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Deprotonated Carbohydrate Anion Fragmentation Chemistry: Structural Evidence from Tandem Mass Spectrometry, Infra-Red Spectroscopy, and Theory

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Key Words: Glycans, Mass spectrometry, Collision-induced Dissociation, Ion Structure, Density functional theory.

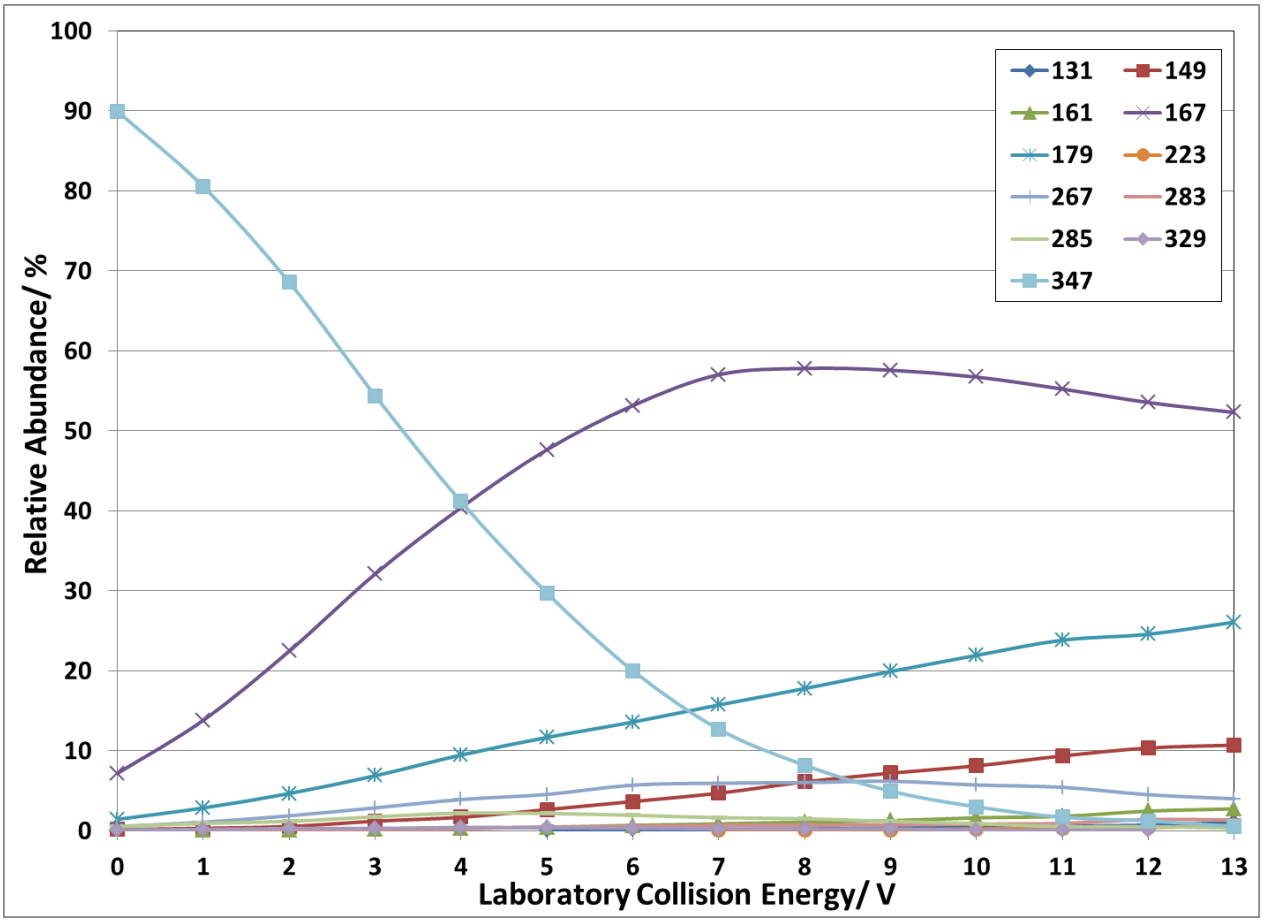

Figure S1: Energy-resolved tandem mass spectra of deprotonated lactose-(glucose-$^{13}C_6$). KEY: *m/z* 347, [lactose-(glucose-$^{13}C_6$)-H]$^-$; *m/z* 167, Z_1 ($^{13}C_6H_9O_5^-$); m/z 179, C_1 ($C_6H_{11}O_6^-$); *m/z* 149, Z_1–H_2O ($^{13}C_6H_7O_4^-$); *m/z* 161, B_1 or C_1-H_2O ($C_6H_9O_5^-$); *m/z* 285, $^{0,2}A_2$ ($^{13}C_4C_6H_{17}O_9^-$); *m/z* 267, $^{0,2}A_2$-H_2O ($^{13}C_4C_6H_{15}O_8^-$).

