SUPPLEMENTARY INFORMATION

Supplemental data, related to NMR results (detailed NMR analyses)

Chemical shift analysis. The four MAG-Tn3 glycosylated peptidic chains were identified as random coil regions on the basis of the chemical shift index (CSI).[1] Indeed large random coil index (RCI) values (*i.e.*, from 0.15 up to 0.5) were obtained for residues 1-18 (Fig. S4)[2] with smaller RCI values from Ser*1 to Lys7, suggesting more restricted motions for this segment. In addition, the slightly larger RCI values obtained for residues 15-18 of the b and b' chains compared to those of the a and a' ones are consistent with the increased flexibility of the lysine side chains compared to that of their peptide backbone. A comparison with two monomeric analogues (*i.e.*, glycopeptide S*T*T*-TT peptide and its non-glycosylated counterpart) indicates that the behaviour of the MAG-Tn3 glycosylated peptide chains is similar to that of the linear glycopeptide, whereas larger RCI values are observed at *N*-ter from Ser1 to Ala8 for the non-glycosylated peptide (Table S1B, C and Fig. S4). These results suggest that the α-glycosylation at *N*-ter locally induces reduced flexibility. Moreover, the Φ and Ψ backbone torsion angles indicate a preferred extended conformation for residues Thr2* to Ile6 (with Φ and Ψ mean values of -120 ± 18 and 137 ± 13, respectively), whereas residues 7-17 are classified as dynamic (with Φ and Ψ mean values of -89 ± 58 and 131 ± 29, respectively).[3]

Coupling constants analysis. Because of signal overlaps, only a few peptide backbone $^{3}J_{NH,H\alpha}$ coupling constants could be extracted; most of the obtained values were between 5.6 and 7.3 Hz, implying the absence of a stable secondary structure (Fig. S3). However, larger values of 9.0 Hz were observed for the glycosylated residues (*i.e.*, Thr2* and Thr3*), corresponding to a Φ torsion angle of approximately -120°, which is consistent with that found in an extended conformation.[4] The $^{3}J_{NH,H\alpha}$ coupling constants measured under the same experimental conditions used for the two linear glycosylated and non-glycosylated analogues were 9.0 and 8.9 Hz for Thr2* and Thr3*, respectively, whereas smaller values of 7.0 and 7.6 Hz were obtained for Thr2 and Thr3, respectively. These results show that this local extended conformation was induced by the α-glycosylation of the threonine residues. In addition, the small $^{3}J_{H\alpha,H\beta}$ values (approximately 3 Hz) observed for the glycosylated Thr2* and Thr3* suggest a limited set of possible values for the χ^{1} torsion angle (N-Cα-Cβ-O_{sugar}). Similarly, the $^{3}J_{H\alpha,H\beta}$ and $^{3}J_{H\alpha,H\beta'}$ values measured for the glycosylated Ser1* (4.3 and 5.1 Hz) were smaller than those (5.4 and 6.1Hz) obtained for the non-glycosylated Ser10 with no conformational preference. Finally, the large $^{3}J_{NH,H2}$ values of 9.6 and 9.7 Hz (Table S1A) obtained for all of the GalNAc residues correspond to torsion angles of approximately 180° between the H2 and NH protons, indicating a preferred orientation for the *N*-acetyl group, as previously reported.[5-7]

^{1}H,^{1}H NOEs. The observation of strong dαN(i,i+1) NOEs for the stretch of residues from Ser1* to Ile15 and medium dNN(i,i+1) NOEs from Ile6 to Phe12 indicates that this central peptidic segment (Ile6-Phe12) is in an unfolded state. In contrast, the dNN(i,i+1) NOEs from Thr2* to Ile6 are absent or weaker, suggesting a preference for an extended conformation in this *N*-ter region (Fig. S3). Besides, the small to medium NOEs observed between the NH proton of the GalNAc residues and the amide proton of the corresponding linked threonine residues (GalNAc2 NH/Thr2* NH and GalNAc3 NH/Thr3* NH) indicate that the torsion angles Ψs ($C1_s$-$O1_s$-Cβ-Cα) adopt values close to 120°, reflecting an eclipsed conformation of the GalNAc-Thr linkage (Table S3).[7,8] In addition, the presence of weak or medium NOEs between the protons of GalNAc3, which are primarly due to its *N*-acetyl group, and the AA protons from the Thr3* to Tyr5 residues confirms a privileged orientation of the *N*-acetyl group relative to the peptidic chain and glycosylation-induced stiffening at *N*-ter to Tyr5.

