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Supporting Information

Solution-Processable Multi-Substituted Buckybowls: Synthesis of Diindeno(1,2,3,4-*defg*:1′,2′,3′,4′-*mnop*)chrysene Derivatives

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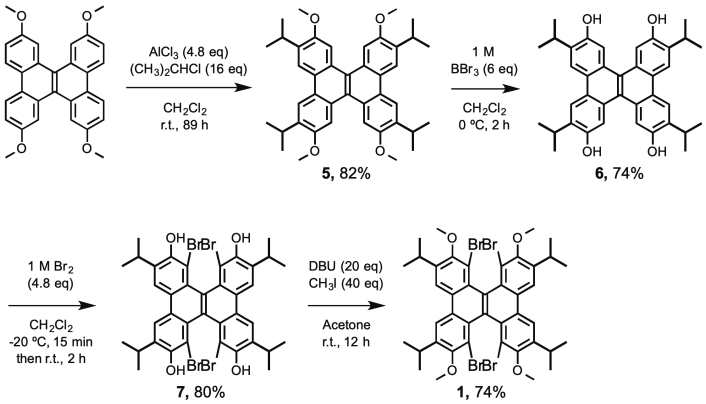
Contents

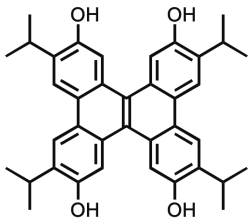
1. General Information. All reactions sensitive to air or moisture were carried out under an argon or a nitrogen atmosphere and anhydrous conditions unless otherwise noted. Dry solvents were purchased and used without further purification and dehydration. All reagents were purchased and used without further purification. Analytical thin layer chromatography was carried out on Merck silica 60F_{254}. Column chromatography was carried out with silica gel 60 $_N$ (Kanto Chemical Co.). LRMS and HRMS were reported on the basis of TOF (time of flight)-MS (MADI-TOF or LCMS-IT-TOF), and DART (Direct Analysis in Real Time)-MS. ^{1}H and ^{13}C NMR spectra were recorded with a 5 mm QNP probe at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in d (ppm) with reference to residual solvent signals [^{1}H NMR: $CHCl_3$ (7.26), C_7H_8 (2.08), C_6H_6 (7.16), CH_2Cl_2 (5.32); ^{13}C NMR: $CDCl_3$ (77.0)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. All melting points were recorded on Yanaco Model MP-500D melting point apparatus and are not corrected.

2. Synthesis of **1** *via* **5**, **6**, and **7** (Scheme S1). 2,7,10,15-tetraisopropyl-3,6,11,14-tetramethoxydibenzo[*g*,*p*]chrysene **5**: Under an Ar atmosphere, to a suspension of the starting DBC having four methoxy groups (4.49 g, 10 mmol) in CH_2Cl_2 (50 mL) was added $AlCl_3$ (6.40 g, 48 mmol) and 2-chloropropane (14.6 mL, 160 mmol). After stirred for 89 h at room temperature, the reaction mixture was quenched at 0 °C with slow addition (10 min) of 1 M aq. HCl (200 mL). The aqueous layer was extracted with CH_2Cl_2 (50 mL × 3), and combined organic phases were washed with brine (50

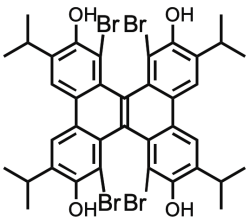


mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 7.51 g of crude products. Purification by short-plugged column chromatography (eluent, hexane/ CH_2Cl_2, 4:1) afforded 5.07 g of **5** in 82% yield as yellow solid materials. Data of **5**: Rf value 0.52 (Hexane/EtOAc, 4:1); M.p. 253-255 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.42 (s, 4H), 8.19 (s, 4H), 3.96 (s, 12H), 3.53 (sept, J = 6.9 Hz, 4H), 1.45 (d, J = 6.9 Hz, 24H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.7, 137.4, 128.2, 127.7, 125.0, 121.0, 108.5, 55.9, 28.0, 23.2 ppm; MS (DART-TOF) *m/z*: 617 $[MH]^+$; IR (neat): 2956, 2865, 1619, 1491, 1459, 1412, 1244, 1045, 877 cm^{-1}; HRMS (DART-TOF) calcd for $C_{42}H_{49}O_4$: 617.3631 $[MH]^+$, found: 617.3626; Anal. Calcd for $C_{42}H_{48}O_4$: C, 82.05; H, 7.54. Found: C, 82.03; H, 7.56.

2,7,10,15-tetraisopropyldibenzo[*g*,*p*]chrysene-3,6,11,14-tetraol **6**: Under an Ar atmosphere, to the solution of **5** (6.79 g, 11 mmol) in dry CH_2Cl_2 (55 mL) at 0 ºC was added BBr_3 (66 mL, 66 mmol, 1 M CH_2Cl_2 solution) dropwise over 5 min. After stirred at 0 °C for 2 h, the mixture was quenched with 1 M aq. HCl (125 mL). The aqueous layer was extracted with EtOAc (50 mL × 3). The combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 5.63 g of crude products as dark green solid materials. Purification by short-plugged column chromatography (eluent, toluene/EtOAc = 9/1) afforded 4.37 g of the desired **6** in 74% yield as green solid materials. Data of **6**: Rf value 0.42 (Hexane/EtOAc, 2:1); M.p. 232-233 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.37 (s, 4H), 8.07 (s, 4H), 5.32 (s, 4H), 3.41 (sept, J = 6.9 Hz, 4H), 1.46 (d, J = 6.9 Hz, 24H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 151.8, 135.3, 128.3, 126.9, 125.6, 121.4, 113.2, 28.4, 23.1 ppm; MS (DART-TOF) *m/z*: 561 $[MH]^+$; IR (neat): 3386, 2956, 2865, 1623, 1499, 1423, 1236, 1152, 989, 877 cm^{-1}; HRMS (DART-TOF) calcd for $C_{38}H_{41}O_4$: 561.3005 $[MH]^+$, found: 561.2988.

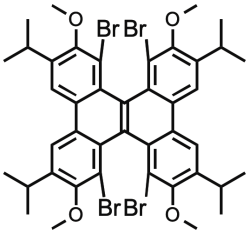


4,5,12,13-tetrabromo-2,7,10,15-tetraisopropyldibenzo[*g*,*p*]chrysene-3,6,11,14-tetraol **7**:



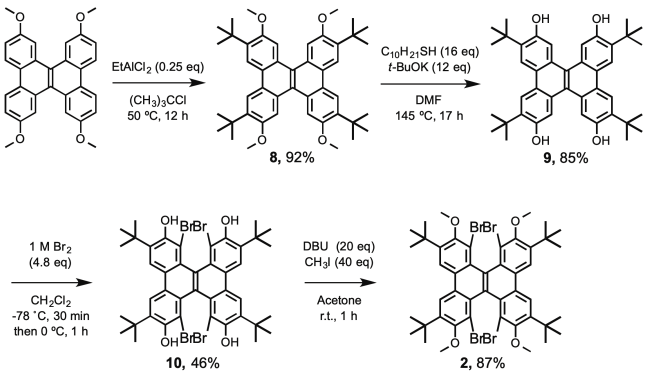
Under an Ar atmosphere, to a 500 mL flask was added **6** (5.89 g, 10.5 mmol) and CH_2Cl_2 (105 mL). After the mixture was stirred for 15 min at -20 ºC, a solution of 1 M Br_2 in CH_2Cl_2 (50.5 mL, 50.5 mmol) was added dropwise over 10 min, and the resultant dark brown suspension was stirred at -20 ºC for 15 min. The reaction mixture was stirred over 2 h at room temperature, and quenched at 0 ºC with saturated aq. $Na_2S_2O_3$ (130 mL). 1 M aqueous HCl (130 mL) was added, and the resultant mixture was diluted with EtOAc, and the aqueous phase was extracted with EtOAc (50 mL × 3). Combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 11.2 g of crude products as brownish yellow solid materials. Purification by short-plugged silica-gel column chromatography (eluent, toluene only) afforded 7.39 g of the desired **7** in 80% yield as yellow solid. Data of **7**: Rf value 0.35 (Hexane/EtOAc, 4:1); M.p. > 300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.39 (s, 4H), 6.17 (s, 4H), 3.55 (qq, J = 6.9, 6.9 Hz, 4H), 1.53 (d, J = 6.9 Hz, 12H), 1.42 (d, J = 6.9 Hz, 12H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 149.7, 136.3, 133.0, 128.0, 122.9, 119.9, 110.3, 28.0, 22.4, 22.2 ppm; MS (DART-TOF) *m/z*: 877 $[MH]^+$; IR (neat): 3438, 2959, 2865, 1144, 752, 582 cm^{-1}; HRMS (DART-TOF) calcd for $C_{38}H_{37}Br_4O_4$: 876.9384 $[MH]^+$, found: 876.9352.

4,5,12,13-tetrabromo-2,7,10,15-tetraisopropyl-3,6,11,14-tetramethoxydibenzo[*g*,*p*]chrysene **1**: Under an Ar atmosphere, to a suspension of **7** (11.0 g, 12.6 mmol) in acetone (200 mL) was added CH_3I (31.4 mL, 504 mmol). The base of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, 37.5 mL, 252 mmol) was added dropwise over 5 min. After stirred at room temperature for 12 h, the reaction was quenched with 3 M aq. HCl (300 mL) at 0 ºC. The aqueous layer was extracted with toluene (70 mL × 3), and combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 10.8 g of crude products.



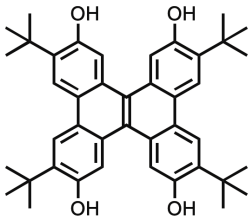
Purification by silica-gel column chromatography (eluent, hexane/EtOAc, 19:1) afforded 8.63 g of **1** as yellow solid materials (74%). Data of **1**: Rf value 0.33 (Hexane/EtOAc, 9:1); M.p. 170-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.42 (s, 4H), 3.99 (s, 12H), 3.56 (qq, J = 6.9, 6.9 Hz, 4H), 1.55 (d, J = 6.9 Hz, 12H), 1.39 (d, J = 6.9 Hz, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.0, 142.2, 134.7, 130.4, 127.4, 121.7, 118.6, 62.1, 29.0, 24.6, 24.5 ppm; MS (DART-TOF) *m/z*: 933 $[MH]^+$; IR (neat): 2955, 2928, 1456, 1389, 1330, 1254, 1040, 784 cm^{-1}; HRMS (DART-TOF) calcd for $C_{42}H_{45}Br_4O_4$: 933.0010 $[MH]^+$, found: 932.9991; Anal. Calcd for $C_{42}H_{44}Br_4O_4$: C, 54.10; H, 4.76. Found: C, 54.39; H, 4.98.

2. Synthesis of **2** *via* **8**, **9**, and **10** (Scheme S2). 2,7,10,15-tetra-*tert*-butyl-3,6,11,14-tetramethoxydibenzo[*g*,*p*]chrysene **8**: Under an Ar atmosphere, to a 200 mL flask was added the starting DBC bearing four methoxy moieties (3.59 g, 8.0 mmol) and *tert*-butyl chloride (40 mL, 360 mmol). The solution was stirred for 10 min, and $EtAlCl_2$ (2 mL, 2.0 mmol, 1.0 M in hexane) was added dropwise over 1 min. After stirred for 12 h at 50 °C, the reaction mixture was quenched at 0 °C by adding H_2O over 5 min (70 mL). The aqueous layer was extracted with toluene (30 mL × 3), and combined organic phases were washed with brine (100 mL × 1), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 5.80 g of crude products. Purification by short-plugged silica-gel column chromatography (eluent, hexane/toluene, 9:1) afforded 4.95 g of of **8** as yellowish white solid materials (92%). Data of **8**: Rf value 0.56 (Hexane/EtOAc, 9:1); M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.53 (s, 4H), 8.21 (s, 4H), 3.98 (s, 12H), 1.59 (s, 36H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 157.2, 138.5, 128.4, 127.4, 124.8,



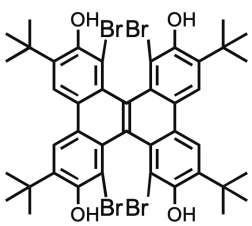
121.6, 109.5, 55.6, 35.7, 30.2 ppm; MS (DART-TOF) *m/z*: 673 $[MH]^+$; IR (neat) 2949, 1610, 1491, 1451, 1404, 1228, 1085, 882, 838 cm^{-1}; HRMS (DART-TOF) calcd for $C_{46}H_{57}O_4$: 673.4257 $[MH]^+$, found; 673.4261; Anal. Calcd for $C_{46}H_{56}O_4$; C, 82.10; H, 8.39. Found: C, 82.10; H, 8.43.

2,7,10,15-tetra-tert-butyldibenzo[g,p]chrysene-3,6,11,14-tetraol **9**: Under an Ar



atmosphere, to a solution of 1-decanethiol (31 mL, 150 mmol) in anhydrous *N,N*-dimethylformamide (180 mL) at 0 °C was added potassium *tert*-butoxide (12.6 g, 112 mmol). After stirred for 15 min at 0 °C, the reaction mixture was allowed to warm to room temperature, then **8** (6.30 g, 9.36 mmol) was added. After the mixture was stirred at 145 °C for 17 h, the reaction was quenched with 1 M aq. HCl at 0 ºC. The aqueous layer was extracted with EtOAc (50 mL × 3), and combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 30.1 g of crude products. Purification by short-plugged silica-gel column chromatography (eluent, toluene/CH_2Cl_2, 4:1) afforded 4.91 g of **9** as greenish yellow solid materials (85%). Data of **9**: Rf value 0.30 (Hexane/EtOAc, 4:1); M.p. > 300 ºC; ^1H NMR (400 MHz, $CDCl_3$) 8.50 (s, 4H), 7.96 (s, 4H), 5.09 (s, 4H), 1.61 (s, 36H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 152.7, 136.6, 128.1, 126.2, 125.0, 121.7, 114.0, 35.3, 29.8 ppm; MS (DART-TOF) *m/z*: 616 $[M]^+$; IR (neat) 3598, 3538, 3379, 2952, 2909, 2865, 1619, 1415, 1165, 882 cm^{-1}; HRMS (DART-TOF) calcd for $C_{42}H_{48}O_4$: 616.3553 $[M]^+$, found; 616.3533.

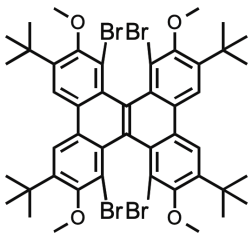
4,5,12,13-tetrabromo-2,7,10,15-tetra-*tert*-butyldibenzo[*g,p*]chrysene-3,6,11,14-tetraol **10**: Under an Ar atmosphere, to a solution of **9** (6.17 g, 10 mmol) in anhydrous CH_2Cl_2



(104 mL) at -78 °C was added a solution of 1 M Br_2 in CH_2Cl_2 (48 mL, 48 mmol) dropwise over 15 min, and then the mixture was stirred at -78 ºC for 30 min. After stirred at 0 ºC for 1 h, the reaction was quenched with 3 M aq. $Na_2S_2O_3$ (15 mL), and followed by additional

stirring for 10 min at 0 °C. The aqueous layer was extracted with EtOAc (50 mL × 3). The combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give 8.32 g of crude products. Purification by short-plugged silica-gel column chromatography (eluent, hexane/toluene, 4:1) afforded 4.31 g of yellow solid materials (46%). Data of **10**: Rf value 0.44 (Hexane/EtOAc, 9:1); M.p. > 300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.52 (s, 4H), 6.38 (s, 4H), 1.61 (s, 36H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.6, 137.0, 133.1, 127.9, 123.8, 121.2, 112.2, 36.1, 29.7 ppm; MS (DART-TOF) *m/z*: 932 $[M]^+$; IR (neat) 3458, 2952, 2908, 2865, 1405, 1385, 1175, 1025, 875, 728 cm^{-1}; HRMS (DART-TOF) calcd for $C_{42}H_{44}Br_4O_4$: 931.9932 $[M]^+$, found; 931.9931.

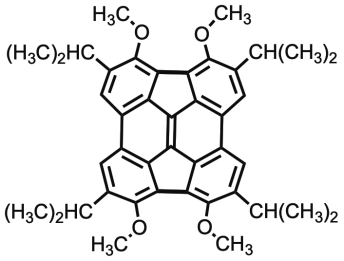
4,5,12,13-tetrabromo-2,7,10,15-tetra-*tert*-butyl-3,6,11,14-tetramethoxydibenzo[*g*,*p*]chrysene **2**: Under an Ar atmosphere, to a suspension of **10**



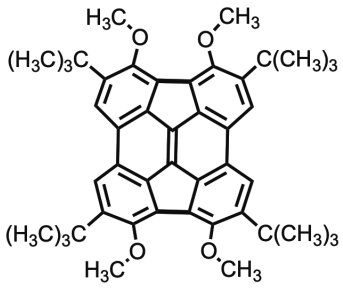
(11.1 g, 12 mmol) in acetone (150 mL) was added CH_3I (30 mL, 480 mmol), and then 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, 36 mL, 240 mmol) was added dropwise over 12 min. After stirred at room temperature for 1 h, the mixture was quenched with 1 M aq. HCl (100 mL), and stirred for 15 min at 0 °C. The aqueous layer was extracted with toluene (100 mL × 3). The combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give 12.5 g of crude products. Purification by short-plugged silica-gel column chromatography (eluent, hexane/toluene = 2/1) afforded 10.3 g of **2** as whitish yellow solid materials (87%). Data of **2**: Rf value 0.41 (Hexane/Toluene, 1:1); M.p. > 300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.53 (s, 4H), 4.15 (s, 12H), 1.59 (s, 36H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 157.1, 142.9, 134.1, 130.5, 126.4, 122.1, 118.6, 61.8, 36.1, 30.9 ppm; MS (DART-TOF) *m/z*: 989 $[MH]^+$; IR (neat) 2955, 2920, 2853, 1373, 1358, 1230, 1207, 1045, 827 cm^{-1}; HRMS (DART-TOF) calcd for $C_{46}H_{53}Br_4O_4$: 989.0636 $[MH]^+$, found; 989.0696; Anal. Calcd for $C_{46}H_{52}Br_4O_4$; C,

55.89; H, 5.30. Found: C, 55.88; H, 5.42.

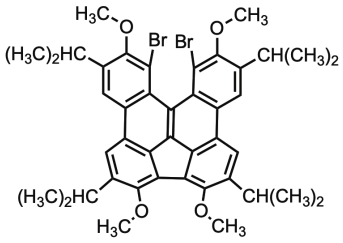
3. Synthesis of 2,5,8,11-tetraisopropyl-1,6,7,12-tetramethoxydiindeno[1,2,3,4-*defg*:1',2',3',4'-*mnop*]chrysene **3** (entry 5 in Table 2; this was described in the experimental section of the manuscript): Under an Ar atmosphere, to a solution of **1** (5.04 g, 5.4 mmol) in anhydrous *N*,*N*-dimethylformamide (100 mL) was added *N*,*N*-diisopropylethylamine (7.2 mL, 43 mmol), and bis(tri-*tert*-butylphosphine)palladium(0) (2.76 g, 5.4 mmol), and tri-*tert*-butylphosphine (10.8 mL, 10.8 mmol, 1.0 M in hexane). The reaction mixture was allowed to warm to 125 ºC, then stirred for 2 h, the reaction mixture was allowed to cool to ambient temperature. The mixture was filtered through a pad of celite, the organic phase was washed with brine (50 mL × 3), and dried over Na_2SO_4, and concentrated *in vacuo* to give products as reddish brown viscous materials. Purification by short-plugged silica-gel column chromatography (eluent, toluene/hexane, 2:1) afforded 2.88 g as yellow solid materials. Purification by silica-gel column chromatography (eluent, hexane/toluene, 2:1) gave 2.05 g of **3** (62%) as yellow solid materials. Data of **3**: Rf value 0.47 (Hexane/EtOAc, 9:1); M.p. > 250 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.22 (s, 4H), 4.09 (s, 12H), 3.67 (sept, J = 6.8 Hz, 4H), 1.44 (d, J = 6.8 Hz, 24H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.5, 145.1, 138.2, 135.7, 130.1, 129.4, 123.7, 64.9, 28.7, 25.2 ppm; MS (DART-TOF) *m/z*: 613 $[MH]^+$; IR (neat) 2955, 2865, 1456, 1405, 1309, 1049, 1029, 989, 867 cm^{-1}; HRMS (DART-TOF) calcd for $C_{42}H_{45}O_4$: 613.3318 $[MH]^+$, found; 613.3314; Anal. Calcd for $C_{42}H_{44}O_4$; C, 82.32; H, 7.24. Found: C, 82.32; H, 7.15.



4. Synthesis of 2,5,8,11-tetra-*tert*-butyl-1,6,7,12-tetramethoxydiindeno[1,2,3,4-*defg*:1',2',3',4'-*mnop*]chrysene **4** (entry 12 in Table 1): Under an Ar atmosphere, to a



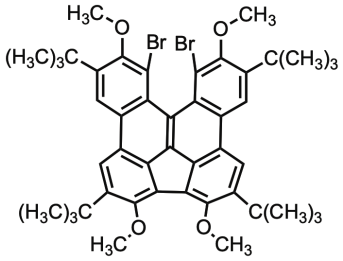
solution of **2** (148 mg, 0.15 mmol) in anhydrous *N*-methylpyrrolidone (3 mL) was added *N*,*N*-diisopropylethylamine (0.2 mL, 1.2 mmol) and bis(tri-*tert*-butylphosphine)palladium(0) (77 mg, 0.15 mmol), and tri-*tert*-butylphosphine (0.3 mL, 0.3 mmol, 1.0 M in hexane). The reaction mixture was allowed to warm to 125 ºC, and additionally stirred for 2 h. Then, the mixture was allowed to cool to ambient temperature, and filtered through a pad of celite. The organic phase was washed with brine (10 mL × 3), and dried over Na_2SO_4, and concentrated *in vacuo* to give a crude product. Purification by silica-gel column chromatography (eluent, hexane/toluene, 2:1) afforded 25 mg of **4** (25%) as yellow solid materials. Data of **4**: Rf value 0.55 (Hexane/Toluene, 4:1); M.p. > 300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.30 (s, 4H), 4.03 (s, 12H), 1.62 (s, 36H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 157.6, 145.9, 138.3, 135.0, 130.1, 127.9, 123.6, 63.6, 37.0, 31.8 ppm; MS (DART-TOF) *m/z*: 669 $[MH]^+$; IR (neat) 2952, 1395, 1292, 1244, 1221, 993 cm^{-1}; HRMS (DART-TOF) calcd for $C_{46}H_{53}O_4$: 669.3944 $[MH]^+$, found; 669.3934; Anal. Calcd for $C_{46}H_{52}O_4$; C, 82.60; H, 7.84. Found: C, 82.60; H, 7.84.



5.Data of side-products **11**, **12**, **13**, and **14**.

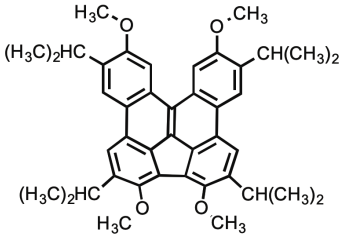
Data of 1,14-dibromo-3,6,9,12-tetraisopropyl-2,7,8,13-tetramethoxybenzo[*p*]indeno[1,2,3,4-*defg*]chrysene **11**: Rf value 0.33 (Hexane/EtOAc, 9:1); M.p. 267-270 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.57 (s, 2H), 8.31 (s, 2H), 4.18 (s, 6H), 4.15 (s, 6H), 3.77 (sept, J = 6.8 Hz, 2H), 3.64 (qq, J = 6.8, 6.8 Hz, 2H) 1.56-1.49 (m, 24H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.8, 153.8, 146.7, 141.2, 134.2, 132.1, 131.4, 130.6, 126.8, 124.4, 122.0, 121.0, 120.7, 120.5, 64.6, 62.2, 28.6, 28.4, 25.0, 24.8, 24.3, 24.2 ppm; MS (DART-TOF) *m/z*: 773 $[MH]^+$; IR (neat) 2955, 2865, 1456, 1405, 1286, 1219, 1057, 993, 871 cm^{-1}; HRMS

(DART-TOF) calcd for $C_{42}H_{45}Br_2O_4$: 773.1664 $[MH]^+$, found; 773.1623; Anal. Calcd for $C_{42}H_{44}Br_2O_4$; C, 65.29; H, 5.74. Found: C, 65.01; H, 5.56.

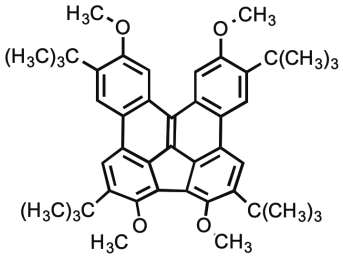


Data of 1,14-dibromo-3,6,9,12-tetra-*tert*-butyl-2,7,8,13-tetramethoxybenzo[*p*]indeno[1,2,3,4-*defg*]chrysene **12**: Rf value 0.42 (Hexane/Toluene, 2:1); M.p. > 300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.68 (s, 2H), 8.41 (s, 2H), 4.35 (s, 6H), 4.14 (s, 6H), 1.67 (s, 18H), 1.65 (s, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 158.5, 156.1, 147.6, 142.34, 142.32, 133.8, 132.7, 132.0, 129.9, 127.2, 123.3, 123.2, 121.52, 121.48, 121.0, 120.8, 63.4, 62.2, 37.0, 36.2, 31.5, 31.3 ppm; MS (DART-TOF) *m/z*: 829 $[MH]^+$; IR (neat) 2952, 1404, 1332, 1244, 1208, 1057, 1029, 993, 806 cm^{-1}; HRMS (DART-TOF) calcd for $C_{46}H_{53}Br_2O_4$: 829.2290 $[MH]^+$, Found; 829.2233. Anal. Calcd for $C_{46}H_{52}Br_2O_4$; C, 66.67; H, 6.32. Found: C, 66.35; H, 6.11.

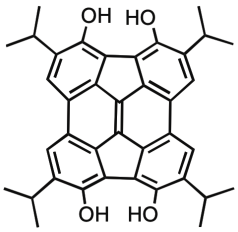
Data of 3,6,9,12-tetraisopropyl-2,7,8,13-tetramethoxybenzo[*p*]indeno[1,2,3,4-*defg*]chrysene **13**: Rf value 0.47 (Hexane/EtOAc, 9:1); M.p. > 300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.74 (s, 2H), 8.64 (s, 2H), 8.35 (s, 2H), 4.18 (s, 6H), 4.17 (s, 6H), 3.79 (sept, J = 6.9 Hz, 2H), 3.61 (sept, J = 6.9 Hz, 2H), 1.55 (d, J = 6.9 Hz, 12H), 1.51 (d, J = 6.9 Hz, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 156.3, 154.9, 145.5, 136.4, 131.8, 131.4, 131.2, 126.9, 126.6, 124.2, 122.4, 122.0, 120.2, 107.5, 64.7, 55.7, 28.2, 28.1, 25.0, 23.1 ppm; MS (DART-TOF) *m/z*: 615 $[MH]^+$; IR (neat) 2956, 2925, 2865, 1403, 1312, 1049, 1034, 989, 874 cm^{-1}; HRMS (DART-TOF) calcd for $C_{42}H_{47}O_4$: 615.3474 $[MH]^+$, found; 615.3453. Anal. Calcd for $C_{42}H_{46}O_4$; C, 82.05; H, 7.54. Found: C, 82.03; H, 7.56.



