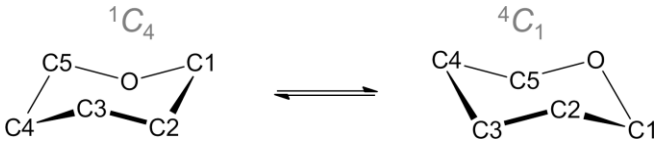
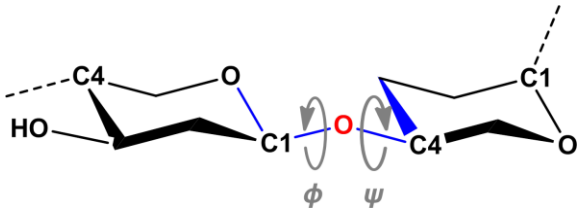
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Figure S1. Nomenclature and structural definitions employed in the manuscript

A: Atom naming convention and example pyranose ring conformations ($^{1}C_{4}$ and $^{4}C_{1}$ chair puckers)



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



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

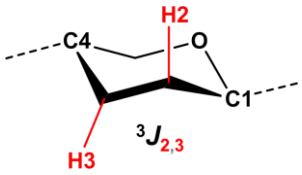
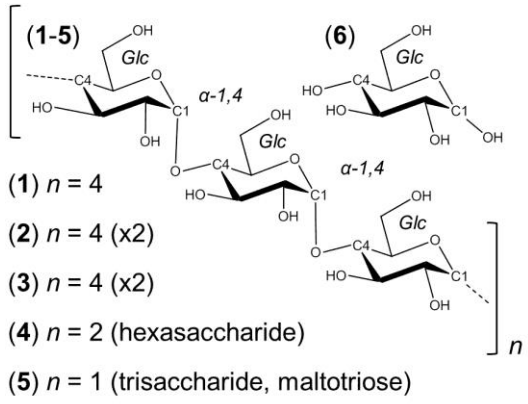


Figure S2. Structures of model amylose fragments **1**-**5**



(**1**) *n* = 4

(**2**) *n* = 4 (x2)

(**3**) *n* = 4 (x2)

(**4**) *n* = 2 (hexasaccharide)

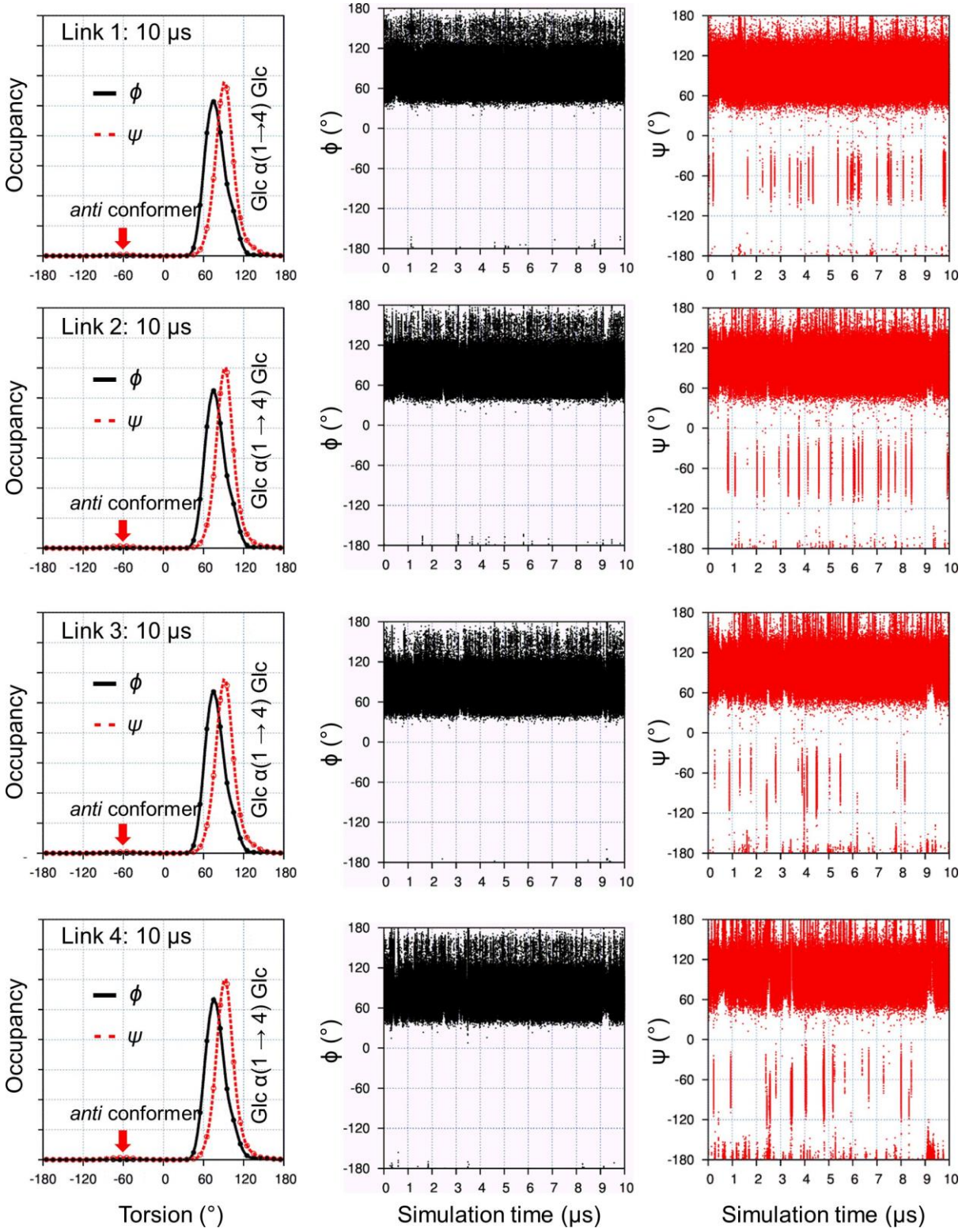
(**5**) *n* = 1 (trisaccharide, maltotriose)

(**2**) Antiparallel double-helix, (**3**) parallel double helix

(**1**-**5**) Terminal Glc residues were (1- or -4 position) hydroxyl terminated

Figure S3. Linkage histograms & time series: 10 *μ*s simulation of **1** (dodecasaccharide)

Glycosidic linkages are numbered from the reducing end; the *anti* conformer is noted



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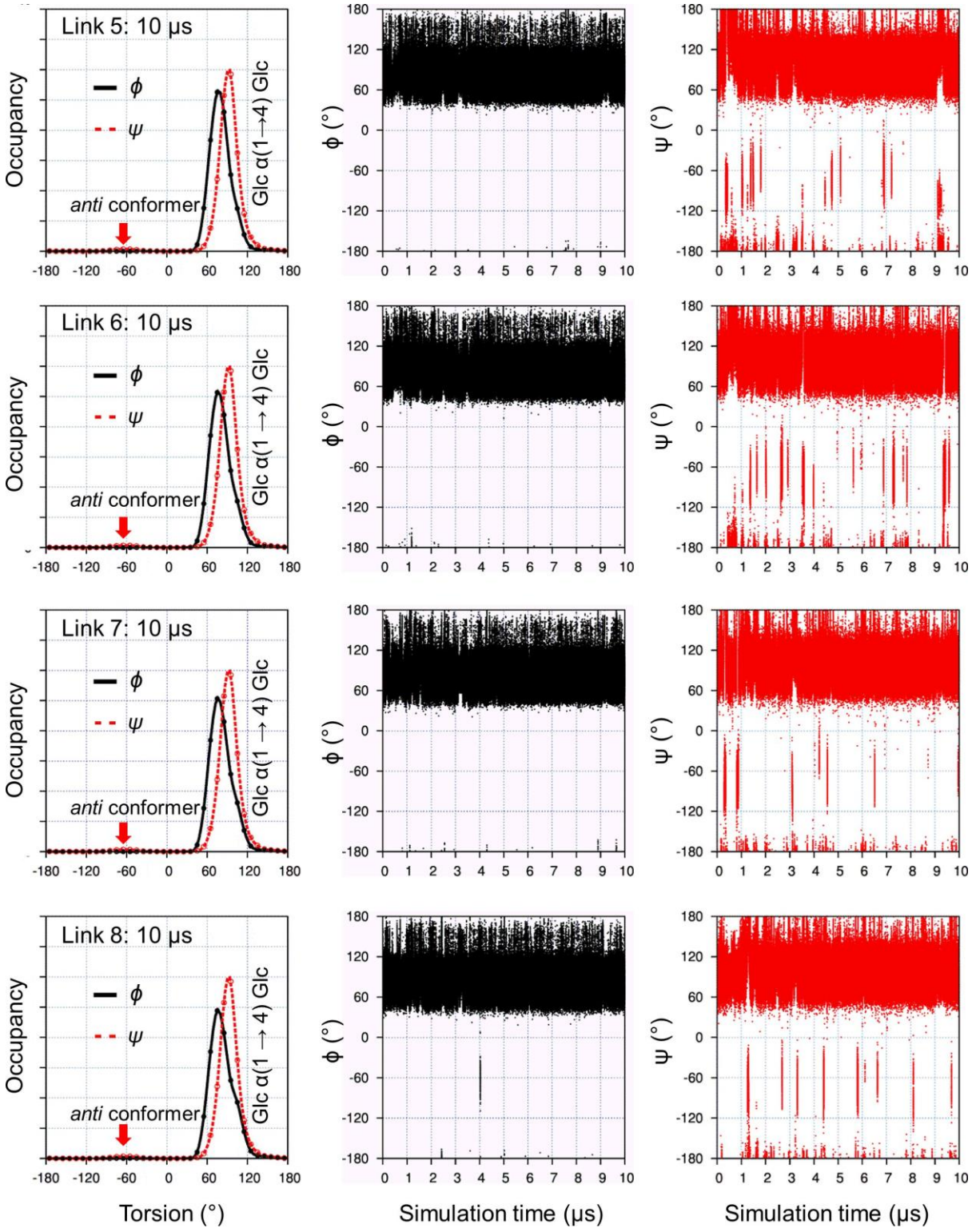
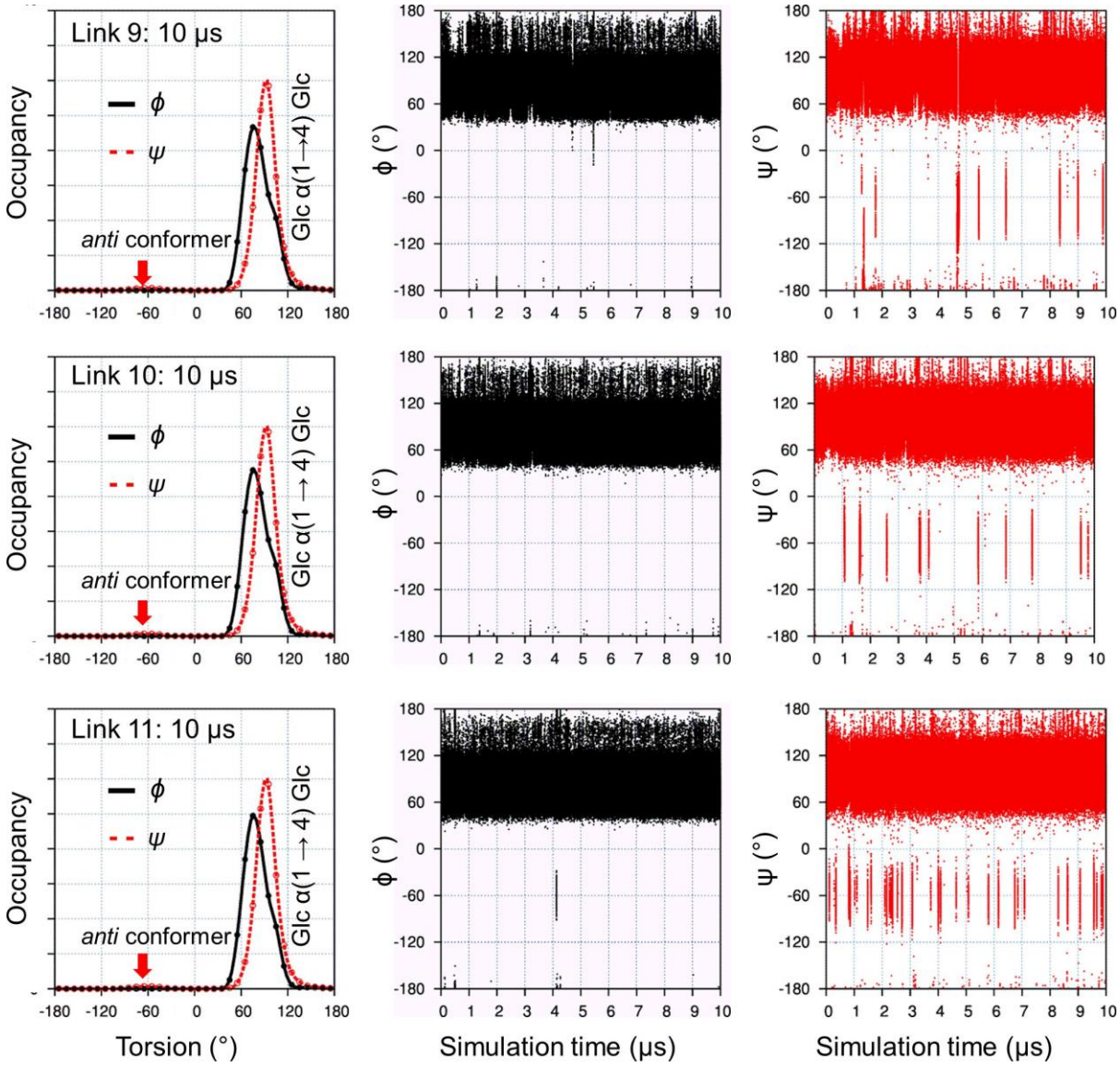


S3 continued

Figure S3. Linkage histograms & time series: 10 *μ*s simulation of **1** (dodecasaccharide)

Glycosidic linkages are numbered from the reducing end; the *anti* conformer is noted



S3 continued

Figure S4. Linkage histograms & time series: 10 *μ*s simulation of **2** (antiparallel double-helix: strand A)

Glycosidic linkages are numbered from the reducing end; the *anti* conformer is noted

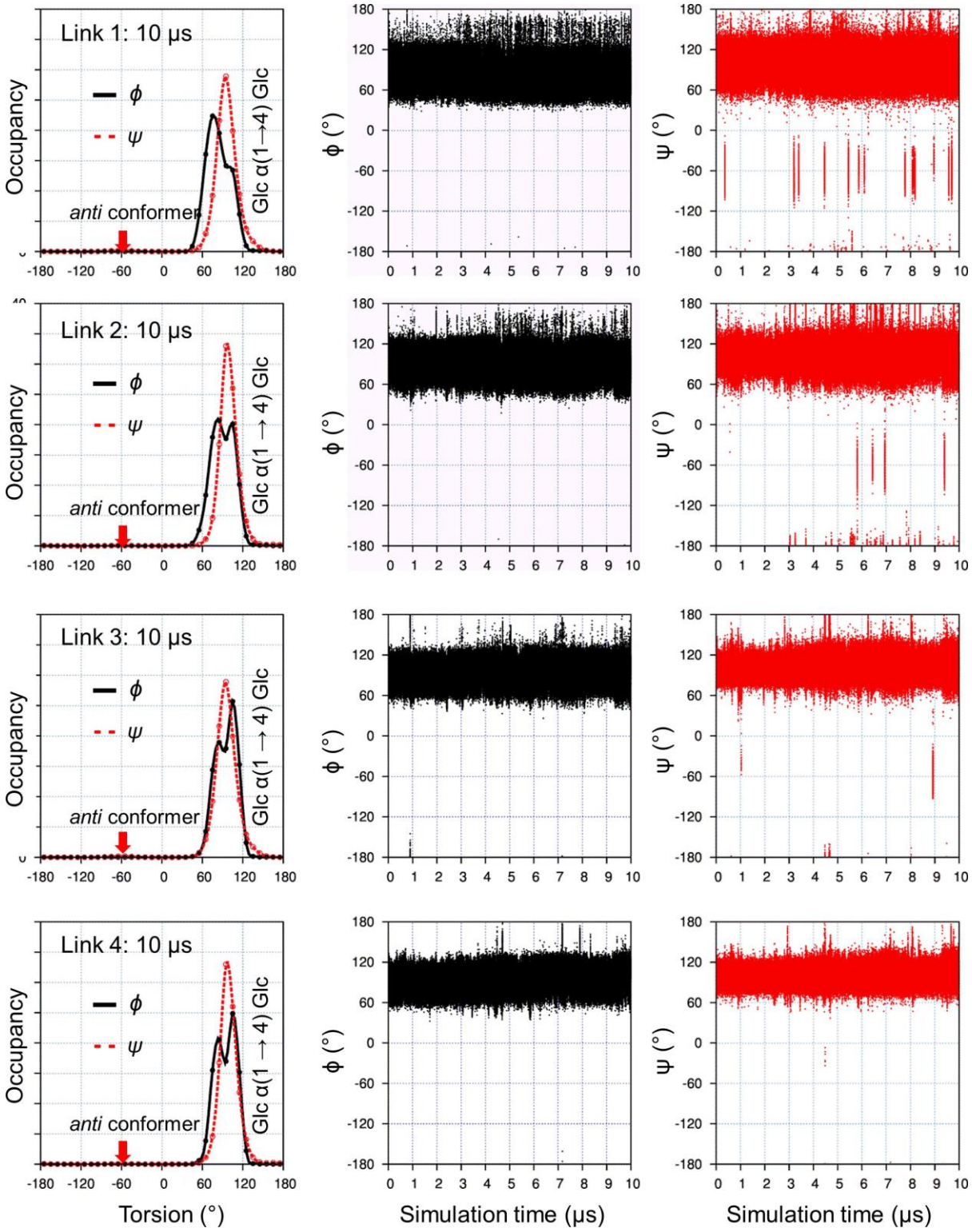
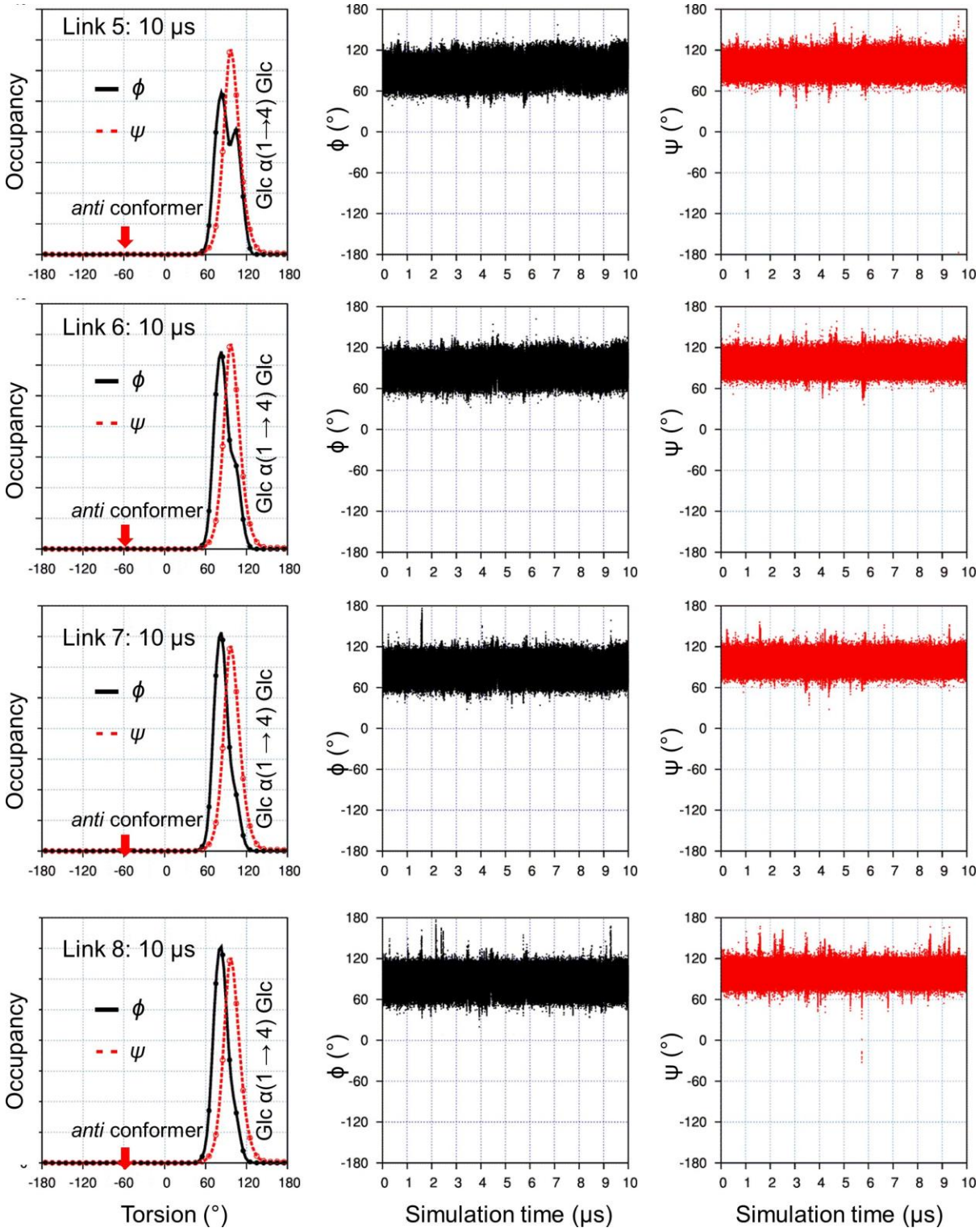


Figure S4. Linkage histograms & time series: 10 μs simulation of **2** (antiparallel double-helix: strand A)

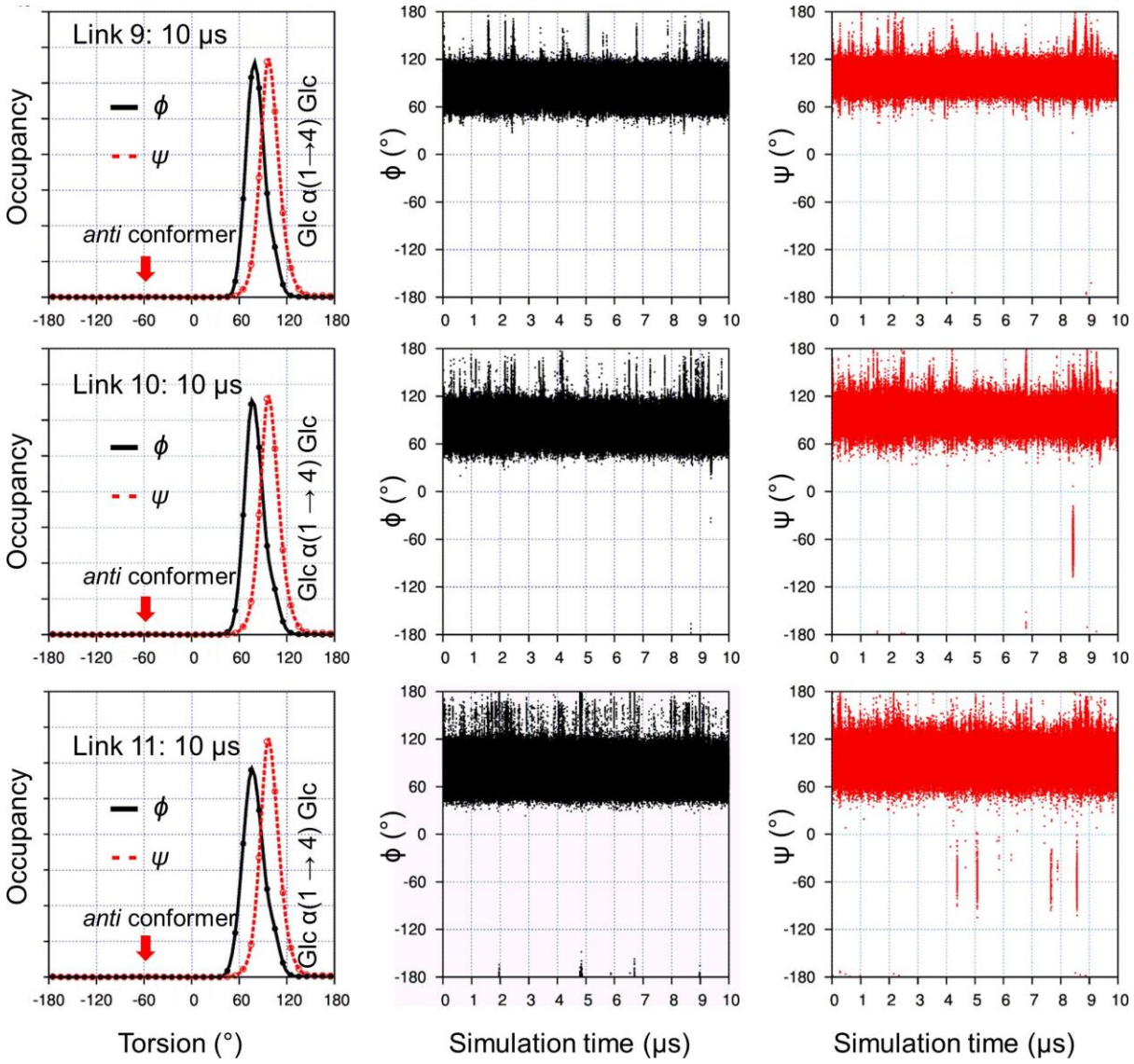
Glycosidic linkages are numbered from the reducing end; the *anti* conformer is noted



S4 continued

Figure S4. Linkage histograms & time series: 10 *μ*s simulation of **2** (antiparallel double-helix: strand A)

Glycosidic linkages are numbered from the reducing end; the *anti* conformer is noted



S4 continued

Figure S5. Linkage histograms & time series: 10 *μ*s simulation of **2** (antiparallel double-helix: strand B)

Glycosidic linkages are numbered from the reducing end; the *anti conformer* is noted

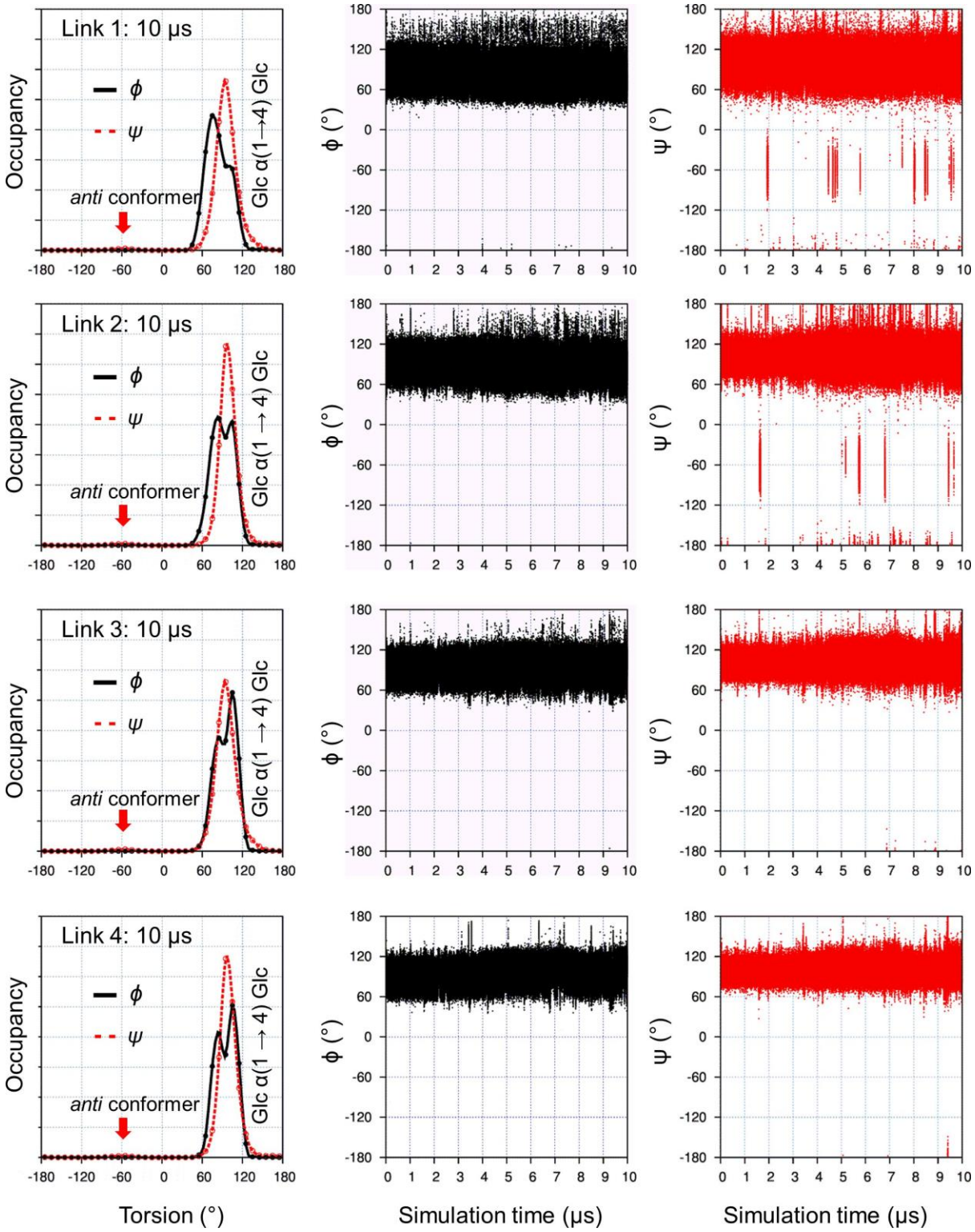
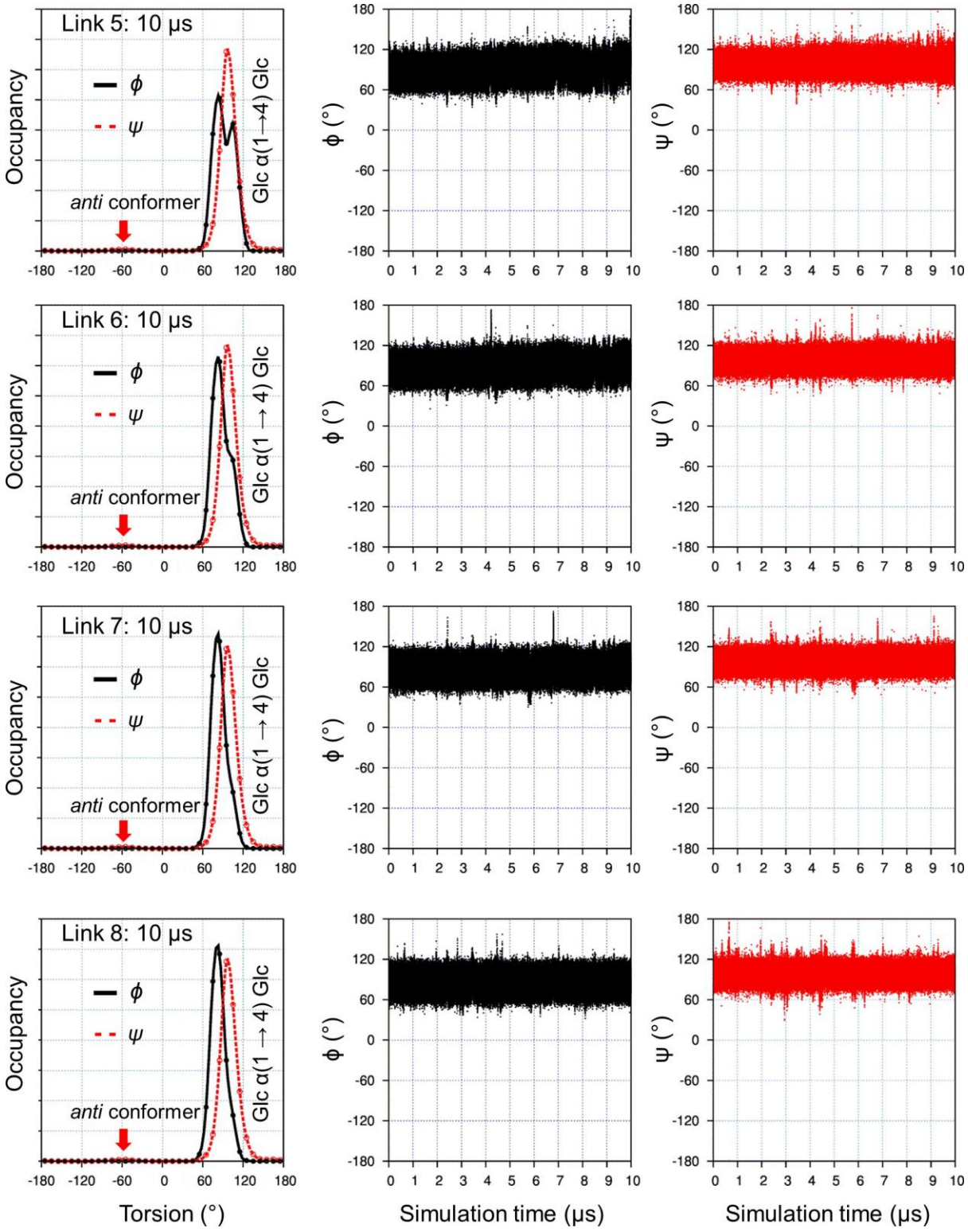


