Supplementary Material (ESI) for Chemical Communications

Supporting Information

Exclusive Enantioselective Recognition of Glucopyranosides by Inherently Chiral Hemicryptophane Hosts.

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I/ General information

Material and methods

Hemicryptophanes **1** and **2** was synthesized and resolved according to previous literature.[1-3] Solvents used were of commercial grade, $CDCl_3$ was stored over molecular sieves. ^{1}H NMR spectra were recorded at 298 K on a Bruker Avance 500 MHz spectrometer. ^{1}H NMR chemical shifts δ are reported in ppm referenced to the protonated residual solvent signal.

^{1}H NMR continuous variation methods (Job's plot)

Stock solutions (5.0 mM in $CDCl_3$) of **1** and each of the guests were prepared and mixed in NMR tubes in different ratios. In this way, relative concentrations α were varied continuously but their sum was kept constant (5.0 mM). ^{1}H NMR spectra were recorded for each sample and values of host's chemical shift δ_{obs} were measured. Job's plots were obtained by plotting $(\delta_{obs} - \delta_{free})\alpha$ versus α, where δ_{free} is the chemical shift of the proton in the uncomplexed host. The stoichiometry of the complexes was obtained from the value of the molar fraction α which corresponds to a maximum of the curve: a 1:1 complexation is obtained for $\alpha_{max} = 0.5$.

^{1}H NMR titrations

Solutions of hosts (between 0.5 and 2.0 mM in $CDCl_3$, 500 µL) were titrated in NMR tubes with 10 µL aliquots of concentrated solutions (between 6.3 and 22.5 mM in $CDCl_3$) of guests. The shifts $\Delta\delta$ of the hosts' protons signals were measured after each addition and plotted as a function of the guest/host ratio. Association constants K_{ass} were obtained by nonlinear least-squares fitting of these plots using WinEQNMR2 program.[4]

[1] P. Dimitrov-Raytchev, O. Perraud, C. Aronica, A. Martinez, J.-P. Dutasta*, J. Org. Chem.* **2010**, *75*, 2099-2102.
[2] A. Gautier, J.-C. Mulatier, J. Crassous, J.-P. Dutasta, *Org. Lett.* **2005**, *7*, 1207-1210.
[3] O. Perraud, P. Dimitrov-Raytchev, A. Martinez, J.-P. Dutasta *Chirality*, 2010, **22**, 885–888.
[4] M. J. Hynes, *J. Chem. Soc. Dalton Trans.* **1993**, 311-312.

II/ Job's plots

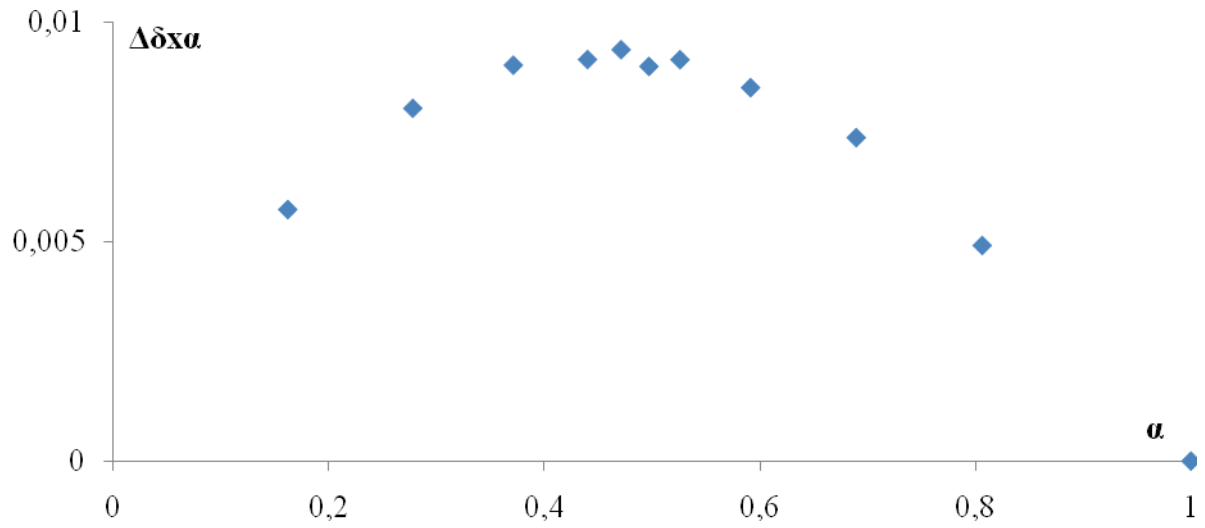

Figure S1. Job's plot of **1** with OctαGlc. The chemical induced shifts Δδ of the H_1 and H_2 protons of **1** were measured, α is the molar ratio of **1**.

