Supporting information for:

Phenyl-β-D-glucopyranoside and Phenyl-β-D-galactopyranoside dimers: Small Structural differences but Very Different Interactions

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Figure S1. Calculated structures the phenyl-β-D-glucopyranoside monomers at M06-2X/6-311+ +G(d,p) level arranged in energetically order respect to the global minimum.

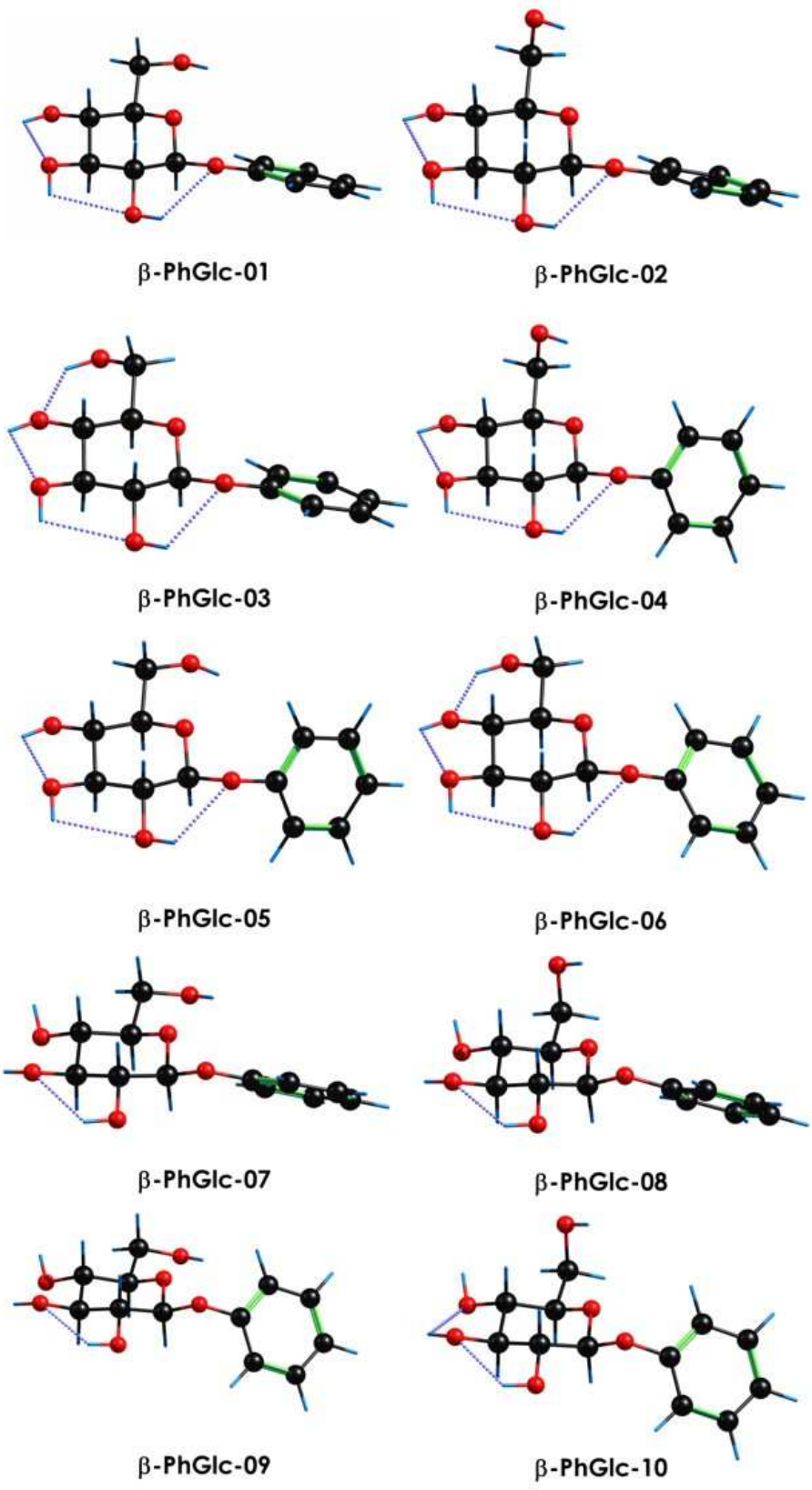


Table S1. Energies, ZPE, BSSE, thermal corrections, relative energies and thermal free energies at 298.15 K (ΔG) calculated at M06-2X/6-311++G(d,p) level for the phenyl-β-D-glucopyranoside monomers.

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

Figure S2. Calculated structures the phenyl-β-D-galactopyranoside monomers at M06-2X/6-311++G(d,p) level arranged in energetically order respect to the global minimum.

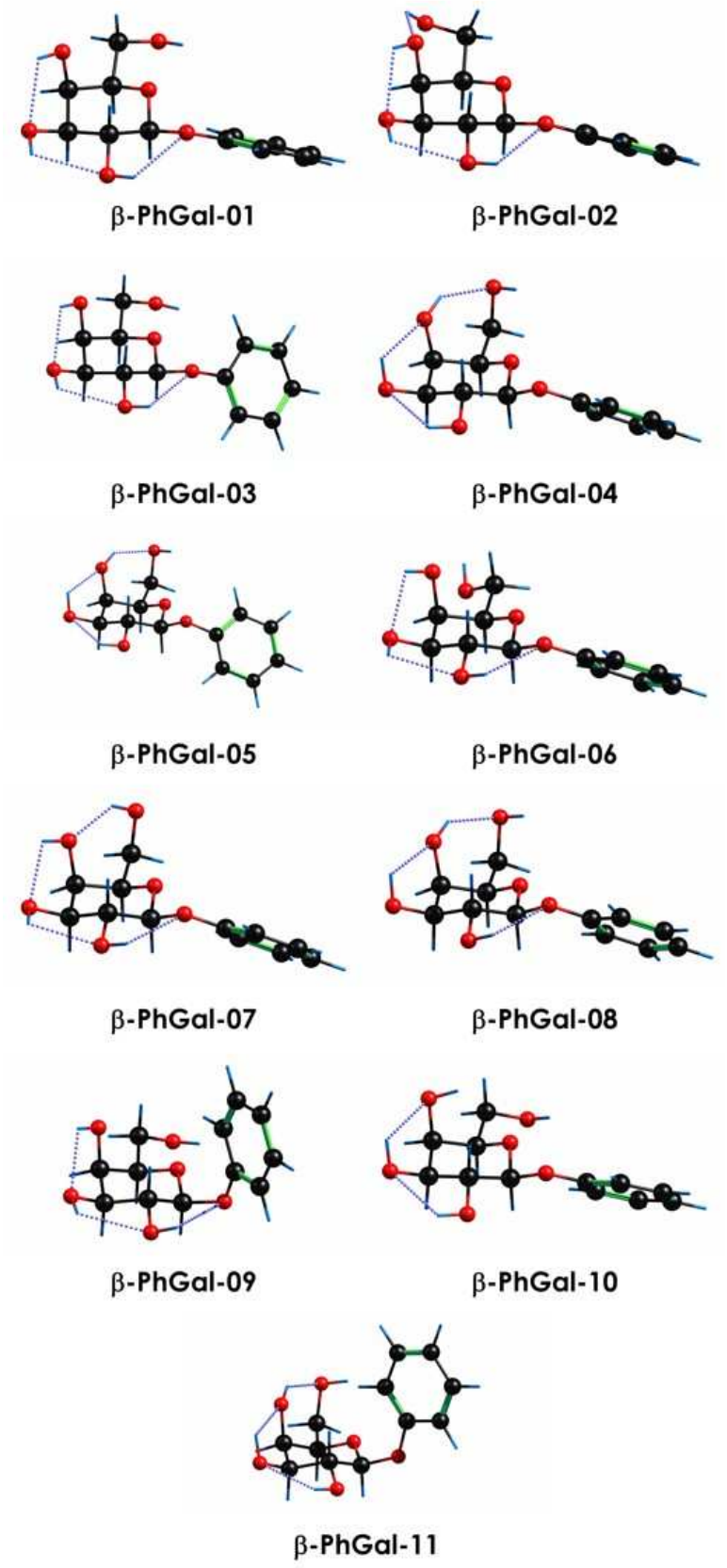


Table S2. Energies, ZPE, BSSE, thermal corrections, relative energies and thermal free energies at 298.15 K (ΔG) calculated at M06-2X/6-311++G(d,p) level for the phenyl-β-D-galactopyranoside monomers.

