Ligand assisted hydrogenation of levulinic acid on Pt(111) from first principles calculations: Supplementary Material

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Area based adsorption energies

If we assume the covered area for the 2AQ modified Pt(111) surface as a rectangular box roughly the size of Figure 4a) we have an area of about 210 Å^2 leading to an adsorption energy of 12.2 meV/Å^2 Ẇhen both ligands are protonated the adsorption energy in this area would be 16.0 meV/Å^2 Ẇhen we assume a rectangular binding similar to Figure S4c) we get an area of about 70 Å^2 and an adsorption energy for LA2 of 11.1 meV/ Å^2 .

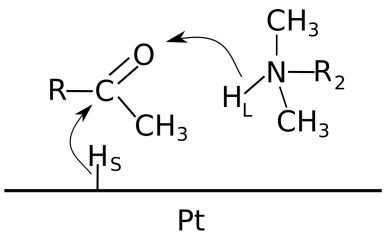

Figure S1: Schematic illustration of the possible reaction mechanisms for the hydrogenation reaction of levulinic acid in the presence of the AQ ligand. 1)In the alkokxy mechanism the surface bound hydrogen H_S is transferred first followed by the ligand bound H_L. 2) In the hydroxy mechanism H_L is transferred first followed by H_S. 3) In a concerted mechanism H_S and H_L are transferred simultaneously.

Table S1: Transition states and their corresponding imaginary frequencies and distances from Fig. 7.

Symbol	imaginary Frequency (cm^{-1})	C/O-H distance Å
TS_1	927.3i	CH=1.45
TS_2	846.5i	CH=1.44
TS_3	175.2i	CH=2.03
TS_4	598.7i	OH=1.55
TS_5	514.6i	OH=1.58
TS_6	353.0i	CH=1.94
TS_7	779.1i	OH=1.40 CH=1.31
TS_8	331.7i	CH=1.72