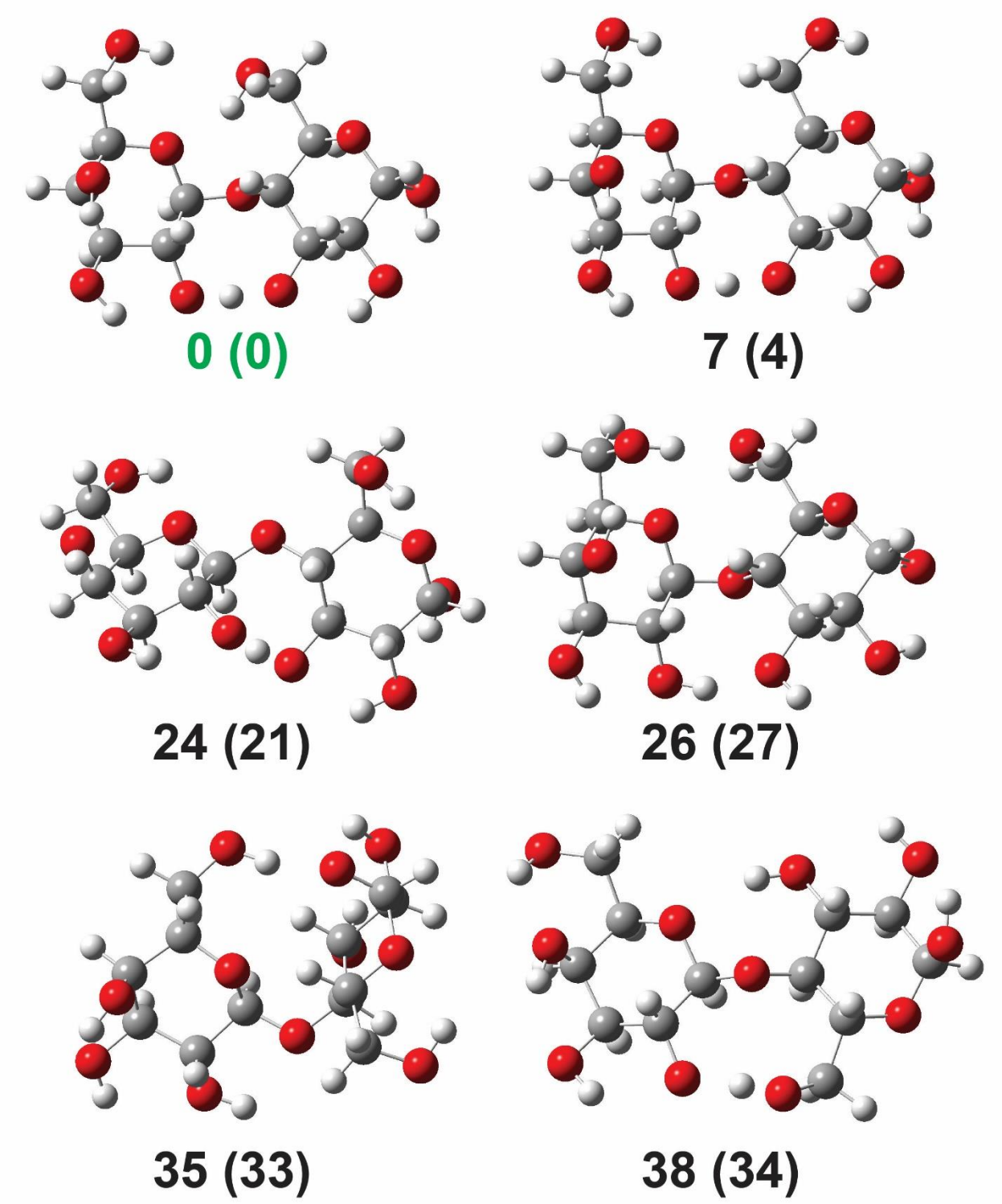

Figure S2: Relative energies of selected low-energy conformers of deprotonated lactose (β-D-galactopyranosyl-(1→4)-α-D-Glucose anomer) calculated at the M06-2X/6-31++G(d,p) level of theory. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}).

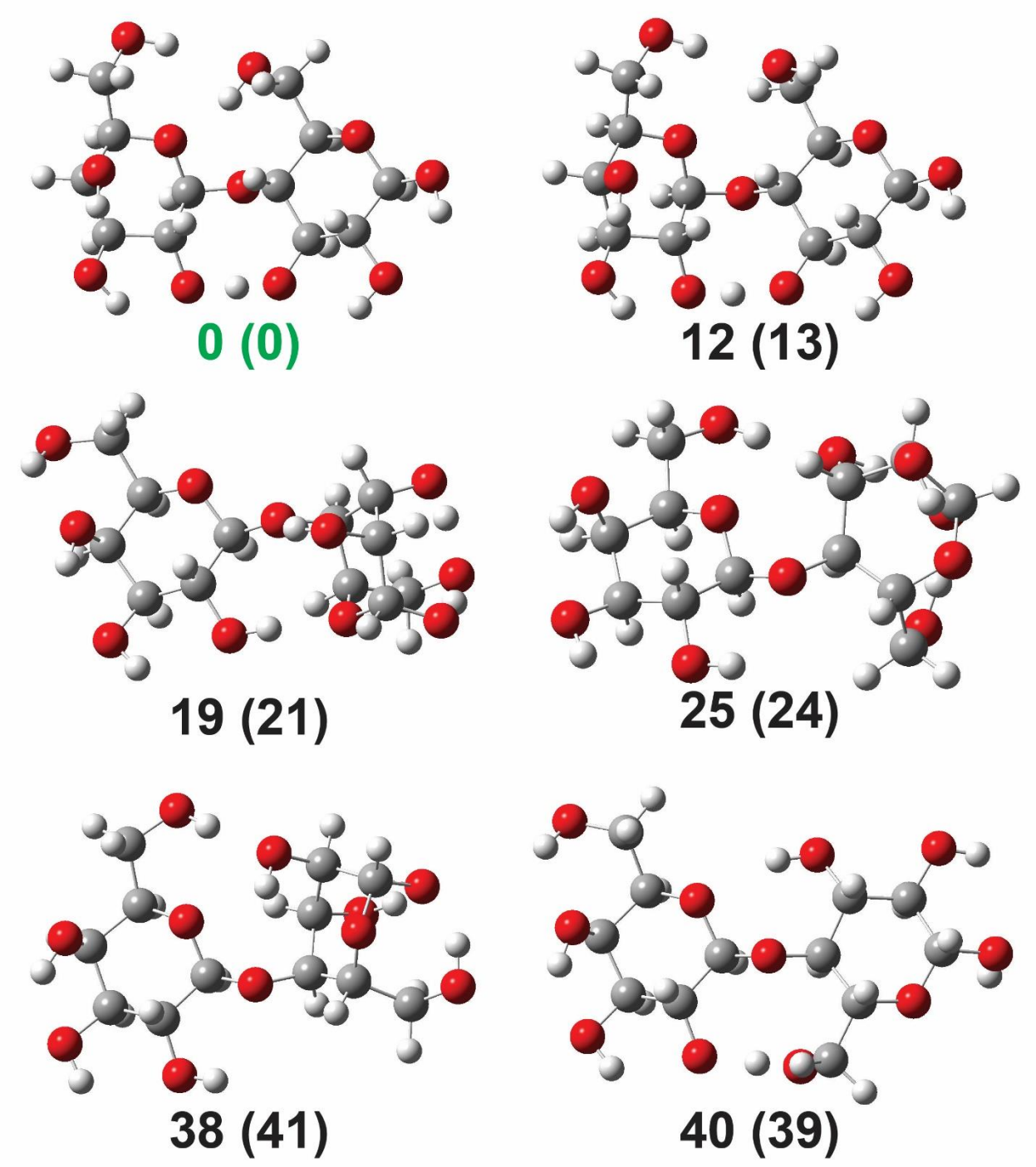

Figure S3: Relative energies of selected low-energy conformers of deprotonated lactose (β-D-galactopyranosyl-(1→4)-β-D-Glucose anomer) calculated at the M06-2X/6-31++G(d,p) level of theory. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}). The β-anomer GM is 5.0 (3.6) kJ mol^{-1}, $\Delta E_{el+ZPE,0K}$ (ΔG_{298}) above the α-anomer (Table 1).

