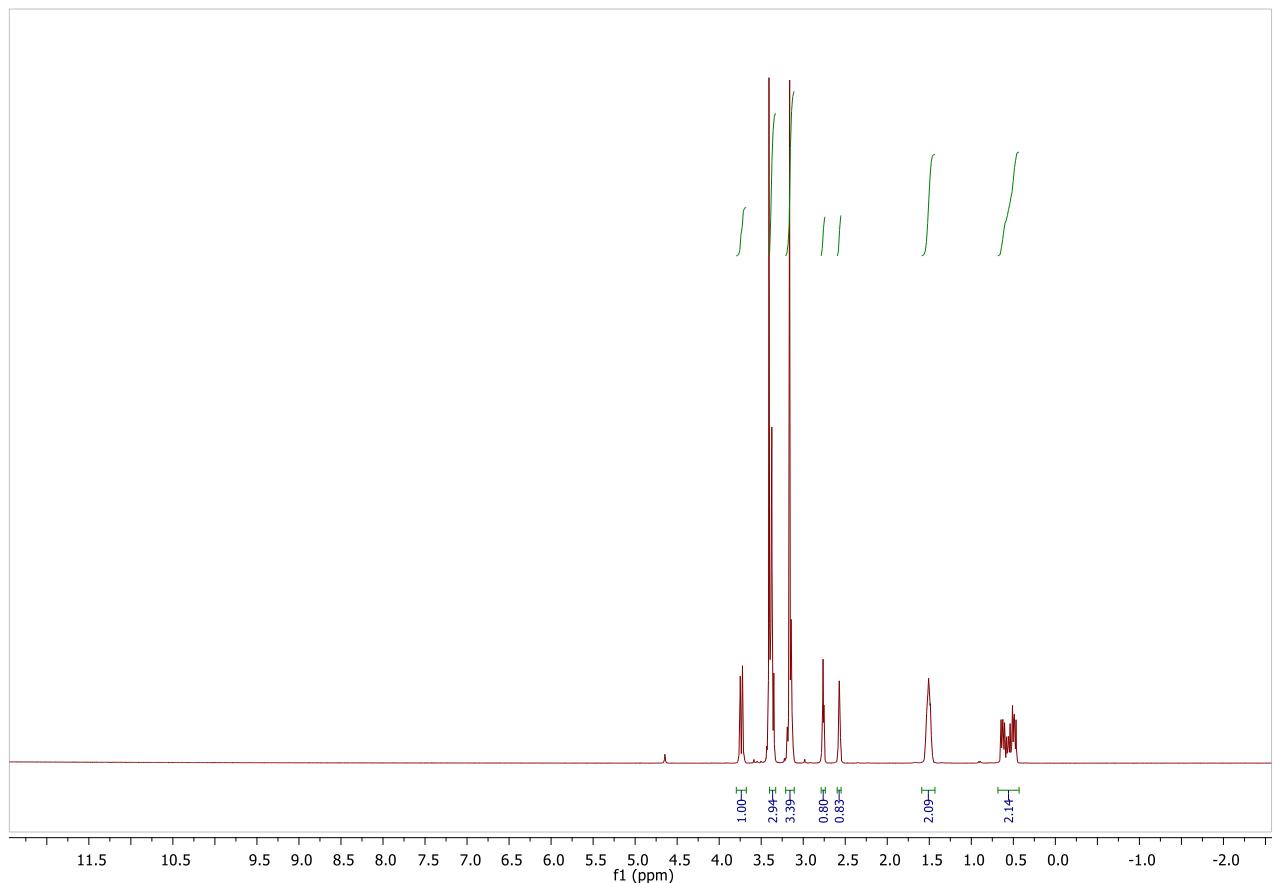


Figure S1. ^1H -NMR of GPTMS (D_2O pH 7).

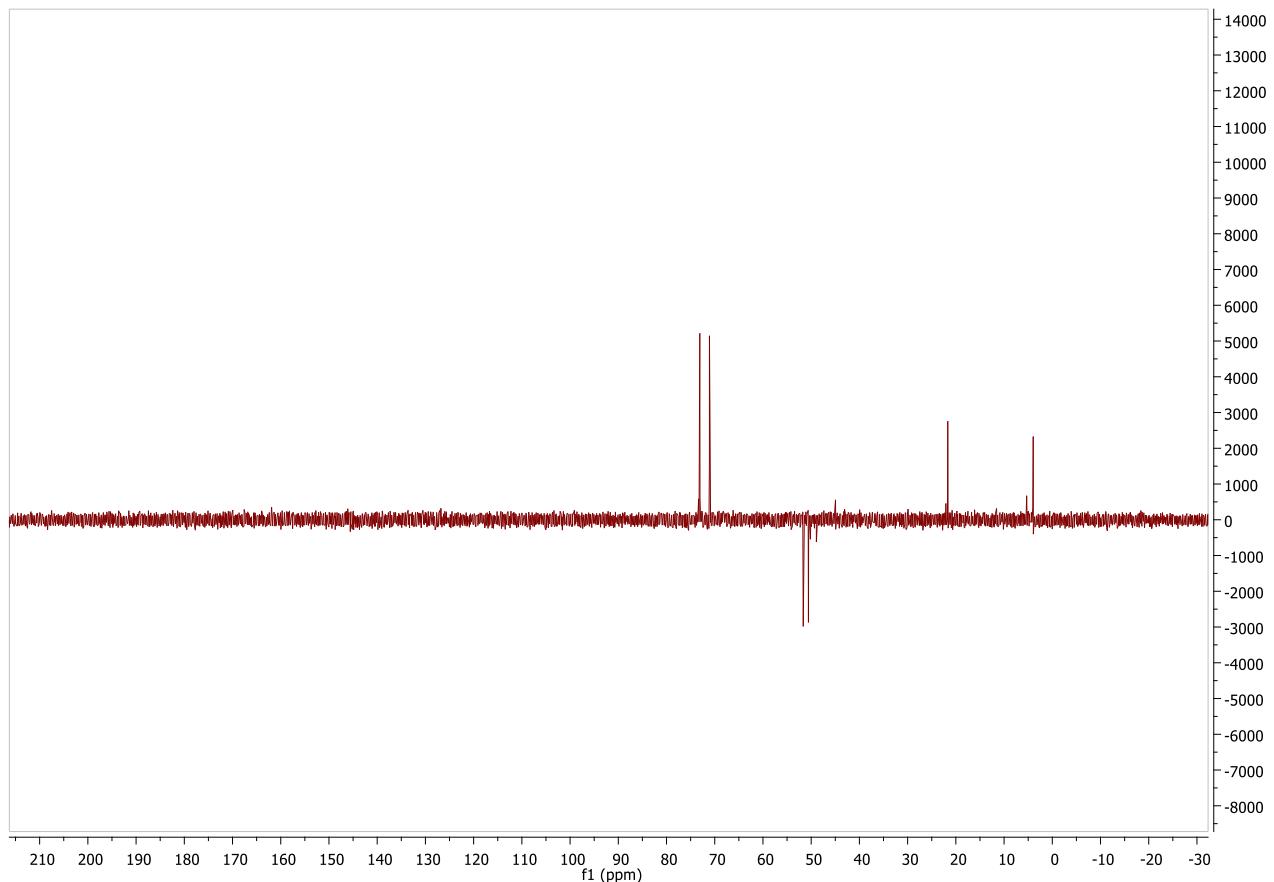


Figure S2. ^{13}C -NMR of GPTMS (D_2O pH 7).

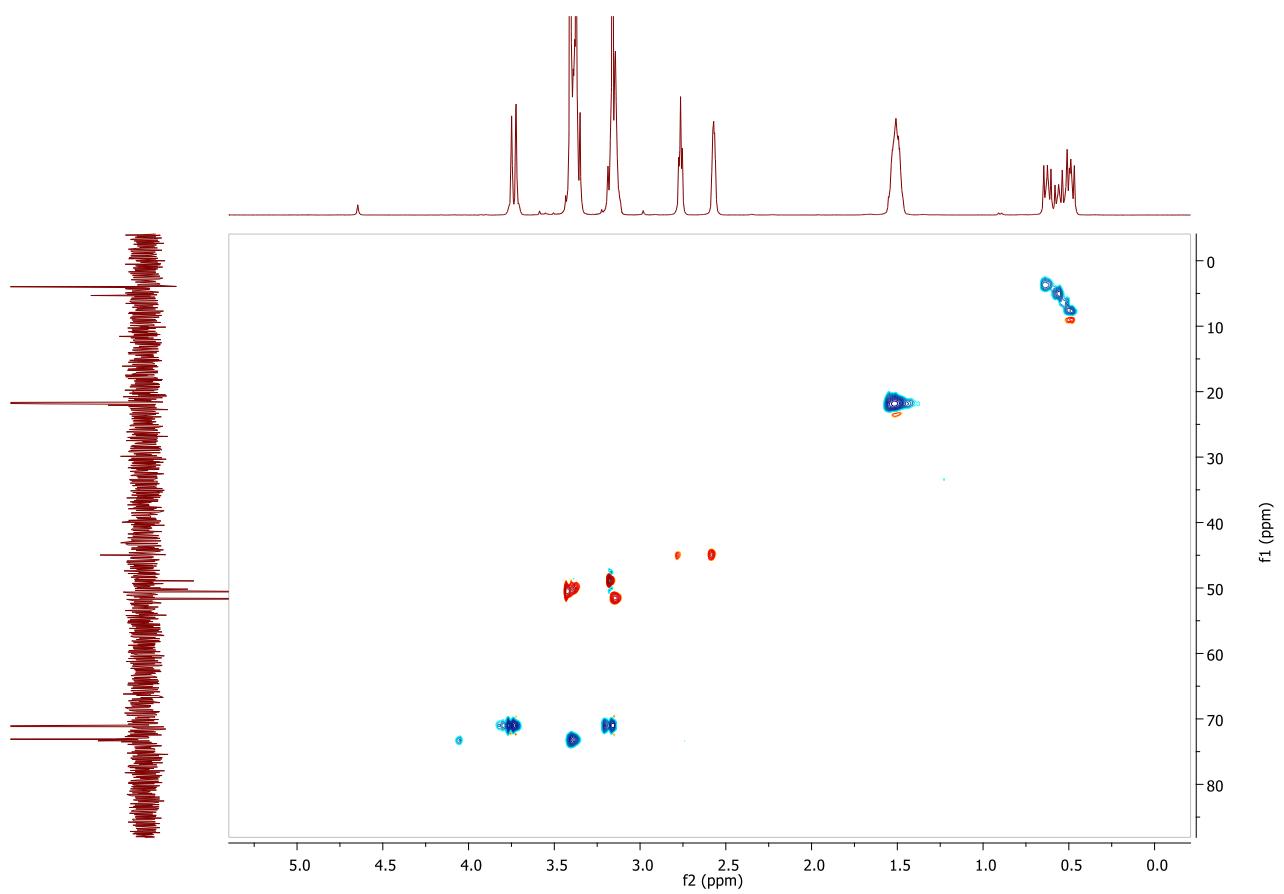


Figure S3. HSQC spectrum of GPTMS (D_2O pH 7).

