Electronic Supplementary Information

Diastereoselective self-assembly of bisheptahelicene on Cu(111)

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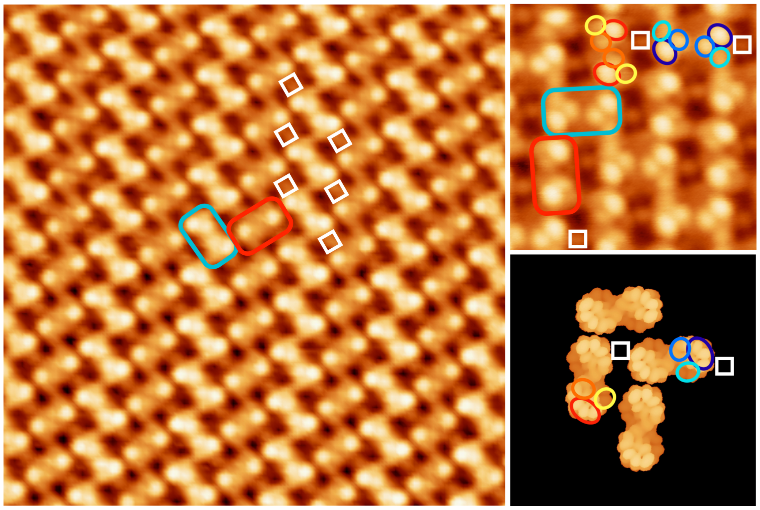

Figure S1. STM image (16.8 nm × 16.8 nm, 1.93 V, 31 pA) showing the zigzag structure made of a succession of rows built with molecules having the same orientation. One row is made of molecules which are rotated by 90° with respect to the adjacent row. The STM image in the top right corner (6.5 nm × 6.5 nm, 2.09 V, 91 pA) is a rotational domain of the left image and allows to determine the handedness of the bis[7]H. Each molecule (for example in the red or blue rectangle) is made of two identical parts with three lobes rotated by 180°. These are therefore a homochiral bishelicenes. By following the lobes of one side of a molecule from dark to bright, one can see that the molecules in the red and blue rectangles have an opposite handedness (*(P,P)* and *(M,M)* respectively). The zigzag structure is therefore a racemate. In between each *(P,P)* and *(M,M)*-9,9'-bis[7]H, there is also a round lobe (white squares). The EHT models (states 138-142 ext. Hückel, LUMO to LUMO+4) are displayed in the bottom right corner and their contrasts are compared to the ones in the STM images using red and blue circles for the *(P,P)* and *(M,M)*-9,9'-bis[7]H respectively. The EHT models were arranged based on the contrasts observed in the STM images.

	Experimental Length (Å)	Theoretical Length (Å)
(M,M)-bis[7]H	18.5 28.9 (four lobes)	18.3
(P,P)-bis[7]H	16.8	18.7

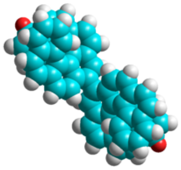

Table S1. Comparison between the experimental and theoretical length of the molecules. For the experimental values, the length was measured along the long axis of the molecule, i.e. in the parallel direction to the long axis of the blue or red rectangle in Figure S1. The *(M,M)*-bis[7]H four-lobes value corresponds to the length when the extra lobe (white squares in Figure S1) is included. The theoretical lengths are measured along the longest axis of the molecules between the two most outer hydrogen (highlighted in red in the *(M,M)*-bis[7]H model on the right).

