Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Cu- and Pd-Catalyzed Ullmann Reaction on a Hexagonal Boron Nitride Layer

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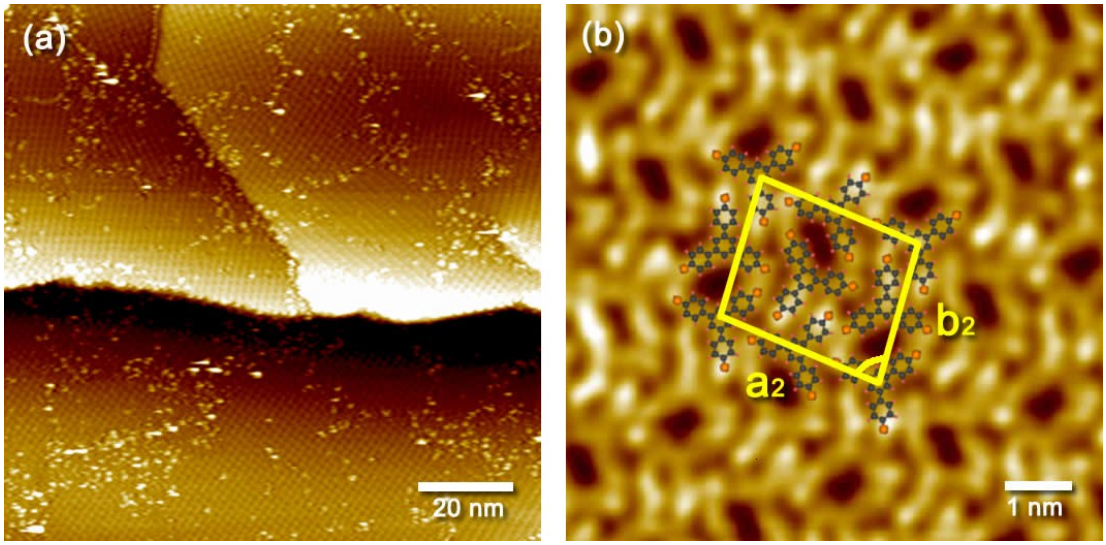

Figure S1: (a) STM images of the large-scale view of the TBB monolayer on h-BN/Ni(111). (b) The other assembly phase in addition to the one shown in Fig. 1a. Ordered domains are separated by the line defects of the h-BN underneath. Unit cell: a_2 = 2.6 nm and b_2 = 2.1 nm with an angle of 84°, containing four molecules. All the molecules are organized via halogen-hydrogen and halogen-halogen interactions.

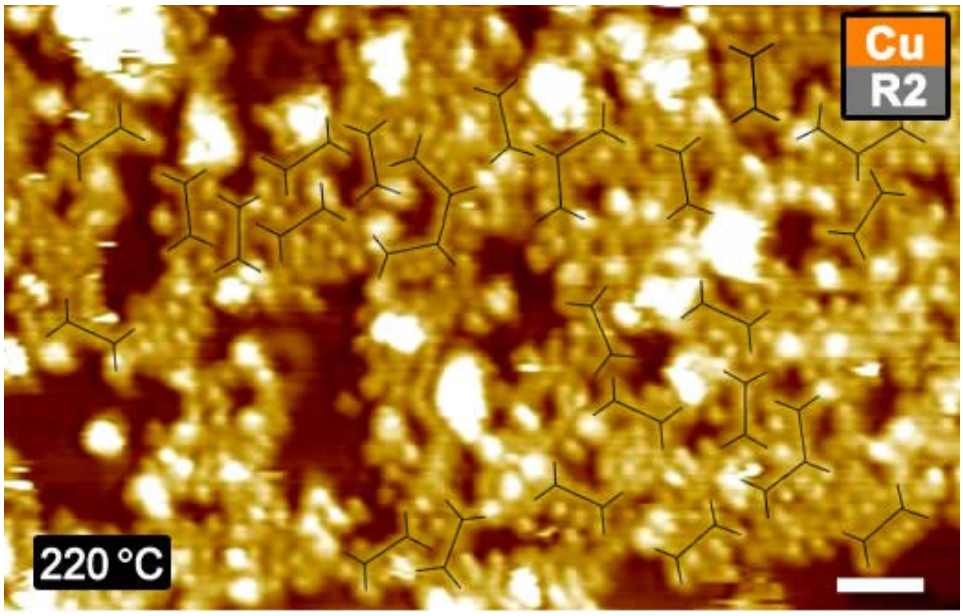

Figure S2: STM image of the oligomers coupled from TBB monomers after 220 ºC annealing using the Cu R2 protocol. As highlighted by the black line symbols, over half of the molecules have been coupled to dimers. Uncoupled monomers still exist and detached Br atoms could be found located around the oligomers. Due to the more dosage of Cu, the clusters make the scanning a hard task. Scale bar: 2 nm.

