European Journal of Organic Chemistry

Supporting Information

Synthesis of an Octacyclic C_{60} Fragment

Naruhiro Yoshida, Ryuhei Akasaka, Tomoya Imai, Michael P. Schramm, Yousuke Yamaoka, Toru Amaya, and Tetsuo Iwasawa*

Contents

1. General Information (Materials and Methods). Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. Solvents for spectrophotometry purchased from commercial suppliers were used for absorption and emission spectra. All reactions were carried out under an argon or a nitrogen atmosphere in dried glassware using standard vacuum-line technique, unless otherwise noted. All work-up operation and purification procedures were carried out with reagent-grade solvent in air, and analytical thin layer chromatography was carried out on Merck silica $60F_{254}$ pre-coated plates. The developed chromatogram was analyzed by UV lamp (254 nm or 354 nm). Flash column chromatography was carried out with silica gel 60 $_{N}$ (Kanto Chemical Co.). All melting points were recorded on the melting point apparatus of “Stanford Research Systems OptiMelt” and are not corrected. IR spectra were reported with a JASCO FT/IR-6000 infrared spectrometer and the data are expressed in cm^{-1}. High-resolution mass spectra (HRMS) were determined on the basis of TOF (time of flight)-MS (MADI-TOF or LCMS-IT-TOF), and DART (Direct Analysis in Real Time)-MS. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECZ400S (^{1}H 400 MHz and ^{13}C 100 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CHCl_3$ (7.26), CH_2Cl_2 (5.32), DMSO (2.50). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (77.0), CD_2Cl_2 (53.8), [D6]-DMSO (39.5). Data are reported as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constants (Hz), and integration. All calculations were conducted using a Gaussian 16 suite program (G16RevC.02).[24] Optimization was performed at the B3LYP/6-31G(d,p). Harmonic vibration frequency analysis was conducted with the optimized structures at the same level of theory to verify all stationary points as local minima (with no imaginary

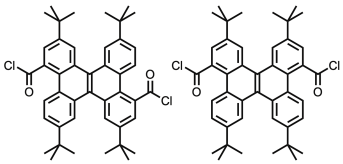
frequency). The computation was carried out using the General Projects on supercomputer "Flow" at Information Technology Center, Nagoya University.

2. Synthesis of **4**/*iso*-**4**, **5**/*iso*-**5**, and **3** (Scheme 1).

1. For **4**/*iso*-**4**, dimethyl 3,6,11,14-tetra-*tert*-butyldibenzo[*g*,*p*]chrysene-1,9-dicarboxylate/dimethyl 3,6,11,14-tetra-*tert*-butyldibenzo[*g*,*p*]chrysene-1,8-dicarboxylate. Under an argon atmosphere, to a solution of **2**/*iso*-**2** (30.8 g, 43.3 mmol) in dry Et_2O (770 mL) at -78 °C was added *n*-BuLi (100 mL, 156 mmol, 1.56 M in hexane) dropwise over 5 min. After the mixture was stirred at -78 °C for 15 min, dimethyl carbonate (18.2 mL, 217 mmol) was added over 10 min. After stirred at -78 °C for 0.5 h, the reaction mixture was allowed to warm to room temperature, and conducted over 2 h. The reaction was quenched with 3 M aq. HCl (300 mL) at 0 °C. The aqueous phase was extracted with toluene (50 mL x 3), combined organic phases were washed with brine (80 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give crude products. Purification by short-plugged silica-gel column chromatography (hexane/toluene, 1:4) yielded 15.8 g of white (colorless) solid materials (55%, **4**/*iso*-**4** = ~1:1). Data of **4**/*iso*-**4**: Rf value 0.23 (hexane/EtOAc, 9/1); M.p. 250 ºC (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 8.78 (d, *J* = 2.0 Hz, 2H), 8.62 (d, *J* = 2.0 Hz, 2H), 8.61 (d, *J* = 2.0 Hz, 2H), 8.45 (d, *J* = 2.0 Hz, 2H), 8.04 (d, *J* = 8.6 Hz, 2H), 8.03 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 2.0 Hz, 2H), 7.81 (d, *J* = 2.0 Hz, 2H), 7.59 (dd, *J* = 2.0, 8.6 Hz, 4H), 4.05 (s, 6H), 4.04 (s, 6H), 1.47-1.39 (m, 72 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 173.3, 173.1, 150.3, 150.2, 149.1, 149.0, 131.2, 130.84, 130.80, 130.3, 130.21, 130.18, 130.06, 129.0, 128.1, 127.49, 127.46, 127.2, 127.1, 127.01, 126.97, 126.93, 126.7, 126.0, 125.6, 125.2, 124.8, 124.0, 123.8, 53.07, 53.05, 35.52, 35.47 (two peaks are overlapped), 35.43, 31.84, 31.82 (two peaks are overlapped), 31.80 ppm; MS (DART-TOF) m/z: 669 $[MH]^+$; IR (neat): 2952, 1718

(C=O), 1599, 1432, 1240, 1141, 882 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{46}H_{53}O_4$ $[MH]^+$: 669.3944, found: 669.3924.

2. For **5**/*iso*-**5**, 3,6,11,14-tetra-*tert*-butyldibenzo[*g*,*p*]chrysene-1,9-dicarbonyl dichloride/

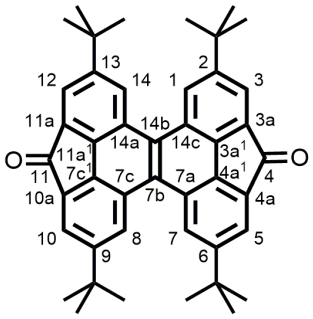


3,6,11,14-tetra-*tert*-butyldibenzo[*g*,*p*]chrysene-1,8-dicarbonyl dichloride. Under an argon atmosphere, to a suspension of potassium *tert*-butoxide (23.9 g, 213 mmol) in dry THF (206 mL) at 0 ºC was added water (0.98 mL, 54.6 mmol). After the mixture was stirred at 0 ºC for 5 min, the starting esters (16.6 g, 24.8 mmol) were added. The reaction was conducted at 70 ºC for 2 h, and quenched with 3 M aq. HCl (206 mL) at 0 ºC. The aqueous phase was extracted with EtOAc (50 mL x 3), and the combined organic phases were washed with brine (100 mL x 1), dried over Na_2SO_4, and concentrated *in vacuo* to give crude products (15.5 g, quant., isomeric molar ratio ~1:1) as whitish brown solid materials. The sample was provided in next step without further purification.

Under an argon atmosphere, to the solution of starting dicarboxylic acids (15.5 g, 24.2 mmol) in sulfurous dichloride (125 mL, 1.72 mol) at room temperature was added catalytic amounts of DMF over 1 min. After stirred at room temperature for 0.5 h, the mixture was concentrated *in vacuo* to give crude products (16.5 g, quant., isomeric molar ratio ~1:1) as yellowish-brown solid materials. The sample was provided in the next step without further purification. Data of **5**/*iso*-**5**: ^{1}H NMR (400 MHz, $CDCl_3$) 8.86 (d, *J* = 1.9 Hz, 2H), 8.63 (d, *J* = 1.9 Hz, 2H), 8.62 (d, *J* = 1.9 Hz, 2H), 8.41 (d, *J* = 1.9 Hz, 2H), 8.25 (d, *J* = 8.6 Hz, 4H), 8.04 (d, *J* = 1.9 Hz, 2H), 7.98 (d, *J* = 1.9 Hz, 2H), 7.69 (dd, *J* = 8.6, 1.9 Hz, 4H), 1.50-1.41 (m, 72H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 172.2, 172.1, 151.5, 151.2, 149.5, 149.3, 135.7, 135.3, 131.7, 130.4, 130.3, 130.22, 130.17, 129.9, 129.2, 129.1, 128.9, 128.8, 126.5, 126.3, 126.2, 126.1, 126.0, 125.8, 125.4, 125.3, 124.8 (two peaks are overlapped),

124.5, 35.7, 35.63, 35.61, 35.57, 31.78 (two peaks are overlapped), 31.75 (two peaks are overlapped) ppm; MS (DART-TOF) *m/z*: 676 $[M]^+$; IR (neat): 2956, 1770 (C=O), 933, 742, 727, 607 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{44}H_{46}Cl_2O_2$ $[M]^+$: 676.2875, found: 676.2862.

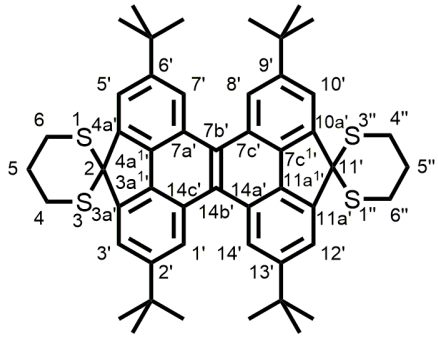
3. For **3**, 2,6,9,13-tetra-*tert*-butyldiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene-4,11-dione.



Under an argon atmosphere, to a solution of the starting acid chlorides (16.3 g, 24.0 mmol) in dry CH_2Cl_2 (220 mL) at 0 ºC was added $AlCl_3$ (8.32 g, 63.4 mmol). After stirred at 0 ºC for 0.5 h, the reaction was quenched with H_2O (120 mL). The aqueous phase was extracted with $CHCl_3$ (100 mL x 3), and the combined organic phases were washed with brine (100 mL x 1), dried over Na_2SO_4, and concentrated *in vacuo* to give crude products. Purification by silica-gel column chromatography (hexane/$CHCl_3$, 1:1) gave 12.2 g of **3** (84%) as yellow solid materials. Data of **3**: Rf value 0.42 (hexane/toluene, 1:4); M.p. > 350 ºC; ^1H NMR (400 MHz, $CDCl_3$) 9.06 (s, 4H, H-1), 8.06 (s, 4H, H-3), 1.57 (s, 36H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 194.7 (C-4), 153.4 (C-2), 137.8 (C-3a), 133.8 (C-3), 128.8 (C-14b), 127.9 (C-14c), 127.0 (C-3a^1), 121.7 (C-1), 36.6 ($\underline{C}(CH_3)_3$), 32.3 (CH_3) ppm; MS (DART-TOFMS) *m/z*: 605 $[MH]^+$; IR (neat): 2952, 1714 (C=O), 1363, 1204, 877, 774 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{44}H_{45}O_2$ $[MH]^+$: 605.3420, found: 605.3397; Anal. Calcd. for $C_{44}H_{44}O_2$; C, 87.38; H, 7.33. Found: C, 87.46; H, 7.25.

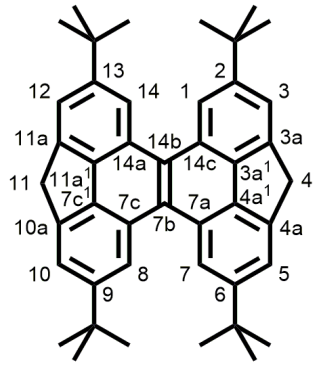
3. Synthesis of **6**, **7**, and **1**. (Scheme 2).

1. For **6**, 2',6',9',13'-tetra-*tert*-butyldispiro[[1,3]dithiane-2,4'-diindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene-11',2''-[1,3]dithiane]. Under an argon atmosphere, to a solution of **3** (2.0 g, 3.3 mmol) in dry CH_2Cl_2 (500 mL) was added 1,3-propanedithiol (3.3 mL, 33 mmol) and boron trifluoride etherate (6.7 mL, 53 mmol). After stirred at room temperature for 30 min, the mixture was quenched with water (200 mL). The



aqueous layer was extracted with $CHCl_3$ (50 mL x 3), and combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 2.9 g of crude products. Purification by short-plugged silica-gel column chromatography (hexane/toluene, 1:1) gave 1.8 g (70%) of **6** as white (colorless) solid materials. (**CAUTION**: All the glass-apparatus were thoroughly washed with aq. 1% v/v sodium hypochlorite of NaClO for the deodorization). Data of **6**: Rf value 0.50 (hexane/CH_2Cl_2, 1:1); M.p. > 300 ºC (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 9.11 (s, 4H, H-1'), 8.18 (s, 4H, H-3'), 3.51 (t, J = 5.7 Hz, 8H, H-4), 2.54-2.53 (m, 4H, H-5), 1.63 (s, 36H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 151.7 (C-2'), 148.3 (C-3a'), 132.6 (C-14c'), 129.9 (C-14b'), 127.6 (C-3a^1'), 122.9 (C-3'), 119.3 (C-1'), 55.7 (C-2), 36.5 ($\underline{C}(CH_3)_3$), 32.7 (CH_3), 28.3 (C-4), 25.1 (C-5) ppm; MS (DART-TOFMS) *m/z*: 785 $[MH]^+$; IR (neat) 2958, 1595, 1415, 1271, 1203, 754, 731, 665 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{50}H_{57}S_4$: 785.3338 $[MH]^+$, found: 785.3329.

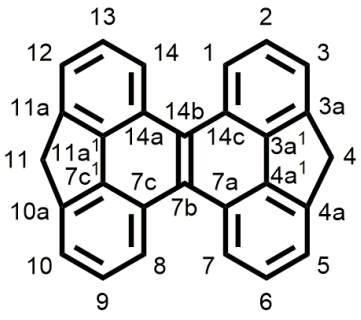
2. For **7**, 2,6,9,13-tetra-*tert*-butyl-4,11-dihydrodiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene.



Under an argon atmosphere, **6** (450 mg, 0.57 mmol) and dry CH_2Cl_2 (324 mL) was charged to a 500 mL flask, and then the mixture was stirred for 20 min (white (colorless) cloudy). With the aid of mild dryer-heating for 5 min, the mixture changed to colorless solution. To the mixture was added sodium iodide (8.5 g, 57 mmol) and trimethylsilyl chloride (7.2 mL, 57 mmol), and then the reaction was monitored at room temperature for 89 h. To the reaction mixture was added H_2O (200 mL), and it was followed by subsequent addition of satd. aq. $Na_2S_2O_3$ (200 mL). The aqueous layer was extracted with $CHCl_3$ (50 mL x 3), and combined organic phases were washed with brine (100 mL), dried over Na_2SO_4,

filtered, and concentrated *in vacuo* to give 1.2 g of crude products. Purification by short-plugged silica-gel column chromatography (hexane/$CHCl_3$, 19:1) gave 242 mg (74%) of **7** as white (colorless) solid materials. Data of **7**: Rf value 0.71 (hexane/ toluene, 2:1); M.p. 214-219 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 9.17 (s, 4H, H-1), 7.92 (s, 4H, H-3), 4.43 (s, 12H, CH_2), 1.63 (s, 36H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 150.7 (C-2), 142.0 (C-3a), 136.8 (C-14c), 129.9 (C-14b), 127.5 (C-3a^1), 120.8 (C-3), 120.2 (C-1), 37.9 (CH_2), 36.4 ($\underline{C}(CH_3)_3$), 32.8 (CH_3) ppm; MS (DART-TOFMS) *m/z*: 577 $[MH]^+$; IR (neat): 2952, 1599, 1412, 1360, 1276, 1214, 846, 756, 732, 665 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{44}H_{49}$: 577.3829 $[MH]^+$, found: 577.3802; Anal. Calcd. for $C_{44}H_{48}$; C, 91.61; H, 8.39. Found: C, 91.68; H, 8.58.

3. For **1**, 4,11-dihydrodiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene. Under an argon atmosphere, to a suspension of **7** (1.4 g, 2.4 mmol) in dry benzene (38 mL) was added aluminum chloride (770 mg, 5.8 mmol). After stirred at room temperature for 0.5 h, the reaction mixture was quenched with H_2O (60 mL) at 0 ºC. The aqueous layer was extracted with CH_2Cl_2 (30 mL x 3), and combined organic phases were washed with brine (60 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 1.2 g of crude products. Purification by short-plugged silica-gel column chromatography (hexane/CH_2Cl_2, 9:1) gave 624 mg (73%) of **1** as white (colorless) solid materials. Data of **1**: Rf value 0.35 (hexane/toluene, 9:1); M.p. 268-274 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 9.11 (dd, J = 6.4 Hz, 6.4 Hz, 4H, H-2), 7.85-7.81 (m, 8H, H-1, H-3), 4.47 (s, 4H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 142.1 (C-3a), 138.7 (C-3a^1), 129.1 (C-14b), 128.2 (C-14c), 127.7 (C-2), 124.6 (C-3), 122.1 (C-1), 37.8 (CH_2) ppm; MS (DART-TOFMS) *m/z*: 353 $[MH]^+$; IR (neat) 2923, 1494, 1442, 1418, 1393, 1085, 1027, 937, 821, 767, 708, 619, 475 cm^{-1}; HRMS



(DART-TOF) calcd. for $C_{28}H_{17}$: 353.1325 $[MH]^+$, found: 353.1314; Anal. Calcd. for $C_{28}H_{16}$; C, 95.42; H, 4.58. Found: C, 95.43; H, 4.43.

