Supporting Information for

Thermochemistry and Kinetics of the Formation of Lignin-Carbohydrate Complex (LCC) Linkages in Lignocellulosic Biomass

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Computational Details for Conformational Screening

The conformational sampling of the model LCC linkages was performed using Car-Parinello molecular dynamics [1] and metadynamics (CPMD-metadynamics). All CPMD and metadynamics calculations in this work were performed with the CPMD software, version 4.3.0 [2] along with the plane-wave-pseudoptential implementation of the Kohn-Sham density functional theory (DFT) [3]. A Martins-Trouiller (MT) pseudopotential [4] using the revised Perdew-Burke-Ernzerhof (revPBE) functional [5, 6] of the generalized gradient approximation (GGA) was used for the exchange and correlation energies for all CPMD calculations, as the revPBE functional has been used for accurate modeling of carbohydrate chemistry [7]. The implemented planewave energy cut-off for energy calculations using the MT pseudopotential, as determined by examining the convergence of the energy, was 70 Ryd. A single k-point (Γ-point) was used for the integration over the Brillouin zone in the reciprocal space. All CPMD calculations were performed at a temperature of 298K and the temperature control was completed using the Nosé-Hoover thermostat [8, 9]. The frequency for the ionic thermostat was selected to be some characteristic frequency of the ionic system to ensure equilibration and the exact value was unnecessary; therefore, it was selected to be 3000 cm^{-1} for all systems, as this is the approximate frequency for the C-H and O-H bond vibrational frequencies. To avoid coupling between the ionic and electronic thermostats the electronic frequency was selected to be 10000 $cm^{-1}$for all systems. The fictitious electron mass was taken as 300 a.u. for all systems. Short molecular dynamics runs were performed without a thermostat to obtain an approximate value around which the fictitious electronic kinetic energy oscillated. As a result, it was selected to be between 0.004 a.u. and 0.005 a.u. for each system for all subsequent calculations. A timestep of 4 a.u. (~0.0968 fs) was chosen for all calculations. Energies, including the fictitious electronic kinetic energy, were monitored to verify the systems did not deviate from the Born-Oppenheimer surface during the molecular dynamics calculations. Trajectories were visualized using the Visual Molecular Dynamics (VMD) software [10].

To accelerate the sampling of the CPMD calculations as well as access conformations with significant energy barriers, the metadynamics technique [11, 12] was used. A detailed description of this technique is provided by Laio and Gervasio [13]. In the present work, two torsion angles were selected as the collective variables. Torsion angle 1 (first collective variable) was chosen to rotate the position of the phenyl ring, whereas torsion angle 2 (second collective variable) rotated the hemicellulose moiety. This ensured the system sampled all major conformation changes, i.e.,, the relative position of the simplified monolignol to the hemicellulose component was varied. Minor conformational changes such as methyl group orientation and hydrogen bonding direction were accounted for in the dynamics (provided kinetic energy) of the system and adequately sampled without any biasing in the system. The torsion angles selected as collective variables are depicted in Figure S.1.

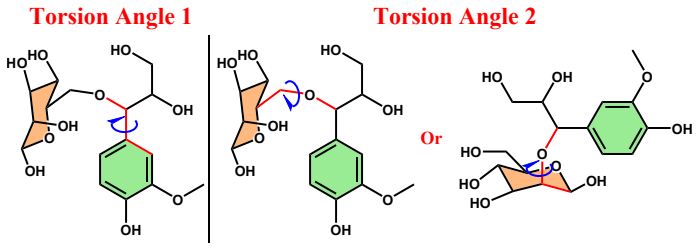

Figure S.1: A schematic of the collective variables (CVs) used in the CPMD-metadynamics calculations. Note, depending on the connection of the sugar molecule, torsion angle 2 was varied.

The parameters for the metadynamics calculations were chosen following the guidelines as previously outlined [14, 15]. Each fictitious particle, $\tilde{s}$, is connected to its actual collective variable, $S(x)$, and the extent of coupling between the two is described by a spring with a specified force constant, k_{cv}. This force constant was chosen in such a way that the typical value of the difference between the fictitious particle and collective variable $\left(\tilde{s} - S(x)\right)$ was smaller than the length on which the free energy varies at the system temperature, T, leading to the condition [13].

$$\langle(\tilde{s} - S(x))^2\rangle \sim \frac{T}{k_{cv}}\left(\langle\tilde{s}^2\rangle - \langle\tilde{s}\rangle^2\right)$$

Where averages were taken at a temperature, T, during a sample metadynamics run without addition of potentials. The fictitious mass, m_{cv}, was selected to ensure the dynamics of the collective variable were slower and thus separable from the nuclear dynamics. It has been shown that the extra terms in the metadynamics extension of the CPMD Lagrangian introduces an additional frequency term proportional to $\sqrt{k_{cv}/m_{cv}}$ [14]. Once the force constant was selected the value of fictitious mass was chosen such that during a sample metadynamics runs of ~200 fs without the addition of potentials, the difference between the fictitious particle and collective variables $\left(\tilde{s} - S(x)\right)$, became minimal [15].

The Gaussian width parameter was chosen as one half the range of fluctuation of the collective variable with the smallest amplitude of oscillation during the sample metadynamics run with no potentials. The height of the potential was kept fixed at ~0.63 kcal/mol. The metadynamics timestep at which Gaussian potential added followed similarly to the procedure outlined by Mushrif et al. [15]. Occasionally collective variables struggled to sample the torsional space and visualizing the trajectory indicated this was typically a result of significant hydrogen bonding occurring between the hemicellulose moiety and simplified monolignol and/or steric interference between the two. In these cases, a scaling factor of 1.2 was implemented for any collective variable that was struggling to sample. Admittedly, the choice of Gaussian potential parameters resulted in a more "hard-driven" simulation; however, since the objective was to screen conformers, rather than identify the global minimum this was deemed an acceptable procedure for the studies objectives.

All metadynamic simulations were performed for a minimum of 1,000,000 CPMD steps and 5000 metadynamic steps. The criteria for rigorously evaluating the convergence of a metadynamic simulation is whether the system begins to rapidly oscillate along the collective variables indicating the free energy surface is filled. However, this was computationally demanding and unnecessary for the present objectives. Therefore, the criteria selected to assess such convergence was the degree each torsional space was sampled. Convergence of the metadynamic simulations were deemed complete if at least one of the torsion angles sampled completely (0-360°) and the other sampled over 90% of the torsional space. The validity of this criteria was reinforced when inspecting the free energy landscape. The free energy surfaces constructed showed all significant minimum wells had dimensions greater than any unsampled region in the simulations, providing confidence no significant conformations were excluded. All structures corresponding to an identifiable minimum were subsequently optimized in all-electron DFT calculations.

The starting set of conformers identified with CPMD+metadynamics were optimized at a M06-2X/6-31G level of theory. All structures within 21 kJ/mol of the lowest energy structure were subsequently optimized at a M06-2X/6-31+G(d) level of theory, this ensured a wide sampling of conformers, and no low energy conformer was excluded from moving forward in the screening process. The top five lowest energy structures

were taken for optimization at a M06-2X/6-311+G(d) level of theory, then the lowest energy structure was further optimized at a M06-2X/6-311++G(d,p) level of theory. As the level of theory increased, no dramatic change in the relative trend of conformers was observed.

Due to a reduced computational cost for the reactant compounds, the initial conformational screening was performed directly using DFT calculations at a M06-2X/6-31G level of theory. All structures within 5 kcal/mol of the lowest energy structure identified in literature for glucose [16], mannose [17] and galactose [18] were taken for optimization. On account of the significantly less degrees of freedom associated with arabinose and xylose, conformation sampling of these compounds was done manually where multiple conformers were generated to maximize hydrogen bonding interactions and subsequently optimized. The conformational space of glucuronic acid was sampled by scanning over two torsion angles, depicted in Figure S.2. Torsion angle 1 was rotated at 30° intervals, whereas torsion angle 2 was rotated at 45° intervals, to generate all possible structures within the 360° periodicity of each torsion angle. Note, two scanning calculations were completed where the hydrogen bonding around the 6-member ring was oriented clockwise as well as counterclockwise. In both scanning calculations a crude free energy surface was developed where all observable minimums were selected for further optimization at the M06-2X/6-31G level of theory where no constraints were imposed. Criteria for subsequent optimization of all reactant compounds follows similarly to the LCC moieties.

Conformation sampling of the quinone methide (QM) intermediate was performed manually.

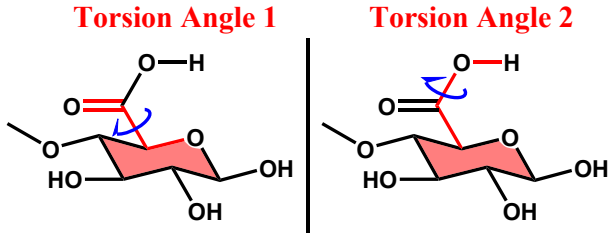

Figure S.2: The schematic of the torsion angles systematically rotated to generate an approximate free energy landscape of glucuronic acid.

Thermochemical Data

Table S.1: The reaction energies from total electronic energies at a M06-2X/6-311++G(d,p) level of theory for nucleophilic addition to the QM intermediate, where the carbon number indicates the location of the nucleophile.

Reaction Energies from Total Electronic Energies (kJ/mol)							
M06-2X/6-311++G(d,p) Gas Phase [Implicit Solvent]							
	Mannose	Glucose	Galactose	Arabinose	Xylose	Glucuronic Acid	Water
Carbon 2	-158.5 [-134.7]	-151.8 [-124.4]	-157.2 [-125.9]	-132.1 [-105.7]	-150.1 [-124.6]	-	-
Carbon 3	-154.2 [-135.6]	-153.9 [-129.5]	-157.3 [-127.5]	-141.8 [-118.7]	-165.1 [-132.7]	-	-
Carbon 4	-	-	-151.4 [-127.0]	-	-	-	-
Carbon 5	-	-	-	-148.9 [-128.4]	-	-	-
Carbon 6	-164.2 [-132.1]	-152.7 [-120.2]	-166.4 [-132.5]	-	-	-146.8 [-120.1]	-
N/A	-	-	-	-	-	-	-143.3 [-109.9]

Table S.2: The reaction energies from zero-point corrected electronic energies at a M06-2X/6-311++G(d,p) level of theory for nucleophilic addition to the QM intermediate, where the carbon number indicates the location of the nucleophile.