Supplementary Figures and Tables

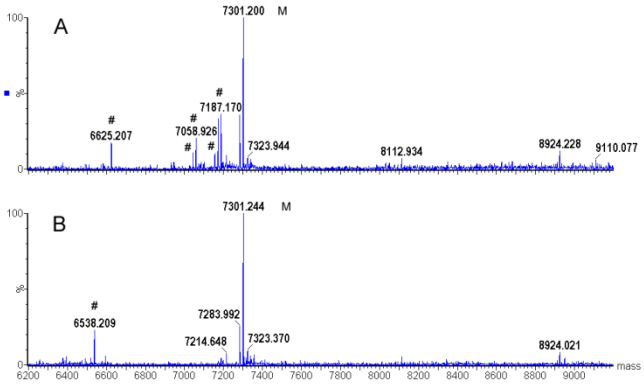

Fig. S1. ESMS analysis of crude peptide **2** synthesized without (*A*) or with (*B*) pseudoproline dipeptides (deconvoluted spectra, calcd M_r 7,301.630). # = deletion products.

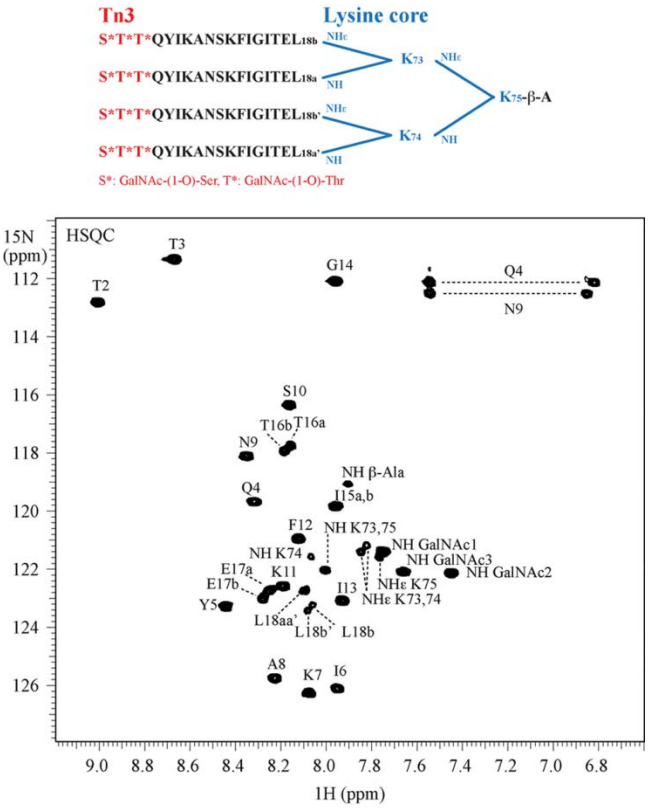

Fig. S2. ^{1}H-^{15}N HSQC spectrum of MAG-Tn3.

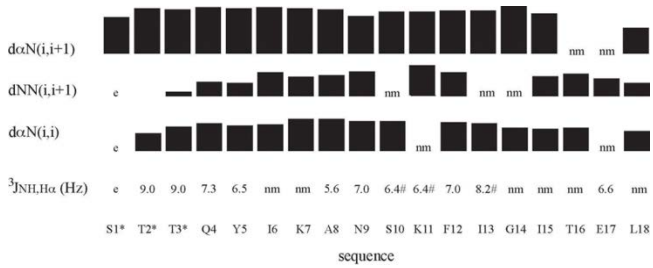

Fig. S3. $^{3}J_{NH,H\alpha}$ coupling constants in Hz and sequential and medium-range $^{1}H,^{1}H$ NOEs measured for MAG-Tn3. The thickness of the lines is proportional to the intensity of the NOEs. # coupling constants measured from 2D NOESY; nm: not measurable due to overlap; e: exchanged NH_2 terminal.

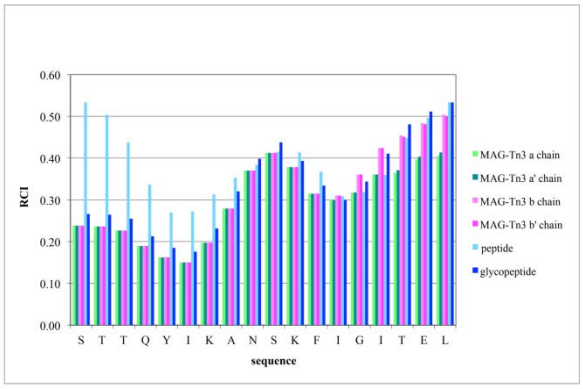

Fig. S4. Random Coil Index (RCI) for MAG-Tn3, the linear glycopeptide S*T*T*QYIKANSKFIGITEL and its non glycosylated analogue.

Table S1.