Figure S5. Linkage histograms & time series: 10 *μ*s simulation of **2** (antiparallel double-helix: strand B)

Glycosidic linkages are numbered from the reducing end; the *anti conformer* is noted



S5 continued

Figure S5. Linkage histograms & time series: 10 μs simulation of **2** (antiparallel double-helix: strand B)

Glycosidic linkages are numbered from the reducing end; the *anti conformer* is noted

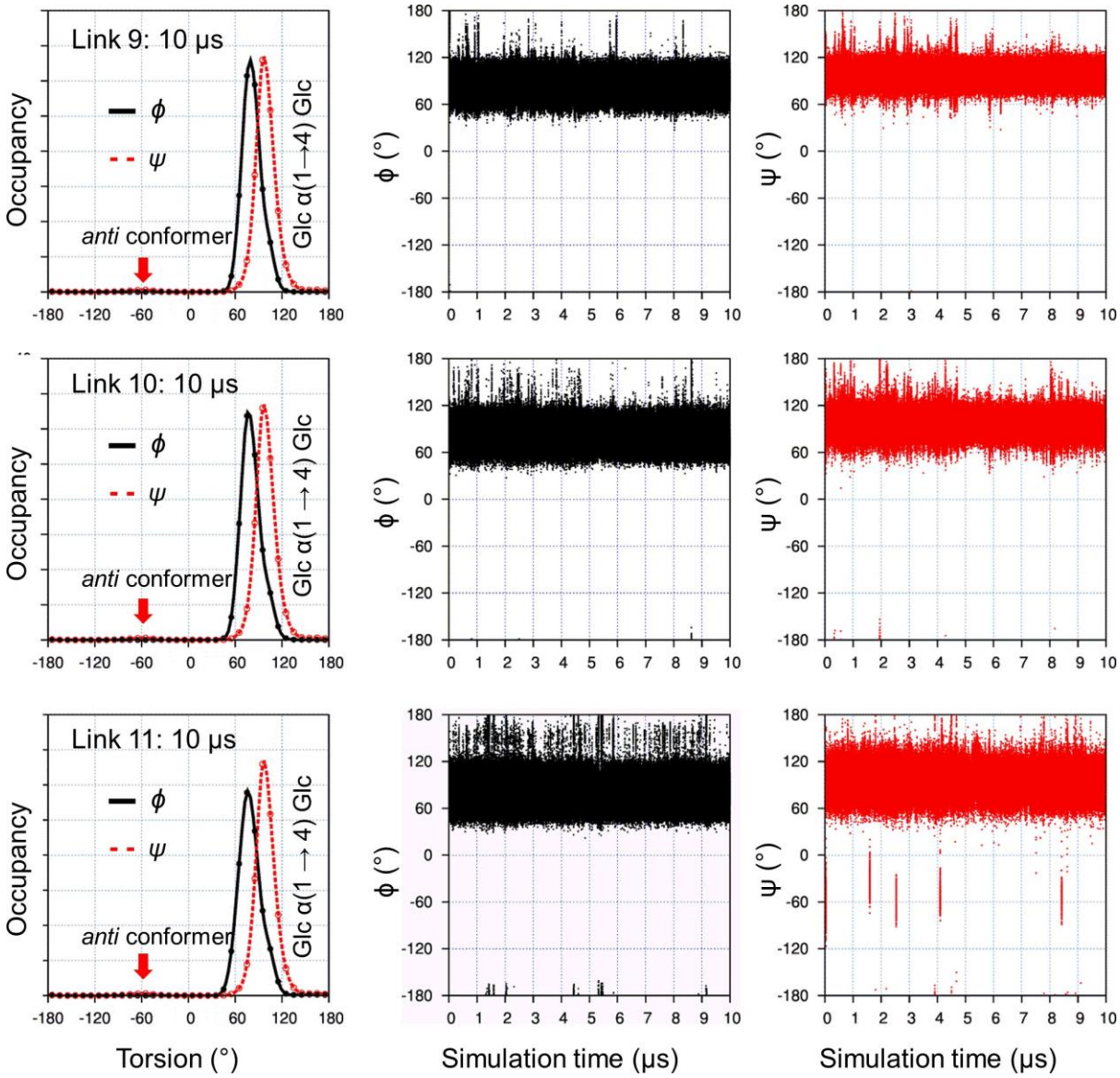


Figure S6. Linkage histograms & time series: 10 *μ*s simulation of **3** (parallel double-helix: strand A)

Glycosidic linkages are numbered from the reducing end; the *anti conformer* is noted

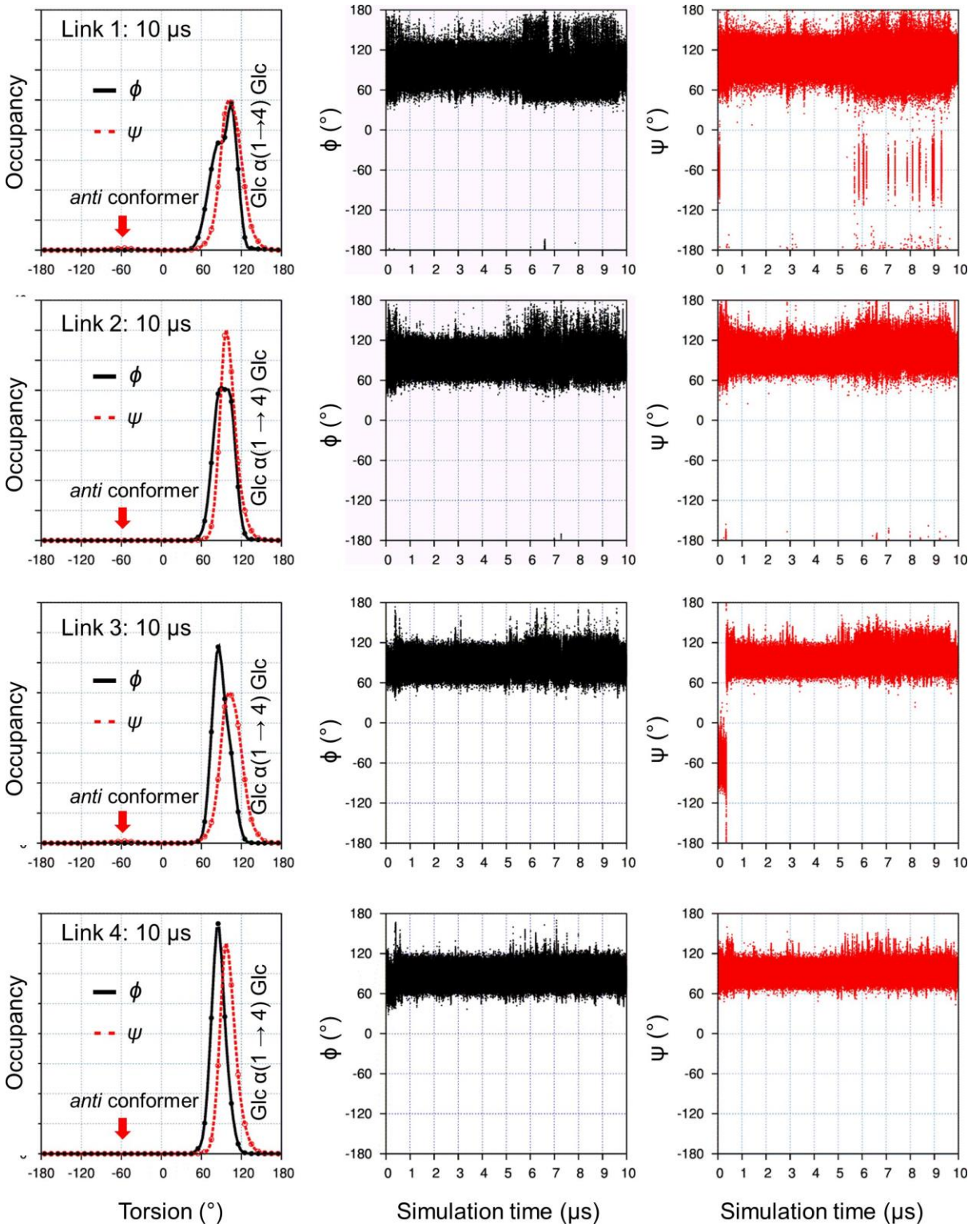
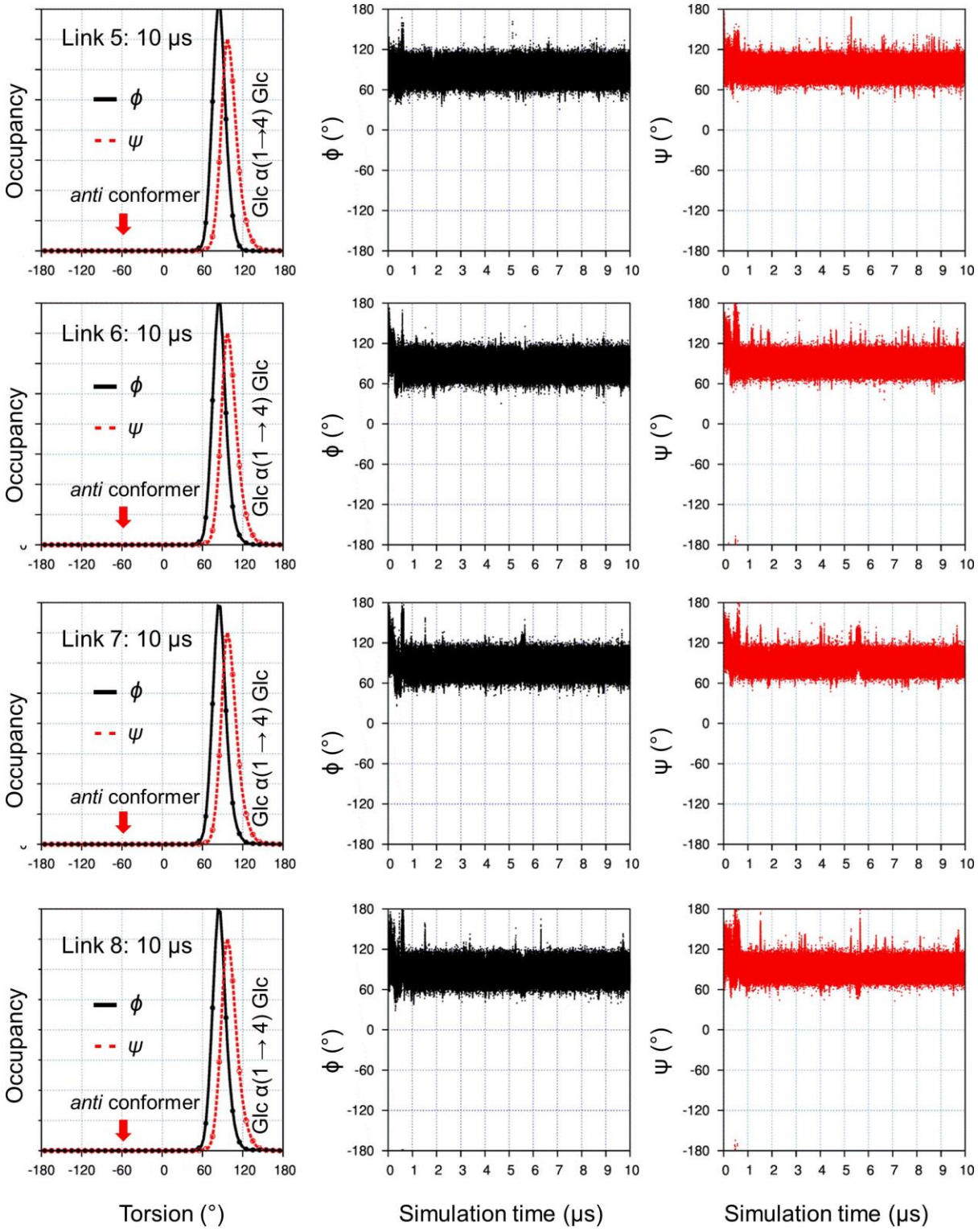


Figure S6. Linkage histograms & time series: 10 *μ*s simulation of **3** (parallel double-helix: strand A)

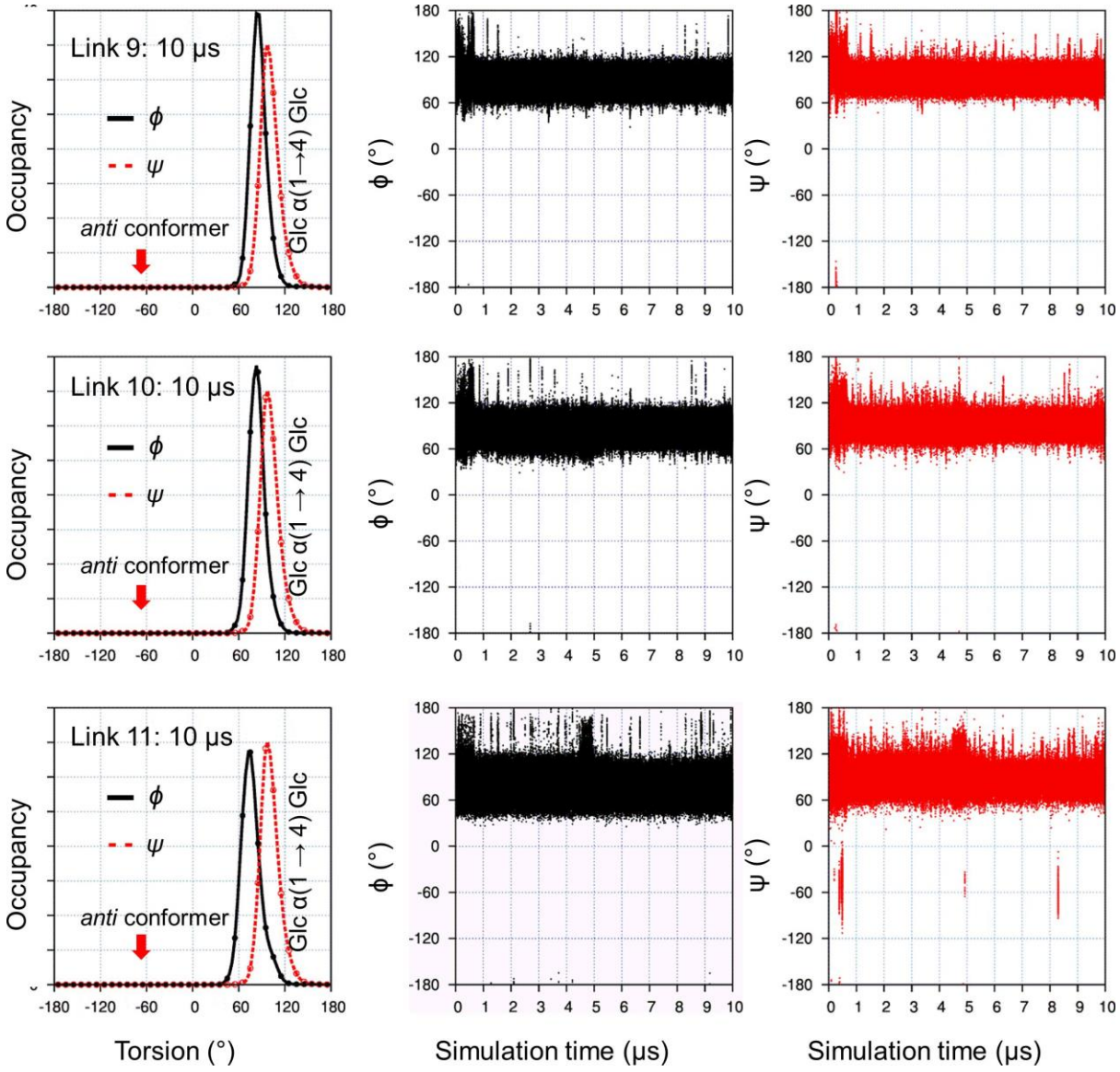
Glycosidic linkages are numbered from the reducing end; the *anti conformer* is noted



S6 continued

Figure S6. Linkage histograms & time series: 10 *μ*s simulation of **3** (parallel double-helix: strand A)

Glycosidic linkages are numbered from the reducing end; the *anti conformer* is noted



S6 continued

Figure S7. Linkage histograms & time series: 10 *μ*s simulation of **3** (parallel double-helix: strand B)

Glycosidic linkages are numbered from the reducing end; the *anti conformer* is noted

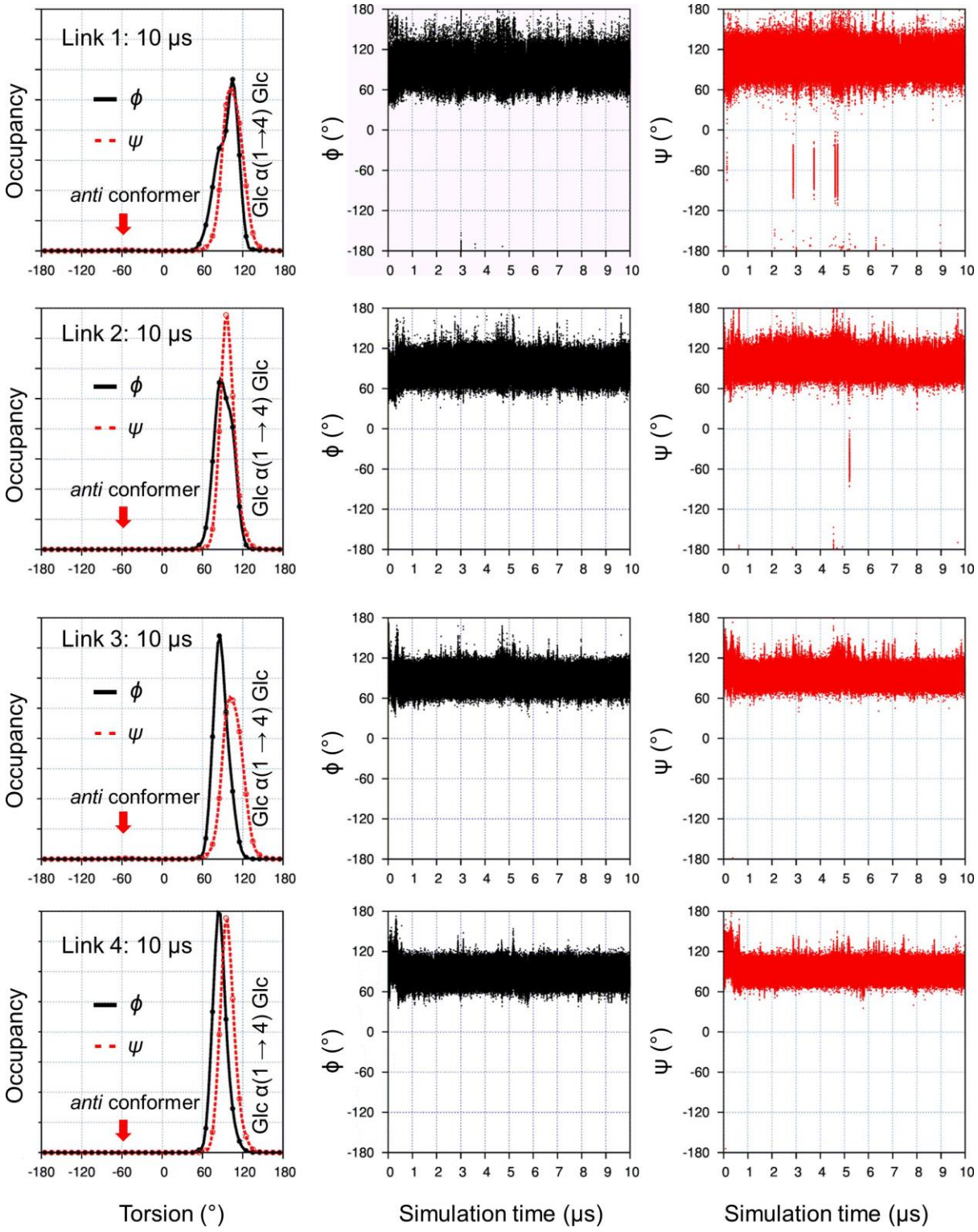
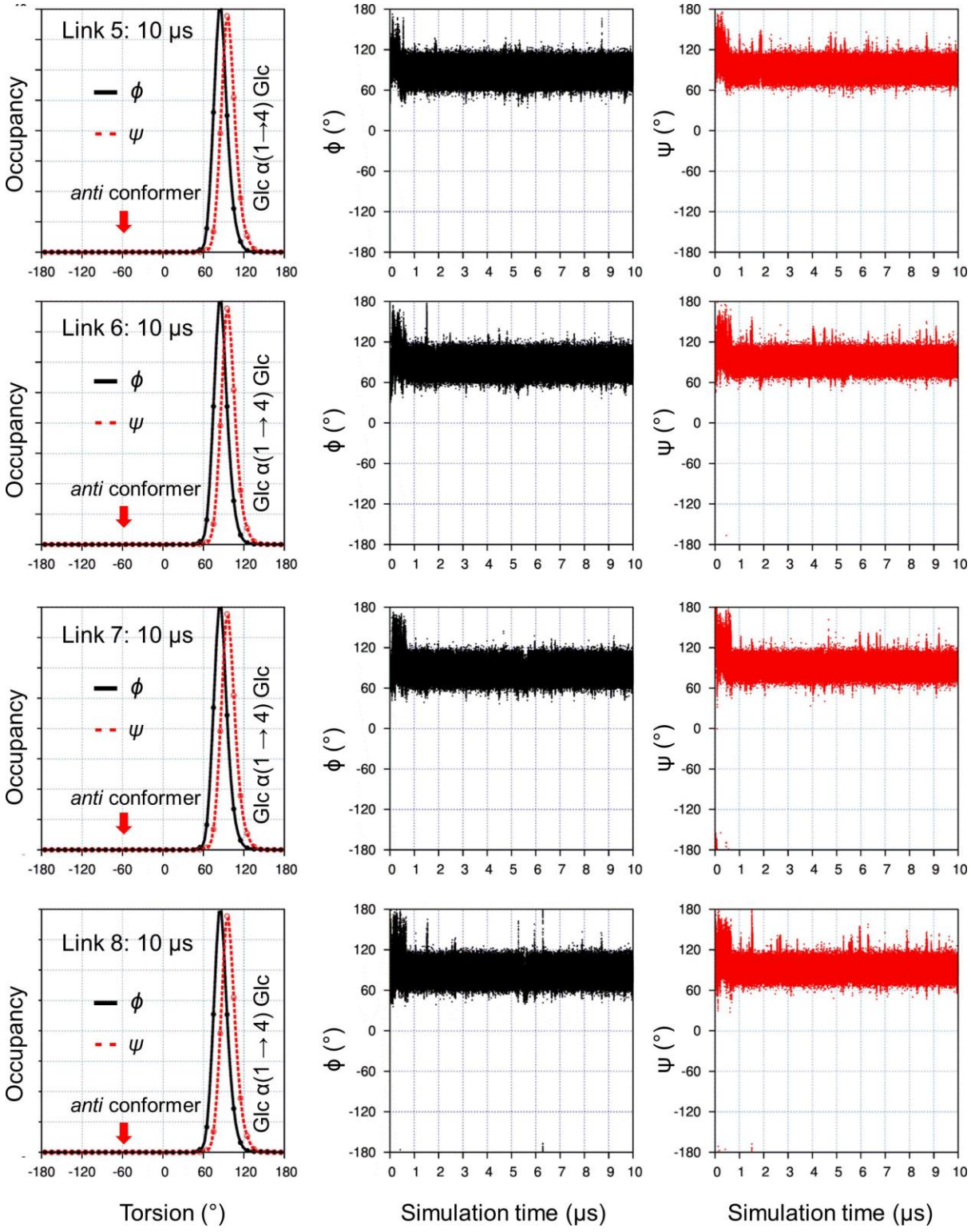


Figure S7. Linkage histograms & time series: 10 *μ*s simulation of **3** (parallel double-helix: strand B)

Glycosidic linkages are numbered from the reducing end; the *anti conformer* is noted



S7 continued

Figure S7. Linkage histograms & time series: 10 *μ*s simulation of **3** (parallel double-helix: strand B)

Glycosidic linkages are numbered from the reducing end; the *anti conformer* is noted

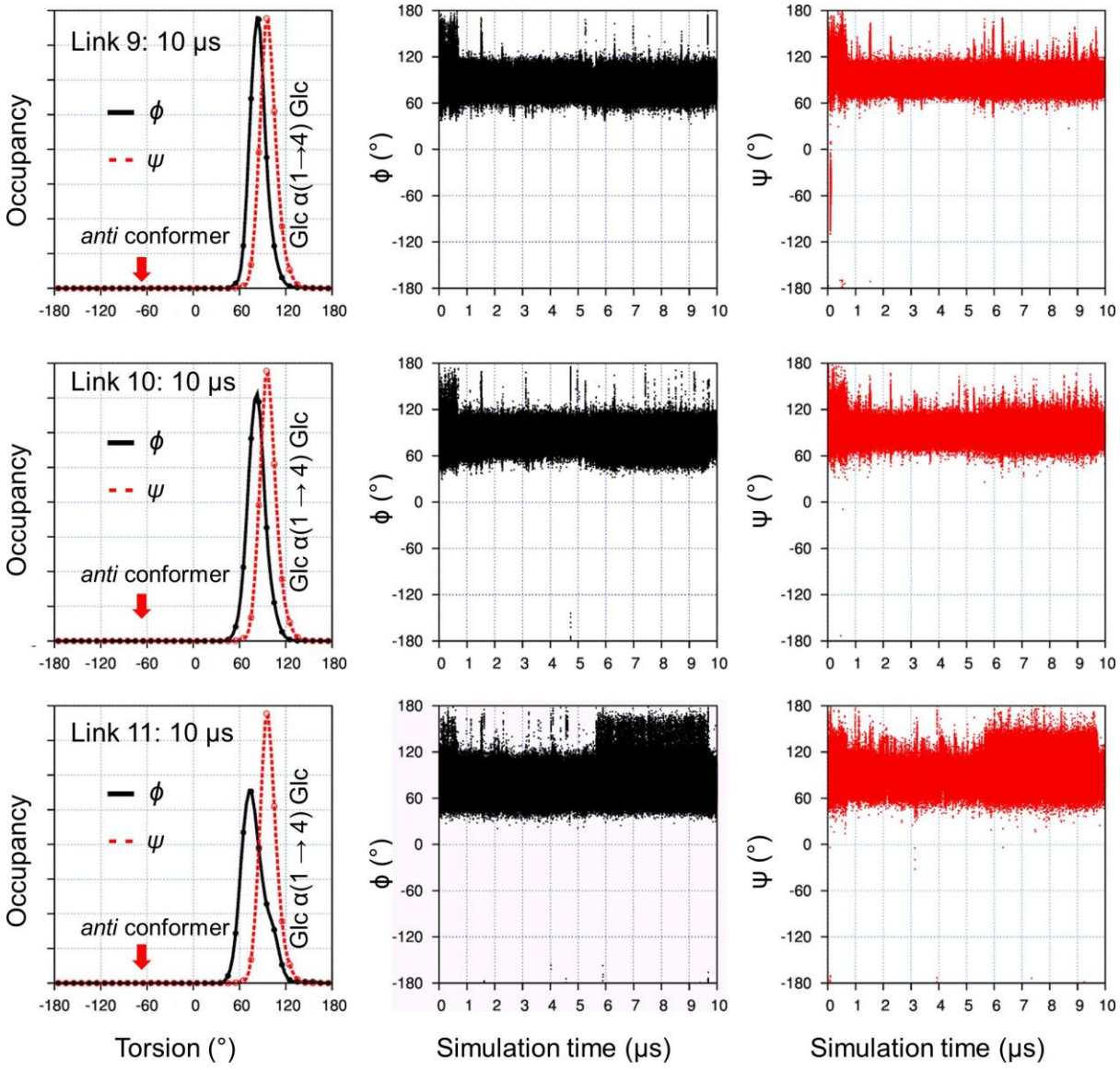


Figure S8. Linkage histograms & time series: 10 μs simulation of **4** (hexasaccharide)

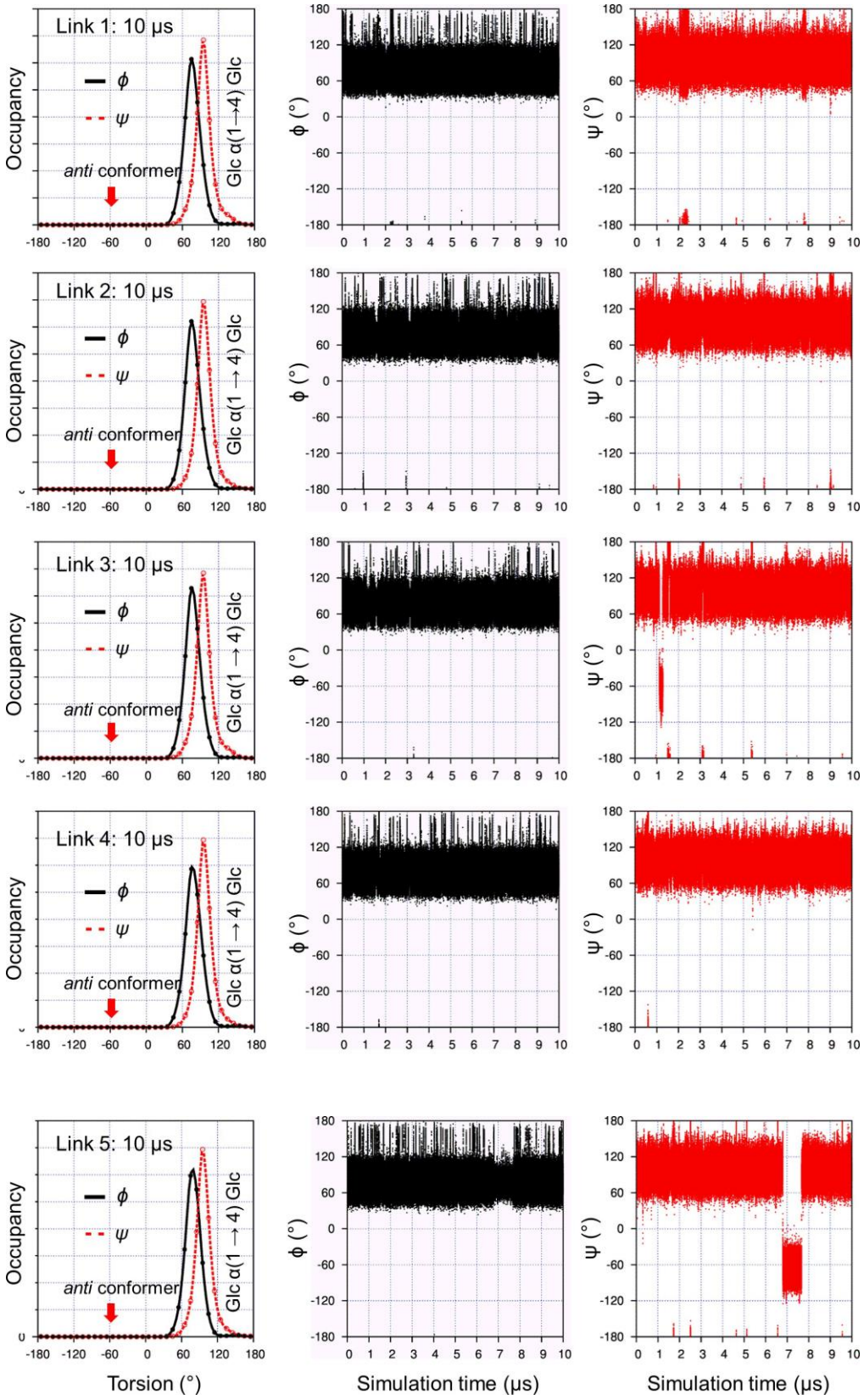


Figure S9. Linkage histograms & time series: 20 *μ*s simulation of **5** (trisaccharide)

Glycosidic linkages are numbered from the reducing end; the *anti* conformer is noted

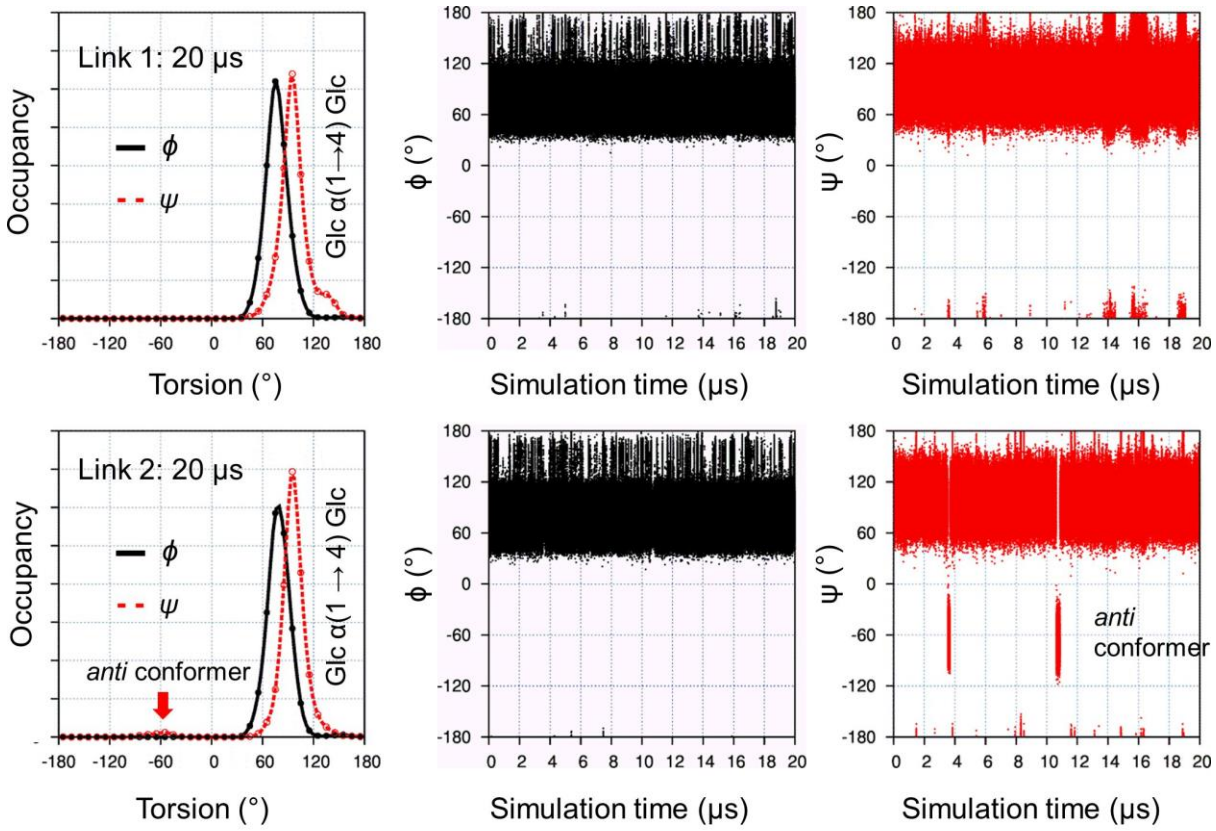


Figure S10. Linkage free energy surfaces: 10 μs simulation of **1** (dodecasaccharide)

