Supporting information for:

SUGAR-PEPTIDIC BOND INTERACTIONS: SPECTROSCOPIC CHARACTERIZATION OF A MODEL SYSTEM

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Scheme S01. Sample rod preparation for mixed solid/liquid samples. While β-phenyl-D-glucopyranoside is a solid at room temperature, n-methyacetamide is a viscous solid (melting point 26 ºC). Preparation of mixtures of solid and liquid samples for laser ablation of mixed solid/liquid is not simple. Furthermore, introduction of the liquid directly in the expansion by simple warming does not result in cluster formation with the ablated sample, at least in our system, because the conditions for the expansion are very different from those required by the solid sample. Therefore, during this work a methodology to prepare samples containing a mixture of solids and liquids was developed. First a drop of liquid glue was deposited on the surface of the cylindrical sample holder. This allowed us to cover the surface of the holder with a thin layer of active carbon. One must allow the mixture to dry for several minutes. Meanwhile a homogeneous mixture of carbon nanotubes and β-phenyl-D-glucopyranoside was done. Once the surface of the sample holder was dry, the mixture of the sugar with the nanotubes was deposited on the surface of the sample holder by pressing the holder against the powdered sugar/nanotubes mixture. Now it is possible to deposit the n-methylacetamide on top of the sugar/nanotubes sample.

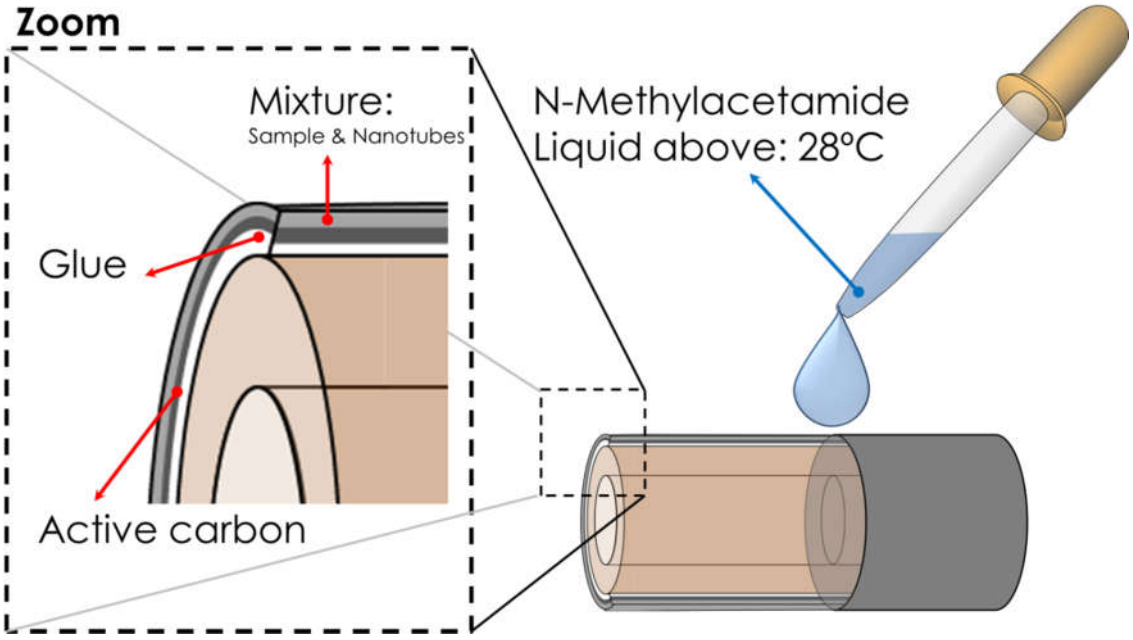
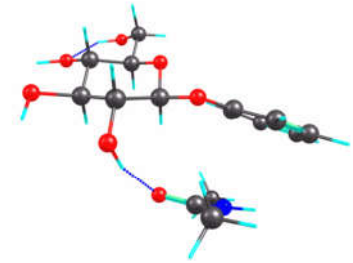
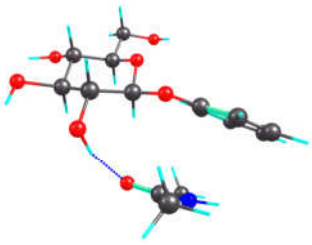


