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

Supplementary Table 1. The xyz coordinates of all adsorption configurations of 2-hydroxybenzaldehyde (presented in Figure 3 of the manuscript) along with their electronic energy and zero point vibrational energy (ZPVE).

Adsorption configurations	xyz coordinates					Electronic energy	ZPVE
1	Tag	Symbol	X	Y	Z	-1942.35	0.113207
	1	Pd	2.982046	-2.96919	-0.2449		
	2	Pd	3.141405	-0.20594	-0.27709		
	3	Pd	3.304592	2.510867	-0.30991		
	4	Pd	0.505901	-4.16767	-0.2282		
	5	Pd	0.673839	-1.45008	-0.26051		
	6	Pd	0.836633	1.2953	-0.29411		
	7	Pd	0.95358	4.095942	-0.32612		
	8	Pd	-1.79454	-2.68198	-0.24315		
	9	Pd	-1.62307	0.063467	-0.27679		
	10	Pd	-1.47844	2.810468	-0.3083		
	11	Pd	-4.0934	-1.17267	-0.25921		
	12	Pd	-3.94393	1.538513	-0.29139		
	13	C	0.019598	0.799016	2.334672		
	14	C	0.213249	-0.58816	2.336918		
	15	C	1.396954	-1.15794	1.706748		
	16	C	2.584966	-0.25985	1.641535		
	17	C	2.393568	1.185112	1.648638		
	18	C	1.030193	1.661709	1.750478		
	19	H	1.617652	-2.16832	2.050032		
	20	H	3.490376	-0.64918	2.114176		
	21	H	3.202393	1.821808	2.007482		
	22	C	-1.15579	1.344505	2.963537		
	23	H	-1.28844	2.438946	2.903738		
	24	O	-0.61979	-1.39905	2.944712		
	25	H	-1.36192	-0.8229	3.300372		
	26	O	-1.98366	0.65665	3.568064		
	27	H	0.898843	2.72884	1.931562		
2	Tag	Symbol	X	Y	Z	-1942.35	0.112316
	1	Pd	3.680081	-1.49465	-0.5732		
	2	Pd	2.708037	1.095701	-0.49573		
	3	Pd	1.758128	3.645563	-0.42013		
	4	Pd	1.910691	-3.59448	-0.40514		
	5	Pd	0.965129	-1.04233	-0.32989		
	6	Pd	0.002987	1.533774	-0.25331		
	7	Pd	-1.02259	4.141015	-0.17109		
	8	Pd	-0.78389	-3.16939	-0.16353		
	9	Pd	-1.73762	-0.59011	-0.08773		
	10	Pd	-2.71672	1.979569	-0.00956		
	11	Pd	-3.48644	-2.72209	0.078641		
	12	Pd	-4.44646	-0.18312	0.155198		