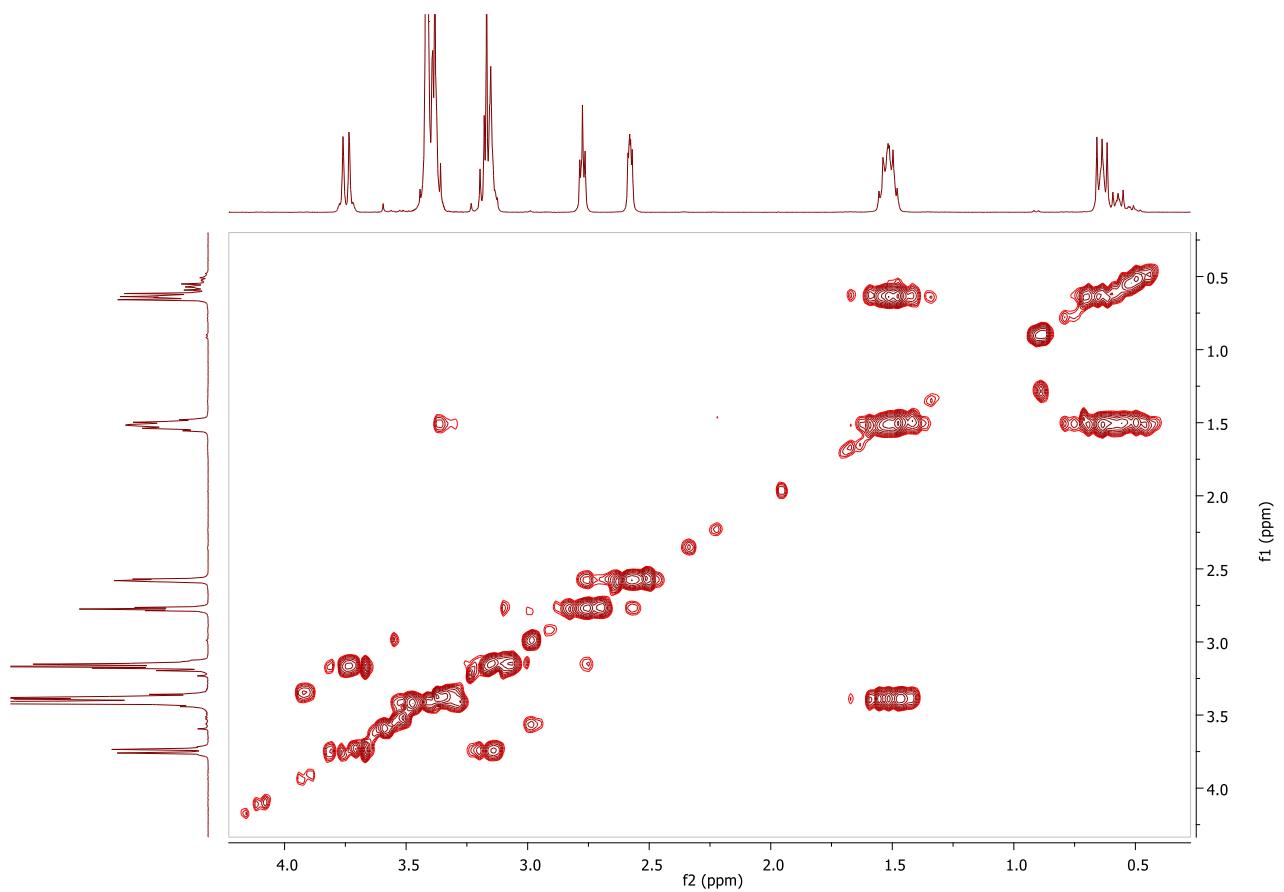


Figure S4. COSY spectrum of GPTMS (D_2O pH 7).

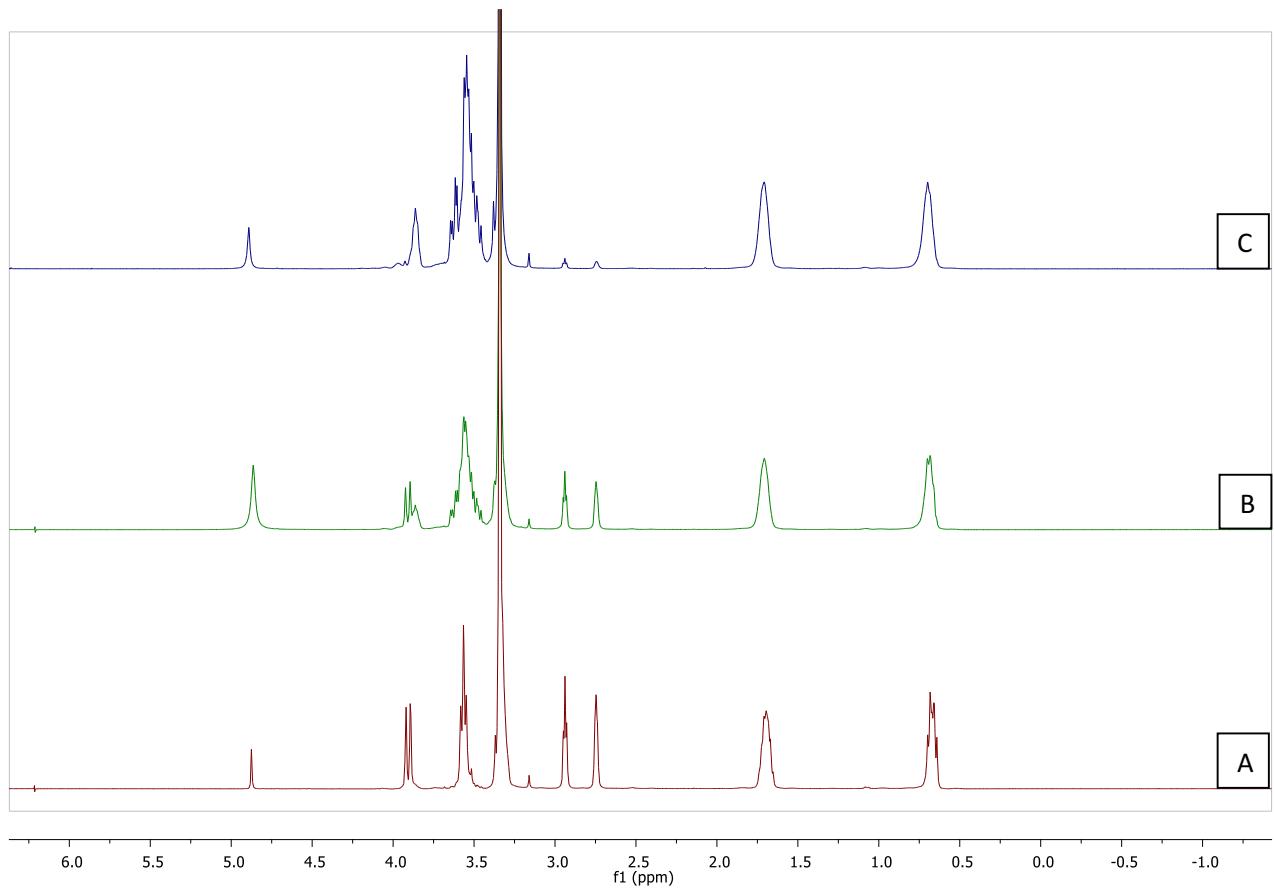


Figure S5. ¹H-NMR comparison between GPTMS at pH 7 (**A**), at pH 2 for 100 h (25°C, **B**) and at pH 2 for 1 month (25°C, **C**).

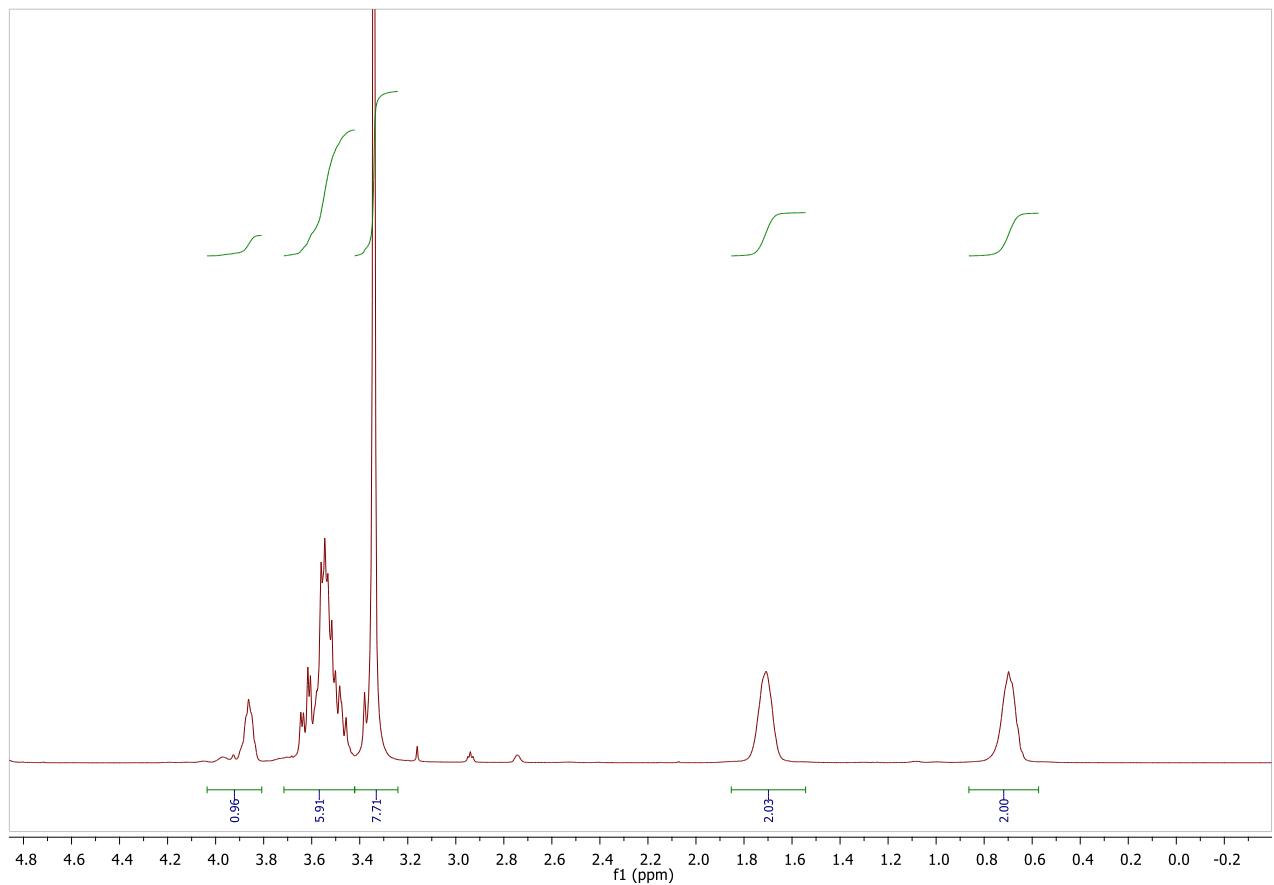


Figure S6. ¹H-NMR of hydrolyzed GPTMS (1 month at pH 2).

