

Supporting Information for

***On-surface synthesis of a phenylene analogue of nonacene***

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**Author contribution:**

I.I performed the STM and STS measurements with the guidance of R.Z. M.K. and M.S. conducted theoretical calculations. S.G. and A.M.E. conceived the experiments and supervised the investigation. O.S and R.B. synthesized the precursors under the supervision of A.M.E. The manuscript was written by S.G. and A.M.E. with input from other authors, who approved the final version.

## 1. Additional BR-STM images

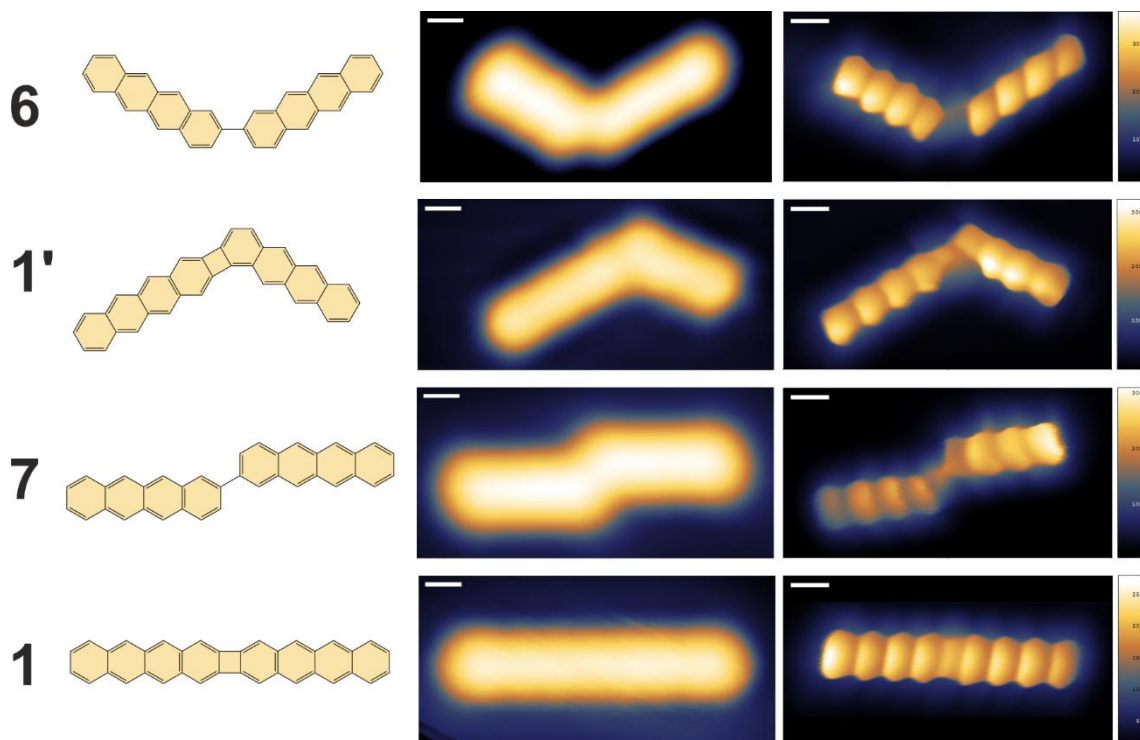


Figure S1. Structural models (left), high-resolution empty-state STM images (middle) and BR-STM images of compounds **1**, **1'**, **6**, **7**.

Figure S1 shows identification of the compounds **1**, **1'**, **6**, **7** based on constant height BR-STM images (right column). Scanning parameters: 10 mV, 30 pA (middle column); 5 mV (right column). Scale bar: 0.3 nm

## 2. $dI/dV$ STS measurements for compounds 1-4

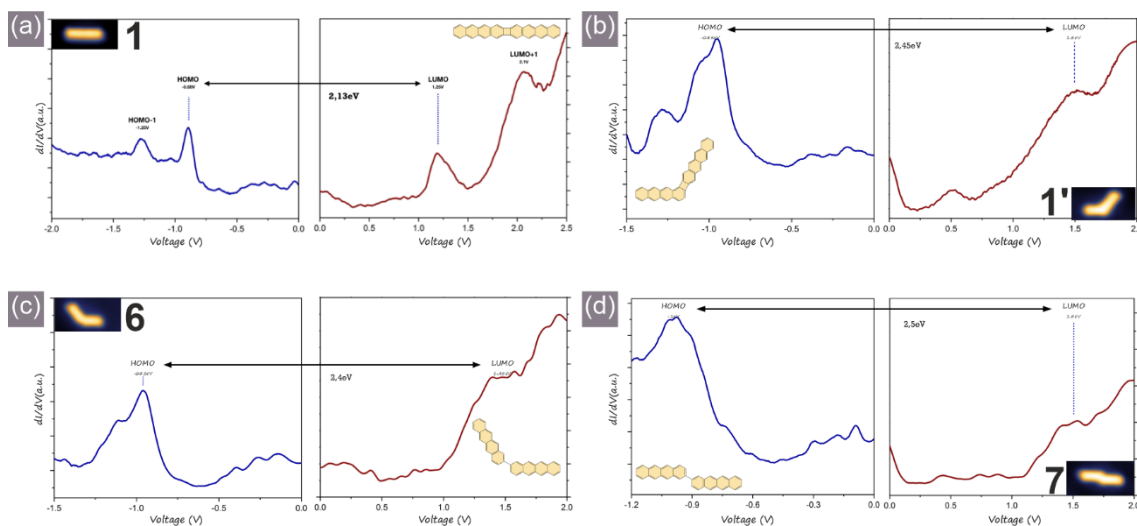


Figure S2. Single point  $dI/dV$  STS data acquired for compounds **1**, **1'**, **6**, **7**. The insets show structural models and corresponding high resolution STM images.

Single point  $dI/dV$  STS data obtained for molecules **1**, **1'**, **6**, **7** and the extracted values of the STS measured transport gap are visualized in Figure S2.

