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Supplementary information

Synthesis of a zigzag carbon nanobelt

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Supplementary Information

Synthesis of a zigzag carbon nanobelt

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1. Materials and Methods

Synthesis and purification

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF), hexane, toluene, and dimethylformamide (DMF) were purified by passing through a solvent purification system (Glass Contour). Compound **3**[1] and 2,9-di-*tert*-butyl-4,7,11,14-tetrahydro-4,7:11,14-diepoxydibenzo[*fg*,*op*]tetracene (**S9**)[1] were prepared according to the procedures reported in the literature. Unless otherwise noted, work-up and purification procedures were performed with reagent-grade solvents under air. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with silica gel 60N (Kanto Chemical Co., spherical, neutral, 40–100 mesh). Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-9204 instrument equipped with JAIGEL-2HR columns using chloroform as an eluent.

Measurements

High-resolution mass spectroscopy (HRMS) was obtained from a JEOL JMS-S3000 SpiralTOF (MALDI-TOF MS) using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix, or Thermo Fisher Q Exactive (APCI MS) with Shimadzu LC 30A system. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz), JEOL ECA 500II (^{1}H 500 MHz, ^{13}C 125 MHz), or JEOL JNM-A-400 (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CHCl_3$ (7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm) or $Cl_2CDCDCl_2$ (δ 73.78 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, sep = septet, m = multiplet), coupling constant (Hz), and integration.

Details of the crystal data and a summary of the intensity data collection parameters for **1** are listed in Supplementary Table 1. A suitable crystal was mounted with mineral oil on a MiTeGen MicroMounts and transferred to the goniometer of the kappa goniometer of a RIGAKU XtaLAB Synergy-S system with 1.2 kW MicroMax-007HF microfocus rotating anode (Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å)) and PILATUS200K hybrid photon-counting detector. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlis^{Pro} (Agilent Technologies, 2010). The structures were solved by direct methods with SHELXT[2] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2018/3)[3] by using Olex2 software package.[4] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. CCDC 1992947 contains the supplementary crystallographic data for this paper.

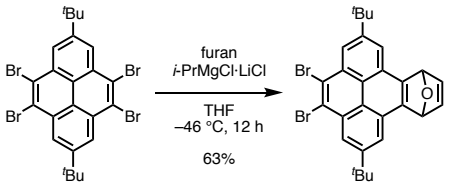
UV–Vis absorption spectra were recorded on a Shimadzu UV-3510 spectrometer with a resolution of 0.5 nm. Emission spectra were measured on Shimadzu RF-6000 spectrometer with a resolution of 0.1 nm. Absolute fluorescence quantum yields (Φ_F) were determined on a Shimadzu RF-6000 using a calibrated integrating sphere system upon excitation at 320 nm. For FL lifetime measurement, Hamamatsu Photonics Quantaurus-Tau® fluorescence lifetime spectrometer C11367-21 with LED as a light source was used (excitation: 340 nm, emission: 407 nm / 432 nm, time range: 202 ns, frequency: 1 MHz). Dilute solutions in spectral grade dichloromethane in a 1 cm square quartz cell were used for measurements.

Theoretical study

The Gaussian 16 program[5] running on a NEC LX 110Rh system was used for optimization (B3LYP/6-31G(d))[6,7] with or without Grimme's D3 type dispersion correction.[8] Structures were optimized without any symmetry assumptions.

2. Experimental section

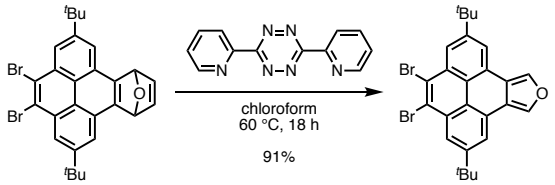
Synthesis of **S1**



To a 500-mL round bottom flask containing 4,5,9,10-tetrabromo-2,7-di-*tert*-butylpyrene (**3**) (12.6 g, 20.0 mmol) filled by N_2 gas were added 400 mL anhydrous THF and furan (14.5 mL, 200 mmol). The resulting mixture was stirred and cooled with an acetonitrile/dry ice cooling bath (–46 °C). *i*-PrMgCl·LiCl (17.0 mL of 1.3 M solution in THF, 22.0 mmol) was added dropwise to the reaction mixture by a syringe pump over 3 hours. The resulting mixture was stirred overnight (ca. 12 hours) before quenching with water. Organic solvent was then evaporated under reduced pressure and the mixture was diluted with dichloromethane. After filtering the mixture through a pad of Celite®, the organic layer was dried with anhydrous Na_2SO_4. Then the mixture was concentrated under reduced pressure and purified by column chromatography on silica gel with hexane/dichloromethane 3:1 to 1:1 (v/v) as eluent. The portion containing the product was further concentrated and precipitated from a solution of methanol/dichloromethane by evaporating dichloromethane under reduced pressure. The resulting solid was filtered and washed with methanol to obtain **S1** as beige solid (6.75 g, 63%).

^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.78 (d, ^4J = 1.8 Hz, 2H), 8.27 (d, ^4J = 1.8 Hz, 2H), 7.40 (t, J = 0.9 Hz, 2H), 6.58 (t, J = 0.9 Hz, 2H), 1.63 (s, 18H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm): 150.2, 148.1, 144.3, 130.8, 127.5, 126.3, 124.6, 121.0, 118.6, 82.5, 35.8, 32.1. HRMS (APCI$^+$): calcd. for $C_{28}H_{27}Br_2O$ ([M+H]$^+$): 537.0423, found:537.0427.

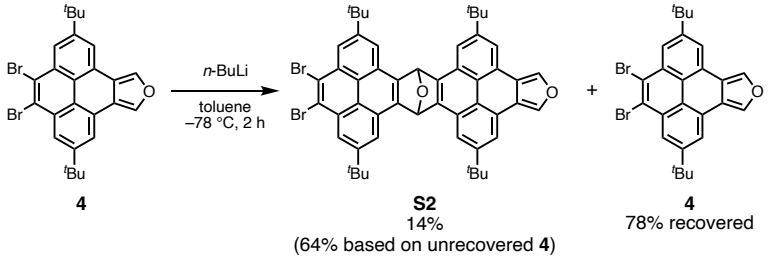
Synthesis of **4**



A solution of compound **S1** (6.46 g, 12.0 mmol) and 3,6-di-2-pyridyl-1,2,4,5-tetrazine (2.98 g, 12.6 mmol) in 60 mL chloroform was heated at 60 °C under N_2 atmosphere in dark overnight (ca. 18 hours). After concentrated under reduced pressure, the mixture was first purified by column chromatography on silica gel with hexane/dichloromethane 1:0 to 20:1 (v/v) as eluent. The product was further precipitated from a solution of methanol/dichloromethane by evaporating dichloromethane under reduced pressure. The resulting solid was filtered and washed with methanol to obtain **4** as light-yellow solid (5.59 g, 91%).

^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.57 (d, ^4J = 1.8 Hz, 2H), 8.45 (s, 2H), 8.29 (d, ^4J = 1.8 Hz, 2H), 1.56 (s, 18H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm): 150.7, 137.0, 131.0, 127.3, 125.2, 124.7, 122.9, 121.4, 120.6, 35.5, 31.8. HRMS (APCI$^+$): calcd. for $C_{26}H_{27}Br_2O$ ([M+H]$^+$): 511.0267, found: 511.0271.

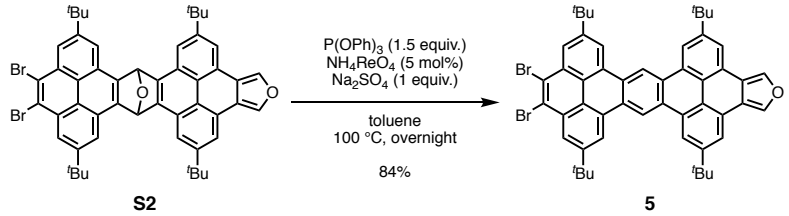
Synthesis of **S2**



A solution of **4** (4.61 g, 9.00 mmol) in 360 mL anhydrous toluene under N_2 atmosphere was cooled to −78 °C with a dry ice/acetone cooling bath. Then *n*-BuLi (2.00 mL of 1.6 M solution in hexane, 3.15 mmol) was added to the reaction mixture by a syringe pump over 1 hour. After complete addition of *n*-BuLi, the reaction mixture was stirred at the same temperature for an additional 1 hour before quenching with 0.2 mL methanol. The resulting mixture was then warmed to room temperature and filtered through a pad of silica gel and washing the silica gel pad with dichloromethane. The mixture was concentrated under reduced pressure and purified by column chromatography on silica gel with hexane/dichloromethane 10/1 to 3/2 (v/v) as eluent. The portion containing unreacted **4** was further concentrated and precipitated from a solution of methanol/dichloromethane by evaporating dichloromethane under reduced pressure. The resulting solid was filtered and washed with methanol to recycle **4** (3.61 g, 78%). The portion containing the product **S2** was further concentrated and precipitated from a solution of methanol/dichloromethane by evaporating dichloromethane under reduced pressure. The resulting solid was filtered and washed with methanol to obtain **S2** as yellow solid (546 mg, 631 μmol, 14% based on used **4** and 64% based on reacted **4**). This reaction was repeated a few times to accumulate a larger amount of **S2**.

^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.72 (d, ^4J = 1.8 Hz, 2H), 8.62 (d, ^4J = 1.8 Hz, 2H), 8.36 (s, 2H), 8.34 (d, ^4J = 2.4 Hz, 2H), 8.17 (d, ^4J = 1.8 Hz, 2H), 7.67 (s, 2H), 1.67 (s, 18H), 1.61 (s, 18H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm): 150.2, 149.5, 148.6, 148.2, 136.8, 130.9, 127.4, 126.8, 126.2, 125.9, 124.8, 122.1, 121.8, 121.3, 119.1, 118.9, 117.4, 82.6, 35.7, 35.3, 32.1, 31.9. HRMS (APCI$^+$): calcd. for $C_{52}H_{49}Br_2O_2$ ([M+H]$^+$): 863.2094, found: 863.2078.

Synthesis of **5**

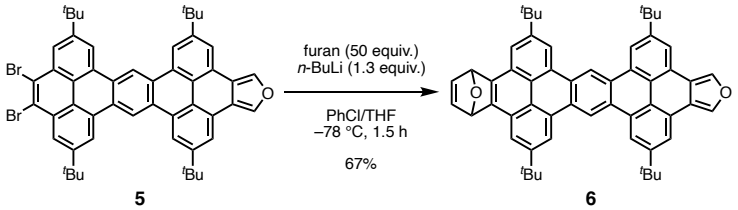


S2 **5**

To a mixture of **S2** (865 mg, 1.00 mmol), ammonium perrhenate (13.4 mg, 50.0 μmol) and sodium sulfate (142 mg, 1.00 mmol) under N_2 atmosphere were added 20 mL anhydrous toluene and triphenyl phosphite (400 μL, 1.50 mmol). The resulting mixture was heated at 100 °C under N_2 atmosphere in dark overnight (ca. 20 hours). The reaction mixture was then diluted with dichloromethane and then filtered through a pad of silica gel. The silica gel pad was further washed with dichloromethane. The filtrate was concentrated under reduced pressure and precipitated from a solution of methanol/dichloromethane by evaporating dichloromethane under reduced pressure. The resulting solid was filtered and washed with methanol to obtain **5** as yellow solid (715 mg, 84%).

