

## Supplementary Material

# Crystal engineering of sterically shielded hexa-*peri*-hexabenzocoronenes (HBCs)

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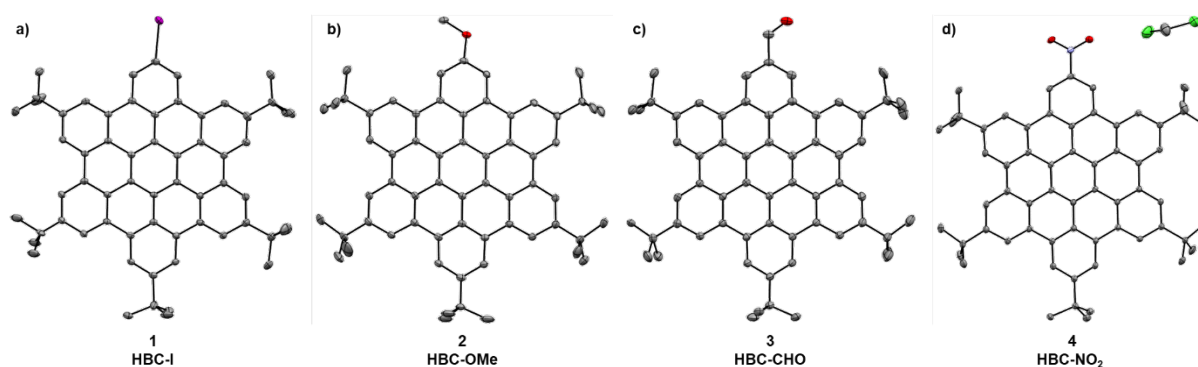
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## 1. General information

All chemicals were purchased from Sigma-Aldrich and used without any further purification. Solvents were distilled prior to usage.  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and EtOAc were distilled from  $\text{K}_2\text{CO}_3$  prior to usage. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F254, detected by UV-light (254 nm, 366 nm). Column chromatography and flash column chromatography were performed on Macherey–Nagel silica gel 60 M (230–400 mesh, 0.04–0.063 mm). NMR spectroscopy was performed on JEOL JNM EX 400 ( $^1\text{H}$ : 400 MHz,  $^{13}\text{C}$ : 100 MHz) and JEOL JNM GX 400 ( $^1\text{H}$ : 400 MHz,  $^{13}\text{C}$ : 100 MHz) and Bruker Avance 400 ( $^1\text{H}$ : 400 MHz,  $^{13}\text{C}$ : 100 MHz). Deuterated solvents were purchased from Sigma Aldrich and used as received. Chemical shifts are referenced to residual protic impurities in the solvents ( $\text{CHCl}_3$ :  $^1\text{H}$ : 7.26 ppm,  $\text{CH}_2\text{Cl}_2$ :  $^1\text{H}$ : 5.32 ppm) or the deuterated solvent itself ( $\text{CDCl}_3$ :  $^{13}\text{C}$ : 77.0 ppm). The resonance multiplicities are indicated as “s” (singlet), “d” (doublet), “t” (triplet), “q” (quartet) and “m” (multiplet). Signals referred to as bs (broad singlet) are not clearly resolved or significantly broadened. For simplicity, *para*-substituted phenylrings with an AA'BB' spin system are termed as doublets. LDI/MALDI-ToF mass spectrometry was performed on a Shimadzu AXIMA Confidence (nitrogen laser, 50 Hz, 337 nm). In case of MALDI, the following matrix were used: 2,5-dihydroxybenzoic acid (DHB), sinapic acid (SIN) or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB). High resolution mass spectrometry was performed on an ESI-ToF mass spectrometer Bruker maXis 4G UHR MS/MS spectrometer or a Bruker micrOTOF II focus TOF MS-spectrometer. Unless otherwise noted, reactions were degassed by the following technique: The reaction mixture was sonicated at 25 °C for 1 min under vacuum, followed by a purge with  $\text{N}_2$ -gas. This cycle was repeated three times.

## 2. X-ray analysis



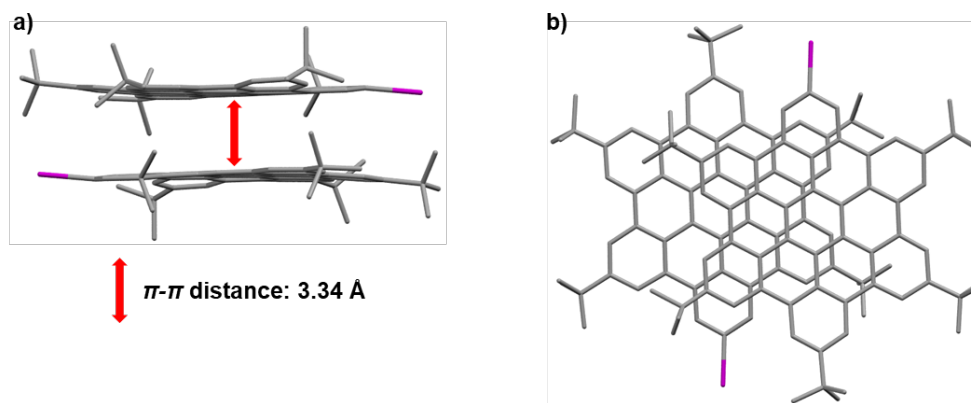
**Figure 1.** Compounds 1 (a), 2 (b), 3 (c) and 4 (d) depicted as ORTEP drawings. All atoms drawn at 30 % probability level. Hydrogen atoms omitted for clarity.

### 2.1. X-ray data for iodo-HBC 1

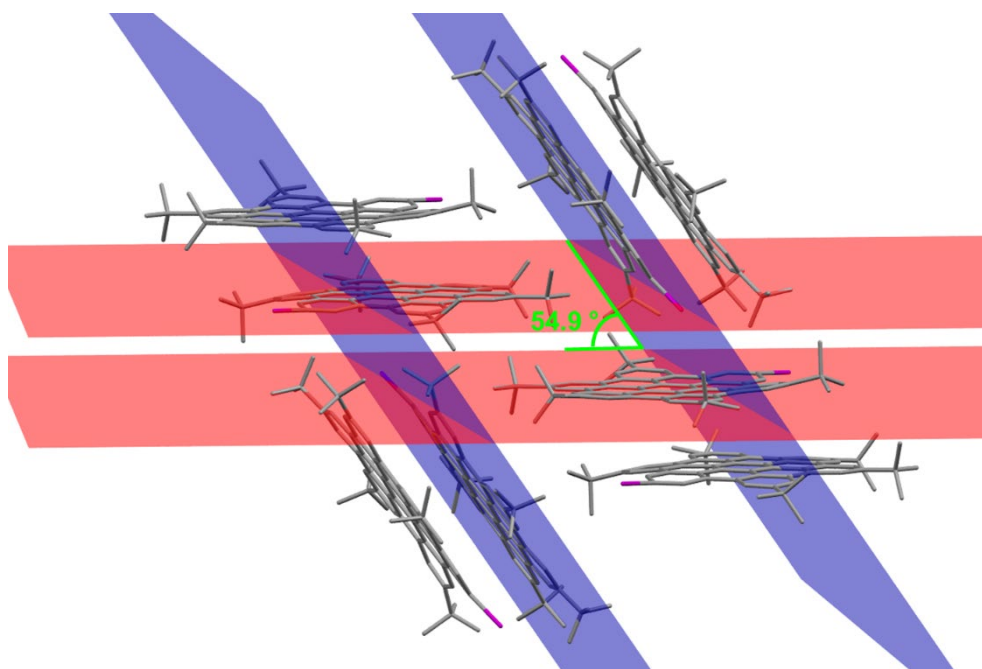
Single crystals of **1** were obtained by solvent diffusion from  $\text{CH}_2\text{Cl}_2$  with EtOH. A suitable crystal was selected and mounted on a loop on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 153.05(10) K during data collection. Using **Olex2**<sup>[S1]</sup>, the structure was solved with the **ShelXT**<sup>[S2]</sup> structure solution program using Intrinsic Phasing and refined with the **ShelXL**<sup>[S3]</sup> refinement package using Least Squares minimization.

**Table 1.** Crystal data and structure refinement for **1**.

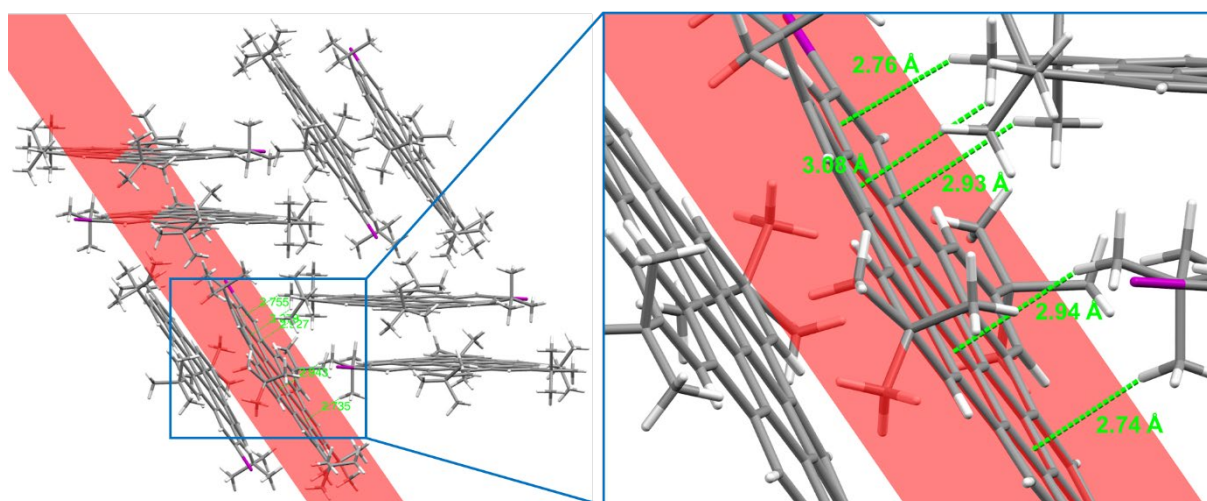
|   |   |
|---|---|
| Identification code                           | 19Jux_DR01  |
| Empirical formula                             | $\text{C}_{62}\text{H}_{57}\text{I}$                          |
| Formula weight                                | 928.97  |
| Temperature/K                                 | 153.05(10)  |
| Crystal system                                | monoclinic  |
| Space group                                   | $C2/c$  |
| $a/\text{\AA}$                                | 30.1288(4)  |
| $b/\text{\AA}$                                | 18.2707(3)  |
| $c/\text{\AA}$                                | 17.0975(2)  |
| $\alpha/^\circ$                               | 90  |
| $\beta/^\circ$                                | 95.6440(10)   |
| $\gamma/^\circ$                               | 90  |
| Volume/ $\text{\AA}^3$                        | 9366.1(2)   |
| Z   | 8   |
| $\rho_{\text{calc}}/\text{cm}^3$              | 1.318   |
| $\mu/\text{mm}^{-1}$                          | 5.664   |
| F(000)  | 3856.0  |
| Crystal size/ $\text{mm}^3$                   | $0.35 \times 0.147 \times 0.115$                              |
| Radiation                                     | $\text{CuK}\alpha$ ( $\lambda = 1.54184$ )                    |
| $2\theta$ range for data collection/ $^\circ$ | 5.896 to 129.08   |
| Index ranges                                  | $-26 \leq h \leq 34, -20 \leq k \leq 17, -19 \leq l \leq 16$  |
| Reflections collected                         | 13888   |
| Independent reflections                       | 7551 [ $R_{\text{int}} = 0.0350, R_{\text{sigma}} = 0.0407$ ] |
| Data/restraints/parameters                    | 7551/159/561  |
| Goodness-of-fit on $F^2$                      | 1.036   |
| Final R indexes [ $I \geq 2\sigma(I)$ ]       | $R_1 = 0.0495, wR_2 = 0.1326$                                 |
| Final R indexes [all data]                    | $R_1 = 0.0548, wR_2 = 0.1387$                                 |
| Largest diff. peak/hole / $e \text{\AA}^{-3}$ | 0.99/-0.77  |
| CCDC Deposition Number                        | 2055850   |



**Figure 3.** Dimer observed for 1. a) Side view with  $\pi$ - $\pi$  distance between the two HBC planes; b) Top view of the dimer. Hydrogens are omitted for clarity.



**Figure 2.** Angles between the dimers of 1. Note that the two red planes and the two blue planes are parallel and therefore all acute angles are 54.9°. Hydrogens are omitted for clarity.



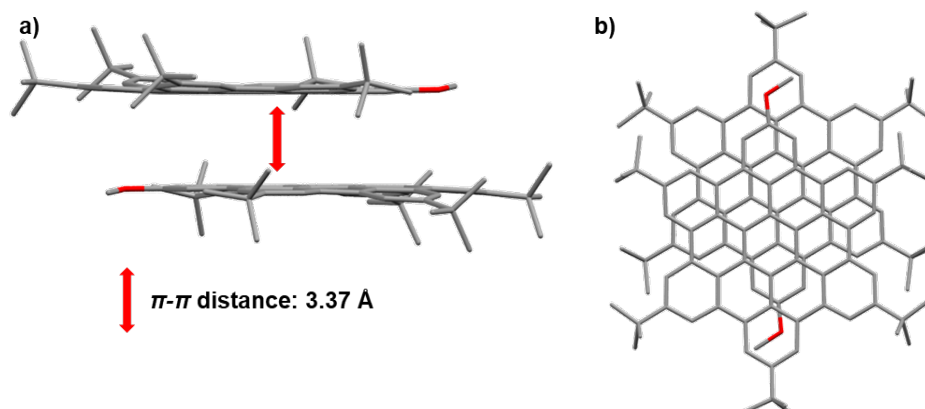
**Figure 4.** Cooperative CH/ $\pi$  interactions between two dimers of 1. CH/ $\pi$  distances around 2.9 Å are marked as this represents the sum of the van der Waals radii of carbon and hydrogen. The marked CH/ $\pi$  interactions are exemplarily for one inter-dimer binding. They occur in the same way between the other dimers as well.

## 2.2. X-ray data for methoxy-HBC 2

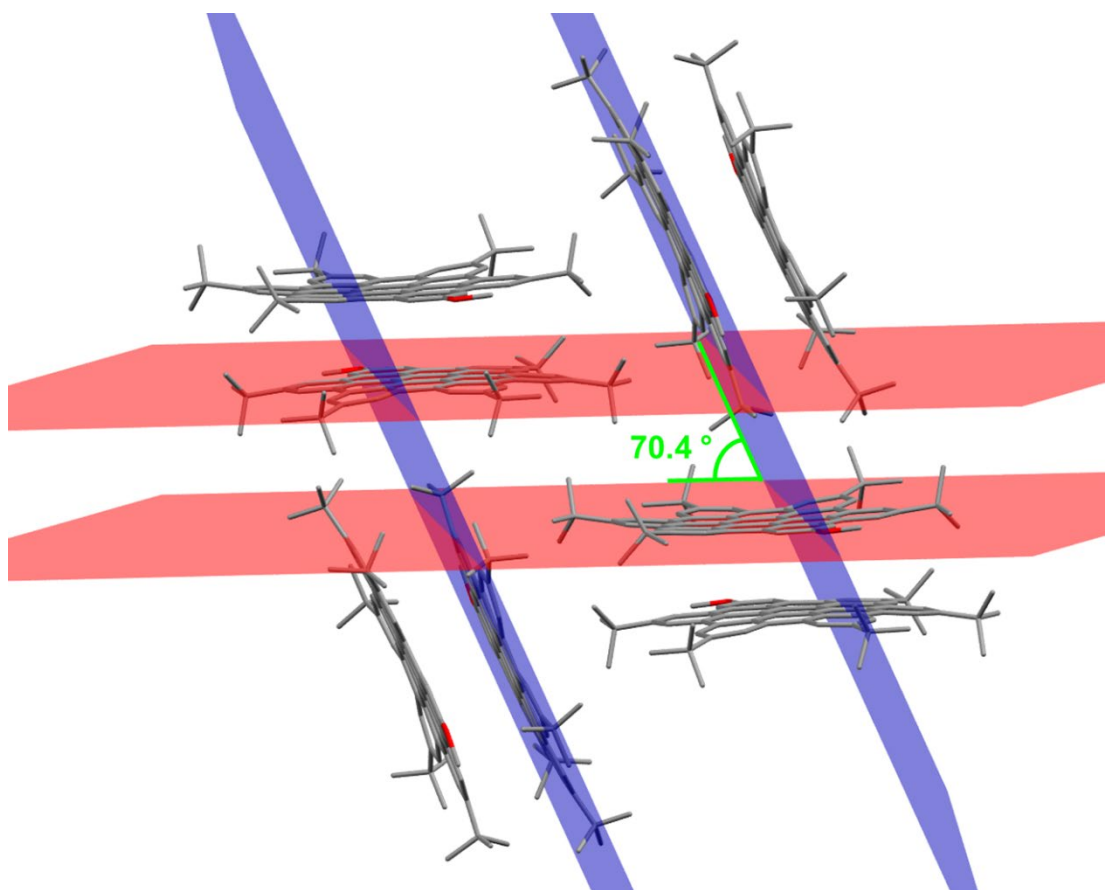
Single crystals of **2** were obtained by solvent diffusion from CH<sub>2</sub>Cl<sub>2</sub> with EtOH. A suitable crystal was selected and mounted on a loop on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 153.00(10) K during data collection. Using **Olex2**<sup>[S1]</sup>, the structure was solved with the **ShelXT**<sup>[S2]</sup> structure solution program using Intrinsic Phasing and refined with the **ShelXL**<sup>[S3]</sup> refinement package using Least Squares minimization.