Glycosidic linkages are numbered from the reducing end; contours at 2, 4 and 6 kcal mol^{-1}

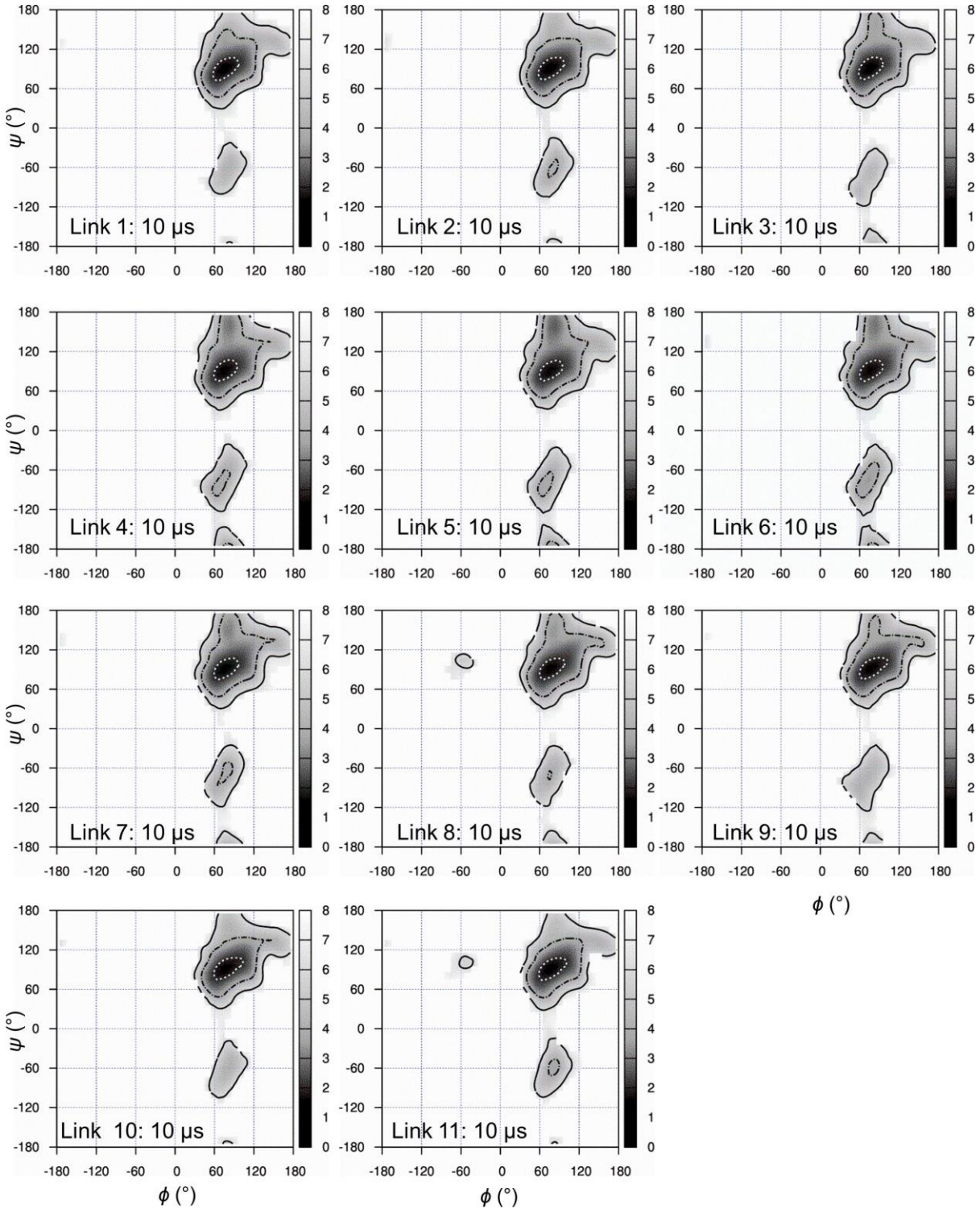


Figure S11. Linkage free energy surfaces: 10 μs simulation of **2** (antiparallel double-helix: strand A)

Glycosidic linkages are numbered from the reducing end; contours at 2, 4 and 6 kcal mol^{-1}

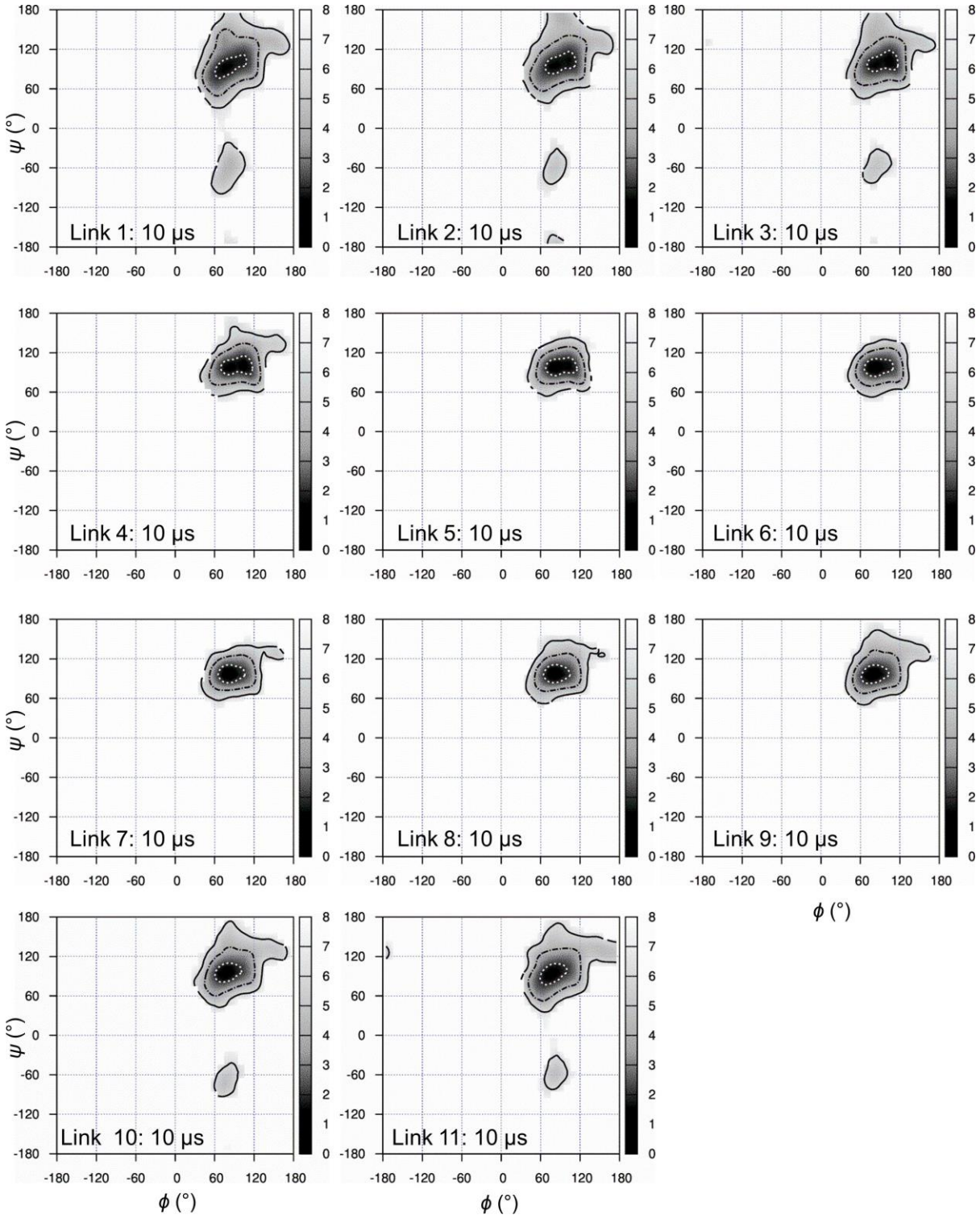
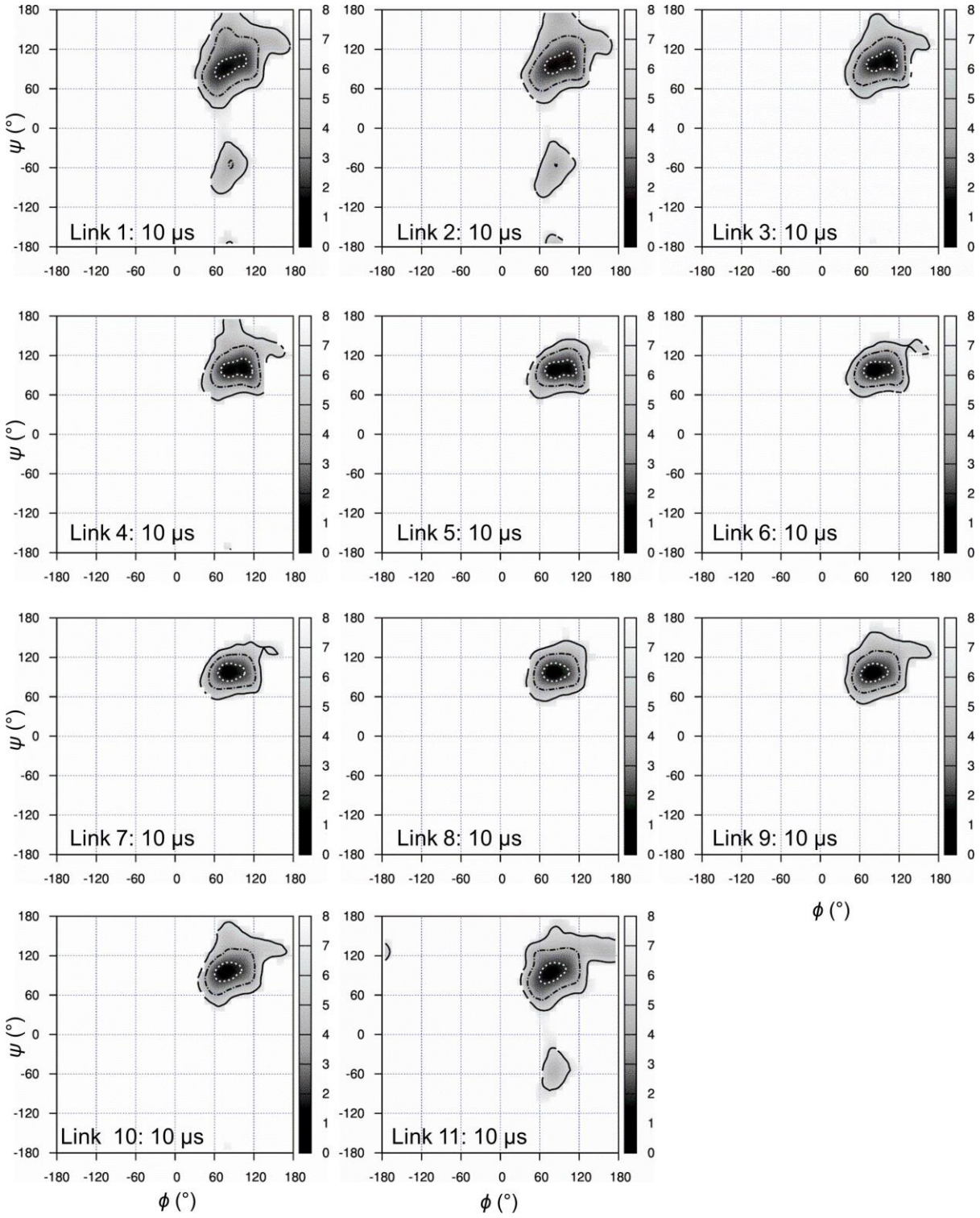


Figure S11. Linkage free energy surfaces: 10 μs simulation of **2** (antiparallel double-helix: strand B)

Glycosidic linkages are numbered from the reducing end; contours at 2, 4 and 6 kcal mol^{-1}



S11 continued

Figure S12. Linkage free energy surfaces: 10 *μ*s simulation of **3** (parallel double-helix: strand A)

Glycosidic linkages are numbered from the reducing end; contours at 2, 4 and 6 kcal mol^{-1}

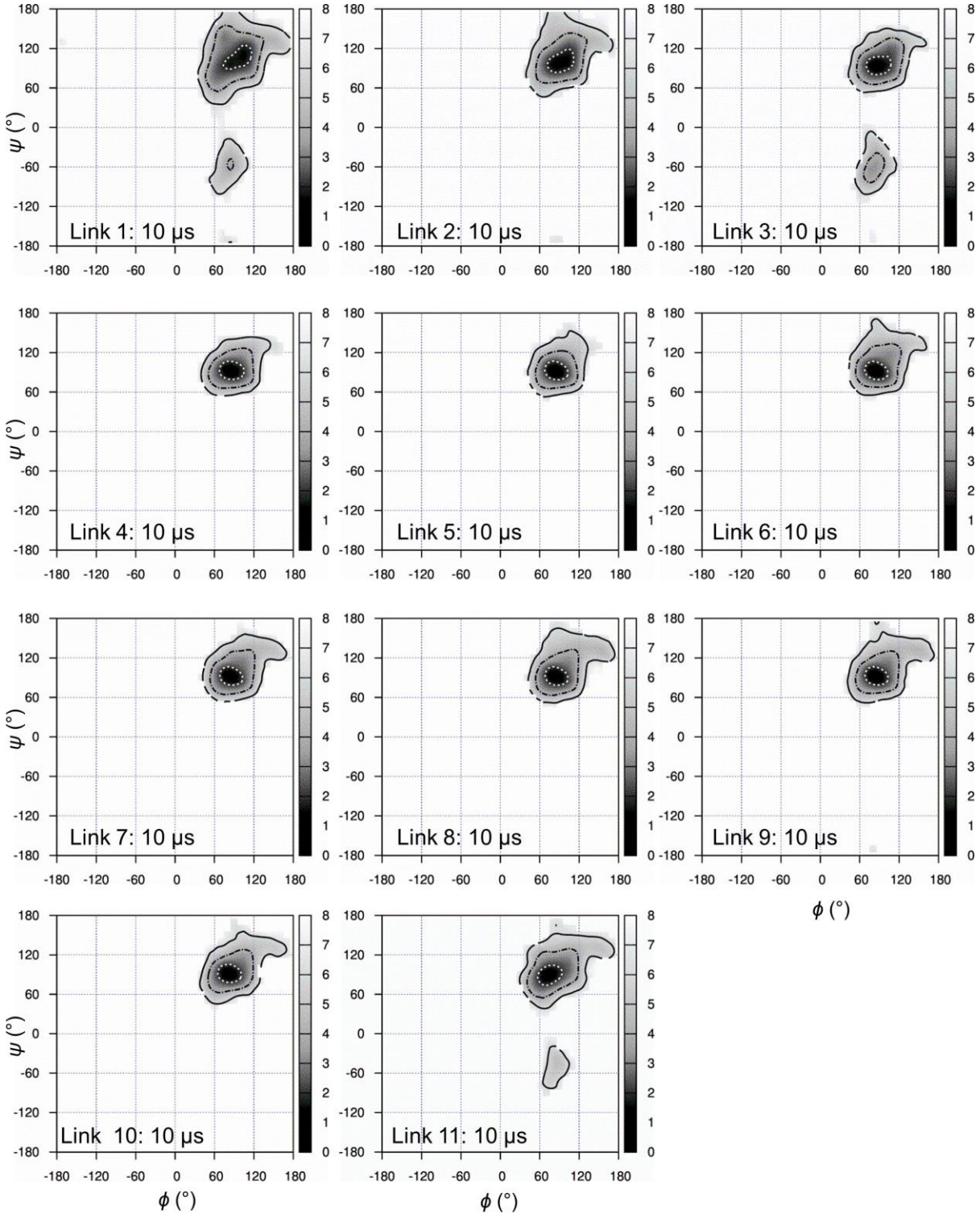
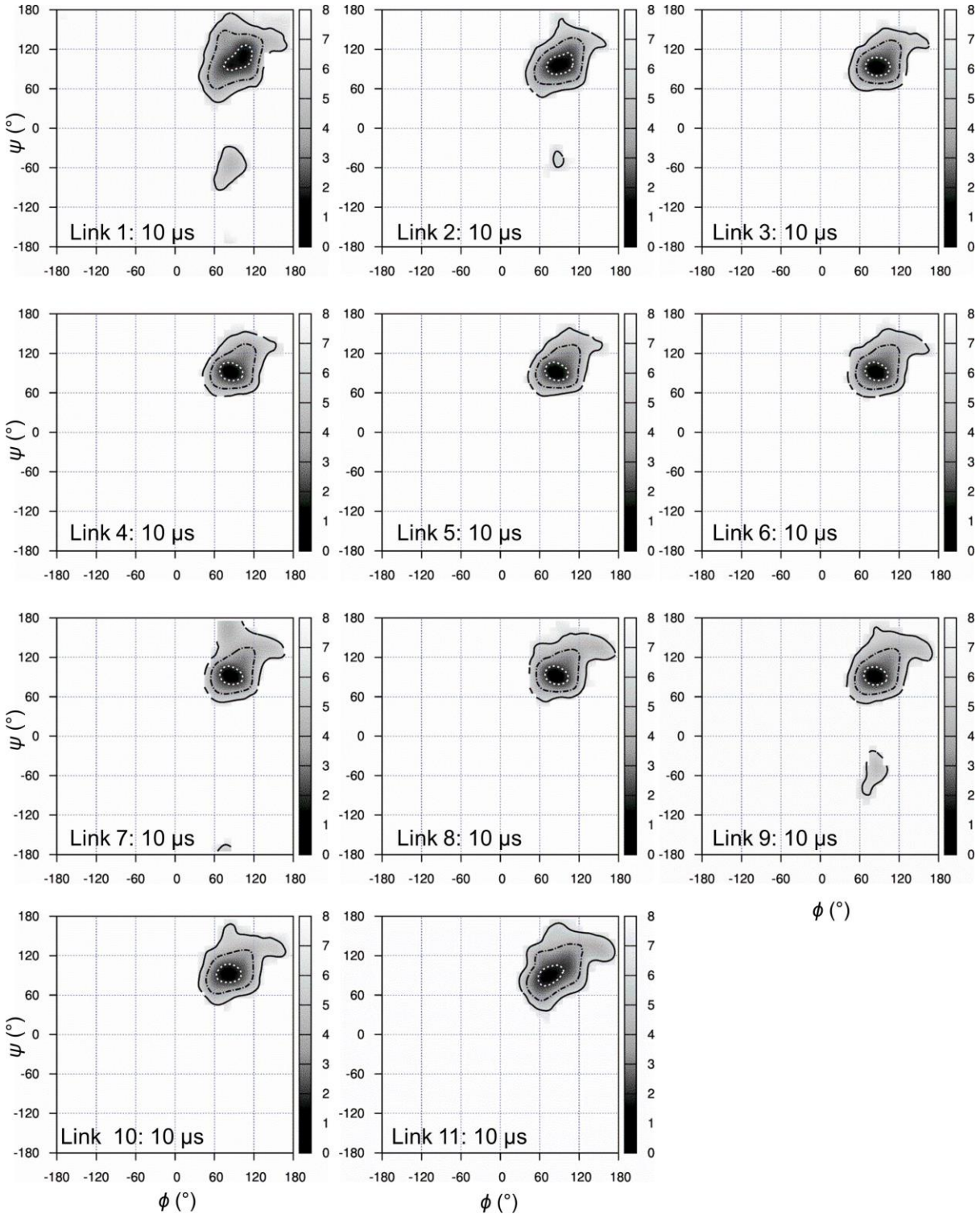


Figure S12. Linkage free energy surfaces: 10 μs simulation of **3** (parallel double-helix: strand B)

Glycosidic linkages are numbered from the reducing end; contours at 2, 4 and 6 kcal mol^{-1}

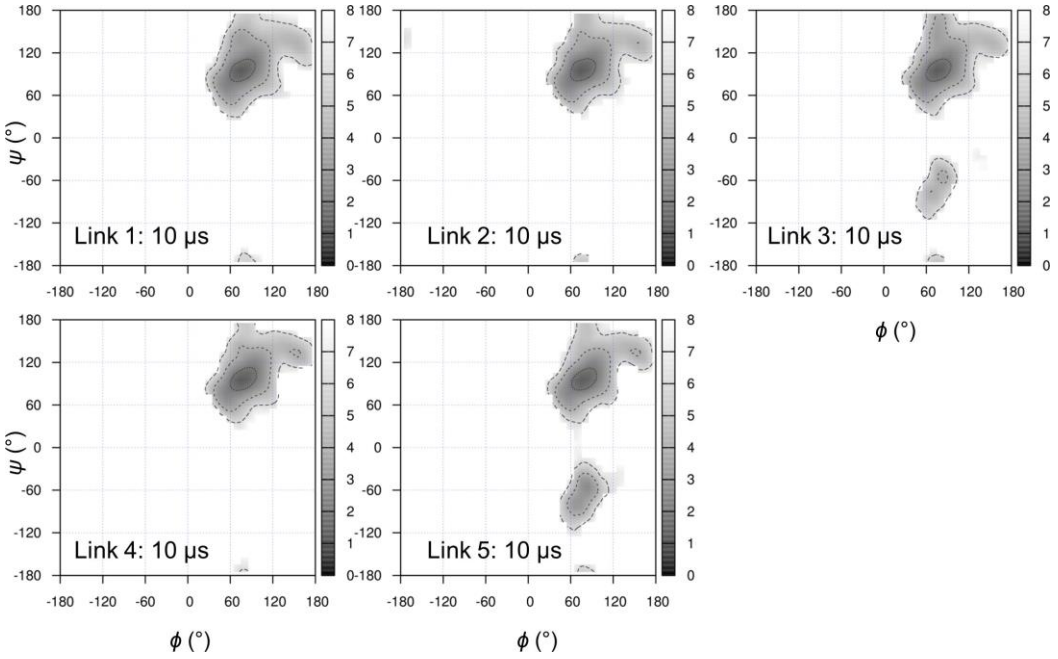


S12 continued

Figure S13. Linkage free energy surfaces: *μ*s simulations of **4** (hexasaccharide) and **5** (trisaccharide)

Glycosidic linkages are numbered from the reducing end; contours at 2, 4 and 6 kcal mol^{-1}

(**4**)



(**5**)

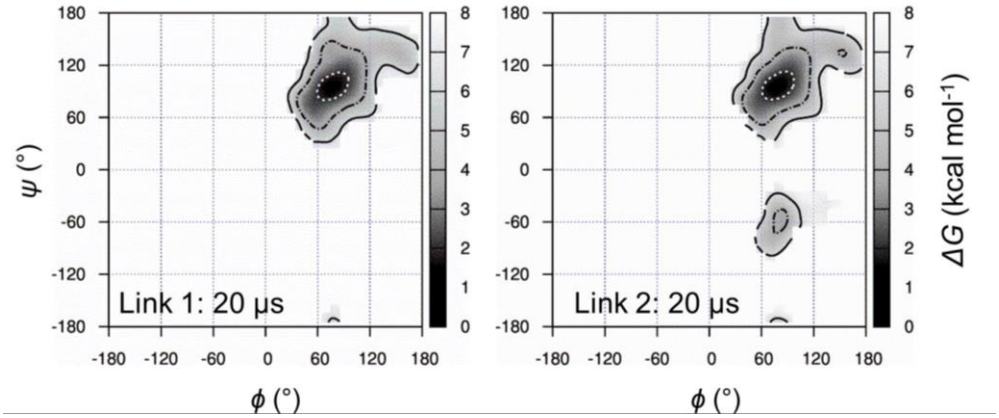
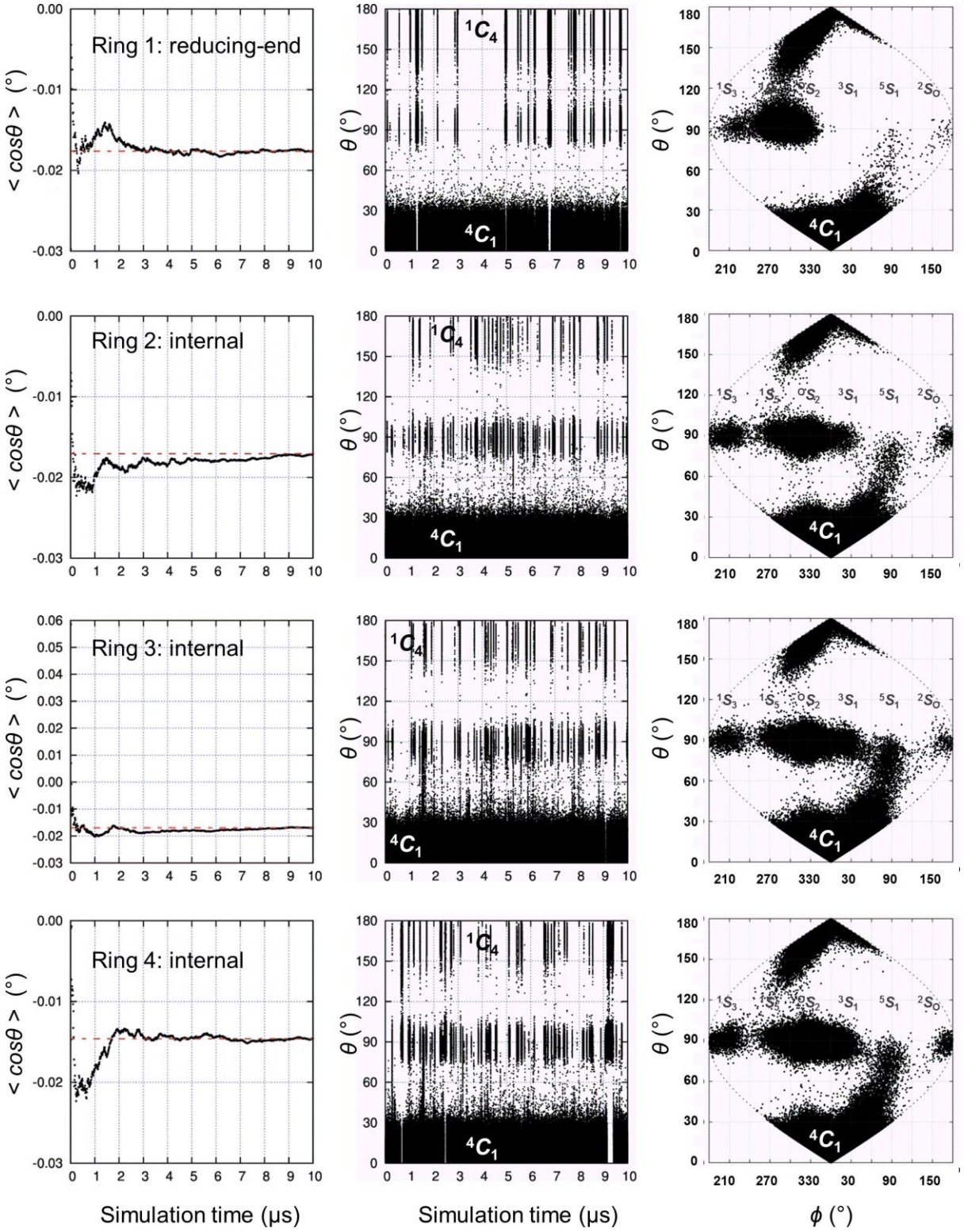


Figure S14. Puckering convergence, time series and sinusoidal projections: 10 μs simulation of **1**

Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



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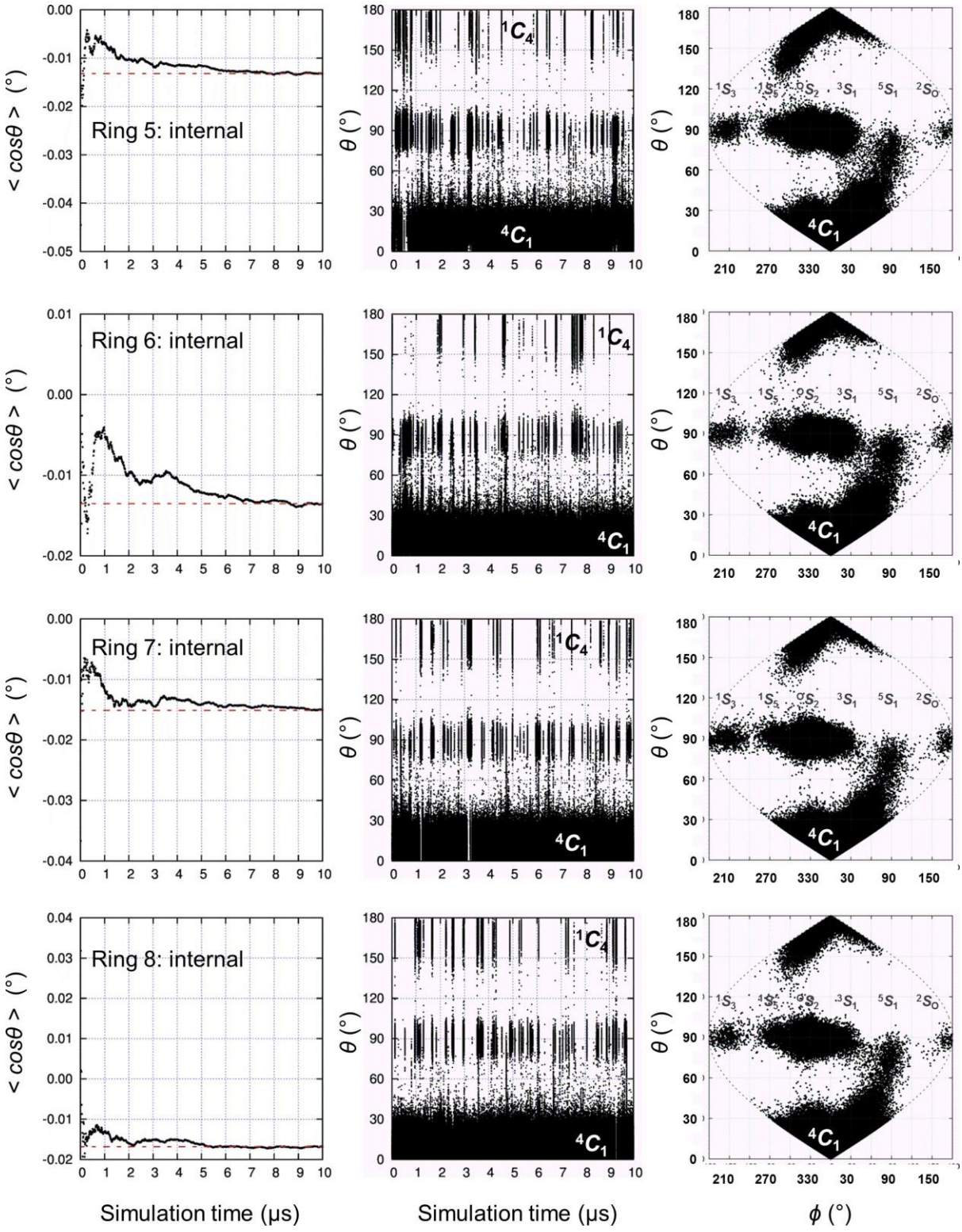

