Electronic Supplementary Information for

Giant Molecular Wheels in Giant Voids: Two-Dimensional Molecular Self-Assembly Goes Big

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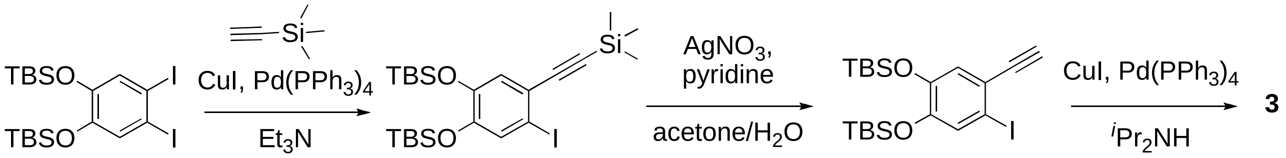
1. Synthesis of DBA 3.



General. All manipulations were performed in an inert gas (nitrogen or argon) atmosphere. All solvents were distilled before use. All commercially available reagents were used as received. $Pd(PPh_3)_4$ was prepared following the literature.[1]

^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured on a Varian Mercury 300 spectrometer. The spectra measured in chloroform-*d* were referenced to residual solvent protons in the ^{1}H NMR spectra (7.26 ppm) and to solvent carbons in the ^{13}C NMR spectra (77.0 ppm). Preparative HPLC was undertaken with a JAI LC-908 chromatograph using 600 mm × 20 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as the eluent. Other spectra were recorded using the following instruments: IR spectra, JACSCO FT/IR-410; Mass spectra, JEOL JMS-700 for EI ionization mode and AXIMA-CFR for LD ionization mode.

Synthesis of 1,2-bis(*tert*-butyldimethylsiloxy)-4-iodo-5-[(trimethylsilyl)ethynyl]benzene. (Trimethylsilyl)acetylene (6.00 mL, 42.4 mmol) was slowly added via a syringe to a mixture of 1,2-bis(*tert*-butyldimethylsiloxy)-4,5-diiodobenzene (25.0 g, 42.4 mmol),[2] $Pd(PPh_3)_4$ (1.05 g, 909 μmol), and CuI (416 mg, 2.18 mmol) in NEt_3 (300 mL). After stirring for 3 h at room temperature,

NH_4Cl aq. and hexane were added to the mixture. The mixture was washed with water and brine, dried over $MgSO_4$ and solvents were evaporated under vacuum. Purification of the reside with silica gel column chromatography (hexane as eluent) gave 1,2-bis(*tert*-butyldimethylsiloxy)-4-iodo-5-[(trimethylsilyl)ethynyl]benzene (10.8 g, 45% yield) as a transparent oil. ^1H NMR (300 MHz, $CDCl_3$, 30 °C) δ 7.23 (s, 1H), 6.92 (s, 1H), 0.98 (s, 9H), 0.97 (s, 9H), 0.27 (s, 9H), 0.20 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) δ 148.5, 147.0, 130.9, 124.7, 122.6, 106.7, 96.6, 90.8, 25.96, 25.91, 25.88, 18.5, 18.4, –0.1, –4.2; IR (neat) 3064, 2957, 2897, 2858, 2153, 2153, 1579, 1539, 1407, 1391, 1369, 1308, 1250, 1200, 1172, 1004, 916, 845, 760 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{41}O_2Si_3I$, 560.1459, found, 560.1462 (M^+).

Synthesis of 1,2-bis(*tert*-butyldimethylsiloxy)-4-ethynyl-5-iodobenzene. 1,2-Bis(*tert*-butyldimethylsiloxy)-4-iodo-5-[(trimethylsilyl)ethynyl]benzene (1.41 g, 2.52 mmol) was dissolved in a mixture of pyridine (60.0 μL ,759 mmol) and acetone (30 mL). Then, $AgNO_3$ (47.9 mg、283 μmol) and water (2.7 mL) were added. Continues stirring for 2 d at 50 °C, brine and hexane were added to the reaction mixture. The organic phase was washed with water and brine, and dried over $MgSO_4$. After removal of solvents under vacuum, the mixture was subject to a silica gel column chromatography (hexane as eluent) to afford 1,2-bis(*tert*-butyldimethylsiloxy)-4-ethynyl-5-iodobenzene (1.16 g, 94% yield) as a transparent oil. ^1H NMR (300 MHz, $CDCl_3$, 30 °C) δ 7.24 (s, 1H), 6.97 (s, 1H), 3.26 (s, 1H), 0.98 (s, 18H), 0.21 (s, 6H), 0.20 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) δ 148.8, 147.1, 130.9, 125.4, 121.6, 89.7, 85.2, 79.1, 25.85, 25.83, 25.76, 18.5, 18.4, –4.2; IR (neat) 3314, 3294, 3065, 2955, 2930, 2886, 2859, 2109, 1579, 1542, 1485, 1390, 1366, 1304, 1256, 1213, 1162, 996, 910, 839, 783, 690 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{33}O_2Si_2I$, 488.1064, found, 488.1076 (M^+).