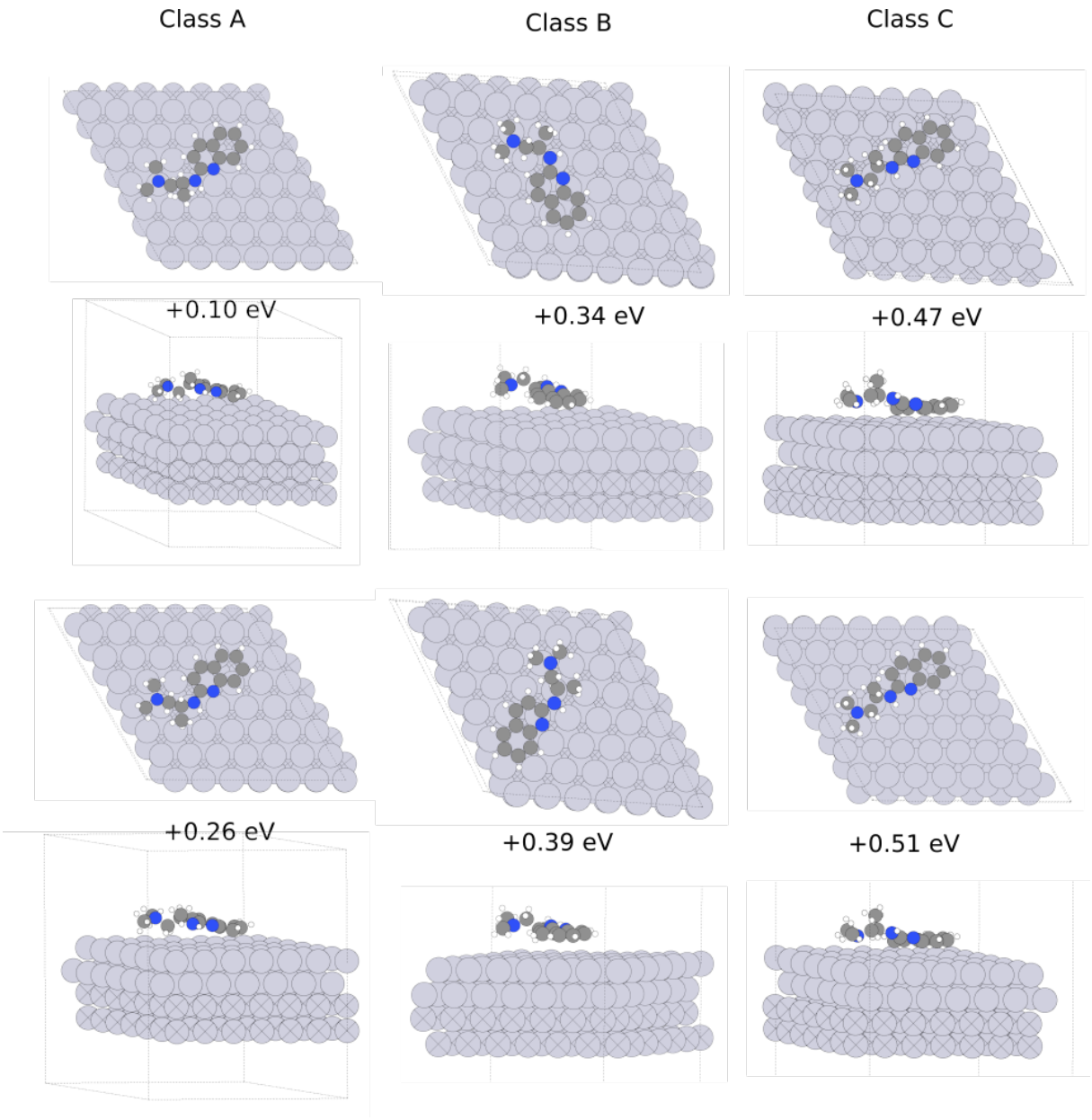

Figure S2: Other isomers of 1AQ adsorbed on Pt(111) sorted by class are presented.