S14 continued

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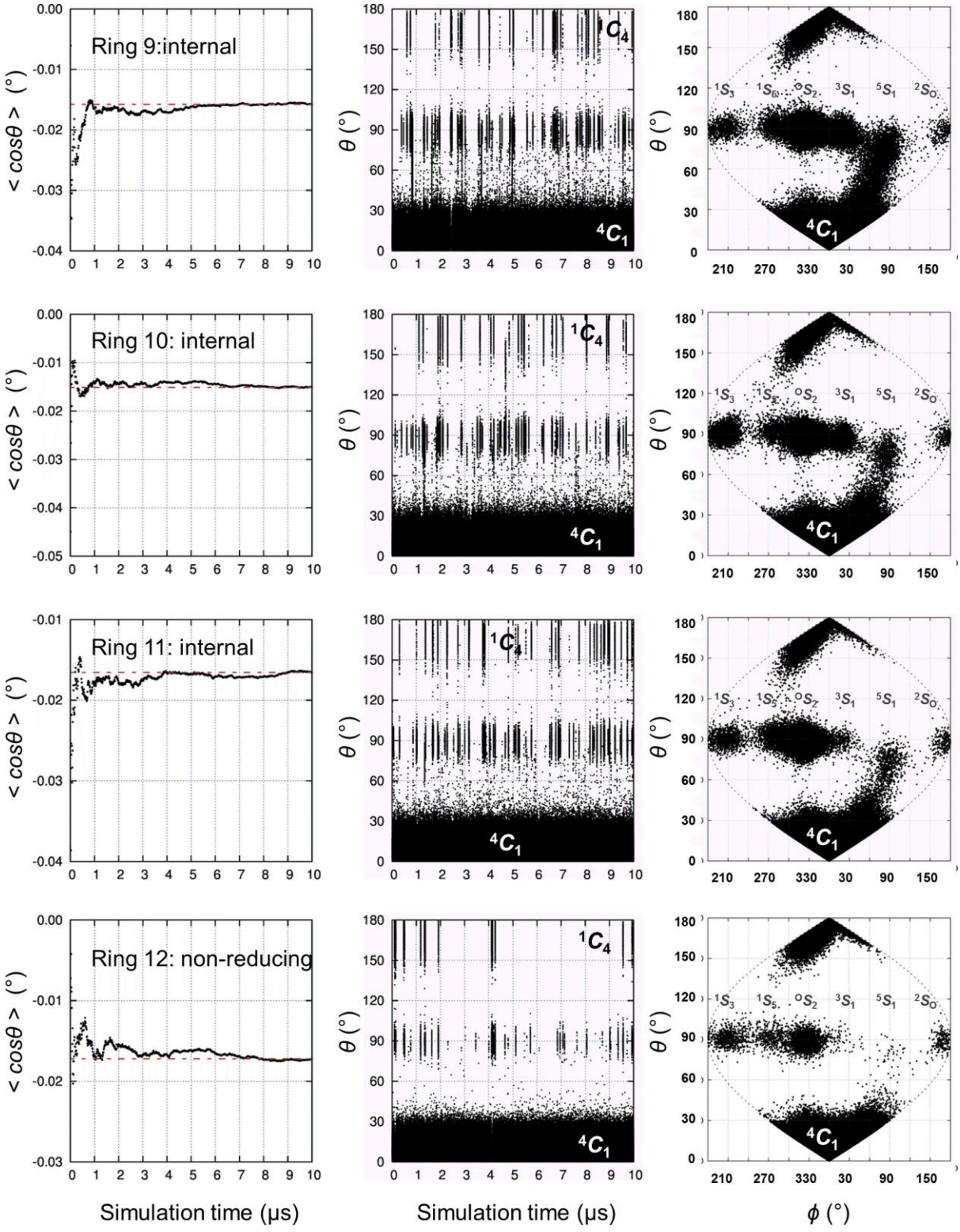
Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



S14 continued

Figure S15. Puckering convergence, time series and sinusoidal projections: **2** (strand A)

Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end

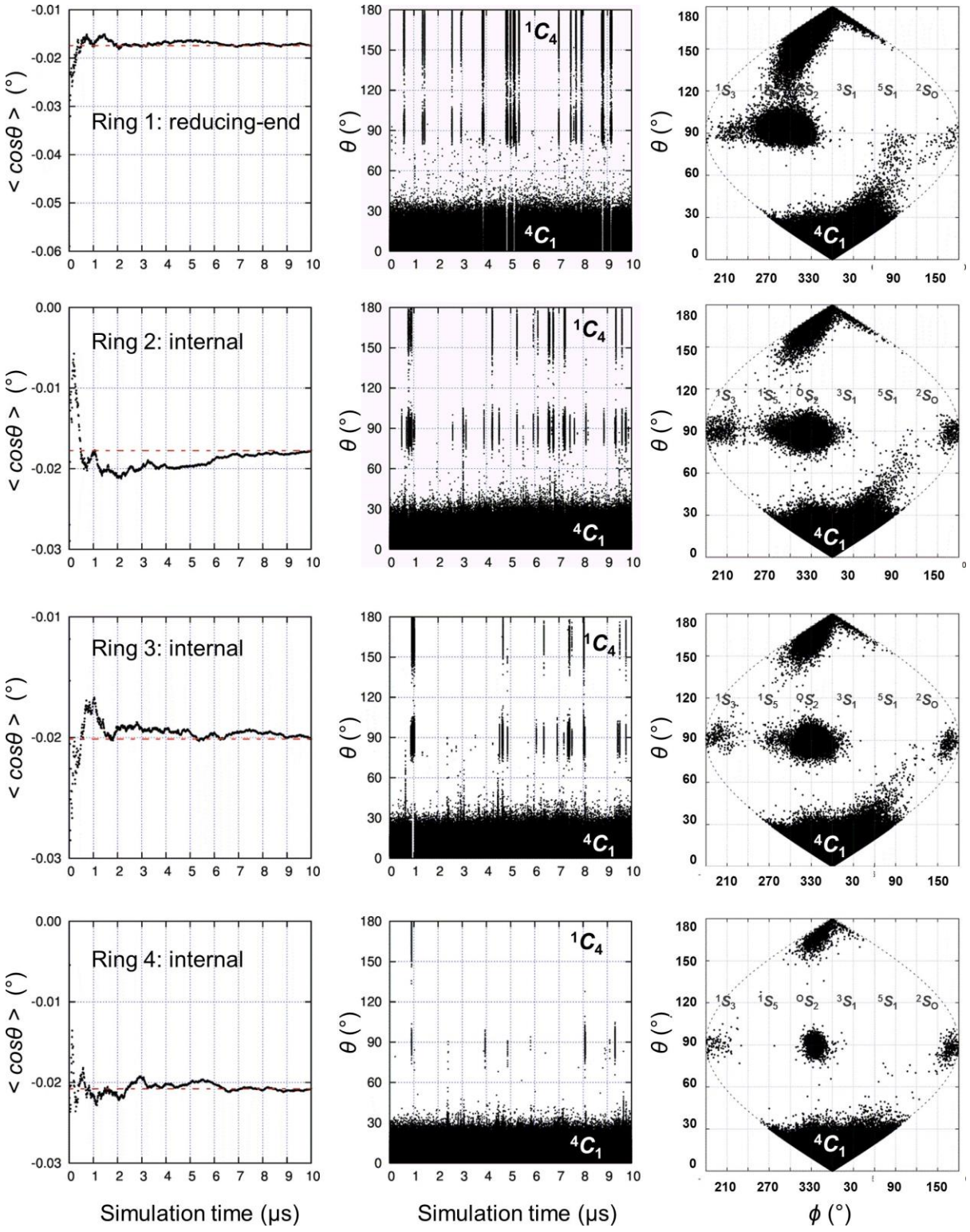
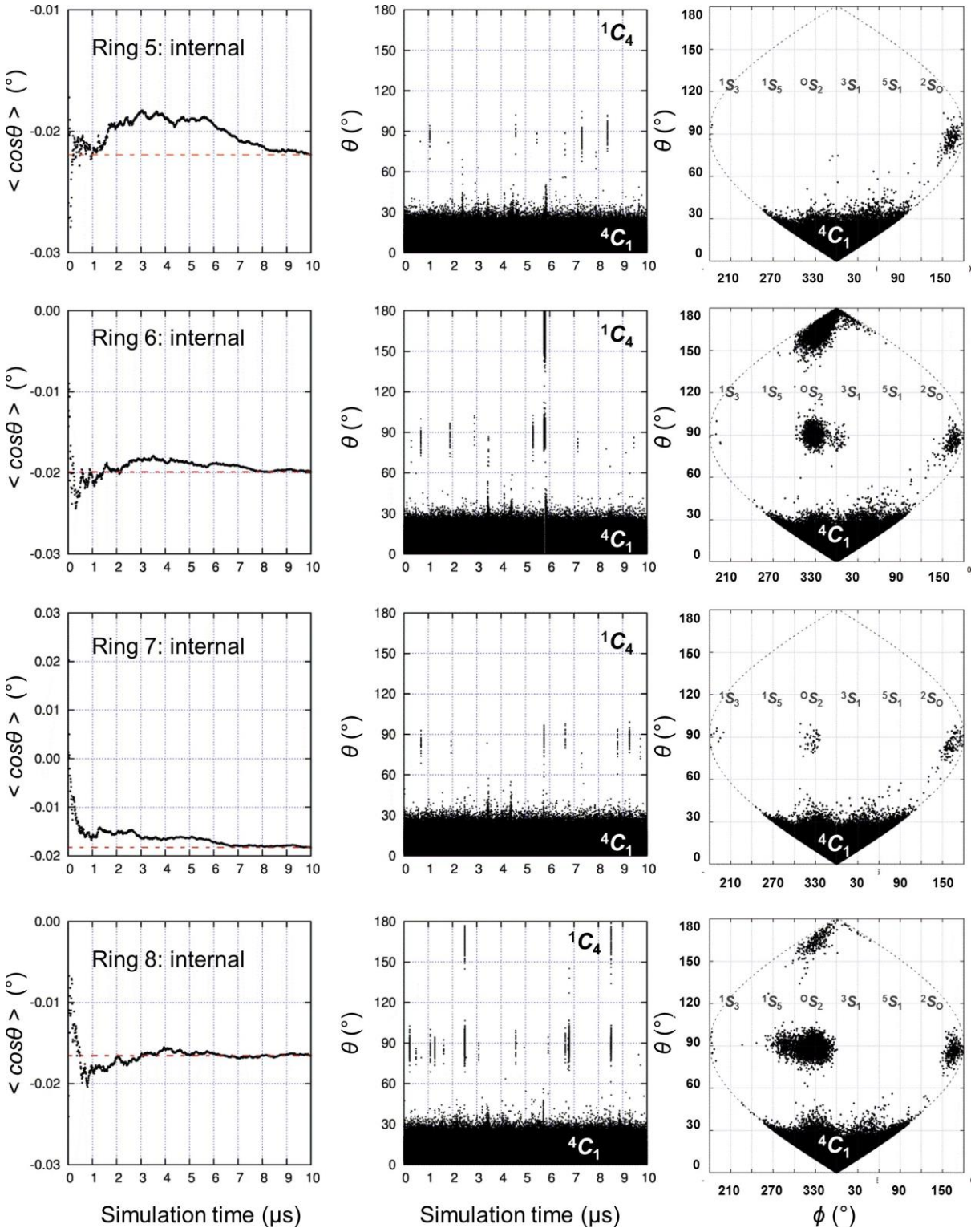


Figure S15. Puckering convergence, time series and sinusoidal projections: **2** (strand A)

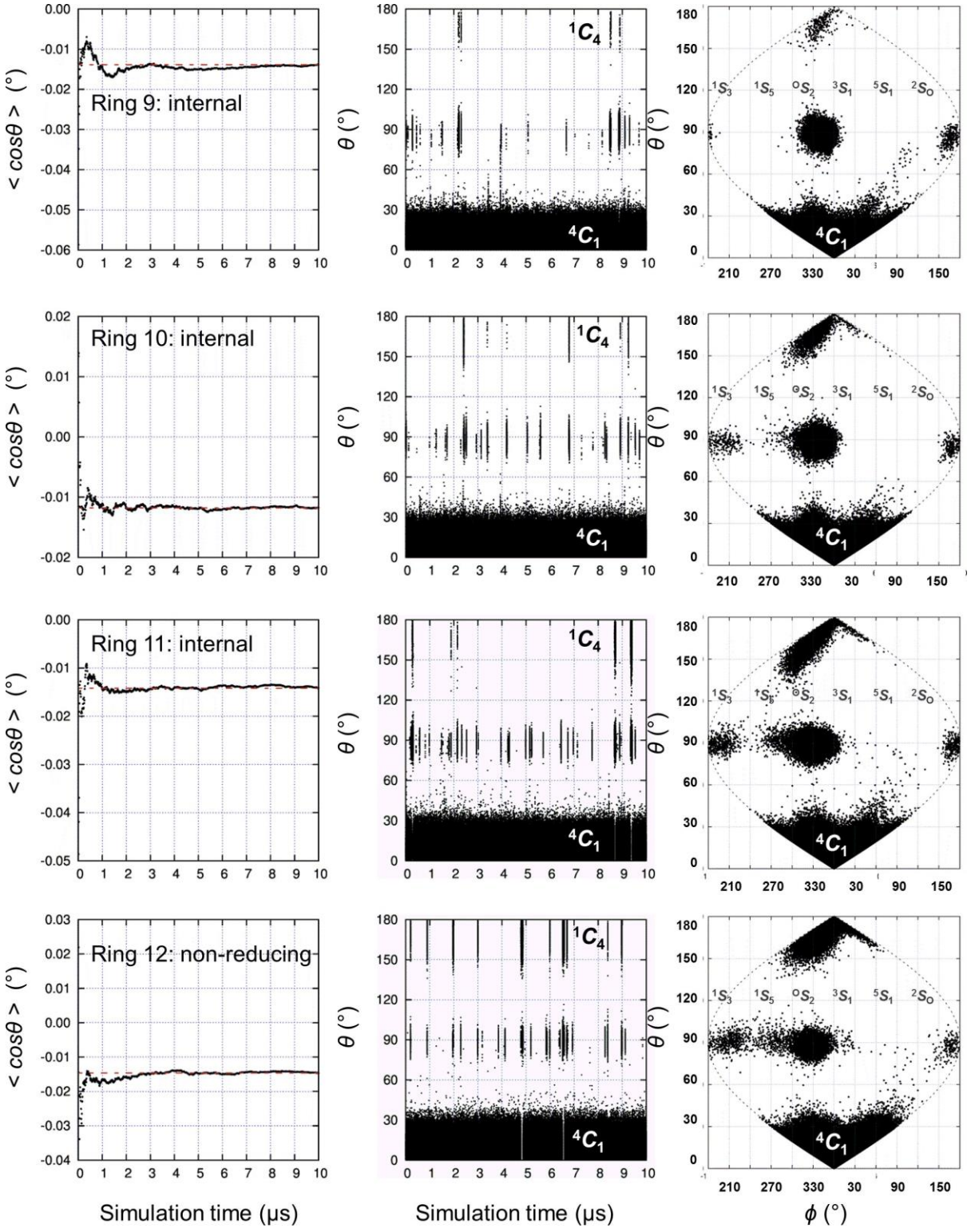
Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



S15 continued

Figure S15. Puckering convergence, time series and sinusoidal projections: **2** (strand A)

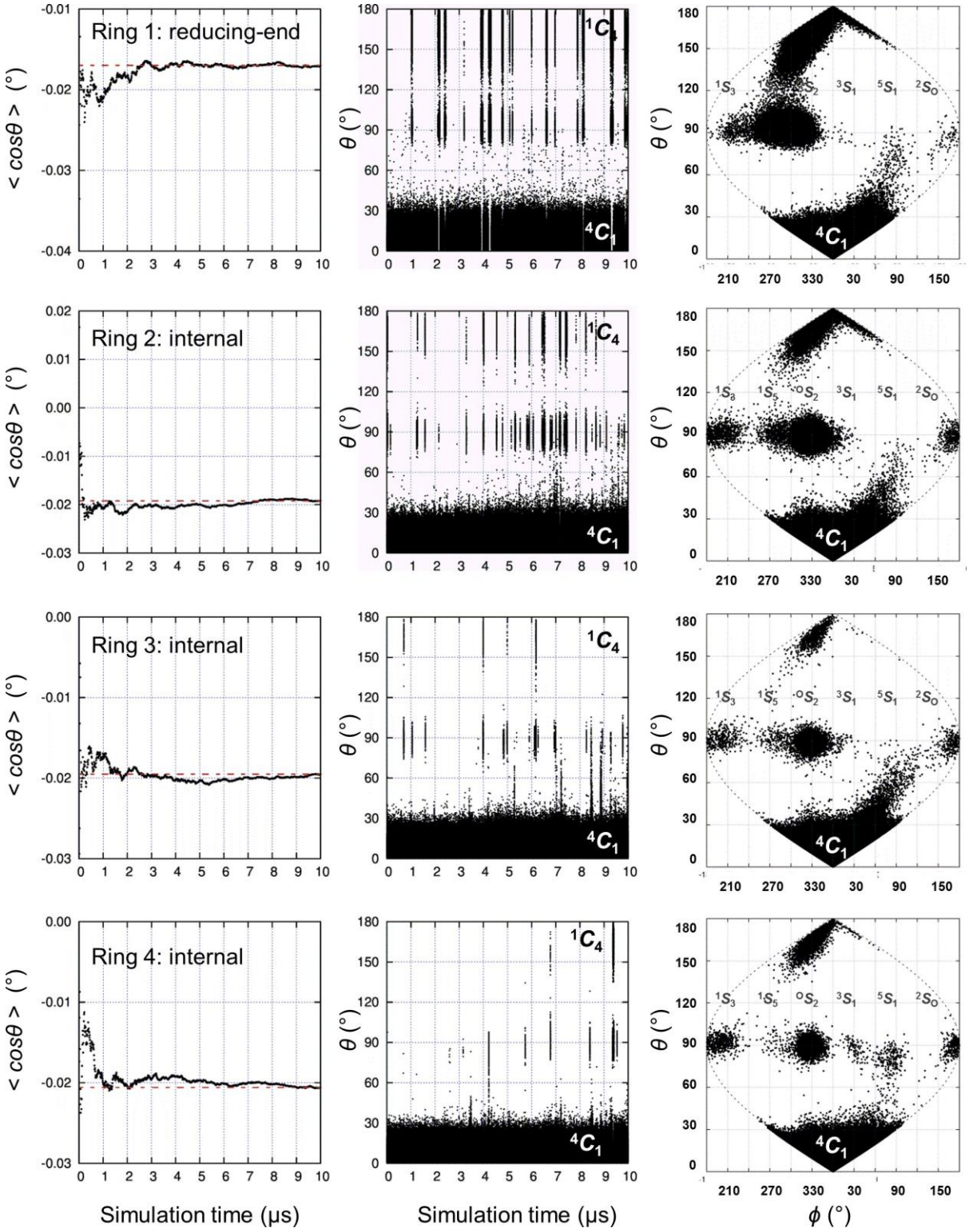
Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



S15 continued

Figure S15. Puckering convergence, time series and sinusoidal projections: **2** (strand B)

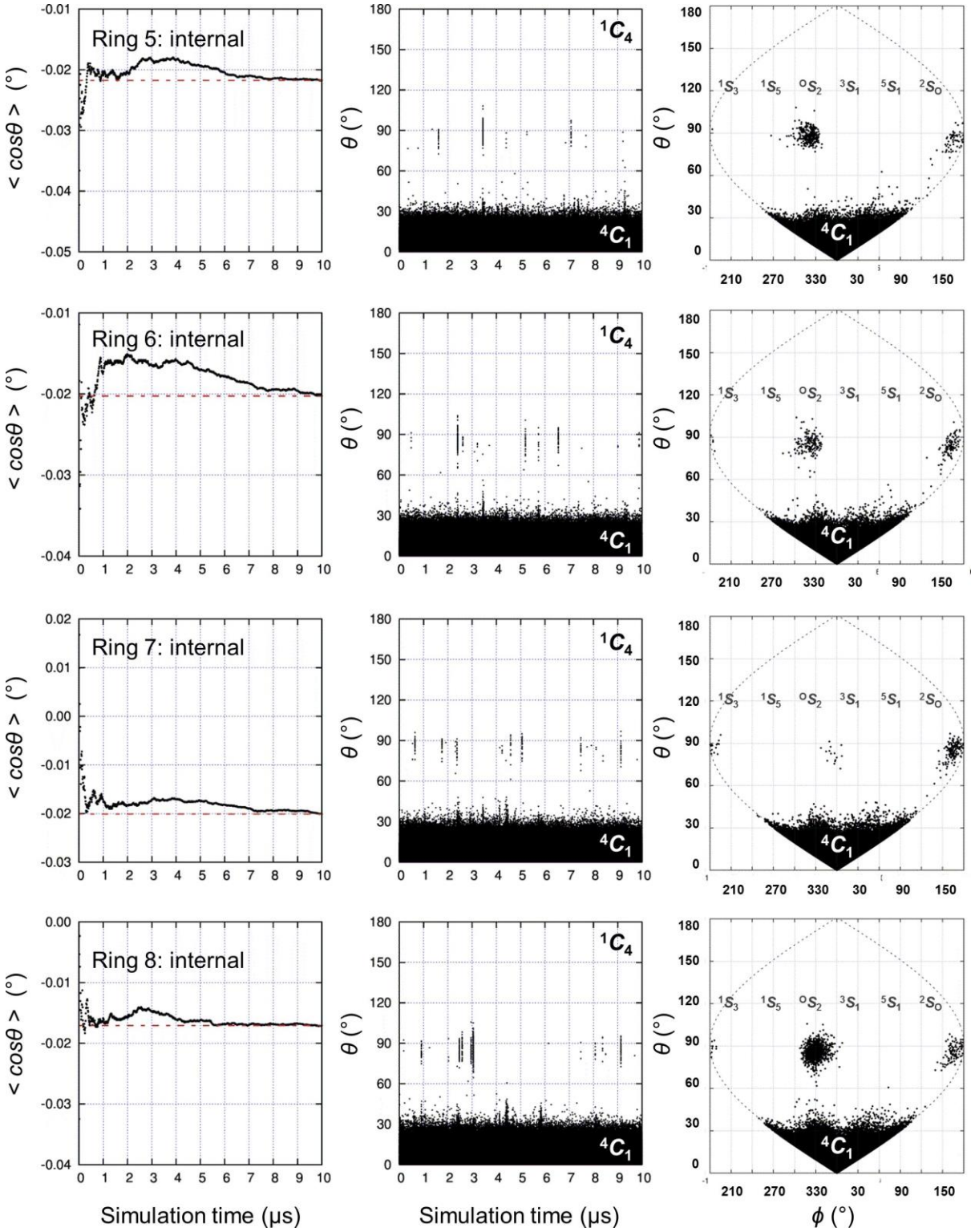
Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



S15 continued

Figure S15. Puckering convergence, time series and sinusoidal projections: **2** (strand B)

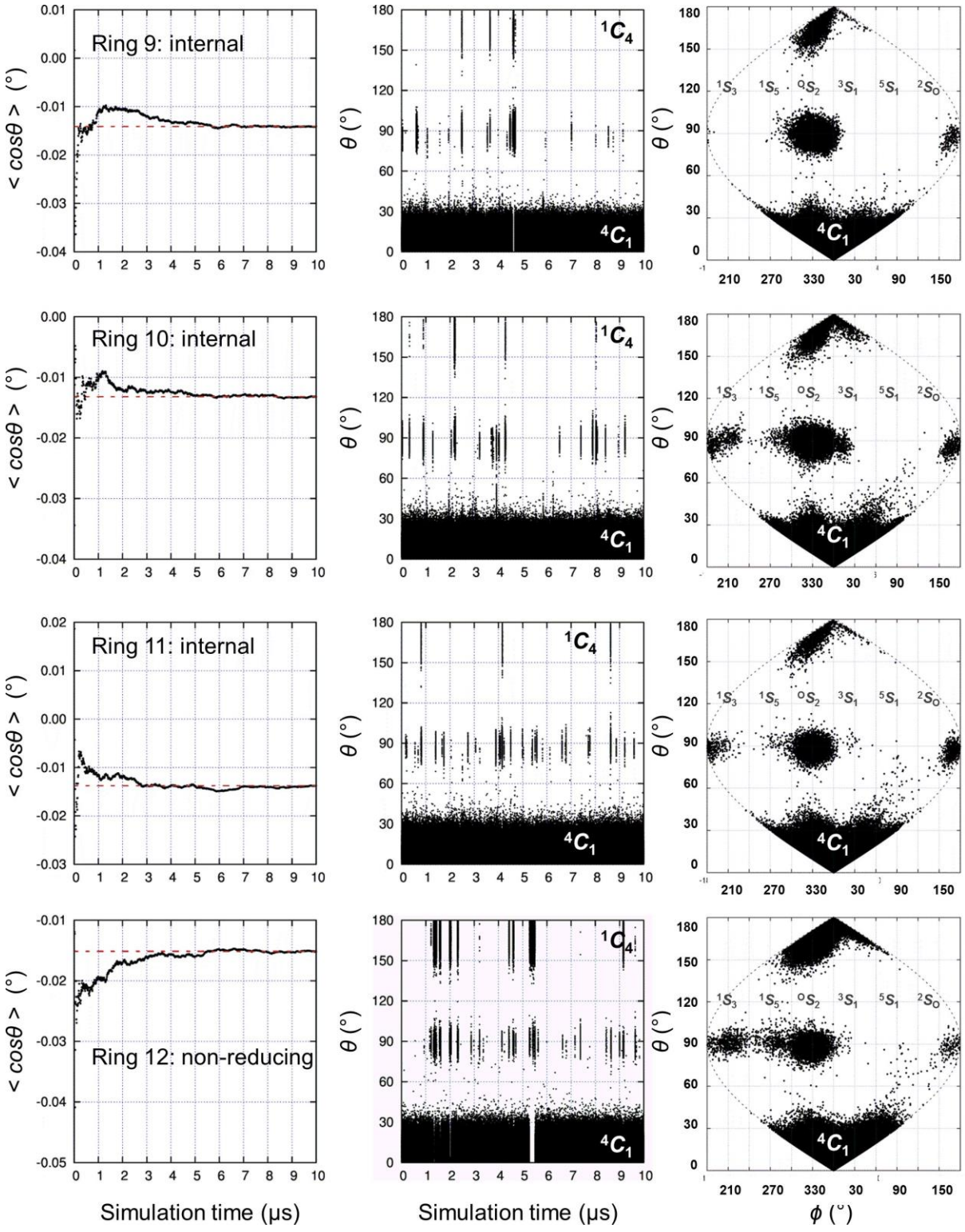
Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



S15 continued

Figure S15. Puckering convergence, time series and sinusoidal projections: **2** (strand B)

Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



S15 continued

Figure S16. Puckering convergence, time series and sinusoidal projections: **3** (strand A)

Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end

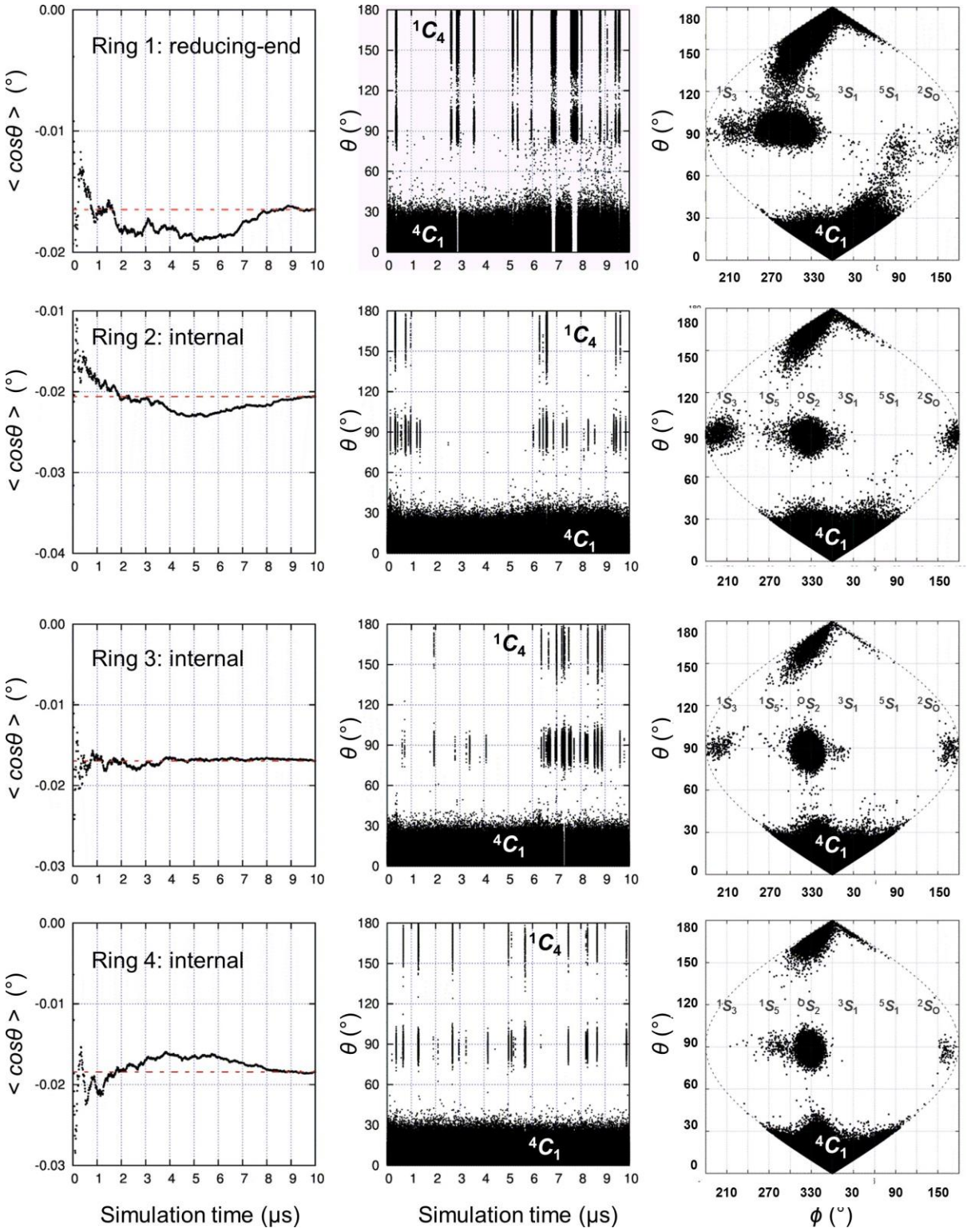
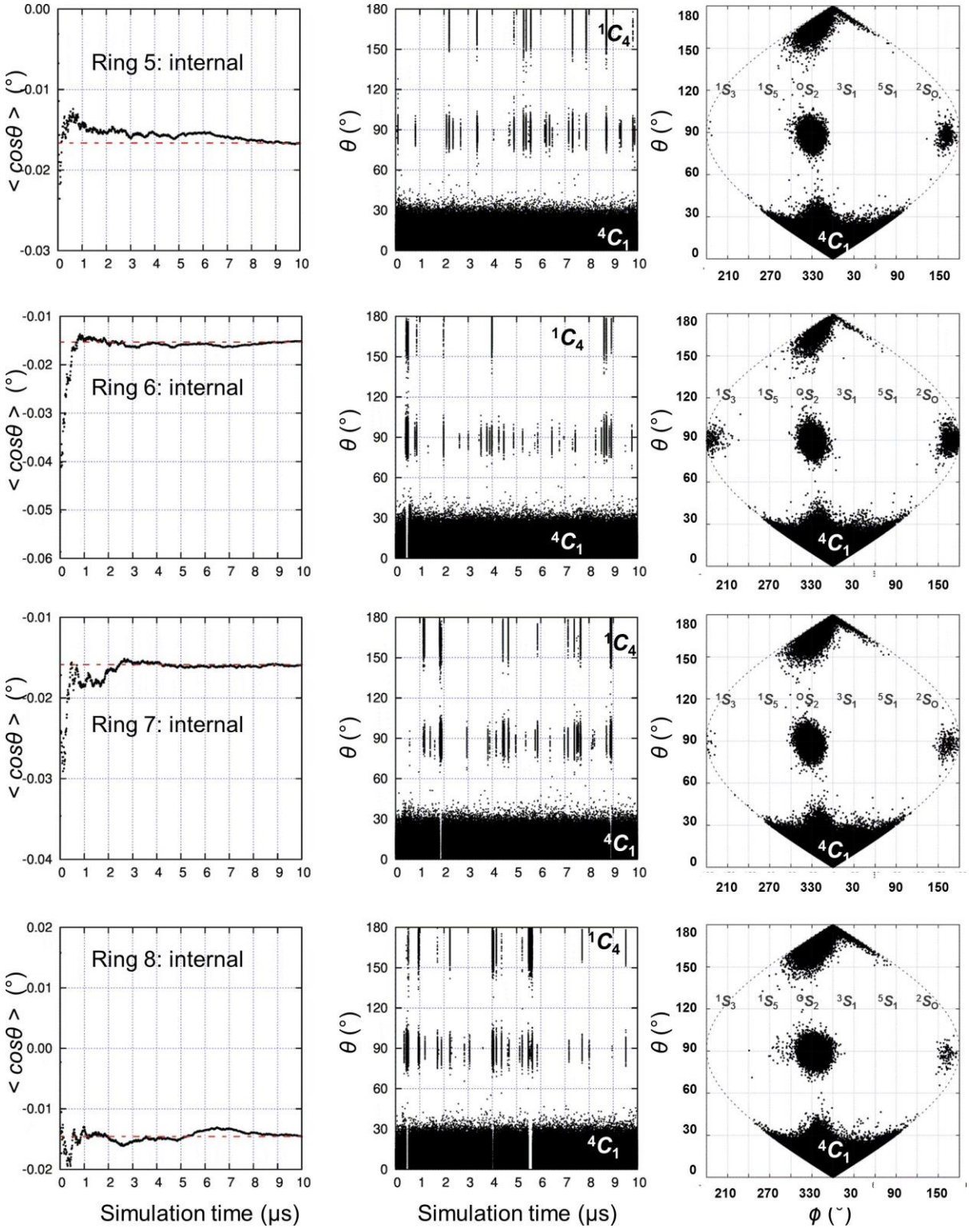