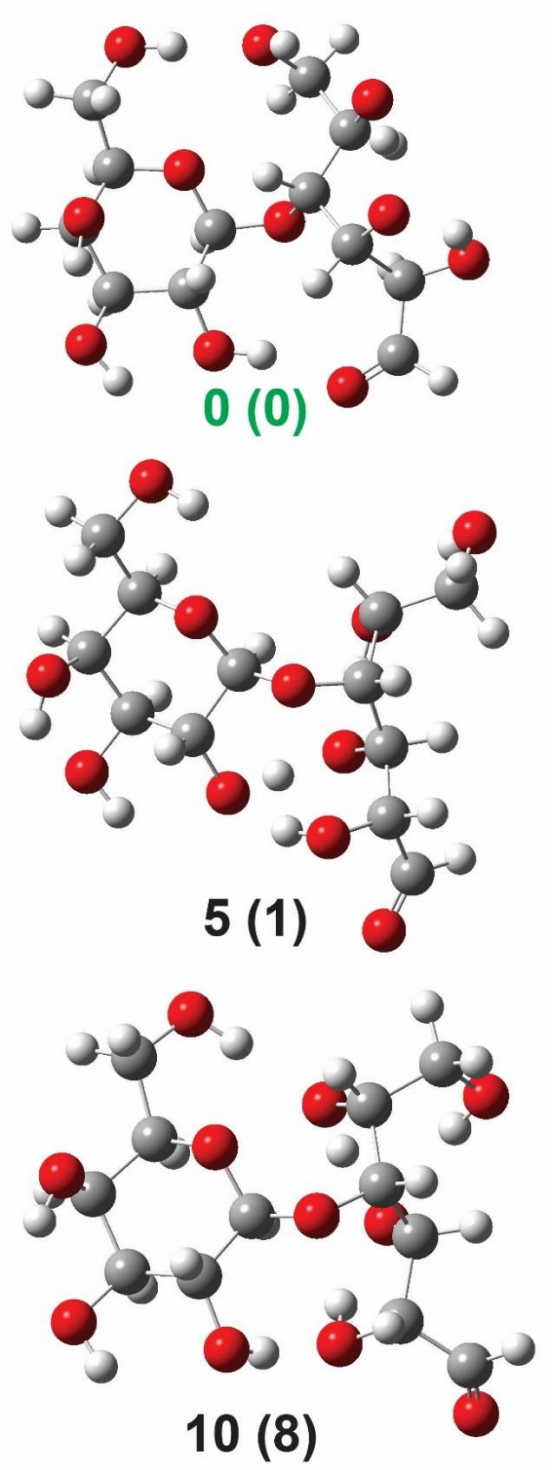

Figure S4: Relative energies of selected low-energy conformers of deprotonated lactose (β-D-galactopyranosyl-(1→4)-β-D-Glucose ring-open) calculated at the M06-2X/6-31++G(d,p) level of theory. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}). The ring-open GM is 32.1 (28.1) kJ mol^{-1}, $\Delta E_{el+ZPE,0K}$ (ΔG_{298}) above the α-anomer (Table 1) and 27.1 (24.5) kJ mol^{-1} above the β-anomer (Table 2).