Reaction Energies from Zero-Point Corrected Electronic Energies (kJ/mol)							
M06-2X/6-311++G(d,p) Gas Phase [Implicit Solvent]							
	Mannose	Glucose	Galactose	Arabinose	Xylose	Glucuronic Acid	Water
Carbon 2	-144.7 [-121.6]	-138.8 [-110.0]	-143.2 [-112.3]	-121.6 [-97.2]	-135.2 [-111.2]	-	-
Carbon 3	-141.2 [-121.3]	-140.4 [-116.5]	-142.8 [-112.4]	-131.2 [-109.0]	-150.5 [-119.2]	-	-
Carbon 4	-	-	-138.5 [-112.8]	-	-	-	-
Carbon 5	-	-	-	-138.0 [-117.2]	-	-	-
Carbon 6	-150.2 [-118.8]	-140.2 [-108.7]	-150.9 [-119.8]	-	-	-133.9 [-107.5]	-
N/A	-	-	-	-	-	-	-120.0 [-88.9]

Coordinates of Model Compounds (Nucleophiles and QM Intermediate)

Table S.3: Coordinates of the lowest energy conformations of arabinose and xylose at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

Arabinose				Xylose			
C	-0.207645	-0.678631	0.904045	C	-0.743555	0.743511	0.204113
C	0.499215	-0.905651	-0.456361	C	0.711157	0.768382	-0.222438
C	-0.73211	0.762735	0.785465	C	-1.407448	-0.52868	-0.292407
C	-1.004498	0.835273	-0.715936	C	1.394417	-0.502968	0.260612
C	2.017097	-0.864321	-0.410063	C	-0.602188	-1.733679	0.180317
O	0.082596	0.173392	-1.31365	O	0.74301	-1.637125	-0.261254
O	-1.232514	-1.617354	1.136833	O	-1.468794	1.837616	-0.318377
O	0.208428	1.727094	1.179477	O	1.294671	1.924153	0.341615
O	-2.20786	0.134343	-0.94913	O	-2.715014	-0.654062	0.217131
O	2.478901	0.414022	0.003277	O	2.699497	-0.472393	-0.214191
H	1.097689	1.390025	0.999701	H	2.218022	1.956171	0.071778
H	0.489181	-0.763065	1.739858	H	-0.787227	0.75419	1.303832
H	0.165378	-1.862563	-0.869608	H	0.776223	0.786448	-1.318244
H	-1.642092	0.904501	1.368017	H	-1.416155	-0.50795	-1.390541
H	-1.037072	1.849523	-1.116919	H	1.372032	-0.544502	1.362918
H	2.424155	-1.113119	-1.394929	H	-0.650558	-1.792256	1.27656
H	2.390019	-1.591891	0.312295	H	-1.009439	-2.65339	-0.235751
H	-1.934046	-1.447221	0.496542	H	-1.015569	2.645813	-0.056734
H	2.325394	1.015186	-0.733486	H	-3.174632	0.171938	0.03262
H	-2.347365	0.070225	-1.898831	H	3.146056	-1.281371	0.052979

Table S.4: Coordinates of the lowest energy conformations of mannose, glucose, galactose at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

Mannose				Glucose				Galactose			
C	0.656459	0.778621	0.196235	C	0.693775	1.026377	0.051684	C	-0.253831	-1.374558	-0.223355
C	-0.594132	1.266725	-0.524112	C	-0.800298	1.185461	-0.163567	C	1.165619	-0.922284	-0.553122
C	0.991279	-0.645322	-0.237491	C	1.185505	-0.25529	-0.61854	C	-1.231855	-0.228059	-0.471195
C	-1.743385	0.295477	-0.285758	C	-1.529977	-0.056645	0.305411	C	1.484463	0.374108	0.167969
C	-1.289788	-1.13502	-0.576465	C	-0.952744	-1.2681	-0.409626	C	0.441973	1.418135	-0.194746
C	2.228306	-1.199398	0.458724	C	2.635564	-0.562669	-0.286733	C	-2.632969	-0.532916	0.025345
O	-0.108396	-1.478126	0.105972	O	0.42986	-1.372931	-0.152897	O	-0.832168	0.966988	0.197452
O	1.759327	1.616246	-0.099808	O	1.401893	2.101038	-0.526426	O	-0.345242	-1.779972	1.123705
O	-0.923171	2.575148	-0.104698	O	-1.211915	2.33768	0.542566	O	2.044862	-1.954776	-0.15549
O	-2.12223	0.447234	1.065298	O	-2.898739	0.119838	0.008226	O	2.783206	0.759857	-0.233558
O	-2.301682	-1.975597	-0.119351	O	-1.593304	-2.390328	0.099502	O	0.757005	2.573237	0.509488
O	3.413718	-0.646853	-0.061937	O	2.808857	-0.799429	1.092996	O	-3.519106	0.520317	-0.288177
H	0.460869	0.766334	1.276854	H	2.201264	-1.504274	1.339599	H	-0.521962	-2.204775	-0.891657
H	-0.375106	1.329183	-1.595478	H	0.894999	0.961038	1.128686	H	1.248608	-0.747995	-1.635442
H	1.164385	-0.66815	-1.324605	H	-0.988911	1.318433	-1.239788	H	-1.270169	-0.032557	-1.553975
H	-2.584222	0.534553	-0.948801	H	1.073997	-0.148441	-1.70791	H	1.429321	0.217308	1.251925
H	-1.124967	-1.2557	-1.659721	H	-1.372155	-0.195342	1.383173	H	0.448143	1.602499	-1.282607
H	2.269124	-2.276176	0.28755	H	-1.113734	-1.175503	-1.49627	H	-2.591139	-0.719906	1.10209
H	2.137911	-1.02871	1.539802	H	3.250248	0.298163	-0.550326	H	-3.009172	-1.429207	-0.471312
H	1.46969	2.528996	0.010901	H	2.956384	-1.427995	-0.878532	H	0.418539	-2.341834	1.299408
H	-1.402111	2.492081	0.72958	H	1.031003	2.914359	-0.16823	H	2.940128	-1.599218	-0.174313
H	-2.624043	-0.334261	1.324107	H	-2.168357	2.410966	0.458333	H	3.000647	1.586486	0.208812
H	-1.953966	-2.87243	-0.082124	H	-3.374051	-0.6611	0.309005	H	0.133256	3.266656	0.276017
H	3.329478	0.313373	-0.02867	H	-1.274858	-3.172053	-0.361258	H	-3.175058	1.310792	0.138322

Table S.5: Coordinates of the lowest energy conformation of glucuronic acid and the QM intermediate at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

Glucuronic Acid				QM Intermediate			
C	-0.967231	1.167684	-0.280773	C	2.787121	-0.64631	-0.152152
C	0.471425	0.792563	0.039373	C	1.862255	0.514143	0.071347
C	-1.921001	0.119896	0.267211	C	1.748462	2.846419	0.34268
C	0.735459	-0.649641	-0.385287	C	0.528273	0.339773	0.183996
C	-1.526332	-1.255805	-0.24218	C	-0.069753	-0.985966	0.081677
C	2.099169	-1.107492	0.113487	C	-1.397306	-1.209106	0.17725
C	1.957101	2.638591	0.083531	C	-2.459649	-0.172216	0.377659
O	-0.205823	-1.55323	0.167586	C	-2.949211	0.391668	-0.95531
O	-1.235155	2.434767	0.277154	C	0.822711	-2.120901	-0.145499
O	1.380604	1.589273	-0.678254	C	2.148975	-1.9704	-0.252556
O	-3.218884	0.479175	-0.156246	O	2.516737	1.677126	0.141047
O	-2.389573	-2.174797	0.333037	O	-3.950725	1.357952	-0.753593
O	2.504546	-2.211945	-0.527279	O	-3.617666	-0.73334	0.987191
O	2.730235	-0.571111	0.977798	O	3.983236	-0.490333	-0.241479
H	-1.078363	1.20387	-1.374922	H	-4.634714	0.945927	-0.215209
H	0.639803	0.880043	1.11995	H	-3.41698	-0.976722	1.894416
H	-1.853061	0.098107	1.363033	H	1.036759	2.99123	-0.476153
H	0.729252	-0.709291	-1.483046	H	1.207907	2.797475	1.293324
H	-1.578504	-1.287543	-1.343017	H	2.455604	3.671504	0.365
H	-2.167299	2.625094	0.126654	H	-0.124101	1.188304	0.340927
H	-3.840392	-0.163745	0.200025	H	-1.768848	-2.225132	0.06521
H	-2.16459	-3.057033	0.022716	H	-2.094922	0.664097	0.985507
H	3.350749	-2.480089	-0.143861	H	-2.121529	0.877492	-1.474582
H	1.185105	3.315875	0.457098	H	-3.310077	-0.440149	-1.573927
H	2.625854	3.177871	-0.58574	H	0.367644	-3.102997	-0.225302
H	2.532308	2.225017	0.918575	H	2.819333	-2.804881	-0.419088

Coordinates of LCC Moieties

Table S.6: Coordinates of the lowest energy conformation for the benzyl ether linkage between the simplified monolignol and arabinose at different bonding locations at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

