Ullmann Reaction of Aryl Chlorides on Various Surfaces and the Application in Stepwise Growth of 2D Covalent Organic Frameworks

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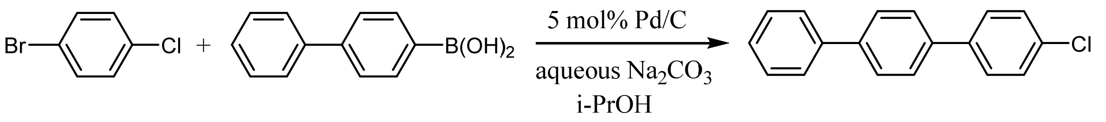
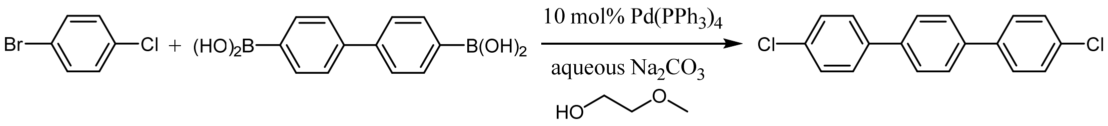
Supporting Information

1. Synthesis of organic molecules

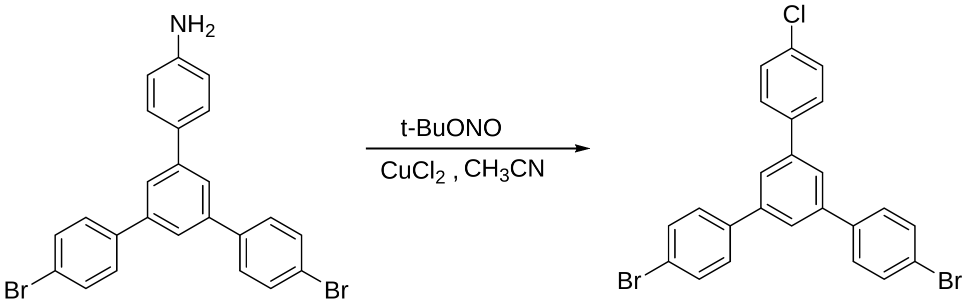


4-Chloro-*p*-terphenyl (CTP).[1] To a solution of 1-bromo-4-chlorobenzene (2.0 mmol), 4-biphenylboronic acid (3.0 mmol) and Pd/C (5% Pd basis, 106 mg) in *i*-PrOH (6 mL) was added 2 M degassed aqueous Na_2CO_3 solution (4 mL) under N_2 atmosphere. The resulting mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the mixture was filtered and the solid residue was washed with ethyl acetate (5 x 30 mL) and petroleum ether (3 x 30 mL). The resulting solid residue was purified by sublimation twice in *vaccum* to give the product as white solid in 15% yield (79 mg). Mp: 223-225 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.35-7.48 (m, 5H), 7.55-7.69 (m, 8H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 127.2, 127.5, 127.6, 127.7, 128.4, 129.0, 129.1, 133.6, 139.0, 139.3, 140.6, 140.7; HRMS (EI, TOF) calcd for $C_{18}H_{13}Cl^+$ $[M]^+$: 264.0706, found: 264.0704.



4, 4''-Dichloro-*p*-terphenyl (DCTP).[2] To a solution of 1-bromo-4-chlorobenzene (7.2 mmol), [1,1'-biphenyl]-4,4'-diyldiboronic acid (3.0 mmol) and $Pd(PPh_3)_4$ (0.3 mmol, 10 mol%) in 2-methoxyethanol (30 mL) was added 2 M degassed aqueous Na_2CO_3 solution (6 mL) under N_2 atmosphere. The resulting mixture was stirred at reflux for 24 h. After cooling to room temperature, the mixture was filtered and the solid residue was washed with ethyl acetate (5 x 30 mL) and petroleum ether (3 x 30 mL). The solid residue was then purified by sublimation twice in *vaccum* to give the product as white solid in 12% yield (107 mg). Mp: 285-288 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.43 (d, J = 8.6 Hz, 4H); 7.56 (d, J = 8.6 Hz, 4H), 7.64 (s, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 127.6, 128.4, 129.2, 133.7, 139.1, 139.4; HRMS

(EI, TOF) calcd for $C_{18}H_{12}Cl_2^+$ $[M]^+$: 298.0316, found: 298.0319 .



4,4''-Dibromo-5'-(4-chlorophenyl)-1,1':3',1''-terphenyl (DBCTP). In a three-necked round-bottom flask, anhydrous copper(II) chloride (1.2 mmol), *tert*-butyl nitrite (1.5 mmol), and anhydrous acetonitrile (4 mL) were added. The resulting mixture was stirred rapidly and warmed to 65 °C. 4"-Bromo-5'-(4-bromophenyl)-[1,1':3',1"-terphenyl]-4-amine[3] (1 mmol) in acetonitrile was slowly added over a period of 5 min to the reaction solution. After 10 min, the reaction solution was cooled to room temperature and then poured into 20 mL of 20% aqueous hydrochloric acid and extracted with 20 mL of ethyl ether, and the organic layer was washed with 20 mL of 20% aqueous hydrochloric acid. The resulting ether solution was dried over anhydrous magnesium sulfate and the ethyl ether was removed under reduced pressure after filtration, then the residue passed through flash column chromatography (petroleum ether) on silica gel to afford the products as white solid. Mp: 239-241 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44-7.55 (6H, m), 7.59-7.62 (6H, m), 7.69 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.2, 125.0, 125.2, 128.7, 129.0, 129.2, 132.1, 132.2, 134.0, 139.3, 139.8, 141.6; HRMS (EI, TOF) calcd for $C_{24}H_{15}Br_2Cl^+$ $[M]^+$: 495.9229, found: 495.9228.

