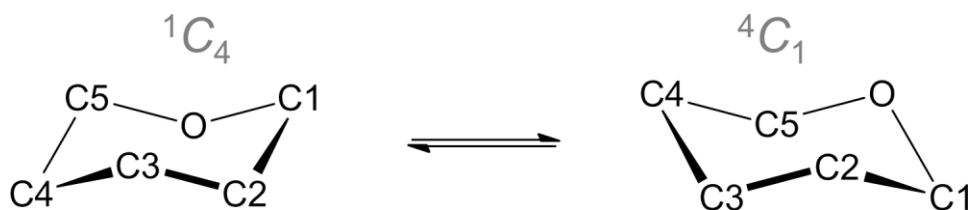


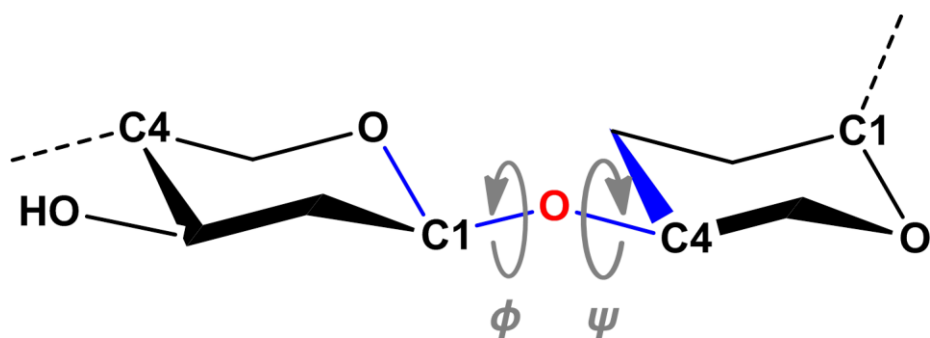
S1	Structural definitions used in the manuscript
S2	Structures of model <i>N</i> -linked oligosaccharides and constituent monosaccharides 1-8
S3-S9	Torsion time series and histograms (100 ns, 10 μ s and 25 μ s simulations of 1-8)
S10-S13	Glycosidic linkage free energy surfaces (100 ns and 10 μ s simulations of 1-8)
S14-S20	Ring puckering convergence and time series (10 μ s and 25 μ s simulations of 1-8)
S21-S24	Computed ring pucker populations and free energies (10 μ s simulations of 1-8)
S25	Calculated and experimental NMR vicinal couplings (10 μ s simulations of 1-8)
S26	Water-oligosaccharide radial distribution functions (10 μ s simulations of 1-2)
S27	Calculation of errors in one-dimensional puckering free energy surfaces
S28-S30	NMR data (800 MHz) for 1 and 2 (nOes, ^1H and ^{13}C chemical shift assignments)
S31	Calculation of order parameters (S^2)
S32-S35	Cartesian coordinates for the most populated conformers of 1 , 2 , 7 and 8

Figure S1. Nomenclature and structural definitions employed in the manuscript

A: Atom naming convention and example pyranose ring conformations (1C_4 and 4C_1 chair puckers)



B: Oligosaccharide glycosidic linkage definitions, $\phi = O_5-C_1-O-C_n$ $\psi = C_1-O-C_n-C_{(n-1)}$



C: Example pyranose ring three bond proton-proton (1H - 1H) vicinal spin-coupling (${}^3J_{H,H}$)

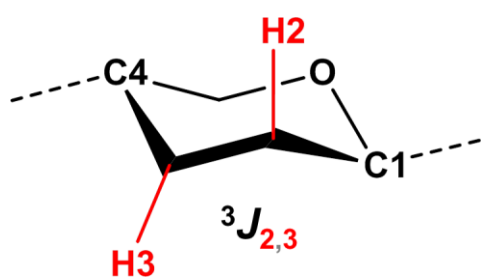


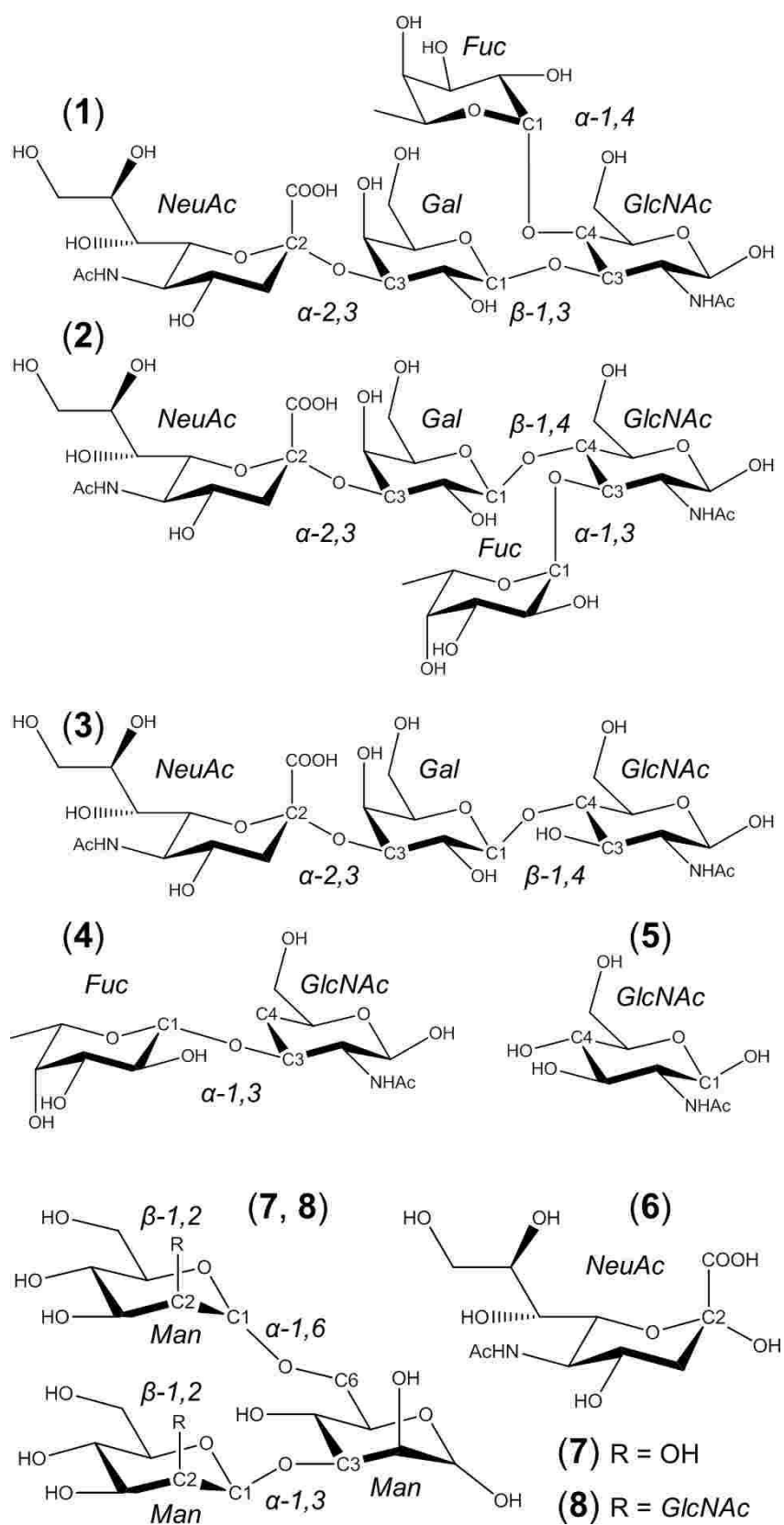
Figure S2. Structures of model oligosaccharides **1-8** (also see Figure 1 caption)

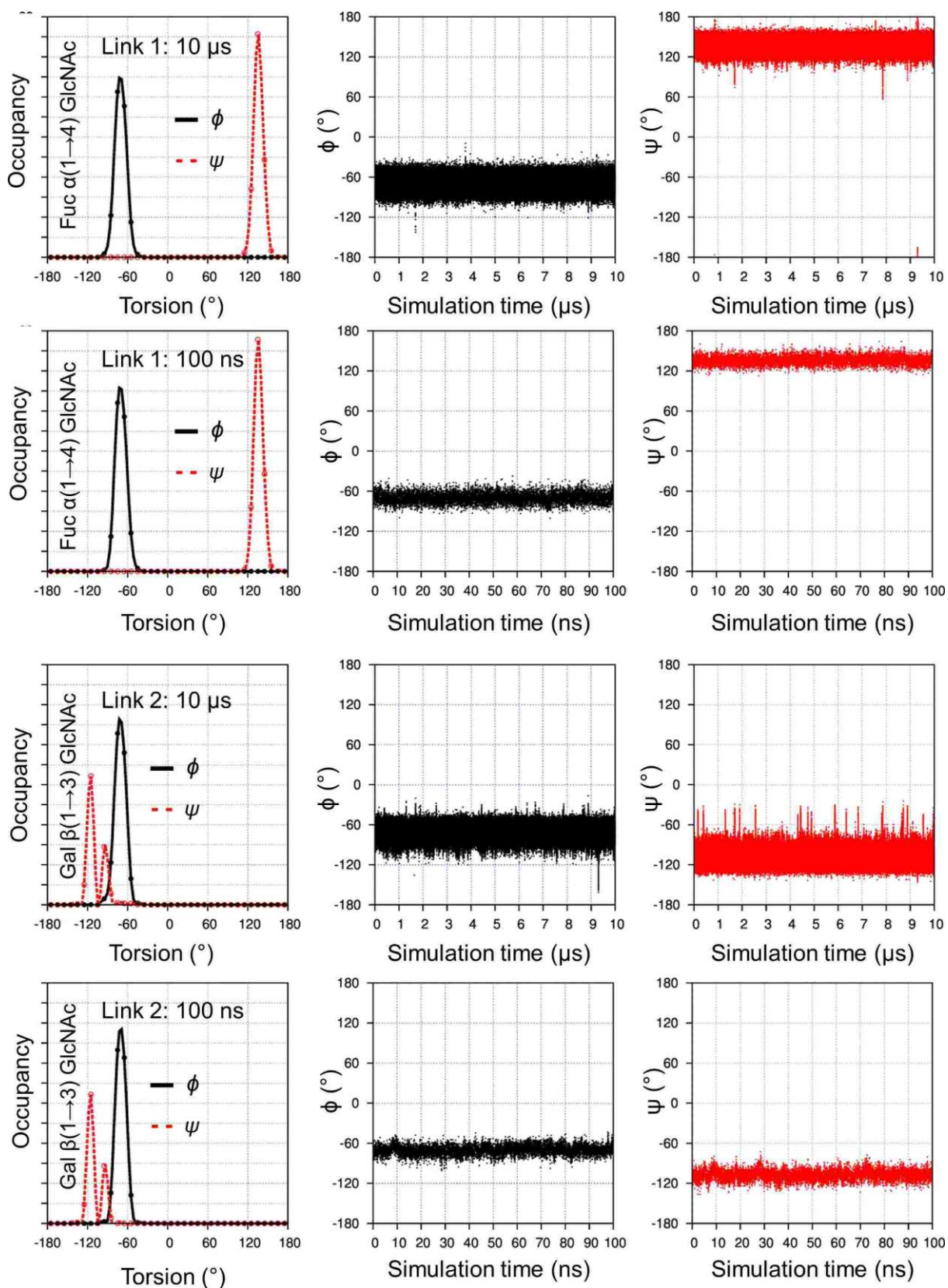
Figure S3. Time series of linkage torsions (10 μ s and initial 100 ns): molecule 1

Figure S3 continued

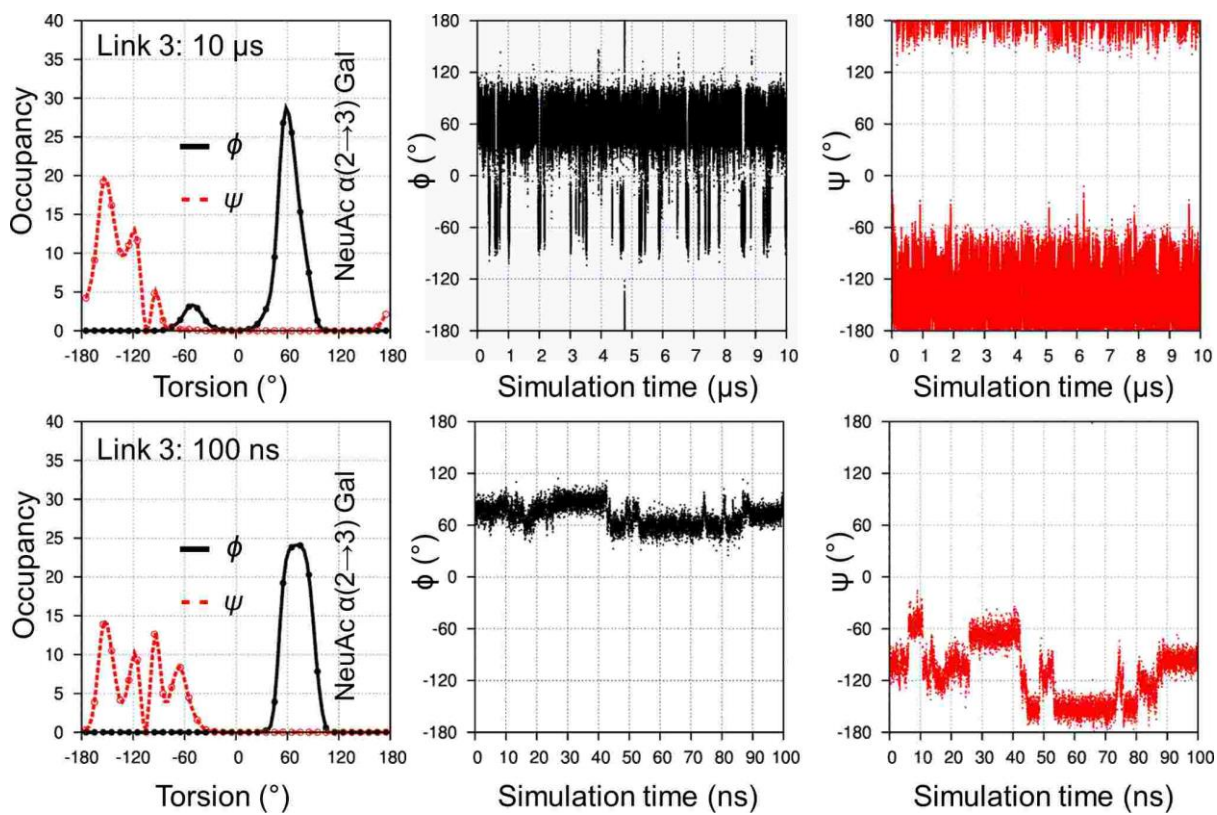


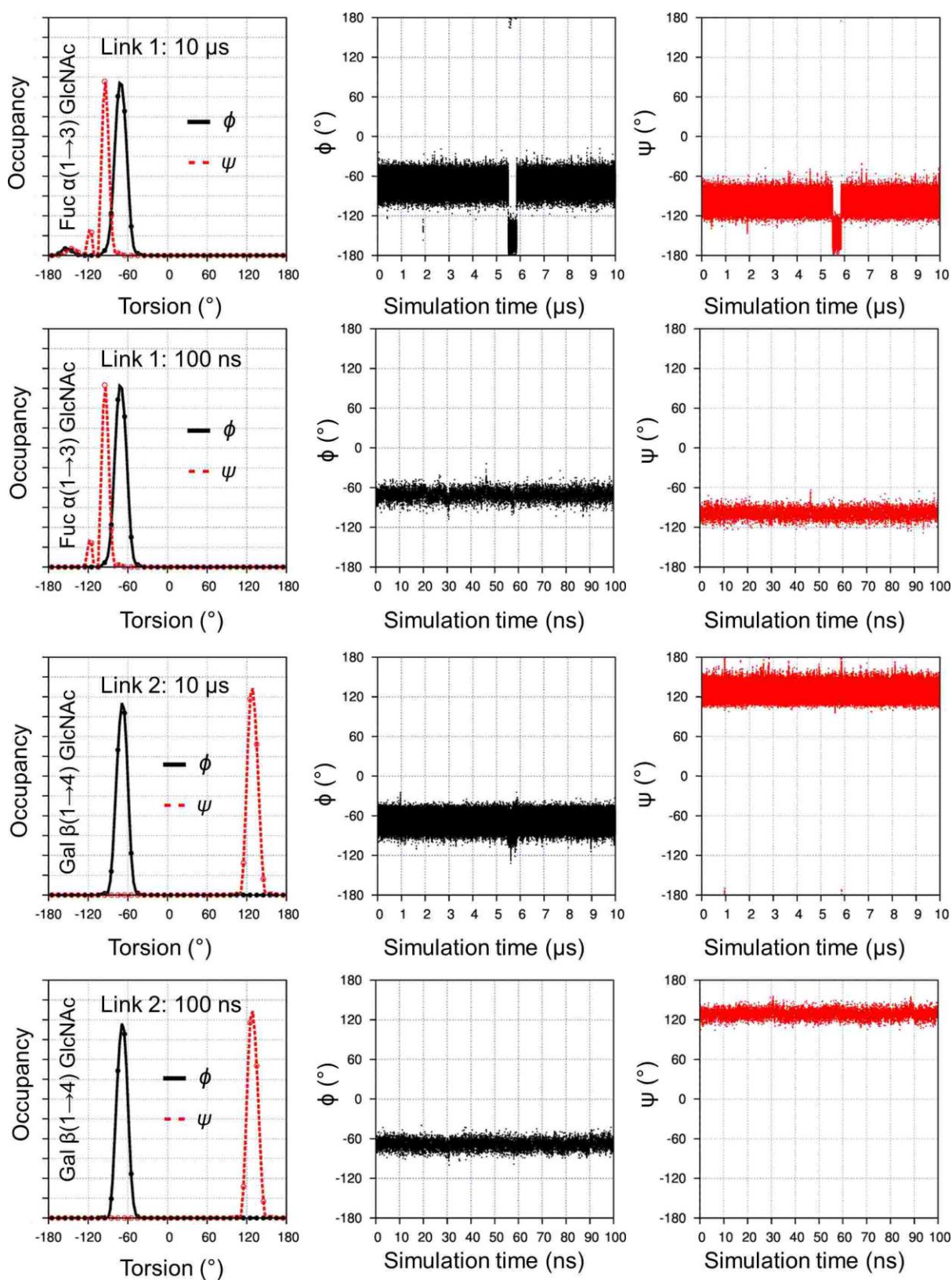
Figure S4. Time series of linkage torsions (10 μ s and initial 100 ns): molecule 2

