

Supporting Information for
Coordination–Controlled C–C Coupling Products *via ortho*-Site C–H Activation

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1. Tip manipulation implemented on product D on Cu(111)

Tip manipulation experiments were performed on a product D in a twofold coordinated chain. The product D could be completely stripped off by pulling apart the connective coordination bonds. The subsequent tip manipulation moved the product D intactly, demonstrating the formation of robust covalent bond on *ortho*-sites.

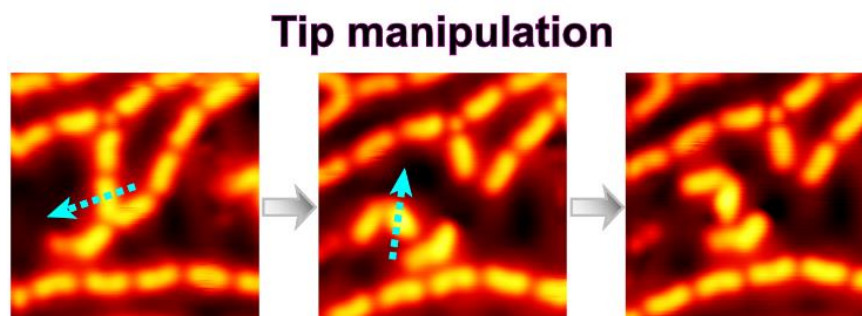


Figure S1 The only product D can be driven away completely from coordinated network and dragged as a whole by a STM tip. Scanning parameters: constant-current mode, $V_b = 10$ mV, $I_t = 50$ pA. Manipulation parameters: $V_b = 1$ mV, $I_t = 12$ nA with closed feedback loop.

2. Reaction path of one pyridyl ring with only flexible Cu adatom but no coordinated Cu adatom on Cu(111)

To clarify the role of the coordinated Cu adatom during C–H activation, we have calculated the reaction path without coordinated Cu adatom. A free Cu adatom approaches the *ortho*-site of a pyridyl ring gradually and then takes the hydrogen atom away. To trigger the dehydrogenation, energy of 1.27 eV is needed to overcome the reaction barrier. This is nearly identical to the reaction barrier shown in Figure 6, in which case both coordinated and free Cu adatoms are included in the calculation. Therefore, the free Cu adatom plays the role of catalyzing dehydrogenation while the coordinated Cu adatom merely imposes spatial restriction on C–C coupling, from an energy point of view.

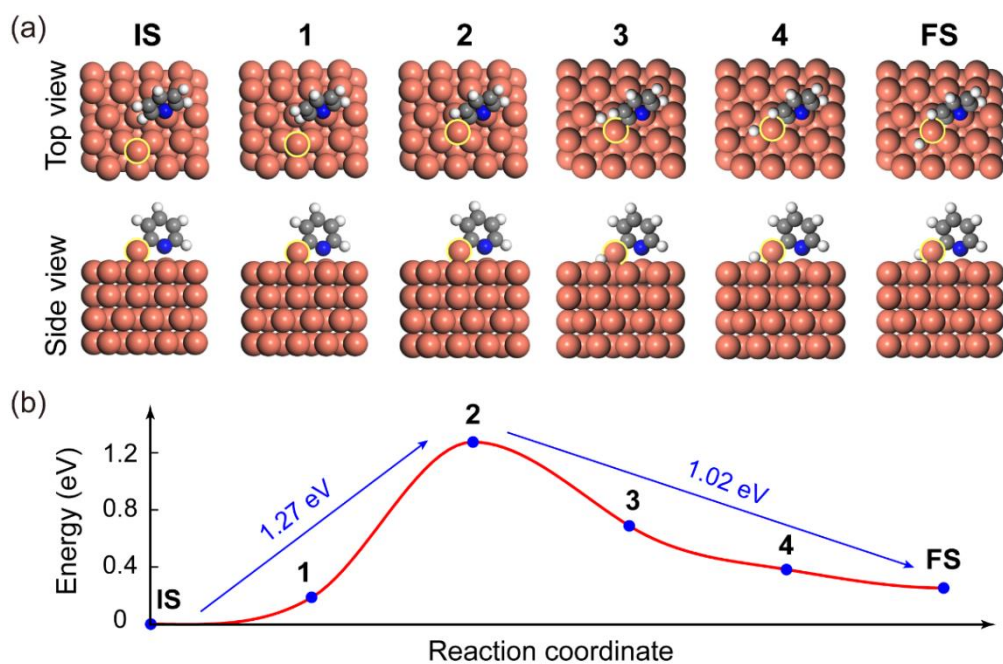


Figure S2 Results of calculated reaction path with only a free Cu adatom. (a) Top and side views of the calculated molecular configurations during the dehydrogenation process. (b) Energies of different states in dehydrogenation process.