^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm): 10.23 (s, 2H), 9.37 (d, ^4J = 1.2 Hz, 2H), 9.11 (d, ^4J = 1.8 Hz, 2H), 8.85 (d, ^4J = 1.2 Hz, 2H), 8.47 (s, 2H), 8.31 (d, ^4J = 1.8 Hz, 2H), 1.75 (s, 18H), 1.70 (s, 18H). ^{13}C NMR ($CDCl_2CDCl_2$, 150 MHz, 120 °C) δ (ppm): 150.3, 149.8, 136.5, 130.8, 129.9, 129.4, 129.0, 129.0, 127.1, 125.5, 125.3, 122.7, 122.5, 121.7, 120.1, 119.1, 118.3, 117.9, 35.5, 35.1, 31.6, 31.4. HRMS (APCI$^+$): calcd. for $C_{52}H_{49}Br_2O$ ($[M+H]^+$): 847.2145, found: 847.2127.

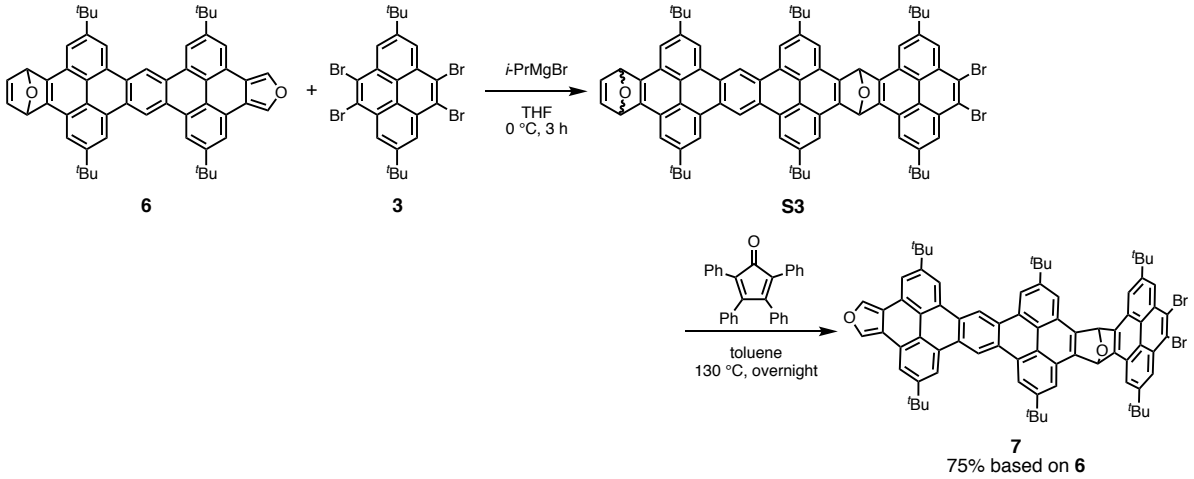
Synthesis of **6**



A mixture of **5** (679 mg, 800 μmol) and 16 mL anhydrous chlorobenzene was heated under N_2 atmosphere with a heat gun to dissolve **5**. NOTE: The following procedures should be performed as soon as possible before **5** starts to precipitate out from the solution. 32 mL anhydrous THF was added to the reaction mixture. The mixture was then cooled to −78 °C in a dryice/acetone cooling bath and furan (2.9 mL, 40 mmol) was added. *n*-BuLi (0.65 mL of 1.6 M solution in hexane, 1.04 mmol) was added dropwise to the reaction mixture within 1 minute. The resulting mixture was further stirred for 1.5 hour at the same temperature before quenching with 0.1 mL methanol. The mixture was filtered through a pad of silica gel. The silica gel pad was further washed with dichloromethane. After concentrating under reduced pressure, the crude mixture was purified by column chromatography on silica gel with hexane/dichloromethane 3:1 to 1:1 (v/v) as eluent. The product was further concentrated and precipitated from a solution of methanol/dichloromethane by evaporating dichloromethane under reduced pressure. The resulting solid was filtered and washed with methanol to obtain **6** as beige solid (407 mg, 67%).

^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm): 10.25 (s, 2H), 9.29 (s, 2H), 9.13 (s, 2H), 8.47 (s, 2H), 8.31 (d, ^4J = 1.8 Hz, 2H), 8.24 (d, ^4J = 1.8 Hz, 2H), 7.45 (s, 2H), 6.61 (s, 2H), 1.75 (s, 18H), 1.70 (s, 18H). ^{13}C NMR ($CDCl_2CDCl_2$, 150 MHz, 100 °C) δ (ppm): 149.6, 149.1, 147.7, 144.0, 136.6, 129.6, 129.6, 129.5, 129.4, 126.9, 125.5, 122.6, 121.7, 121.3, 120.0, 118.1, 117.9, 117.8, 117.5, 82.3, 35.3, 35.1, 31.7, 31.5. HRMS (APCI$^+$): calcd. for $C_{56}H_{53}O_2$ ($[M+H]^+$): 757.4040, found: 757.4032.

Synthesis of **7**



6 **3** **S3**

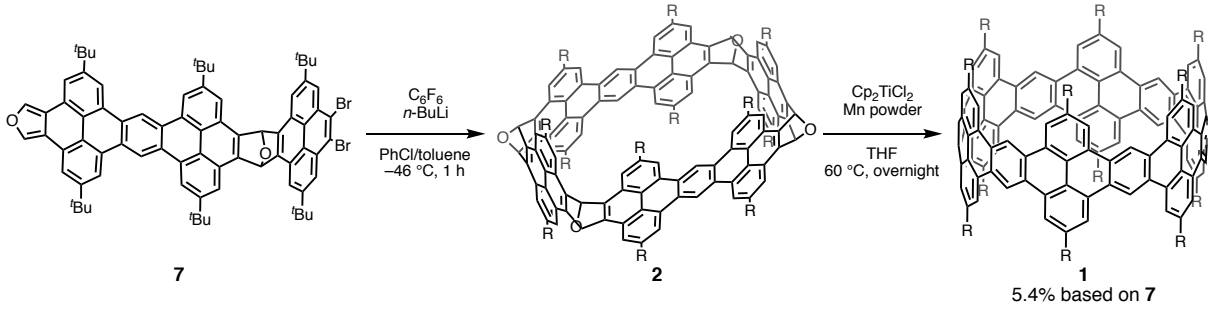
7
75% based on **6**

To a mixture of **6** (379 mg, 500 μmol) and 4,5,9,10-tetrabromo-2,7-di-*tert*-butylpyrene (**3**) (1.26 g, 2.00 mmol) under N_2 atmosphere was added 33 mL anhydrous THF. The mixture was sonicated to give a fine suspension and then cooled in an ice bath. *i*-PrMgBr (1.75 mL of 1.0 M solution in THF, 1.75 mmol) was added dropwise to the reaction mixture in 3 minutes. The resulting mixture was stirred at the same temperature for 3 hours before quenching with 0.1 mL methanol. The mixture was filtered through a pad of silica gel. The silica gel pad was further washed with dichloromethane. After concentrating under reduced pressure, the crude mixture was partially purified by column chromatography on silica gel with hexane/dichloromethane 2:1 to 1:2 (v/v) as eluent. This product **S3** (555 mg) was an isomer mixture and was used directly in the next step. The nonpolar fractions during column chromatography (containing some unreacted 4,5,9,10-tetrabromo-2,7-di-*tert*-butylpyrene (**3**)) were concentrated under reduced pressure and then precipitated from a solution of acetone/dichloromethane by evaporating dichloromethane under reduced pressure. The resulting solid was filtered and washed with acetone to recycle 4,5,9,10-tetrabromo-2,7-di-*tert*-butylpyrene (**3**) as beige solid (430 mg).

The isomer mixture of **S3** (555 mg, 450 μmol) and tetraphenylcyclopentadienone (183 mg, 470 μmol) in 23 mL anhydrous toluene was refluxed vigorously (oil bath temperature 130 °C) in dark overnight (ca. 15 hours). The resulting mixture was concentrated under reduced pressure and triturated with diethyl ether. The resulting solid was filtered and washed with diethyl ether to obtain **7** as light-yellow solid (451 mg, 75% for 2 steps).

^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm): 10.17 (s, 2H), 9.24 (d, ^4J = 1.8 Hz, 2H), 9.07 (d, ^4J = 1.8 Hz, 2H), 8.74 (d, ^4J = 1.8 Hz, 2H), 8.70 (d, ^4J = 1.8 Hz, 2H), 8.62 (d, ^4J = 1.8 Hz, 2H), 8.45 (s, 2H), 8.28 (d, ^4J = 1.8 Hz, 2H), 7.79 (s, 2H), 1.79 (s, 18H), 1.70 (s, 18H), 1.68 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 150.3, 149.5, 149.2, 148.6, 148.2, 136.8, 130.9, 129.75, 129.70, 129.6, 129.5, 127.5, 126.8, 126.2, 125.7, 124.8, 122.8, 121.89, 121.87, 121.3, 120.4, 118.9, 118.32, 118.27, 118.1, 118.0, 82.8, 35.8, 35.7, 35.5, 32.2, 32.1, 31.8. HRMS (APCI$^+$): calcd. for $C_{78}H_{73}Br_2O_2$ ([M+H]$^+$): 1199.3972, found: 1199.3953.

Synthesis of **1**

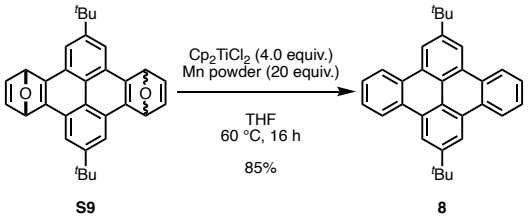


A mixture of compound **7** (240 mg, 200 μmol) and 8 mL anhydrous chlorobenzene was heated to dissolve all solid **7**. After that 8 mL anhydrous toluene was added to the mixture and the mixture was cooled with an acetonitrile/dry ice cooling bath (–46 °C). Hexafluorobenzene (0.11 mL, 1.0 mmol) was then added, followed by dropwise addition of *n*-BuLi (0.5 mL of 1.6 M solution in hexane, 0.8 mmol) by a syringe pump in 15 minutes. After stirring for 1 hour, the reaction mixture was quenched with methanol (0.1 mL) and was filtered through a pad of silica gel with dichloromethane. After evaporating solvent under reduced pressure, this crude mixture was used in the next step directly.

To a Schenk flask were added the above crude mixture, Cp_2TiCl_2 (498 mg, 2.00 mmol), and manganese powder (549 mg, 10.0 mmol). The flask was filled by N_2 gas and 16 mL anhydrous THF was added. The resulting mixture was heated at 60 °C under N_2 atmosphere in dark overnight (ca. 20 hours). The mixture was then filtered through a pad of silica gel with chloroform and the solvent was evaporated under reduced pressure. This crude mixture was diluted with chloroform and filtered again through another pad of silica gel with chloroform. After concentrated under reduced pressure, the mixture was purified by preparative recycling gel permeation chromatography ($CHCl_3$) to give zigzag carbon nanobelt **1** (10.9 mg, 5.4% for 2 steps) as an off-white, light beige solid.

