

## Supporting information

### Thermal cyclotrimerization of tetraphenyl[5]cumulene (tetraphenylhexapentaene) to tricyclodecadiene derivative

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Experimental section

#### **1. General Methods:**

Chemicals were obtained from Tokyo Kasei (Tokyo Chemical Industry), Wako (Wako Pure Chemical Industries), Aldrich, and Merck and used as received if not specified otherwise. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a JEOL EX-400 spectrometer with TMS as an internal standard. HPLC analysis was performed on a JASCO high-performance liquid chromatography system equipped with a 4.6 x 250 mm silica gel column (JASCO Finepak<sup>®</sup> SIL) and a HITACHI diode array detector (HITACHI L-2450; detector wavelength = 254 nm; mobile phase, CH<sub>3</sub>CN : H<sub>2</sub>O = 8:2 v/v). UV-VIS spectra were measured with a Hitachi UV-2000 spectrophotometer. Mass spectra were determined by a Shimadzu GC-MS QP-1000 with a direct inlet attachment using an ionizing voltage of 20 and 70 eV. Elemental analyses were performed by using Yanaco MT-5 instrument at the microanalytical laboratory of this university. X-ray crystallographic analysis was performed with a Rigaku RAXIS-RAPID instrument

(Rigaku Corporation). A software, “CrystalStructure 3.6.0 (Rigaku Corporation)” was used for collecting and solving the data.

## **2. Reaction Details:**

### **Thermal cyclotrimerization of hexapentaene 1 to tricyclodecadiene 2:**

1,1,6,6-Tetraphenyl-1,2,3,4,5-hexapentaene **1** (0.586 g, 1.54 mmol) was refluxed in toluene (50 ml, concentration of the solution 30.8 mmolL<sup>-1</sup>) for 10 ~ 15 min; the color of the solution turned from red to reddish brown. Evaporation of the solvent, separation by column chromatography and recrystallization from EtOAc–hexane afforded nice purple crystals of **2**, 0.392g, (0.343 mmol, 67% yield), mp 168 ~ 170 °C (decomp).

### **Experiments with other concentrations:**

Compound **1** (0.500 g, 1.32 mmol), toluene 30 ml (conc. of the solution 43.8 mmolL<sup>-1</sup>), trimer **2** was obtained 0.341 g (0.299 mmol, 68 % yield).

Compound **1** (0.500 g, 1.32 mmol), toluene 100 ml (conc. of the solution 13.2 mmolL<sup>-1</sup>), trimer **2** was obtained 0.125 g (0.11 mmol, 25 % yield).

Compound **1** (0.500 g, 1.32 mmol), toluene 200 ml (conc. of the solution 6.5 mmolL<sup>-1</sup>). Only uncharacterized gummy materials were afforded.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>ppm</sub> : 6.55–7.60 (m).

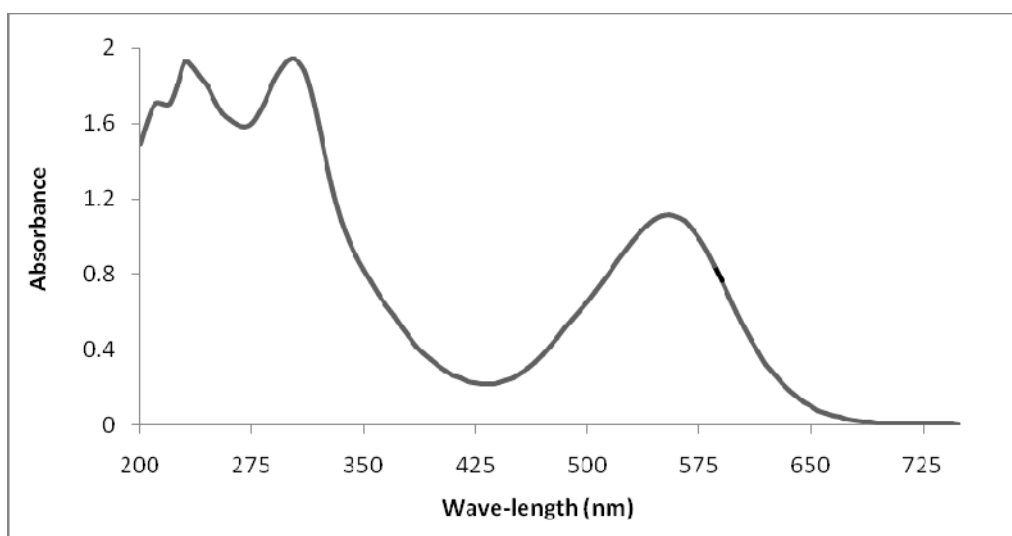
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>ppm</sub>: 117.07, 120.97, 125.95, 126.08, 128.86, 127.09, 127.28, 127.49, 128.52, 130.45, 136.54, 140.53, 144.46, 151.67, 195.74.

