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Supporting Information

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Construction of Multiple Five-Membered Rings in Dibenzo[*g*,*p*]chrysene Core for the Synthesis of a Nona-cycle Buckybowl

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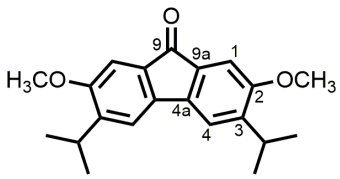
Contents

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 (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 d (ppm) with reference to residual solvent signals [^1H NMR: $CHCl_3$ (7.26), DMSO (2.50); ^{13}C NMR: $CDCl_3$ (77.0), [D6]-DMSO (39.5)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. All melting points were recorded on the melting point apparatus of “Stanford Research Systems OptiMelt” and are not corrected. X-ray single crystal diffraction analyses were performed on a Rigaku XtaLab P200 diffractometer Cu-Kα radiation. Data collection, cell refinement, data reduction and analysis were carried out with the CrysAlisPro (Rigaku Oxford Diffraction), in which the structures were solved by intrinsic phasing methods with the SHELXT program and refines using SHELXL[1] with anisotropic displacement parameters for non-H atoms. CCDC numbers contain the supplementary crystallographic data for this paper, and the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

[1] Sheldrick, G. M. A. Short History of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, 64, 112-122.

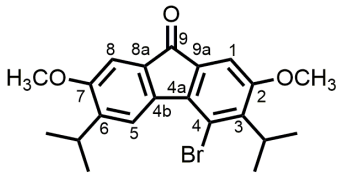
2. Synthesis of **5**, **6**, **7**/*iso*-**7**, and **1**/*iso*-**1** (Scheme 2).

1. For **5**, (3,6-diisopropyl-2,7-dimethoxy-9*H*-fluoren-9-one). Under an argon



atmosphere, to a suspension of the 2,7-dimethoxy-9*H*-fluoren-9-one (10 g, 42 mmol) in 2-chloropropane (172 mL) was added $AlCl_3$ (27 g, 200 mmol). After stirred at 40 ºC (oil bath temp.) for 3 h, the reaction was quenched at 0 ºC with slow addition (10 min) of ice water (400 mL). The aqueous phase was extracted with CH_2Cl_2 (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. Purification by short-plugged silica-gel column chromatography (Toluene only) afforded 12.8 g of products as orange solid materials. Purification by short-plugged column chromatography (Hexane/Toluene, 1:4) afforded 6.4 g of **5** in 48% yield as orange solid materials. Data: *Rf* value 0.43 (Hexane/EtOAc, 4:1); M.p. 164-165 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 7.24 (s, 2H, H-4), 7.11 (s, 2H, H-1), 3.86 (s, 6H, OCH_3), 3.35 (sept, J = 6.8 Hz, 2H, C$\underline{H}$(CH_3)$_2$), 1.25 (d, J = 6.8 Hz, 12H, CH(C$\underline{H}_3$)$_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 194.9 (C=O), 157.4 (C-2), 144.5 (C-3), 138.7 (C-9a), 134.0 (C-4a), 118.0 (C-4), 107.3 (C-1), 56.4 (OCH_3), 27.9 ($\underline{C}$H(CH_3)$_2$), 23.1 (CH($\underline{C}H_3$)$_2$) ppm; MS (DART-TOF) *m/z*: 325 $[MH]^+$; IR (neat) 2956, 1702, 1599, 1447, 1408, 1232, 1045, 877, 774, 591 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{21}H_{25}O_3$: 325.1804 $[MH]^+$, found; 325.1795; Anal. Calcd. for $C_{21}H_{24}O_3$; C, 77.75; H, 7.46. Found: C, 77.97; H, 7.55.

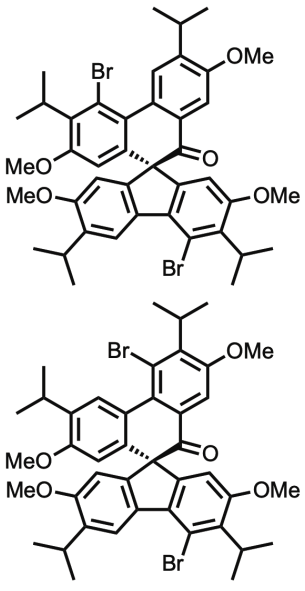
2. For **6**, (4-bromo-3,6-diisopropyl-2,7-dimethoxy-9*H*-fluoren-9-one). Under an argon



atmosphere, to a solution of **5** (19 g, 59 mmol) in dry CH_2Cl_2 (100 mL) at 0 ºC was added a solution of 4.2 M Br_2 in CH_2Cl_2 (84 mL, 350 mmol) dropwise over 5 min, and then the mixture was stirred at room temperature for 4 h. The reaction was quenched with saturated

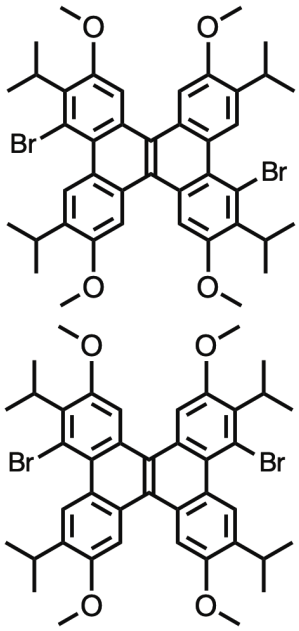
aq. $Na_2S_2O_3$ (180 mL), and the aqueous layer was extracted with CH_2Cl_2 (50 mL x 3). The combined organic phases were washed with brine (100 mL x 3), dried over Na_2SO_4, and concentrated *in vacuo* to give 26 g of crude products. Purification by silica-gel column chromatography (Hexane/CH_2Cl_2, 1:2) afforded 18 g of **6** in 74% yield as orange solid materials. Data: *Rf* value 0.57 (Hexane/CH_2Cl_2, 1:2); M.p. 253-255 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) 8.22 (s, 1H, H-5), 7.14 (s, 1H, H-8), 7.12 (s, 1H, H-1), 3.87 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.78 (sept, J = 7.0 Hz, 1H, C*H*$(CH_3)_2$), 3.35 (sept, J = 7.0 Hz, 1H, C*H*$(CH_3)_2$), 1.33 (d, J = 7.0 Hz, 6H, CH(C*H*$_3)_2$), 1.25 (d, J = 7.0 Hz, 6H, CH(C*H*$_3)_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 193.4 (C=O), 159.6 (C-2), 157.4 (C-7), 144.2 (C-3), 142.1 (C-6), 138.8 (C-8a), 137.4 (C-9a), 135.6 (C-4b), 134.2 (C-4a), 122.0 (C-5), 120.6 (C-4), 107.5 (C-1), 107.1 (C-8), 56.4 (OCH_3), 56.3 (OCH_3), 33.8 (*C*H$(CH_3)_2$), 28.1 (*C*H$(CH_3)_2$), 23.0 (CH(*C*H$_3)_2$), 20.3 (CH(*C*H$_3)_2$) ppm; MS (DART-TOF) *m/z*: 403 $[MH]^+$; IR (neat) 2960, 1714, 1599, 1412, 1244, 1045, 778 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{21}H_{24}BrO_3$: 403.0903 $[MH]^+$, found; 403.0891; Anal. Calcd. for $C_{21}H_{23}BrO_3$; C, 62.54; H, 5.75. Found: C, 62.54; H, 5.56.

3. For **7**/*iso*-**7**, (4,5'-dibromo-3,3',6,6'-tetraisopropyl-2,2',7,7'-tetramethoxy-10'*H*-spiro[fluorene-9,9'-phenanthren]-10'-one/4,4'-dibromo-3,3',6,6'-tetraisopropyl-2,2',7,7'-tetramethoxy-10'*H*-spiro[fluorene-9,9'-phenanthren]-10'-one): The starting fluorenone **6** (38 g, 94 mmol) were added to P(O-*i*Pr)$_3$ (65 mL, 280 mmol), and the resultant orange suspension was stirred at 146 ºC (actual temperature, setting of the heat bath at 170 ºC). After stirred for 43 h, the mixture was cooled to 56 ºC (actual temperature, setting of the heat bath at 60 ºC). To the mixture was slowly added water (65 mL) over 18 min, and the reaction system was re-heated to 82 ºC



(actual temperature, setting of the heat bath at 100 ºC) for hydrolyzing the residual $P(O\textit{i}\text{-}Pr)_3$. After the reaction was conducted for 2 h, the reaction mixture was cooled to room temperature, and the collected precipitates were washed with MeOH (chilled at 0 °C, 10 mL x 3). The resultant residue was dried up with rotary evaporator (60 ºC, 0.5 h), giving 35 g of **7**/*iso*-**7** in 94% yield as whitish yellow solid materials (51:49 molar ratio). The sample was provided to the next step without further purification. Data: *Rf* value 0.57, 0.52 (Hexane/CH_2Cl_2, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.53 (s, 1H), 8.51 (s, 1H), 8.45 (s, 1H), 8.28 (s, 1H), 7.25 (s, 1H), 7.20 (s, 1H), 6.62 (s, 1H), 6.60 (s, 1H), 6.36 (s, 1H), 6.33 (s, 1H), 6.25 (s, 1H), 6.08 (s, 1H), 4.04 (sept, *J* = 7.0 Hz, 1H), 3.90 (sept, *J* = 7.0 Hz, 2H), 3.63 (s, 3H), 3.60 (s, 3H) 3.54 (s, 3H), 3.53 (s, 3H), 3.52 (s, 3H), 3.50 (s, 3H), 3.48 (s, 3H), 3.46 (s, 3H), 3.31 (sept, *J* = 7.0 Hz, 3H), 1.41 (d, *J* = 7.0 Hz, 6H), 1.33 (d, *J* = 7.0 Hz, 24H), 1.32 (d, *J* = 7.0 Hz, 24H), 1.28-1.25 (m, 18H) ppm.

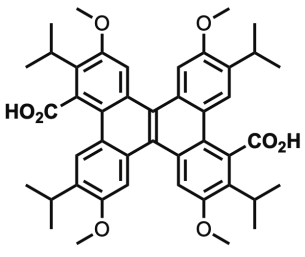
4. For **1**/*iso*-**1**, (1,9-dibromo-2,7,10,15-tetraisopropyl-3,6,11,14-tetramethoxydibenzo[*g*,*p*]chrysene/1,8-dibromo-2,7,10,15-tetraisopropyl-3,6,11,14-tetramethoxydibenzo[*g*,*p*]chrysene): To a solution of **7**/*iso*-**7** (35 g, 44 mmol) in toluene (180 mL) was added methanol (36 mL), and the flask was heated at 45 ºC. To the solution was added $NaBH_4$ (670 mg, 18 mmol) over 30 min (95.7 mg x 7 times at five-minutes intervals). After stirred for 0.5 h, the reaction was quenched with acetone (14 mL) and conducted for additional 0.5 h. The organic layer was washed with H_2O (100 mL x 3) and transferred into a 500 mL flask, and the flask was heated at 120 ºC (oil bath temp.) for azeotropic removal of water, which was followed by additional of CH_3SO_3H (0.03 mL, 0.44 mmol). After stirred for 0.5 h, the reaction mixture was allowed to cool to room temperature, and transferred into a 500 mL



separatory funnel. The organic layer was washed with brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give crude products. Purification by silica-gel column chromatography (Hexane/ CH_2Cl_2, 9:1) afforded 31 g of **1**/*iso*-**1** in 89% yield as yellowish orange solid materials (51:49 molar ratio). Data: *Rf* value 0.38 (Hexane/EtOAc, 9:1); M.p. 283 ºC (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 8.98 (s, 2H), 8.97 (s, 2H), 8.13 (s, 2H), 8.01 (s, 2H), 8.00 (s, 2H), 7.90 (s, 2H), 4.11 (sept, J = 7.0 Hz, 4H), 3.96 (s, 12H), 3.94 (s, 24H), 3.92 (s, 12H), 3.49 (sept, J = 7.0 Hz, 4H), 1.41 (d, J = 7.0 Hz, 48H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 157.7, 157.5, 156.1, 155.9, 137.6, 137.3, 134.7, 134.4, 130.7 (two peaks are overlapped), 129.51, 129.45, 129.3, 129.1, 127.8 (two peaks are overlapped), 127.5 (two peaks are overlapped), 125.8, 125.6, 124.57, 124.55, 124.0, 123.5, 108.8, 108.6, 107.1, 107.0, 56.04, 56.00, 55.84, 55.80, 35.4 (two peaks are overlapped), 27.3 (two peaks are overlapped), 23.3 (two peaks are overlapped), 20.5 (two peaks are overlapped) ppm; MS (DART-TOF) *m/z*: 775 $[MH]^+$; IR (neat) 2959, 2920, 2865,1587, 1452, 1401, 1247, 1053, 831 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{42}H_{47}Br_2O_4$: 775.1821 $[MH]^+$, found; 775.1817.

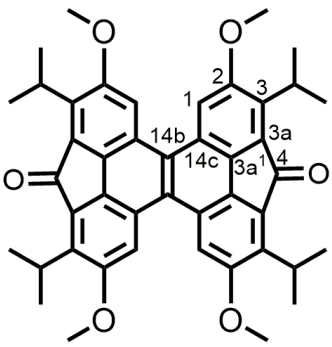
3. Synthesis of **8**/*iso*-**8**, and **2**. (Scheme 3).

1. For **8**/*iso*-**8**, (2,7,10,15-tetraisopropyl-3,6,11,14-tetramethoxydibenzo[*g*,*p*]chrysene-1,9-dicarboxylic acid/2,7,10,15-tetraisopropyl-3,6,11,14-tetramethoxydibenzo[*g*,*p*]chrysene-1,8-dicarboxylic acid). Under an argon atmosphere, to a solution of **1**/*iso*-**1** (3.6 g, 4.7 mmol) in dry Et_2O (216 mL) at -78 ºC was added *n*-BuLi (10.5 mL, 17 mmol, 1.59 M in hexane) dropwise over 5 min. After the mixture was stirred at -78 ºC for 15 min, gaseous carbon dioxide (balloon) was bubbled inside the mixture. While the bubbling kept continuing, the reaction mixture was allowed to warm



to ambient temperature. After conducted for 20 h, the reaction was quenched with 3 M aq. HCl (30 mL) at 0 ºC. The aqueous phase was extracted with EtOAc (30 mL x 3), and combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give crude products. Purification by silica-gel column chromatography (Hexane/EtOAc, 2:1) gave 2.5 g of **8**/*iso*-**8** (76%, ~ 50:50) as whitish yellow solid materials. Data: *Rf* value 0.19 (Hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.45 (s, 2H), 8.28 (s, 2H), 8.17 (s, 2H), 8.10 (s, 2H), 8.0 (s, 2H), 3.97 (s, 12H), 3.93 (s, 12H), 3.46 (sept, *J* = 7.0 Hz, 4H + 4H), 1.50 (d, *J* = 7.0 Hz, 24H), 1.33 (d, *J* = 7.0 Hz, 24H) ppm; MS (DART-TOF) *m/z*: 703 $[M-H]^-$; HRMS (DART-TOF) calcd. for $C_{44}H_{41}O_8$: 703.3271 $[M-H]^-$, found; 703.3252.

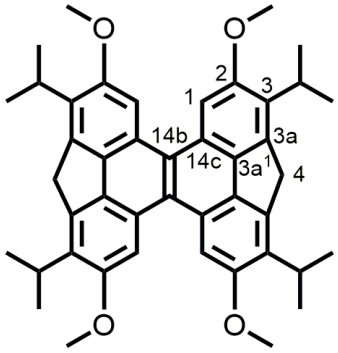
2. For **2**, (3,5,10,12-tetraisopropyl-2,6,9,13-tetramethoxydiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene-4,11-di-one). Under an argon atmosphere, to a suspension of **8**/*iso*-**8** (15 g, 21 mmol) in sulfurous dichloride (140 mL, 1.9 mol) at room temperature was added catalytic amounts of DMF (8 drops over 1 min). After stirred at room temperature for 0.5 h, the mixture was concentrated *in vacuo* to give 15 g of yellow solid products. To a suspension of the sample in dry CH_2Cl_2 (170 mL) at 0 ºC was added $AlCl_3$ (9.6 g, 72 mmol). After stirred at 0 ºC for 0.5 h, the mixture was quenched with 3 M aq. HCl (140 mL) at 0 ºC. The aqueous phase was extracted with CH_2Cl_2 (50 mL x 3), and combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give crude samples. Purification by silica-gel column chromatography (Hexane/Toluene, 1:1) yielded 10 g of **2** in 74% as orange solid materials. Data: *Rf* value 0.55 (Hexane/CH_2Cl_2, 2:1); M.p. 281-328 ºC (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 8.26 (s, 4H, H-1), 4.48 (sept, *J* = 6.9 Hz, 4H, C<u>*H*</u>$(CH_3)_2$), 4.08 (s, 12H, OCH_3) 1.49 (d, *J* = 6.9 Hz, 24H, $CH(C\underline{H}_3)_2$) ppm; ^{13}C NMR (100



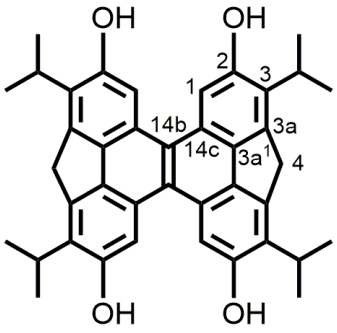
MHz, $CDCl_3$) 195.3 (C=O), 160.0 (C-2), 140.9 (C-3), 132.8 (C-3a), 130.6 (C-14c), 125.9 (C-14b), 124.4 (C-3a^1), 110.7 (C-1), 56.1 (OCH_3), 25.6 ($\underline{C}H(CH_3)_2$), 20.6 ($CH(\underline{C}H_3)_2$) ppm; MS (DART-TOF) *m/z*: 669 $[MH]^+$; IR (neat) 2955, 2920, 2865, 1698 (C=O), 1575, 1452, 1254, 1190, 978, 658 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{44}H_{45}O_6$: 669.3216 $[MH]^+$, found; 669.3210; Anal. Calcd. for $C_{44}H_{44}O_6$: C, 79.02; H, 6.63. Found: C, 79.24; H, 6.63.

