

The first synthesis and X-ray crystallographic analysis of an oxygen-bridged planarized triphenylborane

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1. Experimental Section

General: ^1H , ^{13}C and ^{11}B NMR were recorded with a Bruker Biospin AVANCE III 400 spectrometer at 400, 100 and 128 MHz, respectively. ^1H NMR reported in ppm (δ) were referenced to the chemical shifts of tetramethylsilane at 0.00 ppm, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad). ^{13}C NMR reported in ppm (δ) were referenced to the chemical shifts of solvent signals for CDCl_3 at 77.16 ppm, CD_2Cl_2 at 53.1 ppm, and $\text{THF-}d_8$ at 25.2 ppm. ^{11}B NMR reported in ppm (δ) were referenced to the chemical shifts of $\text{BF}_3\cdot\text{OEt}$ at 0.00 ppm as an external standard. IR spectra were measured on a JASCO FT/IR-350 Fourier-transform infrared spectrometer. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-700 spectrometer operated in a FAB or EI mode at the Department of Instrumental Analysis of the Technical Division, School of Engineering, Tohoku University. Melting points were recorded using a Stuart melting point apparatus SMP3. UV-vis absorption measurements in toluene were performed by a Shimadzu UV-2500 spectrophotometer. The photoluminescence spectra in toluene were recorded on a Hitachi High-Tech F-7000 Spectrophotometer. The solution for UV-vis and photoluminescence experiments was bubbled with N_2 . The absolute photoluminescence quantum yield was measured using Hamamatsu Photonics Quantaury-QY C11347. The transient photoluminescence decay was recorded using Hamamatsu Photonics Quantaury-Tau C11367 equipped with LED light source ($\lambda = 340\text{ nm}$) as an excitation source.

Reactions: All reactions were carried out under N_2 atmosphere in egg-plant shaped flasks unless noted otherwise. Microwave-assisted reactions were performed with a Biotage Initiator+ Sixty (400 W, 2.45 GHz) using a Biotage 20 mL vial sealed with a crimp cap. Column chromatography was performed using spherical silica gel (63–200 μm , Kanto Chemical). Celite short column was performed using Celite® 545RVS (Nacalai Tesque, Inc.).

Materials: All solvents (including super-dehydrated) using in reactions, UV-vis, and photoluminescence experiments were purchased and used as received. Commercially available reagents were used without purification unless noted otherwise.

X-ray Crystallographic analysis: Single crystal of compound **1** was obtained by crystallizing the synthesized **1** from chloroform as a colorless platelet crystal. All measurements for **1** were made on a Rigaku XtaLAB mini diffractometer with graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71075$)

at -123 ± 1 °C at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Data reduction: Of the 4869 reflections were collected, where 1390 were unique ($R_{\text{int}} = 0.0912$). Data were collected and processed using CrystalClear (Rigaku).^{S1} The linear absorption coefficient, μ , for Mo-K α radiation is 1.046 cm^{-1} . An empirical absorption correction was applied which resulted in transmission factors ranging from 0.766 to 0.995. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement: The structure was solved by direct methods^{S2} and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement^{S3} on F^2 was based on 1390 observed reflections and 102 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0529$$

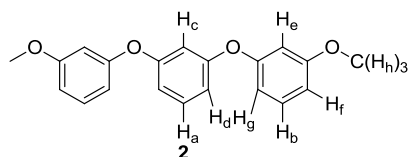
$$wR_2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2} = 0.1337$$

The goodness of fit^{S4} was 0.89. Unit weights were used. Plots of $\Sigma w (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.30 and $-0.26 \text{ e}^-/\text{\AA}^3$, respectively. Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4.^{S5} Anomalous dispersion effects were included in F_{calc} ; ^{S6} the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.^{S7} The values for the mass attenuation coefficients are those of Creagh and Hubbell.^{S8} All calculations were performed using the CrystalStructure^{S9} crystallographic software package except for refinement, which was performed using SHELXL2013.^{S10}

2. Synthesis

1,3-Bis-(3-methoxyphenoxy)benzene (2).

