Supporting Information

Synthesis and Properties of All-Benzene Carbon Nanocages: A Junction Unit of Branched Carbon Nanotubes

Katsuma Matsui,[†] Yasutomo Segawa,*[,†] Tomotaka Namikawa,[‡,§] Kenji Kamada,*[‡,§] and Kenichiro Itami*[,†]

[†] *Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya 464-8602, Japan* [‡] *Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan* [§] *Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda, Hyogo 669-1337, Japan*

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1. Experimental Section

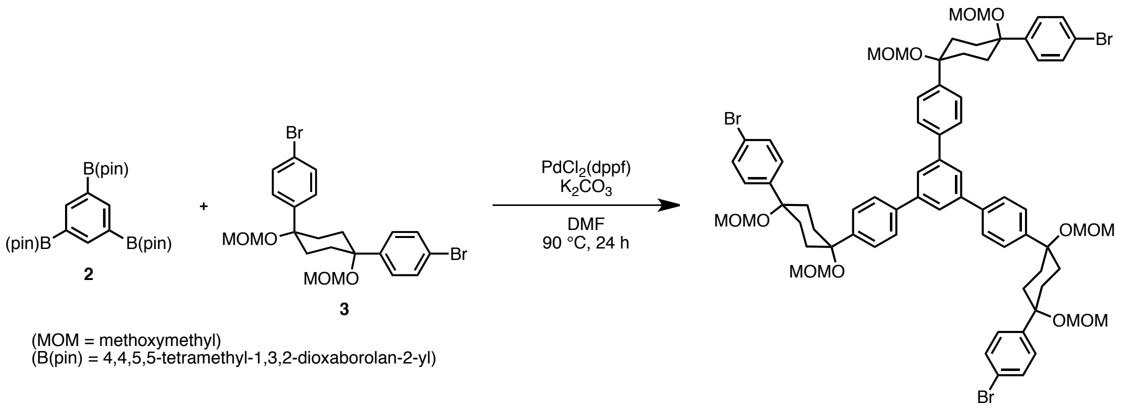
General

Unless otherwise noted, all materials including dry solvents (dimethyl formamide (DMF)) and dimethyl sulfoxide (DMSO) were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF), dichloromethane, and *m*-xylene were purified by passing through a solvent purification system (Glass Contour). All reactions were performed using standard vacuum-line and Schlenk techniques. Work-up and purification procedures were carried out with reagent-grade solvents under air. 1,3,5-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**2**) [S1] and *cis*-1,4-bis(4-dibromophenyl)-1,4-bis(methoxymethyloxy)cyclohexane (**3**) [S2] were synthesized following the reported procedures.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). Preparative thin-layer chromatography (PTLC) was performed using Wako-gel® B5-F silica coated plates (0.75 mm) prepared in our laboratory. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent. High-resolution mass spectra (HRMS) were obtained from JEOL JMS700 (fast atom bombardment mass spectrometry, FAB-MS) or Bruker Daltonics Ultraflex III TOF/TOF (MALDI-TOF-MS) with 9-nitroanthracene as matrix. Melting points were measured on a MPA100 Optimelt automated melting point system. Nuclear magnetic resonance (NMR) spectra were recorded on JEOL JNM-ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CHCl_3$ (δ 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

S1) Liu, Y.; Niu, F.; Lian, J.; Zheg, P.; Niu, H. *Synth. Mat.* **2010**, *160*, 2055.
S2) Omachi, H.; Matsuura, S.; Segawa, Y.; Itami, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 10202.

Synthesis of 4

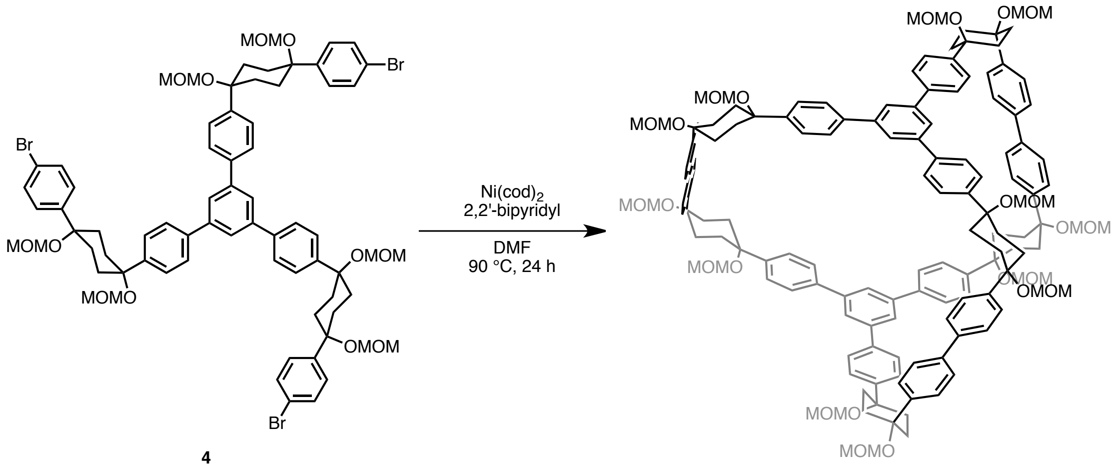


4
53%

To a 500-mL round-bottom flask containing a magnetic stirring bar were added 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene **2** (1.82 g, 3.99 mmol), *cis*-1,4-bis(4-bromophenyl)-1,4-bis(methoxymethoxy)cyclohexane **3** (20.6 g, 40.1 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (32.2 mg, 39.4 μmol), K_2CO_3 (5.53 g, 40.0 mmol), and the flask was evacuated and backfilled with argon three times. Then to this flask was added dry DMF (200 mL). The reaction mixture was stirred at 90 °C for 24 h. After cooled down to room temperature, the mixture was extracted with EtOAc, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 5:1 - 1:1) to afford **4** (2.91 g, 53%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.10 (brs, 12H), 2.35 (brs, 12H), 3.41 (s, 9H), 3.43 (s, 9H), 4.44 (s, 6H), 4.48 (s, 6H), 7.33 (d, J = 8.6 Hz, 6H), 7.45 (d, J = 8.6 Hz, 6H), 7.52 (d, J = 8.1 Hz, 6H), 7.63 (d, J = 8.1 Hz, 6H), 7.73 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.9 (CH_2), 56.0 (CH_3), 77.8 (4°), 78.0 (4°), 92.1 (CH_2), 92.2 (CH_2), 121.6 (4°), 125.0 (CH), 127.2 (CH), 127.3 (CH), 128.7 (CH), 131.5 (CH), 140.2 (4°), 141.7 (4°); HRMS (FAB) *m/z* calcd for $C_{72}H_{81}Br_3O_{12}Na$ $[M+Na]^+$: 1397.3170, found 1397.3158; mp: 103.4–120.0 °C.

Synthesis of 5



4

5
12%

To a 100-mL round-bottom flask containing a magnetic stirring bar were added **4** (139 mg, 101 μmol), $Ni(cod)_2$ (91.1 mg, 331 μmol), and 2,2'-bipyridyl (52.6 mg, 337 μmol). Then to this flask was added dry DMF (50 mL). The reaction mixture was stirred at 90 °C for 24 h. After cooled down to room temperature, the mixture was extracted with EtOAc, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by GPC and PTLC ($CHCl_3$) to afford **5** (13.6 mg, 12%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$, 50 °C) δ 2.13 (brs, 12H), 2.20 (brs, 12H), 2.35–2.48 (m, 24H), 3.41 (s, 18H), 3.43 (s, 18H), 4.47 (s, 24H), 7.48 (d, *J* = 8.4 Hz, 24H), 7.51 (d, *J* = 8.4 Hz, 12H), 7.55 (d, *J* = 8.4 Hz, 12H), 7.63 (d, *J* = 8.4 Hz, 12H), 7.76 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.8 (CH_2), 56.0 (CH_3), 56.1 (CH_3), 78.0 (4°), 92.17 (CH_2), 92.24 (CH_2), 124.7 (CH), 126.8 (CH), 127.0 (CH), 127.2 (CH), 127.5 (CH), 139.6 (4°), 139.9 (4°), 141.5 (4°); HRMS (FAB) *m/z* calcd for $C_{144}H_{162}O_{24}Na$ $[M+Na]^+$: 2298.1348, found 2298.1353; mp: partially decomposed at 300 °C.

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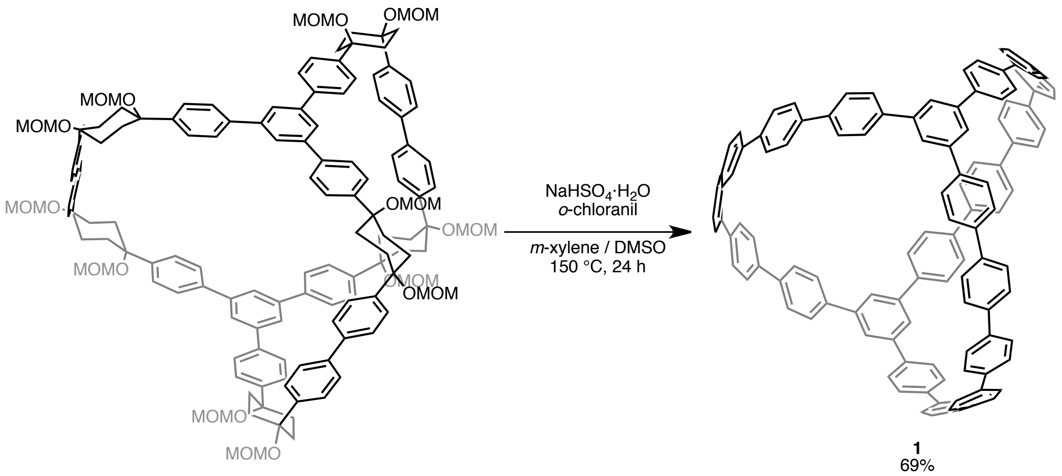
Synthesis of carbon nanocage 1



5

1
69%

To a 20-mL Schlenk tube containing a magnetic stirring bar were added **5** (13.0 mg, 5.71 μmol), $NaHSO_4 \cdot H_2O$ (23.7 mg, 172 μmol), *o*-chloranil (6.96 mg, 28.3 μmol), dry *m*-xylene (2.5 mL) and dry DMSO (0.5 mL). The reaction mixture was stirred at 150 °C for 24 h under air. After cooled down to room temperature, the mixture was extracted with $CHCl_3$, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by PTLC (hexane/CH_2Cl_2 = 1:1) to afford 1,8(1,3,5),2,3,4,5,6,7,9,10,11,12,13,14,15,16,17,18,19,20(1,4)-icosabenzenabicyclo[6.6.6]icosaphane (**1**) (6.0 mg, 69%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.590 (d, *J* = 8.4 Hz, 12H), 7.593 (d, *J* = 8.6 Hz, 24H), 7.67 (d, *J* = 8.6 Hz, 12H), 7.69 (d, *J* = 8.6 Hz, 12H), 7.77 (d, *J* = 8.4 Hz, 12H), 7.85 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 124.6 (CH_2), 127.08 (CH_2), 127.13 (CH_2), 127.4 (CH_2), 127.5 (CH_2), 127.7 (CH_2), 127.8 (CH_2), 138.3 (4º), 138.4 (4º), 138.8 (4º), 139.0 (4º), 139.3 (4º), 139.6 (4º), 141.5 (4º); HRMS (MALDI-TOF) *m/z* calcd for $C_{120}H_{78}$ $[M]^+$: 1518.6104, found 1518.6111; mp: not decomposed nor melted over 300 ºC.