4. Synthesis of **8**, **9**, and **10** (Scheme 3).

1. For **8**, 2,6,9,13-tetra-*tert*-butyl-4,4,11,11-tetrakis(4-methoxyphenyl)-4,11-dihydrodiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene. To a suspension of **3** (2.4 g, 4.0 mmol) in anisole (23 mL) was added methanesulfonic acid (MsOH, 1.6 mL, 24 mmol) at room temperature, and the mixture was stirred for 5 min. The reaction was conducted at 120 ºC, and the starting **3** was totally disappeared on TLC monitoring in 8 h. The reaction was quenched at 0 ºC with saturated aqueous $NaHCO_3$ (45 mL) (pH > 7). The aqueous layer was extracted with toluene (10 mL x 3), washed with brine (30 mL), dried over Na_2SO_4, and filtered, and concentrated *in vacuo* to give 3.6 g of yellow solid materials. Purification by short-plugged silica-gel column chromatography (hexane/toluene, 1:2) afforded 2.8 g of **8** (72%) as pale yellow solid materials. Data of **8**: Rf value 0.40 (hexane/EtOAc, 4/1); M.p. 286 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 9.09 (s, 4H, H-1), 7.77 (s, 4H, H-3), 7.29 (d, J = 9.0 Hz, 8H, phenyl C-2), 6.80 (d, J = 9.0 Hz, 8H, phenyl C-3), 3.76 (s, 12H, phenyl CH_3), 1.55 (s, 36H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 158.6 (phenyl C-4), 151.3 (C-2), 150.3 (C-3a), 138.5 (phenyl C-1), 134.5 (C-14c), 130.2 (C-14b), 129.7 (phenyl C-2), 127.7 (C-3a^1), 121.5 (C-3), 121.0 (C-1), 113.9 (phenyl C-3), 67.1 (C-4), 55.5 (phenyl CH_3), 36.5 ($\underline{C}(CH_3)_3$), 32.7 (CH_3) ppm; MS (DART-TOF) *m*/*z*: 1002 $[MH]^+$; IR (neat): 2949, 1603, 1503, 1244, 1173, 1025 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{72}H_{73}O_4$ $[MH]^+$: 1001.5509, found: 1001.5497; Anal. Calcd. for $C_{72}H_{72}O_4$; C, 86.36; H, 7.25. Found: C, 86.37; H, 6.97.

2. For **9**, (4,4,11,11-tetrakis(4-methoxyphenyl)-4,11-dihydrodiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene). To **8** (2.5 g, 2.5 mmol) in benzene (50 mL) was added $AlCl_3$ (3.2 g, 24 mmol), and the reaction was conducted for 0.5 h. The starting **8** was totally disappeared on TLC monitoring. To the mixture was added aqueous HCl (3 M, 60 mL) at 0 ºC. The mixture was transferred into a separatory funnel, and the aqueous phase was extracted with toluene (30 mL x 3), washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 2.4 g of crude products. Purification by short-plugged silica-gel column chromatography (hexane/toluene, 1:4) afforded 1.6 g of **9** (83%) as whitish yellow solid materials. Data of **9**: Rf value 0.45 (hexane/EtOAc, 2:1); M.p. > 350 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 9.05 (d, *J* = 8.2 Hz, 4H, H-1), 7.81 (dd, *J* = 8.2, 7.3 Hz, 4H, H-2), 7.71 (d, *J* = 7.3 Hz, 4H, H-3), 7.28 (d, *J* = 8.8 Hz, 8H, phenyl H-2), 6.79 (d, *J* = 8.8 Hz, 8H, phenyl H-3), 3.76 (s, 12H, phenyl CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 158.8 (phenyl C-4), 150.6 (phenyl C-1), 137.9 (C-3a), 136.4 (C-3a^1), 129.5 (phenyl C-2), 129.4 (C-14b), 128.5 (C-14c), 128.4 (C-3), 125.3 (C-2), 122.9 (C-1), 114.0 (phenyl C-3), 66.8 (C-4), 55.5 (phenyl CH_3) ppm; MS (DART-TOF) *m/z*: 608 $[M\text{-}OMe\text{-}OMe\text{-}PhOMe]^+$, 777 $[MH]^+$; IR (neat) 3006, 2830, 1606, 1505, 1247, 1173, 1033, 753, 722, 593 cm^{-1}; HRMS (DART-TOF) calcd for $C_{56}H_{41}O_4$: 777.3005 $[MH]^+$, found; 777.3002.

3. For **10**, (4,4',4'',4'''-(4,11-dihydrodiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene-4,4,11,11-tetrayl)tetraphenol). Under an argon atmosphere, to **9** (1.4 g, 1.8 mmol) in dry CH_2Cl_2 (15 mL) at 0 ºC was added BBr_3 (11 mL, 11 mmol, 1 M CH_2Cl_2 solution) dropwise over 10 min. After stirred at 0 ºC for 15 min,

the reaction mixture was allowed to warm to ambient temperature, and conducted over 1 h. The mixture was quenched with water (15 mL). The aqueous layer was extracted with EtOAc (20 mL x 3). The combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give 1.1 g of crude products as greenish white (colorless) materials. Purification by short-plugged silica-gel column chromatography (hexane/acetone, 1:1) afforded 930 mg of **10** in 72% yield as brownish white (colorless) materials. Data of **10**: Rf value 0.55 (hexane/EtOAc, 1:4); M.p. > 350 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) 9.35 (s, 4H, phenyl OH), 9.09 (d, J = 8.4 Hz, 4H, H-1), 7.90 (dd, J = 8.4, 7.2 Hz, 4H, H-2), 7.80 (d, J = 7.2 Hz, 4H, H-3), 7.08 (d, J = 8.7 Hz, 8H, phenyl H-3), 6.67 (d, J = 8.7 Hz, 8H, phenyl H-2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 156.2 (phenyl C-1), 150.3 (phenyl C-4), 135.24 (C-3a), 135.17 (C-3a^1), 128.8 (phenyl C-3), 128.7 (C-14b), 128.3 (C-14c), 127.1 (C-2), 124.7 (C-3), 123.2 (C-1), 115.2 (phenyl C-2), 66.0 (C-4) ppm; MS (DART-TOF) *m/z*: 721 $[MH]^+$; IR (neat) 3523 (OH), 3472 (OH), 2956, 1506, 1170, 832, 784, 725, 592, 517 cm^{-1}; HRMS (DART-TOF) calcd for $C_{52}H_{33}O_4$: 721.2379 $[MH]^+$, found; 721.2386.

5. Molecular packing structures with ORTEP drawing of **3** (Figure S1).

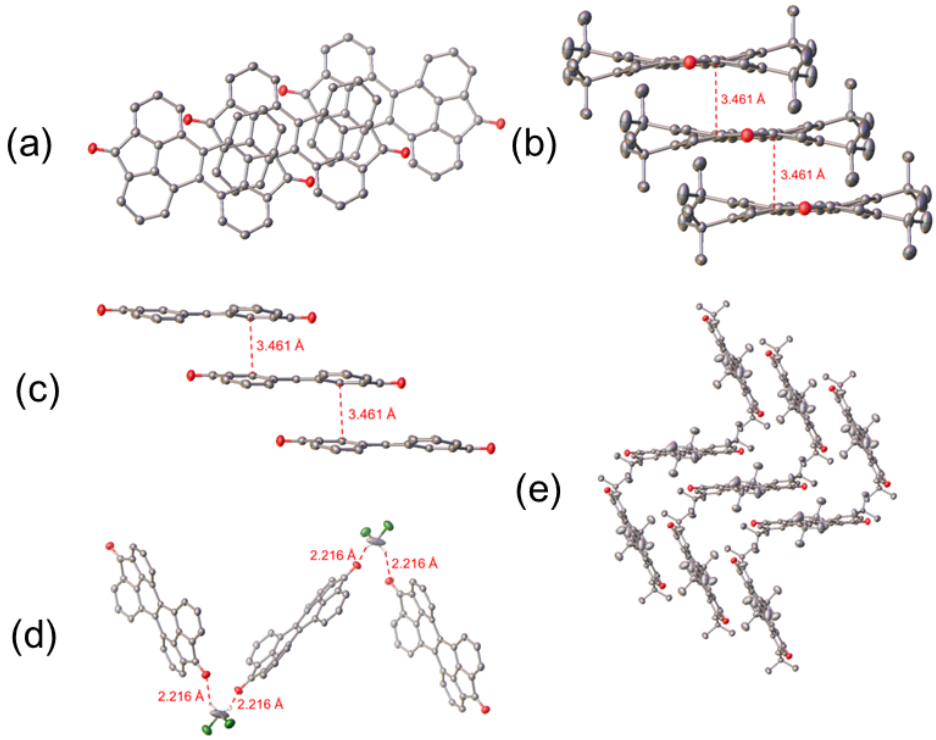


Figure S1. Molecular packing structures with ORTEP drawing of **3** (the hydrogen atoms are omitted for clarity): (a) top view (*tert*-butyl groups are removed for ease of viewing); (b) side view from a ketone moiety, with a description of interlayer distance of 3.461 Å; (c) side view from the *cove* (*tert*-butyl groups are removed); (d) four hydrogen bondings between two CH_2Cl_2 molecules and three compounds of **3**, at a distance of 2.216 Å (*tert*-butyl groups are removed); (e) zigzag-packing view from the *cove* (CH_2Cl_2 molecules are removed for ease of viewing).

6. Molecular packing structures with ORTEP drawing of **1** (Figure S2).

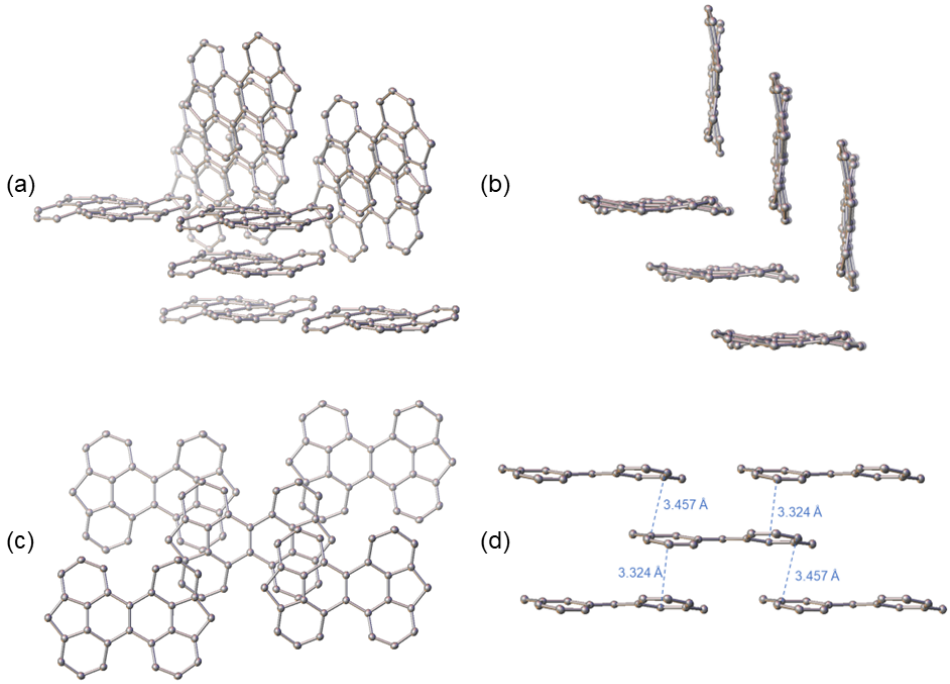


Figure S2. Molecular packing structures with ORTEP drawing of **1** (the hydrogen atoms are omitted for clarity): (a) layered-view from a slanting upper part; (b) side view from five-membered rings; (c) top view; (d) side view from cove regions with a description of interlayer distances, 3.457 Å and 3.324 Å.

7. Molecular packing structures with ORTEP drawing of **8** (Figure S3).

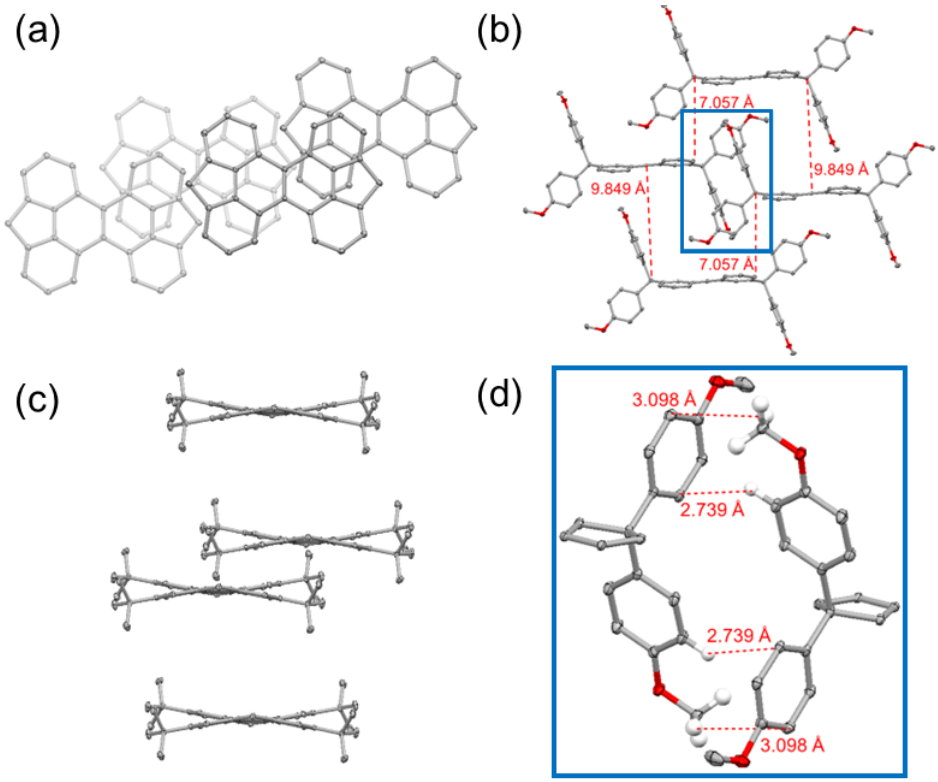


Figure S3. Molecular packing structures with ORTEP drawing of **8** (the hydrogen atoms not engaged in (d) are omitted for clarity): (a) top view (*tert*-butyl groups and anisole moieties are removed for ease of viewing); (b) side view from a cove region with a description of interlayer distances of 9.849 Å and 7.057 Å; (c) side view from a five-membered ring; (d) magnified viewing of the part enclosed with the blue line of (b), with description of selected distances that mean CH•••pi interactions.

8. Optimized structures of **1**, **3**, and **8** (Fig. S4).

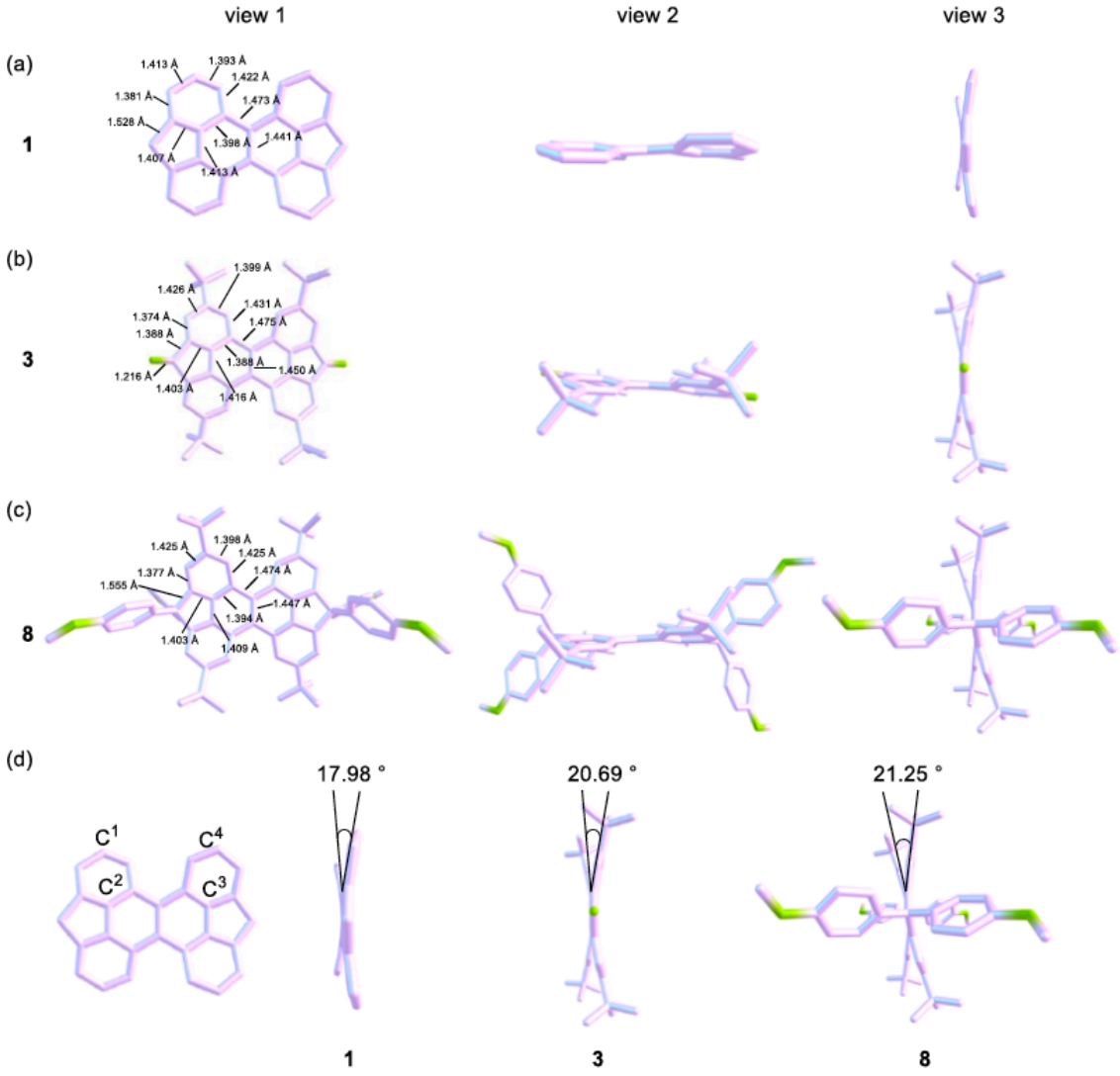


Figure S4. Optimized structures and bond lengths of (a) **1** and (b) **3** with C_{2h} symmetry and (c) **8** with C_i symmetry (B3LYP/6-31G(d,p)), (d) torsion angles, determined by the four carbon atoms of C^1, C^2, C^3, and C^4.

