Supporting Information

Infinitene: A Helically Twisted Figure-Eight [12]Circulene Topoisomer

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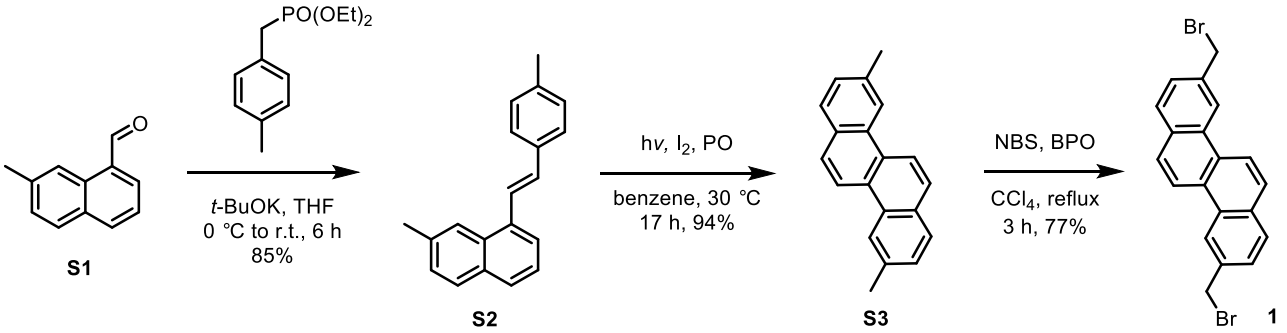
1. General remarks

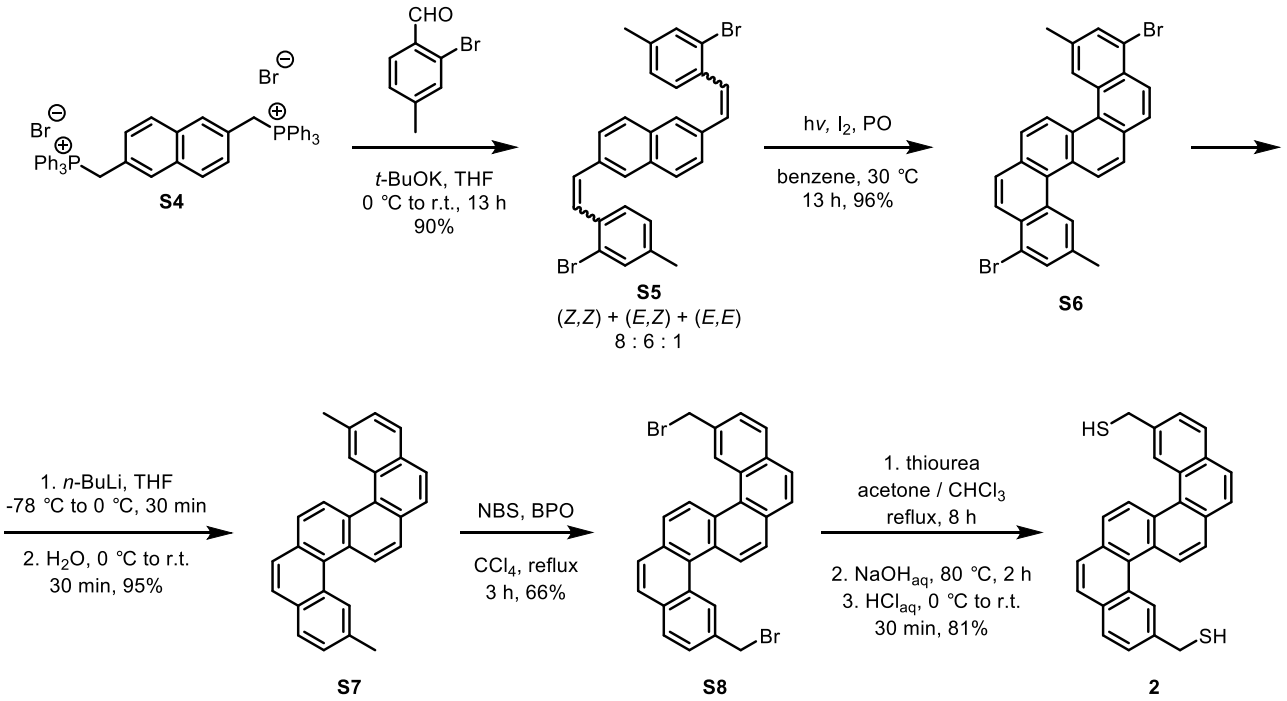
Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. All reagents were purchased from TCI, Aldrich or Wako. Starting materials **S1**[1] and **S4**[2] were synthesized according to the procedures reported in the literature. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen in oven-dried glassware with standard vacuum-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). The developed chromatograms were analyzed by UV lamp (254 nm). Flash column chromatography was performed with KANTO Silica Gel 60N (spherical, neutral, 40-100 μm) or Biotage Isolera® equipped with Biotage SNAP Cartridge KP-Sil columns. Preparative thin-layer chromatography (PTLC) was performed using Wako-gel® B5-F silica coated plates (0.75 mm) prepared in our laboratory. Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard). High-resolution mass spectra (HRMS) were obtained from a Thermo Fisher Scientific Exactive (APCI or ESI) and a JEOL JMS-T100GCV (Direct EI). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-600 (^{1}H 600 MHz, ^{13}C 151 MHz) spectrometer and a JEOL ECA 600II with Ultra COOL™ probe (^{1}H 600 MHz, ^{13}C 151 MHz). Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm), $CDCl_3$ (δ 7.26 ppm), CD_2Cl_2 (δ 5.32 ppm), 1,1,2,2-tetrachloroethane (TCE-d_2, δ 6.00 ppm), dimethylsulfoxide (DMSO-d_6, δ 2.50 ppm) or acetone-d_6 (δ 2.05 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm), CD_2Cl_2 (δ 53.8 ppm), TCE-d_2 (δ 73.8 ppm), dimethylsulfoxide (DMSO-d_6, δ 39.5 ppm) or acetone-d_6 (δ 29.8 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, m = multiplet), coupling constant (Hz), and integration. Chiral HPLC analysis was conducted on a Shimadzu Prominence 2000 instrument equipped with CHIRALPAK® IE column (10 mm × 250 mm). UV-vis absorption spectra were measured with a Shimadzu UV-3150 spectrometer. Circular dichroism spectra were measured with a JASCO FT/IR6100. Steady-state fluorescence measurements were performed with dilute solutions (10^{-6}M, optical density<0.1) contained in standard 1 cm quartz cuvettes at room temperature. Emission spectra were recorded on an F-4500 Hitachi spectrometer with a resolution of 0.4 nm and automatically corrected by instrumental function. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920-02 calibrated integrating sphere system equipped with multichannel spectrometer (PMA-11). Circularly polarized luminescence (CPL) spectra were recorded on a JASCO CPL-300 spectrofluoropolarimeter at 25 °C with 10 × 10 mm quartz cells under the following conditions: scattering angle: 0°, excitation slit width: 5 nm, emission slit width: 5 nm, scan rate: 100 nm min^{-1}, response: 4 s, accumulation: 8 times; data interval: 0.5 nm, solvent: CH_2Cl_2, excitation wavelength: 400 nm, HT voltage (photomultiplier): 650 V.

2. Experimental section

2.1. Preparation of precursors 2 and 3.

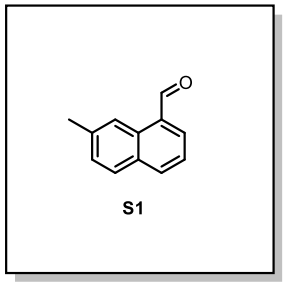


Scheme S1. Synthetic approach towards 3,9-bis(bromomethyl)chrysene (**2**). PO: propylene oxide, BPO: benzoyl peroxide.



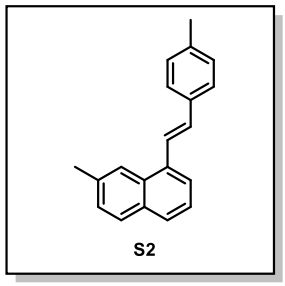
Scheme S2. Synthetic approach towards dibenzo[*c*,*l*]chrysene-3,11-diyldimethanethiol (**3**). PO: propylene oxide, BPO: benzoyl peroxide.

7-Methyl-1-naphthaldehyde (S1)



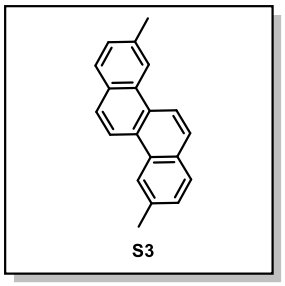
S1 was synthesized according to the literature procedure.[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.38 (s, 1H), 9.06 (d, J = 0.7 Hz, 1H), 8.05 (d, J = 8.1 Hz,1H), 7.95 (dd, J = 7.0, 1.1 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H), 7.55 (dd, J = 7.2, 7.2 Hz, 1H), 7.43 (dd, J = 8.3, 1.5 Hz, 1H), 2.59 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 193.7, 139.4, 136.9, 135.1, 132.0, 130.9, 130.8, 129.1, 128.2, 123.9 (2C), 22.3. Spectral properties were in agreement with those previously reported.

(*E*)-7-Methyl-1-(4-methylstyryl)naphthalene (S2)



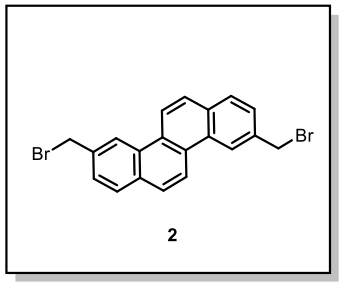
To a solution of **S1** (1.90 g, 11.2 mmol) and diethyl (4-methylbenzyl)phosphonate (3.70 g, 15.3 mmol) in THF (500 mL) was added a solution of potassium *tert*-butoxide (2.09 g, 18.6 mmol) in 20 mL of dry THF dropwise through a syringe at 0 °C for 30 minutes. After stirring the resulting mixture at room temperature for 6 h, the mixture was quenched with 10 mL of 2 M HCl. THF was evaporated, and the resulting aqueous phase was extracted with $CHCl_3$ (3 x 100 mL). The combined organic layers were concentrated under reduced pressure. The crude product was purified by a flash column chromatography (hexane/CH_2Cl_2 = 4:1) and recrystallized from ethanol to afford **S2** (2.45 g, 85%) as pale-yellow needles. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.81 (d, J = 16.2 Hz, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.69 (d, J = 7.1 Hz, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 7.33 (dd, J = 8.4, 1.5 Hz, 1H), 7.21 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 16.2 Hz, 1H), 2.55 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.6, 135.7, 135.0, 134.5, 131.9, 131.6, 131.4, 129.4, 128.4, 128.0, 127.6, 126.6, 125.1, 124.8, 123.6, 122.9, 22.1, 21.3. HRMS (APCI$^+$) *m/z* calcd for $C_{20}H_{19}$ $[M+H]^+$: 259.1481, found 259.1482.

3,9-Dimethylchrysene (S3)



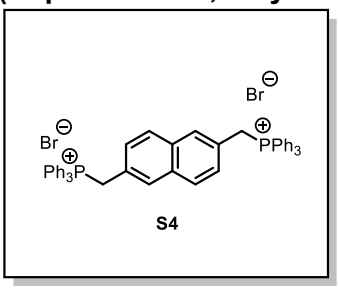
Argon was bubbled through a stirred solution of **S2** (439 mg, 1.70 mmol) and iodine (1.30 g, 5.10 mmol) in dry benzene (500 mL) for 30 min. Then, 3.0 mL of propylene oxide was added, and the reaction mixture was irradiated with a 450 W UV lamp and stirred for additional 24 h at 30 °C. After the reaction was completed, the mixture was washed with aqueous $Na_2S_2O_3$ solution, water, and brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure to give **S3** (425 mg, 94%) as a pale-yellow solid. This procedure was repeated three times to collect 1.29 g of the product. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, J = 8.9 Hz, 2H), 8.55 (s, 2H), 7.94 (d, J = 8.9 Hz, 2H), 7.87 (d, J = 7.9 Hz, 2H), 7.45 (dd, J = 8.1, 1.2 Hz, 2H), 2.65 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.3, 130.7, 130.2, 128.3, 128.2, 128.0, 126.8, 122.7, 120.3, 22.3. HRMS (APCI$^+$) *m/z* calcd for $C_{20}H_{17}$ $[M+H]^+$: 257.1325, found 257.1325.

3,9-Bis(bromomethyl)chrysene (2)



To a solution of **S3** (1.24 g, 4.84 mmol) in CCl_4 (100 mL) were added *N*-bromosuccinimide (1.89 g, 10.6 mmol, 2.2 equiv) and benzoyl peroxide (116 mg, 0.48 mmol, 9.9 mol%). After stirring the resulting mixture at 80 °C for 3 h, the solvent was evaporated and the resulting solid was washed with water, ethanol and diethyl ether, and recrystallized from ethanol to afford **2** (1.54 g, 77%) as a white solid. ^{1}H NMR (600 MHz, $Cl_2CHCHCl_2$, 80 °C) δ 8.80 (s, 2H), 8.75 (d, J = 8.9 Hz, 2H), 8.05 (d, J = 9.3 Hz, 2H), 8.03 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 4.86 (s, 4H). ^{13}C NMR (151 MHz, TCE-d_2, 80 °C) δ 136.1, 131.9, 130.3, 129.2, 128.3, 127.3, 127.1, 123.4, 121.6, 34.2. HRMS (direct EI$^+$ at 200 °C) *m/z* calcd for $C_{20}H_{14}Br_2$ $[M]^+$ (monoisotopic): 411.9462, found: 411.9457.

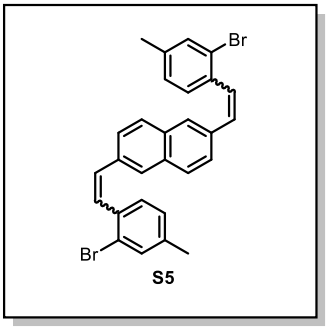
(Naphthalene-2,6-diylbis(methylene))bis(triphenylphosphonium) bromide (S4).



S4

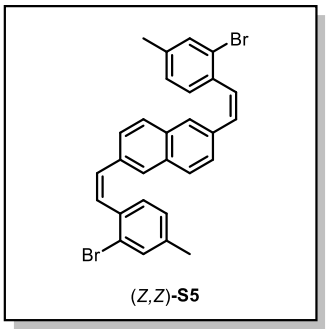
S4 was synthesized according to the literature procedure.[2] ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.93–7.88 (m, 6H), 7.75–7.67 (m, 24H), 7.48 (d, J = 8.6 Hz, 2H), 7.45 (br s, 2H), 7.05 (d, J = 8.6 Hz, 2H), 5.39 (d, J = 15.8 Hz, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 135.1, 134.0 (d, $^2J_{PC}$ = 10.1 Hz), 131.6, 130.07 (d, $^3J_{PC}$ = 13.0 Hz), 128.7, 128.0, 126.5, 126.4, 117.7 (d, $^1J_{PC}$ = 85.3 Hz), 28.2 (d, $^1J_{PC}$ = 4.80 Hz). Spectral properties were in agreement with those previously reported.

2,6-Bis(2-bromo-4-methylstyryl)naphthalene (S5)

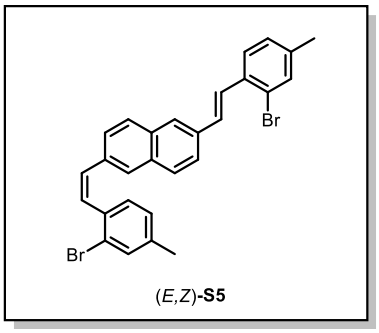


S5

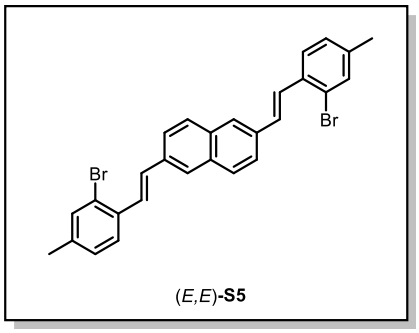
To a solution of 2-bromo-4-methylbenzaldehyde (3.58 g, 18.0 mmol) and **S4** (6.83 g, 8.14 mmol) in dry THF (600 mL) was added a solution of potassium *tert*-butoxide (2.24 g, 20.0 mmol) in 30 mL of dry THF dropwise through a syringe at 0 °C for 30 min. After stirring the resulting mixture at room temperature for 13 h, the mixture was quenched with 100 mL of 2 M HCl and diluted with ethyl acetate. Two layers were separated, and aqueous phase was extracted with AcOEt (3 x 75 mL). Combined organic layers were concentrated under reduced pressure. The crude product was passed through a short pad of silica gel ($CHCl_3$) and purified by a flash column chromatography (hexane/CH_2Cl_2 = 9:1) to afford **S5** (3.80 g, 90%) as a mixture of isomers in a relative ratio of (*Z,Z*)**-S5**/(*E,Z*)**-S5**/(*E,E*)**-S5** = 8:6:1. HRMS (APCI$^+$) *m/z* calcd for $C_{28}H_{23}Br_2$ $[M+H]^+$: 517.0163 (monoisotopic), found 517.0161. Isomers were separated by a gradient flash chromatography (hexane/CH_2Cl_2 = 99:1–95:5).



(*Z,Z*)-**S5**



(*E,Z*)-**S5**



(*E,E*)-**S5**

2,6-Bis((*Z*)-2-bromo-4-methylstyryl)naphthalene ((*Z,Z*)-S5)

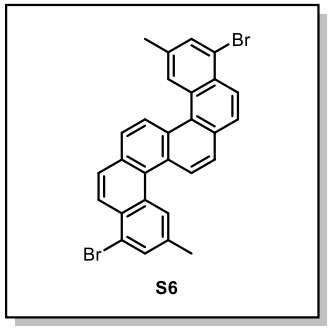
White solid (non-fluorescent on TLC). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (s, 2H), 7.46–7.44 (m, 4H), 7.17 (dd, J = 8.7, 1.3 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 6.86 (d, J = 7.9, 0.7 Hz, 2H), 6.76 (d, J = 12.4 Hz, 2H), 6.65 (d, J = 12.4 Hz, 2H), 2.30 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.1, 134.8, 134.4, 133.1, 132.5, 130.8, 130.6, 129.7, 128.0, 127.9, 127.5, 127.0, 123.7, 20.83.

2-((*E*)-2-Bromo-4-methylstyryl)-6-((*Z*)-2-bromo-4-methylstyryl)naphthalene ((*E,Z*)-S5)

Yellow solid (fluorescent on TLC). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.70 (dd, J = 8.6, 1.7 Hz, 1H), 7.67 (d, J = 8.6 Hz, 1H), 7.63 (s, 1H), 7.590 (d, J = 7.9 Hz, 1H), 7.585 (d, J = 8.6 Hz, 1H), 7.53 (d, J = 16.2 Hz, 1H), 7.46 (d, J = 0.7 Hz, 1H), 7.42 (d, J = 0.7 Hz, 1H), 7.22 (dd, J = 8.6, 0.7 Hz, 1H), 7.12 (d, J = 16.2 Hz, 1H), 7.13–7.11 (m, 1H), 7.09 (d, J = 7.9 Hz, 1H), 6.86 (dd, J = 7.7, 1.0 Hz, 1H), 6.79 (d, J = 12.0 Hz, 1H), 6.68 (d, J = 12.0 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.2, 139.1, 134.9, 134.8, 134.5, 134.2, 133.5, 133.14, 133.07, 132.8, 130.8, 130.6, 130.4, 129.8, 128.5, 128.4, 128.2, 127.9, 127.64, 127.58, 127.3, 126.6, 126.3, 124.0, 123.9, 123.8, 20.84, 20.80.

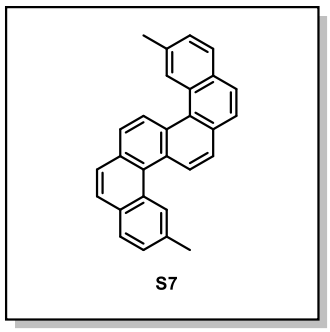
2,6-Bis((*E*)-2-bromo-4-methylstyryl)naphthalene ((*E,E*)-S5)
Bright yellow solid (fluorescent on TLC). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (s, 2H), 7.82 (d, J = 8.3, 2H), 7.23 (d, J = 8.3 Hz, 2H), 7.76 (dd, J = 8.6, 1.4 Hz, 2H), 7.61 (d, J = 7.9 Hz, 2H), 7.56 (d, J = 16.2 Hz, 2H), 7.45–7.43 (m, 2H), 7.15 (d, J = 16.2 Hz, 2H), 7.15–7.13 (m, 2H), 2.35 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.2, 134.9, 134.2, 133.5, 133.4, 130.4, 128.5 (2C), 127.7, 126.7, 126.3, 124.2, 124.0, 20.8.

1,9-Dibromo-3,11-dimethyldibenzo[*c,l*]chrysene (S6)



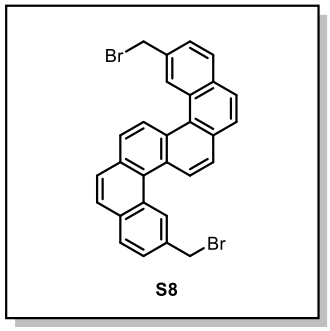
We utilized a strategy of bromine auxiliaries in photosynthesis of helicenes developed by Katz and co-workers.[3] Argon was bubbled through a stirred solution of **S5** (mixture of isomers) (486 mg, 0.94 mmol) and iodine (1.02 g, 4.02 mmol) in dry benzene (500 mL) for 30 min. Then, 3.0 mL of propylene oxide was added, and the mixture was irradiated with a 450 W UV lamp and stirred for additional 13 h at 30 °C. After the reaction was completed, the mixture was washed with aqueous $Na_2S_2O_3$ solution, water, and brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure to give **S6** (463 mg, 96%) as a yellow solid. The procedure was repeated eight times to collect 3.70 g of the product. The corresponding photocyclization reactions using pure (*Z,Z*)-**S5**, (*E,Z*)-**S5**, and (*E,E*)-**S5** gave **S6** in 99%, 98% and 91% yields respectively. These products were used in the next step without further purifications. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.02 (d, J = 8.9 Hz, 2H), 8.77 (s, 2H), 8.37 (d, J = 8.9 Hz, 2H), 7.93 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.6 Hz, 2H), 7.82 (s, 2H), 2.62 (s, 6H). HRMS (direct EI$^+$ at 230 °C) *m/z* calcd for $C_{28}H_{18}Br_2$ $[M+H]^+$: 511.9775 (monoisotopic), found 511.9766.

3,11-Dimethyldibenzo[*c,l*]chrysene (S7)



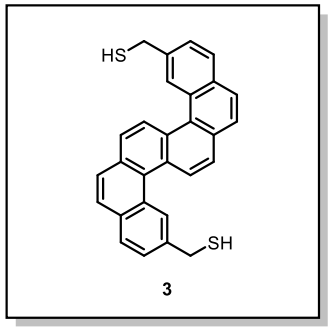
To a stirred solution of **S6** (257 mg, 0.50 mmol) in dry THF (15 mL) was added, a solution of *n*-butyllithium (2.6 M solution in hexane, 0.50 mL, 1.30 mmol, 2.6 equiv) dropwise through a syringe at –78 °C. After stirring for additional 30 min, the resulting mixture was warmed to 0 °C over 30 min. The reaction was quenched with 1.5 mL water at 0 °C, and the mixture was warmed to rt over 30 min. Solvent was evaporated, and the crude product was passed through a short pad of silica gel ($CHCl_3$) giving **S7** (169 mg, 95%) as a pale-yellow solid. A large-scale reaction using **S6** (3.68 g, 7.15 mmol) in dry THF (200 mL), *n*-butyllithium (2.6 M solution in hexane, 6.88 mL, 17.9 mmol, 2.5 equiv) and water (2 mL) gave **S7** (2.25 g, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 (d, J = 8.6 Hz, 2H), 8.85 (s, 2H), 7.95 (d, J = 8.3 Hz, 2H), 7.92 (d, J = 8.6 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.83 (d, J = 8.6 Hz, 2H), 7.48 (dd, J = 8.1, 1.2 Hz, 2H), 2.64 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.0, 131.5, 130.8, 130.4, 130.3, 128.5, 127.9, 127.8, 127.4, 127.3, 126.0, 125.4, 22.2. One quaternary carbon peak can be overlapped. HRMS (APCI$^+$) *m/z* calcd for $C_{28}H_{21}$ $[M+H]^+$: 357.1638, found 357.1632.

3,11-Bis(bromomethyl)dibenzo[*c,l*]chrysene (S8)

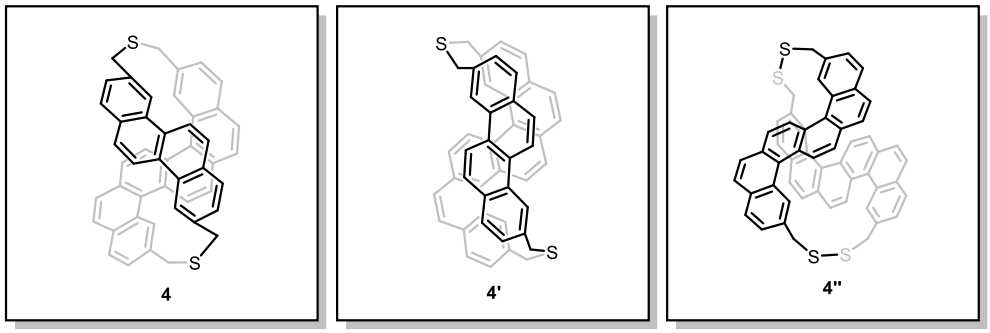


To a solution of **S7** (2.31 g, 6.48 mmol) in CCl_4 (120 mL) were added *N*-bromosuccinimide (2.67 g, 15.0 mmol, 2.3 equiv) and benzoyl peroxide (157 mg, 0.65 mmol, 10 mol%). After stirring the resulting mixture at 80 °C for 3 h, the solvent was evaporated and the crude product was purified by a flash column chromatography (hexane/CH_2Cl_2 = 3:1) to afford **S8** (2.20 g, 66%) as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.08 (d, J = 8.6 Hz, 2H), 9.05–9.04 (br s, 2H), 8.05 (d, J = 8.3 Hz, 2H), 7.99 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 8.6 Hz, 2H), 7.93 (d, J = 8.6 Hz, 2H), 7.70 (dd, J = 8.3, 1.7 Hz, 2H), 4.81 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.7, 133.2, 130.7, 130.6, 130.1, 129.4, 128.7, 127.51, 127.50, 127.4, 127.01, 126.94, 126.4, 34.5. One quaternary carbon peak can be overlapped. HRMS (direct EI$^+$ at 200 °C) *m/z* calcd for $C_{28}H_{18}Br_2$ $[M]^+$: 511.9775 (mono isotopic), found 511.9782.

Dibenzo[*c,l*]chrysene-3,11-diyldimethanethiol (3)



To a solution of **S8** (2.12 g, 4.12 mmol) in 300 mL of 1:1 mixture of acetone and $CHCl_3$ was added thiourea (913 mg, 12.0 mmol, 2.9 equiv), and the resulting mixture was refluxed at 78 °C for 8 h. The resulting thiouronium salt was collected by filtration and dissolved in 100 mL of 6% NaOH solution and stirred at 80 °C for 2 h. Then, the mixture was cooled to 0 °C, and quenched with 6 M HCl. The resulting solid was collected by filtration and washed with water and diethyl ether giving **3** (1.40 g, 81%) as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.09 (d, J = 8.6 Hz, 2H), 8.97 (s, 2H), 8.02 (d, J = 8.3 Hz, 2H), 7.96 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.6 Hz, 2H), 7.64 (dd, J = 8.2, 1.4 Hz, 2H), 4.04 (d, J = 7.6 Hz, 4H), 1.89 (t, J = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.1, 132.5, 130.7, 130.5, 130.2, 129.2, 127.5, 127.42, 127.39, 127.33, 126.4, 126.3, 29.7. One aromatic carbon peak can be overlapped. HRMS (direct EI$^+$ at 300 °C) *m/z* calcd for $C_{28}H_{20}S_2$ $[M]^+$: 420.1006, found 420.1023.



A solution of **2** (1.36 g, 3.28 mmol) in dry DMF (300 mL) heated to 70 °C was slowly cannulated over 28 h to a stirred suspension of Cs_2CO_3 (1.18 g, 3.61 mmol) and **3** (1.38 g, 3.28 mmol) in dry DMF (500 mL) heated to 55 °C. After stirring the mixture for additional 40 h at 55 °C, DMF was evaporated and residue was washed with water, ethanol and diethyl ether. Then the residue was washed with $CHCl_3$ leaving pure **4** (550 mg, 25%). Filtrate was subjected to a flash column chromatography (hexane/CH_2Cl_2 = 3:1) which allowed separation of the side products: conformer **4′** (110 mg, 5%) and disulfide dimer **4″** (220 mg, 16%).

