On-surface synthesis of graphyne nanowires through stepwise reactions

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STM characterization and sample preparation. 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,[1, 2] 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 TBMB and BTBMB molecules were sublimated from the molecular evaporator at RT, respectively. 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.

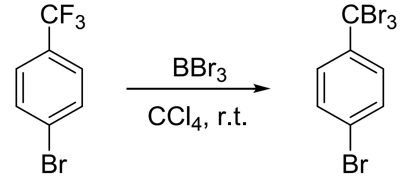
X-ray photoelectron spectroscopy. Photoemission spectroscopy experiments were performed in a UHV chamber with a base pressure of 1×10^{-10} mbar. All of the core level spectra including C 1s and Br 3d were recorded with a Phoibos 100 MCD-5 analyzer using a Mg Kα X-ray source.

DFT calculation. The calculations were performed in the framework of DFT by using the Vienna Ab Initio Simulation Package (VASP) code.[3,4] The projector augmented wave method was used to describe the interaction between ions and electrons,[5,6] and the Perdew-Burke-Ernzerhof generalized gradient approximation exchange−correlation functional was employed.[7] Van der Waals corrections to the PBE density functional were also included using the DFT-D3 method of Grimme.[8] 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 climbing-image nudged elastic band was applied to locate the transition state[9] and the reaction pathway was optimized until the forces acting to the path were converged typically to ≤ 0.05 eV/Å.

According to the Arrhenius equation $v=A\exp(-\Delta E/k_BT)$ (The energy barrier ΔE is defined as the energy difference between the TS and IS, and k_B is Boltzmann's constant. The prefactor A and reaction rate v are normally assigned the rule-of-thumb values of 10^{13} s^{-1} and 1 s^{-1}.), from the DFT calculations, we derived the reaction barrier to be 0.8 eV, then by solving the Arrhenius equation we get the T is about 300 K. Then we state that crossing the 0.8 eV energy barrier corresponds to the reaction taking place at room temperature.

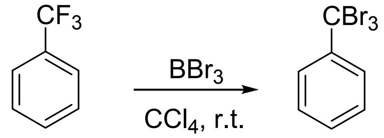
Synthesis. All commercially available chemicals were purchased from Adamas-beta, Aldrich and TCI, and used as received without further purification. ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. The chemical shifts are reported in δ ppm with reference to residual protons of $CDCl_3$ (7.26 ppm in ^{1}H 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 of 1-bromo-4-(tribromomethyl)benzene (BTBMB)[10]: 1-bromo-4-(trifluoromethyl) benzene (1 g, 4.44 mmol) and carbon tetrachloride (5 mL) were added to a flask with a magnetic stir bar. The flask was evacuated and backfilled with nitrogen three times and then left under nitrogen atmosphere. Subsequently, boron tribromide (0.5 mL, 1.336 g, 5.333 mmol) was added dropwise via a syringe. The mixture was stirred at room temperature for 36 h, slowly changing from yellow to amber in color. Then the reaction mixture was added into 30 mL of ice water and extracted with CH_2Cl_2 three times. The combined organic layer was washed with ice water, dried over anhydrous $CaCl_2$, filtered and concentrated to obtain the crude product. The residue was then dissolved in moderate dichloromethane and filtered through silica gel (eluent: petroleum ether, R_f =0.76) and recrystallized from ethanol to afford **BTBMB** (1.017 g, 2.494 mmol, 56% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.53(d, 2H, J = 8.9 Hz), 7.88 (d, 2H, J = 8.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 34.5, 124.7, 128.3, 131.3, 146.2.



Scheme S1. Synthesis of **BTBMB**.

Synthesis of (tribromomethyl)benzene (TBMB) [11]: (trifluoromethyl)benzene (1 g, 6.844 mmol) and carbon tetrachloride (5 mL) were added to a flask with a magnetic stir bar. The flask was evacuated and backfilled with nitrogen three times and then left under nitrogen atmosphere. Subsequently, boron tribromide (0.7 mL, 1.886 g, 7.528 mmol) was added dropwise via a syringe. The mixture was stirred at room temperature for 36 h, slowly changing from yellow to amber in color. Then the reaction mixture was added into 30 mL of ice water and extracted with CH_2Cl_2 three times. The combined organic layer was washed with ice water, dried over anhydrous $CaCl_2$, filtered and concentrated to obtain the crude product. The mixture was purified by silica gel column chromatography (eluent: petroleum ether, R_f = 0.71) to afford **TBMB** (1.34 g, 4.075 mmol, 60% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31-7.36 (m, 1H), 7.38-7.43 (m, 2H), 8.00-8.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 36.4, 126.6, 128.2, 130.3, 147.1.