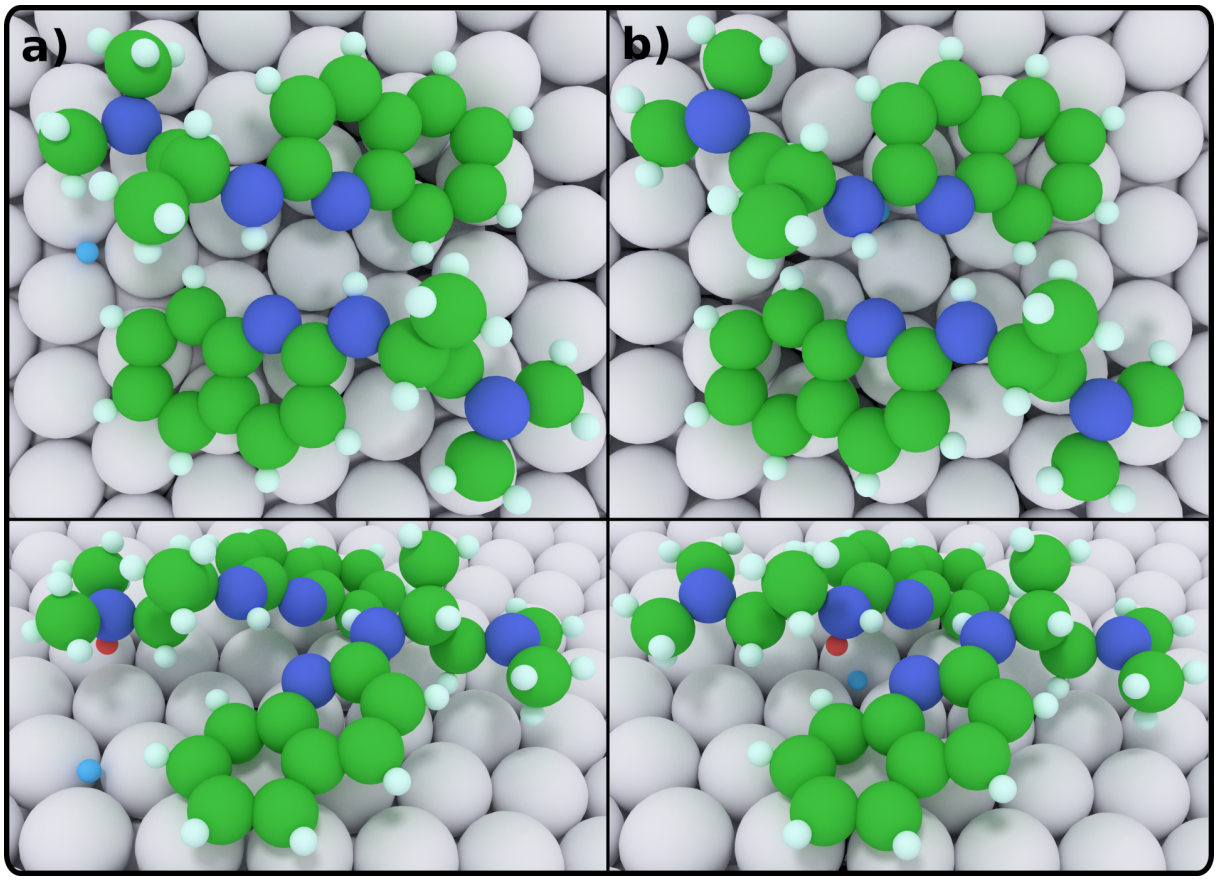

Figure S3: Hydrogen transfer to the AQ ligand in different positions. Difference in energy depending on the positioning of the transferred hydrogen atom. The transferred hydrogen atom is shown in red while the remaining one is displayed blue. The hydrogen transfer to N^3-atom a) is thermodynamically favoured (a 0.00 eV) over the transfer to the to N^2-atom b) (+0.92 eV)

