Supplementary Material

Block-copolymeric Maltodextrin-based Amphiphilic Glycosilicones as Surface-active Systems

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The signals of maltodextrin polymer chain are marked as H1–H6 and C1−C6 in the ^{1}H and ^{13}C NMR spectra, respectively; additional signals corresponding to inevitable impurities such as, e.g., low molecular weight saccharides, are marked by asterisks. The detected impurities are typical for relevant systems as follows from the other reports focused on maltodextrin acetylation, for instance see ref. [M. Elomaa, T. Asplund, P. Soininen, R. Laatikainen, S. Peltonen, S. Hyvarinen, A. Urtti. *Determination of the degree of substitution of acetylated starch by hydrolysis, ^{1}H NMR and TGA/IR*, Carbohydr. Polym. 57 (2004) 261–267; doi: 10.1016/j.carbpol.2004.05.003]. We assume that these additional signals correspond to the incomplete substitution of the hydroxyls of low molecular weight saccharides, which are formed as minor by-products. Remarkably, the ^{1}H NMR integration of the saccharide chain protons and acetyl group protons indicates that all hydroxyl functions in the main product are fully acetylated.

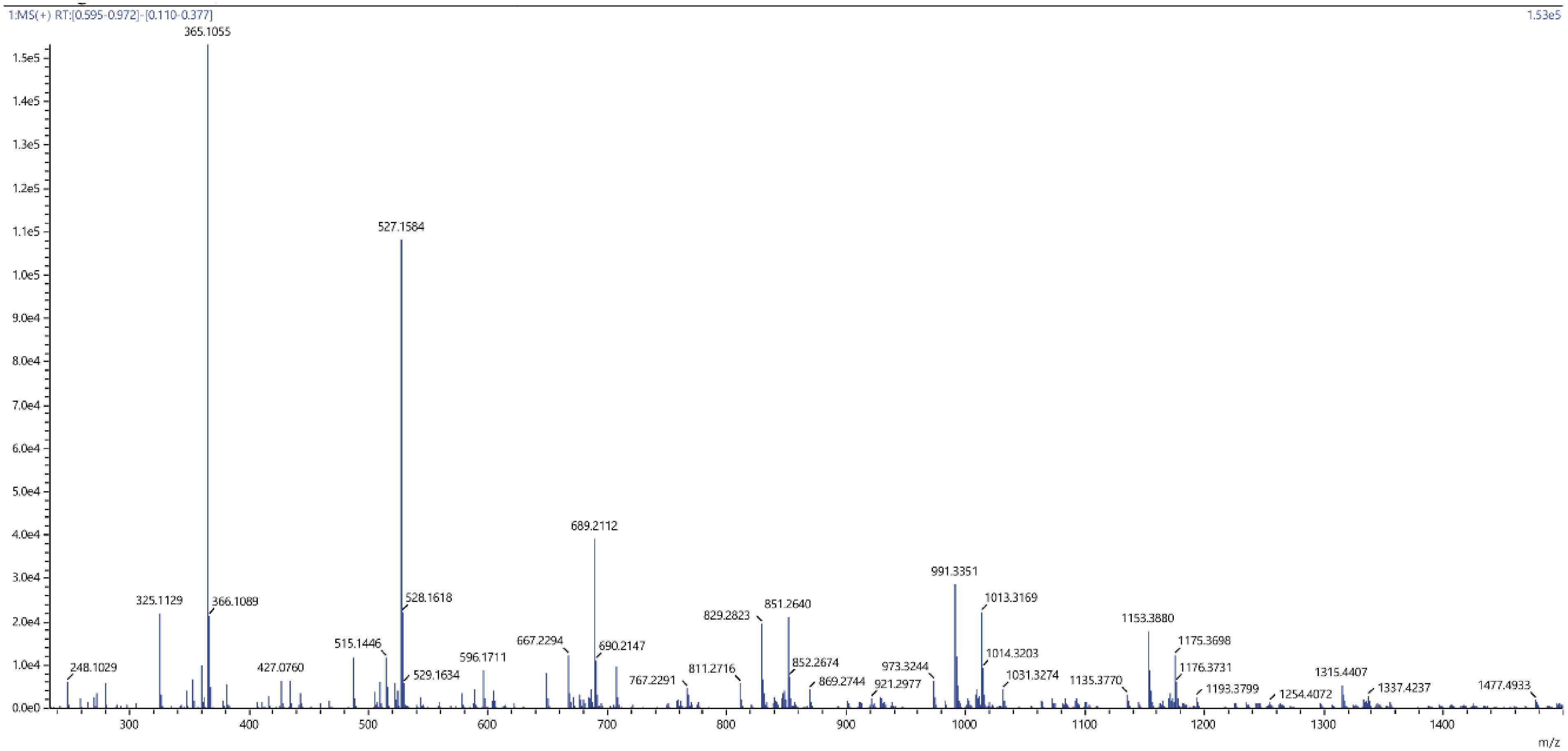

Figure S1. MS ESI spectrum of **malt-1**.

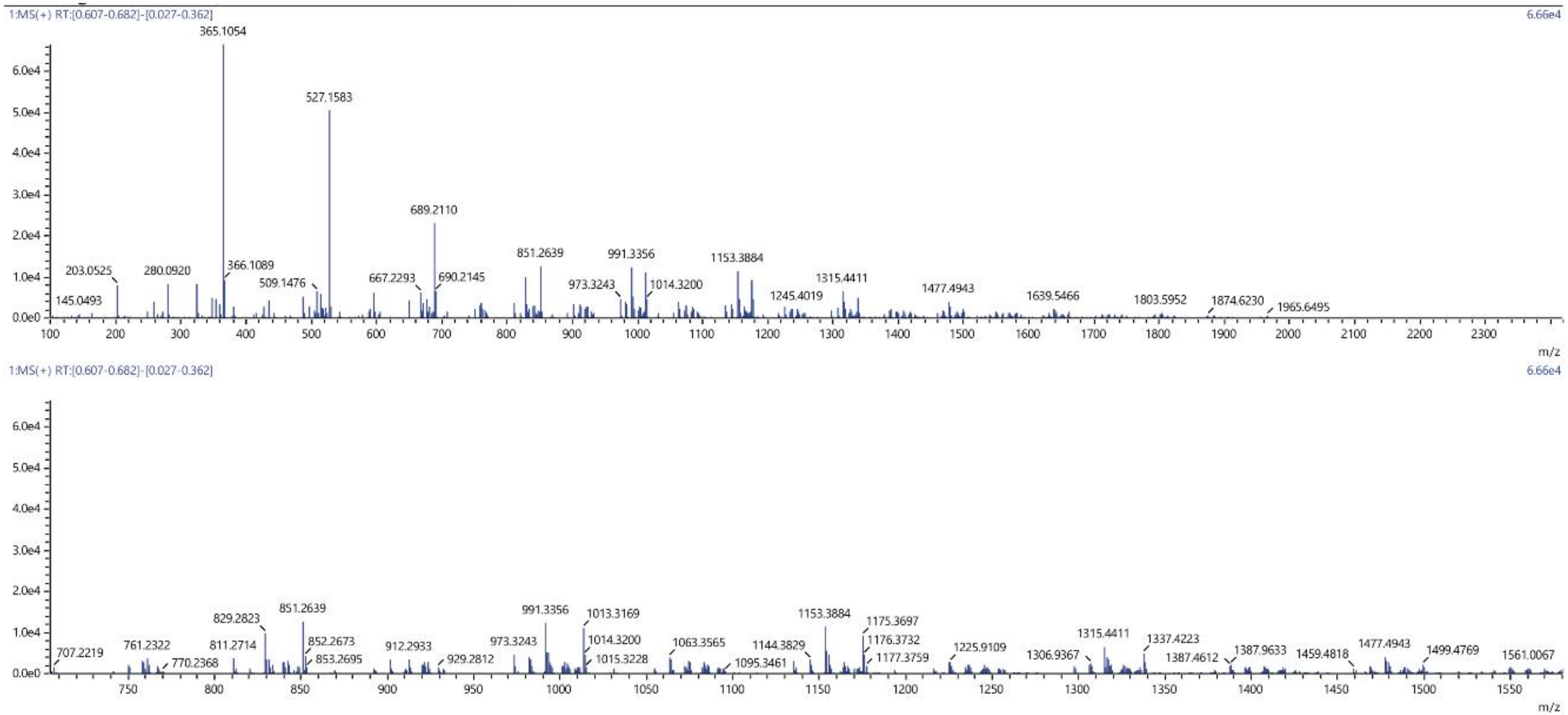

Figure S2. MS ESI spectrum of **malt-2**.

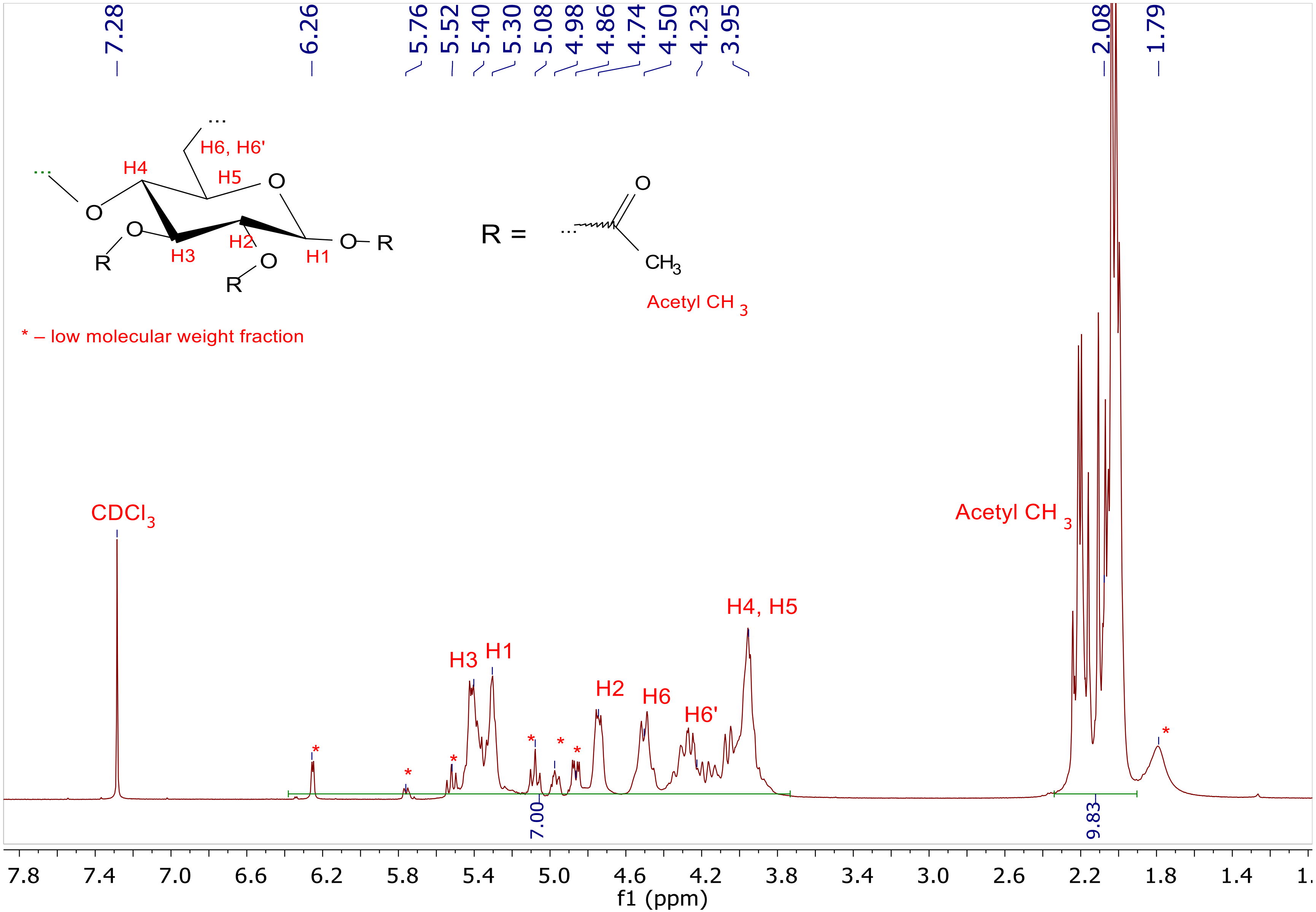

Figure S3. [1]H NMR spectra of **malt-1-ac**.

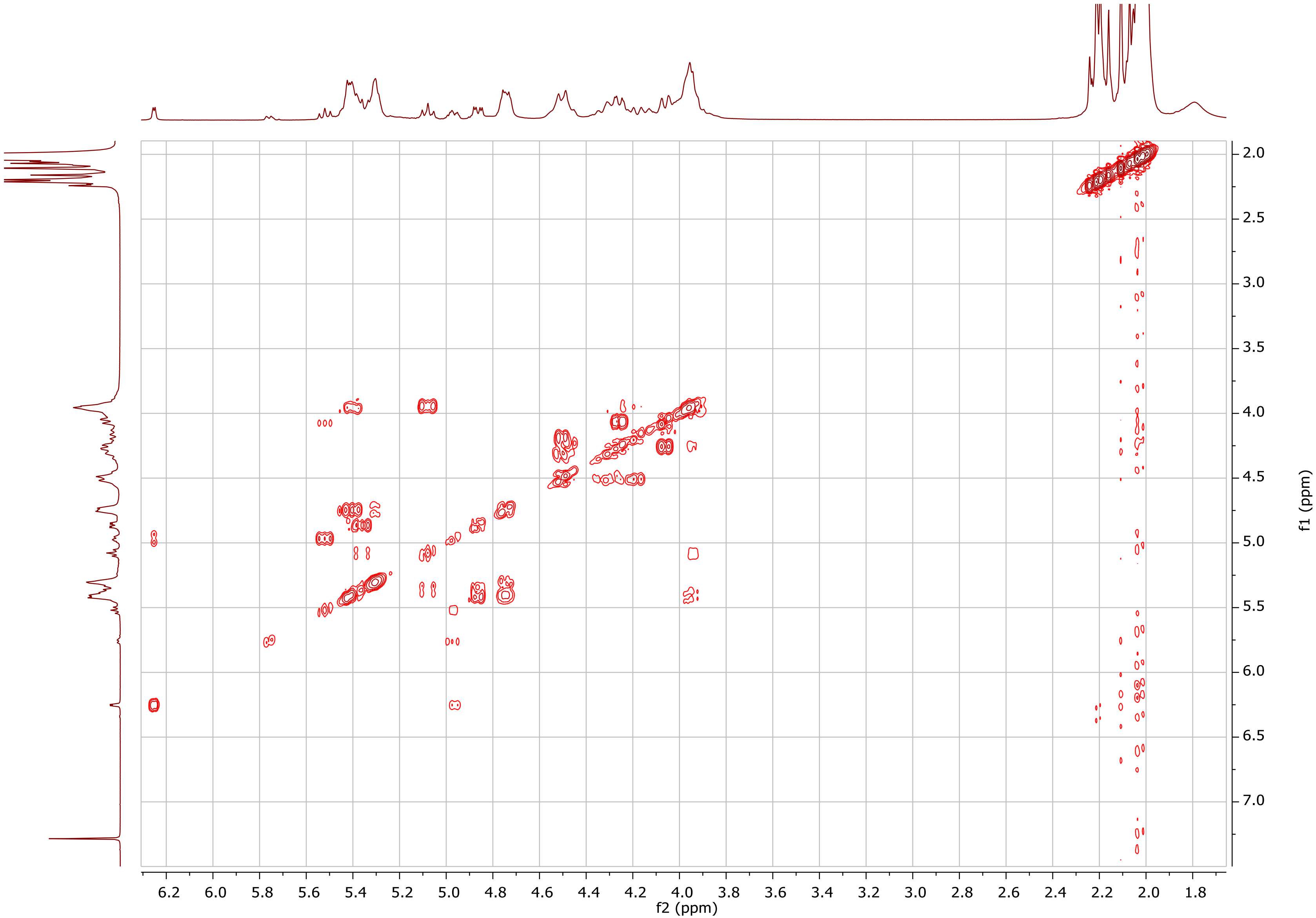

Figure S4. ^{1}H-^{1}H COSY NMR spectra of **malt-1-ac**.