2. Photophysical Study

General

UV/vis absorption spectra were recorded on a Shimadzu UV- 3510 spectrometer with a resolution of 0.5 nm. Emission spectra were measured with an F-4500 Hitachi spectrometer with a resolution of 0.2 nm. Dilute solutions in degassed spectral grade chloroform in a 1 cm square quartz cell were used for measurements. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920-02 calibrated integrating sphere system equipped with multichannel spectrometer (PMA-11). Fluorescence lifetimes were measured with a Hamamatsu Picosecond Fluorescence Measurement System C4780 equipped with a USHO pulsed nitrogen laser (excitation wavelength 337 nm with a repetition rate of 10 Hz).

Two-Photon Absorption

Two-photon absorption (TPA) spectrum was measured by using the open-aperture Z-scan method[S3] with the homemade setup reported previously.[S4] A femtosecond optical parametric amplifier (Spectra-Physics OPA-800) operating at a repetition rate of 1 kHz was used as light source to scan the wide range of excitation wavelength (484–692 nm). The output beam of the parametric amplifier passed through a small iris to obtain near Gaussian spatial profile. The pulsewidth was measured by an autocorrelator (typically 118 fs in FWHM for Gaussian pulse). The Rayleigh range z_R of the optical setup was 7–14 mm depending on the wavelengths employed. The sample solutions were held in a quartz cuvette (path length L = 2 mm), which is shorter then the z_R and satisfied the “optically thin” condition $L << z_R$.[S3] Measurements were repeated at least four times by varying the incident laser power P_i in the range of 0.05–0.35 mW at each wavelength. Prior to each set of measurements, the neat solvent (spectroscopic grade chloroform) was measured under the same conditions, to confirm the absence of unwanted nonlinear optical effects such as induced Raman effect, appearing as sharp dip in Z-scan trace. The on-axis peak intensity I_0 employed was less than 180 GW cm^{-2} at the focus.

Typical recorded Z-scan traces are shown in Figures S1 and S2. Every recorded Z-scan trace was analyzed by the curve fitting procedure with the theoretical model of the transmittance of a spatially and temporally Gaussian pulse through two-photon absorptive media.[S4] From the curve fitting the two-photon absorbance of the sample $q_0 = \alpha^{(2)} I_0 L$ was obtained, where $\alpha^{(2)}$ is

S3) Sheik-Bahae, M.; Said, A. A.; Wei, T.-H.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760.
S4) Kamada, K.; Matsunaga, K.; Yoshino, A.; Ohta, K. *J. Opt. Soc. Am. B* **2003**, *20*, 529.

the TPA coefficient. The proportionality relation of q_0 against I_0, therefore P_i, was confirmed (Figures S3 and S4), which verified that the observed signal arose from the TPA process. TPA cross section $\sigma^{(2)}$ was calculated based on the convention $\sigma^{(2)} = E_{ph}\alpha^{(2)}/N$, where N is the number density of the molecules in the sample calculated from the molar concentration and E_{ph} is the photon energy of the incident laser light. Finally, $\sigma^{(2)}$ spectrum was obtained by repeating the measurements for different wavelengths.

The obtained $\sigma^{(2)}$ values were calibrated based on the reported values of 1,4-bis(2-methylstyryl)benzene (bis-MSB)[S5] as a reference material, measured at the same condition (a chloroform solution, 20 mM). As there are no reported values at a wavelength shorter than 537 nm, we also measured a GaN single crystal (thickness 280 μm, semi-insulating, from Shinyo Co. Ltd.) together with the bis-MSB solution. First, the recorded $\alpha^{(2)}$ spectral shape of GaN was calibrated by using the theoretical equation of the TPA spectral shape of GaN,[S6] then the $\sigma^{(2)}$ values of bis-MSB at wavelengths of 484–537 nm was corrected based on the calibrated $\alpha^{(2)}$ spectrum of GaN, with keeping the consistency with the available reported $\sigma^{(2)}$ values of bis-MSB at 540–600 nm.[S7] Furthermore, at a wavelength longer than 600 nm, our in-house standard compound, 1,4-bis(2,5-dimethoxy-4-{2-[4-(*N*-methyl)pyridin-1-iumyl]ethenyl}phenyl)butadiyne triflate (MPPBT),[S8] was also measured to check the consistency of the reference $\sigma^{(2)}$ values.

The sample solution of **1** in spectroscopic grade chloroform (0.57 mM) was prepared under the ambient condition. The linear oligoparaphenylene, 2''',5'''-didecyl-1,1':4',1'':4'',1''':4''',1'''':4'''',1''''':4''''',1''''''-septiphenyl (2''',5'''-didecyl-*p*-septiphenyl) gifted from Dr. Teruhiro Shiono, Panasonic Corp. was used as received. The chloroform solution of 2''',5'''-didecyl-*p*-septiphenyl (15 mM) was also prepared under the ambient condition. No sign of degradation was observed for both samples after TPA measurements.

S5) Kennedy, S. M.; Lytle, F. E. *Anal. Chem.* **1986**, *58*, 2643.
S6) Sheik-Bahae, M.; Hutchings, D. C.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **1991**, *27*, 1296.
S7) Detailed procedure is in preparation to be presented elsewhere.
S8) Kamada, K.; Iwase, Y.; Sakai, K.; Kondo, K.; Ohta, K. *J. Phys. Chem. C* **2009**, *113*, 11469.

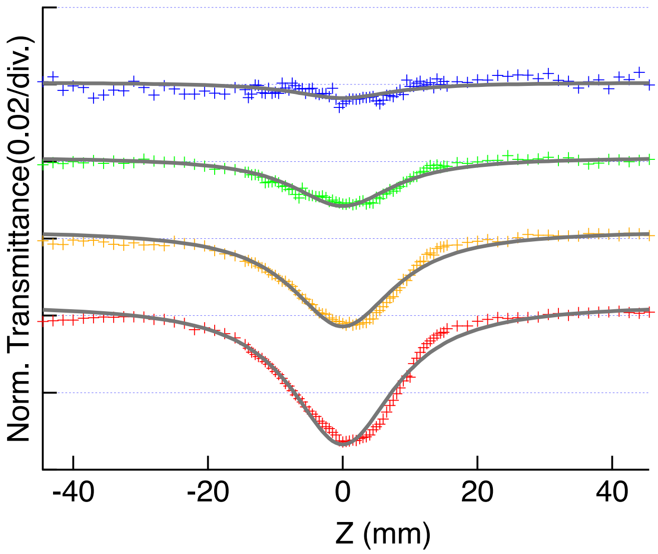


Figure S1. Recorded open-aperture Z-scan traces of **1** in chloroform (0.57 mM) at 573 nm (symbols) with different incident powers (from top to bottom, P = 0.04, 0.12, 0.21, 0.30 mW) with the theoretical curve fits (solid curves). The horizontal axis is the sample position z and the vertical axis is the transmittance normalized to that far away (|z| >> z_R) from the focus (z = 0). Each trace is shifted by 0.02 for readability.

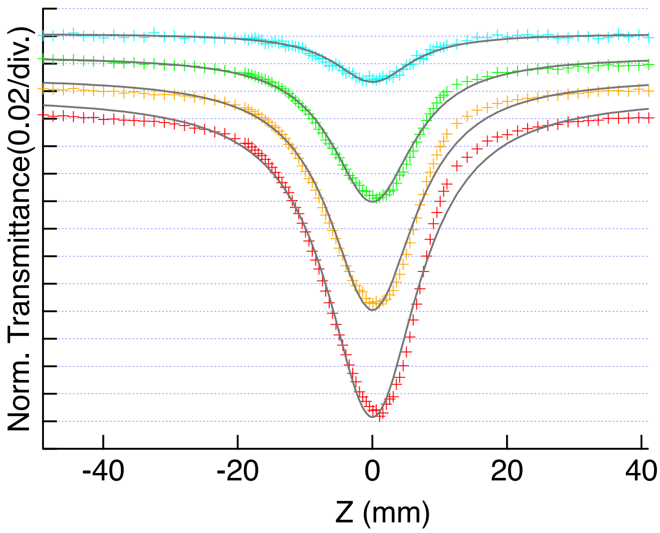


Figure S2. Recorded open-aperture Z-scan traces of 2''',5'''-didecyl-*p*-septiphenyl in chloroform (15 mM) at 510 nm (symbols) with different incident powers (from top to bottom, P_i = 0.05, 0.14, 0.24, 0.34 mW) with the theoretical curve fits (solid curves). The horizontal axis is the sample position z and the vertical axis is the transmittance normalized to that far away (|z| >> z_R) from the focus (z = 0). Each trace is shifted by 0.02 for readability.

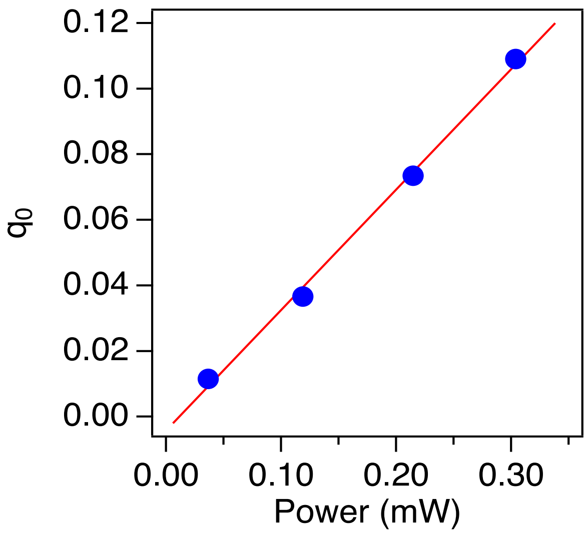


Figure S3. Plot of q_0 versus P_i for the solution of **1**. The q_0 values were obtained from the curve fits in Figure S1.