	13	C	2.886843	0.255849	1.580355		
	14	C	1.62233	-0.22941	2.128244		
	15	C	0.523945	0.628987	2.183444		
	16	C	0.614252	1.979615	1.741413		
	17	C	1.920073	2.606376	1.47862		
	18	C	3.056543	1.691135	1.403232		
	19	H	-0.39681	0.263079	2.620546		
	20	H	-0.18004	2.649293	2.066588		
	21	H	2.093515	3.584965	1.941686		
	22	C	4.034447	-0.6803	1.532256		
	23	H	5.002645	-0.22575	1.24547		
	24	O	1.571649	-1.4101	2.728119		
	25	H	2.470994	-1.83529	2.607964		
	26	O	4.022917	-1.7932	2.123235		
	27	H	4.061139	2.101805	1.493546		
3	Tag	Symbol	X	Y	Z	-1942.37	0.112424
	1	Pd	-1.00372	-4.03346	-0.28625		
	2	Pd	1.539698	-2.96736	-0.05119		
	3	Pd	4.043627	-1.92468	0.179914		
	4	Pd	-3.15401	-2.33158	-0.50442		
	5	Pd	-0.64725	-1.29299	-0.27487		
	6	Pd	1.881587	-0.23741	-0.03938		
	7	Pd	4.44012	0.882888	0.196058		
	8	Pd	-2.82421	0.386693	-0.4951		
	9	Pd	-0.29259	1.434376	-0.26231		
	10	Pd	2.231101	2.506774	-0.02788		
	11	Pd	-2.47291	3.114164	-0.48227		
	12	Pd	0.019472	4.166802	-0.25202		
	13	C	-2.65761	-0.46641	1.461393		
	14	C	-3.24326	0.884177	1.488171		
	15	C	-2.39355	2.083324	1.464608		
	16	C	-0.96321	1.832272	1.673412		
	17	C	-0.41114	0.515967	1.81365		
	18	C	-1.21923	-0.66183	1.637084		
	19	H	-2.81871	2.954005	1.970315		
	20	H	-0.37969	2.662399	2.064174		
	21	H	0.572675	0.41318	2.256149		
	22	C	-3.56021	-1.63547	1.550729		
	23	H	-3.08831	-2.5629	1.929672		
	24	O	-4.53007	1.028502	1.770296		
	25	H	-4.92406	0.092242	1.737987		
	26	O	-4.81549	-1.49094	1.621122		
	27	H	-0.91057	-1.56625	2.162763		
4	Tag	Symbol	X	Y	Z	-1942.35	0.11172
	1	Pd	-2.50598	3.605319	0.02675		
	2	Pd	-3.31715	0.959569	0.078463		

	3	Pd	-4.12109	-1.64063	0.12985		
	4	Pd	0.173707	4.180019	-0.21196		
	5	Pd	-0.63511	1.580579	-0.16023		
	6	Pd	-1.44537	-1.04783	-0.10854		
	7	Pd	-2.2244	-3.73979	-0.06008		
	8	Pd	2.045225	2.189279	-0.39854		
	9	Pd	1.226554	-0.43626	-0.34585		
	10	Pd	0.433201	-3.0702	-0.29638		
	11	Pd	3.909301	0.176394	-0.5856		
	12	Pd	3.120269	-2.42148	-0.5342		
	13	C	2.069402	0.369353	1.532201		
	14	C	3.196764	-0.58006	1.452618		
	15	C	2.844434	-2.01553	1.395768		
	16	C	1.434269	-2.44778	1.602077		
	17	C	0.476082	-1.46179	2.030258		
	18	C	0.780096	-0.10506	1.969882		
	19	H	3.601591	-2.66051	1.854028		
	20	H	1.321638	-3.44785	2.022829		
	21	H	-0.46518	-1.78472	2.459998		
	22	C	2.414326	1.811879	1.656478		
	23	H	1.605965	2.459858	2.041935		
	24	O	4.360063	-0.27039	2.063552		
	25	H	4.376139	0.73444	2.079014		
	26	O	3.626324	2.174562	1.793057		
	27	H	0.054617	0.630364	2.303427		
5	Tag	Symbol	X	Y	Z	-1942.35	0.113507
	1	Pd	-3.95089	-1.90173	-0.00796		
	2	Pd	-1.39954	-2.96646	-0.14014		
	3	Pd	1.107372	-4.01943	-0.26962		
	4	Pd	-4.26476	0.831129	-0.03724		
	5	Pd	-1.75928	-0.22664	-0.16673		
	6	Pd	0.775164	-1.2887	-0.29766		
	7	Pd	3.375536	-2.32585	-0.4334		
	8	Pd	-2.10676	2.510024	-0.19385		
	9	Pd	0.423996	1.439532	-0.32489		
	10	Pd	2.965244	0.394238	-0.45659		
	11	Pd	0.072746	4.179533	-0.35186		
	12	Pd	2.578584	3.141329	-0.48175		
	13	C	0.98895	-0.1828	2.236518		
	14	C	1.786129	0.977904	2.245358		
	15	C	3.115041	0.947453	1.686188		
	16	C	3.711821	-0.31678	1.39507		
	17	C	2.945455	-1.55833	1.442409		
	18	C	1.493432	-1.41323	1.662568		
	19	H	3.742397	1.809062	1.88673		
	20	H	4.796196	-0.38402	1.410818		

