1. Structure of the Transition State (TS) in the Minimum Energy Path from Conformer-3 to Intermediary-1

The NEB method was used to determine the minimum energy path (MEP) from the initial state: 'conform-3', to the final state: intermediate-1. The Structure with the highest energy in the minimum energy path was optimized with the dimer method implemented in CP2K (DIMER Input Sections). Also, the Vibrational_Analysis input section was introduced to perform the frequency calculations. The results are shown in Figure S1. It can be seen that, in the structure of the transition state (TS) there are atoms that form a closed ring of four atoms (oxygen, hydrogen, carbon, and gold), where the hydrogen atom is in the middle of the oxygen and carbon atoms.

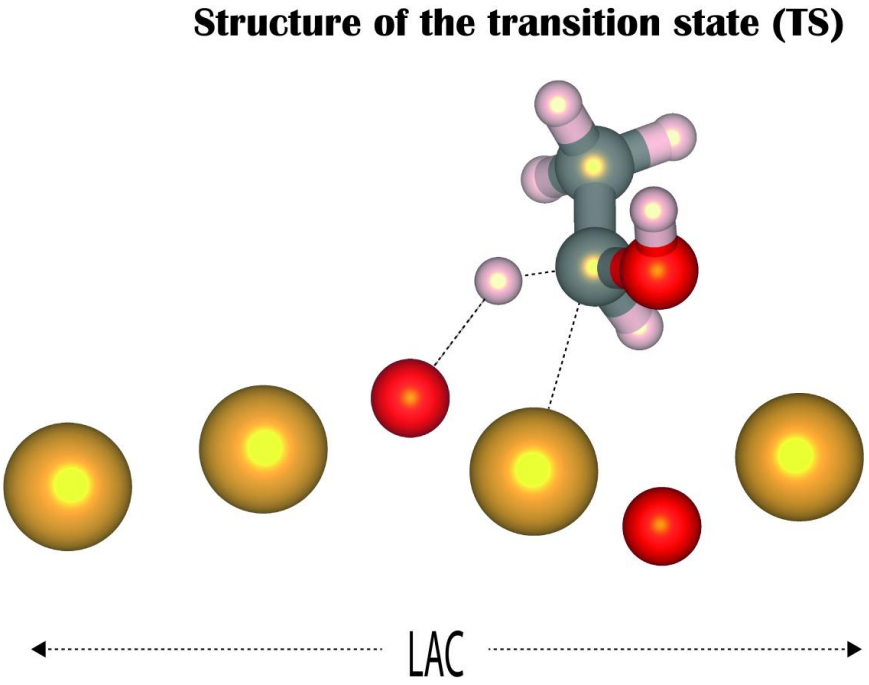

Figure S1 Structure of the transition state (TS) in the minimum energy path from conformer-3 to intermediary-1. Only the LAC part of NW is drawn to focus on the atoms of interest.

2. Acetaldehyde Formation in Pure LAC (Without Oxygen in Its Structure)

Alternatively, NEB analysis was performed to explore the formation of acetaldehyde in the pure LAC (without the presence of oxygen). We take intermediate-1 as the initial state and acetaldehyde as the final state. The result is shown in figure S2. It is observed that the process is endothermic, that is, it needs energy to occur, in this case approximately 0.35 eV. This result makes it clear that the LAC with and without the presence of oxygen lead to different reaction pathways. Therefore, it is easier for the reaction to occur in the presence of oxygen.