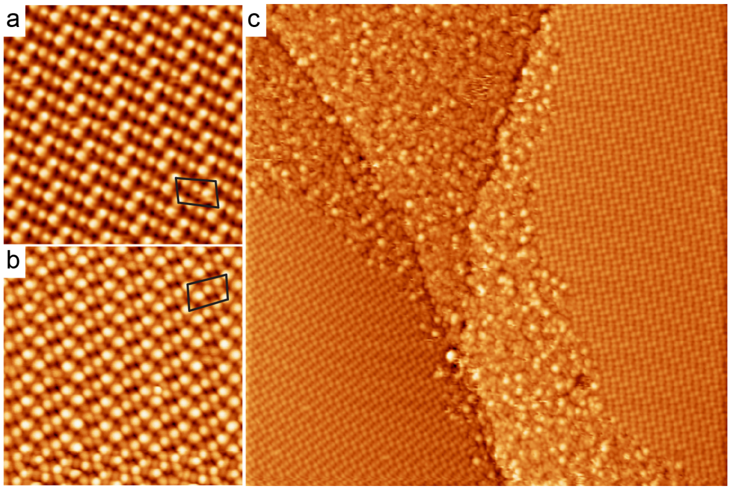

Figure S2. (a, b) Mirror domains of the zigzag structure (a: 20 nm × 20 nm, 2.14 V, 20 pA; b: 20 nm × 20 nm, 1.98 V, 34 pA). The unit cells are highlighted in black. (c) Rotational domains of the zigzag structure observed at sub-monolayer coverage (100 nm × 100 nm, 2.14 V, 24 pA).

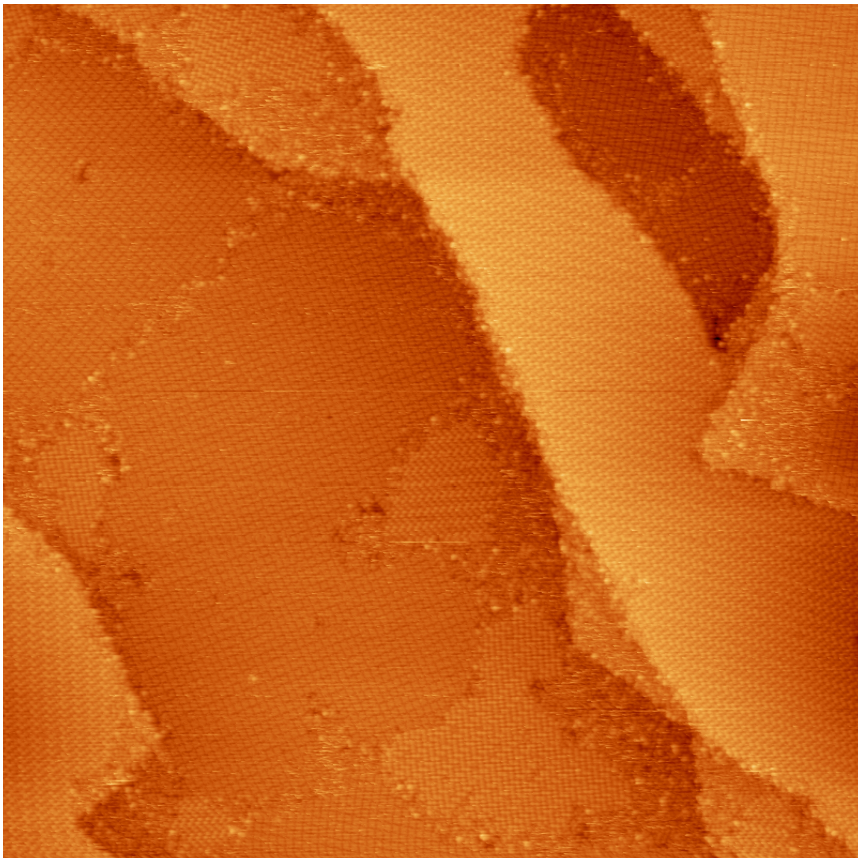

Figure S3. Large scale STM image (200 nm × 200 nm, 25 pA, 2.05 V) of bis7[H] on Cu(111) showing the coexistence of the zigzag and diamond structure close to monolayer coverage.