	21	H	3.423566	-2.42516	1.919281		
	22	C	-0.30395	-0.14483	2.884374		
	23	H	-0.90485	-1.06809	2.847992		
	24	O	1.410542	2.071281	2.874302		
	25	H	0.48392	1.889735	3.216459		
	26	O	-0.72914	0.848645	3.480788		
	27	H	0.984971	-2.31834	2.00072		
6	Tag	Symbol	X	Y	Z	-1942.35	0.112387
	1	Pd	-3.93841	-0.88722	-0.46333		
	2	Pd	-1.70933	-2.5252	-0.3625		
	3	Pd	0.478637	-4.14109	-0.26439		
	4	Pd	-3.59845	1.842115	-0.40783		
	5	Pd	-1.41317	0.222157	-0.3089		
	6	Pd	0.800648	-1.4095	-0.20901		
	7	Pd	3.083478	-3.0322	-0.10601		
	8	Pd	-1.10421	2.962899	-0.25556		
	9	Pd	1.103098	1.324167	-0.15634		
	10	Pd	3.326831	-0.29226	-0.05564		
	11	Pd	1.408626	4.06931	-0.10245		
	12	Pd	3.599445	2.467983	-0.00314		
	13	C	-2.02721	-0.65148	1.592179		
	14	C	-1.06427	0.275737	2.180018		
	15	C	0.269691	-0.1071	2.306531		
	16	C	0.694608	-1.42248	1.962163		
	17	C	-0.2773	-2.45803	1.744828		
	18	C	-1.669	-2.07811	1.588161		
	19	H	0.97565	0.602508	2.719136		
	20	H	1.697086	-1.72061	2.25461		
	21	H	-0.04002	-3.47145	2.057611		
	22	C	-3.46526	-0.28696	1.474443		
	23	H	-4.18223	-1.00408	1.9227		
	24	O	-1.4583	1.451649	2.65963		
	25	H	-2.38874	1.595427	2.362341		
	26	O	-3.80521	0.984106	1.541758		
	27	H	-2.43187	-2.7708	1.95754		

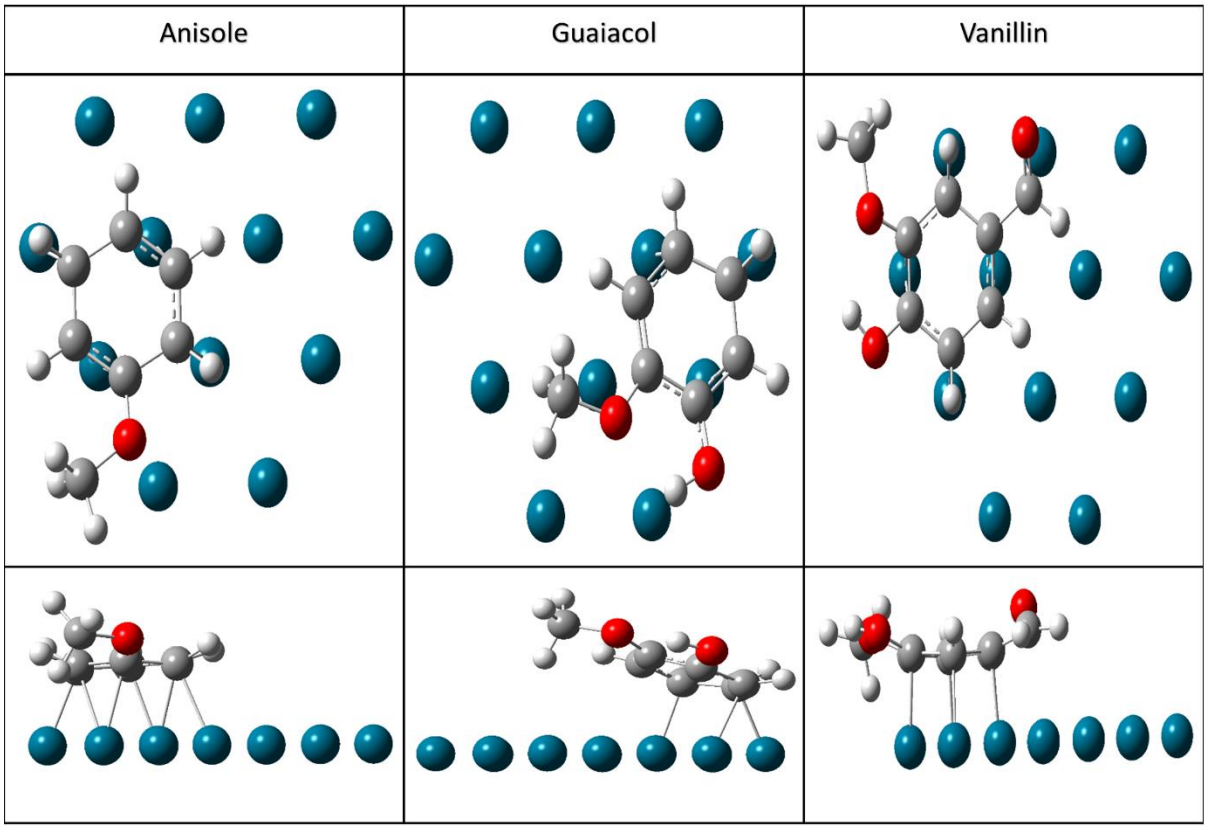
Supplementary Table 2. The xyz coordinates, electronic energy, and ZPVEs of adsorbed species over Pd(111) catalyst surface.

