Electronic Supplementary Material (ESI) for Chemical Science

Saccharide Receptor Achieves Concentration Dependent Mannoside Selectivity Through Two Distinct Cooperative Binding Pathways

Supporting Information

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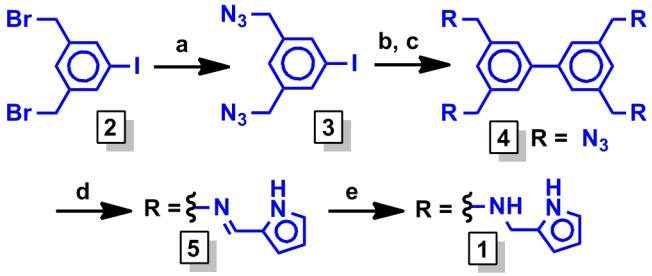
1. Organic synthesis.

General synthetic methods: All solvents were dried using a Pure Solv MD-6 solvent purification system. All reagents and starting materials were purchased from commercial sources and used without further purification unless otherwise noted. Aqueous solutions were prepared from nanopure water purified from a Milli-Q plus system (Millipore Co.), with a resistivity over 18 MΩ cm^{-1}. Chromatography purifications were performed using Sorbent Technologies Silica Gel (60 Å, 65 x 250 mesh). Thin-layer chromatography (TLC) was carried out using aluminum sheets precoated with silica gel 60 (EMD 40−60 mm, 230−400 mesh with 254 nm dye). TLC plates were visualized by UV-light and stained using a *p*-anisaldehyde or phosphomolybdic acid solution if required. All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. Compound **2**,[1] octyl α-D-mannopyranoside,[2] and α-D-*N*-acetylglucosaminopyranoside[3] were synthesized according to published literature procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. NMR spectra were obtained on either a Bruker AVANCE 400 and 500 MHz spectrometers. All chemical shifts are reported in δ units using the solvent residual signal as an internal standard and the coupling constant values (*J*) are reported in Hertz (Hz). The following abbreviations are used for signal multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. Electrospray Ionization Mass Spectroscopy (ESI-MS) spectra were acquired on an Agilent LC/MSD Trap XCT system. High-resolution mass spectral analyses were carried out on an Agilent 6200 LC/MSD TOF System.

Scheme S1. Synthesis of **1**. Reagents and conditions: a) NaN_3, DMF, 84%; b) bis(pinacolato)diborane, $(dppf)PdCl_2$, K_2CO_3, DMF; c) **3**, $(dppf)PdCl_2$, Na_2CO_3, 95%, two steps; d) 1*H*-pyrrole-2-carbaldehyde, PPh_3, C_6H_6; e) $NaBH_4$, MeOH, 80%, two steps.



1,3-Bis(azidomethyl)-5-iodobenzene (3) Compound **2** (1.0 g, 2.6 mmol), DMF (50 mL) and sodium azide (834 mg, 12.8 mmol) were added to a round-bottom flask, and the mixture was heated to 110 °C under N_2. After 16 h, the solution was cooled to room temperature, diluted with 50 mL of CH_2Cl_2, and stirred for an additional 2 h. The resulting mixture was filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (SiO_2, Hexanes) to provide **3** (701 mg, 84%) as a viscous orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (s, 2H), 7.24 (s, 1H), 4.33 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.15, 136.56, 126.69, 94.75, 53.55. HRMS (ESI): *m*/*z* calcd for $C_8H_8IN_4$ $[M+H\text{-}N_2]^+$ 286.9794, Found: 286.9800.

3,3',5,5'-tetrakis(azidomethyl)-1,1'-biphenyl (4) A solution of $(dppf)PdCl_2$ (650 mg, 0.89 mmol), bis-pinacolatoboron (2.50 g, 9.8 mmol), K_2CO_3 (2.40 g, 25.0 mmol), DMF (180 mL), and **3** (2.8 g, 8.9 mmol) were heated to 80 °C under N_2 and stirred for 5 h. Subsequently, DMF (60 mL), **3** (2.81 g, 8.9 mmol), $(dppf)PdCl_2$ (350 mg, 0.48 mmol), and Na_2CO_3 (26.3 mL, 2.0 M aq.) were added to the solution. The reaction mixture was stirred at 80 °C for 16 h, after which the mixture was diluted with water and EtOAc (60 mL 1:1), and extracted with EtOAc (3 x 30 mL). The organic fractions were combined, washed with brine (50 mL), dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and purified by column chromatography (SiO_2, 1:4 EtOAc:hexanes) to yield **4** (3.16 g, 95%) as a pink oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (s, 4H), 7.30 (s, 2H), 4.46 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.46, 136.97, 127.00, 126.77, 54.46. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{15}N_{10}$ $[M+H\text{-}N_2]$ 347.1481, Found: 347.1476.

***N,N',N'',N'''*-([1,1'-biphenyl]-3,3',5,5'-tetrayltetrakis(methylene))tetrakis (1-(1*H*-pyrrol-2-yl)methanamine) (1)** Compound **4**, (0.500 g, 1.34 mmol), PhMe (30 mL) and PPh_3 (1.47 g, 5.6 mmol) were heated to 90 °C and stirred for 1 h before the addition of 1*H*-pyrrole-2-carbaldehyde (530 mg, 5.6 mmol). The reaction mixture was stirred for 12 h at 90 °C, cooled to room temperature and concentrated under reduced pressure. The resulting residue was dissolved in MeOH (30 mL) and $NaBH_4$ (304 mg, 8.04 mmol) was added to the solution over 20 min at room temperature. After stirring for 1 h, the reaction mixture was poured into water/brine (30 mL 1:1) and extracted with CH_2Cl_2 (4 x 70 mL). The organic fractions were combined, dried over anhydrous $MgSO_4$, concentrated under reduced pressure and purified by column chromatography (SiO_2, 9:1:1 CH_2Cl_2:MeOH:NH_3(Conc)) to provide **1** (625 mg, 80%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.73 (s, 4H, br), 7.42 (s, 4H), 7.26 (s, 2H), 6.74 (s, 4H), 6.14 (d, 4H), 6.06 (d, 4H), 3.84 (s, 16H, br), 1.68 ppm (s, 4H, br). ^{13}C NMR (DMSO-D_6, 100 MHz) δ = 141.61 (CH), 140.66 (CH), 131.07 (CH), 127.27 (CH), 125.17 (CH), 117.14 (CH), 107.40 (CH), 106.22 (CH), 79.45 (CH_2), 52.73 (CH_2) ppm. HRMS (ESI): *m*/*z* calcd for $C_{36}H_{43}N_8$ $[M+H]^+$ 587.3532, Found: 587.3638.

Figure S1. ^{1}H NMR of **3** (500 MHz, 25° C) in $CDCl_3$.

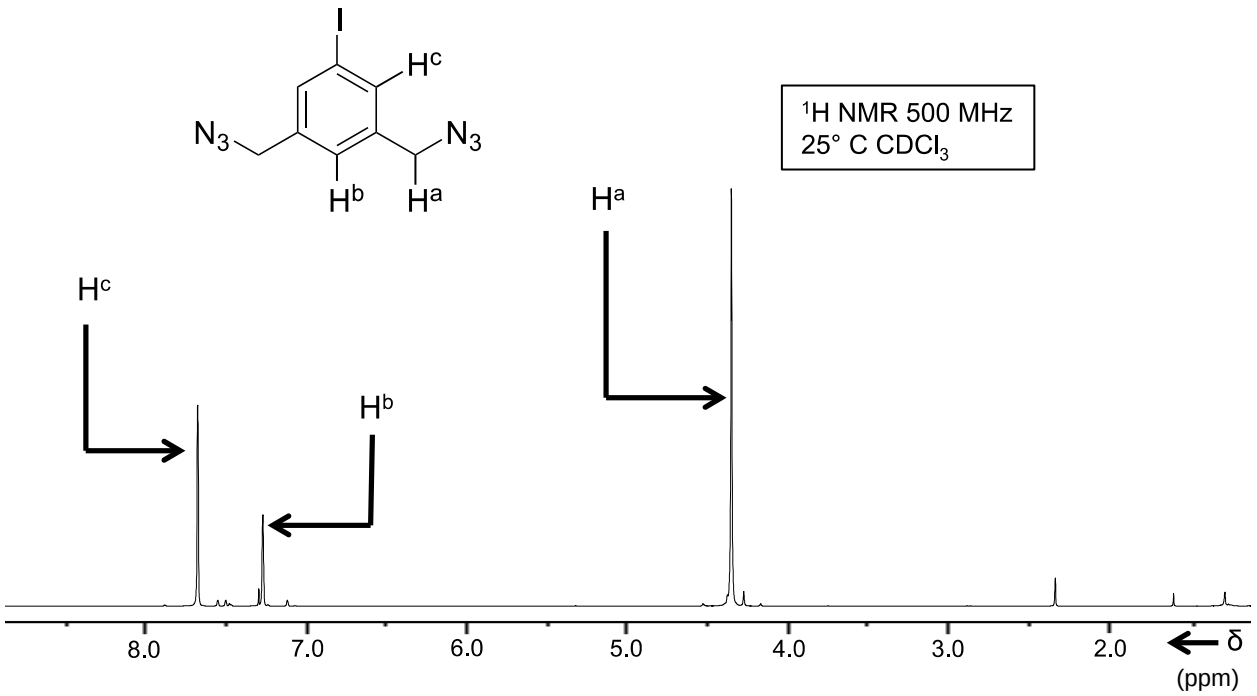


Figure S2. ^{13}C NMR of **3** (100 MHz, 25° C) in $CDCl_3$.

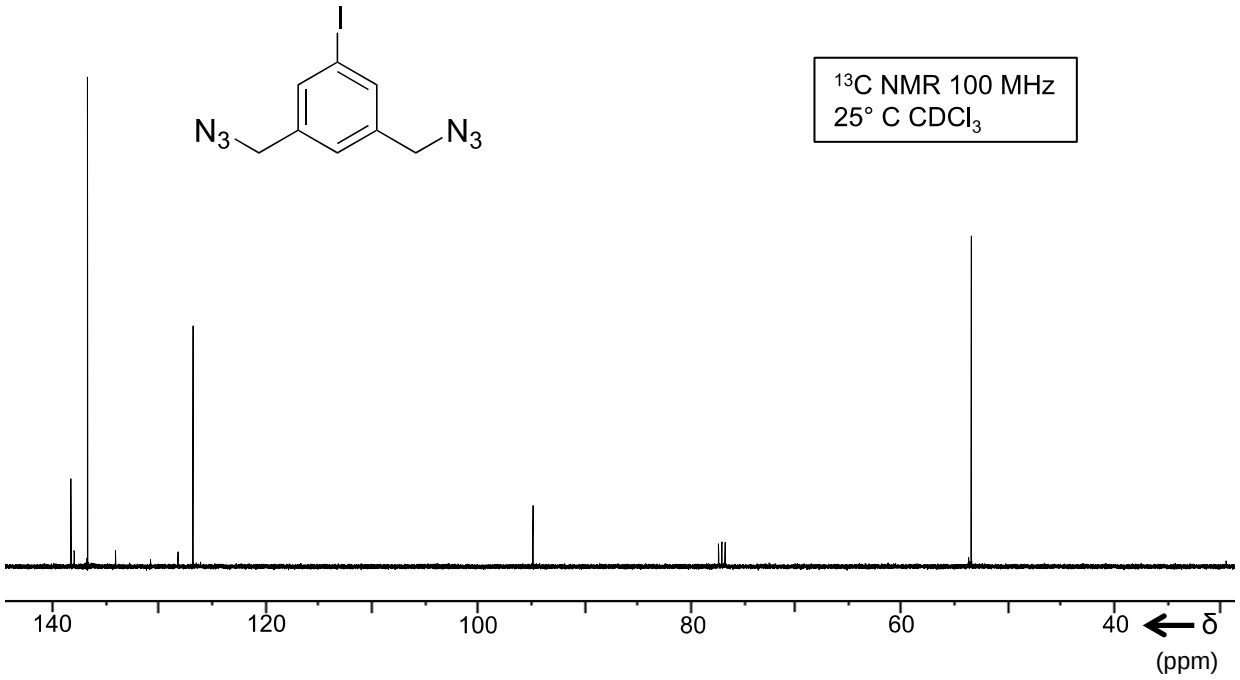
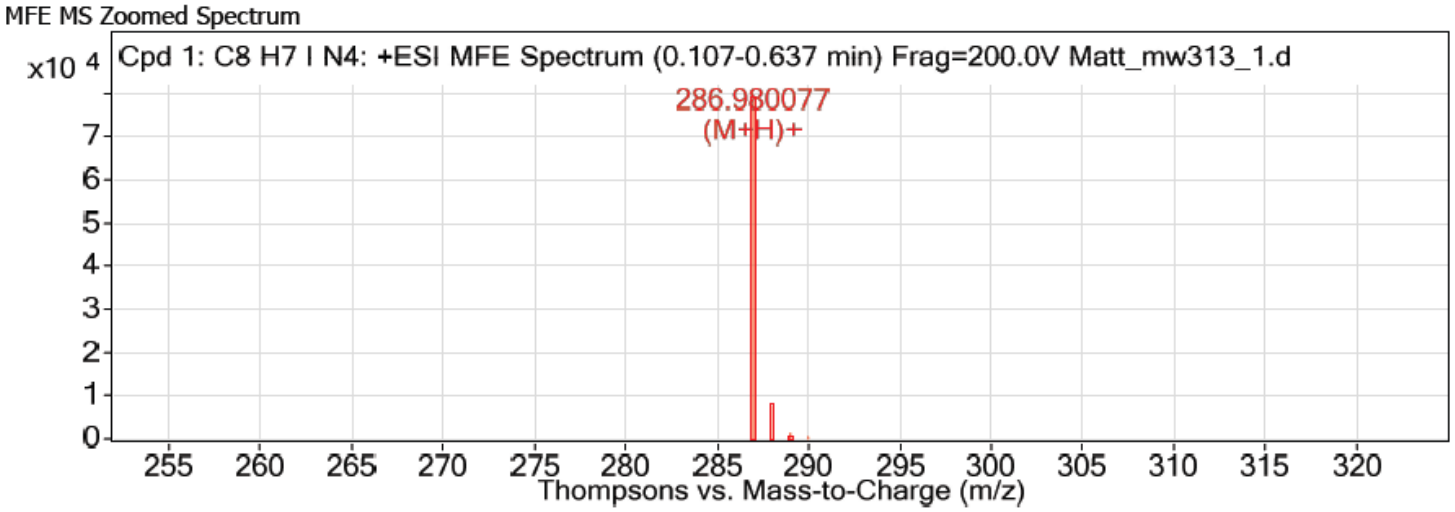


Figure S3. HRMS of **3**.



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
286.980077	1	78094	C8 H8 I N4	(M+H)+
287.98237	1	7777	C8 H8 I N4	(M+H)+
288.992239	1	1172	C8 H8 I N4	(M+H)+
289.977097	1	293	C8 H8 I N4	(M+H)+

Figure S4. ^{1}H NMR of **4** (400 MHz, 25° C) in $CDCl_3$.

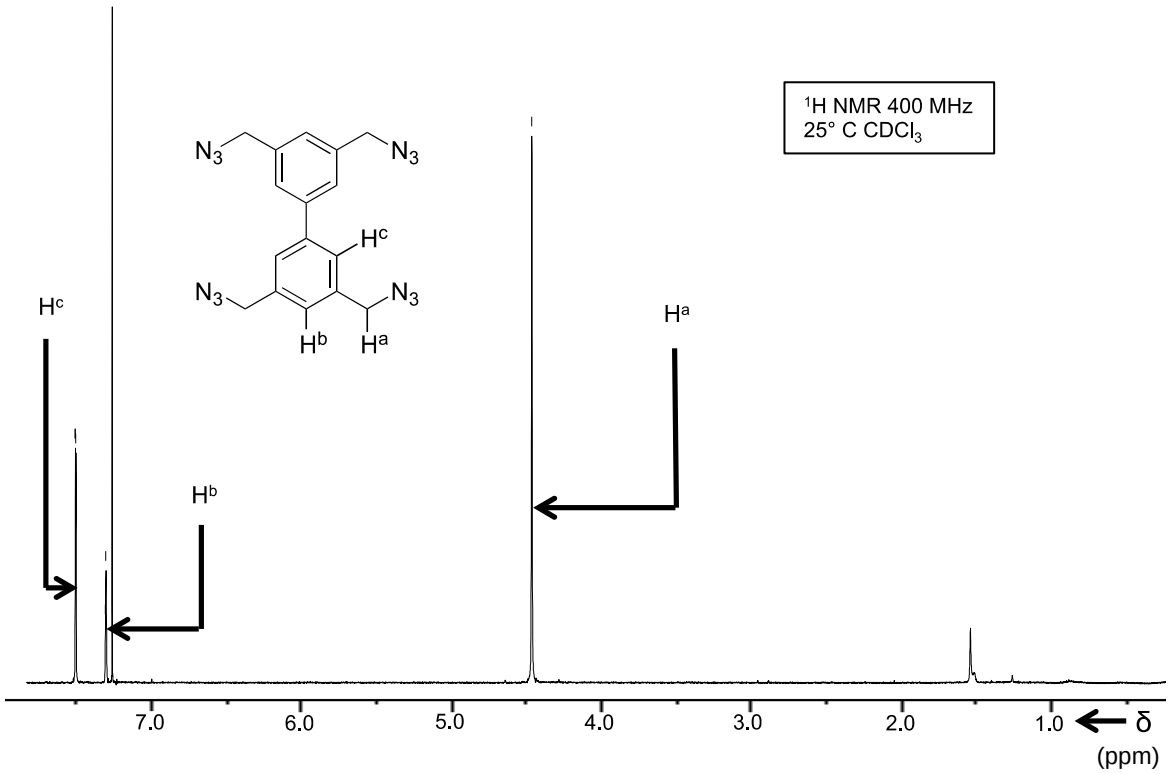


Figure S5. ^{13}C NMR of **4** (100 MHz, 25° C) in $CDCl_3$.

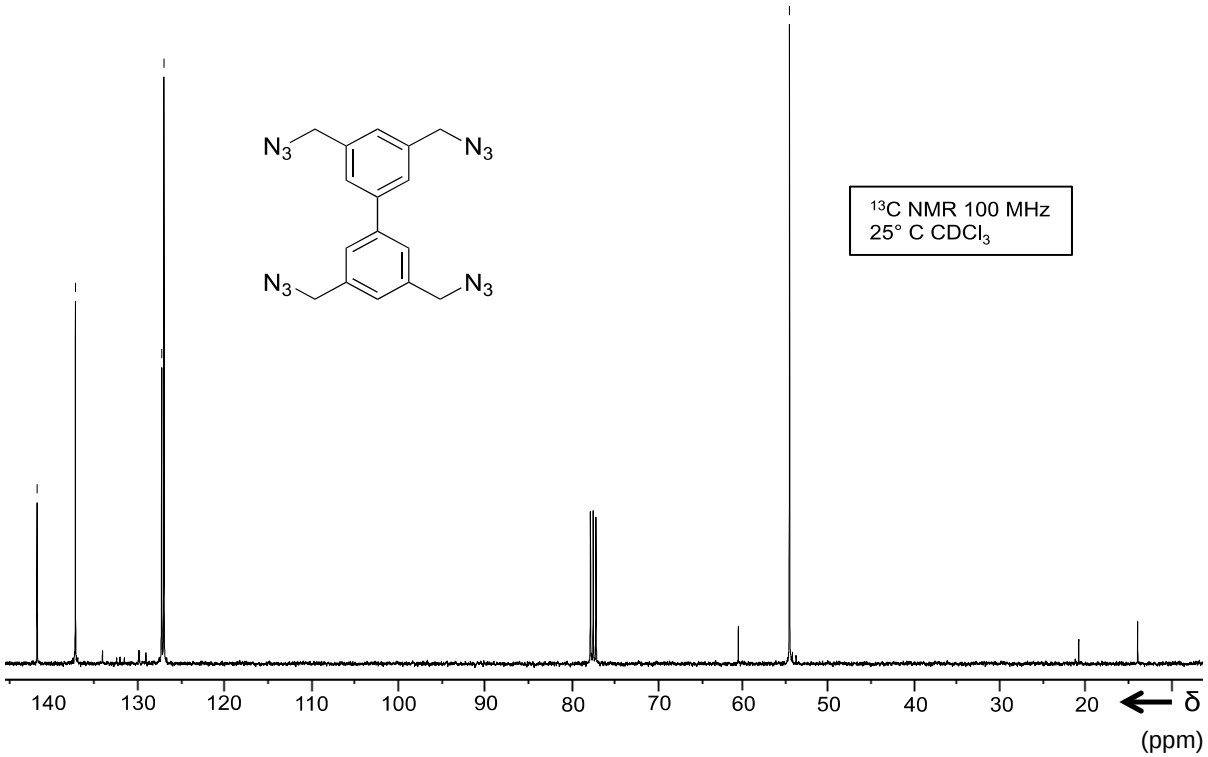
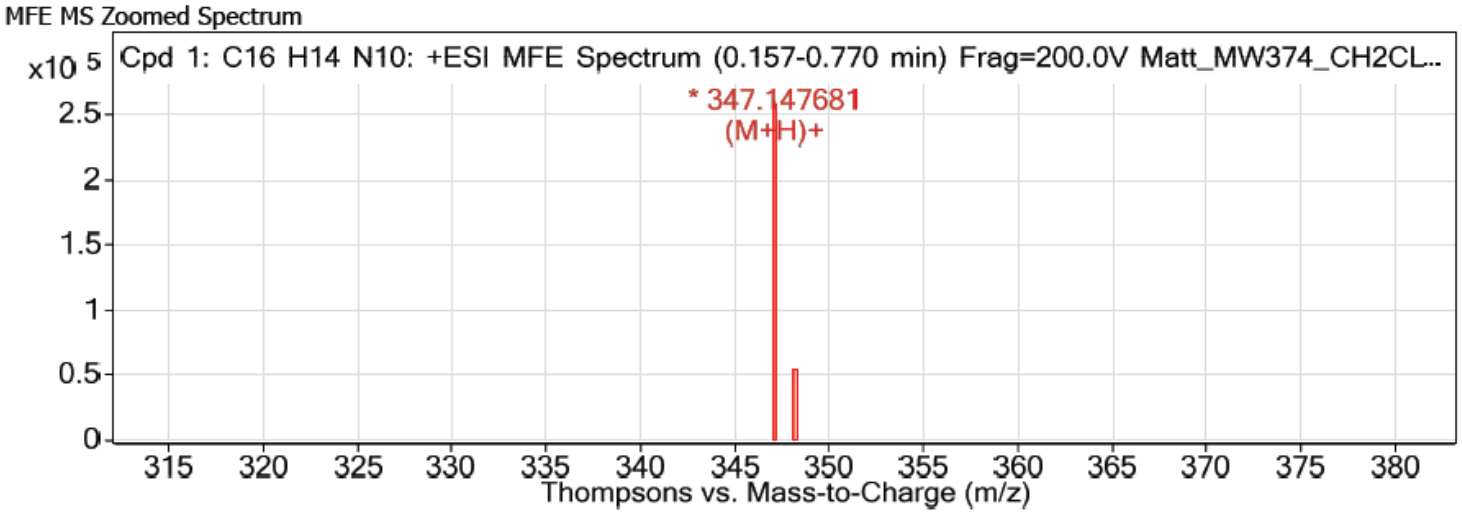


Figure S6. HRMS of **4**



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
347.147681	1	259734	C16 H15 N10	(M+H)+
348.14756	1	53493	C16 H15 N10	(M+H)+

Figure S7. ^{1}H NMR of **1** (400 MHz, 25° C) in $CDCl_3$.