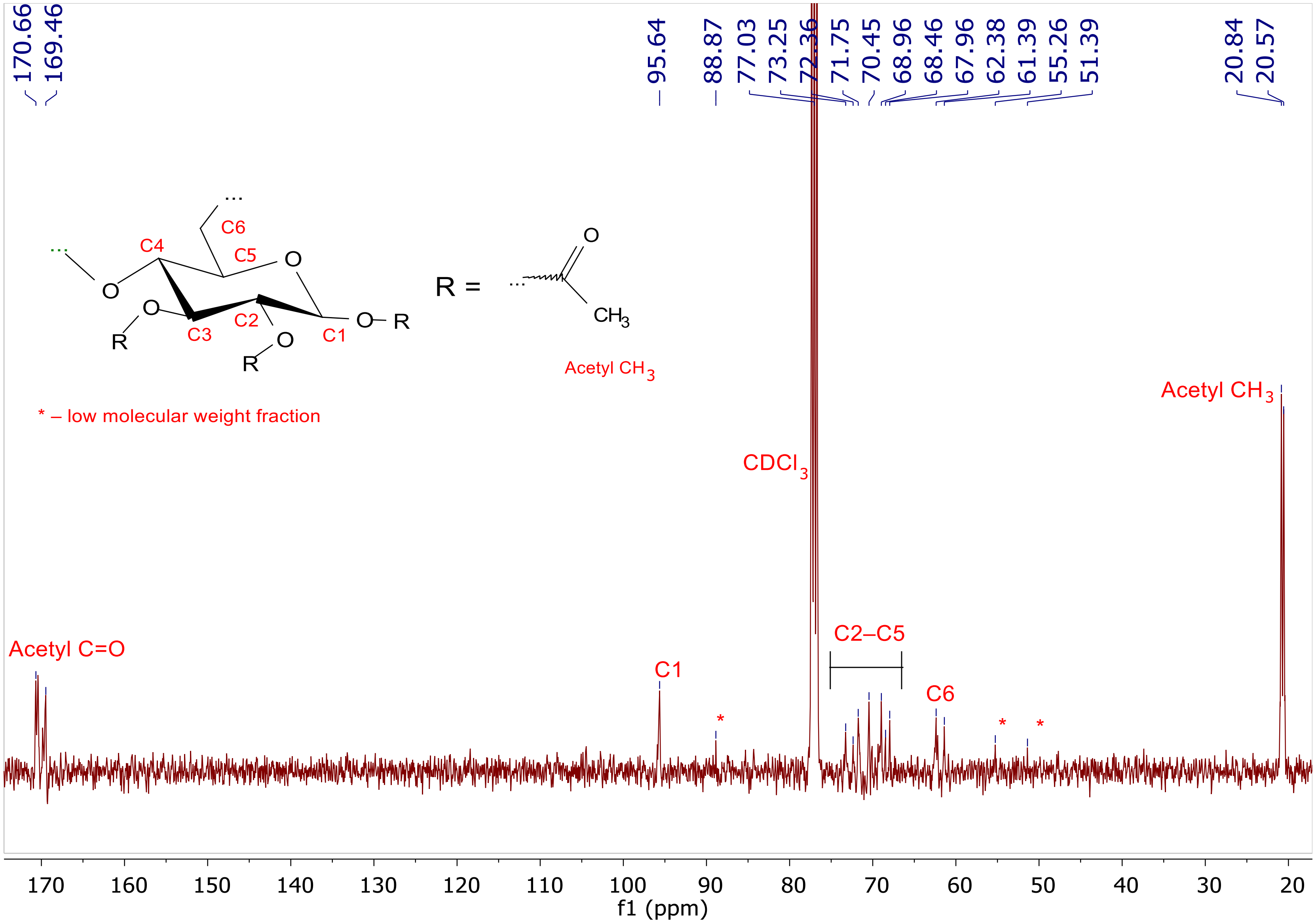

Figure S5. ^{13}C NMR spectra of **malt-1-ac**.

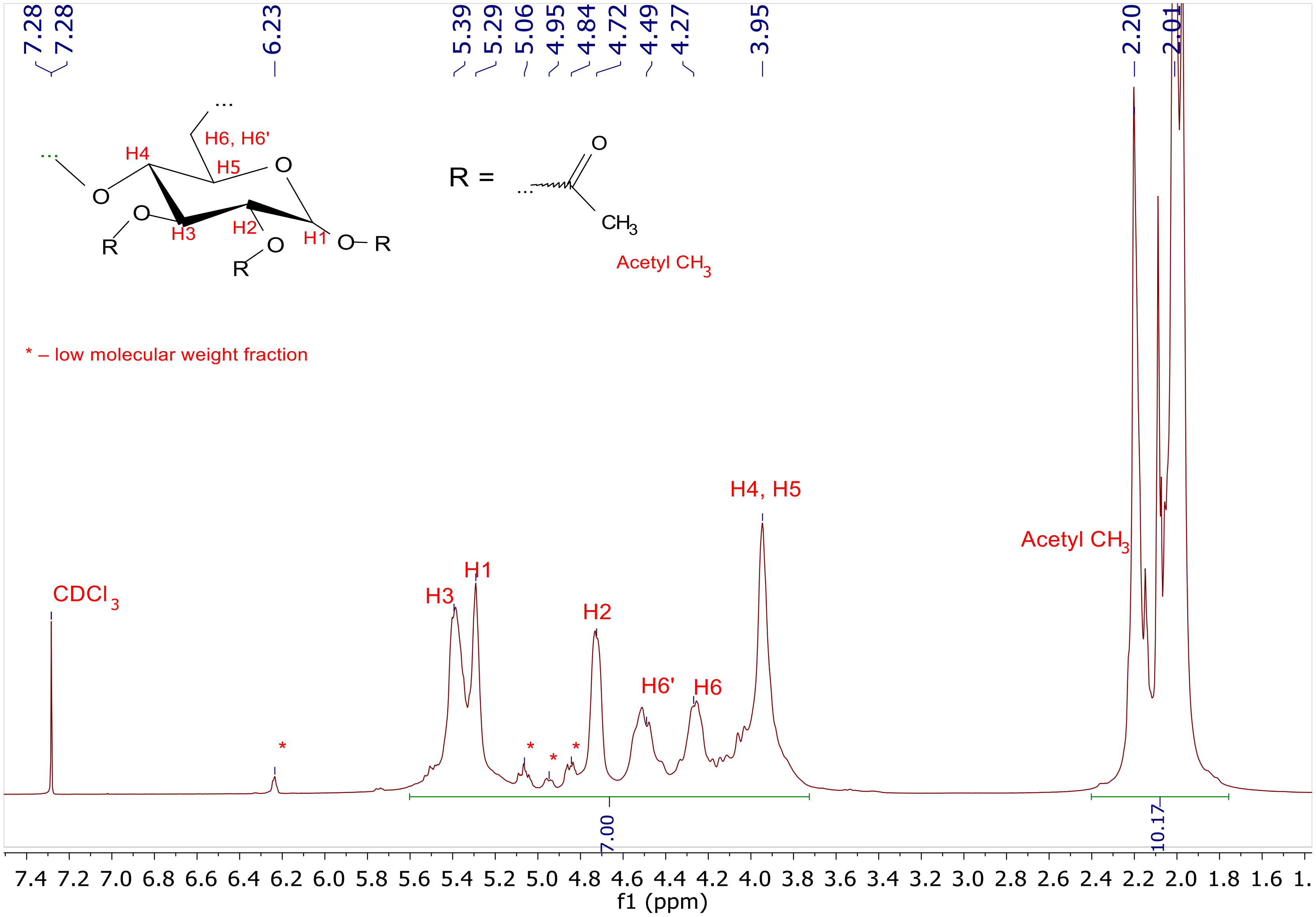

Figure S6. ^{1}H NMR spectra of **malt-2-ac**.

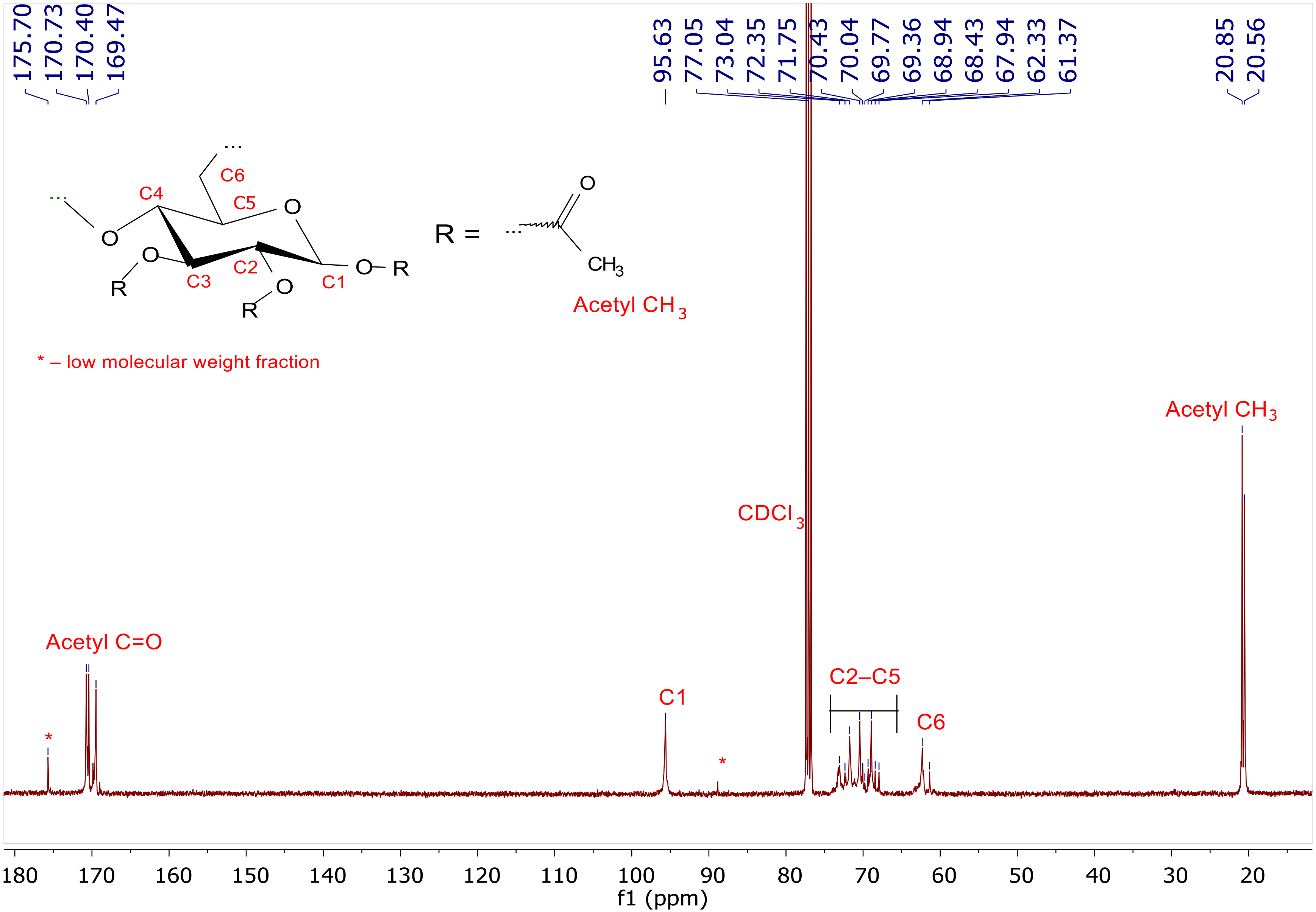

Figure S7. ^{13}C NMR spectra of **malt-2-ac**.

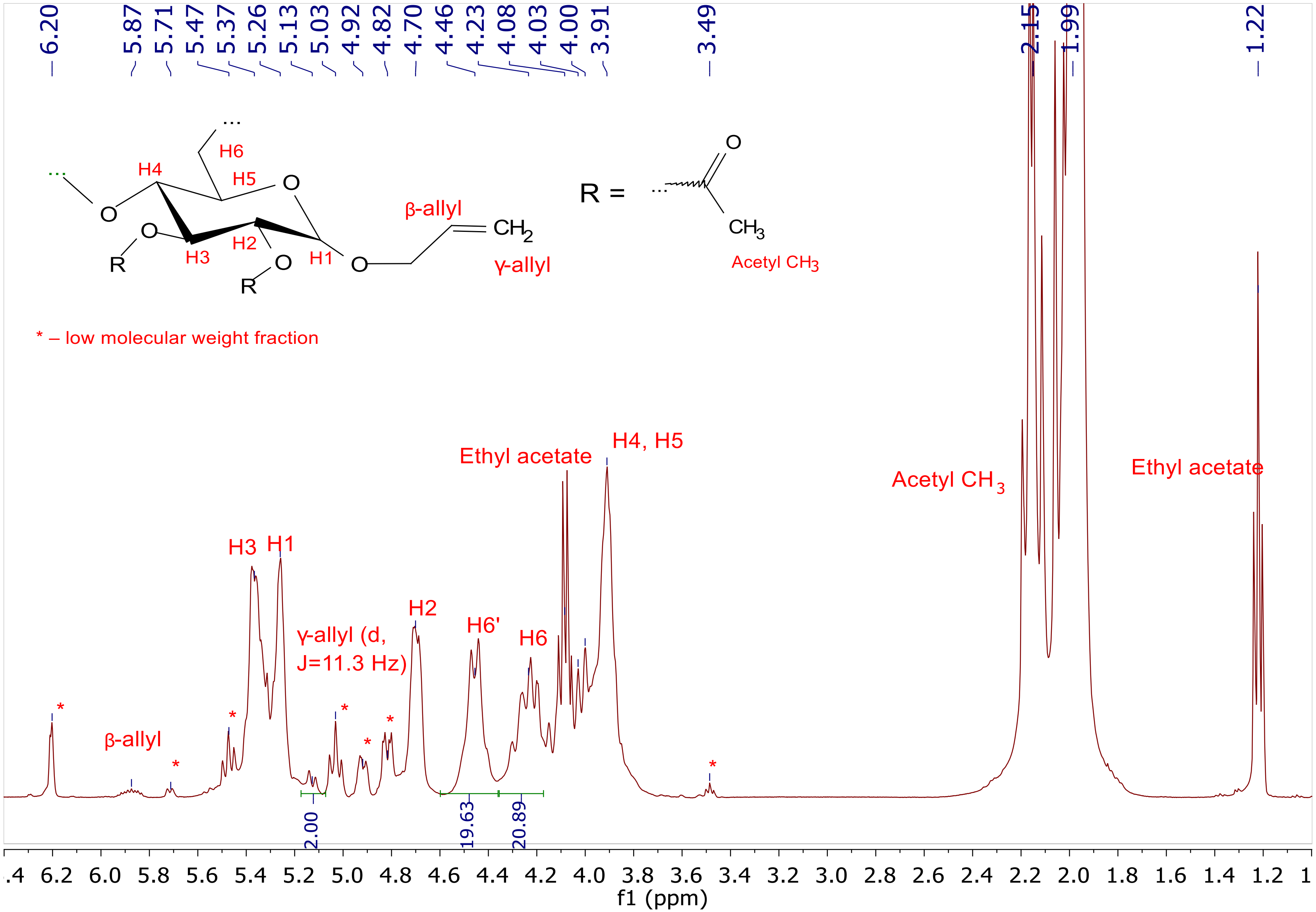

Figure S8. [1]H NMR spectra of **malt-1-ac-allyl**.

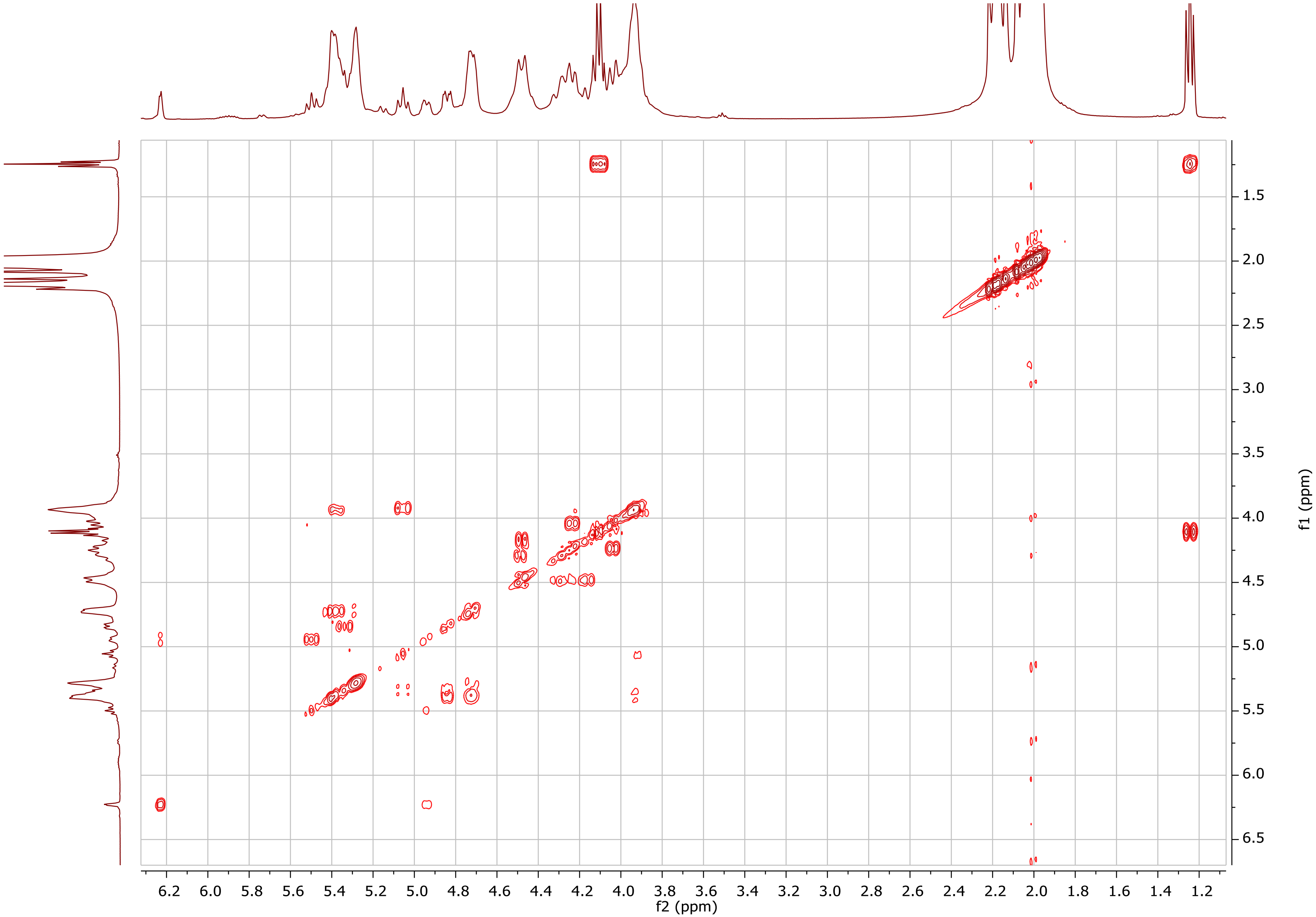

Figure S9. [1]H-[1]H COSY spectra of **malt-1-ac-allyl**.