4. Synthesis of **9**, **10**, **11**, and **3** (Scheme 4).

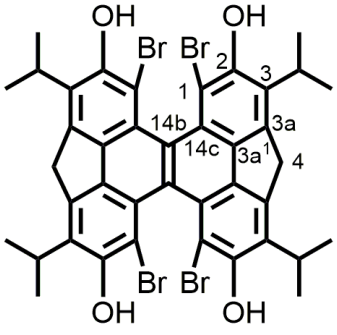
1. For **9**, (3,5,10,12-tetraisopropyl-2,6,9,13-tetramethoxydiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene-4,11-di-one). Under an argon atmosphere, to a 500 mL flask was added starting diketone **2** (9.0 g, 13 mmol) and THF (140 mL) and $AlCl_3$ (9.4 g, 70 mmol) and $NaBH_4$ (4.7 g, 130 mmol). After stirred at 80 °C for 4 h, the mixture was quenched with 3 M aq. HCl (70 mL) dropwise over 8 min. The aqueous layer was extracted with toluene (70 mL x 3), and combined organic phases were washed with brine (100 mL), and dried over Na_2SO_4, and filtered, and concentrated *in vacuo* to give 8.8 g of crude products. Purification by silica-gel column chromatography (Hexane/Toluene, 2:1) afforded 6.2 g of **9** in 71% yield as yellow solid materials. Data: *Rf* value 0.52 (Hexane/ Toluene, 1:1); M.p. 284 ºC (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 8.57 (s, 4H, H-1), 4.52 (s, 4H, CH_2), 4.17 (s, 12H, OCH_3), 3.79 (sept, J = 7.2 Hz, 4H, $C\underline{H}(CH_3)_2$), 1.59 (d, J = 7.2 Hz, 24H, $CH(C\underline{H}_3)_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 157.8 (C-2), 139.3 (C-3a), 132.8 (C-3), 132.7 (C-14c), 127.2 (C-14b), 125.2 (C-3a^1), 105.5 (C-1), 56.2 (OCH_3), 37.0 (CH_2), 28.6 ($\underline{C}H(CH_3)_2$), 21.7 ($CH(\underline{C}H_3)_2$) ppm; MS (DART-TOF) *m/z*: 641 $[MH]^+$; IR (neat): 2944, 2928, 2861, 1595, 1452, 1405, 1191, 1175, 1089, 1057, 820, 661 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{44}H_{49}O_4$ $[MH]^+$: 641.3625, found: 641.3615.



2. For **10**, (3,5,10,12-tetraisopropyl-2,6,9,13-tetramethoxydiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene-4,11-di-one). Under an argon atmosphere, to the solution of **9** (6.1 g, 9.6 mmol) in dry CH_2Cl_2 (80 mL) at 0 ºC was added BBr_3 (57 mL, 1 M CH_2Cl_2 solution) dropwise over 8 min. After stirred for 15 min, reaction mixture was allowed to warm to room temperature and conducted 4 h. The reaction was quenched with 3 M aq. HCl (60 mL) at 0 ºC. The aqueous layer was extracted with EtOAc (50 mL x 3) and the combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 6.4 g of crude products. Purification by silica-gel column chromatography (Toluene/EtOAc, 9:1) afforded 4.7 g of **10** in 85% yield as greenish yellow solid materials. Data: *Rf* value 0.17 (Hexane/EtOAc, 4:1); M.p. 178 ºC (dec.); ^{1}H NMR (400 MHz, DMSO-d_6) 9.42 (s, 4H, OH), 8.39 (s, 4H, H-1), 4.43 (s, 4H, CH_2), 3.67 (sept, J = 7.0 Hz, 4H, C$\underline{H}$(CH_3)$_2$), 1.51 (d, J = 7.0 Hz, 24H, CH(C$\underline{H}_3$)$_2$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 154.8 (C-2), 138.5 (C-3a), 131.3 (C-3), 131.2 (C-14c), 125.6 (C-14b), 124.3 (C-3a^1), 109.2 (C-1), 36.4 (CH_2), 28.0 ($\underline{C}$H(CH_3)$_2$), 21.4 (CH($\underline{C}H_3$)$_2$) ppm; MS (DART-TOF) *m/z*: 585 [MH]$^+$; IR (neat): 3403 (OH), 2949, 2909, 1582, 1475, 1395, 1372, 1240, 1221, 1176, 997, 838 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{40}H_{41}O_4$: 585.3005 [MH]$^+$, found: 585.2993.

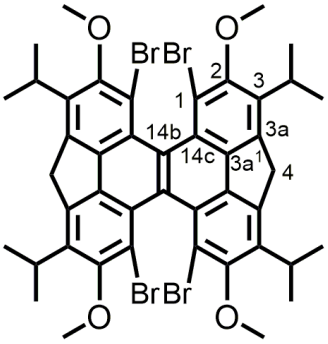


3. For **11**, (3,5,10,12-tetraisopropyl-2,6,9,13-tetramethoxydiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene-4,11-di-one). Under an argon atmosphere, to a suspension of **10** (4.7 g, 8.1 mmol) in dry CH_2Cl_2 (56 mL) at -20 ºC was added a solution of Br_2 (39 mL, 1 M CH_2Cl_2 solution) dropwise over 9 min, and then the mixture was stirred at -20 ºC for 4 h. The reaction was quenched with saturated aq. $Na_2S_2O_3$ (40 mL) and 3 M aq. HCl (60 mL), and the aqueous layer was extracted with EtOAc



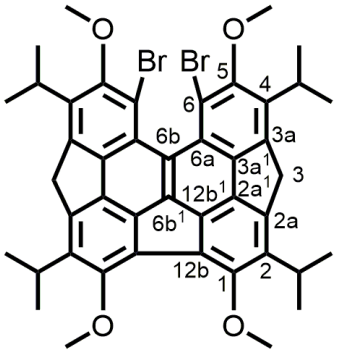
(50 mL x 3). The combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give 8.3 g of crude products. Purification by silica-gel short plugged column chromatography (Hexane/$CHCl_3$, 1:1) yielded 5.4 g of **11** in 73% as yellow solid materials. Data: *Rf* value 0.57 (Hexane/EtOAc, 4:1); M.p. 140 ºC (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 6.26 (s, 4H, OH), 4.49 (s, 4H, CH_2), 3.77 (qq *J* = 7.2, 7.2 Hz, 4H, C*H*$(CH_3)_2$), 1.59 (d, *J* = 7.2 Hz, 12H, CH(C*H*$_3)_2$), 1.57 (d, *J* = 7.2 Hz, 12H, CH(C*H*$_3)_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.9 (C-2), 137.9 (C-3), 132.3 (C-3a), 132.2 (C-14c), 129.7 (C-14b), 122.9 (C-3a^1), 108.4 (C-1), 37.2 (CH_2), 29.8 (*C*H$(CH_3)_2$), 21.5 (CH(*C*H$_3)_2$), 21.4 (CH(*C*H$_3)_2$) ppm; MS (DART-TOF) *m/z*: 899 $[M-H]^-$; IR (neat): 3457 (OH), 3430 (OH), 2967, 2928, 2870, 1578, 1460, 1351, 1164, 1097, 1027, 750 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{40}H_{35}Br_4O_4$ $[M-H]^-$: 898.9228, found: 898.9239.

4. For **3**, (3,5,10,12-tetraisopropyl-2,6,9,13-tetramethoxydiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene-4,11-di-one). Under an argon atmosphere, to a suspension of **11** (4.5 g, 5.0 mmol) in dry CH_2Cl_2 (130 mL) was added 1,8-bis(dimethylamino)naphthalene (Proton Sponge, 19 g, 90 mmol) and trimethyloxonium tetrafluoroborate (Meerwein reagent, 13 g, 90 mmol). After stirred at room temperature for 0.5 h, the reaction was quenched with 3 M aq. HCl (45 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 (80 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give crude products. Purification by silica-gel short plugged column chromatography (Toluene only) afforded 4.5 g of yellow solid materials. Purification by silica-gel column chromatography (Hexane/Toluene, 1:2) yielded 4.0 g of **3** in 83% as yellow solid materials. Data: *Rf* value 0.21 (Toluene only); M.p. 299 ºC (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 4.54 (s, 4H, CH_2), 4.14 (s, 12H, OCH_3), 3.83 (qq,



J = 7.1, 7.1 Hz, 4H, C<u>H</u>$(CH_3)_2$), 1.61 (d, J = 7.1 Hz, 12H, CH(C<u>H</u>$_3)_2$), 1.57 (d, J = 7.1 Hz, 12H, CH(C<u>H</u>$_3)_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.7 (C-2), 139.1 (C-3a), 138.6 (C-3), 135.0 (C-14c), 131.4 (C-14b), 125.7 (C-3a^1), 117.0 (C-1), 62.9 (OCH_3), 38.0 (CH_2), 29.3 (<u>C</u>H$(CH_3)_2$), 23.1 (CH(<u>C</u>$H_3)_2$), 22.9 (CH(<u>C</u>$H_3)_2$) ppm; MS (DART-TOF) *m/z*: 955 [M-H]$^-$; IR (neat): 2960, 2936, 1369, 1329, 1266, 1057, 1031, 901, 647 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{44}H_{43}Br_4O_4$: 954.9854 [M-H]$^-$, found: 954.9868.; Anal. Calcd. for $C_{44}H_{44}Br_4O_4$; C, 55.25; H, 4.64. Found: C, 55.35; H, 4.62.

5. Synthesis of **4** (6,7-dibromo-2,4,9,11-tetraisopropyl-1,5,8,12-tetramethoxy-3,10-dihydroindeno[7,1,2-*pqr*]-*as*-indaceno[3,2,1,8,7-*defghi*]chrysene, Scheme 5). Under an argon atmosphere, to a solution of **3** (1.00 g, 1.05 mmol) in mesitylene (20.0 mL) was added bis(tri-*tert*-butylphosphine)palladium(0) (534 mg, 1.05 mmol). The reaction mixture was allowed to warm to 195 ºC (bath temp.), then stirred for 15 h. The mixture was allowed to cool to ambient temperature, and filtered through a pad of celite. The organic phase was washed with brine (50 mL), and dried over Na_2SO_4, and concentrated *in vacuo* to give crude products as brown solid materials. Purification by short-plugged silica-gel column chromatography (Hexane/Toluene, 1:2) afforded 191 mg of yellow solid materials (24%). Data: *Rf* value 0.53 (Hexane/Toluene, 1:19); M.p. 235 ºC (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 4.83 (d, J = 20 Hz, 2H, CH_2), 4.54 (d, J = 20 Hz, 2H, CH_2), 4.32 (s, 6H, OCH_3), 4.21 (s, 6H, OCH_3), 3.84 (qq, J = 7.0, 7.0 Hz, 2H, C<u>H</u>$(CH_3)_2$), 3.76 (qq, J = 7.0, 7.0 Hz, 2H, C<u>H</u>$(CH_3)_2$), 1.62 (d, J = 7.0 Hz, 6H, CH(C<u>H</u>$_3)_2$), 1.60 (d, J = 7.0 Hz, 6H, CH(C<u>H</u>$_3)_2$), 1.50 (d, J = 7.0 Hz, 6H, CH(C<u>H</u>$_3)_2$), 1.47 (d, J = 7.0 Hz, 6H, CH(C<u>H</u>$_3)_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 158.1 (C-5), 156.2 (C-1), 142.9 (C-3a), 142.3 (C-2a), 139.6 (C-4), 139.0 (C-2), 138.2 (C-6a), 137.3 (C-6b^1), 134.4 (C-12b^1), 130.9 (C-2a^1),



129.6 (C-3a^1), 125.3 (C-12b), 122.5 (C-6b), 118.2 (C-6), 64.7 (OCH_3), 63.4 (OCH_3), 41.7 (CH_2), 29.2 ($\underline{C}H(CH_3)_2$), 28.7 ($\underline{C}H(CH_3)_2$), 23.6 ($CH(\underline{C}H_3)_2$), 23.3 ($CH(\underline{C}H_3)_2$), 22.90 ($CH(\underline{C}H_3)_2$), 22.86 ($CH(\underline{C}H_3)_2$) ppm; MS (DART-TOF) *m/z*: 795 $[MH]^+$; IR (neat): 2963, 2929, 2869, 2836, 1573, 1541, 1443, 1362, 1304, 1231, 1018, 640, 583 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{44}H_{45}Br(79)_2O_4$ $[MH]^+$: 795.1685, found: 795.1704.

6. Data of DFT calculations for **4** and the unsubstituted nona-cycle (Figure 1S):

DFT Calculation: All calculations were conducted using a Gaussian 16 suite program (G16RevC.02).[2] Structure optimization was performed at the B3LYP-D3/6-31G(d,p) level of theory. By using the DFT-D3 dispersion correction method developed by Grimme et al.[3] for the optimization, the bowl structure of compound 4, as observed in the X-ray crystal structure, was accurately reproduced. In contrast, structure optimization of compound 4 using B3LYP/6-31G(d,p) or CAM-B3LYP/6-31G(d,p) resulted in a flattened structure in both cases, and the bowl structure could not be reproduced. Harmonic vibrational frequency analysis was conducted on the optimized structures at the same level of theory (B3LYP-D3/6-31G(d,p)) to verify that all stationary points were local minima (with no imaginary frequencies).

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[2] 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.

[3] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456.

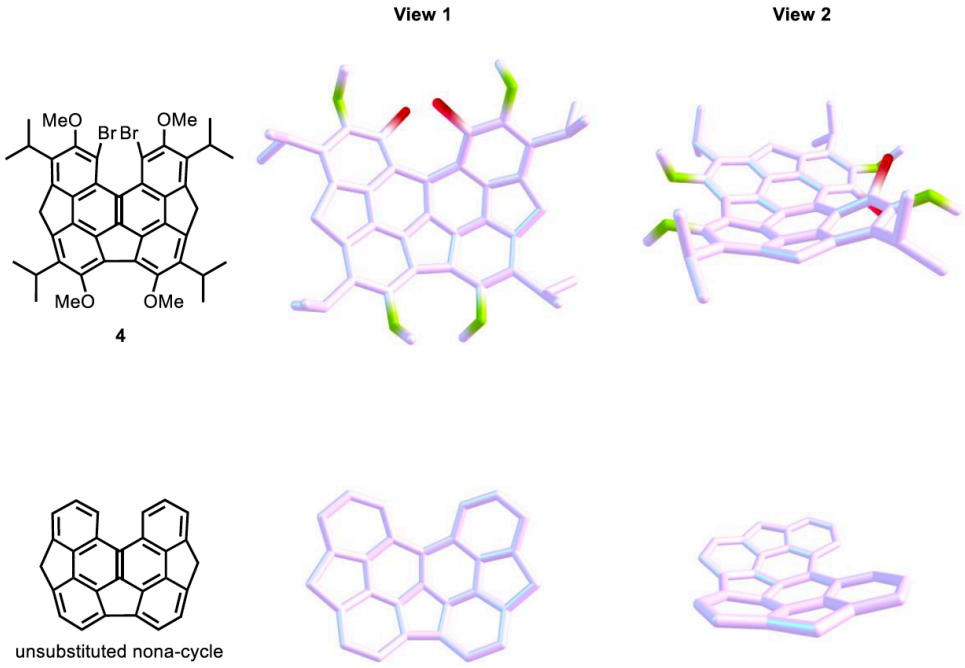


Figure 1S. Optimized structures for **4** and the unsubstituted nona-cycle (B3LYP-D3/6-31G(d,p)).

Cartesian Coordinates of Optimized Structures:

Cartesian coordinates for **4**, optimized at the B3LYP-D3/6-31G(d,p) level of theory.