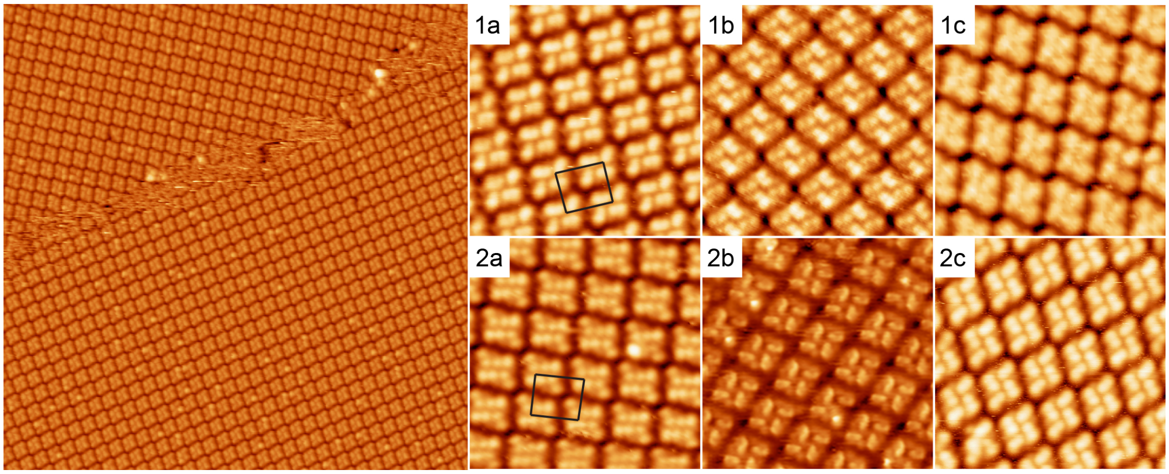

Figure S4. STM image (60 nm × 60 nm, 2.1 V, 20 pA) of two mirror domains of the diamond structure. Rotational domains (10 nm × 10nm) of one mirror domain type are displayed in (1) (a: 1.779 V, 29 pA; b: 2.093 V, 23 pA; c: 1.71 V, 29 pA) and rotational domains of the other mirror domain are displayed in (2) (a: 1.85 V, 25 pA; b: 2.09 V, 29 pA; c: 2.18 V, 32 pA) respectively. The unit cells of the structures 1a and 2a are highlighted in black.

