

Synthesis, Self-assembly and Langerin Recognition Studies of a Resorcinarene-based Glycocluster Exposing a Hyaluronic Acid Thiodisaccharide Mimetic

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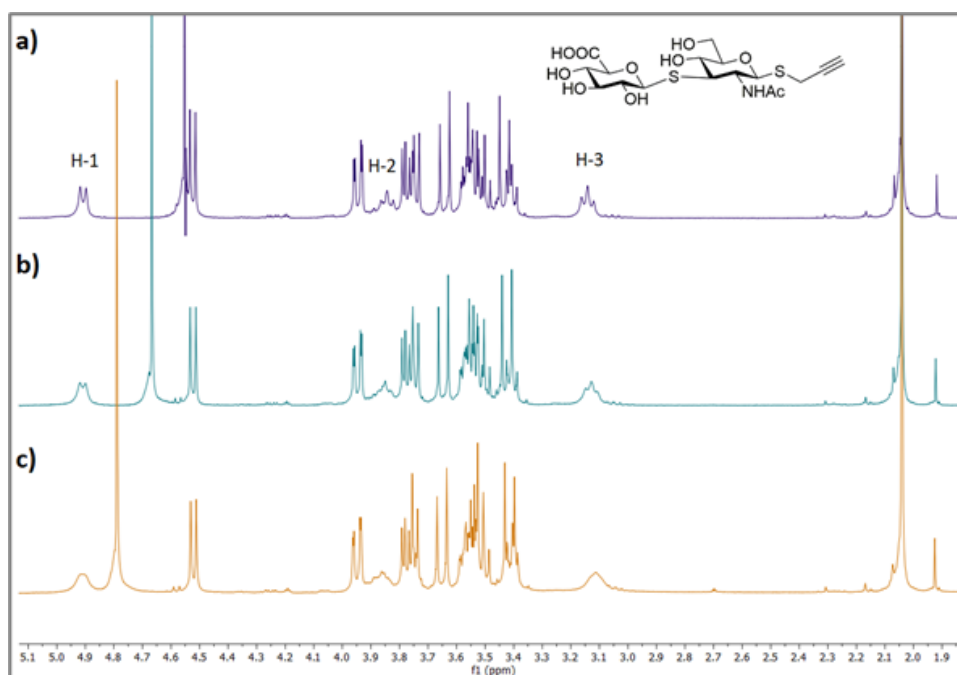


Figure S1. ^1H NMR spectrum (500 MHz) of compound **3** in D_2O at a) 45 °C, b) 35 °C and c) 25 °C.

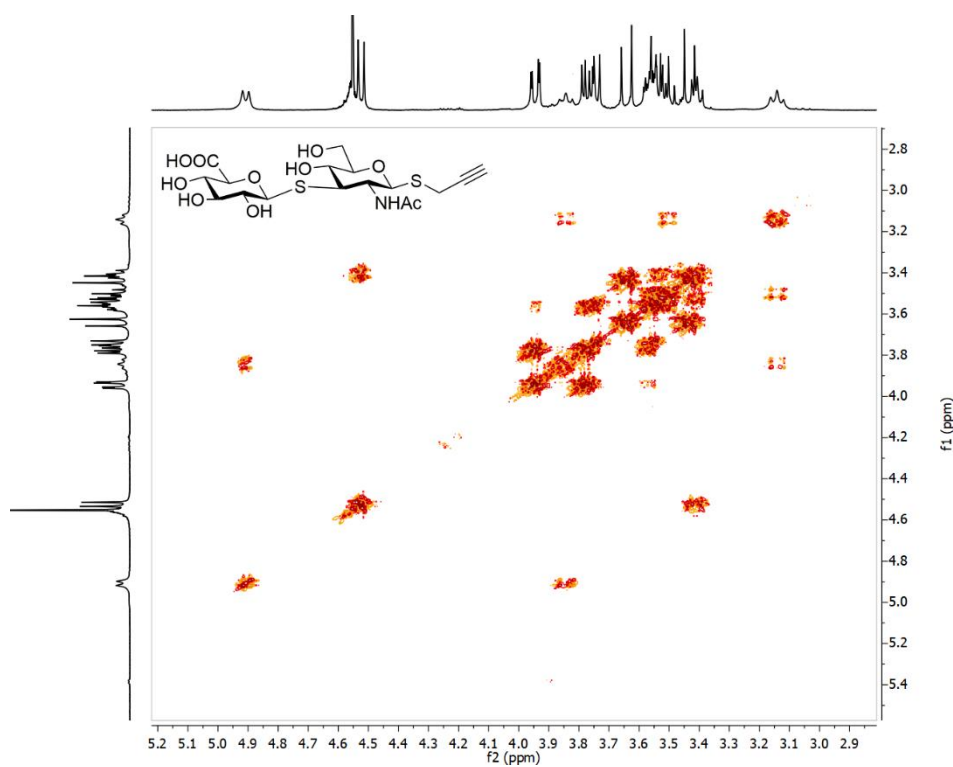


Figure S2. ^1H - ^1H COSY NMR spectrum (500 MHz) of compound **3** in D_2O at 45 °C.

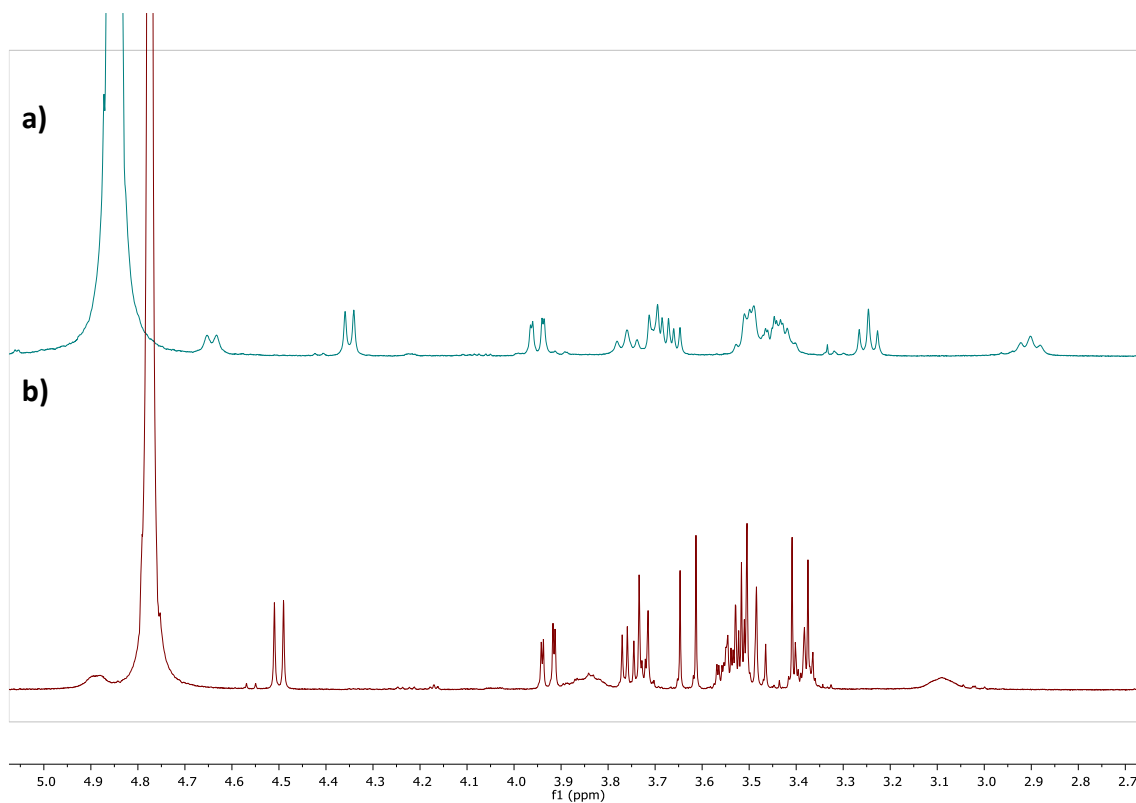


Figure S3. ^1H NMR spectra (500 MHz) of compound **3** in D_2O at pH 12 (a) and pH 5 (b). Alkalinization of the pH 5 sample was performed adding to the NMR tube NaOD (10%) in D_2O .

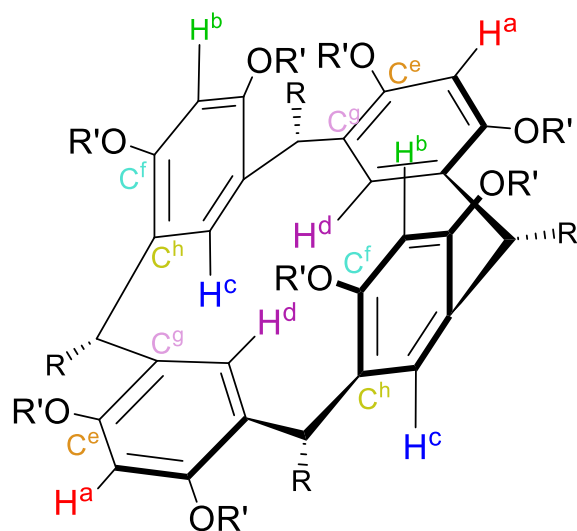


Figure S4. Schematic representation of the resorcinarene aromatic core in its *flattened boat* conformation with C_{2v} symmetry.