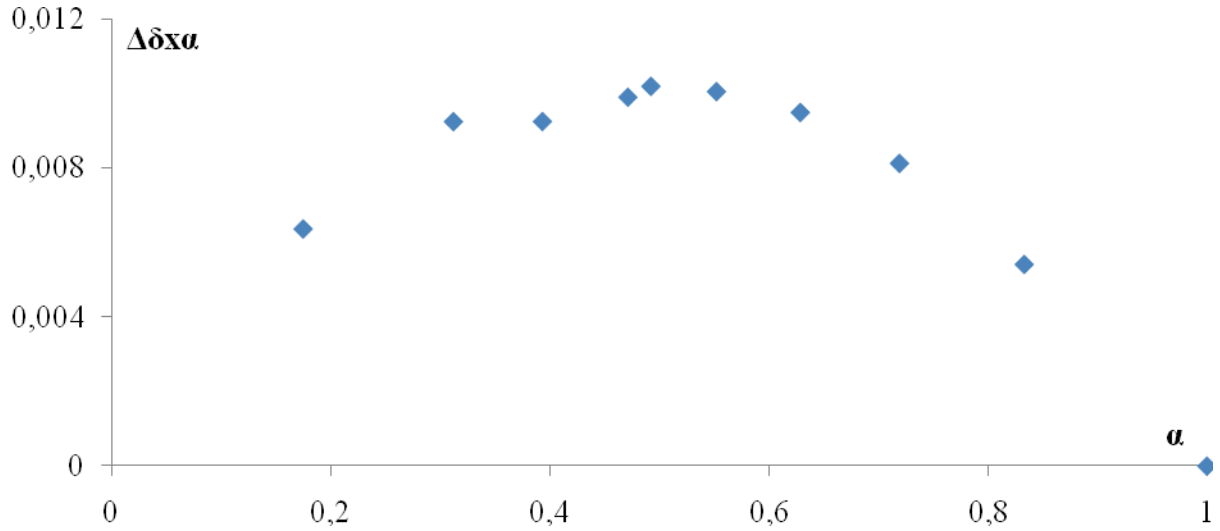

Figure S2. Job's plot of **1** with OctβGlc. The chemical induced shifts Δδ of the H_1 and H_2 protons of **1** were measured, α is the molar ratio of **1**.