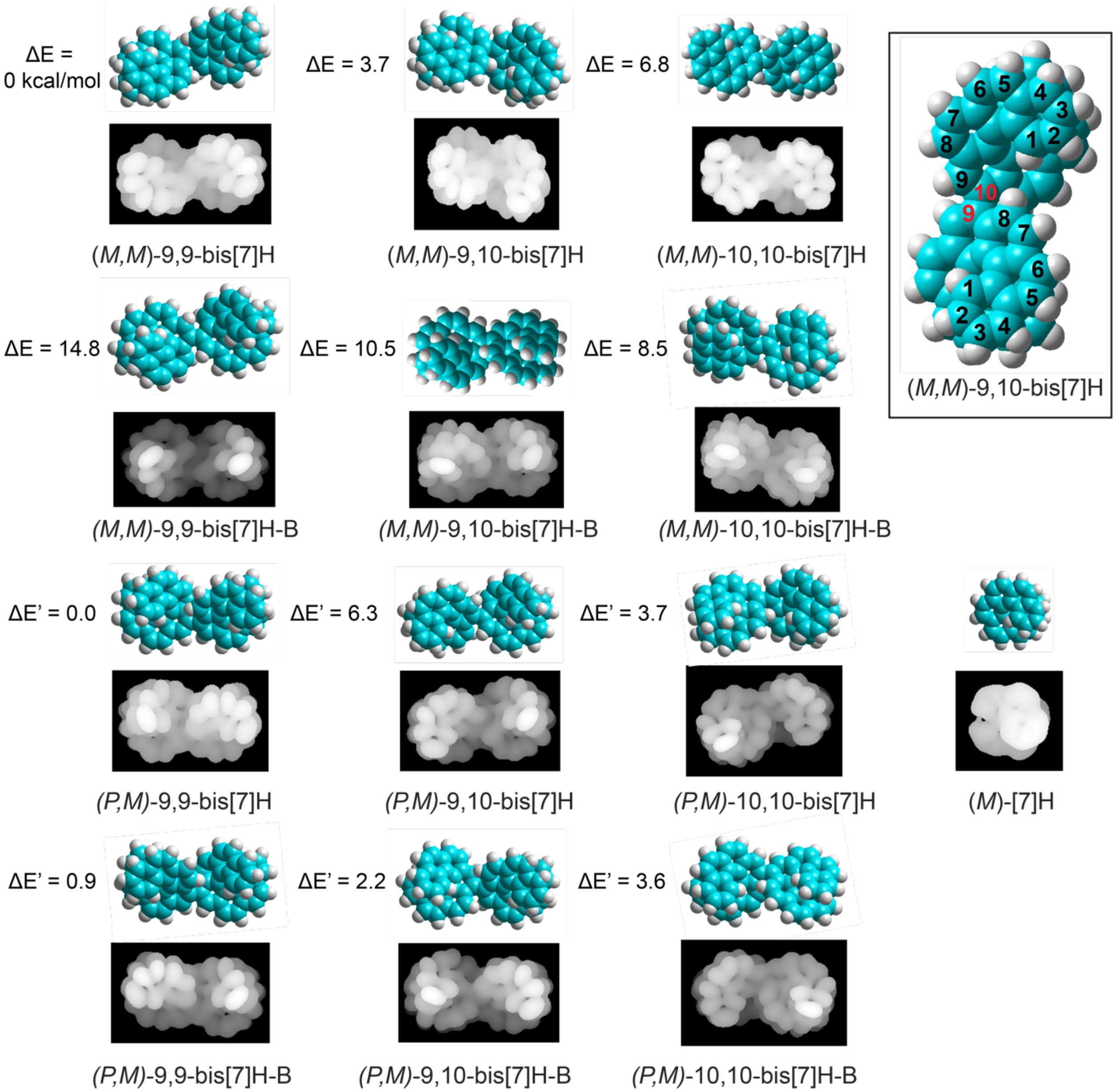

Figure S5. Electron density maps of the frontier orbitals close to the LUMO (LUMO to LUMO+4, states 138 to 142 Extended Hückel, electron density cutoff: 0.0004 e/Å^3) for all possible configurations of bis[7]H with terminal C6 rings parallel to the surface after geometric optimization on a four-layer Cu(111) slab with the AMBER force field. Only the (*M,M*)-enantiomer for the homochiral [7]H combination is presented. For each configuration there are two possible cases, in which either the H atom at C-8 (C-9) or at C-8′ (C-9′) is on top. For the latter, a "B" is added to the name. The relative AMBER force field energy values (kcal/mol) are given next to the molecular models. The 9,9′ conformers are favoured for all diastereomers. Whilst homochiral combinations have a symmetric electron-density appearance, the heterochiral (*P,M*)-combination shows contrast differences between the helical subunits.