**MS** (70 eV) m/e (%):331 (2), 169(8), 168 (62), 167(100), 165(50), 153 (19), 152 (27), 115(11), 91 (30), 89(24), 87(12), 65(21).

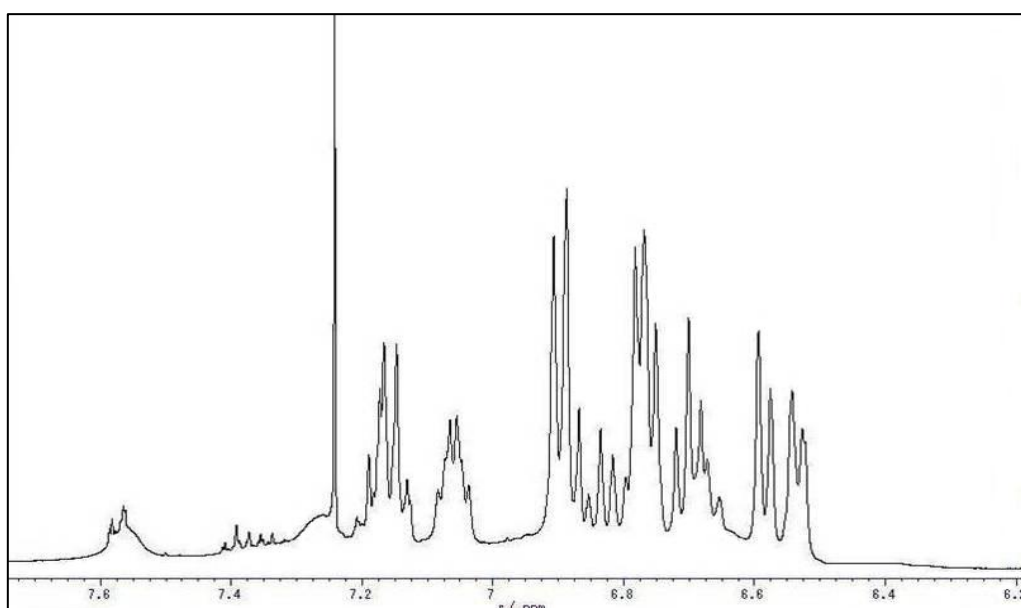
The mass spectrum of the compound does not show the molecular ion peak may be due to less volatility of the compound. A base peak appeared at  $m/e$  167 is assigned to be the cation radical of diphenylmethane.

**UV-VIS** ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 228 (4.10), 302 (3.21), 554(br, 4.81).

**Elemental analysis** for  $\text{C}_{90}\text{H}_{60}\cdot\text{C}_6\text{H}_{14}$ : Found: C, 93.89; H, 6.13; Calcd: C 93.92, H, 6.08



**Fig. 1:** UV-VIS spectrum of trimer **2** in  $\text{CH}_2\text{Cl}_2$



**Fig. 2:**  $^1\text{H}$ -NMR spectrum of trimer **2** in  $\text{CDCl}_3$

### **3. Single Crystal Structure:**

Single crystals of **2** suitable for the determination of X-ray crystal structure were grown by recrystallization from EtOAc–hexane.

**X-ray data:** Empirical formula: C<sub>90</sub>H<sub>60</sub>·C<sub>6</sub>H<sub>14</sub>, Crystal system: Monoclinic, Color: purple, Appearance: prism, Space group: *P2<sub>1</sub>/n*, Unit cell dimensions: *a* = 13.1788(5) Å, *b* = 15.5047(5) Å, *c* = 33.564(1) Å,  $\alpha = 90^\circ$ ,  $\beta = 93.516(1)^\circ$ ,  $\gamma = 90^\circ$ , *V* = 6845.3(4) Å<sup>3</sup>, *Z* = 4, *R* = 0.0690, *R<sub>w</sub>* = 0.1990.