^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm): 9.01 (s, 12H), 8.73 (s, 24H), 1.64 (s, 108H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 149.7, 130.8, 129.7, 124.7, 122.9, 118.6, 35.6, 31.9. HRMS (MALDI-TOF): calcd. for $C_{156}H_{144}$ ($[M]^+$): 2018.1296, found: 2018.1324.

Synthesis of **8**



S9 **8**

To a Schenk flask were added **S9** (96.0 mg, 215 μmol), Cp_2TiCl_2 (214 mg, 860 μmol), and manganese powder (236 mg, 4.30 mmol). The flask was filled by N_2 gas and 4 mL anhydrous THF was added. The resulting mixture was heated at 60 °C under N_2 atmosphere for 16 hours. The mixture was then filtered through a pad of silica gel with dichloromethane and the solvent was evaporated under reduced pressure. This crude mixture was dissolved in a small amount of toluene and loaded onto a pad of silica gel. The silica gel pad was then washed with hexane. The filtrate was concentrated under reduced pressure and the product was further precipitated from a solution of methanol/dichloromethane by evaporating dichloromethane under reduced pressure. The resulting solid was filtered and washed with methanol to obtain 2,9-di-*tert*-butyldibenzo[*fg,op*]tetracene (**8**) as beige solid (76.0 mg, 85%).

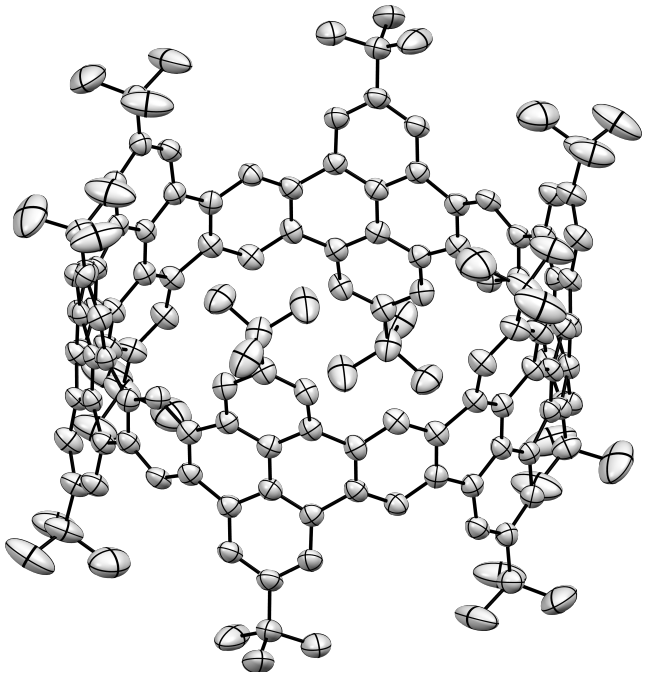
^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 8.97 (s, 4H), 8.85-8.87 (m, 4H), 7.73-7.75 (m, 4H), 1.67 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 148.7, 130.6, 129.1, 127.4,123.8, 122.2, 118.6, 35.8, 32.1. HRMS (MALDI-TOF): calcd. for $C_{32}H_{30}$ ($[M]^+$): 414.2342, found: 414.2332.

3. X-ray Crystallography

Supplementary Table 1. Crystallographic data and structure refinement details of 1·9toluene and the explanations for checkcif alerts.

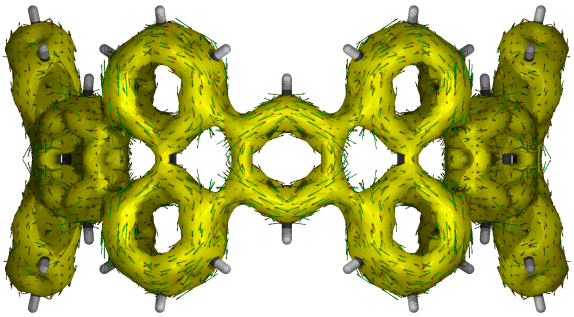
	1·9toluene
CCDC No.	1992947
formula	$C_{219}H_{216}$
fw	2847.91
T (K)	123(2)
λ (Å)	0.71073
cryst syst	*Orthorhombic*
space group	*Pnnm*
a (Å)	14.5786(7)
b (Å)	21.945(2)
c (Å)	28.1707(16)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	9012.6(11)
Z	2
D_{calc} (g·cm^{-3})	1.049
μ(mm^{-1})	0.059
F(000)	3060.0
cryst size (mm)	0.10 × 0.10 × 0.10
2θ range (deg)	2.892–49.998
reflns collected	33780
indep reflns/R_{int}	8118/0.0987
params	679
GOF on F^2	1.261
R_1, wR_2 [$I>2\sigma(I)$]	0.1277, 0.3372
R_1, wR_2 (all data)	0.2190, 0.3959

PLAT084_ALERT_3_B
High wR2 Value (i.e. > 0.25) ..... 0.40 Report
This might be due to a poor quality of the crystal used and severe disordering of toluene molecules.
PLAT097_ALERT_2_B
Large Reported Max. (Positive) Residual Density 0.75 eA-3
This might be due to a poor quality of the crystal used.
PLAT242_ALERT_2_B
Low 'MainMol' Ueq as Compared to Neighbors of C23 Check
This might be due to the thermal rotation mode of the *tert*-butyl group (C23–C26) around C14–C23 bond.
PLAT260_ALERT_2_B
Large Average Ueq of Residue Including C55 0.349 Check
PLAT260_ALERT_2_B
Large Average Ueq of Residue Including C62 0.367 Check
PLAT260_ALERT_2_B
Large Average Ueq of Residue Including C69 0.553 Check
These might be due to a severe disordering of toluene molecules.
PLAT934_ALERT_3_B
Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers .. 3 Check
This might be due to a poor quality of the crystal used and severe disordering of toluene molecules.

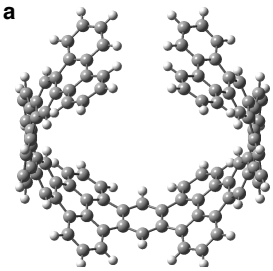


Supplementary Fig. 1. ORTEP drawing of 1 with 50% thermal probability. All hydrogen atoms and solvent molecules are omitted for clarify.

4. Theoretical study

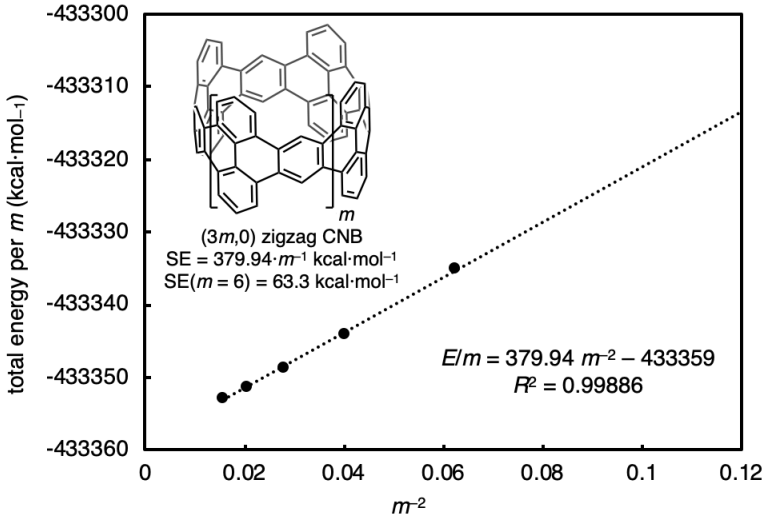


Supplementary Fig. 2. ACID plot of 1'. Magnetic field is applied perpendicularly. Isovalue: 0.04.

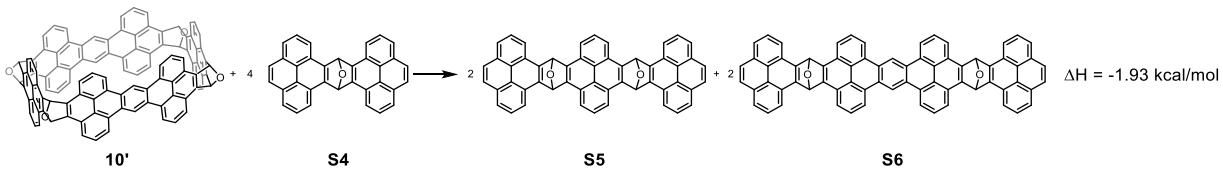


	min	max	total
bond	0.01307643	0.61105758	22.3109305
angle	0.00238678	0.14441399	5.32643547
dihedral	0.00400431	0.66038704	54.3488295
total	0.02004113	1.02730226	81.9861955

Supplementary Fig. 3. Details of StrainViz. (a) The fragment structure for StrainViz calculation of **1'**. (b) Parameters obtained from StrainViz calculations (kcal·mol^{-1}).



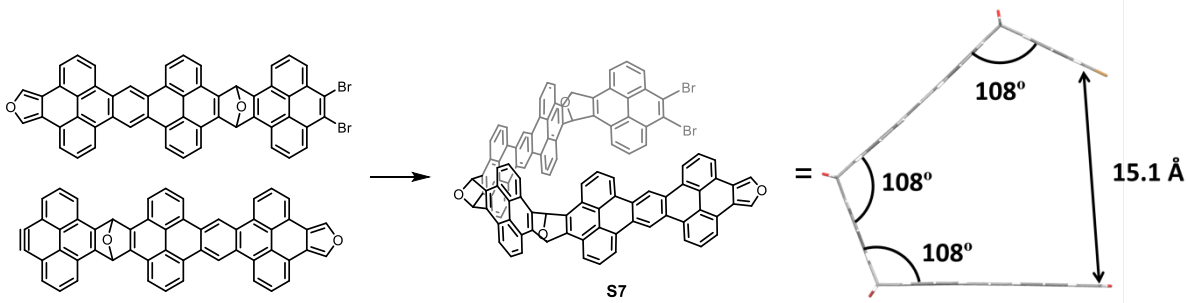
Supplementary Fig. 4. Plot of the total energy per m as a function of m^{-2} with linear regression line.



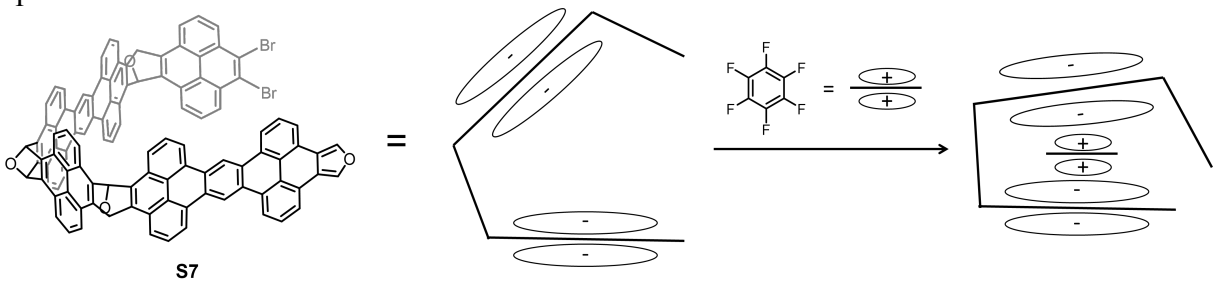
Supplementary Fig. 5. Hypothetical homodesmotic reactions with the enthalpy change for estimation of strain energy of macrocycle **10'.**

Postulated π-π template effect of hexafluorobenzene

In the optimized structure of the model intermediate **S7** (Supplementary Fig. 6) (B3LYP/6-31G(d)), the distance between the two ends is quite large (15.1 Å) and thus difficult to form a macrocycle. By adding hexafluorobenzene, we postulate that the two ends of **S7** can be brought closer together due to π-π template effect to favor the formation of a macrocycle as represented in a simple schematic diagram as shown in Supplementary Fig. 7.