Acquisition Parameter

| | | | | | |
|-------------|------------|-----------------------|-----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 2.7 Bar |
| Focus | Not active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 100 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 6.0 l/min |
| Scan End | 2700 m/z | Set Collision Cell RF | 600.0 Vpp | Set Divert Valve | Source |

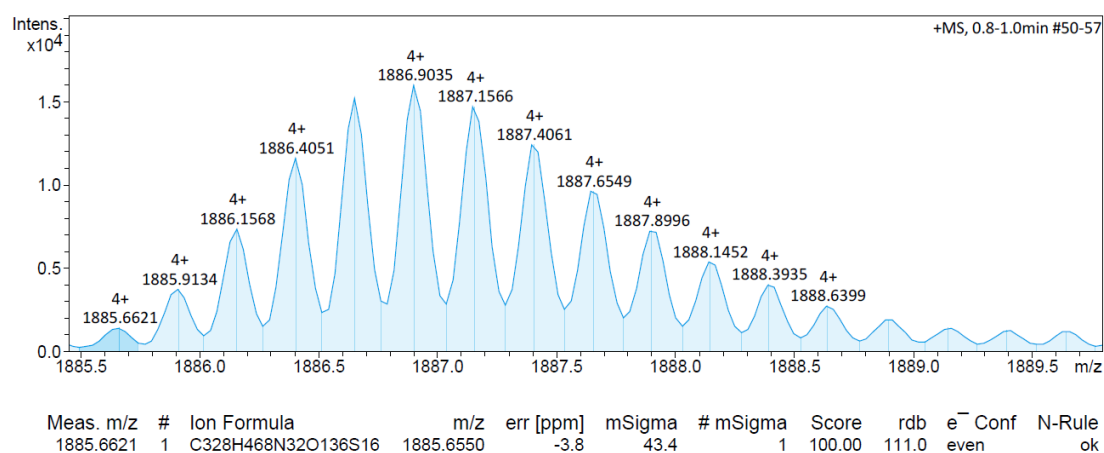


Figure S5. ESI-HRMS spectrum of compound 5.

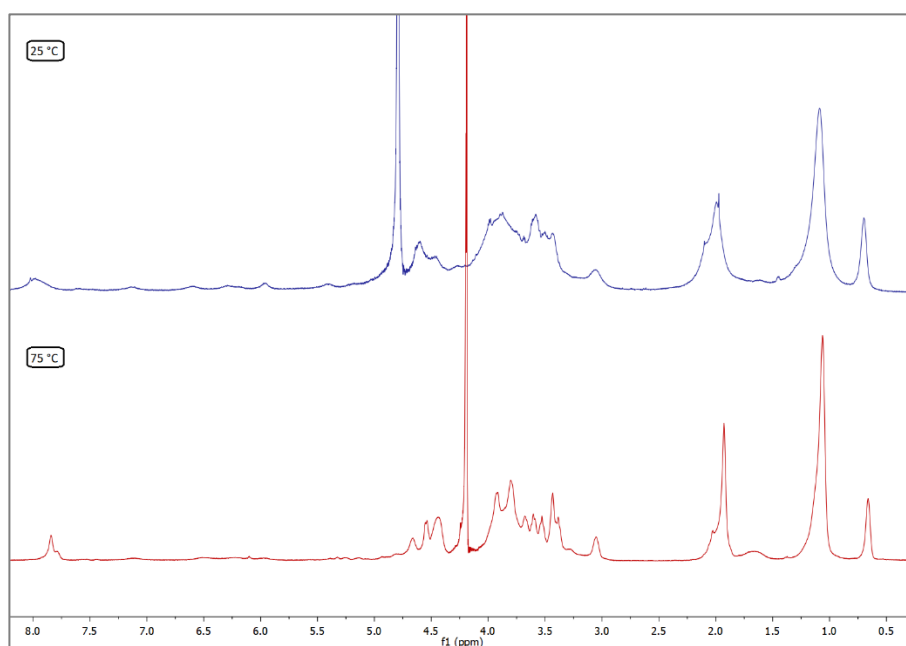


Figure S6. ¹H NMR spectra of compound 6 (500 MHz) in D₂O at 25 °C (up) and 75 °C (down).

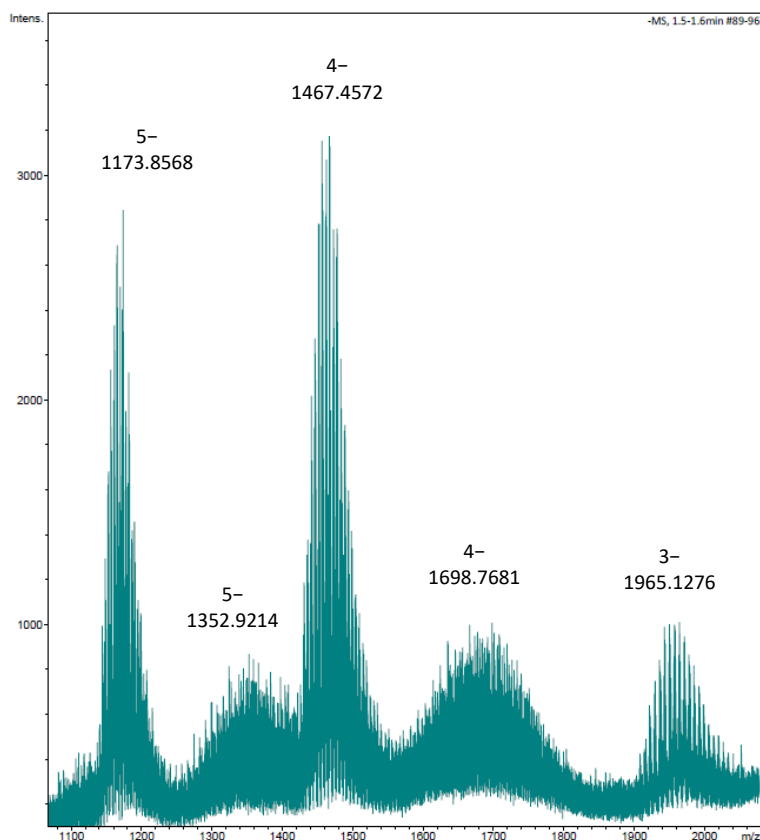


Figure S7. ESI-HRMS spectrum of compound **6**.

