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

SUPPLEMENTARY INFORMATION

Isolating key reaction energetics with prediction of thermodynamic properties during hardwood lignin pyrolysis using model oligomer

Tanzina Azad[1], Maria L. Auad[1, 2], Thomas Elder[3], Andrew J. Adamczyk[1,]*

1Department of Chemical Engineering, Auburn University, Auburn, AL, USA.

2Director, Center for Polymer and Advanced Composites, Auburn, AL, USA.

3United States Department of Agriculture (USDA) Forest Service, Southern Research Station, Auburn, AL, USA.

*Corresponding author: aja0056@auburn.edu

Tables

Table #	Title
S1	Variation of Reaction enthalpies along 9 pathways in the full range of temperature considered in this study (After performing conformational sampling)
S2	Heat capacity C_p (Cal/mol. K) variation with temperature (K) for product 1 structures
S3	Heat capacity C_p (Cal/mol. K) variation with temperature (K) for product 2 structures
S4	Entropy S (Cal/mol. K) variation with temperature (K) for product 1 structures
S5	Entropy S (Cal/mol. K) variation with temperature (K) for product 2 structures
S6	Gibbs free energy G (Hartree) variation with temperature (K) for product 1 structures
S7	Gibbs free energy G (Hartree) variation with temperature (K) for product 2 structures
S8	Variation of Gibbs free energy change ΔG (Hartree) with temperature (K) for 9 reaction pathways
S9	Heat capacity Cp (Cal/mol. K), Entropy S (Cal/mol. K) and Gibbs free energy G (Hartree) variation with temperature (K) for 10-mer reactant structure
S10a)	Spin density and Molecular orbital plots for product 1 species
S10b)	Spin density and Molecular orbital plots for product 2 species
S11	Key results of the Paired T test to identify if statistically significant variation exists between the mean BDEs calculated using soft and hardwood model lignin decamers

Figure #	Title
S1	Heat capacity variation with temperature for 10-mer reactant structure
S2	Entropy variation with temperature for 10-mer reactant structure
S3	Gibbs free energy variation with temperature for 10-mer reactant structure
S4	Gibbs free energy variation with temperature for product 1 radical species
S5	Gibbs free energy variation with temperature for product 2 radical species
S6	Comparison between the current study for BDEs for the hardwood model lignin and the calculated BDEs with a softwood model lignin in our previous study
S7	Comparison between non-bonded interaction energies for all structures between current study (hardwood model lignin with S units) and previous study (softwood model lignin with G units)

Computational methodology (Extended)

Bond dissociation enthalpies were calculated as the difference of the sum of the standard enthalpies of formation of the product fragments and the standard enthalpy of formation of the reactant, as shown in Equation 5,

$$BDE_{298\ (Reactant)} = [\Delta H^{o}_{f,298\ (Product\ 1)} + \Delta H^{o}_{f,298\ (Product\ 2)}] - \Delta H^{o}_{f,298\ (Reactant)} \quad [5]$$

Where $\Delta H^{o}_{f,298}$ is the standard enthalpy of formation of the radical species Products 1 and 2, and the 10-mer lignin molecule as reactant. These standard enthalpy of formation values are calculated using a hybrid methodology based on quantum chemical calculations, statistical thermodynamics, and experimental atomization energies as performed in previous work from our group[64].

The basis for these standard enthalpy of formation values were calculated using Equation [2, 2.1-2.4] to account for the enthalpy correction, then this correction was added to the electronic energy (E_{el}) and zero point energies (ZPE) using Equation [6],

$$H_{298} = E_{el} + ZPE + H\ (T) \quad [6]$$

The standard enthalpy of formation of a given species ($C_xH_yO_z$) was then calculated from its atomization energy using Equation 7,

$$\Delta H^{o}_{f,298}(C_xH_yO_z) = [x\Delta H^{o}_{f,298}(C) + y\Delta H^{o}_{f,298}(H) + z\Delta H^{o}_{f,298}(O)] - \Delta H^{o}_{a,298}(C_xH_yO_z) \quad [7]$$

Where the enthalpies of formation of atomic C, H and O are the experimental values obtained from the NIST-JANAF thermochemical tables ($\Delta H^{o}_{f,298}(C)$ = 172.001 kcal mol^{-1}, $\Delta H^{o}_{f,298}(H)$ = 52.32 kcal mol^{-1}, $\Delta H^{o}_{f,298}(O)$ = 59.803 kcal mol^{-1}) and $\Delta H^{o}_{a,298}(C_xH_yO_z)$ is the atomization enthalpy defined as the enthalpy change upon decomposition of a molecule into its component atoms, which can be evaluated as Equation 7.1,

$$\Delta H^{o}_{a,298}(C_xH_yO_z) = [xH_{298}(C) + yH_{298}(H) + zH_{298}(O)] - H_{298}(C_xH_yO_z) \quad [7.1]$$

Where $H_{298}(C)$, $H_{298}(H)$ and $H_{298}(O)$ are the enthalpies of atomic C, H and O at 298K, respectively, and $H_{298}(C_xH_yO_z)$ is the enthalpy of $C_xH_yO_z$ at the same temperature. These enthalpies can be calculated as previously mentioned in Equation [2, 2.1-2.4, 6]. These quantities are obtained from quantum chemical calculations and statistical thermodynamics.

The enthalpy of reaction at the elevated temperature, or BDE at temperature T, is then calculated using the calculated BDE_{298K} and temperature-dependent heat capacity values following Equation 8,

$$BDE_T = BDE_{298K} + \int_{298K}^{T} \Delta C_{P,Rxn}(T)dT \quad [8]$$

Where $\Delta C_{p,Rxn}$ (T) is the temperature-dependent polynomial defined as the difference between sum of temperature-dependent standard heat capacities of the products and the temperature-dependent standard heat capacity of the reactant.

Vibrational frequency calculations of these optimized structures were performed to determine thermochemical parameters - enthalpy (H), entropy (S), free energy (G), and heat capacity at constant pressure (C_p). These values reported in this work are based on the standard statistical thermodynamic calculations using the standard molecular partition functions of polyatomic gas molecules[70]. The enthalpy correction, H, using the ideal gas approximation is given by Equation 2,

$$H(T) = E_{vib}(T) + E_{rot}(T) + E_{trans}(T) + RT \quad [2],$$

where the subscripts represent vibrational, rotational, and translational contributions, respectively, and R is the ideal gas constant. The contributions are given by,

$$E_{trans} = \frac{3}{2}RT \quad [2.1]$$

$$E_{rot\ (linear)} = RT \quad [2.2]$$

$$E_{rot\ (nonlinear)} = \frac{3}{2}RT \quad [2.3]$$

$$E_{vib} = \frac{R}{k}\frac{1}{2}\sum_i h\nu_i + \frac{R}{k}\sum_i \frac{h\nu_i \exp\left(-\frac{h\nu_i}{kT}\right)}{\left[1 - \exp\left(-\frac{h\nu_i}{kT}\right)\right]} \quad [2.4]$$

Where, k and h are the Boltzmann and Planck's constants, respectively and ν_i is the individual vibrational frequency.

Similarly, heat capacity at constant pressure (C_p) calculations are based on the ideal gas approximation and is given by Equation 3,

$C_p(T) = C_{p,vib}(T) + C_{p,rot}(T) + C_{p,trans}(T) + RT$ [3]

The contributions are given by,

$$C_{p,trans} = \frac{5}{2}RT \quad [3.1]$$

$C_{p,rot\ (linear)} = R$ [3.2]

$$C_{p,rot\ (nonlinear)} = \frac{3}{2}RT \quad [3.3]$$

$$C_{p,vib} = R\sum_i \frac{(\frac{h\nu_i}{kT})^2 \exp(-\frac{h\nu_i}{kT})}{[1-\exp(-\frac{h\nu_i}{kT})]^2} \quad [3.4]$$

The entropy correction is given by Equation 4,

$S(T) = S_{vib}(T) + S_{rot}(T) + S_{trans}(T) + RT$ [4]

The contributions are given by,

$$S_{trans} = \frac{5}{2}R\ln T + \frac{3}{2}R\ln \omega - R\ln p - 2.31482 \quad [4.1]$$

$$S_{rot\ (linear)} = R \ln \frac{8\prod^2 IkT}{\sigma h^2} + R \quad [4.2]$$

$$S_{rot\ (nonlinear)} = \frac{R}{2} \ln [\frac{\prod}{\sqrt{\sigma}} \frac{8\prod^2 cI_A}{h} \frac{8\prod^2 cI_B}{h} \frac{8\prod^2 cI_C}{h} (\frac{Tk_B}{hc})^3] + \frac{3}{2}R \quad [4.3]$$

$$S_{vib} = R\sum_i \frac{\frac{h\nu_i}{k_B T}\exp\left(-\frac{h\nu_i}{k_B T}\right)}{1-\exp\left(-\frac{h\nu_i}{k_B T}\right)} - R\sum_i \ln\left[1-\exp\left(-\frac{h\nu_i}{k_B T}\right)\right] \quad [4.4]$$

Where ω denotes molecular weight, I_x is the moment of inertia about axis X, and σ is the rotational symmetry number.

