

Supplementary Material

Synthesis of cyclodextrin derivatives with monosacharides and their binding with ampicillin and selected lectins

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Dedicated to Professor Michael Orfanopoulos on the occasion of his 67th birthday

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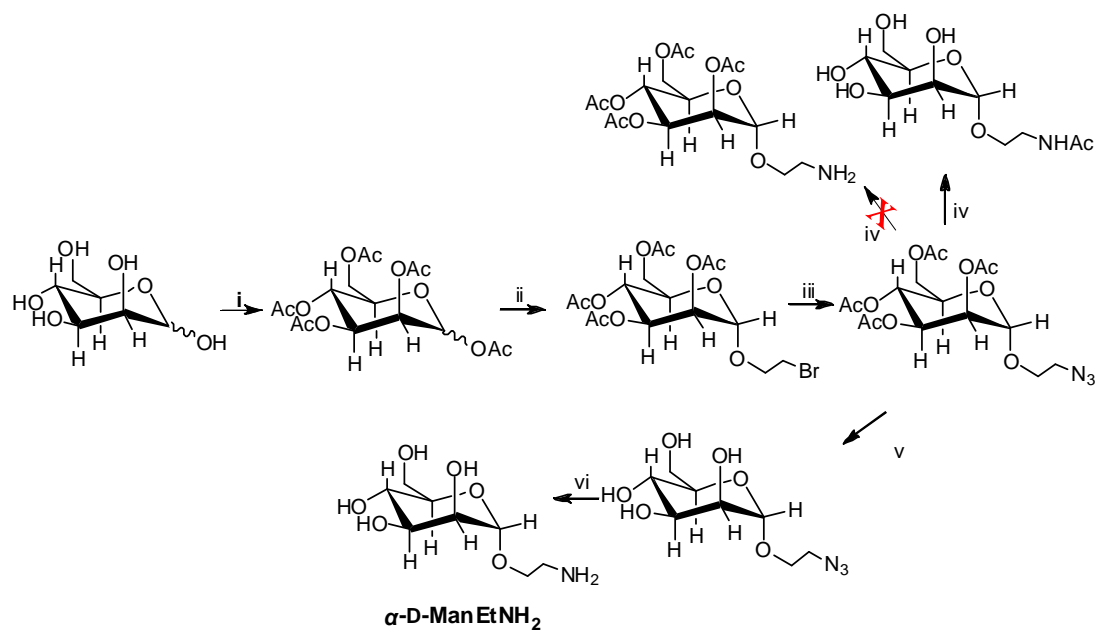


Figure S1. Preparation and NMR spectra of α -D-Man-EtNH₂:¹ i) Acetic anhydride, pyridine, DMAP, rt, 100%; ii) 1-bromoethanol, BF₃·OEt₂, CH₂Cl₂, rt, 67%; iii) NaN₃, DMF, 60 °C, 91%; iv) Pd/C 10%, H₂, MeOH, rt, 25%; v) MeONa, MeOH, rt, 100%; vi) Pd/C 10%, H₂, MeOH, rt, 98%, and ¹H and ¹³C NMR spectra (500 and 125.8 MHz, respectively, D₂O).

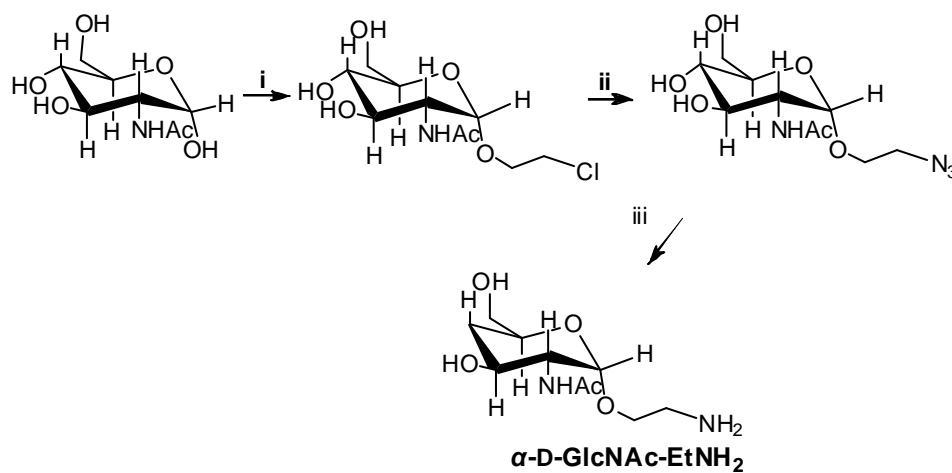


Figure S2: Preparation and NMR spectra of α -D-GlcNAc-EtNH₂:^{2,3} i) 2-Chloroethanol, AcCl, 70 °C, 61-69%; ii) NaN₃, DMF, 60 °C, 100%; iii) Pd/C 10%, H₂, MeOH, rt, 100%, and ¹H and ¹³C NMR spectra (500 and 125.8 MHz, respectively, D₂O).