### 3. Bond length and bond orders of 1

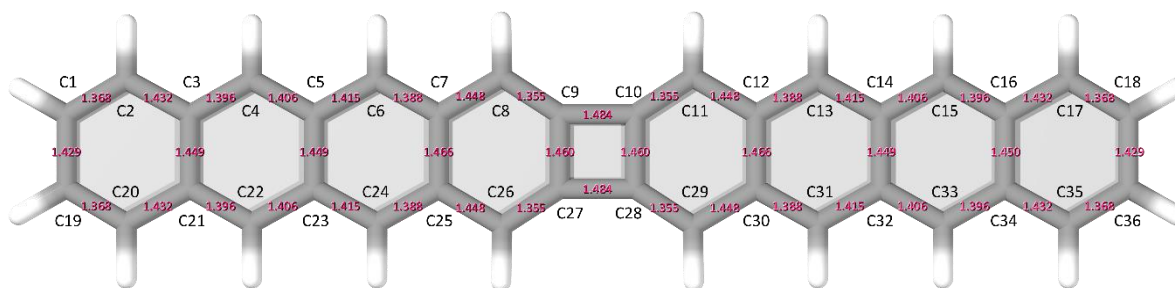


Figure S3. Bond lengths in the optimized geometry of **1** (CBDT; B3LYP/6-31G(d,p), Å).

Table S1. Bond lengths and bond order analysis.

	C1- C2	C2- C3	C3- C4	C4- C5	C5- C6	C6- C7	C7- C8	C8- C9	C9- C10	C9- C27	C1- C19
DFT [Å]	1.36	1.43	1.39	1.40	1.41	1.38	1.44	1.35	1.48	1.46	1.42
Pauling bond order	1.64	1.37	1.51	1.47	1.43	1.55	1.31	1.70	1.18	1.26	1.38

The bond order has been calculated following the formula:

$$n = \exp((r_0 - r) / 0.353),$$

where  $r_0$  is the length of the reference single C-C bond and  $r$  is the length of the analyzed bond, both expressed in Å. The empirical value 0.353 and the length of the reference bond reaching 1.542 Å have been taken from ref [1].

### 4. On surface experimental methods

All experiments were performed using ultra-high vacuum system with the base pressure in the  $1 \cdot 10^{-10}$  mbar range. Atomically clean Au(111) sample was obtained by cycles of Ar<sup>+</sup> ion sputtering and subsequent thermal annealing at 700 K. Precursors 2a/2b were evaporated thermally on a sample kept at 490 K from water-cooled Knudsen cell (Kentax GmbH). The sublimation temperature of 2a/2b was established at 500 K with a flux (0.1 Hz/min) calibrated by a quartz-microbalance. To complete cyclization and dehydrogenation reactions the sample was kept at 610 K for 15 minutes. Thermal annealing was performed in a preparation chamber using resistive heater. All STM/STS data were obtained using a low-temperature scanning tunneling microscope (LT-Nanoprobe STM, ScientaOmicron) operating in 4.5 K. dI/dV measurements were performed using lock-in amplifier (Zurich Instruments MFLI) with frequency of 630 Hz and amplitude of 20 mV. BR-STM data were collected in a constant-height mode using electrochemically etched PtIr tip functionalized with a CO molecule.

### 5. Computational details

All calculations of CDBT on Au(111) were performed using density functional theory (DFT) with the projector augmented waves (PAW)<sup>2</sup> and van der Waals corrected exchange-correlation functional (vdW-DF)<sup>3</sup> available in VASP (Vienna ab-initio simulation package).<sup>4</sup> The optPBE-vdW implementation of the vdW-DF method was used in all the calculations.<sup>5</sup>

The plane wave energy cutoff was set to 700 eV. The Brillouin zone was sampled by a  $1 \times 2 \times 1$  Monkhorst-Pack k-point grid including the  $\Gamma$  point.<sup>6</sup> The convergence criterion for the total energy in the self-consistency cycle was set to  $10^{-6}$  eV.

The Au(111) substrate has been modeled by a slab of 5 atomic layers. Periodic replicas of the slab were separated by a vacuum gap of 12 Å in order to avoid the interaction between surfaces of the slab. All the atomic positions were fully relaxed by a conjugate gradient method, except the bottom layer, until the maximum force in any direction was less than 0.01 eV/Å. During the geometry optimization the Au atoms in the bottom layer were fixed in their bulk positions. The calculations have been performed in the rectangular 12×6 surface unit cell with bulk Au lattice constant  $a_{\text{bulk}} = 4.182 \text{ \AA}$ .

The local density of states maps have been calculated according to the Tersoff-Hamann approach in the constant-current mode.<sup>7</sup>

Magnetic properties of gas phase CBDT were investigated using density functional theory (DFT) calculations as implemented Gaussian 16.<sup>8</sup> The initial geometry optimization was carried out using the hybrid functional B3LYP<sup>9-11</sup> and the 6-31G(d,p) basis set. NICS maps and NICS(1) values were obtained by evaluating GIAO shieldings over a square grid of 151 × 151 points with an extent of 30 × 30 Å and located 1 Å above the plane of the molecule (Figure 3a) or perpendicular to that plane (Figure 3b). ACID<sup>12-13</sup> calculations were performed using the code kindly provided by Prof. Reiner Herge and his group.