Figure S16. Puckering convergence, time series and sinusoidal projections: **3** (strand A)

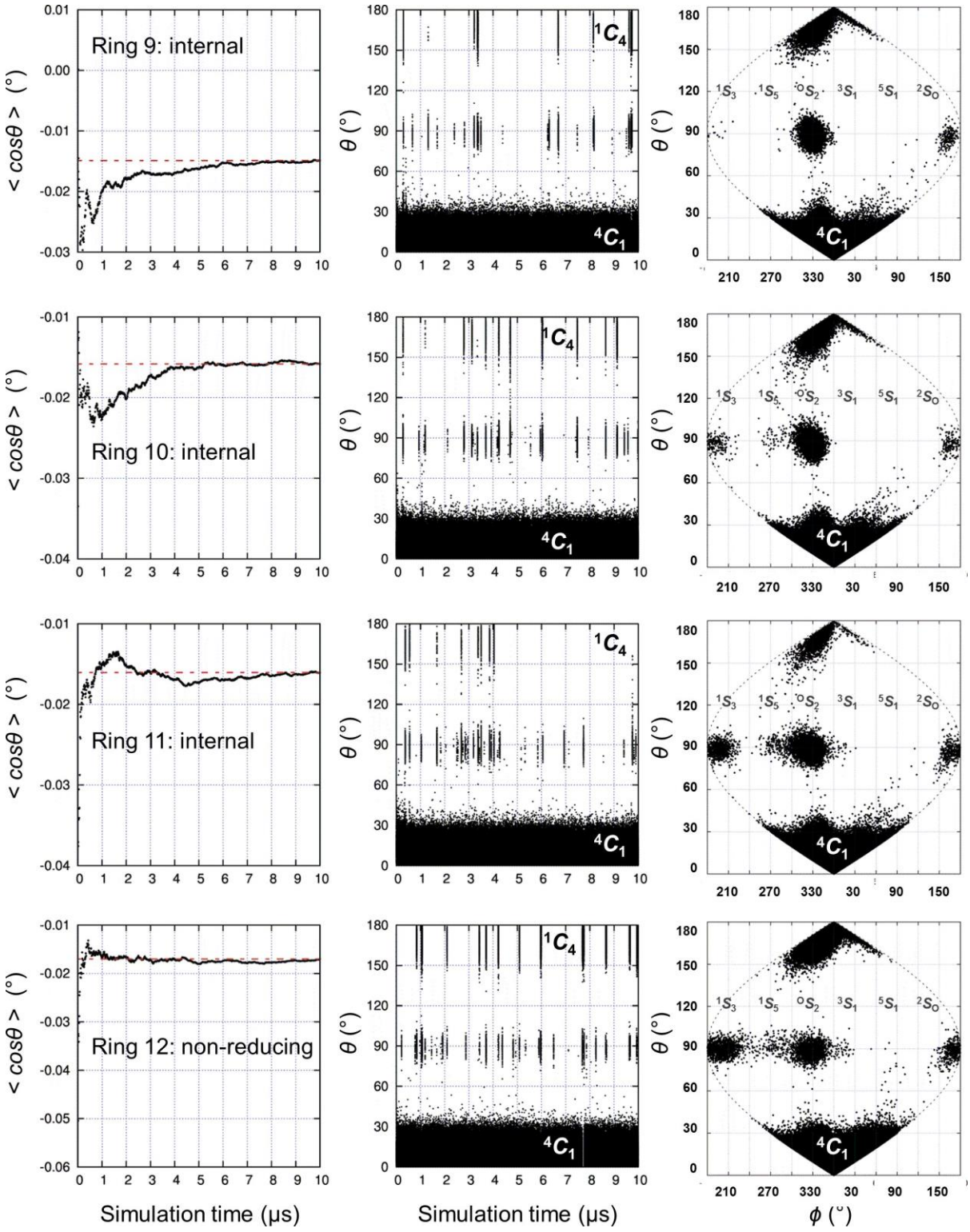
Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



S16 continued

Figure S16. Puckering convergence, time series and sinusoidal projections: **3** (strand A)

Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



S16 continued

Figure S16. Puckering convergence, time series and sinusoidal projections: **3** (strand B)

Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end

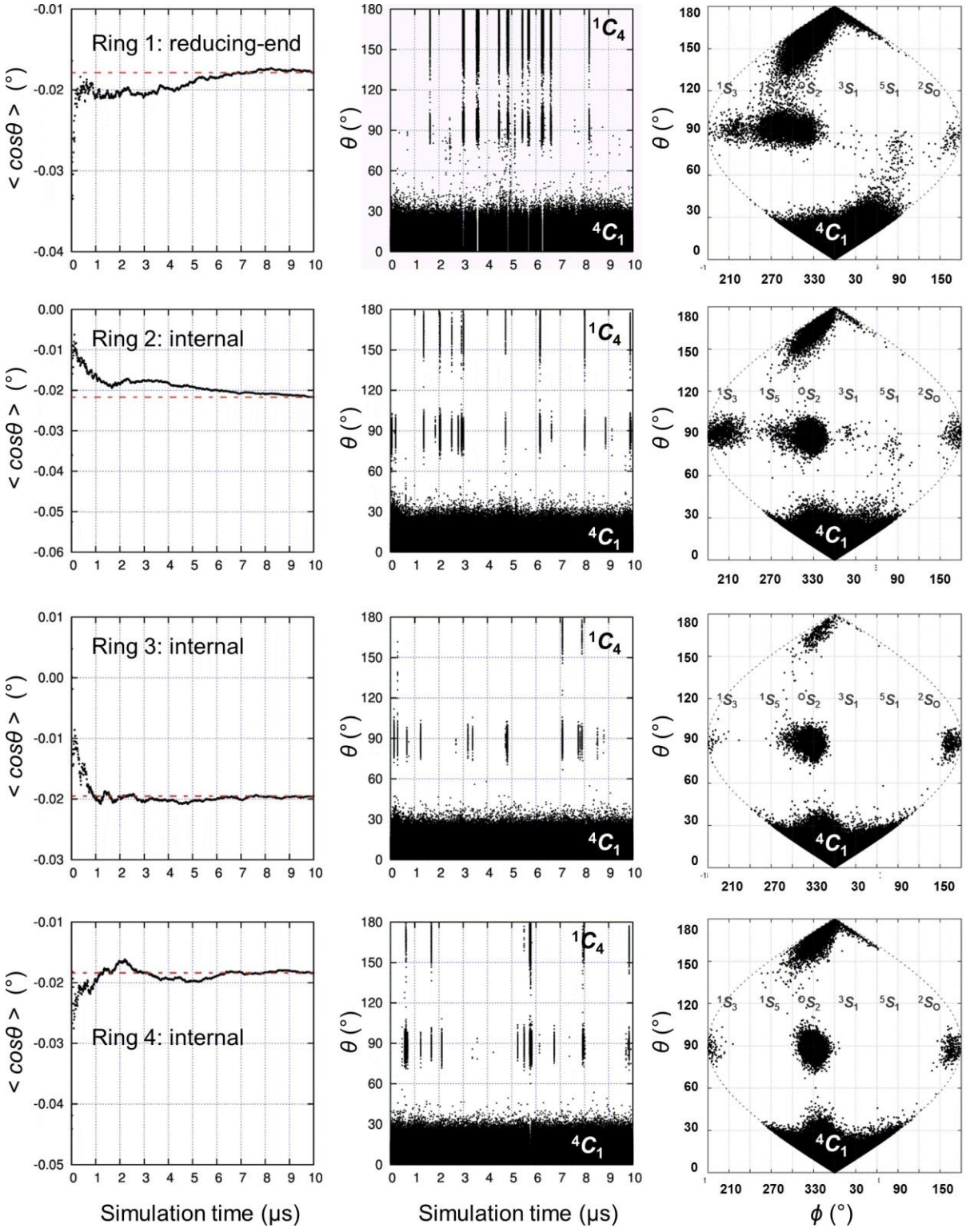
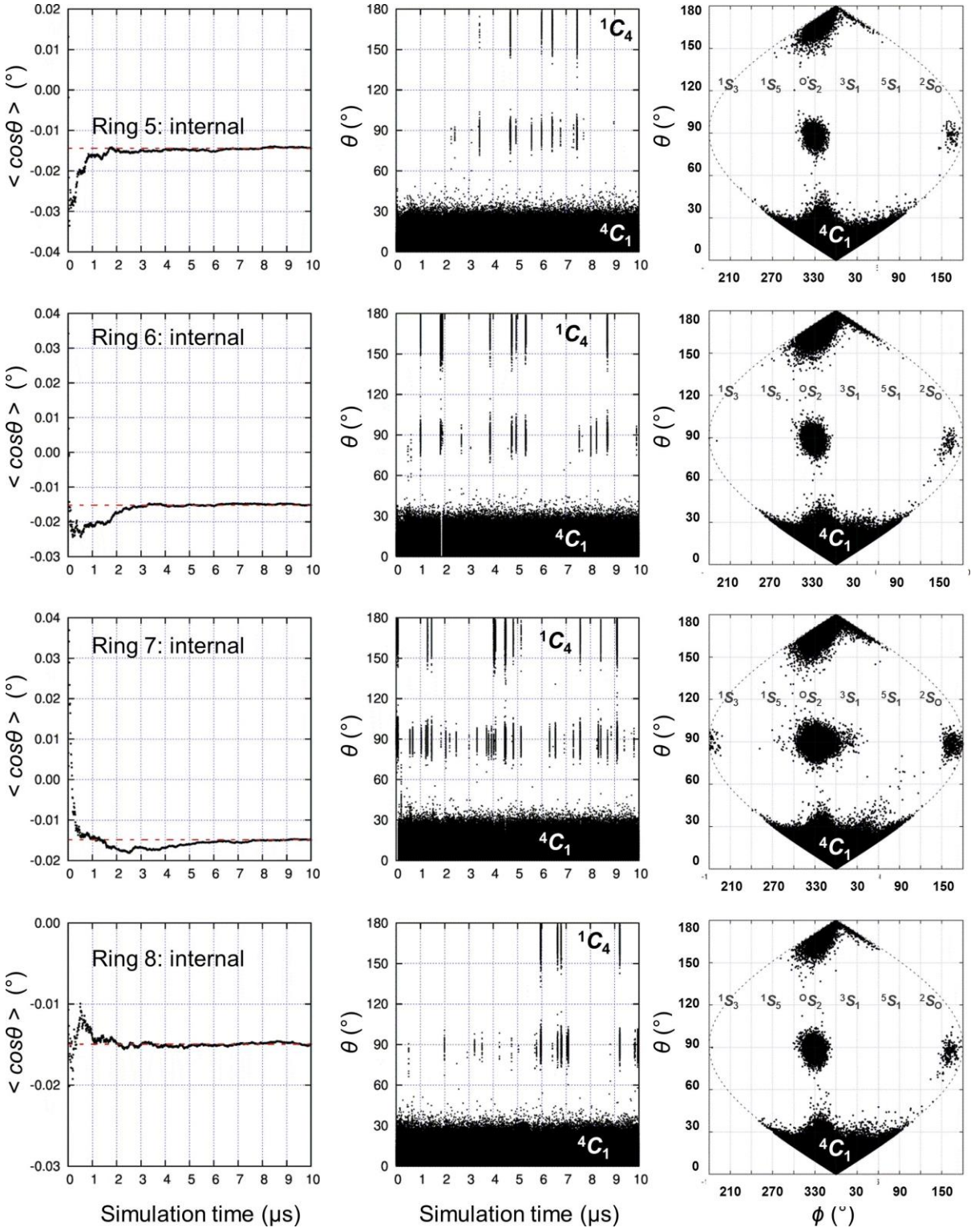


Figure S16. Puckering convergence, time series and sinusoidal projections: **3** (strand B)

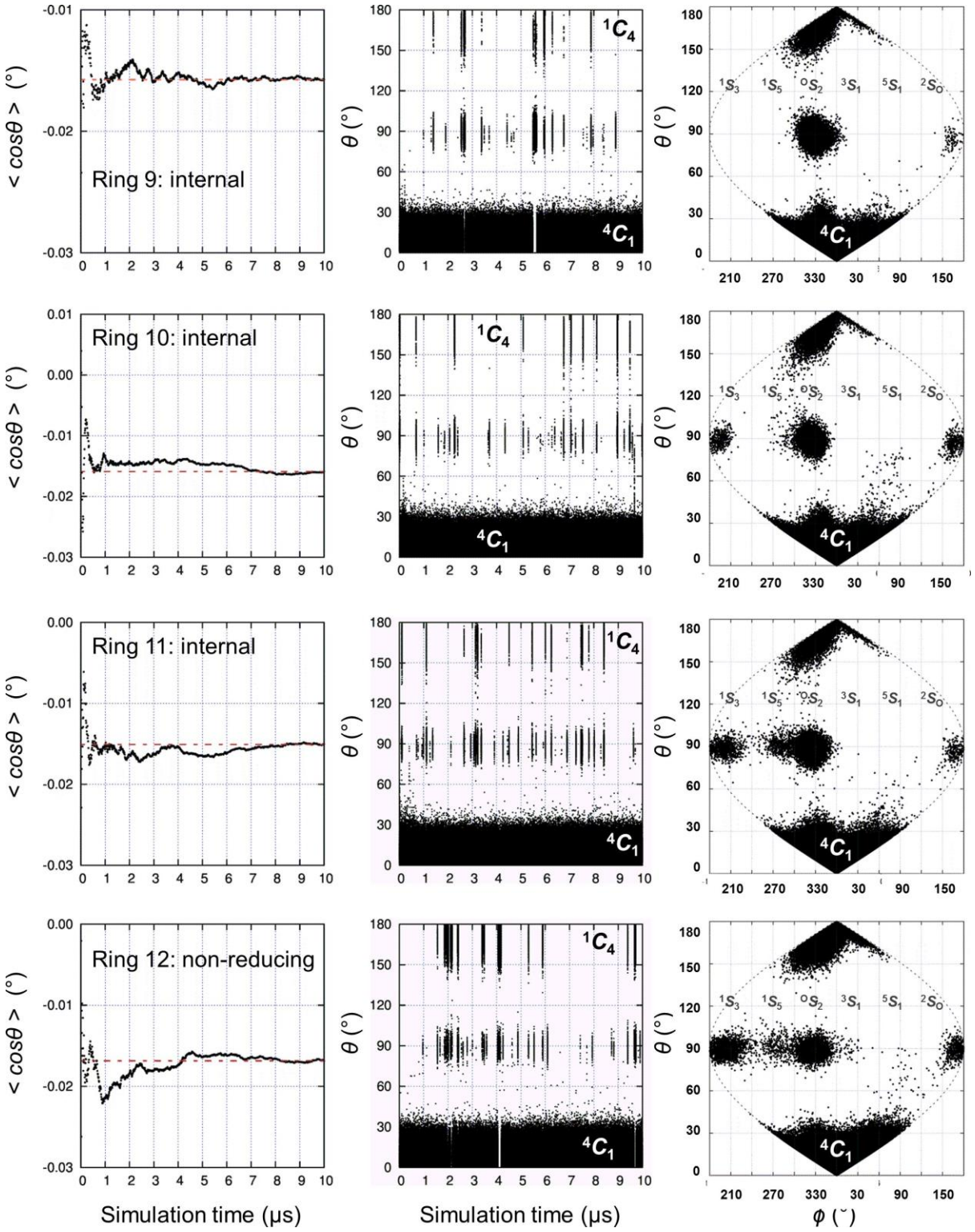
Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



S16 continued

Figure S16. Puckering convergence, time series and sinusoidal projections: **3** (strand B)

Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



S16 continued

Figure S17. Puckering convergence, time series and sinusoidal projections: **4** (hexasaccharide)

Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end

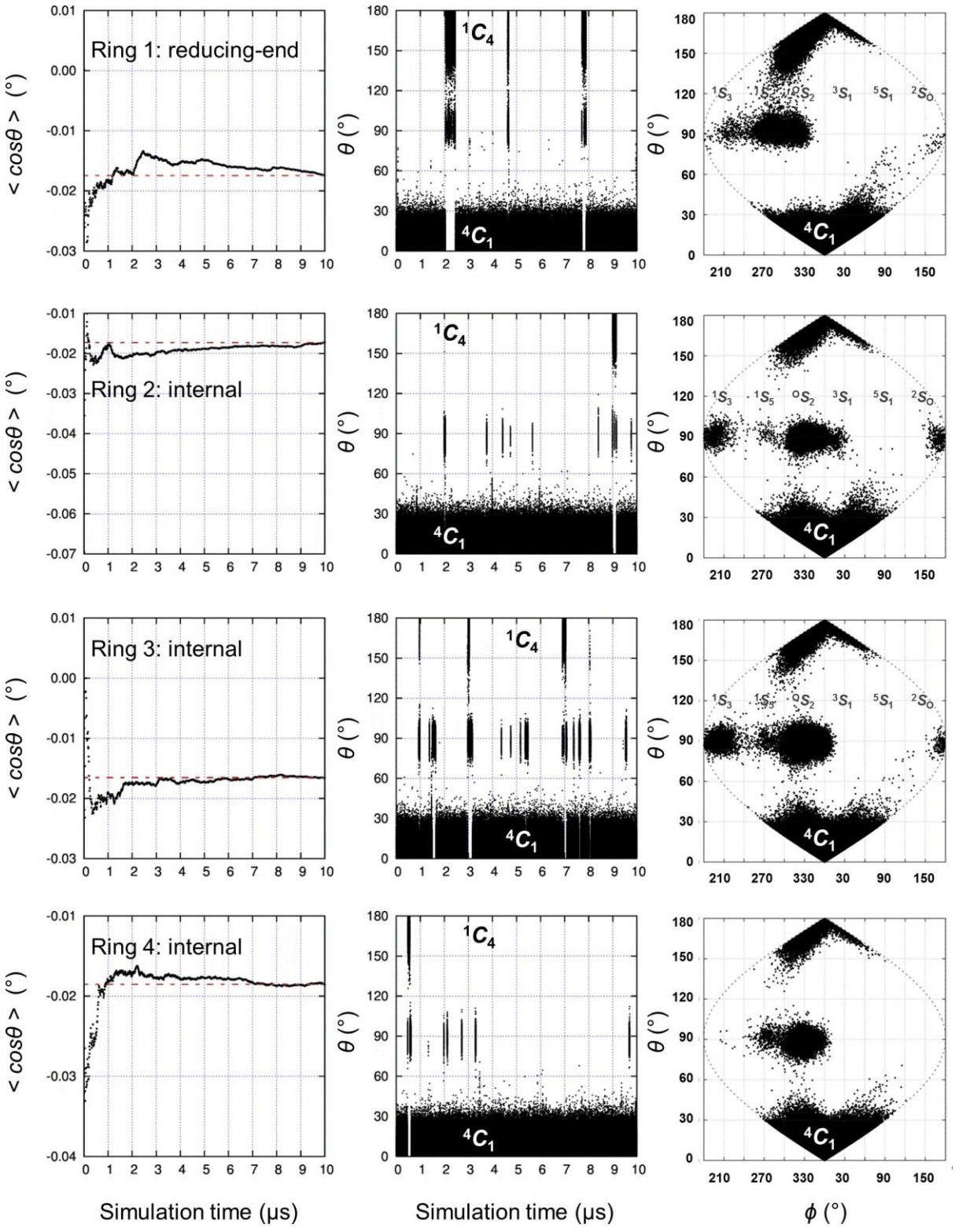
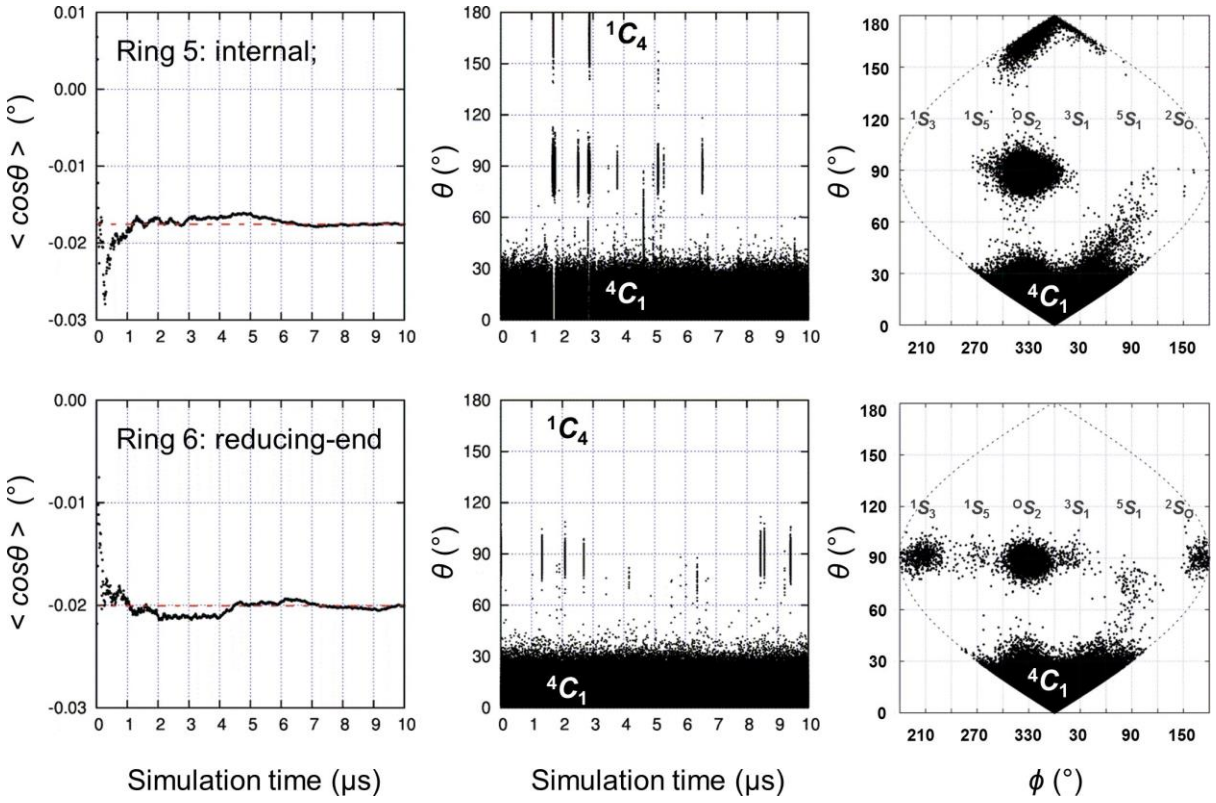


Figure S17. Puckering convergence, time series and sinusoidal projections: **4** (hexasaccharide)

Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end



S17 continued

Figure S18. Puckering convergence, time series and sinusoidal projections: **5** and **6**

Red line denotes simulation average; Glc pyranose rings are numbered from the reducing end

(**5**) - trisaccharide

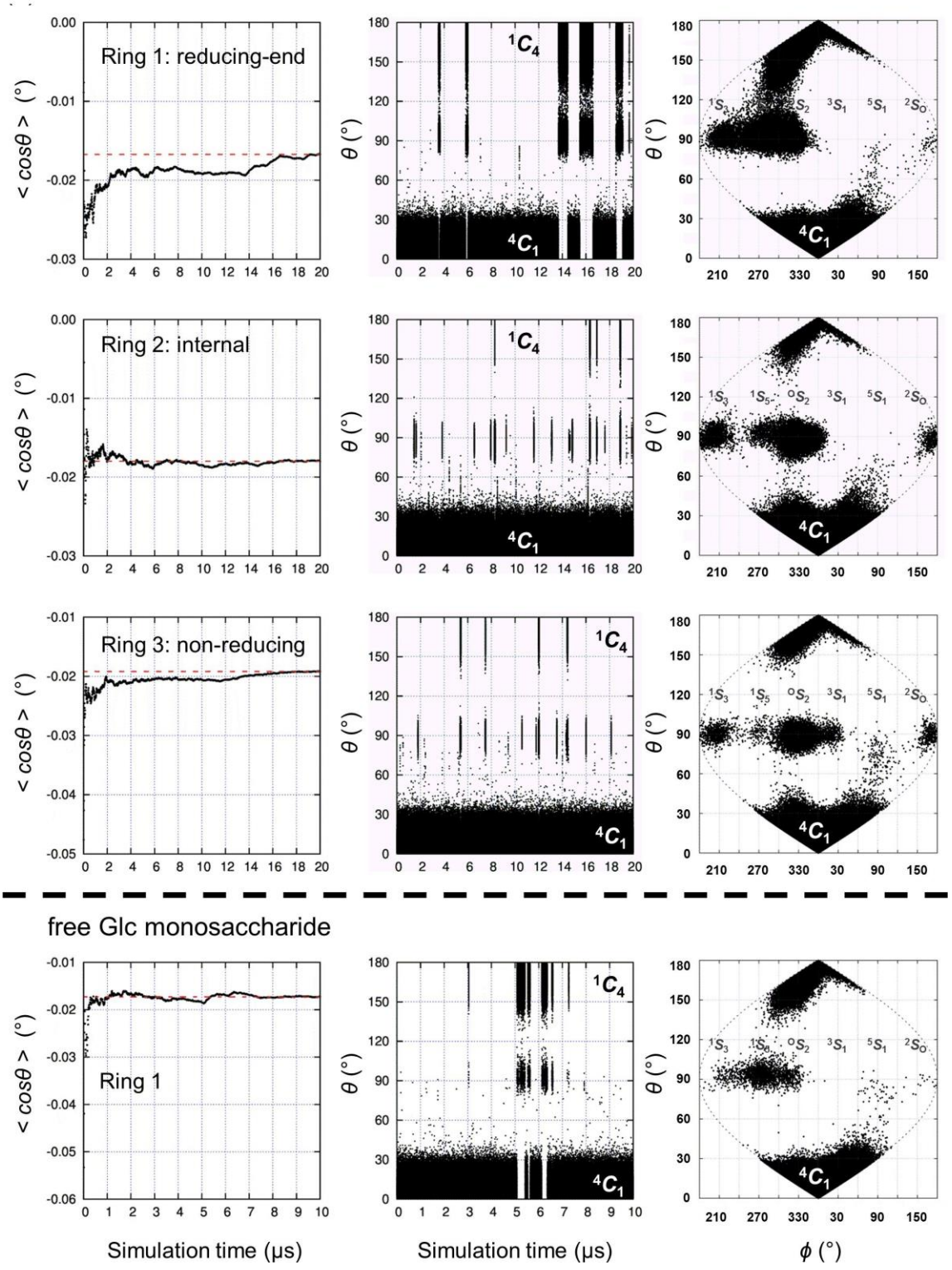


Table S19. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from a 10 μs simulation of **1** (numbered from reducing end)

	Glc:1			Glc:2			Glc:3			Glc:4			Glc:5			Glc:6	
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	92.03	0.05	**4C1**	95.09	0.03	**4C1**	93.24	0.04	**4C1**	88.64	0.07	**4C1**	86.04	0.09	**4C1**	90.88	0.06
1C4	5.47	1.72	**OS2**	2.39	2.21	**OS2**	3.22	2.04	**OS2**	5.46	1.72	**OS2**	5.08	1.77	**3OB**	2.89	2.10
1S5	0.99	2.74	**1C4**	1.20	2.62	**1C4**	1.45	2.51	**1C4**	2.47	2.20	**3OB**	4.30	1.87	**OS2**	2.74	2.13
B25	0.82	2.85	**B25**	0.60	3.04	**B25**	0.66	2.98	**3OB**	1.72	2.41	**1C4**	2.51	2.18	**1C4**	1.70	2.41
OS2	0.29	3.47	**3OB**	0.18	3.76	**3OB**	0.52	3.11	**B25**	0.71	2.93	**3S1**	0.58	3.05	**3S1**	0.51	3.13
5H4	0.12	4.01	**1S5**	0.11	4.03	**2H1**	0.18	3.76	**3S1**	0.18	3.75	**B25**	0.54	3.09	**2H1**	0.30	3.44
14B	0.07	4.33	**1S3**	0.09	4.14	**3S1**	0.16	3.83	**2H1**	0.16	3.80	**2H1**	0.26	3.52	**B25**	0.30	3.44
2H1	0.04	4.61	**2H1**	0.08	4.26	**1S5**	0.11	4.03	**1S5**	0.12	3.98	**E1**	0.20	3.70	**E1**	0.23	3.60
5E	0.04	4.68	**B3O**	0.05	4.55	**E1**	0.09	4.15	**1S3**	0.10	4.08	**1S3**	0.07	4.31	**2E**	0.10	4.11
E4	0.04	4.71	**3S1**	0.04	4.63	**1S3**	0.07	4.34	**E1**	0.10	4.11	**2E**	0.07	4.33	**5S1**	0.08	4.22
E1	0.03	4.77	**E1**	0.04	4.69	**5S1**	0.07	4.34	**B3O**	0.06	4.36	**1S5**	0.06	4.37	**OH1**	0.05	4.49
1S3	0.03	4.87	**2E**	0.02	4.96	**2E**	0.06	4.44	**5H4**	0.04	4.61	**OH1**	0.05	4.46	**1S5**	0.05	4.50
2E	0.01	5.32	**14B**	0.02	5.00	**B3O**	0.03	4.75	**2E**	0.04	4.61	**5H4**	0.05	4.54	**1S3**	0.04	4.68
OH1	0.01	5.82	**5S1**	0.02	5.18	**B14**	0.03	4.83	**5S1**	0.04	4.70	**5S1**	0.05	4.56	**B3O**	0.03	4.78
5S1	0.00	5.99	**E5**	0.01	5.33	**14B**	0.02	5.10	**E4**	0.02	4.99	**E4**	0.03	4.90	**B14**	0.02	4.95
B3O	0.00	5.99	**OH5**	0.01	5.42	**OH1**	0.02	5.12	**14B**	0.02	5.06	**B3O**	0.03	4.92	**25B**	0.01	5.39
2H3	0.00	6.31	**5H4**	0.01	5.53	**E5**	0.01	5.35	**OH1**	0.02	5.12	**B14**	0.01	5.25	**OE**	0.01	5.52
2SO	0.00	6.36	**2SO**	0.01	5.54	**5H4**	0.01	5.36	**B14**	0.02	5.20	**OE**	0.01	5.39	**E5**	0.01	5.57
5HO	0.00	6.51	**OH1**	0.01	5.77	**OH5**	0.01	5.39	**E5**	0.01	5.32	**14B**	0.01	5.44	**2SO**	0.01	5.62
3H4	0.00	6.55	**B14**	0.00	5.92	**2SO**	0.01	5.42	**5E**	0.01	5.32	**5E**	0.01	5.49	**OH5**	0.01	5.62
E5	0.00	6.59	**5E**	0.00	5.99	**25B**	0.01	5.58	**2SO**	0.01	5.39	**E5**	0.01	5.50	**14B**	0.01	5.63
3OB	0.00	6.63	**E4**	0.00	6.01	**OE**	0.01	5.78	**OH5**	0.01	5.52	**OH5**	0.01	5.54	**5H4**	0.01	5.65
OH5	0.00	6.77	**25B**	0.00	6.04	**5E**	0.01	5.78	**25B**	0.01	5.83	**25B**	0.01	5.61	**2H3**	0.01	5.74
B14	0.00	6.96	**2H3**	0.00	6.10	**E4**	0.01	5.80	**OE**	0.01	5.83	**2SO**	0.01	5.82	**5E**	0.00	6.07
25B	0.00	6.96	**4H5**	0.00	6.12	**2H3**	0.01	5.85	**2H3**	0.00	5.94	**2H3**	0.00	6.01	**4H5**	0.00	6.33
E3	0.00	7.04	**OE**	0.00	6.26	**4H5**	0.00	6.01	**5HO**	0.00	6.01	**4H5**	0.00	6.22	**E4**	0.00	6.33
OE	0.00	7.24	**E3**	0.00	6.55	**4E**	0.00	6.72	**4H5**	0.00	6.14	**3H4**	0.00	6.48	**4E**	0.00	6.83
4H3	0.00	7.54	**4E**	0.00	7.04	**5HO**	0.00	6.77	**3H4**	0.00	6.51	**5HO**	0.00	6.51	**5HO**	0.00	6.83
4H5	0.00	7.78	**3H4**	0.00	7.13	**3H4**	0.00	7.04	**4E**	0.00	6.77	**EO**	0.00	6.96	**3H4**	0.00	6.96
4E	0.00	7.78	**5HO**	0.00	7.37	**E3**	0.00	7.13	**EO**	0.00	7.13	**4E**	0.00	7.13	**E3**	0.00	7.13
			4H3	0.00	7.54	**4H3**	0.00	7.54	**4H3**	0.00	7.37	**4H3**	0.00	7.54	**EO**	0.00	7.54
3S1	-	-	**EO**	0.00	8.19				**E3**	0.00	7.37	**E3**	0.00	7.78	**4H3**	0.00	7.78
1H2	-	-	**3E**	0.00	8.19	**1H2**	-	-	**3H2**	0.00	7.78	**1HO**	0.00	7.78	**1H2**	0.00	8.19
1E	-	-				**1E**	-	-	**1E**	0.00	8.19	**1H2**	0.00	8.19	**3E**	0.00	8.19
EO	-	-	**1H2**	-	-	**EO**	-	-	**1HO**	0.00	8.19	**E2**	0.00	8.19	**1HO**	0.00	8.19
3E	-	-	**1E**	-	-	**3E**	-	-	**E2**	0.00	8.19				**E2**	0.00	8.19
1HO	-	-	**1HO**	-	-	**1HO**	-	-				**1E**	-	-			
3H2	-	-	**3H2**	-	-	**3H2**	-	-	**1H2**	-	-	**3E**	-	-	**1E**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**3E**	-	-	**3H2**	-	-	**3H2**	-	-