Figure S4 continued

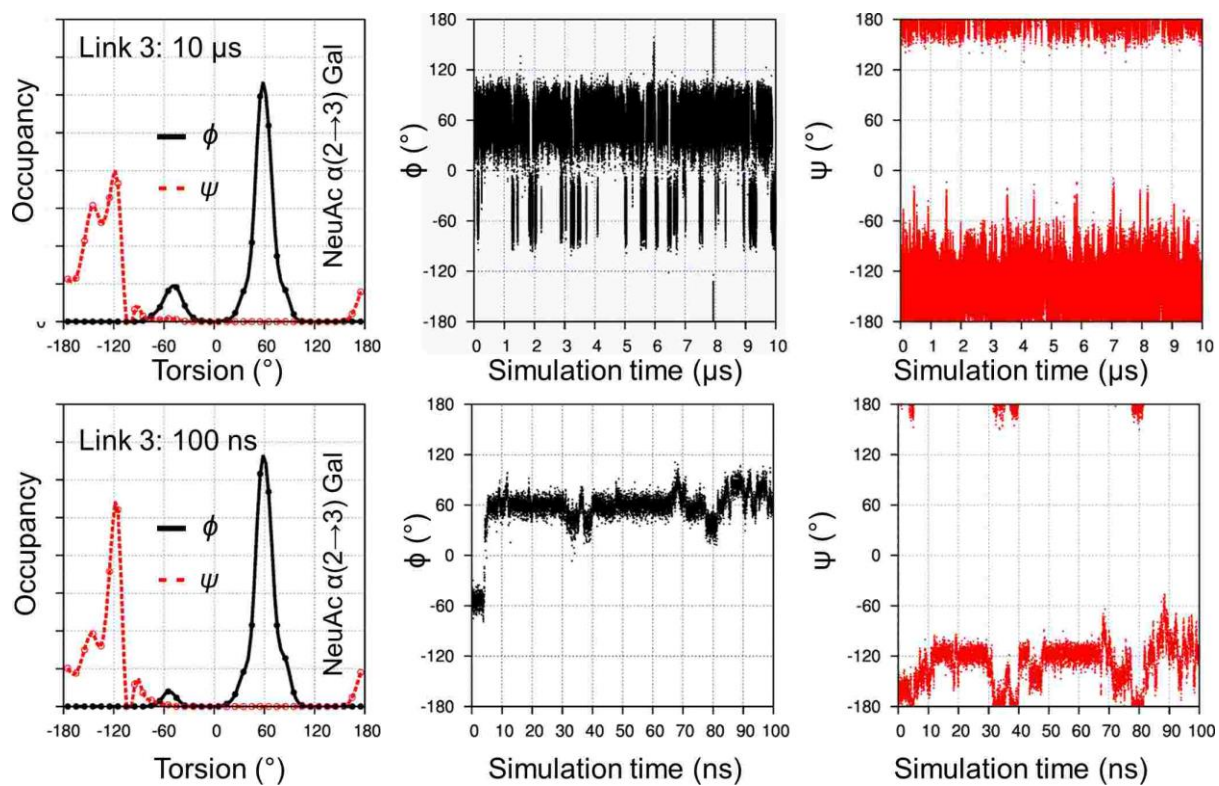


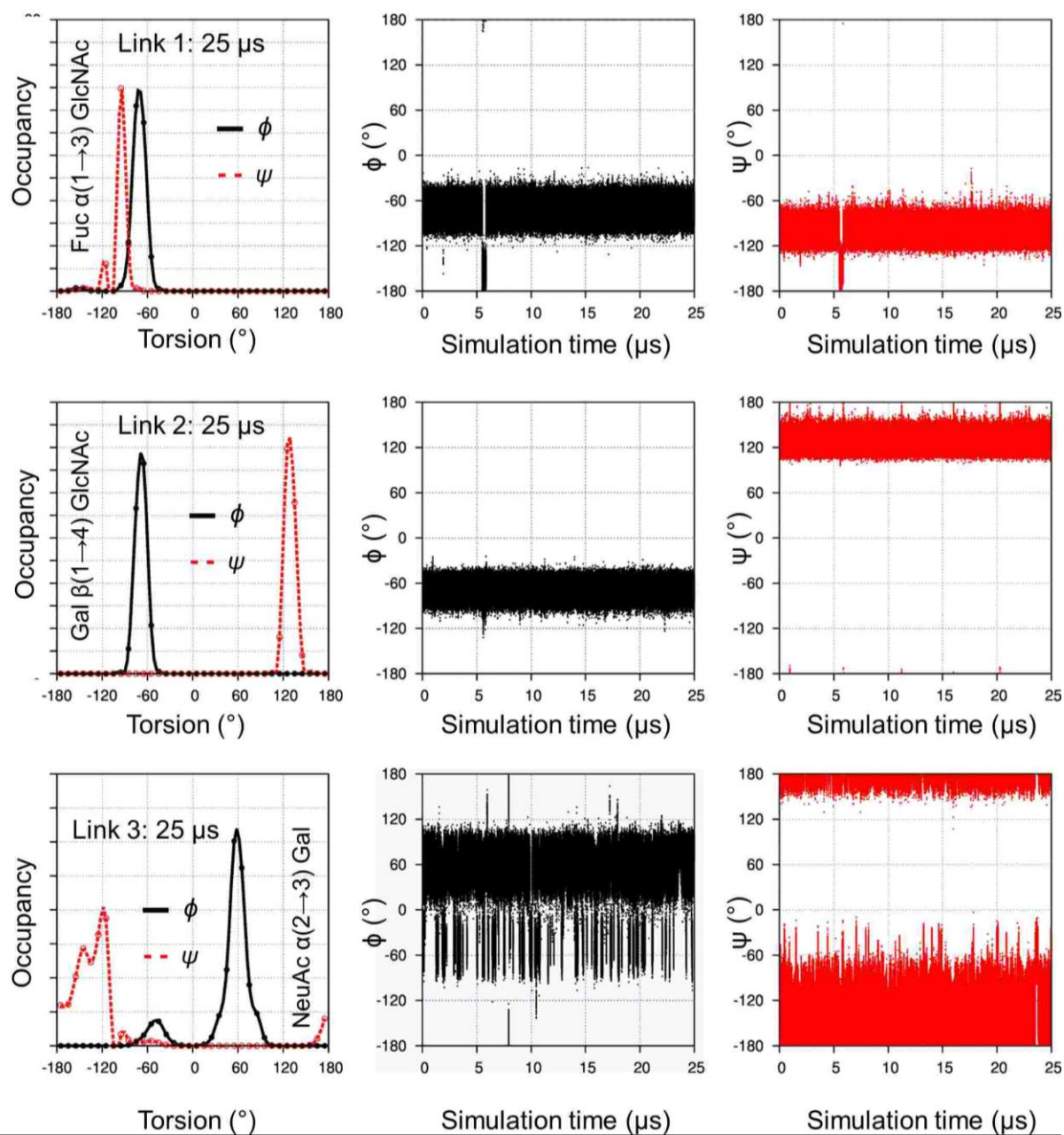
Figure S5. Time series of linkage torsions from a $25\ \mu\text{s}$ simulation of sLe^x: molecule 2

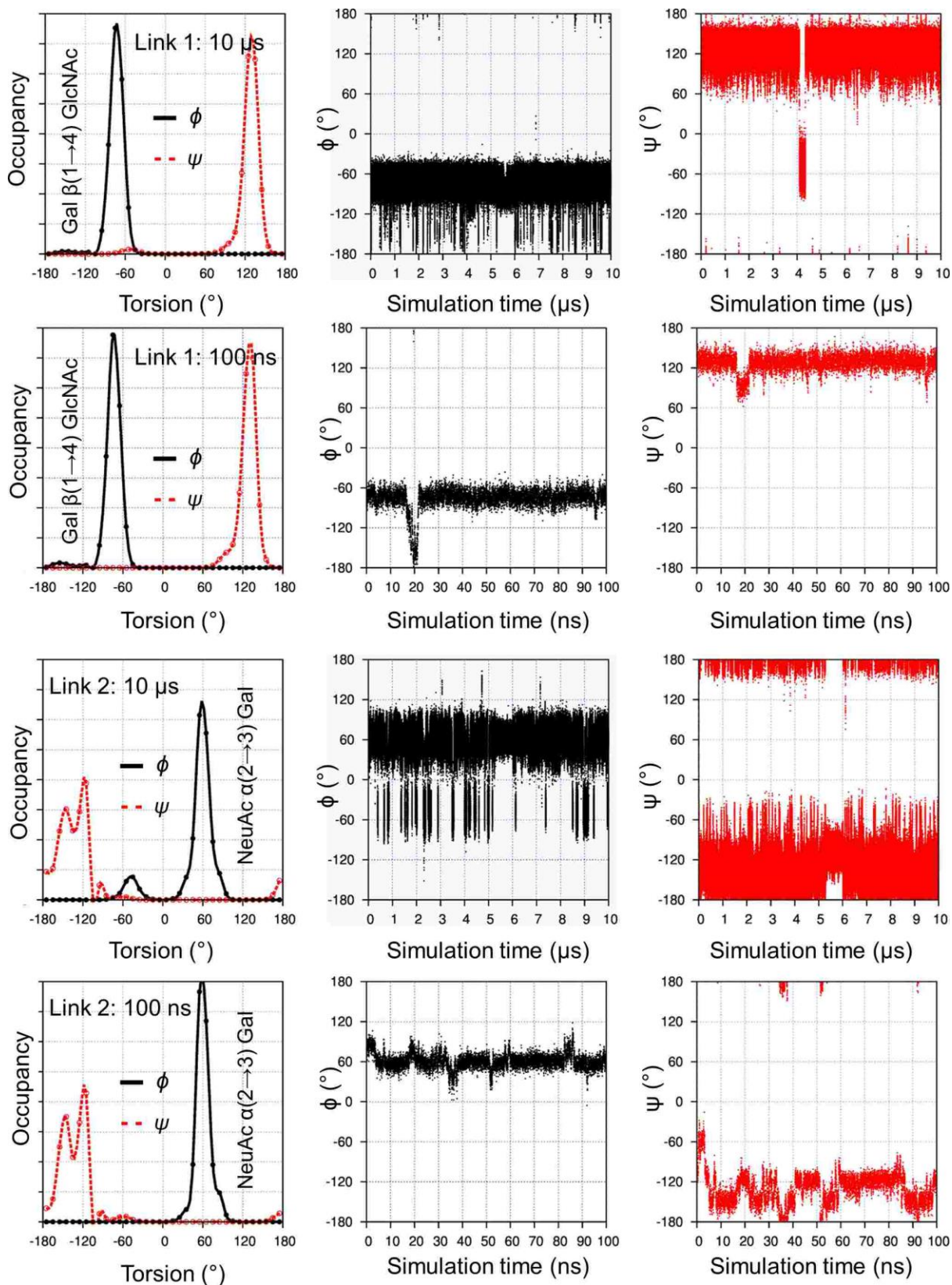
Figure S6. Time series of linkage torsions (10 μ s and initial 100 ns): molecule 3

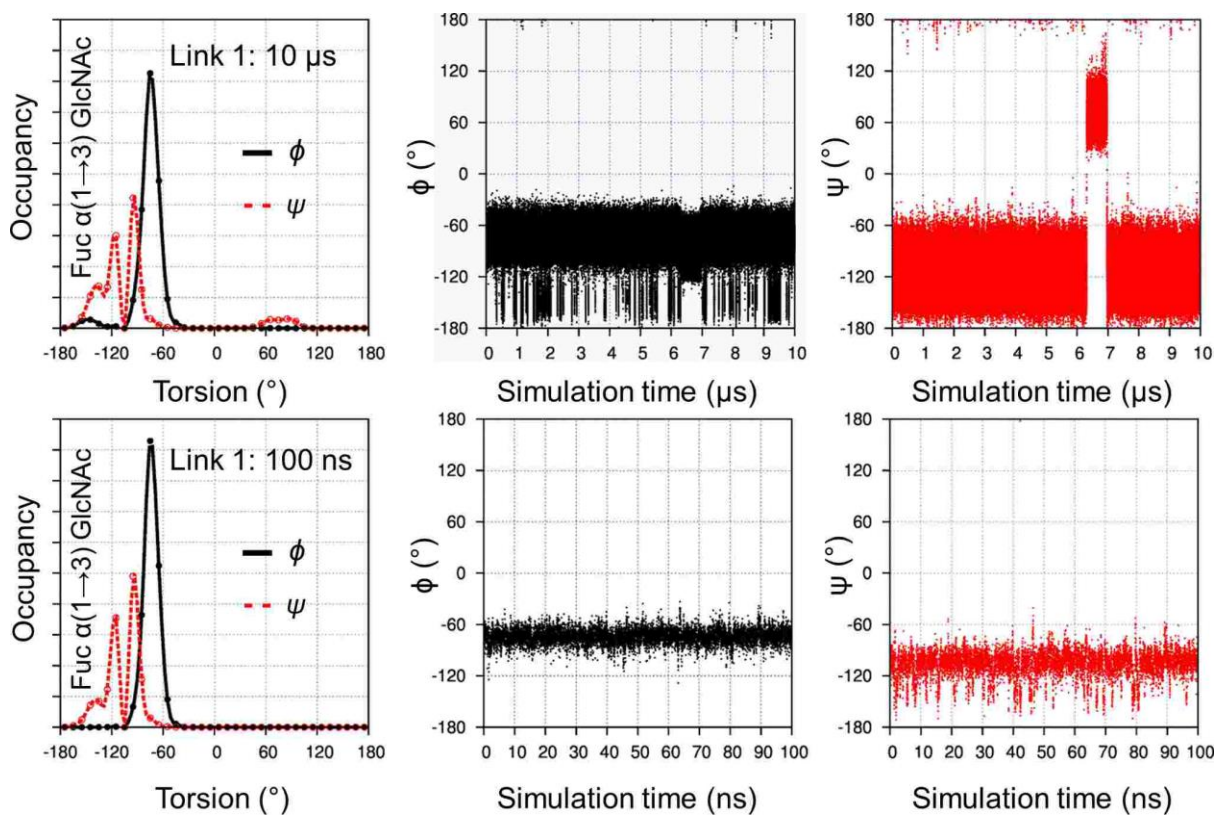
Figure S7. Time series of linkage torsions (10 μ s and initial 100 ns): molecule 4

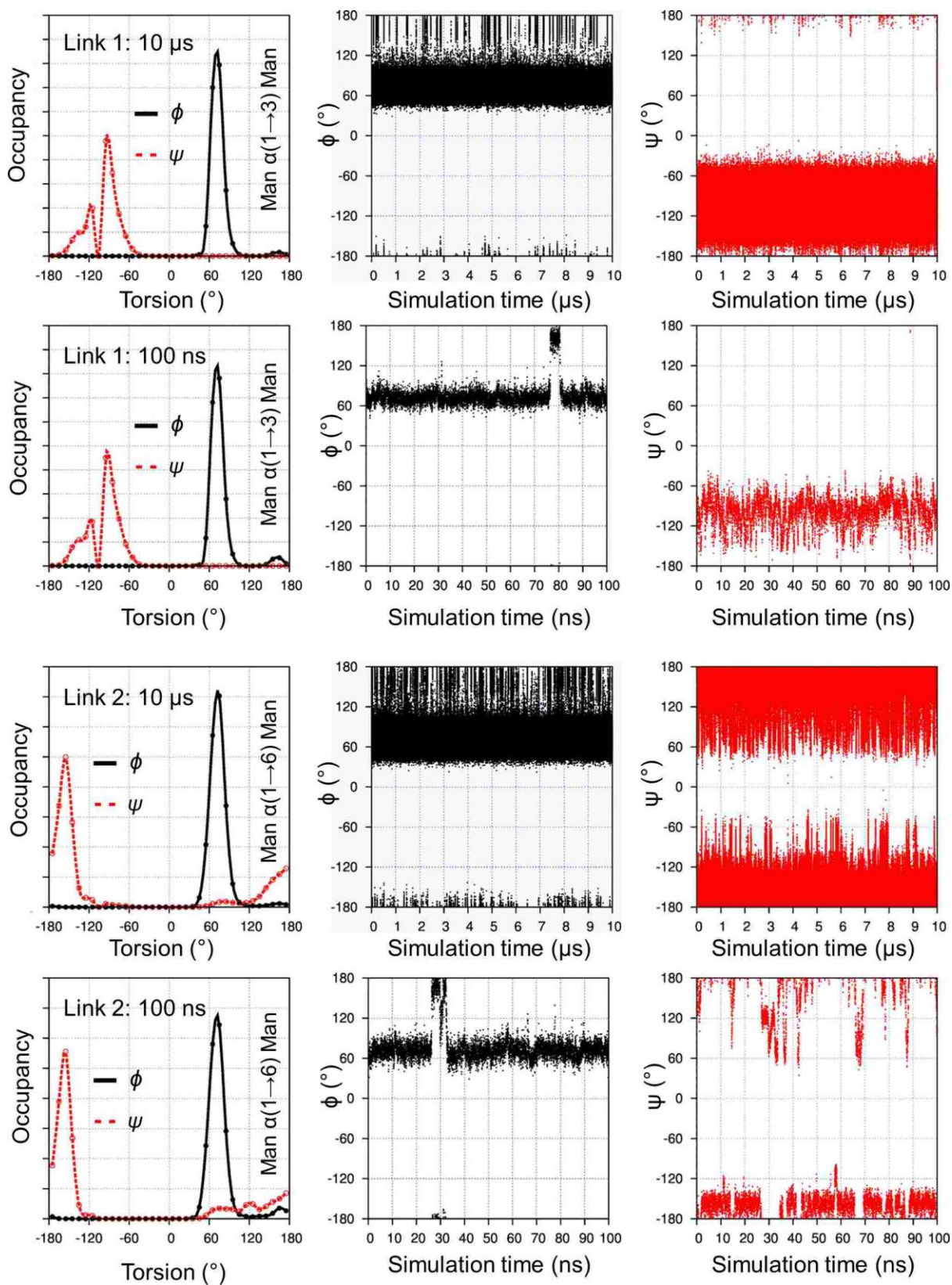
Figure S8. Time series of linkage torsions (10 μ s and initial 100 ns): molecule 7

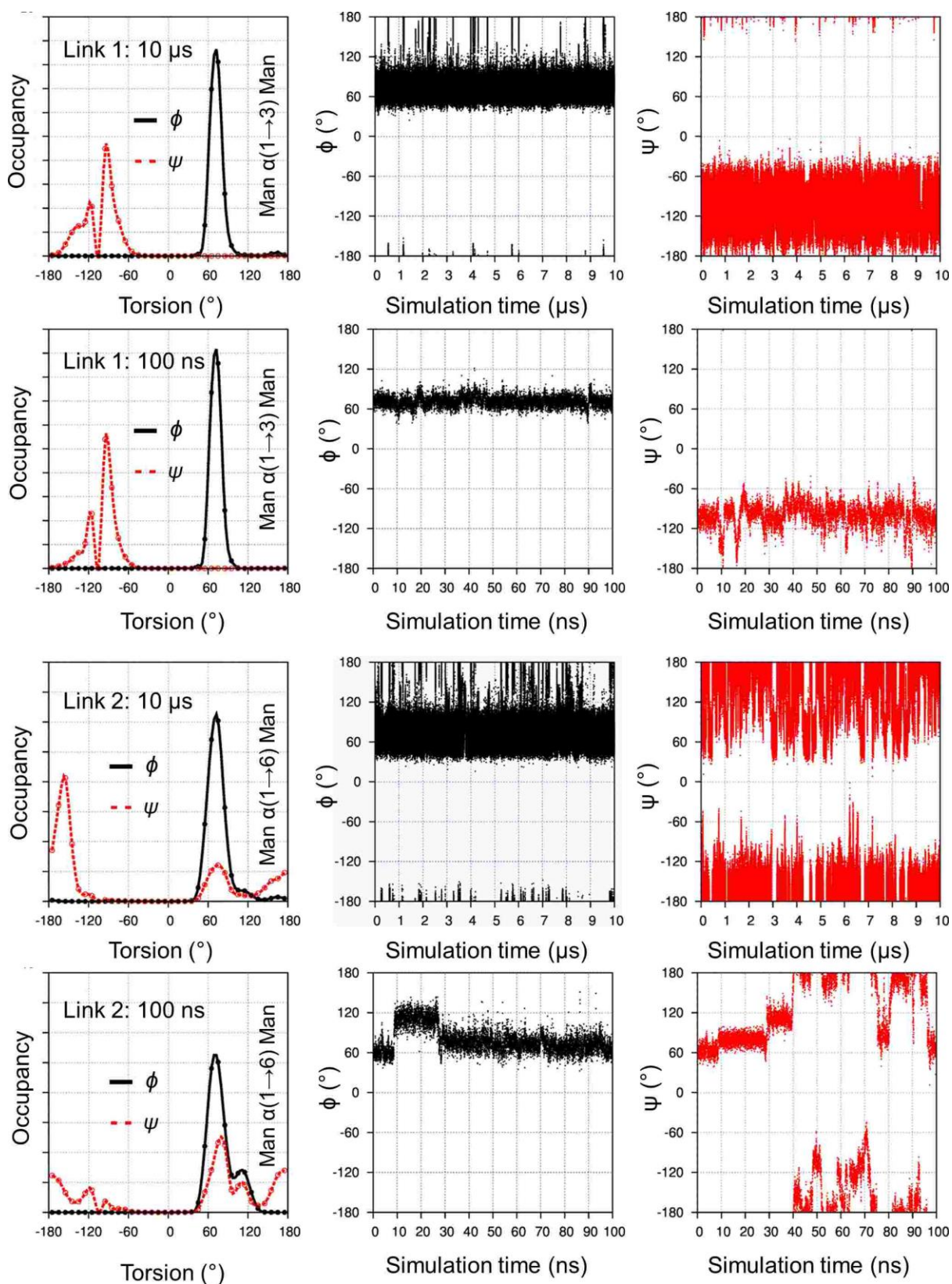
Figure S9. Time series of linkage torsions (10 μ s and initial 100 ns): molecule **8**