Simplified Monolignol + Arabinose (Benzyl Ether)											
Carbon 2				Carbon 3				Carbon 5			
C	3.284506	-1.836814	-0.643371	C	-3.947062	-0.90864	0.911858	C	4.11741	-1.004432	-0.649887
C	2.764353	-1.437316	0.60139	C	-3.244454	-1.068656	-0.295492	C	3.127355	-1.26318	0.315274
C	2.783459	-1.8123	2.9486	C	-3.262903	-2.038318	-2.465126	C	2.494367	-2.614075	2.165995
C	1.84569	-0.40516	0.675101	C	-2.015413	-0.457718	-0.475694	C	1.936805	-0.557557	0.299212
C	1.43048	0.244648	-0.495741	C	-1.469051	0.32256	0.551077	C	1.712501	0.41125	-0.688066
C	0.433199	1.373151	-0.400258	C	-0.161997	1.037942	0.319932	C	0.416798	1.190148	-0.65759
C	0.97938	2.591398	0.339052	C	-0.280526	2.27183	-0.572717	C	0.40397	2.246134	0.442251
C	2.200054	3.190156	-0.337383	C	-1.240651	3.313927	-0.025024	C	1.516238	3.274324	0.2875
C	1.941965	-0.157423	-1.719843	C	-2.162711	0.470575	1.743267	C	2.685926	0.652557	-1.645412
C	2.871118	-1.195987	-1.796075	C	-3.403297	-0.141201	1.924759	C	3.892042	-0.049432	-1.623848
C	-3.029082	0.270074	0.336395	C	1.684663	-0.471866	0.496711	C	-2.639514	-1.439451	0.44812
C	-3.650416	-0.987627	-0.274038	C	2.440465	-1.507446	-0.340341	C	-2.414021	-1.089244	-1.046188
C	-1.733805	0.371273	-0.449379	C	2.799358	0.464632	0.989424	C	-3.547425	-0.290995	0.9406
C	-1.430758	-1.087665	-0.853895	C	3.806295	0.373608	-0.156541	C	-4.309632	0.021178	-0.344441
C	-4.67053	-1.6521	0.623627	C	2.666835	-2.827551	0.373451	C	-1.022075	-0.589663	-1.361352
O	3.247949	-2.154917	1.656546	O	-3.885691	-1.855324	-1.207518	O	3.465113	-2.238872	1.205373
O	2.611858	4.363147	0.327307	O	-1.226589	4.472089	-0.82757	O	1.337831	4.319265	1.23469
O	0.002661	3.616007	0.366066	O	0.979289	2.910829	-0.665045	O	-0.855798	2.879964	0.389043
O	4.180865	-2.849618	-0.708373	O	-5.147313	-1.511977	1.081149	O	5.279574	-1.698031	-0.630717
O	-2.541924	-1.859943	-0.432184	O	3.740193	-0.943305	-0.618227	O	-3.344445	-0.03916	-1.358138
O	-3.791585	1.43858	0.19348	O	0.779227	0.200976	-0.347126	O	-3.237031	-2.707828	0.614442
O	-0.739421	0.999338	0.323817	O	3.315176	-0.10481	2.173875	O	-2.866288	0.830034	1.427055
O	-1.282341	-1.115131	-2.246023	O	3.41049	1.299028	-1.144308	O	-5.279248	-0.998407	-0.510748
O	-5.624528	-0.644244	0.943313	O	3.468393	-3.689303	-0.403277	O	-0.690236	0.361592	-0.371032
H	1.824641	4.906558	0.441138	H	-0.299743	4.690349	-0.975195	H	1.673655	4.02969	2.086978
H	-0.820825	3.228872	0.684235	H	1.633906	2.28934	-1.017064	H	-0.794693	3.685117	0.916423
H	1.701643	-1.956452	3.023367	H	-3.128308	-1.078949	-2.972953	H	1.585522	-2.976756	1.677263
H	3.289746	-2.480723	3.640984	H	-2.294244	-2.533253	-2.3508	H	2.940259	-3.414612	2.751183
H	3.034262	-0.775032	3.188392	H	-3.929515	-2.670544	-3.046666	H	2.249635	-1.772766	2.820416
H	1.419413	-0.106903	1.625162	H	-1.455644	-0.583612	-1.394013	H	1.156871	-0.754393	1.02566
H	0.14178	1.690344	-1.410613	H	0.24483	1.368712	1.284405	H	0.257681	1.693398	-1.622441
H	1.242728	2.298948	1.365519	H	-0.621121	1.951467	-1.567531	H	0.520153	1.725942	1.407341
H	3.033955	2.487681	-0.307626	H	-2.260763	2.928147	-0.021399	H	2.498875	2.804621	0.384428
H	1.955652	3.399736	-1.388516	H	-0.954709	3.551495	1.010484	H	1.444132	3.744186	-0.696808
H	1.602543	0.326807	-2.628631	H	-1.739604	1.069544	2.542646	H	2.51134	1.392249	-2.419783
H	3.279142	-1.523666	-2.744315	H	-3.956365	-0.038399	2.850012	H	4.662154	0.12346	-2.365411
H	4.348518	-3.160099	0.189546	H	-5.358477	-1.990682	0.270521	H	5.242322	-2.326787	0.100173
H	-2.786361	0.071853	1.390855	H	1.168123	-0.92753	1.350455	H	-1.70411	-1.450539	1.006451
H	-4.099354	-0.733747	-1.24393	H	1.922154	-1.666781	-1.288661	H	-2.634521	-1.969944	-1.657308
H	-1.924343	0.947567	-1.363558	H	2.448218	1.49053	1.131376	H	-4.212767	-0.644257	1.728397
H	-0.550153	-1.496201	-0.354105	H	4.840334	0.560164	0.151139	H	-4.758051	1.015559	-0.369972
H	-4.161064	-2.013816	1.524001	H	1.708617	-3.329635	0.52367	H	-1.013057	-0.124079	-2.354567
H	-5.14073	-2.498032	0.113444	H	3.120386	-2.630984	1.352674	H	-0.307868	-1.422733	-1.352972
H	-4.660134	1.254651	0.569818	H	4.025438	0.445222	2.514122	H	-4.127426	-2.655983	0.245757
H	-6.327125	-1.018949	1.477656	H	4.282214	-3.215416	-0.602227	H	-2.215297	1.142282	0.778087
H	-1.0299	-2.004987	-2.509512	H	3.881568	1.093142	-1.957904	H	-5.67505	-0.897471	-1.38202

Table S.7: Coordinates of the lowest energy conformation for the benzyl ether linkage between the simplified monolignol and xylose at different bonding locations at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

Simplified Monolignol + Xylose (Benzyl Ether)							
	Carbon 2				Carbon 3		
C	-3.569505	-0.835872	-0.939758	C	-3.61647	-1.512589	-0.877556
C	-3.099302	-0.715318	0.379225	C	-3.562946	-0.629076	0.215924
C	-3.538022	-1.173875	2.67116	C	-4.726554	0.263733	2.084031
C	-1.883595	-0.099106	0.632625	C	-2.434504	0.140497	0.438436
C	-1.12356	0.410186	-0.42683	C	-1.345417	0.050557	-0.43899
C	0.187247	1.109006	-0.152709	C	-0.137055	0.924419	-0.195271
C	0.097004	2.632517	-0.214024	C	-0.236971	2.317241	-0.83099
C	-0.925706	3.209405	0.749994	C	-1.454849	3.100852	-0.374402
C	-1.593197	0.287755	-1.729997	C	-1.403088	-0.818797	-1.520989
C	-2.813477	-0.336788	-1.985882	C	-2.537755	-1.604386	-1.736545
C	1.532348	-1.520377	-0.279528	C	1.985271	-0.215523	0.133199
C	2.130468	-0.21135	-0.788257	C	3.360925	0.177158	-0.370458
C	2.650661	-2.488715	0.076382	C	1.853881	-1.733236	0.214998
C	3.145369	0.326415	0.222274	C	4.428293	-0.506384	0.471881
C	3.621469	-1.821369	1.040062	C	3.027772	-2.303944	1.004386
O	-3.929167	-1.257918	1.313207	O	-4.687135	-0.63155	0.986186
O	-0.877287	4.616556	0.745393	O	-1.477004	3.232463	1.036895
O	1.343342	3.189126	0.160914	O	0.884844	3.086038	-0.443859
O	-4.751947	-1.444314	-1.184389	O	-4.720812	-2.26981	-1.081049
O	4.144848	-0.635538	0.464765	O	4.263144	-1.902601	0.434679
O	0.727966	-2.162199	-1.244527	O	1.039579	0.348423	-0.750164
O	1.164355	0.762867	-1.13191	O	3.463946	1.584771	-0.283093
O	2.138235	-3.641537	0.703173	O	0.679545	-2.119514	0.892485
O	3.737902	1.454921	-0.334137	O	5.656698	-0.176671	-0.086983
H	0.053115	4.86057	0.804356	H	-0.629341	3.617549	1.286492
H	2.042541	2.793428	-0.378482	H	1.695451	2.56794	-0.563551
H	-3.442073	-0.129768	2.982946	H	-3.944924	0.021486	2.809448
H	-4.326735	-1.655223	3.244116	H	-4.604834	1.296946	1.74655
H	-2.592617	-1.698776	2.83601	H	-5.704207	0.137613	2.542967
H	-1.512792	-0.009471	1.647369	H	-2.379386	0.829947	1.273545
H	0.534589	0.85118	0.854984	H	-0.006513	1.065978	0.883407
H	-0.16078	2.925014	-1.241223	H	-0.274278	2.188453	-1.922209
H	-1.933977	2.915122	0.455109	H	-1.431777	4.084435	-0.856003
H	-0.726311	2.814987	1.758344	H	-2.373926	2.591221	-0.665137
H	-0.994123	0.669692	-2.548727	H	-0.556695	-0.886689	-2.194219
H	-3.193992	-0.444103	-2.994112	H	-2.59959	-2.291111	-2.57173
H	-5.12978	-1.721647	-0.340994	H	-5.355204	-2.065951	-0.383289
H	0.949932	-1.341687	0.637913	H	1.850656	0.201574	1.141708
H	2.677701	-0.406122	-1.715029	H	3.485843	-0.162645	-1.406499
H	3.184446	-2.749656	-0.84738	H	1.87479	-2.138073	-0.805597
H	2.661478	0.578204	1.18165	H	4.35965	-0.157757	1.516589
H	3.105339	-1.603131	1.985943	H	2.953751	-1.970022	2.049179
H	4.466143	-2.475683	1.248432	H	3.004492	-3.39186	0.985701
H	-0.047788	-1.616447	-1.423543	H	4.342104	1.841077	-0.583893
H	1.440295	-3.985948	0.135433	H	-0.086894	-1.892223	0.351567
H	4.450215	1.738664	0.24855	H	6.355186	-0.603404	0.418284

Table S.8: Coordinates of the lowest energy conformation for the benzyl ether linkage between the simplified monolignol and mannose at different bonding locations at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

Simplified Monolignol + Mannose (Benzyl Ether)											
Carbon 2				Carbon 3				Carbon 6			
C	4.483461	-0.508796	-0.610712	C	-4.138356	-1.293042	1.145232	C	0.857208	2.734997	1.261669
C	3.594731	-0.912488	0.403451	C	-3.511288	-1.402553	-0.109708	C	0.848121	2.374426	-0.093351
C	3.299483	-2.2806	2.324841	C	-3.476421	-2.550934	-2.191296	C	0.681766	3.200298	-2.329033
C	2.312674	-0.393006	0.454362	C	-2.407912	-0.621725	-0.409564	C	1.201669	1.097776	-0.488461
C	1.896	0.53249	-0.513728	C	-1.908106	0.274225	0.545251	C	1.532728	0.140431	0.470848
C	0.50573	1.10714	-0.434859	C	-0.730084	1.148648	0.190204	C	1.861091	-1.261881	0.002767
C	0.310212	2.06812	0.739329	C	-1.099723	2.312765	-0.721218	C	3.318016	-1.385966	-0.446124
C	1.117116	3.34533	0.605385	C	-2.234755	3.158197	-0.1693	C	4.317223	-1.140223	0.671081
C	2.77474	0.920738	-1.513615	C	-2.524252	0.370181	1.783893	C	1.534788	0.493138	1.815265
C	4.070087	0.405074	-1.561029	C	-3.642304	-0.408445	2.084502	C	1.20952	1.789496	2.212144
C	-2.557952	-1.815691	0.175667	C	2.054229	-1.106125	-0.520365	C	-2.47881	-2.042498	0.0878
C	-1.643012	-1.770554	-1.045289	C	1.389622	0.013546	0.258108	C	-3.402867	-1.113992	0.871711
C	-3.7313	-0.862196	-0.020157	C	3.345969	-1.502514	0.181088	C	-1.140088	-1.342933	-0.130259
C	-1.234317	-0.332861	-1.335883	C	2.351611	1.183558	0.472361	C	-3.502216	0.25326	0.208618
C	-2.490898	0.540855	-1.481032	C	3.680297	0.683578	1.052781	C	-2.109288	0.786215	-0.123863
C	-4.618855	-0.752181	1.202804	C	4.12302	-2.563643	-0.574121	C	-0.164209	-2.223363	-0.889228
O	4.124791	-1.818001	1.272032	O	-4.089775	-2.317741	-0.936584	O	0.384921	3.354012	-0.943744
O	0.898653	4.197728	1.704265	O	-2.313173	4.29239	-1.022134	O	5.63446	-1.343098	0.213802
O	-1.058664	2.463636	0.806643	O	0.067898	3.108603	-0.857641	O	3.570546	-2.699447	-0.910729
O	5.73435	-1.019667	-0.654869	O	-5.215664	-2.05888	1.43185	O	0.498868	3.984888	1.642179
O	-3.245384	0.454452	-0.283469	O	4.201173	-0.372764	0.266123	O	-1.371209	-0.157302	-0.871791
O	-3.073122	-3.114041	0.366716	O	1.210611	-2.238498	-0.585521	O	-2.259815	-3.237163	0.807816
O	-0.519668	-2.606359	-0.855378	O	0.261284	0.410487	-0.50671	O	-4.674944	-1.707602	1.031979
O	-0.456924	0.072204	-0.220547	O	2.647417	1.832314	-0.740214	O	-4.273122	0.079226	-0.962915
O	-2.222993	1.870209	-1.741252	O	4.610438	1.69935	1.090851	O	-2.288204	1.927774	-0.89523
O	-5.692817	0.13027	0.975306	O	5.329821	-2.869725	0.086533	O	1.097975	-1.626673	-1.139507
H	-0.053154	4.318366	1.785647	H	-2.958105	4.914424	-0.679519	H	5.643921	-2.193588	-0.238242
H	-1.588864	1.688995	1.040722	H	-0.204183	3.951207	-1.24159	H	2.908556	-2.896759	-1.581617
H	3.900907	-2.982471	2.897195	H	-4.064783	-3.324527	-2.678443	H	0.114185	2.369442	-2.757658
H	2.990776	-1.451757	2.96818	H	-3.484204	-1.644421	-2.802901	H	0.383393	4.130816	-2.806267
H	2.416693	-2.791735	1.92916	H	-2.448039	-2.900459	-2.060236	H	1.751741	3.030698	-2.470252
H	1.622608	-0.694295	1.23397	H	-1.915524	-0.696372	-1.371891	H	1.145447	0.796391	-1.526282
H	0.274311	1.638844	-1.364329	H	-0.309464	1.578298	1.108022	H	1.684764	-1.984785	0.812875
H	0.589692	1.561168	1.671695	H	-1.393095	1.912592	-1.701334	H	3.491553	-0.660477	-1.253626
H	2.182451	3.111464	0.58113	H	-3.166821	2.585975	-0.175565	H	4.251016	-0.109927	1.02203
H	0.846925	3.838792	-0.339556	H	-2.00217	3.460086	0.860206	H	4.08501	-1.813698	1.508987
H	2.452838	1.630548	-2.267948	H	-2.131525	1.051971	2.530964	H	1.781463	-0.24872	2.568305
H	4.767438	0.695944	-2.336582	H	-4.130348	-0.351196	3.049483	H	1.207558	2.079331	3.255724
H	5.838546	-1.630615	0.084635	H	-5.393667	-2.625726	0.671453	H	0.321153	4.503503	0.848342
H	-1.982379	-1.491784	1.055042	H	2.29648	-0.732632	-1.523508	H	-2.927285	-2.249083	-0.893888
H	-2.193396	-2.176726	-1.901025	H	1.059385	-0.389008	1.228509	H	-2.984792	-1.000479	1.878102
H	-4.336946	-1.200583	-0.873923	H	3.115796	-1.875001	1.191971	H	-0.718433	-1.09078	0.855296
H	-0.637691	-0.286339	-2.254897	H	1.928259	1.89807	1.191112	H	-3.993237	0.962299	0.886684
H	-3.089165	0.16421	-2.321984	H	3.532813	0.327033	2.080868	H	-1.560334	1.009998	0.806053
H	-4.006529	-0.423055	2.054339	H	4.310002	-2.198847	-1.593018	H	-0.579805	-2.450008	-1.873581
H	-5.036897	-1.731872	1.433524	H	3.533134	-3.478219	-0.630034	H	-0.040188	-3.156849	-0.328727
H	-2.334094	-3.728267	0.29613	H	0.333844	-1.920871	-0.826408	H	-3.121023	-3.548955	1.108149
H	0.139792	-2.088717	-0.375183	H	1.840527	2.287088	-1.026312	H	-5.167588	-1.538081	0.219133