Structure	Energy (Hartree)	ZPE (Hartree)	Thermal correction (Hartree)	Relative Energy(kJ/mol)	Relative Gibbs Free Energy (kJ/mol)
β-PhGal-01	-918.148574	0.281904	0.237912	0.00	0.00
β-PhGal-02	-918.147357	0.282197	0.238096	3.97	3.68
β-PhGal-03	-918.146394	0.281977	0.237452	5.92	4.52
β-PhGal-04	-918.146919	0.282315	0.238305	5.42	5.38
β-PhGal-05	-918.144938	0.282192	0.236327	10.30	5.39
β-PhGal-06	-918.144912	0.281612	0.237134	8.85	7.57
β-PhGal-07	-918.145898	0.282228	0.238413	7.88	8.34
β-PhGal-08	-918.145377	0.282265	0.238273	9.34	9.34
β-PhGal-09	-918.145212	0.282402	0.238557	10.14	10.52
β-PhGal-10	-918.144730	0.282194	0.238276	10.86	11.05
β-PhGal-11	-918.144227	0.282750	0.239054	13.64	14.41

Figure S3. Calculated structures the phenyl-β-D-glucopyranoside dimers at M06-2X/6-311+ +G(d,p) level arranged in energetically order respect to the global minimum.

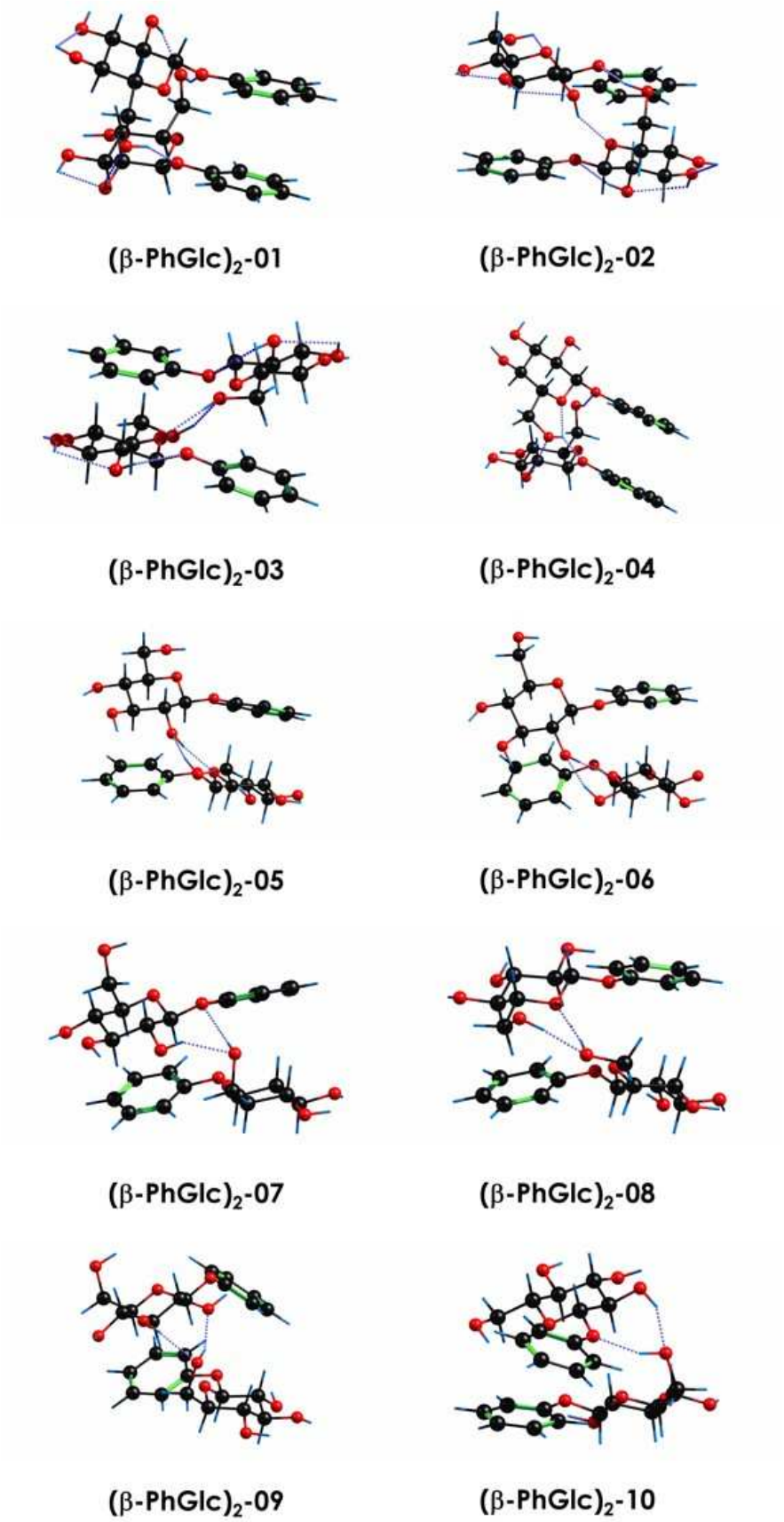
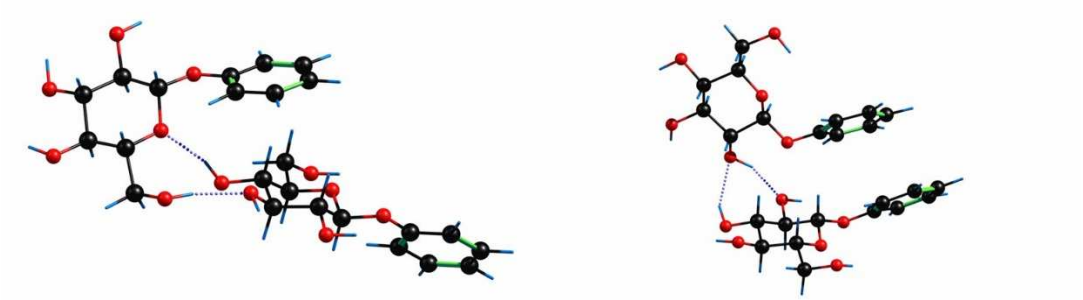


Figure S3. Cont.

$(\beta\text{-PhGlc})_2$-11

$(\beta\text{-PhGlc})_2$-12



$(\beta\text{-PhGlc})_2$-13

$(\beta\text{-PhGlc})_2$-14

Table S3. Energies, ZPE, BSSE, thermal corrections, relative energies and thermal free energies at 298.15 K (ΔG) calculated at M06-2X/6-311++G(d,p) level for the phenyl-β-D-glucopyranoside dimers.