A 100 mL two necked and round bottomed flask equipped with a Teflon coated magnetic stirring bar was charged with resorcinol (1.11 g, 10.0 mmol), 3-iodoanisole (7.07 g, 3.0 equiv, 30.0 mmol), CuCl (994.0 mg, 1.0 equiv, 10.0 mmol), and Cs₂CO₃ (9.77 g, 3.0 equiv, 30.0 mmol), and then evacuated by heating and refilled with N₂. 2,2,6,6-tetramethyl-3,5-heptanedione (415 μ L, 20 mol%, 2.0 mmol) and 30 mL of dry *N*-methyl-2-pyrrolidone (NMP) were added, and then the reaction mixture was stirred at 110 °C for 20 h. After the reaction mixture was diluted with dichloromethane, the resulting solution was passed through a celite short column (dichloromethane). The resulting mixture was washed successively with sat. NH₄Cl aq. and brine, dried over MgSO₄, and evaporated. The remaining NMP was removed in *vacuo* with Kugelrohr at 85 °C for 1 h. The residue was purified by silica gel chromatography using *n*-hexane–dichloromethane (2:1) as an eluent to give the product 2 (3.10 g, 95%) as colorless oil.

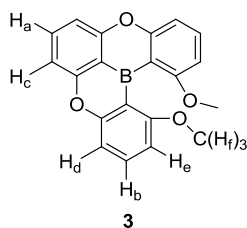


Colorless oil; IR(neat, cm⁻¹): 3002, 2958, 1587, 1482, 1451, 1267, 1194, 1168, 1145, 1042, 980, 847, 770; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 3.77 (s, 6H, CH₃: H_h), 6.58–6.62 (m, 4H, ArH: H_e, H_f), 6.66 (ddd, *J* = 8.3, 2.4, 0.8 Hz, 2H, ArH: H_g), 6.70 (t, *J* = 2.3 Hz, 1H, ArH: H_c), 6.74 (dd, *J* = 8.1, 2.3 Hz, 2H, ArH: H_d), 7.22 (t, *J* = 8.3 Hz, 2H, ArH: H_b), 7.25 (t, *J* = 8.1 Hz, 1H, ArH: H_a); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 161.1, 158.5, 158.1, 130.5, 130.3, 113.7, 111.3, 109.8, 109.4, 105.2, 55.5; HRMS (FAB) *m/z* [M+H]⁺: calcd for C₂₀H₁₉O₄, 323.1283; found, 323.1284.

1,13-Dimethoxy-5,9-dioxa-13b-boranaphtho[3,2,1-*de*]anthracene (3).

A 500 mL two-necked flask equipped with a dropping funnel, a dimroth condenser, and a Teflon coated magnetic stirring bar was charged with **1** (6.94 g, 21.5 mmol), and then evacuated by heating and refilled with N₂. 190 mL of dry tetrahydrofuran and 5.45 mL (1.7 equiv, 36.6 mmol) of *N,N,N',N'*-tetramethylethylenediamine were added, and then *n*-butyllithium (44.7 mL, 3.2 equiv, 68.9 mmol, 1.54 M in *n*-hexane) was added dropwise to the stirred solution at 0 °C for 0.4 h. The reaction mixture was stirred for 0.5 h at 0 °C and gradually warmed to room temperature. After stirring at room temperature for 4 h, dry benzene (100 mL) solution of BF₃·OEt₂ (3.25 mL, 1.2 equiv, 25.8

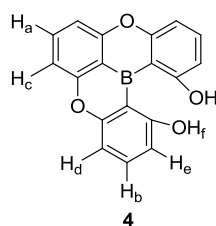
mmol) was added to the stirred solution at $-40\text{ }^{\circ}\text{C}$ for 0.4 h. The reaction mixture was gradually warmed to room temperature and stirred for 2 h at room temperature, and then refluxed ($87\text{ }^{\circ}\text{C}$) for 21 h. After the solvents were removed in *vacuo*, the mixture was dissolved in dichloromethane. The resulting mixture was washed with 1N HCl aq. and brine, dried over MgSO_4 , and evaporated. The residue was purified by silica gel chromatography using hexane–dichloromethane (4:3) as an eluent to give the product **3** (1.55 g, 22%) as colorless crystals.