Synthesis of Hexakis(*tert*-butyldimethylsiloxy)hexadehydrotribenzo[12]annulene 3.

1,2-Bis(*tert*-butyldimethylsiloxy)-4-ethynyl-5-iodobenzene (500 mg, 1.02 mmol), $Pd(PPh_3)_4$ (58.6 mg, 51.0 μmol), and CuI (19.6 mg, 103 μmol) were dissolved in $^{i}Pr_2NH$ (10 mL). After stirring for 5 h at room temperature, NH_4Cl aq. and hexane were added to the mixture. The mixture was washed with water and brine, dried over $MgSO_4$ and solvent was removed under vacuum. Purification was performed with silica gel column chromatography (hexane/CH_2Cl_2 = 9/1) and then by preparative HPLC to give yellow solids. Recrystalization from CH_2Cl_2/MeOH afford hexakis(*tert*-butyldimethylsiloxy)hexadehydrotribenzo[12]annulene (**3**, 48.2 mg, 13% yield) as yellow crystals. mp 80–82 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) δ 6.72 (s, 6H), 0.98 (s, 54H), 0.22 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) δ 147.4, 124.1, 120.3, 91.4, 26.0, 18.6, –3.87. IR (KBr) 2956, 2930, 2896, 2859, 1537, 1506, 1345, 1257, 1228, 933, 890, 841, 826, 783 cm^{-1}; HRMS (EI) calcd for $C_{60}H_{96}O_6Si_6$, 1080.5823, found, 1080.5792 (M^+).

2. STM images of monolayer of DBA 2 at 5.0×10^{-4} mol/L at the TCB/graphite interface.

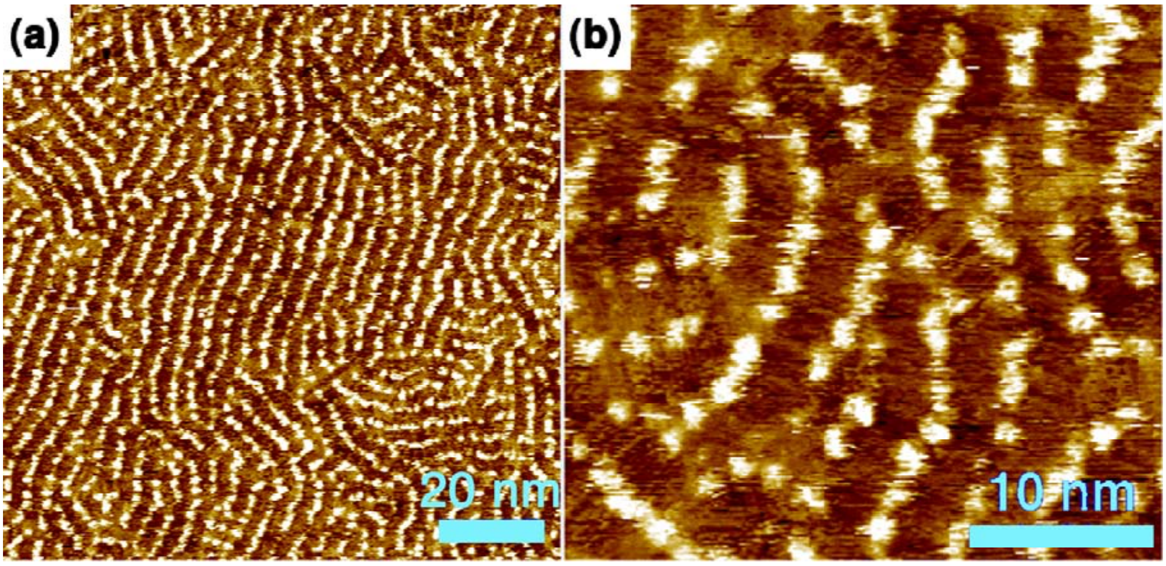


Figure S1. STM images of monolayer of DBA **2** at the TCB/graphite interface forming a nonporous structure (I_{set} = 67 pA. V_{bias} = –0.93 V for (a) and I_{set} = 31 pA. V_{bias} = –0.93 V for (b)).