Table S19. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from a 10 μs simulation of **1** (numbered from reducing end)

	Glc:7			Glc:8			Glc:9			Glc:10			Glc:11			Glc:12	
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	92.34	0.05	**4C1**	91.41	0.05	**4C1**	94.31	0.03	**4C1**	95.61	0.03	**4C1**	95.43	0.03	**4C1**	97.36	0.02
OS2	3.62	1.97	**OS2**	3.94	1.92	**OS2**	2.57	2.17	**OS2**	1.85	2.37	**OS2**	2.48	2.19	**1C4**	2.13	2.28
1C4	1.95	2.33	**1C4**	2.02	2.32	**1C4**	0.97	2.75	**1C4**	1.00	2.73	**1C4**	0.89	2.80	**OS2**	0.26	3.54
3OB	0.91	2.79	**3OB**	1.36	2.55	**3OB**	0.60	3.04	**B25**	0.43	3.24	**B25**	0.59	3.05	**B25**	0.06	4.40
B25	0.51	3.13	**B25**	0.51	3.14	**B25**	0.42	3.25	**1S3**	0.26	3.53	**3OB**	0.11	4.03	**1S3**	0.05	4.49
2H1	0.16	3.83	**2H1**	0.19	3.73	**3S1**	0.32	3.41	**3OB**	0.21	3.65	**1S5**	0.11	4.05	**1S5**	0.03	4.87
3S1	0.10	4.09	**E1**	0.11	4.05	**2H1**	0.23	3.60	**3S1**	0.18	3.74	**2H1**	0.08	4.20	**B3O**	0.02	5.02
E1	0.08	4.24	**1S5**	0.09	4.17	**E1**	0.13	3.95	**2H1**	0.09	4.14	**1S3**	0.07	4.29	**3OB**	0.02	5.14
1S5	0.07	4.27	**3S1**	0.08	4.23	**5S1**	0.11	4.03	**B3O**	0.08	4.24	**E1**	0.04	4.68	**14B**	0.02	5.21
5S1	0.05	4.57	**1S3**	0.07	4.33	**1S5**	0.08	4.26	**1S5**	0.07	4.29	**B3O**	0.04	4.69	**2H1**	0.02	5.22
1S3	0.04	4.58	**2E**	0.05	4.50	**1S3**	0.06	4.45	**E1**	0.05	4.46	**5S1**	0.02	4.94	**2E**	0.01	5.46
2E	0.04	4.64	**5S1**	0.04	4.62	**B14**	0.05	4.46	**5S1**	0.04	4.64	**2E**	0.02	4.98	**2SO**	0.01	5.73
B3O	0.02	5.07	**B3O**	0.04	4.65	**B3O**	0.04	4.70	**2E**	0.02	4.96	**3S1**	0.02	5.06	**E1**	0.01	5.86
B14	0.01	5.26	**14B**	0.02	5.07	**2E**	0.03	4.76	**14B**	0.02	5.21	**14B**	0.02	5.20	**E5**	0.01	5.86
OH1	0.01	5.30	**OH1**	0.02	5.12	**OH1**	0.02	5.15	**B14**	0.02	5.22	**E5**	0.01	5.42	**OH5**	0.00	6.07
OH5	0.01	5.36	**OH5**	0.01	5.42	**OH5**	0.01	5.38	**OH5**	0.01	5.44	**OH5**	0.01	5.48	**2H3**	0.00	6.16
E5	0.01	5.40	**B14**	0.01	5.46	**14B**	0.01	5.40	**OH1**	0.01	5.45	**5H4**	0.01	5.52	**3S1**	0.00	6.33
5H4	0.01	5.43	**E5**	0.01	5.50	**E5**	0.01	5.40	**5H4**	0.01	5.47	**2SO**	0.01	5.67	**5H4**	0.00	6.33
14B	0.01	5.44	**5H4**	0.01	5.62	**2SO**	0.01	5.48	**E5**	0.01	5.50	**OH1**	0.01	5.83	**5S1**	0.00	6.36
5E	0.01	5.76	**2SO**	0.01	5.66	**25B**	0.01	5.55	**E4**	0.01	5.77	**25B**	0.00	5.88	**4H5**	0.00	6.42
25B	0.01	5.83	**25B**	0.01	5.67	**5H4**	0.01	5.64	**2SO**	0.01	5.81	**5E**	0.00	5.94	**OH1**	0.00	6.51
OE	0.01	5.84	**5E**	0.01	5.67	**OE**	0.00	5.90	**OE**	0.00	6.01	**B14**	0.00	5.96	**E4**	0.00	6.59
E4	0.00	5.95	**OE**	0.00	5.96	**4H5**	0.00	6.07	**5E**	0.00	6.16	**E4**	0.00	5.96	**OE**	0.00	6.77
2SO	0.00	5.98	**E4**	0.00	6.07	**2H3**	0.00	6.14	**25B**	0.00	6.18	**OE**	0.00	6.18	**5E**	0.00	6.83
4H5	0.00	6.20	**2H3**	0.00	6.10	**E4**	0.00	6.16	**4H5**	0.00	6.20	**4H5**	0.00	6.24	**B14**	0.00	6.89
2H3	0.00	6.31	**4H5**	0.00	6.36	**5E**	0.00	6.18	**2H3**	0.00	6.31	**2H3**	0.00	6.33	**25B**	0.00	7.04
5HO	0.00	6.45	**5HO**	0.00	6.36	**5HO**	0.00	6.72	**E3**	0.00	7.04	**4E**	0.00	6.96	**4E**	0.00	7.04
4E	0.00	6.89	**4E**	0.00	6.89	**4E**	0.00	7.13	**4E**	0.00	7.13	**5HO**	0.00	6.96	**E3**	0.00	7.04
4H3	0.00	6.96	**3H4**	0.00	7.24	**3H4**	0.00	7.13	**3H4**	0.00	7.24	**3H4**	0.00	6.96	**4H3**	0.00	7.54
E3	0.00	6.96	**E3**	0.00	7.37	**E3**	0.00	7.24	**5HO**	0.00	7.37	**E3**	0.00	7.24	**5HO**	0.00	7.54
3H4	0.00	7.13	**4H3**	0.00	7.54	**EO**	0.00	7.78	**4H3**	0.00	7.78	**4H3**	0.00	7.37	**3H4**	0.00	7.54
EO	0.00	7.78	**EO**	0.00	8.19	**4H3**	0.00	8.19	**EO**	0.00	8.19	**3E**	0.00	8.19	**3E**	0.00	8.19
1HO	0.00	8.19				**3E**	0.00	8.19	**3E**	0.00	8.19	**1HO**	0.00	8.19			
			1H2	-	-	**1HO**	0.00	8.19							**1H2**	-	-
1H2	-	-	**1E**	-	-				**1H2**	-	-	**1H2**	-	-	**1E**	-	-
1E	-	-	**3E**	-	-	**1H2**	-	-	**1E**	-	-	**1E**	-	-	**EO**	-	-
3E	-	-	**1HO**	-	-	**1E**	-	-	**1HO**	-	-	**EO**	-	-	**1HO**	-	-
3H2	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-

S19 continued

Table S20. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from a 10 μs simulation of **2** (strand A, numbered from reducing end)

	Glc:1			Glc:2			Glc:3			Glc:4			Glc:5			Glc:6	
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	93.65	0.04	**4C1**	97.04	0.02	**4C1**	97.13	0.02	**4C1**	99.67	0.00	**4C1**	99.96	0.00	**4C1**	99.26	0.00
1C4	4.88	1.79	**OS2**	1.59	2.46	**OS2**	1.43	2.52	**OS2**	0.13	3.94	**2SO**	0.01	5.42	**1C4**	0.51	3.13
1S5	0.46	3.19	**1C4**	0.74	2.91	**1C4**	0.97	2.75	**1C4**	0.12	3.98	**B3O**	0.01	5.61	**OS2**	0.17	3.77
B25	0.43	3.22	**B25**	0.27	3.50	**3OB**	0.22	3.63	**B3O**	0.02	5.02	**2H1**	0.01	5.86	**B3O**	0.01	5.39
OS2	0.21	3.66	**3OB**	0.11	4.02	**B25**	0.11	4.04	**3OB**	0.01	5.28	**2H3**	0.00	6.07	**2SO**	0.01	5.48
5H4	0.12	4.00	**1S5**	0.05	4.55	**2H1**	0.03	4.80	**2SO**	0.01	5.59	**E1**	0.00	6.31	**3OB**	0.01	5.59
5E	0.05	4.52	**2H1**	0.04	4.68	**B3O**	0.02	5.02	**2H1**	0.01	5.86	**2E**	0.00	6.33	**B25**	0.01	5.74
2H1	0.05	4.54	**B3O**	0.03	4.74	**2E**	0.02	5.16	**1S3**	0.00	5.91	**OH1**	0.00	6.63	**2H1**	0.00	6.02
14B	0.03	4.75	**1S3**	0.03	4.81	**1S5**	0.01	5.28	**E1**	0.00	5.92	**OH5**	0.00	6.89	**E1**	0.00	6.14
E1	0.03	4.78	**E1**	0.02	5.05	**1S3**	0.01	5.32	**2E**	0.00	6.07	**E5**	0.00	6.89	**2H3**	0.00	6.20
E4	0.03	4.84	**2E**	0.02	5.18	**E1**	0.01	5.32	**2H3**	0.00	6.28	**OE**	0.00	6.96	**2E**	0.00	6.36
2E	0.02	5.15	**2SO**	0.01	5.56	**2SO**	0.01	5.36	**OH5**	0.00	6.39	**E3**	0.00	6.96	**E3**	0.00	6.59
1S3	0.01	5.25	**OH5**	0.01	5.64	**OH5**	0.00	6.05	**OE**	0.00	6.45	**3OB**	0.00	7.78	**OH1**	0.00	6.83
5S1	0.01	5.66	**E5**	0.01	5.66	**OH1**	0.00	6.10	**E5**	0.00	6.48	**4H5**	0.00	7.78	**OH5**	0.00	6.89
OH1	0.01	5.87	**14B**	0.01	5.80	**5H4**	0.00	6.12	**OH1**	0.00	6.59	**4H3**	0.00	7.78	**5E**	0.00	6.89
B3O	0.00	5.92	**OH1**	0.01	5.87	**2H3**	0.00	6.14	**E3**	0.00	6.96	**4E**	0.00	8.19	**OE**	0.00	6.96
2SO	0.00	6.14	**5H4**	0.00	5.88	**3S1**	0.00	6.24	**B25**	0.00	7.13				**4H5**	0.00	7.13
2H3	0.00	6.22	**OE**	0.00	6.10	**E5**	0.00	6.33	**3S1**	0.00	7.78	**5S1**	-	-	**E5**	0.00	7.37
5HO	0.00	6.39	**E4**	0.00	6.10	**OE**	0.00	6.42	**4H5**	0.00	7.78	**B14**	-	-	**5HO**	0.00	7.54
3OB	0.00	6.42	**3S1**	0.00	6.26	**5E**	0.00	6.45	**4E**	0.00	7.78	**OS2**	-	-	**5H4**	0.00	7.54
25B	0.00	6.59	**4H5**	0.00	6.26	**14B**	0.00	6.48	**5S1**	0.00	8.19	**B25**	-	-	**4H3**	0.00	7.78
OH5	0.00	6.63	**5E**	0.00	6.26	**25B**	0.00	6.51	**B14**	0.00	8.19	**1S5**	-	-	**3S1**	0.00	8.19
E5	0.00	6.72	**25B**	0.00	6.51	**E4**	0.00	6.63	**1S5**	0.00	8.19	**14B**	-	-			
3H4	0.00	6.72	**5S1**	0.00	6.67	**4H5**	0.00	6.89	**14B**	0.00	8.19	**1S3**	-	-	**5S1**	-	-
B14	0.00	6.77	**2H3**	0.00	6.67	**5HO**	0.00	7.04	**25B**	0.00	8.19	**3S1**	-	-	**B14**	-	-
OE	0.00	6.77	**4E**	0.00	7.04	**E3**	0.00	7.37	**4H3**	0.00	8.19	**25B**	-	-	**1S5**	-	-
4H5	0.00	7.24	**3H4**	0.00	7.04	**4H3**	0.00	7.54	**5HO**	0.00	8.19	**1C4**	-	-	**14B**	-	-
3S1	0.00	7.78	**E3**	0.00	7.24	**3H4**	0.00	7.54	**5E**	0.00	8.19	**1H2**	-	-	**1S3**	-	-
E3	0.00	7.78	**5HO**	0.00	7.37	**5S1**	0.00	7.78	**E4**	0.00	8.19	**1E**	-	-	**25B**	-	-
			B14	0.00	7.54	**4E**	0.00	7.78	**3H4**	0.00	8.19	**5HO**	-	-	**4E**	-	-
4E	-	-	**4H3**	0.00	7.54							**5E**	-	-	**1H2**	-	-
4H3	-	-				**B14**	-	-	**1H2**	-	-	**5H4**	-	-	**1E**	-	-
1H2	-	-	**1H2**	-	-	**1H2**	-	-	**1E**	-	-	**E4**	-	-	**E4**	-	-
1E	-	-	**1E**	-	-	**1E**	-	-	**5H4**	-	-	**3H4**	-	-	**3H4**	-	-
EO	-	-	**EO**	-	-	**EO**	-	-	**EO**	-	-	**EO**	-	-	**EO**	-	-
3E	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-
1HO	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-
3H2	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-

Table S20. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from a 10 μs simulation of **2** (strand A, numbered from reducing end)

Glc:7			Glc:8			Glc:9			Glc:10			Glc:11			Glc:12		
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	99.97	0.00	**4C1**	99.54	0.00	**4C1**	98.27	0.01	**4C1**	98.15	0.01	**4C1**	97.14	0.02	**4C1**	96.90	0.02
B3O	0.01	5.80	**OS2**	0.28	3.48	**OS2**	1.07	2.69	**OS2**	1.11	2.67	**OS2**	1.57	2.46	**1C4**	2.34	2.23
2SO	0.01	5.81	**B25**	0.07	4.28	**3OB**	0.56	3.07	**3OB**	0.37	3.32	**1C4**	0.71	2.94	**OS2**	0.49	3.16
OS2	0.00	6.02	**1C4**	0.03	4.85	**1C4**	0.03	4.92	**1C4**	0.21	3.66	**3OB**	0.21	3.65	**B25**	0.08	4.21
2H3	0.00	6.14	**B3O**	0.02	5.12	**B3O**	0.02	5.12	**B25**	0.06	4.45	**B25**	0.20	3.67	**3OB**	0.04	4.63
E5	0.00	6.22	**1S5**	0.01	5.29	**2SO**	0.01	5.45	**B3O**	0.02	5.01	**B3O**	0.03	4.72	**1S3**	0.03	4.78
2H1	0.00	6.26	**2SO**	0.01	5.29	**B25**	0.01	5.49	**1S3**	0.01	5.24	**1S3**	0.03	4.87	**1S5**	0.02	5.00
E1	0.00	6.42	**3OB**	0.01	5.31	**2H1**	0.01	5.49	**E5**	0.01	5.28	**1S5**	0.02	4.96	**B3O**	0.02	5.16
E3	0.00	6.42	**E5**	0.00	5.95	**E5**	0.01	5.63	**OH5**	0.01	5.30	**2H1**	0.01	5.33	**2E**	0.01	5.28
OH5	0.00	6.48	**OH5**	0.00	6.02	**OH5**	0.01	5.80	**2H1**	0.01	5.67	**OH5**	0.01	5.37	**2H1**	0.01	5.39
2E	0.00	6.83	**2H1**	0.00	6.20	**E1**	0.00	5.88	**2SO**	0.01	5.81	**5H4**	0.01	5.39	**E5**	0.01	5.40
4H5	0.00	7.04	**E3**	0.00	6.20	**E3**	0.00	6.24	**E1**	0.00	5.88	**E5**	0.01	5.41	**14B**	0.01	5.41
OE	0.00	7.04	**2H3**	0.00	6.59	**2E**	0.00	6.24	**1S5**	0.00	6.02	**E1**	0.01	5.72	**OH5**	0.01	5.68
OH1	0.00	7.24	**E1**	0.00	6.67	**2H3**	0.00	6.42	**E3**	0.00	6.20	**2E**	0.01	5.85	**2SO**	0.01	5.73
B25	0.00	7.37	**4H5**	0.00	6.89	**OE**	0.00	6.48	**2E**	0.00	6.31	**2SO**	0.01	5.87	**2H3**	0.00	5.88
1S3	0.00	7.78	**OH1**	0.00	7.04	**4H5**	0.00	6.77	**4H5**	0.00	6.48	**E4**	0.00	5.95	**4H5**	0.00	6.10
4H3	0.00	8.19	**OE**	0.00	7.24	**OH1**	0.00	6.83	**OE**	0.00	6.59	**4H5**	0.00	6.07	**E1**	0.00	6.12
			2E	0.00	7.24	**25B**	0.00	7.04	**OH1**	0.00	6.59	**14B**	0.00	6.24	**3S1**	0.00	6.20
5S1	-	-	**4H3**	0.00	7.37	**5HO**	0.00	7.24	**2H3**	0.00	6.83	**5E**	0.00	6.28	**OE**	0.00	6.45
B14	-	-	**5E**	0.00	7.54	**4H3**	0.00	7.37	**14B**	0.00	6.89	**OE**	0.00	6.39	**5H4**	0.00	6.67
1S5	-	-	**14B**	0.00	7.78	**5S1**	0.00	7.54	**4H3**	0.00	6.89	**E3**	0.00	6.42	**5E**	0.00	6.83
14B	-	-	**E4**	0.00	8.19	**5E**	0.00	7.78	**E4**	0.00	7.13	**2H3**	0.00	6.55	**4E**	0.00	6.89
3OB	-	-				**1S5**	0.00	8.19	**5HO**	0.00	7.24	**OH1**	0.00	6.63	**E3**	0.00	6.89
3S1	-	-	**5S1**	-	-	**1S3**	0.00	8.19	**4E**	0.00	7.37	**3S1**	0.00	6.67	**OH1**	0.00	6.96
25B	-	-	**B14**	-	-	**3S1**	0.00	8.19	**5E**	0.00	7.54	**4H3**	0.00	6.83	**E4**	0.00	6.96
4E	-	-	**1S3**	-	-	**4E**	0.00	8.19	**5H4**	0.00	7.54	**5S1**	0.00	6.96	**5HO**	0.00	7.04
1C4	-	-	**3S1**	-	-				**3S1**	0.00	8.19	**B14**	0.00	7.24	**4H3**	0.00	7.13
1H2	-	-	**25B**	-	-	**B14**	-	-	**EO**	0.00	8.19	**4E**	0.00	7.24	**5S1**	0.00	7.37
1E	-	-	**4E**	-	-	**14B**	-	-				**5HO**	0.00	7.37	**25B**	0.00	7.37
5HO	-	-	**1H2**	-	-	**1H2**	-	-	**5S1**	-	-	**3H4**	0.00	7.54	**B14**	0.00	7.54
5E	-	-	**1E**	-	-	**1E**	-	-	**B14**	-	-	**25B**	0.00	7.78	**3H4**	0.00	8.19
5H4	-	-	**5HO**	-	-	**5H4**	-	-	**25B**	-	-				**EO**	0.00	8.19
E4	-	-	**5H4**	-	-	**E4**	-	-	**1H2**	-	-	**1H2**	-	-			
3H4	-	-	**3H4**	-	-	**3H4**	-	-	**1E**	-	-	**1E**	-	-	**1H2**	-	-
EO	-	-	**EO**	-	-	**EO**	-	-	**3H4**	-	-	**EO**	-	-	**1E**	-	-
3E	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-
1HO	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-
3H2	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-

S20 continued

Table S20. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from a 10 μs simulation of **2** (strand B, numbered from reducing end)

	Glc:1			Glc:2			Glc:3			Glc:4			Glc:5			Glc:6	
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	91.46	0.05	**4C1**	96.81	0.02	**4C1**	99.22	0.00	**4C1**	99.23	0.00	**4C1**	99.95	0.00	**4C1**	99.96	0.00
1C4	6.44	1.63	**OS2**	1.64	2.44	**OS2**	0.40	3.28	**1C4**	0.31	3.42	**OS2**	0.02	4.99	**OS2**	0.01	5.37
1S5	0.74	2.91	**1C4**	0.91	2.79	**2H1**	0.07	4.30	**OS2**	0.27	3.51	**B25**	0.01	5.63	**2SO**	0.01	5.75
B25	0.64	3.00	**B25**	0.21	3.66	**1C4**	0.07	4.31	**B3O**	0.04	4.69	**B3O**	0.00	6.01	**B3O**	0.00	5.99
OS2	0.29	3.47	**3OB**	0.14	3.92	**B25**	0.05	4.49	**1S3**	0.03	4.77	**2SO**	0.00	6.31	**B25**	0.00	6.08
5H4	0.13	3.93	**2H1**	0.05	4.49	**3OB**	0.03	4.78	**B25**	0.03	4.80	**2H3**	0.00	6.39	**2H3**	0.00	6.08
14B	0.05	4.47	**B3O**	0.05	4.54	**2E**	0.03	4.80	**5S1**	0.01	5.25	**2H1**	0.00	6.42	**OH5**	0.00	6.48
5E	0.05	4.50	**1S3**	0.04	4.58	**B3O**	0.03	4.84	**2H1**	0.01	5.42	**E1**	0.00	6.67	**2H1**	0.00	6.59
2H1	0.05	4.51	**1S5**	0.04	4.58	**E1**	0.03	4.92	**3OB**	0.01	5.47	**E3**	0.00	6.83	**E5**	0.00	6.63
E4	0.04	4.66	**E1**	0.02	4.93	**1S3**	0.02	5.03	**3S1**	0.01	5.54	**OH5**	0.00	6.96	**E1**	0.00	6.77
E1	0.03	4.82	**2E**	0.02	5.12	**1S5**	0.01	5.34	**B14**	0.01	5.73	**2E**	0.00	6.96	**E3**	0.00	6.77
1S3	0.02	4.97	**2SO**	0.01	5.42	**2SO**	0.01	5.54	**E1**	0.01	5.75	**E5**	0.00	7.13	**OH1**	0.00	6.89
2E	0.02	5.20	**14B**	0.01	5.64	**OH1**	0.00	5.98	**2SO**	0.00	5.88	**OH1**	0.00	7.13	**2E**	0.00	6.96
5S1	0.01	5.80	**5H4**	0.01	5.66	**OH5**	0.00	6.04	**1S5**	0.00	5.98	**4H3**	0.00	7.37	**4H5**	0.00	7.54
OH1	0.01	5.86	**E5**	0.01	5.67	**E5**	0.00	6.04	**2E**	0.00	6.01	**OE**	0.00	7.54	**OE**	0.00	7.54
B3O	0.00	5.94	**OH1**	0.01	5.81	**14B**	0.00	6.05	**OH1**	0.00	6.33	**1S5**	0.00	7.78	**4E**	0.00	7.78
2SO	0.00	6.14	**OH5**	0.01	5.84	**25B**	0.00	6.10	**OE**	0.00	6.42	**5E**	0.00	8.19	**4H3**	0.00	7.78
2H3	0.00	6.31	**5E**	0.00	6.04	**5S1**	0.00	6.22	**2H3**	0.00	6.45				**1S5**	0.00	8.19
3OB	0.00	6.33	**3S1**	0.00	6.14	**2H3**	0.00	6.26	**E5**	0.00	6.51	**5S1**	-	-	**25B**	0.00	8.19
5HO	0.00	6.55	**2H3**	0.00	6.14	**OE**	0.00	6.31	**14B**	0.00	6.55	**B14**	-	-			
B14	0.00	6.83	**OE**	0.00	6.16	**3S1**	0.00	6.45	**OH5**	0.00	6.55	**14B**	-	-	**5S1**	-	-
E5	0.00	6.83	**E4**	0.00	6.16	**5H4**	0.00	6.89	**5H4**	0.00	6.59	**1S3**	-	-	**B14**	-	-
OE	0.00	6.83	**5S1**	0.00	6.31	**E4**	0.00	6.89	**E4**	0.00	6.83	**3OB**	-	-	**14B**	-	-
OH5	0.00	6.96	**4H5**	0.00	6.42	**B14**	0.00	6.96	**5E**	0.00	7.04	**3S1**	-	-	**1S3**	-	-
3S1	0.00	7.13	**25B**	0.00	7.04	**E3**	0.00	7.13	**E3**	0.00	7.13	**25B**	-	-	**3OB**	-	-
25B	0.00	7.13	**3H4**	0.00	7.13	**4H5**	0.00	7.24	**25B**	0.00	7.24	**4H5**	-	-	**3S1**	-	-
3H4	0.00	7.13	**5HO**	0.00	7.24	**5E**	0.00	7.54	**3H4**	0.00	7.54	**4E**	-	-	**1C4**	-	-
E3	0.00	7.24	**E3**	0.00	7.37	**5HO**	0.00	7.78	**4H5**	0.00	7.78	**1C4**	-	-	**1H2**	-	-
4H5	0.00	7.37	**B14**	0.00	7.54	**4H3**	0.00	8.19	**5HO**	0.00	7.78	**1H2**	-	-	**1E**	-	-
4E	0.00	8.19	**4E**	0.00	7.54				**3E**	0.00	7.78	**1E**	-	-	**5HO**	-	-
4H3	0.00	8.19	**EO**	0.00	8.19	**4E**	-	-	**4H3**	0.00	8.19	**5HO**	-	-	**5E**	-	-
			3E	0.00	8.19	**1H2**	-	-	**EO**	0.00	8.19	**5H4**	-	-	**5H4**	-	-
1H2	-	-				**1E**	-	-				**E4**	-	-	**E4**	-	-
1E	-	-	**4H3**	-	-	**3H4**	-	-	**4E**	-	-	**3H4**	-	-	**3H4**	-	-
EO	-	-	**1H2**	-	-	**EO**	-	-	**1H2**	-	-	**EO**	-	-	**EO**	-	-
3E	-	-	**1E**	-	-	**3E**	-	-	**1E**	-	-	**3E**	-	-	**3E**	-	-
1HO	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-
3H2	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-

S20 continued

Table S20. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from a 10 μs simulation of **2** (strand B, numbered from reducing end)

	Glc:7			Glc:8			Glc:9			Glc:10			Glc:11			Glc:12	
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	99.97	0.00	**4C1**	99.86	0.00	**4C1**	97.88	0.01	**4C1**	98.08	0.01	**4C1**	99.11	0.01	**4C1**	93.96	0.04
B3O	0.01	5.50	**OS2**	0.10	4.09	**OS2**	1.22	2.61	**OS2**	1.08	2.69	**OS2**	0.50	3.14	**1C4**	5.22	1.75
2SO	0.01	5.73	**B3O**	0.01	5.72	**3OB**	0.45	3.21	**1C4**	0.31	3.42	**1C4**	0.13	3.96	**OS2**	0.51	3.13
2H3	0.00	6.20	**3OB**	0.01	5.75	**1C4**	0.30	3.45	**3OB**	0.23	3.60	**3OB**	0.07	4.32	**B25**	0.10	4.12
2H1	0.00	6.26	**2SO**	0.00	5.90	**B25**	0.11	4.04	**B25**	0.15	3.87	**B25**	0.05	4.49	**3OB**	0.05	4.52
OH5	0.00	6.39	**E5**	0.00	5.98	**B3O**	0.01	5.34	**B3O**	0.04	4.63	**B3O**	0.05	4.50	**1S3**	0.04	4.63
E5	0.00	6.48	**OH5**	0.00	6.05	**E5**	0.01	5.53	**1S3**	0.03	4.88	**E5**	0.01	5.28	**1S5**	0.03	4.90
E1	0.00	6.55	**B25**	0.00	6.14	**2SO**	0.01	5.75	**2H1**	0.01	5.31	**OH5**	0.01	5.35	**B3O**	0.02	5.15
E3	0.00	6.59	**E1**	0.00	6.20	**OH5**	0.01	5.87	**E5**	0.01	5.32	**2SO**	0.01	5.40	**14B**	0.01	5.28
3OB	0.00	6.67	**2H1**	0.00	6.31	**E3**	0.00	6.16	**2SO**	0.01	5.49	**2H1**	0.01	5.48	**2E**	0.01	5.38
OH1	0.00	6.83	**2H3**	0.00	6.39	**2H1**	0.00	6.26	**1S5**	0.01	5.50	**1S3**	0.01	5.59	**2H1**	0.01	5.46
2E	0.00	6.96	**E3**	0.00	6.45	**1S5**	0.00	6.36	**OH5**	0.01	5.51	**E1**	0.01	5.63	**E5**	0.01	5.50
OE	0.00	7.37	**2E**	0.00	6.72	**E1**	0.00	6.36	**E1**	0.01	5.57	**1S5**	0.00	5.88	**2SO**	0.01	5.72
4H5	0.00	7.54	**OE**	0.00	6.96	**OE**	0.00	6.39	**3S1**	0.01	5.59	**4H5**	0.00	5.98	**OH5**	0.01	5.84
OS2	0.00	7.78	**4H5**	0.00	7.04	**2H3**	0.00	6.39	**2E**	0.00	5.88	**2E**	0.00	6.02	**4H5**	0.00	5.96
4E	0.00	7.78	**4H3**	0.00	7.04	**4H5**	0.00	6.51	**4H5**	0.00	6.24	**E3**	0.00	6.31	**2H3**	0.00	5.96
4H3	0.00	8.19	**OH1**	0.00	7.13	**OH1**	0.00	7.04	**E3**	0.00	6.24	**3S1**	0.00	6.33	**E1**	0.00	6.10
			4E	0.00	7.78	**5E**	0.00	7.04	**OH1**	0.00	6.26	**OE**	0.00	6.45	**5H4**	0.00	6.10
5S1	-	-				**4H3**	0.00	7.24	**14B**	0.00	6.39	**2H3**	0.00	6.45	**5E**	0.00	6.36
B14	-	-	**5S1**	-	-	**2E**	0.00	7.37	**OE**	0.00	6.67	**OH1**	0.00	6.59	**OE**	0.00	6.48
B25	-	-	**B14**	-	-	**5HO**	0.00	7.37	**2H3**	0.00	6.83	**4H3**	0.00	6.67	**3S1**	0.00	6.72
1S5	-	-	**1S5**	-	-	**5H4**	0.00	7.37	**5H4**	0.00	6.83	**5S1**	0.00	6.89	**E4**	0.00	6.77
14B	-	-	**14B**	-	-	**4E**	0.00	7.78	**4H3**	0.00	7.04	**5H4**	0.00	7.04	**5S1**	0.00	6.89
1S3	-	-	**1S3**	-	-	**3S1**	0.00	8.19	**5E**	0.00	7.13	**5E**	0.00	7.13	**4E**	0.00	7.04
3S1	-	-	**3S1**	-	-				**E4**	0.00	7.24	**14B**	0.00	7.24	**OH1**	0.00	7.04
25B	-	-	**25B**	-	-	**5S1**	-	-	**25B**	0.00	7.37	**4E**	0.00	7.37	**E3**	0.00	7.13
1C4	-	-	**1C4**	-	-	**B14**	-	-	**3H4**	0.00	7.37	**B14**	0.00	7.78	**4H3**	0.00	7.24
1H2	-	-	**1H2**	-	-	**14B**	-	-	**5S1**	0.00	8.19	**25B**	0.00	7.78	**5HO**	0.00	7.24
1E	-	-	**1E**	-	-	**1S3**	-	-	**4E**	0.00	8.19	**5HO**	0.00	7.78	**25B**	0.00	7.37
5HO	-	-	**5HO**	-	-	**25B**	-	-	**5HO**	0.00	8.19				**3H4**	0.00	7.37
5E	-	-	**5E**	-	-	**1H2**	-	-				**1H2**	-	-	**B14**	0.00	7.54
5H4	-	-	**5H4**	-	-	**1E**	-	-	**B14**	-	-	**1E**	-	-	**EO**	0.00	8.19
E4	-	-	**E4**	-	-	**E4**	-	-	**1H2**	-	-	**E4**	-	-	**3H2**	0.00	8.19
3H4	-	-	**3H4**	-	-	**3H4**	-	-	**1E**	-	-	**3H4**	-	-			
EO	-	-	**EO**	-	-	**EO**	-	-	**EO**	-	-	**EO**	-	-	**1H2**	-	-
3E	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-	**1E**	-	-
1HO	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**3E**	-	-
3H2	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**1HO**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-

S20 continued

Table S21. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from a 10 μs simulation of **3** (strand A, numbered from reducing end)