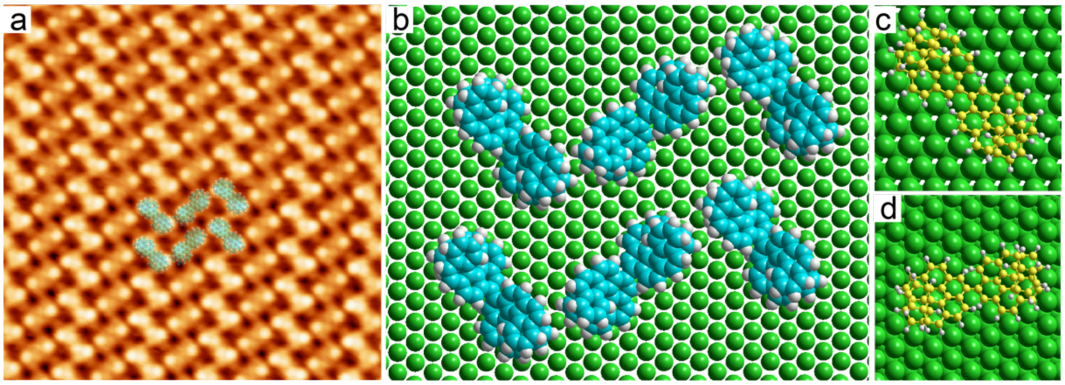

Figure S6. (a) Superposition of the molecular model (b) and an STM image (16.8 nm × 16.8 nm, 1.93 V, 31 pA) of the zigzag structure. (b) Molecular model [in matrix notation: (7, –1; 5, 15)], based on the STM images of the surface. (c, d) Lowest-energy optimized configurations of *(P,P)*-bis[7]H (c) and *(M,M)*-bis[7]H (d), as calculated by molecular mechanics (AMBER-force field). The optimized configurations are in both cases computed on 9,9'-bis[7]H over 420 initial conditions (different x, y, z positions and angle of the molecule with respect to the surface). The calculations were performed under periodic boundary conditions, on a four-layer-Cu(111) slab. The molecule was allowed to relax on the surface without any constrain.

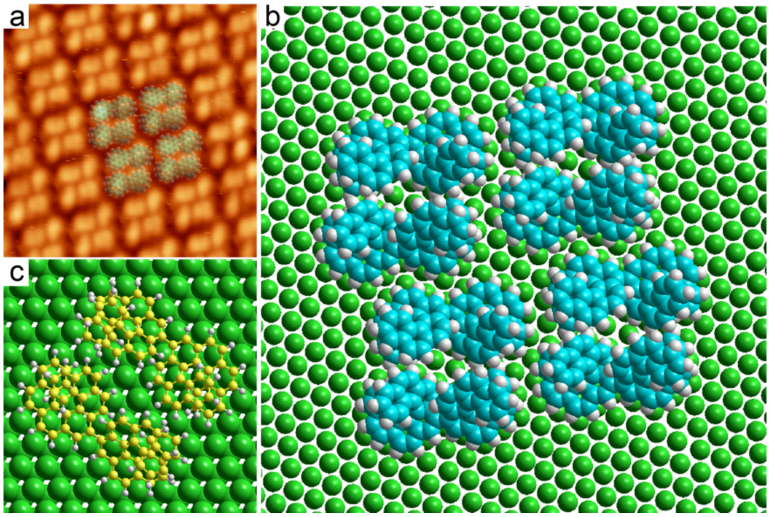

Figure S7. (a) Superposition of the molecular model shown in (b) on an STM image (10 nm × 10 nm, 1.78 V, 29 pA) of the diamond structure. (b) Molecular model based on the STM images of the diamond structure and on force-field calculations. (c) Minimum-energy dimer obtained with Amber-force field geometry optimization calculation. The molecules were allowed to relax freely on the surface. The lateral interaction energy amounts to 8.1 kcal/mol.

Bisheptahelicene synthesis

To a solution of racemic 9-bromo[7]helicene (920 mg, 2.0 mmol) in a mixture of dry benzene (10 ml) and dry THF (2 ml) a solution of tert-butyllithium (2.0 ml, 15% in pentane, 3.1 mmol) was added at -78 °C. The green solution was stirred for 1 h at this temperature, before it was added dropwise to a solution of [Pd(PPh_3)$_2$$Cl_2$] (700 mg, 1.0 mmol) in dry THF (10 ml) at –78 °C. Stirring was continued for 15 min at –78 °C and for 1 h at room temperature before the reaction was quenched by addition of 2n HCl. The organic phase was separated, dried with Na_2SO_4, and evaporated to dryness. Chromatography on silica using a cyclohexane/toluene gradient from 100/1 to 9/1 yielded 350 mg (0.46 mmol, 46%) of a yellow solid (mixture of isomers).

R_f (SiO_2, cyclohexane/toluene 8/2): 0.19.

MS (MALDI-TOF, matrix: norharmane): m/e = 754.

Nuclear magnetic resonance: The spectra (Figs. S8, S9) clearly show the presence of four kinds of molecules, which are assigned to atropisomers of the diastereomers. This becomes particularly clear for the singulets of the 10-H, as indicated by a green rectangle in the HSQC (Figure S10). The spectra also indicate the presence of 3 mass% of cyclohexane.