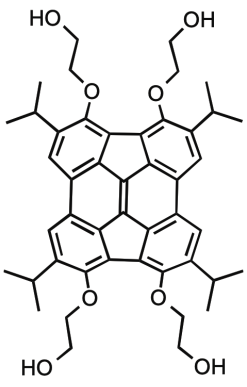
6. Data of 3,6,9,12-tetra-*tert*-butyl-2,7,8,13-tetramethoxybenzo[*p*]indeno[1,2,3,4-*defg*]chrysene **14**: Rf value 0.44 (Hexane/Toluene, 4:1); M.p. > 300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.73 (s, 4H), 8.43 (s, 2H), 4.19 (s, 6H), 4.15 (s, 6H), 1.68 (s, 18H), 1.63 (s, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 157.7, 157.6, 146.3, 137.5, 132.4, 131.4, 130.9, 127.0, 126.7, 123.0, 122.6, 121.2, 120.4, 108.6, 63.6, 55.4, 36.9, 35.7, 31.6, 30.2 ppm; MS (DART-TOF) *m/z*: 671 $[MH]^+$; IR (neat) 2952, 2913, 1451, 1340, 1249, 1208, 1053, 993 cm^{-1}; HRMS (DART-TOF) calcd for $C_{46}H_{55}O_4$: 671.4100 $[MH]^+$, found; 671.4081.



7. Synthesis of **15** and **16** (Scheme 4(a)), 2,5,8,11-tetraisopropyldiindeno[1,2,3,4-*defg*:1',2',3',4'-*mnop*]chrysene-1,6,7,12-tetraol **15**: Under an Ar atmosphere, to a 50 mL flask was added **3** (612 mg, 1.0 mmol) and CH_2Cl_2 (10 mL). After the mixture was stirred for 15 min at 0 ºC, 1 M BBr_3 in CH_2Cl_2 (6.0 mL, 6.0 mmol) was added dropwise over 4 min. The mixture was conducted at 0 ºC for 15 min, then allowed to warm to room temperature over 4 h. The reaction was quenched at 0 ºC with water (20 mL). The resultant mixture was diluted with EtOAc, and the aqueous phase was extracted with EtOAc (20 mL × 3). Combined organic phases were washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give a crude product. Purification by silica-gel column chromatography (eluent, toluene/EtOAc, 19:1) afforded 419 mg of **15** (75%) as yellowish green solid materials. Data of **15**: Rf value 0.56 (Hexane/EtOAc, 1:1); M.p. > 300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.05 (s, 4H), 7.04 (s, 4H), 3.39 (sept, J = 6.8 Hz, 4H), 1.45 (d, J = 6.8 Hz, 24H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 148.2, 139.0, 137.0, 136.3, 127.7, 124.7, 123.0, 27.5, 23.6 ppm; MS (DART-TOF) *m/z*: 557 $[MH]^+$; IR (neat) 3391, 2955, 2928, 1433, 1286, 1190, 1160, 1049, 863, 634, 582 cm^{-1}; HRMS

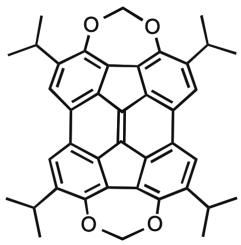


(DART-TOF) calcd for $C_{38}H_{37}O_4$: 557.2692 $[MH]^+$, found; 557.2692.



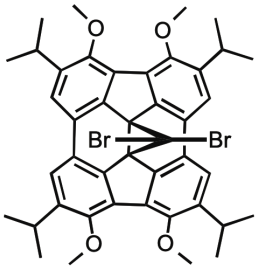
2,2',2'',2'''-((2,5,8,11-tetraisopropyldiindeno[1,2,3,4-*defg*:1',2',3',4'-*mnop*]chrysene-1,6,7,12-tetrayl)tetrakis(oxy))tetrakis(ethan-1-ol) **16**: Under an Ar atmosphere, to a solution of **15** (111 mg, 0.15 mmol) in MeOH (12 mL) was added K_2CO_3 (332 mg, 2.4 mmol) and 2-chloroethanol (0.6 mL, 7.2 mmol). After stirred at 50 ºC for 46 h, the reaction was quenched with 1 M aq. HCl (10 mL) at 0 ºC. The aqueous layer was extracted with EtOAc (10 mL × 3), and combined organic phases were washed with brine (10 mL × 3), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 196 mg of crude products. Purification by silica-gel column chromatography (eluent, EtOAc/hexane, 2:1) afforded 88 mg of **16** as yellow solid materials (61%). Data of **16**: Rf value 0.30 (Hexane/EtOAc, 1:2); M.p. > 300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.26 (s, 4H), 4.28 (t, J = 4.0 Hz, 8H), 4.01 (t, J = 4.0 Hz, 8H), 3.86 (brs, 4H), 3.64 (sept, J = 6.8 Hz, 4H), 1.45 (d, J = 6.8 Hz, 24H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 152.4, 144.6, 137.6, 135.0, 130.2, 129.0, 124.0, 78.8, 62.0, 28.0, 24.7 ppm; MS (DART-TOF) *m/z*: 733 $[MH]^+$; IR (neat) 3347, 2956, 2921, 1425, 1284, 1180, 1053, 870 cm^{-1}; HRMS (DART-TOF) calcd for $C_{46}H_{53}O_8$: 733.3740 $[MH]^+$, found; 733.3724.

8. Synthesis of 10,16,21,27-Tetrakis(isopropyl)-12,14,23,25-tetraoxadecacyclo[17.13.0.$0^{2,30}$.$0^{3,7}$.$0^{4,18}$.$0^{5,15}$.$0^{6,11}$.$0^{8,29}$.$0^{22,32}$.$0^{26,31}$]dotriaconta-1(32),2,4,6,8,10,15,17,19,21,26,28,30-tridecaene **17** (Scheme 4(b)), **17**: Under an Ar atmosphere, to a solution of **15** (168 mg, 0.29 mmol) in DMSO (3.0 mL) and toluene (0.75 mL) was added K_2CO_3 (166 mg, 1.2 mmol) and CH_2BrCl (1.5 mL, 6.0 mmol). After the mixture was stirred at 55 ºC for 2 h, the reaction was quenched with H_2O (3 mL) at 0 ºC, and the



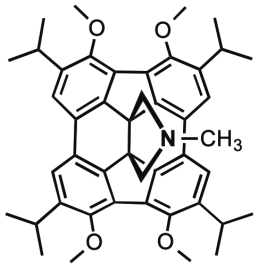
resultant mixture was transferred into a 50 mL separatory funnel. The aqueous phase was extracted with CH_2Cl_2 (10 mL × 3), and the combined organic phases were washed with water (10 mL) and brine (10 mL), and dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 374 mg of crude products. After short-plugged silica-gel column chromatography (eluent, hexane/EtOAc, 9:1) afforded 148 mg of **16** as yellow solid materials (85%). Data of **17**: Rf value 0.62 (Hexane/EtOAc, 4:1); M.p. > 300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 7.82 (s, 4H), 6.68 (d, J = 7.3 Hz, 2H), 6.18 (d, J = 7.3 Hz, 2H), 3.42 (qq, J = 6.9, 6.9 Hz, 4H), 1.44 (d, J = 6.9 Hz, 12H), 1.22 (d, J = 6.9 Hz, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 156.4, 141.8, 141.4, 137.8, 132.0, 126.7, 122.4, 96.6, 28.9, 24.2, 23.7 ppm; MS (DART-TOF) *m/z*: 581 $[MH]^+$; IR (neat) 2955, 1460, 1420, 1298, 1223, 938 cm^{-1}; HRMS (DART-TOF) calcd for $C_{40}H_{37}O_4$: 581.2692 $[MH]^+$, found; 581.2662.

9. Synthesis of 13,13-dibromo-2,5,8,11-tetraisopropyl-1,6,7,12-tetramethoxy-3a^2,3b^2-methanodiindeno[1,2,3,4-*defg*:1',2',3',4'-*mnop*]chrysene **18** (Scheme 4(d)), **18**: To a solution of **14** (183 mg, 0.23 mmol) in benzene (30 mL) was added commercially available 50 % (v/v) aqueous NaOH (15 mL, 287 mmol) and benzyltriethylammonium chloride (34 mg, 0.15 mmol) and bromoform (0.8 mL, 9.0 mmol). After the mixture was stirred at room temperature for 4 h, the reaction was quenched with saturated aq. NH_4Cl (50 mL) at 0 ºC. The aqueous layer was extracted with EtOAc (30 mL × 3), and combined organic phases were washed with brine (30 mL × 3), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give crude products. Purification by short-plugged silica-gel column chromatography (eluent, hexane/CH_2Cl_2, 2:1) afforded 115 mg of **18** as brownish yellow solid materials (49%). Data of **18**: Rf value 0.36 (Hexane/CH_2Cl_2, 2:1); M.p. 291-293 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 7.44 (s, 4H), 3.90 (s, 12H), 3.43 (qq, J =



6.9, 6.9 Hz, 4H), 1.33 (d, J = 6.9 Hz, 12H), 1.25 (d, J = 6.9 Hz, 12H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) 154.3, 144.6, 140.9, 132.9, 128.9, 121.0, 64.1, 55.4, 29.9, 27.9, 24.6, 23.7 ppm; MS (DART-TOF) *m/z*: 785 $[MH]^+$; IR (neat) 2960, 1455, 1225, 1206, 1077, 1001, 1001, 982, 868 cm^{-1}; HRMS (DART-TOF) calcd for $C_{43}H_{45}Br_2O_4$: 785.1664 $[MH]^+$, found; 785.1681.

10. Synthesis of 2,5,8,11-tetraisopropyl-1,6,7,12-tetramethoxy-14-methyl-3a^2,3b^2-(methanoiminomethano)diindeno[1,2,3,4-*defg*:1',2',3',4'-*mnop*]chrysene **19** (Scheme 4(c)), **19**: Under an Ar atmosphere, to a solution of **14** (61 mg, 0.1 mmol) in toluene (30 mL) was added *N*-methylglycine (18 mg, 0.2 mmol) and paraformaldehyde (15 mg, 0.5 mmol). After the mixture was conducted at 125 ºC for 15 min, both the *N*-methylglycine (18 mg) and paraformaldehyde (15 mg) were successively added at 15-min intervals (23 times in all). During the course of reaction progress, the water generated *in situ* was continuously removed with the aid of Dean-Stark apparatus. The reaction mixture was stirred at 125 ºC for 24 h, and allowed to cool to ambient temperature. The mixture was poured into a 50 mL of separatory funnel, and followed by washing with water (10 mL × 3) and brine (10 mL × 1) and drying over Na_2SO_4. The resultant filtrate was concentrated *in vacuo* to give 71 mg of crude products. Purification by silica-gel column chromatography (eluent, hexane/EtOAc, 19:1) afforded 19 mg of **19** as white solid materials (29%). Data of **19**: Rf value 0.26 (Hexane/EtOAc, 9:1); M.p. 202-204 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 7.15 (s, 4H), 3.81 (s, 12H), 3.35 (qq, J = 6.9, 6.9 Hz, 4H), 3.26 (s, 4H), 2.30 (s, 3H), 1.26 (d, J = 6.9 Hz, 12H), 1.23 (d, J = 6.9 Hz, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.2, 153.6, 142.9, 131.3, 125.8, 119.6, 76.8, 63.9, 56.3, 41.8, 27.4, 24.8, 24.1 ppm; MS (DART-TOF) *m/z*: 670 $[MH]^+$; IR (neat) 2956, 2925, 1451, 1404, 1268, 1228, 1073, 1013, 985 cm^{-1}; HRMS (DART-TOF) calcd for



$C_{45}H_{52}NO_4$: 670.3896 $[MH]^+$, found; 670.3864.

11. Data of DFT calculations for **1** and **2**.

DFT Calculation: All calculations were conducted using a Gaussian 16 suite program (G16RevC.01).[1] 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 Coordinates of Optimized Structures: Cartesian coordinates for **1**, optimized at the B3LYP/6-31G(d,p) level of theory.

	Coordinates (Angstroms)		
Atomic Type	X	Y	Z
35	0	1.821167	-3.3583
35	-0.60245	1.678516	3.567706
8	2.06632	2.630561	4.446708
8	-2.8245	1.621333	-4.36475
6	-2.47454	-0.12145	-0.57853
6	3.458395	1.41647	1.310519
1	4.372065	1.504151	0.73782
6	2.370096	0.730125	0.740887
6	-1.28352	0.210257	-1.2816
6	-3.72405	0.154017	-1.16191
1	-4.62423	-0.05096	-0.59409
6	2.170271	1.968099	3.246028
6	-1.44908	0.884041	-2.52095
6	3.405485	2.006866	2.561955
6	-5.2722	0.941467	-2.98405
1	-5.9615	0.573657	-2.21259
6	1.1359	0.640997	1.445975
6	1.059725	1.350581	2.674487
6	0	0	-0.61946
6	-3.87402	0.690644	-2.4308
6	0	0	0.787856
6	-2.69543	1.043	-3.12991

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

6	-2.19812	0.957094	-5.47579
1	-1.65849	0.064189	-5.15019
1	-1.49974	1.645369	-5.9565
1	-2.98147	0.672218	-6.18604
6	-5.56725	2.441709	-3.17656
1	-5.4187	2.993939	-2.24334
1	-6.60656	2.585077	-3.49243
1	-4.91304	2.87397	-3.93705
6	-5.57242	0.140933	-4.26497
1	-4.98792	0.511862	-5.10953
1	-6.63246	0.233896	-4.52512
1	-5.35008	-0.92269	-4.13184
6	2.068744	1.775245	5.597868
1	1.758165	2.393399	6.441981
1	3.075155	1.379657	5.784966
1	1.370349	0.942502	5.474831
6	4.57631	2.771785	3.167067
1	4.530156	2.618737	4.251027
6	4.415648	4.286517	2.920856
1	4.433342	4.508772	1.84816
1	5.23207	4.841876	3.395649
1	3.470382	4.649793	3.331257
6	5.94918	2.280057	2.6862
1	6.064889	1.20022	2.823409
1	6.742128	2.780381	3.251043
1	6.118594	2.507706	1.627942
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35	0.602454	-1.67852	3.567706
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8	2.824497	-1.62133	-4.36475
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6	-3.4584	-1.41647	1.310519
1	-4.37207	-1.50415	0.73782
6	-2.3701	-0.73013	0.740887
6	1.283522	-0.21026	-1.2816
6	3.724051	-0.15402	-1.16191
1	4.624229	0.050957	-0.59409
6	-2.17027	-1.9681	3.246028
6	1.449084	-0.88404	-2.52095
6	-3.40549	-2.00687	2.561955
6	5.272198	-0.94147	-2.98405
1	5.961495	-0.57366	-2.21259
6	-1.1359	-0.641	1.445975
6	-1.05973	-1.35058	2.674487
6	3.874022	-0.69064	-2.4308
6	2.695429	-1.043	-3.12991
6	2.19812	-0.95709	-5.47579
1	1.658492	-0.06419	-5.15019
1	1.499744	-1.64537	-5.9565
1	2.981465	-0.67222	-6.18604
6	5.567245	-2.44171	-3.17656
1	5.418696	-2.99394	-2.24334
1	6.606561	-2.58508	-3.49243
1	4.913043	-2.87397	-3.93705
6	5.572422	-0.14093	-4.26497
1	4.987917	-0.51186	-5.10953

1	6.632455	-0.2339	-4.52512
1	5.350081	0.922687	-4.13184
6	-2.06874	-1.77525	5.597868
1	-1.75817	-2.3934	6.441981
1	-3.07516	-1.37966	5.784966
1	-1.37035	-0.9425	5.474831
6	-4.57631	-2.77179	3.167067
1	-4.53016	-2.61874	4.251027
6	-4.41565	-4.28652	2.920856
1	-4.43334	-4.50877	1.84816
1	-5.23207	-4.84188	3.395649
1	-3.47038	-4.64979	3.331257
6	-5.94918	-2.28006	2.6862
1	-6.06489	-1.20022	2.823409
1	-6.74213	-2.78038	3.251043
1	-6.11859	-2.50771	1.627942

Cartesian Coordinates of Optimized Structures: Cartesian coordinates for **2**, optimized at the B3LYP/6-31G(d,p) level of theory

	Coordinates (Angstroms)		
Atomic Type	X	Y	Z
35	0.297269	3.43568	-1.79921
35	-0.29728	3.435567	1.79918
35	0.297283	-3.43557	1.79918
35	-0.29727	-3.43568	-1.79921
8	-2.5022	4.461246	-2.04233
8	-2.50228	-4.46109	2.042528
8	2.502281	4.461087	2.042528
8	2.5022	-4.46125	-2.04233
6	-1.2894	-2.60489	1.109505
6	-2.45959	-0.66256	0.3025
6	-3.64619	-1.24153	0.788869
1	-4.54791	-0.65074	0.737406
6	-1.23089	1.364789	-0.42228
6	2.492775	3.216077	1.469966
6	-2.49278	-3.21608	1.469966
6	2.459588	0.662561	0.3025
6	1.230905	1.364768	0.422188
6	1.289399	2.60489	1.109505
6	-3.64618	1.241566	-0.78896
1	-4.5479	0.650773	-0.73752
6	-2.49278	3.216152	-1.46993
6	1.28938	-2.60493	-1.10955
6	0	0.703761	-4.9E-05
6	-3.72108	2.513158	-1.339
6	-3.72108	-2.51308	1.338973
6	-2.45959	0.66259	-0.3026
6	2.492775	-3.21615	-1.46993
6	3.646178	-1.24157	-0.78896
1	4.547898	-0.65077	-0.73752
6	3.721077	-2.51316	-1.339
6	-1.23091	-1.36477	0.422188
6	-1.28938	2.604927	-1.10955

6	0	-0.70376	-4.9E-05
6	1.230887	-1.36479	-0.42228
6	3.646185	1.241529	0.788869
1	4.547905	0.65074	0.737406
6	3.721082	2.513084	1.338973
6	5.058237	-3.09659	-1.84538
6	-5.05826	-3.09651	1.845317
6	2.459591	-0.66259	-0.3026
6	-5.05824	3.09659	-1.84538
6	6.231866	-2.12297	-1.61042
1	7.153967	-2.57956	-1.98297
1	6.380487	-1.90263	-0.54799
1	6.098343	-1.17721	-2.14535
6	-6.23189	-2.12291	1.610273
1	-6.38047	-1.90259	0.547825
1	-6.0984	-1.17714	2.145186
1	-7.154	-2.57951	1.982784
6	-1.97423	-5.55449	1.272072
1	-1.59787	-5.21218	0.304996
1	-2.78023	-6.27919	1.115117
1	-1.16235	-6.02516	1.830099
6	4.973652	-3.36521	-3.36811
1	4.779904	-2.43581	-3.914
1	4.181263	-4.07532	-3.60637
1	5.924952	-3.77385	-3.72776
6	-5.39533	4.408638	-1.09743
1	-6.38061	4.771415	-1.41081
1	-4.66847	5.191697	-1.30987
1	-5.42642	4.246674	-0.01463
6	5.058255	3.096509	1.845317
6	-5.39527	-4.40857	1.09733
1	-6.3805	-4.77146	1.410756
1	-4.66832	-5.19157	1.309668
1	-5.42645	-4.24654	0.014543
6	5.395329	-4.40864	-1.09743
1	6.380612	-4.77142	-1.41081
1	4.668466	-5.1917	-1.30987
1	5.426424	-4.24667	-0.01463
6	-1.97428	5.55449	-1.27154
1	-1.59687	5.211768	-0.30502
1	-2.78063	6.278554	-1.11335
1	-1.16323	6.026078	-1.82999
6	-6.23187	2.122971	-1.61042
1	-6.38049	1.90263	-0.54799
1	-6.09834	1.177211	-2.14535
1	-7.15397	2.579562	-1.98297
6	-4.97365	3.365208	-3.36811
1	-5.92495	3.773848	-3.72776
1	-4.7799	2.435805	-3.914
1	-4.18126	4.075319	-3.60637
6	-4.97379	-3.3651	3.368047
1	-4.78012	-2.43567	3.913929

1	-4.1814	-4.07517	3.60641
1	-5.92511	-3.77375	3.727617
6	4.973786	3.365099	3.368047
1	4.780119	2.435674	3.913929
1	4.181398	4.075169	3.60641
1	5.925109	3.773753	3.727617
6	1.974228	5.554493	1.272072
1	1.597869	5.212183	0.304996
1	2.78023	6.279192	1.115117
1	1.162349	6.025156	1.830099

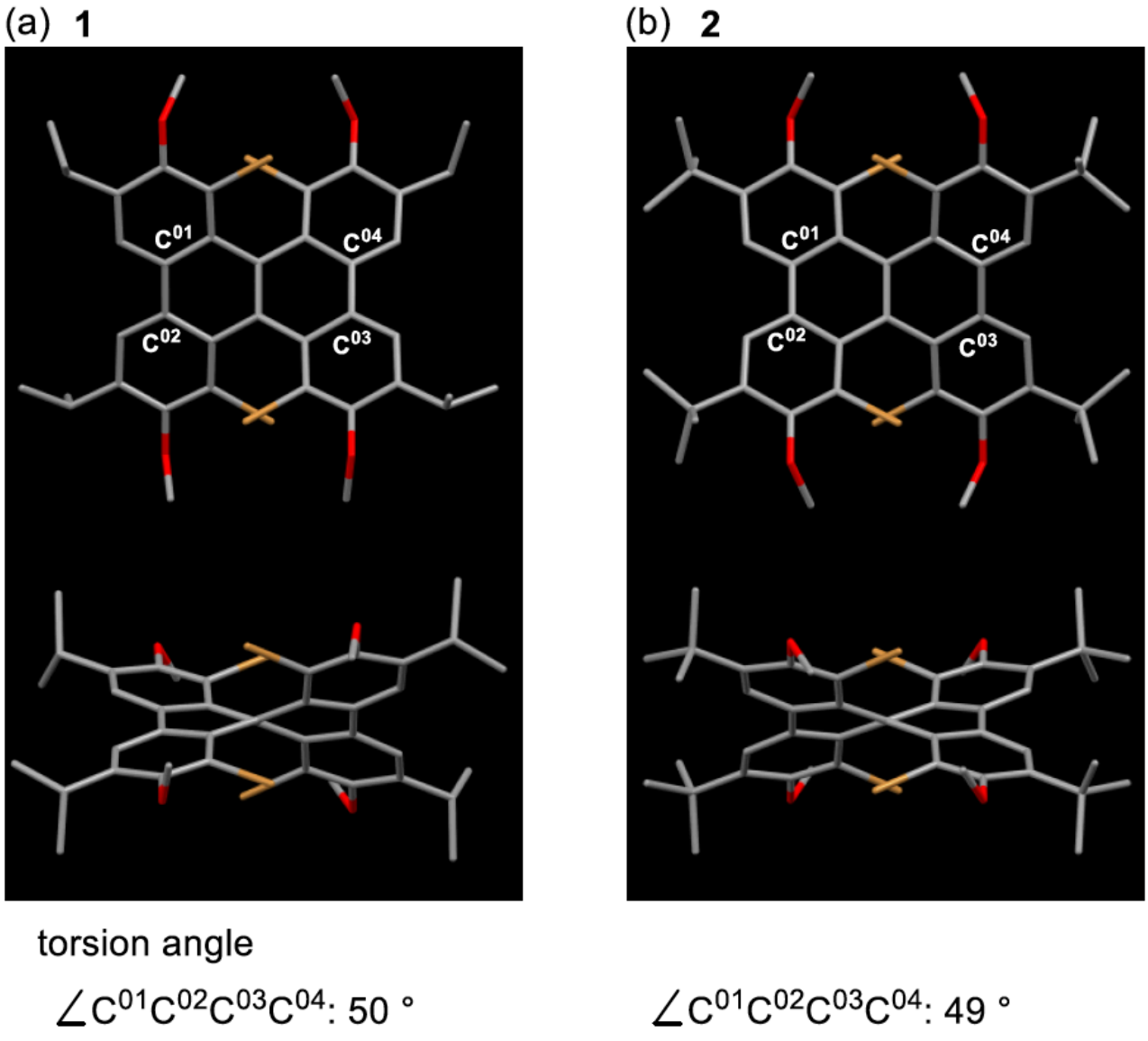


Figure S1. Optimized structures and the torsion angles of ∠$C^{01}C^{02}C^{03}C^{04}$ for (a) **1** and (b) **2**, calculated at the B3LYP/6-31G(d,p) level of theory.

12. Data of POAV angles in **3** and **4** (Table S1).

For POAV angles:

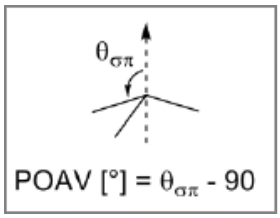
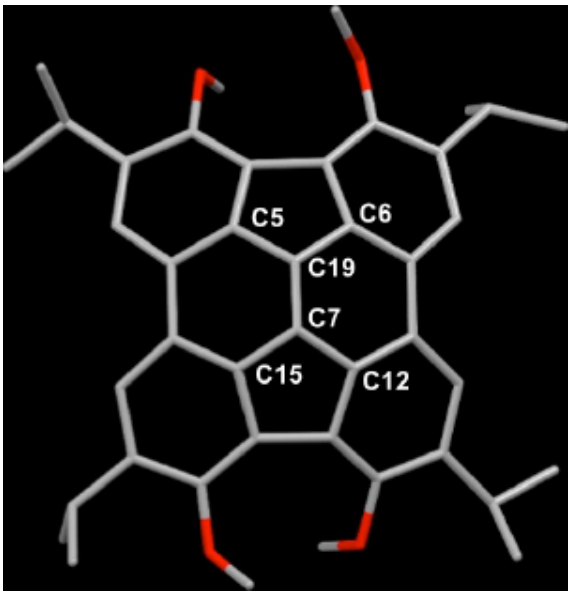
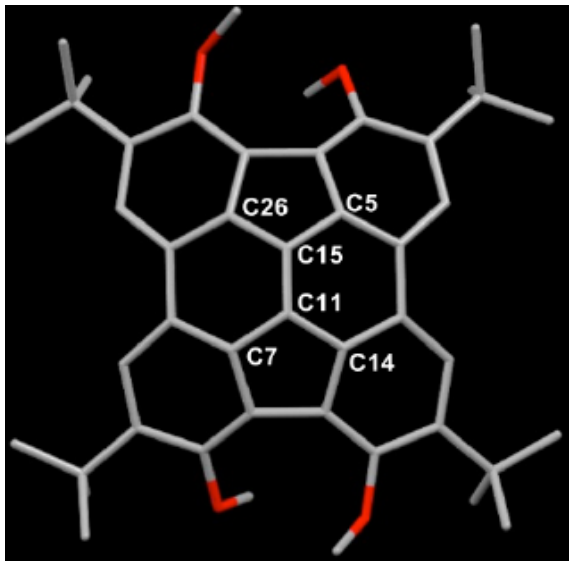


Table S1. POAV angles of Buckybowls **3** and **4**.