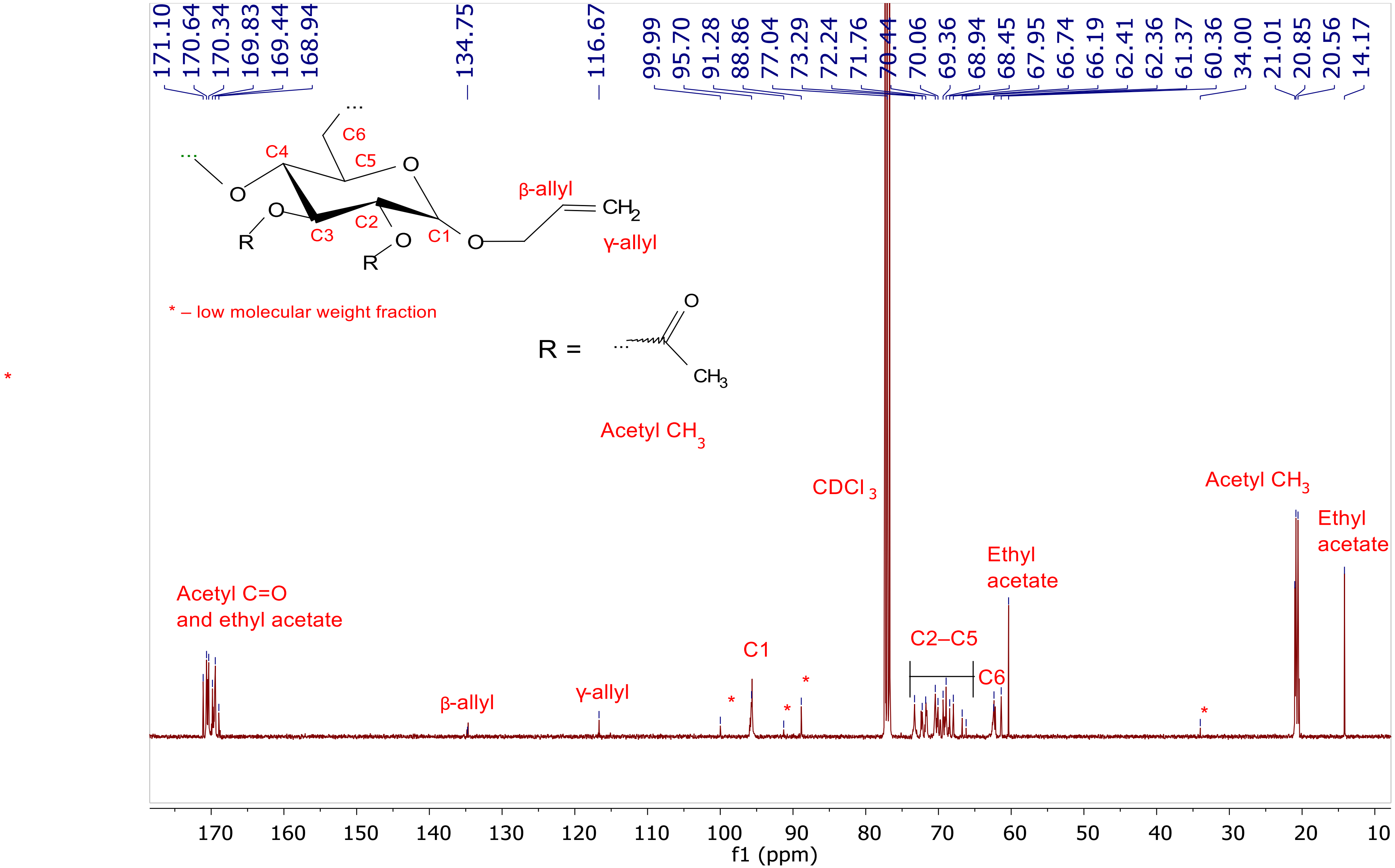

Figure S10. ^{13}C NMR spectra of **malt-1-ac-allyl**.

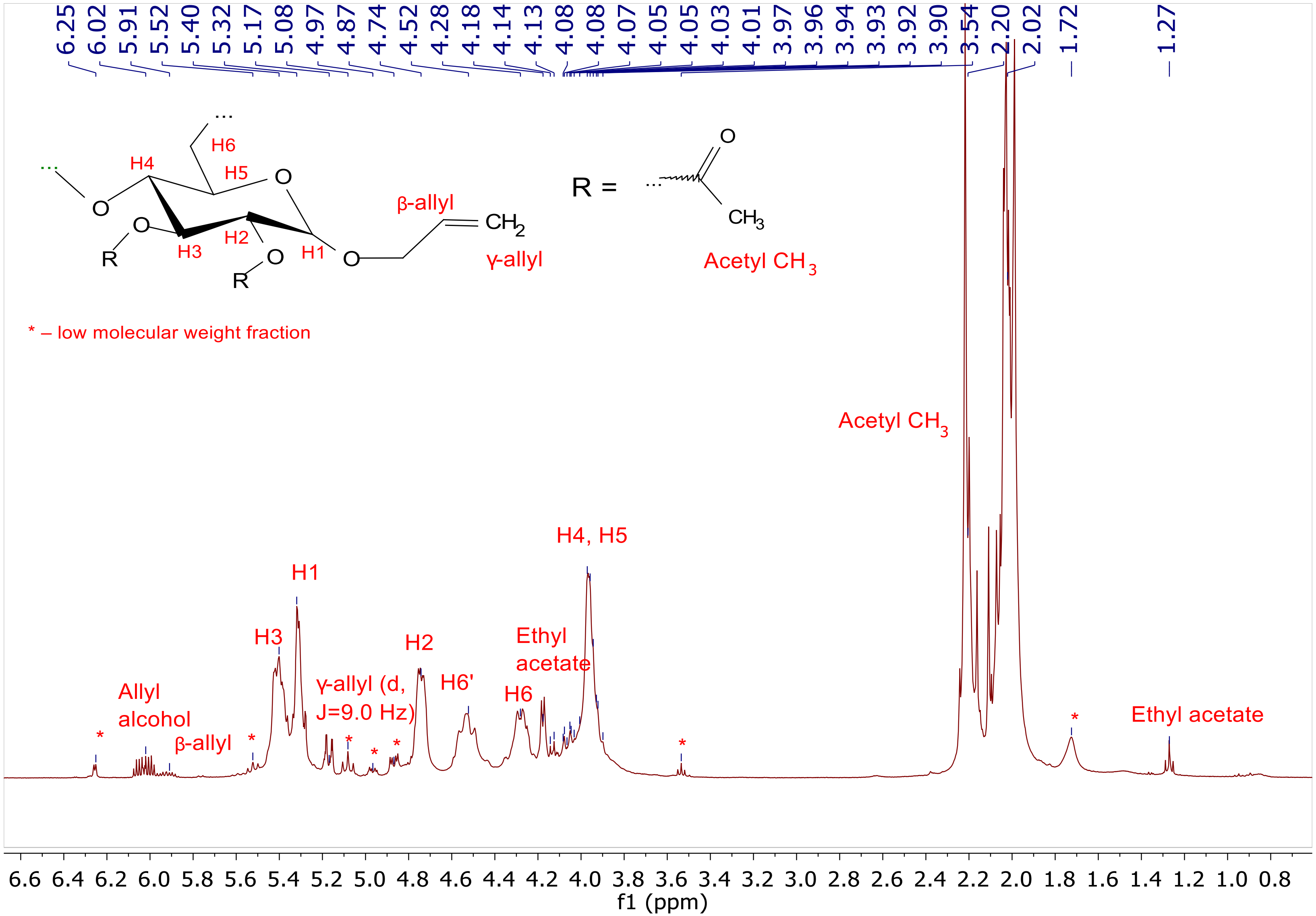

Figure S11. ^{1}H NMR spectra of **malt-2-ac-allyl**.

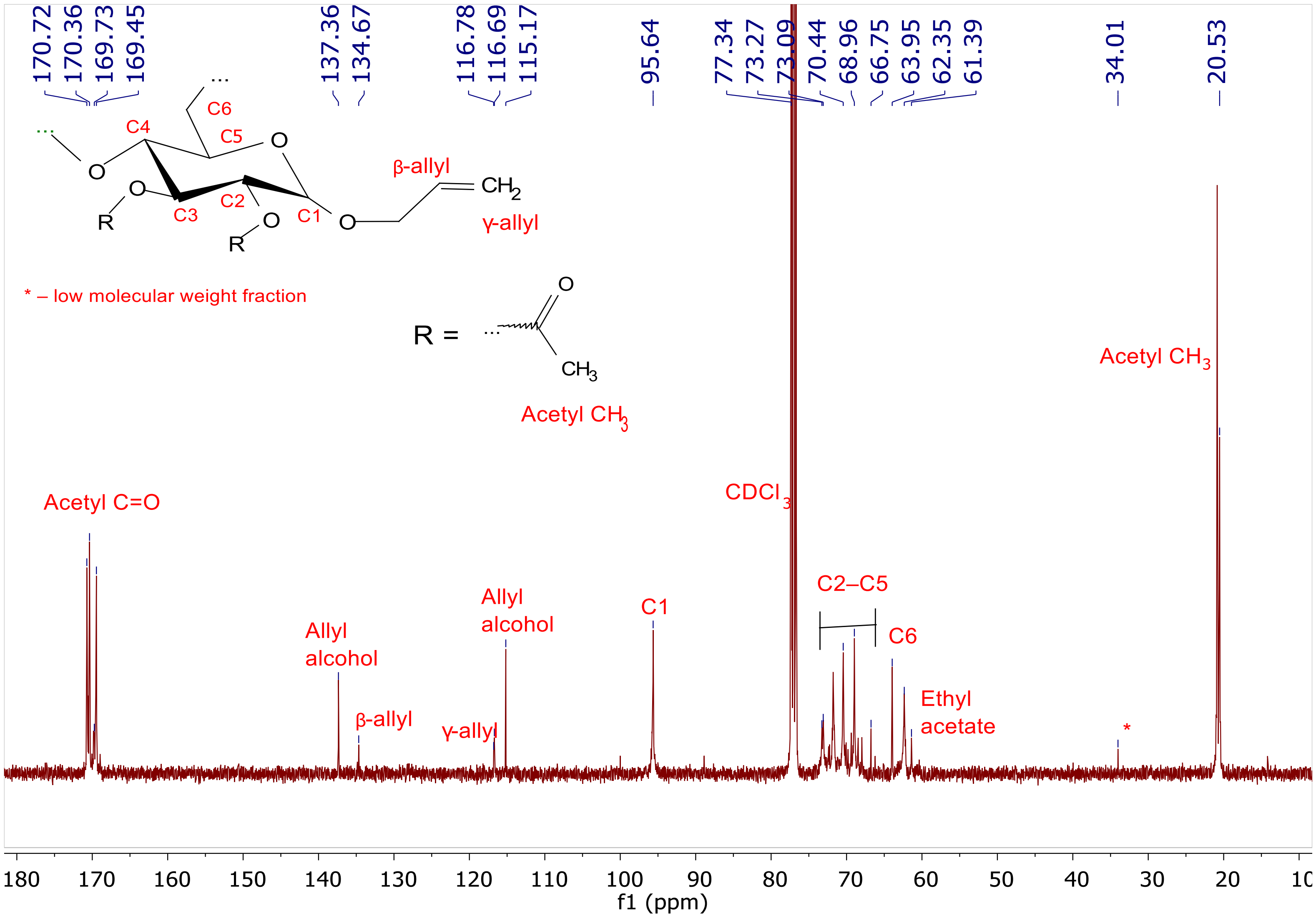

Figure S12. ^{13}C NMR spectra of **malt-2-ac-allyl**.

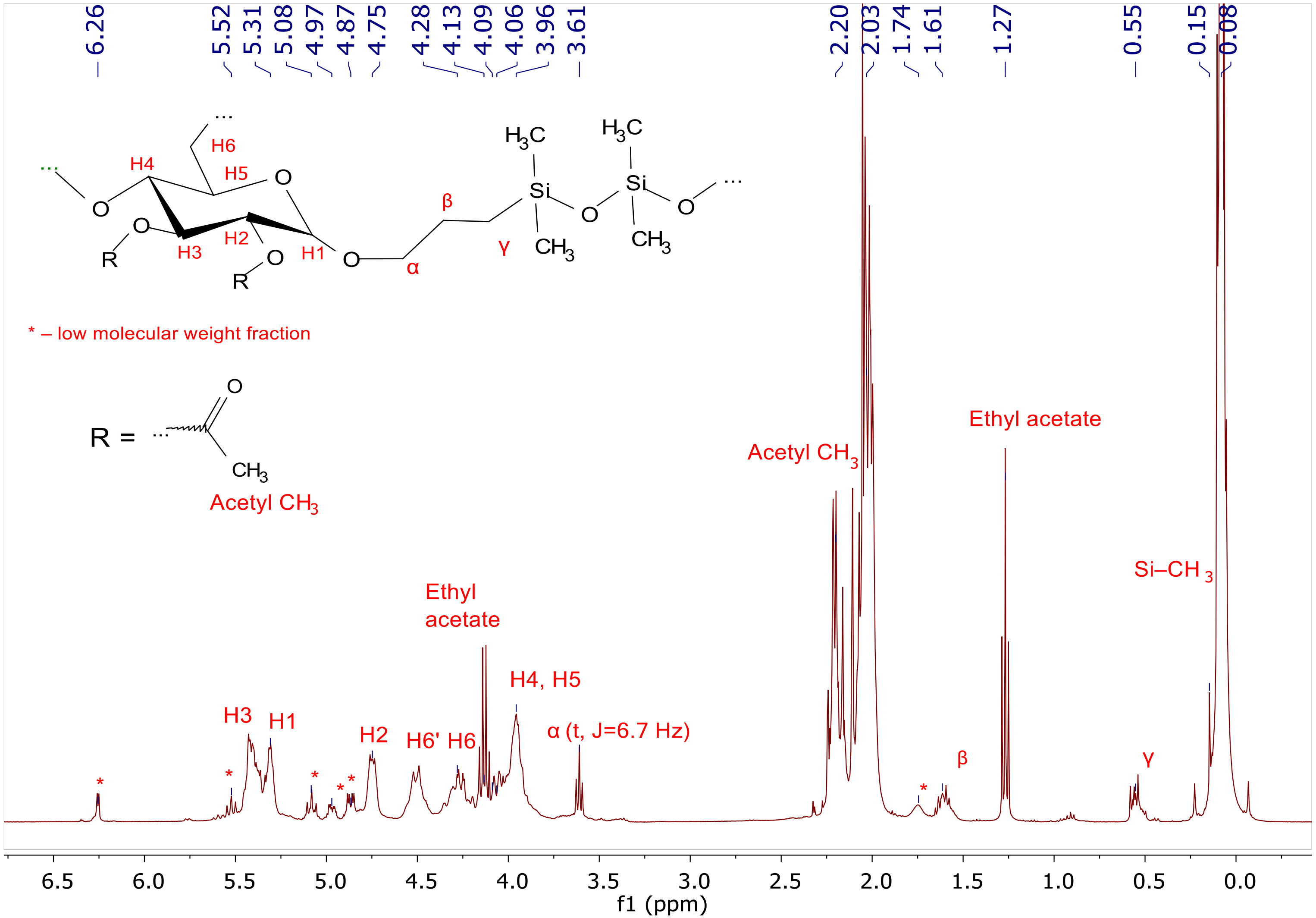

Figure S13. [1]H NMR spectra of **glyc-1-ac**.