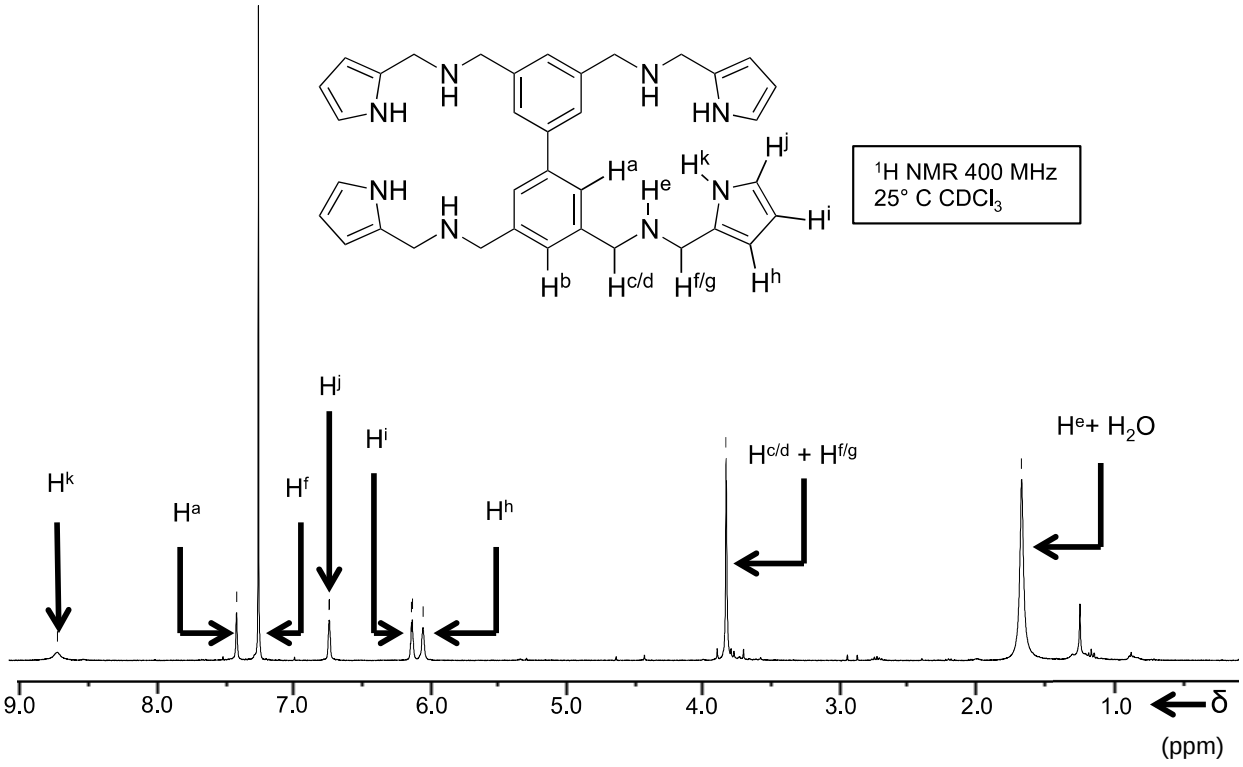


Figure S8. ^{13}C NMR of **1** (100 MHz, 25° C) in DMSO-D_6.

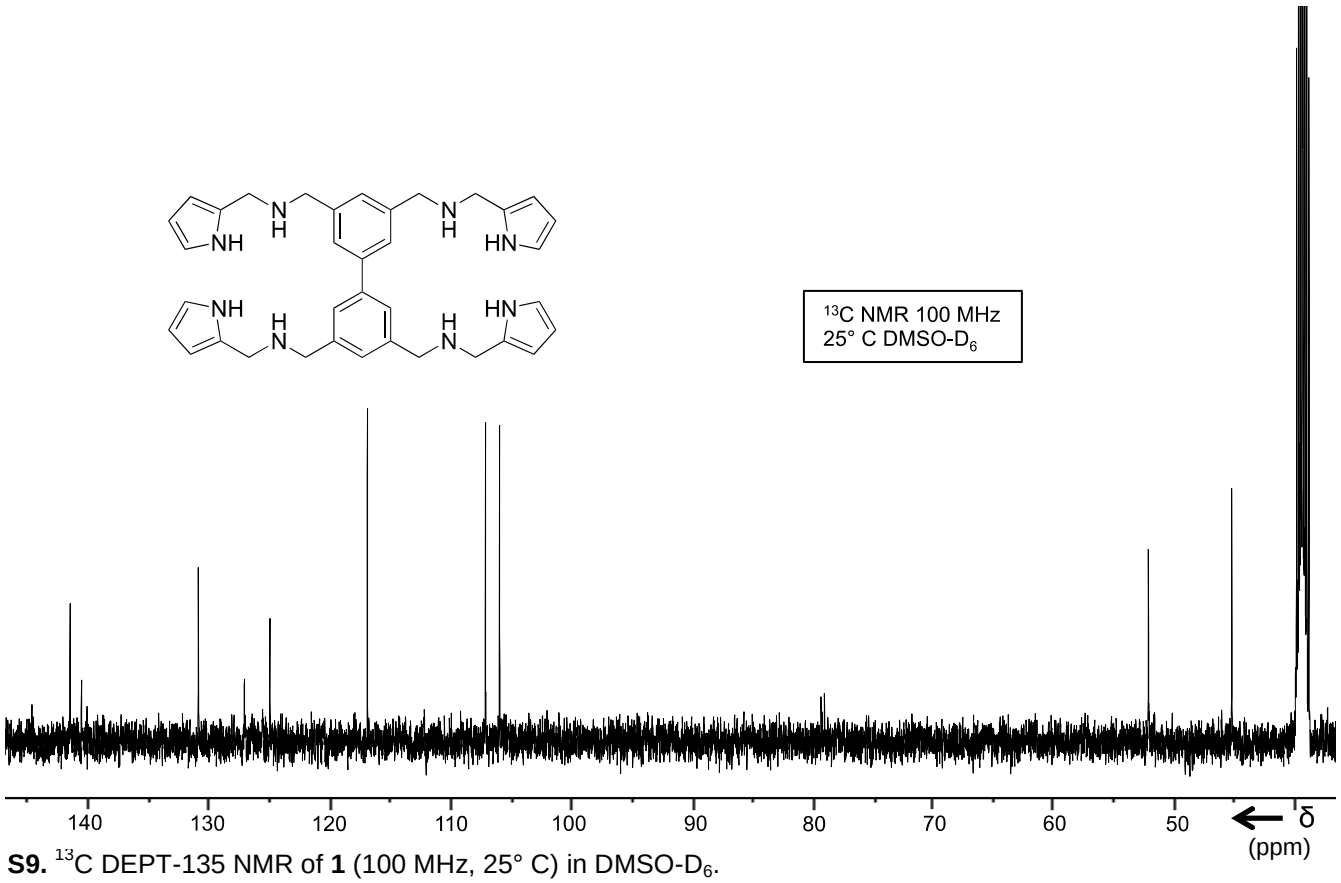


Figure S9. ^{13}C DEPT-135 NMR of **1** (100 MHz, 25° C) in DMSO-D_6.

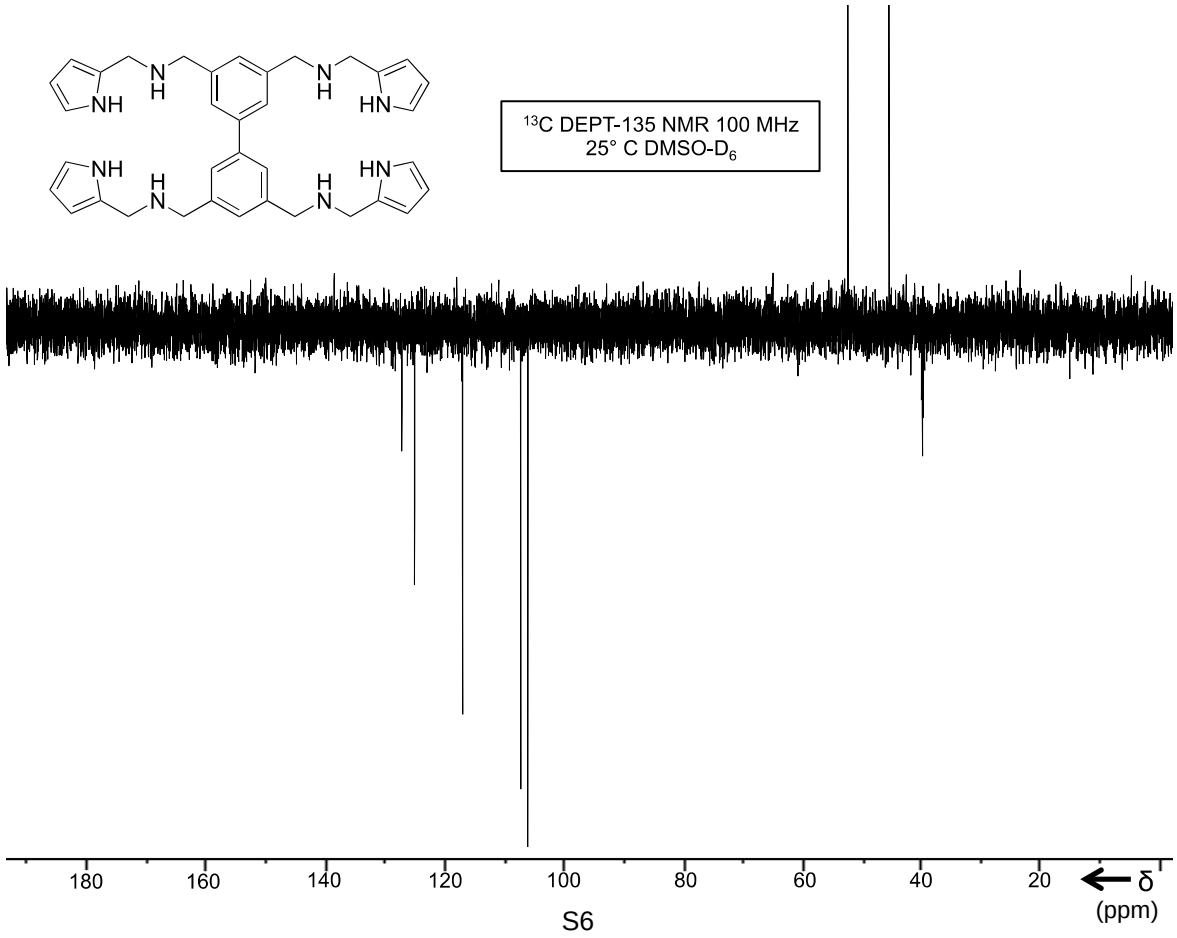
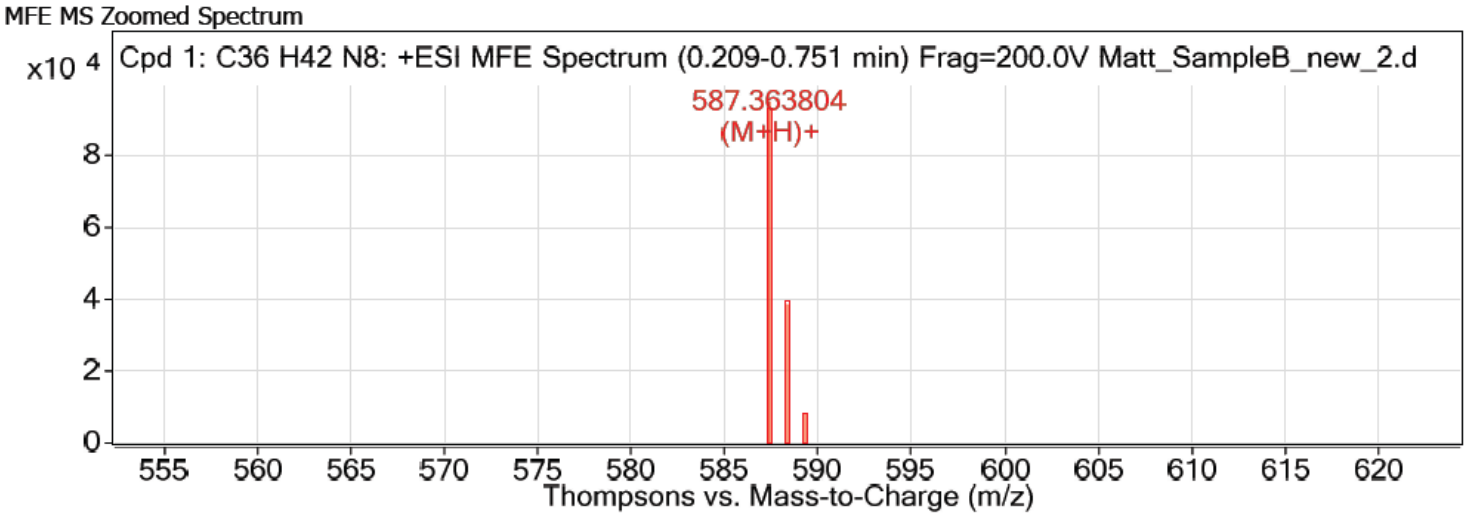


Figure S10. HRMS of **1**



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
587.363804	1	94658	C36 H43 N8	(M+H)+
588.366721	1	38234	C36 H43 N8	(M+H)+
589.370063	1	8153	C36 H43 N8	(M+H)+

2. Variable Temperature NMR

Figure S11. Variable Temperature ^{1}H NMR of 1.0mM solution of **1** in $CDCl_3$.

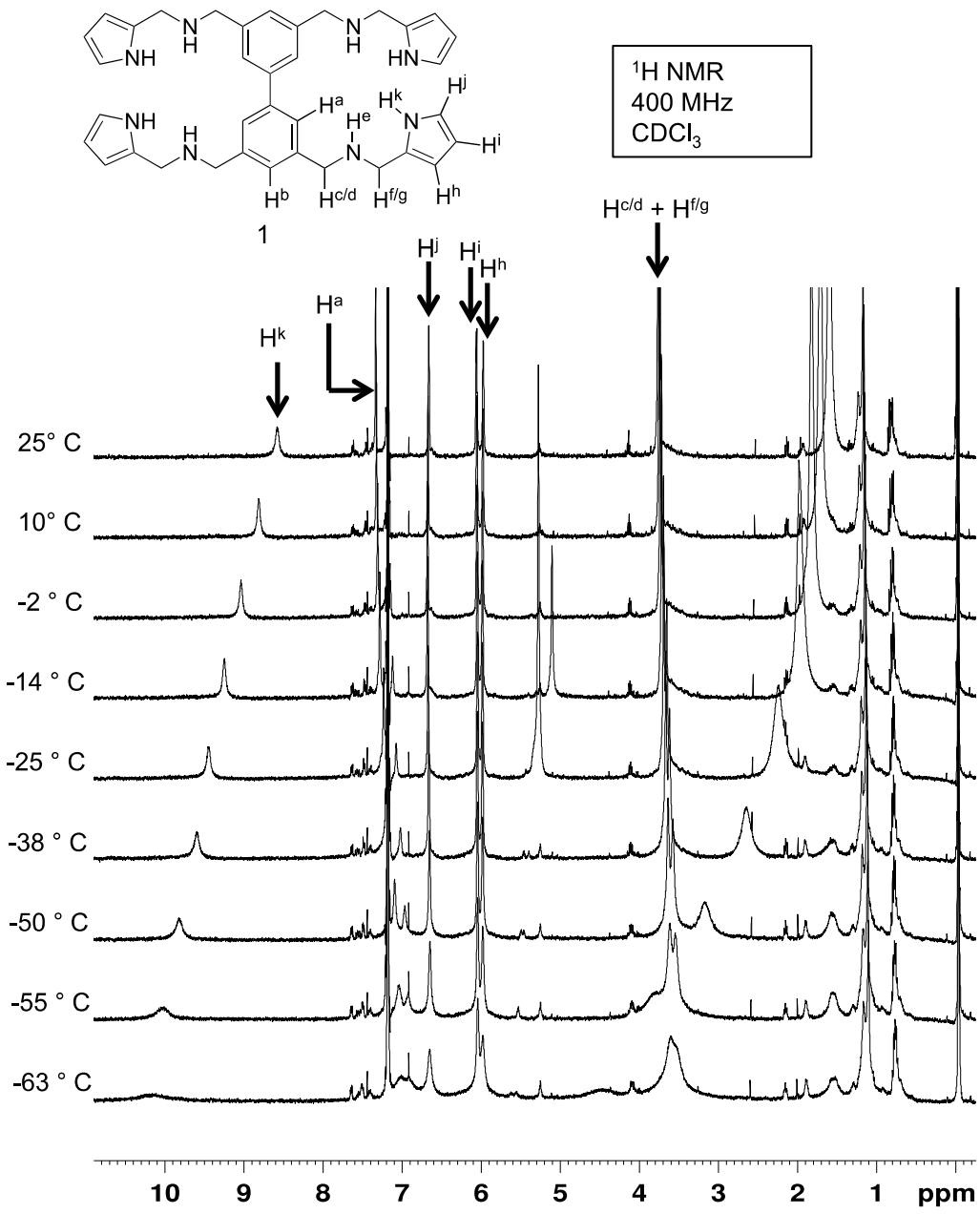
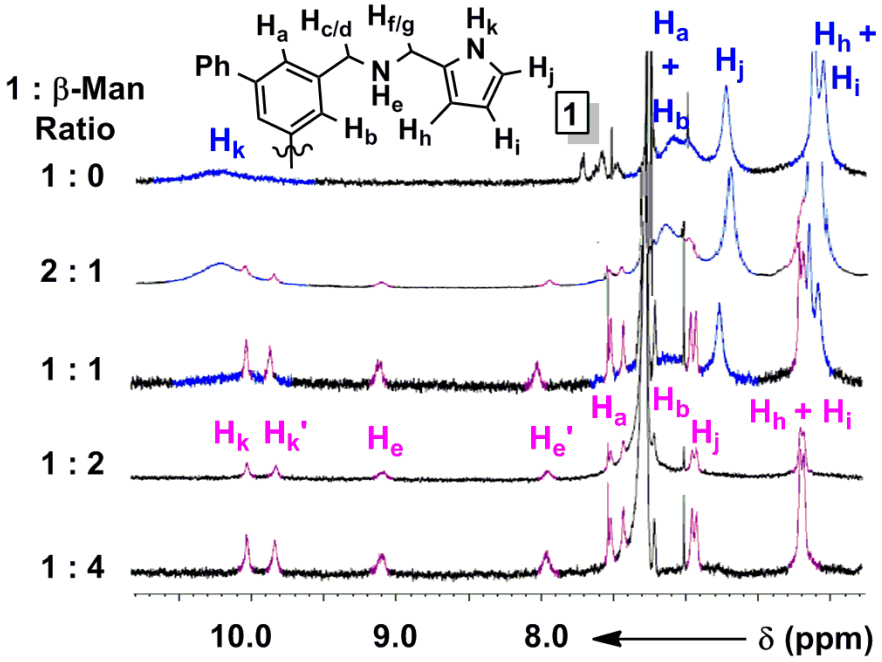


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$, −63°C) of **1** (6.0 mM for 2:1 **1**:β-Man; 1.0mM for all other ratios) and β-Man. The blue and purple signals correspond to **1** and **1**; β-Man_2 respectively.



3. NMR Titrations and Peak Shift Fittings

^{1}H NMR titrations were performed in $CDCl_3$ at a field strength of either 500, 800, or 900 MHz at 25, 20, 15, 10, or 5°C. The ^{1}H NMR resonances corresponding to both pyranoside and host were assigned through ^{1}H-^{1}H COSY and NOESY experiments. The experimental temperatures were verified through calibration with a 100% methanol standard.[4]

Models for ^{1}H NMR Titration Fittings

The addition of **1** to a $CDCl_3$ pyranoside solution or vice versa resulted in the perturbation of the chemical shifts (δ) corresponding to resonances of both **1** and pyranoside. This is the result of an exchange process involving **1** (H) and pyranoside (G) equilibria products interchanging fast on the NMR timescale, resulting in the averaging of chemical shits of protons in differing chemical environments. Accordingly, equilibrium constants can be quantified by first defining a model that includes the correct set of equilibria, calculating the hypothetical concentrations of equilibrium species and the corresponding chemical shifts, and finally fitting the resulting data to the experimental results.

The equilibria involved in a $CDCl_3$ mixture of β-Man and **1** are K_{dimer}, K_1, K_2, and K_3, which are expressed by the following relationships:

(1) $$K_{\text{dimer}} = \frac{[\text{H}_2]}{[\text{H}]^2}$$

(2) $$K_1 = \frac{[\text{HG}]}{[\text{H}][\text{G}]}$$

(3) $$K_2 = \frac{[\text{HG}_2]}{[\text{HG}][\text{G}]}$$

(4) $$K_3 = \frac{[\text{H}_2\text{G}]}{[\text{HG}][\text{H}]}$$

Likewise, mass balance equations relating the known total concentrations of **1** ($[H]_t$) and pyranoside ($[G]_t$) with their corresponding equilibrium concentrations can be derived:

(5) $$[H]_t=[H]+2[H_2]+[HG]+[HG_2]+2[H_2G]$$

(6) $$[G]_t=[G]+[HG]+2[HG_2]+[H_2G]$$

Combining equations (1) through (6) yields the following relationships:

(7) $$[H]_t=[H]+2K_{dimer}[H]^2+K_1[H][G]+K_1K_2[H][G]^2+2K_1K_3[H]^2[G]$$

(8) $$[G]_t=[G]+K_1[H][G]+2K_1K_2[H][G]^2+K_1K_3[H]^2[G]$$

Combining equations (7) and (8) yields equation (9), which can be solved for [G] to give equation (10):

(9) $$[G]_t-2[H]_t=[G]-2[H]-4K_{dimer}[H]^2-K_1[H][G]-3K_1K_3[H]^2[G]$$

(10) $$[G]=\frac{[G]_t-2[H]_t+2[H]+4K_{dimer}[H]^2}{1-K_1[H]-3K_1K_3[H]^2}$$

Combining equations (8) and (10) gives polynomial equation (11), which, when subjected to the boundary conditions specified by equations (7) and (8), can be solved iteratively to obtain the equilibrium concentration of free host for any value of $[H]_t$, $[G]_t$, K_{dimer}, K_1, K_2, and K_3.

(11) $$\begin{aligned}0=&(-6K_{dimer}[K_1K_3]^2)[H]^6+(16K_{dimer}^2K_1K_2-8K_{dimer}K_1^2K_3-3[K_1K_3]^2)[H]^5+\\&(16K_{dimer}K_1K_2-4K_1^2K_3-2K_{dimer}K_1^2+3[K_1K_3]^2[H]_t-6[K_1K_3]^2[G]_t-4K_{dimer}K_1K_3)[H]^4+\\&(-16K_{dimer}K_1K_2[H]_t+8K_{dimer}K_1K_2[G]_t+4K_1K_2+4K_1^2K_3[H]_t-5K_1^2K_3[G]_t-K_1^2-\\&2K_1K_3)[H]^3+(-8K_1K_2[H]_t+4K_1K_2[G]_t+K_1^2[H]_t-K_1^2[G]_t+2K_1K_3[H]_t+2K_1K_3[G]_t+\\&2K_{dimer})[H]^2+(-4K_1K_2[G]_t[H]_t+4K_1K_2[H]_t^2+K_1K_2[G]_t^2+K_1[G]_t+1)[H]-[H]_t\end{aligned}$$

By following a similar protocol, models can be derived for other sets of equilibria, including K_1 and K_2 (Equation (12)) and K_{dimer}, K_1, and K_3 (Equation (13)).

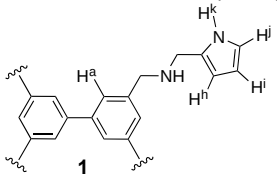
(12) $$0=K_1K_2[G]^3+(-K_1K_2[G]_t+K_1+2K_1K_2[H]_t)[G]^2+(-K_1[G]_t+K_1[H]_t+1)[G]-[G]_t$$

(13) $$\begin{aligned}0=&2K_{dimer}K_1K_3[H]^4+2(K_{dimer}K_1+K_1K_3)[H]^3+(K_1+2K_{dimer}+2K_1K_3[G]_t-K_1K_3)[H]^2\\&+(1+K_1[G]_t-K_1[H]_t)[H]-[H]_t\end{aligned}$$

Fittings were conducted in Microsoft Excel 2007 using the Solver feature. Accordingly, all observable host and guest peaks were simultaneously fitted by minimizing the total sum of squared residuals (the differences between experimental values and fitted values) using the binding constants (K_1 and K_2) and individual chemical shifts (δ_H, δ_{H2}, δ_{HG}, and δ_{H2G}) as fitting parameters. The binding constant describing the dimerization process, K_{dimer}, was determined through ^{1}H NMR dilution experiments and was held constant throughout the fitting process. β-GlcNAc binding constants at 10 and 5° C could not be determined due to significant signal broadenin

Determination of K_1 and K_2

The quantification of K_{dimer}, K_1, K_2, and K_3 from a single ^{1}H NMR titration experiment under the fast exchange regime is possible by fitting the chemical shift changes, $\Delta\delta$, but the large number of fitting parameters often results in multiple points of convergence.[5] Thus, the binding of pyranosides was first studied under conditions where receptor **1** was maintained at a low concentration (<70 μM) to minimize the contribution of the K_{dimer} and K_3 equilibria (Figure 2).



