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

Supplementary Information:

Evidence of Gas-phase Pyranose-to-furanose Isomerization in Protonated Peptidoglycans

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Figure S1

Hydrogen-deuterium exchange MS/MS spectra: (a) GlcNac-β-1-Asn, (b) GlcNac-β-1-Ser, and (c) GalNac-α-1-Ser.

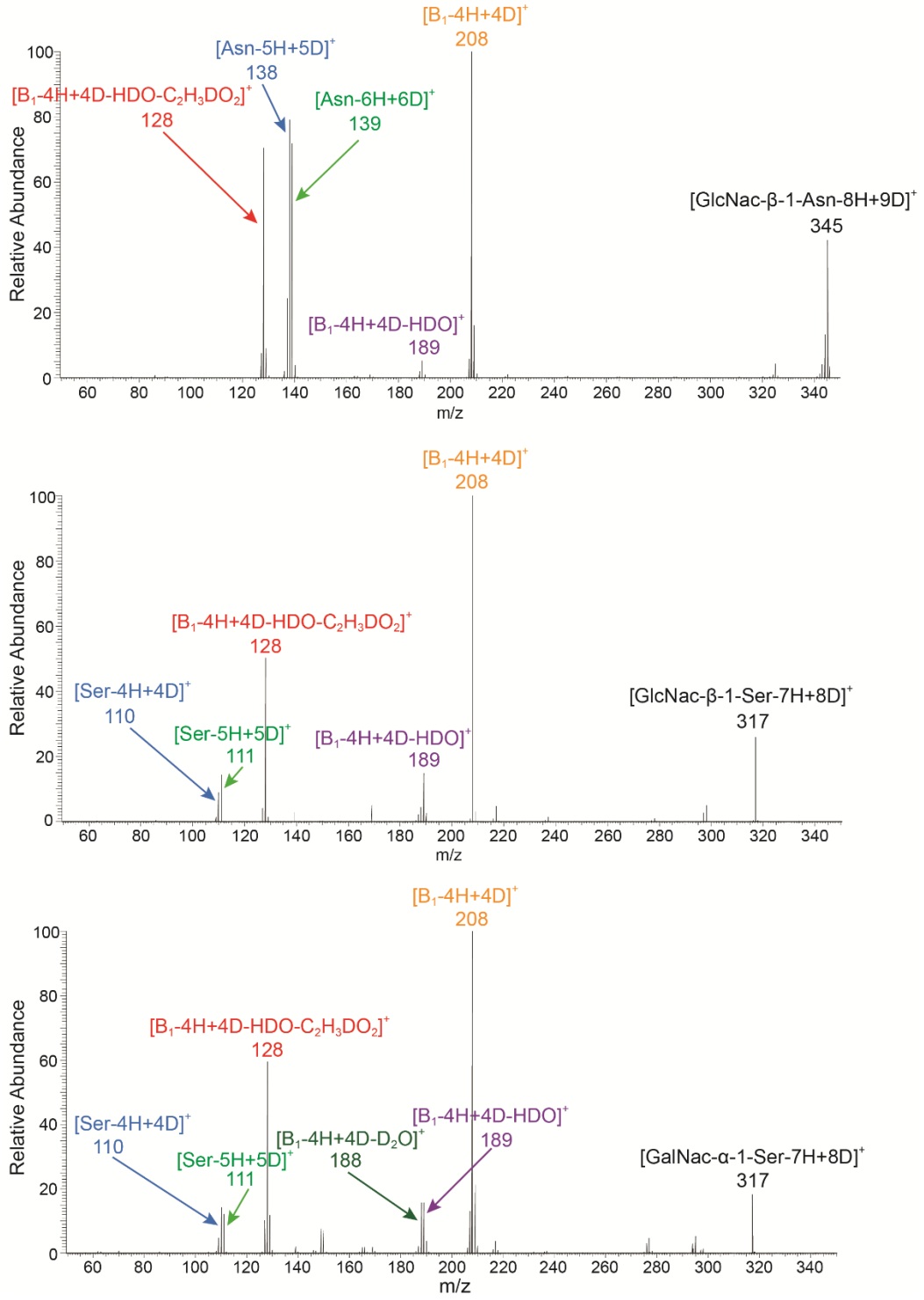


Figure S2
Pyranose form glycosidic bond dissociation pathway of [GlcNac-β-1-Asn+H]$^+$ calculated at B3LYP/6-31+G(d,p) level of theory, (a) Glycosidic bond cleavage TS (b) formation of the glycopyranosyl oxazolinium B_1 ion TS.

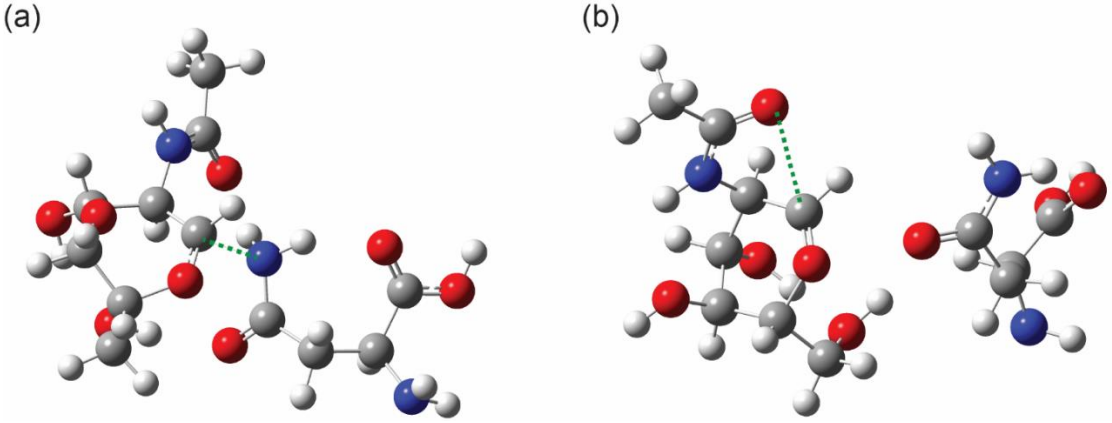


Figure S3
Pyranose form glycosidic bond dissociation reaction calculated at B3LYP/6-31+G(d,p) level of theory, (a) $[GlcNac\text{-}\beta\text{-}1\text{-}Ser+H]^+$ (b) $[GalNac\text{-}\alpha\text{-}1\text{-}Ser+H]^+$.

