Supporting Information

Can Amphipathic Helices Influence CNS Antinociceptive Activity of Glycopeptides Related to β-Endorphin?

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The Supporting Information includes HPLC retention times, CD data, NMR data for the 7 unglycosylated peptides and 14 glycopeptides studied.

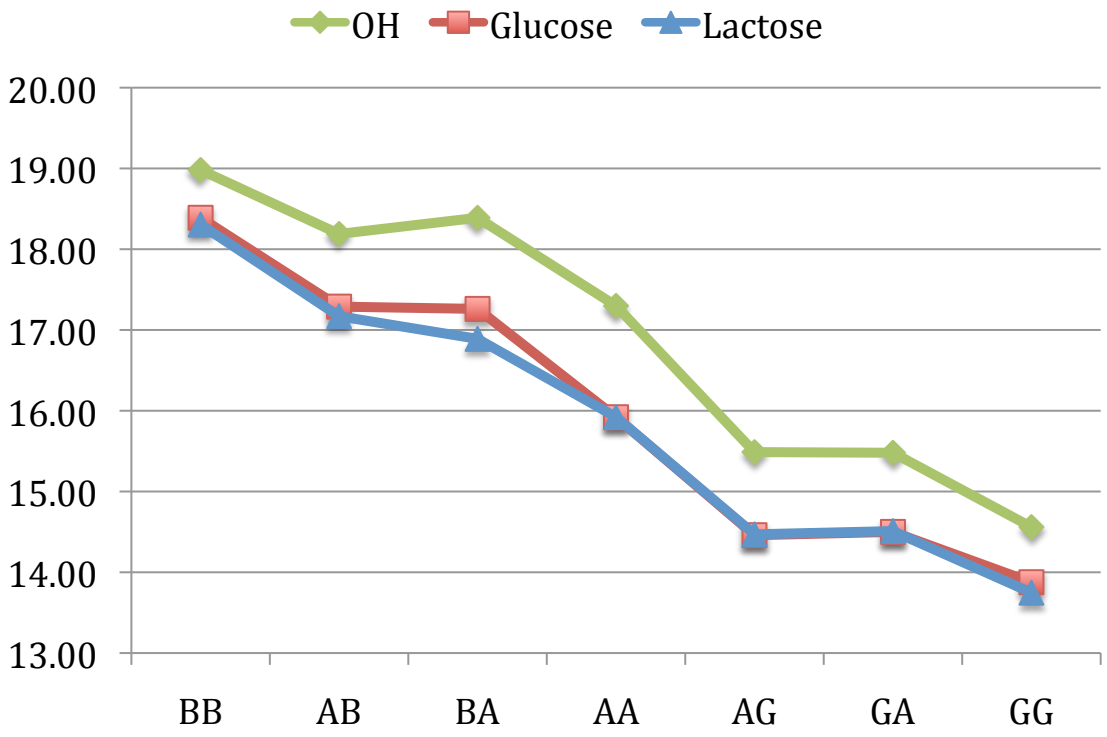
XYL Compound Designations

	BB	AB	BA	AA	AG	GA	GG
Unglycosylated	XYL-5199	XYL-5399	XYL-199	XYL-5299	XYL-5499	XYL-5599	XYL-5699
Glucosides	XYL-5100	XYL-5300	XYL-100	XYL-5200	XYL-5400	XYL-5500	XYL-5600
Lactosides	XYL-5120	XYL-5320	XYL-120	XYL-5220	XYL-5420	XYL-5520	XYL-5620

Isocratic RP-HPLC Retention Times (min)

	OH	Glucose	Lactose
BB	18.98	18.39	18.31
AB	18.19	17.29	17.17
BA	18.39	17.26	16.89
AA	17.30	15.92	15.92
AG	15.49	14.46	14.47
GA	15.48	14.50	14.51
GG	14.56	13.88	13.75

The peptides and glycopeptides were initially purified using a gradient solvent system (95—80% v:v CH_3CN/H_2O containing 0.1% TFA) with a preparative Phenomenex® column (C-18, 250 X 21.9 mm). In order to gauge amphipathicity reversed phase HPLC retention times were measured using an isocratic solvent system (90% v:v CH_3CN/H_2O containing 0.1% TFA) with an analytical Phenomenex® column (C-18, 250 X 4.6 mm). This data is plotted below.



Conformational analysis by circular dichroism. Because circular dichroism (CD) spectra reflect the peptide ensemble average of the alignment of the dipoles of the helix backbone, this simple but powerful technique can be used to quantitatively obtain the secondary structures in both peptides and proteins.[1] The CD spectra provide overall conformation, but do not yield residue-specific information.[2] The structure of the of the final designed peptide sequences was examined in the three different solvent systems of aqueous buffer, TFE-water mixture, and the SDS micelles. The CD spectra of the glycopeptides are shown in **Figure 2**. In aqueous buffer, all the glycopeptides displayed similar spectra that are characteristic of random coil conformation. As noted in a previous study with the parent glycopeptide MD100H, the glycopeptides displayed helical type CD spectra in the presence of TFE and SDS micelles. The calculated helicity per residue, based on the negative maxima at 222 nm ($n\rightarrow p*$ transition band) for each peptide is given in **Table 3**. The helical population increased in the order of solvent water<TFE-water mixture<SDS micelles. The increase in helicity as high as 57% in SDS depends on the amino acids present in address segment. The highest helicity observed were the glycopeptides with two helicogenic α-aminoisobutyric acid (Aib) residues (**G1** and **L2**) and lowest observed were the glycopeptides (**G7** and **L7**) with two glycine residues in the address segment. However, the identity of sugar moieties did not affect the conformation of the glycopeptides significantly, causing only slight changes in the percentages of helical population.

All CD spectra were obtained on OLIS DSM-20 automatic recording spectrophotometer equipped with temperature controller. The glycopeptide stock solutions were prepared by weighing the lyophilized powder, using Cahn/Ventron Instruments Model 21 automatic analytical electrobalance. The samples were prepared by diluting the stock solution to 30μM. All CD spectra were average of three scans recorded with baseline correction between 190 and 250 nm by using integration time of three seconds, a scan step of 0.5 nm in a cell with a path length of 0.1 cm at 20 °C. All spectra were smoothed by KaleidaGraph software (Synergy Software, USA). The molar ellipticities were calculated using the equation $[\theta]=[\theta]_{obs}\bullet(MRW)/10\bullet l\bullet C$, where $[\theta]_{obs}$ is observed ellipticity in millidegrees, MRW is the mean residue weight, l is the cell path length in centimeters and C is the glycopeptide concentration in mg/mL. The percent α-helicity was determined by using the equation $\%helix=[\theta]n\rightarrow p*/-40{,}000(1-2.5/n)\bullet 100$, where n represents the number of amide bonds (including the C-terminal amide) in the glycopeptides and $[\theta]n\rightarrow p*$ is molar ellipticity of $n\rightarrow p*$ transition band at 222 nm. The structure of the final peptide sequences was examined in the three different solvent systems of aqueous buffer, TFE-H_2O mixture, and SDS micelles.

CD TABLE 1. Circular dichroism data for peptides

Name	Solvent	$[\theta]\pi\rightarrow\pi^{*a,b}$ ≅222nm	$[\theta]\pi\rightarrow\pi^{*a,c}$ ≅208nm	% α-helicity by CD[d]
LYX5199	H_2O	N/A	N/A	
	TFE			
	SDS			
LYX5399	H_2O	-4055.9	-10724.0	12.2(±0.5)[f]
	TFE	-17687.0	-19515.0	53.1(±0.9)
	SDS	-20258.0	-13589.0	60.8(±2.5)
LYX199	H_2O	-2468.3	-7313.9	7.4(±4.9)
	TFE	-16671.0	-17612.0	50.0(±1.8)
	SDS	-19511.0	-15731.0	58.5(±5.7)
LYX5299	H_2O	-2394.4	-7534.0	7.2(±2.6)
	TFE	-15603.0	-18431.0	46.8(±1.7)
	SDS	-18132.0	-14934.0	54.4(±1.9)
LYX5499	H_2O	-2912.2	-9579.2	8.7(±1.9)
	TFE	-10021.0	-14495.0	22.7(±4.8)
	SDS	-12594.0	-11926.0	37.8(±2.7)
LYX5599	H_2O	-2379.2	-8559.9	7.1(±1.5)
	TFE	-7549.6	-11490.0	22.6(±4.6)
	SDS	-10989.0	-10564.0	33.0(±3.8)
LYX5699	H_2O	-2691.6	-8294.3	8.1(±3.9)
	TFE	-4802.3	-10180.0	14.4(±3.3)
	SDS	-3670.3	-7091.7	11.0(±3.2)

[a] The units for $[\theta]$ are deg•cm^2•dmol^{-1}; [b] The negative maxima for the $[\theta]\pi\rightarrow\pi^*$ was observed between 205 and 209 nm; [c] The negative maxima for the $[\theta]n\rightarrow\pi^*$ was observed between 222 and 225 nm; [d] The % helicity calculated according to the ref 63; [e] See text for the calculation method; ( )[f] The Standard deviation based on three experiments.

CD TABLE 2. Circular dichroism data for glucosylated peptides

Name	Solvent	$[\theta]\pi\rightarrow\pi^{*a,b}$ ≅222nm	$[\theta]\pi\rightarrow\pi^{*a,c}$ ≅208nm	% α-helicity by CD[d]	% α-helicity by NMR[e]
LYX5100	H_2O	-1468.3	-4301.9	4.4(±2.4)[f]	9.52
	TFE	-11823.0	-12723.0	35.5(±3.2)	
	SDS	-19081.0	-14247.0	57.2(±1.8)	33.47
LYX5300	H_2O	-2528.3	-6128.8	7.6(±1.9)	12.57
	TFE	-10868.0	-12643.0	32.6(±1.6)	
	SDS	-15142.0	-11982.0	45.4(±1.8)	41.90
LYX100	H_2O	-2331.0	-6545.4	7.0(±0.9)	7.23
	TFE	-10801.0	-13720.0	32.4(±1.6)	
	SDS	-12081.0	-9550.1	36.2(±0.7)	32.57
LYX5200	H_2O	-2758.4	-7767.8	8.3(±2.3)	7.14
	TFE	-11164.0	-12343.0	33.5(±2.8)	
	SDS	-12202.0	-10936.0	36.6(±0.8)	36.97
LYX5400	H_2O	1051.1	-6768.0	0.0(±1.3)	0.00
	TFE	-5291.0	-11478.0	15.9(±1.5)	
	SDS	-8466.2	-11779.0	25.4(±3.4)	22.68
LYX5500	H_2O	-327.2	-3853.6	1.0(±0.6)	0.00
	TFE	-2703.9	-6166.0	8.1(±0.3)	
	SDS	-5041.8	-6941.3	15.1(±3.4)	18.93
LYX5600	H_2O	-379.3	-4178.1	1.1(±1.5)	0.00
	TFE	-738.9	-5358.9	2.2(±0.2)	
	SDS	-2354.8	-6506.7	7.1(±0.9)	12.14

[a] The units for $[\theta]$ are deg•cm^2•dmol^{-1}; [b] The negative maxima for the $[\theta]\pi\rightarrow\pi^*$ was observed between 205 and 209 nm; [c] The negative maxima for the $[\theta]n\rightarrow\pi^*$ was observed between 222 and 225 nm; [d] The % helicity calculated according to the ref 63; [e] See text for the calculation method; ( )[f] The Standard deviation based on three experiments.

CD TABLE 3. Circular dichroism data for lactosylated peptides

Name	Solvent	$[\theta]\pi\rightarrow\pi^{*a,b}$ ≅222nm	$[\theta]\pi\rightarrow\pi^{*a,c}$ ≅208nm	% α-helicity by CD[d]	% α-helicity by NMR[e]
LYX5120	H_2O	-238.0	-3143.6	0.7(±6.1)[f]	11.24
	TFE	-11413.0	-10683.0	34.2(±2.4)	
	SDS	-13572.0	-8125.4	40.7(±2.0)	32.57
LYX5320	H_2O	-362.5	-4133.3	1.1(±1.6)	11.24
	TFE	-9333.3	-10974.0	28.0(±2.3)	
	SDS	-11809.0	-9652.7	35.4(±2.3)	44.57
LYX120	H_2O	-350.8	-5860.1	1.1(±4.1)	7.81
	TFE	-9202.2	-11014.0	27.6(±1.5)	
	SDS	-11088.0	-9052.6	33.3(±2.5)	36.19
LYX5220	H_2O	-158.3	-5017.7	0.5(±2.4)	11.25
	TFE	-8774.7	-11338.0	26.3(±5.9)	
	SDS	-10626.0	-9908.1	31.9(±1.3)	37.86
LYX5420	H_2O	636.0	-4088.3	0.0(±0.7)	0.00
	TFE	-4552.9	-7495.8	13.7(±1.7)	
	SDS	-4417.2	-5063.1	13.3(±5.0)	18.93
LYX5520	H_2O	976.6	-1867.9	0.0(±5.0)	0.00
	TFE	-1669.5	-2473.0	5.0(±1.9)	
	SDS	-1960.0	-3647.8	5.1(±4.6)	21.25
LYX5620	H_2O	355.3	-3989.0	0.0(±1.3)	2.32
	TFE	-1323.6	-3717.9	4.0(±3.9)	
	SDS	-1116.9	-3052.3	3.4(±3.0)	13.21

[a] The units for $[\theta]$ are deg•cm^2•dmol^{-1}; [b] The negative maxima for the $[\theta]\pi\rightarrow\pi^*$ was observed between 205 and 209 nm; [c] The negative maxima for the $[\theta]n\rightarrow\pi^*$ was observed between 222 and 225 nm; [d] The % helicity calculated according to the ref 63; [e] See text for the calculation method; ( )[f] The Standard deviation based on three experiments.

Conformational Analysis by NMR. Circular dichroism reflects general information on the overall molecular structure of glycopeptides in different solvents. On the other hand, NMR spectroscopy is well suited to study the local structure at residue specific level. All glycopeptides were characterized for their conformation in aqueous buffer and in SDS micelles by using 2D ^{1}H NMR. The different spin systems were identified with using TOCSY spectra and the sequential assignments were made by the combined use of TOCSY and NOESY/ROESY spectra. Although there were a few overlapping peaks observed, unambiguous ^{1}H chemical shift assignments of all glycopeptides were successfully made based on sequential NOEs such as d_{NN} (i, i+1), $d_{\alpha N}$ (i, i+1), and $d_{\beta N}$ (i, i+1).[3] The complete chemical shift values of the amino acid residues of all glycopeptides are provided in the supplementary data. Standard ROESY experiments worked well for aqueous samples, but it failed for SDS micelle possibly because the association of the glycopeptides with micelles generated high molecular weight and assemblies, increasing the correlation times, resulting in bad quality spectra. Therefore standard NOESY experiments were used for SDS samples.

All the glycopeptides exhibited consecutive strong $d_{\alpha N}$ (i, i+1) NOEs, along with relatively weaker d_{NN} (i, i+1) NOEs throughout the sequence. However, there were no additional NOEs diagnostic of any particular fold observed. Simultaneous observation of $d_{\alpha N}$ (i, i+1) and d_{NN} (i, i+1) without any other medium- or long-range observed NOEs is indicative of nascent helical nature of glycopeptides in aqueous buffer.

Although the spectra are well dispersed with minimum crosspeak crowding in SDS micelles, TOCSY/NOESY spectra enabled the complete sequential assignment of glycopeptides. Unlike NOEs in water, in SDS micelles, a continuous stretch of sequential strong d_{NN} (i, i+1) NOEs are observed for almost the entire length of all glycopeptides. In addition, other helix-specific NOEs, including $d_{\alpha N}$ (i, i+3) and $d_{\alpha N}$ (i, i+4), appear in the C-terminal address domain. The large number of medium- as well as long-range NOEs indicative of helical conformation was observed for glycopeptides with two Aib residues (**G1** and **L1**) in the helical segment. The number of NOEs decreased as Aib residues are replaced with Gly residues. There was a slight difference observed between glucosylated set of peptides and lactosylated set of peptides; the lactosylated glycopeptides appears to be less helical than glucosylated peptides.

It is well established that protein secondary structures can be identified on the basis of $C^{\alpha}H$ chemical shift information. This method, involving the chemical shift index (CSI), is more quantitative and accurate for identifying secondary structure of peptides, and is comparable to CD quality.[4] The magnitude of $C^{\alpha}H$ chemical shift difference, between the observed $C^{\alpha}H$ chemical shift and random coil values, can provide a reliable interpretation of chemical shift changes in structural terms, like an ideal α-helix appears to have an amide proton upfield shift of 0.2 to 0.3 ppm. The observed differences in conformational shift values in SDS micelles are summarized in **Figure 3**. Almost all amino acids showed negative deviations except residue Leu_5 and Ser_{15}. This trend is seen for all the glycopeptides, however, the magnitude of the deviation differs among the

peptides according to the amino acids. It should be noted that there is no random coil reference available for glycosylated serine. However, it is possible to make qualitative comparison of helical content between closely related peptides. Since glycopeptides differ by amino acids in the helical segment, helical content is obtained based on the $C^{\alpha}H$ chemical shift values (**Table 3**). Methods described by Gierasch and co-workers[5] were used. First, the average conformational shift was calculated for each peptide by adding all upfield shifts in the helical regions and dividing by the total number of peptide bonds. Then, to obtain the overall helical contents for each peptide, the average conformational shift was divided by 0.35ppm, which was assigned for 100% helicity. Since there is no random coil value available for the glycoside serine residue and Aib residue lacks the α-proton, they were not included in the calculation. The helical content obtained by this method correlates more closely with the helical content obtained by NMR except for glycopeptide **G1** where the difference is more than 20%. As expected from the design, the helical content varies depending on amino acids present in the helical segment. The presence of two Aib residues increases the helical content where as replacement of those Aib residues with Ala and Gly residues decreases the helical content. According to 2D-NMR results, peptide substituted two Aib residues with two Ala residues do not change the helical content significantly, however, a significant decrease in the helical content was observed by circular dichroism method (**Table 3** and **4**). Interestingly, CD spectra of glycopeptides **G1** (Aib & Aib), **G2** (Ala & Aib), **G3** (Aib, Ala) and **G4** (Ala & Ala) showed almost the same helical content in the TFE-water mixture, but these peptides showed different helical content in SDS micelles. This observation clearly indicates that these glycopeptides should have different interactions with cell membrane that lead different biological activities.

Molecular dynamics simulation with NMR determined restraints was performed on Molecular Operating Environment (**Figure 4)**, showing the 30 low energy structures of **G3** obtained using the Amber99 force field. The glycopeptide address segment as built as a helix and distance restraints were applied. After initial minimization, molecular dynamics is performed using the following parameters: 300K, 50ps equilibration, 1ns molecular dynamics run, saving the output structure every 2ps, with a time step of 0.1fs. Saved output structures are minimized with the 30 low energy structures being aligned by αC from residue 7 through 14. RMSD is calculated as 0.611.

NMR Tables

Table S1: Chemical shift values (p.p.m) of glycopeptides **LYX5100** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.
Table S2: Chemical shift values (p.p.m) of glycopeptides **LYX5100** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.
Table S3: Chemical shift values (p.p.m) of glycopeptides **LYX5120** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.
Table S4: Chemical shift values (p.p.m) of glycopeptides **LYX5120** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.
Table S5: Chemical shift values (p.p.m) of glycopeptides **LYX5200** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.
Table S6: Chemical shift values (p.p.m) of glycopeptides **LYX5200** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.
Table S7: Chemical shift values (p.p.m) of glycopeptides **LYX5220** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.
Table S8: Chemical shift values (p.p.m) of glycopeptides **LYX5220** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.
Table S9: Chemical shift values (p.p.m) of glycopeptides **LYX5300** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.
Table S10: Chemical shift values (p.p.m) of glycopeptides **LYX5300** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.
Table S11: Chemical shift values (p.p.m) of glycopeptides **LYX5320** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.
Table S12: Chemical shift values (p.p.m) of glycopeptides **LYX5320** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.
Table S13: Chemical shift values (p.p.m) of glycopeptides **LYX5400** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.
Table S14: Chemical shift values (p.p.m) of glycopeptides **LYX5400** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.
Table S15: Chemical shift values (p.p.m) of glycopeptides **LYX5420** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.
Table S16: Chemical shift values (p.p.m) of glycopeptides **LYX5420** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.
Table S17: Chemical shift values (p.p.m) of glycopeptides **LYX5500** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.
Table S18: Chemical shift values (p.p.m) of glycopeptides **LYX5500** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.
Table S19: Chemical shift values (p.p.m) of glycopeptides **LYX5520** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.
Table S20: Chemical shift values (p.p.m) of glycopeptides **LYX5520** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.
Table S21: Chemical shift values (p.p.m) of glycopeptides **LYX5600** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.
Table S22: Chemical shift values (p.p.m) of glycopeptides **LYX5600** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.
Table S23: Chemical shift values (p.p.m) of glycopeptides **LYX5620** as

Figure S17: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5520** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.
Figure S18: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5600** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.
Figure S19: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5620** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.
Figure S20: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **MD100H(LYX100)** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.
Figure S21: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **MD120H(LYX120)** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.
Figure S22. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5100** in SDS micelle at pH=5.5 at 30°C.
Figure S23. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5120** in SDS micelle at pH=5.5 at 30°C.
Figure S24. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5200** in SDS micelle at pH=5.5 at 30°C.
Figure S25. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5220** in SDS micelle at pH=5.5 at 30°C.
Figure S26. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5300** in SDS micelle at pH=5.5 at 30°C.
Figure S27. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5320** in SDS micelle at pH=5.5 at 30°C.
Figure S28. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5400** in SDS micelle at pH=5.5 at 30°C.
Figure S29. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5420** in SDS micelle at pH=5.5 at 30°C.
Figure S30. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5500** in SDS micelle at pH=5.5 at 30°C.
Figure S31. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5520** in SDS micelle at pH=5.5 at 30°C.
Figure S32. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5600** in SDS micelle at pH=5.5 at 30°C.
Figure S33. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5620** in SDS micelle at pH=5.5 at 30°C.
Figure S34. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **MD100H(LYX120)** in SDS micelle at pH=5.5 at 30°C.
Figure S35. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **MD120H(LYX120)** in SDS micelle at pH=5.5 at 30°C.
Figure S36: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5100** in SDS micelle at pH=5.5 at 30°C.
Figure S37: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5100** in SDS micelle at pH=5.5 at 30°C.
Figure S38: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5120** in SDS micelle at pH=5.5 at 30°C.
Figure S39: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5120** in SDS micelle at pH=5.5 at 30°C.