Colorless crystal; Mp $226.1\text{--}226.5\text{ }^{\circ}\text{C}$; IR(KBr, cm^{-1}): 3064, 2959, 1619, 1600, 1564, 1468, 1434, 1316, 1290, 1252, 1214, 1090, 1075, 1023, 794, 751; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 3.85 (s, 6H, CH_3 : H_f), 6.71 (d, $J = 8.2\text{ Hz}$, 2H, ArH: H_e), 7.10 (dd, $J = 8.2, 0.8\text{ Hz}$, 2H, ArH: H_d), 7.16 (d, $J = 8.0\text{ Hz}$, 2H, ArH: H_c), 7.57 (t, $J = 8.2\text{ Hz}$, 2H, ArH: H_b), 7.66 (t, $J = 8.0\text{ Hz}$, 1H, ArH: H_a); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 164.4, 161.4, 156.3, 133.8, 133.6, 110.2, 108.4, 103.4, 55.7 (due to the interaction of the boron-bonded carbon atoms with the quadrupole moment of the boron nucleus, two signals of the carbon atoms bonding to the boron were not observed in ^{13}C NMR); ^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 39.5; HRMS (EI) m/z $[\text{M}]^+$: calcd for $\text{C}_{20}\text{H}_{16}\text{BO}_4$, 330.1063; found, 330.1062.

1,13-Dihydroxy-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (**4**).

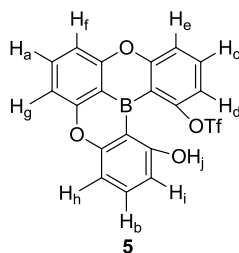
A 300 mL two necked and round bottomed flask equipped with a Teflon coated magnetic stirring bar was charged with **2** (1.08 g, 3.27 mmol), and then evacuated by heating and refilled with N_2 . 95 mL of dry dichloromethane was added, and then BBr_3 (6.9 mL, 2.1 equiv, 6.9 mmol, 1.0 M in dichloromethane) was added dropwise to the stirred solution using syringe driver at $-78\text{ }^{\circ}\text{C}$ for 0.4 h. The reaction mixture was stirred for 0.5 h at $-78\text{ }^{\circ}\text{C}$ and gradually warmed to room temperature overnight, and then stirred at room temperature for 2 h. After the volatile compound was removed in *vacuo*, the mixture was dissolved in ethyl acetate. The resulting mixture was washed with successively with sat. NH_4Cl aq. and brine, dried over MgSO_4 , and evaporated. The residue was purified by recrystallization from dichloromethane–*n*-hexane at $0\text{ }^{\circ}\text{C}$. After filtration and washing with *n*-pentane, the product **4** (929.8 mg, 94%) was obtained as pale yellow crystalline solids.



White crystalline solid; Mp 220.5–220.9 °C; IR(KBr, cm^{-1}): 3467, 3317, 3055, 1610, 1466, 1341, 1304, 1274, 1184, 1156, 1087, 1068, 1030, 1010, 997, 791, 737; ^1H NMR (400 MHz, $\text{THF-}d_8$): δ (ppm) 6.80 (d, $J = 8.0$ Hz, 2H, ArH: H_e), 7.07 (d, $J = 8.0$ Hz, 2H, ArH: H_d), 7.14 (d, $J = 8.3$ Hz, 2H, ArH: H_c), 7.51 (t, $J = 8.0$ Hz, 2H, ArH: H_b), 7.70 (t, $J = 8.3$ Hz, 1H, ArH: H_a), 10.3 (brs, 2H, ArOH: H_f); ^{13}C NMR (100 MHz, $\text{THF-}d_8$): δ (ppm) 162.3, 161.9, 157.3, 134.8, 134.7, 111.6, 110.8, 108.8 (due to the interaction of the boron-bonded carbon atoms with the quadrupole moment of the boron nucleus, two signals of the carbon atoms bonding to the boron were not observed in ^{13}C NMR); ^{11}B NMR (128 MHz, $\text{THF-}d_8$): δ (ppm) 39.4; HRMS (EI) m/z $[\text{M}]^+$: calcd for $\text{C}_{18}\text{H}_{12}\text{BO}_4$, 302.0750; found, 303.0748.

1-Trifluoromethansulfonyloxy-13b-hidroxy-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (5).

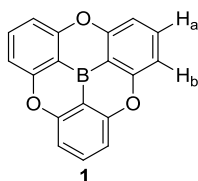
A 300 mL two necked and round bottomed flask equipped with a Teflon coated magnetic stirring bar was charged with **4** (689.3 mg, 2.28 mmol), and then evacuated by heating and refilled with N_2 . *N,N*-Diisopropylethylamine (470 mL, 1.2 equiv, 2.76 mmol) and 114 mL of dry dichloromethane were added, and then dry dichloromethane (10 mL) solution of trifluoromethanesulfonic anhydride (374 μL , 1.0 equiv, 2.28 mmol) was added to the stirred solution using syringe driver at -78 °C for 0.75 h. The reaction mixture was stirred for 0.5 h at -78 °C and gradually warmed to room temperature overnight, and then stirred at room temperature for 3 h. The resulting mixture was washed successively with sat. NH_4Cl aq. and brine, dried over MgSO_4 , and evaporated. The residue was purified by recrystallization from dichloromethane–*n*-hexane at 0 °C. After filtration and washing with *n*-pentane, the product **5** (932.2 mg, 94%) was obtained as colorless crystals.