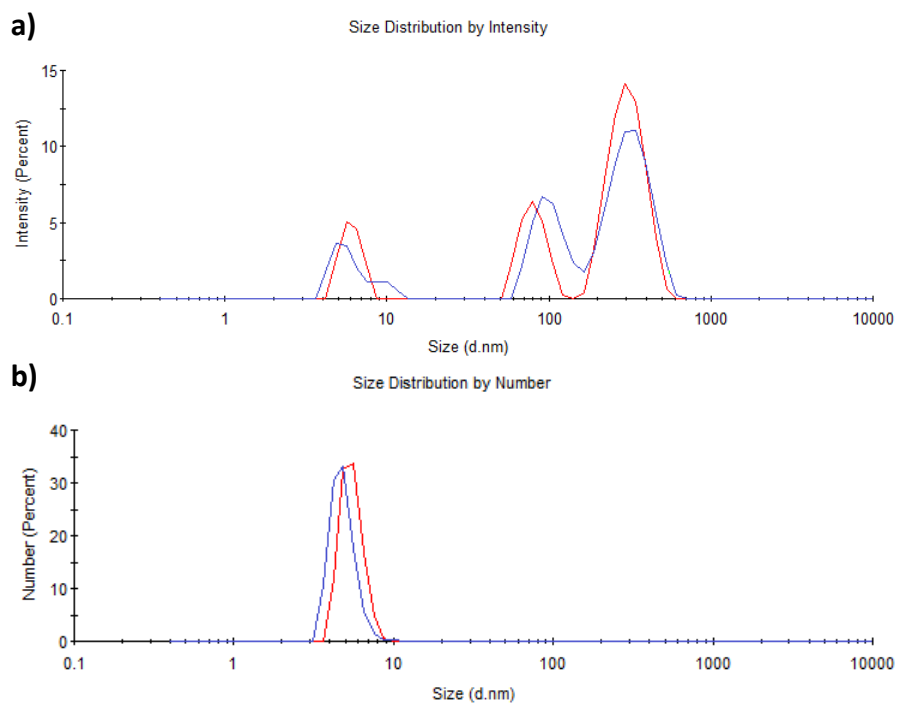
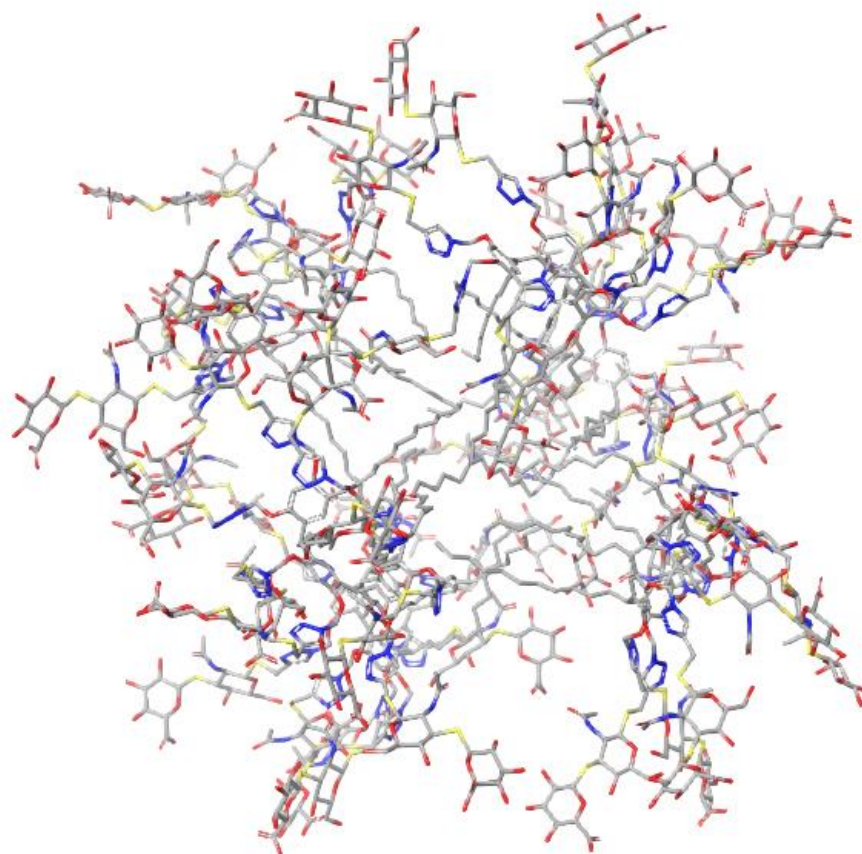
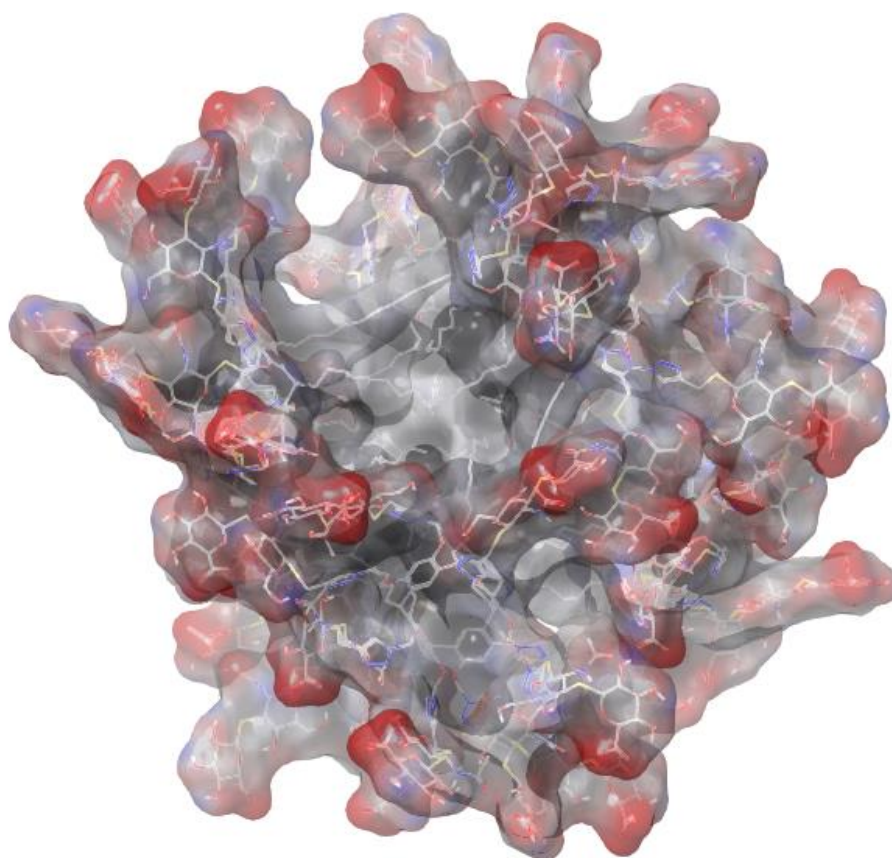


Figure S8. Dynamic light scattering analysis of glycoresorcinarene **6** in water. Particle size distribution by a) intensity and b) number.

a)



b)



c)

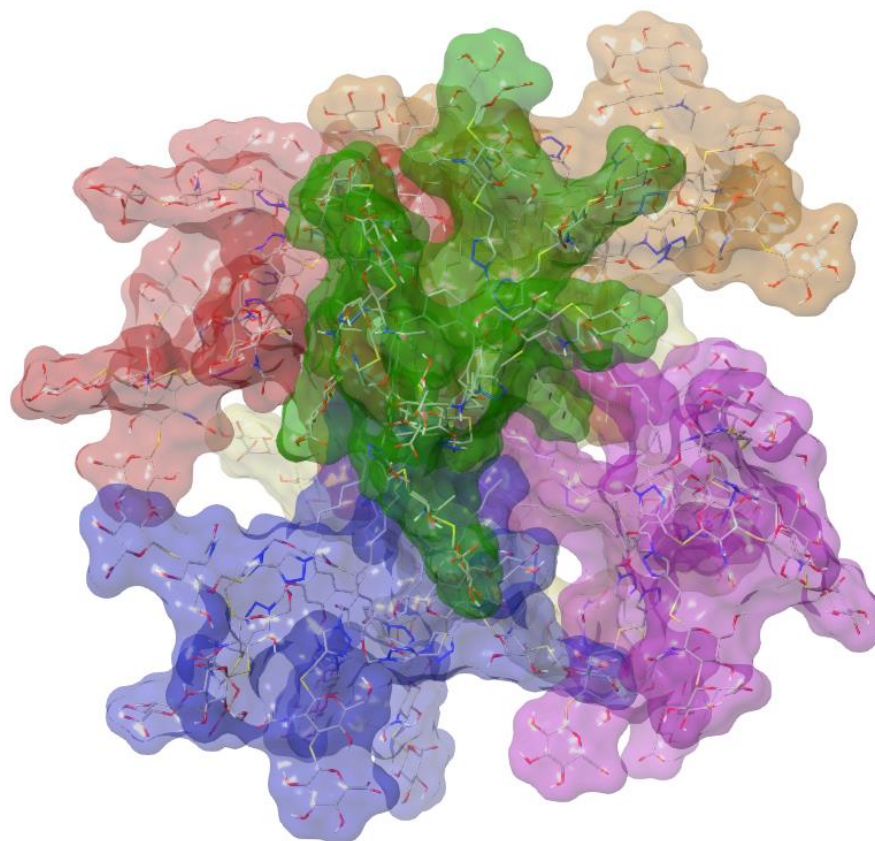
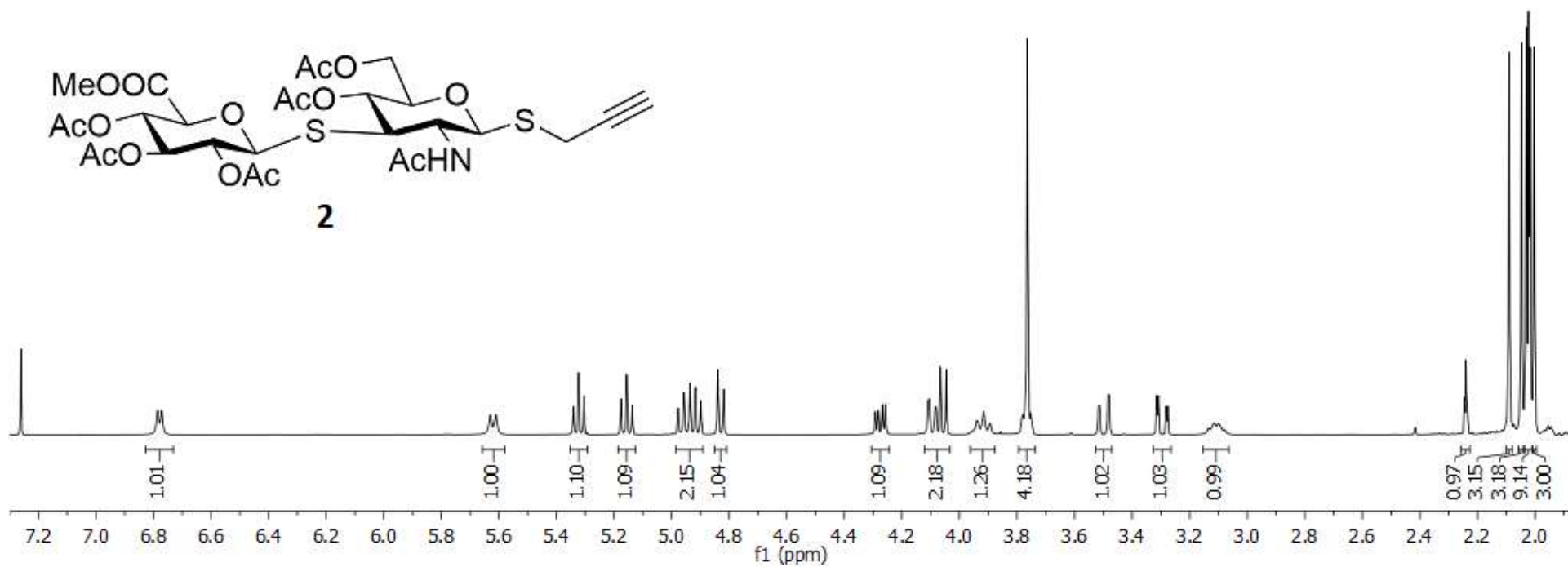
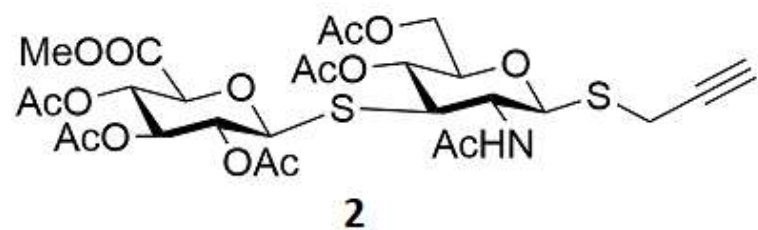
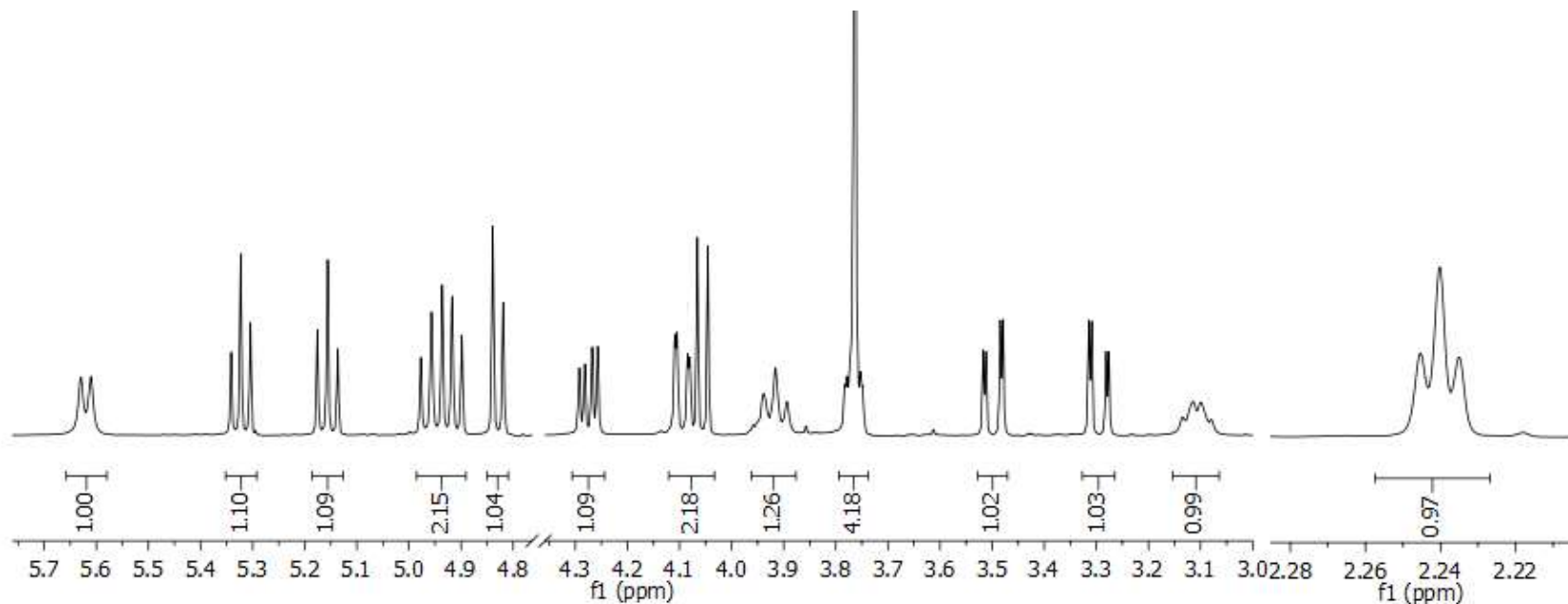