3		4	
Carbons	**POAV[°]**	**Carbons**	**POAV[°]**
C7	8.3	C11	8.8
C19	8.8	C15	9.3
AVE.	**8.6**	**AVE.**	**9.1**
C5	6.4	C5	7.1
C6	6.0	C7	6.6
C12	6.6	C14	5.5
C13	5.1	C26	6.0
AVE.	**6.0**	**AVE.**	**6.3**

13. Data of HOMO/LUMO levels for **4** and unsubstituted DIC (Figure S2, Table S2).

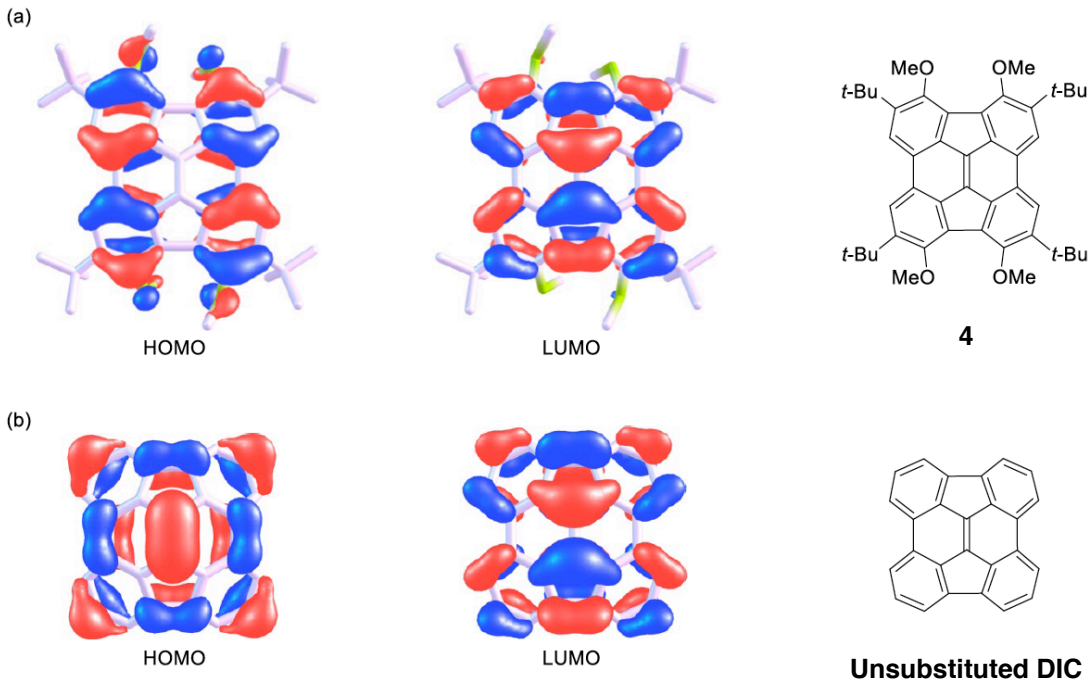


Figure S2. Frontier molecular orbitals calculated at the B3LYP/6-31G(d,p) level of theory (contour value is 0.025), for (a) **4** and (b) unsubstituted DIC.

Table S2. Energy of frontier orbitals calculated at the B3LYP/6-31G(d,p) level of theory, for (a) **4** and (b) unsubstituted DIC.

	Energy [eV]	
	4	**Unsubstituted DIC**
HOMO	-5.34	-5.80
LUMO	-1.84	-1.98
HOMO-LUMO gap	3.50	3.82

DFT Calculation: All calculations were conducted using a Gaussian 16 suite program (G16RevC.01).[1] 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 Coordinates of Optimized Structures: Cartesian coordinates for **4**, optimized at the B3LYP/6-31G(d,p) level of theory.

	Coordinates (Angstroms)		
Atomic Type	X	Y	Z
8	-1.28042	-5.01593	-0.05335
8	1.280423	5.015925	-0.05335
8	1.874591	-4.58219	0.554747
8	-1.87459	4.582189	0.554747
6	-1.26473	1.302054	-0.96687
6	-0.96663	2.639169	-0.56512
6	1.264731	-1.30205	-0.96687
6	-1.56059	-3.69064	-0.28917
6	-3.51293	1.364799	-0.28173
1	-4.48562	0.909438	-0.1461
6	0.052647	-0.66743	-1.26212
6	3.26367	1.896011	-0.30624
1	4.276799	1.579719	-0.09536
6	-1.04945	-1.47785	-0.96971
6	-0.05265	0.667434	-1.26212
6	1.560587	3.690644	-0.28917
6	0.563445	2.766936	-0.61667
6	-2.32346	-0.93059	-0.73574
6	2.930476	3.248498	-0.12785
6	3.512928	-1.3648	-0.28173
1	4.485622	-0.90944	-0.1461
6	-2.43476	0.560713	-0.72211
6	-0.56345	-2.76694	-0.61667
6	2.32346	0.930586	-0.73574
6	2.041482	-3.32702	-0.00107
6	1.049446	1.477849	-0.96971
6	-3.26367	-1.89601	-0.30624
1	-4.2768	-1.57972	-0.09536
6	0.966626	-2.63917	-0.56512
6	-2.93048	-3.2485	-0.12785
6	2.434763	-0.56071	-0.72211
6	-3.35884	2.724574	0.026439
6	-2.04148	3.327022	-0.00107
6	-4.6059	3.575226	0.387318
6	4.028989	4.25759	0.299167
6	-4.02899	-4.25759	0.299167
6	3.35884	-2.72457	0.026439
6	-1.19047	4.585722	1.818008

1	-1.76602	4.036234	2.571363
1	-1.10748	5.632988	2.114262
1	-0.19065	4.157871	1.7339
6	-0.56345	-5.70007	-1.09221
1	-0.49953	-6.7417	-0.77185
1	0.444195	-5.30327	-1.21719
1	-1.11517	-5.64141	-2.03767
6	-5.91712	2.780991	0.200703
1	-6.02072	2.388794	-0.81586
1	-6.76543	3.447195	0.386039
1	-6.00275	1.946113	0.904222
6	4.605904	-3.57523	0.387318
6	5.412488	3.587332	0.442548
1	5.420901	2.813629	1.217091
1	6.145669	4.345869	0.733903
1	5.75698	3.141792	-0.49642
6	0.563445	5.70007	-1.09221
1	-0.4442	5.303273	-1.21719
1	1.115174	5.641414	-2.03767
1	0.499529	6.741695	-0.77185
6	3.686527	4.882372	1.674713
1	2.743513	5.428129	1.647592
1	4.477984	5.578436	1.975951
1	3.615647	4.104734	2.443088
6	-4.58045	4.06106	1.856499
1	-4.44124	3.221708	2.546429
1	-5.53425	4.540732	2.104241
1	-3.79042	4.790508	2.02868
6	-4.67749	4.798233	-0.56114
1	-3.79684	5.43383	-0.4609
1	-5.56322	5.400464	-0.32817
1	-4.75684	4.475306	-1.60466
6	1.190472	-4.58572	1.818008
1	1.107481	-5.63299	2.114262
1	0.190652	-4.15787	1.7339
1	1.766024	-4.03623	2.571363
6	-4.18254	-5.37136	-0.76613
1	-4.42174	-4.94221	-1.74505
1	-5.00184	-6.04345	-0.48626
1	-3.27731	-5.96966	-0.86168
6	4.182543	5.371362	-0.76613
1	4.421738	4.942213	-1.74505
1	5.001842	6.043449	-0.48626
1	3.277311	5.969664	-0.86168
6	4.677491	-4.79823	-0.56114
1	3.796843	-5.43383	-0.4609
1	5.563224	-5.40046	-0.32817
1	4.756844	-4.47531	-1.60466
6	-3.68653	-4.88237	1.674713
1	-2.74351	-5.42813	1.647592
1	-4.47798	-5.57844	1.975951
1	-3.61565	-4.10473	2.443088
6	4.580445	-4.06106	1.856499
1	4.441244	-3.22171	2.546429
1	5.534247	-4.54073	2.104241
1	3.79042	-4.79051	2.02868

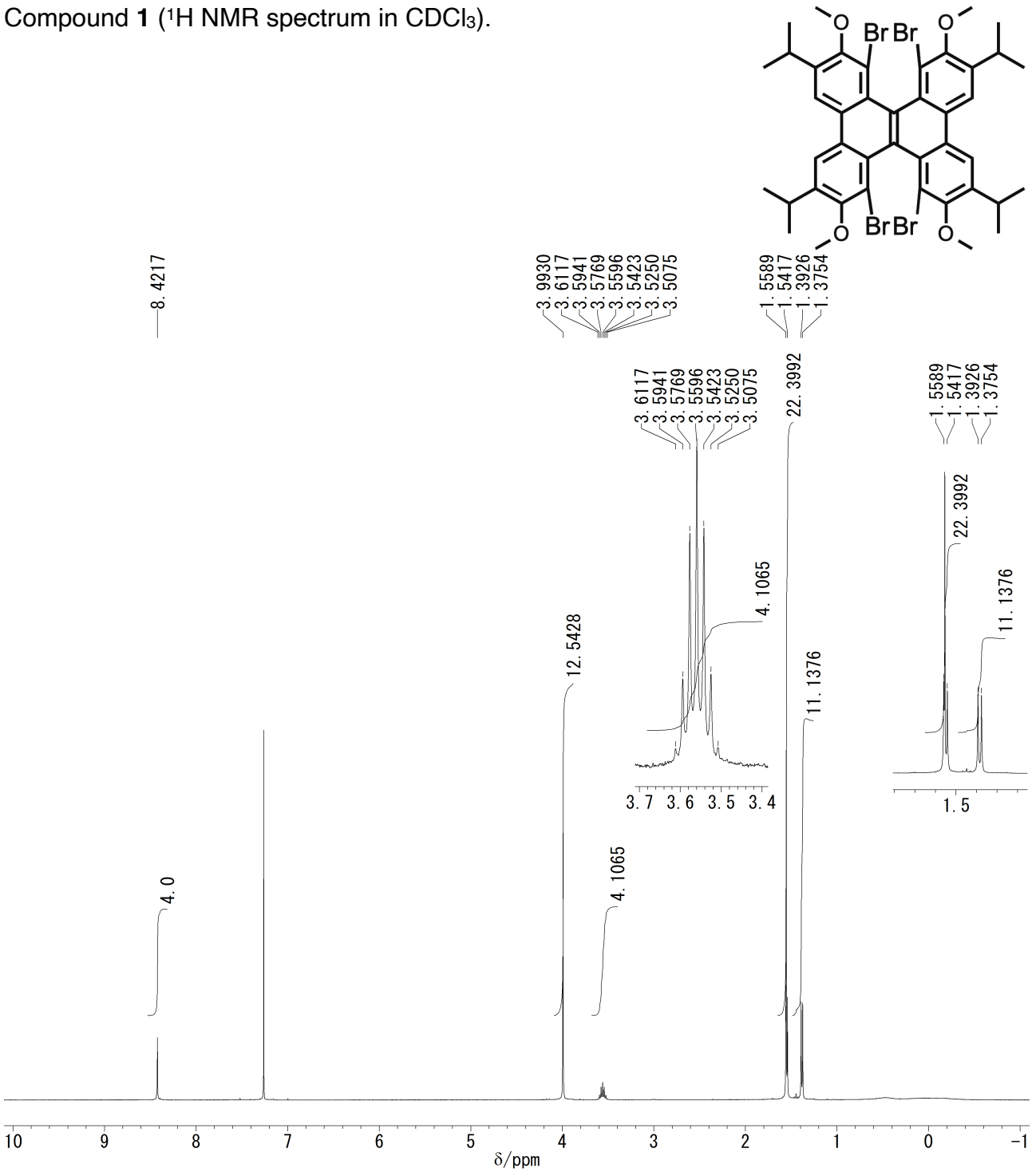
6	-5.41249	-3.58733	0.442548
1	-5.4209	-2.81363	1.217091
1	-6.14567	-4.34587	0.733903
1	-5.75698	-3.14179	-0.49642
6	5.917117	-2.78099	0.200703
1	6.020724	-2.38879	-0.81586
1	6.765425	-3.4472	0.386039
1	6.002746	-1.94611	0.904222

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

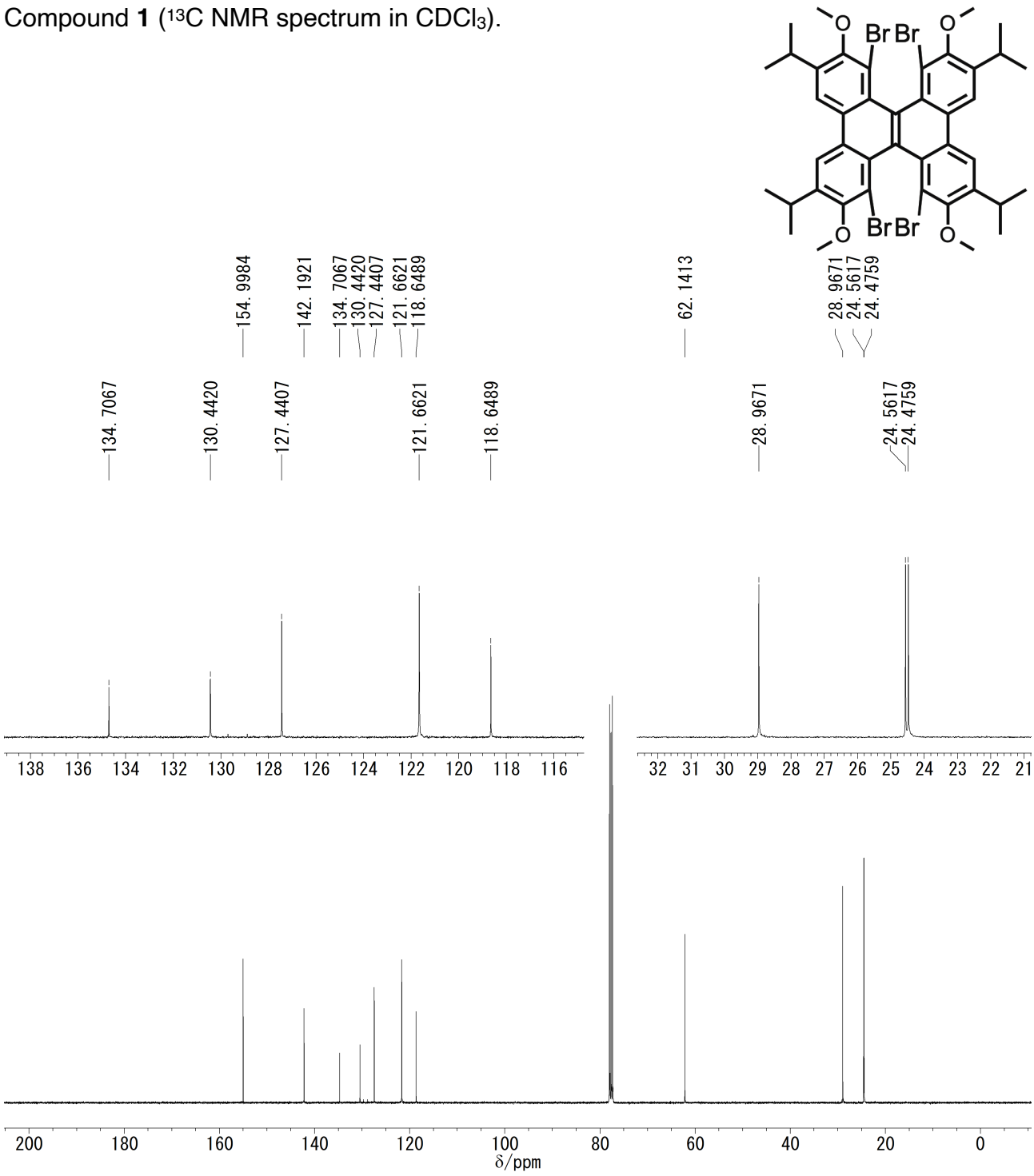
	Coordinates (Angstroms)		
Atomic Type	X	Y	Z
6	-1.16442	1.393886	0.528706
6	-0.76124	2.704142	0.140416
6	0.761241	2.704142	0.140416
6	1.164416	1.393886	0.528706
6	0	0.668513	0.833275
6	0	-0.66851	0.833275
6	1.164416	-1.39389	0.528706
6	0.761241	-2.70414	0.140416
6	-0.76124	-2.70414	0.140416
6	-1.16442	-1.39389	0.528706
6	1.773367	3.51881	-0.35045
6	3.078556	2.972414	-0.46823
6	3.391381	1.633722	-0.20941
6	2.394321	0.749177	0.270722
6	2.394321	-0.74918	0.270722
6	3.391381	-1.63372	-0.20941
6	3.078556	-2.97241	-0.46823
6	1.773367	-3.51881	-0.35045
6	-1.77337	-3.51881	-0.35045
6	-3.07856	-2.97241	-0.46823
6	-3.39138	-1.63372	-0.20941
6	-2.39432	-0.74918	0.270722
6	-2.39432	0.749177	0.270722
6	-3.39138	1.633722	-0.20941
6	-3.07856	2.972414	-0.46823
6	-1.77337	3.51881	-0.35045
1	1.591472	4.534276	-0.69131
1	3.866518	3.61659	-0.8482
1	4.394063	1.278808	-0.43079
1	4.394063	-1.27881	-0.43079
1	3.866518	-3.61659	-0.8482
1	1.591472	-4.53428	-0.69131
1	-1.59147	-4.53428	-0.69131
1	-3.86652	-3.61659	-0.8482
1	-4.39406	-1.27881	-0.43079
1	-4.39406	1.278808	-0.43079
1	-3.86652	3.61659	-0.8482
1	-1.59147	4.534276	-0.69131

14. ^{1}H NMR and ^{13}C NMR spectra for all new compounds of **1**-**19**.

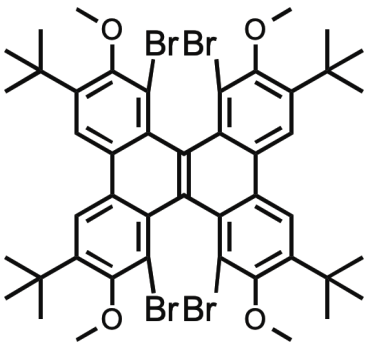
Compound **1** (^{1}H NMR spectrum in $CDCl_3$).

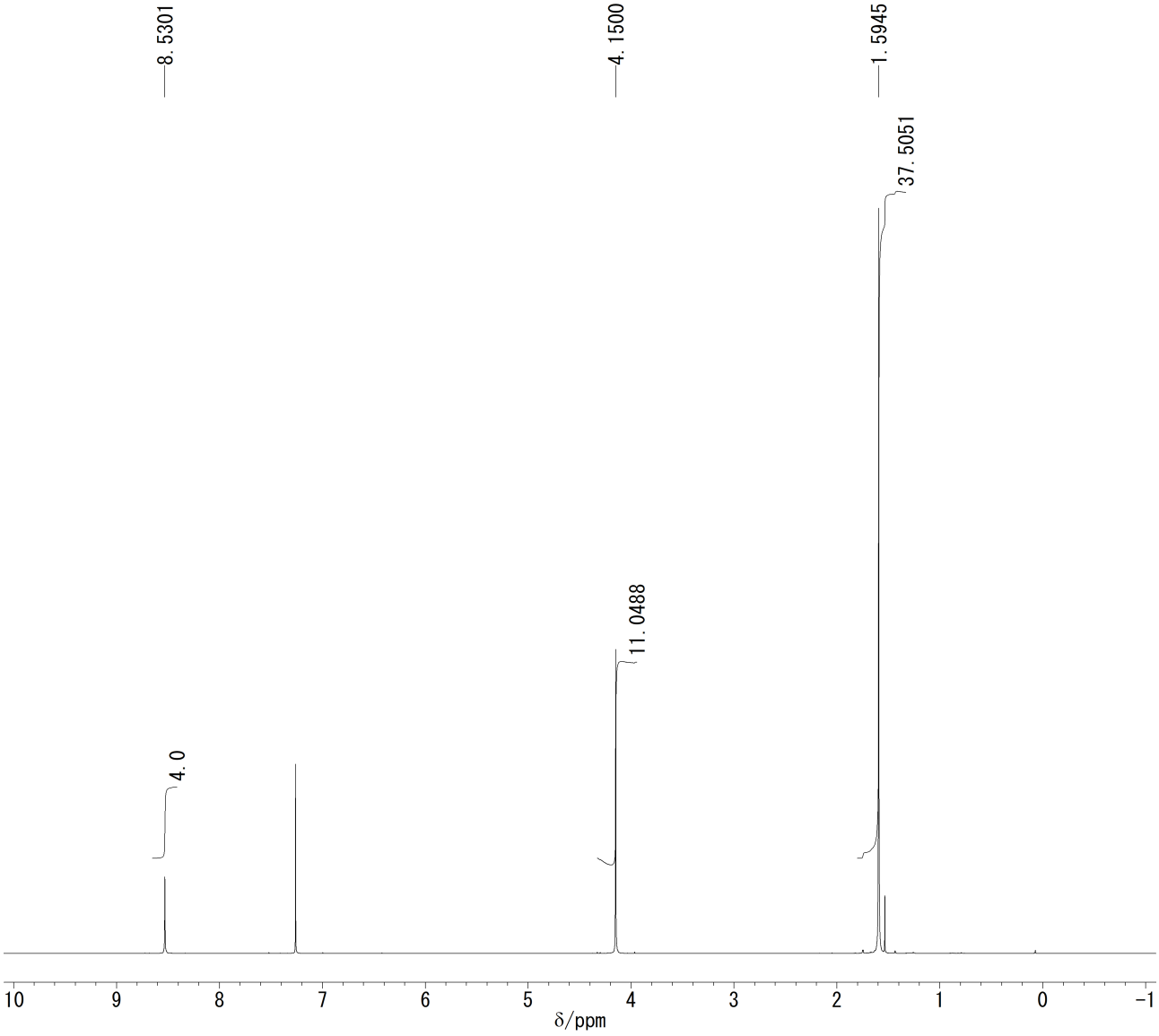


Compound **1** (^{13}C NMR spectrum in $CDCl_3$).

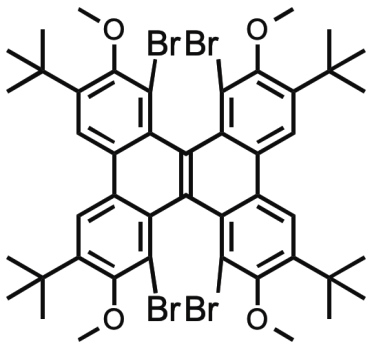


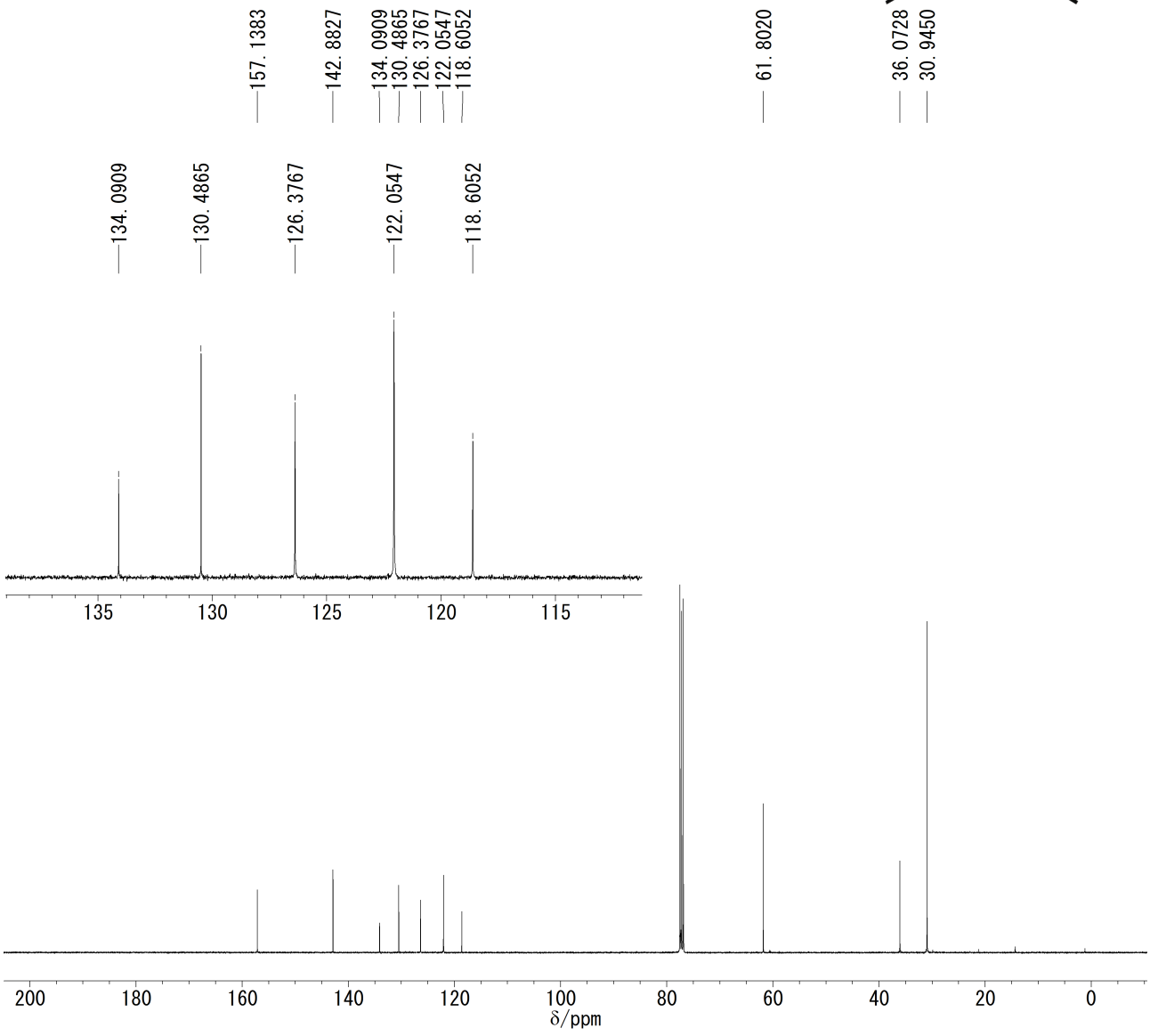
Compound **2** (^{1}H NMR spectrum in $CDCl_3$).