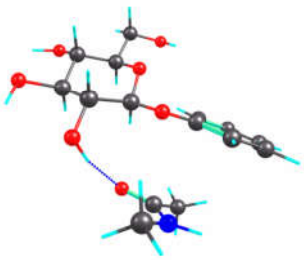
Figure S01. Calculated structures for mAct•β-PhGlc at M06-2X/6-311++G(d,p) level arranged in energetically order respect to the global minimum.



β-PhGlc · mAct-01



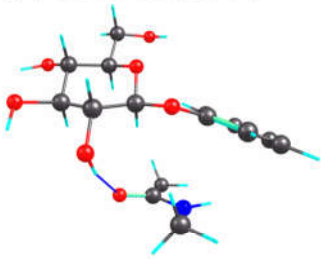
β-PhGlc · mAct-02



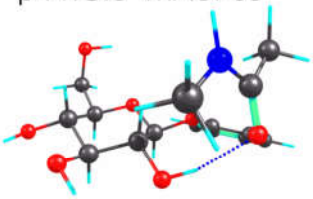
β-PhGlc · mAct-03

β-PhGlc · mAct-04

β-PhGlc · mAct-05



β-PhGlc · mAct-06

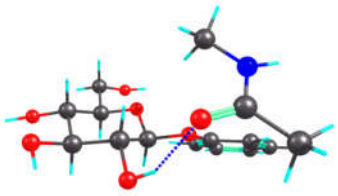


β-PhGlc · mAct-07

β-PhGlc · mAct-08

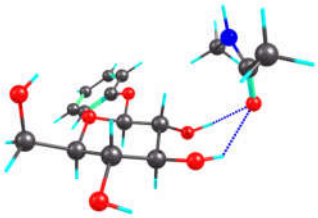
Figure S01. Cont.

β-PhGlc · mAct-09

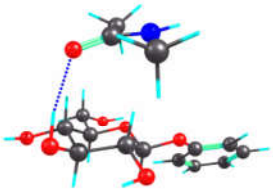


β-PhGlc · mAct-10

β-PhGlc · mAct-11



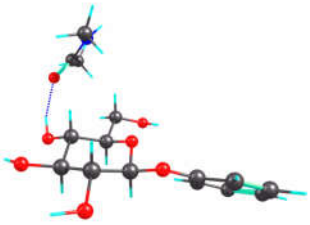
β-PhGlc · mAct-12



β-PhGlc · mAct-13

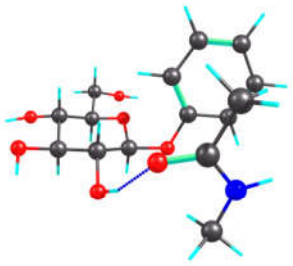
β-PhGlc · mAct-14

β-PhGlc · mAct-15



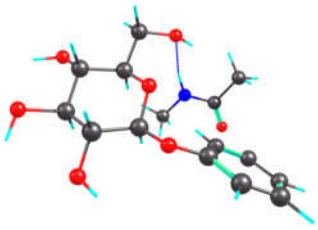
β-PhGlc · mAct-16

Figure S01. Cont.

