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Supporting Information

Reinvestigation of the Internal Glycan Rearrangement of Lewis a and Blood Group Type 1 Epitopes

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Table S1: Unique Conformers after CREST search. The highlighted rows indicate conformers that increased number of unique structures after the second search.

Bond Configuration	Search 1	Search 2	Combined
Fuc_a12a	64	69	37
Fuc_a12b	36	35	23
Fuc_a13a	39	63	59
Fuc_a13b	33	33	29
Fuc_a14a	62	20	34
Fuc_a14b	**47**	**39**	**48**
Fuc_a16a	23	51	30
Fuc_a16b	**39**	**40**	**40**
Fuc_an12a	54	62	46
Fuc_an12b	49	74	45
Fuc_an14a	85	34	70
Fuc_an14b	23	27	11
Fuc_an16a	37	87	74
Fuc_an16b	32	31	28
Fuc_b12a	**79**	**77**	**109**
Fuc_b12b	24	13	19
Fuc_b13a	45	28	45
Fuc_b13b	**54**	**63**	**64**
Fuc_b14a	13	24	20
Fuc_b14b	19	17	18
Fuc_b16a	22	18	15
Fuc_b16b	58	52	58
Fuc_bn12a	96	88	96
Fuc_bn12b	**109**	**87**	**112**
Fuc_bn14a	19	23	19
Fuc_bn14b	73	54	67
Fuc_bn16a	**65**	**87**	**116**
Fuc_bn16b	**82**	**142**	**150**

Table S2: Summary of the number of the individual DFT optimizations in 6-31+G(d,p) basis set (small basis, **SB**), and optimizations + frequency calculations in 6-311+G(d,p) basis set (large basis, **LB**).

Anomer		**alpha**				**beta**			
Bond configuration		**alpha**		**beta**		**alpha**		**beta**	
Fuc Bond		**SB**	**LB**	**SB**	**LB**	**SB**	**LB**	**SB**	**LB**
1-2	**GlcNAc**	46	13	96	22	45	9	112	11
1-4	**GlcNAc**	70	28	19	13	11	6	67	30
1-6	**GlcNAc**	74	37	116	35	28	18	150	41
1-2	**Gal**	37	15	109	66	23	13	19	8
1-3	**Gal**	58	25	45	23	29	13	64	30
1-4	**Gal**	34	17	20	9	48	23	18	7
1-6	**Gal**	30	14	15	7	37	15	58	34
Sum		497	193	420	175	221	97	488	161

Table S3: Benchmark results of most stable conformers of eight molecule's relative free energies based on several functionals with the Mean Absolute Error (MAE) values.

	a12a	**a16a**	**an14a**	**bn16a**	**a12b**	**a16b**	**an14b**	**bn16b**	**MAE**
B3LYP	6.1	6.5	4.6	4.3	5.2	0.0	4.3	7.6	**4.8**
B3LYP+D3	0.5	0.6	0.6	0.5	0.7	0.0	0.5	0.7	**0.5**
PBE1PBE	4.0	4.3	3.1	2.8	3.6	0.0	3.2	5.3	**3.3**
PBE1PBE+D3	0.4	0.4	0.5	0.0	0.7	0.0	0.6	0.1	**0.3**
M062x	0.9	0.3	0.5	0.2	0.8	0.0	0.1	0.4	**0.4**
M06	1.5	1.4	1.8	0.6	1.6	0.0	0.4	1.1	**1.0**
wB97XD	1.0	1.0	0.6	1.3	0.9	0.0	0.2	1.3	**0.8**
HSEH1PBE	3.8	3.9	3.0	2.5	3.6	0.0	3.0	5.2	**3.1**
X3LYP	5.4	5.7	4.0	3.8	4.7	0.0	3.8	6.8	**4.3**
M11	2.8	1.8	1.8	2.0	2.1	0.0	0.8	3.2	**1.8**
MN15	2.9	0.7	1.8	0.8	2.2	0.0	0.4	2.1	**1.4**
CAM-B3LYP	4.1	4.2	2.8	2.5	3.5	0.0	2.8	5.2	**3.1**

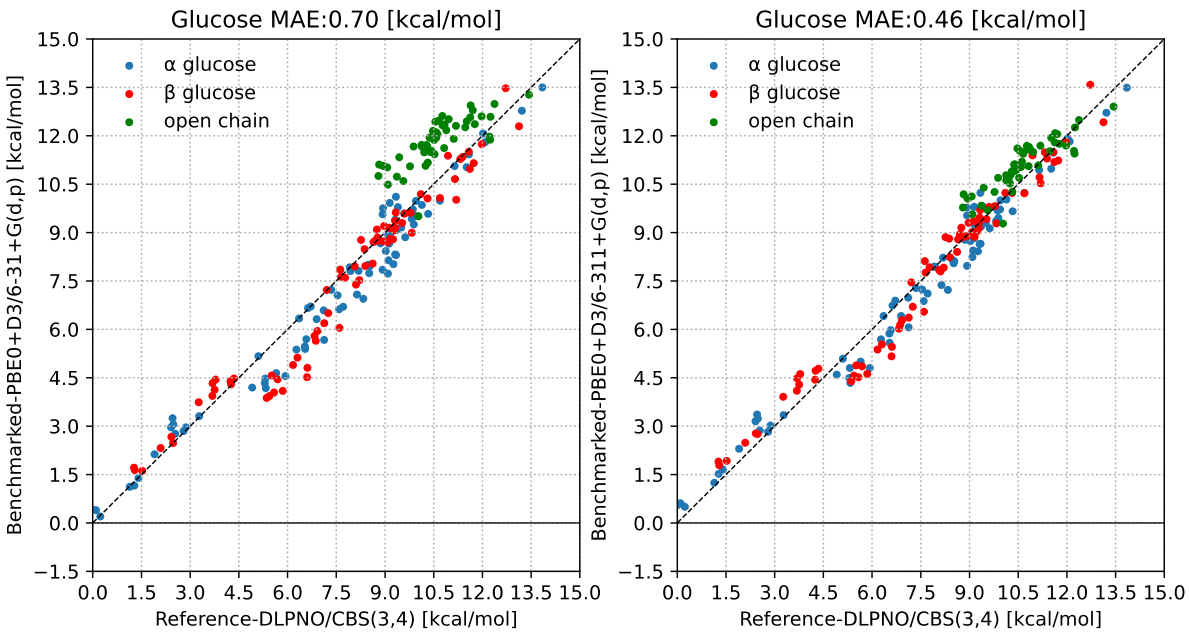

Figure S1: DLPNO/CBS(3,4) energies on x-axis, compared with PBE0+D3/6-31+G(d,p) and PBE0+D3/6-311+G(d,p) energies on y-axis for glucose, respectively. The relative energies (in kcal/mol) are calculated with respect to the lowest-energy conformer. The mean absolute error (MAE) between the two data sets, which includes a shift along the y-axis, is shown above.

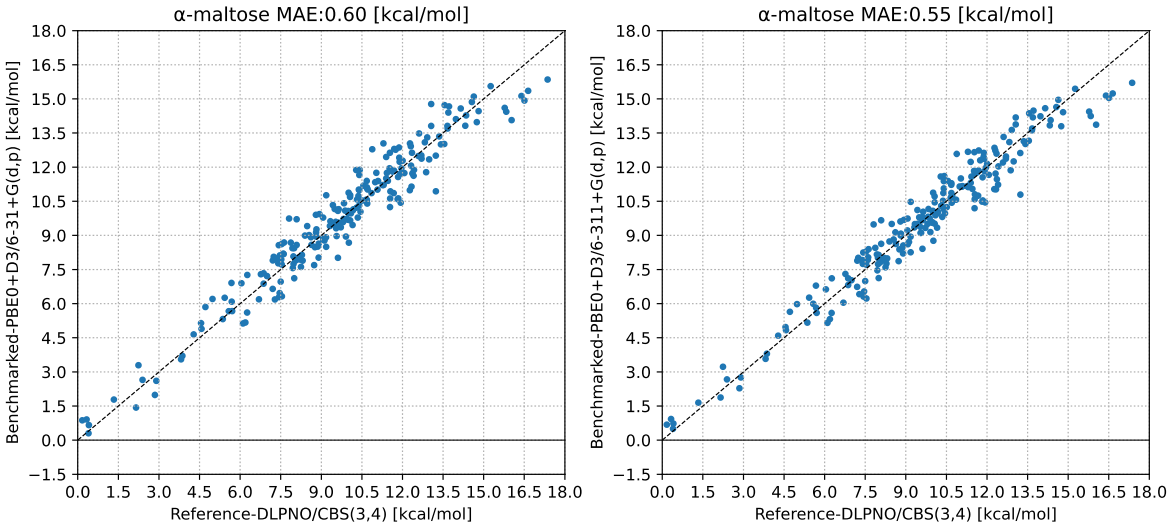

Figure S2: DLPNO/CBS(3,4) energies on x-axis, compared with PBE0+D3/6-31+G(d,p) and PBE0+D3/6-311+G(d,p) energies on y-axis for *α*-maltose, respectively. The relative energies (in kcal/mol) are calculated with respect to the lowest-energy conformer. The mean absolute error (MAE) between the two data sets, which includes a shift along the y-axis, is shown above.

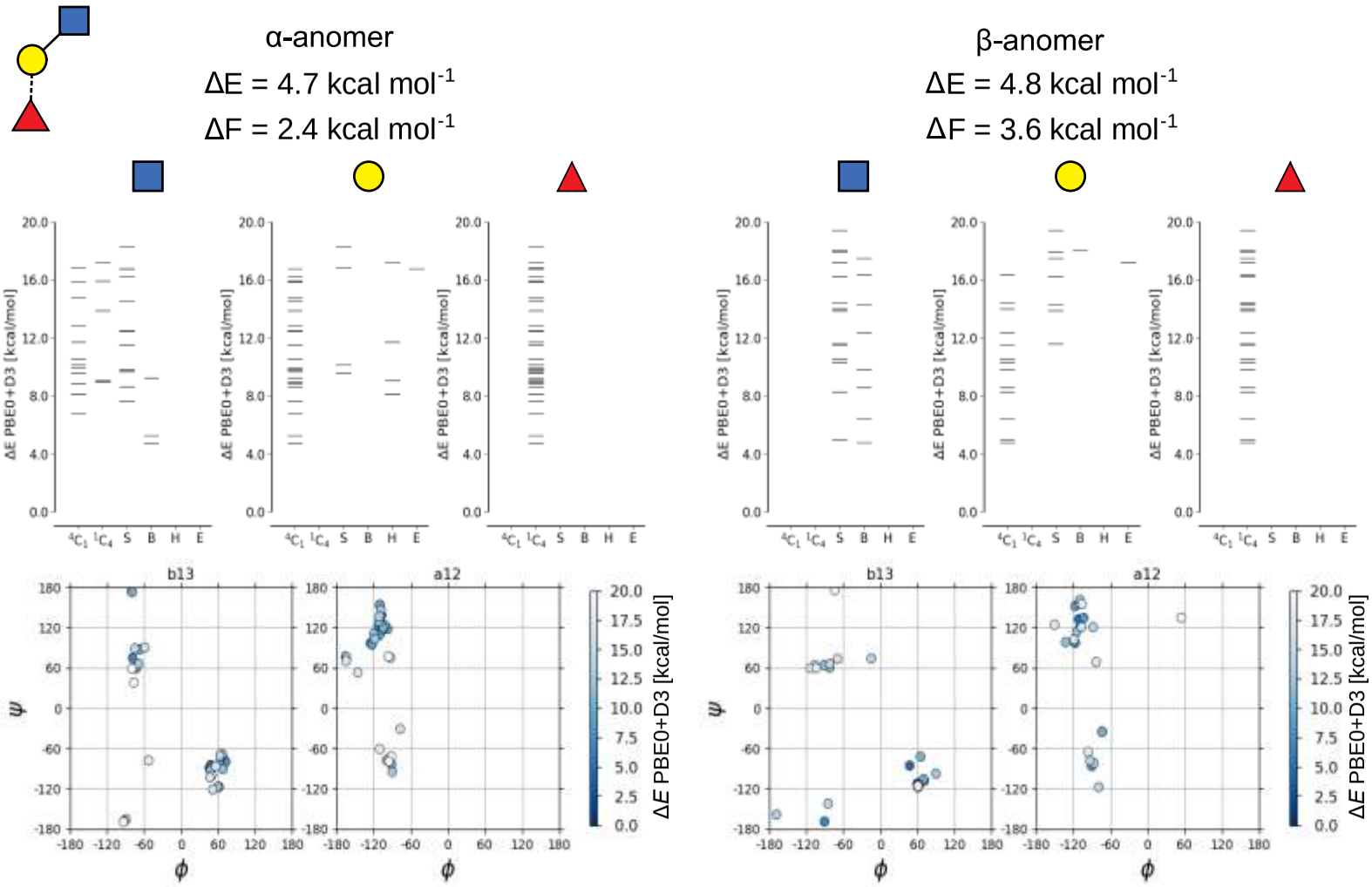

Figure S3:(Top) A comparison is made between the individual ring puckers of the **[BG-H1+H]+** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations. (Bottom) The plots illustrate the distributions of the two glycosidic bond angles between each monomer. The b13 angle corresponds to the bond between GlcNAc and Gal, while the a12 angle represents the bond between Fuc and Gal.

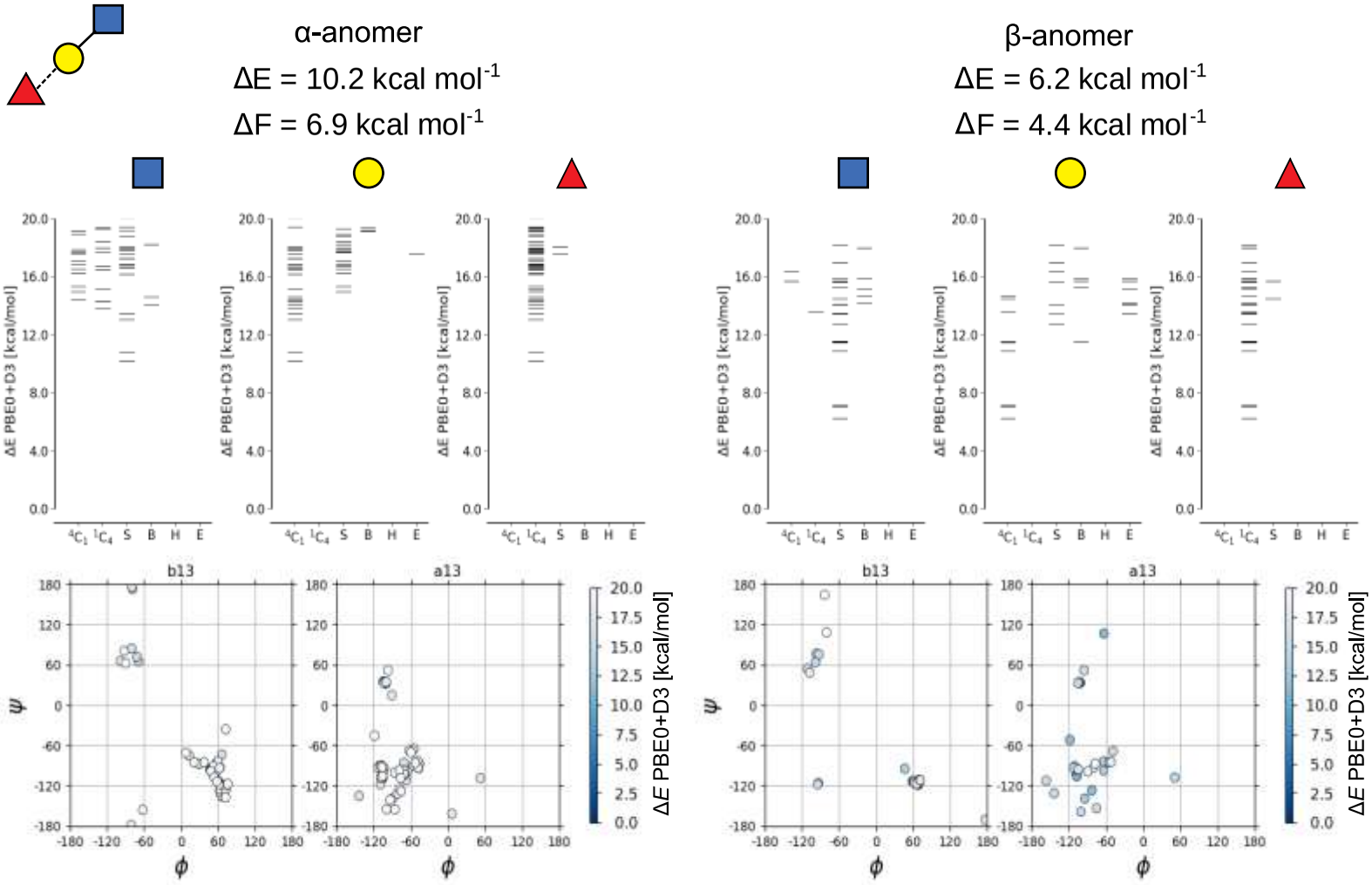

Figure S4: (Top) A comparison is made between the individual ring puckers of the **Fucα(1 → 3)Galβ(1 → 3)GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations.(Bottom) The plots illustrate the distributions of the two glycosidic bond angles between each monomer. The b13 angle corresponds to the bond between GlcNAc and Gal, while the a13 angle represents the bond between Fuc and Gal

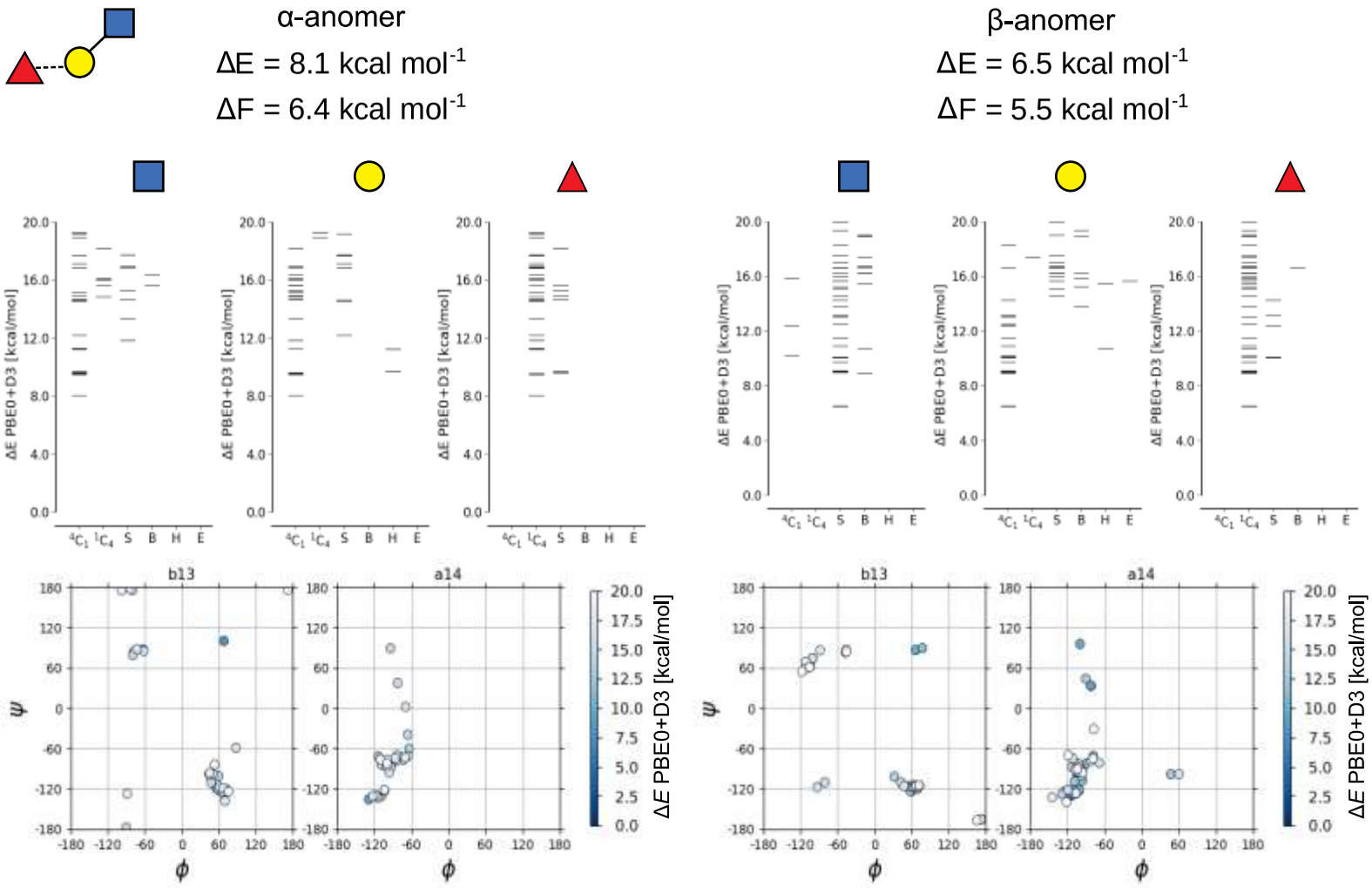

Figure S5: (Top) A comparison is made between the individual ring puckers of the **Fucα(1 → 4)Galβ(1 → 3)GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations.(Bottom) The plots illustrate the distributions of the two glycosidic bond angles between each monomer. The b13 angle corresponds to the bond between GlcNAc and Gal, while the a14 angle represents the bond between Fuc and Gal.

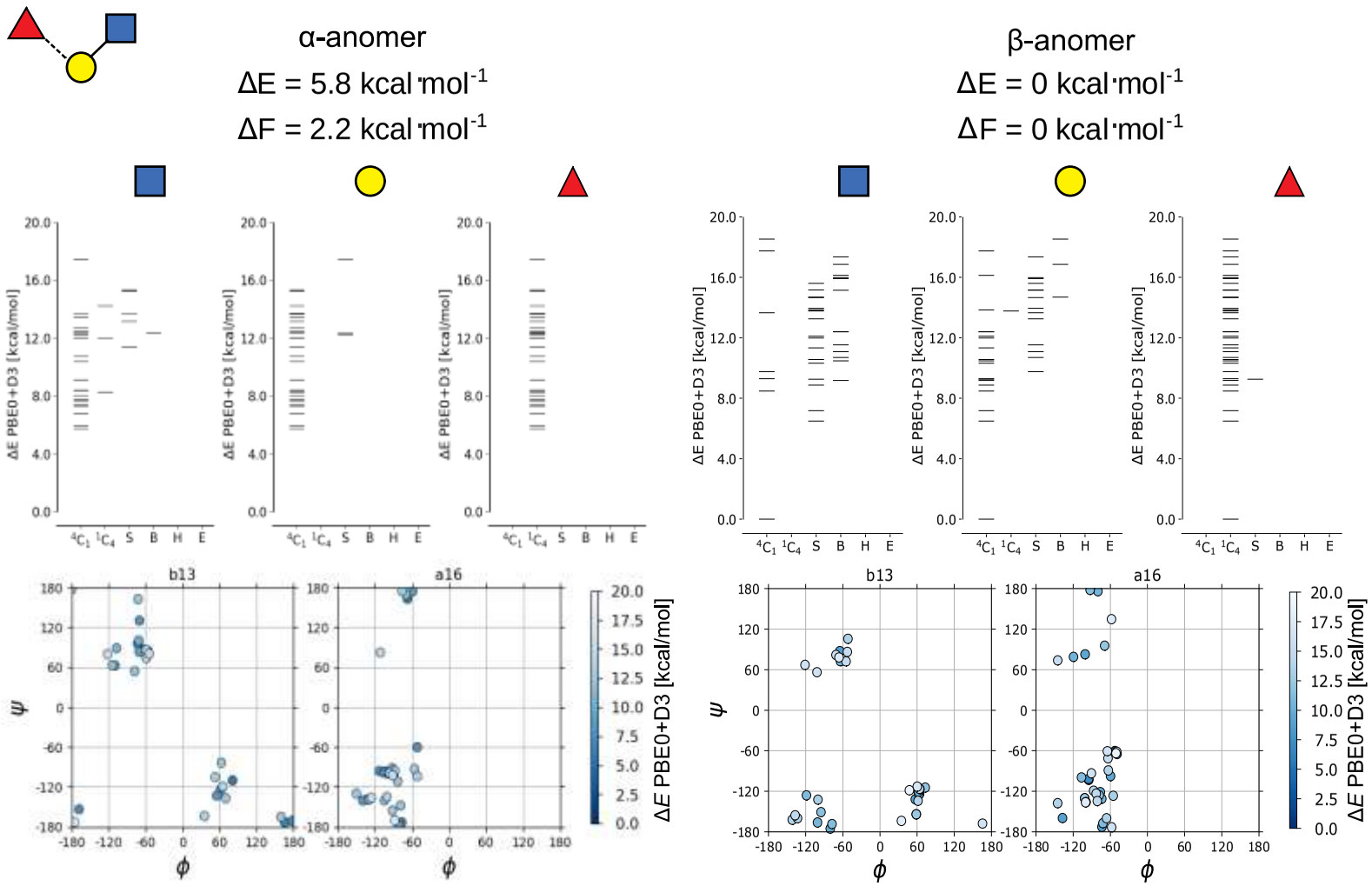

Figure S6: (Top) A comparison is made between the individual ring puckers of the **Fucα(1 → 6)Galβ(1 → 3)GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations.(Bottom) The plots illustrate the distributions of the two glycosidic bond angles between each monomer. The b13 angle corresponds to the bond between GlcNAc and Gal, while the a16 angle represents the bond between Fuc and Gal

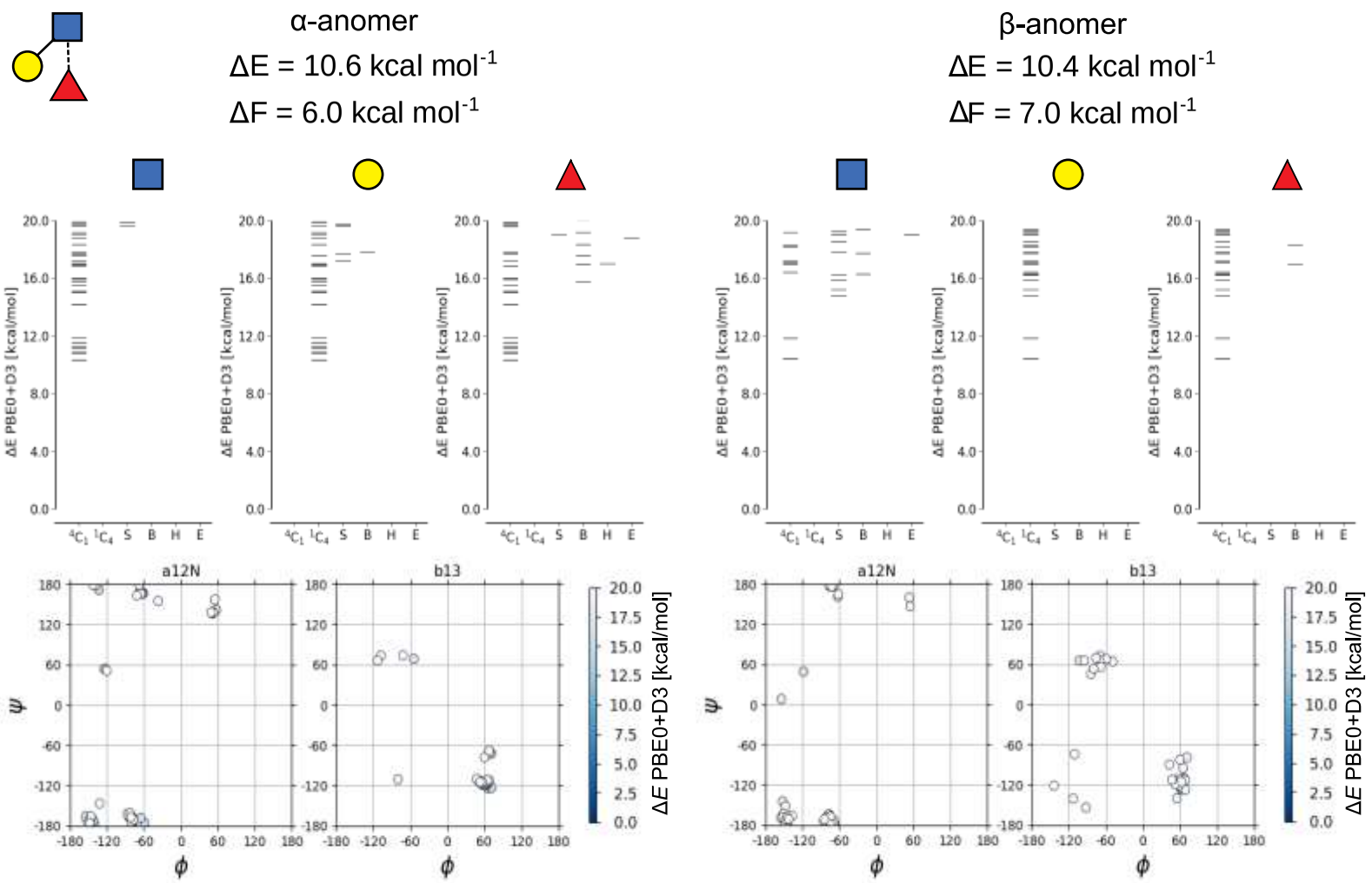

Figure S7: (Top) A comparison is made between the individual ring puckers of the **Galβ(1 → 3)[Fucα(1 → 2)]GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations.(Bottom) Distributions of the two glycosidic bonds angles between each monomer. The b13 corresponds to the bond between the GlcNAc and Gal, and a12 to the bond between Fuc and GlcNAc