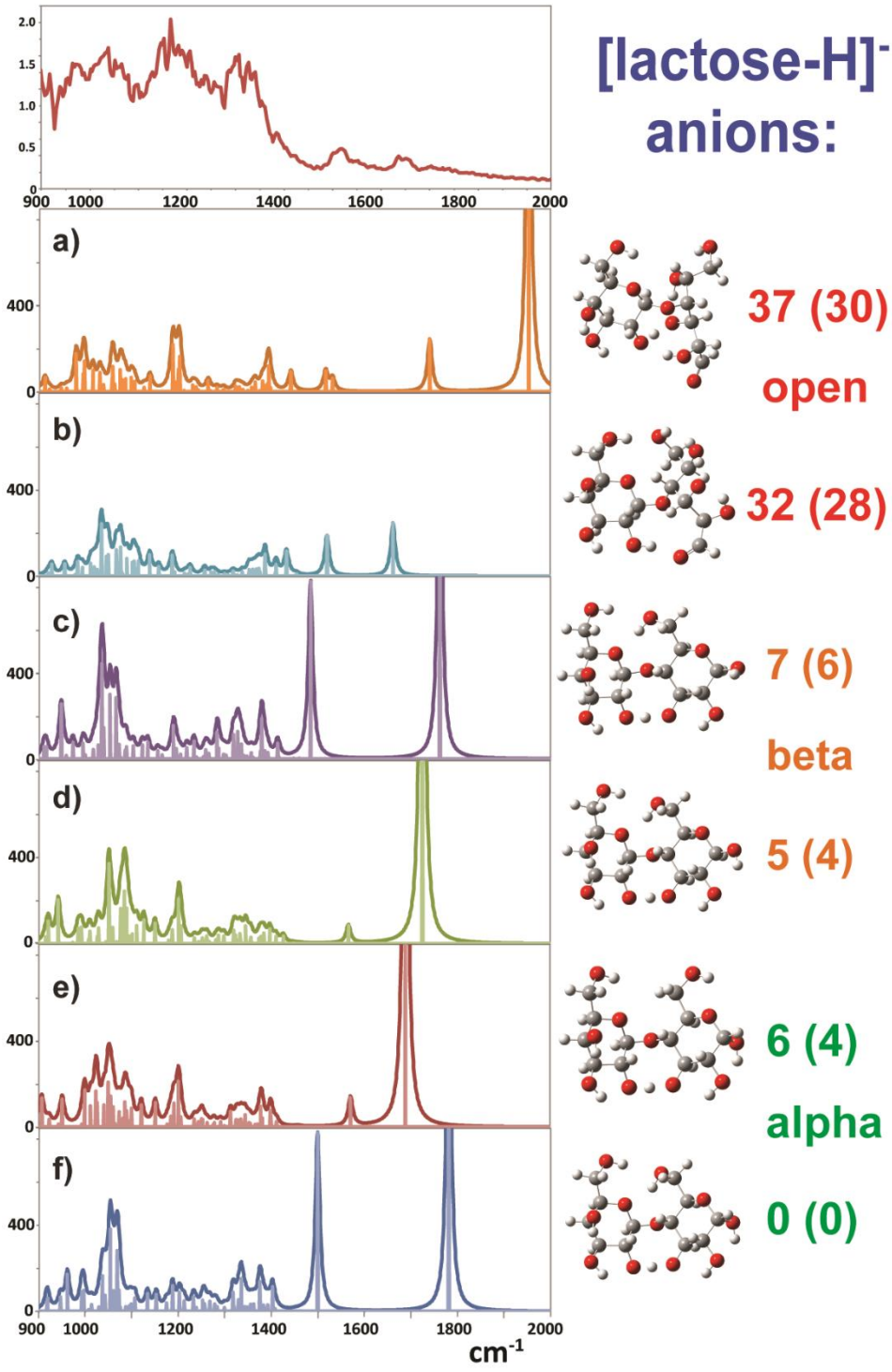

Figure S5: Comparison to the 2 lowest energy structures of deprotonated β-D-galactopyranosyl-(1→4)-D-glucose (*m/z* 341.12 ($C_{12}H_{21}O_{11}^-$)) with frequencies calculated from B3LYP/6-311++G(2d,2p) optimized structures. Panels a and b are ring-open forms, panels c and d β-glucose anomers, while panels e and f are α-glucose forms. Relative energies calculated at the M06-2X/6-31++G(d,p) level of theory. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}) and are normalized to the α-glucose forms. Structural changes between the 2 levels of theory are negligible.

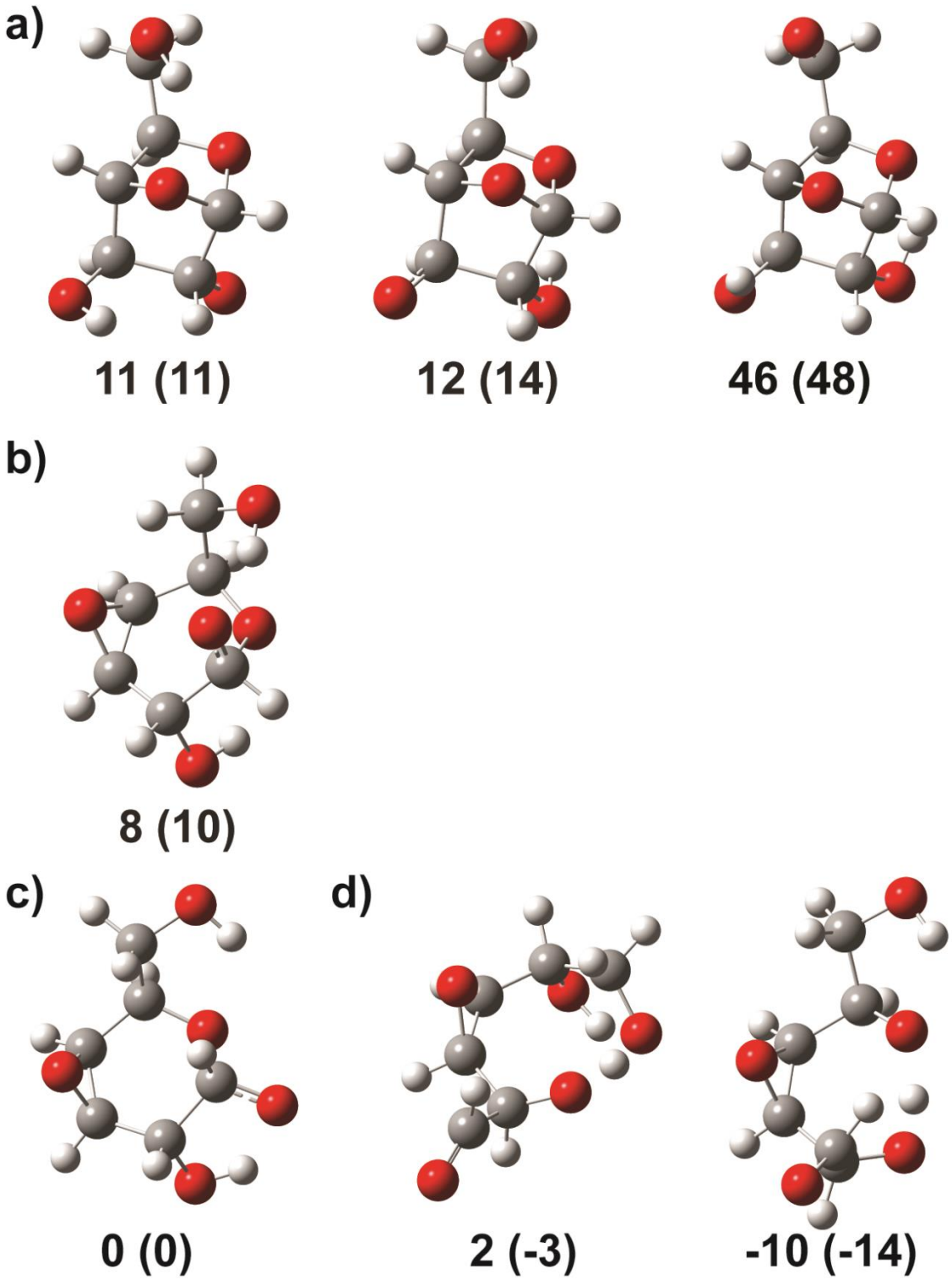

Figure S6: Selected Z_1 anion low-energy conformers calculated at the M06-2X/6-31++G(d,p) level of theory. a) deprotonated 1,4-anhydroglucose structures, [1,4-anhydroglucose-H]$^-$; b) deprotonated 3,4-anhydroglucose, [3,4-anhydro-β-glucose-H]$^-$; c) deprotonated 3,4-anhydroglucose [3,4-anhydro-α-glucose-H]$^-$; d) deprotonated, ring-open aldehyde isomers. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}).

Minima and TSs	E_{el}/H	E_{el+ZPE}/H	$\Delta E_{el+ZPE,0K}$/ kJ mol^{-1}	ΔH_{298}/ kJ mol^{-1}	ΔG_{298}/ kJ mol^{-1}	ΔS_{298} /J mol^{-1}
GM	-1296.986125	-1296.624955	0	0	0	0
C_1-Z_1 TS_1	-1296.909679	-1296.551085	193.9	196.5	190.0	21.8
C_1-Z_1 TS_2	-1296.908922	-1296.550436	195.6	198.7	190.1	28.8
$^{0,2}A_2$ formation TS_1	-1296.949413	-1296.591725	87.2	89.5	83.3	20.7
$^{0,2}A_2$ formation TS_2	-1296.94447	-1296.591076	88.9	92.0	83.5	28.3
Ring-forming TS (α)	-1296.920038	-1296.562144	164.9	161.1	169.1	-26.8
Ring-forming TS (β)	-1296.924404	-1296.566837	152.6	148.7	157.2	-28.2

Table S1: Relative energies of the transition structures of deprotonated lactose (β-D-galactopyranosyl-(1→4)-D-Glucose ring-open) calculated at the M06-2X/6-31++G(d,p) level of theory. The ring-open GM is 32.1 kJ mol^{-1} ($\Delta E_{el+ZPE,0K}$) above the α-anomer (Table 1).