Scheme S2. Synthesis of **TBMB**.

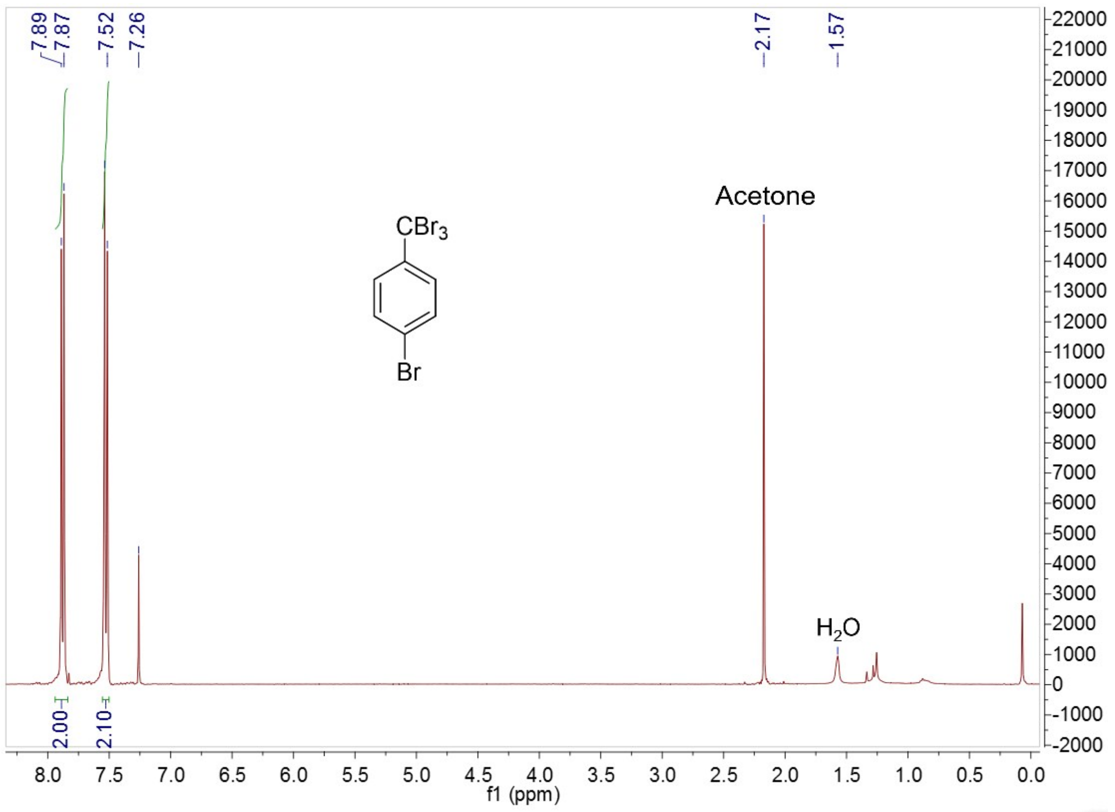


Figure S1. ^{1}H NMR spectrum of **BTBMB** in $CDCl_3$

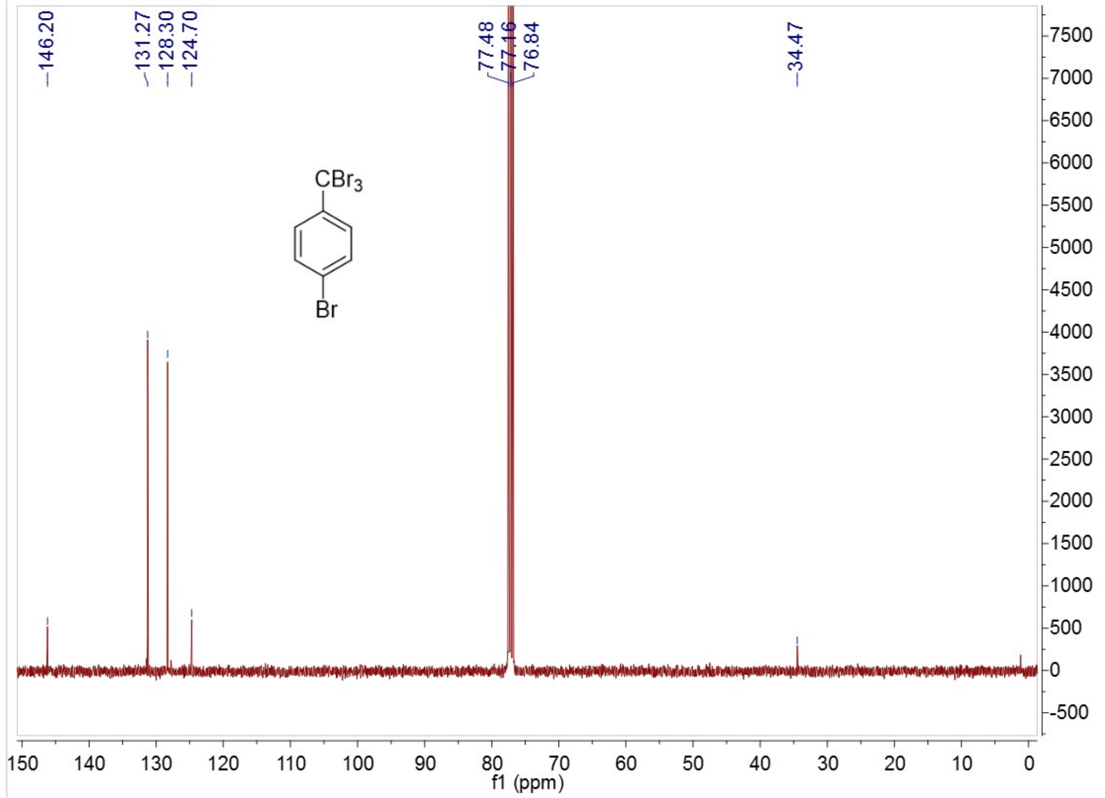


Figure S2. ^{13}C NMR spectrum of **BTBMB** in $CDCl_3$

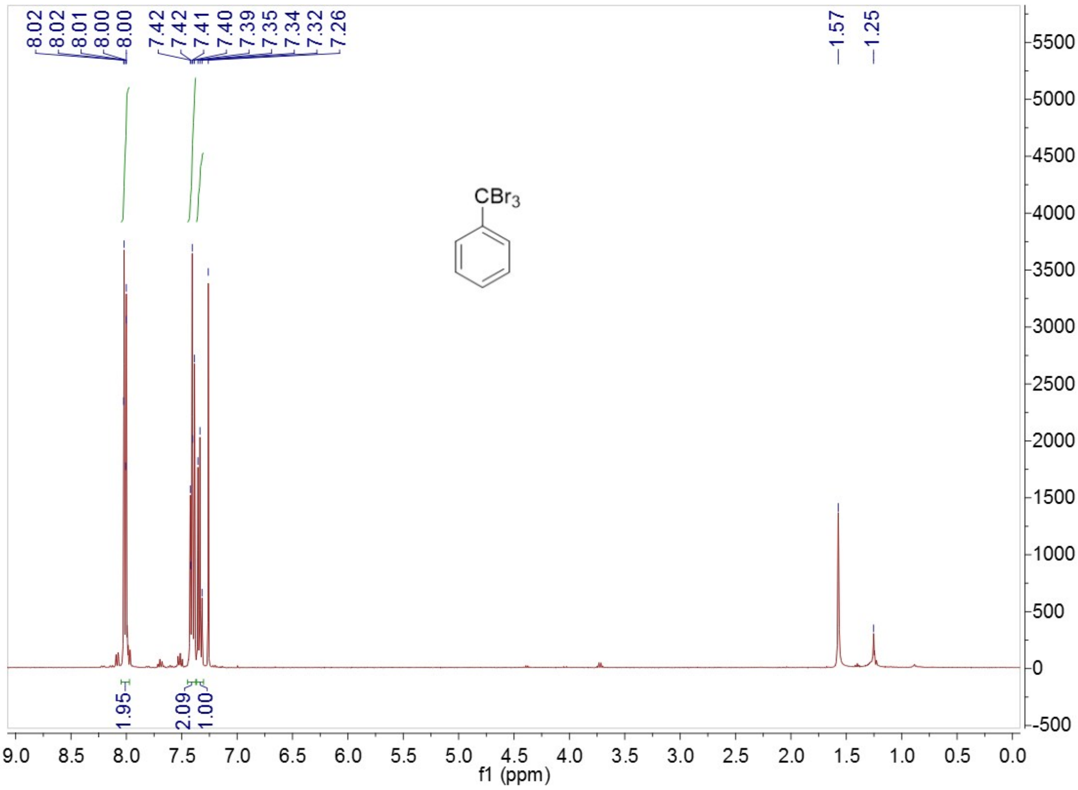


Figure S3. ^{1}H NMR spectrum of **TBMB** in $CDCl_3$

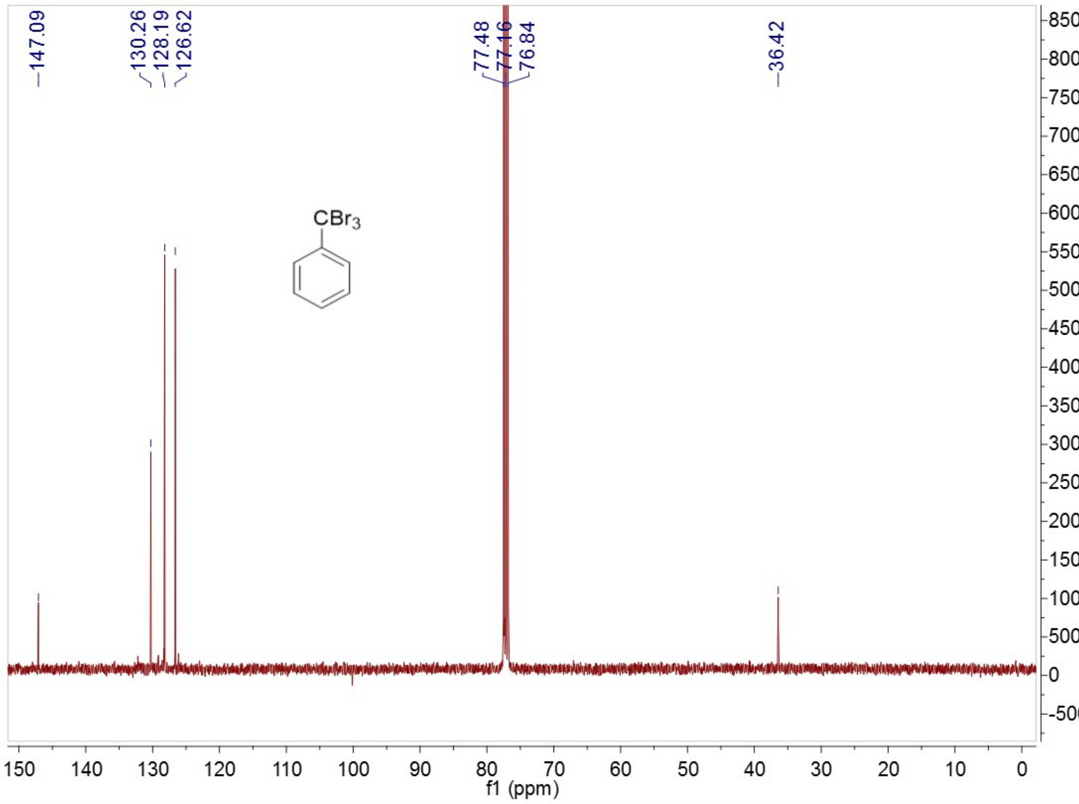


Figure S4. ^{13}C NMR spectrum of **TBMB** in $CDCl_3$

To verify our proposed stepwise reaction process, XPS experiments have been carried out. After deposition of the BTBMB molecules on Au(111) held at RT, the Br 3d signal presents as two doublets