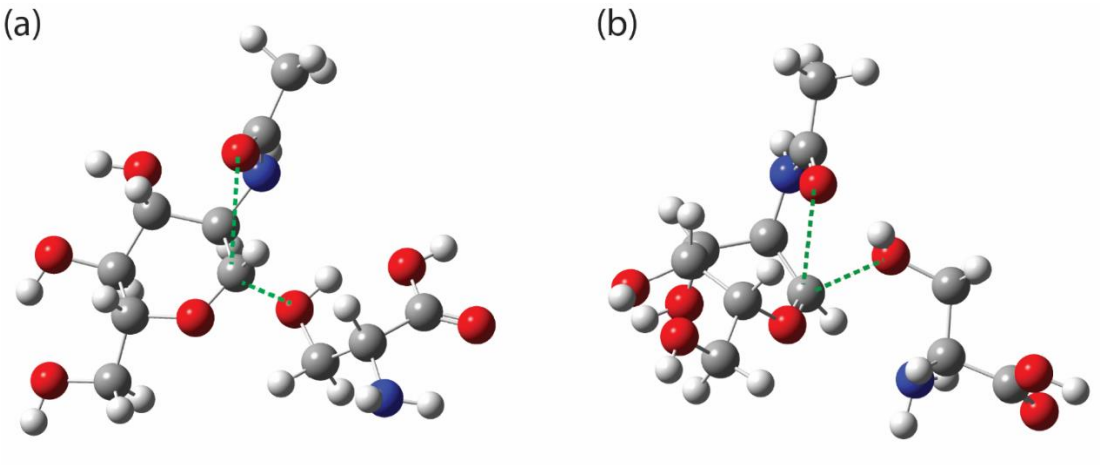


Figure S4
Transition state structures of pyranose to furanose isomerization calculated at B3LYP/6-31+G(d,p) level of theory; (a) S_N2 opening of the pyranose ring of $[GlcNac\text{-}\beta\text{-}1\text{-}Ser+H]^+$, (b) S_N2-like formation of the furanose $[GlcNac\text{-}\beta\text{-}1\text{-}Ser+H]^+$, (c) S_N2 opening of the pyranose ring of $[GalNac\text{-}\alpha\text{-}1\text{-}Ser+H]^+$, (d) S_N2-like formation of the furanose structured $[GalNac\text{-}\alpha\text{-}1\text{-}Ser+H]^+$.

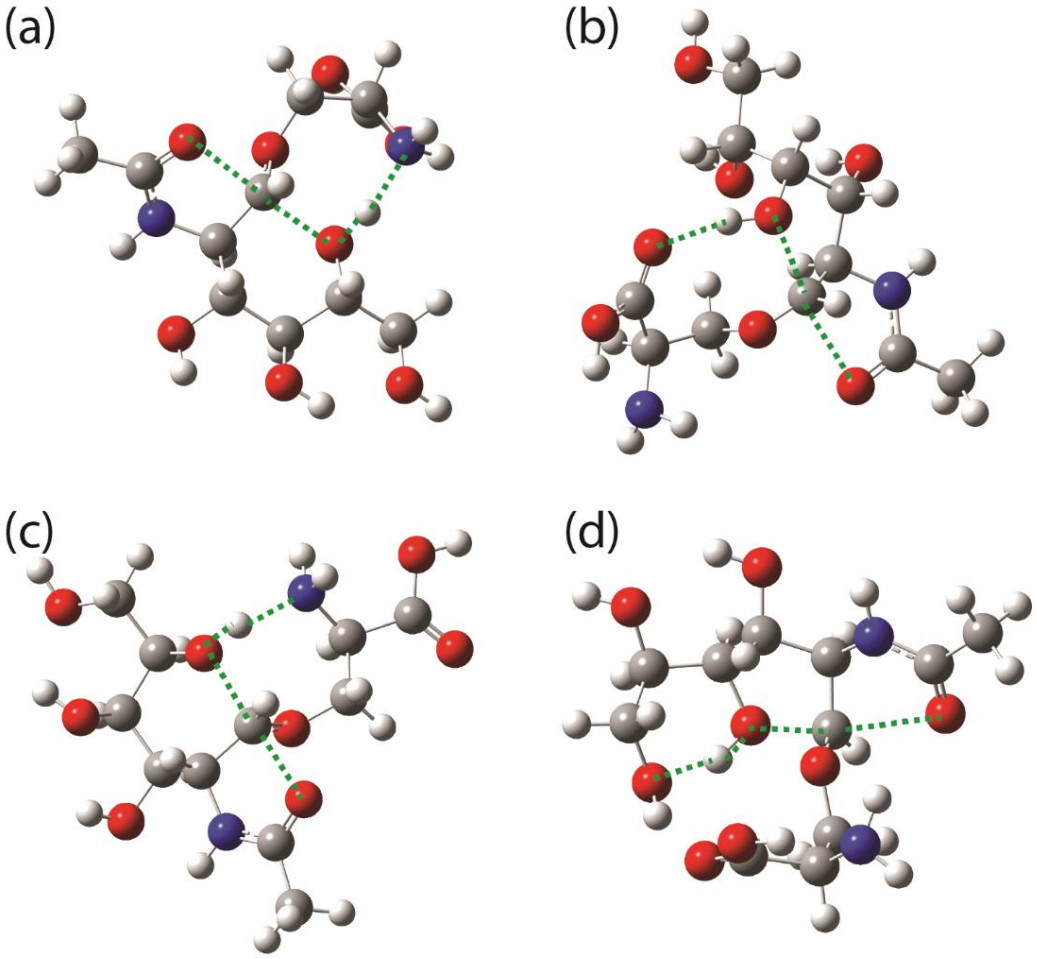


Figure S5
Transition structures of glycosidic bond cleavage reactions after pyranose to furanose isomerization calculated at B3LYP/6-31+G(d,p) level of theory; (a) [GlcNac-β-1-Asn +H]$^+$, (b) [GlcNac-β-1-Ser+H]$^+$, (c) [GalNac-α-1-Ser+H]$^+$.

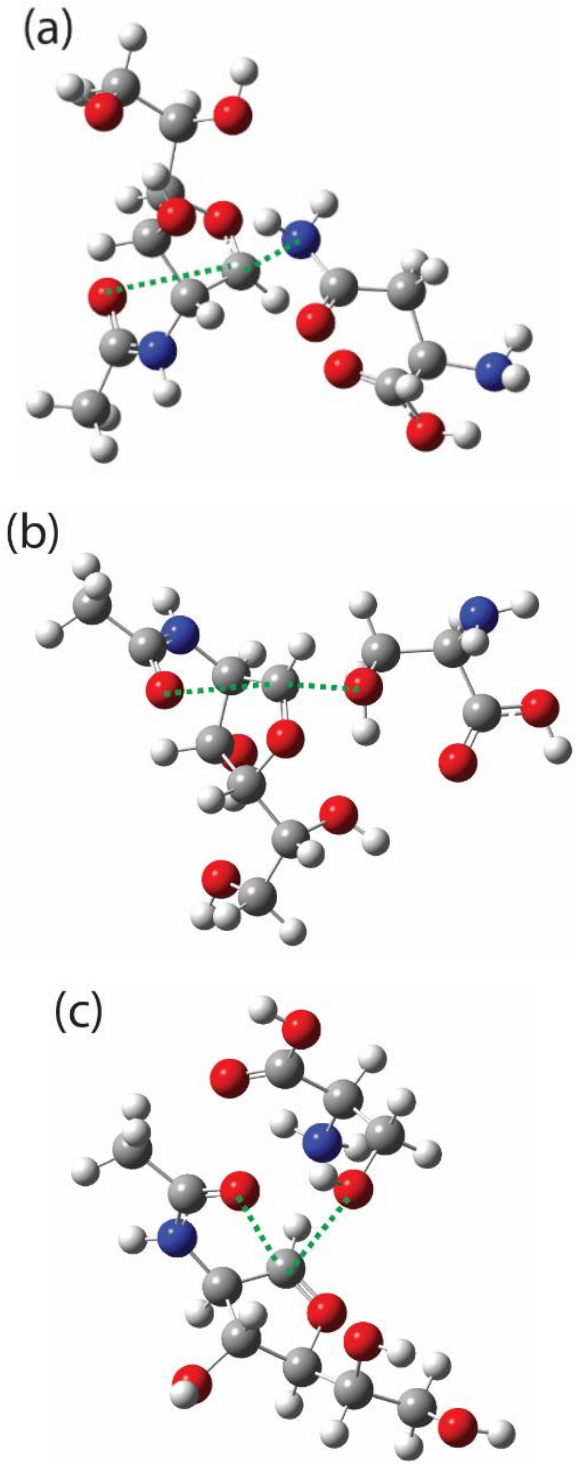


Figure S6
RRKM unimolecular rate constants, k (s^{-1}) calculated for the pyranose glycosidic bond cleavage pathway for $[GlcNac\text{-}\beta\text{-}1\text{-}Asn+H]^+$ at B3LYP/6-31+g(d,p) level of theory.