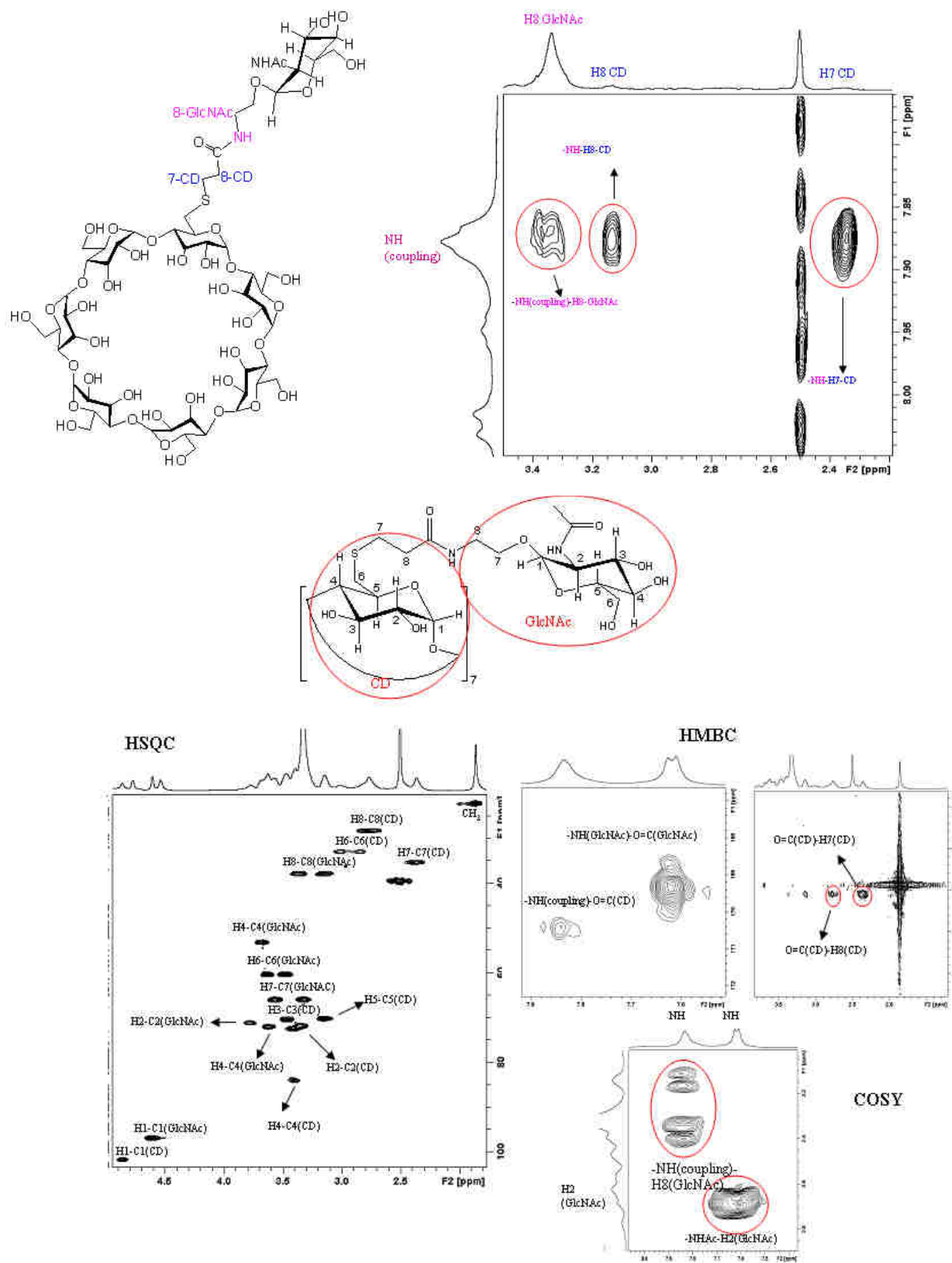


Figure S3. Top: 2D ROESY NMR spectrum of **9**; bottom: HSQC, HMBC and COSY spectra of **5** (500 MHz, DMSO-*d*₆, 298 K) showing the connectivity of the cyclodextrin core with the mono-saccharide.