3. Additional nc-AFM measurements

Occasionally, the C–H bond activation was observed on both *ortho*-sites of the pyridine group of the 1,4-BPyB molecule. Figure S3 shows STM and nc-AFM images showing the existence of clusters composed of four molecules with two additional C–C bonds formed for each pyridine group of the two coupled 1,4-BPyB molecules on Cu(111) after annealing to 400 K.

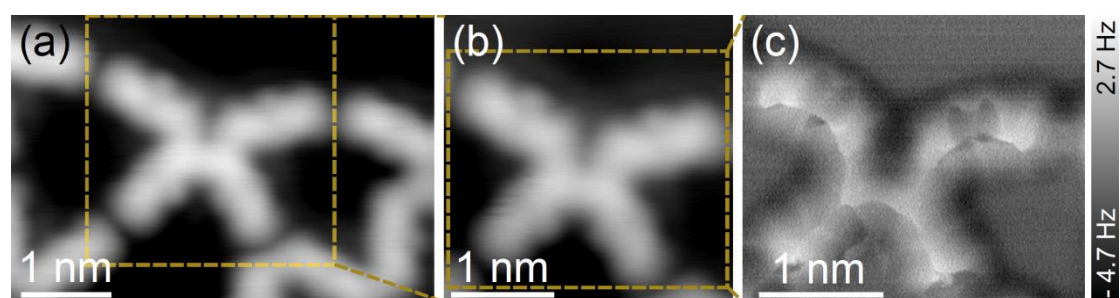


Figure S3 (a) An overview STM image showing the existence of clusters composed of four molecules with two additional C–C bonds formed for each pyridine group on Cu(111) after annealing to 400 K. (b) Close-up STM image of the cluster, where the two lower 1,4-BPyB molecules have two additional C–C bonds. (c) The corresponding frequency shift nc-AFM image revealing the covalent bond formation. Scanning parameters: (a) $V_b = 30$ mV, $I_t = 14$ pA; (b) $V_b = 30$ mV, $I_t = 14$ pA and (c) $V_b = -0.6$

mV. The tip is 10 pm retracted relative to a STM set point of 30 mV and 14 pA on the bare Cu.

4. Relative ratio of type-I and II products in the coordination and non-coordination systems

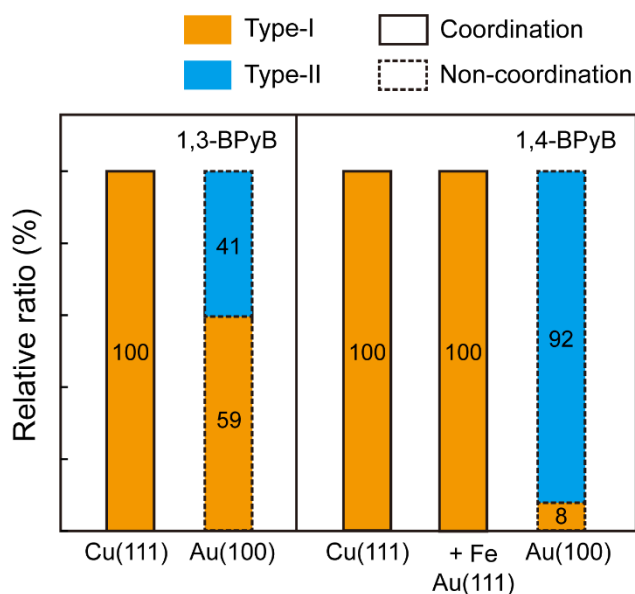


Figure S4 Statistic histograms showing the yields of type-I and II products in the coordination and non-coordination system, respectively. In a coordination system only type-I products are observed, while in a deficient coordination system the two types of products coexist and no selectivity is found. Samples obtained under the same annealing temperature (350 K) were used for statistics here.