9. Optimized structures of (a) **1** and (b) **3** with D_2 symmetry, calculated at the B3LYP/6-31G(d,p) level of theory (Fig. S5).

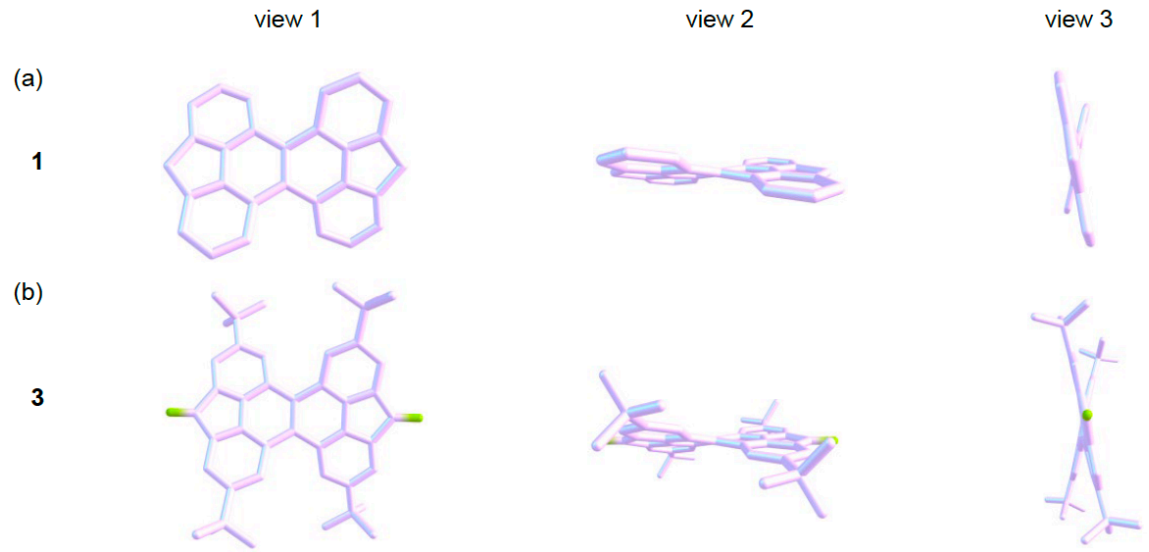


Figure S5**.** Optimized structures of (a) **1** and (b) **3** with D_2 symmetry, calculated at the B3LYP/6-31G(d,p) level of theory.

10. The energy difference between D_2 and C_{2h} symmetry of the DFT-optimized structures for **1** and **3** calculated at the B3LYP/6-31G(d,p) level of theory (Table S1).

Table S1**.** The energy difference between D_2 and C_{2h} symmetry of the DFT-optimized structures for **1** and **3** calculated at the B3LYP/6-31G(d,p) level of theory.

Point group	Energy difference [kcal/mol] [a]	
	1	**3**
D_2	-1.87	-1.94
C_{2h}	0	0

[a] The data after zero-point vibrational energy correction were used.

11. CVs of **1** in CH_2Cl_2 (1.0 mM) including 50 mM NBu_4BF_4 as a supporting electrolyte under argon at 25 ºC (working electrode: Pt) (Fig. S6).

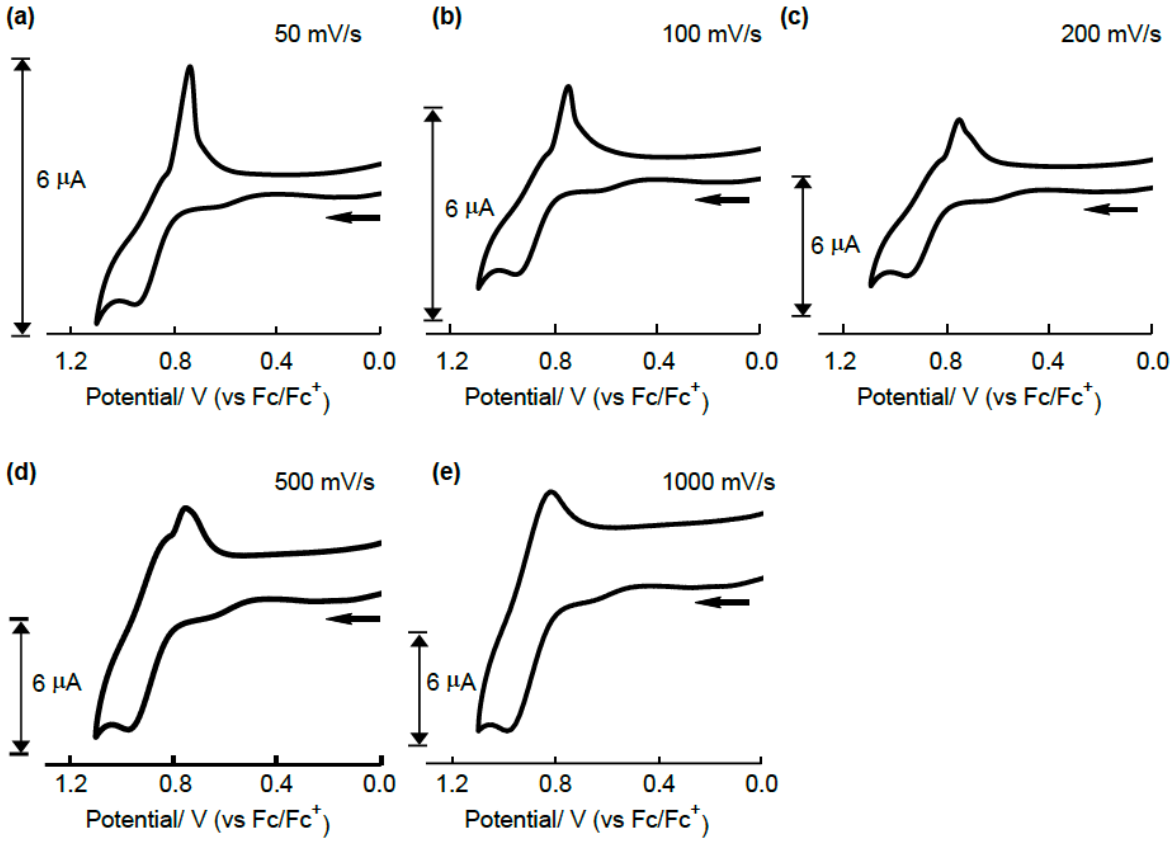


Figure S6. CVs of **1** in CH_2Cl_2 (1.0 mM) including 50 mM NBu_4BF_4 as a supporting electrolyte under argon at 25 °C (working electrode: Pt), where the scan rates are (a) 50 mV/s, (b) 100 mV/s, (c) 200 mV/s, (d) 500 mV/s, and (e) 1000 mV/s, respectively.

12. ^{1}H and ^{13}C NMR spectra for all new compounds. (Fig. S7-S26)

Fig. S7 Compound **1** (^{1}H NMR spectrum in $CDCl_3$).

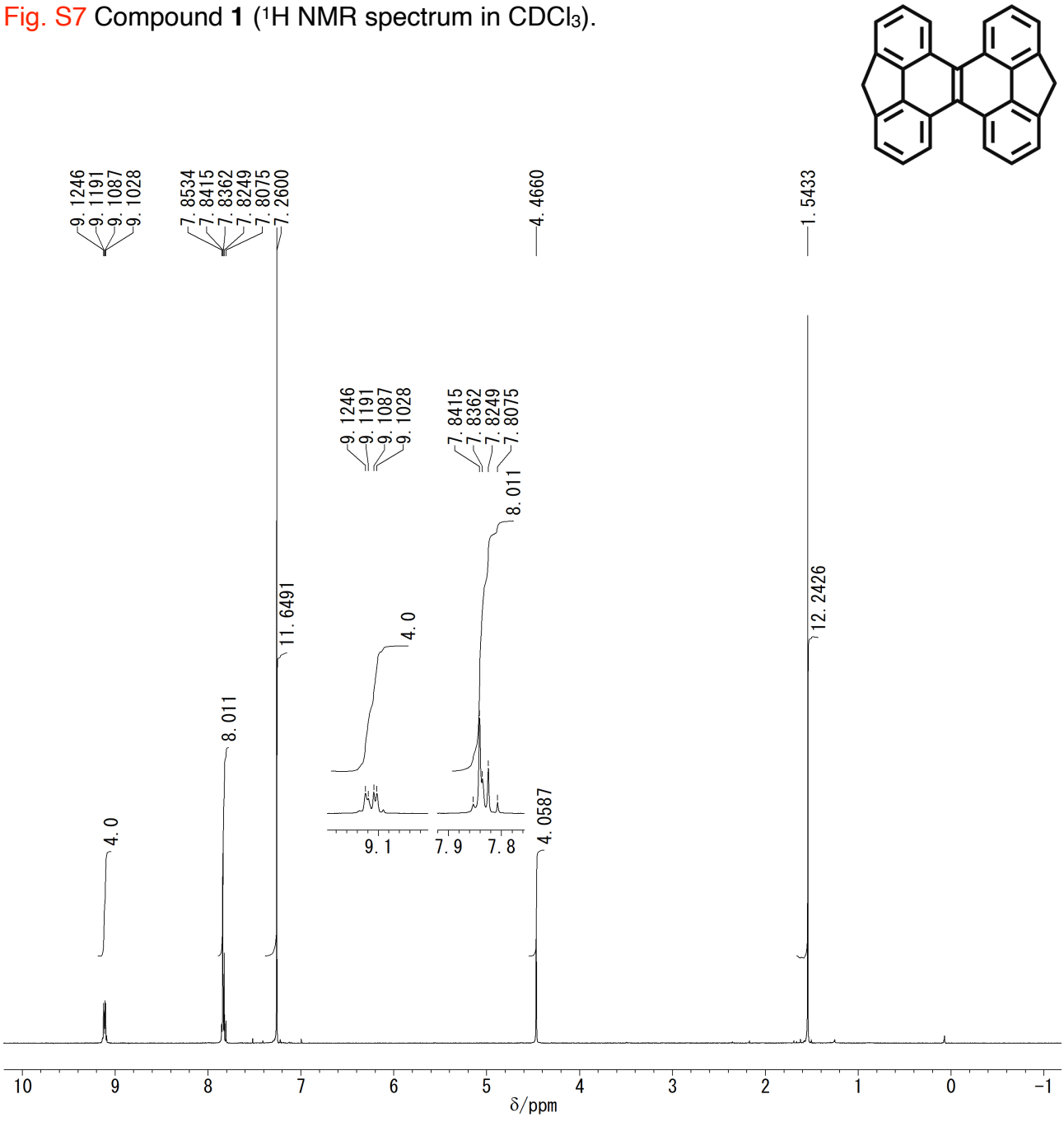


Fig. S8 Compound **1** (^{13}C NMR spectrum in $CDCl_3$).

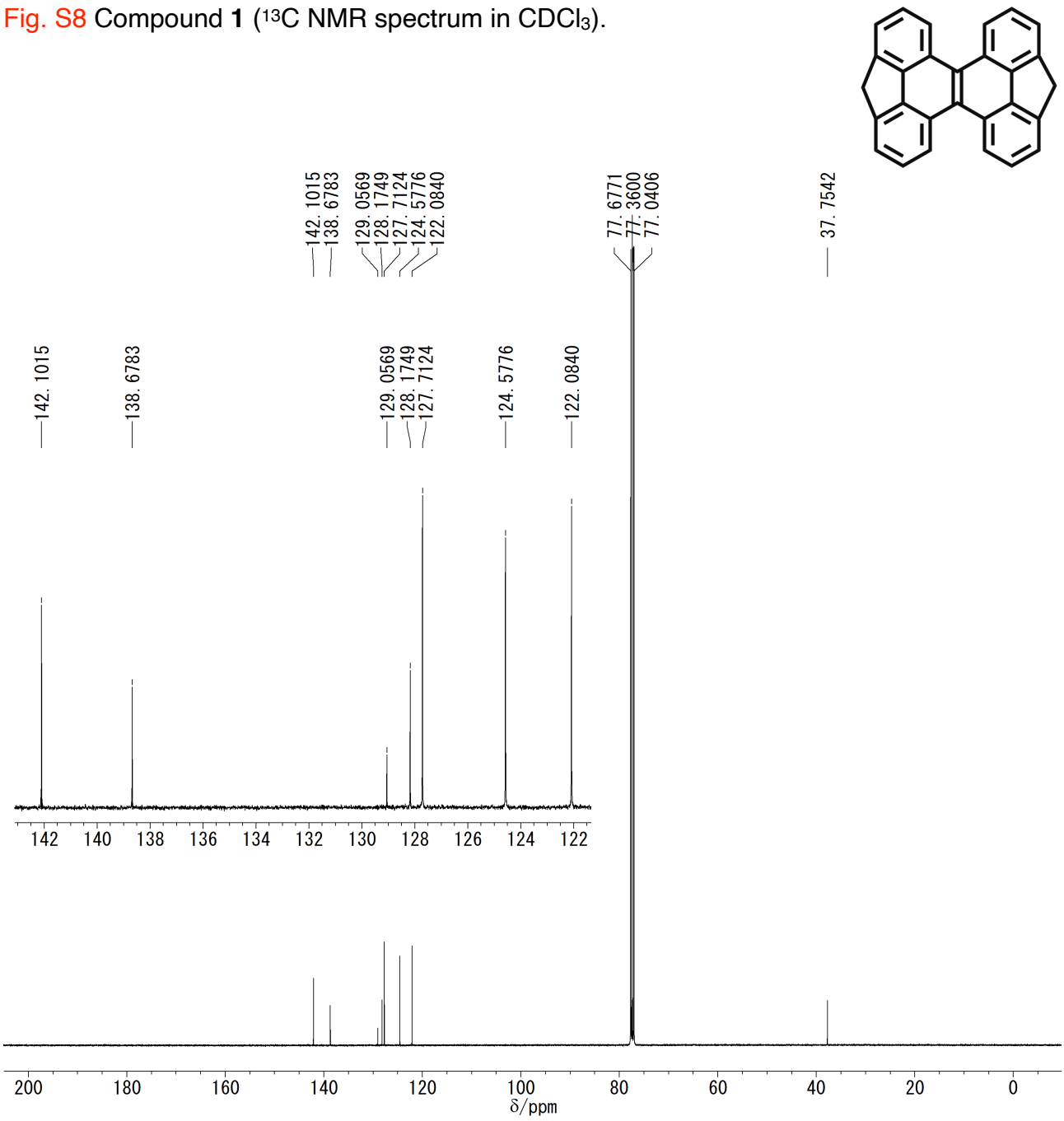
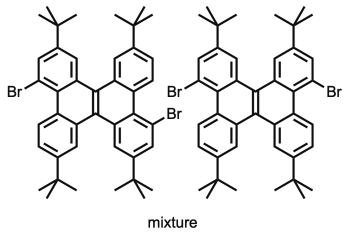


Fig. S9 Compound **2**/*iso*-**2** in 50:50 molar ratio (^{1}H NMR spectrum in $CDCl_3$).