Configuration of conformers were determined by ^{1}H NMR (Figure S1). In the case of conformer **4′**, three upfield-shifted signals (from 6.60 to 6.90 ppm) were observed in the spectrum, assigned to the hydrogen atoms indicated with colored spheres. Particularly indicative is doublet of doublets at 6.90 ppm marked with the red sphere. The corresponding hydrogen atom in **4** would not be affected by any benzene's electron cloud due to its spatial arrangement, hence no upfield shift would be observed.

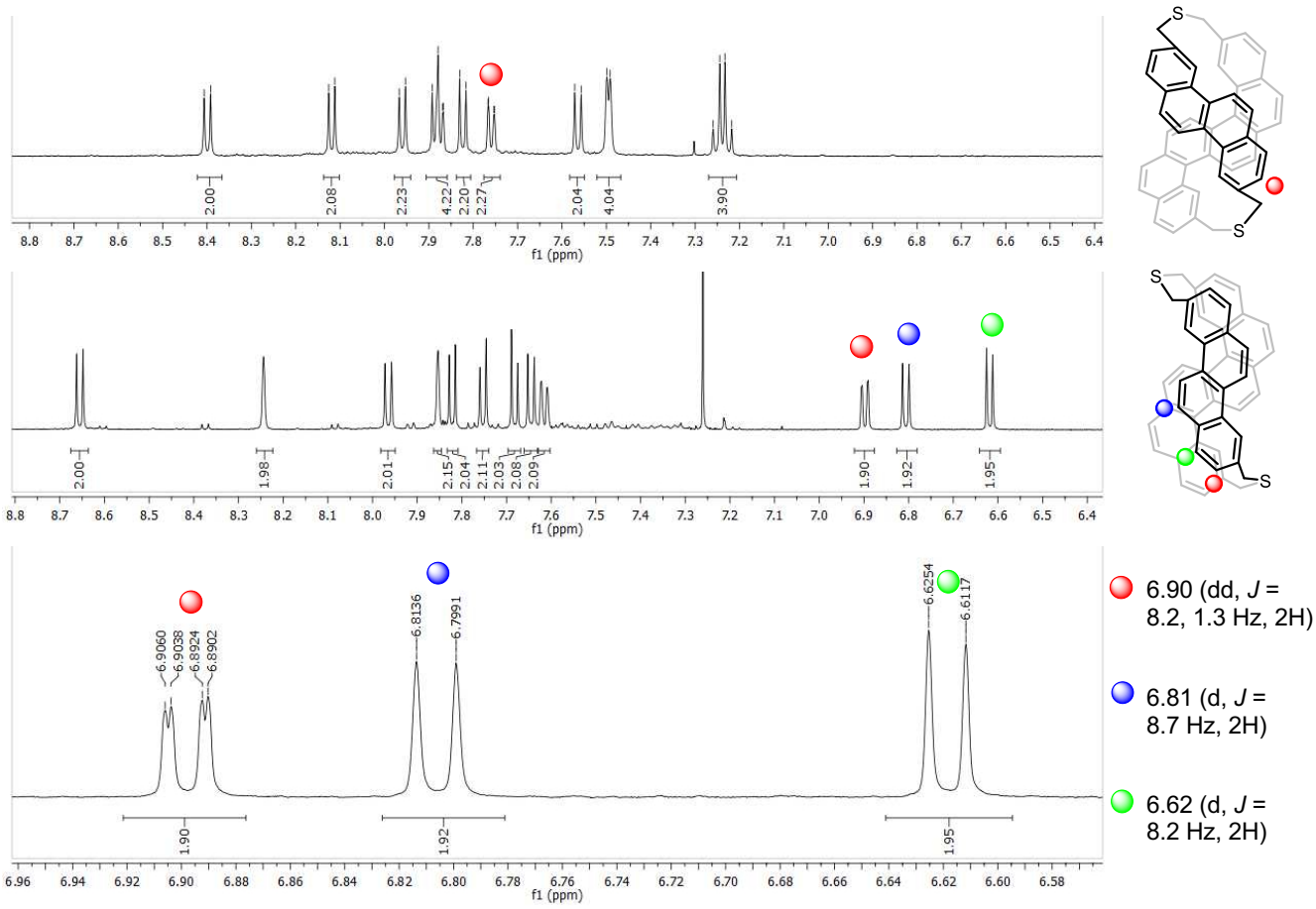


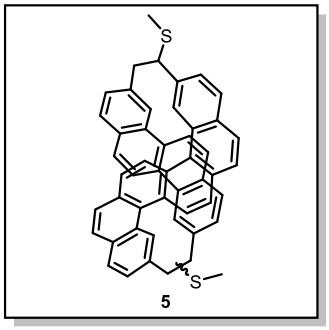
Figure S1. Zoomed-in aromatic region of ^{1}H NMR spectra of conformers **4** (top) and **4′** (center and bottom).

3,7-Dithia-1(3,11)-dibenzo[*c,l*]chrysena-5(3,9)-chrysenacyclooctaphane (4). Yellow solid. ^{1}H NMR (600 MHz, TCE-d_2) δ 8.40 (d, J = 8.7 Hz, 2H), 8.12 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 8.4 Hz, 2H), 7.90–7.86 (m, 4H), 7.82 (d, J = 8.4 Hz, 2H), 7.76 (dd, J = 7.9, 0.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 4.4 Hz, 4H), 7.25 (d, J = 9.1 Hz, 2H), 7.23 (d, J = 9.1 Hz, 2H), 4.22 (d, J = 14.3 Hz, 2H), 4.00 (d, J = 13.8 Hz, 2H), 3.86 (d, J = 13.8 Hz, 2H), 3.71 (d, J = 14.3 Hz, 2H). ^{13}C NMR (151 MHz, TCE-d_2) δ 135.6, 134.7, 131.9, 130.5, 130.2, 129.75, 129.67, 129.1, 128.9, 128.7, 128.2, 127.1, 127.0, 126.8, 126.7, 126.4, 126.3, 126.23, 126.16, 125.5, 124.0, 119.8, 35.66, 34.58. HRMS (APCI^{+}) *m/z* calcd for $C_{48}H_{33}S_2$ [M+H]$^{+}$: 673.2018, found 673.2044.

3,7-Dithia-1(3,11)-dibenzo[*c,l*]chrysena-5(3,9)-chrysenacyclooctaphane conformer (4′)
Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, J = 8.7 Hz, 2H), 8.24 (s, 2H), 7.96 (d, J = 8.9 Hz, 2H), 7.85 (s, 2H), 7.82 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.9 Hz, 2H), 7.61 (dd, J = 8.3, 1.0 Hz, 2H), 6.89 (dd, J = 8.3, 1.4 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 6.61 (d, J = 8.3 Hz, 2H), 4.31 (d, J = 15.1 Hz, 2H), 4.19 (d, J = 14.1 Hz, 2H), 4.03 (d, J = 15.1 Hz, 2H), 3.99 (d, J = 14.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.6, 135.7, 131.1, 130.5, 130.3, 130.2, 128.9, 128.8, 128.5, 127.9, 127.3, 127.1, 126.9, 126.5, 126.30, 126.26, 126.1, 125.9, 125.6, 125.3, 122.5, 119.5, 39.4, 38.1. HRMS (APCI^{+}) *m/z* calcd for $C_{48}H_{33}S_2$ [M+H]$^{+}$: 673.2018, found 673.2018.

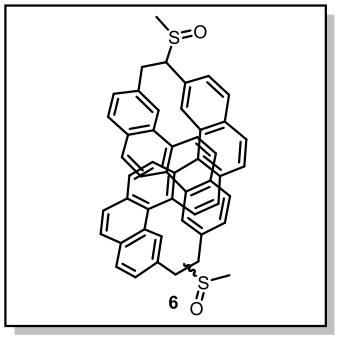
3,4,8,9-Tetrathia-1,6(3,11)-didibenzo[*c,l*]chrysenacyclodecaphane (4″)
Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, J = 7.9 Hz, 4H), 8.25 (br s, 4H), 8.06 (d, J = 8.3 Hz, 4H), 7.84 (d, J = 8.3 Hz, 4H), 7.74 (d, J = 8.3 Hz, 4H), 7.36 (d, J = 8.3 Hz, 4H), 6.55 (d, J = 7.3 Hz, 4H), 4.10 (d, J = 12.7 Hz, 4H), 3.49 (d, J = 12.4 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.4, 132.5, 129.87, 129.85, 129.7, 129.4, 128.9, 126.8, 126.64, 126.57, 126.51, 126.49, 125.5, 44.2. HRMS (APCI^{+}) *m/z* calcd for $C_{56}H_{37}S_4$ [M+H]$^{+}$: 837.1773, found 837.1770.

2,6-Bis(methylthio)-1(3,11)-dibenzo[*c,l*]chrysena-4(3,9)-chrysenacyclohexaphane (5)



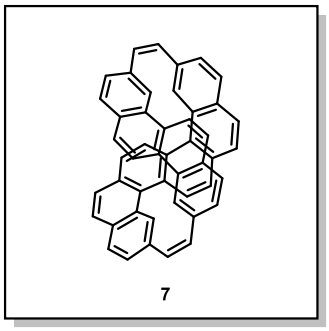
To a stirred solution of dithiacyclophane **4** (67.3 mg, 0.10 mmol) in dry CH_2Cl_2 (2 mL) was added dimethoxycarbenium tetrafluoroborate (the Borch reagent) (97.1 mg, 0.60 mmol in 1 mL of CH_2Cl_2) dropwise at 0 °C. The resulting mixture was stirred at room temperature for 6 h. Then, greenish-yellow solid was filtered and dried, giving intermediate salt in 95% (83.0 mg). The thus-obtained salt was subjected to the next step without further purification. A suspension of the salt (83.0 mg) and 40.0 mg of NaH (60% dispersion) in dry THF (3 mL) was stirred at 55 °C for 48 h giving **5** as a mixture of stereoisomers (40.5 mg, 61%). ^{1}H and ^{13}C NMR (600 MHz, $CDCl_3$): complex mixture due to the presence of regioisomers and diastereomers. HRMS (ESI$^+$) *m/z* calcd for $C_{50}H_{36}S_2Na$ $[M+Na]^+$: 723.2151, found 723.2136. HRMS (APCI$^+$), molecular peak ($C_{50}H_{36}S_2$ $[M]^+$: *m*/*z* 700) was not observed; *m/z* calcd for $C_{49}H_{33}S$ $[M–(CH_3SH)+H]^+$: 653.2297, found 653.2298; *m/z* calcd for $C_{48}H_{29}S$ $[M–(CH_3SH)_2+H]^+$: 605.2264, found 605.2263.

2,6-Bis(methylsulfinyl)-1(3,11)-dibenzo[c,l]chrysena-4(3,9)-chrysenacyclohexaphane (6)



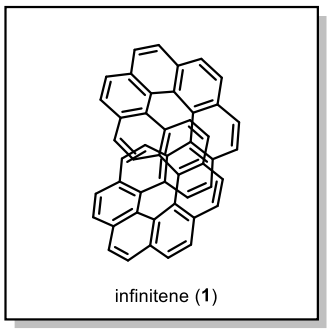
Cyclophane **5** (39.3 mg, 0.056 mmol) and 70% *m*-CPBA (27.8 mg, 0.113 mmol) were dissolved in $CHCl_3$ (4 mL) at 0 °C and the resultant mixture was stirred at room temperature for 13 h. Then, the solution was washed with 3% $NaHCO_3$ and dried. Solvent was evaporated giving pure *S,S′* -bisoxide **6** in 99% yield (40.8 mg). The thus-obtained product was subjected to the next step without further purification. ^{1}H and ^{13}C NMR (600 MHz, $CDCl_3$): complex mixture due to the presence of regioisomers and diastereomers. LRMS (APCI$^+$): molecular peak ($C_{50}H_{36}O_2S_2$ $[M]^+$: *m*/*z* 732) was not found; *m/z* calcd for $C_{49}H_{33}OS$ $[M–CH_3SO]^+$: 669.2, found 669.2. HRMS (APCI$^+$), *m/z* calcd for $C_{48}H_{29}$ $[M–(CH_3SOH)_2+H]^+$: 605.2264, found 605.2263.

(2*Z*,5*Z*)-1(3,11)-Dibenzo[*c,l*]chrysena-4(3,9)-chrysenacyclohexaphane-2,5-diene (7)



S,*S*-bisoxide **6** (25.0 mg, 0.034 mmol) was placed in a round-bottom flask immersed in a sand bath and directly connected to the oil pump through a glass joint. **6** was pyrolyzed at 500 °C (0.04–0.05 Torr) for 1 h to give intensively yellow pyrolysate which sublimed on the side of the flask. Pyrolysate was collected by washing the flask with $CHCl_3$. Solvent was evaporated and the crude product was purified by a flash column chromatography (hexane/CH_2Cl_2 = 95:5) giving **7** (9.5 mg, 46%) as a yellow solid. ^{1}H NMR (600 MHz, CD_2Cl_2) *δ* 8.82 (s, 2H), 8.50 (s, 2H), 8.064 (d, *J* = 8.6 Hz, 2H), 8.058 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.61 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.49 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 12.0 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 12.0 Hz, 2H). ^{13}C NMR (151 MHz, CD_2Cl_2) *δ* 134.4, 134.1, 133.1, 131.6, 131.4, 130.8, 130.4, 129.95, 129.89, 129.5, 129.1, 129.0, 128.7, 127.3, 127.23, 127.20, 127.0, 126.74, 126.71, 126.1 (2C), 125.4, 124.1, 120.0. Other two carbon peaks can be overlapped. HRMS (APCI$^+$) *m/z* calcd for $C_{48}H_{29}$ $[M+H]^+$: 605.2264, found 605.2261.

Cyclo[*c.c.c.c.c.c.e.e.e.e.e.e*]dodecakisbenzene (infinitene, 1)



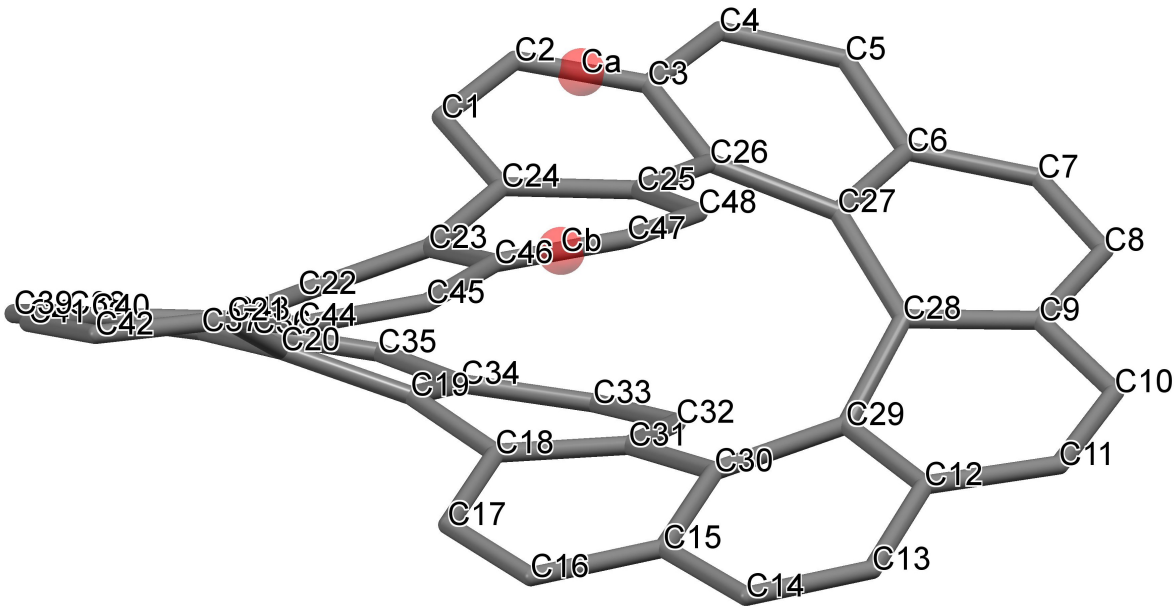
Argon was bubbled through a stirred solution of **7** (9.0 mg, 0.015 mmol) and iodine (12.7 mg, 0.050 mmol) in dry benzene (10 mL) for 10 min. Then, 0.1 mL of propylene oxide was added, and the reaction mixture was irradiated with a 450 W UV lamp and stirred for additional 6 h at room temperature. After the reaction was completed, the mixture was washed with aqueous $Na_2S_2O_3$ solution, water, and brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by a flash column chromatography (hexane/CH_2Cl_2 = 95:5) to give infinitene **1** (8.0 mg, 89%) as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, J = 7.9 Hz, 4H), 8.16 (d, J = 7.9 Hz, 4H), 8.04 (d, J = 7.9 Hz, 4H), 7.60 (d, J = 8.0 Hz, 4H), 6.99 (d, J = 7.9 Hz, 4H), 6.43 (d, J = 8.6 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.1, 133.0, 131.9, 130.7, 128.7, 128.3, 127.9, 127.5, 126.7, 126.5, 122.0, 120.7. One peak of quaternary carbon atom can be overlapped. HRMS (APCI$^+$) *m/z* calcd for $C_{48}H_{25}$ $[M+H]^+$: 601.1951, found 601.1949.

3. X-ray crystallographic analysis

Details of the crystal data and a summary of the intensity data collection parameters are listed in Table S1. 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 CrysAlisPro (Agilent Technologies, 2010). The structures were solved by direct methods with SHELXT[4] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2018/3)[5] by using Olex2 software package.[6] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. CCDC 2113525 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data and structure refinement for **1**.

	Infinitene (**1**)	
CCDC deposition No.	2113525	
Empirical formula	$C_{48}H_{24}$	
Formula weight	600.67	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.2861(14) Å	α = 90°
	b = 13.3592(10) Å	β = 102.261(11)°
	c = 19.508(2) Å	γ = 90°
Volume	2874.2(5) Å^3	
Z	4	
Density (calculated)	1.388 g·cm^{-3}	
Absorption coefficient (μ)	0.079 mm^{-1}	
F(000)	1248.0	
Crystal size	0.100 x 0.100 x 0.010 mm^3	
θ range for data collection	1.861 – 24.999 °	
Index ranges	$-13 \leqq h \leqq 12$, $-15 \leqq k \leqq 15$, $-20 \leqq l \leqq 23$	
Reflections collected	16491	
Independent reflections	5051 [R(int) = 0.0586]	
Completeness to theta = 24.999°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5051 / 0 / 433	
Goodness-of-fit on F^2	1.022	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0639, wR_2 = 0.1497	
R indices (all data)	R_1 = 0.1485, wR_2 = 0.1924	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.793 and -0.223 e Å^{-3}	



splay angle: $\phi_{torsion}$ = ($\phi_{C25\text{-}C26\text{-}C27\text{-}C28}$ + $\phi_{C26\text{-}C27\text{-}C28\text{-}C29}$ + $\phi_{C27\text{-}C28\text{-}C29\text{-}C30}$) / 3 = 20.34°
twist angle: ϕ_{twist} = ($\phi_{C2\text{-}Ca\text{-}Cb\text{-}C46}$) = 22.03°

Figure S2. The molecular structure of **1** with labeled carbon atoms.

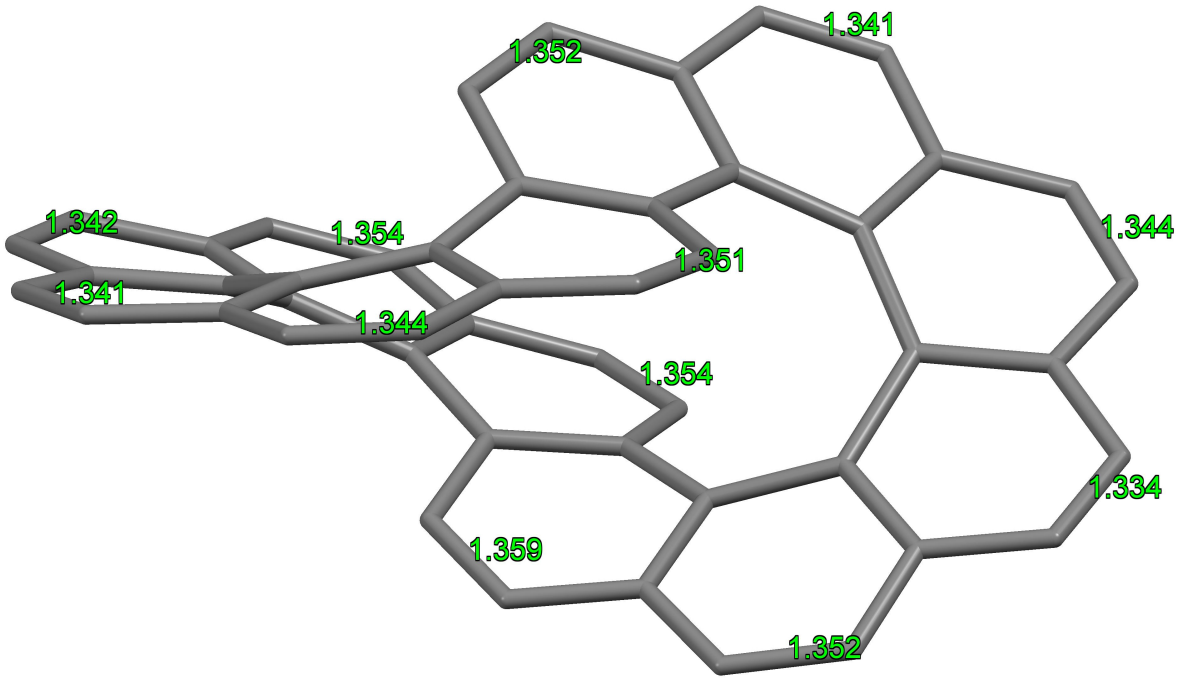


Figure S3. The molecular structure of **1** with listed bond lengths of the corresponding convex-armchair edges.

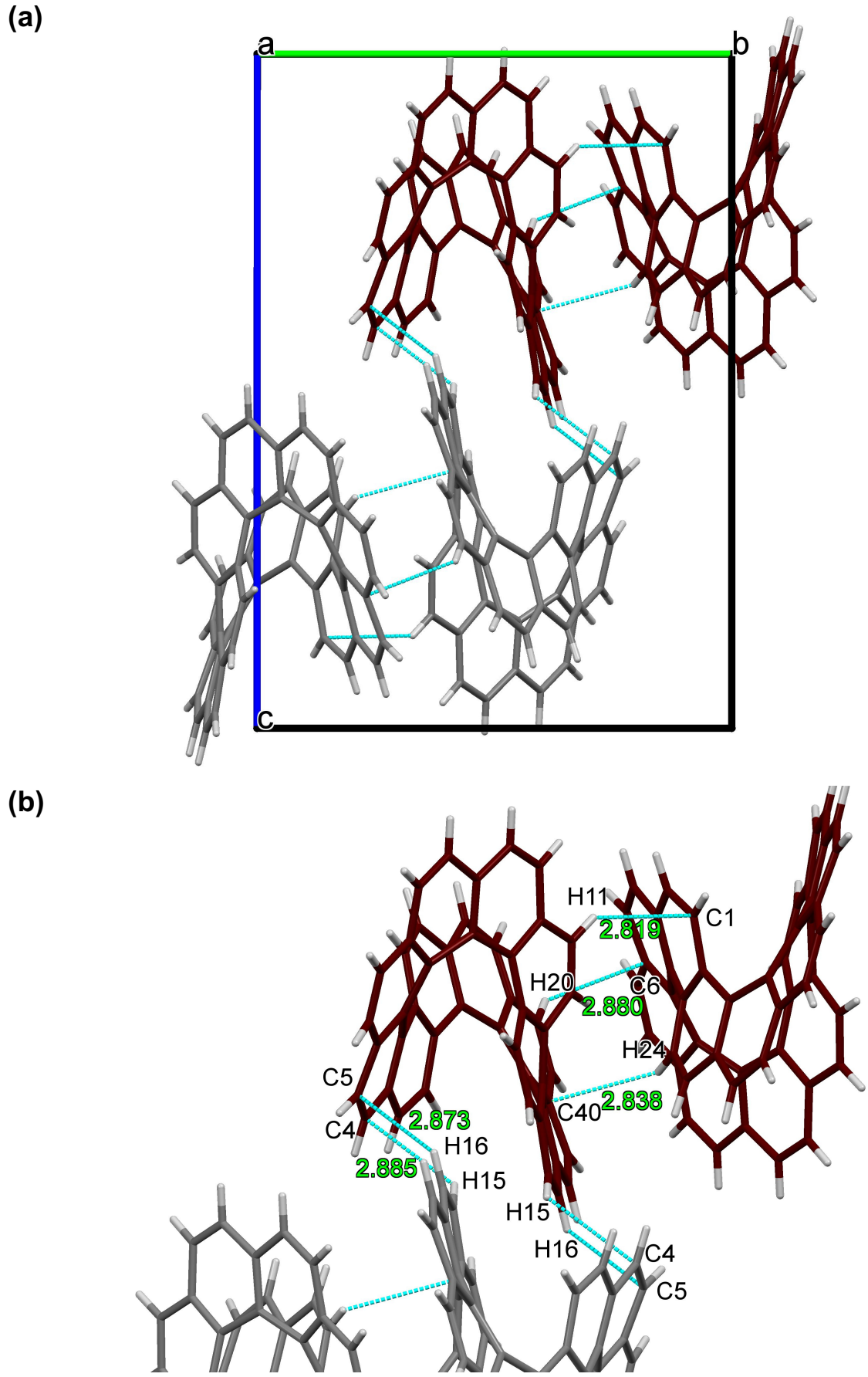


Figure S4. (a) The crystal packing viewed along the *a*-axis. (b) Zoomed-in view emphasizing short contacts. (*P*,*P*)-**1** enantiomer colored in gray, (*M*,*M*)-**1** enantiomer colored in red.

