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Supporting Information

A Secondary Structural Element in a Wide Range of Fucosylated Glycoepitopes

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Supporting Information

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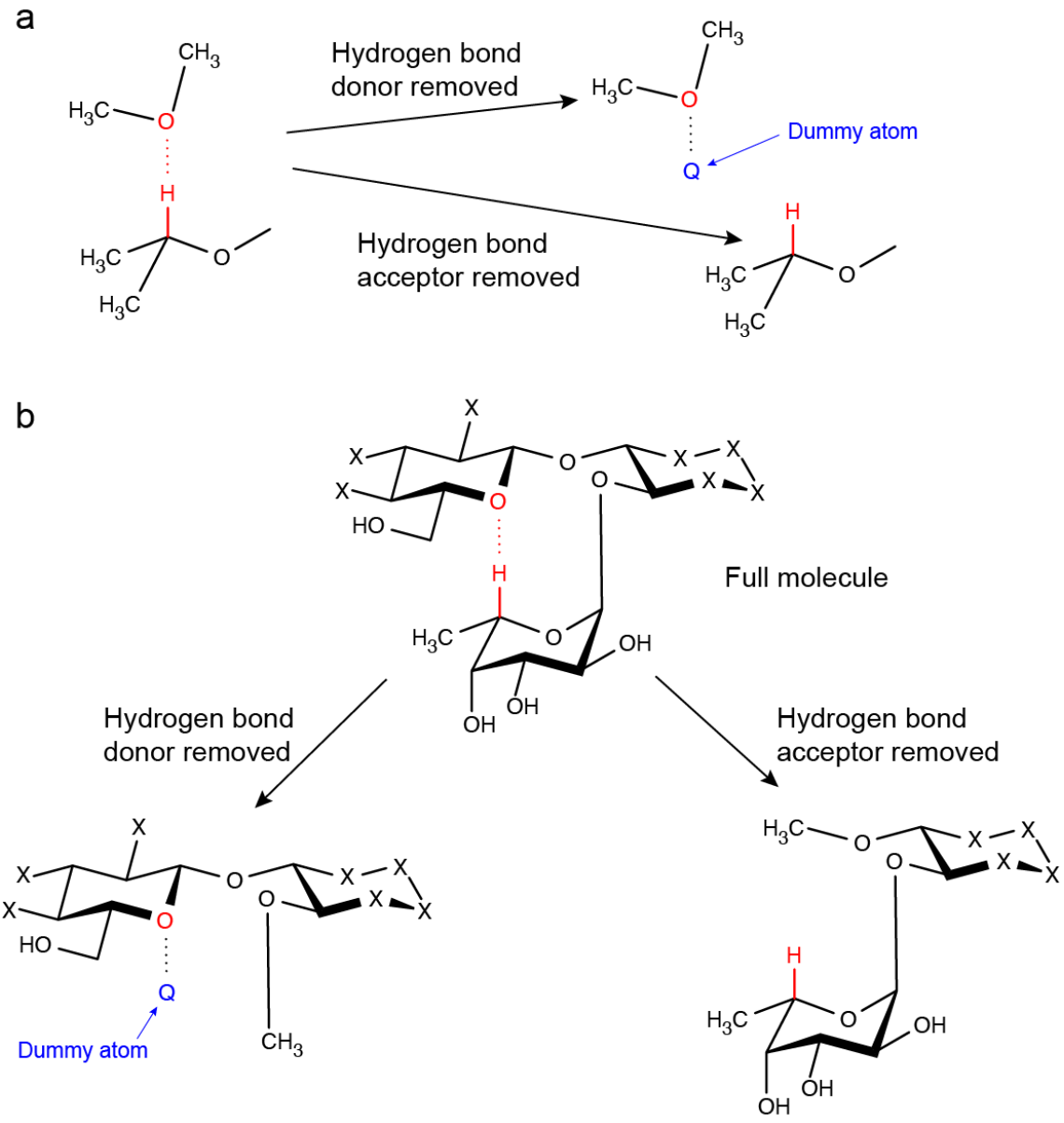

Figure S1. Schematic structures of the model systems used for the calculations of changes in the chemical shielding due to the hydrogen bond, according to Scheiner et al.[1] (a) Simplified model system of iPro-O-Me and Me-O-Me and truncated versions lacking the hydrogen bond donor or acceptor. (b) Trisaccharide cores and truncated versions lacking the hydrogen bond donor or acceptor.

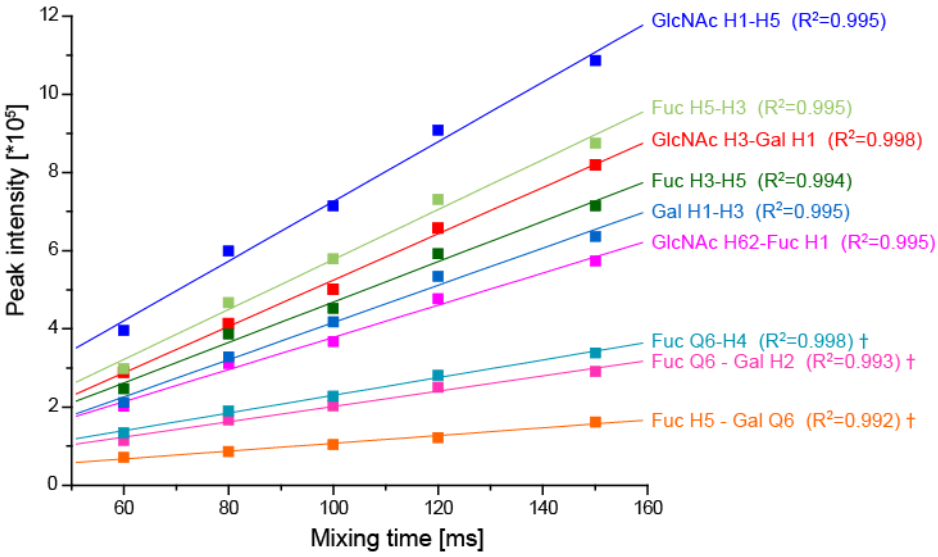

Figure S2. NOE build up curves of Le^a methyl glycoside measured at 275 K at 900 MHz. Shown are the intensities of selected cross-peaks within a 2D NOESY spectra for mixing times ranging between 60 and 150 ms. Spectra were recorded with 88 transients and 480 increments. Intensities of cross-peaks involving CH_3 and CH_2 groups were divided by 3 or 2, respectively, to obtain the intensity per proton (indicated by †). Linear regression was used to fit the data points, the coefficient of determination R^2 is given for each fit.

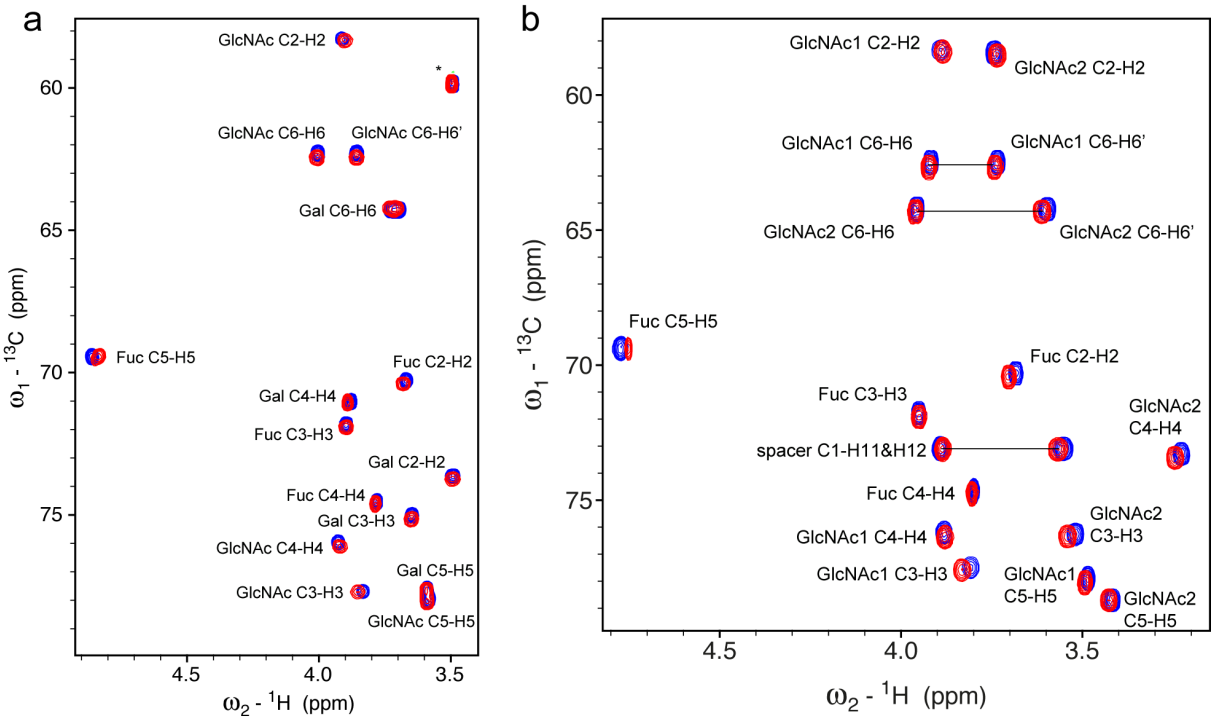

Figure S3. Influence of temperature on the chemical shifts of Le^x methyl glycoside and 3FChB. (a) Overlay of two ^{1}H-^{13}C HSQC spectra of Le^x methyl glycoside (3.7 mM) recorded at 900 MHz and either 277 K (blue) or 298 K (red). The spectra are referenced to DSS. (b) ^{1}H-^{13}C HSQC spectra of 3FChB (2.8 mM) recorded at 900 MHz and either 277 K (blue) or 298 K (red). All spectra are referenced to DSS.

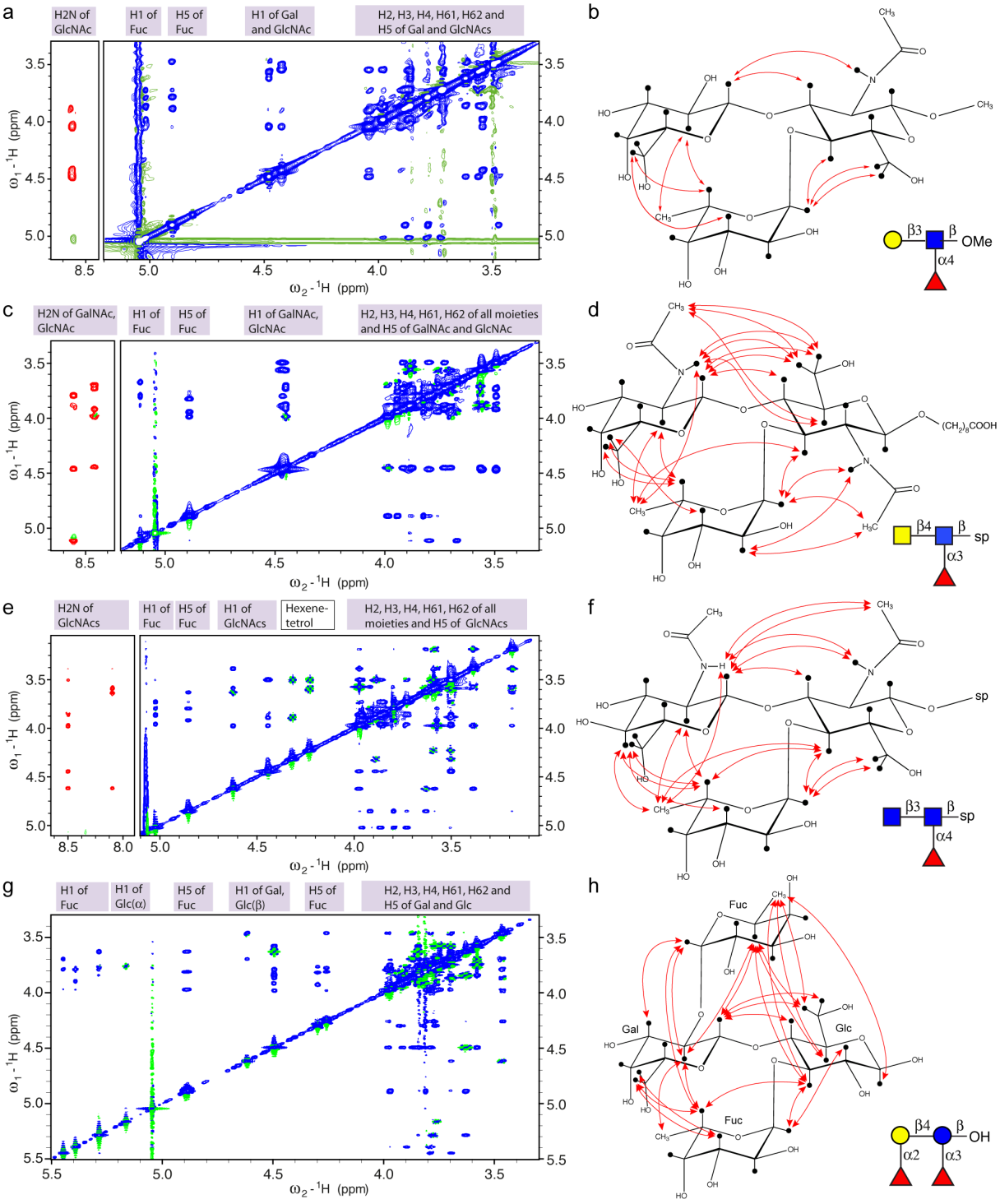

Figure S4. Structure determination of methyl Le^a, LDNF, Bv9 and LDFT. (a) 2D NOESY spectra of methyl Le^a (3.7 mM) in either H_2O (red, left) or in D_2O (blue, right) recorded at 900 MHz and 275 K. On the top, chemical shift assignments of isolated resonances are indicated. (b) Schematic presentation of methyl Le^a displaying the observed inter-residue NOEs by red arrows. (c) 2D NOESY spectra of LDNF (2.2 mM) in either H_2O (red, left) or in D_2O (blue, right) recorded at 900 MHz and 275 K. (d) Schematic presentation of LDNF displaying the observed inter-residue NOEs by red arrows. (e) 2D NOESY spectra of Bv9 (1 mM) in either H_2O (red, left) or in D_2O (blue, right) recorded at 900 MHz and 273 K. (f) Schematic presentation of Bv9 displaying the observed inter-residue NOEs by red arrows. The hexene-tetrol at the reducing end is indicated by 'sp'. (g) 2D NOESY spectrum of LDFT (3.2 mM) in D_2O recorded at 900 MHz and 275 K. (h) Schematic presentation of LDFT(β) displaying the observed inter-residue NOEs by red arrows. Only NOEs of the major β anomer are shown.

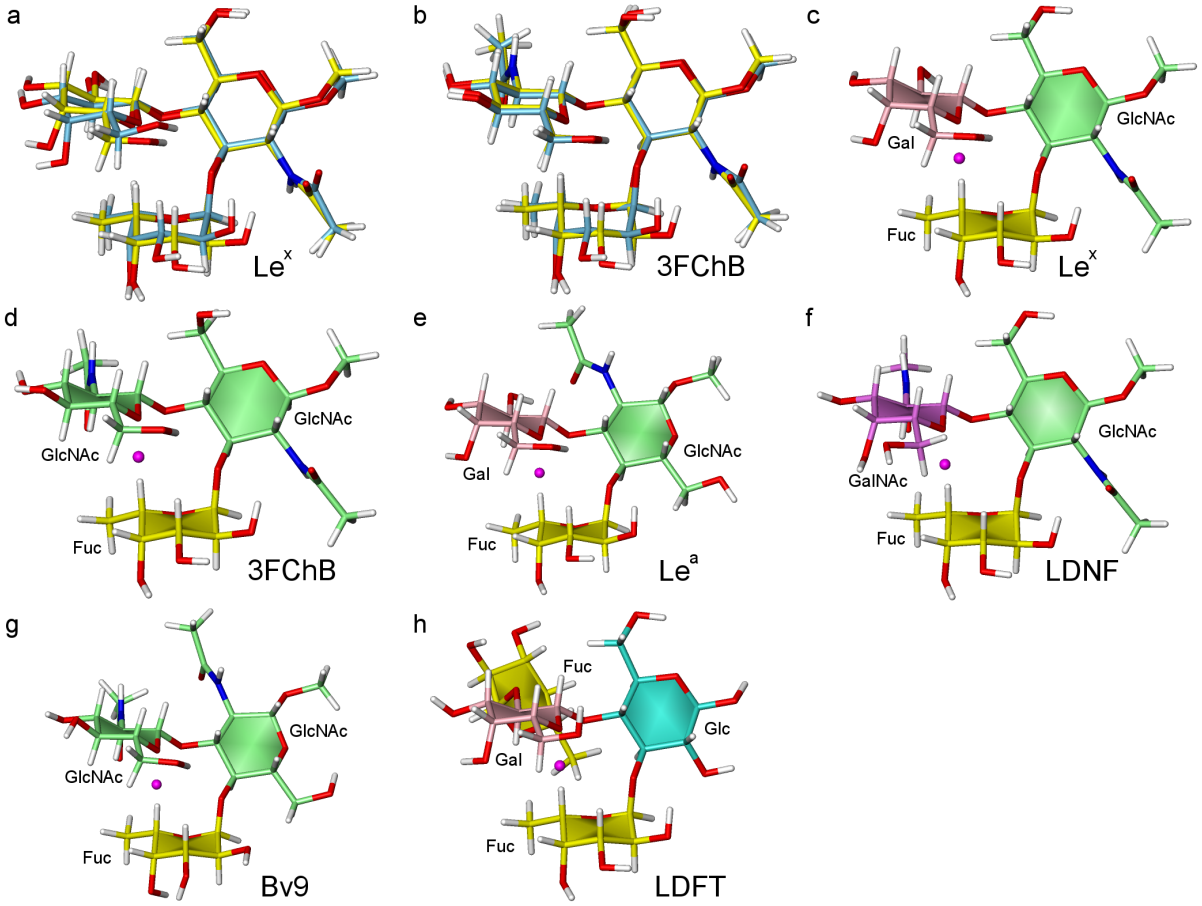

Figure S5. Structures of 3FChB, Le^x, Le^a, LDNF, Bv9 and LDFT optimized with density functional theory (DFT) and bond critical points of the C-H···O hydrogen bonds. (a) Overlay of the DFT-optimized structure (yellow) with the representative NMR structure (sky blue) of Le^x. The latter was used as start structure for the DFT optimization. (b) Comparison of the DFT-optimized structure (yellow) with the representative NMR structure (sky blue) of Le^x. (c) Structure of 3FChB optimized with DFT with the bond critical point of the C-H···O hydrogen bond indicated as magenta sphere. (d) DFT-optimized structure of 3FChB with the bond critical point. (e) DFT-optimized structure of Le^a with the bond critical point. (f) DFT-optimized structure of LDNF with the bond critical point. (g) DFT-optimized structure of Bv9 with the bond critical point. (h) DFT-optimized structure of LDFT with the bond critical point.