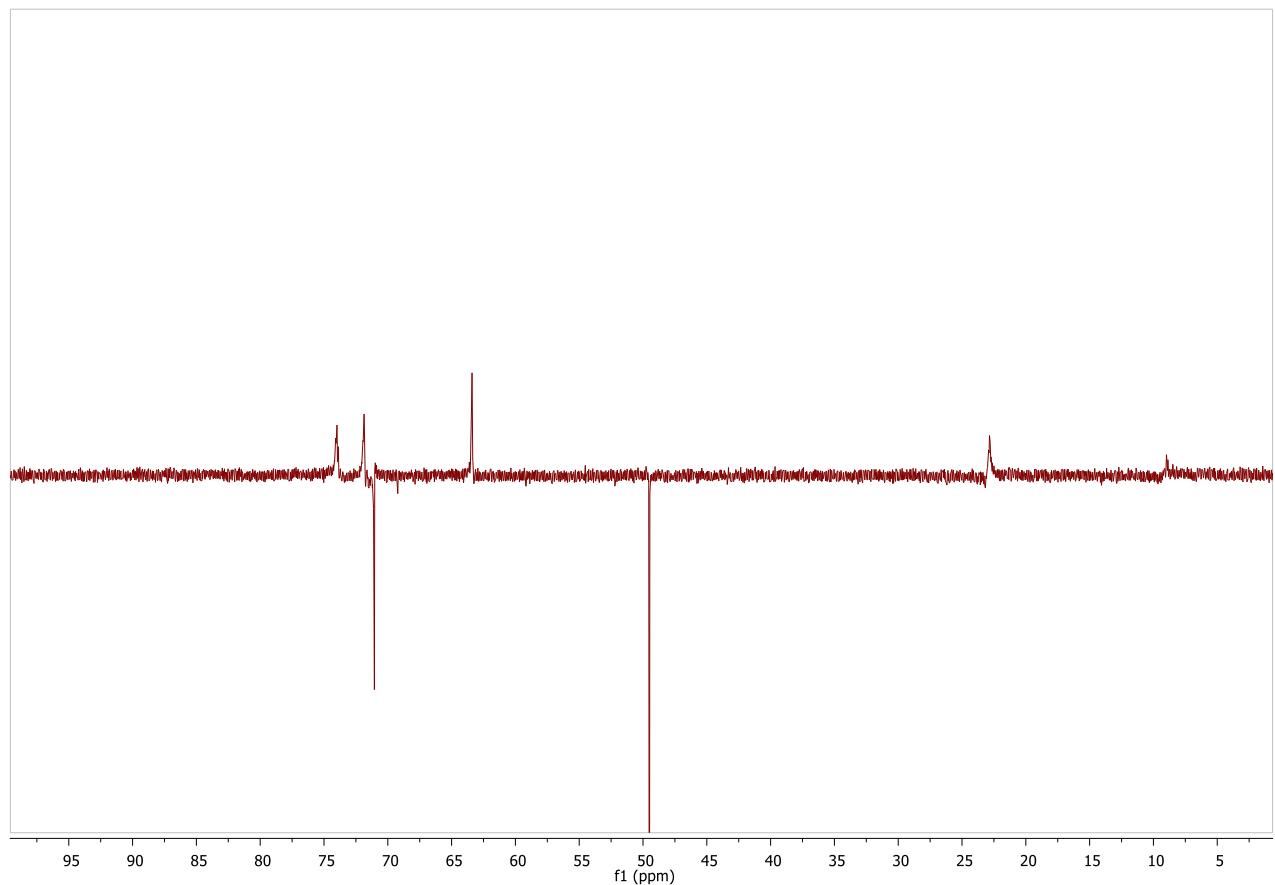


Figure S7. ¹³C-NMR of hydrolyzed GPTMS (1 month at pH 2).

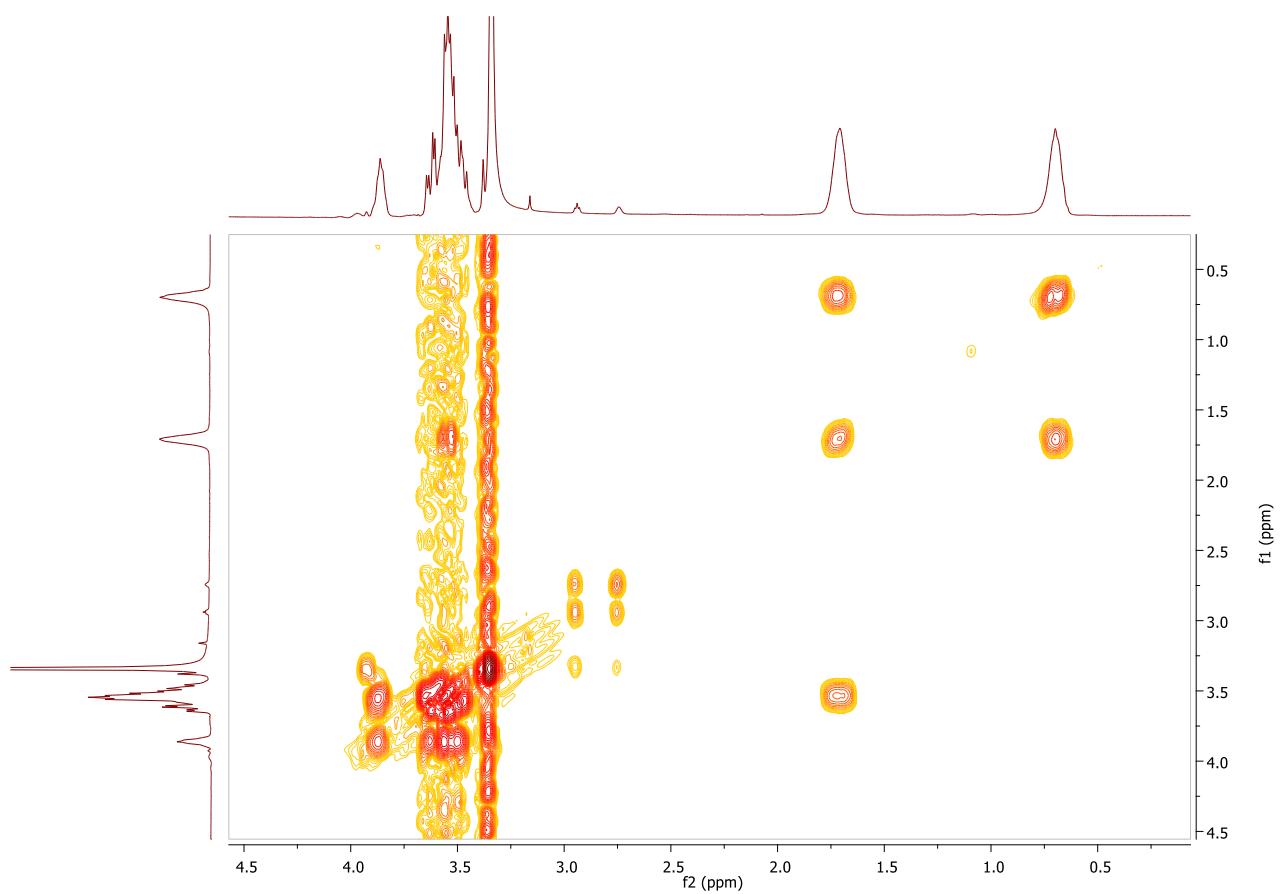


Figure S8. COSY spectra of hydrolyzed GPTMS (1 month at pH 2).