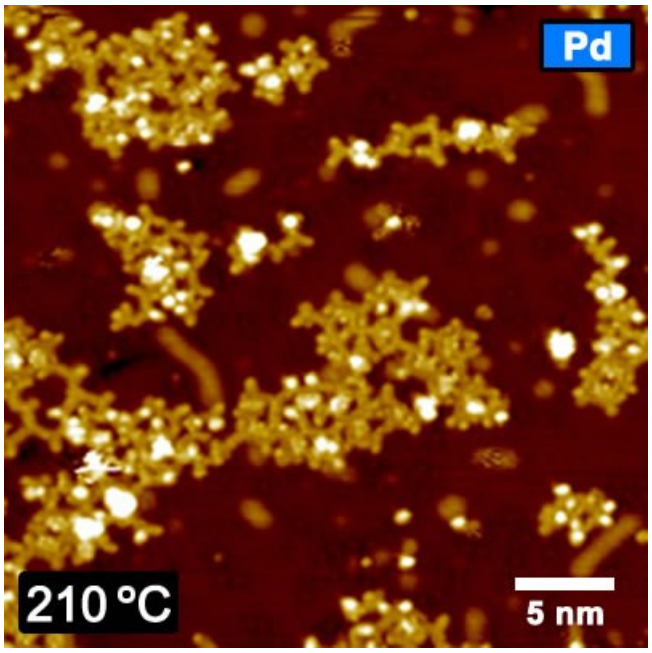

Figure S3: Overview STM image of the oligomers formed by the Pd-catalyzed coupling of TBB molecules on BN/Ni(111) after 210 ºC annealing. Majority of the oligomers are of dimeric size, and Pd-involved intermediates could be hardly observed.

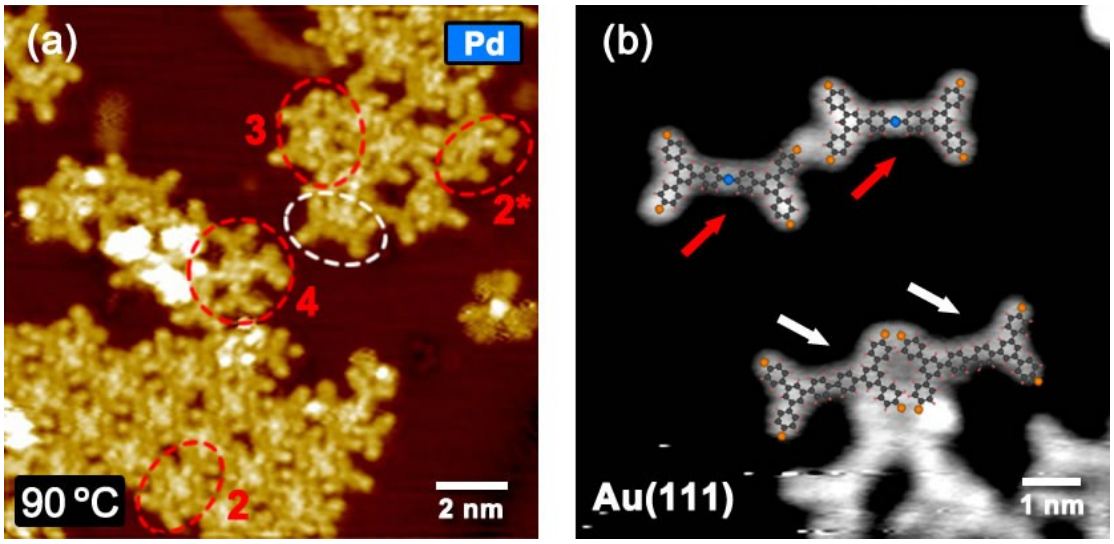

Figure S4: Pd-involved organometallic intermediates on h-BN/Ni(111) (a) and Au(111) (b) surface. White ovals and arrows: covalently coupled dimers; Red ovals and arrows: intermediates with Pd center. Besides the well-arranged island consisting of kinked dimeric units highlighted by red dashed oval with label 2, as discussed in the main text, a deformed structure was also found (marked as 2*). Moreover, similar items made up of more molecules were also observed, such as trimer (marked as 3) and tetramer (marked as 4). All of those items process a little brighter joint than the molecules themselves, which are also assumed to be Pd-connected intermediates.