A) ^{1}H, ^{13}C and ^{15}N NMR chemical shifts (in ppm) and coupling constants ($J_{H,H}$ in Hz) for the MAG-Tn3 GalNAc residues

	H1 $^{3}J_{1,2}$ C1	H2 $^{3}J_{2,3}$ C2	H3 $^{3}J_{3,4}$ C3	H4 $^{3}J_{4,5}$ C4	H5 C5	H66' C6	H (Ac) C	H (NH) $^{3}J_{NH,H2}$ N
α-GalNAc-(1-*O*)-Ser1	4.826 4.1[a] 101.07	4.136 10[b] 52.33	3.847 4[b] 70.76	3.954 ≈ 0 71.30	3.925 74.42	3.74-3.80 64.18	1.999 24.99	7.760 9.6[a] 121.40
α-GalNAc-(1-*O*)-Thr2	4.832 4.1[a] 101.93	4.047 10[b] 52.49	3.828 4[b] 70.96	3.941 ≈ 0 71.30	3.958 74.08	3.72-3.75 64.11	2.018 25.21	7.457 9.7[a] 122.14
α-GalNAc-(1-*O*)-Thr3	4.862 3.8[a] 101.50	4.115 10[b] 52.43	3.806 4[b] 71.10	3.958 ≈ 0 71.30	3.958 74.08	3.72-3.75 64.11	2.033 25.21	7.671 9.6[a] 122.05

[a]Digital resolution 1D ^{1}H spectrum : 0.2 Hz. [b]Digital resolution 2D ^{1}H COSY and TOCSY spectra : 1.5 Hz.

^{1}H, ^{13}C and ^{15}N NMR chemical shifts (in ppm) of the MAG-Tn3 amino acid residues

		H_N N	Hα Cα	Hβ Cβ	Hγ Cγ	Hδ Cδ	Other		
Ser*	1		4.461 55.83	4.221-3.990 69.13					
Thr*	2	9.012 112.82	4.780 59.98	4.393 79.98	1.292 21.14				
Thr*	3	8.671 111.33	4.517 59.33	4.212 79.03	1.174 20.99				
Gln	4	8.327 119.66	4.295 55.24	1.983-1.878 30.53	2.300 33.77		7.550-6.821 NH_2 112.12		
Tyr	5	8.449 123.27	4.456 58.06	2.990-2.881 38.83			7.111 δCH 133.51	6.782 εCH 118.25	
Ile	6	7.957 126.09	3.989 60.42	1.687 38.98	1.367-1.061 27.15	0.773 12.68	0.775 γCH_3 17.26		
Lys	7	8.079 126.25	4.106 56.43	1.754-1.675 32.97	1.397 24.84	1.677 29.27	2.987 εCH_2 42.15	7.774	
Ala	8	8.230 125.76	4.242 52.60	1.348 19.29					
Asn	9	8.354 118.12	4.665 53.28	2.822-2.746 38.83			7.549-6.864 NH_2 112.52		
Ser	10	8.166 116.37	4.364 58.66	3.849-3.788 63.87					
Lys	11	8.194 122.58	4.231 56.49	1.636 32.99	1.252 24.63	1.581 29.03	2.907 εCH2 42.13	7.845	
Phe	12	8.129 120.94	4.629 57.56	3.084-2.964 39.60			7.194 δCH 131.76	7.299 εCH 131.37	7.270 ζCH 129.74
Ile	13	7.934 123.08	4.112 61.12	1.794 38.84	1.392-1.112 27.20	0.802 12.96			
Gly	14	7.952 112.08	3.887 45.33						
Ile	15a	7.954 119.81	4.258 61.30	1.862 39.01	1.433-1.157 27.36	0.829 13.22	0.885 γCH_3 17.69		
	15b	7.971 117.95	4.323 62.18	4.164					
Thr	16a	8.154 117.76	4.291 62.41	4.141 69.71	1.155 21.65				
	16b	8.195	4.323	4.164					

		117.95	62.18				
Glu	17a	8.251	4.321	2.017-1.923	2.307		
		122.71	56.24	29.51	34.10		
	17b	8.284	4.337				
		122.99	56.13				
Leu	18a	8.099	4.306	1.572-1.526	1.550	0.864-0.812	
		122.72	55.29	42.66	27.05	23.62-24.98	
	18a'	8.095	4.332				
		122.72	55.29				
	18b	8.069	4.232				
		123.22	55.48				
	18b'	8.088	4.237				
		123.39	55.48				
Lys	73	8.009	4.167	1.73-1.64	1.30-1.25	1.449	3.149-3.104 εCH_2
		122.05	56.68	33.39	25.13	30.58	41.80
Lys	74	8.073	4.256	1.75-1.67	1.30-1.25	1.455	3.125 εCH_2
		121.56	56.43	33.33	25.13	30.58	41.80
Lys	75	8.009	4.162	1.73-1.64	1.30-1.25	1.448	3.120 εCH_2
		122.05	56.68	33.39	25.13	30.58	41.80
β-Ala	76	7.913	3.423-3.369	2.486			
		119.07	38.50	37.34			

* α-D-GalNAc

β-Ala : -NH-CH_2α-CH_2β-COOH

For the a',b and b' residues, only chemical shifts different from the a residue are shown.