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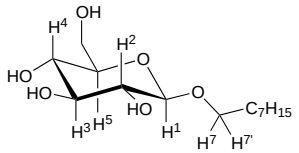
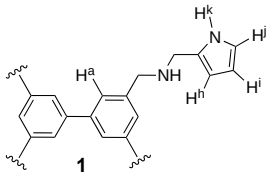


b- Glc

Table S1. ^{1}H NMR (600 MHz, 25° C) chemical shifts (ppm) of a 60 μM solution of **1** [H] in $CDCl_3$ upon incremental addition of β-Glc [G].

Concentration						
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H
0.000058286	0	8.4821	7.4227	6.7435	6.1459	6.0532
5.71431E-05	0.000289725	8.5572	7.4234	6.7448	6.1438	6.0557
5.60442E-05	0.000568308	8.6551	N/A	6.7422	6.1354	6.0559
5.49868E-05	0.000836377	8.722	N/A	6.7434	6.1333	6.0591
5.39685E-05	0.001094519	N/A	N/A	6.7434	6.1296	6.0602
5.29873E-05	0.001343273	N/A	N/A	6.7463	6.1306	6.0639
5.06835E-05	0.001927304	N/A	N/A	6.7492	6.1278	6.0692
4.85717E-05	0.002462667	N/A	N/A	6.7548	6.1291	N/A



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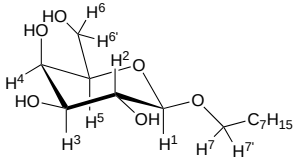
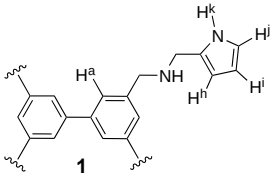


b- Gal

Table S2. ^{1}H NMR (600 MHz, 25° C) chemical shifts (ppm) of a 50 μM solution of **1** [H] in $CDCl_3$ upon incremental addition of β-Gal [G].

Concentration						
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H
0.000047718	0	8.5082	7.4253	6.745	6.145	6.0537
4.67824E-05	0.000288824	8.5108	N/A	6.7443	6.1436	6.0541
4.58827E-05	0.000566538	8.5406	N/A	6.7443	6.1425	6.0539
4.5017E-05	0.000833774	N/A	N/A	6.7435	6.1414	6.0546
4.41833E-05	0.001091111	8.5671	N/A	6.7448	6.1413	6.0543
0.00004338	0.001339091	8.5702	N/A	6.7448	6.1388	6.0538
4.14939E-05	0.001921304	N/A	N/A	6.7455	6.1352	6.0582
0.000039765	0.002455	N/A	N/A	6.7521	6.1337	6.0657

N/A-Peak could not be resolved.



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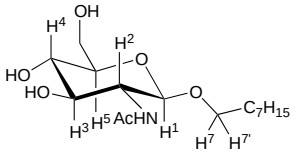
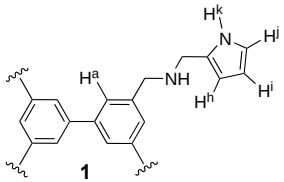


b- GlcNAc

Table S3. ^{1}H NMR (600 MHz, 25° C) chemical shifts (ppm) of a 60 μM solution of **1** [H] in $CDCl_3$ upon incremental addition of β -GlcNAc [G].

Concentration						
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H
0.000058286	0	8.64	7.548	6.7488	6.141	6.0558
5.71431E-05	0.000254843	8.646	7.73	6.7482	6.1407	6.0575
5.60442E-05	0.000499885	8.663	7.4317	6.749	6.1404	6.0582
5.49868E-05	0.000735679	8.681	N/A	6.7496	6.1408	6.0591
5.39685E-05	0.000962741	8.695	N/A	6.7498	6.1409	6.0596
5.29873E-05	0.001181545	8.7105	N/A	6.7505	6.1405	6.0606
5.06835E-05	0.001695261	8.721	N/A	6.7514	6.1392	6.0628
4.85717E-05	0.002166167	8.776	N/A	6.7527	6.1386	6.0656



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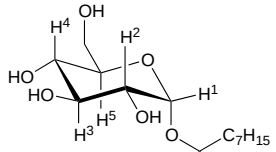
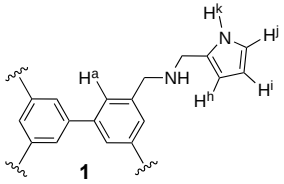


a- Glc

Table S4. ^{1}H NMR (600 MHz, 25° C) chemical shifts (ppm) of a 60 μM solution of **1** [H] in $CDCl_3$ upon incremental addition of α -Glc [G].

Concentration						
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H
0.000058286	0	8.4985	7.4236	6.7445	6.1452	6.0539
5.71431E-05	0.000327255	8.5914	N/A	6.7445	6.1421	6.05689
5.60442E-05	0.000641923	8.6666	N/A	6.7438	6.1396	6.0593
5.49868E-05	0.000944717	8.7373	N/A	6.7441	6.1373	6.062
5.39685E-05	0.001236296	8.799	N/A	6.7444	6.1353	6.0646
5.29873E-05	0.001517273	8.857	N/A	6.7451	6.1335	6.0671
5.06835E-05	0.002176957	8.9497	N/A	6.7456	6.131	6.0715
4.85717E-05	0.002781667	9.04	7.4511	6.7463	6.129	6.076

N/A-Peak could not be resolved.



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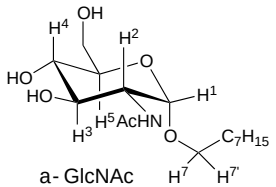
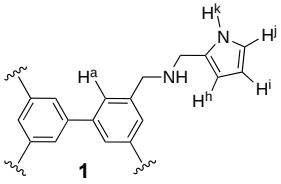


a- GlcNAc

Table S5. ^{1}H NMR (600 MHz, 25° C) chemical shifts (ppm) of a 60 μM solution of **1** [H] in $CDCl_3$ upon incremental addition of α -GlcNAc [G].

Concentration						
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H
0.000058286	0	8.533	7.4272	6.7461	6.1448	6.0545
5.71431E-05	0.000279529	8.614	7.4218	6.7469	6.1428	6.0573
5.60442E-05	0.000548308	8.6868	N/A	6.7478	6.1395	6.0609
5.49868E-05	0.000806943	8.749	7.4496	6.7513	6.138	6.0646
5.39685E-05	0.001056	8.827	7.4592	6.7536	6.1361	6.0686
5.29873E-05	0.001296	N/A	7.4698	6.7572	6.1361	6.0736
5.06835E-05	0.001859478	N/A	N/A	6.7642	6.1329	6.0849
4.85717E-05	0.002376	N/A	7.4317	N/A	N/A	N/A



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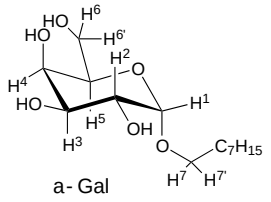
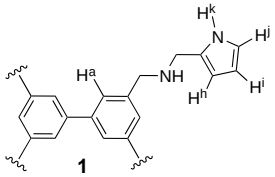


a- Gal

Table S6. ^{1}H NMR (600 MHz, 25° C) chemical shifts (ppm) of a 60 μM solution of **1** [H] in $CDCl_3$ upon incremental addition of α -Gal [G].

Concentration						
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H
0.000047718	0	8.5082	7.4253	6.745	6.145	6.0537
4.67824E-05	0.000312078	8.5108	N/A	6.7443	6.1436	6.0541
4.63282E-05	0.000463573	8.5406	N/A	6.7443	6.1425	6.0539
4.58827E-05	0.000612154	N/A	N/A	6.7435	6.1414	6.0546
4.5017E-05	0.000900906	8.5671	N/A	6.7448	6.1413	6.0543
4.41833E-05	0.001178963	8.5702	N/A	6.7448	6.1388	6.0538
4.22283E-05	0.001831044	N/A	N/A	6.7455	6.1352	6.0582
4.67824E-05	0.000312078	N/A	N/A	6.7521	6.1337	6.0657

N/A-Peak could not be resolved.



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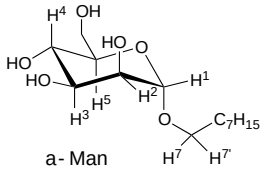


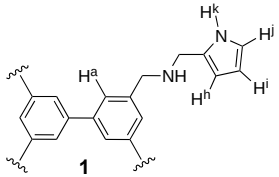
a- Man

Table S7. ^{1}H NMR (600 MHz, 25° C) chemical shifts (ppm) of a 60 μM solution of **1** [H] in $CDCl_3$ upon incremental addition of α-Man [G].

Concentration					
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	j H	i H	h H
0.000058626	0	8.5127	6.7455	6.1451	6.0542
5.83E-05	6.7942E-05	8.5543	6.7462	6.144	6.0561
5.80E-05	0.000136657	8.5892	6.7473	6.1433	6.058
5.77E-05	0.000203481	8.6284	6.7479	6.1415	6.0599
5.74E-05	0.000269461	8.6841	6.7505	6.1416	6.0639
5.69E-05	0.000400268	8.79	6.7556	6.1413	6.0724
5.63E-05	0.000528558	8.8818	6.7597	6.1411	6.0798
5.53E-05	0.000777879	9.0269	6.7705	6.1399	6.0929
5.42E-05	0.001017964	N/A	N/A	N/A	N/A
5.32E-05	0.00124932	9.2026	6.7843	6.1391	6.1117
5.09E-05	0.001792503	9.2883	6.7927	N/A	N/A
4.88E-05	0.00229042	9.3624	N/A	N/A	N/A

N/A-Peak could not be resolved.

Table S8. ^{1}H NMR (600 MHz, 25° C) chemical shifts (ppm) of a 60 μM solution of **1** [H] in $CDCl_3$ upon incremental addition of β-Man [G].



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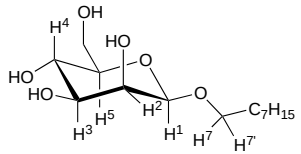


b- Man

Concentration						
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H
0.000058626	0	8.4718	7.4227	6.7439	6.1463	6.0532
5.83E-05	5.82E-05	8.5181	7.4227	6.7442	6.1444	6.055
5.80E-05	0.000124299	8.5664	7.4232	6.7456	6.143	6.0579
5.78E-05	0.00020295	8.6188	7.4243	6.7474	6.1421	6.0608
5.75E-05	0.00027226	8.6754	7.4255	6.7489	6.1409	6.0638
5.69E-05	0.000441141	8.7962	N/A	6.7548	6.1388	6.0727
5.64E-05	0.000541631	8.8984	N/A	6.7605	6.1367	6.0794
5.53E-05	0.000938741	9.0907	7.4426	6.7737	6.1353	6.095
5.43E-05	0.00115231	9.237	7.4522	6.7835	6.1338	6.1055
5.33E-05	0.001411746	9.3172	7.463	6.7904	6.1322	N/A
5.23E-05	0.00168343	9.4077	7.4735	6.7982	6.1319	N/A
5.14E-05	0.00209793	9.4878	7.4227	6.8053	6.1328	N/A
5.05E-05	0.002498138	N/A	N/A	6.8106	6.1326	N/A
4.97E-05	0.00288478	N/A	N/A	6.8149	6.133	N/A

N/A-Peak could not be resolved.

Table S9. ^{1}H NMR (600 MHz, 20° C) chemical shifts (ppm) of a .06 mM solution of **1** [H] in $CDCl_3$ upon incremental addition of β-Man [G].

Concentration						
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H
0.000058626	0	8.4718	7.4227	6.7439	6.1463	6.0532
5.83E-05	5.82E-05	8.5181	7.4227	6.7442	6.1444	6.055
5.80E-05	0.000124299	8.5664	7.4232	6.7456	6.143	6.0579
5.78E-05	0.00020295	8.6188	7.4243	6.7474	6.1421	6.0608
5.75E-05	0.00027226	8.6754	7.4255	6.7489	6.1409	6.0638
5.69E-05	0.000441141	8.7962	N/A	6.7548	6.1388	6.0727
5.64E-05	0.000541631	8.8984	N/A	6.7605	6.1367	6.0794
5.53E-05	0.000938741	9.0907	7.4426	6.7737	6.1353	6.095
5.43E-05	0.00115231	9.237	7.4522	6.7835	6.1338	6.1055
5.33E-05	0.001411746	9.3172	7.463	6.7904	6.1322	N/A
5.23E-05	0.00168343	9.4077	7.4735	6.7982	6.1319	N/A
5.14E-05	0.00209793	9.4878	N/A	6.8053	6.1328	N/A
5.05E-05	0.002498138	N/A	N/A	6.8106	6.1326	N/A
4.97E-05	0.00288478	N/A	N/A	6.8149	6.133	N/A

N/A-Peak could not be resolved.

Table S10. ^{1}H NMR (600 MHz, 15° C) chemical shifts (ppm) of a .06 mM solution of **1** [H] in $CDCl_3$ upon incremental addition of β-Man [G].

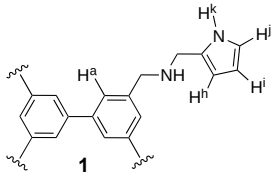
Concentration						
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H
0.000058626	0	8.5121	7.4228	6.7506	6.1473	6.0546
5.83E-05	5.82E-05	8.6072	7.4225	6.7526	6.1448	6.0592
5.80E-05	0.000124299	8.7243	7.4244	6.7574	6.1426	6.0665
5.78E-05	0.00020295	8.8451	7.4269	6.764	6.1407	6.0748
5.75E-05	0.00027226	8.9616	N/A	6.7709	6.1396	6.0831
5.69E-05	0.000441141	9.169	N/A	6.7859	6.1378	6.0989
5.64E-05	0.000541631	9.2981	7.4426	6.7955	6.1369	6.1095
5.53E-05	0.000938741	9.4571	7.4519	6.8084	6.1344	N/A
5.43E-05	0.00115231	9.5324	7.4561	6.8136	6.1338	N/A
5.33E-05	0.001411746	9.5701	7.4619	6.8171	6.134	N/A
5.23E-05	0.00168343	9.6066	7.4662	6.8185	6.1338	N/A
5.14E-05	0.00209793	9.6353	N/A	6.8205	6.1338	N/A
5.05E-05	0.002498138	9.6356	N/A	6.822	6.1334	N/A
4.97E-05	0.00288478	N/A	N/A	6.822	6.1328	N/A

N/A-Peak could not be resolved.

Table S11. ^{1}H NMR (600 MHz, 10° C) chemical shifts (ppm) of a .06 mM solution of **1** [H] in $CDCl_3$ upon incremental addition of β-Man [G].

Concentration						
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H
0.000058626	0	8.5372	7.4225	6.7544	6.1478	6.0554
5.83E-05	5.82E-05	8.6809	7.4226	6.7584	6.1444	6.0633
5.80E-05	0.000124299	8.8619	7.4262	6.7688	6.1419	6.076
5.78E-05	0.00020295	9.035	N/A	6.78	6.1407	6.0879
5.75E-05	0.00027226	9.1713	N/A	6.7901	6.1399	6.0991
5.69E-05	0.000441141	9.3733	7.4419	6.8062	6.1388	6.1153
5.64E-05	0.000541631	9.4782	7.4474	6.8153	6.1371	N/A
5.53E-05	0.000938741	9.5825	7.4532	6.8232	6.1361	N/A
5.43E-05	0.00115231	9.6177	7.4557	6.8255	6.1361	N/A
5.33E-05	0.001411746	9.6392	7.4589	6.8257	6.1357	N/A
5.23E-05	0.00168343	9.6586	7.4671	6.8255	6.1349	N/A
5.14E-05	0.00209793	9.6733	7.4713	6.8258	6.1345	N/A
5.05E-05	0.002498138	9.6911	N/A	6.8255	6.134	N/A
4.97E-05	0.00288478	8.5372	N/A	6.8262	6.1334	N/A

Determination of K_1 and K_3



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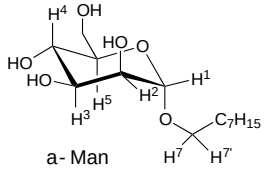
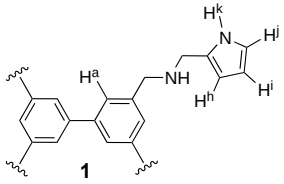


a- Man

Table S12. ^{1}H NMR (900 MHz, 25° C) chemical shifts (ppm) of a 1.0 mM solution of α-Man [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)								
[H] mol L^{-1}	[G] mol L^{-1}	k H	a H	j H	i H	h H	1 G	7 G	5 G	7' G
0.000000	0.000620	N/A	N/A	N/A	N/A	N/A	4.8356	3.6682	3.6223	3.4041
0.000212	0.000618	8.9233	7.4469	6.7571	6.1372	6.0770	4.7961	3.6426	3.5709	3.3827
0.000421	0.000615	8.8783	7.4358	6.7530	6.1371	6.0712	4.7727	3.6376	3.5482	3.3691
0.000630	0.000613	8.8103	7.4285	6.7495	6.1372	6.0652	4.7616	3.6220	3.5297	3.3602
0.000836	0.000610	8.7959	7.4259	6.7480	6.1371	6.0637	4.7490	3.6076	3.5159	3.3566
0.001245	0.000605	8.7710	7.4211	6.7459	6.1375	6.0617	4.7293	3.5948	3.4978	3.3393
0.001647	0.000601	8.7615	7.4182	6.7443	6.1371	6.0602	4.7170	3.5928	3.4847	3.3333
0.002042	0.000596	8.7560	7.4161	6.7434	6.1377	6.0598	4.7071	3.5924	3.4795	3.3263
0.002432	0.000592	8.7551	7.4143	6.7422	6.1377	6.0593	4.7000	3.5912	3.4762	3.3213
0.003933	0.000574	8.7635	7.4083	6.7385	6.1371	6.0578	4.6794	3.5887	3.4573	3.3065
0.008100	0.000525	8.8076	7.3960	6.7286	6.1342	6.0551	4.6550	3.5819	3.4441	3.2895
0.016225	0.000431	8.8968	7.3788	6.7132	6.1300	6.0520	4.6404	N/A	N/A	N/A



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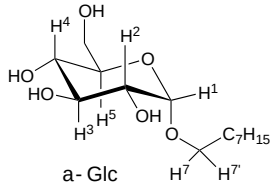


a- Glc

Table S13. ^{1}H NMR (500 MHz, 25° C) chemical shifts (ppm) of a 1.0 mM solution of α-Glc [G] in $CDCl_3$ upon the incremental addition of mM **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)									
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	6 G	4 G	2 G	7' G
0.000000	0.001000	N/A	N/A	N/A	N/A	N/A	4.8657	3.8458	3.5673	3.4699	3.4452
0.000249	0.000996	8.8052	7.4336	6.7459	6.1352	6.0645	4.8514	N/A	3.539	N/A	N/A
0.000496	0.000992	8.8086	7.4322	6.7452	6.1353	6.0649	4.8318	3.8166	3.4972	N/A	N/A
0.000741	0.000988	8.8068	7.4307	6.745	6.1356	6.0638	4.8136	3.7884	3.4597	3.3909	N/A
0.000984	0.000984	8.8038	7.4289	6.7441	6.1357	6.0633	4.7965	3.7778	3.4265	3.3565	3.4026
0.001465	0.000977	8.7925	7.4258	6.7425	6.1361	6.0619	4.7735	3.7583	N/A	3.3151	N/A
0.001938	0.000969	8.7879	7.4231	6.7413	6.1358	6.0606	4.7526	3.7406	3.3497	3.2838	3.361
0.002404	0.000962	8.7813	7.4206	6.7399	6.1361	6.0597	4.7385	3.7242	3.3129	3.2628	3.3462
0.002863	0.000954	8.7805	7.4181	6.7387	6.1358	6.0588	4.7244	3.7091	3.2929	3.2458	3.3476
0.004630	0.000926	8.7788	7.41	6.7335	6.1351	6.0564	4.6956	3.6887	3.2241	3.1992	3.3227
0.009534	0.000847	8.824	7.3953	6.7232	6.1328	6.0537	4.6607	3.6414	3.1817	3.1488	3.2976
0.019097	0.000694	8.9134	7.3766	6.7079	6.1288	6.0514	4.6353	3.6012	3.1241	3.1241	3.2827

N/A-Peak could not be resolved.

Table S14. ^{1}H NMR (500 MHz, 20° C) chemical shifts (ppm) of a 1.0 mM solution of α-Glc [G] in $CDCl_3$ upon the incremental addition of mM **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)									
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	6 G	4 G	2 G	7' G
0.000000	0.001000	N/A	N/A	N/A	N/A	N/A	4.8659	3.8469	3.5697	3.4702	3.4409
0.000249	0.000996	8.8993	7.4369	6.7496	6.1335	6.0687	4.8476	N/A	3.532	N/A	N/A
0.000496	0.000992	8.8943	7.4341	6.7482	6.1336	6.068	4.8213	3.8055	3.4776	N/A	N/A
0.000741	0.000988	8.8819	7.4315	6.747	6.1342	6.0664	4.7989	3.7843	3.4321	3.3672	N/A
0.000984	0.000984	8.8764	7.4289	6.7467	6.1343	6.0655	4.7798	3.7637	3.3925	3.3243	3.3925
0.001465	0.000977	8.8572	7.4248	6.7451	6.1347	6.0636	4.752	3.7381	3.3559	3.2785	N/A
0.001938	0.000969	8.8464	7.4207	6.7433	6.1346	6.0629	4.7297	3.715	3.2933	3.2427	3.3494
0.002404	0.000962	8.8411	7.4179	6.742	6.1348	6.0606	4.7144	3.7003	3.2644	3.2235	3.3402
0.002863	0.000954	8.8394	7.4147	6.74	6.1344	6.0599	4.7006	3.6893	3.2397	3.2032	3.3328
0.004630	0.000926	8.8408	7.4057	6.7346	6.1338	6.057	4.6729	3.6566	3.1806	3.1553	3.3035
0.009534	0.000847	8.8899	7.3877	6.7227	6.131	6.0536	4.6389	3.6049	3.1135	3.1135	3.2795
0.019097	0.000694	8.9853	7.3673	6.7061	6.1268	6.0509	4.6248	3.5875	3.0956	3.0956	3.265

N/A-Peak could not be resolved.

Table S15. ^{1}H NMR (500 MHz, 15° C) chemical shifts (ppm) of a 1.0 mM solution of α-Glc [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)									
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	6 G	4 G	2 G	7' G
0.000000	0.001000	N/A	N/A	N/A	N/A	N/A	4.8661	3.8461	3.5717	3.4734	3.4388
0.000249	0.000996	8.9822	7.4398	6.7517	6.1317	6.0724	4.8428	N/A	3.5246	N/A	N/A
0.000496	0.000992	8.9645	7.4366	6.7506	6.1322	6.0697	4.8106	3.7937	3.458	N/A	N/A
0.000741	0.000988	8.9488	7.4323	6.7495	6.1328	6.0684	4.7848	3.7688	3.405	3.332	3.3876
0.000984	0.000984	8.936	7.429	6.7487	6.1328	6.0673	4.7628	3.7466	3.3602	3.2946	3.3583
0.001465	0.000977	8.9137	7.4235	6.7468	6.1335	6.0647	4.7316	3.7176	3.2973	3.2416	3.3482
0.001938	0.000969	8.8991	7.4187	6.7448	6.1335	6.063	4.7078	3.6954	3.2499	3.2053	3.3337
0.002404	0.000962	8.893	7.4152	6.7426	6.1336	6.0616	4.692	3.6814	3.2204	3.1861	3.3216
0.002863	0.000954	8.8872	7.4112	6.7408	6.1333	6.0603	4.68	3.668	3.1955	3.1646	3.3102
0.004630	0.000926	8.8957	7.401	6.7345	6.1325	6.0573	4.6512	3.6378	3.13	3.13	3.2887
0.009534	0.000847	8.9478	7.3808	6.7217	6.1296	6.0537	4.623	3.5958	3.0848	3.0848	3.2621
0.019097	0.000694	9.0466	7.3588	6.704	6.1248	6.0505	4.6073	3.584	3.0736	3.0736	3.2535

N/A-Peak could not be resolved.