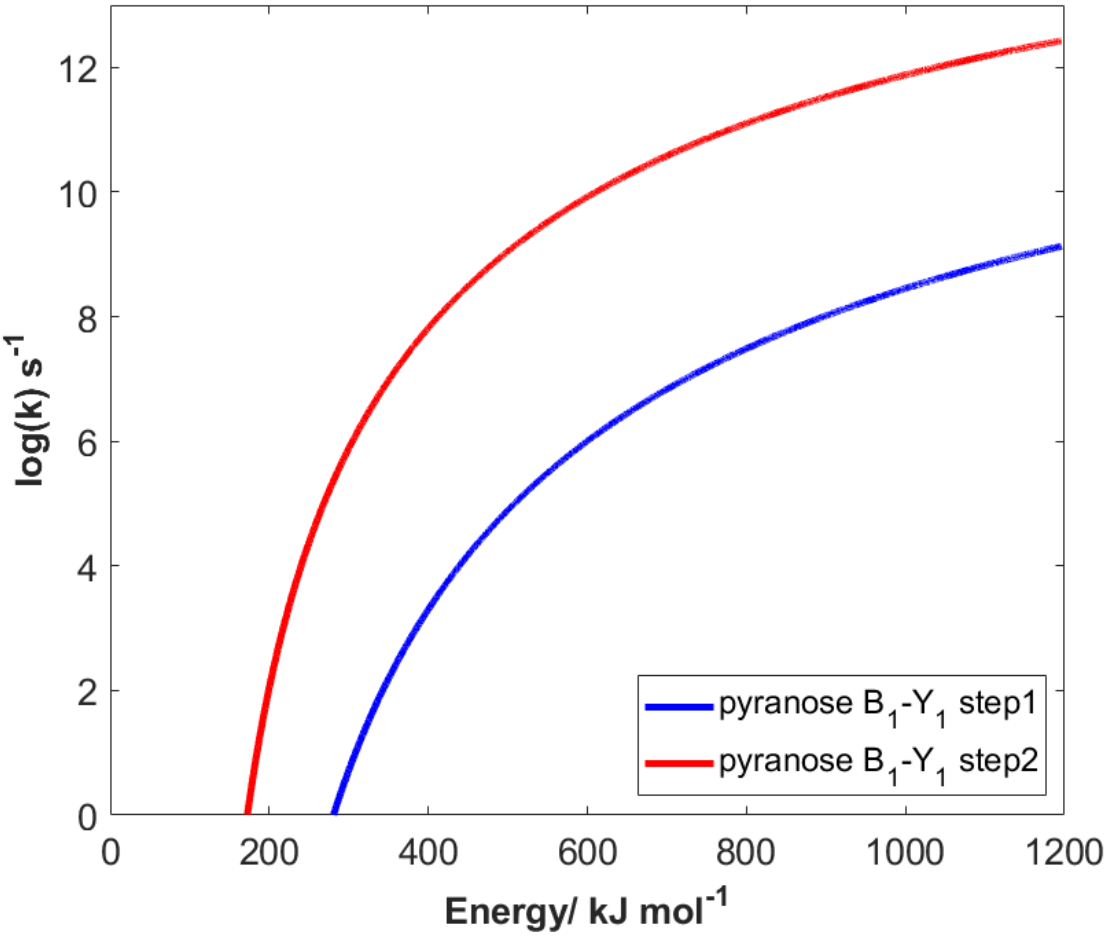


Figure S7
RRKM unimolecular rate constants, k (s^{-1}) calculated for the isomerized furanose glycosidic bond cleavage pathway for $[GlcNac\text{-}\beta\text{-}1\text{-}Asn+H]^+$ at B3LYP/6-31+g(d,p) level of theory.

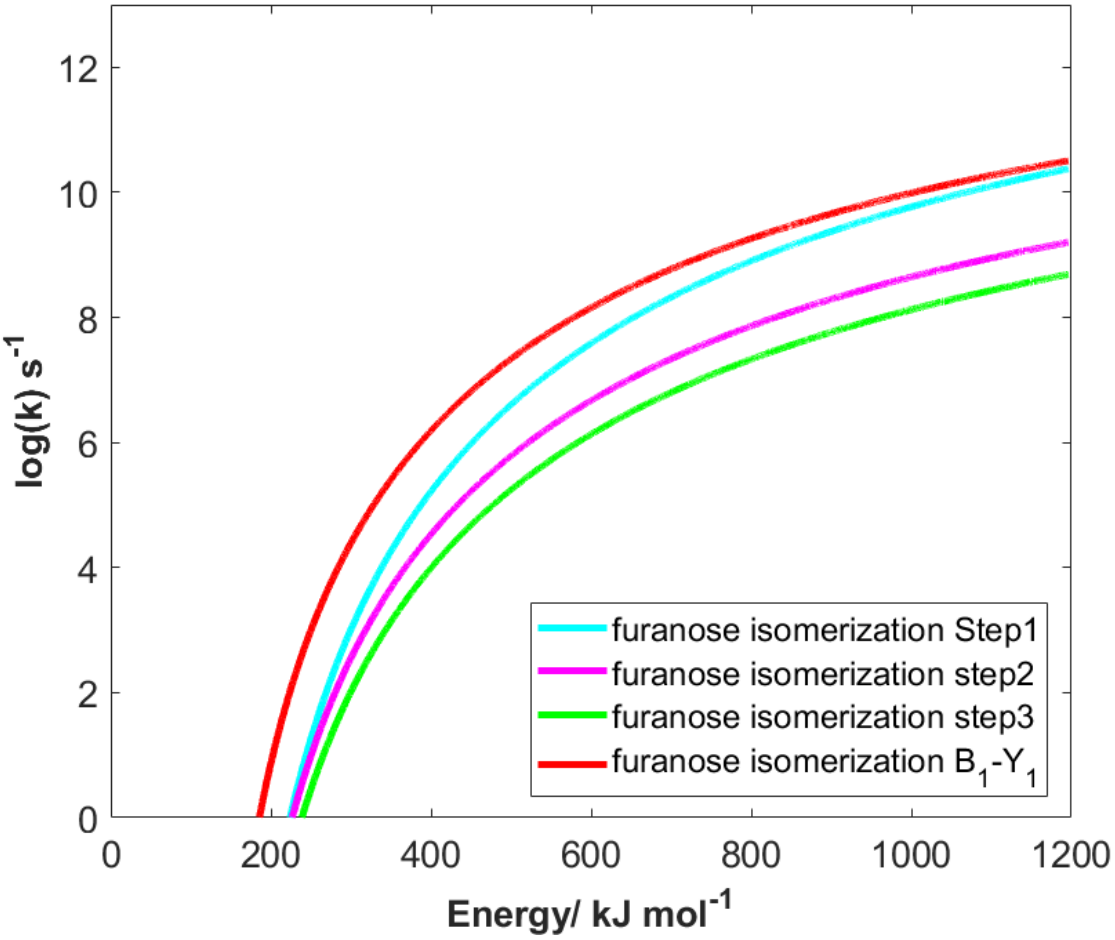


Figure S8
RRKM unimolecular rate constants, k (s^{-1}) calculated for [GlcNac-β-1-Ser+H]$^+$ at B3LYP/6-31+g(d,p) level of theory. i.e., the 2 blue lines are the rate-determining steps for the glycosidic bond cleavage reactions.

