Table S1. Optimized structures of furfural and furfuryl alcohol in the gas phase. Bond lengths are in (Å), and the torsion angle, ω (°), is formed by atoms O1, C2, C6 and O7.

functional	*trans* furfural							
	d_{12}	d_{23}	d_{34}	d_{45}	d_{51}	d_{26}	d_{67}	ω
PW91	1.39	1.38	1.42	1.37	1.36	1.45	1.23	180
PBE	1.39	1.38	1.42	1.38	1.36	1.45	1.23	180
optPBE	1.39	1.38	1.42	1.38	1.37	1.45	1.23	180
optB88	1.39	1.38	1.42	1.37	1.36	1.44	1.23	179
optB86b	1.39	1.38	1.42	1.37	1.36	1.45	1.23	180
PBE-D2	1.39	1.38	1.42	1.38	1.36	1.45	1.23	180
functional	*cis* furfural							
	d_{12}	d_{23}	d_{34}	d_{45}	d_{51}	d_{26}	d_{67}	ω
PW91	1.38	1.38	1.42	1.37	1.36	1.45	1.23	0
PBE	1.38	1.38	1.42	1.37	1.36	1.45	1.23	0
optPBE	1.39	1.38	1.42	1.37	1.37	1.45	1.23	0
optB88	1.38	1.38	1.42	1.37	1.36	1.45	1.23	0
optB86b	1.38	1.38	1.42	1.37	1.36	1.45	1.23	0
PBE-D2	1.38	1.38	1.42	1.38	1.36	1.45	1.23	0
functional	*trans* furfuryl alcohol								
	d_{12}	d_{23}	d_{34}	d_{45}	d_{51}	d_{26}	d_{67}	d_h	ω
PW91	1.38	1.37	1.43	1.36	1.38	1.49	1.43	3.73	157
PBE	1.38	1.37	1.43	1.37	1.38	1.49	1.43	3.70	155
optPBE	1.37	1.37	1.44	1.36	1.37	1.49	1.43	3.74	157
optB88	1.37	1.37	1.44	1.36	1.37	1.49	1.43	3.74	157
optB86b	1.38	1.37	1.43	1.36	1.38	1.49	1.43	3.71	156
PBE-D2	1.38	1.37	1.43	1.37	1.38	1.49	1.43	3.68	152
functional	*cis* furfuryl alcohol								
	d_{12}	d_{23}	d_{34}	d_{45}	d_{51}	d_{26}	d_{67}	d_h	ω
PW91	1.38	1.37	1.43	1.36	1.37	1.48	1.44	2.75	69
PBE	1.38	1.37	1.43	1.37	1.37	1.48	1.44	2.74	69
optPBE	1.39	1.37	1.44	1.37	1.38	1.49	1.45	2.74	69
optB88	1.38	1.37	1.43	1.36	1.37	1.48	1.44	2.75	69
optB86b	1.38	1.37	1.43	1.36	1.37	1.48	1.44	2.74	70
PBE-D2	1.38	1.37	1.43	1.37	1.37	1.48	1.44	2.74	79

Table S2. Total energy (in eV) and energy differences (in eV) for gas-phase furfural and furfuryl alcohol in *cis* and *trans* configurations calculated from PW91, PBE, optPBE, optB88, optB86b, and PBE-D2 functionals.

standard functionals	furfural	furfuryl alcohol
	$\Delta_{(trans\text{-}cis)}$	$\Delta_{(trans\text{-}cis)}$
PW91	-0.026	0.045
PBE	-0.028	0.042
vdW-DF functionals		
optPBE	-0.029	0.048
optB88	-0.049	0.040
optB86b	-0.029	0.040
PBE-D2	-0.025	0.041

Table S3. Binding energies (in eV) of furfural hydrogenation intermediates calculated on Pd(111), Cu(111), and Pt(111) for different functionals according to Eqn. (1) in the main text.

	Pd-PW91	Pd-PBE	Pd-optB86b	Cu-PW91	Cu-PBE	Cu-optB86b	Pt-PW91	Pt-PBE	Pt-optB86b
1 H[§]									
mh2	-1.14	-1.12	-2.34	0.57	0.72	-0.34	-1.76	-1.67	-2.92
mh3	-1.06	-1.01	-2.25	0.02	0.14	-0.71	-1.49	-1.37	-2.61
mh4	-1.00	-0.96	-2.18	0.37	0.53	-0.62	-1.41	-1.30	-2.51
mh5	-1.23	-1.19	-2.35	-0.28	-0.14	-0.89	-1.60	-1.49	-2.66
mh6	-0.96	-0.93	-2.14	-0.89	-0.75	-1.59	-1.43	-1.33	-2.58
mh7	-1.30	-1.28	-2.45	-0.03	0.06	-0.84	-2.00	-1.661	-3.03
2 H[§]									
dh45	-1.77	----	----	----	----	----	----	----	----
dh57	-1.50	----	----	----	----	----	----	----	----
3 H[§]									
th267	-1.95	----	----	----	----	----	----	----	----
th345	-2.07	----	----	----	----	----	----	----	----
th367	-1.87	----	----	----	----	----	----	----	----
th467	-1.89	----	----	----	----	----	----	----	----
th567	-2.02	----	----	----	----	----	----	----	----
4 H[§]									
qh2345	-2.10	----	----	----	----	----	----	----	----
qh3457	-2.39	----	----	----	----	----	----	----	----
5 H[§]									
ph23457	-2.69	----	----	----	----	----	----	----	----