		Coordinates (Angstroms)		
Center Number	Atomic Type	X	Y	Z
1	35	1.442167	-3.4545	-1.76631
2	35	0.158675	-3.19434	1.332163
3	8	4.256747	-3.28852	-0.6619
4	8	0.552809	5.455144	0.142812
5	8	-2.60889	-4.33729	1.080391
6	8	-2.82695	4.799217	-0.26546
7	6	2.394103	0.29769	-0.37653
8	6	1.97151	1.641658	-0.39422
9	6	0.708703	1.939047	-0.77117
10	6	1.531105	-0.79261	-0.66097
11	6	2.893319	2.571235	0.057244

12	6	3.752553	0.27326	-0.03622
13	6	2.402494	3.884116	0.200374
14	6	-0.18671	0.870718	-0.97419
15	6	0.99527	4.165991	-0.09395
16	6	-1.43785	1.511776	-1.02108
17	6	3.620634	-2.07542	-0.5075
18	6	-2.54704	0.738985	-0.92171
19	6	-1.13398	-1.28963	-0.46113
20	6	0.078402	-0.48592	-0.76149
21	6	5.844161	-1.18308	0.371042
22	1	6.08754	-2.22157	0.133612
23	6	4.399172	-0.96302	-0.04908
24	6	0.097452	3.198746	-0.58854
25	6	4.184832	1.740944	0.289436
26	1	4.568505	1.827215	1.311345
27	1	4.991112	2.069692	-0.37415
28	6	2.258197	-1.98569	-0.84859
29	6	-2.39972	-0.65052	-0.65599
30	6	3.284223	5.022406	0.697753
31	1	2.689285	5.937866	0.658816
32	6	-1.38878	2.907574	-0.77421
33	6	-1.27825	-2.50706	0.253144
34	6	-3.65742	-1.13018	-0.25764
35	6	-2.66022	3.463792	-0.55052
36	6	-3.8037	1.263488	-0.61952
37	6	6.007594	-0.99719	1.891746
38	1	5.785343	0.031972	2.193095
39	1	7.035613	-1.21973	2.197827
40	1	5.334704	-1.65826	2.446752
41	6	-3.76732	-2.4223	0.238722

42	6	3.718201	4.806115	2.159902
43	1	4.351058	3.91831	2.26082
44	1	2.853572	4.672958	2.817497
45	1	4.29305	5.665587	2.52174
46	6	-2.53649	-3.10335	0.472888
47	6	6.834409	-0.29788	-0.40579
48	1	6.691249	-0.3981	-1.48572
49	1	7.863455	-0.58922	-0.1698
50	1	6.728429	0.759196	-0.14483
51	6	-3.88063	2.658759	-0.48461
52	6	-5.23501	-3.14669	2.176663
53	1	-4.5054	-3.8684	2.550511
54	1	-6.23855	-3.49207	2.448959
55	1	-5.05678	-2.1895	2.677346
56	6	-5.30093	3.574026	1.381425
57	1	-5.35049	2.602197	1.885791
58	1	-6.20998	4.13226	1.631898
59	1	-4.44115	4.121396	1.776602
60	6	3.982074	-4.23032	0.383519
61	1	2.904776	-4.35865	0.533405
62	1	4.444633	-3.9086	1.325971
63	1	4.421248	-5.17797	0.066466
64	6	4.507285	5.230216	-0.21356
65	1	5.083606	6.102582	0.113323
66	1	4.202297	5.391491	-1.25175
67	1	5.178004	4.365225	-0.19015
68	6	-0.11611	5.626066	1.400133
69	1	-1.04139	5.042328	1.433329
70	1	-0.35732	6.68841	1.476797
71	1	0.537788	5.339517	2.233214

72	6	-2.0851	-5.42686	0.306592
73	1	-2.67996	-5.57374	-0.60293
74	1	-2.16317	-6.31104	0.941853
75	1	-1.03715	-5.26509	0.037574
76	6	-2.32759	5.712713	-1.25481
77	1	-2.79832	5.51881	-2.22624
78	1	-1.24063	5.65245	-1.3428
79	1	-2.60567	6.710041	-0.90808
80	6	-4.683	0.031377	-0.31388
81	1	-5.45199	-0.13244	-1.07886
82	1	-5.2088	0.126515	0.642075
83	6	-5.11441	-3.00094	0.647619
84	1	-5.8645	-2.26612	0.329256
85	6	-5.17265	3.391209	-0.14387
86	1	-5.09271	4.392584	-0.57876
87	6	-5.45616	-4.31947	-0.06939
88	1	-5.32152	-4.22964	-1.15207
89	1	-6.50036	-4.58999	0.121379
90	1	-4.827	-5.13465	0.291464
91	6	-6.4293	2.732925	-0.73217
92	1	-6.30975	2.525011	-1.80019
93	1	-7.2901	3.398462	-0.60962
94	1	-6.67578	1.793268	-0.22976

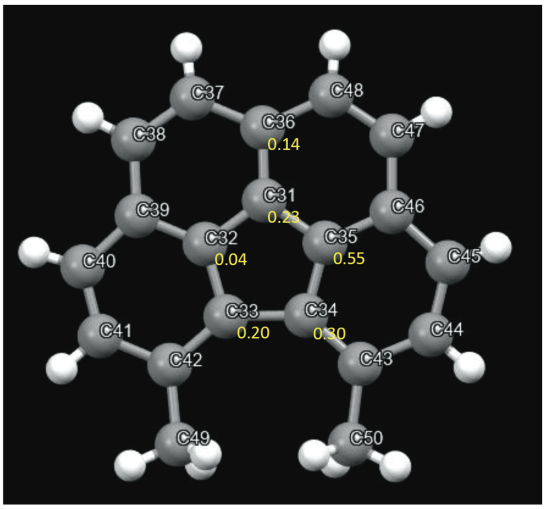
Cartesian coordinates for the unsubstituted nona-cycle, optimized at the B3LYP-D3/6-31G(d,p) level of theory.

		Coordinates (Angstroms)		
Center Number	Atomic Type	X	Y	Z
1	6	0.000059	-1.00889	-0.61637
2	6	-0.000021	0.383404	-0.78004
3	6	-1.104349	1.256006	-0.63009
4	6	-2.317125	0.707656	-0.36707
5	6	-2.436812	-0.69804	-0.26797
6	6	-1.346705	-1.60458	-0.39754
7	6	1.34688	-1.60445	-0.39774
8	6	2.436854	-0.69782	-0.26782
9	6	2.317042	0.707863	-0.36679
10	6	1.104196	1.256071	-0.62978
11	6	1.714785	-2.94777	-0.14054
12	6	3.014054	-3.27093	0.257419
13	6	4.029008	-2.30735	0.473432
14	6	3.726028	-0.98061	0.21752
15	6	3.394536	1.421508	0.153364
16	6	3.140473	2.775355	0.400111
17	6	1.833458	3.347054	0.199652
18	6	0.759119	2.589712	-0.29023
19	6	-3.725922	-0.98089	0.217525
20	6	-4.028776	-2.3076	0.473755
21	6	-3.01363	-3.27107	0.258212
22	6	-1.714362	-2.94781	-0.13967
23	6	-0.759401	2.589627	-0.29034
24	6	-1.833837	3.346902	0.199459
25	6	-3.140768	2.775067	0.399925

26	6	-3.394702	1.421231	0.153003
27	6	4.470363	0.359659	0.466582
28	6	-4.470472	0.359345	0.46618
29	1	0.99347	-3.75002	-0.23272
30	1	3.245928	-4.31486	0.449392
31	1	4.997521	-2.61976	0.853833
32	1	3.903574	3.418977	0.829957
33	1	1.689223	4.376771	0.515765
34	1	-4.997245	-2.62001	0.854269
35	1	-3.245383	-4.31499	0.45041
36	1	-0.992889	-3.74995	-0.23148
37	1	-1.689724	4.376639	0.515567
38	1	-3.90403	3.418669	0.829504
39	1	5.351971	0.461205	-0.17945
40	1	4.829315	0.422369	1.50027
41	1	-5.351943	0.460677	-0.18007
42	1	-4.829627	0.422213	1.499777

7. Data of POAV angles for corannulene and sumanene fragments in Figure 6 (Figure 2S).

(a) Table 1, Entry 6, Corannulene frag.



(b) Table 1, Entry 7, Sumanene frag.

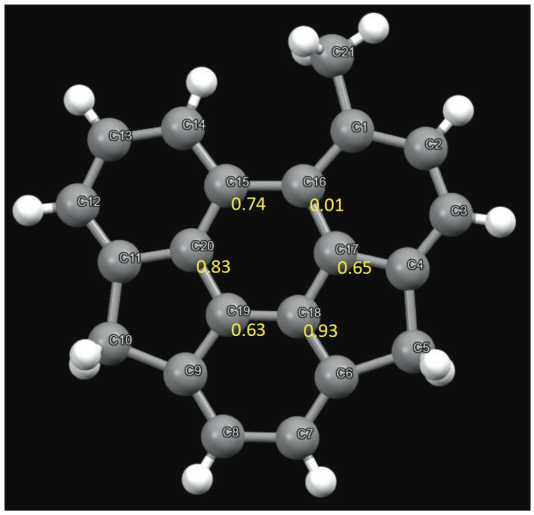
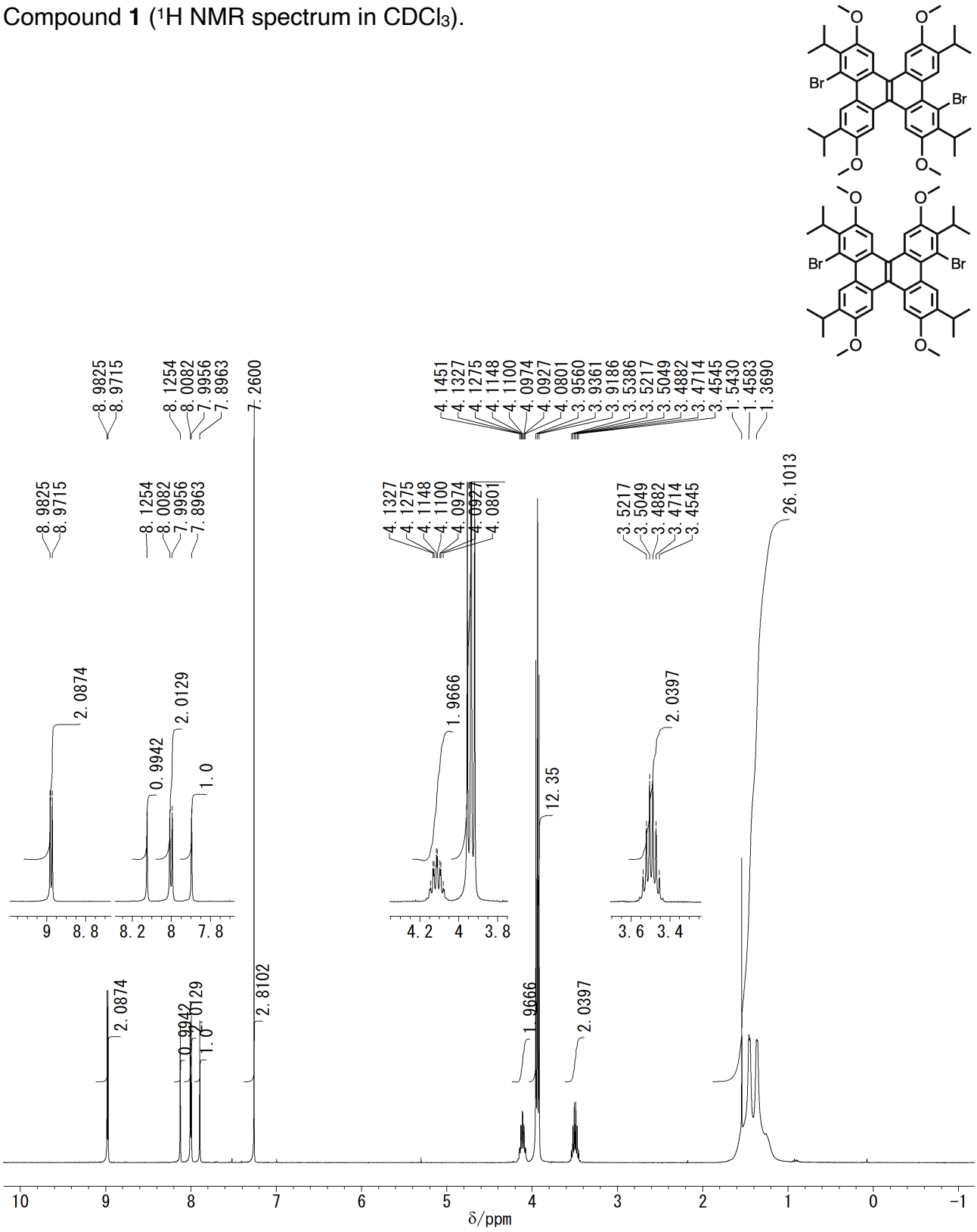


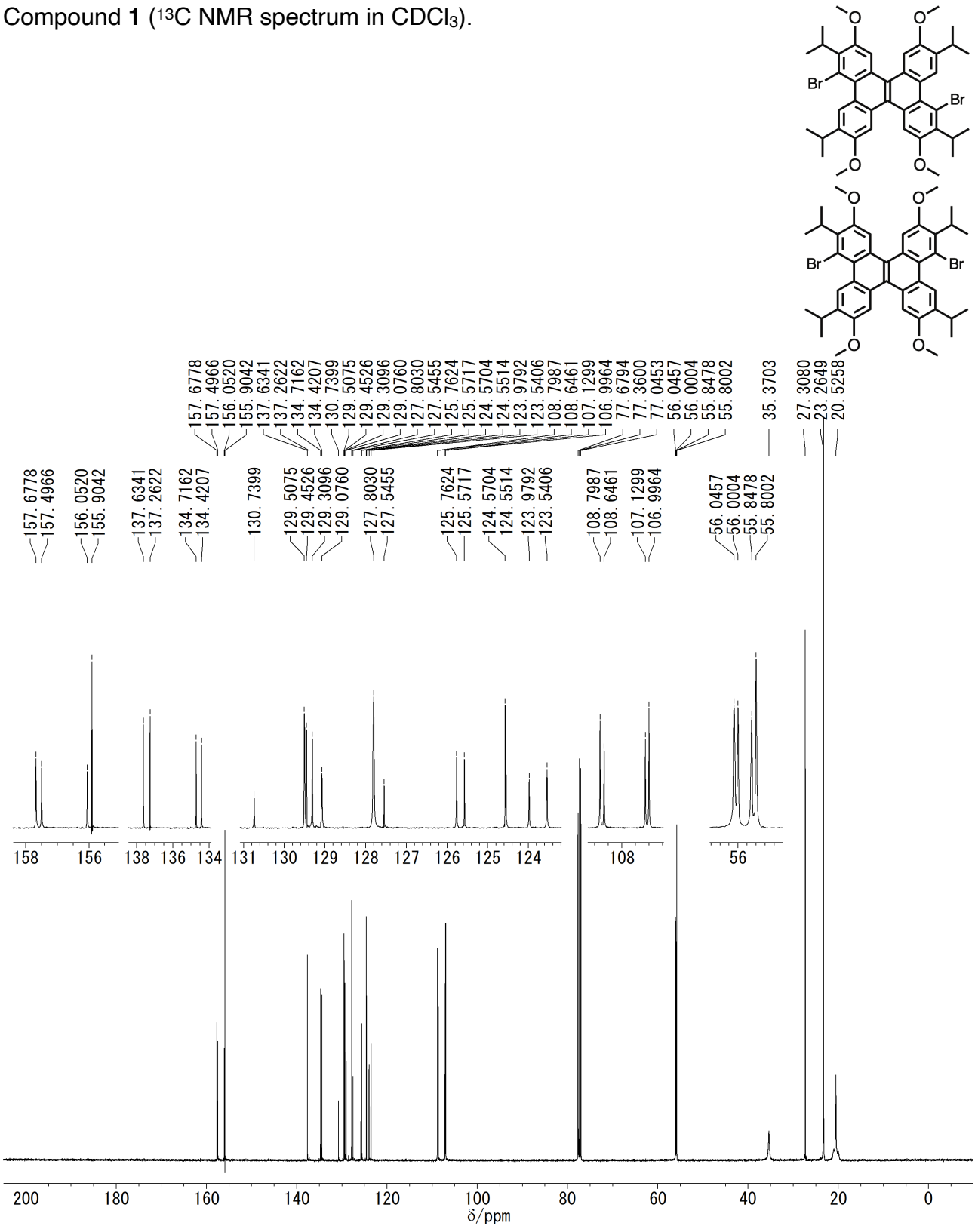
Figure 2S. POAV angles in the X-ray crystal structure of (a) corannulene (CCDC-1874124), and (b) sumanene fragments (CCDC-1290159).

8. ^{1}H NMR and ^{13}C NMR spectra for all new compounds.