5. Calculated dissociation process of Cu–C bond after the occurrence of dehydrogenation on Cu(111)

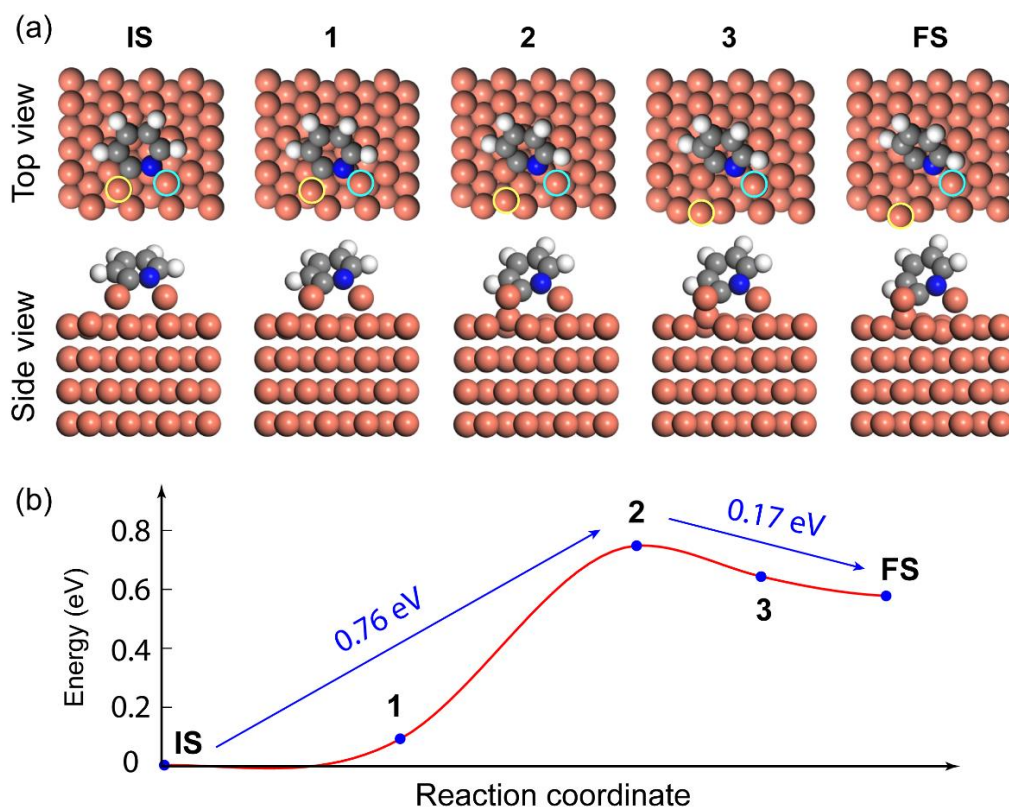


Figure S5 DFT calculation results showing the energy barrier of Cu–C bond dissociation occurring on a dehydrogenative pyridyl ring on Cu(111) with both a free (marked by yellow circle) and a coordinated Cu adatom (marked by blue circle). (a) Top and side views of the calculated molecular configurations throughout Cu–C bond dissociation. (b) Energies of different states in the Cu–C bond dissociation process.

