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Supporting Information

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Carbohydrate-induced Peptide Conformation in Glycopeptides of the Recognition Region of LI-Cadherin**

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1. Justification of conformational analysis based NMR spectra of compounds dissolved in DMSO-d_6 by comparison of NOE contacts using either D_2O or DMSO-d_6 as the solvent

Of course, the natural solvent for peptides and proteins in mammals is H_2O. For recording NMR-experiments it is usually substituted partly or completely by D_2O. Because in the case of diluted NMR samples of compounds **19**- **25**, good results concerning line width and intensity could only be obtained in pure DMSO-d_6, it was checked for a sufficiently water-soluble model glycopeptide whether NOE contacts measured in DMSO-d_6 would match with those measured in D_2O.

In this way, NMR spectra of the glycopeptide Ac-AALDS(GalNAc)QGAI-OH, similar to compound **20**, were recorded at room temperature using DMSO-d_6, D_2O and in a mixture of D_2O/DMSO-d_6 (30:70) as the solvent. Slight differences of the chemical shifts were found with an average deviation of no more than 0.15 ppm compared to those measured in DMSO-d_6 (table 1). Intensities of NH dependent NOE-contacts measured in samples containing D_2O were weak or invisible, NOE-contacts not dependent of exchangeable protons similar to those measured in DMSO-d_6 (table 2). Because of the qualitatively consistent NOE contacts in different solvents in the case of this glycopeptide, DMSO-d_6 was chosen as solvent for NMR measurements for peptide **19** and glycopeptides **20**-**25**.

Table 1: Selected chemical shifts of Ac-AALDS(GalNAc)QGAI-OH

Amino Acid	Proton	Chemical Shift		
		D_2O	DMSO-d_6/D_2O 70:30	DMSO-d_6
A^1-A^3	Ha	4,2-4,3	4,1	4,08-4,24
D	Ha	4,61	4,35	4,48
G	Ha	3,80	3,71	3,69
I	Ha	4,07	3,85	3,79
L	Ha	4,20	4,13	4,26
Q	Ha	4,30	4,07	4,18
S	Ha	4,49	4,37	4,56

Table 2: Isolated NOE-contacts

NOE Proton Contacts			Intensities		
			D_2O	DMSO-d_6/D_2O 70:30	DMSO-d_6
H 3	-	L δ	weak	weak	weak
H 2	-	L δ	very weak	very weak	very weak
H 1	-	Q a	weak	weak	medium
H 1	-	S a	weak	weak	weak
H 1	-	G a	very weak	very weak	very weak
G a	-	S a	weak	medium	medium
G a	-	S β	medium	strong	strong
I γ	-	L δ	weak	medium	medium
A NH	-	NHAc	-	-	weak

1.1 Complete ^{1}H-NMR data of model glycopeptide Ac-AALDS(GalNAc)QGAI-OH

400 MHz-^{1}H-NMR (D_2O), δ[ppm]: 4.88 (d, 1H, H1, ^3J = 3.5 Hz); 4.61 (t, 1H, α-CH Asp, ^3J = 3.1 Hz); 4.49 (m, 1H, α-CH Ser); 4.42-4.20 (m, 5H, α-CH Gln (4.3), 3*α-CH Ala (4.3-4.2), α-CH Leu (4.2)); 4.16 (dd, 1H, H2, $^3J_{2,1}$ = 3.5 Hz, $^3J_{2,3}$ = 11.0 Hz); 4.07 (d, 1H, α-CH Ile); 4.02-3.68 (m, 9H, α-CH_2 Gly (3.8), β-CH_2 $Ser_{a/b}$ (3.9, 3.8), H3 (3.89), H4 (4.02), H5 (3.85), H6 (3.72)); 2.75-2.65 (m, 2H, β-CH_2 Asp); 2.38 (t, 2H, γ-CH_2 Gln, ^3J = 7.0 Hz); 2.01 (m, 4H, β-C$\underline{H}_a$$H_b$ Gln, CH_3 NH$\underline{Ac}$); 1.90 (m, 4H, β-C$H_a$$\underline{H}_b$ Gln, CH_3 GalNH$\underline{Ac}$); 1.86-1.80 (m, 1H, β-CH Ile); 1.68-1.55 (m, 3H, β-CH_2 Leu, γ-CH Leu); 1.41-1.33 (m, 10H, γ-C$\underline{H}_a$$H_b$ Ile, 3*β-CH_3 Ala); 1.18-1.08 (m, 1H, γ-C$H_a$$\underline{H}_b$ Ile); 0.93-0.83 (m, 12H, 2*δ-CH_3 Leu, γ-CH_3 Ile, δ-CH_3 Ile).