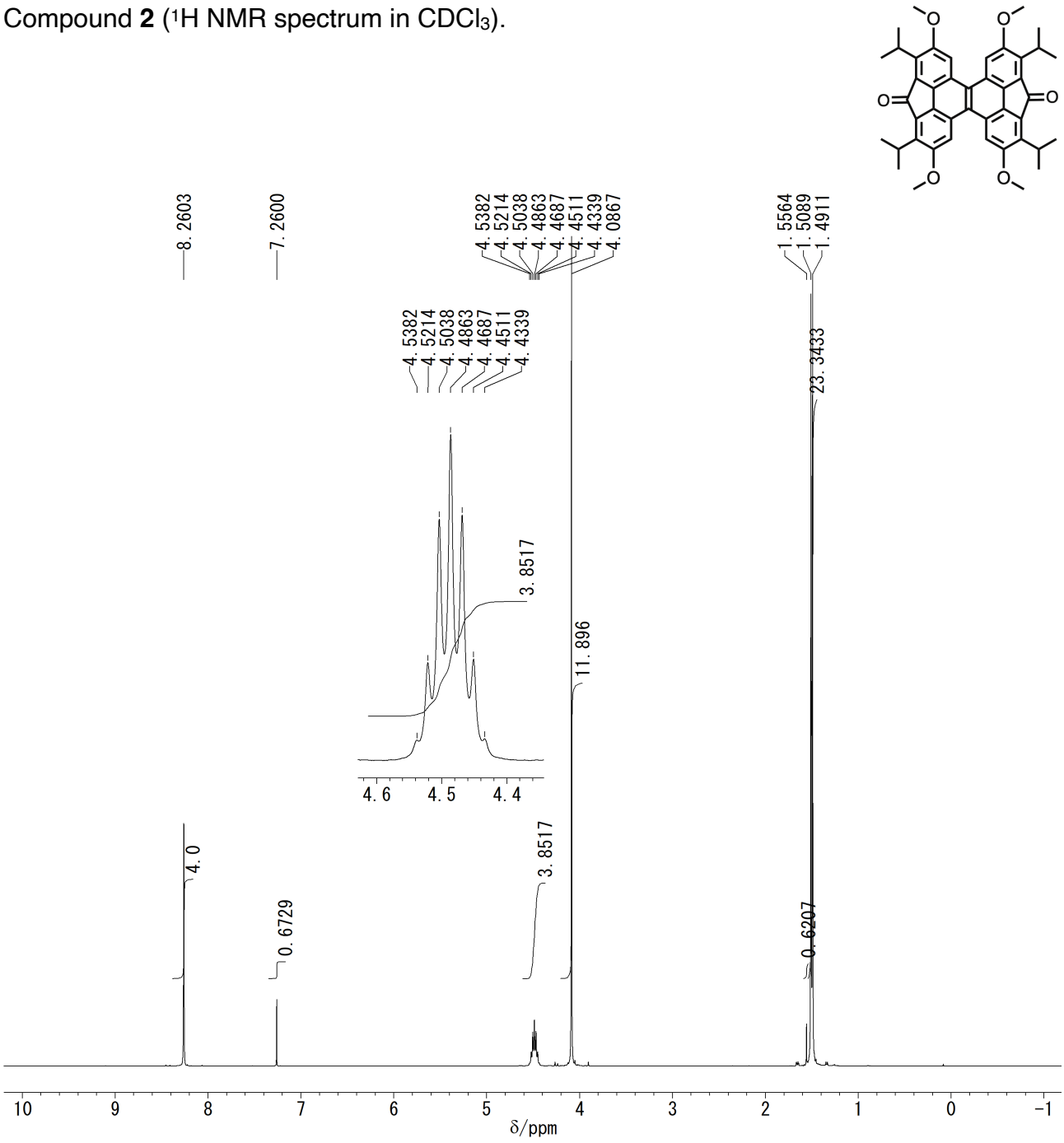
Compound **1** (^{1}H NMR spectrum in $CDCl_3$).



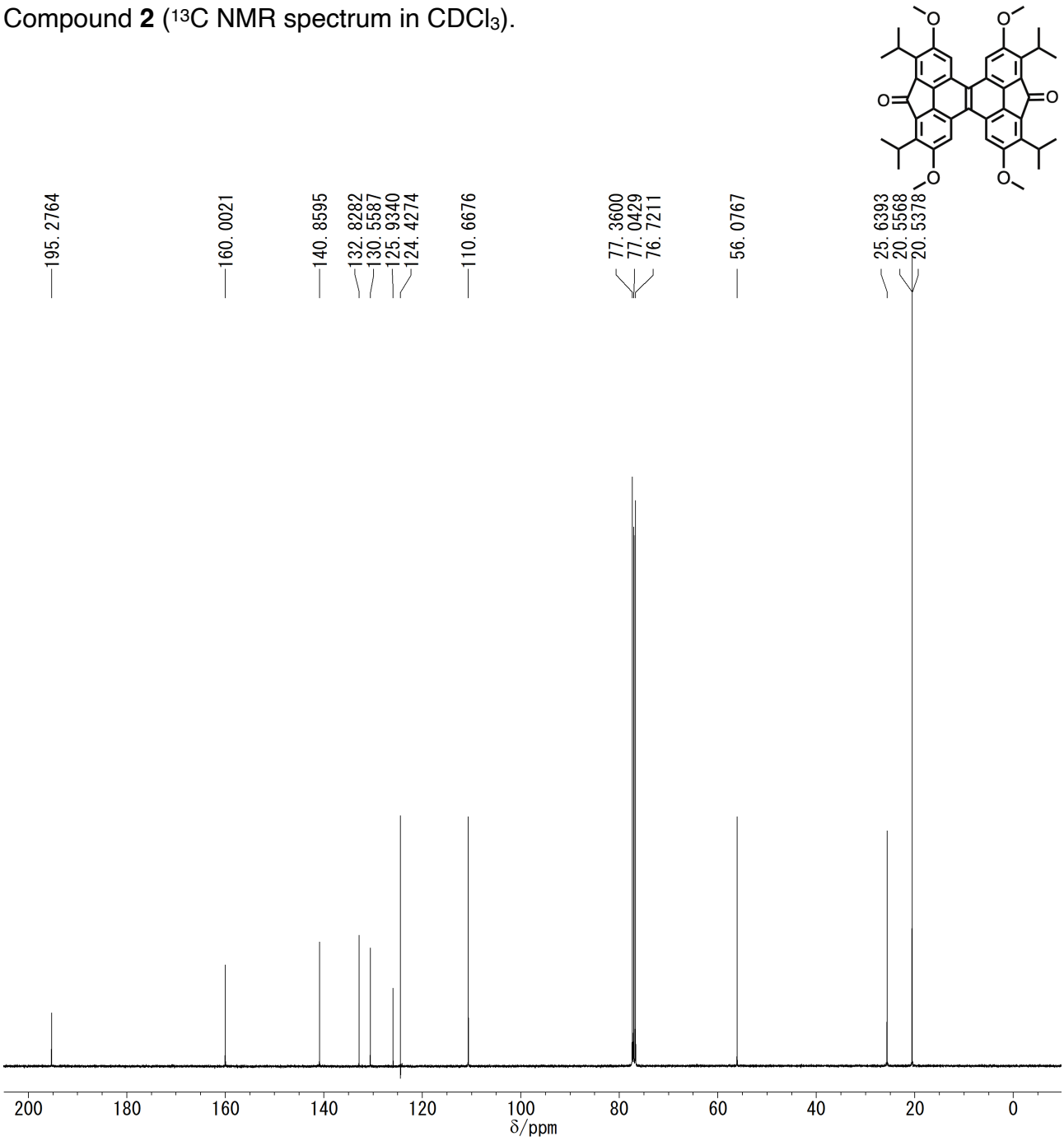
Compound **1** (^{13}C NMR spectrum in $CDCl_3$).



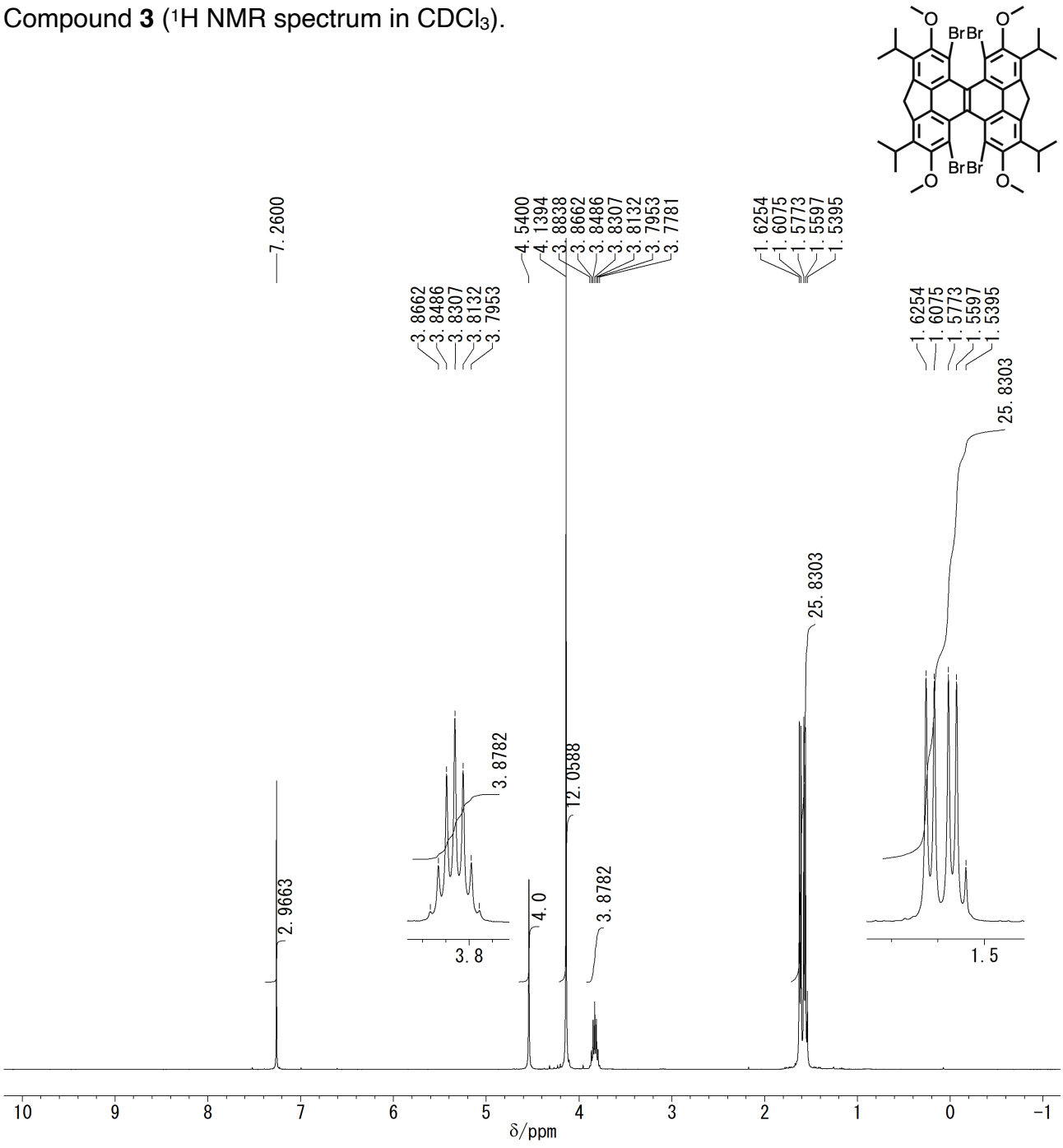
Compound **2** (^{1}H NMR spectrum in $CDCl_3$).



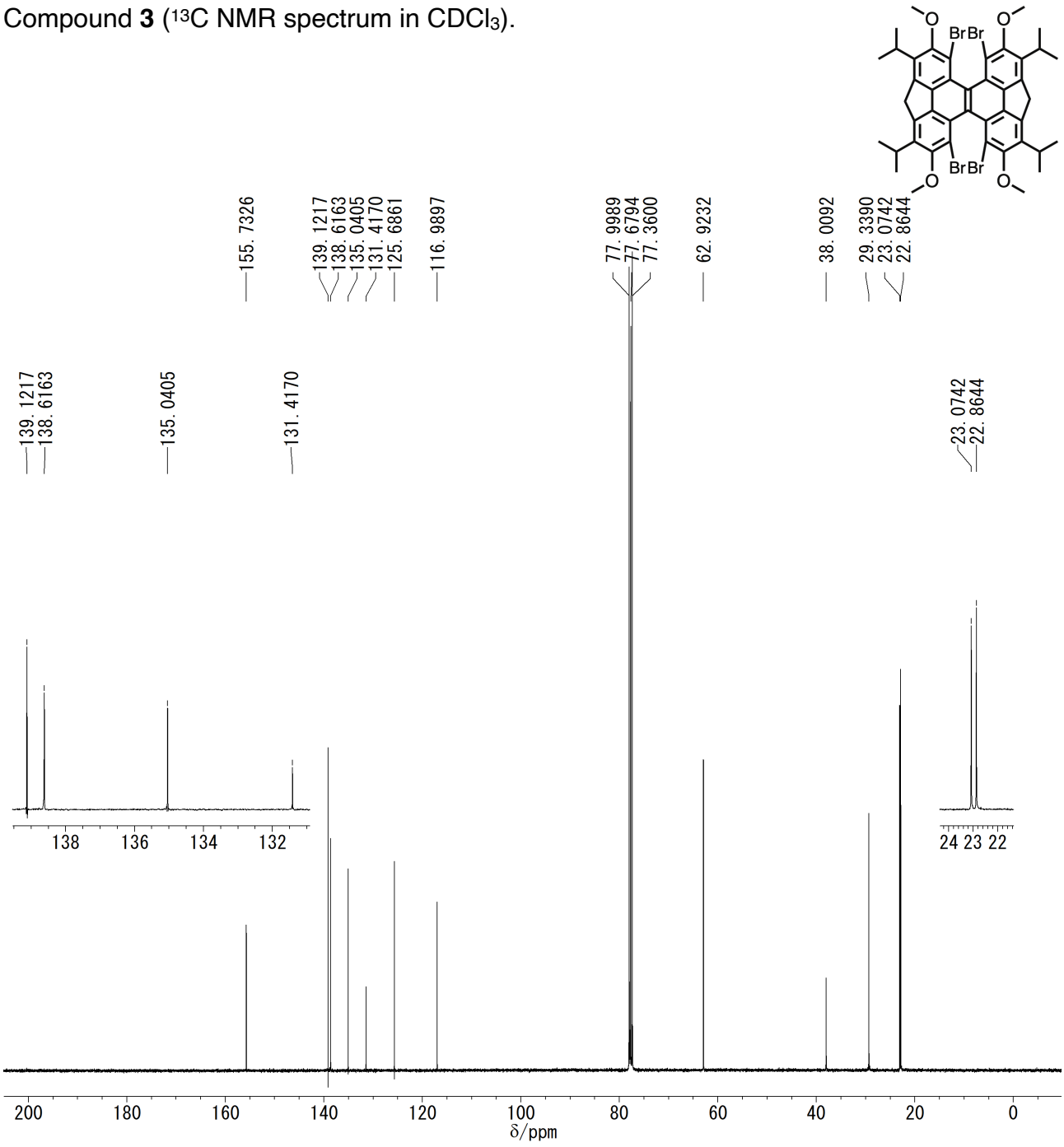
Compound **2** (^{13}C NMR spectrum in $CDCl_3$).



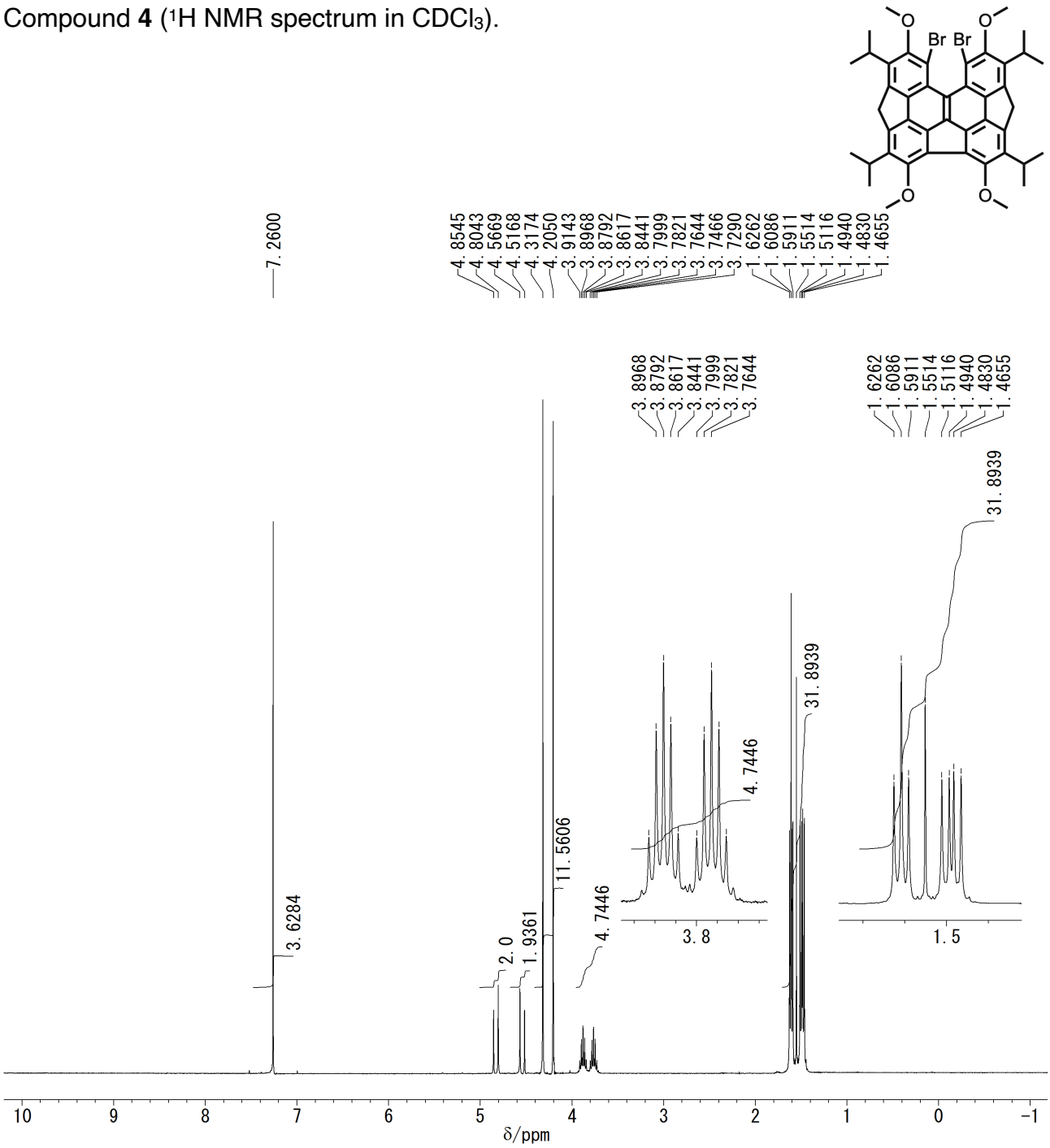
Compound **3** (^{1}H NMR spectrum in $CDCl_3$).