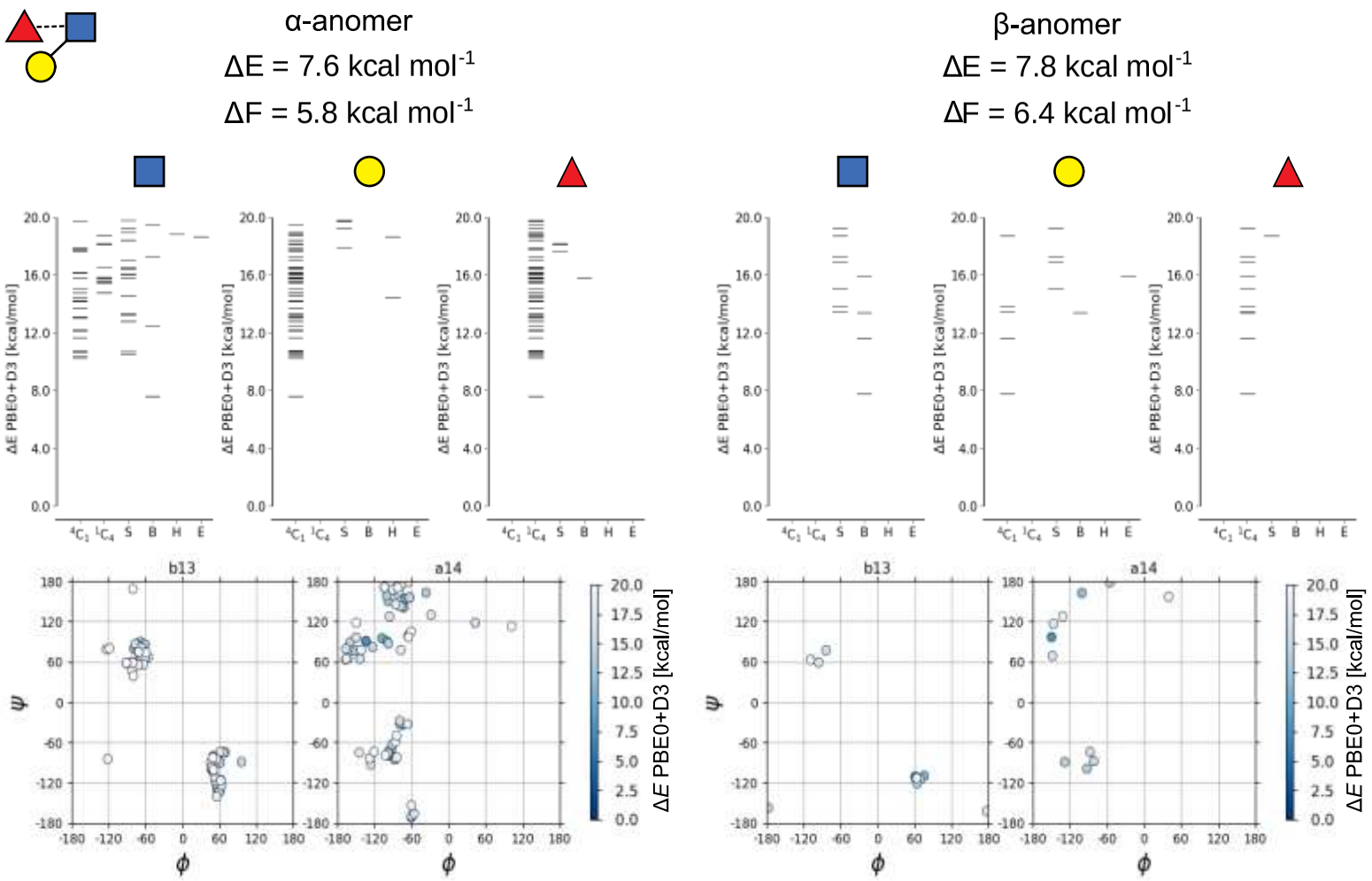

Figure S8: (Top) A comparison is made between the individual ring puckers of the **[Le^a+H]$^+$** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations.(Bottom) Distributions of the two glycosidic bonds angles between each monomer. The b13 corresponds to the bond between the GlcNAc and Gal, and a14 to the bond between Fuc and GlcNAc

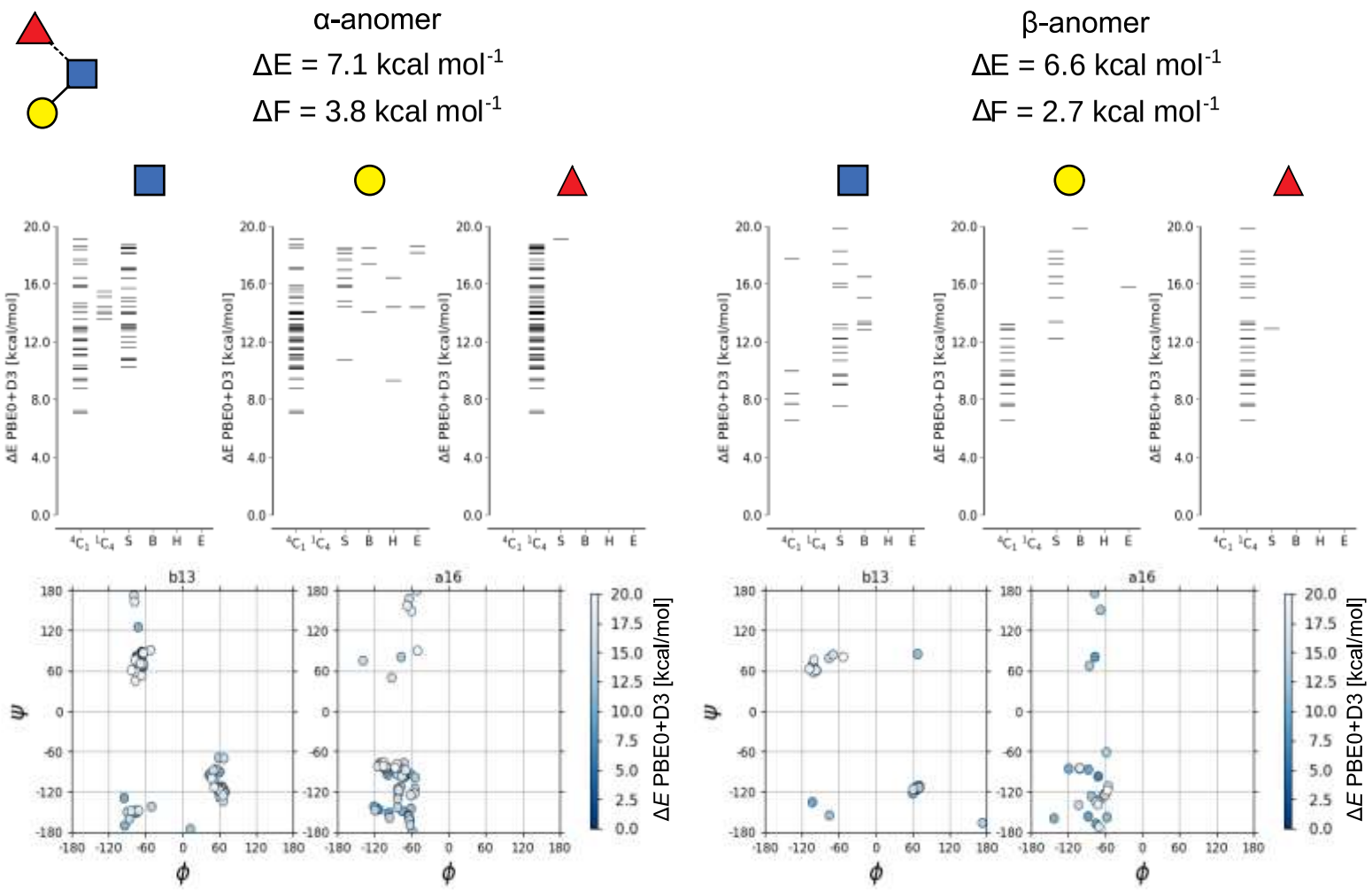

Figure S9: (Top) A comparison is made between the individual ring puckers of the **Galβ(1 → 3)[Fucα(1 → 6)]GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations. (Bottom) Distributions of the two glycosidic bonds angles between each monomer. The b13 corresponds to the bond between the GlcNAc and Gal, and a16 to the bond between Fuc and GlcNAc.

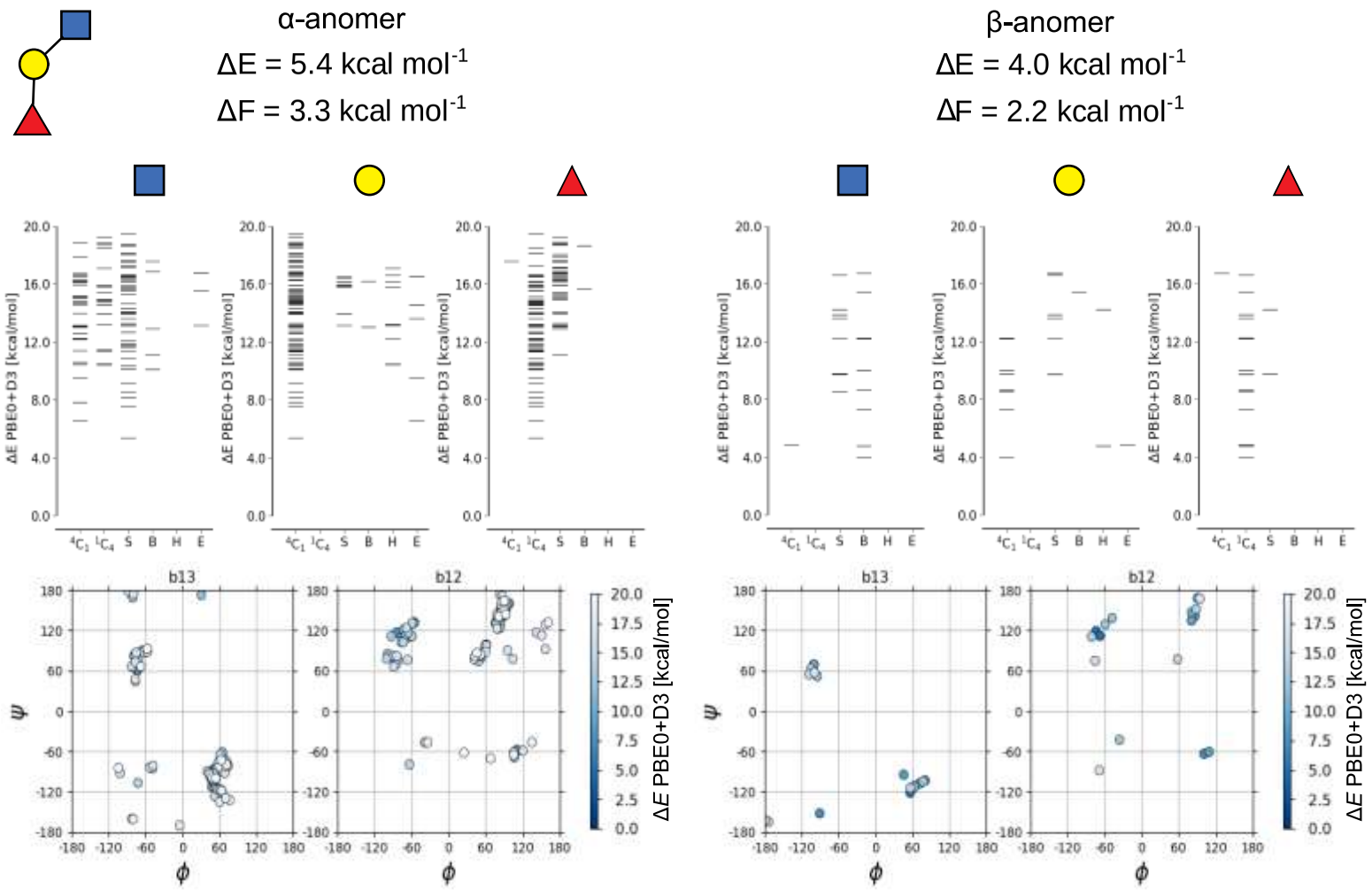

Figure S10: (Top) A comparison is made between the individual ring puckers of the **Fucβ(1 → 2)Galβ(1 → 3)GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations. (Bottom) Distributions of the two glycosidic bonds angles between each monomer. The b13 corresponds to the bond between the GlcNAc and Gal, and b12 to the bond between Fuc and Gal.

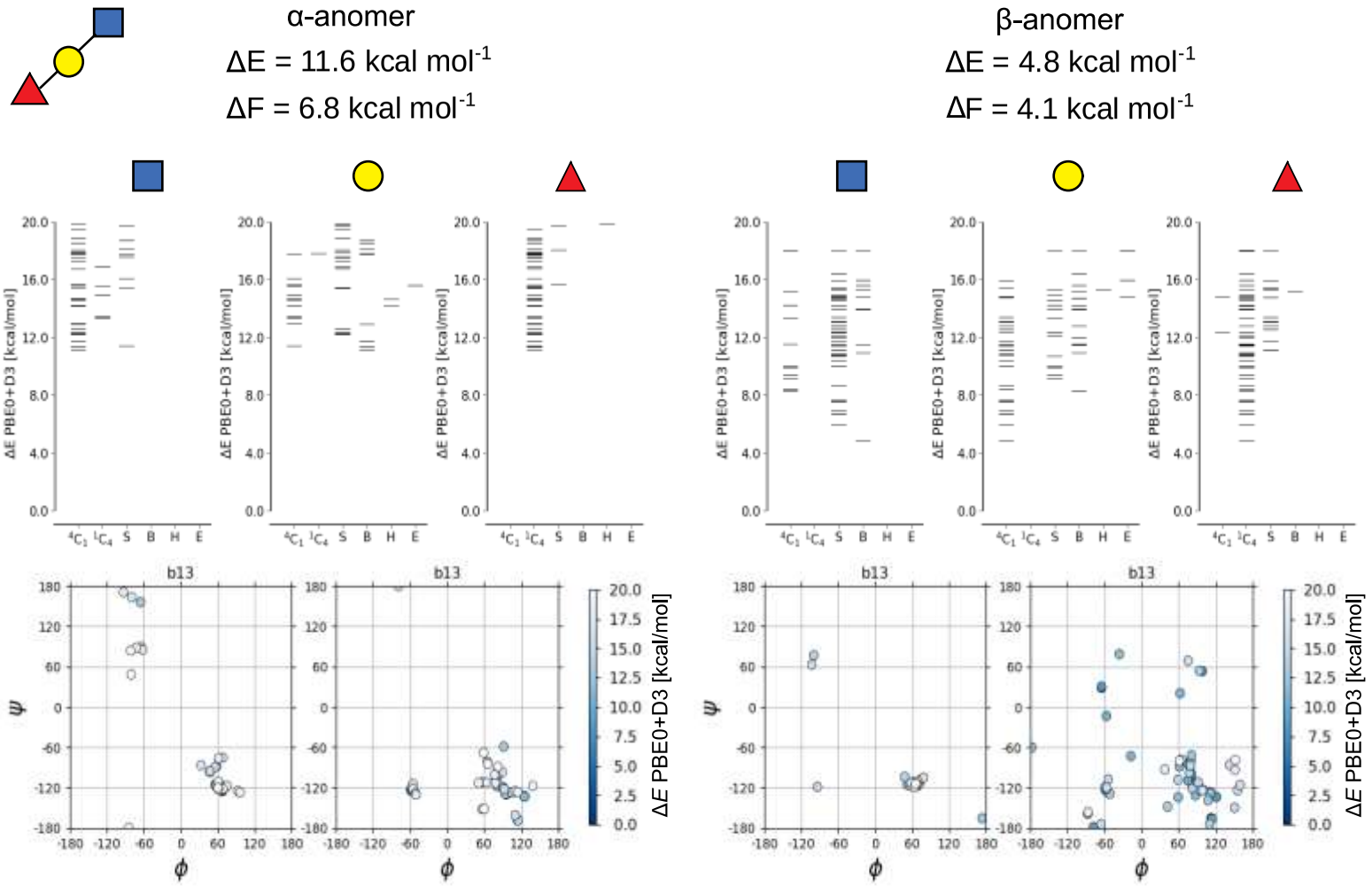

Figure S11: (Top) A comparison is made between the individual ring puckers of the **Fucβ(1 → 3)Galβ(1 → 3)GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations. (Bottom) Distributions of the two glycosidic bonds angles between each monomer. The b13 corresponds to the bond between the GlcNAc and Gal, and b13 to the bond between Fuc and Gal.

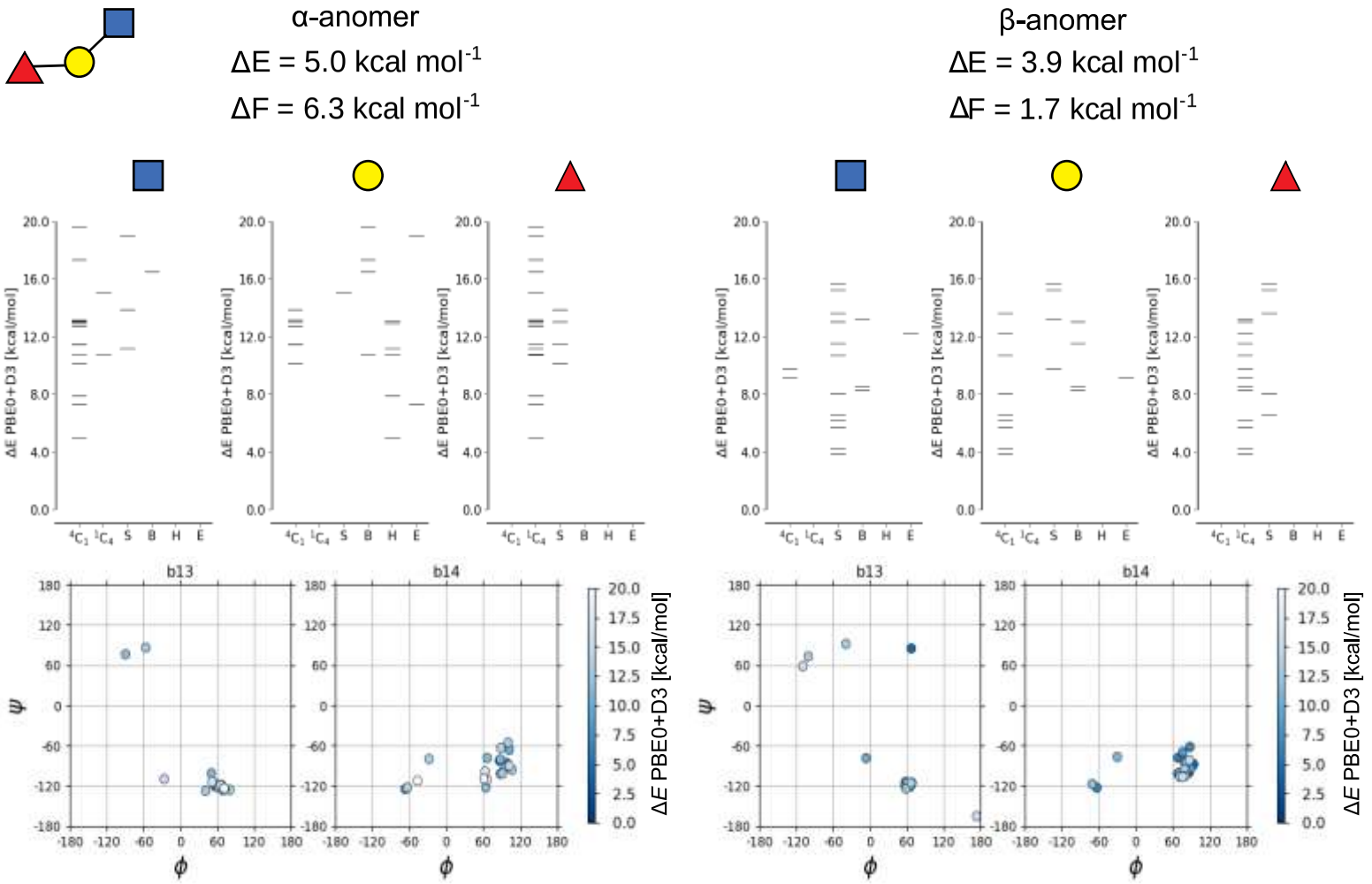

Figure S12: (Top) A comparison is made between the individual ring puckers of the **Fucβ(1 → 4)Galβ(1 → 3)GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations.(Bottom) Distributions of the two glycosidic bonds angles between each monomer. The b13 corresponds to the bond between the GlcNAc and Gal, and b14 to the bond between Fuc and Gal.

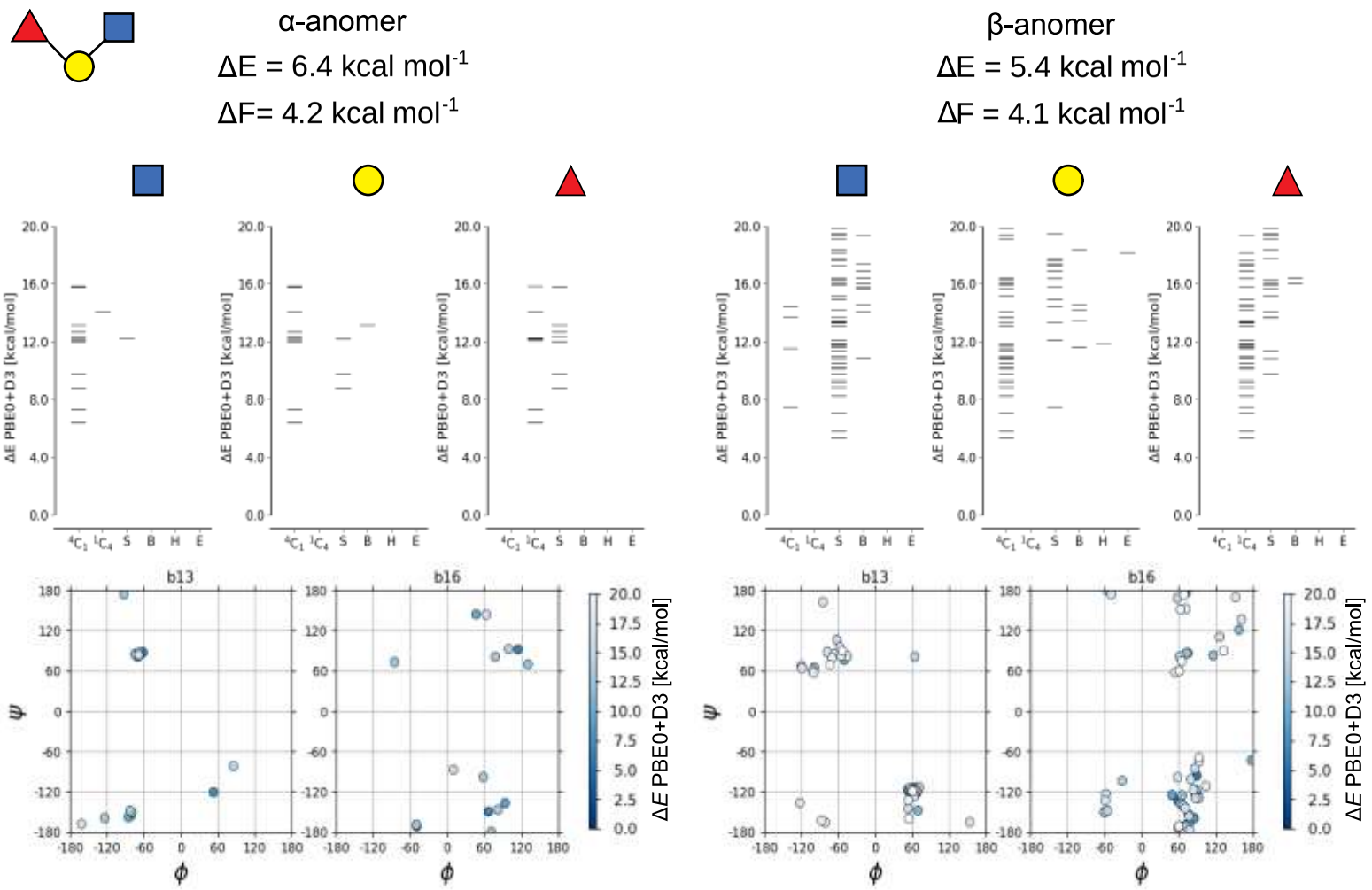

Figure S13: (Top) A comparison is made between the individual ring puckers of the **Fucβ(1 → 6)Galβ(1 → 3)GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations.(Bottom) Distributions of the two glycosidic bonds angles between each monomer. The b13 corresponds to the bond between the GlcNAc and Gal, and b16 to the bond between Fuc and Gal.