Simplified Monolignol + Mannose (Benzyl Ether)											
	Carbon 2				Carbon 3				Carbon 6		
H	-1.876617	2.283906	-0.933302	H	4.562798	2.144446	0.234028	H	-4.138743	0.848852	-1.526894
H	-5.320397	0.954286	0.644581	H	5.779372	-2.032515	0.244642	H	-1.482079	2.458858	-0.897041

Table S.9: Coordinates of the lowest energy conformation for the benzyl ether linkage between the simplified monolignol and glucose at different bonding locations at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

Simplified Monolignol + Glucose (Benzyl Ether)											
	Carbon 2				Carbon 3				Carbon 6		
C	-3.856579	-1.518561	1.086284	C	3.910939	-1.76935	-0.506329	C	-4.633826	-0.731443	1.296327
C	-3.21222	-1.565066	-0.161733	C	3.358355	-1.305424	0.701838	C	-4.270078	-0.860769	-0.055658
C	-2.944063	-2.770712	-2.191015	C	3.440076	-1.431233	3.073846	C	-4.968691	-1.552219	-2.219797
C	-2.214512	-0.654811	-0.468961	C	2.324956	-0.384881	0.69037	C	-3.016727	-0.459429	-0.484316
C	-1.830652	0.301645	0.477511	C	1.827702	0.089804	-0.532356	C	-2.105741	0.076835	0.434436
C	-0.745311	1.2952	0.126407	C	0.727618	1.120637	-0.530965	C	-0.767286	0.574023	-0.053369
C	-1.249569	2.555018	-0.566221	C	1.194517	2.518066	-0.126831	C	-0.861572	1.925477	-0.761862
C	-2.370741	3.254569	0.190622	C	2.285971	3.064637	-1.031787	C	-1.422887	3.027106	0.118237
C	-2.453028	0.328219	1.719174	C	2.372226	-0.377566	-1.721332	C	-2.465981	0.192883	1.769279
C	-3.472806	-0.573216	2.021116	C	3.414565	-1.305328	-1.709983	C	-3.73062	-0.206774	2.201806
C	3.729397	0.360885	0.345286	C	-1.745364	-1.059759	-0.233767	C	3.066466	-1.88358	0.058023
C	2.501714	1.039118	-0.232491	C	-1.566034	0.448213	-0.090061	C	4.454424	-1.259204	-0.014209
C	3.949315	-0.972518	-0.36427	C	-3.190915	-1.374531	-0.610846	C	2.062794	-0.916793	-0.557849
C	1.304508	0.100595	-0.166137	C	-2.595322	1.022733	0.863712	C	4.471032	0.129443	0.606876
C	1.631958	-1.200995	-0.895639	C	-3.986472	0.600323	0.412447	C	3.384202	0.969924	-0.044893
C	5.061426	-1.792545	0.266842	C	-3.478463	-2.862803	-0.631048	C	0.610029	-1.348948	-0.472685
O	-3.650957	-2.564582	-0.977673	O	3.930268	-1.849081	1.813263	O	-5.246403	-1.402595	-0.84031
O	-2.609246	4.532535	-0.386891	O	2.597332	4.394581	-0.686361	O	-1.412314	4.264072	-0.55955
O	-0.135833	3.430095	-0.671485	O	0.115666	3.426449	-0.22557	O	0.438188	2.359262	-1.156332
O	-4.830998	-2.411197	1.379057	O	4.915751	-2.674645	-0.486797	O	-5.860875	-1.129902	1.708304
O	2.77273	-1.773698	-0.283769	O	-4.071832	-0.805087	0.356831	O	2.147509	0.319977	0.130248
O	4.881231	1.150507	0.145808	O	-0.918631	-1.580716	-1.251365	O	3.017744	-3.09688	-0.656978
O	2.279384	2.23498	0.482146	O	-0.286614	0.766082	0.411541	O	5.343645	-2.139843	0.640595
O	0.195059	0.725838	-0.771465	O	-2.462164	2.429091	0.850218	O	5.762335	0.659126	0.395751
O	0.597823	-2.120939	-0.863575	O	-4.881538	1.078206	1.360111	O	3.321198	2.202736	0.582158
O	4.736388	-2.171088	1.587165	O	-4.822461	-3.119673	-0.969327	O	-0.199017	-0.31744	-1.015346
H	-3.177844	4.429465	-1.154181	H	1.756257	4.856764	-0.598139	H	-0.538088	4.364374	-0.950267
H	-0.482014	4.321372	-0.803398	H	-0.629673	3.114562	0.308987	H	0.857799	1.595037	-1.568564
H	-1.879897	-2.932112	-1.997062	H	3.577675	-0.354172	3.205064	H	-5.862398	-1.983327	-2.66467
H	-3.37937	-3.656742	-2.646903	H	2.381351	-1.683811	3.181465	H	-4.759331	-0.582448	-2.68036
H	-3.069486	-1.915372	-2.861074	H	4.021517	-1.96821	3.819289	H	-4.119885	-2.224388	-2.374519
H	-1.68619	-0.698176	-1.412236	H	1.877942	-0.032442	1.611633	H	-2.714267	-0.568543	-1.518337
H	-0.237771	1.620156	1.043963	H	0.291398	1.188292	-1.534694	H	-0.079384	0.688385	0.790328
H	-1.597252	2.277078	-1.572509	H	1.566808	2.475813	0.907007	H	-1.495305	1.81511	-1.652802
H	-3.274153	2.640317	0.204406	H	3.19885	2.476393	-0.927827	H	-2.458339	2.809772	0.381924
H	-2.05934	3.443261	1.22153	H	1.946255	2.999935	-2.076122	H	-0.830336	3.080139	1.043335
H	-2.140372	1.050477	2.466441	H	1.982642	-0.021199	-2.669122	H	-1.759507	0.601501	2.484286
H	-3.965848	-0.570048	2.985266	H	3.846289	-1.683365	-2.628301	H	-4.027512	-0.125843	3.240042
H	-4.936645	-2.997919	0.620277	H	5.124791	-2.874017	0.433921	H	-6.338261	-1.468312	0.941356

Simplified Monolignol + Glucose (Benzyl Ether)											
Carbon 2				Carbon 3				Carbon 6			
H	3.568891	0.170846	1.415112	H	-1.522254	-1.530168	0.734584	H	2.808598	-2.041397	1.115207
H	2.695988	1.265485	-1.291917	H	-1.708733	0.915549	-1.074872	H	4.733411	-1.165654	-1.074835
H	4.198441	-0.772004	-1.417001	H	-3.40839	-0.950267	-1.60243	H	2.316996	-0.770019	-1.619896
H	1.084796	-0.150863	0.88284	H	-2.433787	0.620551	1.872043	H	4.240174	0.059938	1.678004
H	1.837329	-1.003847	-1.955519	H	-4.198862	1.019107	-0.584851	H	3.587304	1.080113	-1.124614
H	5.966578	-1.186604	0.314867	H	-3.229547	-3.282568	0.352755	H	0.330871	-1.554095	0.567364
H	5.251246	-2.672625	-0.358389	H	-2.851028	-3.338131	-1.383986	H	0.459628	-2.255616	-1.059814
H	4.67469	2.033491	0.470616	H	0.005226	-1.490652	-0.98729	H	3.758567	-3.636434	-0.359651
H	1.592685	2.750419	0.029799	H	-3.137309	2.801975	1.426885	H	6.216465	-1.733121	0.64152
H	0.254325	-2.175008	0.03569	H	-5.78046	0.906803	1.064948	H	5.794778	1.540013	0.782068
H	3.90354	-2.651604	1.544188	H	-5.369324	-2.649624	-0.332751	H	2.548712	2.667536	0.232515

Table S.10: Coordinates of the lowest energy conformation for the benzyl ether linkage between the simplified monolignol and galactose at different bonding locations at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