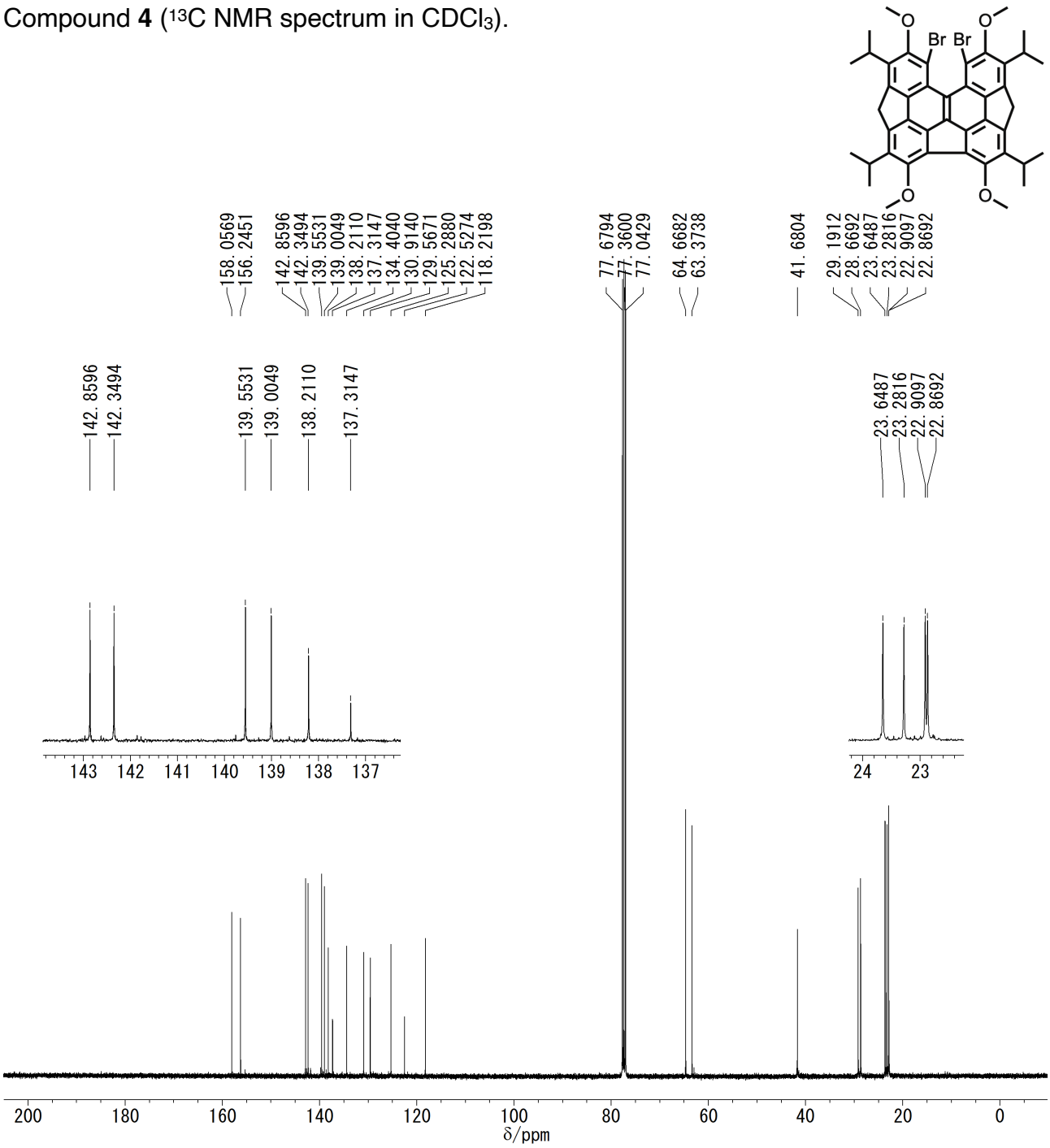
Compound **3** (^{13}C NMR spectrum in $CDCl_3$).



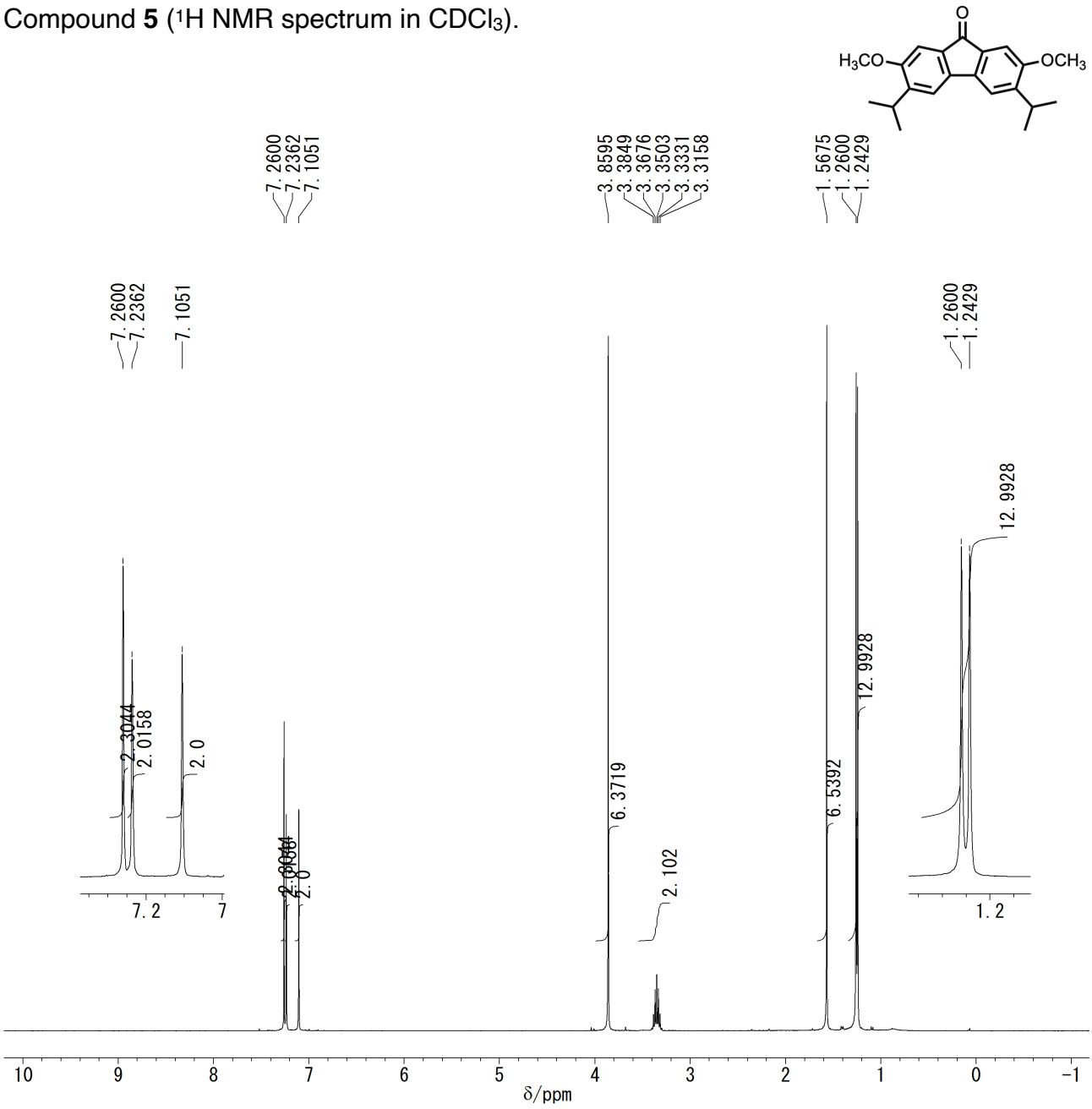
Compound **4** (^{1}H NMR spectrum in $CDCl_3$).



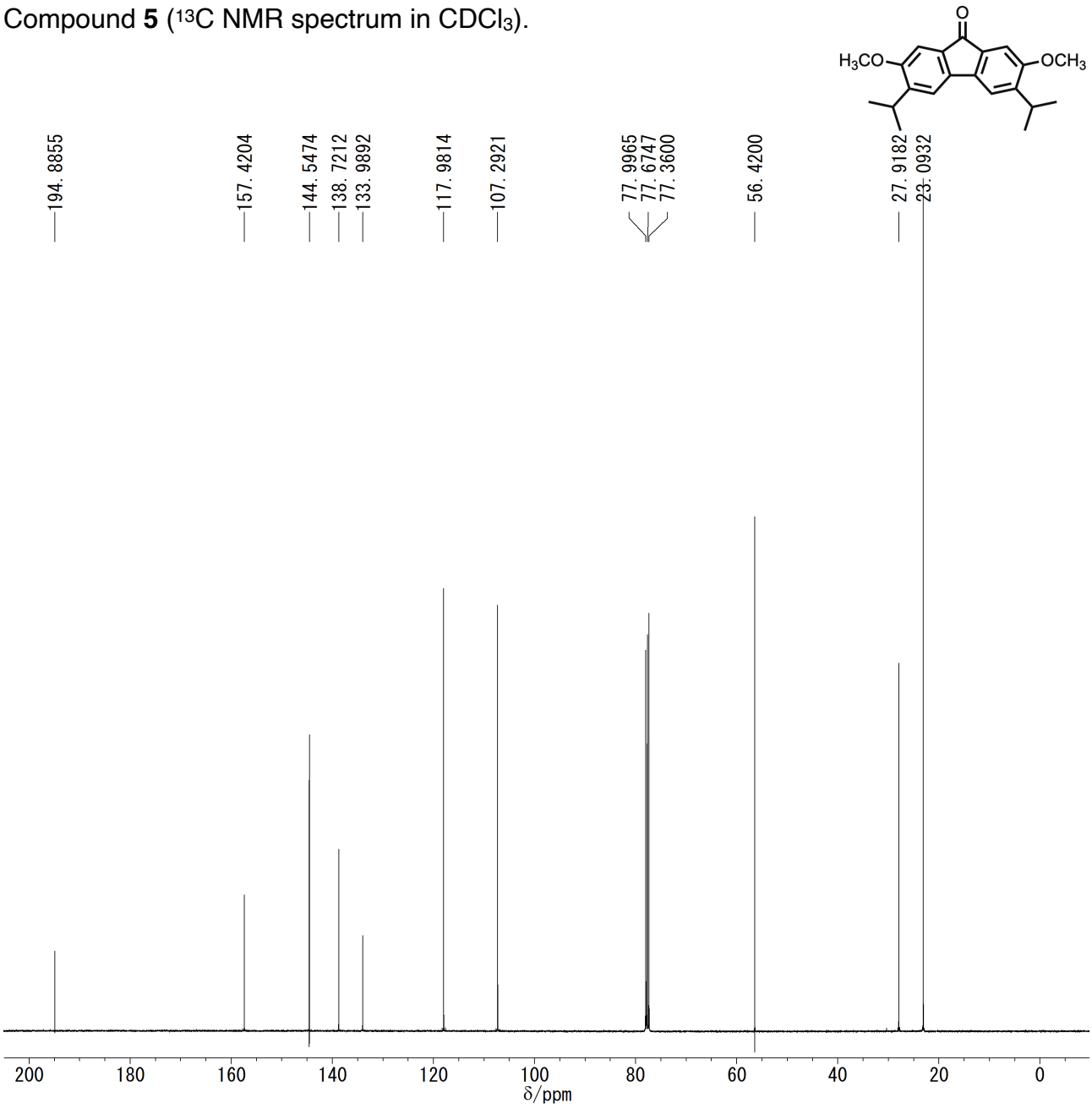
Compound **4** (^{13}C NMR spectrum in $CDCl_3$).



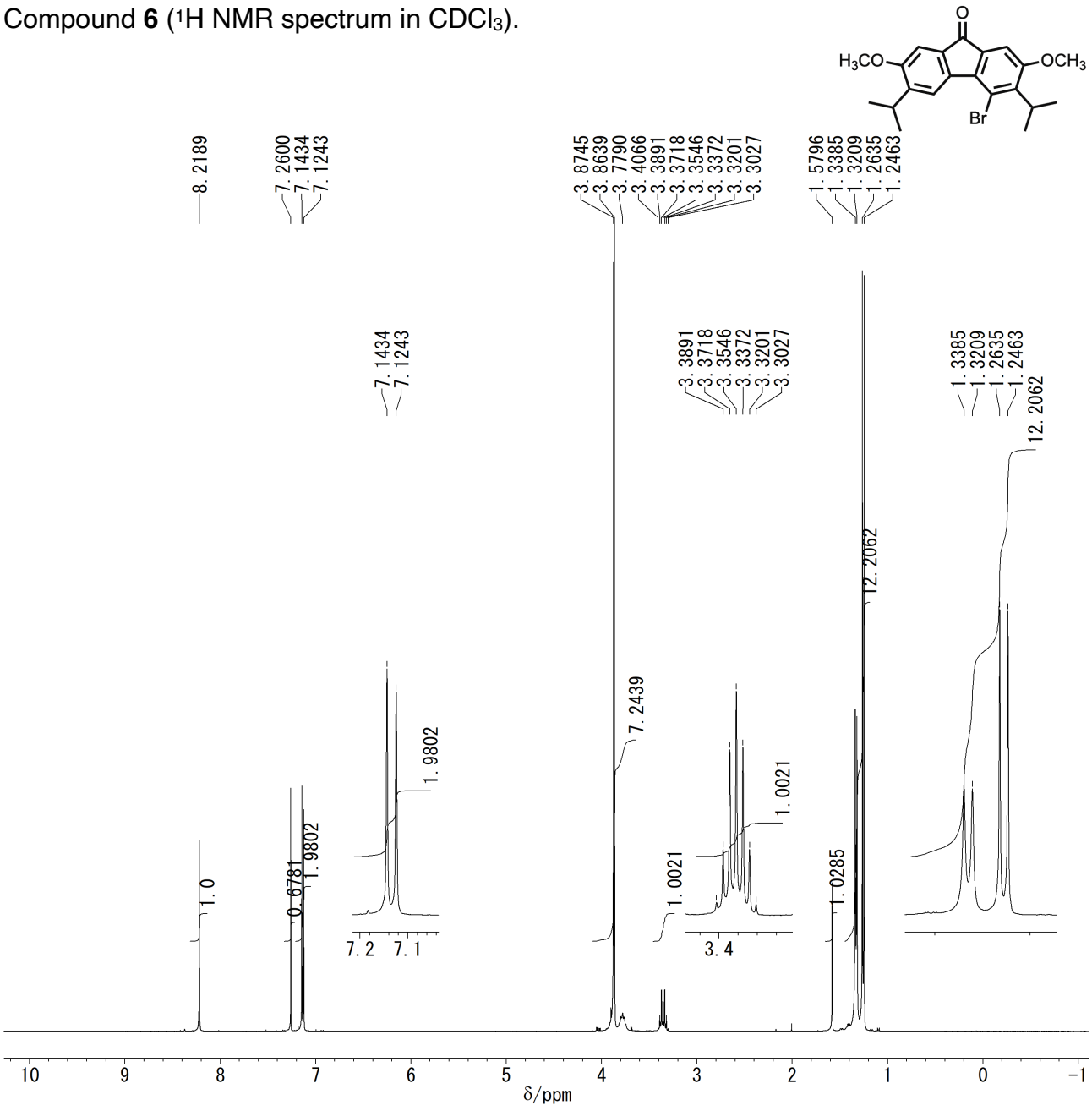
Compound **5** (^{1}H NMR spectrum in $CDCl_3$).