Hγ, Hδ, Hε, NHε of K73 and K74 may be switched.

Sequences from I15 to β-Ala :

-I15a-T16a-E17a-L18a-NHK73Hα-NHεK75Hα-NHβAla

-I15a-T16a-E17a-L18a'-NHK74Hα-NHK75

-I1b-T16b-E17b-L18b-NHεK73 or 74

-I15a-T16a-E17a-L18b'-NHεK73 or 74

B) ^{1}H, ^{13}C and ^{15}N NMR chemical shifts (in ppm) and coupling constants ($J_{H,H}$ in Hz) of the GalNAc residues of the linear glycosylated peptide S*T*T*QYIKANSKFIGITEL

	H1 $^{3}J_{1,2}$ C1	H2 $^{3}J_{2,3}$ C2	H3 C3	H4 C4	H5 C5	H66' C6	H(Ac) C	HN $^{3}J_{NH,H2}$ N
α-GalNAc-(1-*O*)-Ser1	4.842 3.8[a] 101.09	4.151 9[b] 52.41	3.865 70.75	3.973 71.31	3.933 74.43	3.7-3.8 64.17	2.019 25.06	7.756 9.8[a] 121.40
α-GalNAc-(1-*O*)-Thr2	4.852 3.9[a] 101.91	4.070 9[b] 52.55	3.827 70.99	3.963 71.31	3.976 74.15	3.7-3.8 64.17	2.038 25.21	7.447 10.2[a] 122.14
α-GalNAc-(1-*O*)-Thr3	4.881 3.8[a] 101.50	4.132 9[b] 52.46	3.824 71.12	3.973 71.31	3.976 74.15	3.7-3.8 64.17	2.053 25.21	7.661 10.3[a] 122.09

[a]Digital resolution 1D ^{1}H spectrum : 0.2 Hz. [b]Digital resolution 2D ^{1}H spectrum : 1 Hz.

^{1}H, ^{13}C and ^{15}N NMR chemical shifts (in ppm) the amino acid residues of the linear glycosylated peptide S*T*T*QYIKANSKFIGITEL

		H_N N	Hα Cα	Hβ Cβ	Hγ Cγ	Hδ Cδ	Other
Ser*	1		4.48 55.8	4.237-4.003 69.20			
Thr*	2	9.006 112.8	4.78 60.0	4.407 79.99	1.308 21.20		
Thr*	3	8.664	4.53	4.229	1.189		

		111.3	59.3	79.01	20.98				
Gln	4	8.319	4.31	1.994-1.908	2.317		7.544-6.822 NH_2		
		119.7	55.3	30.54	33.81		112.14		
Tyr	5	8.440	4.47	3.015-2.913			7.128 δCH	6.800	
		123.3	58.1	38.86			133.30	118.32	
Ile	6	7.948	4.00	1.708	1.403-1.108	0.792	0.793 γCH_3		
		126.1	60.4	39.01	27.11	12.75	17.28		
Lys	7	8.075	4.12	1.776-1.713	1.410	1.696	3.000 εCH_2		
		126.2	56.4	32.98	24.81	29.29	42.15		
Ala	8	8.226	4.25	1.368					
		125.7	52.6	19.28					
Asn	9	8.348	4.67	2.851-2.767			7.549-6.856 NH_2		
		118.0	53.2	38.86			112.52		
Ser	1	8.148	4.37	3.865-3.813					
		116.2	58.7	63.91					
Lys	1	8.192	4.24	1.675-1.628	1.269	1.603	2.928 εCH2		
		122.5	56.4	32.87	24.67	29.05	42.15		
Phe	1	8.125	4.64	3.122-2.991			7.226 δCH	7.334	7.290 ζCH
		121.0	57.6	39.56			131.92	131.58	129.94
Ile	1	7.927	4.12	1.807	1.424-1.137	0.827	0.866 γCH_3		
		123.1	61.1	38.82	27.18	13.03	17.42		
Gly	1	7.957	3.89						
		112.2	45.3						
Ile	1	7.934	4.26	1.885	1.431-1.157	0.842	0.909 γCH_3		
		119.7	61.1	39.03	27.24	13.18	17.68		
Thr	1	8.192	4.33	4.154	1.173				
		118.3	61.9	69.84	21.51				
Glu	1	8.263	4.38	2.102-1.932	2.380				
		123.8	55.8	29.43	33.71				
Leu	1	7.994	4.22	1.588	1.590	0.846-0.893			
		128.1	56.2	43.07	27.29	23.57-25.07			