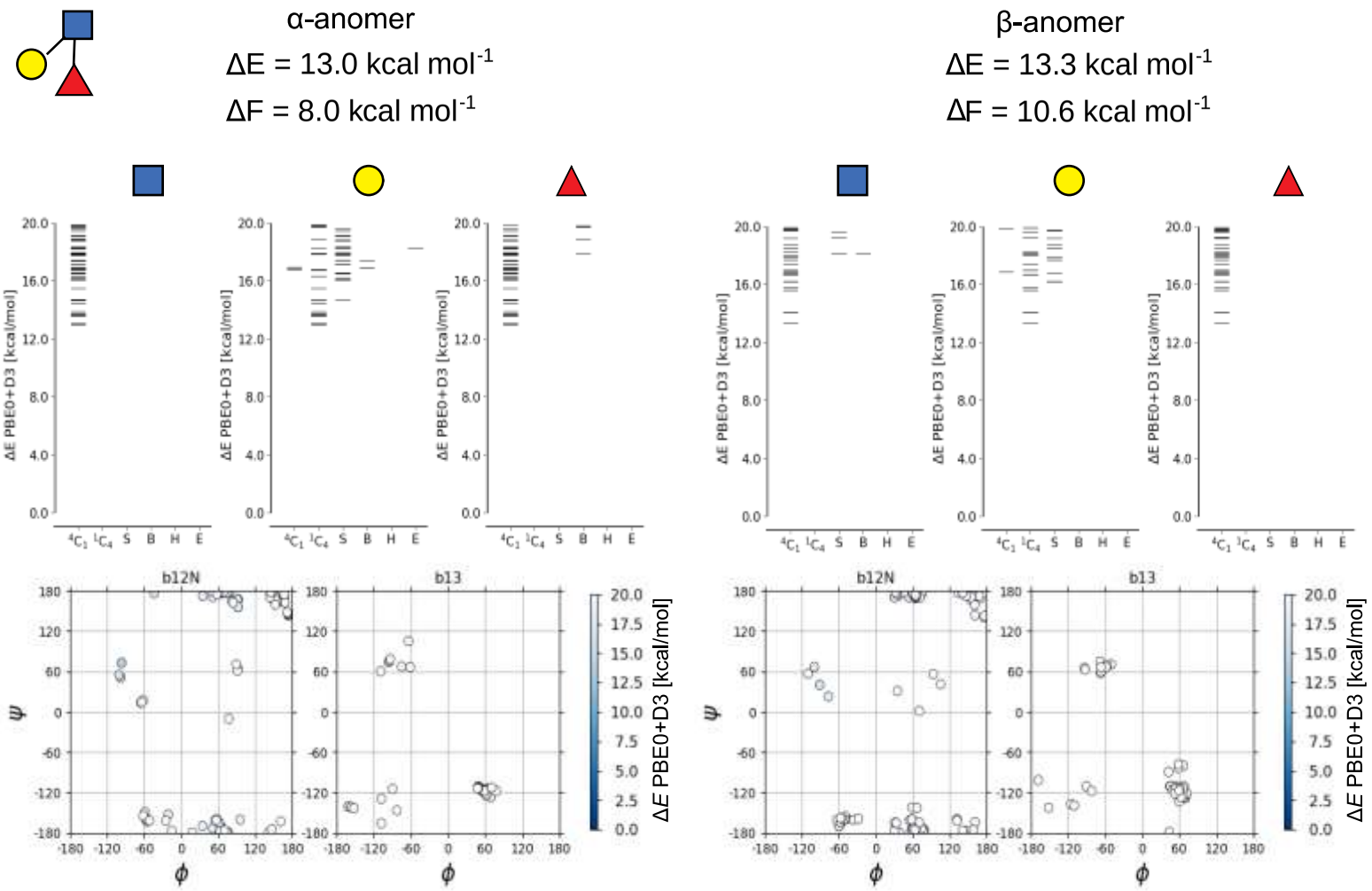

Figure S14: (Top) A comparison is made between the individual ring puckers of the **Galβ(1 → 3)[Fucβ(1 → 2)]GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations.(Bottom) Distributions of the two glycosidic bonds angles between each monomer. The b13 corresponds to the bond between the GlcNAc and Gal, and b12 to the bond between Fuc and

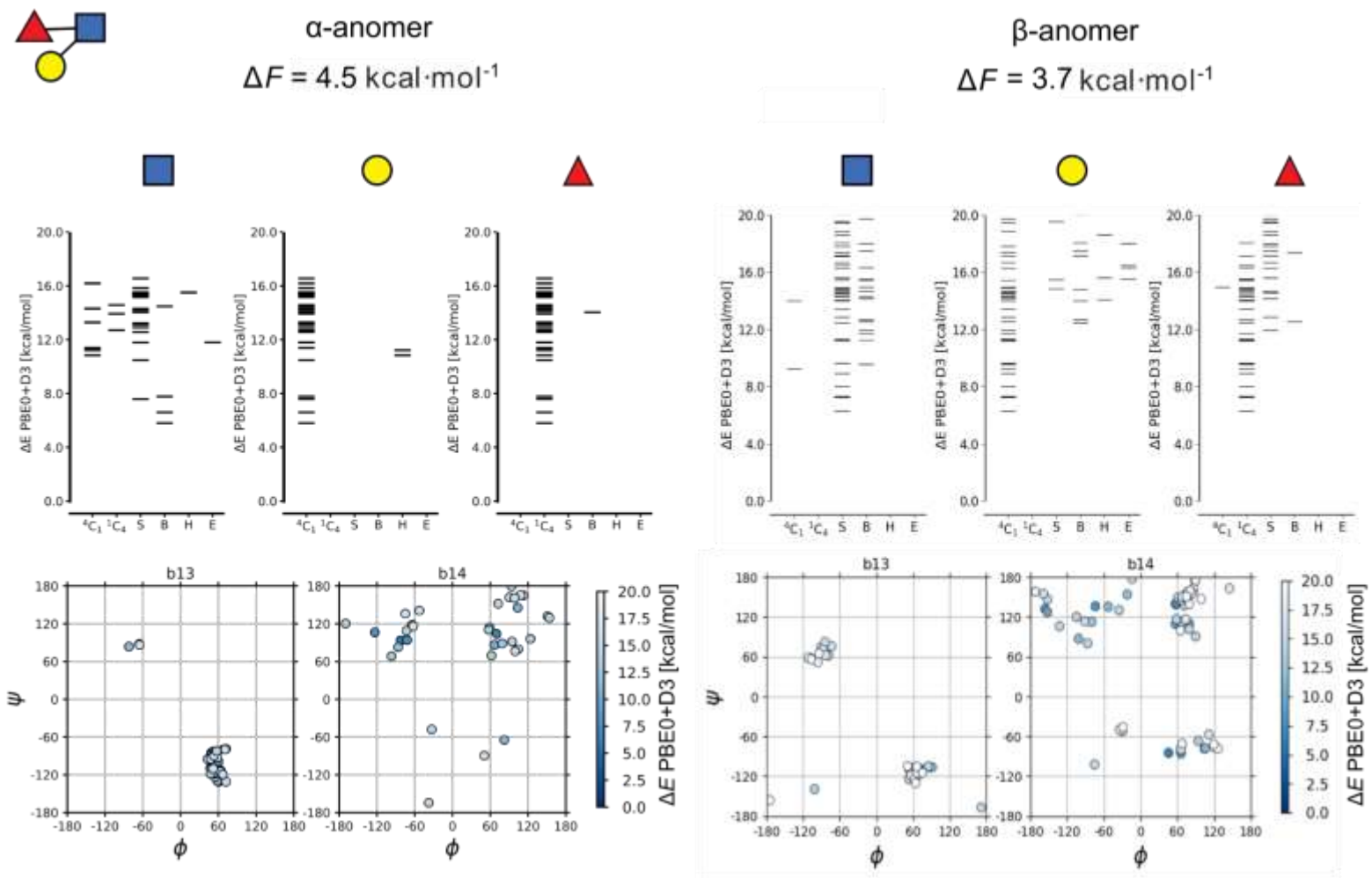

Figure S15: (Top) A comparison is made between the individual ring puckers of the **Galβ(1 → 3)[Fucβ(1 → 4)]GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations.(Bottom) Distributions of the two glycosidic bonds angles between each monomer. The b13 corresponds to the bond between the GlcNAc and Gal, and b14 to the bond between Fuc and

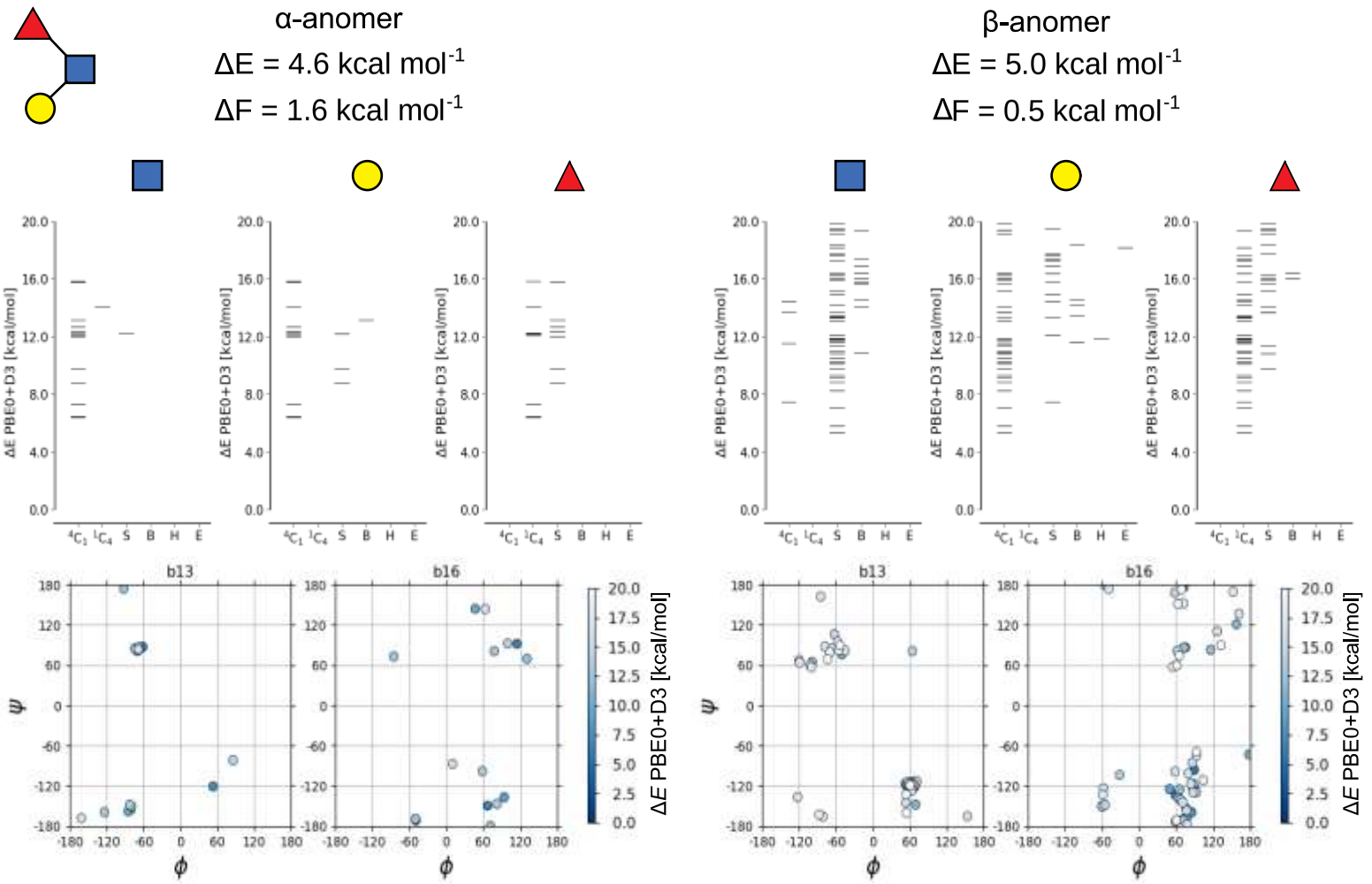

Figure S16: (Top) A comparison is made between the individual ring puckers of the **Galβ(1 → 3)[Fucβ(1 → 6)]GlcNAc** ions and their relative energy with respect to the lowest energy conformer of **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ions. The energy calculations were performed using the PBE0+D3/6-31+(d,p) level of theory. The left plot displays the α-anomer, while the right plot shows the β-anomer. The top portion of each plot indicates the relative energy of the lowest energy conformer (ΔE), while the ΔF value represents the free energy of the ions after higher level theory calculations.(Bottom) Distributions of the two glycosidic bonds angles between each monomer. The b13 corresponds to the bond between the GlcNAc and Gal, and b16 to the bond between Fuc and

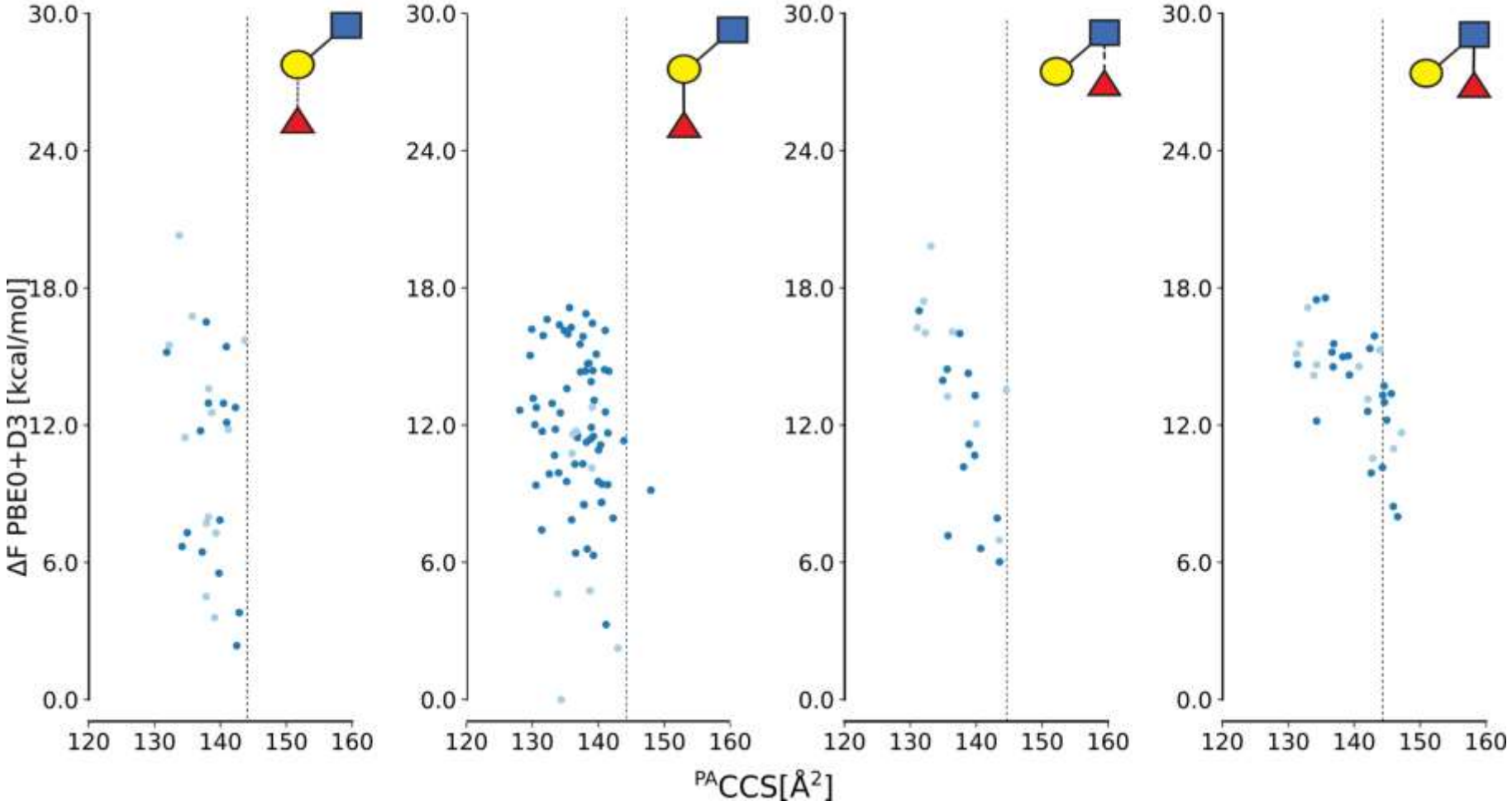

Figure S17: The ^{PA}CCS vs. relative free-energy in a larger 6-311+G(d,p) basis set, evaluated at 300 K of both anomers of ions of respectively: **Fuc*α*(1 → 2)Galβ(1 → 3)GlcNAc, Fucβ (1 → 2)Galβ(1 → 3)GlcNAc, Galβ(1 → 3)[Fuc*α*(1 → 2)]GlcNAc, Galβ(1 → 3)[Fuc*α*(1 → 2)]GlcNAc.** The glycan is shown using SNFG notation above the plots. The y-axis shows the free energy relatively to the lowest free energy conformer of the **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ion**.** The dashed line represents the experimental $^{DT}CCS_{He}$. The conformers highlighted with dark blue represent ***α*** *and light blue* ***β*** *anomers.*

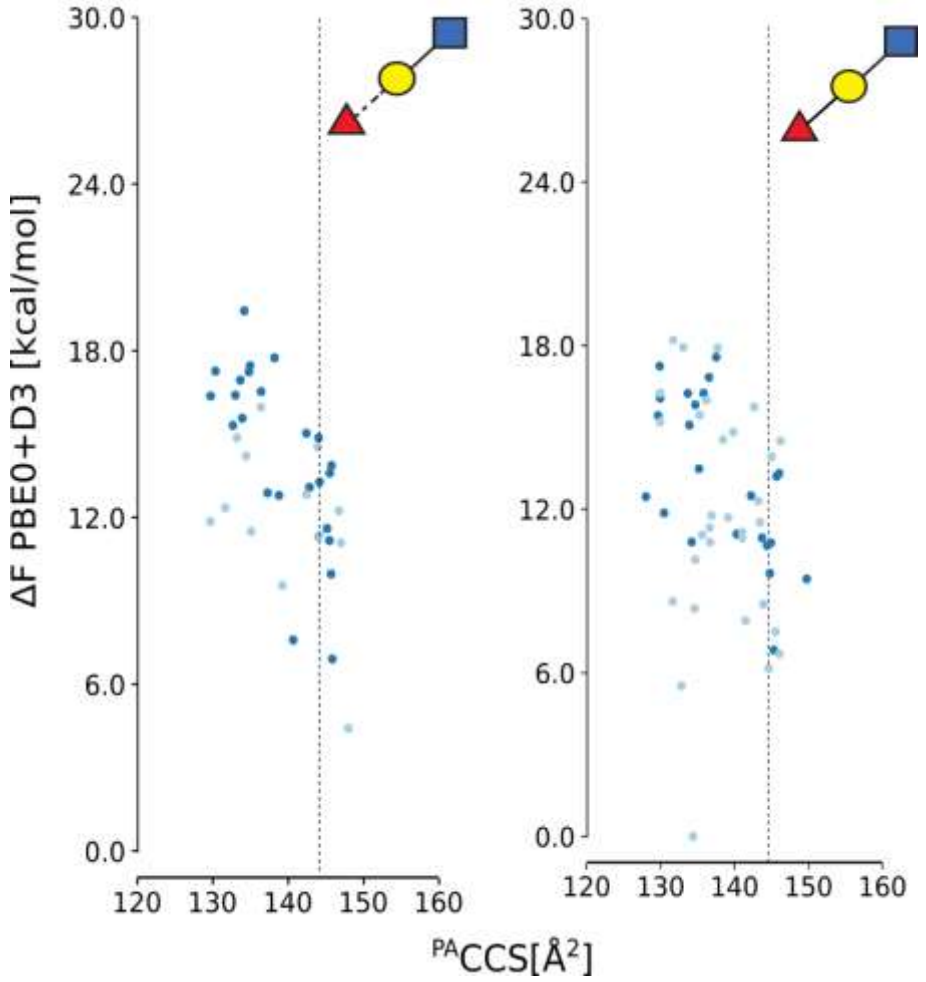

Figure S18: The ^{PA}CCS vs. relative free-energy in a larger 6-311+G(d,p) basis set, evaluated at 300 K of both anomers of ions of respectively: **Fuc*α*(1 → 3)Galβ(1 → 3)GlcNAc, Fucβ (1 → 3)Galβ(1 → 3)GlcNAc,.** The glycan is shown using SNFG notation above the plots. The y-axis shows the free energy relatively to the lowest free energy conformer of the **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ion**.** The dashed line represents the experimental $^{DT}CCS_{He}$. The conformers highlighted with dark blue represent ***α*** *and light blue* ***β*** *anomers.*

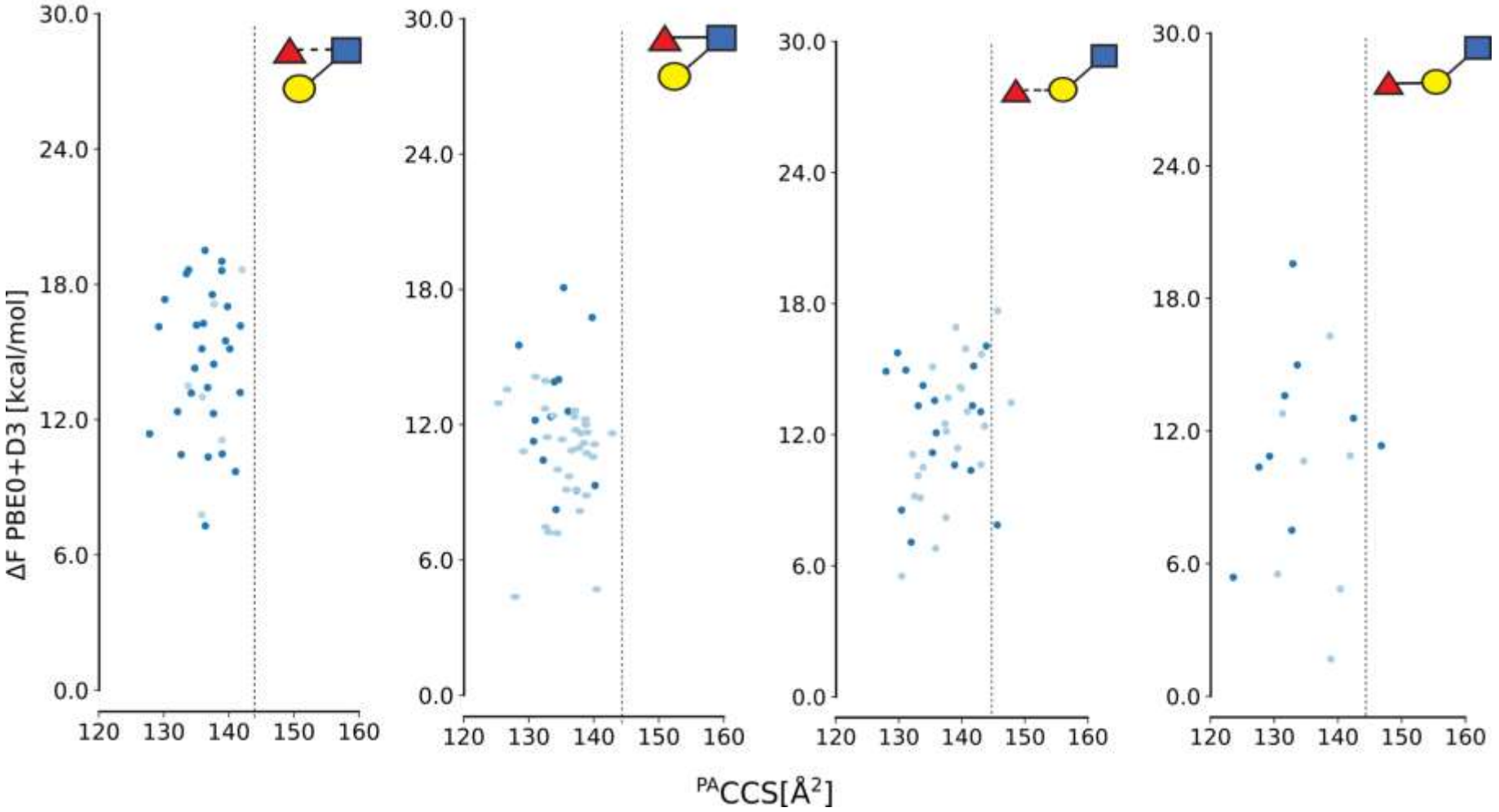

Figure S19: The ^{PA}CCS vs. relative free-energy in a larger 6-311+G(d,p) basis set, evaluated at 300 K of both anomers of ions of respectively: **Fuc*α*(1 → 4)Galβ(1 → 3)GlcNAc, Fucβ (1 → 4)Galβ(1 → 3)GlcNAc, Galβ(1 → 3)[Fuc*α*(1 → 4)]GlcNAc, Galβ(1 → 3)[Fuc*α*(1 → 4)]GlcNAc.** The glycan is shown using SNFG notation above the plots. The y-axis shows the free energy relatively to the lowest free energy conformer of the **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ion**.** The dashed line represents the experimental $^{DT}CCS_{He}$. The conformers highlighted with dark blue represent ***α*** *and light blue* ***β*** *anomers.*

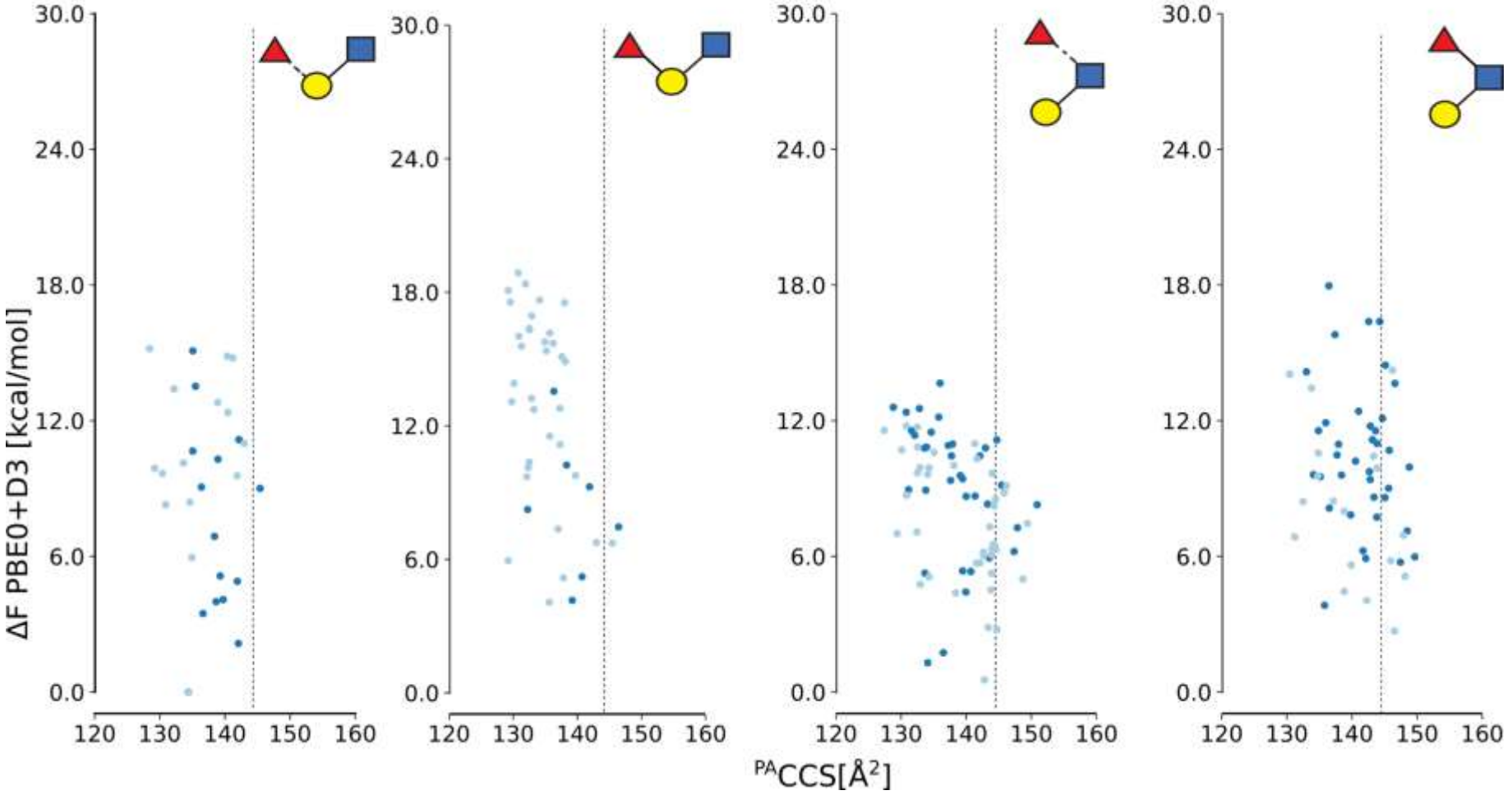

Figure S20: The ^{PA}CCS vs. relative free-energy in a larger 6-311+G(d,p) basis set, evaluated at 300 K of both anomers of ions of respectively: **Fuc*α*(1 → 6)Galβ(1 → 3)GlcNAc, Fucβ (1 → 6)Galβ(1 → 3)GlcNAc, Galβ(1 → 3)[Fuc*α*(1 → 6)]GlcNAc, Galβ(1 → 4)[Fuc*α*(1 → 6)]GlcNAc.** The glycan is shown using SNFG notation above the plots. The y-axis shows the free energy relatively to the lowest free energy conformer of the **Fucα(1 → 6)Galβ(1 → 3)GlcNAcβ** ion**.** The dashed line represents the experimental $^{DT}CCS_{He}$. The conformers highlighted with dark blue represent ***α*** *and light blue* ***β*** *anomers.*

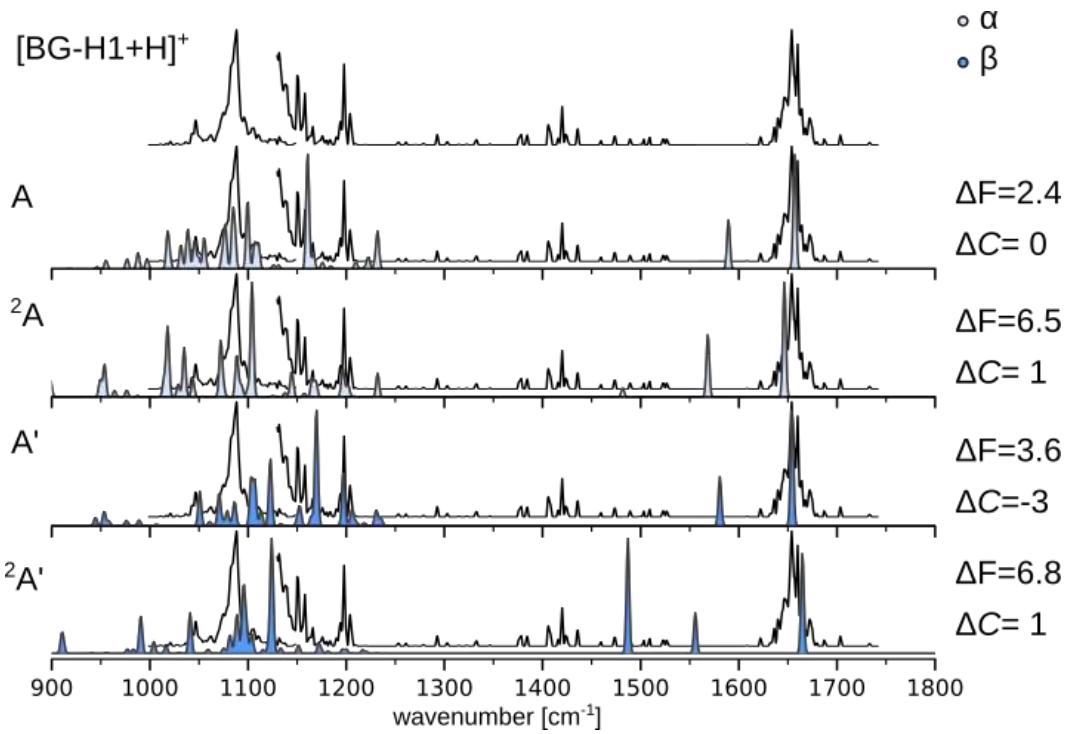

Figure S21: Simulated vibrational spectra of the lowest-free energy conformers of $[BG\text{-}H1+H]^+$ ions. (A) and (^{2}A) represent the most stable and second most stable conformers of alpha anomers respectively. The (A') and (^{2}A'), represent beta anomers of the same ions above. All spectra are compared to the experimental IR spectrum of $[BG\text{-}H1+H]^+$ (Top spectrum). The disconnected experimental line indicates two regions where a different laser power was used. The spectra between 1000-1250 cm^{-1} is computed using anharmonic corrections, while the amide I band is calculated using harmonic vibrations. ΔF indicates relative free energy with respect to the global minimum (in kcal mol^{-1}), and ΔC indicates a difference in CCS from experimental value of 144 $Å^2$.