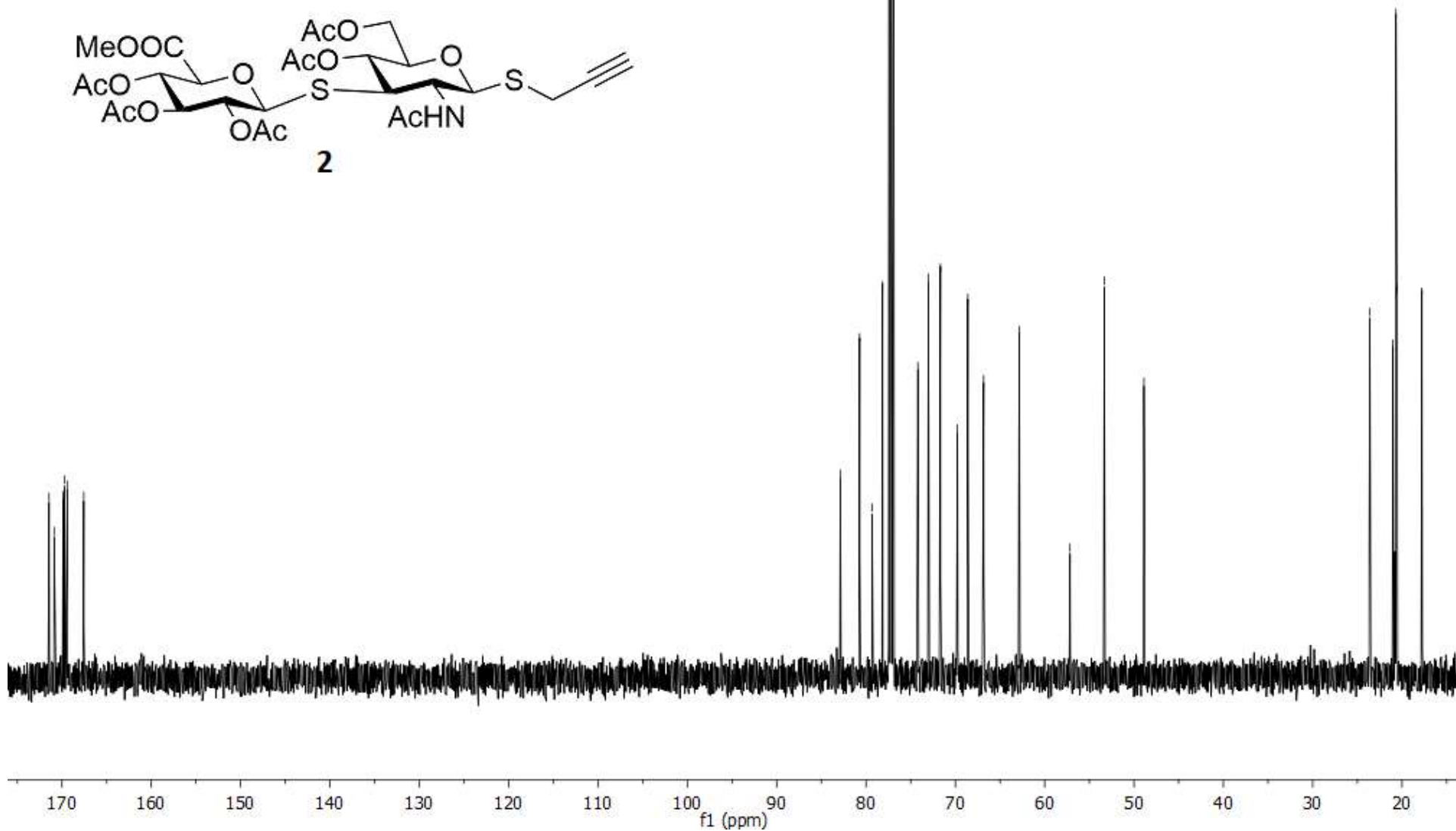
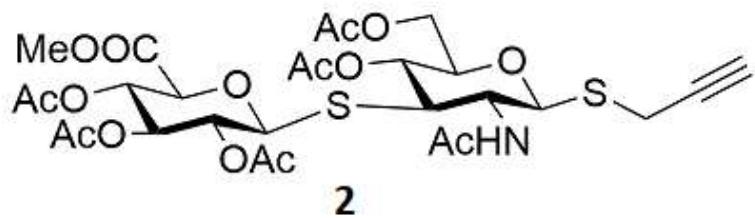
Figure S9. Proposed hexameric assembly of glycoresorcinarene **6**. a) All-atom structure of the micelle obtained by MM and restrained MD simulations, b) Surface of the micelle mapping electrostatic potential, c) Surface of the hexamer with monomers distinguished by colour.