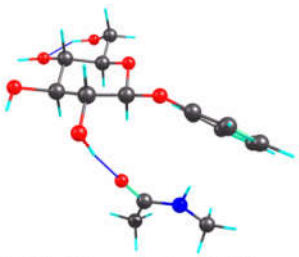


β-PhGlc · mAct-17

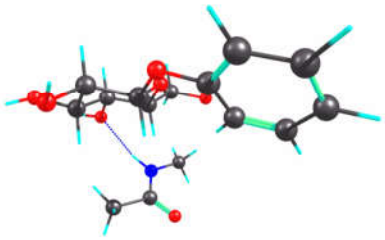
β-PhGlc · mAct-18



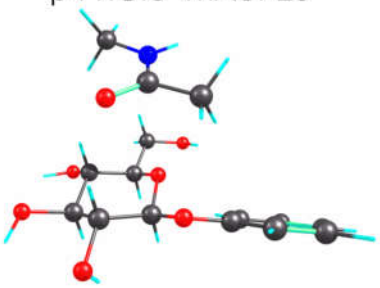
β-PhGlc · mAct-19



β-PhGlc · mAct-20



β-PhGlc · mAct-21



β-PhGlc · mAct-22

Figure S02. Calculated structures for mAct and β-PhGlc monomers at M06-2X/6-311++G(d,p) level arranged in energetically order respect to the global minimum.

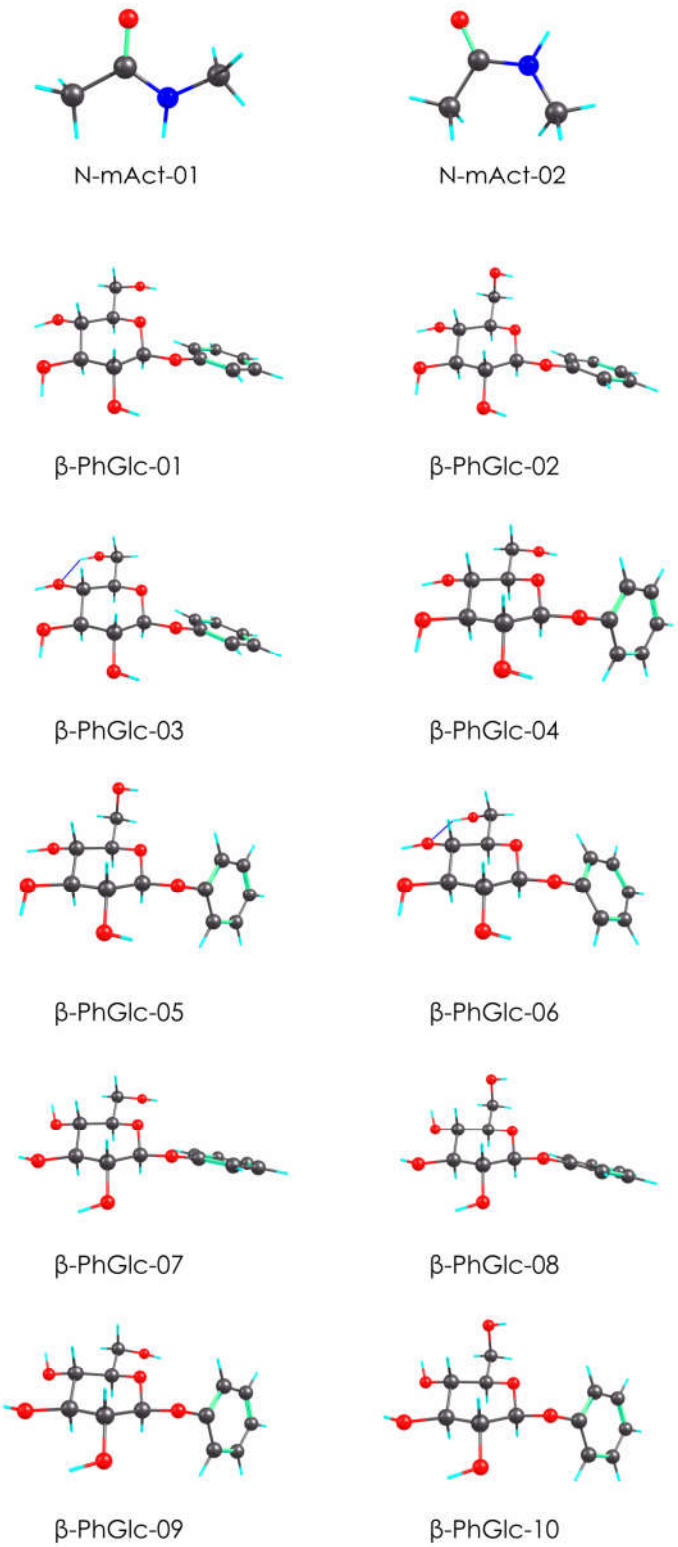


Table S01. Energies, ZPE, BSSE, thermal corrections, relative energies, sum of electronic and thermal free energies at 298.15 K (ΔG), and the equilibrium temperature calculated at M06-2X/6-311++G(d,p) level for the mAct•β-PhGlc.