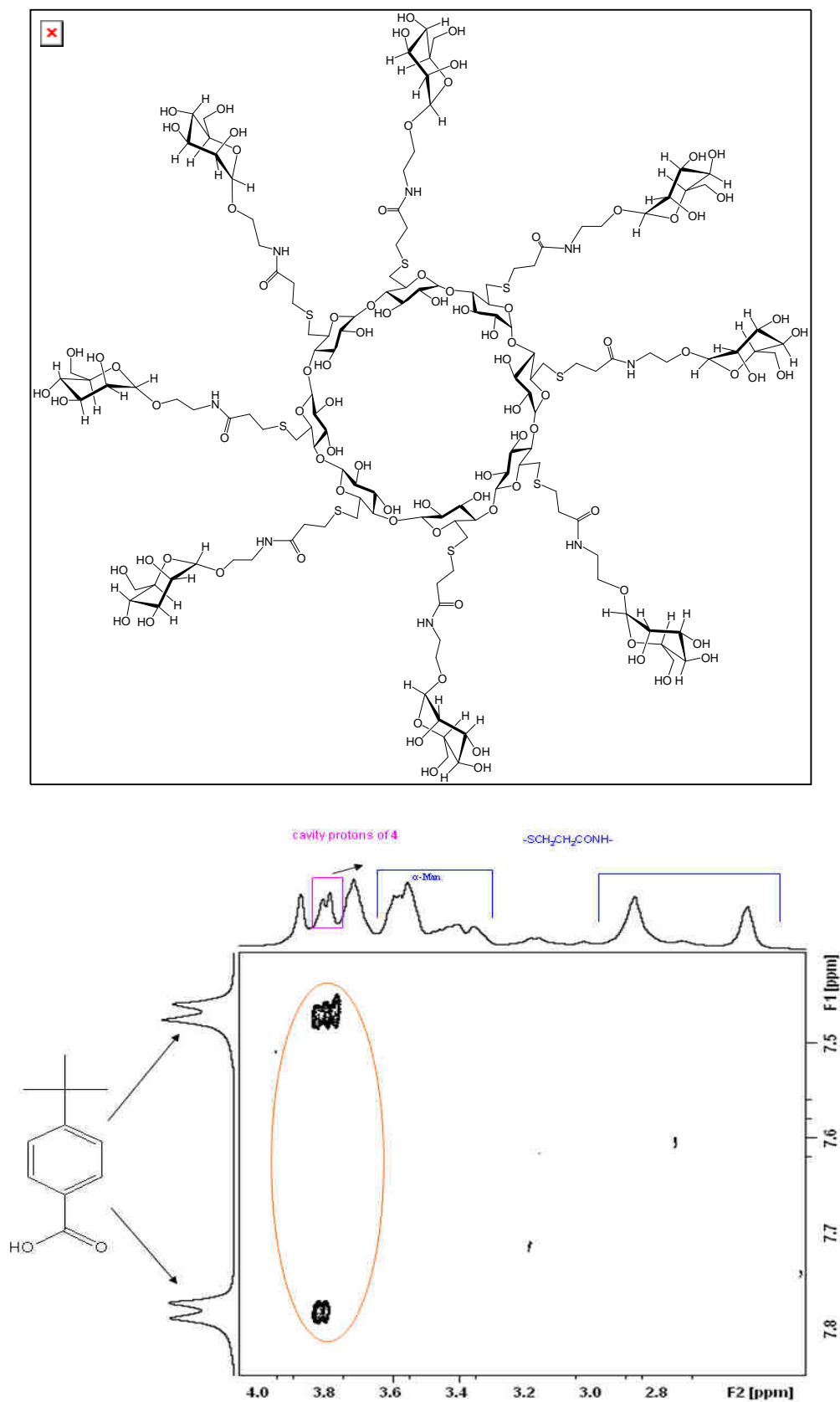


Figure S4. Partial ROESY spectrum of **4** in the presence of excess *p*-tert-butylbenzoic acid (500 MHz, D₂O, 298 K, pH ~8).