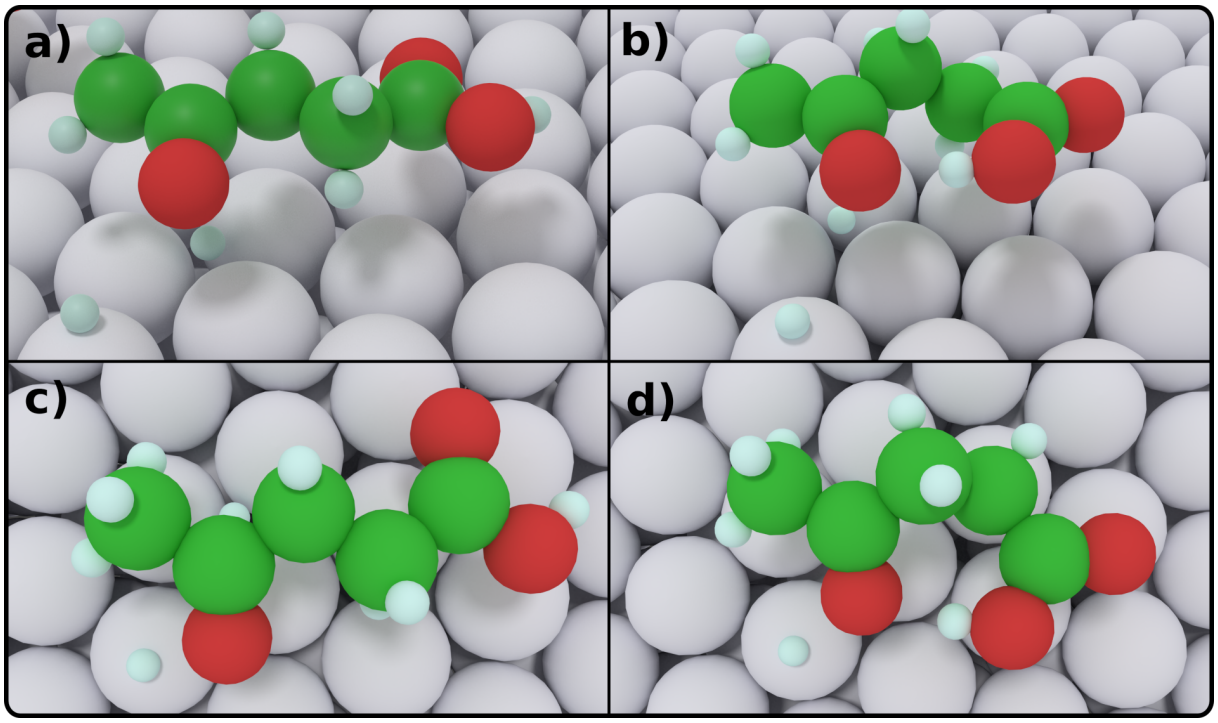

Figure S4: Adsorbed structures of LA1 (b, d) and LA2 (a, c) on 2H pre-covered Pt(111).

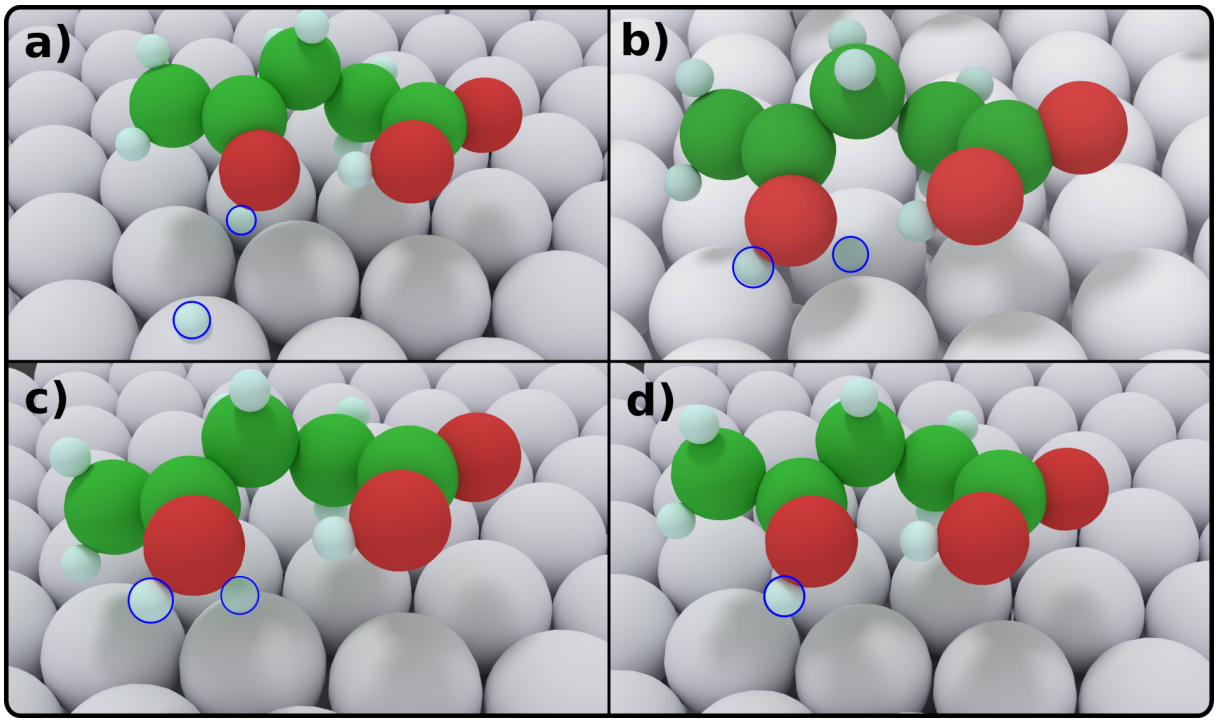

Figure S5: Initial I_3 (a), intermediate I_5 (b), transition TS_3 (c) and final (d) state structure for levulinic acid with an internal hydrogen bond (LA1) . Color code is as following: Carbon=green, Hydrogen=white, Oxygen=red, Platinum=grey, Nitrogen=blue.

