

Supporting Information for:

Unexpected Phenyl Group Rearrangement during an Intramolecular Scholl Reaction Leading to an Alkoxy-substituted Hexa-*peri*-hexabenzocoronene

*Xi Dou, Xiaoyin Yang, Graham J. Bodwell[†], Manfred Wagner, Volker Enkelmann and Klaus Müllen**

Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

Fax: +49-6131-379350

Email: muellen@mpip-mainz.mpg.de

[†]Department of Chemistry, Memorial University, St. John's NL, Canada A1B 3X7

Experimental Details

General Methods:

Chemicals were obtained from Fluka, Aldrich, and ABCR and used as received. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DPX 250, Bruker DRX 500 or Bruker DRX 700 spectrometer with use of the solvent proton or carbon signal as an internal standard. Field Desorption (FD) mass spectra were obtained on a VG Instruments ZAB 2-SEFPD instrument. MALDI-TOF mass spectra were measured using a Bruker Reflex II-TOF spectrometer using a 337 nm nitrogen laser and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as matrix. Data collections for the crystal structure analysis were performed on a Nonius KCCD diffractometer with graphite monochromated Mo-K α radiation at a temperature of 120 K. Elemental analyses were carried out on a Foss Heraeus Vario EL apparatus in the Institute for Organic Chemistry at the Johannes Gutenberg University, Mainz.

Synthesis:

1,4-Bis(4-methoxyphenyl)-2,3,5,6-tetrakis(dodecylphenyl)benzene (2). A mixture of 1,4-diiodo-2,3,5,6-tetrakis(4-dodecylphenyl)benzene (**1**)¹ (1.3 g, 1.0 mmol), 4-methoxyphenylboronic acid (0.76 g, 5.0 mmol), Pd(PPh₃)₄ (60 mg, 0.050 mmol), K₂CO₃ (2.7

g, 19.6 mmol), Aliquat[®] 336 (7 mg, 0.02 mmol) and toluene (30 mL) in a 100 mL Schlenk reaction flask was thoroughly degassed using the “freeze-thaw” method. The mixture was heated to 100 °C under an argon atmosphere. After 48 h, the reaction was quenched by adding distilled water (30 mL). Dichloromethane (200 mL) was added and the layers were separated. The organic phase was dried over MgSO₄. The residue was purified by column chromatography using petroleum ether (PE) / dichloromethane (DCM) 8/1 as eluent (*R_f* = 0.2). Compound **2** (1.15 g, 91%) was isolated as a colorless oil. **MS** (FD, 8 kV): *m/z* (%) = 1267.6 (100%, M⁺) (calcd. for C₉₂H₁₃₀O₂ = 1268.06 g mol⁻¹); **¹H-NMR** (250 MHz, CD₂Cl₂): δ = 6.73-6.64 (m, 20H, aryl-*H*), 6.40 (d, ³*J* = 8.8 Hz, 4H, aryl-*H*), 3.59 (s, 6H, -OCH₃), 2.37 (t, ³*J* = 6.8 Hz, 8H, α-CH₂), 1.43-1.13 (m, 80H, alkyl-*H*), 0.88 (m, 12H, -CH₃); **¹³C-NMR** (62.5 MHz, CD₂Cl₂): δ = 157.3, 140.9, 140.2, 139.8, 138.7, 133.9, 132.8, 131.6, 126.9, 112.2, 55.2, 35.6, 32.3, 31.6, 30.09, 30.06, 30.0, 29.9, 29.82, 29.76, 29.3, 23.1, 14.3; **Elemental Analysis** C 87.03%, H 10.01%, (calcd. for C₉₂H₁₃₀O₂: C 87.14%, H 10.33%).