III/ ^{1}H NMR titrations

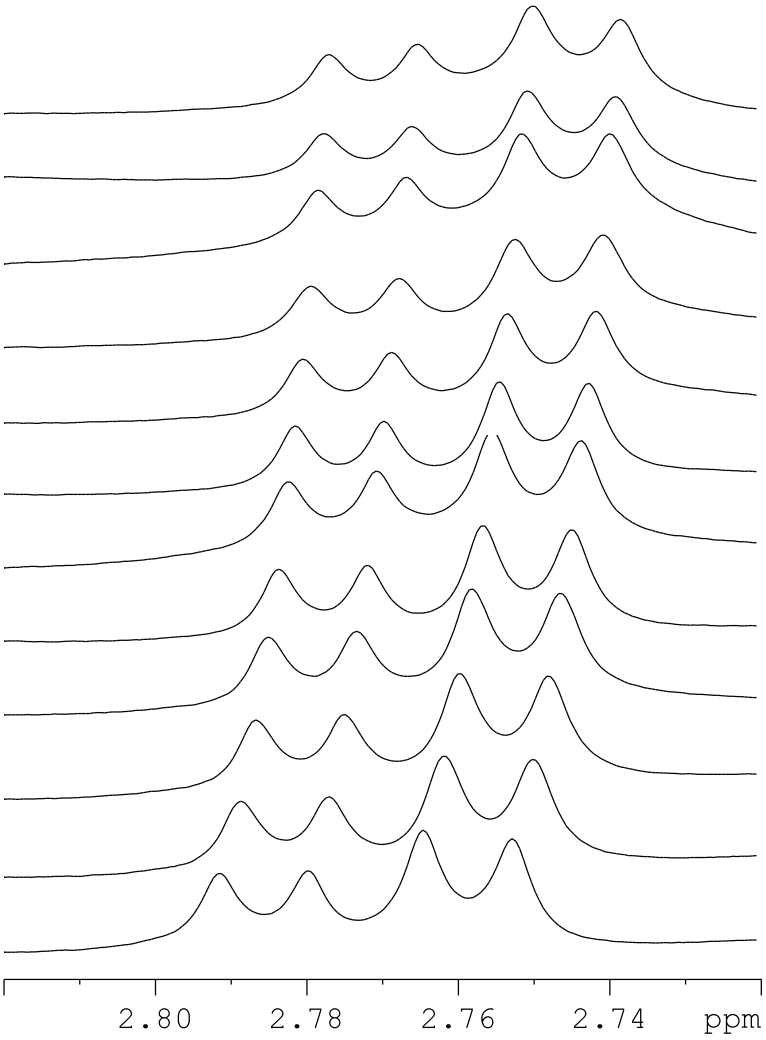

Figure S3. Illustration of the evolution of ^{1}H NMR spectra during titrations: this figure is focused on the NCH_2's NMR signal used to calculate K_{ass} for the titration of RRR-*M*-**2** with OctβGlc (0; 0.45; 0.9; 1.35; 1.8; 2.25; 2.7; 3.38; 4.05; 4.95; 5.85; 6.75 equivalents from bottom to top).

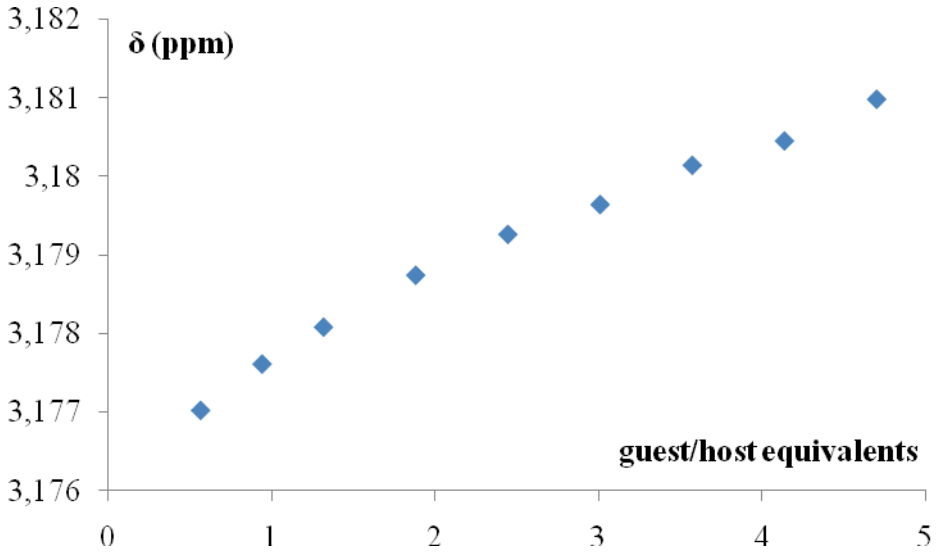

Figure S4. Titration curve of *M*-**1** (c = 0.7 mM) with OctαGlc (c = 6.3 mM). The chemical induced shifts Δδ of the H_1 and H_2 protons of *M*-**1** were measured and plotted as a function of the ratio [OctαGlc]/[*M*-**1**].
K_{ass} = 216 ± 15 M^{-1}.