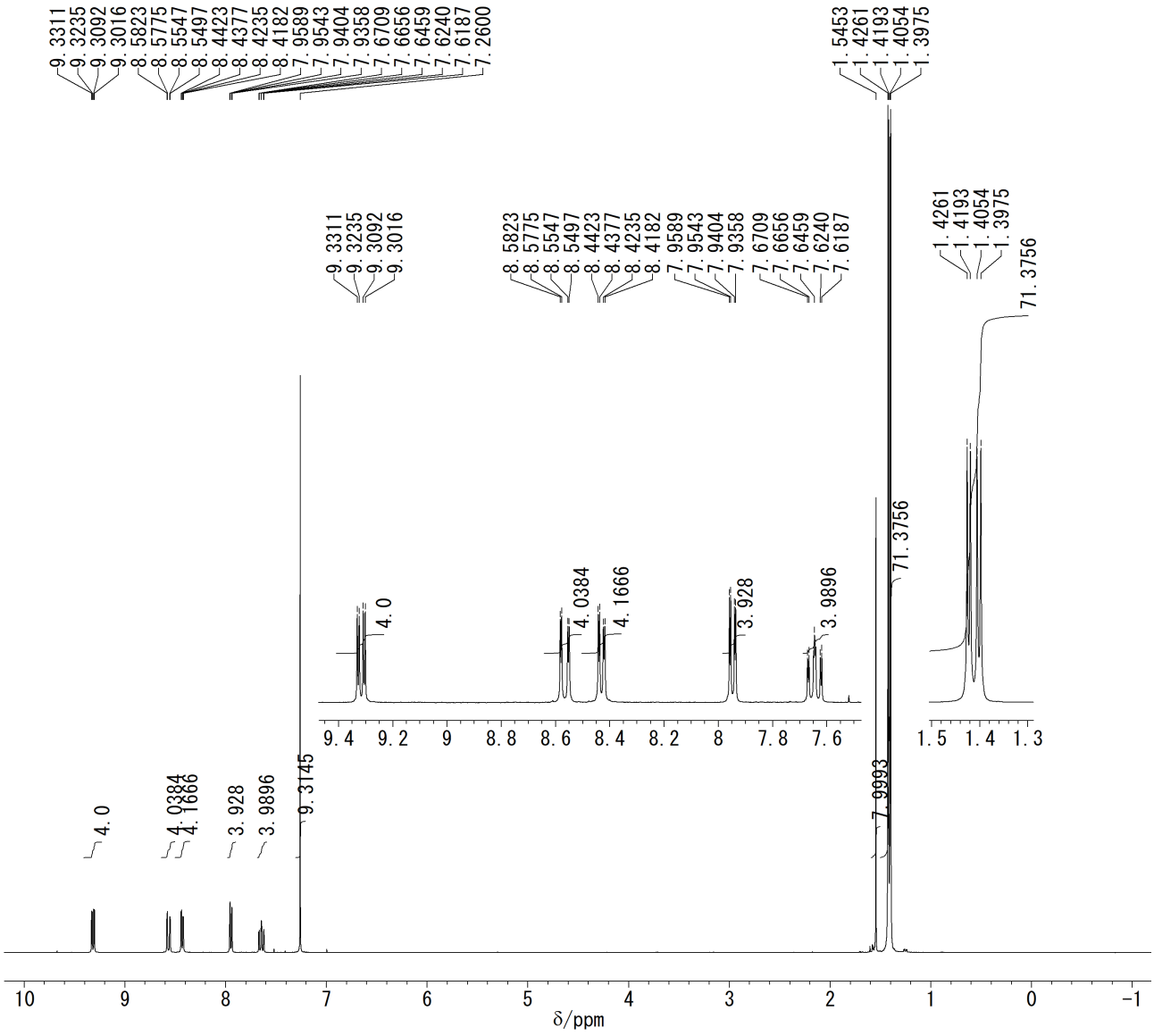
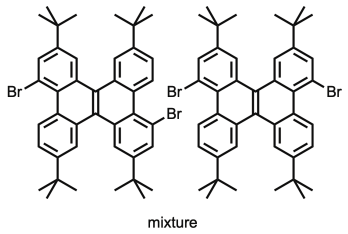


Fig. S10 Compound **2**/*iso*-**2** in 50:50 molara ratio (^{13}C NMR spectrum in $CDCl_3$).



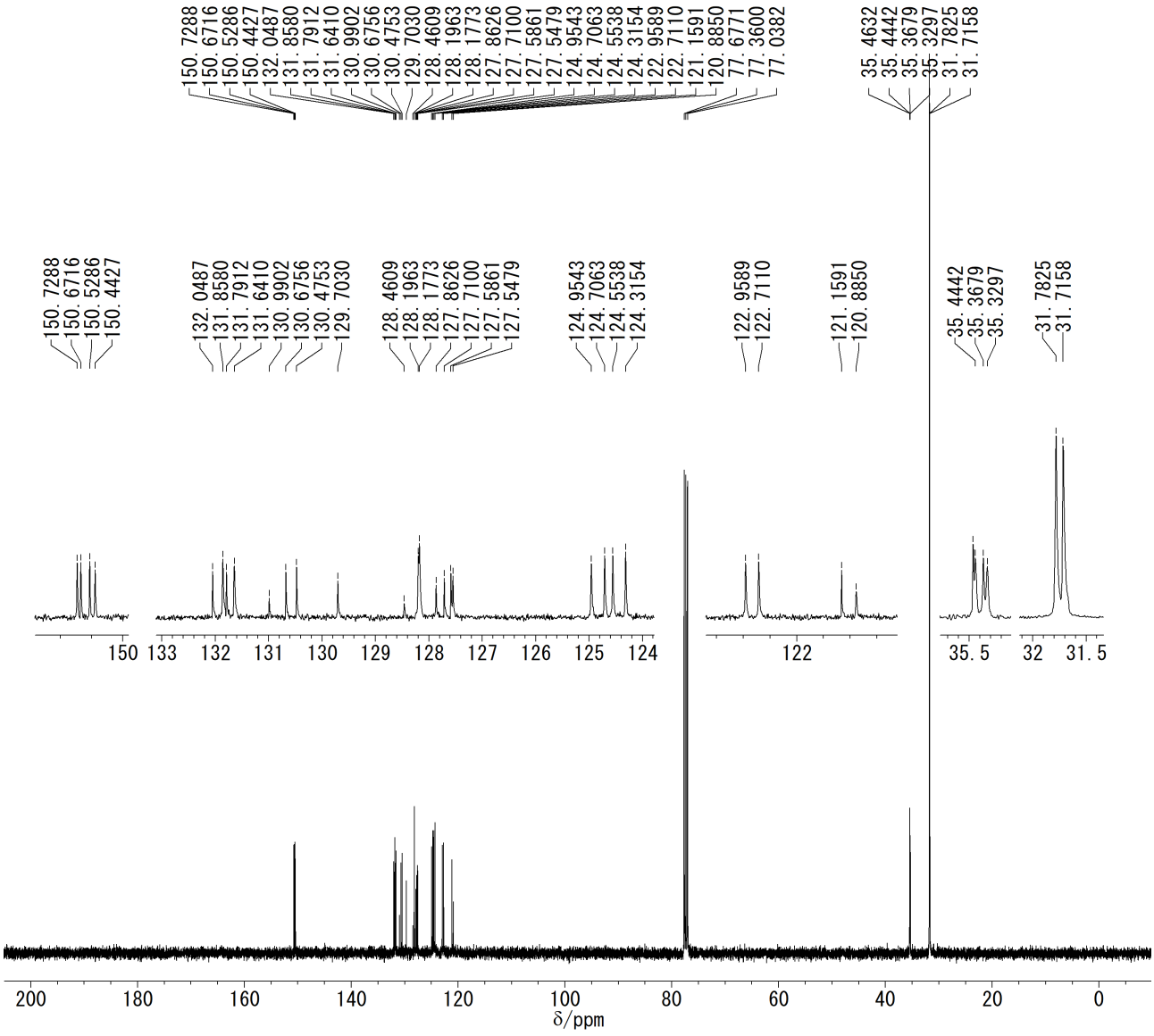


Fig. S11 Compound **3** (^{1}H NMR spectrum in $CDCl_3$).

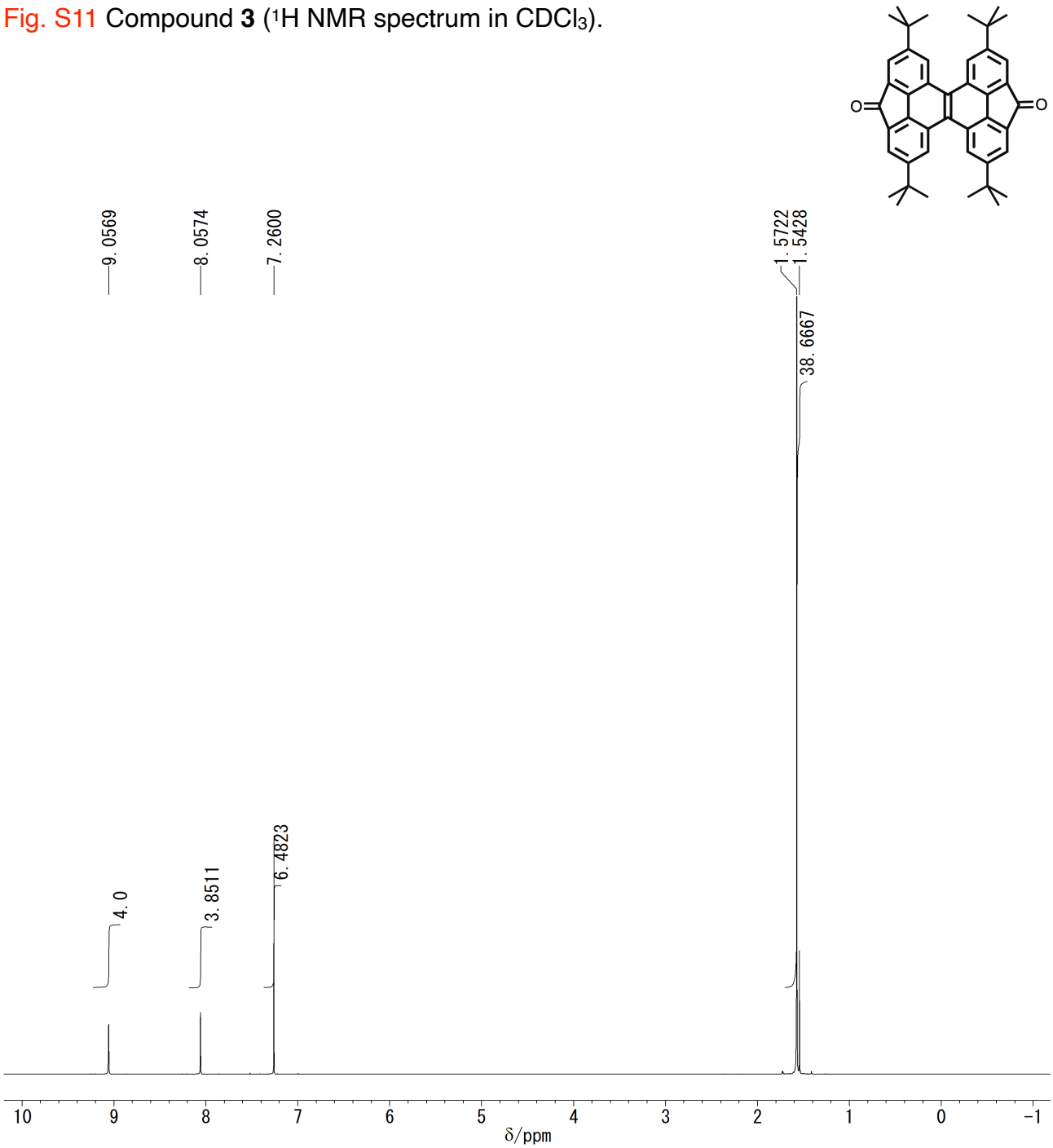


Fig. S12 Compound **3** (^{13}C NMR spectrum in $CDCl_3$).

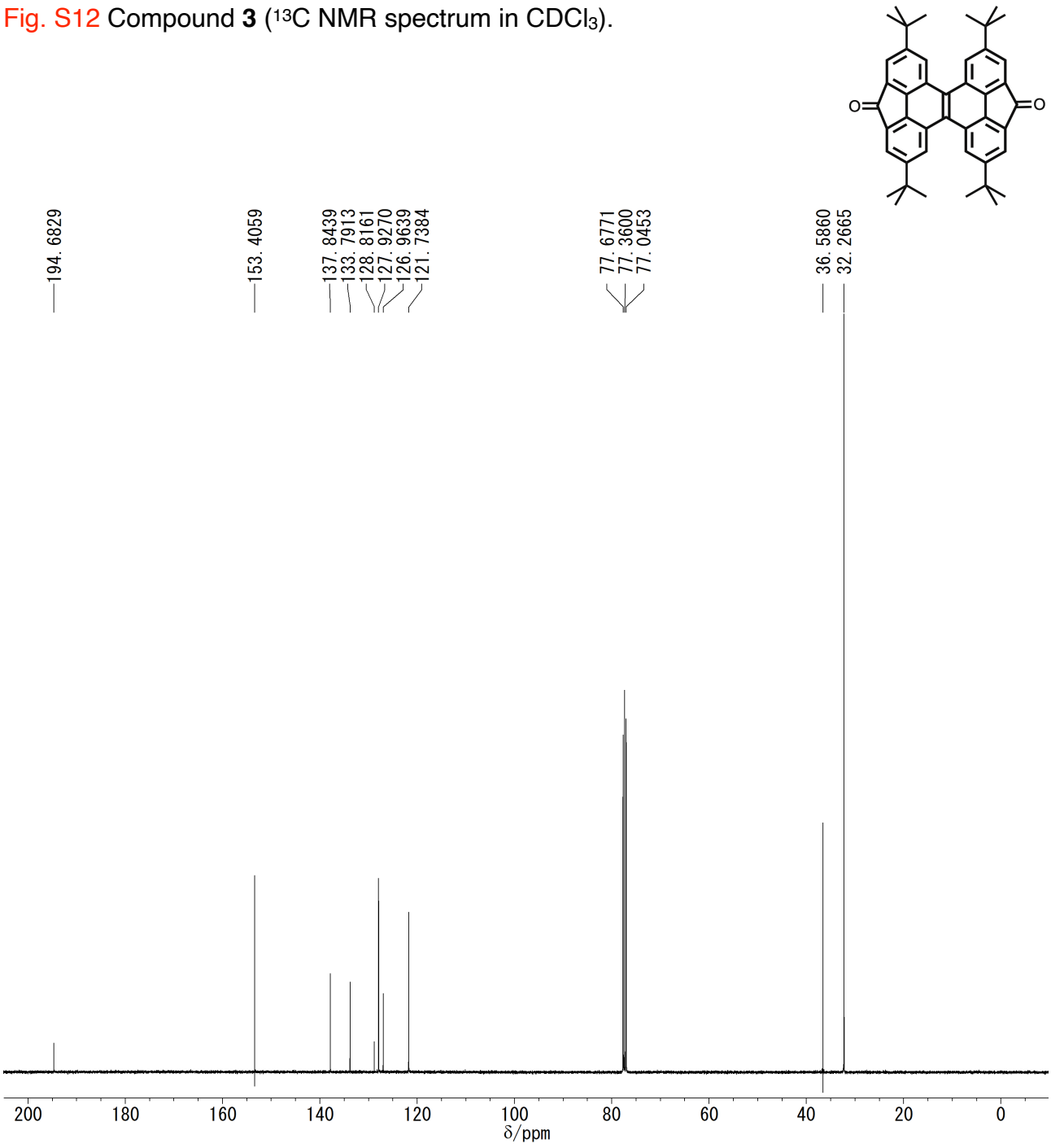
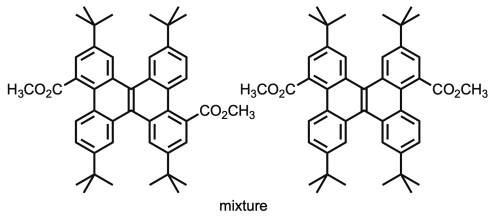


Fig. S13 Compound **4**/*iso*-**4** in 50:50 molara ratio (^{1}H NMR spectrum in $CDCl_3$).



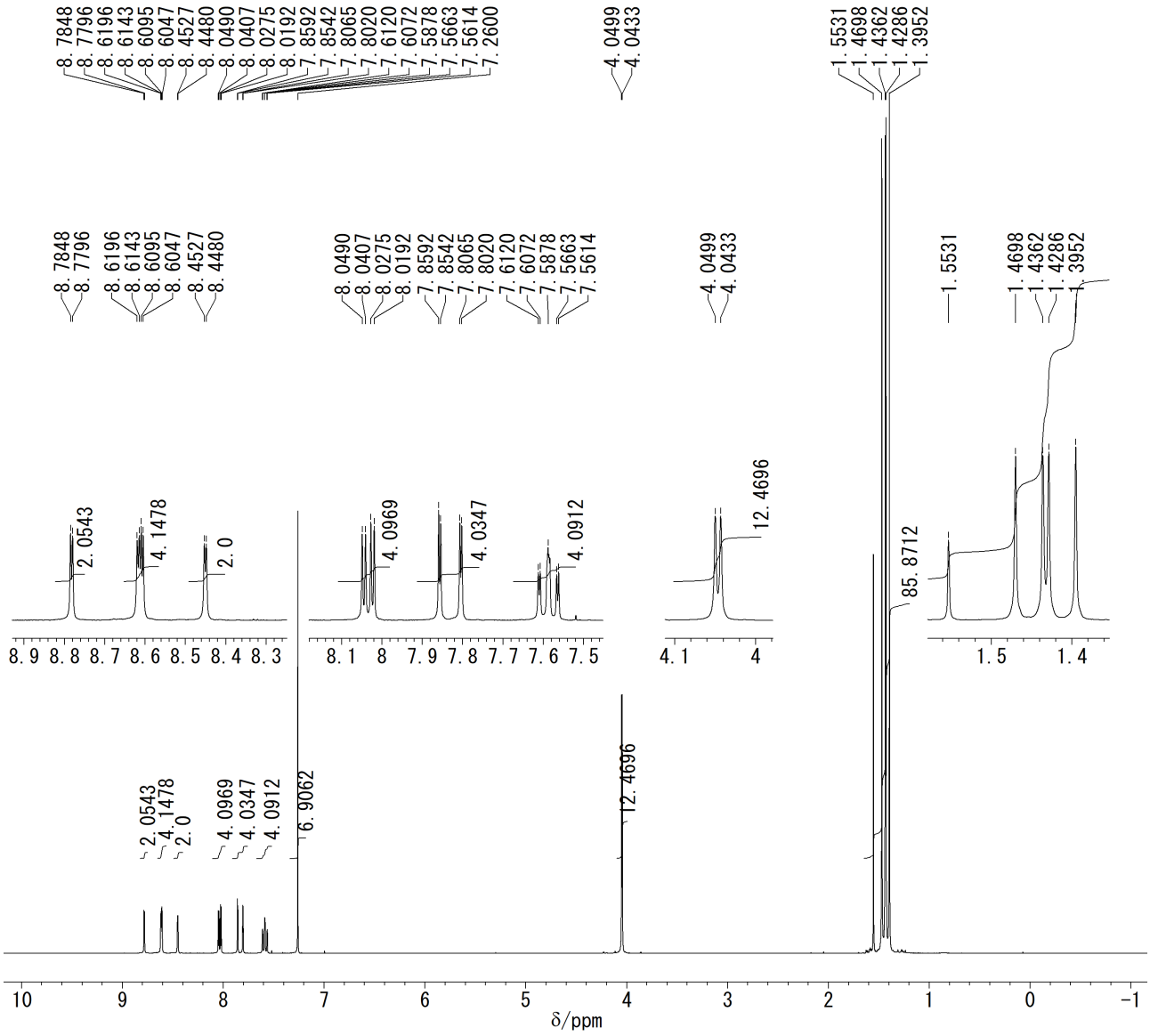
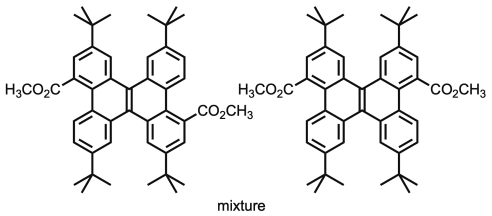


Fig. S14 Compound **4**/*iso*-**4** in 50:50 molara ratio (^{13}C NMR spectrum in $CDCl_3$).