400 MHz-^{1}H-NMR (DMSO-d_6/D_2O 70:30), δ[ppm]: 8.23 (m, 1H, NH Gln); 4.59 (d, 1H, H1, ^3J = 3.4 Hz); 4.39-4.33 (m, 2H, α-CH Asp (4.35), α-CH Ser(4.37)); 4.35-4.00 (m, 6H, H2 (4.16), 3*α-CH Ala (4.1), α-CH Leu (4.13), α-CH Gln (4.07)); 3.85 (d, 1H, α-CH Ile, ^3J = 5.1 Hz); 3.74-3.43 (m, 9H, α-CH_2 Gly (3.71), H3 (3.70), H4 (3.61), H5 (3.61), β-CH_2 Ser (3.47), H6 (3.46)); 2.41 (m, 2H, β-CH_2 Asp); 2.12 (t, 2H, γ-CH_2 Gln, ^3J = 7.4 Hz); 1.95-1.80 (m, 8H, β-C$\underline{H}_a$$H_b$ Gln (1.91), CH_3 NH$\underline{Ac}$ (1.84), β-C$H_a$$\underline{H}_b$ Gln (1.82), CH_3 GalNH$\underline{Ac}$ (1.81)); 1.68-1.60 (m, 1H, β-CH Ile); 1.55-1.41 (m, 3H, γ-CH Leu (1.51), β-CH_2 Leu (1.43)); 1.35-1.12 (m, 10H, γ-C$\underline{H}_a$$H_b$ Ile (1.3), 3*β-CH_3 Ala (1.2)); 0.93 (m, 1H, γ-C$H_a$$\underline{H}_b$ Ile); 0.79-0.68 (m, 12H, 2*δ-CH_3 Leu (0.74), δ-CH_3 Ile (0.72), γ-CH_3 Ile (0.70)).

400 MHz-^{1}H-NMR (DMSO-d_6), δ[ppm]: 8.71 (d, 1H, NH Ile, ^3J = 8.2 Hz); 8.68-8.10 (m, 7H, NH Ala (8.6, 8.45 ^3J = 7.4 Hz), NH Asp (8.43), NH Ser (8.35), NH Leu, NH Gly, NH GalN$\underline{H}$Ac); 7.79 (d, 1H, NH Ala, ^3J = 8.2 Hz); 7.50 (s_b, 1H, NH ε-Gln); 6.71 (s_b, 1H, NH ε-Gln); 4.62 (d, 1H, H1, ^3J = 3.1 Hz); 4.56 (m, 1H, α-CH Ser); 4.48 (m, 1H, α-CH Asp (4.35)); 4.35-4.00 (m, 6H, H2 (4.26), 3*α-CH Ala (4.24, 4,08), α-CH Leu (4.26), α-CH Gln (4.18)); 3.74-3.43 (m, 10H, α-CH Ile (3.79), H3 (3.71), α-CH_2 Gly (3.69), H5 (3.63), H4 (3.62), β-C$\underline{H}_a$$H_b$ Ser (3.51), H6 (3.48), β-C$H_a$$\underline{H}_b$ Ser (3.42)); 2.40 (m, 2H, β-CH_2 Asp); 2.08 (t, 2H, γ-CH_2 Gln, ^3J = 7.4 Hz); 1.95-1.80 (m, 8H, β-CH_2 Gln (1.92), CH_3 NH$\underline{Ac}$ (1.84), CH_3 GalNH$\underline{Ac}$ (1.81)); 1.72-1.55 (m, 2H, β-CH Ile (1.70), γ-CH Leu (1.58)); 1.55-1.41 (m, 2H, β-CH_2 Leu (1.45), γ-C$\underline{H}_a$$H_b$ Ile (1.44)); 1.35-1.02 (m, 10H, 3*β-CH_3 Ala (1.22, 1.15), γ-C$H_a$$\underline{H}_b$ Ile (1.07)); 0.89-0.70 (m, 12H, 2*δ-CH_3 Leu (0.85, 0.79), δ-CH_3 Ile (0.79), γ-CH_3 Ile (0.74)).

2. NOE/ROE proton contacts used for MM2-calculations of peptide 19 and glycopeptides 20-25 in DMSO-d_6 at 298 K.

NOESY and ROESY NMR spectra were recorded using mixing times of 300 ms in all cases. For discussion of the NOE/ROE NMR spectra and conformational analysis amino acids were numbered from *N*- to *C*-terminus of LI-cadherin peptide sequence **I** in the following way: L^1 A^2 A^3 L^4 D^5 S^6 Q^7 G^8 A^9 I^{10} V^{11}.
^{1}H signals of the saccharide portions were indicated as:
N-acetyl-D-galactosamine (no apostrophe); D-galactose ('); *N*-acetyl-neuraminic acid ('').

Proton-proton distances were calculated from NOESY and ROESY intensities according to the formula V = k/r^6. Constant "k" was derived from the known distance between co-axial protons within a monosaccharide residue.
The available software *Chem3D* V 9.0 used in this work does not fully support ensemble calculations. Therefore, random structures of molecules **19-25** were generated by the *molecular dynamics* procedure in *Chem3D* V 9.0. For each molecule eight to ten different random structures were created and subjected to MM2 energy minimization calculations based on proton-proton distances obtained from the NOE/ROE intensities (formula, se above). The following upper limits of these intensity-derived distances of the related protons were assigned:

intensity	strong	medium	weak	very weak
distance (upper limit)	3.0 Å	3.6 Å	4.3 Å	5.0 Å