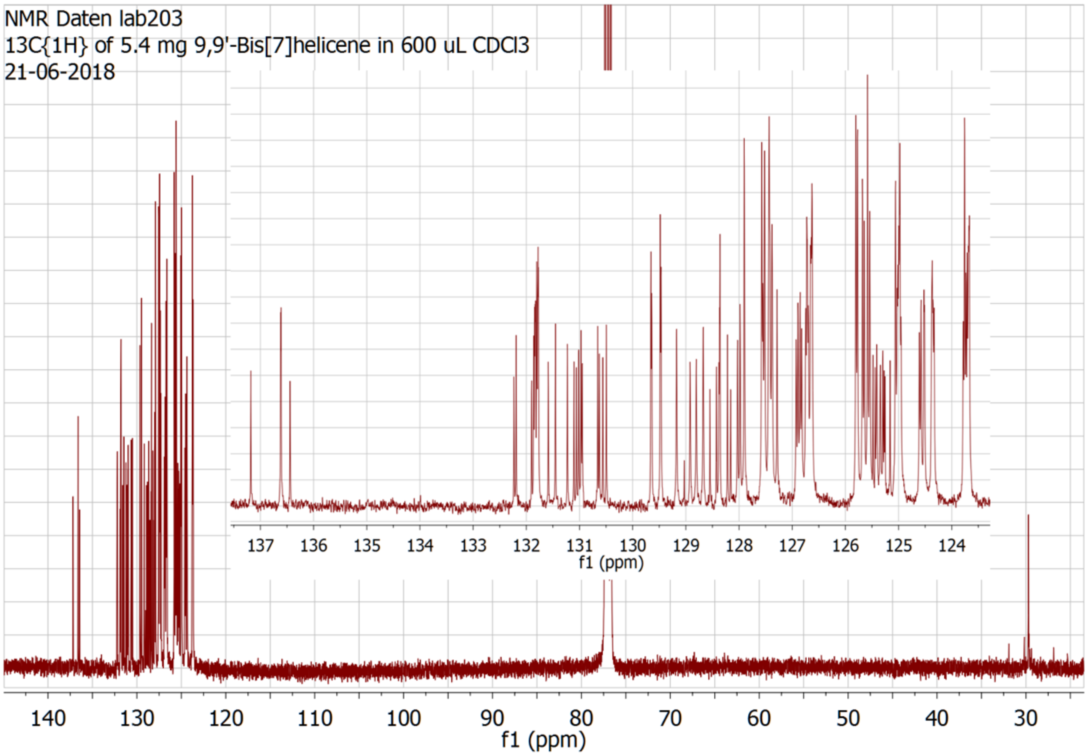

Figure S8. ^{13}C NMR spectra of bisheptahelicene after purification and crystallization from cyclohexane.