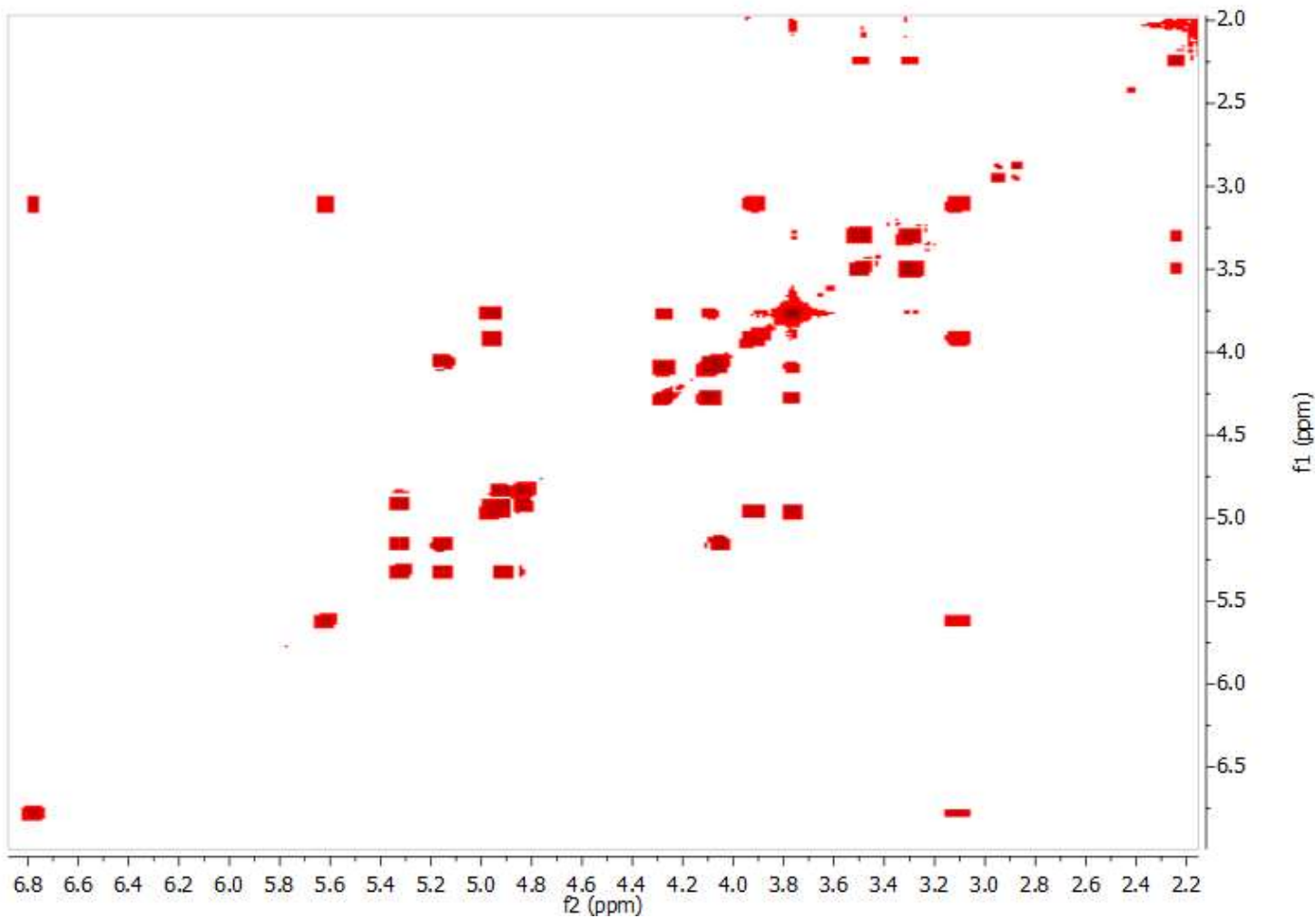
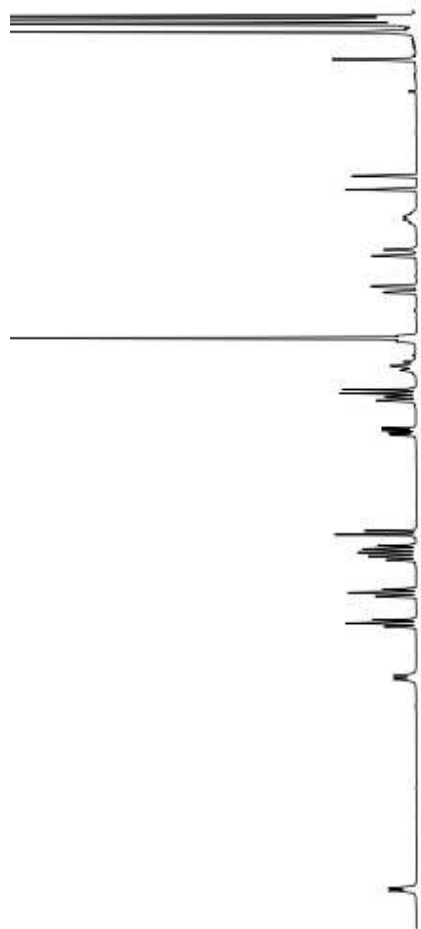
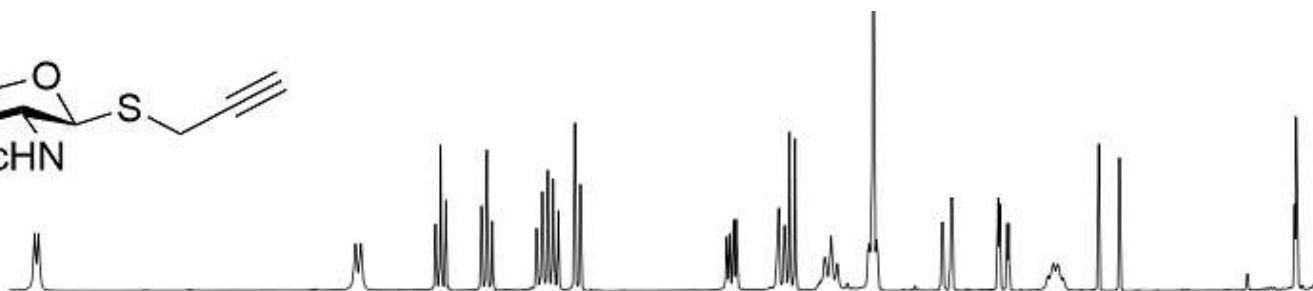
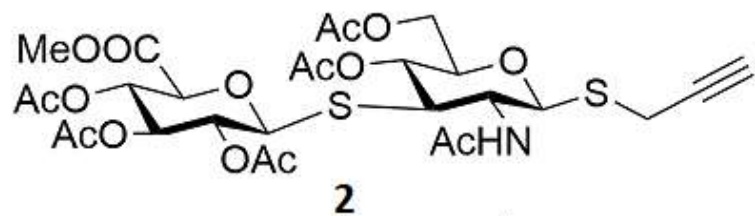