These upper limits were used in MM2 energy minimization calculations the following way: At first, two or three NOE restraints were included in the calculations, the resulting values fixed and the next two or three NOE restraints included. Subsequently, for refinement about a fifth of all restraints were allowed to vary, the newly obtained values were fixed again, and new restraints were varied. This was repeated until the distances did not change any more. In the last step, about 60 % and finally all fixations were removed, and the final structure was calculated by energy minimization. The calculations led to nearly identical results regarding the turn region. In most cases, only few NOE-contacts between saccharide and peptide were found. The relative position of the saccharide obviously shows greatest variation in these compounds

NOE Proton Contacts of 19	ROE/NOE intensity
A^{2} α - L^{4} β	medium
A^{2} α - A^{9} β	strong
A^{2} β - A^{9} NH	very weak
L^{4} NH - A^{9} NH	weak
L^{4} α - A^{9} NH	strong
L^{4} γ - A^{9} NH	strong
D^{5} NH - A^{9} NH	medium
Q^{7} α - V^{11} α	strong
A^{9} α - I^{10} NH	medium

NOE Proton Contacts of 20	ROE/NOE intensity
V^{11} α - L^{4} α	weak
I^{10} α - L^{4} β	strong
S^{6} NH - G^{8} α	weak
S^{6} α - H 1	medium
S^{6} β - A^{9} NH	weak
G^{8} NH - A^{9} NH	weak
G^{8} NH - I^{10} α	very weak

NOE Proton Contacts of 21	ROE/NOE intensity
I^{10} β - L^{4} NH	strong
I^{10} β - V^{11} NH	strong
I^{10} β - NHCO$\underline{CH}_{3}$	very weak
Q^{7} α - H 4	medium
I^{10} NH - G^{8} NH	very weak
$I^{10}\gamma^{CH3}$ - L^{4} γ	weak
V^{11} NH - L^{4} β	medium
D^{5} α - NHCO$\underline{CH}_{3}$	very weak
H 3 - H 1’	weak
H 3 - H 3’	weak
H 3 - H 5’	weak

NOE Proton Contacts of 22	ROE/NOE intensity
A^{3} NH - L^{1} α	very weak
S^{6} β - H 2	medium
I^{10} NH - A^{2} α	weak
I^{10} NH - A^{3} α	medium
V^{11} NH - A^{2} α	weak
V^{11} NH - A^{3} α	medium
V^{11} NH - A^{9} α	medium
V^{11} NH - I^{10} α	medium
A^{9} α - N$\underline{H}$COCH$_{3}$	weak

NOE Proton Contacts of 23			ROE/NOE intensity
L^4 α	-	$I^{10}\gamma^{CH3}$	medium
L^4 γ	-	$I^{10}\gamma^{CH3}$	weak
D^5 β	-	I^{10} δ	very weak
Q^7 γ	-	I^{10} α	very weak
Q^7 NH^{ω}	-	NHCOCH$_3$	weak
Q^7 α	-	$I^{10}\gamma^{CH3}$	weak
Q^7 NH	-	I^{10} α	very weak
G^8 NH	-	A^9 β	weak
G^8 NH	-	H 5	weak
A^9 NH	-	NHCOCH$_3$	very weak

NOE Proton Contacts of 24			ROE/NOE intensity
L^4 NH	-	V^{11} α	weak
Q^7 α	-	S^6 β	weak
Q^7 α	-	I^{10} β	very weak
$I^{10}\gamma^{CH2}$	-	L^4 β	very weak
I^{10} δ	-	A^9 β	weak
$I^{10}\gamma^{CH3}$	-	A^3 α	weak
$I^{10}\gamma^{CH3}$	-	L^4 β	very weak
$I^{10}\gamma^{CH3}$	-	Q^7 α	very weak
NHCOCH$_3$	-	A^9 β	strong
NHCOCH$_3$	-	D^5 α	very weak
NHCOCH$_3$	-	H 5’’	weak

NOE Proton Contacts of 25			ROE/NOE intensity
G^8 NH	-	H 2	medium
L^4 β	-	$I^{10}\gamma^{CH2}$	weak
L^4 β	-	I^{10} δ	strong
L^4 γ	-	I^{10} δ	medium

The structures of (glycol)peptides **19 - 25** shown in Figure 2 in this publication are those ones fitting all NOE restrictions and having lowest energy.

3. Complete ^{1}H-NMR data of compounds 19 - 25

Denomination of the saccharide portions:
N-acetyl-D-galactosamine (no apostrophe); D-galactose (’); *N*-acetyl-neuraminic acid (’’).