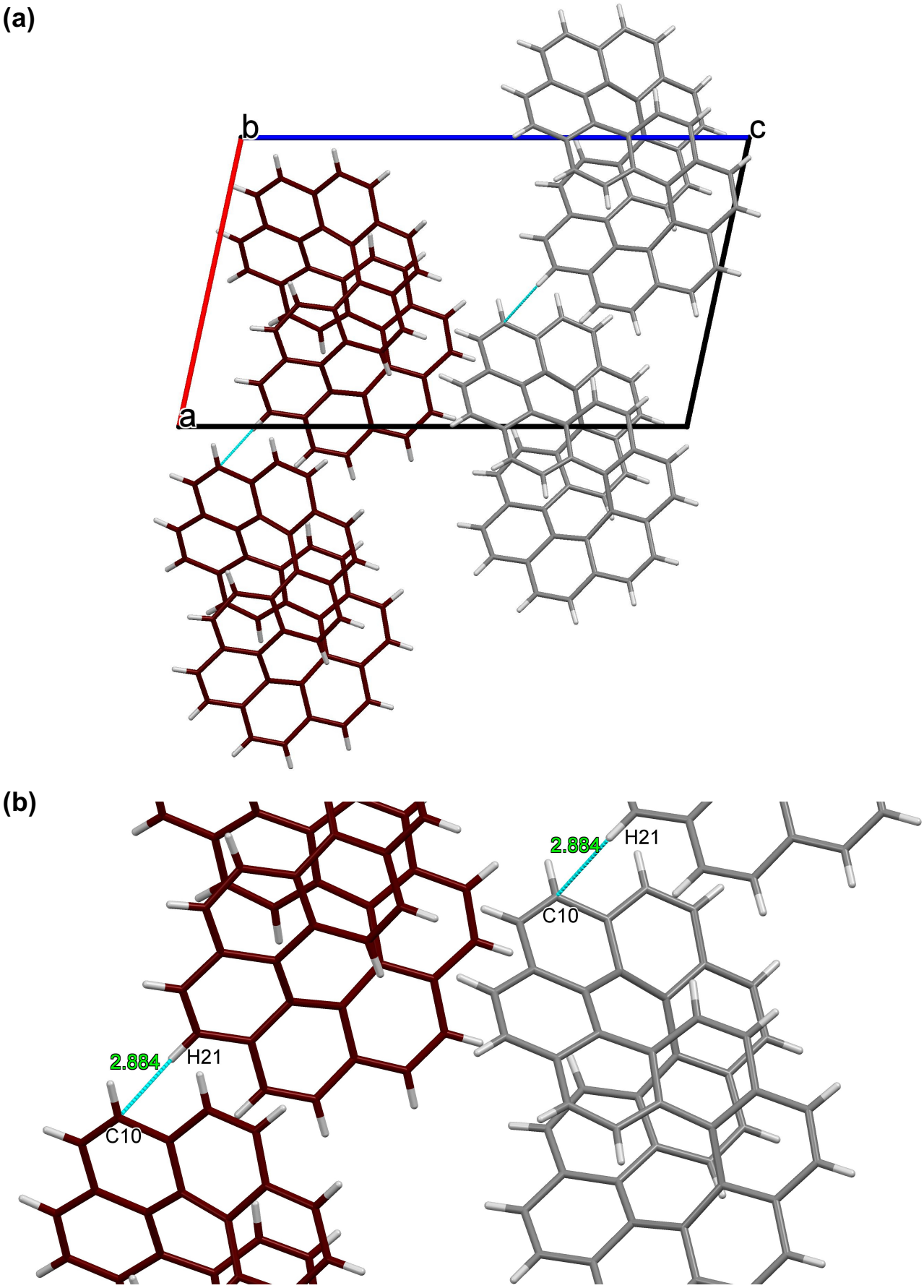
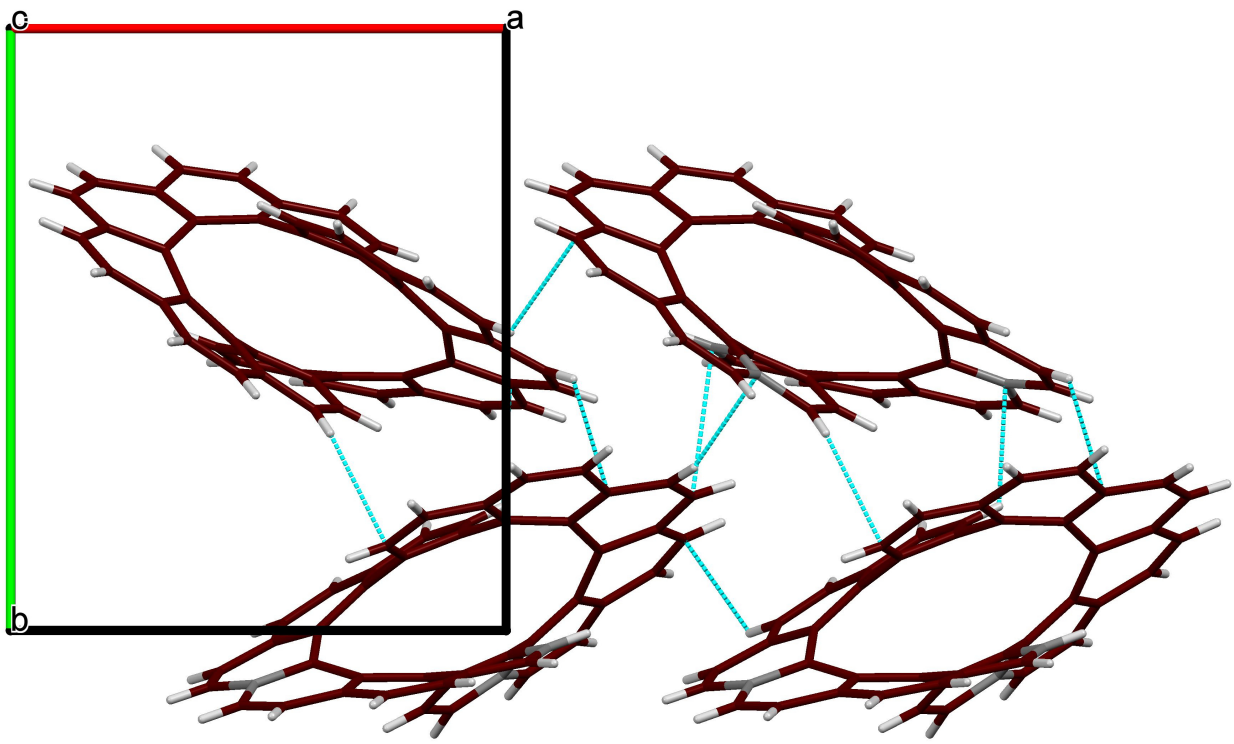


Figure S5. (a) The crystal packing viewed along the *b*-axis. (b) Zoomed-in view emphasizing short contacts. (*P*,*P*)-**1** enantiomer colored in gray, (*M*,*M*)-**1** enantiomer colored in red.

(a)



(b)

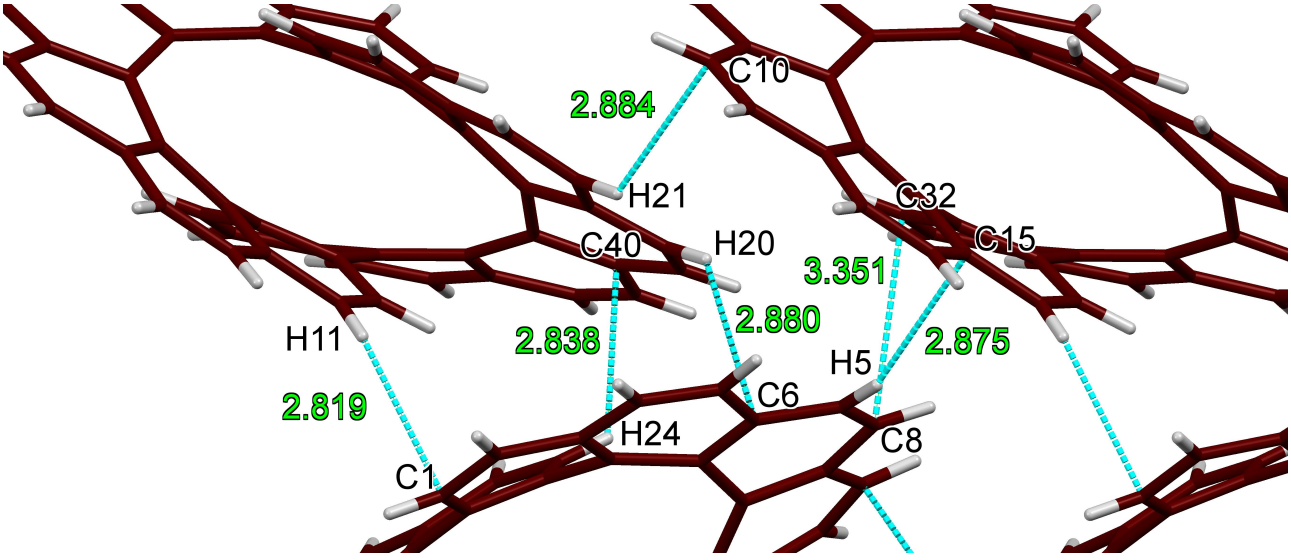


Figure S6. (a) The crystal packing viewed along the *c*-axis. (b) Zoomed-in view emphasizing short contacts.

4. Photophysical properties

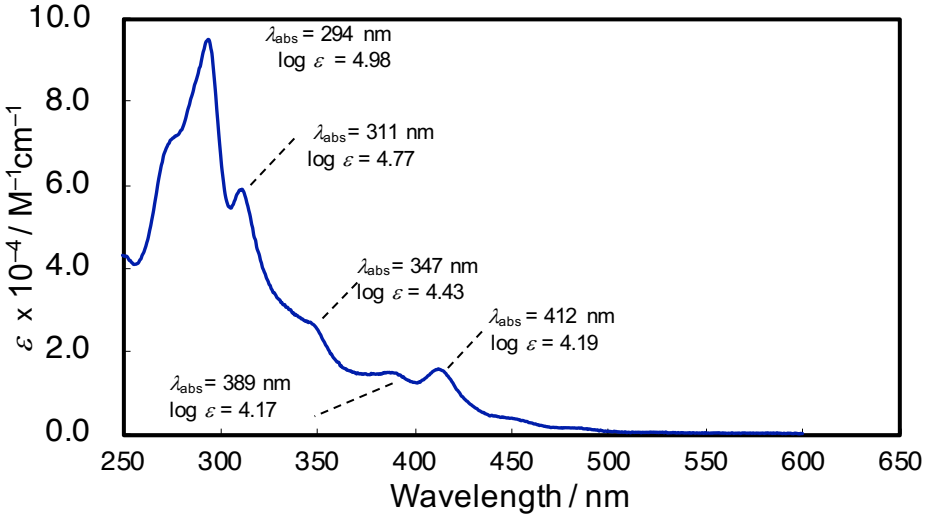


Figure S7. UV-vis absorption spectrum of **1** measured in CH_2Cl_2.

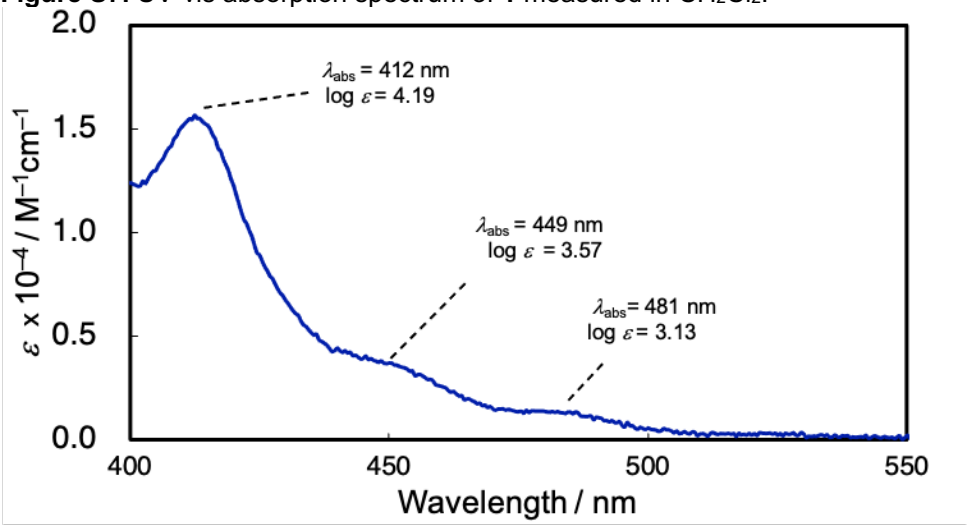


Figure S8. Zoomed-in region (400- 550 nm) of absorption spectrum of **1**.

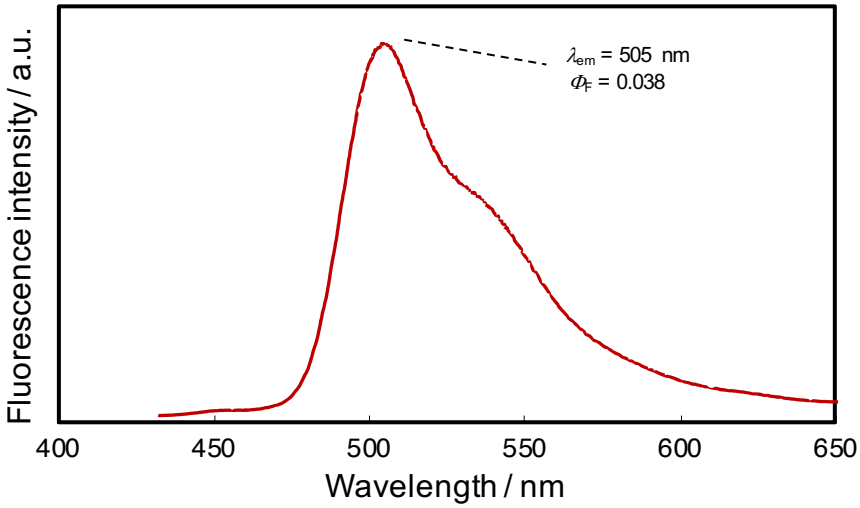


Figure S9. Emission spectrum of **1** measured in CH_2Cl_2.

5. Chiral HPLC analyses and CD spectra

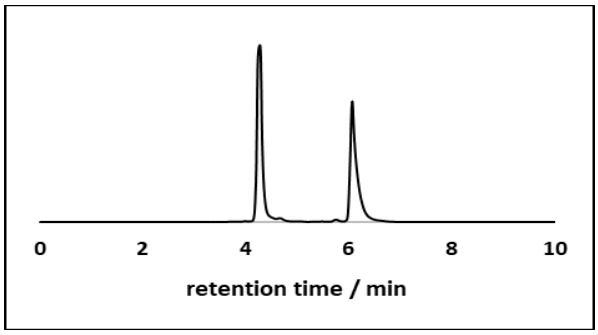


Figure S10. Chromatogram for the resolution of *rac*-**1** using UV (315 nm) detectors in *n*-hexane/CH_2Cl_2 (35:65, *v*/*v*) at the flow rate of 1.0 mL/min. Optical resolution was carried out with a DAICEL CHIRALPAK® IE column (0.46(i.d.) × 25 cm) at 30 °C.

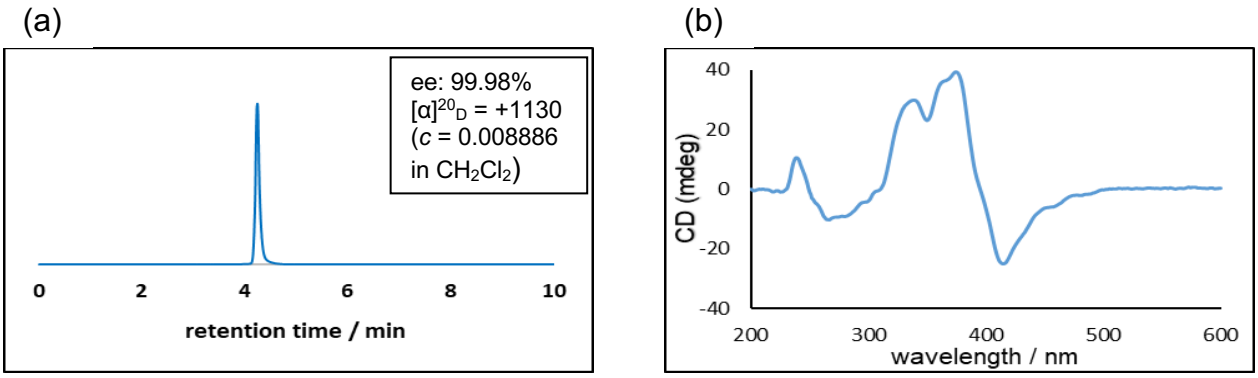


Figure S11. (a) Chromatogram of the eluted first fraction assigned as (+)-(*P*,*P*)-**1**. (b) CD spectrum of (+)-(*P*,*P*)-**1** measured in CH_2Cl_2.

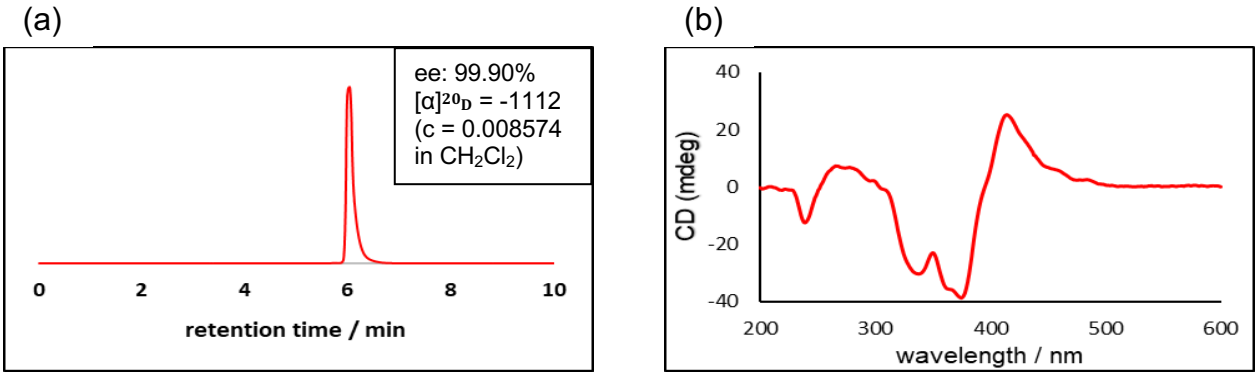


Figure S12. (a) Chromatogram of the eluted second fraction assigned as (–)-(*M*,*M*)-**1**. (b) CD spectrum of (–)-(*M*,*M*)-**1** measured in CH_2Cl_2.

Table S2. The anisotropy factors $|g_{CD}|$ of selected transitions for **1**.

Wavelength (nm)	265	339	375	415	457	484
ε ($M^{-1}cm^{-1}$)	51549	28859	14485	15181	3021	1297
$\lvert\Delta\varepsilon\rvert$ ($M^{-1}cm^{-1}$)[a]	17.82	52.48	68.97	43.78	10.36	3.04
$\lvert g_{CD}\rvert$[b]	3.5×10^{-4}	1.8×10^{-3}	4.8×10^{-3}	2.9×10^{-3}	3.4×10^{-3}	2.3×10^{-3}

[a] $\Delta\varepsilon = (\theta \cdot 0.1 \cdot M) / (c \cdot l \cdot 3298)$; *M*: molecular weight (g/mol); *c*: concentration (g/L); *l*: cell length (cm). [b] $|g_{CD}| = |\Delta\varepsilon| / \varepsilon$

6. Circularly polarized luminescence

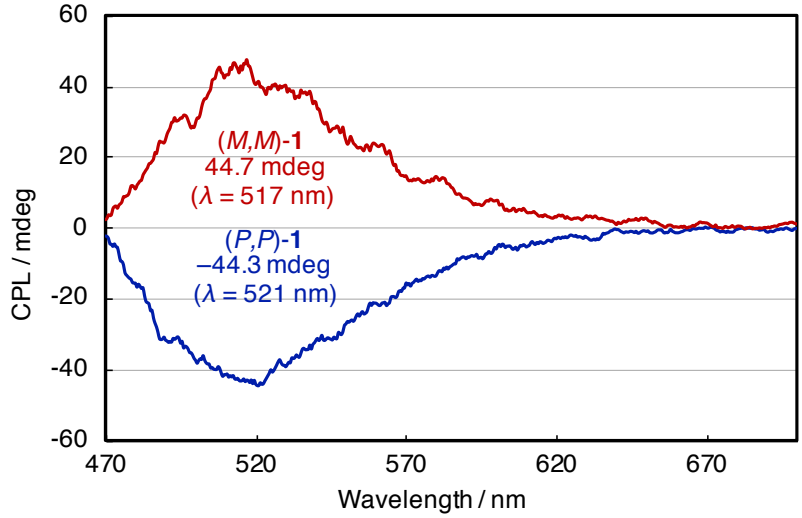
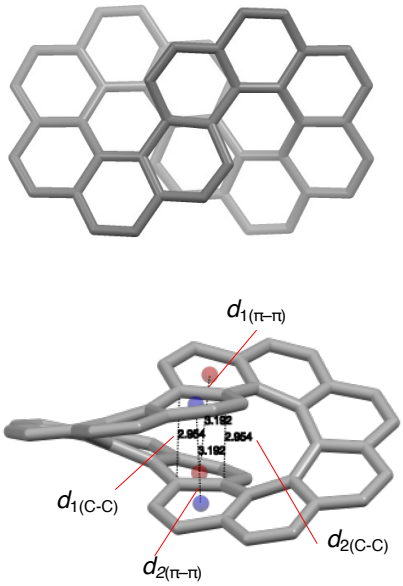


Figure S13. Circularly polarized luminescence (CPL) spectra of (*P*,*P*)-**1** (c = 2.4 × 10^{-6} M, blue line) and (*M*,*M*)-**1** (2.9 × 10^{-6} M, red line) in CH_2Cl_2 at 25 °C with a 10 × 10 mm cells. CPL = $\Delta I = I_L - I_R$; I_L, I_R: intensities of left and right circularly polarized radiations. The spectra of dissymmetry factor were depicted in Figure 8 of the main text. g_{CPL} (g_{lum}) = (ΔI) / (I) = (ΔI) / [(1/2)(I_L+I_R)].

7. DFT calculations

The computations were performed using Research Center for Computational Science, Okazaki, Japan. We carried out the computational studies by using the density functional theory (DFT) in Gaussian 16[7] package (revision C. 01). All geometry optimizations of minima were conducted by using PBE0[8]/6-311+G(d,p) in gas phase at 273.15 K. Frequency analyses were carried out at the same level to evaluate the zero-point vibrational energy and thermal corrections at 273.15. The nature of the stationary points was determined in each case according to the appropriate number of negative eigenvalues of the Hessian matrix. Calculations of single point energies, molecular orbitals and TD-DFT for all DFT-optimized structures were obtained by using the B3LYP[9]/6-311++G(d,p), and GIAO-NMR[10] and NICS(0)/NICS(1)[11] were calculated using B3LYP/6-311+G(2d,p) with SMD (CHCl3) model.[12] Visualization of molecular orbitals was performed by the use of GaussView 6.0.16 software with 0.02 of isovalue.[13]



optimized structure by PBE0/6-311+G(d,p)

Red color: difference within 0.015 Å
Orange color: difference within 0.020 Å
Yellow color: difference within 0.040 Å

Structure or basis sets	Closest C···C distance $d_{1(\pi-\pi)}$ (Å)	Closest C···C distance $d_{2(C-C)}$ (Å)	Distance between centroids $d_{1(\pi-\pi)}$ (Å)	Distance between centroids $d_{2(\pi-\pi)}$ (Å)	Cost (day, hour)
Experimental (X-ray)	2.94166	2.91976	3.19245	3.15195	
B3LYP/6-31+G(d,p)	3.00522		3.26052		2d17h
B3LYP/6-311+G(d,p)	3.00195		-		4d15h
B3LYP/6-311+G(2d,p)	3.00437		-		7d5h
B3LYP/6-311++G(2d,p)	3.00450		-		8d0h
B3LYP/cc-pVDZ	2.99892		-		9h
B3LYP/cc-PVTZ	3.00565		-		6d16h
B3PW91/6-31+G(d,p)	2.96991		-		2d18h
M06-2X/6-31+G(d,p)	2.97353		-		3d7h
M06-2X/6-311+G(2d,p)	2.96972		-		9d11h
BMK/6-31G(d)	2.99800		-		3d2h
CAM-B3LYP/6-31+G(d,p)	2.97869		-		1d23h
mPW1PW91/6-31+G(d,p)	2.96071		3.19917		2d19h
PBE0/6-31G(d)	2.95666		-		7h
PBE0/6-31G(d,p)	2.95682		-		8h
PBE0/6-311G(d,p)	2.95316		3.18465		1d1h
PBE0/6-31+G(d)	2.95955		-		2d2h
PBE0/6-31+G(d,p)	2.95992		-		2d20h
PBE0/6-311+G(d,p)	2.95429		3.19221		4d21h
B3LYP-D3/6-31+G(d,p)	3.00153		-		2d9h
B3LYP-D3/cc-PVDZ	2.99795		-		11h
B3LYP-D3/cc-PVTZ	3.00214		-		6d6h
M06-2X-D3/6-31+G(d,p)	2.97532		3.15530		3d9h
M06-2X-D3/6-311+G(2d,p)	2.97149		-		10d13h
BMK-D3/6-31+G(d,p)	2.97620		-		2d18h
CAM-B3LYP-D3/6-31+G(d,p)	2.97796		-		2d1h
B3PW91-D3/6-31+G(d,p)	2.97523		-		2d19h
PBE0-D3/6-31G(d)	2.96325		3.15865		7h
PBE0-D3/6-31G(d,p)	2.96377		-		8h
PBE0-D3/6-31+G(d)	2.96436		-		2d10h
PBE0-D3/6-31+G(d,p)	2.96493		-		2d19h
PBE0-D3/6-311+G(d,p)	2.96074		-		4d18h

Figure S14. Comparison of basis sets for geometry optimization of inifintene (**1**). Calculation cost: job cpu time in Gaussian.

Table S3. Uncorrected and thermal-corrected (298.15 K, 1 atm) energies of stationary points (Hartree) calculated by PBE0/6-311+G(d,p).[a]

structure	*E*	*E* + *ZPE*	*H*	*G*
(*P*,*P*)-**1**	-1841.879574	-1841.318388	-1841.287702	-1841.372361
benzene	-232.019728	-231.918919	-231.913580	-231.946378
phenanthrene	-539.016349	-538.821262	-538.810864	-538.856141

a) *E*: electronic energy; *ZPE*: zero-point energy; *H*: sum of electronic and thermal correction to enthalpies; *G*: sum of electronic and thermal correction to free energies.

Table S4. TD-DFT (B3LYP/6-311++(d,p)//PBE0/6-311+G(d,p)) vertical one-electron excitations (5 states) calculated for inifinitene (**1**).

Exited state	Energy / eV	Wavelength / nm	Oscillator strength	Description
1	2.5748	481.54	0.0001	HOMO-1 to LUMO
2	2.5983	477.18	0.0113	HOMO to LUMO+1
3	2.7572	449.67	0.0024	HOMO to LUMO+2
4	2.8860	429.60	0.1226	HOMO-1 to LUMO+2
5	2.9834	415.58	0.0214	HOMO-2 to LUMO+1

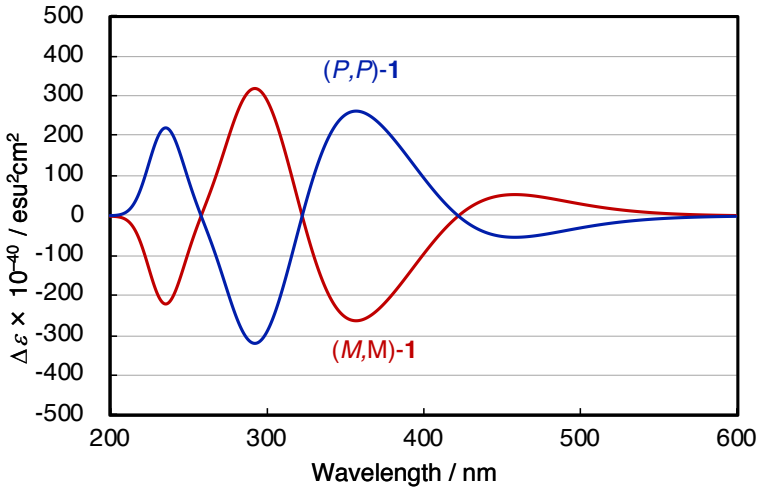
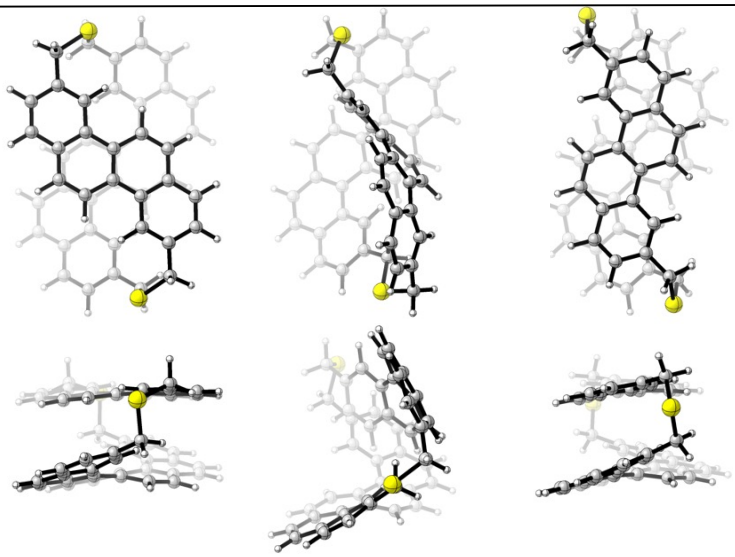


Figure S15. CD spectra of (*P*,*P*)-**1** and (*M*,*M*)-**1** simulated by TD-DFT (B3LYP/6-311++(d,p)//PBE0/6-311+G(d,p) with *N* state = 100).

We optimized cyclic sulfides **4** and its conformer **4′**, compound **7** and its conformer **7′** for evaluating a possibility of interconversion and relative stabilities (Table S5). As a result, compounds **4** and **4′** show almost the same stability, and weak intramolecular π-π interactions (ca. 3.6–3.8 Å) were observed (Table S5a). An activation energy from **4** to **4′** are estimated to be 28.4 kcal/mol by PBE0/def2-TZVP//PBE0-D3/6-31G(d), which means that both compounds are even stable at room temperature but the interconversion can be possible at higher temperature. The structures of **7** and **7′** are more strained compared to **4** and **4′**, which are rationalized by smaller sizes of macrocycles in **7** and **7′** than **4** and **4′**. Compound **7** was more stable than **7′** by 6 kcal/mol (Table S5b). Interconversions corresponding to the rotation of a chrysene moiety or a dibenzochrysene moiety can be potentially expected, while any distinct transition states were not obtained due to those highly bent and strained structures. Therefore, we expected that not only the interconversion from **7** to **7′** but also racemization would be difficult, and the optical resolution of enantiomers of **7** would also be possible.

Table S5. DFT calculations for estimating relative stabilities of (a) **4**/**4′**, (b) **7**/**7′**, and the transition states of those interconversions.