* α-D-GalNAc

C) ^{1}H, ^{13}C and ^{15}N NMR chemical shifts (in ppm) of the amino acid residues of the non-glycosylated analogue STTQYIKANSKFIGITEL

		H_N	Hα	Hβ	Hγ	Hδ	Other		
		N	Cα	Cβ	Cγ	Cδ			
Ser	1		4.233	3.986					
			57.28	62.99					
Thr	2	8.648	4.460	4.231	1.197				
		115.46	61.90	69.82	21.44				
Thr	3	8.219	4.260	4.096	1.099				
		117.40	62.17	69.82	21.43				
Gln	4	8.311	4.277	1.939-	2.204		7.392-6.791 NH_2		
		123.19	55.88	29.63	33.74		112.16		
Tyr	5	8.194	4.542	2.978-			7.044 δCH	6.762 εCH	
		122.13	57.78	38.67			133.26	118.22	
Ile	6	7.969	4.051	1.755	1.403-	0.793	0.835 γCH_3		
		123.66	60.80	38.92	27.18	12.70	17.33		
Lys	7	8.241	4.191	1.773-	1.400	1.657	2.964 εCH_2		
		125.97	56.43	32.91	24.72	29.09	42.21		
Ala	8	8.258	4.246	1.348					
		125.57	52.60	19.25					
Asn	9	8.354	4.656	2.816-			7.534-6.848 NH_2		
		117.95	-	38.77			112.57		
Ser	10	8.145	4.351	3.849-					
		116.17	58.62	63.81					
Lys	11	8.190	4.226	1.773-	1.259	1.582	2.905 εCH2		
		122.49	56.42	32.91	24.71	29.08	42.21		
Phe	12	8.128	4.625	3.088-			7.197 δCH	7.300 εCH	7.266 ζCH
		120.99	-	39.49			131.91	131.50	129.86
Ile	13	7.946	4.115	1.792	1.403-	0.826	0.835 γCH_3		
		123.08	61.08	38.80	27.18	12.95	17.33		
Gly	14	7.965	3.874						
		112.26	45.21						
Ile	15	7.943	4.245	1.866	1.403-	0.826	0.886 γCH_3		
		119.82	61.09	38.93	27.18	12.95	17.61		
Thr	16	8.193	4.317	4.129	1.150				
		118.37	61.90	69.83	21.70				
Glu	17	8.262	4.367	2.074-	2.367				

		123.81	55.88	29.36	33.47	
Leu	18	8.009	4.210	1.574	1.569	0.874-0.827
		128.00	56.16	43.06	27.18	25.06-23.41

Table S2.
List of NOEs obtained for MAG-Tn3 in solution in 85% H_2O at pH 3.9 and at a concentration of 0.77 M from a NOESY experiment acquired at 303 K and 14 T with a mixing time of 200 ms. The NOEs are classified in strong (s), medium (m) and weak (w) intensities.