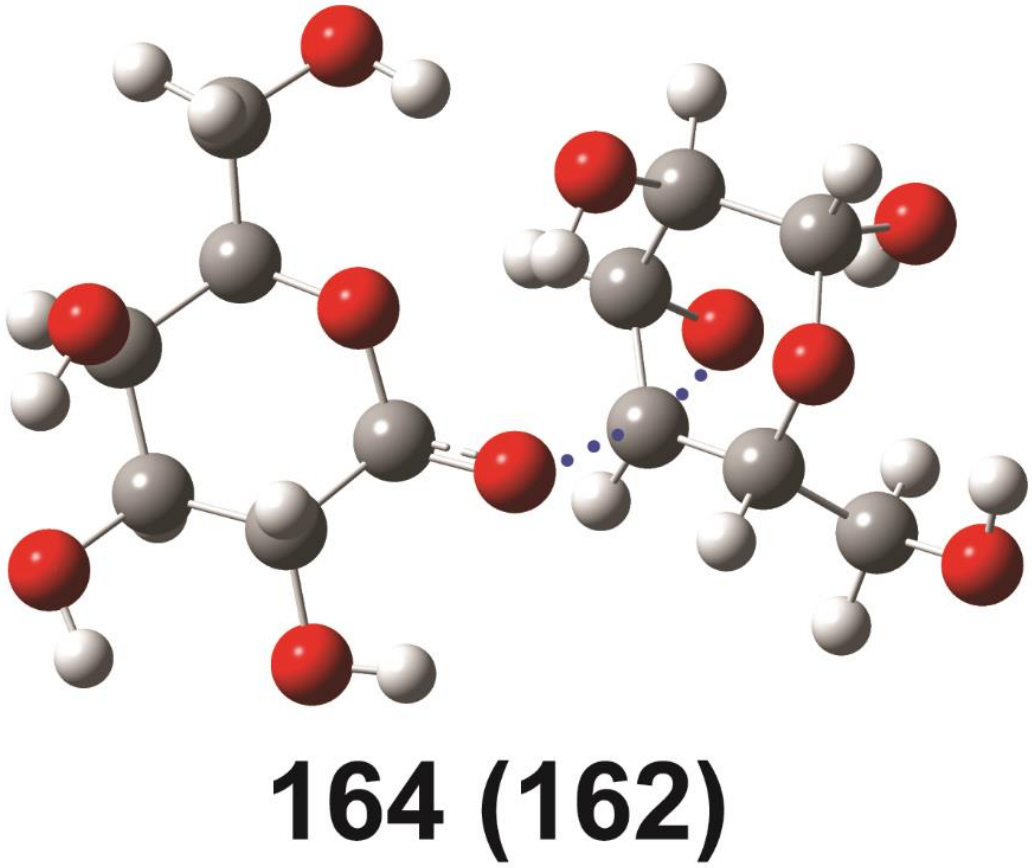

Figure S7: The higher-energy 3,4-anhydroglucose-forming C_1-Z_1 transition structures of deprotonated lactose (β-D-galactopyranosyl-(1→4)-β-D-Glucose) calculated at the M06-2X/6-31++G(d,p) level of theory. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}). The reaction coordinate is illustrated with blue dots.

