Supporting Information

Regio-Defined Multi-Hydroxylation of Dibenzo[*g*,*p*]chrysene

Naoki Yoshida, Shinsuke Kamiguchi, Kazuki Sakao, Ryuhei Akasaka, Yoshino Fujii,

Tomoyuki Maruyama, Tetsuo Iwasawa*

Department of Materials Chemistry, Ryukoku University, Seta, Otsu, 520-2194, Japan

Corresponding author's email address: iwasawa@rins.ryukoku.ac.jp

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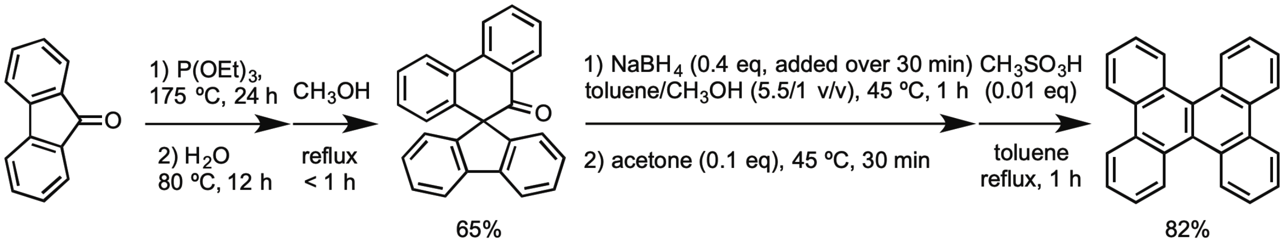
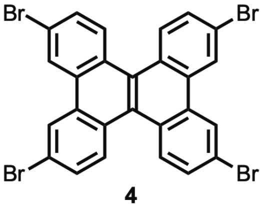
1. General informations: All reactions sensitive to air or moisture were carried out under an argon or a nitrogen atmosphere and anhydrous conditions unless otherwise noted. Dry solvents were purchased and used without further purification and dehydration. All reagents were purchased and used without 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.). HRMS were reported on the basis of TOF (time of flight)-MS (MALDI-TOF or LCMS-IT-TOF), and DART (Direct Analysis in Real Time)-MS. ^1H 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 δ (ppm) with reference to residual solvent signals [^1H NMR: $CHCl_3$ (7.26), CH_2Cl_2 (5.32), DMSO (2.50); ^{13}C NMR: $CDCl_3$ (77.0), DMSO (39.5)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.
2. Synthesis of dibenzo[*g*,*p*]chrysene (Scheme 1): To a 1 L flask charged with 9-fluorenone (80 g, 444 mmol) was added $P(OEt)_3$ (153 mL, 888 mmol), and the mixture was stirred at 175 °C. After stirred for 24 h, the mixture was cooled to 60 °C. To the mixture was slowly added water (160 mL, 8.88 mol) over 10 min, and the mixture was heated to 80 °C for hydrolyzing the residual $P(OEt)_3$. After stirred for more than 12 h, the reaction mixture was filtered, and the precipitates were washed with methanol (500 mL). The collected solid materials in methanol (252 mL, 6.21 mol) was refluxed in 1 h, and the mixture was filtered and washed again with methanol (400 mL). The resultant sample was dried up with rotary evaporator (70 °C, 0.5 h), giving 49.7 g of desired pale yellow solid materials in 65% yield. ^1H NMR (400 MHz, $CDCl_3$) 8.20 (dd, J = 7.8, 1.2



Hz, 1H), 8.10 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.81 - 7.77 (m, 3H), 7.45 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.41 - 7.35 (m, 3H), 7.18 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 7.18 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.08 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.04 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 2H), 6.61 (dd, *J* = 7.8, 1.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 197.6, 147.4 (two peaks are overlapped), 142.0, 138.4, 135.2, 130.9, 130.4, 129.6, 128.9, 128.7 (two peaks are overlapped), 128.6, 128.4, 128.3 (two peaks are overlapped), 125.1 (two peaks are overlapped), 124.5, 123.6, 120.9 (two peaks are overlapped), 69.0 ppm; MS (DART-TOF) *m/z*: 345 $[MH]^+$; IR (neat): 3068, 1686 (C=O), 1603, 1478, 1447, 1256, 1132, 746, 718 cm^{-1}; HRMS (DART-TOF) calcd for $C_{26}H_{17}O$: 345.1279 $[MH]^+$, Found: 345.1276. This spiro-ketone molecule was provided in next step without further purification. To a 500 mL flask charged with the spiro-ketone (30 g, 87.1 mmol) was added toluene (132 mL) and methanol (24 mL), and the flask was heated at 45 °C. To the flask was slowly added $NaBH_4$ (1.32 g, 34.8 mmol) over 30 min (189 mg x 7 times at five-minutes intervals). After stirred for 1 h, the reaction was quenched with acetone (0.64 mL, 8.4 mmol) and treated for additional 0.5 h. The organic layer was washed with water (100 mL x 3), and transferred into 500 mL flask, and the flask was heated at 120 °C for azeotropic removal of water, which was followed by addition of CH_3SO_3H (0.06 mL, 0.87 mmol). After 1 h, the second azeotropic removal of water from the reaction solvent of toluene was carried out, and the reaction mixture was allowed to cool to room temperature when crystallization was observed. The crystals were collected in 23.5 g of dibenzo[*g,p*]chrysene (82%) as yellow crystals. All data are identified with authentic sample that are commercialized in TCI. ^{1}H NMR (400 MHz, $CDCl_3$) 8.72 (dd, *J* = 8.0, 1.3 Hz, 4H) 8.71 (dd, *J* = 8.0, 1.3 Hz, 4H), 7.69 (ddd, *J* = 8.0, 8.0, 1.3 Hz, 4H), 7.64 (ddd, *J* = 8.0, 8.0, 1.3 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 130.8, 129.2, 128.9, 127.4, 126.5 (two peaks are overlapped), 123.6 ppm.

3. Synthesis of tetra-bromide **4** (Scheme 2): To the cloudy state of dibenzo[*g*, *p*]chrysene (2.63 g, 8.0 mmol) in dry CH_2Cl_2 (24 mL) was added Br_2 (6.6 mL, 128 mmol, 5.7 M in CH_2Cl_2) dropwise over 10 min. After the mixture was stirred for 2 h at room temperature, the resultant precipitates were filtered off, and washed with methanol, and concentrated *in vacuo* to give crude products. Purification by recrystallization from toluene (350 - 140 = 210 mL/g) afforded 3.72 g of **4** as white solid materials in 72% yield. ^1H NMR (400 MHz, $CDCl_3$) 8.73 (d, *J* = 1.8 Hz, 4H), 8.41 (d, *J* = 8.8 Hz, 4H), 7.75 (dd, *J* = 8.8, 1.8 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 131.6, 130.9, 130.5, 128.0, 127.0, 122.0 ppm; MS (DART-TOF) *m/z*: 640 $[M]^+$; IR (neat): 3076, 1587, 1514, 1475, 1408, 1085, 1021, 894, 858, 806, 567 cm^{-1}; HRMS (DART-TOF) calcd for $C_{26}H_{12}Br_4$: 639.7673 $[M]^+$, Found 639.7683; Anal. Calcd for $C_{26}H_{12}Br_4$: C, 48.49; H, 1.88. Found: C, 48.26; H, 1.79.



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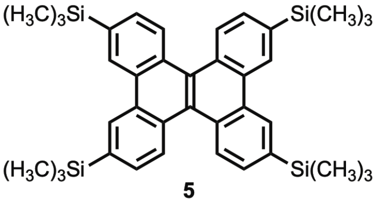
4. Synthesis of tetra-trimethylsilyl **5** (Scheme 3): Under an argon atmosphere, to the suspension of **4** (515 mg, 0.8 mmol) in dry THF (16 mL) at -78 °C was added *n*-BuLi (3.1 mL, 4.8 mmol, 1.6 M in hexane) dropwise over 5 min. After the mixture was stirred at -78 °C for 30 min, chlorotrimethylsilane (0.9 mL, 7.2 mmol) was added over 1 min. The reaction mixture was allowed to warm to ambient temperature and conducted for 2 h. The reaction was quenched with methanol (10 mL) at 0 °C, and followed by concentration to give 521 mg of crude products as yellow solid materials. Purification with silica-gel column chromatography (eluent, hexane only) afforded 365 mg of **5** in 74% as white solid materials. ^1H NMR (400 MHz, $CDCl_3$) 8.89 (s, 4H), 8.66 (d, *J* = 8.2 Hz, 4H), 7.76 (d, *J* = 8.2 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 138.9, 131.4, 130.3, 129.9, 128.9, 128.4, 128.3, -0.62 ppm; MS (DART-TOF) *m/z*: 616 $[M]^+$; IR (neat): 2952, 1391, 1249, 1105, 814, 659, 583 cm^{-1}; HRMS (DART-TOF) calcd for



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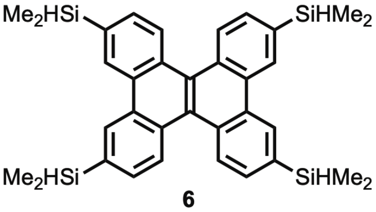
$C_{38}H_{48}Si_4$: 616.2833 [M]$^+$, Found 616.2846; Anal. Calcd for $C_{38}H_{48}Si_4$: C, 73.87; H, 7.83. Found: C, 73.96; H, 7.84.

5. Synthesis of tetra-silyl **6** (Scheme 4): Under an argon atmosphere, to a suspension of **4** (1.03 g, 1.6 mmol) in anhydrous THF (32 mL) at -78 ºC was added *n*-BuLi (6.0 mL, 1.59 M hexane solution) dropwise over 5 min. The suspension was stirred at -78 ºC for 30 min, and chlorodimethylsilane (1.0 mL, 14.4 mmol) was added *quickly in just 5 seconds*. After stirred for 2 h at room temperature, the reaction was quenched with satd. aq. NH_4Cl (20 mL). The mixture was diluted with toluene, and the aqueous phase was extracted with toluene (15 mL x 3). Combined organic phases were washed with brine (30 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give the crude products. Purification by silica-gel column chromatography (eluent, hexane only) gave 674 mg of **6** (75%) as white solid materials. ^1H NMR (400 MHz, $CDCl_3$) 8.93 (s, 4H), 8.66 (d, J = 8.1 Hz, 4H), 7.78 (d, J = 8.1 Hz, 4H), 4.69 (sept, J = 3.8 Hz, 4H), 0.53 (d, J = 3.8 Hz, 24H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 136.0, 131.8, 130.3, 130.1, 129.8, 128.4, 128.3, -3.3 ppm; MS (DART-TOF) *m/z*: 560 [M]$^+$; IR (neat): 2956, 2109 (Si-H), 1388, 1240, 1109, 862, 814 cm^{-1}; HRMS (DART-TOF) calcd for $C_{34}H_{40}Si_4$: 560.2207 [M]$^+$, Found : 560.2223.



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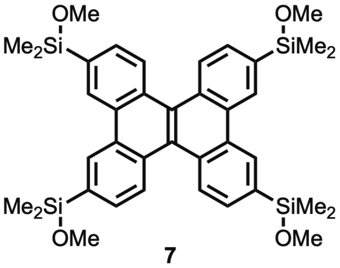
6. Synthesis of tetra-methoxysilyl **7** (Scheme 4): Under an Ar atmosphere, to a solution of **6** (1.12 g, 2.0 mmol) in toluene and MeOH (each 16 mL) was added 10 wt% Pd/C (416 mg, 0.4 mmol) at room temperature, and the mixture was stirred for 30 min. Filtration through a pad of celite (eluent, toluene), and the following concentration gave 1.28 g of crude products as white solid materials. The products were provided in next step without further purification. ^1H NMR (400 MHz, $CDCl_3$) 8.99



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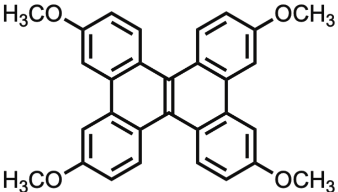
(s, 4 H), 8.70 (d, *J* = 8.2 Hz, 4 H), 7.83 (d, *J* = 8.2 Hz, 12 H), 3.57 (s, 12 H), 0.56 (s, 24 H) ppm.

7. Synthesis of tetra-methoxy **8** (Scheme 4): To a solution of **7** in THF and MeOH (each 5 mL) was added $KHCO_3$ (200 mg, 2.0 mmol), 30% aq. H_2O_2 (1.4 mL, 12 mmol) dropwise over 3 min, and KF (116 mg, 2.0 mmol). After stirred for 4 h at room temperature, the mixture was quenched with 1 M aq. HCl (40 mL), and stirred for 10 min at 0 °C. The aqueous phase was extracted with EtOAc (20 mL x 3), and the combined organic phases were washed with brine, dried over Na_2SO_4, and filtered, and concentrated *in vacuo* to give 295 mg of crude products as dark green solid materials. The products were washed with $CHCl_3$, and followed by purification with short plugged column chromatography (SiO_2, eluted with THF). The resultant dark green solid materials (153 mg) included **1**; however, further purification of this state was very difficult owing to troublesome impurities. Hence, the products were provided in next step to convert into the corresponding tetra-methoxy **8**. To this product was added DMF (2.5 mL), K_2CO_3 (525 mg, 3.8 mmol) and MeI (0.47 mL, 7.6 mmol). The mixture was stirred for 10 h at 55 °C, and the starting material was totally disappeared by TLC monitoring. The reaction mixture was diluted with toluene, and the resultant mixture was filtered through a pad of celite, and the filtrate was evaporated off. The residue dissolved in toluene was washed with water (40 mL), and the aqueous phase was extracted with toluene (30 mL x 3), and combined organic phases were washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give 180 mg of crude products as dark green solid materials. Purification with silica-gel short column chromatography (eluent, toluene) afforded 65 mg of **8** in pure form as orange solid materials 30% yield in 2 steps. ^1H NMR (400 MHz, $CDCl_3$) 8.55 (d, *J* = 9.0 Hz, 4H), 8.00 (d, *J* = 2.4 Hz, 4H), 7.23 (dd, *J* = 9.0, 2.4 Hz, 4H), 4.05 (s, 12H) ppm; ^{13}C NMR



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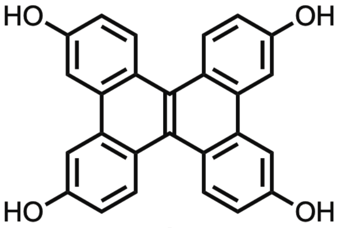
(100 MHz, $CDCl_3$) 158.1, 131.8, 130.6, 124.8, 124.3, 115.4, 106.4, 55.9 ppm; MS (DART -TOF) *m/z*: 449 $[MH]^+$; IR (neat): 2928, 2829, 1606, 1451, 1419, 1224, 1034, 826, 778 cm^{-1}; HRMS (DART -TOF) calcd for $C_{30}H_{25}O_4$: 449.1753 $[MH]^+$, Found: 449.1734; Anal. Calcd for $C_{30}H_{24}O_4$: C, 80.34; H, 5.39. Found: C, 80.19; H, 5.39.