Table S1. Variation of Reaction enthalpies (kcal mol^{-1}) along 9 pathways in the full range of temperature considered in this study

T(K)	RXN_S1	RXN_S2	RXN_S3	RXN_S4	RXN_S5	RXN_S6	RXN_S7	RXN_S8	RXN_S9
25	69.0957656	58.92284	45.88937	47.80884	67.47497	66.46422	77.66425	64.30142	68.08188
50	69.2457656	59.11784	46.04337	47.91984	67.57997	66.58022	77.60325	64.33442	68.16088
75	69.4367656	59.35684	46.22537	48.02884	67.68197	66.65622	77.52625	64.41042	68.20988
100	69.6727656	59.62984	46.45937	48.14984	67.77297	66.71922	77.44425	64.49342	68.24888
125	69.9407656	59.93584	46.73637	48.27684	67.83997	66.77022	77.34825	64.55242	68.27488
150	70.2317656	60.26884	47.04537	48.40784	67.88897	66.81522	77.24325	64.57742	68.28788
175	70.5387656	60.63184	47.38137	48.54784	67.91797	66.85622	77.12925	64.57442	68.28588
200	70.8567656	61.01584	47.73937	48.69884	67.93197	66.89922	77.00725	64.54342	68.27288
225	71.1827656	61.42084	48.11537	48.86284	67.92997	66.94522	76.87725	64.49042	68.24888
250	71.5087656	61.84084	48.50637	49.04084	67.91597	66.99622	76.73825	64.41642	68.21588
275	71.8367656	62.27384	48.90837	49.23184	67.88897	67.05322	76.59125	64.32642	68.17488
298.15	**72.1387656**	**62.68084**	**49.28637**	**49.41784**	**67.85297**	**67.10922**	**76.44825**	**64.23042**	**68.13088**
300	72.1617656	62.71384	49.31637	49.43484	67.84897	67.11522	76.43625	64.22242	68.12588
325	72.4867656	63.16184	49.73337	49.64584	67.79797	67.18022	76.27225	64.10742	68.07088
350	72.8067656	63.61284	50.15337	49.86584	67.73497	67.25022	76.10025	63.98142	68.00888
375	73.1227656	64.06684	50.57537	50.09284	67.66297	67.32022	75.92025	63.84442	67.94188
400	73.4347656	64.52384	50.99937	50.32484	67.57997	67.39422	75.73325	63.70142	67.87088
425	73.7437656	64.97984	51.42437	50.56084	67.48797	67.46722	75.53825	63.54942	67.79388
450	74.0487656	65.43584	51.84937	50.80084	67.38697	67.54022	75.33725	63.39142	67.71288
475	74.3507656	65.89184	52.27437	51.04284	67.27697	67.61222	75.13025	63.22842	67.62788
500	74.6477656	66.34484	52.69837	51.28584	67.16097	67.68522	74.91825	63.05842	67.54088
525	74.9417656	66.79584	53.12137	51.53084	67.03597	67.75522	74.70025	62.88442	67.44888
550	75.2317656	67.24484	53.54237	51.77684	66.90597	67.82322	74.47925	62.70442	67.35488
575	75.5197656	67.69284	53.96137	52.02384	66.76897	67.89122	74.25325	62.52042	67.25788
600	75.8057656	68.13784	54.38037	52.27284	66.62597	67.95722	74.02325	62.33542	67.15788
625	76.0877656	68.58184	54.79737	52.52184	66.47697	68.02122	73.79125	62.14442	67.05688
650	76.3677656	69.02184	55.21237	52.77084	66.32397	68.08522	73.55525	61.95042	66.95288
675	76.6447656	69.45984	55.62637	53.02084	66.16397	68.14522	73.31525	61.75342	66.84588
700	76.9207656	69.89584	56.03937	53.26984	66.00097	68.20422	73.07525	61.55342	66.73888
725	77.1947656	70.32984	56.45037	53.52084	65.83397	68.26122	72.83125	61.35242	66.62988
750	77.4667656	70.76284	56.86037	53.77084	65.66197	68.31922	72.58525	61.14842	66.51888
775	77.7357656	71.19184	57.26837	54.02184	65.48597	68.37322	72.33725	60.94142	66.40588
800	78.0047656	71.61984	57.67637	54.27184	65.30797	68.42622	72.08825	60.73242	66.29188
825	78.2727656	72.04684	58.08237	54.52384	65.12497	68.47822	71.83725	60.52242	66.17688
850	78.5377656	72.47084	58.48837	54.77484	64.94097	68.53022	71.58525	60.30942	66.06088
875	78.8047656	72.89484	58.89337	55.02684	64.75297	68.58022	71.33225	60.09642	65.94388
900	79.0677656	73.31684	59.29737	55.27684	64.56197	68.62722	71.07825	59.88142	65.82488

925	79.3297656	73.73784	59.70037	55.52884	64.36897	68.67522	70.82125	59.66442	65.70588
950	79.5917656	74.15584	60.10237	55.77984	64.17297	68.72022	70.56325	59.44642	65.58488
975	79.8527656	74.57384	60.50437	56.03284	63.97297	68.76622	70.30525	59.22642	65.46388
1000	80.1127656	74.98984	60.90437	56.28384	63.77397	68.81022	70.04625	59.00542	65.34188

Table S2. Heat capacity C_p (Cal mol^{-1} K^{-1}) variation with temperature (K) for product 1 structures

Temperature (K)	Product1: 1-mer	Product1: 2-mer	Product1: 3-mer	Product1: 4-mer	Product1: 5-mer	Product1: 6-mer	Product1: 7-mer	Product1: 8-mer	Product1: 9-mer
25	11.418	13.831	21.982	25.242	25.585	33.735	31.492	35.555	43.624
50	15.614	22.687	36.557	45.648	51.519	68.716	70.708	76.661	92.006
75	20.002	32.543	52.149	66.869	78.932	104.352	111.696	117.294	143.987
100	24.478	42.618	67.704	87.858	105.589	138.375	150.901	154.356	194.436
125	28.779	52.292	82.496	107.708	130.765	169.984	187.401	188.323	241.58
150	32.84	61.428	96.411	126.339	154.494	199.395	221.404	220.161	285.544
175	36.72	70.143	109.664	144.091	177.164	227.248	253.62	250.888	327.224
200	40.51	78.614	122.539	161.366	199.219	254.204	284.811	281.365	367.597
225	44.28	86.983	135.256	178.465	221.003	280.747	315.547	312.157	407.396
250	48.064	95.325	147.933	195.539	242.697	307.132	346.13	343.503	447.008
275	51.869	103.656	160.593	212.609	264.333	333.414	376.626	375.371	486.512
298.15	55.395	111.333	172.266	228.355	284.251	357.587	404.703	405.163	522.883
300	55.676	111.944	173.194	229.608	285.835	359.508	406.935	407.548	525.775
325	59.458	120.138	185.656	246.422	307.069	385.257	436.87	439.733	564.552
350	63.186	128.179	197.886	262.924	327.884	410.479	466.217	471.608	602.564
375	66.828	136.01	209.802	278.998	348.141	435.009	494.777	502.883	639.553
400	70.364	143.587	221.334	294.549	367.727	458.71	522.389	533.323	675.308
425	73.774	150.878	232.431	309.51	386.559	481.486	548.936	562.752	709.68
450	77.048	157.861	243.061	323.838	404.585	503.278	574.345	591.053	742.574
475	80.18	164.527	253.211	337.513	421.784	524.059	598.585	618.16	773.948
500	83.169	170.875	262.877	350.533	438.154	543.83	621.652	644.047	803.801
525	86.014	176.912	272.069	362.909	453.71	562.611	643.57	668.718	832.162
550	88.722	182.646	280.8	374.662	468.479	580.436	664.378	692.201	859.082
575	91.296	188.091	289.092	385.82	482.498	597.35	684.125	714.538	884.625
600	93.744	193.262	296.967	396.414	495.804	613.401	702.867	735.781	908.866
625	96.073	198.174	304.447	406.475	508.441	628.64	720.663	755.986	931.879
650	98.288	202.844	311.559	416.038	520.448	643.116	737.571	775.211	953.741
675	100.398	207.287	318.324	425.133	531.867	656.881	753.649	793.515	974.526
700	102.409	211.517	324.764	433.79	542.735	669.979	768.951	810.953	994.305
725	104.327	215.548	330.902	442.039	553.088	682.455	783.527	827.578	1013.144
750	106.157	219.393	336.756	449.905	562.961	694.35	797.425	843.44	1031.105

775	107.906	223.064	342.344	457.413	572.384	705.701	810.689	858.585	1048.243
800	109.578	226.571	347.682	464.585	581.384	716.542	823.358	873.057	1064.611
825	111.178	229.924	352.787	471.443	589.989	726.906	835.469	886.895	1080.257
850	112.709	233.133	357.671	478.004	598.222	736.819	847.056	900.136	1095.225
875	114.176	236.206	362.348	484.285	606.104	746.31	858.149	912.814	1109.553
900	115.582	239.15	366.829	490.304	613.656	755.403	868.777	924.96	1123.279
925	116.931	241.973	371.125	496.074	620.896	764.118	878.965	936.602	1136.436
950	118.225	244.681	375.245	501.608	627.84	772.477	888.737	947.767	1149.055
975	119.468	247.28	379.2	506.919	634.504	780.498	898.115	958.48	1161.163
1000	120.661	249.775	382.996	512.018	640.903	788.199	907.118	968.763	1172.788

Table S3. Heat capacity C_p (Cal mol^{-1} K^{-1}) variation with temperature (K) for product 2 structures