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)$_2$-01	-1836.332575	0.567165	0.006956476772	0.503037	0.00	0.00	272
(β-PhGlc)$_2$-02	-1836.331146	0.566203	0.006490184206	0.502709	0.00	2.89	260
(β-PhGlc)$_2$-03	-1836.329972	0.566612	0.006116207510	0.502269	3.18	4.82	255
(β-PhGlc)$_2$-04	-1836.330135	0.567077	0.006934590446	0.50348	6.12	7.57	250
(β-PhGlc)$_2$-05	-1836.327923	0.565411	0.006235304946	0.500405	5.72	5.30	251
(β-PhGlc)$_2$-06	-1836.326824	0.566154	0.006257571858	0.501707	10.61	11.61	250
(β-PhGlc)$_2$-07	-1836.326379	0.566496	0.006000402052	0.501955	12.00	13.43	250
(β-PhGlc)$_2$-08	-1836.326669	0.566811	0.006197535162	0.503208	12.58	15.96	250
(β-PhGlc)$_2$-09	-1836.32562	0.565840	0.005519274596	0.500802	11.01	12.39	250
(β-PhGlc)$_2$-10	-1836.324568	0.566470	0.006239633524	0.501322	17.32	16.52	244
(β-PhGlc)$_2$-11	-1836.324307	0.566313	0.004744947095	0.499141	13.66	11.48	250
(β-PhGlc)$_2$-12	-1836.322879	0.566677	0.006002146014	0.501038	21.67	20.21	214
(β-PhGlc)$_2$-13	-1836.321023	0.565728	0.004193866938	0.497847	19.30	16.70	250
(β-PhGlc)$_2$-14	-1836.320174	0.564996	0.004788501152	0.497721	21.17	18.60	241

Figure S4. IR spectra of phenyl-β-D-glucopyranoside dimers and the predicted spectra for the structures in Figure S03 calculated at M06-2X/6-311++G(d,p). Correction factors of 0.938 and 0.953 for OH and CH stretching modes respectively were employed to account for the anharmonicity

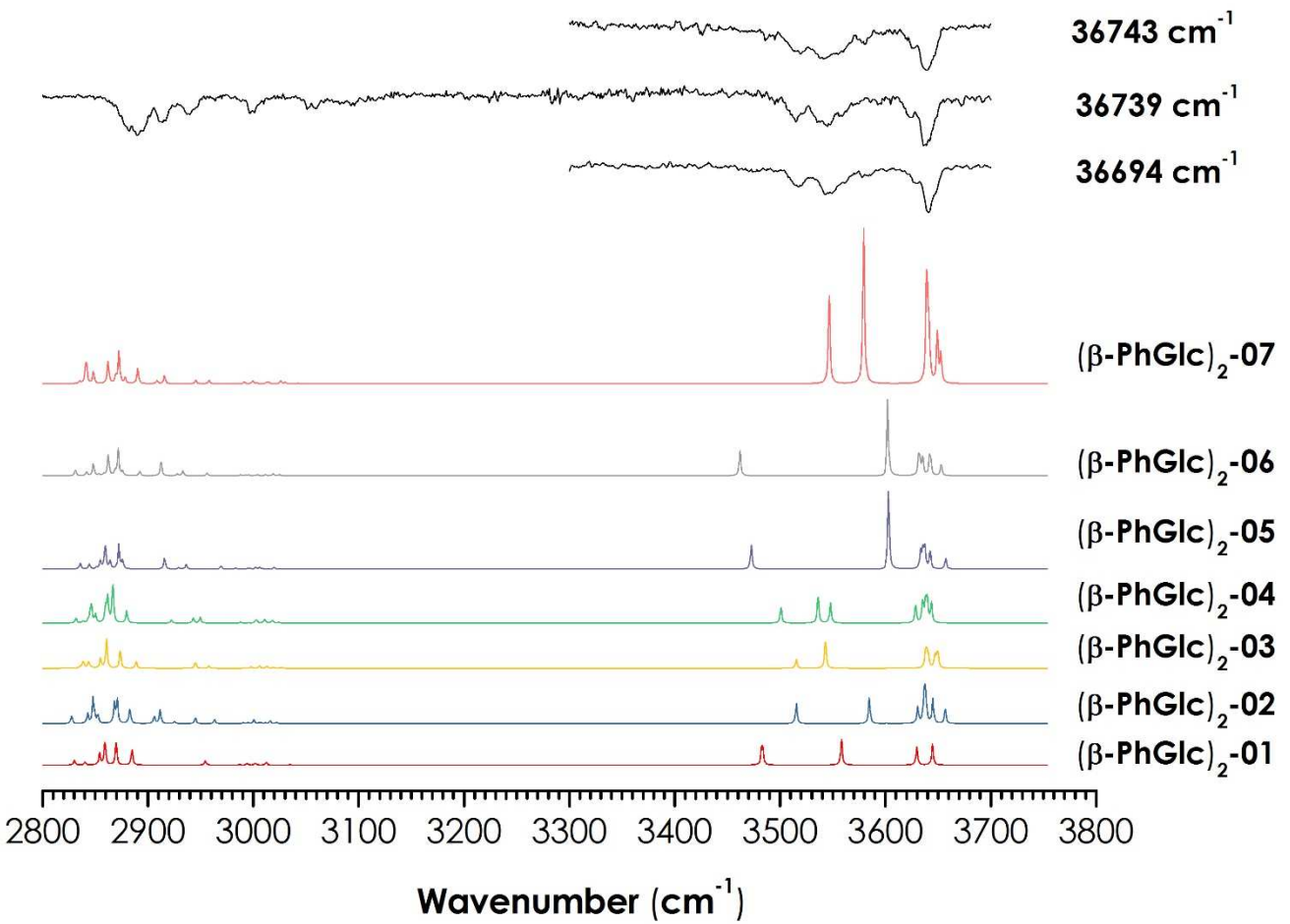


Figure S4. Cont.