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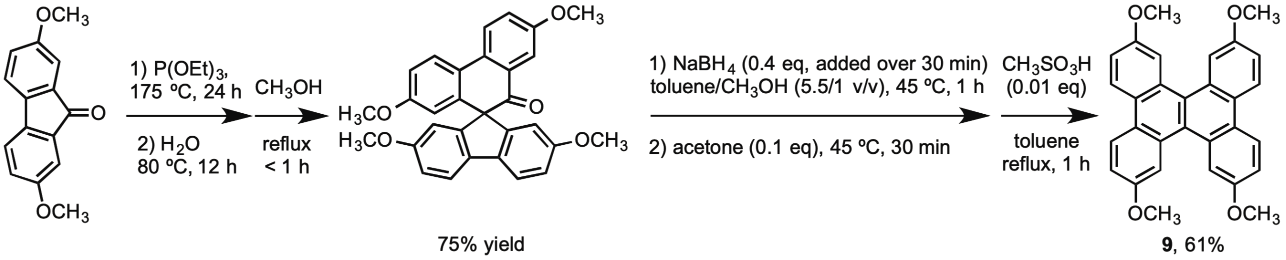
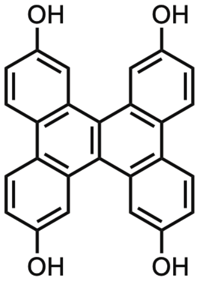
8. Synthesis of tetrol **1** (Scheme 4): Under an argon atmosphere, to the solution of **8** (100 mg, 0.2 mmol) in dry CH_2Cl_2 (2 mL) at 0 °C was added BBr_3 (1.2 mL, 1 M CH_2Cl_2 solution) dropwise over 3 min. After stirred at room temperature for 4 h, the mixture was quenched with water (2 mL) at 0 °C. The resultant precipitates were filtered off, and washed with water (20 mL), and concentrated *in vacuo* to give **1** (63 mg, 81%) in pure form as blue solid materials. ^{1}H NMR (400 MHz, DMSO-d_6) 9.91 (s, 4H), 8.34 (d, $J = 7.2$ Hz, 4H), 7.80 (d, $J = 1.9$ Hz, 4H), 7.12 (dd, $J = 7.2$, 1.9 Hz, 4H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 155.8, 131.0, 129.9, 123.2, 122.1, 116.6, 107.6 ppm; MS (DART -TOF) *m/z*: 393 $[MH]^+$; IR (neat): 3180 (O-H), 1606, 1436, 1340, 1200, 1165, 965, 802 cm^{-1}; HRMS (DART -TOF) calcd for $C_{26}H_{17}O_4$: 393.1121 $[MH]^+$, Found : 393.1112.

9. Synthesis of tetra-methoxy **9** (Scheme 5): To a 1 L flask charged with 2,7-dimethoxy-9-fluorenone (80 g, 333 mmol) was added $P(OEt)_3$ (115 mL, 666 mmol), and the resultant brown solution was stirred at 175 °C. After stirred for 24 h, the mixture was cooled to 60 °C. To the mixture was slowly added water (120 mL, 6.66 mol) over 10 min, and the mixture was heated to 80 °C for hydrolyzing the residual $P(OEt)_3$. After stirred for more than 12 h, the reaction mixture was filtered, and the precipitates were washed with



methanol (450 mL). The collected solid materials in methanol (189 mL, 4.66 mol) was refluxed in 1 h, and the mixture was filtered and washed again with methanol (400 mL). The resultant sample was dried up with rotary evaporator (70 °C, 0.5 h), giving 57.7 g of desired yellow solid materials in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) 7.99 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 2.8 Hz, 1H), 7.30 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.89 (dd, *J* = 8.4, 2.3 Hz, 2H), 6.87 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.57 (d, *J* = 2.3 Hz, 2H), 6.15 (d, *J* = 2.8 Hz, 1H), 3.85 (s, 3H), 3.68 (s, 6H), 3.60 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 197.4, 159.7, 159.3, 159.1, 148.6, 140.7, 134.7, 131.9, 130.4, 125.2, 124.6, 123.8, 123.4, 120.7, 114.1, 113.9, 113.5, 110.9, 110.7, 69.0, 55.8, 55.7, 55.4 ppm; MS (DART-TOF) *m/z*: 465 $[MH]^+$; IR (neat): 2936, 2833, 1683, 1604, 1469, 1427, 1215, 1041, 809, 783 cm^{-1}; HRMS (DART-TOF) calcd for $C_{30}H_{25}O_5$: 465.1702 $[MH]^+$, Found: 465.1690. This spiro-ketone molecule was provided in next step without further purification. To a 500 mL flask charged with the spiro-ketone (30 g, 65 mmol) was added toluene (122 mL) and methanol (24 mL), and the flask was heated at 45 °C. To the flask was slowly added $NaBH_4$ (977 mg, 26 mmol) over 30 min (140 mg x 7 times at five-minutes intervals). After stirred for 1 h, the reaction was quenched with acetone (0.5 mL, 6.5 mmol) and treated for additional 0.5 h. The organic layer was washed with water (100 mL x 3), and transferred into 500 mL flask, and the flask was heated at 120 °C for azeotropic removal of water, which was followed by addition of CH_3SO_3H (0.04 mL, 0.65 mmol). After 1 h, the reaction mixture was allowed to cool to room temperature, and concentrated *in vacuo*. The resultant sample was recrystallized from CH_2Cl_2/EtOH (4/1 v/v, 25 mL/g - 7 mL/g = 18 mL/g), which afforded 17.8 g of **9** in 61% yield as yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$) 8.51 (d, *J* = 9.0 Hz, 4H), 8.23 (d, *J* = 2.6 Hz, 4H), 7.28 (dd, *J* = 9.0, 2.6 Hz, 4H), 0.94 (s, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 157.8, 129.9, 128.8, 125.3, 124.9, 116.4, 110.3, 55.7 ppm; MS (DART-TOF) *m/z*: 449 $[MH]^+$; IR (neat): 2825, 1603, 1479, 1466, 1427, 1238, 1214, 1008, 798 cm^{-1}; HRMS (DART-TOF) calcd for $C_{30}H_{25}O_4$: 449.1747 [MH]$^+$, Found: 449.1771; Anal. Calcd for $C_{30}H_{24}O_4$: C, 80.34; H, 5.39. Found: C, 80.34; H, 5.18.

10. Synthesis of tetrol **2** (Scheme 5): Under an Ar atmosphere, to the solution of **9** (428 mg, 0.95 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C was added BBr_3 (5.7 mL, 1 M CH_2Cl_2 solution) dropwise over 4 min. After stirred for 4 h at room temperature, the reaction system was quenched with water (10 mL) at 0 °C. The resultant precipitates were filtered off, and washed with water (40 mL), and concentrated *in vacuo* to give **2** (354 mg, 96%) in pure form as green solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) 9.72 (s, 4H), 8.49 (d, *J* = 8.9 Hz, 4H), 8.00 (d, *J* = 2.4 Hz, 4H), 7.15 (dd, *J* = 8.9, 2.4 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.3, 129.1, 127.3, 124.7, 123.6, 116.7, 112.0 ppm; MS (DART-TOF) *m/z*: 393 [MH]$^+$; IR (neat): 3240 (O-H), 1610, 1578, 1447, 1244, 1169, 782, 452, cm^{-1}; HRMS (DART-TOF) calcd for $C_{26}H_{17}O_4$: 393.1122 [MH]$^+$, Found: 393.1131.



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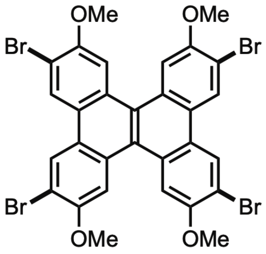
11. Synthesis of tetra-bromo **10** (Scheme 6): Under an argon atmosphere, to a solution of **9** (897 mg, 2.0 mmol) in anhydrous CH_2Cl_2 (8 mL) at room temperature was added Br_2 (1.6 mL, 32 mmol, 5.7 M in CH_2Cl_2) dropwise over 3 min. After stirred at room temperature for 2 h, the reaction was quenched with satd. aq. $NaHCO_3$ (20 mL), and followed by additional stirring for 10 min at 0 °C. The aqueous layer was extracted with CH_2Cl_2 (10 mL x 3). The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give 1.58 g of crude products. Purification by short-plugged silica-gel column chromatography (eluent, CH_2Cl_2 only) yielded 1.42 g of orange solid materials. Reprecipitation of the sample from $CHCl_3$/MeOH (1/8 v/v) gave 1.24 g of whitish yellow solid materials, and the following recrystallization from toluene (63 - 26 = 37 mL/g) yielded 758 mg of the yellowish white solid in 50%. ^{1}H NMR (400



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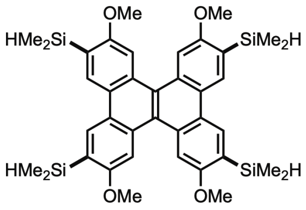
MHz, $CDCl_3$) 8.66 (s, 4H), 8.09 (s, 4H), 3.99 (s, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 154.4, 128.9, 128.5, 128.1, 125.0, 113.3, 109.4, 56.7 ppm; MS (DART-TOF) *m/z*: 764 $[MH]^+$; IR (neat): 2952, 2928, 2832, 1595, 1475, 1464, 1395, 1249, 1161, 1057, 1025, 866 cm^{-1}; HRMS (DART-TOF) calcd for $C_{30}H_{20}Br_4O_4$: 763.8054 $[M]^+$, Found: 763.8074; Anal. Calcd for $C_{30}H_{20}Br_4O_4$: C, 47.16; H, 2.64. Found: C, 47.12; H, 2.77.

12. Synthesis of tetra-silyl **11** (Scheme 6): Under an argon atmosphere, to a solution of **10** (760 mg, 1.0 mmol) in anhydrous THF (20 mL) at -78 °C was added *n*-BuLi (3.8 mL, 6.0 mmol, 1.6 M in hexane) dropwise over 3 min. After the mixture was stirred at -78 °C for 30 min, chlorodimethylsilane (0.62 mL, 9 mmol) was added *quickly in just 5 seconds*. The reaction was allowed to warm to room temperature, and stirred for additional 1 h. The reaction was quenched with satd. aq. $NaHCO_3$ (20 mL). The aqueous phase was extracted with toluene (20 mL x 3), and combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give crude products as yellow solid materials. Purification by silica-gel column chromatography (eluent, hexane/toluene = 1/1) afforded 513 mg of **11** as yellow solid materials in 75% yield. ^1H NMR (400 MHz, $CDCl_3$) 8.74 (s, 4H), 8.14 (s, 4H), 4.65 - 4.62 (sept, $J = 3.7$ Hz, 4H), 3.95 (s, 12H), 0.50 (d, $J = 3.7$ Hz, 24H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 162.4, 131.8, 131.4, 129.6, 127.1, 125.0, 107.2, 55.9, -3.2 ppm; MS (DART-TOF) *m/z*: 681 $[MH]^+$; IR (neat): 2949, 2900, 2821, 2113 (Si-H), 1599, 1459, 1395, 1236, 1081, 862, 834 cm^{-1}; HRMS (DART-TOF) calcd for $C_{38}H_{49}O_4Si_4$: 681.2702 $[MH]^+$, Found: 681.2724; Anal. Calcd for $C_{38}H_{48}O_4Si_4$: C, 67.01; H, 7.10. Found: C, 67.00; H, 7.14.



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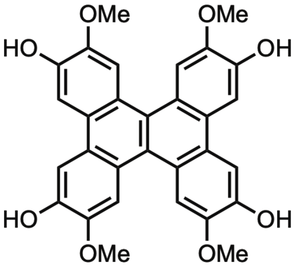
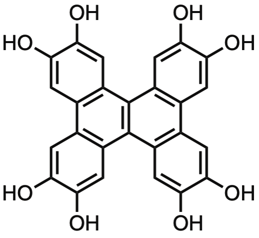
13. Synthesis of tetra-methoxy **12** (Scheme 6): Under an argon atmosphere, to a solution of 11 (905 mg, 1.3 mmol) in toluene and MeOH (each 12 mL) was added 10% Pd/C (277 mg, 0.26 mmol) at room temperature. The mixture was stirred for 30 min, and



12

then filtered through a pad of celite (eluent, toluene), and concentrated *in vacuo* to give 1.09 g of crude products as white solid materials. To the crude products (320 mg) was added THF and MeOH (each 4 mL), $KHCO_3$ (160 mg, 1.6 mmol), and 30% aq. H_2O_2 (1.0 mL, 9.6 mmol, dropwise over 3 min), and KF (93 mg, 1.6 mmol). After stirred at room temperature for 17 h, the mixture was quenched with 1 M aq. HCl (8 mL), and stirred at 0 °C for 10 min. The aqueous phase was extracted with EtOAc (20 mL x 2), and the combined organic phases were washed with brine, dried over Na_2SO_4, and filtered, and concentrated *in vacuo* to give 236 mg of crude products as dark green solid materials. Purification by silica-gel short -plugged column chromatography (eluent, hexane/EtOAc = 1/2) afforded 80 mg of 12 (39%) in 2 steps as dark green solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) 8.14 (s, 4H), 8.00 (s, 4H), 5.89 (s, 4H), 4.01 (s, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 146.2, 145.4, 125.6, 125.5, 123.5, 108.9, 56.3 ppm; MS (DART-TOF) *m/z*: 513 $[MH]^+$; IR (neat): 3307 (O-H), 2933, 2829, 1503, 1249, 1141, 1034, 858 cm^{-1}; HRMS (DART TOF) calcd for $C_{30}H_{25}O_8$: 513.1544 $[MH]^+$, Found: 513.1562.