Intra residue	Intensity	sequential	Intensity	i,i+n, n>1	Intensity
nh, h1 GalNAc1	w	h1 GalNAc1, hb S1	m		
nh, h2 GalNAc1	m	h1 GalNAc1, hb' S1	m		
nh, h3 GalNAc1	m				
nh, ch3 GalNAc1	m				
h1, h2 GalNAc1	m				
h1, h3 GalNAc1	m				
h1, h5 GalNAc1	w				
h2, h3 GalNAc1	s				
nh, h1 GalNAc2	m	h1 GalNAc2, hb T2	s	nh GalNAc2, ha T3	w
nh, h2 GalNAc2	m	nh GalNAc2, nh T2	w		
nh, h3 GalNAc2	m	h66' GalNAc, hc T2	m		
nh, ch3 GalNAc2	s				
h1, h2 GalNAc2	m				
h1, h3 GalNAc2	m				
h2, h3 GalNAc2	s				
nh, h1 GalNAc3	m	h1 GalNAc3, hb T3	s	h1 GalNAc3, nh Q4	m
nh, h2 GalNAc3	m	nh GalNAc3, nh T3	m	nh GalNAc3, nh Q4	w
nh, h3 GalNAc3	m	ch3 GalNAc3, nh T3	w	ch3 GalNAc3, hb Y5	w
nh, ch3 GalNAc3	s	h66' GalNAc, hc T3	m	ch3 GalNAc3, hb' Y5	w
nh, h4 GalNAc3	w			ch3 GalNAc3, nh Y5	w
h1, h2 GalNAc3	m			ch3 GalNAc3, h26 Y5	w
h1, h3 GalNAc3	w				
h2, h3 GalNAc3	s				
ha, hb S1	m	ha S1, nh T2	s		
ha, hb' S1	m	hb S1, nh T2	m		
hb, hb' S1	s	h'b S1, nh T2	w		
ha, nh T2	m	ha T2, nh T3	s		
ha, hb T2	m	hb T2, nh T3	m		
nh, hb T2	w	ch3c T2, nh T3	m		
nh, ch3c T2	m				
hb, hc T2	m				
ha, nh T3	m	ha T3, nh Q4	s		
ha, hb T3	m	hb T3, nh Q4	s		
ha, hc T3	w	hc T3, nh Q4	m		
nh, hb T3	m	nh T3, nh Q4	w		
nh, ch3c T3	m				
hb, hc T3	s				
ha, nh Q4	m	ha Q4, nh Y5	s		
ha, hb Q4	m	ha Q4, h26 Y5	w		
ha, hb' Q4	m	hb Q4, nh Y5	w		
ha, hc Q4	m	h'b Q4, nh Y5	m		
nh, hb Q4	m	hc Q4, nh Y5	w		
nh, hb' Q4	m	nh Q4, nh Y5	m		
nh, hc Q4	w				
nh2d Q4	s				
ha, nh Y5	m	ha Y5, nh I6	s	h26 Y5, ha K7	w
ha, hb Y5	m	hb Y5, nh I6	w	h35 Y5, ha K7	m
ha, hb' Y5	m	h'b Y5, nh I6	m	h26 Y5, nh K7	w
ha, h26 Y5	s	h26 Y5, nh I6	m	h35 Y5, hb K7	w
hb, hb' Y5	s	nh Y5, nh I6	w		
nh, hb Y5	s				
nh, h'b Y5	m				
nh, h26 Y5	m				
h26, hb' Y5	s				
h26, hb Y5	s				
h35, hb' Y5	w				
h35, hb Y5	w				
h26, h35 Y5	s				
ha, nh I6	m	ha I6, nh K7	s	ch3c or d I6, nh A8	w
ha, hb I6	m	nh I6, nh K7	m		

ha, hc I6	w	ch3c or d I6, nh K7	m		
ha, hc' I6	w				
ha, ch3c or d I6	s				
hb, hc I6	w				
hb,ch3c or d I6	m				
hc, hc' I6	s				
hc, ch3d or c I6	s				
hc', ch3d or c I6	m				
nh, hb I6	m				
nh, hc I6	m				
nh, hc' I6	m				
nh, ch3c I6	m				
ha, nh K7	s	ha K7, nh A8	s		
ha, hb K7	s	hb K7, nh A8	w		
ha, hb' K7	s	h'b K7, nh A8	m		
ha, hc K7	m	nh K7, nh A8	m		
hc, hd K7	s				
hc, he K7	w				
hd, he K7	m				
nh, hb K7	s				
nh, hb' K7	m				
nh, ch2c K7	w				
ha, nh A8	s	ha A8, nh N9	s	hb A8, nh S10	w
ha, hb A8	s	nh A8, nh N9	m		
nh, ch3b A8	s	ch3b A8, nh N9	m		
ha, nh N9	m	ha N9, nh S10	s	ha N9, nh K11	w
ha, hb N9	w	hb N9, nh S10	w	hb' N9, h26 F12	w
ha, hb' N9	w	hb' N9, nh S10	w		
hb, hb' N9	s	nh N9, nh S10	m		
hb, nhc N9	w				
hb, nhc' N9	m				
hb', nhc N9	w				
hb', nhc' N9	m				
nh2c N9	s				
nh, hb N9	m				
nh, h'b N9	m				
ha, nh S10	m	ha S10, nh K11	s		
ha, hb S10	m	hb S10, nh K11	m		
ha, hb' S10	m	h'b S10, nh K11	m		
nh, hb S10	m	nh S10, nh K11			
nh, h'b S10	m				
ha, nh K11 + ha I15, nh T16b'	s	ha K11,nh F12	s	ha K11, nh I13	w
hc, hd K11	m	ha K11, h26 F12	w		
hd, he K11	s	ch2b K11, nh F12	m		
nh, hb K11	m	ch2c K11, nh F12	w		
nh, hb' K11	m	nh K11, h26 F12	w		
nh,hc K11	m	ch2e K11, h35 F12	w		
		nh K11, nh F12	m		
ha, nh F12	m	ha F12, nh I13	s	h35 F12, ch2a G14	w
ha, hb F12	w	hb F12, nh I13	w	h35 F12, nh G14	w
ha, hb' F12	w	hb' F12, nh I13	m	h26 F12, ch2a G14	w
ha, h26 F12	m	h26 F12, nh I13	m	h35 F12, ch3d I15	w
ha, h35 F12	m	h26 F12, ch3d I13	w	h26 F12, hc' I15	w
hb,hb' F12	s	nh F12, nh I13	m		
hb, h26 F12	s				
hb, h35 F12	m				
hb', h26 F12	s				
hb', h35 F12	m				
h35, h26 F12	s				
nh, hb F12	m				
nh, hb' F12	m				
nh, h26 F12	m				
nh, h35 F12	w				
ha, nh I13	m	ha I13, nh G14	s		
ha, hc I13	m	ch3c I13, ha G14	w		
ha, hc' I13	m	nh I13,ha G14	w		
ha, ch3c I13	s				
ha, ch3d I13	m				