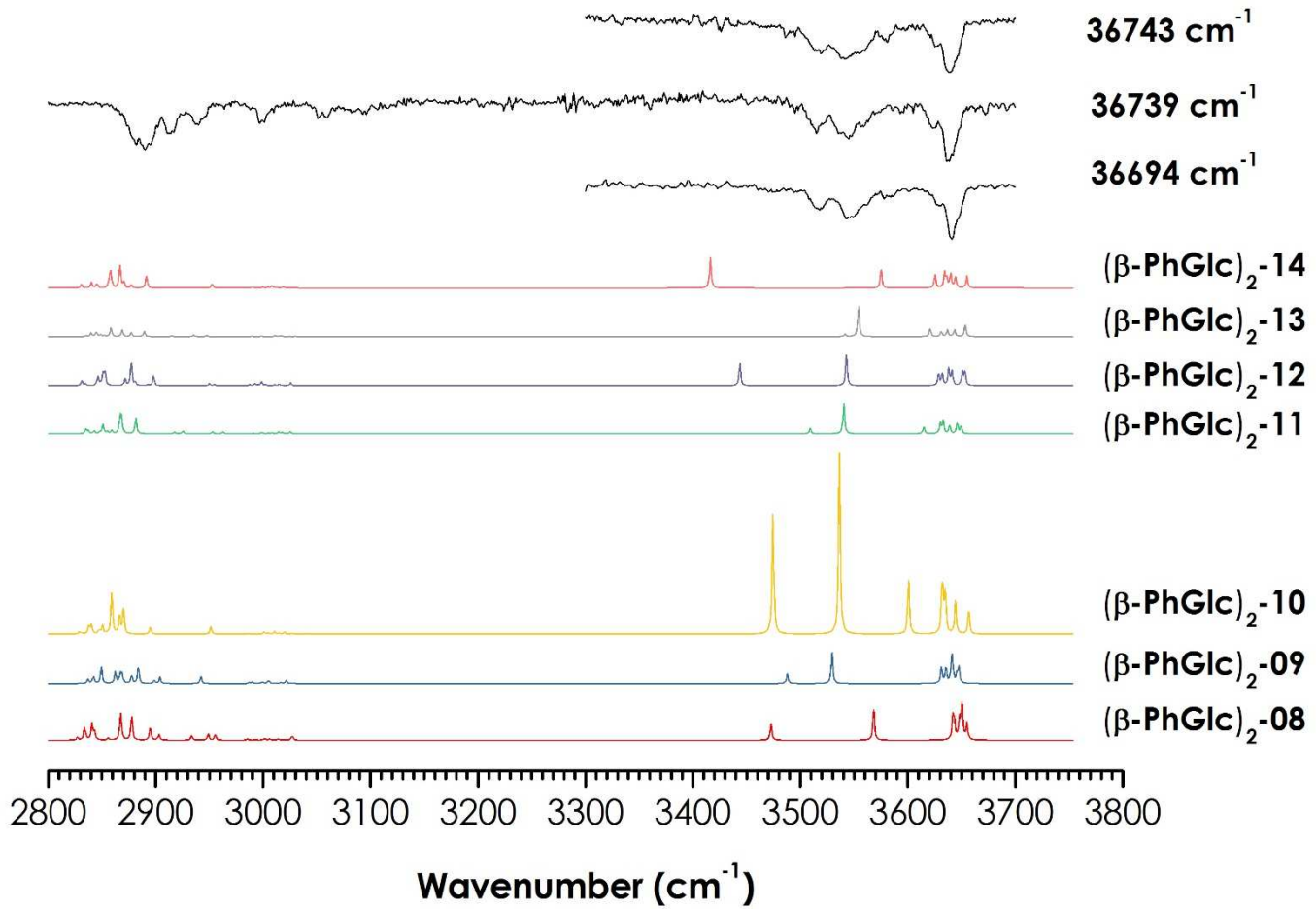


Figure S5. IR spectra of phenyl-β-D-glucopyranoside dimers and the sum of the predicted spectra for the three most relevant structures in Figure S03 calculated at M06-2X/6-311++G(d,p). Their relative abundance was taking into account. A correction factor of 0.938 was employed to account for the anharmonicity.

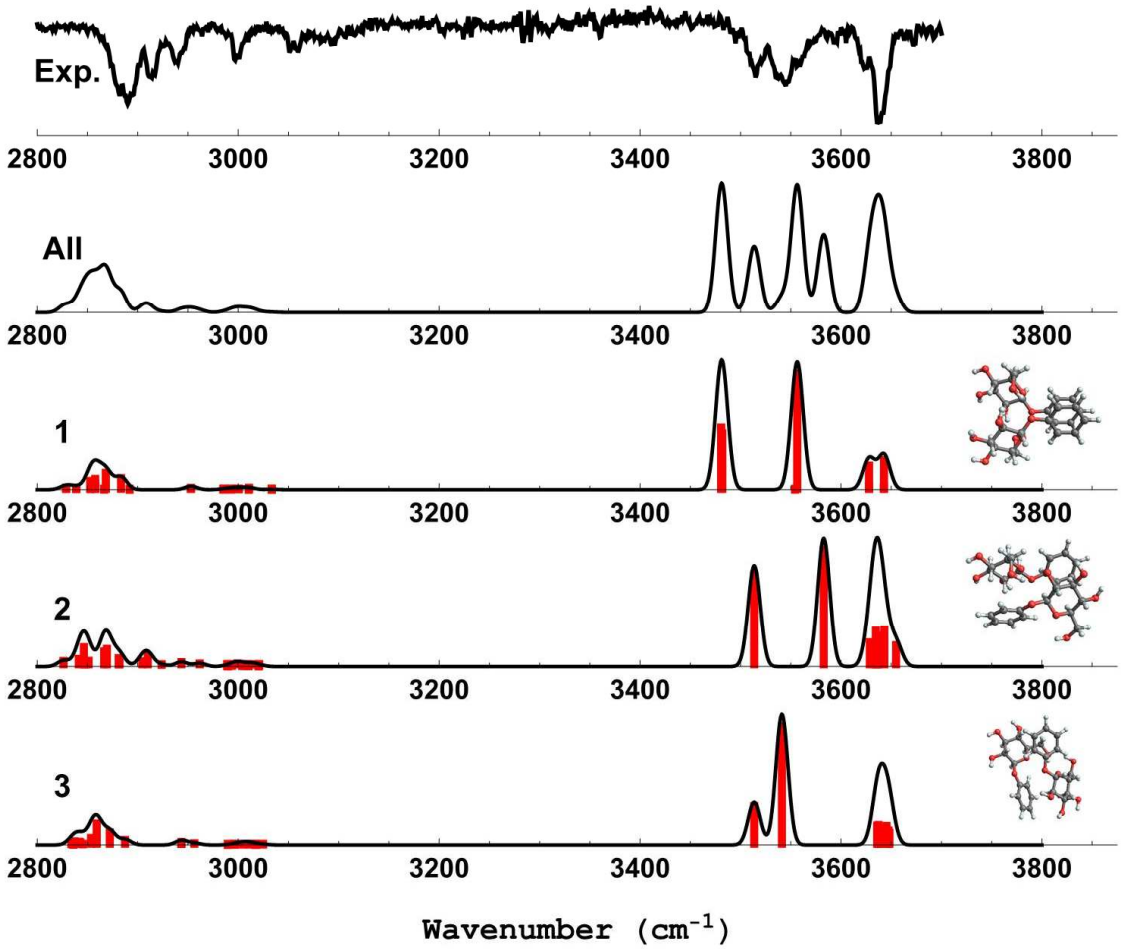


Figure S6. Calculated structures the phenyl-β-D-galactopyranoside dimers at M06-2X/6-311++G(d,p) level arranged in energetically order respect to the global minimum.