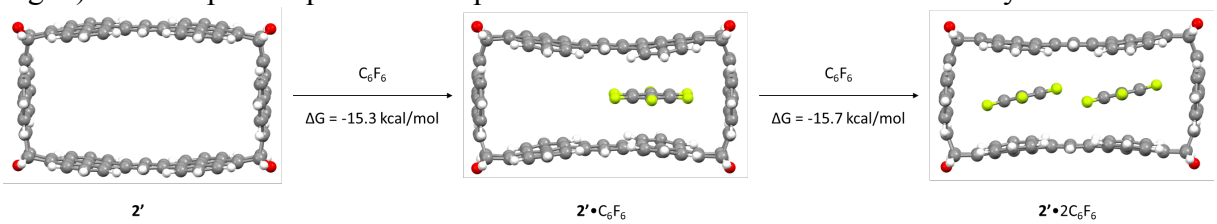


Supplementary Fig. 6. Chemical structure of the model intermediate **S7** together with DFT optimized structure.

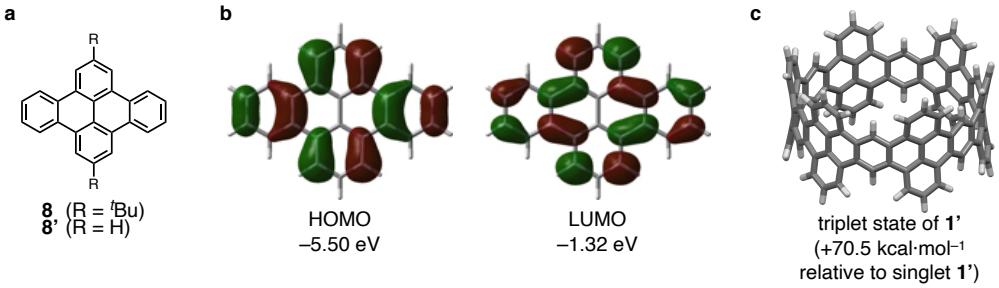


Supplementary Fig. 7. Schematic diagram of the postulate π-π template effect between model intermediate **S7** and hexafluorobenzene.

Moreover, by using DFT calculation at B3LYP-D3/6-31G(d) level of theory, the intermediate macrocycle **2'** was found to be able to bind to one or two hexafluorobenzene (Supplementary Fig. 8). This helps to explain the template effect of hexafluorobenzene in the synthesis of **2**.



Supplementary Fig. 8. Binding of hexafluorobenzenes with macrocycle **2'**.

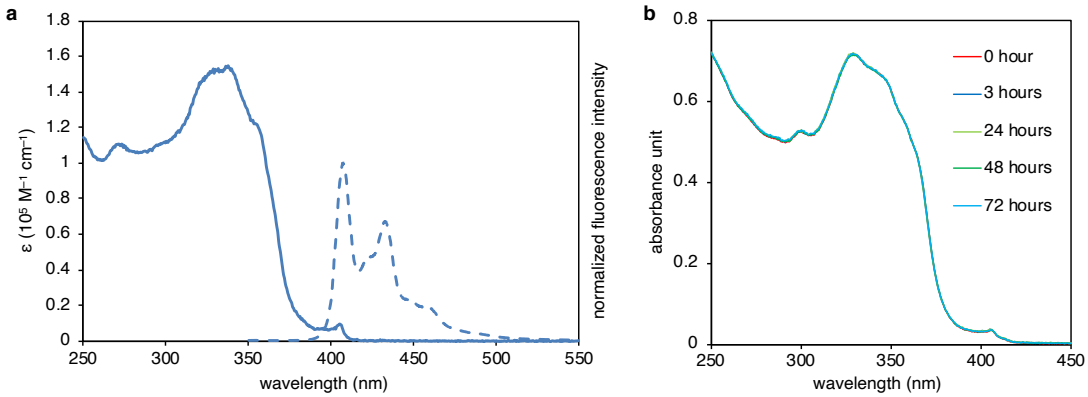


Supplementary Fig. 9. Calculations for reference molecules. (**a**) Structure of **8** and **8'**. (**b**) Frontier molecular orbitals of **8'** and their energies calculated by using B3LYP/6-31G(d) level of theory (isovalue: 0.04). (c) Optimized structure of triplet state of **1'**. Singlet biradical state could not be found by stable=opt method.

Supplementary Table 2. Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree): *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.

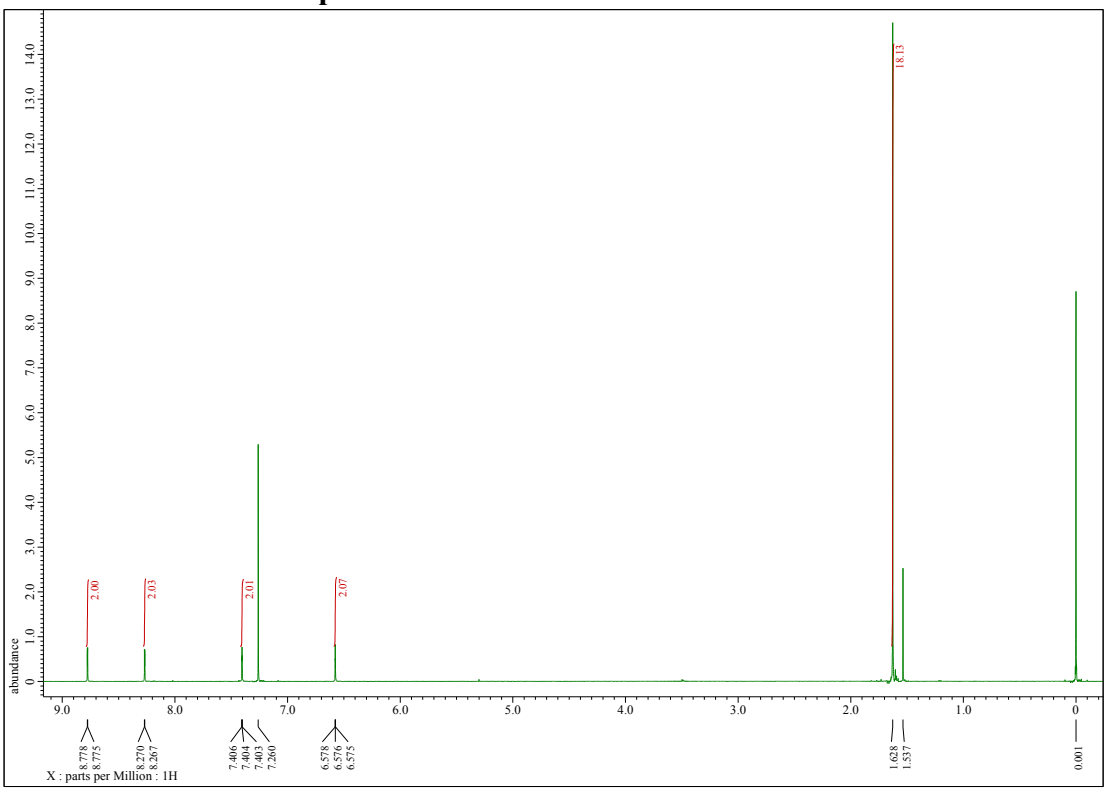
molecule	***E*** (Hartree)	***E+ZPE*** (Hartree)	***H*** (Hartree)	***G*** (Hartree)
(12,0)CNB	-2763.0987888	-2762.298751	-2762.254631	-2762.364872
(15,0)CNB	-3453.9473604	-3452.946087	-3452.890344	-3453.024434
(18,0)CNB (**1'**)	-4144.7822763	-4143.579860	-4143.512438	-4143.670837
(18,0)CNB (**1'**) triplet	-4144.6699797			
(21,0)CNB	-4835.6092986	-4834.205870	-4834.126724	-4834.312322
(24,0)CNB	-5526.4314399	-5524.827104	-5524.736190	-5524.947004
2'	-4445.4675902	-4444.246981	-4444.176951	-4444.345190
S4	-1381.7363399	-1381.323558	-1381.300636	-1381.373777
S5	-2147.6992668	-2147.081468	-2147.046500	-2147.145979
S6	-2838.5095165	-2837.691754	-2837.644786	-2837.772203
S7	-9588.9005799	-9587.680987	-9587.604925	-9587.800343
C_6F_6 (B3LYP-D3)	-827.6050233	-827.553742	-827.542977	-827.588984
2' (B3LYP-D3)	-4445.676424	-4444.455451	-4444.385184	-4444.555153
2'·C_6F_6 (B3LYP-D3)	-5273.3285624	-5272.054127	-5271.972533	-5272.168569
2'·2C_6F_6 (B3LYP-D3)	-6100.9874117	-6099.659966	-6099.567445	-6099.782514
8'	-923.059311475	-922.757889	-922.742035	-922.797932

5. Photophysical measurement

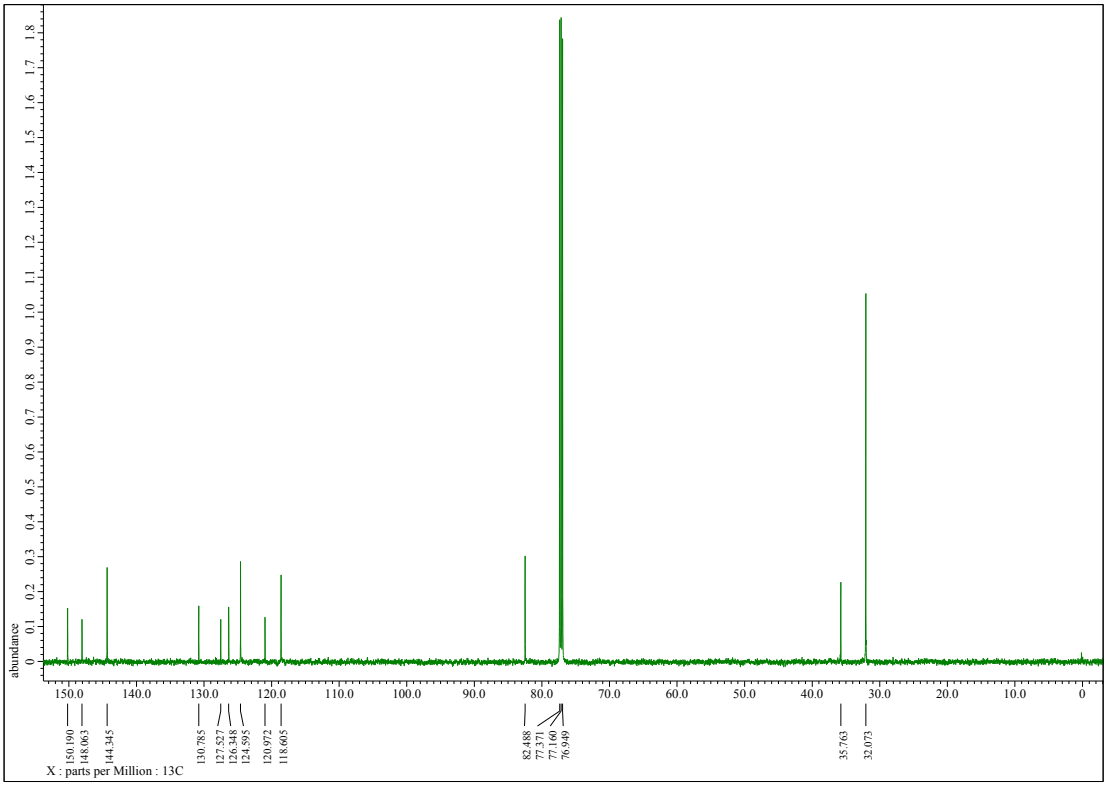


Supplementary Fig. 10. (**a**) UV–vis absorption (solid line) and fluorescence (broken line) of the dichloromethane solution of **1** and **8**. Fluorescence spectra were taken upon excitation at 320 nm and 330 nm for **1** and **8**, respectively. (**b**) Photostability experiment of **1** in CH_2Cl_2 under room light.