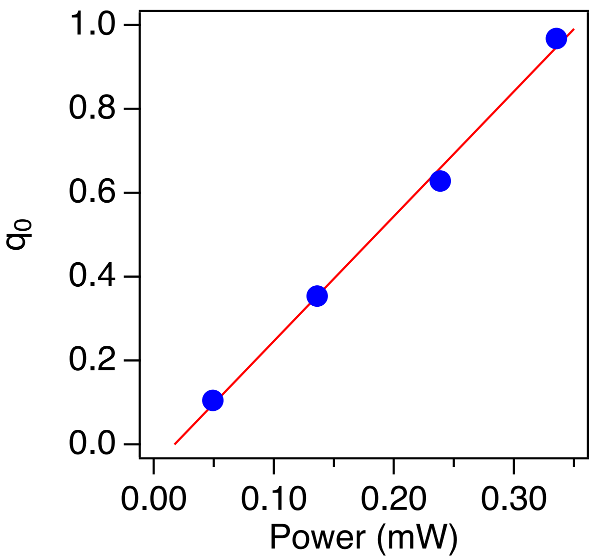


Figure S4. Plot of q_0 versus P_i for the solution of 2''',5'''-didecyl-*p*-septiphenyl. The q_0 values were obtained from the curve fits in Figure S2.

3. Computational Study

The Gaussian 09 program[S9] running on a SGI Altix4700 system was used for optimization, TD-DFT (B3LYP/6-31G(d)).[S10] Structure of **1** was optimized with D_3 symmetry assumptions and other structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies. Harmonic vibration frequency calculation at the same level was performed to verify all stationary points as local minima (with no imaginary frequency). Visualization of the results was performed by use of GaussView 5.0.9 software.

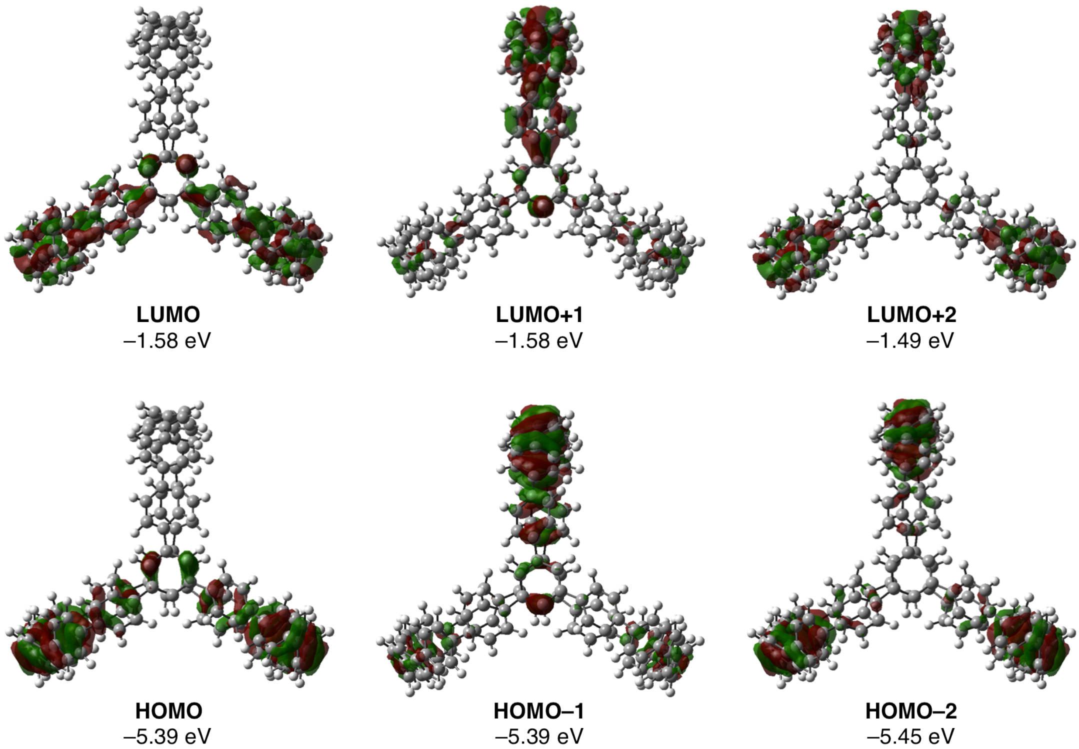


Figure S5. Frontier molecular orbitals of **1**.

S9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
S10) a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652; b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

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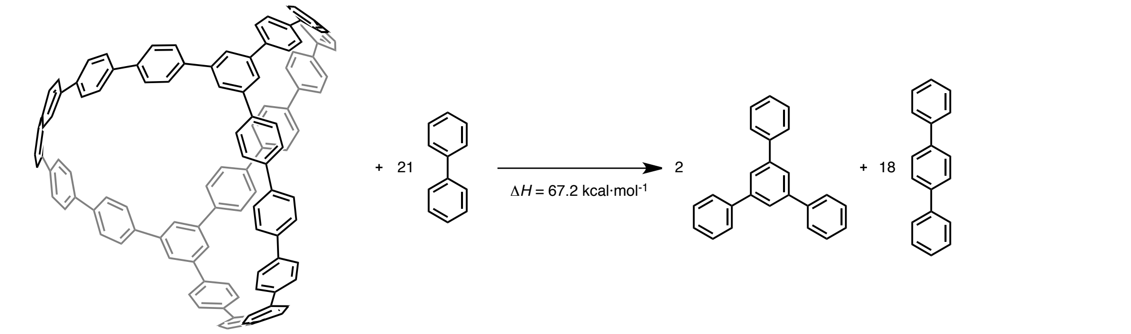
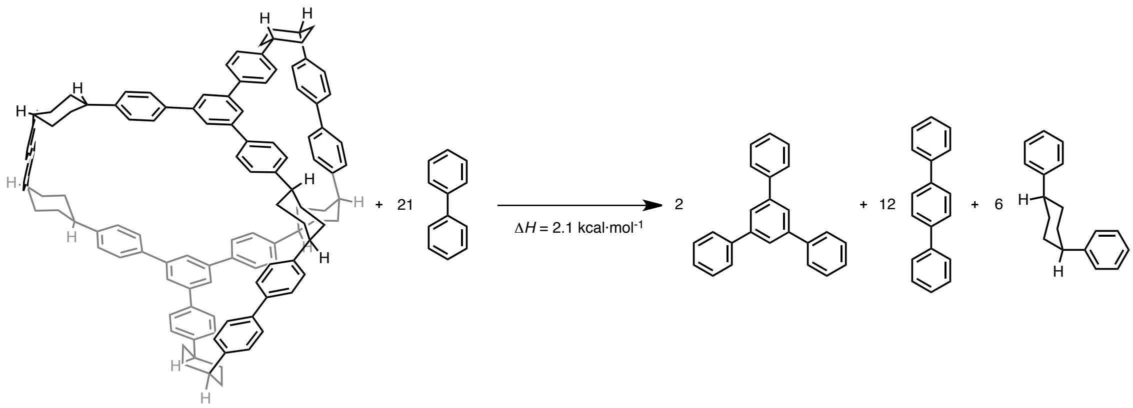


1



5-H

Scheme S1. Structure of **1**, model structure of **5** (**5-H**), and homodesmotic reactions for calculation of strain energies for **1** and **5-H**.

Table S1. Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree).[a]

compound	*E*	*E* + *ZPE*	*H*	*G*
Ph_3benzene	-925.058193	-925.076505	-925.057249	-925.124685
5-H	-4639.497600	-4639.593794	-4639.496655	-4639.735677
1	-4618.161421	-4618.250896	-4618.160477	-4618.381245

a) E: electronic energy; ZPE: zero-point energy; H (= E + ZPE + E_{vib} + E_{rot} + E_{trans} + RT): sum of electronic and thermal enthalpies; G (= $H - TS$): sum of electronic and thermal free energies.

Table S2. Cartesian coordinates for 1,3,5-triphenylbenzene, **5-H**, and **1**.

1,3,5-triphenylbenzene

C	-1.38791600	0.05242900	-0.01231700	C	0.65097200	-1.23167500	-0.01529800	H	1.15975500	-2.19127900	-0.01680600
C	-0.65822500	1.24819200	-0.01287800	C	-0.75057700	-1.19609300	-0.01616600	C	-1.54259400	-2.45493100	-0.00800700
C	0.74277200	1.17720100	-0.01437000	H	-2.47423500	0.09135000	-0.01141600	C	-1.12929400	-3.57112400	-0.75381000
C	1.41177000	-0.05472200	-0.01328500	H	1.32311700	2.09613000	-0.01499100	C	-2.72222900	-2.56281900	0.74897600

C	-1.86568900	-4.75458700	-0.74208100	C	3.65539300	0.79573900	-0.77049200	C	-0.86867800	3.63537200	0.76069900
H	-0.23307800	-3.49976700	-1.36427700	C	4.97655700	-1.10557600	0.77798000	C	-2.52097000	2.76347500	-0.76274000
C	-3.45897100	-3.74588600	0.76131400	H	3.01824000	-1.74874900	1.39061500	C	-1.52483900	4.86550400	0.77059100
H	-3.04605800	-1.72056000	1.35529800	C	5.04858900	0.74889900	-0.76131800	H	0.01680900	3.49005100	1.37369100
C	-3.03508900	-4.84684600	0.01494800	H	3.14680500	1.52066000	-1.40013500	C	-3.17974400	3.99203500	-0.75051700
H	-1.52772400	-5.60397200	-1.33082000	C	5.71605300	-0.20114800	0.01307600	H	-2.90265300	1.95710100	-1.38241900
H	-4.36298000	-3.81022900	1.36186100	H	5.48364200	-1.84405900	1.39346000	C	-2.68431900	5.04881800	0.01501900
H	-3.61170300	-5.76819400	0.02202900	H	5.61355300	1.45290600	-1.36761700	H	-1.13382400	5.67797000	1.37751700
C	2.89787400	-0.10756800	-0.00563300	H	6.80244700	-0.23503500	0.02002300	H	-4.07723200	4.12778000	-1.34920600
C	3.58357200	-1.05719500	0.77034900	C	-1.35383200	2.56272100	-0.00722000	H	-3.19838700	6.00661500	0.02226200