The CIF data of the crystal suggest to contain the hexane solvent molecule. But the molecule precluded a fully acceptable refinement with extremely large thermal ellipsoids and unlikely bond lengths and angles. Although we elaborated to refine the spatial arrangement of solvent molecules by putting a few molecules of hexane in arbitrary positions, we failed to refine the structure even under such conditions. The hydrogens are not positioned due to the same reason. It may be caused by the limitation of our structure-solving software. Under the present circumstances, we decide to leave the hydrogen atoms off. A few of the phenyl rings seem to be also disordered slightly, but the refinement could not be fully done as a result of a similar trial of the refinement of the hexane molecule.

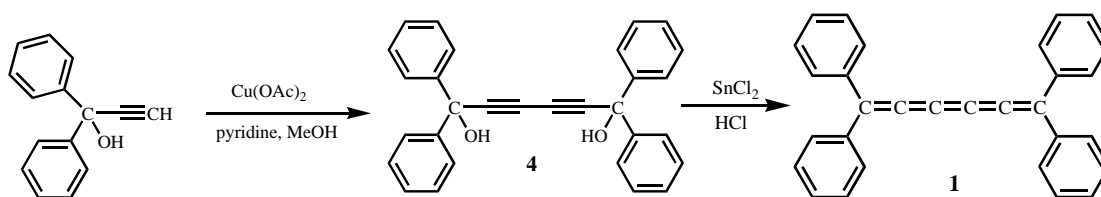
### **4. Procedure for the synthesis of tetraarylhexapentaene 1:**

Tetraarylhexapentaene **1** was prepared following a standard procedure<sup>13</sup>.

**Synthesis of diol 4:** To a stirred solution of 13.082 g (65.52 mmol) of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O in methanol-pyridine (1:1, 100 ml) was added a solution of 6.823 g (32.76 mmol) of 1,1-diphenyl-2-propyn-1-ol in 100 ml of methanol-pyridine (1:1) at 60 °C and the

solution was stirred for 10 hrs at the same temperature. After cooling to room temperature, the solvent was evaporated in *vacuo* and a mixture of 100 ml of ether-CS<sub>2</sub> (v/v = 4/1) and 250 ml of 2M HCl was added to the residue. The aqueous phase was extracted with 2x100 ml of ether-CS<sub>2</sub> (v/v = 4/1) and the combined organic phase was washed successively with 2M HCl, water and brine, and then dried over MgSO<sub>4</sub>. After removal of the solvent in *vacuo*, the residue was purified by recrystallization from ether-hexane to give the diol (11.189 g, 82%), colorless crystals, mp 148-149 °C [Lit<sup>13</sup> 150-151 °C].

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>ppm</sub> : 2.48 (s, 2H), 7.10-7.60 (m, 20H).



**Synthesis of tetraphenylhexapentaene 1:** A solution of 2.071 g (4.99 mmol) of the diol **4** in 25 ml of dry ether was cooled to - 40 °C and then 1.24g (5.50 mmol) of SnCl<sub>2</sub>·2H<sub>2</sub>O and 6.0 ml of ether saturated with gaseous HCl was added. The mixture was allowed to warm to 0 °C and stirred for 1 hr. The resulting orange solid was filtered off and were washed successively with water, EtOH and ether to give cumulene **1** (1.66 g, 87%), mp >290 °C [Lit<sup>13</sup> 298 °C].

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>ppm</sub> : 7.12-7.60 (m).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ<sub>ppm</sub> : 79.3, 113.94, 124.84, 126.10, 130.84, 130.96, 136.71, 196.90.

MS (70 eV) m/e (%): 380(M<sup>+</sup>, 67), 368 (66), 305 (87), 227(100).

**UV-VIS** (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 360 (2.50), 472 (5.98).

Elemental analysis for C<sub>30</sub>H<sub>20</sub>: Found: C, 94.59; H, 5.41; Calcd: C, 94.70; H, 5.30.