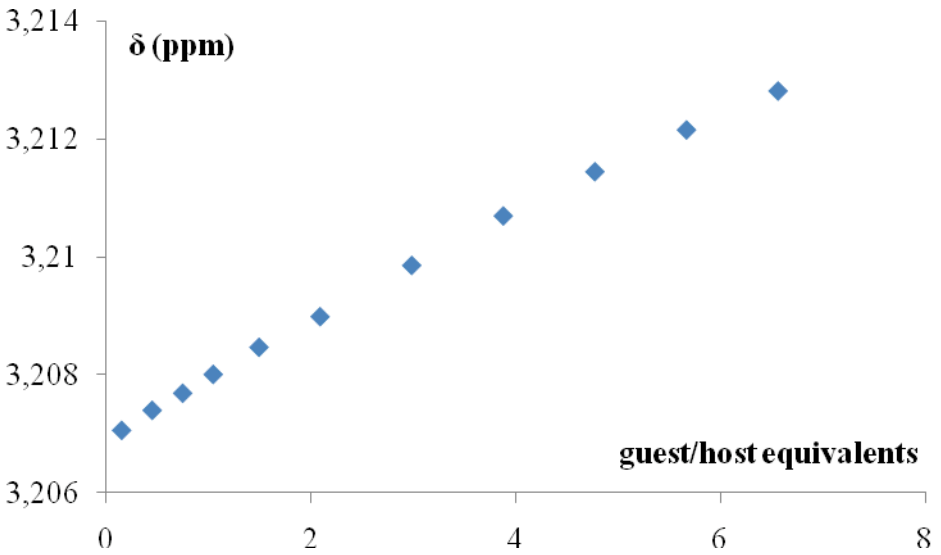

Figure S5. Titration curve of *M*-**1** (c = 0.7 mM) with OctβGlc (c = 10.0 mM). The chemical induced shifts Δδ of the H_1 and H_2 protons of *M*-**1** were measured and plotted as a function of the ratio [OctβGlc]/[*M*-**1**].
K_{ass} = 64 ± 6 M^{-1}.

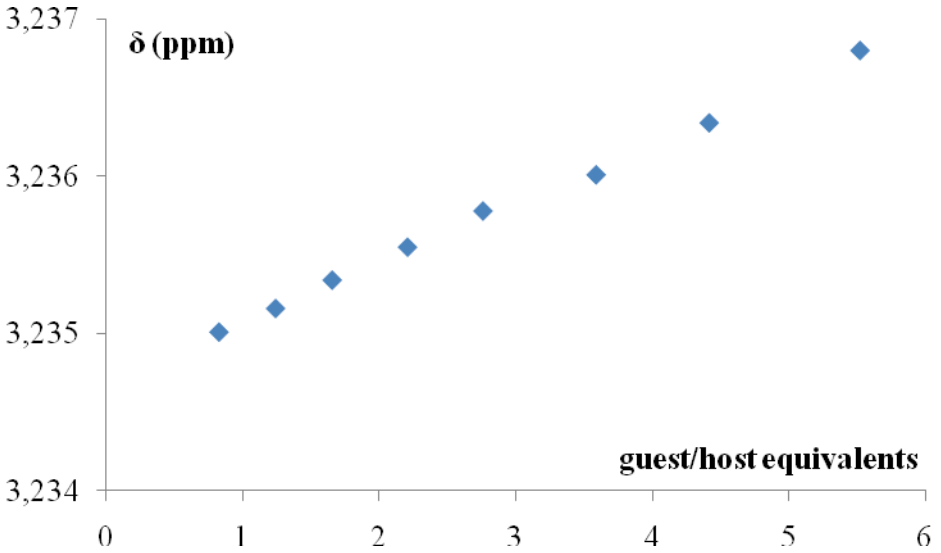

Figure S6. Titration curve of *P*-**1** (c = 0.5 mM) with OctαGlc (c = 7.2 mM). The chemical induced shifts Δδ of the H_1 and H_2 protons of *P*-**1** were measured and plotted as a function of the ratio [OctαGlc]/[*M*-**1**].
$K_{ass} = 31 \pm 5\ M^{-1}$.

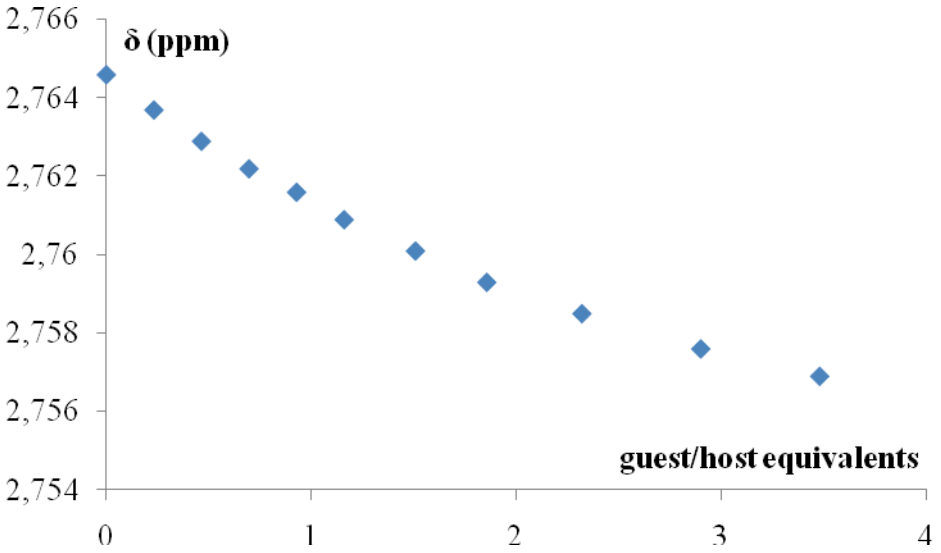

Figure S7. Titration curve of RRR-*M*-**2** (c = 2.0 mM) with OctαGlc (c = 11.6 mM). The chemical induced shifts Δδ of the NCH_2 protons of RRR-*M*-**2** were measured and plotted as a function of the ratio [OctαGlc]/[RRR-*M*-**2**].
$K_{ass} = 123 \pm 3\ M^{-1}$.