5-H

C	1.33993100	-0.75197900	6.09711700	C	-2.17078600	-3.41277300	6.69788200	H	-5.28281000	-5.86685100	6.40633300
C	0.28546000	-1.67491200	6.04320800	C	-4.26523100	-2.95272500	4.93343000	C	-7.94509200	-5.53423400	5.53490700
C	-1.05151600	-1.25410900	6.02536300	H	-3.23251800	-1.14370500	4.41351800	H	-6.90500200	-3.70224000	4.99774100
C	-1.32413500	0.12037400	6.07193700	C	-3.21808500	-4.32784700	6.59342400	H	-6.90274500	-4.04519200	6.71642200
C	-0.29293100	1.06844600	6.13072400	H	-1.36542300	-3.59632900	7.40441500	C	-6.41906500	-6.99518900	4.16530200
C	1.03389400	0.61558600	6.14487800	C	-4.28699500	-4.11990800	5.71193800	H	-5.38676400	-5.24302000	3.41528300
H	0.50878300	-2.73711700	6.00072100	H	-5.06249800	-2.76083000	4.22001000	H	-4.32857600	-6.41497500	4.19124400
H	-2.35628900	0.45815800	6.05022600	H	-3.20730400	-5.22093700	7.21504400	C	-7.84209700	-6.38129200	4.24594600
H	1.84276700	1.33968400	6.18008800	C	-0.60249600	2.52184200	6.14421900	H	-8.91673900	-5.02660100	5.58304100
C	2.75350300	-1.20934100	6.06549000	C	-1.64811100	3.04072500	6.92420600	H	-7.92753900	-6.23260000	6.38324600
C	3.73187900	-0.63122400	6.88945400	C	0.13248500	3.42309900	5.35849200	H	-6.30425800	-7.57096500	3.23993600
C	3.16003600	-2.22526000	5.18639200	C	-1.94229500	4.40245800	6.91235100	H	-6.30597700	-7.71089100	4.99277600
C	5.05866000	-1.05287700	6.82927800	H	-2.21972600	2.37362700	7.56419200	H	-8.54438800	-7.22044700	4.35874400
H	3.44552800	0.14000200	7.59984100	C	-0.17321000	4.78242000	5.34165200	C	6.93965700	-2.43704100	5.84371800
C	4.48994700	-2.63492800	5.12207500	H	0.93419200	3.04873100	4.72751300	C	7.19208100	-3.94685600	5.65705900
H	2.42977300	-2.67749000	4.52062000	C	-1.21830900	5.30308700	6.11799900	C	7.63635000	-1.64102500	4.71336100
C	5.47013700	-2.05711300	5.94162100	H	-2.75181200	4.77658500	7.53630200	H	7.41779800	-2.14253100	6.79091200
H	5.79276300	-0.59246200	7.48783700	H	0.40890500	5.43967900	4.70216400	C	8.69165200	-4.26146300	5.55968400
H	4.76273300	-3.40898800	4.41031400	C	-5.40545000	-5.14213800	5.58676500	H	6.69933300	-4.30016500	4.74261000
C	-2.15879000	-2.24063200	5.92727000	C	-6.80829800	-4.51240200	5.72785500	H	6.74441800	-4.50337300	6.49002300
C	-3.22901500	-2.02962800	5.04294600	C	-5.31323300	-5.93674800	4.26383900	C	9.12635400	-1.99985300	4.57590800

H	7.10558400	-1.83957100	3.77442300	H	-1.21466600	8.33892100	0.22237800	H	9.44815800	-6.11782900	3.54998700
H	7.53102300	-0.56578400	4.90568100	C	1.04221100	9.74441700	-0.34863500	C	8.27192300	-3.80780400	0.70021400
C	9.38316400	-3.51201300	4.39142400	C	2.44648800	9.78723900	-0.36647700	H	8.52041000	-2.19065600	2.06533900
H	8.83917000	-5.34335400	5.47135800	C	0.38697100	9.70198900	-1.58743300	C	8.33993500	-5.18816600	0.46487000
H	9.18583500	-3.96065000	6.49469300	C	3.15246300	9.74688700	-1.56433500	H	8.88201300	-7.06962800	1.37416400
H	9.58305800	-1.42352300	3.76220200	H	2.99310800	9.81663400	0.57231000	H	7.92271000	-3.14745800	-0.08884600
H	9.64713500	-1.68746000	5.49183300	C	1.10040700	9.66290200	-2.78576800	C	7.93843400	-5.75829800	-0.84441400
H	10.46617400	-3.67354900	4.50371900	H	-0.69926300	9.71312600	-1.61859100	C	7.25111600	-6.98102000	-0.92926200
C	-1.61756000	6.77017300	6.07160600	H	4.23874200	9.77481400	-1.52819100	C	8.19904000	-5.08592200	-2.04675800
C	-0.43022000	7.75042700	5.98922600	H	0.54065300	9.64106500	-3.71467200	C	6.81427600	-7.47754300	-2.15307800
C	-2.59985100	7.03532100	4.90496700	C	-8.22967500	-5.67813300	2.94290800	H	7.02493200	-7.53259500	-0.02062700
H	-2.15665200	6.99100800	7.00607600	C	-8.28087000	-6.43103600	1.75687800	C	7.75890200	-5.58904600	-3.27126400
C	-0.90544700	9.20986200	5.95438900	C	-8.55662000	-4.32028300	2.84173900	H	8.76790400	-4.16015900	-2.02947400
H	0.15923500	7.55134000	5.08529200	C	-8.59372800	-5.85283600	0.53192700	H	6.28066300	-8.42479600	-2.16853300
H	0.24095300	7.59372400	6.84296400	H	-8.07863000	-7.49925600	1.79463100	H	7.99970900	-5.03148700	-4.16976300
C	-3.03388800	8.50981400	4.83112900	C	-8.86022000	-3.73213400	1.61302900	C	6.50351500	-7.37240100	-4.66825500
H	-2.11487800	6.72905800	3.97001400	H	-8.56773200	-3.69316000	3.72631000	C	6.79035400	-6.54227900	-5.93968700
H	-3.48386500	6.39518400	5.01854000	C	-8.86919000	-4.47794600	0.42569300	C	4.98064300	-7.66000700	-4.60805200
C	-1.85177700	9.50126600	4.76061400	H	-8.64090100	-6.47973800	-0.35430700	H	7.00772200	-8.34209600	-4.79677300
H	-0.04007000	9.88139800	5.93842500	H	-9.05740700	-2.66437300	1.57668100	C	5.92669300	-5.27374400	-6.07661500
H	-1.45051900	9.43509900	6.88228900	C	-9.12334900	-3.83362700	-0.88649300	H	6.59274900	-7.19194200	-6.80367800
H	-3.72184400	8.66249400	3.99069700	C	-9.97620500	-2.72259500	-1.01164100	H	7.85418500	-6.28074600	-5.99934200
H	-3.61009300	8.74915900	5.73584400	C	-8.49401700	-4.28915600	-2.05380000	C	4.13873300	-6.37902600	-4.66276900
H	-2.26445600	10.50928100	4.91912300	C	10.14735000	-2.08142100	-2.23334800	H	4.71932100	-8.29929400	-5.46382600
C	-1.11858100	9.54581800	3.41448500	H	10.52517900	-2.36654300	-0.14415200	H	4.73026500	-8.23310800	-3.70857900
C	0.02108000	10.35458500	3.26345100	C	-8.67801600	-3.64822600	-3.27972300	C	4.41589500	-5.56828300	-5.95000300
C	-1.55161500	8.85033400	2.27709700	H	-7.81772800	-5.13784500	-2.00175900	H	6.12737500	-4.79690400	-7.04456400
C	0.71008200	10.43603300	2.05693200	H	10.82089100	-1.22868900	-2.28611300	H	6.21262900	-4.54457000	-5.31082900
H	0.37548100	10.94671800	4.10342600	H	-8.16597300	-4.04773000	-4.14814800	H	3.07161800	-6.62831500	-4.61080000
C	-0.86497100	8.92782100	1.06595400	C	9.00480700	-4.07170500	3.01441400	H	4.35610900	-5.75511900	-3.78544300
H	-2.43352100	8.22097500	2.32352700	C	9.10097100	-5.45151800	2.76441300	H	4.13169900	-6.20712400	-6.80026100
C	0.28916700	9.71173700	0.92897000	C	8.59975600	-3.26503400	1.94183700	C	-9.69938400	-1.73094900	-4.69700500
H	1.57686300	11.08749100	1.98231000	C	8.77626100	-5.99867900	1.52632100	C	-9.06675300	-2.33940600	-5.96929300

C	-9.23488300	-0.25606300	-4.56564100	C	2.93657400	6.93400400	-5.52248400	C	0.95444900	-0.85096700	-6.06926600
H	10.78684900	-1.70802400	-4.86173800	H	1.43719800	8.05186600	-6.62846800	H	-0.85331900	-2.01930300	-6.10704000
C	-7.54271900	-2.14648100	-6.08942000	H	1.10547200	7.91136400	-4.91182600	C	1.47565000	0.44981000	-6.02395800
H	-9.54431900	-1.85417900	-6.83197100	H	4.49084800	6.27145500	-4.15509400	H	2.55248400	0.59123800	-6.00579700
H	-9.31585200	-3.40519700	-6.04805800	H	3.04577100	6.87406900	-3.35340300	C	2.30918700	5.55694200	-5.67016600
C	-7.70774200	-0.11486400	-4.58991900	H	3.66195900	7.05592400	-6.34153100	C	2.84178600	4.61564700	-6.56069100
H	-9.66201400	0.31518400	-5.40281200	C	2.50177200	9.65682500	-2.80670400	C	1.20908700	5.16186200	-4.89388100
H	-9.63719000	0.18978600	-3.64900300	C	7.03218400	-6.78428800	-3.35603900	C	2.30753000	3.33218900	-6.67022600
C	-7.10691600	-0.67770400	-5.89828600	C	-9.48584100	-2.51033300	-3.39726900	H	3.69051900	4.89263900	-7.18291500
H	-7.20719300	-2.50424900	-7.07125600	C	-5.59763700	-0.49904200	-5.94898300	C	0.66466600	3.88572300	-5.00730800
H	-7.02762200	-2.76554700	-5.34748100	C	-4.73613200	-1.27324500	-5.15704200	H	0.77495300	5.85281000	-4.17580900
H	-7.42610500	0.93984700	-4.48115400	C	-5.01691700	0.47552800	-6.77125900	C	1.20542900	2.94140100	-5.89490800
H	-7.27298600	-0.64457600	-3.73154700	C	-3.35675500	-1.08975500	-5.19647300	H	2.73624500	2.63129400	-7.38187300
H	-7.53560800	-0.09334400	-6.72688000	H	-5.14394300	-2.02611400	-4.48772400	H	-0.17324900	3.60379000	-4.37528100
C	3.33714800	9.58728100	-4.08964800	C	-3.63674300	0.67229100	-6.80529400	C	3.55358800	-4.31787700	-6.01304300
C	2.53578000	9.46761400	-5.40544000	H	-5.65692400	1.08904800	-7.40229600	C	2.45276900	-4.25019700	-6.87702600
C	4.37566000	8.43622700	-4.04787500	C	-2.77739000	-0.11182000	-6.02101000	C	3.79104100	-3.21366500	-5.18055300
H	3.90354700	10.52938500	-4.14170500	H	-2.71817000	-1.69347300	-4.55720500	C	1.61536200	-3.13587700	-6.90398600
C	1.90811300	8.08032300	-5.63757200	H	-3.21765100	1.42502300	-7.46801400	H	2.24637300	-5.08660400	-7.54187700
H	3.23044600	9.67918300	-6.23032200	C	-1.30445900	0.08528200	-6.04425600	C	2.96482800	-2.09335800	-5.21171500
H	1.76204200	10.24355800	-5.45958800	C	-0.75224100	1.37299000	-6.00016600	H	4.62317100	-3.23052400	-4.48137700
C	3.72460900	7.05545000	-4.19741700	C	-0.43769000	-1.01611300	-6.08115500	C	1.85465400	-2.03346300	-6.06967000
H	5.08974900	8.58961200	-4.87005700	C	0.63578700	1.57184800	-5.98539500	H	0.77716100	-3.11107800	-7.59550600
H	4.96073900	8.47434400	-3.12243600	H	-1.41374800	2.23385500	-5.96378600	H	3.16163100	-1.26458200	-4.53679700