Colorless crystal; Mp 210.6–211.1 °C; IR(KBr, cm^{-1}): 3306, 3069, 1608, 1588, 1469, 1304, 1243, 1206, 1139, 1066, 1032, 1004, 972, 914, 863, 798, 754; ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 5.74 (brs, 1H, OH: H_j), 6.72 (d, $J = 8.3$ Hz, 1H, ArH: H_i), 7.10 (d, $J = 8.3$ Hz, 1H, ArH: H_h), 7.21 (d, $J = 8.5$ Hz, 1H, ArH: H_e), 7.23 (d, $J = 8.6$ Hz, 2H, ArH: H_g , H_f), 7.53 (t, $J = 8.3$ Hz, 1H, ArH: H_b), 7.57 (d, $J = 8.5$ Hz, 1H, ArH: H_d), 7.69 (t, $J = 8.5$ Hz, 1H, ArH: H_c), 7.73 (t, $J = 8.6$ Hz, 1H, ArH: H_a); ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 160.5, 160.3, 159.7, 155.9, 155.6, 152.0, 114.0, 133.7, 132.4, 118.2 (q, $J = 320$ Hz), 117.9, 115.2, 109.5, 109.0, 108.8, 108.2 (due to the interaction of the boron-bonded carbon atoms with the quadrupole moment of the boron nucleus, three signals of the carbon atoms bonding to the boron were not observed in ^{13}C NMR); ^{11}B NMR (128 MHz, CD_2Cl_2): δ (ppm) 39.1; HRMS (FAB) m/z $[\text{M}]^+$: calcd for $\text{C}_{19}\text{H}_{10}\text{BF}_3\text{O}_6\text{S}$, 434.0243; found, 434.0246.

4,8,12-Trioxa-12c-boradibenzo[cd,mn]pyrene (1).

A 20 mL vial was charged with **5** (520.8 mg, 1.20 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (540 μL , 3.0 equiv, 3.60 mmol), and dry dimethylformamide (DMF, 12.0 mL). The vial sealed with a crimped cap, and then the reaction mixture was heated in a microwave reactor at 240 °C for 4 h. After cooling to room temperature, the DMF was removed in *vacuo* with Kugelrohr at 75 °C for 0.5 h, and then dissolved in 20 mL of dry tetrahydrofuran (THF). The resulting mixture was poured into 2 M HCl aq. (130 mL) and then stirred vigorously at room temperature for 2 h. The precipitate was collected by filtration and washed with water and *n*-hexane. The crude product was purified by recrystallization from dichloromethane–*n*-hexane at 0 °C. After filtration and washing with *n*-pentane, the product **5** (295.2 mg, 87%) was obtained as white crystalline solids.



White crystalline solids; Mp 308.3–308.8 °C (slowly sublimation from 200 °C); IR(KBr, cm^{-1}): 3063, 1638, 1611, 1513, 1466, 1376, 1310, 1286, 1228, 1194, 1144, 1040, 974, 930, 792, 745; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.22 (d, $J = 8.0$ Hz, 6H, ArH: H_b), 7.74 (t, $J = 8.0$ Hz, 3H, ArH: H_a); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.3, 135.9, 110.5 (due to the interaction of the boron-bonded carbon atoms with the quadrupole moment of the boron nucleus, one signal of the carbon atom bonding to the boron was not observed in ^{13}C NMR); ^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 34.2; HRMS (EI) m/z $[\text{M}]^+$: calcd for $\text{C}_{18}\text{H}_9\text{BO}_3$, 284.0645; found, 284.0644.

3. X-ray crystallographic analysis of 1

Table S1. Crystal data and structure refinement for compound 1.