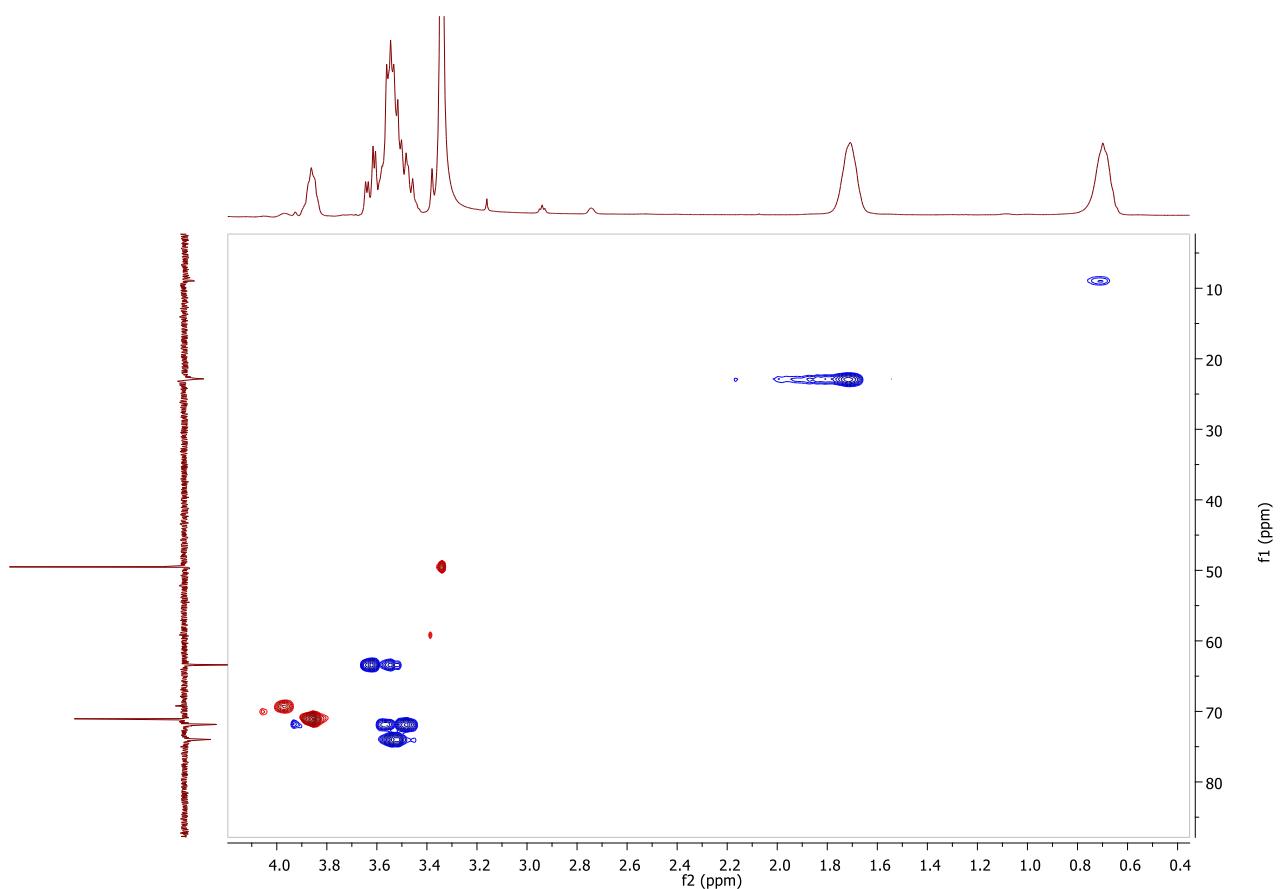


Figure S9. HSQC spectra of hydrolyzed GPTMS (1 month at pH 2).

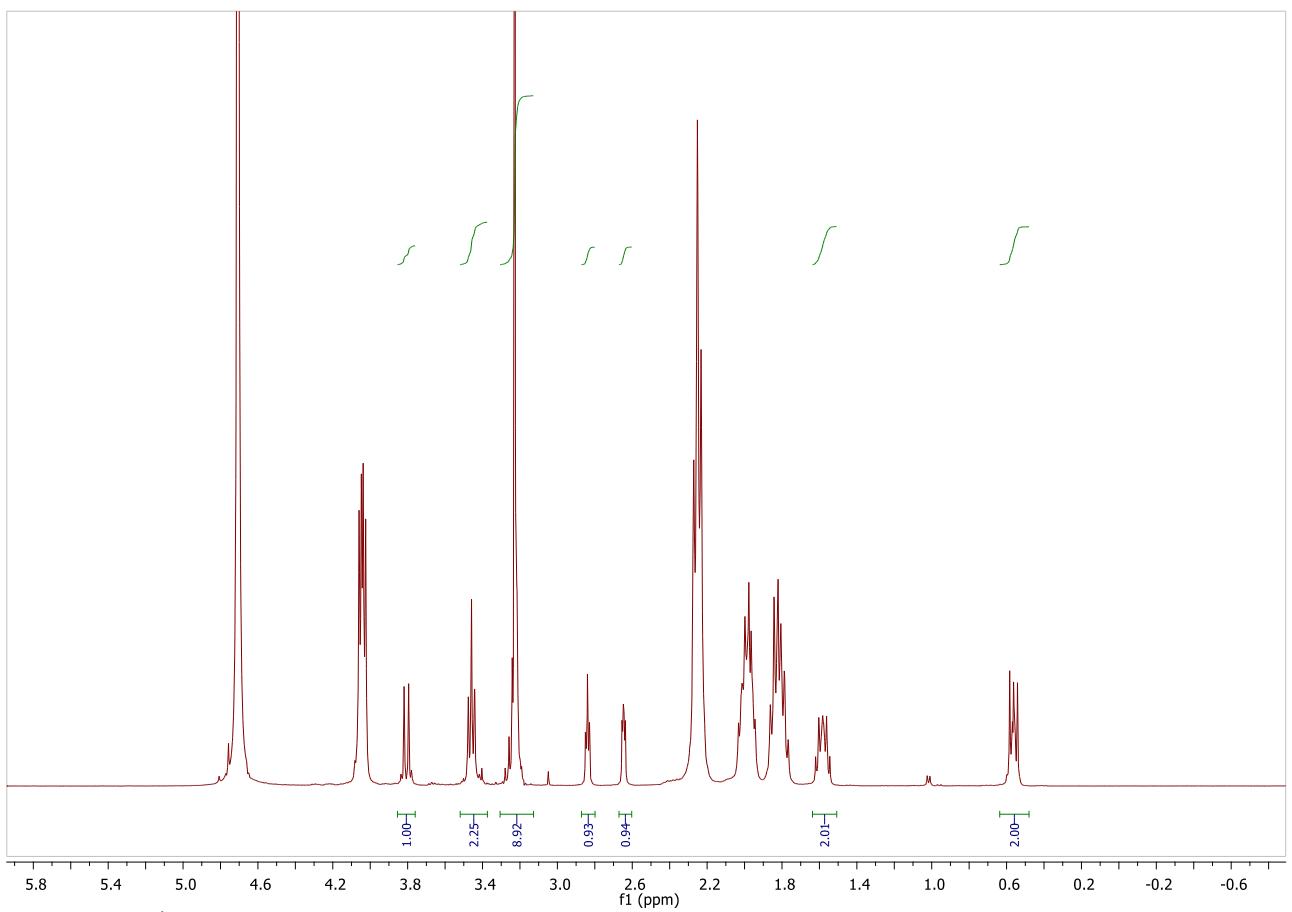


Figure S10. ¹H-NMR of the reaction PGA/GPTMS (12 h 40°C).

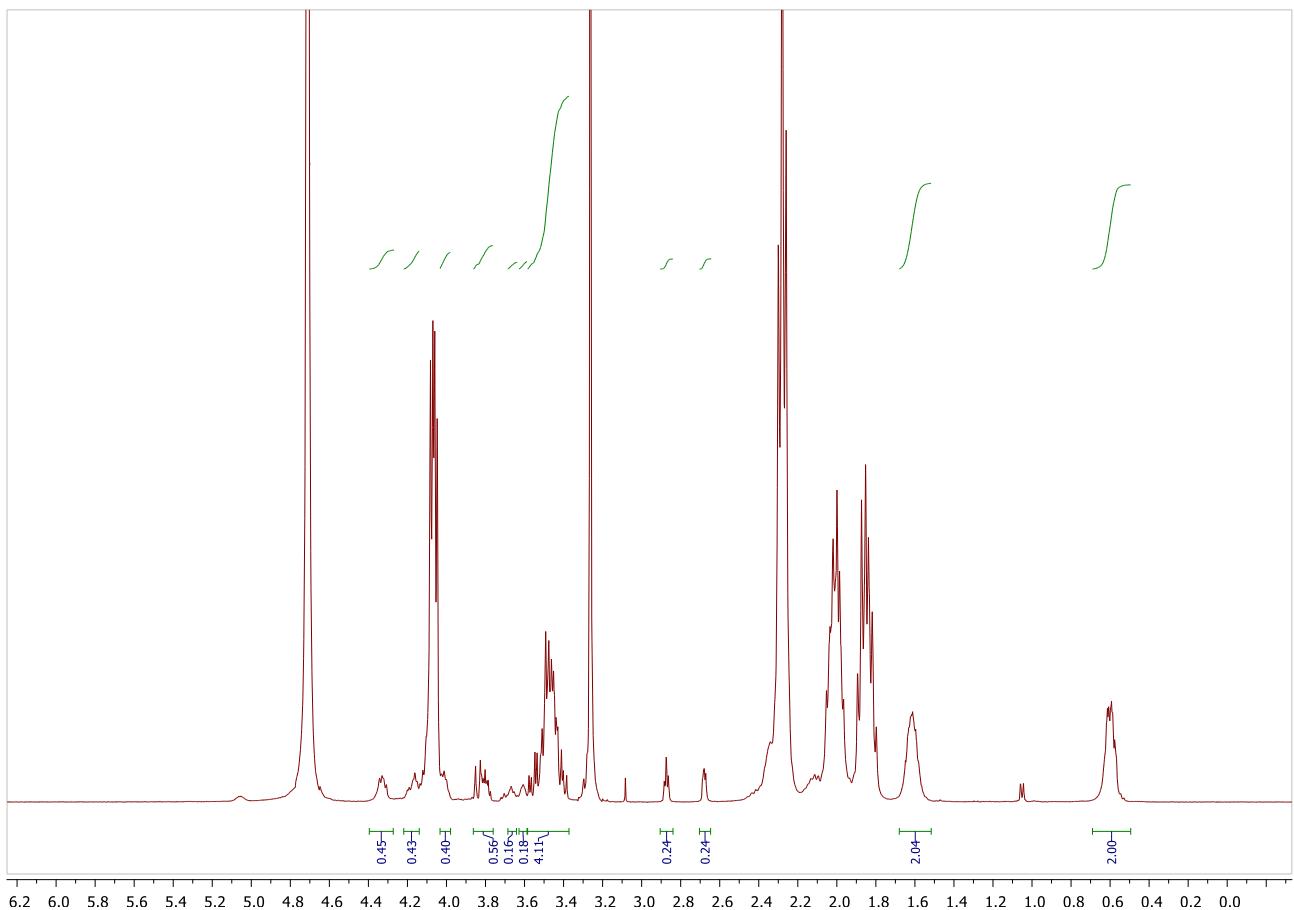


Figure S11. ¹H-NMR of the reaction PGA/GPTMS (96 h 40°C).