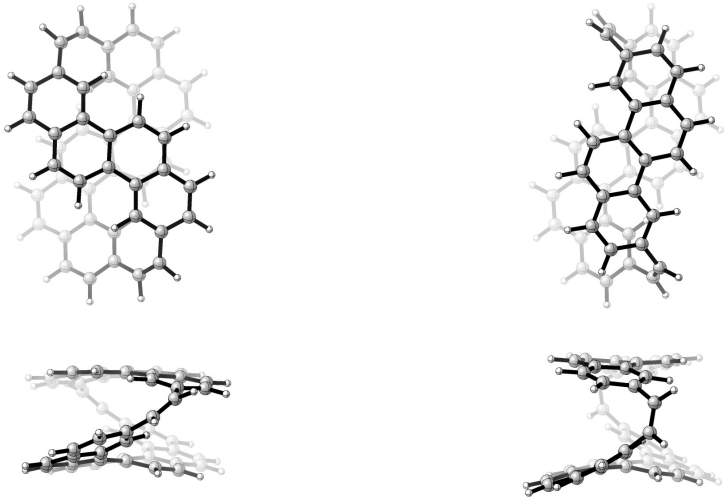
(a) Interconversion of **4** to **4′**



Basis sets (sp calc.//geom. optimization)	**4**	**TS$_{4–4'}$**	**4′**
PBE0/6-311+G(d,p)//PBE0-D3/6-31G(d)	0.03	30.4	0.00
PBE0/def2-TZVP//PBE0-D3/6-31G(d)	0.02	28.4	0.00
PBE0-D3/def2-TZVP//PBE0-D3/6-31G(d)	0.03	35.5	0.00
PBE0-D3/6-31G(d)	0.04	37.0	0.00

ΔG values (kcal/mol) are shown

(b) Optimizations of **7** and **7′**



Basis sets (sp calc.//geom. optimization)	**7**	**TS$_{7–7'}$**	**7′**
PBE0/6-311+G(d,p)//PBE0-D3/6-31G(d)	0.00	not located	6.19
PBE0/def2-TZVP//PBE0-D3/6-31G(d)	0.00	not located	6.30
PBE0-D3/def2-TZVP//PBE0-D3/6-31G(d)	0.00	not located	10.07
PBE0-D3/6-31G(d)	0.00	not located	11.06

ΔG values (kcal/mol) are shown

Table S6. Uncorrected and thermal-corrected (298.15 K, 1 atm) energies of stationary points (Hartree) calculated by PBE0-D3/6-31G(d).[a]

structure	*E*	*E* + *ZPE*	*H*	*G*	Δ_{ZPE}	Δ_H	Δ_G
4	-2642.491233	-2641.831783	-2641.794579	-2641.897272	0.659450	0.696655	0.593962
4′	-2642.491236	-2641.831809	-2641.794598	-2641.897332	0.659427	0.696638	0.593904
TS$_{4-4'}$	-2642.433001	-2641.774315	-2641.737887	-2641.838408	0.658686	0.695114	0.594594
7	-1843.956216	-1843.346127	-1843.312921	-1843.407502	0.610090	0.643296	0.548714
7′	-1843.937261	-1843.328625	-1843.295247	-1843.389885	0.608636	0.642014	0.547376

a) *E*: electronic energy; *ZPE*: zero-point energy (Δ_{ZPE}); *H*: sum of electronic and thermal correction to enthalpies ($E + \Delta_H$); *G*: sum of electronic and thermal correction to free energies ($E + \Delta_G$); Δ_{ZPE}*:* Zero-point energy correction; Δ_H*:* thermal correction to enthalpy; Δ_G*:* thermal correction to free energy.

Table S7. Single point calculations of electronic energies (*E*: Hartree) of each stationary points obtained by PBE0-D3/6-31G(d).[a]

structure	*E* (PBE0/6-311+G(d,p)	*E* (PBE0/def2-TZVP)	*E* (PBE0-D3/def2-TZVP)
4	-2642.842991	-2643.052520	-2643.137646
4′	-2642.842976	-2643.052501	-2643.137641
TS$_{4-4'}$	-2642.795226	-2643.007859	-2643.081688
7	-1844.266608	-1844.470821	-1844.542359
7′	-1844.255405	-1844.459439	-1844.524982

a) *E*: electronic energy; *ZPE*: zero-point energy (Δ_{ZPE}); *H*: sum of electronic and thermal correction to enthalpies ($E + \Delta_H$); *G*: sum of electronic and thermal correction to free energies ($E + \Delta_G$); Δ_{ZPE}*:* Zero-point energy correction; Δ_H*:* thermal correction to enthalpy; Δ_G*:* thermal correction to free energy.

Table S8. Summary of free energies (*G*: Hartree) of each stationary points obtained by PBE0-D3/6-31G(d).[a]

structure	*G* (PBE0/6-311+G(d,p)	*G* (PBE0/def2-TZVP)	*G* (PBE0-D3/def2-TZVP)	*G* (PBE0-D3/6-31G(d))
4	-2642.249029	-2642.458558	-2642.543684	-2641.897272
4′	-2642.249072	-2642.458597	-2642.543737	-2641.897332
TS$_{4-4'}$	-2642.200632	-2642.413265	-2642.487094	-2641.838408
7	-1843.717894	-1843.922107	-1843.993645	-1843.407502
7′	-1843.708029	-1843.912063	-1843.977606	-1843.389885

a) *G*: sum of electronic and thermal correction to free energies ($E + \Delta_G$); Δ_G*:* thermal correction to free Energy obtained by PBE0-D3/6-31G(d).

8. Cartesian coordinates of optimized structures

(*P,P*)-**1**

C	-1.7549160	1.3330810	-1.2727700
C	-1.9289940	2.4151310	-0.4688610
C	-1.6363140	2.3466800	0.9196360
C	-1.7126740	3.5219750	1.7029970
C	-1.4569160	3.4601450	3.0340750
C	-0.9837590	2.2636440	3.6334300
C	-0.7733460	2.2764920	5.0351400
C	-0.3860840	1.1453450	5.6687950
C	0.0000000	0.0000000	4.9246020
C	0.3860840	-1.1453450	5.6687950
C	0.7733460	-2.2764920	5.0351400
C	0.9837590	-2.2636440	3.6334300
C	0.7524840	-1.0879580	2.8612350
C	0.0000000	0.0000000	3.4992600
C	-0.7524840	1.0879580	2.8612350
C	-1.2798180	1.1097850	1.5133260
C	-1.4757990	-0.0630220	0.7045480
C	-1.7549160	-1.3330810	1.2727700
C	-1.4757990	0.0630220	-0.7045480
C	-1.9289940	-2.4151310	0.4688610
C	-1.2798180	-1.1097850	-1.5133260
C	-1.6363140	-2.3466800	-0.9196360
C	-0.7524840	-1.0879580	-2.8612350
C	-1.7126740	-3.5219750	-1.7029970
C	-0.9837590	-2.2636440	-3.6334300
C	0.0000000	0.0000000	-3.4992600
C	-1.4569160	-3.4601450	-3.0340750
C	-0.7733460	-2.2764920	-5.0351400
C	0.0000000	0.0000000	-4.9246020
C	0.7524840	1.0879580	-2.8612350
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C	0.9837590	2.2636440	-3.6334300
C	1.2798180	1.1097850	-1.5133260
C	0.7733460	2.2764920	-5.0351400
C	1.4569160	3.4601450	-3.0340750
C	1.6363140	2.3466800	-0.9196360
C	1.7126740	3.5219750	-1.7029970
C	1.4757990	-0.0630220	-0.7045480
C	1.4757990	0.0630220	0.7045480
C	1.4569160	-3.4601450	3.0340750
C	1.7549160	1.3330810	1.2727700
C	1.9289940	2.4151310	0.4688610
C	1.2798180	-1.1097850	1.5133260
C	1.9289940	-2.4151310	-0.4688610
C	1.7549160	-1.3330810	-1.2727700
C	1.7126740	-3.5219750	1.7029970
C	1.6363140	-2.3466800	0.9196360
H	-2.2392930	3.3684460	-0.8851660
H	-2.0134520	4.4515360	1.2296440
H	-1.5825920	4.3326040	3.6680320
H	-0.9888310	3.1868630	5.5856190
H	-0.3169590	1.1016610	6.7511970
H	0.3169590	-1.1016610	6.7511970
H	0.9888310	-3.1868630	5.5856190
H	-2.2392930	-3.3684460	0.8851660
H	-2.0134520	-4.4515360	-1.2296440
H	-1.5825920	-4.3326040	-3.6680320
H	-0.9888310	-3.1868630	-5.5856190
H	-0.3169590	-1.1016610	-6.7511970
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H	0.9888310	3.1868630	-5.5856190
H	1.5825920	4.3326040	-3.6680320
H	2.0134520	4.4515360	-1.2296440
H	-1.8969130	-1.4136950	2.3435870
H	-1.8969130	1.4136950	-2.3435870
H	1.8969130	1.4136950	2.3435870
H	2.2392930	3.3684460	0.8851660
H	1.8969130	-1.4136950	-2.3435870
H	1.5825920	-4.3326040	3.6680320
H	2.0134520	-4.4515360	1.2296440
H	2.2392930	-3.3684460	-0.8851660

(*M,M*)-**1**

C	-1.7549160	1.3330810	1.2727700
C	-1.9289940	2.4151310	0.4688610
C	-1.6363140	2.3466800	-0.9196360
C	-1.7126740	3.5219750	-1.7029970
C	-1.4569160	3.4601450	-3.0340750
C	-0.9837590	2.2636440	-3.6334300
C	-0.7733460	2.2764920	-5.0351400
C	-0.3860840	1.1453450	-5.6687950
C	0.0000000	0.0000000	-4.9246020
C	0.3860840	-1.1453450	-5.6687950
C	0.7733460	-2.2764920	-5.0351400
C	0.9837590	-2.2636440	-3.6334300
C	0.7524840	-1.0879580	-2.8612350
C	0.0000000	0.0000000	-3.4992600
C	-0.7524840	1.0879580	-2.8612350
C	-1.2798180	1.1097850	-1.5133260
C	-1.4757990	-0.0630220	-0.7045480
C	-1.7549160	-1.3330810	-1.2727700
C	-1.4757990	0.0630220	0.7045480
C	-1.9289940	-2.4151310	-0.4688610
C	-1.2798180	-1.1097850	1.5133260
C	-1.6363140	-2.3466800	0.9196360
C	-0.7524840	-1.0879580	2.8612350
C	-1.7126740	-3.5219750	1.7029970
C	-0.9837590	-2.2636440	3.6334300
C	0.0000000	0.0000000	3.4992600
C	-1.4569160	-3.4601450	3.0340750
C	-0.7733460	-2.2764920	5.0351400
C	0.0000000	0.0000000	4.9246020
C	0.7524840	1.0879580	2.8612350
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C	1.2798180	1.1097850	1.5133260
C	0.7733460	2.2764920	5.0351400
C	1.4569160	3.4601450	3.0340750
C	1.6363140	2.3466800	0.9196360
C	1.7126740	3.5219750	1.7029970
C	1.4757990	-0.0630220	0.7045480
C	1.4757990	0.0630220	-0.7045480
H	-2.2392930	3.3684460	0.8851660
H	-2.0134520	4.4515360	-1.2296440
H	-1.5825920	4.3326040	-3.6680320
H	-0.9888310	3.1868630	-5.5856190
H	-0.3169590	1.1016610	-6.7511970
H	0.3169590	-1.1016610	-6.7511970
H	0.9888310	-3.1868630	-5.5856190
H	-2.2392930	-3.3684460	-0.8851660
H	-2.0134520	-4.4515360	1.2296440
H	-1.5825920	-4.3326040	3.6680320
H	-0.9888310	-3.1868630	5.5856190
H	-0.3169590	-1.1016610	6.7511970
H	0.3169590	1.1016610	6.7511970
H	0.9888310	3.1868630	5.5856190
H	1.5825920	4.3326040	3.6680320
H	2.0134520	4.4515360	1.2296440
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H	-1.8969130	1.4136950	2.3435870
C	1.4569160	-3.4601450	-3.0340750
C	1.7549160	1.3330810	-1.2727700
C	1.9289940	2.4151310	-0.4688610
H	1.8969130	1.4136950	-2.3435870
H	2.2392930	3.3684460	-0.8851660
C	1.2798180	-1.1097850	-1.5133260
C	1.9289940	-2.4151310	0.4688610
C	1.7549160	-1.3330810	1.2727700
H	1.8969130	-1.4136950	2.3435870
C	1.7126740	-3.5219750	-1.7029970
H	1.5825920	-4.3326040	-3.6680320
C	1.6363140	-2.3466800	-0.9196360
H	2.0134520	-4.4515360	-1.2296440
H	2.2392930	-3.3684460	0.8851660

(*P*,*P*)-**1** for NICS(0) and NICS(1) calculations

C	-1.8934679	1.3886487	-1.2874533
C	-2.0675459	2.4706987	-0.4835443
C	-1.7748659	2.4022477	0.9049527
C	-1.8512259	3.5775427	1.6883137
C	-1.5954679	3.5157127	3.0193917
C	-1.1223109	2.3192117	3.6187467
C	-0.9118979	2.3320597	5.0204567
C	-0.5246359	1.2009127	5.6541117
C	-0.1385519	0.0555677	4.9099187
C	0.2475321	-1.0897773	5.6541117
C	0.6347941	-2.2209243	5.0204567
C	0.8452071	-2.2080763	3.6187467
C	0.6139321	-1.0323903	2.8465517
C	-0.1385519	0.0555677	3.4845767
C	-0.8910359	1.1435257	2.8465517
C	-1.4183699	1.1653527	1.4986427
C	-1.6143509	-0.0074543	0.6898647
C	-1.8934679	-1.2775133	1.2580867
C	-1.6143509	0.1185897	-0.7192313
C	-2.0675459	-2.3595633	0.4541777
C	-1.4183699	-1.0542173	-1.5280093
C	-1.7748659	-2.2911123	-0.9343193
C	-0.8910359	-1.0323903	-2.8759183
C	-1.8512259	-3.4664073	-1.7176803
C	-1.1223109	-2.2080763	-3.6481133
C	-0.1385519	0.0555677	-3.5139433
C	-1.5954679	-3.4045773	-3.0487583
C	-0.9118979	-2.2209243	-5.0498233
C	-0.1385519	0.0555677	-4.9392853
C	0.6139321	1.1435257	-2.8759183
C	-0.5246359	-1.0897773	-5.6834783
C	0.2475321	1.2009127	-5.6834783
C	0.8452071	2.3192117	-3.6481133
C	1.1412661	1.1653527	-1.5280093
C	0.6347941	2.3320597	-5.0498233
C	1.3183641	3.5157127	-3.0487583
C	1.4977621	2.4022477	-0.9343193
C	1.5741221	3.5775427	-1.7176803
C	1.3372471	-0.0074543	-0.7192313
C	1.3372471	0.1185897	0.6898647
H	-2.3778449	3.4240137	-0.8998493
H	-2.1520039	4.5071037	1.2149607
H	-1.7211439	4.3881717	3.6533487
H	-1.1273829	3.2424307	5.5709357
H	-0.4555109	1.1572287	6.7365137
H	0.1784071	-1.0460933	6.7365137
H	0.8502791	-3.1312953	5.5709357
H	-2.3778449	-3.3128783	0.8704827
H	-2.1520039	-4.3959683	-1.2443273
H	-1.7211439	-4.2770363	-3.6827153
H	-1.1273829	-3.1312953	-5.6003023
H	-0.4555109	-1.0460933	-6.7658803
H	0.1784071	1.1572287	-6.7658803
H	0.8502791	3.2424307	-5.6003023
H	1.4440401	4.3881717	-3.6827153
H	1.8749001	4.5071037	-1.2443273
H	-2.0354649	-1.3581273	2.3289037
H	-2.0354649	1.4692627	-2.3582703
C	1.3183641	-3.4045773	3.0193917
C	1.6163641	1.3886487	1.2580867
C	1.7904421	2.4706987	0.4541777
H	1.7583611	1.4692627	2.3289037
H	2.1007411	3.4240137	0.8704827
C	1.1412661	-1.0542173	1.4986427
C	1.7904421	-2.3595633	-0.4835443
C	1.6163641	-1.2775133	-1.2874533
H	1.7583611	-1.3581273	-2.3582703
C	1.5741221	-3.4664073	1.6883137
H	1.4440401	-4.2770363	3.6533487
C	1.4977621	-2.2911123	0.9049527
H	1.8749001	-4.3959683	1.2149607
H	2.1007411	-3.3128783	-0.8998493
Bq	-0.6211641	-1.0733388	-4.2850936
Bq	-1.4422128	-2.2427968	-2.2921331
Bq	0.3440602	1.1844742	-4.2850936
Bq	1.1651089	2.3539322	-2.2921331
Bq	-1.7304919	1.2563472	0.1005385
Bq	-1.7304919	-1.1452118	-0.1299051
Bq	-0.7481974	-1.2811727	-0.0010173
Bq	-2.7103735	-1.0044036	-0.2713446
Bq	-0.4980905	-2.4738364	-2.0570716
Bq	-2.3808629	-1.9912563	-2.5280639
Bq	-1.5448436	-0.7028878	-4.3829823
Bq	0.3138521	-1.4352112	-4.1630563
Bq	1.2677397	0.8140231	-4.3829823
Bq	-0.5816984	1.5427637	-4.1642646
Bq	2.1037590	2.1023916	-2.5280639
Bq	0.2209867	2.5849717	-2.0570716
Bq	-0.7481974	1.3923080	-0.0283493
Bq	-2.7103735	1.1155389	0.2419780

benzene

C	-1.1820870	-0.7330860	0.0000000
C	-1.2259210	0.6571660	0.0000000
C	-0.0438320	1.3902510	0.0000000
C	1.1820870	0.7330860	0.0000000
C	1.2259210	-0.6571660	0.0000000
C	0.0438320	-1.3902510	0.0000000
H	-2.1044460	-1.3051040	0.0000020
H	-2.1824800	1.1699510	-0.0000010
H	-0.0780280	2.4750480	-0.0000010
H	2.1044460	1.3051040	0.0000010
H	2.1824800	-1.1699510	-0.0000010
H	0.0780280	-2.4750480	-0.0000010

phenanthrene

C	3.5454770	-0.2964380	0.0000000
C	2.8251730	0.8750330	0.0000000
C	1.4161380	0.8620470	0.0000000
C	0.7255560	-0.3772390	0.0000000
C	1.4911120	-1.5599830	0.0000000
C	2.8681910	-1.5241130	0.0000000
C	0.6771420	2.0864110	0.0000000
C	-0.7255560	-0.3772390	0.0000000
C	-1.4161380	0.8620470	0.0000000
C	-0.6771420	2.0864110	0.0000000
C	-2.8251730	0.8750330	0.0000000
H	-3.3359980	1.8335980	0.0000000
C	-3.5454770	-0.2964380	0.0000000
C	-2.8681910	-1.5241130	0.0000000
C	-1.4911120	-1.5599830	0.0000000
H	1.2292250	3.0216340	0.0000000
H	4.6301870	-0.2728710	0.0000000
H	3.3359980	1.8335980	0.0000000
H	0.9970930	-2.5243980	0.0000000
H	3.4303360	-2.4522790	0.0000000
H	-1.2292250	3.0216340	0.0000000
H	-4.6301870	-0.2728710	0.0000000
H	-3.4303360	-2.4522790	0.0000000
H	-0.9970930	-2.5243980	0.0000000

4

S	-6.0883620	0.5588900	-1.6148670
S	6.0789700	-0.5634280	-1.6293040
C	1.2486880	1.3863230	-1.6340500
C	0.4536450	2.4887680	-1.5609730
C	-0.9618390	2.3775710	-1.6512170
C	-1.7949420	3.5162060	-1.6314800
C	-3.1583090	3.3995960	-1.7711220
C	-3.7511650	2.1326190	-1.9587030
C	-4.9297390	-0.4863410	0.7160870
C	-5.5526760	-1.7332760	0.9215400
C	-4.8087190	-2.8070520	1.3458880
C	-3.4336200	-2.6783530	1.6392700
C	-2.8047350	-1.4013720	1.5361880
C	-1.5514330	1.0897570	-1.7719940
C	-0.7063500	-0.0817980	-1.7235610
C	-1.2591670	-1.3941610	-1.6284820
C	0.6956550	0.0736910	-1.7236030
C	-0.4639330	-2.4960970	-1.5493800
C	1.5408350	-1.0979020	-1.7670320
C	0.9516060	-2.3851630	-1.6397290
C	1.7851330	-3.5234130	-1.6144420
C	3.7405840	-2.1410660	-1.9515880
C	3.1483100	-3.4071690	-1.7562690
C	4.9371160	0.4930870	0.7054890
C	2.8136950	1.4082340	1.5295940
C	5.5602680	1.7401950	0.9088510
C	3.4426910	2.6852850	1.6311400
C	1.4132170	1.2794440	1.8902200
C	4.8170580	2.8140610	1.3344630
C	2.6758610	3.8342670	1.9787020
C	0.6814920	2.4650730	2.1259520
C	1.3356890	3.7309270	2.1726200
C	0.7175550	0.0180540	2.0104860
C	-0.7073810	-0.0115620	2.0121850
C	-2.6660180	-3.8275020	1.9845700
C	-1.3879600	1.2129730	2.2698640
C	-0.7133440	2.3920990	2.3685480
C	-1.4033820	-1.2728640	1.8933530
C	0.7243010	-2.3858260	2.3657590
C	1.3986890	-1.2066570	2.2659950
C	-1.3252890	-3.7244230	2.1748300
C	-0.6711420	-2.4586180	2.1268620
C	-5.7249130	0.6721500	0.1861970
C	-5.2380830	2.0528780	-2.2128310
C	5.2267510	-2.0627130	-2.2107790
C	5.7311310	-0.6661190	0.1754240
C	2.9381400	-1.0177690	-1.9426140
C	3.5919310	0.3546520	0.9930740
C	-3.5840200	-0.3477870	1.0009900
C	-2.9489390	1.0091490	-1.9454950
H	0.8958520	3.4739750	-1.4355920
H	-1.3374170	4.4953580	-1.5094360
H	-3.7855190	4.2886300	-1.7585300
H	-6.6128770	-1.8486140	0.7078970
H	-5.2712950	-3.7854240	1.4543970
H	-0.9061240	-3.4806930	-1.4192680
H	1.3280080	-4.5020360	-1.4867690
H	3.7757360	-4.2959960	-1.7398880
H	6.6200480	1.8555680	0.6931400
H	5.2798040	3.7924920	1.4417130
H	3.1780840	4.7963100	2.0468970
H	0.7363600	4.6115620	2.3911540
H	-2.3336770	-1.5184510	-1.5539130
H	2.3231690	1.5107260	-1.5591140
H	-2.4479710	1.1944050	2.4881610
H	-1.2454420	3.3037990	2.6286800
H	2.4592130	-1.1882960	2.4817250
H	-3.1681980	-4.7894900	2.0538700
H	-0.7254650	-4.6051930	2.3914460
H	1.2570860	-3.2976960	2.6238520
H	-6.6860290	0.7409900	0.7061680
H	-5.1908350	1.6129070	0.3484760
H	-5.7355320	2.9391000	-1.8016380
H	-5.4401570	2.0581030	-3.2918920
H	5.4251170	-2.0775720	-3.2904460
H	5.7260580	-2.9450880	-1.7935520
H	6.6968630	-0.7290490	0.6875080
H	5.2014070	-1.6075070	0.3480290
H	-3.4278680	0.0447170	-2.0762010
H	-3.1098010	0.5927530	0.7513740
H	3.4166260	-0.0539350	-2.0792060
H	3.1174100	-0.5860770	0.7449240

4′

S	-6.6127190	1.1745450	1.6464780
S	6.6129130	1.1661330	-1.6528160
C	0.1523330	1.7179130	-1.8658990
C	-1.1504730	1.6808500	-2.2609410
C	-2.2046310	1.8330870	-1.3188460
C	-3.5542670	1.9099790	-1.7313740
C	-4.5621370	2.1196440	-0.8248960
C	-4.2622670	2.2574030	0.5476680
C	-4.9973000	-0.8591070	0.5353430
C	-5.8604920	-1.1814110	-0.5304280
C	-5.3371370	-1.6166710	-1.7218430
C	-3.9477610	-1.8062660	-1.8894210
C	-3.0674460	-1.6027140	-0.7859570
C	-1.8902580	1.9279890	0.0622430
C	-0.5114550	1.8325400	0.4822010
C	-0.1519490	1.7239470	1.8579780
C	0.5118190	1.8306680	-0.4904670
C	1.1508740	1.6871090	2.2530270
C	1.8906860	1.9267290	-0.0708790
C	2.2051170	1.8358820	1.3104480
C	3.5548540	1.9134050	1.7226240
C	4.2627510	2.2536230	-0.5575640
C	4.5626920	2.1200470	0.8153930
C	4.9971770	-0.8616780	-0.5319390
C	3.0671240	-1.5981740	0.7931030
C	5.8602260	-1.1781980	0.5356630
C	3.9472640	-1.7952090	1.8978950
C	1.6506830	-1.8732560	0.9599730
C	5.3366870	-1.6068400	1.7293870
C	3.4226910	-2.1216320	3.1808080
C	1.1772170	-2.1030800	2.2720220
C	2.0813740	-2.2174960	3.3685530
C	0.7009670	-1.9576080	-0.1284020
C	-0.7012250	-1.9568860	0.1374070
C	-3.4233300	-2.1405030	-3.1703960
C	-1.1127500	-2.1951820	1.4802980
C	-0.2084060	-2.3003700	2.4933040
C	-1.6510530	-1.8788980	-0.9513410
C	0.2079610	-2.3148400	-2.4822400
C	1.1124060	-2.2033940	-1.4699680
C	-2.0820370	-2.2376320	-3.3577230
C	-1.1777270	-2.1166190	-2.2620240
C	-5.5522440	-0.3038270	1.8200050
C	-5.3532920	2.4963890	1.5502100
C	5.3538210	2.4886610	-1.5610480
C	5.5520930	-0.3127880	-1.8193280
C	2.9526200	2.1451610	-0.9771420
C	3.6388410	-1.0608960	-0.3851470
C	-3.6389460	-1.0586420	0.3892700
C	-2.9522190	2.1496740	0.9677110
H	-1.4035930	1.5541380	-3.3105270
H	-3.7811740	1.8046840	-2.7894790
H	-5.5983800	2.1616150	-1.1491940
H	-6.9302160	-1.0225910	-0.4219880
H	-5.9905440	-1.8058390	-2.5706430
H	1.4039400	1.5633600	3.3029830
H	3.7818970	1.8108490	2.7809680
H	5.5990350	2.1624360	1.1392960
H	6.9299940	-1.0201530	0.4265490
H	5.9899860	-1.7913700	2.5792910
H	4.1143280	-2.2548790	4.0093230
H	1.6708700	-2.4224980	4.3544430
H	-0.9305100	1.6234410	2.6065450
H	0.9308290	1.6145750	-2.6141470
H	-2.1543740	-2.4031640	1.6866270
H	-0.5432340	-2.5548960	3.4961750
H	2.1540490	-2.4122710	-1.6752490
H	-4.1150550	-2.2786560	-3.9980330
H	-1.6716740	-2.4485780	-4.3424170
H	0.5427880	-2.5751090	-3.4836370
H	-6.2036110	-1.0433600	2.3011250
H	-4.7472240	-0.0803530	2.5289490
H	-4.9262310	2.6531310	2.5468040
H	-5.9322350	3.3930790	1.2987060
H	5.9330570	3.3860790	-1.3128230
H	4.9266820	2.6419530	-2.5581460
H	6.2032850	-1.0546990	-2.2970210
H	4.7470270	-0.0924730	-2.5292100
H	-2.7395880	2.2697560	2.0262480
H	-2.9878570	-0.7146950	1.1830110
H	2.7398840	2.2619900	-2.0360220
H	2.9879190	-0.7216370	-1.1810310