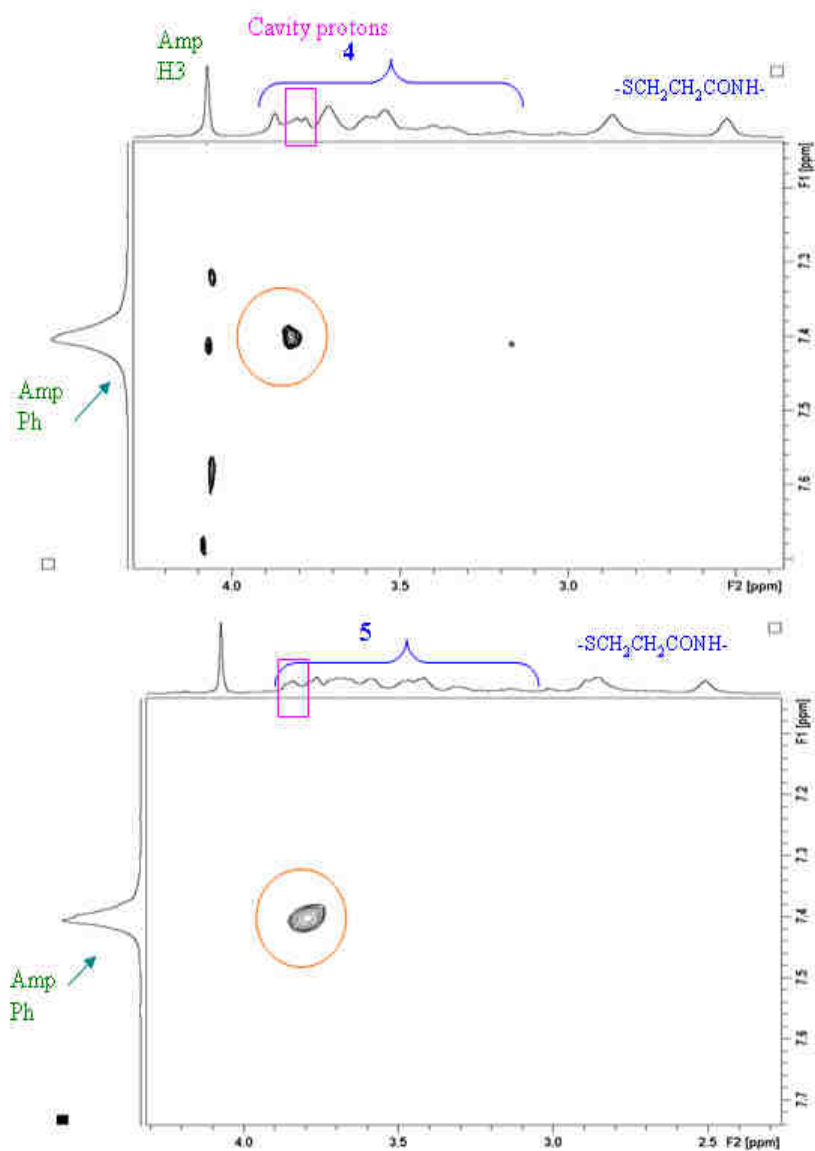


Figure S5. Partial ROESY spectrum of **4** (top) and **5** (bottom) with excess ampicillin (500 MHz, D₂O, 298 K, pH ~8). The dipolar interactions of ampicillin's phenyl group with the cavity protons of the hosts are shown.