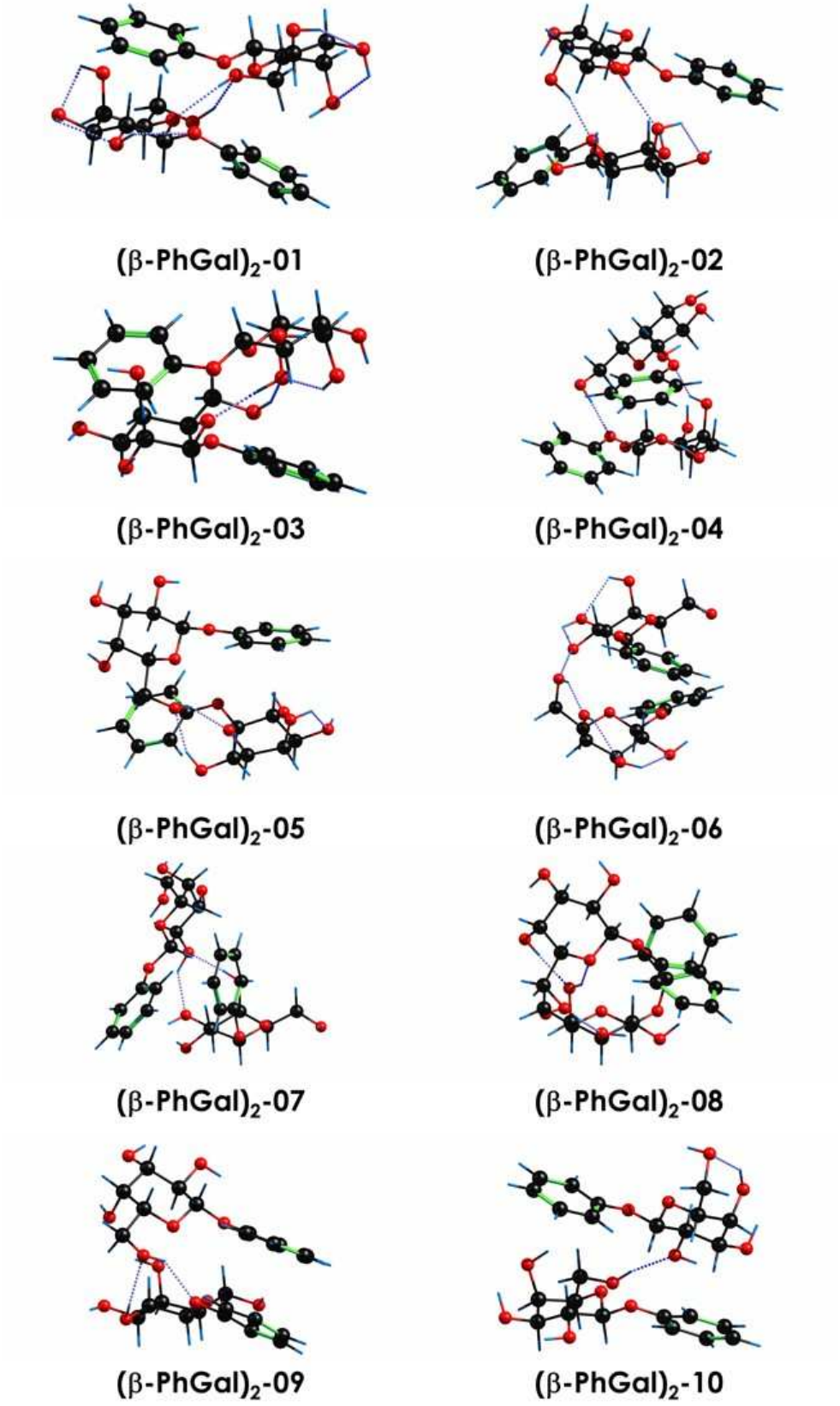


Figure S6. Cont.

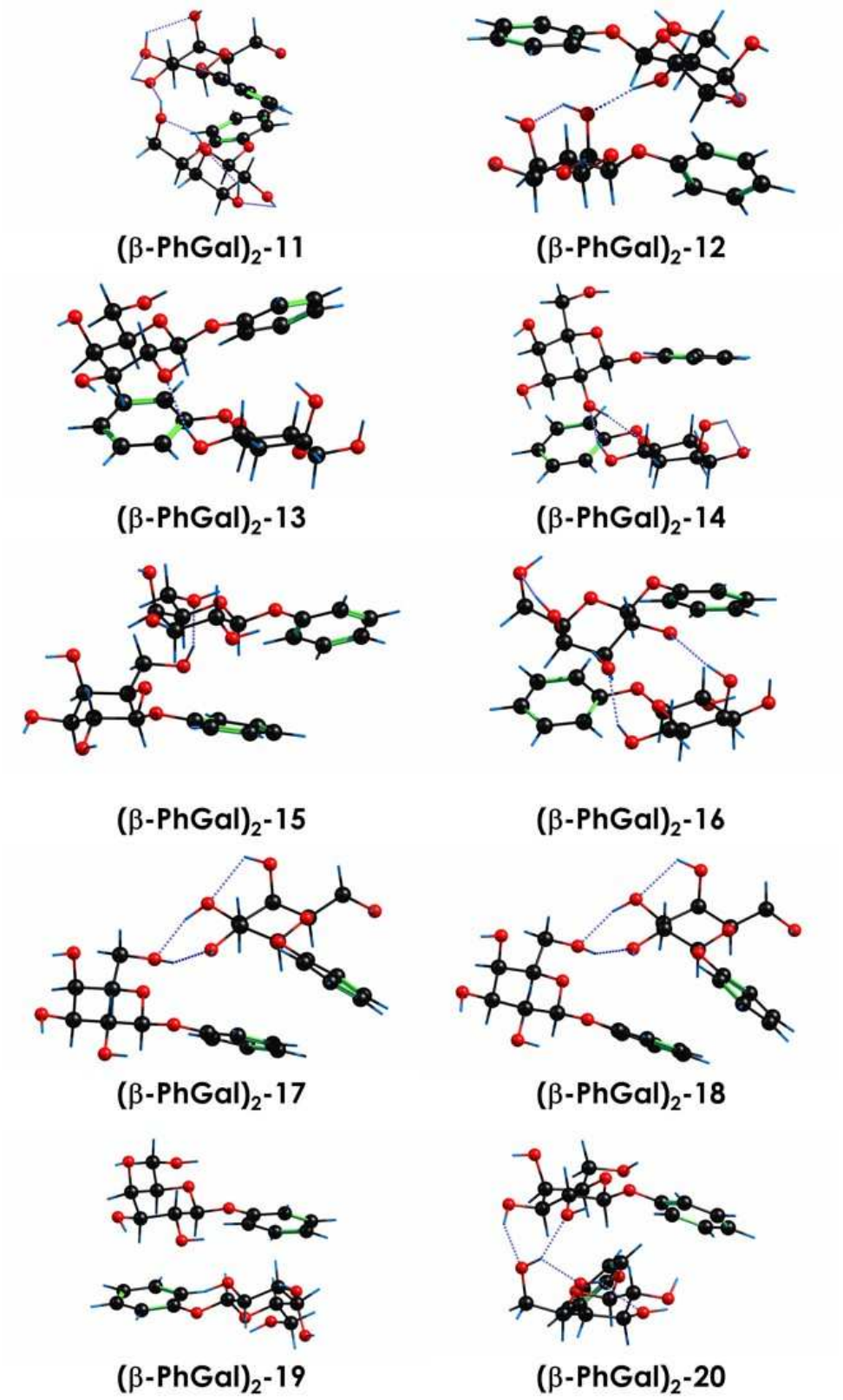


Table S4. Energies, ZPE, BSSE, thermal corrections, relative energies and thermal free energies at 298.15 K (ΔG) calculated at M06-2X/6-311++G(d,p) level for the phenyl-β-D-galactopyranoside dimers.

Structure	Energy (Hartree)	ZPE (Hartree)	Thermal correction (Hartree)	BSSE (Hartree)	Relative Energy (kJ/mol)	Relative Gibbs Free Energy (kJ/mol)	Equilibrium Temperature (K)
(β-PhGal)$_2$-01	-1836.331018	0.566575	0.503001	0.0066005	0.00	0.12	303.1
(β-PhGal)$_2$-02	-1836.330387	0.567512	0.504073	0.0066507	4.25	4.59	299.2
(β-PhGal)$_2$-03	-1836.329399	0.56697	0.503304	0.0065108	5.05	5.17	278.1
(β-PhGal)$_2$-04	-1836.329498	0.567385	0.504725	0.0066528	6.25	8.64	276.9
(β-PhGal)$_2$-05	-1836.328534	0.566711	0.502744	0.0064132	6.39	5.97	273.8
(β-PhGal)$_2$-06	-1836.328361	0.566684	0.500298	0.0063722	6.66	0.00	287.1
(β-PhGal)$_2$-07	-1836.326602	0.566607	0.501992	0.0049400	7.32	9.07	267.0
(β-PhGal)$_2$-08	-1836.328432	0.567489	0.505031	0.0060931	7.86	12.24	260.6
(β-PhGal)$_2$-09	-1836.329328	0.567493	0.505015	0.0070840	8.12	9.85	261.9
(β-PhGal)$_2$-10	-1836.327267	0.567051	0.503222	0.0058742	9.19	10.55	277.0
(β-PhGal)$_2$-11	-1836.326824	0.566324	0.502089	0.0062717	9.49	8.74	250.9
(β-PhGal)$_2$-12	-1836.326534	0.566338	0.501547	0.0060673	9.75	8.08	259.0
(β-PhGal)$_2$-13	-1836.326589	0.5666	0.502319	0.0060269	10.19	9.96	267.3
(β-PhGal)$_2$-14	-1836.326775	0.566645	0.50262	0.0063389	10.64	10.26	265.7
(β-PhGal)$_2$-15	-1836.324837	0.566121	0.499262	0.0050091	10.86	6.53	253.8