Figure S40: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5200** in SDS micelle at pH=5.5 at 30°C.
Figure S41: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5200** in SDS micelle at pH=5.5 at 30°C.
Figure S42: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5220** in SDS micelle at pH=5.5 at 30°C.
Figure S43: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5220** in SDS micelle at pH=5.5 at 30°C.
Figure S44: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5300** in SDS micelle at pH=5.5 at 30°C.
Figure S45: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5300** in SDS micelle at pH=5.5 at 30°C.
Figure S46: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5320** in SDS micelle at pH=5.5 at 30°C.
Figure S47: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5320** in SDS micelle at pH=5.5 at 30°C.
Figure S48: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5400** in SDS micelle at pH=5.5 at 30°C.
Figure S49: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5400** in SDS micelle at pH=5.5 at 30°C.
Figure S50: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5420** in SDS micelle at pH=5.5 at 30°C.
Figure S51: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5420** in SDS micelle at pH=5.5 at 30°C.
Figure S52: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5500** in SDS micelle at pH=5.5 at 30°C.
Figure S53: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5500** in SDS micelle at pH=5.5 at 30°C.
Figure S54: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5520** in SDS micelle at pH=5.5 at 30°C.
Figure S55: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5520** in SDS micelle at pH=5.5 at 30°C.
Figure S56: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5600** in SDS micelle at pH=5.5 at 30°C.
Figure S57: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5600** in SDS micelle at pH=5.5 at 30°C.
Figure S58: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5620** in SDS micelle at pH=5.5 at 30°C.
Figure S59: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5620** in SDS micelle at pH=5.5 at 30°C.
Figure S60: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX100** in SDS micelle at pH=5.5 at 30°C.
Figure S61: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX100** in SDS micelle at pH=5.5 at 30°C.
Figure S62: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX120** in SDS micelle at pH=5.5 at 30°C.

Figure S63: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX120** in SDS micelle at pH=5.5 at 30°C.

Table S1: Chemical shift values (p.p.m) of glycopeptides **LYX5100** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.70, 6.99	
D-Thr2		4.16	4.11	γ 0.88	-0.23
Gly3	8.48	3.89			-0.12
Phe4	8.12	4.63	3.09 3.02	δ 7.36; ε 7.19; ζ 6.89	0.01
Leu5	8.30	4.62	1.60	γ 1.55; δ 0.93	0.27
Pro6		4.33	3.12	γ 2.29, 2.01 δ 3.69, 3.64	-0.11
Asn7	8.58	4.67	2.88 2.81		-0.09
Leu8	8.29	4.21	1.70	γ 1.62; δ 0.95, 0.88	-0.14
Aib9			1.46		
Glu10	8.26	4.15	2.03	γ 2.29	-0.14
Lys11	8.02	4.14	1.88	γ 1.70; δ1.55, 1.43 ε 3.02	-0.18
Aib12			1.46		
Leu13	7.81	4.30	1.69	γ 1.61; δ 0.95, 0.89	-0.05
Lys14	8.16	4.31	1.89 1.83	γ 1.71; δ 1.49; ε 3.02	-0.01
Ser15	8.51	4.62	4.25 3.96		0.13
Leu16	8.33	4.33	1.71	γ 1.64; δ 0.96, 0.89	-0.02
-$CONH_2$	7.45 7.25				

Table S2: Chemical shift values (p.p.m) of glycopeptides **LYX5100** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.51, 6.85	
D-Thr2	8.61	4.34		γ 1.15	-0.05
Gly3	8.41	3.94			-0.07
Phe4	7.84	4.61	3.21 3.07	δ 7.31; ε 7.23; ζ 6.88	-0.01
Leu5	8.05	4.32	1.86	γ 1.65; δ 1.00, 0.94	-0.03
Pro6		4.26	2.31	γ 2.07, 1.95; δ 3.58	-0.18
Asn7	7.68	4.54	2.87 2.81		-0.24
Leu8	7.83	4.00	1.69	γ 1.64; δ 0.96, 0.92	-0.35
Aib9			1.40		
Glu10	7.60	3.93	2.10	γ 2.42, 2.31	-0.36
Lys11	8.02	4.14	1.88	γ 1.70; δ1.55, 1.43 ε 3.02	-0.18
Aib12			1.40		
Leu13	7.71	3.93	1.84 1.76	γ 1.63; δ 0.90	-0.42
Lys14	7.90	4.13	1.94	γ 1.71, 1.62 δ 1.52, 1.49; ε 3.00	-0.19
Ser15	7.82	4.69	4.17 4.12		0.20
Leu16	7.85	4.25	1.78 1.75	γ 1.64, 1.62; δ 0.90	-0.10
$-CONH_2$	7.27 6.90				

Table S3: Chemical shift values (p.p.m) of glycopeptides **LYX5120** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.70, 6.98	
D-Thr2	8.59	4.15		γ 0.88	-0.24
Gly3	8.49	3.88			-0.13
Phe4	8.11	4.63	3.08 3.03	δ 7.38; ε 7.25; ζ 6.89	0.01
Leu5	8.29	4.61	1.61 1.59	γ 1.55, 1.53 δ 0.94, 0.91	0.26
Pro6		4.34	3.20 3.12	γ 2.29, 2.02 δ 3.69, 3.63	-0.10
Asn7	8.57	4.66	2.87 2.82		-0.10
Leu8	8.26	4.20	1.70	γ 1.64, 1.60 δ 0.96, 0.89	-0.15
Aib9			1.47		
Glu10	8.23	4.14	2.09 2.03	γ 2.30	-0.15
Lys11	8.02	4.12	1.88	γ 1.69; δ1.54; ε 3.00	-0.20
Aib12			1.47		
Leu13	7.79	4.29	1.69	γ 1.61; δ 0.94, 0.88	-0.06
Lys14	8.14	4.30	1.89 1.84	γ 1.69; δ 1.51, 1.44 ε 3.01	-0.02
Ser15	8.48	4.61	4.24 3.97		0.12
Leu16	8.30	4.32	1.70	γ 1.62; δ 0.95, 0.89	-0.03
-$CONH_2$	7.43 7.25				

Table S4: Chemical shift values (p.p.m) of glycopeptides **LYX5120** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1		4.45		δ 7.52, 6.83	-0.11
D-Thr2	8.54	4.35		γ 1.15	-0.04
Gly3	8.38	3.96			-0.05
Phe4	7.90	4.55	3.24 3.05	δ 7.28; ε 7.21; ζ 6.85	-0.07
Leu5	8.18	4.25	1.87	γ 1.66, 1.55; δ 0.99	-0.10
Pro6		4.22	2.28 2.11	γ 1.90; δ 3.59	-0.22
Asn7	7.58	4.48	2.87 2.76		-0.28
Leu8	7.89	3.97	1.66	γ 1.59; δ 0.94	-0.38
Aib9			1.38		
Glu10	7.69	3.90	2.14 2.08	γ 2.49, 2.35	-0.39
Lys11	7.75	4.14	1.98 1.91	γ 1.68, 1.62; δ1.40 ε 2.98	-0.18
Aib12			1.38		
Leu13	7.88	4.00	1.84	γ 1.62; δ 0.90	-0.35
Lys14	7.94	4.10	1.93	γ 1.70, 1.61 δ 1.52, 1.48; ε 2.98	-0.22
Ser15	7.82	4.71	4.23 4.11		0.22
Leu16	7.85	4.22	1.78	γ 1.62; δ 0.90	-0.13
$-CONH_2$	7.27 6.89				

Table S5: Chemical shift values (p.p.m) of glycopeptides **LYX5200** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.70, 6.99	
D-Thr2		4.16	4.11		-0.23
Gly3	8.47	3.88			-0.13
Phe4	8.12	4.62	3.08 3.02	δ 7.35; ε 7.18; ζ 6.89	0.00
Leu5	8.29	4.61	1.70	γ 1.58; δ 0.93	0.26
Pro6		4.34	2.29	γ 2.01, 1.86; δ 3.63	-0.10
Asn7	8.58	4.66	2.86 2.81		-0.10
Leu8	8.32	4.28	1.69	γ 1.64; δ 0.95, 0.88	-0.07
Ala9	8.26	4.26	1.41		-0.08
Glu10	8.25	4.19	2.05 2.00	γ 2.31, 2.26	-0.10
Lys11	8.28	4.23	1.86 1.80	γ 1.70; δ1.44; ε 3.01	-0.09
Ala12	8.19	4.31	1.40		-0.03
Leu13	8.17	4.31	1.68	γ 1.59; δ 0.95, 0.90	-0.04
Lys14	8.27	4.32	1.86	γ 1.70; δ 1.44; ε 3.01	0.00
Ser15	8.55	4.63	4.25 3.96		0.14
Leu16	8.35	4.32	1.71	γ 1.63; δ 0.95, 0.89	-0.03
-$CONH_2$	7.45 6.99				

Table S6: Chemical shift values (p.p.m) of glycopeptides **LYX5200** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1		4.45		δ 7.53, 6.84	-0.11
D-Thr2	8.60	4.32		γ 1.14	-0.07
Gly3	8.42	3.93			-0.08
Phe4	7.86	4.58	3.19 3.05	δ 7.30; ε 7.22; ζ 6.86	-0.04
Leu5	8.05	4.32	1.85	γ 1.65, 1.54; δ 0.97	-0.05
Pro6		4.26	2.30 2.07	γ 1.93, 1.89; δ 3.60	-0.18
Asn7	7.77	4.53	2.85 2.81		-0.23
Leu8	7.93	4.04	1.67	γ 1.61; δ 0.93, 0.88	-0.31
Ala9	8.28	3.96	1.43		-0.38
Glu10	7.85	4.00	2.13	γ 2.45, 2.35	-0.29
Lys11	7.71	4.05	1.95 1.90	γ 1.70; δ 1.47; ε 2.99	-0.27
Ala12	8.14	4.17	1.43		-0.17
Leu13	8.13	4.13	1.80	γ 1.60, 1.55; δ 0.90	-0.22
Lys14	7.76	4.12	1.90	γ 1.70; δ 1.48; ε 2.99	-0.20
Ser15	7.96	4.61	4.16 4.06		0.12
Leu16	7.91	4.23	1.77	γ 1.59; δ 0.92, 0.89	-0.12
$-CONH_2$	7.23 6.90				

Table S7: Chemical shift values (p.p.m) of glycopeptides **LYX5220** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.68, 6.96	
D-Thr2	8.63	4.17	4.13		-0.22
Gly3	8.54	3.91			-0.10
Phe4	8.16	4.57	3.08	δ 7.36; ε 7.19; ζ 6.90	-0.05
Leu5	8.26	4.28	1.55	γ 1.41; δ 0.93, 0.87	-0.07
Pro6		4.34	3.12	γ 1.70; δ 3.20	-0.10
Asn7	8.36	4.64	2.83 2.78		-0.12
Leu8	8.12	4.18	1.66	γ 1.57; δ 0.93, 0.87	-0.17
Ala9	8.21	4.19	1.39		-0.15
Glu10	8.28	4.16	2.12 2.04	γ 2.31	-0.13
Lys11	8.05	4.23	1.91 1.85	γ 1.70; δ 1.54, 1.45 ε 3.01	-0.09
Ala12	7.95	4.28	1.42		-0.06
Leu13	8.07	4.32	1.70	γ 1.59; δ 0.96, 0.90	-0.03
Lys14	8.26	4.32	1.86 1.81	γ 1.55; δ 1.45; ε 3.01	0.00
Ser15	8.53	4.63	4.25 3.96		0.14
Leu16	8.33	4.33	1.71	γ 1.63; δ 0.96, 0.89	-0.02
$-CONH_2$	7.44 7.25				

Table S8: Chemical shift values (p.p.m) of glycopeptides **LYX5220** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1		4.45		δ 7.54, 6.83	-0.11
D-Thr2	8.55	4.33		γ 1.12	-0.06
Gly3	8.39	3.96			-0.05
Phe4	7.89	4.56	3.21 3.05	δ 7.30; ε 7.21; ζ 6.87	-0.20
Leu5	8.12	4.29	1.85	γ 1.64, 1.52; δ 0.97	-0.06
Pro6		4.24	2.29 2.09	γ 1.92; δ 3.60	-0.20
Asn7	7.74	4.52	2.87 2.80		-0.24
Leu8	7.97	4.03	1.66	γ 1.44; δ 0.92, 0.87	-0.32
Ala9	8.27	3.96	1.43		-0.38
Glu10	7.87	3.98	2.13	γ 2.45, 2.31	-0.31
Lys11	7.72	4.04	1.94	γ 1.58; δ 1.41; ε 2.98	-0.28
Ala12	8.17	4.16	1.43		-0.18
Leu13	8.15	4.12	1.80	γ 1.61; δ 0.90	-0.23
Lys14	7.77	4.12	1.94	γ 1.58; δ 1.41; ε 2.99	-0.20
Ser15	7.94	4.64	4.13		0.15
Leu16	7.91	4.22	1.78	γ 1.59; δ 0.92, 0.89	-0.13
$-CONH_2$	7.24 6.89				

Table S9: Chemical shift values (p.p.m) of glycopeptides **LYX5300** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.70, 6.99	
D-Thr2		4.16	4.10	γ 0.90	-0.23
Gly3	8.47	3.89			-0.12
Phe4	8.12	4.63	3.11 3.04	δ 7.36; ε 7.19; ζ 6.89	0.01
Leu5	8.30	4.62	1.61	δ 0.95	0.27
Pro6		4.34	2.30	γ 2.03; δ 3.70, 3.64	-0.10
Asn7	8.59	4.67	2.91 2.83		-0.09
Leu8	8.33	4.26	1.71	γ 1.63; δ 0.97	-0.09
Ala9	8.25	4.26	1.44		-0.08
Glu10	8.17	4.18	2.09 2.06	γ 2.33, 2.28	-0.11
Lys11	8.18	4.15	1.87	γ 1.71; δ 1.53; ε 3.02	-0.17
Aib12			1.25		
Leu13	7.76	4.29	1.69	γ 1.61; δ 0.93, 0.88	-0.06
Lys14	8.16	4.30	1.90	γ 1.73; δ 1.61; ε 3.03	-0.16
Ser15	8.48	4.62	4.25 3.98		0.13
Leu16	8.32	4.32	1.73	γ 1.64; δ 0.97, 0.90	-0.03
-$CONH_2$	7.44 7.25				

Table S10: Chemical shift values (p.p.m) of glycopeptides **LYX5300** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1		4.46		δ 7.54, 6.85	-0.10
D-Thr2	8.59	4.33		γ 1.15	-0.06
Gly3	8.41	3.94			-0.07
Phe4	7.85	4.59	3.20 3.06	δ 7.31; ε 7.22; ζ 6.86	-0.03
Leu5	8.08	4.30	1.82	γ 1.55; δ 0.97, 0.92	-0.05
Pro6		4.24	2.31 2.08	γ 1.93, 1.85 δ 3.59	-0.20
Asn7	7.73	4.52	2.88 2.81		-0.25
Leu8	7.94	4.04	1.70	γ 1.65; δ 0.97, 0.92	-0.31
Ala9	8.35	3.93	1.43		-0.41
Glu10	7.82	3.95	2.12 2.10	γ 2.46, 2.32	-0.34
Lys11	7.61	3.92	1.95 1.90	γ 1.71, 1.63 δ 1.41 ε 2.98	-0.40
Aib12			1.48		
Leu13	8.09	4.01	1.82	γ 1.63; δ 0.97, 0.91	-0.34
Lys14	7.78	4.11	1.94	γ 1.70, 1.61; δ 1.49 ε 2.98	-0.21
Ser15	7.84	4.67	4.16 4.12		0.18
Leu16	7.86	4.23	1.75	γ 1.61; δ 0.89	-0.12
$-CONH_2$	7.27 6.90				

Table S11: Chemical shift values (p.p.m) of glycopeptides **LYX5320** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.70, 6.98	
D-Thr2	8.59	4.15		γ 0.89	-0.24
Gly3	8.49	3.89			-0.12
Phe4	8.12	4.62	3.08 3.02	δ 7.52; ε 7.17; ζ 6.90	0.00
Leu5	8.29	4.61	1.72	γ 1.58; δ 0.93, 0.91	0.26
Pro6		4.34	3.20 3.12	γ 2.29, 2.02 δ 3.69, 3.63	-0.10
Asn7	8.58	4.66	2.87 2.82		-0.10
Leu8	8.31	4.25	1.68	γ 1.43; δ 0.95, 0.88	-0.10
Ala9	8.24	4.25	1.43		-0.09
Glu10	8.16	4.18	2.03	γ 2.32, 2.28	-0.11
Lys11	8.17	4.14	1.82	γ 1.70; δ 1.52, 1.43 ε 3.00	-0.18
Aib12			1.43		
Leu13	7.76	4.28	1.69	γ 1.61; δ 0.93, 0.88	-0.07
Lys14	8.14	4.29	1.88 1.83	γ 1.70; δ 1.51, 1.45 ε 3.01	-0.03
Ser15	8.45	4.61	4.25 3.97		0.12
Leu16	8.29	4.32	1.71	γ 1.59; δ 0.95, 0.89	-0.03
-$CONH_2$	7.43 7.24				

Table S12: Chemical shift values (p.p.m) of glycopeptides **LYX5320** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1		4.43		δ 7.52, 6.83	-0.13
D-Thr2	8.50	4.32		γ 1.09	-0.07
Gly3	8.36	3.96			-0.05
Phe4	7.91	4.54	3.23 3.05	δ 7.26; ε 7.18; ζ 6.85	-0.08
Leu5	8.19	4.23	1.87	γ 1.65; δ 0.96	-0.12
Pro6		4.20	1.86	γ 1.60; δ 2.27	-0.24
Asn7	7.65	4.46	2.87 2.77		-0.30
Leu8	8.00	4.03	1.66	δ 0.91, 0.87	-0.32
Ala9	8.36	3.96	1.41		-0.38
Glu10	7.93	3.92	2.15 2.10	γ 2.53, 2.35	-0.37
Lys11	7.65	3.89	1.95 1.90	γ 1.67; δ 1.61; ε 2.97	-0.43
Aib12			1.41		
Leu13	8.09	3.98	1.82	γ 1.37; δ 0.88	-0.37
Lys14	7.82	4.09	1.92	γ 1.69, 1.61; δ 1.46 ε 2.98	-0.23
Ser15	7.83	4.70	4.21 4.11		0.21
Leu16	7.87	4.20	1.86	γ 1.60; δ 0.89	-0.15
$-CONH_2$	7.27 6.89				

Table S13: Chemical shift values (p.p.m) of glycopeptides **LYX5400** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.69, 6.99	
D-Thr2		4.17		γ 0.89	-0.22
Gly3	8.47	3.89			-0.12
Phe4	8.12	4.63	3.08 3.03	δ 7.36; ε 7.18; ζ 6.90	0.01
Leu5	8.36	4.31	1.68	γ 1.64; δ 0.96, 0.89	-0.04
Pro6		4.33	3.01	γ 2.29, 2.01 δ 3.69, 3.64	-0.11
Asn7	8.57	4.66	2.87 2.79		-0.10
Leu8	8.33	4.29	1.68	γ 1.64; δ 0.95, 0.88	-0.06
Ala9	8.26	4.27	1.41		-0.07
Glu10	8.24	4.24	2.06 1.99	γ 2.28	-0.05
Lys11	8.36	4.31	1.89 1.81	γ 1.71; δ 1.50, 1.45 ε 3.01	-0.01
Gly12	8.44	3.95			-0.06
Leu13	8.10	4.36	1.66	γ 1.62; δ 0.94, 0.89	0.01
Lys14	8.39	4.33	1.85 1.80	γ 1.70; δ 1.47; ε 3.00	0.01
Ser15	8.58	4.63	4.25 3.95		0.14
Leu16	8.28	4.62	1.59	γ 1.56; δ 0.93, 0.91	0.27
-$CONH_2$	7.45 7.24				

