

Supplementary Materials for
**Stereoselective synthesis of dienes through
dehalogenative homocoupling of terminal alkenyl
bromide on Cu(110)**

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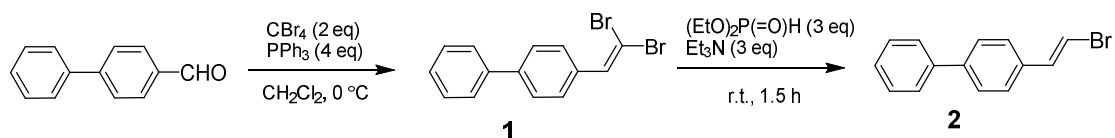
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I. Synthesis of the BVBP molecules.

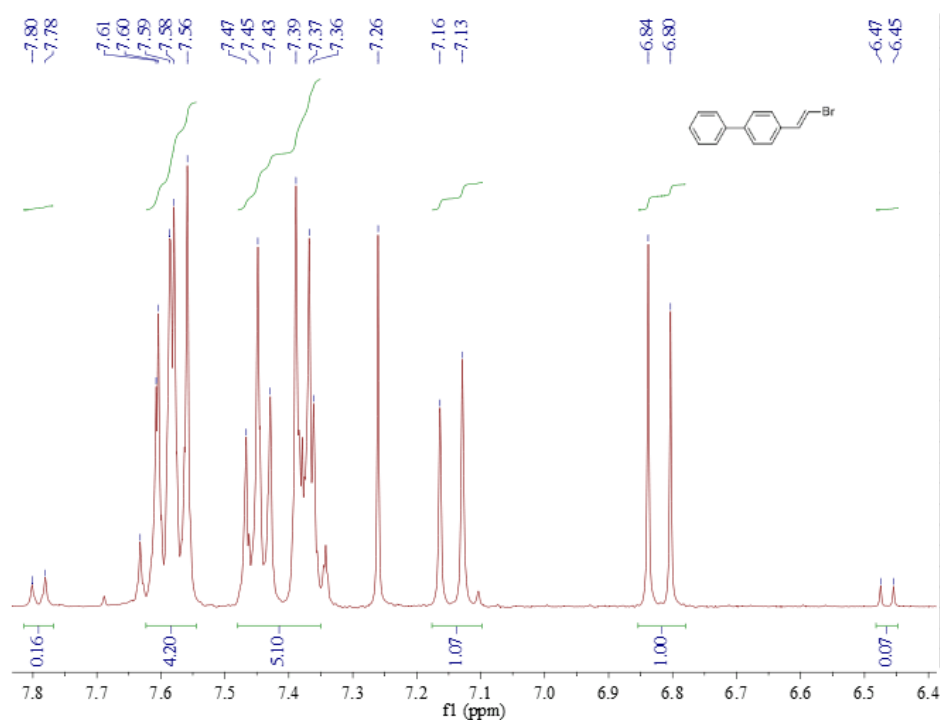
Materials and Methods. All commercially available chemicals were purchased from Adamas, Aldrich and TCI, and used as received without further purification except triethylamine which was distilled over CaH_2 . ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. The chemical shifts are reported in δ ppm with reference to residual protons and carbons of CDCl_3 (7.26 ppm in ^1H NMR and 77.16 ppm in ^{13}C NMR). Thin layer chromatography (TLC) was performed on glass plates coated with 0.20 mm thickness of silica gel. Column chromatography was performed using neutral silica gel PSQ100B.

Synthesis.



4-(2,2-dibromovinyl)-1,1'-biphenyl (1): To a CH_2Cl_2 solution of CBr_4 (3.31 g, 10.00 mmol) was added slowly a CH_2Cl_2 solution of PPh_3 (5.25 g, 20.00 mmol) followed by a CH_2Cl_2 solution of 4-phenylbenzaldehyde (0.91 g, 5.00 mmol) at 0°C . After the addition, the solvent was concentrated and the resulting crude was purified by column chromatography on silica gel (eluent: petroleum ether, $R_f = 0.54$) to afford **1** (0.418 g, 1.24 mmol, 29% yield) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.35 (m, 3H), 7.52 (s, 1H), 7.65 – 7.60 (m, 6H).