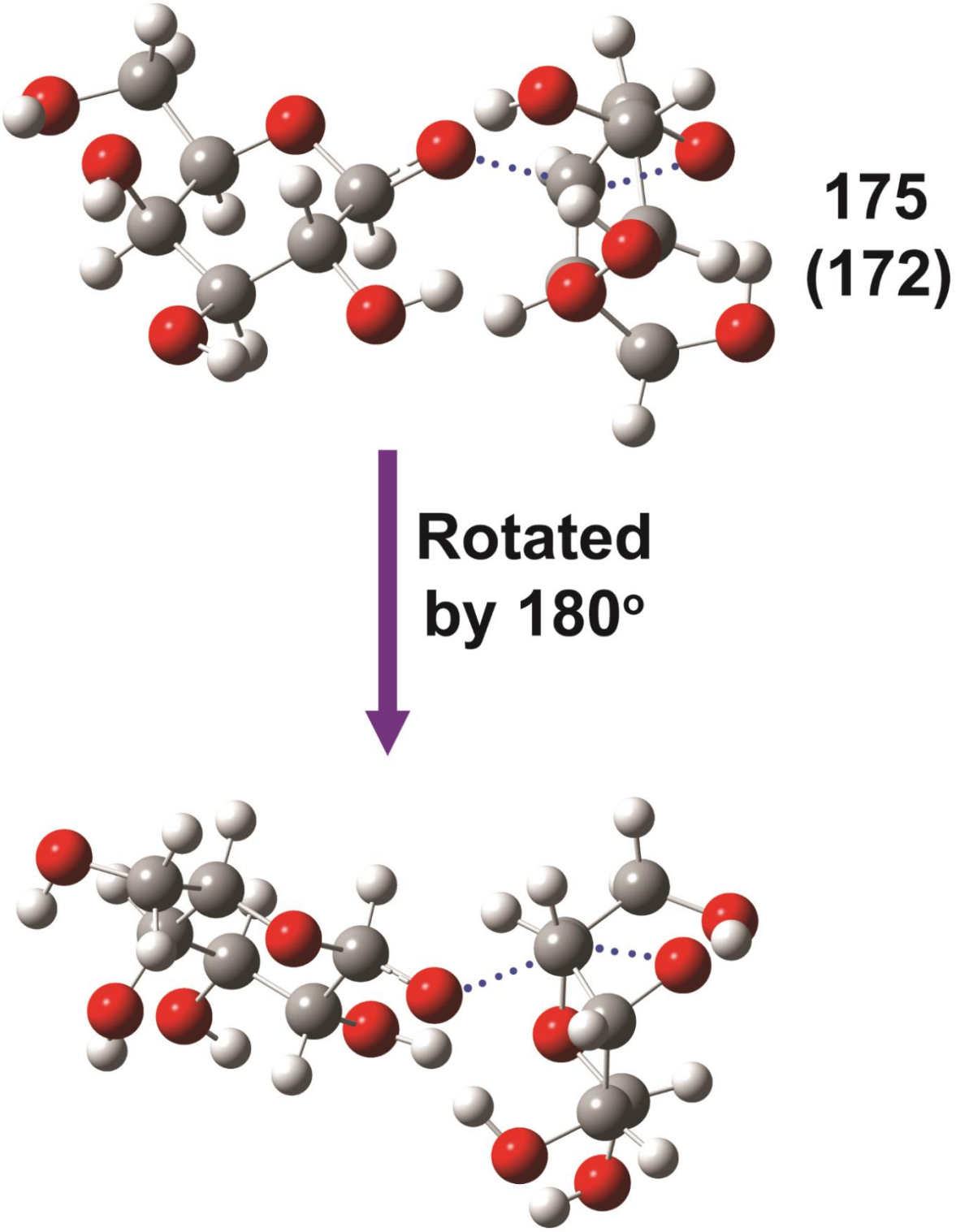

Figure S8: The lowest-energy 3,4-anhydroglucose-forming C_1-Z_1 transition structure of deprotonated lactose (β-D-galactopyranosyl-(1→4)-α-D-Glucose) calculated at the M06-2X/6-31++G(d,p) level of theory. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}). The reaction coordinate is illustrated with blue dots.

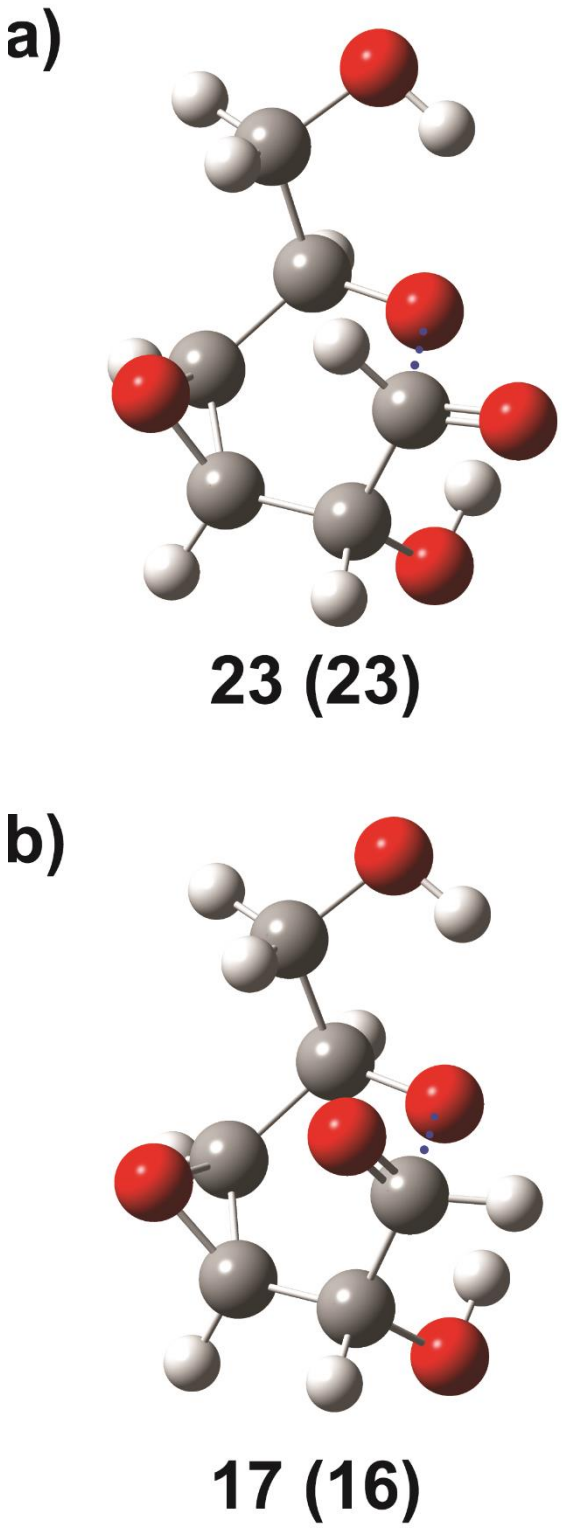

Figure S9: The low-energy Z_1-ring-opening isomerization transition structures generated from of the a) deprotonated 3,4-anhydro-α-glucose anion and b) deprotonated 3,4-anhydro-β-glucose anion structures. Relative energies calculated at the M06-2X/6-31++G(d,p) level of theory. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}). The reaction coordinate is illustrated with blue dots.

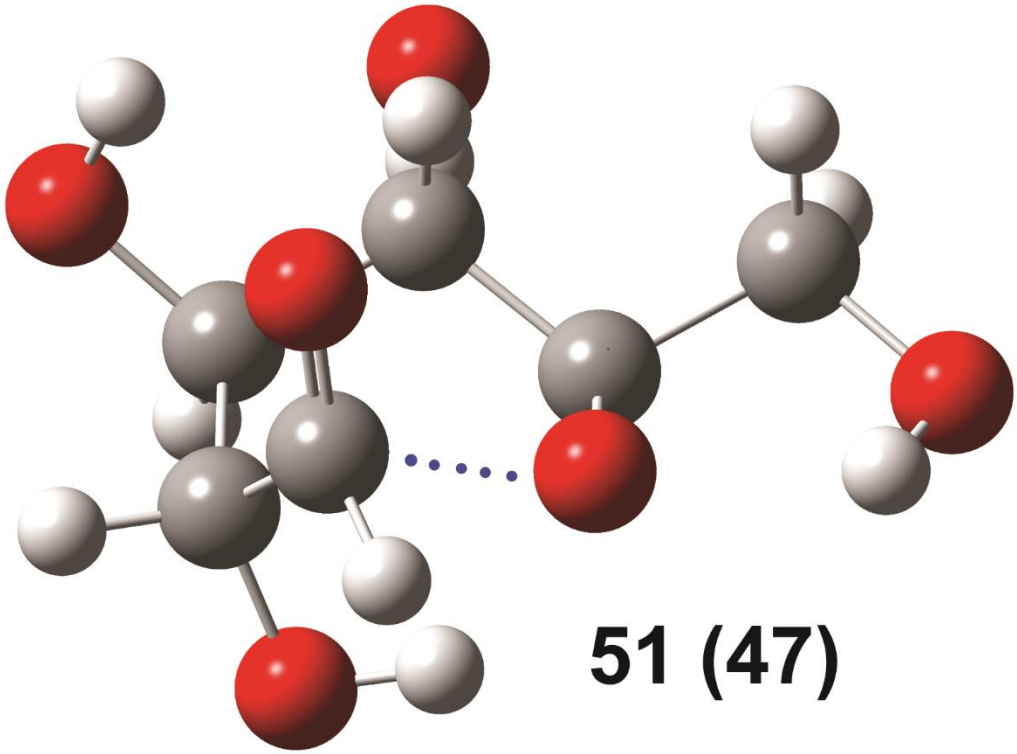

Figure S10: The low-energy C_1-ring-opening isomerization transition structures generated from the deprotonated β-D-galactopyranose anion structures. Relative energies calculated at the M06-2X/6-31++G(d,p) level of theory. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}). The reaction coordinate is illustrated with blue dots.