14. Synthesis of octol **3** (Scheme 6): Under an argon atmosphere, to the solution of **12** (80 mg, 0.16 mmol) in dry CH_2Cl_2 (2 mL) at 0 °C was added BBr_3 (0.96 mL, 1 M CH_2Cl_2 solution) dropwise over 3 min. The mixture was stirred for 20 h at room temperature, and then quenched with water (3 mL) at 0 °C. The resultant precipitates were filtered off, and washed with water (40 mL), and concentrated *in vacuo* to give **3** (73 mg, 100%) in pure form as blue solid materials. ^{1}H NMR (400 MHz, DMSO-d_6) 9.47 (s, 4H), 9.28 (s, 4H), 7.94 (s, 4H), 7.67 (s, 4H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 145.4, 144.6, 123.4, 123.3, 122.2, 113.0, 107.8 ppm; MS (DART-TOF) *m/z*: 457 $[MH]^+$; IR (neat): 3295 (O-H), 1515, 1272, 1225, 1129, 846 cm^{-1}; HRMS (DART -TOF) calcd for $C_{26}H_{17}O_8$: 457.0918

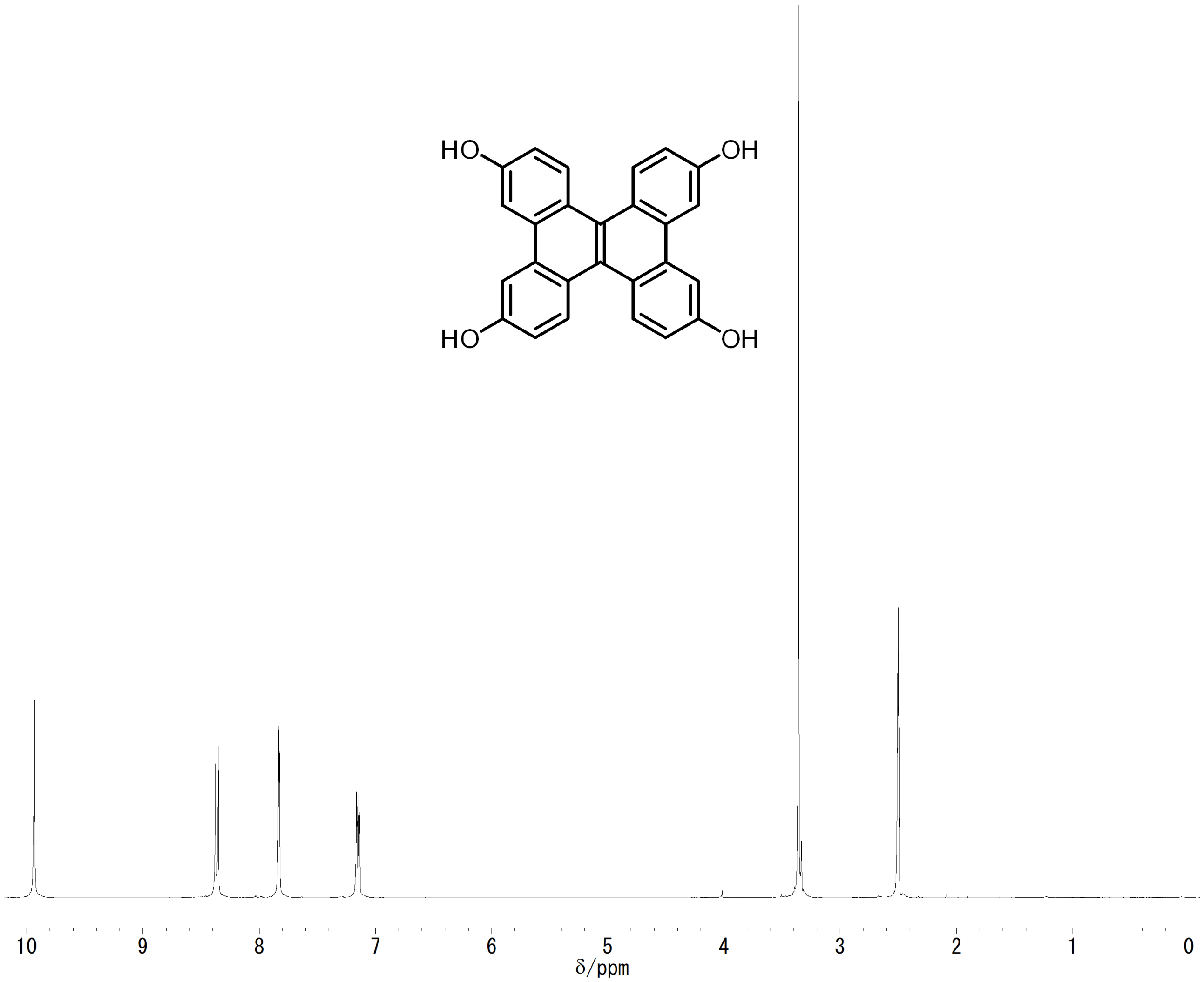


3

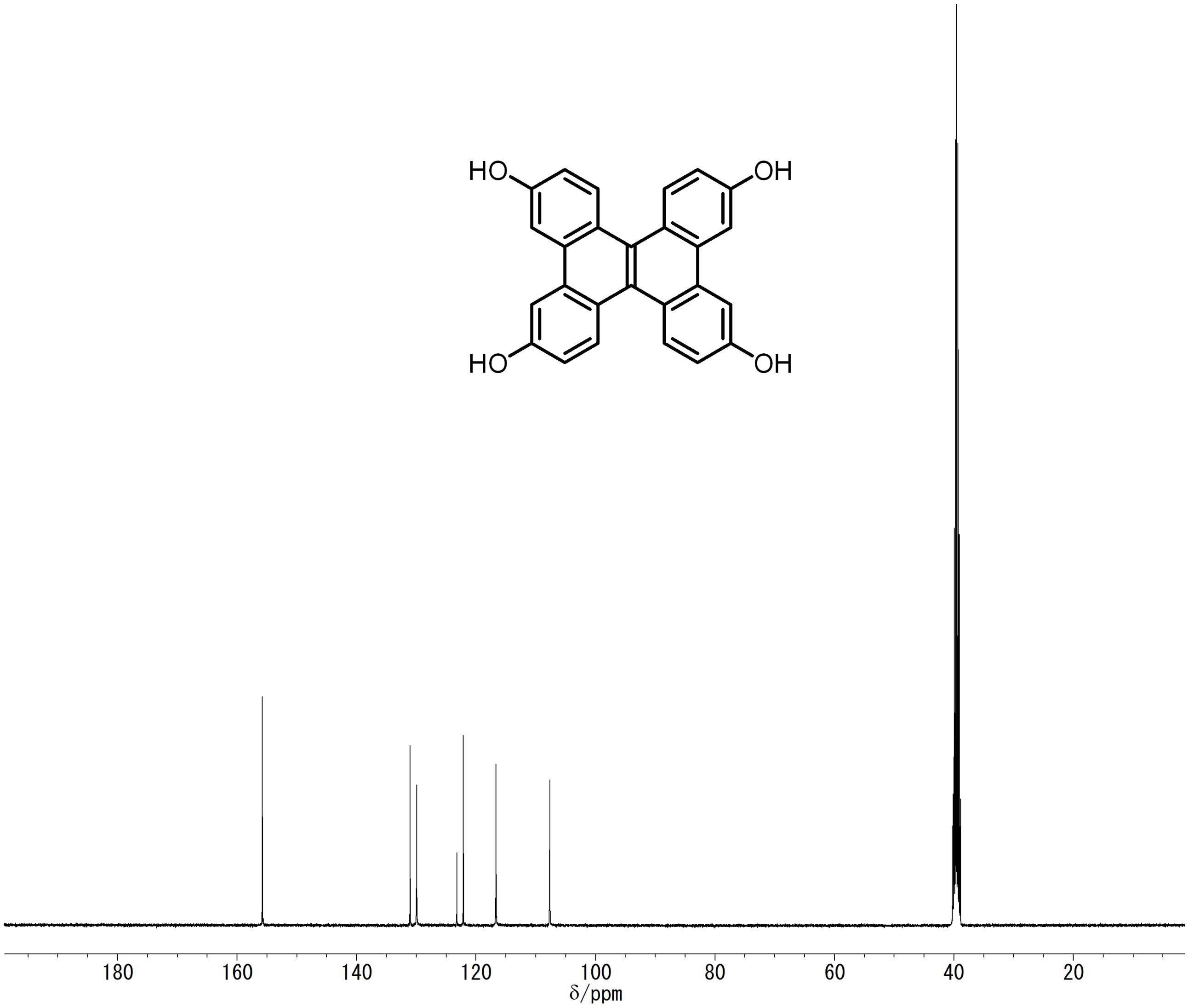
$[MH]^+$, Found : 457.0904.

15. ^{1}H NMR and ^{13}C NMR spectra for all new compounds of **1**-**12**.

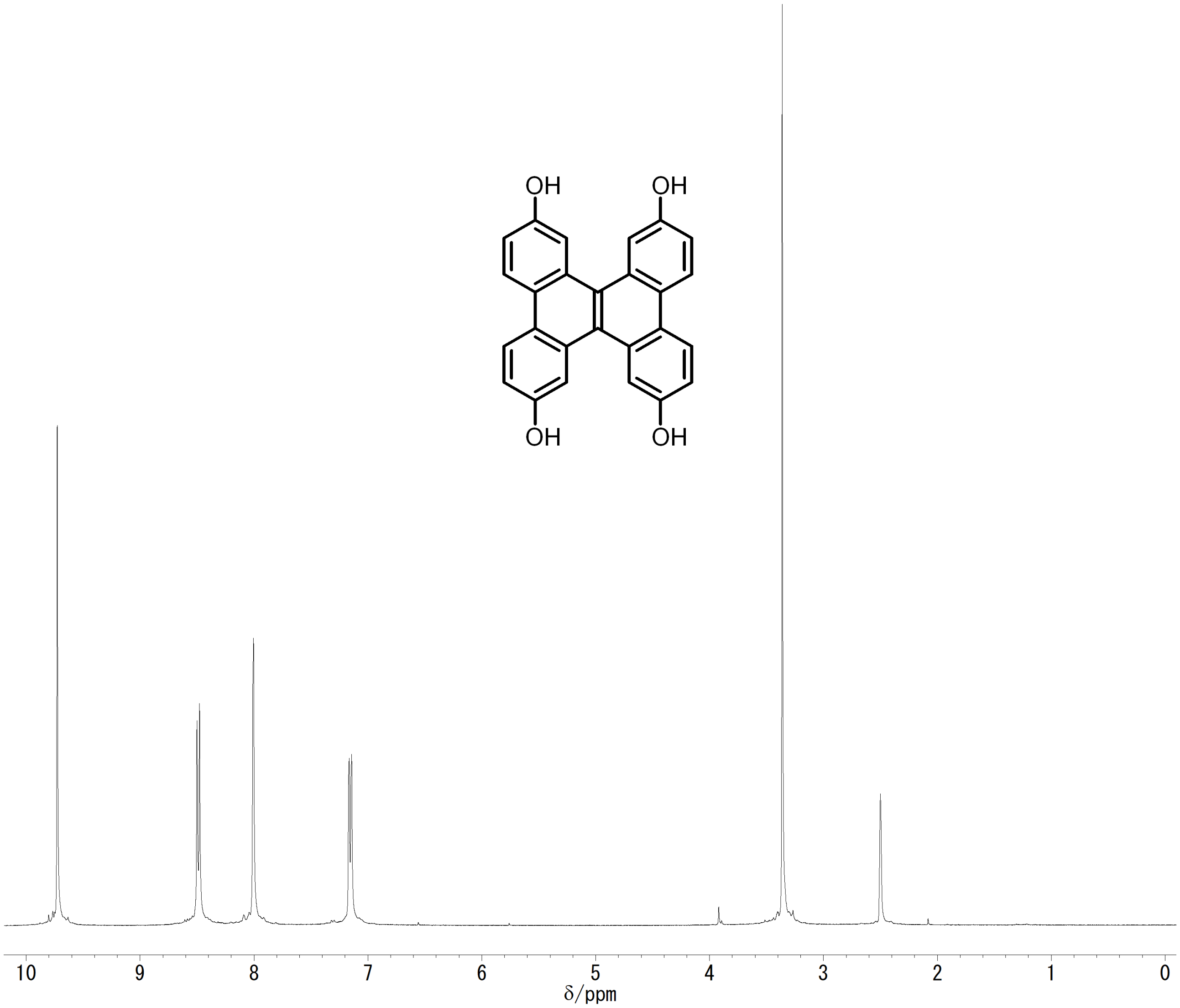
Compound **1** (^{1}H NMR spectrum in DMSO-d_6)