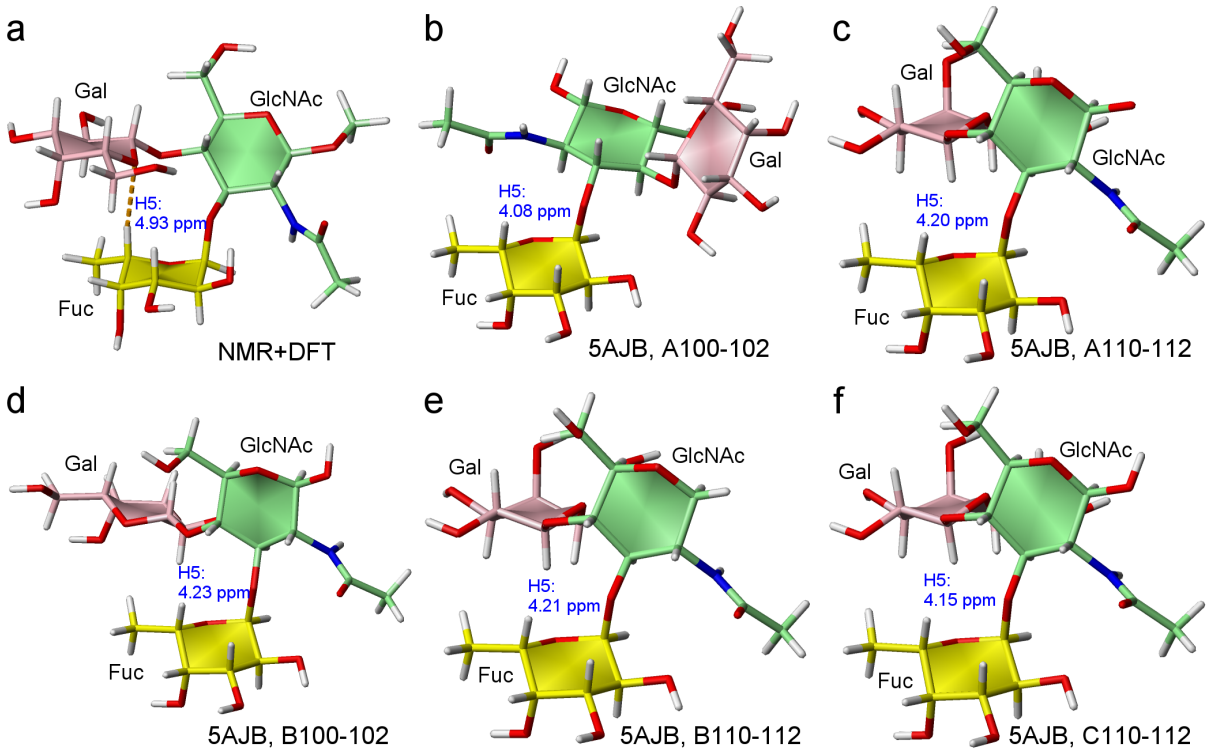

Figure S6. Chemical shifts of Fuc H5 of Le^x calculated from 3D coordinates of open conformations found in the crystal structure 5AJB[2] in comparison with a closed conformation. a) DFT minimized structure of closed Le^x with calculated chemical shift. b-f) open Le^x structures observed in the crystal structure 5AJB with calculated chemical shifts.

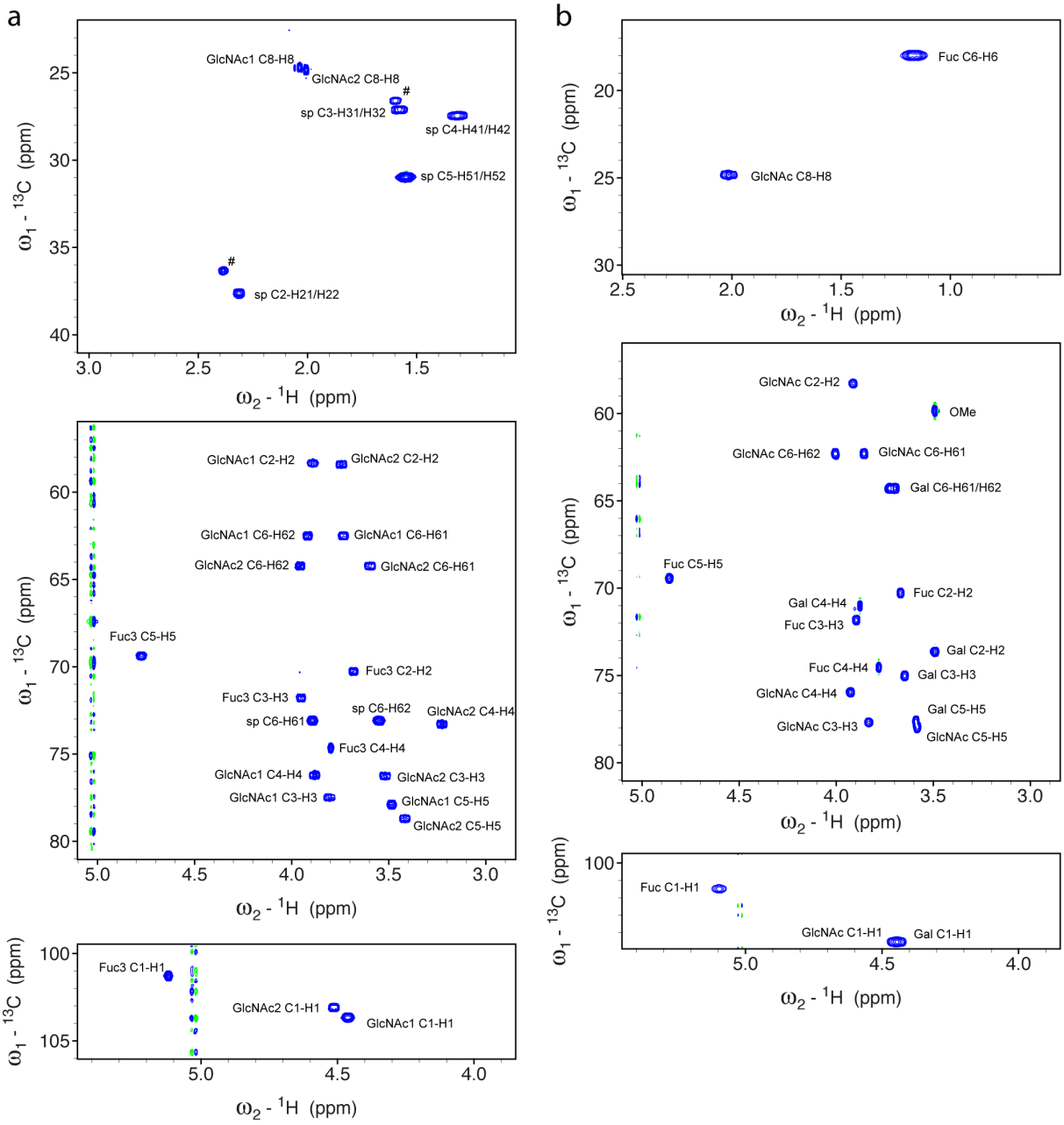

Figure S7. ^{1}H-^{13}C HSQC spectra of all investigated oligosaccharides referenced to DSS. (a) Three regions of the ^{1}H-^{13}C HSQC spectrum of α1,3-fucosylated chitobiose (2.8 mM) measured at 600 MHz and 277 K. The proximal N-acetylglucosamine that harbours the α1,3 branch is indicated as "GlcNAc1", the distal N-acetylglucosamine that stacks to the fucose is labeled "GlcNAc2". The signals of the linker 6-hydroxy hexanoate (-O-$(CH_2)_5$COOH) remaining from the chemical synthesis are labeled with "sp". The two correlations indicated with "#" originate from an impurity. (b) ^{1}H-^{13}C HSQC spectrum of Le^{x} methylglycoside (3.7 mM) measured at 900 MHz and 277 K. (c) ^{1}H-^{13}C HSQC spectrum of Le^{a} methylglycoside (3.7 mM) spectrum measured at 275 K. The two regions on the top are recorded at 900 MHz. The anomeric region (bottom) of a spectrum recorded at 500 MHz is shown at the bottom (better perfomance of ^{13}C decoupling compared to 900 MHz spectrum). (d) ^{1}H-^{13}C HSQC spectrum of LDNF with a β–$(CH_2)_8$COOH linker (2.2 mM) measured at 900 MHz and 275 K.

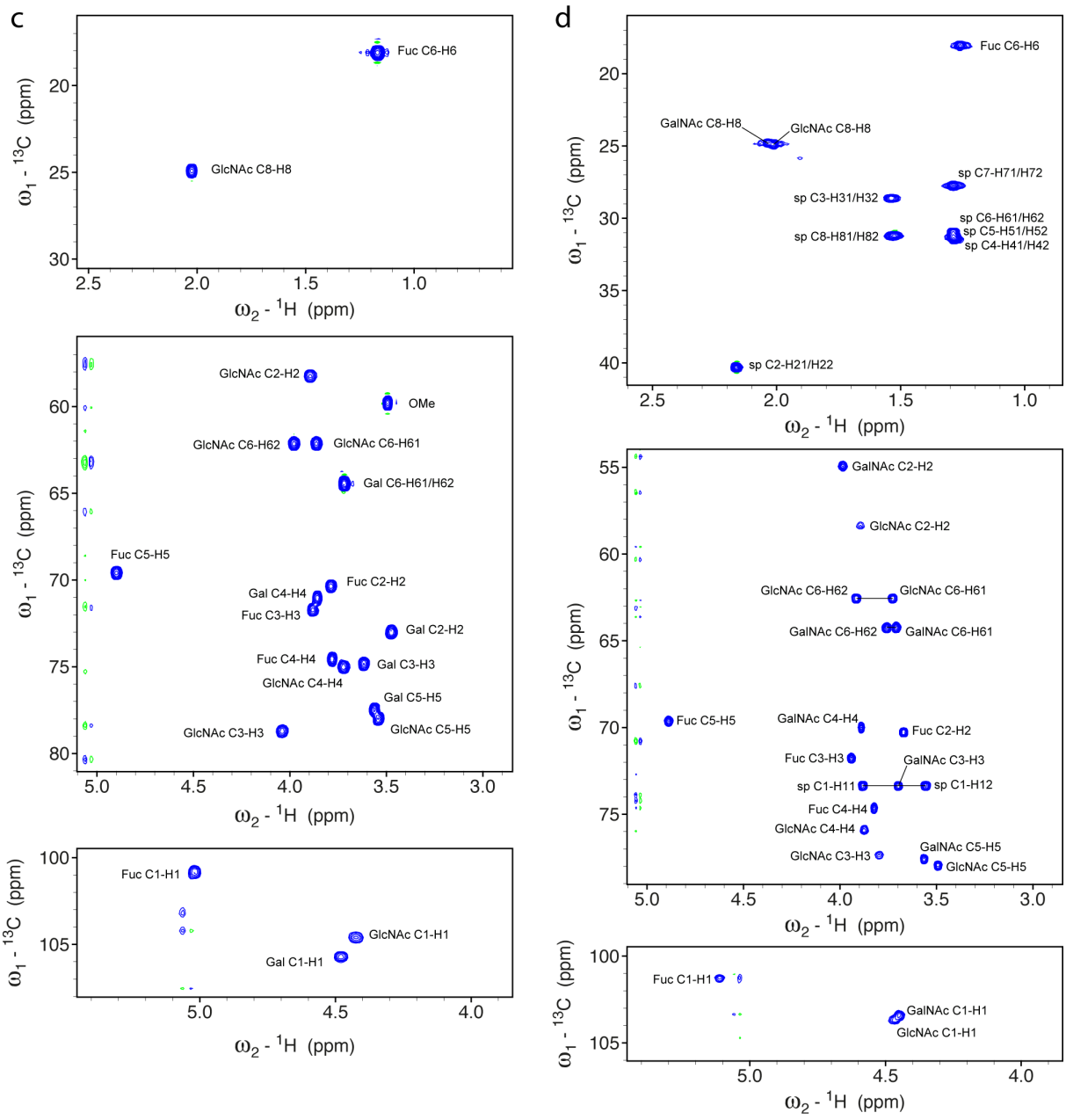

Figure S7 (continuation). (e) ^{1}H-^{13}C HSQC spectrum of Bv9 with a β–hexene-tetrol moiety at the reducing end (1 mM) measured at 500 MHz and 273 K. Please note that 273 K was required so that the water signal was not overlapping with Fuc3 H1 but upfield of it. The proximal N-acetylglucosamine that harbours the α1,3 branch is indicated as "GlcNAc1", the distal N-acetylglucosamine that stacks to the fucose is labeled "GlcNAc2". (f) ^{1}H-^{13}C HSQC spectrum LDFT with free OH at the reducing end (3.2 mM) measured at 500 MHz and 275 K. The spectrum is referenced to DSS. Fuc3 corresponds to the α1,2-linked fucose, Fuc4 to the α1,3-linked fucose. Signals depending on the anomeric state of the glucose are labeled with (α) or (β).

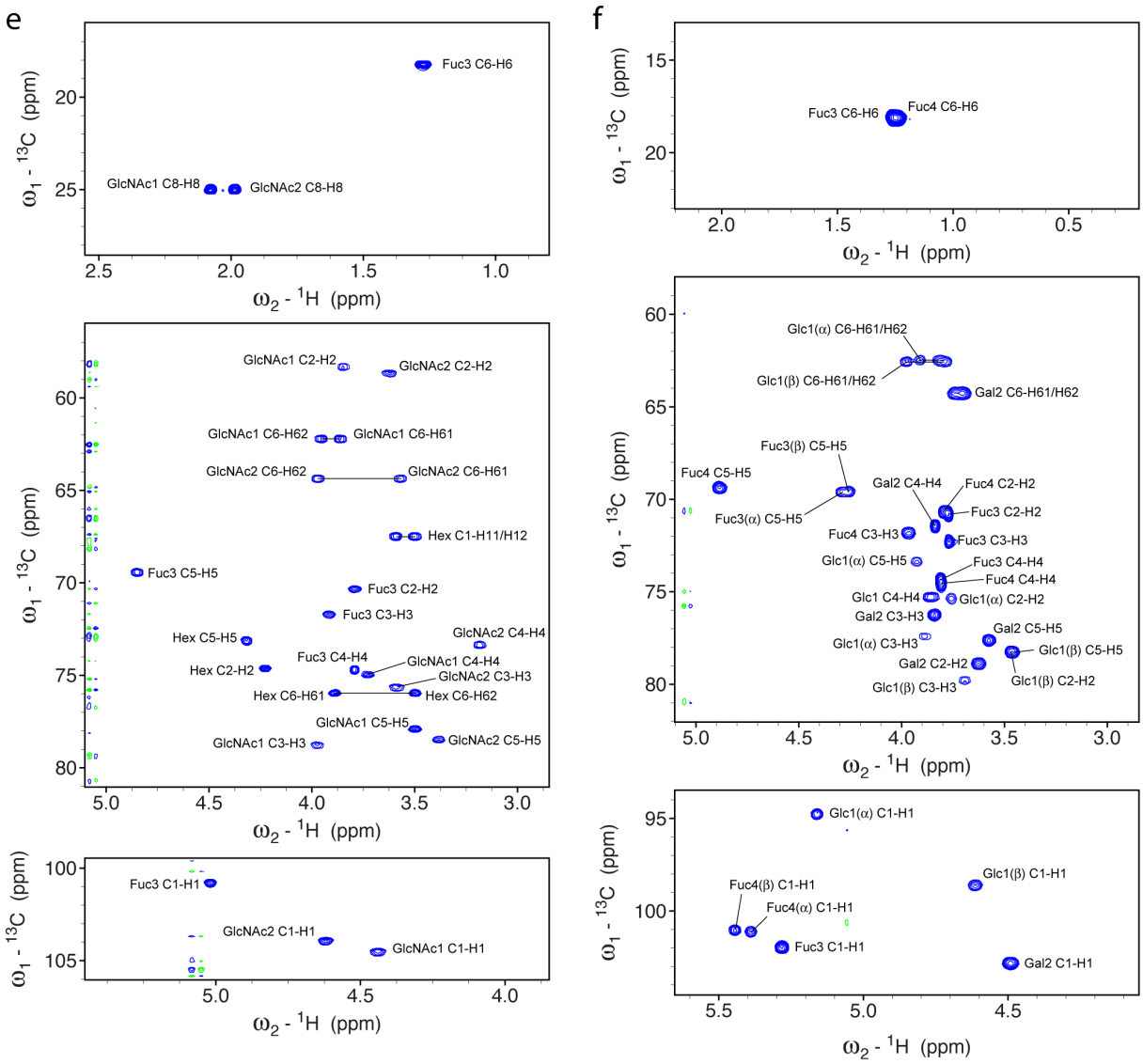

Figure S7 (continuation).