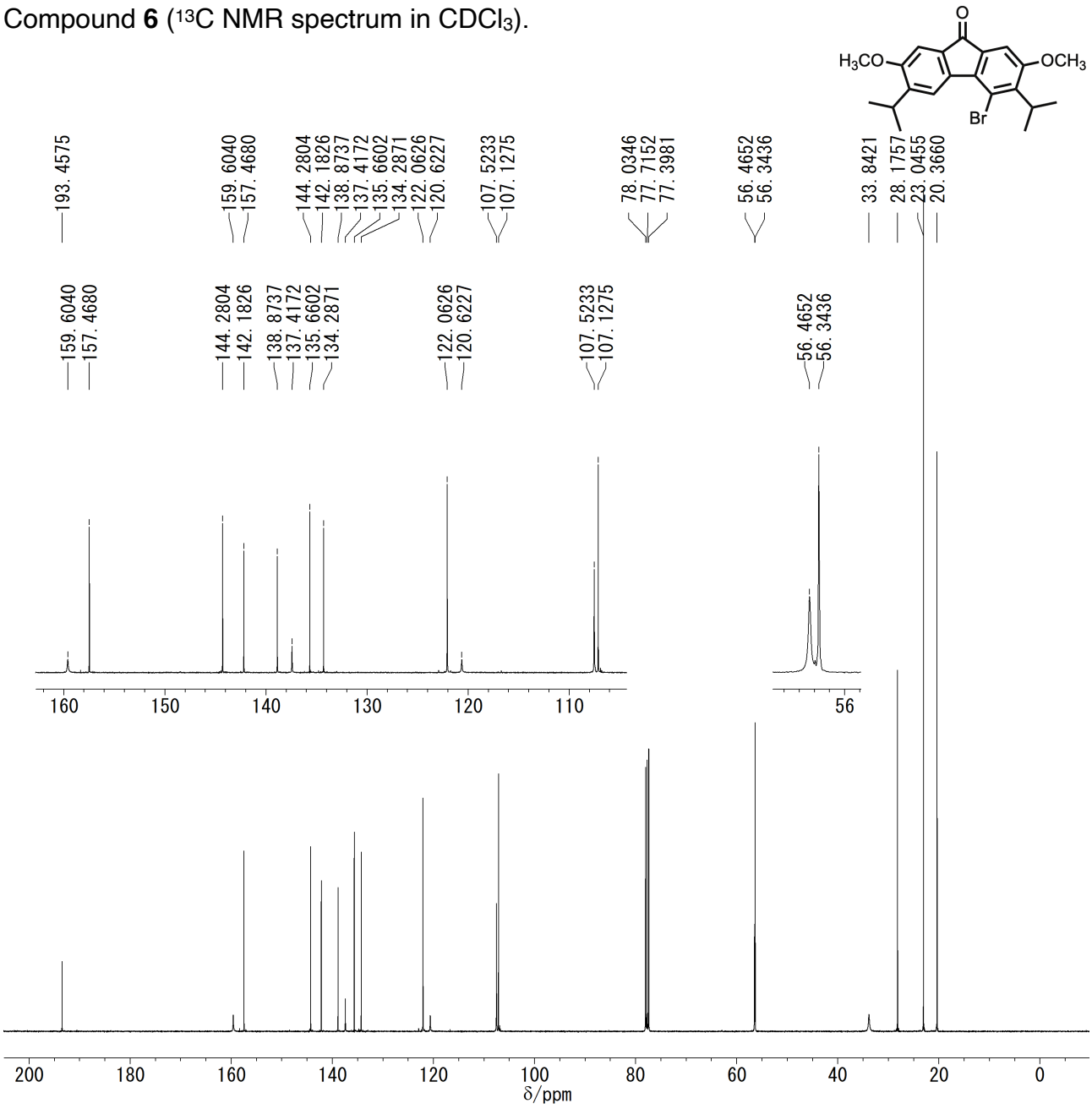
Compound **5** (^{13}C NMR spectrum in $CDCl_3$).



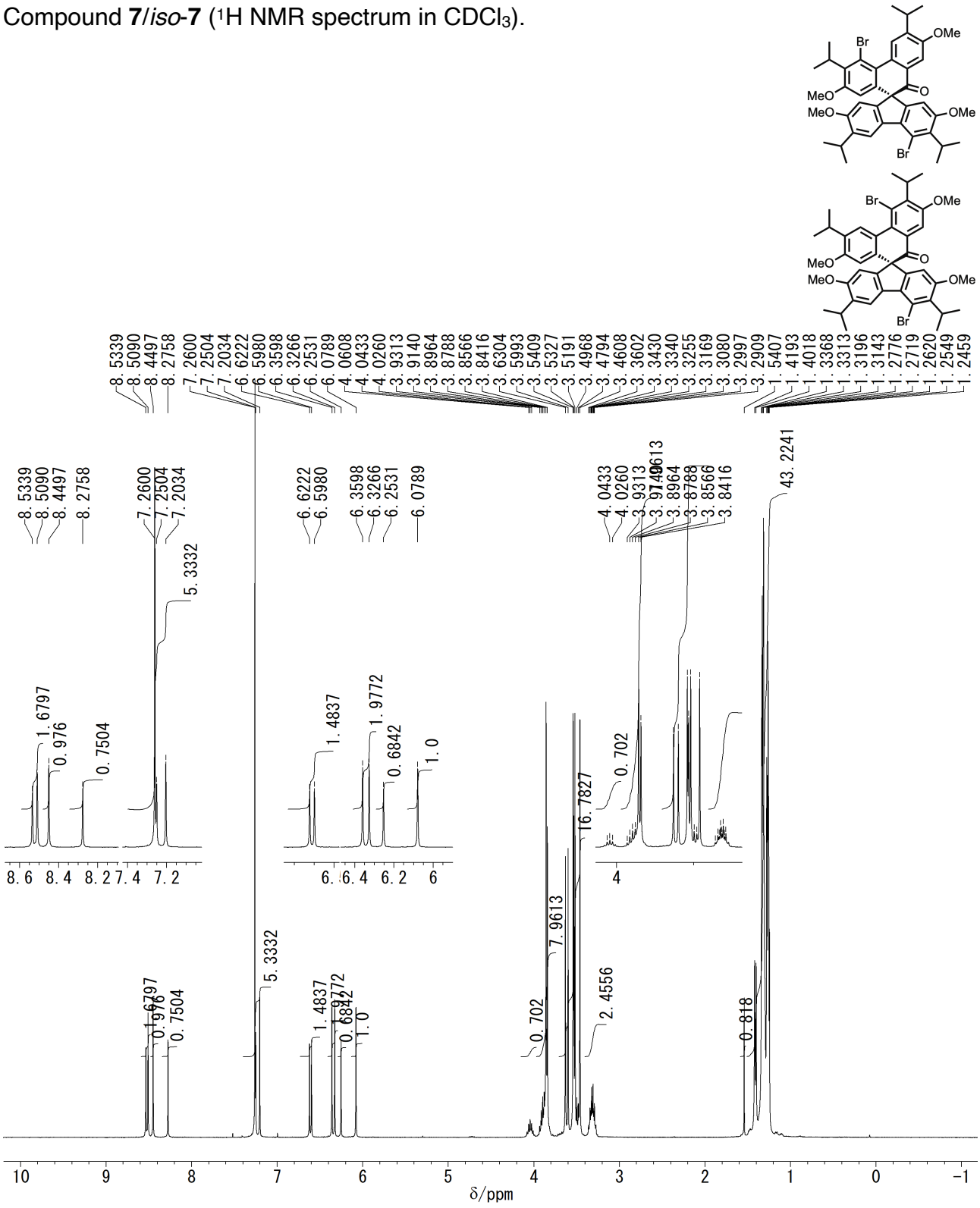
Compound **6** (^{1}H NMR spectrum in $CDCl_3$).



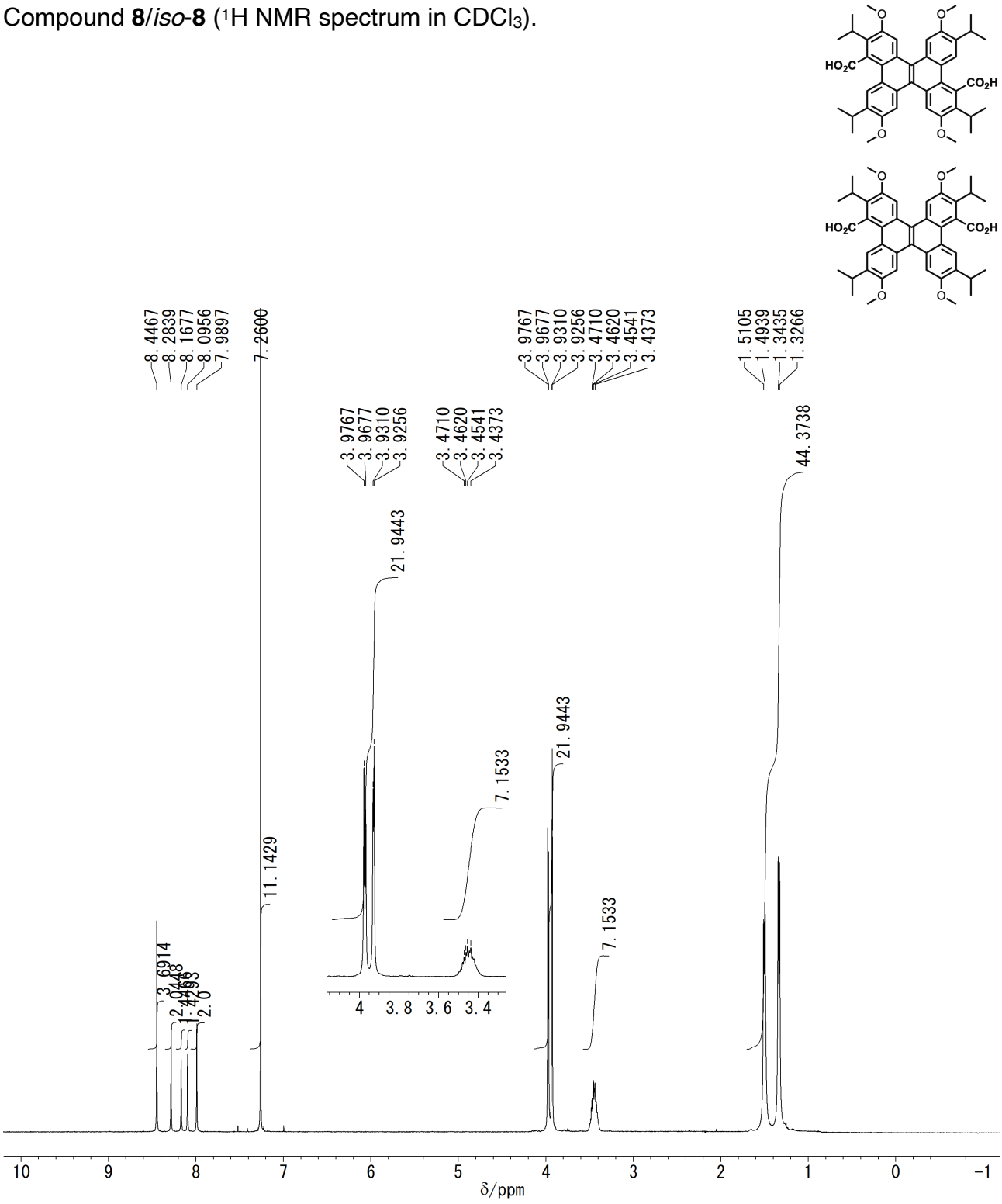
Compound **6** (^{13}C NMR spectrum in $CDCl_3$).



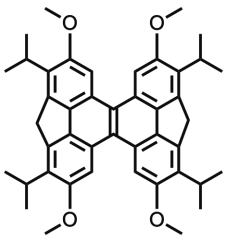
Compound **7**/*iso*-**7** (^{1}H NMR spectrum in $CDCl_3$).

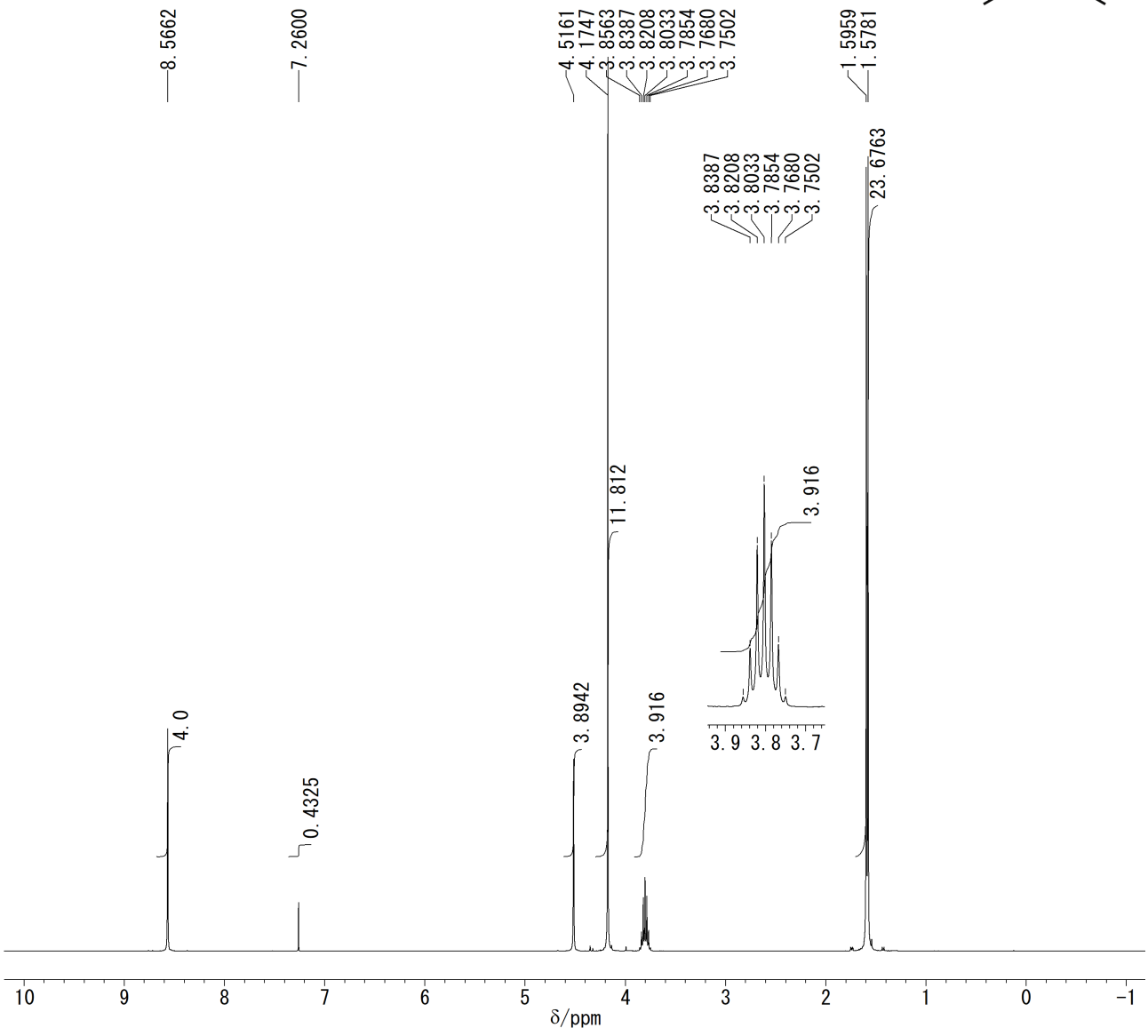


Compound **8**/*iso*-**8** (^{1}H NMR spectrum in $CDCl_3$).

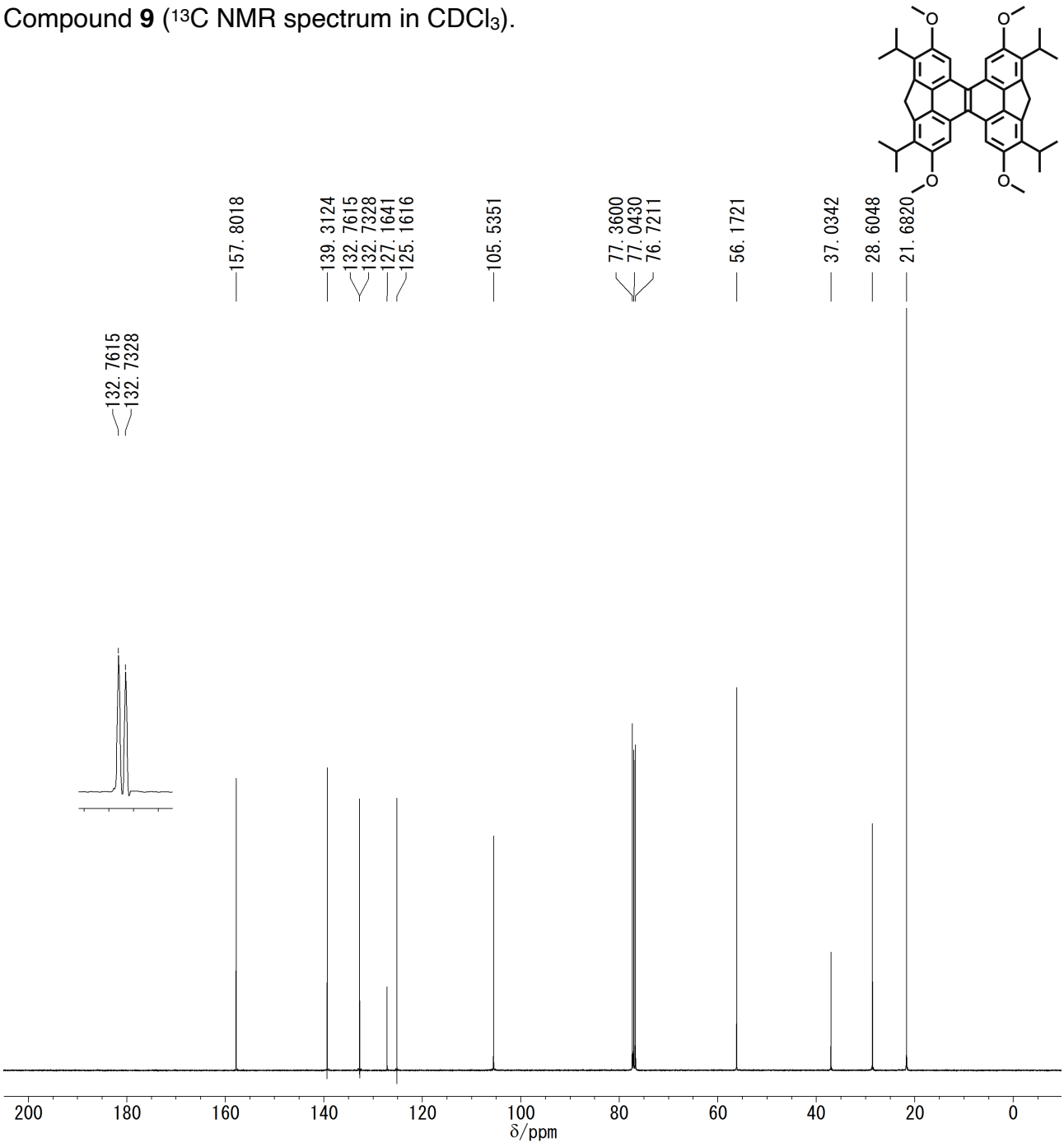


Compound **9** (^{1}H NMR spectrum in $CDCl_3$).