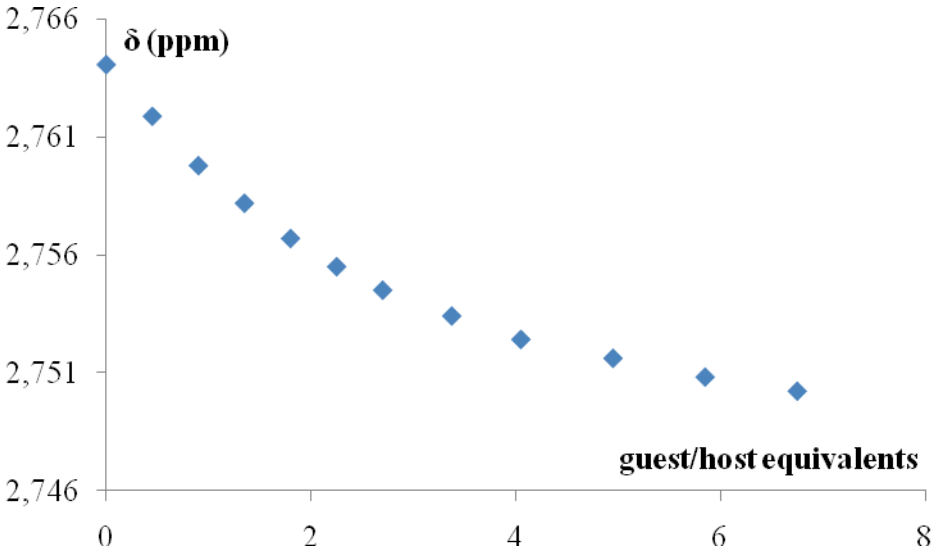

Figure S8. Titration curve of RRR-*M*-**2** (c = 2.0 mM) with OctβGlc (c = 22.5 mM). The chemical induced shifts Δδ of the NCH_2 protons of RRR-*M*-**2** were measured and plotted as a function of the ratio [OctβGlc]/[RRR-*M*-**2**].
K_{ass} = 226 ± 2 M^{-1}.

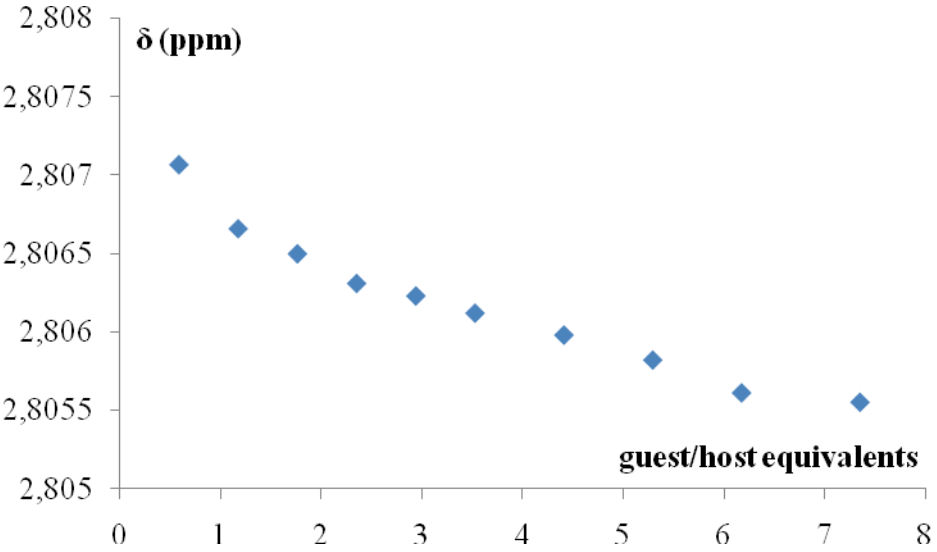

Figure S9. Titration curve of SSS-*P*-**2** (c = 1.4 mM) with OctβGlc (c = 20.0 mM). The chemical induced shifts Δδ of the NCH_2 protons of SSS-*P*-**2** were measured and plotted as a function of the ratio [OctβGlc]/[SSS-*P*-**2**].
K_{ass} = 115 ± 8 M^{-1}.