6. Reaction path of one pyridyl ring with only free Au adatom but no coordinated Fe adatom on Au(111)

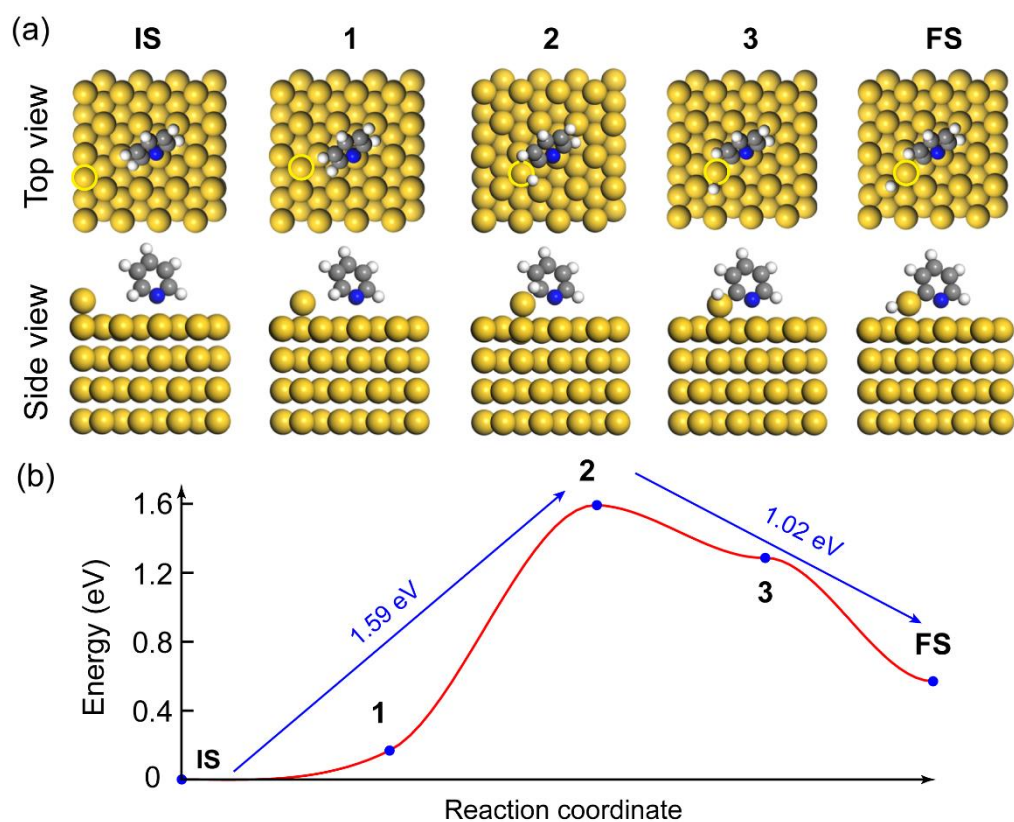


Figure S6 DFT calculation results of the dehydrogenative reaction path of a pyridyl ring on Au(111) with only a free Au adatom but no coordinated Fe adatom. (a) Top and side views of the calculated molecular configurations during the dehydrogenation process. The free Au adatom is highlighted by a yellow circle. (b) Energies of different states in dehydrogenation process.

7. Dehydrogenation process of pyridyl ring on Cu(111) with isolated hydrogen atom surrounded

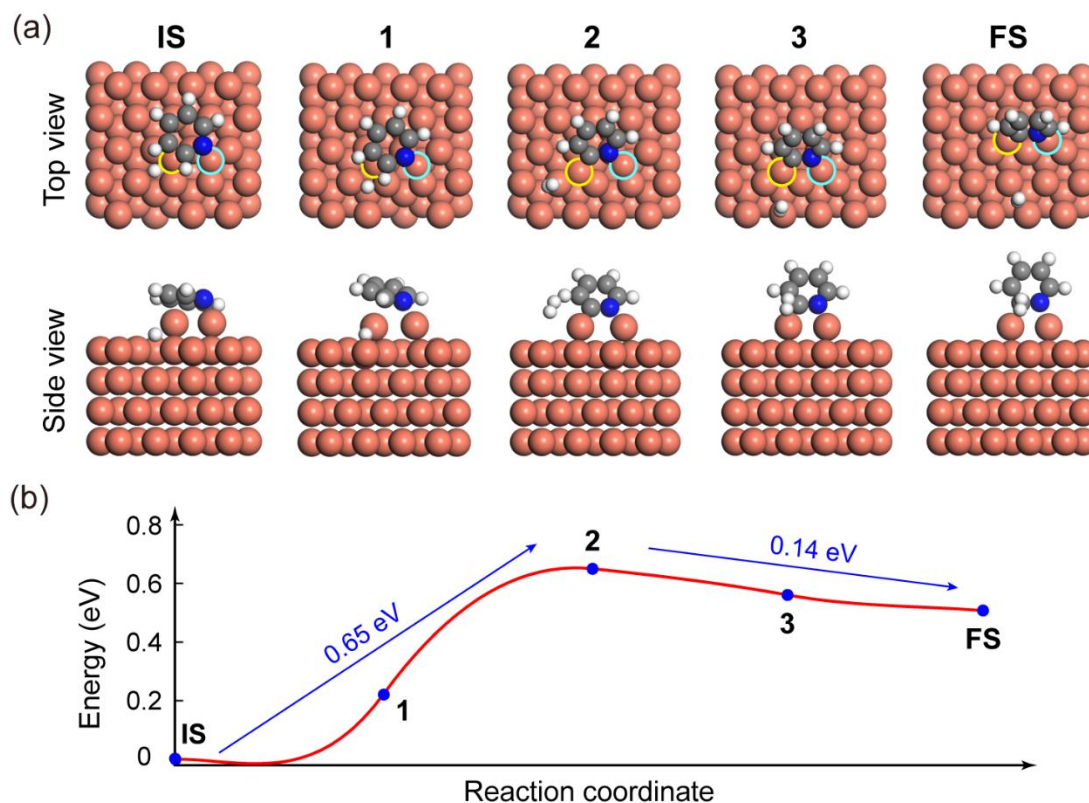


Figure S7 Calculated dehydrogenation process and barrier of a pyridyl ring on Cu(111) with an isolated hydrogen atom surrounded. The pyridyl ring keeps coordinating to a Cu adatom (marked by blue circle) and dehydrogenation occurs with the aid of a free Cu adatom (yellow circle). (a) Top and side views of the calculated molecular configurations during the dehydrogenation process. (b) Energies of different states in dehydrogenation process.