Structure	Energy (Hartree)	ZPE (Hartree)	BSSE (Hartree)	Thermal Correction (Hartree)	Relative Energy (kJ/mol)	Relative Gibbs Free Energy (kJ/mol)	Equilibrium Temperature(K)
β-PhGlc · mAct-1	-1166.659012	0.387328	0.0025429	0.334014	1.01	0.00	257.6
β-PhGlc · mAct-2	-1166.66023	0.388116	0.0025868	0.335947	0.00	1.88	250.3
β-PhGlc · mAct-3	-1166.658745	0.387539	0.0025876	0.33498	2.39	3.24	242.4
β-PhGlc · mAct-4	-1166.658122	0.387425	0.0026193	0.334614	3.81	3.91	237.7
β-PhGlc · mAct-5	-1166.654933	0.386865	0.0020097	0.331464	9.11	4.01	237.5
β-PhGlc · mAct-6	-1166.659098	0.388665	0.0026451	0.336132	4.57	5.34	232.1
β-PhGlc · mAct-7	-1166.654346	0.38665	0.0020734	0.331818	10.25	6.48	224.2
β-PhGlc · mAct-8	-1166.652053	0.387038	0.002045	0.330148	17.22	8.12	204.8
β-PhGlc · mAct-9	-1166.654058	0.386738	0.0020318	0.332191	11.13	8.22	216.3
β-PhGlc · mAct-10	-1166.65441	0.387221	0.0021562	0.332689	11.80	8.60	212.6
β-PhGlc · mAct-11	-1166.651872	0.387322	0.0013796	0.330815	16.69	10.35	204.6
β-PhGlc · mAct-12	-1166.652939	0.387024	0.0019942	0.33194	14.72	10.50	201.8
β-PhGlc · mAct-13	-1166.650993	0.386461	0.0021083	0.33016	18.65	10.94	189.9
β-PhGlc · mAct-14	-1166.650403	0.386606	0.0019432	0.33065	20.15	13.77	176.6
β-PhGlc · mAct-15	-1166.651961	0.387133	0.0018169	0.332573	17.11	14.73	183.9
β-PhGlc · mAct-16	-1166.650015	0.386881	0.0014999	0.330815	20.72	15.22	175.7
β-PhGlc · mAct-17	-1166.652754	0.387338	0.0025232	0.333814	17.42	15.91	174.6
β-PhGlc · mAct-18	-1166.649871	0.386562	0.0015352	0.33109	20.36	16.32	164.1
β-PhGlc · mAct-19	-1166.651372	0.387065	0.0017518	0.332672	18.30	16.54	178.3
β-PhGlc · mAct-20	-1166.651388	0.387738	0.0021485	0.333154	21.07	17.76	145.1
β-PhGlc · mAct-21	-1166.647822	0.386426	0.0017138	0.330232	25.85	19.45	143.7
β-PhGlc · mAct-22	-1166.648724	0.38607	0.0023895	0.331251	24.32	19.76	172.1

Table S02. Energies, ZPE, thermal corrections, relative energies and the sum of electronic and thermal free energies at 298.15 K (ΔG) calculated at M06-2X/6-311++G(d,p) level for the mAct•β-PhGlc.