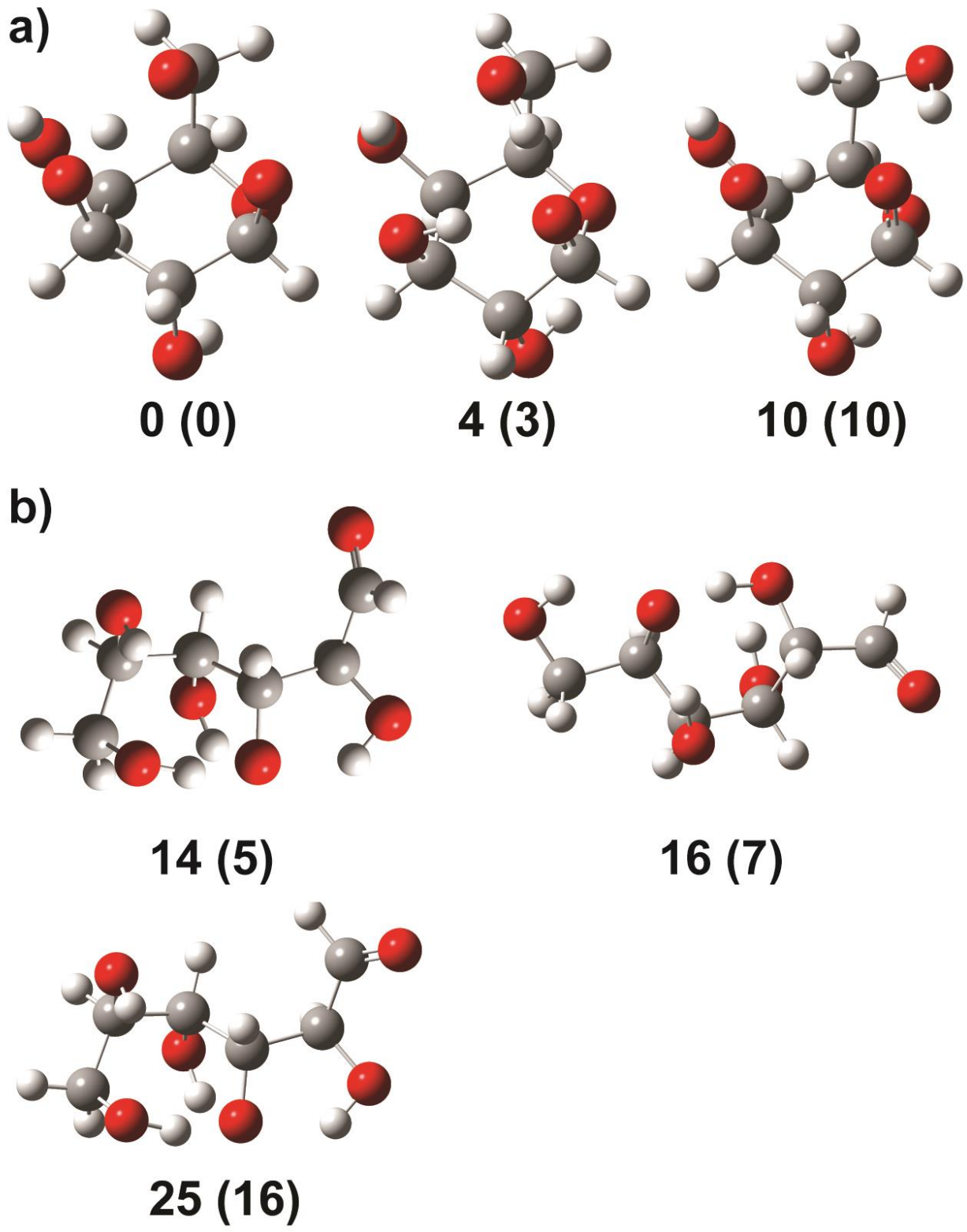

Figure S11: Selected C_1 anion low-energy conformers calculated at the M06-2X/6-31++G(d,p) level of theory. a) deprotonated β-D-galactose C_1 structures, [β-D-galactose-H]$^-$; b) deprotonated, ring-open aldehyde C_1 structures. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}).