Simplified Monolignol + Galactose (Benzyl Ether)							
Carbon 2				Carbon 6			
C	3.958137	-1.010157	-1.125436	C	-0.736651	2.822497	-1.051417
C	3.565612	-0.994444	0.224604	C	-0.733913	2.341518	0.265627
C	4.026594	-1.790217	2.416189	C	-0.446476	2.92221	2.564709
C	2.451145	-0.270095	0.620356	C	-1.166348	1.059755	0.551959
C	1.709758	0.443529	-0.332666	C	-1.574172	0.21787	-0.483739
C	0.510458	1.249148	0.108492	C	-1.988235	-1.198493	-0.144204
C	0.870566	2.632101	0.660489	C	-3.449836	-1.281449	0.299142
C	1.629496	3.479438	-0.347847	C	-4.432244	-0.879673	-0.787453
C	2.102295	0.424192	-1.664322	C	-1.571356	0.691099	-1.790966
C	3.226275	-0.299692	-2.060319	C	-1.163435	1.992767	-2.076366
C	-2.503671	-1.870849	-0.532799	C	2.269943	-2.230713	-0.392533
C	-1.1789	-1.146044	-0.293093	C	3.324314	-1.262735	-0.924295
C	-3.626186	-0.859556	-0.725554	C	1.008996	-1.448588	-0.018367
C	-1.357081	-0.13075	0.83491	C	3.500776	-0.085024	0.016771
C	-2.521615	0.820407	0.527929	C	2.150481	0.568316	0.265958
C	-4.99979	-1.498416	-0.809929	C	-0.020509	-2.354567	0.636426
O	4.364227	-1.736394	1.042107	O	-0.205018	3.213182	1.189886
O	0.874005	3.648811	-1.532672	O	-5.759289	-1.067333	-0.353341
O	-0.31128	3.350533	0.951704	O	-3.772444	-2.617897	0.639602
O	5.043504	-1.72153	-1.50744	O	-0.301781	4.076377	-1.324674
O	-3.695833	0.066957	0.356105	O	1.303234	-0.385312	0.87055
O	-2.814314	-2.703315	0.562733	O	2.740697	-2.917079	0.744421
O	-0.233635	-2.141217	0.040858	O	4.528834	-1.98896	-1.069265
O	-0.182688	0.584922	1.16618	O	4.417514	0.79614	-0.598268
O	-2.723865	1.731261	1.559729	O	2.353001	1.638435	1.126893
O	-5.987031	-0.529964	-1.087043	O	-1.247492	-1.719861	0.950133
H	0.035825	4.043354	-1.267529	H	-5.806135	-1.95387	0.020698
H	-0.928912	2.791595	1.444099	H	-3.126958	-2.907756	1.292827
H	3.028963	-2.217213	2.553861	H	-0.089912	3.785447	3.121687
H	4.767395	-2.432961	2.885557	H	-1.51549	2.778532	2.738211

Simplified Monolignol + Galactose (Benzyl Ether)							
	Carbon 2				Carbon 6		
H	4.066939	-0.793577	2.864717	H	0.106544	2.030309	2.872056
H	2.128308	-0.254482	1.654554	H	-1.113921	0.66389	1.557456
H	-0.146163	1.415536	-0.750787	H	-1.860025	-1.85057	-1.021716
H	1.483794	2.494139	1.562904	H	-3.58379	-0.626858	1.172031
H	1.855012	4.446772	0.114166	H	-4.317087	0.176337	-1.033591
H	2.566783	2.998646	-0.629498	H	-4.226656	-1.475668	-1.688873
H	1.537586	0.992619	-2.396287	H	-1.879339	0.039303	-2.602521
H	3.545364	-0.328115	-3.094884	H	-1.155612	2.375844	-3.089176
H	5.415914	-2.147322	-0.725836	H	-0.090592	4.511974	-0.490261
H	-2.41128	-2.465777	-1.451811	H	2.017712	-2.943089	-1.191013
H	-0.888464	-0.638947	-1.223728	H	2.99435	-0.875008	-1.898684
H	-3.43597	-0.302089	-1.655774	H	0.597105	-1.033616	-0.952045
H	-1.622359	-0.684631	1.74128	H	3.874659	-0.438638	0.985653
H	-2.323556	1.425927	-0.367476	H	1.6974	0.908065	-0.681619
H	-5.19992	-2.02702	0.127017	H	0.380936	-2.722169	1.580087
H	-5.017132	-2.219946	-1.628906	H	-0.202366	-3.209453	-0.029588
H	-2.018249	-3.209076	0.76366	H	3.646784	-3.187353	0.554487
H	0.640178	-1.737005	0.106427	H	5.236702	-1.354115	-1.22512
H	-5.931063	0.136979	-0.395329	H	4.50407	1.570734	-0.03314
H	-2.99229	1.240523	2.345488	H	1.625564	2.267458	1.047148

Simplified Monolignol + Galactose (Benzyl Ether)							
	Carbon 3				Carbon 4		
C	4.109919	-1.129473	-0.44136	C	-3.956365	-1.223235	0.16036
C	3.330361	-1.067468	0.725558	C	-2.906281	-1.32938	-0.766815
C	3.075415	-1.835199	2.961811	C	-2.09025	-2.462169	-2.689856
C	2.188978	-0.281798	0.763757	C	-1.781088	-0.530453	-0.647893
C	1.807648	0.446948	-0.370837	C	-1.688178	0.383661	0.407194
C	0.581365	1.322579	-0.321414	C	-0.484371	1.28679	0.511001
C	0.83999	2.717045	0.264163	C	-0.625253	2.568447	-0.316212
C	1.797938	3.535117	-0.585307	C	-1.826705	3.413631	0.080341
C	2.582845	0.383778	-1.520957	C	-2.722956	0.476599	1.328068
C	3.734169	-0.401463	-1.555935	C	-3.859128	-0.321148	1.203832
C	-1.66815	-0.944751	-0.705214	C	1.84527	0.669756	0.812884
C	-1.664735	0.45561	-0.083883	C	3.031031	0.854657	-0.128281
C	-3.09141	-1.397542	-1.033618	C	2.05587	-0.626252	1.607428
C	-2.712766	0.603806	0.998581	C	3.176353	-0.373058	-1.007585
C	-4.058568	0.155805	0.452931	C	3.338865	-1.601349	-0.125636
C	-3.143679	-2.897359	-1.32527	C	0.881024	-0.982756	2.499234
O	3.808746	-1.828904	1.751966	O	-3.11747	-2.266762	-1.736421
O	1.298663	3.695585	-1.899713	O	-1.826995	4.632509	-0.62562
O	-0.370588	3.447091	0.300599	O	0.508773	3.392926	-0.119852
O	5.222334	-1.901198	-0.473509	O	-5.052081	-2.01084	0.037747
O	-3.986777	-1.187193	0.049797	O	2.226513	-1.735977	0.727246
O	-1.083009	-1.887509	0.17224	O	0.672231	0.599668	0.033579
O	-0.41354	0.725759	0.512399	O	2.847445	2.018664	-0.906405
O	-2.736474	1.969023	1.368764	O	4.310276	-0.160413	-1.823102
O	-4.97583	0.274821	1.4897	O	3.403202	-2.702673	-0.970304
O	-2.11369	-3.297467	-2.201138	O	1.147154	-2.151769	3.242306
H	0.423693	4.090295	-1.814973	H	-0.926595	4.972799	-0.574245
H	-1.038017	2.961441	0.808178	H	1.280276	2.993992	-0.549483

Simplified Monolignol + Galactose (Benzyl Ether)							
	Carbon 3				Carbon 4		
H	2.065681	-2.225404	2.802316	H	-1.163344	-2.778386	-2.202349
H	3.616086	-2.489406	3.641582	H	-2.440243	-3.24571	-3.35782
H	3.018176	-0.829441	3.387696	H	-1.91111	-1.546224	-3.260312
H	1.583216	-0.220738	1.660203	H	-0.955683	-0.615804	-1.342486
H	0.189814	1.453478	-1.335456	H	-0.338501	1.577104	1.559846
H	1.258713	2.594787	1.273394	H	-0.713694	2.285166	-1.37427
H	1.946552	4.507065	-0.102288	H	-2.755612	2.894933	-0.157058
H	2.763337	3.034201	-0.667137	H	-1.794021	3.591402	1.166023
H	2.292904	0.959852	-2.393968	H	-2.649814	1.176283	2.154154
H	4.348506	-0.464435	-2.44561	H	-4.673338	-0.262869	1.915372
H	5.31384	-2.331253	0.385274	H	-4.932752	-2.568819	-0.73998
H	-1.100788	-0.911443	-1.645095	H	1.802499	1.522612	1.501154
H	-1.880629	1.201708	-0.861416	H	3.943474	0.956149	0.476814
H	-3.430388	-0.82313	-1.909028	H	2.957479	-0.520538	2.230875
H	-2.465908	-0.039923	1.850696	H	2.266829	-0.502403	-1.606305
H	-4.347486	0.785327	-0.40653	H	4.256591	-1.511969	0.479821
H	-4.093458	-3.142588	-1.801405	H	-0.015995	-1.097934	1.880483
H	-3.087636	-3.419967	-0.366726	H	0.711098	-0.180129	3.220972
H	-0.266443	-1.492733	0.504343	H	3.483666	1.995596	-1.630141
H	-3.425106	2.092746	2.030298	H	4.421395	-0.927777	-2.393034
H	-1.302499	-3.339419	-1.683797	H	1.302825	-2.858645	2.608673
H	-5.836758	-0.024891	1.182577	H	3.56517	-3.493938	-0.448474

Table S.11: Coordinates of the lowest energy conformation for the LCC moiety containing benzyl ester linkage between the simplified monolignol and glucuronic acid at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

Simplified Monolignol + Glucuronic Acid Benzyl Ester			
C	5.13939	-1.205921	-0.033201
C	4.263042	-0.829602	0.999997
C	3.940472	-0.70937	3.352084
C	3.023906	-0.289521	0.703842
C	2.638218	-0.126838	-0.633162
C	1.322951	0.519872	-0.959462
C	1.277374	2.013167	-0.62586
C	2.26831	2.820291	-1.448124
C	3.502625	-0.508442	-1.648625
C	4.755326	-1.043178	-1.350797
C	-4.452011	-0.929386	0.397201
C	-3.214658	-1.194973	-0.446958
C	-4.581337	0.554004	0.699443
C	-1.995786	-0.526424	0.180014
C	-3.302817	1.065254	1.34154
C	-0.813783	-0.53627	-0.781671
C	-3.306532	-3.196799	-1.714344
O	4.759585	-1.052407	2.251325
O	2.147118	4.194071	-1.160815

Simplified Monolignol + Glucuronic Acid Benzyl Ester			
O	-0.000876	2.545638	-0.921224
O	6.35002	-1.732533	0.264444
O	-2.213191	0.854116	0.459069
O	-5.578134	-1.401914	-0.305655
O	-2.921626	-2.567627	-0.501298
O	-5.688002	0.70503	1.561409
O	-3.454588	2.426665	1.545886
O	0.265763	-0.051175	-0.154944
O	-0.867093	-0.85998	-1.93118
H	1.212179	4.410819	-1.243817
H	-0.669388	2.141639	-0.352353
H	3.008816	-1.282375	3.335729
H	4.508573	-0.961581	4.244302
H	3.715883	0.361258	3.35035
H	2.338694	-0.008548	1.493774
H	1.073675	0.371165	-2.011876
H	1.506483	2.143618	0.441032
H	3.289851	2.523673	-1.207122
H	2.087408	2.622509	-2.514196
H	3.201725	-0.393038	-2.683832
H	5.440881	-1.348281	-2.131356
H	6.435665	-1.766267	1.224817
H	-4.343204	-1.470717	1.349237
H	-3.367427	-0.784158	-1.452537
H	-4.727683	1.109693	-0.236595
H	-1.720091	-1.063177	1.098332
H	-3.105836	0.533182	2.286108
H	-6.359103	-1.172148	0.209316
H	-5.808749	1.643269	1.738385
H	-2.715578	2.764389	2.060101
H	-4.385	-3.110535	-1.869604
H	-2.765678	-2.752367	-2.555937
H	-3.032048	-4.246278	-1.619912

Kinetic Data

Reaction Half-Life Calculations

Under the framework of the transition state theory, one can approximate the reaction rate using the Eyring equation:

$$k_r = \frac{\kappa k_B T}{h} e^{\frac{-\Delta G_a}{RT}}$$

where $k_r$is the reaction rate constant, κ is the transmission coefficient and assumed to be 1, $k_B$is the Boltzmann constant, h is Planck's constant, ΔG_a is the activation energy and T is the reaction temperature. Assuming that the reaction is first order, the rate law is given as

$$[A] = [A_o]e^{-k_r t}$$

where $[A]$ is an arbitrary concentration with the subscript, o, denoting the initial state and t is the time. The reaction half-life is then given by

$$t_{1/2} = \frac{ln(2)}{k_r}$$

Table S.12: The calculated activation energy, rate constant as well as reaction half-life for the nucleophilic addition to the QM intermediate of the most thermodynamically favorable reaction sites on the model compounds considered. Un-bracketed numbers indicate gas phase calculations and bracketed numbers indicate implicit solvent calculations.