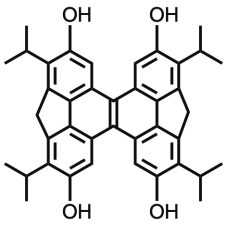


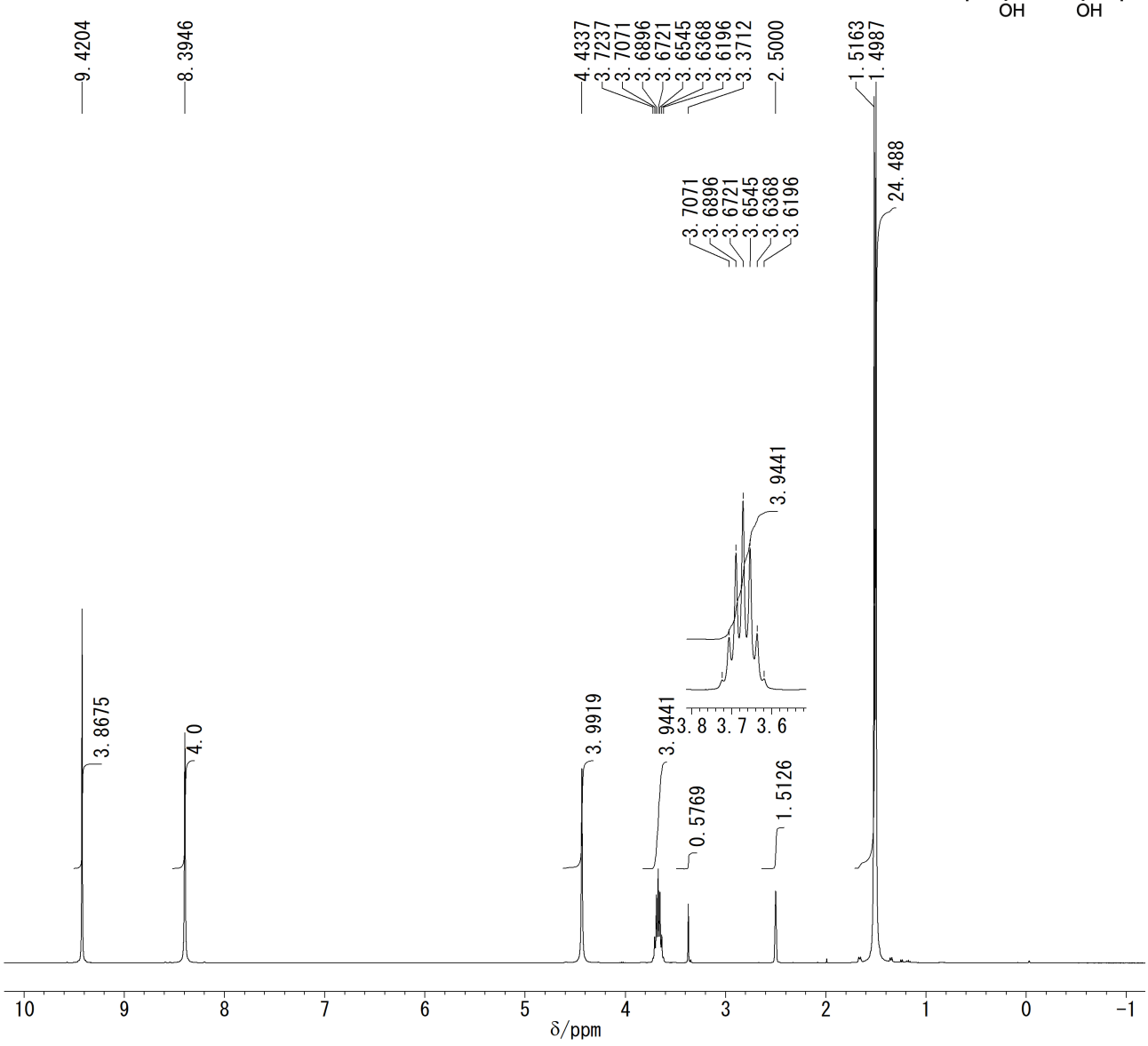


Compound **9** (^{13}C NMR spectrum in $CDCl_3$).

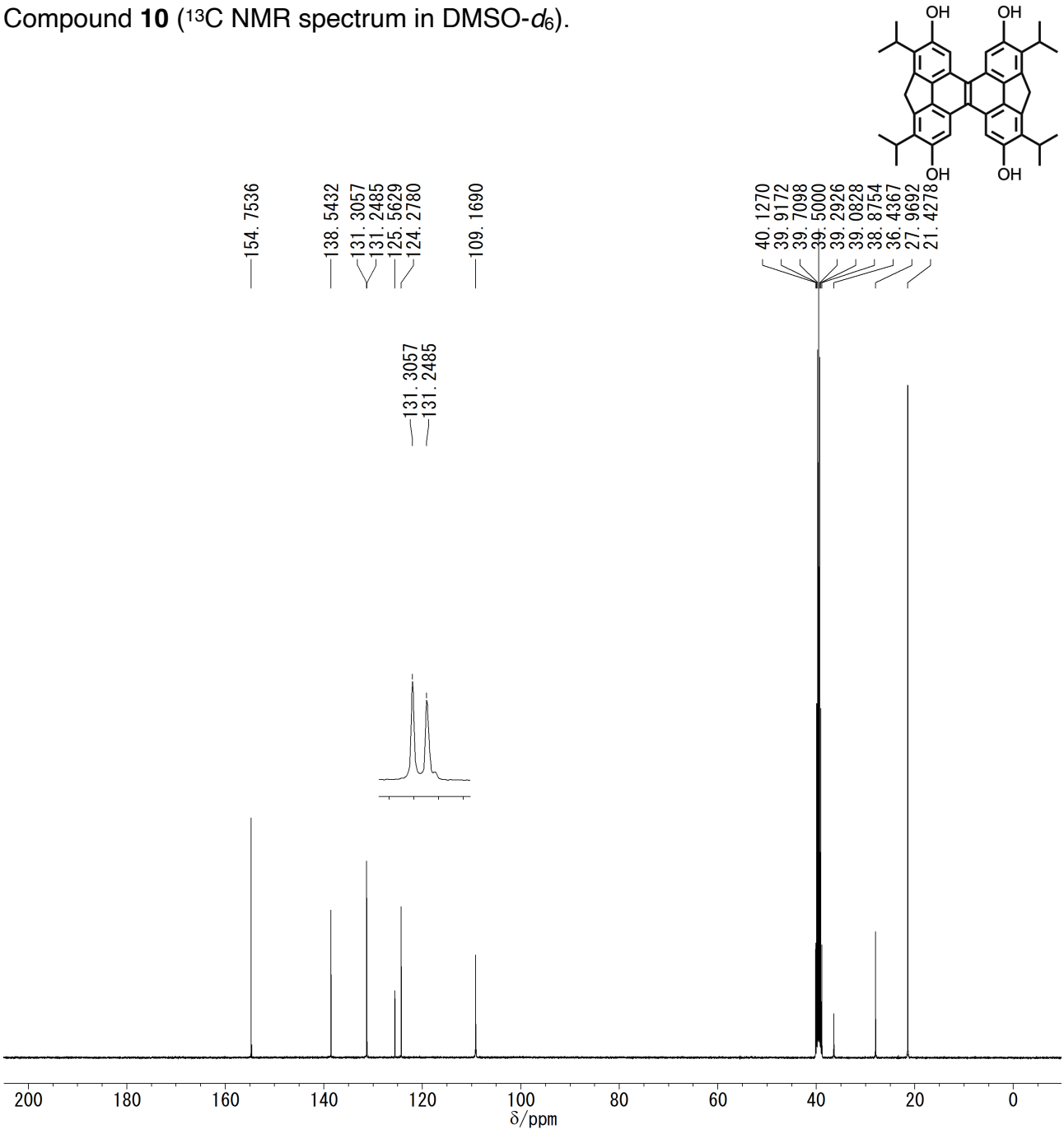


Compound **10** (^{1}H NMR spectrum in DMSO-d_6).

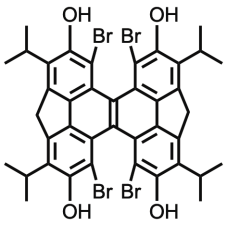


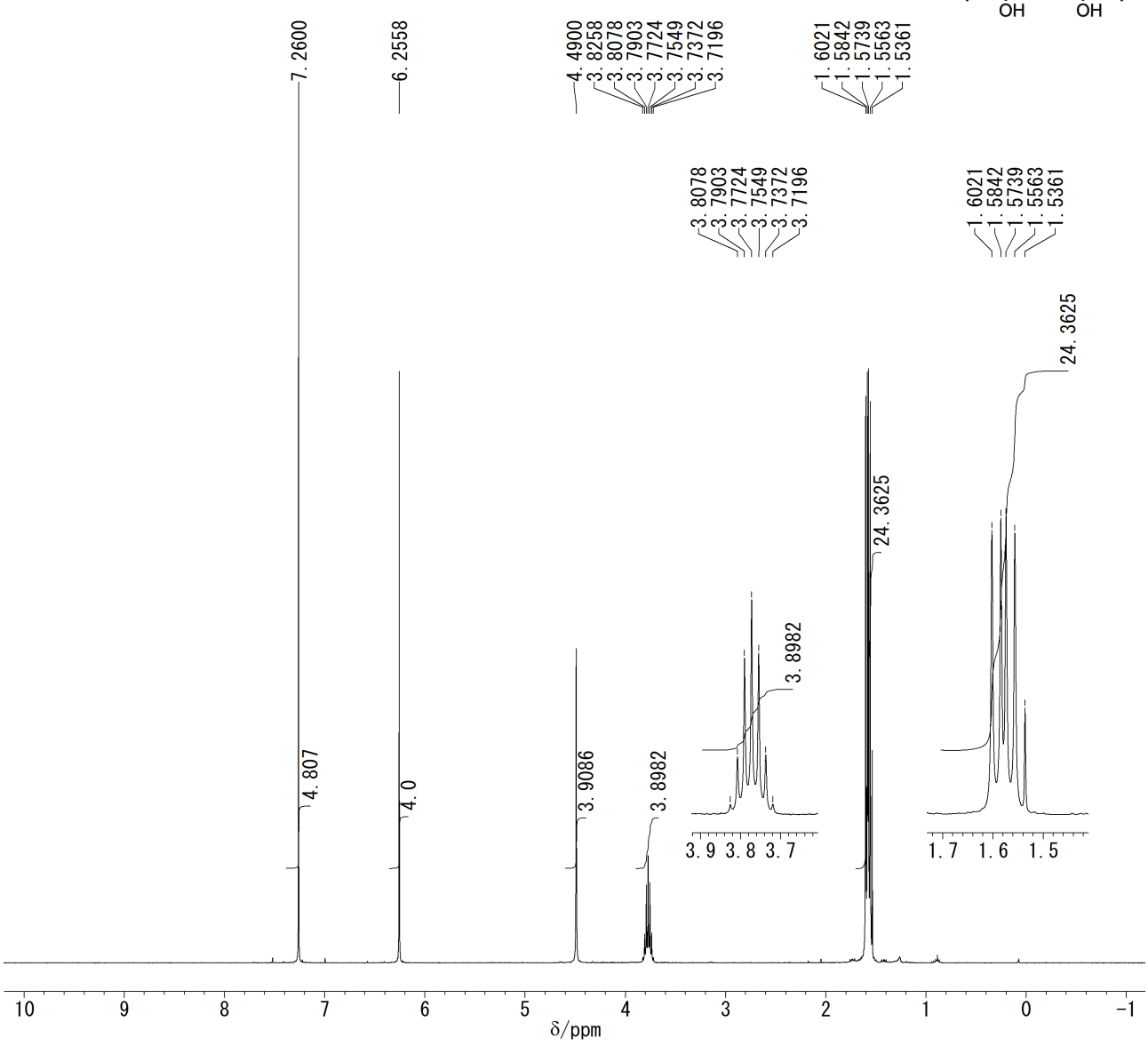


Compound **10** (^{13}C NMR spectrum in DMSO-d_6).

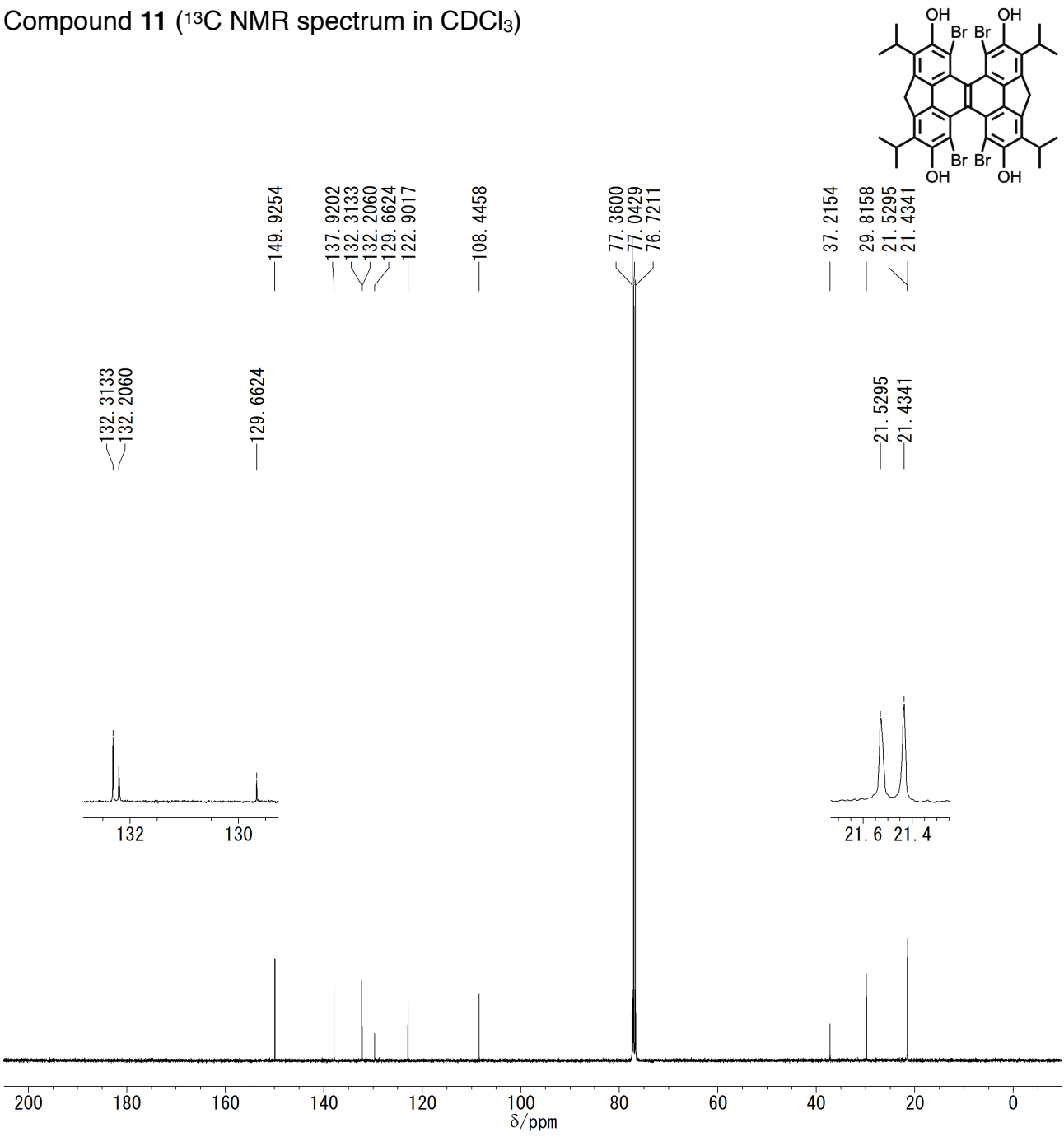


Compound **11** (^{1}H NMR spectrum in $CDCl_3$).