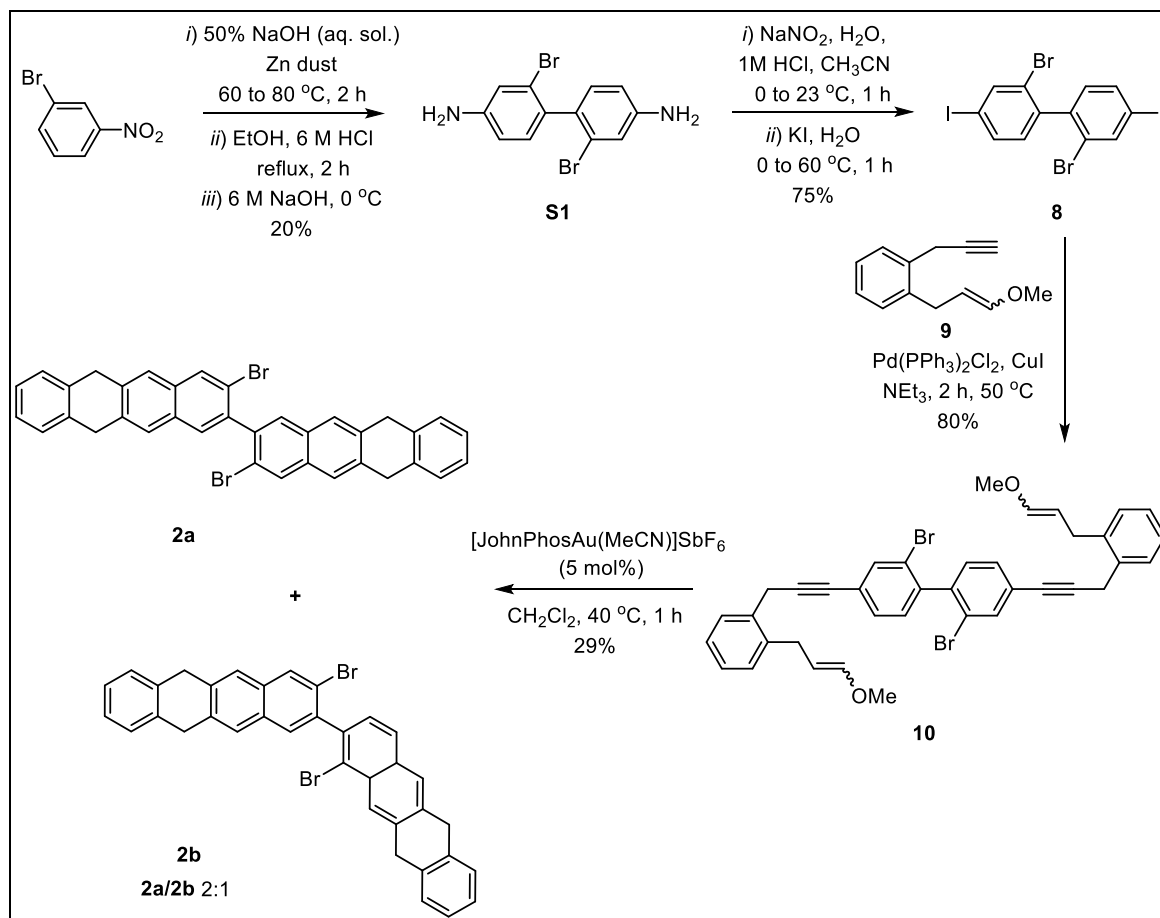
## 6. Synthetic methods: general information

Reactions under argon atmosphere were carried out in oven-dried glassware, using solvents dried by passing through an activated alumina column on a PureSolv™ solvent purification system (Innovative Technologies, Inc., MA). Analytical thin layer chromatography was carried out using TLC-aluminum sheets with 0.2 mm of silica gel (Merck GF234) using UV light as the visualizing agent and an acidic solution of vanillin in ethanol as the developing agent. Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-63 μm). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. All reagents were used as purchased, without further purification.

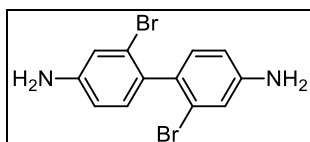
NMR spectra were recorded at 23 °C on a Bruker Avance 300, 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. Chemical shifts ( $\delta$ ) are given as parts per million (ppm) downfield from tetramethylsilane, with calibration on the residual protio-solvent used ( $\delta_{\text{H}} = 7.26 \text{ ppm}$  and  $\delta_{\text{C}} = 77.00 \text{ ppm}$  for  $\text{CDCl}_3$ ). Mass spectra were recorded on a Waters Micromass LCT Premier Spectrometer (APCI) or on an Autoflex Bruker Daltonics (MALDI). Melting point was determined using a Mettler Toledo MP70 apparatus.

## 7. Experimental Procedures and Characterization

### Synthesis of precursor 2a



1,7-Enyne **9** was prepared according to our previously reported procedures.<sup>14</sup>



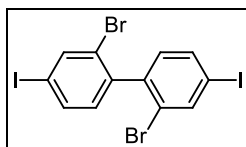
**2,2'-Dibromo-[1,1'-biphenyl]-4,4'-diamine (S1).** To a stirred solution of 1-bromo-3-nitrobenzene (1.0 equiv, 5.50 g, 27.2 mmol) in ethanol (60 mL) and aqueous sodium hydroxide (2.3 equiv, 2.50 g, 62.5 mmol, 15 mL), zinc dust (5.6 equiv, 10 g, 153 mmol) was added portionwise, so that the temperature does not exceed 70 °C. After stirring at this temperature for 15 min, more zinc (3.4 equiv, 6 g, 92 mmol) was added. The transparent mixture was then left to stir under reflux for 2 h and filtered through a Celite pad after cooling down to 23 °C. The zinc residue was washed with ethanol (2 × 30 mL). The combined filtrate was diluted with ethyl acetate (200 mL) and water (100 mL). The organic phase was extracted with more ethyl acetate (3 × 100 mL) and then washed with water and brine, dried (MgSO<sub>4</sub>) and the solvent was evaporated *in vacuo*. The resulting yellow oil was slowly poured onto 20% H<sub>2</sub>SO<sub>4</sub> (ca. 150 mL) at 0 °C and stirred at this temperature for ca. 40 min. This afforded the desired hydrazine as a pale orange solid which was isolated through vacuum filtration (ca. 3.500 g).

The crude hydrazine was dissolved in ethanol (60 mL), added to 6 M HCl (60 mL) and stirred at reflux for 2 h. After this time, the dark orange solution was cooled on ice. Thus, some solid benzidine hydrochloride precipitated. Then, a solution of 25% aq. NaOH (120 mL) was added dropwise through a dropping funnel at 0 °C to make the solution basic to a pH of 11. The brown solution was extracted with diethyl ether (3 × 150 mL) and the extracts were dried (MgSO<sub>4</sub>), filtered, and evaporated. The

crude benzidine was crystallized from an ethanol-water mixture and was obtained as a pale orange solid (1.834 g, 5.362 mmol, 20% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.00 (d,  $J$  = 8.2 Hz, 2H), 6.97 (d,  $J$  = 2.4 Hz, 2H), 6.64 (dd,  $J$  = 8.2, 2.4 Hz, 2H), 3.74 (s, 4H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.0, 132.2, 132.2, 124.9, 118.4, 113.9. Spectral data are in agreement with the literature.