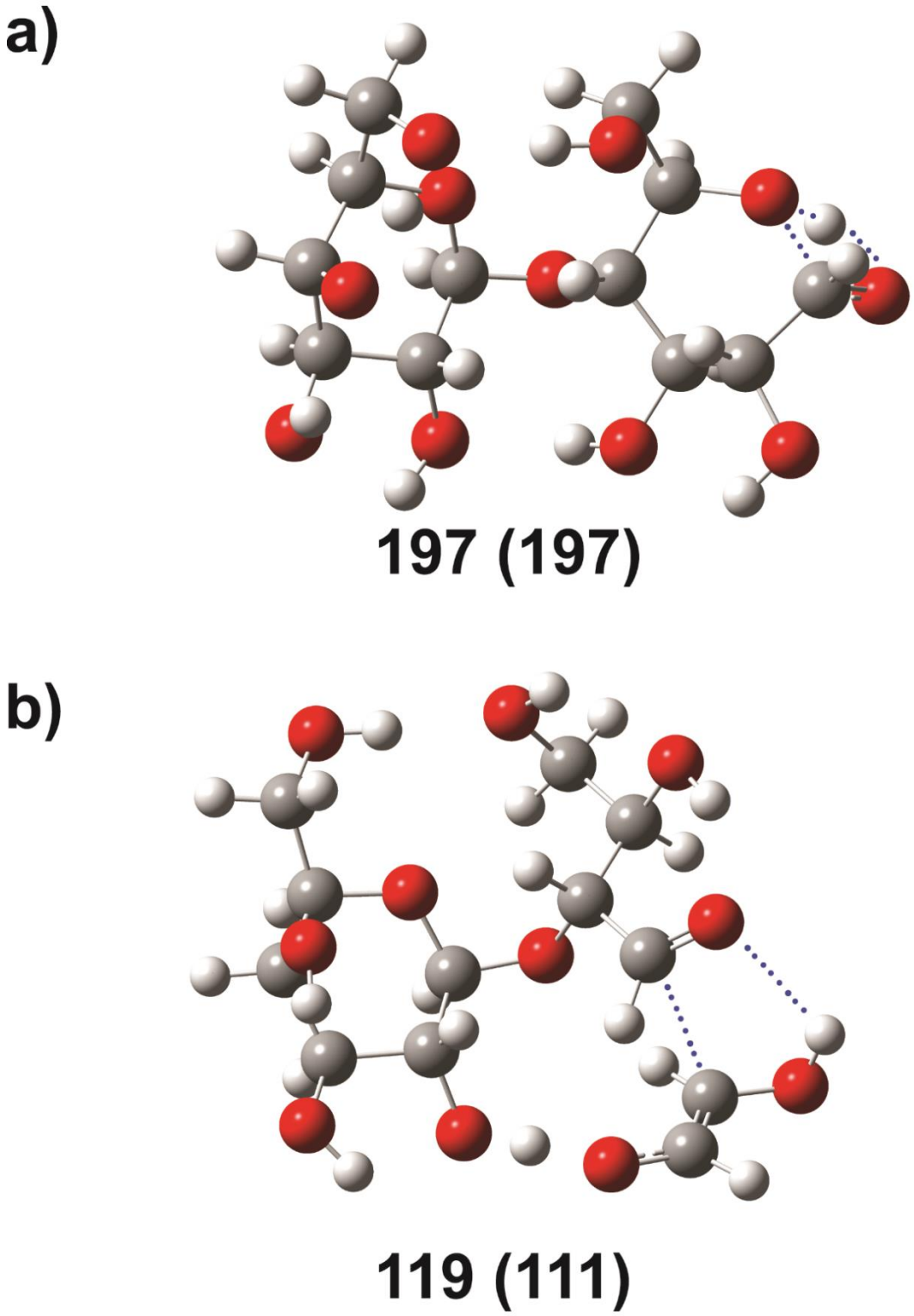

Figure S12: The lowest-energy $^{0,2}A_2$-forming transition structures of deprotonated lactose (β-D-galactopyranosyl-(1→4)-α-D-Glucose) calculated at the M06-2X/6-31++G(d,p) level of theory. a) ring-opening TS; b) $^{0,2}A_2$ formation TS_A. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}). The reaction coordinate is illustrated with blue dots.

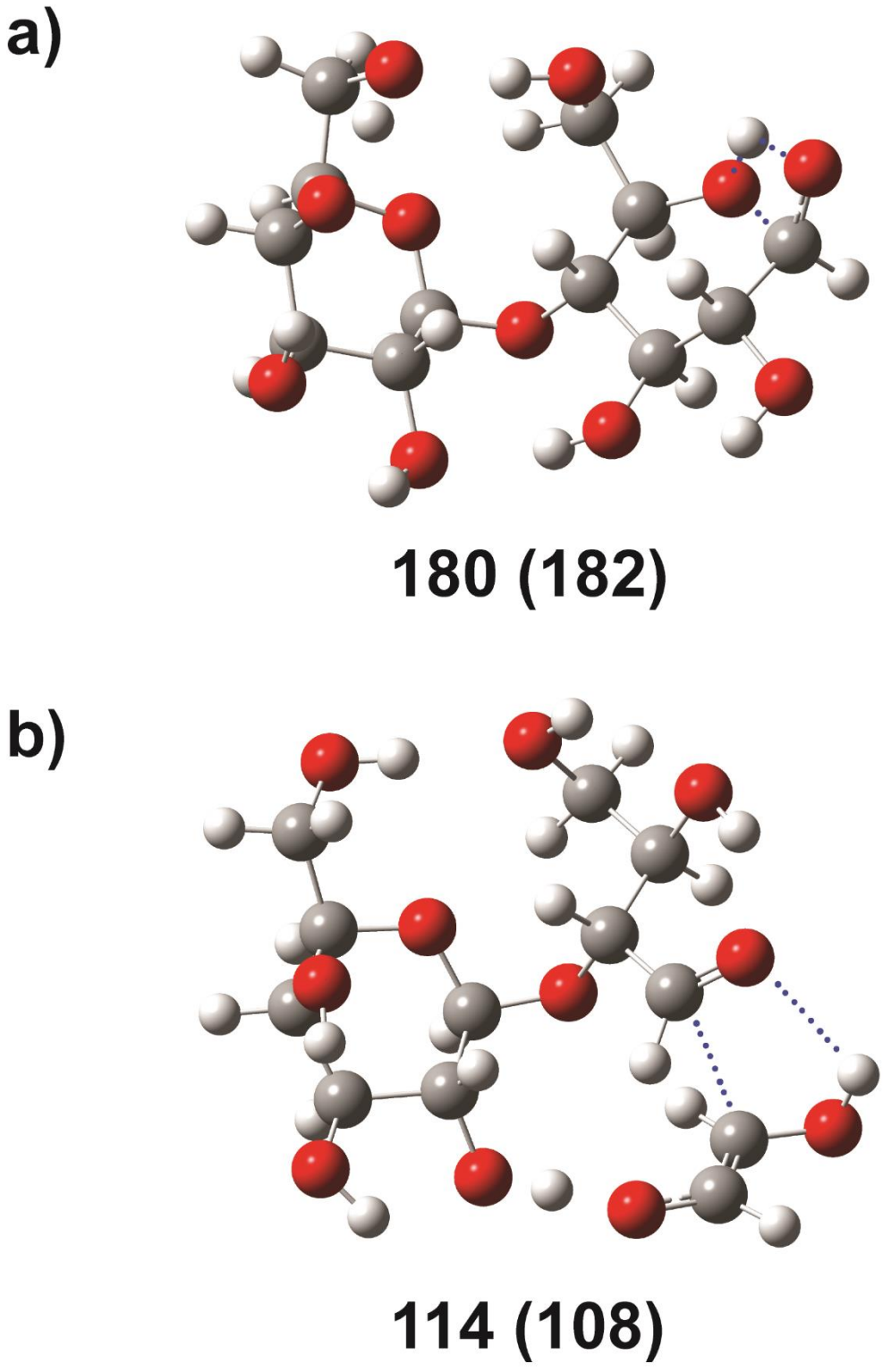

Figure S13: The lowest-energy $^{0,2}A_2$-forming transition structures of deprotonated lactose (β-D-galactopyranosyl-(1→4)-β-D-Glucose) calculated at the M06-2X/6-31++G(d,p) level of theory. a) ring-opening TS; b) $^{0,2}A_2$ formation TS_A. Values in kJ mol^{-1}: $\Delta E_{el+ZPE,0K}$ (ΔG_{298}). The reaction coordinate is illustrated with blue dots.