Nucleophile (Reaction Site)	Activation Energy (kJ)	Rate Constant (s^{-1})	Half-Life (s)
Mannose (C2)	41.1 [34.5]	3.9E+05 [5.6E+06]	1.8E-06 [1.2E-07]
Mannose (C6)	36.5 [32.5]	2.4E+06 [1.2E+07]	2.8E-07 [5.6E-08]
Glucose (C3)	30.4 [29.5]	3.0E+07 [4.2E+07]	2.3E-08 [1.6E-08]
Glucose (C6)	26.9 [26.1]	1.2E+08 [1.7E+08]	5.8E-09 [4.2E-09]
Galactose (C6)	21.3 [21.7]	1.2E+09 [9.9E+08]	6.0E-10 [7.0E-10]
Arabinose (C5)	16.7 [13.8]	7.2E+09 [2.4E+10]	9.6E-11 [2.9E-11]
Xylose (C3)	27.2 [31.5]	1.1E+08 [1.9E+07]	6.5E-09 [3.7E-08]
Glucuronic Acid (C6)	60.8 [82.3]	1.4E+02 [2.3E-02]	5.1E-03 [3.0E+01]
Water	38.8 [28.8]	1.0E+06 [5.5E+07]	6.9E-07 [1.3E-08]

Coordinates of Transition States via the Concerted Mechanism

Table S.13: Transition state coordinates for the nucleophilic addition of water to the QM intermediate via the concerted mechanism, at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

QM Intermediate + Water			
C	1.37767	2.252966	0.003685
C	1.052881	0.858768	-0.042334
C	1.9072	-1.348642	-0.172675
C	-0.260467	0.45985	-0.049636
C	-1.300821	1.427111	0.009944
C	-2.671553	1.056779	0.017306
C	-3.142293	-0.258858	0.553572
C	-2.983665	-0.290798	2.081176
C	-0.969417	2.795831	0.054701
C	0.345351	3.20047	0.06083
O	2.127794	0.051483	-0.082221
O	-3.507689	-1.493507	2.578885
O	-4.517965	-0.484873	0.288909
O	2.612912	2.668219	-0.004621
O	-3.229537	0.762942	-1.770383
O	-2.265734	-1.552883	-2.275084
O	-3.924116	-3.027736	-0.767892
O	4.696206	1.20546	-0.286182
O	5.095459	-1.32421	0.732025
O	7.315888	-2.80322	-0.062074
H	-4.467837	-1.436784	2.565475
H	-4.755895	-0.097911	-0.561772
H	1.347199	-1.704641	0.697679
H	1.363258	-1.592139	-1.090155

QM Intermediate + Water			
H	2.89554	-1.799552	-0.184336
H	-0.504021	-0.59171	-0.126309
H	-3.383493	1.867641	0.161003
H	-2.548403	-1.080927	0.139746
H	-1.924216	-0.259134	2.338504
H	-3.480096	0.582416	2.520426
H	-1.761386	3.535686	0.106262
H	0.623344	4.2455	0.105709
H	-2.893989	1.48771	-2.312821
H	-2.807083	-0.1043	-2.083659
H	-2.034434	-1.891497	-3.144462
H	-2.827788	-2.228293	-1.832975
H	-4.405288	-2.447125	-0.161119
H	-3.933558	-3.912457	-0.395082
H	4.806236	0.302587	0.069215
H	5.524959	1.66967	-0.148889
H	5.095471	-1.434624	1.686191
H	5.859239	-1.834367	0.409728
H	8.215377	-2.478976	-0.153672
H	7.31325	-3.694804	-0.41906
H	3.328557	1.963756	-0.095941

Table S.14: Transition state coordinates for the nucleophilic addition of mannose at different bonding locations to the QM intermediate via the concerted mechanism, at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

QM Intermediate + Mannose							
Carbon 2				Carbon 6			
H	-9.088762	3.161867	0.293347	H	9.137722	1.177006	-1.899484
C	-2.884211	-1.749807	0.391465	C	2.319227	-1.580551	-0.389984
C	-2.891185	-0.398385	-0.048764	C	2.567752	-0.257056	0.05875
C	-4.127468	-0.069205	-2.021656	C	3.916914	-0.090658	1.980849
C	-1.787392	0.401013	0.115168	C	1.603182	0.715444	-0.037725
C	-0.606289	-0.122797	0.693216	C	0.337224	0.410379	-0.590585
C	0.580855	0.645899	0.923791	C	-0.725515	1.356102	-0.756077
C	0.548396	2.080862	1.422208	C	-0.489899	2.843675	-0.935043
C	1.898789	2.799573	1.396597	C	-1.759967	3.697077	-0.89829
C	-0.5934	-1.478241	1.097925	C	0.096763	-0.90754	-1.03493
C	-1.711451	-2.267444	0.967807	C	1.062547	-1.880816	-0.941535
C	3.962507	-0.421645	0.261235	C	-2.740286	-1.398026	1.254853
C	3.750367	0.334918	-1.043171	C	-3.348774	-2.747875	0.900522
C	3.393642	-1.844643	0.166055	C	-3.467326	-0.341646	0.422178
C	2.319369	0.197279	-1.549158	C	-3.301058	-2.997615	-0.604264
C	1.895496	-1.268224	-1.575666	C	-3.805114	-1.796382	-1.410836
C	3.401912	-2.547544	1.507683	C	-3.130784	1.087304	0.7657
O	-4.042174	0.097859	-0.596643	O	3.812205	0.030934	0.554608
O	2.089624	3.295383	0.0711	O	-2.095321	3.89367	0.470233
O	-0.437319	2.875967	0.819159	O	0.462427	3.369204	-0.044416
O	-3.927175	-2.534773	0.280769	O	3.216864	-2.534994	-0.316842

QM Intermediate + Mannose							
Carbon 2				Carbon 6			
H	-9.088762	3.161867	0.293347	H	9.137722	1.177006	-1.899484
O	2.047637	-1.80897	-0.274963	O	-3.200744	-0.579871	-0.945179
O	5.359945	-0.460567	0.518087	O	-2.930333	-1.200062	2.644217
O	4.065815	1.70616	-0.90169	O	-2.648724	-3.812391	1.500161
O	1.370154	0.944369	-0.750508	O	-1.972639	-3.2316	-1.028445
O	0.607215	-1.455281	-2.009378	O	-3.520717	-1.930417	-2.745752
O	2.744253	-1.698395	2.441903	O	-1.69786	1.310897	0.838796
O	-6.195773	-1.78536	-0.720716	O	-3.239615	6.358881	0.375281
O	-6.695069	0.817185	-0.332348	O	5.593	-2.213115	0.695002
O	-8.598186	2.524266	0.817866	O	6.545033	0.24409	0.200582
O	6.633522	1.138649	-1.393712	O	8.69378	1.485512	-1.105871
H	3.013921	3.168878	-0.193955	H	-2.561017	4.743956	0.572103
H	-0.014764	3.46951	0.186875	H	-0.002824	3.923387	0.593369
H	-3.324382	0.490652	-2.507818	H	4.955899	0.117192	2.227782
H	-4.066019	-1.127947	-2.284032	H	3.255597	0.633481	2.463884
H	-5.099136	0.322262	-2.31472	H	3.663301	-1.106074	2.294237
H	-1.841326	1.432428	-0.204763	H	1.840262	1.713682	0.303382
H	1.381963	0.062531	1.376133	H	-1.554312	0.981912	-1.357146
H	0.26761	1.942129	2.477191	H	-0.080421	2.90172	-1.954012
H	1.871768	3.640679	2.09161	H	-1.554259	4.660457	-1.370733
H	2.708211	2.121586	1.680418	H	-2.571679	3.204365	-1.443825
H	0.317067	-1.885875	1.520816	H	-0.869136	-1.155368	-1.455381
H	-1.721099	-3.299878	1.292851	H	0.886124	-2.887895	-1.297534
H	3.45525	0.113853	1.067713	H	-1.676842	-1.395975	0.992075
H	4.404336	-0.112538	-1.80429	H	-4.39808	-2.740266	1.230041
H	4.010608	-2.423038	-0.53798	H	-4.550257	-0.431281	0.613532
H	2.245859	0.611172	-2.558405	H	-3.931771	-3.860608	-0.846836
H	2.547611	-1.804837	-2.277476	H	-4.891521	-1.694423	-1.300433
H	4.436197	-2.742272	1.811582	H	-3.534625	1.323845	1.751716
H	2.878842	-3.50212	1.402783	H	-3.56534	1.761956	0.025618
H	5.511621	-0.532788	1.464425	H	-2.173116	-0.736625	3.010153
H	5.017567	1.804013	-1.095423	H	-2.646822	-3.679989	2.453852
H	1.633226	1.899919	-0.733395	H	-1.598928	-3.91491	-0.458783
H	-0.000655	-0.991536	-1.41922	H	-2.676813	-2.39344	-2.827984
H	2.662369	-2.153197	3.28427	H	-1.603997	2.216842	1.18986
H	-6.543066	-0.881599	-0.558889	H	-2.822973	7.172138	0.673889
H	-6.926196	-2.403252	-0.648615	H	-4.164688	6.571983	0.224174
H	-5.826694	1.080644	-0.010379	H	6.096676	-1.394345	0.498127
H	-7.357414	1.391778	0.08248	H	6.192408	-2.957369	0.608895
H	-4.75673	-2.117112	-0.097131	H	5.727488	0.639906	-0.119468
H	-9.116688	2.372995	1.611694	H	7.285432	0.662012	-0.266548
H	6.73202	0.474166	-0.70028	H	9.334993	2.018636	-0.62946
H	7.507496	1.415325	-1.677235	H	4.105352	-2.272698	0.06043