[§]The hydrogenation intermediates are represented in short-hand notation throughout this paper, where *mh*, *dh*, *th*, *qh*, and *ph* correspond to intermediates from different levels of hydrogenation as classified in Table S3. Numerical labels represent the hydrogenation sites, indicated in Fig. 1 in the main text.

The reference states correspond to gas phase furfural, stoichiometrically appropriate amounts of hydrogen, and the corresponding clean metal surface for each functional.

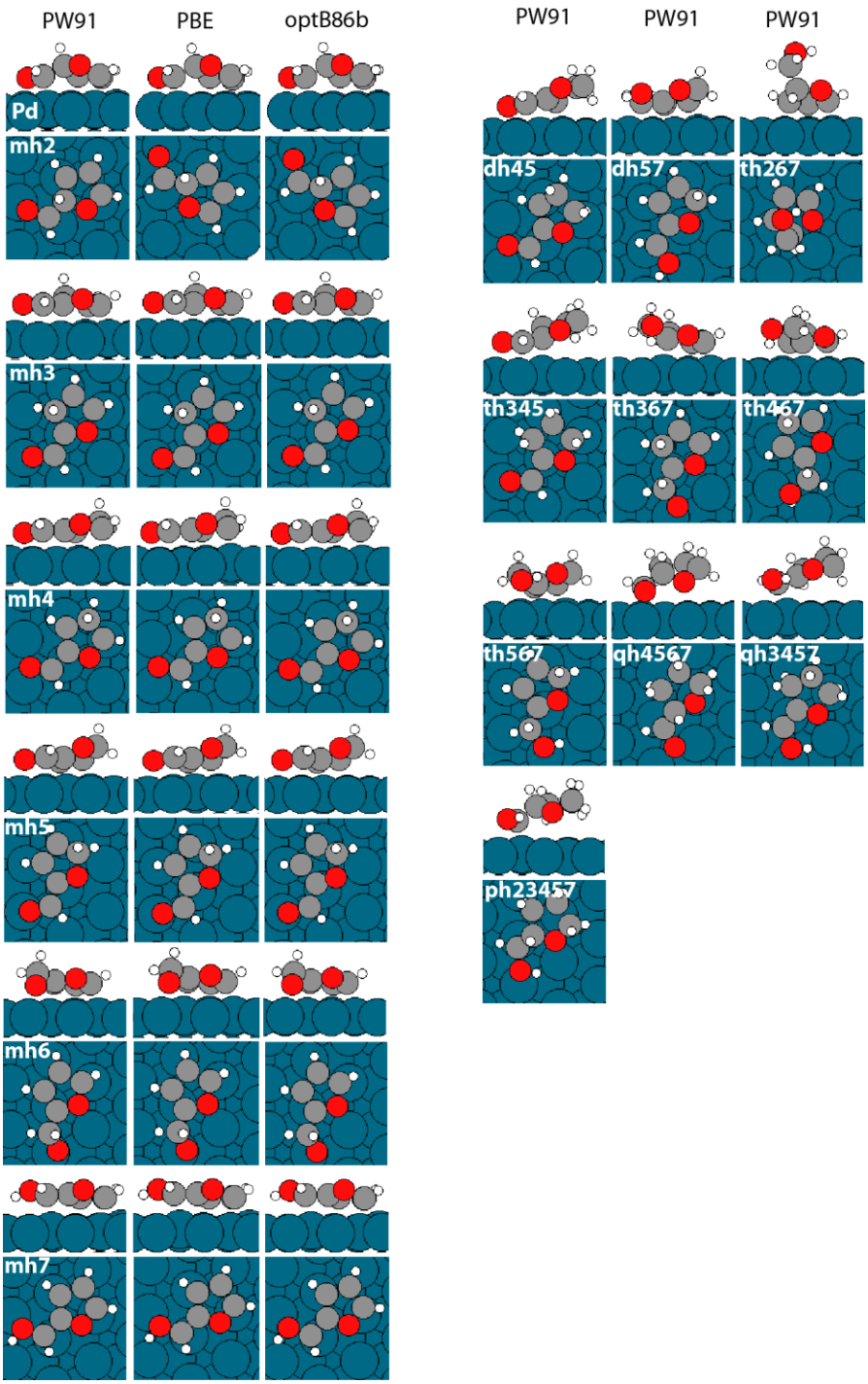

Fig. S1. Optimized geometries of furfural hydrogenation intermediates on Pd(111) for PW91, PBE (mono-hydrogenation intermediates only), and optB86b functionals (mono-hydrogenation intermediates only).