Table S14: Chemical shift values (p.p.m) of glycopeptides **LYX5400** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1		4.45		δ 7.50, 6.84	-0.11
D-Thr2	8.62	4.32		γ 1.15	-0.07
Gly3	8.42	3.91			-0.10
Phe4	7.82	4.57	3.14 3.04	δ 7.29; ε 7.20; ζ 6.86	-0.05
Leu5	7.91	4.40	1.81	γ 1.62, 1.53 δ 0.97, 0.92	0.05
Pro6		4.31	2.27 1.99	γ 1.94, 1.83; δ 3.58	-0.13
Asn7	7.94	4.60	2.82		-0.16
Leu8	7.90	4.07	1.71	γ 1.63; δ 0.92, 0.86	-0.28
Ala9	8.11	4.12	1.44		-0.22
Glu10	7.79	4.16	2.14 2.05	γ 2.38, 2.33	-0.13
Lys11	7.74	4.24	1.91	γ 1.67; δ 1.51; ε 2.98	-0.08
Gly12	7.98	3.93			-0.08
Leu13	8.09	4.23	1.70	γ 1.57; δ 0.93, 0.88	-0.12
Lys14	7.87	4.15	1.86 1.82	γ 1.70; δ 1.49; ε 2.99	-0.17
Ser15	7.98	4.60	4.19 4.00		0.11
Leu16	7.88	4.21	1.76	γ 1.57; δ 0.94, 0.88	-0.14
$-CONH_2$	7.27 7.21				

Table S15: Chemical shift values (p.p.m) of glycopeptides **LYX5420** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.69, 6.99	
D-Thr2	8.59	4.16	4.11	γ 0.89	-0.23
Gly3	8.49	3.89			-0.12
Phe4	8.11	4.62	3.08 3.03	δ 7.36; ε 7.19; ζ 6.90	0.00
Leu5	8.34	4.33	1.66	γ 1.44; δ 0.95, 0.88	-0.02
Pro6		4.34	3.19 3.13	γ 2.28, 2.01 δ 3.67, 3.63	-0.10
Asn7	8.56	4.66	2.87 2.80		-0.10
Leu8	8.32	4.29	1.66	γ 1.63; δ 0.94, 0.87	-0.06
Ala9	8.25	4.27	1.41		-0.07
Glu10	8.23	4.24	2.07 1.99	γ 2.29	-0.05
Lys11	8.35	4.30	1.89 1.81	γ 1.70; δ 1.50; ε 3.00	-0.02
Gly12	8.44	3.95			-0.06
Leu13	8.10	4.35	1.66	γ 1.61; δ 0.94, 0.89	0.00
Lys14	8.39	4.33	1.85 1.80	γ 1.70; δ 1.46; ε 3.00	0.01
Ser15	8.58	4.62	4.25 3.95		0.13
Leu16	8.28	4.61	1.58	γ 1.54; δ 0.93, 0.91	0.26
-$CONH_2$	7.45 7.24				

Table S16: Chemical shift values (p.p.m) of glycopeptides **LYX5420** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1		4.49		δ 7.54, 6.87	-0.07
D-Thr2	8.64	4.36		γ 1.18	-0.03
Gly3	8.44	3.96			-0.05
Phe4	7.87	4.59	3.19 3.08	δ 7.32; ε 7.26; ζ 6.95	-0.03
Leu5	8.00	4.41	1.85 1.68	γ 1.56; δ 1.02, 1.00	0.06
Pro6		4.34	2.31 2.05	γ 1.98, 1.89; δ 3.63	-0.10
Asn7	7.94	4.62	2.85		-0.14
Leu8	7.93	4.10	1.73 1.68	γ 1.46; δ 0.97, 0.91	-0.25
Ala9	8.15	4.14	1.49		-0.20
Glu10	7.84	4.19	2.19 2.12	γ 2.46, 2.42	-0.10
Lys11	7.80	4.26	1.95	γ 1.71; δ 1.54; ε 3.01	-0.06
Gly12	8.05	3.95			-0.06
Leu13	8.09	4.23	1.75	γ 1.55; δ 0.95, 0.90	-0.12
Lys14	7.92	4.19	1.89	γ 1.74; δ 1.54; ε 3.04	-0.13
Ser15	8.02	4.65	4.23 4.05		0.16
Leu16	7.92	4.25	1.82	γ 1.61; δ 0.98, 0.94	-0.10
$-CONH_2$	7.26 6.92				

Table S17: Chemical shift values (p.p.m) of glycopeptides **LYX5500** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.72, 6.98	
D-Thr2	8.59	4.16		γ 0.89	-0.23
Gly3	8.47	3.89			-0.12
Phe4	8.11	4.63	3.08 3.03	δ 7.35; ε 7.19 ζ 6.90	0.01
Leu5	8.36	4.32	1.71	γ 1.63 δ 0.95, 0.89	-0.03
Pro6		4.24	2.28	γ 2.05, 1.98 δ 3.97	-0.20
Asn7	8.59	4.68	2.86 2.79		-0.08
Leu8	8.41	4.34	1.70	γ 1.63; δ 0.94, 0.88	-0.01
Gly9	8.46	3.95			-0.06
Glu10	8.30	4.24	2.06 2.00	γ 2.28	-0.05
Lys11	8.41	4.27	1.85	γ 1.79; δ 1.49, 1.44 ε 3.02	-0.05
Ala12	8.24	4.33	1.33		-0.01
Leu13	8.21	4.32	1.67 1.58	γ 1.39; δ 0.95, 0.90	-0.03
Lys14	8.29	4.33	1.85	γ 1.80; δ 1.46 ε 3.01	0.01
Ser15	8.56	4.63	4.25 3.95		0.14
Leu16	8.28	4.62	1.70	γ 1.58; δ 0.93	0.27
-$CONH_2$	7.45 7.25				

Table S18: Chemical shift values (p.p.m) of glycopeptides **LYX5500** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1		4.45		δ 7.53, 6.84	-0.11
D-Thr2	8.62	4.28		γ 1.14	-0.11
Gly3	8.41	3.89			-0.12
Phe4	7.79	4.58	3.11 3.05	δ 7.27; ε 7.20; ζ 6.86	-0.04
Leu5	7.85	4.49	1.79	γ 1.59, 1.53 δ 0.96, 0.92	0.14
Pro6		4.34	2.26 1.95	γ 1.87, 1.83 δ 3.62, 3.57	-0.10
Asn7	8.08	4.71	2.85 2.78		-0.05
Leu8	7.84	4.13	1.69	γ 1.53; δ 0.96, 0.90	-0.22
Gly9	8.45	3.95 3.79			-0.06
Glu10	7.93	4.16	2.12 2.04	γ 2.36, 2.29	-0.13
Lys11	7.90	4.19	1.91	γ 1.68; δ 1.51, 1.44 ε 2.98	-0.13
Ala12	8.03	4.25	1.41		-0.09
Leu13	8.02	4.16	1.76	γ 1.60; δ 0.92, 0.87	-0.19
Lys14	7.73	4.14	1.86	γ 1.69; δ 1.50, 1.44 ε 3.00	-0.18
Ser15	7.98	4.61	4.18 4.03		0.12
Leu16	7.89	4.22	1.77	γ 1.58; δ 0.93, 0.88	-0.13
$-CONH_2$	7.23 6.89				

Table S19: Chemical shift values (p.p.m) of glycopeptides **LYX5520** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.72, 6.98	
D-Thr2	8.59	4.16		γ 0.89	-0.23
Gly3	8.48	3.89			-0.12
Phe4	8.11	4.63	3.08 3.03	δ 7.35; ε 7.19 ζ 6.90	+0.01
Leu5	8.33	4.33	1.71	γ 1.63 δ 0.95, 0.89	-0.02
Pro6		4.34	3.20 3.12	γ 2.28, 2.01 δ 3.68, 3.63	-0.10
Asn7	8.60	4.67	2.86 2.79		-0.10
Leu8	8.40	4.34	1.70	γ 1.63; δ 0.94, 0.87	-0.01
Gly9	8.47	3.95			-0.06
Glu10	8.30	4.24	2.06 1.99	γ 2.29	-0.05
Lys11	8.40	4.26	1.86 1.79	γ 1.70; δ 1.49, 1.44 ε 3.01	-0.06
Ala12	8.22	4.28	1.39		-0.06
Leu13	8.20	4.32	1.67	γ 1.59; δ 0.95, 0.89	-0.03
Lys14	8.29	4.32	1.85 1.80	γ 1.70; δ 1.46 ε 3.01	0.00
Ser15	8.55	4.63	4.25 3.96		+0.13
Leu16	8.28	4.62	1.59	γ 1.53 δ 0.93, 0.91	+0.27
-$CONH_2$	7.44 7.25				

Table S20: Chemical shift values (p.p.m) of glycopeptides **LYX5520** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1		4.44		δ 7.52, 6.84	-0.12
D-Thr2	8.59	4.28		γ 1.11	-0.11
Gly3	8.39	3.91			-0.10
Phe4	7.81	4.57	3.13 3.05	δ 7.29; ε 7.22; ζ 6.87	-0.05
Leu5	7.88	4.45	1.77	γ 1.57; δ 0.92, 0.88	0.10
Pro6		4.32	2.25 1.94	γ 1.86, 1.82; δ 3.60	-0.12
Asn7	8.03	4.69	2.84 2.78		-0.07
Leu8	7.85	4.12	1.69	γ 1.45; δ 0.93, 0.88	-0.23
Gly9	8.43	3.92 3.79			-0.09
Glu10	7.95	4.14	2.12 2.05	γ 2.38, 2.31	-0.15
Lys11	7.89	4.17	1.89	γ 1.68; δ 1.51; ε 2.82	-0.15
Ala12	8.04	4.23	1.68		-0.11
Leu13	8.02	4.14	1.76	γ 1.60; δ 0.92	-0.21
Lys14	7.74	4.13	1.86	γ 1.69; δ 1.50, 1.45 ε 2.99	-0.19
Ser15	7.97	4.63	4.18 4.06		0.14
Leu16	7.88	4.22	1.77	γ 1.57; δ 0.92, 0.88	-0.13
$-CONH_2$	7.45 7.25				

Table S21: Chemical shift values (p.p.m) of glycopeptides **LYX5600** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.72, 6.98	
D-Thr2	8.58	4.16		γ 0.89	-0.23
Gly3	8.47	3.89			-0.12
Phe4	8.11	4.63	3.08 3.03	δ 7.36; ε 7.19 ζ 6.90	0.01
Leu5	8.29	4.62	1.58	γ 1.54; δ 0.94, 0.91	0.27
Pro6		4.34	3.01	γ 2.28, 2.01 δ 3.69,3.63	-0.10
Asn7	8.60	4.67	2.87 2.79		-0.09
Leu8	8.42	4.34	1.70	γ 1.63; δ 0.94, 0.87	-0.01
Gly9	8.45	3.95			-0.06
Glu10	8.31	4.27	2.07 1.99	γ 2.28	-0.02
Lys11	8.49	4.31	1.89 1.81	γ 1.70; δ 1.50,1.44 ε 3.00	-0.01
Gly12	8.41	3.95			-0.06
Leu13	8.10	4.35	1.65	γ 1.62; δ 0.94, 0.89	0.00
Lys14	8.39	4.33	1.85 1.80	γ 1.70; δ 1.46,1.80 ε 3.00	0.01
Ser15	8.57	4.63	4.25 3.95		0.14
Leu16	8.36	4.33	1.70	γ 1.63; δ 0.95, 0.88	0.01
$-CONH_2$	7.45 7.25				

Table S22: Chemical shift values (p.p.m) of glycopeptides **LYX5600** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.53, 6.83	
D-Thr2	8.62	4.27		γ 1.14	-0.12
Gly3	8.41	3.89			-0.12
Phe4	7.78	4.58	3.08 3.05	δ 7.29; ε 7.21 ζ 6.87	-0.04
Leu5	7.78	4.52	1.77	γ 1.58, 1.53 δ 0.97, 0.93	0.17
Pro6		4.35	2.25	γ 1.95, 1.86 δ 3.60	-0.09
Asn7	8.15	4.73	2.86 2.75		-0.03
Leu8	7.84	4.16	1.71	γ 1.65; δ 0.94, 0.88	-0.19
Gly9	8.38	4.02 3.91			0.01
Glu10	7.99	4.26	2.15 1.99	γ 2.31, 2.27	-0.03
Lys11	7.99	4.31	1.91	γ 1.68; δ 1.49 ε 2.98	0.01
Gly12	7.94	3.95			-0.06
Leu13	8.03	4.18	1.71	γ 1.57; δ 0.94, 0.88	-0.17
Lys14	7.92	4.14	1.86 1.82	γ 1.71; δ 1.49, 1.44 ε 3.00	-0.18
Ser15	7.95	4.59	4.20 3.97		0.10
Leu16	7.89	4.21	1.80 1.78	γ 1.57 δ 0.94, 0.88	-0.14
$-CONH_2$	7.20 6.86				

Table S23: Chemical shift values (p.p.m) of glycopeptides **LYX5620** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.72, 6.98	
D-Thr2	8.58	4.16		γ 0.89	-0.23
Gly3	8.48	3.89			-0.12
Phe4	8.11	4.63	3.08 3.03	δ 7.36; ε 7.19 ζ 6.90	0.01
Leu5	8.28	4.62	1.58	γ 1.54; δ 0.93, 0.91	0.27
Pro6		4.34	3.20 3.12	γ 2.28, 2.01 δ 3.69,3.63	-0.10
Asn7	8.60	4.68	2.86 2.78		-0.08
Leu8	8.42	4.34	1.70	γ 1.63; δ 0.94, 0.87	-0.01
Gly9	8.45	3.95			-0.06
Glu10	8.31	4.27	2.07 1.99	γ 2.28	-0.02
Lys11	8.49	4.31	1.89 1.81	γ 1.72; δ 1.50,1.44 ε 3.01	-0.01
Gly12	8.42	3.93			-0.08
Leu13	8.11	4.35	1.66	γ 1.61; δ 0.94, 0.89	0.00
Lys14	8.39	4.33	1.85 1.80	γ 1.70; δ 1.46 ε 3.00	0.01
Ser15	8.57	4.63	4.25 3.94		0.14
Leu16	8.34	4.33	1.70	γ 1.62; δ 0.95, 0.88	-0.02
$-CONH_2$	7.45 7.25				

Table S24: Chemical shift values (p.p.m) of glycopeptides **LYX5620** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.52, 6.83	
D-Thr2	8.60	4.27		γ 1.12	-0.12
Gly3	8.40	3.89			-0.12
Phe4	7.78	4.57	3.09 3.04	δ 7.28; ε 7.27 ζ 7.2	-0.05
Leu5	7.79	4.50	1.77	γ 1.57, 1.52 δ 0.97, 0.92	0.15
Pro6		4.34	2.25 1.95	γ 1.86, 1.82 δ 3.61	-0.10
Asn7	8.13	4.72	2.85 2.75		-0.04
Leu8	7.84	4.16	1.70	γ 1.57; δ 0.94, 0.88	-0.19
Gly9	8.37	4.01 3.90			0.00
Glu10	7.98	4.25	2.14 1.99	γ 2.32, 2.28	-0.04
Lys11	7.99	4.30	1.90	γ 1.68; δ 1.48 ε 2.98	-0.02
Gly12	7.95	3.96			-0.05
Leu13	8.03	4.17	1.65	γ 1.57; δ 0.94, 0.88	-0.18
Lys14	7.92	4.14	1.86 1.81	γ 1.70; δ 1.48, 1.43 ε 2.99	-0.18
Ser15	7.94	4.60	4.20 3.99		0.11
Leu16	7.88	4.20	1.80 1.76	γ 1.58, 1.55 δ 0.94, 0.87	-015
$-CONH_2$	7.20 6.86				

Table S25: Chemical shift values (p.p.m) of glycopeptides **MD100H(LYX100)** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.70, 6.99	
D-Thr2		4.10			-0.29
Gly3	8.48	3.89			-0.13
Phe4	8.12	4.63	3.09 3.03	δ 7.36; ε 7.19; ζ 6.90	-0.01
Leu5	8.30	4.62	1.61 1.59	γ 1.55, 1.53 δ 0.94, 0.91	0.27
Pro6		4.33	3.19 3.14	γ 2.29, 2.02 δ 3.69, 3.64	-0.11
Asn7	8.57	4.66	2.85 2.80		-0.11
Leu8	8.28	4.23	1.66	γ 1.58; δ 0.95, 0.88	-0.12
Aib9			1.46		
Glu10	8.36	4.16	2.10 2.04	γ 2.30	-0.13
Lys11	8.08	4.25	1.93 1.85	γ 1.70; δ1.45; ε 3.01	-0.07
Ala12	7.96	4.29	1.42		-0.05
Leu13	8.10	4.32	1.70	γ 1.42; δ 0.96, 0.89	-0.03
Lys14	8.28	4.33	1.86	γ 1.80; δ 1.70; ε 3.02	0.01
Ser15	8.56	4.63	4.26 3.96		0.14
Leu16	8.36	4.33	1.70 1.62	γ 1.47; δ 0.96, 0.89	-0.02
$-CONH_2$	7.45 7.25				

Table S26: Chemical shift values (p.p.m) of glycopeptides **MD100H(LYX100)** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

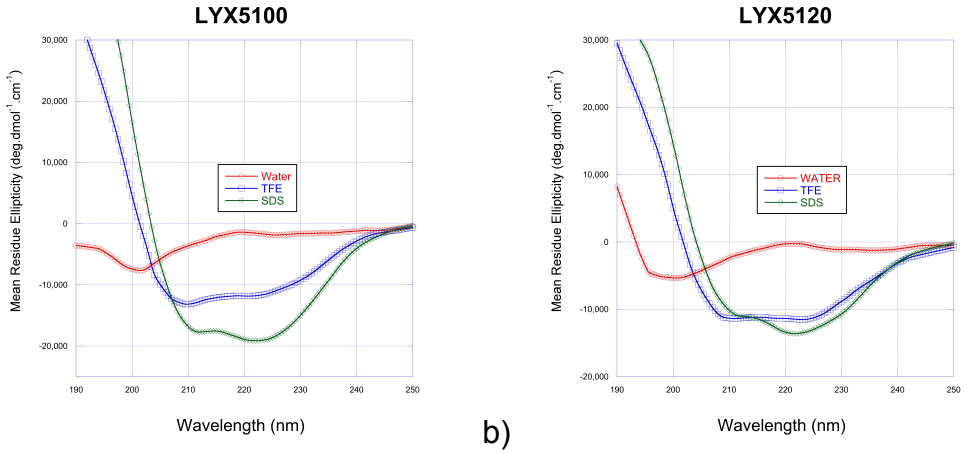
Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1		4.46		δ 7.52, 6.85	-0.10
D-Thr2	8.61	4.34		γ 1.15	-0.05
Gly3	8.42	3.94			-0.07
Phe4	7.86	4.58	3.21 3.06	δ 7.30; ε 7.23; ζ 6.88	-0.04
Leu5	8.07	4.31	1.86	γ 1.65; δ 0.99	-0.31
Pro6		4.25	2.30 2.08	γ 1.93; δ 3.59	-0.19
Asn7	7.66	4.52	2.86 2.80		-0.24
Leu8	7.83	3.99	1.67	γ 1.64; δ 0.94, 0.90	-0.36
Aib9			1.49		
Glu10	7.71	3.97	2.12	γ 2.45, 2.37	-0.32
Lys11	7.80	4.03	2.00 1.91	γ 1.70; δ1.45; ε 2.99	-0.29
Ala12	8.01	4.19	1.44		-0.15
Leu13	8.03	4.15	1.79	γ 1.54, 1.48; δ 0.90	-0.20
Lys14	7.84	4.14	1.91	γ 1.70; δ 1.61; ε 3.00	-0.18
Ser15	7.95	4.63	4.16 4.08		0.14
Leu16	7.91	4.24	1.76	γ 1.60; δ 0.92, 0.89	-0.11
$-CONH_2$	7.25 6.92				

Table S27: Chemical shift values (p.p.m) of glycopeptides **MD120H(LYX120)** as measured in H_2O:D_2O (9:1) at 3.1mM concentration, pH=5.5 and at 15 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1				δ 7.69, 6.98	
D-Thr2	8.58	4.15	4.11	γ 0.89	-0.24
Gly3	8.48	3.96			-0.05
Phe4	8.12	4.63	3.08 3.03	δ 7.35; ε 7.19; ζ 6.90	0.01
Leu5	8.29	4.61	1.59	γ 1.54; δ 0.94, 0.91	0.26
Pro6		4.34	3.20 3.12	γ 2.28, 2.02 δ 3.68, 3.63	-0.10
Asn7	8.56	4.65	2.84 2.80		-0.11
Leu8	8.25	4.22	1.66	γ 1.60; δ 0.95, 0.87	-0.13
Aib9					
Glu10	8.33	4.16	2.09 2.03	γ 2.30	-0.13
Lys11	8.07	4.24	1.92 1.84	γ 1.69; δ 1.54,1.45 ε 3.01	-0.08
Ala12	7.97	4.28	1.42		-0.06
Leu13	8.08	4.32	1.70	γ 1.60; δ 0.95, 0.90	-0.03
Lys14	8.26	4.33	1.86 1.80	γ 1.70; δ 1.47; ε 3.01	0.01
Ser15	8.54	4.63	4.25 3.96		0.14
Leu16	8.33	4.33	1.71	γ 1.63; δ 0.95, 0.89	-0.02
$-CONH_2$	7.44 7.24				

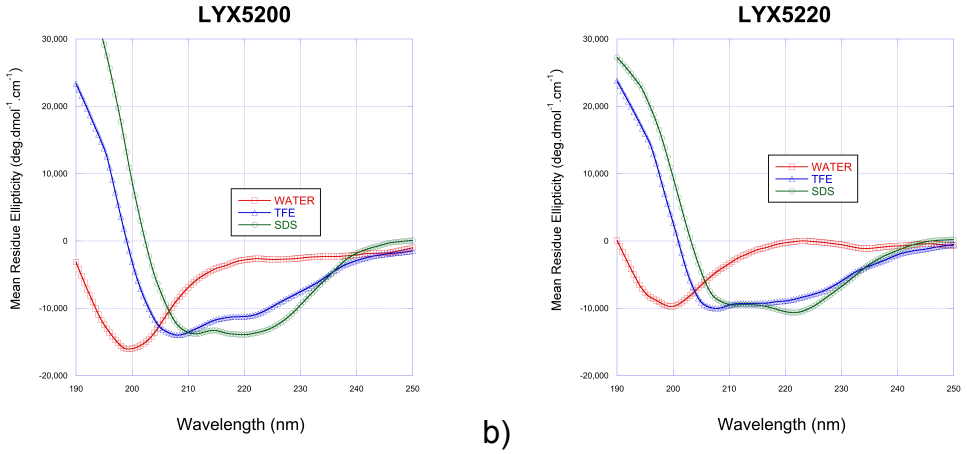
Table S28: Chemical shift values (p.p.m) of glycopeptides **MD120H(LYX120)** as measured in SDS micelle at 3.3mM concentration, pH=5.5 and at 30 °C.