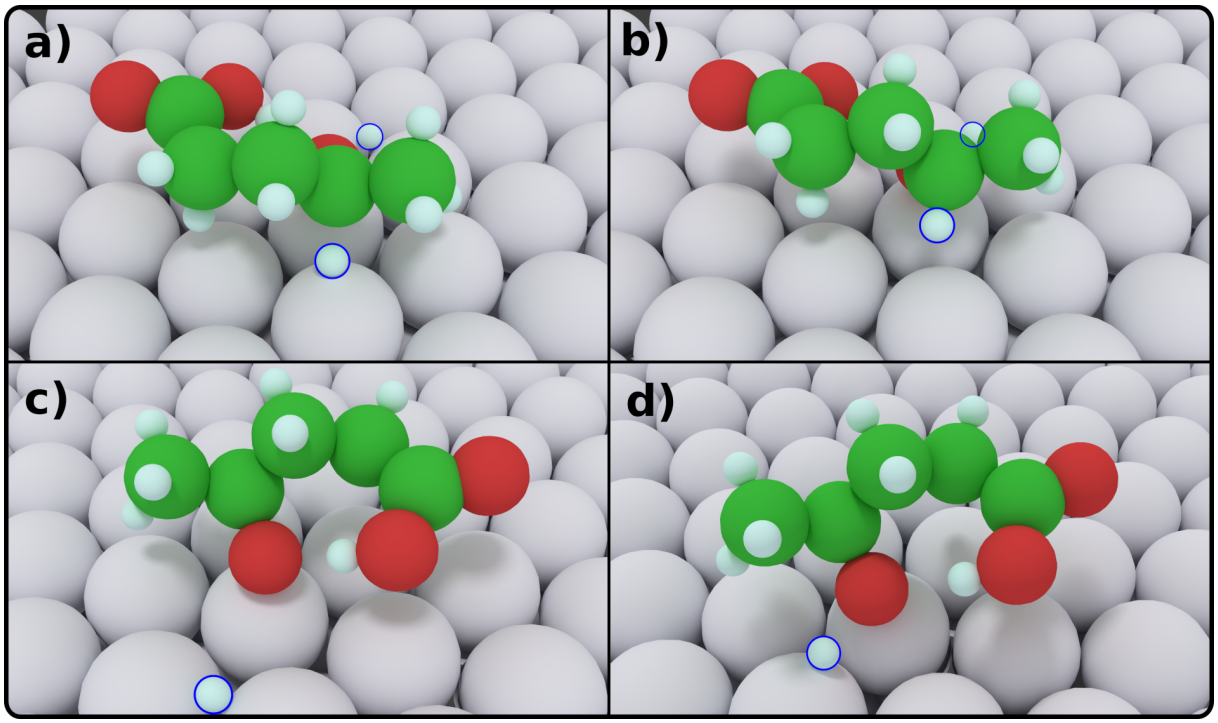

Figure S6: TS_1 (a), Alkoxy intermediate I_6 (b) and (c) and TS_4 (d) from Fig. 7 and Table 2 of levulinic acid (LA1) Color code is as following: Carbon=green, Hydrogen=white, Oxygen=red, Platinum=grey, Nitrogen=blue.