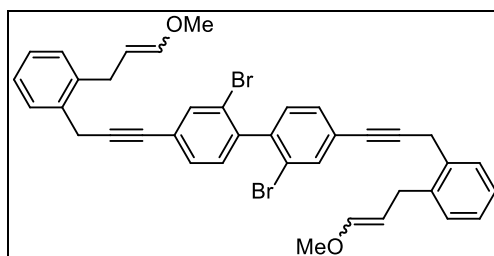
**2,2'-Dibromo-4,4'-diiodo-1,1'-biphenyl (8).** Benzidine **S1** (1.0 equiv, 600 mg, 1.75 mmol) was dissolved in acetonitrile (0.141 M, 20 mL) and 1 M HCl (10 mL) and the resulting slurry was cooled to 0 °C. Then a solution of sodium nitrite (2.4 equiv, 289 mg, 4.19 mmol) in water (5 mL) was slowly added. The reaction mixture was then stirred for 30 min at 0 °C and then added to a second RBF containing a solution of potassium iodide (10 equiv, 2.91 g, 17.5 mmol) in water (10 mL) cooled to 0 °C. After that, the solution was allowed to warm to 23 °C with stirring for 1 h and was then heated to 60 °C for another hour. The reaction was allowed to cool to 23 °C and was diluted with water and EtOAc. The product was extracted with EtOAc (3  $\times$  50 mL) and the organic phase was washed with  $\text{NaHSO}_3$  and brine, dried ( $\text{MgSO}_4$ ), filtered and the solvent was removed *in vacuo*. Purification by column chromatography (cyclohexane) gave the title compound as a white solid (738 mg, 1.310 mmol, 75% yield).

Melting point = 78–81 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J$  = 1.7 Hz, 2H), 7.70 (dd,  $J$  = 8.1, 1.7 Hz, 2H), 6.94 (d,  $J$  = 8.1 Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 140.8, 136.5, 132.2, 124.3, 94.2. Spectral data are in agreement with the literature.<sup>15</sup>

HRMS (APCI+)  $m/z$  calc. for  $\text{C}_{12}\text{H}_6\text{Br}_2\text{I}_2$   $[\text{M}]^+$ : 561.6920, found: 561.6918.

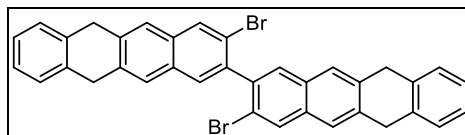


**2,2'-Dibromo-4,4'-bis(3-(2-(3-methoxyallyl)phenyl)prop-1-yn-1-yl)-1,1'-biphenyl (10).**  $\text{PdCl}_2(\text{PPh}_3)_2$  (25.0 mg, 36  $\mu\text{mol}$ , 10 mol%) and  $\text{CuI}$  (13.5 mg, 71  $\mu\text{mol}$ , 20 mol%) were suspended in  $\text{Et}_3\text{N}$  (1.8 mL) and the mixture was bubbled with Ar for 10 min. A solution of **8** (1.0 equiv, 353  $\mu\text{mol}$ , 200 mg) and **9** (3.0 equiv, 198 mg, 1.06 mmol) in a mixture of degassed  $\text{NEt}_3$  (1.8 mL) was subsequently added and the reaction was stirred at 40 °C for 2 h. Then the mixture was diluted with EtOAc (10 mL), filtered through a short pad of silica gel compacted with EtOAc/ $\text{NEt}_3$  99:1 and concentrated under reduced pressure. Purification by column chromatography (cyclohexane/EtOAc 98:2) afforded the title compound as a pale yellow oil (192 mg, 0.282 mmol, 80% yield).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (dd,  $J$  = 6.1, 1.5 Hz, 2.5H), 7.50 – 7.47 (m, 2.5H), 7.42 (ddd,  $J$  = 7.9, 5.0, 1.6 Hz, 2.5H), 7.24 – 7.22 (m, 7.5H), 7.14 (dd,  $J$  = 7.9, 1.7 Hz, 2.5H), 6.37 (dt, 2H, *E*), 6.02 (dt,  $J$  = 6.1, 1.5 Hz, 0.5H, *Z*), 4.90 (dt,  $J$  = 12.5, 7.0 Hz, 2H, *E*), 4.50 (td,  $J$  = 7.4, 6.2 Hz, 0.5H, *Z*), 3.84 (s, 1H, *Z*), 3.83 (s, 4H, *E*), 3.67 (s, 1.5H, *Z*), 3.53 (s, 6H, *E*), 3.49 (dd,  $J$  = 7.3, 1.5 Hz, 1H, *Z*), 3.37 (dd,  $J$  = 7.0, 1.1 Hz, 4H, *E*);

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  148.5, 146.9, 141.19, 141.15, 139.38, 139.18, 138.16, 135.55, 134.53, 134.42, 130.73, 130.71, 130.42, 130.41, 129.44, 129.27, 128.99, 128.73, 127.48, 127.40, 127.27, 126.79, 126.56, 125.40, 123.15, 104.53, 100.99, 89.72, 89.70, 81.33, 81.25, 59.87, 56.14, 56.12, 53.56, 31.27, 31.22, 27.79, 23.58, 23.36 (peaks missing due to overlapping).

HRMS (APCI+)  $m/z$  calc. for  $\text{C}_{38}\text{H}_{33}\text{Br}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : 679.0842, found: 679.0844.



**3,3'-Dibromo-6,6',11,11'-tetrahydro-2,2'-bitetracene (2).** To a solution of **10** (1 equiv, 65 mg, 0.096 mmol) in HPLC grade  $\text{CH}_2\text{Cl}_2$  (0.1 M, 1.0 mL) was added cationic gold catalyst  $[\text{JohnPhosAu}(\text{MeCN})]\text{SbF}_6$  (3.7 mg, 5 mol%) and the mixture was stirred at  $40^\circ\text{C}$  for 1 hour under air. After cooling to  $23^\circ\text{C}$ ,  $\text{NEt}_3$  (0.1 mL) was added and then the solvents were evaporated under reduced pressure. Purification by column chromatography (cyclohexane/ $\text{CH}_2\text{Cl}_2$  9:1) afforded the title compound as a 2.7:1 mixture of isomers – symmetric **2a** and non-symmetric **2b**, with **2a** being the major one (17 mg, 28  $\mu\text{mol}$ , 29% yield).