(β-PhGal)$_2$-16	-1836.327532	0.567185	0.504342	0.0067614	11.18	12.79	257.8
(β-PhGal)$_2$-17	-1836.323947	0.566529	0.500362	0.0039771	11.56	11.76	259.1
(β-PhGal)$_2$-18	-1836.323947	0.566531	0.500367	0.0039758	11.56	11.77	267.6
(β-PhGal)$_2$-19	-1836.324579	0.566031	0.50039	0.0052305	11.88	10.17	263.1
(β-PhGal)$_2$-20	-1836.326160	0.567074	0.502091	0.0058207	12.02	10.49	264.6
(β-PhGal)$_2$-21	-1836.325180	0.566785	0.501182	0.0052756	12.40	10.67	274.4
(β-PhGal)$_2$-22	-1836.324068	0.565984	0.499846	0.0051336	12.84	10.08	274.3
(β-PhGal)$_2$-23	-1836.324789	0.566426	0.501661	0.0054270	12.88	12.96	251.9
(β-PhGal)$_2$-24	-1836.325910	0.567461	0.502933	0.0057186	13.42	13.35	244.6
(β-PhGal)$_2$-25	-1836.323826	0.566328	0.49982	0.0048282	13.58	10.65	240.5
(β-PhGal)$_2$-26	-1836.324151	0.566707	0.500171	0.0050370	14.27	10.72	264.1
(β-PhGal)$_2$-27	-1836.324909	0.566356	0.502112	0.0061650	14.32	13.83	251.0
(β-PhGal)$_2$-28	-1836.325113	0.5666	0.502412	0.0061635	14.42	14.08	246.3
(β-PhGal)$_2$-29	-1836.324218	0.566501	0.502009	0.0056949	15.28	15.37	237.0
(β-PhGal)$_2$-30	-1836.324207	0.566569	0.500997	0.0058390	15.87	12.74	234.4
(β-PhGal)$_2$-31	-1836.323866	0.566397	0.501189	0.0056974	15.94	14.14	238.6
(β-PhGal)$_2$-32	-1836.324101	0.5662	0.501232	0.0061847	16.08	13.64	239.1
(β-PhGal)$_2$-33	-1836.324049	0.566512	0.501257	0.0059132	16.33	13.84	230.5
(β-PhGal)$_2$-34	-1836.324004	0.566135	0.501144	0.0063823	16.69	13.66	238.2
(β-PhGal)$_2$-35	-1836.322335	0.565827	0.501336	0.0058889	18.97	18.55	240.4
(β-PhGal)$_2$-36	-1836.321611	0.566177	0.500606	0.0048239	18.99	18.53	244.1

(β-PhGal)$_2$-37	-1836.322282	0.566951	0.499959	0.0047466	19.06	15.07	236.3
(β-PhGal)$_2$-38	-1836.320661	0.566151	0.497521	0.0039701	19.17	12.93	247.7
(β-PhGal)$_2$-39	-1836.322704	0.566211	0.501083	0.0060023	19.30	16.91	218.5
(β-PhGal)$_2$-40	-1836.320658	0.56603	0.498585	0.0041389	19.31	15.73	223.3
(β-PhGal)$_2$-41	-1836.323136	0.566508	0.502803	0.0061713	19.39	20.30	226.6
(β-PhGal)$_2$-42	-1836.322413	0.565701	0.500718	0.0064652	19.94	16.72	229.0
(β-PhGal)$_2$-43	-1836.321578	0.566584	0.501219	0.0047879	20.05	20.23	217.8
(β-PhGal)$_2$-44	-1836.322125	0.566878	0.501322	0.0050584	20.10	19.06	223.6
(β-PhGal)$_2$-45	-1836.322903	0.566625	0.503502	0.0061946	20.37	22.74	209.6
(β-PhGal)$_2$-46	-1836.320819	0.566975	0.500749	0.0042210	21.58	20.99	207.8
(β-PhGal)$_2$-47	-1836.319481	0.566274	0.499485	0.0037355	21.98	21.18	221.4
(β-PhGal)$_2$-48	-1836.320741	0.566378	0.499323	0.0049743	22.20	17.45	210.0
(β-PhGal)$_2$-49	-1836.321918	0.566667	0.499192	0.0059923	22.54	14.01	213.7
(β-PhGal)$_2$-50	-1836.321472	0.566269	0.502172	0.0059645	22.59	23.01	221.9
(β-PhGal)$_2$-51	-1836.321367	0.566235	0.500959	0.0059054	22.62	20.10	225.7
(β-PhGal)$_2$-52	-1836.321925	0.567111	0.503332	0.0056423	22.77	24.86	221.4
(β-PhGal)$_2$-53	-1836.321782	0.566804	0.502007	0.0058874	22.98	21.76	202.9
(β-PhGal)$_2$-54	-1836.319504	0.566631	0.499599	0.0038863	23.25	21.42	198.1
(β-PhGal)$_2$-55	-1836.319061	0.566367	0.499862	0.0038273	23.57	23.27	200.6
(β-PhGal)$_2$-56	-1836.320962	0.56608	0.501199	0.0060724	23.72	21.79	207.2
(β-PhGal)$_2$-57	-1836.320279	0.566645	0.50068	0.0049219	23.97	22.22	208.3

(β-PhGal)$_2$-58	-1836.319672	0.566038	0.499386	0.0049316	24.00	20.42	201.1
(β-PhGal)$_2$-59	-1836.320059	0.565869	0.50042	0.0055637	24.20	22.12	212.0
(β-PhGal)$_2$-60	-1836.319518	0.566778	0.500431	0.0041543	24.30	23.57	197.8
(β-PhGal)$_2$-61	-1836.322042	0.566716	0.503495	0.0069491	24.85	24.98	214.3
(β-PhGal)$_2$-62	-1836.320340	0.565916	0.501176	0.0061073	25.01	23.36	190.4
(β-PhGal)$_2$-63	-1836.320122	0.566606	0.501489	0.0052186	25.06	24.76	208.7
(β-PhGal)$_2$-64	-1836.320122	0.566608	0.501486	0.0052190	25.07	24.75	201.8
(β-PhGal)$_2$-65	-1836.317960	0.5659	0.498579	0.0038783	25.36	22.79	194.3
(β-PhGal)$_2$-66	-1836.319454	0.566064	0.498848	0.0053346	25.70	19.58	194.3
(β-PhGal)$_2$-67	-1836.317972	0.565644	0.498503	0.0043045	25.78	22.56	195.0
(β-PhGal)$_2$-68	-1836.318095	0.566694	0.500212	0.0041912	27.92	26.73	182.7
(β-PhGal)$_2$-69	-1836.318472	0.566609	0.500434	0.0047781	28.24	26.32	187.5
(β-PhGal)$_2$-70	-1836.316379	0.56588	0.497418	0.0037561	29.14	23.90	191.5
(β-PhGal)$_2$-71	-1836.318503	0.566863	0.50184	0.0050384	29.51	29.93	178.7
(β-PhGal)$_2$-72	-1836.317572	0.566762	0.500166	0.0045512	30.41	27.98	172.3

Figure S7. IR spectra of phenyl-β-D-galactopyranoside dimers and the predicted spectra for the structures in Figure S06 calculated at M06-2X/6-311+ +G(d,p). Correction factors of 0.938 and 0.953 for OH and CH stretching modes respectively were employed to account for the anharmonicity.

