Table S1. Estimated distances r (Å) for various conformers of a pseudorotational itinerary of 4NP-S-Glc bound to HvβII. The data in the last column were used for deduction of conformational changes.

H/H	r (Å)	r (Å)	r (Å)	r (Å)	r (Å)	r (Å)	r (Å)	Experimental r (Å)
	$^{4}C_{1}$	$^{3}S_{5}$	$^{O}S_{2}$	$^{O}S_{4}$	$^{1}C_{4}$	$^{1}S_{3}$	$^{1}S_{5}$	estimated error (10%)
H1/H2	3.1	3.0	2.8	3.1	2.5	2.5	2.5	2.9* (H2 overlaps with H4)
H1/H3	2.6	2.8	4.3	3.6	4.3	3.9	4.2	3.0
H1/H4	4.0	4.5	4.5	3.9	4.9	3.8	3.7	- (no NOE assumed)
H1/H5	2.4	4.0	2.5	2.5	4.1	4.1	4.0	3.7
H2/H3	3.1	3.1	2.6	2.8	2.5	3.2	2.5	2.8 (H2/H3 + H4/H3)
H2/H4	2.7	2.7	4.3	4.2	4.4	2.7	3.8	overlap
H2/H5	4.0	4.1	3.9	4.5	5.0	4.3	4.0	2.8 (H2/H5 + H4/H5)
H3/H4	3.1	3.1	2.8	2.5	2.6	2.9	3.2	2.8 (H3/H4 + H3/H2)
H3/H5	2.6	3.5	3.7	4.2	4.4	2.0	2.7	Too close to diagonal
H4/H5	3.1	2.8	3.1	2.8	2.5	3.2	2.9	2.8 (H4/H5 + H2/H5)

Table S2. Estimated distances r (Å) for various conformers of a pseudorotational itinerary of 4NP-S-Man bound to HvβII. The data in the last column were used for deduction of conformational changes.

H/H	r (Å)	r (Å)	r (Å)	r (Å)	r (Å)	r (Å)	r (Å)	Experimental r (Å)
	$^{4}C_{1}$	$^{3}S_{5}$	$^{O}S_{4}$	$^{O}S_{2}$	$^{1}C_{4}$	$^{1}S_{5}$	$^{1}S_{3}$	estimated error (10 %)
H1/H2	2.5	2.2	2.3	2.3	2.4	2.4	2.5	2.5
H1/H3	2.6	2.9	3.9	4.3	4.3	4.2	3.9	2.6
H1/H4	4.0	4.4	4.1/4.0	4.5	4.9	3.7	3.8	- (no NOE)
H1/H5	2.4	4.0	2.3/2.4	2.5	4.1	4.0	4.1	2.5
H2/H3	2.5	2.5	2.4	2.5	2.5	2.5	2.4	2.5
H2/H4	3.9	3.8	4.0/3.9	3.8	3.8	3.8	3.7	- (no NOE)
H2/H5	4.0	4.8	3.8/3.9	2.5	4.1	2.8	3.7	- (no NOE)
H3/H4	3.1	3.1	2.5	2.7	2.6	3.2	2.9	3.0
H3/H5	2.6	3.2	4.2	3.8	4.4	2.7	2.0	2.6
H4/H5	3.1	2.9	2.9/2.8	3.1	2.5	2.9	3.2	3.0

Table S3. Parameters of optimized conformers for 4NP-O-Glc (in $^{1}S_{3,}$ $^{3}S_{5}$ and $^{4}C_{1}$ or 1B, 1S and 1C), 4NP-S-Glc (in $^{1}S_{3,}$ $^{3}S_{5}$ and $^{4}C_{1}$ or 2B, 2S and 2C), 4NP-O-Man (in $^{1}S_{3,}$ $^{3}S_{5}$ and $^{4}C_{1}$ or 3B, 3S and 3C) and 4NP-S-Man (in $^{1}S_{3,}$ $^{3}S_{5}$ and $^{4}C_{1}$ or 4B, 4S and 4C) obtained at the M05-2X/6-31+G* level of theory.

	1B	**1S**	**1C**	**2B**	**2S**	**2C**	**3B**	**3S**	**3C**	**4B**	**4S**	**4C**
Q(C1)	0.36	0.32	0.36	-0.02	-0.08	-0.01	0.05	0	0.33	-0.10	-0.51	-0.68
Q(X1)[b]	-0.54	-0.45	-0.45	-0.24	-0.15	-0.14	-0.38	-0.29	-0.44	-0.11	-0.07	-0.01
Q(O4)	-0.53	-0.44	-0.36	-0.27	-0.38	-0.40	-0.52	-0.42	-0.37	-0.43	-0.29	-0.22
d(C1-X)	1.43	1.44	1.41	1.92	1.89	1.86	1.43	1.42	1.41	1.87	1.89	1.85
d(X1-C7)	1.36	1.37	1.37	1.80	1.82	1.82	1.37	1.37	1.38	1.80	1.82	1.82
α(C1-X1-C7)	117.2	115.9	116.6	92.1	94.4	86.9	117.9	116.6	115.7	94.7	93.5	94.2
Θ(C5-O4-C1-X1)	-64.4	-86.1	173.6	-106.2	-96.9	163.9	-66.8	-89.8	174.1	-78.1	-92.4	164.9
Φ(O4-C1-X1-C7)	-62.0	-81.7	-68.4	-30.4	-65.8	-79	-55.2	-67.3	-70.6	-49	-66.4	-78.8
Ψ(C1-X1-C7-C8)	-10.5	28.7	-1.5	-54.1	45.4	76.1	-5.4	28.1	0.8	-16.3	46.5	34.8

[a] The relative energy (Q) in kcal/mol, lengths (*d*) in Å, and (α, Θ, Φ, Ψ) angles in degrees.
[b] X represents oxygen in the O-linked and sulfur in the S-linked glycosides, respectively.