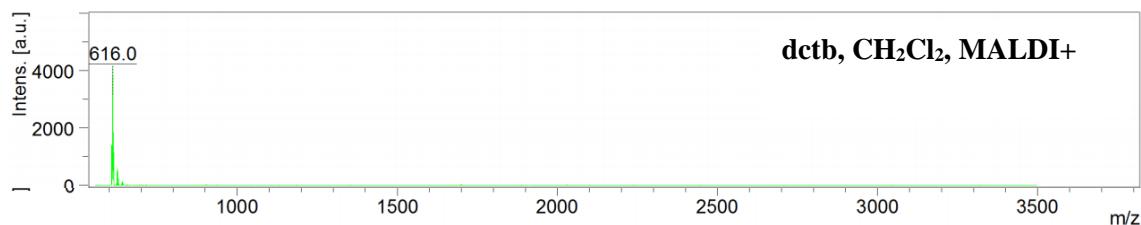
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (s, 1H), 8.15 (s, 1H), 8.14 (s, 1.4H), 7.85 – 7.82 (m, 2H), 7.74 (d,  $J$  = 2.2 Hz, 5.5H), 7.38 – 7.33 (m, 5.5H), 7.23 (dt,  $J$  = 9.9, 3.6 Hz, 5.5H), 4.16 (d,  $J$  = 12.9 Hz, 3H), 4.10 (d,  $J$  = 14.7 Hz, 8H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 140.1, 139.8, 139.2, 138.1, 138.0, 137.4, 137.4, 137.1, 136.9, 136.9, 136.8, 136.8, 133.0, 133.0, 132.9, 131.2, 131.1, 131.0, 130.5, 130.3, 129.5, 129.3, 127.8, 127.6, 127.5, 127.4, 127.4, 126.9, 126.8, 126.5, 126.5, 125.7, 125.4, 125.4, 125.3, 124.2, 121.4, 120.9.

HRMS (APCI+)  $m/z$  calc. for  $\text{C}_{36}\text{H}_{23}\text{Br}_2$   $[\text{M}-\text{H}]^+$ : 613.0140, found: 613.0161 (isotopic composition:  $^{79}\text{Br}$ ).

MALDI-MS spectrum of hydroacene **2**:

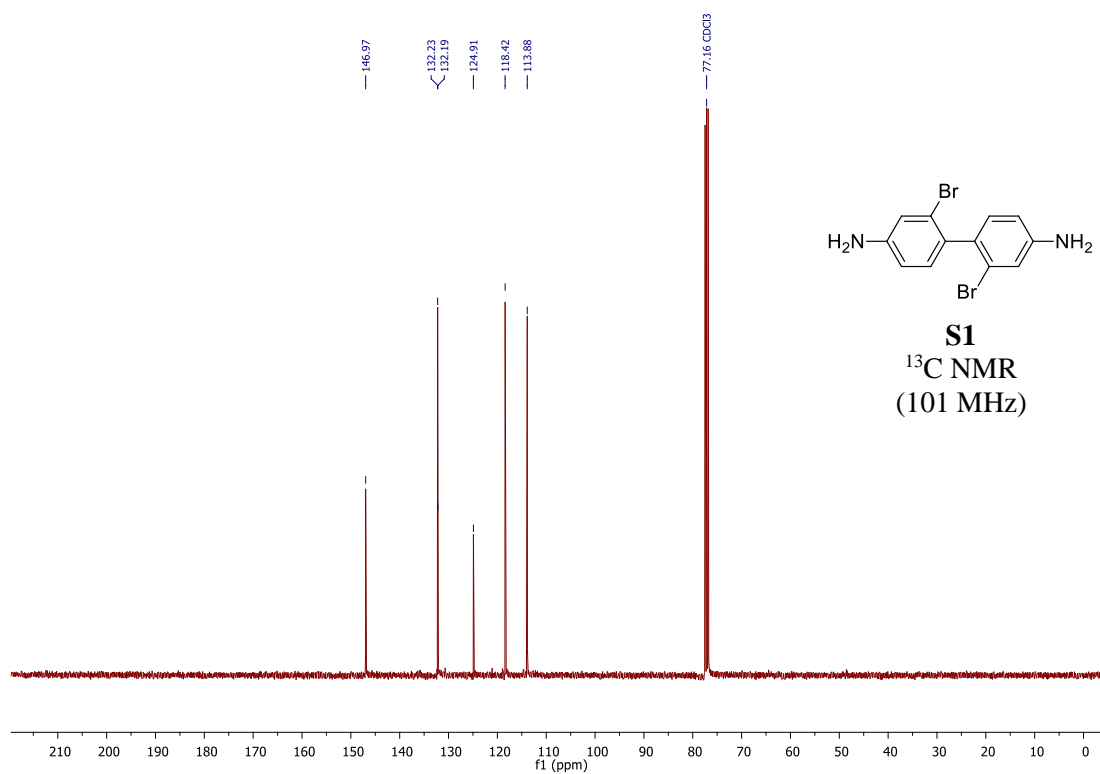
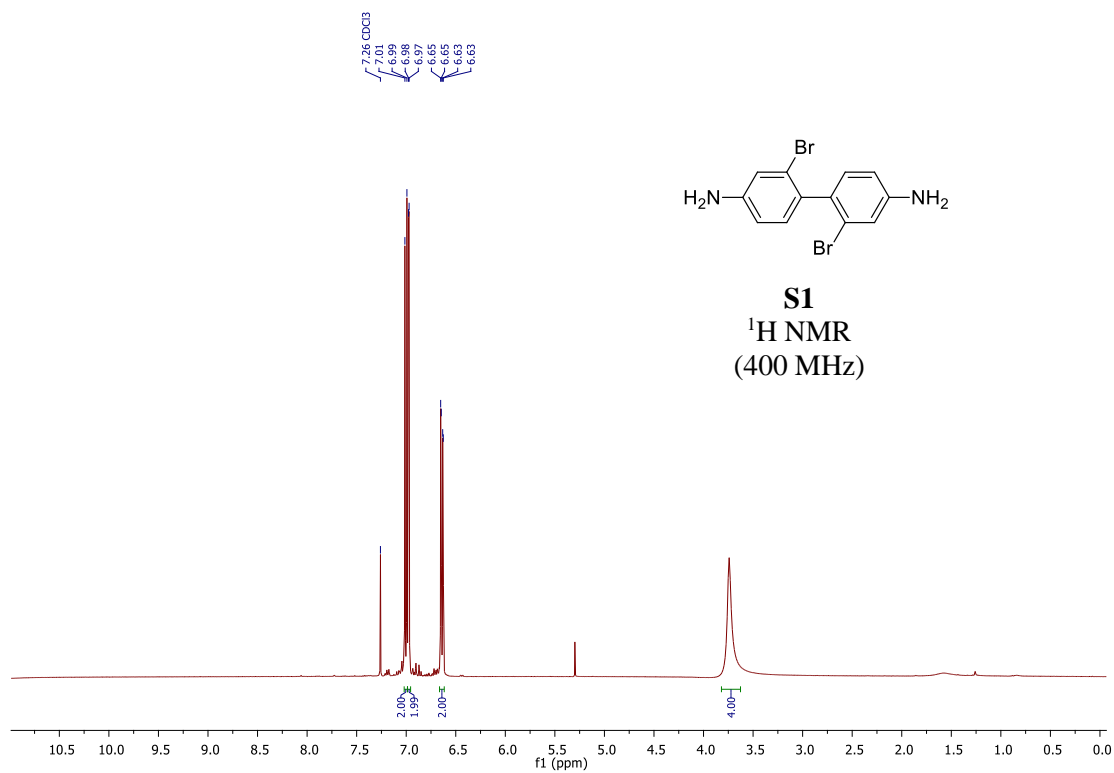
(MALDI+)  $m/z$  calc. for  $\text{C}_{36}\text{H}_{24}\text{Br}_2$   $[\text{M}]^+$ : 616.0, found: 616.0