Table S16. ^{1}H NMR (500 MHz, 10° C) chemical shifts (ppm) of a 1.0 mM solution of α-Glc [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)									
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	6 G	4 G	2 G	7' G
0.000000	0.001000	N/A	N/A	N/A	N/A	N/A	4.8667	3.8476	3.5743	3.475	3.4342
0.000249	0.000996	9.0832	7.4453	6.7546	6.1295	6.0766	4.8365	N/A	3.5136	3.4265	3.4139
0.000496	0.000992	9.0528	7.4387	6.7527	6.1297	6.0739	4.7964	3.7809	3.4315	N/A	N/A
0.000741	0.000988	9.0323	7.4333	6.7516	6.1313	6.071	4.7652	3.7499	3.3671	3.297	3.3709
0.000984	0.000984	9.0147	7.4287	6.7505	6.1312	6.0696	4.7392	3.7278	3.3161	3.2536	3.3516
0.001465	0.000977	8.9838	7.4218	6.7483	6.1322	6.0663	4.705	3.6948	3.2481	3.1957	3.3291
0.001938	0.000969	8.9646	7.4157	6.7458	6.1324	6.064	4.6813	3.671	3.2	3.1581	3.3096
0.002404	0.000962	8.961	7.4114	6.744	6.1322	6.0626	4.6665	3.6563	3.1723	3.1353	3.2992
0.002863	0.000954	8.9546	7.4068	6.7417	6.1321	6.0612	4.6534	3.6433	3.1475	3.1154	3.2888
0.004630	0.000926	8.9653	7.3949	6.7351	6.131	6.0581	N/A	3.6144	3.0904	3.0904	3.2692
0.009534	0.000847	9.0218	7.3718	6.72	6.1278	6.0535	N/A	3.5832	3.0543	3.0543	3.2446
0.019097	0.000694	9.1238	7.3481	6.7012	6.1226	6.0499	N/A	3.5767	3.0522	3.0522	3.2317

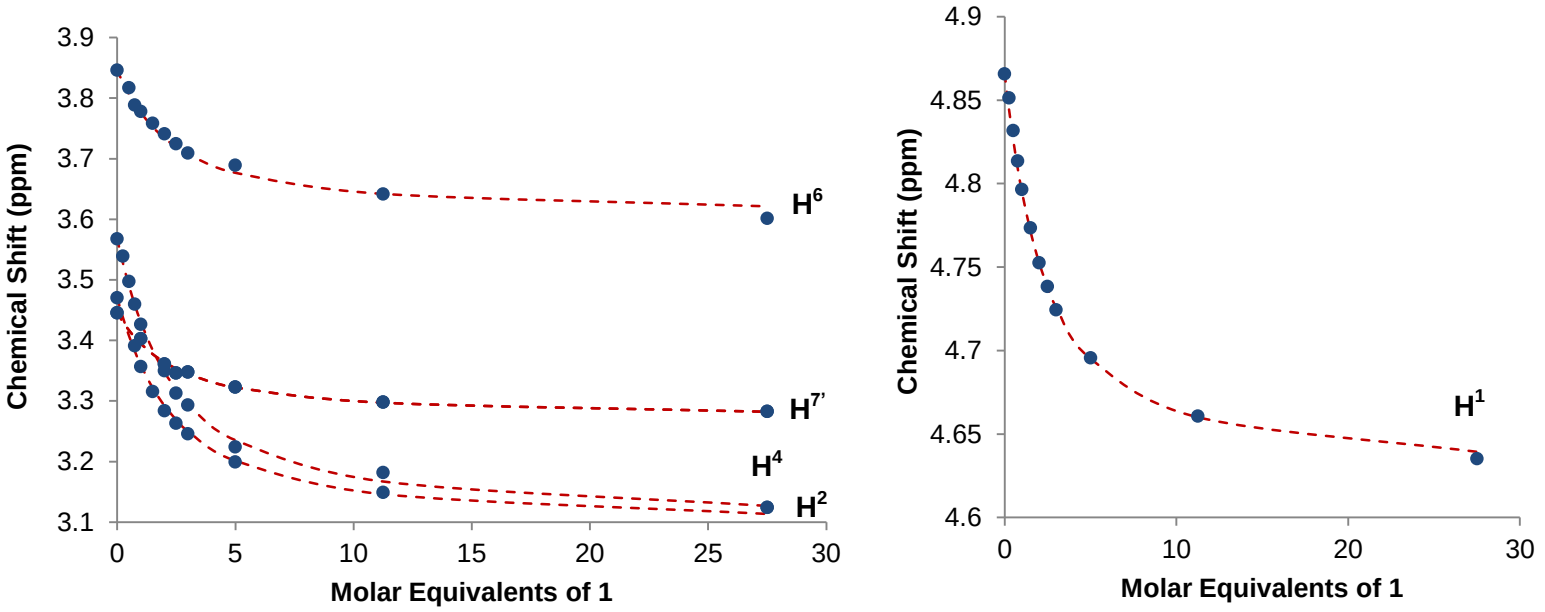
N/A-Peak could not be resolved.

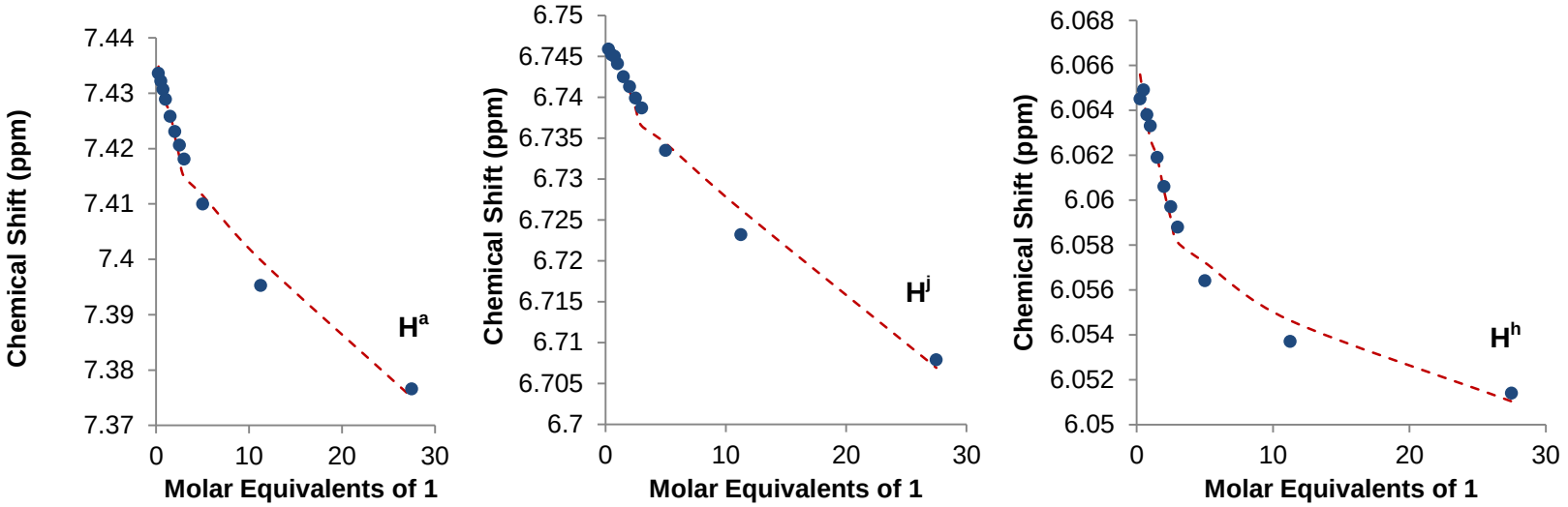
Table S17. ^{1}H NMR (500 MHz, 5° C) chemical shifts (ppm) of a 1.0 mM solution of α-Glc [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

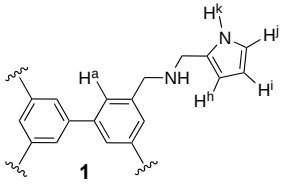
Concentration		^{1}H NMR Peak Shift (δ)									
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	6 G	4 G	2 G	7' G
0.000000	0.001000	N/A	N/A	N/A	N/A	N/A	4.8669	3.8463	3.5769	3.4778	3.4305
0.000249	0.000996	9.208	7.4515	6.7567	6.1262	6.082	4.8272	N/A	3.498	3.4061	3.4061
0.000496	0.000992	9.1593	7.4418	6.7549	6.1273	6.0775	4.7779	3.7634	3.3984	3.3183	3.3731
0.000741	0.000988	9.1254	7.4344	6.7531	6.1285	6.074	4.7398	3.7287	3.3219	3.2515	3.3506
0.000984	0.000984	9.1019	7.4286	6.7522	6.129	6.0717	4.7114	3.7025	3.265	3.2036	3.3318
0.001465	0.000977	9.0625	7.4193	6.7495	6.1301	6.0677	4.6747	3.6681	3.1924	3.1439	3.3046
0.002404	0.000962	9.0372	7.4058	6.7441	6.1307	6.0632	4.6364	3.6292	3.1184	3.0852	3.2744
0.002863	0.000954	9.0334	7.4009	6.7422	6.1303	6.0619	4.6238	3.6173	3.0963	3.0649	3.2654
0.004630	0.000926	9.0468	7.3862	6.7339	6.1292	6.0581	4.5995	3.5866	3.0421	3.0421	3.2441
0.009534	0.000847	9.1079	7.3604	6.7178	6.1254	6.0531	4.5822	3.557	3.0185	3.0185	3.2207
0.019097	0.000694	9.2099	7.3346	6.6973	6.1201	6.0491	N/A	3.5455	3.0243	3.0243	3.2139

N/A-Peak could not be resolved.

Figure S13: Fitting of experimental data (blue circles) with the 1:1 model (dashed red line) corresponding to the ^{1}H NMR titration of α-Glc with **1** at 25°C.







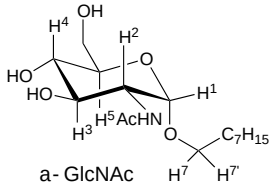


Table S18. ^{1}H NMR (800 MHz, 25° C) chemical shifts (ppm) of a 1.0 mM solution of α-GlcNAc [G] in $CDCl_3$ upon the incremental addition of **1** [H].

Concentration		^{1}H NMR Peak Shift (δ)									
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	7 G	4 G	7' G	Ac G
0.000000	0.001006	N/A	N/A	N/A	N/A	N/A	4.7835	3.648	3.5822	3.4	2.068
0.000214	0.001002	8.8449	7.4439	6.7497	6.1357	6.0667	4.7639	3.6321	3.5363	3.3895	2.0577
0.000427	0.000998	8.8393	7.4439	6.7493	6.1359	6.0663	4.7458	3.6177	3.4935	3.3796	2.0478
0.000638	0.000994	8.8396	7.4366	6.7499	6.1366	6.0675	4.7272	3.6029	3.4505	3.3693	2.0382
0.000847	0.000990	8.8327	7.4364	6.7489	6.1368	6.0665	4.7105	3.5908	3.4124	3.3602	2.0294
0.001261	0.000982	8.8212	7.4316	6.7482	6.1374	6.0656	4.6873	3.5719	3.3515	3.3515	2.0174
0.001668	0.000975	8.8091	7.4289	6.7462	6.1374	6.0639	4.6596	3.5516	3.2962	3.3322	2.0034
0.002069	0.000967	8.804	7.4253	6.7452	6.1377	6.0632	4.6397	3.5362	3.2509	3.3211	1.9929
0.002464	0.000960	8.7976	7.4228	6.7436	6.1375	6.0622	4.6227	3.524	3.2137	3.3119	1.9843
0.003985	0.000931	8.7951	7.4138	6.7382	6.1367	6.0593	4.5799	N/A	3.1135	3.2881	N/A
0.008207	0.000853	8.8671	7.3942	6.7273	6.1343	6.0573	4.5221	3.4468	2.9864	3.2564	N/A
0.016439	0.000699	8.9676	7.3722	6.7122	6.1301	6.0547	4.501	3.4275	2.939	3.2415	N/A

N/A-Peak could not be resolved.

Table S19. ^{1}H NMR (800 MHz, 20° C) chemical shifts (ppm) of a 1.0 mM solution of α-GlcNAc [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)									
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	7 G	4 G	7' G	Ac G
0.000000	0.001006	N/A	N/A	N/A	N/A	N/A	4.7821	3.6464	3.5845	3.3964	2.0699
0.000214	0.001002	8.9414	7.4526	6.7532	6.1339	6.0695	4.7568	3.6257	3.5245	3.3821	2.0562
0.000427	0.000998	8.927	7.4457	6.7533	6.1347	6.0696	4.7344	3.6078	3.4722	3.3699	2.044
0.000638	0.000994	8.9202	7.4412	6.7534	6.1354	6.0697	4.7113	3.5393	3.4183	3.3572	2.0319
0.000847	0.000990	8.9078	7.4378	6.7524	6.1357	6.0689	4.6915	3.5743	3.3721	3.347	2.0214
0.001261	0.000982	8.8912	7.4337	6.7512	6.1363	6.0673	4.6642	3.5538	3.3221	3.3221	2.0073
0.001668	0.000975	8.8713	7.4284	6.7492	6.1365	6.0653	4.6331	3.5298	3.2383	3.3147	1.991
0.002069	0.000967	8.8648	7.4247	6.7479	6.1368	6.0644	4.6113	3.5135	3.1894	3.3024	1.9798
0.002464	0.000960	8.8608	7.4199	6.7458	6.1364	6.0631	4.5936	3.4993	3.1488	3.2922	1.9699
0.003985	0.000931	8.8555	7.4097	6.7399	6.1356	6.0599	4.5529	3.467	3.0517	3.2702	N/A
0.008207	0.000853	8.9273	7.3862	6.7272	6.1329	6.0573	4.5003	3.4277	2.9391	3.2408	N/A
0.016439	0.000699	9.0375	7.362	6.7107	6.1287	6.0545	4.4853	3.4123	2.9046	3.2294	N/A

N/A-Peak could not be resolved.

Table S20. ^{1}H NMR (800 MHz, 15° C) chemical shifts (ppm) of a 1.0 mM solution of α-GlcNAc [G] in $CDCl_3$ upon the incremental addition of mM **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)									
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	7 G	4 G	7' G	Ac G
0.000000	0.001006	N/A	N/A	N/A	N/A	N/A	4.7807	3.6443	3.5877	3.3926	2.0715
0.000214	0.001002	9.0503	7.4615	6.7568	6.1321	6.0727	4.7482	3.6172	3.5105	3.3747	2.054
0.000427	0.000998	9.0242	7.449	6.7572	6.133	6.073	4.7212	3.5952	3.4464	3.3597	2.0387
0.000638	0.000994	9.0075	7.4465	6.7565	6.1337	6.072	4.693	3.573	3.3801	3.3442	2.0239
0.000847	0.000990	8.9907	7.4401	6.7558	6.1343	6.0712	4.6701	3.5562	3.3296	3.3296	2.0116
0.001261	0.000982	8.9662	7.4363	6.7544	6.1349	6.0692	4.6482	3.5345	3.266	3.3173	1.9983
0.001668	0.000975	8.9381	7.4281	6.752	6.1356	6.0668	4.6048	3.5066	3.1763	3.296	1.9774
0.002069	0.000967	8.9298	7.4235	6.7504	6.1358	6.0655	4.5817	3.4891	3.1243	3.2832	1.9655
0.002464	0.000960	8.9239	7.4173	6.748	6.135	6.064	4.5636	3.4745	3.084	3.2734	1.9552
0.003985	0.000931	8.9205	7.4046	6.7412	6.1346	6.0606	4.5253	3.4458	2.9943	3.2518	N/A
0.008207	0.000853	8.9961	7.3775	6.7269	6.1314	6.0573	4.4815	3.4111	2.8983	3.2252	N/A
0.016439	0.000699	9.1093	7.3511	6.7087	6.1269	6.0541	4.4729	3.4008	2.8779	3.217	N/A

N/A-Peak could not be resolved.

Table S21. ^{1}H NMR (800 MHz, 10° C) chemical shifts (ppm) of a 1.0 mM solution of α-GlcNAc [G] in $CDCl_3$ upon the incremental addition of **1** [H].

Concentration		^{1}H NMR Peak Shift (δ)									
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	7 G	4 G	7' G	Ac G
0.000000	0.001006	N/A	N/A	N/A	N/A	N/A	4.779	3.6408	3.5924	3.388	2.073
0.000214	0.001002	9.1712	7.4715	6.76	6.13	6.076	4.7386	3.607	3.4939	3.3655	2.0505
0.000427	0.000998	9.1297	7.4544	6.7607	6.1312	6.0767	4.7066	3.5811	3.4167	3.348	2.0324
0.000638	0.000994	9.1058	7.4519	6.7597	6.1319	6.0748	4.6727	3.5549	3.3334	3.3334	2.0143
0.000847	0.000990	9.0784	7.4435	6.7593	6.1329	6.074	4.647	3.5353	3.2758	3.3152	2.0004
0.001261	0.000982	9.0604	7.4402	6.7581	6.1332	6.0724	4.6324	3.5216	3.2423	3.3049	1.9933
0.001668	0.000975	9.011	7.4275	6.7545	6.1343	6.0684	4.5746	3.4816	3.1106	3.2763	1.9623
0.002069	0.000967	9.0006	7.4213	6.7528	6.1345	6.0668	4.5518	3.4651	3.0591	3.2644	1.9504
0.002464	0.000960	8.9931	7.4137	6.7499	6.1337	6.0647	4.5341	3.4512	3.0206	3.2539	1.9403
0.003985	0.000931	8.9885	7.398	6.742	6.1332	6.061	4.4994	3.4236	2.9381	3.2336	N/A
0.008207	0.000853	9.0723	7.3671	6.726	6.1297	6.0574	4.4649	3.3965	2.863	3.2113	N/A
0.016439	0.000699	9.1884	7.3388	6.7061	6.1248	6.0536	4.4623	3.3891	2.8543	3.2044	N/A

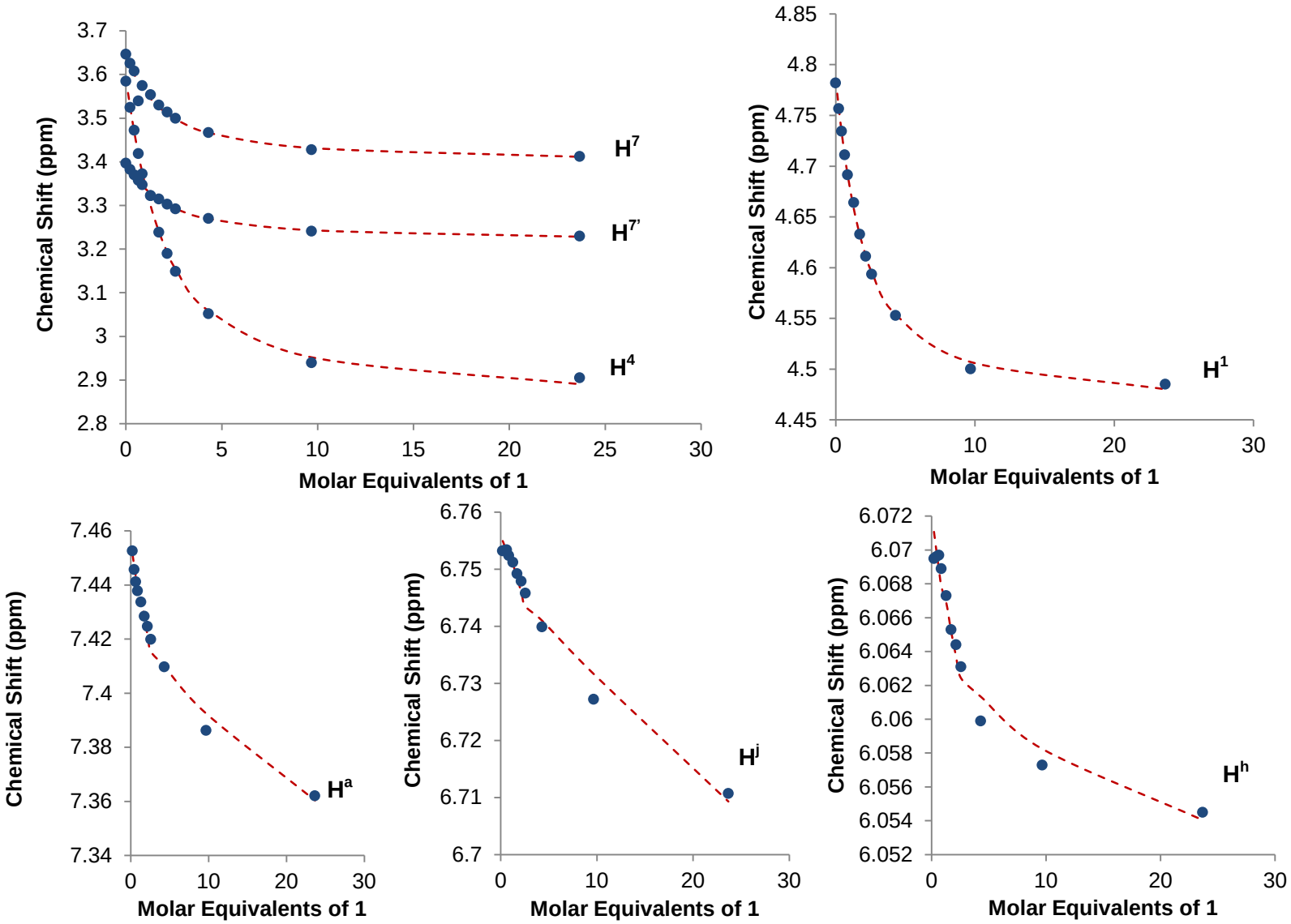
N/A-Peak could not be resolved.

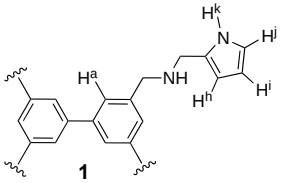
Table S22. ^{1}H NMR (800 MHz, 5° C) chemical shifts (ppm) of a 1.0 mM solution of α-GlcNAc [G] in $CDCl_3$ upon the incremental addition of **1** [H].

Concentration		^{1}H NMR Peak Shift (δ)									
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	7 G	4 G	7' G	Ac G
0.000000	0.001006	N/A	N/A	N/A	N/A	N/A	4.7769	3.6371	3.599	3.383	2.0738
0.000214	0.001002	9.2919	7.4817	6.7633	6.127	6.0797	4.7278	3.5955	3.4766	3.3556	2.0462
0.000427	0.000998	9.2385	7.4603	6.7643	6.1292	6.0803	4.6906	3.5656	3.3852	3.3354	2.0251
0.000638	0.000994	9.2061	7.4574	6.7627	6.13	6.0776	4.6511	3.5353	3.3034	3.3034	2.0038
0.000847	0.000990	9.169	7.4464	6.762	6.1311	6.0764	4.6222	3.5136	3.2233	3.2988	1.9883
0.001261	0.000982	9.1543	7.4435	6.7614	6.1315	6.0751	4.61	3.5014	3.1952	3.2893	1.9822
0.001668	0.000975	9.0862	7.4264	6.7569	6.1331	6.0699	4.5466	3.4587	3.0507	3.2583	1.9479
0.002069	0.000967	9.0734	7.4187	6.7544	6.1332	6.0678	4.5229	3.4415	2.9979	3.2452	1.9353
0.002464	0.000960	9.0643	7.4096	6.7515	6.1325	6.0658	4.5072	3.4287	2.9629	3.2356	1.9263
0.003985	0.000931	9.0574	7.3904	6.7423	6.1317	6.0612	4.4768	3.4047	2.89	3.2171	N/A
0.008207	0.000853	9.1501	7.3566	6.7248	6.1281	6.0572	4.4514	3.3827	2.8342	3.1989	N/A
0.016439	0.000699	9.2652	7.3252	6.7029	6.1227	6.0525	4.4537	3.3789	N/A	3.1927	N/A

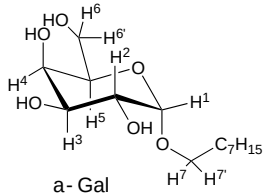
N/A-Peak could not be resolved.