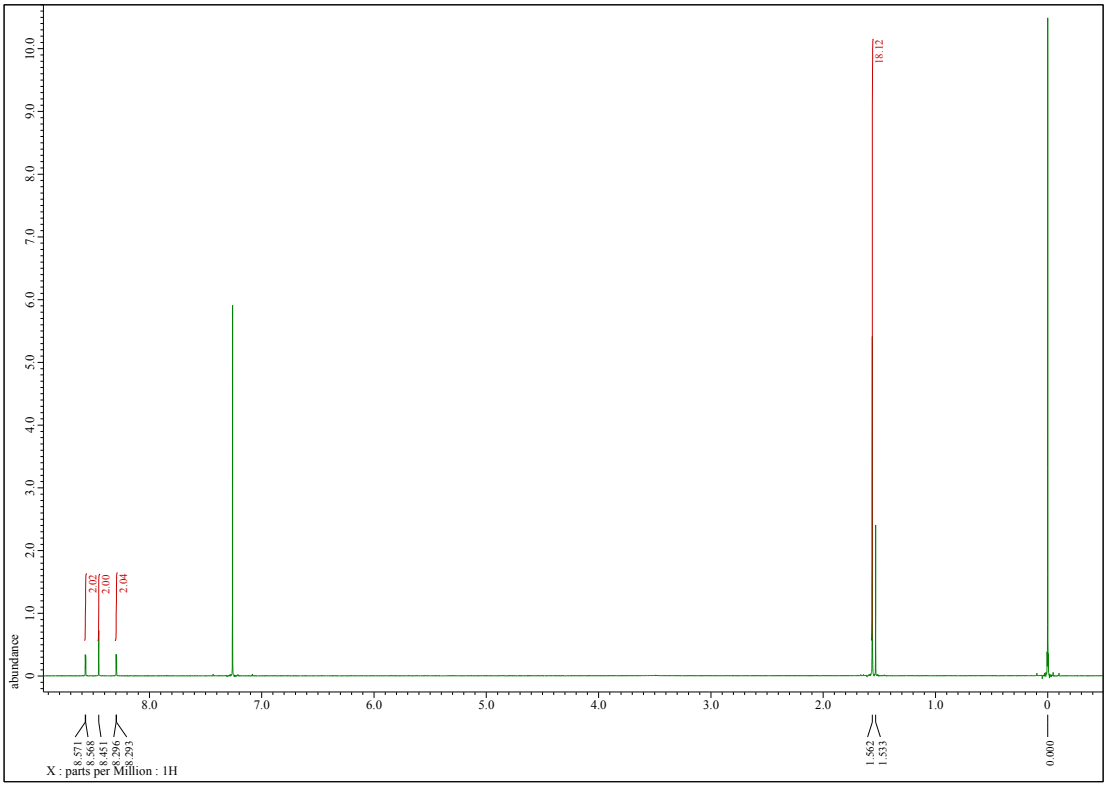
5. ^{1}H NMR and ^{13}C NMR spectra



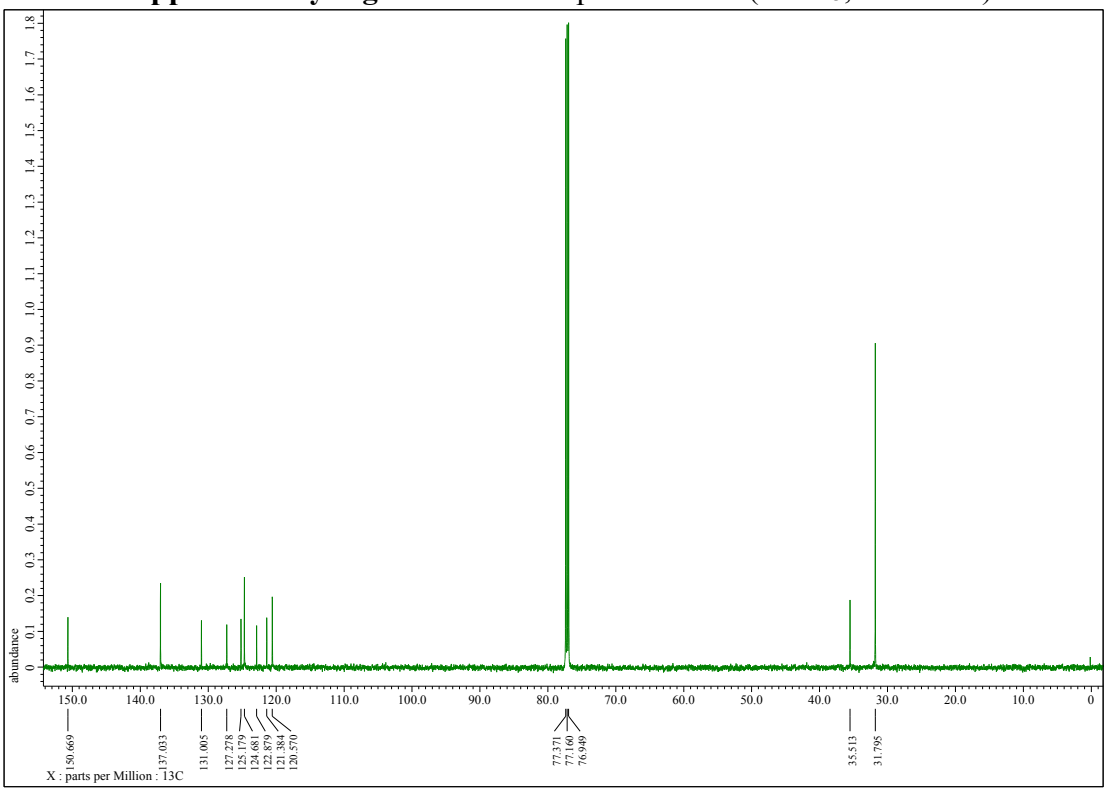
Supplementary Fig. 11. ^{1}H NMR spectrum of **S1** ($CDCl_3$, 600 MHz)



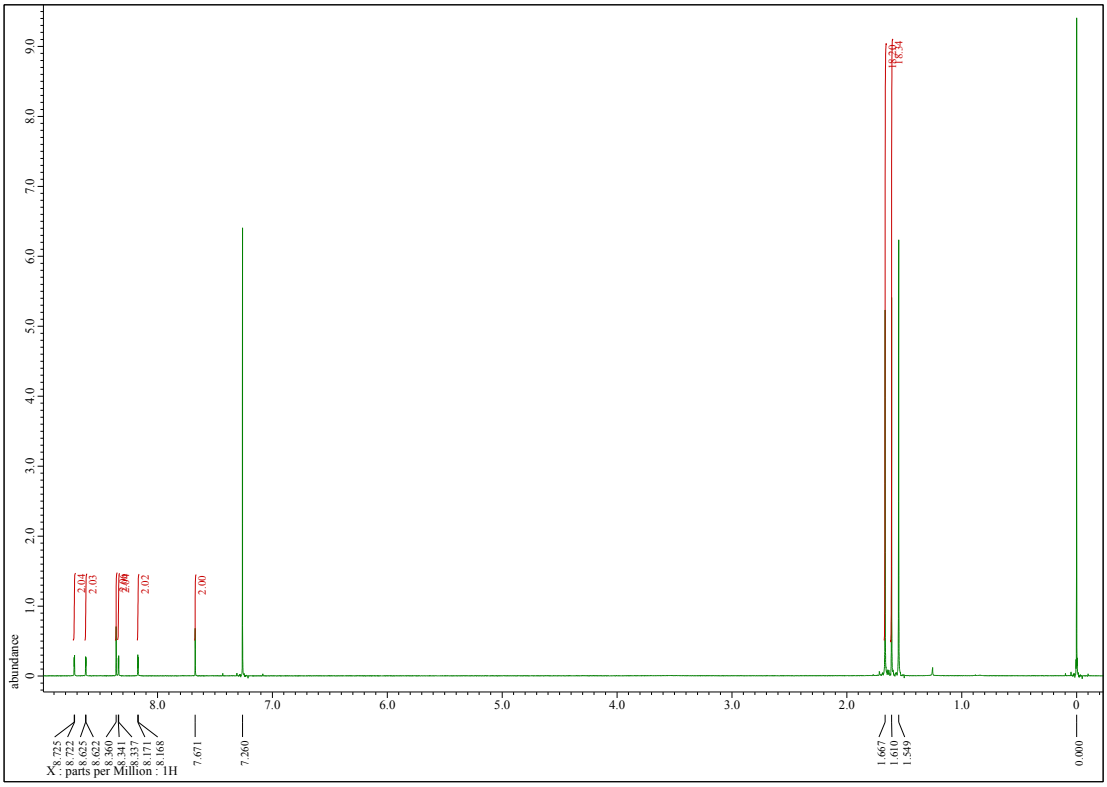
Supplementary Fig. 12. ^{13}C NMR spectrum of **S1** ($CDCl_3$, 150 MHz)