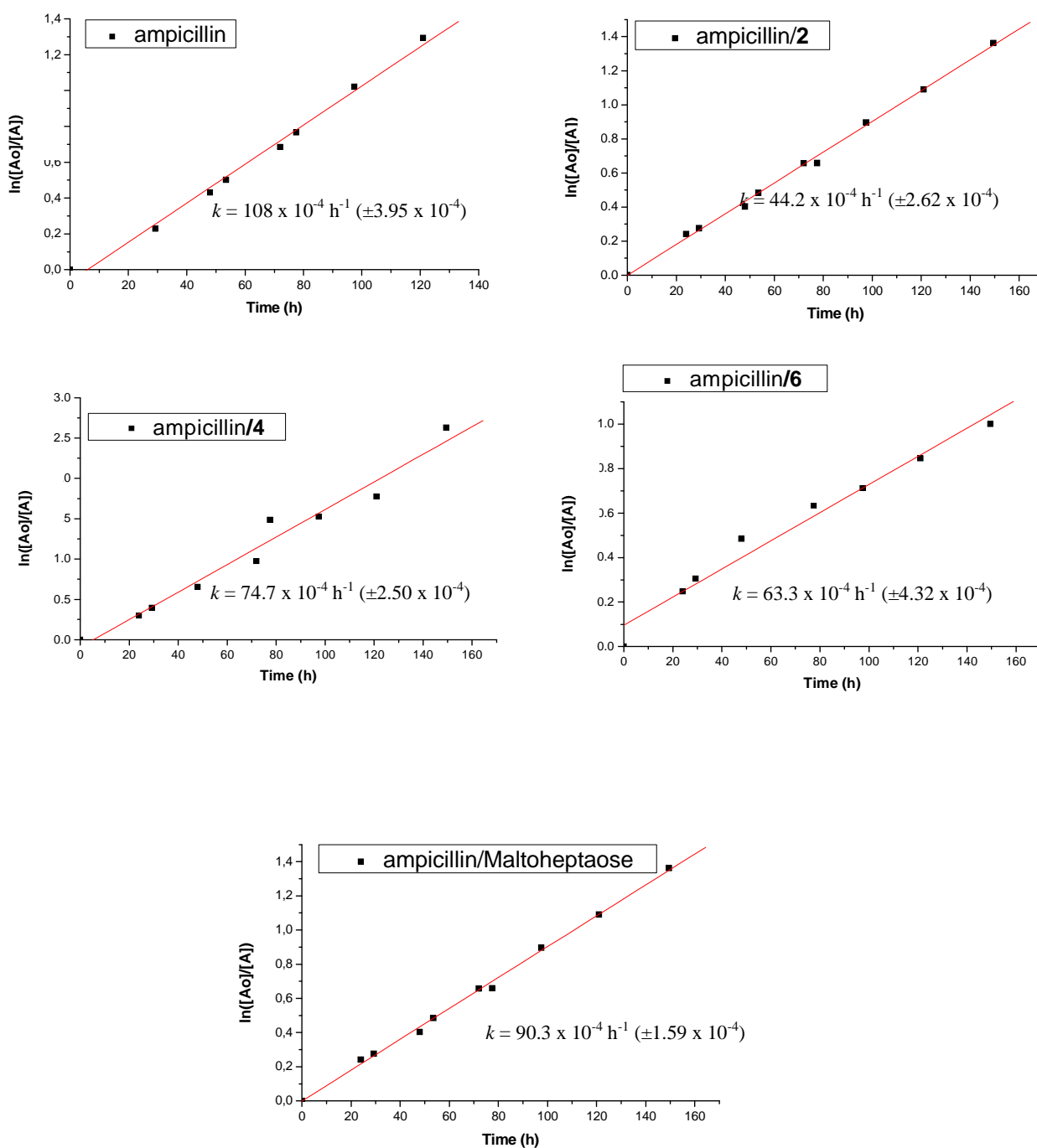


Figure S6. Linear fitting of experimental data from the enzymatic hydrolysis of ampicillin by β -lactamase in the presence either of glycoclusters or linear maltoheptaose according to the equation $\ln([A_0]/[A]) = kt$, where $[A_0]$ is the initial ampicillin concentration and $[A]$ is the concentration at time t .

Analysis of WLRs Curves

From the binding curves the *on* (layer build-up) and *off* (wash off) parts were analysed separately.

The binding of the compounds with the immobilized proteins were processed assuming a first order reaction and a mono-exponential growth equation:

$$y = a(1 - e^{-bt}), \text{ where}$$

$$y = \Delta\lambda_{max}$$

$$t = \text{time (s)}$$

$$b(s^{-1}) = k_{on} \cdot [\text{compound}] \Rightarrow k_{on} = (b/[\text{compound}]) (s^{-1} \cdot M^{-1}) \Rightarrow k_{on} = b \cdot [\text{compound}]^{-1} (s^{-1} \cdot M^{-1})$$

Therefore, the association rate constant k_{on} depends only on the concentration of the compound introduced in the WLRs setup. For the dissociation process the following mono-exponential decay equation was used:

$$y = A_1 e^{-x/t_1}, \text{ where}$$

$$y = \Delta\lambda_{max}$$

$$t = \text{time (s)}$$

$$t_1 = 1/k_{off}$$

$$k_{off} = 1/t_1 (s^{-1})$$

The results of the exponential fittings are presented in Table 2 (main text).

References

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