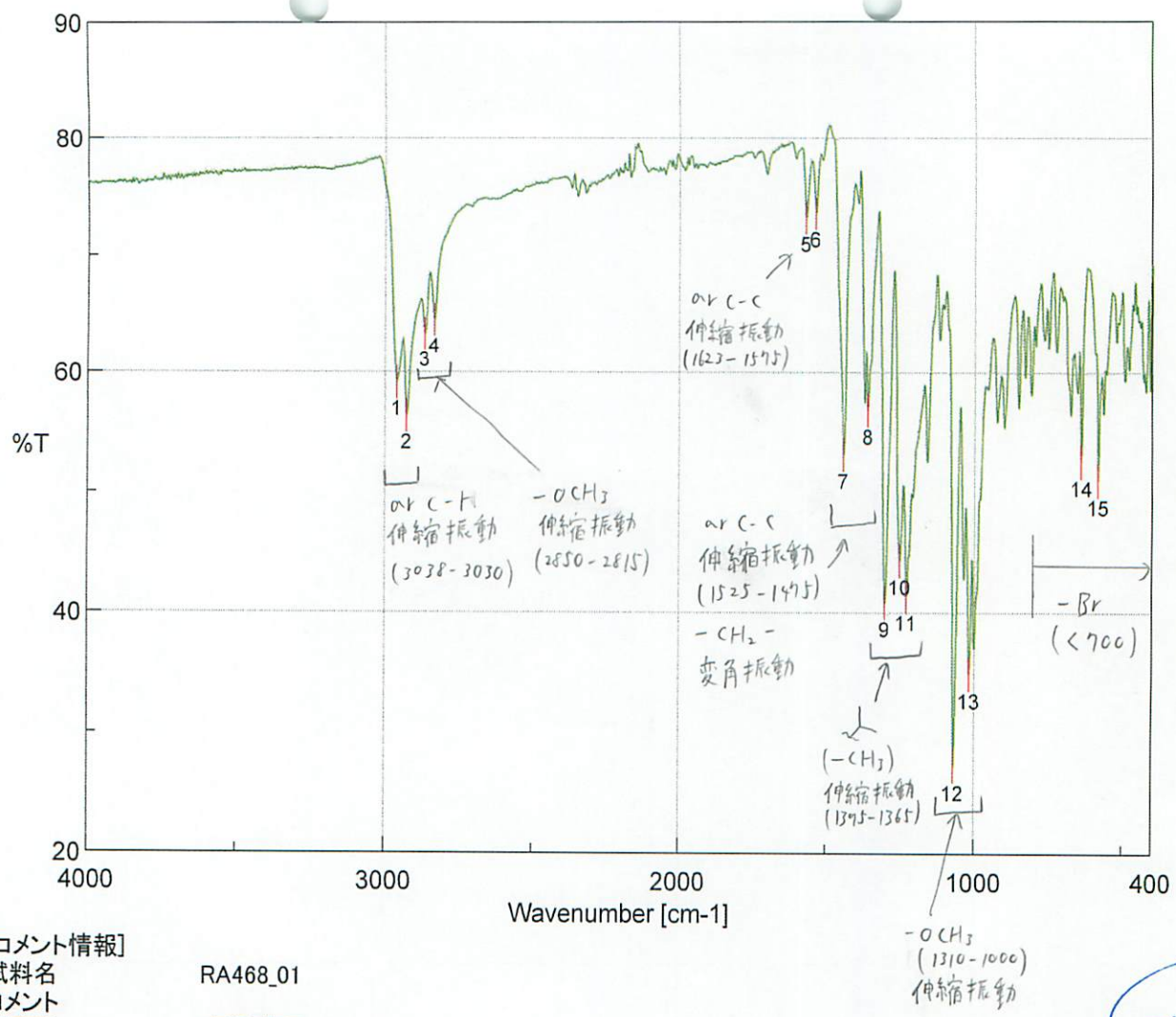




Compound **11** (^{13}C NMR spectrum in $CDCl_3$)



9. IR and MS spectra of nona-cycle compound **4**.



[コメント情報]

試料名	RA468_01
コメント	
測定者	赤阪 龍平
所属	
会社	龍谷大学

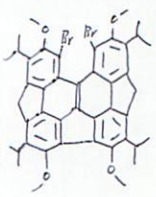
[データ情報]

作成日時	2023/01/31 14:58
データタイプ	等間隔データ
横軸	Wavenumber [cm-1]
縦軸	%T
スタート	399.193 cm-1
エンド	4000.6 cm-1
データ間隔	0.964233 cm-1
データ数	3736

[測定情報]

機種名	FT/IR-4600typeA
シリアル番号	D086761786
付属品名	ATR PRO ONE
付属品シリアルNo.	B086561809
入射角	45 度
測定日時	2023/01/31 14:58
光源	標準光源
検出器	TGS
積算回数	64
分解	4 cm-1
ゼロフィリング	On
アポダイゼーション	Cosine
ゲイン	Auto (8)
アパーチャー	Auto (7.1 mm)
スキャンスピード	Auto (2 mm/sec)
フィルタ	Auto (30000 Hz)

RA468
片架橋ブロモ体



IR (neat): 2963, 2929, 2869, 2836, 1573, 1541, 1443, 1362, 1304, 1231, 1018, 640, 583 cm-1

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度
1	2963.09	59.2742	2	2929.34	56.4893	3	2868.59	63.4379
4	2835.81	64.6188	5	1572.66	73.2695	6	1540.85	73.6658
7	1443.46	53.2262	8	1361.5	56.9452	9	1303.64	40.9308
10	1253.5	44.4911	11	1231.33	41.4999	12	1071.26	27.3958
13	1018.23	34.9814	14	640.251	52.6654	15	583.361	51.0841

RA468

==== Shimadzu LCMSsolution 分析レポート ====

サンプルID :
データファイル : RA468@450oC_002.lcd

分析日時 : 2023/02/17 10:52:39

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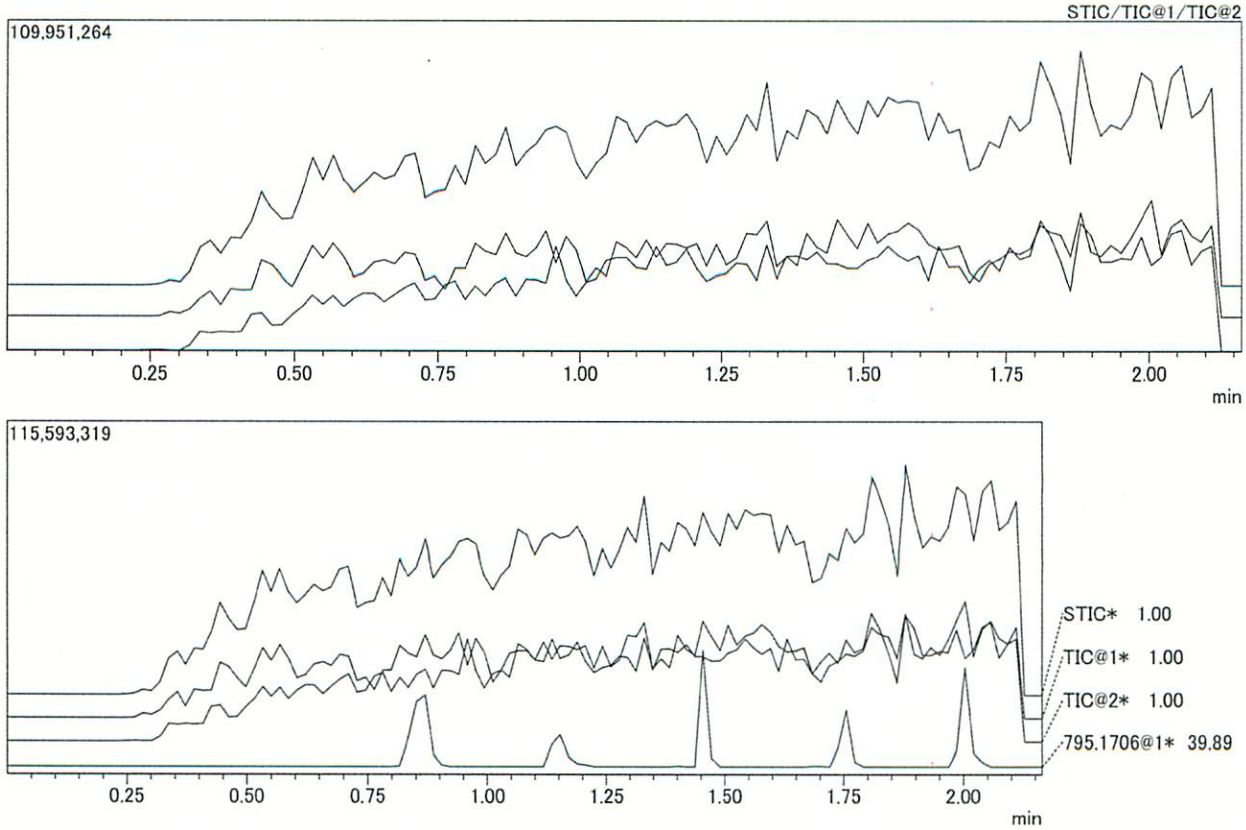

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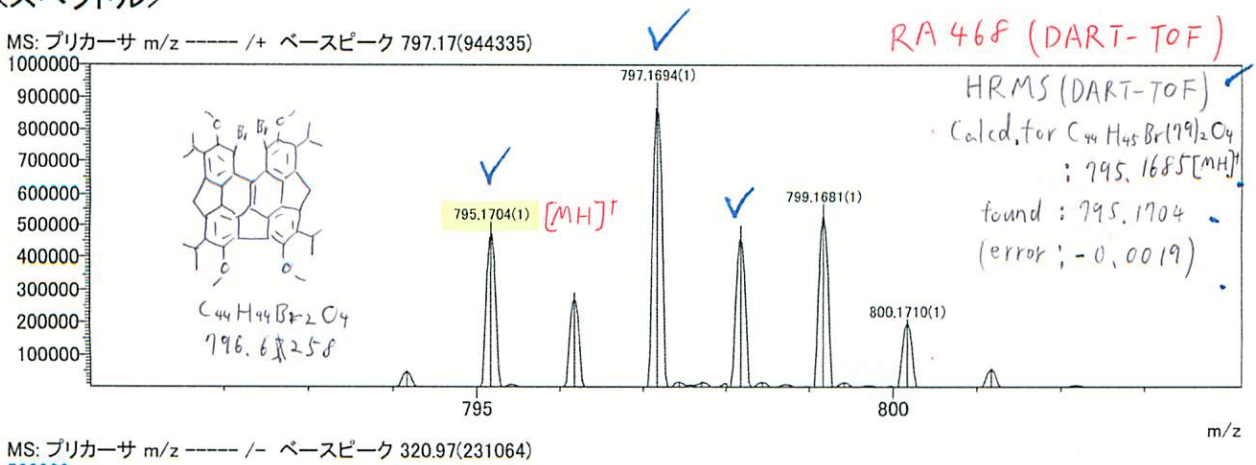
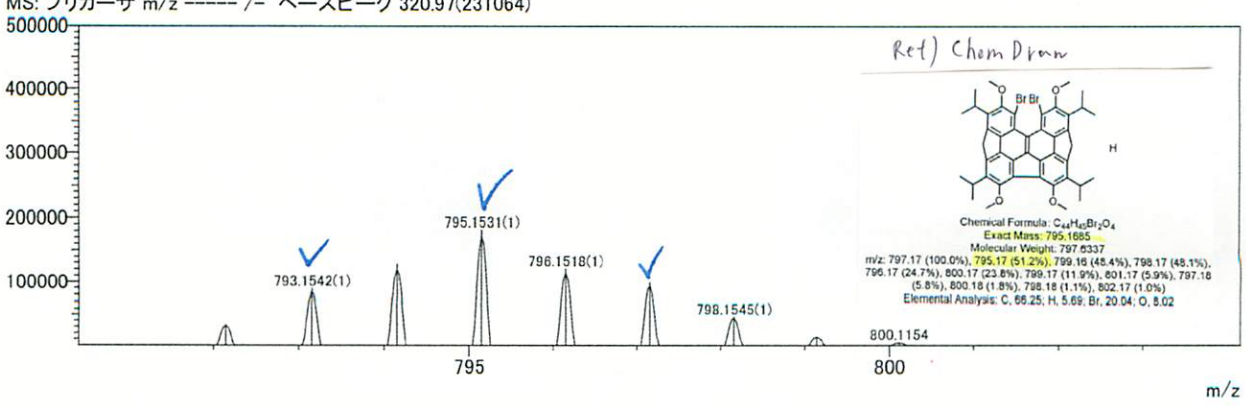
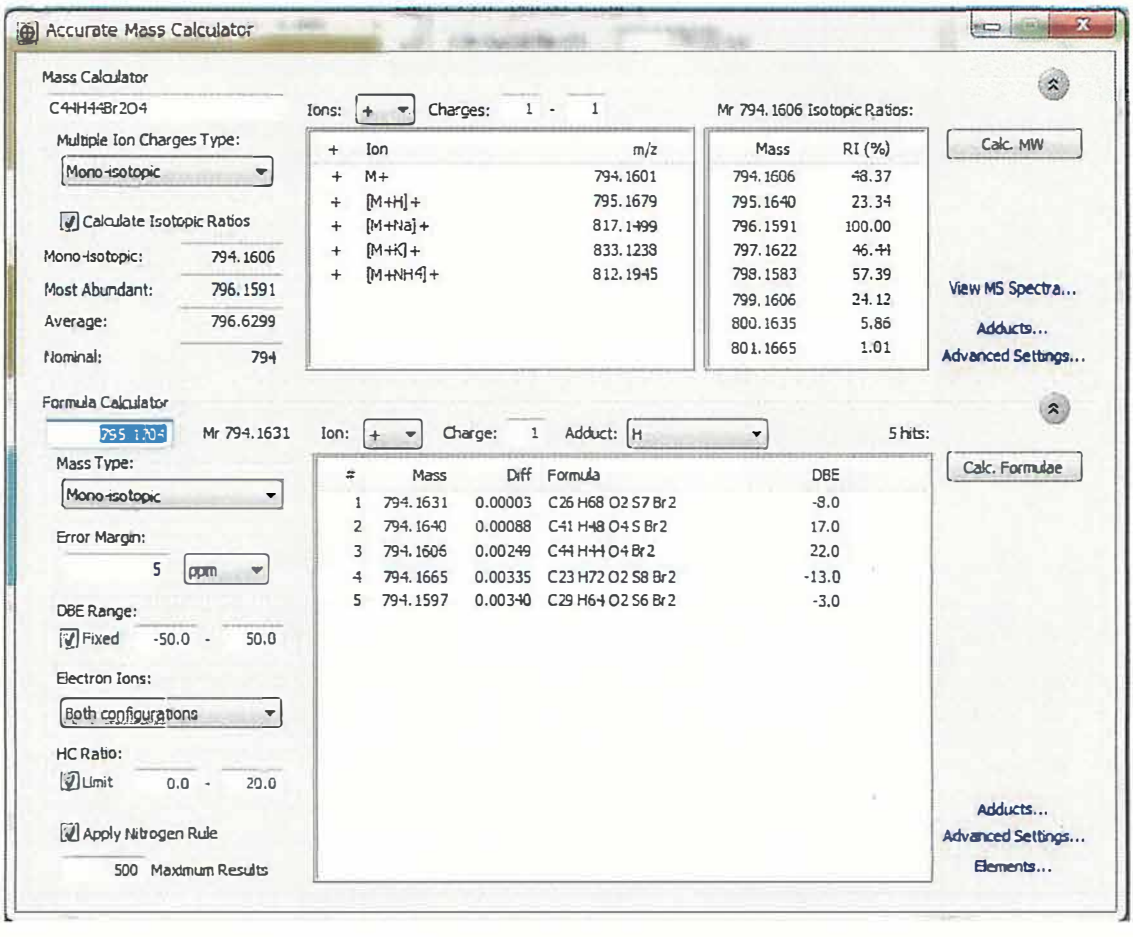




RA468

RA468


Accurate Mass Calculator
Mass Calculator
C44H44Br2O4
Multiple Ion Charges Type:
Mono-isotopic
Calculate Isotopic Ratios
Mono-isotopic: 794.1606
Most Abundant: 796.1591
Average: 796.6299
Nominal: 794
Ions: + Charges: 1 - 1
+ Ion m/z
+ M+ 794.1601
+ [M+H]+ 795.1679
+ [M+Na]+ 817.1499
+ [M+K]+ 833.1238
+ [M+NH4]+ 812.1945
Mr 794.1606 Isotopic Ratios:
Mass RI (%)
794.1606 48.37
795.1640 23.34
796.1591 100.00
797.1622 46.41
798.1583 57.39
799.1606 24.12
800.1635 5.86
801.1665 1.01
Calc. MW
View MS Spectra...
Adducts...
Advanced Settings...
Formula Calculator
795.1704
Mr 794.1631
Ion: + Charge: 1 Adduct: H
5 hits:
Mass Type:
Mono-isotopic
Error Margin:
5 ppm
DBE Range:
Fixed -50.0 - 50.0
Electron Ions:
Both configurations
HC Ratio:
Limit 0.0 - 20.0
Apply Nitrogen Rule
500 Maximum Results
Mass Diff Formula DBE
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2 794.1640 0.00088 C41 H48 O4 S Br2 17.0
3 794.1606 0.00249 C44 H44 O4 Br2 22.0
4 794.1665 0.00335 C23 H72 O2 S8 Br2 -13.0
5 794.1597 0.00340 C29 H64 O2 S6 Br2 -3.0
Calc. Formulae
Adducts...
Advanced Settings...
Elements...