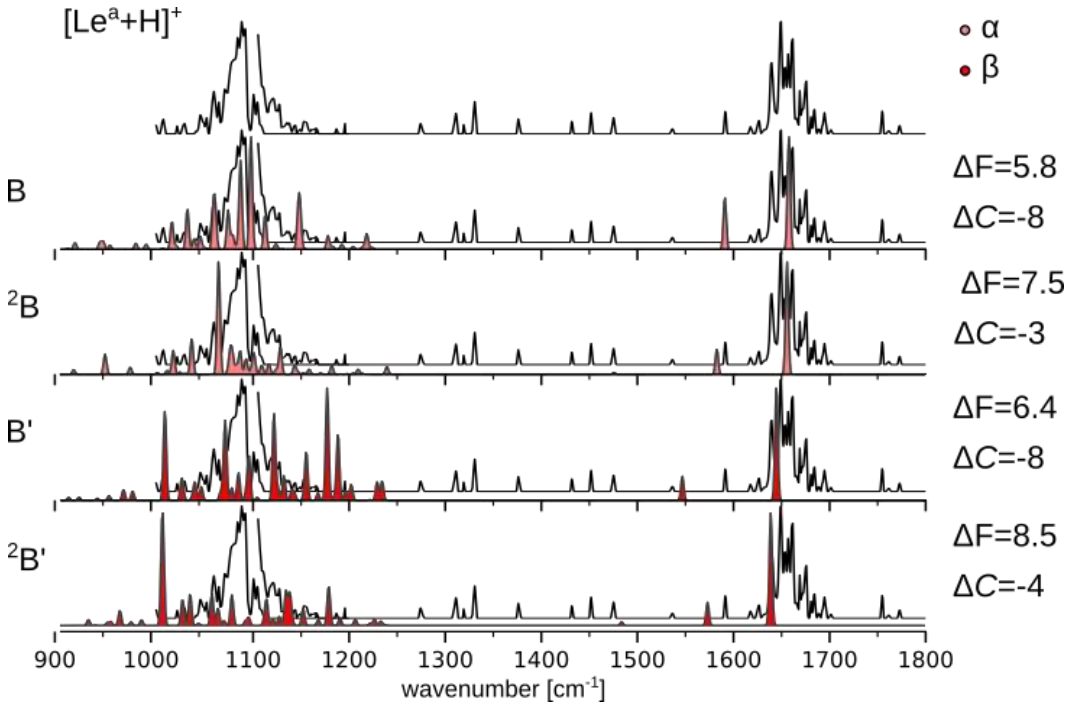

Figure S22: Simulated vibrational spectra of the lowest-free energy conformers of $[Le^a+H]^+$ ions. (B) and (^{2}B) represent the most stable and second most stable conformers of alpha anomers respectively. The (B') and (^{2}B') represent beta anomers of the ions following. All spectra are compared to the experimental IR spectrum of $[Le^a+H]^+$ (Top spectrum). The disconnected experimental line indicates two regions where a different laser power was used. The spectra between 1000-1250 cm^{-1} is computed using anharmonic corrections, while the amide I band is calculated using harmonic vibrations. ΔF indicates relative free energy with respect to the global minimum (in kcal mol^{-1}), and ΔC indicates a difference in CCS from experimental value of 144 Å^2.

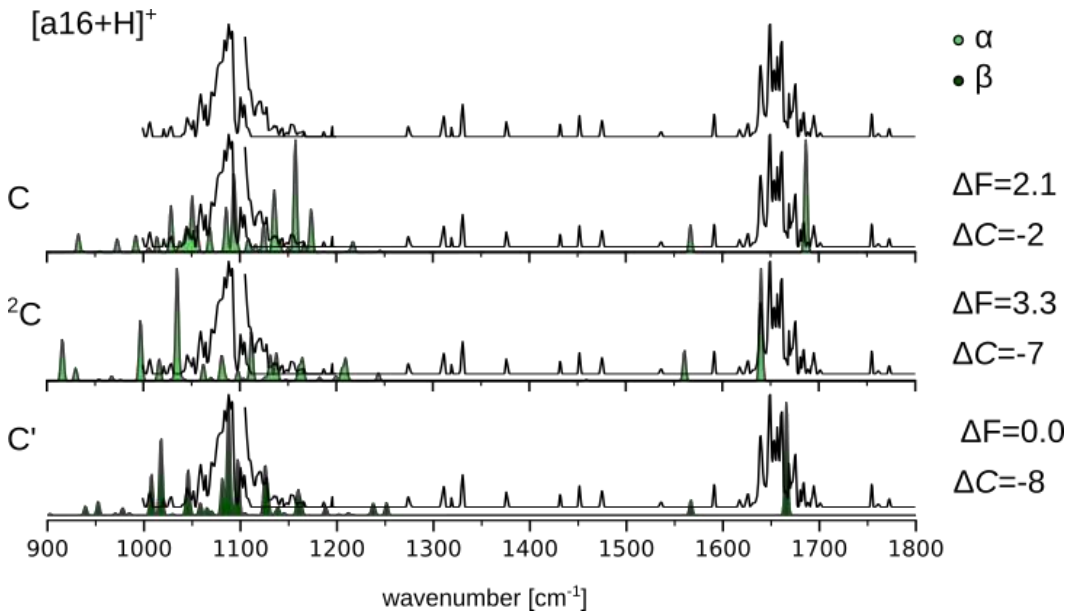

Figure S23: Simulated vibrational spectra of the lowest-free energy conformers of $[a16+H]^+$ ions. (C) and (^{2}C) represent the most stable and second most stable conformers of alpha anomers respectively. (C') represents the most stable beta anomers of the same ions above. All spectra are compared to the experimental IR spectrum of $[Le^a+H]^+$ (Top spectrum). The disconnected experimental line indicates two regions where a different laser power was used. The spectra between 1000-1250 cm^{-1} is computed using anharmonic corrections, while the amide I band is calculated using harmonic vibrations. ΔF indicates relative free energy with respect to the global minimum (in kcal mol^{-1}), and ΔC indicates a difference in CCS from experimental value of 144 Å^2.

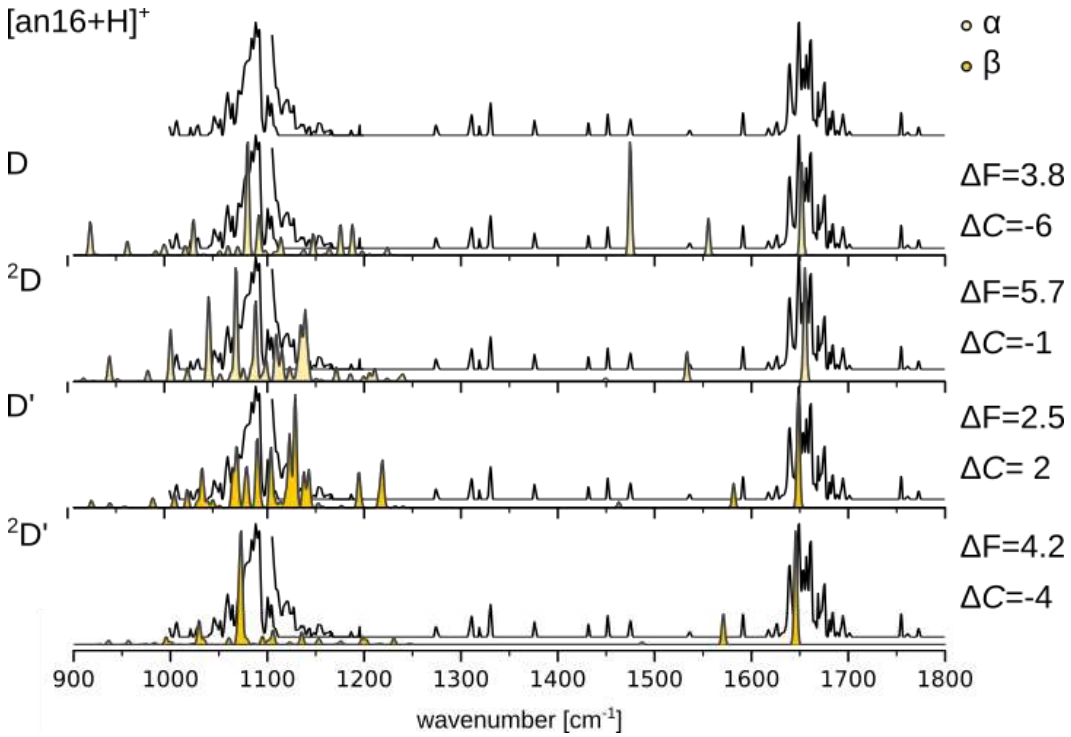

Figure S24: Simulated vibrational spectra of the lowest-free energy conformers of $[an16+H]^+$ ions. (D) and (^{2}D) represent the most stable and second most stable conformers of alpha anomers respectively. (D') and (^{2}D'), represent the most stable beta anomers of the same ion. All spectra are compared to the experimental IR spectrum of $[Le^a+H]^+$ (Top spectrum). The disconnected experimental line indicates two regions where a different laser power was used. The spectra between 1000-1250 cm^{-1} is computed using anharmonic corrections, while the amide I band is calculated using harmonic vibrations. ΔF indicates relative free energy with respect to the global minimum (in kcal mol^{-1}), and ΔC indicates a difference in CCS from experimental value of 144 $Å^2$.

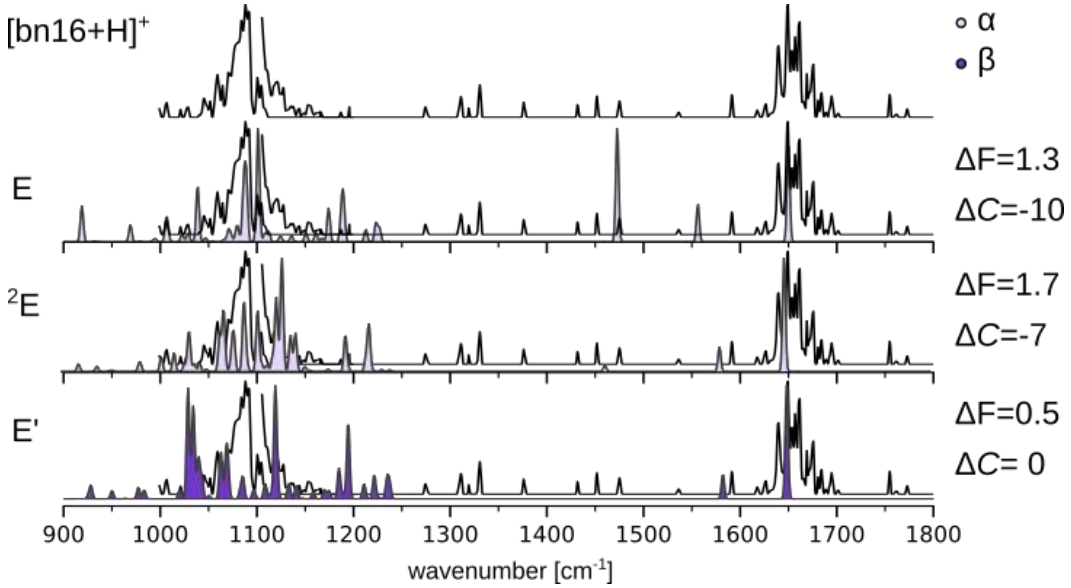

Figure S25: Simulated vibrational spectra of the lowest-free energy conformers of $[an16+H]^+$ ions. (E) and (^{2}E) represent the most stable and second most stable conformers of alpha anomers respectively. (E) represents the most stable beta anomer of the same ion. All spectra are compared to the experimental IR spectrum of $[Le^a+H]^+$ (Top spectrum). The disconnected experimental line indicates two regions where a different laser power was used. The spectra between 1000-1250 cm^{-1} is computed using anharmonic corrections, while the amide I band is calculated using harmonic vibrations. ΔF indicates relative free energy with respect to the global minimum (in kcal mol^{-1}), and ΔC indicates a difference in CCS from experimental value of 144 $Å^2$.

Table S4: Vibrational mode assignment of **[α-BG-H1+H]$^+$ ion (A)**

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
965.20	945.29	2.87E-03	β(CCH), β(CCO)
972.76	948.69	4.91E-03	β(CCH), β(CCO)
989.59	976.05	2.54E-02	β(CCH), β(CCO)
997.63	985.25	8.75E-02	vs(COC) in glycosidic linkage, β(COH)
1004.80	984.95	2.98E-03	vs(COC) in glycosidic linkage, β(COH)
1018.50	1006.80	1.04E-01	Bending H+ on Acetyl Oxygen
1032.83	1017.89	1.64E-01	β(COH), ν(CC)
1045.38	1027.10	1.04E-01	ν(CC),ν(CO)
1047.55	1048.11	3.52E-01	ν(CO), ν(CC), β(COH)
1059.64	1050.72	7.18E-02	*ν(CC), ν(CO), β(COH)*
1069.27	1068.14	2.36E-01	*β(CH2)*
1073.48	1061.62	2.32E-01	ν(COC) in glycosidic linkage,β(CO), ν(COH), β(CH)
1088.65	1074.97	6.20E-02	γ(CH2), ν(CC), ν(CN)
1094.01	1079.67	1.05E-01	*ν(CC), ν(CO), β(COH)*
1099.88	1085.34	2.95E-01	*ν(CC), ν(CO), β(COH)*
1106.83	1075.72	2.13E-01	γ(CH2), ν(CC), ν(CN)
1110.24	1106.84	3.82E-01	ν(CO), ring def.??
1119.63	1103.83	1.27E-01	ν(CC),ν(CO)
1123.86	1108.14	1.77E-02	ν(CC),ν(CO)
1128.38	1114.42	4.42E-01	ν(CC),ν(CO), ν(CC), β(COH)
1130.07	1116.76	1.21E-01	ν(COC) in glycosidic linkage, β(CO), ν(COH), β(CH)
1132.43	1116.41	1.33E-01	β(CO), ν(COH), β(CH)
1138.24	1069.43	1.80E-01	???
1146.81	1128.23	3.98E-03	ν(CC),ν(CO), β(CH)
1147.97	1129.58	6.16E-01	ν(CC),ν(CO)
1152.85	1123.82	6.00E-03	β(COH), ν(CC)
1153.26	1136.80	2.31E-01	β(COH), β(HC:CH), β(CC)
1157.84	1140.54	2.28E-01	β(COH), β(HC:CH), β(CC)
1164.94	1156.18	3.54E-02	ν(CC),ν(CO)
1166.85	1161.02	3.63E-02	ν(CC),ν(CO)
1175.99	1154.45	3.86E-03	β(CO), ν(COH), β(CH)
1187.51	1174.19	1.64E-03	ν(COC) in glycosidic linkage,β(CO), ν(COH), β(CH)
1204.24	1190.71	9.85E-01	ν(CC),ν(CO)
1205.00	1238.87	1.86E-02	β(COH)
1212.49	1205.81	5.75E-02	β(CO), ν(COH), β(CH)
1219.09	1196.57	1.39E-01	ν(CO), β(COH), β(CH)
1220.15	1214.19	2.78E-02	ν(CO), β(COH), β(CH)
1240.05	1225.19	3.93E-04	ν(CO), β(COH), β(CH)
1245.72	1228.85	1.02E-03	β(COH), β(CC)
1250.99	1240.20	4.29E-02	β(COH), β(CC)
1254.11	1221.05	3.63E-03	β(COH), τ(CH), δ(CC)
1269.48	1249.16	5.98E-03	β(COH), τ(CH2)
1271.05	1248.03	1.28E-02	β(COH), β(CH)
1275.44	1252.57	1.00E-01	β(COH), β(CH)
1281.09	1262.01	2.95E-01	β(COH), β(CH)
1291.68	1259.37	4.22E-02	β(COH), β(CH)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S5 Vibrational mode assignment of ***[α-BG-H1+H]⁺ ion (^{2}A):***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
965.36	942.148	3.10E-04	β(CH2), Bending H+ on Acetyl Oxygen
973.13	940.3	6.40E-05	Bending H+ on Acetyl Oxygen, β(CCH), β(CCO)
984.62	970.503	1.45E-04	β(HCCH), β(CH3)
999.17	985.593	5.57E-04	β(HCCH), β(CH3)
1013.47	1006.56	2.23E-03	Bending H+ on Acetyl Oxygen, β(CH3)
1023.06	1019.76	1.88E-03	τ(CH3), Bending H+ on Acetyl Oxygen
1023.55	1007.11	3.66E-03	δ(HCCH), τ(CH3)
1040.58	1013.10	2.88E-03	Bending H+ on Acetyl Oxygen, β(CH3), δ(HCOH)
1045.60	1020.69	7.53E-03	Bending H+ on Acetyl Oxygen, β(CH3), δ(HCOH)
1055.23	1046.32	6.31E-04	β(CH3), δ(HCOH), ν(CC), ν(CO)
1059.46	1033.97	2.22E-03	Bending H+ on Acetyl Oxygen, β(CH3)
1071.80	1059.76	4.35E-04	β(CH3), δ(HCOH), ν(CC), ν(CO)
1082.31	1070.89	6.12E-04	δ(HCOH), ν(CC), ν(CO)
1090.62	1070.97	6.21E-04	Bending H+ on Acetyl Oxygen, β(CH3), δ(HCOH), ν(CC), ν(CO)
1101.33	1090.10	1.26E-02	δ(HCOH), δ(HCCH), ν(CC), ν(CO)
1102.15	1088.55	1.67E-04	δ(HCOH), δ(HCCH), ν(CC), ν(H2C:OH)
1110.36	1096.83	8.83E-04	δ(HCOH), ν(CN), ν(CO), τ(CH3)
1117.41	1106.86	4.24E-05	Bending H+ on Acetyl Oxygen, δ(HCOH), ν(CN), ν(CO), τ(CH3)
1117.84	1104.98	9.40E-04	Bending H+ on Acetyl Oxygen, δ(HCOH), ν(CO), τ(CH3)
1125.56	1111.54	1.01E-03	νas(COC) in glycosidic linkage, νas(COC), ν(CO), δ(HCCH), β(CO)
1129.03	1117.31	3.81E-04	β(CH3), δ(HCCH), , δ(HCOH)
1132.16	1119.34	2.60E-04	νas(COC) in glycosidic linkage, δ(HCCH), , δ(HCOH)
1138.40	1127.88	4.54E-04	τ(HCCH) , β(CH2), δ(HCOH)
1141.08	1125.28	4.51E-04	νas(COC) in glycosidic linkage, νas(COC), ν(CO), δ(HCCH), β(CO)
1146.22	1129.87	4.30E-05	νas(COC) in glycosidic linkage, νas(COC), ν(CO), ν(CC)
1149.50	1133.89	1.63E-06	ν(COC) in glycosidic linkage, ν(CO), δ(HCOH), δ(HCCH)
1158.59	1145.23	2.10E-04	ν(CO), ν(CC), δ(HCOH)
1163.62	1163.24	1.89E-04	τ(HCCH) , β(CH2), δ(HCOH)
1168.58	1150.46	1.96E-04	τ(HCCH) , β(CH2), δ(HCOH), ν(CO)
1173.39	1154.01	5.99E-05	δ(HCOH), ν(CO), νas(COC), ν(CN)
1175.46	1151.77	1.29E-05	δ(HCOH), ν(CO), ν(CCC), τ(CH2)
1179.41	1155.86	9.36E-04	δ(HCOH), ν(CO), νas(COC), ν(CCC)
1188.24	1173.67	2.54E-03	νas(COC) in glycosidic linkage, νas(COC), ν(CO), δ(HCCH), β(CH3)
1197.23	1181.40	9.29E-05	νas(COC) in glycosidic linkage, δ(HCCH), δ(HCOH)
1209.08	1201.93	1.44E-04	δ(HCCH), δ(HCOH)
1213.33	1204.42	4.71E-05	νas(COC) in glycosidic linkage, δ(HCCH), δ(HCOH)
1221.75	1211.33	1.29E-04	δ(HCCH), δ(HCOH), β(CH3)
1240.15	1226.32	5.23E-04	δ(HCCH), δ(HCOH), τ(CH2)
1242.60	1230.08	5.61E-04	δ(HCCH), δ(HCOH), τ(CH2)
1250.23	1235.96	4.79E-03	δ(HCCH), δ(HCOH), τ(CH2)
1258.41	1228.81	9.43E-04	δ(HCCH), δ(HCOH), τ(CH2)
1265.36	1247.23	1.51E-03	δ(HCOH), δ(HCNH), τ(CH2)
1273.73	1246.21	1.39E-04	δ(HCCH), δ(HCOH), τ(CH2)
1278.84	1250.58	4.45E-04	δ(HCCH), δ(HCOH)
1289.77	1261.18	4.55E-03	δ(HCCH), δ(HCOH), δ(HCNH)
1304.21	1269.34	2.49E-04	δ(HCCH), δ(HCOH), τ(CH2)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S6: Vibrational mode assignment of **[*β-BG-H1+H*]$^+$ *ion (A'):***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
966.63	915.28	4.33E-03	β(CCH), β(CCO), β(CNH)
975.60	931.39	2.43E-03	β(CCH), β(CCO), β(CNH)
989.48	974.55	8.12E-02	β(CCH), β(CCO)
998.13	983.43	1.45E-01	vs(COC) in glycosidic linkage, β(COH)
1009.84	987.99	4.55E-02	vs(COC) in glycosidic linkage, β(COH)
1019.68	1006.09	4.79E-02	β(CO), β (CH)
1033.85	1019.02	5.19E-02	β(CO), β (CH)
1041.27	1036.61	9.54E-03	β(CO), β (CH)
1045.44	1025.39	6.73E-02	ν(CO), ν(CC), β(COH)
1059.48	1043.80	1.29E-01	β(CO), β (CH)
1069.76	1062.56	3.23E-01	τ(CH2)
1070.53	1059.20	5.70E-01	τ(CH2), β(CCO), ν(CO)
1089.59	1075.38	3.51E-02	ν(CN), β(CCH), β(CCO), γ(CH2)
1093.89	1077.32	1.22E-01	vas(COC) in glycosidic linkage, β(COH)
1100.88	1084.79	6.84E-01	β(CCH), β(CCO),γ(CH2), ν(CN)
1110.39	1090.94	1.47E-02	ν(CC), β(CO), β(CH)
1111.27	1100.57	2.99E-01	vs(COC) in glycosidic linkage, β(COH), β(CH)
1112.91	1104.33	4.15E-02	vs(COC) in glycosidic linkage, β(COH), β(CH)
1125.02	1108.80	1.31E-01	β(CO), β (CH)
1128.86	1115.63	1.10E-02	β(CO), β (CH)
1129.72	1116.45	8.39E-02	β(CO), β (CH)
1130.37	1115.48	6.37E-02	ν(CC), β(CO), β(CH)
1139.07	1112.52	1.30E-02	β(CO), β(CH)
1145.26	1116.90	7.04E-02	ν(CO), β(CO), τ(CH2)
1150.75	1133.09	3.96E-01	ν(CO), β(CO)
1152.97	1134.96	4.53E-02	β(CO), β(CH)
1157.28	1136.91	3.78E-01	β(CO), β(CH)
1161.23	1080.84	3.17E-01	Bending H+ on Acetyl Oxygen
1165.73	1143.32	1.33E-01	ν(CC), β(CO), β(CH)
1175.21	1152.74	5.84E-01	ν(CO), β(CO)
1180.59	1163.32	1.32E-02	ν(CC), β(CO), β(CH)
1192.03	1180.82	7.70E-02	vas(COC) in glycosidic linkage, β(COH), β(CH)
1198.94	1183.00	1.35E-01	vas(COC) in glycosidic linkage, β(COH), β(CH)
1208.44	1199.68	9.85E-01	Bending H+ on Acetyl Oxygen, ν(CO), β(CO)
1211.21	1194.50	7.75E-02	β(CO), β(CH)
1215.49	1227.21	4.27E-01	β(CO), β(CH)
1236.94	1224.03	8.42E-04	β(CO), β(CH)
1247.04	1239.19	2.27E-02	β(CO), β(CH)
1249.05	1231.88	1.09E-02	β(CO), β(CH)
1252.66	1236.01	1.34E-01	β(CO), β(CH)
1253.98	1225.58	1.16E-03	β(CO), τ(CH2)
1271.97	1241.07	1.09E-02	β(CO), β(CH)
1274.59	1248.28	1.98E-02	β(CO), τ(CH2), β(CH)
1283.39	1262.25	3.37E-02	β(CO), τ(CH2), β(CH)
1290.01	1260.39	1.04E-01	β(CO), τ(CH2), β(CH)
1301.49	1265.62	5.28E-02	β(CO), β(CH)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S7: Vibrational mode assignment of ***[β-BG-H1+H]⁺ (^{2}A'):***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
985.27	928.78	1.03E-03	β(NH)
989.22	965.42	5.26E-05	β(NH), β(HCCH)
1000.90	979.40	3.07E-03	β(NH), β(HCCH), β(HCOH)
1005.75	983.78	1.53E-04	β(NH), β(HCCH), β(HCOH)
1016.18	994.03	4.28E-04	Bending H+ on Acetyl Oxygen, δ(HCOH), ν(CO)
1019.28	1006.41	2.27E-03	β(CH3), β(HCCH)
1026.69	1017.27	3.88E-04	τ(CH3)
1052.54	1030.46	5.43E-04	τ(CH3), β(OH)
1059.92	1047.52	2.48E-03	τ(CH3), β(OH), ν(CO)
1063.35	1051.98	4.41E-04	τ(CH3), β(OH), ν(CO)
1069.10	1048.31	3.84E-03	τ(CH3), β(OH), ν(CO)
1071.26	1058.93	5.25E-05	β(CH3), β(NH)
1079.81	1058.60	2.97E-05	τ(CH3), β(OH), ν(CO), ν(CN)
1086.64	1064.92	4.82E-05	Bending H+ on Acetyl Oxygen, τ(CH3), β(OH), ν(CO)
1088.69	1044.34	2.39E-04	Bending H+ on Acetyl Oxygen, τ(CH3), β(OH)
1095.04	1073.78	6.34E-04	Bending H+ on Acetyl Oxygen, τ(CH3), τ(CH2), β(OH)
1102.04	1083.23	8.66E-04	Bending H+ on Acetyl Oxygen, τ(CH3), τ(CH2), β(OH)
1119.58	1102.12	5.63E-06	τ(CH2), β(OH), β(HCCH)
1122.47	1103.85	2.00E-04	Bending H+ on Acetyl Oxygen, τ(CH2), β(OH)
1125.35	1105.30	9.96E-04	Bending H+ Acetyl Oxygen, τ(CH3), τ(CH2), β(OH), vas(COC)
1134.12	1118.47	8.09E-04	β(CH2), β(HCCH)
1135.81	1121.16	2.71E-04	β(OH), β(HCCH)
1140.64	1123.53	1.37E-03	τ(CH3), β(OH), β(HCCH)
1145.32	1133.73	6.29E-04	τ(CH2), β(OH), β(HCCH)
1148.92	1129.74	1.32E-05	τ(CH2), β(OH), β(HCCH)
1151.28	1134.25	5.72E-05	τ(CH2), β(OH), β(HCCH)
1169.02	1154.96	2.06E-06	τ(CH3), β(OH), β(HCCH)
1169.86	1154.76	1.12E-06	τ(CH3), β(OH), β(HCCH)
1171.53	1159.33	1.18E-04	β(OH), β(HCCH)
1178.86	1167.69	1.07E-03	τ(CH2), β(OH)
1184.52	1173.71	1.44E-06	τ(CH2), β(OH)
1188.90	1175.04	1.10E-03	τ(CH3), β(OH), β(HCCH), ν(CC)
1192.87	1179.59	2.69E-05	τ(CH3), β(OH), β(HCCH)
1202.65	1187.32	1.11E-03	β(NH), β(HCCH), β(OH)
1210.92	1195.30	2.07E-03	vas(COC) in glycosidic linkage, β(NH), β(HCCH), β(OH)
1216.14	1199.17	4.13E-04	τ(CH2), β(OH), β(HCCH)
1234.50	1228.59	4.31E-04	β(OH), β(HCCH)
1241.53	1226.37	9.92E-05	β(OH), β(HCCH)
1247.37	1231.95	4.34E-05	τ(CH2), β(OH), β(HCCH)
1254.09	1245.21	1.13E-03	β(OH), β(HCOH)
1255.27	1238.13	3.64E-07	β(OH), β(HCCH)
1259.78	1236.83	3.10E-03	β(OH), β(HCCH)
1274.56	1242.36	6.17E-04	τ(CH2), β(OH), β(HCCH)
1282.76	1261.10	1.37E-04	β(OH), β(HCOH)
1294.15	1262.11	2.87E-03	β(OH), β(HCOH)
1296.25	1259.35	1.03E-03	β(OH), β(HCOH)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S8: Vibrational mode assignment of **[*α-Le^a+H]$^+$ ion (B):***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
958.75	937.12	1.16E-02	β(CO), β(CH2), β(NH)
971.43	944.60	6.61E-02	β(CO), β(CH2), β(NH), ν(CO)
984.97	974.00	7.45E-02	β(CH2), νs(COC) in glycosidic linkage
986.16	970.65	6.77E-02	β(CH3), ν(CO)
1000.97	980.94	4.06E-02	β(CH3), νs(COC) in glycosidic linkage, β(NH)
1019.23	1008.01	5.59E-02	δ(HCCH), ν(CO)
1030.84	1018.68	4.67E-02	β(CH3), β(NH), Bending H+ on Acetyl Oxygen
1044.52	1050.11	3.12E-02	β(CH3), Bending H+ on Acetyl Oxygen
1054.71	1035.89	1.18E-02	β(CH3), Bending H+ on Acetyl Oxygen, β(CO)
1062.59	1045.54	2.46E-01	β(CH3), Bending H+ on Acetyl Oxygen, β(CO)
1071.07	1068.74	9.21E-02	β(CH3), β(NH)
1076.68	1061.68	3.48E-01	β(CH3), β(NH), Bending H+ on Acetyl Oxygen, β(CO)
1080.05	1063.47	1.29E-03	δ(HCCH), ν(CO), β(COH), β(CH3)
1089.91	1075.13	1.12E-01	β(CH3), Bending H+ on Acetyl Oxygen, ν(CC)
1093.84	1079.89	1.69E-02	ν(CO), β(HCCH), β(CO)
1104.26	1090.66	2.21E-01	Bending H+ on Acetyl Oxygen, β(CO)
1110.75	1093.27	4.76E-04	Bending H+ on Acetyl Oxygen, β(CO)
1117.51	1104.04	3.23E-01	ν(CO), β(CO)
1120.21	1113.23	1.97E-02	ν(CO), β(CO)
1124.20	1108.57	1.22E-01	ν(CC), ν(CO)
1125.71	1113.03	8.47E-03	ν(CC), ν(CC), Bending H+ on Acetyl Oxygen
1134.93	1091.52	3.26E-02	Bending H+ on Acetyl Oxygen
1135.79	1116.99	7.21E-01	β(CO)
1141.30	1088.83	3.27E-01	Bending H+ on Acetyl Oxygen, β(CO)
1144.76	1127.78	9.06E-01	ν(CC), ν(CO)
1149.40	1132.26	8.78E-03	ν(CC), ν(CO)
1150.35	1128.61	8.17E-03	ν(CO), τ(CH2), Bending H+ on Acetyl Oxygen
1160.90	1142.52	2.76E-01	β(CO), τ(CH2), δ(HCOH)
1168.76	1153.76	4.42E-02	β(CO), τ(CH2), δ(HCOH), ν(CO)
1175.21	1156.98	2.55E-03	νas(COC) in glycosidic linkage, ν(CC)
1179.99	1160.37	6.07E-03	β(CH3), β(CO), νas(COC) in glycosidic linkage
1191.64	1177.03	2.55E-01	β(CH3), β(CO), νas(COC) in glycosidic linkage
1198.51	1183.72	4.69E-03	ν(CC), ν(CO), β(CH3)
1202.00	1178.94	2.80E-01	νas(COC) in glycosidic linkage, β(HCCH)
1224.48	1212.94	2.43E-02	β(CO), β(HCCH)
1227.49	1207.98	1.04E-01	β(CO), τ(CH2), ν(CO)
1239.00	1222.36	3.82E-02	β(CO), τ(CH2), ν(CO)
1239.54	1224.76	1.40E-03	β(CO)
1245.77	1221.12	2.57E-04	β(CO), β(HCCH), τ(CH2)
1252.56	1243.77	1.95E-02	ν(CO), τ(CH2)
1259.20	1234.14	2.25E-02	β(CO), τ(CH2)
1262.86	1247.80	5.22E-02	β(CO)
1272.19	1253.13	7.91E-03	β(CO), τ(CH2)
1281.02	1254.38	9.80E-03	β(CO), τ(CH2)
1283.77	1248.62	6.83E-02	δ(HCOH)
1288.64	1273.81	4.17E-04	β(CO), β(HCCH)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S9: Vibrational mode assignment of **[*α-Le^a+H]$^+$ (B'):***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
963.121	899.649	2.33E-02	β(CO), β(CH2)
966.858	944.343	1.01E-02	Bending H+ on Acetyl Oxygen, β(HCOH)
976.096	919.302	4.50E-03	Bending H+ on Acetyl Oxygen, β(HCOH)
990.368	954.618	3.17E-02	β(HCCH), β(CO), β(CH3)
992.234	976.535	3.54E-02	β(HCCH), β(CO)
1017.299	977.476	2.75E-02	β(HCCH), β(CO), νs(COC) in glycosidic linkage
1032.224	1003.245	1.40E-02	β(CH3), β(CO)
1048.925	1031.464	2.03E-02	β(CH3), β(HCCH),β(CH3), β(CH2)
1057.257	1041.69	4.86E-02	β(CH3), β(CO), ν(CC), β(CH2)
1064.891	1048.044	7.70E-03	β(CH3)
1066.109	1069.899	1.14E-02	β(CH3), β(CO), ν(CC)
1070.73	1060.182	1.62E-02	νs(COC), δ(HCCH), β(CH3)
1084.191	1054.922	5.86E-02	νs(COC), νas(COC), δ(HCCH), β(CH3)
1097.038	1067.22	3.18E-02	β(CH3), β(CO), ν(CC),ν(CO)
1102.104	1088.22	8.24E-03	β(CO), ν(CC),ν(CO)
1109.919	1095.262	1.03E-01	β(CO), β(CH2), νas(COC) in glycosidic linkage
1113.694	1105.118	1.68E-02	β(HCCH), ν(CC),ν(CO)
1114.663	1107.297	4.31E-02	β(HCCH), ν(CC), β(CH3)
1117.185	1109.503	4.13E-02	β(HCOH), ν(CC), β(HCCH)
1123.339	1113.618	2.86E-02	β(HCCH), ν(CO), β(CH2)
1129.458	1117.633	4.71E-02	β(HCCH), ν(CO), β(CH2)
1139.58	1123.788	3.79E-02	νas(COC) in glycosidic linkage, νas(COC), β(HCCH)
1144.665	1129.108	2.16E-02	ν(CC), β(HCCH)
1148.197	1132.106	4.38E-02	ν(CC), ν(CO), β(HCCH)
1155.456	1138.428	1.10E-02	ν(CC), ν(CO), β(CH2)
1158.947	1140.292	2.79E-02	ν(CC), ν(CO), β(CH2)
1162.674	1147.601	3.14E-02	Bending H+ on Acetyl Oxygen, ν(CC), ν(CO)
1169.168	1154.735	2.16E-02	β(HCOH), τ(CH2)
1178.089	1159.305	4.82E-02	β(HCCH), ν(CC)
1180.209	1160.704	1.46E-02	ν(CC), β(CH3)
1190.309	1174.31	2.88E-02	β(CH3), β(HCCH), ν(CC)
1194.331	1177.606	1.52E-02	νas(COC) in glycosidic linkage, νas(COC), β(HCOH)
1199.017	1183.569	1.29E-02	νas(COC) in glycosidic linkage, β(HCCH)
1205.566	1189.46	2.19E-02	νas(COC) in glycosidic linkage, β(HCCH)
1215.353	1201.285	1.22E-02	β(HCCH), β(HCOH)
1222.887	1212.97	2.74E-02	β(HCCH), β(HCOH), β(CH2)
1238.306	1222.21	7.12E-03	β(HCCH), β(HCOH), β(CH2)
1240.22	1228.762	8.69E-03	β(HCCH), β(HCOH)
1249.65	1240.452	2.12E-02	β(HCCH), β(HCOH), β(CH3)
1257.279	1235.347	1.15E-02	β(HCCH), β(HCOH)
1264.456	1244.898	1.03E-02	β(HCCH), β(HCOH)
1277.466	1253.372	1.42E-03	β(HCCH), β(HCOH), β(CH2)
1281.368	1250.226	5.50E-03	β(HCOH), β(CH2)
1286.588	1270.706	1.55E-02	β(HCCH), β(HCOH), β(CH3)
1301.259	1270.204	2.06E-02	β(HCCH), β(HCOH)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S10: *Vibrational mode assignment of* ***[β-Le^a+H]$^+$ ion (B')***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
973.65	948.94	3.65E-02	β(CO), β(CH2)
982.05	967.85	2.51E-02	β(CH3), β(CO), ν(CC)
992.595	938.06	3.49E-02	Bending H+ on Acetyl Oxygen, β(HCOH)
997.051	980.02	4.29E-02	β(HCCH), β(CO), β(CH2)
1002.091	980.49	6.80E-03	β(HCCH), β(CO), β(CH2)
1019.572	1004.59	9.27E-02	β(CH3), β(CO)
1025.619	1026.37	4.67E-03	β(CH3), δ(HCCH)
1036.645	995.18	1.07E-01	β(CH3), β(CO)
1050.108	1038.27	6.00E-01	β(CH3), β(CO), ν(CC)
1052.948	1038.18	2.42E-01	β(CH3), β(CO), ν(CC), ν(CO)
1067.258	1055.66	1.91E-01	β(CH3), β(CO)
1071.226	1057.67	3.91E-02	β(CH3), β(CO)
1072.102	1066.01	1.87E-02	β(CH3)
1082.2	1069.14	1.50E-01	β(CH3), β(CO), ν(CO), ν(CO) in glycosidic linkage
1087.621	1071.00	4.11E-02	β(CH3), Bending H+ on Acetyl Oxygen, vas(CC)
1093.566	1076.18	1.27E-01	ν(CC), vas(COC) in glycosidic linkage, ν(CO), β(CO)
1107.163	1096.15	6.91E-02	ν(CC), ν(CO), β(CO)
1114.063	1099.27	1.11E-01	ν(CC), ν(CO), β(CO)
1118.298	1101.15	6.53E-01	ν(CC), ν(CO), β(CO)
1124.132	1114.92	7.43E-02	β(CH3), β(CO)
1124.624	1114.85	1.69E-01	ν(CO), β(CO), β(CH3)
1128.909	1107.88	1.13E-01	ν(CO), β(CO)
1135.695	1122.53	6.06E-02	ν(CC), ν(CO), β(CO)
1138.917	1125.97	1.29E-02	ν(CO), β(CO), β(CH3), ν(CC)
1145.28	1125.70	1.70E-01	ν(CC), ν(CO), β(CO)
1146.522	1125.54	2.09E-01	Bending H+ on Acetyl Oxygen, ν(CC)
1153.025	1134.19	2.89E-02	ν(CO), β(CO), β(CH2)
1162.964	1155.78	9.97E-02	β(CH3), β(CO)
1164.947	1162.15	2.09E-01	β(CH3), β(CO)
1168.378	1151.77	7.37E-01	β(CH2), β(CO), ν(CC)
1187.468	1170.18	7.96E-02	β(CH3), β(CO), vas(CO)
1193.929	1173.12	5.91E-02	vas(COC) in glycosidic linkage, β(CO), β(CH2)
1197.559	1182.37	2.05E-02	ν(CO) in glycosidic linkage, β(CO), β(CH3)
1208.065	1185.40	4.03E-01	β(CH3), β(CO), ν(CC)
1218.062	1207.12	9.06E-01	vas(COC) in glycosidic linkage, β(CO), β(CH3)
1221.366	1213.41	2.85E-02	β(CO), β(CH3), β(CH2)
1221.901	1218.35	5.37E-01	β(CO), β(CH2)
1231.663	1197.53	6.37E-02	ν(CC), β(CO)
1236.218	1222.75	5.85E-05	β(CO), β(CH2)
1247.209	1226.16	7.75E-02	β(CO), β(CH3)
1253.624	1233.63	4.79E-03	β(CO), β(CH2), ν(CO)
1257.268	1232.13	1.25E-01	β(CO), β(CH2), β(HCCH)
1274.553	1251.62	7.80E-03	β(CO), β(CH2), β(HCCH)
1291.243	1259.00	1.34E-01	β(CO), β(CH2), β(HCCH)
1293.553	1260.37	1.51E-02	β(CO), β(CH2)
1306.537	1264.31	1.51E-01	β(CO), β(CH2), β(HCCH)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S11: *Vibrational mode assignment of* ***[β-Le^a+H]$^+$ ion (^{2}B')***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
970.849	959.573	2.62E-02	β(HCCH), β(CH3)
977.682	967.062	8.53E-03	Bending H+ on Acetyl Oxygen, β(HCCH), β(CH3)
992.018	979.366	1.89E-02	β(HCCH)
997.87	982.909	2.10E-02	β(HCCH)
1007.175	992.28	4.05E-02	Bending H+ on Acetyl Oxygen, β(HCCH), β(CH3)
1019.391	1003.862	2.04E-02	β(HCCH), β(CH3)
1023.694	1014.804	2.47E-02	β(HCCH), β(CH3)
1041.449	1036.668	1.05E-01	β(CH2), ν(CC), β(CH3)
1049.704	1038.533	1.54E-02	β(CH3)
1060.876	1036.032	3.16E-02	β(CH2), ν(CC), β(CH3)
1070.613	1057.689	4.40E-02	β(CH2), ν(CC), β(CH3)
1071.598	1065.364	5.63E-02	τ(CH3)
1083.037	1057.042	2.89E-02	τ(CH2), β(HCCH)
1088.282	1075.987	5.37E-03	ν(CO), β(CH3)
1092.32	1074.008	1.49E-02	ν(CO), β(HCCH)
1099.578	1094.361	4.16E-02	ν(CC), β(HCCH), β(HCOH)
1113.476	1066.727	8.84E-03	Bending H+ on Acetyl Oxygen
1116.065	1100.49	2.24E-02	ν(CO), β(HCCH), β(HCOH)
1119.631	1107.956	1.68E-02	τ(CH2), β(HCCH), β(HCOH)
1123.74	1088.15	5.61E-02	Bending H+ on Acetyl Oxygen, τ(CH2)
1130.017	1108.976	5.25E-02	τ(CH2), β(HCCH), β(HCOH)
1133.375	1122.877	2.02E-02	τ(CH3), β(HCCH), β(HCOH)
1141.004	1124.037	6.40E-03	τ(CH2), β(HCCH), β(HCOH)
1141.86	1126.436	2.78E-02	τ(CH2), β(HCCH), β(HCOH)
1154.88	1141.93	7.37E-03	τ(CH2), β(HCCH), β(HCOH)
1157.607	1144.962	4.85E-02	τ(CH3), β(HCCH), β(HCOH)
1159.051	1142.707	2.12E-02	β(HCCH), ν(CO), ν(CC)
1164.717	1158.079	2.91E-02	β(HCOH), ν(CO), ν(CC)
1166.58	1151.631	2.50E-02	β(HCCH), β(HCOH), β(CH3), ν(CN)
1179.74	1165.165	5.68E-02	β(HCCH), β(HCOH), β(CH3), ν(CO)
1185.255	1169.088	5.34E-02	νas(COC), β(HCCH), β(CH3)
1188.441	1171.374	2.11E-02	ν(CC), β(HCCH), β(CH3)
1200.98	1183.02	3.93E-02	β(HCCH), β(HCOH), β(CH3), ν(CN)
1211.219	1218.43	3.03E-03	β(HCCH), β(HCOH)
1215.915	1198.841	2.30E-02	β(HCCH), β(HCOH), β(CH3)
1220.176	1210.361	1.11E-02	τ(CH2), β(HCCH), β(HCOH)
1222.203	1211.034	9.68E-03	β(CH2), β(HCCH), β(HCOH)
1226.93	1209.565	5.82E-02	τ(CH2), β(HCCH), β(HCOH)
1239.668	1221.362	2.56E-02	β(HCOH)
1244.952	1236.229	6.51E-04	τ(CH2), β(HCCH), β(HCOH)
1248.514	1237.255	2.36E-02	β(HCCH), β(HCOH)
1275.413	1252.762	1.49E-02	τ(CH2), β(HCCH), β(HCOH)
1282.107	1248.806	2.90E-03	τ(CH2), β(HCCH)
1286.179	1263.725	1.95E-02	β(HCCH), β(HCOH)
1291.791	1267.498	9.63E-03	τ(CH2), β(HCCH), β(HCOH)
1294.09	1257.312	2.39E-02	τ(CH2), β(HCCH), β(HCOH)