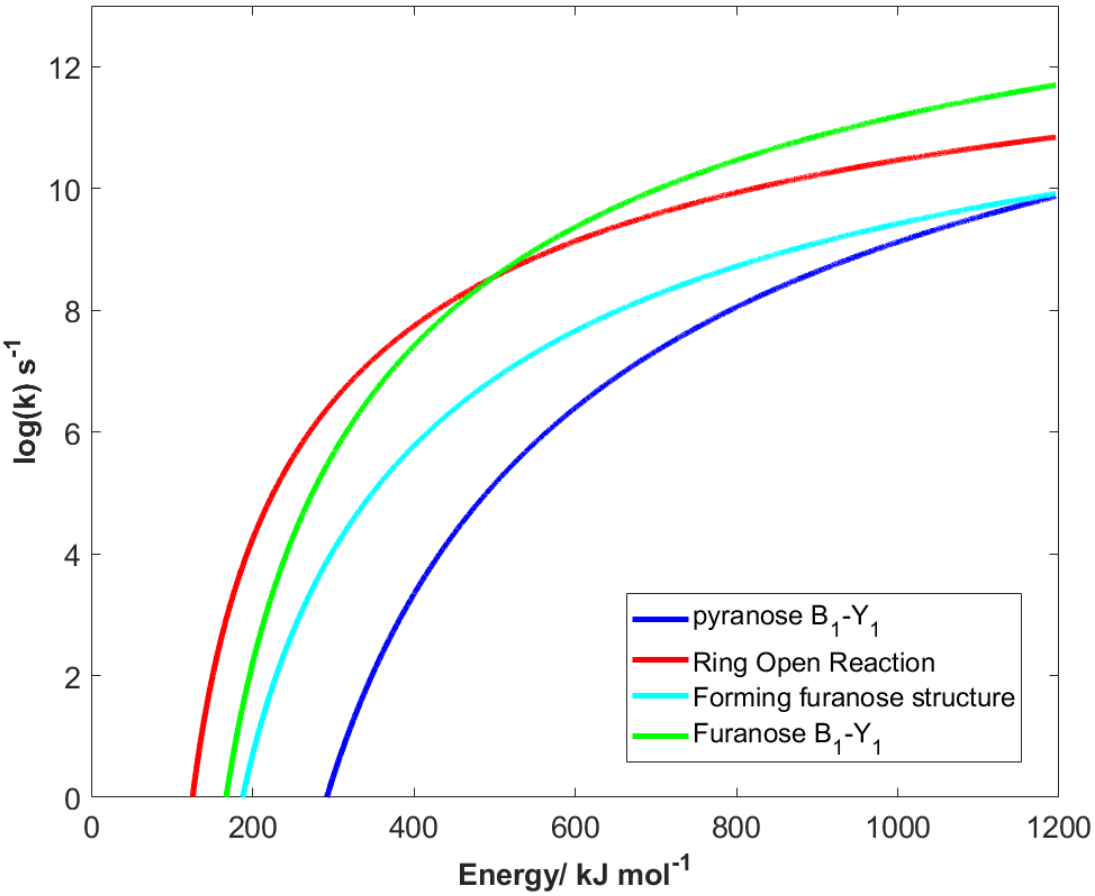


Figure S9
RRKM unimolecular rate constants, k (s^{-1}) calculated for $[GalNac-\alpha-1-Ser+H]^+$ at B3LYP/6-31+g(d,p) level of theory. i.e., the green line is the rate-determining step for the Furnose isomerization then B1-Y1 reaction whereas the dark blue line is for the direct, pyranose dissociation reaction.

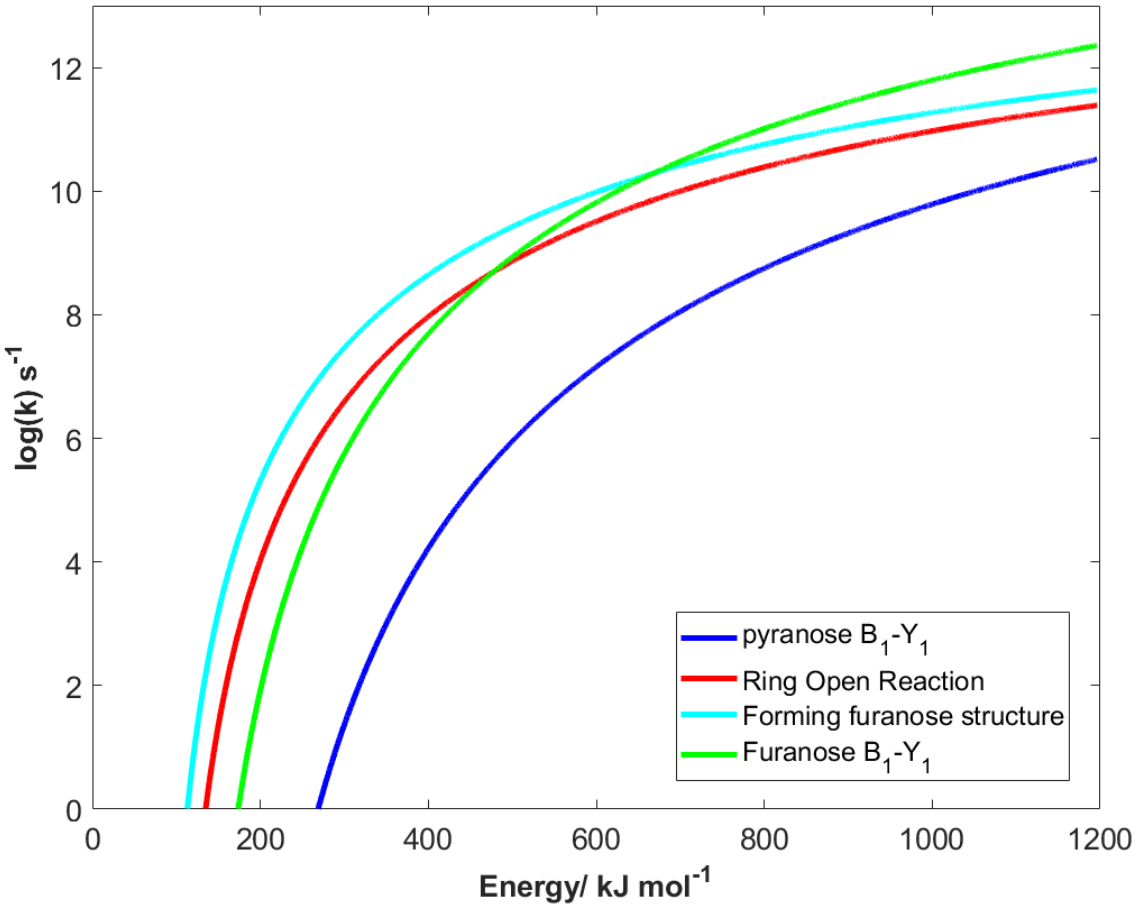
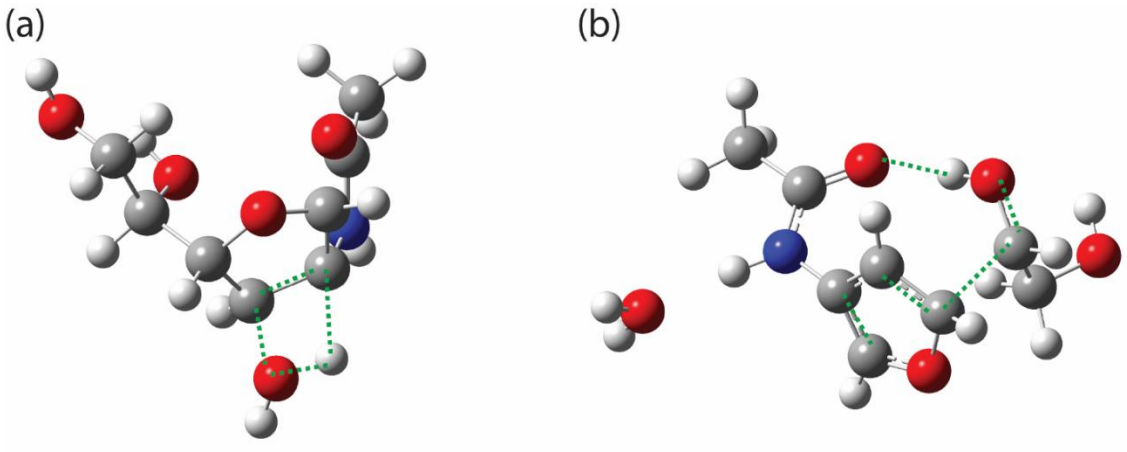