**Table 2.** Crystal data and structure refinement for **2**.

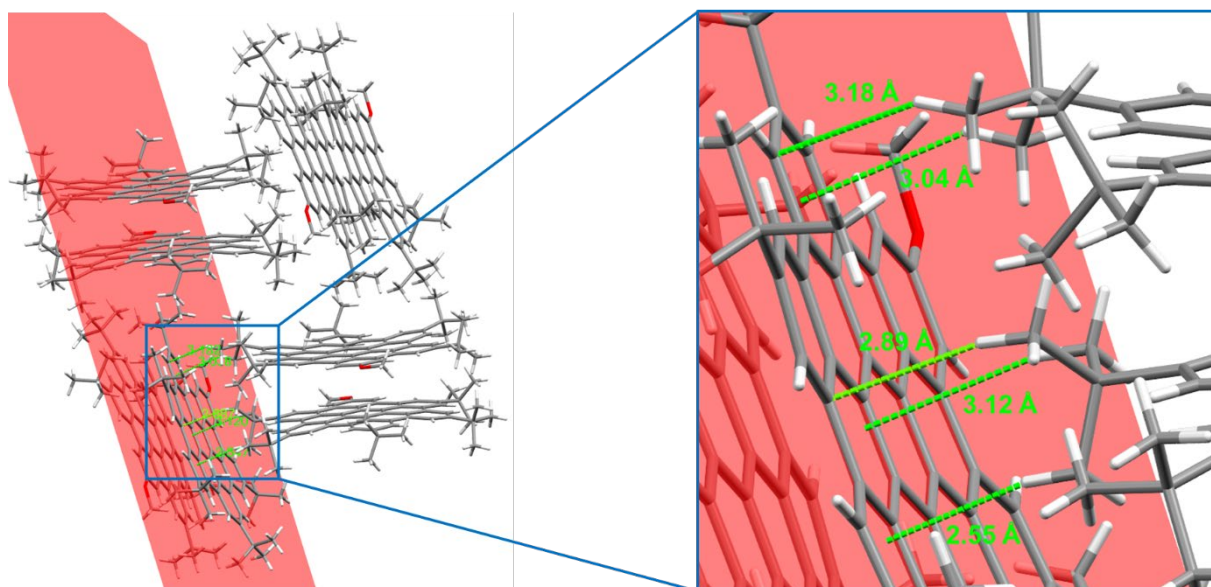
|   |   |
|---|---|
| Identification code                         | 18Jux DR07  |
| Empirical formula                           | C <sub>63</sub> H <sub>60</sub> O                             |
| Formula weight                              | 833.11  |
| Temperature/K                               | 153.00(10)  |
| Crystal system                              | monoclinic  |
| Space group                                 | P2 <sub>1</sub> /c  |
| a/Å   | 14.6195(2)  |
| b/Å   | 19.8826(3)  |
| c/Å   | 18.7072(3)  |
| α/°   | 90  |
| β/°   | 92.1010(10)   |
| γ/°   | 90  |
| Volume/Å <sup>3</sup>                       | 5434.04(14)   |
| Z   | 4   |
| ρ <sub>calc</sub> /cm <sup>3</sup>          | 1.018   |
| μ/mm <sup>-1</sup>                          | 0.442   |
| F(000)                                      | 1784.0  |
| Crystal size/mm <sup>3</sup>                | 0.228 × 0.192 × 0.079   |
| Radiation                                   | CuKα (λ = 1.54184)  |
| 2θ range for data collection/°              | 6.05 to 129.114   |
| Index ranges                                | -16 ≤ h ≤ 14, -17 ≤ k ≤ 22, -14 ≤ l ≤ 21                      |
| Reflections collected                       | 16372   |
| Independent reflections                     | 8763 [R <sub>int</sub> = 0.0211, R <sub>sigma</sub> = 0.0234] |
| Data/restraints/parameters                  | 8763/30/595   |
| Goodness-of-fit on F <sup>2</sup>           | 1.043   |
| Final R indexes [I ≥ 2σ (I)]                | R <sub>1</sub> = 0.0614, wR <sub>2</sub> = 0.1809             |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0764, wR <sub>2</sub> = 0.1963             |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.34/-0.34  |
| CCDC Deposition Number                      | 2055849   |



**Figure 5.** Dimer observed for **2**. a) Side view with  $\pi$ - $\pi$  distance between the two HBC planes; b) Top view of the dimer. Hydrogens are omitted for clarity.

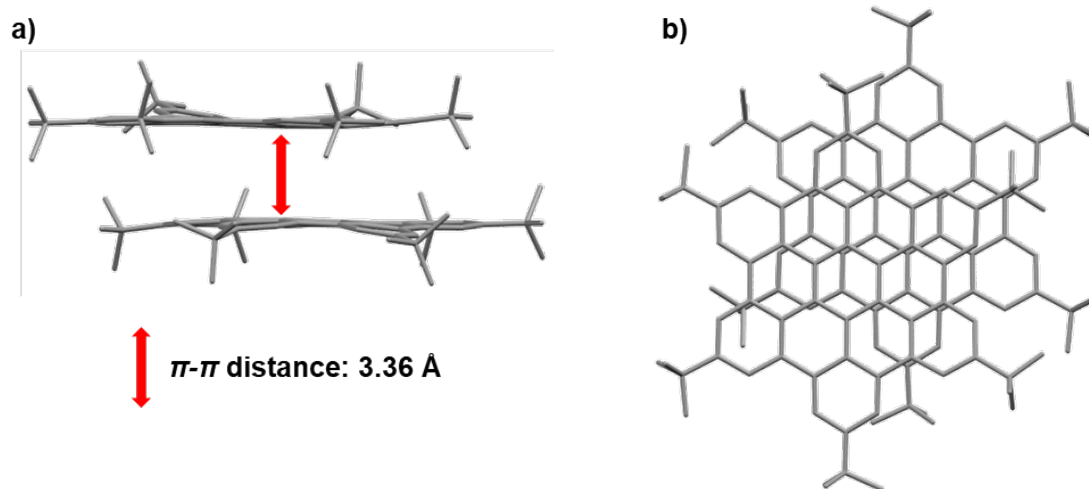


**Figure 6.** Angles between the dimers of **2**. Note that the two red planes and the two blue planes are parallel and therefore all acute angles are  $70.4^\circ$ . Hydrogens are omitted for clarity.

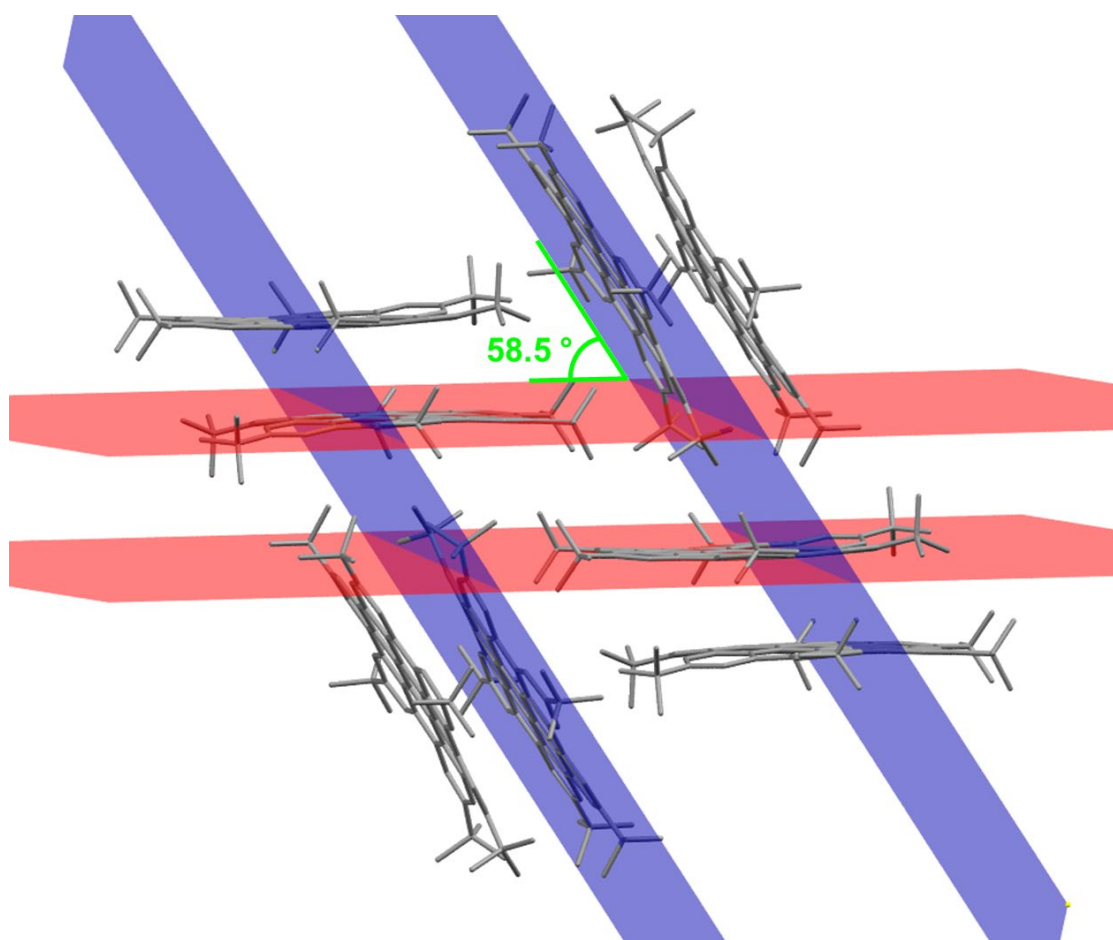


**Figure 7.** Cooperative CH/ $\pi$  interactions between two dimers of **2**. CH/ $\pi$  distances around 2.9 Å are marked as this represents the sum of the van der Waals radii of carbon and hydrogen. The marked CH/ $\pi$  interactions are exemplarily for one inter-dimer binding. They occur in the same way between the other dimers as well.

### 2.3. Reference hexa *tert*-butyl HBC<sup>[S4]</sup>

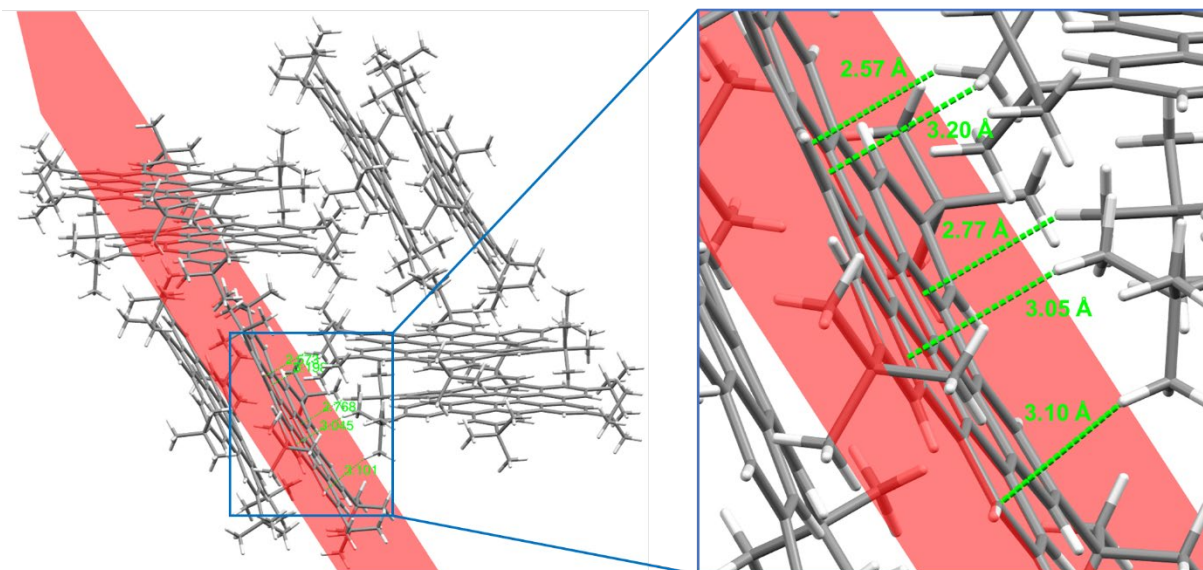


**Figure 8.** Dimer observed for hexa *tert*-butyl HBC reference. a) Side view with  $\pi$ - $\pi$  distance between the two HBC planes; b) Top view of the dimer. Hydrogens are omitted for clarity.



**Figure 9.** Angles between the dimers of the hexa *tert*-butyl HBC reference. Note that the two red planes and the two blue planes are parallel and therefore all acute angles are 58.5°. Hydrogens are omitted for clarity.





**Figure 10.** Cooperative CH/ $\pi$  interactions between two dimers of the hexa *tert*-butyl HBC reference. CH/ $\pi$  distances around 2.9 Å are marked as this represents the sum of the van der Waals radii of carbon and hydrogen. The marked CH/ $\pi$  interactions are exemplarily for one inter-dimer binding. They occur in the same way between the other dimers as well.

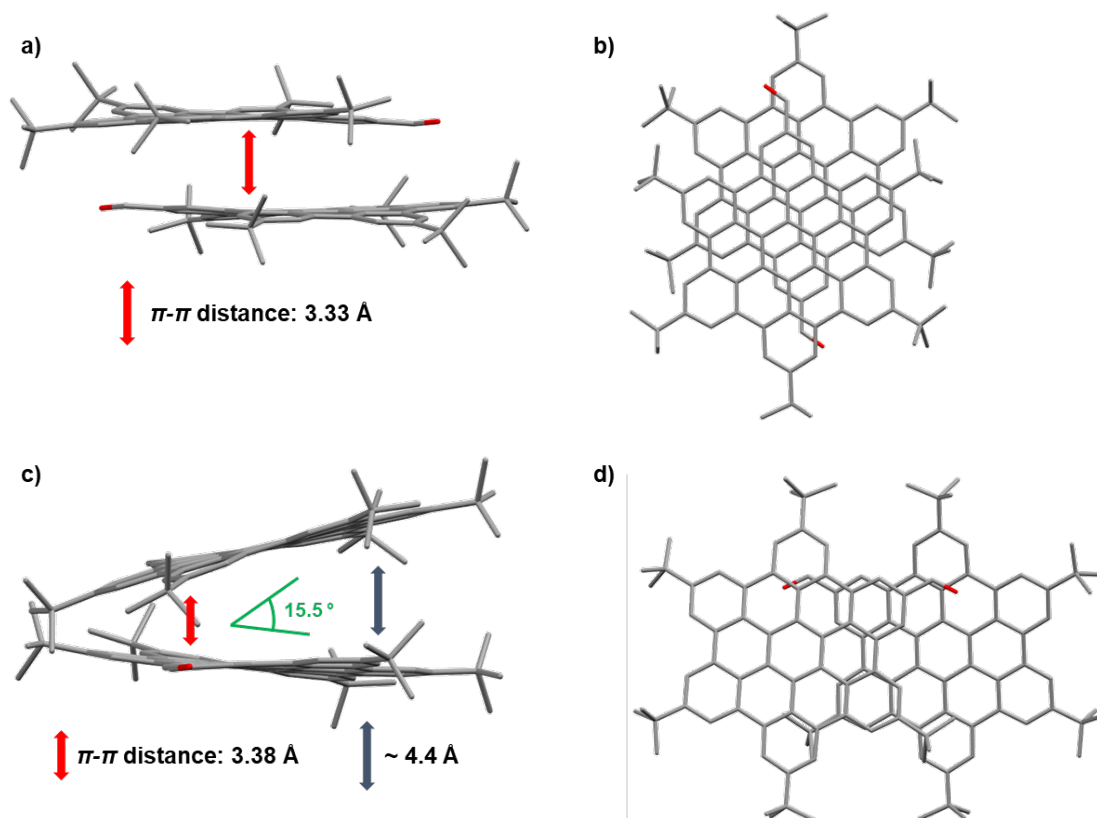
## 2.4. X-ray data for formyl-HBC 3

Single crystals of **3** were obtained by solvent diffusion from CH<sub>2</sub>Cl<sub>2</sub> with EtOH. A suitable crystal was selected and mounted on a loop on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 153.00(10) K during data collection. Using **Olex2**<sup>[S1]</sup>, the structure was solved with the **ShelXT**<sup>[S2]</sup> structure solution program using Intrinsic Phasing and refined with the **ShelXL**<sup>[S3]</sup> refinement package using Least Squares minimization.

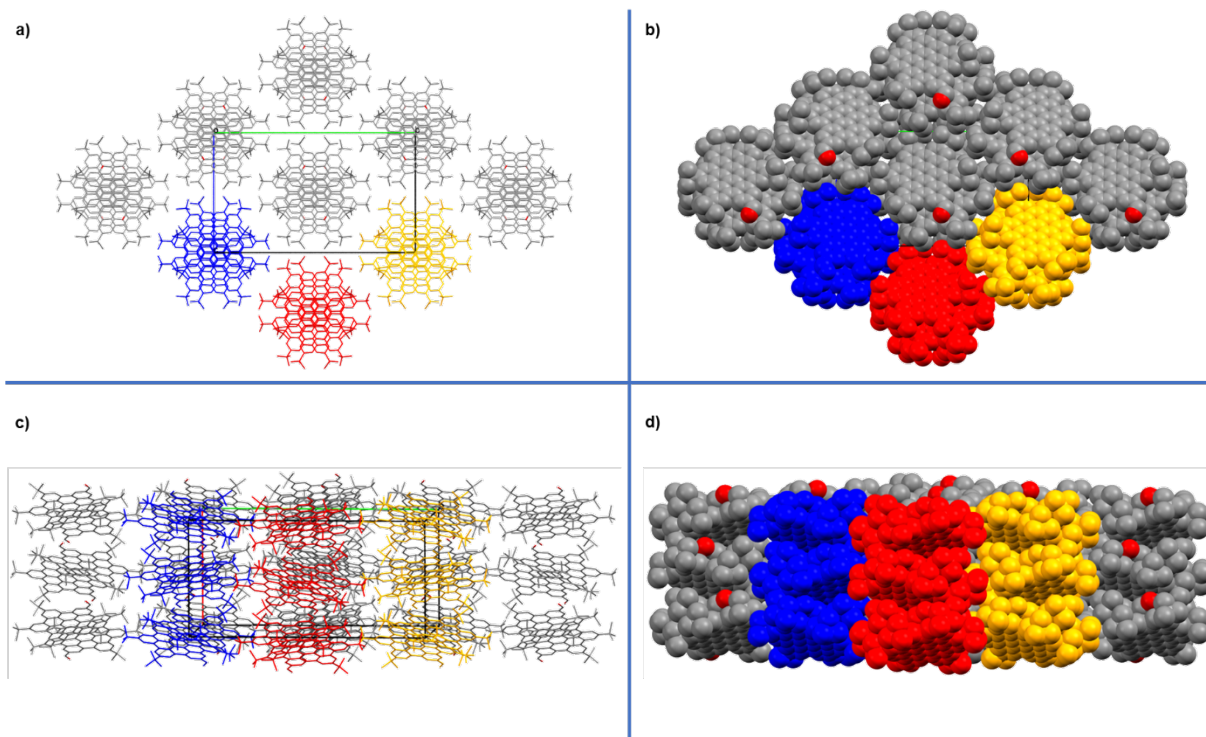
The selected crystals of **3** with an obvious lower quality showed very low diffraction intensities at higher diffraction angles, which by far did not improve the overall data set. Therefore, data collection was ended at a bit lower diffraction angles than usual. Nevertheless, this does not influence the quality of all non-hydrogen positions at all. Hydrogen positions were calculated in idealized positions anyway and will not get discussed.

**Table 3.** Crystal data and structure refinement for **3**.

|   |   |
|---|---|
| Identification code                         | 18Jux DR05 2  |
| Empirical formula                           | C <sub>63</sub> H <sub>58</sub> O                             |
| Formula weight                              | 831.09  |
| Temperature/K                               | 153.00(10)  |
| Crystal system                              | monoclinic  |
| Space group                                 | I2/a  |
| a/Å   | 16.1772(3)  |
| b/Å   | 32.8021(4)  |
| c/Å   | 19.5162(3)  |
| α/°   | 90  |
| β/°   | 90.802(2)   |
| γ/°   | 90  |
| Volume/Å <sup>3</sup>                       | 10355.2(3)  |
| Z   | 8   |
| ρ <sub>calc</sub> /cm <sup>3</sup>          | 1.066   |
| μ/mm <sup>-1</sup>                          | 0.464   |
| F(000)                                      | 3552.0  |
| Crystal size/mm <sup>3</sup>                | 0.387 × 0.28 × 0.197  |
| Radiation                                   | CuKα (λ = 1.54184)  |
| 2θ range for data collection/°              | 8.954 to 146.898  |
| Index ranges                                | -13 ≤ h ≤ 19, -40 ≤ k ≤ 21, -21 ≤ l ≤ 23                      |
| Reflections collected                       | 15159   |
| Independent reflections                     | 9338 [R <sub>int</sub> = 0.0205, R <sub>sigma</sub> = 0.0291] |
| Data/restraints/parameters                  | 9338/60/656   |
| Goodness-of-fit on F <sup>2</sup>           | 1.077   |
| Final R indexes [I ≥ 2σ (I)]                | R <sub>1</sub> = 0.0651, wR <sub>2</sub> = 0.2011             |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0749, wR <sub>2</sub> = 0.2124             |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.20/-0.36  |
| CCDC Deposition Number                      | 2055848   |



**Figure 11.** Dimers observed for **3**. a) Side view of dimer A with  $\pi$ - $\pi$  distance between the two HBC planes; b) Top view of the dimer A; c) Sideview of dimer B with  $\pi$ - $\pi$  distance between the two HBC planes. Note that the two HBC planes are not parallel here but in a V-shaped arrangement with an angle of  $15.5^\circ$ . Therefore, the  $\pi$ - $\pi$  distance is smaller on the side of the -CHO substituent; d) Top view of dimer B. Hydrogens are omitted for clarity.