The values of the nominal mass (shown above in the MALDI-MS spectrum) and the exact mass are different because of the isotopic composition of the compound: ca. 50%  $^{79}\text{Br}$  and 50%  $^{81}\text{Br}$ .

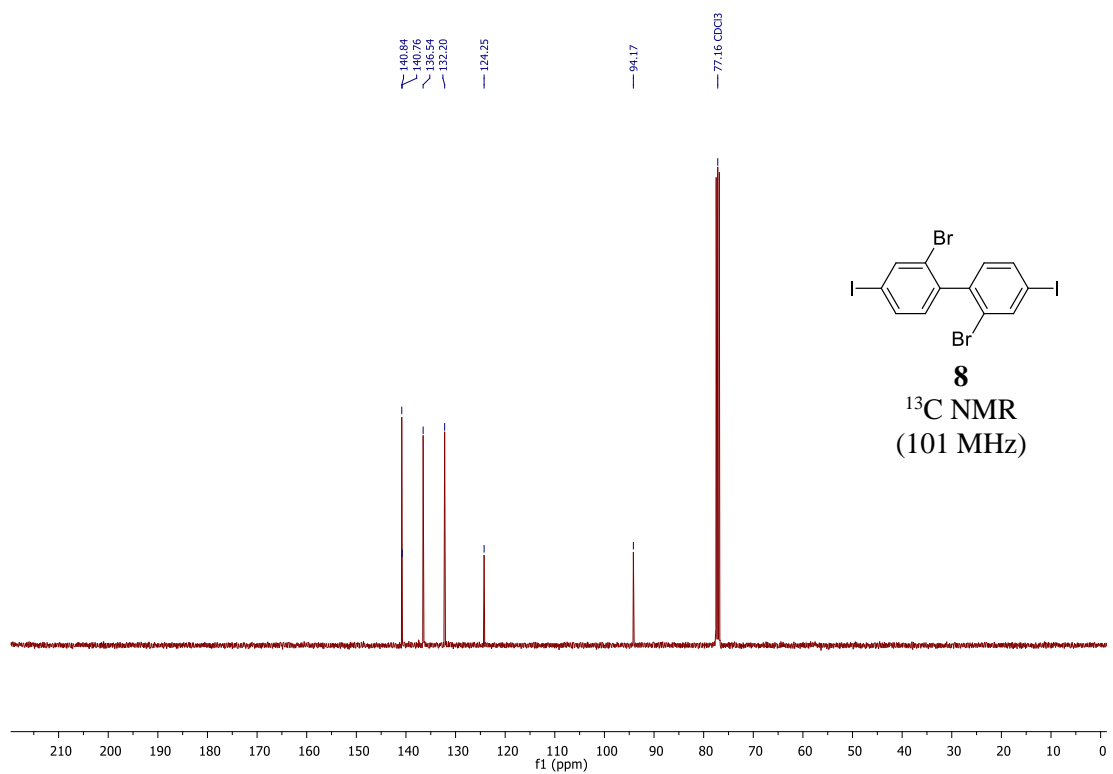
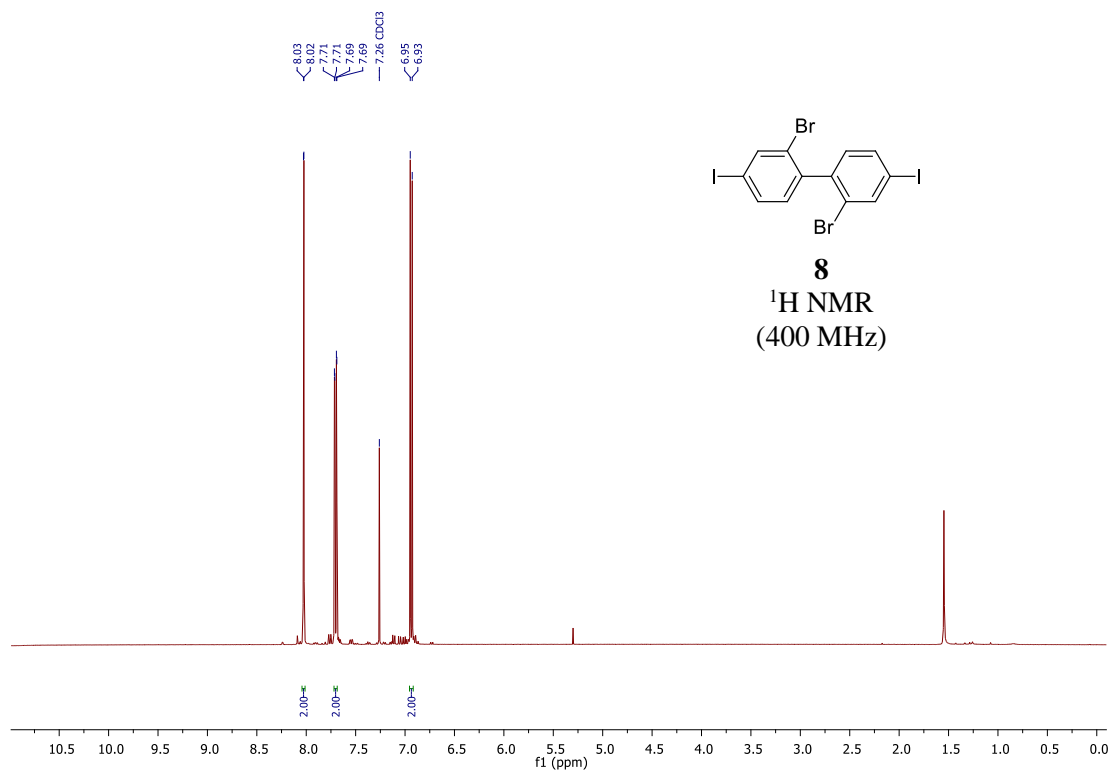
## 8. NMR Spectra