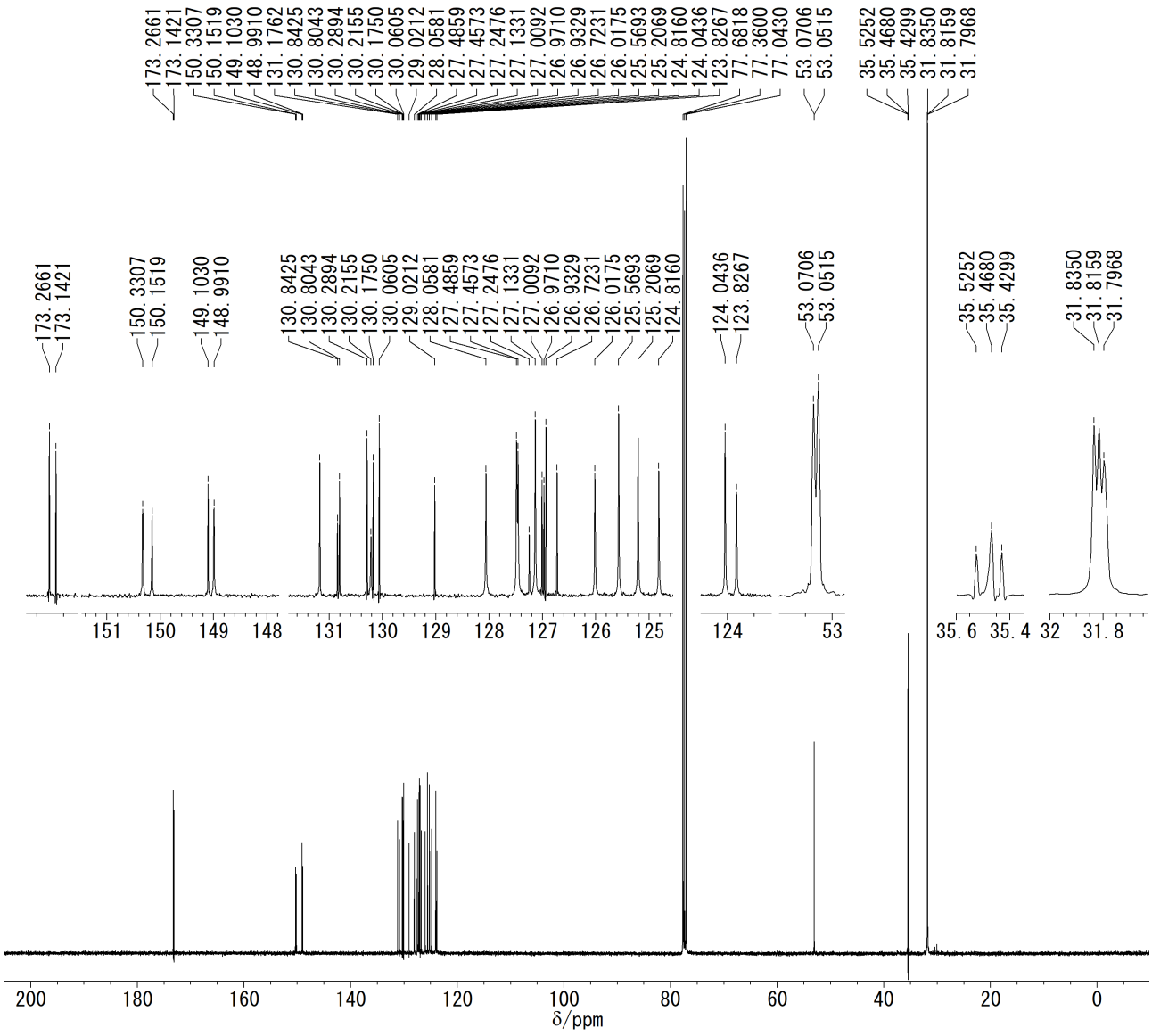
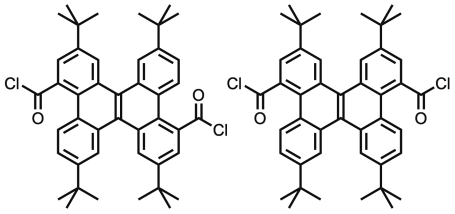


Fig. S15 Compound **5**/*iso*-**5** in 50:50 molara ratio (^{1}H NMR spectrum in $CDCl_3$).



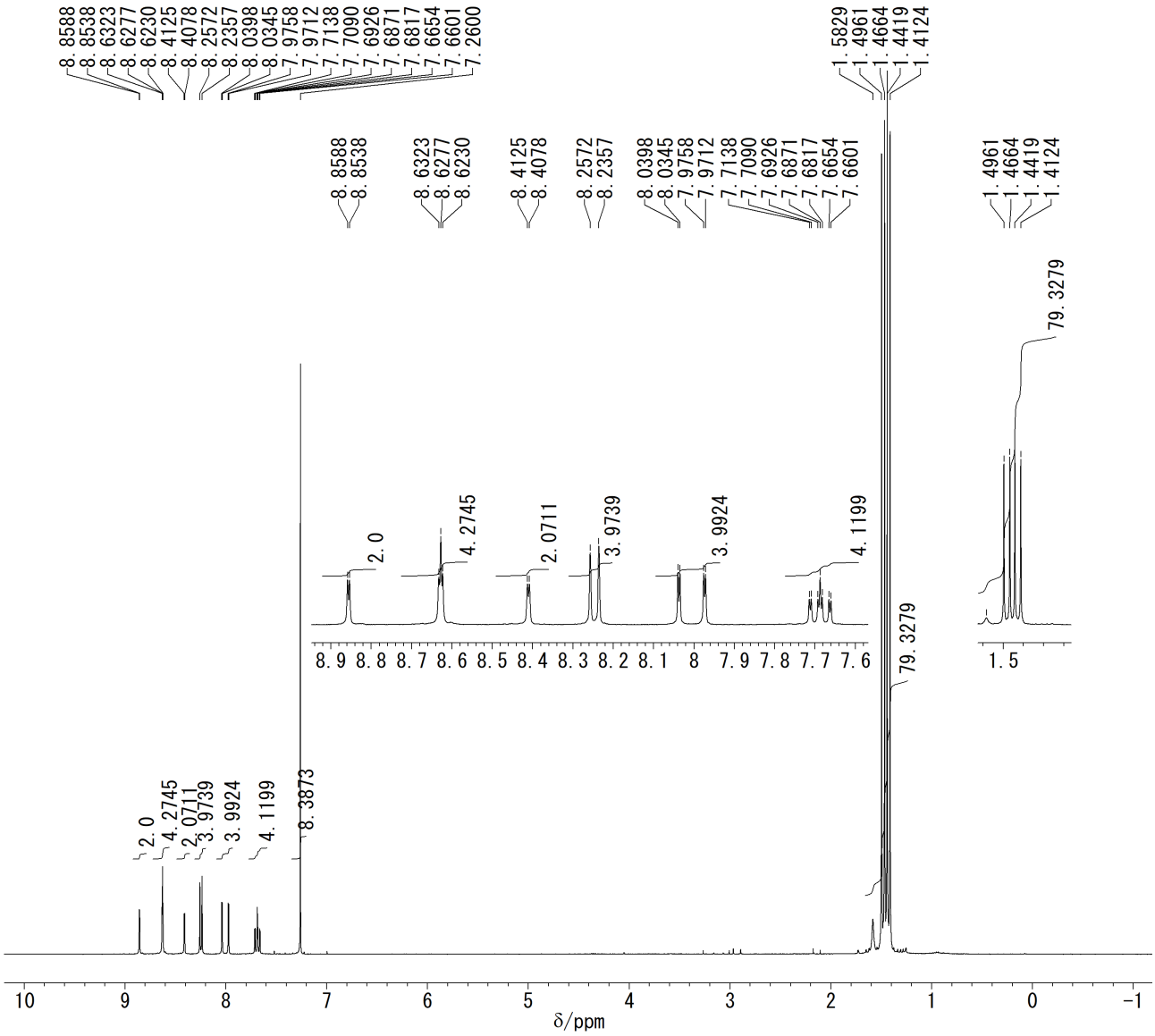
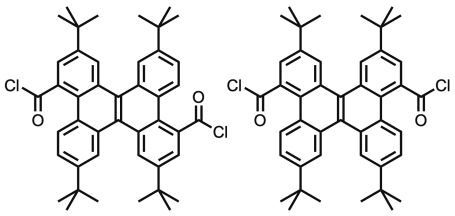


Fig. S16 Compound **5**/*iso*-**5** in 50:50 molara ratio (^{13}C NMR spectrum in $CDCl_3$).



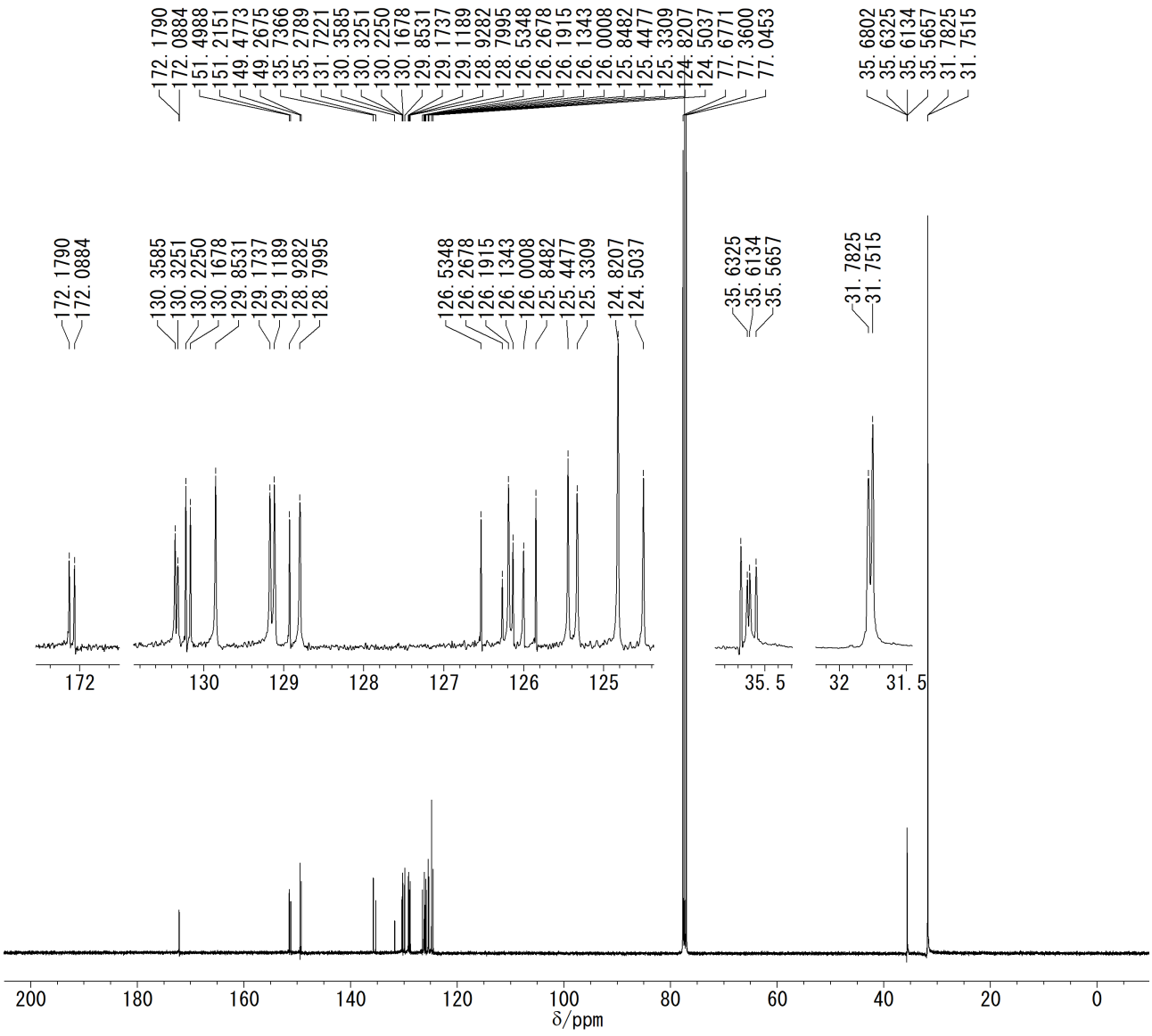


Fig. S17 Compound **6** (^{1}H NMR spectrum in $CDCl_3$).

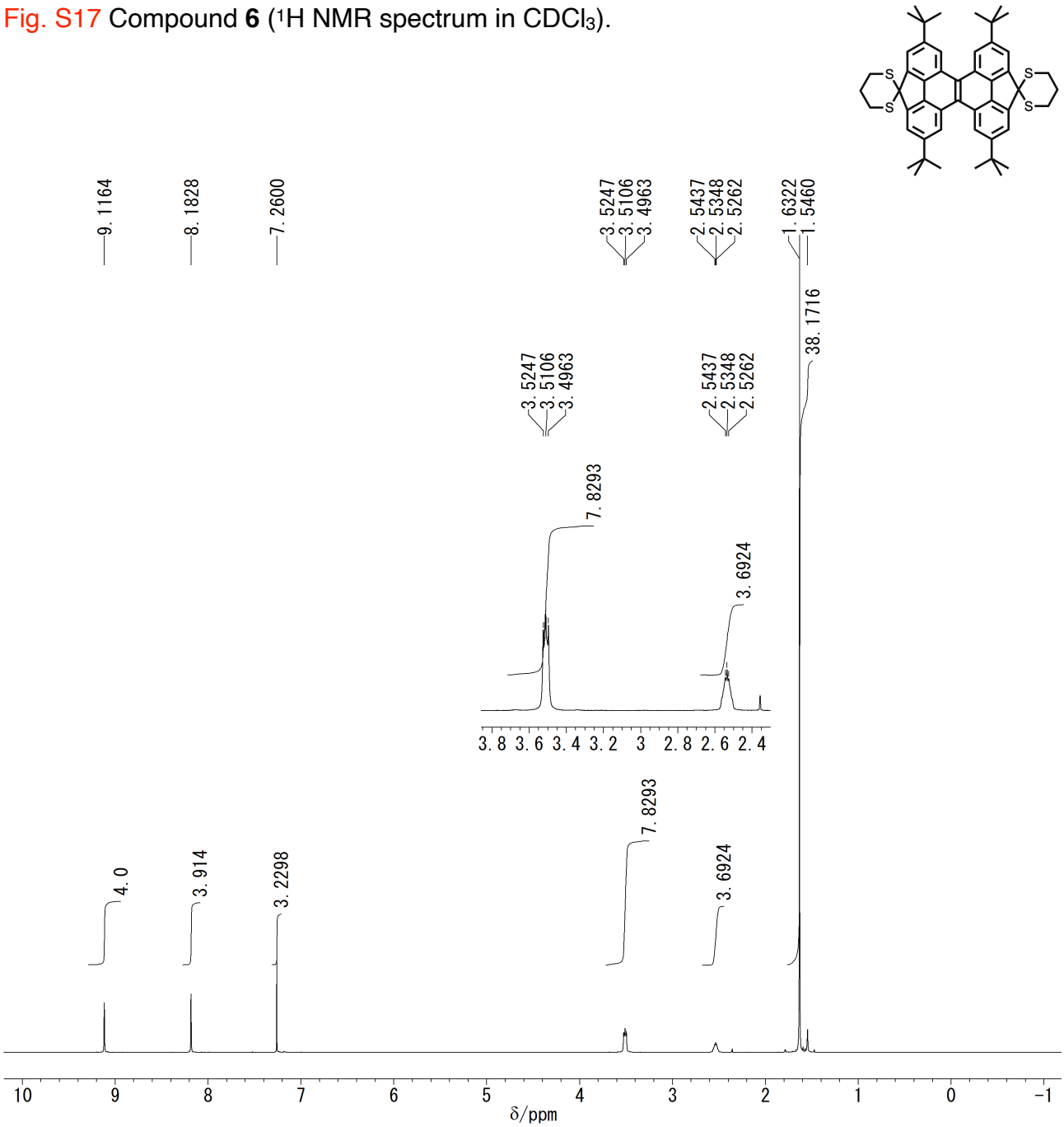


Fig. S18 Compound **6** (^{13}C NMR spectrum in $CDCl_3$).