Figure S9 continued

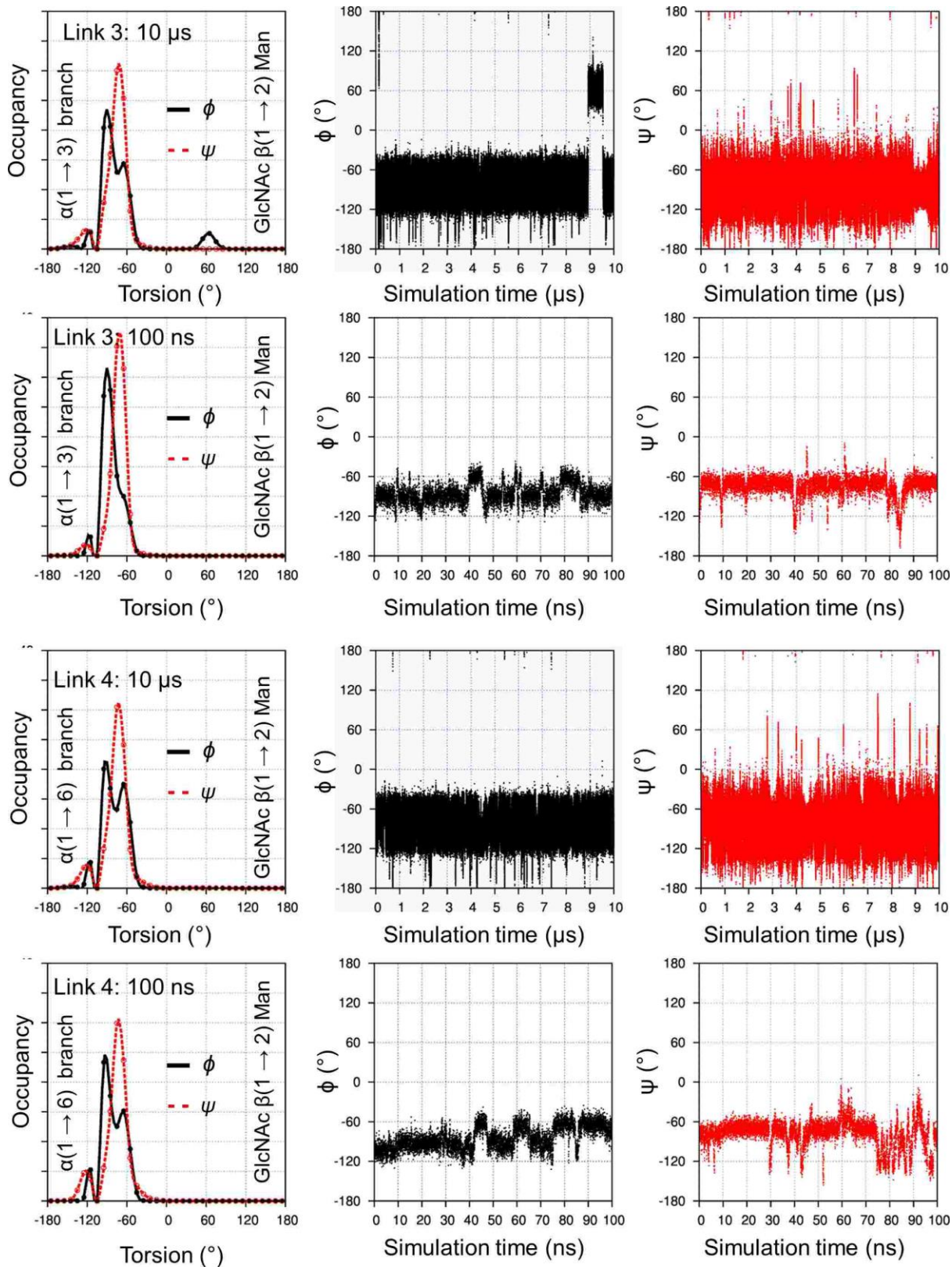


Figure S10. Linkage free energy surfaces (10 μ s): molecules **1-4** (contours at 2, 4 and 6 kcal mol⁻¹)

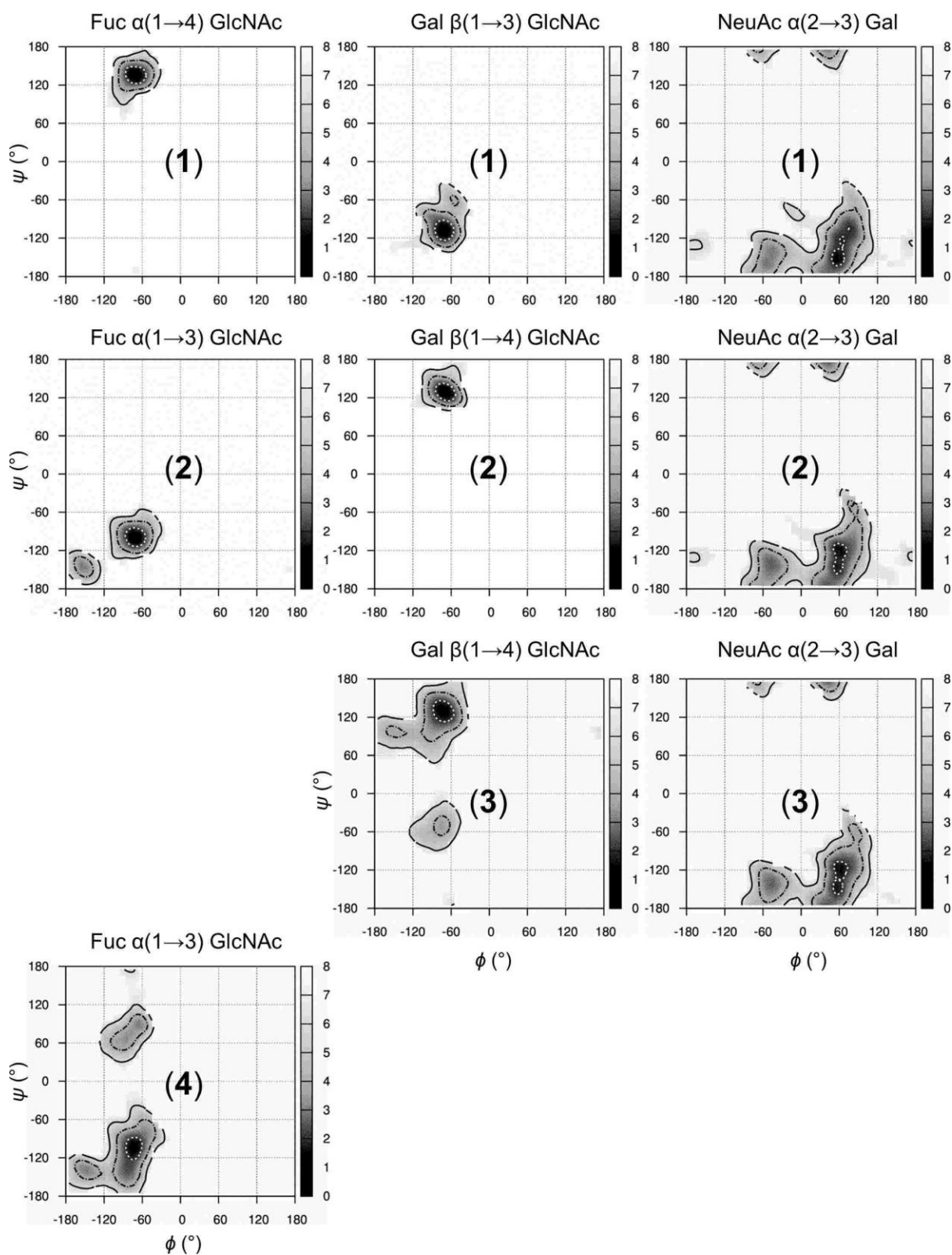


Figure S11. Linkage free energy surfaces (100 ns): molecules **1-4** (contours at 2, 4 and 6 kcal mol⁻¹)

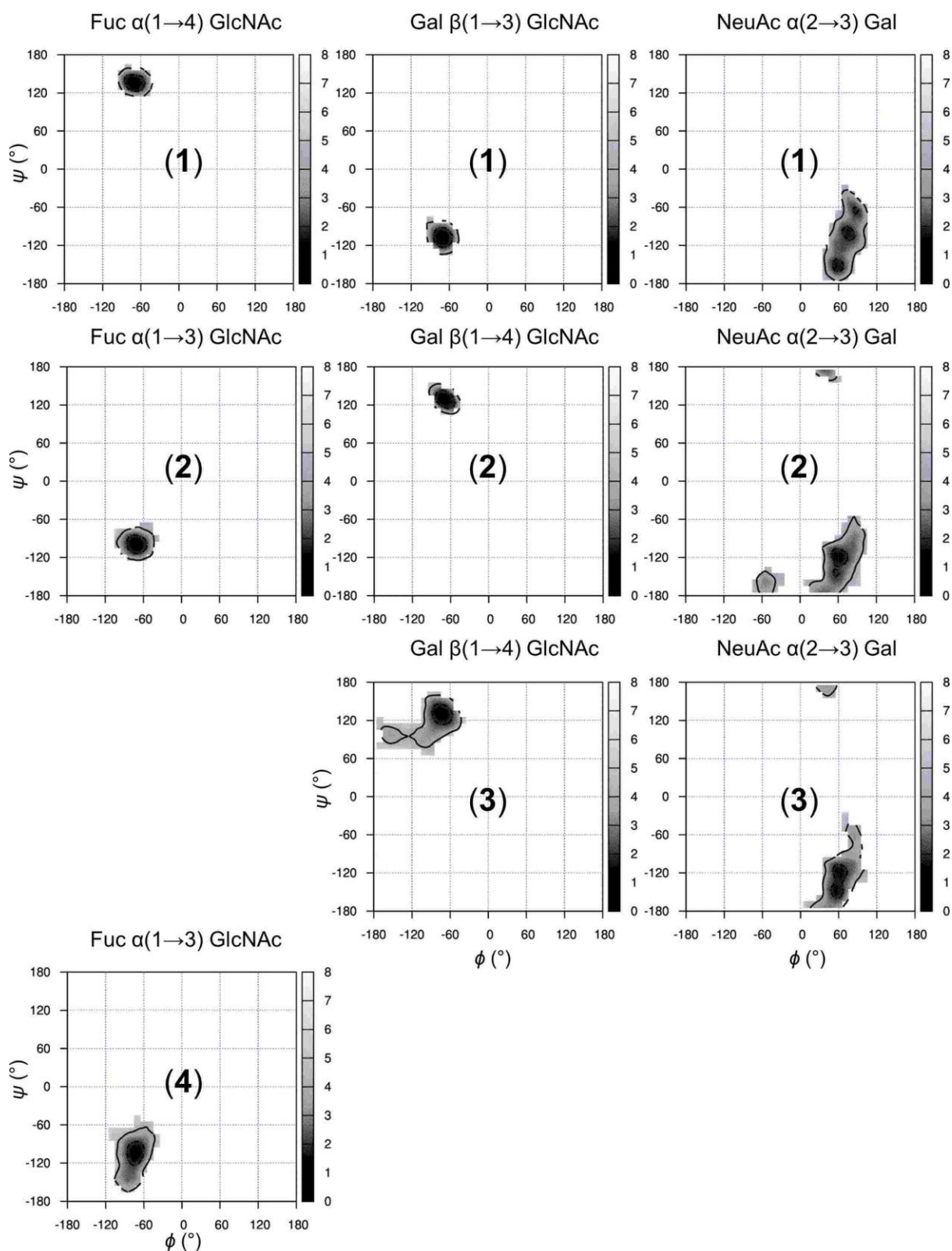
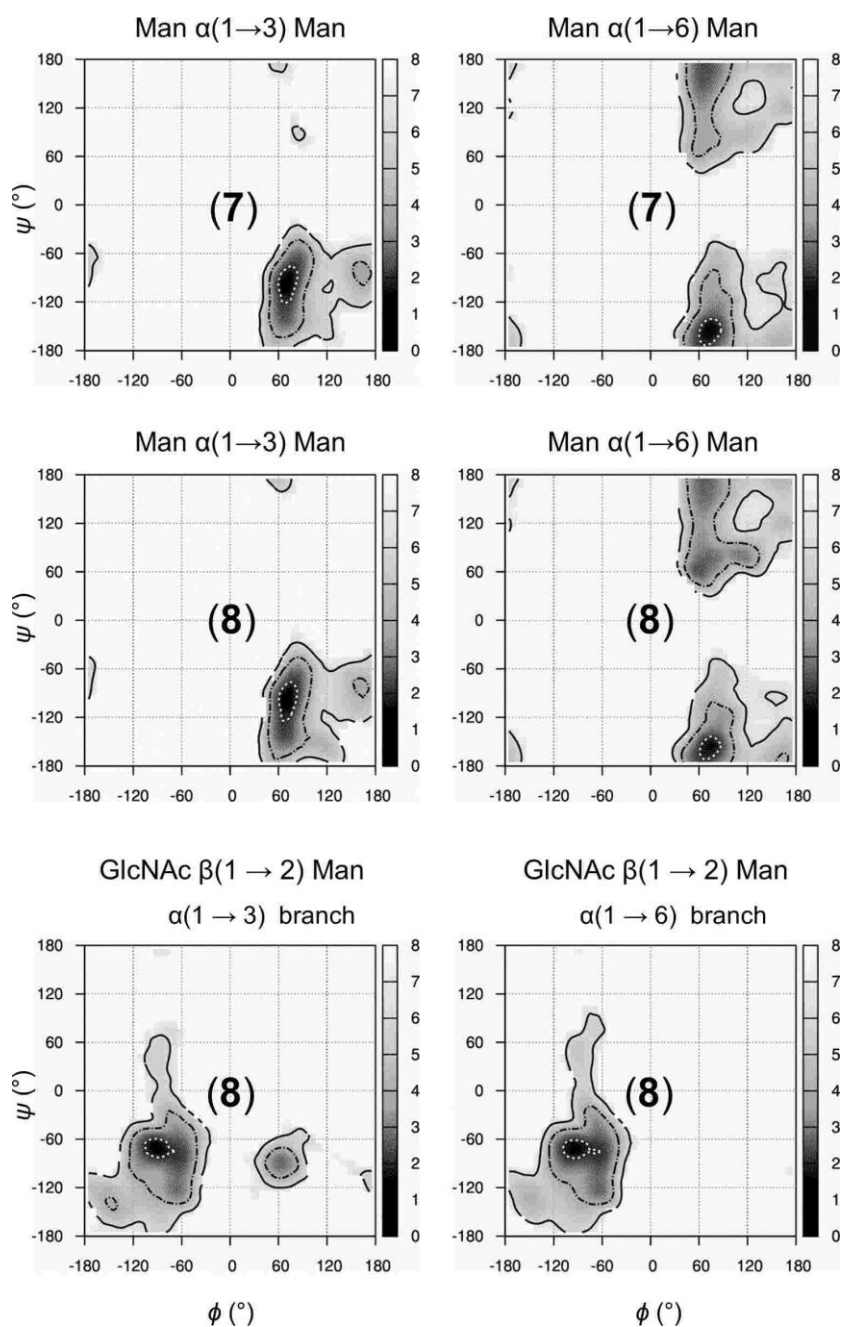


Figure S12. Linkage free energy surfaces (10 μ s): molecules **7-8** (contours at 2, 4 and 6 kcal mol⁻¹)



Computed average $\alpha(1-6)$ ω torsions in **7** and **8**: (also see Table 1 Legend)

Torsion	Mol	CAL (μ s)		CAL (ns)		NMR ¹	
		ω ($\pm\sigma$)	min	ω ($\pm\sigma$)	min	ω ($\pm\sigma$)	min
Man-Man	7	54 (52)	2	53 (10)	1	60	>1
Man-Man	8	51 (41)	2	-120 (99)	2	60	>1

(1) Sayers, E. W.; Prestegard, J. H. *Biophys J* **2000**, *79*, 3313.