	Glc:1			Glc:2			Glc:3			Glc:4			Glc:5			Glc:6	
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	90.04	0.06	**4C1**	98.15	0.01	**4C1**	96.44	0.02	**4C1**	98.20	0.01	**4C1**	97.97	0.01	**4C1**	97.97	0.01
1C4	8.72	1.45	**OS2**	1.00	2.73	**OS2**	3.10	2.06	**OS2**	1.27	2.59	**OS2**	1.26	2.59	**OS2**	1.55	2.47
B25	0.34	3.36	**1C4**	0.53	3.10	**1C4**	0.23	3.60	**1C4**	0.43	3.23	**1C4**	0.66	2.98	**1C4**	0.28	3.50
1S5	0.34	3.37	**B25**	0.11	4.04	**B25**	0.14	3.89	**B25**	0.05	4.49	**B25**	0.03	4.89	**B3O**	0.08	4.22
OS2	0.17	3.80	**B3O**	0.06	4.45	**3OB**	0.02	5.09	**3OB**	0.01	5.28	**2SO**	0.03	4.91	**2SO**	0.04	4.68
5H4	0.13	3.95	**1S3**	0.05	4.48	**B3O**	0.02	5.15	**OH5**	0.01	5.43	**3OB**	0.02	5.06	**3OB**	0.03	4.73
2H1	0.05	4.57	**3OB**	0.03	4.83	**1S3**	0.01	5.29	**1S5**	0.01	5.52	**OH5**	0.01	5.28	**B25**	0.02	5.20
5E	0.04	4.59	**5H4**	0.01	5.62	**OH5**	0.01	5.44	**2SO**	0.01	5.75	**B3O**	0.01	5.38	**OH5**	0.01	5.25
E4	0.04	4.61	**1S5**	0.01	5.65	**2SO**	0.01	5.68	**E5**	0.00	6.12	**E5**	0.00	5.90	**1S3**	0.00	5.92
14B	0.03	4.80	**2H1**	0.01	5.67	**E5**	0.01	5.85	**B3O**	0.00	6.26	**OE**	0.00	6.33	**OE**	0.00	6.14
E1	0.03	4.89	**E5**	0.01	5.67	**5H4**	0.00	6.05	**E3**	0.00	6.67	**5E**	0.00	6.55	**E5**	0.00	6.18
1S3	0.02	5.06	**OH5**	0.01	5.84	**OE**	0.00	6.22	**OE**	0.00	6.83	**E3**	0.00	6.72	**E3**	0.00	6.48
2E	0.02	5.20	**2SO**	0.01	5.85	**2H1**	0.00	6.36	**5H4**	0.00	6.89	**4H5**	0.00	6.89	**E1**	0.00	6.63
5S1	0.01	5.37	**E1**	0.00	5.91	**E4**	0.00	6.36	**5E**	0.00	6.96	**5H4**	0.00	6.96	**2H3**	0.00	6.63
B3O	0.01	5.75	**2E**	0.00	6.12	**E1**	0.00	6.48	**14B**	0.00	7.04	**2H3**	0.00	7.37	**5HO**	0.00	6.67
2SO	0.01	5.86	**14B**	0.00	6.16	**1S5**	0.00	6.59	**2H3**	0.00	7.37	**2E**	0.00	7.37	**5E**	0.00	6.72
OH1	0.00	5.95	**4H5**	0.00	6.20	**3S1**	0.00	6.83	**2H1**	0.00	7.54	**2H1**	0.00	7.54	**2H1**	0.00	6.96
2H3	0.00	6.10	**E4**	0.00	6.20	**14B**	0.00	6.89	**4H3**	0.00	7.54	**E4**	0.00	7.54	**OH1**	0.00	7.04
25B	0.00	6.26	**5E**	0.00	6.36	**2E**	0.00	6.89	**E4**	0.00	7.54	**E1**	0.00	7.78	**5H4**	0.00	7.24
3OB	0.00	6.48	**OE**	0.00	6.51	**5E**	0.00	6.89	**1S3**	0.00	7.78	**4H3**	0.00	7.78	**4H5**	0.00	7.54
5HO	0.00	6.63	**2H3**	0.00	6.51	**E3**	0.00	6.96	**E1**	0.00	7.78	**5HO**	0.00	7.78	**4H3**	0.00	7.54
3S1	0.00	6.72	**OH1**	0.00	6.63	**2H3**	0.00	6.96	**4H5**	0.00	7.78	**1S5**	0.00	8.19	**2E**	0.00	7.78
3H4	0.00	6.77	**3S1**	0.00	6.72	**4H5**	0.00	7.13	**4E**	0.00	7.78	**25B**	0.00	8.19	**3H4**	0.00	7.78
OE	0.00	6.96	**4E**	0.00	7.13	**5HO**	0.00	7.24	**5HO**	0.00	7.78	**OH1**	0.00	8.19	**14B**	0.00	8.19
B14	0.00	7.04	**5S1**	0.00	7.37	**OH1**	0.00	7.37	**OH1**	0.00	8.19	**3E**	0.00	8.19	**25B**	0.00	8.19
E5	0.00	7.04	**E3**	0.00	7.37	**3H4**	0.00	7.54	**2E**	0.00	8.19	**3H2**	0.00	8.19	**E4**	0.00	8.19
E3	0.00	7.04	**3H4**	0.00	7.37	**4H3**	0.00	7.78	**3H4**	0.00	8.19				**3E**	0.00	8.19
OH5	0.00	7.24	**4H3**	0.00	7.54	**3E**	0.00	8.19	**3E**	0.00	8.19	**5S1**	-	-	**3H2**	0.00	8.19
4H5	0.00	8.19	**25B**	0.00	7.78	**3H2**	0.00	8.19				**B14**	-	-			
3E	0.00	8.19	**5HO**	0.00	7.78				**5S1**	-	-	**14B**	-	-	**5S1**	-	-
			3E	0.00	8.19	**5S1**	-	-	**B14**	-	-	**1S3**	-	-	**B14**	-	-
4E	-	-				**B14**	-	-	**3S1**	-	-	**3S1**	-	-	**1S5**	-	-
4H3	-	-	**B14**	-	-	**25B**	-	-	**25B**	-	-	**4E**	-	-	**3S1**	-	-
1H2	-	-	**1H2**	-	-	**4E**	-	-	**1H2**	-	-	**1H2**	-	-	**4E**	-	-
1E	-	-	**1E**	-	-	**1H2**	-	-	**1E**	-	-	**1E**	-	-	**1H2**	-	-
EO	-	-	**EO**	-	-	**1E**	-	-	**EO**	-	-	**3H4**	-	-	**1E**	-	-
1HO	-	-	**1HO**	-	-	**EO**	-	-	**1HO**	-	-	**EO**	-	-	**EO**	-	-
3H2	-	-	**3H2**	-	-	**1HO**	-	-	**3H2**	-	-	**1HO**	-	-	**1HO**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-

Table S21. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from a 10 μs simulation of **3** (strand A, numbered from reducing end)

	Glc:7			Glc:8			Glc:9			Glc:10			Glc:11			Glc:12	
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	96.94	0.02	**4C1**	95.72	0.03	**4C1**	98.33	0.01	**4C1**	98.42	0.01	**4C1**	99.15	0.01	**4C1**	96.76	0.02
OS2	1.87	2.36	**1C4**	2.17	2.27	**OS2**	0.82	2.85	**1C4**	0.76	2.89	**OS2**	0.44	3.22	**1C4**	2.86	2.11
1C4	1.05	2.70	**OS2**	1.81	2.38	**1C4**	0.76	2.90	**OS2**	0.70	2.94	**1C4**	0.15	3.85	**OS2**	0.15	3.84
B25	0.08	4.23	**3OB**	0.22	3.62	**B25**	0.02	4.93	**B25**	0.04	4.63	**B25**	0.09	4.15	**1S3**	0.07	4.34
OH5	0.02	5.21	**B25**	0.04	4.69	**3OB**	0.01	5.26	**B3O**	0.02	5.19	**B3O**	0.05	4.56	**B3O**	0.05	4.46
2SO	0.01	5.35	**OH5**	0.01	5.26	**OH5**	0.01	5.31	**OH5**	0.01	5.28	**1S3**	0.04	4.62	**B25**	0.03	4.79
B3O	0.01	5.36	**2SO**	0.01	5.67	**2SO**	0.01	5.41	**3OB**	0.01	5.47	**2SO**	0.01	5.23	**3OB**	0.01	5.35
3OB	0.01	5.45	**B3O**	0.00	5.99	**B3O**	0.01	5.59	**2SO**	0.01	5.61	**OH5**	0.01	5.34	**2SO**	0.01	5.40
E5	0.00	5.96	**E5**	0.00	6.10	**2H1**	0.00	6.05	**1S3**	0.01	5.68	**3OB**	0.01	5.38	**1S5**	0.01	5.47
OE	0.00	6.36	**OE**	0.00	6.28	**E5**	0.00	6.12	**2H1**	0.00	5.94	**1S5**	0.01	5.39	**14B**	0.01	5.62
E3	0.00	6.55	**5E**	0.00	6.45	**OE**	0.00	6.28	**E5**	0.00	5.99	**2H1**	0.01	5.84	**2H1**	0.01	5.84
5E	0.00	6.59	**E3**	0.00	6.51	**E1**	0.00	6.36	**1S5**	0.00	6.02	**E5**	0.01	5.87	**E5**	0.01	5.86
5H4	0.00	6.67	**1S5**	0.00	6.55	**2H3**	0.00	6.51	**E1**	0.00	6.28	**2H3**	0.00	6.20	**2E**	0.00	6.01
5HO	0.00	6.77	**5H4**	0.00	6.63	**5H4**	0.00	6.59	**5H4**	0.00	6.42	**E1**	0.00	6.24	**OH5**	0.00	6.12
E1	0.00	7.24	**E1**	0.00	6.96	**2E**	0.00	6.72	**OE**	0.00	6.45	**2E**	0.00	6.28	**2H3**	0.00	6.24
2H1	0.00	7.37	**2H3**	0.00	7.13	**5E**	0.00	6.77	**E3**	0.00	6.48	**E3**	0.00	6.42	**E1**	0.00	6.42
2H3	0.00	7.37	**5HO**	0.00	7.13	**E3**	0.00	6.83	**2E**	0.00	6.48	**OE**	0.00	6.59	**3S1**	0.00	6.48
E4	0.00	7.37	**E4**	0.00	7.37	**1S3**	0.00	7.24	**5E**	0.00	6.51	**5H4**	0.00	6.63	**E3**	0.00	6.51
4H5	0.00	7.54	**4H3**	0.00	7.54	**E4**	0.00	7.24	**2H3**	0.00	7.04	**14B**	0.00	6.77	**5H4**	0.00	6.55
OH1	0.00	7.54	**2H1**	0.00	7.78	**1S5**	0.00	7.37	**OH1**	0.00	7.13	**4H5**	0.00	6.83	**OE**	0.00	6.72
2E	0.00	7.78	**4H5**	0.00	7.78	**OH1**	0.00	7.37	**5HO**	0.00	7.13	**5E**	0.00	6.83	**4H5**	0.00	6.77
4E	0.00	8.19	**3H4**	0.00	7.78	**4H5**	0.00	7.78	**E4**	0.00	7.13	**3S1**	0.00	6.96	**5S1**	0.00	6.89
4H3	0.00	8.19	**14B**	0.00	8.19	**5HO**	0.00	7.78	**14B**	0.00	7.54	**E4**	0.00	6.96	**E4**	0.00	6.96
3E	0.00	8.19	**3S1**	0.00	8.19	**5S1**	0.00	8.19	**3H4**	0.00	7.78	**4H3**	0.00	7.04	**OH1**	0.00	7.04
			4E	0.00	8.19	**25B**	0.00	8.19	**4H5**	0.00	8.19	**OH1**	0.00	7.13	**5E**	0.00	7.13
5S1	-	-	**OH1**	0.00	8.19	**4E**	0.00	8.19	**4H3**	0.00	8.19	**5HO**	0.00	7.13	**4E**	0.00	7.54
B14	-	-	**2E**	0.00	8.19	**4H3**	0.00	8.19	**EO**	0.00	8.19	**4E**	0.00	7.24	**5HO**	0.00	7.54
1S5	-	-				**EO**	0.00	8.19				**25B**	0.00	7.54	**B14**	0.00	7.78
14B	-	-	**5S1**	-	-				**5S1**	-	-				**4H3**	0.00	7.78
1S3	-	-	**B14**	-	-	**B14**	-	-	**B14**	-	-	**5S1**	-	-	**3H4**	0.00	8.19
3S1	-	-	**1S3**	-	-	**14B**	-	-	**3S1**	-	-	**B14**	-	-	**3E**	0.00	8.19
25B	-	-	**25B**	-	-	**3S1**	-	-	**25B**	-	-	**1H2**	-	-	**3H2**	0.00	8.19
1H2	-	-	**1H2**	-	-	**1H2**	-	-	**4E**	-	-	**1E**	-	-			
1E	-	-	**1E**	-	-	**1E**	-	-	**1H2**	-	-	**3H4**	-	-	**25B**	-	-
3H4	-	-	**EO**	-	-	**3H4**	-	-	**1E**	-	-	**EO**	-	-	**1H2**	-	-
EO	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-	**1E**	-	-
1HO	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**EO**	-	-
3H2	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**1HO**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-

S21 continued

Table S21. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from a 10 μs simulation of **3** (strand B, numbered from reducing end)

	Glc:1			Glc:2			Glc:3			Glc:4			Glc:5			Glc:6	
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	94.71	0.03	**4C1**	98.19	0.01	**4C1**	99.28	0.00	**4C1**	98.37	0.01	**4C1**	99.37	0.00	**4C1**	98.02	0.01
1C4	4.57	1.83	**OS2**	1.21	2.62	**OS2**	0.56	3.08	**OS2**	1.03	2.71	**1C4**	0.32	3.40	**1C4**	1.46	2.51
1S5	0.21	3.65	**1C4**	0.31	3.42	**B25**	0.06	4.42	**1C4**	0.49	3.16	**OS2**	0.27	3.51	**OS2**	0.46	3.19
B25	0.19	3.72	**B25**	0.11	4.03	**1C4**	0.03	4.72	**B25**	0.03	4.91	**OH5**	0.01	5.23	**B25**	0.02	5.16
OS2	0.09	4.16	**1S3**	0.06	4.45	**B3O**	0.02	5.07	**B3O**	0.02	4.98	**B25**	0.01	5.73	**OH5**	0.01	5.35
5H4	0.06	4.37	**B3O**	0.04	4.62	**2SO**	0.02	5.19	**3OB**	0.02	5.01	**2SO**	0.00	5.88	**2SO**	0.01	5.59
2H1	0.03	4.89	**1S5**	0.01	5.23	**OH5**	0.01	5.60	**OH5**	0.01	5.39	**B3O**	0.00	6.04	**3OB**	0.00	5.96
14B	0.03	4.92	**3OB**	0.01	5.54	**3OB**	0.01	5.85	**2SO**	0.01	5.41	**3OB**	0.00	6.18	**E5**	0.00	6.12
E4	0.02	5.05	**E5**	0.01	5.69	**E5**	0.00	6.07	**E5**	0.00	6.08	**E5**	0.00	6.18	**B3O**	0.00	6.20
5E	0.02	5.06	**14B**	0.01	5.75	**OE**	0.00	6.31	**OE**	0.00	6.36	**E3**	0.00	6.42	**OE**	0.00	6.33
1S3	0.02	5.07	**OH5**	0.01	5.76	**1S5**	0.00	6.33	**5H4**	0.00	6.45	**OE**	0.00	6.55	**5H4**	0.00	6.48
E1	0.02	5.09	**2H1**	0.00	5.99	**E3**	0.00	6.45	**E3**	0.00	6.77	**2H3**	0.00	6.72	**E3**	0.00	6.55
2E	0.01	5.46	**2SO**	0.00	6.01	**2H3**	0.00	6.67	**1S3**	0.00	6.83	**2E**	0.00	7.24	**5E**	0.00	6.63
B3O	0.01	5.75	**3S1**	0.00	6.02	**4H5**	0.00	6.83	**5E**	0.00	6.83	**5E**	0.00	7.37	**2H3**	0.00	6.72
5S1	0.01	5.84	**5S1**	0.00	6.05	**1S3**	0.00	7.13	**2H3**	0.00	6.89	**4H3**	0.00	7.54	**5HO**	0.00	7.37
2H3	0.00	6.08	**5H4**	0.00	6.28	**4H3**	0.00	7.13	**2E**	0.00	7.13	**5H4**	0.00	7.78	**2H1**	0.00	7.54
OH1	0.00	6.14	**E1**	0.00	6.31	**5H4**	0.00	7.13	**E4**	0.00	7.13	**2H1**	0.00	8.19	**E1**	0.00	7.54
2SO	0.00	6.20	**E4**	0.00	6.33	**2H1**	0.00	7.37	**5HO**	0.00	7.37	**OH1**	0.00	8.19	**4H5**	0.00	7.54
3OB	0.00	6.45	**4H5**	0.00	6.36	**OH1**	0.00	7.37	**3H4**	0.00	7.54	**3H4**	0.00	8.19	**OH1**	0.00	7.54
5HO	0.00	6.63	**OE**	0.00	6.36	**5E**	0.00	7.37	**2H1**	0.00	7.78				**2E**	0.00	7.78
3H4	0.00	6.67	**2E**	0.00	6.55	**E1**	0.00	7.54	**4H3**	0.00	7.78	**5S1**	-	-	**E4**	0.00	7.78
3S1	0.00	6.89	**5E**	0.00	6.55	**4E**	0.00	8.19	**OH1**	0.00	8.19	**B14**	-	-	**4E**	0.00	8.19
25B	0.00	7.24	**B14**	0.00	6.77	**2E**	0.00	8.19	**3E**	0.00	8.19	**1S5**	-	-	**4H3**	0.00	8.19
OH5	0.00	7.24	**OH1**	0.00	6.96	**5HO**	0.00	8.19				**14B**	-	-	**EO**	0.00	8.19
E5	0.00	7.24	**E3**	0.00	7.24	**E4**	0.00	8.19	**5S1**	-	-	**1S3**	-	-	**3E**	0.00	8.19
B14	0.00	7.37	**2H3**	0.00	7.24				**B14**	-	-	**3S1**	-	-			
4H5	0.00	7.37	**4E**	0.00	7.78	**5S1**	-	-	**1S5**	-	-	**25B**	-	-	**5S1**	-	-
E3	0.00	7.37	**5HO**	0.00	7.78	**B14**	-	-	**14B**	-	-	**E1**	-	-	**B14**	-	-
OE	0.00	7.78	**25B**	0.00	8.19	**14B**	-	-	**3S1**	-	-	**4H5**	-	-	**1S5**	-	-
3E	0.00	7.78	**3H4**	0.00	8.19	**3S1**	-	-	**25B**	-	-	**4E**	-	-	**14B**	-	-
						25B	-	-	**E1**	-	-	**1H2**	-	-	**1S3**	-	-
4E	-	-	**4H3**	-	-	**1H2**	-	-	**4H5**	-	-	**1E**	-	-	**3S1**	-	-
4H3	-	-	**1H2**	-	-	**1E**	-	-	**4E**	-	-	**5HO**	-	-	**25B**	-	-
1H2	-	-	**1E**	-	-	**3H4**	-	-	**1H2**	-	-	**E4**	-	-	**1H2**	-	-
1E	-	-	**EO**	-	-	**EO**	-	-	**1E**	-	-	**EO**	-	-	**1E**	-	-
EO	-	-	**3E**	-	-	**3E**	-	-	**EO**	-	-	**3E**	-	-	**3H4**	-	-
1HO	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-
3H2	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-

S21 continued

Table S21. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from a 10 μs simulation of **3** (strand B, numbered from reducing end)

	Glc:7			Glc:8			Glc:9			Glc:10			Glc:11			Glc:12	
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	96.83	0.02	**4C1**	98.99	0.01	**4C1**	96.50	0.02	**4C1**	98.47	0.01	**4C1**	97.64	0.01	**4C1**	95.04	0.03
OS2	1.52	2.48	**OS2**	0.53	3.10	**OS2**	2.30	2.24	**1C4**	0.68	2.96	**OS2**	1.29	2.58	**1C4**	4.38	1.86
1C4	1.35	2.55	**1C4**	0.41	3.26	**1C4**	0.98	2.74	**OS2**	0.64	2.99	**1C4**	0.73	2.92	**OS2**	0.24	3.58
3OB	0.18	3.75	**2SO**	0.01	5.27	**B25**	0.11	4.02	**B25**	0.08	4.21	**B25**	0.15	3.87	**1S3**	0.11	4.04
B25	0.04	4.60	**OH5**	0.01	5.27	**3OB**	0.07	4.34	**B3O**	0.04	4.70	**1S3**	0.06	4.44	**B3O**	0.07	4.33
B3O	0.02	4.96	**B25**	0.01	5.37	**OH5**	0.01	5.29	**1S3**	0.02	5.17	**B3O**	0.04	4.67	**B25**	0.05	4.50
2SO	0.02	5.03	**3OB**	0.01	5.68	**2SO**	0.00	5.90	**2SO**	0.01	5.25	**1S5**	0.03	4.79	**1S5**	0.02	4.98
OH5	0.01	5.32	**B3O**	0.01	5.77	**E5**	0.00	5.96	**OH5**	0.01	5.28	**3OB**	0.01	5.25	**3OB**	0.02	5.09
3S1	0.01	5.76	**E5**	0.00	6.01	**B3O**	0.00	6.02	**2H1**	0.01	5.77	**OH5**	0.01	5.46	**14B**	0.01	5.28
2H1	0.00	6.04	**2H3**	0.00	6.48	**2H1**	0.00	6.36	**3OB**	0.01	5.86	**2SO**	0.01	5.60	**2SO**	0.01	5.30
E5	0.00	6.33	**OE**	0.00	6.63	**OE**	0.00	6.42	**5H4**	0.00	5.88	**2H1**	0.01	5.61	**2H1**	0.01	5.49
E3	0.00	6.51	**E3**	0.00	6.67	**2E**	0.00	6.48	**E1**	0.00	5.96	**E5**	0.01	5.64	**2E**	0.01	5.58
5E	0.00	6.51	**2H1**	0.00	6.96	**5E**	0.00	6.48	**E5**	0.00	6.01	**14B**	0.01	5.85	**2H3**	0.00	5.88
E1	0.00	6.55	**E1**	0.00	6.96	**5H4**	0.00	6.67	**1S5**	0.00	6.16	**5H4**	0.00	6.12	**E1**	0.00	6.08
OE	0.00	6.59	**5E**	0.00	7.13	**E3**	0.00	6.72	**5E**	0.00	6.22	**2E**	0.00	6.14	**E5**	0.00	6.16
2E	0.00	6.72	**2E**	0.00	7.24	**5HO**	0.00	6.77	**E3**	0.00	6.28	**E1**	0.00	6.20	**3S1**	0.00	6.26
5H4	0.00	6.72	**OH1**	0.00	7.37	**E1**	0.00	6.89	**2E**	0.00	6.39	**5E**	0.00	6.45	**OH5**	0.00	6.28
1S5	0.00	6.83	**4H3**	0.00	7.54	**E4**	0.00	6.96	**OE**	0.00	6.51	**4H5**	0.00	6.55	**OH1**	0.00	6.59
5HO	0.00	6.96	**5HO**	0.00	7.54	**4H5**	0.00	7.13	**2H3**	0.00	6.51	**OE**	0.00	6.55	**5E**	0.00	6.67
OH1	0.00	7.24	**5H4**	0.00	7.78	**OH1**	0.00	7.13	**5S1**	0.00	6.67	**E3**	0.00	6.77	**4H5**	0.00	6.72
2H3	0.00	7.37	**4E**	0.00	8.19	**4H3**	0.00	7.37	**E4**	0.00	6.77	**2H3**	0.00	6.77	**E3**	0.00	6.72
4H5	0.00	7.54				**2H3**	0.00	7.54	**4H5**	0.00	7.04	**OH1**	0.00	6.83	**5S1**	0.00	6.83
E4	0.00	7.78	**5S1**	-	-	**1S5**	0.00	7.78	**5HO**	0.00	7.04	**E4**	0.00	6.89	**5H4**	0.00	6.83
5S1	0.00	8.19	**B14**	-	-	**3H4**	0.00	8.19	**B14**	0.00	7.37	**5HO**	0.00	6.96	**E4**	0.00	6.83
14B	0.00	8.19	**1S5**	-	-				**OH1**	0.00	7.37	**4H3**	0.00	7.04	**OE**	0.00	6.96
1S3	0.00	8.19	**14B**	-	-	**5S1**	-	-	**4E**	0.00	7.54	**4E**	0.00	7.37	**5HO**	0.00	7.04
4H3	0.00	8.19	**1S3**	-	-	**B14**	-	-	**3H4**	0.00	7.78	**25B**	0.00	7.78	**25B**	0.00	7.54
3H4	0.00	8.19	**3S1**	-	-	**14B**	-	-	**3S1**	0.00	8.19	**3H4**	0.00	7.78	**3H4**	0.00	7.54
			25B	-	-	**1S3**	-	-	**25B**	0.00	8.19	**3S1**	0.00	8.19	**B14**	0.00	7.78
B14	-	-	**4H5**	-	-	**3S1**	-	-	**4H3**	0.00	8.19	**3E**	0.00	8.19	**4E**	0.00	7.78
25B	-	-	**1H2**	-	-	**25B**	-	-							**4H3**	0.00	7.78
4E	-	-	**1E**	-	-	**4E**	-	-	**14B**	-	-	**5S1**	-	-			
1H2	-	-	**E4**	-	-	**1H2**	-	-	**1H2**	-	-	**B14**	-	-	**1H2**	-	-
1E	-	-	**3H4**	-	-	**1E**	-	-	**1E**	-	-	**1H2**	-	-	**1E**	-	-
EO	-	-	**EO**	-	-	**EO**	-	-	**EO**	-	-	**1E**	-	-	**EO**	-	-
3E	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-	**EO**	-	-	**3E**	-	-
1HO	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-
3H2	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-

S21 continued

Table S22. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from a 10 μs simulations of **4** (from reducing end)

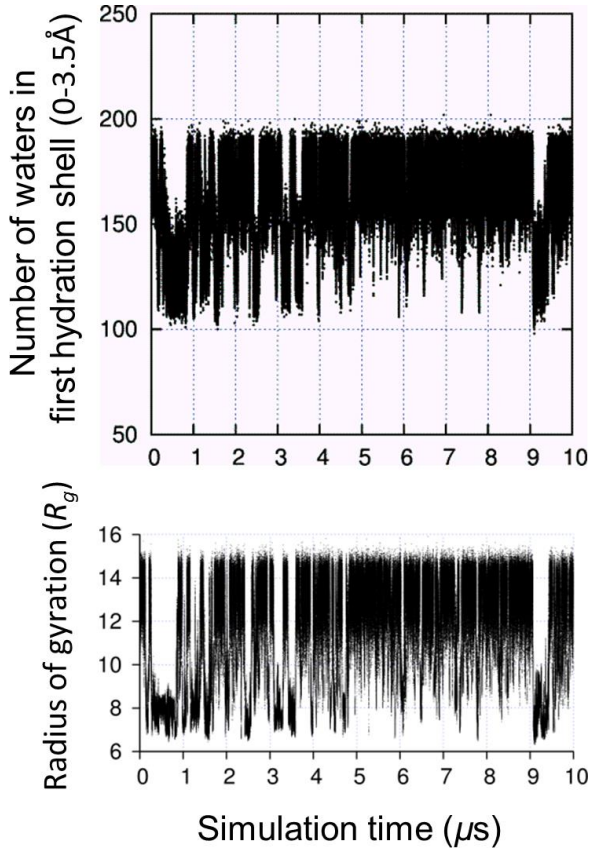
	(4) Glc:1			(4) Glc:2			(4) Glc:3			(4) Glc:4			(4) Glc:5			(4) Glc:6	
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	93.59	0.04	**4C1**	97.28	0.02	**4C1**	91.25	0.05	**4C1**	97.38	0.02	**4C1**	97.60	0.01	**4C1**	99.30	0.00
1C4	5.56	1.71	**1C4**	1.51	2.49	**OS2**	5.18	1.76	**OS2**	1.46	2.50	**OS2**	1.72	2.41	**OS2**	0.49	3.16
1S5	0.26	3.54	**OS2**	0.74	2.91	**1C4**	1.56	2.47	**1C4**	0.83	2.84	**1C4**	0.26	3.53	**1S3**	0.04	4.60
B25	0.24	3.57	**3OB**	0.19	3.71	**3OB**	1.24	2.60	**B25**	0.13	3.94	**B25**	0.16	3.82	**3OB**	0.04	4.64
OS2	0.15	3.86	**B3O**	0.06	4.45	**B25**	0.41	3.27	**3OB**	0.10	4.11	**3OB**	0.15	3.86	**B25**	0.03	4.74
5H4	0.07	4.35	**1S3**	0.05	4.50	**1S3**	0.17	3.78	**1S5**	0.03	4.78	**2H1**	0.03	4.75	**B3O**	0.02	4.96
14B	0.03	4.89	**B25**	0.05	4.50	**B3O**	0.06	4.40	**E5**	0.02	5.14	**E5**	0.02	5.19	**2H1**	0.01	5.46
5E	0.02	4.95	**3S1**	0.02	5.02	**1S5**	0.03	4.73	**OH5**	0.01	5.37	**E1**	0.02	5.19	**E5**	0.01	5.49
1S3	0.02	5.08	**E5**	0.02	5.03	**E5**	0.02	5.02	**2H1**	0.01	5.66	**OH5**	0.01	5.44	**3S1**	0.01	5.73
2H1	0.02	5.18	**E1**	0.01	5.32	**14B**	0.01	5.25	**4H5**	0.01	5.73	**2E**	0.01	5.51	**2SO**	0.01	5.74
E4	0.02	5.19	**2H1**	0.01	5.34	**OH5**	0.01	5.35	**E1**	0.00	5.96	**1S5**	0.00	5.88	**2E**	0.01	5.76
E1	0.01	5.32	**OH5**	0.01	5.42	**5H4**	0.01	5.56	**2E**	0.00	6.12	**4H5**	0.00	5.88	**1S5**	0.01	5.82
2E	0.01	5.73	**1S5**	0.01	5.49	**2H1**	0.01	5.68	**14B**	0.00	6.24	**2H3**	0.00	6.36	**OH5**	0.01	5.86
B3O	0.00	5.99	**4H5**	0.01	5.53	**4H5**	0.01	5.75	**5H4**	0.00	6.33	**OH1**	0.00	6.45	**14B**	0.01	5.87
2SO	0.00	6.42	**2SO**	0.01	5.56	**E1**	0.00	5.88	**2H3**	0.00	6.42	**3S1**	0.00	6.67	**E1**	0.00	5.92
E5	0.00	6.63	**2E**	0.01	5.78	**2E**	0.00	5.90	**OE**	0.00	6.77	**4E**	0.00	6.67	**5S1**	0.00	5.98
OH1	0.00	6.63	**14B**	0.00	6.26	**E4**	0.00	6.16	**5E**	0.00	6.77	**OE**	0.00	6.67	**4H5**	0.00	5.99
2H3	0.00	6.63	**OE**	0.00	6.36	**5E**	0.00	6.26	**OH1**	0.00	6.83	**5S1**	0.00	6.72	**2H3**	0.00	6.36
OH5	0.00	6.72	**5H4**	0.00	6.39	**2H3**	0.00	6.36	**E4**	0.00	6.83	**5E**	0.00	6.77	**OH1**	0.00	6.59
5HO	0.00	6.83	**4E**	0.00	6.45	**2SO**	0.00	6.48	**4E**	0.00	6.89	**25B**	0.00	6.89	**OE**	0.00	6.63
E3	0.00	6.96	**2H3**	0.00	6.67	**4E**	0.00	6.55	**1S3**	0.00	7.13	**5H4**	0.00	6.96	**B14**	0.00	6.89
OE	0.00	7.04	**OH1**	0.00	6.77	**OE**	0.00	6.59	**5HO**	0.00	7.13	**2SO**	0.00	7.13	**25B**	0.00	6.89
5S1	0.00	7.13	**E4**	0.00	6.83	**5HO**	0.00	6.96	**4H3**	0.00	7.37	**E3**	0.00	7.13	**E3**	0.00	6.96
3H4	0.00	7.13	**E3**	0.00	7.24	**3S1**	0.00	7.04	**E3**	0.00	7.37	**5HO**	0.00	7.13	**4E**	0.00	7.04
4H5	0.00	7.37	**4H3**	0.00	7.54	**25B**	0.00	7.04	**3E**	0.00	8.19	**E4**	0.00	7.78	**4H3**	0.00	7.54
4H3	0.00	7.37	**5E**	0.00	7.54	**E3**	0.00	7.13				**4H3**	0.00	8.19	**5E**	0.00	8.19
3OB	0.00	7.54	**5S1**	0.00	7.78	**OH1**	0.00	7.13	**5S1**	-	-	**EO**	0.00	8.19	**3E**	0.00	8.19
25B	0.00	7.78	**B14**	0.00	8.19	**3H4**	0.00	7.54	**B14**	-	-				**3H2**	0.00	8.19
3E	0.00	8.19	**5HO**	0.00	8.19	**EO**	0.00	7.78	**B3O**	-	-	**B14**	-	-			
			3H4	0.00	8.19	**3E**	0.00	8.19	**3S1**	-	-	**14B**	-	-	**1C4**	-	-
B14	-	-	**EO**	0.00	8.19				**2SO**	-	-	**1S3**	-	-	**1H2**	-	-
3S1	-	-	**3H2**	0.00	8.19	**5S1**	-	-	**25B**	-	-	**B3O**	-	-	**1E**	-	-
4E	-	-				**B14**	-	-	**1H2**	-	-	**1H2**	-	-	**5HO**	-	-
1H2	-	-	**25B**	-	-	**4H3**	-	-	**1E**	-	-	**1E**	-	-	**5H4**	-	-
1E	-	-	**1H2**	-	-	**1H2**	-	-	**3H4**	-	-	**3H4**	-	-	**E4**	-	-
EO	-	-	**1E**	-	-	**1E**	-	-	**EO**	-	-	**3E**	-	-	**3H4**	-	-
1HO	-	-	**3E**	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-	**EO**	-	-
3H2	-	-	**1HO**	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-	**1HO**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-