3. STM images of assembly of a mixture of DBA 2 and wheel 4 at the TCB/graphite interface.

Figure S2 shows the voids with featureless large bright spots as indicated by red arrows. Desorption (red arrows in Figure S3) and adsorption events (green arrows in Figure S3) of molecular wheel **4** were observed. Though the area is typically smaller than that of DBA, monolayer domains of wheel **4** were also observed (Figures S3).

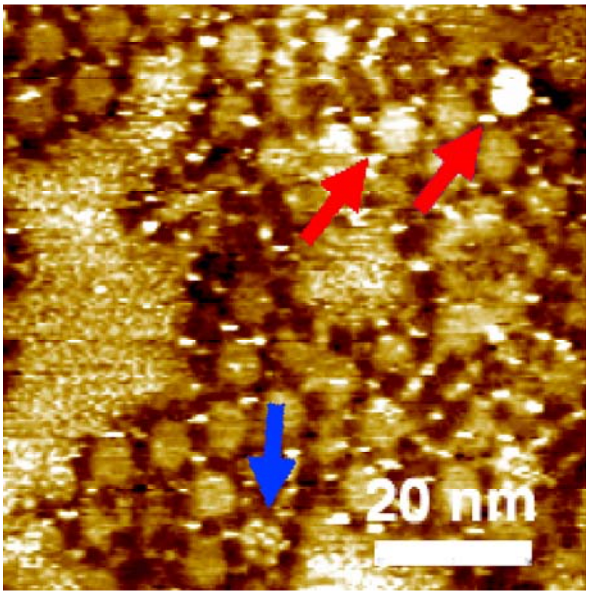


Figure S2. An STM image of monolayer of a mixture of DBA **2** and wheel **4** at the TCB/graphite interface (I_{set} = 48 pA. V_{bias} = –0.42 V). The red arrows indicate the positions of featureless bright spots in the voids. The blue arrow indicates the position of an adsorbed wheel molecule with seven bright spots.