Figure S13. Linkage free energy surfaces (100 ns): molecules **7-8** (contours at 2, 4 and 6 kcal mol⁻¹)

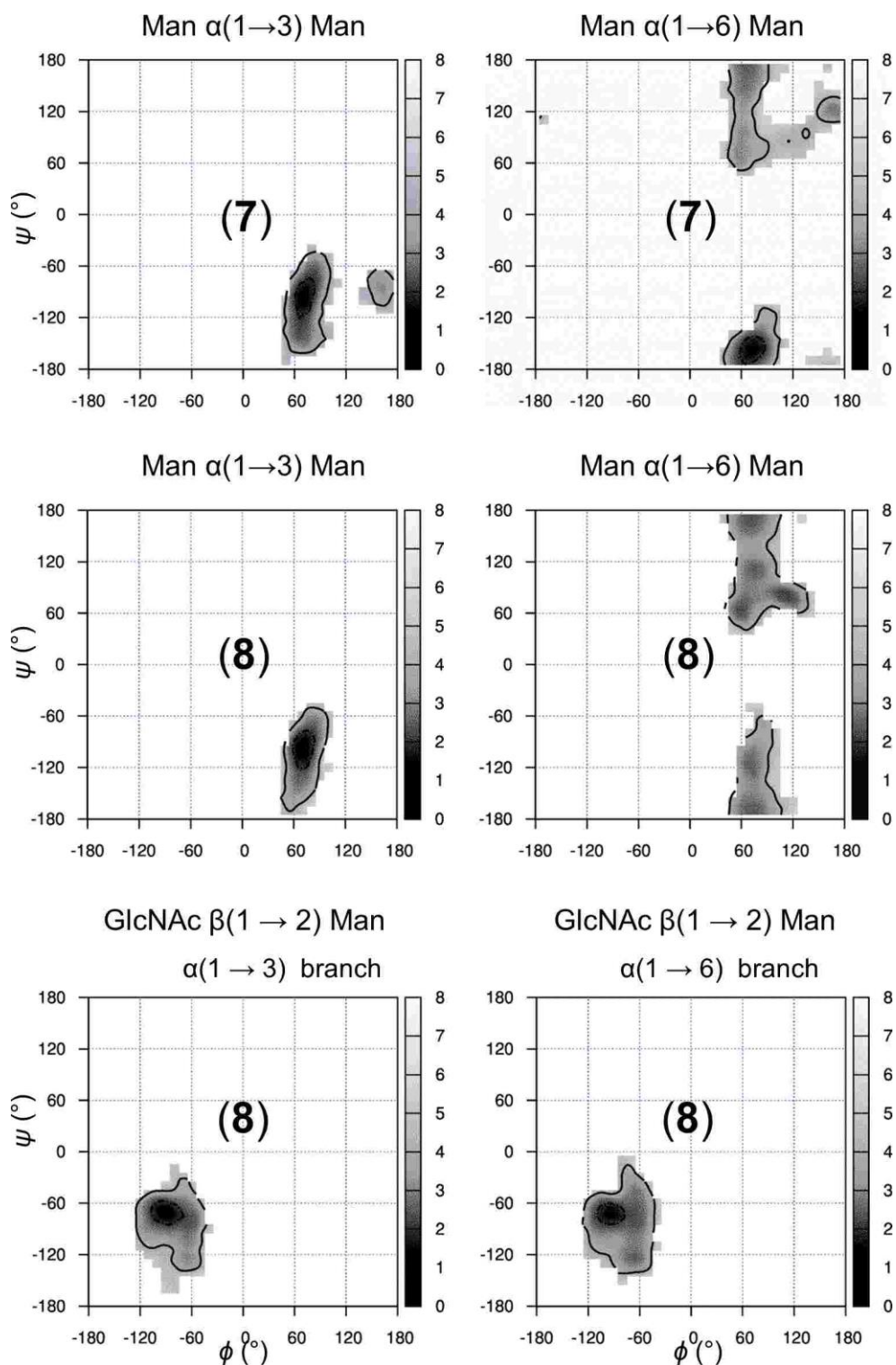


Figure S14. Puckering convergence (red line denotes simulation average) and time series: molecule 1

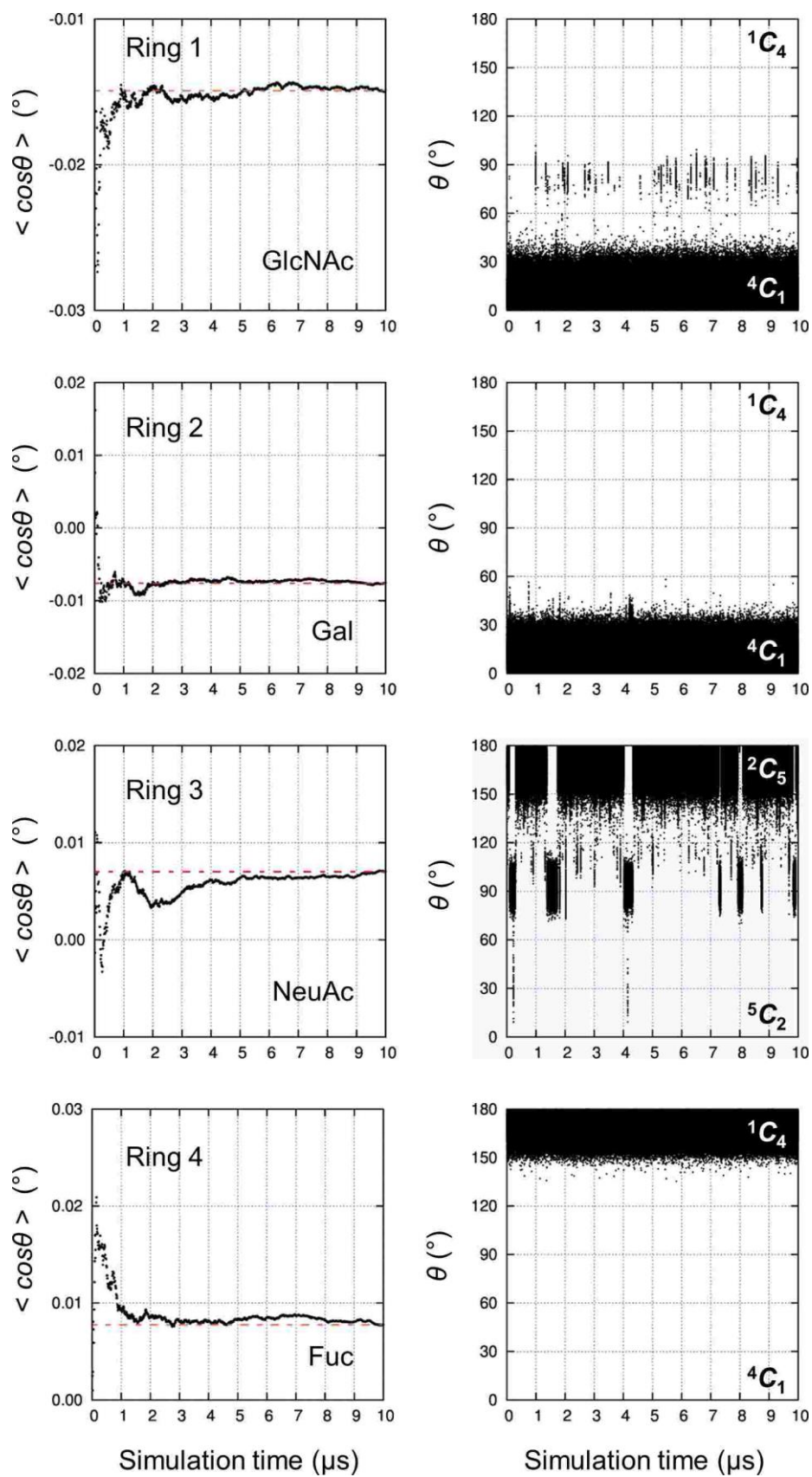


Figure S15. Puckering convergence (red line denotes simulation average) and time series: molecule 2

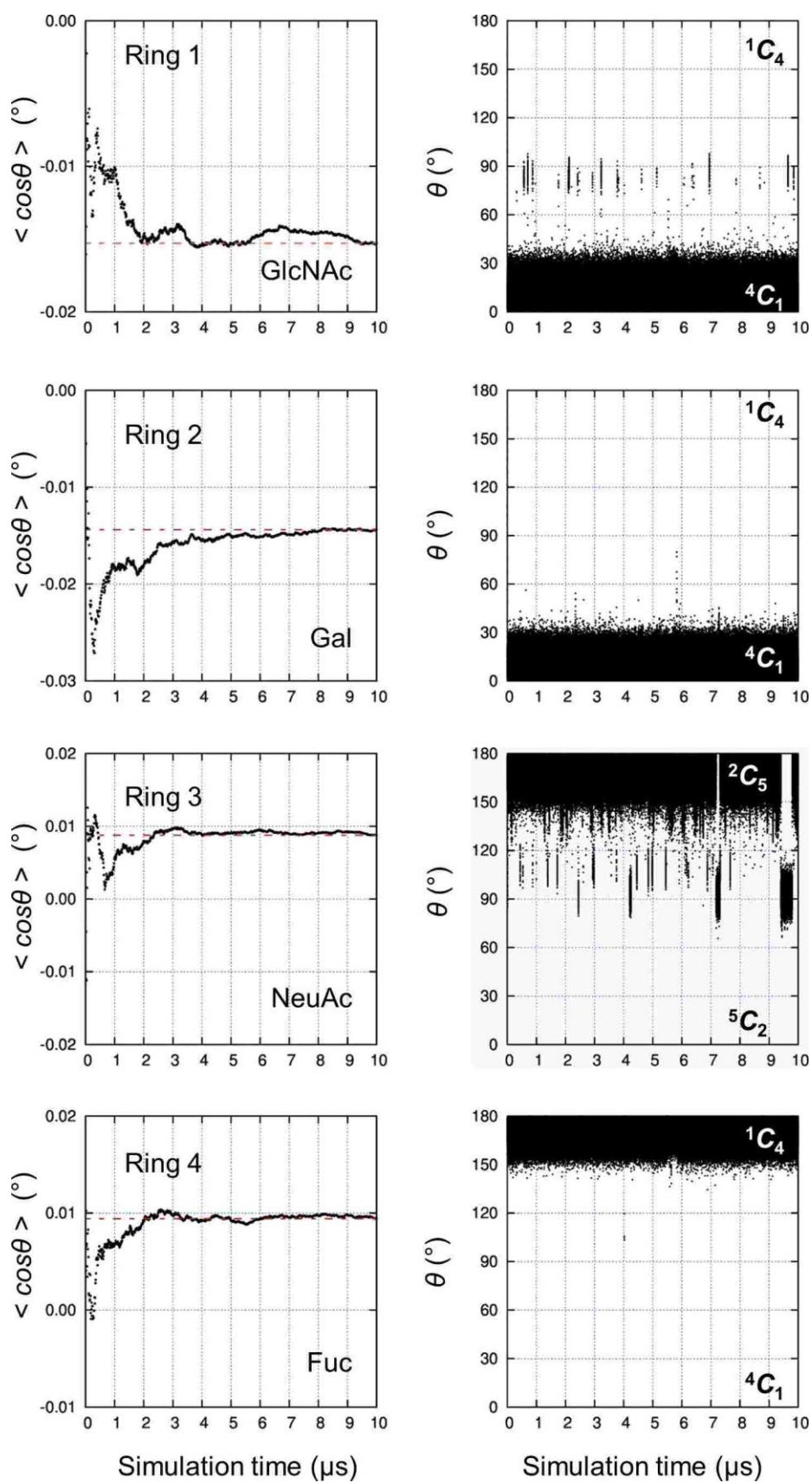


Figure S16. Puckering convergence (red line denotes simulation average) and time series: molecule 2

25 μ s simulation

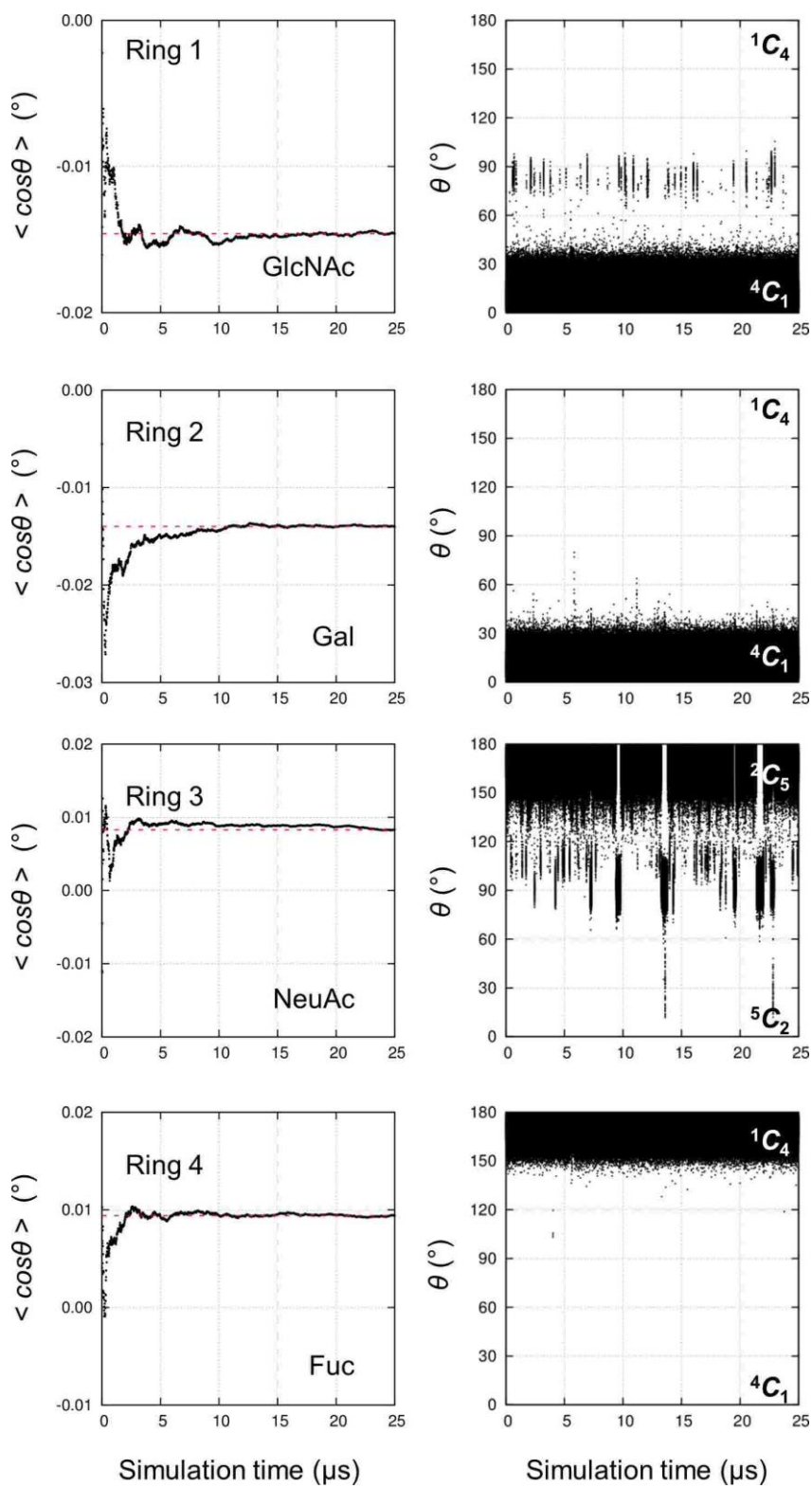


Figure S17. Puckering convergence (red line denotes simulation average) and time series: molecule 3

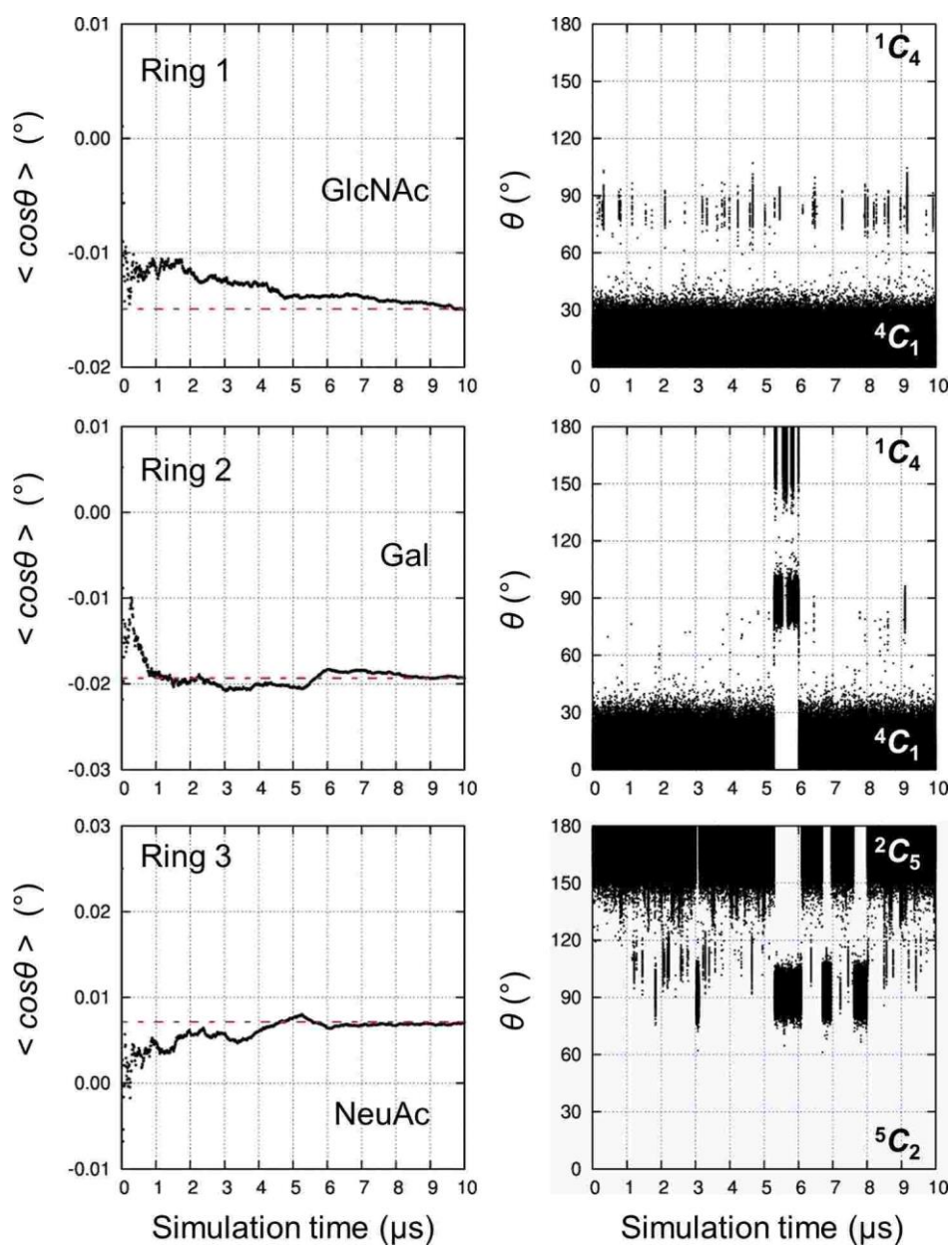
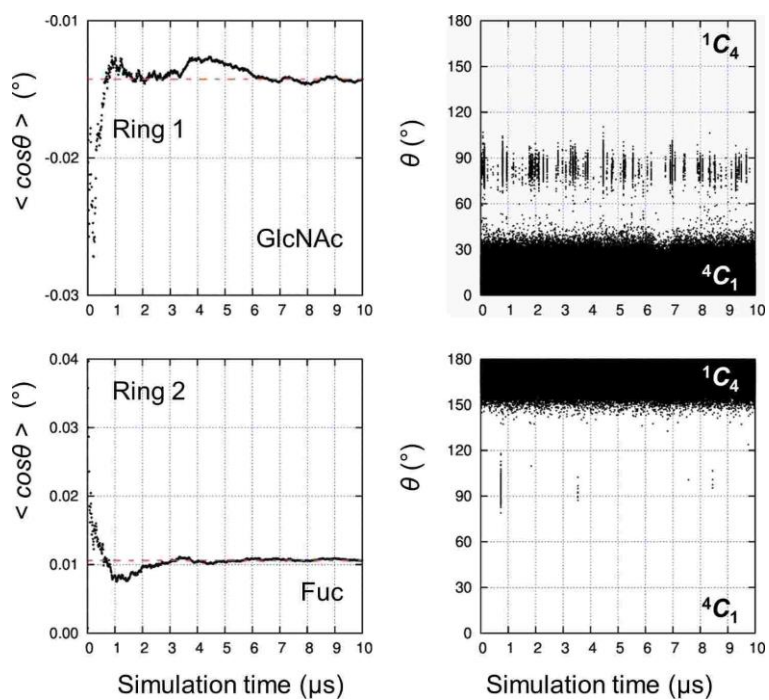
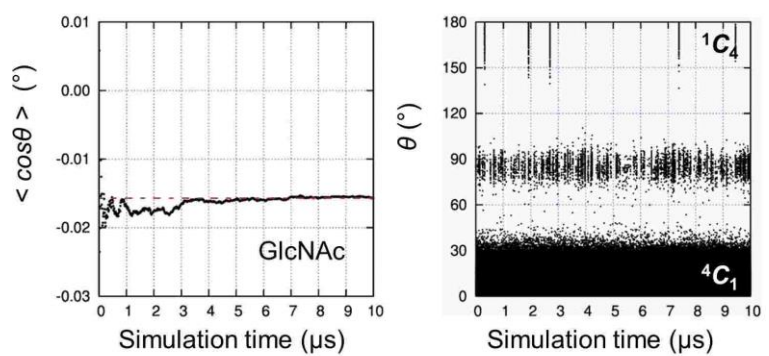