19: L-Leucyl-L-alanyl-L-alanyl-L-leucyl-L-asparagyl-L-seryl-L-glutaminyl-glycyl-L-alanyl-L-isoleucyl-L-valin
400 MHz-^{1}H-NMR (DMSO-d$_6$), δ[ppm]: 8.66 (d, 1H, NH Ala^1, ^3J = 7.4 Hz); 8.24 (d, 1H, NH Asp, ^3J = 7.4 Hz); 8.12-8.04 (m, 5H, NH Leu$^{\omega}$ (8.10), NH Leu^2 (8.10), NH Gly (8.06), NH Gln (8.06)); 7.93-7.84 (m, 4H, NH Ala^2 (7.91), NH Val (7.88), NH Ile (7.86), NH Ala^3 (7.86)); 7.71 (d, 1H, NH Ser, ^3J = 7.4 Hz); 7.24 (s$_b$, 1H, NH$_a$H$_b$ ε-Gln); 6.77 (s$_b$, 1H, NH$_a$H$_b$ ε-Gln); 4.55 (dd, 1H, α-CH Asp, ^3J_a = 7.4 Hz, ^3J_b = 13.3 Hz); 4.40-4.18 (m, 7H, α-CH Ala^1 (4.38), α-CH Ala^2 (4.35), α-CH Leu^2 (4.28), α-CH Ala^3 (4.28), α-CH Ser (4.25), α-CH Ile (4.23), α-CH Gln (4.20)); 4.11 (dd, 1H, α-CH Val, ^3J_a = 5.5 Hz, ^3J_b = 8.2 Hz); 3.77 (m, 1H, α-CH ω-Leu); 3.72+3.67 (2*d, 2H, α-CH$_a$H$_b$ Gly, $^3J_{a,b}$ = 5.7 Hz); 3.62-3.48 (m, 2H, β-CH$_a$H$_b$ Ser (3.60), β-CH$_a$H$_b$ Ser (3.50)); 2.72 (dd, 1H, β-CH$_a$H$_b$ Asp, $^3J_{a,b}$ = 5.9 Hz, $^3J_{a,a}$ = 16.4 Hz); 2.51 (m, 1H, β-CH$_a$H$_b$ Asp); 2.10 (t, 2H, γ-CH$_2$ Gln, ^3J = 6.9 Hz); 2.05-1.90 (m, 2H, β-CH Val (2.03), β-CH$_a$H$_b$ Gln (1.92)); 1.77-1.41 (m, 9H, β-CH$_a$H$_b$ Gln (1.75), β-CH Ile (1.71), γ-CH ω-Leu (1.63), γ-CH Leu^2 (1.57), β-CH$_2$ ω-Leu (1.51), β-CH$_2$ Leu^2 (1.43), γ-CH$_a$H$_b$ Ile (1.43)); 1.25-1.15 (m, 9H, β-CH$_3$ Ala^1 (1.23), β-CH$_3$ Ala^3 (1.19), β-CH$_3$ Ala^2 (1.17)); 1.07 (m, 1H, γ-CH$_a$H$_b$ Ile); 0.91-0.77 (m, 24H, 4*δ-CH$_3$ Leu, 2*γ-CH$_3$ Val (0.87, 0.85), γ-CH$_3$ Ile (0.83), δ-CH$_3$ Ile (0.79)).

20: L-Leucyl-L-alanyl-L-alanyl-L-leucyl-L-asparagyl-L-seryl-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-L-glutaminyl-glycyl-L-alanyl-L-isoleucyl-L-valin

400 MHz-^{1}H-NMR (DMSO-d$_6$), δ[ppm]: 8.65 (d, 1H, NH Ala^3, ^3J = 7.4 Hz); 8.24 (d, 1H, NH Asp, ^3J = 7.0 Hz); 8.18-7.85 (m, 10H, NH Gly (8.16), ω-NH$_2$ Leu (8.10), NH Ala^2 (8.09), NH Gln (7.98), NH Ala^1 (7.95), NH Ser (7.91), NH Ile, Leu, Val (7.87)); 7.33-7.24 (m, 2H, NH GalNHAc (7.31), N$\underline{H_a}$H$_b$ ε-Gln (7.26)); 6.78 (s$_b$, 1H, NH$_a\underline{H_b}$ ε-Gln); 4.60 (d, 1H, H1, $^3J_{1,2}$ = 3.1 Hz); 4.54 (dd, 1H, α-CH Asp, $^3J_{\alpha,\beta a}$ = 7.4 Hz, $^3J_{\alpha,\beta b}$ = 13.3 Hz); 4.44-3.40 (m, 19H, α-CH Ser (4.42), α-CH Ala^3 (4.37), α-CH Ala^1 (4.34), α-CH Leu (4.29), α-CH Ala^2 (4.26), α-CH Ile (4.21), α-CH Gln (4.20), α-CH Val (4.10), H2 (4.05), α-C$\underline{H_a}$H$_b$ Gly (3.80), α-CH ω-Leu (3.76), H5 (3.70), β-C$\underline{H_a}$H$_b$ Ser (3.62), α-CH$_a\underline{H_b}$ Gly (3.60), H4 (3.57), H3 (3.57), β-CH$_a\underline{H_b}$ Ser (3.50), H6a (3.50), H6b (3.42)); 2.71 (m, 1H, β-C$\underline{H_a}$H$_b$ Asp); 2.52 (m, 1H, β-CH$_a\underline{H_b}$ Asp); 2.12-2.00 (m, 3H, γ-CH$_2$ Gln (2.10), β-CH Val (2.02)); 1.92-1.40 (m, 12H, β-C$\underline{H_a}$H$_b$ Gln (1.88), CH$_3$ NHAc (1.85), β-CH$_a\underline{H_b}$ Gln (1.76), β-CH Ile (1.71), γ-CH ω-Leu (1.62), γ-CH Leu (1.56), β-CH$_2$ ω-Leu (1.49), γ-C$\underline{H_a}$H$_b$ Ile (1.43) β-CH$_2$ Leu (1.42)); 1.23-1.13 (m, 9H, β-CH$_3$^{3} Ala (1.21), β-CH$_3$^{2} Ala (1.18), β-CH$_3$^{1} Ala (1.15)); 1.04 (m, 1H, γ-CH$_a\underline{H_b}$ Ile); 0.90-0.77 (m, 24H, 4*δ-CH$_3$ Leu, 2*γ-CH$_3$ Val (0.85), γ-CH$_3$ Ile (0.82), δ-CH$_3$ Ile (0.79)).