Table S1: Calculated isotropic chemical shielding (ppm) of the full oligosaccharide molecules and truncated derivatives together with the resulting chemical shift changes (ppm).[a]

		iPro-O-Me/ Me-O-Me	3FChB	Le^x	Le^a	LDNF	Bv9	LDFT (β)
NMR isotropic shielding σ	full molecule	27.53	26.85	26.81	26.81	26.88	26.63	26.84
	proton acceptor removed	28.35	27.54	27.60	27.61	27.55	27.34	27.53
	$\Delta\sigma$	-0.82	-0.69	-0.79	-0.80	-0.67	-0.71	-0.69
	proton donor removed	0.10	-0.14	-0.10	-0.12	-0.14	-0.08	-0.27
	$\Delta\sigma_{HB}$	-0.91	-0.55	-0.69	-0.68	-0.53	-0.63	-0.42
Chemical shift change due to hydrogen bond	$\Delta\delta_{HB}$	0.91	0.55	0.69	0.68	0.53	0.63	0.42

[a] The tri- and tetrasaccharides of the calculations were β-methyl glycosides except for LDFT for which the free OH as β-anomer was used. Calculations were performed with a basis set of B3LYP/6-31G(d,p) according to Scheiner et al. [1]

Table S2: Carbohydrate structures with a characteristic Fuc H5 chemical shift between 4.6 and 5.0 ppm found by a GLYCOSCIENCES.DE database search, ordered in respect to the central glyco-motifs, together with 21 additional values from the literature (marked by +).

# [a]	Carbohydrate structure [b]	Motif [c]	Chemical shift of Fuc H5 [d]	LINUCS ID or Reference[e]
	Le^x containing carbohydrates			
1	**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Galβ1,3GlcNAcβ1,3]Galβ1,4Glc	Le^x	4.866	1670
2	**Galβ1,4[Fucα1,3]GlcNAcβ**1,4[Galβ1,4GlcNAcβ1,2]Manα1,3[Galβ1,4GlcNAcβ1,2 Manβ1,6]Manβ1,4GlcNAcβ1,4GlcNAcβ-Asn	Le^x	4.835	274
3	**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Galβ1,3]GalNAc-ol	Le^x	4.835	4286
4	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Gal**β**1,4GlcNAcβ1,6**[**Fucα1,2Gal**β**1,4GlcNAc**β**1,3]GalNAc-ol	Le^x	4.835	12503
5	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,4GlcNAcβ1,6[Fucα1,2Galβ1,3GlcNAc**β**1,3]GalNAc-ol	Le^x	4.834	12501
6	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,3GalNAc-ol	Le^x	4.833	4285
7	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,4Glc	Le^x	4.832	212
8	**Galβ1,4[Fucα1,3]GlcNAcβ**1,4[Galβ1,4GlcNAcβ1,2]Manα1,3[Galβ1,4GlcNAcβ1,6[Galβ1,4GlcNAcβ1,2]Manβ1,6]Manβ1,4GlcNAcβ1,4GlcNAcβ-Asn	Le^x	4.832	275
9	**Galβ1,4[Fucα1,3]GlcNAcβ**1,2[Galβ1,4GlcNAcβ1,6]Manα1,6[Galβ1,4GlcNAcβ1,4[Galβ1,4GlcNAcβ1,2]Manβ1,3]Manβ1,4GlcNAcβ1,4GlcNAcβ-Asn	Le^x	4.832	276
10	**Galβ1,4[Fucα1,3]GlcNAcβ**1,4[Galβ1,4GlcNAcβ1,2]Manα1,6[Galβ1,4GlcNAcβ1,4[Galβ1,4GlcNAcβ1,2]Manβ1,3]Manβ1,4GlcNAcβ1,4GlcNAcβ-Asn	Le^x	4.832	277
11	Neu5Acα2,3Galβ1,3[Neu5Acα2,6]GalNAcβ1,3[**Galβ1,4[Fucα1,3]GlcNAcβ1,6**]Galβ1,4Glc	Le^x	4.832	1174
12	**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,6[Galβ1,3]GlcNAcβ1,3]Galβ1,4Glc	Le^x	4.832	2835
13	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3[Fucα1,2]Galβ1,4GlcNAcβ1,6[GlcNAc**β**1,3]GalNAc-ol	Le^x	4.831	12496
14	**Galβ1,4[Fucα1,3]GlcNAcβ**1,2Manα1,6Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn	Le^x	4.83	273
15	**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[GlcNAcβ1,3]GalNAc-ol	Le^x	4.83	4288
16	**Galβ1,4[Fucα1,3]GlcNAcβ**1,4Manα1,3Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn	Le^x	4.83	12533
17	**Galβ1,4[Fucα1,3]GlcNAcβ**1,2Manα1,3[Manα1,6]Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn	Le^x	4.83	12538
18	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,4GlcNAcβ1,2Manα1,6Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn	Le^x	4.83	12548
19	**Galβ1,4[Fucα1,3]GlcNAcβ**1,2Manα1,6[Neu5Acα2,6Galβ1,4GlcNAcβ1,2Manβ1,3]Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn	Le^x	4.829	278
20	**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Gal**β**1,4GlcNAcβ1,3]GalNAc-ol	Le^x	4.829	4294
21	**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Le^x	4.829	4298
22	Neu5Acα2,6Galβ1,4GlcNAc**β**1,3[**Galβ1,4[Fucα1,3]GlcNAcβ1,6]**Galβ1,4Glc	Le^x	4.829	8313
23	**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3]Galβ1,4Glc	Le^x	4.827	2838
24	**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3GlcNAcβ1,6]Galβ1,4Glc	Le^x	4.825	2837
25	**Galβ1,4[Fucα1,3]GlcNAcβ**1,2Manα1,3Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn	Le^x	4.822	272
26	**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Galβ1,4GlcNAcβ1,2]Manα1,3[Galβ1,4GlcNAcβ1,2Manβ1,6]Manβ1,4GlcNAcβ1,4GlcNAcβ-Asn	Le^x	4.82	279
27	**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Fucα1,2Gal**β**1,3GlcNAcβ1,3]Galβ1,4Glc	Le^x	4.819	1668
28	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3[KDNα2,6]GalNAc-ol	Le^x	4.818	3508
29	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3GalNAc-o	Le^x	4.813	4278
30	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3[Galβ1,4[Fucα1,3]GlcNAcβ1,6]Galβ1,4Glc	Le^x	4.829	6680
31	Galβ1,4[Fucα1,3]GlcNAcβ1,3[**Galβ1,4[Fucα1,3]GlcNAcβ**1,6]Galβ1,4Glc	Le^x	4.821	6680
32	**Galβ1,4[Fucα1,3]GlcNAcβ**1,2[Galβ1,4[Fucα1,3]GlcNAcβ1,6]Manα1,6Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn	Le^x	4.83	12544
33	Galβ1,4[Fucα1,3]GlcNAcβ1,2[**Galβ1,4[Fucα1,3]GlcNAcβ**1,6]Manα1,6Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn	Le^x	4.83	12544
34	Galβ1,4[Fucα1,3]GlcNAcβ1,2 Manα1,3[**Galβ1,4[Fucα1,3]GlcNAcβ**1,2 Manα1,6]Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn	Le^x	4.829	12545
35	Galβ1,4[Fucα1,3]GlcNAcβ1,2Manα1,3[**Galβ1,4[Fucα1,3]GlcNAcβ**1,2 Manα1,6]Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn	Le^x	4.829	12546
36	**Galβ1,4[Fucα1,3]GlcNAcβ**1,2Manα1,3[Galβ1,4[Fucα1,3]GlcNAcβ1,2Manα1,6]Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn	Le^x	4.829	12546
37	**Galβ1,4[Fucα1,3]GlcNAcβ**1,2 Manα1,3[Galβ1,4[Fucα1,3]GlcNAcβ1,2	Le^x	4.822	12545

	Manα1,6]Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAcβ-Asn			
38	Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3**[Galβ1,4[Fucα1,3]GlcNAcβ**1,6]Galβ1,4GlcNAc**β**1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Le^x	4.81	12417
39	Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3[**Galβ1,4[Fucα1,3]GlcNAcβ**1,6]Galβ1,4Glc	Le^x	4.823	8107
40	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,4[Fucα1,3]GlcNAcβ1,3Gal**β**1,3GalNAc-ol	Le^x	4.851	12507
41	Neu5Acα2,3Galβ1,3[Fucα1,4]GlcNAcβ1,3[**Galβ1,4[Fucα1,3]GlcNAcβ**1,6]Galβ1,4Glc	Le^x	4.795	4124
42	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,4GlcNAcβ1,6[Neu5Acα2,3Galβ1,3[Fucα1,4]GalNAcβ1,3]Galβ1,4Glc	Le^x	4.789	4222
43	**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Galβ1,3[Fucα1,4]GlcNAcβ1,3]Galβ1,4Glc	Le^x	4.873	1671
44	Galβ1,3GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Int Le^x	4.806	12413
45	Galβ1,4GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Int Le^x	4.806	12414
46	Galβ1,3GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Galβ1,3]GalNAc-ol	Int Le^x	4.806	12419
47	Galβ1,3GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Fucα1,2Galβ1,3GlcNAcβ1,3]Galβ1,4Glc	Int Le^x	4.801	14252
48	Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3[Galβ1,4GlcNAcβ1,6]**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Int Le^x	4.81	12418
49	Galβ1,3[Fucα1,4]GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Galβ1,3GlcNAcβ1,3]Galβ1,4Glc	Int Le^x	4.801	2727
50	Galβ1,3[Fucα1,4]GlcNAcβ1,3Galβ1,4GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Int Le^x	4.81	12416
51	Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3 **Galβ1,4[Fucα1,3]GlcNAcβ1,3**Galβ1,4Glc	Int Le^x	4.811	14239
52	GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,9-9-hydroxy-Nonanoate-OMe	Int Le^x	4.82	9296
53	Galβ1,4GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,9-9-hydroxy-Nonanoate-OMe	Int Le^x	4.82	9297
54	Neu5Acα2,6Galβ1,4GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,9-9-hydroxy-Nonanoate-OMe	Int Le^x	4.82	9299
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56	Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,4[Fucα1,3]GlcNAcβ1,3Galβ1,4Glc	Int Le^x	4.812	12761
57	Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3Galβ1,4[Fucα1,3]GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,4Glc	Int Le^x	4.812	12761
58	Fucα1,2Galβ1,3GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3]Galβ1,4Glc	Int Le^x	4.814	12762
59	Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3]Galβ1,4Glc	Int Le^x	4.8	12763
60	Galβ1,4[Fucα1,3]GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,3GalNAc-ol	Int Le^x	4.865	12507
61	Neu5Acα2,3Galβ1,4[Fucα1,3]GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,9-9-hydroxy-Nonanoate-OMe	Int Le^x	4.82	8861
62	Galβ1,4GlcNAcβ1,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3[Fucα1,4]GalNAcβ1,3]Galβ1,4Glc	Int Le^x	4.776	4221
63	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Galβ1,4GlcNAcβ1,3]GalNAc-ol	Sia Le^x	4.83	12342
64	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Fucα1,2Galβ1,3GlcNAcβ1,3]GalNAc-ol	Sia Le^x	4.821	12697
65	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,3GalNAc-ol	Sia Le^x	4.82	12340
66	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[GlcNAcβ1,3]GalNAc-ol	Sia Le^x	4.82	12341
67	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Fucα1,2Galβ1,3]GalNAc-ol	Sia Le^x	4.82	12388
68	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,3[Neu5Acα2,6]GalNAc-ol	Sia Le^x	4.819	17378
69	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,3[Neu5Acα2,6]GalNAc-ol	Sia Le^x	4.804	12408
70	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3]Galβ1,4Glc	Sia Le^x	4.798	6665
71	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,4[Fucα1,3]GlcNAcβ1,9-9-hydroxy-Nonanoate-OMe	Sia Le^x	4.82	8861
72	3S-**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Fucα1,2Galβ1,3]GalNAc-ol	3S-Le^x	4.806	17382
73	3S-**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	3S-Le^x	4.805	17388
74	3S-**Galβ1,4[Fucα1,3]GlcNAcβ**1,3[Neu5Acα2,6]GalNAc-ol	3S-Le^x	4.802	12406
75	**Galβ1,4**[6S]-[**Fucα1,3]GlcNAcβ**1,3[6S]Galβ1,4[6S]GlcNAc-ol	6S-Le^x	4.783	4412
76	**Galβ1,4**[6S]-[**Fucα1,3]GlcNAcβ**1,3Galβ1,4[6S]GlcNAc-ol	6S-Le^x	4.782	4410
77	**Galβ1,4**[6S]-[**Fucα1,3]GlcNAcβ**1,3[6S]Galβ1,4[6S]GlcNAc**β**1,3Gal-ol	6S-Le^x	4.778	3526
78	**Galβ1,4**[6S]-[**Fucα1,3]GlcNAcβ**1,3Galβ1,4[6S]-[Fucα1,3]GlcNAc-ol	6S-Le^x	4.782	4408
79	Galβ1,3[Fucα1,4]GlcNAcβ1,3**Galβ1,4**[6S]-[**Fucα1,3]GlcNAcβ**1,3Galβ1,4Glcβ	Int 6S-Le^x	4.805	22552

80	Fucα1,2Galβ1,3GlcNAcβ1,3**Galβ1,4**[6S]**[Fucα1,3]GlcNAcβ**1,3Galβ1,4Glcβ	Int 6S-Le^x	4.823	22550
81	Fucα1,2Galβ1,3GlcNAcβ1,3**Galβ1,4**[6S]**[Fucα1,3]GlcNAcβ**1,3Galβ1,4Glcα	Int 6S-Le^x	4.823	22551
82	Galβ1,3[Fucα1,4]GlcNAcβ1,3**Galβ1,4**[6S]**[Fucα1,3]GlcNAcβ**1,3Galβ1,4Glcβ	Int 6S-Le^x	4.805	22553
83	Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3**Galβ1,4**[6S]**[Fucα1,3]GlcNAcβ**1,3Galβ1,4Glcα	Int 6S-Le^x	4.819	22556
84	Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3**Galβ1,4**[6S]**[Fucα1,3]GlcNAcβ**1,3Galβ1,4Glcβ	Int 6S-Le^x	4.819	22557
85	Neu5Acα2,3**Galβ1,4**[6S]**[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	6S-Sia Le^x	4.802	17385
	Le^y containing carbohydrates			
86	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,6Galβ1,4GlcNAcβ1,3]Galβ1,4Glc	Le^y	4.88	8312
87	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,3**[**Fucα1,2]Gal**β**1,4GlcNAcβ1,6**[**GlcNAcβ1,3]GalNAc-ol	Le^y	4.88	12499
88	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,3[Fucα1,2]Gal**β**1,4GlcNAcβ1,6**[**Fucα1,2GlcNAcβ1,3]GalNAc-ol	Le^y	4.88	12504
89	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,3[Neu5Acα2,3Gal**β**1,4GlcNAc**β**1,6]GalNAc-ol	Le^y	4.877	12695
90	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Fucα1,2Galβ1,3GlcNAcβ1,3]GalNAc-ol	Le^y	4.874	8956
91	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,3[Neu5Acα2,6]GalNAc-ol	Le^y	4.874	12386
92	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,3**[**Gal**β**1,4GlcNAcβ1,6**]**Galβ1,3GalNAc-ol	Le^y	4.874	12508
93	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,3**[**Fucα1,2Gal**β**1,4GlcNAcβ1,6**]**Galβ1,3GalNAc-ol	Le^y	4.874	12511
94	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,3 Galβ1,3GalNAc-ol	Le^y	4.873	6679
95	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[GlcNAcβ1,3]GalNAc-ol	Le^y	4.872	8949
96	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Fucα1,2Galβ1,3]GalNAc-ol	Le^y	4.871	1667
97	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Le^y	4.87	12286
98	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,3[Fucα1,2Galβ1,4GlcNAcβ1,6]GalNAc-ol	Le^y	4.867	8953
99	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,3GalNAc-ol	Le^y	4.866	4284
100	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Gal**β**1,3]GalNAc-ol	Le^y	4.85	4292
101	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,3[Fucα1,2Galβ1,4[Fucα1,3]GlcNAcβ1,6]GalNAc-ol	Le^y	4.873	12510
102	Fucα1,2Galβ1,4[Fucα1,3]GlcNAcβ1,3[Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**1,6]GalNAc-ol	Le^y	4.873	12510
103	Fucα1,2**Galβ1,4**[6S]**[Fucα1,3]GlcNAcβ**1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	6S-Le^y	4.854	17381
	Le^a containing carbohydrates			
104	**Galβ1,3[Fucα1,4]GlcNAc**	Le^a	4.881	1708
105	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3[Neu5Acα2,6Galβ1,4GlcNAcβ1,6]Galβ1,4Glc	Le^a	4.876	2836
106	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	Le^a	4.871	1223
107	**Galβ1,3[Fucα1,4]GlcNAcβ**	Le^a	4.78	668
108	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4[6S][Fucα1,3]GlcNAcβ1,3Galβ1,4Glcβ	Le^a	4.883	22552
109	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4[6S][Fucα1,3]GlcNAcβ1,3Galβ1,4Glcβ	Le^a	4.883	22553
110	Galβ1,4[Fucα1,3]GlcNAcβ1,6[**Galβ1,3[Fucα1,4]GlcNAcβ**1,3]Galβ1,4Glc	Le^a	4.915	1671
111	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ1,3[**Galβ1,4[Fucα1,3]GlcNAcβ1,6**]**Galβ1,4GlcNAc**β**1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Le^a	4.86	12417
112	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4[Fucα1,3]GlcNAcβ1,6[Galβ1,3GlcNAc**β**1,3]Galβ1,4Glc	Le^a	4.869	2727
113	**Galβ1,3[Fucα1,4]GlcNAcβ1,3**Galβ1,4GlcNAc**β**1,3Galβ1,4[Fucα1,3]GlcNAcβ1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Le^a	4.86	12416
114	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4GlcNAcβ1,6[Neu5Acα2,3Galβ1,3[Fucα1,4]GalNAcβ1,3]Galβ1,4Glc	Le^a	4.839	4223
115	Neu5Acα2,3Galβ1,4[Fucα1,3]GlcNAcβ1,6[**Galβ1,3[Fucα1,4]GlcNAcβ**1,3]Galβ1,4Glc	Le^a	4.873	2826
116	Neu5Acα2,3**Galβ1,3**[Neu5Acα2,6]**[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	Int. Le^a	4.878	2780
117	Neu5Acα2,3**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	Sia Le^a	4.864	1632
118	Galβ1,3GlcNAcβ1,3Galβ1,4GlcNAcβ1,6[Neu5Acα2,3**Galβ1,3[Fucα1,4]GlcNAcβ**1,3]Galβ1,4Glc	Sia Le^a	4.838	4220
119	Neu5Acα2,3**Galβ1,3[Fucα1,4]GlcNAcβ**1,3[Neu5Acα2,6Galβ1,4GlcNAcβ1	Sia Le^a	4.837	4125