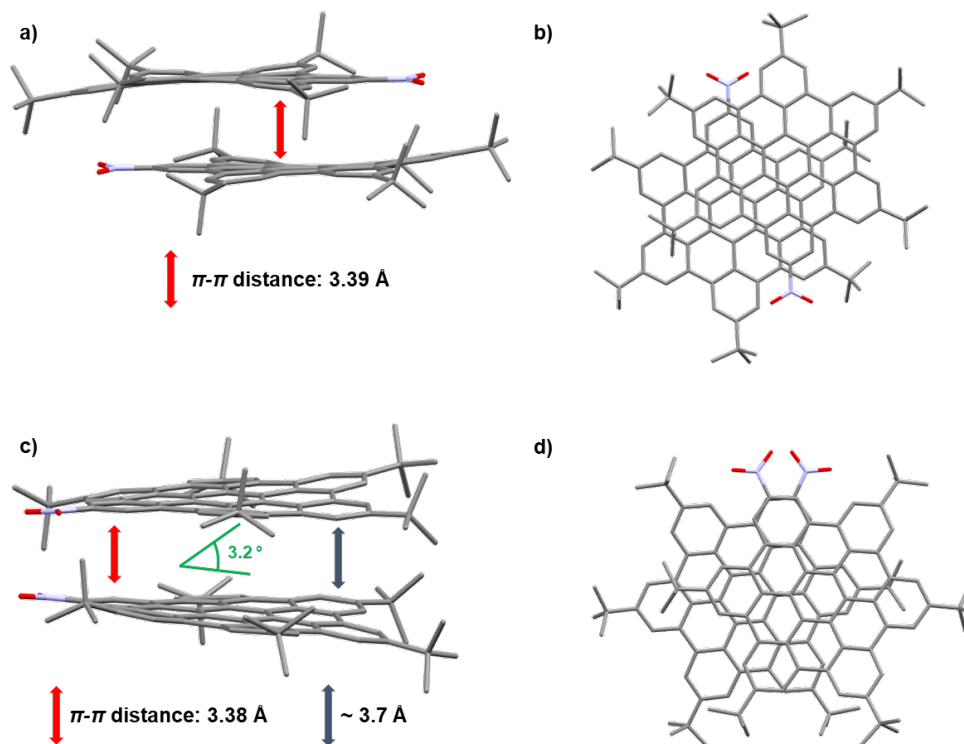
**Figure 12.** Larger view of the crystal packing of **3**. a) Top view of the stacks along crystallographic a-axis showing nicely the columns that are separated by their *tert*-butyl substituents; b) Top view of the stacks along crystallographic a-axis in a space-fill model showing the densely packed superstructure; c) Side view of the stacks along crystallographic c-axis (slightly shifted); d) Side view of the stacks along crystallographic c-axis (slightly shifted) in a space-fill model. Here the V-shaped gaps caused by the arrangement of dimer B are visible with the HBCs close enough for  $\pi$ - $\pi$  aggregation only on one side of the dimer. Hydrogen atoms are omitted for clarity.

## 2.5. X-ray data for nitro-HBC 4

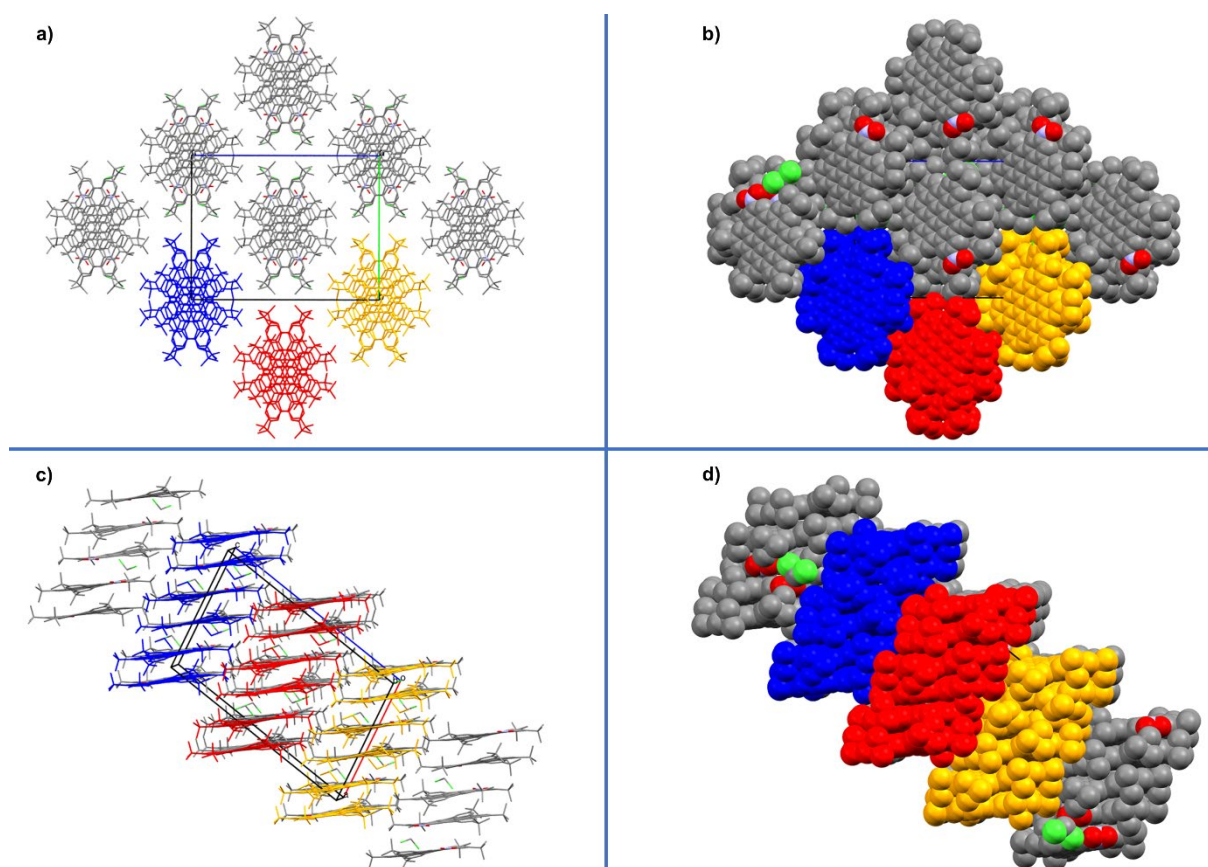
Single crystals of **4** were obtained by solvent diffusion from CH<sub>2</sub>Cl<sub>2</sub> with EtOH. A suitable crystal was selected and mounted on a loop on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 153.00(10) K during data collection. Using **Olex2**<sup>[S1]</sup>, the structure was solved with the **ShelXT**<sup>[S2]</sup> structure solution program using Intrinsic Phasing and refined with the **ShelXL**<sup>[S3]</sup> refinement package using Least Squares minimization.

**Table 4.** Crystal data and structure refinement for **4**.

|   |   |
|---|---|
| Identification code                         | 18Jux DR03  |
| Empirical formula                           | C <sub>63</sub> H <sub>59</sub> Cl <sub>2</sub> NO <sub>2</sub> |
| Formula weight                              | 933.01  |
| Temperature/K                               | 153.00(10)  |
| Crystal system                              | monoclinic  |
| Space group                                 | I2/a  |
| a/Å   | 17.0400(2)  |
| b/Å   | 20.8535(2)  |
| c/Å   | 27.8412(4)  |
| α/°   | 90  |
| β/°   | 102.6900(10)  |
| γ/°   | 90  |
| Volume/Å <sup>3</sup>                       | 9651.5(2)   |
| Z   | 8   |
| ρ <sub>calc</sub> /cm <sup>3</sup>          | 1.284   |
| μ/mm <sup>-1</sup>                          | 1.572   |
| F(000)                                      | 3952.0  |
| Crystal size/mm <sup>3</sup>                | 0.394 × 0.126 × 0.095   |
| Radiation                                   | CuKα (λ = 1.54184)  |
| 2θ range for data collection/°              | 6.8 to 129.21   |
| Index ranges                                | -19 ≤ h ≤ 17, -23 ≤ k ≤ 23, -32 ≤ l ≤ 32                        |
| Reflections collected                       | 26634   |
| Independent reflections                     | 7979 [R <sub>int</sub> = 0.0237, R <sub>sigma</sub> = 0.0181]   |
| Data/restraints/parameters                  | 7979/0/628  |
| Goodness-of-fit on F <sup>2</sup>           | 1.050   |
| Final R indexes [I >= 2σ (I)]               | R <sub>1</sub> = 0.0548, wR <sub>2</sub> = 0.1549               |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0606, wR <sub>2</sub> = 0.1621               |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.57/-0.57  |
| CCDC Deposition Number                      | 2055847   |

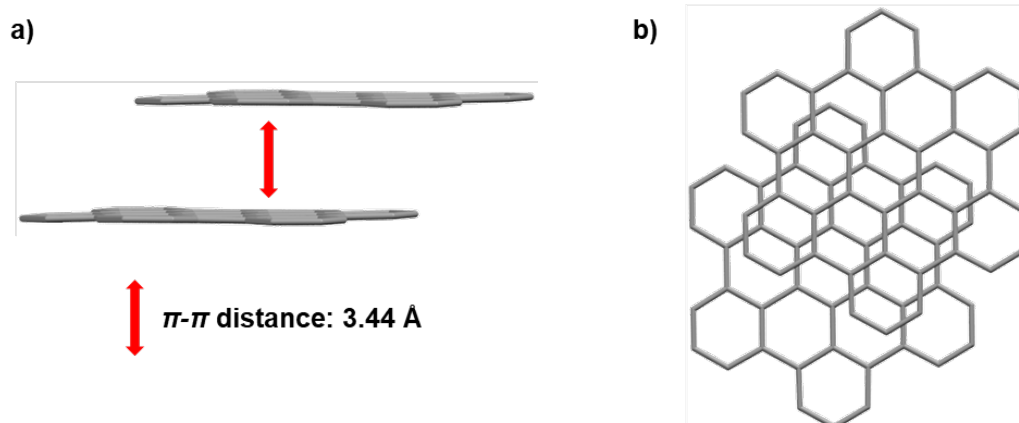


**Figure 13.** Dimers observed for **4**. a) Side view of dimer A with  $\pi$ - $\pi$  distance between the two HBC planes; b) Top view of the dimer A; c) Sideview of dimer B with  $\pi$ - $\pi$  distance between the two HBC planes. Note that the two HBC planes are not exactly parallel here but in a slightly V-shape arrangement with an angle of  $3.2^\circ$ . Therefore, the  $\pi$ - $\pi$  distance is smaller on the side of the  $-\text{NO}_2$  substituents; d) Top view of dimer B. Hydrogens are omitted for clarity.

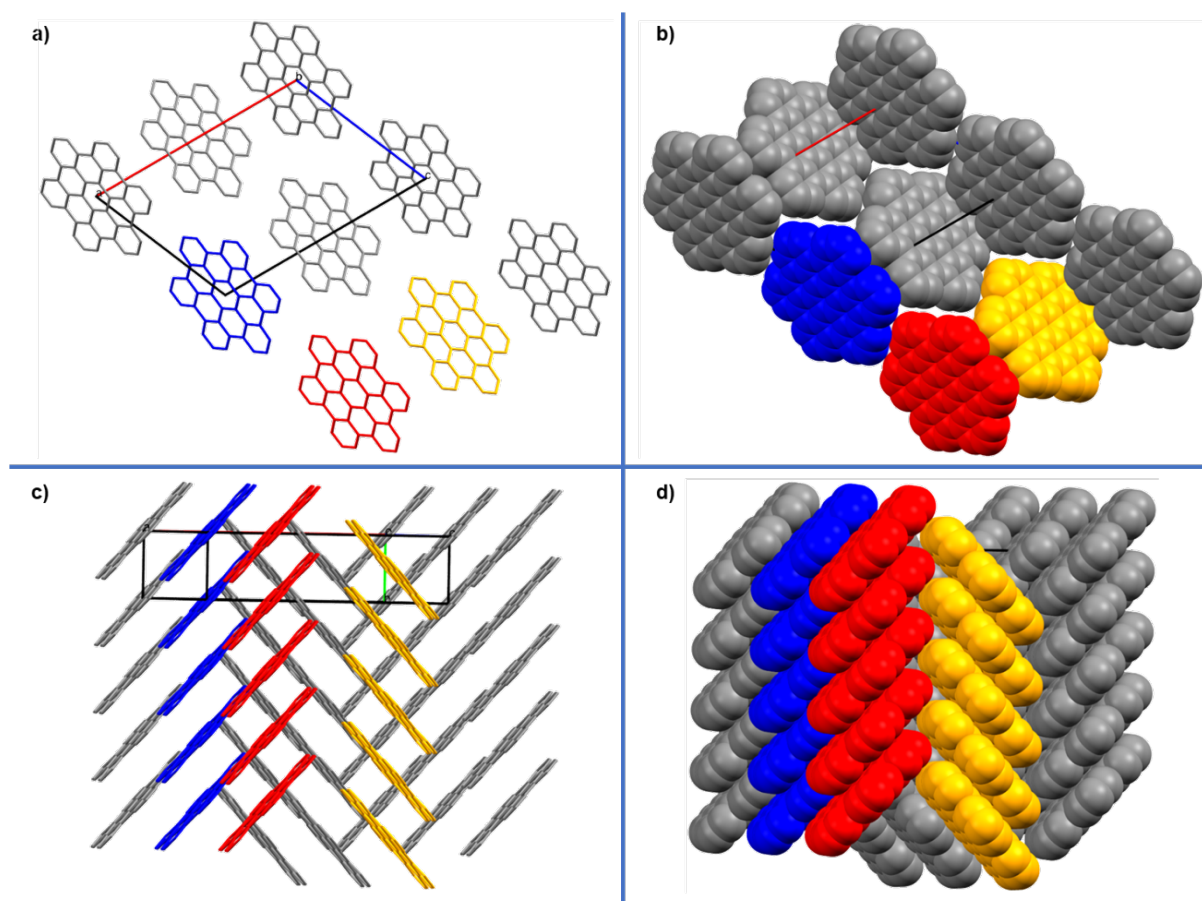


**Figure 14.** Larger view of the crystal packing of **4**. a) Top view of the stacks along crystallographic a-axis showing nicely the columns that are separated by their *tert*-butyl substituents; b) Top view of the stacks along crystallographic a-axis in a space-fill model showing the densely packed superstructure; c) Side view of the stacks along crystallographic c-axis (slightly shifted) showing the well-ordered columns; d) Side view of the stacks along crystallographic c-axis (slightly shifted) in a space-fill model. Here, all the HBCs are densely packed with tight  $\pi$ - $\pi$  aggregation. Hydrogen atoms are omitted for clarity. Green colored atoms belong to the  $\text{CH}_2\text{Cl}_2$  located between the *tert*-butyl groups at the rim of the columns.

## 2.6. Reference unsubstituted HBC<sup>[S5]</sup>



**Figure 15.** Dimer observed for unsubstituted HBC as a reference. a) Side view of the dimer with  $\pi$ - $\pi$  distance between the two HBC planes; b) Top view of the dimer. Hydrogens are omitted for clarity.



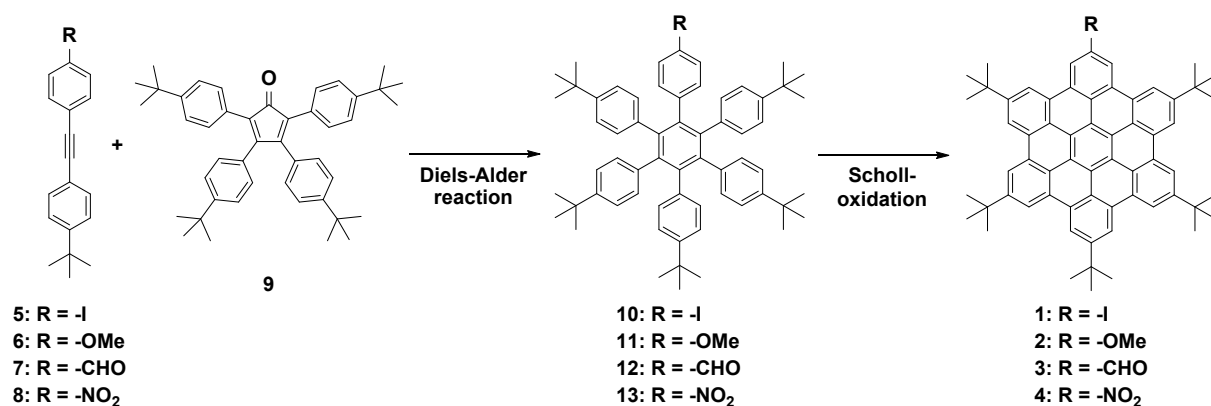
**Figure 16.** Larger view of the crystal packing of unsubstituted HBC as a reference. a) Top view of the stacks along crystallographic b-axis showing nicely the columns; b) Top view of the stacks along crystallographic b-axis in a space-fill model showing the densely packed superstructure; c) Side view of the stacks along crystallographic ac-plane showing the well-ordered columns that are arranged in a herringbone fashion; d) Side view of the stacks along crystallographic ac-plane in a space-fill model. All the HBCs are densely packed with tight  $\pi$ - $\pi$  aggregation. Hydrogen atoms and are omitted for clarity.

### 3. Synthesis

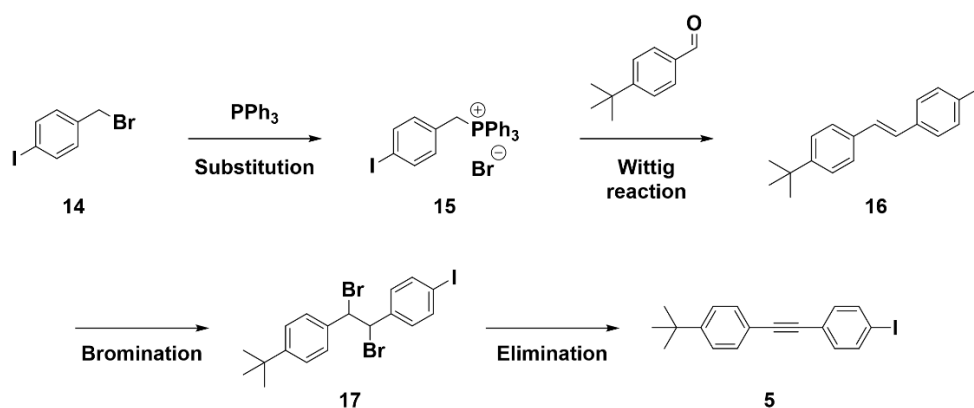
The material of compounds **2**<sup>[S6]</sup> and **4**<sup>[S7]</sup> stems from the same batches as in our previous publications. For synthetic details and spectra please see these publications. Compounds **1**<sup>[S8]</sup> and **3**<sup>[S7]</sup> were previously reported as well, either by our group or by others. However, the materials used in this study here stems from different batches. Therefore, we included the synthetic details and spectra.