Figure S14: Fitting of experimental data (blue circles) with the 1:1 model (dashed red line) corresponding to the ^{1}H NMR titration of α-GlcNAc with **1** at 25°C.





1



a- Gal

Table S23. ^{1}H NMR (500 MHz, 25° C) chemical shifts (ppm) of a 0.684 mM solution of α-Gal [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	6 G	7' G	5 G	7 G	4 G
0.000000	0.000684	N/A	N/A	N/A	N/A	N/A	4.9572	3.7332	3.4543	3.8264	3.7233	4.0991
0.000175	0.000679	8.6229	7.409	6.7412	6.1399	6.0596	4.9495	N/A	3.4484	N/A	N/A	4.0817
0.000348	0.000675	8.6167	7.4118	6.7423	6.1406	6.0591	4.9426	N/A	3.4431	3.808	N/A	4.0651
0.000519	0.000671	8.6181	7.4125	6.7424	6.1411	6.0587	4.9353	N/A	3.4378	3.7975	N/A	4.0485
0.000689	0.000667	8.6167	7.4127	6.7415	6.1411	6.0583	4.9288	N/A	3.4325	3.7904	N/A	4.0338
0.001021	0.000660	8.6181	7.4119	6.741	6.1411	6.0579	4.9166	N/A	3.4231	N/A	N/A	4.004
0.001346	0.000652	8.6204	7.4111	6.7401	6.141	6.0576	4.9065	3.7001	3.4149	3.7617	3.6869	3.9793
0.001664	0.000645	8.624	7.4102	6.7395	6.1412	6.0574	4.8974	N/A	3.4076	N/A	N/A	3.9574
0.002575	0.000624	8.6276	7.4076	6.7372	6.1409	6.0563	4.8753	3.636	3.3901	N/A	3.6556	3.9028
0.004735	0.000573	8.6432	7.4003	6.7327	6.1402	6.0547	4.8385	3.5746	3.3591	3.6704	3.6235	N/A
0.007782	0.000502	8.6737	7.3916	6.7267	6.1389	6.0534	4.8083	3.531	N/A	3.6322	N/A	N/A
0.009535	0.000462	8.6922	7.3867	6.7232	6.1386	6.0527	4.7967	3.5135	N/A	3.6178	N/A	N/A

N/A-Peak could not be resolved.

Table S24. ^{1}H NMR (500 MHz, 20° C) chemical shifts (ppm) of a 0.684 mM solution of α-Gal [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	6 G	7' G	5 G	7 G	4 G
0.000000	0.000684	N/A	N/A	N/A	N/A	N/A	4.9589	3.732	3.451	3.826	3.7222	4.1015
0.000175	0.000679	8.6862	7.4057	6.746	6.1387	6.062	4.9487	3.7298	3.4427	3.8103	3.7135	4.0778
0.000348	0.000675	8.6754	7.4084	6.7456	6.1395	6.0614	4.9392	N/A	3.4356	3.799	N/A	4.0557
0.000519	0.000671	8.6758	7.4091	6.745	6.14	6.0609	4.9296	3.7147	3.4279	3.7888	3.6977	4.0325
0.000689	0.000667	8.6735	7.4094	6.7445	6.1404	6.0603	4.9215	N/A	3.4215	3.7753	N/A	4.013
0.001021	0.000660	8.6715	7.4088	6.7433	6.1402	6.0596	4.9053	3.6777	3.4084	3.7578	3.6779	3.9738
0.001346	0.000652	8.6688	7.4079	6.7426	6.1404	6.0589	4.8934	3.6638	3.399	3.7496	3.6537	3.9435
0.001664	0.000645	8.6712	7.4065	6.7414	6.1402	6.0584	4.882	3.6381	3.3895	N/A	N/A	3.9153
0.002575	0.000624	8.6751	7.4032	6.7392	6.1402	6.0572	4.8566	3.5962	3.3686	N/A	3.6354	N/A
0.004735	0.000573	8.6936	7.3943	6.7334	6.1395	6.0553	4.8164	3.5289	3.3354	3.6352	3.6012	N/A
0.007782	0.000502	8.7272	7.3836	6.7267	6.1382	6.0537	4.7878	3.4853	3.3134	3.594	N/A	N/A

N/A-Peak could not be resolved.

Table S25. ^{1}H NMR (500 MHz, 15° C) chemical shifts (ppm) of a 0.684 mM solution of α-Gal [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	6 G	7' G	5 G	7 G	4 G
0.000000	0.000684	N/A	N/A	N/A	N/A	N/A	4.9606	3.7305	3.4472	3.8231	3.7208	4.1046
0.000175	0.000679	8.7692	7.4005	6.7487	6.1371	6.0654	4.9466	3.7254	3.4359	3.8052	3.7092	4.0722
0.000348	0.000675	8.7474	7.4041	6.748	6.138	6.0638	4.9343	3.7017	3.4261	3.7922	N/A	4.0417
0.000519	0.000671	8.7402	7.4048	6.7472	6.1381	6.0631	4.9215	N/A	3.4159	3.7731	N/A	4.0112
0.000689	0.000667	8.7366	7.4054	6.7469	6.1387	6.0625	4.911	3.682	3.4077	3.76	N/A	3.985
0.001021	0.000660	8.7304	7.4041	6.7455	6.1391	6.0612	4.8909	3.6468	3.391	3.7452	3.6623	3.9352
0.001346	0.000652	8.7258	7.4035	6.7445	6.1394	6.0602	4.8762	3.6218	3.3789	3.7115	3.6492	3.8966
0.001664	0.000645	8.7279	7.4016	6.7433	6.139	6.0594	4.8629	3.5981	3.368	3.6938	3.6381	N/A
0.002575	0.000624	8.7282	7.3978	6.7404	6.1393	6.0581	4.8345	3.5487	3.344	3.6555	3.6143	N/A
0.004735	0.000573	8.7498	7.3868	6.7337	6.1381	6.0554	4.7933	3.4808	3.3082	3.5979	N/A	N/A
0.007782	0.000502	8.7904	7.3736	6.726	6.1369	6.0535	4.7668	3.4432	3.2885	3.5632	N/A	N/A

N/A-Peak could not be resolved.

Table S26. ^{1}H NMR (500 MHz, 10° C) chemical shifts (ppm) of a 0.684 mM solution of α-Gal [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	6 G	7' G	5 G	7 G	4 G
0.000000	0.000684	N/A	N/A	N/A	N/A	N/A	4.9625	3.7296	3.444	3.8227	3.7201	4.1066
0.000175	0.000679	8.8491	7.3957	6.7517	6.1348	6.0683	4.9446	N/A	3.4297	3.8012	3.7048	4.0655
0.000348	0.000675	8.8212	7.3997	6.7508	6.1364	6.0667	4.9283	3.7073	3.4167	3.7785	3.691	4.0253
0.000519	0.000671	8.8116	7.4004	6.7496	6.1366	6.0657	4.9123	3.6995	3.4036	3.7572	3.6773	3.9865
0.000689	0.000667	8.803	7.401	6.7491	6.1371	6.0648	4.8991	N/A	3.3925	3.7386	N/A	3.9534
0.001021	0.000660	8.7942	7.3997	6.7475	6.1377	6.0632	4.8751	3.6326	3.3727	3.7063	3.6454	3.8914
0.001346	0.000652	8.7863	7.3987	6.7464	6.1383	6.0621	4.8579	3.6007	3.3583	3.6823	3.6302	N/A
0.001664	0.000645	8.787	7.3969	6.745	6.138	6.0611	4.843	3.576	3.351	3.6621	3.6175	N/A
0.002575	0.000624	8.7863	7.3917	6.7416	6.1384	6.0588	4.8128	3.5211	3.3198	3.6197	3.5908	N/A
0.004735	0.000573	8.8086	7.3782	6.7337	6.1375	6.0557	4.773	3.4531	3.2848	3.5623	3.5562	N/A
0.007782	0.000502	8.8565	7.3628	6.7249	6.1357	6.0535	4.7493	3.4201	3.266	3.5352	N/A	N/A

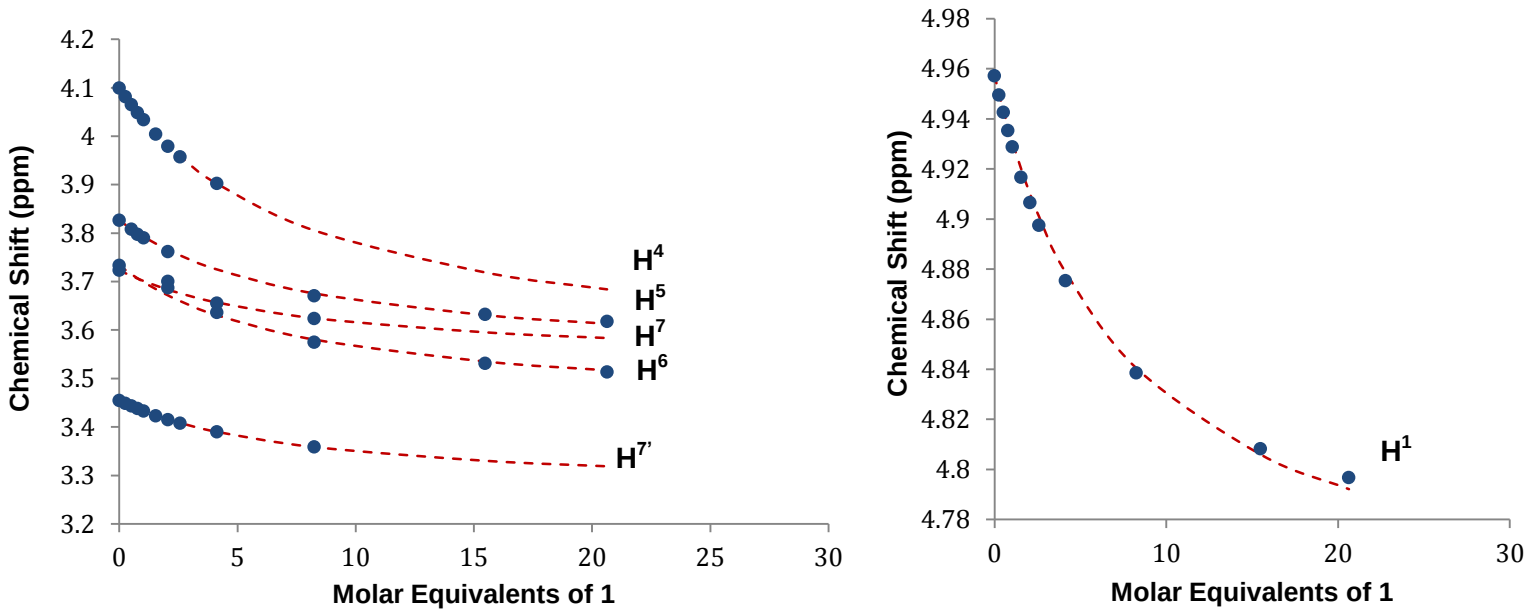
N/A-Peak could not be resolved.

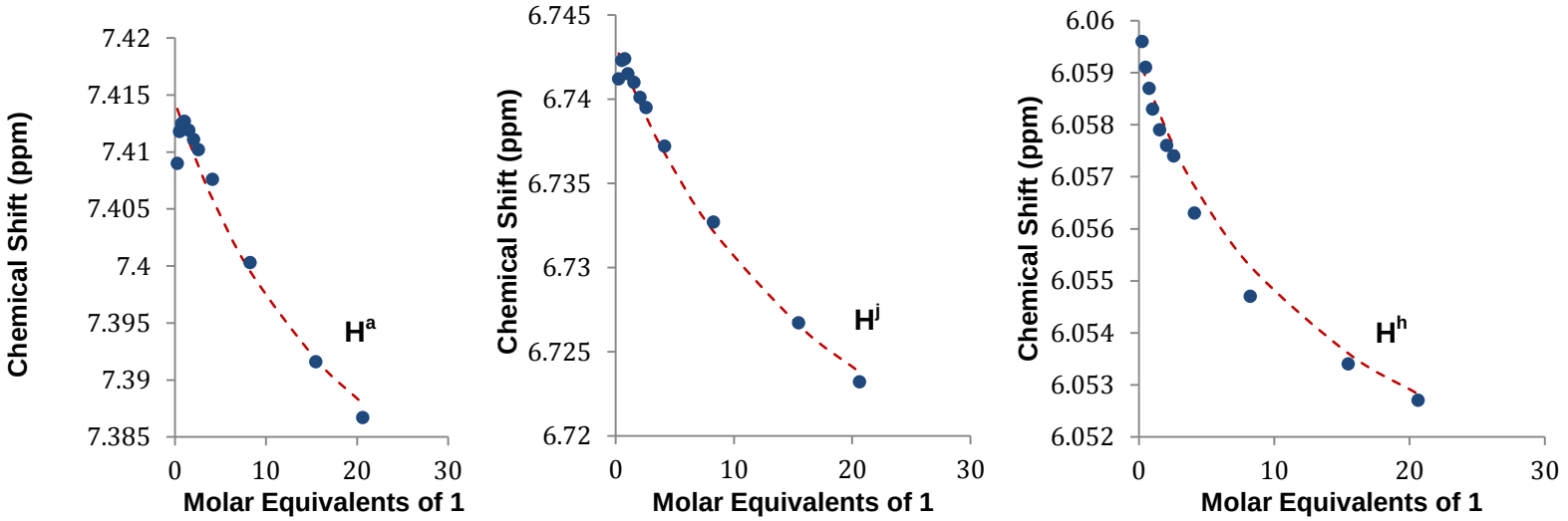
Table S27. ^{1}H NMR (500 MHz, 5° C) chemical shifts (ppm) of a 0.684 mM solution of α-Gal [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

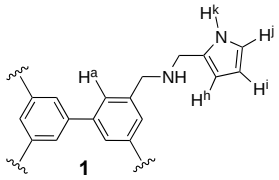
Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	6 G	7' G	5 G	7 G	4 G
0.000000	0.000684	N/A	N/A	N/A	N/A	N/A	4.964	3.728	3.4402	3.8222	3.7189	4.1088
0.000175	0.000679	8.9367	7.3905	6.7541	6.1331	6.0712	4.9419	N/A	3.4228	N/A	N/A	4.0575
0.000348	0.000675	8.9061	7.3946	6.753	6.1341	6.0702	4.9208	N/A	3.4054	3.7665	N/A	4.004
0.000519	0.000671	8.889	7.3953	6.7519	6.135	6.0682	4.9011	N/A	3.3893	3.7384	N/A	3.9561
0.000689	0.000667	8.8777	7.3958	6.7508	6.1354	6.0671	4.8848	N/A	3.3756	3.7154	N/A	3.9145
0.001021	0.000660	8.8624	7.3947	6.7488	6.136	6.0648	4.8571	3.5928	3.3521	3.6771	3.6265	N/A
0.001346	0.000652	8.8522	7.3931	6.7476	6.1368	6.0636	4.8369	3.5567	3.3349	3.6486	3.6106	N/A
0.001664	0.000645	8.8512	7.3911	6.7458	6.1366	6.0624	4.8216	3.5266	3.3215	3.6272	3.5822	N/A
0.002575	0.000624	8.8491	7.3844	6.7421	6.1369	6.0599	4.7898	3.4689	3.2952	3.5825	3.5703	N/A
0.004735	0.000573	8.8758	7.3681	6.7334	6.1361	6.0561	4.7542	3.4075	3.2631	N/A	N/A	N/A
0.007782	0.000502	8.932	7.3498	6.7231	6.134	6.0531	4.7339	N/A	3.2423	3.5132	N/A	N/A

N/A-Peak could not be resolved.

Figure S15: Fitting of experimental data (blue circles) with the 1:1 model (dashed red line) and 2:1 model (solid black line) corresponding to the ^{1}H NMR titration of α-Gal with **1** at 25°C.







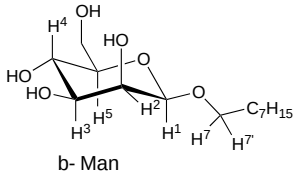


Table S28. ^{1}H NMR (900 MHz, 25° C) chemical shifts (ppm) of a 1.0 mM solution of β-Man [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)								
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	7’ G	3 G	5 G
0.000000	0.000976	N/A	N/A	N/A	N/A	N/A	4.5329	3.5455	3.5154	3.2891
0.000249	0.000972	9.045	7.4475	6.7657	6.1319	6.0845	4.5012	3.531	3.4825	3.2336
0.000496	0.000968	8.976	7.4454	6.7603	6.1326	6.0788	4.4853	3.5239	3.4573	3.205
0.000741	0.000964	8.937	7.4399	6.7565	6.1332	6.074	4.4701	3.5169	3.4349	3.1781
0.000984	0.000961	8.9033	7.4365	6.7538	6.1334	6.071	4.4609	3.5123	3.4175	3.1615
0.001465	0.000953	8.8533	7.432	6.7498	6.1342	6.0663	4.4413	3.5034	3.3882	3.1267
0.001938	0.000946	8.8271	7.4288	6.7474	6.1345	6.0638	4.4305	3.4977	3.3685	3.1096
0.004198	0.000910	8.7938	7.4176	6.7399	6.1348	6.0583	4.3967	3.4803	3.3242	3.0653
0.008247	0.000847	8.1808	7.4043	6.7308	6.1338	6.0552	4.376	3.4707	3.2995	3.0388
0.018855	0.000682	8.8992	7.3821	6.7122	6.1301	6.052	N/A	3.468	3.287	3.012

N/A-Peak could not be resolved.

Table S29. ^{1}H NMR (900 MHz, 20° C) chemical shifts (ppm) of a 1.0 mM solution of β-Man [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)								
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	7' G	3 G	5 G
0.000000	0.000976	N/A	N/A	N/A	N/A	N/A	4.5307	3.5408	3.5198	3.2865
0.000249	0.000972	9.197	7.4551	6.7751	6.1297	6.0918	4.4916	3.5228	3.4751	3.2168
0.000496	0.000968	9.109	7.4496	6.7676	6.1311	6.0846	4.472	3.5147	3.4434	3.1794
0.000741	0.000964	9.0411	7.4413	6.7623	6.1319	6.0788	4.4545	3.5068	3.4135	3.1468
0.000984	0.000961	8.9919	7.4365	6.7587	6.132	6.0746	4.4442	3.5022	3.3928	3.1275
0.001465	0.000953	8.9275	7.4311	6.7534	6.1329	6.0685	4.4237	3.4931	3.359	3.0909
0.001938	0.000946	8.8911	7.4268	6.7503	6.1331	6.0653	4.4133	3.4881	3.3432	3.0759
0.004198	0.000910	8.8565	7.4136	6.7417	6.1332	6.0589	4.3827	3.472	3.3026	3.0408
0.008247	0.000847	8.8742	7.3978	6.7308	6.132	6.0549	4.3643	3.4646	3.2843	3.0268
0.018855	0.000682	8.9714	7.3727	6.7103	6.1275	6.0511	4.3538	3.463	3.279	3.017

N/A-Peak could not be resolved.

Table S30. ^{1}H NMR (900 MHz, 15° C) chemical shifts (ppm) of a 1.0 mM solution of β-Man [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)								
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	7' G	3 G	5 G
0.000000	0.000976	N/A	N/A	N/A	N/A	N/A	4.5273	3.5353	3.5244	3.2827
0.000249	0.000972	9.317	7.4599	6.7864	6.1294	6.1025	4.4813	3.5146	3.4657	3.1963
0.000496	0.000968	9.2286	7.4502	6.7768	6.1306	6.0922	4.4582	3.5056	3.4215	3.1495
0.000741	0.000964	9.1452	7.4422	6.7699	6.1314	6.0851	4.4389	3.4971	3.3902	3.1127
0.000984	0.000961	9.0833	7.4372	6.765	6.1316	6.0793	4.4276	3.4929	3.3656	3.0905
0.001465	0.000953	9.0093	7.43	6.7578	6.1319	6.072	4.4071	3.4833	3.331	3.0557
0.001938	0.000946	8.9647	7.4252	6.7539	6.1323	6.0676	4.398	3.4794	3.3137	3.0393
0.004198	0.000910	8.9245	7.4091	6.7434	6.1318	6.0597	4.3702	3.4655	3.2863	3.0161
0.008247	0.000847	8.9463	7.3904	6.7308	6.1305	6.0552	4.3549	3.462	3.269	3.007
0.018855	0.000682	9.0499	7.3621	6.7078	6.1251	6.0504	4.342	3.4593	3.27	2.9909

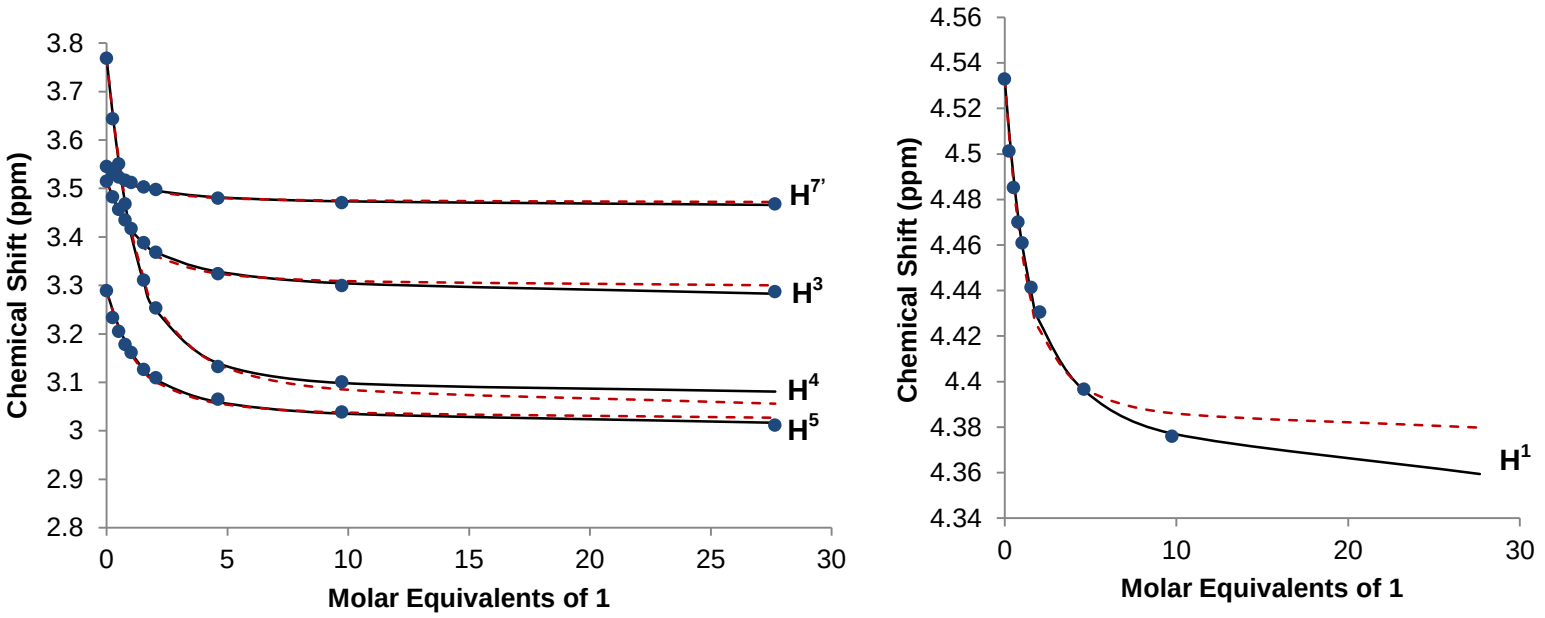
N/A-Peak could not be resolved.