$TS_{4-4'}$

S	-4.6719350	-3.3225520	-1.8606330
S	5.8865760	1.2400600	0.2527860
C	1.6833360	-1.6190970	1.7458750
C	0.4506780	-1.1214860	1.4806080
C	-0.2972400	-1.6232480	0.3802860
C	-1.3793860	-0.8847850	-0.1192600
C	-2.1093550	-1.3645250	-1.1671220
C	-1.9183310	-2.6723980	-1.6397710
C	-5.3099860	-0.9301560	-0.4445930
C	-5.9818080	-1.5055540	0.6542870
C	-5.7983180	-0.9994080	1.9174900
C	-4.8840450	0.0506800	2.1596980
C	-4.2594490	0.7050260	1.0597170
C	0.0977520	-2.8200280	-0.2740960
C	1.4494610	-3.2880740	-0.0404270
C	2.0585480	-4.2941580	-0.8523940
C	2.2646730	-2.5933760	0.8780020
C	3.4143210	-4.4392460	-0.9133290
C	3.6973680	-2.6844810	0.7602260
C	4.2738740	-3.5546890	-0.1978540
C	5.6458430	-3.4087110	-0.5128990
C	5.8022220	-1.4659340	0.9198280
C	6.3784970	-2.3540750	-0.0156240
C	3.3317270	2.3923980	-0.0581730
C	1.1161320	3.2548660	-0.6869650
C	3.9341200	3.3202470	-0.9266720
C	1.7479430	4.0835500	-1.6609410
C	-0.3368910	3.2447390	-0.6216280
C	3.1538320	4.1302390	-1.7205800
C	0.9609080	4.7790990	-2.6271580
C	-1.0550380	3.7990950	-1.7052840
C	-0.3812710	4.5844350	-2.6897170
C	-1.1002850	2.7115980	0.4788910
C	-2.4721520	2.3758070	0.2944880
C	-4.4767950	0.3491080	3.4925720
C	-3.1319940	2.8583790	-0.8677100
C	-2.4588980	3.6084890	-1.7896950
C	-3.1665440	1.6278800	1.3195510
C	-1.3505250	2.2346470	2.8455300
C	-0.5716040	2.6432090	1.8020940
C	-3.3590970	1.0903420	3.7138370
C	-2.6369160	1.6669300	2.6273600
C	-5.3689780	-1.6056730	-1.7944360
C	-2.9740640	-3.1927760	-2.5733330
C	6.4405920	-0.1660960	1.3105690
C	4.1243570	1.3636520	0.7226280
C	4.5246830	-1.7195050	1.3698990
C	1.9470110	2.3857780	0.0599950
C	-4.5537410	0.2083000	-0.2348300
C	-0.8041260	-3.3783010	-1.2193400
H	0.0297480	-0.3077580	2.0671430
H	-1.5887580	0.0841130	0.3116510
H	-2.8784140	-0.7603080	-1.6196620
H	-6.6073280	-2.3817640	0.5025140
H	-6.2894940	-1.4654440	2.7684470
H	3.8554370	-5.1677970	-1.5894880
H	6.0921830	-4.0902040	-1.2335220
H	7.3958930	-2.1859930	-0.3606310
H	5.0161670	3.3645650	-1.0116010
H	3.6219470	4.7925820	-2.4450610
H	1.4673590	5.4087260	-3.3546280
H	-0.9742790	5.0455070	-3.4758030
H	1.4342450	-4.9076800	-1.4945520
H	2.2528300	-1.2221510	2.5790070
H	-4.2047660	2.7239780	-0.9598420
H	-2.9948800	4.0631420	-2.6193460
H	0.4261670	3.0242640	1.9901000
H	-5.0111310	-0.1124690	4.3192600
H	-2.9740830	1.2278310	4.7213600
H	-0.9712290	2.2855920	3.8634130
H	-6.4119320	-1.7510180	-2.0977730
H	-4.8970500	-0.9990530	-2.5747940
H	-3.0375460	-2.5748180	-3.4774310
H	-2.7623130	-4.2176250	-2.8965200
H	7.5268920	-0.1796430	1.1758770
H	6.2364370	0.0842340	2.3579450
H	4.0657600	1.5800880	1.7982460
H	3.6563340	0.3869140	0.5590510
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H	-4.0629670	0.6625380	-1.0869970
H	4.1131420	-1.0535700	2.1192150
H	1.4859130	1.6296530	0.6902520

7

C	-1.3181860	1.3315970	2.2028930
C	-0.5826890	2.4753130	2.1369660
C	0.8344690	2.4288060	2.0415850
C	1.5993110	3.5982060	1.8379500
C	2.9529450	3.5286200	1.6079770
C	3.6091320	2.2766530	1.6037210
C	5.0087340	2.1755870	1.1683890
C	5.5474370	1.2374230	0.3632850
C	5.7077980	-1.0430820	-0.5893940
C	5.1375410	-2.1713120	-1.1278930
C	3.7693800	-2.2121910	-1.4691300
C	2.9780250	-1.0291030	-1.3437450
C	1.4898160	1.1676160	2.1008740
C	0.7036920	-0.0431060	2.1980750
C	1.3181180	-1.3315840	2.2030500
C	-0.7037600	0.0431180	2.1980400
C	0.5826240	-2.4753050	2.1371850
C	-1.4898790	-1.1676110	2.1008910
C	-0.8345280	-2.4288060	2.0417310
C	-1.5993600	-3.5982220	1.8381450
C	-3.6091650	-2.2766850	1.6036900
C	-2.9529800	-3.5286510	1.6080830
C	-5.0087400	-2.1756560	1.1682640
C	-4.9186490	-0.0998540	-0.3304590
C	-2.9779910	1.0291090	-1.3437450
C	-5.5474250	-1.2375120	0.3631230
C	-5.7077810	1.0430340	-0.5894570
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C	-1.5690950	1.0774650	-1.7091790
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C	-0.7090720	-0.0801170	-1.8102390
C	0.7091190	0.0801610	-1.8102170
C	3.1649540	-3.4387680	-1.8663880
C	1.2235480	1.3858540	-2.0532640
C	0.3962940	2.4618160	-2.1711800
C	1.5691380	-1.0774290	-1.7092180
C	-0.3962410	-2.4617460	-2.1713720
C	-1.2234970	-1.3857920	-2.0533950
C	1.8216010	-3.5099510	-2.0519600
C	1.0009400	-2.3464000	-1.9589260
C	-2.8853090	-1.1436570	1.9351900
C	-3.5913690	-0.0905920	-0.7451020
C	3.5913930	0.0905580	-0.7450210
C	2.8852560	1.1436480	1.9352550
C	4.9186660	0.0997960	-0.3303530
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H	5.6728760	2.9702570	1.5087130
H	6.6221370	1.3126830	0.1945470
H	6.7593640	-1.0416400	-0.3117450
H	5.7329710	-3.0707990	-1.2671840
H	1.0782570	-3.4426620	2.1114600
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H	-6.7593540	1.0415720	-0.3118310
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H	-3.7905820	4.3227640	-1.9640960
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H	-2.3986080	1.4123050	2.2312890
H	2.2807480	1.5132250	-2.2488690
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H	3.7906230	-4.3227190	-1.9642950
H	1.3440630	-4.4562100	-2.2948570
H	-0.8053700	-3.4362400	-2.4261570
H	3.4193630	0.2021650	1.9625310
H	2.9901130	0.9593240	-0.5254420
H	-3.4194160	-0.2021730	1.9623710
H	-2.9900900	-0.9593680	-0.5255540

7′

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C	1.5161640	2.8524720	2.0322860
C	2.3917650	2.6841000	0.9239510
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C	4.5882140	2.1587330	0.0548530
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C	4.8710260	1.3876970	-2.3027280
C	5.2917240	0.1184450	-2.1931110
C	5.8964180	-1.3282000	-0.2338690
C	5.5288470	-1.9363610	0.9432600
C	4.1716220	-2.0699350	1.3083370
C	3.1557480	-1.6745460	0.3892050
C	1.8484780	2.6293220	-0.3881640
C	0.4209920	2.7574800	-0.5669710
C	-0.1648640	2.8498180	-1.8640870
C	-0.4201930	2.7573660	0.5647520
C	-1.5152200	2.8547300	-2.0345070
C	-1.8477750	2.6303650	0.3858070
C	-2.3909530	2.6862250	-0.9263000
C	-3.7775120	2.5022220	-1.1116380
C	-4.0480920	2.0207590	1.2409960
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C	-5.2926040	0.1221870	2.1909060
C	-5.8967030	-1.3282670	0.2345220
C	-4.1718760	-2.0737550	-1.3058330
C	-1.7633580	-1.9119400	-0.7281670
C	-5.5291070	-1.9393550	-0.9410780
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C	0.9159980	-2.1195630	-1.6138100
C	-0.1122850	-2.3162130	-2.4864910
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C	-0.9162120	-2.1145270	1.6166760
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H	2.3123740	2.1732280	-2.4545710
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H	-2.3123450	2.1741730	2.4520350
H	-2.8267780	-0.4879030	1.3839210

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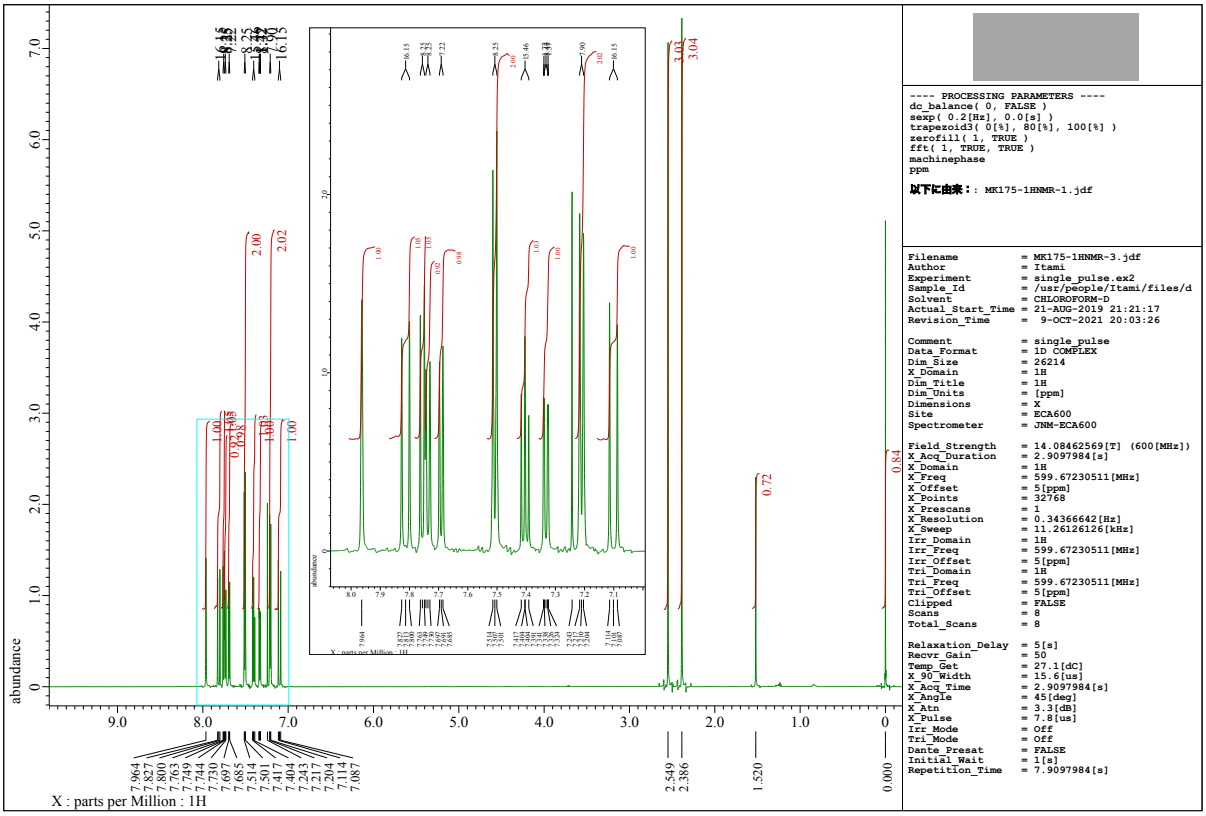
10. ^{1}H and ^{13}C NMR spectra of synthesized compounds

(a)



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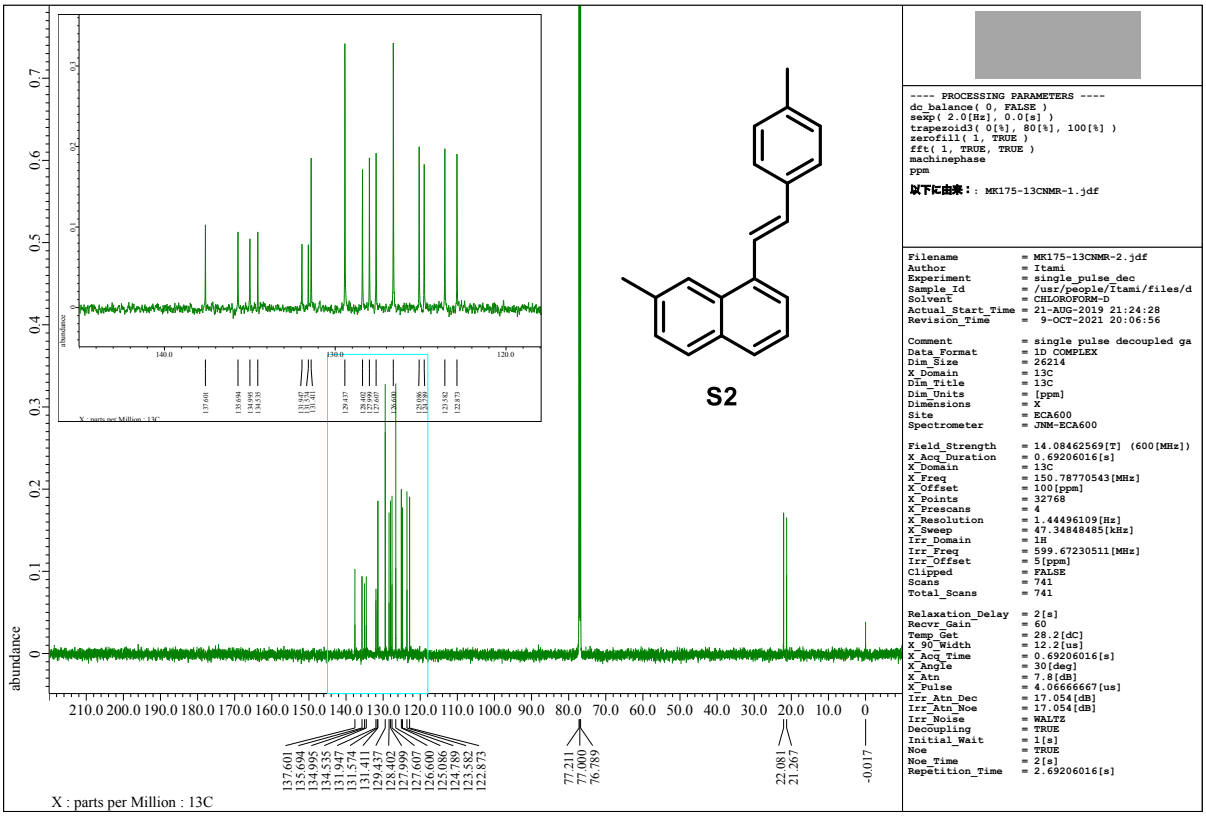
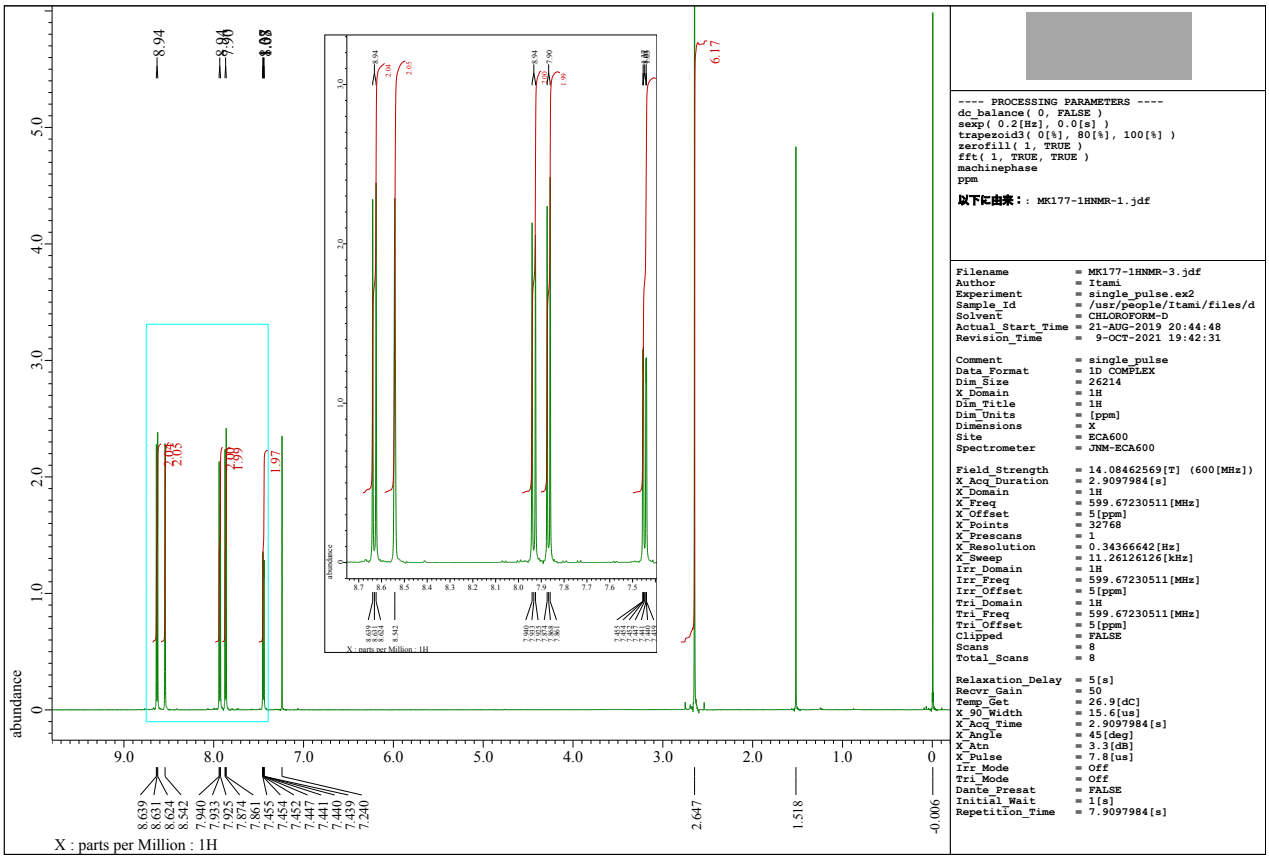


Figure S16. (a) ^{1}H NMR of **S2** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of **S2** (151 MHz, $CDCl_3$)

(a)



(b)

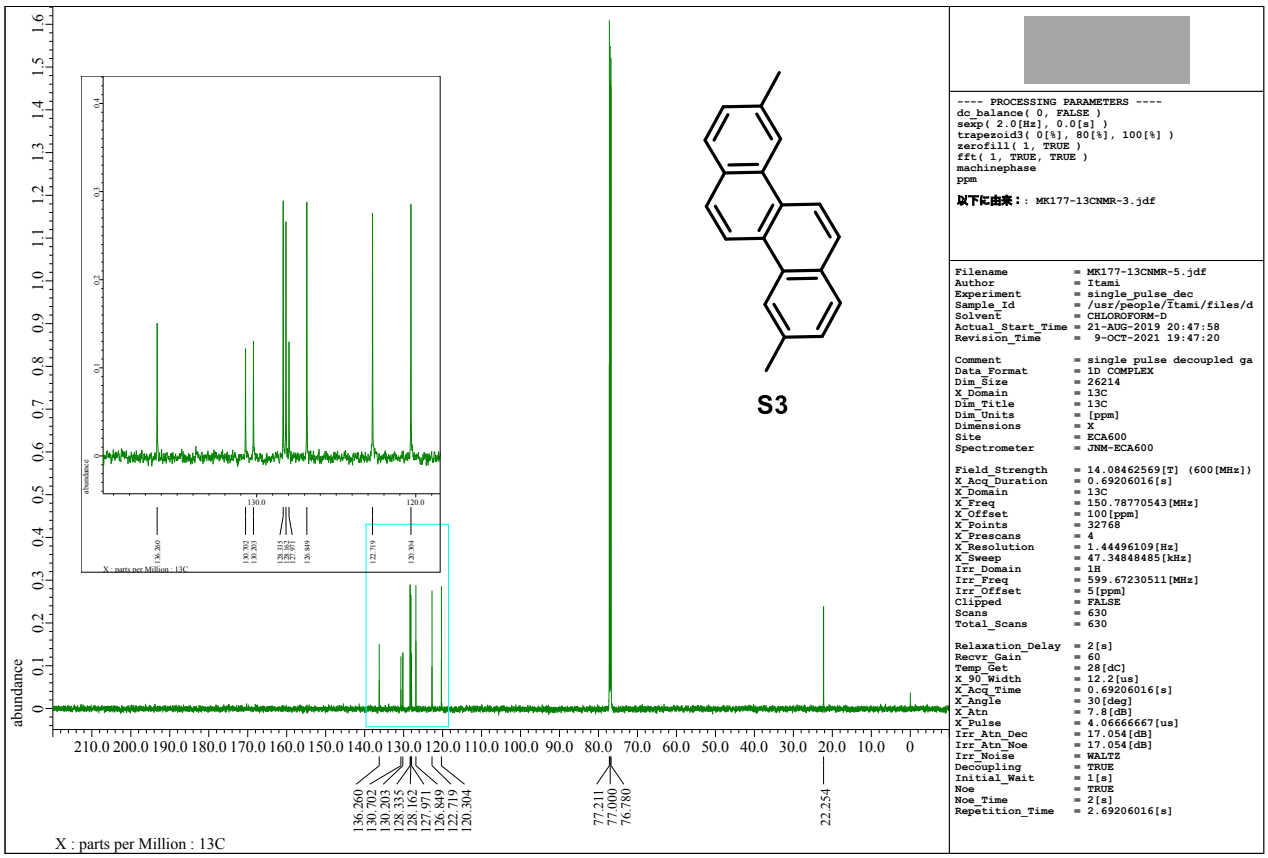
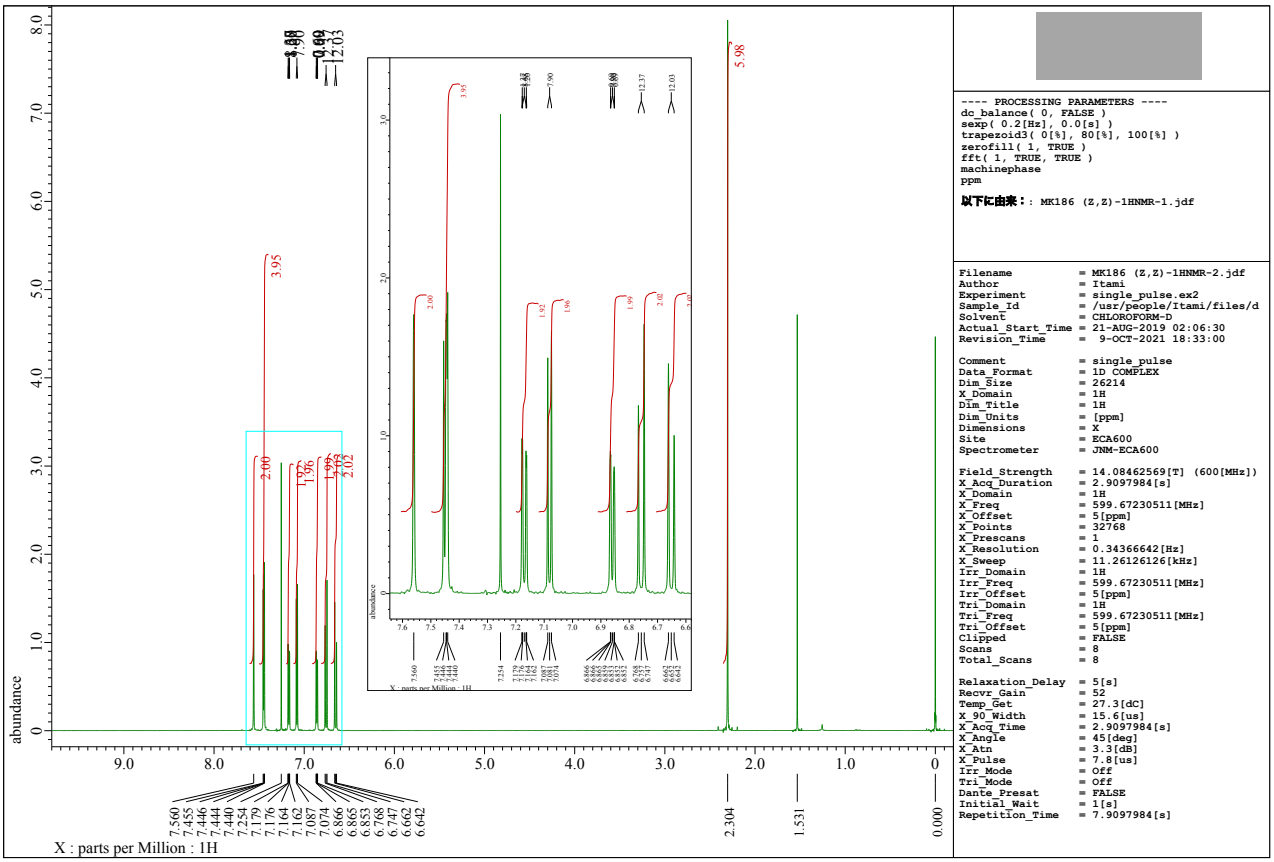


Figure S17. (a) ^{1}H NMR of **S3** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of **S3** (151 MHz, $CDCl_3$)

(a)



(b)

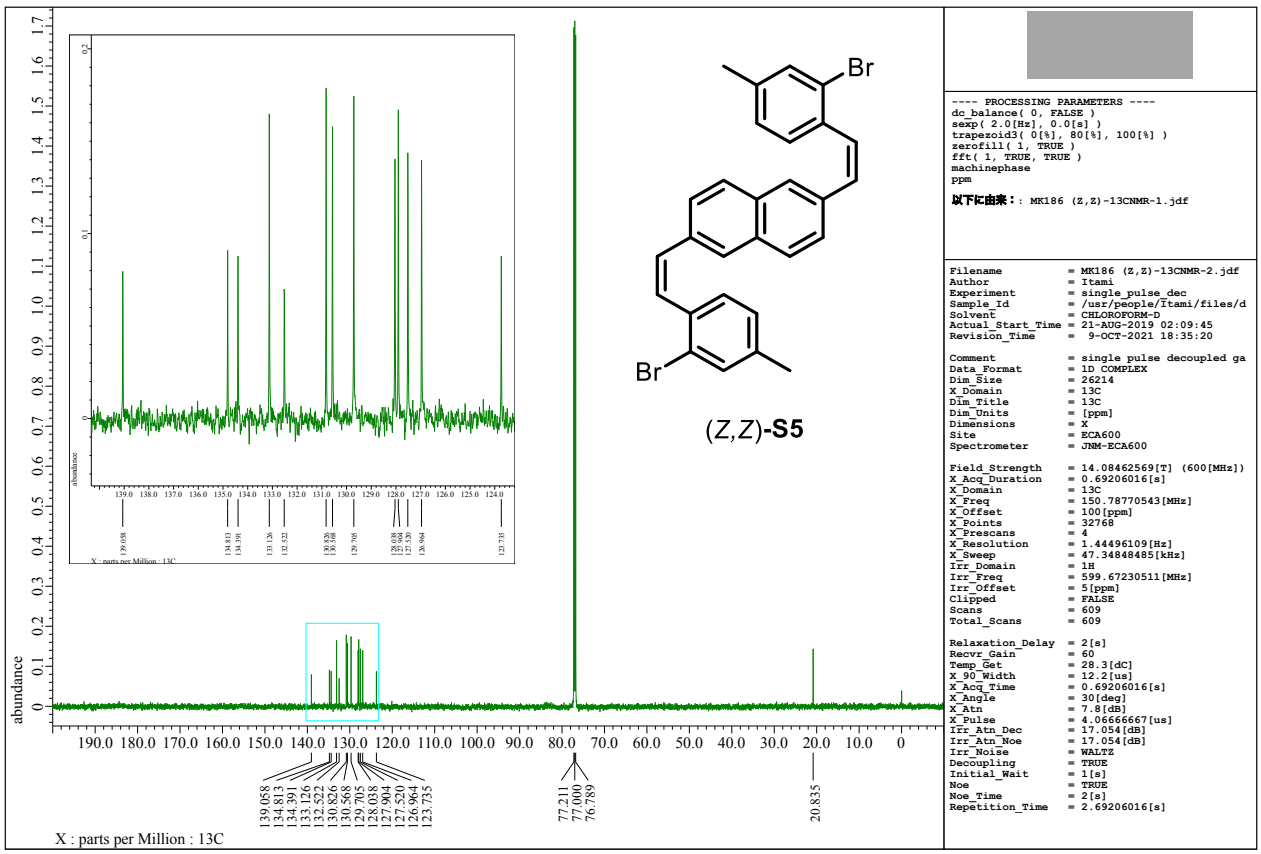
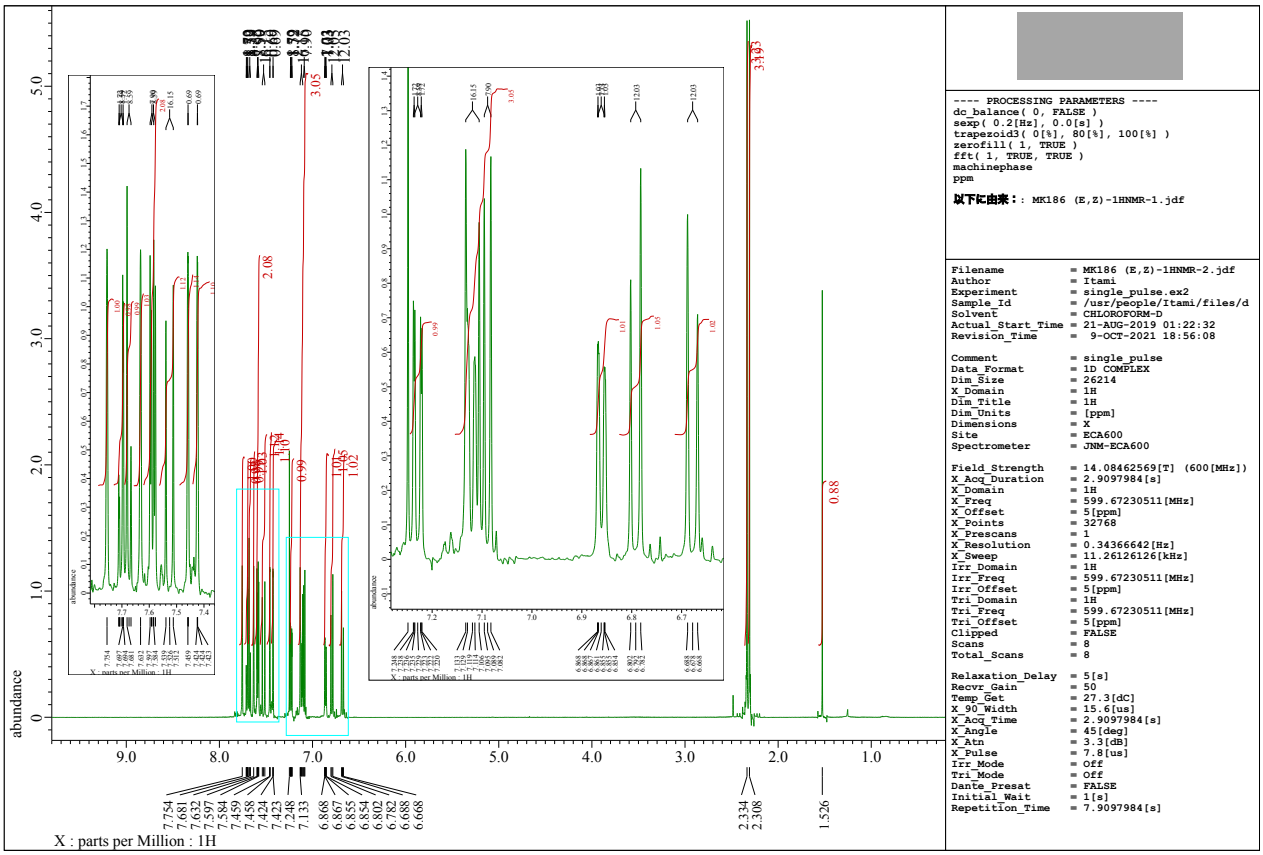