2. General procedure for the STM experiment

The STM experiments were performed in a commercial UHV system (base pressure 2×10^{-10} mbar) equipped with a variable temperature scanning tunneling microscope (SPECS, Aarhus 150), a molecular evaporator, and standard facilities for sample preparation. The single-crystalline Cu(111), Ag(111), Au(111) surfaces were cleaned by cycles of argon-ion sputtering and annealing. After thorough degas, the molecules CTP (53 ^{o}C), DCTP (96 ^{o}C) and DBCTP (135 ^{o}C) were deposited by thermal sublimation onto the corresponding substrates and annealed to the indicated temperature. The subsequent samples measurements were carried out at ~110 K.

3. General procedure for the calculation

The calculations were carried out in the framework of DFT by using the Vienna Ab Initio Simulation Package (VASP).[4,5] The projector augmented wave method was used to describe the interaction between ions and electrons.[6,7] We used the generalized gradient approximation (GGA) with Perdew−Burke−Ernzerhof(PBE) formulism to treat exchange−correlation interaction,[8] and van der Waals (vdW) interactions were considered by using the DFT-D2 developed by Grimme.[9] The structures were relaxed until the forces on all unconstrained atoms were ≤0.015 eV/Å. All surfaces were modeled by four layered slabs separated by at least 20 Å of vacuum, a p(5×5) surface unit cell for Au(111), Ag(111), Cu(111) was used. Calculated lattice constants of 4.11 Å for Au, 4.14 Å for Ag, and 3.59 Å for Cu were used (experimental lattice constants: 4.08, 4.09, and 3.61 Å for Au, Ag, and Cu, respectively).[10] All calculations were done with a 2×2 k-point sampling and a 450 eV kinetic energy cutoff.

4. Supplemental STM images

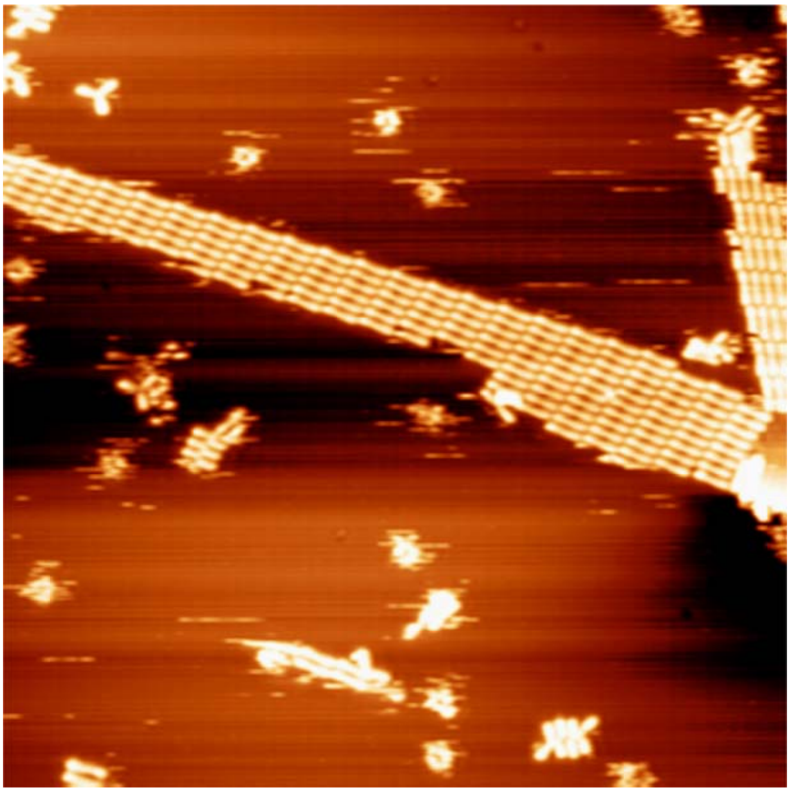


Figure S1. CTP on Cu(111) after annealing at 80 °C (65×65 nm^2, -1.6 V, -0.09 nA)

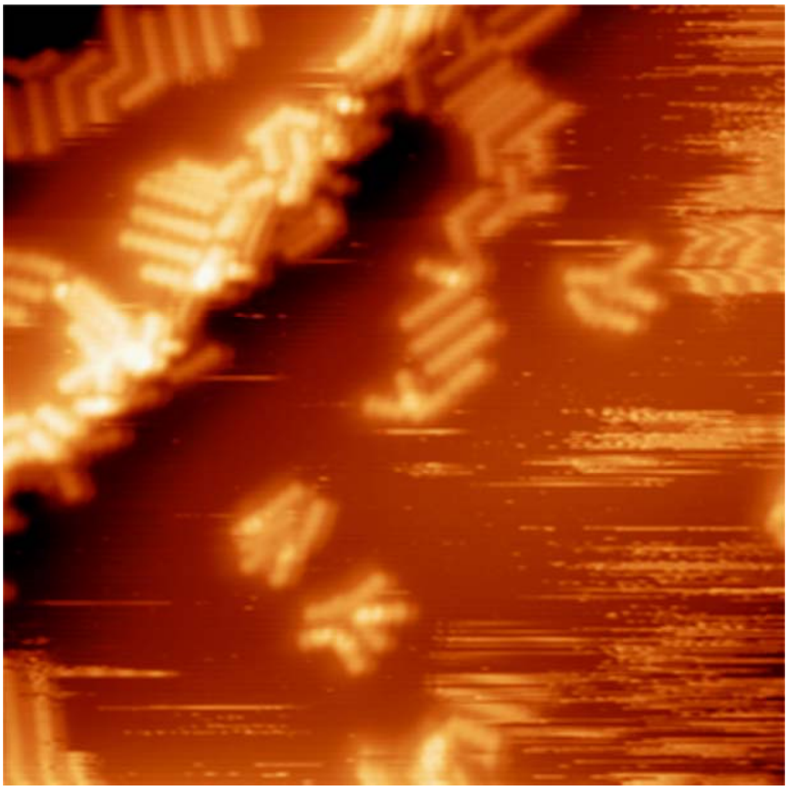


Figure S2. CTP on Cu(111) after annealing at 160 °C (26×26 nm^2, -1.5 V, -0.07 nA)