Residue	NH ppm	$C_\alpha H$ ppm	$C_\beta H$ ppm	Others ppm	Δδ(Obs.-r.c.) ppm
Tyr1		4.45		δ 7.52, 6.82	-0.11
D-Thr2	8.54	4.34		γ 1.12	-0.05
Gly3	8.38	3.97			-0.04
Phe4	7.91	4.54	3.24 3.04	δ 7.27; ε 7.21; ζ 6.86	-0.08
Leu5	8.17	4.25	1.87 1.67	γ 1.52, 1.42 δ 0.99, 0.93	-0.10
Pro6		4.24	2.27 2.11	γ 1.91, 1.84 δ 3.58	-0.20
Asn7	7.59	4.48	2.86 2.76		-0.28
Leu8	7.87	3.97	1.65	γ 1.59; δ 0.92, 0.88	-0.38
Aib9			1.48		
Glu10	7.76	3.93	2.12	γ 2.48, 2.36	-0.36
Lys11	7.81	4.01	2.00 1.91	γ 1.66; δ 1.46 ε 2.98	-0.31
Ala12	8.04	4.17	1.44		-0.17
Leu13	7.86	4.13	1.80	γ 1.61; δ 0.90	-0.22
Lys14	7.78	4.11	1.90	γ 1.70; δ 1.55, 1.46 ε 3.00	-0.21
Ser15	7.92	4.65	4.13		0.16
Leu16	7.90	4.22	1.77	γ 1.61, 1.58 δ 0.92, 0.89	-0.13
$-CONH_2$	7.25 6.90				



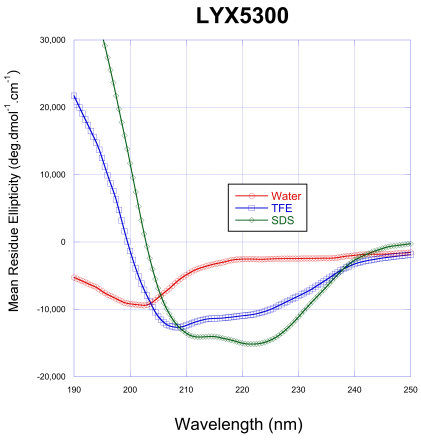
a) b)

Figure S3: Far-UV CD spectra of glycopeptides a) **LYX5100** and b) **LYX5120** as a function of Water, 30%TFE and SDS solution.

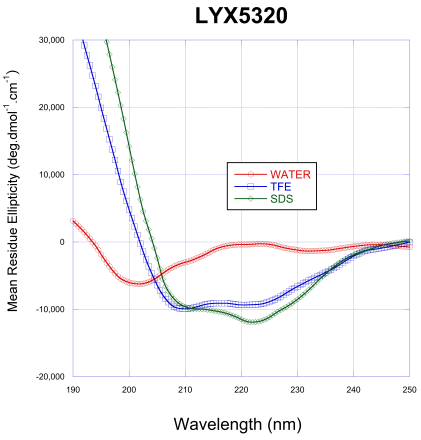


a) b)

Figure S3: Far-UV CD spectra of glycopeptides a) **LYX5200** and b) **LYX5220** as a function of Water, 30%TFE and SDS solution.

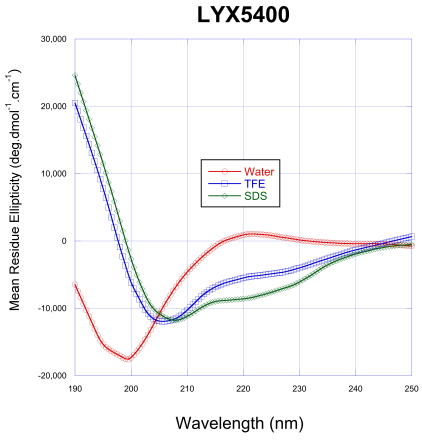


a)

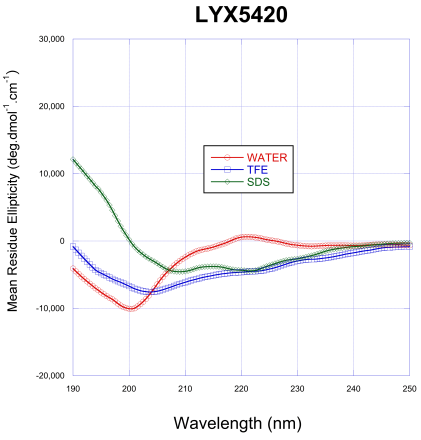


b)

Figure S3: Far-UV CD spectra of glycopeptides a) **LYX5300** and b) **LYX5320** as a function of Water, 30%TFE and SDS solution.

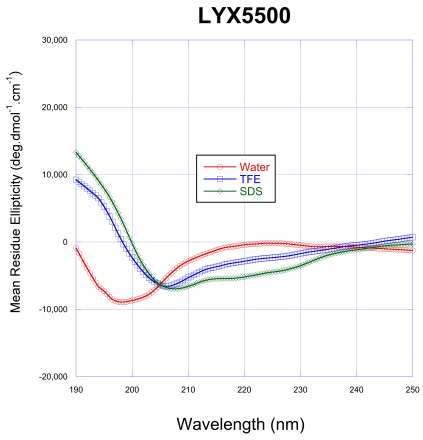


a)

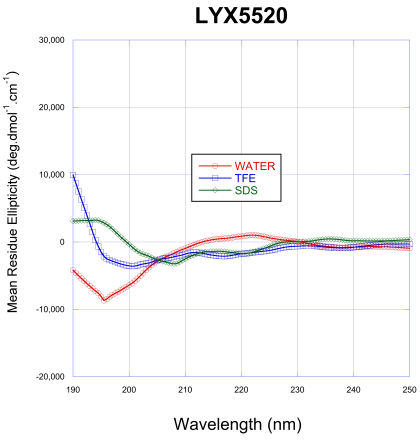


b)

Figure S4: Far-UV CD spectra of glycopeptides a) **LYX5400** and b) **LYX5420** as a function of Water, 30%TFE and SDS solution.

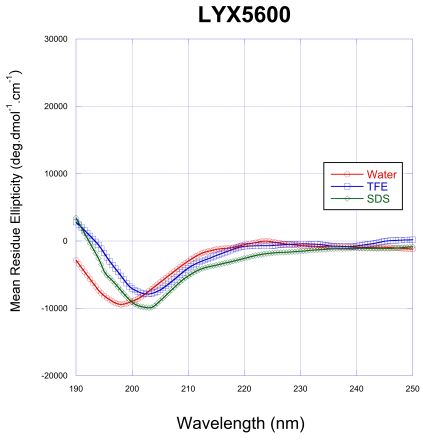


a)

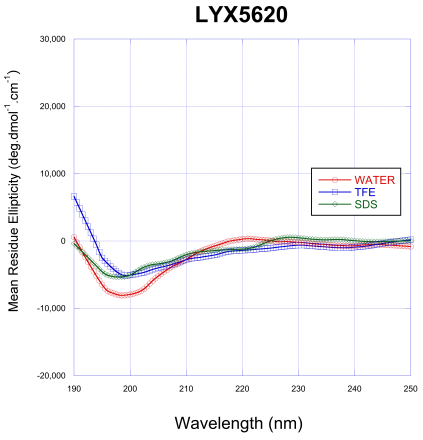


b)

Figure S5: Far-UV CD spectra of glycopeptides a) **LYX5500** and b) **LYX5520** as a function of Water, 30%TFE and SDS solution.

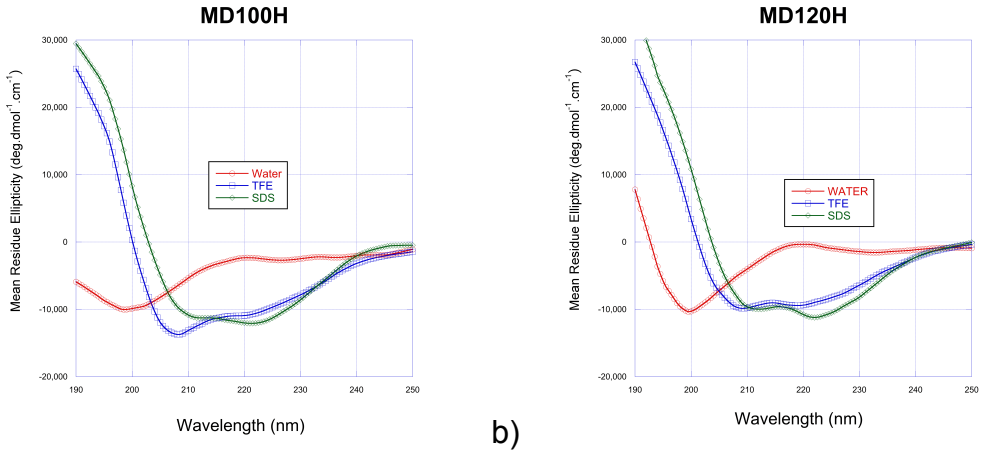


a)



b)

Figure S6: Far-UV CD spectra of glycopeptides a) **LYX5600** and b) **LYX5620** as a function of Water, 30%TFE and SDS solution.



a) b)

Figure S7: Far-UV CD spectra of glycopeptides a**) MD100H(LYX100)** and b) **MD120H(LYX120)** as a function of Water, 30%TFE and SDS solution.

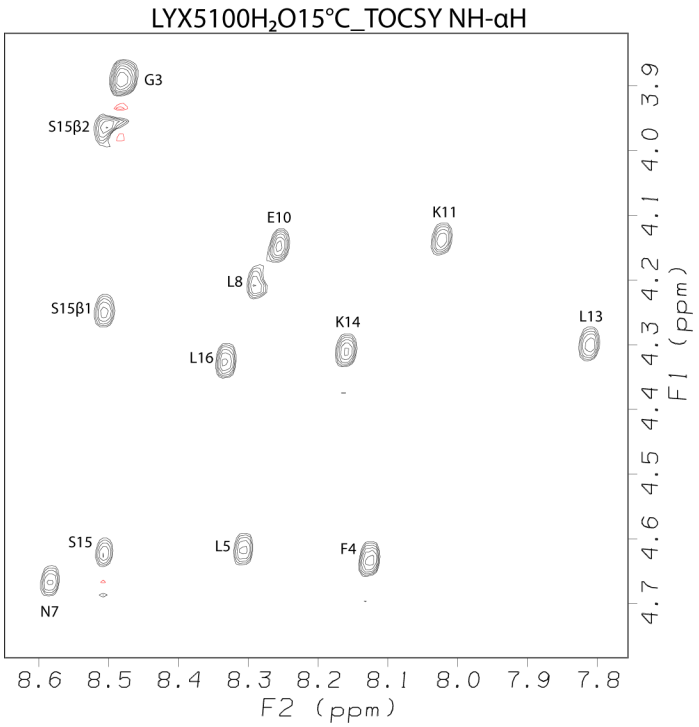


Figure S8: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5100** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

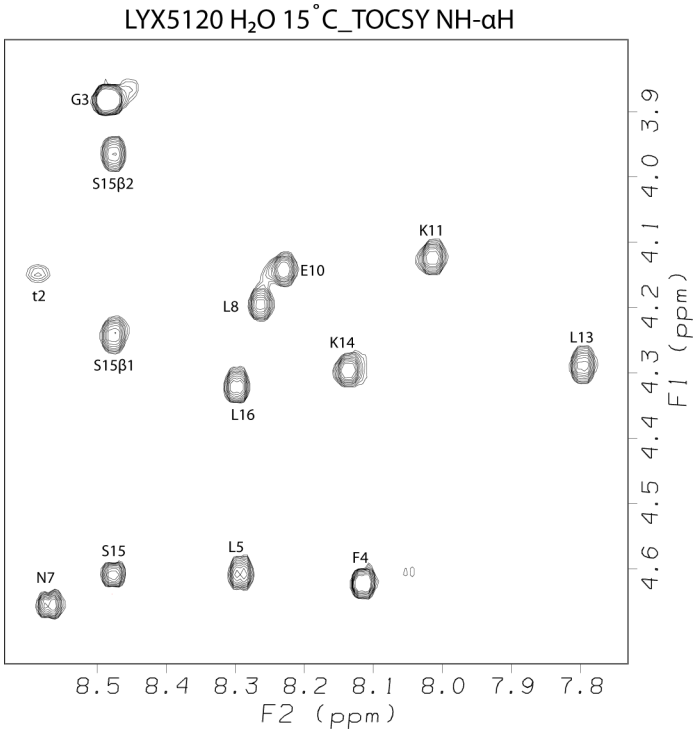


Figure S9: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5120** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

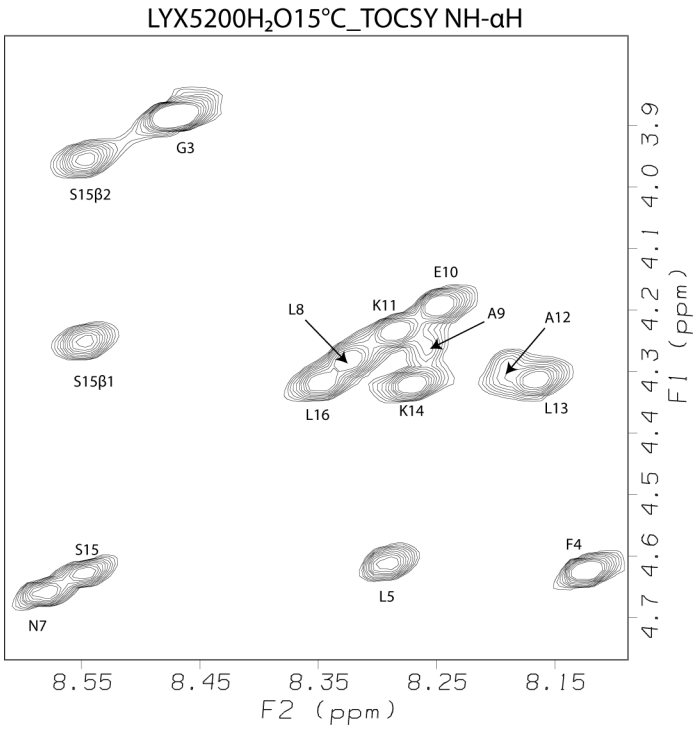


Figure S10: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5200** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

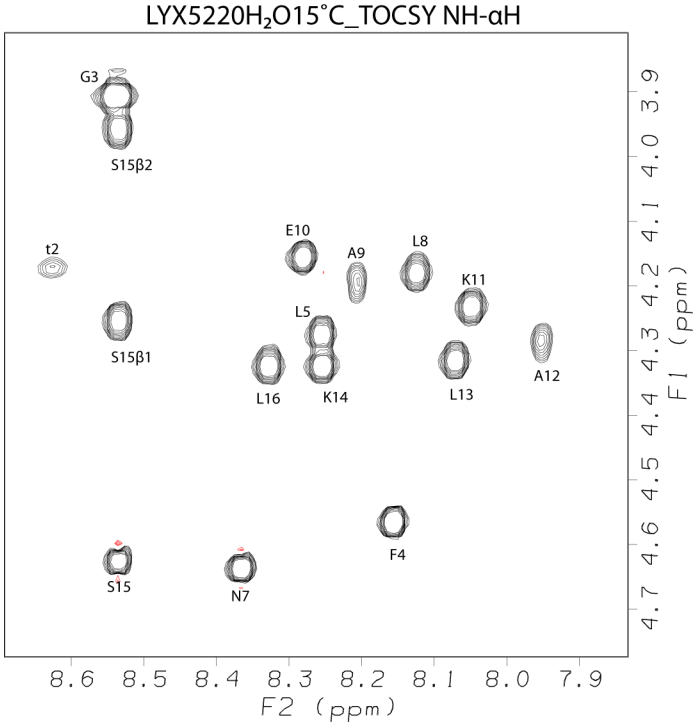


Figure S11: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5220** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

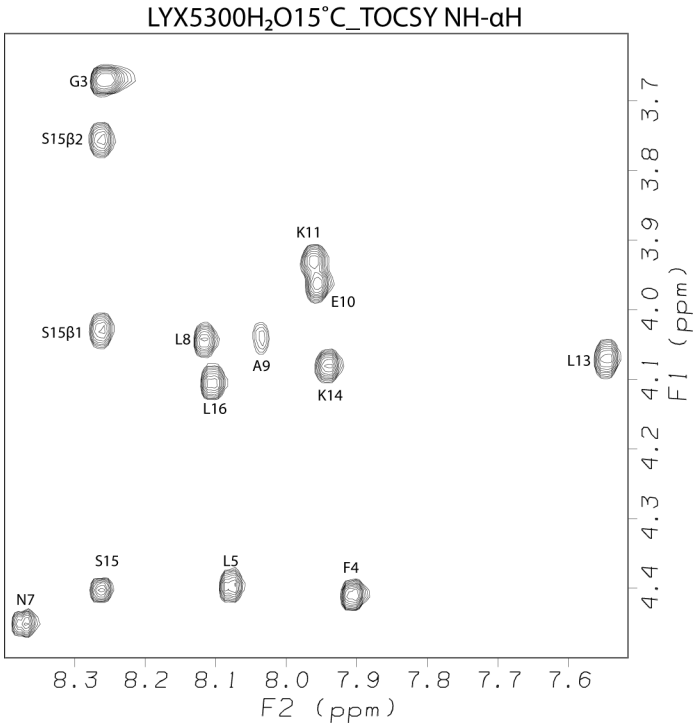


Figure S12: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5300** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

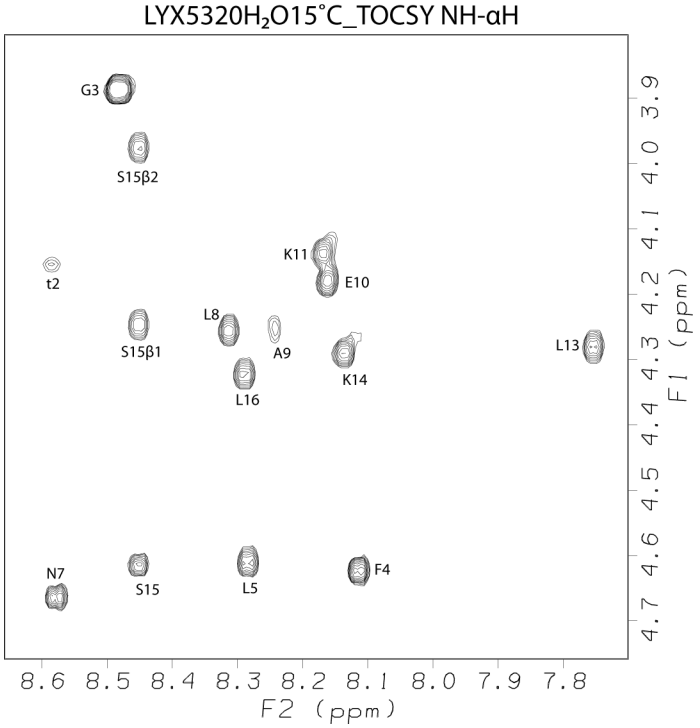


Figure S13: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5320** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