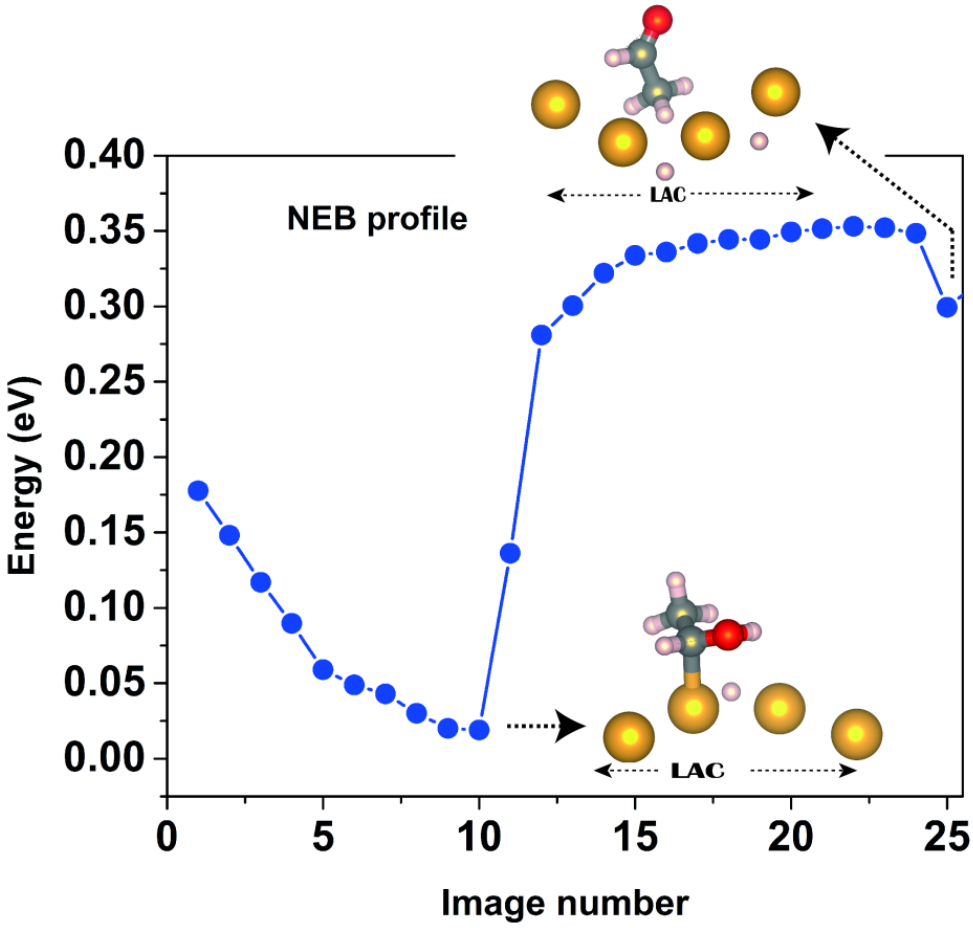

Figure S2 NEB of minimum energy pathway in the formation of acetaldehyde from an intermediate-1. This reaction occurs in pure LAC, that is, without the presence of oxygen atoms in its structure. The formation of acetaldehyde takes place with a high energy cost, since an endothermic process occurs.

3. Structure of the Transition State (Ts) in the Minimum Energy Path from Intermediary-1 to Intermediary-2

The NEB method was used to determine the minimum energy path (MEP) from the initial state: 'intermediary-1', to the final state: intermediate-2. The Structure with the highest energy in the minimum energy path was optimized with the dimer method implemented in CP2K (DIMER Input Sections). Also, the Vibrational_Analysis input section was introduced to perform the frequency calculations. The results are shown in Figure S3. It can be seen that in the transition state (TS) structure the carbon atom attached to the -OH group is between the gold and the oxygen atoms of the LAC.