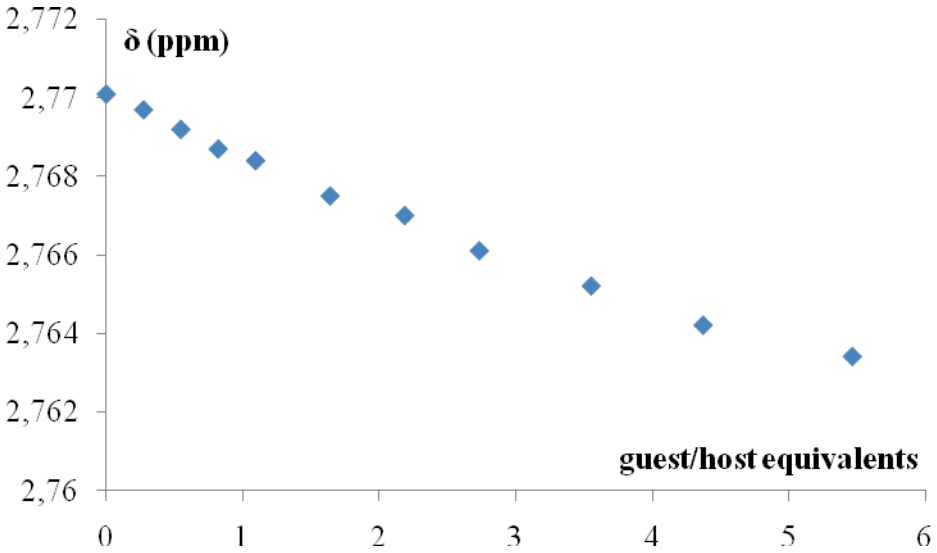

Figure S10. Titration curve of SSS-*M*-**2** (c = 0.5 mM) with OctαGlc (c = 6.9 mM). The chemical induced shifts Δδ of the NCH_2 protons of SSS-*M*-**2** were measured and plotted as a function of the ratio [OctαGlc]/[SSS-*M*-**2**]. $K_{ass} = 115 \pm 4\ M^{-1}$.

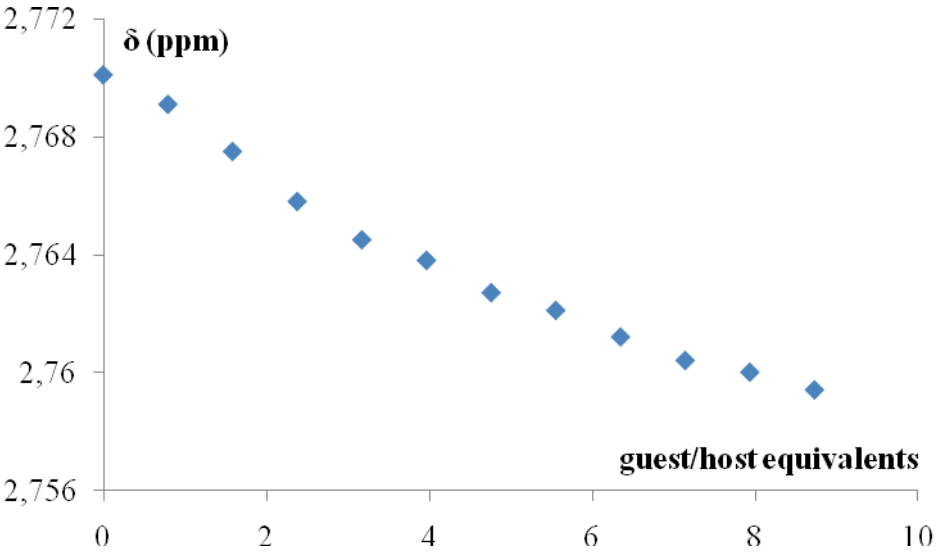

Figure S11. Titration curve of SSS-*M*-**2** (c = 0.5 mM) with OctβGlc (c = 20.0 mM). The chemical induced shifts Δδ of the NCH_2 protons of SSS-*M*-**2** were measured and plotted as a function of the ratio [OctβGlc]/[SSS-*M*-**2**]. $K_{ass} = 184 \pm 5\ M^{-1}$.