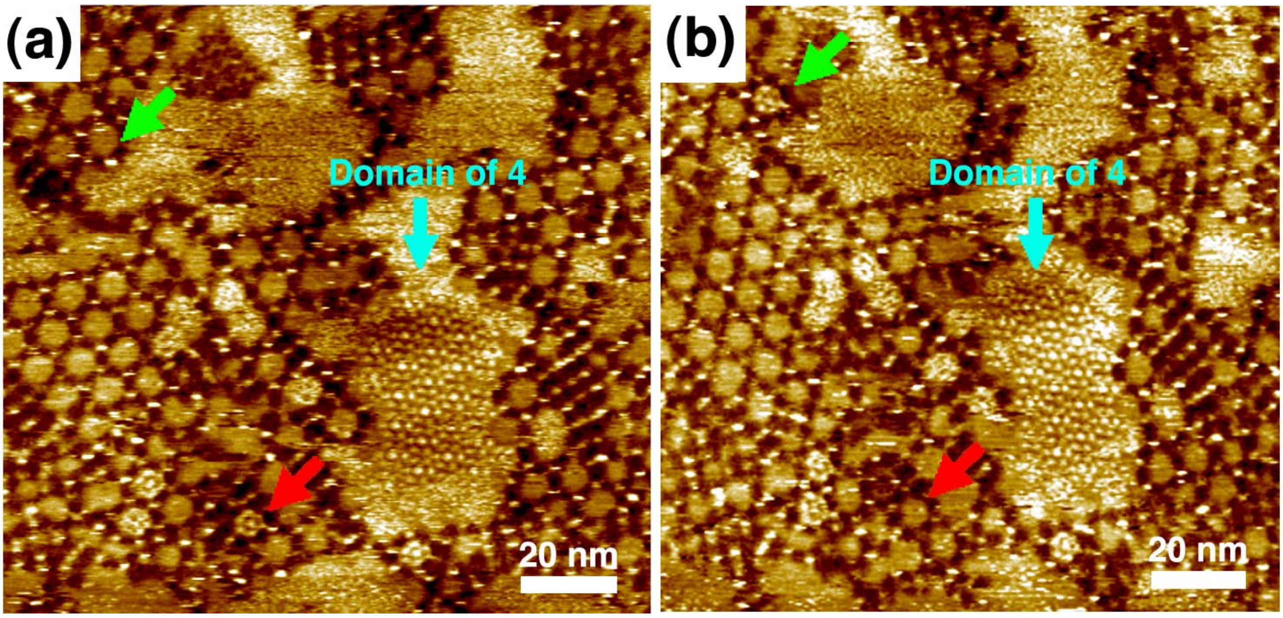


Figure S3. Sequence of STM images of a monolayer of a mixture of DBA **2** and wheel **4** at the TCB/graphite interface (I_{set} = 48 pA. V_{bias} = –0.42 V). (a) First scan. (b) Second scan. It takes 84 seconds for the acquisition of an image. The turquoise colored arrows indicate pure domains of **4**. The red and green arrows indicate sites where desorption and adsorption events of wheel molecule **4** were observed, respectively.

4. ^{1}H and ^{13}C NMR spectra of all compounds.