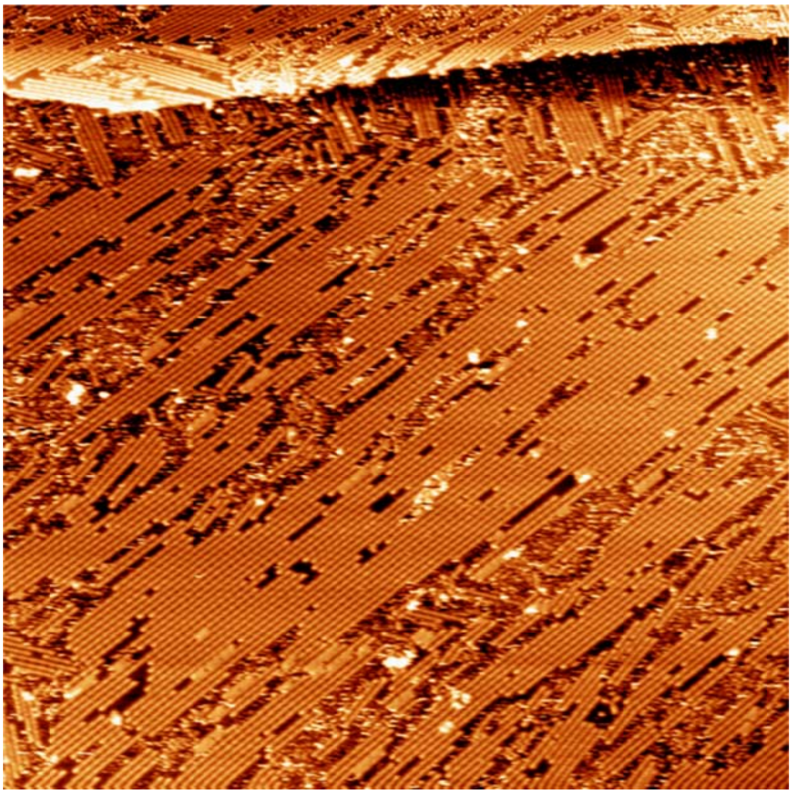


Figure S3. DCTP on Cu(111) after annealing at 80 °C (130×130 nm^2, -1.0 V, -0.07 nA)

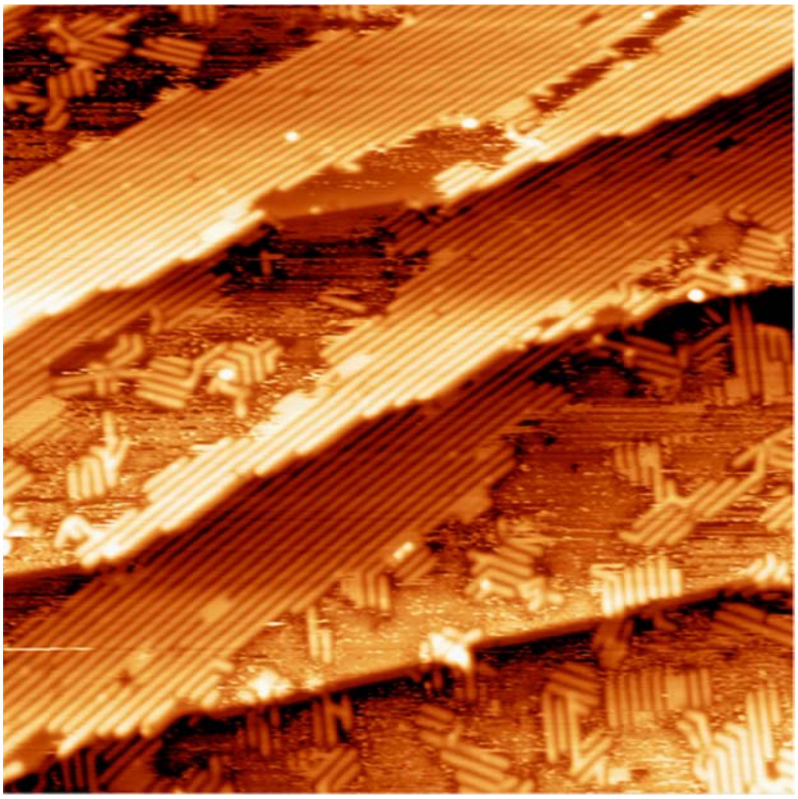


Figure S4. DCTP on Cu(111) after annealing at 160 °C (65×65 nm^2, 1.0 V, 0.05 nA)