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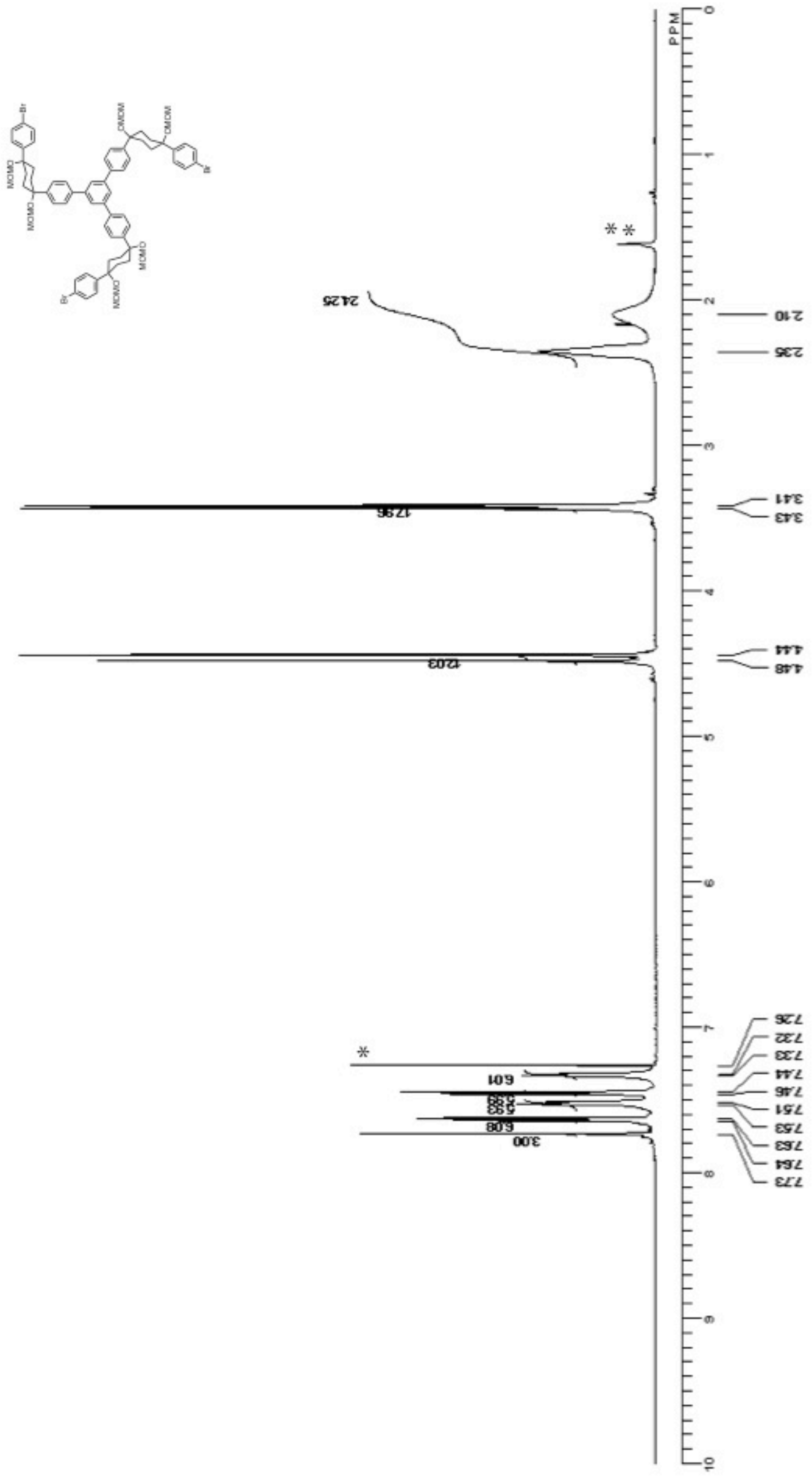
C	0.19301900	-1.37694200	9.19997000	C	-0.37928000	2.85096400	8.89111200	C	-3.59821900	-1.40691600	9.23655900
C	-1.11514400	-0.87108700	9.18018500	C	3.55882700	-0.37990200	8.08387100	C	-1.45040900	3.27198600	8.08387100
C	-1.28897700	0.52131200	9.19997000	C	4.69720300	-0.97929700	7.55917300	C	-1.50050600	4.55754600	7.55917300
C	-0.19681100	1.40128700	9.18018500	C	4.15013800	-3.01976800	8.69775800	C	0.54012700	5.10400900	8.69775800
C	1.09595700	0.85563100	9.19997000	C	3.01753500	-2.41269100	9.23655900	C	0.58068400	3.81960700	9.23655900
C	1.31195600	-0.53020000	9.18018500	C	-2.10841800	-2.89208400	8.08387100	C	-0.19301900	-1.37694200	-9.19997000
C	2.65864700	-1.09701600	8.89111200	C	-3.19669800	-3.57824900	7.55917300	C	-1.31195600	-0.53020000	-9.18018500
C	-2.27936700	-1.75394800	8.89111200	C	-4.69026500	-2.08424100	8.69775800	C	-1.09595700	0.85563100	-9.19997000

C	0.19681100	1.40128700	-9.18018500	H	3.77590800	-0.57429700	-9.91179900	H	1.72858900	6.54371700	6.64834100
C	1.28897700	0.52131200	-9.19997000	H	5.69593100	-1.76196000	-8.95544300	H	-2.41578400	8.83448300	5.21811200
C	1.11514400	-0.87108700	-9.18018500	H	3.02049400	-4.39272100	-6.86261900	H	1.80774400	8.14019000	4.80192200
C	2.27936700	-1.75394800	-8.89111200	H	1.11153200	-3.18941700	-7.77485700	C	-7.27818800	-4.55559600	4.81935300
C	-2.65864700	-1.09701600	-8.89111200	H	-2.38531000	-2.98288400	-9.91179900	C	7.58435500	-4.02529700	4.81935300
C	0.37928000	2.85096400	-8.89111200	H	-4.37386700	-4.05184100	-8.95544300	C	-0.30616800	8.58089300	4.81935300
C	3.59821900	-1.40691600	-9.23655900	H	-5.31445400	-0.41946400	-6.86261900	C	-7.96579200	-2.86576500	-5.51948700
C	4.69026500	-2.08424100	-8.69775800	H	-3.31788200	0.63209300	-7.77485700	C	-6.47783300	-4.73776700	-5.31448200
C	4.51329200	-3.15264200	-7.80177300	H	-1.39059800	3.55718100	-9.91179900	C	-7.19203100	-2.36492800	-6.56188700
C	3.19669800	-3.57824900	-7.55917300	H	-1.32206300	5.81380000	-8.95544300	H	-8.85877900	-2.32511100	-5.21811200
C	2.10841800	-2.89208400	-8.08387100	H	2.29396100	4.81218500	-6.86261900	C	-5.71052700	-4.24375700	-6.36448000
C	-3.01753500	-2.41269100	-9.23655900	H	2.20635000	2.55732300	-7.77485700	H	-6.14573900	-5.63564700	-4.80192200
C	-4.15013800	-3.01976800	-8.69775800	C	-4.51329200	-3.15264200	7.80177300	C	-6.00775300	-3.00802500	-6.96302300
C	-4.98691400	-2.33230400	-7.80177300	C	4.98691400	-2.33230400	7.80177300	H	-7.49047500	-1.44050900	-7.04950000
C	-4.69720300	-0.97929700	-7.55917300	C	-0.47362200	5.48494600	7.80177300	H	-4.80273100	-4.76886000	-6.64834100
C	-3.55882700	-0.37990200	-8.08387100	C	-5.60890300	-3.69885400	6.96302300	C	7.34194300	-3.24108500	-5.31448200
C	-0.58068400	3.81960700	-9.23655900	C	-6.53046500	-2.82358300	6.36448000	C	6.46472100	-5.46569600	-5.51948700
C	-0.54012700	5.10400900	-8.69775800	C	-5.64410300	-5.04601800	6.56188700	C	6.53046500	-2.82358300	-6.36448000
C	0.47362200	5.48494600	-7.80177300	C	-7.34194300	-3.24108500	5.31448200	H	7.95348300	-2.50454200	-4.80192200
C	1.50050600	4.55754600	-7.55917300	H	-6.53131900	-1.77485700	6.64834100	C	5.64410300	-5.04601800	-6.56188700
C	1.45040900	3.27198600	-8.08387100	C	-6.46472100	-5.46569600	5.51948700	H	6.44299500	-6.50937200	-5.21811200
H	0.34611800	-2.44851300	9.13596800	H	-4.99275500	-5.76668800	7.04950000	C	5.60890300	-3.69885400	-6.96302300
H	-2.29353300	0.92451000	9.13596800	H	-7.95348300	-2.50454200	4.80192200	H	6.53131900	-1.77485700	-6.64834100
H	1.94741600	1.52400300	9.13596800	H	-6.44299500	-6.50937200	5.21811200	H	4.99275500	-5.76668800	-7.04950000
H	3.31788200	0.63209300	7.77485700	C	6.00775300	-3.00802500	6.96302300	C	1.50107100	8.33146000	-5.51948700
H	5.31445400	-0.41946400	6.86261900	C	5.71052700	-4.24375700	6.36448000	C	-0.86411000	7.97885200	-5.31448200
H	4.37386700	-4.05184100	8.95544300	C	7.19203100	-2.36492800	6.56188700	C	1.54792800	7.41094600	-6.56188700
H	2.38531000	-2.98288400	9.91179900	C	6.47783300	-4.73776700	5.31448200	H	2.41578400	8.83448300	-5.21811200
H	-1.11153200	-3.18941700	7.77485700	H	4.80273100	-4.76886000	6.64834100	C	-0.81993800	7.06734000	-6.36448000
H	-3.02049400	-4.39272100	6.86261900	C	7.96579200	-2.86576500	5.51948700	H	-1.80774400	8.14019000	-4.80192200
H	-5.69593100	-1.76196000	8.95544300	H	7.49047500	-1.44050900	7.04950000	C	0.39885000	6.70688000	-6.96302300
H	-3.77590800	-0.57429700	9.91179900	H	6.14573900	-5.63564700	4.80192200	H	2.49772100	7.20719600	-7.04950000
H	-2.20635000	2.55732300	7.77485700	H	8.85877900	-2.32511100	5.21811200	H	-1.72858900	6.54371700	-6.64834100
H	-2.29396100	4.81218500	6.86261900	C	-0.39885000	6.70688000	6.96302300	C	-7.58435500	-4.02529700	-4.81935300
H	1.32206300	5.81380000	8.95544300	C	-1.54792800	7.41094600	6.56188700	C	0.30616800	8.58089300	-4.81935300
H	1.39059800	3.55718100	9.91179900	C	0.81993800	7.06734000	6.36448000	C	7.27818800	-4.55559600	-4.81935300
H	-0.34611800	-2.44851300	-9.13596800	C	-1.50107100	8.33146000	5.51948700	C	-8.16251800	-4.37680700	-3.49794100
H	-1.94741600	1.52400300	-9.13596800	H	-2.49772100	7.20719600	7.04950000	C	-8.12817000	-5.68490600	-2.98052600
H	2.29353300	0.92451000	-9.13596800	C	0.86411000	7.97885200	5.31448200	C	-8.58252000	-3.35529000	-2.62774100