	,6]Galβ1,4Glc			
120	Neu5Acα2,3**Galβ1,3[Fucα1,4]GlcNAcβ**1,3[Galβ1,4GlcNAcβ1,6]Galβ1,4Glc	Sia Le^a	4.836	4123
121	Galβ1,4[Fucα1,3]GlcNAcβ1,3Galβ1,4GlcNAcβ1,6[Neu5Acα2,3**Galβ1,3[Fucα1,4]GlcNAcβ**1,3]Galβ1,4Glc	Sia Le^a	4.839	4222
122	Neu5Acα2,3**Galβ1,3[Fucα1,4]GlcNAcβ**1,3[Galβ1,4[Fucα1,3]GlcNAcβ1,6]Galβ1,4Glc	Sia Le^a	4.836	4124
123	Galβ1,3[Fucα1,4]GlcNAcβ1,3Galβ1,4GlcNAcβ1,6[Neu5Acα2,3**Galβ1,3[Fucα1,4]GlcNAcβ**1,3]Galβ1,4Glc	Sia Le^a	4.839	4223
124	Galβ1,4GlcNAcβ1,3Galβ1,4[Fucα1,3]GlcNAcβ1,6[Neu5Acα2,3**Galβ1,3[Fucα1,4]GlcNAcβ**1,3]Galβ1,4Glc	Sia Le^a	4.838	4221
125	3S-**Galβ1,3[Fucα1,4]GlcNAcα**	3S-Le^a	4.874	13788
126	3S-**Galβ1,3[Fucα1,4]GlcNAcβ**	3S-Le^a	4.861	13788
	Le^b containing carbohydrates			
127	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,3GalNAc-ol	Le^b	4.88	5022
128	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3[Neu5Acα2,6Galβ1,4GlcNAcβ1,6]Galβ1,4Glc	Le^b	4.866	2839
129	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ1,3**Galβ1,4GlcNAcβ1,6[GlcNAcβ1,3]GalNAc-ol	Le^b	4.866	12497
130	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Gal**β**1,4GlcNAcβ1,6**[**Galβ1,4GlcNAcβ1,3]GalNAc-ol	Le^b	4.866	12506
131	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Gal**β**1,4GlcNAcβ1,6**[**Fucα1,2Galβ1,3]GalNAc-ol	Le^b	4.865	12502
132	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,3[Galβ1,4GlcNAcβ1,6]GalNAc-ol	Le^b	4.865	12514
133	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	Le^b	4.86	1225
134	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ1,3**Galβ1,4GlcNAcβ1,3Galβ1,4GlcNAcβ1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Le^b	4.86	12415
135	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3**[**Fucα1,2]Galβ1,4GlcNAcβ1,6**[**GlcNAcβ1,3]GalNAc-ol	Le^b	4.855	12505
136	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,6[Galβ1,4GlcNAcβ1,3]GalNAc-ol	Le^b	4.82	4291
137	Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3Galβ1,4[Fucα1,3]GlcNAcβ1,6[Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3]Galβ1,4Glc	Le^b	4.853	12763
138	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4[Fucα1,3]GlcNAcβ1,6[Fucα1,2Galβ1,3[Fucα1,4]GlcNAcβ1,3]Galβ1,4Glc	Le^b	4.853	12763
139	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3[Galβ1,4[Fucα1,3]GlcNAcβ1,6]Galβ1,4Glc	Le^b	4.861	8107
140	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4[6S][Fucα1,3]GlcNAcβ1,3Galβ1,4Glcα	Le^b	4.871	22556
141	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4[6S][Fucα1,3]GlcNAcβ1,3Galβ1,4Glcβ	Le^b	4.871	22557
142	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3 Galβ1,4[Fucα1,3]GlcNAcβ1,3Galβ1,4Glc	Le^b	4.86	14239
143	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ1,3[**Galβ1,4[Fucα1,3]GlcNAcβ1,6**]**Galβ1,4GlcNAcβ1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Le^b	4.86	12417
144	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ1,3[**Galβ1,4GlcNAcβ1,6**]**Galβ1,4[Fucα1,3]GlcNAcβ1,6[Neu5Acα2,3Galβ1,3]GalNAc-ol	Le^b	4.86	12418
145	Fucα1,2Galβ1,3GlcNAcβ1,3Galβ1,4[Fucα1,3]GlcNAcβ1,6[Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3]Galβ1,4Glc	Le^b	4.868	12762
146	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4[Fucα1,3]GlcNAcβ1,3Galβ1,4[Fucα1,3]GlcNAcβ1,3Galβ1,4Glc	Le^b	4.853	12761
147	GalNAcα1,3[Fucα1,2]**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Gal**β**1,4Glc	Int Le^b	4.853	1271
148	GalNAcα1,3[Fucα1,2]**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Gal	Int Le^b	4.853	14257
	3-Fucosylated chitobiose containing carbohydrates			
149	Manα1,6[Xylβ1,2]Manβ1,4**GlcNAcβ1,4[Fucα1,3]GlcNAcβ**-Asn	3FChB	4.722	4566
150	Manα1,6[Manα1,3][Xylβ1,2]Manβ1,4**GlcNAcβ1,4[Fucα1,3]GlcNAc**	3FChB	4.721	1024
151	Manα1,6[Manβ1,3]Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn	3FChB	4.72	12525
152	Manα1,6[Manβ1,3]Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAc**	3FChB	4.71	2900
	4-Fucosylated GlcNAcβ1,3GlcNAc cont. carbohydrates			
153	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,4GalAα1,3Fucα		4.71	26716
+1	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6-Hexene-tetrol		4.816	Coppin 2003
+2	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[Galβ1,3]GalNAc-ol		4.809	Coppin 2003
+3	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[GlcNAcα1,4Galβ1,3]GalNAc-ol		4.805	Coppin 2003
+4	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[Fucα1,2Galβ1,3]GalNAc-ol		4.809	Coppin

				2003
+5	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[Kdnα2,3Galβ1,3]GalNAc-ol		4.807	Coppin 2003
+6	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[Kdnα2,3[Galβ1,4]Galβ1,3]GalNAc-ol		4.809	Coppin 2003
+7	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[Kdnα2,3[GlcNAcα1,4Galβ1,4]Galβ1,3] GalNAc-ol		4.811	Coppin 2003
+8	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[NeuAcα2,3[Galβ1,4]Galβ1,3]GalNAc-ol		4.809	Coppin 2003
+9	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[NeuGcα2,3Galβ1,3]GalNAc-ol		4.809	Coppin 2003
+10	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[NeuGcα2,3[Galβ1,4]Galβ1,3]GalNAc-ol		4.807	Coppin 2003
+11	**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[NeuGcα2,3[GlcNAcα1,4Galβ1,4]Galβ 1,3]GalNAc-ol		4.812	Coppin 2003
+12	Galβ1,4**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[Kdnα2,3Galβ1,3]GalNAc-ol		4.79	Coppin 2003
+13	GlcNAcα1,4Galβ1,4**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[GlcNAcα1,4Galβ1 ,3]GalNAc-ol		4.775	Coppin 2003
+14	GlcNAcα1,4Galβ1,4**GlcNAcβ1,3[Fucα1,4]GlcNAcβ**1,6[Kdnα2,3Galβ1,3] GalNAc-ol		4.78	Coppin 2003
	3-Fucosylated LAcDiNAc (LDNF) cont. carbohydrates			
154	**GalNAcβ1,4[Fucα1,3]GlcNAcβ**1,2Manα1,3[GalNAcβ1,4GlcNAcβ1,2Man β1,6]Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAc	LDNF	4.862	13355
155	**GalNAcβ1,4[Fucα1,3]GlcNAcβ**1,2Manα1,6[GalNAcβ1,4GlcNAcβ1,2Man β1,3]Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAc	LDNF	4.862	13356
156	**GalNAcβ1,4[Fucα1,3]GlcNAcβ**1,2Manα1,3[Neu5Acα2,3Galβ1,4GlcNAcβ 1,2Manβ1,6]Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAc	LDNF	4.861	13760
157	**GalNAcβ1,4[Fucα1,3]GlcNAcβ**1,6[Galβ1,3]GalNAc-ol	LDNF	4.85	13039
158	**GalNAcβ1,4[Fucα1,3]GlcNAcβ**1,3GalNAc-ol	LDNF	4.841	13884
159	**GalNAcβ1,4[Fucα1,3]GlcNAcβ**1,2Manα1,3[GalNAcβ1,4[Fucα1,3]GlcNAc β1,2Manβ1,6]Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAc	LDNF	4.853	13757
160	GalNAcβ1,4[Fucα1,3]GlcNAcβ1,2Manα1,3[**GalNAcβ1,4[Fucα1,3]GlcNAc β**1,2Manβ1,6]Manβ1,4GlcNAcβ1,4[Fucα1,6]GlcNAc	LDNF	4.853	13757
161	GalNAcα1,2**Fucα1,3[GalNAcβ1,4]GlcNAcβ**1,3GalNAc-ol	iLDNF	4.837	2816
+15	Tyvα1,3**GalNAcβ1,4[Fucα1,3]GlcNAcβ**OMe	iLDNF	4.82	Zhang 1996
+16	Tyvβ1,3**GalNAcβ1,4[Fucα1,3]GlcNAcβ**OMe	iLDNF	4.84	Zhang 1996
	Le^x-like containing carbohydrates			
162	**Galβ1,4[Fucα1,3]Glc**β	Le^x like	4.78	27042
163	Neu5Acα2,3Galβ1,3[Neu5Acα2,6]GlcNAcβ1,3**Galβ1,4[Fucα1,3]Glcα**	int Le^x like	4.82	2781
164	Neu5Acα2,3Galβ1,4GlcNAcβ1,3**Galβ1,4[Fucα1,3]Glcα**	int Le^x like	4.819	2737
165	Neu5Acα2,3Galβ1,3[Neu5Acα2,6]GlcNAcβ1,3**Galβ1,4[Fucα1,3]Glcβ**	int Le^x like	4.81	2781
166	Neu5Acα2,3Galβ1,4GlcNAcβ1,3**Galβ1,4[Fucα1,3]Glcβ**	int Le^x like	4.806	2737
167	Neu5Acα2,3**Galβ1,4[Fucα1,3]Glcβ**	Sia Le^x like	4.81	1630
168	Neu5Acα2,3**Galβ1,4[Fucα1,3]Glcα**	Sia Le^x like	4.82	1630
	Le^y-like containing carbohydrates			
169	Galα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcα**	int Le^y like	4.872	3993
170	Galα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	int Le^y like	4.854	3993
171	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcα**	int Le^y like	4.851	1273
172	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	int Le^y like	4.835	1273
+17	Fucα1,2**Galβ1,4[Fucα1,3]Glcβ**	Le^y like	4.88	Ishizuka 1999
	Le^a-like containing carbohydrates			
+18	3S-**Galβ1,3[Fucα1,4]Glcβ**-sp	3S-Le^a like	4.840	Kurutz 1997
+19	6S-**Galβ1,3[Fucα1,4]Glcβ**-sp	6S-Le^a	4.839	Kurutz 1997

		like		
+20	3S,6S-**Galβ1,3[Fucα1,4]Glcβ**-sp	3S,6S-Le[a] like	4.873	Kurutz 1997
	Le[b]-like containing carbohydrates			
173	Galα1,3[Fucα1,2]**Galβ1,3[Fucα1,4]Glc**	int Le[b] like	4.97	14260
174	GalNAcα1,3[Fucα1,2]**Galβ1,3[Fucα1,4]Glc**	int Le[b] like	4.969	14259
	4-Fucosylated chitobiose-like containing carbohydrates			
175	Glcα1,2Glcβ1,3**GlcNAcβ1,3[Fucα1,4]Glc**αP	3FChB like	4.84	27088
	3-Fucosylated chondroitin sulfate			
+21	3S-GlcAβ1,3[4S]**GalNAcβ1,4[Fucα1,3]GlcAβ**1,3[4S]GalNAc		4.80	Kitagawa 1997
	Miscellaneous carbohydrates			
176	**Galα1,3[Fucα1,2]Galβ**1,3[Fucα1,4]Glc		4.665	14260
177	**GalNAcα1,3[Fucα1,2]Galβ**1,3[Fucα1,4]Glc		4.662	14259
178	**Manα1,3[Fucα1,2]Rha**αOMe		(4.96)[f]	27238

[a] Consecutive numbering of the results from the database search. Few additional data found in the literature are indicated by a + sign.
[b] The motif with the characteristic Fuc H5 chemical shift is indicated in bold.
[c] The following abbreviations are used to indicate the Glyco motif: Le^x – $Lewis^x$; Int Le^x – internal $Lewis^x$; Sia Le^x – sialyl $Lewis^x$; 3S-Le^x – 3-sulfo $Lewis^x$; 6S-Le^x – 6-sulfo $Lewis^x$; Int 6S-Le^x – internal 6-sulfo $Lewis^x$; 6S-Sia Le^x – 6-sulfo sialyl $Lewis^x$; Le^y – $Lewis^y$; 6S-Le^y – 6-sulfo $Lewis^y$; Le^a – $Lewis^a$; Int Le^a – internal $Lewis^a$; Sia Le^a – sialyl $Lewis^a$; 3S-Le^a – 3-sulfo $Lewis^a$; Le^b – $Lewis^b$; Int Le^b – internal $Lewis^b$; 3FChB – α1,3-fucosylated chitobiose; LDNF – fucosylated LacDiNAc; iLDNF – internal fucosylated LacDiNAc;
[d] Chemical shift values are given in ppm.
[e] Additional data are used, indicated with an +: from five publications [3].
[f] Probably an artifact of the database, Kochetkov et al. reports an H5 chemical shift of 4.09 ppm for the same compound (number 13) [4].

Table S3: Intra- and inter-residual NOEs of Le^x β-methyl glycoside at 277 K and 900 MHz and their corresponding distances.

proton pair	average S/N of NOEs cross peaks	corresponding ^{1}H-^{1}H distance[b] [Å]
intra		
Gal2 H1-H2	345[a]	2.76
Gal2 H1-H3	433[a]	2.65
Gal2 H1-H5	824	2.38
Gal2 H3-H4	616[a]	2.50
Gal2 H4-H5	992	2.31
Gal2 H4-Q6	375[a]	3.05[e]
GlcNAc1 H1-H3	240[a]	2.93
GlcNAc1 H1-H5	837	2.38
GlcNAc1 H1-Q1	345	3.31
GlcNAc1 H5-H62	312[a]	2.80
GlcNAc1 H5-H61	456[a]	2.63[f]
GlcNAc1 HN2-H1	87	2.84
GlcNAc1 HN2-H2	42[a]	3.20
GlcNAc1 HN2-H3	114[a]	2.71
GlcNAc1 HN2-Q8	203[a]	2.96[e]
Fuc3 H1-H2	403	2.69
Fuc3 H3-H5 [c]	437.5	2.65
(Fuc3 H3-H5, H2O)[d]	131[a]	(2.65)
Fuc3 H4-H5	823	2.39
Fuc3 H4-Q6	472[a]	3.14[e]
Fuc3 H5-Q6	1580[a]	2.57[e,f]
inter		
Gal2 H1 - GlcNAc1 H4	744[a]	2.43
Gal2 H1 - GlcNAc1 H61	416[a]	2.67
Gal2 H1 - GlcNAc1 H62	312[a]	2.80
Gal2 H2 - Fuc3 H5	323[a]	2.79
Gal2 H2 - Fuc3 Q6	288[a]	3.41[e]
Gal2 Q6 - Fuc3 H3	381[a]	3.04[e]
GlcNAc1 H3 - Fuc3 H1	258[a]	2.89
GlcNAc1 HN2 - Fuc3 H1	143[a]	2.61
GlcNAc1 Q8 - Fuc3 H1	90[a]	4.14[e]

[a] Only one cross-peak was used because of artifacts or severe spectral overlap.