Figure S18. (a) ^{1}H NMR of (*Z*,*Z*)-**S5** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of (*Z*,*Z*)-**S5** (151 MHz, $CDCl_3$)

(a)



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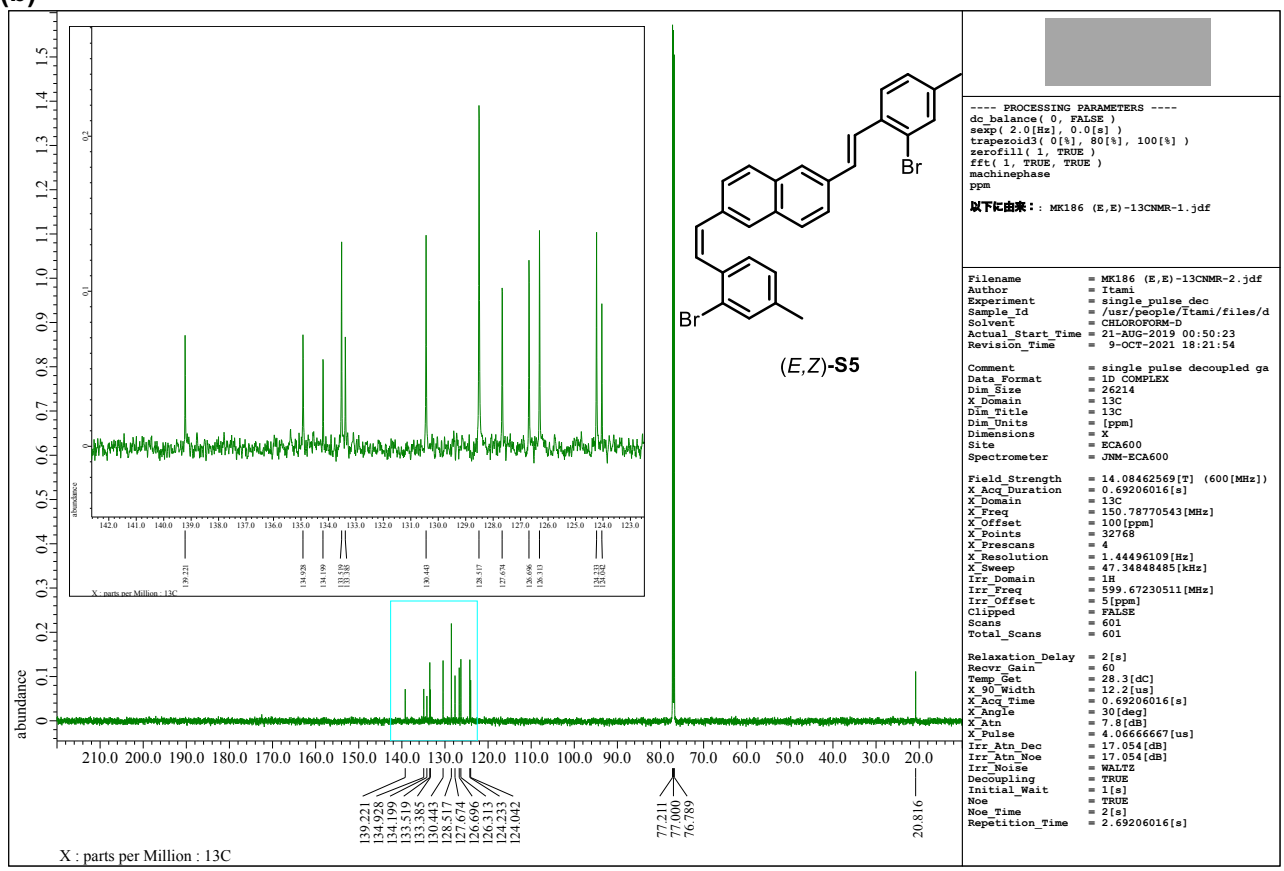
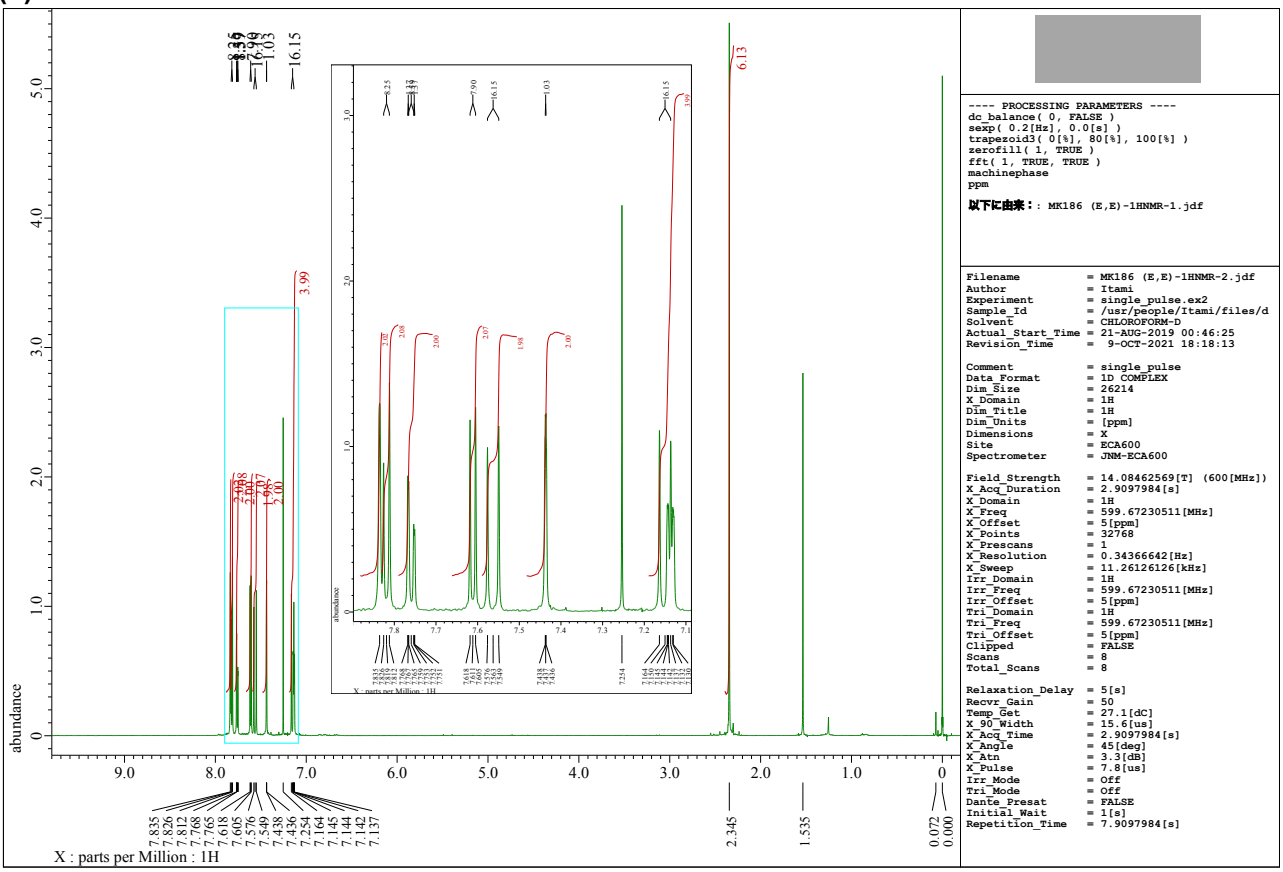


Figure S19. (a) ^{1}H NMR of (*E,Z*)-**S5** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of (*E,Z*)-**S5** (151 MHz, $CDCl_3$)

(a)



(b)

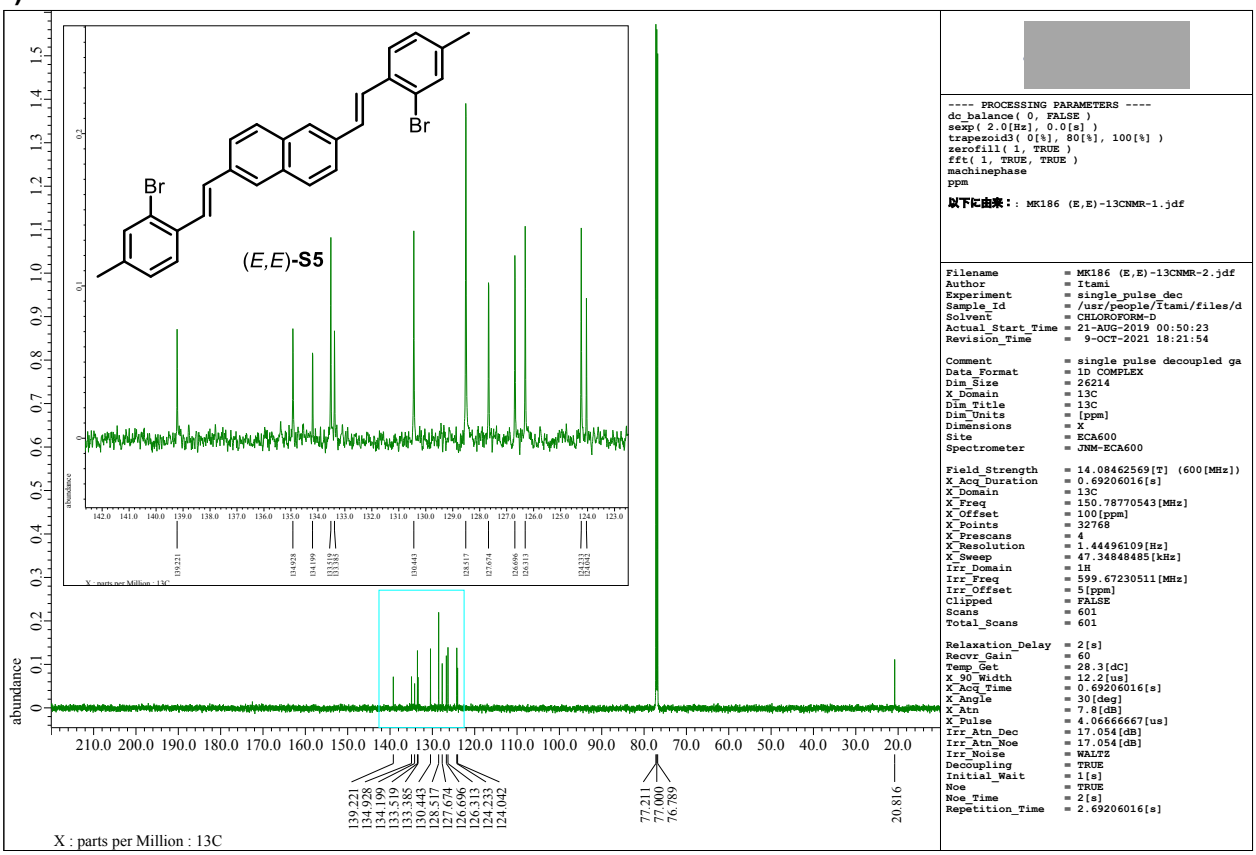
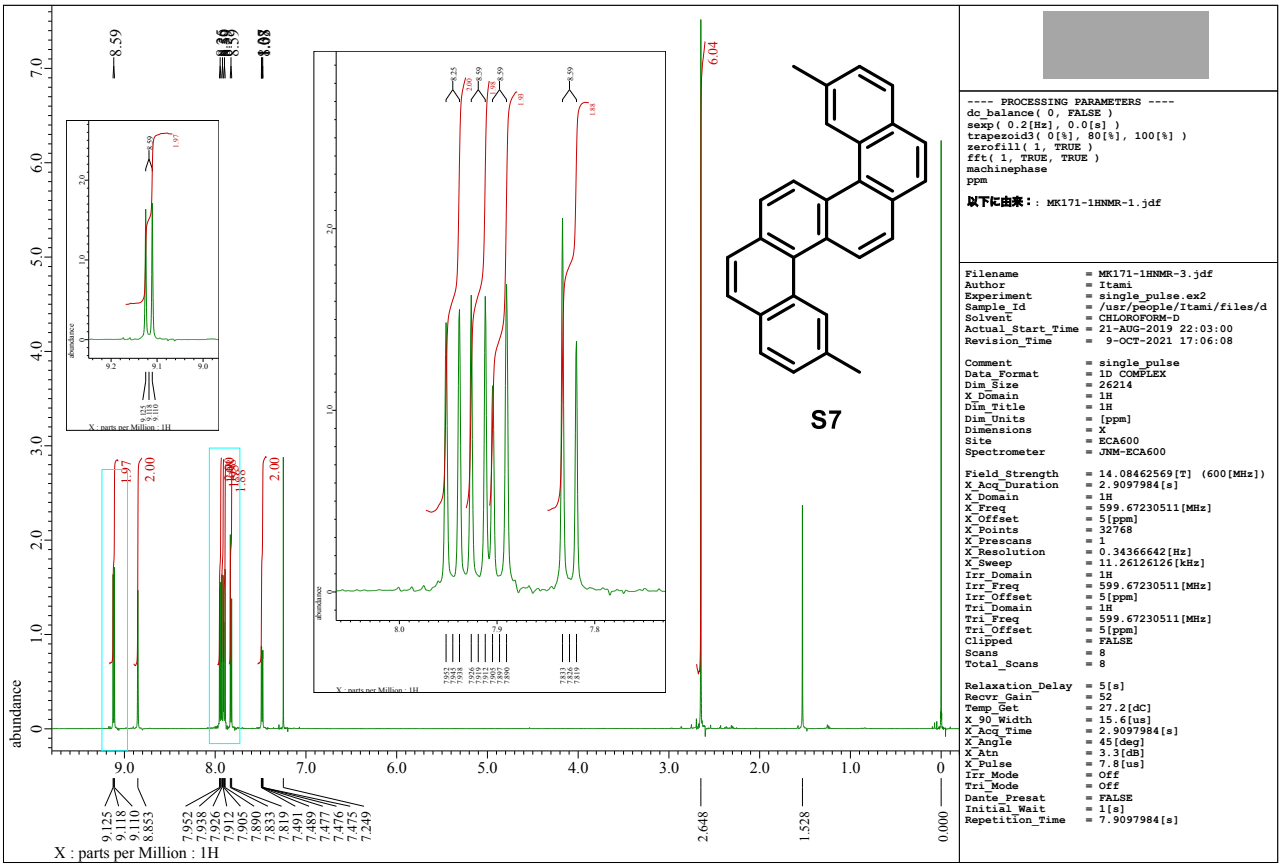


Figure S20. (a) ^{1}H NMR of (*E,E*)-**S5** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of (*E,E*)-**S5** (151 MHz, $CDCl_3$)

(a)



(b)

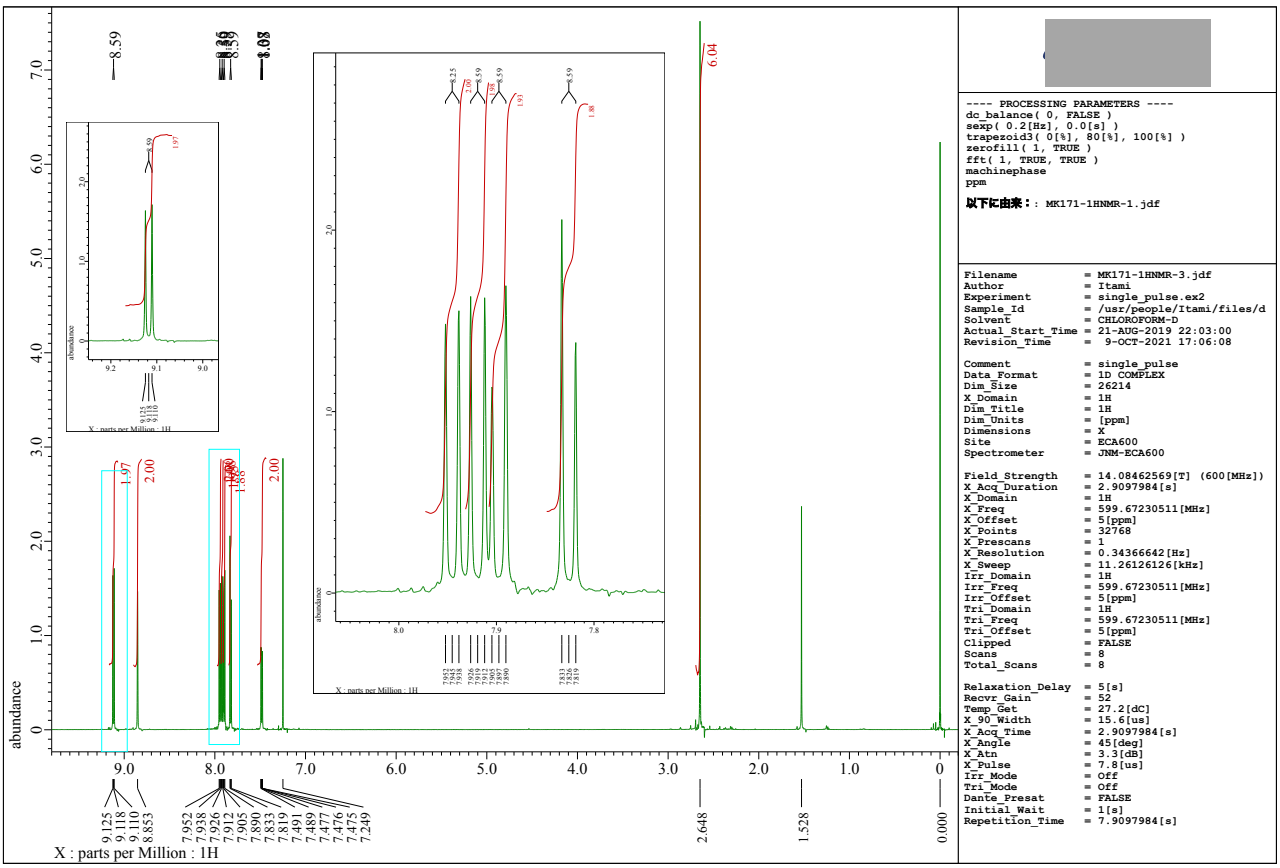
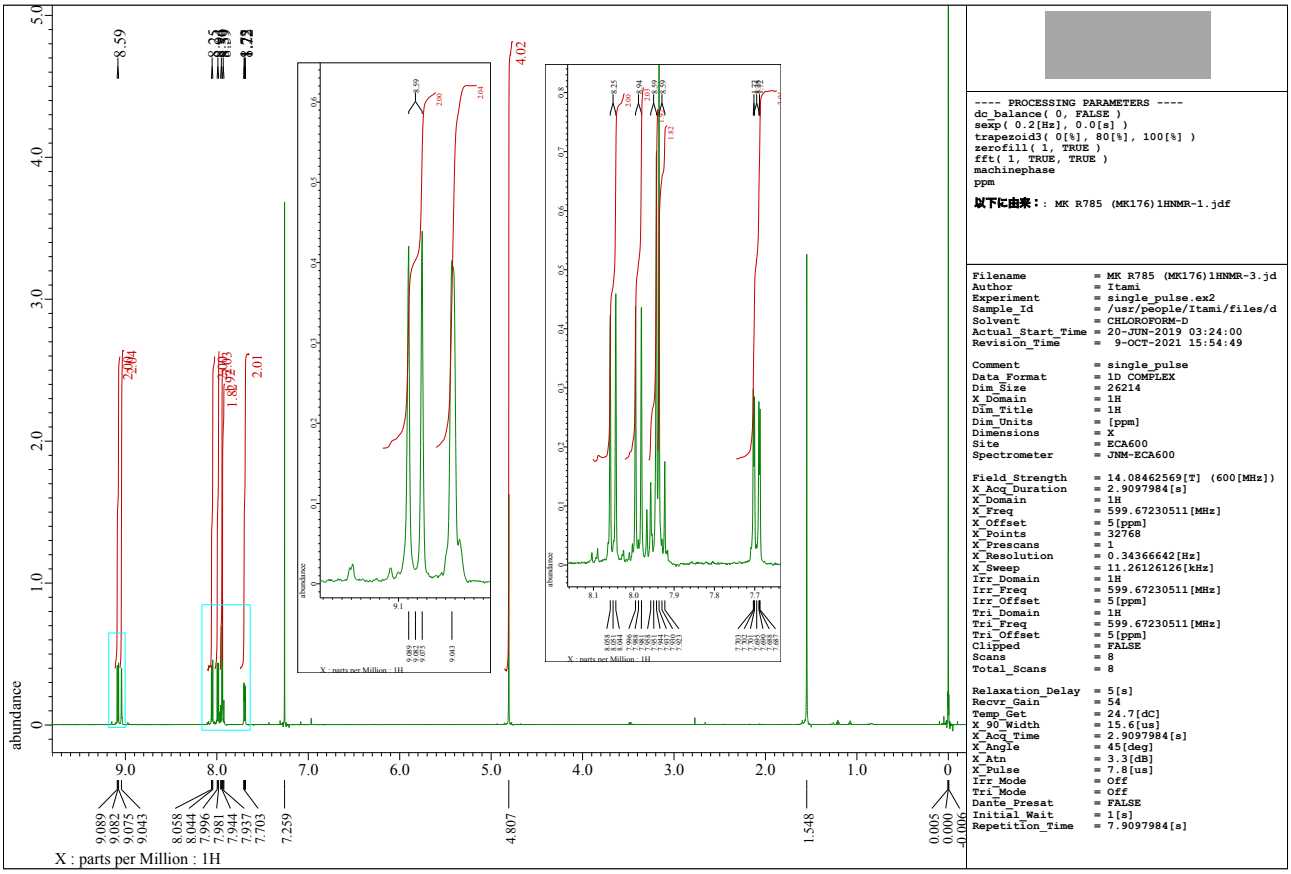


Figure S21. (a) ^{1}H NMR of **S7** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of **S7** (151 MHz, $CDCl_3$)

(a)