4-(bromovinyl)-1,1'-biphenyl (2): To a solution of **1** (0.40 g, 1.18 mmol) in diethyl phosphonate (0.609 g, 4.41 mmol) was added triethylamine (4.80 mL). The reaction mixture was stirred at r.t. for 14 h. Diethyl ether was added, and the salts were removed by filtration. After evaporation of the filtrate, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether, $R_f = 0.42$) to afford **2** as a white solid (0.26 g, 1.02 mmol, 86% yield): ^1H NMR (400 MHz, CDCl_3) δ 7.63 – 7.56 (m, 4H), 7.47 – 7.36 (m, 5H), 7.15 (d, $J = 14.0$ Hz, 1H), 6.82 (d, $J = 14.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.0, 140.4, 136.7, 134.9, 132.5, 131.9, 129.4, 128.8, 127.5, 127.4, 127.0, 126.9, 126.5, 106.5.



The major products are its trans-isomer i.e., trans-BVBP.^[1]

II. Experimental and theoretical details.

The STM experiments were carried out in a UHV chamber with a base pressure of 1×10^{-10} mbar. The whole system is equipped with a variable-temperature “Aarhus-type” scanning tunneling microscope,^{2,3} a molecular evaporator, and standard facilities for sample preparation. The metal substrates were prepared by several cycles of 1.5 keV Ar⁺ sputtering followed by annealing resulting in clean and flat terraces separated by monatomic steps. After the system was thoroughly degassed, the BVBP molecules were sublimated at 300 K. The sample was thereafter transferred within the UHV chamber to the microscope, where measurements were carried out in a typical temperature range of 100~150 K.

All of the calculations were performed 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 employed the Perdew-Burke-Ernzerhof generalized gradient approximation exchange-correlation functional,⁸ and van der Waals (vdW) interactions were included using the dispersion corrected DFT-D2 method of Grimme.⁹ The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in VASP until the forces on all unconstrained atoms were ≤ 0.03 eV/Å for geometry optimization. The simulated STM image was obtained using the Tersoff-Hamann method,¹⁰ in which the local density of states (LDOS) is used to approximate the tunneling current. The climbing-image nudged elastic band was applied to locate the transition state¹¹ and the reaction pathway was optimized until the forces acting to the path were converged typically to ≤ 0.03 eV/Å.

III. Supplementary STM images and DFT calculations.

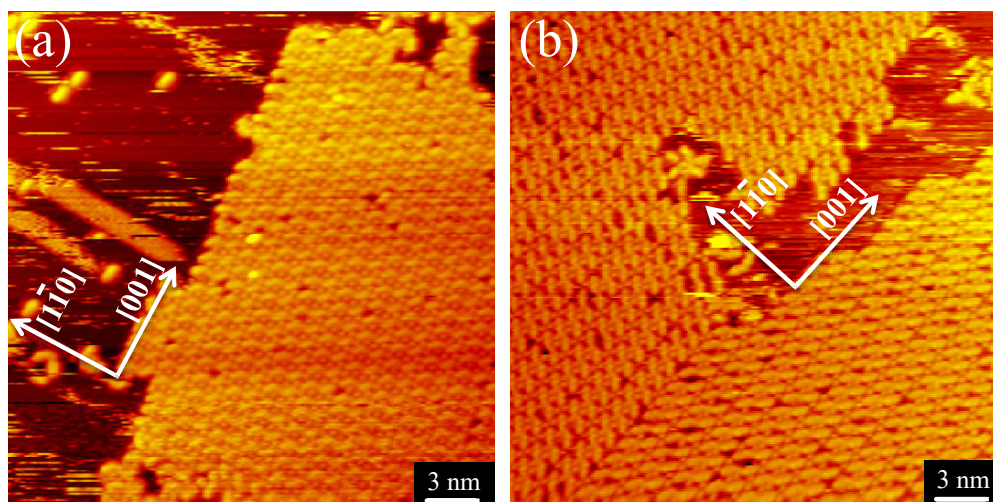


Figure S1. Large-scale STM images showing (a) after deposition of BVBP on Cu(110) at RT, and (b) annealing the sample to ~ 400 K.