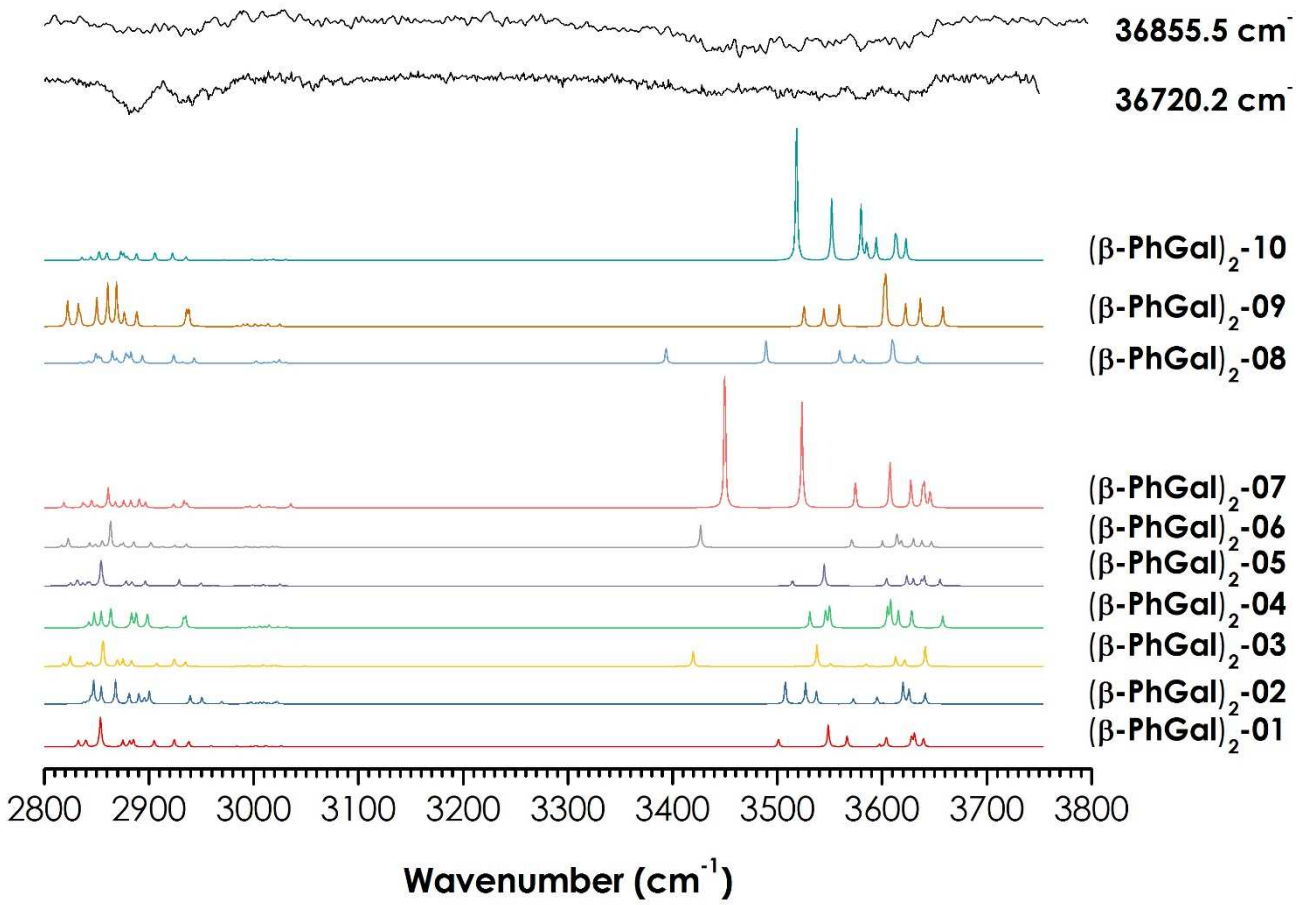


Figure S7. Cont.

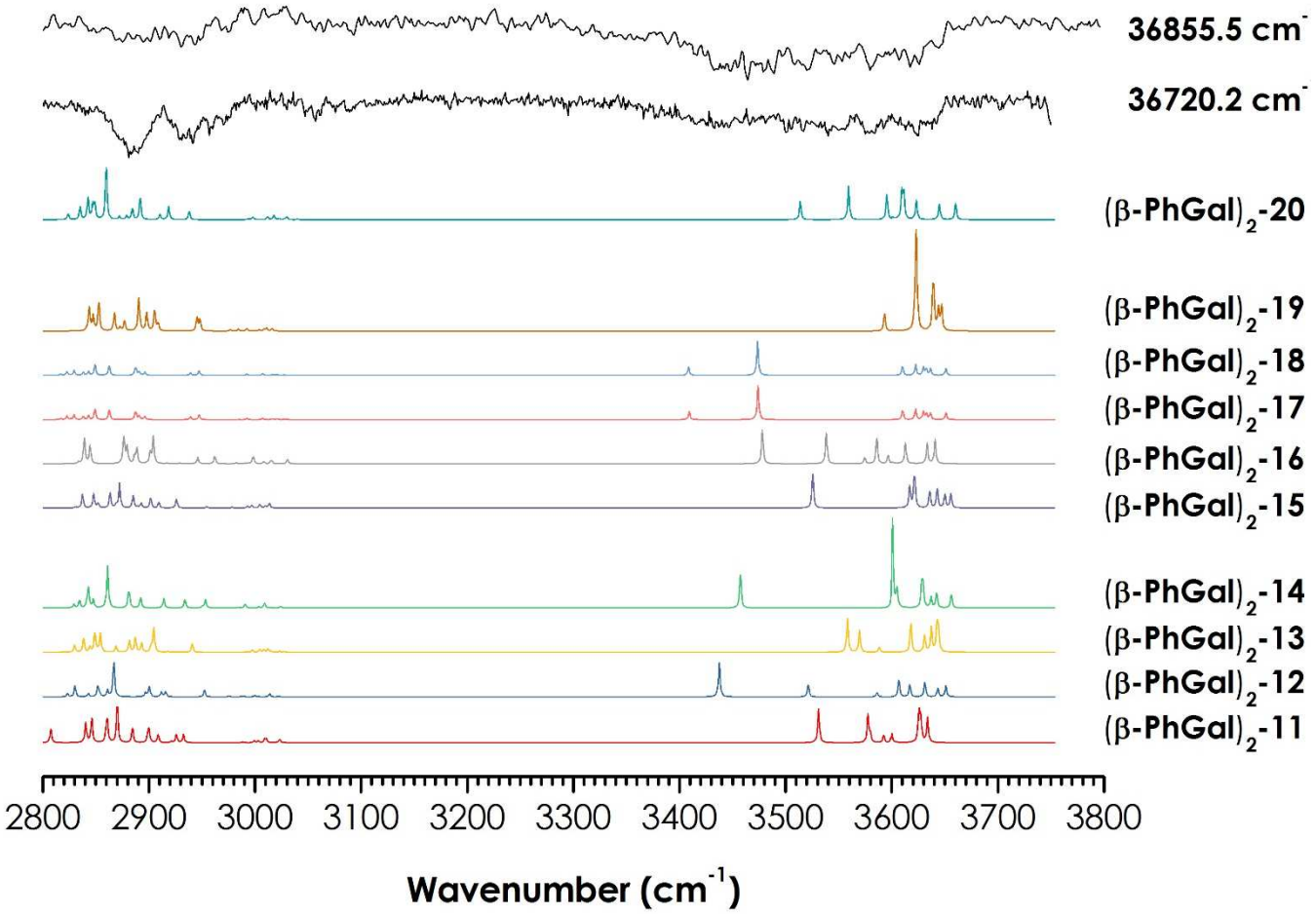


Figure S8. IR spectra of phenyl-β-D-galactopyranoside dimers and the sum of the predicted spectra for the three most relevant structures in Figure S06 calculated at M06-2X/6-311++G(d,p). Their relative abundance was taking into account. A correction factor of 0.938 was employed to account for the anharmonicity.