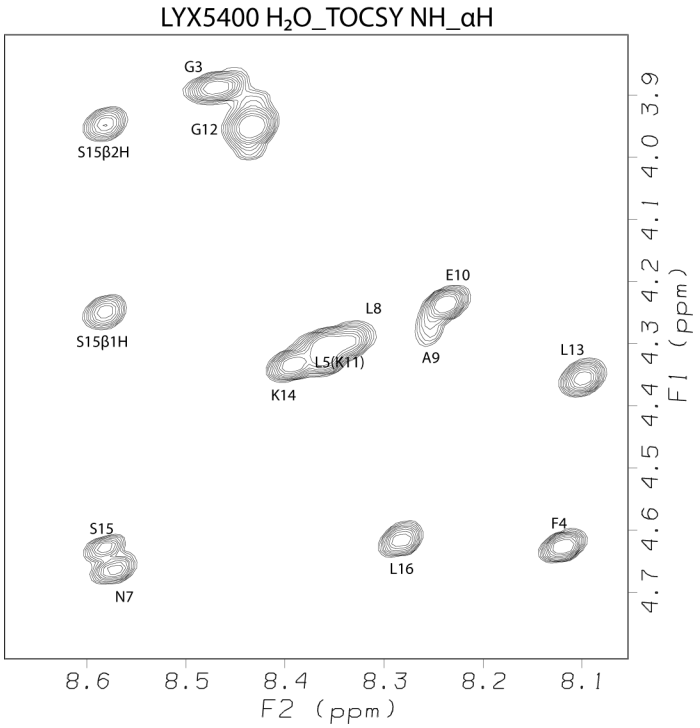


Figure S14: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5400** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

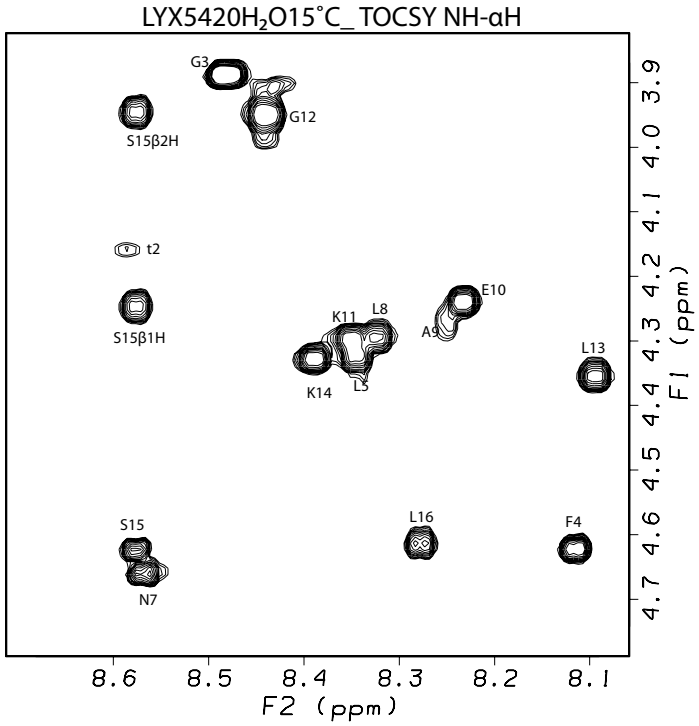


Figure S15: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5420** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

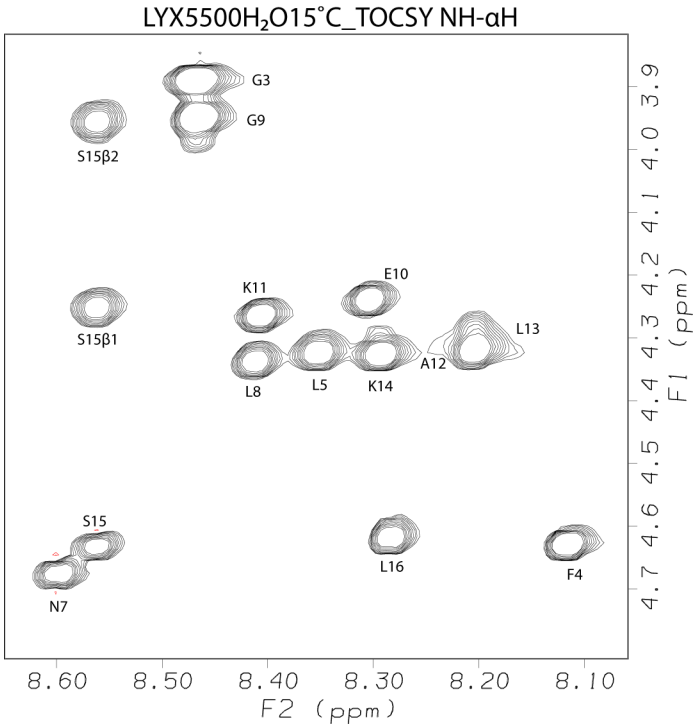


Figure S16: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5500** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

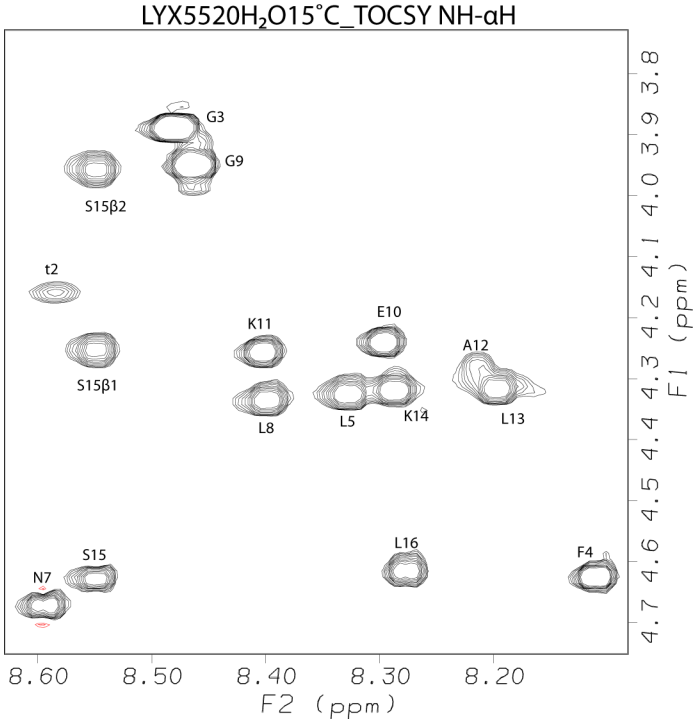


Figure S17: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5520** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

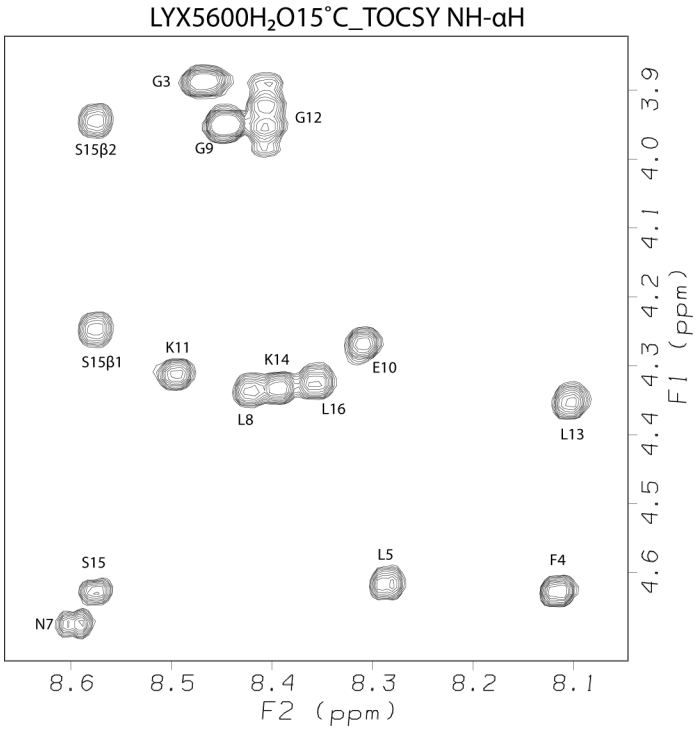


Figure S18: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5600** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

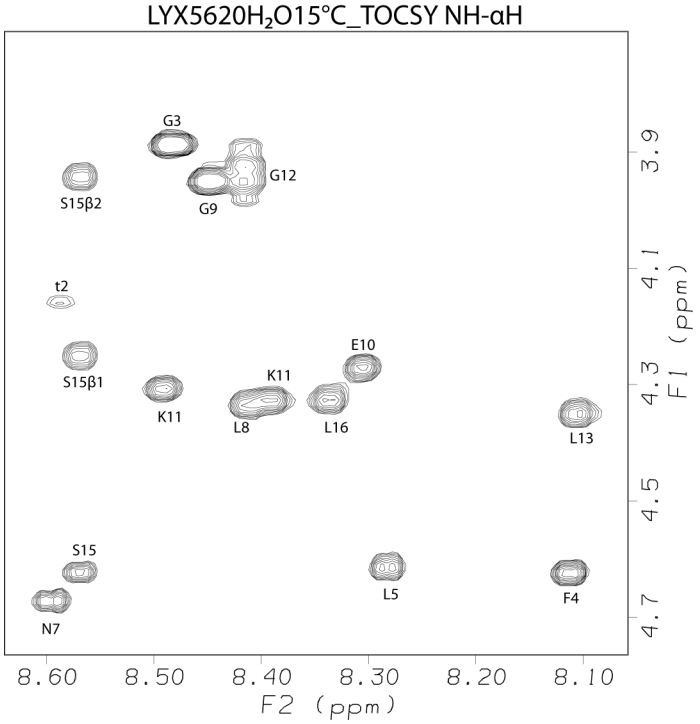


Figure S19: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **LYX5620** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

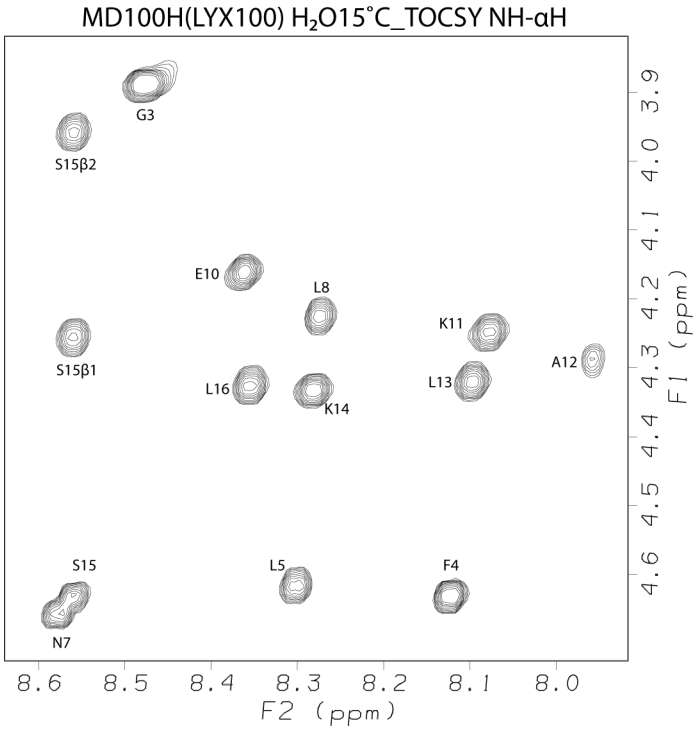


Figure S20: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **MD100H(LYX100)** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

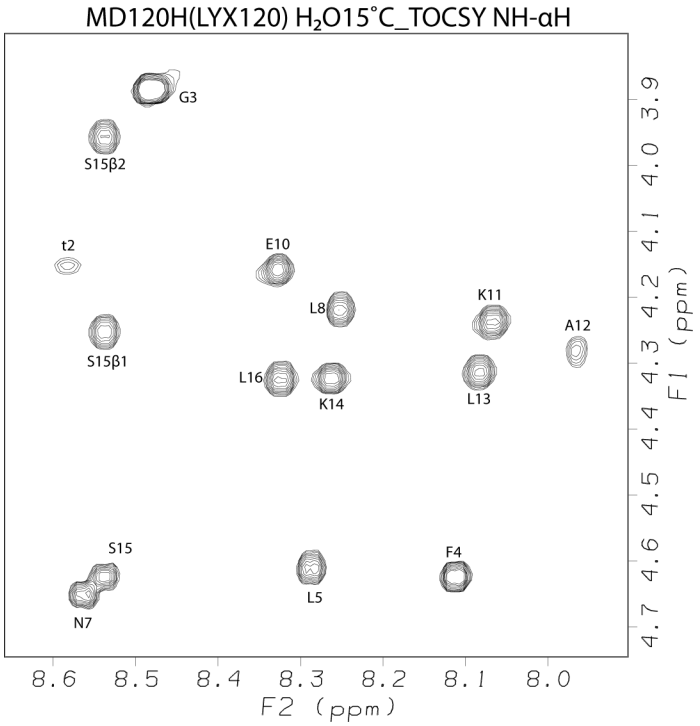


Figure S21: Finger print (NH-αH) region of TOCSY (mixing time = 300ms) spectra of glycopeptide **MD120H(LYX120)** in H_2O:D_2O(9:1) at pH=5.5 at 15°C.

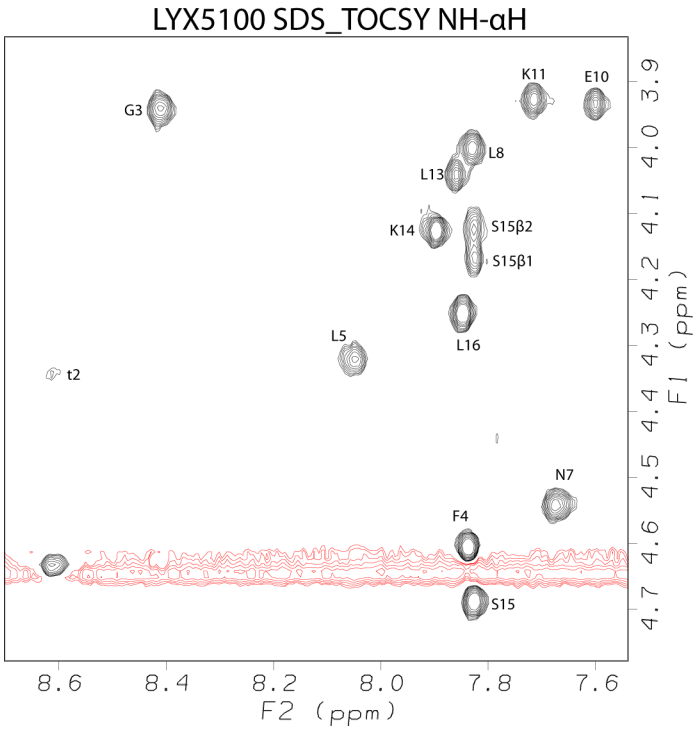


Figure S22. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5100** in SDS micelle at pH=5.5 at 30°C.

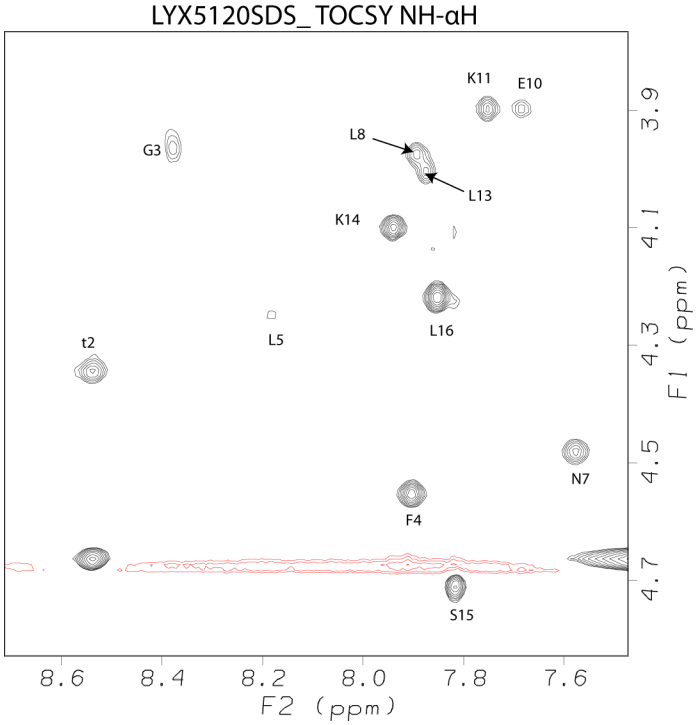


Figure S23. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5120** in SDS micelle at pH=5.5 at 30°C.

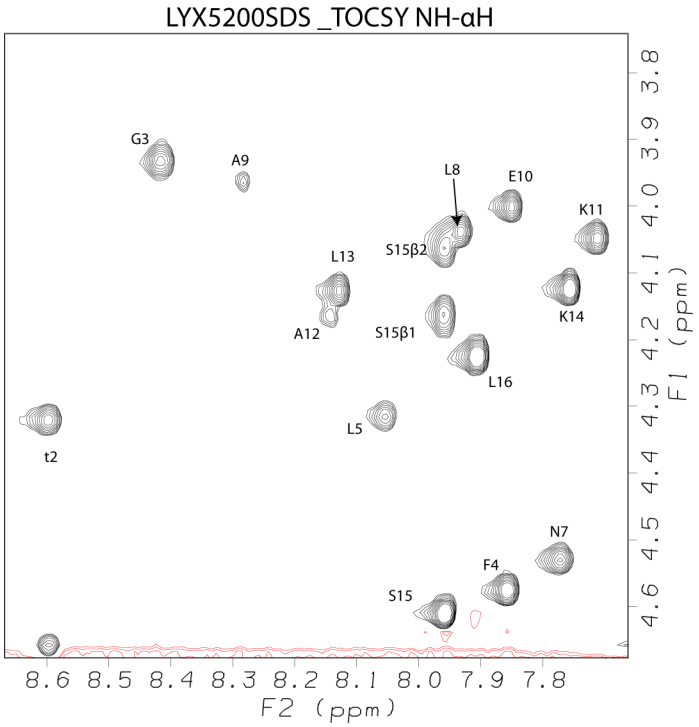


Figure S24. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5200** in SDS micelle at pH=5.5 at 30°C.

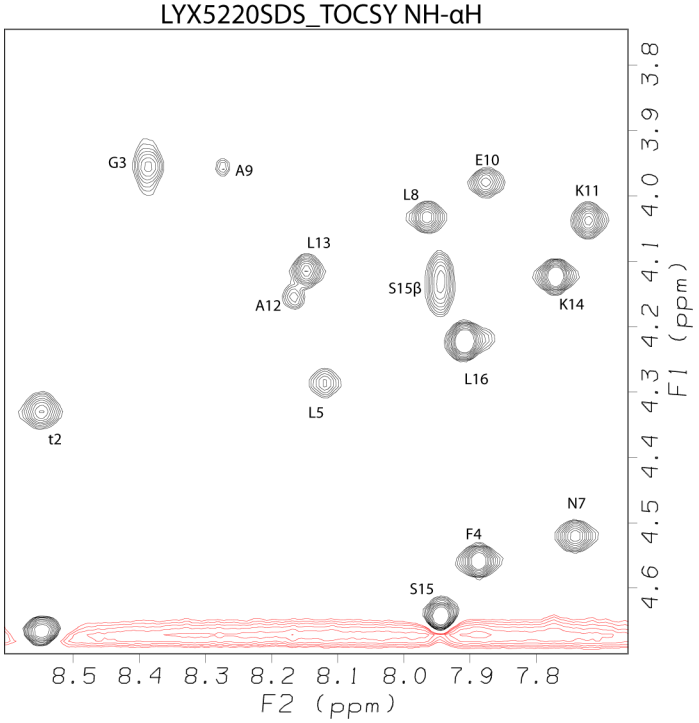


Figure S25. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5220** in SDS micelle at pH=5.5 at 30°C.

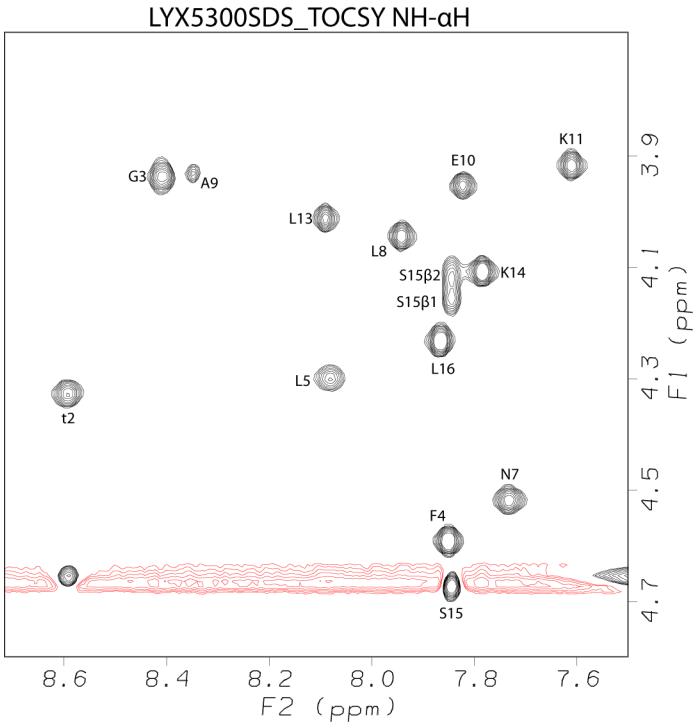


Figure S26. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5300** in SDS micelle at pH=5.5 at 30°C.