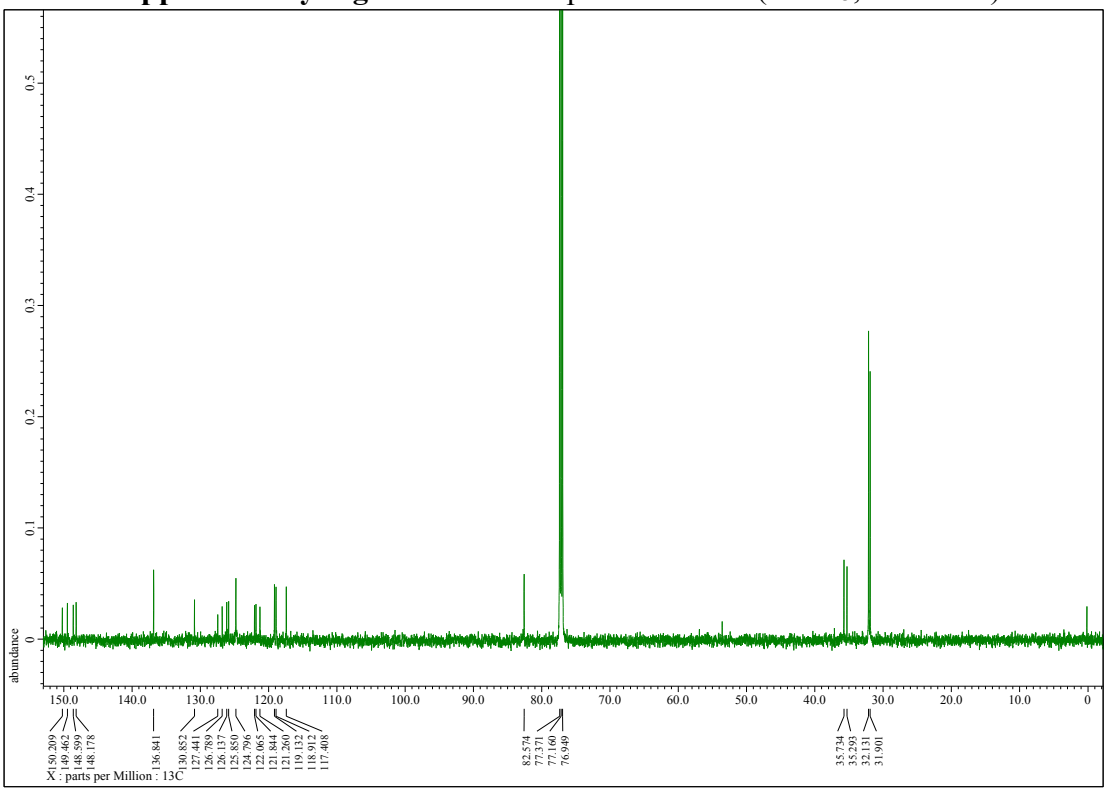
Supplementary Fig. 13. ^{1}H NMR spectrum of **4** ($CDCl_3$, 600 MHz)



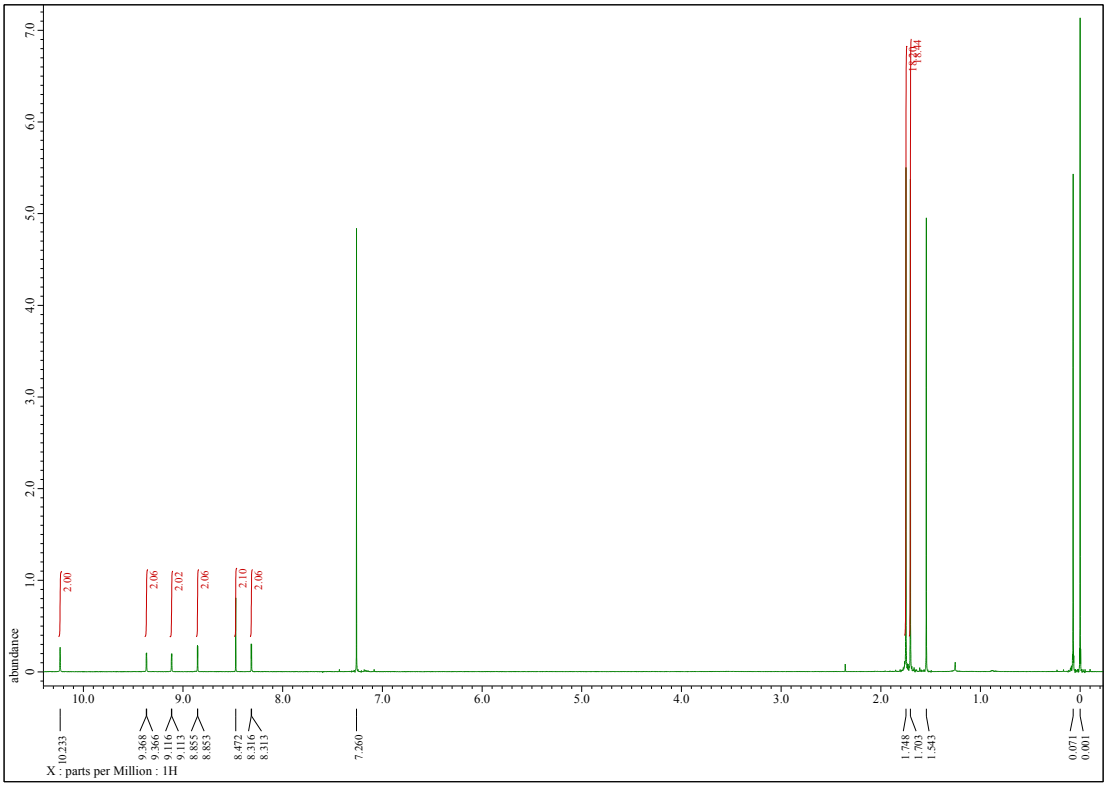
Supplementary Fig. 14. ^{13}C NMR spectrum of **4** ($CDCl_3$, 150 MHz)



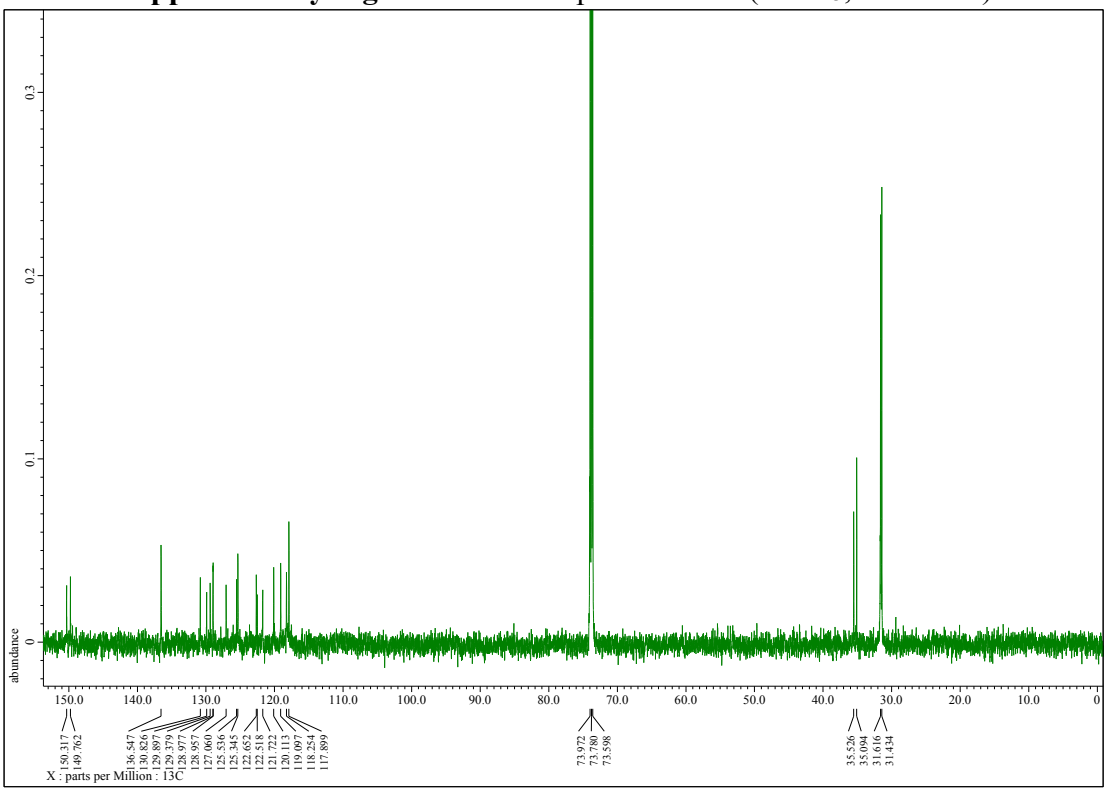
Supplementary Fig. 15. ^{1}H NMR spectrum of **S2** ($CDCl_3$, 600 MHz)



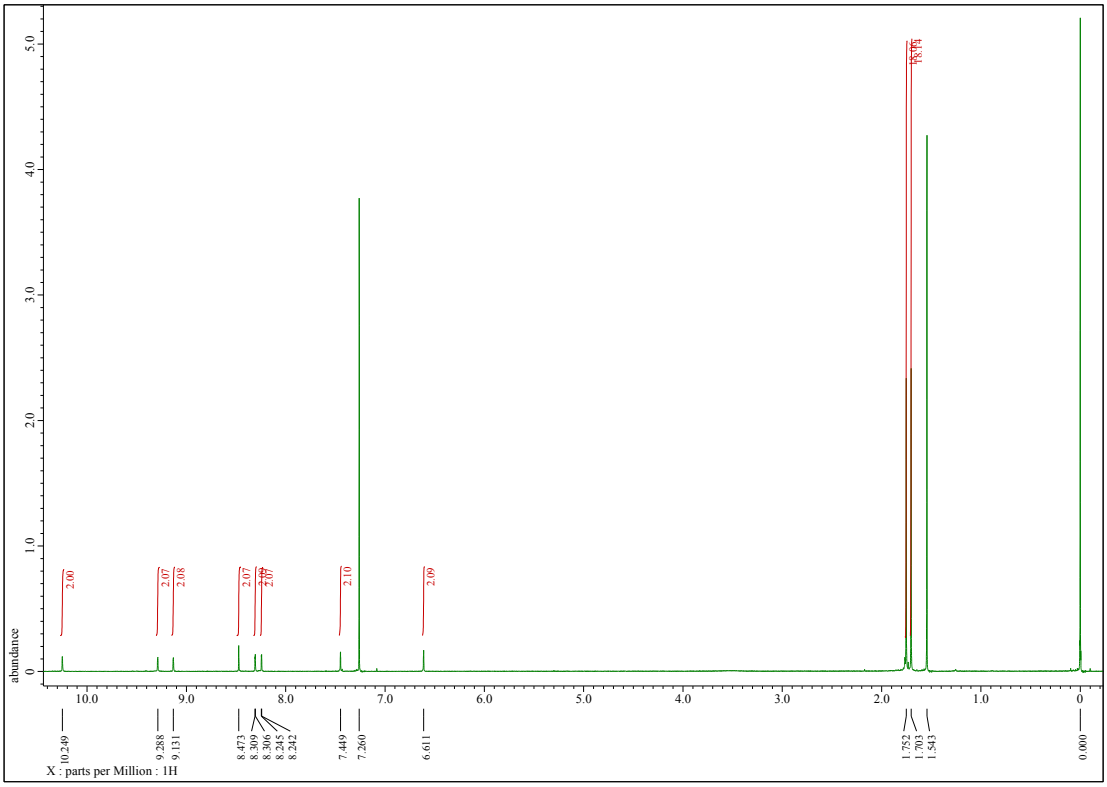
Supplementary Fig. 16. ^{13}C NMR spectrum of **S2** ($CDCl_3$, 150 MHz)