Temperature (K)	Product 2: 1-mer	Product 2: 2-mer	Product 2:3-mer	Product 2: 4-mer	Product 2:5-mer	Product 2: 6-mer	Product 2:7-mer	Product 2: 8-mer	Product 2: 9-mer
25	11.669	13.208	17.941	22.352	29.538	30.6	32.35	40.48	41.503
50	16.17	21.31	32.251	41.513	58.531	62.143	65.458	81.774	86.834
75	21.033	30.765	48.399	62.744	88.263	96.124	100.751	122.318	133.165
100	26.098	40.093	64.751	84.347	116.825	129.637	134.095	160.476	177.165
125	31.085	48.815	80.488	105.091	143.448	161.256	164.709	195.931	217.887
150	35.888	56.998	95.422	124.689	168.248	190.88	193.273	229.246	255.916
175	40.525	64.866	109.693	143.361	191.723	219.008	220.734	261.303	292.316
200	45.053	72.642	123.533	161.459	214.416	246.241	247.899	292.938	328.099
225	49.523	80.476	137.141	179.277	236.743	273.046	275.291	324.732	363.967
250	53.964	88.432	150.629	196.98	258.927	299.679	303.134	356.949	400.253
275	58.378	96.505	164.024	214.605	281.02	326.2	331.405	389.58	436.97
298.15	62.426	104.04	176.313	230.811	301.339	350.588	357.809	419.998	471.18
300	62.747	104.643	177.288	232.098	302.954	352.527	359.923	422.43	473.916
325	67.048	112.77	190.35	249.358	324.595	378.505	388.426	455.213	510.777
350	71.251	120.807	203.125	266.264	345.792	403.954	416.639	487.62	547.216
375	75.33	128.684	215.534	282.705	366.403	428.708	444.31	519.372	582.922
400	79.264	136.342	227.515	298.592	386.315	452.628	471.233	550.24	617.64
425	83.041	143.739	239.022	313.86	405.444	475.618	497.257	580.056	651.179
450	86.65	150.848	250.028	328.468	423.742	497.618	522.279	608.706	683.414
475	90.09	157.651	260.522	342.401	441.186	518.599	546.243	636.129	714.274
500	93.362	164.145	270.505	355.659	457.777	538.563	569.126	662.304	743.735
525	96.469	170.332	279.99	368.254	473.534	557.529	590.934	687.238	771.804
550	99.419	176.219	288.993	380.211	488.487	575.533	611.691	710.963	798.515
575	102.218	181.817	297.539	391.558	502.671	592.619	631.435	733.524	823.919
600	104.876	187.141	305.65	402.329	516.13	608.834	650.213	754.973	848.075
625	107.402	192.204	313.353	412.557	528.907	624.232	668.074	775.371	871.048
650	109.803	197.021	320.674	422.276	541.044	638.861	685.07	794.777	892.905

675	112.088	201.609	327.638	431.519	552.583	652.773	701.252	813.25	913.714
700	114.265	205.979	334.267	440.317	563.564	666.014	716.67	830.847	933.537
725	116.341	210.148	340.584	448.7	574.025	678.629	731.37	847.623	952.435
750	118.322	214.126	346.609	456.695	583.999	690.658	745.396	863.629	970.467
775	120.216	217.925	352.361	464.326	593.519	702.139	758.79	878.911	987.684
800	122.027	221.557	357.857	471.617	602.613	713.108	771.59	893.514	1004.136
825	123.76	225.031	363.114	478.588	611.308	723.594	783.831	907.479	1019.869
850	125.421	228.357	368.144	485.26	619.629	733.629	795.545	920.841	1034.923
875	127.013	231.543	372.962	491.648	627.596	743.237	806.762	933.636	1049.338
900	128.541	234.597	377.579	497.771	635.231	752.444	817.51	945.894	1063.149
925	130.007	237.526	382.006	503.641	642.552	761.271	827.814	957.646	1076.389
950	131.415	240.336	386.254	509.273	649.576	769.739	837.696	968.918	1089.087
975	132.768	243.035	390.332	514.679	656.318	777.867	847.18	979.734	1101.273
1000	134.069	245.626	394.248	519.871	662.794	785.673	856.285	990.118	1112.971

Table S4. Entropy S (Cal mol^{-1} K^{-1}) variation with temperature (K) for product 1 structures

Temperature (K)	Product 1: 1-mer	Product 1: 2-mer	Product 1:3-mer	Product 1: 4-mer	Product 1: 5-mer	Product 1: 6-mer	Product 1:7-mer	Product 1: 8-mer	Product 1:9-mer
25	57.093	64.211	77.468	80.423	81.109	85.583	86.311	94.319	99.15
50	66.293	76.453	97.092	104.141	106.599	119.583	119.862	131.306	143.804
75	73.446	87.492	114.845	126.646	132.672	154.208	156.307	170.184	190.927
100	79.814	98.239	131.99	148.778	159.061	188.942	193.87	209.087	239.328
125	85.743	108.798	148.704	170.539	185.356	223.26	231.514	247.228	287.844
150	91.352	119.147	164.987	191.84	211.315	256.881	268.72	284.403	335.818
175	96.708	129.275	180.851	212.657	236.843	289.725	305.287	320.656	382.987
200	101.859	139.196	196.338	233.029	261.945	321.836	341.197	356.146	429.327
225	106.848	148.939	211.506	253.023	286.668	353.312	376.52	391.059	474.925
250	111.709	158.535	226.412	272.71	311.077	384.258	411.35	425.565	519.899
275	116.469	168.012	241.106	292.147	335.223	414.764	445.771	459.796	564.358
298.15	120.801	176.696	254.552	309.96	357.383	442.678	477.333	491.322	605.132
300	121.145	177.387	255.62	311.376	359.147	444.896	479.843	493.836	608.376
325	125.751	186.671	269.977	330.42	382.866	474.691	513.6	527.729	651.995
350	130.294	195.87	284.184	349.288	406.387	504.169	547.054	561.486	695.23
375	134.778	204.982	298.246	367.979	429.703	533.33	580.199	595.094	738.07
400	139.205	214.003	312.156	386.485	452.801	562.166	613.018	628.526	780.495
425	143.574	222.928	325.91	404.794	475.663	590.663	645.49	661.747	822.473
450	147.884	231.751	339.498	422.893	498.273	618.806	677.591	694.72	863.976
475	152.134	240.466	352.914	440.772	520.612	646.578	709.299	727.408	904.972
500	156.323	249.068	366.15	458.418	542.666	673.966	740.594	759.779	945.436
525	160.451	257.553	379.2	475.822	564.424	700.958	771.459	791.804	985.346
550	164.515	265.916	392.06	492.979	585.874	727.546	801.882	823.459	1024.685

575	168.516	274.156	404.727	509.881	607.011	753.723	831.855	854.726	1063.441
600	172.454	282.271	417.198	526.527	627.829	779.489	861.37	885.589	1101.607
625	176.328	290.261	429.474	542.915	648.328	804.84	890.426	916.038	1139.179
650	180.14	298.126	441.554	559.046	668.505	829.781	919.024	946.066	1176.158
675	183.889	305.865	453.44	574.919	688.363	854.312	947.164	975.669	1212.545
700	187.577	313.481	465.134	590.538	707.903	878.44	974.851	1004.845	1248.347
725	191.204	320.974	476.639	605.905	727.131	902.17	1002.091	1033.595	1283.57
750	194.772	328.347	487.956	621.025	746.049	925.508	1028.89	1061.92	1318.222
775	198.282	335.601	499.09	635.9	764.663	948.462	1055.255	1089.825	1352.313
800	201.735	342.739	510.044	650.537	782.979	971.04	1081.195	1117.314	1385.854
825	205.131	349.762	520.822	664.938	801.002	993.249	1106.718	1144.393	1418.855
850	208.473	356.674	531.426	679.11	818.738	1015.098	1131.832	1171.068	1451.328
875	211.761	363.477	541.862	693.058	836.193	1036.594	1156.548	1197.345	1483.284
900	214.998	370.172	552.133	706.786	853.374	1057.747	1180.873	1223.231	1514.735
925	218.183	376.764	562.243	720.299	870.287	1078.564	1204.816	1248.734	1545.692
950	221.319	383.253	572.195	733.602	886.938	1099.053	1228.387	1273.861	1576.168
975	224.406	389.642	581.994	746.701	903.334	1119.223	1251.595	1298.619	1606.173
1000	227.446	395.935	591.643	759.599	919.479	1139.081	1274.447	1323.016	1635.718

Table S5. Entropy S (Cal mol^{-1} K^{-1}) variation with temperature (K) for product 2 structures

Temperature (K)	Product 2: 1-mer	Product 2: 2-mer	Product 2: 3-mer	Product 2: 4-mer	Product 2: 5-mer	Product 2: 6-mer	Product 2:7-mer	Product 2: 8-mer	Product 2: 9-mer
25	58.254	65.223	71.512	76.475	83.088	83.96	90.989	96.285	96.804
50	67.71	76.729	88.172	97.703	112.348	114.474	123.276	136.985	139.291
75	75.173	87.143	104.272	118.506	141.715	145.964	156.508	177.868	183.294
100	81.917	97.283	120.444	139.525	171.06	178.105	190.126	218.348	227.706
125	88.279	107.178	136.598	160.596	200.026	210.351	223.383	258.013	271.672
150	94.374	116.808	152.604	181.505	228.396	242.311	255.962	296.707	314.793
175	100.256	126.188	168.392	202.138	256.108	273.799	287.826	334.463	356.99
200	105.964	135.357	183.947	222.467	283.196	304.78	319.074	371.421	398.361
225	111.529	144.364	199.284	242.515	309.742	335.295	349.85	407.757	439.073
250	116.977	153.254	214.432	262.32	335.834	365.411	380.292	443.634	479.295
275	122.327	162.06	229.418	281.922	361.55	395.191	410.506	479.182	519.162
298.15	127.207	170.161	243.166	299.915	385.075	422.507	438.344	511.883	555.844
300	127.595	170.806	244.26	301.346	386.944	424.68	440.564	514.488	558.767
325	132.787	179.503	258.968	320.608	412.05	453.904	470.5	549.596	598.158
350	137.911	188.155	273.544	339.708	436.884	482.869	500.321	584.521	637.348
375	142.966	196.76	287.983	358.642	461.448	511.569	530.013	619.25	676.324
400	147.954	205.31	302.279	377.398	485.734	539.989	559.552	653.76	715.059
425	152.874	213.8	316.419	395.961	509.733	568.108	588.906	688.019	753.516
450	157.723	222.218	330.395	414.318	533.429	595.907	618.042	721.99	791.656