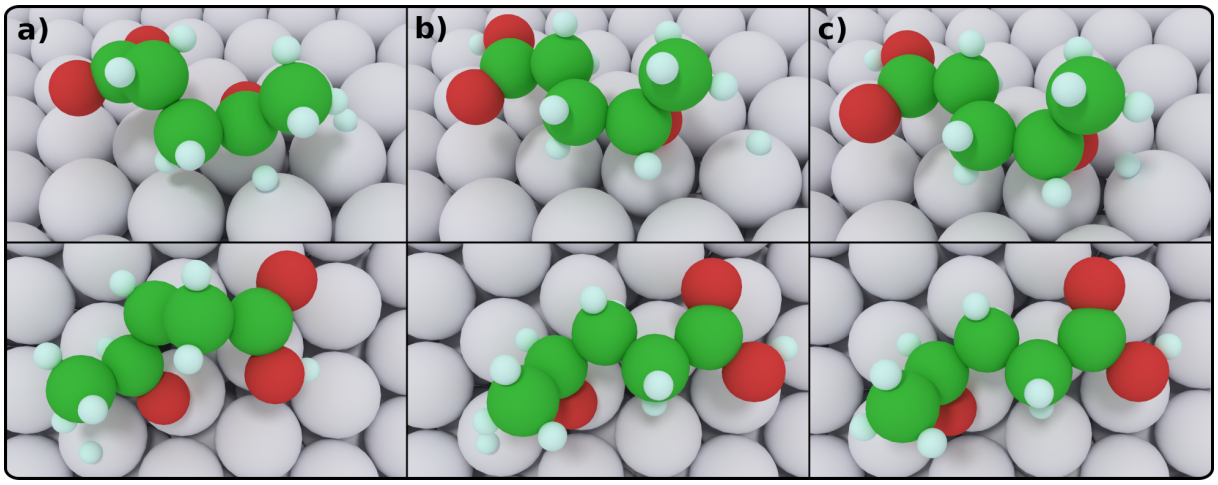

Figure S7: TS_2 (a), Alkoxy intermediate I_7 (b) and TS_5 (c) from Fig. 7 and Table 2 of levulinic acid (LA2) in the side view (top) and top view (bottom). Color code is as following: Carbon=green, Hydrogen=white, Oxygen=red, Platinum=grey, Nitrogen=blue.