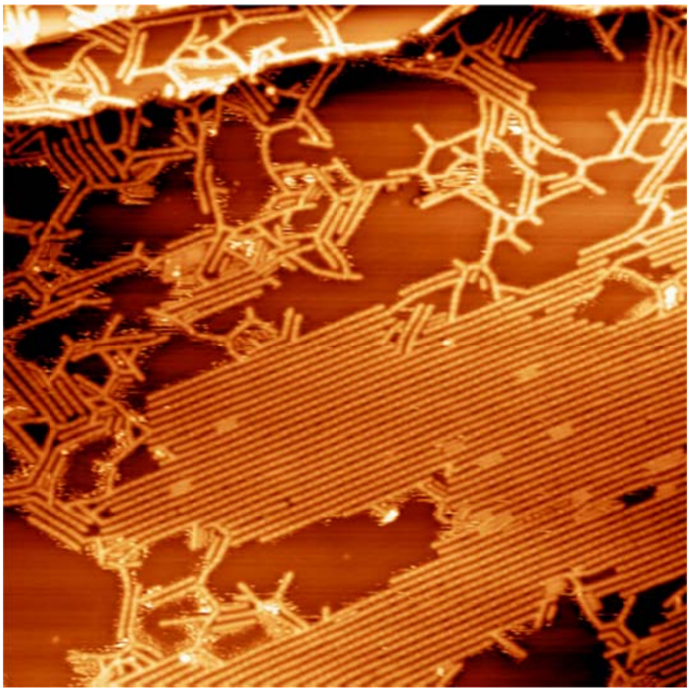


Figure S5. DCTP on Ag(111) after annealing at 120 ^{o}C (65×65 nm^2, -1.5 V, -0.09 nA)

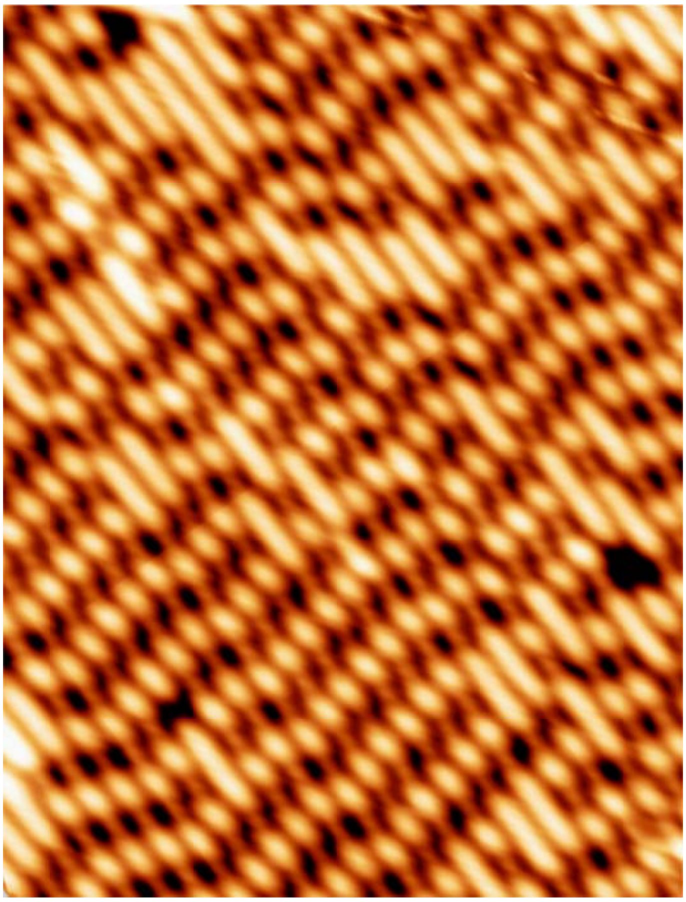


Figure S6. DCTP on Ag(111) after annealing at 120 ^{o}C (15×20 nm^2, 2.5 V, 0.05 nA)

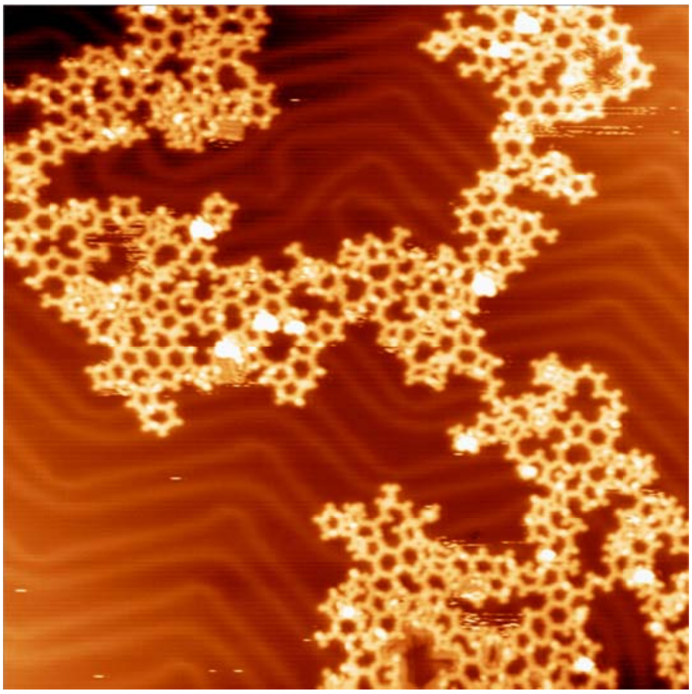


Figure S7. 1,3,5-tris(4-chlorophenyl)benzene and Cu on Au(111) after annealing at 300 ^{o}C (65×65 nm^2, -1.5 V, -0.11 nA)