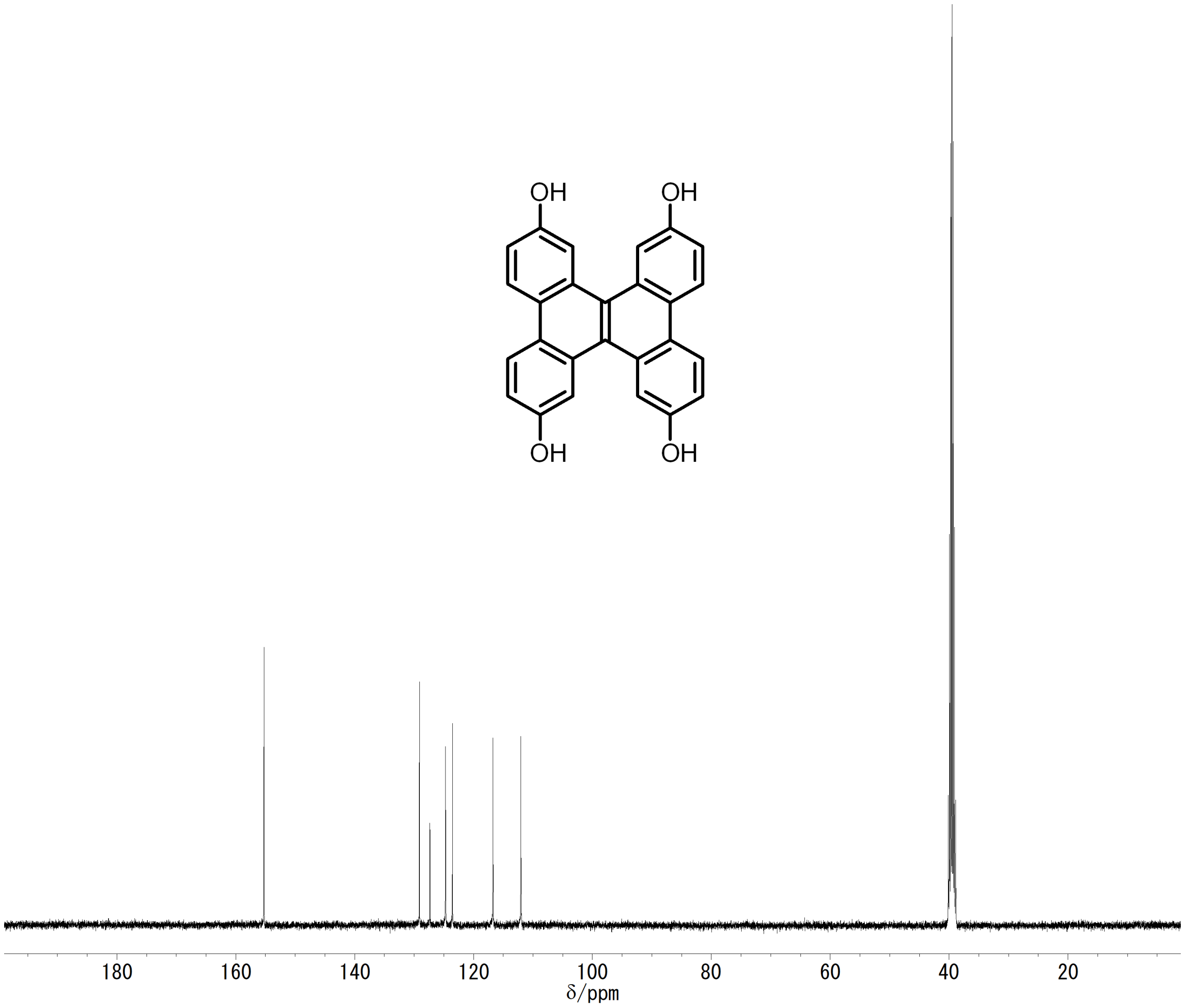
Compound **1** (^{13}C NMR spectrum in DMSO-d_6)



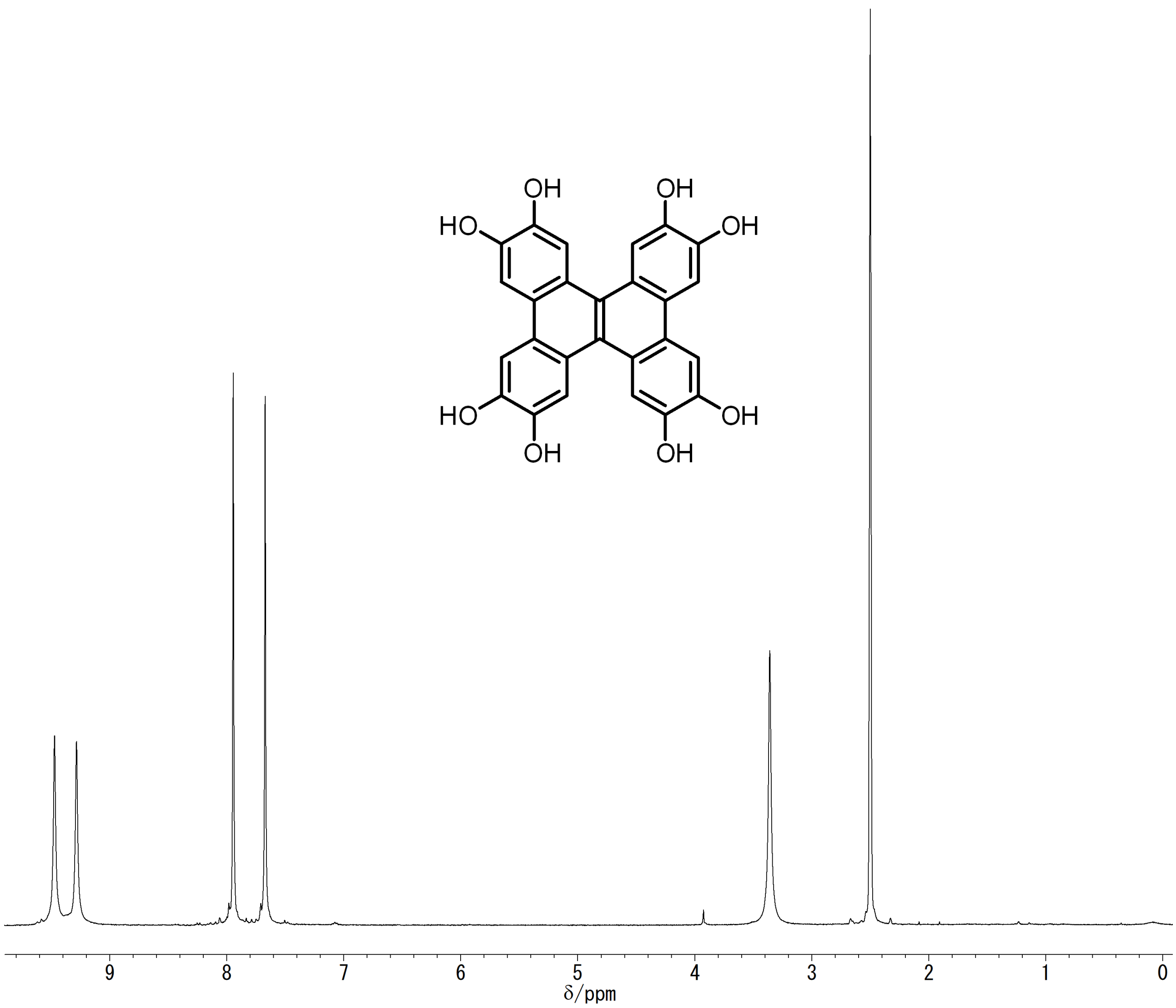
Compound **2** (^{1}H NMR spectrum in DMSO-d_6)



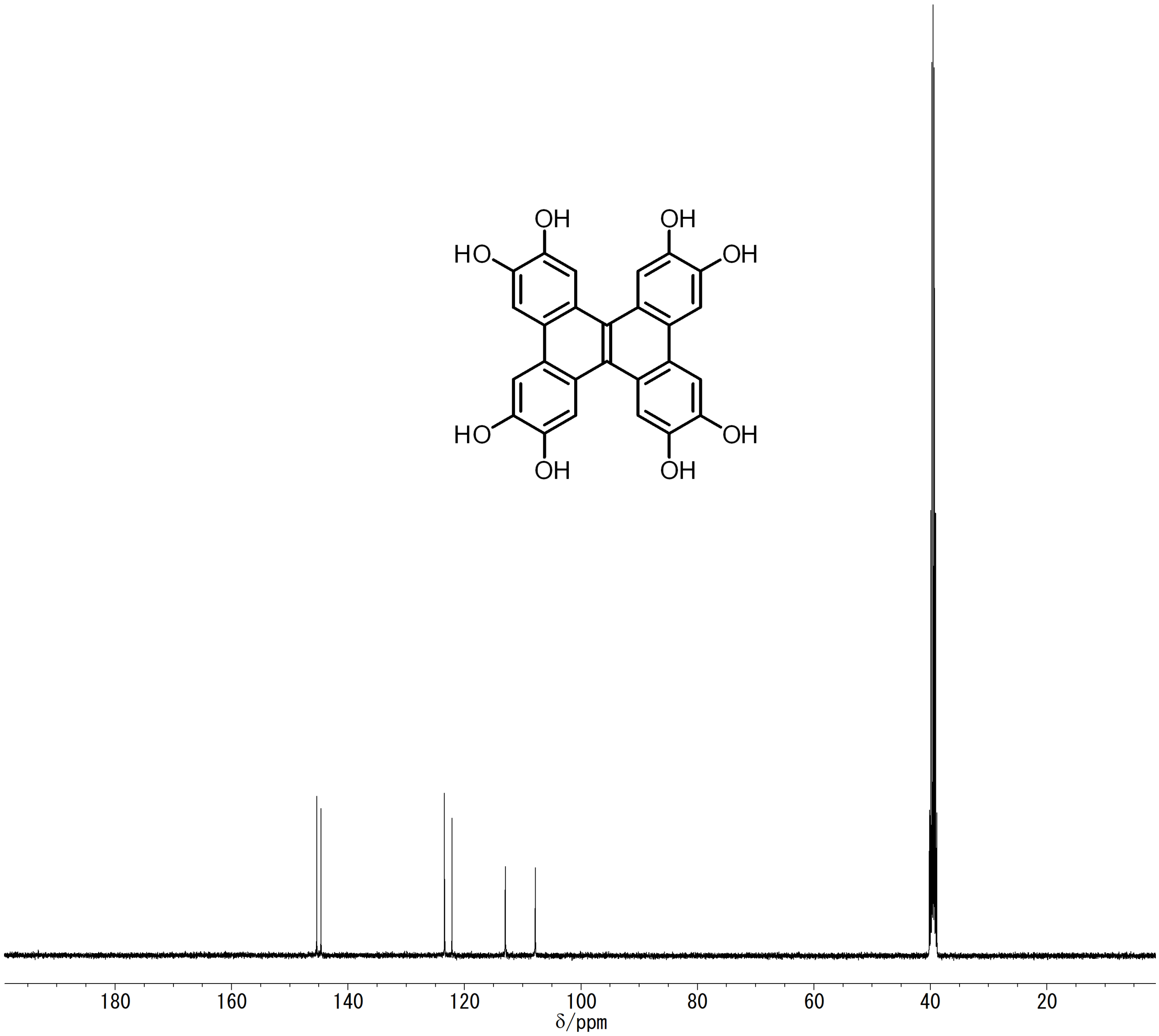
Compound **2** (^{13}C NMR spectrum in DMSO-d_6)



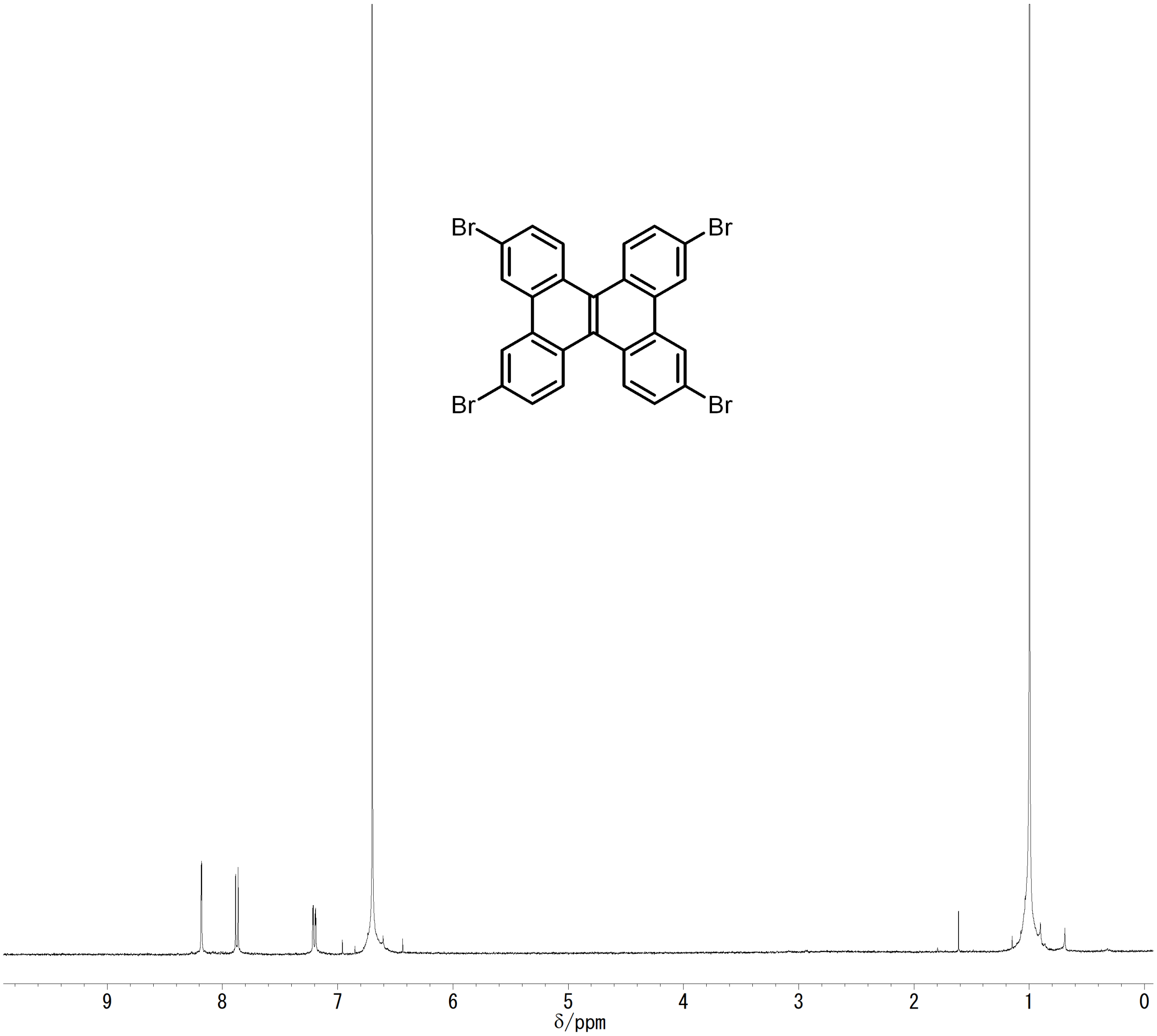
Compound **3** (^{1}H NMR spectrum in DMSO-d_6)