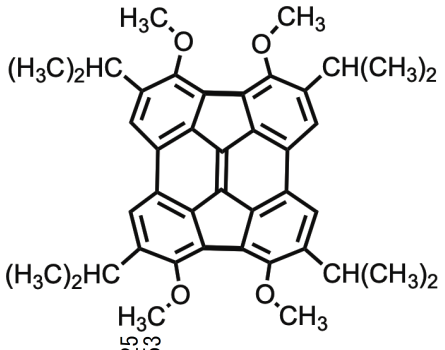


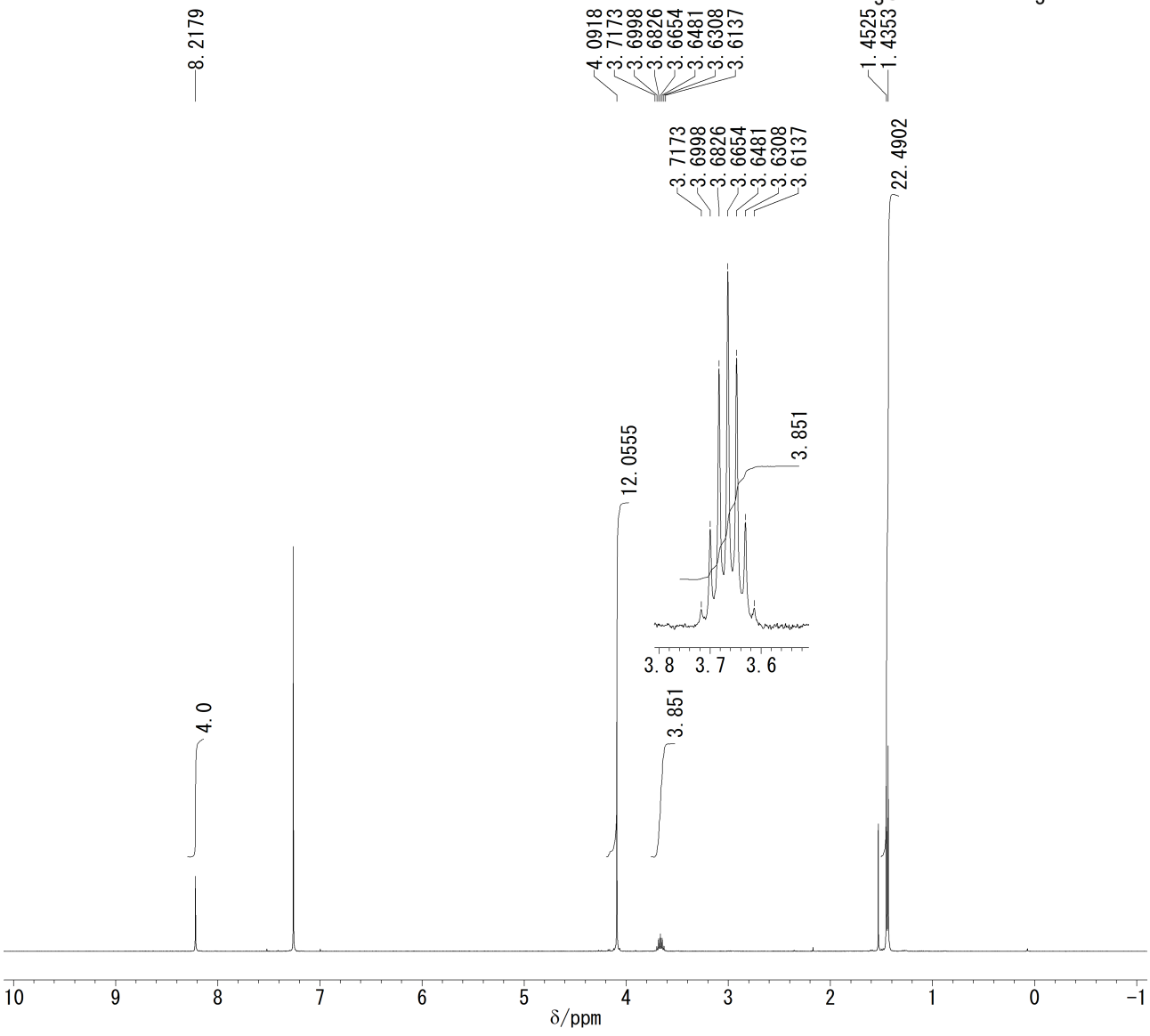
Compound **2** (^{13}C NMR spectrum in $CDCl_3$).



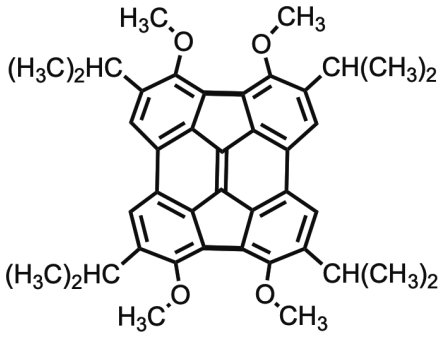


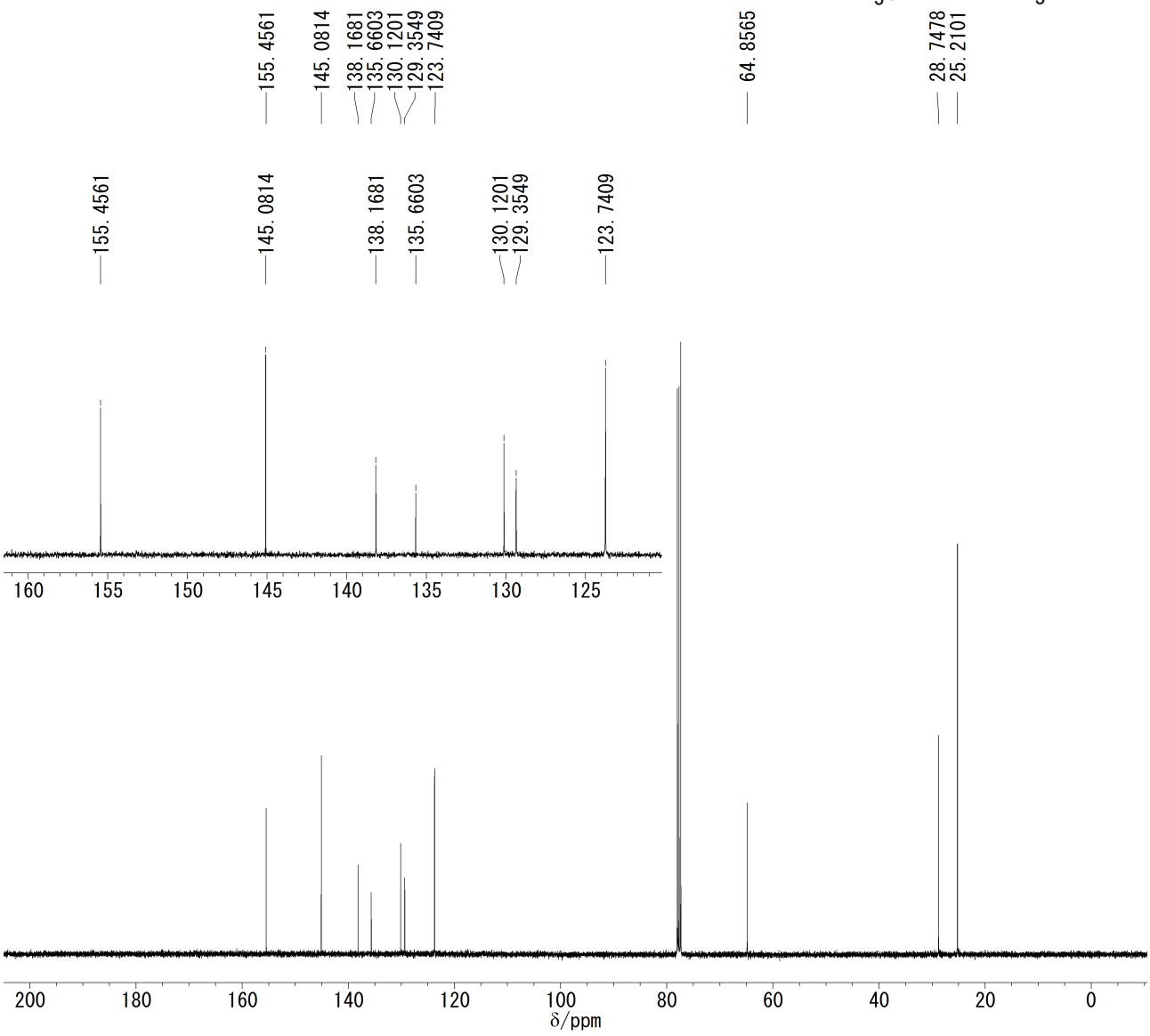
Compound **3** (^{1}H NMR spectrum in $CDCl_3$).



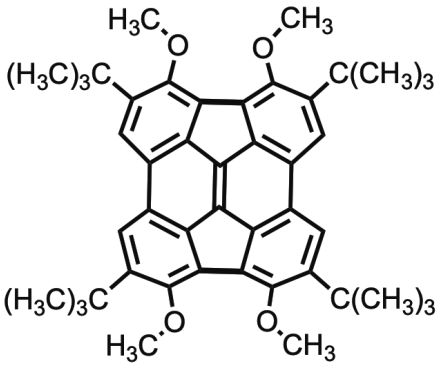


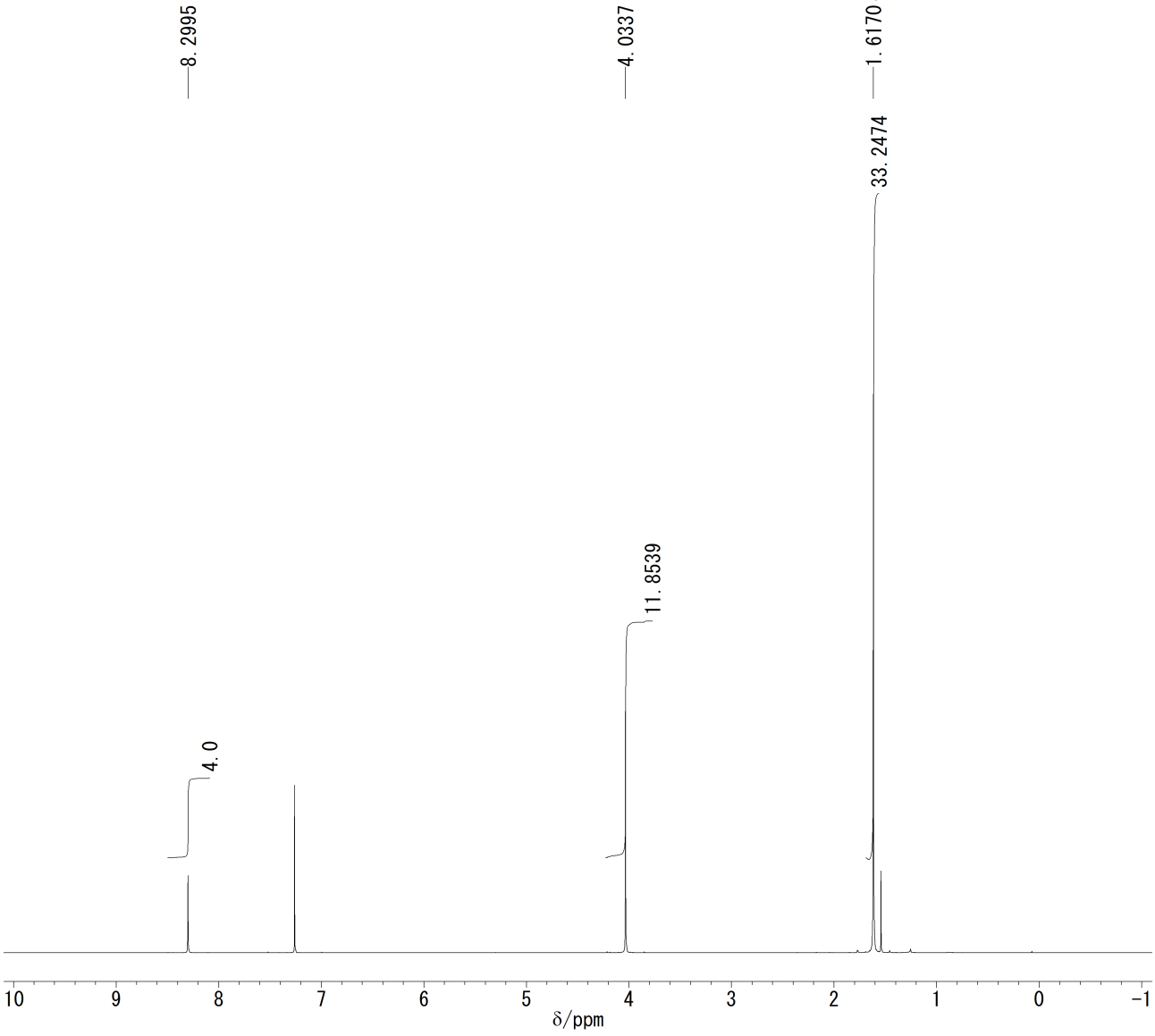
Compound **3** (^{13}C NMR spectrum in $CDCl_3$).



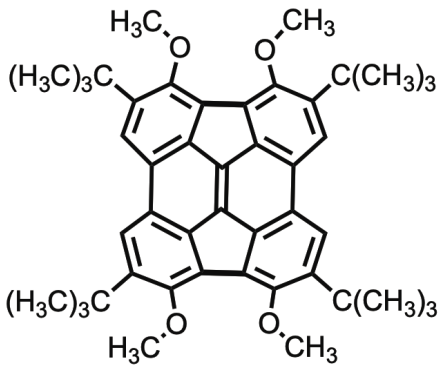


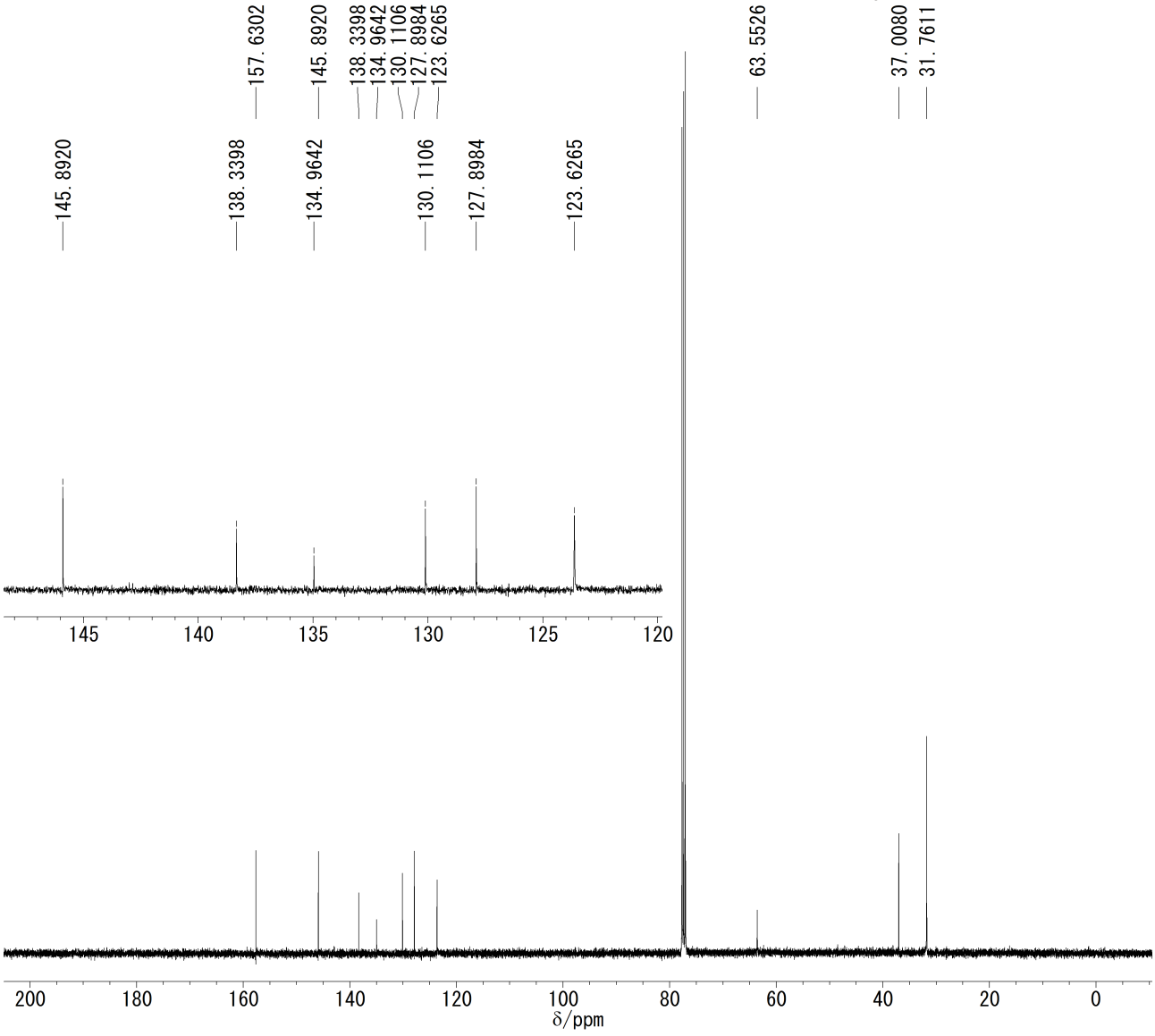
Compound **4** (^{1}H NMR spectrum in $CDCl_3$).



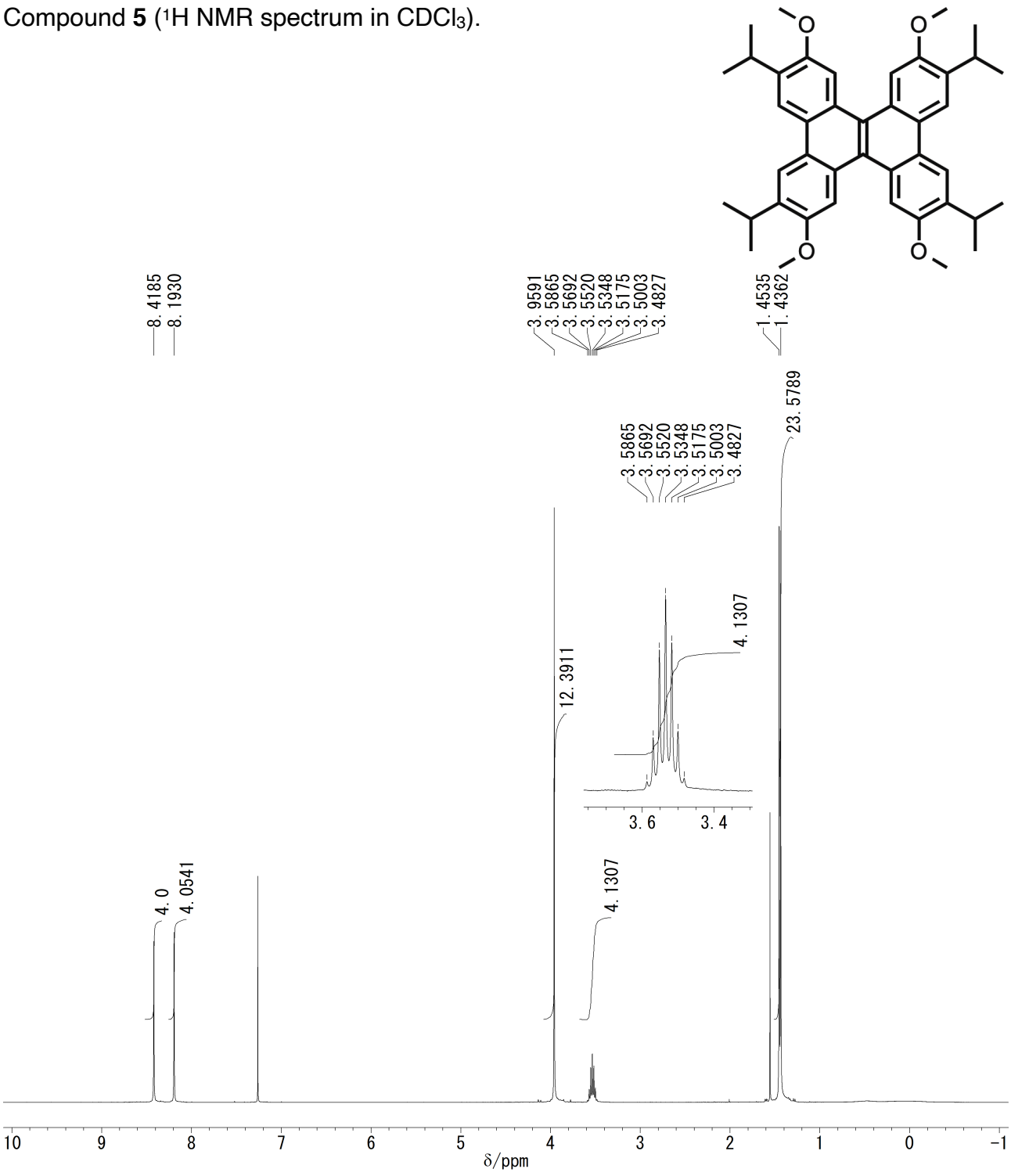


Compound **4** (^{13}C NMR spectrum in $CDCl_3$).

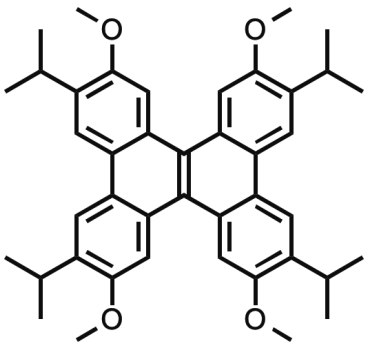


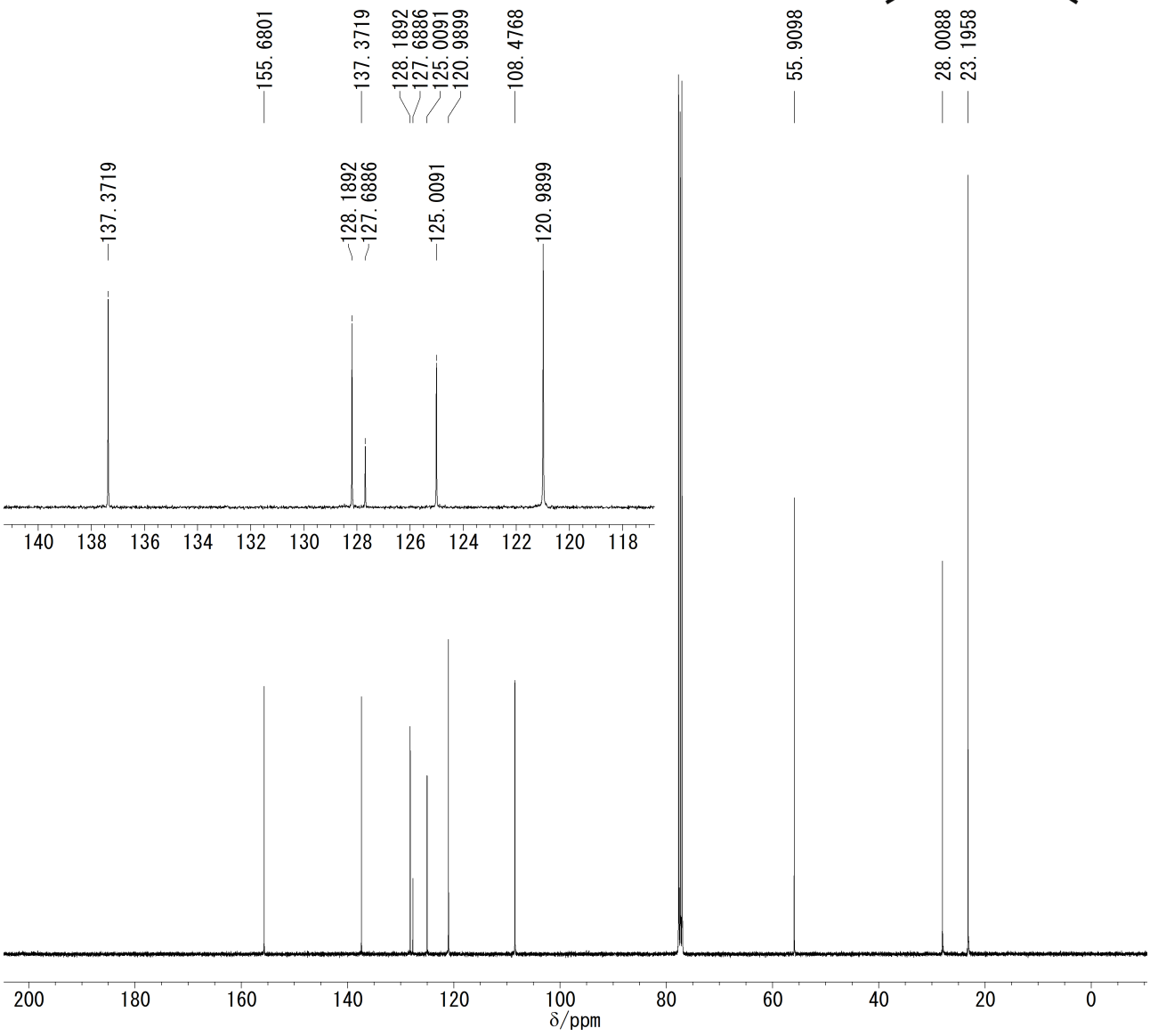


Compound **5** (^{1}H NMR spectrum in $CDCl_3$).