v-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S12: Vibrational mode assignment of **[*α-a16+H*]$^+$ *ion (C):***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
978.20	961.91	1.87E-01	β(CCH), β(CCO)
997.16	966.51	5.77E-03	β(CCH), β(CCO)
997.53	983.92	1.84E-02	vs(COC) in glycosidic linkage, β(COH)
1017.24	1002.16	1.33E-01	β(CCH), β(CCO)
1020.46	1034.78	4.94E-02	β(CCH), β(CCO)
1026.23	966.78	8.81E-03	Bending H+ on Acetyl Oxygen
1032.90	1021.46	1.65E-01	β(CCH), β(CCO), ν(CO)
1054.46	1043.37	1.50E-01	β(CCH), β(CCO), ν(CO)
1062.25	1057.52	3.68E-02	β(CCH), β(CCO)
1069.71	1061.99	9.80E-03	β(CCH), β(CCO)
1076.40	1058.02	3.88E-01	β(CCH), β(CCO), ν(CO)
1078.51	1067.00	1.03E-01	β(CCH), β(CCO)
1086.99	1071.57	9.06E-02	vas(COC) in glycosidic linkage, β(COH)
1092.10	1074.36	2.15E-01	vas(COC) in glycosidic linkage, β(COH)
1095.29	1084.97	1.79E-01	β(CCH), β(CCO)
1102.64	1084.22	6.41E-02	β(CCH), β(CCO), ν(CO)
1107.26	1079.89	5.00E-01	ν(CC), ν(CO)
1114.71	1098.09	2.21E-01	β(CCH), β(CCO)
1123.10	1108.24	8.08E-03	β(CCH), β(CCO)
1127.10	1115.24	3.87E-01	β(CCH), β(CCO)
1129.75	1112.52	1.51E-02	β(CCH), β(CCO)
1137.39	1123.05	6.31E-01	ν(CC), ν(CO), β(CO)
1139.42	1125.41	1.23E-01	vas(CC), ν(CO), β(CO)
1142.40	1128.86	1.63E-02	ν(CO), β(CCH)
1146.49	1145.67	7.15E-02	ν(CC), β(CO)
1153.97	1137.61	1.02E-01	β(CCH), β(CCO),γ(CH2), ν(CN)
1158.29	1140.11	4.18E-02	β(CCH), β(CCO),γ(CH2), ν(CN)
1166.69	1154.04	2.45E-01	β(CCH), β(CCO),γ(CH2), ν(CN)
1170.94	1155.94	2.05E-03	vas(COC) in glycosidic linkage, ν(CN), β(CCH)
1177.57	1164.31	3.02E-01	β(CCO), ν(CO)
1181.03	1165.79	2.76E-01	β(CCH), β(CCO)
1193.00	1170.55	1.04E-01	β(CCH), vas(CO)
1193.65	1179.37	3.79E-02	β(CCH), β(CCO)
1200.57	1186.86	9.06E-01	β(CCH), β(CCO)
1208.33	1196.07	6.48E-02	β(CCH), β(CCO)
1223.45	1203.25	3.49E-01	γ(CH2), γ(HC:OH)
1235.13	1223.41	2.45E-03	β(COH), β(CCH), vas(COC) in glycosidic linkage,
1242.23	1216.32	7.43E-03	β(CCH), β(CCO)
1243.88	1234.20	2.18E-03	β(CCH), β(CCO)
1254.56	1246.65	8.17E-02	β(CCH), β(CCO)
1256.09	1274.54	1.87E-02	β(CCH), β(CCO)
1261.46	1244.56	1.41E-02	τ(CH2), β(CCH), β(CCO)
1263.11	1242.36	8.31E-03	τ(CH2), β(CCH), β(CCO)
1269.00	1238.99	6.38E-03	τ(CH2), β(CCH), β(CCO)
1287.59	1266.85	6.95E-05	τ(CH2), β(CCH), β(CCO)
1288.75	1268.42	1.52E-03	τ(CH2), β(CCH), β(CCO)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S13: Vibrational mode assignment of **[*α-a16+H*]$^+$ *ion* (^{2}*A*).**

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
974.667	956.484	1.20E-02	Bending H+ on Acetyl Oxygen, β(HCOH), β(CH2)
980.024	965.865	3.38E-02	β(HCOH), β(HCCH), β(CH2)
996.675	980.751	8.16E-03	β(HCCH)
1000.171	986.556	3.22E-02	β(HCOH), β(HCCH), β(CH2)
1014.178	998.44	1.00E-02	β(HCOH), β(HCCH)
1017.802	1004.147	1.57E-02	β(HCCH), β(CH3)
1022.506	1013.37	2.28E-02	Bending H+ on Acetyl Oxygen, β(CH3)
1041.677	1030.531	2.67E-02	β(HCOH), β(HCCH)
1047.231	1038.782	9.11E-03	Bending H+ on Acetyl Oxygen, β(CH3)
1056.308	1025.305	4.43E-02	Bending H+ on Acetyl Oxygen, β(CH3), β(HCCH)
1067.354	1052.707	1.81E-02	Bending H+ on Acetyl Oxygen, β(CH3), β(HCCH)
1069.702	1064.303	3.36E-02	β(CH3)
1076.585	1064.081	1.40E-02	νas(COC) in glycosidic linkage, β(HCOH), β(HCCH)
1080.736	1059.308	2.27E-02	β(HCOH), β(HCCH), β(CH2), β(CH3)
1087.976	1090.16	4.02E-02	β(HCOH), β(HCCH)
1089.01	1073.041	5.95E-03	β(HCOH), β(CH3)
1103.813	1059.413	7.44E-02	Bending H+ on Acetyl Oxygen
1116.034	1102.872	1.56E-01	νas(COC) in glycosidic linkage, β(HCOH), β(HCCH)
1119.09	1108.199	3.80E-02	β(HCOH), β(HCCH)
1121.338	1100.445	9.44E-02	Bending H+ on Acetyl Oxygen, β(HCOH), β(HCCH)
1126.087	1111.104	1.45E-02	Bending H+ on Acetyl Oxygen, β(HCOH), β(HCCH)
1129.328	1114.967	1.05E-02	β(HCOH), β(HCCH), β(CH3)
1132.638	1116.051	1.12E-02	ν(CO), β(HCOH), β(HCCH)
1146.804	1130.982	3.25E-02	β(HCOH), β(HCCH)
1148.048	1124.854	4.36E-02	β(HCOH), β(HCCH)
1153.226	1137.201	1.05E-02	ν(CO), β(HCOH), β(HCCH)
1154.432	1135.659	5.72E-02	β(HCOH), β(HCCH), β(CH2)
1168.68	1152.862	2.37E-02	β(HCOH), β(HCCH), β(CH3)
1172.957	1155.501	5.83E-03	ν(CO), β(HCOH), β(HCCH)
1175.796	1165.251	4.39E-02	β(HCOH), β(HCCH), β(CH2)
1182.617	1165.735	3.08E-02	β(HCCH), β(HCNH)
1188.85	1172.895	8.08E-03	β(HCOH), β(HCCH)
1196.457	1182.025	2.85E-02	β(HCOH), β(HCCH), β(CH3)
1209.37	1184.04	2.83E-02	β(HCOH), β(HCCH), β(CH2)
1218.801	1201.11	1.37E-02	β(HCOH), β(HCCH), β(CH2)
1233.583	1231.98	3.28E-02	β(HCOH), β(HCCH), β(CH2)
1236.744	1205.811	2.79E-02	β(HCOH), β(HCCH)
1237.678	1227.807	3.40E-02	β(HCOH), β(HCCH)
1240.901	1228.294	1.62E-02	β(HCOH), β(HCCH)
1253.928	1246.464	7.56E-03	β(HCOH)
1261.071	1246.543	1.23E-02	β(HCOH), β(HCCH), β(CH2)
1261.427	1243.356	1.01E-02	β(HCOH), β(HCCH), β(CH2)
1275.735	1246.323	6.37E-03	β(HCOH), β(HCCH), β(CH2)
1285.449	1268.977	1.83E-03	β(HCOH), β(HCCH)
1297.621	1260.489	3.65E-02	β(HCOH), β(HCCH)
1306.216	1277.084	1.65E-02	β(HCOH), β(HCCH)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S14: Vibrational mode assignment of **[*β-a16+H*]$^+$ *ion.(C')***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
981.65	932.34	2.21E-02	Bending H+ on Acetyl Oxygen, β(CCH)
997.40	969.26	1.14E-01	Bending H+ on Acetyl Oxygen, β(CCH), β(CCO)
1001.64	982.47	1.71E-01	β(CCH), β(CCO), β(CNH)
1015.80	1000.28	2.72E-02	δ(CH2)
1019.92	1007.84	8.77E-02	δ(CH2)
1032.54	1014.82	2.88E-02	β(CCH), β(CCO)
1041.09	1047.97	3.13E-03	β(CCH), β(CCO)
1053.71	1037.68	4.80E-01	ν(CO), ν(CC), β(COH)
1057.17	1073.37	3.80E-02	δ(CH2)
1061.53	1047.58	9.00E-01	ν(CC), β(COH)
1073.67	1059.66	1.80E-02	νas(COC) in glycosidic linkage, β(COH), ν(CO)
1077.10	1078.72	1.88E-02	β(COH), β(CH)
1086.07	1075.78	4.92E-01	β(CCH), β(CCO)
1088.44	1073.50	1.55E-02	β(CCH), β(CCO)
1102.58	1095.20	8.13E-02	β(CCH), β(CCO), ν(CC)
1106.87	1088.42	1.38E-01	δ(HCOH), ν(CO), τ(CH2)
1113.04	1099.94	4.63E-02	β(CCH), β(CCO)
1113.62	1097.26	2.91E-03	β(CCH), β(CCO), ν(CO)
1120.70	1111.24	4.01E-01	β(CCH), β(CCO)
1124.27	1116.74	2.45E-01	β(CCH), β(CCO)
1128.11	1118.22	1.27E-01	β(CCH), β(CCO)
1133.87	1117.95	9.06E-01	νas(CO), ν(CO), β(CO), β(CH)
1141.36	1124.91	9.75E-02	ν(CC), β(CO), β(CH)
1147.42	1127.45	5.76E-01	νas(CO), ν(CO), β(CO), β(CH)
1150.72	1134.44	2.79E-02	ν(CO), β(CO), β(CH)
1160.89	1142.91	4.12E-03	ν(CC), β(CO), β(CH)
1167.63	1150.51	7.77E-04	ν(CC), β(CO), β(CH)
1174.04	1155.27	4.84E-01	ν(CO), β(COC), β(CH)
1176.85	1158.19	2.37E-01	β(CCO), ν(CO), β(CH)
1184.29	1166.01	2.45E-02	β(CCO), ν(CO), β(CH)
1187.86	1169.02	7.30E-02	β(CCO), ν(CO), β(CH)
1190.94	1175.31	2.66E-02	γ(CH2), γ(HC:OH)
1191.85	1168.27	7.61E-03	γ(CH2), γ(HC:OH)
1202.43	1188.73	2.60E-03	δ(HCCH), ν(CO), β(COH)
1212.28	1192.66	1.13E-01	β(COH), β(CCH), νas(COC) in glycosidic linkage,
1220.16	1189.58	2.41E-01	β(CCH), β(CCO)
1235.25	1217.90	5.66E-02	δ(HCCH), β(COH)
1242.33	1231.98	1.39E-02	δ(HCCH), β(COH)
1251.26	1218.79	3.01E-02	τ(CH2)
1255.97	1246.00	6.71E-03	β(CCH), β(CCO)
1258.42	1281.33	1.20E-01	δ(HCOH)
1265.92	1241.76	2.53E-02	γ(CH2), γ(HC:OH)
1283.82	1263.92	1.11E-02	γ(CH2), γ(HC:OH)
1290.42	1270.33	5.75E-03	β(CH3), β(CCH), β(CCO)
1296.20	1267.49	1.14E-01	β(CH3), β(CCH), β(CCO)
1300.81	1269.51	5.12E-03	β(CH3), β(CCH), β(CCO)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S15 *Vibrational mode assignment of* ***[α-an16+H]⁺ ion.(D)***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
967.50	953.84	1.06E-03	β(OH), β(HCCH), τ(CH2), τ(CH3)
977.24	947.21	7.96E-05	Bending H+ on Acetyl Oxygen, β(HCNH)
980.30	967.42	5.95E-04	β(HCCH), β(OH)
997.00	985.50	3.54E-04	β(OH), β(HCCH), τ(CH2)
1015.13	1009.74	3.97E-03	Bending H+ on Acetyl Oxygen, τ(CH3)
1021.35	1014.72	8.52E-03	Bending H+ on Acetyl Oxygen, τ(CH3), β(HCCH)
1024.51	1023.84	3.26E-04	Bending H+ on Acetyl Oxygen, τ(CH3)
1049.47	1022.08	2.16E-03	Bending H+ on Acetyl Oxygen, τ(CH3)
1058.49	1045.16	2.44E-03	β(OH), β(HCCH), τ(CH2), τ(CH3), ν(CO)
1062.27	1024.67	5.22E-04	Bending H+ on Acetyl Oxygen, τ(CH3)
1071.98	1053.14	3.71E-04	Bending H+ on Acetyl Oxygen, τ(CH3), β(HCCH)
1074.92	1064.18	3.53E-04	νs(COC) in glycosidic linkage, δ(HCOH)
1077.20	1054.08	1.80E-03	Bending H+ on Acetyl Oxygen
1089.66	1080.92	2.52E-05	Bending H+ on Acetyl Oxygen, β(OH)
1090.82	1078.84	7.77E-05	β(OH), β(HCCH), τ(CH2), τ(CH3), ν(CO)
1100.64	1089.47	1.26E-04	β(OH), β(HCCH), ν(CC)
1110.10	1101.51	5.62E-04	Bending H+ on Acetyl Oxygen, β(OH)
1113.19	1099.24	2.21E-03	Bending H+ on Acetyl Oxygen, β(OH), β(HCOH),
1114.38	1099.63	7.44E-04	Bending H+ on Acetyl Oxygen, β(OH), β(HCOH),
1119.49	1109.43	1.50E-04	β(OH), δ(HCOH), τ(CH3)
1122.98	1109.64	3.10E-03	β(OH), δ(HCOH), τ(CH3)
1130.66	1119.54	2.96E-03	β(OH), δ(HCOH)
1135.89	1120.74	4.51E-05	β(OH), δ(HCOH), τ(CH2)
1138.16	1122.06	4.30E-04	νas(COC), δ(HCOH)
1139.44	1127.92	8.28E-05	β(OH), δ(HCOH)
1151.41	1137.36	1.04E-04	β(OH), δ(HCOH)
1158.31	1141.11	1.40E-04	β(OH), δ(HCOH)
1161.00	1144.14	6.33E-05	β(OH), δ(HCOH), τ(CH2)
1169.74	1152.69	2.07E-05	νs(COC) in glycosidic linkage, δ(HCOH), β(OH)
1172.59	1154.58	7.21E-04	β(OH), β(HCOH)
1182.30	1165.13	1.23E-05	δ(HCOH), τ(CH3)
1185.93	1167.83	1.53E-04	δ(HCCH), ν(CN)
1192.95	1177.33	4.19E-03	β(OH), δ(HCOH), τ(CH3)
1201.53	1193.99	7.42E-05	δ(HCCH), δ(HCOH)
1204.33	1188.64	1.73E-03	β(OH), δ(HCOH), τ(CH3)
1214.89	1205.55	4.92E-05	δ(HCCH), δ(HCOH)
1222.83	1217.88	5.47E-04	δ(HCCH), δ(HCOH)
1231.95	1219.20	5.11E-04	δ(HCCH), δ(HCOH)
1239.39	1227.95	6.56E-04	δ(HCCH), δ(HCOH)
1246.50	1244.21	1.10E-03	β(OH), β(HCCH)
1257.77	1251.47	4.85E-04	δ(HCOH)
1262.72	1235.60	1.69E-03	β(OH), δ(HCOH), τ(CH2)
1273.31	1260.50	1.63E-04	β(OH), δ(HCOH), τ(CH2)
1275.75	1258.34	2.54E-03	β(OH), δ(HCOH), τ(CH2)
1281.23	1254.01	4.81E-04	β(OH), δ(HCOH), τ(CH2)
1297.58	1261.93	3.96E-05	β(OH), β(HCCH)

v-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S16: Vibrational mode assignment of **[*α-an16+H*]$^+$ *ion* (^{2}*D*)**