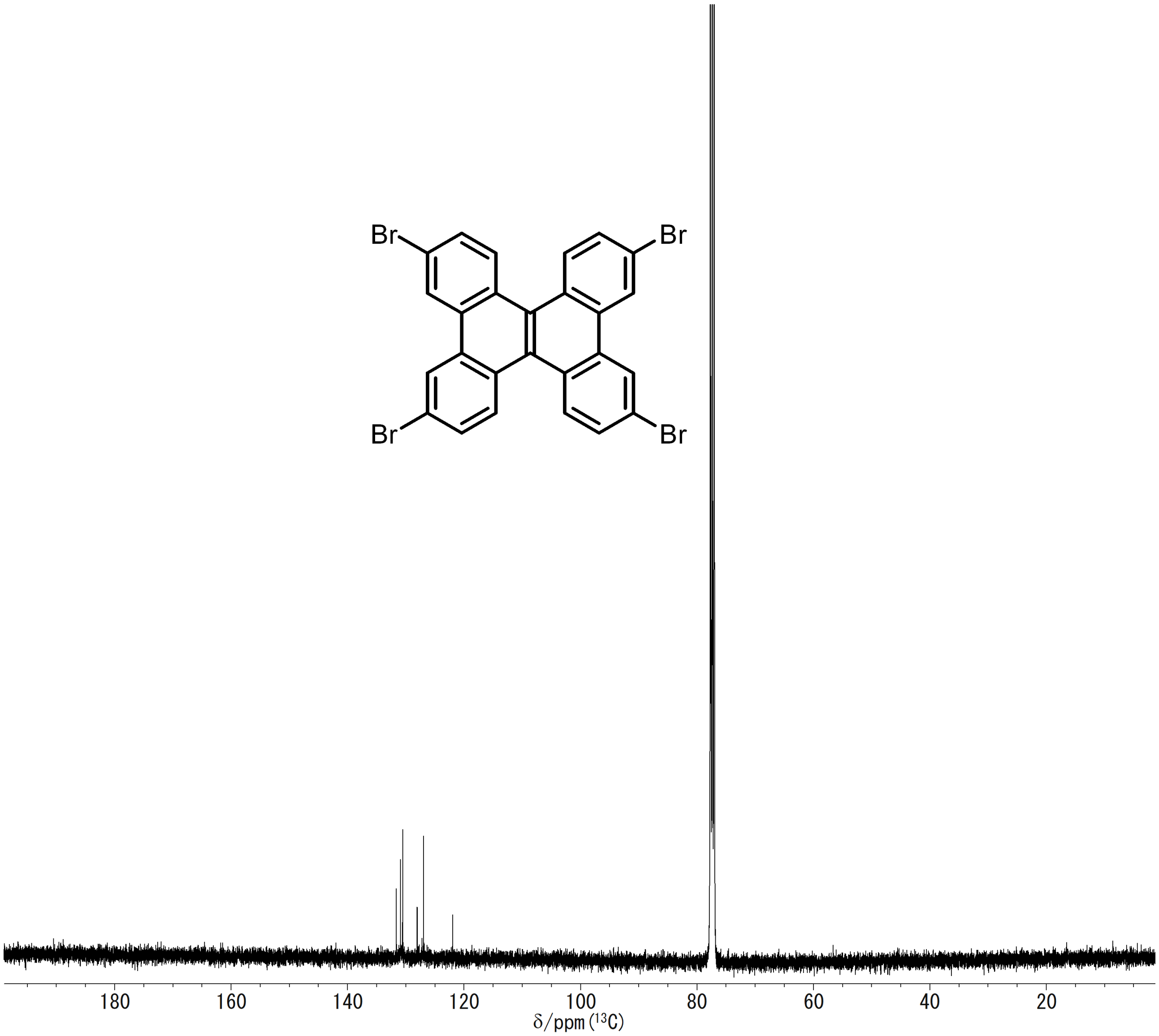
Compound **3** (^{13}C NMR spectrum in DMSO-d_6)



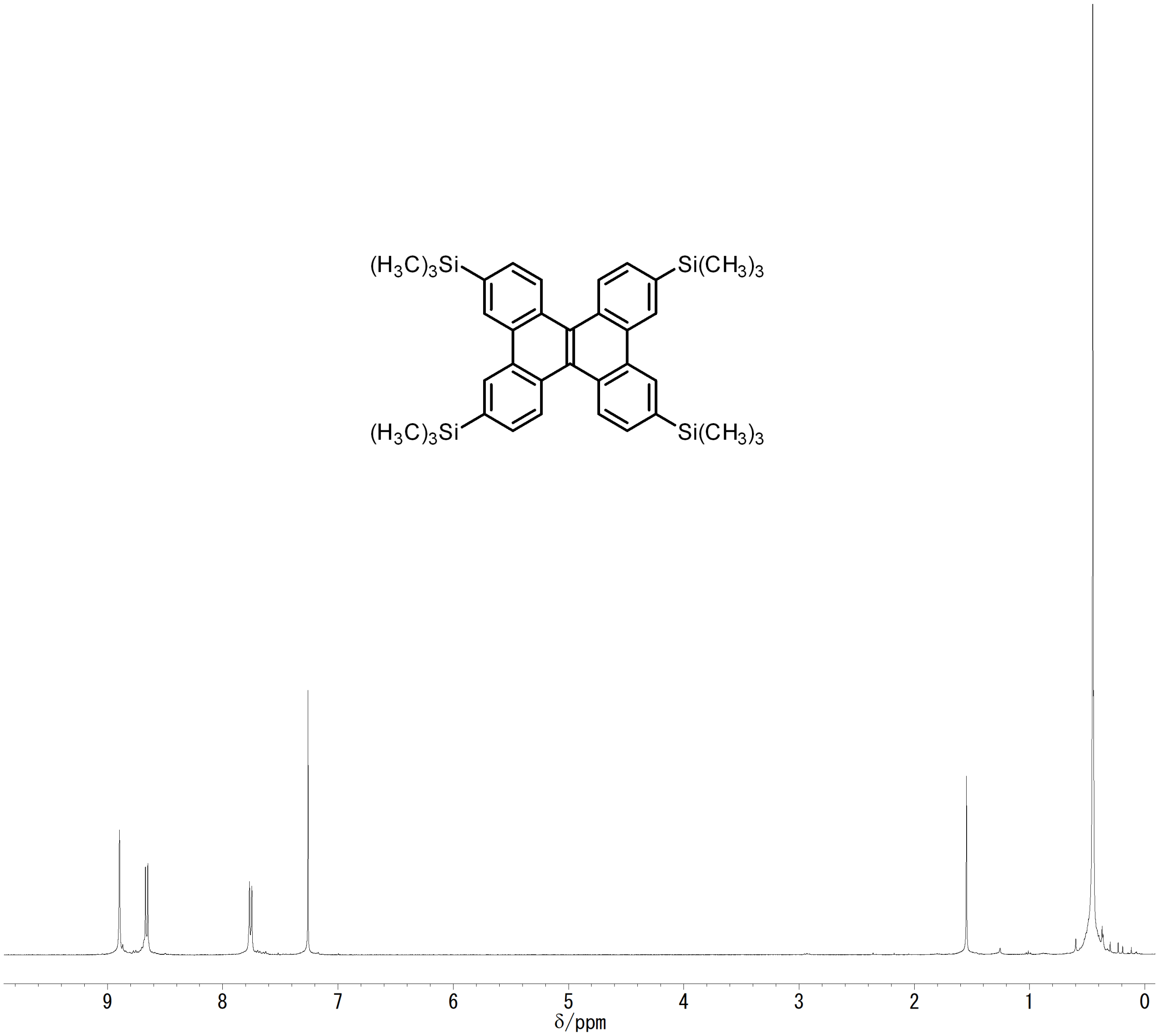
Compound **4** (^{1}H NMR spectrum in $CDCl_3$)



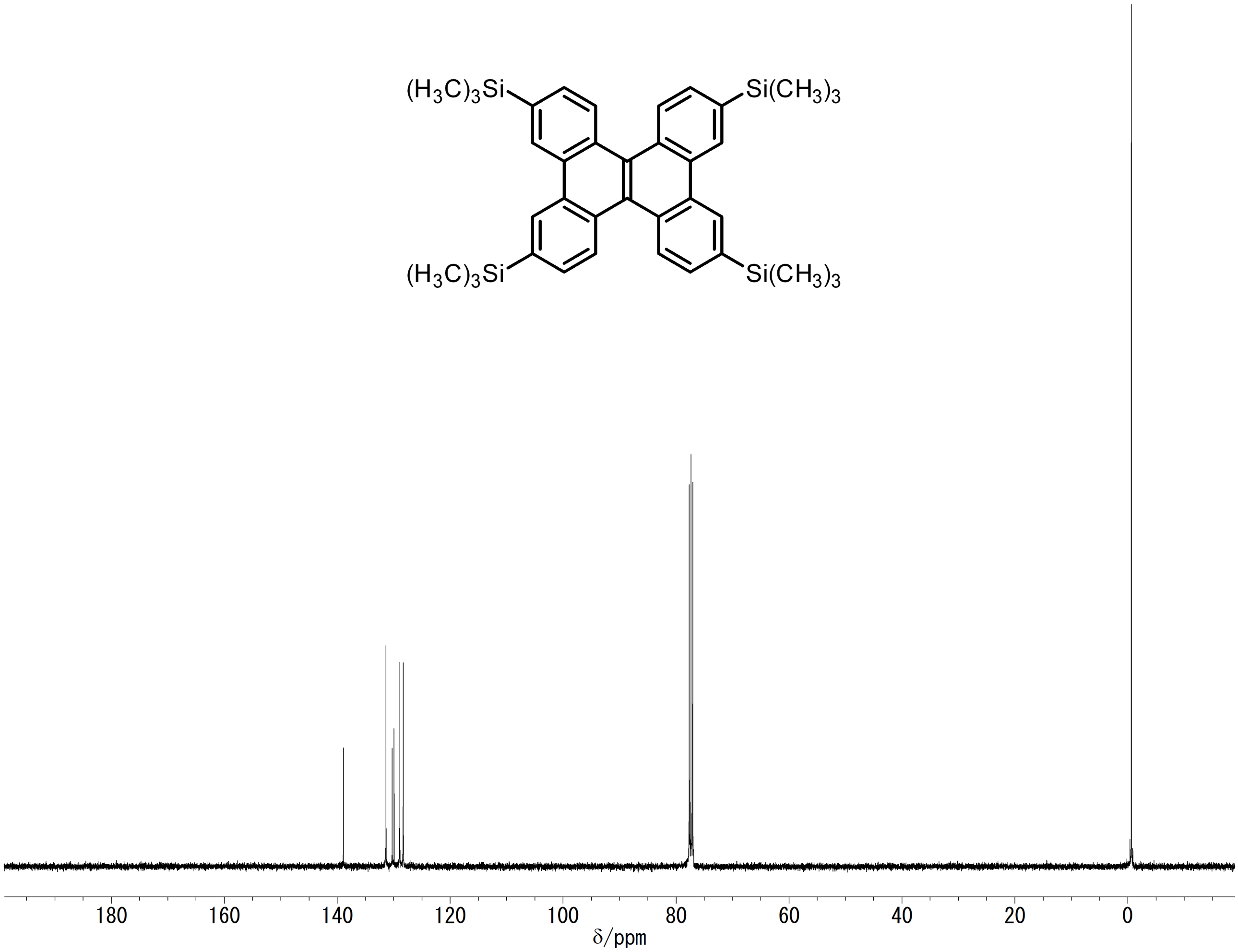
Compound **4** (^{13}C NMR spectrum in $CDCl_3$)