Structures	xyz Coordinates					Electronic energy	ZPVE
2-hydroxy-benzaldehyde	Same as adsorption configuration 3						
Phenol	Tag	Symbol	X	Y	Z	-1829.05	0.102996
	1	Pd	-3.1373	-3.06425	0.057086		
	2	Pd	-0.38016	-3.17619	-0.16851		
	3	Pd	2.330022	-3.29013	-0.39592		
	4	Pd	-4.37348	-0.61485	0.17495		
	5	Pd	-1.66353	-0.73143	-0.05268		
	6	Pd	1.075331	-0.84424	-0.28173		
	7	Pd	3.868078	-0.91088	-0.5135		
	8	Pd	-2.93418	1.714527	0.065656		
	9	Pd	-0.19542	1.592425	-0.1631		
	10	Pd	2.544323	1.497533	-0.391		
	11	Pd	-1.47069	4.040074	-0.04483		
	12	Pd	1.233627	3.939605	-0.27019		
	13	C	3.142494	-1.36807	1.495129		
	14	C	1.894817	-0.59716	1.593773		
	15	C	2.066306	0.875381	1.626837		
	16	C	3.362608	1.454131	1.798098		
	17	C	4.513042	0.660119	1.814076		
	18	C	4.417786	-0.73135	1.628216		
	19	H	1.210189	1.443636	1.978181		
	20	H	3.422158	2.500444	2.06316		
	21	H	5.50742	1.128047	1.948893		
	22	H	3.049679	-2.41594	1.77713		
	23	O	0.976548	-1.12157	2.482226		
	24	H	0.073786	-1.09472	2.104943		
	25	H	5.296762	-1.34821	1.785966		
Benzene	Tag	Symbol	X	Y	Z	-1753.84	0.099492
	1	Pd	-2.20661	3.494186	-0.25589		
	2	Pd	-2.91974	0.821196	-0.29775		
	3	Pd	-3.62704	-1.80711	-0.33727		
	4	Pd	0.457724	4.170487	-0.12151		
	5	Pd	-0.25537	1.541409	-0.1621		
	6	Pd	-0.96828	-1.115	-0.19923		
	7	Pd	-1.64714	-3.83445	-0.23744		
	8	Pd	2.405834	2.248599	-0.01947		
	9	Pd	1.686439	-0.40528	-0.06089		
	10	Pd	0.990934	-3.06651	-0.10046		
	11	Pd	4.351722	0.30727	0.076843		