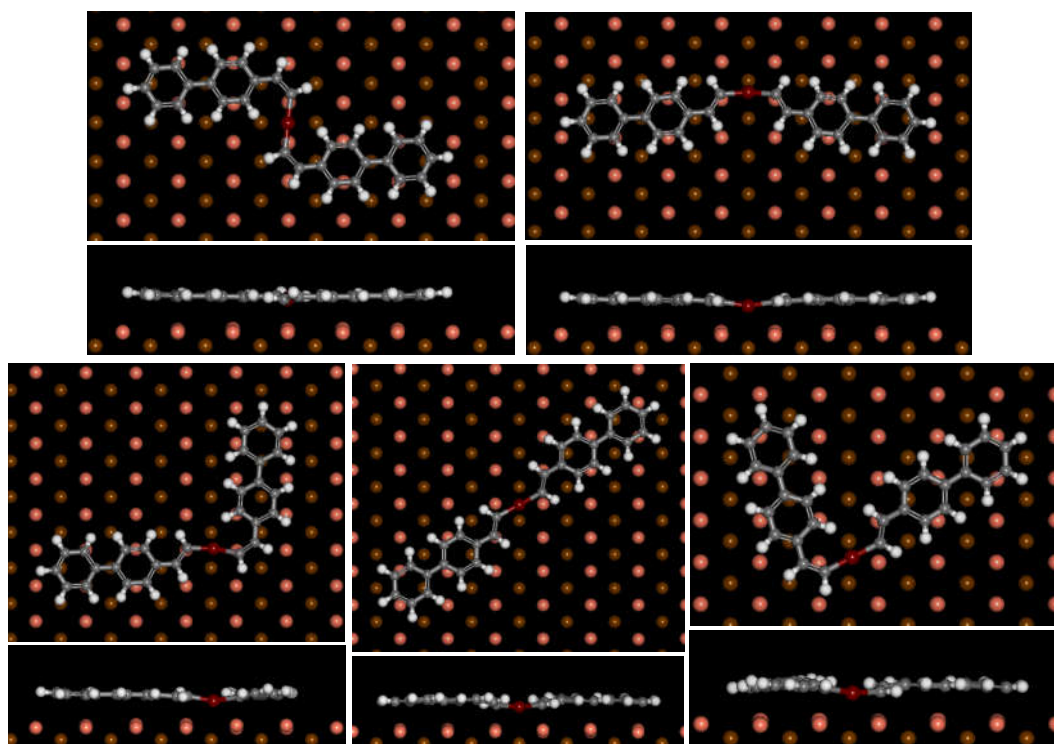


Figure S2. DFT relaxed models of C-Cu-C organometallic intermediates with different configurations on Cu(110).

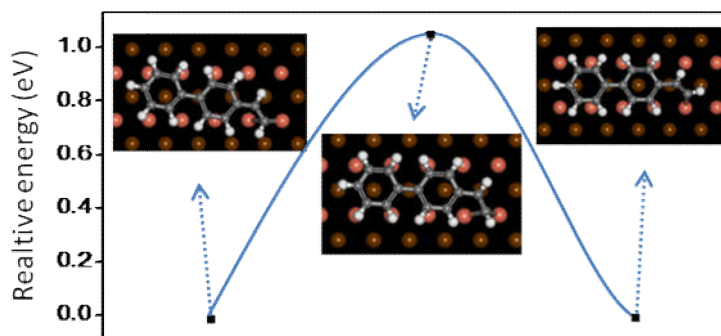


Figure S3. DFT-calculated energy diagram for the cis/trans isomerization of the BVBP molecule on Cu(110), which shows an energy barrier of 1.04 eV. The structural models of the initial state, transition state and final state along the pathway are also shown. Considering that the reaction barrier of such a trans/cis isomerization is prohibitively large in the gas phase, which is about 2.5 eV, our calculations show that such a barrier is largely reduced for the case on the Cu(110) surface.

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