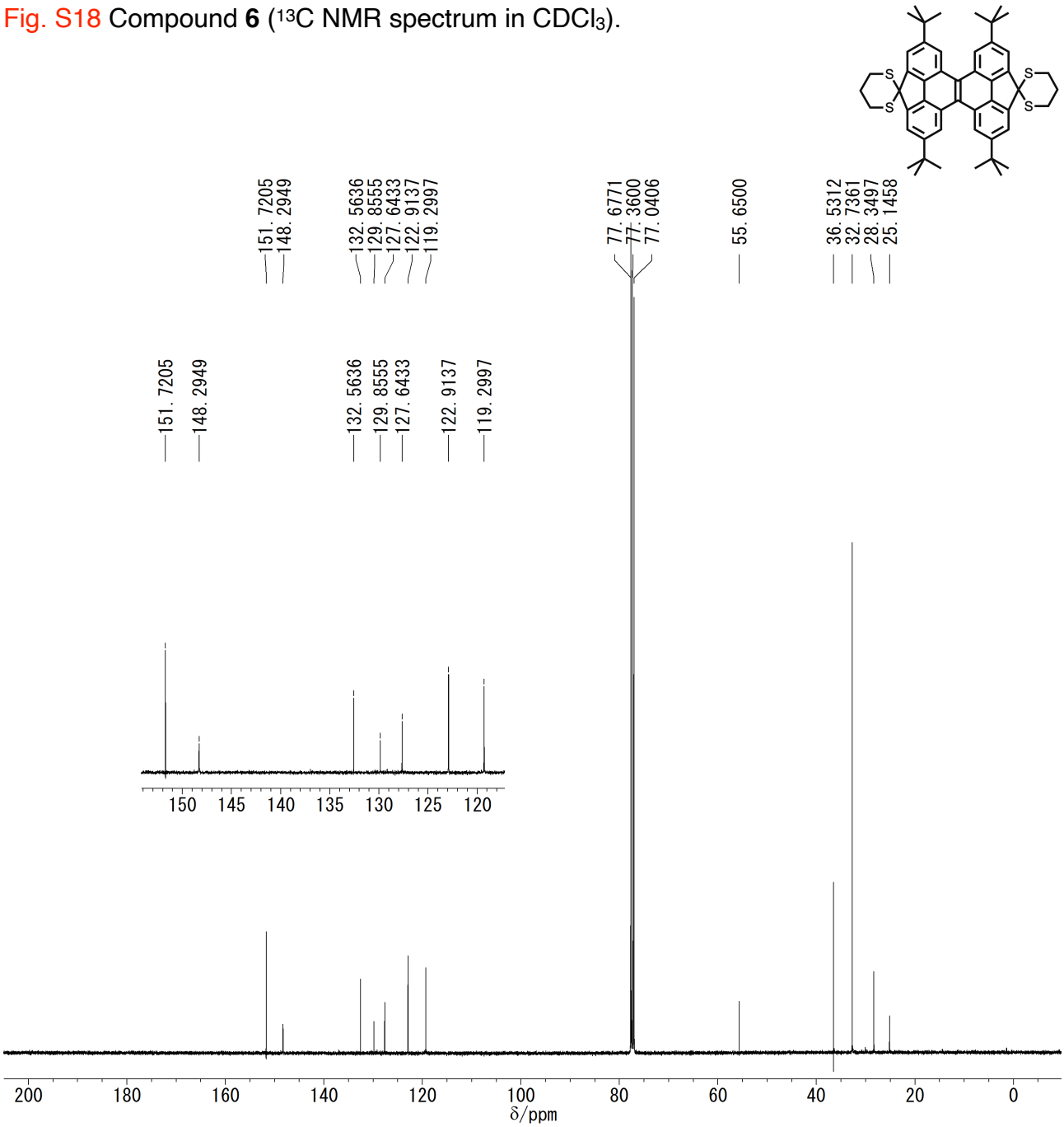
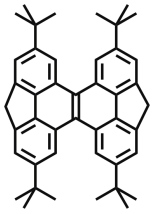


Fig. S19 Compound **7** (^{1}H NMR spectrum in $CDCl_3$).



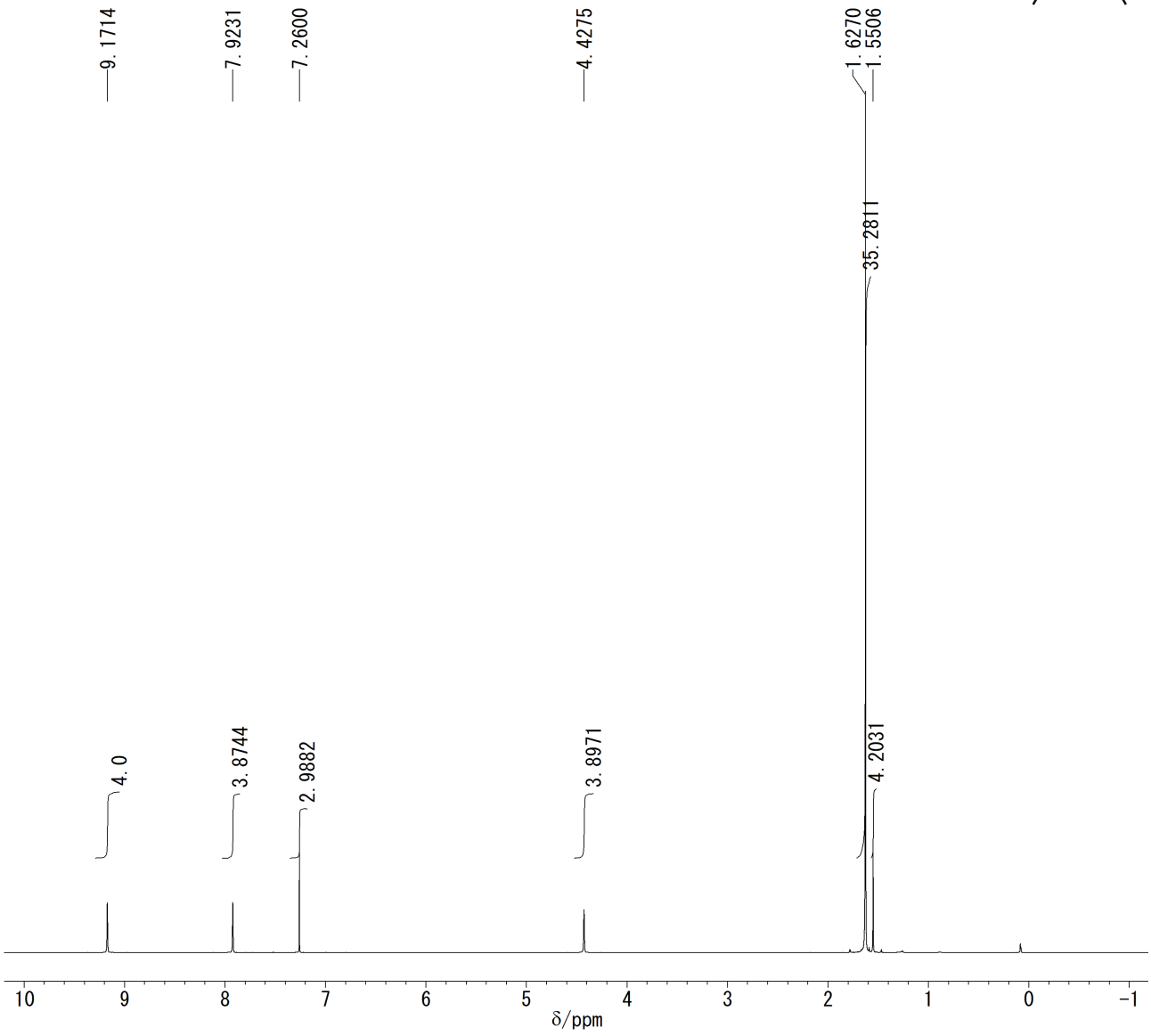
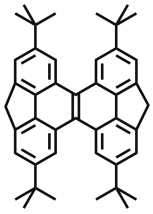


Fig. S20 Compound **7** (^{13}C NMR spectrum in $CDCl_3$).



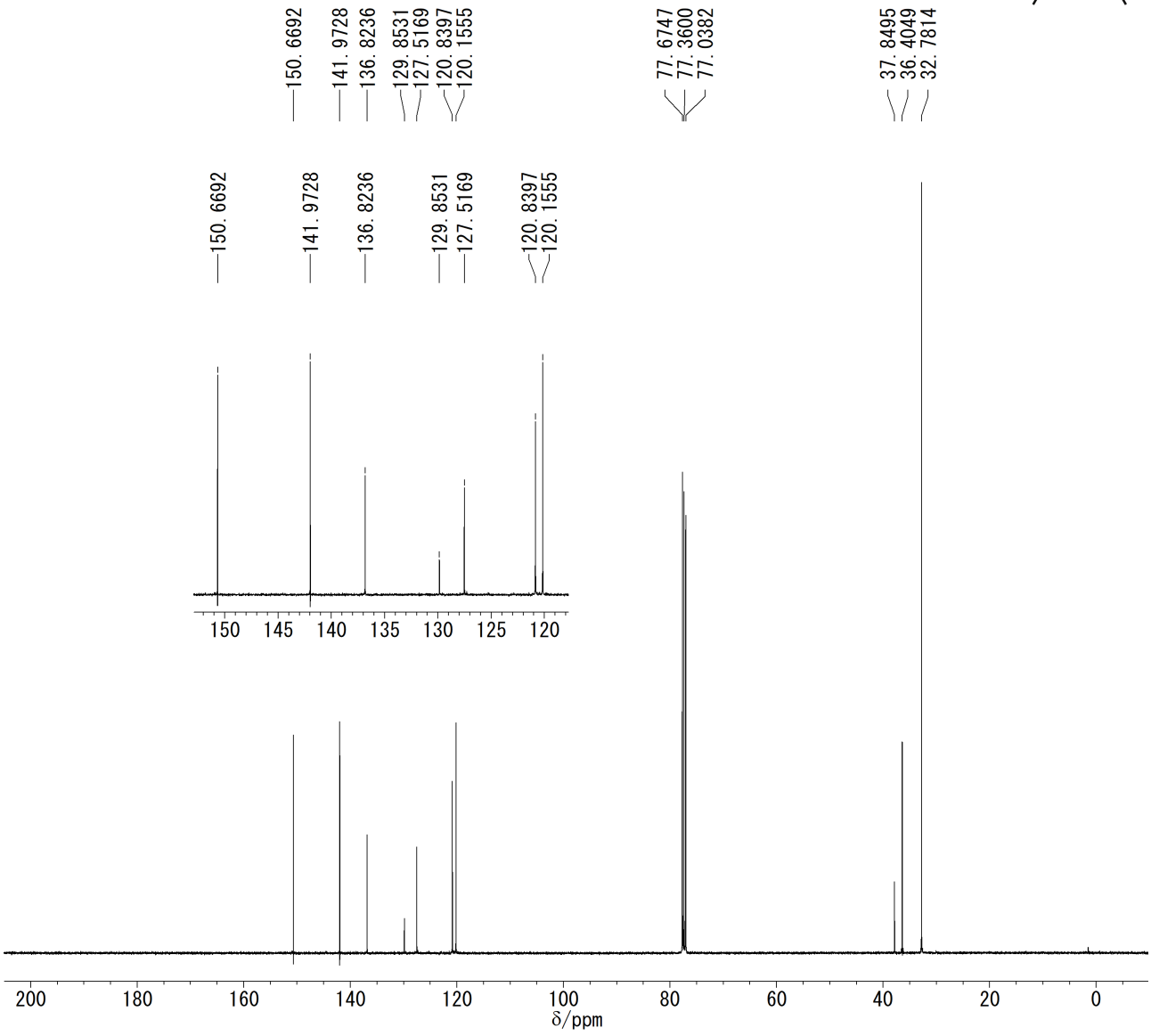


Fig. S21 Compound **8** (^{1}H NMR spectrum in $CDCl_3$).

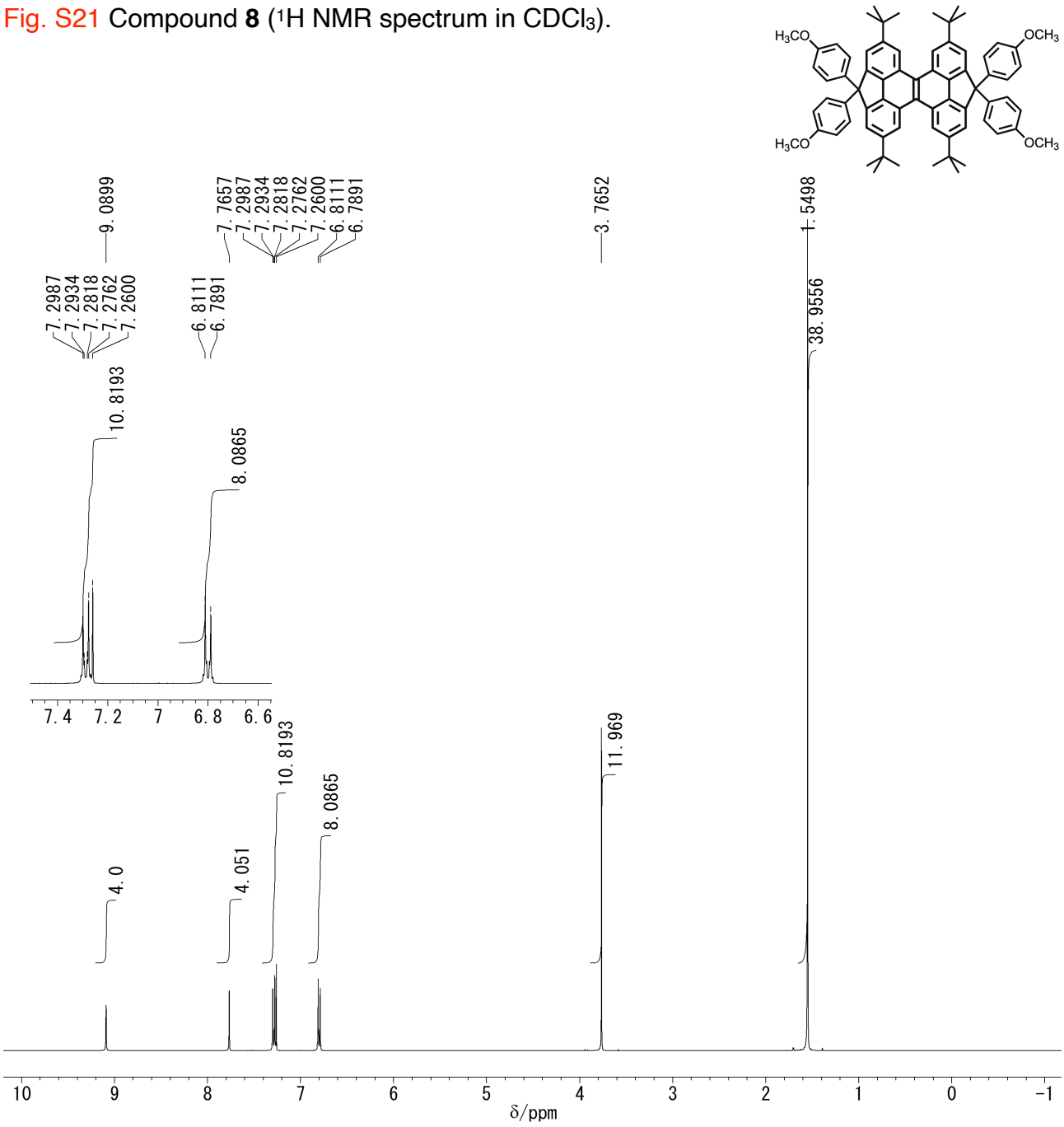


Fig. S22 Compound **8** (^{13}C NMR spectrum in $CDCl_3$).