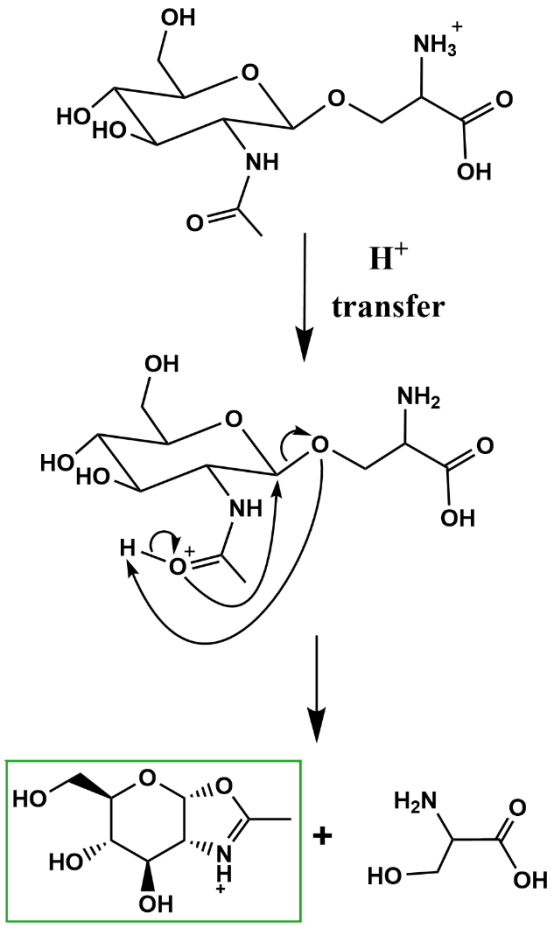
Figure S10

Transition structures of producing m/z 126 ion from the α-GalNAc-originated bicyclic furanose oxazolinium structured B_1 ion; (a) loss of H_2O; (b) loss the $C_2H_4O_2$.



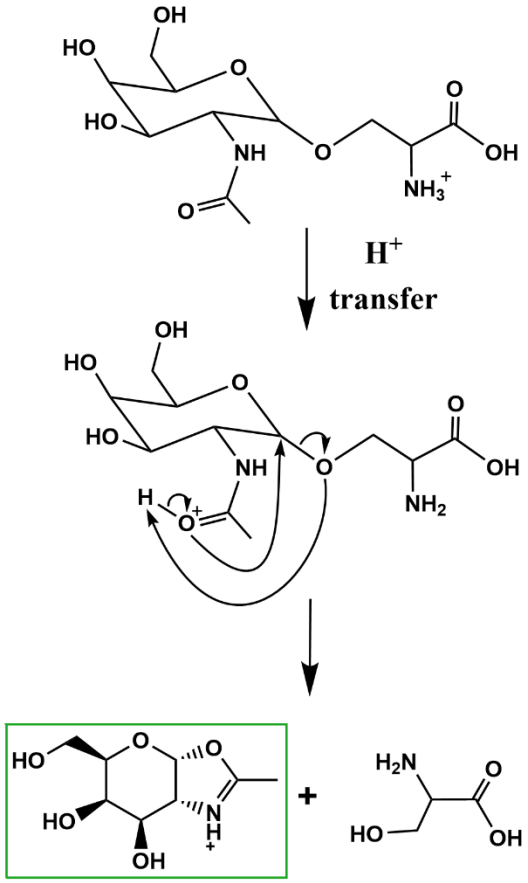
Scheme S1

Direct glycosidic bond cleavage reaction of pyranose form [GlcNac-β-1-Ser+H]$^+$ results in a glycopyranosyl oxazolinium structured B_1 ion and neutral serine.



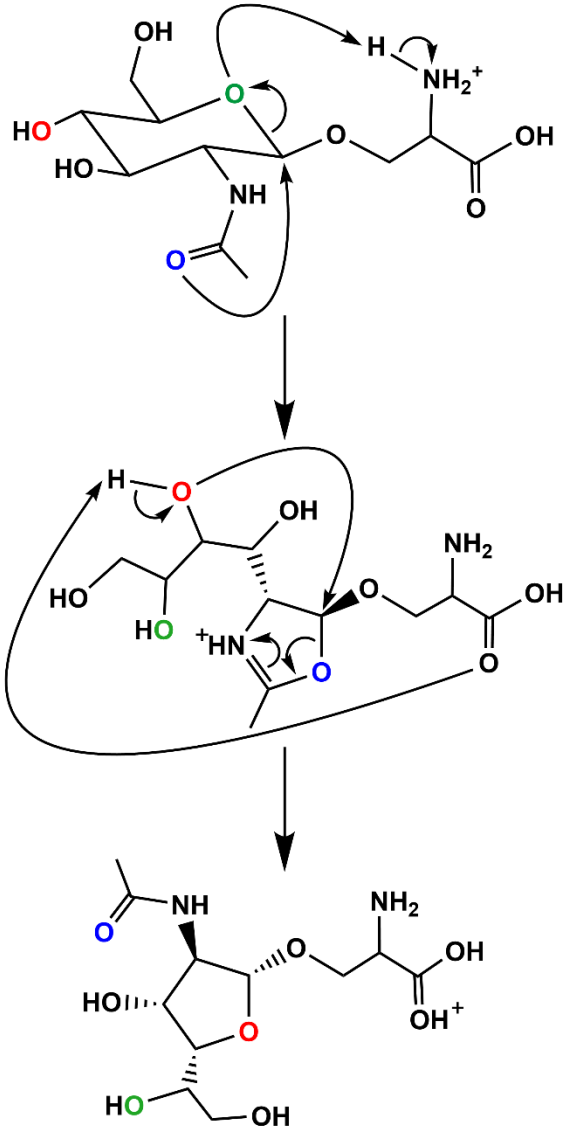
Scheme S2

Direct glycosidic bond cleavage reaction of pyranose form of $[GalNac\text{-}\alpha\text{-}1\text{-}Ser+H]^+$ producing glycopyranosyl oxazolinium structured B_1 ion and neutral serine.