Figure S18. Puckering convergence (red line denotes simulation average) and time series: mols 4-6



GlcNAc (5)



NeuAc (6)

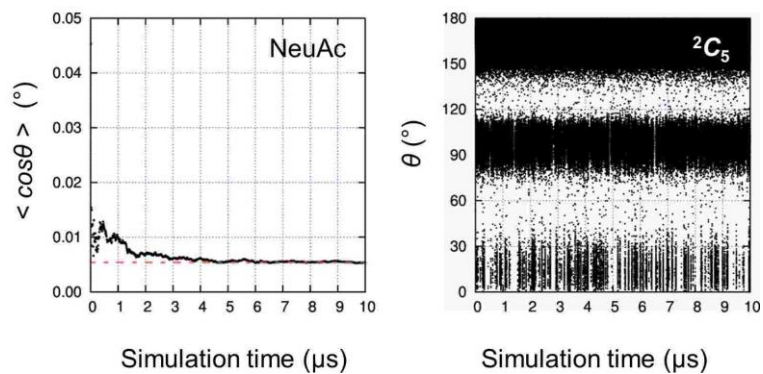


Figure S19. Puckering convergence (red line denotes simulation average) and time series: molecule 7

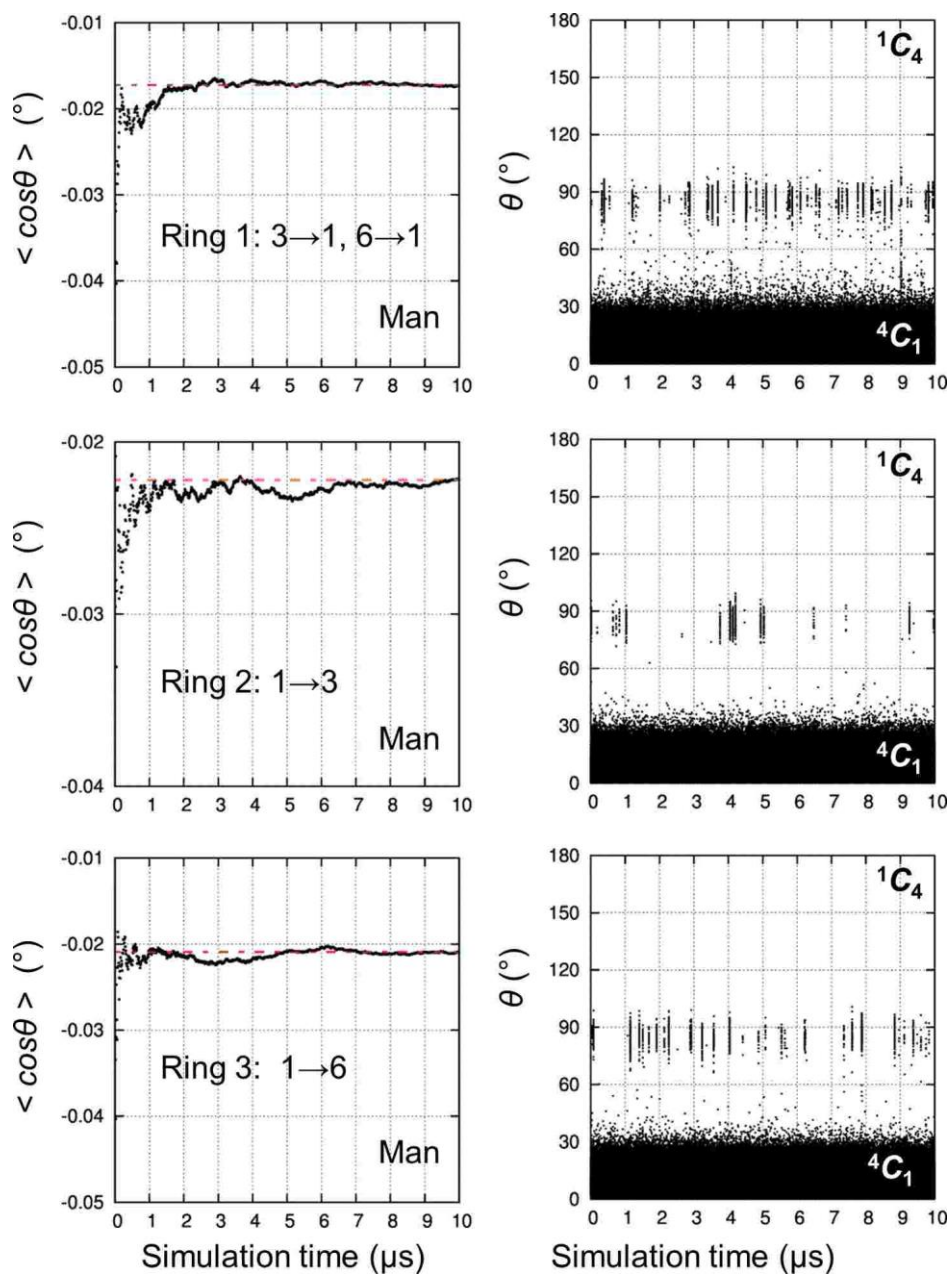


Figure S20. Puckering convergence (red line denotes simulation average) and time series: molecule 8

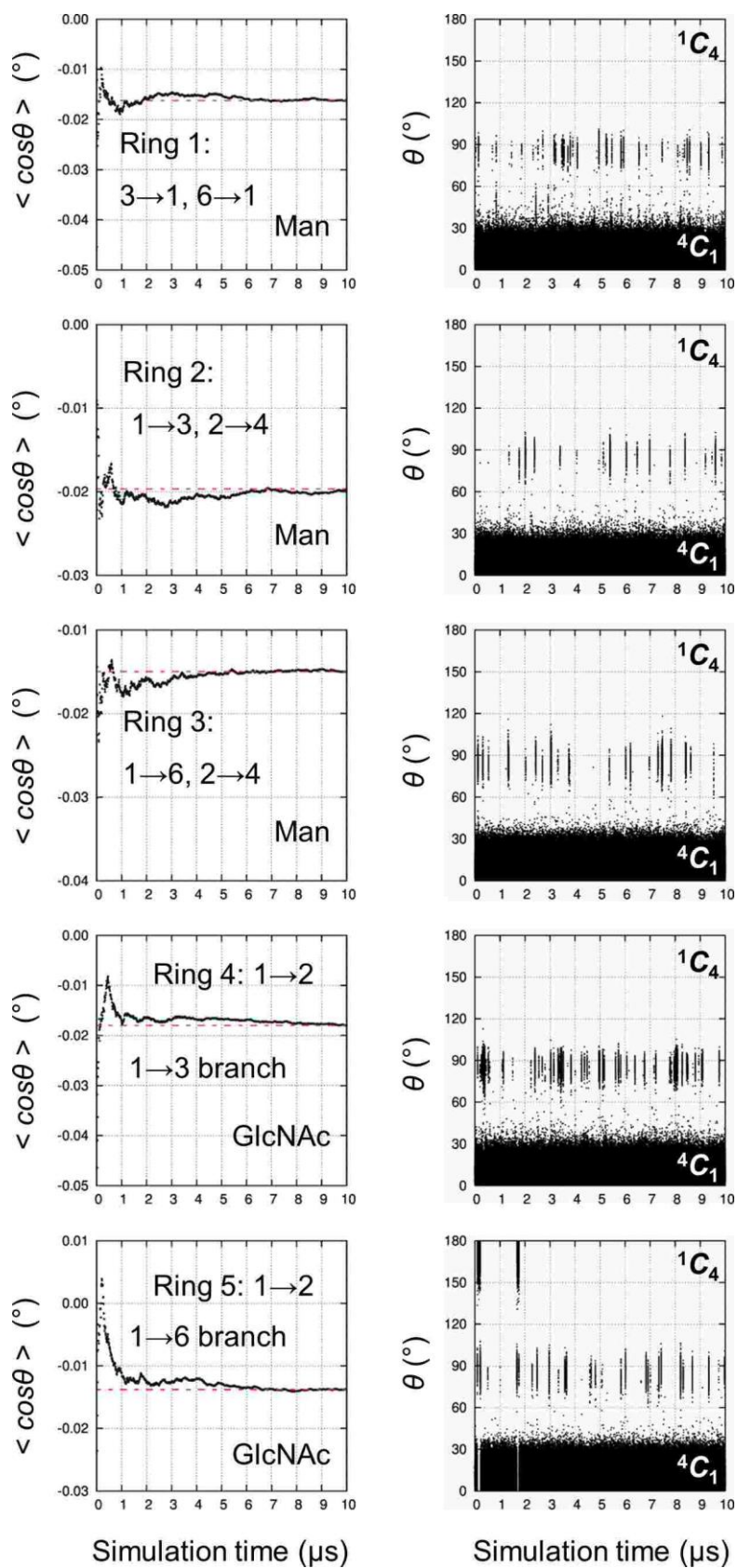


Table S21. Calculated pyranose ring puckering populations (%) and relative free energies (ΔG , kcal mol⁻¹) from the 10 μ s simulations: GlcNAc

Mol (1) GlcNAc			Mol (2) GlcNAc			Mol (3) GlcNAc			Mol (4) GlcNAc			Mol (8) 1→3 branch GlcNAc			Mol (8) 1→6 branch GlcNAc		
Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG
4C1	99.7310	0.00	4C1	99.8474	0.00	4C1	99.6651	0.00	4C1	99.4440	0.00	4C1	98.8646	0.01	4C1	97.1438	0.02
1S3	0.0717	4.29	1S3	0.0289	4.83	OS2	0.0579	4.42	1S3	0.1346	3.92	B3O	0.3325	3.38	1C4	1.8959	2.35
B3O	0.0369	4.69	14B	0.0282	4.85	1S3	0.0562	4.44	B3O	0.0640	4.36	2SO	0.2553	3.54	B3O	0.2735	3.50
14B	0.0277	4.86	1S5	0.0181	5.11	3OB	0.0444	4.58	3S1	0.0637	4.36	1S3	0.1865	3.73	1S3	0.1770	3.76
E5	0.0241	4.94	B3O	0.0126	5.32	14B	0.0323	4.77	2SO	0.0568	4.43	14B	0.1283	3.95	2SO	0.1449	3.88
4H5	0.0177	5.12	4H5	0.0112	5.39	3S1	0.0298	4.81	14B	0.0453	4.57	3S1	0.0579	4.42	14B	0.0728	4.28
OH5	0.0158	5.19	E5	0.0109	5.41	B3O	0.0230	4.97	3OB	0.0223	4.99	1S5	0.0497	4.51	3S1	0.0715	4.30
2SO	0.0140	5.26	OH5	0.0089	5.53	1S5	0.0141	5.26	OH5	0.0160	5.18	3OB	0.0252	4.91	3OB	0.0582	4.42
4H3	0.0131	5.30	4H3	0.0064	5.73	2SO	0.0113	5.39	OE	0.0154	5.21	OS2	0.0139	5.27	1S5	0.0438	4.59
4E	0.0127	5.32	4E	0.0060	5.76	4H3	0.0099	5.47	1S5	0.0145	5.24	OH5	0.0121	5.35	OS2	0.0347	4.72
E3	0.0081	5.59	E3	0.0049	5.88	4E	0.0070	5.67	E3	0.0144	5.25	OE	0.0100	5.46	E5	0.0098	5.47
OE	0.0072	5.66	OE	0.0045	5.94	OH5	0.0065	5.72	OH1	0.0141	5.26	E5	0.0076	5.62	OH5	0.0090	5.52
2H3	0.0053	5.84	2SO	0.0036	6.07	4H5	0.0061	5.75	B14	0.0137	5.28	B14	0.0072	5.66	OE	0.0090	5.52
1S5	0.0038	6.04	2H3	0.0028	6.22	E3	0.0061	5.75	E5	0.0111	5.40	E3	0.0072	5.66	B14	0.0071	5.66
OH1	0.0037	6.05	2E	0.0018	6.48	B25	0.0056	5.81	2H3	0.0111	5.40	4H3	0.0057	5.80	E3	0.0071	5.66
2E	0.0031	6.16	OH1	0.0016	6.55	OE	0.0056	5.81	4H3	0.0106	5.43	2H3	0.0053	5.84	OH1	0.0069	5.68
2H1	0.0024	6.31	E1	0.0014	6.63	E5	0.0055	5.82	5S1	0.0084	5.57	5S1	0.0049	5.88	4H3	0.0068	5.69
E1	0.0016	6.55	2H1	0.0008	6.96	OH1	0.0038	6.04	4H5	0.0075	5.63	OH1	0.0042	5.98	4H5	0.0053	5.84
25B	0.0001	8.19				2H3	0.0028	6.22	2E	0.0070	5.67	4H5	0.0040	6.01	2H3	0.0049	5.88
						2E	0.0027	6.24	4E	0.0065	5.72	2E	0.0038	6.04	E1	0.0040	6.01
						E1	0.0026	6.26	E1	0.0064	5.73	2H1	0.0035	6.08	2E	0.0038	6.04
						2H1	0.0009	6.89	OS2	0.0047	5.91	4E	0.0030	6.18	2H1	0.0022	6.36
						B14	0.0007	7.04	2H1	0.0039	6.02	25B	0.0028	6.22	B25	0.0021	6.39
						25B	0.0001	8.19	25B	0.0021	6.39	E1	0.0026	6.26	5S1	0.0016	6.55
									B25	0.0018	6.48	B25	0.0017	6.51	25B	0.0015	6.59
									1HO	0.0001	8.19	E4	0.0003	7.54	4E	0.0014	6.63
												EO	0.0001	8.19	1H2	0.0007	7.04
												3H2	0.0001	8.19	5HO	0.0002	7.78
															5H4	0.0002	7.78
															E2	0.0002	7.78
															5E	0.0001	8.19

Table S22. Calculated pyranose ring puckering populations (%) and relative free energies (ΔG , kcal mol⁻¹) from the 10 μ s simulations: Gal and Fuc

Mol (1) Gal			Mol (2) Gal			Mol (3) Gal			Mol (1) Fuc			Mol (2) Fuc			Mol (4) Fuc		
Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG	1C4			Puck	%	ΔG
4C1	99.9168	0.00	4C1	99.981	0.00	4C1	92.6621	0.05	1C4	99.9951	0.00	1C4	99.9959	0.00	1C4	99.9514	0.00
E5	0.0383	4.67	E5	0.005	5.83	OS2	4.2504	1.87	1E	0.0017	6.51	EO	0.0009	6.89	3S1	0.0352	4.72
4H5	0.0152	5.21	OH5	0.004	5.99	1C4	2.3229	2.23	1HO	0.0011	6.77	1E	0.0007	7.04	B14	0.0040	6.01
OH5	0.0114	5.38	4E	0.003	6.20	B25	0.2715	3.50	EO	0.0009	6.89	5HO	0.0003	7.54	1E	0.0028	6.22
4H3	0.0084	5.57	4H5	0.002	6.31	3OB	0.2158	3.64	1H2	0.0006	7.13	1HO	0.0003	7.54	1HO	0.0021	6.39
4E	0.0072	5.66	4H3	0.002	6.48	1S5	0.1216	3.98	5HO	0.0003	7.54	3OB	0.0002	7.78	3OB	0.0016	6.55
E3	0.0023	6.33	E3	0.002	6.59	1S3	0.0496	4.51	E2	0.0002	7.78	3S1	0.0001	8.19	1H2	0.0013	6.67
2H3	0.0004	7.37	2H3	0.001	7.24	B3O	0.0282	4.85	5E	0.0001	8.19	E2	0.0001	8.19	5S1	0.0004	7.37
			1S3	0.000	7.78	14B	0.0175	5.13							E2	0.0004	7.37
						E5	0.0126	5.32							EO	0.0003	7.54
						4H5	0.0120	5.35							5E	0.0002	7.78
						4E	0.0102	5.45							3H2	0.0002	7.78
						4H3	0.0079	5.60							5HO	0.0001	8.19
						EO	0.0044	5.95									
						OH5	0.0039	6.02									
						2SO	0.0036	6.07									
						E3	0.0014	6.63									
						5HO	0.0011	6.77									
						1HO	0.0011	6.77									
						5E	0.0009	6.89									
						OE	0.0004	7.37									
						2H3	0.0004	7.37									
						5H4	0.0002	7.78									
						3S1	0.0001	8.19									
						OH1	0.0001	8.19									
						2E	0.0001	8.19									

Table S23. Calculated pyranose puckering populations (%) and relative free energies (ΔG , kcal mol⁻¹) from the 10 μ s simulations: NeuAc

NB: In this table $\theta=O5-C1-C2-C3-C4-C5$ (not $O6-C2-C3-C4-C5-C6$), therefore the carbon number should be incremented by 1 (i.e. ¹C₄=²C₅, ⁵S₁=⁶S₂ etc.)