with the binding energy (E_B) of Br $3d_{5/2}$ at 69.2 eV (blue line) and 67.3 eV (green line), respectively. The E_B (Br $3d_{5/2}$) = 69.2 eV is indicative of intact C-Br bonds, in agreement with previous work,[12] which should be attributed to the intact aryl C(sp^2)-Br groups. The E_B (Br $3d_{5/2}$) = 67.3 eV is indicative of bromine atoms adsorbed on the Au(111) surface,[12,13] which should come from the dissociated C-Br bonds of C(sp^3)-Br groups. The corresponding C 1s XP spectrum obtained at RT supports the interpretation of the C(sp^2)-Br groups remaining intact: the peak located at 284.8 eV (blue line) is assigned to carbon bound to bromine, in accord with previous work.[14] The other two peaks located at 284.2 eV and 283.8 eV (red line and orange line) originate from the C-C and C-H carbons, respectively. Furthermore, the area ratio of C-Br:C-C:C-H is 1:1.9:4.4, in accordance with the stoichiometric ratio (1:2:4) in the acetylenic intermediate. Further annealing the sample to 500K, only the green doublet survives in Br 3d XP spectrum, which indicates complete debromination of the molecules, and it is also supported by C 1s XP spectrum. Therefore, we confirm that the reaction should go through a stepwise reaction pathway.