21: L-Leucyl-L-alanyl-L-alanyl-L-leucyl-L-asparagyl-L-seryl-*O*-(2-acetamido-2-desoxy-3-*O*-[β-D-galactopyranosyl]-α-D-galactopyranosyl)-L-glutaminyl-glycyl-L-alanyl-L-isoleucyl-L-valin

400 MHz-^{1}H-NMR (DMSO-d$_6$), δ[ppm]: 8.66 (d, 1H, NH Ala^3, ^3J = 7.4 Hz); 8.30-8.22 (m, 2H, NH Asp (8.28), NH Gly (8.24)); 8.14 (d, 1H, NH Ala$^{1/2}$, ^3J = 7.4 Hz); 8.09 (m, 1H, NH Leu^1); 8.01 (m, 2H, NH Ser, NH Gln); 7.95 (d, 1H, NH Ile, ^3J = 7.4 Hz); 7.92-7.87 (m, 3H, NH Val (7.90), NH Leu^2 (7.89), NH Ala$^{1/2}$); 7.47 (d, 1H, NH GalNHAc, ^3J = 8.61 Hz); 7.30 (s$_b$, 1H, N$\underline{H_a}$H$_b$ ε-Gln); 6.82 (s$_b$, 1H, NH$_a\underline{H_b}$ ε-Gln); 4.69 (d, 1H, H1, $^3J_{1,2}$ = 3.1 Hz); 4.57-4.20 (m, 10H, α-CH Asp (4.55), α-CH Ser (4.45), α-CH Ala^{1,3} (4.38), α-CH Ile (4.35), α-CH Leu^2 (4.33), α-CH Ala^2 (4.31), H1'(4.30), H2 (4.24), α-CH Gln (4.22)); 4.12 (dd, 1H, α-CH Val, ^3J_a = 5.9 Hz, ^3J_b = 8.2 Hz); 3.94 (m, 1H, H4); 3.85-3.25 (m, 15H, α-C$\underline{H_a}$H$_b$ Gly (3.83), α-CH Leu^1 (3.78), H3 (3.70), β-C$\underline{H_a}$H$_b$ Ser (3.69), H5 (3.62), H4'(3.62), α-CH$_a\underline{H_b}$ Gly (3.62), H6'/H6$_a$ (3.52), β-CH$_a\underline{H_b}$ Ser (3.51), H6'/H6$_b$ (3.44), H5'(3.35), H2'(3.34), H3'(3.27)); 2.72 (dd, 1H, β-C$\underline{H_a}$H$_b$ Asp, $^3J_{a,b}$ = 5.1 Hz, $^3J_{a,b}$ = 17.2 Hz); 2.54 (m, 1H, β-CH$_a\underline{H_b}$ Asp); 2.14-2.02 (m, 3H, γ-CH$_2$ Gln (2.12), β-CH Val (2.04)); 1.92-1.41 (m, 13H, β-C$\underline{H_a}$H$_b$ Gln (1.90), NH$\underline{Ac}$ (1.81), β-CH$_a\underline{H_b}$ Gln (1.77), β-CH Ile(1.72), γ-CH Leu^1 (1.64), γ-CH Leu^2 (1.59), β-CH$_2$ Leu^1 (1.52), γ-C$\underline{H_a}$H$_b$ Ile (1.45), β-CH$_2$ Leu^2 (1.43)); 1.24-1.15 (m, 9H, β-CH$_3$ Ala (3: 1.22, 2: 1.18, 1: 1.17)); 1.05 (m, 1H, γ-CH$_a\underline{H_b}$ Ile); 0.92-0.78 (m, 24H, 4*δ-CH$_3$ Leu, 2*γ-CH$_3$ Val (0.87), γ-CH$_3$ Ile (0.83), δ-CH$_3$ Ile (0.80)).

22: L-Leucyl-L-alanyl-L-alanyl-L-leucyl-L-asparagyl-L-seryl-*O*-{2-acetamido-2-desoxy-3-*O*-[4-*O*-acetyl-3-*O*-(5-acetamido-3,5-dideoxy-α-D-glycero-D-galacto-2-nonulopyranosyl)-β-D-galactopyranosyl]-α-D-galactopyranosyl}-L-glutaminyl-glycyl-L-alanyl-L-isoleucyl-L-valin

400 MHz-^{1}H-NMR (DMSO-d$_6$), δ[ppm]: 8.64 (d, 1H, NH Ala^A, ^3J = 7.4 Hz); 8.37 (d, 1H, NH Asp, ^3J = 8.2 Hz); 8.21-7.80 (m, 11H, NH: Gly (8.19), NeuNHAc (8.19), Gln (8.11), Val (8.09), Ala^B (8.08), Leu^1 (NH$_2$, 8.05), Ala^C (7.89), Leu^4 (7.89), Ser (7.88), GalNHAc (7.88), Ile (7,82)); 7.24+7.11+6.96 (s, 3-6H, NH$_3^+$ ε-Gln, Leu^1); 4.62-3.92 (m, 14H, H1 (4.60), α-CH