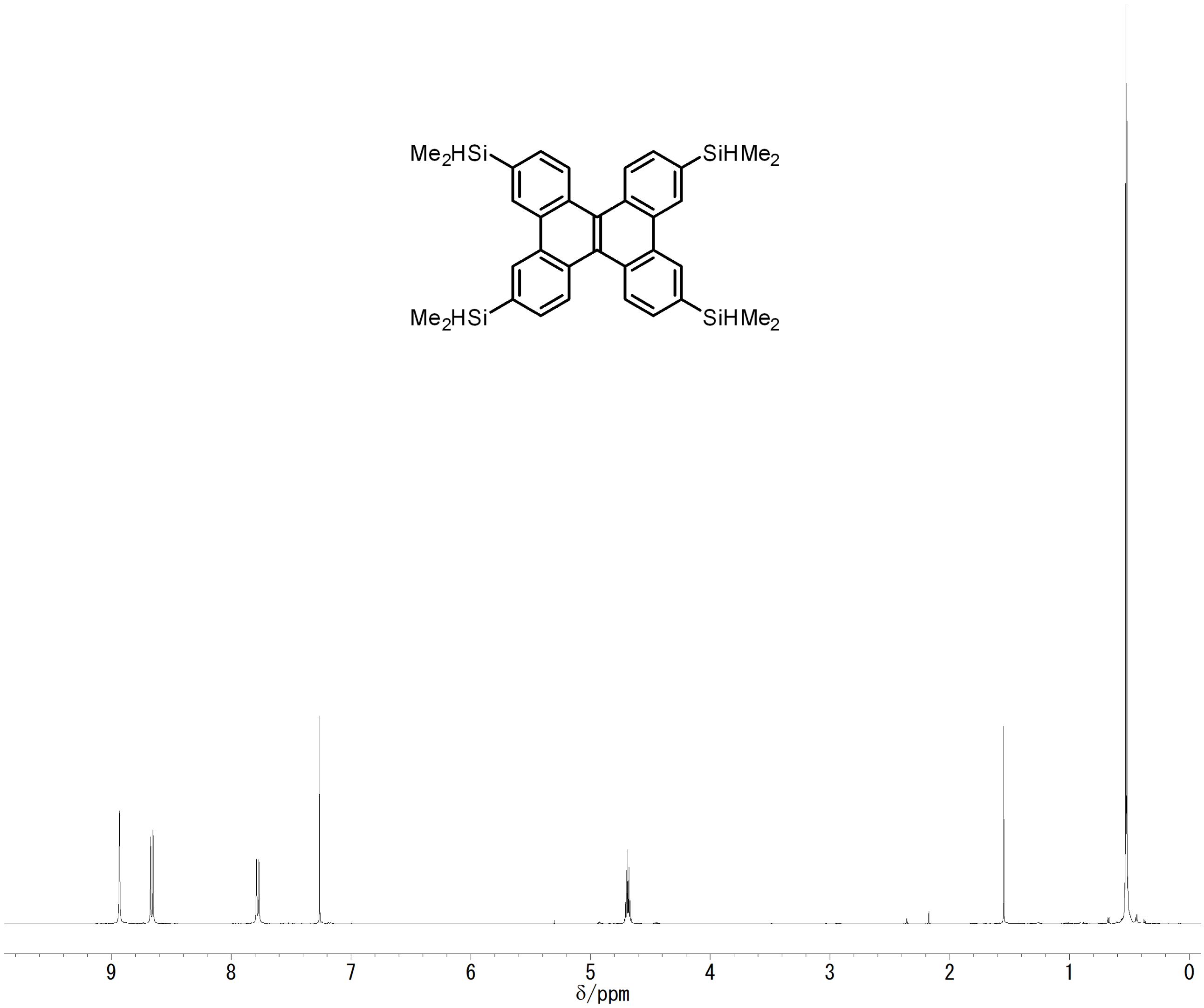
Compound **5** (^{1}H NMR spectrum in $CDCl_3$)



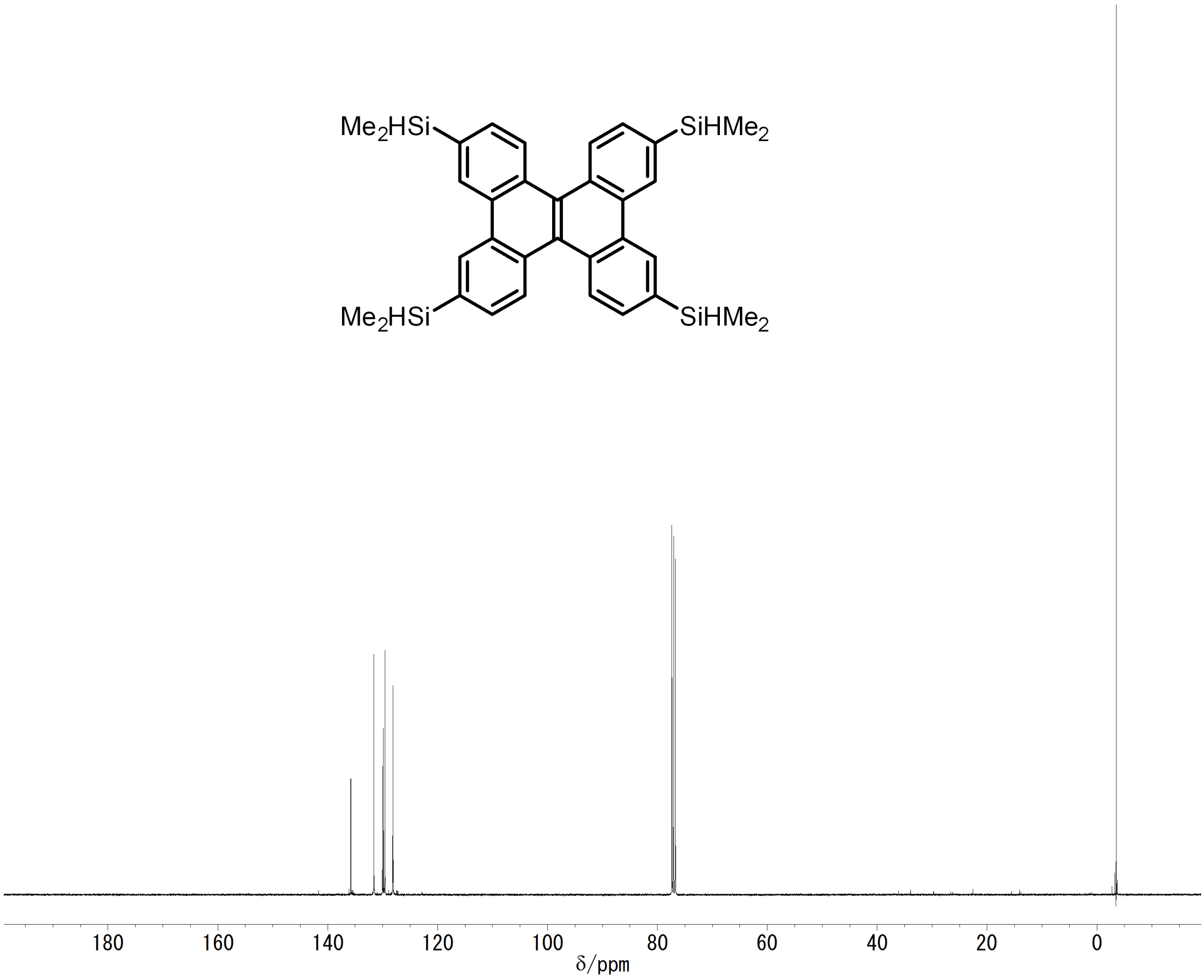
Compound **5** (^{13}C NMR spectrum in CDCl$_3$)



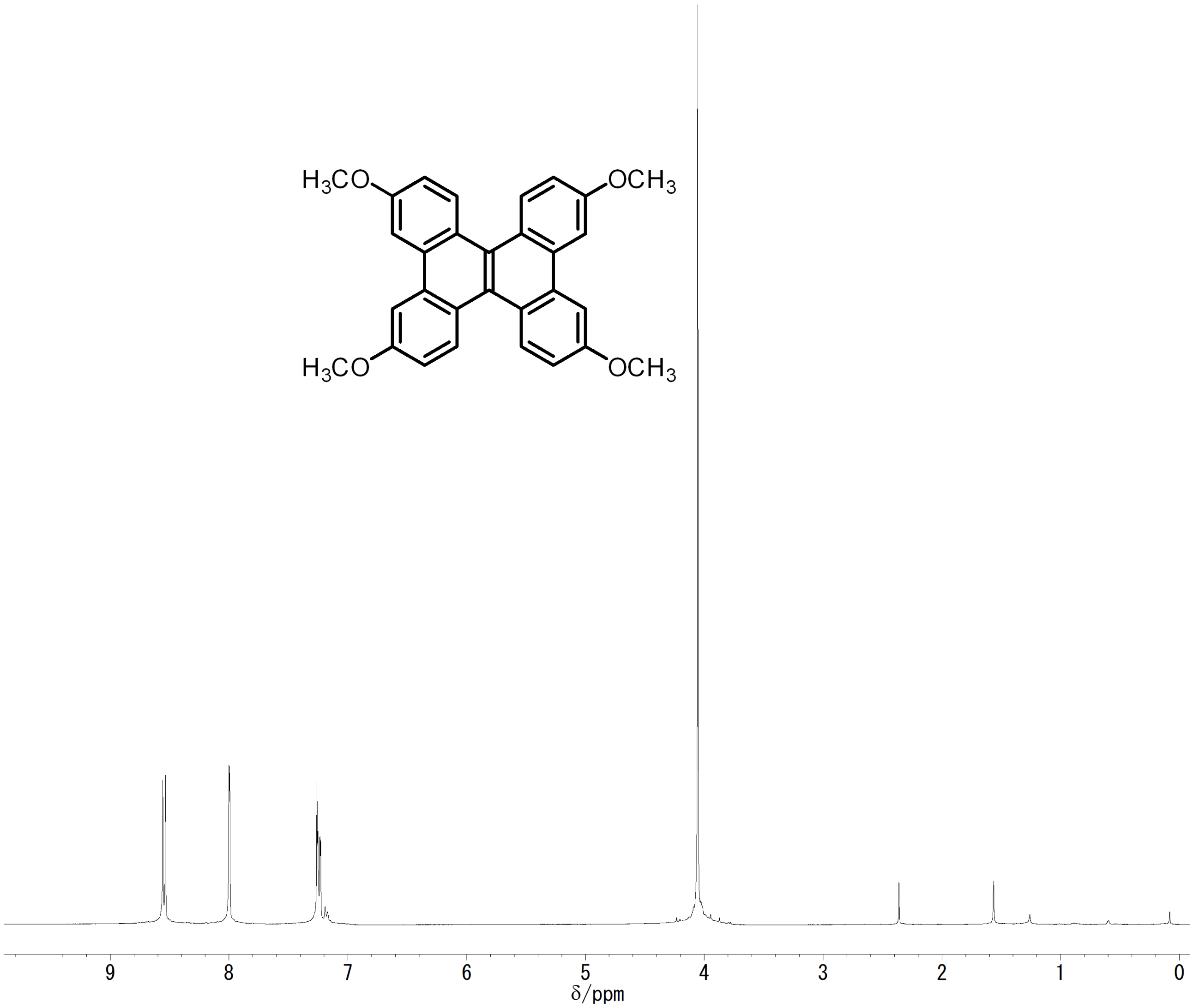
Compound **6** (^{1}H NMR spectrum in $CDCl_3$)



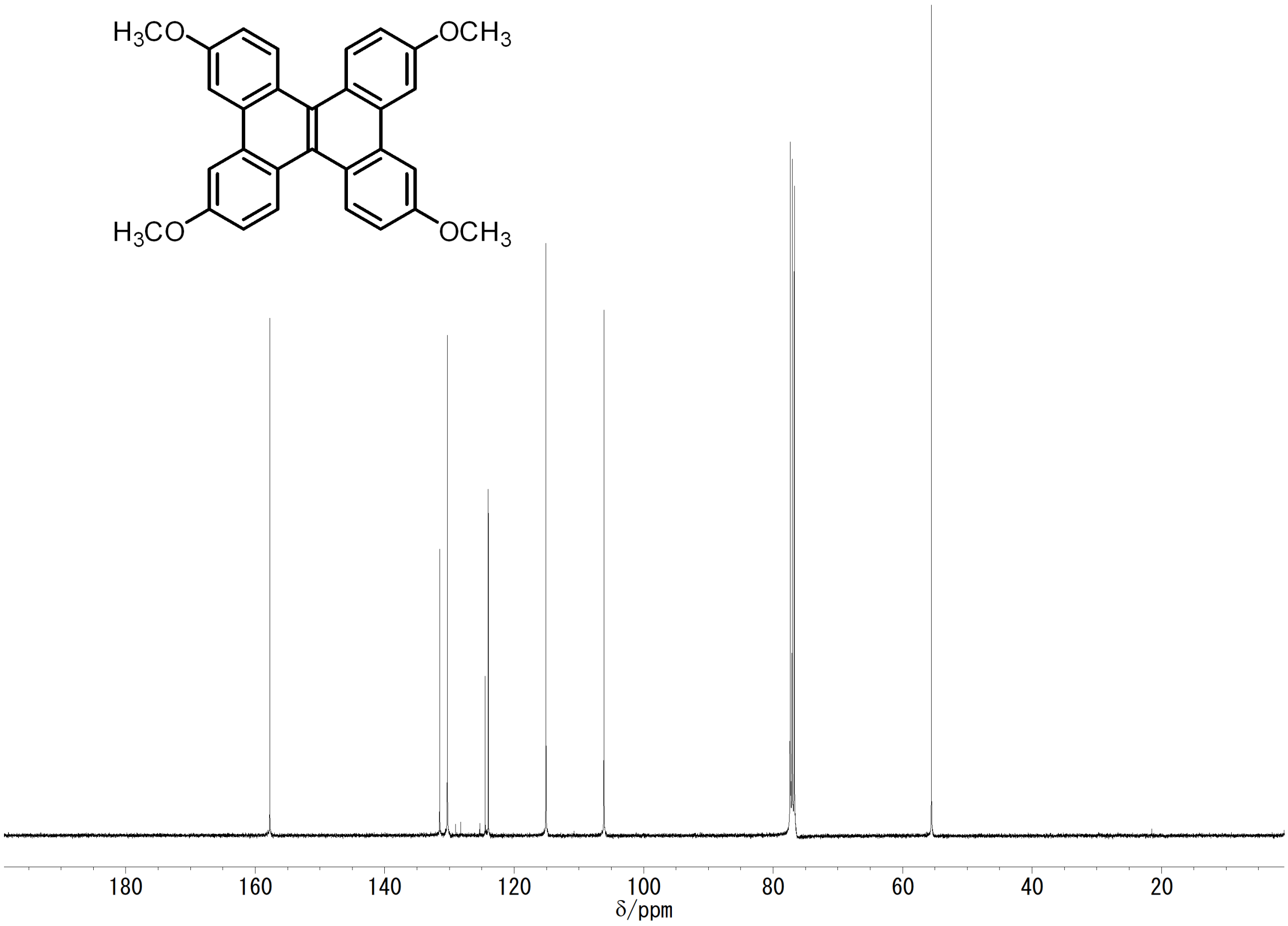
Compound **6** (^{13}C NMR spectrum in $CDCl_3$)