Coordinates of Transition States via the Step-Wise Mechanism

Table S.15: Transition state coordinates for the nucleophilic addition of water to the QM intermediate via the second step in the step-wise mechanism, at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

QM Intermediate + Water			
C	-3.280892	-0.517157	0.005386
C	-2.335182	0.535150	0.180339
C	-2.067485	2.851428	0.643224
C	-0.993633	0.274309	0.079042
C	-0.558073	-1.052493	-0.195052
C	0.812641	-1.387903	-0.262930
C	1.880908	-0.597727	0.410909
C	1.806548	-0.824884	1.935245
C	-1.510475	-2.076079	-0.386312
C	-2.859008	-1.816178	-0.278133
O	-2.914004	1.725741	0.430094
O	2.852276	-0.130462	2.554741
O	3.176948	-0.996761	0.013854
O	-4.571355	-0.258121	0.105335
O	1.474227	-0.954450	-2.115158
O	1.567444	1.634086	-1.940188
O	3.795675	1.745416	-0.423265
H	3.668503	-0.623257	2.427057
H	3.179147	-1.174056	-0.935207
H	-1.422330	2.681387	1.508888
H	-1.465323	3.048030	-0.247448
H	-2.728641	3.691307	0.835605
H	-0.272643	1.075532	0.175282
H	1.053161	-2.437765	-0.416802
H	1.745249	0.474402	0.231563
H	0.867199	-0.423268	2.317813
H	1.846175	-1.899424	2.147464
H	-1.172405	-3.084563	-0.597988
H	-3.608051	-2.587220	-0.403634
H	-4.705632	0.679978	0.309040
H	0.929704	-1.347160	-2.807166
H	1.442639	0.043227	-2.201942
H	1.480341	2.265238	-2.660302
H	2.406442	1.840039	-1.474212
H	4.011582	0.899704	-0.007606
H	4.323109	2.423481	0.005980

Table S.16: Transition state coordinates for the nucleophilic addition of arabinose and xylose to the QM intermediate via the second step in the step-wise mechanism, at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

QM Intermediate + Arabinose				QM Intermediate + Xylose			
Carbon 5				Carbon 3			
C	-4.029094	-0.593735	-0.623989	C	3.995932	-1.642987	-0.065199
C	-3.248774	-0.245234	0.514274	C	3.897639	-0.345241	0.500555
C	-3.107731	1.191707	2.399646	C	4.927862	1.223765	1.960183
C	-1.998432	-0.781292	0.682882	C	2.857389	0.484051	0.161338
C	-1.47306	-1.659768	-0.307705	C	1.87969	0.032061	-0.763678
C	-0.16257	-2.179946	-0.277354	C	0.770706	0.817073	-1.189637

QM Intermediate + Arabinose				QM Intermediate + Xylose			
	Carbon 5				Carbon 3		
C	0.744072	-2.299266	0.918205	C	0.710308	2.325709	-1.178653
C	2.188778	-2.680321	0.586709	C	-0.705003	2.890891	-1.331409
C	-2.264877	-1.98718	-1.434317	C	1.991731	-1.261759	-1.312332
C	-3.532184	-1.472016	-1.588901	C	3.039954	-2.091806	-0.973826
C	0.368326	1.772933	0.154822	C	-1.885697	-0.257223	-0.181573
C	0.742507	1.636318	-1.345157	C	-2.596137	-0.530798	1.138843
C	1.727384	2.038712	0.836899	C	-1.671485	-1.555044	-0.942103
C	2.529095	2.606881	-0.326193	C	-3.853178	-1.365821	0.927528
C	0.341048	0.345293	-2.02029	C	-2.997984	-2.320027	-1.009003
O	-3.87323	0.617149	1.338612	O	4.907314	-0.06349	1.354441
O	2.906348	-1.578196	0.041864	O	-1.256989	2.917753	-0.022343
O	0.633942	-1.276246	1.856157	O	1.357292	2.930923	-0.090378
O	-5.236089	-0.07702	-0.76809	O	5.008544	-2.432064	0.267673
O	5.474382	-2.456621	0.233174	O	-3.892901	2.54963	-0.110449
O	2.170293	1.75686	-1.3985	O	-3.512264	-2.566584	0.279254
O	-0.597396	2.767974	0.388175	O	-0.635263	0.380255	0.131685
O	2.321741	0.846325	1.312006	O	-2.912698	0.721212	1.724429
O	2.063071	3.910248	-0.525969	O	-1.232474	-1.220573	-2.249838
O	0.882836	-0.803043	-1.381981	O	-4.348125	-1.637582	2.187748
H	3.855387	-1.808926	0.042659	H	-2.224431	3.058915	-0.061922
H	1.297042	-0.57555	1.703807	H	0.679789	3.287404	0.498709
H	-2.804868	0.418977	3.109914	H	4.998452	2.002946	1.197197
H	-2.23688	1.711067	1.989595	H	4.032568	1.37283	2.569065
H	-3.768595	1.900448	2.890573	H	5.811248	1.243699	2.592101
H	-1.405453	-0.552893	1.555964	H	2.777444	1.476047	0.577891
H	0.05475	-2.913007	-1.049929	H	0.196374	0.382176	-2.003123
H	0.329044	-3.211385	1.387855	H	1.270222	2.578595	-2.093692
H	2.662837	-3.001767	1.517531	H	-0.645375	3.9048	-1.734037
H	2.189197	-3.522137	-0.114687	H	-1.300867	2.268792	-2.008092
H	-1.862086	-2.655381	-2.187688	H	1.24312	-1.59458	-2.021675
H	-4.156151	-1.717667	-2.438364	H	3.153503	-3.081738	-1.396545
H	-5.42401	0.514997	-0.023132	H	5.583172	-1.969576	0.895438
H	6.058003	-2.285922	0.977711	H	-3.894367	1.974688	0.670841
H	6.020494	-2.844346	-0.456196	H	-4.708092	3.057728	-0.108086
H	-0.049529	0.844254	0.539981	H	-2.493828	0.420486	-0.797294
H	0.279669	2.463721	-1.893709	H	-1.928361	-1.103687	1.792468
H	1.635393	2.729458	1.67318	H	-0.918109	-2.156759	-0.417433
H	3.613436	2.556083	-0.212347	H	-4.582725	-0.812101	0.311156
H	0.653976	0.351075	-3.067653	H	-3.709953	-1.742168	-1.615936
H	-0.747722	0.242733	-1.982853	H	-2.849106	-3.292505	-1.480638
H	-0.224626	3.621831	0.135208	H	-3.21714	0.561221	2.62561
H	2.746709	0.357917	0.592679	H	-1.274237	-1.998789	-2.815449
H	2.529326	4.315703	-1.264532	H	-5.152913	-2.161859	2.119044
H	1.840556	-0.757241	-1.206331	H	-0.876242	1.270522	0.480423

Table S.17: Transition state coordinates for nucleophilic addition of mannose at different bonding locations to the QM intermediate via the second step in the step-wise mechanism, at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

QM Intermediate + Mannose							
Carbon 2				Carbon 6			
C	4.024754	-1.04649	-0.165106	C	0.578964	3.609003	-0.301618
C	3.767485	0.327759	0.091398	C	-0.781936	3.471237	0.085581
C	4.708287	2.376627	0.844246	C	-2.679099	4.60898	0.956263
C	2.529777	0.862365	-0.167492	C	-1.429049	2.270116	-0.058105
C	1.50048	0.021618	-0.671594	C	-0.722385	1.162973	-0.603853
C	0.185643	0.486679	-0.991627	C	-1.296116	-0.119581	-0.833819
C	-0.091782	1.822554	-1.652938	C	-2.773858	-0.366701	-1.037968
C	-1.549448	2.289088	-1.584656	C	-3.190951	-1.839428	-1.002033
C	1.765489	-1.343413	-0.89757	C	0.626452	1.317545	-0.977807
C	3.022741	-1.868198	-0.667844	C	1.273778	2.527293	-0.832373
C	-2.813884	-1.301801	-0.024656	C	1.902572	-1.279538	1.351567
C	-2.825593	-0.366524	1.171739	C	3.385359	-1.416076	1.036866
C	-1.921538	-2.513052	0.265817	C	1.15502	-2.260133	0.447144
C	-1.416489	-0.021091	1.627502	C	3.65334	-1.21694	-0.452145
C	-0.623137	-1.30832	1.847881	C	2.694943	-2.026268	-1.332229
C	-1.746911	-3.398664	-0.949659	C	-0.316454	-2.401587	0.743542
O	4.844398	0.986929	0.574777	O	-1.30937	4.617376	0.575098
O	-1.687751	2.924515	-0.320256	O	-3.330217	-2.204972	0.364569
O	0.762079	2.858058	-1.252197	O	-3.601637	0.384786	-0.18733
O	5.231022	-1.544901	0.075455	O	1.186144	4.780169	-0.158034
O	-0.631511	-2.063691	0.64764	O	1.3365	-1.85984	-0.897489
O	-4.164472	-1.65609	-0.249498	O	1.736852	-1.585572	2.723289
O	-3.523956	0.82396	0.858819	O	4.15607	-0.447902	1.70915
O	-0.711072	0.810399	0.688214	O	3.477205	0.141269	-0.809635
O	0.671235	-1.080023	2.24362	O	2.770964	-1.641205	-2.64706
O	-1.319871	-2.572047	-2.027777	O	-0.975448	-1.117326	0.832362
O	-4.181562	3.457556	0.439296	O	-5.294113	-4.075054	0.239757
H	-2.61301	3.211695	-0.150116	H	-3.994173	-2.914994	0.447287
H	0.260725	3.443805	-0.670042	H	-3.974725	-0.220082	0.466242
H	4.441317	2.917691	-0.067019	H	-3.311695	4.35951	0.100672
H	3.952652	2.541891	1.616635	H	-2.845501	3.894692	1.76666
H	5.67829	2.710354	1.201669	H	-2.901995	5.615103	1.300234
H	2.330722	1.908695	0.001583	H	-2.46351	2.159343	0.227223
H	-0.476126	-0.304445	-1.340772	H	-0.658077	-0.798821	-1.398703
H	0.134538	1.587777	-2.705098	H	-2.925354	-0.009679	-2.068923
H	-1.735002	3.006026	-2.387038	H	-4.151003	-1.94652	-1.512081
H	-2.240239	1.445016	-1.679787	H	-2.448857	-2.462125	-1.512602
H	0.966578	-1.977478	-1.260293	H	1.162221	0.467622	-1.377604
H	3.251456	-2.909808	-0.8515	H	2.305978	2.659074	-1.129442
H	5.805578	-0.845191	0.41875	H	0.561969	5.422421	0.210804
H	-2.41578	-0.766985	-0.89164	H	1.573173	-0.258895	1.126338
H	-3.323044	-0.886749	2.002829	H	3.6984	-2.429672	1.326799
H	-2.37612	-3.107326	1.072443	H	1.579125	-3.266986	0.597423
H	-1.4531	0.537582	2.567672	H	4.677071	-1.535018	-0.68039
H	-1.102924	-1.886021	2.648384	H	2.937019	-3.094177	-1.272153
H	-2.698344	-3.889497	-1.181699	H	-0.437882	-2.896846	1.70938
H	-1.001187	-4.16505	-0.719885	H	-0.792395	-3.007508	-0.031135
H	-4.281012	-1.963114	-1.152944	H	1.013326	-1.067767	3.084862
H	-4.346933	0.554133	0.429284	H	3.995252	-0.53099	2.654963
H	-1.200346	1.673335	0.551414	H	3.993996	0.670993	-0.19001
H	1.102151	-0.49373	1.609244	H	2.975965	-0.697729	-2.67533