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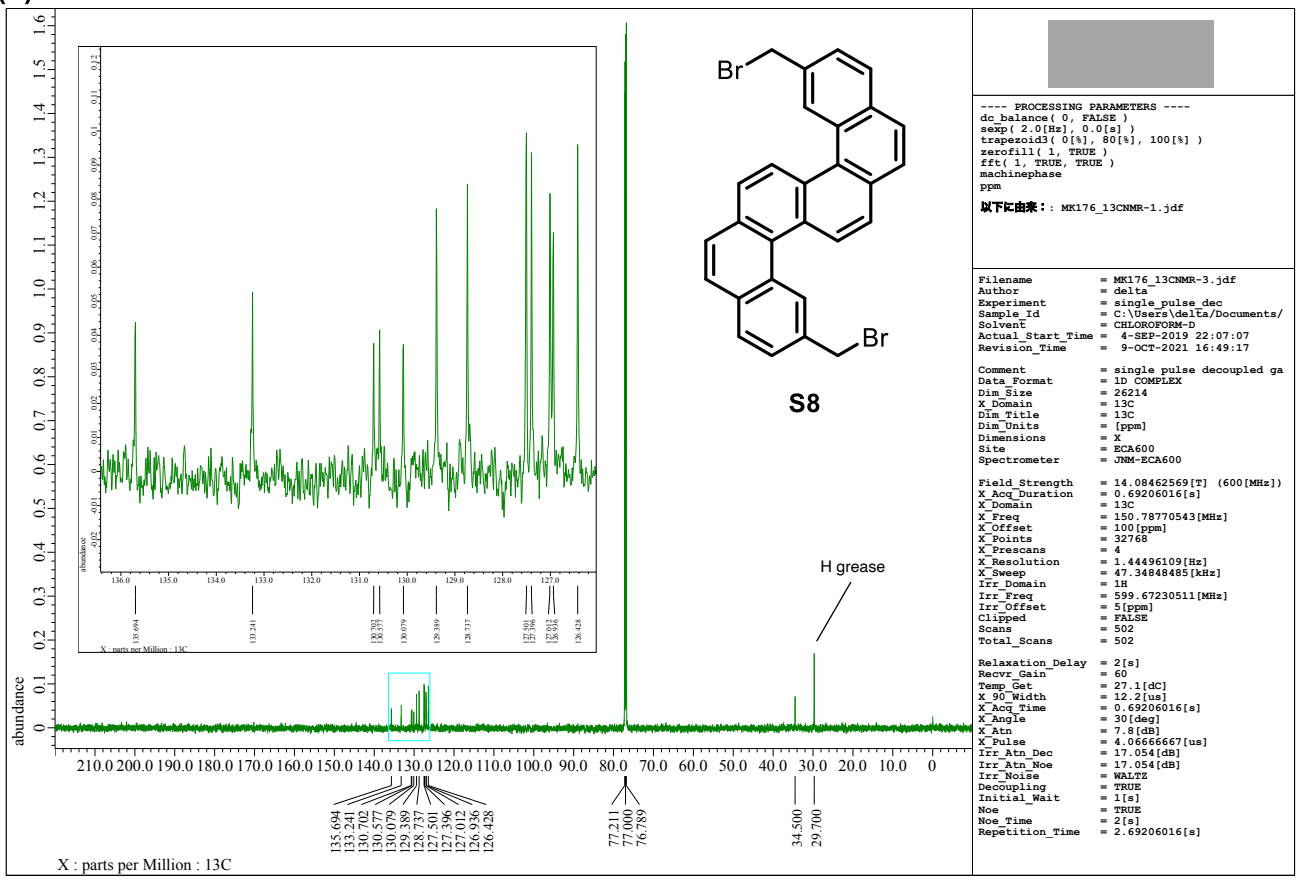
X_Angle           = 45[deg]
X_Atn             = 3.3[dB]
X_Pulse           = 7.8[us]
Irr_Mode          = Off
Tri_Mode          = Off
DanTe_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 7.9097984[s]
```

(b)




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid3( 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
以下に由来： MK176_13CNMR-1.jdf

Filename          = MK176_13CNMR-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = C:\Users\delta/Documents/
Solvent           = CHLOROFORM-D
Actual_Start_Time =  4-SEP-2019 22:07:07
Revision_Time     =  9-OCT-2021 16:49:17

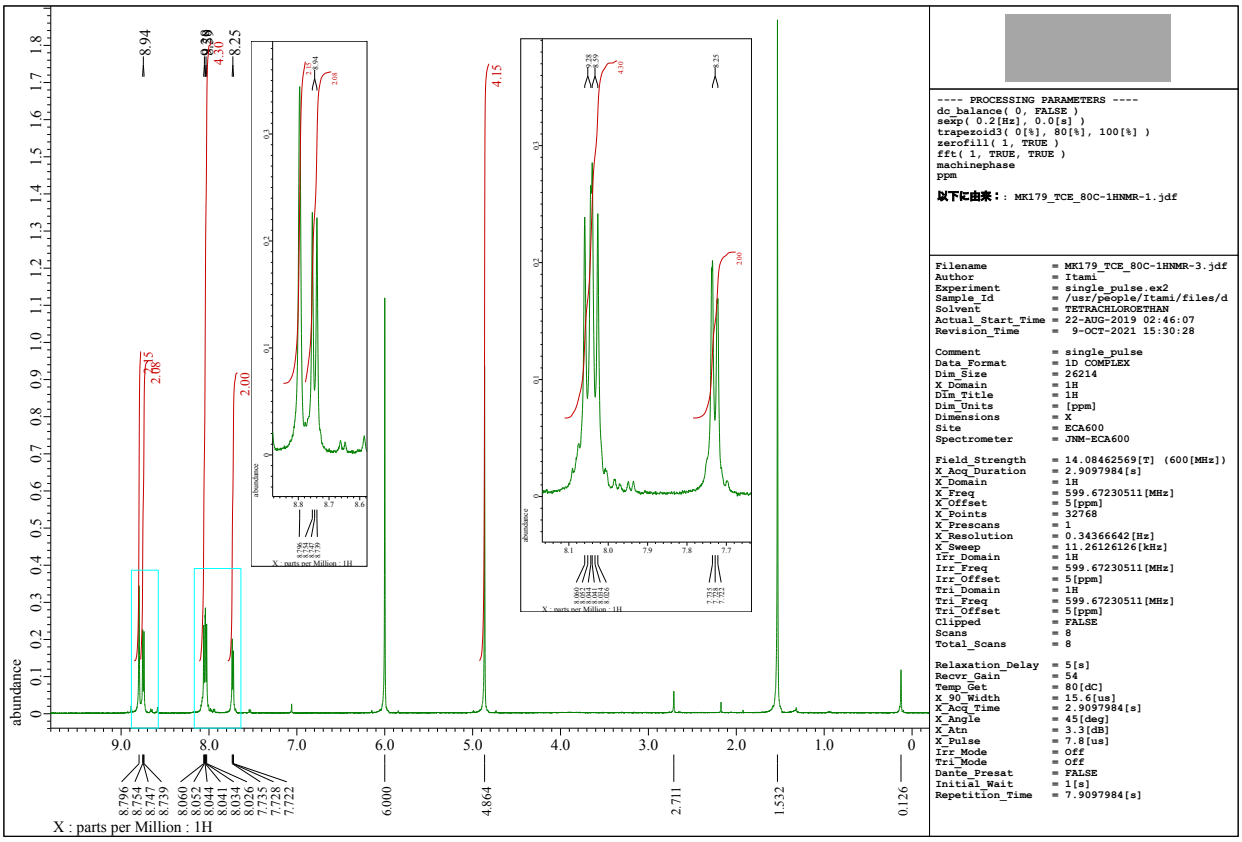
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = 13C
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = JNM-ECA600

Field_Strength    = 14.08462569[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.78770543[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
Irr_Domain        = 1H
Irr_Freq          = 599.67230511[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 502
Total_Scans       = 502

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 27.1[dC]
X_90_Width        = 12.2[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 7.8[dB]
X_Pulse           = 4.06666667[us]
Irr_Atn_Dec       = 17.054[dB]
Irr_Atn_Noe       = 17.054[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```

Figure S22. (a) ^{1}H NMR of **S8** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of **S8** (151 MHz, $CDCl_3$)

(a)



(b)

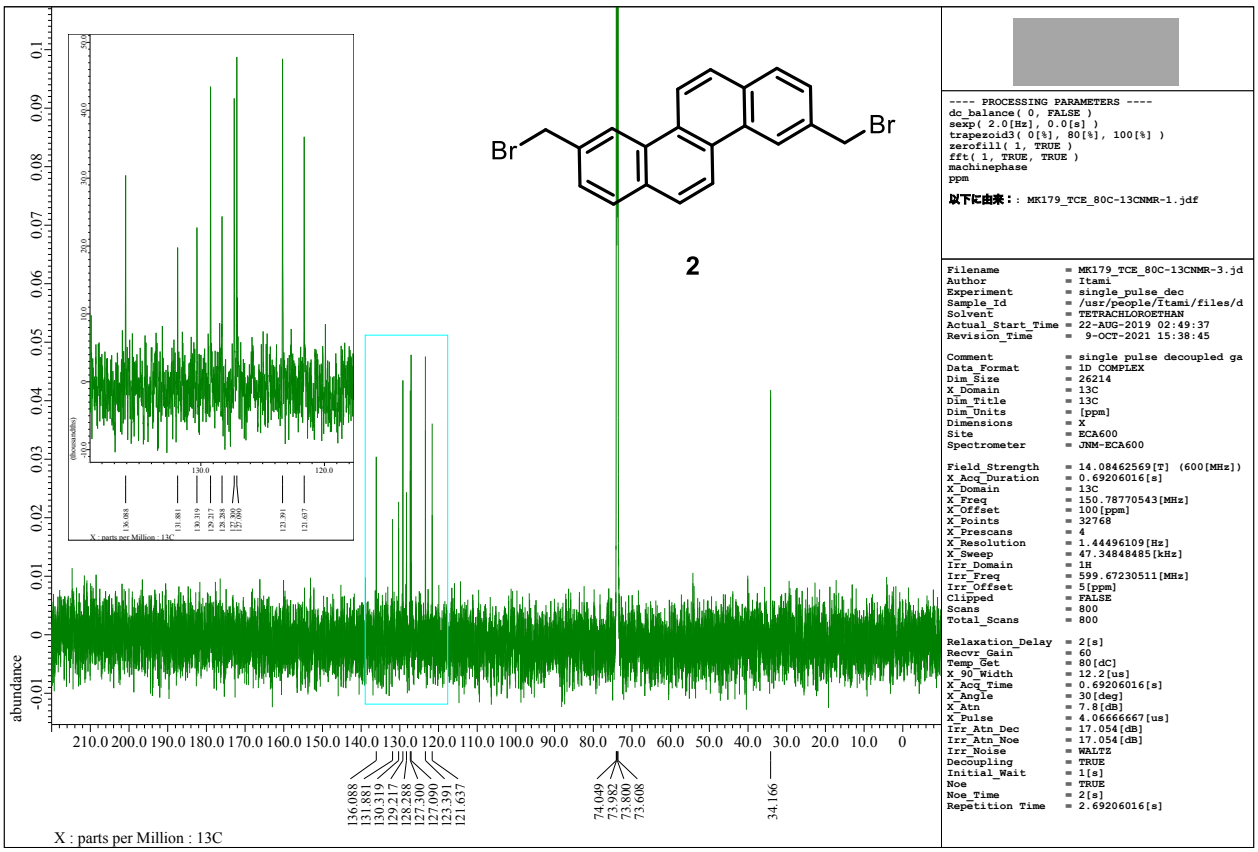