475	162.501	230.558	344.197	432.453	556.811	623.365	646.927	755.642	829.439
500	167.206	238.811	357.816	450.356	579.866	650.465	675.532	788.942	866.832
525	171.837	246.97	371.246	468.016	602.586	677.193	703.831	821.864	903.803
550	176.394	255.031	384.48	485.426	624.963	703.538	731.805	854.387	940.329
575	180.875	262.989	397.517	502.579	646.993	729.492	759.435	886.492	976.39
600	185.282	270.84	410.353	519.473	668.673	755.051	786.709	918.168	1011.97
625	189.615	278.583	422.988	536.106	690.004	780.211	813.617	949.404	1047.06
650	193.875	286.216	435.421	552.478	710.986	804.974	840.153	980.196	1081.652
675	198.062	293.739	447.655	568.59	731.624	829.341	866.314	1010.54	1115.744
700	202.178	301.15	459.692	584.443	751.92	853.316	892.097	1040.437	1149.335
725	206.224	308.452	471.533	600.042	771.88	876.903	917.505	1069.887	1182.426
750	210.202	315.644	483.181	615.39	791.51	900.109	942.537	1098.895	1215.022
775	214.113	322.727	494.641	630.49	810.816	922.939	967.199	1127.464	1247.126
800	217.958	329.704	505.915	645.348	829.804	945.401	991.493	1155.601	1278.745
825	221.74	336.575	517.008	659.968	848.481	967.502	1015.425	1183.311	1309.887
850	225.459	343.343	527.924	674.355	866.855	989.25	1039	1210.602	1340.558
875	229.118	350.008	538.665	688.514	884.932	1010.652	1062.224	1237.481	1370.768
900	232.718	356.574	549.237	702.451	902.72	1031.717	1085.103	1263.955	1400.523
925	236.26	363.042	559.643	716.17	920.225	1052.451	1107.643	1290.033	1429.834
950	239.746	369.414	569.887	729.676	937.455	1072.864	1129.852	1315.723	1458.71
975	243.177	375.692	579.974	742.975	954.416	1092.961	1151.735	1341.031	1487.158
1000	246.555	381.878	589.906	756.071	971.114	1112.752	1173.299	1365.968	1515.188

Table S6. Gibbs free energy G (Hartree) variation with temperature (K) for product 1 structures

Temperature (K)	Product 1: 1-mer	Product 1: 2-mer	Product 1: 3-mer	Product 1: 4-mer	Product 1: 5-mer	Product 1: 6-mer	Product 1: 7-mer	Product 1: 8-mer	Product 1: 9-mer
25	-727.787	-1531.45	-2335.13	-3138.8	-3942.48	-4746.19	-5549.82	-6353.54	-7157.17
50	-727.789	-1531.45	-2335.13	-3138.8	-3942.48	-4746.2	-5549.82	-6353.54	-7157.18
75	-727.792	-1531.46	-2335.14	-3138.81	-3942.48	-4746.2	-5549.83	-6353.55	-7157.18
100	-727.795	-1531.46	-2335.14	-3138.81	-3942.49	-4746.21	-5549.83	-6353.55	-7157.19
125	-727.798	-1531.47	-2335.15	-3138.82	-3942.5	-4746.22	-5549.84	-6353.56	-7157.2
150	-727.802	-1531.47	-2335.15	-3138.82	-3942.5	-4746.23	-5549.85	-6353.57	-7157.21
175	-727.806	-1531.48	-2335.16	-3138.83	-3942.51	-4746.24	-5549.86	-6353.59	-7157.23
200	-727.81	-1531.48	-2335.17	-3138.84	-3942.52	-4746.25	-5549.87	-6353.6	-7157.24
225	-727.814	-1531.49	-2335.18	-3138.85	-3942.53	-4746.26	-5549.88	-6353.61	-7157.26
250	-727.818	-1531.49	-2335.19	-3138.86	-3942.55	-4746.28	-5549.9	-6353.63	-7157.28
275	-727.823	-1531.5	-2335.2	-3138.87	-3942.56	-4746.29	-5549.91	-6353.65	-7157.3
298.15	-727.827	-1531.51	-2335.2	-3138.88	-3942.57	-4746.31	-5549.93	-6353.67	-7157.33
300	-727.827	-1531.51	-2335.2	-3138.88	-3942.57	-4746.31	-5549.93	-6353.67	-7157.33
325	-727.832	-1531.51	-2335.22	-3138.89	-3942.59	-4746.33	-5549.95	-6353.69	-7157.35
350	-727.837	-1531.52	-2335.23	-3138.9	-3942.6	-4746.35	-5549.97	-6353.71	-7157.38

375	-727.843	-1531.53	-2335.24	-3138.92	-3942.62	-4746.37	-5549.99	-6353.73	-7157.41
400	-727.848	-1531.54	-2335.25	-3138.93	-3942.64	-4746.39	-5550.01	-6353.76	-7157.44
425	-727.854	-1531.55	-2335.26	-3138.95	-3942.66	-4746.41	-5550.03	-6353.78	-7157.47
450	-727.86	-1531.55	-2335.28	-3138.96	-3942.68	-4746.44	-5550.05	-6353.81	-7157.5
475	-727.866	-1531.56	-2335.29	-3138.98	-3942.7	-4746.46	-5550.08	-6353.84	-7157.54
500	-727.872	-1531.57	-2335.3	-3138.99	-3942.72	-4746.49	-5550.1	-6353.87	-7157.58
525	-727.878	-1531.58	-2335.32	-3139.01	-3942.74	-4746.52	-5550.13	-6353.9	-7157.61
550	-727.885	-1531.59	-2335.33	-3139.03	-3942.76	-4746.54	-5550.16	-6353.93	-7157.65
575	-727.891	-1531.61	-2335.35	-3139.05	-3942.79	-4746.57	-5550.19	-6353.96	-7157.7
600	-727.898	-1531.62	-2335.37	-3139.07	-3942.81	-4746.6	-5550.22	-6354	-7157.74
625	-727.905	-1531.63	-2335.38	-3139.09	-3942.84	-4746.64	-5550.25	-6354.03	-7157.78
650	-727.912	-1531.64	-2335.4	-3139.11	-3942.86	-4746.67	-5550.28	-6354.07	-7157.83
675	-727.919	-1531.65	-2335.42	-3139.13	-3942.89	-4746.7	-5550.32	-6354.11	-7157.88
700	-727.927	-1531.66	-2335.44	-3139.15	-3942.92	-4746.74	-5550.35	-6354.15	-7157.93
725	-727.934	-1531.68	-2335.46	-3139.18	-3942.95	-4746.77	-5550.38	-6354.19	-7157.98
750	-727.942	-1531.69	-2335.48	-3139.2	-3942.98	-4746.81	-5550.42	-6354.23	-7158.03
775	-727.95	-1531.7	-2335.49	-3139.22	-3943.01	-4746.85	-5550.46	-6354.27	-7158.08
800	-727.958	-1531.72	-2335.51	-3139.25	-3943.04	-4746.88	-5550.5	-6354.32	-7158.14
825	-727.966	-1531.73	-2335.54	-3139.27	-3943.07	-4746.92	-5550.54	-6354.36	-7158.19
850	-727.974	-1531.74	-2335.56	-3139.3	-3943.1	-4746.96	-5550.58	-6354.41	-7158.25
875	-727.982	-1531.76	-2335.58	-3139.33	-3943.13	-4747	-5550.62	-6354.46	-7158.31
900	-727.991	-1531.77	-2335.6	-3139.35	-3943.17	0.56728	-5550.66	-6354.5	-7158.37
925	-728	-1531.79	-2335.62	-3139.38	-3943.2	0.524724	-5550.7	-6354.55	-7158.43
950	-728.008	-1531.8	-2335.64	-3139.41	-3943.24	0.481343	-5550.75	-6354.6	-7158.49
975	-728.017	-1531.82	-2335.67	-3139.44	-3943.27	0.437154	-5550.79	-6354.66	-7158.55
1000	-728.026	-1531.83	-2335.69	-3139.47	-3943.31	0.392166	-5550.84	-6354.71	-7158.62

Table S7. Gibbs free energy G (Hartree) variation with temperature (K) for product 2 structures

Temperature (K)	Product 2: 1-mer	Product 2: 2-mer	Product 2: 3-mer	Product 2: 4-mer	Product 2: 5-mer	Product 2: 6-mer	Product 2: 7-mer	Product 2: 8-mer	Product 2: 9-mer
25	-804.185	-1607.86	-2411.56	-3215.16	-4018.88	-4822.58	-5626.3	-6429.96	-7233.61
50	-804.188	-1607.87	-2411.57	-3215.17	-4018.89	-4822.59	-5626.3	-6429.96	-7233.61
75	-804.191	-1607.87	-2411.57	-3215.17	-4018.89	-4822.59	-5626.31	-6429.97	-7233.62
100	-804.194	-1607.87	-2411.58	-3215.18	-4018.9	-4822.6	-5626.32	-6429.98	-7233.62
125	-804.197	-1607.88	-2411.58	-3215.18	-4018.9	-4822.61	-5626.32	-6429.99	-7233.63
150	-804.201	-1607.88	-2411.59	-3215.19	-4018.91	-4822.62	-5626.33	-6430	-7233.65
175	-804.205	-1607.89	-2411.59	-3215.2	-4018.92	-4822.63	-5626.35	-6430.01	-7233.66
200	-804.209	-1607.89	-2411.6	-3215.21	-4018.93	-4822.64	-5626.36	-6430.02	-7233.67
225	-804.213	-1607.9	-2411.61	-3215.22	-4018.94	-4822.65	-5626.37	-6430.04	-7233.69