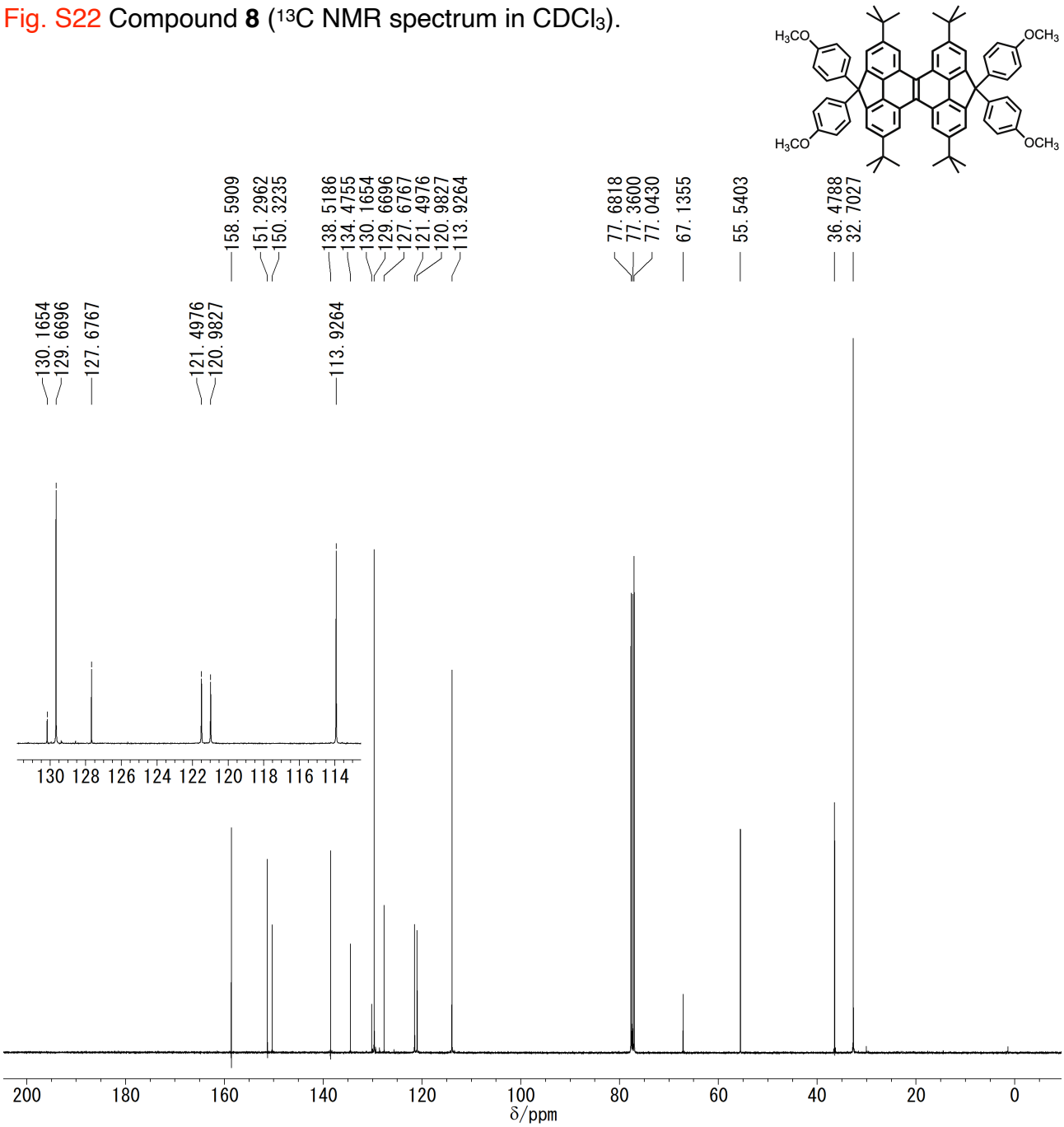


Fig. S23 Compound **9** (^{1}H NMR spectrum in $CDCl_3$).

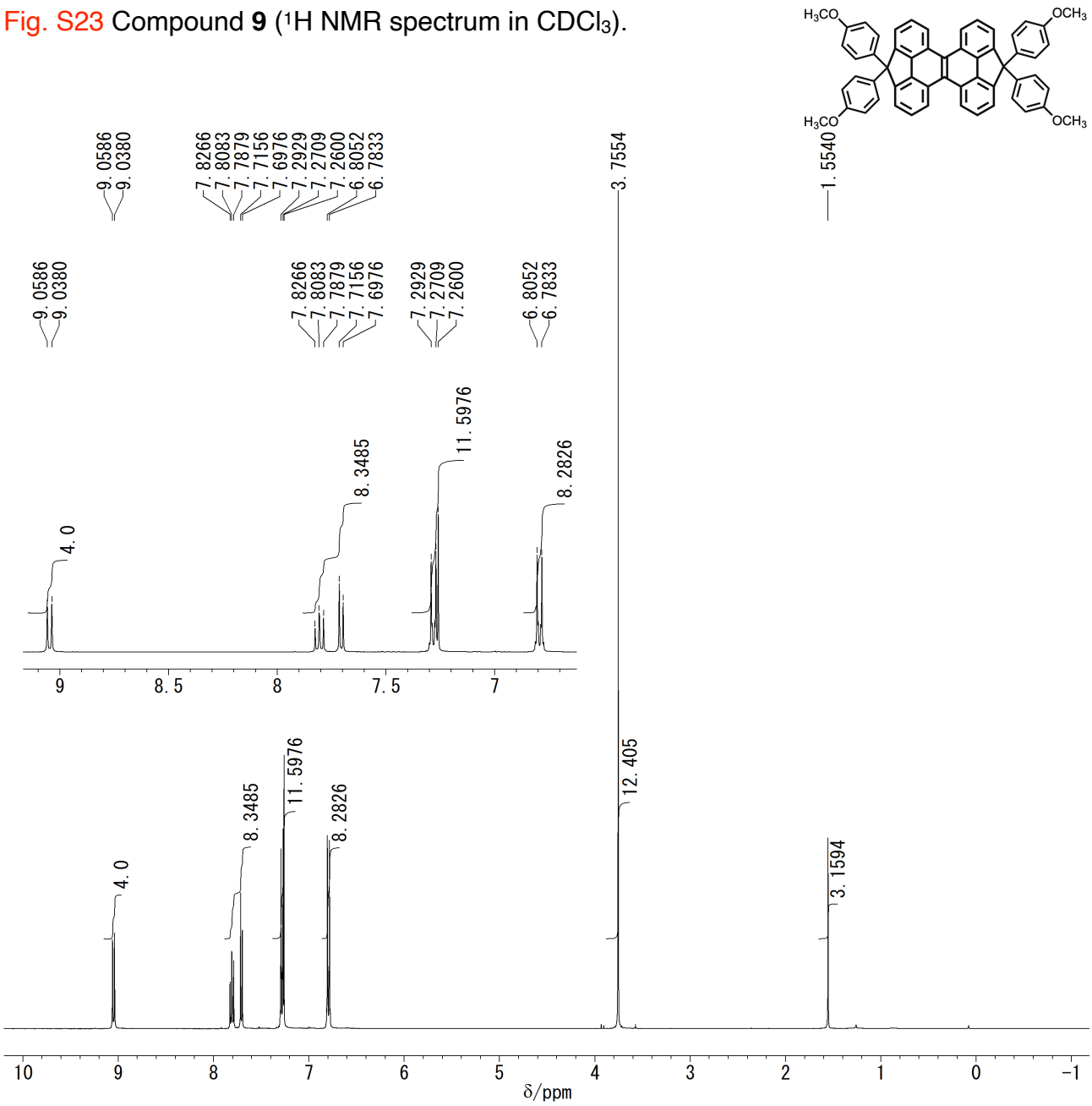
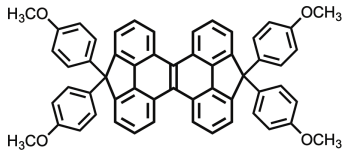


Fig. S24 Compound **9** (^{13}C NMR spectrum in $CDCl_3$).



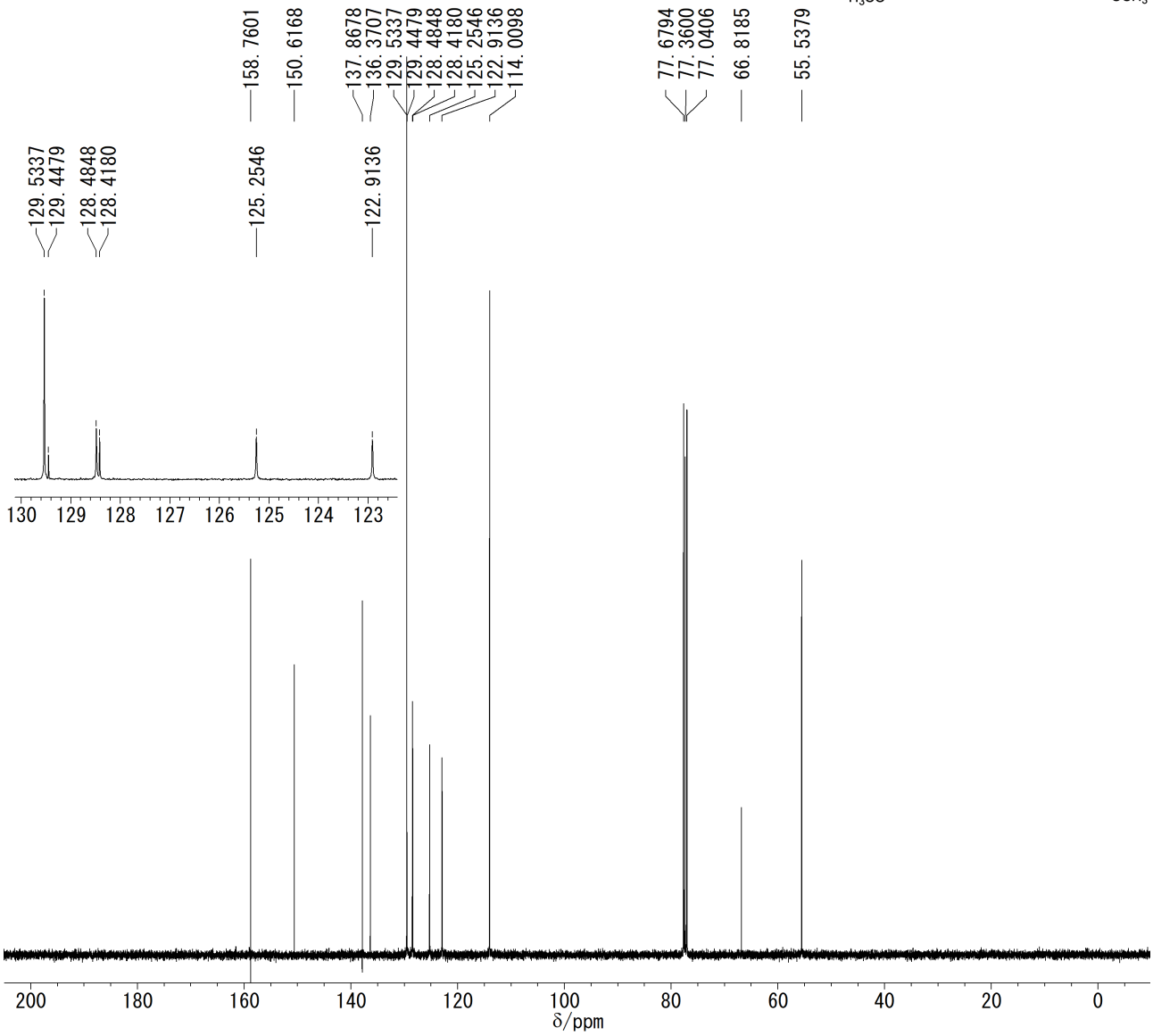
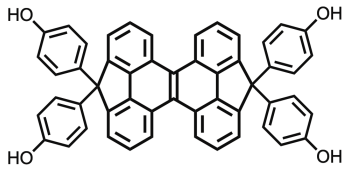


Fig. S25 Compound **10** (^{1}H NMR spectrum in DMSO-d_6).



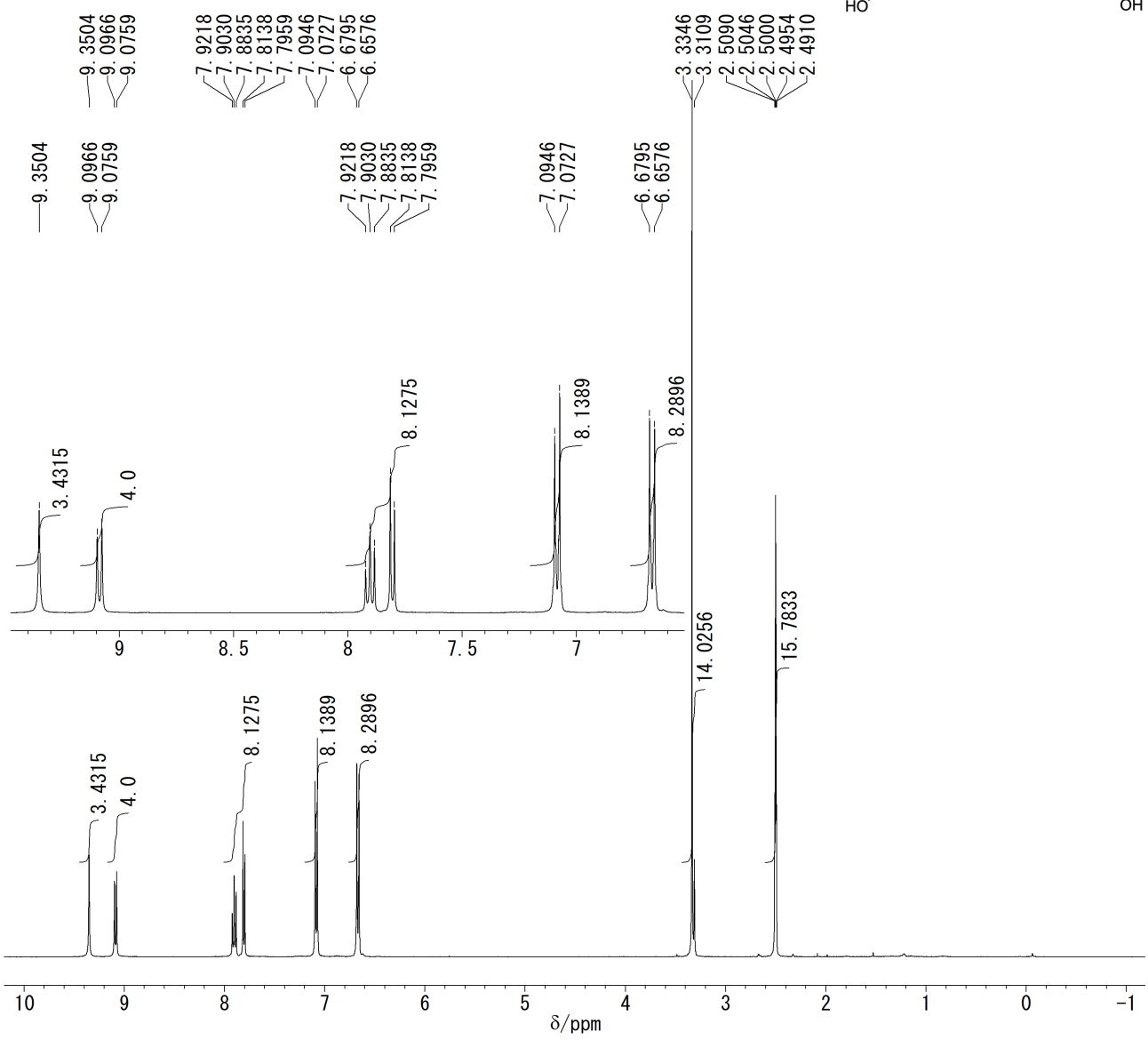
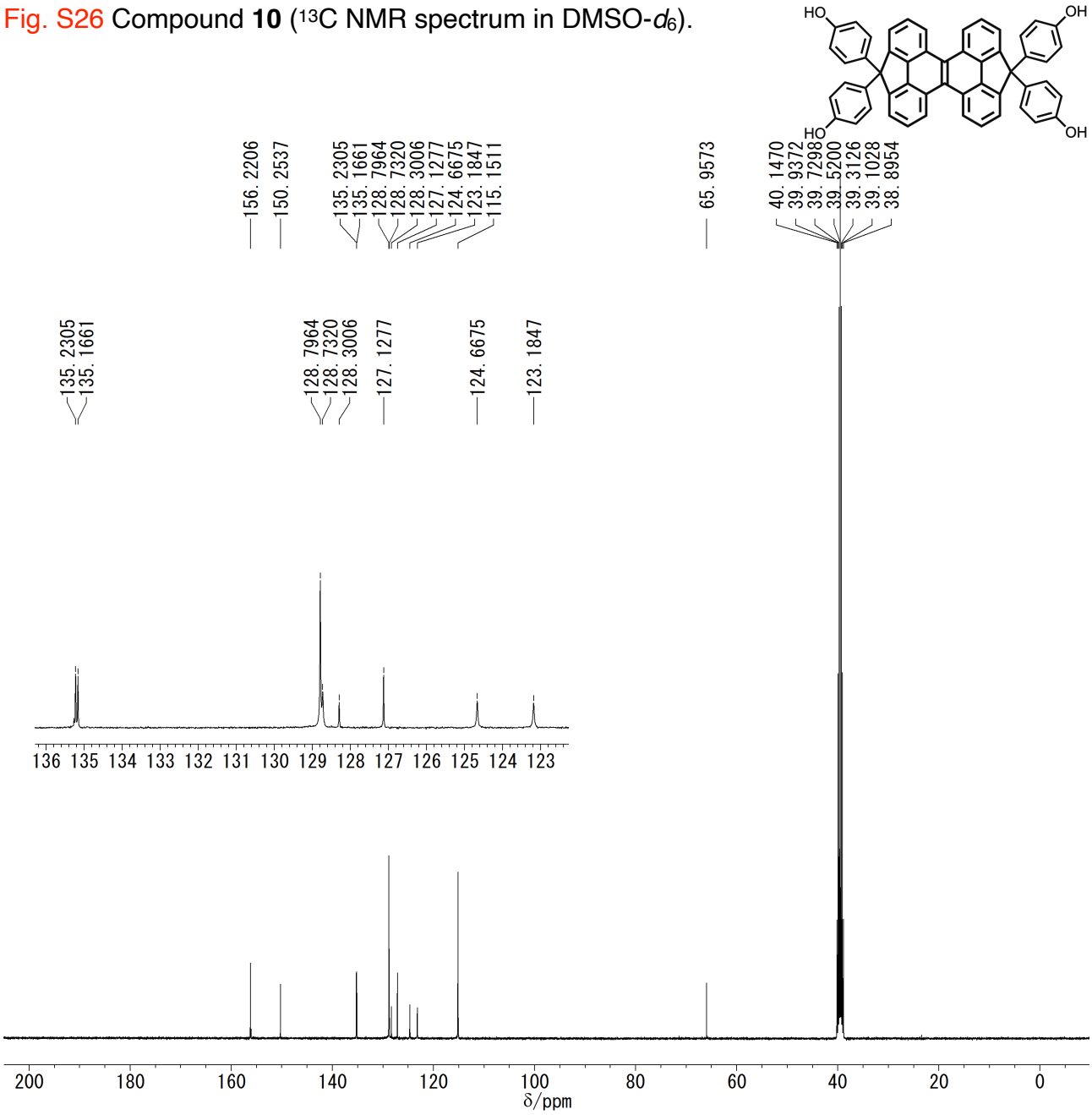


Fig. S26 Compound **10** (^{13}C NMR spectrum in DMSO-d_6).