Mol (1) NeuAc			Mol (2) NeuAc			Mol (3) NeuAc			Mol (6) NeuAc		
Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG
1C4	86.9965	0.08	1C4	93.7913	0.04	1C4	83.9744	0.10	1C4	87.8913	0.08
5S1	10.4665	1.34	5S1	4.8863	1.79	5S1	12.1260	1.25	3OB	2.7366	2.13
B14	1.5216	2.48	B14	0.3887	3.29	25B	2.3730	2.22	3S1	2.0671	2.30
25B	0.3201	3.41	25B	0.2434	3.57	B14	0.7873	2.87	OS2	2.0656	2.30
2SO	0.2003	3.68	1HO	0.1390	3.90	2SO	0.1705	3.78	5S1	1.4890	2.49
EO	0.1144	4.02	EO	0.1382	3.90	1HO	0.1240	3.97	4C1	1.1169	2.67
1HO	0.0957	4.12	5HO	0.1260	3.96	5HO	0.1182	4.00	B14	0.8522	2.83
5HO	0.0949	4.13	2SO	0.0989	4.10	EO	0.1135	4.02	25B	0.6225	3.01
OS2	0.0382	4.67	OS2	0.0776	4.25	OS2	0.0945	4.13	EO	0.3871	3.29
5H4	0.0349	4.72	5H4	0.0296	4.82	5H4	0.0268	4.88	2SO	0.3608	3.34
E4	0.0192	5.07	E4	0.0194	5.07	E4	0.0179	5.12	5HO	0.1805	3.75
B3O	0.0158	5.19	1E	0.0181	5.11	1E	0.0148	5.23	1HO	0.0488	4.52
5E	0.0157	5.19	5E	0.0149	5.23	5E	0.0145	5.24	5H4	0.0372	4.68
1E	0.0144	5.25	3OB	0.0081	5.59	3OB	0.0098	5.47	5E	0.0329	4.76
1S3	0.0083	5.57	B3O	0.0066	5.71	B3O	0.0084	5.57	2H1	0.0209	5.02
3S1	0.0068	5.69	1H2	0.0033	6.12	3S1	0.0068	5.69	E4	0.0164	5.17
1H2	0.0068	5.69	3H4	0.0029	6.20	1H2	0.0039	6.02	E1	0.0158	5.19
E2	0.0066	5.71	E2	0.0017	6.51	1S3	0.0032	6.14	B25	0.0102	5.45
4C1	0.0060	5.76	1S5	0.0012	6.72	1S5	0.0031	6.16	B3O	0.0098	5.47
3OB	0.0053	5.84	3S1	0.0011	6.77	B25	0.0025	6.28	1E	0.0087	5.54
B25	0.0031	6.16	3H2	0.0011	6.77	3H4	0.0022	6.36	2E	0.0061	5.75
2H3	0.0031	6.16	1S3	0.0009	6.89	E2	0.0019	6.45	1H2	0.0046	5.92
3H4	0.0019	6.45	2H3	0.0006	7.13	3H2	0.0012	6.72	E2	0.0042	5.98
3H2	0.0012	6.72	14B	0.0004	7.37	2H1	0.0004	7.37	2H3	0.0036	6.07
E3	0.0009	6.89	2H1	0.0003	7.54	2H3	0.0004	7.37	3H4	0.0035	6.08
1S5	0.0007	7.04	B25	0.0002	7.78	E3	0.0003	7.54	1S3	0.0032	6.14
3E	0.0005	7.24	3E	0.0002	7.78	E1	0.0002	7.78	E3	0.0010	6.83
2H1	0.0003	7.54				3E	0.0002	7.78	3H2	0.0010	6.83
4H3	0.0002	7.78				14B	0.0001	8.19	1S5	0.0008	6.96
2E	0.0001	8.19							3E	0.0006	7.13
									14B	0.0005	7.24
									E5	0.0002	7.78
									4H3	0.0002	7.78
									4E	0.0001	8.19
									OH1	0.0001	8.19

Table S24. Calculated pyranose ring puckering populations (%) and relative free energies (ΔG , kcal mol⁻¹) from the 10 μ s simulations: Man

Mol (7) Man (1→3,1→6)			Mol (7) Man (1→3)			Mol (7) Man (1→6)			Mol (8) Man (1→3,1→6)			Mol (8) Man (1→3)			Mol (8) Man (1→6)		
Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG	Puck	%	ΔG
4C1	99.6457	0.00	4C1	99.8996	0.00	4C1	99.7982	0.00	4C1	99.5905	0.00	4C1	99.4711	0.00	4C1	97.9142	0.01
B3O	0.2304	3.60	B3O	0.0579	4.42	B3O	0.1127	4.03	B3O	0.2858	3.47	B3O	0.3989	3.28	B3O	1.3841	2.54
2SO	0.0398	4.64	2SO	0.0255	4.91	2SO	0.0675	4.33	2SO	0.0417	4.62	2SO	0.0856	4.19	2SO	0.6024	3.03
2E	0.0270	4.87	2H3	0.0059	5.77	2H3	0.0075	5.63	2E	0.0285	4.84	2H3	0.0113	5.39	1S3	0.0398	4.64
2H3	0.0242	4.94	2E	0.0058	5.78	2E	0.0060	5.76	2H3	0.0233	4.96	2E	0.0112	5.39	2H3	0.0204	5.04
2H1	0.0110	5.41	2H1	0.0025	6.28	E3	0.0032	6.14	2H1	0.0129	5.31	1S3	0.0074	5.64	E3	0.0134	5.29
1S3	0.0106	5.43	E3	0.0010	6.83	2H1	0.0021	6.39	E3	0.0079	5.60	2H1	0.0055	5.82	2E	0.0115	5.38
E3	0.0068	5.69	1S3	0.0005	7.24	1S3	0.0015	6.59	1S3	0.0047	5.91	E3	0.0033	6.12	2H1	0.0048	5.90
4H3	0.0032	6.14	E1	0.0004	7.37	4H3	0.0008	6.96	4H3	0.0028	6.22	5S1	0.0021	6.39	4H3	0.0030	6.18
E1	0.0006	7.13	4H3	0.0004	7.37	E1	0.0003	7.54	4E	0.0006	7.13	4H3	0.0012	6.72	E5	0.0013	6.67
4E	0.0004	7.37	25B	0.0003	7.54	4E	0.0002	7.78	25B	0.0005	7.24	E5	0.0004	7.37	4E	0.0011	6.77
25B	0.0002	7.78	4E	0.0002	7.78				E1	0.0003	7.54	4H5	0.0004	7.37	OH5	0.0008	6.96
E5	0.0001	8.19							5S1	0.0002	7.78	4E	0.0004	7.37	4H5	0.0008	6.96
									4H5	0.0002	7.78	25B	0.0003	7.54	E1	0.0007	7.04
									OH1	0.0001	8.19	E1	0.0003	7.54	5S1	0.0005	7.24
												OH5	0.0003	7.54	25B	0.0005	7.24
												OH1	0.0002	7.78	OH1	0.0003	7.54
												B14	0.0001	8.19	OE	0.0002	7.78
															14B	0.0001	8.19
															3H4	0.0001	8.19

Table S25: Calculated and experimental (EXP) NMR three-bond vicinal couplings (Hz): molecules **1-8**

All calculated data for **1-8** are derived from 10 μ s simulations (also see Computational Methods).

Key:

- Reference calculated and experimental values not from this work are italicised and underlined
- Mono: data for the free aqueous monosaccharide (calculated or experimental)
- DP3: the trisaccharide NeuAc- α (2 \rightarrow 3)-Gal- β (1 \rightarrow 4)-Glc
- HA: mean values from NMR for internal GlcNAc rings in a hyaluronan oligosaccharide
- Experimental errors are estimated to be ± 0.2 Hz
- 10 μ s simulations were split into 1 μ s sub-sets to compute standard deviations (at most ± 0.4 Hz)

A. GlcNAc

	(1)	(2)	(3)	(4)	(5)	(8) ^{1\rightarrow3}	(8) ^{1\rightarrow6}	<i>EXP Mono</i> ²	<i>EXP HA</i> ²
$J_{1,2}$	7.5	7.5	7.5	7.5	7.5	7.5	7.4	<u>8.5</u>	<u>8.6</u>
$J_{2,3}$	8.7	8.5	8.7	8.7	8.6	8.5	8.4	<u>10.4</u>	<u>10.3</u>
$J_{3,4}$	8.0	7.8	8.0	8.0	7.6	7.6	7.5	<u>8.8</u>	<u>8.7</u>
$J_{4,5}$	8.4	8.4	8.3	8.3	8.2	8.2	8.1	<i>n/d</i>	<u>9.9</u>

n/d = not determined

B. Gal

	(1)	(2)	(3)	<i>CAL Mono</i> ³	<i>EXP MonoA</i> ⁴	<i>EXP MonoB</i> ⁵	<i>EXP DP3</i> ⁵
$J_{1,2}$	7.9	8.1	7.7	<u>8.1</u>	<u>8.0</u>	<u>7.9</u>	<u>7.8</u>
$J_{2,3}$	8.2	8.3	7.8	<u>8.3</u>	<u>10.0</u>	<u>9.9</u>	<u>9.0</u>
$J_{3,4}$	2.4	2.3	2.6	<u>2.5</u>	<u>3.8</u>	<u>3.5</u>	<u>3.1</u>
$J_{4,5}$	0.7	0.8	1.0	<u>0.8</u>	<u>1.0</u>	<u>1.5</u>	<u>1.5</u>

C. NeuAc

	(1)	(2)	(3)	(6)	<i>EXP MonoA</i> ⁵	<i>EXP MonoB</i> ⁶	<i>EXP DP3</i> ⁵
$J_{3ax,4}$	9.8	10.4	9.5	10.4	<u>12.3</u>	<u>11.8</u>	<u>11.5</u>
$J_{3eq,4}$	4.9	4.7	4.8	4.7	<u>5.0</u>	<u>5.0</u>	<u>4.5</u>
$J_{4,5}$	8.2	8.4	8.0	8.3	<u>10.2</u>	<u>10.4</u>	<u>10.4</u>
$J_{5,6}$	8.9	8.9	8.9	8.6	<u>10.3</u>	<u>10.7</u>	<u>9.9</u>

Table S25 continued

D. Fuc

	(1)	(2)	(4)	CAL Mono ³	EXP Mono ⁷
$J_{1,2}$	1.7	1.6	1.7	<u>3.5</u>	<u>4.0</u>
$J_{2,3}$	8.4	8.4	8.4	<u>8.4</u>	<u>10.0</u>
$J_{3,4}$	2.2	2.2	2.3	<u>2.4</u>	<u>4.2</u>
$J_{4,5}$	0.8	0.9	0.8	<u>0.9</u>	<u>0.9</u>

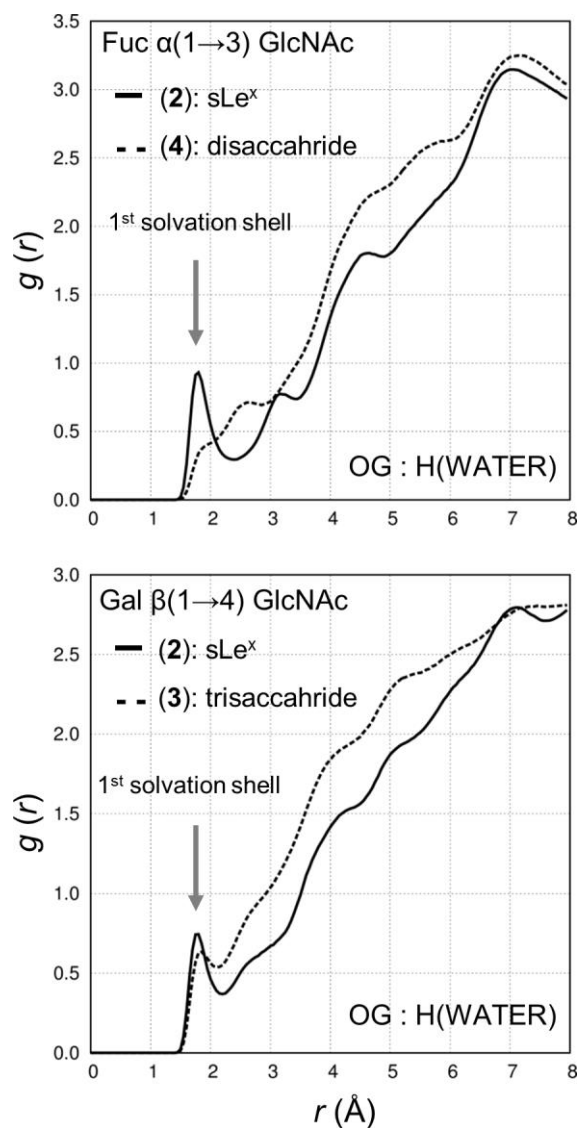
E. Man

Mol 7		(7) ^{1→3, 1→6}	(7) ^{1→3}	(7) ^{1→6}	Mono ^{3,4}
CAL	$J_{1,2}$	2.3	2.4	2.4	<u>2.3</u>
CAL	$J_{2,3}$	2.6	2.6	2.6	<u>2.6</u>
CAL	$J_{3,4}$	8.3	8.3	8.3	<u>8.3</u>
CAL	$J_{4,5}$	8.3	8.2	8.3	<u>8.2</u>
EXP ¹	$J_{1,2}$	<u>1.8</u>	<u>1.8</u>	<u>1.6</u>	<u>1.8</u>
EXP ¹	$J_{2,3}$	<u>3.3</u>	<u>3.6</u>	<u>3.3</u>	<u>3.8</u>
EXP ¹	$J_{3,4}$	<u>9.5</u>	<u>9.5</u>	<u>8.8</u>	<u>10.0</u>
EXP ¹	$J_{4,5}$	<u>9.8</u>	<u>8.0</u>	<u>10.3</u>	<u>9.8</u>

Mol 8		(8) ^{1→3, 1→6}	(8) ^{1→3}	(8) ^{1→6}
CAL	$J_{1,2}$	2.3	2.4	2.4
CAL	$J_{2,3}$	2.6	2.6	2.6
CAL	$J_{3,4}$	8.3	8.3	8.3
CAL	$J_{4,5}$	8.3	8.2	8.3

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S26. Radial distribution functions for through-space interaction of glycosidic bond oxygen atoms and TIP3P water hydrogen atoms around the $\alpha(1\rightarrow3)$ and $\beta(1\rightarrow4)$ linkages in **2**, **3** and **4**.



Data are calculated from 10 μ s simulations of **1** and **2**.

S27. Calculation of errors in one-dimensional puckering free energy surfaces (Figures 6 and 7)

Errors in computed puckering relative free energies (derived from populations, relative to the lowest energy pucker), were calculated by splitting each 10 μs trajectory into 10 x 1 μs sub-trajectories, in which the 3D-data were randomly selected. The puckering populations and free energies were then calculated using successively more randomly selected data. These analyses showed that using 80% of the randomly selected data (equivalent to an 8 μs trajectory of random 3D-data) gave extremely small errors in computed relative free energies ($\pm 0.01 \text{ kcal mol}^{-1}$) for pucker less than or equal to 5 kcal mol^{-1} above the lowest energy pucker. At 7 kcal mol^{-1} above the lowest energy pucker the error was $\pm 0.2 \text{ kcal mol}^{-1}$ and the largest calculated errors were $\pm 0.6 \text{ kcal mol}^{-1}$, which were evident at $> 9 \text{ kcal mol}^{-1}$ above the lowest energy pucker.

S28: Calculation of nuclear Overhauser effects (nOes) from 800 MHz NMR of molecules **1** and **2**

Four conformationally independent reference nOe intensities (from cross-peaks of protons in fixed geometric arrangement: Fuc:H1-H2, Fuc:H4-H5, Gal:H1-H3 and Gal:H1-H5) were used to parameterise a model relating cross-peak intensity (I) to proton-proton distance (r) using the relationship $I = \frac{k}{r^6}$. The constant of proportionality (k) was then derived from a linear plot of $\frac{1}{r^6}$ and intensity (I) for the reference nOes.

Standard (*Std*) and back-predicted (*Pred*) distances (Å) for calibration / reference nOes

nOe	Molecule 1					Molecule 2				
	<i>Std*</i>	<i>Pred</i>	<i>Std-Pred</i>	<i>S</i> ²	<i>nOe intensity</i>	<i>Std*</i>	<i>Pred</i>	<i>Std-Pred</i>	<i>S</i> ²	<i>Intensity</i>
Fuc:H1-H2	2.4	1.9	0.5	0.87	27116350	2.4	2.2	0.2	0.76	31682622
Fuc:H4-H5	2.5	2.0	0.5	0.86	20723074	2.5	2.8	-0.3	0.75	6777185
Gal:H1-H3	3.1	2.0	1.1	0.96	20263030	2.9	2.5	0.4	0.85	15013054
Gal:H1-H5	2.5	2.0	0.5	0.89	20543788	2.5	2.3	0.2	0.76	21058458
STDEV			0.3					0.3		

*Standard (*Std*) distances were measured from initial (energy minimised) starting structures

Order parameters (*S*²) calculated from 10 μ s-dynamics (see S31); smaller value indicates greater mobility

Distances (Å) for an inter-ring nOe (\pm STDEV)

- derived from NMR (*Pred NMR*) and 10 μ s-dynamics (simulation average, *Pred MD*)

Molecule 1

nOe	<i>Pred MD</i>	<i>Pred NMR</i>	<i>S</i> ²
Gal:H2-Fuc:H5	2.5 (\pm 0.4)	2.1 (\pm 0.3)	0.84

Molecule 2

nOe	<i>Pred MD</i>	<i>Pred NMR</i>	<i>S</i> ²
Gal:H2-Fuc:H5	2.6 (\pm 0.8)	2.6 (\pm 0.3)	0.90

Order parameters (*S*²) calculated from 10 μ s-dynamics (see S31); smaller value indicates greater mobility

Table S29. Assigned ^1H and ^{13}C chemical shifts in molecules **1** and **2** (800 MHz NMR spectroscopy)

	Atom	Mol (1)		Mol (2)	
		^{13}C	^1H	^{13}C	^1H
Fuc	1	98.05	5.01	98.59	5.09
Fuc	2	67.82	3.79	67.71	3.67
Fuc	3	69.12	3.88	69.21	3.89
Fuc	4	71.95	3.78	71.90	3.77
Fuc	5	66.83	4.88	66.65	4.82
Fuc	Me	15.34	1.17	15.24	1.16
Gal	1	102.84	4.54	101.62	4.52
Gal	2	68.79	3.50	69.25	3.53
Gal	3	75.64	4.05	75.64	4.08
Gal	4	66.90	3.91	67.29	3.93
Gal	5	74.65	3.53	74.92	3.58
Gal	6	61.63	3.69	61.52	3.69
NeuAc	3	40.04	1.76	39.79	1.79
NeuAc	3	40.04	2.77	39.79	2.76
NeuAc	4	68.43	3.67	68.24	3.68
NeuAc	5	51.65	3.84	51.69	3.84
NeuAc	6	72.73	3.62	72.90	3.65
NeuAc	7	68.02	3.61	68.12	3.59
NeuAc	8	71.86	3.85	71.86	3.89
NeuAc	9	62.27	3.82	62.60	3.87
NeuAc	9	62.27	3.65	62.60	3.64
NeuAc	Me	22.08	2.04	21.88	2.02
α-GlcN	1	94.77	4.71	94.77	4.72
α-GlcN	2	56.84	3.85	56.92	3.87
α-GlcN	3	76.02	4.06	74.84	3.84
α-GlcN	4	72.32	3.74	73.29	3.95
α-GlcN	5	75.59	3.55	75.37	3.59
α-GlcN	6	59.72	3.95	59.65	3.97
α-GlcN	6	59.72	3.87	59.65	3.91
α-GlcN	Me	22.16	2.03	22.10	2.02
β-GlcN	1	91.00	5.11	91.11	5.09
β-GlcN	2	54.00	4.14	54.12	4.15
β-GlcN	3	74.13	4.17	72.74	4.00
β-GlcN	4	72.37	3.75	73.29	3.95
β-GlcN	5	71.43	3.98	71.18	4.01
β-GlcN	6	59.74	3.95	59.58	3.93
β-GlcN	6	59.68	3.87	59.59	3.89
β-GlcN	Me	22.16	2.03	22.10	2.03

Figure S30. Example nOes evidencing Gal and Fuc ring stacking in **1** and **2** from 800 MHz NMR