250	-804.218	-1607.9	-2411.62	-3215.23	-4018.96	-4822.66	-5626.39	-6430.06	-7233.71
275	-804.223	-1607.91	-2411.62	-3215.24	-4018.97	-4822.68	-5626.4	-6430.07	-7233.73
298.15	-804.227	-1607.92	-2411.63	-3215.25	-4018.99	-4822.69	-5626.42	-6430.09	-7233.75
300	-804.228	-1607.92	-2411.63	-3215.25	-4018.99	-4822.7	-5626.42	-6430.09	-7233.75
325	-804.233	-1607.92	-2411.64	-3215.26	-4019	-4822.71	-5626.44	-6430.11	-7233.77
350	-804.238	-1607.93	-2411.65	-3215.27	-4019.02	-4822.73	-5626.46	-6430.14	-7233.8
375	-804.244	-1607.94	-2411.67	-3215.29	-4019.04	-4822.75	-5626.48	-6430.16	-7233.82
400	-804.25	-1607.95	-2411.68	-3215.3	-4019.06	-4822.77	-5626.5	-6430.19	-7233.85
425	-804.256	-1607.96	-2411.69	-3215.32	-4019.08	-4822.79	-5626.52	-6430.21	-7233.88
450	-804.262	-1607.96	-2411.7	-3215.33	-4019.1	-4822.82	-5626.54	-6430.24	-7233.91
475	-804.268	-1607.97	-2411.72	-3215.35	-4019.12	-4822.84	-5626.57	-6430.27	-7233.94
500	-804.275	-1607.98	-2411.73	-3215.37	-4019.14	-4822.87	-5626.6	-6430.3	-7233.98
525	-804.281	-1607.99	-2411.74	-3215.39	-4019.16	-4822.89	-5626.62	-6430.33	-7234.01
550	-804.288	-1608	-2411.76	-3215.41	-4019.19	-4822.92	-5626.65	-6430.37	-7234.05
575	-804.295	-1608.01	-2411.78	-3215.43	-4019.21	-4822.95	-5626.68	-6430.4	-7234.09
600	-804.303	-1608.02	-2411.79	-3215.45	-4019.24	-4822.98	-5626.71	-6430.44	-7234.13
625	-804.31	-1608.03	-2411.81	-3215.47	-4019.27	-4823.01	-5626.74	-6430.47	-7234.17
650	-804.318	-1608.05	-2411.83	-3215.49	-4019.3	-4823.04	-5626.78	-6430.51	-7234.21
675	-804.326	-1608.06	-2411.84	-3215.51	-4019.32	-4823.07	-5626.81	-6430.55	-7234.26
700	-804.334	-1608.07	-2411.86	-3215.53	-4019.35	-4823.11	-5626.85	-6430.59	-7234.3
725	-804.342	-1608.08	-2411.88	-3215.56	-4019.38	-4823.14	-5626.88	-6430.64	-7234.35
750	-804.35	-1608.09	-2411.9	-3215.58	-4019.42	-4823.18	-5626.92	-6430.68	-7234.4
775	-804.359	-1608.11	-2411.92	-3215.61	-4019.45	-4823.21	-5626.96	-6430.72	-7234.44
800	-804.367	-1608.12	-2411.94	-3215.63	-4019.48	-4823.25	-5627	-6430.77	-7234.49
825	-804.376	-1608.13	-2411.96	-3215.66	-4019.51	-4823.29	-5627.04	-6430.82	-7234.55
850	-804.385	-1608.15	-2411.98	-3215.68	-4019.55	-4823.33	-5627.08	-6430.86	-7234.6
875	-804.394	-1608.16	-2412	-3215.71	-4019.58	-4823.37	-5627.12	-6430.91	-7234.65
900	-804.403	-1608.17	-2412.02	-3215.74	-4019.62	-4823.41	-5627.16	-6430.96	-7234.71
925	-804.412	-1608.19	-2412.04	-3215.77	-4019.65	-4823.45	-5627.21	-6431.01	-7234.76
950	-804.422	-1608.2	-2412.07	-3215.8	-4019.69	-4823.49	-5627.25	-6431.06	-7234.82
975	-804.432	-1608.22	-2412.09	-3215.83	-4019.73	-4823.54	-5627.3	-6431.12	-7234.88
1000	-804.441	-1608.23	-2412.11	-3215.86	-4019.77	-4823.58	-5627.34	-6431.17	-7234.94

Table S8. Variation of Gibbs free energy ΔG (Hartree) change with temperature (K) for 9 Reaction pathway

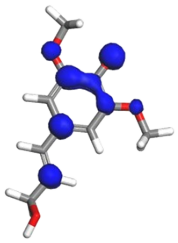
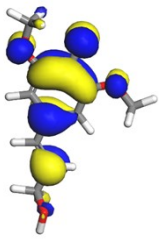
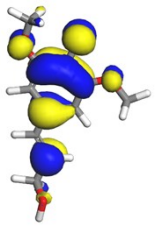
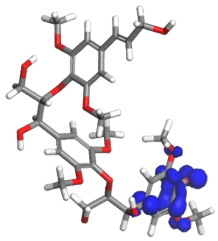
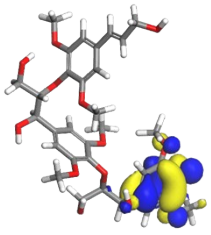
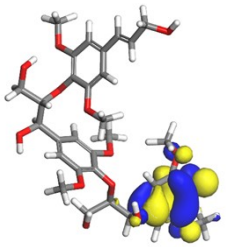
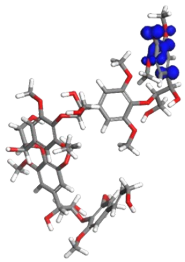
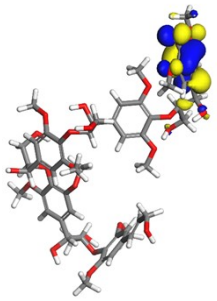
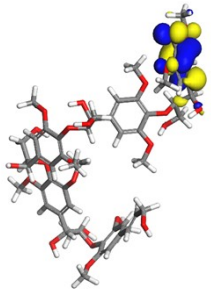
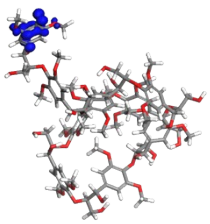
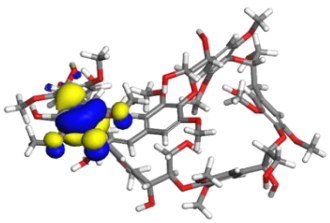
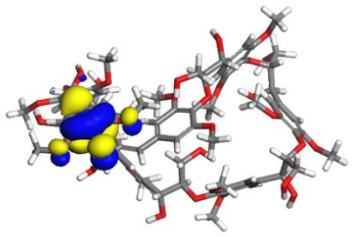
Temperature (K)	RXN 1	RXN 2	RXN 3	RXN 4	RXN 5	RXN 6	RXN 7	RXN 8	RXN 9
25	0.108057	0.091581	0.070495	0.118261	0.143005	0.144851	0.11951	0.10019	0.144242
50	0.105915	0.089152	0.067765	0.115995	0.140396	0.142317	0.117364	0.097894	0.141915