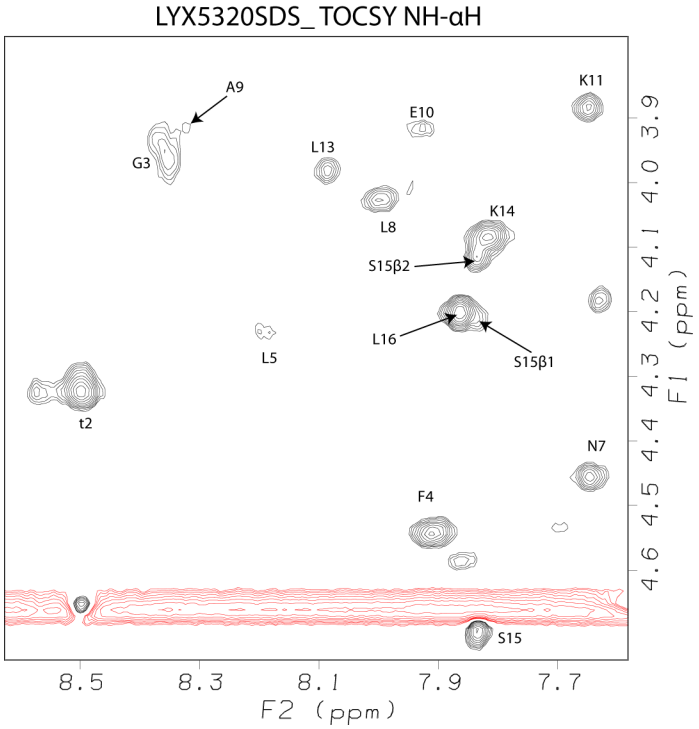


Figure S27. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5320** in SDS micelle at pH=5.5 at 30°C.

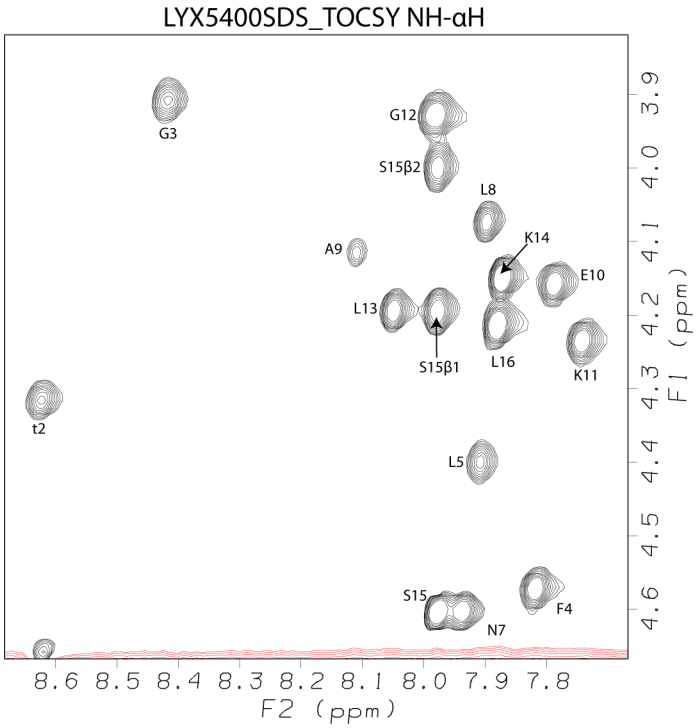


Figure S28. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5400** in SDS micelle at pH=5.5 at 30°C.

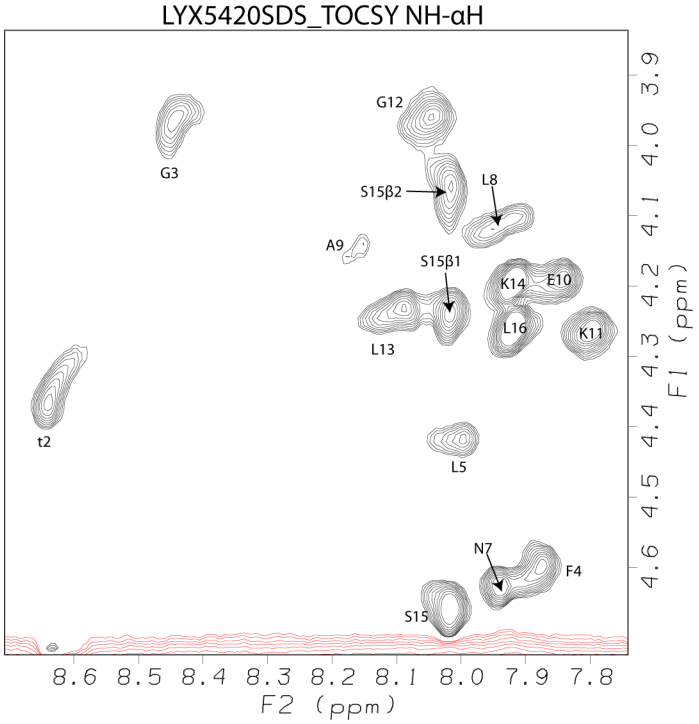


Figure S29. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5420** in SDS micelle at pH=5.5 at 30°C.

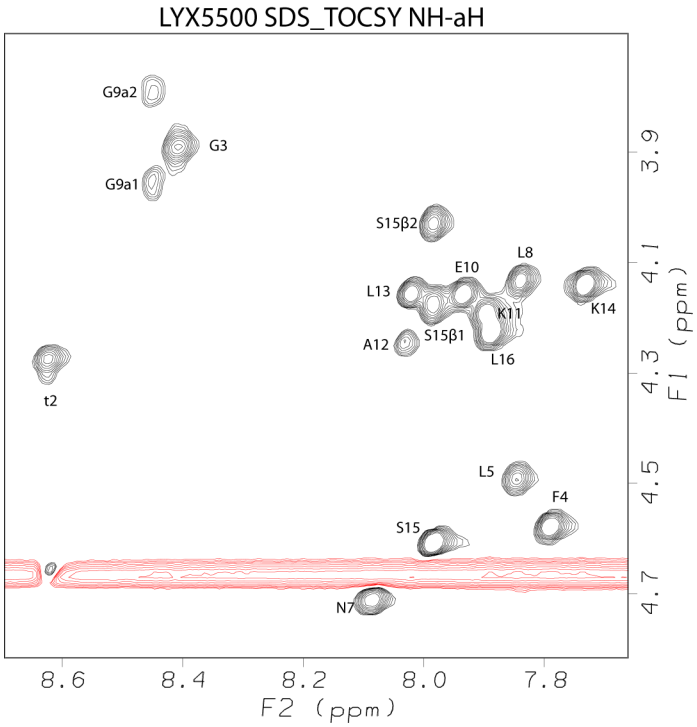


Figure S30. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5500** in SDS micelle at pH=5.5 at 30°C.

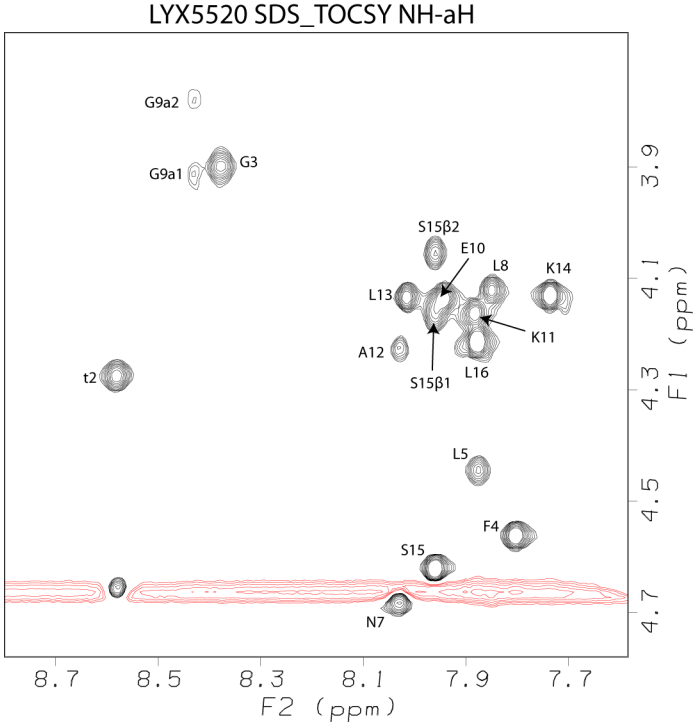


Figure S31. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5520** in SDS micelle at pH=5.5 at 30°C.

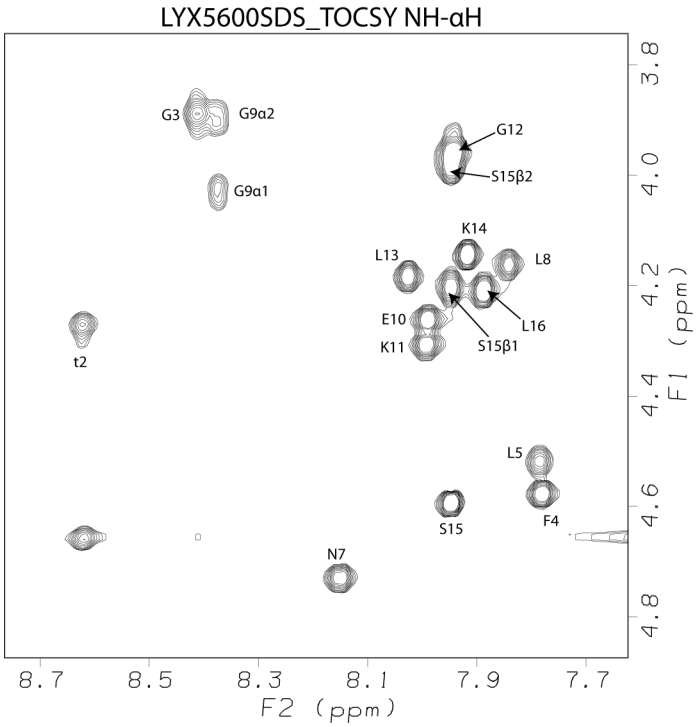


Figure S32. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5600** in SDS micelle at pH=5.5 at 30°C.

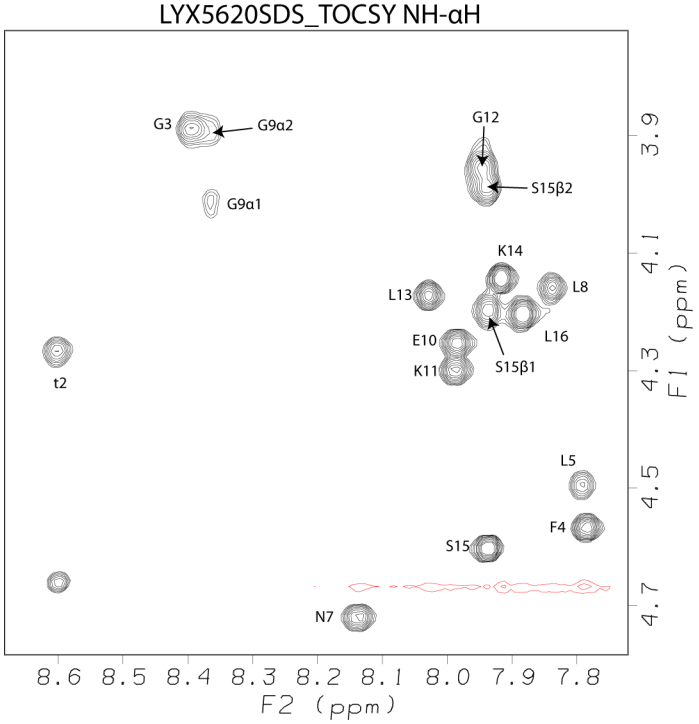


Figure S33. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **LYX5620** in SDS micelle at pH=5.5 at 30°C.

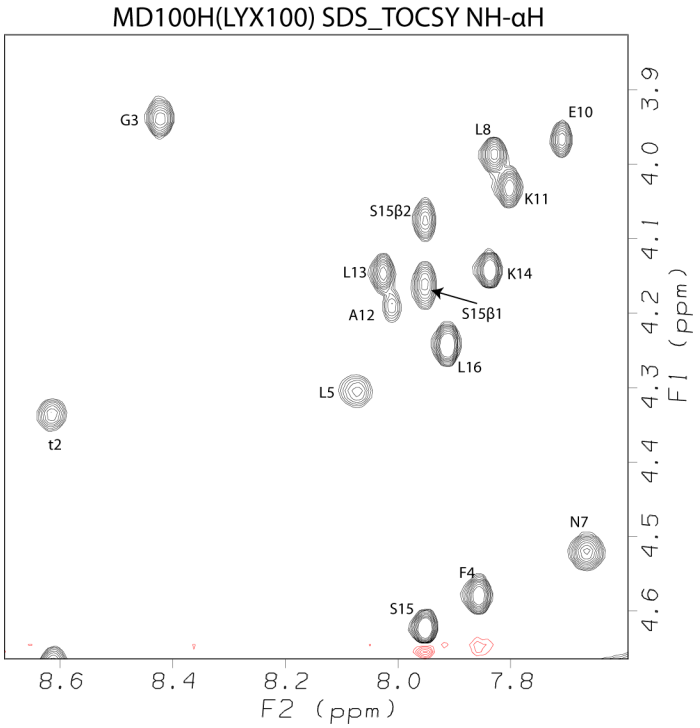


Figure S34. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **MD100H(LYX100)** in SDS micelle at pH=5.5 at 30°C.

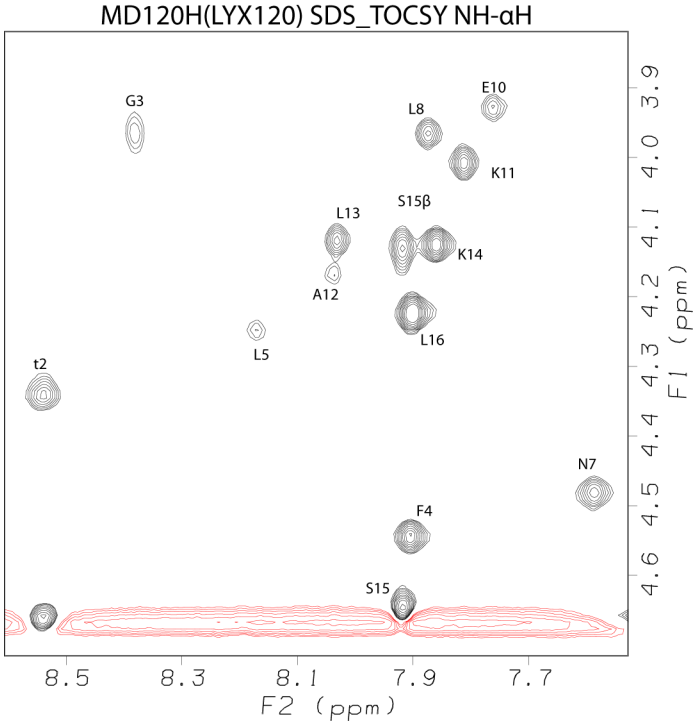


Figure S35. Finger print region of (NH-αH) of TOCSY (mixing time = 150ms) spectra of glycopeptide **MD120H(LYX120)** in SDS micelle at pH=5.5 at 30°C.

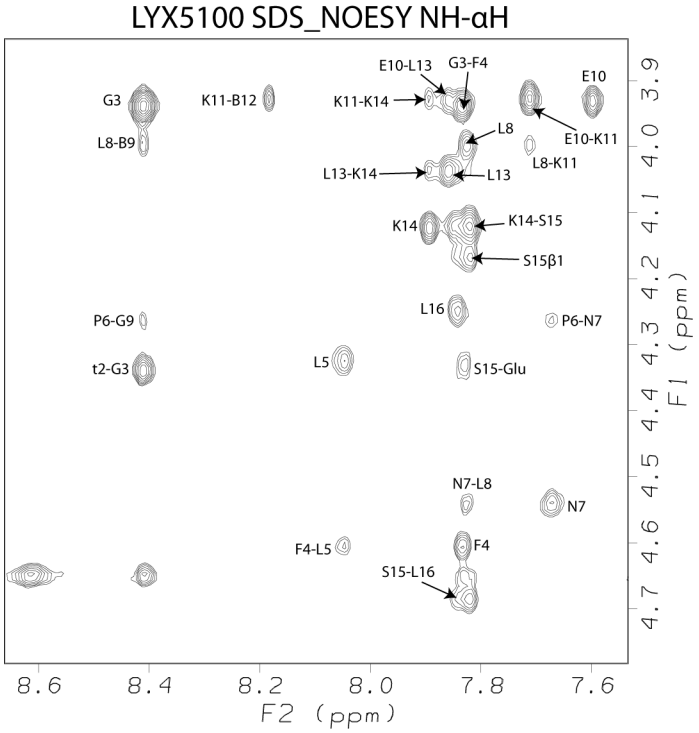


Figure S36: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5100** in SDS micelle at pH=5.5 at 30°C.

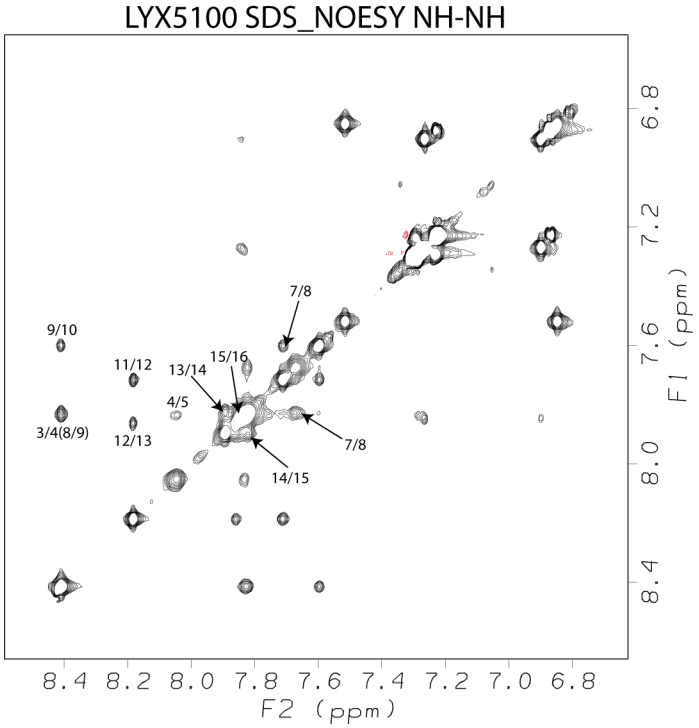


Figure S37: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5100** in SDS micelle at pH=5.5 at 30°C.

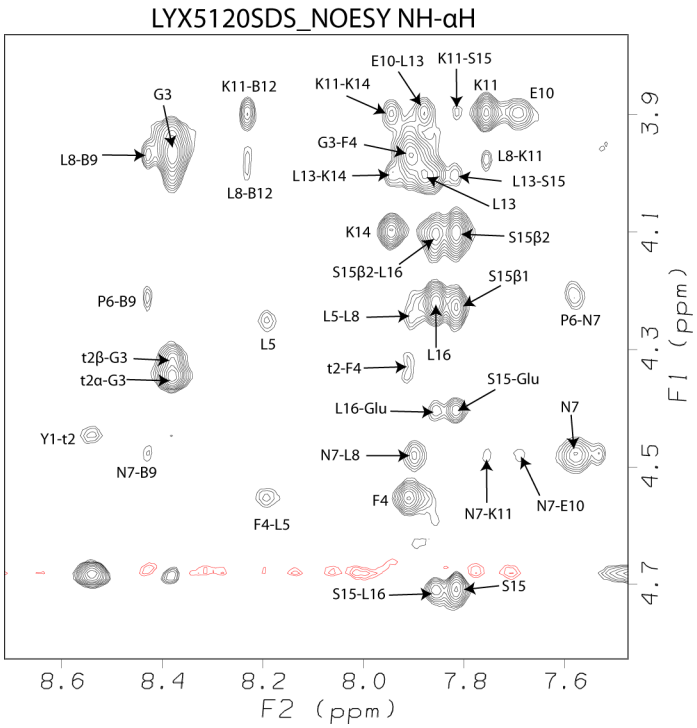


Figure S38: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5120** in SDS micelle at pH=5.5 at 30°C.