Table S23. Pyranose pucker populations (%) and relative free energies (Δ*G*, kcal mol^{-1}) from 20 and 10 μs simulations of **5** and **6** (from reducing end)

	(6) Glc:1			(5) Glc:1			(5) Glc:2			(5) Glc:3	
Pucker	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***	**Pucker**	**%**	**Δ*G***
4C1	92.54	0.05	**4C1**	85.83	0.09	**4C1**	96.96	0.02	**4C1**	97.87	0.01
1C4	7.21	1.56	**1C4**	12.21	1.25	**OS2**	2.09	2.29	**1C4**	1.14	2.65
1S5	0.09	4.14	**1S5**	0.62	3.02	**1C4**	0.39	3.29	**OS2**	0.74	2.91
B25	0.05	4.56	**B25**	0.57	3.06	**B25**	0.18	3.73	**3OB**	0.08	4.26
14B	0.02	5.00	**OS2**	0.37	3.33	**3OB**	0.17	3.77	**B25**	0.05	4.47
2H1	0.02	5.18	**5H4**	0.14	3.90	**1S3**	0.05	4.46	**1S3**	0.03	4.90
OS2	0.02	5.22	**14B**	0.07	4.28	**B3O**	0.03	4.81	**B3O**	0.02	5.14
2E	0.01	5.37	**1S3**	0.06	4.42	**1S5**	0.03	4.88	**3S1**	0.01	5.30
5H4	0.01	5.38	**5E**	0.06	4.45	**E5**	0.02	5.07	**E5**	0.01	5.49
E1	0.01	5.48	**E4**	0.03	4.76	**2H1**	0.02	5.18	**2H1**	0.01	5.56
1S3	0.01	5.52	**2H1**	0.02	5.18	**E1**	0.01	5.30	**1S5**	0.01	5.70
5E	0.01	5.78	**E1**	0.01	5.43	**OH5**	0.01	5.41	**2E**	0.01	5.74
E4	0.00	5.96	**2E**	0.00	5.89	**4H5**	0.01	5.66	**2SO**	0.01	5.78
5S1	0.00	6.31	**B3O**	0.00	5.98	**14B**	0.01	5.78	**OH5**	0.00	5.90
2H3	0.00	6.31	**3OB**	0.00	6.22	**2E**	0.01	5.83	**E1**	0.00	6.04
OH1	0.00	6.51	**5HO**	0.00	6.31	**2SO**	0.00	5.95	**4H5**	0.00	6.07
25B	0.00	6.72	**OH1**	0.00	6.53	**2H3**	0.00	6.37	**5S1**	0.00	6.11
5HO	0.00	6.72	**2H3**	0.00	6.51	**4E**	0.00	6.43	**14B**	0.00	6.12
B14	0.00	6.83	**5S1**	0.00	6.61	**OH1**	0.00	6.48	**2H3**	0.00	6.31
2SO	0.00	6.89	**3H4**	0.00	6.72	**5E**	0.00	6.53	**5H4**	0.00	6.77
E3	0.00	6.89	**2SO**	0.00	6.77	**OE**	0.00	6.63	**OE**	0.00	6.86
B3O	0.00	6.96	**OH5**	0.00	6.77	**5H4**	0.00	6.65	**B14**	0.00	7.13
E5	0.00	7.13	**E5**	0.00	6.86	**E4**	0.00	7.18	**25B**	0.00	7.18
OE	0.00	7.13	**E3**	0.00	6.92	**4H3**	0.00	7.24	**OH1**	0.00	7.18
OH5	0.00	7.24	**4H5**	0.00	7.65	**3S1**	0.00	7.45	**5E**	0.00	7.18
3OB	0.00	7.37	**OE**	0.00	7.45	**5HO**	0.00	7.45	**E4**	0.00	7.18
4H5	0.00	8.19	**4E**	0.00	7.78	**3H4**	0.00	7.45	**E3**	0.00	7.37
4H3	0.00	8.19	**B14**	0.00	8.19	**5S1**	0.00	7.65	**4E**	0.00	7.54
3H4	0.00	8.19	**25B**	0.00	8.19	**E3**	0.00	7.54	**3H4**	0.00	7.95
						B14	0.00	8.60			
3S1	-	-	**3S1**	-	-	**25B**	0.00	8.19	**4H3**	-	-
4E	-	-	**4H3**	-	-				**1H2**	-	-
1H2	-	-	**1H2**	-	-	**1H2**	-	-	**1E**	-	-
1E	-	-	**1E**	-	-	**1E**	-	-	**5HO**	-	-
EO	-	-	**EO**	-	-	**EO**	-	-	**EO**	-	-
3E	-	-	**3E**	-	-	**3E**	-	-	**3E**	-	-
1HO	-	-	**1HO**	-	-	**1HO**	-	-	**1HO**	-	-
3H2	-	-	**3H2**	-	-	**3H2**	-	-	**3H2**	-	-
E2	-	-	**E2**	-	-	**E2**	-	-	**E2**	-	-

S24: Time series of first hydration shell water occupancy and R_g in **1** (dodecasaccharide)

Water occupancy was computed using the Amber12 tool ptraj (keyword “watershell”)



S25: Experimental ^{1}H-^{1}H three-bond vicinal spin-couplings ($^{3}J_{HH}$)

- Experimental errors are estimated to be ± 0.2 Hz

Experimental Data

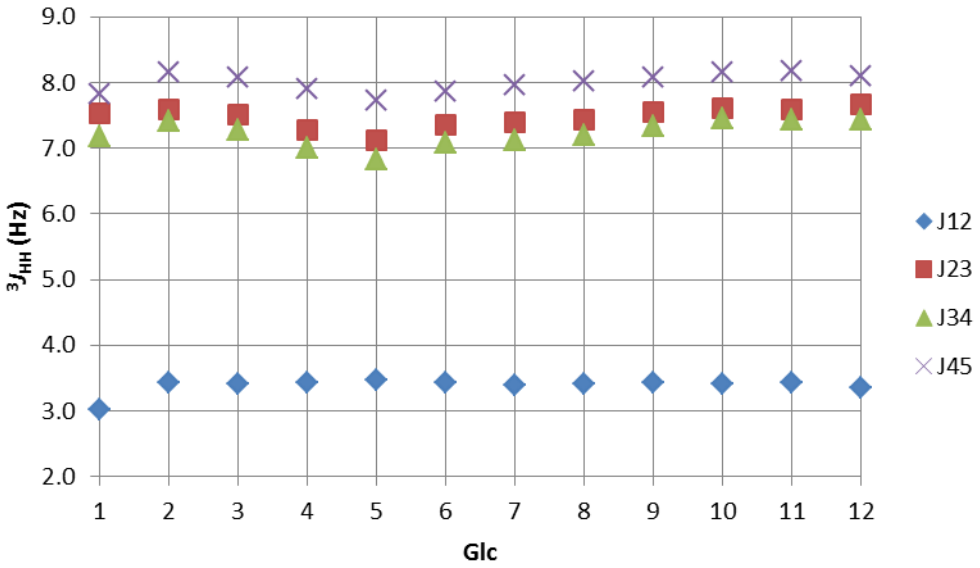
	Tafazzoli et. al.[1]	Roshind el. al.[2]	Roshind et. al[2]
	1	**1**	**2**
J_{12}	3.8	3.8	3.9
J_{23}	9.8	9.9	9.9
J_{34}	9.1	9.0	9.2
J_{45}	10.0	10.1	10.1

(1) Tafazzoli, M.; Grhiasi, M. *Carbohyd Res* **2007**, *342*, 2086.
(2) Roshind, M. U.; Tahtinen, P.; Niemitz, M.; Sjhohn, R. *Carbohyd Res* **2008**, *343*, 101

S26 Calculated ^{1}H-^{1}H three-bond vicinal spin-couplings ($^{3}J_{HH}$): **1** (dodecasaccharide, 10 μs simulation)

- μs simulations were split into 1 μs sub-sets to compute standard deviations (STDEV)
- $^{3}J_{HH}$ values were calculated using substituent-adjusted Karplus equations of Altona and Haasnoot
- Glc pyranose rings are numbered from the reducing end

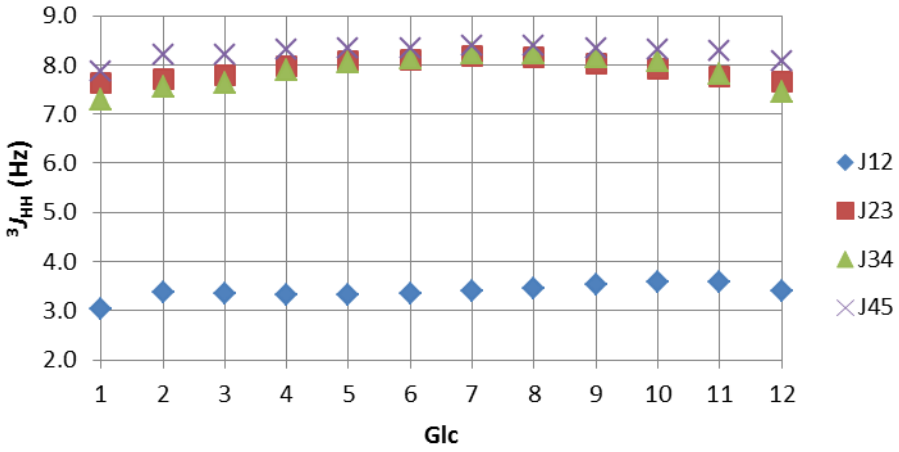
Glc	1	2	3	4	5	6	7	8	9	10	11	12
J_{12}	3.0	3.4	3.4	3.4	3.5	3.4	3.4	3.4	3.4	3.4	3.4	3.3
J_{23}	7.5	7.6	7.5	7.3	7.1	7.4	7.4	7.4	7.5	7.6	7.6	7.7
J_{34}	7.2	7.4	7.3	7.0	6.8	7.1	7.1	7.2	7.3	7.4	7.4	7.4
J_{45}	7.8	8.2	8.1	7.9	7.7	7.9	8.0	8.0	8.1	8.1	8.2	8.1
J_{12} ± STDEV	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.1
J_{23} ± STDEV	0.3	0.1	0.2	0.4	0.6	0.4	0.3	0.2	0.1	0.1	0.1	0.2
J_{34} ± STDEV	0.3	0.1	0.3	0.5	0.8	0.5	0.3	0.3	0.1	0.2	0.2	0.2
J_{45} ± STDEV	0.3	0.1	0.1	0.3	0.5	0.3	0.2	0.2	0.1	0.1	0.1	0.2



S27: Calculated $^{3}J_{HH}$ values: antiparallel double-helix **2** (10 μs simulation), strand A

- μs simulations were split into 1 μs sub-sets to compute standard deviations (STDEV)
- $^{3}J_{HH}$ values were calculated using substituent-adjusted Karplus equations of Altona and Haasnoot
- Glc pyranose rings are numbered from the reducing end

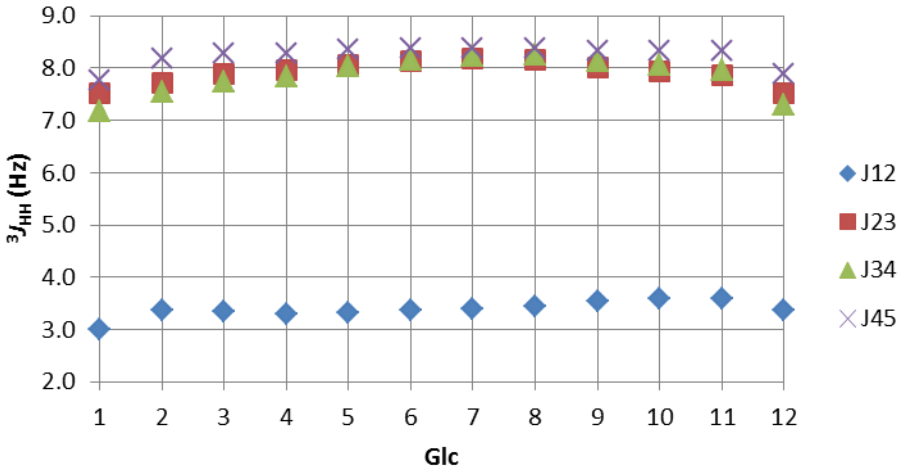
Glc	1	2	3	4	5	6	7	8	9	10	11	12
J_{12}	3.0	3.4	3.3	3.3	3.3	3.3	3.4	3.5	3.5	3.6	3.6	3.4
J_{23}	7.6	7.7	7.8	8.0	8.1	8.1	8.2	8.1	8.0	7.9	7.8	7.6
J_{34}	7.3	7.6	7.6	7.9	8.0	8.1	8.2	8.2	8.1	8.1	7.8	7.4
J_{45}	7.9	8.2	8.2	8.3	8.3	8.3	8.4	8.4	8.3	8.3	8.3	8.1
J_{12} ± STDEV	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.1
J_{23} ± STDEV	0.2	0.2	0.2	0.1	0.1	0.1	0.0	0.1	0.2	0.1	0.1	0.2
J_{34} ± STDEV	0.2	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.3	0.1	0.2	0.2
J_{45} ± STDEV	0.2	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.1	0.1	0.2



S27: Calculated $^{3}J_{HH}$ values: antiparallel double-helix **2** (10 μs simulation), strand B

- μs simulations were split into 1 μs sub-sets to compute standard deviations (STDEV)
- $^{3}J_{HH}$ values were calculated using substituent-adjusted Karplus equations of Altona and Haasnoot
- Glc pyranose rings are numbered from the reducing end

Glc	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
J_{12}	3.0	3.4	3.3	3.3	3.3	3.4	3.4	3.5	3.5	3.6	3.6	3.4
J_{23}	7.5	7.7	7.9	8.0	8.1	8.1	8.2	8.2	8.0	7.9	7.9	7.5
J_{34}	7.2	7.6	7.7	7.8	8.0	8.2	8.2	8.2	8.1	8.1	8.0	7.3
J_{45}	7.8	8.2	8.3	8.3	8.3	8.4	8.4	8.4	8.3	8.3	8.3	7.9
J_{12} **± STDEV**	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.1
J_{23} **± STDEV**	0.3	0.2	0.1	0.2	0.1	0.1	0.0	0.0	0.2	0.1	0.0	0.4
J_{34} **± STDEV**	0.4	0.3	0.2	0.3	0.2	0.1	0.0	0.1	0.3	0.2	0.1	0.4
J_{45} **± STDEV**	0.4	0.2	0.0	0.1	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.5

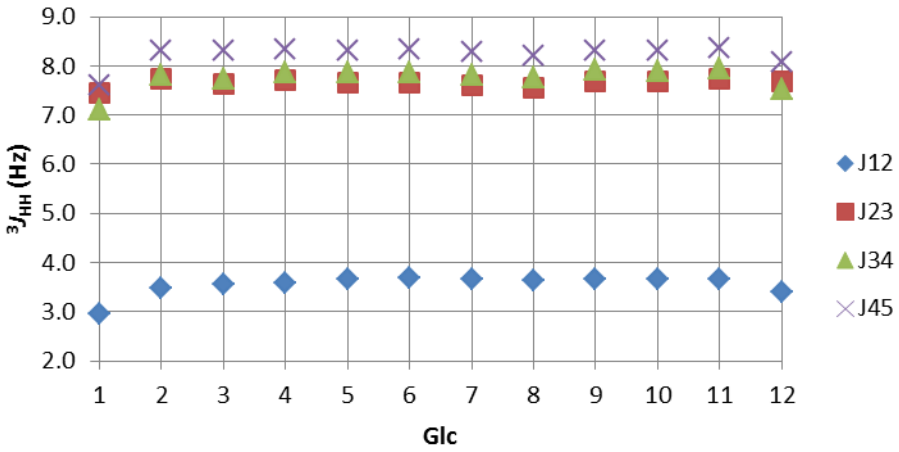


S27 continued

S28: Calculated $^{3}J_{HH}$ values: parallel double-helix **3** (10 μs simulation), strand A

- μs simulations were split into 1 μs sub-sets to compute standard deviations (STDEV)
- $^{3}J_{HH}$ values were calculated using substituent-adjusted Karplus equations of Altona and Haasnoot
- Glc pyranose rings are numbered from the reducing end

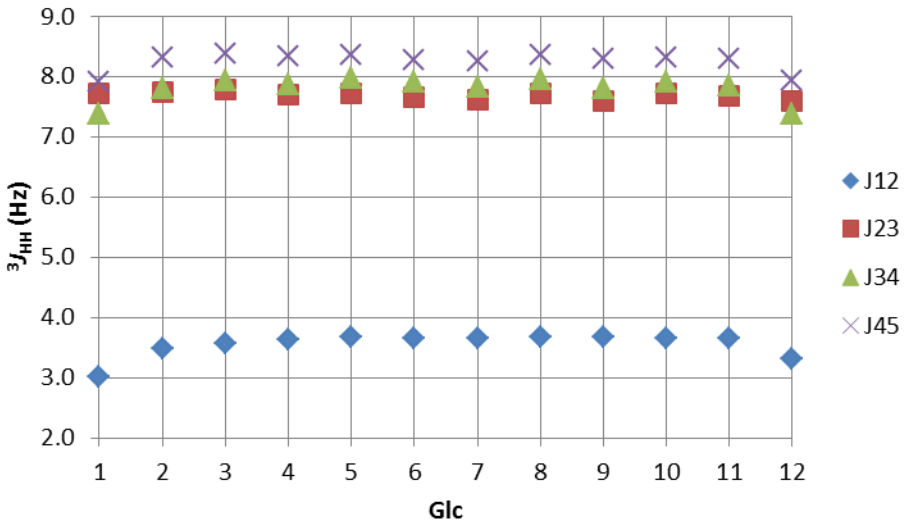
Glc	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
J_{12}	3.0	3.5	3.6	3.6	3.7	3.7	3.7	3.6	3.7	3.7	3.7	3.4
J_{23}	7.5	7.7	7.6	7.7	7.7	7.7	7.6	7.6	7.7	7.7	7.7	7.7
J_{34}	7.1	7.8	7.7	7.9	7.9	7.9	7.8	7.8	7.9	7.9	8.0	7.5
J_{45}	7.6	8.3	8.3	8.3	8.3	8.3	8.3	8.2	8.3	8.3	8.4	8.1
J_{12} **± STDEV**	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.0
J_{23} **± STDEV**	0.5	0.1	0.3	0.1	0.1	0.2	0.2	0.3	0.1	0.1	0.0	0.1
J_{34} **± STDEV**	0.5	0.2	0.4	0.1	0.1	0.4	0.3	0.4	0.1	0.1	0.1	0.1
J_{45} **± STDEV**	0.6	0.1	0.1	0.0	0.1	0.1	0.1	0.4	0.1	0.1	0.0	0.1



S28: Calculated $^{3}J_{HH}$ values: parallel double-helix **3** (10 μs simulation), strand B

- μs simulations were split into 1 μs sub-sets to compute standard deviations (STDEV)
- $^{3}J_{HH}$ values were calculated using substituent-adjusted Karplus equations of Altona and Haasnoot
- Glc pyranose rings are numbered from the reducing end

Glc	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
J_{12}	3.0	3.5	3.6	3.6	3.7	3.7	3.7	3.7	3.7	3.6	3.6	3.3
J_{23}	7.7	7.7	7.8	7.7	7.7	7.7	7.6	7.7	7.6	7.7	7.7	7.6
J_{34}	7.4	7.8	7.9	7.9	8.0	7.9	7.8	8.0	7.8	7.9	7.9	7.4
J_{45}	7.9	8.3	8.4	8.3	8.4	8.3	8.3	8.4	8.3	8.3	8.3	7.9
J_{12} **± STDEV**	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
J_{23} **± STDEV**	0.3	0.1	0.1	0.1	0.0	0.2	0.2	0.1	0.3	0.1	0.1	0.2
J_{34} **± STDEV**	0.3	0.2	0.1	0.2	0.1	0.2	0.3	0.1	0.4	0.1	0.1	0.2
J_{45} **± STDEV**	0.4	0.0	0.0	0.1	0.0	0.2	0.2	0.1	0.2	0.1	0.1	0.4

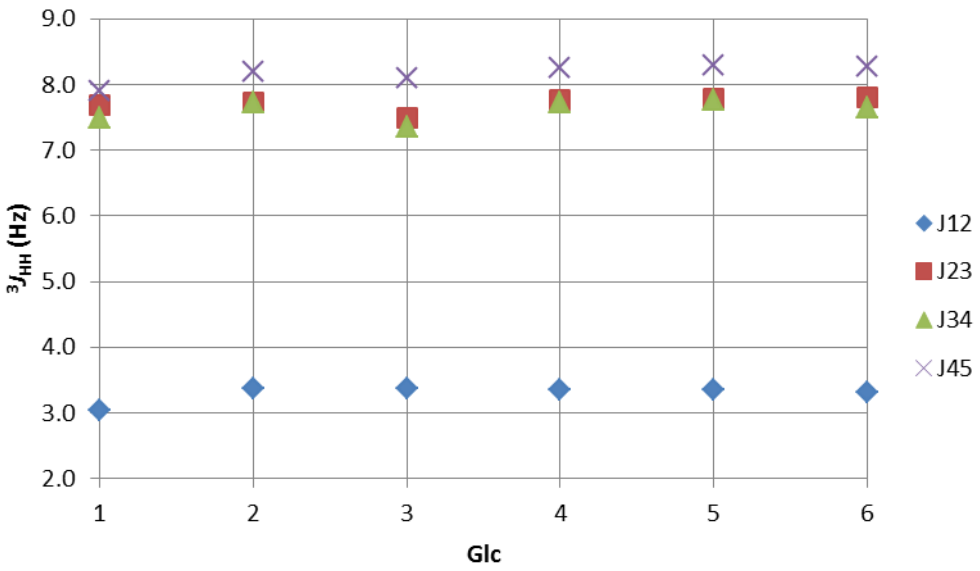


S28 continued

S29: Calculated $^{3}J_{HH}$ values: **4** (hexasaccharide, 10 μs simulation)

- μs simulations were split into 1 μs sub-sets to compute standard deviations (STDEV)
- $^{3}J_{HH}$ values were calculated using substituent-adjusted Karplus equations of Altona and Haasnoot
- Glc pyranose rings are numbered from the reducing end

	CAL	CAL	CAL	CAL	CAL	CAL
Glc	**1**	**2**	**3**	**4**	**5**	**6**
J_{12}	3.0	3.4	3.4	3.3	3.4	3.3
J_{23}	7.7	7.7	7.5	7.8	7.8	7.8
J_{34}	7.5	7.7	7.4	7.7	7.8	7.6
J_{45}	7.9	8.2	8.1	8.2	8.3	8.3
J_{12} **± STDEV**	0.2	0.1	0.1	0.0	0.0	0.0
J_{23} **± STDEV**	0.7	0.2	0.3	0.2	0.2	0.0
J_{34} **± STDEV**	0.7	0.3	0.4	0.3	0.3	0.0
J_{45} **± STDEV**	0.9	0.3	0.2	0.2	0.1	0.0



S30: Calculated $^{3}J_{HH}$ values: **5** (trisaccharide) and **6** (monosaccharide) (10 and 20 μs simulations)

- μs simulations were split into 1 μs sub-sets to compute standard deviations (STDEV)
- $^{3}J_{HH}$ values were calculated using substituent-adjusted Karplus equations of Altona and Haasnoot
- Glc pyranose rings are numbered from the reducing end

	(6) **1**	**(5)** **1**	**(5)** **2**	**(5)** **3**
J_{12}	3.0	2.9	3.4	3.3
J_{23}	7.6	7.3	7.7	7.7
J_{34}	7.1	7.1	7.7	7.6
J_{45}	7.7	7.4	8.3	8.2
J_{12} ± STDEV	0.3	0.3	0.0	0.0
J_{23} ± STDEV	0.8	1.0	0.2	0.1
J_{34} ± STDEV	0.7	1.1	0.3	0.2
J_{45} ± STDEV	1.1	1.3	0.1	0.2

S30 continued

Table S31: Analysis of α-D-Glc puckers in 174 high-resolution Protein Data Bank entries (< 2Å)

Computed Cremer-Pople parameters are tabulated for entries with non-$^4C_1$ Glc puckers ($\theta > 60°$).

PDB_ID	Ring	θ(°)	ϕ(°)	Q	Unique
4BFN	1	67	215	0.60	
4BFN	4	90	222	0.76	1
2BQP	1	180	152	0.61	1
3U2W	1	77	226	0.66	1
3TSA	1	84	192	0.52	1
3GD9	1	63	238	0.51	1
3L2M	13	88	134	0.73	1
3UYL	1	66	230	0.59	1
2BHY	2	60	227	0.56	1
2VXJ	2	74	205	0.65	1
1GEG	2	90	191	0.73	
1GEG	3	89	207	0.74	
1GEG	4	90	212	0.74	
1GEG	5	89	196	0.74	
1GEG	6	87	179	0.75	
1GEG	7	89	209	0.75	
1GEG	8	90	186	0.73	1
1JDC	4	62	197	0.51	1
1Q6C	2	85	232	0.74	1
1UH4	7	76	179	0.59	1
1PPF	1	93	330	0.72	1
4AFC	2	99	194	0.74	1
1QSG	1	76	257	0.72	1
3U2V	1	90	211	0.80	
3U2V	3	84	213	0.75	1
3U2V	8	92	234	0.76	
3U2V	9	99	233	0.76	1
1QJW	1	92	157	0.67	
1QJW	3	91	155	0.68	1
Total					19

PDB entries analysed (< 1.5 Å resolution): 1C58, 1EU1, 1GWM, 1H5V, 1HX0, 1K3I, 1OJJ, 1PWB, 1S5M, 1UOZ, 1W8T, 1WDR, 2J72, 2J73, 2JEN, 2X6W, 2X6X, 2X6Y, 3AXI, 3BC9, 3CHB, 3O8M, 3OEA, 3OG2, 3OGV, 3U2U, 4BFN, 4BFO, 4FCH

29 in total

PDB entries analysed (1.5-2.0 Å resolution): 1ANF, 1BYB, 1CEL, 1CXL, 1CZA, 1D3C, 1DO1, 1DO3, 1DO4, 1DO7, 1E3Z, 1E5J, 1ELJ, 1EZ9, 1FQA, 1FQB, 1G94, 1GEG, 1GWW, 1H5U, 1JDC, 1JDD, 1JG9, 1K72, 1KCL, 1L5W, 1LAX, 1LES, 1NE7, 1NSZ, 1OFC, 1OGO, 1OH3, 1OJK, 1P2D, 1PPF, 1Q2E, 1Q6C, 1Q6E, 1QFO, 1QJW, 1QSG, 1RPI, 1TYW, 1UA4, 1UH4, 1UKS, 1V2B, 1V3H, 1V3I, 1VEM, 1WDS, 1WLW, 1WPC, 1XIF, 1Y4C, 1Z32, 2A2Q, 2AER, 2ASV, 2ATI, 2B3B, 2BHY, 2BQP, 2BWA, 2BXY, 2BXZ, 2BY0, 2BY1, 2BY2, 2BY3, 2C3W, 2C4F, 2CN3, 2D3N, 2ESR, 2F2E, 2FH6, 2FH8, 2FHB, 2FHC, 2FHF, 2GJP, 2GVY, 2HIS, 2HYR, 2JJB, 2PYD, 2V8L, 2VJJ, 2VXJ, 2X85, 2XG9, 2Z8G, 2ZOX, 2ZYO, 3A4A, 3AXH, 3AZT, 3BLP, 3BMW, 3BZ4, 3C6S, 3CZG, 3DHP, 3F9M, 3FW3, 3GD9, 3HG3, 3L2M, 3LSM, 3MBP, 3MKK, 3O0W, 3OGR, 3OGS, 3OLE, 3OLI, 3S9C, 3SIT, 3T7O, 3TSA, 3U2V, 3U2W, 3UYL, 3V0W, 3VEV, 3VF6, 3VMO, 3W7S, 3WBA, 3WBE, 4AD4, 4AD5, 4AF9, 4AFC, 4AL9, 4B4R, 4DCH, 4DGR, 4DO6, 4H7V, 4ISE, 4KWU, 4MBP

145 in total

S32: Radii of gyration: averages, means and standard deviations

Averages (AVE), means and standard deviations of R_g from each 1 μs time window during each 10 μs simulation of **1**, **2**, and **3**

(1) Single-stranded amylose		
μs	**AVE**	**STDEV**
1	9.4	2.5
2	10.4	2.5
3	11.4	2.5
4	10.7	2.7
5	11.9	2.2
6	12.8	1.4
7	12.2	1.9
8	12.3	2.0
9	12.8	1.4
10	10.7	2.6
MEAN(1-10)	**11.5**	
STDEV(1-10)	**1.1**	

(2) Antiparallel double-helix		
μs	**AVE**	**STDEV**
1	12.7	1.0
2	13.6	0.8
3	13.8	0.7
4	13.5	1.0
5	13.4	0.8
6	12.8	1.0
7	13.2	0.8
8	12.8	0.8
9	12.9	0.8
10	13.0	1.0
MEAN(2-10)	**13.2**	
STDEV(2-10)	**0.3**	

(3) Parallel double-helix		
μs	**AVE**	**STDEV**
1	11.7	2.2
2	14.2	0.7
3	14.4	0.3
4	14.4	0.2
5	14.5	0.3
6	14.3	0.5
7	14.4	0.5
8	14.6	0.3
9	14.5	0.4
10	14.5	0.3
MEAN(2-10)	**14.4**	
STDEV(2-10)	**0.1**	

Underlined values indicate the initial 1 μs excluded for calculation of molecular properties for **2** and **3**

S33: Occupancy of the *anti* ψ geometry in each linkage from 10 and 20 μs simulations of **1**-**5**

Link	1	strandA 2	strandB 2	strandA 3	strandB 3	Hexa- 4	Tri- 5
1	0.9	0.7	1.1	1.2	0.5	0.0	0.1
2	1.6	0.3	1.1	0.0	0.0	0.1	1.9
3	0.9	0.2	0.0	3.5	0.0	1.7	
4	2.7	0.0	0.0	0.0	0.0	0.0	
5	2.9	0.0	0.0	0.0	0.0	8.8	
6	4.1	0.0	0.0	0.0	0.0		
7	2.0	0.0	0.0	0.0	0.1		
8	1.5	0.0	0.0	0.0	0.0		
9	1.5	0.0	0.0	0.0	0.3		
10	1.0	0.2	0.0	0.0	0.0		
11	1.5	0.2	0.5	0.3	0.0		

Table reports percentage residence of negative glycosidic ψ torsion values (derived from time series).

Linkages are numbered from the reducing end.

S34: Classification of the 38 canonical pyranose ring puckers

4C1	-1	<	θ°	<	36	&	-16	<	ϕ°	<	345
OE	36	<	θ°	<	72	&	-16	<	ϕ°	<	15
OH1	36	<	θ°	<	72	&	15	<	ϕ°	<	45
E1	36	<	θ°	<	72	&	45	<	ϕ°	<	75
2H1	36	<	θ°	<	72	&	75	<	ϕ°	<	105
2E	36	<	θ°	<	72	&	105	<	ϕ°	<	135
2H3	36	<	θ°	<	72	&	135	<	ϕ°	<	165
E3	36	<	θ°	<	72	&	165	<	ϕ°	<	195
4H3	36	<	θ°	<	72	&	195	<	ϕ°	<	225
4E	36	<	θ°	<	72	&	225	<	ϕ°	<	255
4H5	36	<	θ°	<	72	&	255	<	ϕ°	<	285
E5	36	<	θ°	<	72	&	285	<	ϕ°	<	315
OH5	36	<	θ°	<	72	&	315	<	ϕ°	<	345
3OB	72	<	θ°	<	108	&	-16	<	ϕ°	<	15
3S1	72	<	θ°	<	108	&	15	<	ϕ°	<	45
B14	72	<	θ°	<	108	&	45	<	ϕ°	<	75
5S1	72	<	θ°	<	108	&	75	<	ϕ°	<	105
25B	72	<	θ°	<	108	&	105	<	ϕ°	<	135
2SO	72	<	θ°	<	108	&	135	<	ϕ°	<	165
B3O	72	<	θ°	<	108	&	165	<	ϕ°	<	195
1S3	72	<	θ°	<	108	&	195	<	ϕ°	<	225
14B	72	<	θ°	<	108	&	225	<	ϕ°	<	255
1S5	72	<	θ°	<	108	&	255	<	ϕ°	<	285
B25	72	<	θ°	<	108	&	285	<	ϕ°	<	315
OS2	72	<	θ°	<	108	&	315	<	ϕ°	<	345
EO	108	<	θ°	<	144	&	-16	<	ϕ°	<	15
1HO	108	<	θ°	<	144	&	15	<	ϕ°	<	45
1E	108	<	θ°	<	144	&	45	<	ϕ°	<	75
1H2	108	<	θ°	<	144	&	75	<	ϕ°	<	105
E2	108	<	θ°	<	144	&	105	<	ϕ°	<	135
3H2	108	<	θ°	<	144	&	135	<	ϕ°	<	165
3E	108	<	θ°	<	144	&	165	<	ϕ°	<	195
3H4	108	<	θ°	<	144	&	195	<	ϕ°	<	225
E4	108	<	θ°	<	144	&	225	<	ϕ°	<	255
5H4	108	<	θ°	<	144	&	255	<	ϕ°	<	285
5E	108	<	θ°	<	144	&	285	<	ϕ°	<	315
5HO	108	<	θ°	<	144	&	315	<	ϕ°	<	345
1C4	144	<	θ°	<	180	&	-16	<	ϕ°	<	345

θ and ϕ are the Cremer-Pople azimuthal and meridian angles, respectively.