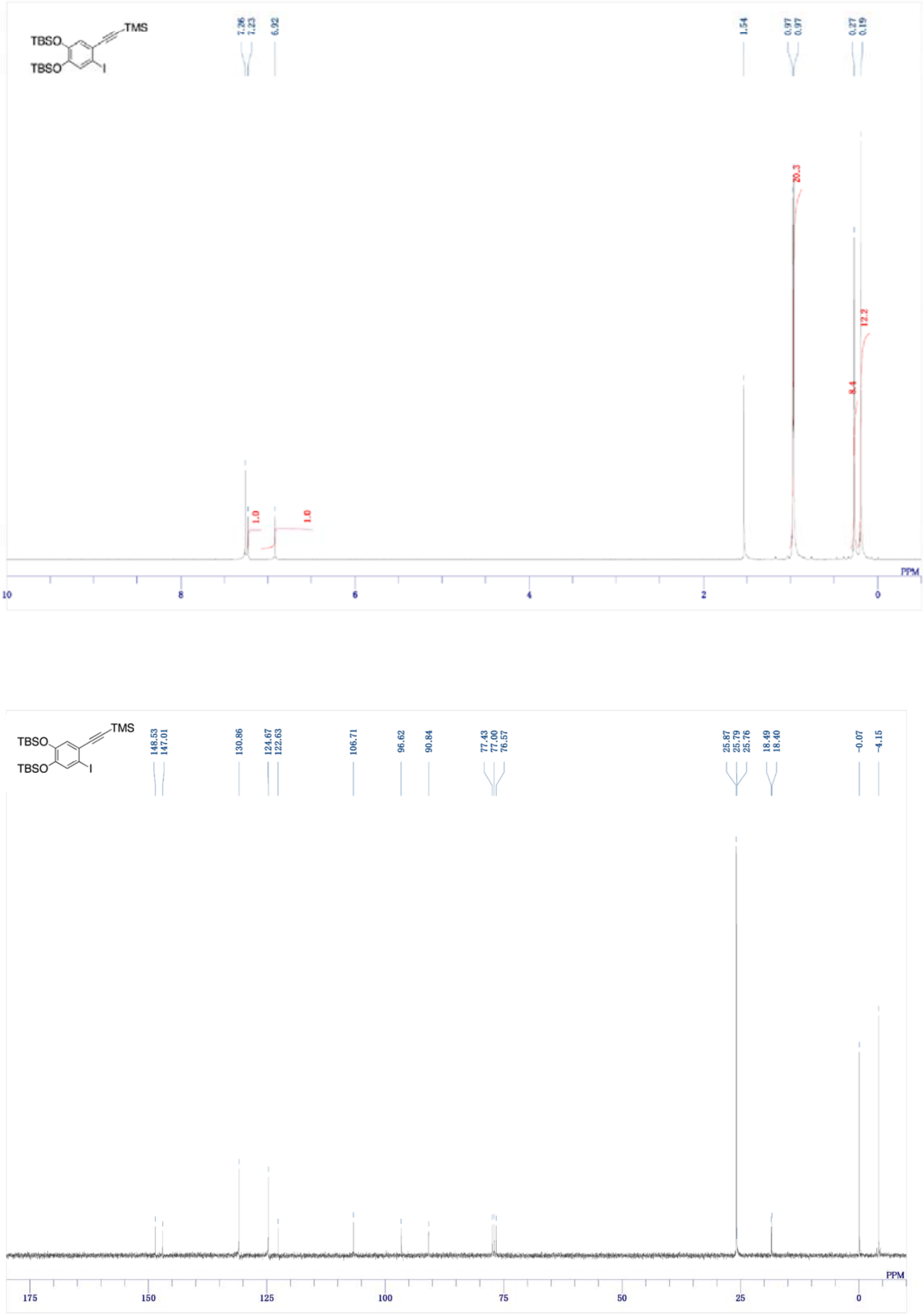


Figure S4. ^{1}H (upper) and ^{13}C (lower) NMR spectra of 1,2-bis(*tert*-butyldimethylsiloxy)-4-iodo-5-[(trimethylsilyl)ethynyl]benzene in $CDCl_3$ at 30 °C.

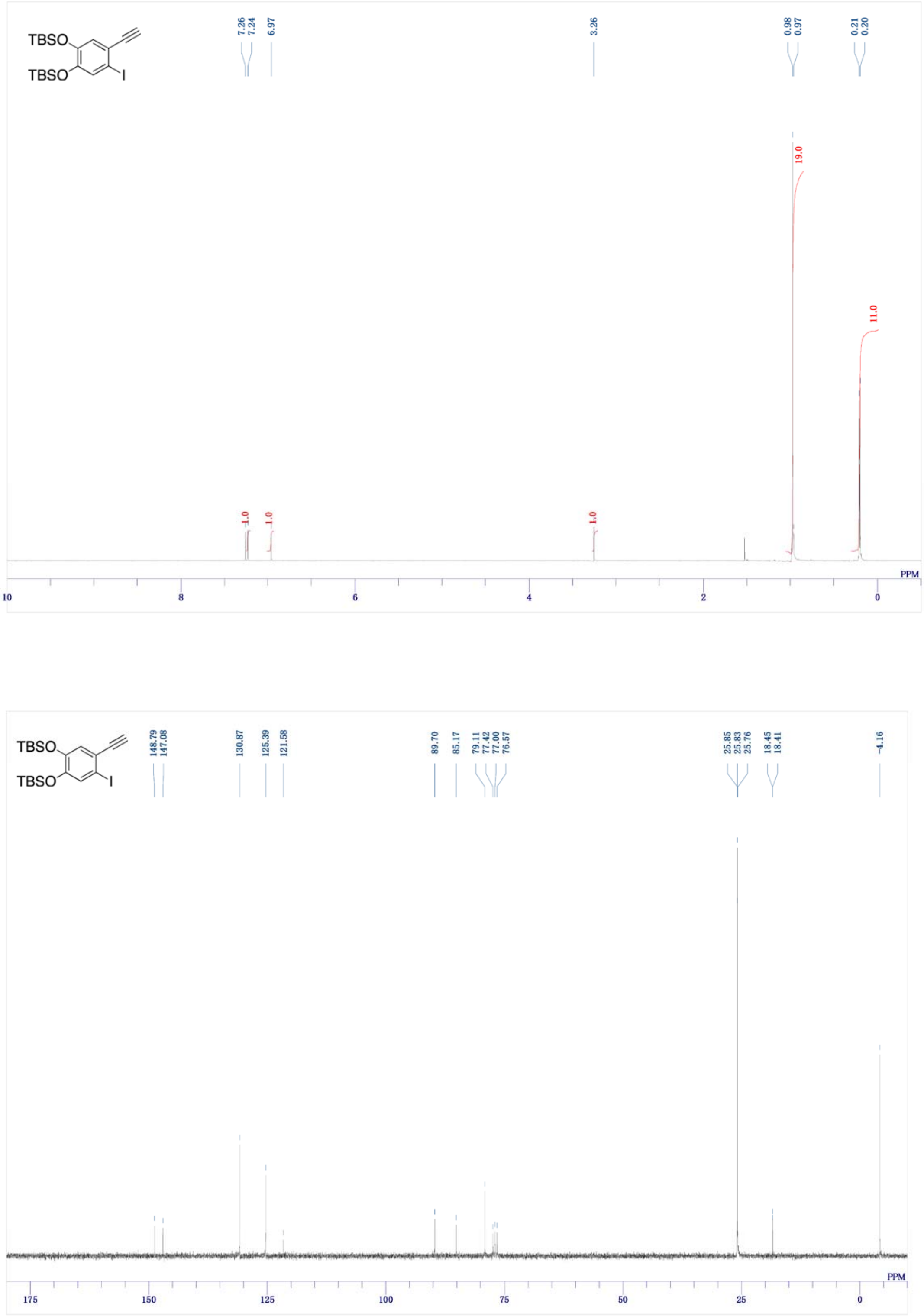


Figure S5. ^{1}H (upper) and ^{13}C (lower) NMR spectra of 1,2-bis(*tert*-butyldimethylsiloxy)-4-ethynyl-5-iodobenzene in $CDCl_3$ at 30 °C.