[b] The ^{1}H-^{1}H distances were calculated from experimentally obtained NOE intensities using the H3-H5 cross-peak of Fuc3 as a reference with a distance of 2.65 Å assuming a $1/r^6$ dependence of the NOE intensities. For the structure calculations the herein reported distances were increased by 0.2 Å tolerance and used as upper limit restraints.

[c] Reference restraint for the NOESY measured in D_2O.

[d] Reference restraint for the NOESY measured in H_2O.

[e] Signal to noise ratios from cross-peaks involving methyl or methylene protons were divided by 3 and 2 for the calculation, respectively.

[f] Because of overlap and close artifacts, the distance is not reliable and we used 6 Å as a conservative restraint.

Table S4. Intra- and inter-residual NOEs of 3FChB at 277 K and 900 MHz and their corresponding distances.

proton pair	average S/N of NOEs cross peaks	corresponding ^{1}H-^{1}H distance[b] [Å]
intra		
GlcNAc2 H1-H2	489[a]	2.79
GlcNAc2 H1-H3	553	2.73
GlcNAc2 H1-H5	1151.5	2.41
GlcNAc2 H2-H4	398.5	2.88
GlcNAc2 H2-Q8	100[a]	4.36[e]
GlcNAc2 H3-H5	499[a]	2.78
GlcNAc2 H4-H62	409	2.87
GlcNAc2 H4-H61	255	3.11
GlcNAc2 H5-H62	462	2.81
GlcNAc2 H5-H61	684.5	2.63
(GlcNAc2 H61-H62, D_2O)[c]	7424.5	(1.77)
(GlcNAc2 H61-H62, H_2O)[d]	3303.5	(1.77)
GlcNAc2 HN2-H1	150.5	2.96
GlcNAc2 HN2-H2	219	2.78
GlcNAc2 HN2-H3	373	2.55
GlcNAc2 HN2-Q8	490	2.92[e]
GlcNAc1 H1-H3	421.5	2.86
GlcNAc1 H1-H5	1256	2.38
GlcNAc1 H3-H5	496.5	2.78
GlcNAc1 H5-H61	750[a]	2.59
GlcNAc1 H5-H62	762[a]	2.59
GlcNAc1 HN2-H1	157	2.94
GlcNAc1 HN2-H2	108[a]	3.13
GlcNAc1 HN2-H3	257.5	2.71
GlcNAc1 HN2-Q8	559.5	2.86[e]
Fuc3 H1-H2	636	2.67
Fuc3 H1-H5	24[a]	4.60
Fuc3 H1-Q6	117[a]	4.25[e]
Fuc3 H3-H4	374[a]	2.91
Fuc3 H3-H5	655.5	2.65
(Fuc3 H3-H5, H2O)	244[a]	(2.73)
Fuc3 H4-H5	1354	2.35
Fuc3 H4-Q6	940[a]	3.00[e]
Fuc3 H5-Q6	3583.5	2.40[e]
inter		
GlcNAc2 H1 - GlcNAc1 H4	1029[a]	2.46
GlcNAc2 H1 - GlcNAc1 H62	444[a]	2.83
GlcNAc2 HN2 - GlcNAc1 H62	140	3.00
GlcNAc2 H2 - Fuc3 H5	475[a]	2.80
GlcNAc2 H2 - Fuc3 Q6	545[a]	3.29[e]
GlcNAc2 H62 - Fuc3 H4	204.5	3.22
GlcNAc2 H4 - Fuc3 H5	102.5	3.61
GlcNAc1 H3 - Fuc3 H1	406[a]	2.87
GlcNAc1 H2 - Fuc3 H1	104[a]	3.61[e]
GlcNAc1 HN2 - Fuc3 H1	347[a]	2.58
GlcNAc1 Q8 - Fuc3 H1	237[a]	3.77[e]

[a] Only one cross-peak was used because of artifacts or severe spectral overlap.
[b] The ^{1}H-^{1}H distances were calculated from experimentally obtained NOE intensities using the H3-H5 cross-peak of Fuc3 as a reference with a distance of 2.65 Å assuming a $1/r^6$ dependence of the NOE intensities. For

the structure calculations the herein reported distances were increased by 0.2 Å tolerance and used as upper limit restraints.

[c] Reference restraint for the NOESY measured in D_2O.

[d] Reference restraint for the NOESY measured in H_2O.

[e] Signal to noise ratios from cross-peaks involving methyl or methylene protons were divided by 3 and 2 for the calculation, respectively.

Table S5. NMR structure determination statistics of 3FChB (fucosylated chitobiose, GlcNAcβ1,4[Fucα1,3]GlcNAcβ), methyl Le^x, methyl Le^a, LDNF (fucosylated LacdiNAc, GalNAcβ1,4[Fucα1,3]GlcNAcβ) the amphibian glycan Bv9 (GlcNAcβ1,3[Fucα1,4]GlcNAcβ) and LDFT (Lactodifucotetraose β anomer, Fucα1,2Galβ1,4[Fucα1,3]GlcNAcβ).

	3FChB	**methyl Le^x**	**methyl Le^a**	**LDNF**	**Bv9**	**LDFT(β)**
NMR distance and dihedral constraints						
Distance restraints						
Total NOE	42	29	29	42	32	42
Intra-residue	31	20	20	21	15	19
Inter-residue	11	9	9	21	17	23
Total dihedral angle restraints	2	0	0	0	0	0
HN-CO peptide bonds of acetamido	2	0	0	0	0	0
Structure statistics						
Violations (mean and s.d.)						
Number of distance violations > 0.1 Å	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
Number of dihedral angle violations > 5º	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
Max. dihedral angle violation (º)	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
Max. distance constraint violation (Å)	0.04±0.00	0.07±0.00	0.00±0.00	0.09±0.00	0.01±0.01	0.09±0.01
Deviations from idealized geometry						
Bond lengths (Å)	0.01463± 0.0001	0.01537± 0.0002	0.0155± 0.0001	0.0143± 0.0001	0.0147± 0.0001	0.0166± 0.0002
Bond angles (º)	1.84±0.02	1.90±0.05	1.90±0.04	1.97±0.06	1.82±0.04	2.05±0.02
Average pairwise r.m.s. deviation* (Å)						
all heavy	0.05±0.02	0.15±0.15	0.14±0.13	0.26±0.16	0.14±0.13	0.07±0.03

* Pairwise r.m.s. deviation was calculated among 20 refined structures.

Table S6: Intra- and inter-residual NOEs of Le[a] β-methyl glycoside at 275 K and 900 MHz and their corresponding distances.

proton pair	average S/N of NOEs cross peaks	corresponding ^{1}H-^{1}H distance[b] [Å]
intra		
Gal2 H1-H3	194.5	2.78
Gal2 H1-H5	394.5	2.47
Gal2 H3-H4	286[a]	2.60
Gal2 H4-H5	369[a]	2.49
Gal2 H4-Q6	556[a]	2.62[e]
Gal2 H5-Q6	1011[a]	2.37[e]
GlcNAc1 H1-H2	67.5	3.31
GlcNAc1 H1-H3	131	2.96
GlcNAc1 H1-H5	360.5	2.50
GlcNAc1 H2-H3	394	2.47[f]
GlcNAc1 H3-H5	190	2.79
GlcNAc1 H5-H62	275[a]	2.62[f]
GlcNAc1 H5-H61	260[a]	2.64
GlcNAc1 HN2-H1	283[a]	3.04
GlcNAc1 HN2-H3	533.5	2.74
GlcNAc1 HN2-Q8	962[a]	2.98[e]
Fuc3 H1-H2	367.5	2.50
Fuc3 H3-H5 [c]	257	2.65
(Fuc3 H3-H5, H2O)[d]	645[a]	(2.65)
Fuc3 H4-H5	419.5	2.44
Fuc3 H4-Q6	229[a]	2.70
inter		
Gal2 H1 - GlcNAc1 H3	248.5	2.66
Gal2 H1 - GlcNAc1 HN2	440[a]	3.50
Gal2 H2 - Fuc3 H5	212.5	2.74
Gal2 H2 - Fuc3 Q6	225[a]	3.25[e]
Gal2 Q6 - Fuc3 H3	427	2.73[e]
Gal2 Q6 - Fuc3 H5	70	3.69[e]
GlcNAc1 H4 - Fuc3 H1	335.5	2.53
GlcNAc1 H62 - Fuc3 H1	286[a]	2.60
GlcNAc1 H61 - Fuc3 H1	134[a]	2.95

[a] Only one cross-peak was used because of artifacts or severe spectral overlap.
[b] The ^{1}H-^{1}H distances were calculated from experimentally obtained NOE intensities using the H3-H5 cross-peak of Fuc3 as a reference with a distance of 2.65 Å assuming a $1/r^{6}$ dependence of the NOE intensities. For the structure calculations the herein reported distances were increased by 0.2 Å tolerance and used as upper limit restraints.
[c] Reference restraint for the NOESY measured in D_2O.
[d] Reference restraint for the NOESY measured in H_2O.
[e] Signal to noise ratios from cross-peaks involving methyl or methylene protons were divided by 3 and 2 for the calculation, respectively.
[f] Because of overlap and close artifacts, the distance is not reliable and we used 6 Å as a conservative restraint.

Table S7. Intra- and inter-residual NOEs of LDNF at 275 K and 900 MHz and their corresponding distances.

proton pair	average S/N of NOEs cross peaks	corresponding ^{1}H-^{1}H distance[b] [Å]
intra		
GalNAc H1-H3	880	2.68
GalNAc H1-H5	1977	2.34
GalNAc HN2-H1	270	2.78
GalNAc HN2-H3	447	2.56
GalNAc HN2-H5	35	3.91
GalNAc HN2-Q8	530[a]	2.49
GlcNAc H1-H3	416.5	3.04
GlcNAc H1-H5	1490.5	2.46
GlcNAc H3-H5	533	2.92
GlcNAc H5-H61	770[a]	2.74
GlcNAc H5-H62	652[a]	2.84
GlcNAc HN2-H1	192.5	2.94
GlcNAc HN2-H3	284.5	2.76
GlcNAc HN2-H5	28	4.06
GlcNAc HN2-Q8	618[a]	2.91[e]
Fuc H1-H2	965.5	2.64
Fuc H1-H5	150	3.60
Fuc H3-H4	1855	2.37
Fuc H3-H5[c]	948	2.65
(Fuc H3-H5, H2O)[d]	361[a]	(2.65)
Fuc H4-H5	1877	2.36
Fuc H4-Q6	1098[a]	3.11[e]
inter		
GalNAc H1 - GlcNAc H4	1579	2.43
GalNAc H1 - GlcNAc H62	1326[a]	2.51
GalNAc H1 - GlcNAc H61	792[a]	2.73
GalNAc Q8 - GlcNAc H5	69[a]	4.93[e]
GalNAc Q8 - GlcNAc H62	115[a]	4.52[e]
GalNAc Q8 - GlcNAc H61	113[a]	4.54[e]
GalNAc HN2 - GlcNAc H5	26.5	4.10
GalNAc HN2 - GlcNAc H62	213.5	2.89
GalNAc HN2 - GlcNAc H61	178.5	2.98
GalNAc H2 - Fuc H5	796.5	2.73
GalNAc H61 - Fuc H5	78.5	4.01
GalNAc H62 - Fuc H3	771	2.74
GalNAc H62 - Fuc H5	134.5	3.67
GalNAc H2 - Fuc Q6	734	3.32[e]
GalNAc HN2 - Fuc Q6	18[a]	5.25[e]
GlcNAc H3 - Fuc H1	721	2.77
GlcNAc H3 - Fuc Q6	119[a]	4.50[e]
GlcNAc HN2 - Fuc H1	543[a]	2.48
GlcNAc HN2 - Fuc H2	22	4.22
GlcNAc Q8 - Fuc H1	358.5	3.74[e]
GlcNAc Q8 - Fuc H2	63[a]	5.00[e]

[a] Only one cross-peak was used because of artifacts or severe spectral overlap.
[b] The ^{1}H-^{1}H distances were calculated from experimentally obtained NOE intensities using the H3-H5 cross-peak of Fuc as a reference with a distance of 2.65 Å assuming a $1/r^{6}$ dependence of the NOE intensities. For the structure calculations the herein reported distances were increased by 0.2 Å tolerance and used as upper limit restraints.
[c] Reference restraint for the NOESY measured in D_2O.
[d] Reference restraint for the NOESY measured in H_2O.

[e] Signal to noise ratios from cross-peaks involving methyl or methylene protons were divided by 3 and 2 for the calculation, respectively.

Table S8. Intra- and inter-residual NOEs of Bv9 at 273 K and 900 MHz and their corresponding distances.

proton pair	average S/N of NOEs cross peaks	corresponding ^{1}H-^{1}H distance[b] [Å]
intra		
GlcNAc2 H1-H3	174.5	2.83
GlcNAc2 H1-H5	393.5	2.47
GlcNAc2 HN2-H1	123[a]	2.93
GlcNAc2 HN2-H2	34[a]	3.63
GlcNAc2 HN2-H3	264[a]	2.58
GlcNAc2 HN2-H5	15[a]	4.16
GlcNAc1 H1-H3	166.5	2.86
GlcNAc1 H3-H5	250[a]	2.67
GlcNAc1 H5-H62	256[a]	2.66
GlcNAc1 HN2-H1	189[a]	2.72
GlcNAc1 HN2-H3	159[a]	2.80
Fuc3 H1-H2	525.5	2.36
Fuc3 H3-H4	661.5	2.27
Fuc3 H3-H5[c]	260.5	2.65
(Fuc3 H3-H5, H2O)[d]	223[a]	(2.65)
Fuc3 H4-Q6	401	2.96[e]
inter		
GlcNAc2 H1 - GlcNAc1 H3	254	2.66
GlcNAc2 H1 - GlcNAc1 HN2	276[a]	2.56
GlcNAc2 H1 - GlcNAc1 Q8	57[a]	4.10[e]
GlcNAc2 HN2 - GlcNAc1 HN2	15.5	4.13
GlcNAc2 HN2 - GlcNAc1 Q8	77[a]	3.80[e]
GlcNAc2 H2 - Fuc3 H5	190.5	2.79
GlcNAc2 H4 - Fuc3 H5	40	3.62
GlcNAc2 H62 - Fuc3 H3	161[a]	2.87
GlcNAc2 H62 - Fuc3 H5	34.5	3.71
GlcNAc2 H2 - Fuc3 Q6	255	3.19[e]
GlcNAc2 H4 - Fuc3 Q6	69[a]	3.97[e]
GlcNAc2 HN2 - Fuc3 Q6	17[a]	4.89[e]
GlcNAc1 H4 - Fuc3 H1	425	2.44
GlcNAc1 H61 - Fuc3 H1	377[a]	2.49
GlcNAc1 H62 - Fuc3 H1	699[a]	2.25
GlcNAc1 H4 - Fuc3 H5	61.5	3.37
GlcNAc1 H4 - Fuc3 Q6	47[a]	4.23[e]

[a] Only one cross-peak was used because of artifacts or severe spectral overlap.
[b] The ^{1}H-^{1}H distances were calculated from experimentally obtained NOE intensities using the H3-H5 cross-peak of Fuc3 as a reference with a distance of 2.65 Å assuming a $1/r^{6}$ dependence of the NOE intensities. For the structure calculations the herein reported distances were increased by 0.2 Å tolerance and used as upper limit restraints.
[c] Reference restraint for the NOESY measured in D_2O.
[d] Reference restraint for the NOESY measured in H_2O.
[e] Signal to noise ratios from cross-peaks involving methyl or methylene protons were divided by 3 and 2 for the calculation, respectively.

Table S9. Intra- and inter-residual NOEs of LDFT at 275 K and 900 MHz and their corresponding distances.

proton pair[a]	average S/N of NOEs cross peaks	corresponding ^{1}H-^{1}H distance[b] [Å]
intra		
Fuc3 H1-H2 (β)	1857[c]	2.12
Fuc3 H1-H5 (β)	112[c]	3.39
(Fuc3 H3-H5 (β))[d]	488[c]	(2.65)
Fuc3 H4-H5 (β)	731[c]	2.48
Fuc3 H4-Q6	670[c]	3.74[f]
Gal2 H1-H3	1403[c]	2.75
(Gal2 H1-H5)[e]	1759	(2.65)
Gal2 H3-H5	2823.5	2.45
Glc1 H1-H3 (β)	332	2.83
Glc1 H1-H5 (β)	1137[c]	2.30
Glc1 H2-H4 (β)	808[c]	2.44
Glc1 H3-H5 (β)	777[c]	2.45
Glc1 H5-H61 (β)	446.5	2.69
Fuc4 H1-H2 (β)	595[c]	2.56
Fuc4 H1-H3 (β)	95[c]	3.48
Fuc4 H1-H5 (β)	80	3.58
Fuc4 H1-Q6 (β)	72[c]	4.38 [f]
Fuc4 H3-H5 (β)	703	2.49
Fuc4 H3-Q6 (β)	87[c]	4.24 [f]
Fuc4 H4-H5 (β)	1033[c]	2.34
Fuc4 H4-Q6	814[c]	3.62[f]
inter		
Fuc3 H1 - Gal2 H2	1218[c]	2.82
Fuc3 H1 - Gal2 H3	236	3.70
Fuc3 H5 - Gal2 H1 (β)	105[c]	3.42
Fuc3 H5 - Gal2 H2 (β)	66[c]	3.70
Fuc3 H5 - Glc1 H3 (β)	49[c]	3.89
Fuc3 H5 - Glc1 H5 (β)	483	2.65
Fuc3 H5 - Glc1 H61 (β)	177.5	3.14
Fuc3 Q6 - Glc1 H1 (β)	45[c]	4.73[f]
Fuc3 Q6 - Glc1 H3 (β)	187[c]	3.73[f]
Fuc3 Q6 - Glc1 H5 (β)	81[c]	4.29[f]
Fuc3 Q6 - Glc1 H61 (β)	161[c]	3.83[f]
Fuc3 H1 - Fuc4 Q6	223[c]	4.49[f]
Gal2 H1 - Glc1 H4 (β)	550[c]	2.60
Gal2 H1 - Glc1 H61	465[c]	3.31
Gal2 H1 - Glc1 H62 (β)	691[c]	2.50
Gal2 H2 - Fuc4 H5 (β)	604	2.56
Gal2 H2 - Fuc4 Q6	786[c]	3.64[f]
Gal2 H61 - Fuc4 H3	597[c]	3.17
Gal2 H62 - Fuc4 H3	194[c]	3.83
Gal2 H61 - Fuc4 H5	65[c]	4.59
Glc1 H2 - Fuc H1 (β)	72.5	3.64
Glc1 H3 - Fuc H1 (β)	640.5	2.53
Glc1 H3 - Fuc H5 (β)	106[c]	3.42

[a] The nomenclature of the residues is as follows, Glc1: reducing end Glc; Gal2: stacking Gal; Fuc3: α1,2-linked Fuc; Fuc4: α1,3-linked Fuc. If the cross-peaks can be distinguished between the anomers at the reducing end, only the β-anomer is used and indicated by "β".