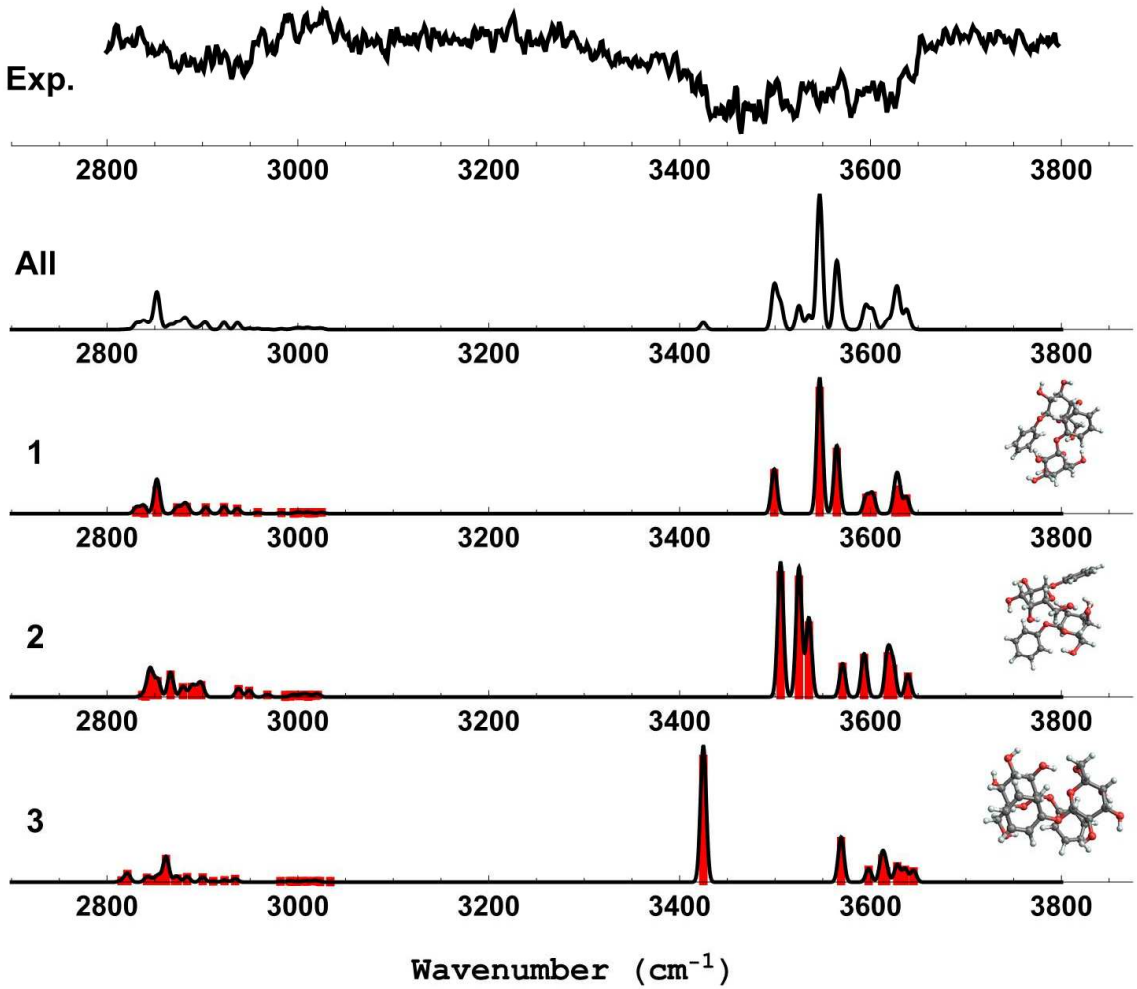


Figure S9. Despite the absence of discrete features, it is possible to extract the vibrational information of different conformers system by tuning the laser to different wavelengths and recording the IR spectra. The IR spectra of phenyl-β-D-glucopyranoside dimers is shown below.

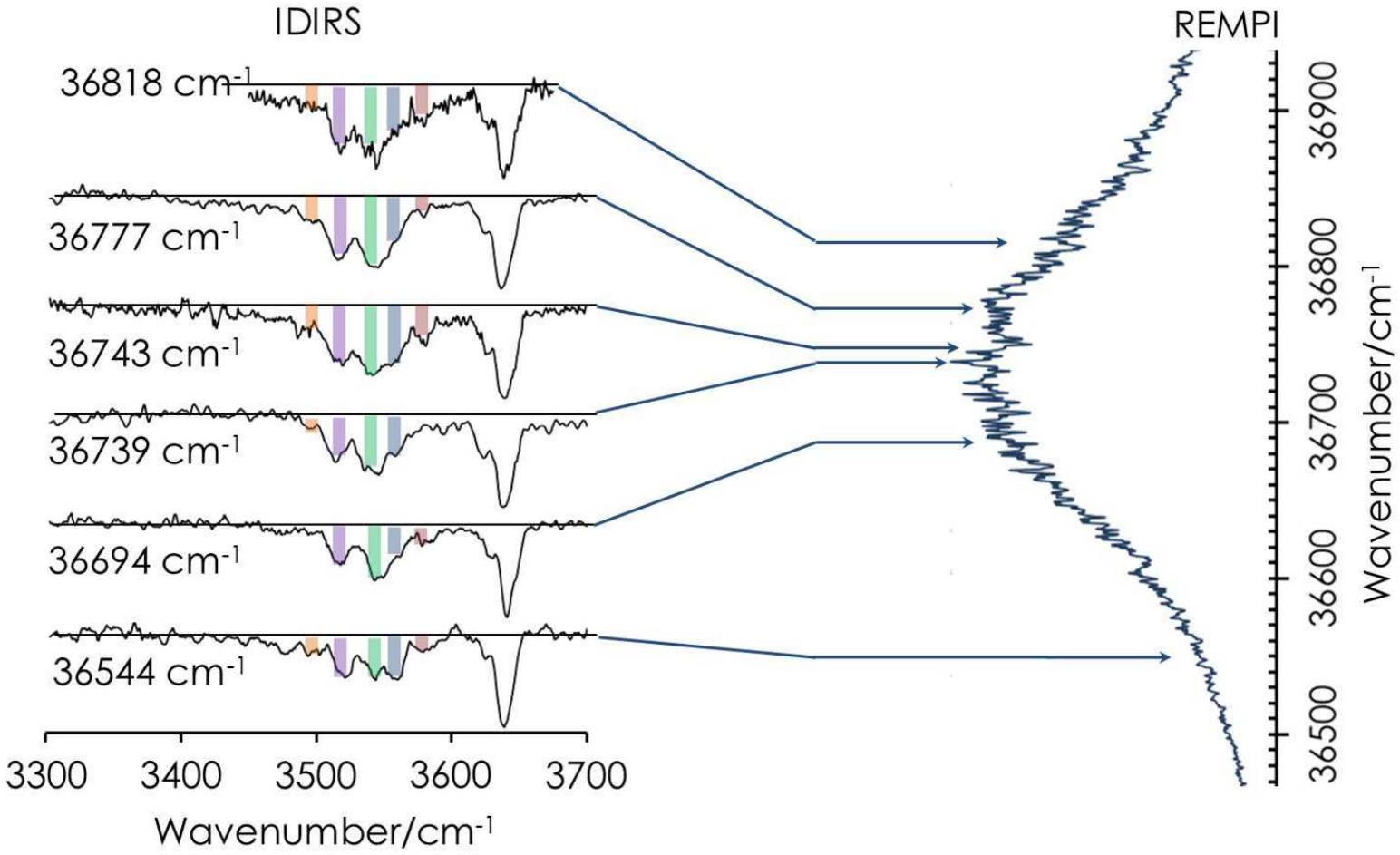


Figure S10. Possible relaxation pathways of phenyl-β-D-glucopyranoside dimers: isomers 04, 05 and 07 are structurally related to the more stable isomers 01 and 02 and are very likely to relax into the more stable structures.