13. Data of DFT calculations for **1**, **3**, and **8**.

DFT Calculation: All calculations were conducted using a Gaussian 16 suite program (G16RevC.01). Optimization was performed at the B3LYP/6-31G(d,p) level of theory. Harmonic vibration frequency analysis was conducted with the optimized structures at the same level of theory to verify all stationary points as local minima (with no imaginary frequency).

Cartesian Coordination of Optimized Structures: Cartesian coordinates for **1**, optimized at the B3LYP/6-31G(d,p) level of theory.

		Coordinates (Angstroms)		
Center Number	Atomic Type	X	Y	Z
1	6	-0.12907	2.438894	0.706572
2	6	0	0	0.720485
3	6	0.04405	1.273079	-1.45926
4	6	0.04405	1.273079	1.459259
5	6	0.297828	1.519826	2.836045
6	6	0.029434	3.954344	2.549695
7	6	-0.12907	2.438894	-0.70657
8	6	-0.1428	3.758835	1.193141
9	6	0.297828	1.519826	-2.83605
10	6	-0.1428	3.758835	-1.19314
11	6	0.269708	2.814173	-3.34895
12	6	0.269708	2.814173	3.348952
13	6	0.029434	3.954344	-2.5497
14	6	-0.24969	4.70741	0
15	6	0.129074	-2.43889	-0.70657
16	6	0	0	-0.72049
17	6	-0.04405	-1.27308	1.459259
18	6	-0.04405	-1.27308	-1.45926

19	6	-0.29783	-1.51983	-2.83605
20	6	-0.02943	-3.95434	-2.5497
21	6	0.129074	-2.43889	0.706572
22	6	0.142798	-3.75884	-1.19314
23	6	-0.29783	-1.51983	2.836045
24	6	0.142798	-3.75884	1.193141
25	6	-0.26971	-2.81417	3.348952
26	6	-0.26971	-2.81417	-3.34895
27	6	-0.02943	-3.95434	2.549695
28	6	0.249693	-4.70741	0
29	1	0.577216	0.721353	3.506996
30	1	0.036824	4.944671	2.996423
31	1	0.577216	0.721353	-3.507
32	1	0.472254	2.952398	-4.40733
33	1	0.472254	2.952398	4.407329
34	1	0.036824	4.944671	-2.99642
35	1	-1.20022	5.258001	0
36	1	0.546944	5.461022	0
37	1	-0.57722	-0.72135	-3.507
38	1	-0.03682	-4.94467	-2.99642
39	1	-0.57722	-0.72135	3.506996
40	1	-0.47225	-2.9524	4.407329
41	1	-0.47225	-2.9524	-4.40733
42	1	-0.03682	-4.94467	2.996423
43	1	1.200216	-5.258	0
44	1	-0.54694	-5.46102	0

Cartesian Coordination of Optimized Structures: Cartesian coordinates for **3**, optimized at the B3LYP/6-31G(d,p) level of theory.

		Coordinates (Angstroms)		
Center Number	Atomic Type	X	Y	Z
1	8	-5.83844	-0.76329	0
2	6	-2.40466	-0.35791	0.708022
3	6	-2.40466	-0.35791	-0.70802
4	6	-3.71502	-0.46642	1.198809
5	6	-2.84672	0.068187	3.38131
6	6	0	0	-0.72486
7	6	-1.27418	-0.07502	1.462225
8	6	-1.56048	0.176209	2.841588
9	1	-0.77267	0.523318	3.490192
10	6	-1.27418	-0.07502	-1.46223
11	6	-3.94497	-0.28196	2.541139
12	1	-4.95305	-0.34426	2.937633
13	6	-3.71502	-0.46642	-1.19881
14	6	-4.63211	-0.61245	0
15	6	-2.84672	0.068187	-3.38131
16	6	-3.94497	-0.28196	-2.54114
17	1	-4.95305	-0.34426	-2.93763
18	6	-1.56048	0.176209	-2.84159
19	1	-0.77267	0.523318	-3.49019
20	6	-3.14564	0.364911	4.865555
21	6	-3.14564	0.364911	-4.86556
22	6	-3.76868	-0.89174	5.520349
23	1	-4.69831	-1.19287	5.02917
24	1	-3.99902	-0.69555	6.573313
25	1	-3.07767	-1.73988	5.476236
26	6	-4.14525	1.543252	4.962613
27	1	-3.72703	2.448889	4.511512
28	1	-4.37334	1.760471	6.011934

29	1	-5.09008	1.324357	4.457379
30	6	-1.88792	0.743147	5.667266
31	1	-1.15167	-0.06615	5.671563
32	1	-2.16283	0.941832	6.707873
33	1	-1.40804	1.647036	5.277564
34	6	-3.76868	-0.89174	-5.52035
35	1	-3.07767	-1.73988	-5.47624
36	1	-3.99902	-0.69555	-6.57331
37	1	-4.69831	-1.19287	-5.02917
38	6	-4.14525	1.543252	-4.96261
39	1	-5.09008	1.324357	-4.45738
40	1	-4.37334	1.760471	-6.01193
41	1	-3.72703	2.448889	-4.51151
42	6	-1.88792	0.743147	-5.66727
43	1	-1.40804	1.647036	-5.27756
44	1	-2.16283	0.941832	-6.70787
45	1	-1.15167	-0.06615	-5.67156
46	8	5.83844	0.763289	0
47	6	2.404662	0.357907	-0.70802
48	6	2.404662	0.357907	0.708022
49	6	3.715018	0.466415	-1.19881
50	6	2.846722	-0.06819	-3.38131
51	6	0	0	0.724858
52	6	1.274184	0.075018	-1.46223
53	6	1.56048	-0.17621	-2.84159
54	1	0.772673	-0.52332	-3.49019
55	6	1.274184	0.075018	1.462225
56	6	3.944973	0.28196	-2.54114
57	1	4.953045	0.344257	-2.93763
58	6	3.715018	0.466415	1.198809

59	6	4.63211	0.612449	0
60	6	2.846722	-0.06819	3.38131
61	6	3.944973	0.28196	2.541139
62	1	4.953045	0.344257	2.937633
63	6	1.56048	-0.17621	2.841588
64	1	0.772673	-0.52332	3.490192
65	6	3.145644	-0.36491	-4.86556
66	6	3.145644	-0.36491	4.865555
67	6	3.768677	0.891744	-5.52035
68	1	4.698307	1.192869	-5.02917
69	1	3.999018	0.695554	-6.57331
70	1	3.07767	1.739877	-5.47624
71	6	4.145249	-1.54325	-4.96261
72	1	3.727028	-2.44889	-4.51151
73	1	4.373344	-1.76047	-6.01193
74	1	5.090076	-1.32436	-4.45738
75	6	1.887918	-0.74315	-5.66727
76	1	1.151672	0.066147	-5.67156
77	1	2.162826	-0.94183	-6.70787
78	1	1.408038	-1.64704	-5.27756
79	6	3.768677	0.891744	5.520349
80	1	3.07767	1.739877	5.476236
81	1	3.999018	0.695554	6.573313
82	1	4.698307	1.192869	5.02917
83	6	4.145249	-1.54325	4.962613
84	1	5.090076	-1.32436	4.457379
85	1	4.373344	-1.76047	6.011934
86	1	3.727028	-2.44889	4.511512
87	6	1.887918	-0.74315	5.667266
88	1	1.408038	-1.64704	5.277564

89	1	2.162826	-0.94183	6.707873
90	1	1.151672	0.066147	5.671563

Cartesian Coordination of Optimized Structures: Cartesian coordinates for **8**, optimized at the B3LYP/6-31G(d,p) level of theory.

		Coordinates (Angstroms)		
Center Number	Atomic Type	X	Y	Z
1	8	-6.91705	0.788699	5.619633
2	8	-8.5167	-0.54736	-3.88626
3	6	-2.43725	-0.66016	0.217793
4	6	-2.41787	0.747742	0.156645
5	6	-3.75845	-1.12768	0.267665
6	6	-5.35625	0.236684	1.766988
7	6	-1.25355	1.478565	-0.07683
8	6	-3.97874	-2.47658	0.107106
9	1	-4.98827	-2.87439	0.110235
10	6	-7.93782	-0.89514	-1.53007
11	1	-8.86265	-1.41186	-1.30215
12	6	0.01076	0.722812	-0.02586
13	6	-1.57503	-2.82042	-0.19555
14	1	-0.77311	-3.48453	-0.47332
15	6	-1.48661	2.844744	-0.40753
16	1	-0.66302	3.46286	-0.72482
17	6	-3.90144	2.596196	-0.09973
18	1	-4.89513	3.030985	-0.12418
19	6	-5.79011	-0.03188	-0.74207
20	6	-3.7261	1.253983	0.150328
21	6	-1.29738	-1.44148	0.032931

22	6	-2.87421	-3.337	-0.15525
23	6	-7.6735	-0.42036	-2.81812
24	6	-2.76922	3.402129	-0.41262
25	6	-4.72678	0.082716	0.365592
26	6	-6.99889	-0.69748	-0.51325
27	1	-7.22714	-1.06568	0.481579
28	6	-3.02428	4.875305	-0.79664
29	6	-5.54139	0.426747	-2.04681
30	1	-4.61046	0.9372	-2.26809
31	6	-3.17759	-4.82382	-0.43717
32	6	-4.92347	-0.5086	2.873472
33	1	-4.15563	-1.26341	2.746229
34	6	-6.89932	1.418785	3.250316
35	1	-7.66849	2.172692	3.369308
36	6	-6.34988	1.198583	1.986556
37	1	-6.71993	1.786057	1.151923
38	6	-6.46421	0.242345	-3.06798
39	1	-6.26847	0.603911	-4.07223
40	6	-6.45161	0.663456	4.34057
41	6	-7.91337	1.764347	5.876384
42	1	-8.13032	1.700774	6.943775
43	1	-8.83283	1.565822	5.310284
44	1	-7.56121	2.776904	5.640429
45	6	-4.10116	-4.93542	-1.67473
46	1	-5.04795	-4.4077	-1.53043
47	1	-4.33328	-5.98629	-1.88222
48	1	-3.61715	-4.51272	-2.56103
49	6	-5.45969	-0.30329	4.140256
50	1	-5.12196	-0.88523	4.991579
51	6	-1.91124	-5.65219	-0.71758

52	1	-1.36908	-5.28832	-1.59645
53	1	-2.18883	-6.69342	-0.9111
54	1	-1.22745	-5.6475	0.136332
55	6	-1.73053	5.643981	-1.1189
56	1	-1.05433	5.675152	-0.2596
57	1	-1.97382	6.677984	-1.38408
58	1	-1.1928	5.205845	-1.96607
59	6	-3.93382	4.932859	-2.04818
60	1	-3.45532	4.438788	-2.90017
61	1	-4.13212	5.973942	-2.32735
62	1	-4.89801	4.445311	-1.87903
63	6	-3.88788	-5.44445	0.790013
64	1	-3.25097	-5.38977	1.679052
65	1	-4.11979	-6.49908	0.602829
66	1	-4.8275	-4.9347	1.021349
67	6	-3.7243	5.598369	0.379346
68	1	-4.68137	5.134914	0.635053
69	1	-3.92079	6.644872	0.119911
70	1	-3.09671	5.582341	1.276317
71	6	-9.74983	-1.21859	-3.68785
72	1	-9.59998	-2.25815	-3.36866
73	1	-10.2571	-1.21053	-4.6538
74	1	-10.3774	-0.70561	-2.94749
75	8	6.917048	-0.7887	-5.61963
76	8	8.516697	0.547358	3.886264
77	6	2.437254	0.660159	-0.21779
78	6	2.417871	-0.74774	-0.15665
79	6	3.758446	1.127676	-0.26767
80	6	5.356252	-0.23668	-1.76699
81	6	1.253551	-1.47857	0.076831

82	6	3.978736	2.476579	-0.10711
83	1	4.988267	2.874393	-0.11024
84	6	7.937819	0.89514	1.530068
85	1	8.86265	1.411855	1.302152
86	6	-0.01076	-0.72281	0.025864
87	6	1.575031	2.820416	0.195551
88	1	0.773114	3.484525	0.473316
89	6	1.486609	-2.84474	0.40753
90	1	0.663021	-3.46286	0.72482
91	6	3.901437	-2.5962	0.099733
92	1	4.895131	-3.03099	0.124179
93	6	5.790108	0.031877	0.742068
94	6	3.7261	-1.25398	-0.15033
95	6	1.297379	1.441477	-0.03293
96	6	2.874207	3.337004	0.15525
97	6	7.673498	0.420362	2.81812
98	6	2.769216	-3.40213	0.412615
99	6	4.726775	-0.08272	-0.36559
100	6	6.998887	0.697476	0.513247
101	1	7.227142	1.065677	-0.48158
102	6	3.024284	-4.87531	0.79664
103	6	5.54139	-0.42675	2.046806
104	1	4.610461	-0.9372	2.268089
105	6	3.177588	4.823823	0.437168
106	6	4.923469	0.508604	-2.87347
107	1	4.155632	1.263414	-2.74623
108	6	6.899317	-1.41879	-3.25032
109	1	7.668494	-2.17269	-3.36931
110	6	6.349884	-1.19858	-1.98656
111	1	6.719929	-1.78606	-1.15192

112	6	6.464208	-0.24235	3.067975
113	1	6.268474	-0.60391	4.072228
114	6	6.451614	-0.66346	-4.34057
115	6	7.913368	-1.76435	-5.87638
116	1	8.130316	-1.70077	-6.94378
117	1	8.832829	-1.56582	-5.31028
118	1	7.561208	-2.7769	-5.64043
119	6	4.101158	4.935421	1.674726
120	1	5.047952	4.407703	1.530426
121	1	4.33328	5.986285	1.882215
122	1	3.617145	4.512721	2.561034
123	6	5.459686	0.303288	-4.14026
124	1	5.121964	0.885227	-4.99158
125	6	1.911244	5.652185	0.717583
126	1	1.369077	5.288317	1.596449
127	1	2.188827	6.693422	0.911102
128	1	1.227451	5.647496	-0.13633
129	6	1.730533	-5.64398	1.1189
130	1	1.054334	-5.67515	0.2596
131	1	1.973818	-6.67798	1.384079
132	1	1.192804	-5.20585	1.966066
133	6	3.933815	-4.93286	2.048179
134	1	3.45532	-4.43879	2.900168
135	1	4.132123	-5.97394	2.327353
136	1	4.89801	-4.44531	1.879031
137	6	3.88788	5.444451	-0.79001
138	1	3.250972	5.389765	-1.67905
139	1	4.119787	6.499076	-0.60283
140	1	4.827496	4.934695	-1.02135
141	6	3.724298	-5.59837	-0.37935

142	1	4.681373	-5.13491	-0.63505
143	1	3.920785	-6.64487	-0.11991
144	1	3.096707	-5.58234	-1.27632
145	6	9.749832	1.218592	3.687852
146	1	9.59998	2.258152	3.36866
147	1	10.25707	1.210534	4.653797
148	1	10.37744	0.70561	2.947487