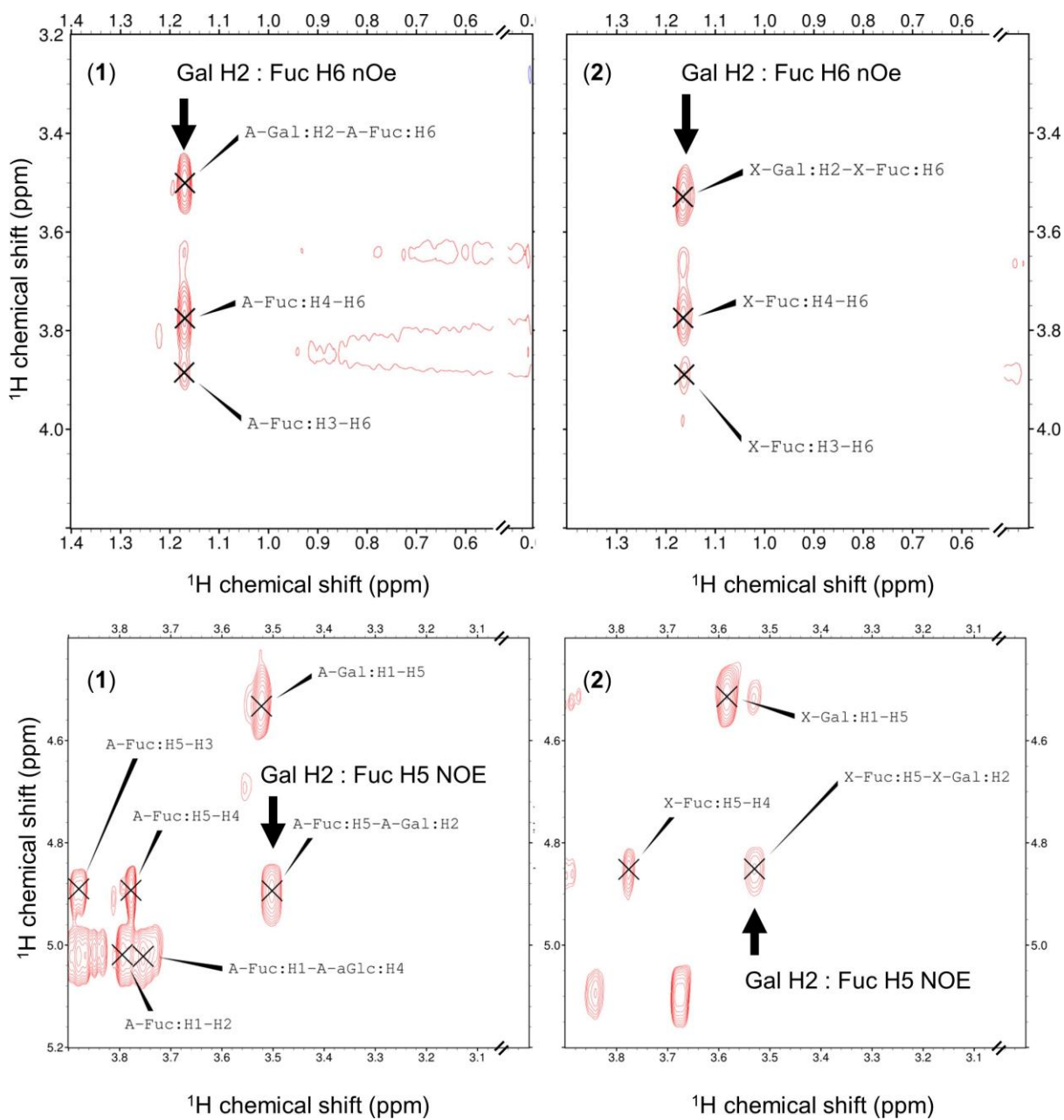


Table S31. Calculation of order parameters

Order parameters (S^2 , tabulated in S28) were derived using the Amber tool ptraj and the method of Prompers & Brüschweiler (JACS 2002, 124, 4522). A step and correlation time of 10 ps and 10 ns were employed. The following double exponential function was used to fit the time correlation curve and extract S^2 (as parameter c, where x=time).

$$f(x) = c + a \cdot \exp(-t/k_1) + b \cdot \exp(-t/k_2)$$

Autocorrelation function and the fitting function $f(t)$ for the Gal-H2LFuc-H5 bond vector in molecule 1.

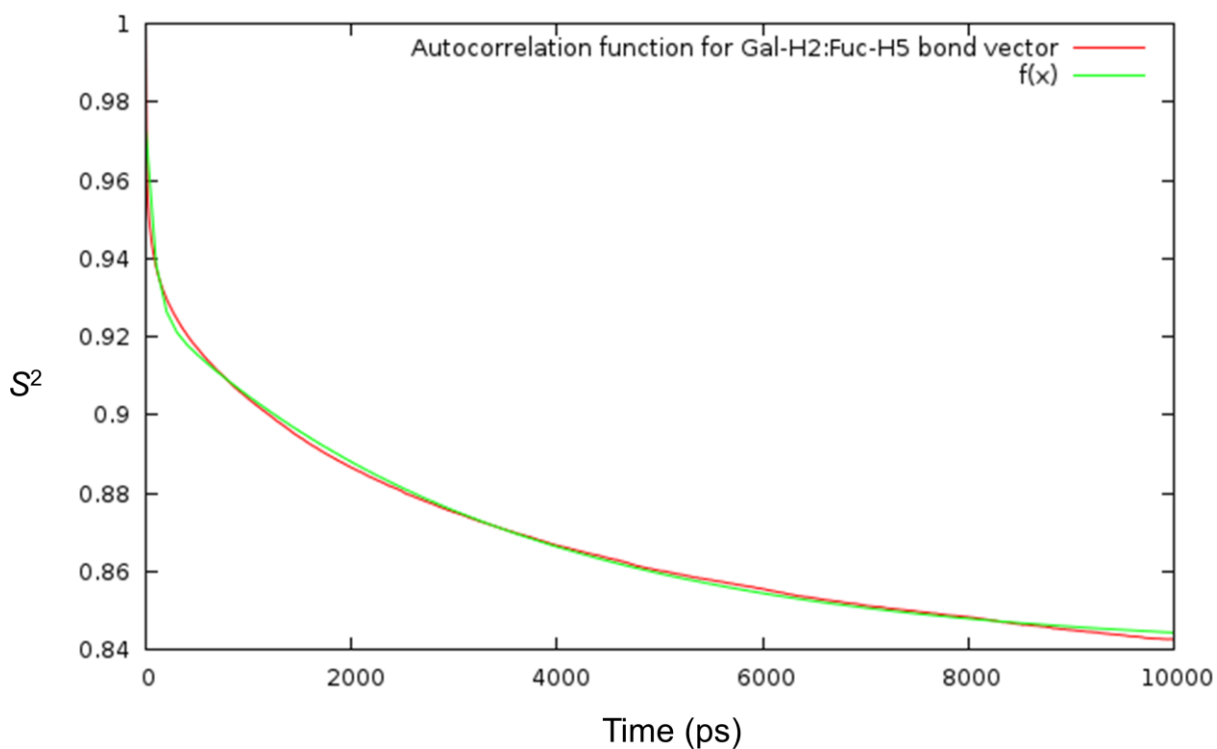


Figure S32: Cartesian coordinates of most populated conformer (GLYCAM naming convention): 1

Derived from the 10 μ s simulation

ATOM	1	HO1	ROH	X	1	2.453	-21.454	0.987
ATOM	2	O1	ROH	X	1	1.664	-21.529	0.446
ATOM	3	C1	WYB	X	2	1.638	-20.402	-0.437
ATOM	4	H1	WYB	X	2	1.990	-20.652	-1.438
ATOM	5	O5	WYB	X	2	2.476	-19.490	0.258
ATOM	6	C5	WYB	X	2	2.710	-18.257	-0.528
ATOM	7	H5	WYB	X	2	3.112	-18.466	-1.520
ATOM	8	C6	WYB	X	2	3.747	-17.455	0.347
ATOM	9	H62	WYB	X	2	3.997	-16.576	-0.247
ATOM	10	H61	WYB	X	2	4.657	-18.045	0.461
ATOM	11	O6	WYB	X	2	3.118	-17.009	1.519
ATOM	12	H6O	WYB	X	2	3.771	-16.429	1.918
ATOM	13	C4	WYB	X	2	1.305	-17.513	-0.686
ATOM	14	H4	WYB	X	2	0.830	-17.227	0.253
ATOM	15	O4	WYB	X	2	1.663	-16.392	-1.475
ATOM	16	C3	WYB	X	2	0.393	-18.486	-1.473
ATOM	17	H3	WYB	X	2	0.836	-18.577	-2.465
ATOM	18	C2	WYB	X	2	0.266	-19.804	-0.713
ATOM	19	H2	WYB	X	2	-0.264	-19.732	0.236
ATOM	20	N2	WYB	X	2	-0.494	-20.771	-1.588
ATOM	21	H2N	WYB	X	2	0.012	-21.370	-2.226
ATOM	22	C2N	WYB	X	2	-1.788	-20.994	-1.381
ATOM	23	O2N	WYB	X	2	-2.409	-20.295	-0.565
ATOM	24	CME	WYB	X	2	-2.514	-22.125	-2.092
ATOM	25	H3M	WYB	X	2	-3.512	-22.202	-1.662
ATOM	26	H2M	WYB	X	2	-2.649	-22.029	-3.170
ATOM	27	H1M	WYB	X	2	-1.956	-22.999	-1.757
ATOM	28	O3	WYB	X	2	-0.892	-17.836	-1.511
ATOM	29	C1	3LB	X	3	-1.558	-17.765	-2.815
ATOM	30	H1	3LB	X	3	-1.645	-18.773	-3.223
ATOM	31	O5	3LB	X	3	-0.711	-16.953	-3.728
ATOM	32	C5	3LB	X	3	-1.289	-16.773	-5.058
ATOM	33	H5	3LB	X	3	-1.359	-17.759	-5.516
ATOM	34	C6	3LB	X	3	-0.418	-15.964	-5.977
ATOM	35	H62	3LB	X	3	-0.040	-15.096	-5.437
ATOM	36	H61	3LB	X	3	-0.987	-15.766	-6.885
ATOM	37	O6	3LB	X	3	0.678	-16.867	-6.265
ATOM	38	H6O	3LB	X	3	1.398	-16.606	-5.687
ATOM	39	C4	3LB	X	3	-2.659	-16.153	-4.958
ATOM	40	H4	3LB	X	3	-3.055	-16.072	-5.971
ATOM	41	O4	3LB	X	3	-2.431	-14.843	-4.448
ATOM	42	H4O	3LB	X	3	-3.319	-14.481	-4.389
ATOM	43	C3	3LB	X	3	-3.617	-16.892	-4.080
ATOM	44	H3	3LB	X	3	-3.853	-17.895	-4.436
ATOM	45	C2	3LB	X	3	-2.943	-17.134	-2.694
ATOM	46	H2	3LB	X	3	-2.851	-16.128	-2.287
ATOM	47	O2	3LB	X	3	-3.804	-17.942	-1.868
ATOM	48	H2O	3LB	X	3	-3.889	-18.790	-2.311
ATOM	49	O3	3LB	X	3	-4.900	-16.262	-3.827
ATOM	50	C2	OSA	X	4	-5.940	-16.560	-4.683
ATOM	51	C1	OSA	X	4	-5.677	-15.980	-6.180
ATOM	52	O1A	OSA	X	4	-5.530	-14.770	-6.340
ATOM	53	O1B	OSA	X	4	-5.586	-16.842	-7.109
ATOM	54	C3	OSA	X	4	-7.139	-15.877	-4.065
ATOM	55	H3E	OSA	X	4	-7.061	-14.791	-4.111
ATOM	56	H3A	OSA	X	4	-7.151	-16.104	-2.999
ATOM	57	C4	OSA	X	4	-8.372	-16.442	-4.823
ATOM	58	H4	OSA	X	4	-8.267	-16.185	-5.876
ATOM	59	C5	OSA	X	4	-8.533	-17.922	-4.711
ATOM	60	H5	OSA	X	4	-8.726	-18.104	-3.654
ATOM	61	C6	OSA	X	4	-7.292	-18.575	-5.293
ATOM	62	H6	OSA	X	4	-7.253	-18.345	-6.358
ATOM	63	C7	OSA	X	4	-7.280	-20.106	-5.109
ATOM	64	H7	OSA	X	4	-8.223	-20.465	-5.520
ATOM	65	C8	OSA	X	4	-5.999	-20.712	-5.778
ATOM	66	H8	OSA	X	4	-5.050	-20.298	-5.437
ATOM	67	C9	OSA	X	4	-5.830	-22.156	-5.731

ATOM	68	H9S	OSA	X	4	-6.865	-22.465	-5.585
ATOM	69	H9R	OSA	X	4	-5.493	-22.493	-6.712
ATOM	70	O9	OSA	X	4	-5.065	-22.592	-4.600
ATOM	71	H9O	OSA	X	4	-5.236	-23.531	-4.506
ATOM	72	O8	OSA	X	4	-6.084	-20.420	-7.163
ATOM	73	H8O	OSA	X	4	-5.274	-19.928	-7.311
ATOM	74	O7	OSA	X	4	-7.405	-20.385	-3.674
ATOM	75	H7O	OSA	X	4	-7.898	-21.169	-3.421
ATOM	76	O6	OSA	X	4	-6.204	-17.989	-4.620
ATOM	77	N5	OSA	X	4	-9.717	-18.312	-5.517
ATOM	78	H5N	OSA	X	4	-9.691	-18.190	-6.519
ATOM	79	C5N	OSA	X	4	-10.658	-19.109	-5.026
ATOM	80	CME	OSA	X	4	-11.887	-19.307	-5.928
ATOM	81	H3M	OSA	X	4	-11.721	-20.194	-6.538
ATOM	82	H2M	OSA	X	4	-11.851	-18.471	-6.626
ATOM	83	H1M	OSA	X	4	-12.848	-19.346	-5.415
ATOM	84	O5N	OSA	X	4	-10.594	-19.558	-3.879
ATOM	85	O4	OSA	X	4	-9.591	-15.728	-4.276
ATOM	86	H4O	OSA	X	4	-10.197	-15.839	-5.012
ATOM	87	C1	OfA	X	5	1.630	-15.073	-0.868
ATOM	88	H1	OfA	X	5	2.310	-15.185	-0.024
ATOM	89	O5	OfA	X	5	0.268	-14.766	-0.416
ATOM	90	C5	OfA	X	5	-0.735	-14.538	-1.550
ATOM	91	H5	OfA	X	5	-0.818	-15.437	-2.161
ATOM	92	C6	OfA	X	5	-2.060	-14.287	-0.850
ATOM	93	H61	OfA	X	5	-2.813	-14.032	-1.595
ATOM	94	H62	OfA	X	5	-2.010	-13.515	-0.082
ATOM	95	H63	OfA	X	5	-2.484	-15.119	-0.288
ATOM	96	C4	OfA	X	5	-0.172	-13.443	-2.370
ATOM	97	H4	OfA	X	5	-0.917	-13.158	-3.114
ATOM	98	O4	OfA	X	5	0.081	-12.217	-1.486
ATOM	99	H4O	OfA	X	5	-0.758	-11.759	-1.394
ATOM	100	C3	OfA	X	5	1.147	-13.891	-3.003
ATOM	101	H3	OfA	X	5	1.070	-14.848	-3.521
ATOM	102	O3	OfA	X	5	1.501	-12.863	-3.973
ATOM	103	H3O	OfA	X	5	2.417	-13.042	-4.200
ATOM	104	C2	OfA	X	5	2.150	-14.079	-1.906
ATOM	105	H2	OfA	X	5	2.393	-13.104	-1.483
ATOM	106	O2	OfA	X	5	3.286	-14.535	-2.560
ATOM	107	H2O	OfA	X	5	3.937	-13.910	-2.232

Figure S33: Cartesian coordinates of most populated conformer (GLYCAM naming convention): 2

Derived from the 25 μ s simulation

ATOM	1	HO1	ROH	X	1	-22.801	-7.834	11.511	0	0
ATOM	2	O1	ROH	X	1	-23.416	-7.107	11.633	0	0
ATOM	3	C1	WYB	X	2	-22.903	-6.059	10.816	0	0
ATOM	4	H1	WYB	X	2	-23.772	-5.769	10.224	0	0
ATOM	5	O5	WYB	X	2	-21.879	-6.644	10.035	0	0
ATOM	6	C5	WYB	X	2	-21.135	-5.712	9.145	0	0
ATOM	7	H5	WYB	X	2	-21.781	-5.101	8.513	0	0
ATOM	8	C6	WYB	X	2	-20.133	-6.534	8.275	0	0
ATOM	9	H62	WYB	X	2	-19.822	-5.912	7.435	0	0
ATOM	10	H61	WYB	X	2	-20.656	-7.403	7.873	0	0
ATOM	11	O6	WYB	X	2	-19.038	-7.095	9.012	0	0
ATOM	12	H6O	WYB	X	2	-18.99	-8.048	8.902	0	0
ATOM	13	C4	WYB	X	2	-20.411	-4.709	9.963	0	0
ATOM	14	H4	WYB	X	2	-19.817	-5.259	10.692	0	0
ATOM	15	O4	WYB	X	2	-19.66	-3.81	9.083	0	0
ATOM	16	C3	WYB	X	2	-21.395	-3.846	10.754	0	0
ATOM	17	H3	WYB	X	2	-21.998	-3.26	10.061	0	0
ATOM	18	C2	WYB	X	2	-22.221	-4.838	11.588	0	0
ATOM	19	H2	WYB	X	2	-21.519	-5.214	12.332	0	0
ATOM	20	N2	WYB	X	2	-23.219	-4.153	12.369	0	0
ATOM	21	H2N	WYB	X	2	-24.009	-3.852	11.817	0	0
ATOM	22	C2N	WYB	X	2	-23.306	-3.949	13.711	0	0
ATOM	23	O2N	WYB	X	2	-22.382	-4.374	14.382	0	0
ATOM	24	CME	WYB	X	2	-24.487	-3.422	14.209	0	0
ATOM	25	H3M	WYB	X	2	-24.359	-3.123	15.25	0	0
ATOM	26	H2M	WYB	X	2	-24.619	-2.427	13.782	0	0
ATOM	27	H1M	WYB	X	2	-25.298	-4.1	13.941	0	0
ATOM	28	O3	WYB	X	2	-20.633	-2.872	11.557	0	0
ATOM	29	C1	3LB	X	3	-18.21	-3.793	9.162	0	0
ATOM	30	H1	3LB	X	3	-17.866	-4.825	9.227	0	0
ATOM	31	O5	3LB	X	3	-17.759	-3.106	10.324	0	0
ATOM	32	C5	3LB	X	3	-16.306	-2.968	10.519	0	0
ATOM	33	H5	3LB	X	3	-15.902	-3.975	10.417	0	0
ATOM	34	C6	3LB	X	3	-16.049	-2.515	11.967	0	0
ATOM	35	H62	3LB	X	3	-16.88	-1.896	12.304	0	0
ATOM	36	H61	3LB	X	3	-15.077	-2.033	12.072	0	0
ATOM	37	O6	3LB	X	3	-16.053	-3.755	12.83	0	0
ATOM	38	H6O	3LB	X	3	-15.483	-4.42	12.438	0	0
ATOM	39	C4	3LB	X	3	-15.855	-1.928	9.416	0	0
ATOM	40	H4	3LB	X	3	-14.781	-1.781	9.528	0	0
ATOM	41	O4	3LB	X	3	-16.466	-0.671	9.628	0	0
ATOM	42	H4O	3LB	X	3	-16.032	-0.118	8.974	0	0
ATOM	43	C3	3LB	X	3	-16.206	-2.566	8.041	0	0
ATOM	44	H3	3LB	X	3	-15.487	-3.364	7.859	0	0
ATOM	45	C2	3LB	X	3	-17.661	-3.028	7.888	0	0
ATOM	46	H2	3LB	X	3	-18.374	-2.215	7.75	0	0
ATOM	47	O2	3LB	X	3	-17.698	-3.893	6.772	0	0
ATOM	48	H2O	3LB	X	3	-17.457	-3.386	5.993	0	0
ATOM	49	O3	3LB	X	3	-15.963	-1.52	7.023	0	0
ATOM	50	C2	OSA	X	4	-14.967	-1.906	6.09	0	0
ATOM	51	C1	OSA	X	4	-13.45	-1.837	6.721	0	0
ATOM	52	O1A	OSA	X	4	-12.645	-2.79	6.561	0	0
ATOM	53	O1B	OSA	X	4	-13.138	-0.88	7.458	0	0
ATOM	54	C3	OSA	X	4	-15.143	-0.719	5.164	0	0
ATOM	55	H3E	OSA	X	4	-14.736	0.219	5.542	0	0
ATOM	56	H3A	OSA	X	4	-16.206	-0.513	5.048	0	0
ATOM	57	C4	OSA	X	4	-14.532	-1.043	3.793	0	0
ATOM	58	H4	OSA	X	4	-13.455	-1.062	3.96	0	0
ATOM	59	C5	OSA	X	4	-15	-2.436	3.226	0	0
ATOM	60	H5	OSA	X	4	-16.08	-2.37	3.087	0	0
ATOM	61	C6	OSA	X	4	-14.722	-3.559	4.192	0	0
ATOM	62	H6	OSA	X	4	-13.637	-3.639	4.248	0	0
ATOM	63	C7	OSA	X	4	-15.271	-4.912	3.855	0	0
ATOM	64	H7	OSA	X	4	-14.962	-5.057	2.82	0	0
ATOM	65	C8	OSA	X	4	-14.685	-5.994	4.753	0	0
ATOM	66	H8	OSA	X	4	-14.977	-5.818	5.788	0	0
ATOM	67	C9	OSA	X	4	-15.056	-7.424	4.306	0	0