5,11,14,17-Tetradodecyl-2,8-dimethoxy-hexa-*peri*-hexabenzocoronene (3). Compound **2** (200 mg, 0.16 mmol) was dissolved in dichloromethane (200 mL) and the solution was bubbled with argon for 20 min. FeCl₃/CH₃NO₂ solution (1.7 mL, 1.89 M, 3.2 mmol) was then added dropwise. The reaction was quenched by adding methanol (300 mL) after 20 min. The solvent was removed under reduced pressure and the crude product was filtered through a short silica-pad with hot toluene. Compound **3** (40 mg, 20%) was obtained as a yellow powder after purification by recrystallization from toluene. **MS** (MALDI-TOF, TCNQ): *m/z* (%) = 1256 (100%, M⁺) (calcd. for C₉₂H₁₁₈O₂ = 1255.97 g mol⁻¹); **¹H-NMR** (500 MHz, CDCl₃): δ = 7.91 (s, 2H, aryl-*H_a*), 7.87 (s, 2H, aryl-*H_b*), 7.67 (s, 2H, aryl-*H_c*), 7.40 (s, 2H, aryl-*H_f*), 7.36 (s, 2H, aryl-*H_d*), 7.21 (s, 2H, aryl-*H_e*), 3.75 (s, 6H, -OCH₃), 2.78 (t, ³*J* = 7.7 Hz, 2H, *H₂*), 2.65 (t, ³*J* = 7.7 Hz, 4H, *H₁*), 2.36 (t, ³*J* = 7.7 Hz, 2H, *H₃*), 1.85 (m, 2H, β-CH₂), 1.77 (m, 6H, β-CH₂), 1.52-1.23 (m, 86H, alkyl-*H*), 0.88 (m, 12H, -CH₃); **¹³C-NMR** (125 MHz,

CDCl₃): δ = 148.0, 130.3, 130.1, 130.0, 121.9, 121.8, 120.4, 120.3, 119.8, 119.6, 113.9, 113.7, 111.9, 111.8, 111.7, 110.5, 110.4, 110.2, 110.1, 109.9, 108.8, 108.5, 97.1, 97.0, 46.2, 28.4, 28.2, 27.9, 23.4, 23.3, 23.1, 22.9, 21.3, 21.3, 21.2, 21.1, 21.0, 20.9, 20.8, 20.5, 13.8, 5.1;

Elemental Analysis C 87.25%, H 9.88%, (calcd. for C₉₂H₁₁₈O₂: C 87.98%, H 9.47%).

5,11-Bis[4'-dodecylphenyl]-2,8-didodecyl-6,12-bis[spiro(6'-oxo-cyclohexa-1',4'-diene)-

3']indeno[1,2-*b*]fluorene (4). The mother liquor, which was used for the recrystallization of

compound **3**, was concentrated. Column chromatography was used for the purification with

an eluent of PE/DCM (2/3) (*R_f* = 0.1). The resulting product was further recrystallized from a

DCM/acetone (1/1) mixture to afford compound **4** (138 mg, 70%) as brown crystal. **MS** (FD,

8 kV): *m/z* (%) = 1236.8 (100%, M⁺), 618.2 (21%, M²⁺), (calcd. for C₉₀H₁₂₂O₂ = 1235.97 g

mol⁻¹); **¹H-NMR** (250 MHz, CD₂Cl₂): δ = 7.19 (s, 8H, aryl-*H*), 6.82 (s, 2H, aryl-*H*), 6.81 (d,

³*J* = 8.6 Hz, 2H, aryl-*H*), 6.54 (d, ³*J* = 9.8 Hz, 4H, ethenyl-*H*), 6.19 (d, ³*J* = 7.9 Hz, 2H, aryl-

H), 6.05 (d, ³*J* = 9.8 Hz, 4H, ethenyl-*H*), 2.69 (t, ³*J* = 7.2 Hz, 4H, α -CH₂), 2.46 (t, ³*J* = 7.7 Hz,

4H, α -CH₂), 1.67 (m, 4H, β -CH₂), 1.39-1.21 (m, 76H, alkyl-*H*), 0.91-0.84 (m, 12H, -CH₃);

¹³C-NMR (62.5 MHz, CD₂Cl₂): δ = 185.7, 149.9, 144.0, 143.4, 143.3, 142.8, 139.7, 139.2,

136.2, 133.9, 130.0, 129.3, 128.9, 128.4, 124.5, 123.7, 56.9, 36.1, 32.3, 32.3, 31.9, 31.9, 30.1,

30.1, 29.99, 29.97, 29.91, 29.8, 29.7, 29.6, 23.1, 14.3, 14.2; **Elemental Analysis** C 87.35%,

H 9.98%, (calcd. for C₉₀H₁₂₂O₂: C 87.46%, H 9.95%).