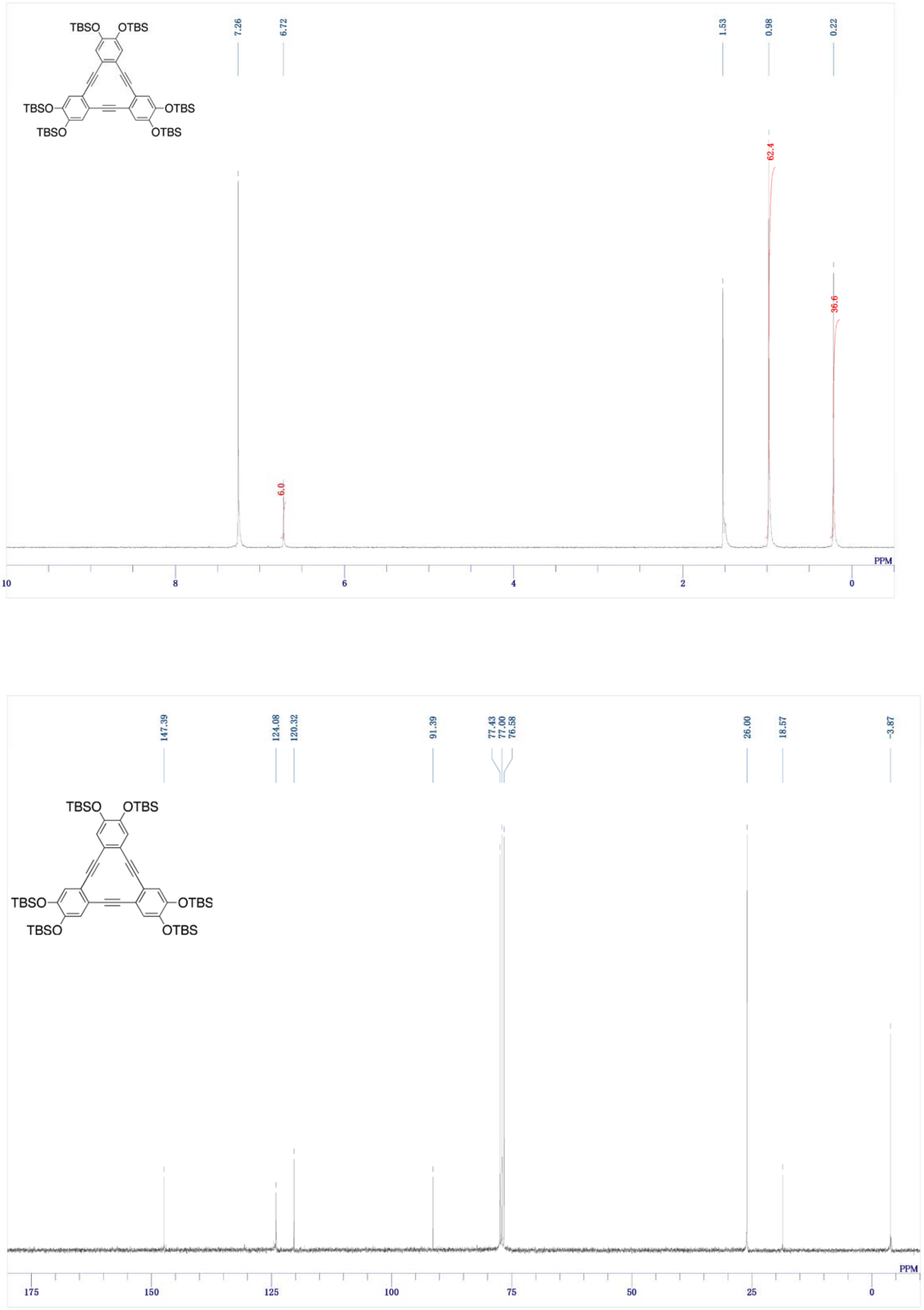


Figure S6. ^{1}H (upper) and ^{13}C (lower) NMR spectra of **3** in $CDCl_3$ at 30 °C.