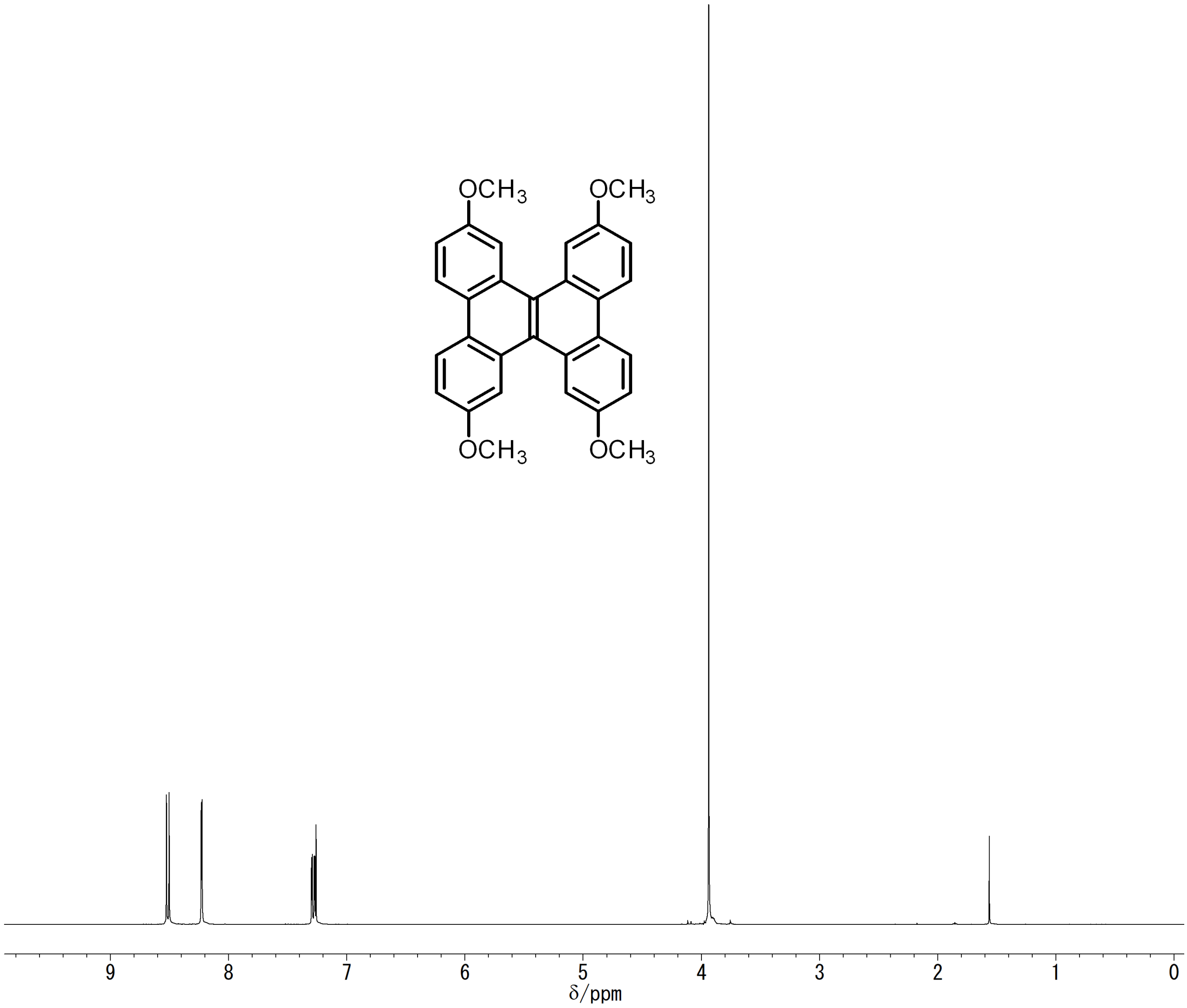
Compound **8** (^{1}H NMR spectrum in $CDCl_3$)



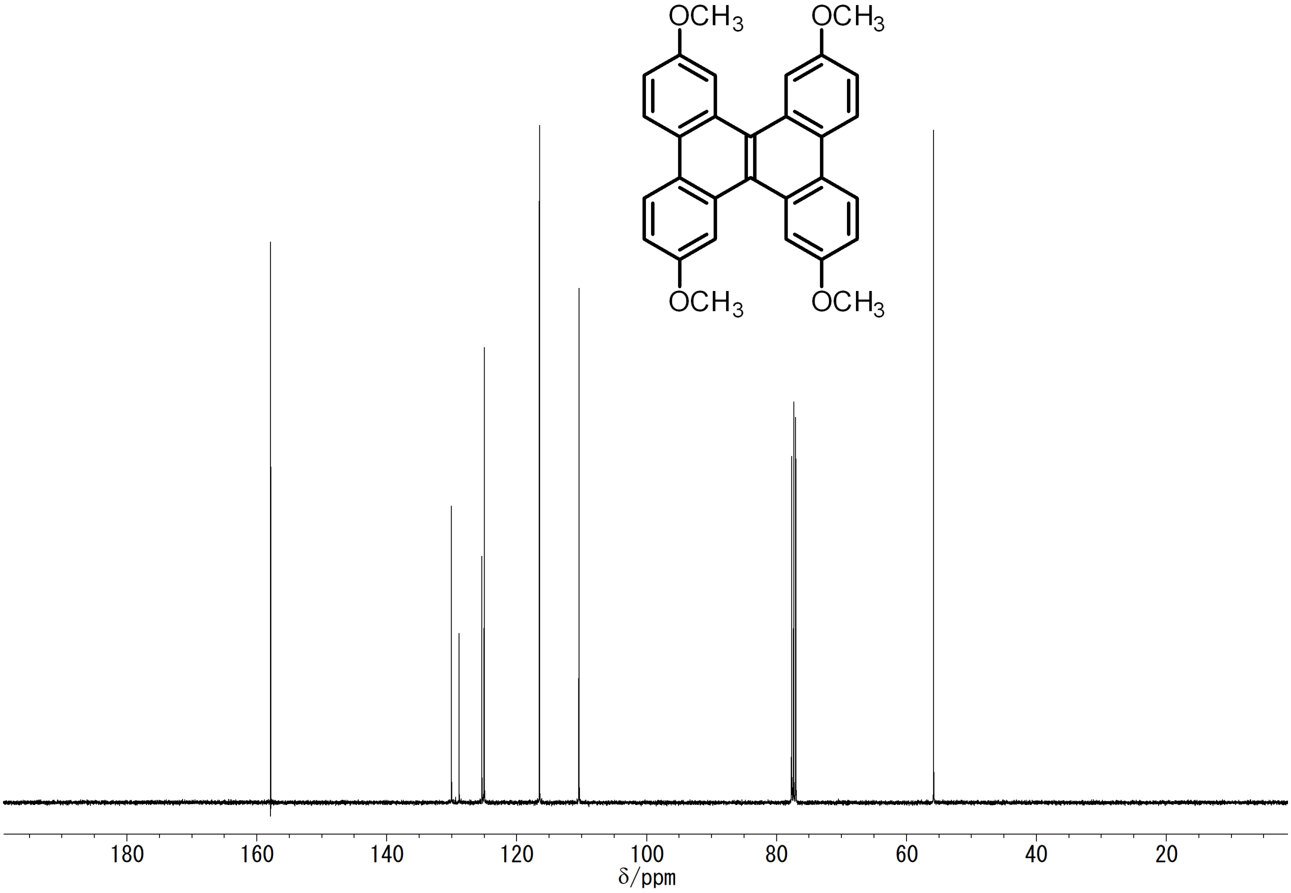
Compound **8** (^{13}C NMR spectrum in $CDCl_3$)



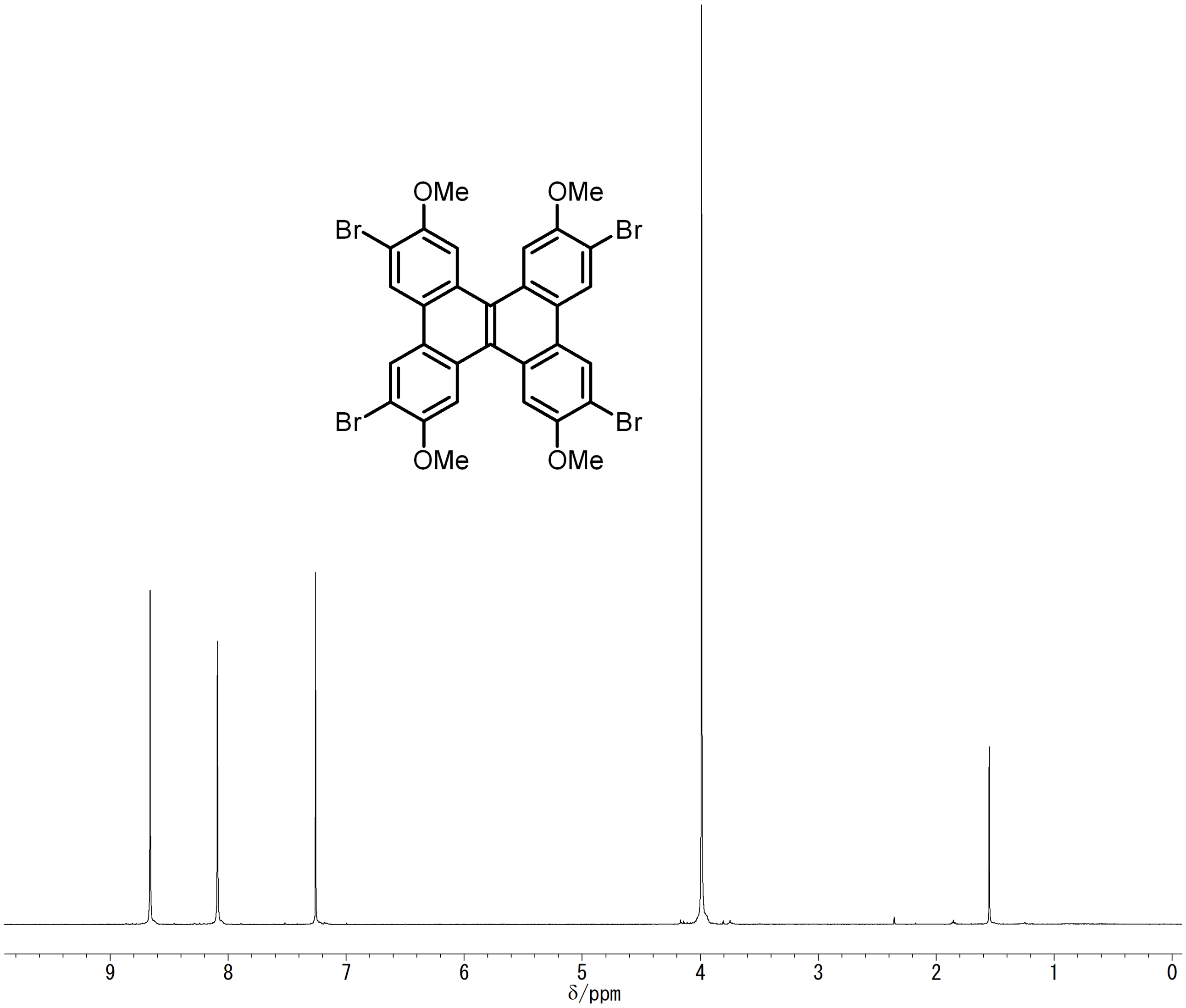
Compound **9** (^{1}H NMR spectrum in $CDCl_3$)