5. Line profile of poly(*p*-phenylene)

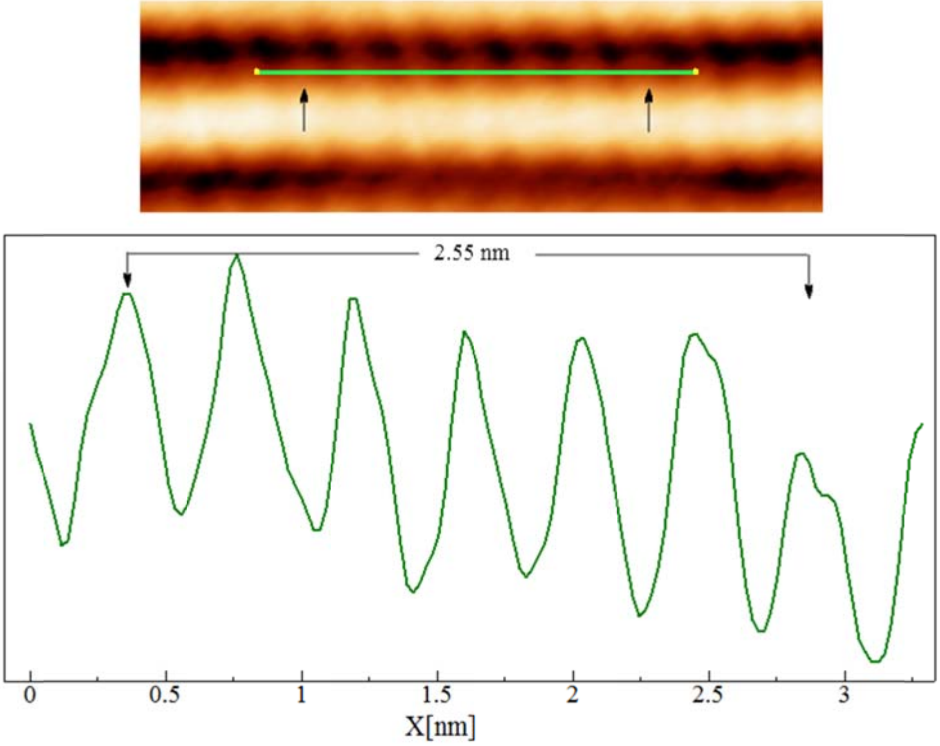


Figure S8. line profile of poly(*p*-phenylene) on Cu(111)

6. DFT-calculated lengths

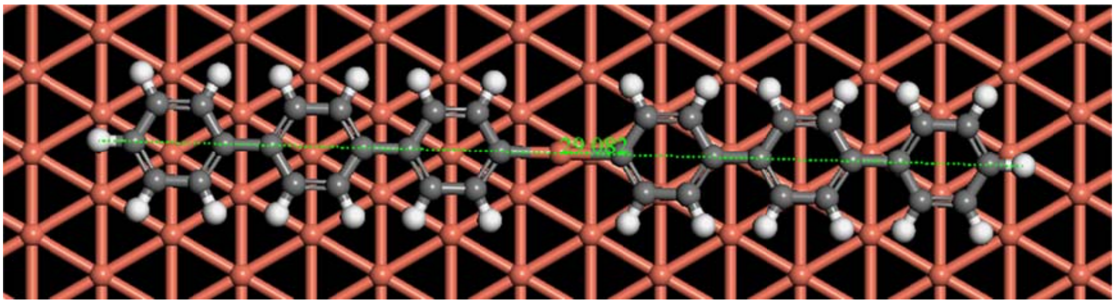


Figure S9. DFT-predicted length(Å) of the CTP intermediate on Cu(111)

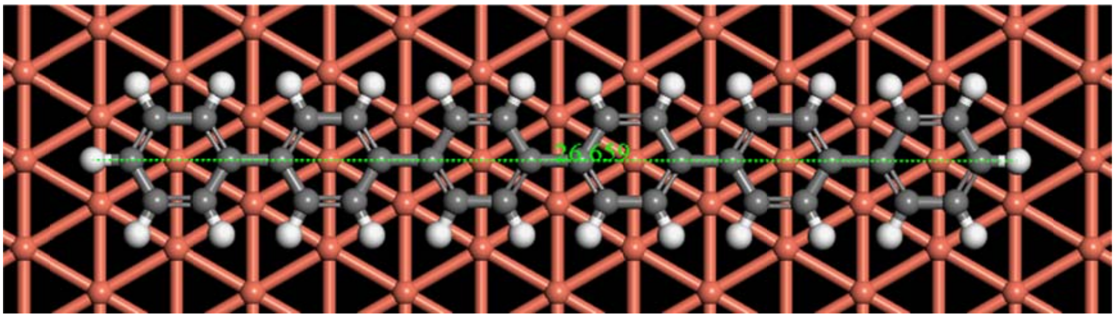


Figure S10. DFT-predicted length(Å) of the CTP coupling product on Cu(111)

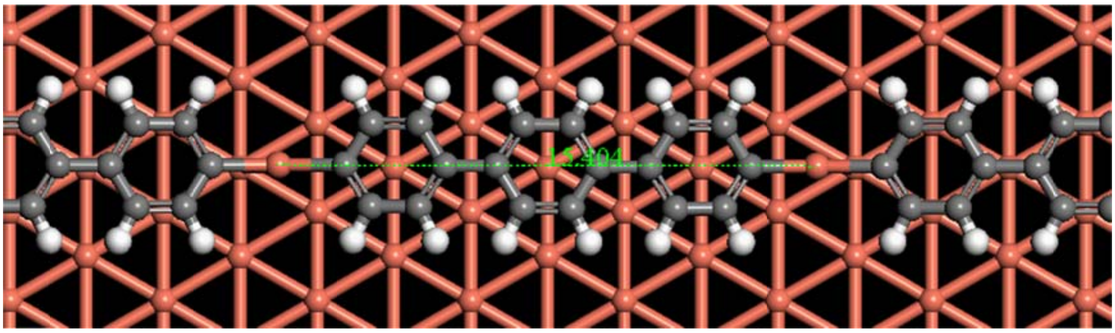


Figure S11. DFT-predicted length(Å) of the DCTP intermediate on Cu(111)