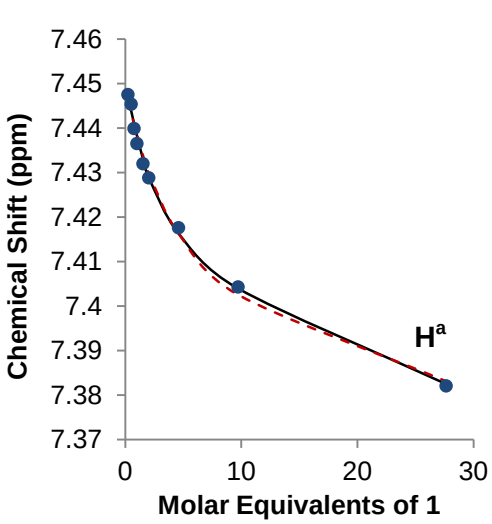
Table S31. ^{1}H NMR (900 MHz, 10° C) chemical shifts (ppm) of a 1.0 mM solution of β-Man [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

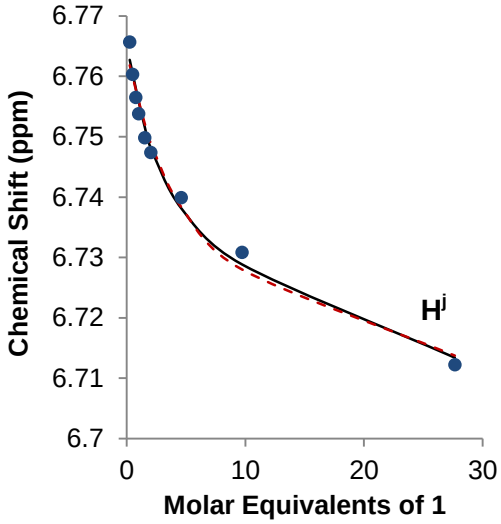
Concentration		^{1}H NMR Peak Shift (δ)								
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	7' G	3 G	5 G
0.000000	0.000976	N/A	N/A	N/A	N/A	N/A	4.5216	3.5274	3.5343	3.2738
0.000249	0.000972	9.439	7.4657	6.7966	6.1299	6.1124	4.4707	3.5061	3.4587	3.1762
0.000496	0.000968	9.3526	7.4538	6.7869	6.1305	6.1006	4.4436	3.496	3.4033	3.1196
0.000741	0.000964	9.2565	7.4434	6.7782	6.1309	6.0915	4.4231	3.4882	3.3633	3.0787
0.000984	0.000961	9.1815	7.438	6.7716	6.131	6.0845	4.4109	3.4845	3.339	3.054
0.001465	0.000953	9.0896	7.4287	6.7623	6.1312	6.0752	4.3917	3.4748	3.304	3.0213
0.001938	0.000946	9.0398	7.4229	6.7575	6.1313	6.0701	4.3835	3.4715	3.2882	3.0099
0.004198	0.000910	8.9997	7.4034	6.7448	6.1306	6.0604	4.3595	3.4554	3.2673	2.9942
0.008247	0.000847	9.0286	7.3817	6.7305	6.1285	6.0554	4.3472	3.4462	3.261	2.984
0.018855	0.000682	9.132	7.3503	6.705	6.1228	6.0498	N/A	3.4403	3.2652	2.9841

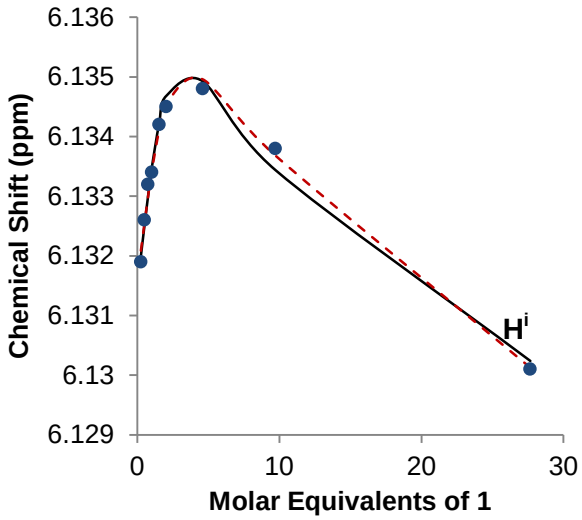
N/A-Peak could not be resolved.

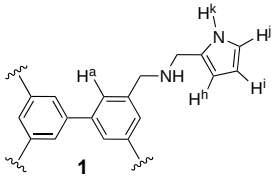
Figure S16: Fitting of experimental data (blue circles) with the 1:1 model (dashed red line) and 2:1 model (solid black line) corresponding to the ^{1}H NMR titration of β-Man with **1** at 25°C.











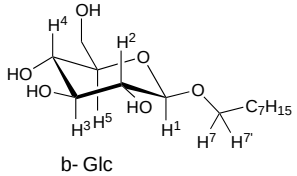


Table S32. ^{1}H NMR (900 MHz, 25° C) chemical shifts (ppm) of a 1.0 mM solution of β-Glc [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	4 G	3 G	7' G	5 G	2 G
0.000000	0.000954	N/A	N/A	N/A	N/A	N/A	4.3107	3.6064	3.5795	3.5287	3.4041	3.355
0.000249	0.000950	9.021	7.4519	6.748	6.1259	6.0749	4.2842	3.5417	3.5319	3.5073	3.3642	3.2483
0.000496	0.000946	8.9789	7.4459	6.7467	6.1272	6.0718	4.2645	N/A	N/A	N/A	3.3337	3.1693
0.000741	0.000943	8.9121	7.4378	6.7441	6.1289	6.0673	4.2258	3.3944	N/A	N/A	3.2772	3.0152
0.000984	0.000939	8.8921	7.4352	6.7436	6.1297	6.066	4.2119	3.3605	3.4134	3.4475	3.2576	2.9595
0.001465	0.000932	8.8518	7.4302	6.7417	6.1311	6.0634	4.1885	3.3043	3.373	3.4279	3.2255	2.8696
0.001938	0.000924	8.8314	7.4269	6.7408	6.1321	6.0615	4.1713	3.2639	3.3468	3.4138	3.2006	2.8048
0.002404	0.000917	8.8143	7.4243	6.7396	6.1324	6.06	4.1593	3.2365	3.3267	3.4027	3.1859	2.7624
0.002863	0.000910	8.8056	7.4219	6.7385	6.1328	6.0592	4.1496	3.2144	3.3103	3.3946	3.1707	2.7252
0.004630	0.000883	8.7885	7.4144	6.7343	6.1334	6.0562	4.126	3.161	3.2739	3.3742	3.1418	2.6491
0.009534	0.000808	8.8154	7.3998	6.7247	6.132	6.0531	4.1086	N/A	3.2437	3.3569	N/A	2.6081
0.019097	0.000663	8.8849	7.3817	6.7103	6.1291	6.0507	4.1038	3.0871	3.2391	3.3427	3.1133	2.6271

N/A-Peak could not be resolved.

Table S33. ^{1}H NMR (900 MHz, 20° C) chemical shifts (ppm) of a 1.0 mM solution of β-Glc [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	4 G	3 G	7' G	5 G	2 G
0.000000	0.000954	N/A	N/A	N/A	N/A	N/A	4.3113	3.6089	3.5822	3.5256	3.4047	3.3567
0.000249	0.000950	9.1372	7.4606	6.7519	6.1231	6.0811	4.2778	3.5282	3.5192	3.4993	3.3524	3.2196
0.000496	0.000946	9.0914	7.4533	6.7502	6.1241	6.0768	4.2524	N/A	N/A	3.463	3.3145	3.1162
0.000741	0.000943	8.9969	7.4413	6.7472	6.1271	6.0707	4.2067	3.3458	3.4064	3.4412	3.2485	2.9307
0.000984	0.000939	8.9713	7.4375	6.7463	6.1278	6.0688	4.1907	3.3068	3.3799	3.4274	3.2255	2.8674
0.001465	0.000932	8.9183	7.4308	6.7441	6.1295	6.0651	4.1655	3.2467	3.3389	3.4056	3.1912	2.7692
0.001938	0.000924	8.896	7.4267	6.743	6.1304	6.0631	4.1488	3.2065	3.3114	3.3907	3.1711	2.7057
0.002404	0.000917	8.8734	7.4231	6.7414	6.1312	6.0614	4.1383	3.1789	3.2948	3.3823	3.1568	2.6676
0.002863	0.000910	8.8672	7.4203	6.7404	6.1315	6.0601	4.1285	N/A	3.2796	3.3732	N/A	2.6344
0.004630	0.000883	8.8463	7.4109	6.7352	6.1319	6.0568	4.1106	3.1148	3.2501	3.3536	3.1148	2.5789
0.009534	0.000808	8.8832	7.3935	6.7243	6.1304	6.0533	4.0954	3.0869	3.2293	3.3411	3.0869	2.5565
0.019097	0.000663	8.9532	7.3728	6.7086	6.1275	6.0501	4.0935	3.0778	3.2296	3.334	3.0994	2.5969

N/A-Peak could not be resolved.

Table S34. ^{1}H NMR (900 MHz, 15° C) chemical shifts (ppm) of a 1.0 mM solution of β-Glc [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	4 G	3 G	7' G	5 G	2 G
0.000000	0.000954	N/A	N/A	N/A	N/A	N/A	4.3122	3.6112	3.5843	3.5225	3.3582	N/A
0.000249	0.000950	9.2619	7.4716	6.7561	6.1195	6.0862	4.2705	3.5153	3.5086	3.4908	3.3405	3.1876
0.000496	0.000946	9.201	7.4613	6.7535	6.121	6.0819	4.2388	3.4231	N/A	N/A	3.2921	3.0572
0.000741	0.000943	9.0841	7.4449	6.7496	6.1244	6.0736	4.186	3.2924	3.3733	3.4214	3.2182	2.8409
0.000984	0.000939	9.0568	7.4402	6.7488	6.1256	6.0714	4.1687	3.2489	3.3449	3.4068	3.1953	2.7697
0.001465	0.000932	8.9899	7.4312	6.7461	6.1275	6.0667	4.1431	3.1843	3.3041	3.3836	3.1618	2.6685
0.001938	0.000924	8.9645	7.4261	6.7447	6.1287	6.0644	4.1276	N/A	3.2806	3.3707	N/A	2.6119
0.002404	0.000917	8.9384	7.4215	6.7429	6.1295	6.0623	4.118	N/A	3.263	3.3613	N/A	2.5767
0.002863	0.000910	8.9348	7.418	6.7417	6.1299	6.0611	4.1095	3.11	3.251	3.3522	3.11	2.5501
0.004630	0.000883	8.9127	7.4064	6.7356	6.1303	6.0571	4.0939	N/A	3.2275	3.3381	N/A	2.508
0.009534	0.000808	8.9576	7.3854	6.7233	6.1284	6.053	4.084	3.0654	3.2137	3.3233	3.0654	2.5134
0.019097	0.000663	9.03	7.3623	6.706	6.1251	6.0496	4.0882	3.0657	3.2222	3.3222	3.0657	2.5674

N/A-Peak could not be resolved.

Table S35. ^{1}H NMR (900 MHz, 10° C) chemical shifts (ppm) of a 1.0 mM solution of β-Glc [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	4 G	3 G	7' G	5 G	2 G
0.000000	0.000954	N/A	N/A	N/A	N/A	N/A	4.3126	3.6138	3.5862	3.5195	3.4031	3.3602
0.000249	0.000950	9.3744	7.4842	6.7596	6.1171	6.0912	4.263	N/A	N/A	N/A	3.3237	3.1567
0.000496	0.000946	9.3082	7.4701	6.7569	6.1184	6.0864	4.2247	3.3868	3.4382	3.4517	3.2675	2.9981
0.000741	0.000943	9.1732	7.4489	6.7522	6.1219	6.0768	4.1652	3.2375	3.3405	3.4016	3.1839	2.7499
0.000984	0.000939	9.1385	7.4428	6.751	6.1232	6.0738	4.1468	3.1909	3.312	3.3865	3.1622	2.6776
0.001465	0.000932	9.0658	7.4315	6.7477	6.1254	6.068	4.1216	3.1271	3.272	3.3631	3.1271	2.5771
0.001938	0.000924	9.045	7.4267	6.7467	6.1266	6.0662	4.1103	N/A	3.2524	3.3522	N/A	2.5358
0.002404	0.000917	9.0107	7.4195	6.7441	6.1278	6.0631	4.0985	N/A	3.237	3.342	3.0906	2.4999
0.002863	0.000910	9.0053	7.415	6.7425	6.128	6.0617	4.0916	3.0587	3.226	3.3371	3.0801	2.4785
0.004630	0.000883	8.9884	7.4012	6.7361	6.1287	6.0577	4.0797	3.0412	3.12	3.3233	3.065	2.4561
0.009534	0.000808	9.038	7.3764	6.7219	6.1261	6.0529	4.0734	3.0316	3.2022	3.3094	3.0467	2.4759
0.019097	0.000663	9.1131	7.3507	6.7032	6.1227	6.049	4.0796	3.0518	3.2158	3.3097	3.0518	2.5417

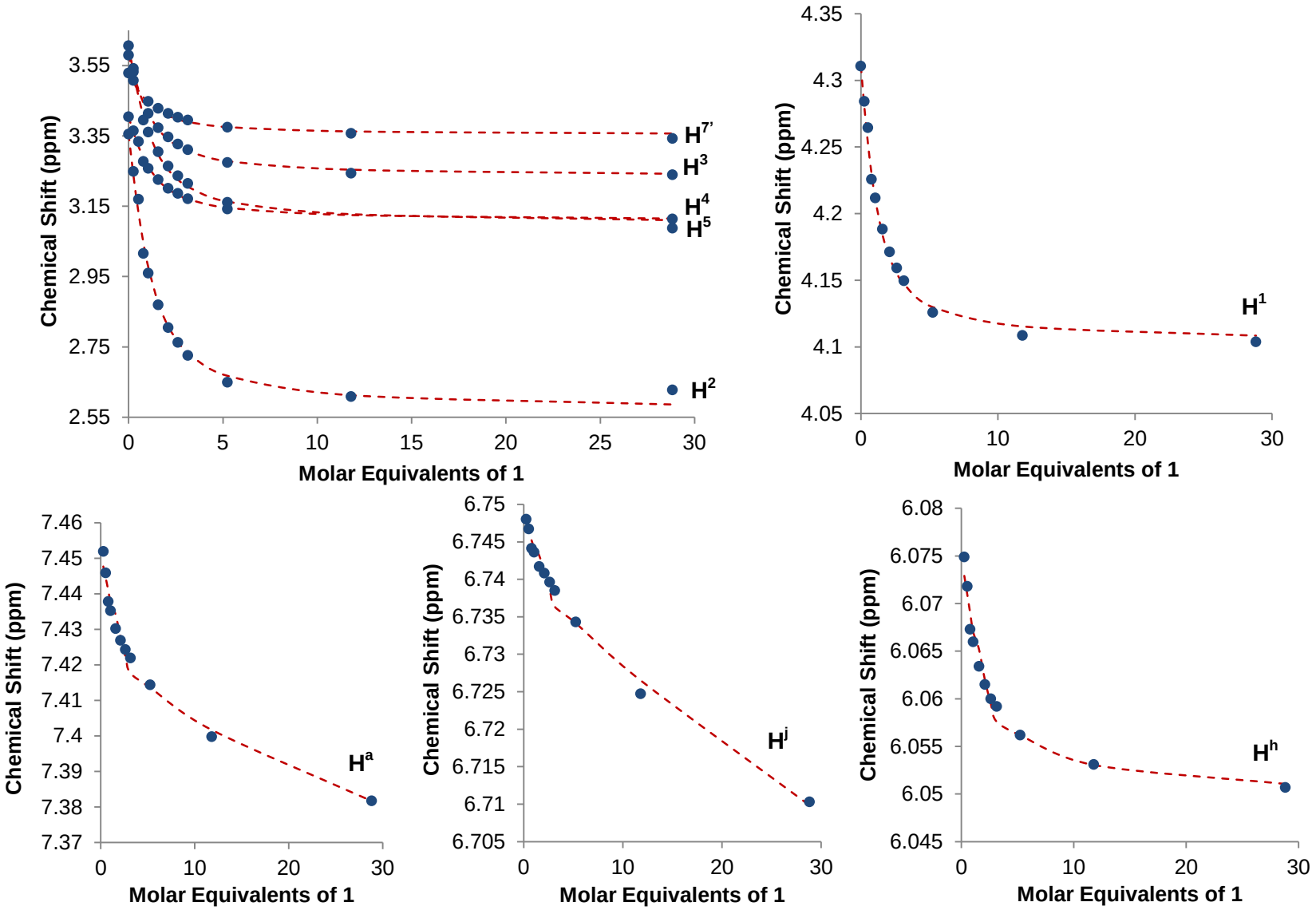
N/A-Peak could not be resolved.

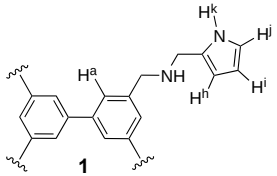
Table S36. ^{1}H NMR (900 MHz, 5° C) chemical shifts (ppm) of a 1.0 mM solution of β-Glc [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	4 G	3 G	7' G	5 G	2 G
0.000000	0.000954	N/A	N/A	N/A	N/A	N/A	4.3123	3.6172	3.5852	3.516	3.3953	3.3621
0.000249	0.000950	9.4746	7.4963	6.7642	6.115	6.0969	4.2554	N/A	N/A	N/A	3.3079	3.1292
0.000496	0.000946	9.4003	7.4790	6.7598	6.1152	6.0901	4.2109	3.3513	3.4145	3.4386	3.2402	2.9415
0.000741	0.000943	9.2602	7.4527	6.7545	6.1198	6.0794	4.1446	3.1819	3.3091	3.3833	3.1551	2.6644
0.000984	0.000939	9.2195	7.4453	6.7528	6.1211	6.0760	4.1273	3.1309	3.2822	3.3682	3.1313	2.5949
0.001465	0.000932	9.1439	7.4317	6.7493	6.1238	6.0698	4.1021	3.0754	3.2446	3.3442	3.0920	2.4983
0.001938	0.000924	9.1235	7.4263	6.7478	6.1245	6.0677	4.0923	3.0607	3.2311	3.3372	3.0802	2.4685
0.002404	0.000917	9.0891	7.4171	6.7450	6.1259	6.0643	4.0817	3.0293	3.2151	3.325	3.0696	2.4331
0.002863	0.000910	9.0801	7.4110	6.7427	6.1261	6.0620	4.0768	3.0193	3.207	3.3292	3.0573	2.4158
0.004630	0.000883	9.0725	7.3947	6.7355	6.1263	6.0578	4.067	3.0032	3.1949	3.3084	3.0468	2.4040
0.009534	0.000808	9.1209	7.3664	6.7199	6.1239	6.0526	4.0651	3.0114	3.1942	3.298	3.0337	2.4446
0.019097	0.000663	9.2015	7.3373	6.6994	6.1200	6.0481	4.0755	3.0381	3.2082	3.2981	3.0381	2.5305

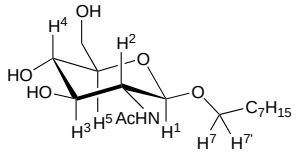
N/A-Peak could not be resolved.

Figure S17. Fitting of experimental data (blue circles) with the 1:1 model (dashed red line) corresponding to the ^{1}H NMR titration of β-Glc with **1** at 25°C.





1



b- GlcNAc

Table S37. ^{1}H NMR (900 MHz, 25° C) chemical shifts (ppm) of a 1.0 mM solution of β-GlcNAc [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	N-H G	1 G	4 G	7' G	5 G	2 G
0.000000	0.000996	N/A	N/A	N/A	N/A	N/A	5.724	4.4278	3.5471	3.4832	3.4191	3.3542
0.000212	0.000992	8.7698	7.4371	6.75	6.1378	6.0634	5.7389	4.4159	3.5089	3.4726	3.3984	3.3423
0.000421	0.000988	8.7863	7.437	6.7496	6.1374	6.0643	5.7613	4.4036	N/A	N/A	3.3779	3.3304
0.000630	0.000984	8.7759	7.4342	6.7486	6.1376	6.063	5.7687	4.3959	N/A	N/A	3.365	3.3237
0.000836	0.000980	8.7819	7.4337	6.748	6.1373	6.0628	5.7838	4.3888	N/A	N/A	3.3512	3.3176
0.001245	0.000973	8.7753	7.4305	6.7464	6.137	6.0616	5.797	4.3773	3.3787	3.4385	N/A	N/A
0.001647	0.000965	8.7786	7.4286	6.745	6.1366	6.0606	5.8125	4.3675	3.3499	3.4292	3.3081	3.3081
0.002042	0.000958	8.778	7.4264	6.744	6.1366	6.0601	5.8234	4.3595	N/A	3.4208	N/A	N/A
0.002432	0.000950	8.7797	7.4245	6.7426	6.1359	6.0591	5.8316	4.3529	N/A	N/A	N/A	N/A
0.003933	0.000922	8.7797	7.4172	6.7383	6.1354	6.057	5.8408	4.3342	N/A	3.3941	N/A	3.2691
0.008100	0.000844	8.8118	7.4029	6.7293	6.1338	6.0545	5.8553	4.3042	3.1397	3.364	3.1807	3.2441
0.016225	0.000692	8.8798	7.3841	6.7156	6.1301	6.0517	5.9014	4.2796	3.0687	3.3392	3.1332	3.2324

N/A-Peak could not be resolved.

Table S38. ^{1}H NMR (900 MHz, 20° C) chemical shifts (ppm) of a 1.0 mM solution of β-GlcNAc [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	N-H G	1 G	4 G	7' G	5 G	2 G
0.000000	0.000996	N/A	N/A	N/A	N/A	N/A	5.7463	4.4232	3.5415	3.4772	3.4155	3.3537
0.000212	0.000992	8.8258	7.4385	6.7544	6.1379	6.0661	5.7627	4.4065	N/A	N/A	3.3883	3.337
0.000421	0.000988	8.8615	7.4401	6.7545	6.1367	6.0677	5.7991	4.3899	N/A	N/A	3.3591	3.323
0.000630	0.000984	8.8319	7.4344	6.7525	6.1375	6.0651	5.8012	4.3802	3.4048	3.4419	3.3342	3.3137
0.000836	0.000980	8.8484	7.4348	6.7519	6.1366	6.0653	5.8265	4.3712	3.3743	3.4345	N/A	N/A
0.001245	0.000973	8.8305	7.4296	6.7497	6.1366	6.0629	5.8331	4.358	3.3313	3.4216	N/A	N/A
0.001647	0.000965	8.8402	7.4278	6.7482	6.1359	6.0622	5.8591	4.3463	N/A	3.4114	N/A	N/A
0.002042	0.000958	8.8383	7.4249	6.7469	6.1357	6.0615	5.8682	4.3375	N/A	3.4027	N/A	N/A
0.002432	0.000950	8.7852	7.4108	6.7395	6.1331	6.0606	N/A	4.3349	N/A	N/A	N/A	N/A
0.003933	0.000922	8.8409	7.4142	6.7408	6.1348	6.0581	5.8816	4.3101	3.1732	3.3754	3.2063	3.2559
0.008100	0.000844	8.8761	7.397	6.7299	6.1324	6.0549	5.8909	4.2784	3.0774	3.3417	3.1486	3.2327
0.016225	0.000692	8.9526	7.3758	6.7146	6.1287	6.052	N/A	4.2508	3.0122	3.3196	3.1035	3.2258

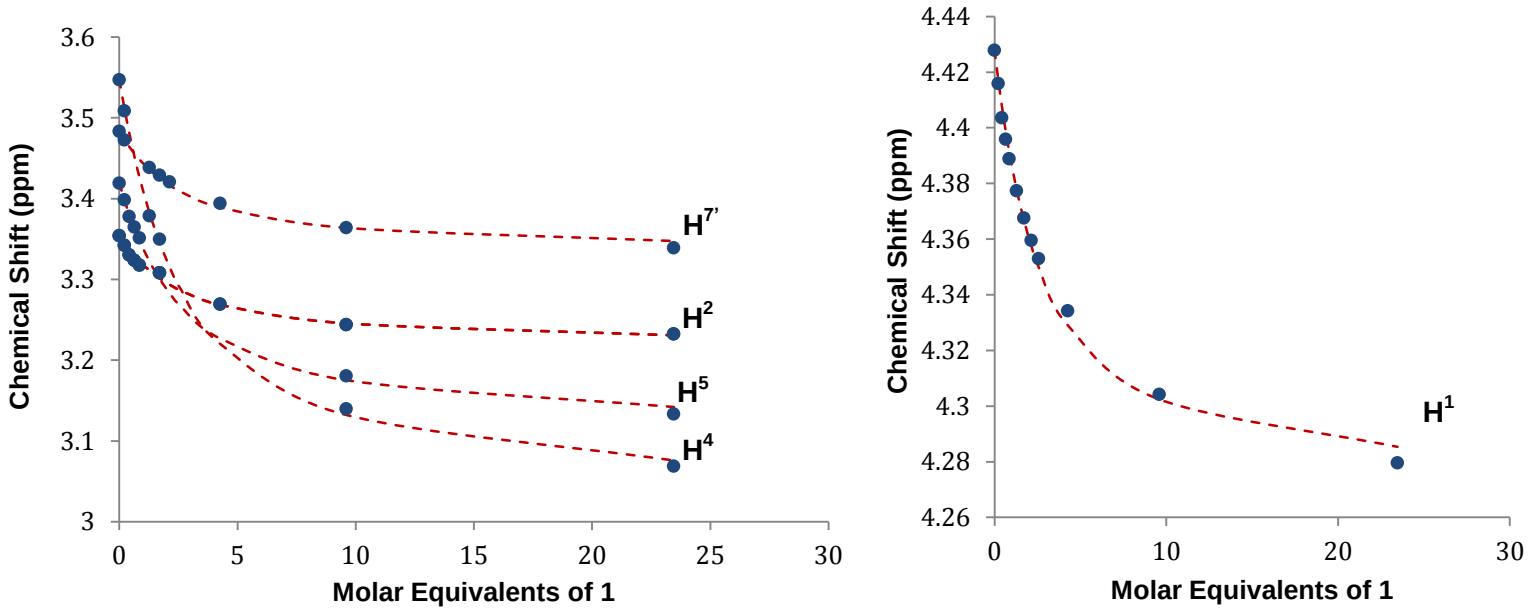
N/A-Peak could not be resolved.