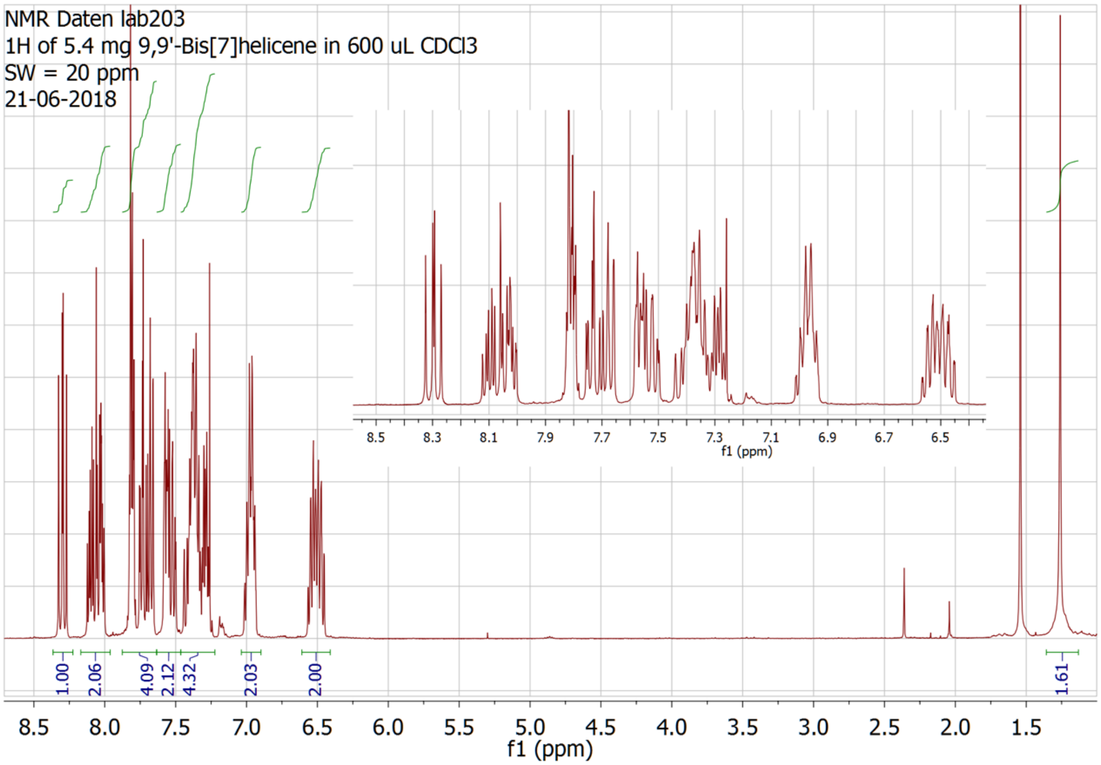

Figure S9. ^{1}H NMR spectra of bisheptahelicene after purification and crystallization from cyclohexane.

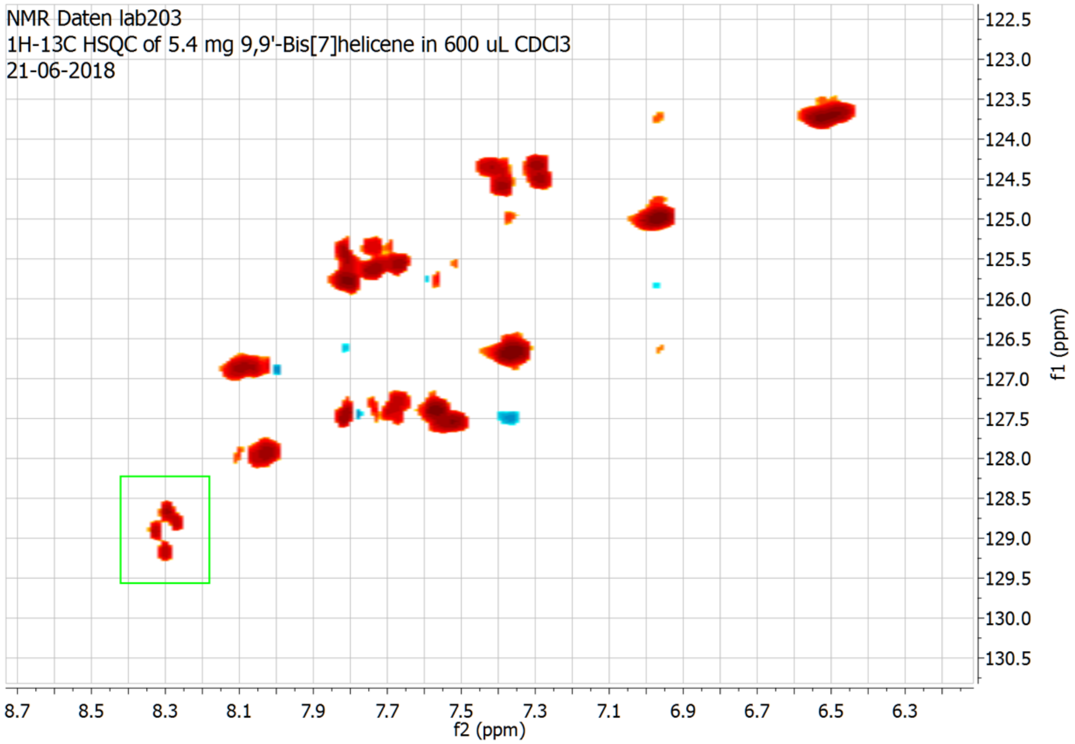

Figure S10. HSQC NMR plot of 9,9’-bisheptahelicene after purification and crystallization from cyclohexane.