### 2,2'-Dibromo-[1,1'-biphenyl]-4,4'-diamine (S1)

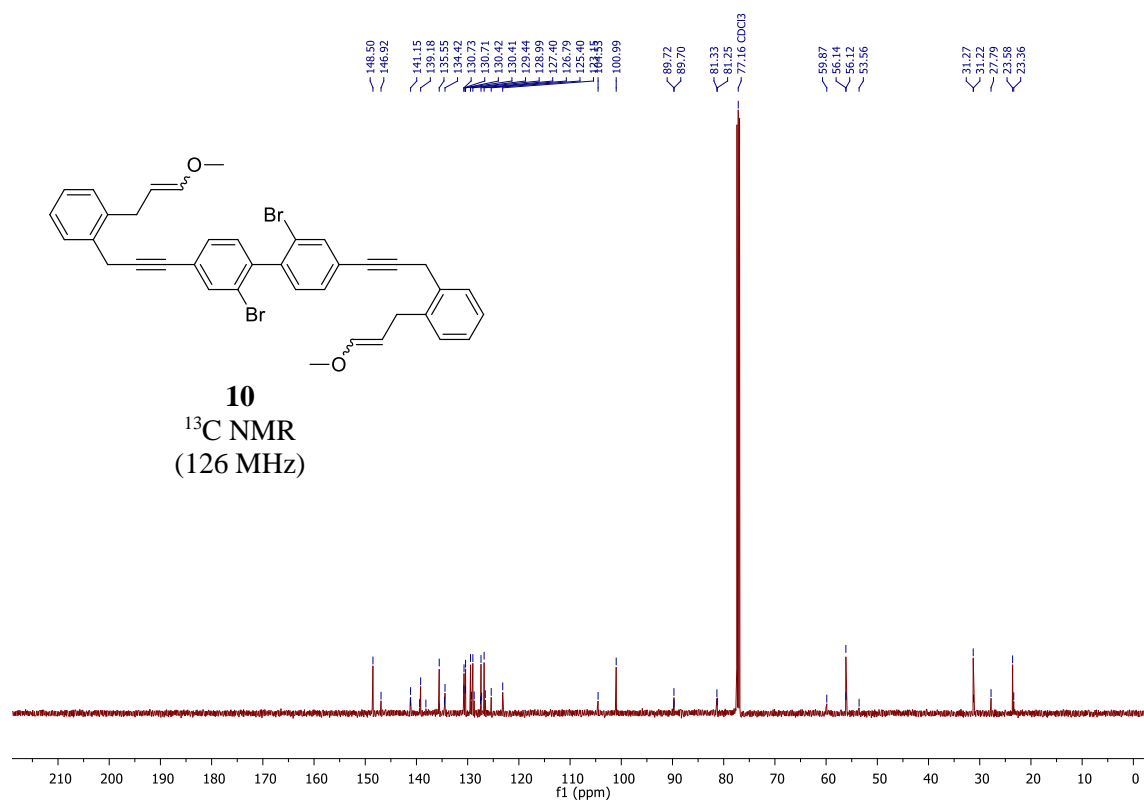
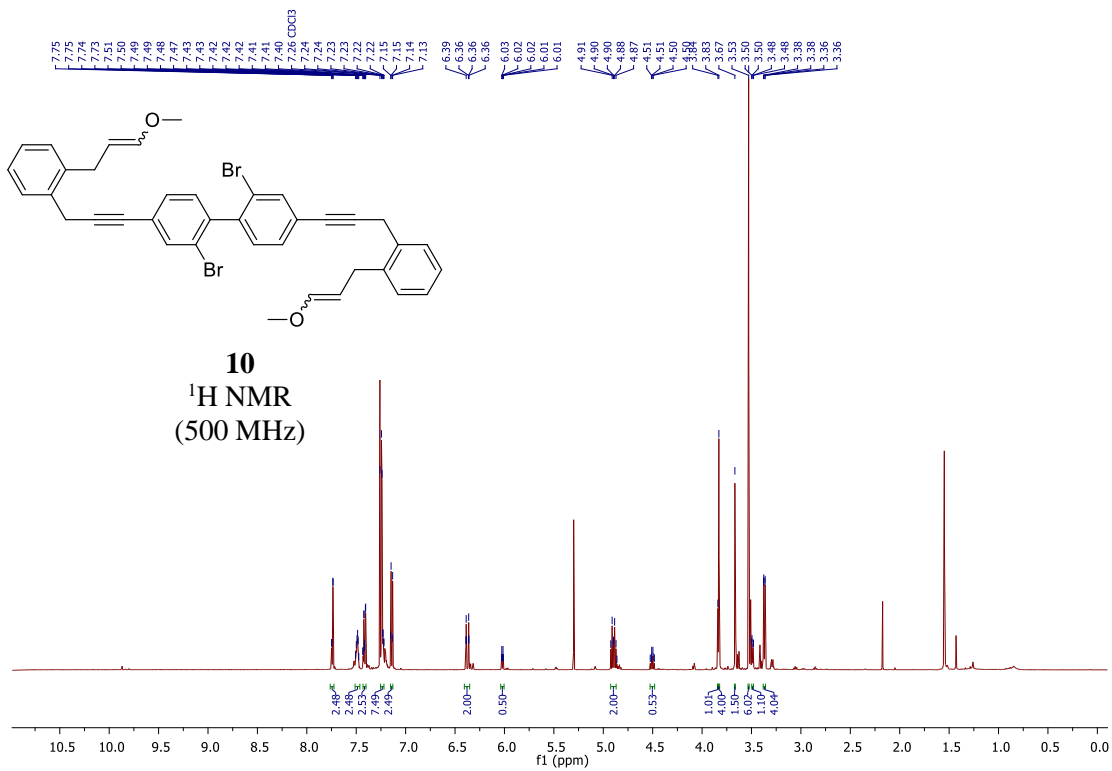