ATOM	68	H9S	OSA	X	4	-16.143	-7.5	4.283	0	0
ATOM	69	H9R	OSA	X	4	-14.609	-7.588	3.325	0	0
ATOM	70	O9	OSA	X	4	-14.517	-8.386	5.188	0	0
ATOM	71	H9O	OSA	X	4	-14.987	-9.223	5.154	0	0
ATOM	72	O8	OSA	X	4	-13.273	-5.961	4.626	0	0
ATOM	73	H8O	OSA	X	4	-12.936	-6.488	5.354	0	0
ATOM	74	O7	OSA	X	4	-16.71	-4.854	3.827	0	0
ATOM	75	H7O	OSA	X	4	-16.911	-3.937	4.027	0	0
ATOM	76	O6	OSA	X	4	-15.269	-3.162	5.49	0	0
ATOM	77	N5	OSA	X	4	-14.322	-2.65	1.884	0	0
ATOM	78	H5N	OSA	X	4	-13.337	-2.432	1.837	0	0
ATOM	79	C5N	OSA	X	4	-15.018	-3.198	0.928	0	0
ATOM	80	CME	OSA	X	4	-14.26	-3.296	-0.426	0	0
ATOM	81	H3M	OSA	X	4	-13.3	-3.809	-0.361	0	0
ATOM	82	H2M	OSA	X	4	-14.141	-2.298	-0.848	0	0
ATOM	83	H1M	OSA	X	4	-14.872	-3.78	-1.186	0	0
ATOM	84	O5N	OSA	X	4	-16.183	-3.592	0.996	0	0
ATOM	85	O4	OSA	X	4	-14.797	0.116	2.972	0	0
ATOM	86	H4O	OSA	X	4	-14.531	0.904	3.452	0	0
ATOM	87	C1	OfA	X	5	-21.211	-1.564	11.766	0	0
ATOM	88	H1	OfA	X	5	-22.269	-1.695	11.994	0	0
ATOM	89	O5	OfA	X	5	-21.139	-0.76	10.564	0	0
ATOM	90	C5	OfA	X	5	-19.754	-0.147	10.406	0	0
ATOM	91	H5	OfA	X	5	-19.141	-1.034	10.244	0	0
ATOM	92	C6	OfA	X	5	-19.685	0.541	9.018	0	0
ATOM	93	H61	OfA	X	5	-18.778	0.179	8.533	0	0
ATOM	94	H62	OfA	X	5	-19.696	1.629	8.967	0	0
ATOM	95	H63	OfA	X	5	-20.572	0.35	8.413	0	0
ATOM	96	C4	OfA	X	5	-19.321	0.619	11.635	0	0
ATOM	97	H4	OfA	X	5	-18.377	1.102	11.381	0	0
ATOM	98	O4	OfA	X	5	-20.321	1.607	11.912	0	0
ATOM	99	H4O	OfA	X	5	-20.172	2.333	11.302	0	0
ATOM	100	C3	OfA	X	5	-19.331	-0.36	12.806	0	0
ATOM	101	H3	OfA	X	5	-18.772	-1.239	12.486	0	0
ATOM	102	O3	OfA	X	5	-18.729	0.231	13.961	0	0
ATOM	103	H3O	OfA	X	5	-19.049	1.121	14.126	0	0
ATOM	104	C2	OfA	X	5	-20.766	-0.837	13.072	0	0
ATOM	105	H2	OfA	X	5	-21.409	0.015	13.294	0	0
ATOM	106	O2	OfA	X	5	-20.597	-1.811	14.152	0	0
ATOM	107	H2O	OfA	X	5	-19.691	-2.13	14.141	0	0

Figure S34: Cartesian coordinates of most populated conformer (GLYCAM naming convention): 7

Derived from the 10 μ s simulation

ATOM	1	HO1	ROH	X	1	6.960	-11.486	11.865
ATOM	2	O1	ROH	X	1	6.146	-11.519	11.358
ATOM	3	C1	VMA	X	2	5.726	-10.257	11.411
ATOM	4	H1	VMA	X	2	5.204	-10.046	12.345
ATOM	5	C2	VMA	X	2	4.773	-10.083	10.192
ATOM	6	H2	VMA	X	2	4.125	-10.959	10.152
ATOM	7	O2	VMA	X	2	3.898	-8.920	10.424
ATOM	8	H2O	VMA	X	2	3.274	-8.788	9.706
ATOM	9	C3	VMA	X	2	5.509	-10.075	8.839
ATOM	10	H3	VMA	X	2	5.779	-11.125	8.730
ATOM	11	C4	VMA	X	2	6.722	-9.149	8.888
ATOM	12	H4	VMA	X	2	6.315	-8.138	8.892
ATOM	13	C5	VMA	X	2	7.688	-9.485	10.042
ATOM	14	H5	VMA	X	2	8.135	-10.470	9.907
ATOM	15	C6	VMA	X	2	8.820	-8.421	10.243
ATOM	16	H62	VMA	X	2	9.420	-8.592	11.137
ATOM	17	H61	VMA	X	2	9.546	-8.508	9.435
ATOM	18	O6	VMA	X	2	8.260	-7.089	10.229
ATOM	19	O5	VMA	X	2	6.858	-9.422	11.281
ATOM	20	O4	VMA	X	2	7.413	-9.240	7.652
ATOM	21	H4O	VMA	X	2	7.691	-10.153	7.552
ATOM	22	O3	VMA	X	2	4.622	-9.742	7.764
ATOM	23	C1	OMA	X	3	4.312	-10.873	6.935
ATOM	24	H1	OMA	X	3	5.245	-11.361	6.651
ATOM	25	C2	OMA	X	3	3.552	-10.350	5.672
ATOM	26	H2	OMA	X	3	4.086	-9.555	5.154
ATOM	27	C3	OMA	X	3	2.202	-9.853	6.090
ATOM	28	H3	OMA	X	3	2.369	-9.002	6.751
ATOM	29	C4	OMA	X	3	1.318	-10.852	6.883
ATOM	30	H4	OMA	X	3	1.101	-11.653	6.175
ATOM	31	C5	OMA	X	3	2.123	-11.308	8.043
ATOM	32	H5	OMA	X	3	2.162	-10.488	8.761
ATOM	33	C6	OMA	X	3	1.279	-12.551	8.609
ATOM	34	H62	OMA	X	3	0.240	-12.267	8.777
ATOM	35	H61	OMA	X	3	1.357	-13.268	7.792
ATOM	36	O6	OMA	X	3	1.720	-13.120	9.850
ATOM	37	H6O	OMA	X	3	2.034	-14.001	9.634
ATOM	38	O5	OMA	X	3	3.458	-11.782	7.784
ATOM	39	O4	OMA	X	3	0.202	-10.190	7.465
ATOM	40	H4O	OMA	X	3	-0.643	-10.516	7.146
ATOM	41	O3	OMA	X	3	1.496	-9.292	4.956
ATOM	42	H3O	OMA	X	3	1.864	-8.417	4.813
ATOM	43	O2	OMA	X	3	3.436	-11.434	4.754
ATOM	44	H2O	OMA	X	3	3.031	-11.076	3.961
ATOM	45	C1	OMA	X	4	9.362	-6.171	9.856
ATOM	46	H1	OMA	X	4	10.256	-6.505	10.384
ATOM	47	C2	OMA	X	4	8.767	-4.747	10.282
ATOM	48	H2	OMA	X	4	8.491	-4.814	11.334
ATOM	49	C3	OMA	X	4	7.496	-4.410	9.444
ATOM	50	H3	OMA	X	4	6.798	-5.234	9.595
ATOM	51	C4	OMA	X	4	7.879	-4.479	7.911
ATOM	52	H4	OMA	X	4	8.668	-3.801	7.583
ATOM	53	C5	OMA	X	4	8.327	-5.919	7.608
ATOM	54	H5	OMA	X	4	7.546	-6.646	7.834
ATOM	55	C6	OMA	X	4	8.731	-6.151	6.092
ATOM	56	H62	OMA	X	4	9.033	-7.155	5.790
ATOM	57	H61	OMA	X	4	7.840	-5.891	5.521
ATOM	58	O6	OMA	X	4	9.889	-5.304	5.760
ATOM	59	H6O	OMA	X	4	9.749	-5.074	4.839
ATOM	60	O5	OMA	X	4	9.533	-6.265	8.388
ATOM	61	O4	OMA	X	4	6.642	-4.253	7.220
ATOM	62	H4O	OMA	X	4	6.472	-3.316	7.095
ATOM	63	O3	OMA	X	4	6.923	-3.162	9.907
ATOM	64	H3O	OMA	X	4	5.989	-3.235	9.696
ATOM	65	O2	OMA	X	4	9.787	-3.714	10.213

ATOM 66 H2O OMA X 4 9.621 -3.113 10.943

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Figure S35: Cartesian coordinates of most populated conformer (GLYCAM naming convention): 8

Derived from the 10 μ s simulation

ATOM	1	HO1	ROH	X	1	5.944	11.587	-12.385
ATOM	2	O1	ROH	X	1	5.196	11.245	-12.879
ATOM	3	C1	VMA	X	2	5.144	11.793	-14.157
ATOM	4	H1	VMA	X	2	5.462	12.834	-14.098
ATOM	5	C2	VMA	X	2	3.702	11.832	-14.694
ATOM	6	H2	VMA	X	2	3.006	12.277	-13.983
ATOM	7	O2	VMA	X	2	3.693	12.603	-15.914
ATOM	8	H2O	VMA	X	2	4.046	13.476	-15.731
ATOM	9	C3	VMA	X	2	3.115	10.505	-14.922
ATOM	10	H3	VMA	X	2	3.003	9.997	-13.964
ATOM	11	C4	VMA	X	2	3.977	9.640	-15.759
ATOM	12	H4	VMA	X	2	4.062	10.004	-16.783
ATOM	13	C5	VMA	X	2	5.418	9.542	-15.344
ATOM	14	H5	VMA	X	2	5.470	8.918	-14.451
ATOM	15	C6	VMA	X	2	6.292	8.890	-16.439
ATOM	16	H62	VMA	X	2	7.357	8.844	-16.213
ATOM	17	H61	VMA	X	2	6.054	7.832	-16.546
ATOM	18	O6	VMA	X	2	6.107	9.499	-17.792
ATOM	19	O5	VMA	X	2	5.931	10.960	-15.042
ATOM	20	O4	VMA	X	2	3.437	8.285	-15.845
ATOM	21	H4O	VMA	X	2	2.748	8.314	-16.512
ATOM	22	O3	VMA	X	2	1.660	10.534	-15.512
ATOM	23	C1	2MA	X	3	0.705	9.946	-14.596
ATOM	24	H1	2MA	X	3	0.979	9.037	-14.059
ATOM	25	C2	2MA	X	3	-0.554	9.655	-15.336
ATOM	26	H2	2MA	X	3	-0.362	9.096	-16.251
ATOM	27	C3	2MA	X	3	-1.223	10.965	-15.711
ATOM	28	H3	2MA	X	3	-0.662	11.564	-16.430
ATOM	29	C4	2MA	X	3	-1.339	11.845	-14.527
ATOM	30	H4	2MA	X	3	-1.980	11.326	-13.814
ATOM	31	C5	2MA	X	3	0.004	12.278	-13.998
ATOM	32	H5	2MA	X	3	0.542	12.661	-14.865
ATOM	33	C6	2MA	X	3	-0.101	13.339	-12.898
ATOM	34	H62	2MA	X	3	-0.388	14.297	-13.330
ATOM	35	H61	2MA	X	3	-0.826	13.069	-12.130
ATOM	36	O6	2MA	X	3	1.197	13.491	-12.277
ATOM	37	H6O	2MA	X	3	1.496	12.669	-11.883
ATOM	38	O5	2MA	X	3	0.625	11.016	-13.633
ATOM	39	O4	2MA	X	3	-2.068	13.058	-15.009
ATOM	40	H4O	2MA	X	3	-2.998	12.890	-15.175
ATOM	41	O3	2MA	X	3	-2.558	10.579	-16.307
ATOM	42	H3O	2MA	X	3	-3.044	10.088	-15.640
ATOM	43	O2	2MA	X	3	-1.494	8.923	-14.484
ATOM	44	C1	OYB	X	4	-1.241	7.567	-14.259
ATOM	45	H1	OYB	X	4	-0.167	7.516	-14.428
ATOM	46	O5	OYB	X	4	-1.996	6.696	-15.082
ATOM	47	C5	OYB	X	4	-1.776	5.291	-14.735
ATOM	48	H5	OYB	X	4	-0.702	5.148	-14.843
ATOM	49	C6	OYB	X	4	-2.617	4.340	-15.605
ATOM	50	H62	OYB	X	4	-2.566	3.360	-15.129
ATOM	51	H61	OYB	X	4	-2.232	4.235	-16.620
ATOM	52	O6	OYB	X	4	-4.044	4.805	-15.715
ATOM	53	H6O	OYB	X	4	-4.592	4.518	-14.981
ATOM	54	C4	OYB	X	4	-2.149	5.075	-13.233
ATOM	55	H4	OYB	X	4	-3.215	5.165	-13.024
ATOM	56	O4	OYB	X	4	-1.748	3.718	-13.021
ATOM	57	H4O	OYB	X	4	-2.128	3.452	-12.180
ATOM	58	C3	OYB	X	4	-1.347	6.005	-12.271
ATOM	59	H3	OYB	X	4	-0.301	5.722	-12.397
ATOM	60	O3	OYB	X	4	-1.806	5.757	-10.890
ATOM	61	H3O	OYB	X	4	-2.758	5.883	-10.890
ATOM	62	C2	OYB	X	4	-1.607	7.404	-12.809
ATOM	63	H2	OYB	X	4	-2.669	7.613	-12.678
ATOM	64	N2	OYB	X	4	-0.838	8.345	-12.004
ATOM	65	H2N	OYB	X	4	0.111	8.040	-11.840
ATOM	66	C2N	OYB	X	4	-1.409	9.451	-11.568

ATOM	67	O2N	OYB	X	4	-2.499	9.773	-11.965
ATOM	68	CME	OYB	X	4	-0.611	10.211	-10.461
ATOM	69	H3M	OYB	X	4	-0.503	11.241	-10.800
ATOM	70	H2M	OYB	X	4	-1.179	10.196	-9.531
ATOM	71	H1M	OYB	X	4	0.375	9.746	-10.427
ATOM	72	C1	2MA	X	5	6.494	8.570	-18.855
ATOM	73	H1	2MA	X	5	7.510	8.301	-18.566
ATOM	74	C2	2MA	X	5	6.549	9.291	-20.231
ATOM	75	H2	2MA	X	5	7.321	10.059	-20.257
ATOM	76	C3	2MA	X	5	5.127	9.772	-20.482
ATOM	77	H3	2MA	X	5	4.782	10.461	-19.712
ATOM	78	C4	2MA	X	5	4.204	8.607	-20.543
ATOM	79	H4	2MA	X	5	4.390	7.973	-21.409
ATOM	80	C5	2MA	X	5	4.344	7.733	-19.286
ATOM	81	H5	2MA	X	5	3.849	8.236	-18.455
ATOM	82	C6	2MA	X	5	3.563	6.431	-19.573
ATOM	83	H62	2MA	X	5	2.690	6.611	-20.200
ATOM	84	H61	2MA	X	5	4.213	5.671	-20.005
ATOM	85	O6	2MA	X	5	3.108	6.056	-18.251
ATOM	86	H6O	2MA	X	5	3.729	6.252	-17.545
ATOM	87	O5	2MA	X	5	5.703	7.374	-19.057
ATOM	88	O4	2MA	X	5	2.875	9.134	-20.568
ATOM	89	H4O	2MA	X	5	2.264	8.553	-21.029
ATOM	90	O3	2MA	X	5	5.171	10.362	-21.727
ATOM	91	H3O	2MA	X	5	4.274	10.598	-21.973
ATOM	92	O2	2MA	X	5	6.956	8.287	-21.252
ATOM	93	C1	OYB	X	6	8.395	7.888	-21.269
ATOM	94	H1	OYB	X	6	8.813	7.969	-20.266
ATOM	95	O5	OYB	X	6	9.066	8.868	-22.114
ATOM	96	C5	OYB	X	6	10.513	8.552	-22.168
ATOM	97	H5	OYB	X	6	10.870	8.630	-21.141
ATOM	98	C6	OYB	X	6	11.259	9.692	-22.905
ATOM	99	H62	OYB	X	6	12.294	9.363	-23.013
ATOM	100	H61	OYB	X	6	11.231	10.702	-22.495
ATOM	101	O6	OYB	X	6	10.647	9.891	-24.142
ATOM	102	H6O	OYB	X	6	10.380	10.813	-24.164
ATOM	103	C4	OYB	X	6	10.760	7.195	-22.784
ATOM	104	H4	OYB	X	6	10.535	7.153	-23.850
ATOM	105	O4	OYB	X	6	12.239	6.976	-22.678
ATOM	106	H4O	OYB	X	6	12.608	7.256	-23.519
ATOM	107	C3	OYB	X	6	10.046	6.114	-22.056
ATOM	108	H3	OYB	X	6	10.530	5.972	-21.090
ATOM	109	O3	OYB	X	6	10.201	4.904	-22.796
ATOM	110	H3O	OYB	X	6	11.130	4.685	-22.903
ATOM	111	C2	OYB	X	6	8.548	6.494	-21.717
ATOM	112	H2	OYB	X	6	8.010	6.487	-22.665
ATOM	113	N2	OYB	X	6	8.008	5.490	-20.844
ATOM	114	H2N	OYB	X	6	8.563	5.224	-20.043
ATOM	115	C2N	OYB	X	6	6.829	5.059	-20.954
ATOM	116	O2N	OYB	X	6	6.100	5.531	-21.786
ATOM	117	CME	OYB	X	6	6.393	4.202	-19.851
ATOM	118	H3M	OYB	X	6	5.750	3.373	-20.148
ATOM	119	H2M	OYB	X	6	7.268	3.661	-19.489
ATOM	120	H1M	OYB	X	6	6.092	4.921	-19.090

S35 continued