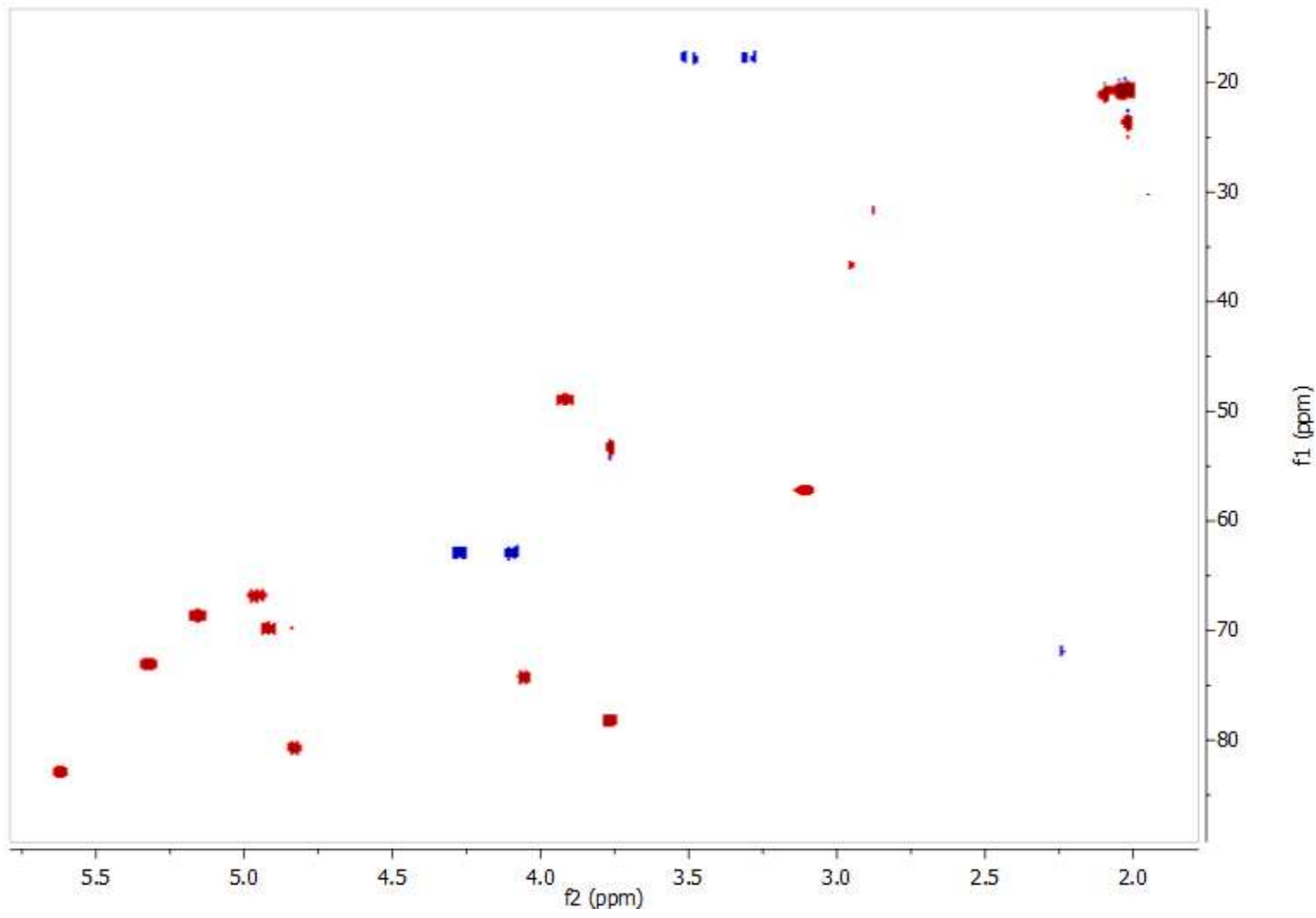
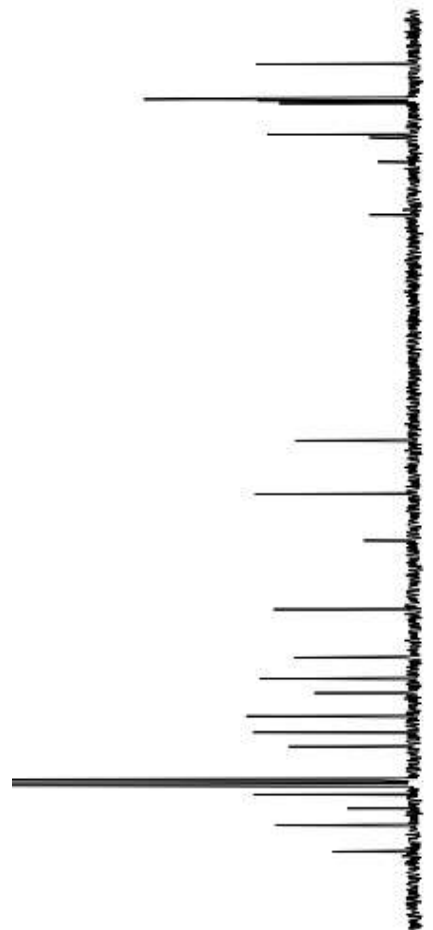
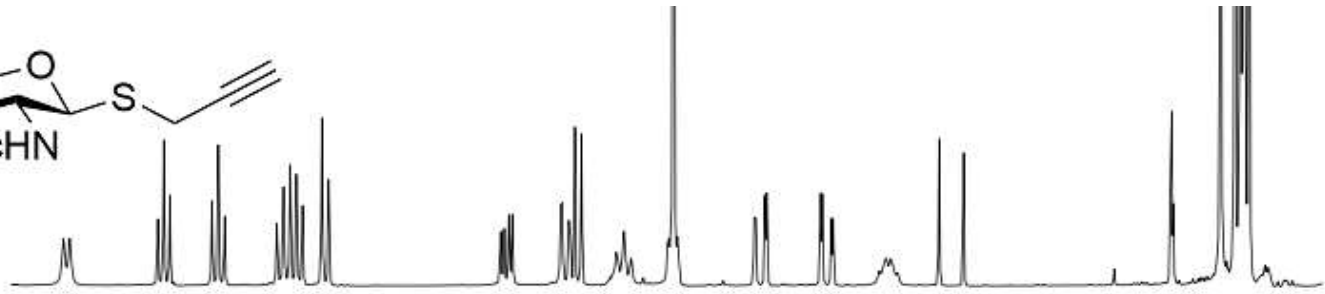
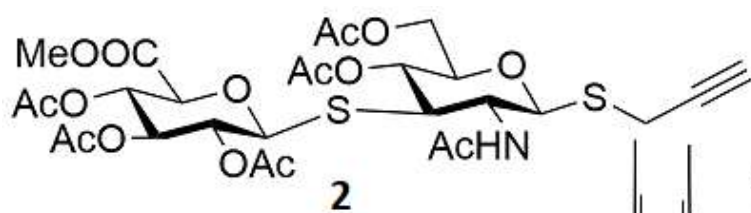
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170.9
169.9
169.7
169.4
169.4
167.6

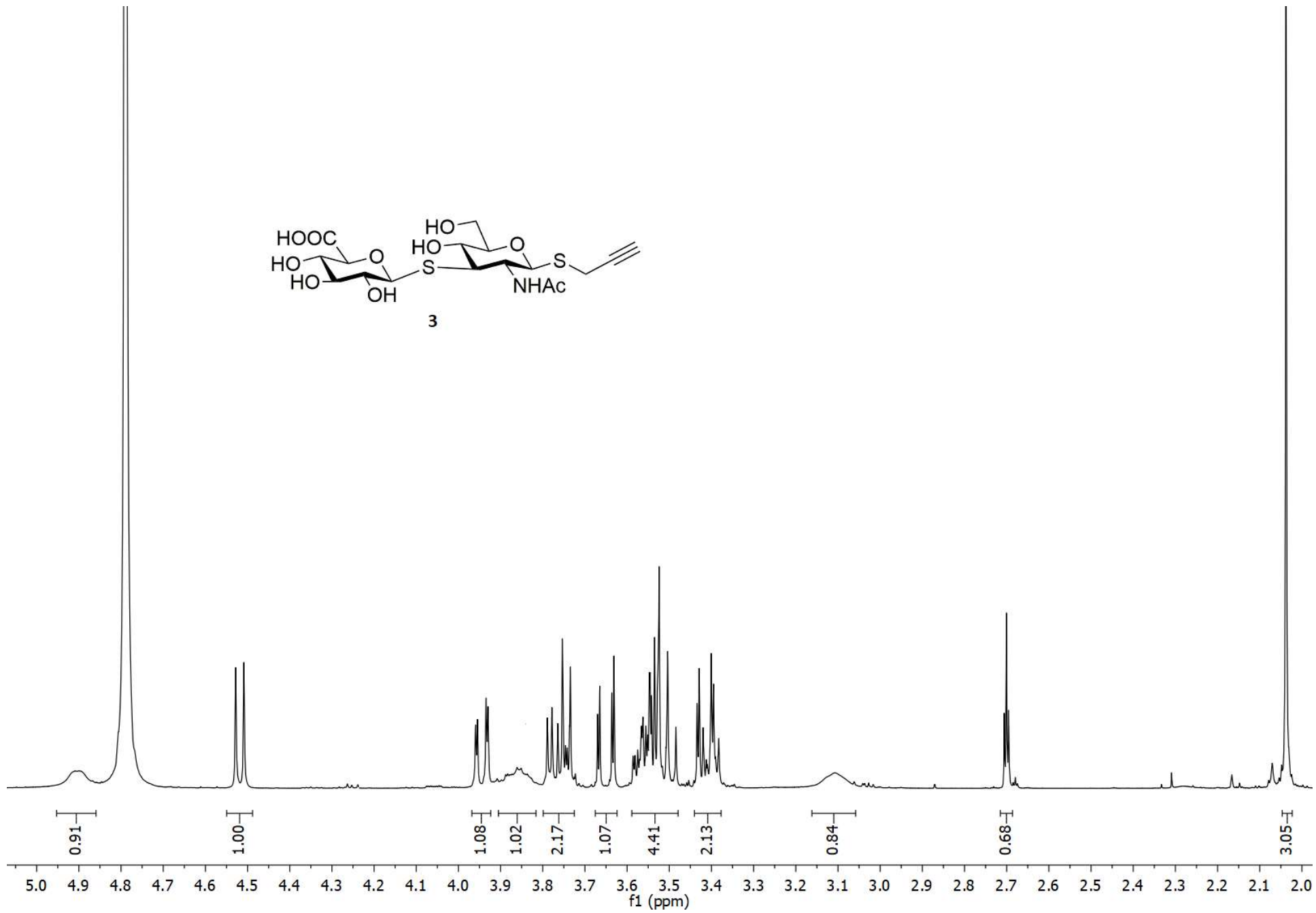
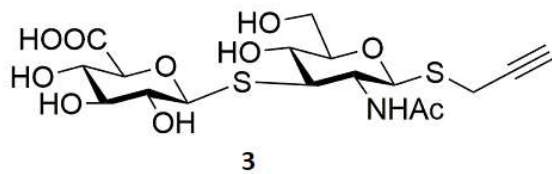
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80.7
79.3
78.1
74.2
73.0
71.7
69.8
68.6
66.8
62.8
57.2
53.3
48.9