¹ Yang, X.; Dou, X; Müllen, K. *Efficient Synthesis of Symmetrically and Unsymmetrically substituted Hexaphenylbenzene (HPB) Analogues via Sterically Hindered Suzuki-Miyaura Coupling Reaction*, in preparation.

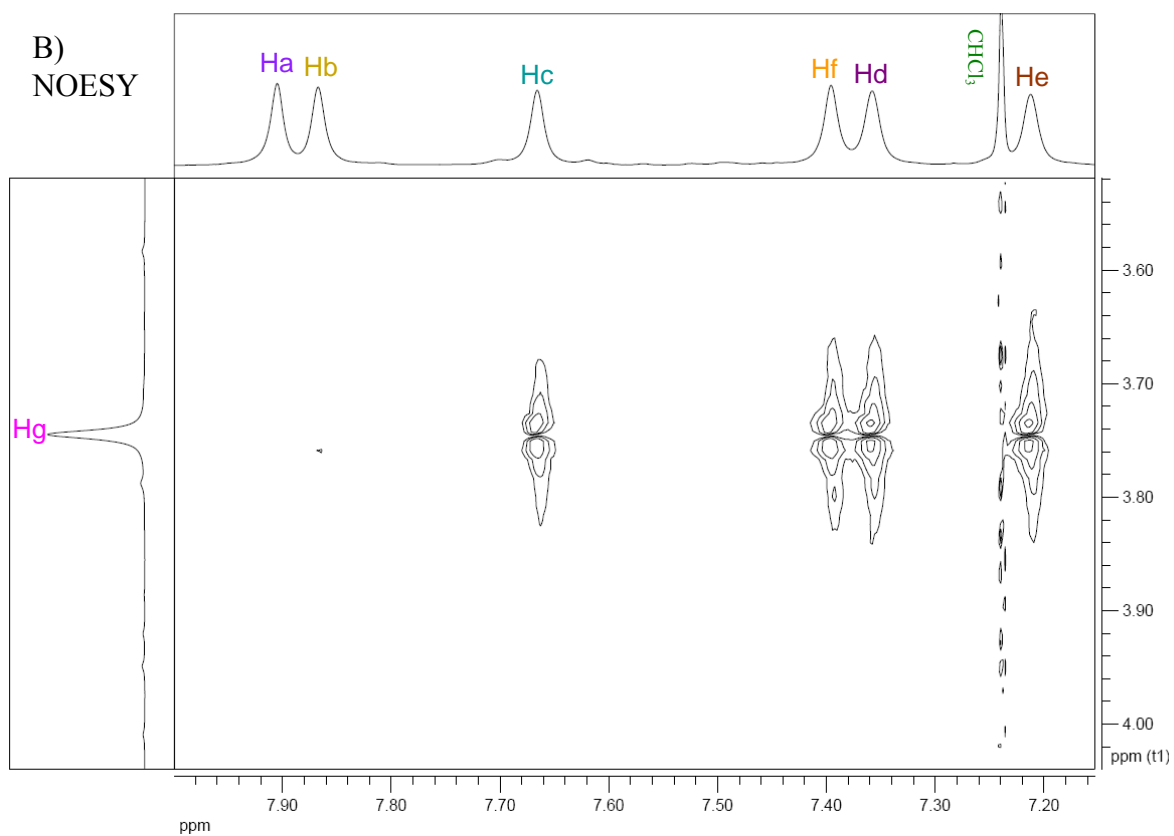
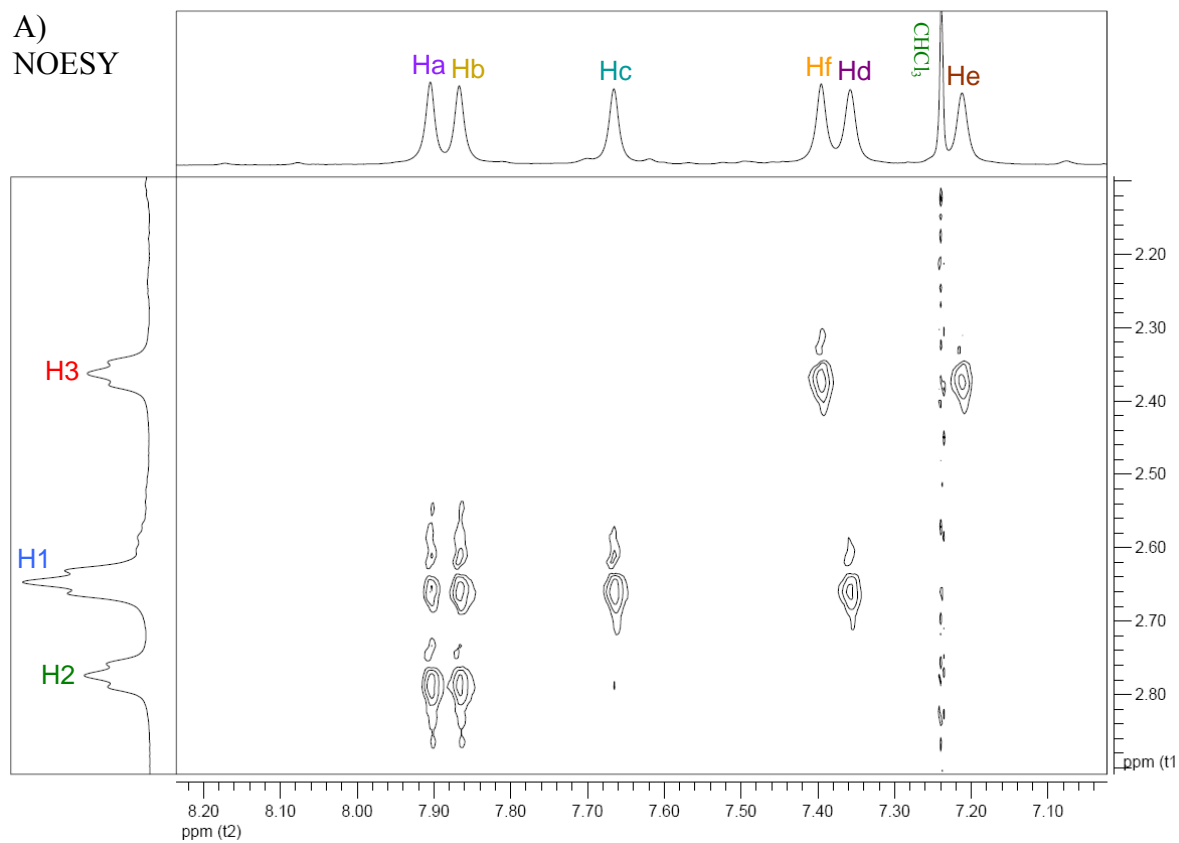
Structure assignment of compound 3:

On the one-dimensional ^1H -NMR (Figure 1a), the three triplet peaks with a coupling constant $^3J = 7.5$ Hz in the region from 2.79 to 2.35 ppm were assigned to the three different alkyl α -protons next to aromatic core. According to their integral values, the triplet peak around 2.65 ppm with an integral value two times bigger than the values of the other two triplet peaks were attributed to H_1 , which coupled with four aromatic protons, H_a , H_b , H_c and H_d on ^1H , ^1H NOESY spectrum (Figure 1b for correlations, Figure S1A for NOESY spectra). The alkyl α -proton signal at 2.78 ppm, which only showed correlation peaks with two aromatic protons (H_a and H_b , which also coupled with H_1) on ^1H , ^1H NOESY spectrum, was evaluated as H_2 . The remaining one at 2.36 ppm was naturally justified as H_3 , which showed two coupling signals with another two aromatic protons, H_c and H_f , in the ^1H , ^1H NOESY spectrum. The singlet peak at 3.75 ppm represented six protons on two methoxyl groups, H_g , with same chemical environment. This assignment was further confirmed by its correlation with four nearby aromatic protons, H_c , H_d , H_e and H_f on ^1H , ^1H NOESY spectrum (Figure S1B).

The differentiation between the aromatic protons H_a and H_b ; H_c and H_d ; H_e and H_f were further achieved by the ^1H , ^1H COSY spectrum (Figure S1D) and supplemented with data from ^1H , ^1H NOESY spectrum (Figure S1C). In the ^1H , ^1H COSY spectrum, the two protons at 7.91 and 7.40 ppm each showed only one over-five-bond coupling signal with the protons at 7.87 and 7.21 ppm, respectively. The one at 7.91 ppm was substantiated as H_a because it did not correlate with the protons on methoxyl group, H_g , according to ^1H , ^1H NOESY spectrum. The signal at 7.40 ppm was therefore proved for H_f coupling with H_g as described before. Consequently, H_b and H_e were separately verified at 7.87 and 7.21 ppm as solely coupled protons of H_a and H_f on ^1H , ^1H COSY spectrum. Theoretically, H_b should correlate not only with H_a over five aromatic bonds but also with H_c over four bonds. Thus, the signal at 7.67 ppm, the other coupling signal of H_b , was allocated to H_c . H_d was assigned to the signal at

7.36 ppm due to its correlation with both H_e and H_c in a similar way. All the assignments were further proved by aromatic proton coupling on ¹H, ¹H NOESY spectrum, which showed correlations between H_a and H_b, H_c and H_d, H_e and H_f.

H,H NOESY spectra for 3:



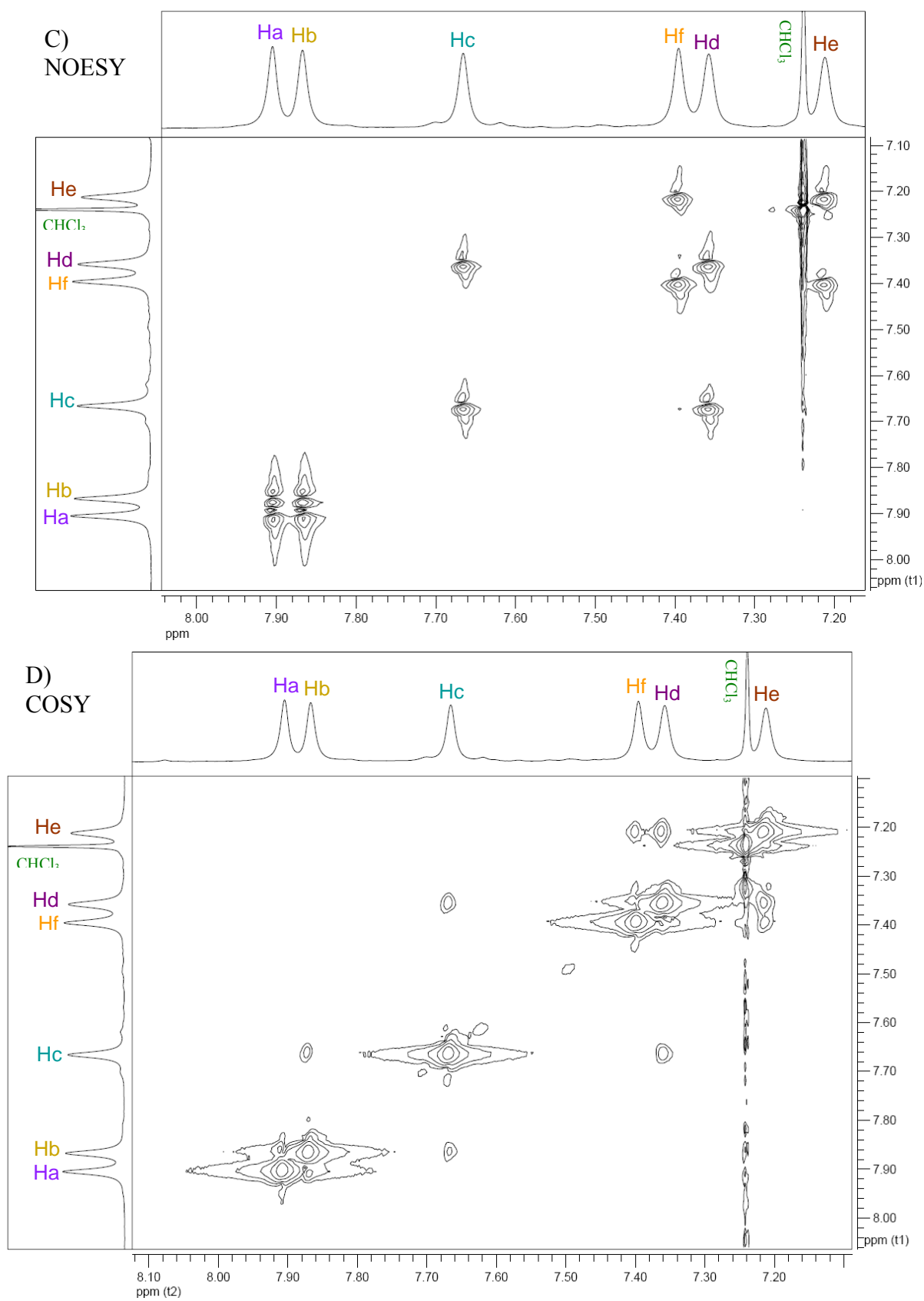