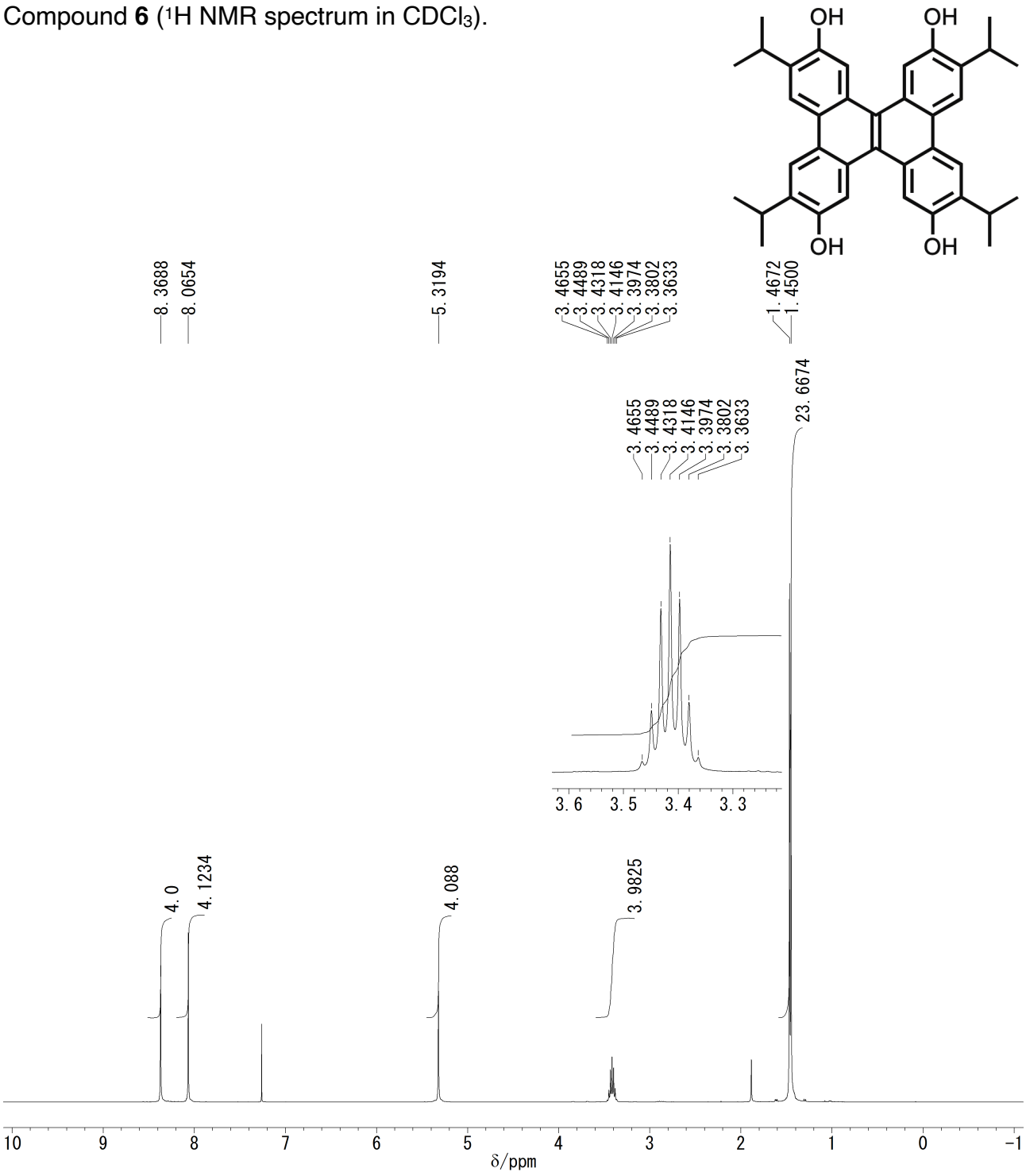


Compound **5** (^{13}C NMR spectrum in $CDCl_3$).

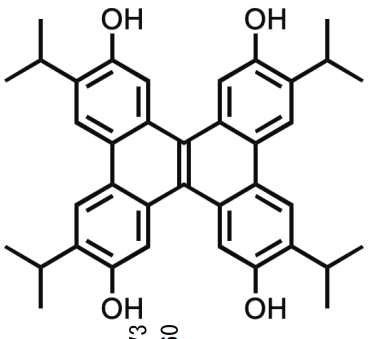


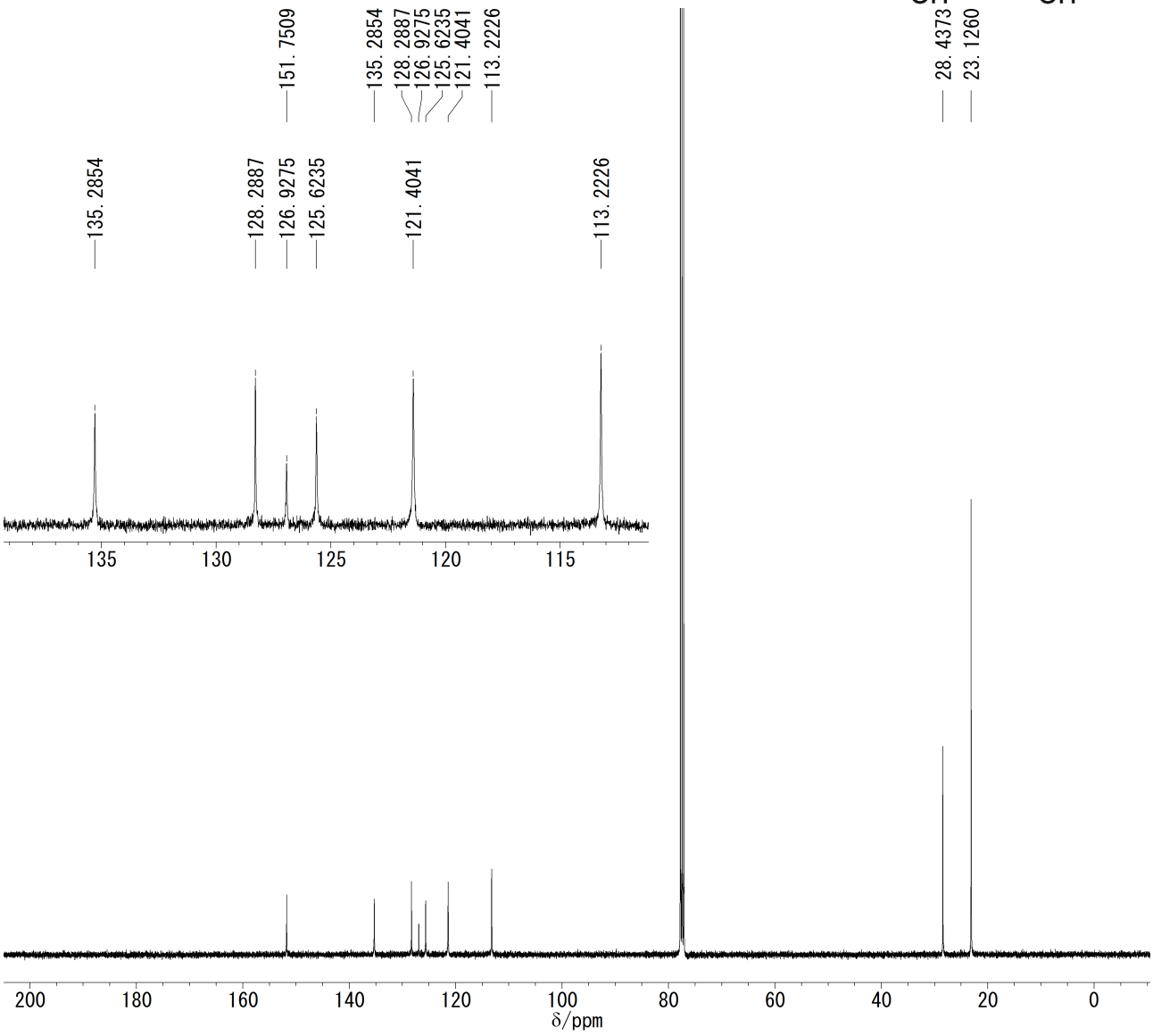


Compound **6** (^{1}H NMR spectrum in $CDCl_3$).

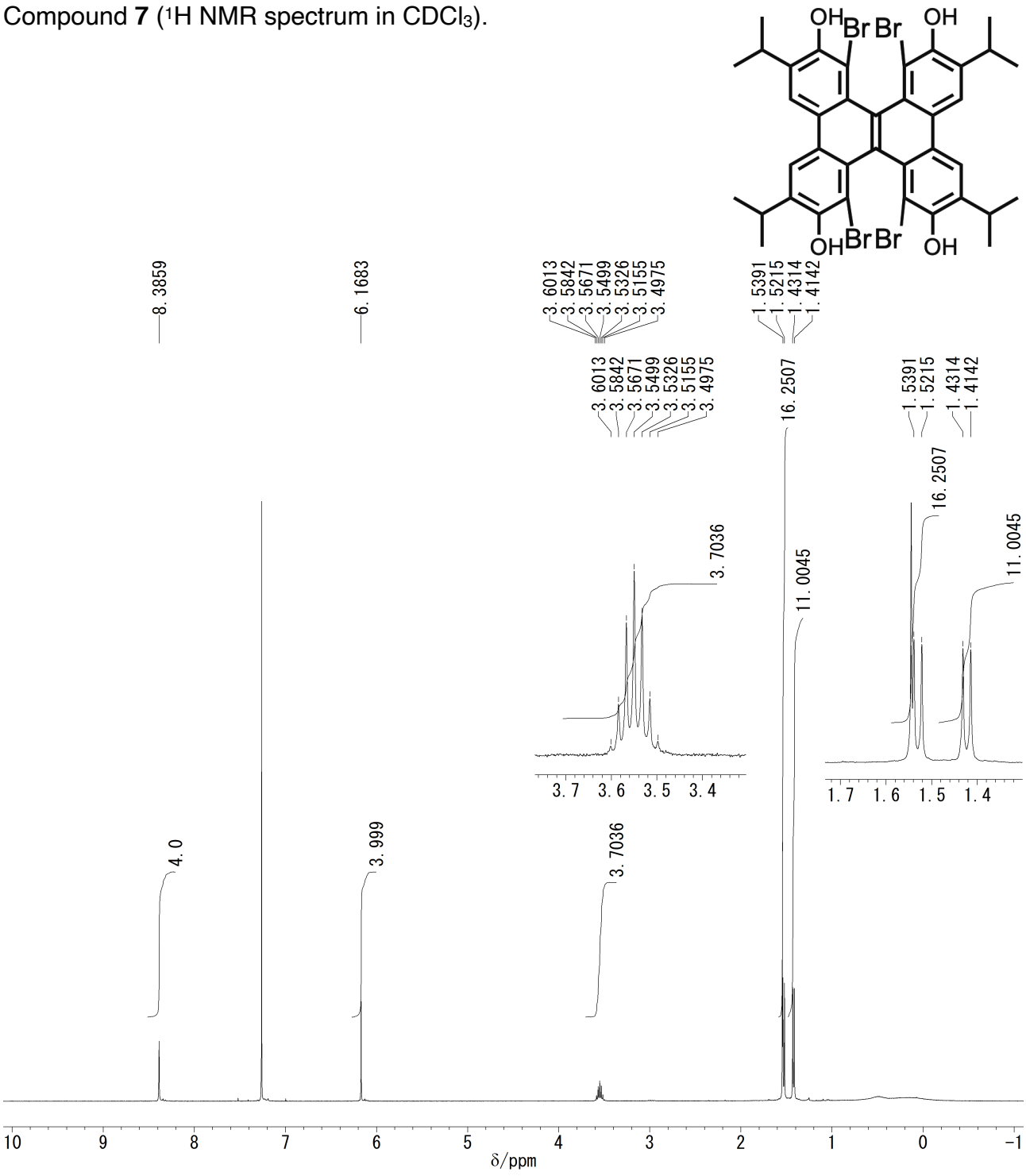


Compound **6** (^{13}C NMR spectrum in $CDCl_3$).

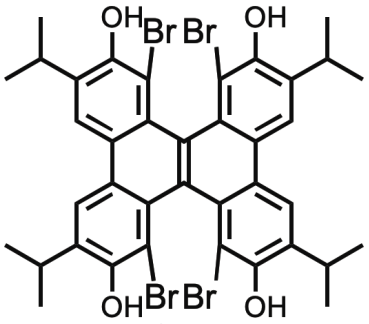


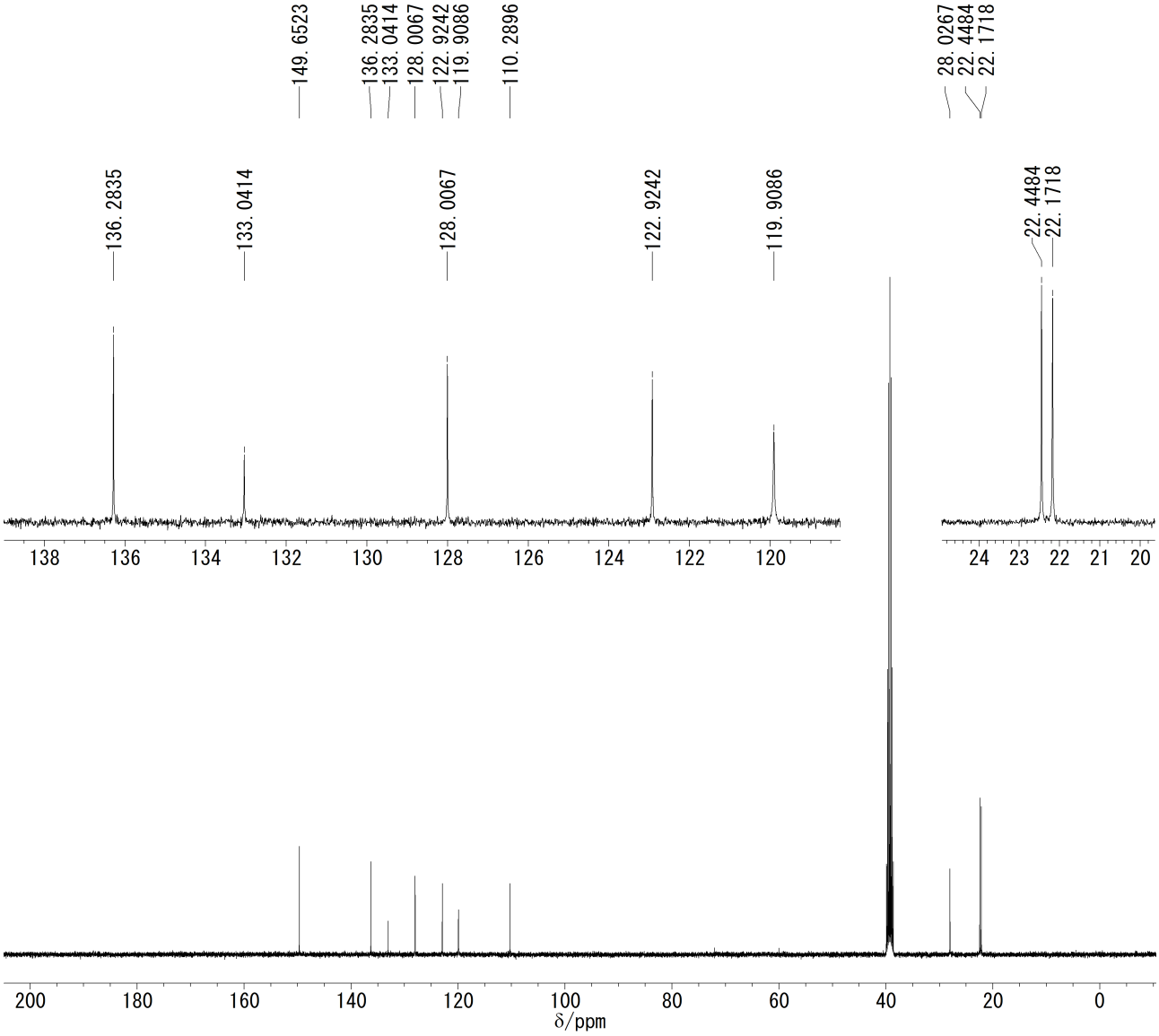


Compound **7** (^{1}H NMR spectrum in $CDCl_3$).

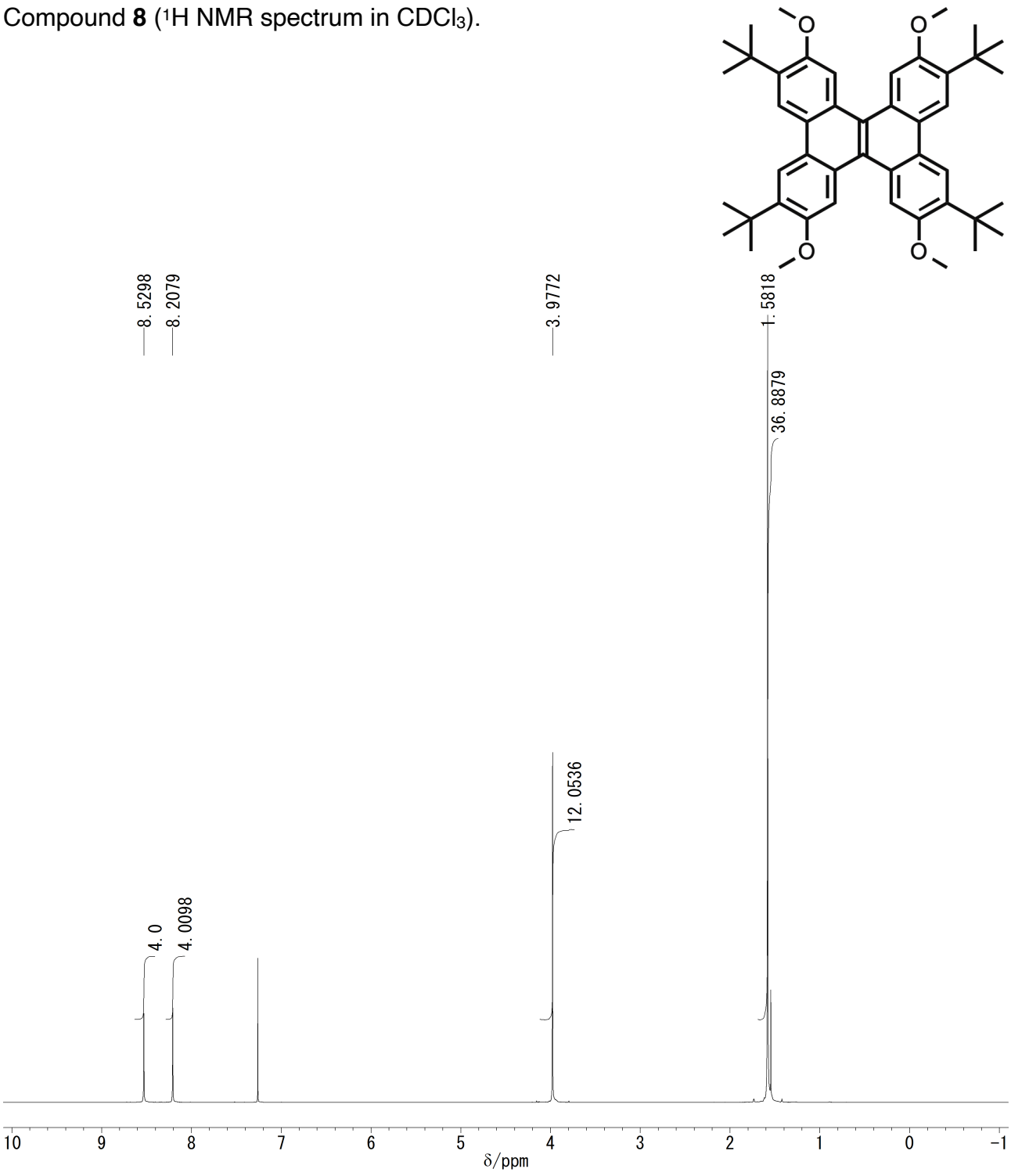


Compound **7** (^{13}C NMR spectrum in DMSO-d_6).

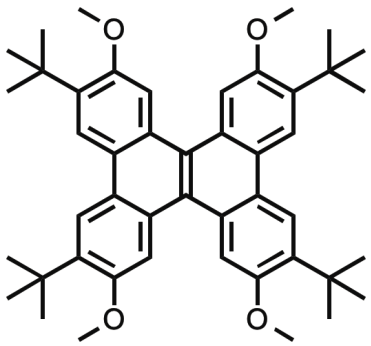


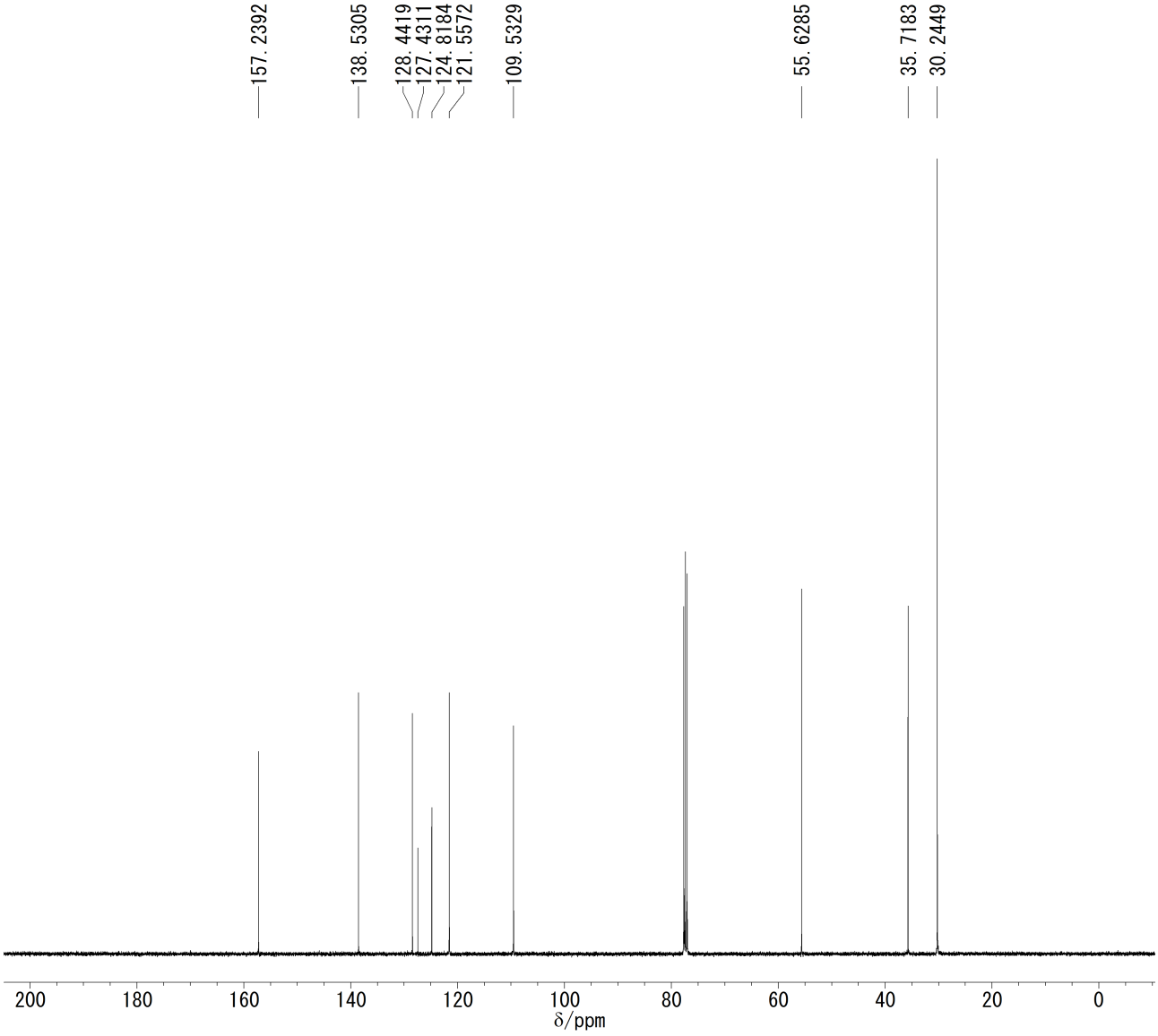


Compound **8** (^{1}H NMR spectrum in $CDCl_3$).

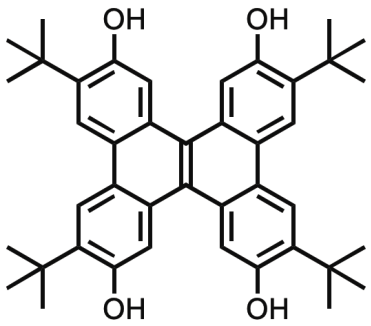


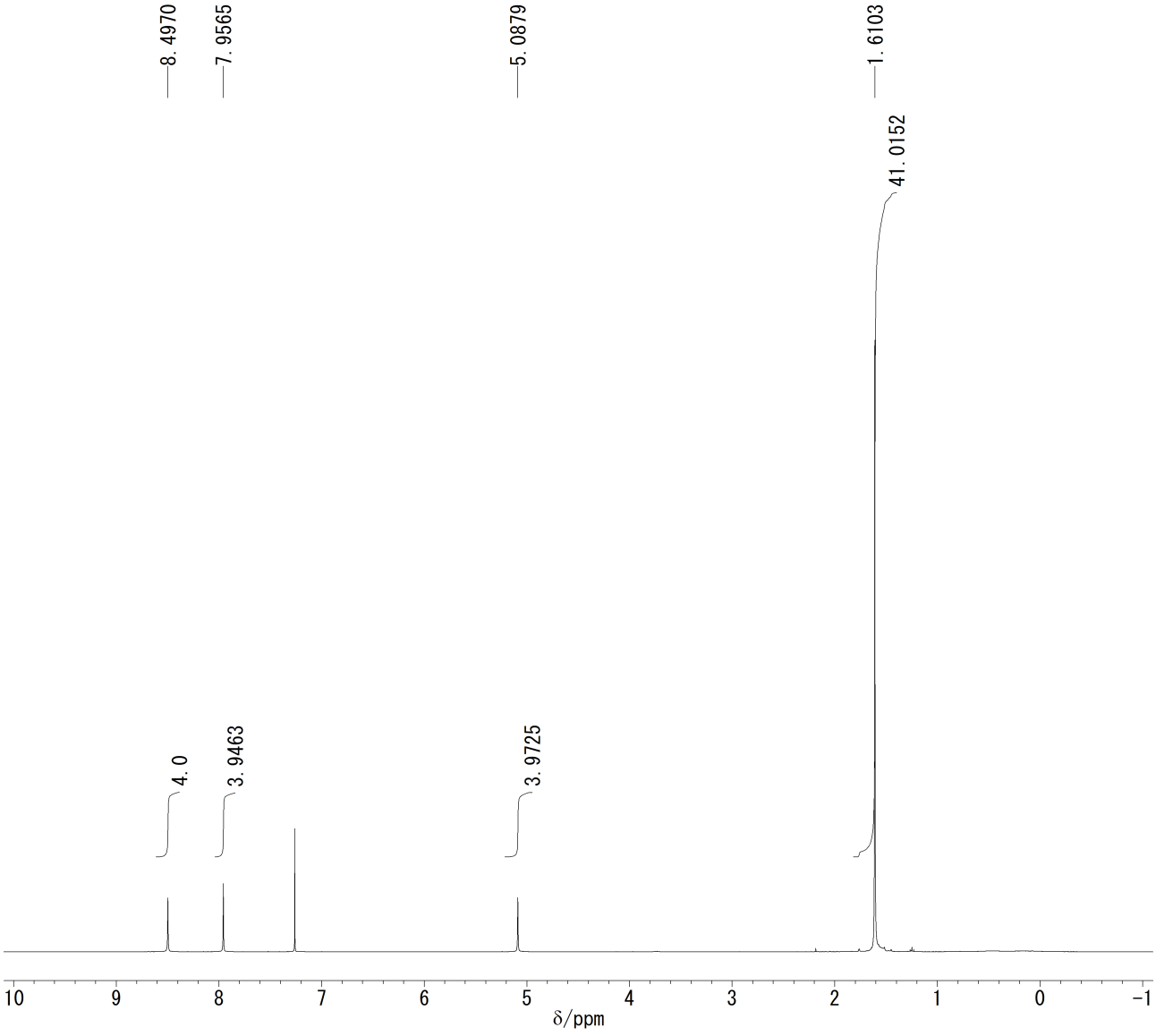
Compound **8** (^{13}C NMR spectrum in $CDCl_3$).