QM Intermediate + Mannose							
	Carbon 2				Carbon 6		
H	-1.179788	-3.113585	-2.809007	H	-1.881003	-1.324932	1.128912
H	-4.26118	2.829762	1.166565	H	-6.197724	-3.949764	0.542923
H	-4.623418	4.269079	0.702983	H	-5.196676	-5.015464	0.066134

Table S.18: Transition state coordinates for nucleophilic addition of glucose at different bonding locations to the QM intermediate via the second step in the step-wise mechanism, at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

QM Intermediate + Glucose							
	Carbon 3				Carbon 6		
C	3.896452	-2.094816	0.101961	C	1.473509	3.217117	-0.487452
C	4.072753	-0.746962	0.510019	C	0.208916	3.362409	0.147684
C	5.442623	0.747340	1.752231	C	-1.154295	4.806342	1.453719
C	3.194106	0.224443	0.098594	C	-0.743637	2.384548	0.026962
C	2.108964	-0.130861	-0.745589	C	-0.449119	1.212245	-0.724617
C	1.158305	0.801545	-1.249204	C	-1.385862	0.173509	-0.957927
C	1.393089	2.281970	-1.429461	C	-2.877999	0.372842	-1.083940
C	0.109852	3.090440	-1.642990	C	-3.705637	-0.917058	-1.061695
C	1.948333	-1.475281	-1.137327	C	0.815261	1.078388	-1.338473
C	2.832729	-2.449574	-0.724964	C	1.760535	2.079065	-1.235680
C	-1.629876	-1.038897	-0.598396	C	1.367913	-1.640786	1.431027
C	-1.601019	0.370430	-0.025716	C	2.841865	-1.872295	1.132938
C	-3.045471	-1.623937	-0.485985	C	0.544099	-2.438801	0.414294
C	-2.273064	0.426189	1.339544	C	3.125953	-1.480056	-0.304372
C	-3.647791	-0.225195	1.298690	C	2.188604	-2.213238	-1.257597
C	-3.102524	-3.098441	-0.859225	C	-0.944913	-2.332233	0.619249
O	5.156258	-0.570925	1.299498	O	0.089972	4.527535	0.824022
O	-0.385458	3.387628	-0.344196	O	-3.924901	-1.255736	0.301164
O	2.182030	2.876639	-0.433057	O	-3.416929	1.309444	-0.189465
O	4.753926	-3.022524	0.505012	O	2.379366	4.177048	-0.371864
O	-3.043433	3.497494	-0.363667	O	0.841065	-1.994336	-0.898229
O	-3.505572	-1.552806	0.853191	O	1.109653	-2.088077	2.748347
O	-1.234813	-0.931993	-1.958538	O	3.682553	-1.086012	1.943930
O	-0.248176	0.828302	0.146533	O	2.293378	-1.714340	-2.552263
O	-2.366695	1.790031	1.714709	O	-1.352600	-0.953653	0.718787
O	-4.117913	-0.211717	2.597408	O	-6.34237	-2.472342	0.186043
O	-4.417247	-3.579713	-0.824542	O	4.430533	-1.812641	-0.711702
H	-1.312590	3.697192	-0.394396	H	-4.763206	-1.747995	0.388588
H	1.607752	3.428038	0.114112	H	-3.915814	0.819051	0.476063
H	5.613131	1.413983	0.903275	H	-1.959676	4.824902	0.715055
H	4.622588	1.124483	2.368349	H	-1.366471	4.059950	2.223575
H	6.347094	0.670451	2.348978	H	-1.047305	5.786350	1.910275
H	3.320626	1.253578	0.396761	H	-1.713904	2.493816	0.485934
H	0.474552	0.394531	-1.988625	H	-1.004252	-0.645562	-1.566443
H	1.960849	2.304080	-2.374068	H	-2.957084	0.788073	-2.101919
H	0.350632	4.015362	-2.172104	H	-4.663094	-0.732124	-1.553482
H	-0.616797	2.517624	-2.229241	H	-3.182979	-1.718549	-1.593530
H	1.120717	-1.734344	-1.786627	H	1.037721	0.191519	-1.920552

QM Intermediate + Glucose							
	Carbon 3				Carbon 6		
H	2.737168	-3.483826	-1.029017	H	2.724334	2.007108	-1.724043
H	5.435422	-2.612297	1.057839	H	2.019021	4.897964	0.165403
H	-3.133316	3.042909	0.488161	H	1.141958	-0.573423	1.318507
H	-3.755522	4.138024	-0.436604	H	3.064883	-2.940992	1.270246
H	-0.317645	1.792521	0.347308	H	0.800204	-3.504934	0.518136
H	-0.926635	-1.668912	-0.034936	H	2.405020	-3.293160	-1.228803
H	-2.124328	1.041762	-0.721081	H	-1.213852	-2.832957	1.552132
H	-3.718708	-1.056378	-1.145999	H	-1.465839	-2.816849	-0.211922
H	-1.667062	-0.131909	2.062601	H	0.528183	-1.469396	3.195720
H	-4.317656	0.321452	0.614060	H	3.593631	-1.381258	2.855716
H	-2.444478	-3.655931	-0.179545	H	3.222877	-1.761644	-2.807957
H	-2.750856	-3.253013	-1.883224	H	-2.296451	-0.984660	0.969571
H	-1.426692	-1.751187	-2.424740	H	-6.526037	-3.407112	0.057152
H	-2.653717	1.829130	2.634800	H	-7.171108	-2.071697	0.463430
H	-5.018650	-0.549570	2.629862	H	2.94633	-0.401295	-0.408763
H	-4.733888	-3.521450	0.082201	H	5.054003	-1.432228	-0.082980

Table S.19: Transition state coordinates for nucleophilic addition of galactose to the QM intermediate via the second step in the step-wise mechanism, at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

QM Intermediate + Galactose			
	Carbon 6		
C	0.899543	3.304416	-1.163182
C	0.403339	3.037047	0.147217
C	0.833484	3.313336	2.465920
C	-0.671901	2.210364	0.319094
C	-1.271400	1.604882	-0.824152
C	-2.394835	0.771450	-0.729814
C	-3.320044	0.706868	0.471938
C	-4.538244	-0.180886	0.240347
C	-0.749959	1.869631	-2.113155
C	0.314579	2.722376	-2.286955
C	1.200238	-0.708346	0.385442
C	2.449132	-1.071923	1.176463
C	0.598180	-1.971378	-0.232115
C	3.396426	-1.888399	0.314977
C	2.666167	-3.101284	-0.243032
C	-0.551105	-1.640240	-1.172108
O	1.111044	3.661361	1.111517
O	-4.122639	-1.519125	0.024256
O	-2.645993	0.403808	1.666904
O	1.939351	4.106796	-1.308236
O	-6.388000	-2.936443	0.576292
O	1.545151	-2.680159	-1.002024
O	1.521310	0.194162	-0.650061
O	3.048382	0.145428	1.579719
O	4.475617	-2.252089	1.143512
O	3.554226	-3.758159	-1.072759

QM Intermediate + Galactose Carbon 6			
O	-1.641518	-1.132209	-0.399699
H	-4.873805	-2.120112	0.176985
H	-2.247463	-0.468602	1.561018
H	-0.188019	3.595463	2.731212
H	0.988560	2.241064	2.612357
H	1.538595	3.876893	3.070222
H	-1.063570	1.991888	1.303531
H	-2.834290	0.456727	-1.674196
H	-3.701923	1.730286	0.587284
H	-5.172710	-0.117979	1.128022
H	-5.101209	0.194823	-0.622827
H	-1.214450	1.406499	-2.976980
H	0.724078	2.948352	-3.262609
H	2.227753	4.422462	-0.437778
H	-7.063121	-3.222459	-0.044964
H	-6.583827	-3.374870	1.408792
H	0.461133	-0.258310	1.066441
H	2.169387	-1.669964	2.054367
H	0.219016	-2.607522	0.583794
H	3.730320	-1.289854	-0.541568
H	2.320790	-3.751668	0.578177
H	-0.855238	-2.533812	-1.718373
H	-0.227154	-0.872971	-1.880774
H	2.232794	0.755825	-0.317353
H	3.929229	-0.058083	1.916505
H	5.114259	-2.748388	0.620838
H	3.167886	-4.583155	-1.381822
H	-2.454059	-1.677002	-0.436986

Table S.20: Transition state coordinates for nucleophilic addition of glucuronic acid to the QM intermediate via the second step in the step-wise mechanism, at a M06-2X/6-311++G(d,p) level of theory in the gas phase.

QM Intermediate + Glucuronic Acid			
C	-3.721499	-2.422485	-0.147752
C	-4.042104	-1.077495	-0.441350
C	-5.682005	0.390003	-1.345109
C	-3.152045	-0.069832	-0.127569
C	-1.925103	-0.396001	0.481539
C	-0.939472	0.656234	0.804251
C	-1.496358	2.055166	1.197178
C	-0.556890	2.762980	2.156675
C	-1.609933	-1.721787	0.762370
C	-2.512491	-2.732761	0.452076
C	4.161578	-1.004744	-0.546937
C	3.232256	0.059055	-1.124146
C	3.363440	-2.162603	0.022144
C	2.178903	0.428966	-0.044023

QM Intermediate + Glucuronic Acid			
C	2.397122	-1.628342	1.064410
C	1.165902	1.376588	-0.630055
O	-5.256657	-0.923517	-1.023384
O	0.764138	2.730943	1.647259
O	-1.616907	2.767885	-0.060338
O	-4.590753	-3.397005	-0.444899
O	1.515047	-0.704469	0.442500
O	5.008185	-1.533698	-1.534312
O	4.048473	1.149884	-1.459532
O	4.175527	-3.098331	0.683489
O	1.577192	-2.610453	1.588936
O	-0.188112	1.029081	-0.515450
O	1.421288	2.352378	-1.265834
O	0.175006	4.788954	-0.238909
H	0.978372	3.599380	1.286862
H	-1.190833	3.653309	-0.031756
H	-5.743893	1.006222	-0.443594
H	-5.001352	0.848572	-2.067980
H	-6.669772	0.289057	-1.786677
H	-3.399608	0.960929	-0.355364
H	-0.166363	0.312982	1.483001
H	-2.492393	1.948619	1.626104
H	-0.896203	3.788015	2.335651
H	-0.577000	2.231955	3.111725
H	-0.656522	-1.971521	1.214105
H	-2.295252	-3.770812	0.669552
H	-5.376857	-3.009800	-0.851792
H	4.747385	-0.541761	0.261075
H	2.722058	-0.356452	-2.002682
H	2.779297	-2.636510	-0.778778
H	2.687643	0.986616	0.757738
H	2.953036	-1.108914	1.861606
H	5.593328	-0.838266	-1.852799
H	3.562913	1.776579	-2.004198
H	4.857695	-3.404203	0.075142
H	2.115015	-3.400187	1.730370
H	-0.809651	1.949666	-0.689731
H	0.125637	5.744607	-0.347859
H	0.726100	4.451055	-0.958148

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