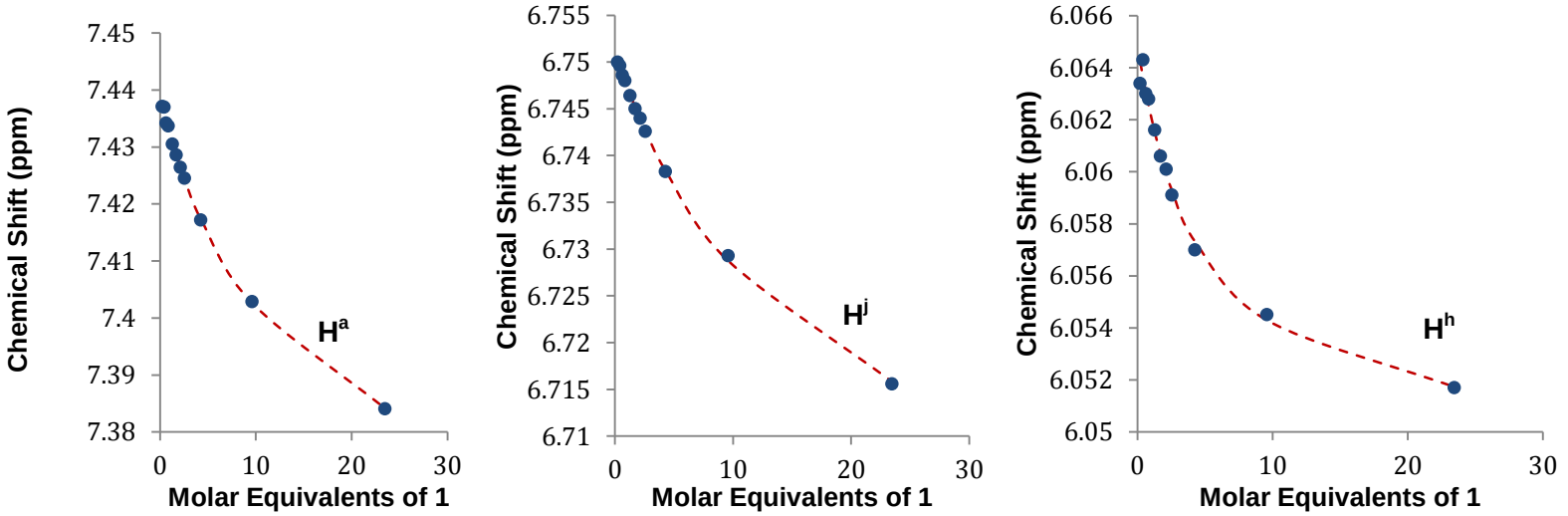
Table S39. ^{1}H NMR (900 MHz, 15° C) chemical shifts (ppm) of a 1.0 mM solution of β-GlcNAc [G] in $CDCl_3$ upon the incremental addition of **1** [H].

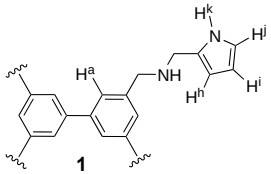
Concentration		^{1}H NMR Peak Shift (δ)										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	N-H G	1 G	4 G	7' G	5 G	2 G
0.000000	0.000996	N/A	N/A	N/A	N/A	N/A	5.7673	4.4162	3.533	3.4701	3.4099	3.3497
0.000212	0.000992	8.8849	7.4396	6.7585	6.1374	6.0683	5.7897	4.3936	N/A	N/A	3.3728	3.3292
0.000421	0.000988	8.9386	7.4426	6.7592	6.1358	6.0711	5.8416	4.3719	3.3968	3.4367	3.3356	3.3164
0.000630	0.000984	8.8872	7.4339	6.756	6.1367	6.0666	5.8328	4.3597	3.351	3.4253	N/A	N/A
0.000836	0.000980	8.9188	7.4355	6.7558	6.1353	6.0674	5.8717	4.3489	N/A	3.4175	N/A	N/A
0.001245	0.000973	8.8901	7.428	6.7529	6.1358	6.0642	5.869	4.3332	N/A	3.4026	N/A	N/A
0.001647	0.000965	8.9079	7.4265	6.7514	6.1347	6.0639	N/A	4.3203	N/A	3.3913	N/A	3.2684
0.002042	0.000958	8.9046	7.4227	6.7497	6.1347	6.0627	N/A	4.3101	3.1935	3.3819	3.2239	3.2627
0.002432	0.000950	8.9071	7.42	6.748	6.1341	6.0618	N/A	4.3018	3.1693	3.3745	3.2092	3.2563
0.003933	0.000922	8.9102	7.4096	6.7422	6.1331	6.0589	N/A	4.2811	3.1028	3.3567	3.1705	3.2412
0.008100	0.000844	8.9494	7.3894	6.7297	6.1306	6.0552	N/A	4.2479	3.0148	3.3235	3.1147	3.2235
0.016225	0.000692	9.0302	7.3661	6.7131	6.1267	6.0517	N/A	4.2208	2.9716	3.2991	3.0735	3.2208

N/A-Peak could not be resolved.

Figure S18: Fitting of experimental data (blue circles) with the 1:1 model (dashed red line) corresponding to the ^{1}H NMR titration of β-GlcNAc with **1** at 25°C.







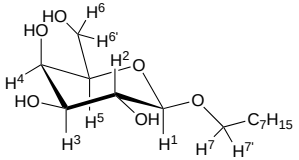


Table S40. ^{1}H NMR (500 MHz, 25° C) chemical shifts (ppm) of a 1.0 mM solution of β-Gal [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	3 G	5 G	7' G
0.000000	0.000684	N/A	N/A	N/A	N/A	N/A	4.2567	3.6425	3.5636	3.5186
0.000175	0.000680	8.6616	7.422	6.7405	6.1372	6.0586	4.2419	3.6056	3.5413	3.5019
0.000349	0.000676	8.6642	7.4212	6.7404	6.1378	6.0584	4.2281	N/A	3.5213	3.4863
0.000520	0.000672	8.6614	7.4207	6.7399	6.1378	6.0582	4.2166	N/A	3.5047	3.4731
0.000689	0.000668	8.6611	7.4198	6.7397	6.138	6.0582	4.2061	N/A	3.4869	3.4602
0.001022	0.000660	8.6504	7.4184	6.739	6.1384	6.0576	4.188	3.5012	3.4588	N/A
0.001347	0.000653	8.6477	7.4165	6.7384	6.1386	6.0569	4.1725	3.4743	N/A	N/A
0.001664	0.000645	8.6426	7.4161	6.7378	6.1388	6.0565	4.1624	3.462	3.4167	N/A
0.002575	0.000624	8.6366	7.4118	6.736	6.1394	6.0553	4.1298	3.4076	3.3425	N/A
0.004736	0.000574	8.6418	7.4041	6.7322	6.1394	6.0541	4.0977	N/A	3.2645	N/A
0.007782	0.000503	8.6661	7.3945	6.7272	6.1387	6.0525	4.071	N/A	3.2239	N/A

N/A-Peak could not be resolved.

Table S41. ^{1}H NMR (500 MHz, 20° C) chemical shifts (ppm) of a 1.0 mM solution of β-Gal [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	3 G	5 G	7' G
0.000000	0.000684	N/A	N/A	N/A	N/A	N/A	4.2567	3.6425	3.5636	3.5186
0.000175	0.000680	8.6616	7.422	6.7405	6.1372	6.0586	4.2419	3.6056	3.5413	3.5019
0.000349	0.000676	8.6642	7.4212	6.7404	6.1378	6.0584	4.2281	N/A	3.5213	3.4863
0.000520	0.000672	8.6614	7.4207	6.7399	6.1378	6.0582	4.2166	N/A	3.5047	3.4731
0.000689	0.000668	8.6611	7.4198	6.7397	6.138	6.0582	4.2061	N/A	3.4869	3.4602
0.001022	0.000660	8.6504	7.4184	6.739	6.1384	6.0576	4.188	3.5012	3.4588	N/A
0.001347	0.000653	8.6477	7.4165	6.7384	6.1386	6.0569	4.1725	3.4743	N/A	N/A
0.001664	0.000645	8.6426	7.4161	6.7378	6.1388	6.0565	4.1624	3.462	3.4167	N/A
0.002575	0.000624	8.6366	7.4118	6.736	6.1394	6.0553	4.1298	3.4076	3.3425	N/A
0.004736	0.000574	8.6418	7.4041	6.7322	6.1394	6.0541	4.0977	N/A	3.2645	N/A
0.007782	0.000503	8.6661	7.3945	6.7272	6.1387	6.0525	4.071	N/A	3.2239	N/A

N/A-Peak could not be resolved.

Table S42. ^{1}H NMR (500 MHz, 15° C) chemical shifts (ppm) of a 0.684 mM solution of β-Gal [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	3 G	5 G	7' G
0.000000	0.000684	N/A	N/A	N/A	N/A	N/A	4.26	3.6429	3.5661	3.5112
0.000175	0.000680	8.8371	7.4211	6.7442	6.1323	6.0634	4.2323	N/A	3.5261	3.48
0.000349	0.000676	8.8291	7.4195	6.7434	6.1328	6.0627	4.2091	N/A	3.4918	3.4518
0.000520	0.000672	8.812	7.4181	6.7432	6.1338	6.0619	4.1904	3.5045	3.4488	3.4304
0.000689	0.000668	8.803	7.4164	6.7428	6.1342	6.0615	4.1729	3.4749	N/A	N/A
0.001022	0.000660	8.7788	7.4139	6.7421	6.1354	6.0601	4.1478	3.4326	3.3542	3.3692
0.001347	0.000653	8.7652	7.4113	6.7412	6.1359	6.0591	4.1272	3.3987	3.3031	N/A
0.001664	0.000645	8.7562	7.4102	6.7407	6.1363	6.0588	4.1122	3.383	3.2817	N/A
0.002575	0.000624	8.7392	7.4038	6.7382	6.1373	6.0569	4.0854	3.328	3.2058	N/A
0.004736	0.000574	8.7428	7.3921	6.7337	6.1378	6.0546	4.0535	N/A	3.1519	N/A
0.007782	0.000503	8.7816	7.3782	6.7268	6.1364	6.0531	4.0352	N/A	3.136	N/A
0.009535	0.000462	8.8051	7.3718	6.7235	6.1359	6.0523	4.0303	N/A	3.1375	N/A

N/A-Peak could not be resolved.

Table S43. ^{1}H NMR (500 MHz, 10° C) chemical shifts (ppm) of a 0.684 mM solution of β-Gal [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	3 G	5 G	7' G
0.000000	0.000684	N/A	N/A	N/A	N/A	N/A	4.262	3.6451	3.5675	3.5081
0.000175	0.000680	8.9336	7.4217	6.7449	6.1293	6.0658	4.2266	N/A	3.5166	3.4675
0.000349	0.000676	8.9176	7.4189	6.7442	6.1299	6.0654	4.1971	3.5155	N/A	3.4328
0.000520	0.000672	8.8944	7.417	6.744	6.1312	6.0639	4.1744	3.4772	N/A	N/A
0.000689	0.000668	8.8782	7.4145	6.7434	6.1317	6.063	4.1545	3.4438	3.3637	3.382
0.001022	0.000660	8.8451	7.4118	6.7434	6.1343	6.0622	4.1265	3.397	3.2911	3.35
0.001347	0.000653	8.8263	7.4081	6.7415	6.1344	6.0599	4.1204	3.3601	3.2367	N/A
0.001664	0.000645	8.8142	7.4064	6.7413	6.1352	6.0592	4.1106	N/A	3.2132	N/A
0.002575	0.000624	8.7943	7.3983	6.7386	6.1364	6.0572	4.0636	N/A	3.1471	N/A
0.004736	0.000574	8.8007	7.3843	6.7334	6.1368	6.0546	4.0354	N/A	3.108	N/A
0.007782	0.000503	8.8463	7.368	6.7261	6.1358	6.0527	4.0198	N/A	3.1092	N/A
0.009535	0.000462	8.8732	7.3604	6.7221	6.1347	6.0522	4.0158	N/A	N/A	N/A

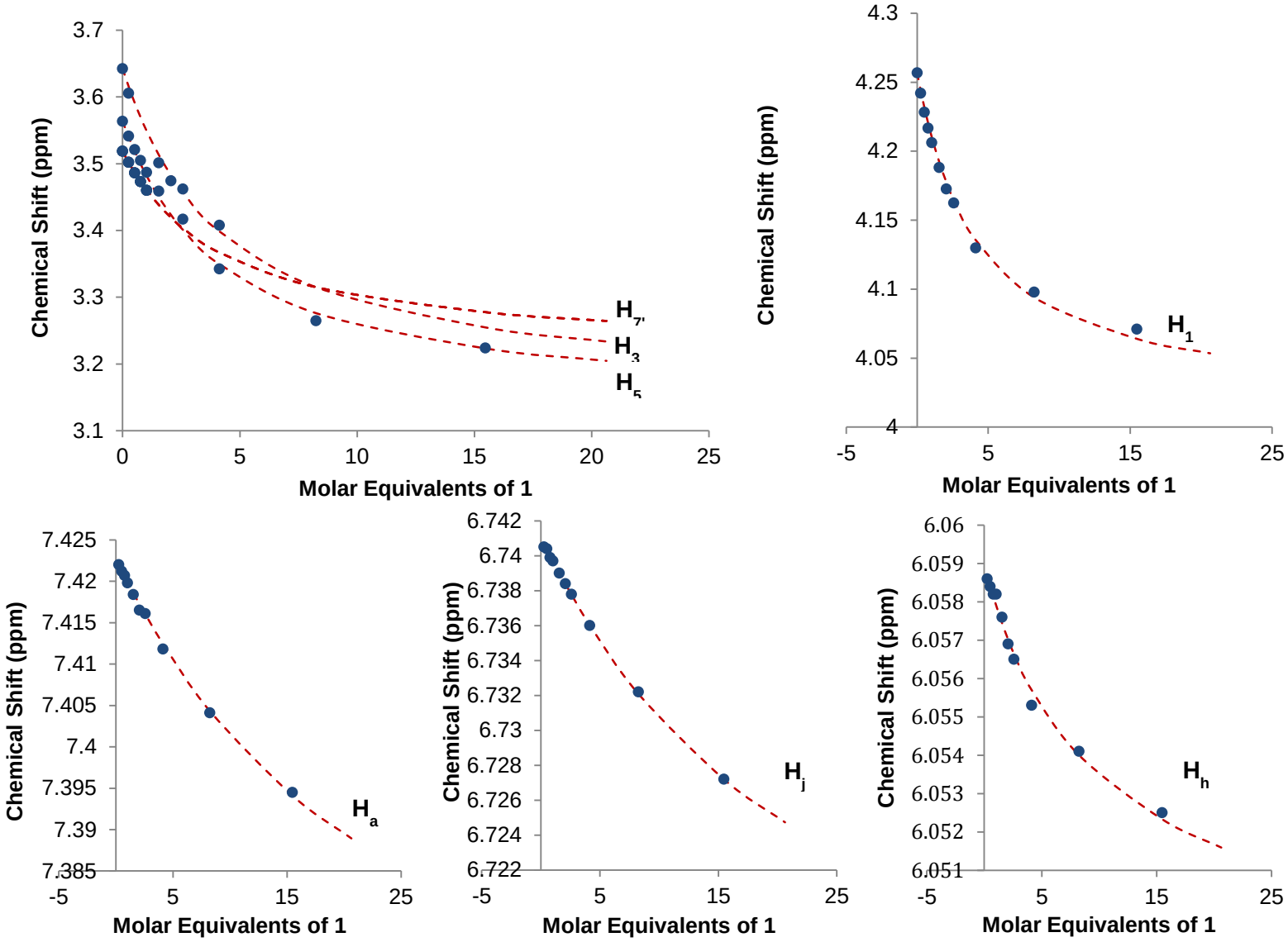
N/A-Peak could not be resolved

Table S44. ^{1}H NMR (500 MHz, 10° C) chemical shifts (ppm) of a 0.684 mM solution of β-Gal [G] in $CDCl_3$ upon the incremental addition of **1** [H]**.**

Concentration										
$[H]_t$ mol L^{-1}	$[G]_t$ mol L^{-1}	k H	a H	j H	i H	h H	1 G	3 G	5 G	7' G
0.000000	0.000684	N/A	N/A	N/A	N/A	N/A	4.2663	3.6462	3.5687	3.5046
0.000175	0.000680	9.0393	7.422	6.7449	6.1249	6.0685	4.2196	3.5528	3.5048	3.4538
0.000349	0.000676	9.0125	7.4185	6.7442	6.1264	6.0671	4.1841	3.4919	3.4312	3.4124
0.000520	0.000672	8.9805	7.4153	6.7439	6.1278	6.0656	4.1565	3.446	3.3646	3.3804
0.000689	0.000668	8.9571	7.4123	6.7433	6.1289	6.0642	4.1343	3.4088	3.303	3.3535
0.001022	0.000660	8.9167	7.4076	6.7425	6.1309	6.0623	4.103	3.3576	3.224	N/A
0.001347	0.000653	8.896	7.4037	6.7415	6.1322	6.0608	4.0818	3.3197	3.1734	N/A
0.001664	0.000645	8.8757	7.4008	6.7409	6.1332	6.0597	4.0708	N/A	3.1461	N/A
0.002575	0.000624	8.8536	7.3917	6.7385	6.1347	6.0575	4.0432	3.2592	3.0956	N/A
0.004736	0.000574	8.8684	7.3745	6.7325	6.135	6.0553	4.018	N/A	3.0705	N/A
0.007782	0.000503	8.9189	7.3556	6.7242	6.1338	6.0527	4.0053	3.2051	N/A	N/A
0.009535	0.000462	8.9508	7.347	6.7205	6.1325	6.0519	4.0011	N/A	N/A	N/A

N/A-Peak could not be resolved

Figure S19: Fitting of experimental data (blue circles) with the 1:1 model (dashed red line) and 2:1 model (solid black line) corresponding to the ^{1}H NMR titration of β-Gal with **1** at 25°C.



4. Complete Table of Binding Constants.

Table S45. Complete table of binding constants at all temperatures observed by ^{1}H NMR titrations for each pyranoside in $CDCl_3$ with **1.**

Sugar	Temperature (°C)	Log K_1	Log K_2	Log K_3
α-Glc	25	2.73 ± 0.01	-	-
	20	2.86 ± 0.01	-	-
	15	3.02 ± 0.02	-	-
	10	3.20 ± 0.02	-	-
	5	3.38 ± 0.03	-	-
β-Glc	25	3.23 ± 0.02	-	-
	20	3.47 ± 0.03	-	-
	15	3.65 ± 0.04	-	0.45 ± 0.04
	10	3.87 ± 0.08	-	0.57 ± 0.04
	5	4.12 ± 0.11	-	0.63 ± 0.04
α-GlcNAc	25	2.69 ± 0.03	-	-
	20	2.83 ± 0.02	-	-
	15	2.98 ± 0.03	-	-
	10	3.16 ± 0.03	-	-
	5	3.22 ± 0.04	-	-
β-GlcNAc	25	2.65 ± 0.02	-	-
	20	2.84 ± 0.02	-	-
	15	2.93 ± 0.02	-	-
α-Man	25	2.57 ± 0.19	3.71 ± 0.10	-
β-Man	25	2.46 ± 0.31	3.34 ± 0.11	2.45 ± 0.09
	20	2.75 ± 0.12	3.57 ± 0.04	2.57 ± 0.04
	15	2.97 ± 0.08	3.89 ± 0.03	2.74 ± 0.07
	10	3.27 ± 0.07	4.10 ± 0.03	2.87 ± 0.07
α-Gal	25	2.18 ± 0.02	-	-
	20	2.31 ± 0.03	-	-
	15	2.51 ± 0.03	-	-
	10	2.66 ± 0.04	-	-
	5	2.87 ± 0.05	-	-
β-Gal	25	2.59 ± 0.03	-	-
	20	2.78 ± 0.03	-	-
	15	3.05 ± 0.04	-	-
	10	3.20 ± 0.04	-	-
	5	3.40 ± 0.05	-	-

5. Van't Hoff Analysis.

Figure S20: Van't Hoff Plot of K_1 and K_3 of β-Glc and α-Glc binding to **1** in $CDCl_3$.