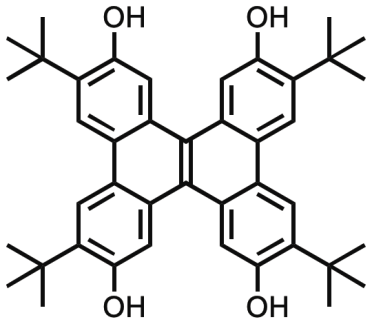


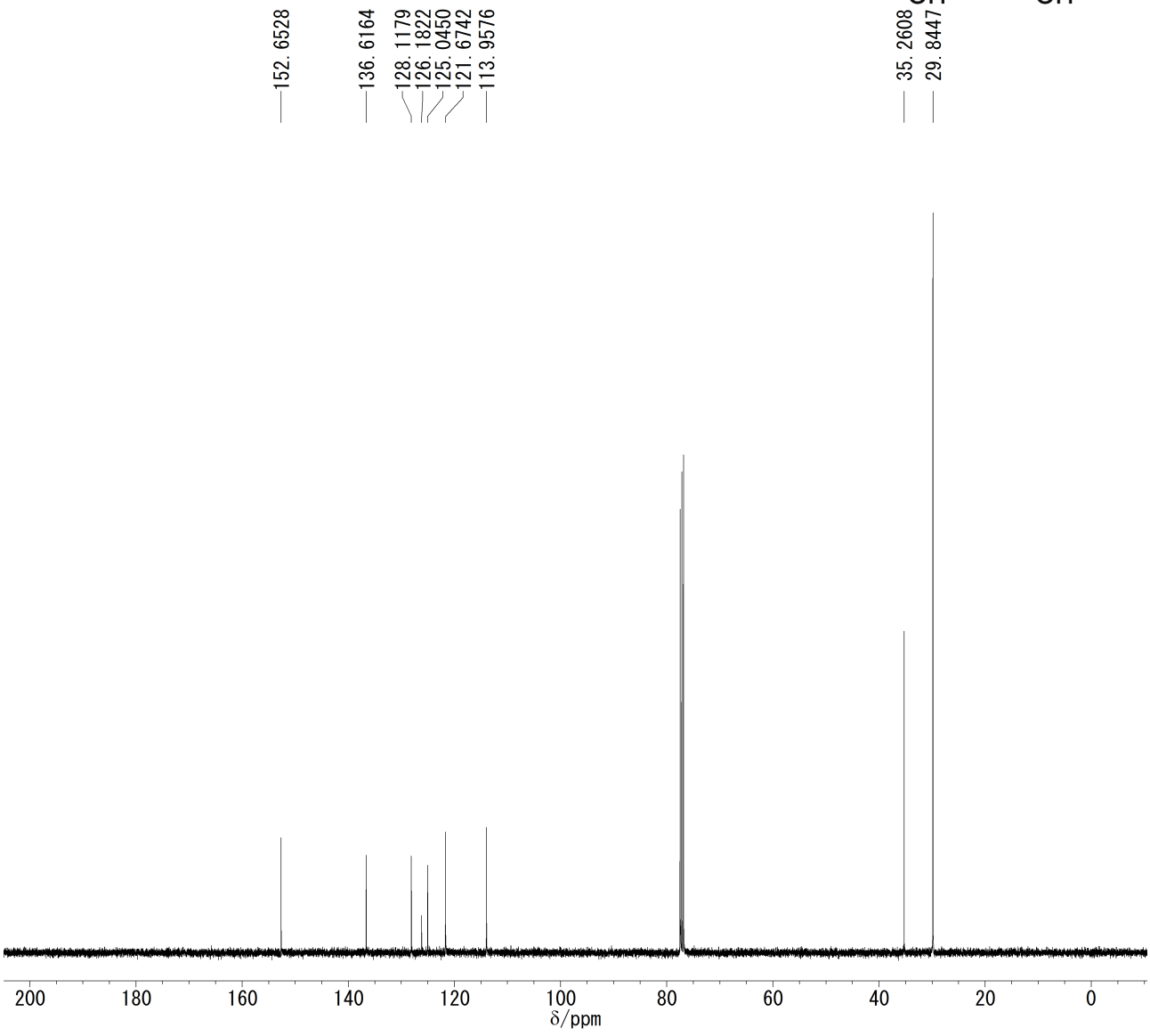
Compound **9** (^{1}H NMR spectrum in $CDCl_3$).



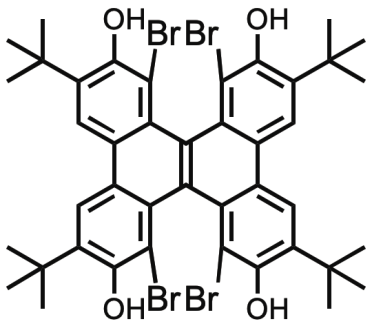


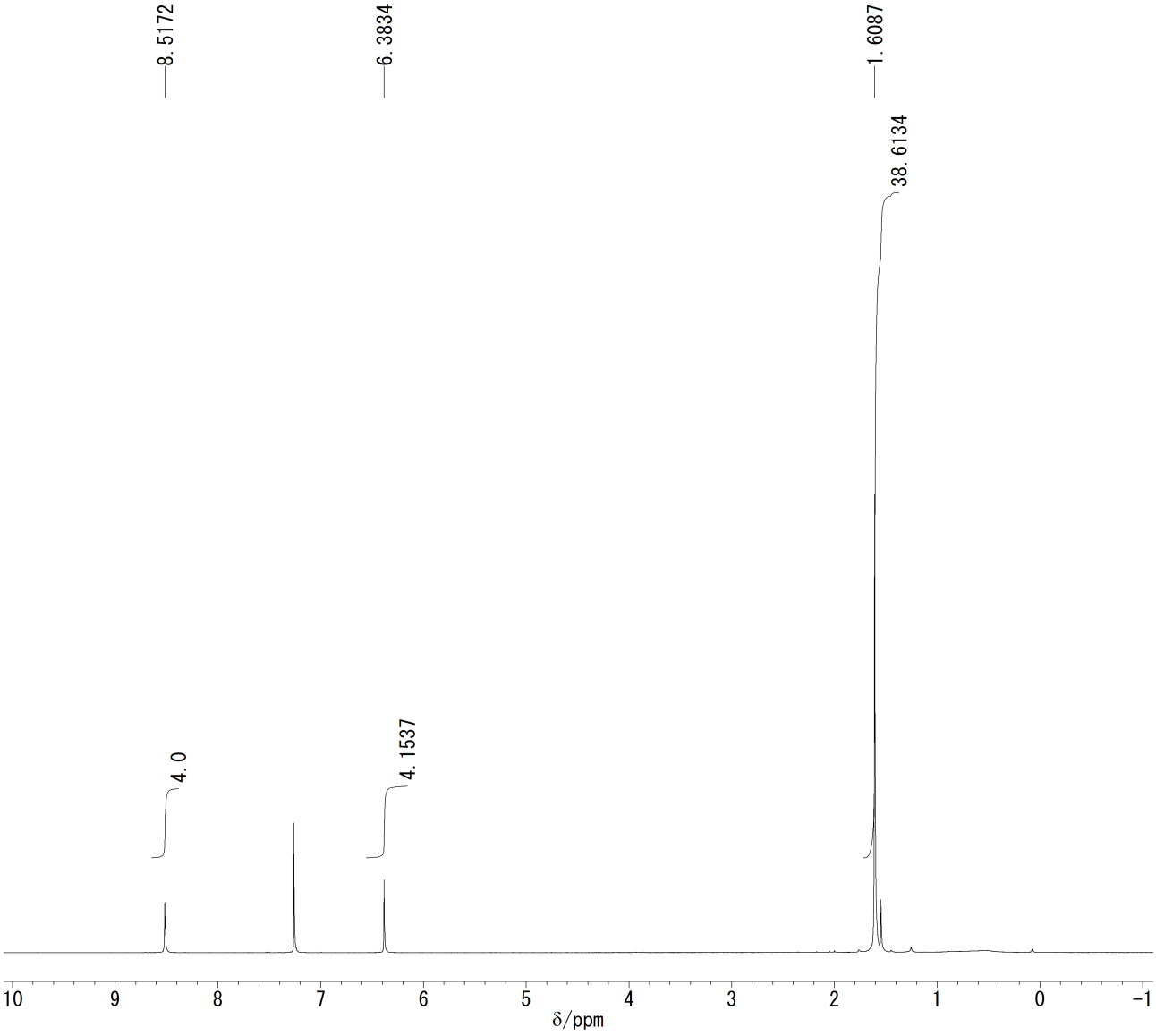
Compound **9** (^{13}C NMR spectrum in $CDCl_3$).



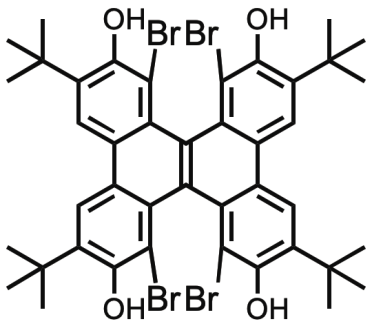


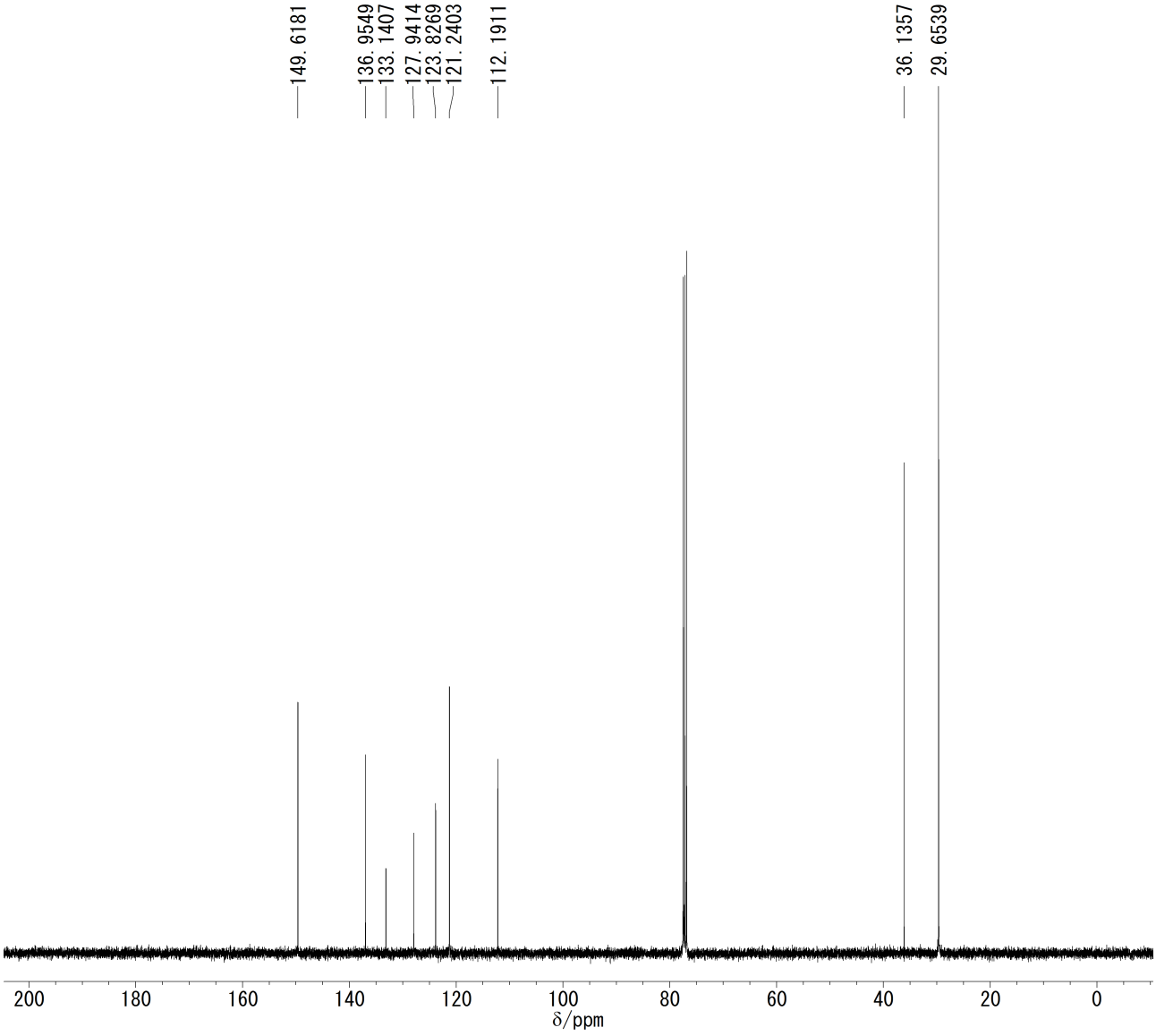
Compound **10** (^{1}H NMR spectrum in $CDCl_3$).



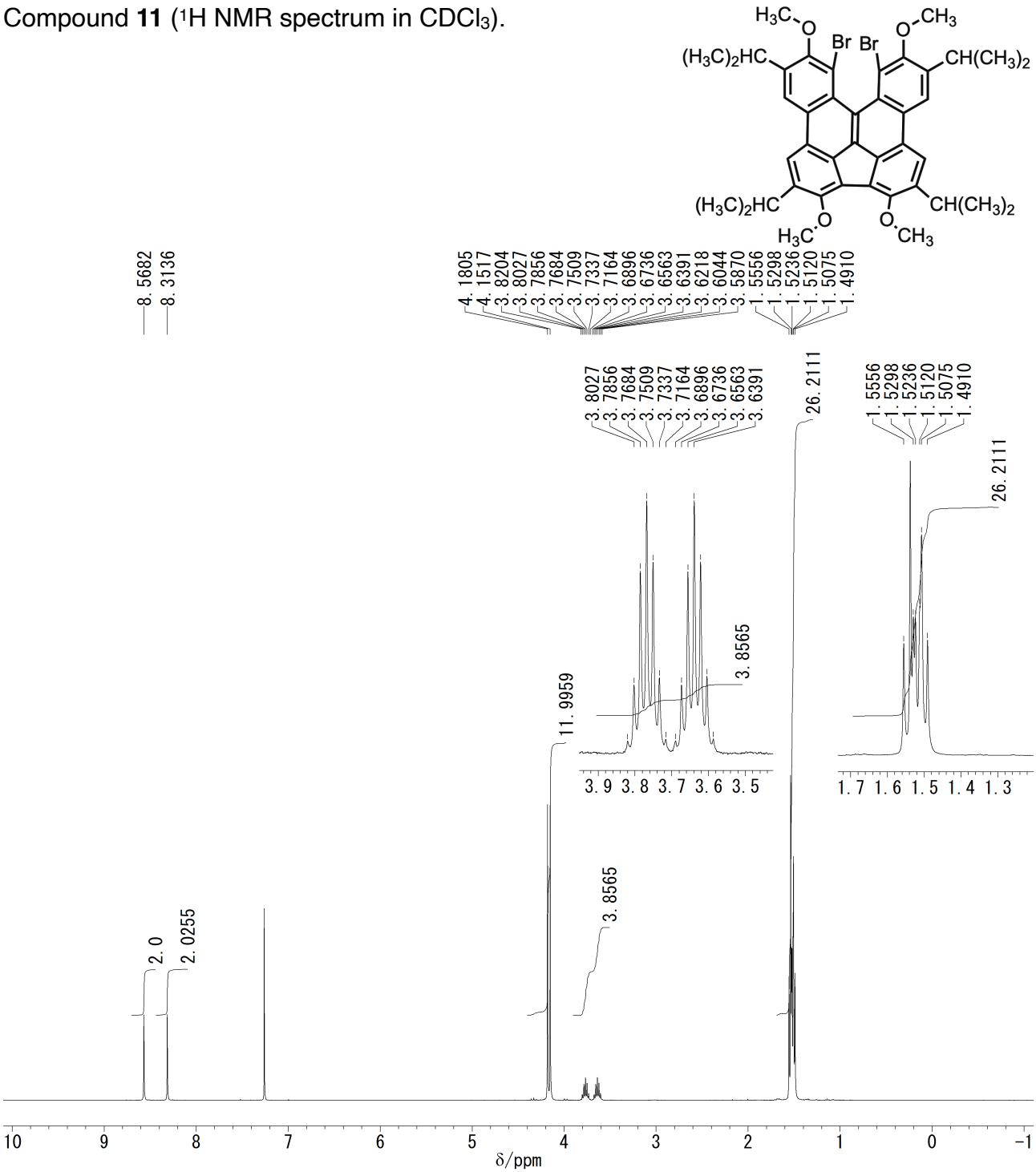


Compound **10** (^{13}C NMR spectrum in $CDCl_3$).

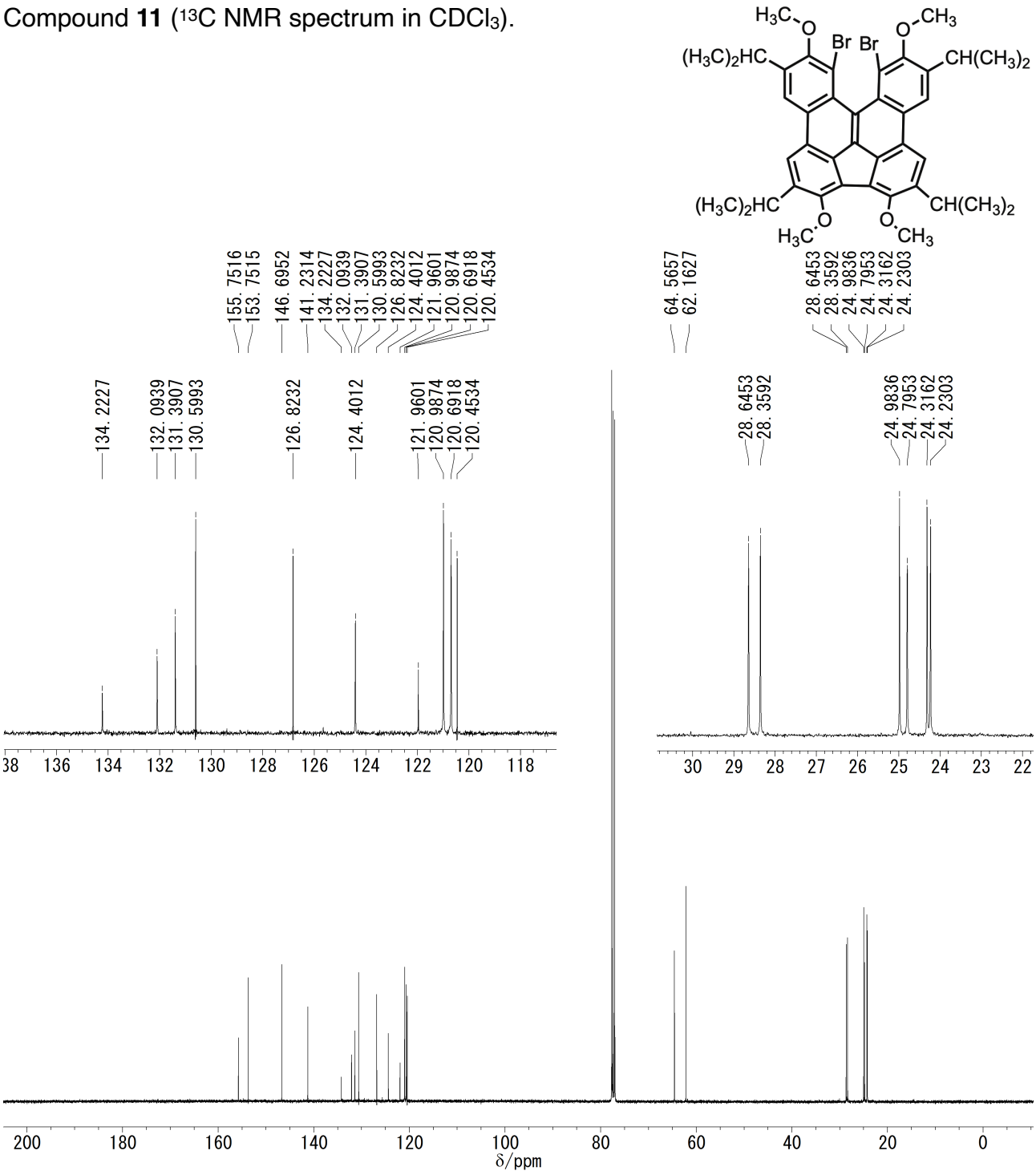




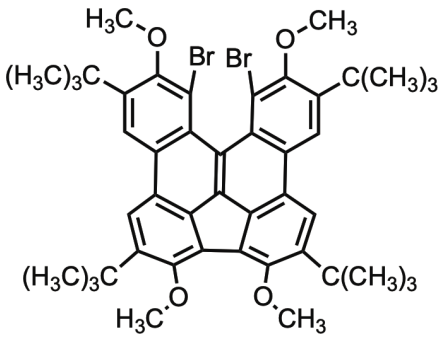
Compound **11** (^{1}H NMR spectrum in $CDCl_3$).

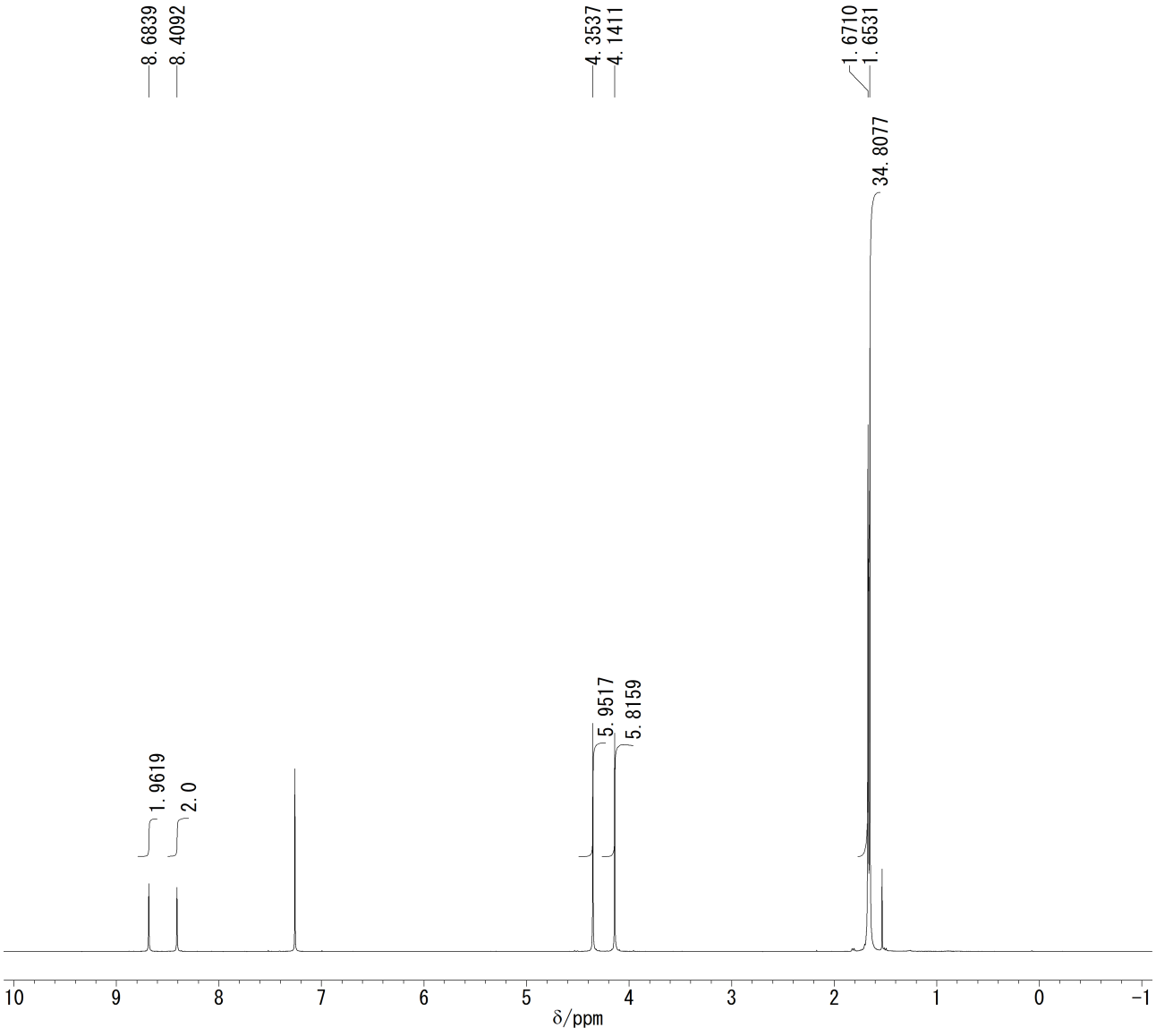


Compound **11** (^{13}C NMR spectrum in $CDCl_3$).

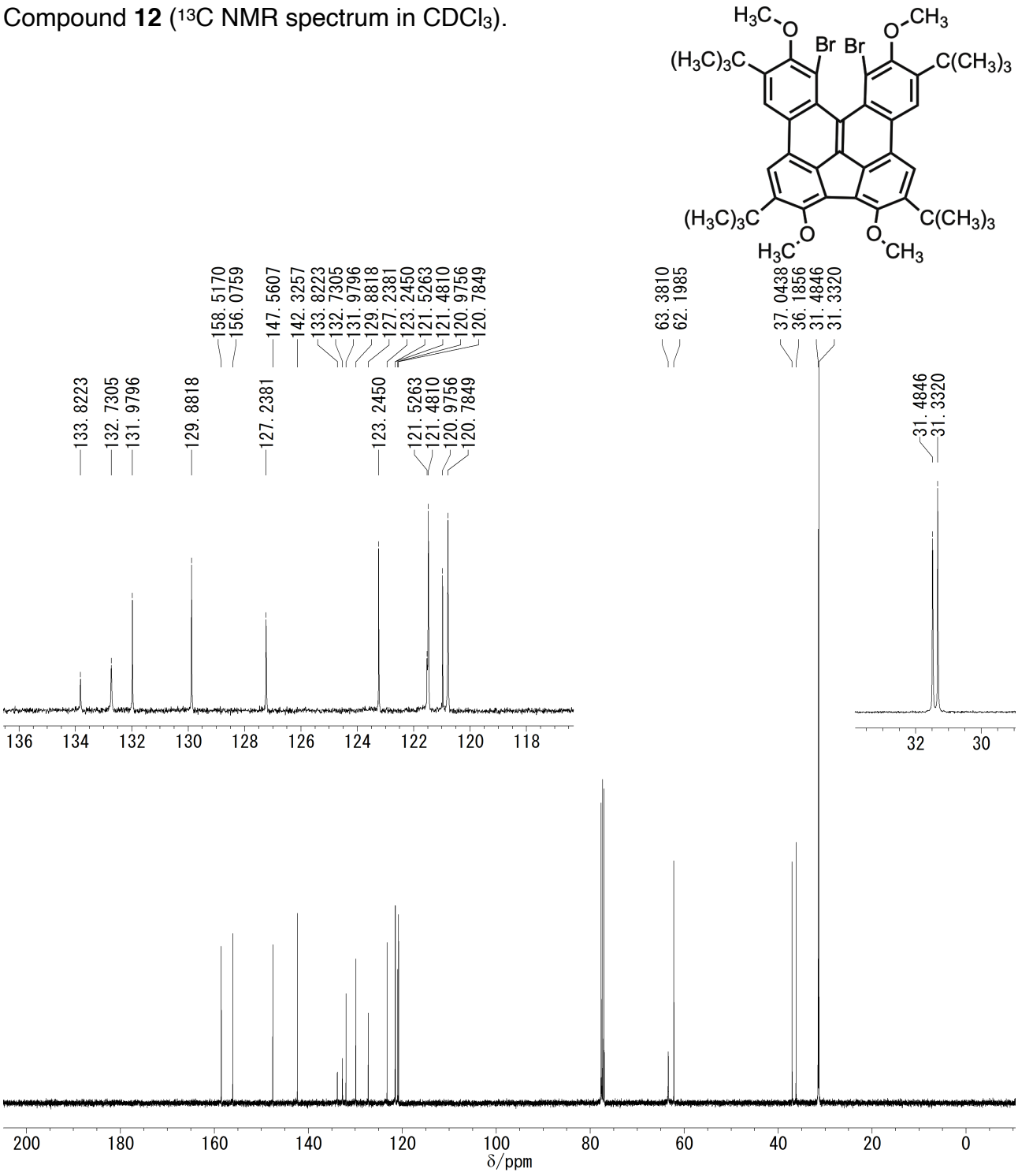


Compound **12** (^{1}H NMR spectrum in $CDCl_3$).