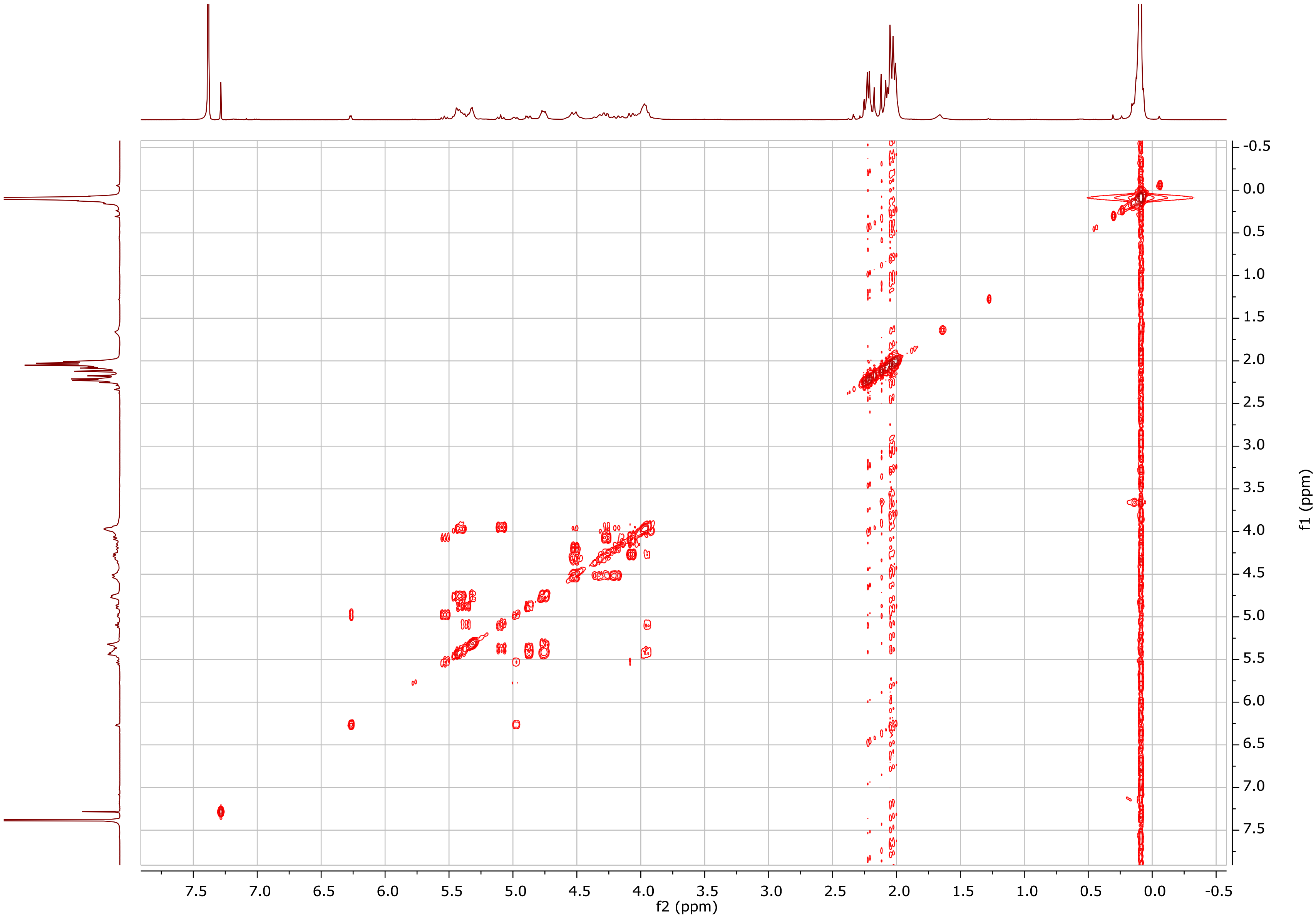

Figure S14. ^{1}H-^{1}H COSY spectra of **glyc-1-ac**.

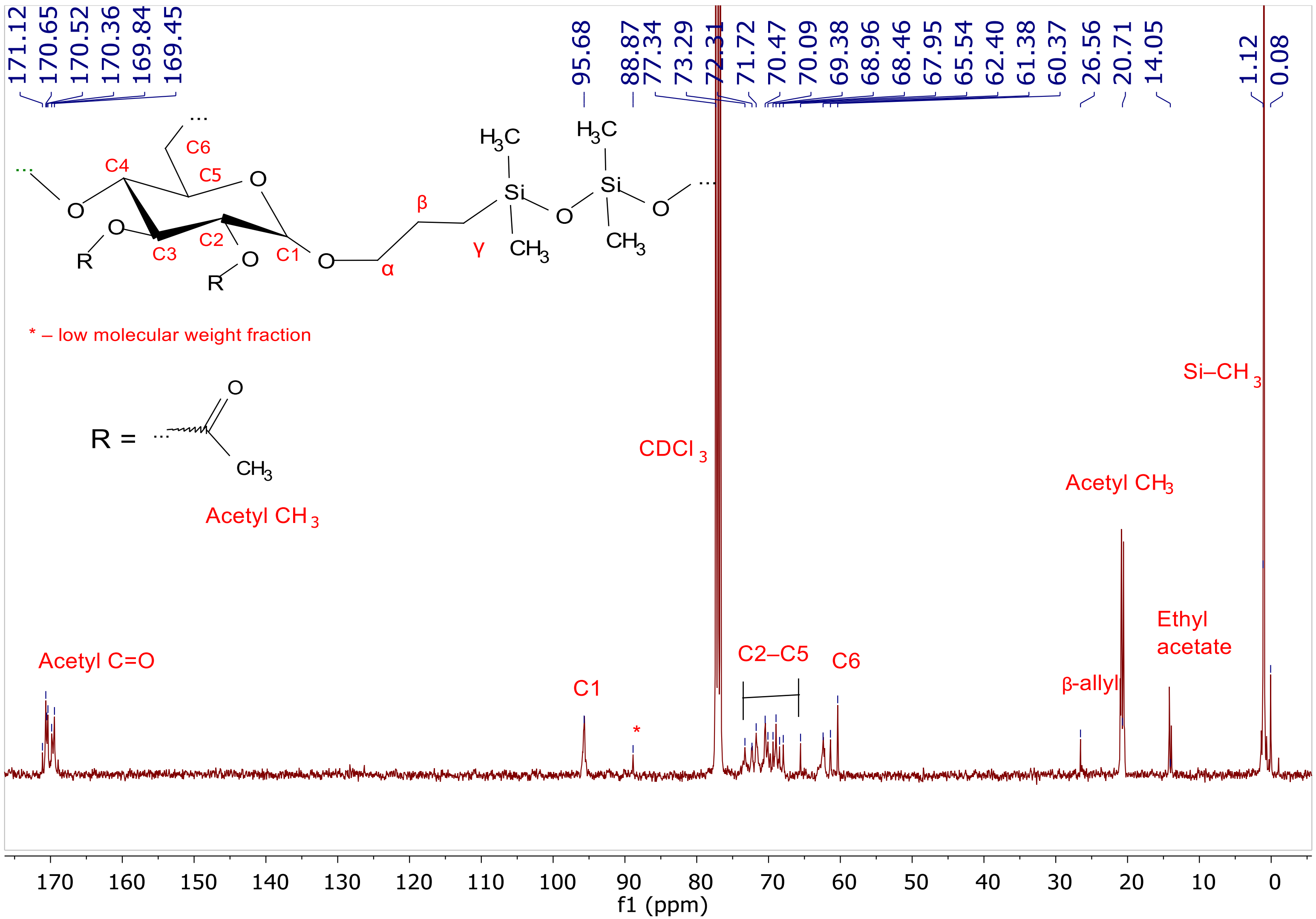

Figure S15. ^{13}C NMR spectra of **glyc-1-ac**.

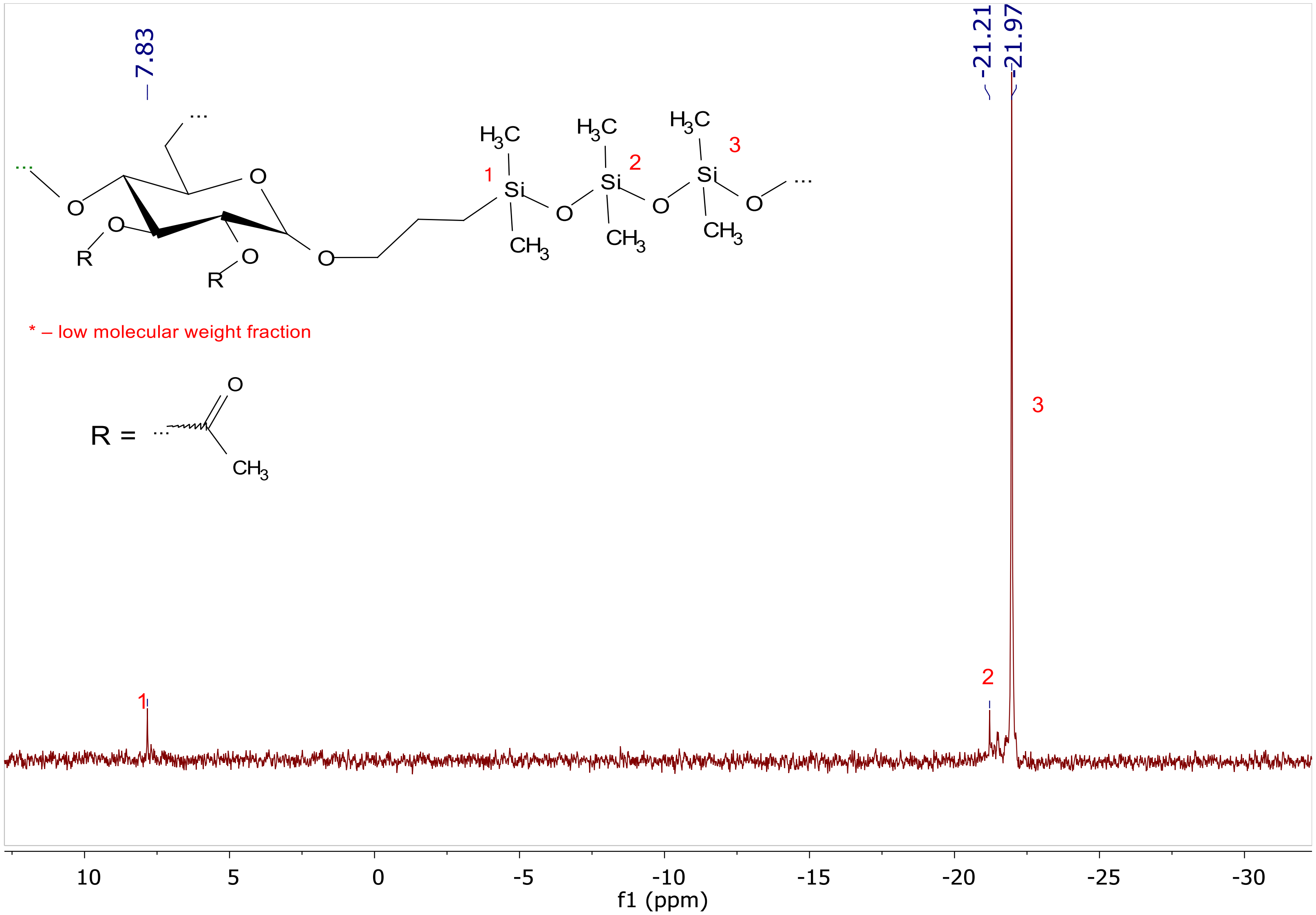

Figure S16. ^{29}Si NMR spectra of **glyc-1-ac**.

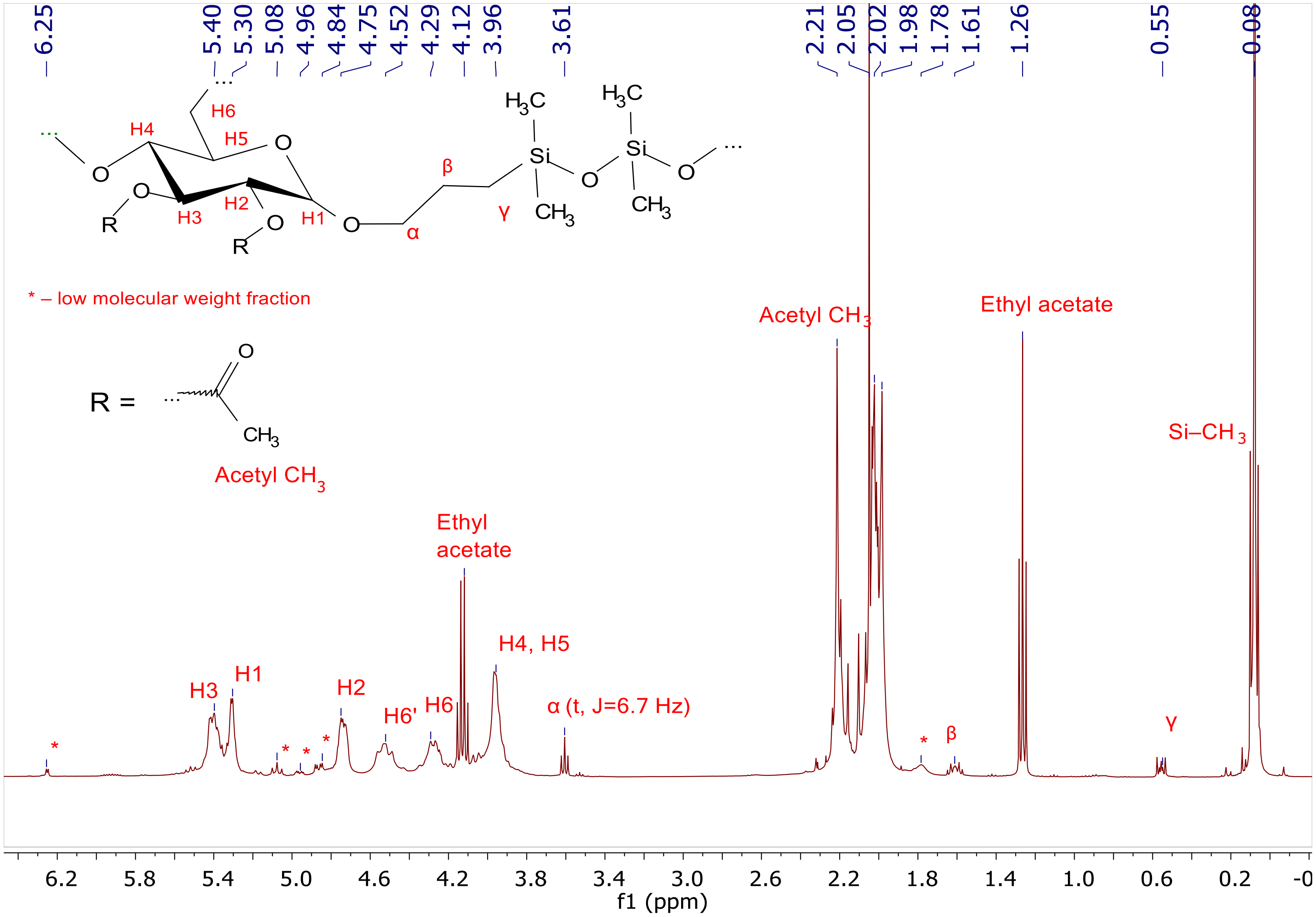

Figure S17. ^{1}H NMR spectra of **glyc-2-ac**.