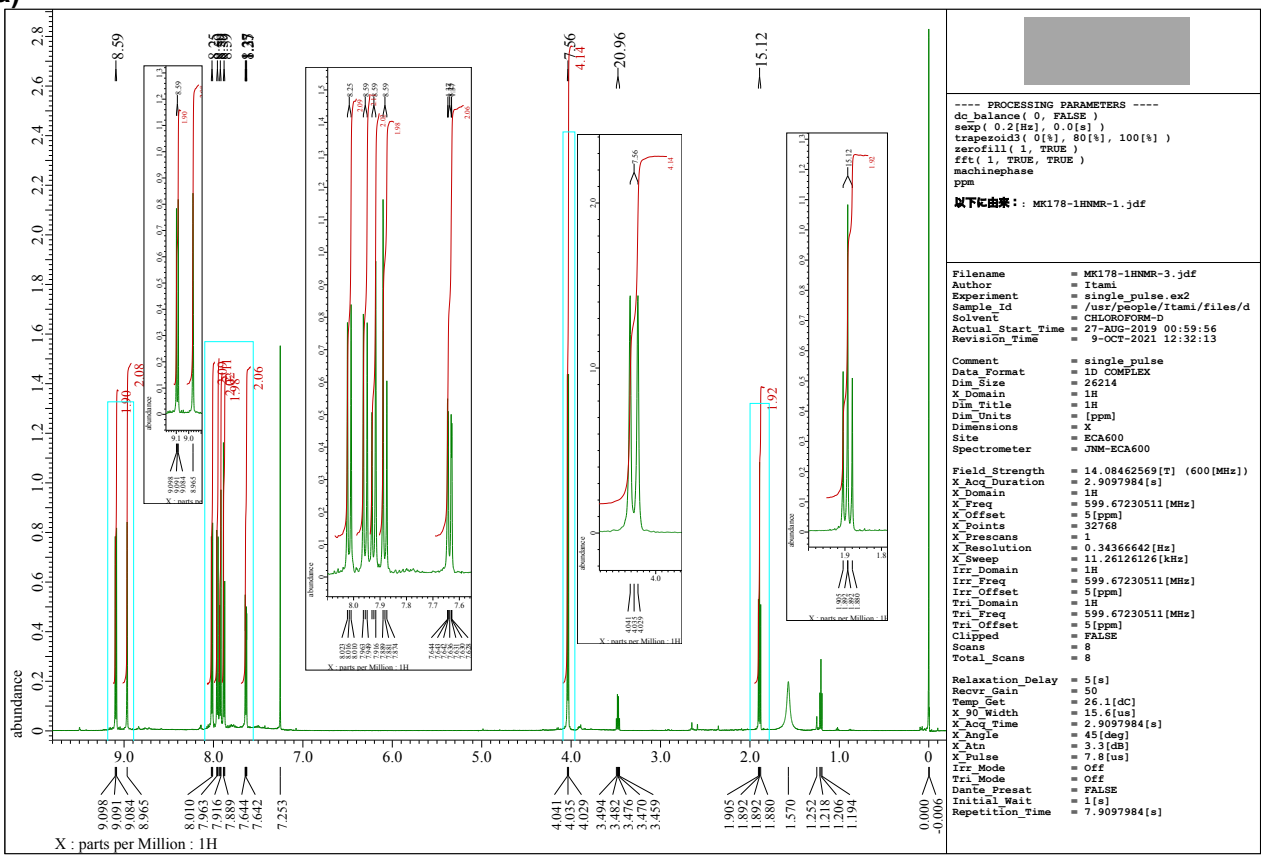


Figure S23. (a) ^{1}H NMR of **2** (600 MHz, $Cl_2CDCDCl_2$, 80 °C); (b) ^{13}C NMR of **2** (151 MHz, $Cl_2CDCDCl_2$, 80 °C)

(a)



(b)

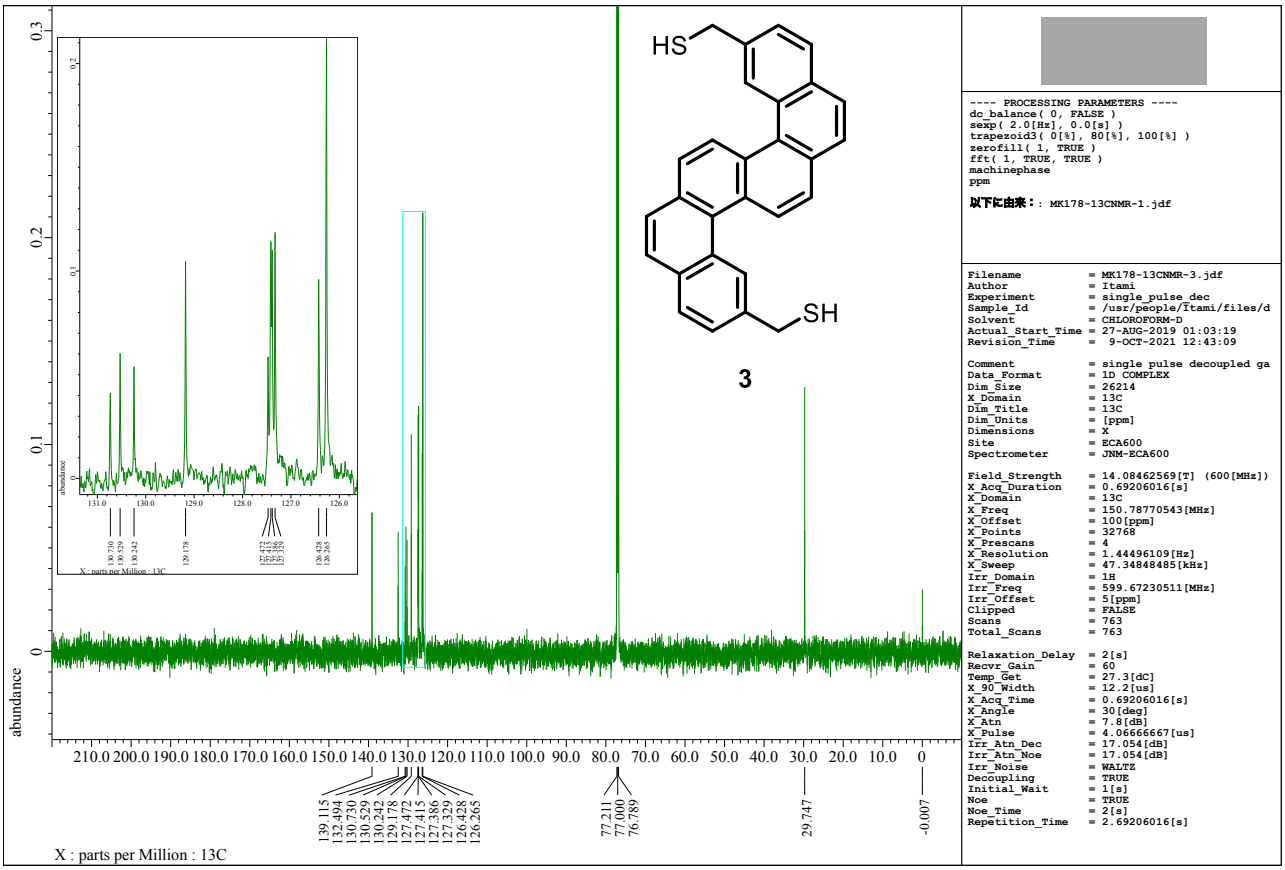
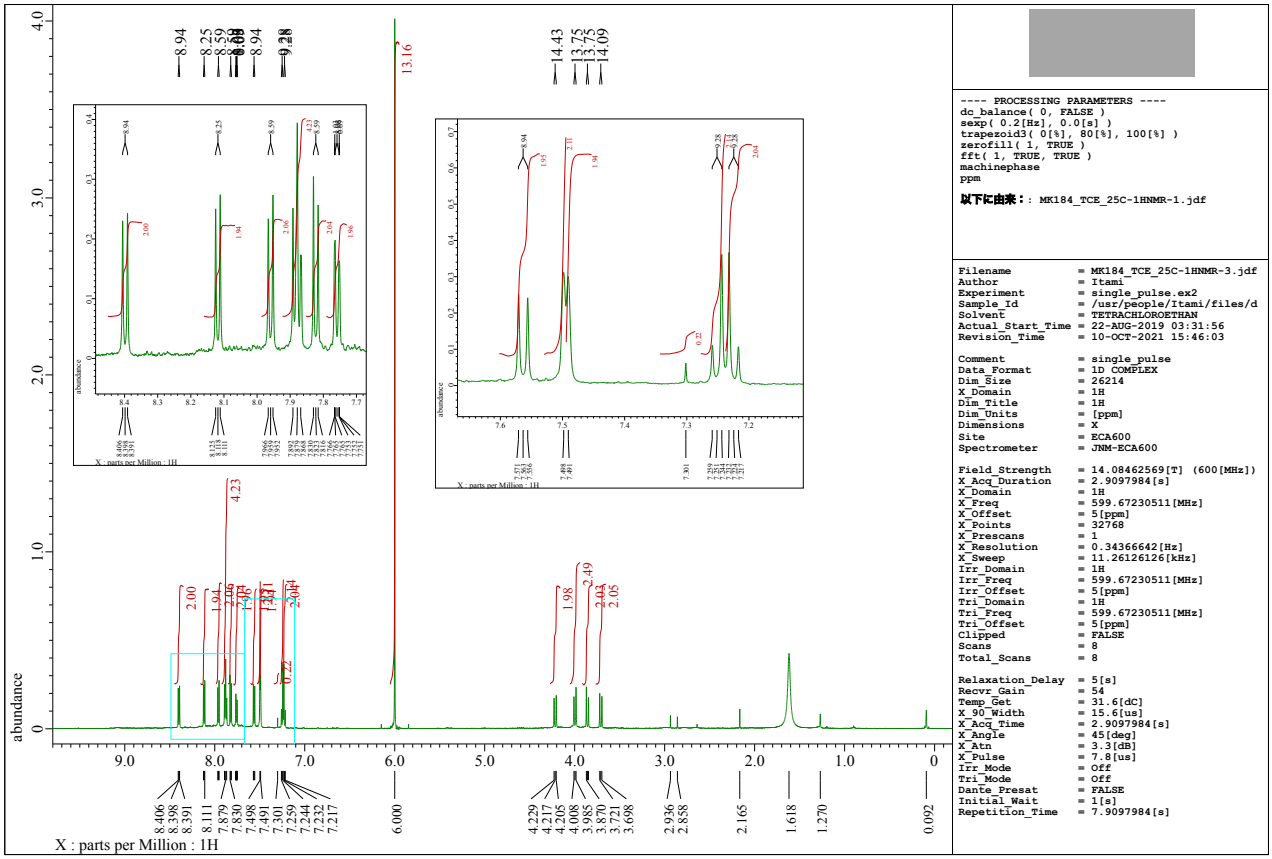


Figure S24. (a) ^{1}H NMR of **3** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of **3** (151 MHz, $CDCl_3$)

(a)



(b)

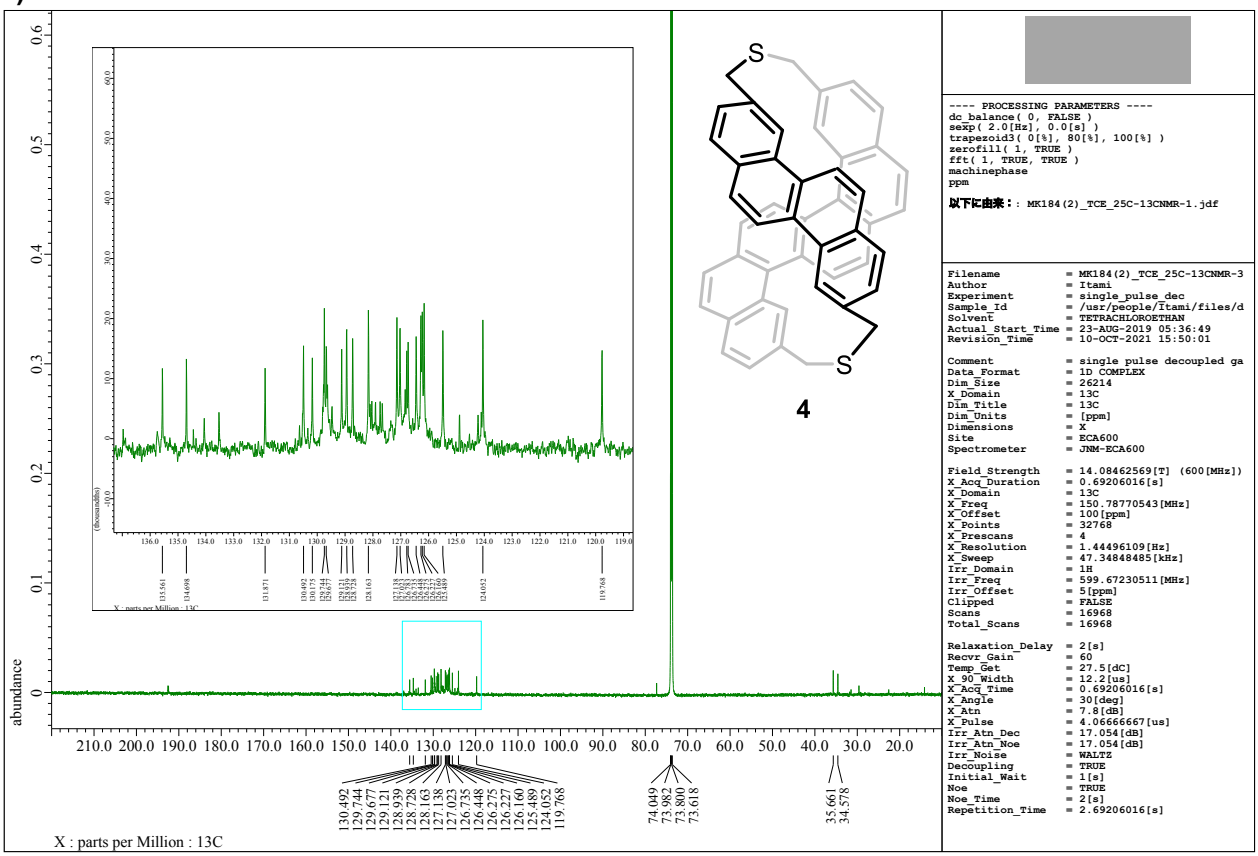
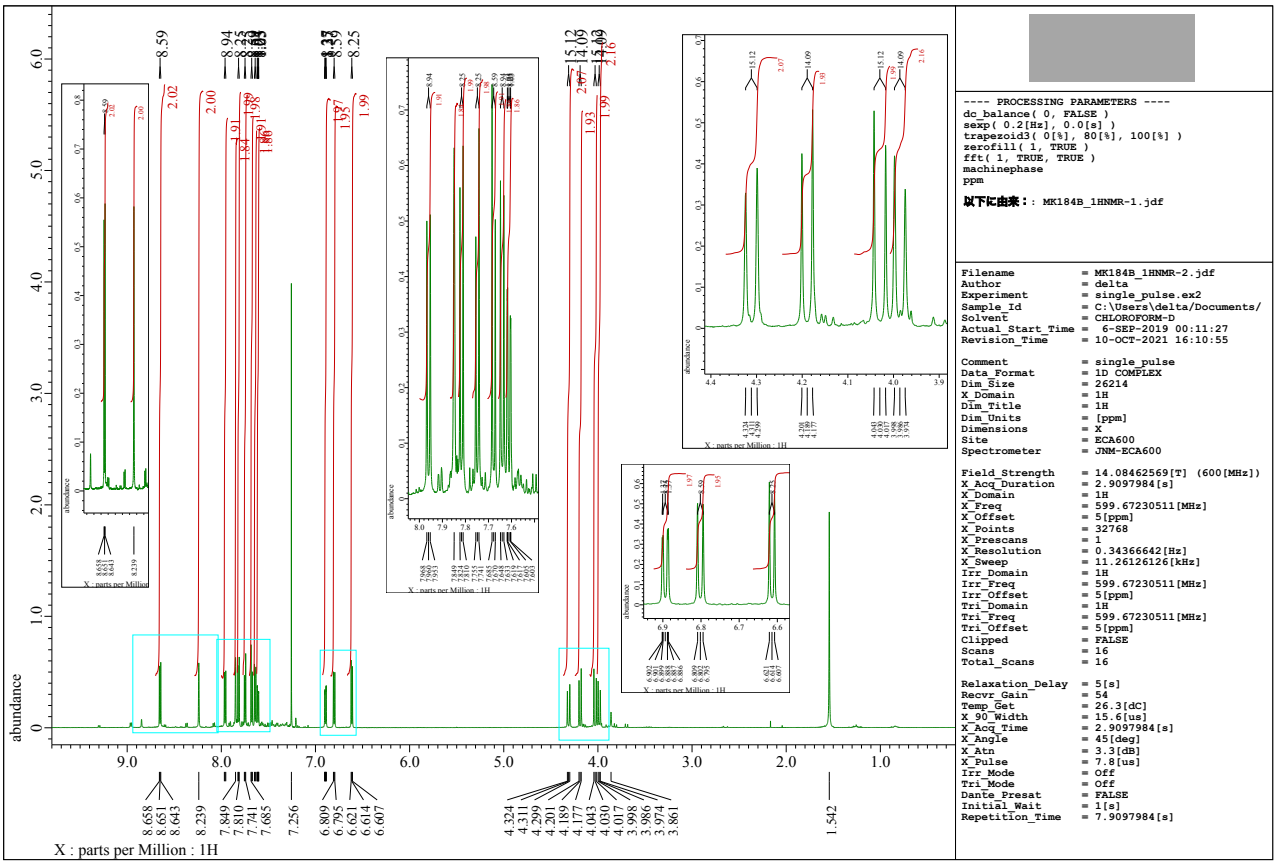


Figure S25. (a) ^{1}H NMR of **4** (600 MHz, $Cl_2CDCDCl_2$,); (b) ^{13}C NMR of **4** (151 MHz, $Cl_2CDCDCl_2$,)

(a)



(b)

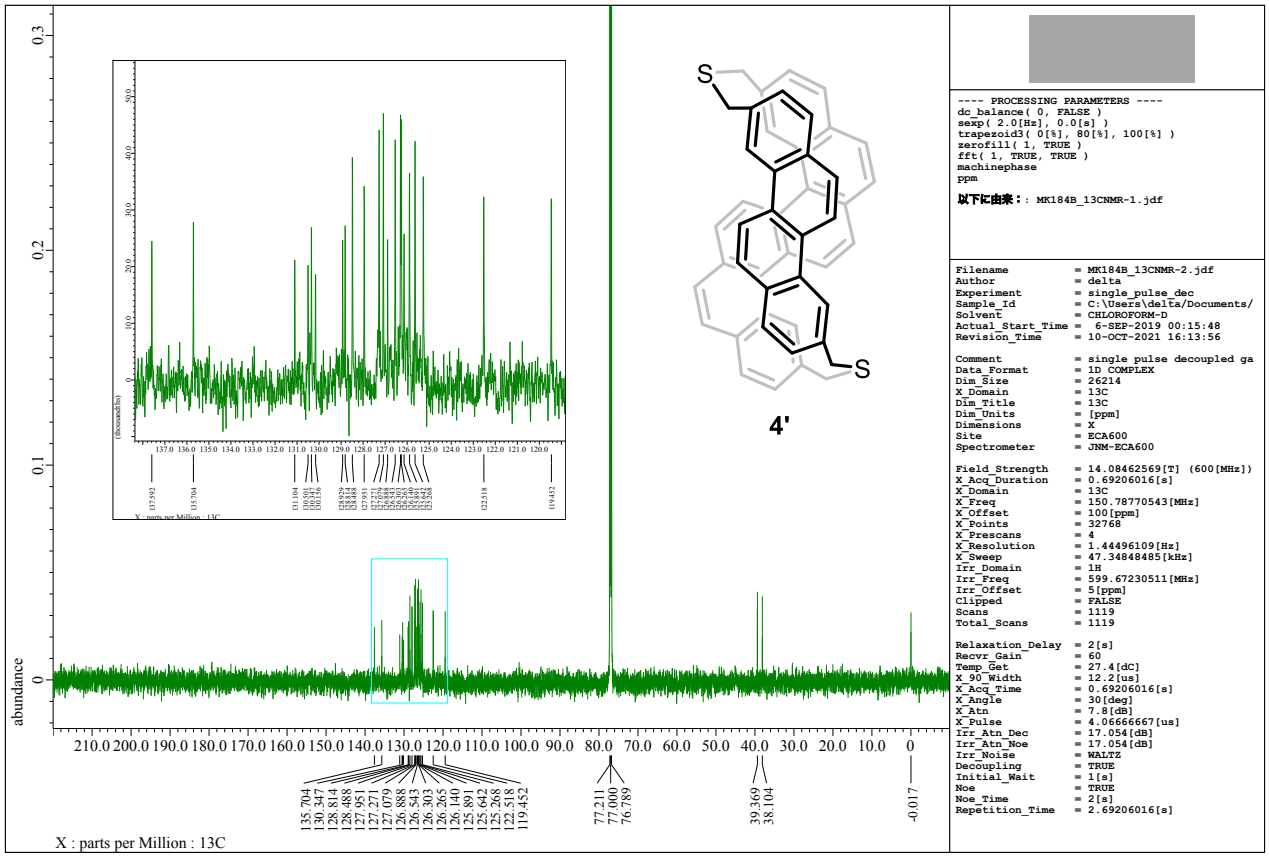
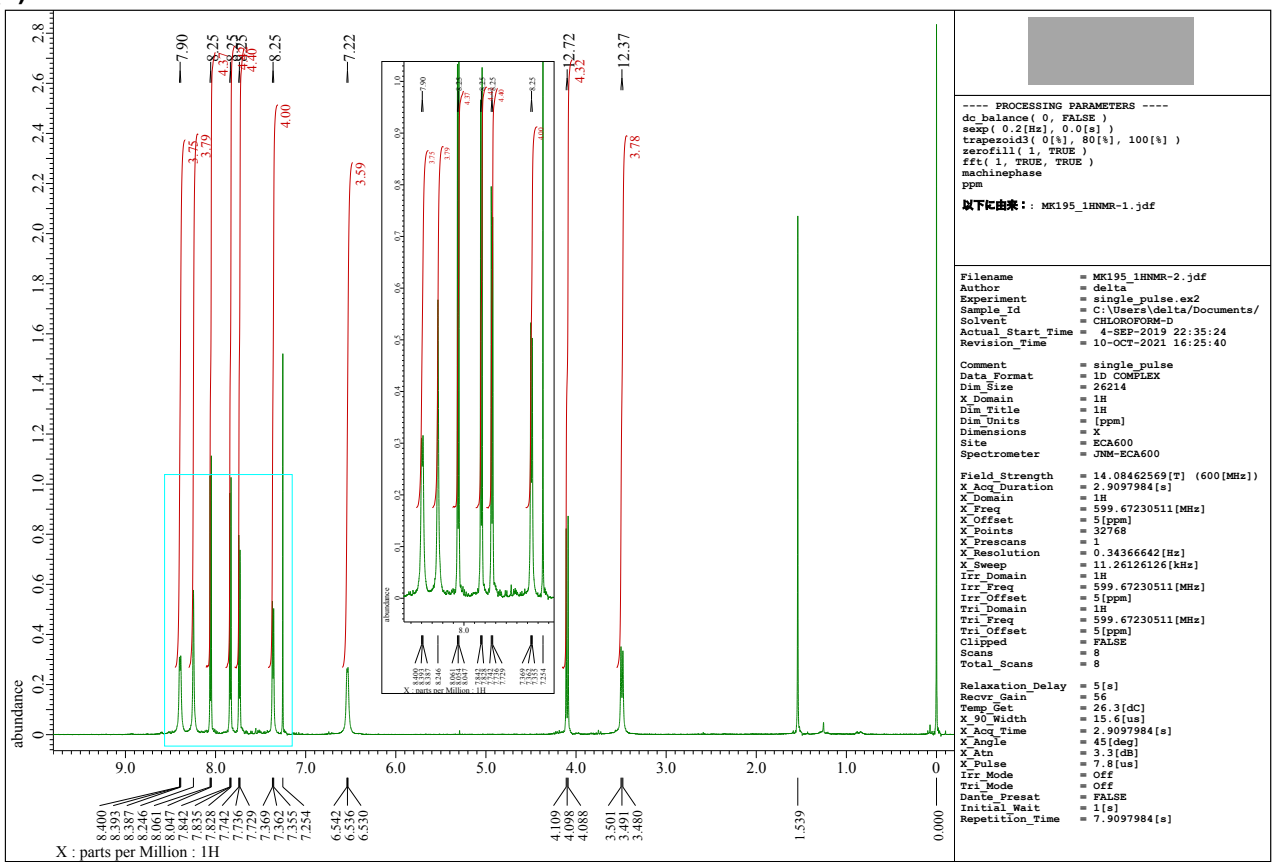


Figure S26. (a) ^{1}H NMR of **4′** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of **4′** (151 MHz, $CDCl_3$)

(a)



(b)

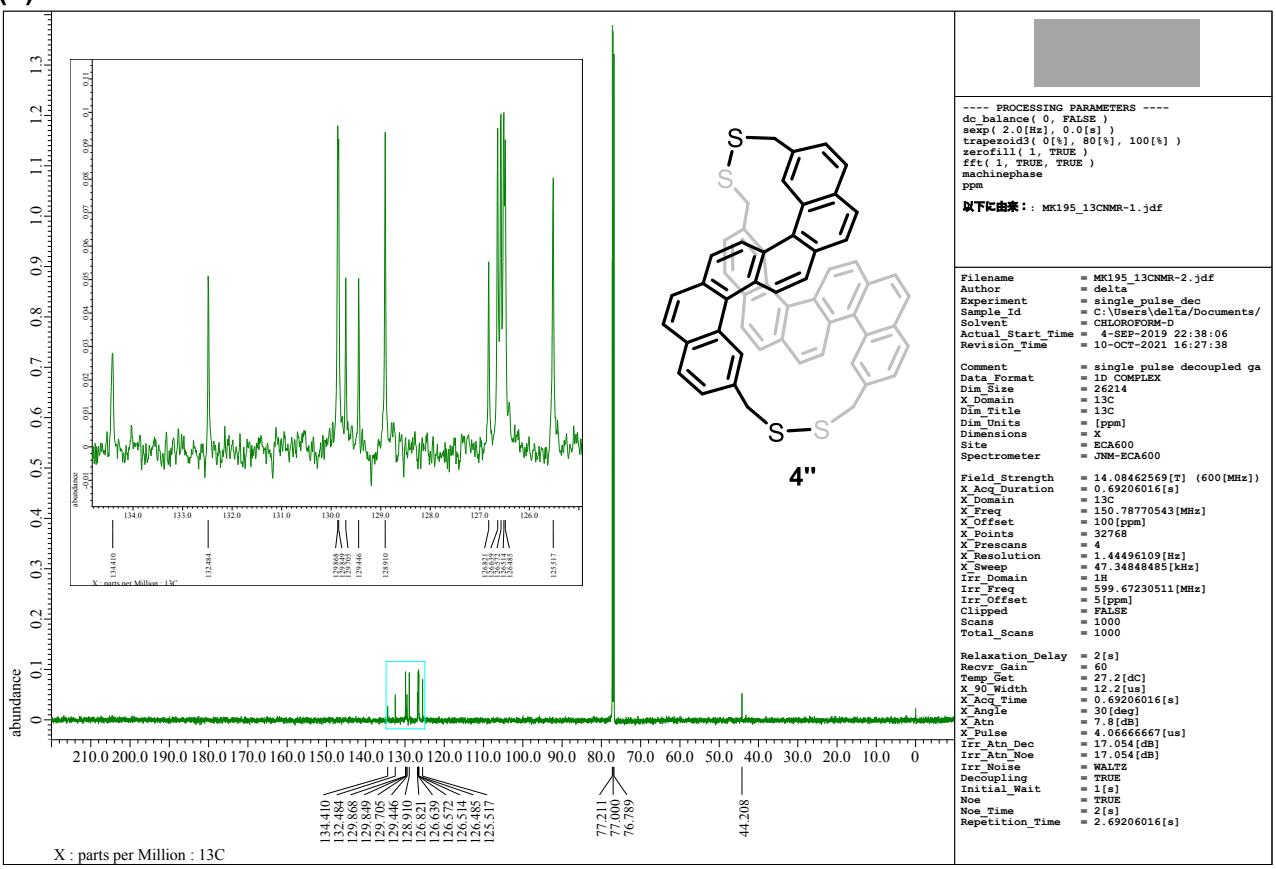
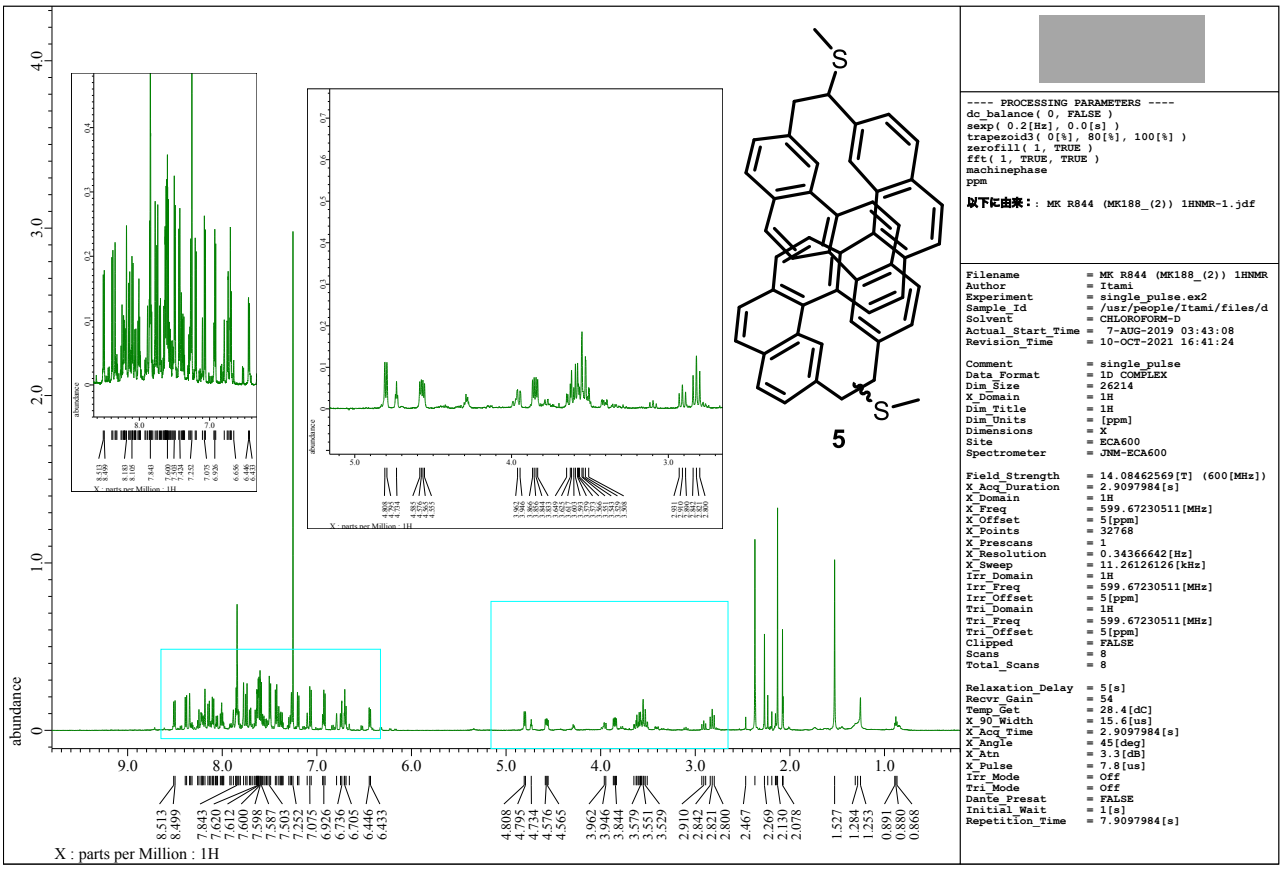


Figure S27. (a) ^{1}H NMR of **4″**(600 MHz, $CDCl_3$); (b) ^{13}C NMR of **4″** (151 MHz, $CDCl_3$)

(a)



(b)

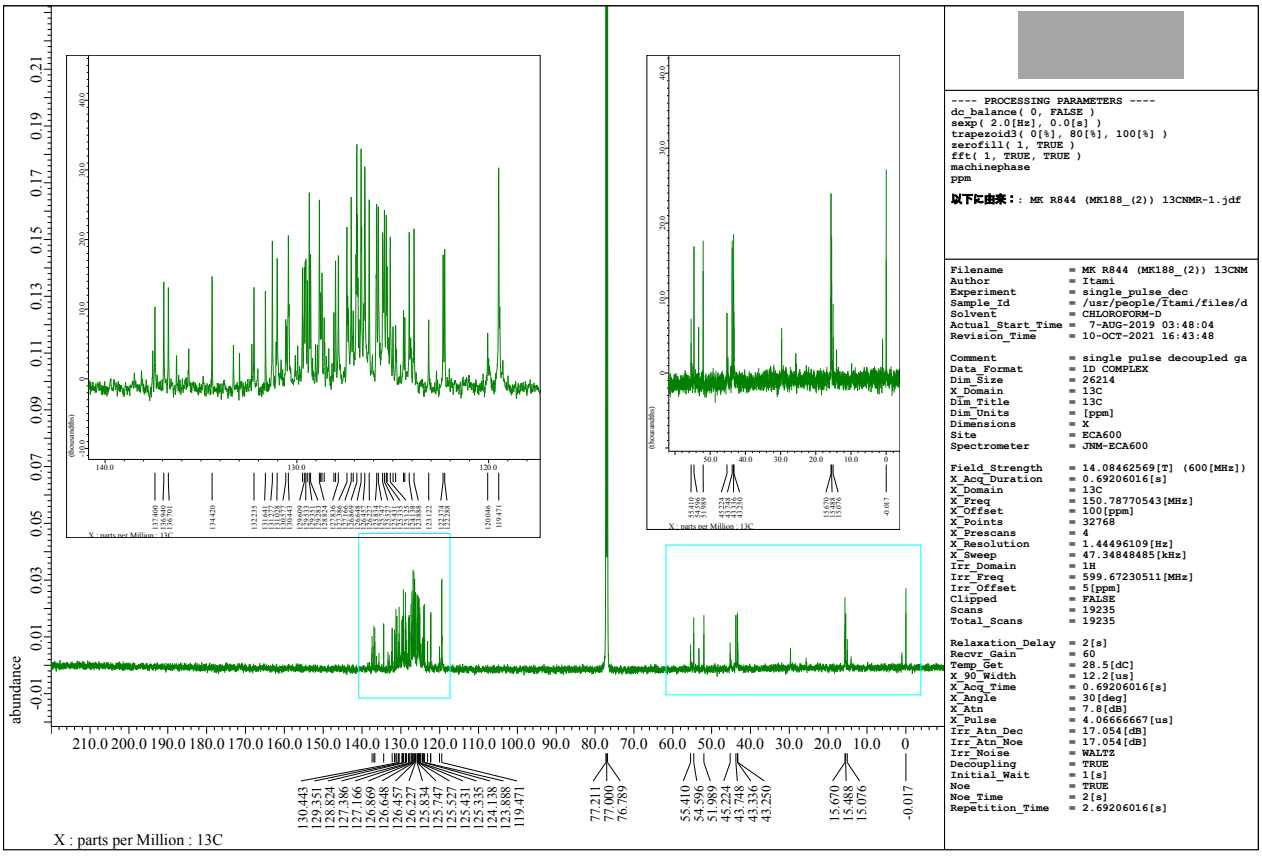
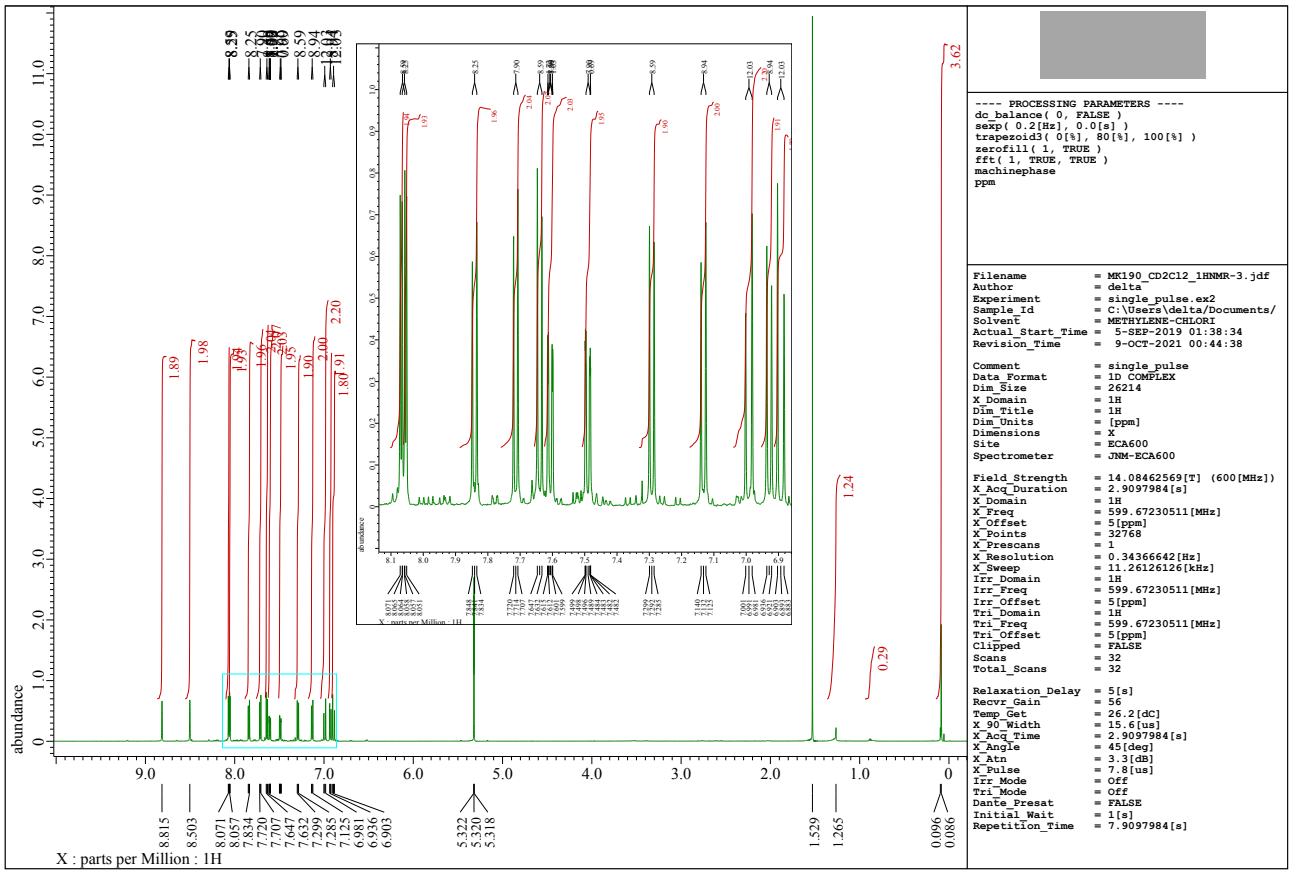


Figure S28. (a) ^{1}H NMR of **5** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of **5** (151 MHz, $CDCl_3$)

(a)



(b)

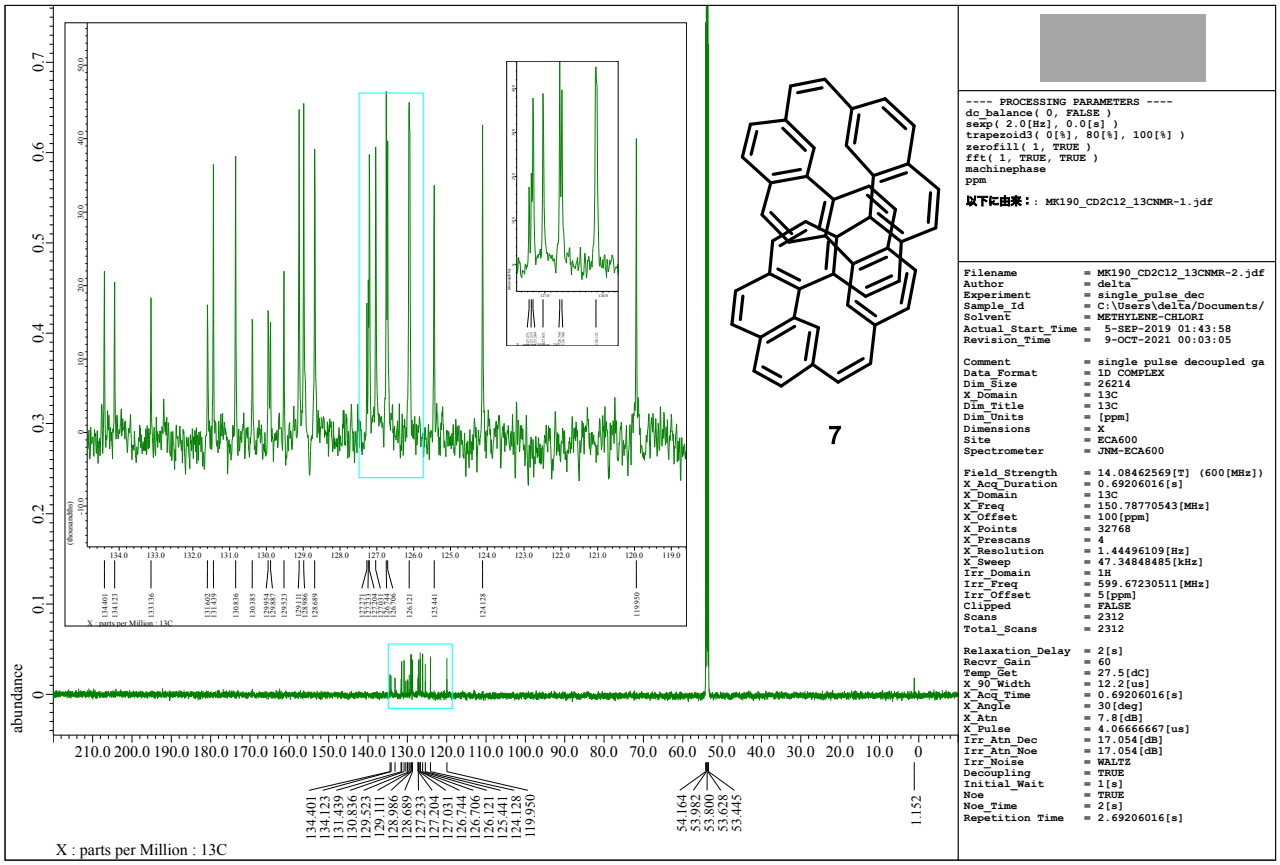
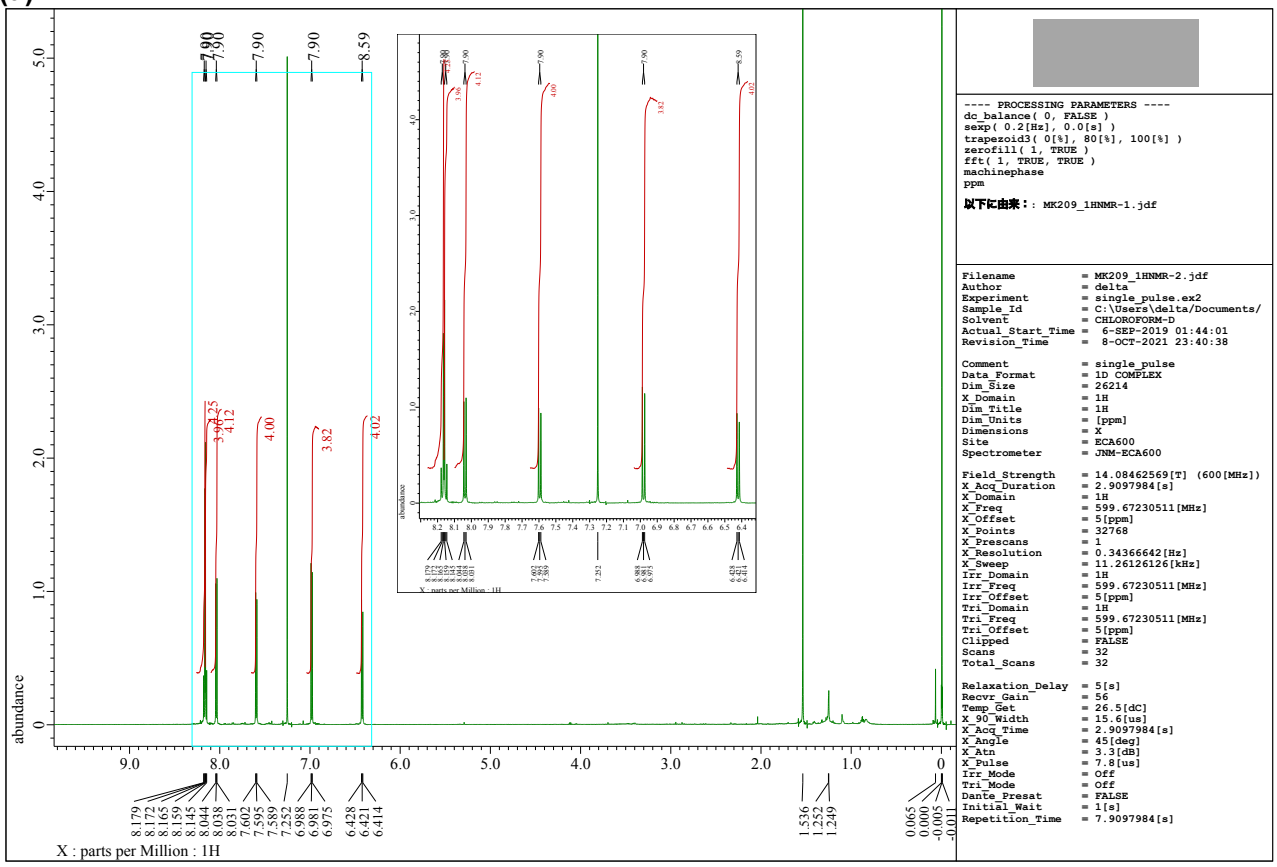


Figure S29. (a) ^{1}H NMR of **7** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of **7** (151 MHz, $CDCl_3$)

(a)



(b)

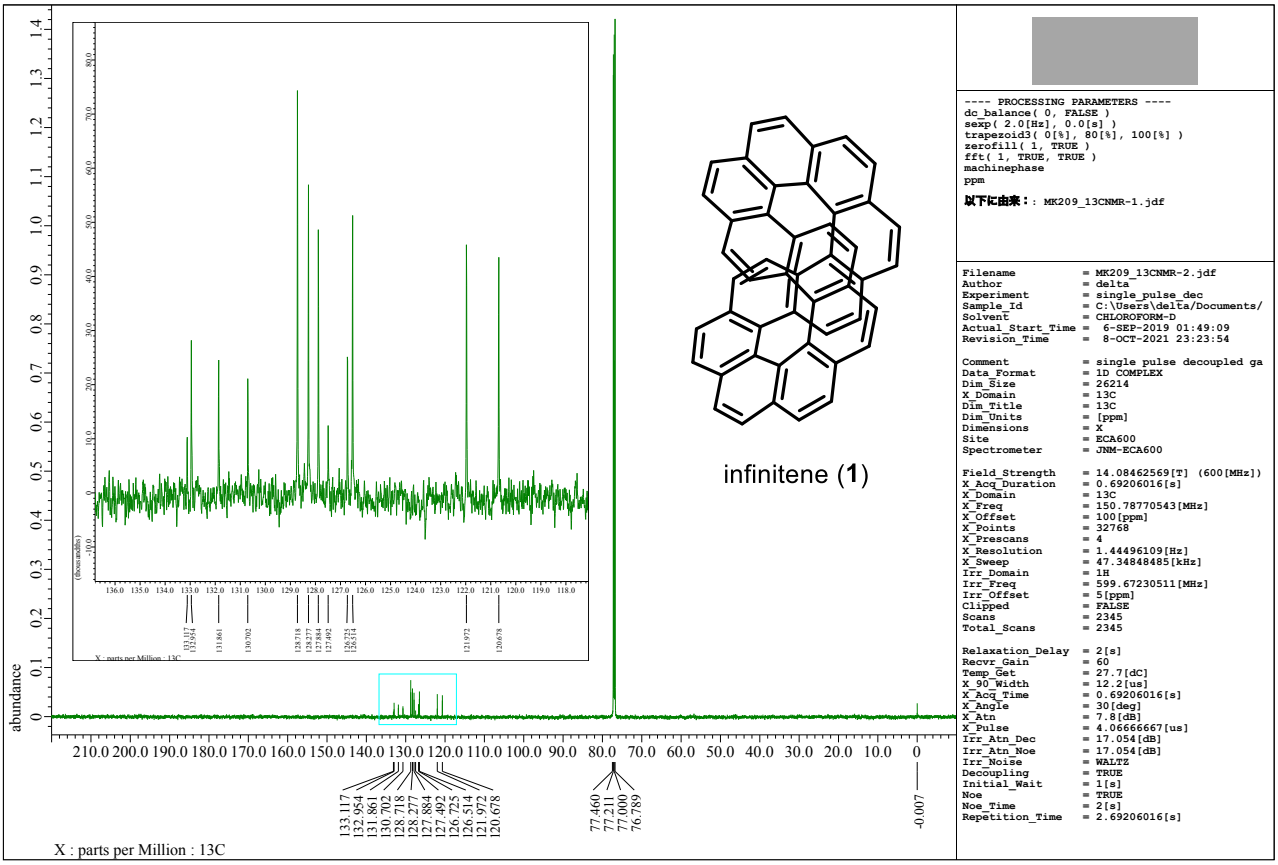


Figure S30. (a) ^{1}H NMR of **1** (600 MHz, $CDCl_3$); (b) ^{13}C NMR of **1** (151 MHz, $CDCl_3$)