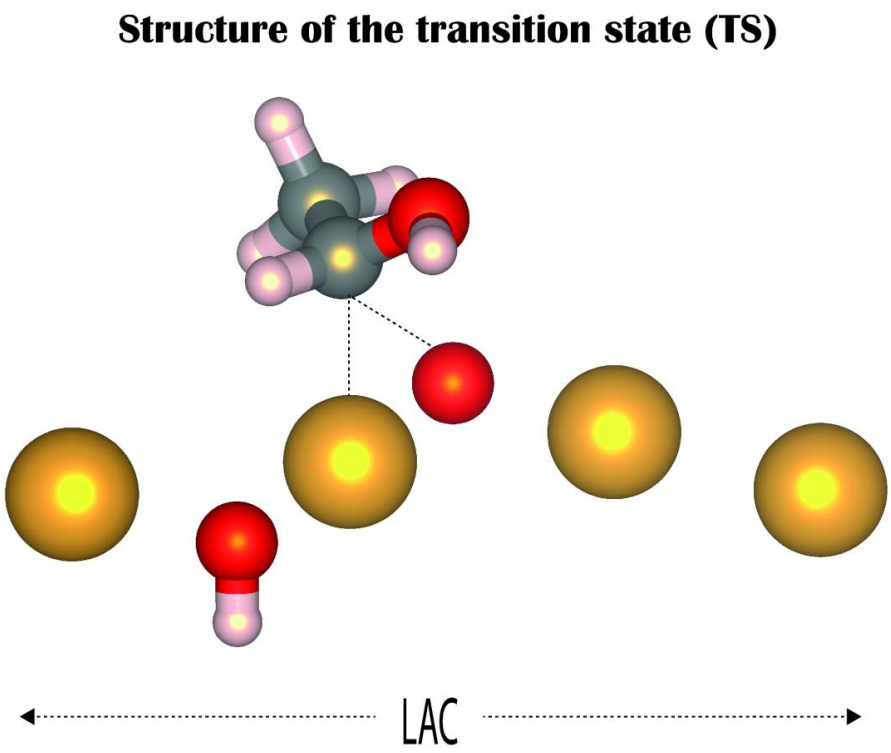

Figure S3 Structure of the transition state (TS) in the minimum energy path from intermediary-1 to intermediary-2. Only the LAC part of NW is drawn to focus on the atoms of interest.

4. Structure of the Transition State (TS) in the Minimum Energy Path from Intermediary-2 to the Acetic Acid

The NEB method was used to determine the minimum energy path (MEP) from the initial state: 'intermediary-2', to the final state: acetic acid. The Structure with the highest energy in the minimum energy path was optimized with the dimer method implemented in CP2K (DIMER Input Sections). Also, the Vibrational_Analysis input section was introduced to perform the frequency calculations. The TS structures of both reaction pathways (path 1 and path 3) were optimized. The results are shown in Figure S4. It can be seen that in the transition state (TS) structure of path 1 the hydrogen atom is in the middle of the gold and carbon atoms. Also, the TS structure of path3 shows that the hydrogen atom is in the middle between the oxygen and carbon atoms.

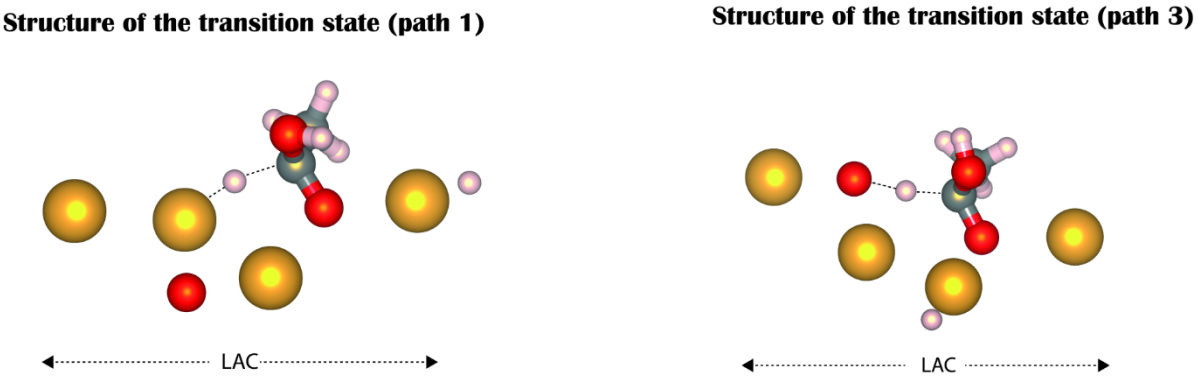

Figure S4 Structure of the transition state (TS) in the minimum energy path from intermediary-2 to the acid acetic. This graph shows the two reaction paths (path 1 and path 3). Only the LAC part of NW is drawn to focus on the atoms of interest.