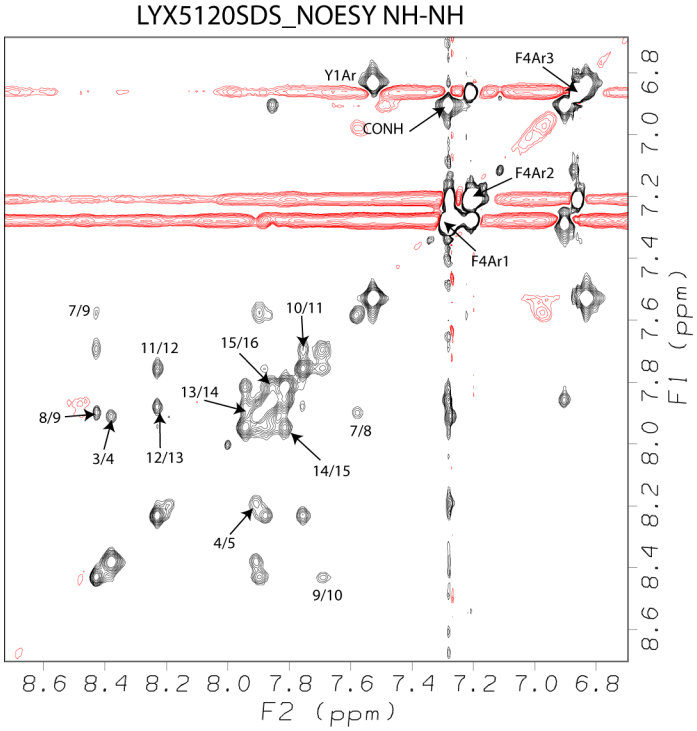


Figure S39: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5120** in SDS micelle at pH=5.5 at 30°C.

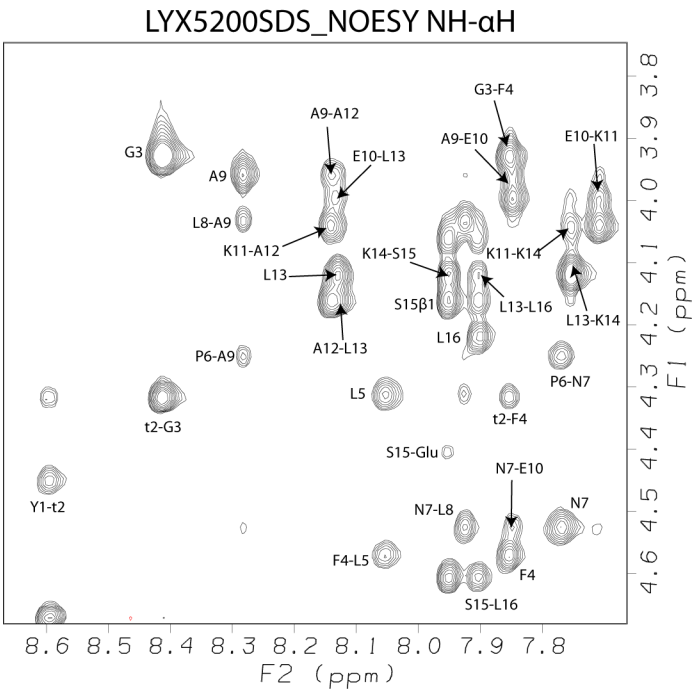


Figure S40: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5200** in SDS micelle at pH=5.5 at 30°C.

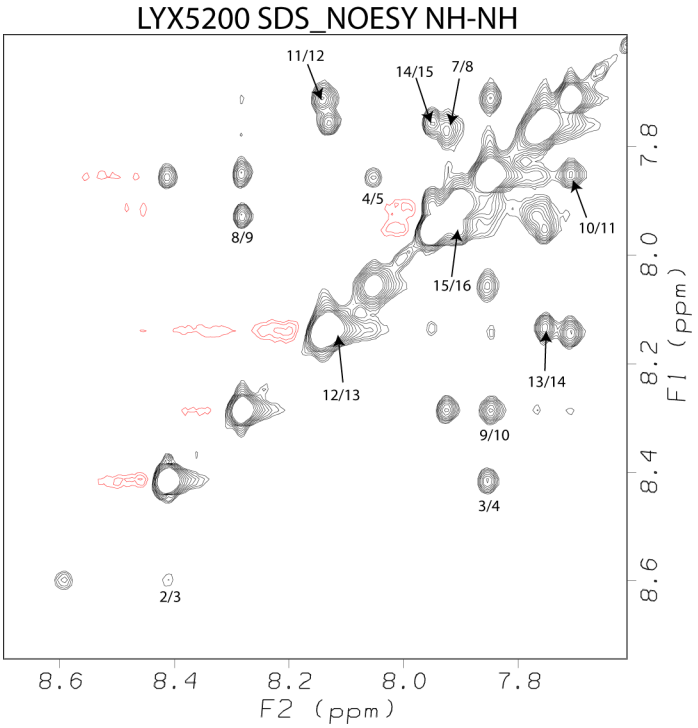


Figure S41: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5200** in SDS micelle at pH=5.5 at 30°C.

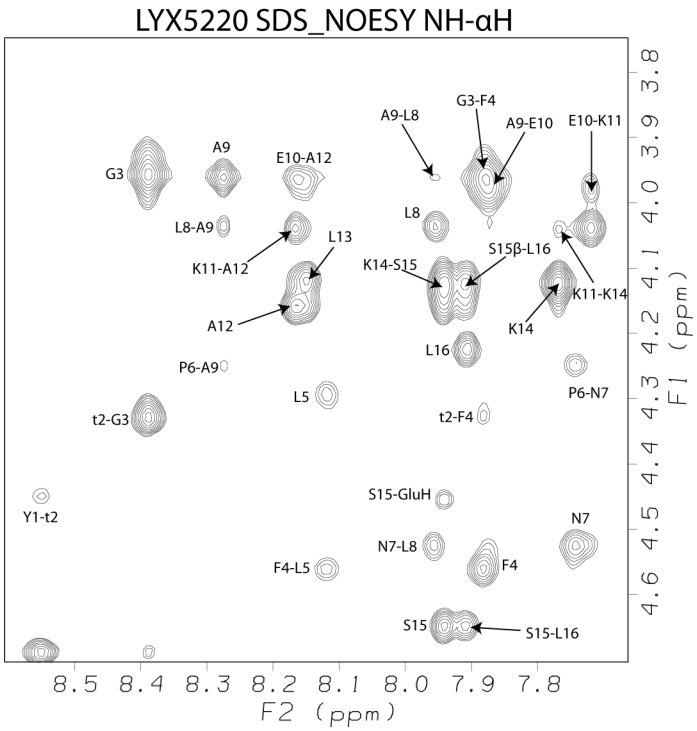


Figure S42: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5220** in SDS micelle at pH=5.5 at 30°C.

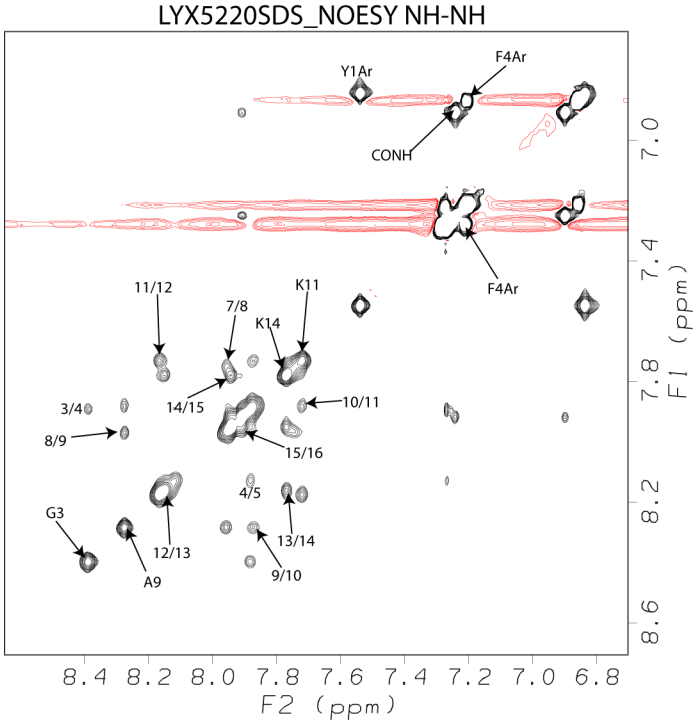


Figure S43: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5220** in SDS micelle at pH=5.5 at 30°C.

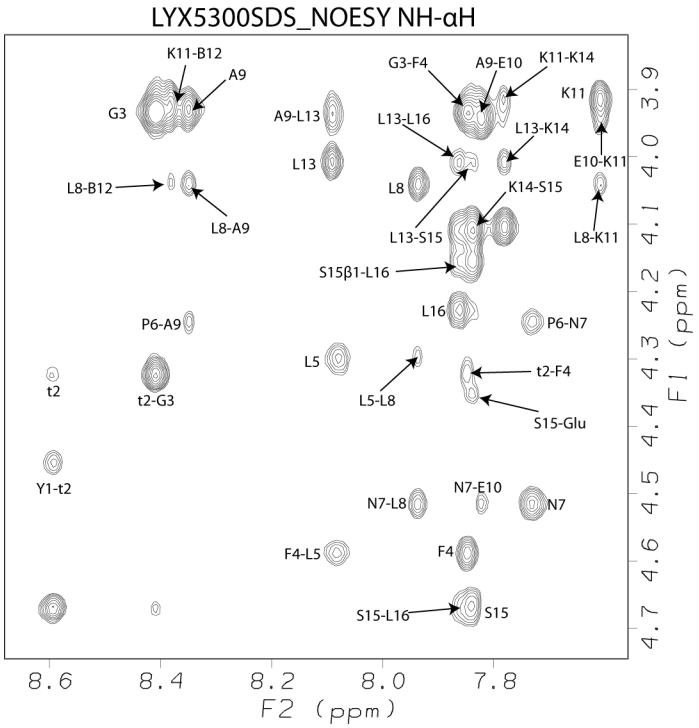


Figure S44: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5300** in SDS micelle at pH=5.5 at 30°C.

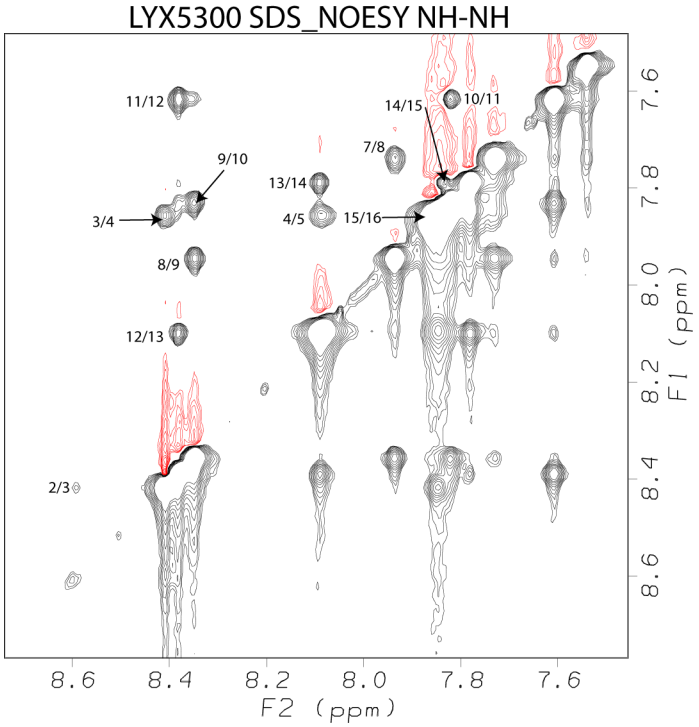


Figure S45: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5300** in SDS micelle at pH=5.5 at 30°C.

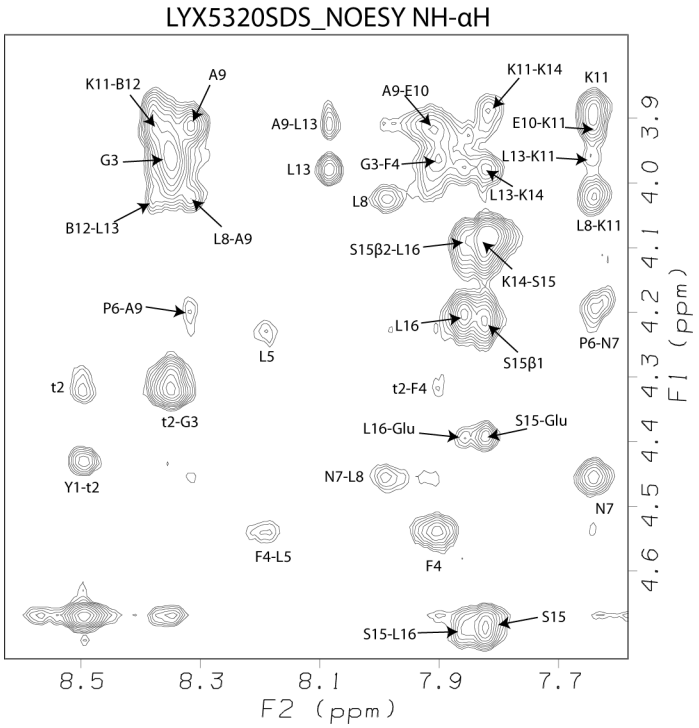


Figure S46: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5320** in SDS micelle at pH=5.5 at 30°C.

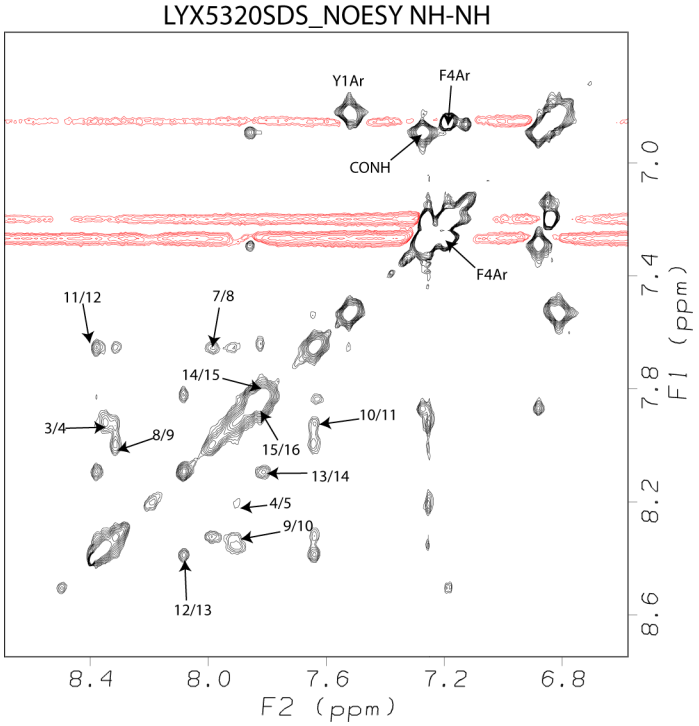


Figure S47: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5320** in SDS micelle at pH=5.5 at 30°C.

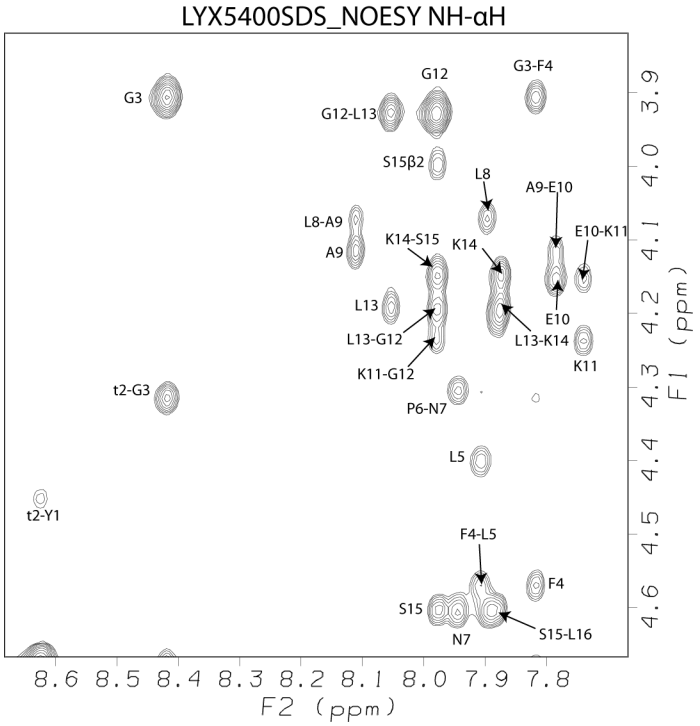


Figure S48: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5400** in SDS micelle at pH=5.5 at 30°C.

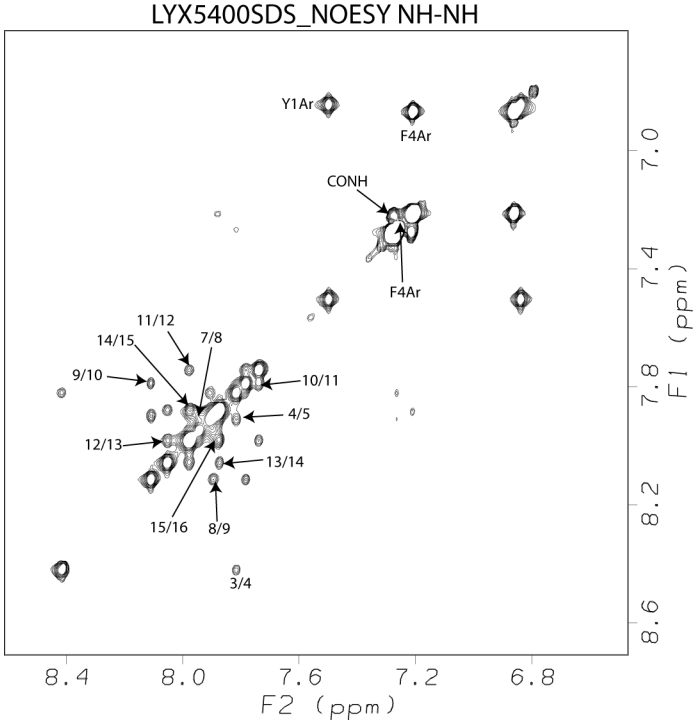


Figure S49: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5400** in SDS micelle at pH=5.5 at 30°C.

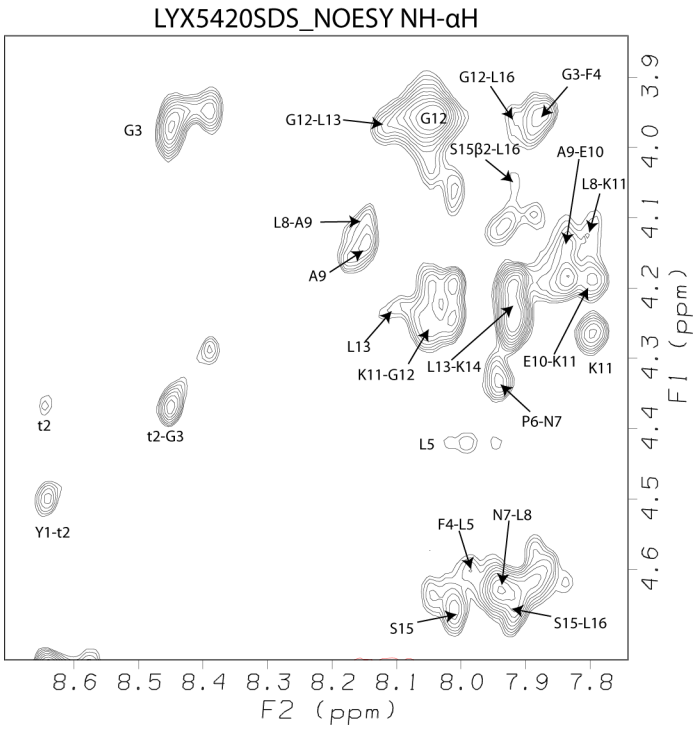


Figure S50: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5420** in SDS micelle at pH=5.5 at 30°C.

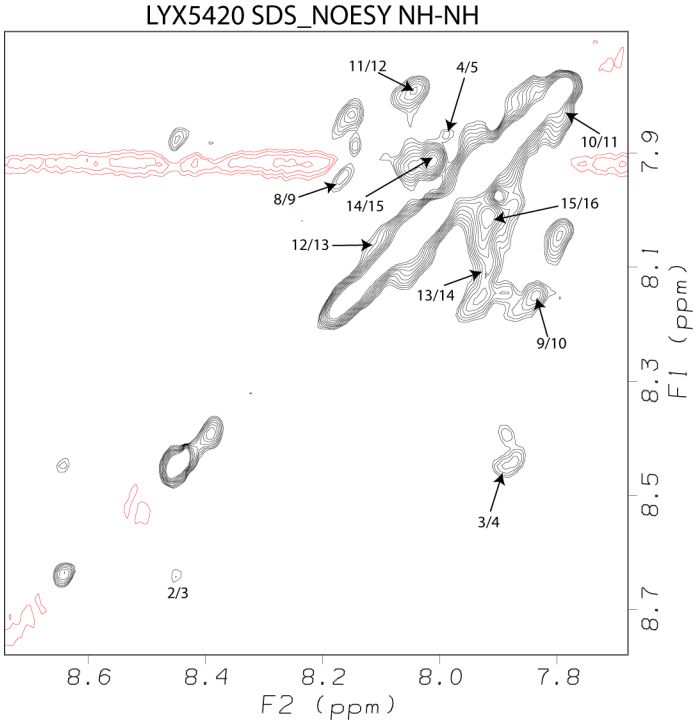


Figure S51: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5420** in SDS micelle at pH=5.5 at 30°C.