Generally, the necessary diphenylacetylenes were synthesized via Sonogashira coupling followed by a Diels-Alder reaction with tetra-(4-*tert*-butylphenyl)cyclopentadienone **9**<sup>[S6]</sup> to obtain the corresponding hexaarylbenzenes derivatives (**10-13**). Those were then closed via Scholl oxidation to the HBC derivatives (**1-4**) (Scheme 1).

Diphenylacetylene precursor **5** was synthesised in different way as reported in the literature for this compound. To avoid the more common, statistical Sonogashira-coupling starting from 1,4-diiodobenzene and 4-*tert*-butylphenylacetylene we utilized a route known in the literature for other asymmetric diphenylacetylenes.<sup>[S9]</sup> A reaction sequence of a Wittig reaction, followed by bromination of the double bond and elimination of two times HBr to obtain the desired acetylene (Scheme 2) is used. As this route is non-statistical, multigram synthesis is easily possible. The synthesis of **5** in that way is not yet presented in the literature and the procedures are described here.

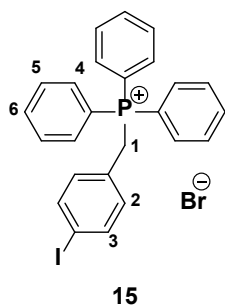


**Scheme 1.** General synthesis of HBC derivatives **1-4** from the corresponding diphenylacetylenes **5-8** and tetra-(4-*tert*-butylphenyl)cyclopentadienone **9** via hexaarylbenzenes derivatives **10-13**.



**Scheme 2.** Alternative synthesis of diphenylacetylene **5** via a reaction cascade including the synthesis of a phosphonium salt **15** for the Wittig reaction to obtain **16** followed by a bromination to **17** and elimination to obtain **5**.

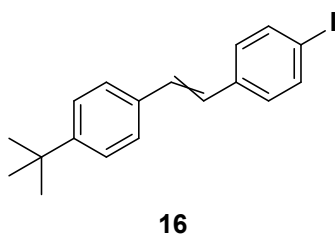
#### 4-Iodobenzyltriphenylphosphonium bromide **15**



A round-bottom flask (500 mL) equipped with a magnetic stirring bar and a reflux condenser was charged with 4-Iodobenzylbromide (14.8 g, 50.0 mmol) and toluene (200 mL). PPh<sub>3</sub> (14.4 g, 55.0 mmol) was added and the resulting solution was stirred for 18 h under reflux (heat-on set to 130 °C). During that time a white solid precipitated. The suspension was allowed to cool to rt. and the precipitate was filtered off through a glass-frit (P4). It was washed with hexanes (100 mL) and dried under vacuum. The product was obtained as a white solid in a yield of 99 % (27.8 g, 49.7 mmol). As **15** is already known in the literature<sup>[S10]</sup> its purity was only checked by <sup>1</sup>H NMR.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, rt.): δ[ppm] = 7.78 – 7.71 (m, 9H, 4,6), 7.61 – 7.56 (m, 6H, 5), 7.36 (dd, <sup>3</sup>J<sub>1H-1H</sub> = 8.4 Hz, <sup>5</sup>J<sub>1H-31P</sub> = 0.8 Hz, 2H, 3), 6.92 (dd, <sup>3</sup>J<sub>1H-1H</sub> = 8.4 Hz, <sup>4</sup>J<sub>1H-31P</sub> = 2.6 Hz, 2H, 2), 5.55 (d, <sup>2</sup>J<sub>1H-31P</sub> = 14.8 Hz, 2H, 1).

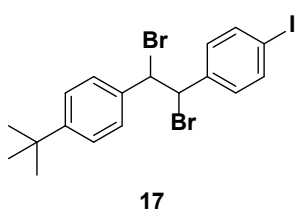
#### 4-Iodo-4'-*tert*-butyl stilbene (E/Z mixture) **16**



A round-bottom Schlenk-flask (500 mL) equipped with a magnetic stirring bar and a reflux condenser was flame dried under vacuum and subsequently charged with **15** (25.2 g, 45 mmol) and dry THF (120 mL). The suspension was degassed via ultrasound + vacuum (4 x 1 min)/N<sub>2</sub> cycles. It was cooled to 0 °C and KOtBu (5.89 g, 52.5 mmol) was added in 5 portions. The cooling was removed, and the mixture was stirred for 1 h at 80 °C. The now deeply orange suspension was allowed to cool to rt. again and 4-*tert*-butylbenzaldehyde (6.08 g, 6.27 mL, 37.5 mmol) was added. The reaction mixture was again stirred for 1 h at 80 °C. After cooling to rt. EtOAc (100 mL) and H<sub>2</sub>O (150 mL) were added, the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 100 mL). The combined organic phases were washed with brine (2 x 50 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvents the crude product was first filtered over a pad of silica gel with hexanes/CH<sub>2</sub>Cl<sub>2</sub> 2/1 and again over short silica gel column with pure CH<sub>2</sub>Cl<sub>2</sub> to remove some remaining baseline impurities. All fractions containing the products (E and Z isomer!) were collected. The solvents were evaporated, and remaining solids were dried under vacuum. 14.5 g, 40.0 mmol of product were obtained which still contained some impurities according to NMR spectroscopy (No yield determined). Despite the small impurities the products were used without further purification. E and Z isomers were not separated as this is not necessary for the following reactions. The product was only characterized by <sup>1</sup>H NMR spectroscopy and as it is an E/Z product mixture the peaks are just listed without assignment. For a detailed characterization see literature.<sup>[S10]</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, rt.): δ[ppm] = 7.68 (d, <sup>3</sup>J = 8.4 Hz), 7.58 – 7.55 (m), 7.45 (d, <sup>3</sup>J = 8.4 Hz), 7.40 (d, <sup>3</sup>J = 8.4 Hz), 7.27 – 7.24 (m), 7.18 (d, <sup>3</sup>J = 8.3 Hz), 7.10 (d, <sup>3</sup>J = 16.3 Hz), 7.04 – 7.00 (m), 6.96 – 6.92 (m), 6.59 (d, <sup>3</sup>J = 12.9 Hz), 6.46 (d, <sup>3</sup>J = 12.2 Hz), 1.35 (s), 1.31 (s).

#### 1-(4-*tert*-butylphenyl)-1-bromo-2-(4-iodophenyl)-2-bromoethane (Isomeric mixture) **17**



A round-bottom flask (250 mL) equipped with a magnetic stirring bar and a dropping funnel was charged with **16** (14.5 g, 40.0 mmol) and CHCl<sub>3</sub> (100 mL). The solution was cooled to 0 °C. The dropping funnel was charged with Br<sub>2</sub> (7.03 g, 2.25 mL, 44.0 mmol) dissolved in CHCl<sub>3</sub> (44 mL). The Br<sub>2</sub> solution was added dropwise over 40 min. After complete addition the cooling was removed and the orange suspension was stirred for additional 15 min at rt. The reaction mixture was quenched with 10 % aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> x 5 H<sub>2</sub>O (100 mL) and stirred until the mixture turned colorless. H<sub>2</sub>O (50 mL) and CH<sub>2</sub>Cl<sub>2</sub> (50 mL) were added and the phases were separated. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 50 mL), the combined

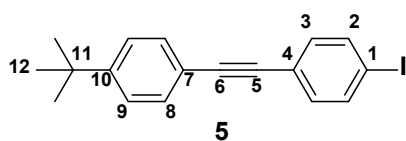


organic phases were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvents the product was dried under vacuum and obtained as a white solid in a yield of 97 % (20.2 g, 38.7 mmol). For **17** the isomers were not separated as it is not necessary for the following elimination reaction. The mixture was only characterized by <sup>1</sup>H NMR spectroscopy.

The product was only characterized by <sup>1</sup>H NMR spectroscopy and as it is mixture of enantiomers the peaks are just listed without assignment.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, rt.): δ[ppm] = 7.78 (d, <sup>3</sup>J = 8.5 Hz), 7.55 (d, <sup>3</sup>J = 8.5 Hz), 7.45 – 7.45 (m), 7.29 (d, <sup>3</sup>J = 8.5 Hz), 7.24 (d, <sup>3</sup>J = 8.5 Hz), 7.13 (d, <sup>3</sup>J = 8.5 Hz), 6.99 (d, <sup>3</sup>J = 8.5 Hz), 5.48 (s), 1.35 (s), 1.26 (s).

#### 4-iodo-4'-tert-butyl diphenylacetylene **5**



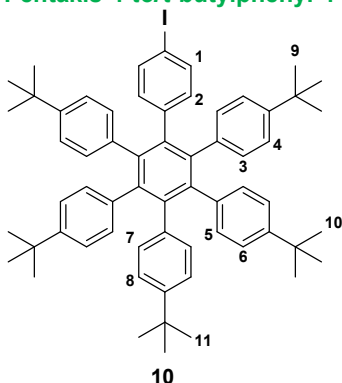
A round-bottom flask (500 mL) equipped with a magnetic stirring bar was charged with **17** (20.2 g, 38.7 mmol) and THF (390 mL). The solution was cooled to 0 °C and KO<sup>t</sup>Bu (13.0 g, 0.12 mol) was added in 7 portions over 35 min. After complete addition the cooling was removed and the reaction

mixture was stirred for further 15 min at rt. H<sub>2</sub>O (100 mL), Et<sub>2</sub>O (50 mL) and brine (50 mL) were added, and the phases were separated. The aqueous phase was extracted with Et<sub>2</sub>O (5 x 50 mL), the combined organic phases were washed with brine (100 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvents a brownish solid was obtained. The solid was suspended in refluxing pentane (60 mL). The suspension was cooled in the fridge to ~6 °C and filtered off through a glass-frit (P4). The product was dried under vacuum and obtained as an off-white solid in a yield of 79 % (11.0 g, 30.5 mmol).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, rt.): δ[ppm] = 7.68 (d, <sup>3</sup>J = 8.4 Hz, 2H, 2), 7.46 (d, <sup>3</sup>J = 8.5 Hz, 2H, 8), 7.37 (d, <sup>3</sup>J = 8.5 Hz, 2H, 9), 7.25 (d, <sup>3</sup>J = 8.5 Hz, 2H, 3), 1.33 (s, 9H, 12).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, rt.): δ[ppm] = 151.8 (10), 137.4, 133.1, 131.3, 125.4 (2,3,8,9), 123.0, 119.8 (4,7), 93.8, 91.0, 87.8 (1,5,6), 34.8 (11), 31.1 (12).

#### Pentakis-4-tert-butylphenyl-4-iodo-HAB **10**



A round-bottom pressure-flask (100 mL) equipped with a magnetic stirring bar was charged with **5** (1.08 g, 3.00 mmol), **9** (1.83 g, 3.00 mmol) and toluene (9.00 mL). The reaction mixture was purged with N<sub>2</sub> and the flask was closed. The reaction mixture was stirred for 30 h at 220 °C. After cooling to room temperature, upon stirring MeOH (30 mL) was added to the brownish mixture and a white solid precipitated. The suspension was placed in the fridge for 1 h and the white solid was filtered off through a glass frit (P4) and washed with an excess of MeOH. The remaining solid was dried under vacuum. The product was obtained as a white solid in a yield of 83 % (2.34 g, 2.49 mmol).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, rt.): 7.16 (d, <sup>3</sup>J = 8.4 Hz, 2H, 2), 6.86-6.79 (m, 10H, 3,4,5,6,7,8), 6.68-6.63 (m, 10H, 3,4,5,6,7,8), 6.59 (d, <sup>3</sup>J = 8.4 Hz, 2H, 3), 1.13 (s, 18H, 9,10,11), 1.10 (s, 27H, 9,10,11).

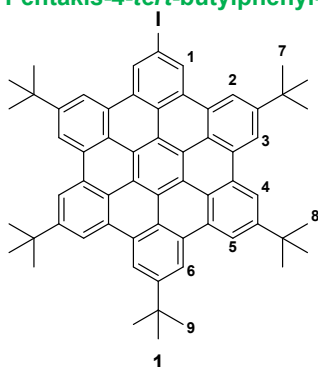
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, rt.): 147.8, 147.5, 147.4, 140.83, 140.78, 140.7, 140.0, 138.5, 137.73, 137.69, 137.5, 135.5, 133.6, 131.02, 130.96, 129.0, 128.2, 125.3, 123.4, 123.1, 123.0, 90.6, 34.1, 34.0, 31.20, 31.17.

HRMS (APPI, toluene): m/z (calculated for C<sub>62</sub>H<sub>69</sub>I): 940.4439

m/z (measured): 940.4433

error [ppm]: 0.6

#### Pentakis-4-*tert*-butylphenyl-4-iodo-HBC 1



A round-bottom Schlenk-flask (250 mL) equipped with a magnetic stirring bar was charged with **10** (0.58 g, 0.62 mmol), 7 eq. DDQ (0.99 g, 4.34 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (160 mL). The yellow suspension was degassed via N<sub>2</sub> bubbling for 15 min and meanwhile cooled to -20 °C. 14 eq. Triflic acid (1.30 g, 0.76 mL, 8.68 mmol) was added over 1 min. The reaction mixture was stirred for 2.5 h at -20 °C and then quenched with MeOH (100 mL). All solvents were evaporated, the remaining solids were taken up in CH<sub>2</sub>Cl<sub>2</sub>/hexanes 1/1 and filtered over a pad of silica gel. The obtained yellow solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and reprecipitated by addition of MeOH (40 mL). The suspension was cooled in the fridge for complete

precipitation. The solids were filtered off through a glass-frit (P4), washed with an excess of MeOH and dried under vacuum. The product was obtained as a yellow solid in a yield of 76 % (0.44 g, 0.47 mmol).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, rt.):** 9.18 (s, 2H, 1,2,3,4,5,6), 9.12 (s, 2H, 1,2,3,4,5,6), 9.05 (s, 2H, 1,2,3,4,5,6), 8.94 (s, 2H, 1,2,3,4,5,6), 8.85 (s, 2H, 1,2,3,4,5,6), 8.68 (s, 2H, 1,2,3,4,5,6), 1.93 (s, 9H, 9), 1.89 (s, 18H, 7,8), 1.80 (s, 18H, 7,8).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, rt.):** 148.5, 148.32, 148.25, 131.8, 130.2, 129.91, 129.87, 129.63, 129.55, 128.2, 123.2, 123.0, 119.7, 119.0, 118.8, 118.7, 118.5, 35.8, 35.7, 35.6, 32.20, 32.16, 32.1.

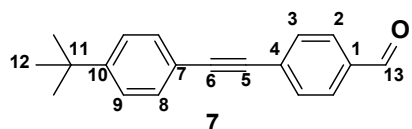
**MS (MALDI, dctb):** m/z (relative intensity) = 928 [M<sup>+</sup>] (100 %)

**HRMS (MALDI, dctb):** m/z (calculated for C<sub>62</sub>H<sub>57</sub>I): 928.3500

m/z (measured): 928.3517

error [ppm]: 1.9

#### 4-formyl-4'-*tert*-butyl diphenylacetylene 7



A round-bottom Schlenk-flask (250 mL) equipped with a magnetic stirring bar and a reflux condenser was charged with 4-bromobenzaldehyde (2.78 g, 15.0 mmol), 2 mol% Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.21 g, 0.30 mmol), 1 mol% CuI (28.6 mg, 0.15 mmol), THF (50 mL) and NEt<sub>3</sub> (50 mL). The mixture

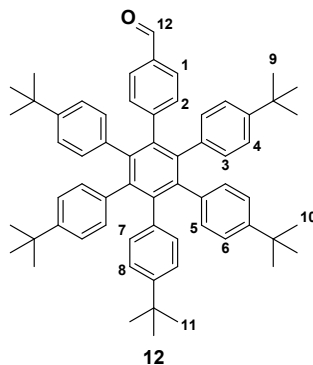
was degassed by N<sub>2</sub> bubbling for 20 min and finally 4-*tert*-butylphenylacetylene (2.50 g, 2.85 mL, 15.8 mmol) was added. The reaction mixture was stirred for 18 h at 80 °C. All solvents were evaporated and the crude product were filtered over a pad of silica gel with CH<sub>2</sub>Cl<sub>2</sub>/hexanes 3/2. The product was than purified via column chromatography over silica gel with CH<sub>2</sub>Cl<sub>2</sub>/hexanes 2/3. A brownish solid was obtained which was recrystallized from hexanes. The product was obtained as a off white solid and was dried under vacuum. The product was obtained in a yield of 73 % (2.87 g, 10.9 mmol).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, rt.):** 10.02 (s, 1H, 13), 7.86 (d, <sup>3</sup>J = 8.4 Hz, 2H, 2), 7.67 (d, <sup>3</sup>J = 8.2 Hz, 2H, 3), 7.49 (d, <sup>3</sup>J = 8.6 Hz, 2H, 8), 7.40 (d, <sup>3</sup>J = 8.6 Hz, 2H, 9), 1.34 (s, 9H, 12).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, rt.):** 191.4 (13), 152.4 (10), 135.3 (1,4,7), 132.0 (2,3,8,9), 131.5 (2,3,8,9), 129.9 (1,4,7), 129.6 (2,3,8,9), 125.5 (2,3,8,9), 119.4 (1,4,7), 93.8, 88.0 (5,6), 34.9 (11), 31.1 (12).

**HRMS (APPI, toluene):** m/z (calculated for C<sub>19</sub>H<sub>18</sub>O): 262.1352  
m/z (measured): 262.1355  
error [ppm]: -1.0

#### Pentakis-4-*tert*-butylphenyl-4-formyl-HAB 12



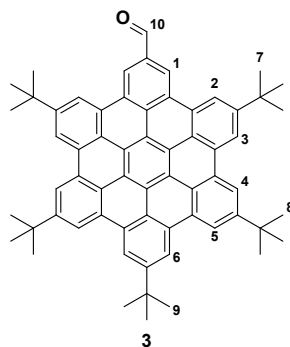
A round-bottom pressure-flask (250 mL) equipped with a magnetic stirring bar was charged with **7** (1.31 g, 5.00 mmol), **9** (3.04 g, 5.00 mmol) and toluene (15 mL). The dark suspension was purged with N<sub>2</sub> and the flask was closed. The reaction mixture was stirred for 24 h at 220 °C. After cooling to room temperature, MeOH (50 mL) was added and a white solid precipitated. The suspension was placed in the fridge for complete precipitation. All solids were filtered off through a glass-frit (P4) and washed with an excess of MeOH. As the product was not pure yet, the solids were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and reprecipitated by addition of MeOH (100 mL). The suspension was cooled in the fridge for 1 h, the solids were filtered off through a glass-frit (P4), washed with an excess of MeOH and dried under vacuum. The product was obtained as a white solid in a yield of 79 % (3.32 g, 3.94 mmol).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, rt.):** 9.76 (s, 1H, 12), 7.37 (d, <sup>3</sup>J = 8.3 Hz, 1), 7.03 (d, <sup>3</sup>J = 8.1 Hz, 2), 6.83-6.80 (m, 10H, 3,4,5,6,7,8), 6.69-6.64 (m, 10H, 3,4,5,6,7,8), 1.10 (s, 45H, 9,10,11).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, rt.):** 191.4, 148.5, 148.1, 147.61, 147.57, 141.2, 140.8, 139.9, 138.6, 137.62, 137.51, 137.3, 133.1, 132.3, 131.00, 130.96, 128.00, 123.4, 123.11, 123.09, 34.10, 34.05, 34.04, 31.17, 31.15.

