Supplementary Material (ESI) for PCCP

Supporting Information

An *ab initio* insight into the Cu(111)–mediated Ullmann reaction

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Absorption of Phenyl on Cu(111)

Figure S1B illustrates the general geometry of PG on a substrate, in which Φ is the angle between the C_1C_4 axis and the surface plane; ω is the angle describing the rotation of the mirror symmetry plane of PG about C_1C_4, which is set to be zero when this plane is orthogonal to the surface. Starting with various initial geometries, we find different stable high–symmetry optimized positions of PG on Cu(111) (Fig. S1C–F).

Migration of Phenyl on Cu(111)

Figure S2 provides other diffusion pathways of Phenyl on Cu(111). It is found that these transitions require much higher acvitvation energies compared to the path presented in the main manuscript.

Absorption of Biphenyl on Cu(111)

Figure S3 shows some high-symmetry adsorption positions of biphenyl on Cu(111). In the gas phase, the torsion angle between the two π-planes of biphenyl is about 44.4°.[1] However, the adsorbed molecule in our calculations becomes almost planar, in agreement with experimental observations[2]. Stable adsorption geomtries of biphenyl on Cu(111) are similar to the case of benzene, a relative of biphenyl, on the same surface.[3] The binding energy of the most stable structure is -1.3 eV.

Adsorption of two approaching Phyenyls on Cu(111)

Figure S4 presents several adsortion geometries of two phenyls when the approach each other. Total energy of the system is significantly lowered when the spacing between them decreases and their adsorption positions are similar to the favorable one of single phenyls (as shown in Figure S1.C)

By performing the routine B→J→E→P (all in Figure S4), the system can reach the lowest energy structure (Figure S4.P) from the "well separated" geometry (Figure S4.B). The activation energy for this process is 0.09 eV.

References:

[1] A. Almenningen, O. Bastiansen, L. Fernholt, B. N. Cyvin, S. J. Cyvin, S. Samdal. *J. Mol. Struct.* **128**, 59 (1985)

[2] M. Xi and B. E. Bent, *Surf. Sci.* **278**,19 (1992)

[3] K. Berland, T. L. Einstein, P. Hyldgaard, *Phys. Rev. B.* **80**, 155431 (2009)

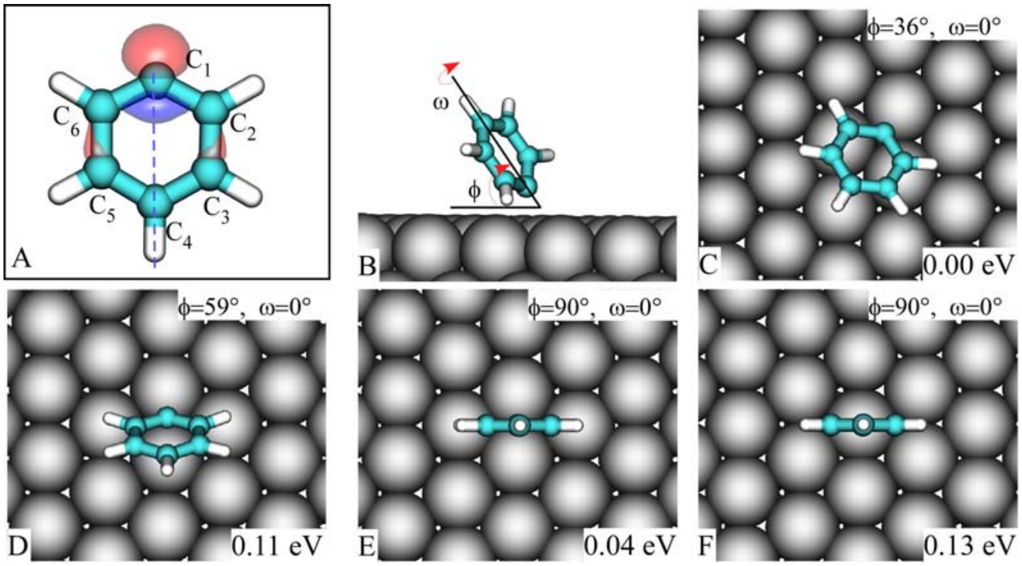

Figure S1. Phenyl and its single occupied molecular orbital (A), general geometry of phenyl on Cu(111) (B) and the most stable geometries of phenyl on Cu(111) (C-F). Total energies are relative to the lowest one.