Structure	Energy (Hartree)	ZPE (Hartree)	Thermal Correction (Hartree)	Relative Energy (kJ/mol)	Relative Gibbs Free Energy (kJ/mol)
b-PhGlc-1	-918.148769	0.281637	0.237167	0.00	0.00
b-PhGlc-2	-918.148303	0.281844	0.237559	1.77	2.25
b-PhGlc-3	-918.147723	0.282161	0.238269	4.12	5.64
b-PhGlc-5	-918.146287	0.281640	0.236675	6.52	5.22
b-PhGlc-4	-918.146551	0.281975	0.237231	6.71	5.99
b-PhGlc-6	-918.145782	0.281954	0.237133	8.67	7.75
b-PhGlc-8	-918.144428	0.281832	0.237328	11.91	11.82
b-PhGlc-7	-918.142671	0.281169	0.236572	14.78	14.45
b-PhGlc-10	-918.142498	0.281676	0.235892	16.57	13.12
b-PhGlc-9	-918.140614	0.281679	0.236713	21.52	20.22

Structure	Energy (Hartree)	ZPE (Hartree)	Thermal Correction (Hartree)	Relative Energy (kJ/mol)	Relative Gibbs Free Energy (kJ/mol)
N-mAct-01	-248.486064	0.102554	0.072236	0.00	0.00
N-mAct-02	-248.482527	0.102665	0.072858	9.58	10.92

Figure S03. IR spectra of mAct•β-PhGlc and the predicted spectra for the structures in Figure S01 calculated at M06-2X/6-311++G(d,p). A correction factor of 0.939 was employed to account for the anharmonicity.