hb, hc' I13	m				
hb, ch3c I13	m				
hb, ch3d I13	m				
hc, ch3d I13	s				
hc', ch3d I13	s				
hc, hc' I13	s				
nh, hb I13	m				
nh, hc' I13	m				
nh, hc I13	m				
nh, ch3c I13	m				
ha, nh G14	s	ha G14, nh I15a	s		
		ha G14, nh I15b	s		
		ha G14, ch3c I15	w		
ha, nh I15a	m	ha I15, nh T16b	s	ch3c I15, nh E17a	w
ha, nh I15b	m	ha I15, nh T16a	s	ch3c I15, nh E17a'	w
ha, hb I15ab	m	ha I15ab, hc T16ab	m	ch3c I15, nh E17b	w
ha, hc' I15ab	m	ha I15, nh T16b' + ha, nh K11	**s**	ha I15b or L18b', nh E17b	w
ha, hd I15ab	m	hb I15, nh T16a	w		
ha, ch3c I15ab	s	hb I15, nh T16b	m		
hb, hc' I15ab	m	hb I15, nh T16b'	w		
hb, ch3c I15ab	s	ch3c I15, nh T16b'	w		
hb, ch3d I15ab	m	ch3c I15, nh T16a	m		
hc, ch3c I15	s	ch3c I15, nh T16b	m		
hc, ch3d I15	s	nh I15, nh T16	m		
hc', ch3c I15	m	nh I15a, ha T16ab	w		
hc', ch3d I15	s	nh I15b, ha T16ab	w		
hc, hc' I15	s				
nh, hb I15a	m				
nh, hb I15b	m				
nh, hc I15a	m				
nh, hc I15b	m				
nh, hc' I15a	m				
nh, hc' I15b	m				
nh, ch3c I15a	m				
nh, ch3c I15b	m				
nh, ch3d I15a	m				
nh, ch3d I15b	m				
ha, nh T16a	m	ha T16a + ha E17a, nh E17a	s	ch3c T16ab, nh L18aa'b'	w
ha, nh T16b	m	ha T16a + ha E17a', nh E17a'	s		
ha, hb T16ab	s	ha T16b + ha E17b, nh E17b	s		
ha, hb T16ab	s	hb T16a, nh E17a'	m		
ha, hc T16ab	m	hb T16a, nh E17a	m		
hb, hc T16ab	s	hb T16b, nh E17b	m		
nh T16a, hb T16	m	hc T16, nh E17a	m		
nh T16b', hb T16	m	hc T16, nh E17a'	m		
nh, hc T16a	m	hc T16, nh E17b	w		
nh, hc T16b'	m	nh T16a, nh E17a	m		
nh T16b, hb T16	m	nh T16b, nh E17b	m		
nh, hc T16b	m				
haT16a + ha E17a, nh E17a	s				
ha T16a + ha E17a', nh E17a'	s				
ha T16b + ha E17b, nh E17b	s				
ha, hb E17ab	m	ha E17a, nh L18aa'	s		
ha, hb' E17ab	m	ha E17b, nh L18b	s		
ha, hc E17ab	m	ha E17b, nh L18b'	s		
nh, hb E17a	m	hb E17ab, nh L18aa'bb'	w		
nh, h'b E17a	m	hb' E17ab, nh L18aa'bb'	w		
nh, hb E17a'	m	hc E17ab, nh L18aa'bb'	w		
nh, h'b E17a'	m	nh E17a, nh L18aa'	m		
nh, hb E17b	m	nh E17b, nh L18bb'	m		
nh, hb' E17b	m				
nh, hc E17a	m				
nh, hc E17a'	m				
nh, hc E17b	m				
ha, nh L18a	s	ha L18a , nh K73	m		
ha, nh L18a'	s	ha L18a', nh K74	m		
ha, nh L18b	m	ha L18b, nhe K73	m		
ha, nh L18b'	m	ha L18b', nhe K74	m		