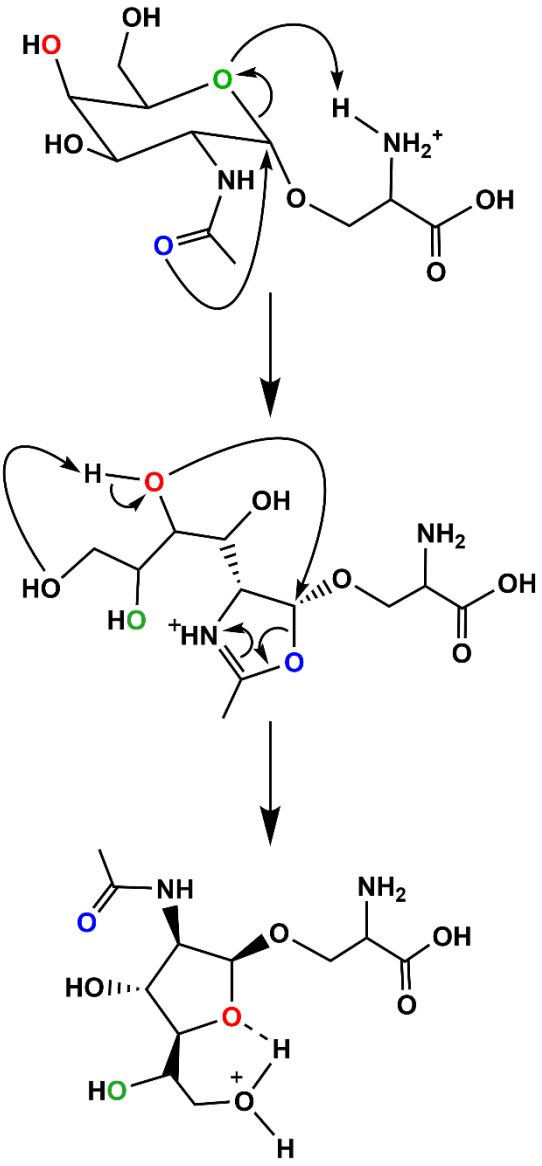
Scheme S3

Pyranose structure to furanose Isomerization reaction for $[GlcNac\text{-}\beta\text{-}1\text{-}Ser+H]^+$.

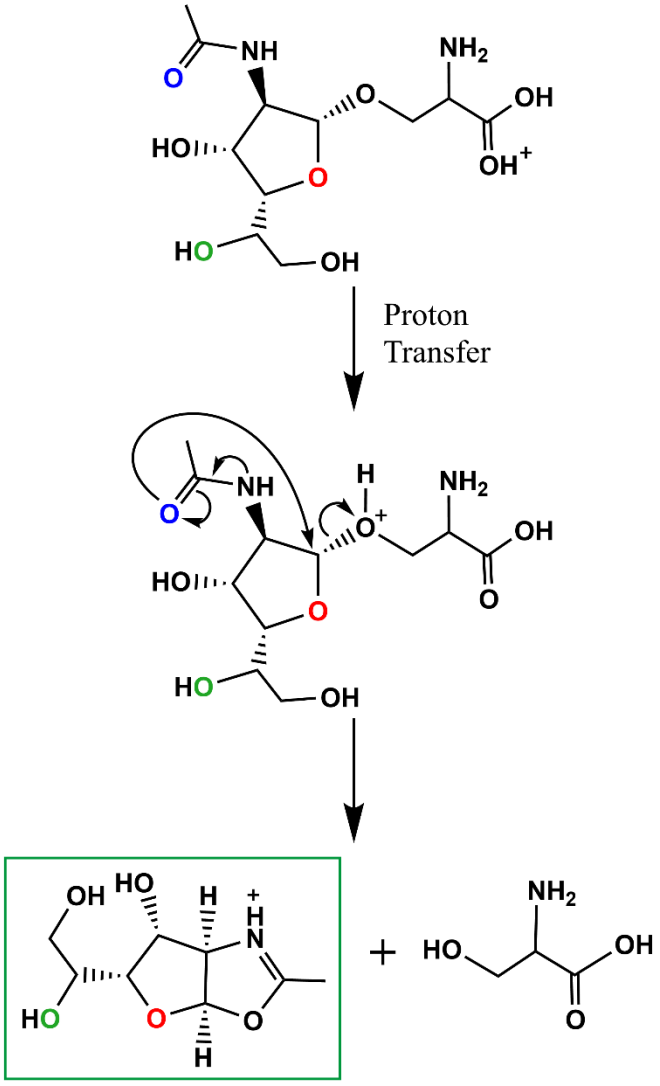


Scheme S4

Pyranose structure to furanose Isomerization reaction for $[GalNac\text{-}\alpha\text{-}1\text{-}Ser+H]^+$.



Scheme S5
Glycosidic bond dissociation of [GlcNac-β-1-Ser+H]$^+$ after the Pyranose-furanose isomerization.



Scheme S6

Glycosidic bond dissociation of [GalNac-α-1-Ser+H]$^+$ after the Pyranose-furanose isomerization.

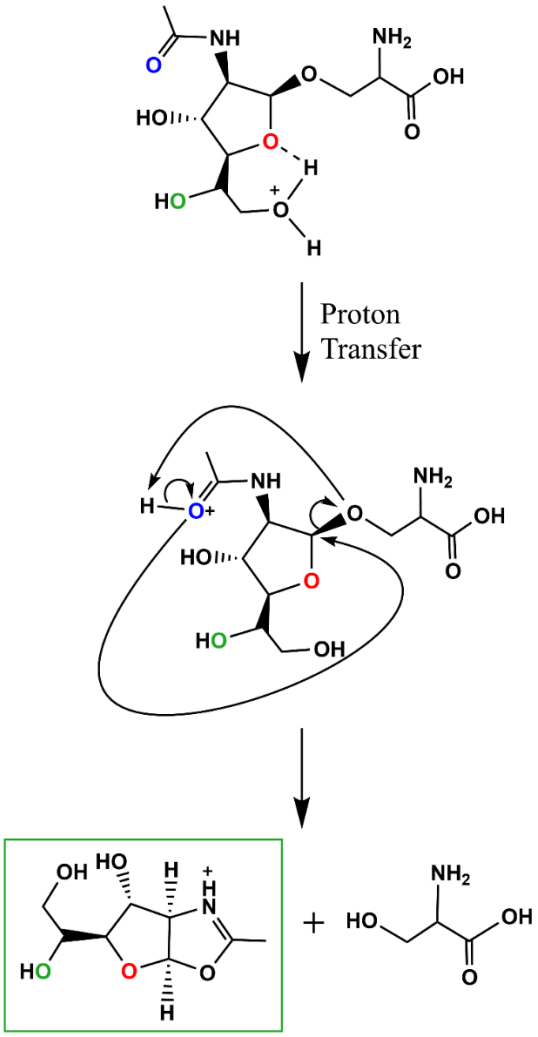


Table S1

Relative Energies of the Minima, Transition Structures, and Separated Products of $[GlcNac-\beta-1-Asn+H]^+$, Calculated at the B3LYP/6-31+G(d,p) Level of Theory. GM is the Global Minimum of Potential Energy Surface of $[GlcNac-\beta-1-Asn+H]^+$.