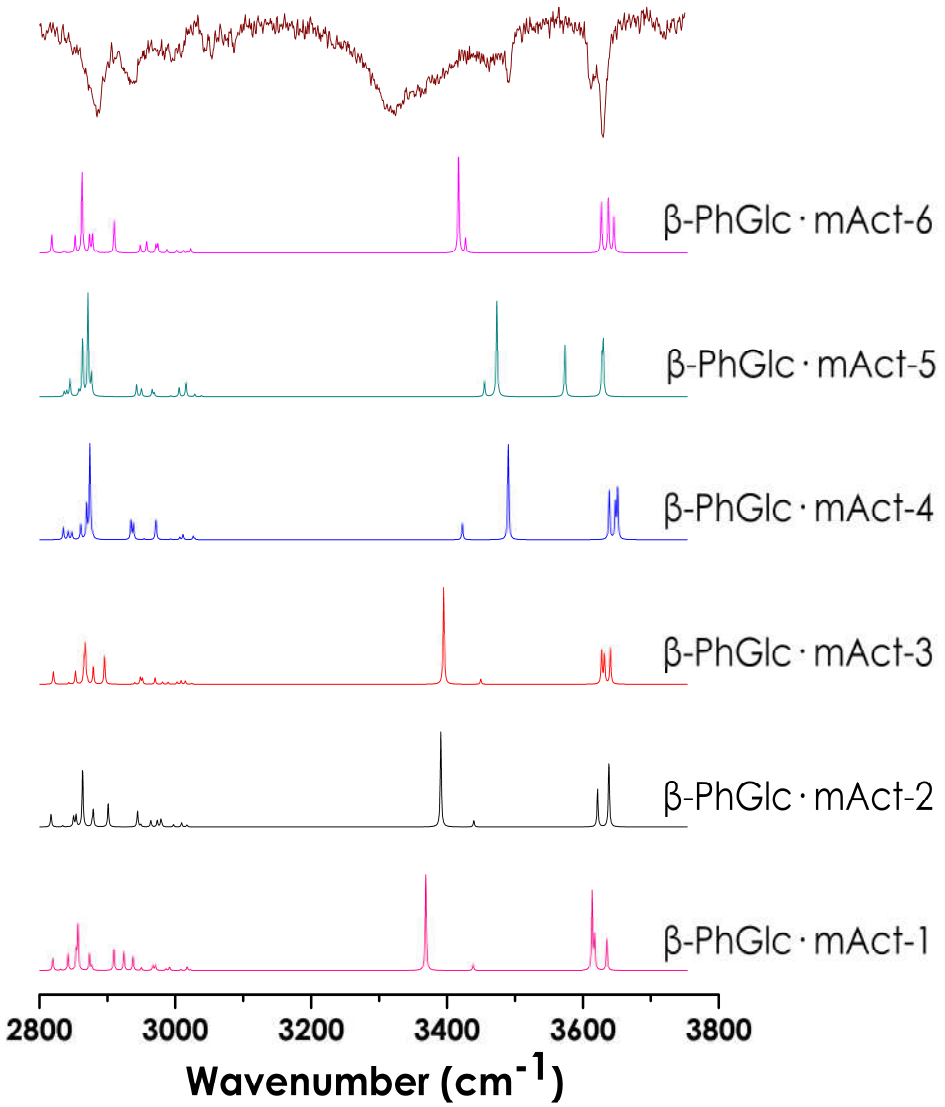


Figure S03. Cont.

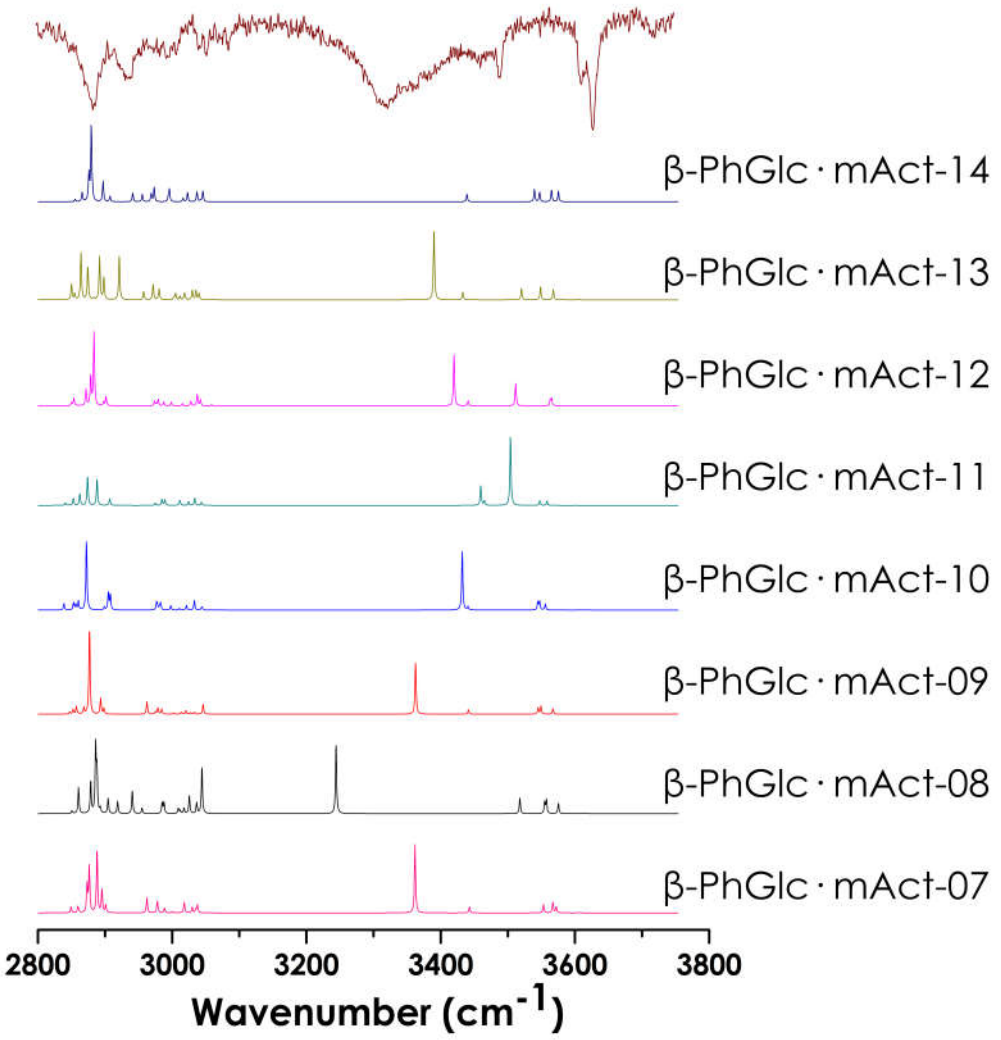


Figure S03. Cont.