7. Calculated states of the dechlorination reaction of phenyl chloride on Cu(111), Ag(111) and Au(111)

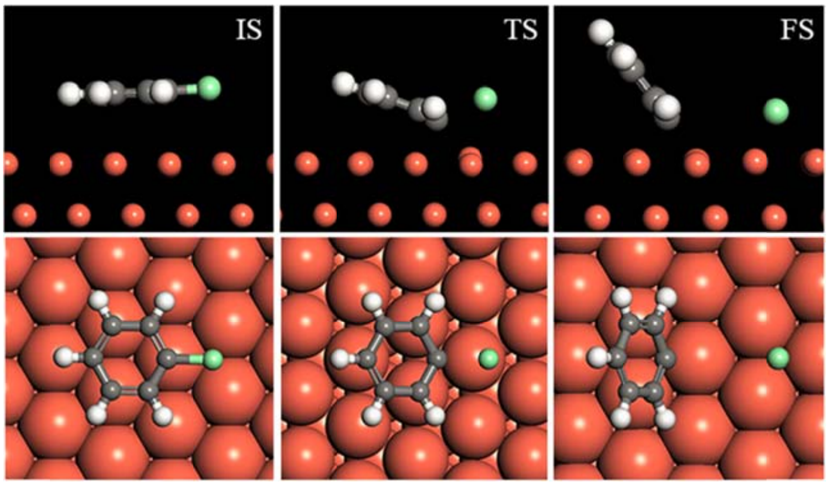


Figure S12. Top and side views of the initial state (**IS**), transition state (**TS**) and final state (**FS**) of the dechlorination reaction of phenyl chloride on Cu(111).

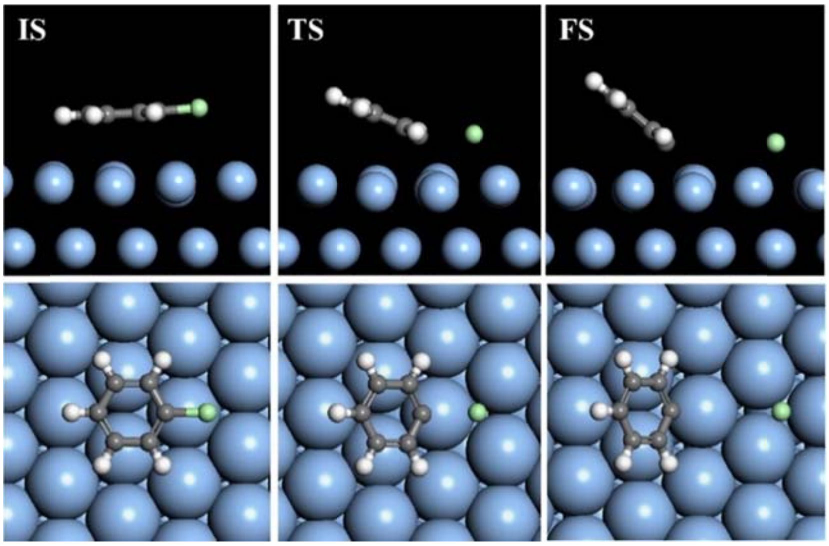


Figure S13. Top and side views of the initial state (**IS**), transition state (**TS**) and final state (**FS**) of the dechlorination reaction of phenyl chloride on Ag(111).

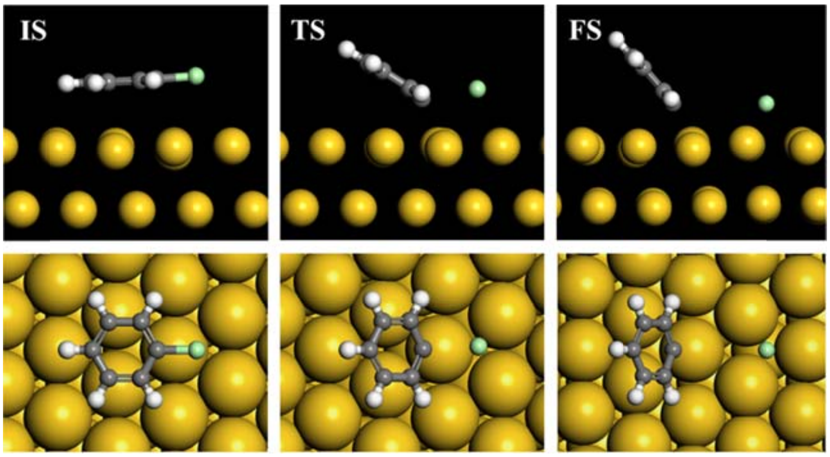


Figure S14. Top and side views of the initial state (**IS**), transition state (**TS**) and final state (**FS**) of the dechlorination reaction of phenyl chloride on Au(111).

8. Calculated debromination reaction of phenyl bromide on Cu(111).

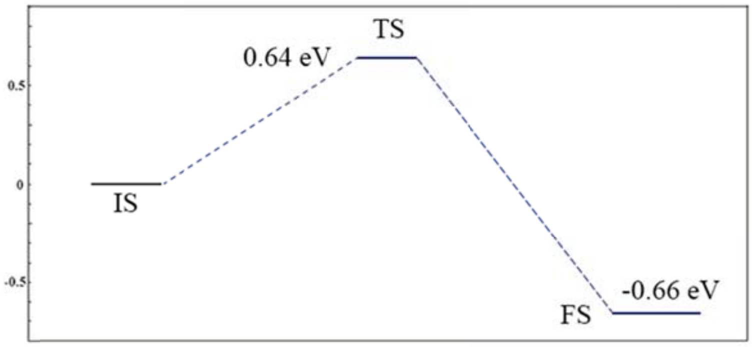


Figure S15. Calculated energy diagrams of debromination of phenyl bromide on Cu(111)