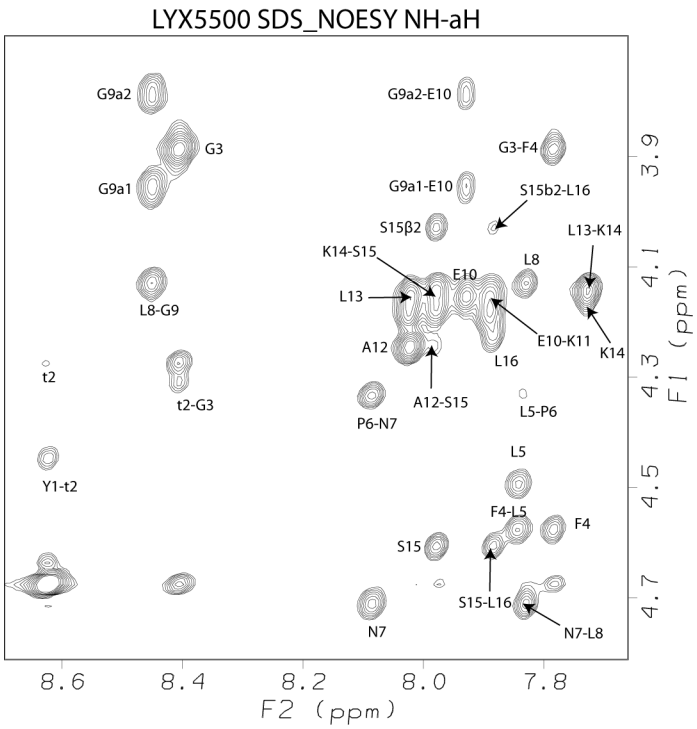


Figure S52: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5500** in SDS micelle at pH=5.5 at 30°C.

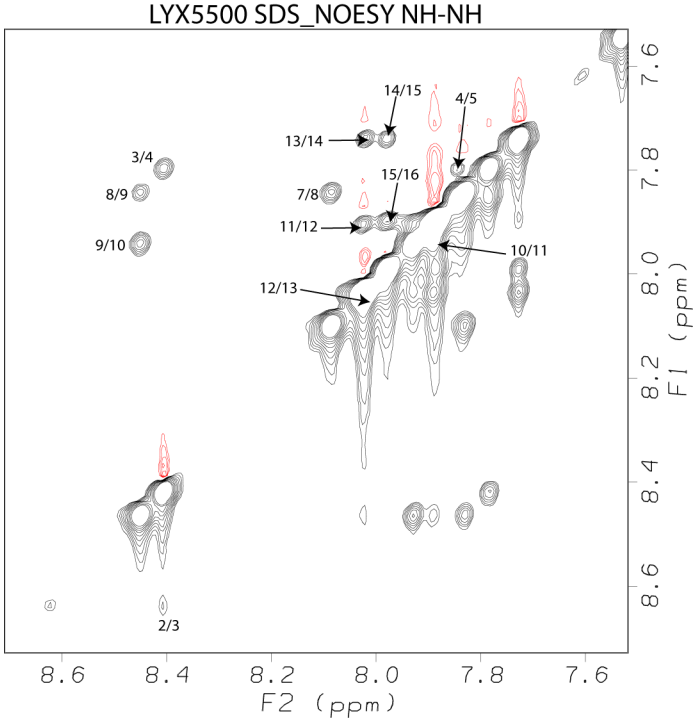


Figure S53: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5500** in SDS micelle at pH=5.5 at 30°C.

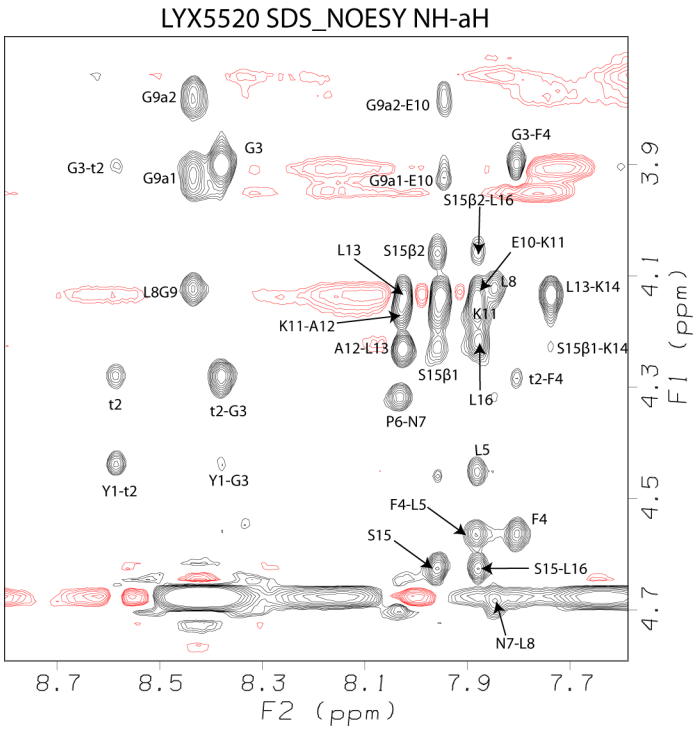


Figure S54: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5520** in SDS micelle at pH=5.5 at 30°C.

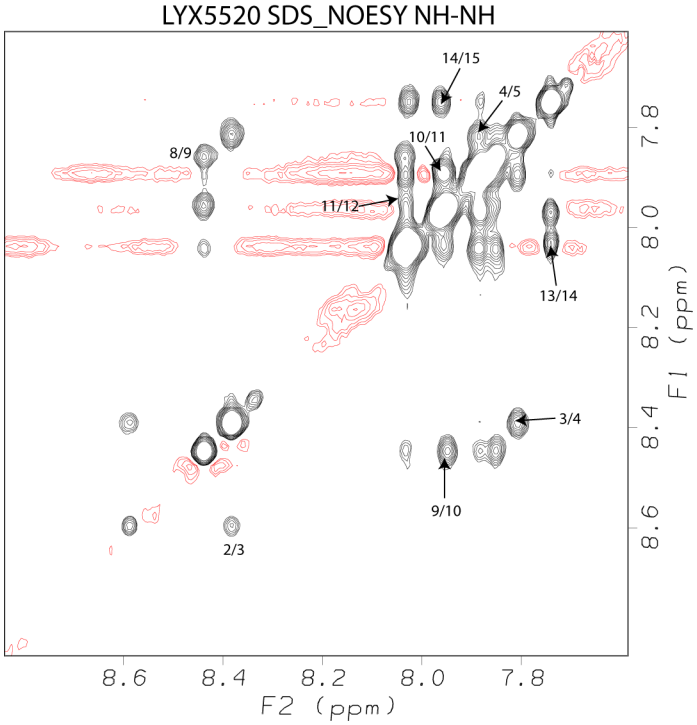


Figure S55: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5520** in SDS micelle at pH=5.5 at 30°C.

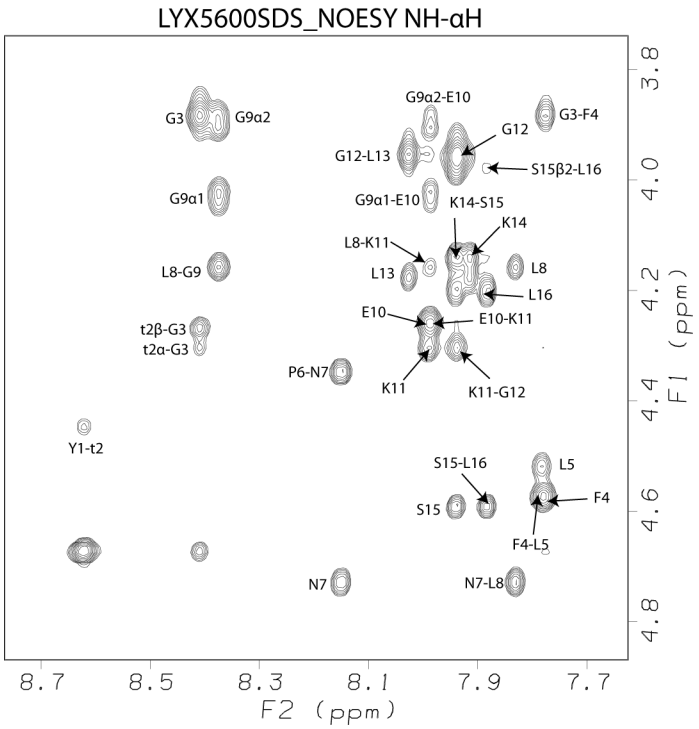


Figure S56: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5600** in SDS micelle at pH=5.5 at 30°C.

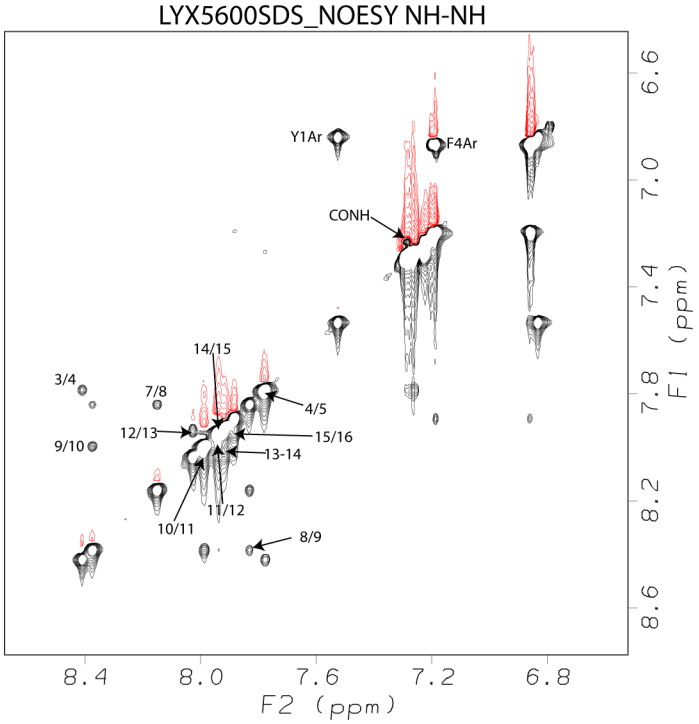


Figure S57: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5600** in SDS micelle at pH=5.5 at 30°C.

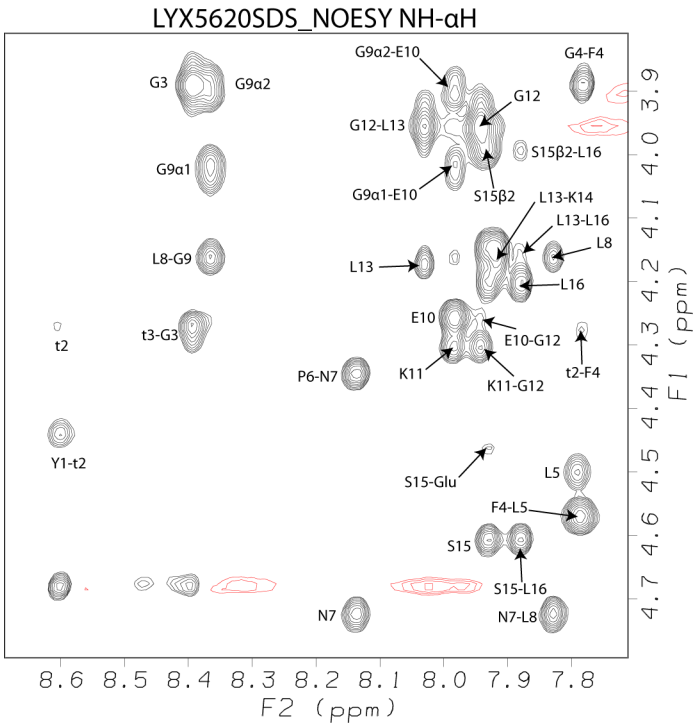


Figure S58: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5620** in SDS micelle at pH=5.5 at 30°C.

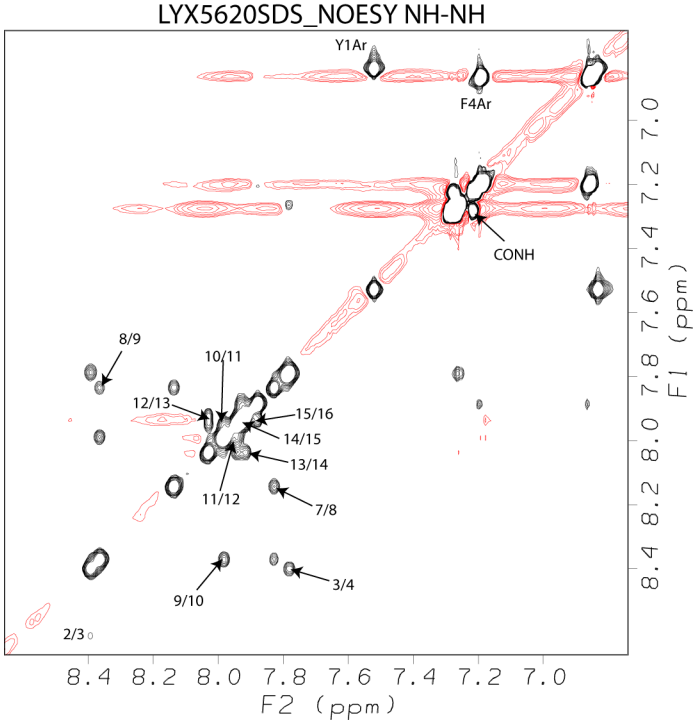


Figure S59: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **LYX5620** in SDS micelle at pH=5.5 at 30°C.

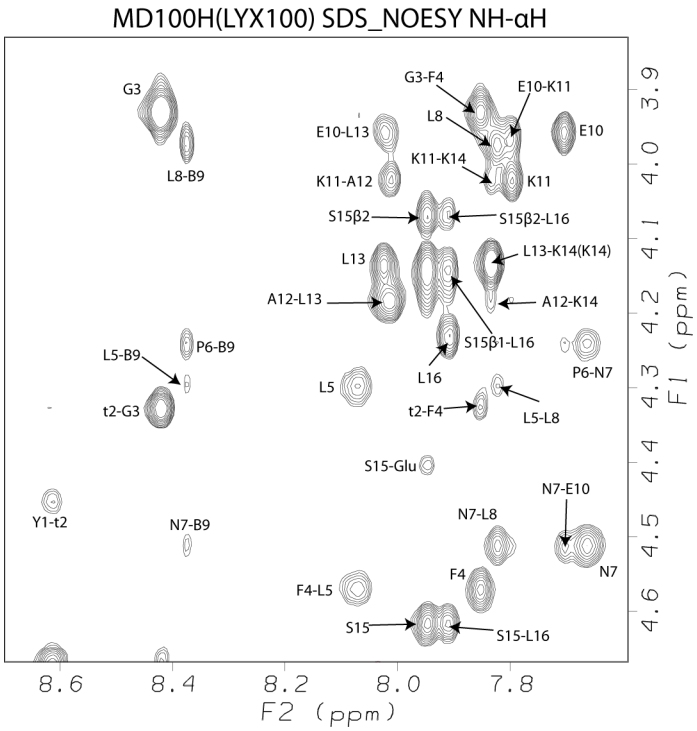


Figure S60: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **MD100H(LYX100)** in SDS micelle at pH=5.5 at 30°C.

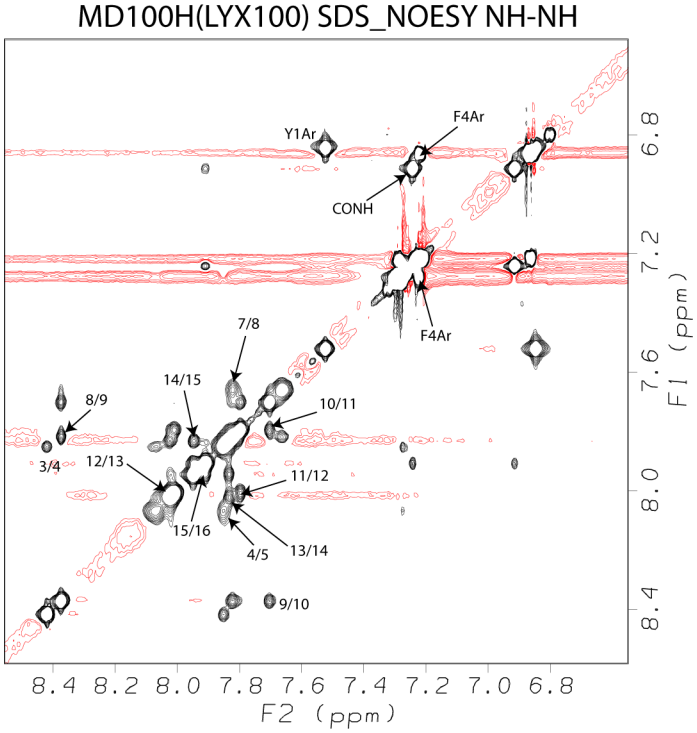


Figure S61: Finger print region of (NH-NH) of NOESY (mixing time = 150ms) spectra of glycopeptide **MD100H(LYX100)** in SDS micelle at pH=5.5 at 30°C.

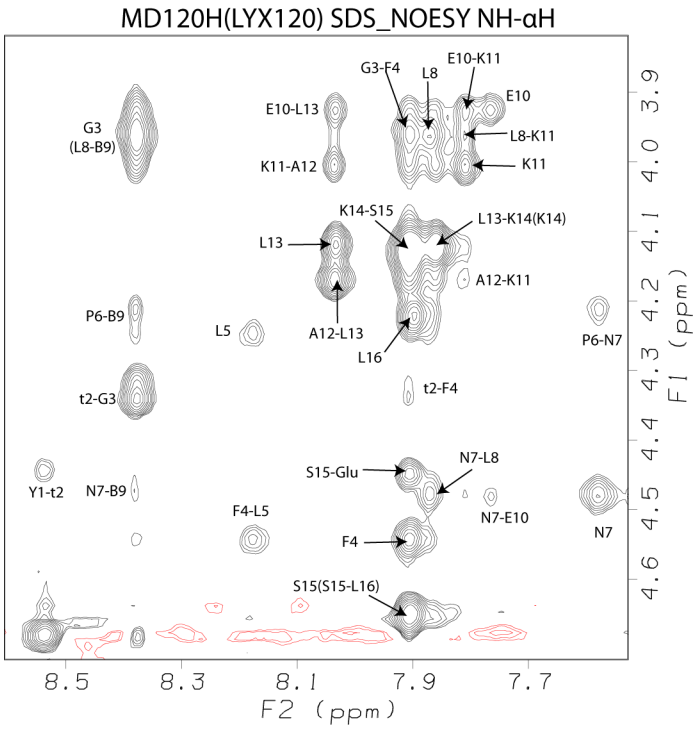


Figure S62: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **MD120H(LYX120)** in SDS micelle at pH=5.5 at 30°C.

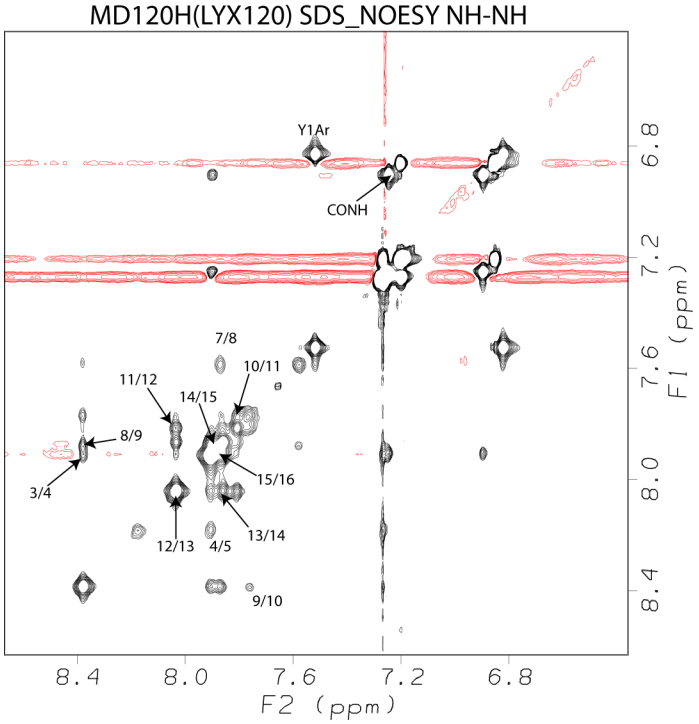


Figure S63: Finger print region of (NH-αH) of NOESY (mixing time = 150ms) spectra of glycopeptide **MD120H(LYX120)** in SDS micelle at pH=5.5 at 30°C.

Citations

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[3] Wuthrich, K., *NMR of Proteins and Nucleic Acids*. Wiley Press, **1986**.

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[5] Rizo, J.; Blanco, F. J.; Kobe, B.; Bruch, M. D.; Gierasch, L. M., Conformational Behavior of Escherichia-Coli Ompa Signal Peptides in Membrane Mimetic Environments. *Biochemistry* **1993,** *32* (18), 4881-4894.