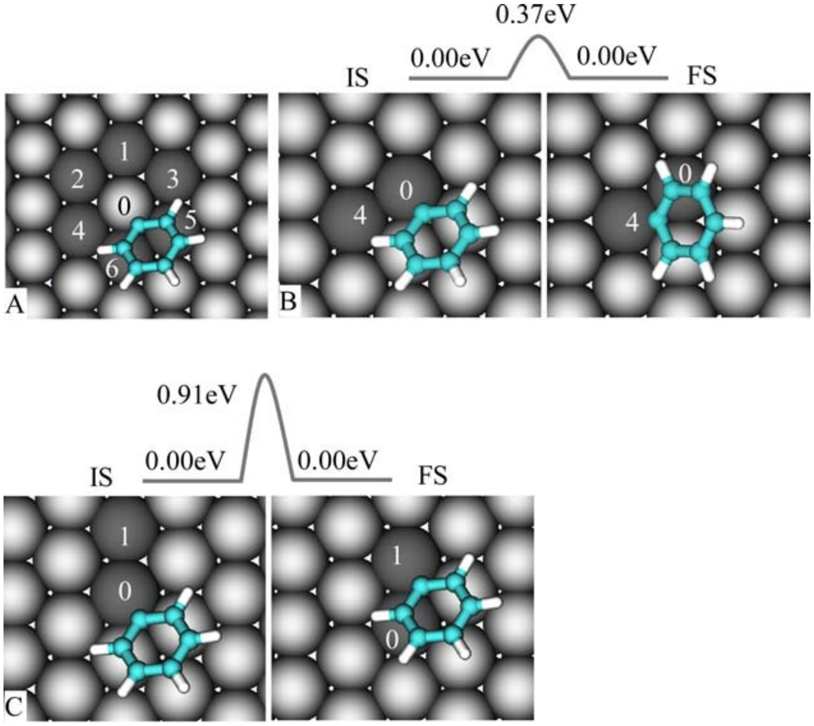

Figure S2. Direct diffusion pathways of Phenyl on Cu(111): Cu_0-Cu_4 (B) and Cu_0-Cu_1 (C) transitions

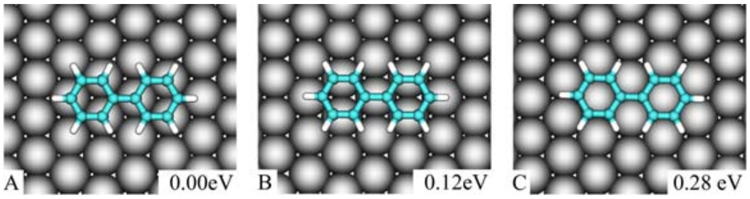

Figure S3. Some high-symmetry adsorption geometries of biphenyl on Cu(111) with total energies relative to the lowest one (A)

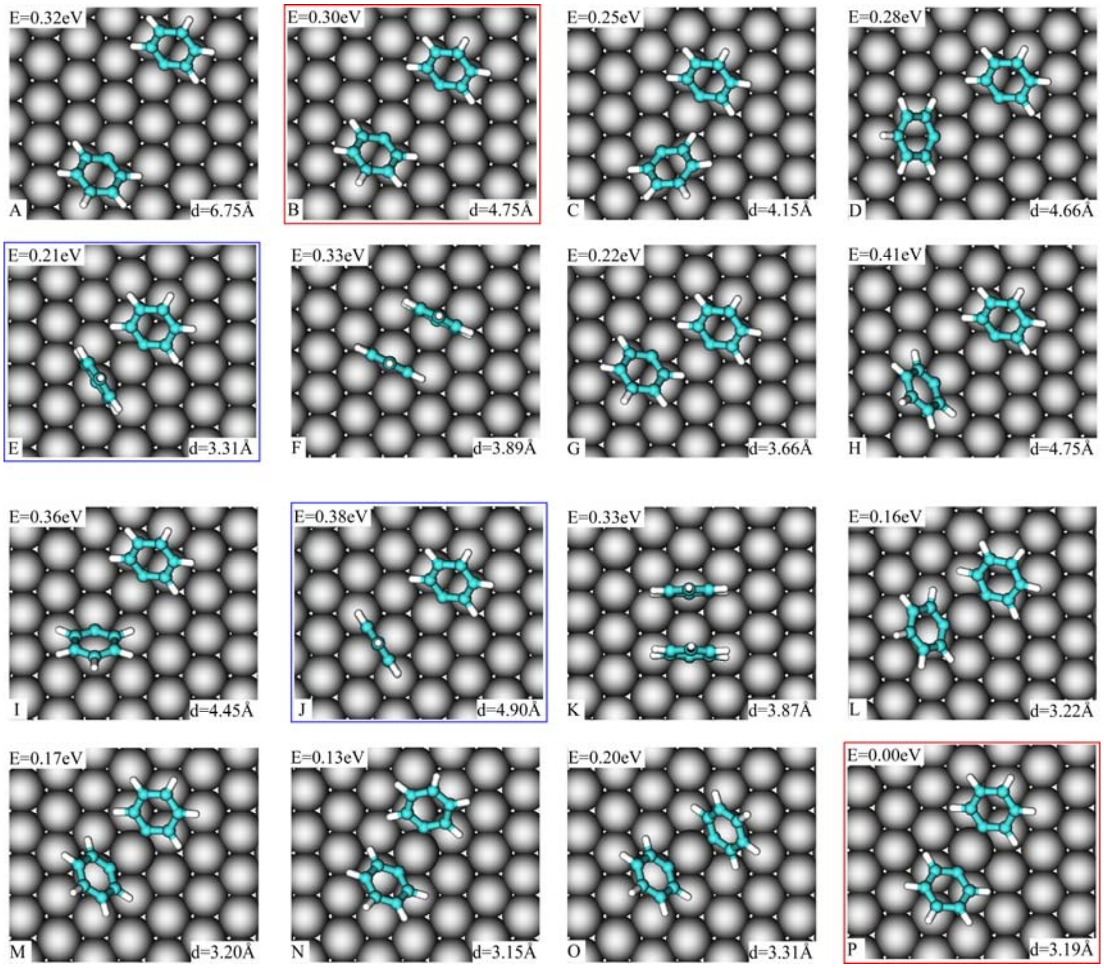

Figure S4. Adsorption position, energy relative to the lowest one and C_1–C_1 separation in various geometries of two PGs on Cu(111) when they approach each other. The dashed red lines in M and N indicate the initial positions (before relaxations) of the C_1C_4 axes of PGs. The red frames highlight the two typical configurations with both PGs are in the favorable positions, they are connected by the geometries in the blue frames.