Asp (4.56), H1’ (4.50), α-CH Ala^{A} (4.38), α-CH Ala^{C} (4.33), H3’ (4.30), α-CH Leu^{4} (4.29), α-CH Ala^{B} (4.26), α-CH Ile (4.23), α-CH Gln (4.14), α-CH Val (4.13), α-CH Ser (4.11), H2 (4.10), H3 (3.90)); 3.81-3.50 (14H, m, α-CH Leu^{1} (3.79), β-C$\underline{H_A}H_B$ Ser (3.74), α-CH_2 Gly (3.70+3.64), H6’’ (3.67), H4, H4’, H5, H9a’’(3.60), H4’’ (3.55), H5’’, H6, H6’, β-C$H_A\underline{H_B}$ Ser (3.50), H9b’’ (3.40), H5’(3.35), H2’, H7’’, H8’’ (3.30)); 2.81-2.50 (m, 3H, β-CH_2 Asp (2.79-2.66), H3$_{eq}$’’ (2.50)); 2.10-2.01 (m, 3H, γ-CH_2 Gln (2.08), β-CH Val (2.03)); 1.90-1.70 (m, 14H, 4’OAc (1.88), β-C$\underline{H_a}H_b$ Gln (1.85), NH$\underline{Ac}$ Gal (1.84), NH$\underline{Ac}$ Neu (1.76), β-CH Ile (1.72)); 1.70-1.40 (m, 9H, β-C$H_a\underline{H_b}$ Gln (1.69), γ-CH Leu^{1} (1.62), γ-CH Leu^{4} (1.58), H3$_{ax}$’’ (1.50), β-CH_2 Leu^{1} (1.48), γ-C$\underline{H_a}H_b$ Ile (1.43), β-CH_2 Leu^{4} (1.42)); 1.24-1.14 (m, 9H, β-CH_3 Ala^{A} (1.22), β-CH_3 Ala^{B} (1.18), β-CH_3 Ala^{C} (1.16)); 1.05 (m, 1H, γ-C$H_a\underline{H_b}$ Ile); 0.89-0.78 (m, 24H, 4*δ-CH_3 Leu, 2*γ-CH_3 Val (0.87+0.86), γ-CH_3 Ile (0.83), δ-CH_3 Ile (0.80)).

23: L-Leucyl-L-alanyl-L-alanyl-L-leucyl-L-asparagyl-L-seryl-*O*-{2-acetamido-3,4-di-*O*-acetyl-2-deoxy-6-*O*-[benzyl-(5-acetamido-3,5-dideoxy-α-D-glycero-D-galacto-2-nonulopyranosyl)onat]-α-D-galactopyranosyl}-L-glutaminyl-glycyl-L-alanyl-L-isoleucyl-L-valin

400 MHz-^{1}H-NMR (DMSO-d_6), δ[ppm]: 8.64 (d, 1H, NH Ala^{1}, ^{3}J = 7.4 Hz); 8.23 (d, 1H, NH Asp, ^{3}J = 7.1 Hz); 8.16 (m, 1H, NH Gly); 8.11-8.06 (m, 3H, NH Ala^{3} (8.09), NH Leu$^{\omega}$ (8.08)); 7.99-7.85 (m, 7H, NH Gln (7.97), NH Ser (7.96), NH Ala^{2} (7.95), $\underline{NH}$Ac Neu (7.94), NH Ile (7.89), NH Leu^{2} (7.87), NH Val (7.87)); 7.28-7.24 (m, 2H, N$\underline{H_a}H_b$ ε-Gln, $\underline{NH}$Ac Gal); 6.78 (s_b, 1H, N$H_a\underline{H_b}$ ε-Gln); 4.61 (d, 1H, H1, $^{3}J_{1,2}$ = 3.1 Hz); 4.56 (dd, 1H, α-CH Asp, $^{3}J_a$ = 7.4 Hz, $^{3}J_b$ = 13.3 Hz); 4.45-4.21 (m, 7H, α-CH Ser (4.43), α-CH Ala^{1} (4.38), α-CH Ala^{2} (4.34), α-CH Leu^{2} (4.31), α-CH Ala^{3} (4.28), α-CH Gln (4.24), α-CH Ile (4.23)); 4.13-4.04 (m, 2H, α-CH Val (4.11), H2 (4.06)); 3.84 (d, 1H, α-C$\underline{H_a}H_b$ Gly, $^{3}J_{a,b}$ = 6.3 Hz); 3.80-3.49 (m, 12H, α-CH ω-Leu (3.78), β-C$\underline{H_a}H_b$ Ser (3.65), H5 (3.64), H4 (3.63), H6a (3.61), H9a’’ (3.61), H8’’ (3.61), α-C$H_a\underline{H_b}$ Gly (3.58), H3 (3.56), H5’’ (3.55), H4’’ (3.52), β-C$H_a\underline{H_b}$ Ser (3.51)); 3.40-3.36 (m, 3H, H6b, H9b’’, H7’’); 3.27 (m, 1H, H6’’); 2.72 (dd, 1H, β-C$\underline{H_a}H_b$ Asp, $^{3}J_{a,b}$ = 4.9 Hz, $^{3}J_{a,a}$ = 16.6 Hz); 2.57-2.47 (m, 2H, β-C$H_a\underline{H_b}$ Asp (2.55), H3$_{eq}$’’ (2.49)); 2.13-2.00 (m, 3H, γ-CH_2 Gln (2.11), β-CH Val (2.02)); 1.90-1.84 (m, 4H, β-C$\underline{H_a}H_b$ Gln (1.88), NH$\underline{Ac}$ Neu (1.86)); 1.77-1.41 (m, 13H, β-C$H_a\underline{H_b}$ Gln (1.75), NH$\underline{Ac}$ Gal (1.74), β-CH Ile (1.71), γ-CH ω-Leu (1.64), γ-CH Leu^{2} (1.57), H3$_{ax}$’’ (1.55), β-CH_2 ω-Leu (1.52), β-CH_2 Leu^{2} (1.43), γ-C$\underline{H_a}H_b$ Ile (1.43)); 1.24-1.15 (m, 9H, β-CH_3 Ala^{1} (1.22), β-CH_3 Ala^{3} (1.18), β-CH_3 Ala^{2} (1.16)); 1.05 (m, 1H, γ-C$H_a\underline{H_b}$ Ile); 0.92-0.77 (m, 24H, 4*δ-CH_3 Leu, 2*γ-CH_3 Val (0.86, 0.85), γ-CH_3 Ile (0.82), δ-CH_3 Ile (0.79)).