75	0.103634	0.08654	0.064898	0.113598	0.137501	0.139487	0.115219	0.095553	0.139333
100	0.101239	0.083793	0.061921	0.111044	0.134307	0.136359	0.113045	0.09317	0.136481
125	0.098745	0.080929	0.058844	0.108296	0.130804	0.132921	0.11082	0.090757	0.13334
150	0.09616	0.077963	0.055673	0.105334	0.126994	0.129168	0.108537	0.08833	0.129904
175	0.093494	0.074907	0.052414	0.102143	0.122879	0.125101	0.106188	0.0859	0.126172
200	0.090756	0.071761	0.049074	0.098725	0.118463	0.120725	0.103773	0.083473	0.122148
225	0.087956	0.068538	0.045665	0.095077	0.113762	0.116051	0.101294	0.081057	0.11784
250	0.085097	0.065243	0.042184	0.091208	0.108782	0.11109	0.09875	0.078647	0.11326
275	0.082184	0.061877	0.038642	0.087122	0.103539	0.105853	0.096146	0.076255	0.108415
298.15	0.079448	0.058706	0.035309	0.083155	0.098459	0.100771	0.093681	0.07405	0.10371
300	0.079228	0.058451	0.035042	0.082832	0.098044	0.100357	0.093485	0.073876	0.103324
325	0.076226	0.054964	0.031384	0.078343	0.092307	0.094612	0.090765	0.07151	0.097992
350	0.073183	0.051423	0.027679	0.073667	0.086345	0.088628	0.087993	0.069161	0.092433
375	0.070105	0.047829	0.023921	0.06881	0.080165	0.082419	0.085171	0.066823	0.086656
400	0.066994	0.044188	0.020122	0.063785	0.073781	0.076	0.082302	0.064502	0.080674
425	0.063853	0.040502	0.016278	0.058596	0.067201	0.069374	0.079389	0.062196	0.074495
450	0.060682	0.036771	0.012398	0.053254	0.060435	0.062553	0.076435	0.059906	0.068127
475	0.057485	0.033001	0.008476	0.047764	0.05349	0.055549	0.073439	0.057629	0.06158
500	0.054261	0.029193	0.004521	0.042132	0.046379	0.048371	0.070404	0.055366	0.054865
525	0.051015	0.025348	0.00053	0.036366	0.039102	0.04102	0.067335	0.053116	0.047984
550	0.047746	0.021469	-0.00349	0.030473	0.031676	0.033512	0.064232	0.05088	0.040946
575	0.044457	0.017558	-0.00754	0.024456	0.024102	0.025849	0.061096	0.048659	0.033761
600	0.041147	0.013616	-0.01162	0.01832	0.016387	0.018038	0.057931	0.046448	0.026427
625	0.037819	0.009643	-0.01573	0.012072	0.008535	0.010088	0.054734	0.044251	0.018957
650	0.034474	0.005644	-0.01987	0.005715	0.000554	0.002	0.051512	0.042066	0.011356
675	0.031109	0.001617	-0.02403	-0.00075	-0.00755	-0.00622	0.048259	0.039892	0.003625
700	0.02773	-0.00244	-0.02821	-0.00731	-0.01578	-0.01456	0.044983	0.03773	-0.00423
725	0.024334	-0.00651	-0.03242	-0.01397	-0.02412	-0.02303	0.041682	0.035581	-0.0122
750	0.020924	-0.01061	-0.03665	-0.02072	-0.03257	-0.03161	0.038358	0.033443	-0.02029
775	0.017499	-0.01474	-0.04091	-0.02757	-0.04113	-0.04031	0.035008	0.031314	-0.02849
800	0.014062	-0.01888	-0.04518	-0.0345	-0.0498	-0.04912	0.031639	0.029196	-0.03679
825	0.01061	-0.02305	-0.04947	-0.04152	-0.05856	-0.05803	0.028248	0.027089	-0.0452
850	0.007144	-0.02724	-0.05379	-0.04862	-0.06743	-0.06705	0.024836	0.024992	-0.05372
875	0.003666	-0.03145	-0.05812	-0.0558	-0.07639	-0.07616	0.021405	0.022906	-0.06233
900	0.000178	-0.03567	-0.06247	-0.06306	-0.08544	-0.08537	0.017953	0.020829	-0.07103
925	-0.00332	-0.03992	-0.06684	-0.07039	-0.09458	-0.09468	0.014486	0.018761	-0.07983
950	-0.00684	-0.04418	-0.07123	-0.07779	-0.1038	-0.10407	0.010999	0.016702	-0.08871
975	-0.01036	-0.04847	-0.07563	-0.08527	-0.11312	-0.11356	0.007493	0.014652	-0.09769
1000	-0.01389	-0.05276	-0.08005	-0.09282	-0.12251	-0.12313	0.003971	0.012612	-0.10675

Table S9. Heat capacity Cp (Cal mol^{-1} K^{-1}), Entropy S (Cal mol^{-1} K^{-1}) and Gibbs free energy G (Hartree) variation with temperature (K) for 10-mer reactant structure

Temperature (K)	Cp (Cal mol^{-1} K^{-1})	S (Cal mol^{-1} K^{-1})	G (Hartree)
25	50.485	102.317	-7961.5
50	105.941	149.937	-7961.51
75	163.227	198.002	-7961.51
100	219.207	246.096	-7961.52
125	271.898	293.604	-7961.53
150	321.22	340.209	-7961.54
175	368.042	385.864	-7961.56
200	413.392	430.688	-7961.58
225	458.058	474.862	-7961.59
250	502.463	518.566	-7961.61
275	546.694	561.944	-7961.63
298.15	587.375	601.904	-7961.66
300	590.609	605.09	-7961.66
325	633.941	648.051	-7961.68
350	676.386	690.834	-7961.71
375	717.664	733.421	-7961.74
400	757.547	775.776	-7961.77
425	795.87	817.853	-7961.8
450	832.535	859.606	-7961.83
475	867.496	900.988	-7961.87
500	900.755	941.96	-7961.9
525	932.347	982.485	-7961.94
550	962.33	1022.535	-7961.98
575	990.777	1062.085	-7962.02
600	1017.771	1101.117	-7962.07
625	1043.398	1139.62	-7962.11
650	1067.743	1177.585	-7962.16
675	1090.888	1215.007	-7962.21
700	1112.914	1251.885	-7962.26
725	1133.893	1288.219	-7962.31
750	1153.896	1324.014	-7962.36
775	1172.984	1359.273	-7962.41
800	1191.216	1394.004	-7962.47
825	1208.645	1428.213	-7962.52
850	1225.319	1461.908	-7962.58
875	1241.284	1495.099	-7962.64
900	1256.579	1527.794	-7962.7
925	1271.241	1560.002	-7962.76

950	1285.305	1591.734	-7962.82

Structure	Spin density	HOMO	LUMO
Product 1: 1-mer			
Product 1: 3-mer			
Product 1: 5-mer			
Product 1: 7-mer			

975	1298.803	1622.998	-7962.89
1000	1311.762	1653.805	-7962.95

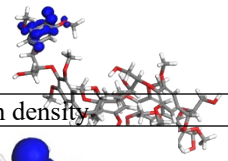
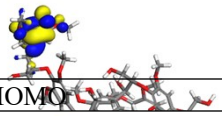
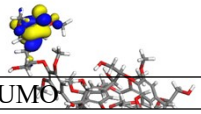
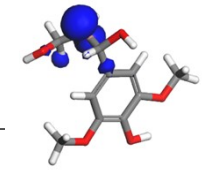
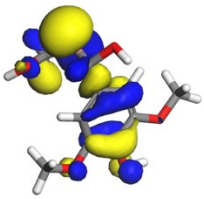
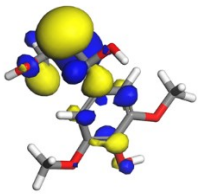
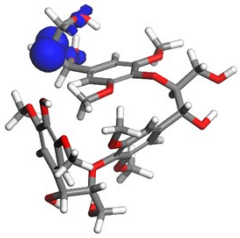
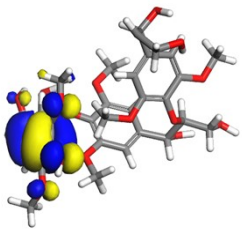
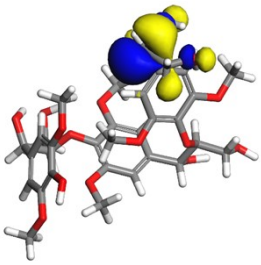
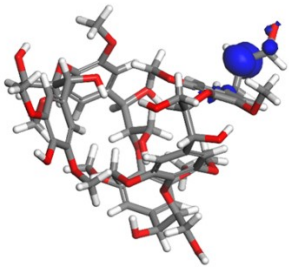
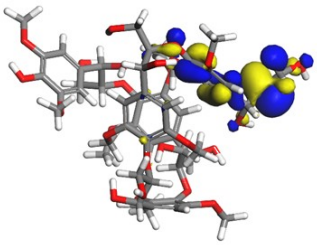
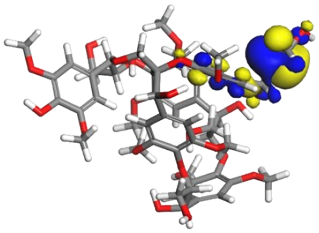
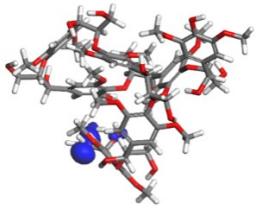
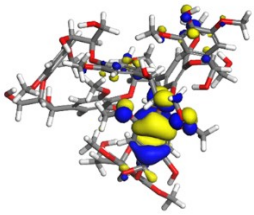
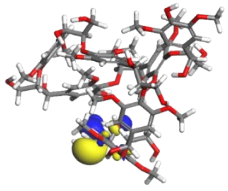
Structure	Spin density	HOMO	LUMO
Product 1: 9-mer			
Product 2: 1-mer			
Product 2: 3-mer			
Product 2: 5-mer			
Product 2: 7-mer			

Table S10a: Spin density and Molecular orbital plots for product 1 species

Table S10b: Spin density and Molecular orbital plots for product 2 species

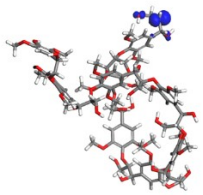
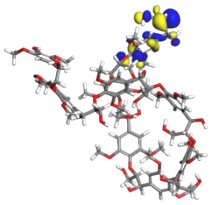
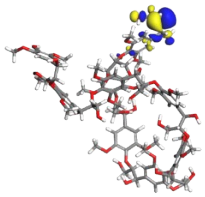
Product 2: 9-mer			

Table S11. Key results of the Paired T test to identify if statistically significant variation exists between the mean BDEs calculated using soft and hardwood model lignin decamers

Temperature (K)	P(T<=t) two-tail for all reaction pathways studied with model lignin decamers consisting of Guaicyl and Syringyl monolignols (assumed α = 0.05)
298.25	0.261870227
400	0.246180446
500	0.24047412
600	0.248023298
700	0.273068126
800	0.320542329
900	0.390688541
1000	0.478746282