[b] The ^{1}H-^{1}H distances were calculated from experimentally obtained NOE intensities using the H3-H5 cross-peak of Fuc and Gal as a reference with a distance of 2.65 Å assuming a $1/r^{6}$ dependence of the NOE

intensities. For the structure calculations the herein reported distances were increased by 0.2 Å tolerance and used as upper limit restraints.

[c] Only one cross-peak was used because of artifacts or severe spectral overlap.

[d] Reference restraint for signals corresponding to the β-anomer at the reducing end (separated signals for α and β; NOESY measured in D_2O).

[e] Reference restraint for signals indistinguishable for both anomers (no separate signals for α and β; NOESY measured in D_2O).

[f] Signal to noise ratios from cross-peaks involving methyl or methylene protons were divided by 3 and 2 for the calculation, respectively.

Table S10: The hydrogen bond lenght (H...O), electron density $\rho(r_c)$, the Laplacian of the electron density $\nabla^2 \rho(r_c)$ and the ellipticity ε at the bond critical points of the DFT-minimized structures.

carbohydrate	Distance (H...O) [Å]	$\rho(r_c)$ at bond critical point [au]	$\nabla^2 \rho(r_c)$ at bond critical point [au]	ε at bond critical point [au]
3FChB	2.35	0.013	0.037	0.045
Le^x	2.32	0.014	0.039	0.041
Le^a	2.33	0.013	0.038	0.046
LDNF	2.41	0.012	0.034	0.019
Bv9	2.33	0.013	0.038	0.049
LDFT	2.47	0.010	0.030	0.031

Table S11: Experimental chemical shift assignments and calculated chemical shifts using the GIAO method.

carbohy-drates	Fucα1,3 GlcNAc	3FChB		Le^x		Le^a		LDNF		Bv9		LDFT (β)	
	exp.	exp.	GIAO calc.	exp.	GIAO calc.	exp.	GIAO calc.	exp.	GIAO calc.	exp.	GIAO calc.	exp.	GIAO calc.
GlcNAc/Glc (reducing end)													
H1	4.55	4.46	4.30	4.45	4.33	4.43	4.30	4.47	4.29	4.44	4.18	4.62	4.64
H2	3.83	3.89	3.92	3.91	3.95	3.90	3.98	3.89	3.94	3.85	3.99	3.47	3.38
H3	3.64	3.81	3.55	3.83	3.57	4.04	3.60	3.80	3.49	3.97	3.62	3.70	3.74
H4	3.49	3.88	3.91	3.93	3.43	3.73	3.41	3.88	3.47	3.73	3.33	3.87	3.65
H5	3.47	3.49	3.12	3.58	3.42	3.55	3.46	3.49	3.36	3.50	3.32	3.46	3.43
H61	3.72	3.92	3.93	3.86	4.06	3.98	4.29	3.91	3.94	3.96	4.18	3.98	3.87
H62	3.91	3.74	3.84	4.00	3.70	3.87	3.78	3.73	3.70	3.87	3.64	3.79	3.64
Q8	2.02	2.01	(1.83)	2.02	(1.84)	2.03	(1.84)	2.01	(1.83)	2.08	(1.88)	—	—
GlcNAc/Gal /GalNAc (stacking with Fuc)													
H1	—	4.52	4.80	4.44	4.21	4.48	4.44	4.45	4.14	4.62	4.64	4.49	4.28
H2	—	3.75	3.87	3.49	3.66	3.48	3.53	3.99	4.11	3.63	3.92	3.63	3.85
H3	—	3.52	3.44	3.65	3.62	3.62	3.55	3.70	3.66	3.59	3.51	3.84	3.77
H4	—	3.23	3.37	3.88	3.82	3.86	3.75	3.89	3.99	3.19	3.22	3.84	3.50
H5	—	3.42	3.52	3.59	3.59	3.57	3.57	3.56	3.64	3.39	3.42	3.58	3.35
H61	—	3.96	3.92	3.72	3.57	3.72	4.02	3.71	3.78	3.97	3.86	3.75	3.84
H62	—	3.60	3.68	3.70	4.05	3.72	3.57	3.76	4.13	3.57	3.61	3.70	3.95
Q8	—	2.04	(1.80)	—	—	—	—	2.03	(1.84)	1.99	(1.91)	—	—
Fuc (stacking)													
H1	4.98	5.12	5.02	5.10	5.02	5.02	4.67	5.11	4.97	5.02	4.70	5.45	5.30
H2	3.70	3.68	3.55	3.67	3.54	3.79	3.60	3.67	3.51	3.80	3.49	3.79	3.65
H3	3.83	3.95	3.62	3.90	3.60	3.88	3.67	3.94	3.60	3.92	3.44	3.97	3.78
H4	3.80	3.80	3.85	3.78	3.86	3.78	3.86	3.82	3.83	3.80	3.58	3.81	3.88
H5	**4.33**	**4.78**	**4.88**	**4.86**	**4.92**	**4.90**	**4.92**	**4.89**	**4.85**	**4.85**	**5.10**	**4.89**	**4.89**
Q6	1.16	1.26	(1.27)	1.17	(1.13)	1.17	(1.14)	1.26	(1.37)	1.27	(1.26)	1.24	(1.31)

[a] The carbohydrates of which the experimental shifts were obtained were either β-methyl glycosides (Le^x, Le^a), contained a free OH (LDFT) or a spacer (-$[CH_2]_3$-NH_2 in case of Fucα1,3GlcNAc and LDNF; -$[CH_2]_5$-COONa in 3FChB and hexenetetrol in Bv9). Calculations were obtained for the β-methyl glycosides except for LDFT for which the free OH as β-anomer was used.

[b] Experimental values were measured at 273-278 K (see experimental section, the slightly different values were necessary to avoid overlap with the water signal) and referenced to DSS (0.00 ppm corresponds to 0.00 ppm referenced to TMS). Fuc H5 is shown in bold. The methylene groups H61 and H62 were not stereospecifically assigned.

[c] Obtained with the GIAO chemical shift calculation in Gaussian 09 for a water environment (CPCM), values were referenced to TMS (separate calculation). These values are comparable to the experimental values because both TMS and DSS have identical ^{1}H chemical shifts (0.00 ppm). The predicted methyl group chemical shifts are the average of the three calculated chemical shifts, but since methyl groups rotate fast and sample a full cone, the average of three individual positions is not a good approximation. Therefore the values are in brackets.

Table S12: Three-dimensional coordinates of representatives for most structural motifs found in the Protein Databank (PDB) and the Cambridge Structural database (CSD).

PDB or CSD accession code	Chain and residue numbers	Carbohydrate structure (trisaccharide motifs are shown in bold)	Distance H5–O5	Distance C5–O5	Resolution	Refinement program
		Le^x containing carbohydrates				
ABUCEF	1	**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe (pure carbohydrate)	2.3	3.3		direct
ABUCEF	2	**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe (pure carbohydrate)	2.3	3.3		direct
1FWU	A 2001-2003	3S-**Galβ1,4[Fucα1,3]GlcNAcβ**	2.4 [a]	3.5	1.9	CNS
1G1R	A 901-904	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.6 [a]	3.6	3.4	CNS
1G1R	B 901-904	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.0 [a]	3.1	3.4	CNS
1G1R	D 901-904	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.4 [a]	3.5	3.4	CNS
1G1S	C 629-634	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Galβ1,3]GalNacα-Thr616	2.4 [a]	3.4	1.9	CNS
1G1S	D 629-634	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**1,6[Galβ1,3]GalNacα-Thr616	2.3 [a]	3.4	1.9	CNS
1G1T	A 901-904	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.4 [a]	3.4	1.5	CNS
1KMB	1 222-224	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.3 [a]	3.4	2.1	X-PLOR 3.54
1KMB	2 222-224	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.3 [a]	3.3	2.1	X-PLOR 3.54
1KMB	3 222-224	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.3 [a]	3.3	2.1	X-PLOR 3.54
1SL5	C 1-4	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Gal	2.8 [a]	3.7	1.7	CNS 1.1
1SL6	G 1-3	**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.4	2.25	CNS 1.1
1SL6	H 1-3	**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.4	2.25	CNS 1.1
1SL6	I 1-3	**Galβ1,4[Fucα1,3]GlcNAcα**	2.9 [a]	3.9	2.25	CNS 1.1
1SL6	J 1-3	**Galβ1,4[Fucα1,3]GlcNAcα**	2.9 [a]	3.9	2.25	CNS 1.1
1SL6	K 1-3	**Galβ1,4[Fucα1,3]GlcNAcα**	3.0 [a]	4.00	2.25	CNS 1.1
1SL6	L 1-3	**Galβ1,4[Fucα1,3]GlcNAcα**	3.0 [a]	3.9	2.25	CNS 1.1
1UZ8	A 1213-1214	**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.4 [a]	3.5	1.8	REFMAC 5.2
1UZ8	H 1213-1214	**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.2 [a]	3.3	1.8	REFMAC 5.2
2KMB	1 222-224	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.3 [a]	3.4	2.0	X-PLOR 3.54
2KMB	2 222-224	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.2 [a]	3.3	2.0	X-PLOR 3.54
2KMB	3 222-224	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.3 [a]	3.3	2.0	X-PLOR 3.54
2OX9	E 1-3	**Galβ1,4[Fucα1,3]GlcNAcβ**	2.1 [a]	3.2	1.95	CNS 1.1
2OX9	F 1-3	**Galβ1,4[Fucα1,3]GlcNAcβ**	2.3 [a]	3.3	1.95	CNS 1.1
2OX9	G 1-3	**Galβ1,4[Fucα1,3]GlcNAcβ**	2.2 [a]	3.3	1.95	CNS 1.1
2OX9	H 1-3	**Galβ1,4[Fucα1,3]GlcNAcβ**	2.3 [a]	3.4	1.95	CNS 1.1
2R61	A 601-604	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	2.3 [a]	3.4	2.75	REFMAC 5.3
2RDG	A 601-604	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcα**	2.3 [a]	3.4	1.6	REFMAC 5.3
2Z8L	A 601-604	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	2.3 [a]	3.4	1.65	REFMAC 5.3
3AP9	A 155-160	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ1,4Glc	2.8 [a]	3.8	1.33	REFMAC 5.5
3KMB	1 222-224	3S-**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.2 [a]	3.2	2.0	X-PLOR 3.54
3KMB	3 222-224	3S-**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.1 [a]	3.1	2.0	X-PLOR 3.54
3PVD	A 1-4	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcα**	2.2 [a]	3.3	1.9	PHENIX
3PVD	B 1-4	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcα**	2.3 [a]	3.4	1.9	PHENIX
3ZNL	A 1322-1325	Neu5Acα2,3**Galβ1,4[Fucα1,3][6S]GlcNAcβ**	2.5 [a]	3.4	2.5	REFMAC 5.7
3ZNL	C 1322-1325	Neu5Acα2,3**Galβ1,4[Fucα1,3][6S]GlcNAcβ**	1.9 [a]	2.9	2.5	REFMAC 5.7
3ZNL	E 1322-1325	Neu5Acα2,3**Galβ1,4[Fucα1,3][6S]GlcNAcβ**	2.4 [a]	3.4	2.5	REFMAC 5.7
3ZNM	A 1324-1327	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	2.6 [a]	3.6	2.4	REFMAC 5.7

3ZNM	C 1324-1327	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	2.7 [a]	3.7	2.4	REFMAC 5.7
3ZNM	E 1324-1327	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	2.5 [a]	3.5	2.4	REFMAC 5.7
3ZW1	A 105-108	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ	(4.3) [a,b,c]	(4.6) [b,c]	1.6	REFMAC 5.5
3ZW1	B 99-103	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galα/β	(4.6) [a,b,c]	(4.9) [b,c]	1.6	REFMAC 5.5
4CSY	A 301-304	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.3 [a]	3.3	2.41	Buster 2.10
4CSY	A 301-304	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.3 [a]	3.3	2.41	Buster 2.10
4DXG	A 301-304	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.4	2.5	REFMAC 5.5
4KMB	1 222-224	4S-**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.4 [a]	3.4	2.0	X-PLOR 3.54
4KMB	3 222-224	4S-**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.4 [a]	3.4	2.0	X-PLOR 3.54
4P2N	A 601-603	**Galβ1,4[Fucα1,3]GlcNAcβ**	2.2 [a]	3.3	1.7	PHENIX
4P2N	B 601-603	**Galβ1,4[Fucα1,3]GlcNAcβ**	2.2 [a]	3.2	1.7	PHENIX
4P2N	C 601-603	**Galβ1,4[Fucα1,3]GlcNAcβ**	2.2 [a]	3.2	1.7	PHENIX
4P2N	D 601-603	**Galβ1,4[Fucα1,3]GlcNAcβ**	2.2 [a]	3.2	1.7	PHENIX
4RCO	A 401-404	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcα**	2.3 [a]	3.4	1.9	REFMAC 5.7
4RCO	B 401-404	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.4	1.9	REFMAC 5.7
4RFB	A 301-304	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	2.4 [a]	3.4	1.93	REFMAC 5.7
4RFB	B 301-304	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	2.4 [a]	3.5	1.93	REFMAC 5.7
4RFB	C 301-304	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	2.6 [a]	3.6	1.93	REFMAC 5.7
4RFB	D 301-304	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	2.6 [a]	3.6	1.93	REFMAC 5.7
4UNZ	A 701-704	Neu5Acα2,3**Galβ1,4[Fucα1,3]|[6S]GlcNAcβ**	(2.8) [a,d]	(3.6) [d]	2.9	REFMAC 5.8
4UNZ	C 701-704	Neu5Acα2,3**Galβ1,4[Fucα1,3]|[6S]GlcNAcβ**	(2.8) [a,d]	(3.6) [d]	2.9	REFMAC 5.8
4UNZ	E 701-704	Neu5Acα2,3**Galβ1,4[Fucα1,3]|[6S]GlcNAcβ**	(3.7) [a,d]	(4.3) [d]	2.9	REFMAC 5.8
4UO2	A 701-704	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	(3.1) [a,d]	(4.0) [d]	2.7	REFMAC 5.8
4UO2	C 701-704	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	(2.6) [a,d]	(3.6) [d]	2.7	REFMAC 5.8
4UO2	E 701-704	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	(4.8) [a,d]	(4.2) [d]	2.7	REFMAC 5.8
4UO6	A 701-704	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	3.1 [a]	3.9	2.9	REFMAC 5.8
4UO7	A 701-704	Neu5Acα2,3**Galβ1,4[Fucα1,3]|[6S]GlcNAcβ**	2.4 [a]	3.5	3.0	REFMAC 5.8
4UO7	C 701-704	Neu5Acα2,3**Galβ1,4[Fucα1,3]|[6S]GlcNAcβ**	2.7 [a]	3.6	3.0	REFMAC 5.8
4UO7	E 701-704	Neu5Acα2,3**Galβ1,4[Fucα1,3]|[6S]GlcNAcβ**	2.4 [a]	3.4	3.0	REFMAC 5.8
4USO	A 200-203	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcβ**	2.6 [a]	3.6	1.95	REFMAC 5.8
4X0C	A 604-606	**Galβ1,4[Fucα1,3]GlcNAcα**	2.1 [a,e]	3.2 [e]	1.72	PHENIX
4X0C	B 604-606	**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.4	1.72	PHENIX
5A70	A 201-204	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ	2.5 [a]	3.5	1.6	REFMAC 5.8
5A70	B 201-204	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ	2.5 [a]	3.6	1.6	REFMAC 5.8
5A70	C 201-204	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ	2.4 [a]	3.5	1.6	REFMAC 5.8
5A70	D 201-204	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galβ	2.4 [a]	3.5	1.6	REFMAC 5.8
5AJB	A 100-102	**Galβ1,4[Fucα1,3]GlcNAcβ**	(7.0) [a,b,f]	(7.5) [b,f]	1.8	REFMAC 5.8
5AJB	A 110-103	**Galβ1,4[Fucα1,3]GlcNAcβ**1,3Galα	(5.2) [a,b,f]	(5.3) [b,f]	1.8	REFMAC 5.8
5AJB	B 100-102	**Galβ1,4[Fucα1,3]GlcNAcβ**	(4.4) [a,b,f]	(4.4) [b,f]	1.8	REFMAC 5.8
5AJB	B 110-112	**Galβ1,4[Fucα1,3]GlcNAc**	(5.1) [a,b,f]	(5.3) [b,f]	1.8	REFMAC 5.8
5AJB	C 110-112	**Galβ1,4[Fucα1,3]GlcNAcβ**	(5.1) [a,b,f]	(5.3) [b,f]	1.8	REFMAC 5.8
5AJC	A 100-102	**Galβ1,4[Fucα1,3]GlcNAcα**	(7.1) [a,b,g]	(7.6) [b,g]	2.6	REFMAC 5.8
5AJC	C 100-104	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcα**	(7.4) [a,b,g]	(7.8) [b,g]	2.6	REFMAC 5.8
5I4D	A 401-404	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.5	1.75	REFMAC 5.8
5I4D	B 401-405	Neu5Acα2,3**Galβ1,4[Fucα1,3]GlcNAcα/β**	2.4 [a]	3.5	1.75	REFMAC 5.8
		Le^y containing carbohydrates				
1CLY	H 228-231	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**–sp	2.3 [a]	3.4	2.5	X-PLOR
1CLZ	H 232-235	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**–sp	2.4 [a]	3.5	2.8	X-PLOR