	12	Pd	3.658833	-2.31836	0.037754		
	13	C	-1.0884	1.026034	1.823188		
	14	C	-0.72925	-0.36391	1.928575		
	15	C	-1.70509	-1.39585	1.834528		
	16	C	-3.12079	-1.11311	1.681667		
	17	C	-3.49458	0.283272	1.702748		
	18	C	-2.5096	1.322797	1.760503		
	19	H	-1.4172	-2.39705	2.139323		
	20	H	-3.82115	-1.83489	2.108329		
	21	H	-4.52969	0.537694	1.909138		
	22	H	-0.44079	1.757272	2.301361		
	23	H	-2.8274	2.323044	2.039962		
	24	H	0.266522	-0.6172	2.275775		
Benzaldehyde	Tag	Symbol	X	Y	Z	-1867.15	0.107952
	1	Pd	3.955516	0.62475	-0.45492		
	2	Pd	1.857583	2.42503	-0.32011		
	3	Pd	-0.20143	4.200591	-0.18791		
	4	Pd	3.411292	-2.07168	-0.4132		
	5	Pd	1.354898	-0.29179	-0.28172		
	6	Pd	-0.72752	1.500661	-0.14719		
	7	Pd	-2.88072	3.289892	-0.00894		
	8	Pd	0.841408	-3.0023	-0.24103		
	9	Pd	-1.23546	-1.20287	-0.10773		
	10	Pd	-3.32946	0.575982	0.026584		
	11	Pd	-1.74605	-3.91721	-0.06828		
	12	Pd	-3.80889	-2.15627	0.064295		
	13	C	2.360472	-0.50429	1.656744		
	14	C	0.980691	-0.15888	1.870224		
	15	C	0.539456	1.20171	1.867872		
	16	C	1.552752	2.237703	1.767291		
	17	C	2.941012	1.897641	1.726321		
	18	C	3.376273	0.541997	1.59524		
	19	H	-0.41183	1.446766	2.333546		
	20	H	1.272987	3.234317	2.101739		
	21	H	3.674307	2.664272	1.950092		
	22	C	2.776609	-1.93453	1.608731		
	23	H	3.783365	-2.14128	2.021912		
	24	O	1.90541	-2.88384	1.670357		
	25	H	4.378892	0.285826	1.947056		
	26	H	0.301285	-0.94828	2.17482		

Adsorption of anisole, guaiacol, and vanillin

The most stable adsorption configurations of anisole, guaiacol, and vanillin over Pd(111) catalyst model can be seen in Supplementary Figure 1. All of these phenolic bio-oil model species adsorb in bridge 30° configurations similar to other species, i.e., benzene, phenol, benzaldehyde, and 2-hydroxybenzaldehyde considered in the present study. The spin multiplicities of these adsorbed substrates over Pd(111) model suggest the ground state structures in quintet states; however, bare catalyst surface lies in septet state as of already defined in manuscript. The adsorption energies of anisole, guaiacol, and vanillin are calculated as -33.40 kcal/mol, -32.60 kcal/mol, and -36.19 kcal/mol, respectively, which are in correct order compared to adsorption energies of other aforementioned phenols. In the adsorption of anisole, the methyl group attached to oxygen atom is slightly out-located from the catalyst boundary and this is because of lower coordination number of metals at the boundary. Similar phenomena can be seen in the case of vanillin as well where methoxy and hydroxyl groups are out-located from the catalyst boundary. In the case of guaiacol, oxygen atom of hydroxyl group is slightly outside of catalyst surface and, both oxy-functional groups sense repulsion from the surface which is the reason of bend of both oxy-groups from the plane. The same is true for the case of formyl group of vanillin. It should be noticed that despite slightly out-location of oxy-groups of substrates over present surface, the benzenoid rings of all three compounds are still interacting with the catalyst surface.



Supplementary Figure 1. The adsorption configurations of anisole, guaiacol, and vanillin.