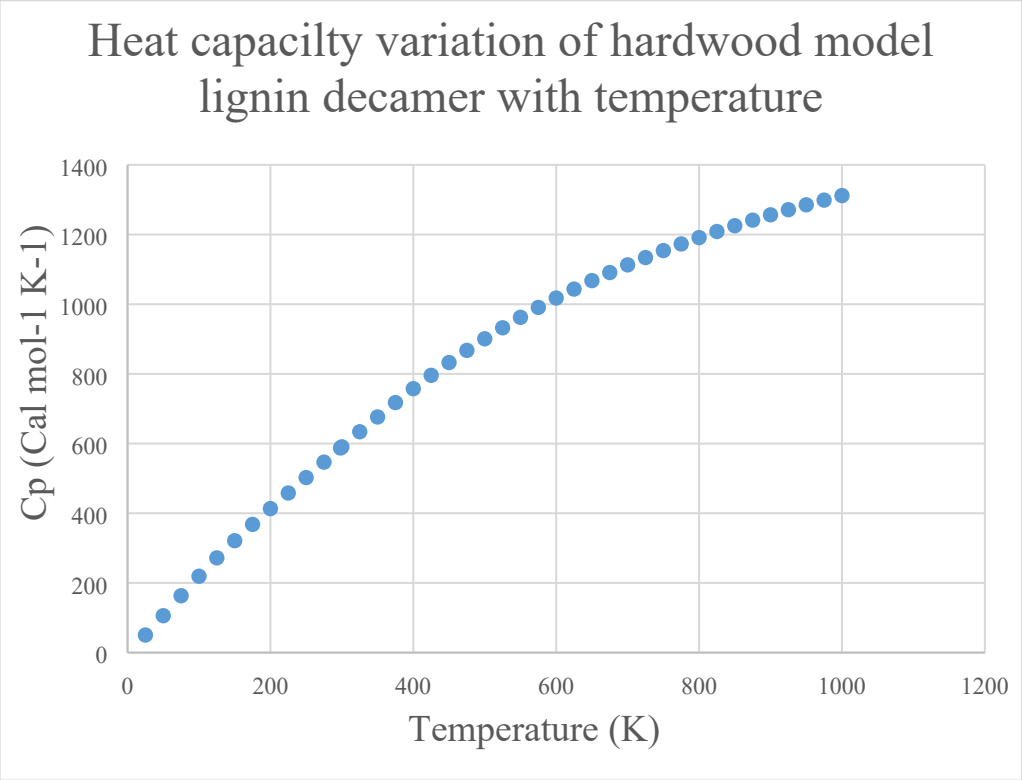


Figure S1. Heat capacity variation with temperature for 10-mer reactant structure of hardwood model lignin

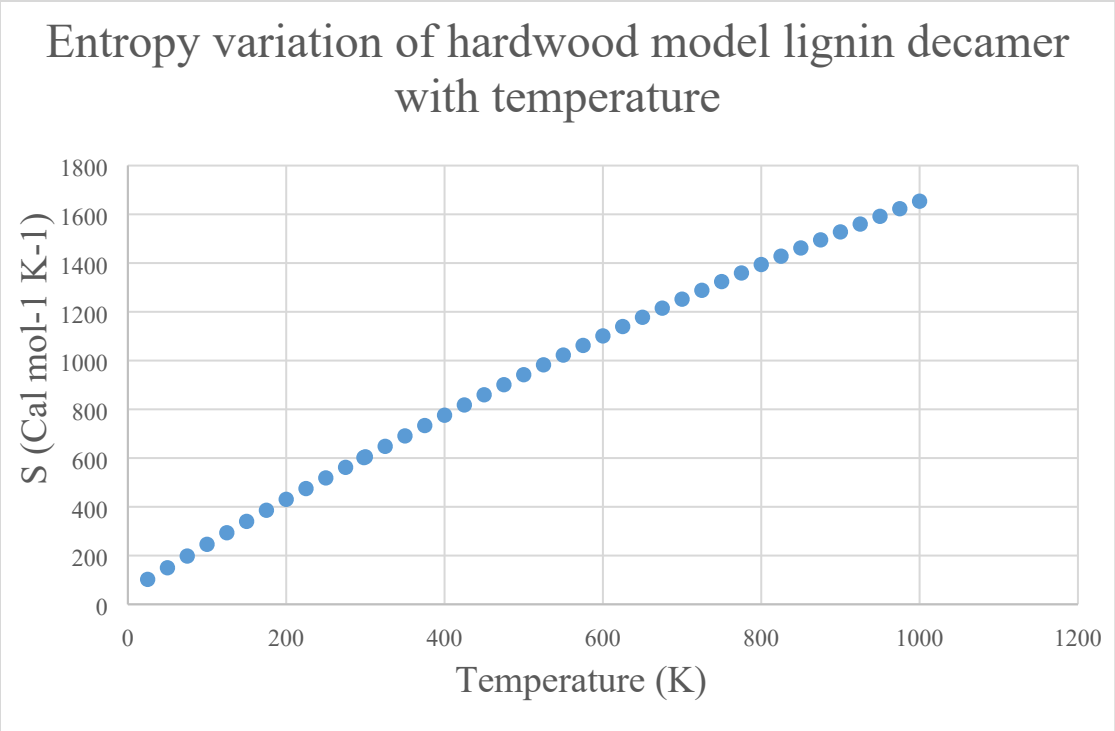


Figure S2. Entropy variation with temperature for 10-mer reactant structure of hardwood model lignin

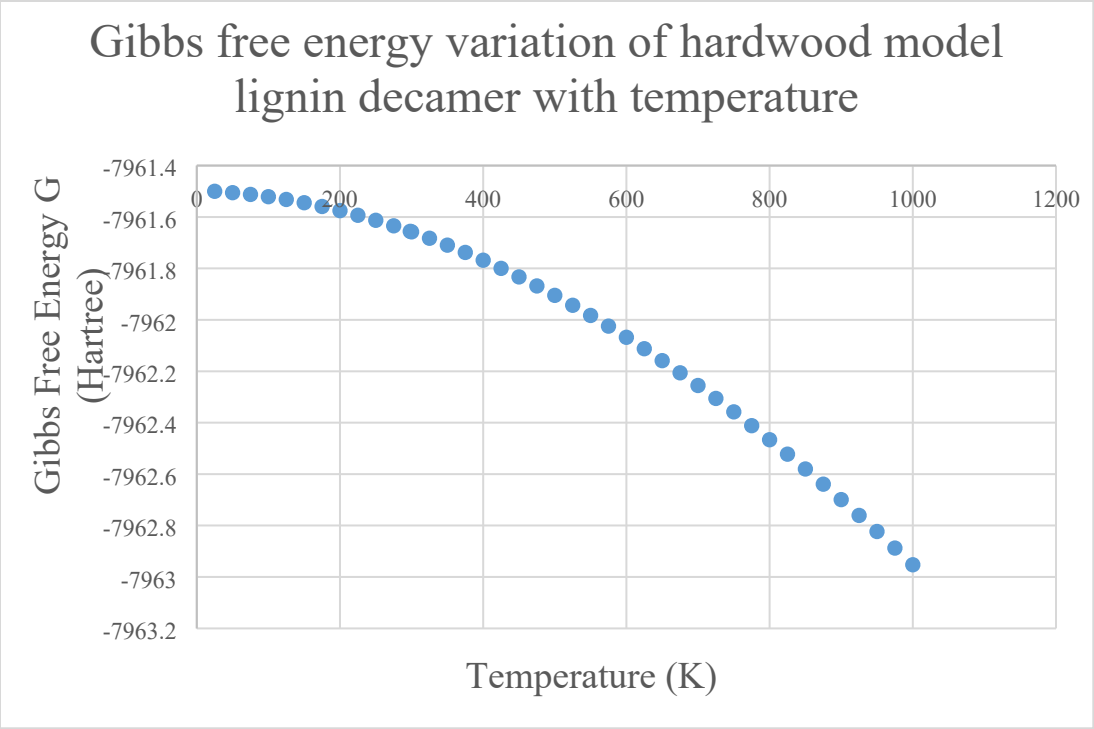


Figure S3. Gibbs free energy variation with temperature for 10-mer reactant structure of hardwood model lignin

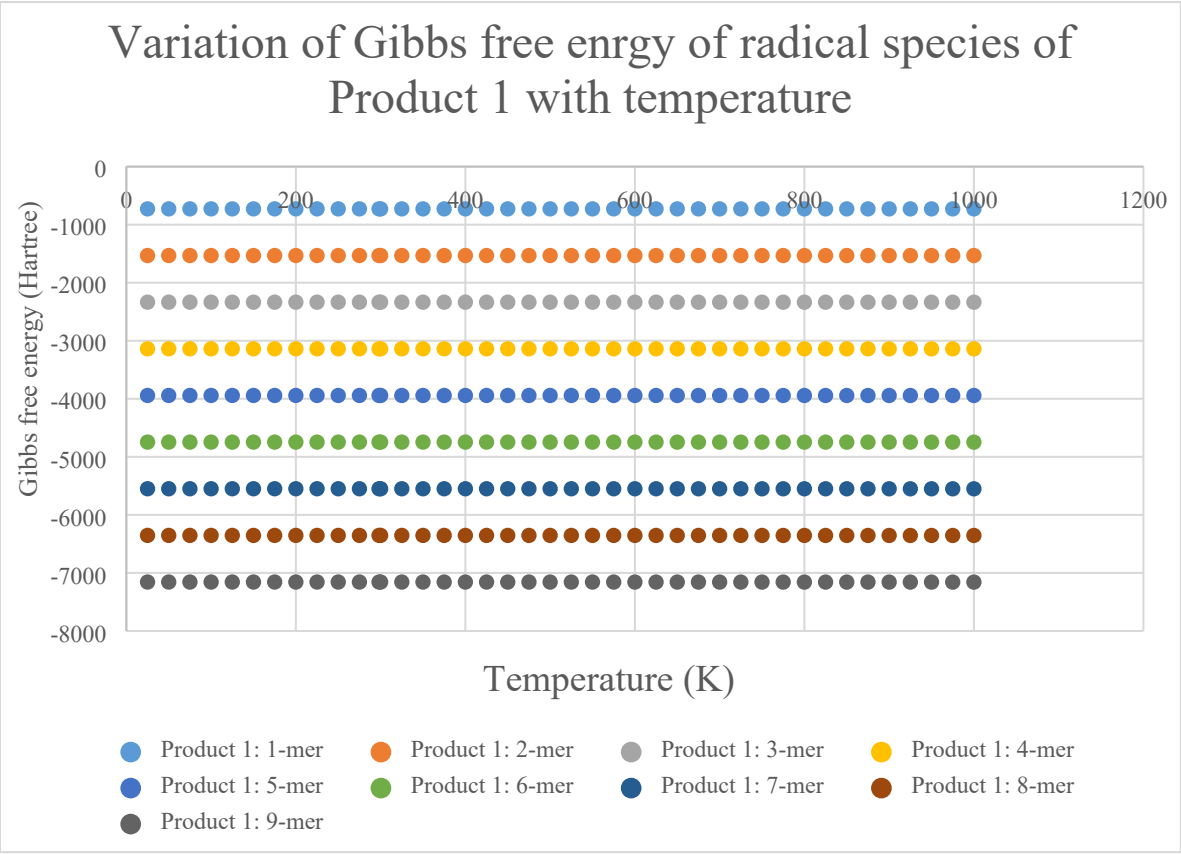


Figure S4. Gibbs free energy variation with temperature for product 1 radical species