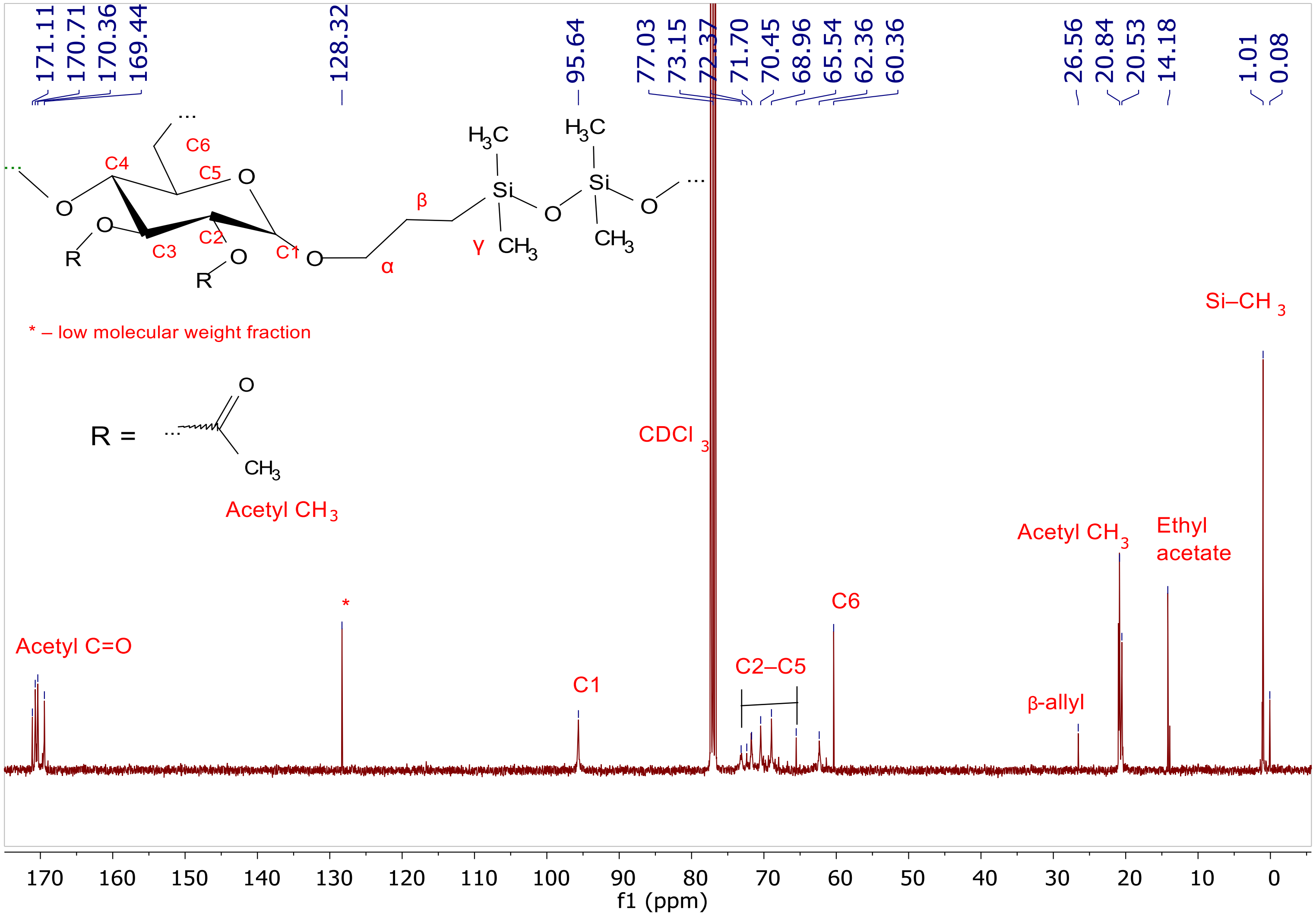

Figure S18. ^{13}C NMR spectra of **glyc-2-ac**.

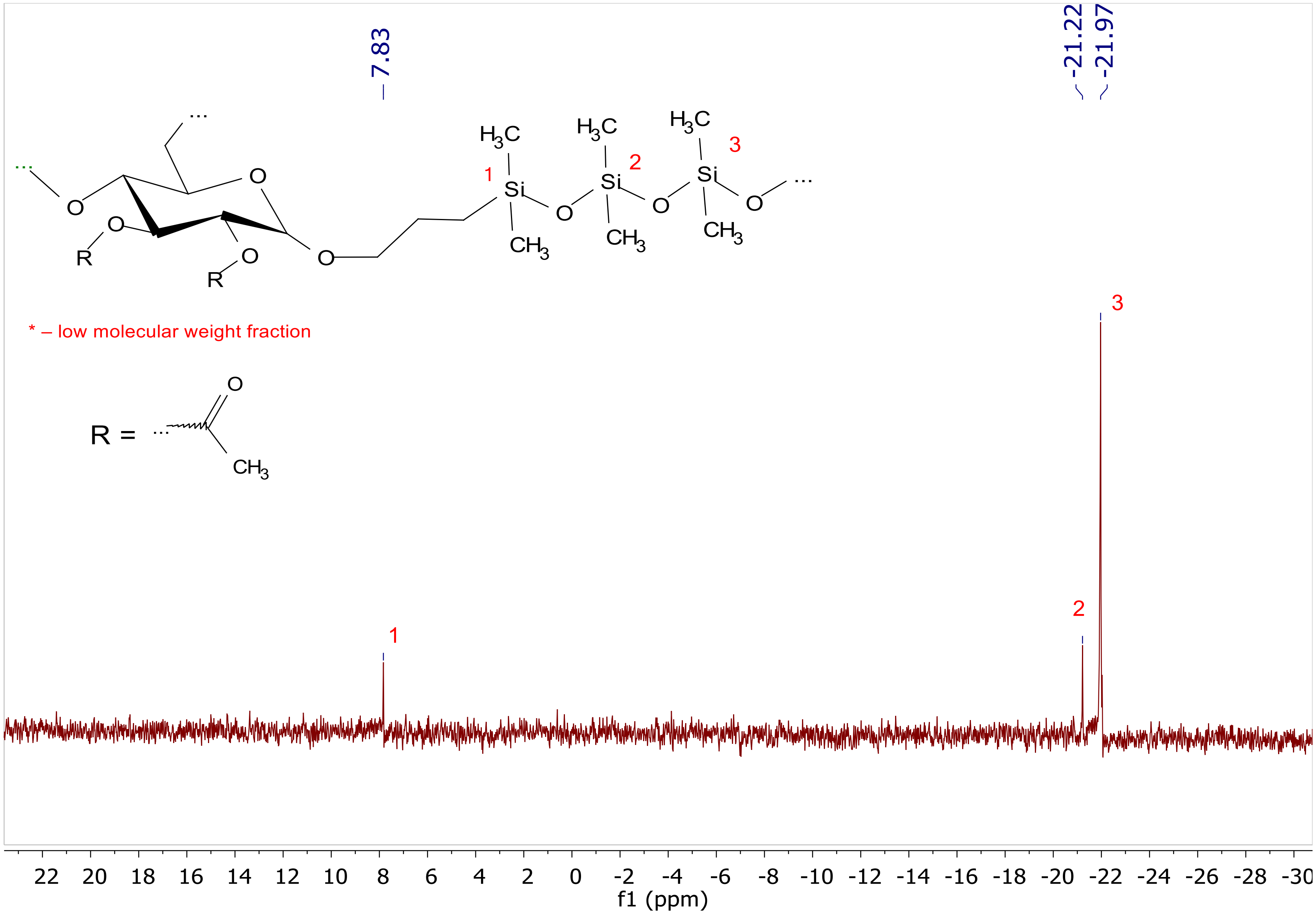

Figure S19. ^{29}Si NMR spectra of **glyc-2-ac**.

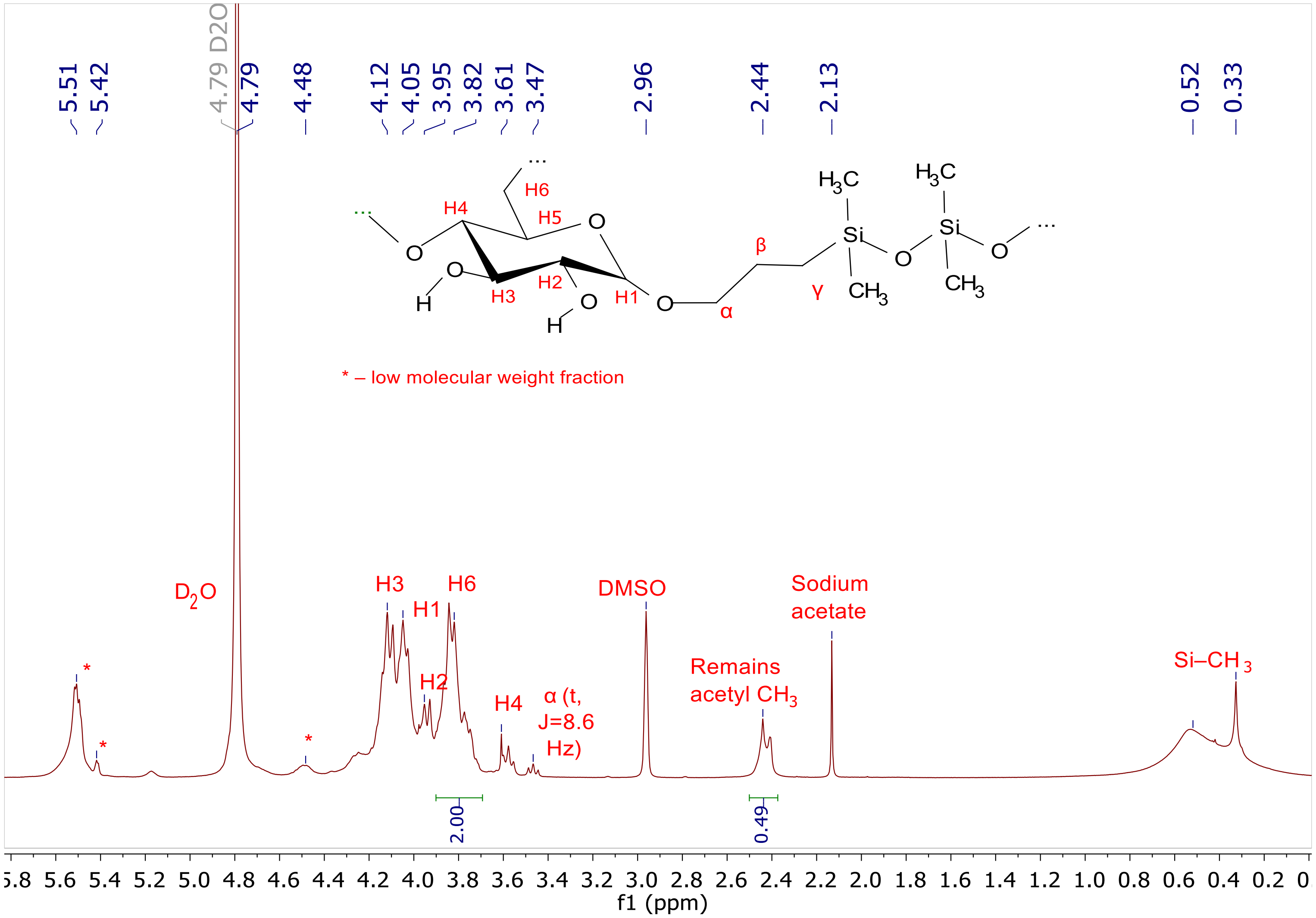

Figure S20. ^{1}H NMR spectra of **glyc-1**.

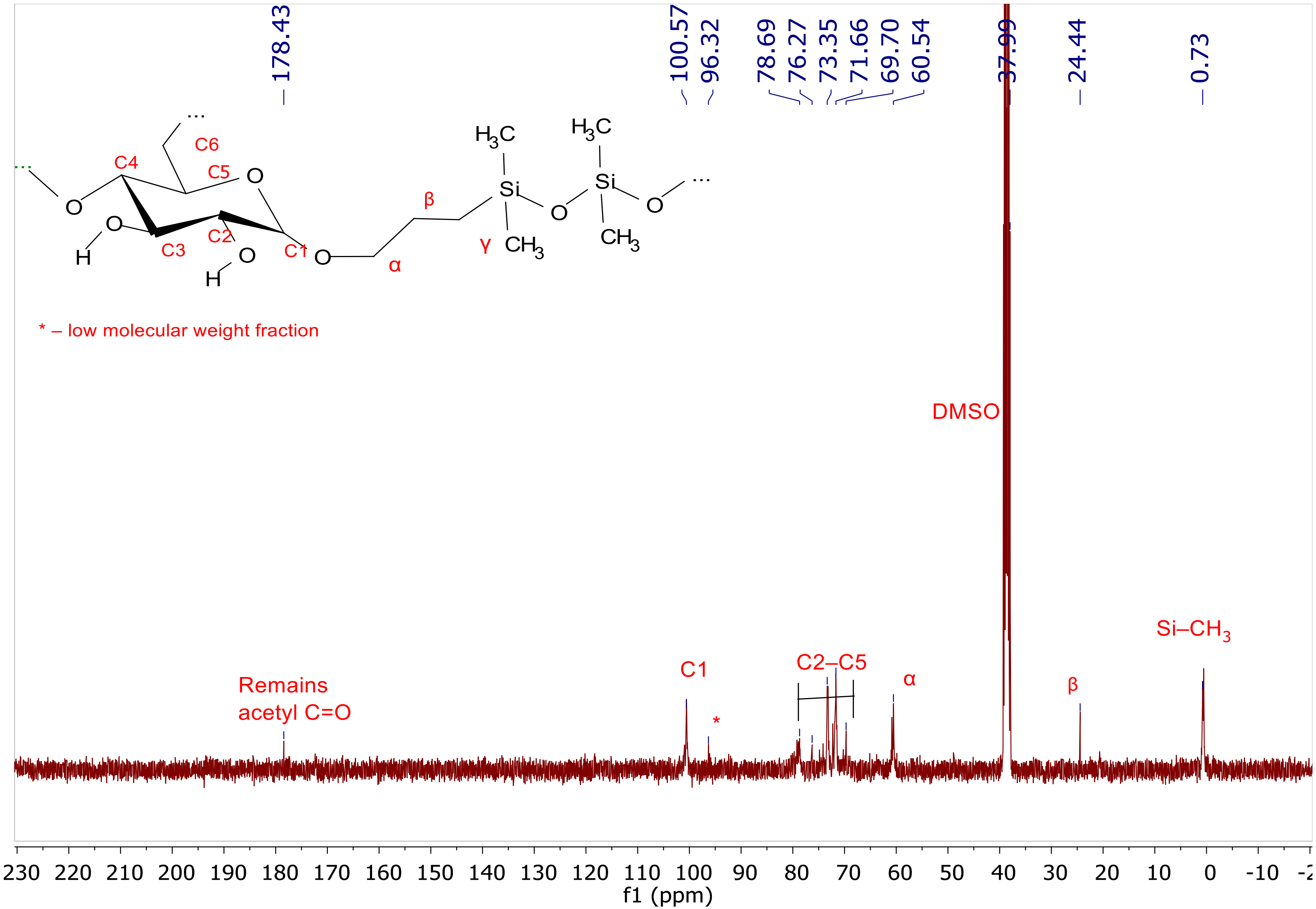

Figure S21. ^{13}C NMR spectra of **glyc-1**.

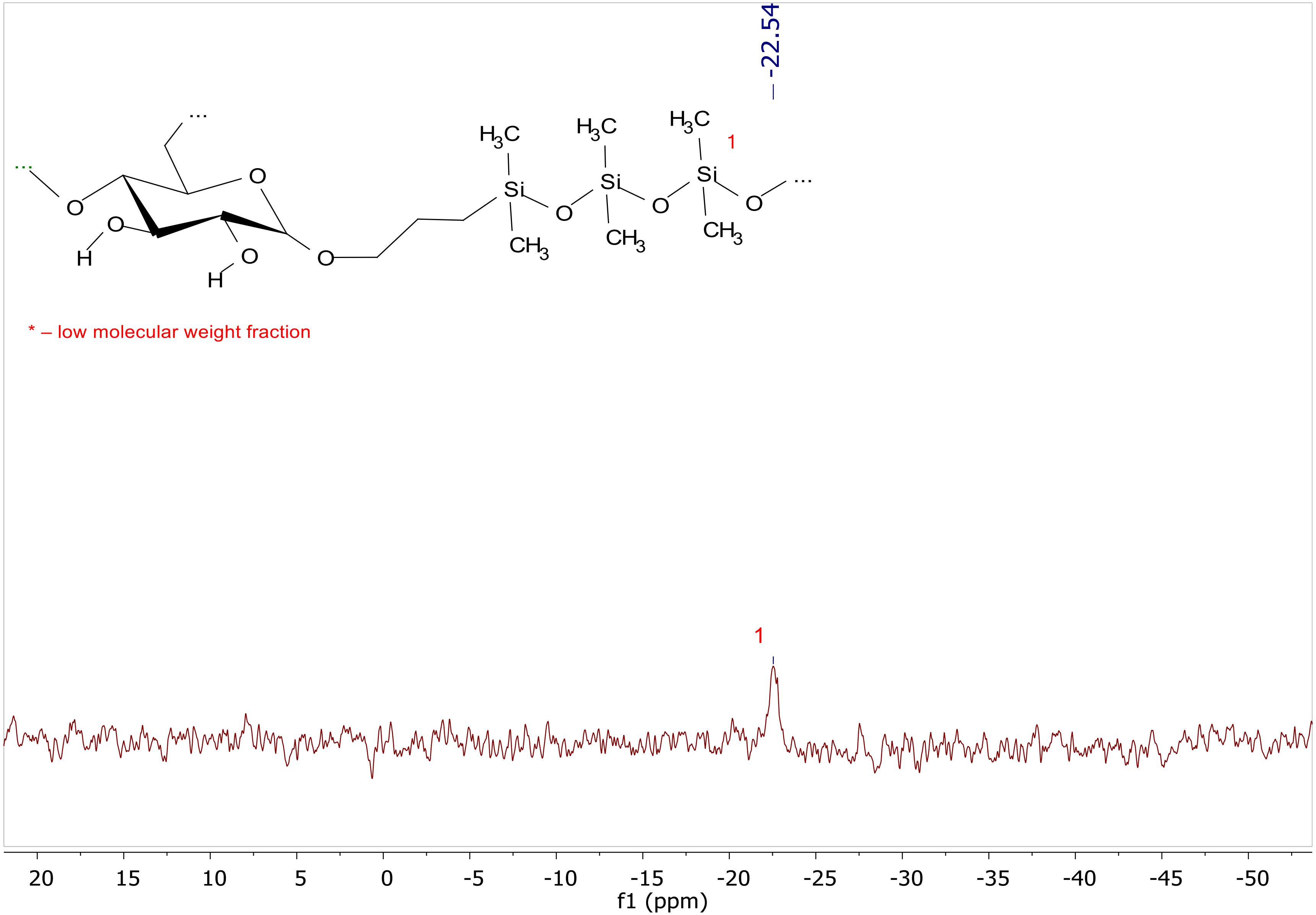

Figure S22. ^{29}Si NMR spectra of **glyc-1**.