**HRMS (APPI, toluene):** m/z (calculated for C<sub>63</sub>H<sub>70</sub>O): 842.5421  
m/z (measured): 842.5423  
error [ppm]: -0.2

#### Pentakis-4-*tert*-butylphenyl-4-formyl-HBC 3



A round-bottom Schlenk-flask (500 mL) equipped with a magnetic stirring bar was charged with **12** (0.51 g, 0.60 mmol). The precursor was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (360 mL) and the solution was degassed via N<sub>2</sub> bubbling for 40 min and meanwhile cooled to 0 °C. 16 eq. FeCl<sub>3</sub> (1.56 g, 9.60 mmol), dissolved in MeNO<sub>2</sub> (5.20 g) was added over 25 min. During that time and for further 45 min the cooling and N<sub>2</sub> bubbling were continued. N<sub>2</sub> bubbling and cooling were stopped and the reaction mixture was stirred for further 18 h at room temperature. The reaction mixture was quenched with MeOH (200 mL), all solvents were evaporated and the crude product was purified via column chromatography over silica gel with CH<sub>2</sub>Cl<sub>2</sub>/hexanes 1/1. For complete purification the obtained solids were dissolved in CH<sub>2</sub>Cl<sub>2</sub> and reprecipitated by addition of MeOH (100 mL). The suspension was cooled in the fridge for 30 min, the solids were filtered off through a glass-frit (P4) and dried under vacuum. The product was obtained as a yellow solid in a yield of 62 % (0.31 g, 0.37 mmol).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, rt.):** 10.12 (s, 1H, 10), 9.25 (s, 1,2,3,4,5,6), 9.19 (s, 1,2,3,4,5,6), 9.04 (s, 1,2,3,4,5,6), 8.90 (s, 1,2,3,4,5,6), 8.71 (s, 1,2,3,4,5,6), 8.62 (s, 1,2,3,4,5,6), 1.94 (s, 9), 1.88 (s, 7,8), 1.69 (s, 7,8).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, rt.):** 192.3, 149.1, 148.6, 148.4, 132.4, 130.5, 130.1, 130.0, 129.8, 129.6, 129.0, 128.5, 123.4, 123.2, 122.9, 121.2, 121.0, 120.6, 119.8, 118.88, 118.85, 118.8, 118.64, 118.62, 35.8, 35.7, 35.5, 32.1, 32.0.

**MS (MALDI, dctb):** m/z (relative intensity) = 830 [M<sup>+</sup>] (100 %)

**HRMS (LDI):** m/z (calculated for C<sub>63</sub>H<sub>56</sub>O): 830.4482  
m/z (measured): 830.4484  
error [ppm]: 0.2

## 4. Measurement data

### 4-Iodobenzyltriphenylphosphonium bromide 15

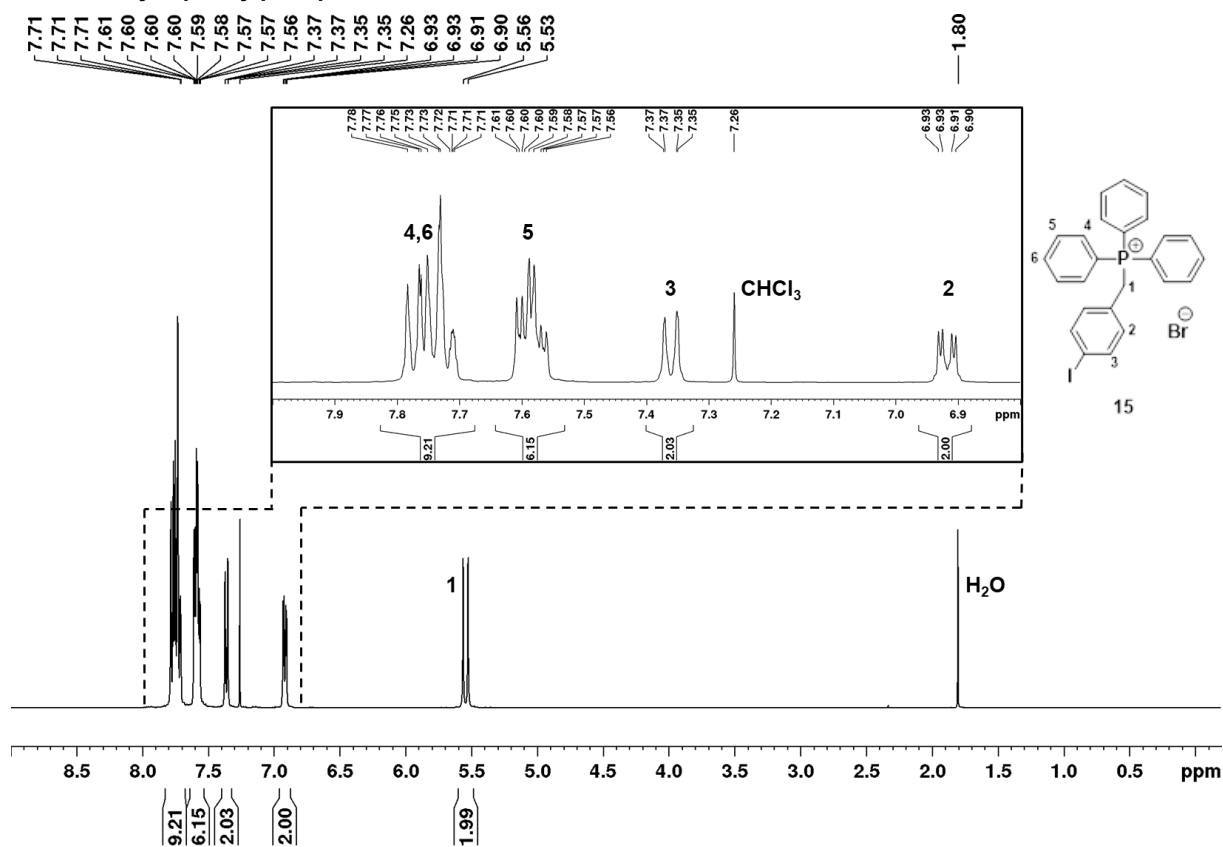


Figure 17. <sup>1</sup>H NMR spectrum of 15 (CDCl<sub>3</sub>, 400 MHz, rt.).

### 4-Iodo-4'-tert-butyl stilbene (E/Z mixture) 16

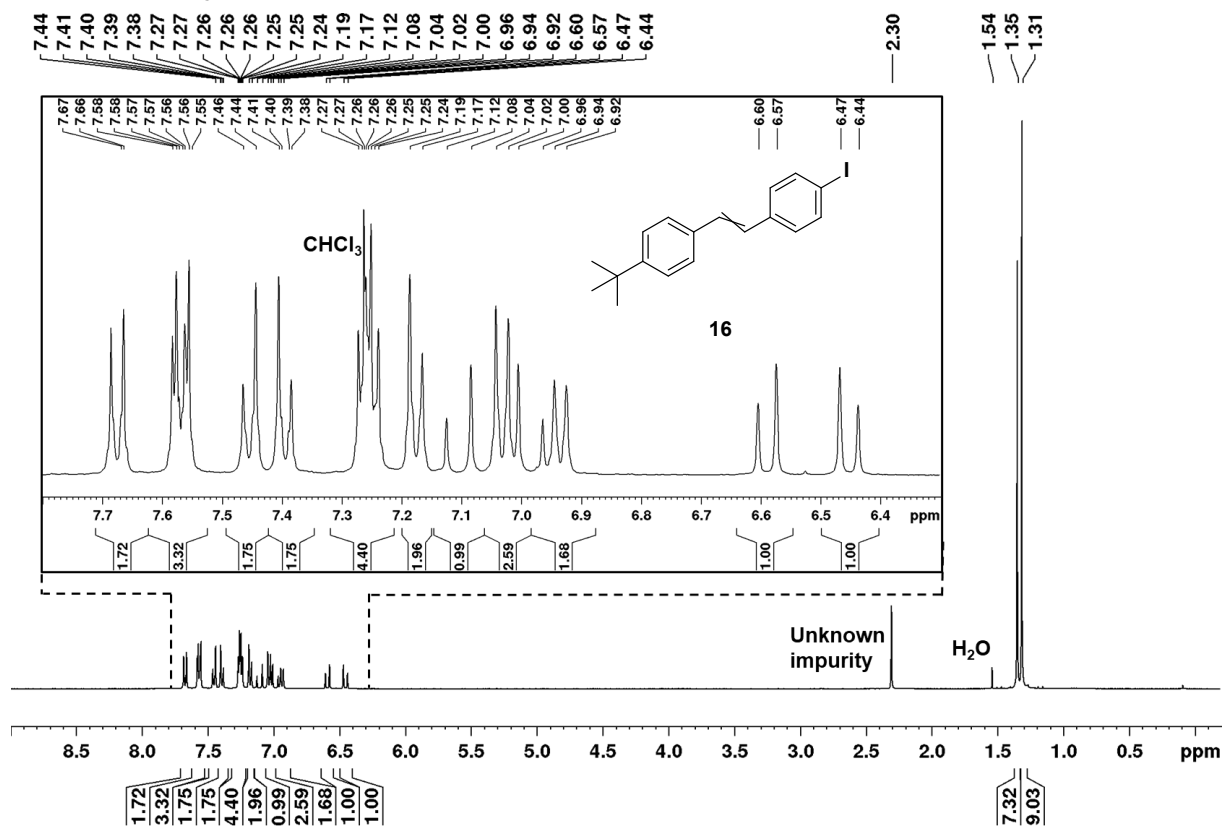


Figure 18. <sup>1</sup>H NMR spectrum of 16 (CDCl<sub>3</sub>, 400 MHz, rt.).

1-(4-*tert*-butylphenyl)-1-bromo-2-(4-iodophenyl)-2-bromoethane (Isomeric mixture) 17

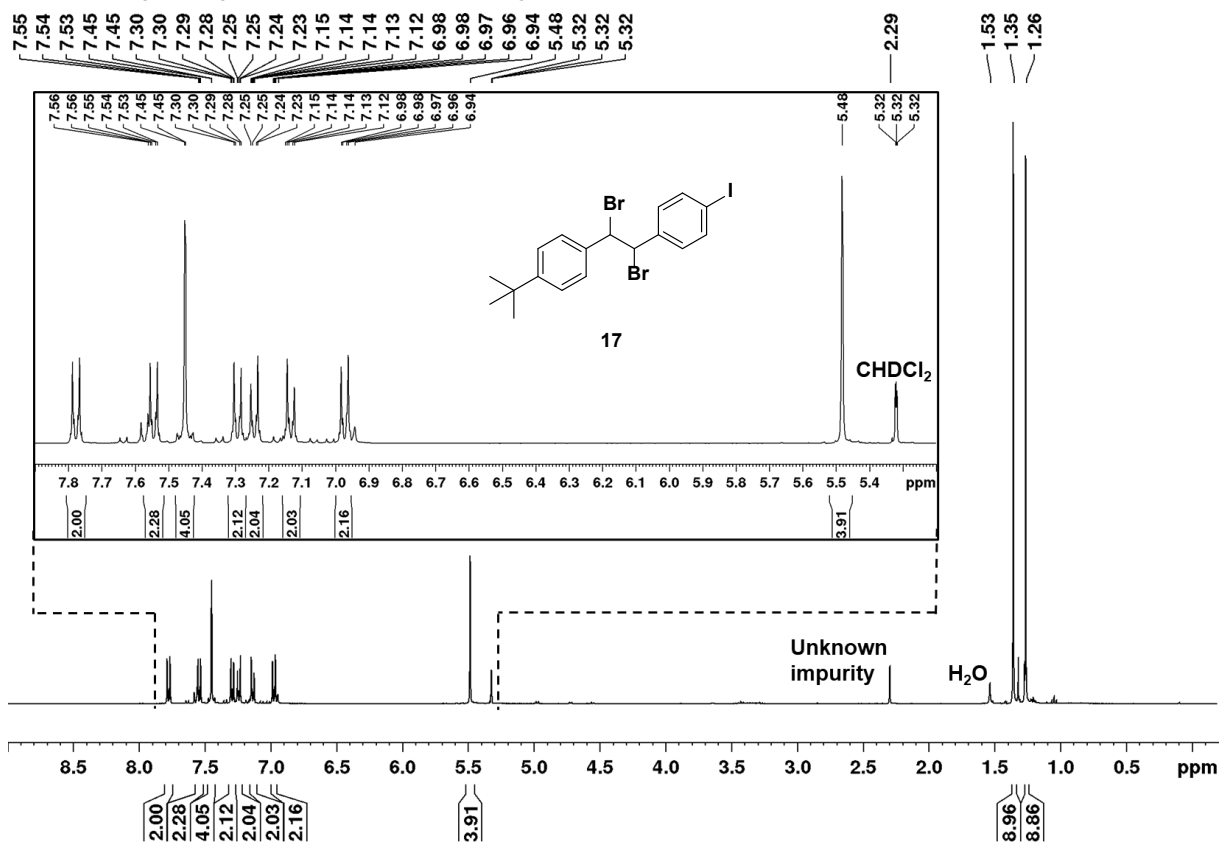


Figure 19. <sup>1</sup>H NMR spectrum of 17 (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, rt.).

4-iodo-4'-*tert*-butyl diphenylacetylene 5

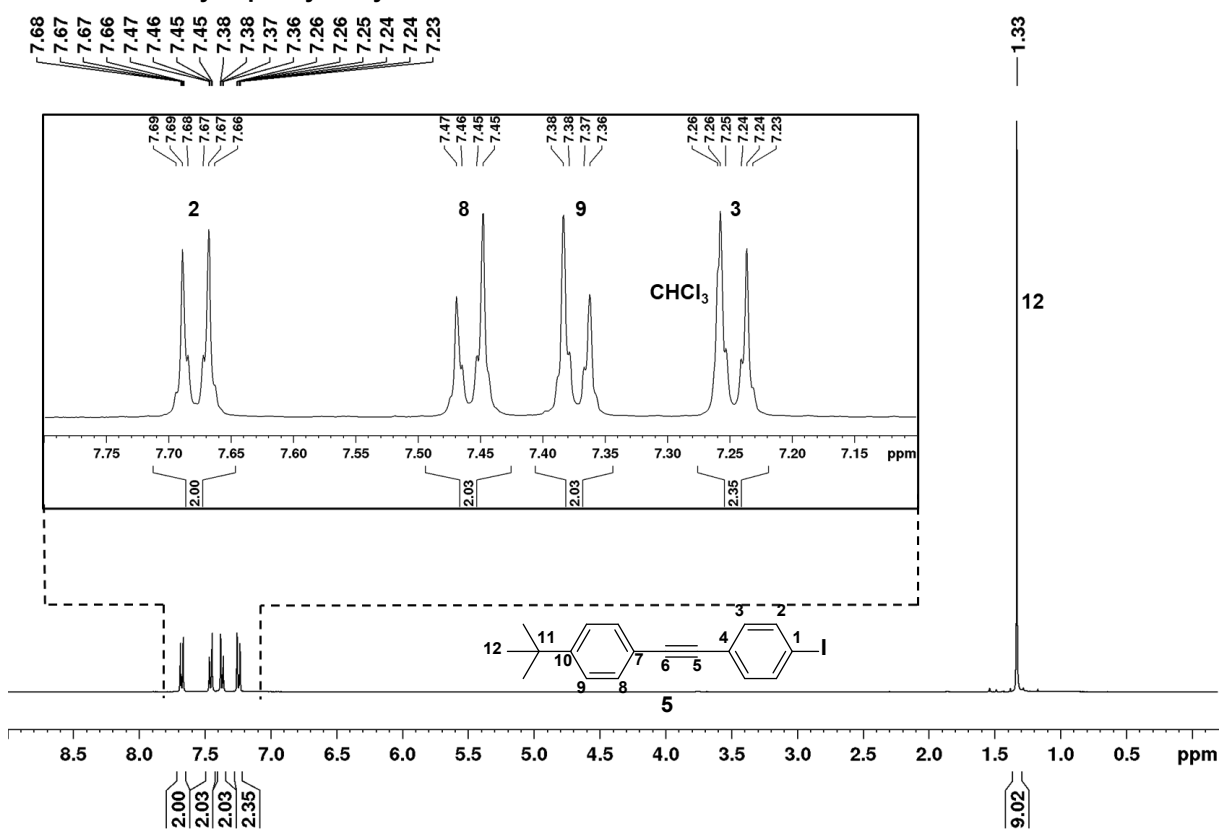


Figure 20. <sup>1</sup>H NMR spectrum of 5 (CDCl<sub>3</sub>, 400 MHz, rt.).

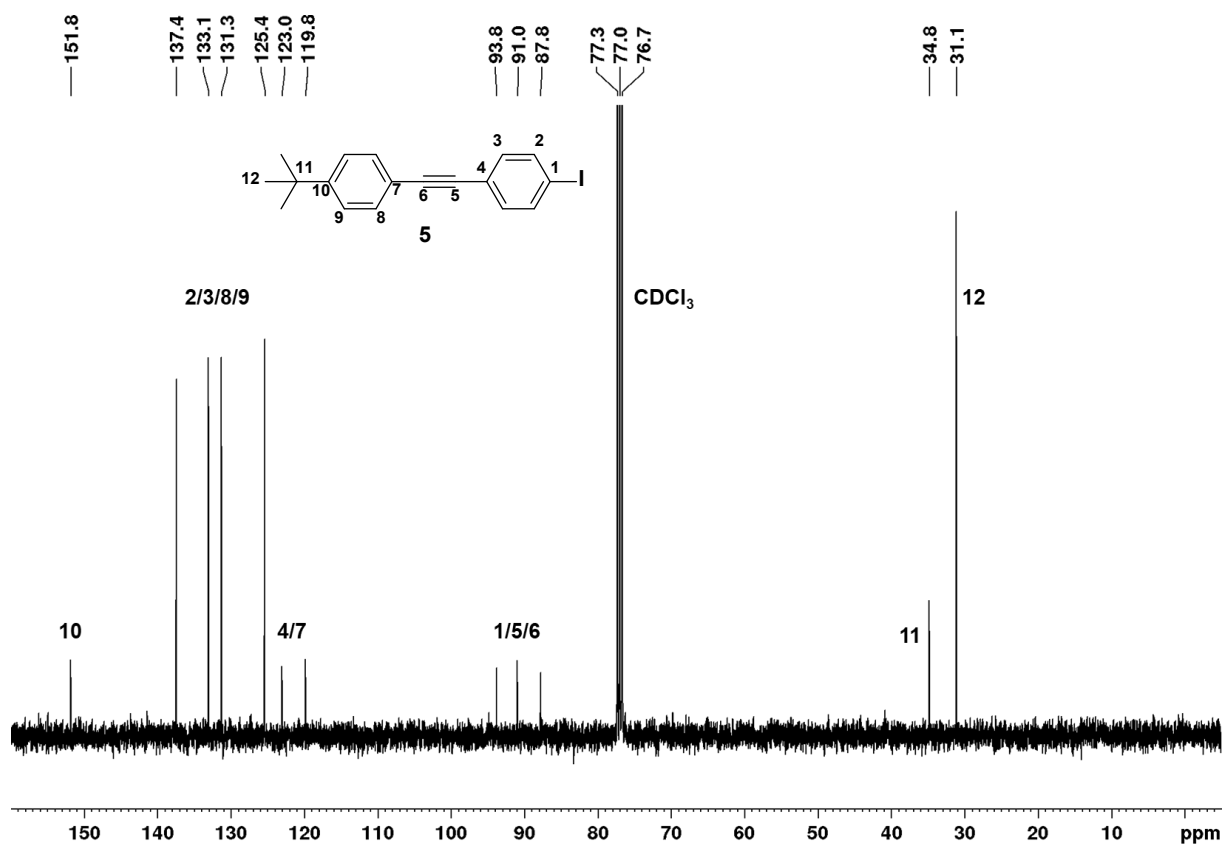


Figure 21. <sup>13</sup>C NMR spectrum of **5** (CDCl<sub>3</sub>, 100 MHz, rt.).