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
958.776	939.879	1.40E-02	β(HCOH), β(CH2)
965.394	950.152	6.23E-03	β(HCCH), β(CH2)
983.841	966.711	3.86E-02	Bending H+ on Acetyl Oxygen, β(HCNH)
990.314	974.485	3.04E-03	β(HCCH)
993.907	974.973	1.14E-02	β(HCCH)
1017.728	1006.407	2.49E-02	β(HCCH), β(CH3)
1025.122	1015.024	2.77E-03	β(HCCH), β(CH3)
1034.303	1030.262	8.69E-03	β(CH3)
1045.053	1029.905	5.24E-02	β(CH3)
1058.255	1046.319	9.39E-03	β(HCCH), τ(CH3)
1061.11	1047.428	2.58E-02	β(HCCH), τ(CH3)
1080.298	1068.876	5.95E-02	νs(COC) in glycosidic linkage, β(HCOH)
1085.484	1070.469	3.85E-02	νas(COC) in glycosidic linkage, β(HCOH), τ(CH2)
1092.836	1081.065	1.96E-02	τ(CH2), β(HCOH)
1103.637	1094.16	5.20E-03	β(HCOH)
1109.288	1092.33	2.03E-02	β(HCOH), β(HCCH)
1113.726	1097.405	7.75E-02	β(HCOH), β(HCCH)
1117.794	1105.012	2.57E-02	β(HCOH), β(HCCH)
1125.676	1113.195	2.64E-02	ν(CO), β(HCOH), β(HCCH)
1128.93	1117.966	4.52E-02	ν(CO), β(HCOH), β(HCCH)
1135.023	1117.389	4.64E-02	ν(CO), β(HCOH), β(HCCH)
1139.222	1124.598	1.80E-02	ν(CC), β(HCOH), β(HCCH)
1142.448	1128.477	3.30E-02	νas(COC) in glycosidic linkage, ν(CC), β(HCOH)
1153.399	1138.712	4.65E-02	ν(CC), β(HCOH), β(HCCH)
1156.254	1140.862	2.02E-02	ν(CC), νas(COC), β(HCOH), β(HCCH)
1160.386	1144.882	3.95E-02	β(HCCH)
1162.397	1152.777	2.64E-02	β(HCOH), β(HCCH)
1173.156	1155.829	1.10E-02	ν(CO), β(HCOH), β(HCCH)
1179.323	1161.099	2.77E-02	β(HCCH), τ(CH3)
1180.82	1164.481	5.21E-02	νas(COC), β(HCOH), β(HCCH)
1186.932	1168.904	5.74E-02	ν(CO), β(HCOH), β(HCCH), β(CH3)
1191.736	1171.935	3.00E-02	νas(COC), β(HCOH), β(HCCH)
1194.79	1180.177	1.15E-02	νas(COC) in glycosidic linkage, ν(CC), β(HCOH)
1202.951	1185.306	8.97E-03	νas(COC) in glycosidic linkage, β(HCOH), β(HCCH)
1217.874	1201.015	2.56E-02	β(HCOH), β(HCCH)
1220.991	1215.613	1.88E-02	β(HCCH), β(HCOH), τ(CH2)
1238.84	1226.956	2.84E-03	β(HCOH), β(HCCH)
1242.694	1229.352	1.51E-02	β(HCCH), β(HCOH), τ(CH2)
1250.478	1240.669	2.43E-02	β(HCOH), β(HCCH)
1251.959	1235.388	2.00E-02	β(HCOH), β(HCCH), β(HCNH)
1269.828	1253.488	1.16E-02	β(HCCH), β(HCOH), τ(CH2)
1279.717	1256.012	2.69E-03	β(HCCH), β(HCOH), τ(CH2)
1286.255	1269.787	1.78E-02	β(HCCH), β(HCOH)
1288.293	1266.141	1.56E-03	β(HCOH), β(HCCH), β(HCNH)
1298.122	1266.36	1.22E-02	β(HCNH), τ(CH2)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S17: *Vibrational mode assignment of* ***[β-an16+H]$^+$ (D')***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
970.10	948.31	2.25E-04	β(OH), τ(CH2)
983.24	967.42	2.79E-03	β(OH), δ(HCCH), τ(CH3)
993.31	980.85	1.46E-05	δ(HCCH), τ(CH3)
1000.53	983.71	1.54E-03	δ(HCCH), τ(CH3)
1016.63	1011.34	8.58E-04	τ(CH3)
1017.22	1012.99	3.15E-03	τ(CH3)
1044.61	1034.05	5.77E-04	β(OH), δ(HCCH), τ(CH3)
1052.17	1063.16	4.24E-05	β(OH), νs(COC), τ(CH3)
1058.21	1047.28	2.78E-03	β(OH), ν(CO), τ(CH3)
1068.71	1057.86	3.40E-04	β(OH), τ(CH3)
1072.79	1068.15	4.34E-05	δ(HCCH), τ(CH3)
1075.76	1062.26	2.98E-04	β(OH), ν(CO), τ(CH2), τ(CH3)
1088.87	1073.74	3.28E-03	β(HCCH), ν(CC), β(OH)
1091.39	1080.51	6.25E-04	β(HCCH), ν(CC), β(OH)
1103.51	1094.47	2.82E-04	β(HCCH), ν(CC), β(OH)
1110.89	1100.13	4.85E-03	β(HCCH), β(OH)
1114.86	1098.43	1.59E-03	β(HCCH), β(OH), νas(COC)
1117.41	1107.99	1.68E-03	β(OH), δ(HCCH), τ(CH2)
1120.01	1109.16	2.16E-04	β(OH), δ(HCCH), τ(CH3)
1123.63	1107.02	6.85E-05	β(OH), δ(HCCH), τ(CH2)
1132.28	1119.47	5.20E-06	β(OH), δ(HCCH), τ(CH3)
1139.34	1122.15	1.03E-04	β(HCCH), β(OH), ν(CO)
1141.14	1126.76	1.51E-03	β(OH), δ(HCCH), τ(CH3)
1152.32	1133.69	1.61E-04	β(HCCH), β(OH), ν(CO)
1153.02	1137.67	9.60E-05	β(HCCH), ν(CC)
1155.03	1140.39	5.11E-04	β(OH), δ(HCCH), τ(CH2)
1160.25	1143.43	1.88E-03	β(HCCH), β(OH), ν(CO)
1162.08	1153.03	5.24E-05	β(OH), δ(HCCH), τ(CH3), ν(CN)
1172.77	1149.10	8.35E-05	β(HCCH), ν(CO)
1173.29	1157.55	4.65E-05	β(HCCH), β(CH3)
1179.10	1158.89	3.07E-05	β(HCCH), ν(CO)
1182.84	1167.82	4.18E-04	Bending H+ on Acetyl Oxygen, β(OH), νas(COC)
1188.11	1172.88	2.81E-04	νas(COC) in glycosidic linkage, β(CH3), β(OH)
1196.79	1182.57	5.39E-05	δ(HCOH), τ(CH3)
1206.82	1187.26	6.19E-05	νas(COC) in glycosidic linkage, β(HCCH), β(OH)
1222.02	1205.70	3.93E-04	β(HCOH), τ(CH2)
1225.68	1206.61	1.83E-04	β(HCOH), β(HCCH), τ(CH2)
1235.37	1224.47	7.26E-04	β(HCOH), β(HCCH), τ(CH3)
1241.17	1227.11	7.95E-04	β(HCOH), β(HCCH), τ(CH2)
1249.78	1246.92	9.23E-04	β(HCOH)
1259.94	1245.75	3.25E-04	β(HCOH)
1270.72	1248.95	3.44E-04	β(HCOH), β(HCCH), τ(CH2)
1275.22	1253.01	1.27E-03	β(HCOH), β(HCCH), τ(CH2)
1283.57	1262.00	4.07E-04	β(HCOH), β(HCCH), τ(CH2)
1290.57	1270.27	1.26E-04	β(HCOH), β(HCCH), τ(CH2)
1295.59	1270.05	1.60E-03	β(HCOH), β(HCCH), τ(CH2

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S18: *Vibrational mode assignment of* ***[β-an16+H]$^+$ (^{2}D')***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
974.667	956.484	1.20E-02	Bending H+ on Acetyl Oxygen, β(HCOH), β(CH2)
980.024	965.865	3.38E-02	β(HCOH), β(HCCH), β(CH2)
996.675	980.751	8.16E-03	β(HCCH)
1000.171	986.556	3.22E-02	β(HCOH), β(HCCH), β(CH2)
1014.178	998.44	1.00E-02	β(HCOH), β(HCCH)
1017.802	1004.147	1.57E-02	β(HCCH), β(CH3)
1022.506	1013.37	2.28E-02	Bending H+ on Acetyl Oxygen, β(CH3)
1041.677	1030.531	2.67E-02	β(HCOH), β(HCCH)
1047.231	1038.782	9.11E-03	Bending H+ on Acetyl Oxygen, β(CH3)
1056.308	1025.305	4.43E-02	Bending H+ on Acetyl Oxygen, β(CH3), β(HCCH)
1067.354	1052.707	1.81E-02	Bending H+ on Acetyl Oxygen, β(CH3), β(HCCH)
1069.702	1064.303	3.36E-02	β(CH3)
1076.585	1064.081	1.40E-02	vas(COC) in glycosidic linkage, β(HCOH), β(HCCH)
1080.736	1059.308	2.27E-02	β(HCOH), β(HCCH), β(CH2), β(CH3)
1087.976	1090.16	4.02E-02	β(HCOH), β(HCCH)
1089.01	1073.041	5.95E-03	β(HCOH), β(CH3)
1103.813	1059.413	7.44E-02	Bending H+ on Acetyl Oxygen
1116.034	1102.872	1.56E-01	vas(COC) in glycosidic linkage, β(HCOH), β(HCCH)
1119.09	1108.199	3.80E-02	β(HCOH), β(HCCH)
1121.338	1100.445	9.44E-02	Bending H+ on Acetyl Oxygen, β(HCOH), β(HCCH)
1126.087	1111.104	1.45E-02	Bending H+ on Acetyl Oxygen, β(HCOH), β(HCCH)
1129.328	1114.967	1.05E-02	β(HCOH), β(HCCH), β(CH3)
1132.638	1116.051	1.12E-02	ν(CO), β(HCOH), β(HCCH)
1146.804	1130.982	3.25E-02	β(HCOH), β(HCCH)
1148.048	1124.854	4.36E-02	β(HCOH), β(HCCH)
1153.226	1137.201	1.05E-02	ν(CO), β(HCOH), β(HCCH)
1154.432	1135.659	5.72E-02	β(HCOH), β(HCCH), β(CH2)
1168.68	1152.862	2.37E-02	β(HCOH), β(HCCH), β(CH3)
1172.957	1155.501	5.83E-03	ν(CO), β(HCOH), β(HCCH)
1175.796	1165.251	4.39E-02	β(HCOH), β(HCCH), β(CH2)
1182.617	1165.735	3.08E-02	β(HCCH), β(HCNH)
1188.85	1172.895	8.08E-03	β(HCOH), β(HCCH)
1196.457	1182.025	2.85E-02	β(HCOH), β(HCCH), β(CH3)
1209.37	1184.04	2.83E-02	β(HCOH), β(HCCH), β(CH2)
1218.801	1201.11	1.37E-02	β(HCOH), β(HCCH), β(CH2)
1233.583	1231.98	3.28E-02	β(HCOH), β(HCCH), β(CH2)
1236.744	1205.811	2.79E-02	β(HCOH), β(HCCH)
1237.678	1227.807	3.40E-02	β(HCOH), β(HCCH)
1240.901	1228.294	1.62E-02	β(HCOH), β(HCCH)
1253.928	1246.464	7.56E-03	β(HCOH)
1261.071	1246.543	1.23E-02	β(HCOH), β(HCCH), β(CH2)
1261.427	1243.356	1.01E-02	β(HCOH), β(HCCH), β(CH2)
1275.735	1246.323	6.37E-03	β(HCOH), β(HCCH), β(CH2)
1285.449	1268.977	1.83E-03	β(HCOH), β(HCCH)
1297.621	1260.489	3.65E-02	β(HCOH), β(HCCH)
1306.216	1277.084	1.65E-02	β(HCOH), β(HCCH)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S19: *Vibrational mode assignment of* ***[α-bn16+H]$^+$ ion. (E)***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
971.81	961.28	6.94E-03	β(HCCH), β(CH3)
977.30	948.91	3.40E-01	Bending H+ on Acetyl Oxygen, β(NH)
980.30	964.71	3.77E-03	β(HCCH), β(CO)
1011.42	999.10	1.53E-01	β(HCCH), β(CH3)
1014.17	1008.76	6.81E-03	Bending H+ on Acetyl Oxygen, β(CH3)
1023.63	1025.06	2.74E-02	Bending H+ on Acetyl Oxygen, β(CH3)
1048.42	1022.47	1.12E-02	Bending H+ on Acetyl Oxygen, β(CH3)
1050.18	1036.21	8.69E-02	Bending H+ on Acetyl Oxygen, β(CH3)
1060.64	1036.00	7.14E-02	Bending H+ on Acetyl Oxygen, β(CH3)
1066.73	1037.74	9.40E-02	Bending H+ on Acetyl Oxygen, β(CH3)
1071.02	1052.77	7.19E-02	β(HCCH), β(CO), ν(CO)
1078.05	1058.68	7.62E-02	Bending H+ on Acetyl Oxygen, β(HCCH), β(CO)
1082.41	1068.65	4.70E-01	β(CO), vas(COC)
1089.59	1083.52	6.14E-03	β(CO), β(HCCH)
1090.99	1076.92	3.52E-02	Bending H+ on Acetyl Oxygen, β(CH3), β(CO)
1101.08	1096.44	1.62E-02	β(CO), vs(COC) in glycosidic linkage
1103.59	1094.94	7.58E-03	β(CO), vs(COC) in glycosidic linkage
1111.95	1100.70	9.85E-02	β(CO), vs(COC) in glycosidic linkage
1113.51	1103.42	4.41E-02	vas(COC), β(CO)
1122.36	1108.87	8.77E-02	vas(COC), β(CO), ν(CO)
1130.10	1110.53	7.06E-02	Bending H+ on Acetyl Oxygen, β(CO)
1134.52	1118.98	5.00E-01	vas(OCO), β(CO)
1136.43	1116.37	4.39E-01	vas(COC) in glycosidic linkage, ν(CO)
1140.37	1128.98	1.51E-02	β(HCCH), β(CO), ν(CO)
1146.01	1131.28	9.06E-01	vas(COC), β(CO), ν(CO)
1155.09	1142.07	4.32E-02	β(CH3), β(CO), ν(CO)
1157.61	1138.23	6.94E-02	ν(CC), vas(COC) in glycosidic linkage, ν(CO)
1162.67	1142.40	4.01E-02	β(CO), τ(CH2), ν(CO)
1171.10	1153.59	2.15E-02	β(CO), β(CH3)
1173.98	1154.91	2.86E-02	ν(CC), vas(COC) in glycosidic linkage, ν(CO)
1176.53	1166.00	2.30E-02	β(CO), ν(CO)
1186.33	1165.75	2.58E-02	ν(CN), vas(COC), β(CC)
1192.93	1180.68	6.90E-02	β(CO), β(CH3)
1203.09	1191.04	7.10E-02	vas(COC) in glycosidic linkage, δ(HCCH)
1214.44	1197.41	2.93E-02	vas(COC) in glycosidic linkage, δ(HCCH), β(CO)
1216.66	1204.16	2.52E-01	vas(COC) in glycosidic linkage, δ(HCCH), β(CO)
1223.81	1219.54	2.95E-01	δ(HCOH), β(CO)
1226.82	1217.44	1.94E-01	δ(HCOH), β(CO)
1230.92	1215.36	1.28E-02	δ(HCOH), β(CO), τ(CH2)
1255.00	1242.72	8.83E-02	δ(HCOH), β(CO), β(CH3)
1257.24	1252.78	1.78E-02	δ(HCOH)
1268.00	1241.66	1.77E-03	Bending H+ on Acetyl Oxygen, β(HCCH), β(CO)
1269.57	1253.25	1.19E-01	Bending H+ on Acetyl Oxygen, δ(HCOH)
1281.81	1255.88	5.38E-03	δ(HCOH), β(CO), δ(HCCH), τ(CH2)
1284.99	1256.83	9.56E-02	δ(HCCH), δ(HCOH)
1295.21	1265.17	3.58E-03	δ(HCCH), δ(HCOH)

v-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S20: *Vibrational mode assignment of* ***[α-bn16+H]$^+$) ion (^{2}E).***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
971.805	961.281	9.07E-03	β(HCOH), β(HCCH), β(CH3)
977.303	948.905	6.34E-02	Bending H+ on Acetyl Oxygen, β(HCOH), β(HCNH)
980.302	964.713	6.68E-03	β(HCOH), β(HCCH)
1011.423	999.101	4.26E-02	β(HCCH), β(CH3)
1014.167	1008.762	8.98E-03	Bending H+ on Acetyl Oxygen, β(CH3)
1023.632	1025.062	1.80E-02	Bending H+ on Acetyl Oxygen, β(CH3)
1048.423	1022.469	1.15E-02	Bending H+ on Acetyl Oxygen, β(CH3), β(CH2)
1050.178	1036.208	3.21E-02	Bending H+ on Acetyl Oxygen, β(CH3)
1060.641	1036.002	2.91E-02	Bending H+ on Acetyl Oxygen, β(CH3), β(CH2)
1066.734	1037.735	3.34E-02	Bending H+ on Acetyl Oxygen, β(CH3)
1071.021	1052.766	2.92E-02	β(HCOH), β(HCCH)
1078.053	1058.678	3.00E-02	Bending H+ on Acetyl Oxygen, β(HCOH)
1082.414	1068.65	7.46E-02	Bending H+ on Acetyl Oxygen, β(HCOH), ν(CC)
1089.593	1083.523	8.53E-03	β(HCOH), β(HCCH)
1090.985	1076.915	2.04E-02	Bending H+ on Acetyl Oxygen, β(HCOH)
1101.082	1096.435	1.39E-02	β(HCOH), β(HCCH)
1103.588	1094.938	9.48E-03	β(HCOH), β(HCCH)
1111.954	1100.701	3.42E-02	β(HCOH), β(HCCH), β(HCNH), νs(COC) in glycosidic linkage
1113.506	1103.418	2.29E-02	β(HCOH), β(HCCH), β(CH2)
1122.36	1108.867	3.22E-02	ν(CO), β(HCOH), β(HCCH), β(CH3)
1130.1	1110.532	2.89E-02	β(HCOH), β(HCNH)
1134.52	1118.977	7.70E-02	ν(CO), β(HCOH), β(HCCH)
1136.434	1116.372	7.21E-02	ν(CO), β(HCOH), β(HCCH)
1140.372	1128.981	1.34E-02	ν(CO), β(HCOH), β(HCCH)
1146.014	1131.282	1.04E-01	β(HCOH), β(HCNH)
1155.089	1142.067	2.26E-02	β(HCOH), β(HCCH), β(CH3)
1157.606	1138.233	2.87E-02	ν(CC), β(HCOH), β(HCCH)
1162.666	1142.4	2.18E-02	β(HCOH), β(HCCH), β(CH2)
1171.097	1153.593	1.60E-02	β(HCOH), β(HCCH), β(CH3)
1173.981	1154.906	1.84E-02	ν(CO), β(HCOH), β(HCCH)
1176.531	1166.003	1.65E-02	ν(CO), β(HCOH), β(HCCH)
1186.325	1165.752	1.75E-02	ν(CO), ν(CN), β(HCOH), β(HCCH)
1192.927	1180.68	2.86E-02	β(HCOH), β(HCCH), β(CH3)
1203.086	1191.04	2.90E-02	νas(COC) in glycosidic linkage, β(HCOH), β(HCCH)
1214.443	1197.407	1.86E-02	νas(COC) in glycosidic linkage, β(HCOH), β(HCCH)
1216.66	1204.155	5.46E-02	νas(COC) in glycosidic linkage, β(HCOH), β(HCCH)
1223.806	1219.54	5.91E-02	β(HCOH), β(HCCH)
1226.815	1217.44	4.79E-02	β(HCOH), β(HCCH)
1230.92	1215.355	1.23E-02	β(HCOH), β(HCCH), β(CH2)
1254.998	1242.717	3.23E-02	β(HCOH), β(HCCH)
1257.243	1252.782	1.45E-02	β(HCOH), β(HCCH)
1268.001	1241.658	4.58E-03	β(HCOH), β(HCCH), β(HCNH)
1269.565	1253.25	3.75E-02	β(HCOH), β(HCCH)
1281.805	1255.879	7.98E-03	β(HCOH), β(HCCH), β(CH2)
1284.993	1256.828	3.36E-02	β(HCOH), β(HCCH), β(HCNH)
1295.207	1265.168	6.51E-03	β(HCOH), β(HCCH)

ν-stretching, as–asymmetric, s-symmetric, β–in-plane bending, γ–out-of-plane bending, δ-scissoring, τ-twisting

Table S21: *Vibrational mode assignment of* ***[β-bn16+H]$^+$ ion (E').***

Harmonic Vib	Anharmonic Vib	Intensity	Assignment
970.00	955.97	3.97E-02	τ(CH2), δ(HCOH), β(CH3)
972.52	958.34	1.36E-01	τ(CH2), δ(HCOH), β(CH3)
995.16	980.07	8.52E-02	δ(HCOH), δ(HCCH)
1005.34	993.56	6.07E-03	τ(CH2), β(CO), β(CH3), Bending H+ on Acetyl Oxygen
1016.26	1007.32	1.18E-01	δ(HCCH), β(CH3)
1019.88	1013.40	8.94E-02	δ(HCCH), β(CH3)
1054.11	1050.13	9.04E-02	β(CH3), β(CO)
1060.37	1058.93	2.32E-01	β(CH3), β(CO)
1071.84	1064.23	9.06E-01	β(CH3)
1074.32	1068.92	1.16E-01	β(CH3), β(CO)
1077.41	1058.79	8.53E-01	β(CH3), β(CO), ν(HCCH3)
1081.75	1069.76	2.94E-01	β(CO), δ(HCOH), νas(COC), ν(CC)
1089.95	1073.09	2.00E-01	β(CO), δ(HCOH), ν(CC). ν(CO)
1094.16	1080.43	3.47E-02	β(CH3), ν(HCCH), δ(HCOH)
1101.23	1092.60	4.53E-01	ν(HCCH), δ(HCOH)
1104.92	1100.65	8.18E-02	ν(HCCH), δ(HCOH)
1108.69	1097.97	3.01E-01	νas(COC) in glycosidic linkage, δ(HCOH)
1116.80	1099.51	2.57E-01	νas(COC), β(CC)
1126.79	1112.92	8.00E-02	β(CO), ν(HCCH)
1131.29	1115.61	1.95E-01	ν(CO), β(CO)
1138.88	1125.85	1.48E-02	ν(CO), β(CO)
1139.56	1127.00	7.51E-02	ν(CO), β(CO)
1145.96	1129.61	4.53E-03	β(CO), ν(HCCH)
1150.42	1138.41	7.72E-02	β(CH3), β(CO), ν(HCCH)
1153.32	1138.51	6.55E-02	ν(HCCH), δ(HCOH)
1156.95	1144.14	3.72E-02	ν(HCCH), δ(HCOH)
1163.36	1148.81	3.93E-01	νas(COC), δ(HCOH), ν(CO)
1164.61	1149.10	5.69E-01	ν(NC), ν(CO)
1170.28	1151.01	1.40E-01	δ(HCCH), ν(CO)
1174.63	1163.63	6.27E-02	δ(HCOH), β(CH3)
1179.32	1162.55	8.03E-02	δ(HCCH), ν(CO), δ(HCOH)
1181.39	1170.92	1.14E-01	δ(HCCH), ν(CO), δ(HCOH)
1192.11	1177.14	7.74E-03	δ(HCCH), β(CH3), δ(HCOH)
1208.01	1188.28	6.60E-02	δ(HCCH), ν(CO)
1215.86	1199.87	7.98E-02	δ(HCOH), νas(COC) in glycosidic linkage
1221.57	1214.91	2.61E-01	δ(HCOH), δ(HCCH)
1223.91	1218.92	4.12E-02	δ(HCOH), δ(HCCH)
1231.65	1204.48	7.28E-02	δ(HCOH), δ(HCCH)
1241.62	1224.50	6.54E-01	δ(HCOH), δ(HCCH), β(CH2)
1255.87	1252.07	5.24E-02	δ(HCOH), δ(HCCH), β(CH3)
1258.77	1240.61	9.64E-02	δ(HCOH), δ(HCCH)
1263.25	1251.27	1.52E-01	δ(HCOH), δ(HCCH)
1269.30	1241.72	3.41E-02	δ(HCOH), δ(HCCH)
1281.94	1256.03	1.16E-02	δ(HCOH), δ(HCCH)
1290.75	1264.67	1.65E-01	δ(HCOH), δ(HCCH), τ(CH2)
1295.87	1267.31	1.25E-01	δ(HCOH), β(HCCH)

ν-stretching,as–asymmetric,s-symmetric,β–in-plane bending,γ–out-of-plane bending, δ-scissoring,τ-twisting

Table S22: XYZ-coordinates of [***α-BG-H1+H]***$^+$ ion (A).