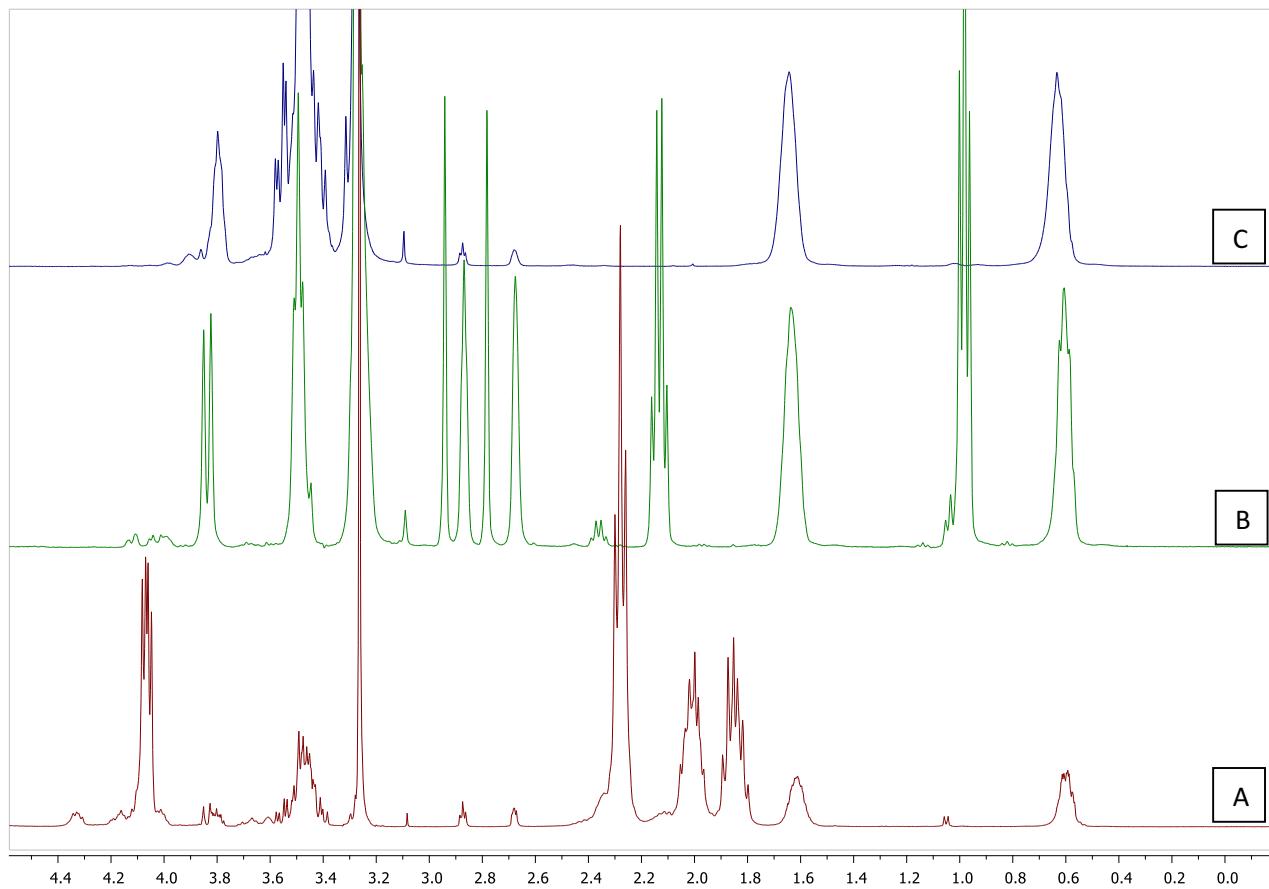


Figure S12. ¹H-NMR comparison between reaction PGA/GPTMS at 40°C for 96 h (**A**), Propanoic Acid/GPTMS¹ at 40°C for 24 h (**B**) and at pH 2 for 1 month (25°C, **C**).

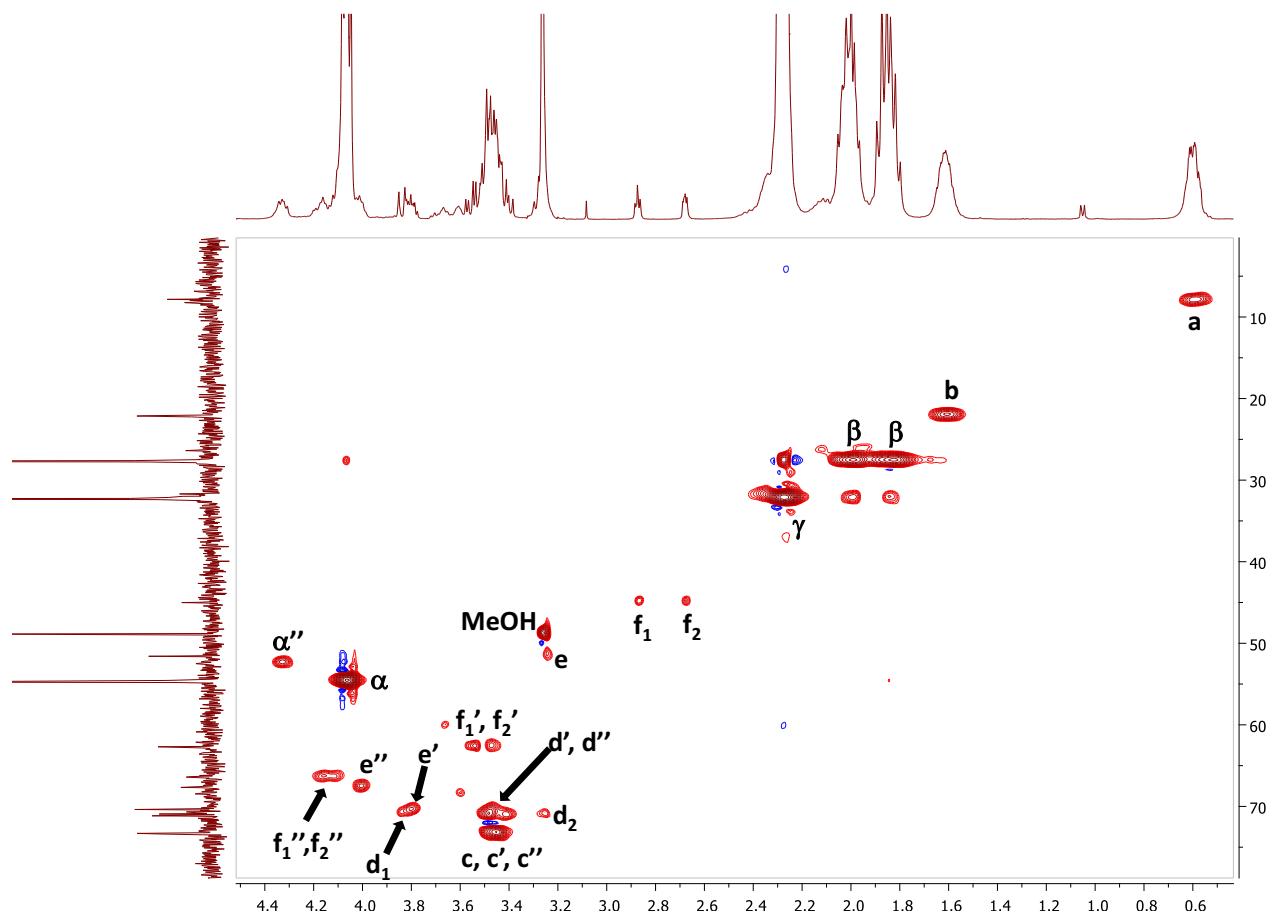


Figure S13. HSQC of reaction PGA/GPTMS at 40°C for 96 h.

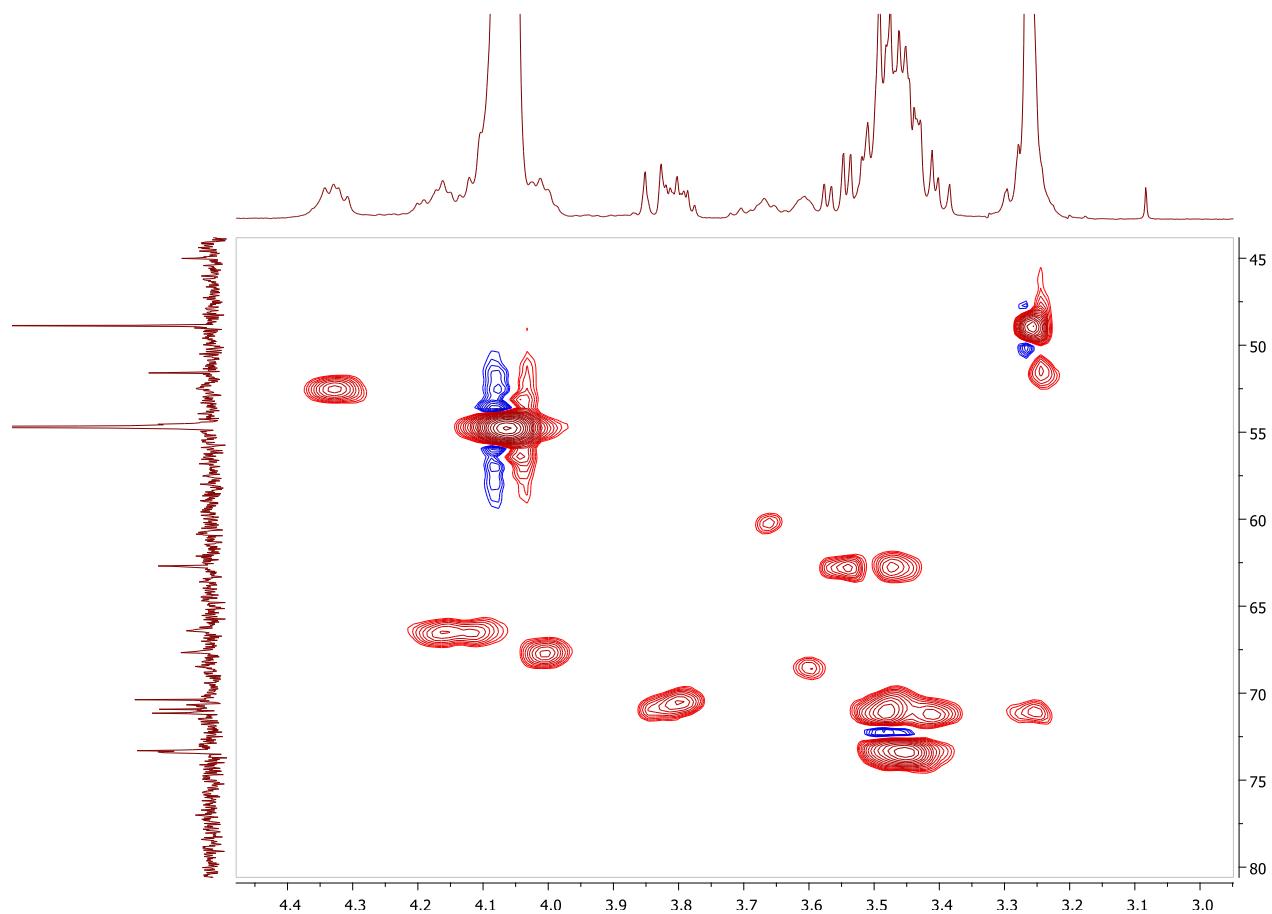


Figure S14. HSQC of reaction PGA/GPTMS at 40°C for 96 h (Zoom).