ha, ch2b L18aa'	m	ha L18b, ch2e K73	w
ha L18bb', ch2b + hc L18	m	ha L18bb', hb K73 or K75	m
ha, ch3d L18aa'	m	ch2b + hc L18b, nhe K74	w
ha, ch3d' L18aa'	m	hc L18, nh K73 or K75	w
hc, ch3d L18	m	ch3dd' L18, ha K73 or K75	w
hc, ch3d' L18	s	nh L18b, nhe K73	w
nh, ch2b + hc L18aa'bb'	m	nh L18b', nhe K74	w
nh, ch3d L18aa'bb'	w		
nh, ch3d' L18aa'bb'	w		
ha, nh K73 + K75	m	ha K73, nhe K75	m
ha, hb K73 + K75	m	nh K73, nhe K75	w
ha, hb' K73 + K75	m	nh K73, nhe K75	w
ha,hc K73 + K75	m	hb' K73 or K75, nhe K75	w
ha, hc' K73 + K75	m		
ha, ch2d K73 + K75	m		
ha, ch2e K73 + K75	w		
hb, ch2e K73 + K74 + K75	w		
hb', ch2e K73 + K74 + K75	w		
ch2c, ch2e K73 + K74 + K75	w		
ch2d, ch2e K73 + K74 + K75	m		
nhe, ch2d K73	m		
nhe, he K73	m		
nhe, he' K73	m		
nh, hb K73 + K75	m		
nh, hb' K73 + K75	m		
nh, hc K73 + K75	m		
nh, hc' K73+ K75	m		
nh, ch2d K73 + K75	m		
ha, nh K74	m	ha K74, nh K75	m
ha, hb K74	m		
ha, hb' K74	m		
nh, hc K74	w		
nh, hc' K74	w		
nhe, ch2d K74	m		
nhe, ch2e K74	m		
nhe, hc K75	w	ha K75, nh b-Ala	m
nhe, h'c K75	w	hb' K75, nh b-Ala	w
nhe, ch2d K75	m	nh K75, nh b-Ala	w
nhe, ch2e K75	m		
ha, nh b-Ala	m		
ha', nh b-Ala	m		
hb, ch2b b-Ala	w		
nh, ch2b b-Ala	w		

Table S3.

^{1}H, ^{1}H NOEs between GalNAc and amino acid residues around the S*T*T* antigen motif of MAG-Tn3. Strong, medium and weak NOEs are written in bold, normal and italic characters, respectively.

	Ser1	Thr2	Thr3	Gln4	Tyr5
α-GalNAc1	H1, Hββ'				
α-GalNAc2		**H1, Hβ**	*NH, Hα*		
		H66', CH3γ			
		NH, NH			
α-GalNAc3			**H1, Hβ**	H1, NH	*CH3, NH*
			NH, NH	*NH, NH*	CH3, H2,6
			H66', CH3γ		*CH3, Hββ'*
			CH3, NH		

Supplementary References

1 D. S. Wishart and B. D. Sykes, *J. Biomol. NMR,* 1994, **4**, 171-180.
2 M. V. Berjanskii and D. S. Wishart, *J. Am. Chem. Soc.*, 2005, **127**, 14970-14971.
3 Y. Shen, F. Delaglio, G. Cornilescu and A. Bax, *J. Biomol. NMR,* 2009, **44**, 213-223.
4 A. Pardi, M. Billeter and K. Wuthrich, *J. Mol. Biol.*, 1984, **180**, 741-751.
5 A. Borgert, J. Heimburg-Molinaro, X. Song, Y. Lasanajak, T. Ju, M. Liu, P. Thompson, G. Ragupathi, G. Barany, D. F. Smith, R. D. Cummings and D. Live, *ACS Chem. Biol.*, 2012, **7**, 1031-1039.
6 D. M. Coltart, A. K. Royyuru, L. J. Williams, P. W. Glunz, D. Sames, S. D. Kuduk, J. B. Schwarz, X. T. Chen, S. J. Danishefsky and D. H. Live, *J. Am. Chem. Soc.*, 2002, **124**, 9833-9844.
7 F. Corzana, J. H. Busto, M. Garcia de Luis, J. Jimenez-Barbero, A. Avenoza and J. M. Peregrina, *Chemistry,* 2009, **15**, 3863-3874.
8 F. Corzana, J. H. Busto, G. Jimenez-Oses, M. Garcia de Luis, J. L. Asensio, J. Jimenez-Barbero, J. M. Peregrina and A. Avenoza, *J. Am. Chem. Soc.*, 2007, **129**, 9458-9467.