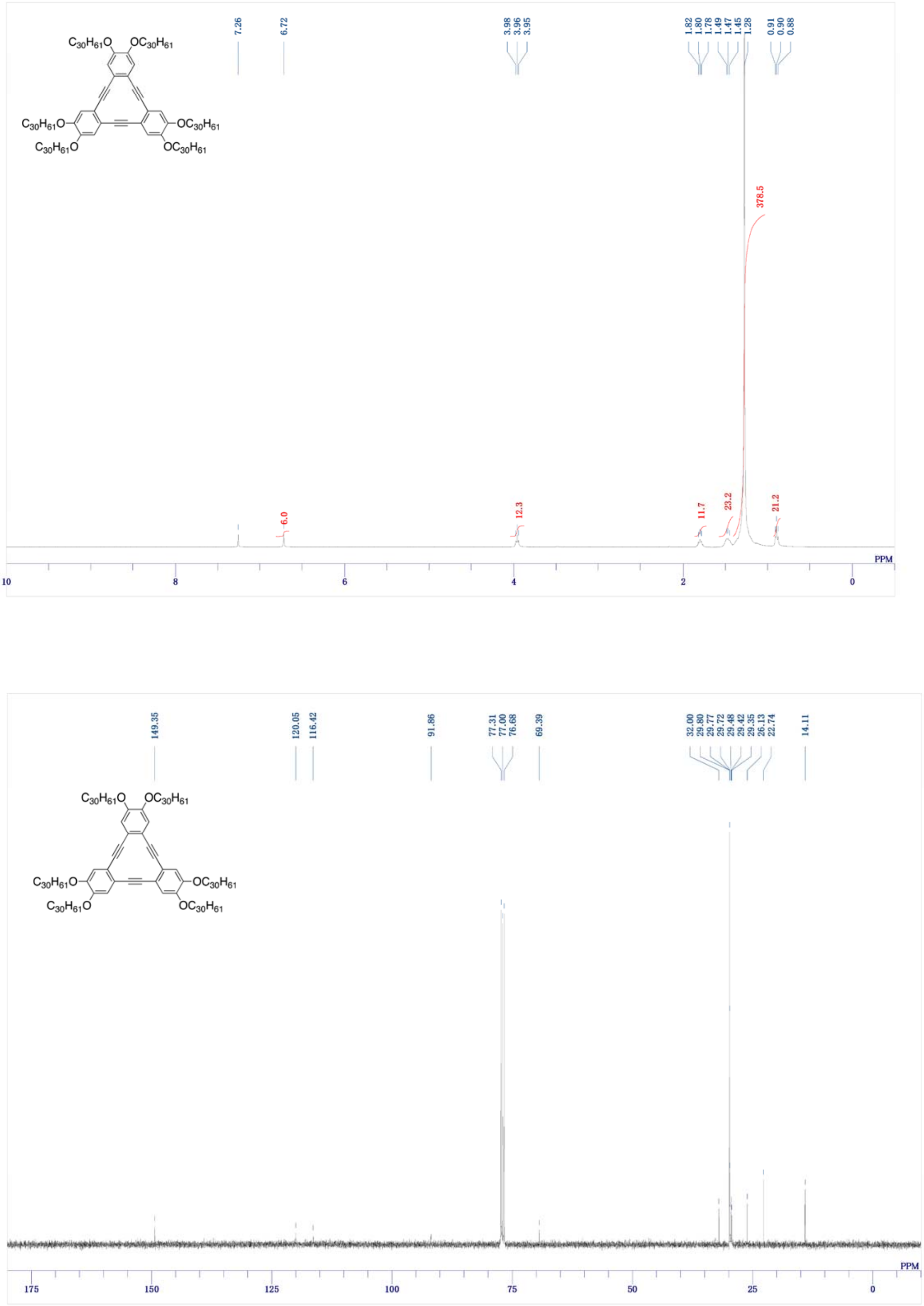


Figure S7. ^{1}H (upper) and ^{13}C (lower) NMR spectra of **2** in $CDCl_3$ at 30 °C.

5. References.

(1) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121–124.

(2) Kinder, J. D.; Youngs, W. J. *Organometallics* **1996**, *15*, 460–463.