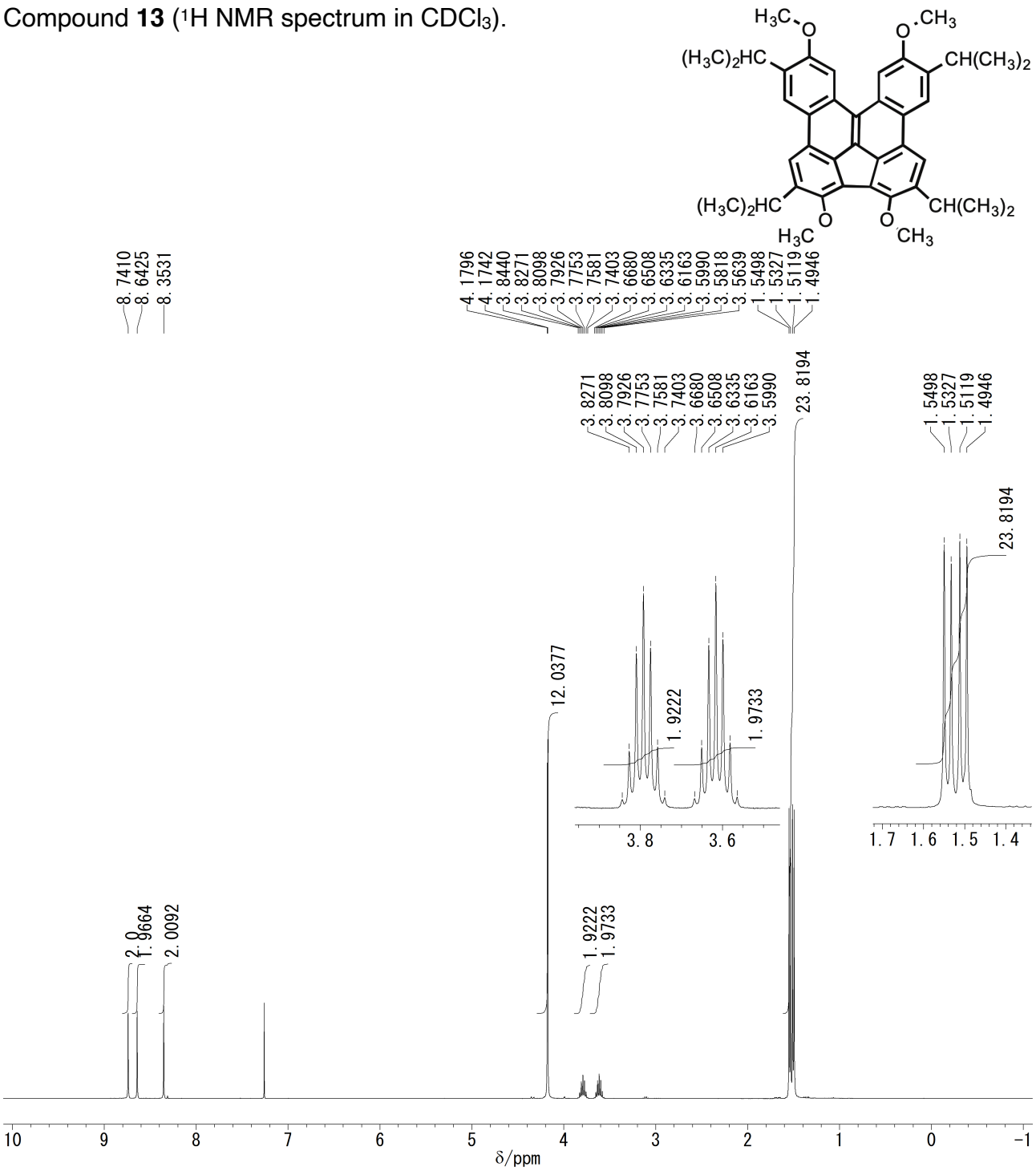




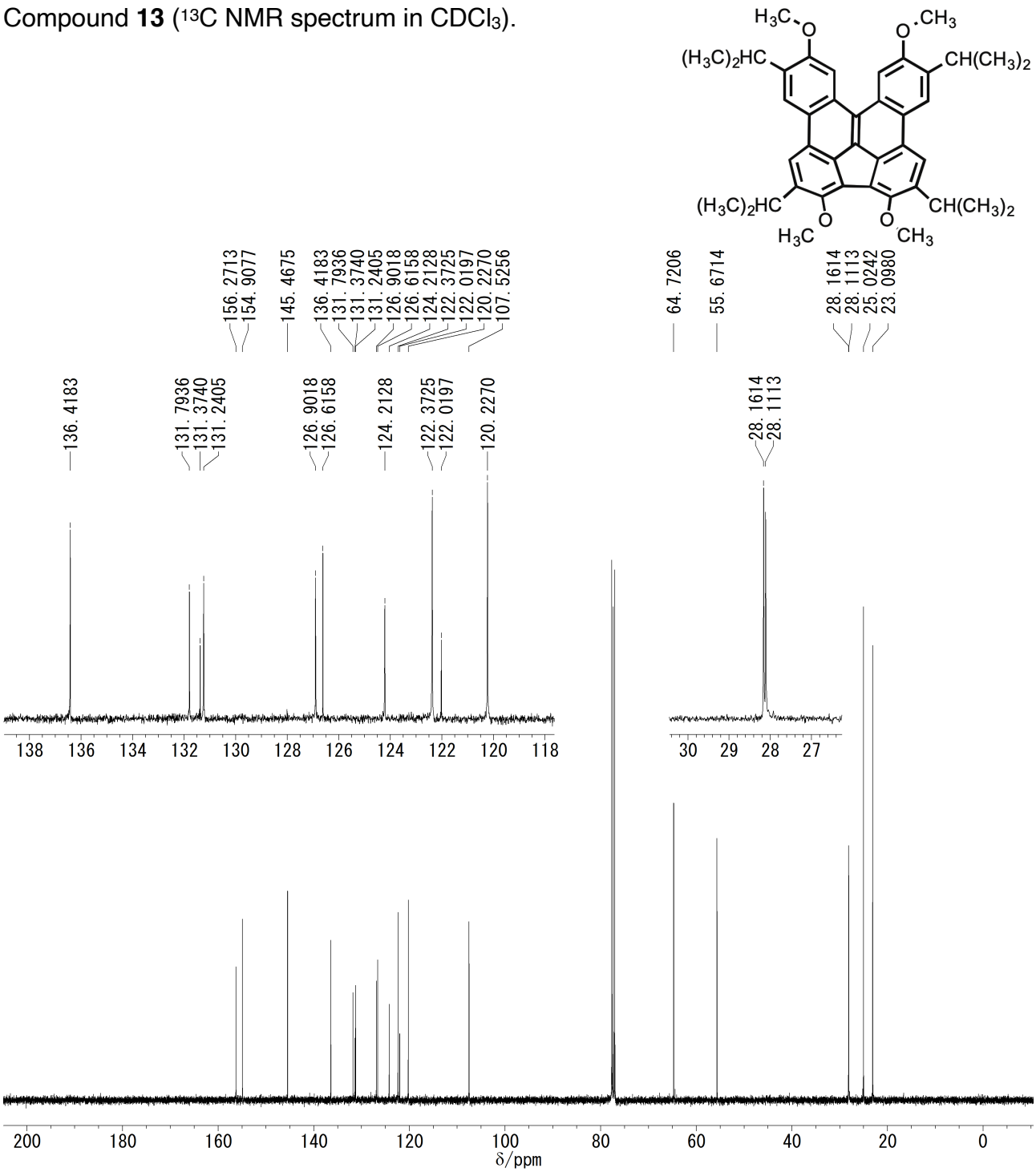
Compound **12** (^{13}C NMR spectrum in $CDCl_3$).



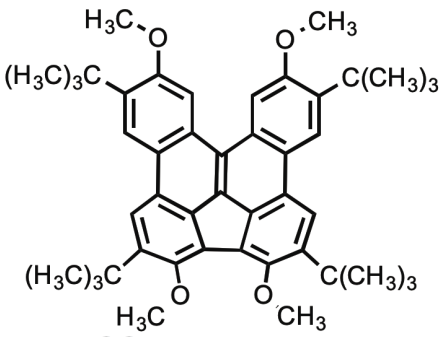
Compound **13** (^{1}H NMR spectrum in $CDCl_3$).

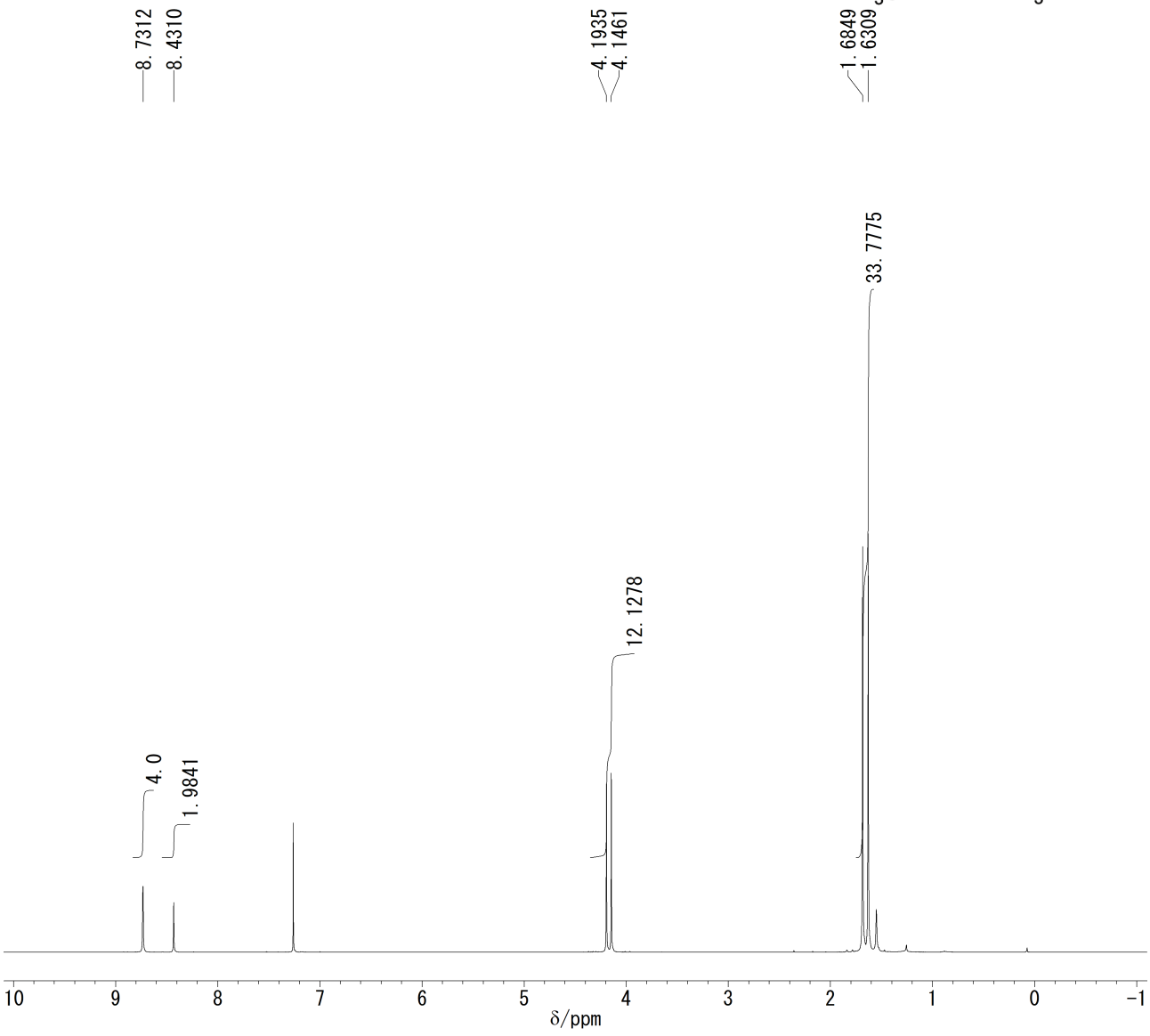


Compound **13** (^{13}C NMR spectrum in $CDCl_3$).

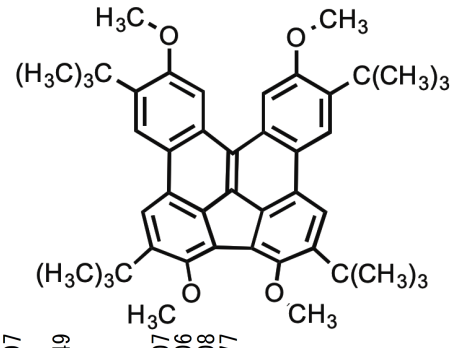


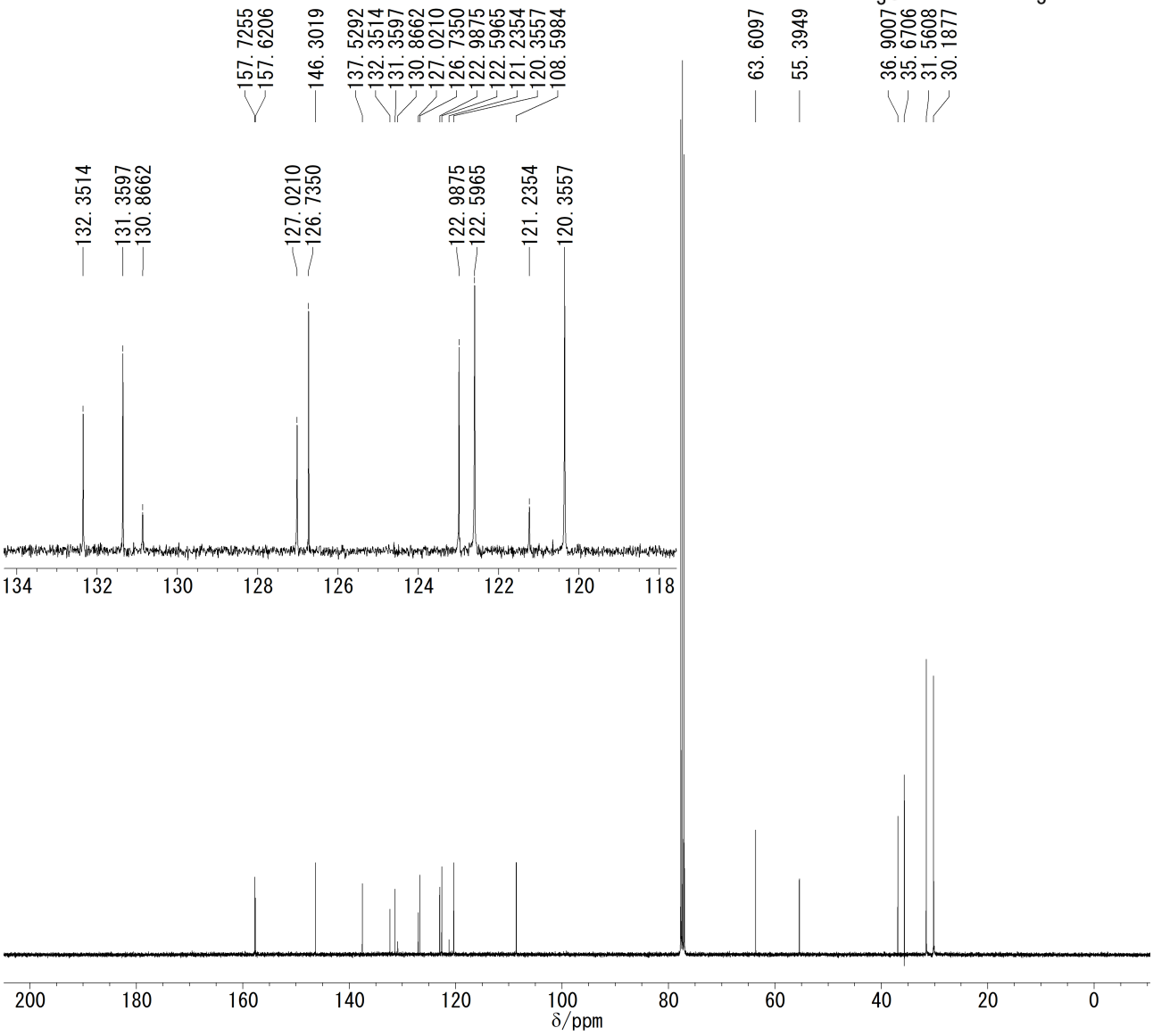
Compound **14** (^{1}H NMR spectrum in $CDCl_3$).



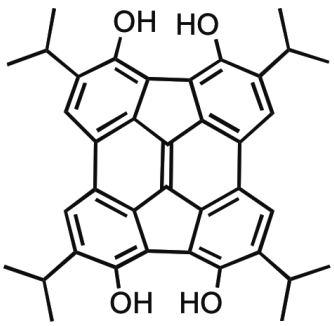


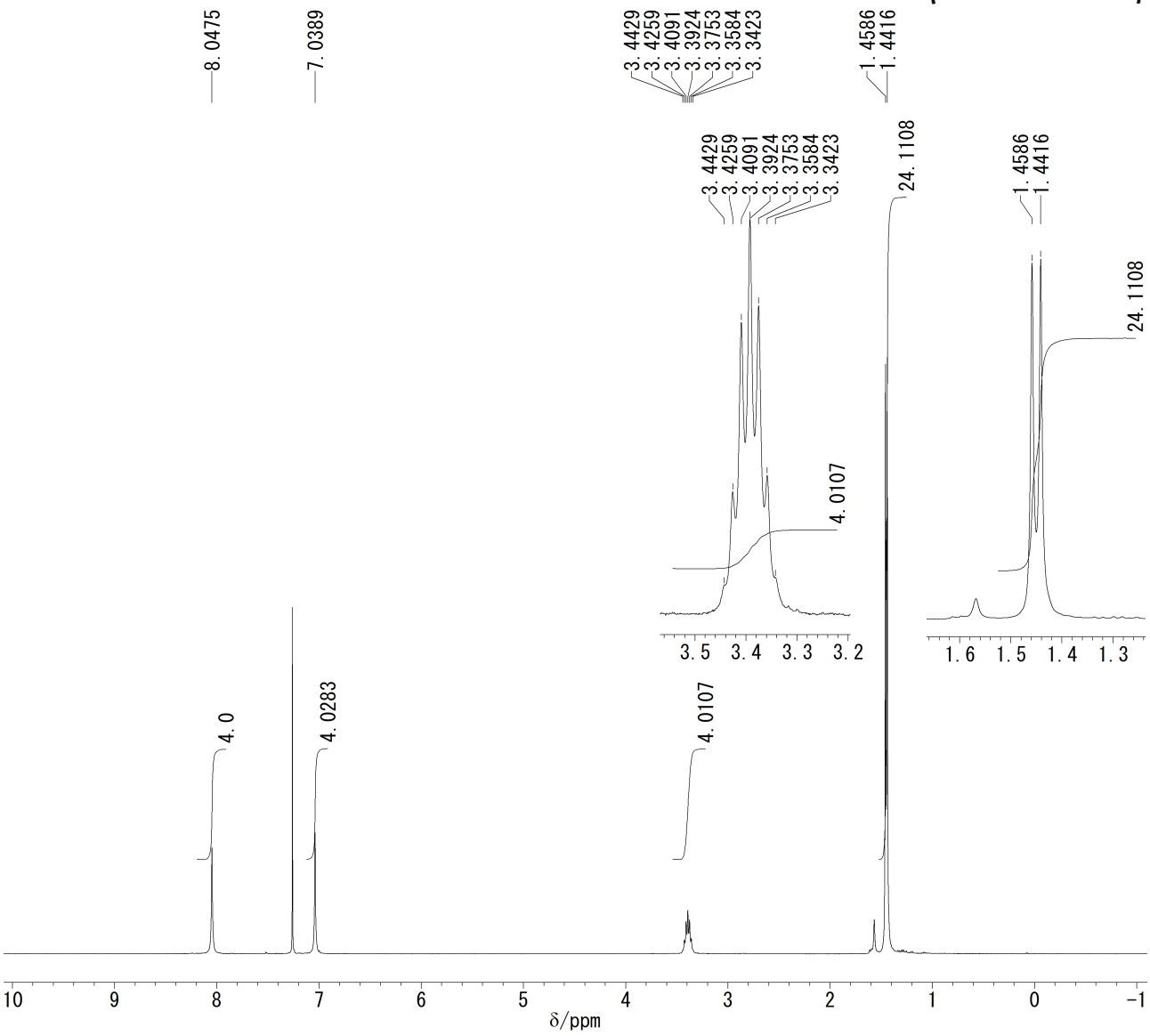
Compound **14** (^{13}C NMR spectrum in $CDCl_3$).



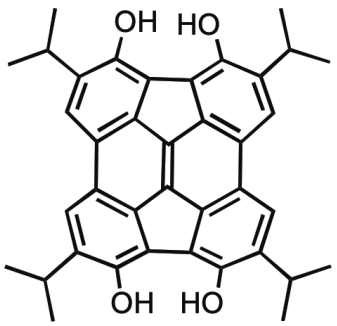


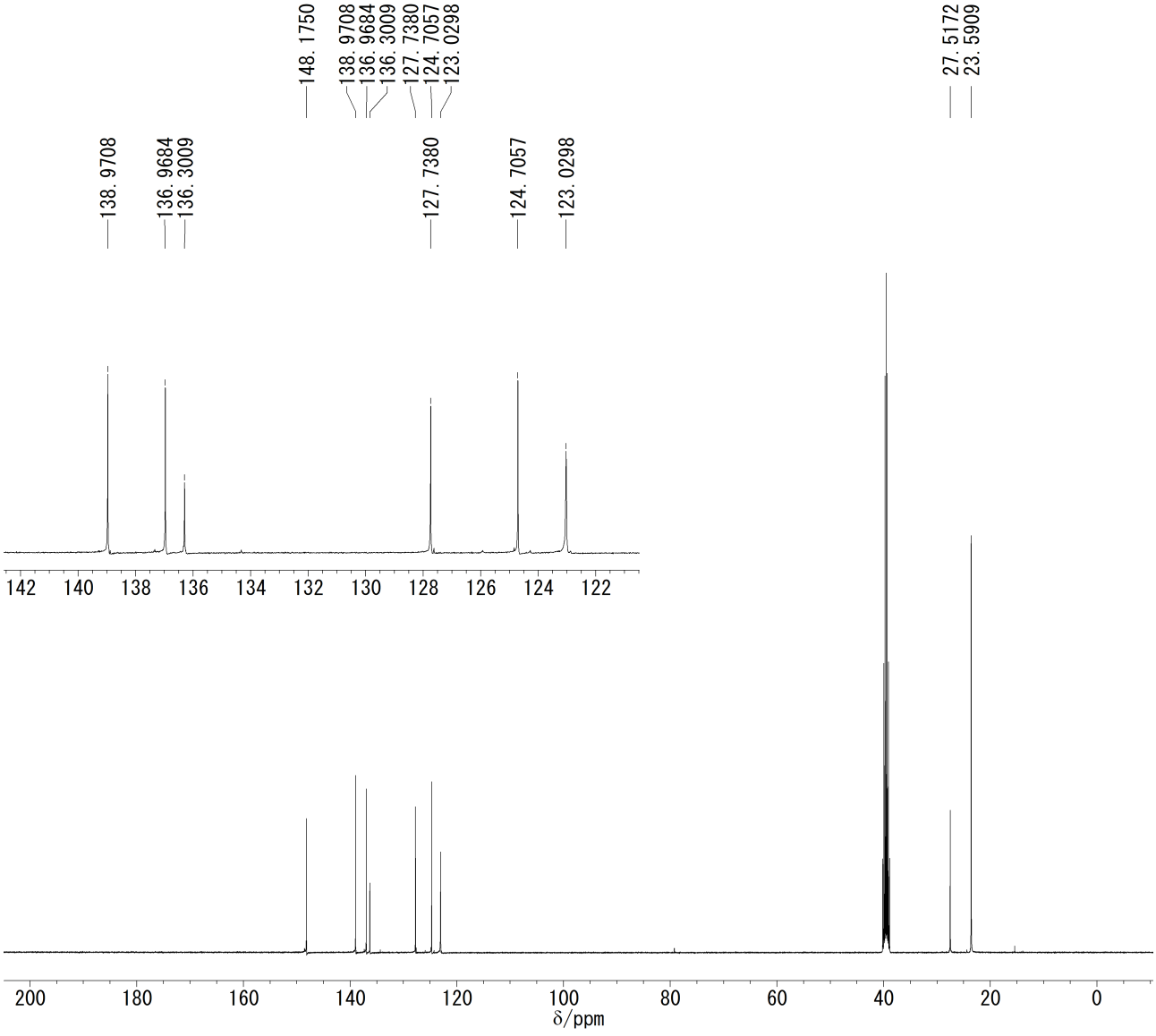
Compound **15** (^{1}H NMR spectrum in $CDCl_3$).