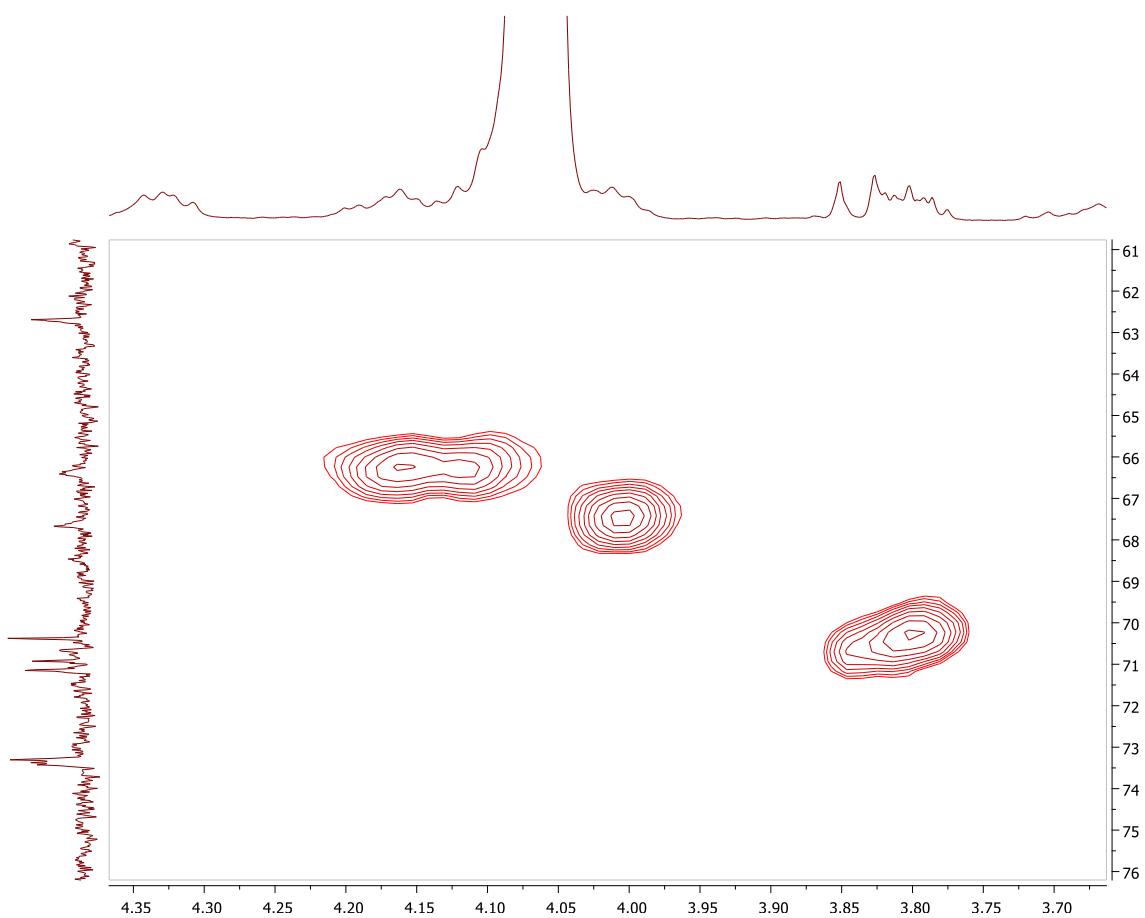


Figure S15. HSQC of reaction PGA/GPTMS at 40°C for 96 h (Zoom).

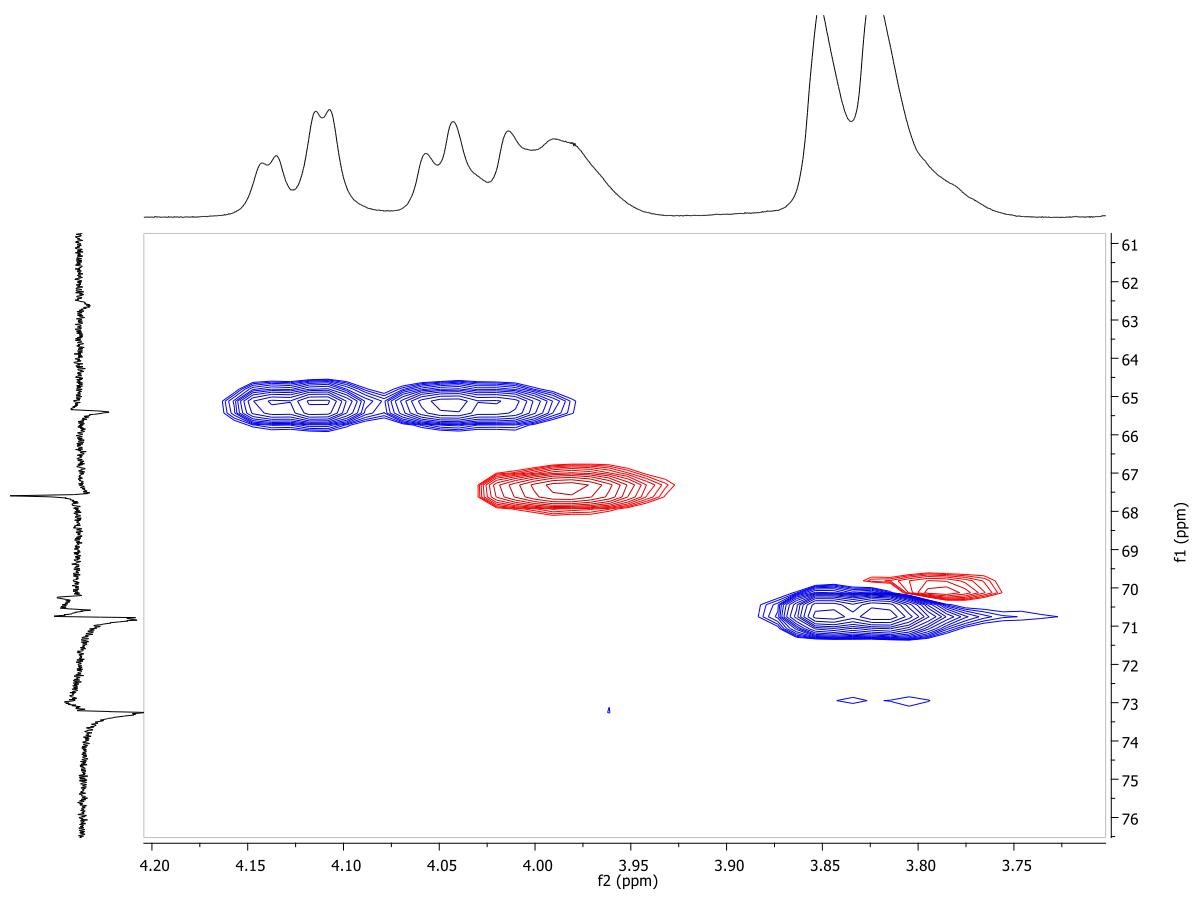


Figure S16. HSQC of reaction propanoic acid/GPTMS at 40°C for 48 h (Zoom).¹

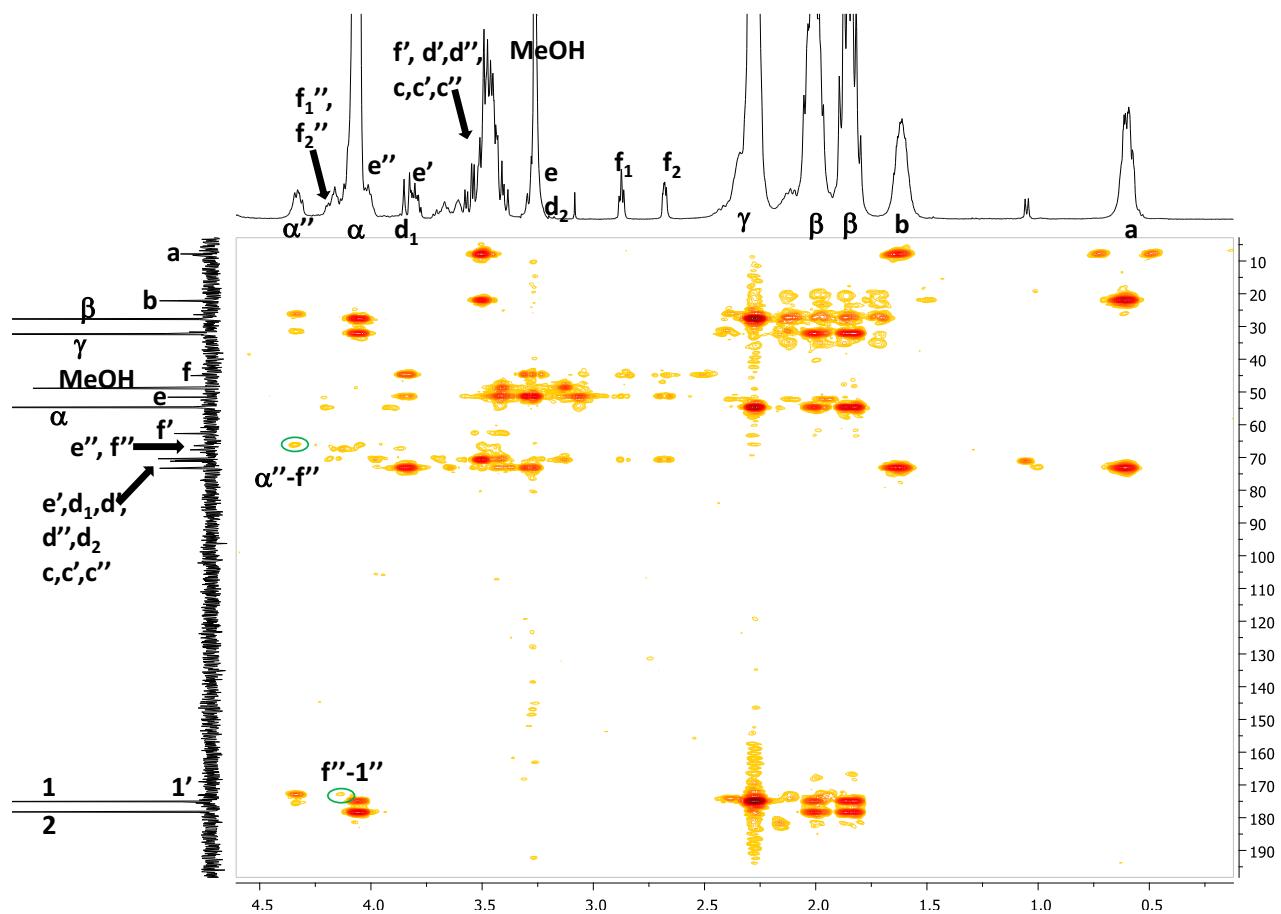


Figure S17. HMBC spectra of reaction PGA/GPTMS at 40°C for 96 h (Zoom).