1GSL	A 252-255	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**-OMe	2.5 [a]	3.5	2.00	X-PLOR
1S3K	H 223-226	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.5	1.9	CNS 1.0
2J1T	A 1150-1153	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**	2.5 [a]	3.5	1.6	REFMAC 5.1
2WMG	A 1590-1593	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**	(5.4) [a,b,h]	(6.2) [b,h]	2.3	REFMAC 5.2
2WMK	A 2006-2010	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]GlcNAcβ**	(5.0) [a,b,h]	(5.8) [b,h]	1.9	REFMAC 5.2
2WMK	B 2006-2010	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]GlcNAcβ**	(5.0) [a,b,h]	(5.8) [b,h]	1.9	REFMAC 5.2
3EYV	H 223-226	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.3 [a]	3.4	2.5	CNS 1.0
3LEG	A 1186	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**	2.8 [a]	3.8	2.0	REFMAC 5.5
3PA2	A 1-4	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**	2.7 [a]	3.7	1.48	PHENIX
3PUN	A 1-4	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.5	2.05	PHENIX
3PUN	B 1-4	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.2 [a]	3.3	2.05	PHENIX
4D4U	A 930-933	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	(4.2) [a,b,i]	(4.2) [b,i]	1.99	REFMAC 5.8
4D4U	A 960-963	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.5 [a]	3.5	1.99	REFMAC 5.8
4D4U	B 930-933	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	(4.4) [a,b,i]	(4.4) [b,i]	1.99	REFMAC 5.8
4GWI	A 205	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**	2.5 [a]	3.5	1.6	REFMAC5
4P25	A 601-604	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**	2.1 [a]	3.1	1.5	PHENIX
4P25	B 601-604	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**	2.4 [a]	3.4	1.5	PHENIX
4P25	C 601-604	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**	2.2 [a]	3.2	1.5	PHENIX
4P25	D 601-604	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**	2.1 [a]	3.1	1.5	PHENIX
4RDL	A 601-604	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.5 [a]	3.5	1.45	PHENIX
4RDL	B 601-604	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.5 [a]	3.5	1.45	PHENIX
4WZE	A 602-605	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.5 [a]	3.5	1.46	PHENIX
4WZE	B 602-605	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.5 [a]	3.5	1.46	PHENIX
5ELB	A 207-210	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.8 [a,e]	3.8 [e]	1.08	REFMAC 5.8
5ELB	B 207-210	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.9 [a,e]	3.9 [e]	1.08	REFMAC 5.8
5ELB	C 207-210	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.7 [a,e]	3.8 [e]	1.08	REFMAC 5.8
5ELB	D 207-210	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.5 [a,e]	3.6 [e]	1.08	REFMAC 5.8
5ELB	E 207-210	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.6 [a]	3.6	1.08	REFMAC 5.8
5ELB	F 1203-1206	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.4	1.08	REFMAC 5.8
5ELB	G 204-207	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.9 [a,e]	3.9 [e]	1.08	REFMAC 5.8
5ELB	H 1203-1206	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.5 [a]	3.5	1.08	REFMAC 5.8
5ELB	I 1203-1207	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα/β**	2.3 [a,e]	3.3 [e]	1.08	REFMAC 5.8
5ELB	J 1203-1207	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα/β**	2.4 [a,e]	3.5 [e]	1.08	REFMAC 5.8
5ELC	A 205-208	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.5 [a]	3.5	1.50	REFMAC 5.8
5ELC	B 205-209	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα/β**	2.5 [a,e]	3.5 [e]	1.50	REFMAC 5.8
5ELC	C 205-209	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα/β**	2.7 [a,e]	3.7 [e]	1.50	REFMAC 5.8
5ELC	D 205-208	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**	2.3 [a]	3.3	1.50	REFMAC 5.8
5ELC	E 205-208	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.5	1.50	REFMAC 5.8
5ELC	G 201-204	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcβ**	2.6 [a]	3.6	1.50	REFMAC 5.8
5ELC	H 201-204	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.8 [a]	3.9	1.50	REFMAC 5.8
5ELC	I 201-205	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα/β**	2.4 [a,e]	3.4 [e]	1.50	REFMAC 5.8
5ELC	J 201-204	Fucα1,2**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.4	1.50	REFMAC 5.8
5ELD	A 203-207	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]GlcNAcα**	2.3 [a,e]	3.3 [e]	1.40	REFMAC 5.8
5ELD	C 204-208	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]GlcNAcα**	2.3 [a,e]	3.4 [e]	1.40	REFMAC 5.8
5ELD	D 203-207	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]GlcNAcα**	2.5 [a,e]	3.5 [e]	1.40	REFMAC 5.8
5ELD	E 204-208	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]GlcNAcα**	2.4 [a]	3.5	1.40	REFMAC 5.8
5ELE	D 205-209	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]GlcNAcα**	2.3 [a]	3.4	1.60	REFMAC 5.8

5ELE	G 201-206	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]GlcNAcα/β**	2.4 [a,e]	3.4 [e]	1.60	REFMAC 5.8
5ELE	J 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]GlcNAcα**	2.5 [a]	3.6	1.60	REFMAC 5.8
		Le[a] containing carbohydrates				
1FWV	A 2001-2003	3S-**Galβ1,3[Fucα1,4]GlcNAcβ**	2.6 [a]	3.6	2.2	CNS
1W8H	A 331-333	**Galβ1,3[Fucα1,4]GlcNAcα/β**	2.4 [a]	3.5	1.75	REFMAC 5.1
1W8H	B 331-333	**Galβ1,3[Fucα1,4]GlcNAcα/β**	2.4 [a]	3.5	1.75	REFMAC 5.1
1W8H	C 331-333	**Galβ1,3[Fucα1,4]GlcNAcα/β**	2.3 [a]	3.4	1.75	REFMAC 5.1
1W8H	D 331-333	**Galβ1,3[Fucα1,4]GlcNAcβ**	2.3 [a]	3.4	1.75	REFMAC 5.1
3ASR	A 1002-1004	**Galβ1,3[Fucα1,4]GlcNAcβ**-O-p-nitrophenol	2.3 [a]	3.3	1.6	COOT, REFMAC5
3ASR	B 1002-1004	**Galβ1,3[Fucα1,4]GlcNAcβ**-O-p-nitrophenol	2.4 [a]	3.4	1.6	COOT, REFMAC5
3UET	A 502-504	**Galβ1,3[Fucα1,4]GlcNAcβ**	(4.4) [a,b,j]	(4.4) [b,j]	2.1	COOT, REFMAC5
3UET	B 502-504	**Galβ1,3[Fucα1,4]GlcNAcβ**	(4.2) [a,b,j]	(4.2) [b,j]	2.1	COOT, REFMAC5
4P3I	A 601-603	**Galβ1,3[Fucα1,4]GlcNAcβ**	2.6 [a]	3.7	1.69	PHENIX
4P3I	B 601-603	**Galβ1,3[Fucα1,4]GlcNAcβ**	2.2 [a]	3.1	1.69	PHENIX
4P3I	C 601-603	**Galβ1,3[Fucα1,4]GlcNAcβ**	2.8 [a]	3.6	1.69	PHENIX
4P3I	D 601-603	**Galβ1,3[Fucα1,4]GlcNAcβ**	2.0 [a]	3.1	1.69	PHENIX
4RM0	A 601-603	**Galβ1,3[Fucα1,4]GlcNAcβ**	2.4 [a]	3.4	2.0	PHENIX
4RM0	B 601-603	**Galβ1,3[Fucα1,4]GlcNAcα**	2.4 [a]	3.4	2.0	PHENIX
4UT5	A 400-403	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ	2.6 [a]	3.6	1.75	REFMAC 5.8
4UT5	B 399-403	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galα	2.6 [a]	3.6	1.75	REFMAC 5.8
4UT5	C 399-403	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galα/β	2.7 [a]	3.7	1.75	REFMAC 5.8
4UT5	D 401-403	**Galβ1,3[Fucα1,4]GlcNAcβ**	2.6 [a]	3.7	1.75	REFMAC 5.8
4WZL	A 607-609	**Galβ1,3[Fucα1,4]GlcNAcα**	2.3 [a]	3.3	1.7	PHENIX
4WZL	B 607-609	**Galβ1,3[Fucα1,4]GlcNAcα**	2.3 [a]	3.3	1.7	PHENIX
5A6Z	A 201-204	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galα	2.4 [a]	3.5	1.5	REFMAC 5.8
5A6Z	B 201-203	**Galβ1,3[Fucα1,4]GlcNAcβ**	2.4 [a]	3.5	1.5	REFMAC 5.8
5A6Z	C 201-204	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ	2.4 [a]	3.5	1.5	REFMAC 5.8
5A6Z	D 201-204	**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galα	2.4 [a]	3.5	1.5	REFMAC 5.8
		Le[b] containing carbohydrates				
1LED	A 252-255	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**-OMe	2.6 [a]	3.6	2.0	X-PLOR, PROLSQ
3ASS	A 1001-1005	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**-O-p-nitrophenol	2.5 [a]	3.5	1.6	COOT, REFMAC5
3ASS	B 1001-1005	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**-O-p-nitrophenol	2.5 [a]	3.5	1.6	COOT, REFMAC5
3AST	A 1001-1005	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**-O-p-nitrophenol	2.5 [a]	3.5	1.4	COOT, REFMAC5
3AST	B 1001-1005	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**-O-p-nitrophenol	2.5 [a]	3.5	1.4	COOT, REFMAC5
3LEK	A1185	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcα**	2.7 [a]	3.7	2.2	COOT, REFMAC5
3SEJ	B 1-6	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	1.9 [a]	2.9	3.04	REFMAC
3SEJ	C 1-6	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	2.5 [a]	3.4	3.04	REFMAC
3SEJ	C 532-537	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	1.8 [a]	2.9	3.04	REFMAC
3SEJ	D 1-6	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	1.8 [a]	2.8	3.04	REFMAC
3SEJ	E 1-6	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	2.2 [a]	3.2	3.04	REFMAC
3SEJ	F 1-6	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	2.2 [a]	3.1	3.04	REFMAC
3SEJ	G 1-6	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	1.8 [a]	2.7	3.04	REFMAC
3SEJ	J 1-6	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glc	2.0 [a]	2.9	3.04	REFMAC
4GWJ	A 205-208	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**	2.5 [a]	3.6	1.6	REFMAC5
4OPO	B 605-608	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**	2.3 [a]	3.3	1.4	PHENIX

4OPO	B 609-612	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**	2.3 [a]	3.4	1.4	PHENIX
4OPS	B 601-604	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**	2.0 [a]	3.0	1.76	PHENIX
4RDK	A 601-604	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcα**	2.5 [a]	3.5	1.63	PHENIX
4RDK	B 601-604	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcα**	2.5 [a]	3.6	1.63	PHENIX
4ZH7	A 601-605	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ	2.4 [a]	3.5	2.12	REFMAC 5.8
5F8R	A 501-506	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glcβ	2.5 [a]	3.5	2.44	REFMAC 5.8
5F8R	B 501-506	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glcβ	2.7 [a]	3.7	2.44	REFMAC 5.8
5F7M	A 501-506	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glcβ	2.5 [a]	3.5	2.72	REFMAC 5.8
5F7M	B 501-506	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glcβ	2.7 [a]	3.8	2.72	REFMAC 5.8
5F7N	A 501-505	GalNAcα1,3[Fucα1,2]**Galβ1,3[Fucα1,4]GlcNAcβ**	2.7 [a]	3.7	2.28	REFMAC 5.8
5F7N	B 501-505	GalNAcα1,3[Fucα1,2]**Galβ1,3[Fucα1,4]GlcNAcβ**	2.8 [a]	3.9	2.28	REFMAC 5.8
5F7W	A 501-507	Galα1,3[Fucα1,2]**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4 Glcβ	2.5 [a]	3.6	2.81	REFMAC 5.8
5F7W	B 501-507	Galα1,3[Fucα1,2]**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4 Glcβ	2.7 [a]	3.8	2.81	REFMAC 5.8
5F9A	A 1001-1006	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glcβ	2.4 [a]	3.5	2.44	REFMAC 5.8
5F9D	A 1001-1007	Galα1,3[Fucα1,2]**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4 Glcβ	2.8 [a]	3.8	2.59	REFMAC 5.8
5F93	A 501-506	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glcα	2.4 [a]	3.4	2.99	REFMAC 5.8
5F93	B 501-506	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glcα	2.6 [a]	3.6	2.99	REFMAC 5.8
5F93	E 501-506	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glcα	(3.8) [a,b,k]	(4.9) [b,k]	2.99	REFMAC 5.8
5F93	G 501-506	Fucα1,2**Galβ1,3[Fucα1,4]GlcNAcβ**1,3Galβ1,4Glcα	2.7 [a]	3.7	2.99	REFMAC 5.8
		3-Fucosylated chitobiose containing carbohydrates (selection)				
1E4M	M 941-945	Xylβ1,2Manβ1,4**GlcNAcβ1,4[Fucα1,3]GlcNAcβ**-Asn265	2.5 [a]	3.5	1.2	REFMAC
1E4M	M 951-957	Manα1,3[Manα1,6][Xylβ1,2]Manβ1,4**GlcNAcβ1,4[Fucα1 ,3]GlcNAcβ**-Asn292	2.5 [a]	3.5	1.2	REFMAC
1E6Q	M 941-945	Xylβ1,2Manβ1,4**GlcNAcβ1,4[Fucα1,3]GlcNAcβ**-Asn265	2.5 [a]	3.5	1.35	REFMAC
1E6Q	M 951-957	Manα1,3[Manα1,6][Xylβ1,2]Manβ1,4**GlcNAcβ1,4[Fucα1 ,3]GlcNAcβ**-Asn292	2.7 [a]	3.7	1.35	REFMAC
1E6S	M 941-945	Xylβ1,2Manβ1,4**GlcNAcβ1,4[Fucα1,3]GlcNAcβ**-Asn265	2.5 [a]	3.5	1.35	REFMAC
1E6S	M 951-957	Manα1,3[Manα1,6][Xylβ1,2]Manβ1,4**GlcNAcβ1,4[Fucα1 ,3]GlcNAcβ**-Asn292	2.6 [a]	3.6	1.35	REFMAC
1JU2	B 544-547	Manβ1,4**GlcNAcβ1,4[Fucα1,3]GlcNAcβ**-Asn392	2.3 [a]	3.4	1.45	CNS 1.1
1JU2	A 539-543	Manα1,6Manβ1,4**GlcNAcβ1,4[Fucα1,3]GlcNAcβ**-Asn135	2.2 [a]	3.3	1.45	CNS 1.1
1JU2	B 539-543	Manα1,6Manβ1,4**GlcNAcβ1,4[Fucα1,3]GlcNAcβ**-Asn135	2.3 [a]	3.4	1.45	CNS 1.1
1JU2	A 544-548	Manβ1,3Manβ1,4**GlcNAcβ1,4[Fucα1,3]GlcNAcβ**-Asn392	2.4 [a]	3.4	1.45	CNS 1.1
1LK9	A 500-503	Manβ1,4**GlcNAcβ1,4[Fucα1,3]GlcNAcβ**-Asn146	2.2 [a]	3.3	1.53	REFMAC 4.0.6
1YM0	A 1-5	Manβ1,3Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAc β**-Asn161	2.4 [a]	3.5	2.06	CNS
2B9L	A 416-419	**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn32	2.6 [a]	3.6	2.0	CNS 1.1
2F9N	B 1000-1003	**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn113	2.5 [a]	3.5	1.6	CNS 1.1
2F9N	D 1000-1003	**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn113	2.4 [a]	3.5	1.6	CNS 1.1
2QQM	D 1-4	**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn261	2.6 [a]	3.6	2.0	REFMAC 5
3L9R	A 501-507	Manβ1,3Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAc β**-Asn57	2.3 [a]	3.4	2.3	REFMAC 5.5
3L9R	C 501-507	Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn57	2.5 [a]	3.6	2.3	REFMAC 5.5
3L9R	E 501-507	Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn57	2.3 [a]	3.4	2.3	REFMAC 5.5
3L9R	G 501-507	Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn57	2.4 [a]	3.5	2.3	REFMAC 5.5
3QW9	A 187-191	Manα1,3[Manα1,6]Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1 ,6]**GlcNAcβ**-Asn14(B)	2.3 [a]	3.3	1.84	REFMAC 5
3QW9	A 200-204	Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn14	2.4 [a]	3.4	1.84	REFMAC 5
3U0P	A 301-304	**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn20	(5.6) [a,b,l]	(5.9) [b,l]	2.8	PHENIX