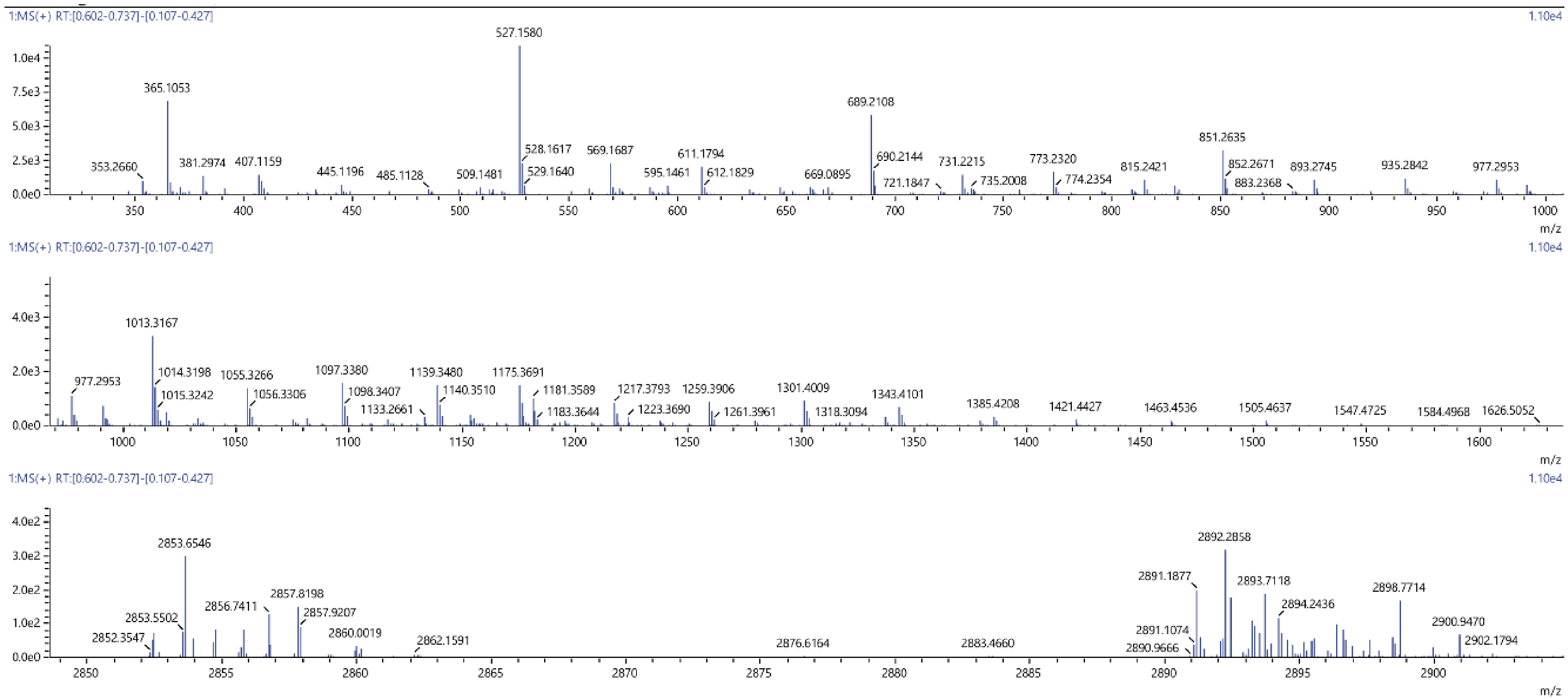

Figure S23. MS ESI spectrum of **glyc-1**.

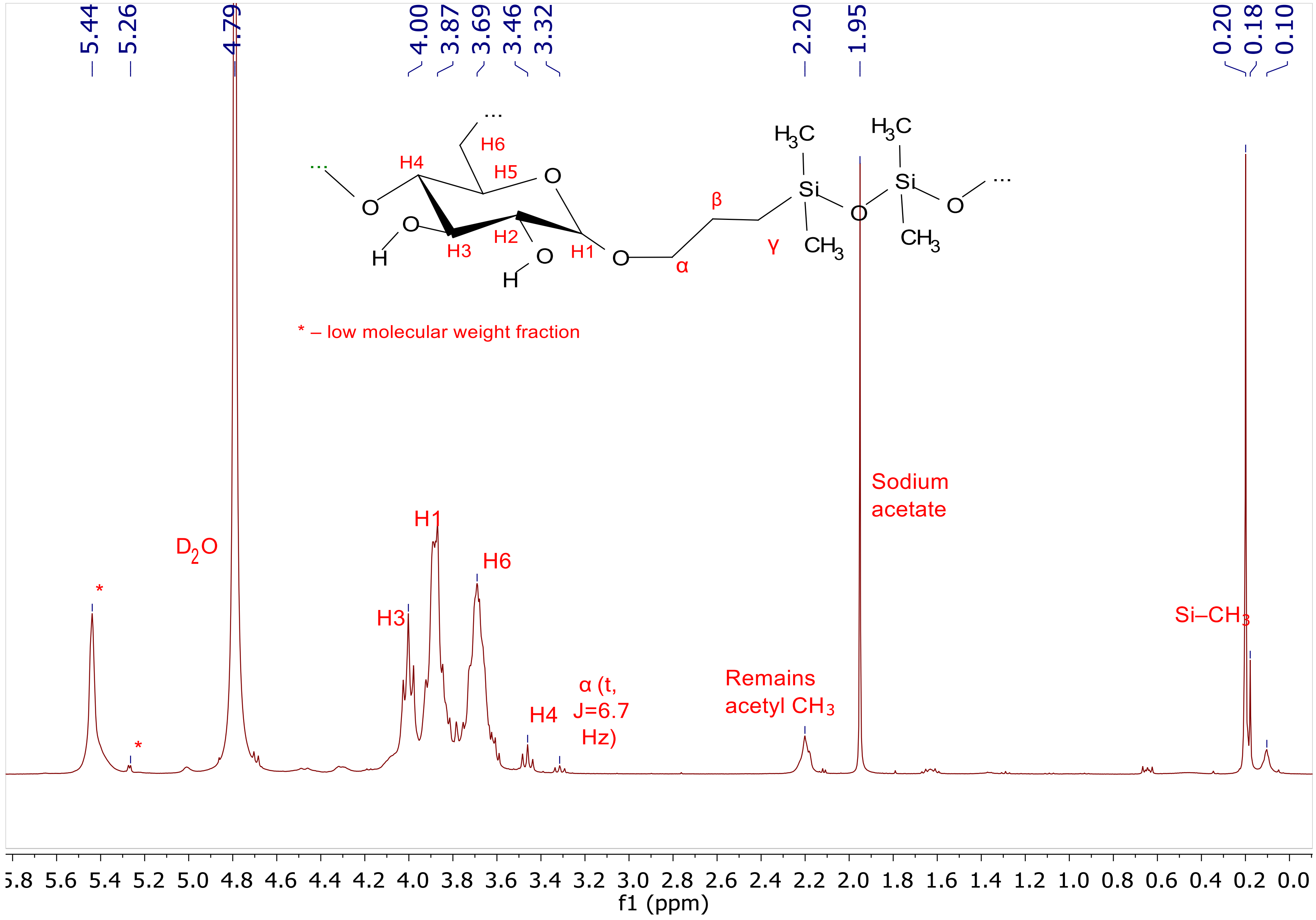

Figure S24. ^{1}H NMR spectra of **glyc-2**.

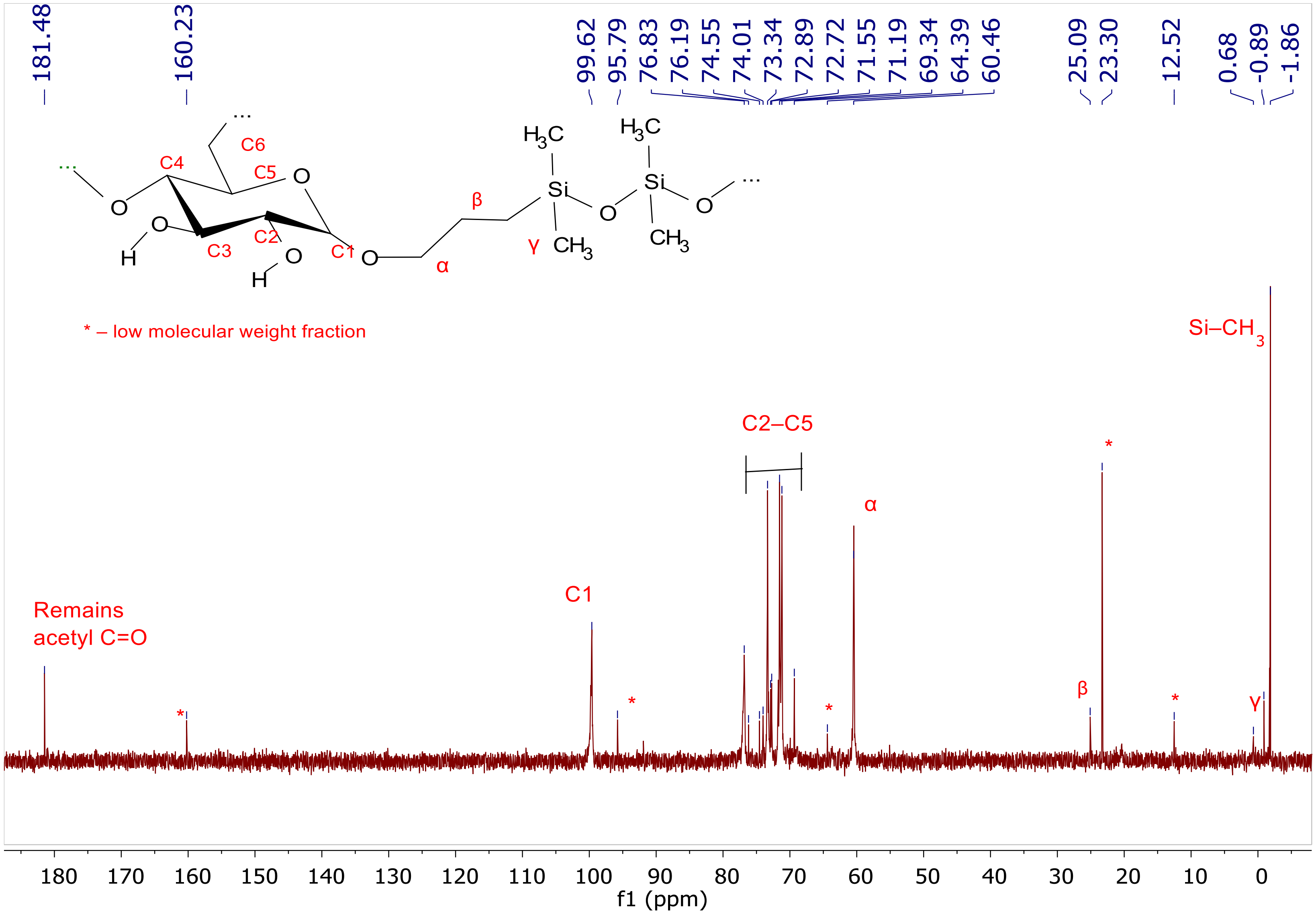

Figure S25. ^{13}C NMR spectra of **glyc-2**.

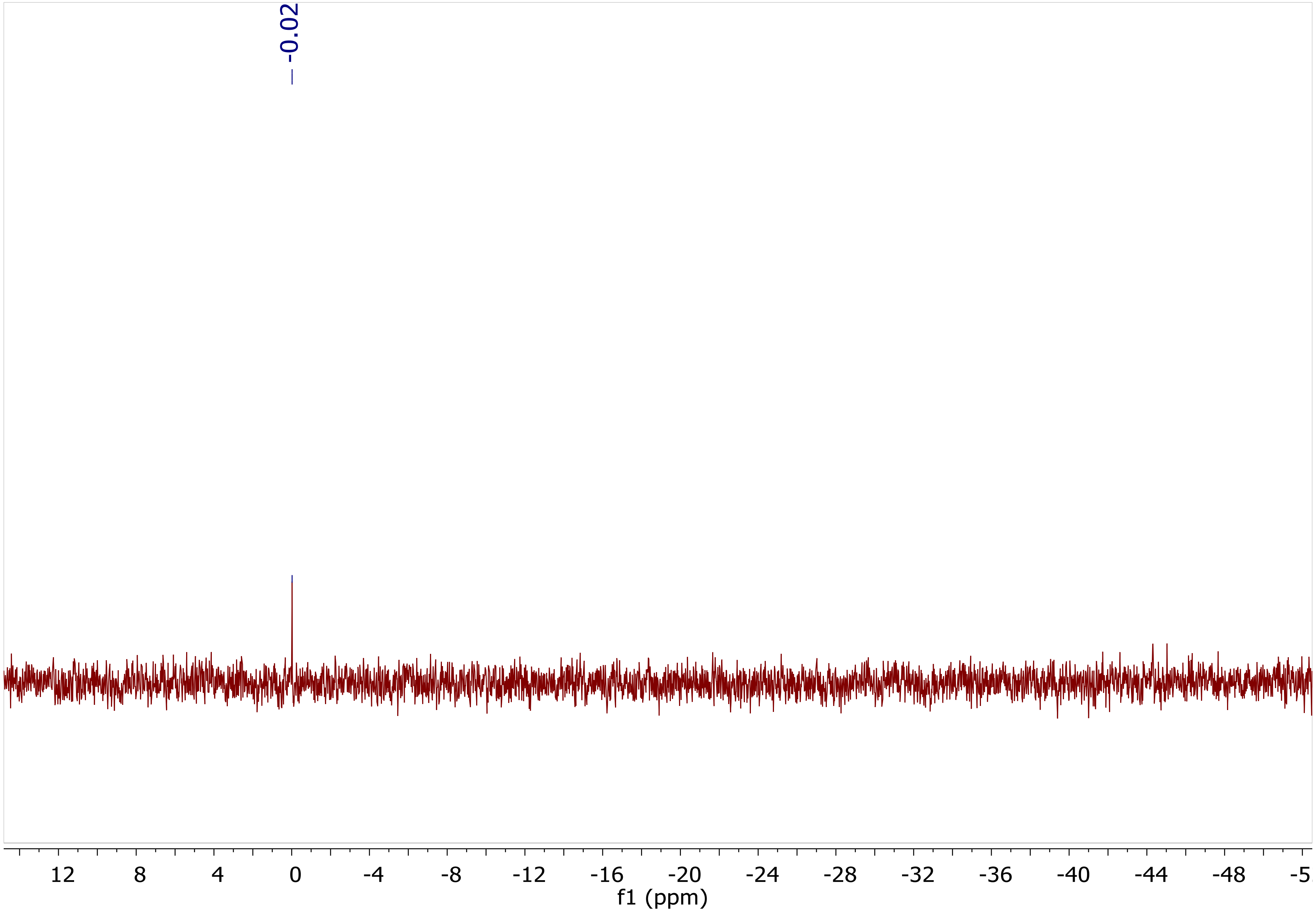

Figure S26. ^{29}Si NMR spectra of **glyc-2**.

Table S1. Optimization of the hydrosilylation reaction conditions between **malt-1-ac-allyl** and **PDMS-H**.

Catalyst	Temperature, °C	Time, h	Conversion degree, %	Signals of allyl group (5.87; 5.12 ppm) in **glyc-1-ac** ^{1}H NMR	Signals of siloxane chain in **glyc-1** (0 ppm) ^{1}H and ^{13}C NMR
Karstedt's catalyst	20	24	50[1]	+	+
Karstedt's catalyst	80	4	25[1]	+	+
Karstedt's catalyst	80	24	100[2]	–	+
$Rh(acac)(CO)_2$	80	24	100[2]	–	+
Wilkinson's catalyst	80	24	no reaction	+	–

[1] The Si-H groups conversion was calculated according to IR data on Si-H peaks intensity as proportion of signal intensity after and before the reaction.

[2] The vinyl groups conversion was calculated according to NMR data on vinyl peaks presence.