C	-3.457437	1.818169	-0.806872
H	-2.945627	2.451034	-1.539870
O	-4.781088	1.612472	-1.101698
H	-5.198382	2.456838	-1.298909
C	-2.068572	2.903283	0.867448
H	-1.992249	2.687992	1.937396
O	-3.388699	2.484435	0.463582
C	-2.746547	0.479936	-0.709061
H	-2.673260	0.076373	-1.718318
N	-3.480493	-0.537708	0.054180
H	-3.317357	-1.509253	-0.254693
C	-4.221031	-0.436552	1.129462
O	-4.467154	0.656196	1.759005
C	-4.842358	-1.651440	1.715005
H	-4.752681	-2.516439	1.061782
H	-5.893744	-1.434340	1.913202
H	-4.367626	-1.858004	2.678749
C	-1.297689	0.679863	-0.186604
H	-1.163111	0.073105	0.715676
O	0.135054	2.197081	1.038527
H	0.973339	2.013848	0.576609
C	-0.951116	2.131268	0.159385
H	-0.723003	2.633087	-0.789891
O	-0.353298	0.328891	-1.187205
C	-1.942018	4.393544	0.653838
H	-0.961611	4.709895	1.030645
H	-2.726946	4.902305	1.225539
O	-2.079680	4.634228	-0.733979
H	-2.031651	5.577206	-0.900706
C	0.011103	-1.011468	-1.289610
H	0.539432	-1.089098	-2.249992
C	-0.982709	-3.182584	-1.415200
H	-0.488078	-3.419421	-2.370066
O	-1.166572	-1.779548	-1.303137
C	0.945315	-1.459627	-0.170392
H	0.501505	-1.214274	0.801734
O	2.187854	-0.812924	-0.329295
C	1.201370	-2.959641	-0.220027
H	1.790463	-3.173741	-1.125302
O	1.862515	-3.400401	0.933603
H	2.672879	-2.875485	1.071289
C	-0.106214	-3.728870	-0.297489
H	0.114273	-4.782708	-0.515248
O	-0.797793	-3.627283	0.937873
H	-0.148921	-3.802477	1.631745
C	-2.378974	-3.781413	-1.433887
H	-2.309316	-4.874884	-1.469819
H	-2.912719	-3.444872	-2.324729
O	-3.137951	-3.356229	-0.314820
H	-2.600913	-3.574600	0.464535
C	2.642355	0.037286	0.684469
H	1.986419	-0.021738	1.558697
C	3.436501	1.685933	-0.859083
H	3.091513	1.080051	-1.706870
O	2.611242	1.378562	0.274938
C	4.063946	-0.357303	1.047367
H	4.384160	0.285860	1.876181
O	4.063753	-1.712813	1.447903
H	4.983107	-2.004701	1.461059
C	4.988448	-0.138819	-0.140895
H	4.670076	-0.795871	-0.955347

O	6.301035	-0.516335	0.195998
H	6.687308	0.223813	0.680544
C	4.895939	1.310645	-0.596343
H	5.452563	1.421964	-1.536679
O	5.499684	2.073084	0.432969
H	5.767298	2.929932	0.096071
C	3.236065	3.152622	-1.154745
H	3.505068	3.759562	-0.286645
H	2.191544	3.354059	-1.402657
H	3.846968	3.456096	-2.009274
H	-4.056727	1. 478527	1.319589

Table S23: XYZ-coordinates of [***α-BG-H1+H]***$^{+}$ ion (^{2}A).

C	-3.777383	2.184448	0.678761
H	-4.837487	1.967781	0.510793
O	-3.561533	2.690759	1.968323
H	-4.153937	3.431775	2.124078
C	-2.043010	3.469502	-0.345746
H	-1.800612	4.008710	0.577960
O	-3.416405	3.065247	-0.333744
C	-2.947614	0.903243	0.588832
H	-3.196736	0.376525	-0.330819
N	-3.237802	0.012458	1.701159
H	-2.991446	0.355264	2.620652
C	-3.610311	-1.236416	1.583034
O	-4.053682	-1.636142	0.454589
C	-3.516724	-2.159892	2.742194
H	-4.451573	-2.711529	2.856459
H	-3.274157	-1.640904	3.669271
H	-2.719836	-2.882372	2.533408
C	-1.458714	1.259384	0.629029
H	-1.242660	1.734784	1.592161
O	0.197445	2.733553	-0.321664
H	0.789299	2.058023	0.044803
C	-1.115485	2.260067	-0.456762
H	-1.275752	1.818370	-1.451599
O	-0.616453	0.113737	0.639845
C	-1.890909	4.398783	-1.533806
H	-0.847673	4.712464	-1.598446
H	-2.511152	5.289013	-1.372419
O	-2.210199	3.758028	-2.745990
H	-3.157224	3.599123	-2.752721
C	-0.428593	-0.642717	-0.513287
H	-0.287103	-0.009289	-1.401568
C	-1.422709	-2.449363	-1.701765
H	-1.217301	-1.976504	-2.675319
O	-1.560524	-1.466023	-0.690366
C	0.830160	-1.453657	-0.248894
H	0.754987	-1.844145	0.773143
O	1.960149	-0.625993	-0.392817
C	1.019342	-2.624943	-1.195009
H	1.340448	-2.230933	-2.171250
O	1.960753	-3.529828	-0.680783
H	2.646911	-3.035759	-0.195423
C	-0.275490	-3.397453	-1.390499
H	-0.150505	-4.091921	-2.232271
O	-0.600005	-4.122397	-0.213972
H	0.223288	-4.522924	0.098084
C	-2.757680	-3.165527	-1.811586
H	-2.685524	-3.979090	-2.538658
H	-3.534230	-2.473752	-2.140902

O	-3.192730	-3.690829	-0.551189
H	-2.416983	-4.129116	-0.150126
C	2.503998	-0.061404	0.780398
H	1.839252	-0.255283	1.625890
C	3.492884	1.825427	-0.328880
H	3.146903	1.492905	-1.317012
O	2.571607	1.325426	0.659631
C	3.876484	-0.670403	1.021190
H	4.239247	-0.307081	1.990230
O	3.735671	-2.081320	1.047637
H	4.630982	-2.441044	1.068971
C	4.853839	-0.251613	-0.063576
H	4.506506	-0.649641	-1.021659
O	6.115748	-0.824900	0.183860
H	6.556928	-0.255491	0.826339
C	4.901265	1.264174	-0.135148
H	5.504303	1.562051	-1.003788
O	5.523487	1.679585	1.067286
H	5.810770	2.591341	0.990634
C	3.444018	3.332726	-0.244094
H	2.440521	3.699284	-0.463821
H	4.133489	3.772068	-0.970632
H	3.717906	3.667280	0.759911
H	-3.756068	-2.604596	0.166031

Table S24: XYZ-coordinates of [***β-BG-H1+H***]$^+$ ion (A').

C	3.513637	1.805175	0.811557
H	4.593648	1.671357	0.962299
O	2.927519	2.512694	1.828957
H	2.888813	3.455741	1.587051
C	2.114278	2.822479	-0.925238
H	2.083009	2.521116	-1.977596
O	3.435884	2.480588	-0.445098
C	2.791494	0.464931	0.721455
H	2.715409	0.081556	1.737960
N	3.533776	-0.558232	-0.028593
H	3.346609	-1.533697	0.260990
C	4.295036	-0.453930	-1.088540
O	4.571802	0.648811	-1.695431
C	4.914065	-1.665347	-1.682239
H	5.964842	-1.450725	-1.885936
H	4.433679	-1.865010	-2.645007
H	4.821873	-2.534153	-1.034248
C	1.344587	0.645129	0.186093
H	1.227825	0.019578	-0.706720
O	-0.072844	2.088735	-1.133195
H	-0.922513	1.941270	-0.680619
C	0.983884	2.079846	-0.211142
H	0.717027	2.609121	0.708161
O	0.389899	0.299599	1.175722
C	1.963841	4.325674	-0.861157
H	0.984575	4.588947	-1.275713
H	2.750673	4.787186	-1.467407
O	2.073118	4.724692	0.496864
H	2.088767	5.682102	0.556189
C	0.031993	-1.039982	1.281288
H	-0.496061	-1.119457	2.241572
C	1.032577	-3.208070	1.414410
H	0.540712	-3.442540	2.371131

O	1.212494	-1.805461	1.295655
C	-0.897074	-1.496280	0.160709
H	-0.451004	-1.253768	-0.810959
O	-2.141406	-0.848394	0.313550
C	-1.152383	-2.995877	0.219318
H	-1.739698	-3.205405	1.126579
O	-1.815232	-3.444476	-0.930761
H	-2.645637	-2.948225	-1.047477
C	0.156499	-3.762309	0.299948
H	-0.061654	-4.815452	0.522704
O	0.848567	-3.665494	-0.936175
H	0.204125	-3.855709	-1.629920
C	2.431261	-3.801027	1.432175
H	2.368717	-4.894751	1.465968
H	2.964500	-3.462371	2.322405
O	3.186024	-3.369571	0.311188
H	2.649275	-3.594612	-0.466794
C	-2.610359	-0.034890	-0.716314
H	-1.973088	-0.123735	-1.601844
C	-3.334647	1.640875	0.833824
H	-2.989939	0.984205	1.640149
O	-2.570523	1.327299	-0.352355
C	-4.044652	-0.426601	-1.035021
H	-4.362322	0.170777	-1.901245
O	-4.074800	-1.796976	-1.372256
H	-4.999623	-2.071370	-1.372303
C	-4.959329	-0.121490	0.143045
H	-4.677384	-0.772180	0.977105
O	-6.286591	-0.442506	-0.195272
H	-6.655721	0.324905	-0.650453
C	-4.803220	1.338086	0.564189
H	-5.378440	1.505187	1.479888
O	-5.373857	2.187629	-0.414126
H	-4.723935	2.340383	-1.107235
C	-3.050814	3.081219	1.180465
H	-3.350052	3.751298	0.371859
H	-1.986267	3.220586	1.382543
H	-3.607666	3.362998	2.076954
H	4.136005	1.469444	-1.280975

Table S25: XYZ-coordinates of [***β-BG-H1+H]***$^{+}$ *ion (*^{2}*A').*

C	3.010512	-2.399101	-0.483986
H	2.447526	-3.149361	-1.044940
O	3.794867	-3.132753	0.442875
H	4.447819	-2.499979	0.817963
C	4.216580	-0.398833	-1.124573
H	4.468884	0.016046	-2.102521
O	3.756629	-1.717783	-1.420717
C	2.033442	-1.489945	0.296811
H	2.515847	-1.192598	1.237298
N	0.815041	-2.212444	0.636762
H	-0.095592	-1.869644	0.267944
C	0.769454	-3.255781	1.425105
O	1.824159	-3.820324	1.907318
C	-0.527855	-3.844932	1.831181
H	-1.371904	-3.375179	1.328734
H	-0.627729	-3.734112	2.915279
H	-0.509979	-4.916505	1.620390
C	1.771105	-0.215973	-0.489905
H	1.418883	-0.436997	-1.506919
O	3.090601	1.657019	-1.356832

H	2.507546	2.298815	-0.920468
C	3.117523	0.513361	-0.548405
H	3.362112	0.781256	0.490259
O	0.780321	0.514686	0.214400
C	5.486681	-0.406643	-0.303295
H	5.846023	0.624244	-0.215873
H	6.243827	-1.012203	-0.811345
O	5.205507	-0.946470	0.991277
H	5.975818	-0.850953	1.557200
C	0.195960	1.607801	-0.419881
H	0.189996	1.460717	-1.512355
C	0.402776	3.984675	-0.596631
H	0.310601	3.929367	-1.693602
O	0.960643	2.762240	-0.103973
C	-1.223931	1.751351	0.104412
H	-1.180881	1.737828	1.199594
O	-2.031115	0.706526	-0.387422
C	-1.889091	3.047524	-0.341155
H	-2.067530	2.997527	-1.420793
O	-3.148413	3.168600	0.276304
H	-3.000862	3.598765	1.129342
C	-0.990075	4.228799	-0.020027
H	-1.397214	5.132536	-0.497637
O	-1.018879	4.345635	1.382549
H	-0.292118	4.921828	1.659034
C	1.397418	5.082810	-0.265296
H	1.037252	6.025656	-0.683291
H	2.364572	4.860107	-0.732102
O	1.538500	5.286102	1.127747
H	2.021972	4.542602	1.497625
C	-2.220508	-0.410691	0.433059
H	-1.683313	-0.280632	1.377567
C	-2.296800	-1.966194	-1.406406
H	-2.228425	-1.129888	-2.111903
O	-1.665459	-1.552567	-0.173271
C	-3.711077	-0.583707	0.693630
H	-3.829982	-1.373158	1.441523
O	-4.267624	0.580088	1.244278
H	-4.006722	1.348647	0.709716
C	-4.437899	-1.024597	-0.568565
H	-4.401879	-0.212402	-1.310145
O	-5.769063	-1.378378	-0.278590
H	-6.143980	-0.691024	0.282087
C	-3.765529	-2.256899	-1.157486
H	-4.235488	-2.486503	-2.125177
O	-3.865777	-3.355400	-0.281329
H	-4.792348	-3.417961	-0.023164
C	-1.528715	-3.157327	-1.925423
H	-1.599704	-3.994429	-1.228562
H	-0.478622	-2.902741	-2.092903
H	-1.950098	-3.478988	-2.880231
H	2.691397	-3.555542	1.449153

Table S26: XYZ-coordinates of [***α-Le^a+H]$^+$*** *ion (B).*

C	-1.074992	3.127270	-0.746336
H	-0.410356	3.172352	-1.616077
O	-2.091064	4.044844	-0.803183
H	-1.731723	4.908226	-1.031189
C	0.890916	2.595853	0.593936

H	0.900325	2.298402	1.648730
O	-0.287884	3.414148	0.420040
C	-1.668333	1.730386	-0.620870
H	-2.095387	1.472290	-1.589045
N	-2.787917	1.648809	0.323013
H	-3.532570	0.980933	0.062080
C	-2.961876	2.220236	1.487885
O	-2.127660	3.019449	2.051402
C	-4.194874	1.944951	2.268108
H	-4.565317	2.889717	2.669176
H	-3.936578	1.308501	3.119986
H	-4.962294	1.463898	1.665734
C	-0.551962	0.686620	-0.322719
H	-0.757979	0.202107	0.638750
O	-0.447934	-0.268231	-1.365738
C	0.828479	1.337763	-0.267802
H	1.104018	1.601965	-1.295022
O	1.795398	0.468978	0.275448
C	2.124043	3.430343	0.290283
H	3.004093	2.910267	0.682015
H	2.025020	4.384415	0.815405
O	2.245624	3.687479	-1.085024
H	2.843197	3.015963	-1.440549
C	-1.342727	-1.343378	-1.376940
H	-1.215771	-1.797013	-2.369576
C	-3.692326	-1.764233	-1.278982
H	-3.703386	-2.253395	-2.265254
O	-2.638140	-0.815249	-1.226214
C	-1.049300	-2.394610	-0.308484
H	-1.057997	-1.919014	0.682874
O	0.150485	-3.074191	-0.551449
H	0.924190	-2.511034	-0.374254
C	-2.134929	-3.460266	-0.335625
H	-2.055462	-3.996042	-1.293765
O	-1.995193	-4.352154	0.743512
H	-1.089997	-4.679761	0.736388
C	-3.520554	-2.854577	-0.230718
H	-4.266778	-3.637295	-0.422288
O	-3.722728	-2.305606	1.063468
H	-3.457350	-2.979181	1.701078
C	-4.977157	-0.969658	-1.121318
H	-5.834062	-1.653157	-1.114309
H	-5.094011	-0.286364	-1.964502
O	-4.951481	-0.174596	0.052536
H	-4.762954	-0.790100	0.779713
C	2.486143	-0.363035	-0.632245
H	1.951089	-0.402983	-1.582713
C	3.152505	-1.826696	1.149653
H	2.685390	-1.129322	1.854142
O	2.491476	-1.673774	-0.131294
C	3.923234	0.093917	-0.832468
H	4.358921	-0.580262	-1.584055
O	3.951858	1.417383	-1.327227
H	4.878111	1.689901	-1.300581
C	4.724233	-0.023553	0.454495
H	4.316577	0.680608	1.187652
O	6.055450	0.361929	0.212335
H	6.523721	-0.421859	-0.102933
C	4.618868	-1.442686	1.004558
H	5.094151	-1.478495	1.989667
O	5.353256	-2.332801	0.186291
H	4.798004	-2.616099	-0.546810
C	2.932485	-3.249583	1.600109

H	3.366313	-3.961023	0.894632
H	1.865825	-3.460900	1.696232
H	3.406301	-3.404767	2.571970
H	-1.322837	3.245606	1.469265

Table S27: XYZ-coordinates of [***α-Le^a+H]$^+$*** ion (^{2}B).

C	-1.114720	3.450734	-0.222555
H	-1.927766	4.039568	-0.656353
O	-0.783504	3.962273	1.068269
H	-0.617626	4.910124	1.018698
C	1.130197	2.850995	-0.680074
H	1.451747	3.244255	0.291762
O	-0.054060	3.549639	-1.092627
C	-1.537398	1.987871	-0.072195
H	-1.815342	1.688232	-1.081917
N	-2.747042	1.734228	0.719188
H	-3.403068	1.065738	0.287309
C	-2.987373	1.985393	1.979515
O	-2.238363	2.724275	2.725162
C	-4.175914	1.394208	2.636893
H	-4.628771	2.134446	3.297281
H	-3.841408	0.555549	3.256511
H	-4.898043	1.036076	1.905095
C	-0.352562	1.111311	0.373719
H	-0.050020	1.386911	1.389096
O	-0.696278	-0.255564	0.497321
C	0.839365	1.361700	-0.542645
H	0.644077	0.978449	-1.551569
O	2.015899	0.785793	-0.019206
C	2.226595	3.116032	-1.705612
H	3.190978	3.001513	-1.202170
H	2.129787	4.156794	-2.030588
O	2.143709	2.273878	-2.824052
H	2.830063	1.600125	-2.719148
C	-1.190099	-0.961430	-0.605247
H	-0.542968	-0.844101	-1.488721
C	-3.381213	-1.200168	-1.663393
H	-3.052129	-1.243104	-2.712207
O	-2.467819	-0.443086	-0.886253
C	-1.216875	-2.420235	-0.167564
H	-1.608132	-2.433998	0.858653
O	0.053207	-3.008185	-0.247427
H	0.699805	-2.497247	0.268197
C	-2.133184	-3.255294	-1.043183
H	-1.691752	-3.324788	-2.049235
O	-2.316334	-4.536198	-0.490467
H	-1.448441	-4.901235	-0.289814
C	-3.507908	-2.624927	-1.156589
H	-4.100427	-3.196835	-1.883509
O	-4.166040	-2.610146	0.098787
H	-4.104746	-3.498929	0.467554
C	-4.684200	-0.411190	-1.578215
H	-5.503893	-1.000328	-2.004682
H	-4.597870	0.512864	-2.154217
O	-4.960567	-0.032883	-0.240843
H	-4.977325	-0.862013	0.262048
C	2.388217	-0.488435	-0.461653
H	1.772131	-0.796823	-1.311986
C	2.903954	-1.211179	1.762230
H	2.641033	-0.204909	2.107614
O	2.186306	-1.462129	0.535431
C	3.860514	-0.487672	-0.843534

H	4.081659	-1.491640	-1.234106
O	4.091493	0.468232	-1.852613
H	5.047932	0.560189	-1.939685
C	4.733131	-0.230906	0.376961
H	4.537161	0.783919	0.738282
O	6.088516	-0.277960	0.002572
H	6.360642	-1.203675	0.045192
C	4.400640	-1.237309	1.476772
H	4.944527	-0.962724	2.385718
O	4.875221	-2.520733	1.114811
H	4.223093	-2.945382	0.548627
C	2.445546	-2.241001	2.764672
H	2.675832	-3.253909	2.427629
H	1.368410	-2.158591	2.925699
H	2.950921	-2.081375	3.719814
H	-1.562151	3.238603	2.194067

Table S28: XYZ-coordinates of [***β-Le^a+H]$^+$*** ion (B').

C	1.511538	-2.713679	1.043008
H	2.469286	-2.680219	1.567766
O	1.392392	-4.041874	0.571502
H	0.461648	-4.193139	0.287077
C	-0.727029	-1.975791	1.557801
H	-1.108977	-1.349878	2.368693
O	0.583200	-2.342320	1.987778
C	1.569141	-1.753647	-0.181634
H	1.142295	-2.273888	-1.048342
N	2.956888	-1.464257	-0.498481
H	3.276289	-0.488704	-0.441503
C	3.797321	-2.387736	-0.879119
O	3.478263	-3.639224	-0.941606
C	5.173554	-2.034970	-1.293844
H	5.849010	-2.850247	-1.036023
H	5.488979	-1.107598	-0.815473
H	5.191054	-1.912782	-2.381828
C	0.697653	-0.524753	0.052314
H	1.050126	0.040889	0.919808
O	0.622098	0.284856	-1.107915
C	-0.694366	-1.114386	0.291313
H	-0.908422	-1.734140	-0.585810
O	-1.696856	-0.137330	0.413688
C	-1.620721	-3.196129	1.421849
H	-2.666275	-2.883403	1.385358
H	-1.473336	-3.840213	2.290868
O	-1.297464	-3.958342	0.265325
H	-1.839512	-3.622426	-0.460038
C	1.262179	1.529216	-1.067749
H	1.107492	1.956546	-2.066244
C	3.488123	2.371836	-0.645709
H	3.493885	3.013928	-1.539147
O	2.630703	1.258932	-0.851579
C	0.667233	2.482253	-0.022387
H	0.520366	1.941846	0.921120
O	-0.533740	3.049919	-0.472962
H	-1.251568	2.395772	-0.525624
C	1.589349	3.657362	0.265713
H	1.589038	4.314876	-0.616740
O	1.158796	4.359513	1.407194
H	0.235049	4.595077	1.277243

C	3.011852	3.208421	0.525669
H	3.653245	4.096518	0.606074
O	3.104042	2.427960	1.705476
H	2.696837	2.932827	2.418220
C	4.880867	1.790073	-0.456051
H	5.566155	2.584576	-0.136776
H	5.244362	1.399430	-1.410018
O	4.877792	0.705762	0.448441
H	4.510350	1.034551	1.280674
C	-2.416981	0.132324	-0.782239
H	-1.745855	0.038847	-1.639217
C	-3.762607	1.809264	0.285686
H	-3.294700	1.614126	1.259520
O	-2.814136	1.464738	-0.743916
C	-3.636226	-0.762411	-0.947161
H	-4.101805	-0.474619	-1.898166
O	-3.256856	-2.129893	-0.991712
H	-4.089287	-2.619773	-0.962628
C	-4.631997	-0.528374	0.176992
H	-4.164563	-0.796939	1.129232
O	-5.741007	-1.379002	0.010059
H	-6.337705	-0.938811	-0.608727
C	-5.018525	0.941900	0.206386
H	-5.621203	1.135634	1.104159
O	-5.786255	1.150442	-0.963546
H	-6.287478	1.965006	-0.891137
C	-4.041954	3.284369	0.128452
H	-3.121739	3.861244	0.236542
H	-4.747540	3.620617	0.893071
H	-4.455023	3.492962	-0.861493
H	2.613118	-3.902635	-0.496648

Table S29: XYZ-coordinates of [***β-Le^a+H]$^+$*** ion (^{2}B').

C	1.771711	2.633160	-1.033260
H	2.464078	2.236970	-1.780202
O	2.271543	3.918915	-0.702820
H	1.590623	4.345132	-0.137132
C	-0.645208	2.653325	-0.846032
H	-1.443165	2.417320	-1.555789
O	0.537491	2.657466	-1.650385
C	1.797378	1.739781	0.228280
H	1.617039	2.366020	1.111370
N	3.096423	1.096372	0.385825
H	3.105349	0.067607	0.464359
C	4.224433	1.734681	0.578886
O	4.323078	3.016944	0.508243
C	5.456138	0.989267	0.921293
H	5.479124	0.833752	2.005223
H	6.326370	1.580767	0.641305
H	5.466746	0.017914	0.420550
C	0.664399	0.726276	0.132193
H	0.723592	0.215066	-0.832841
O	0.679885	-0.186610	1.207558
C	-0.638827	1.509186	0.199790
H	-0.725027	1.907594	1.219217
O	-1.695357	0.599325	-0.035069
C	-0.942724	4.027262	-0.283241
H	-1.932154	4.016715	0.184788
H	-0.949007	4.751718	-1.104096
O	0.052667	4.377728	0.682611
H	-0.215920	5.170908	1.153494
C	1.033613	-1.510379	0.962273

H	0.744603	-2.046440	1.875335
C	2.980374	-2.871461	0.671406
H	2.780707	-3.428607	1.599271
O	2.438900	-1.557486	0.797698
C	0.365268	-2.145242	-0.253698
H	0.708077	-1.640243	-1.166576
O	-1.031713	-2.130403	-0.157203
H	-1.321818	-1.201316	-0.165414
C	0.820317	-3.588237	-0.370774
H	0.495873	-4.141420	0.523979
O	0.312888	-4.185565	-1.537591
H	-0.630266	-3.998558	-1.584689
C	2.338460	-3.642617	-0.472857
H	2.660321	-4.690280	-0.396093
O	2.770926	-3.090962	-1.701897
H	2.244996	-3.498616	-2.400260
C	4.485050	-2.710500	0.520239
H	4.928999	-3.698192	0.340265
H	4.899867	-2.327246	1.456317
O	4.832133	-1.788697	-0.484917
H	4.409102	-2.086258	-1.301892
C	-2.987540	1.058672	0.372600
H	-2.930988	2.133100	0.566559
C	-3.697041	-0.908437	1.536925
H	-2.773776	-1.468827	1.344998
O	-3.390902	0.492689	1.565459
C	-3.978844	0.794465	-0.746927
H	-4.925410	1.256642	-0.435215
O	-3.495789	1.392008	-1.924427
H	-4.034185	1.057111	-2.650085
C	-4.214984	-0.698757	-0.910354
H	-3.284375	-1.186575	-1.215307
O	-5.139303	-0.928927	-1.946324
H	-6.016998	-0.798850	-1.565687
C	-4.681022	-1.270911	0.421842
H	-4.715817	-2.366291	0.345961
O	-5.983140	-0.746424	0.615594
H	-6.445433	-1.253135	1.285708
C	-4.210334	-1.254500	2.914499
H	-5.102565	-0.669140	3.150311
H	-3.452450	-1.028860	3.666505
H	-4.448823	-2.320053	2.978174
H	3.517606	3.489751	0.106064

Table S30: XYZ-coordinates of [***α-a16+H]***$^{+}$ ion (C).

C	-3.569188	-2.339486	1.057256
H	-3.289177	-3.354217	1.357873
O	-3.954976	-1.571382	2.168810
H	-4.624821	-2.045697	2.669678
C	-5.099456	-1.287671	-0.406576
H	-5.505219	-0.658616	0.395018
O	-4.585832	-2.502572	0.127331
C	-2.363132	-1.616023	0.446239
H	-1.875390	-2.270981	-0.276536
N	-1.433228	-1.326788	1.522589
H	-1.854116	-0.898984	2.338657
C	-0.135811	-1.481408	1.525273
O	0.421471	-2.048256	0.523824
C	0.618028	-1.044475	2.730868
H	0.252755	-1.587071	3.606882
H	0.448655	0.023513	2.888035

H	1.680820	-1.240623	2.613883
C	-2.774850	-0.315566	-0.249364
H	-3.025667	0.430474	0.511440
O	-1.725342	0.120217	-1.089010
H	-5.309776	0.693795	-1.908316
C	-4.001505	-0.508649	-1.128381
H	-3.689850	-1.065680	-2.024579
O	-4.448513	0.783639	-1.471944
C	-6.217937	-1.714613	-1.340263
H	-6.993020	-2.227692	-0.760975
H	-5.812029	-2.413864	-2.082051
O	-6.723129	-0.542634	-1.958406
H	-7.420571	-0.770369	-2.576168
C	-0.977736	1.256137	-0.806702
H	-0.513906	1.512994	-1.769474
C	1.015565	1.946424	0.181434
H	1.350356	2.171517	-0.844299
O	0.038492	0.923043	0.123059
C	-1.753414	2.463462	-0.285214
H	-2.187744	2.218546	0.695452
O	-2.717731	2.930439	-1.184225
H	-3.390700	2.243896	-1.333948
C	-0.784422	3.619766	-0.067946
H	-0.427442	3.945774	-1.056881
O	-1.418221	4.681688	0.603148
H	-2.245947	4.863436	0.145792
C	0.416038	3.212930	0.773407
H	1.160058	4.022099	0.733191
O	0.043148	2.950250	2.108046
H	-0.527346	3.678587	2.379920
C	2.206059	1.454509	0.966201
H	1.958350	1.342923	2.027065
H	3.012038	2.191810	0.881719
O	2.610211	0.209368	0.419312
C	3.852912	-0.230699	0.869626
H	3.914681	-0.168166	1.964491
C	5.030032	0.612076	-1.029510
H	4.068961	0.946000	-1.440363
O	4.920012	0.550260	0.404310
C	4.034963	-1.658695	0.384822
H	4.944942	-2.047830	0.855641
O	2.940023	-2.480079	0.796830
H	3.096415	-3.342521	0.385469
C	4.188392	-1.724544	-1.125772
H	3.244655	-1.421315	-1.590760
O	4.423027	-3.064237	-1.494913
H	5.377972	-3.203996	-1.445680
C	5.302101	-0.784954	-1.575009
H	5.321379	-0.751962	-2.668819
O	6.552159	-1.311185	-1.170014
H	6.770651	-0.959656	-0.300947
C	6.106963	1.619246	-1.350026
H	5.852676	2.590700	-0.922623
H	6.206674	1.728574	-2.432440
H	7.074319	1.309033	-0.949606
H	1.428941	-2.091960	0.604672

Table S31: XYZ-coordinates of [***α-a16+H]***$^{+}$ ion (^{2}C).

