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-EtNH$_2$:\textsuperscript{2,3} i) 2-Chloroethanol, AcCl, 70 °C, 61-69%; ii) NaN$_3$, DMF, 60 °C, 100%; iii) Pd/C 10%, H$_2$, MeOH, rt, 100%, and $^1$H and $^{13}$C NMR spectra (500 and 125.8 MHz, respectively, D$_2$O).
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, D$_2$O, 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 glyoclusters 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:

\[ y = a(1-e^{-bt}), \]

where

\[ y = \Delta \lambda_{\text{max}}, \]

\[ t = \text{time (s)} \]

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

Therefore, the association rate constant \( k_{\text{on}} \) 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:

\[ y = A_1e^{-\frac{t}{t_1}}, \]

where

\[ y = \Delta \lambda_{\text{max}}, \]

\[ t = \text{time (s)} \]

\[ t_1 = 1/k_{\text{off}} \]

\[ k_{\text{off}} = 1/t_1 (s^{-1}) \]

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

References