4ARN	C 501-507	Manα1,3[Manα1,6]Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn140	2.4 [a]	3.5	2.41	BUSTER
4GWM	A 706-712	Manα1,3[Manα1,6]Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn370	2.2 [a]	3.3	1.85	BUSTER
4GWM	B 705-710	Manα1,3Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn370	2.2 [a]	3.3	1.85	BUSTER
4GWM	B 711-714	**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn445	2.3 [a]	3.4	1.85	BUSTER
4GWN	A 705-711	Manα1,3[Manα1,6]Manβ1,4**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn370	2.6 [a]	3.6	3.0	BUSTER
4GZT	D 508-511	**GlcNAcβ1,4[Fucα1,3]**[Fucα1,6]**GlcNAcβ**-Asn146	2.2 [a]	3.3	2.19	REFMAC 5.5
		Le^x-like containing carbohydrates				
1W8F	A 1118-1121	GalNAcα1,3**Galβ1,4[Fucα1,3]Glcβ**	2.3 [a]	3.4	1.05	REFMAC 5.1
1W8F	B 1118-1122	Galβ1,4GalNAcα1,3**Galβ1,4[Fucα1,3]Glcβ**	2.4 [a]	3.5	1.05	REFMAC 5.1
1W8F	C 1118-1120	**Galβ1,4[Fucα1,3]Glcβ**	2.4 [a]	3.5	1.05	REFMAC 5.1
1W8F	D 1118-1122	Galβ1,4GalNAcα1,3**Galβ1,4[Fucα1,3]Glcβ**	2.4 [a]	3.4	1.05	REFMAC 5.1
		Le^y-like containing carbohydrates				
2O2L	N 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.3 [a]	3.4	2.53	REFMAC
2O2L	O 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.4 [a]	3.5	2.53	REFMAC
2O2L	P 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.6 [a]	3.6	2.53	REFMAC
2O2L	Q 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.8 [a]	3.7	2.53	REFMAC
2O2L	R 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.6 [a]	3.6	2.53	REFMAC
2O2L	S 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	(4.3) [a,b,m]	(5.1) [b,m]	2.53	REFMAC
2O2L	T 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.6 [a]	3.6	2.53	REFMAC
2O2L	U 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.5 [a]	3.5	2.53	REFMAC
2O2L	V 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.4 [a]	3.5	2.53	REFMAC
2O2L	W 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.6 [a]	3.7	2.53	REFMAC
3EFX	D 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.6 [a]	3.6	1.94	REFMAC
3EFX	E 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.2 [a]	3.3	1.94	REFMAC
3EFX	F 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.3 [a]	3.4	1.94	REFMAC
3EFX	G 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.5 [a]	3.6	1.94	REFMAC
3EFX	H 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.3 [a]	3.3	1.94	REFMAC
3EFX	I 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.5 [a]	3.5	1.94	REFMAC
3EFX	J 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.5 [a]	3.4	1.94	REFMAC
3EFX	K 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.4 [a]	3.4	1.94	REFMAC
3EFX	L 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.6 [a]	3.6	1.94	REFMAC
3EFX	M 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.7 [a]	3.7	1.94	REFMAC
5ELF	A 205-209	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcα**	2.4 [a]	3.4	1.55	REFMAC 5.8
5ELF	D 205-210	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcα/β**	2.5 [a,e]	3.5 [e]	1.55	REFMAC 5.8
5ELF	E 205-209	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcα**	2.5 [a]	3.5	1.55	REFMAC 5.8
5ELF	F 202-206	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcβ**	2.4 [a]	3.5	1.55	REFMAC 5.8
5ELF	G 201-206	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcα/β**	2.5 [a,e]	3.5 [e]	1.55	REFMAC 5.8
5ELF	I 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcα**	2.4 [a]	3.4	1.55	REFMAC 5.8
5ELF	J 201-205	GalNAcα1,3[Fucα1,2]**Galβ1,4[Fucα1,3]Glcα**	2.4 [a,e]	3.5 [e]	1.55	REFMAC 5.8

[a] protons were added to the structures by Maestro (Schrödinger) because the crystal structures lacked protons; disances are in brackets when the heavy atoms are characterized by high B-factors

[b] flipped away, open conformation, value not used for average distance

[c] the electron density is of good quality and the resolution is good; in this case the interactions with the protein seem to be so favorable that Le^x is distorted into an elongated conformation; however, the oligosaccharides might be distorted due to crystal packing, they are in close contact to other symmetry related molecules and forms several hydrogen bonds with them; values were not used for average distance but for the histogram

[d] the two structures 4UNZ, 4UO2 determined at low resolution (2. 9 and 2.7 Å) contain errors in sugar geometry, for example in 4UNZ, Fuc 704 has wrong chirality at C1; values were not used for average distance, but for the histogram

[e] two conformations present for oligosaccharide, used distances of first conformation

[f] in the structure 5AJB that contains 5 Le^x motifs in an open conformation, four of these five ligands might be distorted due to crystal packing, they are in close contact to other symmetry related molecules and form several hydrogen bonds with them; only B 110-112 is at least 4.2 Å away from symmetry neighboring molecules; it is possible that the protein stabilizes an open conformation as discussed in Topin et al. [2]; values were not used for average distance, but for the histogram

[g] in the structure 5AJC that contains one Le^x and one sLe^x ligand both in an open conformation, the sLe^x ligand is in close contact with a neighboring molecule with which it is also forming three hydrogen bonds, Le^x is far away from neighboring molecules; it could be that the protein stabilizes a open conformation as discussed in Topin et al. [2]; values were not used for average distance, but for the histogram

[h] the two structures 2WMG and 2WMK of glycoside hydrolases (GH98, inactivated enzymes by a point mutant) show very unusual Galβ1,4GlcNAc phi angles, however in that case this might be linked with the function of the WT enzymes – cleaving the very same Galβ1,4GlcNAc linkage; values were not used for average distance, but for the histogram

[i] the electron density seems to be of good quality, the resolution is with 2 Å moderate; in this case the interactions with the protein seem to be so favorable that Le^y is distorted into an elongated conformation; values were not used for average distance, but for the histogram

[j] the inactive double mutant D172A/E217A of the 1,3 -1,4-α-L-fucosynthase crystallized with Galβ1,3[Fuc1,4]GlcNAcβ1,3Galβ1,4Glc (LNFP II) showed only electron density of three moieties of which Fuc and Gal could be clearly assigned but GlcNAc was 'partially ambiguous' as stated in the corresponding publication [5]; the fucosynthase is based on a natural fucosidase and in this context it might be plausible that the Fuc1,4GlcNAc linkage gets distorted by the enzyme to facilitate cleavage; values were not used for average distance, but for the histogram

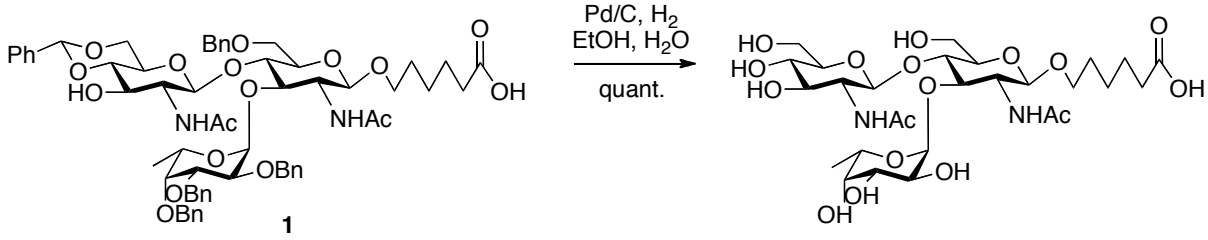
[k] Gal E504 is in a boat conformation, O5 is flipped up; the fact that this conformation is only found in one of the four binding sites makes it unlikely that it is a property of the protein to stabilize this conformation; values were not used for average distance, but for the histogram

[l] high B-factors (96-163) compared to an average B-factor of 68 for the protein; sugar puckers are very distorted including two boat conformations; axial O2,O3 and O4 in Fuc302; axial O3,O4 and acetamide at C2 in GlcNAc303; phi-psi angles in disallowed regions; value not used for average distance distance, but for the histogram

[m] sugar chain S in the binding site of protein chain I does show only very weak intensity at the fucose position; according to the associated publication [6] this site is characterized by weak electron density for Fucα1,3 and Glcβ; the occupancy in the pdb file is only 50%; all other nine binding sites that are equivalent in the two pentamers of the asymetric unit show the expected stacked structure; value not used for average distance, but for the histogram

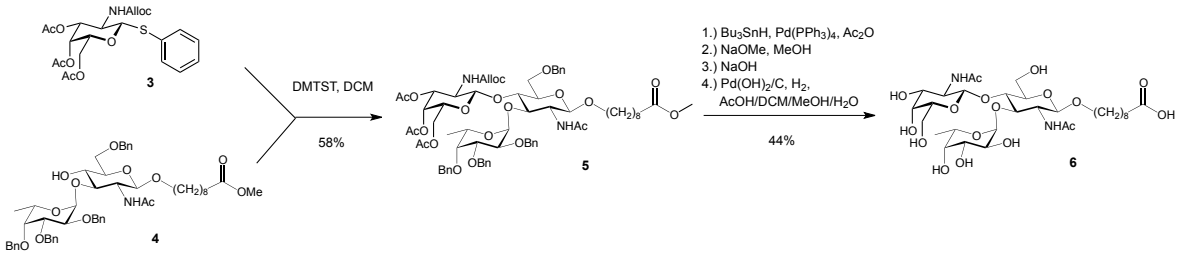
SI Methods

Synthesis and characterisation of GlcNAcβ1,4[Fucα1,3]GlcNAcβ1-O-(CH$_2$)$_5$-COOH.



1 [7] (28 mg, 24 µmol) was dissolved in a mixture of ethanol (2 mL) and water (1 mL). Pd/C 10% (12 mg) was added and the solution was stirred. Vacuum and H_2 were alternated and the mixture was allowed to stir under H_2 overnight. The mixture was filtered off through Celite and concentrated. The residue was dissolved in water and filtered through a 0.45 µm syringe filter and concentrated. The residue was purified on a G15 column to give, after lyophilisation, 14 mg of the desired product (99%) as a white solid. $[\alpha]_D^{25}$ -80 (c = 1.0 in H_2O). MS FAB+-HRMS: *m/z*: Calcd for $C_{30}H_{53}O_{17}N_2$ $[M+C_2H_5]^+$: 713.3344, found 713.3357. A ^{1}H-^{13}C HSQC spectrum with chemical shift assignment is shown in Figure S7a. Chemical shifts are deposited in the BMRB under the accession number 21032.

Synthesis and characterisation of GalNAcβ1,4[Fucα1,3]GlcNAcβ1-O-(CH$_2$)$_8$-COOH.



Compound **4** [8] (590 mg, 0.66 mmol) and thioglycoside **3** (791 mg, 1.64 mmol) were dissolved in dry DCM (25 mL) and stirred together with powdered 4Å activated molecular sieves (4 g) for 4 h at rt. DMTST (509 mg, 1.97 mmol) was dissolved in DCM (15 mL) and stirred together with powdered 4 Å activated molecular sieves (2 g) for 4 h at room temperature as well. Both suspensions were combined and stirred for 16 h at room temperature. The mixture was filtered over a short pad of celite, diluted with DCM (50 mL), and washed with a saturated solution of $NaHCO_3$ (40 mL) and water (40 mL). The aqueous phases were extracted with DCM (3× 30 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed *in vacuo*. The crude product was purified by flash

chromatography (petroleum ether/EtOAc, 40% to 70%) to yield **5** as a colorless oil (268 mg, 211 mmol, 32%). Reactant **4** was recovered in 45% yield (263 mg, 293 µmol). $[\alpha]_d^{25}$ -44.2 (*c* = 2.5 in $CHCl_3$); ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.42 – 7.22 (m, 20H, Ar-H), 5.94 – 5.83 (m, 1H, CH_2=C*H*-CH_2), 5.31 – 5.18 (m, 3H, 2x CH_2=CH-CH_2, Gal*N*Ac-H4), 5.16 – 5.09 (br s, 1H, Fuc-H1), 4.95 (d, *J* = 11.8 Hz, 1H, Ph-CH_2), 4.87 – 4.67 (m, 6H, 4x Ph-CH_2, Gal*N*Ac-H3, Glc*N*Ac-H1), 4.68 (d, *J* = 11.8 Hz, 1H, Ph-CH_2), 4.64 – 4.53 (m, 2H, Ph-CH_2, CH_2=CH-CH_2), 4.49 (dd, *J* = 13.3, 5.4 Hz, 1H, CH_2=CH-CH_2), 4.46 – 4.35 (m, 2H, Ph-CH_2, Gal*N*Ac-H1), 4.26 – 4.16 (m, 1H, Fuc-H5), 4.17 – 4.07 (m, 3H, Gal*N*Ac-H6, Fuc-H2, Glc*N*Ac-H3), 4.00 (dd, *J* = 10.8, 5.9 Hz, 1H, Gal*N*Ac-H6'), 3.92 (t, *J* = 6.2 Hz, 1H, Glc*N*Ac-H4), 3.88 – 3.83 (m, 1H, Fuc-H3), 3.78 – 3.67 (m, 5H, CH_2 linker, Glc*N*Ac-H6, Glc*N*Ac-H6', Gal*N*Ac-H2, Glc*N*Ac-H2), 3.65 (s, 3H, COO-Me), 3.65 – 3.53 (m, 3H, Fuc-H4, Gal*N*Ac-H5, Glc*N*Ac-H5), 3.40 – 3.32 (m, 1H, CH_2 linker), 2.28 (t, *J* = 7.5 Hz, 2H, CH_2 linker), 2.02 – 1.92 (m, 9H, 3x Ac), 1.83 – 1.75 (s, 3H, NH-CO-CH_3), 1.63 – 1.54 (m, 2H, CH_2 linker), 1.52 – 1.43 (m, 2H, CH_2 linker), 1.32 – 1.18 (m, 8H, CH_2 linker), 1.15 (d, *J* = 6.5 Hz, 3H, Fuc-H6); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 174.4, 170.5, 170.3, 170.3, 170.1 (4x Me-*C*OO, *C*OO-Me), 156.2 (NH-*C*O), 139.0, 138.7, 137.9, 128.8 – 127.3 (24x Ar-C), 132.7 (CH_2=*C*H-CH_2), 117.9 (*C*H_2=CH-CH_2), 100.2 (Gal*N*Ac-C1), 100.0 (Glc*N*Ac-C1), 97.3 (Fuc-C1), 79.8 (Fuc-C3), 77.2 (Fuc-C4), 76.6 (Fuc-C2), 74.5 (Ph-*C*H_2), 74.4 (Glc*N*Ac-C5), 74.3 (Glc*N*Ac-C3), 73.9 (Glc*N*Ac-C4), 73.6 (Ph-*C*H_2), 73.4 (Ph-*C*H_2), 72.7 (Ph-*C*H_2), 70.4 (Gal*N*Ac-C3), 70.4 (Gal*N*Ac-C5), 70.1 (Gal*N*Ac-C2), 69.6 (CH_2 linker), 69.3 (Glc*N*Ac-C6), 66.7 (Fuc-C5), 66.3 (Gal*N*Ac-C4), 66.0 (CH_2=CH-*C*H_2), 60.7 (Gal*N*Ac-C6), 52.5 (Glc*N*Ac-C2), 51.6 (COO-Me), 34.2, 29.5, 29.3, 29.3, 29.2, 25.9, 25.0 (7x CH_2 linker), 23.2 (NH-CO-*C*H_3), 20.7 (3x *C*H_3-COO), 16.9 (Fuc-C6); ESI-MS: *m/z*: Calcd for $C_{68}H_{88}N_2NaO_{21}$ [*M*+Na]$^+$: 1291.58, found: 1291.65.

Compound **5** (87.0 mg, 68.5 µmol) was dissolved in DCM (2 mL) and $Pd(PPh_3)_4$ (1.6 mg, 1.37 µmol) and Bu_3SnH (21.9 mg, 75.4 µmol) were added. The solution was stirred for 5 min and Ac_2O (7.8 µl, 82.2 µmol) was added. The reaction mixture was stirred for 1 h at ambient temperature. The solvent was removed under reduced pressure and purified by flash chromatography (EtOAc/MeOH, 100% to 80%) to yield the intermediate (50.0 mg, 40.7 µmol, 60%) as a white solid. The intermediate (39.4 mg, 32.1 µmol) was suspended in MeOH (0.5 mL), treated with NaOMe/MeOH (320 µL, 0.02 M) and stirred for 16 h at room temperature. An aqueous solution of NaOH (64 µL, 10 M) was added and the reaction mixture stirred for 16 h at room temperature. The reaction was quenched with two drops of glacial acetic acid and concentrated *in vacuo*. The resulting alcohol was dissolved in DCM/MeOH/AcOH/H_2O (1:1:2:2, 4 mL) and $Pd(OH)_2$/C (10.0 mg) was added. The suspension was stirred under an atmosphere of hydrogen for 18 h. The reaction mixture was filtered and purified by size exclusion chromatography to yield **6** as a white foam (17.5 mg, 23.6 µmol, 74%). $[\alpha]_D^{22}$ -49.0 (*c* = 5.6 in H_2O); HRMS: *m/z*: Calcd for $C_{31}H_{54}N_2NaO_{17}$ [*M*+Na]$^+$: 749.3320, found: 749.3323; A ^{1}H-^{13}C HSQC spectrum with chemical shift assignment is given in Figure S7d. Chemical shifts are deposited in the BMRB under the accession number 21053.

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