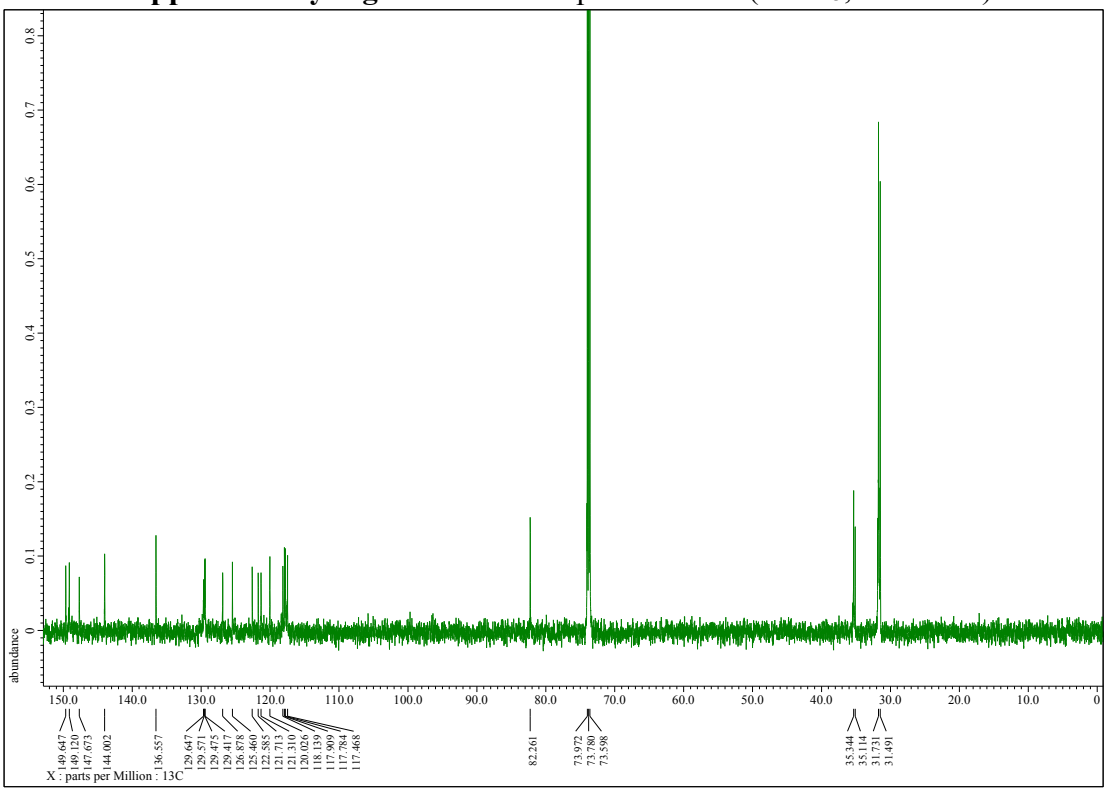
Supplementary Fig. 17. ^{1}H NMR spectrum of **5** ($CDCl_3$, 600 MHz)



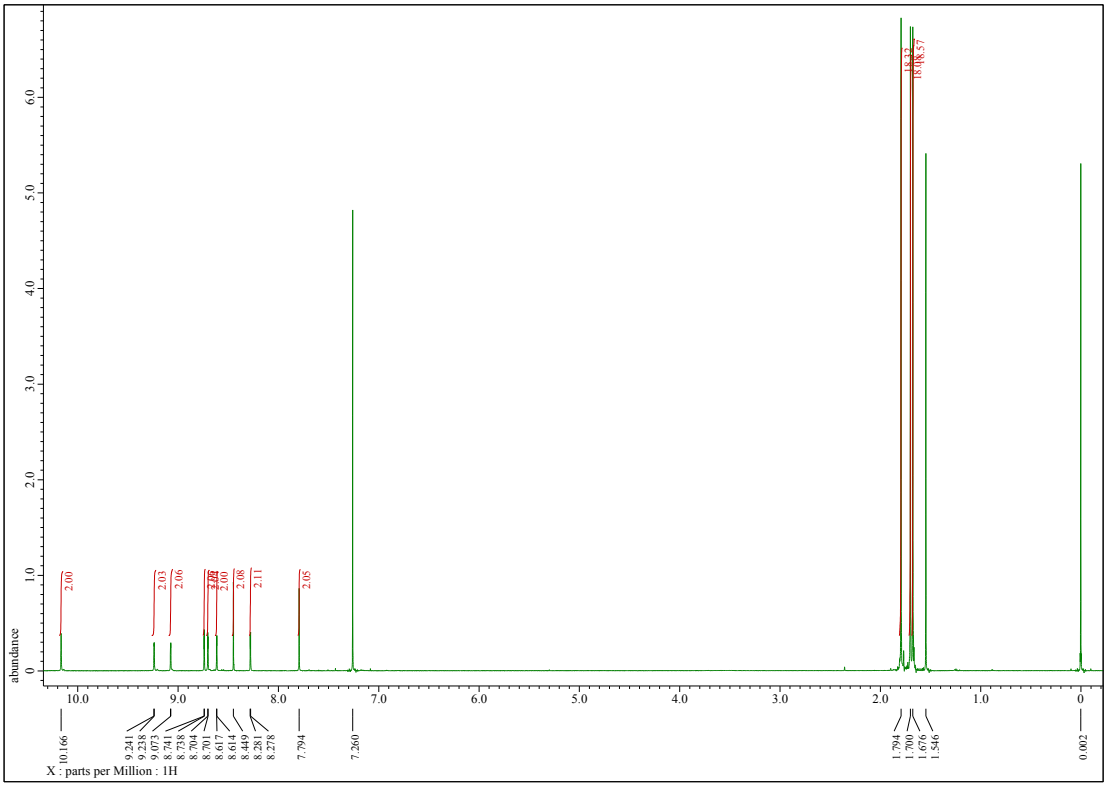
Supplementary Fig. 18. ^{13}C NMR spectrum of **5** ($CDCl_2CDCl_2$, 150 MHz, 120 °C)



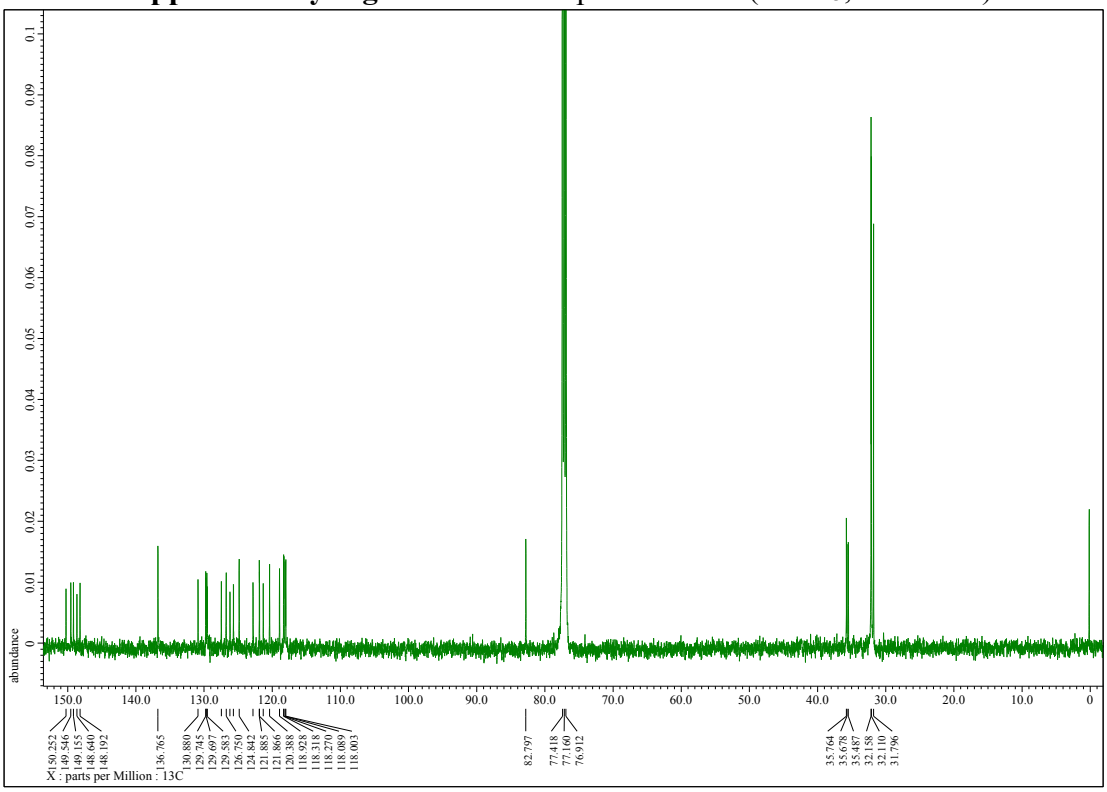
Supplementary Fig. 19. ^{1}H NMR spectrum of **6** ($CDCl_3$, 600 MHz)



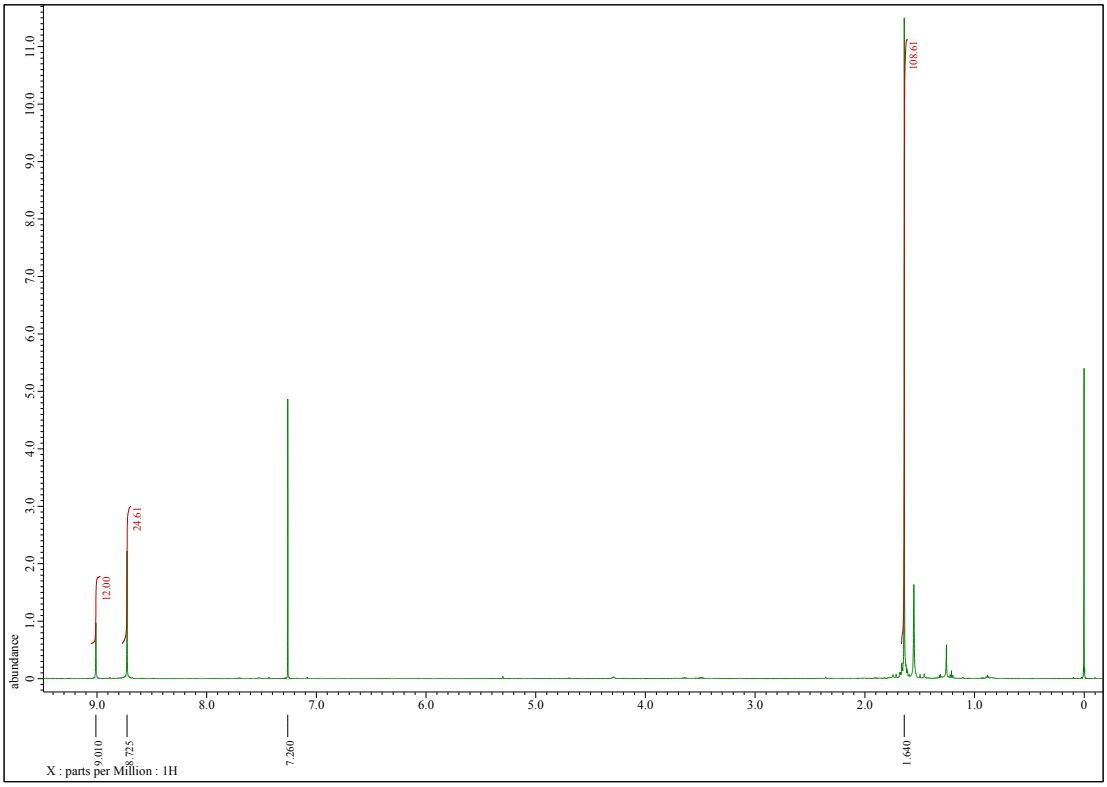
Supplementary Fig. 20. ^{13}C NMR spectrum of **6** ($CDCl_2CDCl_2$, 150 MHz, 100 °C)