23.6
21.0
20.8
20.7
20.6
17.8





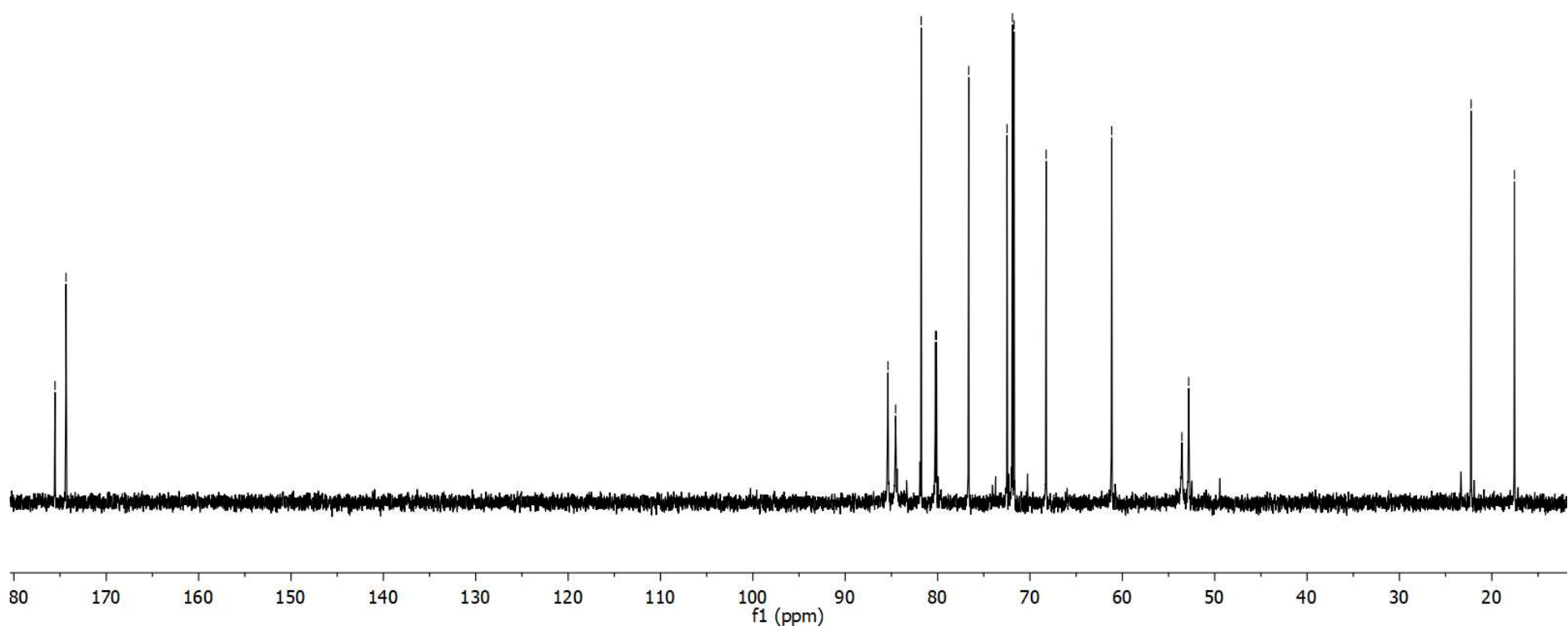
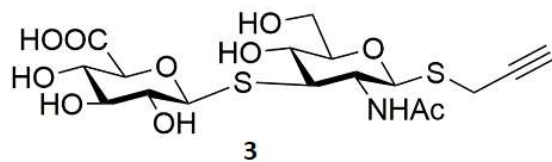


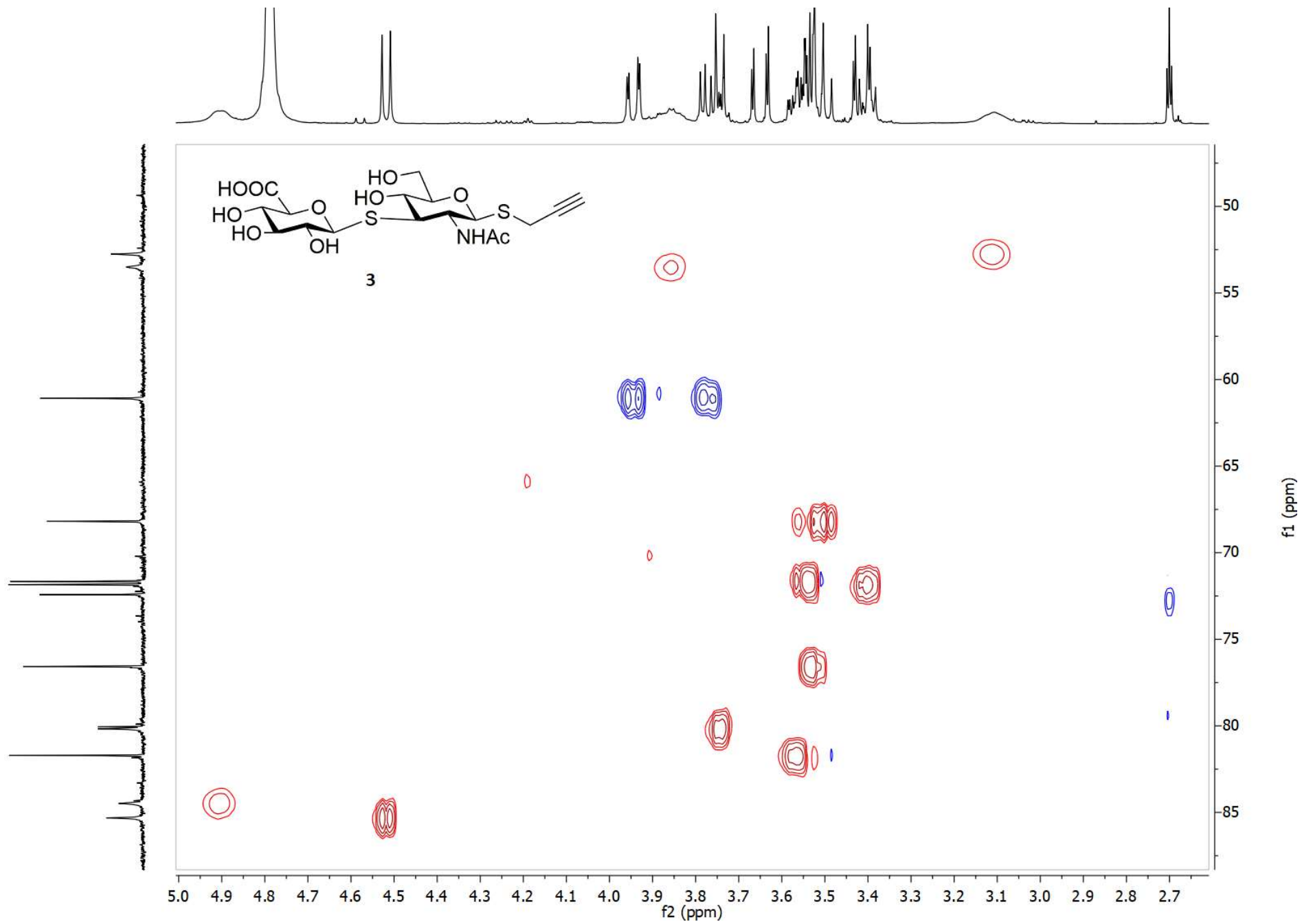


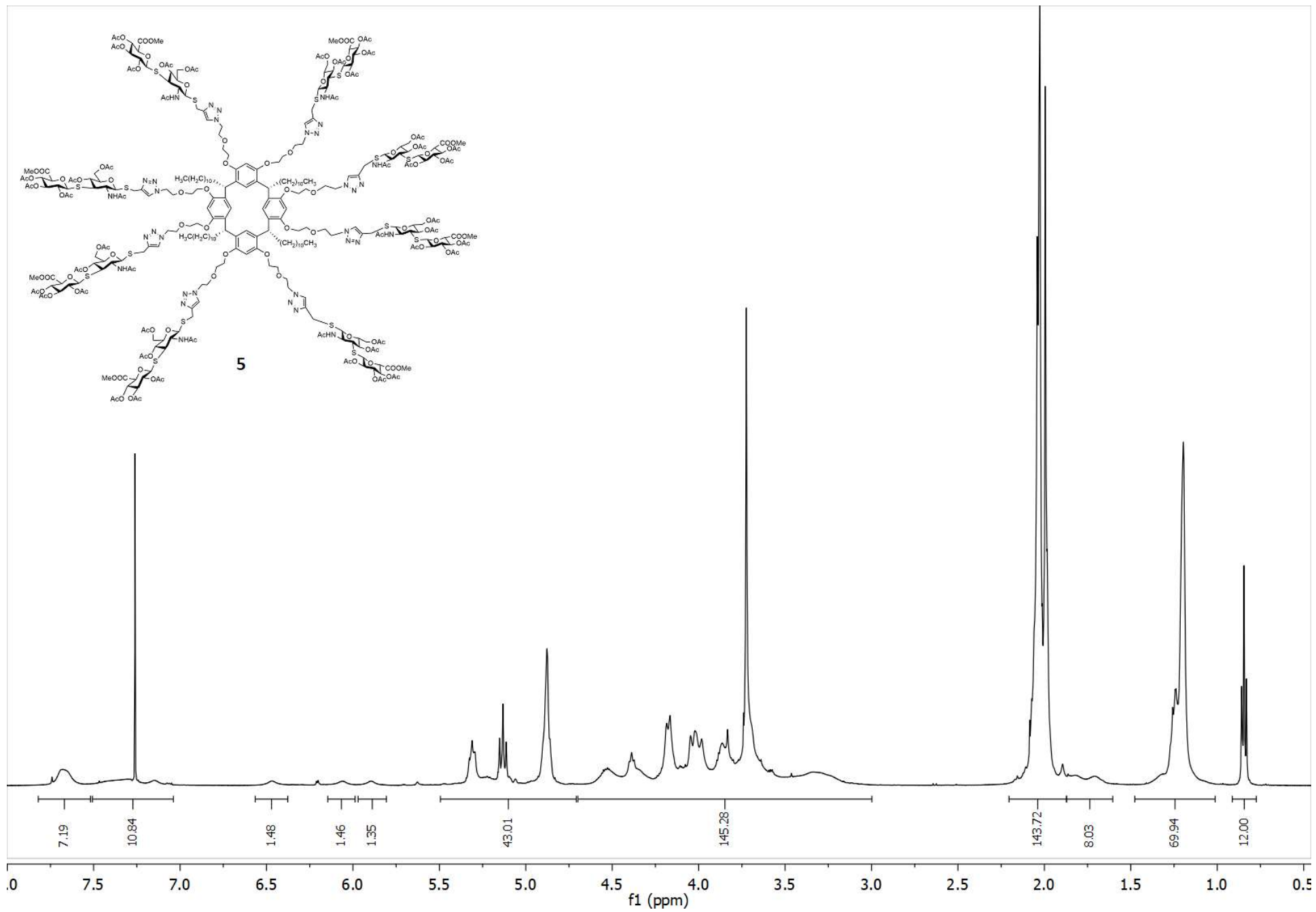
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174.4