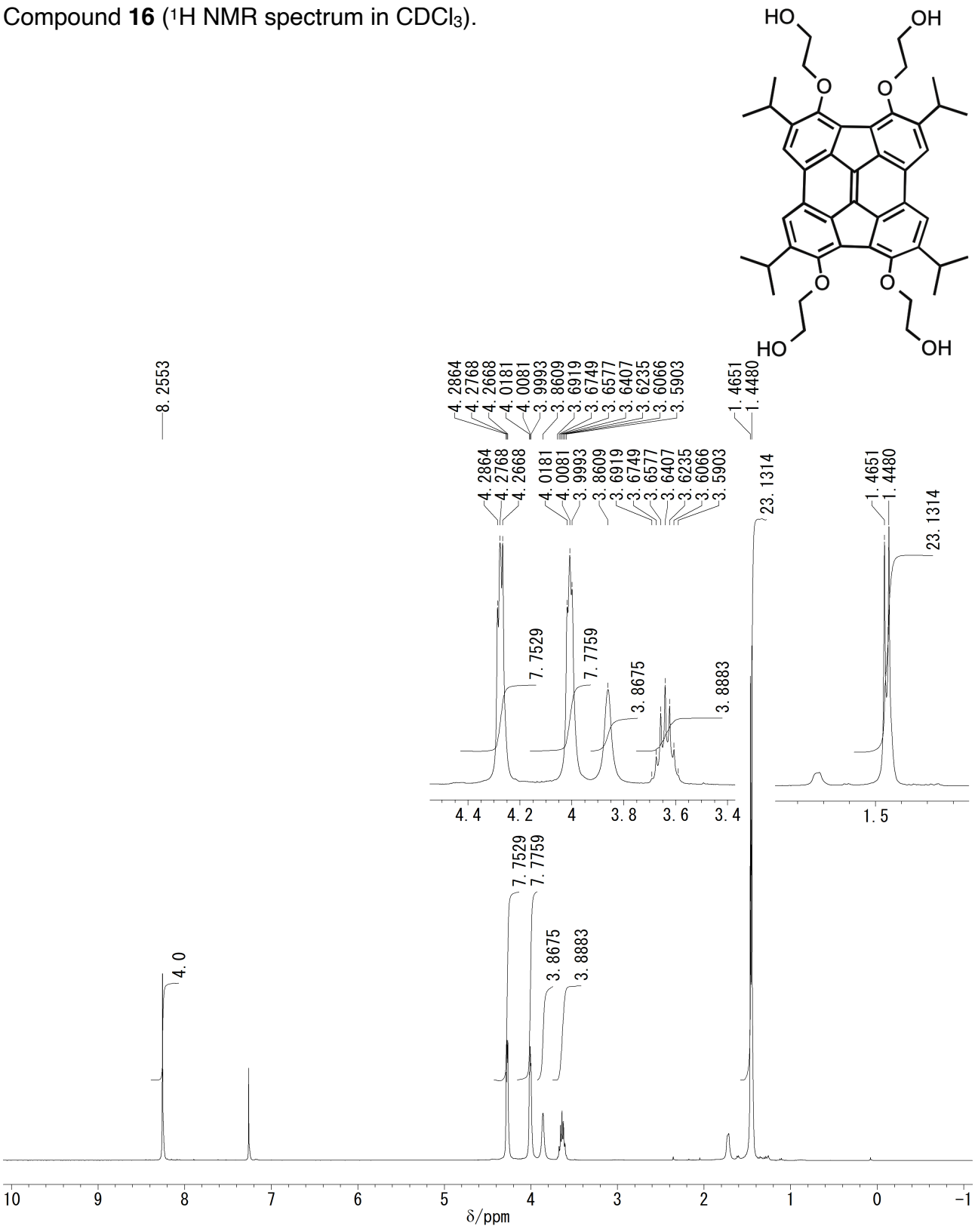


Compound **15** (^{13}C NMR spectrum in DMSO-d_6).

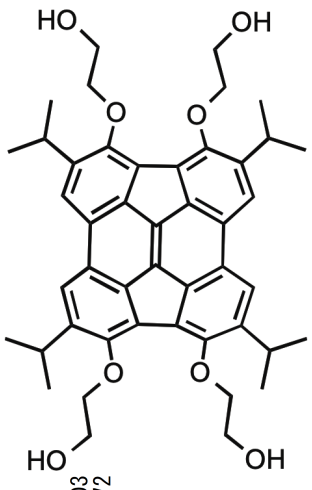


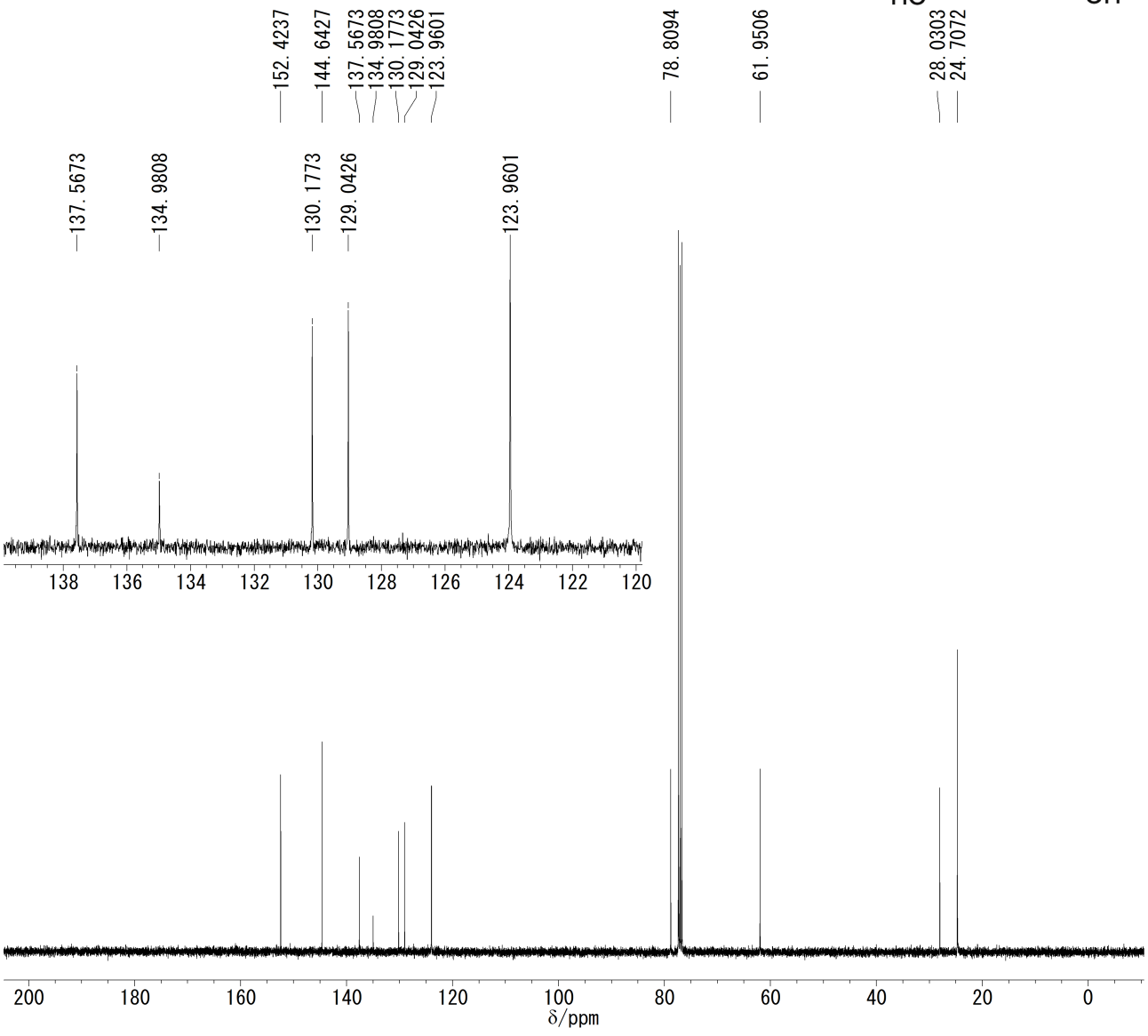


Compound **16** (^{1}H NMR spectrum in $CDCl_3$).

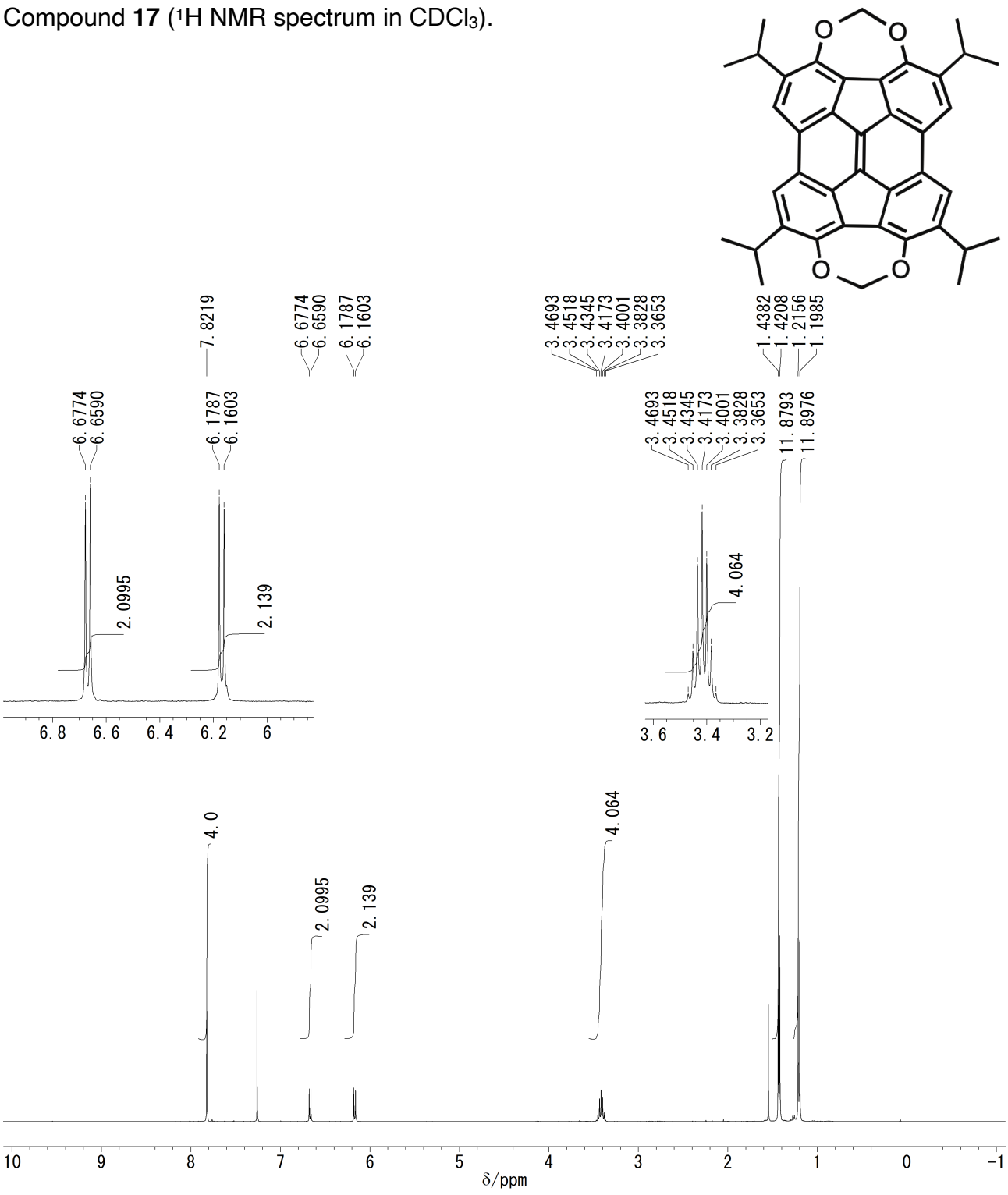


Compound **16** (^{13}C NMR spectrum in $CDCl_3$).

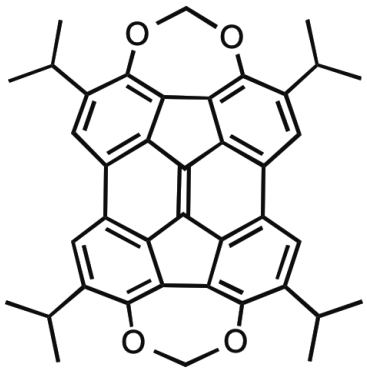


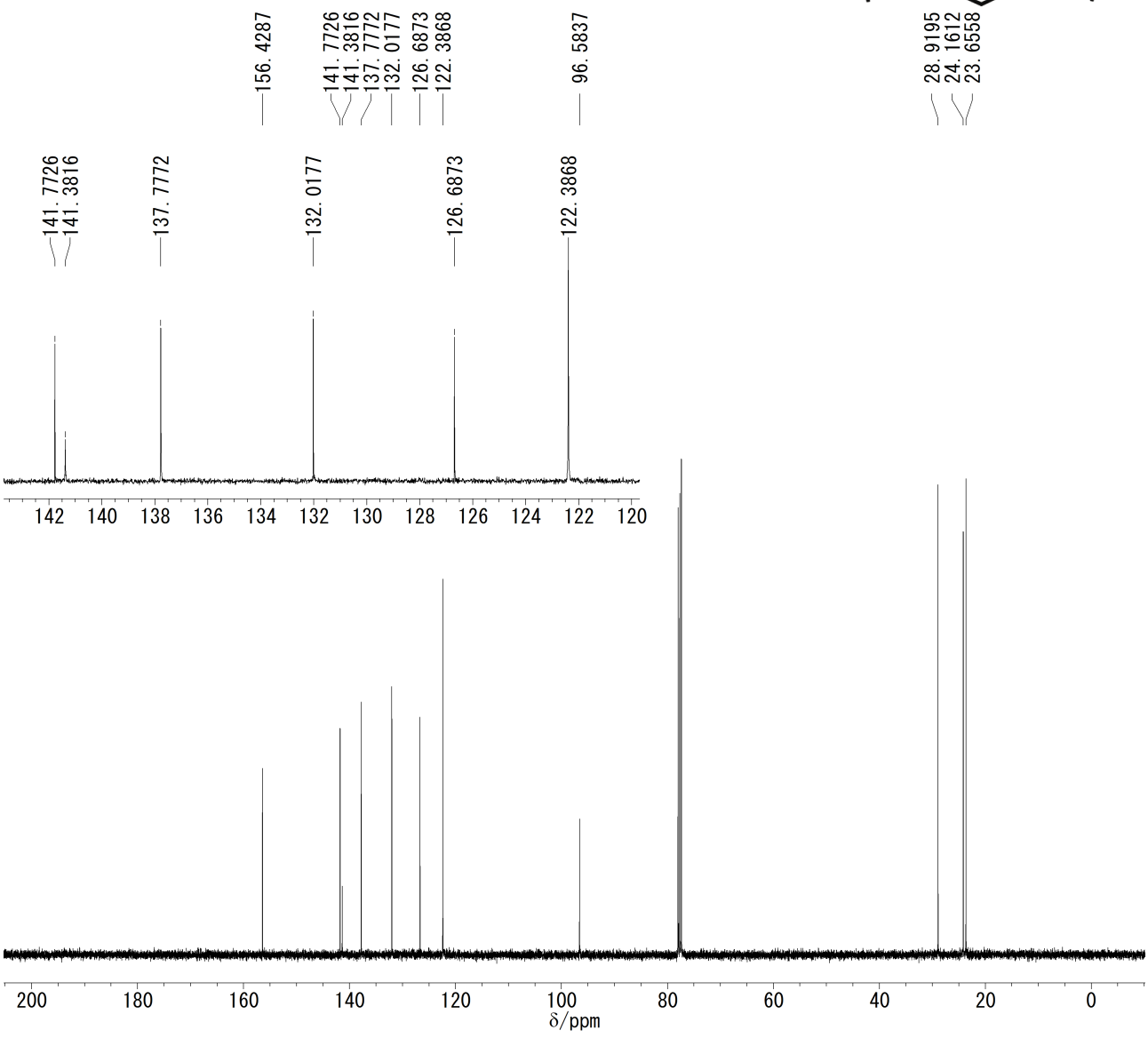


Compound **17** (^{1}H NMR spectrum in $CDCl_3$).

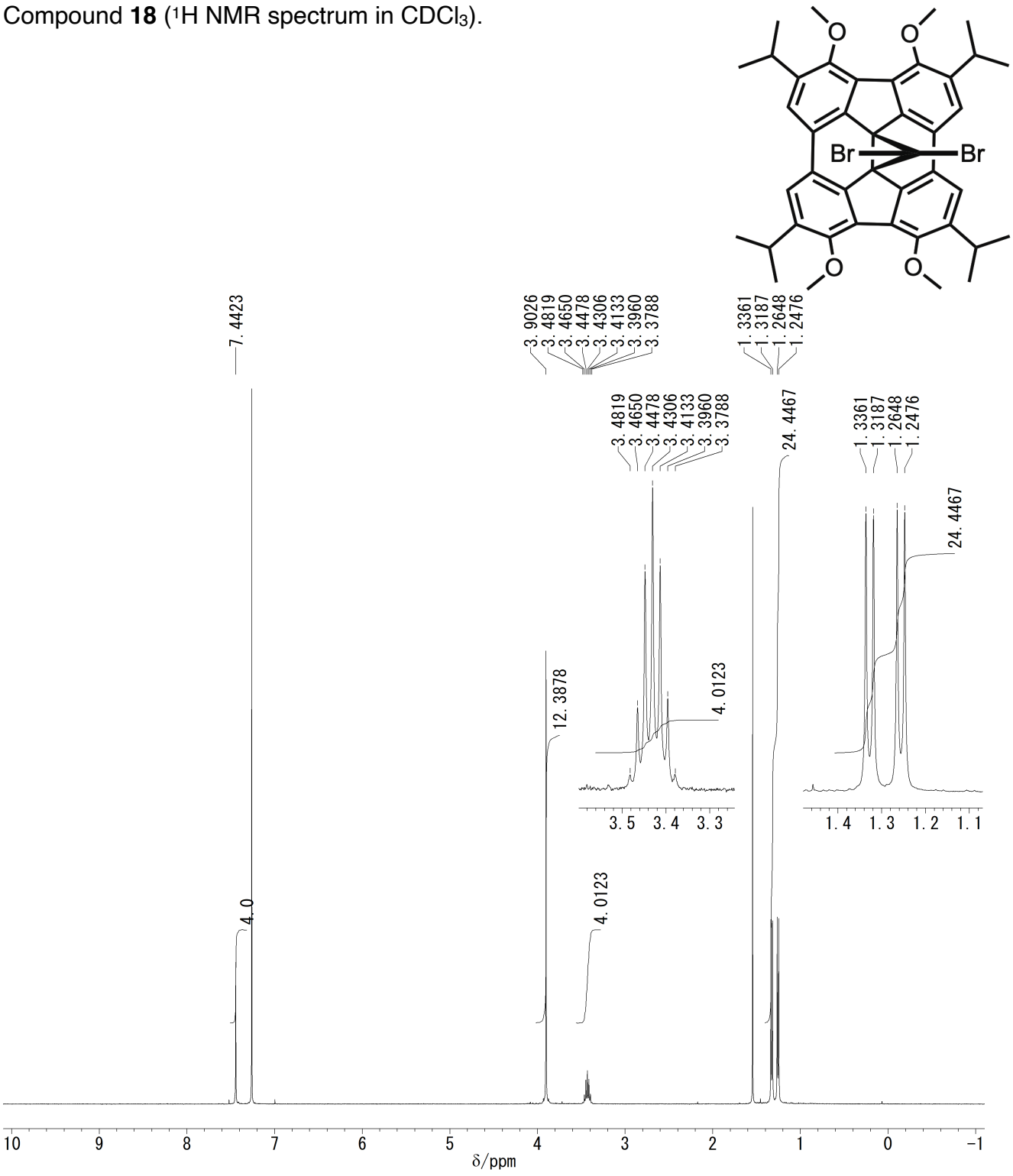


Compound **17** (^{13}C NMR spectrum in $CDCl_3$).

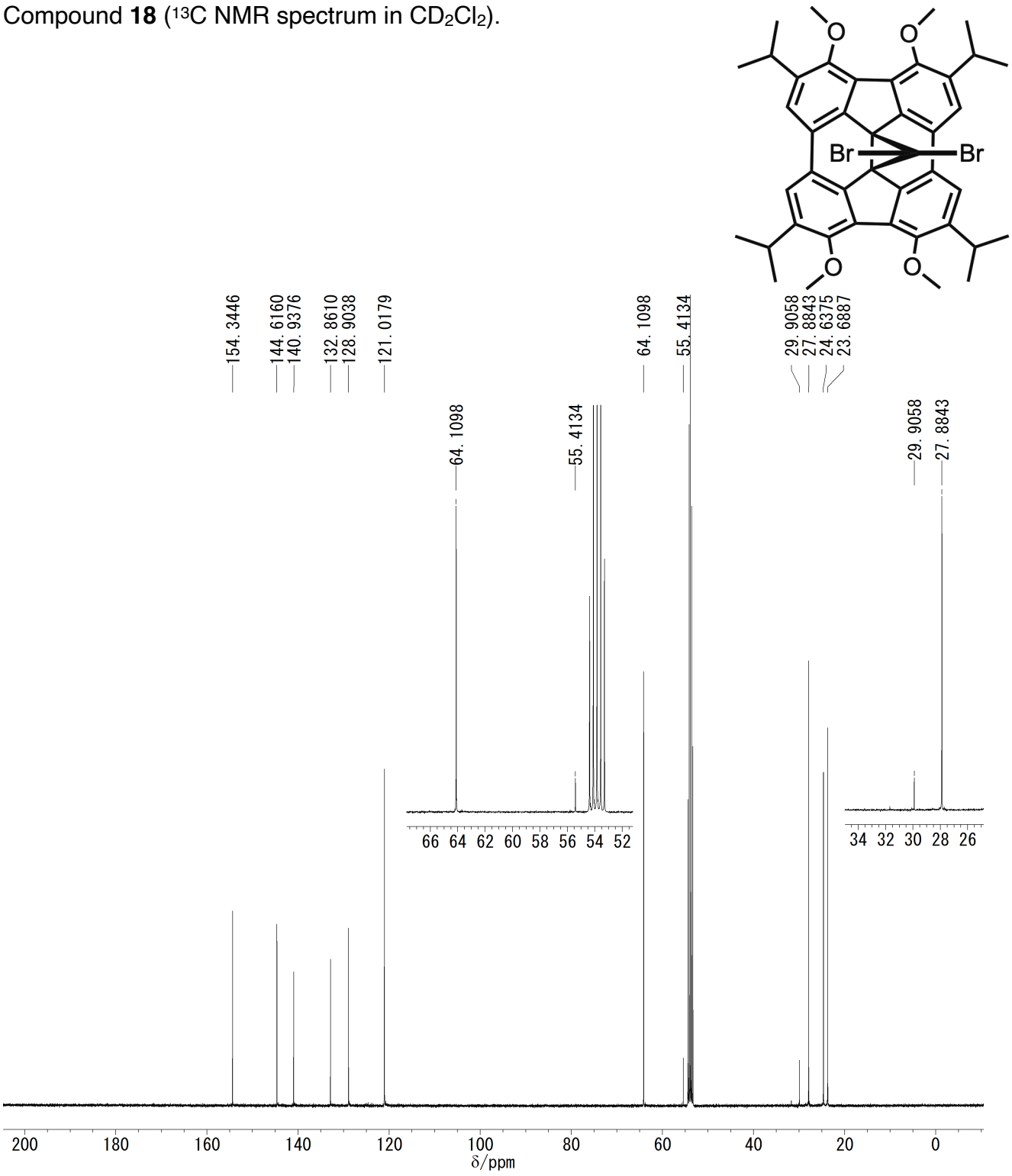




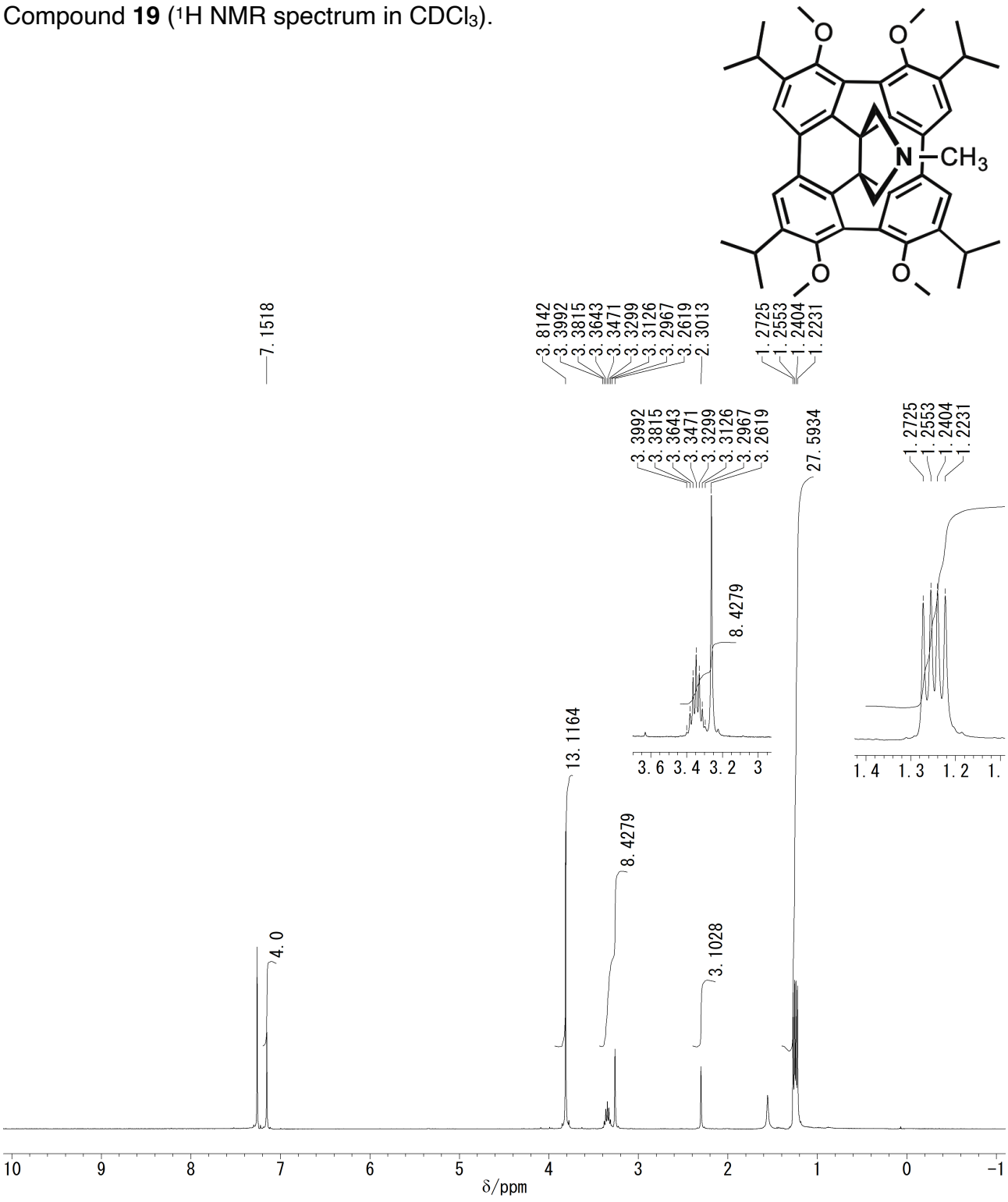
Compound **18** (^{1}H NMR spectrum in $CDCl_3$).



Compound **18** (^{13}C NMR spectrum in CD_2Cl_2).



Compound **19** (^{1}H NMR spectrum in $CDCl_3$).



Compound **19** (^{13}C NMR spectrum in $CDCl_3$).