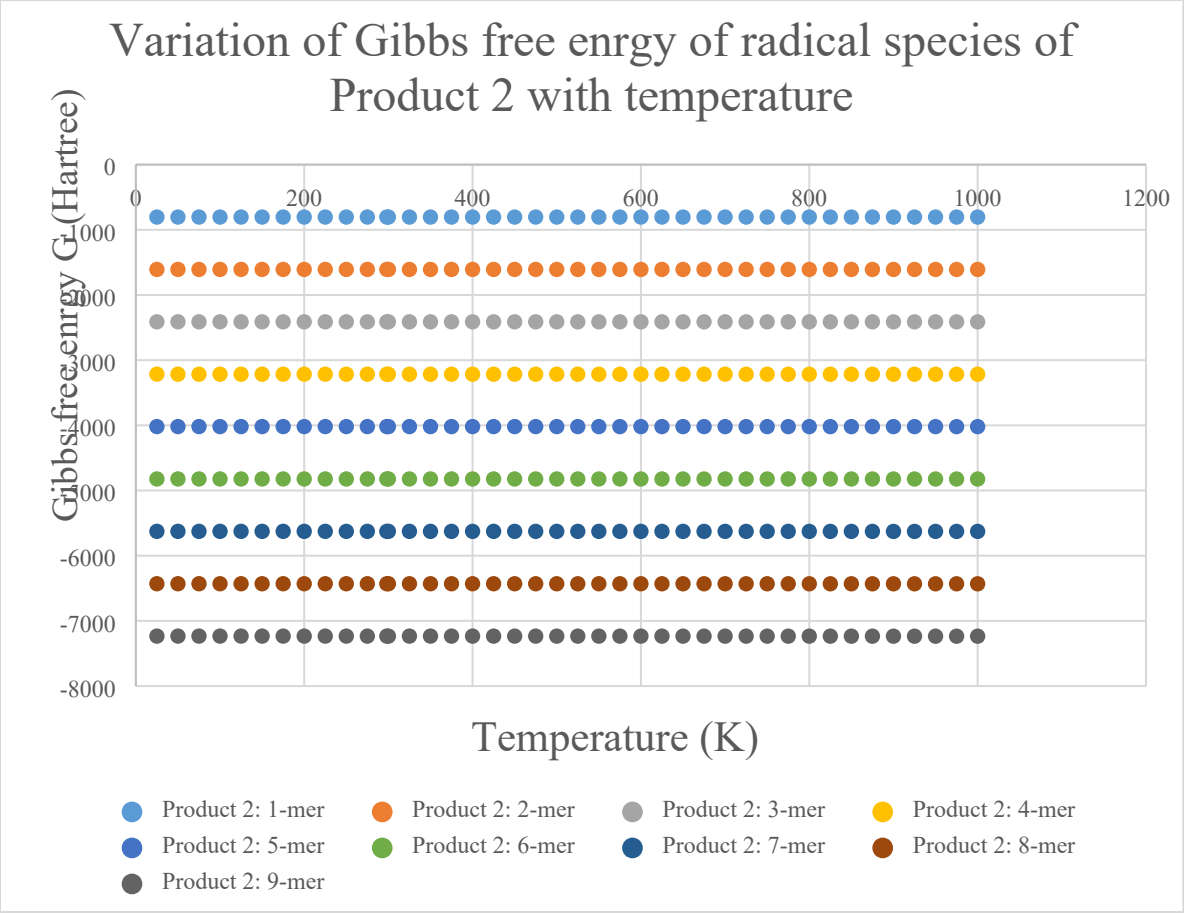


Figure S5. Gibbs free energy variation with temperature for product 2 radical species

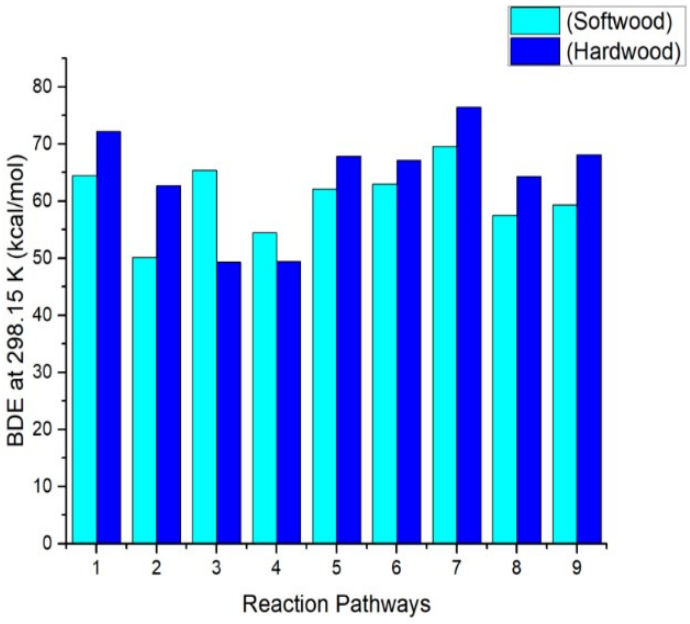


Figure S6. Comparison between the current study for BDEs for the hardwood model lignin and the calculated BDEs with a softwood model lignin in our previous study.

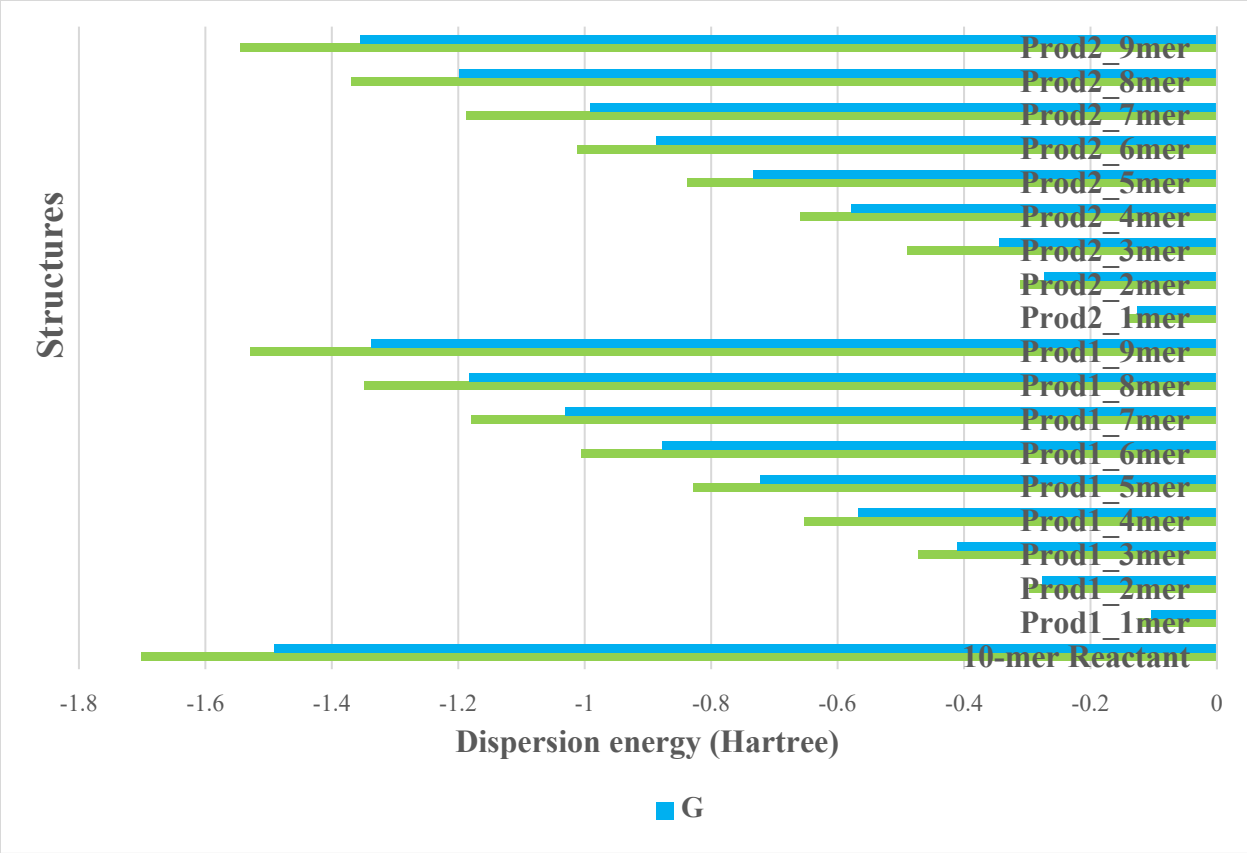


Figure S7. Comparison between non-bonded interaction energies for all structures between current study (hardwood model lignin with S units) and previous study (softwood model lignin with G units)