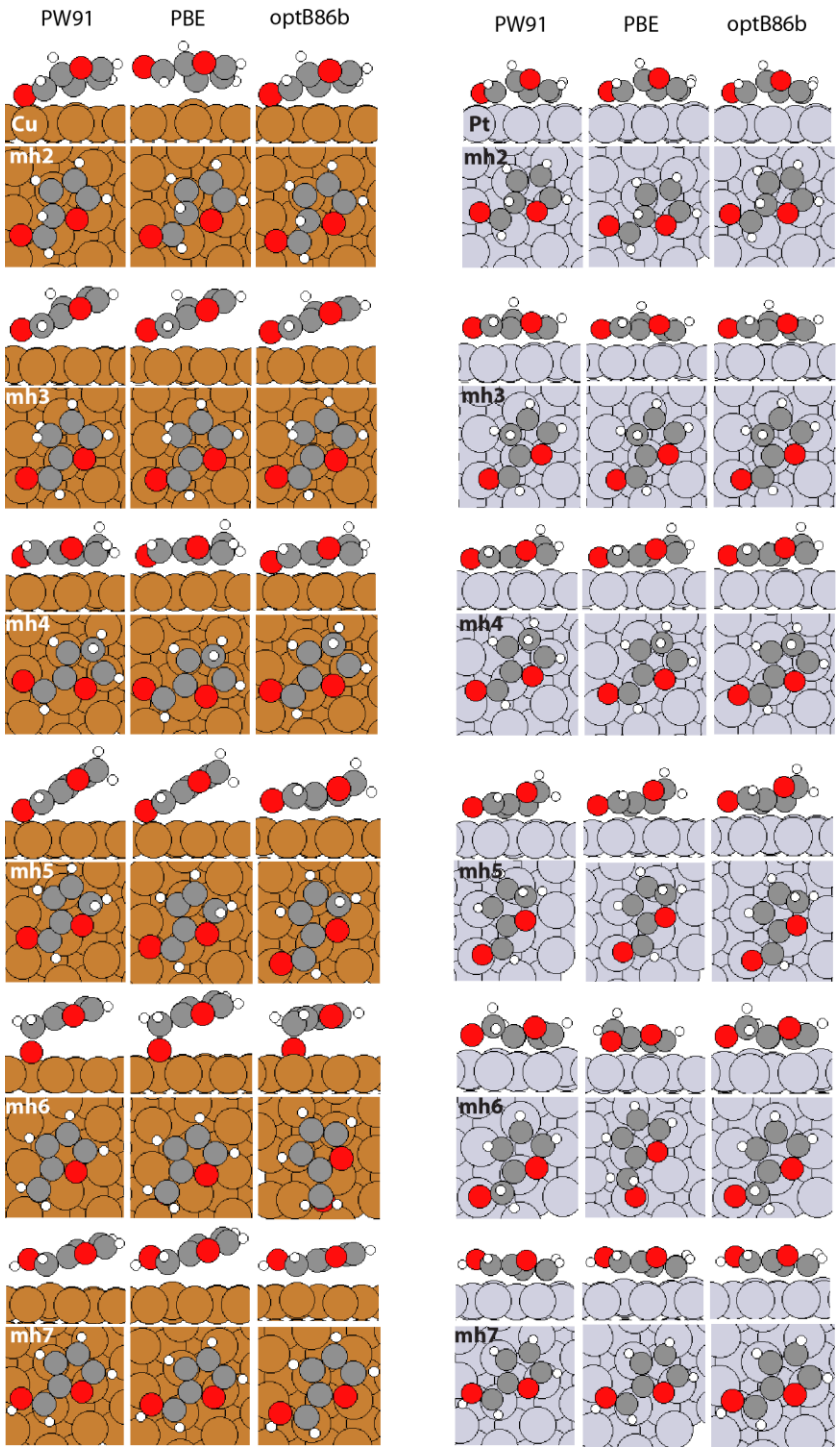

Fig. S2. Optimized geometries of furfural hydrogenation intermediates on Cu(111) and Pt(111) for PW91, PBE (mono-hydrogenation intermediates only), and optB86b functionals (mono-hydrogenation intermediates only).