24: L-Leucyl-L-alanyl-L-alanyl-L-leucyl-L-asparagyl-L-seryl-*O*-(2-acetamido-4-*O*-acetyl-2-deoxy-3-*O*-β-D-galactopyranosyl-6-*O*-[benzyl-(5-acetamido-3,5-dideoxy-α-D-glycero-D-galacto-2-nonulopyranosyl)onat]-α-D-galactopyranosyl)-L-glutaminyl-glycyl-L-alanyl-L-isoleucyl-L-valin

400 MHz-^{1}H-NMR (DMSO-d_6), δ[ppm]: 8.66 (d, 1H, NH Ala^{I}, ^{3}J = 7.4 Hz); 8.30-8.23 (m, 2H, NH Asp (8.28), NH Gly (8.25)); 8.19-8.02 (m, 4H, NH Ser (8.17), NH Ala^{III} (8.14), NH Leu^{1} (8.10), Neu$\underline{NH}$Ac (8.04)); 7.96-7.87 (m, 5H, Ala^{II} (7.94), NH Leu^{4} (7.88), NH Ile, Gln (7.91), NH Val (7.89)); 7.57 (d, 1H, Gal$\underline{NH}$Ac, ^{3}J = 8.2 Hz); 7.28 (s_b, 1H, N$\underline{H_a}H_b$ ε-Gln); 6.81 (s_b, 1H, N$H_a\underline{H_b}$ ε-Gln); 5.30 (s_b, 1H, H4); 4.79 (d, 1H, H1, $^{3}J_{1,2}$ = 2.7 Hz); 4.56-4.17 (m, 10H, α-CH Asp (4.54), α-CH Ser (4.46), α-CH Ala^{I} (4.39), α-CH Ala^{II} (4.37), α-CH Leu^{4} (4.36), α-CH Ala^{III} (4.32), H1’ (4.29), α-CH Ile (4.24), α-CH Gln (4.23), H2 (4.19)); 4.12 (dd, 1H, α-CH Val, $^{3}J_{a,b}$ = 5.9 Hz, $^{3}J_{a\,NH,}$ = 8.2 Hz); 3.99-3.75 (m, 5H, H3’(3.97), H3 (3.95), α-C$\underline{H_a}H_b$

Gly (3.85), α-CH Leu^{1} (3.78), β-C$\underline{H_a}$H$_b$ Ser (3.77)); 3.65-3.43 (m, 11H, H9a’’ (3.63), α-CH$_a\underline{H_b}$ Gly (3.61), H4’(3.61), H5 (3.60), H6a/H6a’/H4’’ (3.55), H5’’(3.50), β-CH$_a\underline{H_b}$ Ser (3.49), H6b/H6b’ (3.45)); 3.41-3.22 (m, 6H, H9b’’ (3.39), H5’/H7’’ (3.32), H6’’ (3.30), H8’’ (3.25), H2’(3.24)); 2.70 (m, 1H, β-C$\underline{H_a}$H$_b$ Asp); 2.56-2.47 (m, 2H, β-CH$_a\underline{H_b}$ Asp (2.54), H3$_{eq}$’’ (2.49)); 2.13-1.68 (m, 15H, γ-CH$_2$ Gln (2.11), β-CH Val (2.03), H4:OAc (2.01), β-C$\underline{H_a}$H$_b$ Gln (1.90), NH$\underline{Ac}$ Neu (1.87), NH$\underline{Ac}$ Gal (1.83), β-CH$_a\underline{H_b}$ Gln (1.77), β-CH Ile (1.70)); 1.66-1.42 (m, 8H, γ-CH Leu^{1} (1.64), γ-CH Leu^{4} (1.59), β-CH$_2$ Leu^{1} (1.51), H3$_{ax}$’’ (1.48), γ-C$\underline{H_a}$H$_b$ Ile (1.46), β-CH$_2$ Leu^{4} (1.44)); 1.24-1.15 (m, 9H, β-CH$_3$ Ala^{I} (1.22), β-CH$_3$ Ala^{III} (1.18), β-CH$_3$ Ala^{II} (1.17)); 1.07 (m, 1H, γ-CH$_a\underline{H_b}$ Ile); 0.94-0.78 (m, 24H, 4*δ-CH$_3$ Leu (0.90-0.86, 0.82), 2*γ-CH$_3$ Val (0.87-0.86), γ-CH$_3$ Ile (0.84), δ-CH$_3$ Ile (0.80)).