### 2,2'-Dibromo-4,4'-diiodo-1,1'-biphenyl (8)

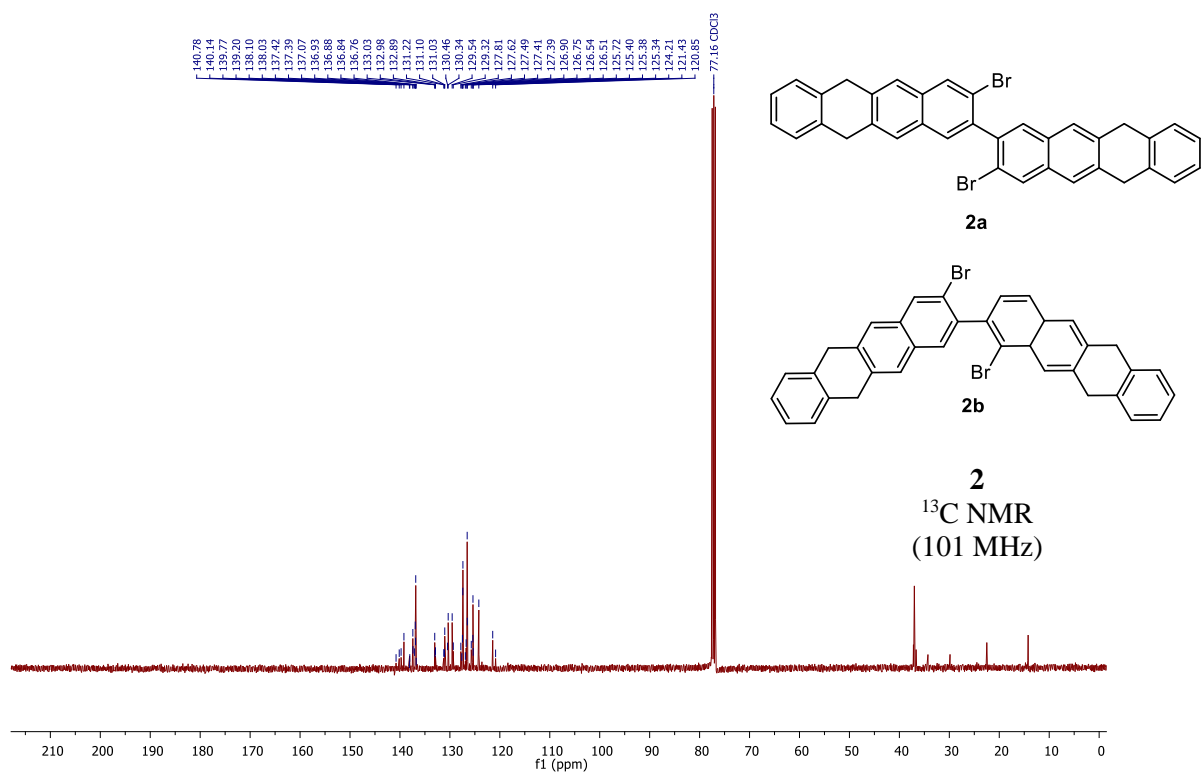
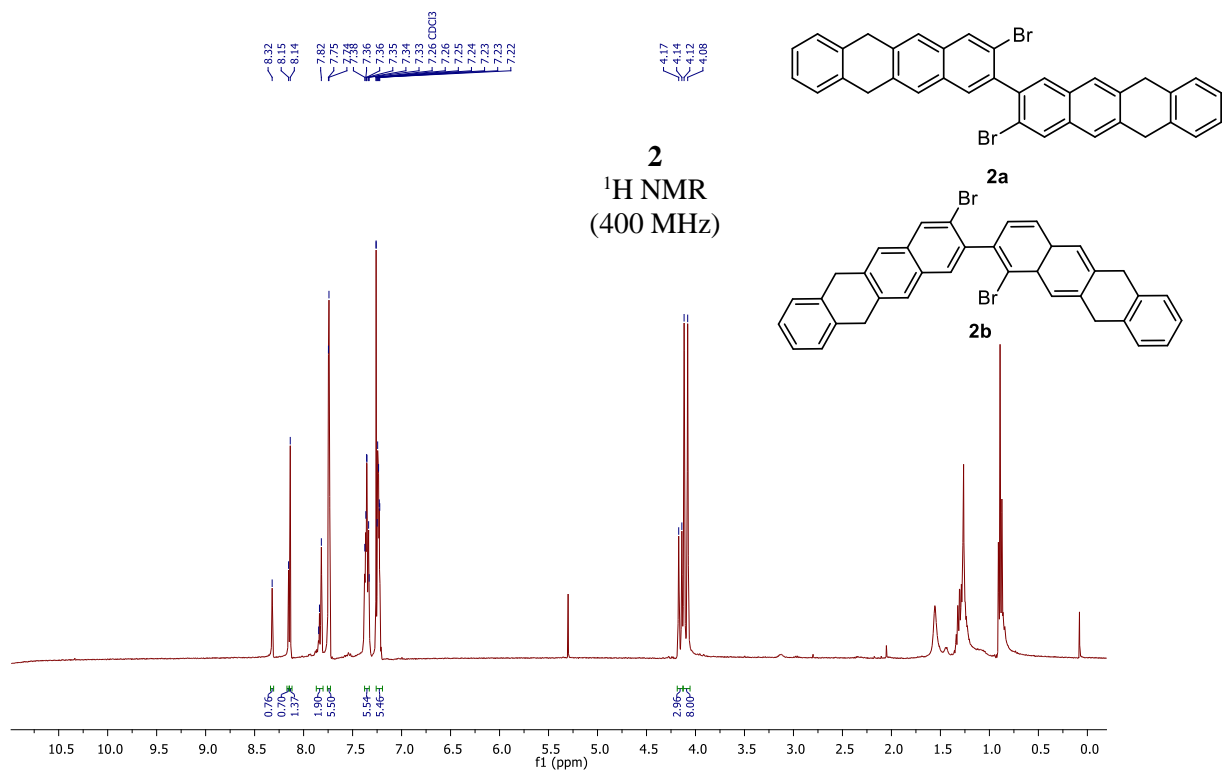




**2,2'-Dibromo-4,4'-bis(3-(2-(3-methoxyallyl)phenyl)prop-1-yn-1-yl)-1,1'-biphenyl (10)**



**3,3'-Dibromo-6,6',11,11'-tetrahydro-2,2'-bitetracene (2)**



## 9. References

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