Name	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	0	0	0	0	0	0
Direct glycosidic bond cleavage reaction (pyranose form)						
Glycosidic bond cleavage TS (pyranose form)	-1236.423538	-1236.053009	149.9	149.3	148.2	3.7
Form pyranose oxazolinium double ring TS	-1236.433832	-1236.06481	118.9	120.6	106.1	48.9
Products: B_1 (charged) + Asn	-1236.439628	-1236.070006	105.2	105.6	50.1	185.9
Products: B_1 (double ring neutral) + $[Asn+H]^+$	-1236.392259	-1236.022854	229.0	228.5	174.8	180.4
Products: B_1 (double bond neutral) + $[Asn+H]^+$	-1236.395925	-1236.027955	215.7	217.9	157.1	204.1
Pyranose-Furanose isomerized glycosidic bond cleavage pathway						
Pyranose-Furanose isomerization Step1 TS	-1236.430097	-1236.060155	131.1	132.4	128.2	14
Pyranose-Furanose isomerization Step2 TS	-1236.433743	-1236.06222	125.7	124.7	127.5	-9.5
Pyranose-Furanose isomerization Step3 TS	-1236.429947	-1236.06135	128	125.6	130.6	-16.8
Glycosidic bond cleavage TS (furanose form)	-1236.437078	-1236.06638	114.8	115	112.4	8.9
Products: B_1(charged) + Asn(neutral)	-1236.442415	-1236.072682	98.2	98.4	40.5	193.9
Products: B_1(double ring neutral) + $[Asn+H]^+$	-1236.399144	-1236.029788	210.8	210.2	156.5	180
Products: B_1(double bond neutral) + $[Asn+H]^+$	-1236.397629	-1236.030497	209	212.3	148	215.3
204 (furanose oxazolinium B_1) producing 126 TS						
Proton extraction TS (extract H from C2)	-1236.3591	-1235.99794	294.5	296.9	233.3	213.4
H_2O loss TS	-1236.411049	-1236.045567	169.4	171.9	108.5	212.7
Generate 126 TS	-1236.395226	-1236.036412	193.4	203.4	117.7	287.2
Products	-1236.412012	-1236.056868	139.7	150.3	-15.8	556.9
204(pyranose oxazolinium B_1) -H_2O TS						
Proton extraction TS	-1236.359382	-1235.997975	294.4	296.7	234.2	209.7
H_2O loss TS	-1236.402981	-1236.037805	189.8	192.5	128.5	214.2
Products	-1236.402493	-1236.040732	182.1	189.3	82.6	357.8

Table S2

Relative Energies of the Minima, Transition Structures, and Separated Products of [GlcNac-β-1-Asn+H]$^+$, Calculated at the M06-2X/6-31+G(d,p) Level of Theory. GM is the Global Minimum of Potential Energy Surface of [GlcNac-β-1-Asn+H]$^+$.

Name	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	0	0	0	0	0	0
Direct glycosidic bond cleavage reaction (pyranose form)						
Glycosidic bond cleavage TS (pyranose form)	-1235.918343	-1235.542859	176.2	177.5	164.2	44.7
Form pyranose oxazolinium double ring TS	-1235.9258	-1235.550316	156.6	158.0	152.5	18.5
Products: B_1(charged) + Asn	-1235.932328	-1235.55663	140.0	140.5	83.9	189.8
Products: B_1 (double ring neutral) + $[Asn+H]^+$	-1235.888498	-1235.512944	254.7	254.9	199	187.6
Products: B_1 (double bond neutral) + $[Asn+H]^+$	-1235.881913	-1235.508235	267.1	270.6	206.2	216.2
Pyranose-Furanose isomerized glycosidic bond cleavage pathway						
Pyranose-Furanose isomerization Step1 TS	-1235.929959	-1235.553753	147.6	148.5	146.7	6.3
Pyranose-Furanose isomerization Step2 TS	-1235.930349	-1235.554473	145.7	144.7	146.1	-4.8
Pyranose-Furanose isomerization Step3 TS	-1235.936876	-1235.563636	121.6	117.8	126.7	-29.8
Glycosidic bond cleavage TS (furanose form)	-1235.937561	-1235.561231	127.9	128.6	127.2	4.8
Products: B_1(charged) + Asn	-1235.931297	-1235.555624	142.7	143.2	83.1	201.5
Products: B_1(double ring neutral) + $[Asn+H]^+$	-1235.892815	-1235.517269	243.4	243.6	186.4	192
Products: B_1(double bond neutral) + $[Asn+H]^+$	-1235.883687	-1235.509505	263.7	265.9	205.0	204.1
204 (furanose oxazolinium B_1) producing 126 TS						
Proton extraction TS (extract H from C2)	-1235.84111	-1235.473912	357.2	360	294.8	218.9
H_2O loss TS	-1235.886423	-1235.516096	246.4	250.9	181	234.4
Generate 126 TS	-1235.880534	-1235.513875	252.3	257.9	185.4	242.9
Products	-1235.865041	-1235.504558	276.7	288.3	117.2	574
204 (pyranose oxazolinium B_1) -H_2O TS						
Proton extraction TS	-1235.838679	-1235.469076	369.9	369.5	314.1	185.7
H_2O loss TS	-1235.840096	-1235.468012	372.7	373.4	315	195.8
Products	-1235.878935	-1235.511119	259.5	267.2	157.5	367.8

Table S3

Relative Energies of the Minima, Transition Structures, and Separated Products of [GlcNac-β-1-Ser+H]$^+$, Calculated at the B3LYP/6-31+G(d,p) Level of Theory. GM is the Global Minimum of Potential Energy Surface of [GlcNac-β-1-Ser+H]$^+$.

Name	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	0	0	0	0	0	0
Direct glycosidic bond cleavage reaction (pyranose form)						
Glycosidic bond cleavage TS (pyranose form)	-1142.919371	-1142.571968	166.2	167.9	161.6	21.1
Products: B_1(charged)+Ser	-1142.947513	-1142.600174	92.1	92.9	40.0	177.4
Products: B_1(double ring neutral) + $[Ser+H]^+$	-1142.926706	-1142.577819	150.8	150.4	99.4	170.0
Products: B_1(double bond neutral) + $[Ser+H]^+$	-1142.930372	-1142.58292	137.4	139.8	81.7	194.8
Pyranose-Furanose isomerized glycosidic bond cleavage pathway						
Pyranose-Furanose isomerization Step1	-1142.949846	-1142.601493	88.7	88.3	89.4	-3.7
Pyranose-Furanose isomerization Step2	-1142.940145	-1142.591302	115.4	115.2	117.3	-6.8
Glycosidic bond cleavage TS (furanose form)	-1142.938973	-1142.591919	113.8	116	108.4	25.3
Products: B_1(charged)+Ser	-1142.950300	-1142.60285	85.1	85.7	30.4	185.5
Products: B_1(double ring neutral) + $[Ser+H]^+$	-1142.933591	-1142.584753	132.6	132.1	81.2	170.7
Products: B_1(double bond neutral) + $[Ser+H]^+$	-1142.932076	-1142.585462	130.7	134.1	72.7	206.0
204 (furanose oxazolinium B_1) producing 126 TS						
Proton extraction TS (extract H from C2)	-1142.866985	-1142.528108	281.3	284.3	223.1	205.0
H_2O loss TS	-1142.918933	-1142.575735	156.3	159.2	98.3	204.2
Generate 126 TS	-1142.903111	-1142.56658	180.3	190.7	107.6	278.8
Products	-1142.919896	-1142.587036	126.6	137.6	-25.9	548.4
204 (pyranose oxazolinium B_1) -H_2O TS						
Proton extraction	-1142.867267	-1142.528143	281.2	284.0	224.0	201.0
H_2O loss	-1142.910866	-1142.567973	176.7	179.8	118.3	206.3
Products	-1142.910377	-1142.5709	169.0	176.6	72.5	349.4

Table S4

Relative Energies of the Minima, Transition Structures, and Separated Products of [GlcNac-β-1-Ser+H]$^+$, Calculated at the M062X/6-31+G(d,p) Level of Theory. GM is the Global Minimum of Potential Energy Surface of [GlcNac-β-1-Ser+H]$^+$.