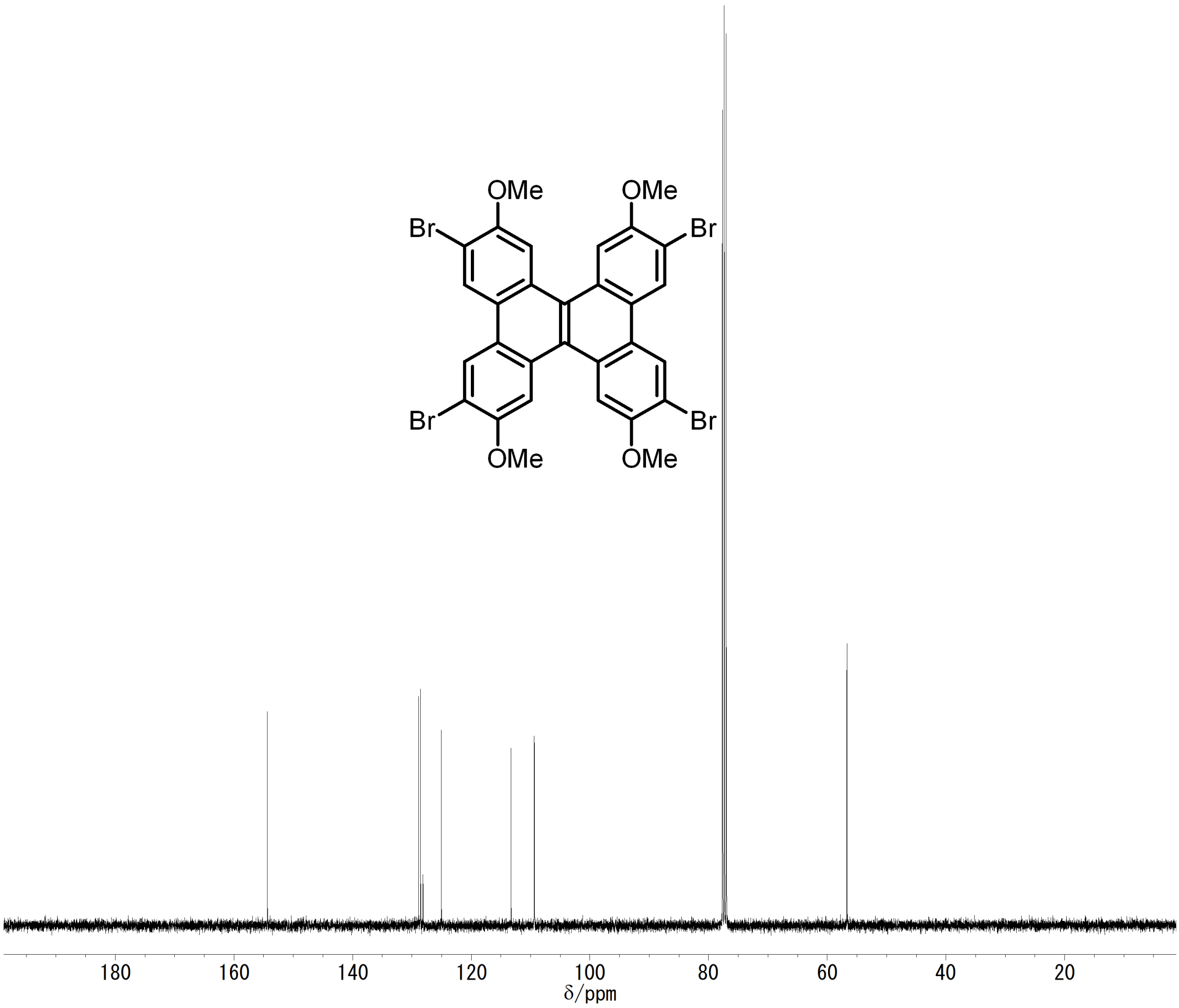
Compound **9** (^{13}C NMR spectrum in $CDCl_3$)



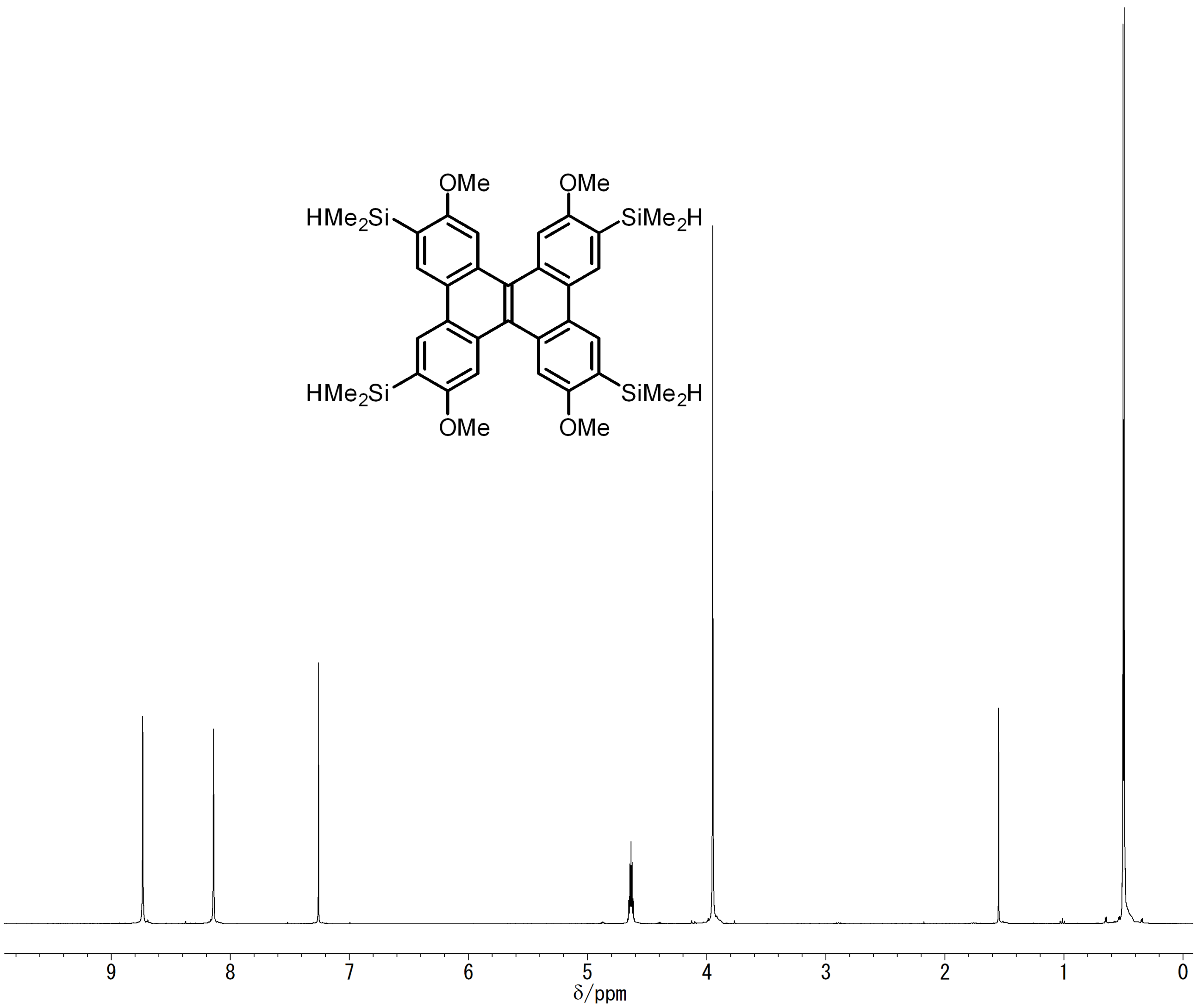
Compound **10** (^{1}H NMR spectrum in $CDCl_3$)



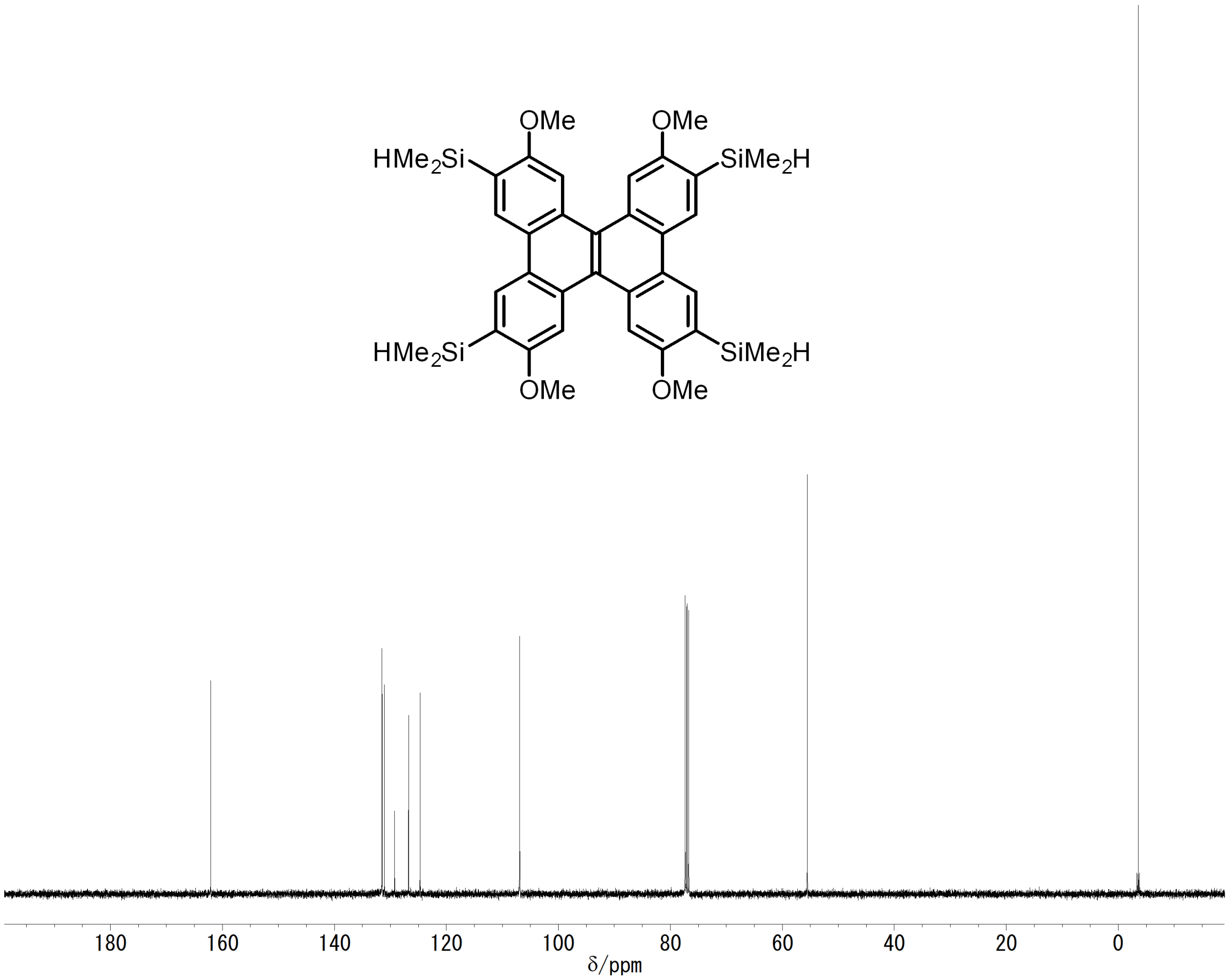
Compound **10** (^{13}C NMR spectrum in CDCl$_3$)



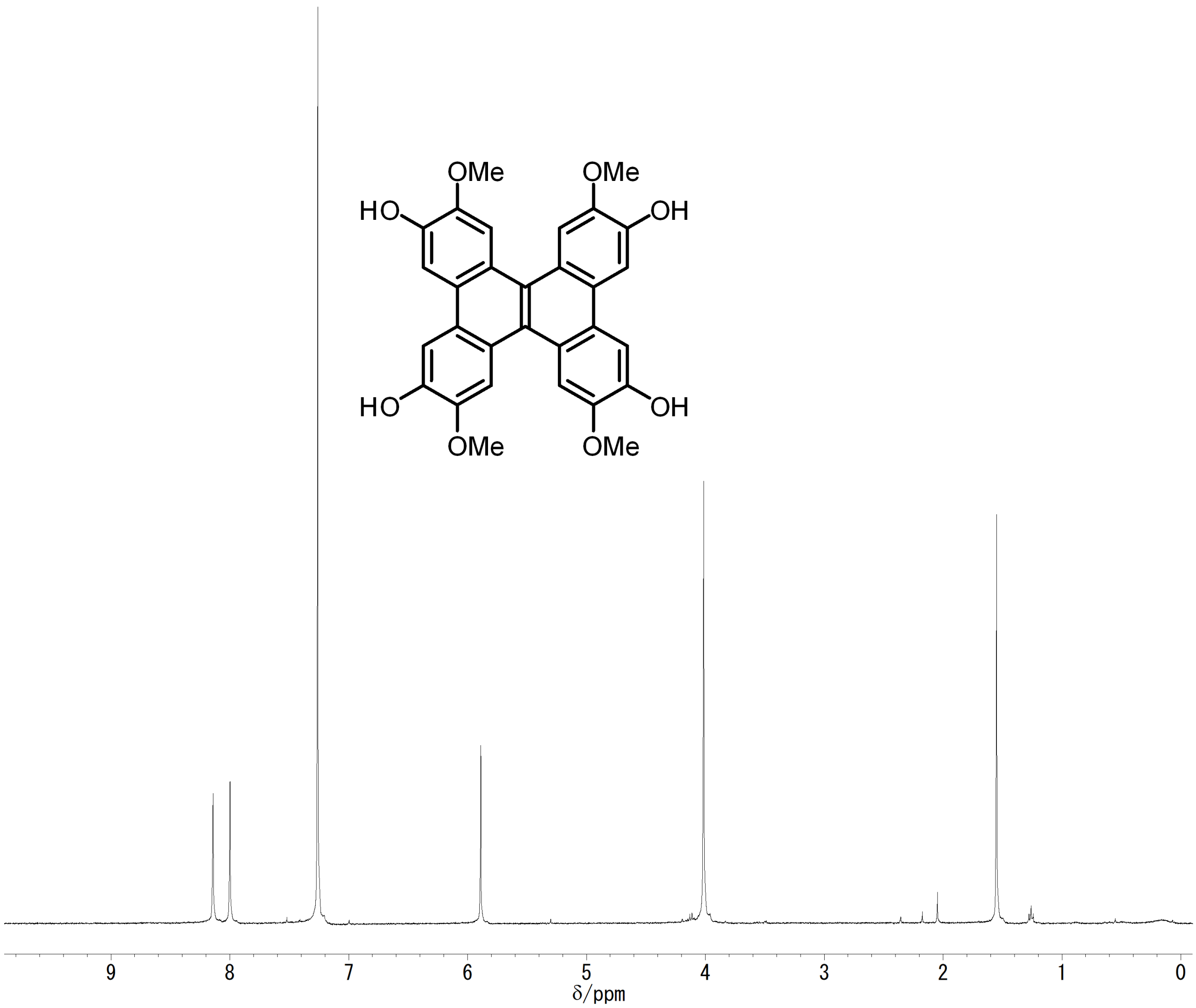
Compound **11** (^{1}H NMR spectrum in $CDCl_3$)



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 $CDCl_3$)