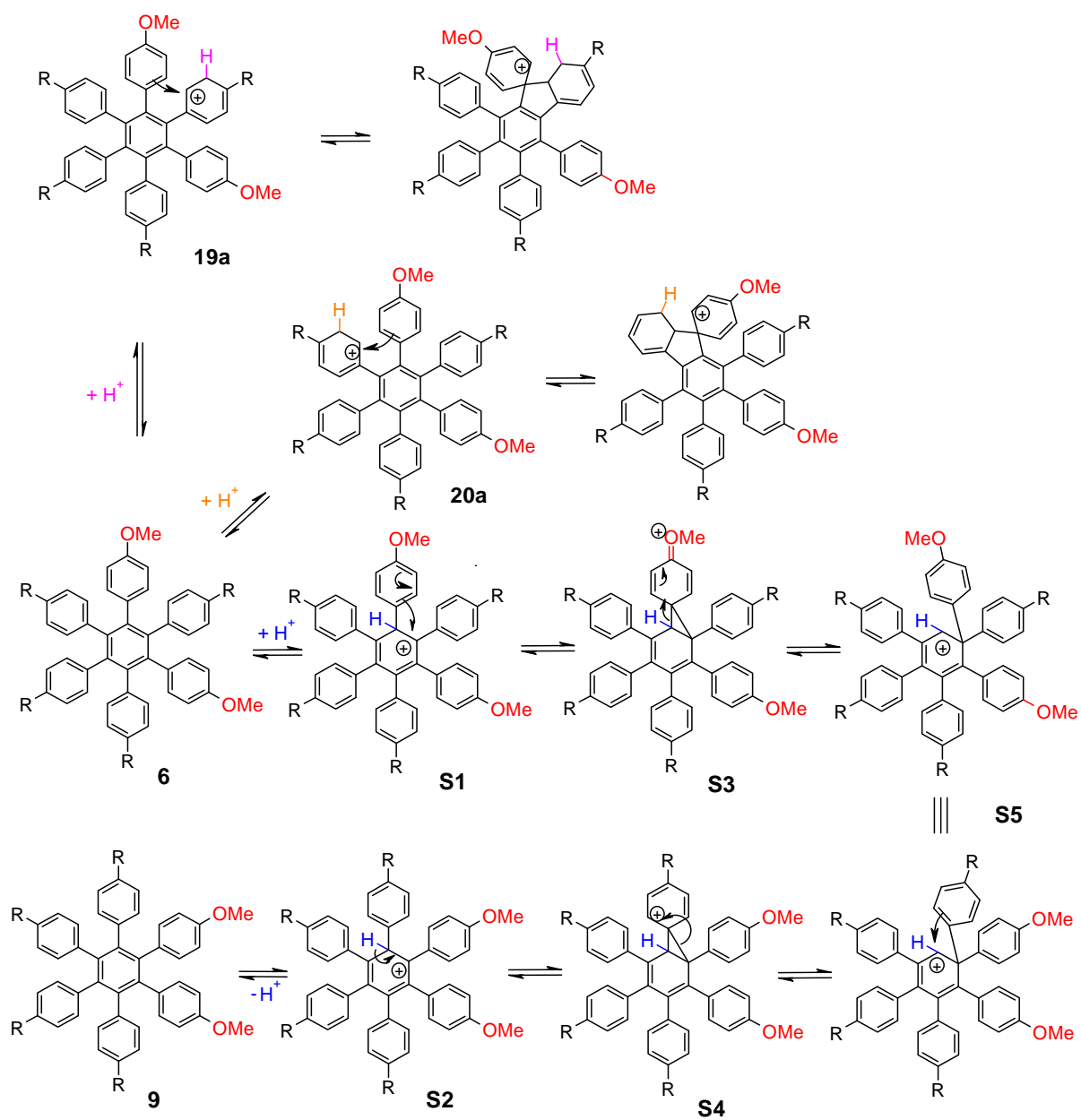