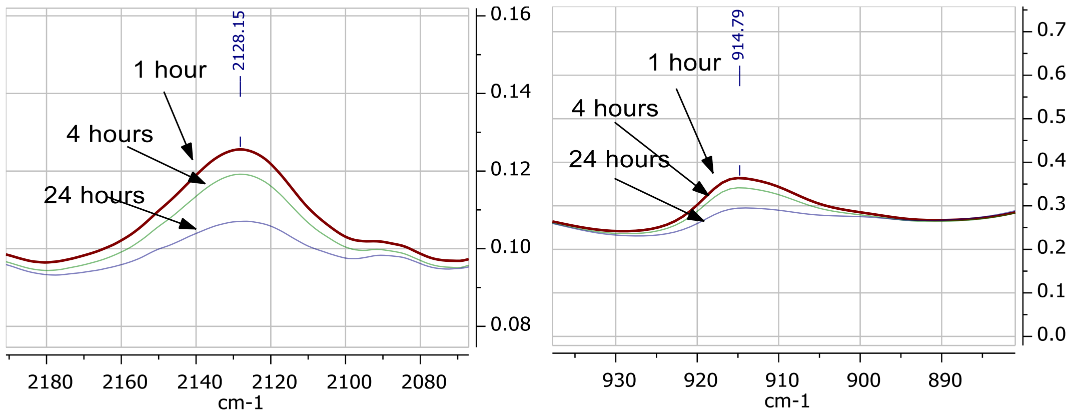

Figure S27. Dynamics of Si–H peaks in IR spectra of the hydrosilylation process of **malt-1-ac-allyl** and **PDMS-H**, catalyzed by Karstedt's catalyst at RT.

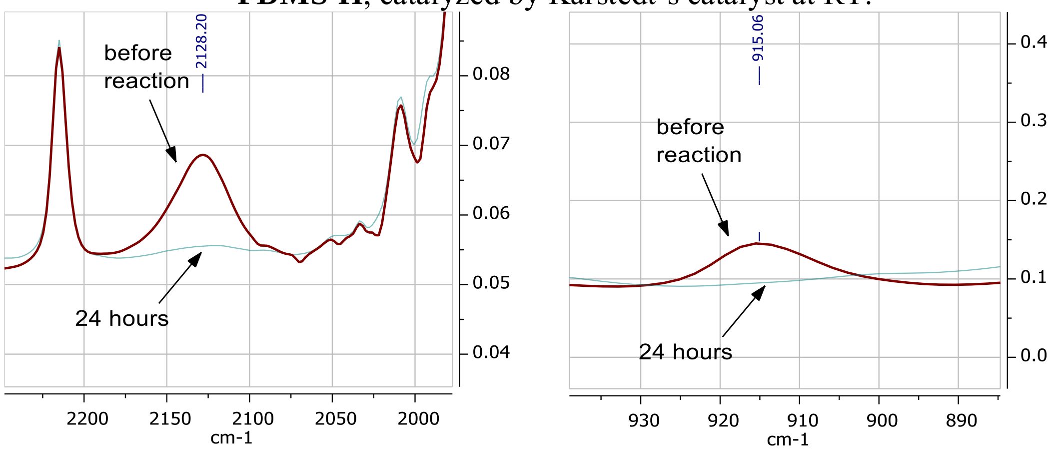

Figure S28. Dynamics of Si–H peaks in IR spectra of the hydrosilylation process of **malt-1-ac-allyl** and **PDMS-H**, catalyzed by Karstedt's catalyst at 80 °C.

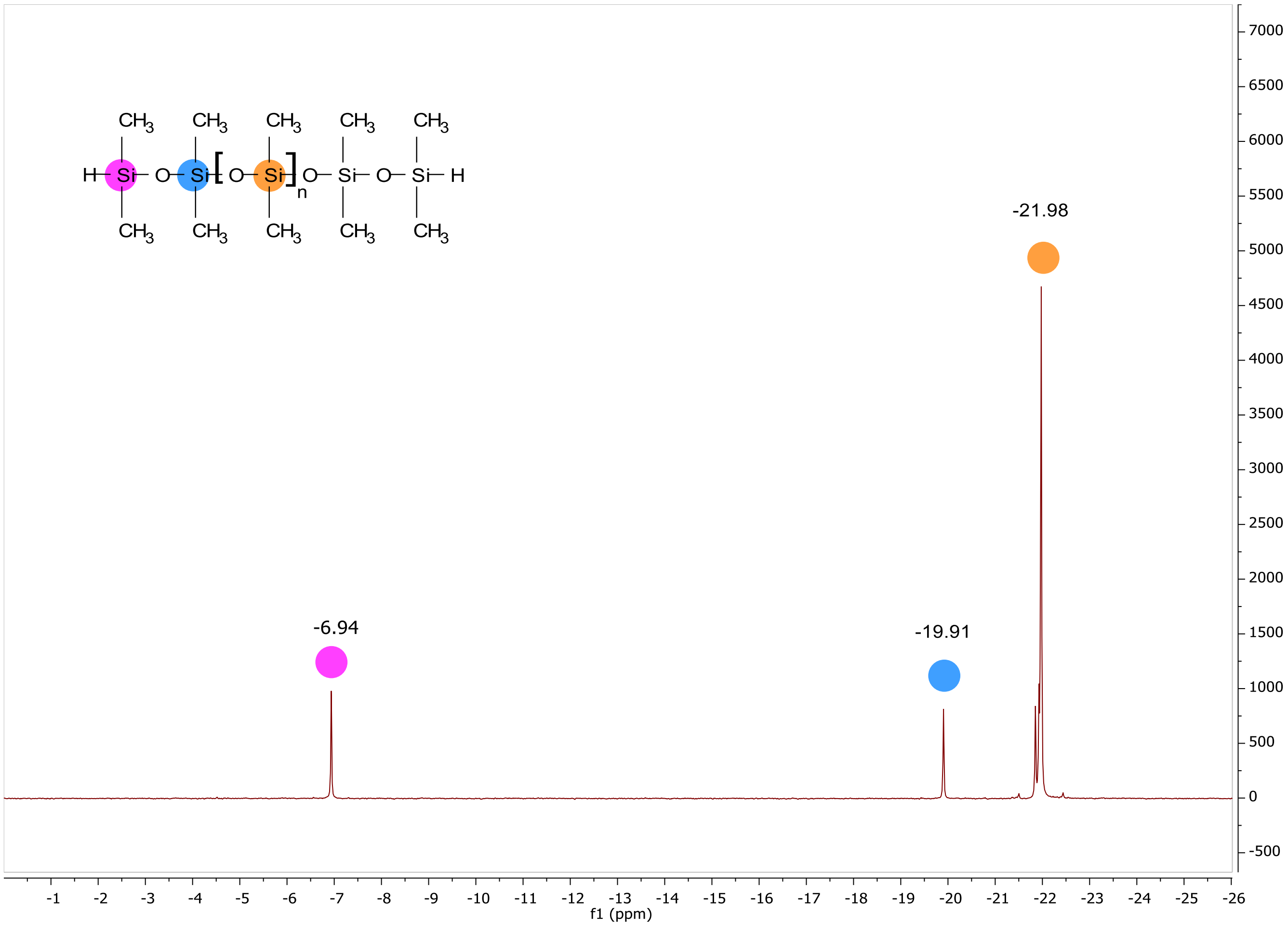

Figure S29. ^{29}Si NMR spectra of **PDMS-H**.

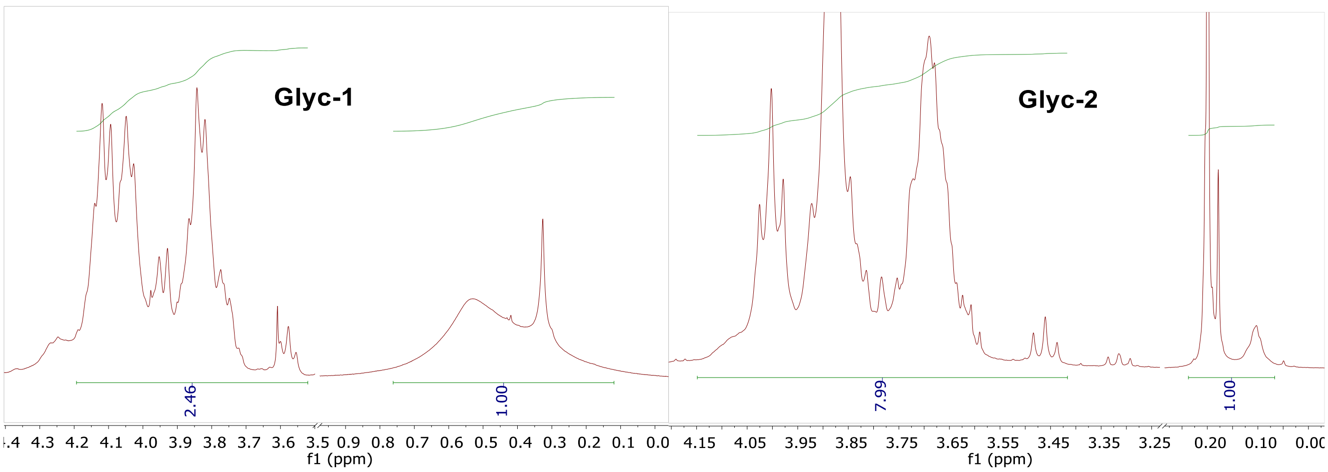

Figure S30. Integration of **glyc-1** and **glyc-2** ^{1}H NMR signals for calculation of diblock/triblock structure.

To approximate the diblock/triblock structure of the resulting glycosilicones **glyc-1** and **glyc-2** ^{1}H NMR was used.

If we have 1 mole of glycosilicone, then calculated integral intensity of maltodextrin part of the molecule is expected to be: $M_{maltodextrin}/M_{maltodextrin\ chain\ unit}\times1$ for diblock and $M_{maltodextrin}/M_{maltodextrin\ chain\ unit}\times2$ for triblock. $M_{maltodextrin\ chain\ unit}$ is 177 g/mol. We are using 1100 and 3100 as $M_{maltodextrin}$ for **glyc-1** and **glyc-2**, respectively.

Theoretical integral intensity of H1–H6 interval for **glyc-1** is 37.2 (diblock) or 74.6 (triblock).

Theoretical integral intensity of H1–H6 interval for **glyc-2** is 105.1 (diblock) or 210.2 (triblock).

Theoretical integral intensity of polysiloxane part should be $M_{polysiloxane}/M_{polysiloxane\ chain\ unit} \times 6$ or $900/74 \times 6 = 72.9$.

Theoretical ratios CH_3–Si/H1–H6 for **glyc-1** are 1:0.5 (diblock) or 1:1.02 (triblock).

Theoretical ratios CH_3–Si/H1–H6 for **glyc-2** are 1:1.44 (diblock) or 1:2.9 (triblock).

From the ^{1}H NMR experiments we obtained ratios of 1:2.5 for **glyc-1** and 1:8 for **glyc-2**.

We assumed, that a diblock copolymer is a polymer consisting of two homopolymers linked together in one chain; a triblock copolymer is a polymer consisting of three homopolymers, linked together in one chain.

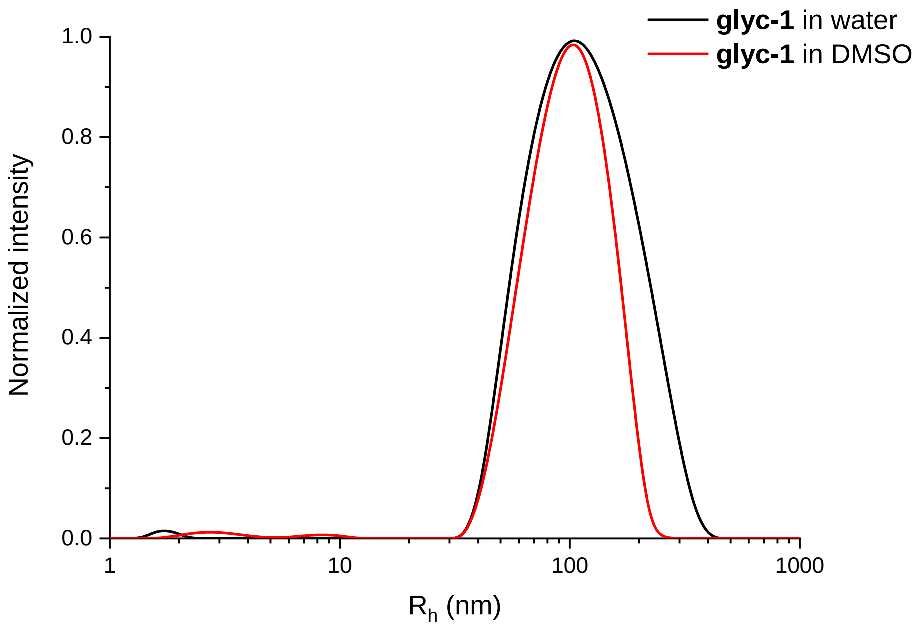

Figure S31. Dynamic light scattering results of **glyc-1** solutions.

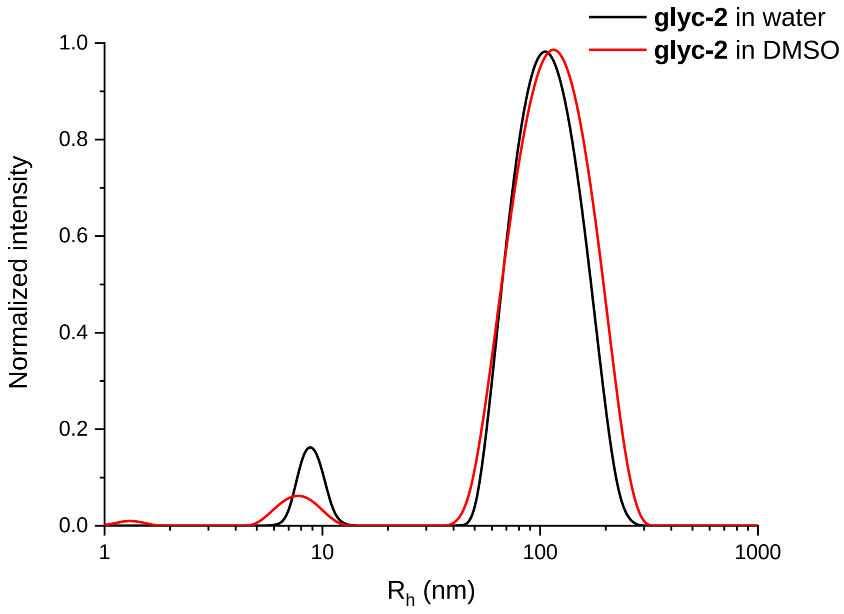

Figure S32. Dynamic light scattering results of **glyc-2** solutions.

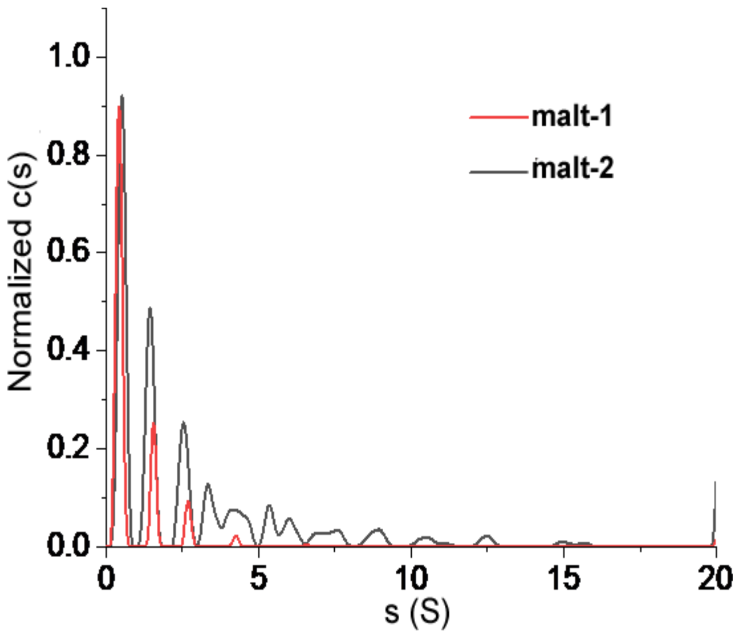

Figure S33. Differential distributions of the sedimentation coefficients for **malt-1** and **malt-2** in water (n = 42000 rpm, c = 0.1% w/w).

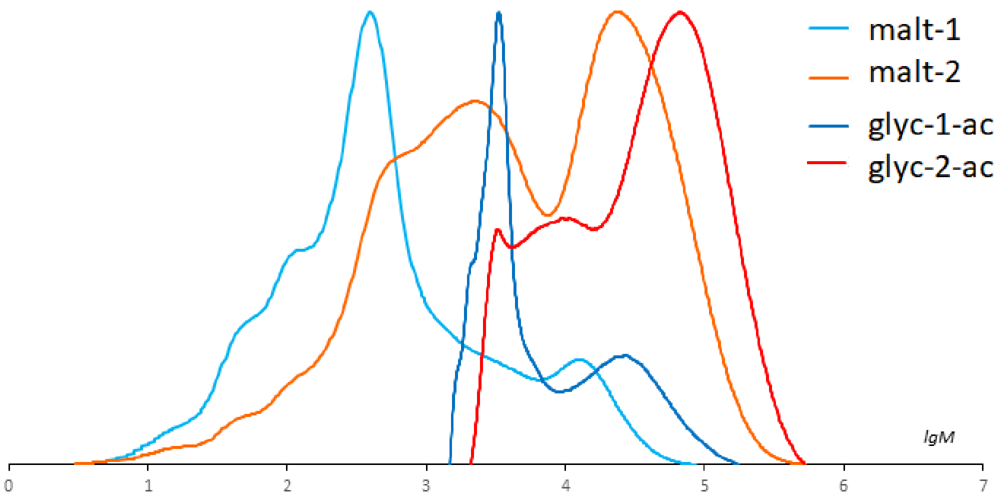

Figure S34. SEC of **malt-1** and **malt-2**, **glyc-1-ac** and **glyc-2-ac**.