Empirical formula	C ₁₈ H ₉ BO ₃
Formula weight	284.08
Temperature	150 K
Wavelength (Mo K α)	0.71075 Å
Crystal system	Monoclinic
Space group	C2/c (#15)
Unit cell dimensions	$a = 17.055(9)$ Å $\alpha = 90^\circ$ $b = 10.409(6)$ Å $\beta = 110.071(10)^\circ$ $c = 7.301(4)$ Å $\gamma = 90^\circ$
Volume	1209.4(12) Å ³
Z	4
Density (calculated)	1.560 g·cm ⁻³
μ (Mo K α)	0.1046 mm ⁻¹
$F(000)$	584.0
Crystal dimensions	0.240×0.150×0.050 mm ³
Theta range for data collection	3.415 to 27.468°
Reflections collected	4869
Independent reflections	1390 [$R(\text{int}) = 0.0912$]
Refinement method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	1390 / 0 / 102
Goodness-of fit on F^2	0.890
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0529$, $wR_2 = 0.1170$
R indices (all data)	$R_1 = 0.1062$, $wR_2 = 0.1337$
Largest diff. peak and hole	0.30 and -0.26 e ⁻ ·Å ⁻³

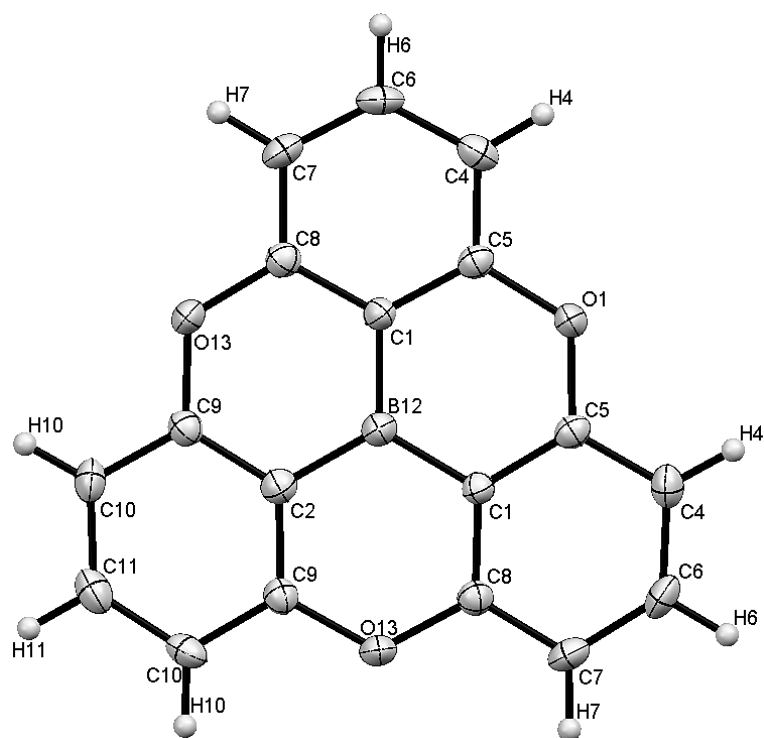


Figure S1. Thermal ellipsoid drawing of compound **1** with thermal ellipsoids at 50% probability.

Table S1. Selected bond lengths and angles of compound **1**.

Length / Å		Angle / °	
C1–B12	1.459(2)	C1–B12–C1 ¹	120.6(2)
C2–B12	1.461(4)	C1 ¹ –B12–C2	119.70(12)
O1–C5	1.4098(17)	C1–B12–C2	119.70(12)
O13–C8	1.400(2)		
O13–C9	1.4081(19)		
O1–C5 ¹	1.4098(17)		

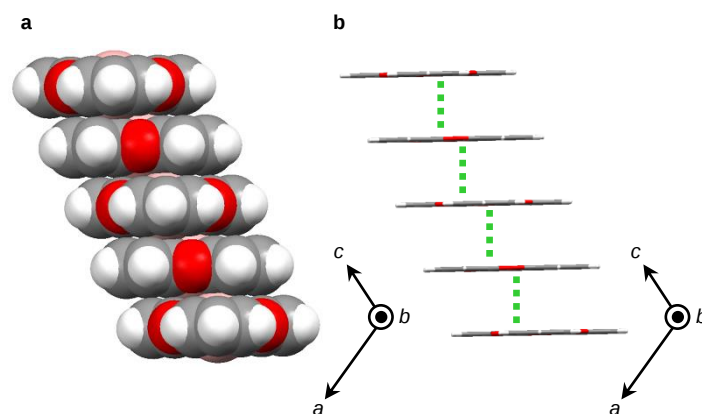


Figure S2. π - π Stacking rod structure of compound **1** depicted in (a) spacefill and (b) capped sticks models. Green dotted line indicates a π -interaction (interplanar distance = 3.379 Å).