Figure S1. ^1H , ^1H -NOESY and COSY spectra of compound **3** (CDCl_3 , rt, 500 MHz); coupling between A) alkyl α -protons and aromatic, B) methoxy protons and aromatic, aromatic, C) aromatic protons in NOESY spectrum and D) aromatic protons in COSY spectrum



Scheme S1. Proposed mechanism for the five-membered-ring closure of "meta"-dimethoxy HPB **6** and the formation of a possible intermediate "ortho"-dimethoxy HPB **9**.

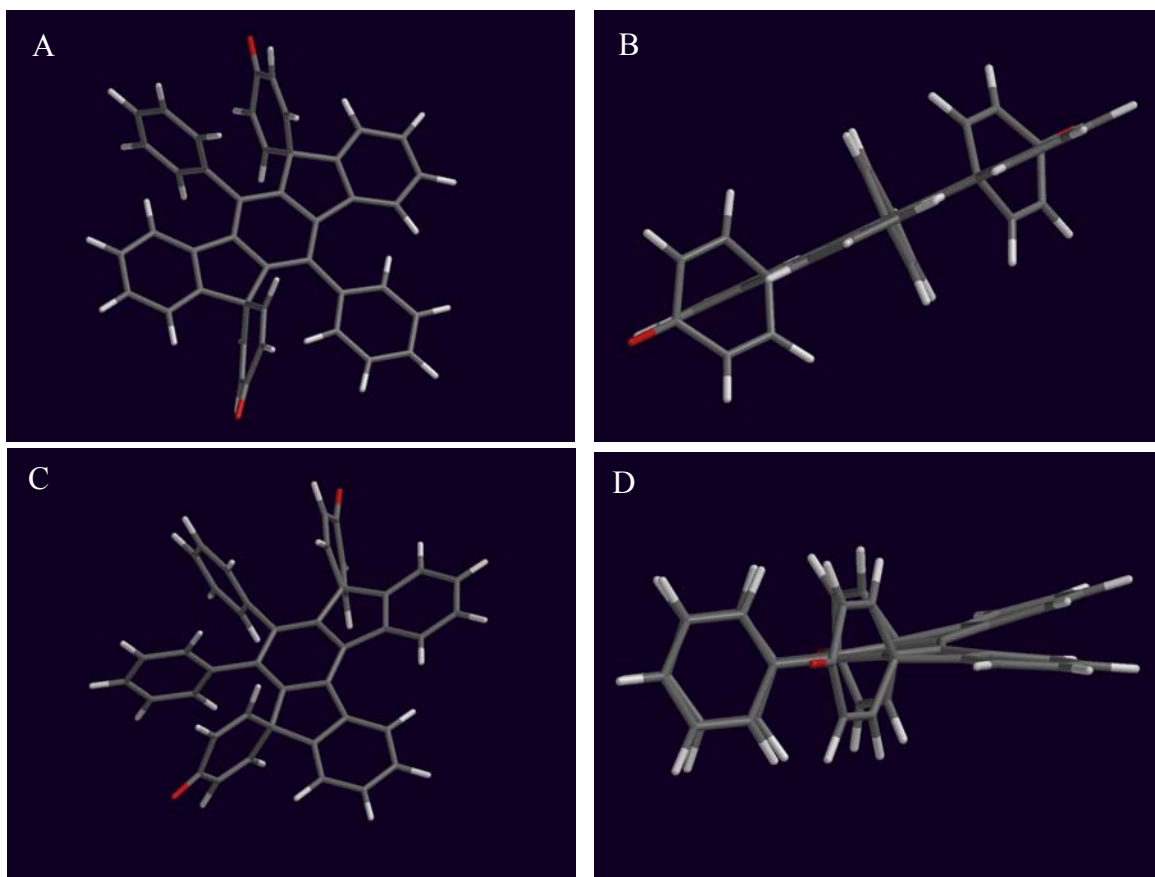


Figure S2. PM3-calculated molecular geometry of compound **4** (A, top view; B, side view) and **7** (C, top view; D, side view). All alkyl chains are neglected to simplify the calculation.