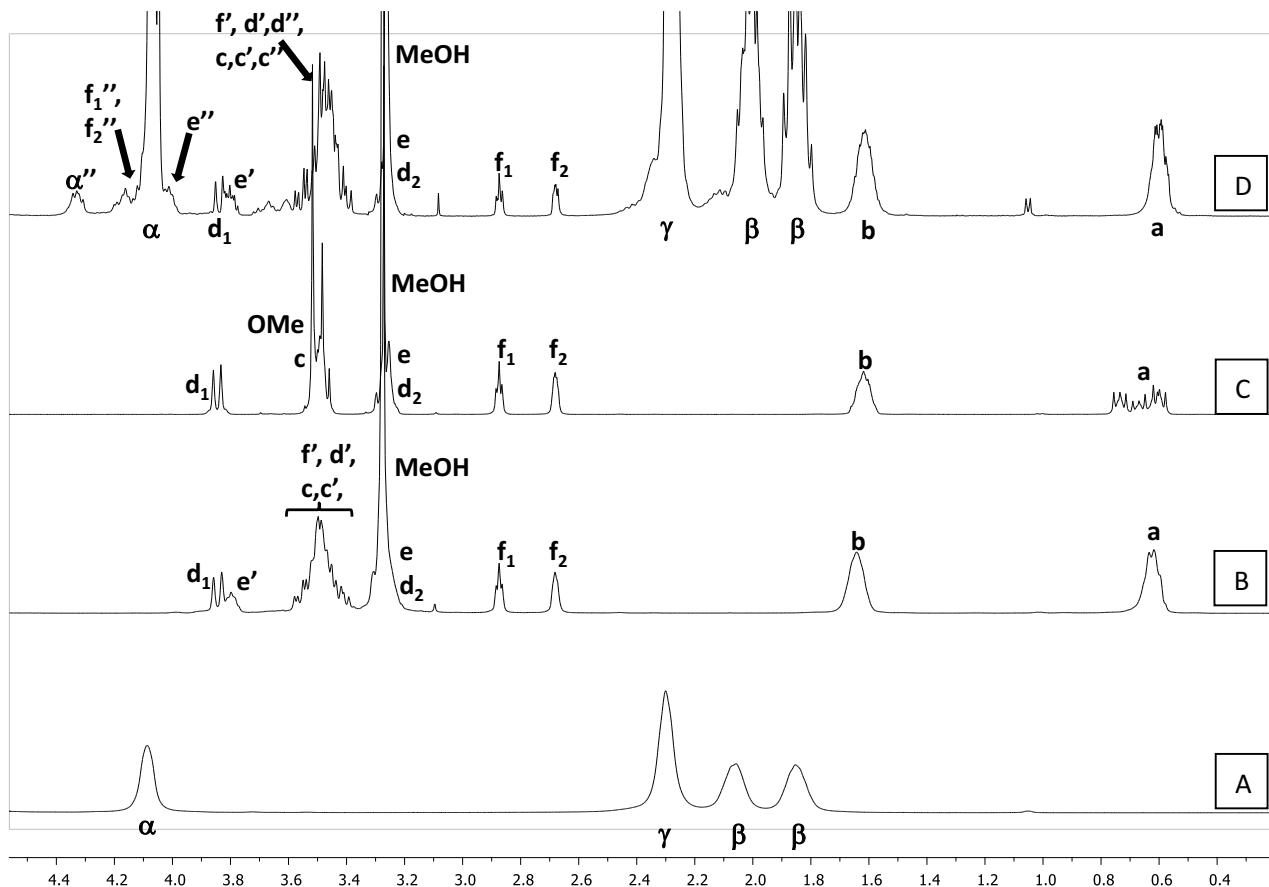


Figure S18. ^1H -NMR of PGA (**A**), GPTMS at pH 2 for 100 h (25°C, **B**), at pH 7 (25°C, **C**) and reaction of PGA/GPTMS (96 h, 40°C, **D**) in D_2O .

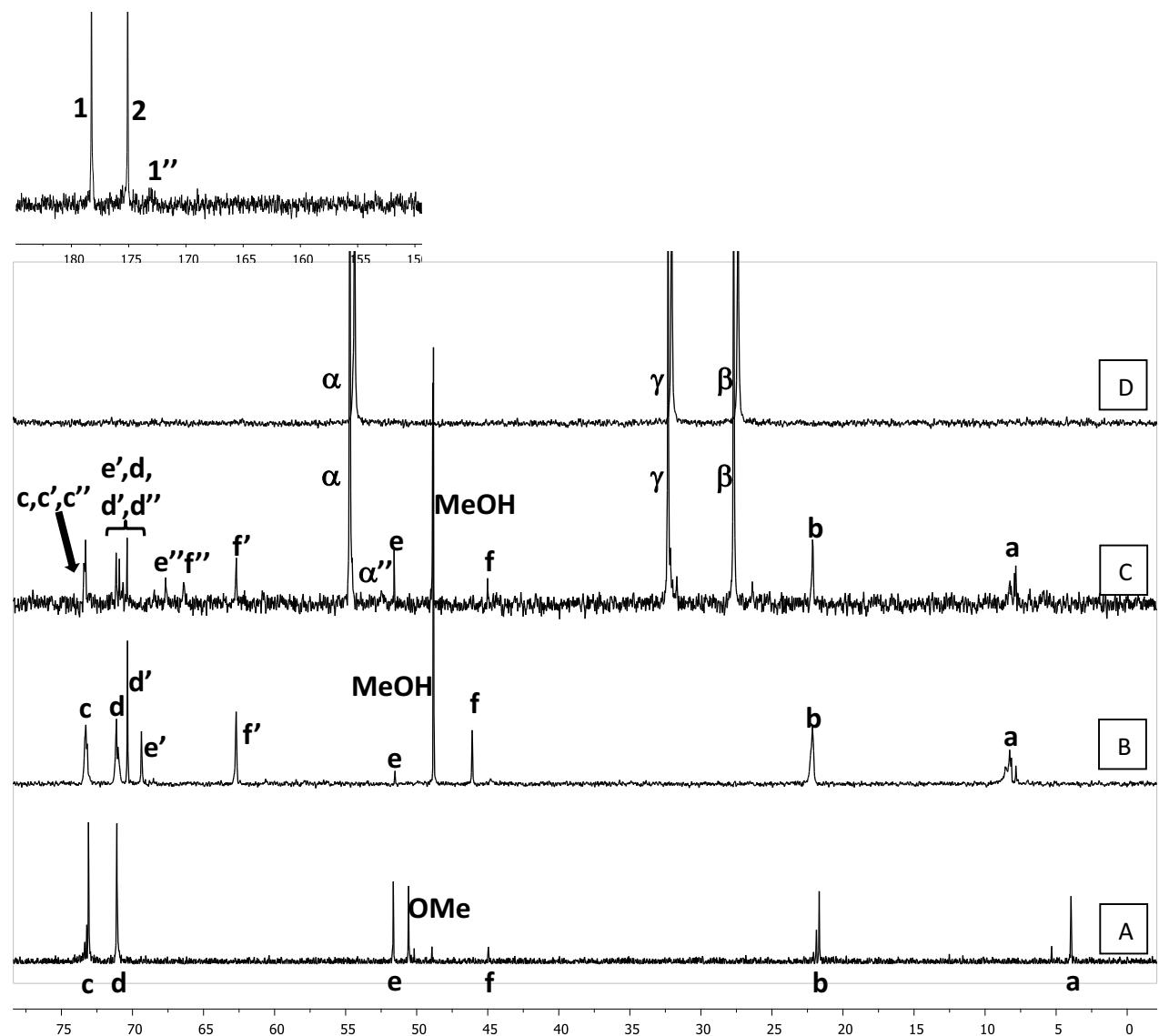


Figure S19. ¹³C-NMR of (A), GPTMS at pH7 (25°C, A), at pH 2 for 100 h (25°C, B), reaction of PGA/GPTMS (96 h, 40°C, C) and PGA (D). Inset: carboxylic signal of spectra PGA/GPTMS (96 h, 40°C, C).