Table S2. Molecular weight characteristics of **malt-1** and **malt-2**, **glyc-1-ac** and **glyc-2-ac**, obtained by SEC.

Sample		$M_w \times 10^{-3}$ (*Đ*), Da		
	Mass concentration of high molecular weight fraction, %	High molecular weight fraction	Low molecular weight fraction	Total
malt-1 *	16.6	16.8 (1.28)	0.91 (6.09)	3.57 (19.8)
malt-2 *	54.5	44 (1.84)	2.09 (5.51)	25.0 (30.4)
glyc-1-ac **	30.8	29.3 (1.44)	3.71 (1.15)	12.0 (2.71)
glyc-2-ac **	59.9	76.6 (1.71)	7.25 (1.31)	51.0 (4.10)

* 0.5 M $NaNO_3$, 0.05% NaN_3, 30 °C, TSKgel SuperAW-H, SuperAW4000, SuperAW2500, pullulan standards;
** 0.1 M $LiN(SO_2CF_3)_2$, DMF, 60 °C, TSKgel Guard, $G5000H_{HR}$, polystyrene standards.

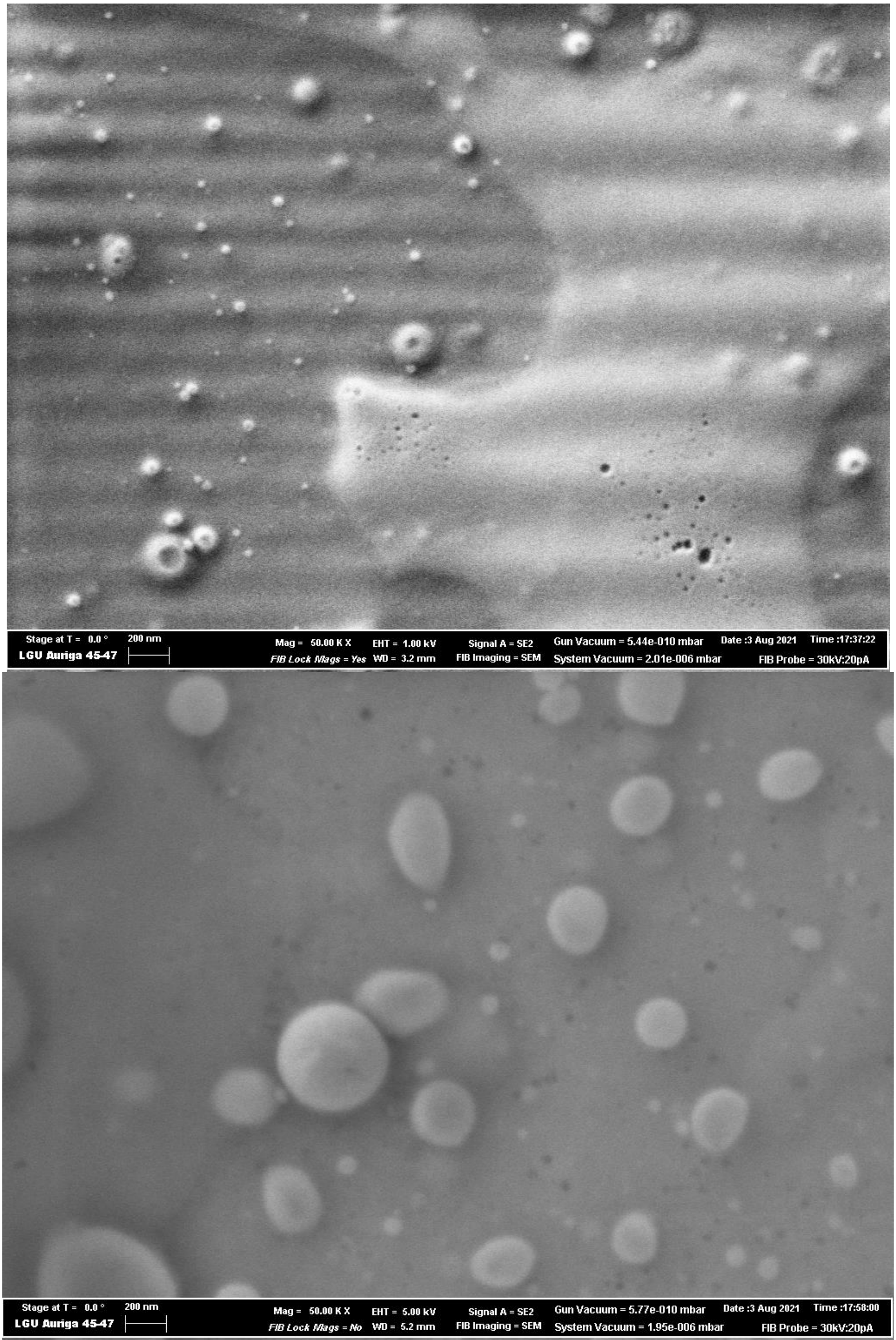

Figure S35. SEM images of **glyc-1**, obtained from aqueous solutions.

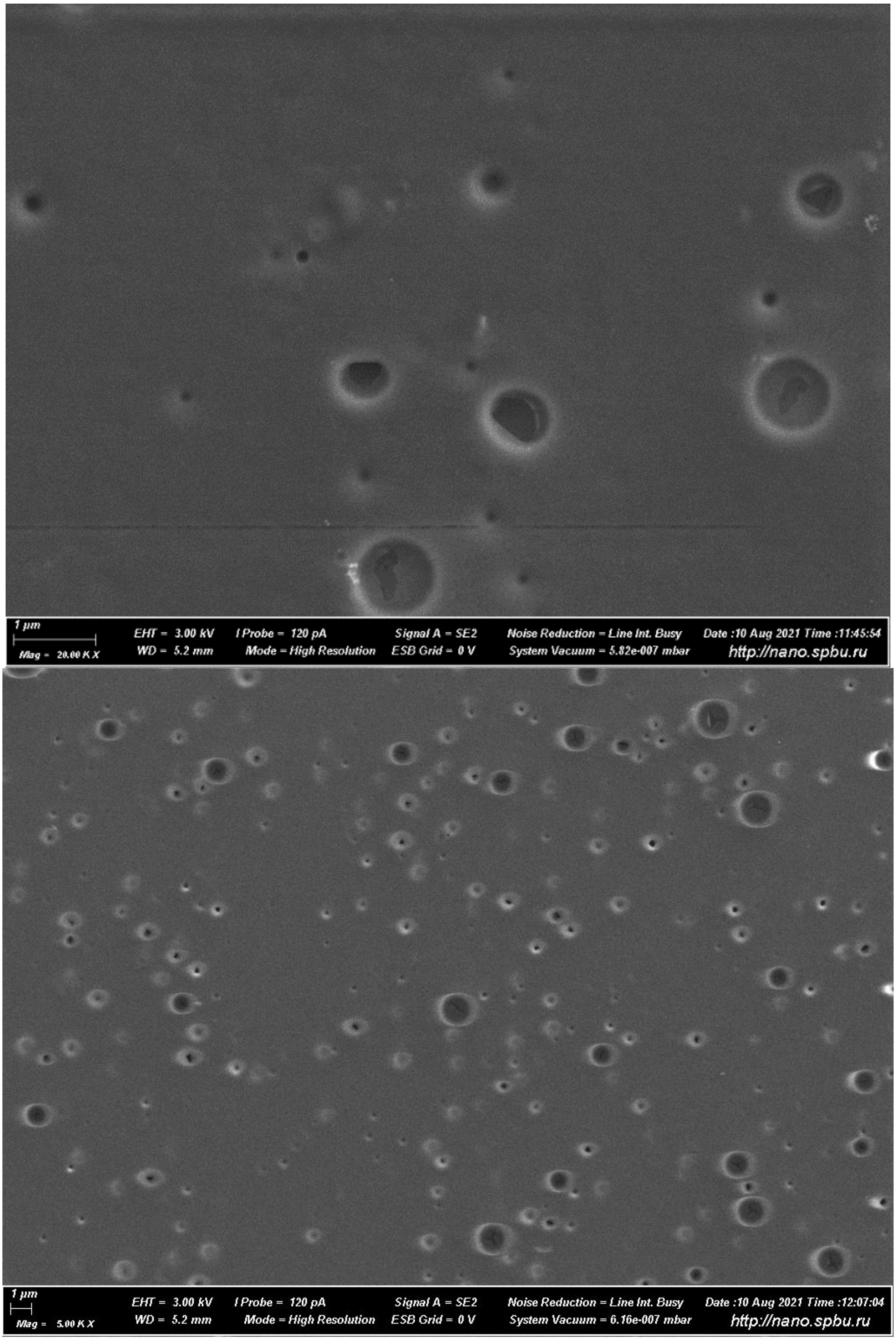

Figure S36. SEM images of **glyc-2**, obtained from aqueous solutions.

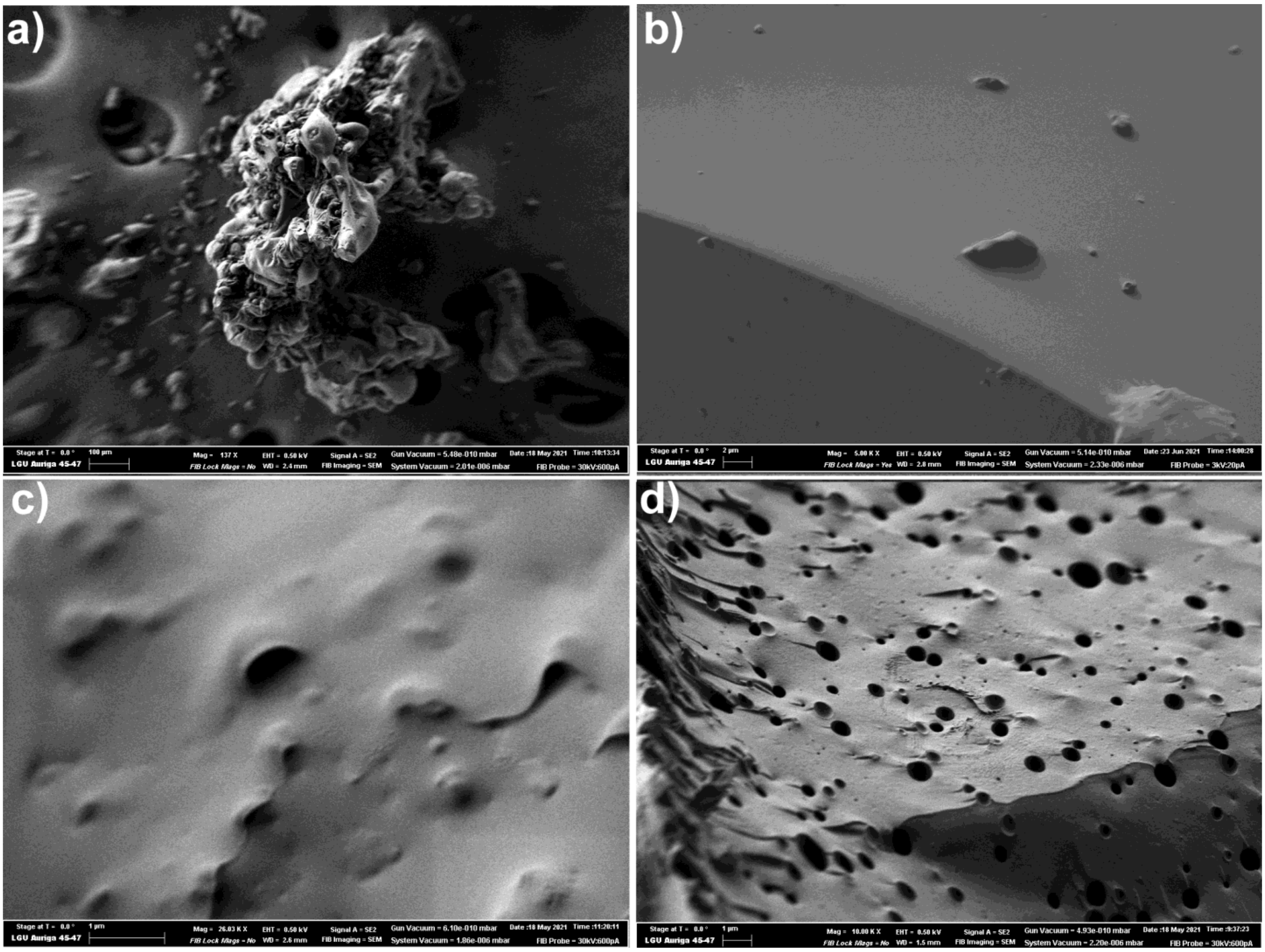

Figure S37. SEM images of solid **malt-2** (a), silicone rubber[1] (b), **glyc-1** (c) and **glyc-2** (d).

[1] Obtained from α,ω-hexavinylpolydimethylsiloxane and poly(dimethyl-*co*-methylhydrosiloxane) with Karstedt's catalyst according to previously published method from Dobrynin, M. V., Pretorius, C., Kama, D. V., Roodt, A., Boyarskiy, V. P., & Islamova, R. M. (2019). Rhodium(I)-catalysed cross-linking of polysiloxanes conducted at room temperature. Journal of Catalysis, 372, 193–200. https://doi.org/10.1016/j.jcat.2019.03.004

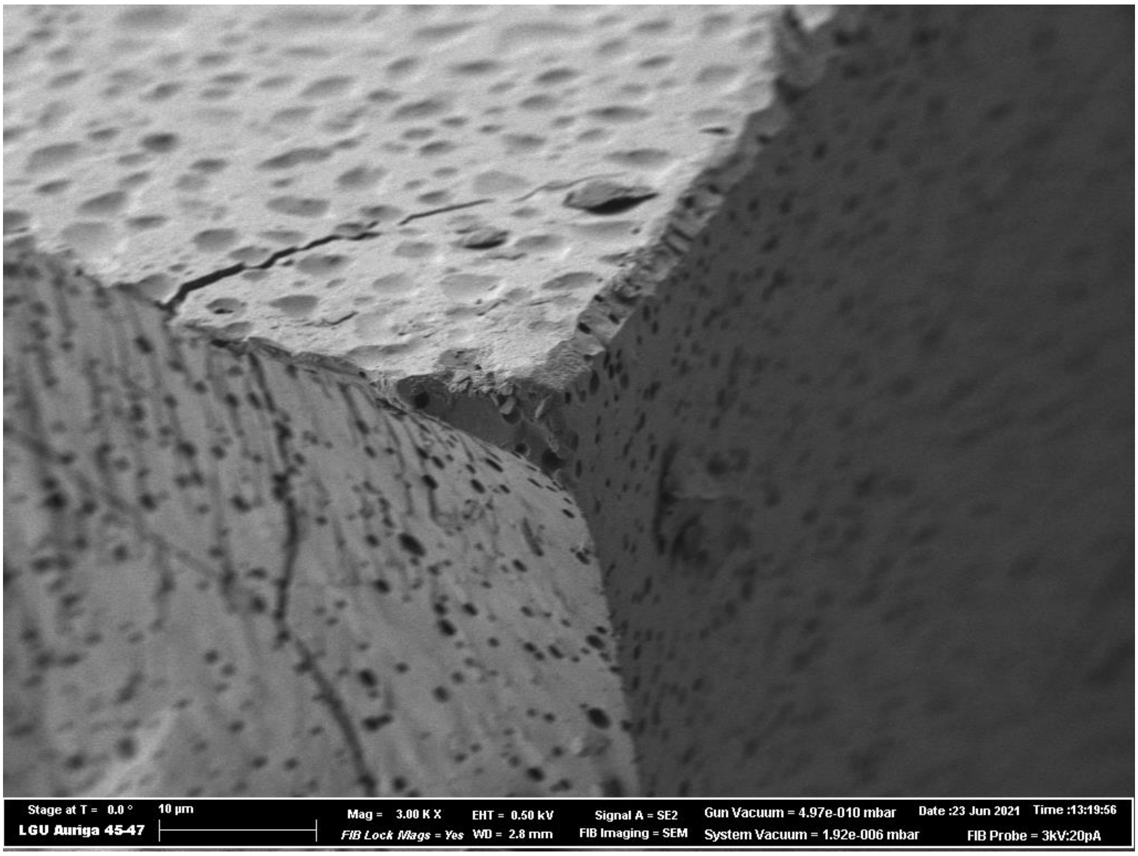

Figure S38. SEM image of solid **glyc-2**.