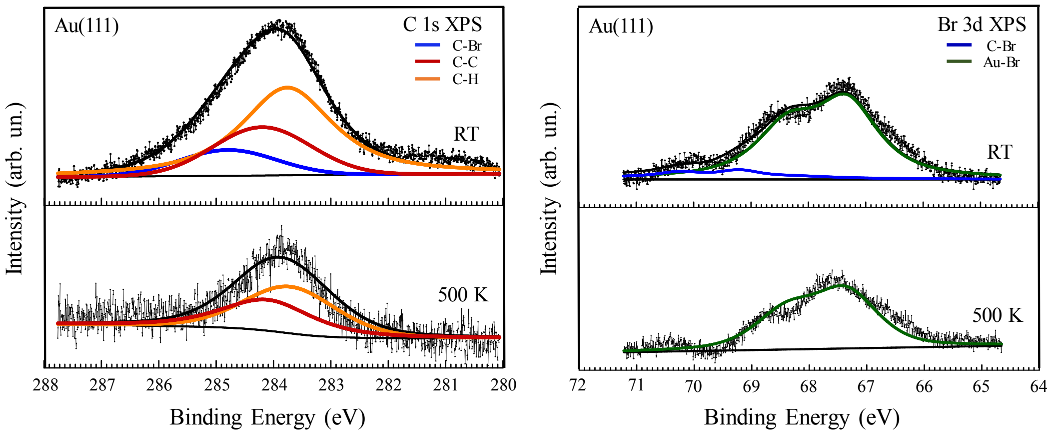


Figure S5. The C 1s and Br 3d spectra of BTBMB on Au(111) deposited at RT followed by annealing to 500 K.

Additional STM experiments were performed on Cu(111) and Cu(110) surfaces as shown below. After the deposition of BTBMB molecules on Cu(111) and Cu(110) surfaces held at RT and further annealing of the sample at 530K and 550K, respectively, we could also form the graphyne nanowires. Since the polymerization outcome was rather similar, this suggests a negligible influence of orientation on Au and Ag surfaces.

We believe that the products shown here mainly depend on the reactivity of the functional groups. As is well-known, the Ullmann reaction (i.e. the aryl C(sp^2)-Br functional groups) has been well studied on various surfaces.[15,16] Although the reaction pathways may be different from different substrates, the corresponding C-C single bonded products are eventually formed. This is an indication of the universality of the reactivity of aryl C(sp^2)-Br functional groups. We observe that the tribromomethyl groups (i.e. C(sp^3)-3Br groups) also have also demonstrated universality since the C-C triple bonds were formed on all the Cu(110), Cu(111), Ag(110) and Au(111) surfaces, respectively.

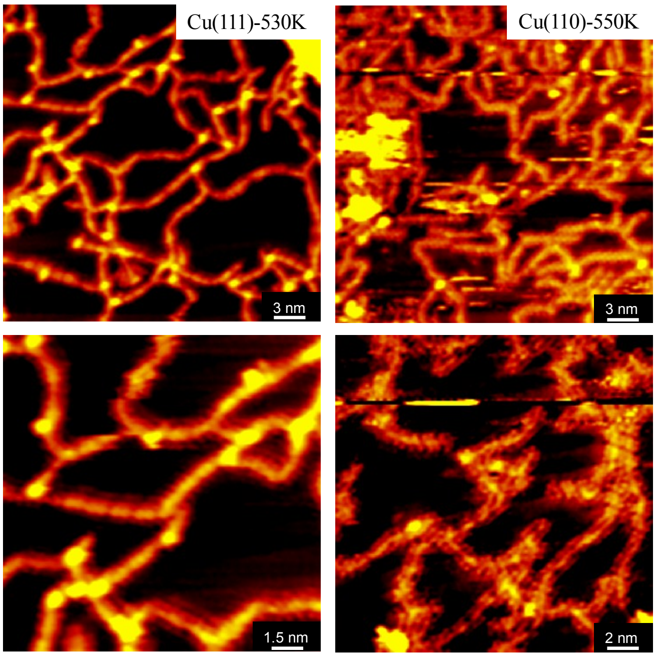


Figure S6. The STM images show the formation of graphyne nanowires on the Cu(111) and Cu(110) surfaces, respectively.

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