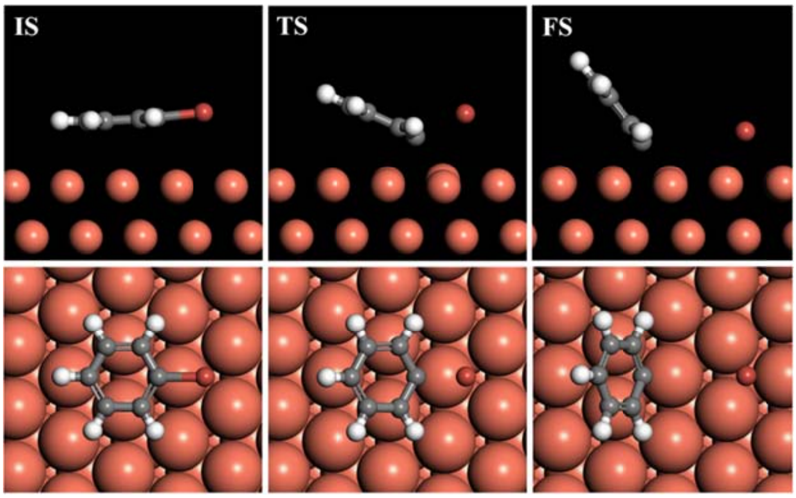


Figure S16. Top and side views of the initial state (**IS**), transition state (**TS**) and final state (**FS**) of the debromination reaction of phenyl bromide on Cu(111).

9. References

(1) Taylor, R. H.; Felpin, F.-X. *Org. Lett.*, **2007**, 9, 2911.

(2) Hart, H.; Harada, K.; Du, C.-J. F. *J. Org. Chem.* **1985**, 50, 3104.

(3) Eichhorn, J.; Strunskus, T.; Rastgoo-Lahrood, A.; Samanta, D.; Schmittel, M.; Lackinger, M. *Chem. Comm.*, **2014**, *50*, 7680-7682.

(4) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *48*, 13115.

(5) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.

(6) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.

(7) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.

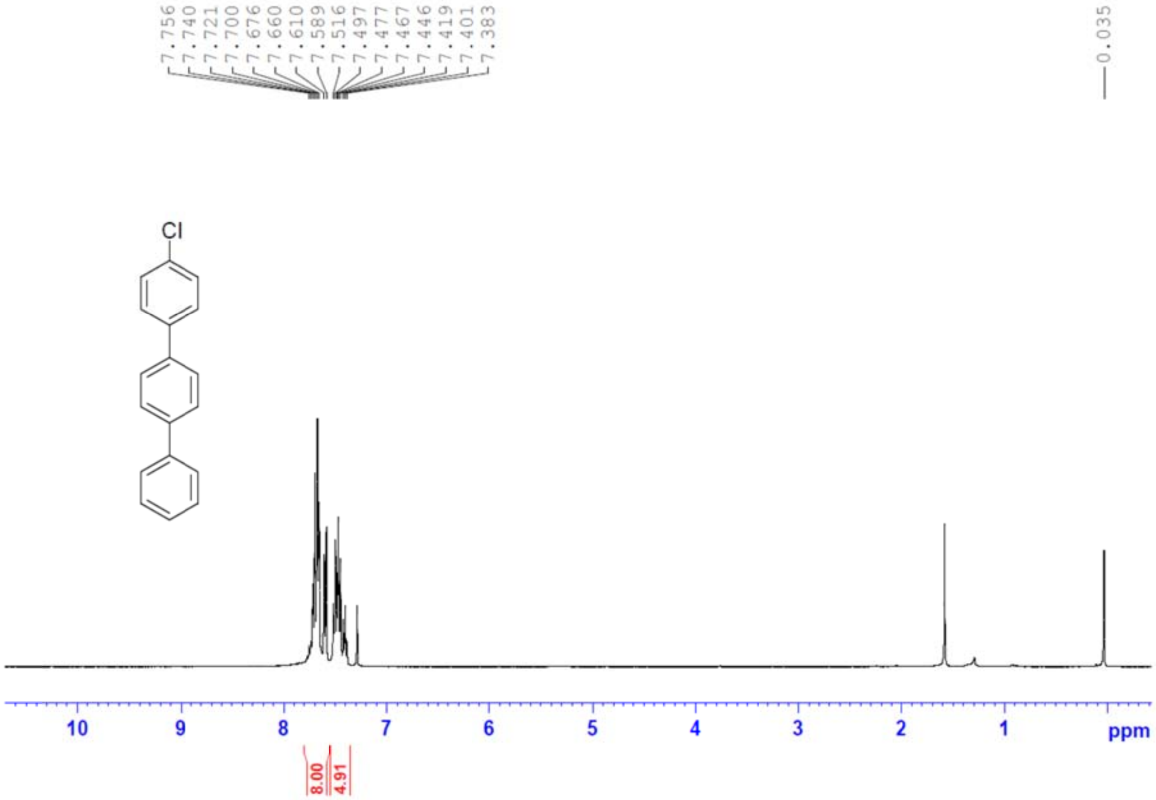
(8) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(9) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.