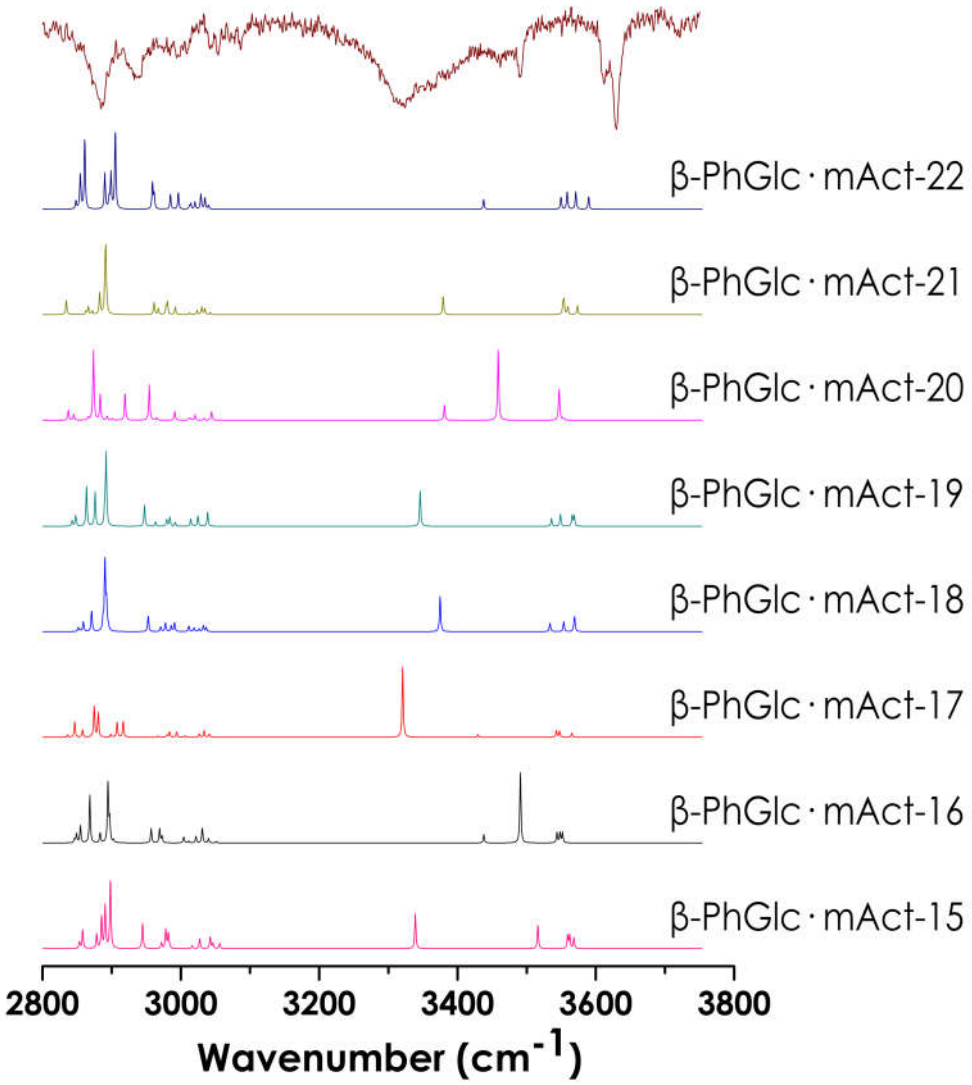


Figure S04. Gibbs relative free energy of the conformations for mAct·β-PhGlc for the structures in Figure S01. The red bar indicates the temperature at which most of the organic compounds decompose, while the blue bar indicates the temperature of decomposition of pyranose. The orange bar indicates where ΔG becomes positive and therefore, the cluster is no longer stable.