25: L-Leucyl-L-alanyl-L-alanyl-L-leucyl-L-asparagyl-L-seryl-*O*-{2-acetamido-2-desoxy-3-*O*-[4-*O*-acetyl-3-*O*-(5-acetamido-3,5-dideoxy-α-D-glycero-D-galacto-2-nonulopyranosyl)-β-D-galactopyranosyl]-6-*O*-(5-acetamido-3,5-dideoxy-α-D-glycero-D-galacto-2-nonulo-pyranosyl)-α-D-galactopyranosyl}-L-glutaminyl-glycyl-L-alanyl-L-isoleucyl-L-valin
H: α-GalNAc, H’: β-Gal-4OAc, H’’: (2→3)-α-NeuNAc, H’’’: (2→6)-α-NeuNAc
400 MHz-^{1}H-NMR (DMSO-d$_6$), δ[ppm]: 9.41 (s, 1H (bis zu 4H möglich), COOH); 8.67 (d, 1H, NH Ala^{A}, ^{3}J = 7.8 Hz); 8.22-8.10 (m, 7H, NH: 2*NeuNHAc (8.20+8.05), Gly (8.18), Asp (8.15), Leu^{1} (NH$_2$, 8.12), Gln (8.12)); 9.94-7.83 (m, 7H, NH: Ala^{B,C} (7.92), Leu^{4} (7.91), Ser (7.91), GalNHAc (7.91/7.85), Val (7.90), Ile (7,85)); 6.83+6.67 (s, 3-6H, NH$_3^+$ ε-Gln, Leu^{1}); 4.84 (m, 1H, H4’); 4.63-4.56 (m, 3H, H1’ (4.61), H1 (4.59), α-CH Asp (4.59)); 4.40-4.09 (m, 9H, α-CH Ala^{A} (4.38), α-CH Ala^{C} (4.36), α-CH Leu^{4} (4.30), α-CH Ala^{B} (4.30), α-CH Ile (4.23), α-CH Ser (4.21), H2 (4.21), α-CH Gln (4.14), α-CH Val (4.11)); 3.97-3.29 (m, 25H, H3’ (3.95), α-CH$_2$ Gly (3.83+3.68), H5 (3.83), α-CH Leu^{1} (3.78), H4 (3.72), H2’ (3.70), H4’’’ (3.68), β-CH$_2$ Ser (3.68-3.66), H3 (3.66), H6 (3.64+3.61), H5’’+H5’’’ (3.59+3.48), H4’’ (3.56), H6’ (3.47), H6’’ (3.67), H9’’+H9’’’ (3.46+3.42), H6’’+H6’’’ (3.35+3.30); H7’’+H7’’’ (3.34), H5’ (3.31)); 3.19 (m, 2H, H8’’, H8’’’); 2.75-2.47 (m, 4H, β-CH$_2$ Asp (2.73+2.58), *H3$_{eq}$’’+ H3$_{eq}$’’’ (2.50)*); 2.20-1.83 (m, 16H, 4’OAc (2.18), γ-CH$_2$ Gln (2.11), NH$\underline{Ac}$ Gal (2.07), β-CH Val (2.03), 2*NH$\underline{Ac}$ Neu (1.87), β-C$\underline{H_a}$H$_b$ Gln (1.85)); 1.82-1.42 (m, 11H, *H3$_{ax}$’’’ (1.80)*, β-CH Ile (1.72), β-CH$_a\underline{H_b}$ Gln (1.70), γ-CH Leu^{1} (1.66), γ-CH Leu^{4} (1.58), β-CH$_2$ Leu^{1} (1.52), *H3$_{ax}$’’ (1.50)*, γ-C$\underline{H_a}$H$_b$ Ile (1.46), β-CH$_2$ Leu^{4} (1.44)); 1.24-1.15 (m, 9H, β-CH$_3$ Ala^{A} (1.22), β-CH$_3$ Ala^{B} (1.18), β-CH$_3$ Ala^{C} (1.17)); 1.07 (m, 1H, γ-CH$_a\underline{H_b}$ Ile); 0.90-0.78 (m, 24H, 4*δ-CH$_3$ Leu, 2*γ-CH$_3$ Val (0.88+0.87), γ-CH$_3$ Ile (0.83), δ-CH$_3$ Ile (0.80)).