Name	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	0	0	0	0	0	0
Direct glycosidic bond cleavage reaction (pyranose form)						
Glycosidic bond cleavage TS (pyranose form)	-1142.456763	-1142.102904	190.0	191.3	181.2	33.7
Products: B_1(charged)+ Ser	-1142.478651	-1142.125735	130.1	131.5	70.5	204.6
Products: B_1(double ring neutral) + $[Ser+H]^+$	-1142.461386	-1142.10673	180.0	180.2	121.3	197.4
Products: B_1 (double bond neutral) + $[Ser+H]^+$	-1142.454800	-1142.102021	192.3	195.9	128.5	226.0
Pyranose-Furanose isomerized glycosidic bond cleavage pathway						
Pyranose-Furanose isomerization Step1	-1142.481824	-1142.128481	122.8	123.7	114.6	30.6
Pyranose-Furanose isomerization Step2	-1142.47271	-1142.120165	144.7	147.3	135.2	40.6
Glycosidic bond cleavage TS (furanose form)	-1142.474462	-1142.120805	143.0	144.2	137.0	24.0
Products: B_1(charged)+Ser	-1142.477620	-1142.124729	132.7	134.2	69.7	216.2
Products: B_1(double ring neutral) + $[Ser+H]^+$	-1142.465703	-1142.111055	168.6	168.9	108.7	201.8
Products: B_1(double bond neutral) + $[Ser+H]^+$	-1142.456574	-1142.103291	189.0	191.1	127.4	213.9
204 (furanose oxazolinium B_1) producing 126 TS						
Proton extraction TS (extract H from C2)	-1142.387433	-1142.043017	347.2	351.0	281.3	233.6
H_2O loss TS	-1142.432746	-1142.085201	236.5	241.8	167.5	249.1
Generate 126 TS	-1142.426857	-1142.08298	242.3	248.8	172.0	257.7
Products	-1142.411364	-1142.073663	266.8	279.3	103.7	588.7
204 (pyranose oxazolinium B_1) -H_2O TS						
Proton extraction	-1142.385002	-1142.038181	359.9	360.4	300.7	200.4
H_2O loss	-1142.386419	-1142.037117	362.7	364.3	301.6	210.5
Products	-1142.425258	-1142.080224	249.5	258.1	144.1	382.5

Table S5

Relative Energies of the Minima, Transition Structures, and Separated Products of [GalNac-α-1-Ser+H]$^+$, Calculated at the B3LYP/6-31+G(d,p) Level of Theory. GM is the Global Minimum of Potential Energy Surface of [GalNac-α-1-Ser+H]$^+$.

Name	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	0	0	0	0	0	0
Direct glycosidic bond cleavage reaction (pyranose form)						
Glycosidic bond cleavage TS (pyranose form)	-1142.92162	-1142.573399	160.9	163.0	153.9	30.6
Products: B_1(charged)+Ser	-1142.941419	-1142.593209	108.9	109.5	54.4	184.5
Products: B_1(double ring neutral) + $[Ser+H]^+$	-1142.927357	-1142.577738	149.5	149.1	97.6	172.6
Products: B_1 (double bond neutral) + $[Ser+H]^+$	-1142.939246	-1142.590434	116.2	117.3	61.9	185.9
Pyranose-Furanose isomerized glycosidic bond cleavage pathway						
Pyranose-Furanose isomerization Step1	-1142.947085	-1142.597886	96.7	97.1	93.5	12.3
Pyranose-Furanose isomerization Step2	-1142.950657	-1142.602305	85.1	85.5	82.6	9.8
Glycosidic bond cleavage TS (furanose form)	-1142.934749	-1142.589317	119.2	123.4	111.7	39.2
Products: B_1(charged)+Ser	-1142.950877	-1142.603782	81.2	83.1	24.7	195.8
Products: B_1(double ring neutral) + $[Ser+H]^+$	-1142.929852	-1142.581293	140.2	140.7	85.5	185.1
Products: B_1(double bond neutral) + $[Ser+H]^+$	-1142.933302	-1142.586365	126.9	130.6	65.4	218.6
204 (furanose oxazolinium B_1) producing 126 TS						
H_2O loss TS (extract H from C2)	-1142.85303	-1142.512383	321.1	323.0	264.7	195.5
Generate 126 TS	-1142.905079	-1142.566392	179.3	188.6	107.8	271.2
Products	-1142.905859	-1142.572362	163.7	175.6	6.1	568.4
204 (furanose oxazolinium B_1) -H_2O (extract H from oxazolinium nitrogen)						
Proton extraction TS	-1142.858511	-1142.515147	313.9	313.1	261.0	174.8
H_2O loss TS	-1142.870569	-1142.527705	280.9	283.4	223.2	201.8
Products	-1142.934979	-1142.593005	109.5	114.8	13.4	340.0
204 (pyranose oxazolinium B_1) -H_2O TS						
TS	-1142.864257	-1142.524136	290.3	293.1	230.2	211.0
Products	-1142.91277	-1142.573187	161.5	170.1	62.3	361.6

Table S6

Relative Energies of the Minima, Transition Structures, and Separated Products of [GalNac-α-1-Ser+H]$^+$, Calculated at the M062X/6-31+G(d,p) Level of Theory. GM is the Global Minimum of Potential Energy Surface of [GalNac-α-1-Ser+H]$^+$.

Name	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	**0**	**0**	**0**	**0**	**0**	**0**
Glycosidic bond cleavage (pyranose form)						
Glycosidic bond cleavage TS (pyranose form)	-1142.456045	-1142.102363	184.9	187.0	181.3	18.8
Products: B_1(charged) + Ser	-1142.471982	-1142.118515	142.5	143.2	88.7	182.7
Products: B_1(double ring neutral) + [Ser+H]$^+$	-1142.461408	-1142.106169	174.9	174.5	123.7	170.3
Products: B_1(double bond neutral) + [Ser+H]$^+$	-1142.462957	-1142.108711	168.3	169.9	112.9	191.0
Pyranose-Furanose isomerized glycosidic bond cleavage pathway						
Pyranose-Furanose isomerization Step1	-1142.480143	-1142.125577	124.0	124.5	122.0	8.4
Pyranose-Furanose isomerization Step2	-1142.482697	-1142.129169	114.5	115.5	113.0	8.1
Glycosidic bond cleavage TS (furanose form)	-1142.466252	-1142.115131	151.4	155.0	147.9	24.0
Products: B_1(charged)+Ser	-1142.480541	-1142.127645	118.5	119.9	63.8	188.4
Products: B_1(double ring neutral)+ [Ser+H]$^+$	-1142.459041	-1142.105057	177.8	178.7	122.7	187.8
Products: B_1(double bond neutral) + [Ser+H]$^+$	-1142.454473	-1142.102502	184.6	188.6	125.0	213.3
204 (furanose oxazolinium B_1) producing 126 TS						
H_2O loss TS (extract H from C2)	-1142.381835	-1142.03469	362.6	363.7	309.8	180.8
Generate 126 TS	-1142.413148	-1142.069156	272.1	281.1	203.6	259.7
Products	-1142.404325	-1142.065900	280.7	290.8	127.5	547.6
204 (furanose oxazolinium B_1) -H_2O (extract H from oxazolinium nitrogen)						
Proton extraction TS	-1142.389039	-1142.039718	349.4	348.1	297.8	168.7
H_2O loss TS	-1142.395088	-1142.046096	332.6	334.2	278.4	187.2
Products	-1142.458009	-1142.110569	163.4	168.6	69.1	333.7
204 (pyranose oxazolinium B_1) -H_2O TS						
TS	-1142.382731	-1142.037681	354.7	356.0	297.5	196.4
Products	-1142.42778	-1142.081995	238.4	246.1	140.7	353.6