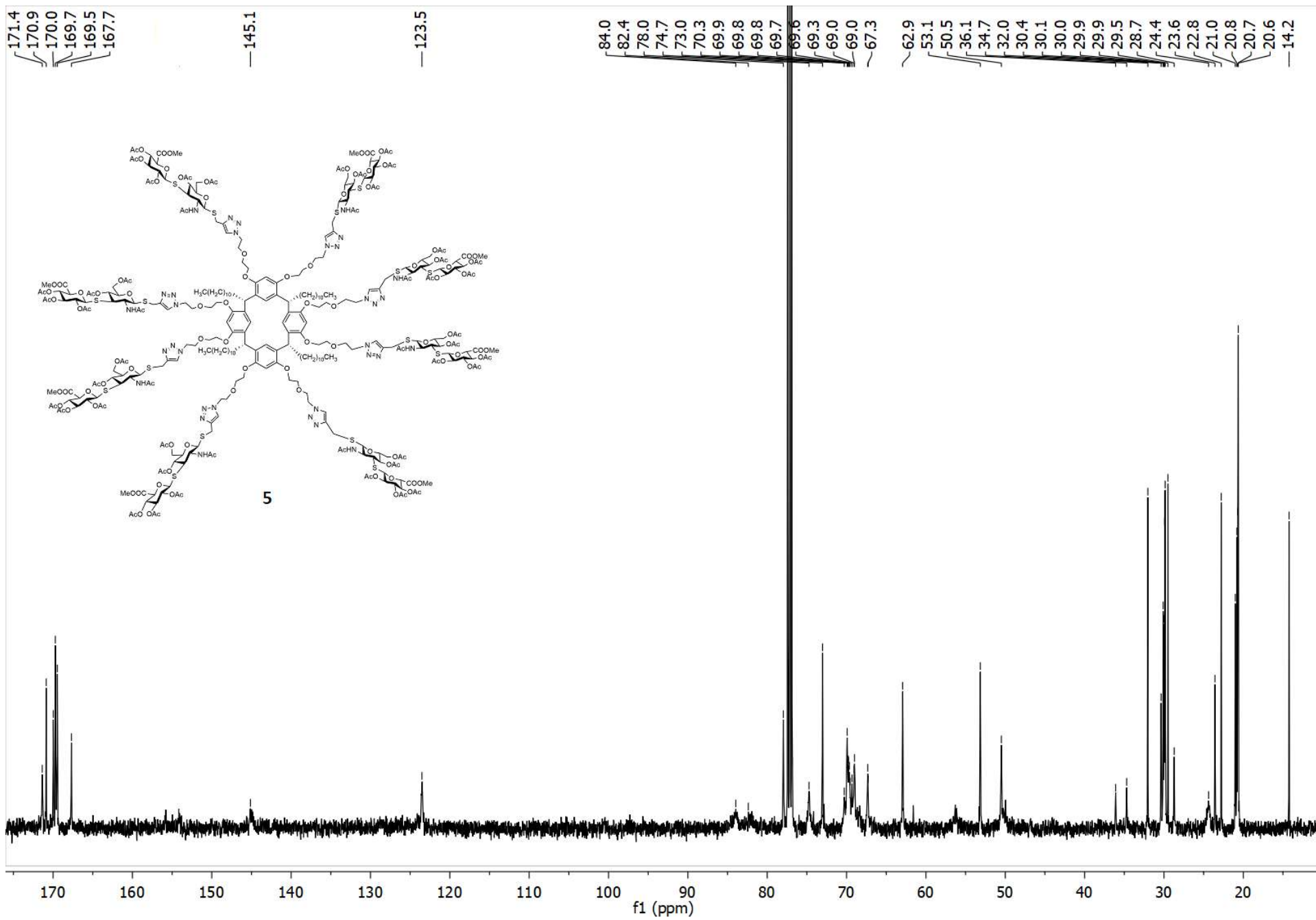
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84.5
81.8
80.2
80.1
76.6
72.5
71.9
71.7
68.2
61.1
53.6
52.8

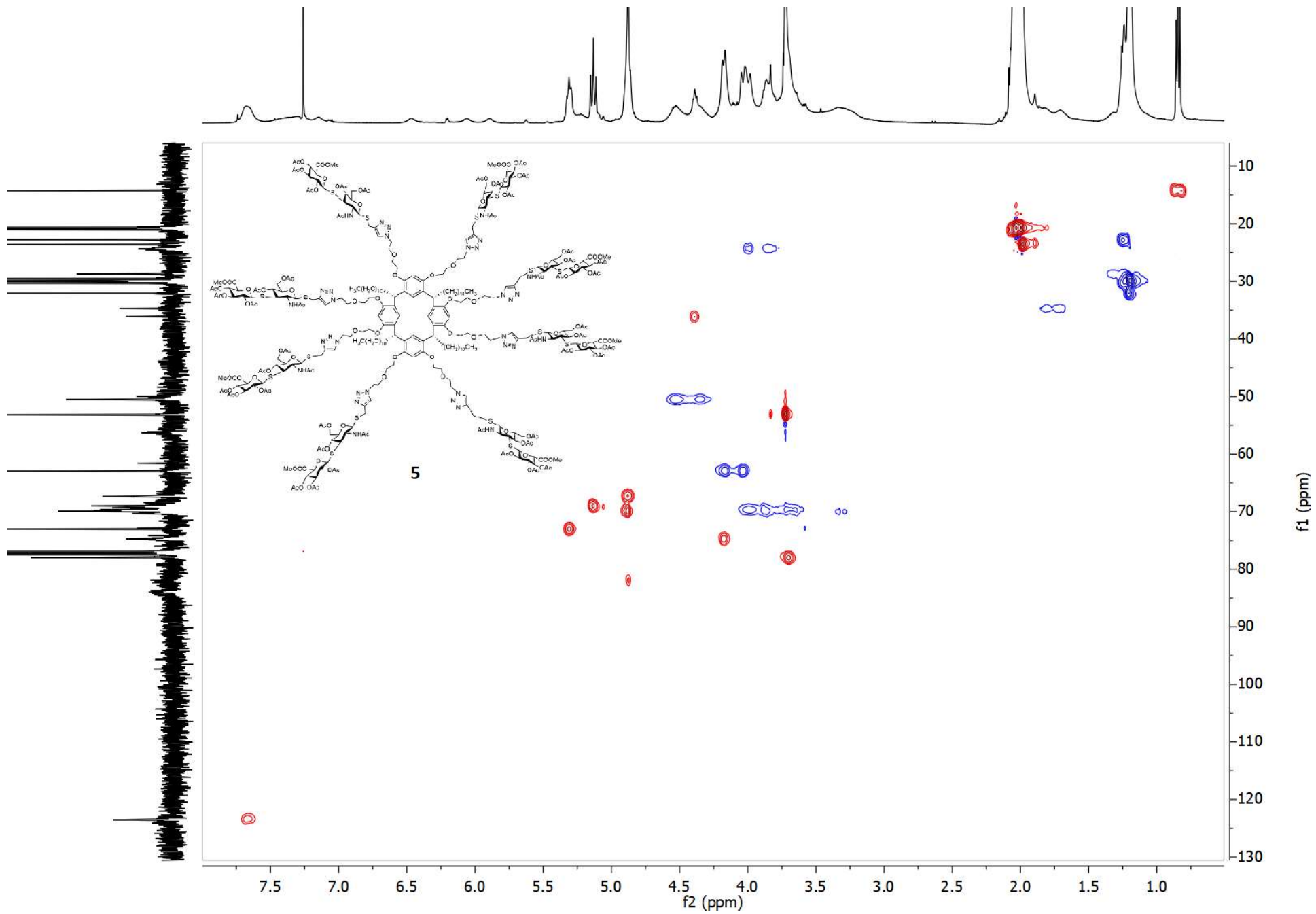
22.2
17.6

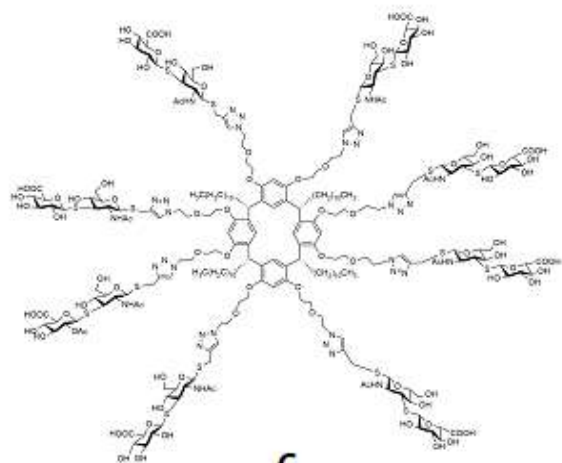












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