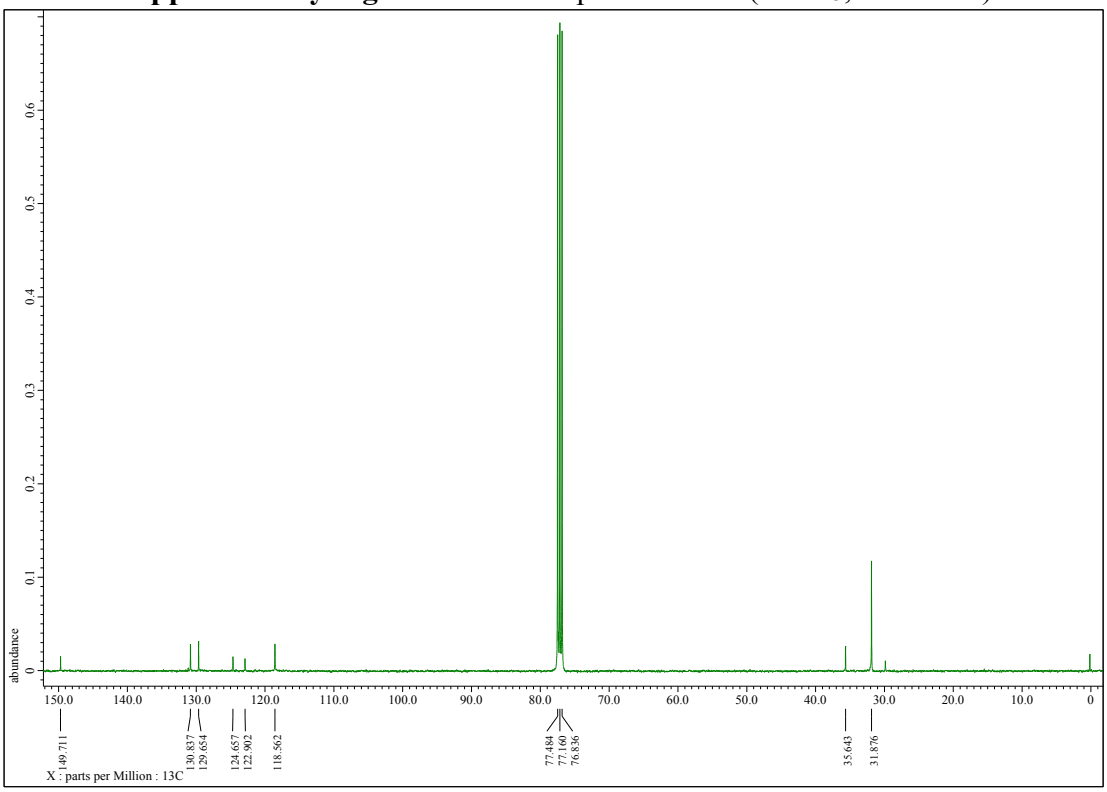
Supplementary Fig. 21. ^{1}H NMR spectrum of **7** ($CDCl_3$, 600 MHz)



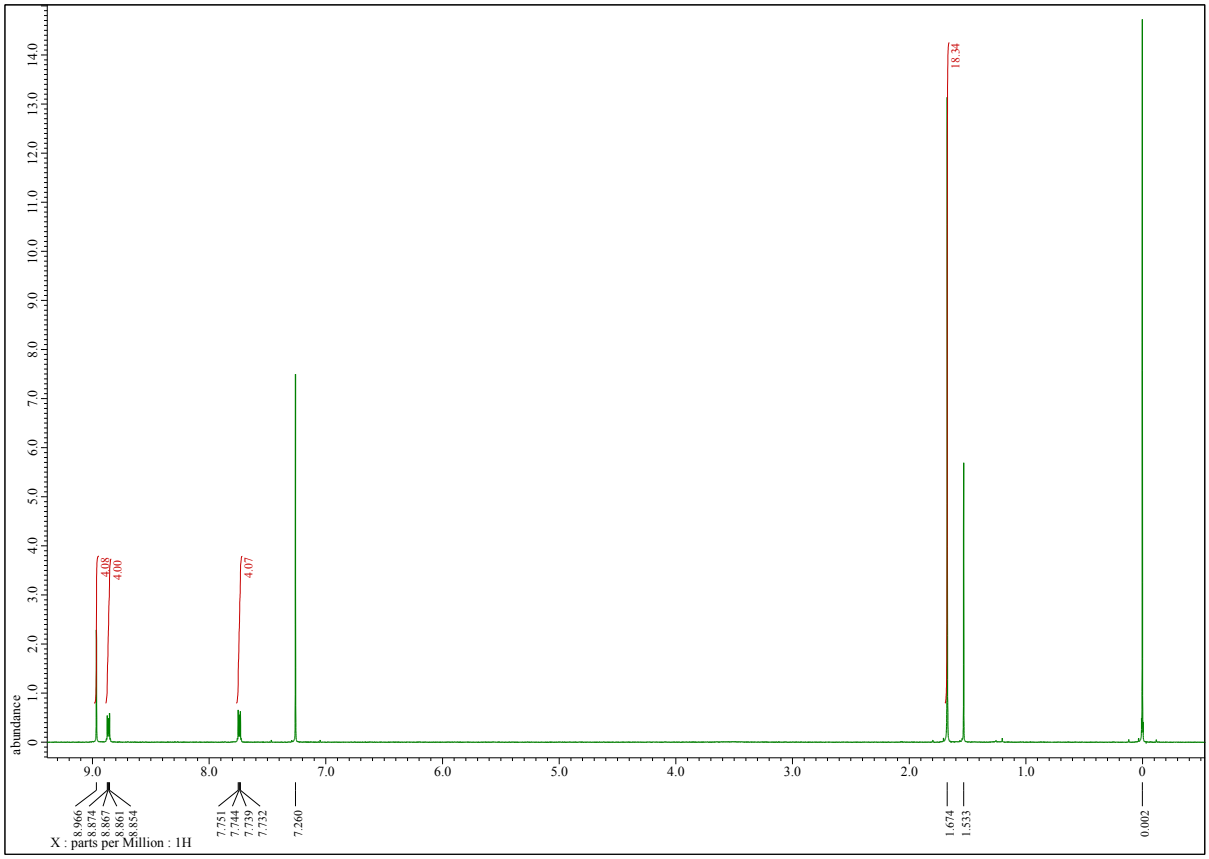
Supplementary Fig. 22. ^{13}C NMR spectrum of **7** ($CDCl_3$, 125 MHz)



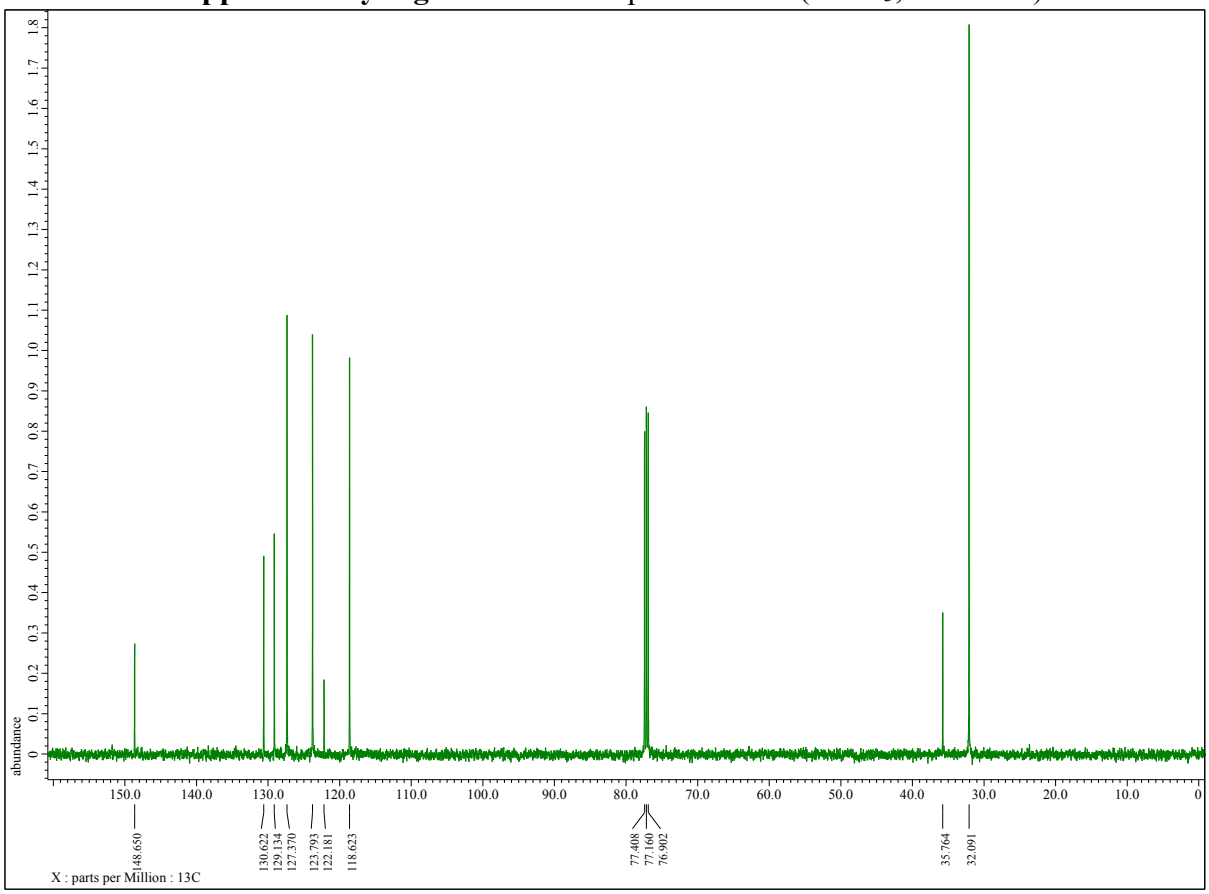
Supplementary Fig. 23. ^{1}H NMR spectrum of **1** ($CDCl_3$, 600 MHz)



Supplementary Fig. 24. ^{13}C NMR spectrum of **1** ($CDCl_3$, 100 MHz)



Supplementary Fig. 25. ^{1}H NMR spectrum of **8** ($CDCl_3$, 500 MHz)



Supplementary Fig. 26. ^{13}C NMR spectrum of **8** ($CDCl_3$, 125 MHz)

7. Supplementary References

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