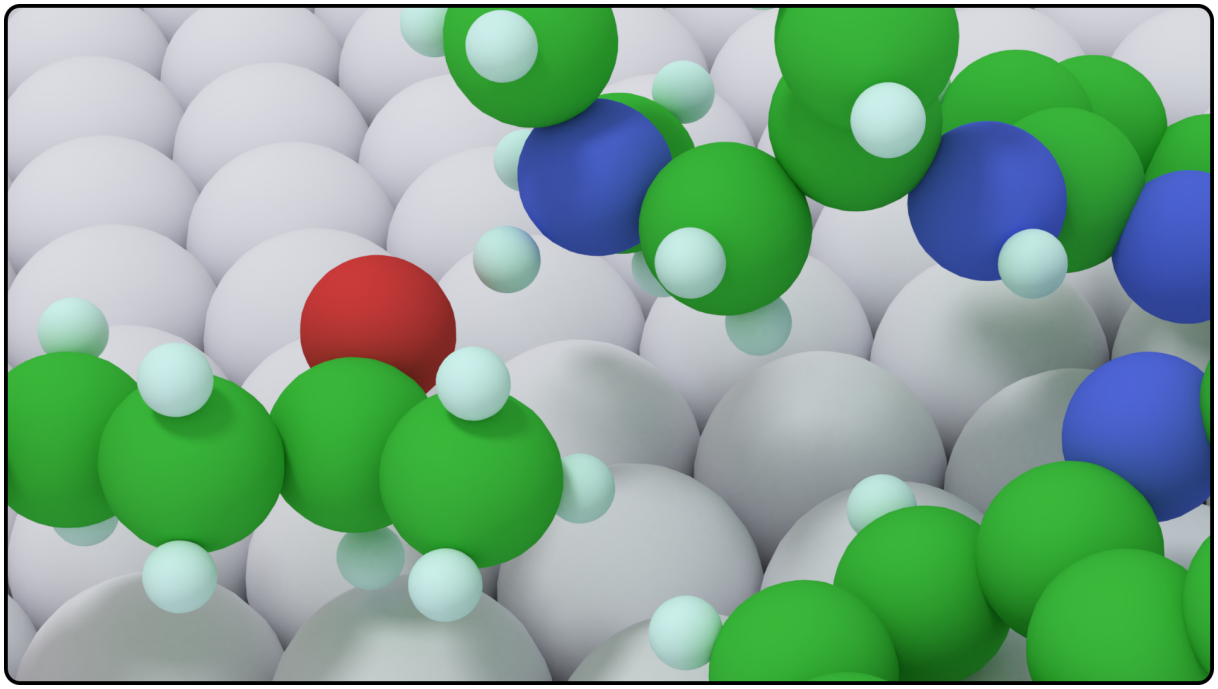

Figure S8: Detailed view of TS_7 from Fig. 7.

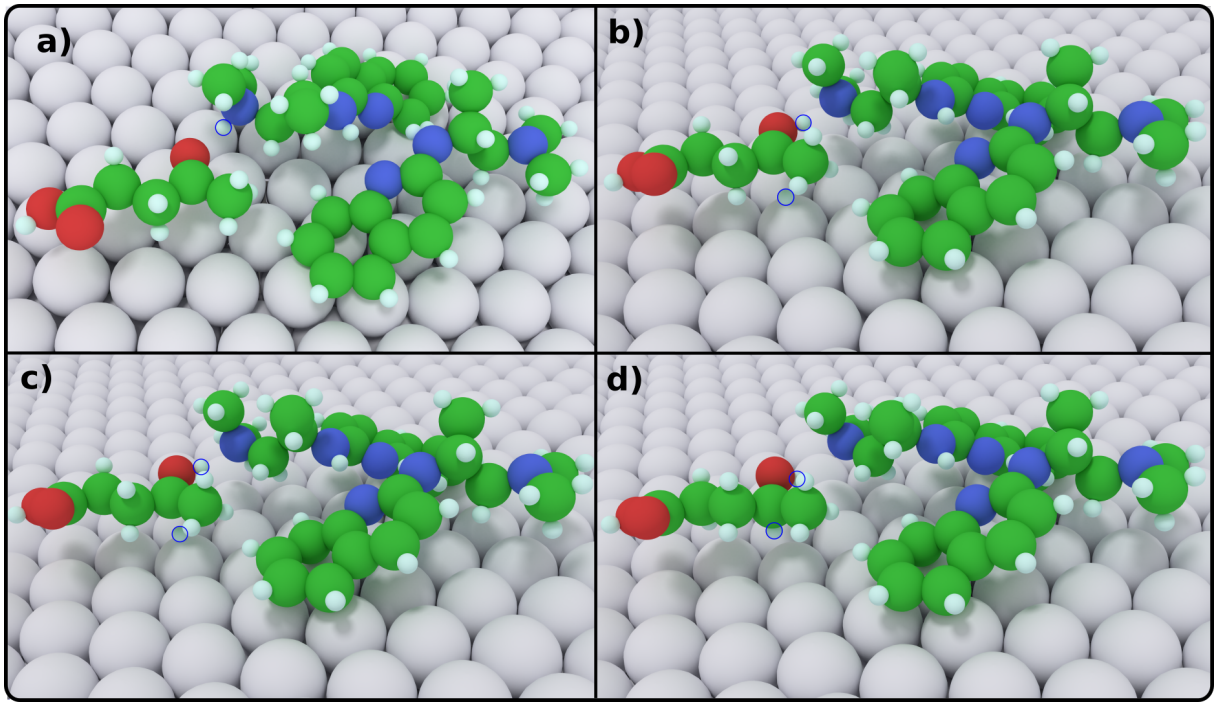

Figure S9: Structures for the hydrogenation reaction of levulinic acid on a Pt(111) surface in the presence of the 2AQH ligand via the hydroxy pathway. a) I_{12} , b) I_{13}, c) TS_8 and d) I_{14} from Fig. 7 .