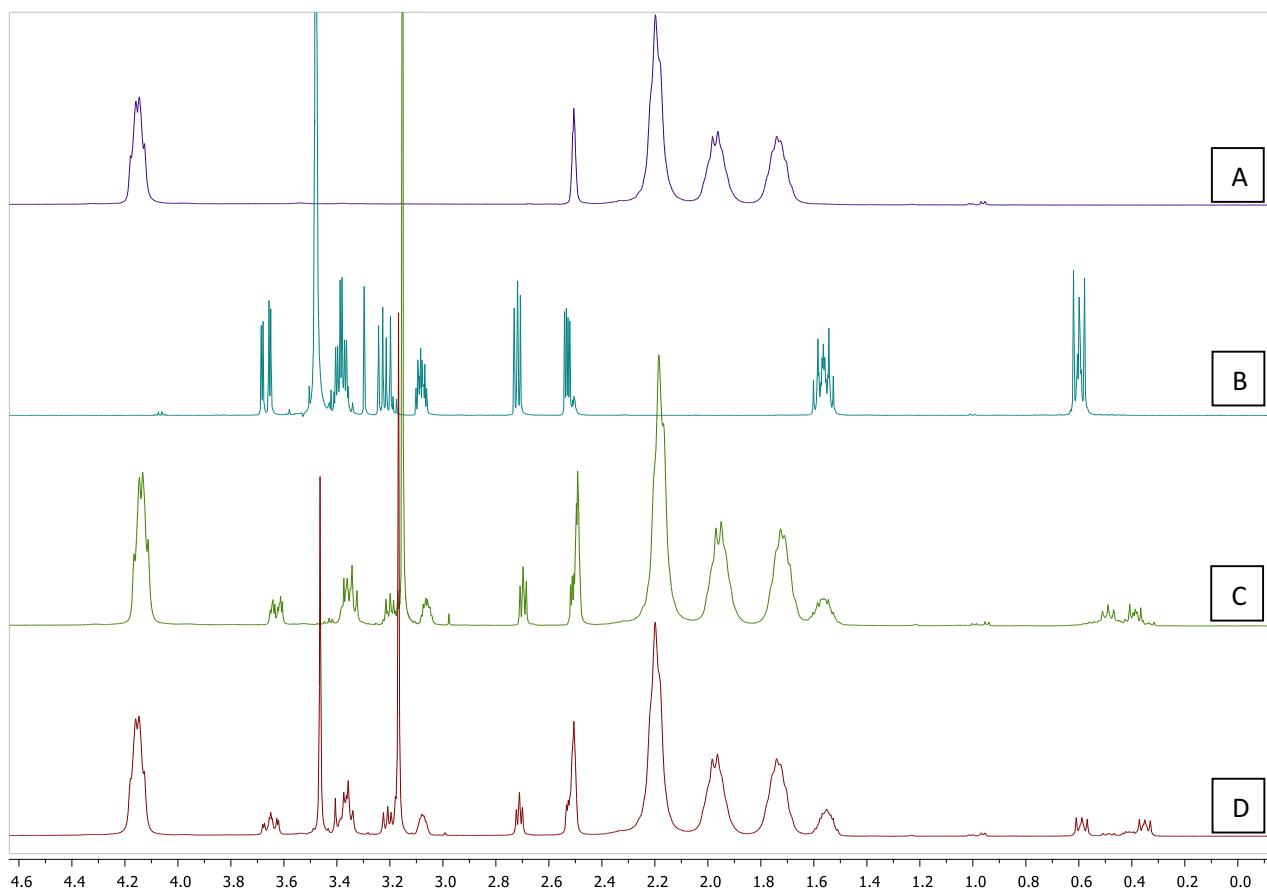


Figure S20. ¹H-NMR of PGA (**A**), GPTMS (25°C, **B**) and reaction of PGA/GPTMS after 24 h (40°C, **C**) and 96 h, (40°C, **D**) in d6-DMSO.

	<i>1H</i>	<i>13C</i>
β_1	1,84	27,6
β_2	1,99	27,6
γ	2,27	32,3
α	4,05	54,5
α''	4,33	52,5
a	0,59	8,0
b	1,61	22,2
f_1	2,87	45,1
f_2	2,67	45,1
e	3,24	51,6
f'	3,47- 3,53	62,8
d_1	3,84	71,0
d_2	3,25	71,0
f_1''	4,16	66,5
f_2''	4,12	66,5
e''	4,00	67,7
$d', d'', c, c',$ c''	3,54- 3,36	70,9- 73,4

Table S1. Reaction between PGA and GPTMS: summary of the characteristic ^1H ^{13}C -NMR signals.

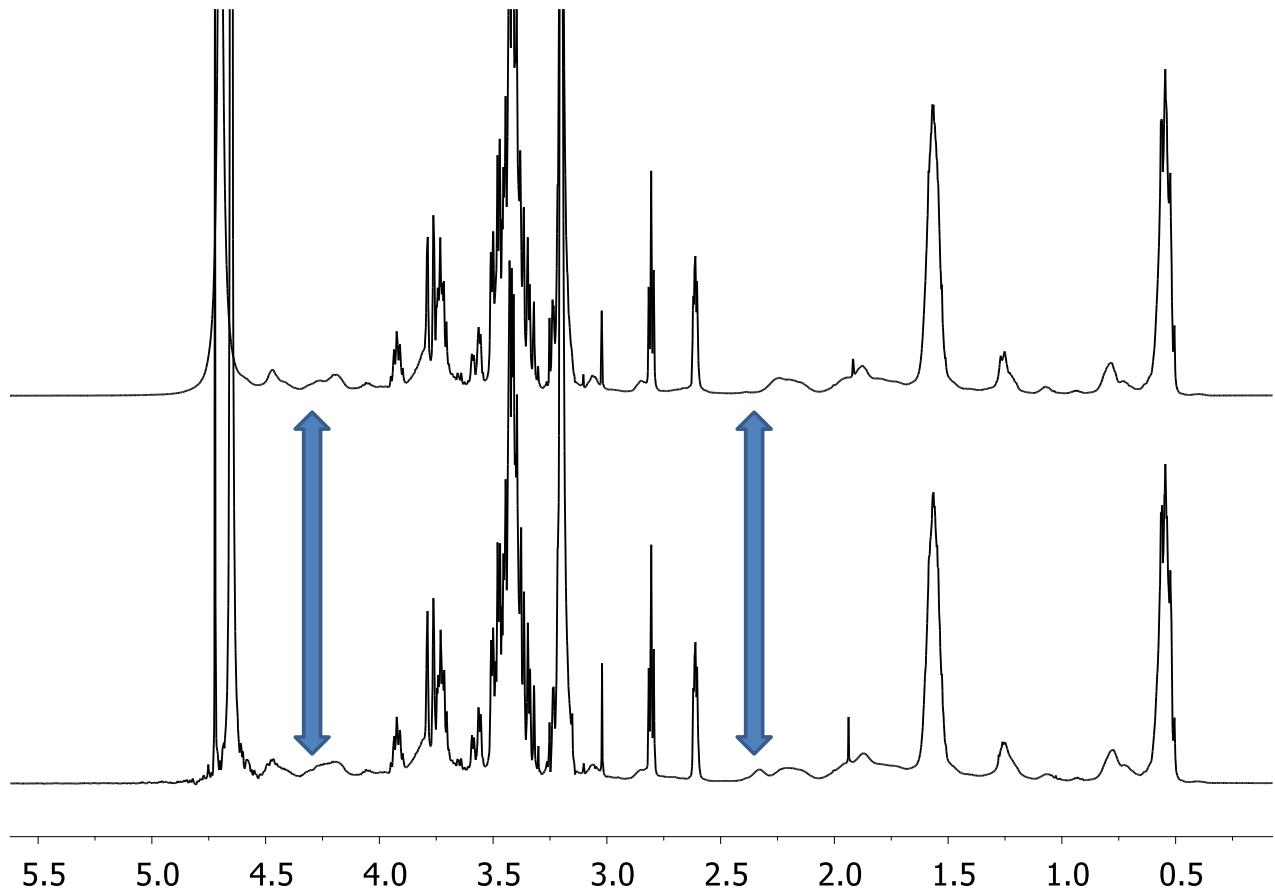


Figure S21. Reaction gelatin/GPTMS after 24 h (top) and 48 h (bottom) at pH 5.

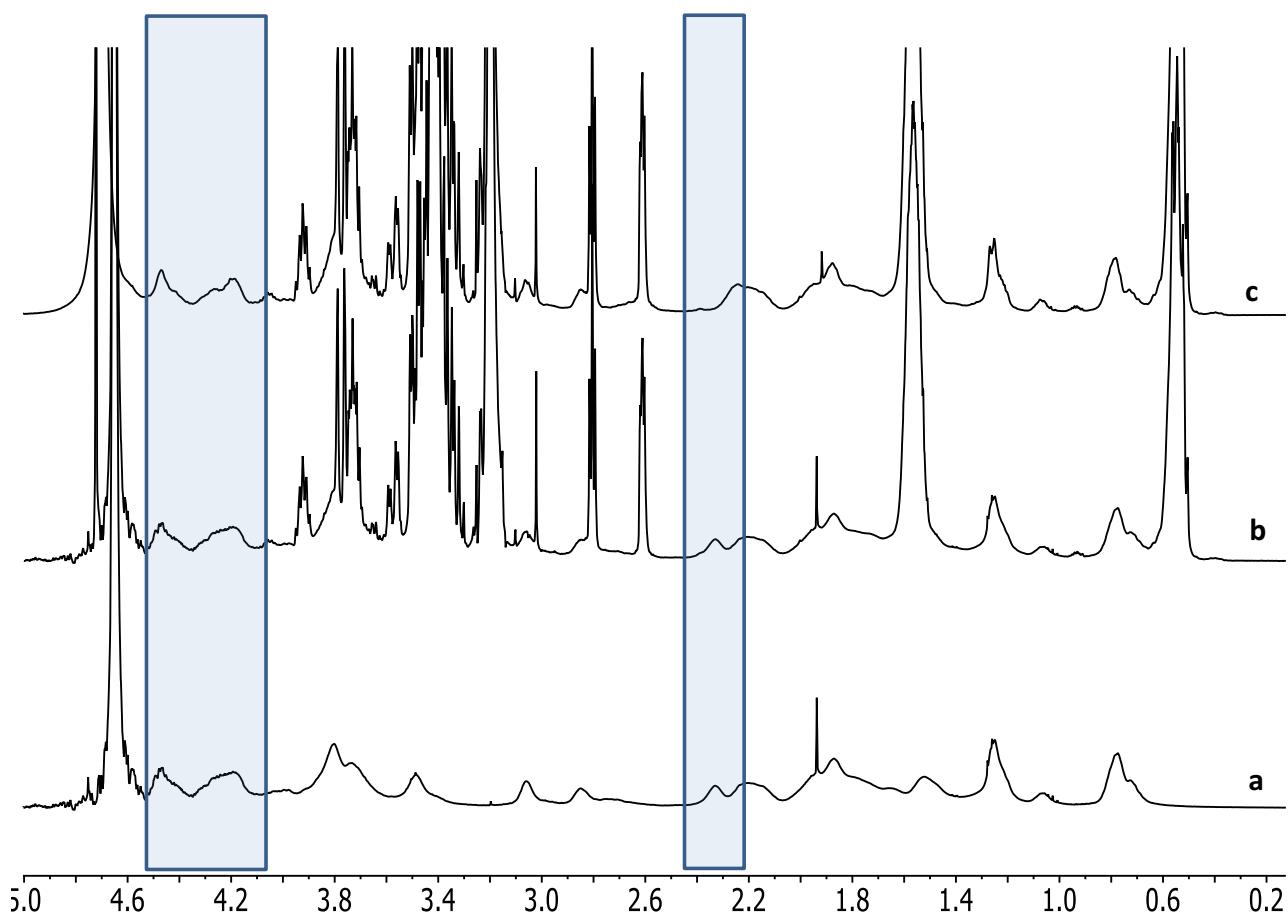


Figure S22. ¹H-NMR spectra of Gelatin, after 48 h (a) and reaction of Gelatin/GPTMS after 24 (b) and 48 (c) hours at pH 5, 40 °C.

1 "Exploring GPTMS reactivity against simple nucleophiles: chemistry beyond hybrid materials fabrication." L. Gabrielli, L. Connell, L. Russo, J. Jiménez-Barbero, F. Nicotra, L. Cipolla, J. R. Jones, *RSC Ad.*, **2014**, *4*, 1841-1848.