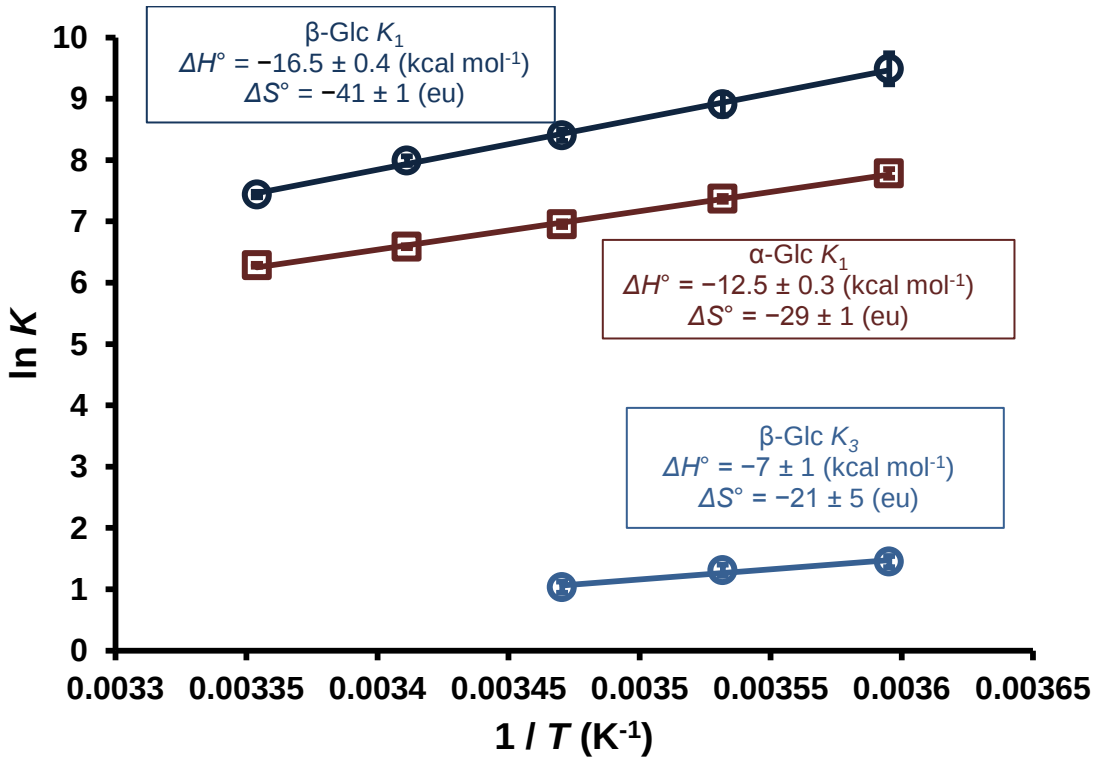


Figure S21: Van't Hoff Plot of K_1 of α-GlcNAc and β-GlcNAc binding to **1** in $CDCl_3$

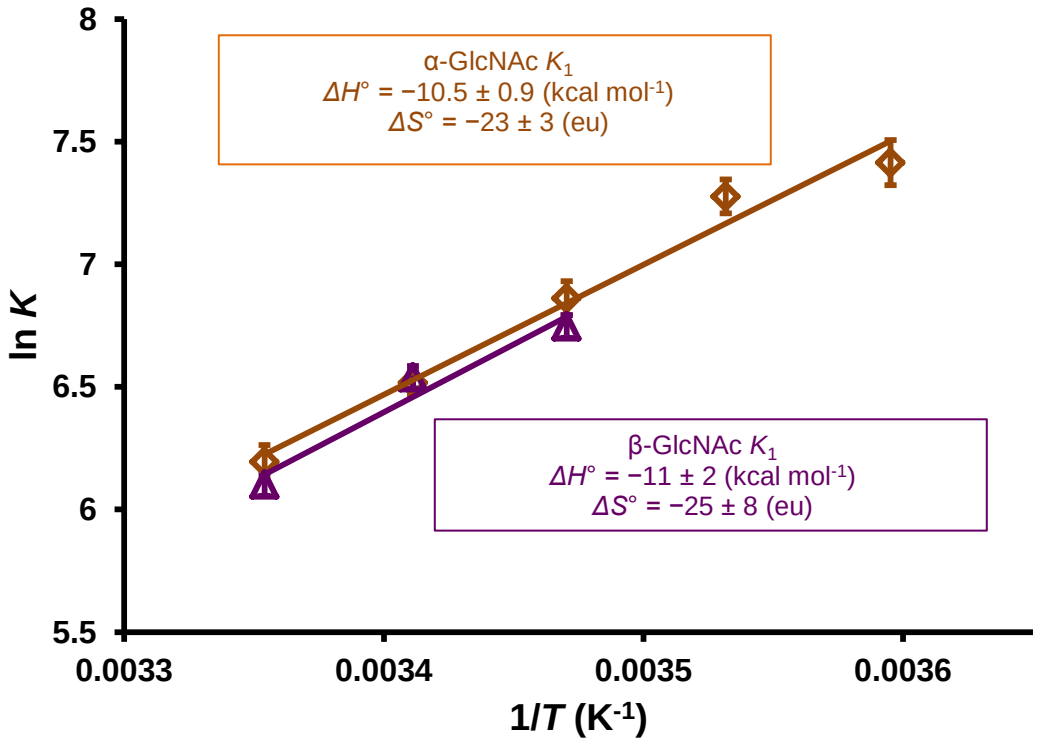


Figure S22: Van't Hoff Plot of K_1 of α-Gal and β-Gal binding to **1** in $CDCl_3$.

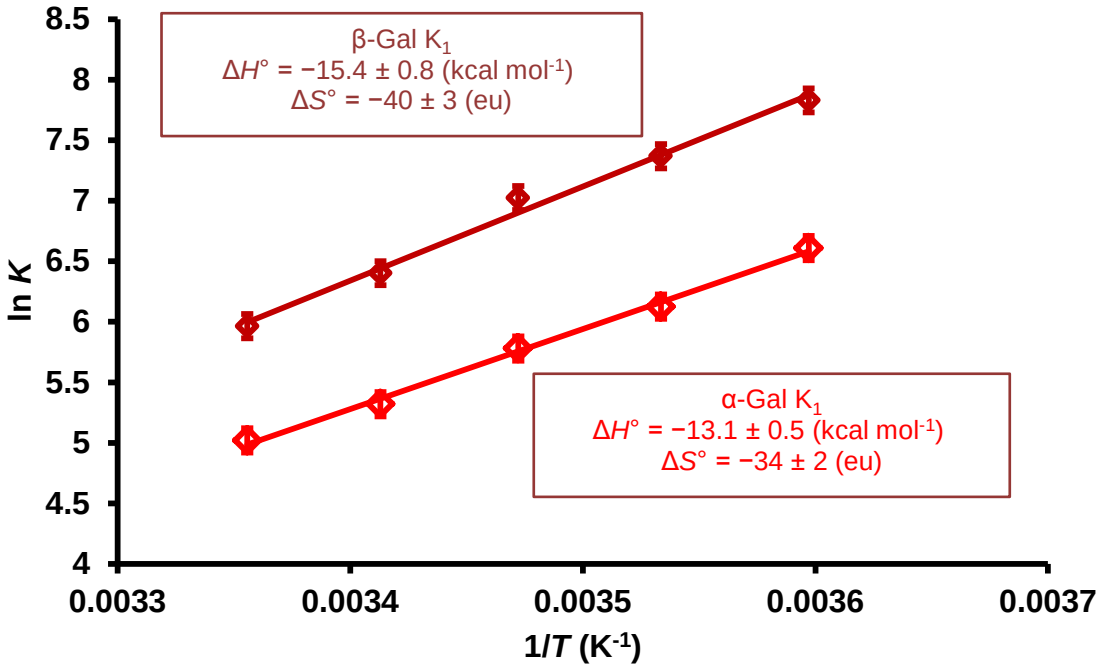
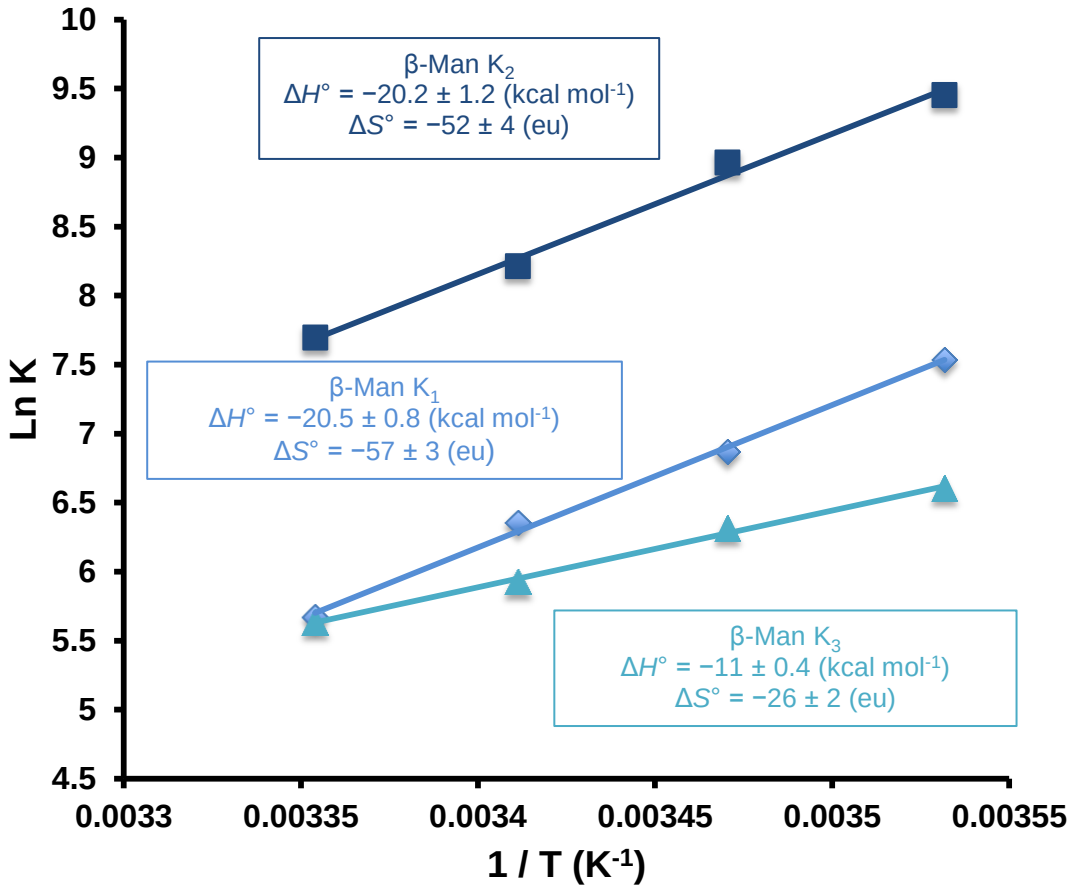


Figure S23: Van't Hoff Plot of K_1, K_2 and K_3 of β-Man binding to **1** in $CDCl_3$.



6. ROESY NMR Experiments

Figure S24. ^{1}H-^{1}H ROESY spectrum of β-Man(12.0 mM) with **1** (6.0 mM) at −60° C 400 MHz in $CDCl_3$.

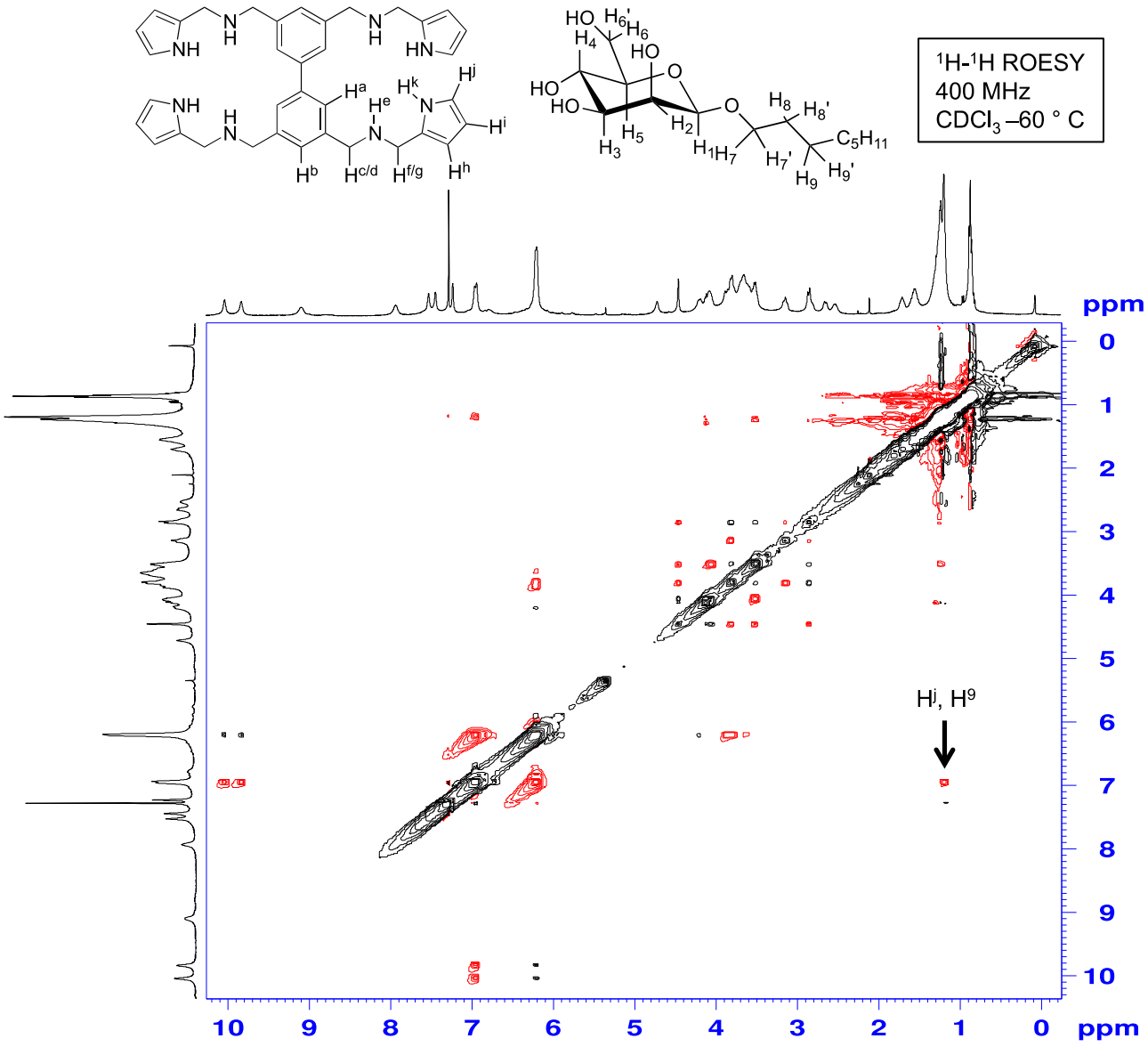


Figure S25. ^{1}H-^{1}H ROESY spectrum of β-Man(1.0 mM) with **1** (0.5 mM) at 25° C 600 MHz in $CDCl_3$.

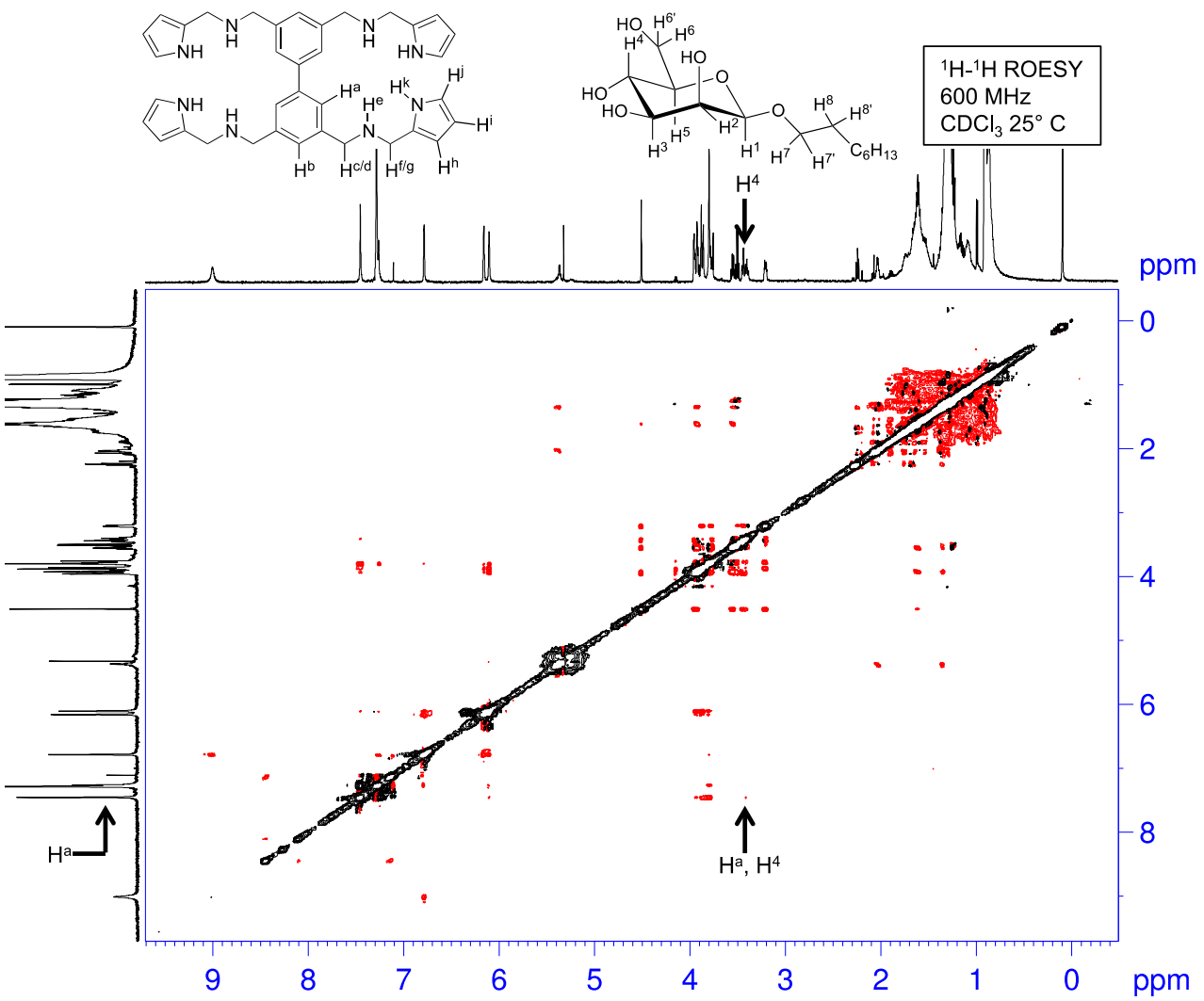


Table S46. Complexation induced shifts for each observable pyranoside proton obtained from ^{1}H NMR titrations. The observed intermolecular cross-peaks obtained from a ^{1}H-^{1}H ROESY analysis. The corresponding distance between the protons in the calculated structures is indicated in parenthesis.

Glycoside	Complexation-Induced Shifts (ppm)	Observed Intermolecular Cross-Peaks and Calculated Distances (Å)
βGlc	H_1 – 0.207 H_2 – 0.728 H_3 – 0.340 H_4 – 0.519 H_5 – 0.291 $H_{7'}$ – 0.186	**1**:β-Glc H_1,H_a – w (2.94) H_2,H_a – m (3.06) H_3,H_a – w (3.83) H_4,H_a – m (2.92) H_5,H_a – w (3.06)
βMan	H_1 – 0.157 H_3 – 0.228 H_4 – 0.730 H_5 – 0.277 $H_{7'}$ – 0.078	**1**:β-Man H_4,H_a – m (3.33) **1**$_2$:β-Man H_J,H_8 H_J,H_9 H_i,H_9 H_h,H_9

Figure S26. ^{1}H-^{1}H ROESY spectrum of β-Glc (1.0mM) and **1** (3.0mM) at 20° C 500 MHz in $CDCl_3$.

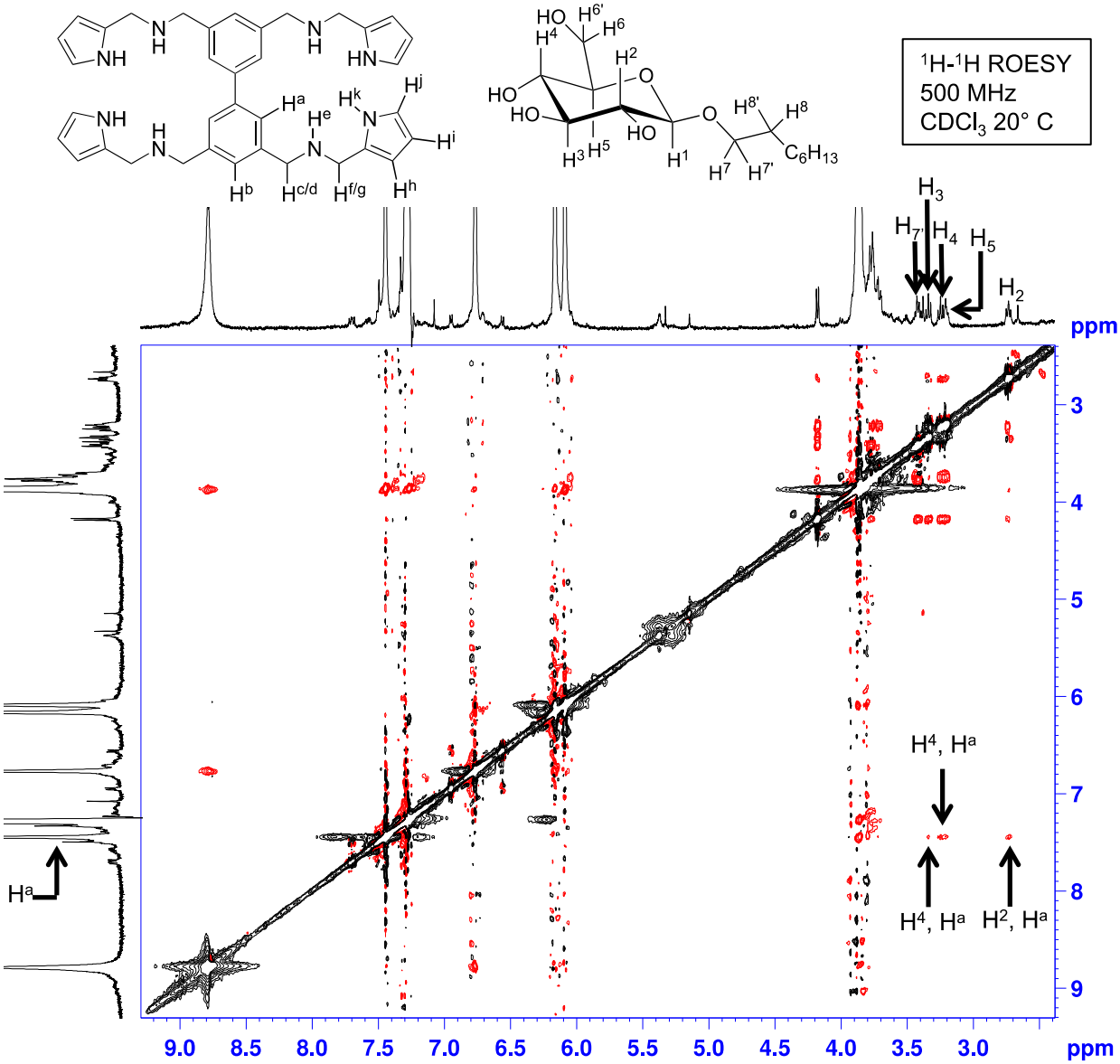
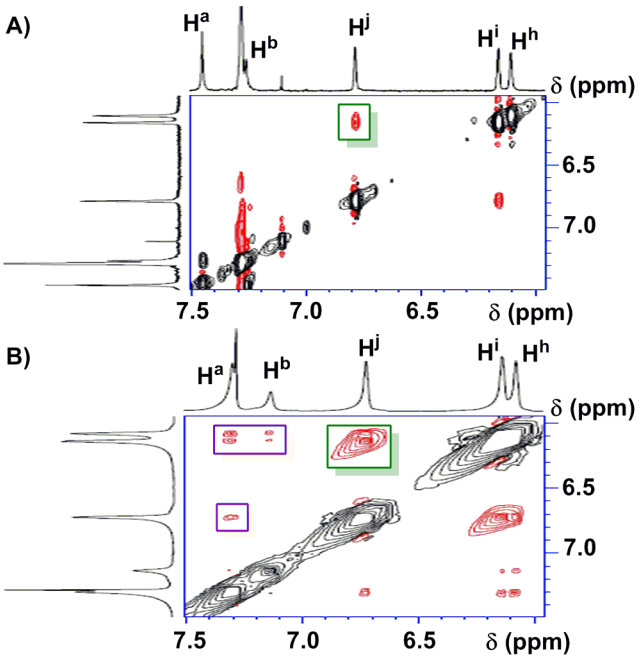


Figure S27. Selected portions of a ^{1}H-^{1}H ROESY spectra corresponding to a) a $CDCl_3$ solution of β-Man (1.0 mM) with 0.50 molar equivalents of **1** at 600 MHz, 25°C, and with a 600 ms mixing time, and b) a $CDCl_3$ solution of β-Man (6.0 mM) with 2.0 molar equivalents of **1** at 400 MHz, –10°C, and with a 500 ms mixing time.



7. References:

1. A. V. Rukavishnikov, A. Phadke, M. D. Lee, D. H. Lamunyon, P. A. Petukhov and J. F. W. Keana, *Tet. Lett.*, 1999, **40**, 6353-6356.
2. M. Polakova, M. Belanova, L. Petrus and K. Mukusova, *Carb. Res.*, 2010, **345**, 1339-1347.
3. B. Aguilera, L. Romero-Ramirez, J. Abad-Rodriguez, G. Corrales, M. Nieto-Sampedro and A. Fernandez-Mayoralas, *J. Med. Chem.*, 1998, **41**, 4599-4606.
4. C. Ammann, P. Meier and A. E. Merbach, *J. Magn. Reson.*, 1982, **46**, 319-321.
5. P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305-1323.