C	0.258211	3.116220	1.102832
H	-0.310753	3.017939	2.032501
O	1.142197	4.205677	1.162068
H	0.658257	4.996033	1.419187

C	-0.176369	3.239762	-1.238881
H	0.495448	4.099684	-1.356662
O	-0.695833	3.228035	0.097347
C	1.128868	1.875346	0.892404
H	0.475628	1.008464	1.012746
N	2.149696	1.864914	1.927157
H	2.486551	2.781973	2.200330
C	2.663264	0.822104	2.527976
O	2.371363	-0.391461	2.243738
C	3.635487	1.008232	3.632866
H	4.588534	0.559358	3.341657
H	3.275714	0.464126	4.509434
H	3.784242	2.056870	3.886897
C	1.751029	1.884934	-0.508282
H	2.374922	2.775050	-0.628735
O	2.669454	0.804780	-0.648005
H	0.444600	1.797910	-3.431059
C	0.610669	1.949628	-1.508171
H	-0.072124	1.103341	-1.354606
O	1.158285	1.938785	-2.801920
C	-1.349170	3.405403	-2.190124
H	-0.957345	3.720289	-3.162613
H	-1.980341	4.220190	-1.818224
O	-2.072199	2.216859	-2.382262
H	-2.813630	2.167721	-1.760061
C	2.196795	-0.426897	-1.058013
H	1.626308	-0.353417	-1.992756
C	0.797454	-2.220539	-0.344891
H	0.328710	-2.147840	-1.335908
O	1.338139	-0.928066	-0.031352
C	3.394921	-1.351468	-1.200681
H	3.951827	-1.314642	-0.253703
O	4.206504	-1.000345	-2.291219
H	4.563097	-0.119290	-2.148894
C	2.942038	-2.785512	-1.441335
H	2.480879	-2.835541	-2.439715
O	4.025966	-3.675023	-1.348626
H	4.723573	-3.367829	-1.935994
C	1.917715	-3.237718	-0.404788
H	1.503755	-4.203664	-0.728576
O	2.487503	-3.335784	0.876055
H	3.301261	-3.844446	0.786237
C	-0.290250	-2.502631	0.661239
H	0.105835	-2.477868	1.684110
H	-0.710039	-3.499661	0.479326
O	-1.240722	-1.485124	0.454706
C	-2.279254	-1.369647	1.377524
H	-1.915898	-1.536466	2.398308
C	-3.863855	-2.295114	-0.140697
H	-3.061364	-2.465047	-0.869998
O	-3.294852	-2.317442	1.177226
C	-2.844416	0.034146	1.205828
H	-3.662268	0.149321	1.930985
O	-1.846769	0.992279	1.455192
H	-2.073532	1.782556	0.947617
C	-3.397462	0.150171	-0.206295
H	-2.575101	0.018534	-0.914637
O	-3.903595	1.456920	-0.427042
H	-4.819817	1.471426	-0.120746
C	-4.455232	-0.920071	-0.443331
H	-4.763416	-0.891495	-1.493423
O	-5.614337	-0.612903	0.310252
H	-5.526637	-0.998761	1.187446

C	-4.867311	-3.420180	-0.213176
H	-4.377978	-4.371386	0.002977
H	-5.305353	-3.470016	-1.212825
H	-5.676777	-3.278534	0.505820
H	1.897724	-0.583792	1.362198

Table S32: XYZ-coordinates of [***β-a16+H]***$^{+}$ *ion (C').*

C	0.807114	-2.500324	-0.061823
H	0.443580	-1.919429	-0.917120
O	-0.139500	-3.467625	0.284354
H	-0.854893	-3.427886	-0.382643
C	2.979025	-2.243746	-0.872034
H	2.604731	-1.760305	-1.787848
O	2.010122	-3.143747	-0.364718
C	1.074134	-1.573043	1.127998
H	1.550784	-2.164887	1.919320
N	-0.116844	-0.945909	1.685653
H	-0.193032	0.073773	1.556672
C	-0.985849	-1.542949	2.449949
O	-1.022718	-2.827734	2.579208
C	-1.974784	-0.763840	3.228720
H	-2.969942	-1.189020	3.087220
H	-1.964694	0.286885	2.946934
H	-1.726146	-0.861360	4.290294
C	2.019838	-0.488533	0.627298
H	1.527173	-0.010665	-0.223659
O	2.281323	0.463509	1.643495
H	4.803583	-0.563993	-0.939995
C	3.307391	-1.131043	0.140172
H	3.834823	-1.563769	1.003644
O	4.083019	-0.119971	-0.464253
C	4.187586	-3.098868	-1.206125
H	3.908708	-3.826775	-1.974757
H	4.498319	-3.639709	-0.303820
O	5.209088	-2.226189	-1.663188
H	6.004491	-2.724153	-1.861512
C	1.847894	1.763422	1.393728
H	2.155008	2.342311	2.272357
C	-0.250461	2.914845	0.967545
H	-0.077296	3.661193	1.759218
O	0.423533	1.711769	1.306780
C	2.445228	2.374489	0.128477
H	2.236311	1.715086	-0.722102
O	3.823041	2.569561	0.260904
H	4.235182	1.702688	0.118751
C	1.801603	3.713131	-0.178020
H	2.023489	4.424206	0.631505
O	2.254117	4.207652	-1.414943
H	3.214590	4.127637	-1.427576
C	0.295435	3.542943	-0.302748
H	-0.168089	4.532260	-0.414243
O	-0.002236	2.754227	-1.445556
H	0.551788	3.104444	-2.157644
C	-1.752735	2.603038	0.983565
H	-2.301167	3.389102	0.453190
H	-2.094180	2.610711	2.022740
O	-2.053520	1.323198	0.470253
C	-2.569390	1.240411	-0.839034
H	-2.302228	2.136567	-1.403437
C	-4.521991	0.057776	-0.174174
H	-4.162577	0.069270	0.863652

O	-3.964767	1.185395	-0.858433
C	-1.954429	0.000042	-1.497478
H	-2.273955	0.002535	-2.549820
O	-0.551091	0.017373	-1.417874
H	-0.261656	0.943903	-1.483347
C	-2.498829	-1.249425	-0.820615
H	-2.145154	-1.252920	0.210510
O	-2.007921	-2.443522	-1.408582
H	-2.547267	-2.630200	-2.187809
C	-4.023313	-1.230417	-0.819929
H	-4.384503	-2.085255	-0.238154
O	-4.496093	-1.428470	-2.137989
H	-4.575378	-0.572559	-2.571613
C	-6.023058	0.212645	-0.196010
H	-6.406221	0.212909	-1.218453
H	-6.308226	1.152475	0.279424
H	-6.495674	-0.611525	0.343625
H	-0.596015	-3.268910	1.774487

Table S33: XYZ-coordinates of [***α- an16+H]***$^{+}$ *ion (D).*

C	-0.159276	3.576135	-0.639307
H	-0.136687	3.846504	-1.700268
O	-0.677945	4.618463	0.139707
H	-0.213107	5.433708	-0.069011
C	1.368152	2.765347	1.006666
H	1.205531	3.581506	1.721566
O	1.153529	3.235108	-0.325486
C	-1.069924	2.374076	-0.413137
H	-0.721753	1.561152	-1.047024
N	-2.449424	2.632908	-0.785296
H	-2.971822	3.274402	-0.203510
C	-3.104334	1.907661	-1.658686
O	-2.433375	1.176039	-2.461162
C	-4.587545	1.946897	-1.710723
H	-4.920178	2.096089	-2.739590
H	-5.007187	2.719596	-1.066897
H	-4.961588	0.974284	-1.372089
C	-1.003353	1.947317	1.058221
H	-1.318815	2.776680	1.697799
O	-1.932584	0.913810	1.355133
H	1.155364	0.484813	2.745360
C	0.438208	1.599151	1.361091
H	0.734362	0.760771	0.722157
O	0.576198	1.260746	2.712063
C	2.813378	2.316606	1.092573
H	3.074975	2.173816	2.146183
H	3.463169	3.086562	0.663775
O	2.941207	1.102782	0.376031
C	-1.628823	-0.398575	1.025533
H	-0.617352	-0.677125	1.354383
C	-1.572100	-1.866474	-0.855391
H	-0.568208	-2.249725	-0.613148
O	-1.732128	-0.539190	-0.378103
C	-2.664692	-1.256785	1.731785
H	-3.655232	-0.869875	1.455158
O	-2.480155	-1.253645	3.124618
H	-2.515795	-0.344751	3.438012
C	-2.555069	-2.701800	1.283547
H	-1.595869	-3.105811	1.640873
O	-3.631219	-3.472374	1.762926
H	-3.713964	-3.322595	2.710137

C	-2.590571	-2.808921	-0.230452
H	-2.340055	-3.838026	-0.519209
O	-3.884560	-2.477059	-0.720452
H	-4.529097	-2.957085	-0.185997
C	-1.691555	-1.799116	-2.367476
H	-1.623360	-2.803218	-2.794753
H	-0.887728	-1.189625	-2.782718
O	-2.919507	-1.188142	-2.790214
H	-3.627934	-1.607047	-2.262814
C	3.821606	0.124508	0.844189
H	4.304074	0.441226	1.774326
C	4.381111	-0.462449	-1.383664
H	3.709032	0.331464	-1.730468
O	4.852169	-0.114172	-0.073491
C	3.051148	-1.176968	1.045454
H	3.769474	-1.929125	1.395677
O	2.044391	-1.004917	2.028217
H	1.604091	-1.854932	2.130865
C	2.457947	-1.620421	-0.282595
H	1.740376	-0.862091	-0.612381
O	1.736301	-2.827828	-0.120745
H	2.382995	-3.541764	-0.205510
C	3.571007	-1.755389	-1.319244
H	3.126342	-1.946753	-2.301694
O	4.346051	-2.900845	-1.010184
H	5.077331	-2.635685	-0.443183
C	5.588178	-0.542575	-2.286392
H	5.280814	-0.783653	-3.306829
H	6.288945	-1.310723	-1.952032
H	6.108295	0.416466	-2.294223
H	-2.801401	0.200634	-2.658657

Table S34: XYZ-coordinates of [***α- an16+H]***$^{+}$ ion (^{2}D).

C	-0.563560	-2.669783	-0.970535
H	-0.438314	-3.735053	-0.750866
O	-1.513128	-2.469430	-1.982075
H	-1.303596	-3.034037	-2.731903
C	0.781081	-0.803413	-1.540047
H	0.076975	-0.543656	-2.340689
O	0.705891	-2.211069	-1.293395
C	-1.109910	-1.937427	0.261091
H	-0.487571	-2.228245	1.114074
N	-2.467382	-2.391603	0.521225
H	-3.064849	-2.564037	-0.286881
C	-3.034715	-2.361037	1.694737
O	-2.447714	-1.819405	2.715271
C	-4.335018	-3.016560	1.934170
H	-4.827093	-3.278215	0.998213
H	-4.965629	-2.363708	2.538127
H	-4.154352	-3.928459	2.513653
C	-1.031851	-0.426093	0.078181
H	-1.708269	-0.145170	-0.732089
O	-1.449938	0.197637	1.297395
H	1.425263	1.586771	-0.127244
C	0.399157	-0.050807	-0.260359
H	1.056729	-0.398832	0.545172
O	0.522983	1.338280	-0.420509
C	2.178322	-0.464337	-2.011092
H	2.131458	0.459794	-2.598076
H	2.550027	-1.269237	-2.654728
O	3.009920	-0.274422	-0.887220

C	-2.575658	1.057386	1.173733
H	-2.694519	1.499333	2.170757
C	-4.864134	0.748483	0.371818
H	-5.419465	1.205430	1.204798
O	-3.641451	0.204468	0.849918
C	-2.354484	2.163032	0.146748
H	-2.002295	1.725281	-0.791892
O	-1.431024	3.105663	0.611360
H	-0.560054	2.734907	0.404207
C	-3.661881	2.858552	-0.177383
H	-4.063705	3.345805	0.724326
O	-3.478099	3.792272	-1.211409
H	-2.710699	4.329705	-0.986661
C	-4.658981	1.826729	-0.676366
H	-5.625614	2.318281	-0.849394
O	-4.200890	1.222726	-1.874765
H	-3.987394	1.934143	-2.489498
C	-5.666685	-0.442996	-0.146625
H	-6.561157	-0.067387	-0.659433
H	-6.005936	-1.045224	0.698477
O	-4.914086	-1.299812	-0.977597
H	-4.597605	-0.759720	-1.713935
C	4.078080	0.615584	-1.041434
H	3.891484	1.289012	-1.885477
C	5.689722	-0.978455	-0.328713
H	4.873001	-1.695676	-0.180948
O	5.283493	-0.030789	-1.331099
C	4.214078	1.402646	0.252770
H	4.984867	2.167036	0.089852
O	2.984571	2.043152	0.551509
H	3.059917	2.379450	1.453003
C	4.649357	0.495267	1.391376
H	3.849287	-0.224807	1.592325
O	4.817094	1.259467	2.563431
H	5.713767	1.617708	2.534089
C	5.917916	-0.254490	0.994373
H	6.156892	-0.987028	1.771812
O	7.006958	0.650299	0.956321
H	7.065878	1.022600	0.070614
C	6.911008	-1.690099	-0.857179
H	7.737020	-0.994688	-1.020377
H	6.678033	-2.178959	-1.804584
H	7.241366	-2.448213	-0.143134
H	-1.849900	-1.089079	2.403051

Table S35: XYZ-coordinates of [***β-an16+H]***$^{+}$ ion (*D'*).

C	-1.027909	2.781461	0.641427
H	-1.193876	2.354830	1.644697
O	-1.488983	4.099216	0.584514
H	-0.931338	4.678858	1.114312
C	0.960108	1.537510	0.409169
H	0.869808	1.130507	1.428043
O	0.324634	2.807506	0.334846
C	-1.777248	1.979622	-0.422213
H	-1.583584	2.457670	-1.390336
N	-3.221990	1.916385	-0.199936
H	-3.621001	0.970477	-0.085204
C	-4.081266	2.877157	-0.425387
O	-3.727350	4.097888	-0.653813
C	-5.532340	2.592690	-0.452599
H	-5.789485	2.169947	-1.429421

H	-6.089449	3.516881	-0.311778
H	-5.779808	1.861305	0.320648
C	-1.215231	0.557262	-0.435268
H	-1.477902	0.080902	0.517707
O	-1.763131	-0.157593	-1.524466
H	1.658128	-0.902721	-0.332193
C	0.308671	0.541725	-0.559653
H	0.566865	0.815417	-1.593020
O	0.692874	-0.776052	-0.264849
C	2.413861	1.840667	0.058756
H	2.894231	2.406195	0.863331
H	2.416075	2.463272	-0.840536
O	3.130909	0.665149	-0.240235
C	-2.583040	-1.253758	-1.251444
H	-2.814394	-1.676265	-2.236591
C	-4.750174	-1.711096	-0.302031
H	-5.116196	-2.195081	-1.219823
O	-3.759985	-0.745205	-0.643275
C	-1.940609	-2.319430	-0.366617
H	-1.632761	-1.864505	0.583226
O	-0.853325	-2.927540	-1.001314
H	-0.115309	-2.301099	-0.922962
C	-2.948639	-3.403747	-0.032615
H	-3.235555	-3.922820	-0.960083
O	-2.411752	-4.310043	0.898875
H	-1.537524	-4.564974	0.584489
C	-4.189169	-2.797685	0.598042
H	-4.953017	-3.580093	0.705103
O	-3.889683	-2.235281	1.863451
H	-3.400382	-2.901333	2.360657
C	-5.897719	-0.940612	0.332784
H	-6.628273	-1.654270	0.733636
H	-6.403317	-0.346897	-0.433049
O	-5.452317	-0.037046	1.318873
H	-4.964542	-0.555222	1.973698
C	3.914701	0.150279	0.809509
H	3.342796	0.139994	1.745148
C	5.946683	1.065911	-0.039518
H	5.389942	1.464247	-0.896858
O	5.038886	0.934232	1.071897
C	4.317920	-1.256669	0.400738
H	4.810942	-1.716656	1.268232
O	3.155844	-1.986945	0.071729
H	3.446043	-2.791046	-0.375195
C	5.299082	-1.224925	-0.762493
H	4.779556	-0.843535	-1.647491
O	5.707323	-2.538620	-1.062742
H	6.440142	-2.746242	-0.469104
C	6.472668	-0.309868	-0.430064
H	7.111661	-0.215559	-1.313537
O	7.274296	-0.905736	0.573981
H	6.929355	-0.650461	1.435418
C	7.019548	2.041181	0.377660
H	7.715290	2.205997	-0.448393
H	7.588266	1.664657	1.230326
H	6.572453	2.997937	0.653383
H	-2.795236	4.277500	-0.365805

Table S36: XYZ-coordinates of [***β-an16+H]***$^{+}$ ion (^{2}D').

C	0.311274	0.485989	1.888925
H	-0.349412	1.005406	2.587695

O	1.525361	1.221237	1.909627
H	2.162192	0.705631	1.368605
C	0.767947	-1.870123	1.505016
H	0.508024	-2.765758	2.073938
O	0.431263	-0.796772	2.385534
C	-0.278895	0.548582	0.461072
H	0.545131	0.613417	-0.260244
N	-1.105197	1.742939	0.309457
H	-2.082209	1.601584	0.026073
C	-0.663966	2.971218	0.396646
O	0.540912	3.258852	0.746475
C	-1.555779	4.108057	0.067415
H	-2.591975	3.860837	0.305146
H	-1.469439	4.323576	-1.002624
H	-1.235153	4.990487	0.619444
C	-1.066908	-0.715456	0.180448
H	-1.857509	-0.838879	0.927082
O	-1.593364	-0.704025	-1.141512
H	-1.421128	-3.139779	-0.497881
C	-0.108963	-1.898122	0.242599
H	0.522742	-1.811541	-0.654796
O	-0.797213	-3.117578	0.243759
C	2.255515	-1.931558	1.224830
H	2.477016	-2.803562	0.601960
H	2.804955	-2.031634	2.164797
O	2.693688	-0.737753	0.575286
C	-2.965213	-0.635298	-1.315274
H	-3.115334	-0.719368	-2.399672
C	-4.772548	0.915443	-1.006451
H	-5.038750	0.896578	-2.074777
O	-3.389215	0.631587	-0.857103
C	-3.742715	-1.741144	-0.608904
H	-3.532176	-1.712268	0.467176
O	-3.320506	-2.964051	-1.165003
H	-3.864409	-3.660064	-0.779933
C	-5.235432	-1.523394	-0.780435
H	-5.493028	-1.633235	-1.842455
O	-5.869750	-2.523434	-0.001061
H	-6.721082	-2.750922	-0.382989
C	-5.625354	-0.127913	-0.300765
H	-6.677360	0.064177	-0.560542
O	-5.433490	-0.003057	1.093101
H	-5.850209	-0.759279	1.521482
C	-4.978334	2.330563	-0.482212
H	-6.054528	2.542483	-0.438958
H	-4.530204	3.039178	-1.183588
O	-4.349170	2.541668	0.758463
H	-4.698876	1.885682	1.374890
C	3.371958	-0.902558	-0.652160
H	2.753532	-1.498558	-1.332736
C	5.544249	-0.995676	0.334150
H	5.087068	-0.791957	1.311142
O	4.558092	-1.618141	-0.512067
C	3.640494	0.480954	-1.223359
H	4.009950	0.322289	-2.246269
O	2.444218	1.230325	-1.256348
H	2.697804	2.119834	-1.531248
C	4.717802	1.216511	-0.435323
H	4.327522	1.469953	0.556973
O	5.001678	2.435896	-1.079090
H	5.676315	2.248656	-1.744656
C	5.953986	0.338836	-0.274280
H	6.663279	0.840325	0.391415

O	6.608270	0.205443	-1.522007
H	6.236769	-0.551193	-1.986851
C	6.677319	-1.978976	0.491901
H	7.150532	-2.195174	-0.468027
H	6.307780	-2.914323	0.915642
H	7.436927	-1.568151	1.160937
H	1.066825	2.477786	1.140182

Table S37: XYZ-coordinates of [***α-bn16+H]***$^{+}$ ion (E).

C	-1.624388	3.394047	-0.604686
H	-1.863689	3.649747	-1.642581
O	-2.347869	4.200459	0.290119
H	-2.211452	5.126175	0.067733
C	0.337294	3.140930	0.734257
H	0.018154	3.822327	1.533300
O	-0.249444	3.532441	-0.508401
C	-2.047733	1.956627	-0.301050
H	-1.603446	1.316824	-1.063431
N	-3.494648	1.858257	-0.387075
H	-3.998500	2.679183	-0.070337
C	-4.197402	0.815041	-0.755174
O	-3.700526	-0.303620	-1.121687
C	-5.678485	0.897410	-0.785660
H	-6.046574	1.891621	-0.536004
H	-6.084447	0.167019	-0.081191
H	-6.024011	0.615518	-1.782978
C	-1.548708	1.532739	1.084450
H	-2.008134	2.163229	1.850217
O	-1.994679	0.213116	1.387378
H	1.324570	1.050821	2.254224
C	-0.047356	1.709717	1.112365
H	0.399058	1.055018	0.354791
O	0.428690	1.392659	2.390643
C	1.839178	3.262254	0.559259
H	2.327044	3.134889	1.529986
H	2.076752	4.256863	0.172515
O	2.299401	2.294911	-0.374988
C	-1.204683	-0.837957	0.950492
H	-0.167960	-0.737376	1.293241
C	-0.437483	-1.867969	-1.069322
H	0.594538	-1.777951	-0.701984
O	-1.227047	-0.823943	-0.474969
C	-1.813568	-2.131175	1.458504
H	-2.860962	-2.168055	1.127762
O	-1.706268	-2.248036	2.854918
H	-2.189977	-1.527783	3.268545
C	-1.063272	-3.314869	0.866369
H	-0.041362	-3.312268	1.274503
O	-1.715288	-4.526275	1.160152
H	-1.868343	-4.566952	2.109256
C	-0.977583	-3.223426	-0.651097
H	-0.278580	-3.994419	-1.003788
O	-2.250656	-3.409153	-1.238761
H	-2.642183	-4.191115	-0.832298
C	-0.461564	-1.618748	-2.568458
H	0.036390	-2.459100	-3.071120
H	0.111207	-0.714195	-2.789671
O	-1.760506	-1.399144	-3.057191
H	-2.276404	-2.191778	-2.861727
C	3.243485	1.383169	0.061414
H	4.106585	1.891672	0.524779

C	3.528990	-0.526439	1.467923
H	4.436698	-0.058277	1.879092
O	2.651089	0.512397	1.014971
C	3.663185	0.593192	-1.167305
H	2.745880	0.171472	-1.600782
O	4.349291	1.392102	-2.098517
H	3.753305	2.080637	-2.406231
C	4.589959	-0.544452	-0.786946
H	5.532887	-0.119166	-0.412079
O	4.830775	-1.391268	-1.886766
H	5.116998	-0.847708	-2.627525
C	3.964927	-1.402074	0.303262
H	4.725268	-2.103597	0.674090
O	2.854969	-2.114697	-0.206799
H	3.163062	-2.512850	-1.030059
C	2.812107	-1.291082	2.554844
H	2.548374	-0.633707	3.386500
H	3.457890	-2.081887	2.942749
H	1.905330	-1.755760	2.163849
H	-2.708301	-0.464072	-1.005276

Table S38: XYZ-coordinates of [***α-bn16+H]***$^{+}$ ion (^{2}E).

C	-0.985574	3.703172	-0.369026
H	-1.227100	4.080616	-1.368158
O	-1.549354	4.509120	0.628428
H	-1.316457	5.427365	0.464863
C	0.978866	3.087318	0.848646
H	0.824633	3.761976	1.700669
O	0.405709	3.649219	-0.332078
C	-1.561508	2.304633	-0.171506
H	-1.170270	1.663141	-0.958429
N	-3.008552	2.264644	-0.280235
H	-3.539945	2.705910	0.458528
C	-3.640633	1.481365	-1.120507
O	-2.989412	1.004412	-2.109001
C	-5.078706	1.169329	-0.924131
H	-5.528246	1.758166	-0.124859
H	-5.159259	0.109097	-0.659743
H	-5.624142	1.326149	-1.856554
C	-1.128800	1.766643	1.197648
H	-1.471587	2.443072	1.985639
O	-1.747378	0.527438	1.512668
H	1.653597	0.798070	2.263959
C	0.381662	1.719574	1.190865
H	0.701019	1.029256	0.401714
O	0.836929	1.284674	2.442086
C	2.469162	2.960838	0.588504
H	2.978924	2.695353	1.519119
H	2.856035	3.919519	0.233410
O	2.702943	1.983774	-0.418511
C	-1.231291	-0.640319	0.971012
H	-0.140298	-0.698102	1.086160
C	-1.177744	-1.858390	-1.070136
H	-0.083750	-1.974859	-1.022338
O	-1.571210	-0.672493	-0.401357
C	-1.895962	-1.788000	1.710528
H	-2.983068	-1.642887	1.639391
O	-1.472826	-1.863876	3.048458
H	-1.646221	-1.018701	3.473886
C	-1.526178	-3.110523	1.064149
H	-0.450625	-3.283987	1.216073

O	-2.286096	-4.171946	1.593441
H	-2.228473	-4.136588	2.553488
C	-1.803898	-3.088721	-0.428610
H	-1.364662	-3.986423	-0.883274
O	-3.205206	-3.067457	-0.673484
H	-3.608929	-3.734579	-0.104647
C	-1.583231	-1.686915	-2.523482
H	-1.365910	-2.598229	-3.087460
H	-1.034295	-0.858858	-2.973960
O	-2.975978	-1.368543	-2.661046
H	-3.456982	-1.999840	-2.090322
C	3.474468	0.883808	-0.088750
H	4.461149	1.187264	0.302162
C	3.470807	-1.112323	1.225517
H	4.496496	-0.873594	1.547442
O	2.803801	0.111081	0.896106
C	3.607152	0.080623	-1.373026
H	2.584776	-0.110542	-1.727080
O	4.365755	0.758106	-2.343850
H	3.917520	1.581335	-2.557477
C	4.288096	-1.249173	-1.120649
H	5.331960	-1.062545	-0.828121
O	4.234404	-2.069305	-2.266295
H	4.567243	-1.561459	-3.012910
C	3.586917	-2.003719	-0.001087
H	4.199868	-2.874521	0.270542
O	2.303192	-2.427437	-0.421732
H	2.446383	-2.834741	-1.284650
C	2.716750	-1.753571	2.365969
H	2.703532	-1.098739	3.240320
H	3.201219	-2.689079	2.654298
H	1.689139	-1.977269	2.074855
H	-3.157694	-0.011289	-2.367122

Table S39: XYZ-coordinates of [***β-bn16+H***]$^+$ *ion (E').*

C	-0.915180	2.802992	1.029579
H	-1.483213	2.516673	1.931390
O	-1.161089	4.139023	0.697739
H	-0.766541	4.729485	1.348360
C	0.817966	1.357079	1.628890
H	0.224160	1.042242	2.502407
O	0.447756	2.680715	1.256035
C	-1.348692	1.949128	-0.166193
H	-0.820332	2.327344	-1.049856
N	-2.791041	1.992403	-0.414619
H	-3.280439	1.084316	-0.383830
C	-3.459306	2.982588	-0.948803
O	-2.957216	4.159110	-1.121538
C	-4.849510	2.781728	-1.412371
H	-5.360234	3.741580	-1.463577
H	-5.369937	2.093626	-0.742353
H	-4.823393	2.344423	-2.416080
C	-0.935409	0.493220	0.069076
H	-1.541745	0.090939	0.890739
O	-1.141252	-0.244280	-1.117838
H	1.814208	-0.997948	0.721490
C	0.533124	0.416845	0.457797
H	1.135071	0.742543	-0.398943
O	0.842057	-0.908327	0.806543
C	2.275234	1.362493	2.040548
H	2.483540	0.437394	2.585601

H	2.453190	2.212248	2.707143
O	3.113235	1.471004	0.903018
C	-2.076589	-1.278168	-1.086781
H	-2.009942	-1.743148	-2.077743
C	-4.457897	-1.564587	-0.863434
H	-4.549854	-2.078213	-1.832151
O	-3.347307	-0.674301	-0.906391
C	-1.821603	-2.323733	-0.003343
H	-1.808718	-1.833149	0.978494
O	-0.629241	-3.018590	-0.228080
H	0.086232	-2.416060	0.033506
C	-2.952899	-3.334649	0.026918
H	-2.964786	-3.886687	-0.925447
O	-2.802819	-4.216874	1.111673
H	-1.895367	-4.539787	1.099810
C	-4.285471	-2.629023	0.206031
H	-5.095128	-3.362659	0.091061
O	-4.364662	-2.014584	1.480391
H	-4.112561	-2.679411	2.131953
C	-5.689595	-0.696845	-0.653417
H	-6.557685	-1.343857	-0.476264
H	-5.886545	-0.122110	-1.561990
O	-5.511597	0.237683	0.387167
H	-5.294511	-0.267564	1.182569
C	4.117973	0.519566	0.811753
H	4.705413	0.476646	1.745436
C	4.463592	-1.816455	0.426982
H	5.079497	-1.859831	1.338009
O	3.520326	-0.743416	0.581425
C	5.000140	0.899646	-0.362365
H	4.358470	0.960292	-1.250791
O	5.686731	2.107057	-0.132498
H	5.046837	2.822843	-0.104266
C	6.049169	-0.174076	-0.584525
H	6.714293	-0.197355	0.292722
O	6.787182	0.072269	-1.756936
H	7.098053	0.982401	-1.728268
C	5.391805	-1.538354	-0.747320
H	6.181652	-2.304317	-0.738329
O	4.652327	-1.598426	-1.940598
H	5.226641	-1.266035	-2.639096
C	3.671469	-3.091665	0.270627
H	3.031313	-3.256193	1.140918
H	4.349825	-3.943152	0.183561
H	3.063301	-3.049193	-0.634820
H	-2.138845	4.303974	-0.577802