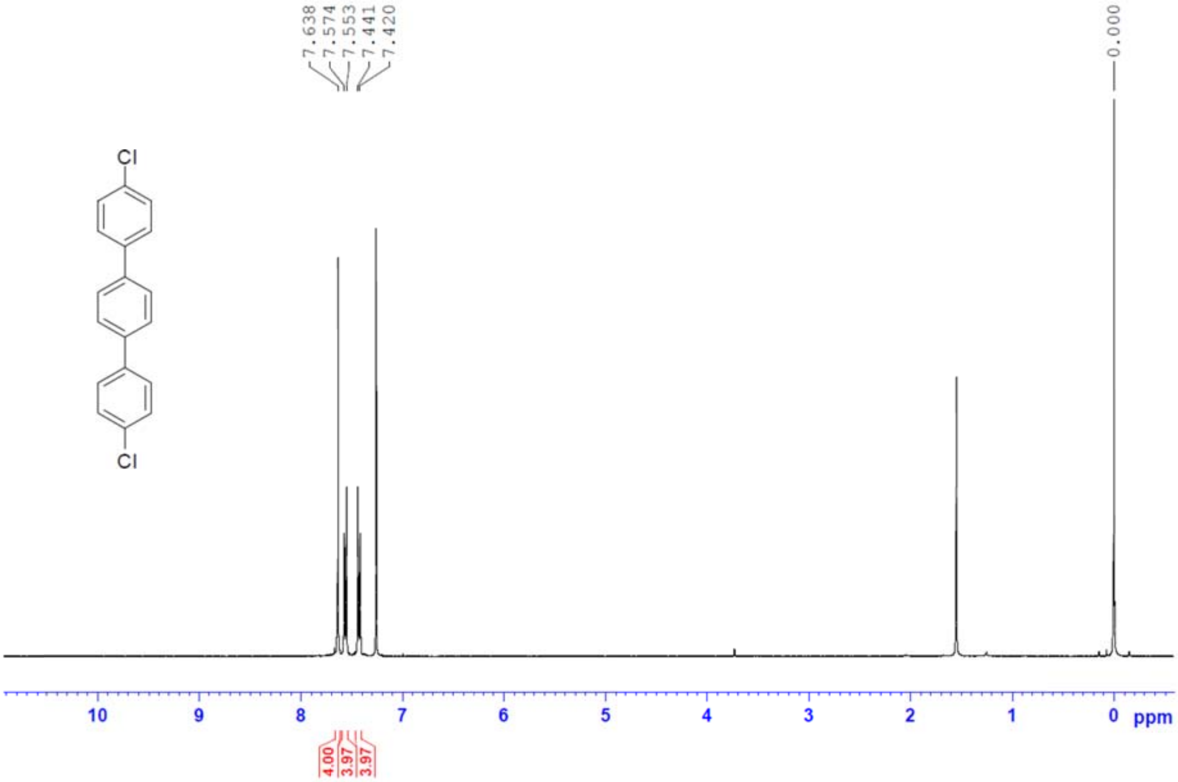
(10) Kittel, C. *Introduction to Solid State Physics*, 8th ed.; John Wiley & Sons, Inc.: New York, 2005.

10. Copies of ^{1}H and ^{13}C NMR spectra for the molecules

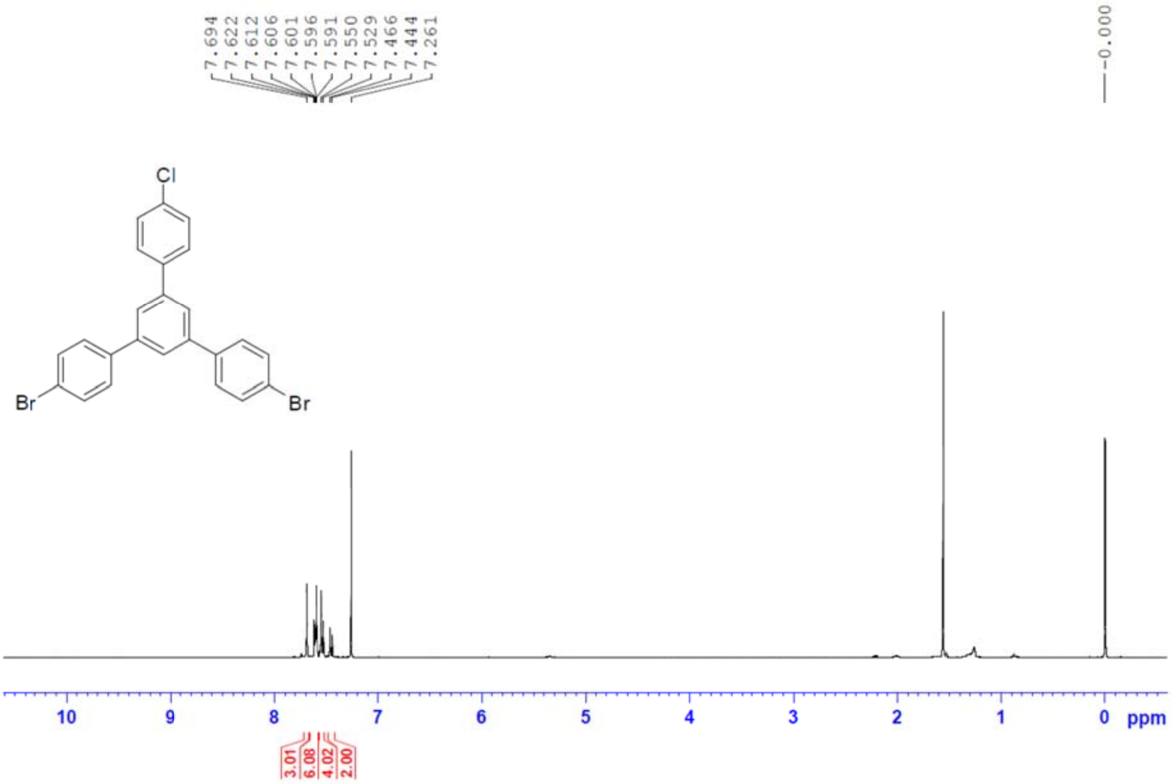
^{1}H NMR of 4-chloro-1,1':4',1''-terphenyl (CTP).



^{1}H NMR of 4,4''-dichloro-1,1':4',1''-terphenyl (DCTP).



^{1}H NMR of 4,4''-dibromo-5'-(4-chlorophenyl)-1,1':3',1''-terphenyl (DBCTP)



^{13}C NMR of 4,4''-dibromo-5'-(4-chlorophenyl)-1,1':3',1''-terphenyl (DBCTP)