### Pentakis-4-*tert*-butylphenyl-4-iodo-HAB **10**

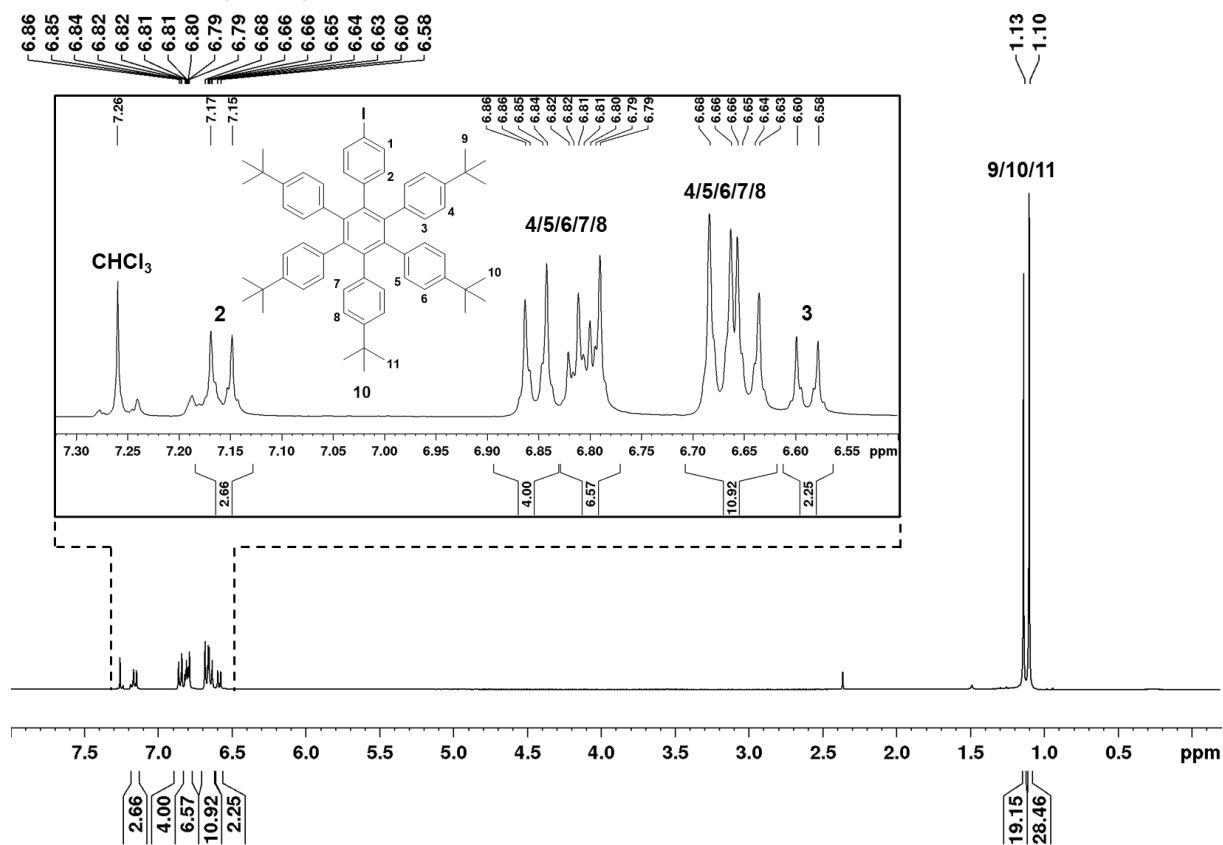


Figure 22. <sup>1</sup>H NMR spectrum of **10** (CDCl<sub>3</sub>, 400 MHz, rt.).

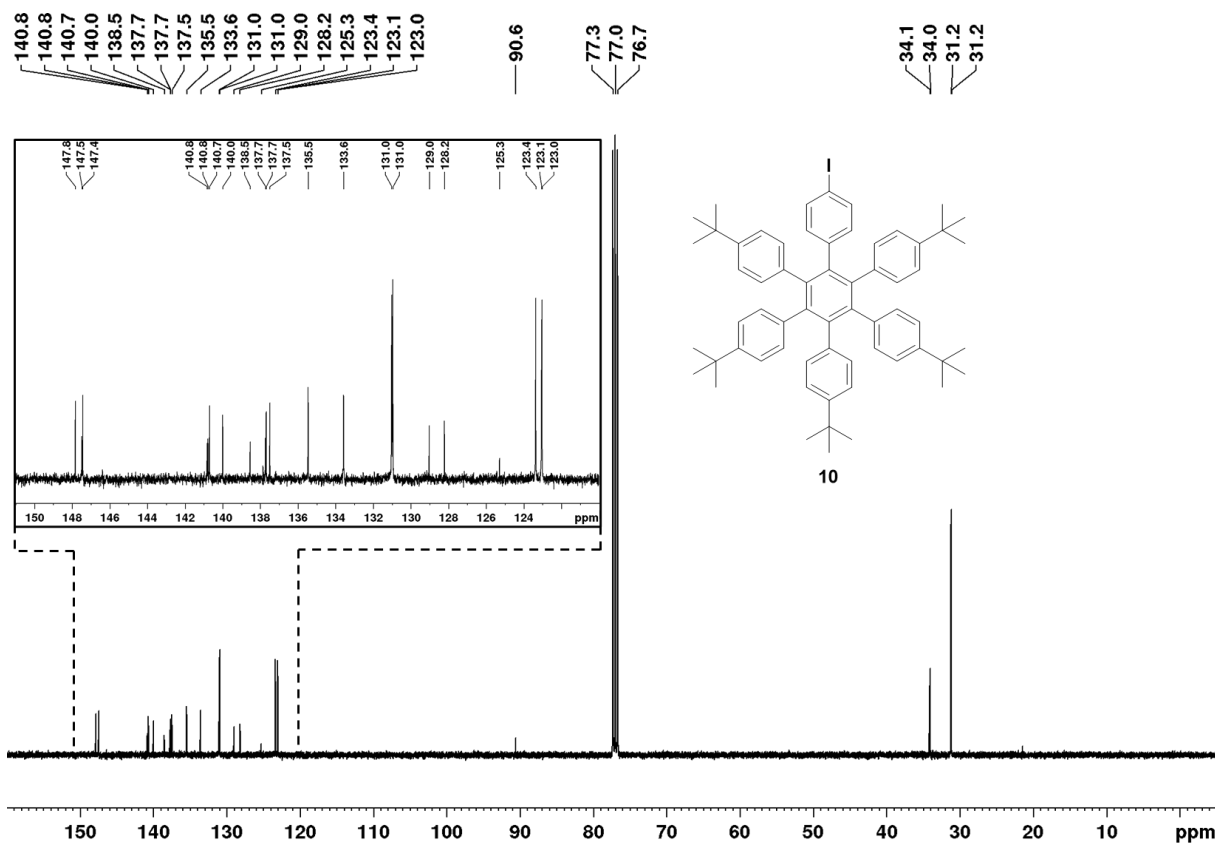


Figure 24.  $^{13}\text{C}$  NMR spectrum of 10 ( $\text{CDCl}_3$ , 100 MHz, rt.).

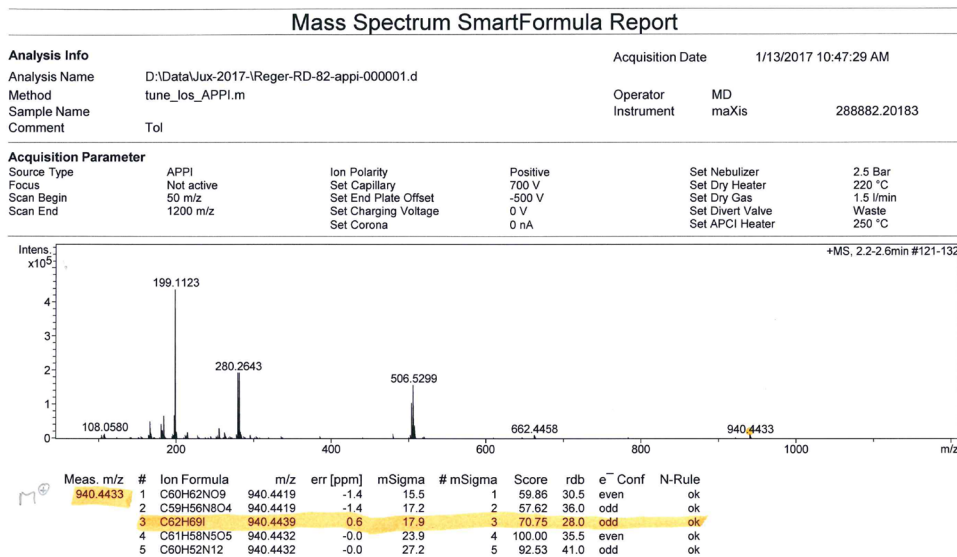


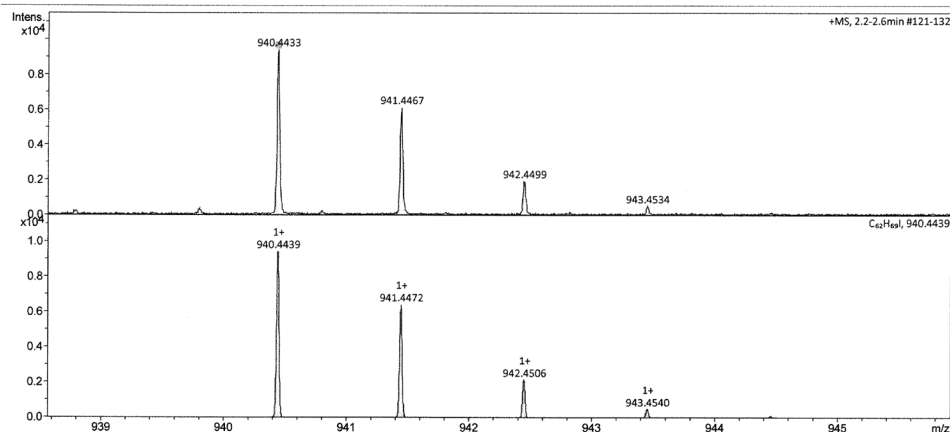
Figure 23. HRMS (APPI, toluene) spectrum of 10 (overview).



## Display Report

|                      |  |                  |                       |  |
|----------------------|--|------------------|-----------------------|--|
| <b>Analysis Info</b> |  | Acquisition Date | 1/13/2017 10:47:29 AM |  |
| Analysis Name        | D:\Data\Uux-2017-1\Reger-RD-82-appi-000001.d | Operator         | MD                    |  |
| Method               | tune_los_APPI.m                              | Instrument       | maXis                 |  |
| Sample Name          |  |                  | 288882.20183          |  |
| Comment              | Tol  |                  |                       |  |

|                              |            |                      |          |                  |           |
|------------------------------|------------|----------------------|----------|------------------|-----------|
| <b>Acquisition Parameter</b> |            |                      |          |                  |           |
| Source Type                  | APPI       | Ion Polarity         | Positive | Set Nebulizer    | 2.5 Bar   |
| Focus                        | Not active | Set Capillary        | 700 V    | Set Dry Heater   | 220 °C    |
| Scan Begin                   | 50 m/z     | Set End Plate Offset | -500 V   | Set Dry Gas      | 1.5 l/min |
| Scan End                     | 1200 m/z   | Set Charging Voltage | 0 V      | Set Divert Valve | Waste     |
|                              |            | Set Corona           | 0 nA     | Set APPI Heater  | 250 °C    |



Reger-RD-82-appi-000001.d  
Bruker Compass DataAnalysis 4.2

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by: MD

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Figure 25. HRMS (APPI, toluene) spectrum of **10** (zoom on product peak); measured (top), calculated (bottom).

### Pentakis-4-*tert*-butylphenyl-4-iodo-HBC **1**

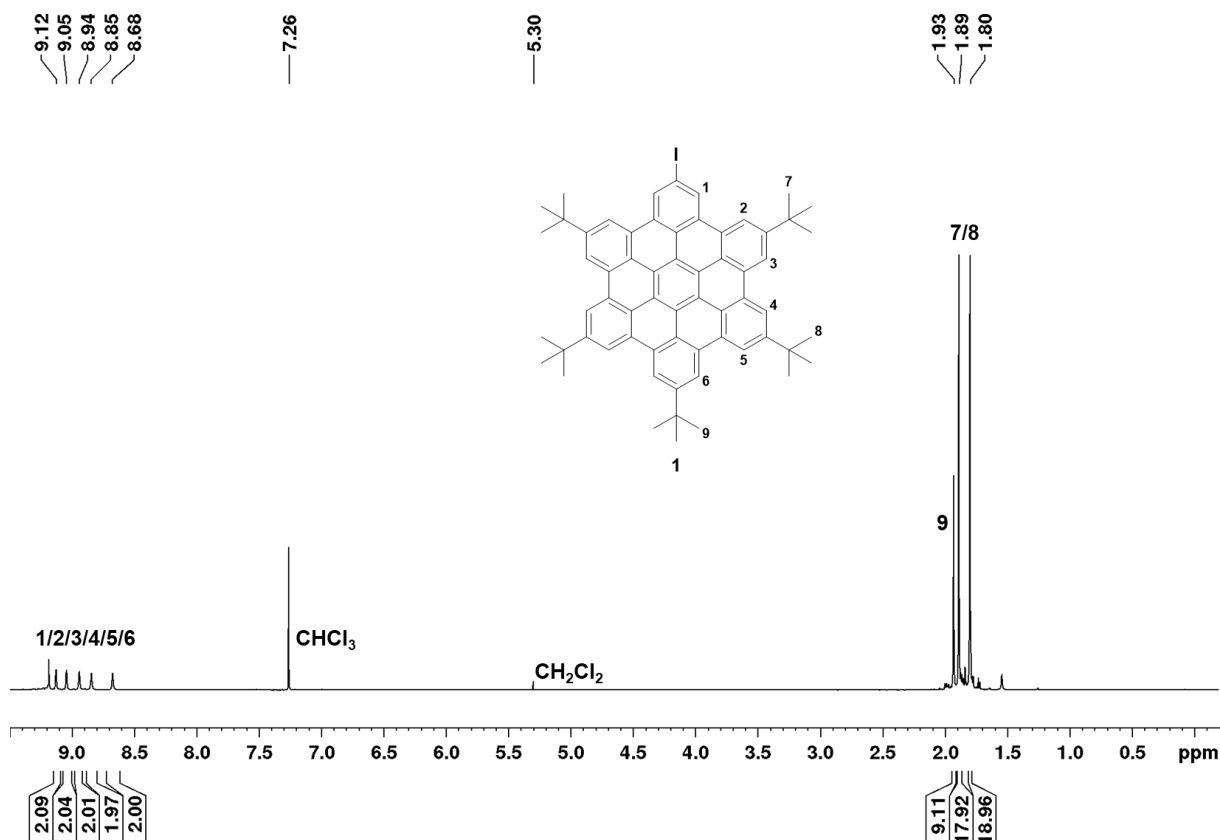


Figure 26. <sup>1</sup>H NMR spectrum of **1** (CDCl<sub>3</sub>, 400 MHz, rt.).

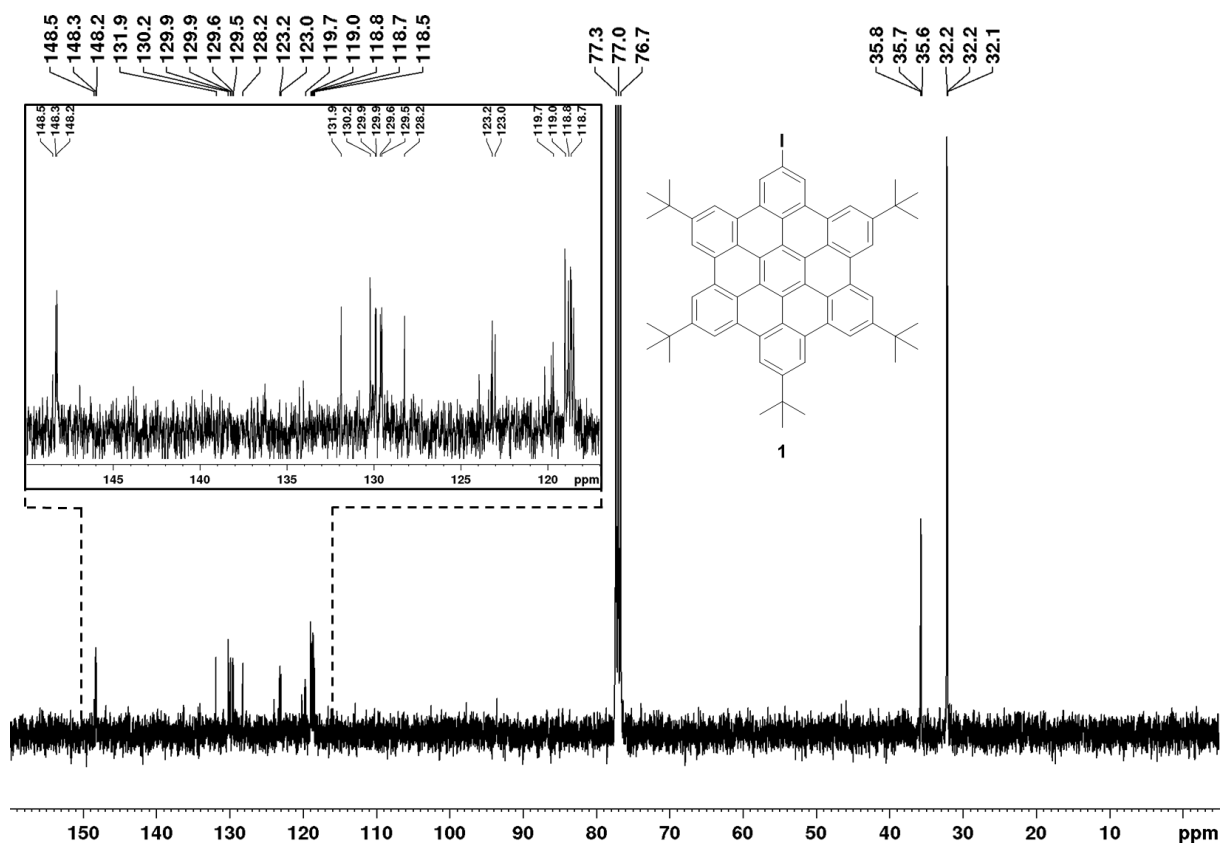


Figure 27.  $^{13}\text{C}$  NMR spectrum of **1** ( $\text{CDCl}_3$ , 100 MHz, rt.).