C	-8.36175400	-5.93451600	-1.63099800	H	9.58169000	-3.56495400	-3.63509000	C	-9.32031900	-4.27423300	1.63099800
H	-7.87818600	-6.51551000	-3.63509000	C	7.53441500	-5.83922700	-1.28181100	C	-7.53441500	-5.83922700	1.28181100
C	-8.82412600	-3.60538100	-1.28181100	H	6.32525500	-6.29687100	-2.98174400	C	-8.98735800	-4.19674900	2.98052600
H	-8.61587800	-2.32939600	-2.98174400	H	10.16365300	-3.69848700	-1.25857400	H	10.16365300	-3.69848700	1.25857400
H	-8.28481000	-6.95273900	-1.25857400	H	6.92005300	-6.44510000	-0.62206400	C	-7.19702600	-5.75503500	2.62774100
H	-9.04164700	-2.77039200	-0.62206400	C	-8.65059100	-4.88866100	-0.73618000	H	-6.92005300	-6.44510000	0.62206400
C	0.29083300	9.25735200	-3.49794100	C	0.09159100	9.93596200	-0.73618000	C	-7.87168500	-4.88054500	3.49794100
C	-0.85918800	9.88165500	-2.98052600	C	8.55900000	-5.04730200	-0.73618000	H	-9.58169000	-3.56495400	3.63509000
C	1.38549400	9.11032500	-2.62774100	C	-0.09159100	9.93596200	0.73618000	H	-6.32525500	-6.29687100	2.98174400
C	-0.95856500	10.20874900	-1.63099800	C	0.95856500	10.20874900	1.63099800	C	8.65059100	-4.88866100	0.73618000
H	-1.70350400	10.08046400	-3.63509000	C	-1.28971100	9.44460800	1.28181100	C	8.36175400	-5.93451600	1.63099800
C	1.28971100	9.44460800	-1.28181100	C	0.85918800	9.88165500	2.98052600	C	8.82412600	-3.60538100	1.28181100
H	2.29062300	8.62626700	-2.98174400	H	1.87884300	10.65122600	1.25857400	C	8.12817000	-5.68490600	2.98052600
H	-1.87884300	10.65122600	-1.25857400	C	-1.38549400	9.11032500	2.62774100	H	8.28481000	-6.95273900	1.25857400
H	2.12159400	9.21549100	-0.62206400	H	-2.12159400	9.21549100	0.62206400	C	8.58252000	-3.35529000	2.62774100
C	7.87168500	-4.88054500	-3.49794100	C	-0.29083300	9.25735200	3.49794100	H	9.04164700	-2.77039200	0.62206400
C	8.98735800	-4.19674900	-2.98052600	H	1.70350400	10.08046400	3.63509000	C	8.16251800	-4.37680700	3.49794100
C	7.19702600	-5.75503500	-2.62774100	H	-2.29062300	8.62626700	2.98174400	H	7.87818600	-6.51551000	3.63509000
C	9.32031900	-4.27423300	-1.63099800	C	-8.55900000	-5.04730200	0.73618000	H	8.61587800	-2.32939600	2.98174400

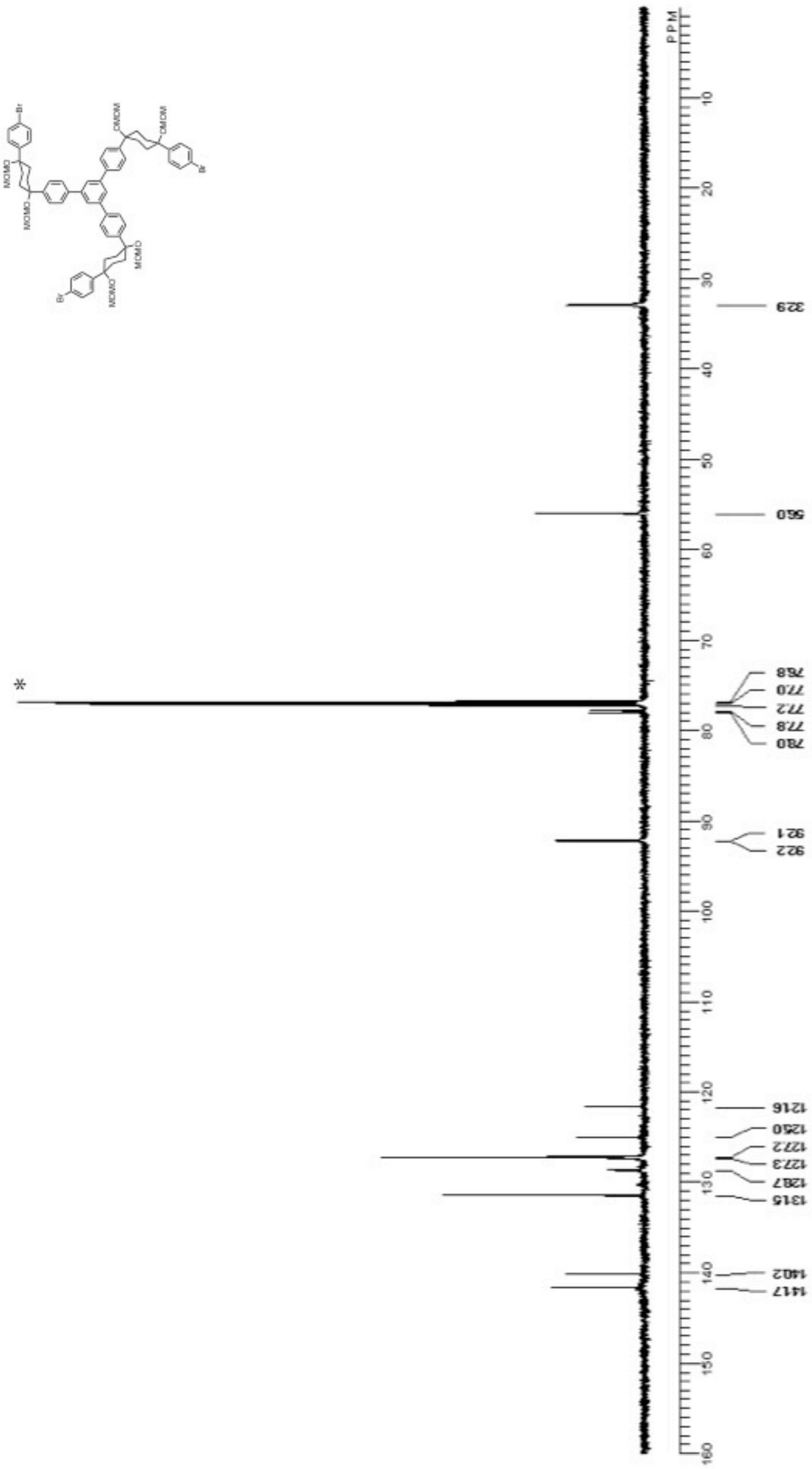
4. Spectra of New Products

^{1}H NMR spectrum of **4** ($CDCl_3$)



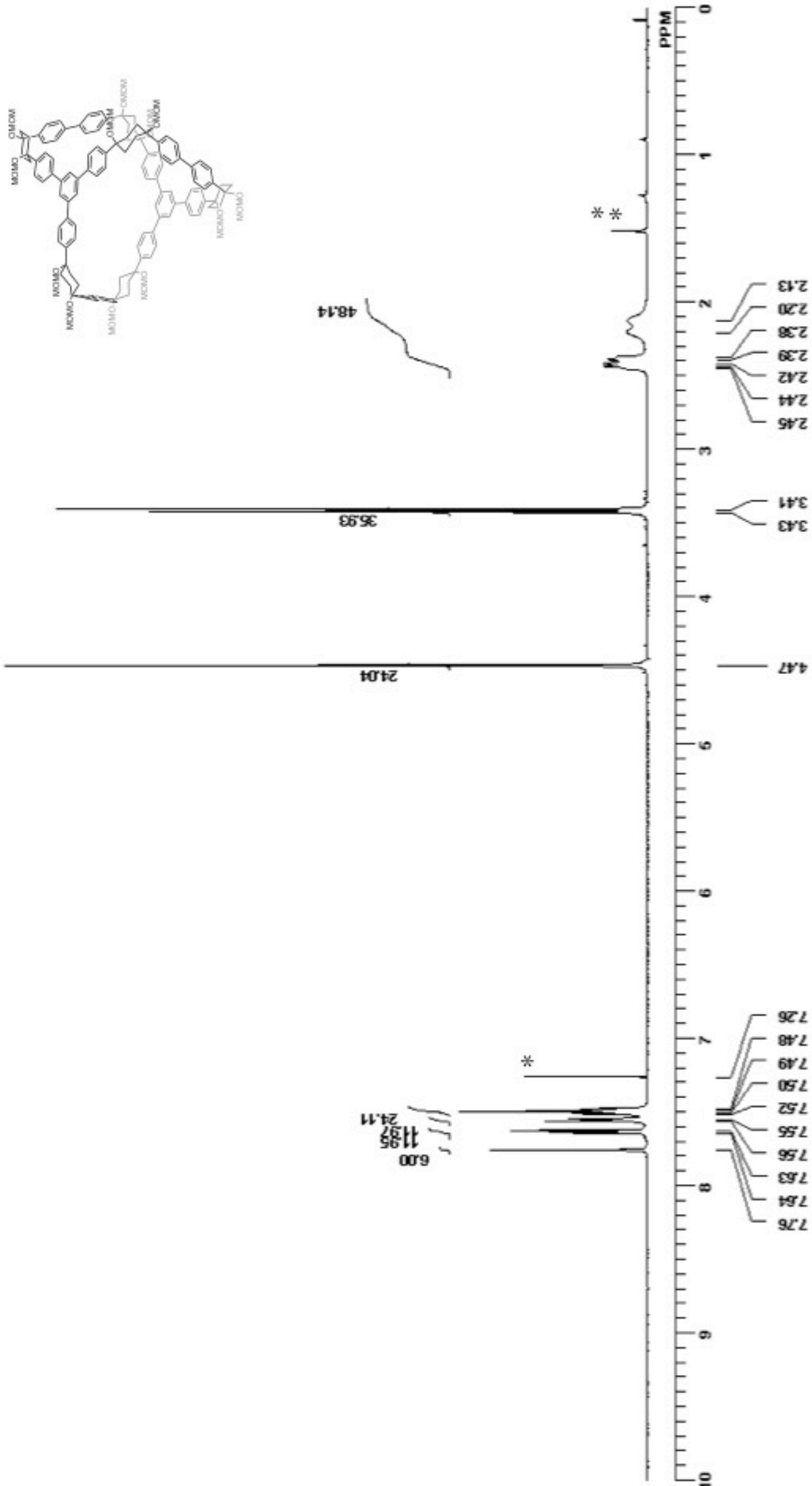
*: $CHCl_3$, **: H_2O

^{13}C NMR spectrum of **4** ($CDCl_3$)



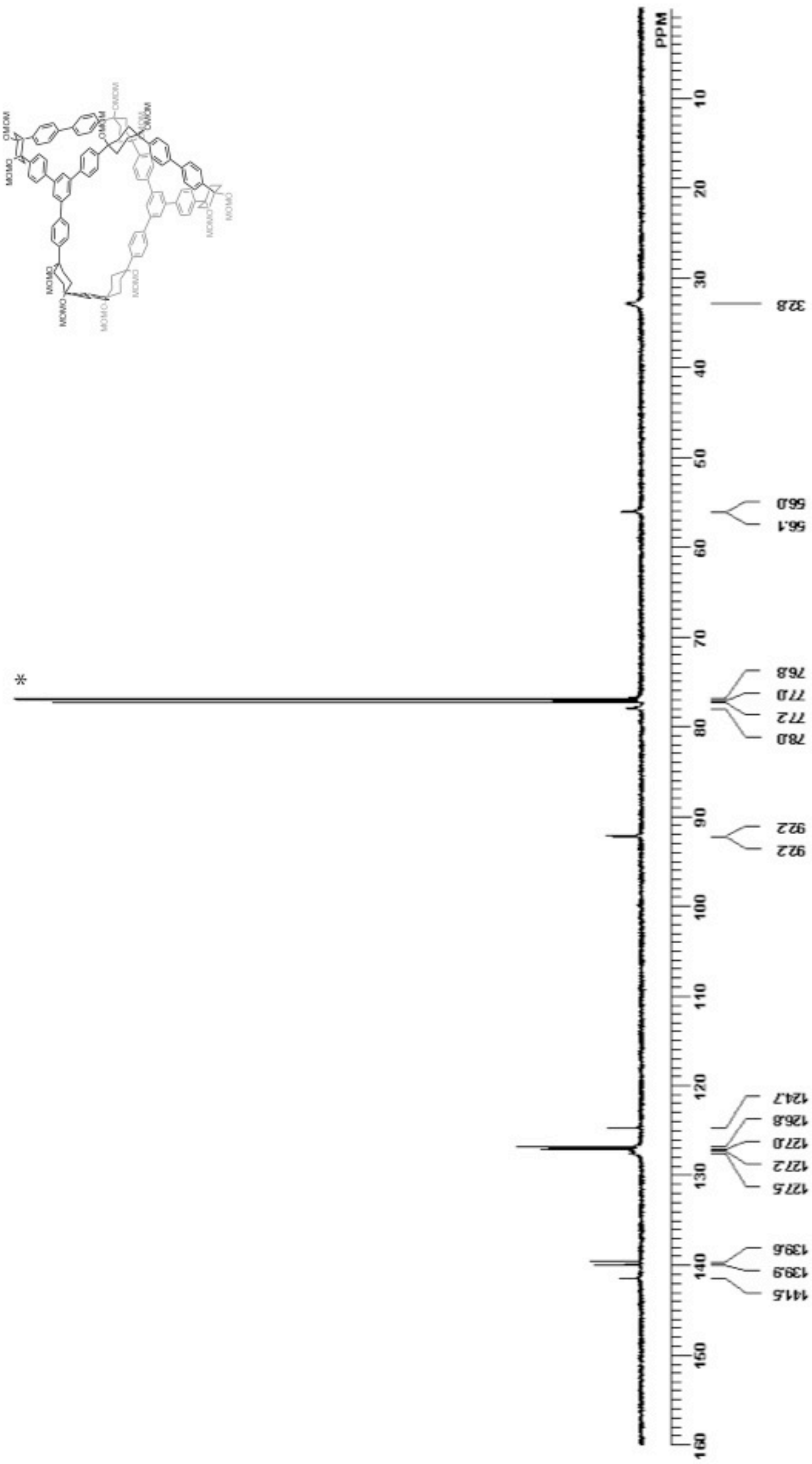
*: $CDCl_3$

^{1}H NMR spectrum of **5** ($CDCl_3$, 50 °C)



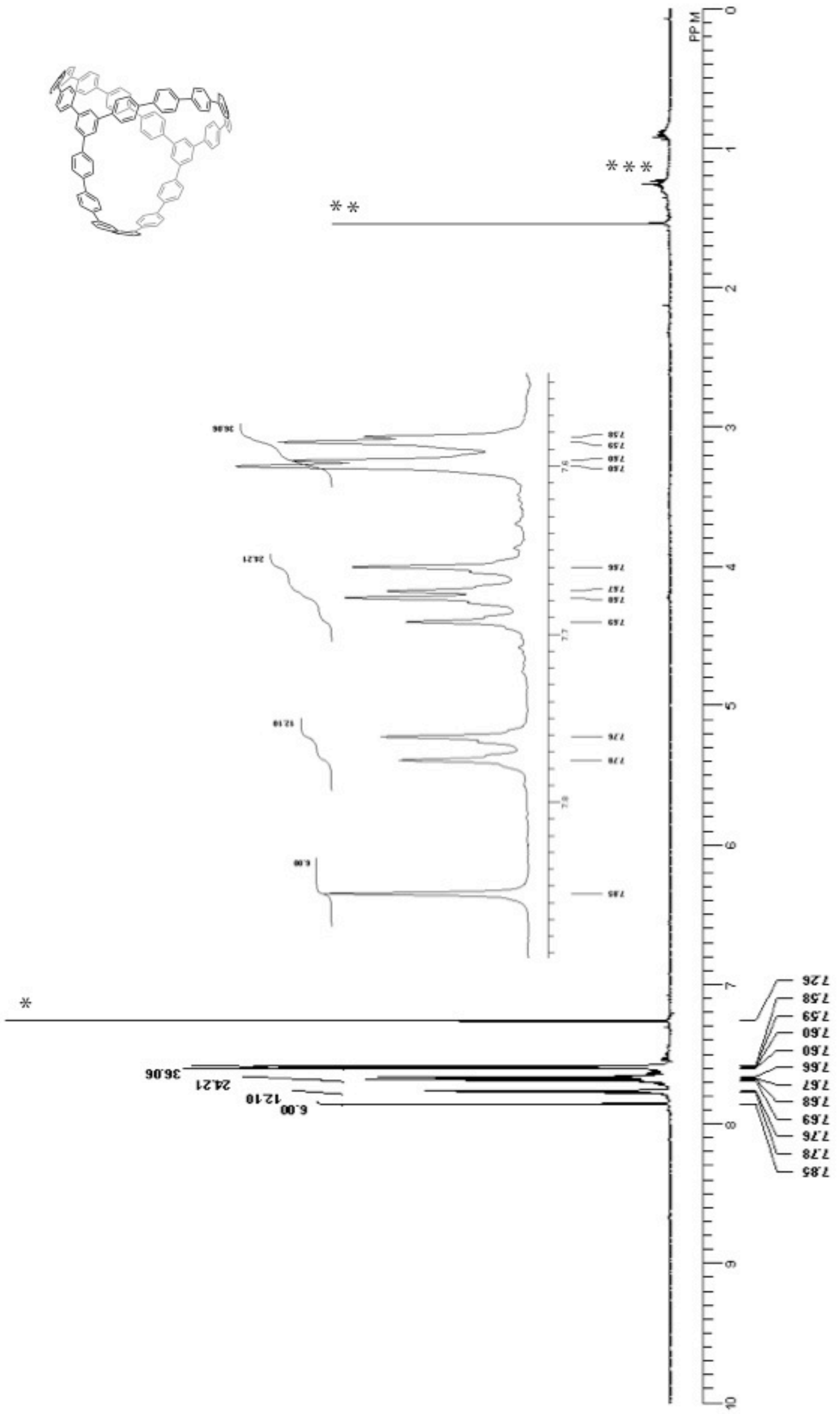
*: $CHCl_3$, **: H_2O

^{13}C NMR spectrum of **5** ($CDCl_3$)