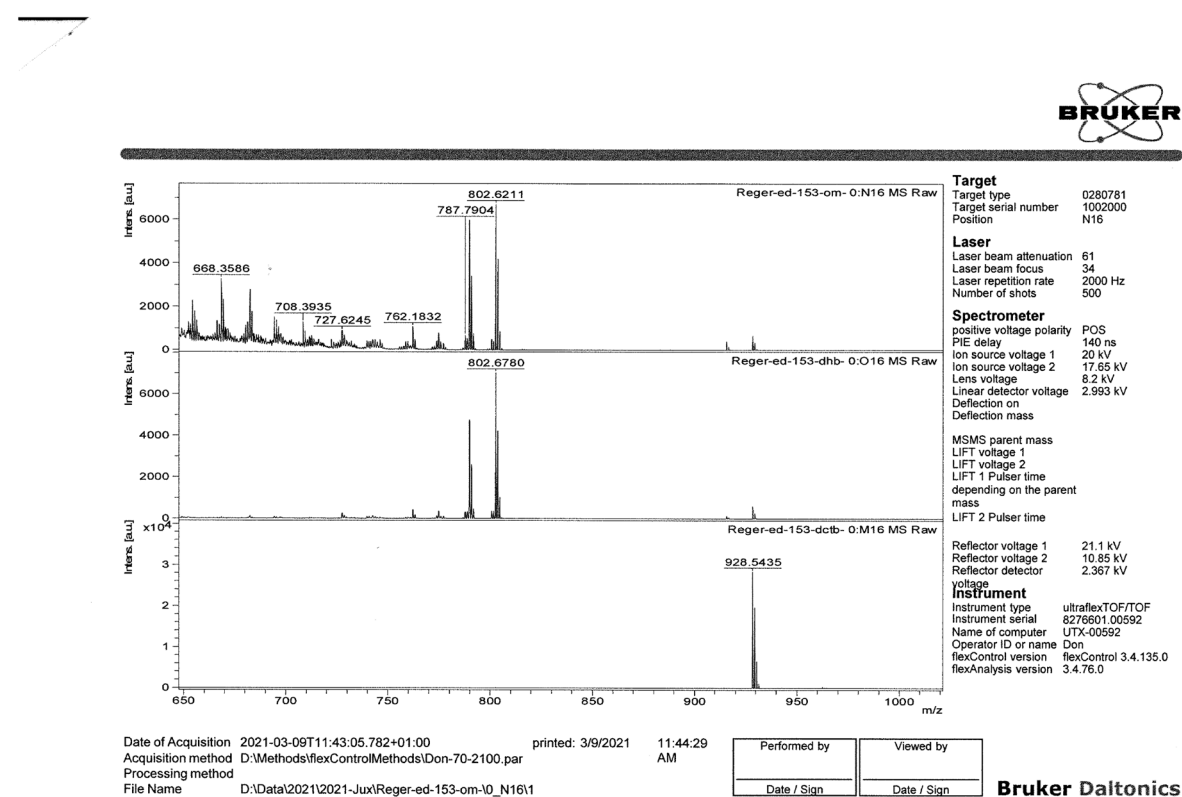
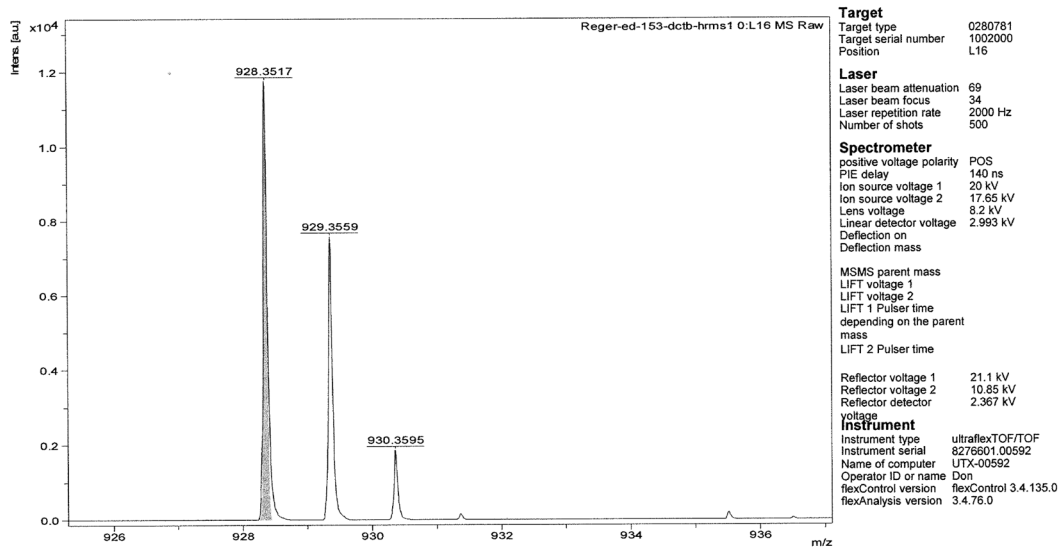


Figure 28. MS (MALDI) of **1**; top (without matrix), middle (dihb), bottom (dctb).

| Formula                         | Mass     | Error  | mSigma  | DbtEq | N rule | Electron Configuration |
|---------------------------------|----------|--------|---------|-------|--------|------------------------|
| C <sub>62</sub> H <sub>57</sub> | 928.3500 | 1.8612 | 40.2202 | 34.00 | ok     | odd                    |



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 Processing method:  
 File Name: D:\Data\2021\2021-Jux\Reger-ed-153-dctb-hrms1\0\_L16\1

printed: 3/9/2021 11:47:31 AM

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|              |             |
| Date / Sign  | Date / Sign |

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Figure 29. HRMS (MALDI, dctb) of 1. Inset (top left): Calculated value for C<sub>62</sub>H<sub>57</sub>l.

### 4-formyl-4'-*tert*-butyl diphenylacetylene 7

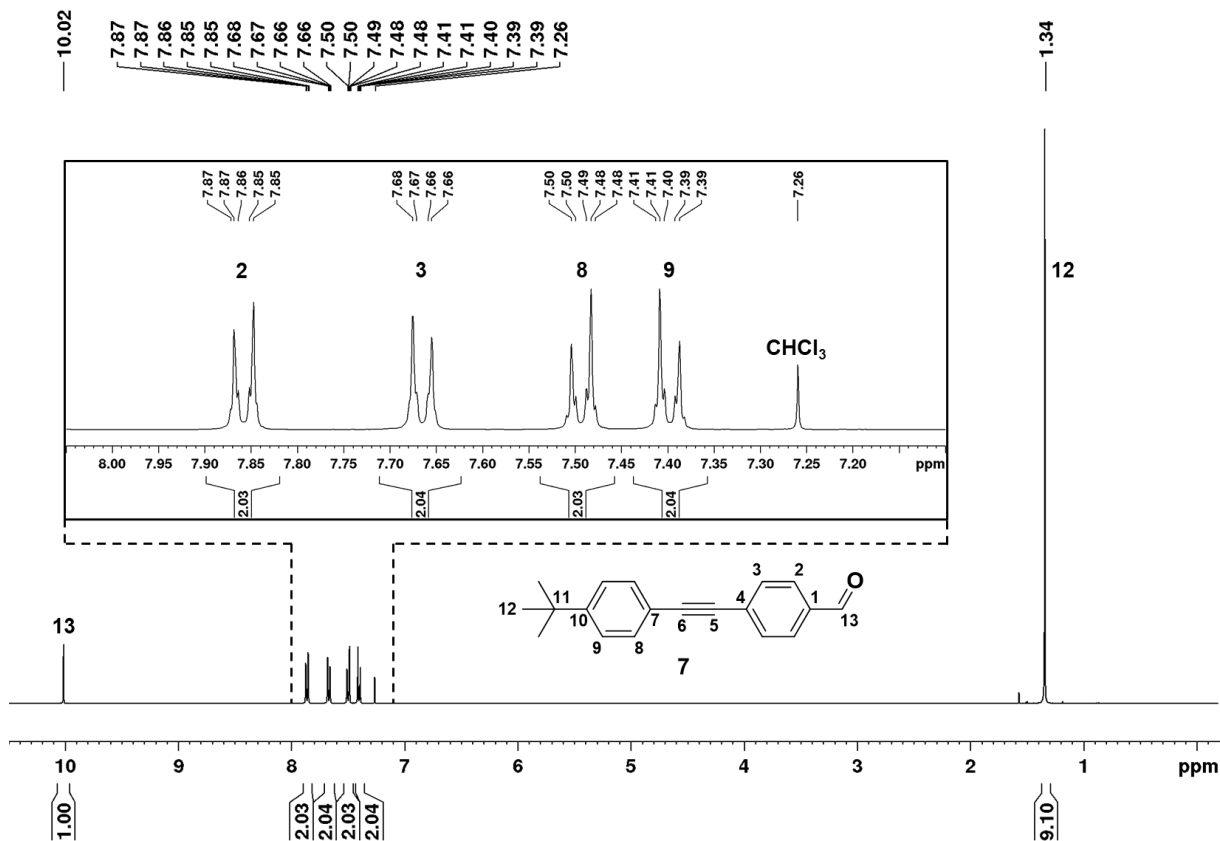


Figure 30. <sup>1</sup>H NMR spectrum of 7 (CDCl<sub>3</sub>, 400 MHz, rt.).

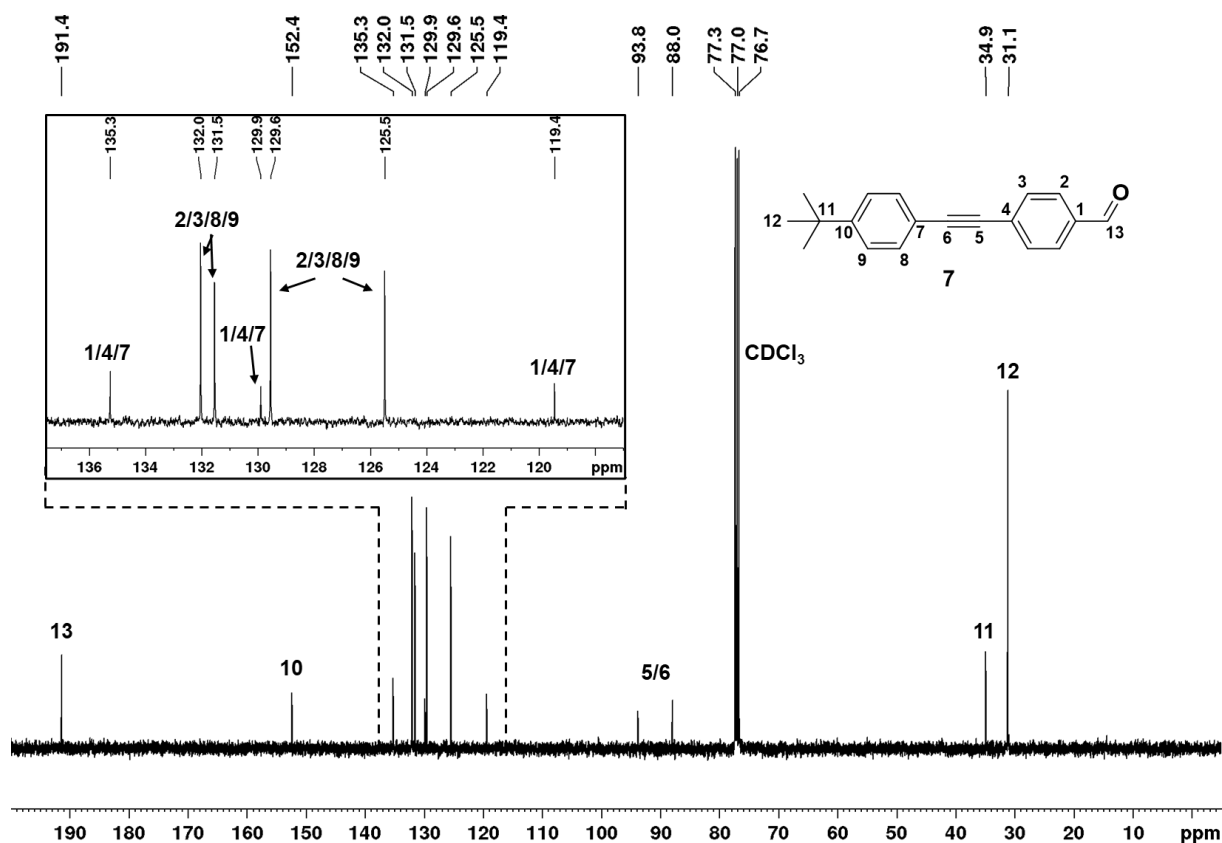


Figure 31.  $^{13}\text{C}$  NMR spectrum of **7** ( $\text{CDCl}_3$ , 100 MHz, rt.).

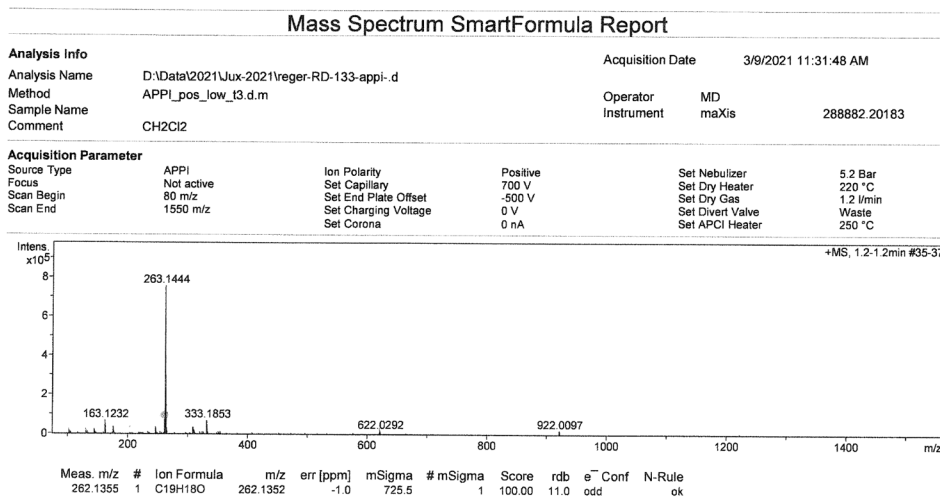
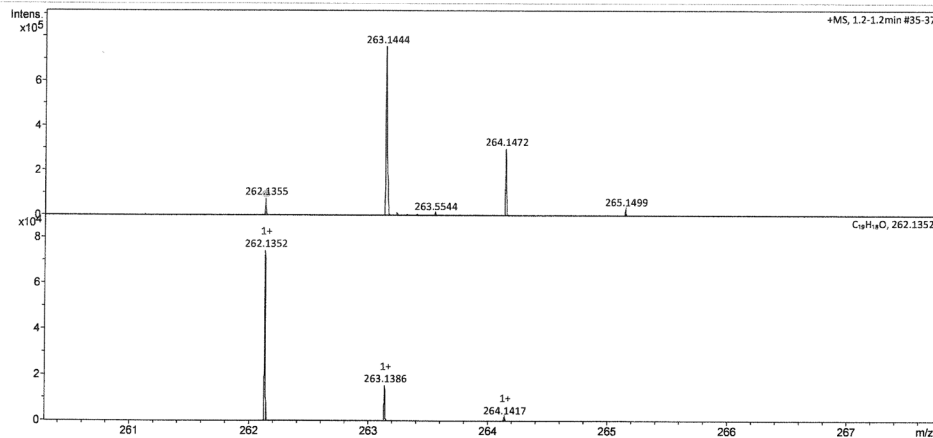


Figure 32. HRMS (APPI,  $\text{CH}_2\text{Cl}_2$ ) spectrum of **7** (overview).

## Display Report

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| Analysis Name        | D:\Data\2021\Lux-2021\reger-RD-133-appi-d | Operator         | MD    |                      |  |
| Method               | APPI_pos_low_t3.d.m                       | Instrument       | maXis | 288882.20183         |  |
| Sample Name          |   |                  |       |                      |  |
| Comment              | CH2Cl2                                    |                  |       |                      |  |

|                              |            |                      |          |                  |           |
|------------------------------|------------|----------------------|----------|------------------|-----------|
| <b>Acquisition Parameter</b> |            |                      |          |                  |           |
| Source Type                  | APPI       | Ion Polarity         | Positive | Set Nebulizer    | 5.2 Bar   |
| Focus                        | Not active | Set Capillary        | 700 V    | Set Dry Heater   | 220 °C    |
| Scan Begin                   | 80 m/z     | Set End Plate Offset | -500 V   | Set Dry Gas      | 1.2 l/min |
| Scan End                     | 1550 m/z   | Set Charging Voltage | 0 V      | Set Divert Valve | Waste     |
|                              |            | Set Corona           | 0 nA     | Set APGI Heater  | 250 °C    |



reger-RD-133-appi-d  
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 Page 1 of 1

Figure 33. HRMS (APPI, CH<sub>2</sub>Cl<sub>2</sub>) spectrum of **7** (zoom on product peak); measured (top), calculated (bottom).

### Pentakis-4-*tert*-butylphenyl-4-formyl-HAB **12**

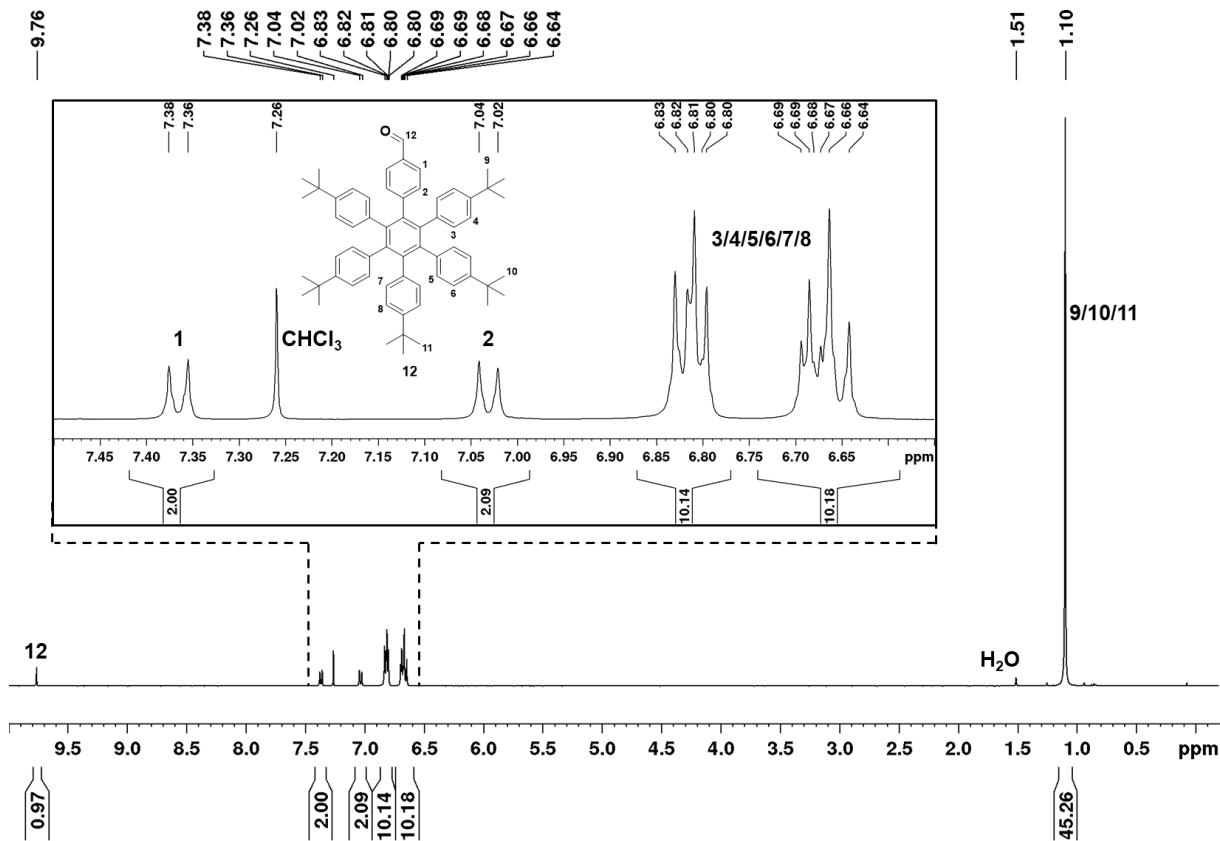


Figure 34. <sup>1</sup>H NMR spectrum of **12** (CDCl<sub>3</sub>, 400 MHz, rt.).