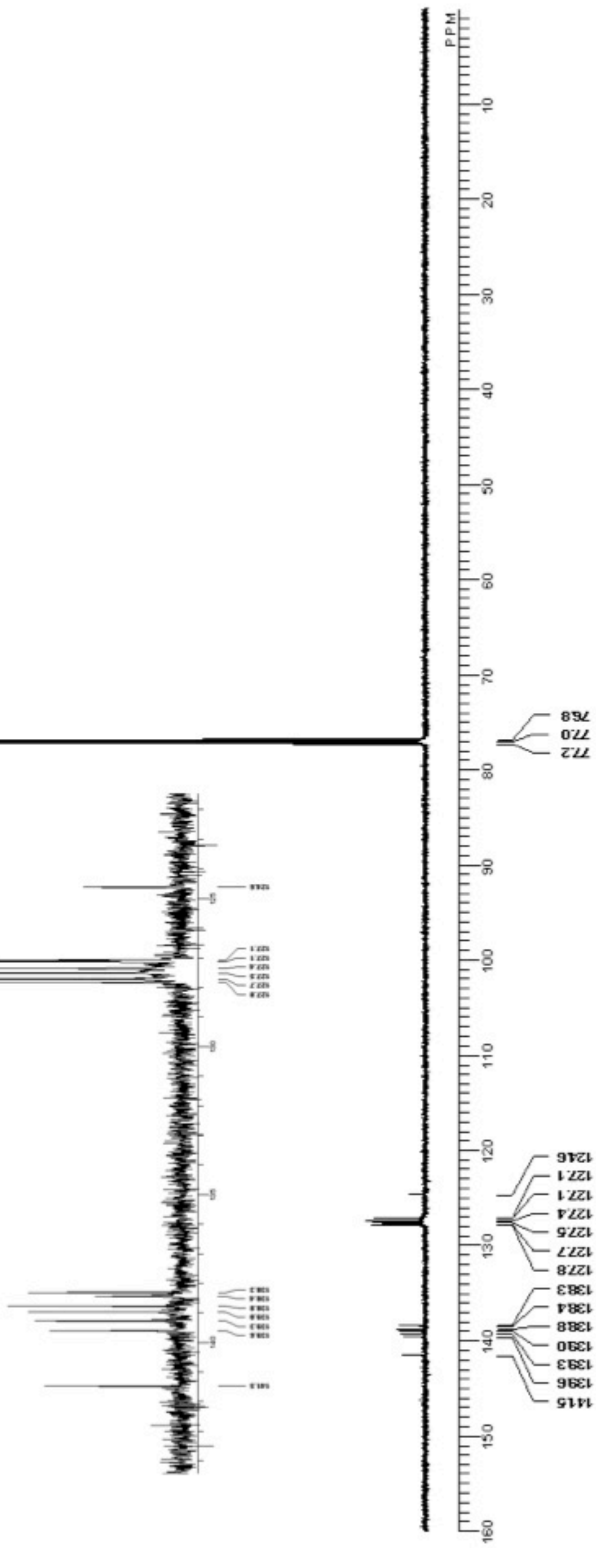
*: $CDCl_3$

^{1}H NMR spectrum of **1** ($CDCl_3$)



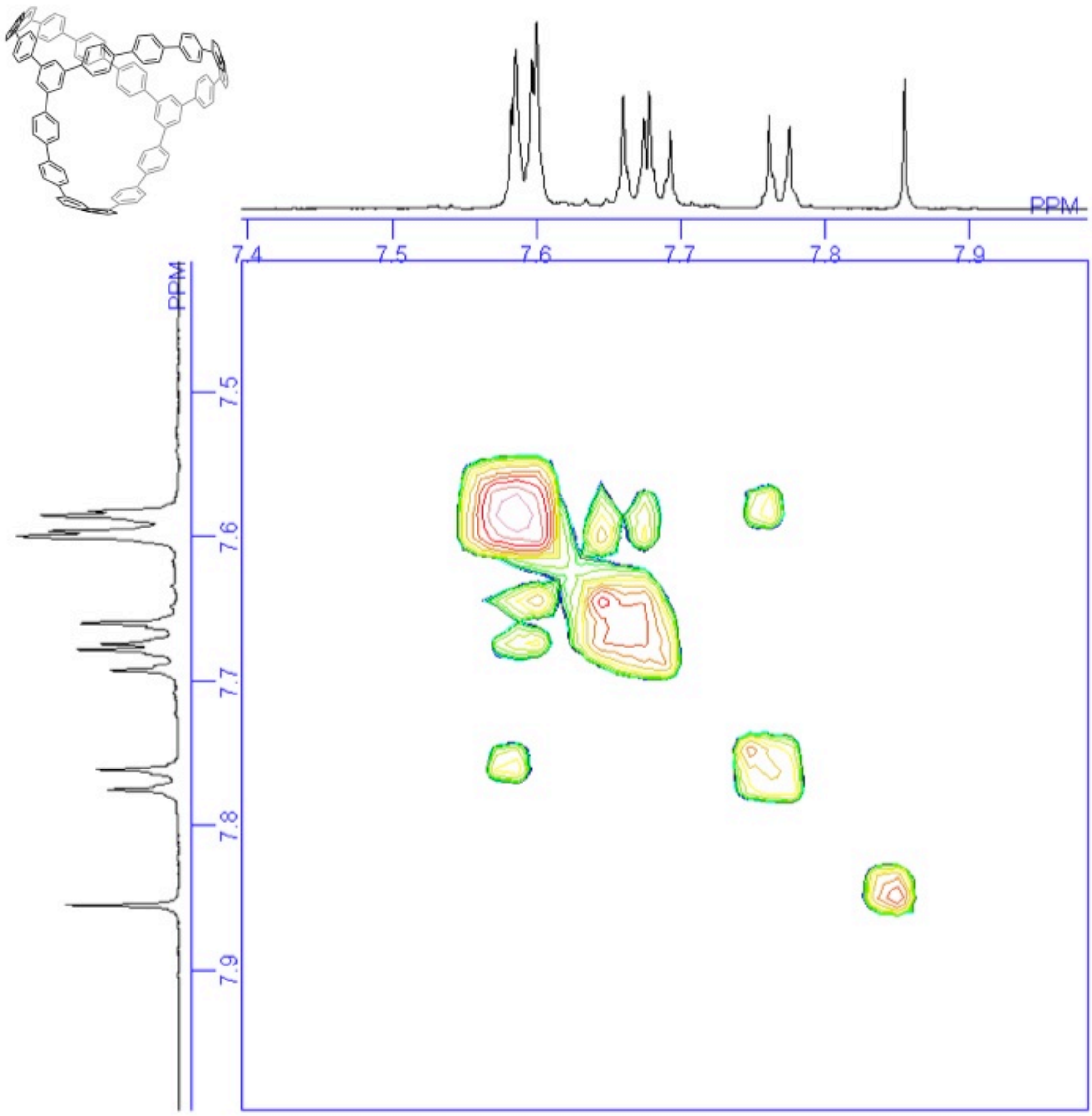
*: $CHCl_3$, **: H_2O, ***: hexane

^{13}C NMR spectrum of **1** ($CDCl_3$)

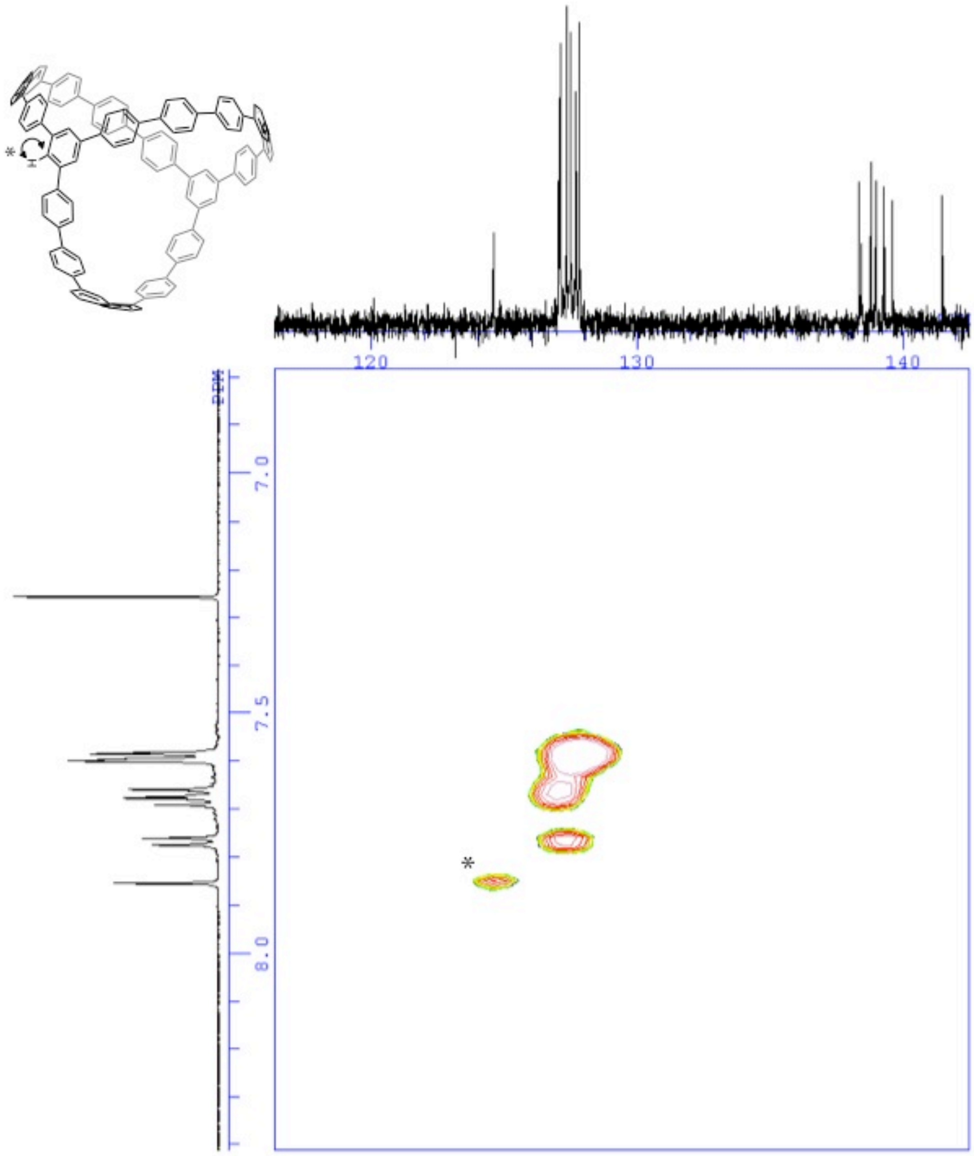


*: $CDCl_3$

HH COSY spectrum of **1** ($CDCl_3$)



HMQC spectrum of **1** ($CDCl_3$)



Mass spectrum of **1** (MALDI-TOF MS)