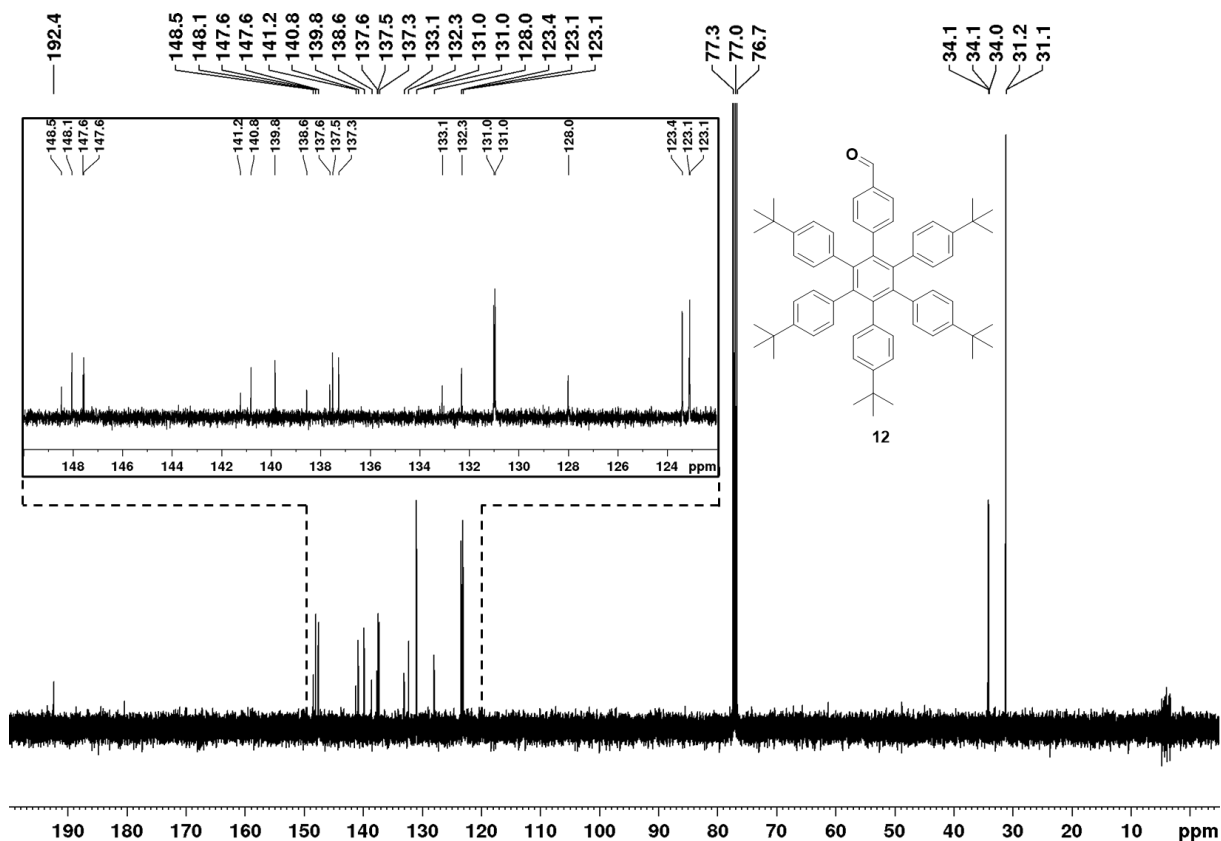


Figure 35. <sup>13</sup>C NMR spectrum of 12 (CDCl<sub>3</sub>, 100 MHz, rt.).

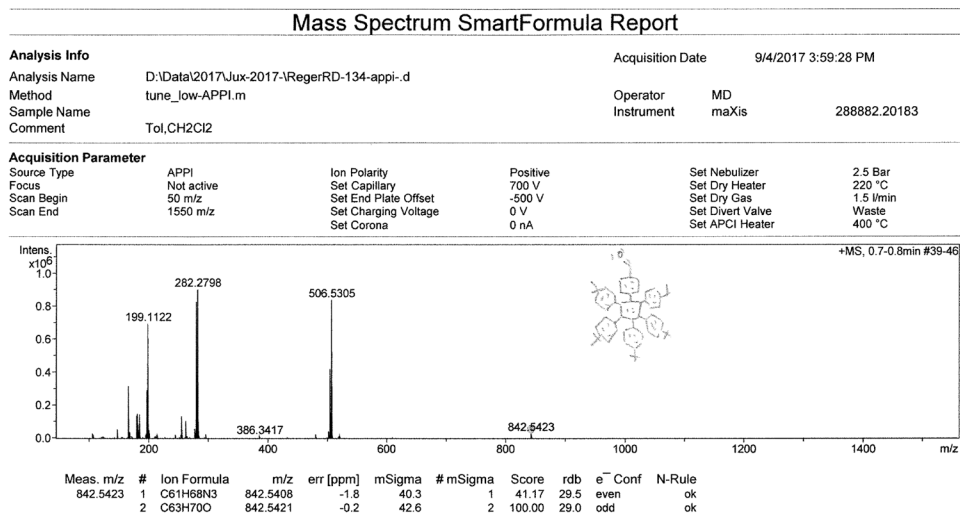


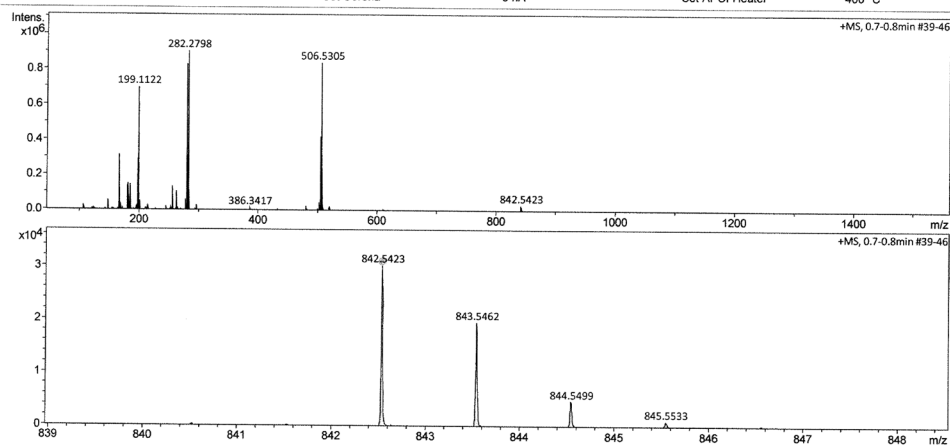
Figure 36. HRMS (APPI, toluene, CH<sub>2</sub>Cl<sub>2</sub>) spectrum of 12 (overview).

## Display Report

|                      |   |                  |                     |  |
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| Method               | tune_low-APPI.m                           | Instrument       | maXis               |  |
| Sample Name          |   |                  | 288882.20183        |  |
| Comment              | Tol,CH2Cl2                                |                  |                     |  |

### Acquisition Parameter

|             |            |                      |          |                  |           |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | APPI       | Ion Polarity         | Positive | Set Nebulizer    | 2.5 Bar   |
| Focus       | Not active | Set Capillary        | 700 V    | Set Dry Heater   | 220 °C    |
| Scan Begin  | 50 m/z     | Set End Plate Offset | -500 V   | Set Dry Gas      | 1.5 l/min |
| Scan End    | 1550 m/z   | Set Charging Voltage | 0 V      | Set Divert Valve | Waste     |
|             |            | Set Corona           | 0 nA     | Set APPI Heater  | 400 °C    |



RegerRD-134-appi-d  
Bruker Compass DataAnalysis 4.2

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by: MD

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Figure 37. HRMS (APPI, toluene, CH<sub>2</sub>Cl<sub>2</sub>) spectrum of **12**; overview (top) and zoom on product peak (bottom).

### Pentakis-4-*tert*-butylphenyl-4-formyl-HBC **12**

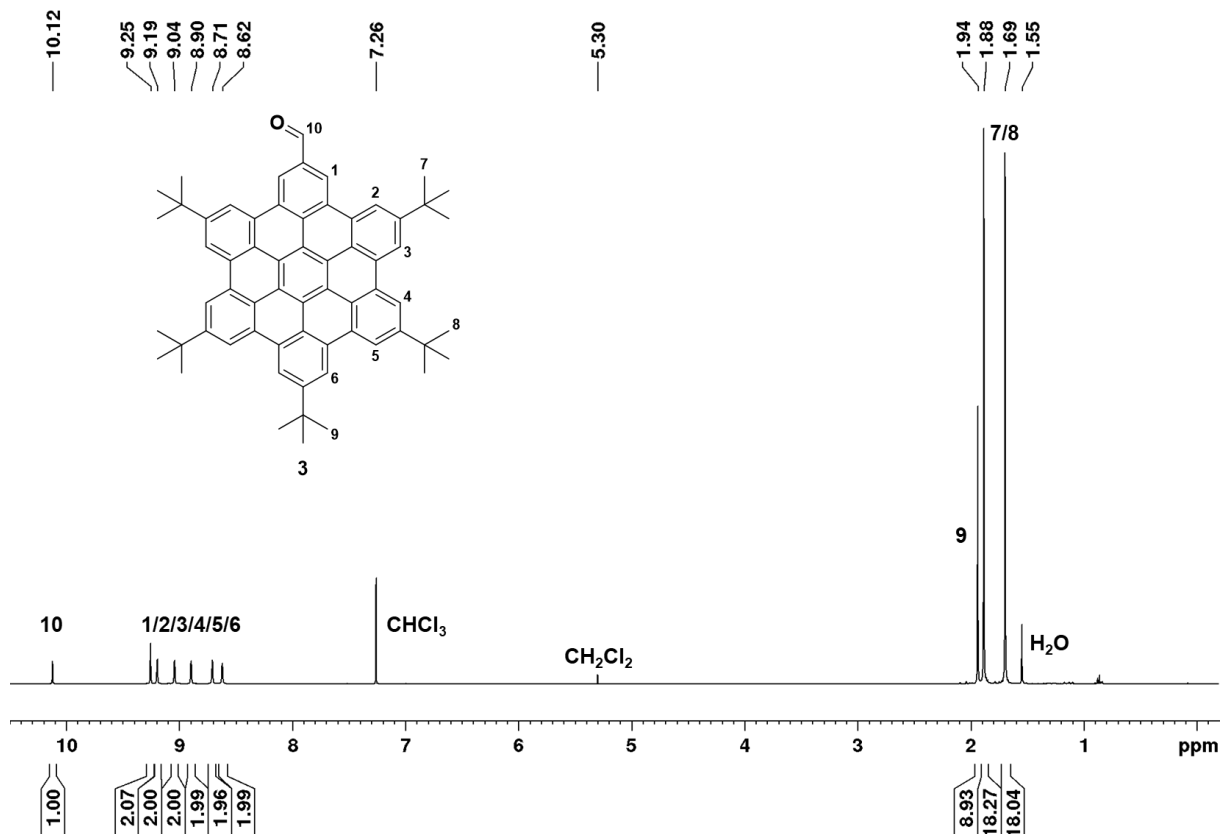


Figure 38. <sup>1</sup>H NMR spectrum of **3** (CDCl<sub>3</sub>, 400 MHz, rt.).

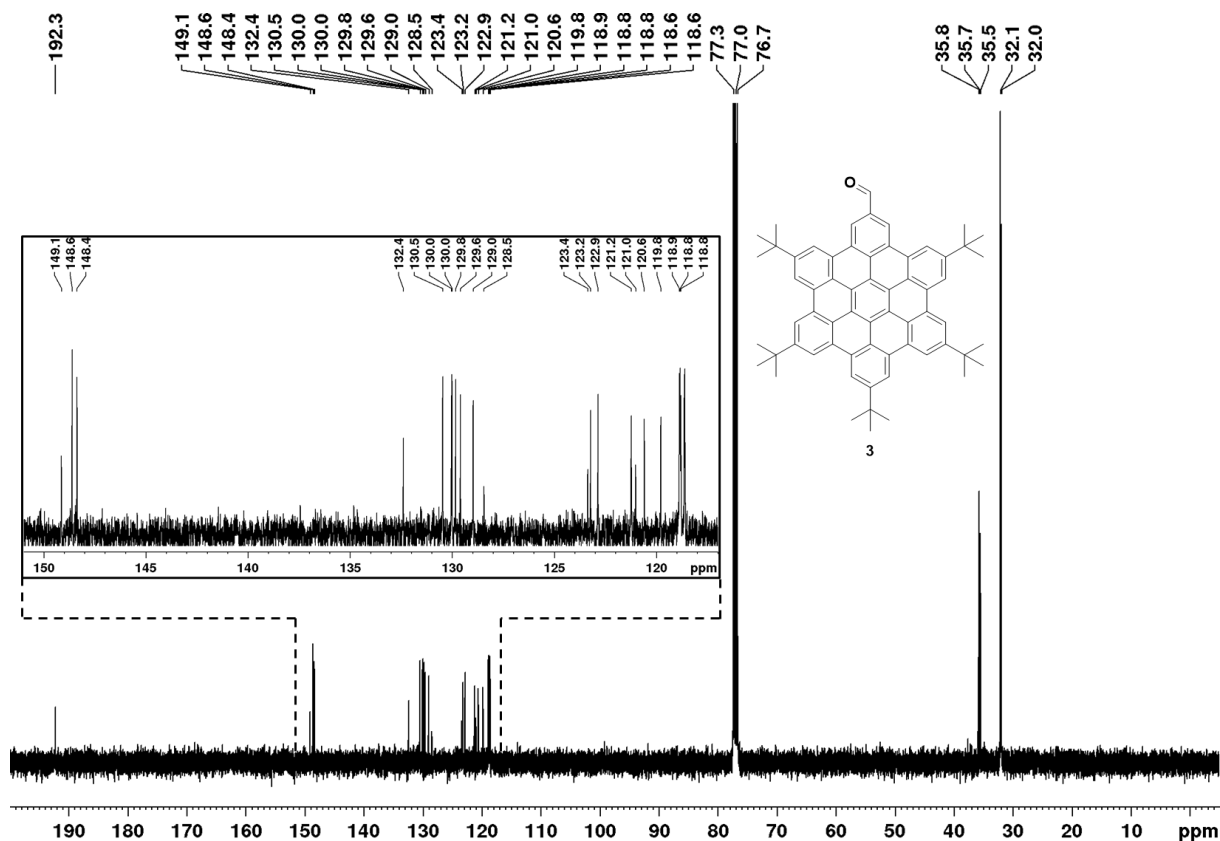


Figure 40.  $^{13}\text{C}$  NMR spectrum of **3** ( $\text{CDCl}_3$ , 100 MHz, rt.).

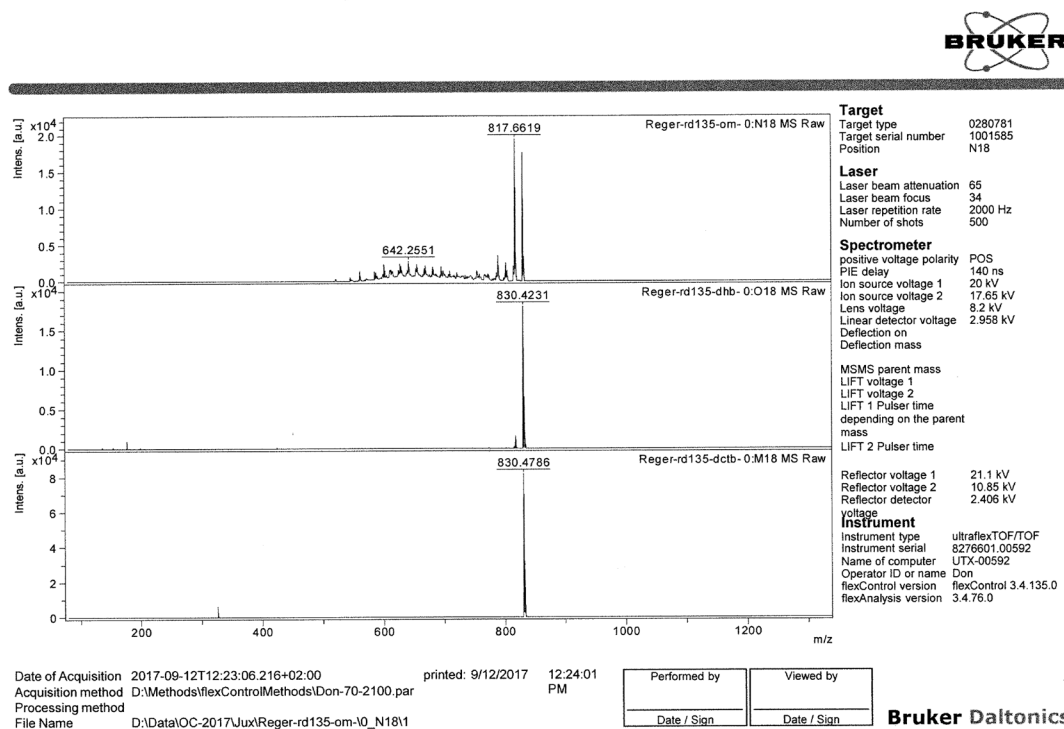
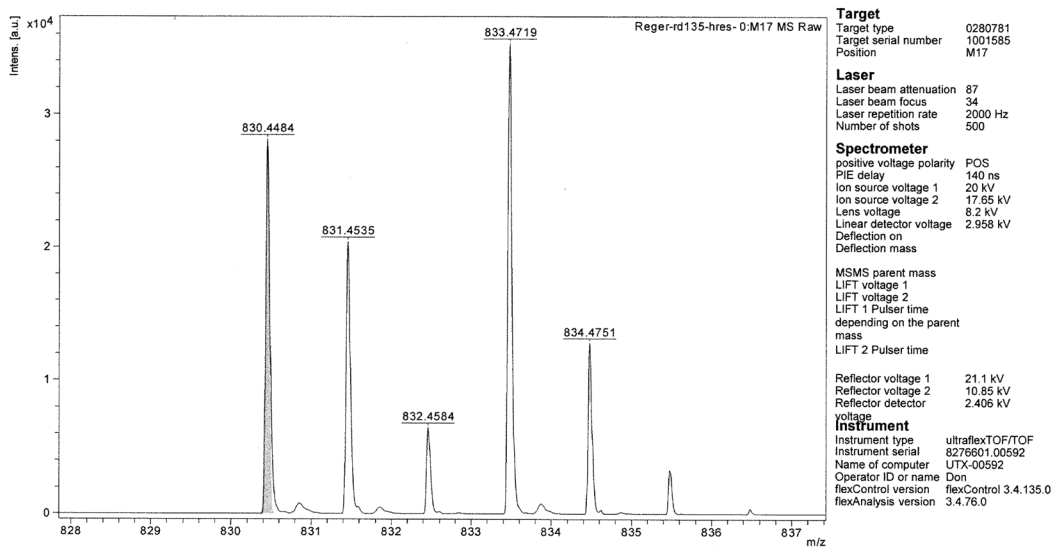


Figure 39. MS (MALDI) of **3**; top (without matrix), middle (dihb), bottom (dctb).



|           |          |        |          |       |    |     |
|-----------|----------|--------|----------|-------|----|-----|
| C 63 H 58 | 830.4482 | 0.2117 | 464.2782 | 35.00 | ok | odd |
| O         |          |        |          |       |    |     |



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printed: 9/12/2017 12:28:08 PM

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| Performed by | Viewed by   |
| Date / Sign  | Date / Sign |

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Figure 41. HRMS (MALDI, without matrix) of 3. Inset (top left): Calculated value for C<sub>63</sub>H<sub>58</sub>O.

## 5. Literature

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