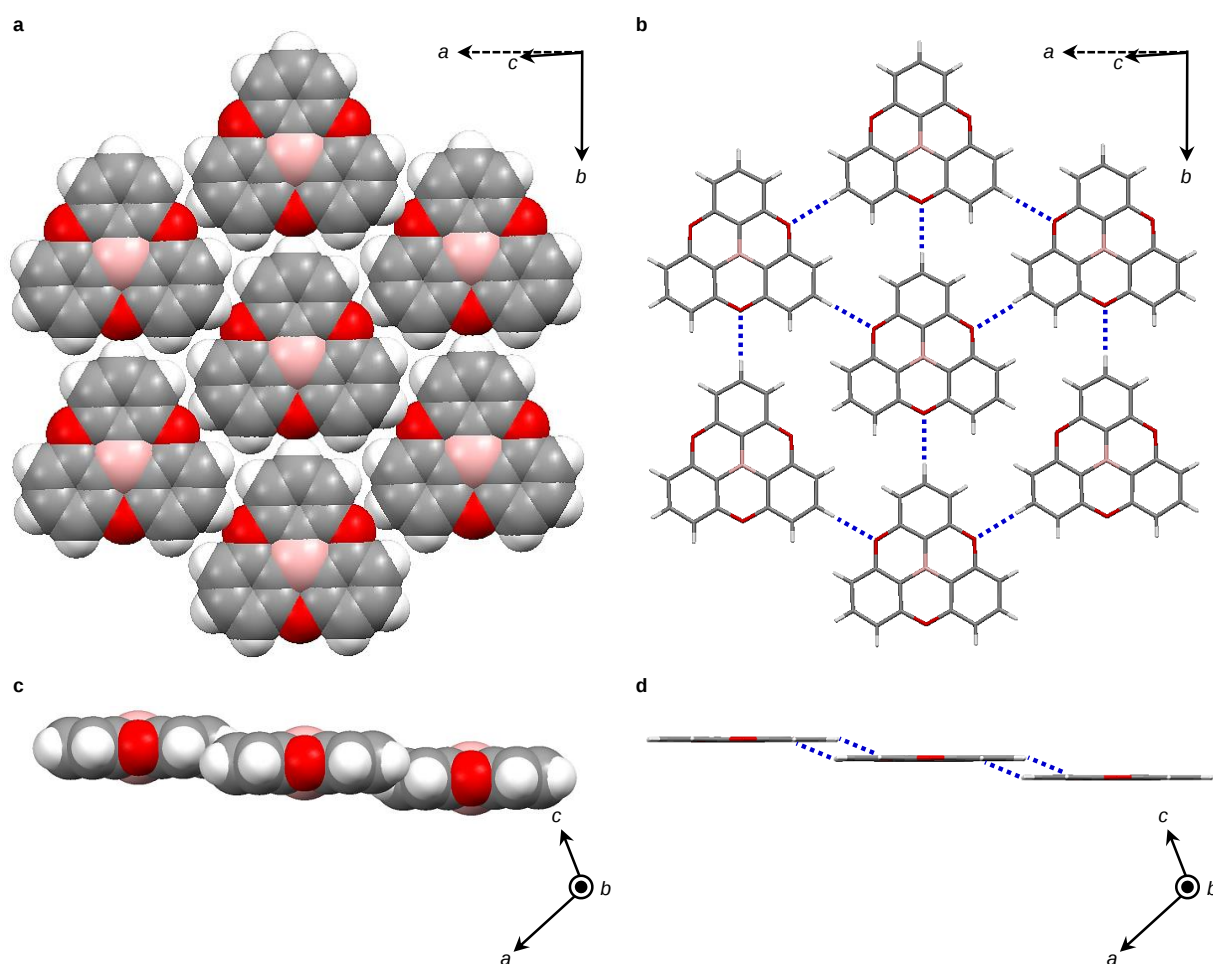


Figure S3. The motif of $\text{CH}\cdots\text{O}$ intermolecular hydrogen bonds of compound **1** along the direction of π -planar plane of (a, b) top and (c, d) side views depicted in spacefill and capped sticks models. Green dotted line indicates a $\text{CH}\cdots\text{O}$ intermolecular hydrogen bond (intermolecular distance = 2.519–2.620 Å, $\text{C-H}\cdots\text{O}$ angles = 159.6, 180.0°).

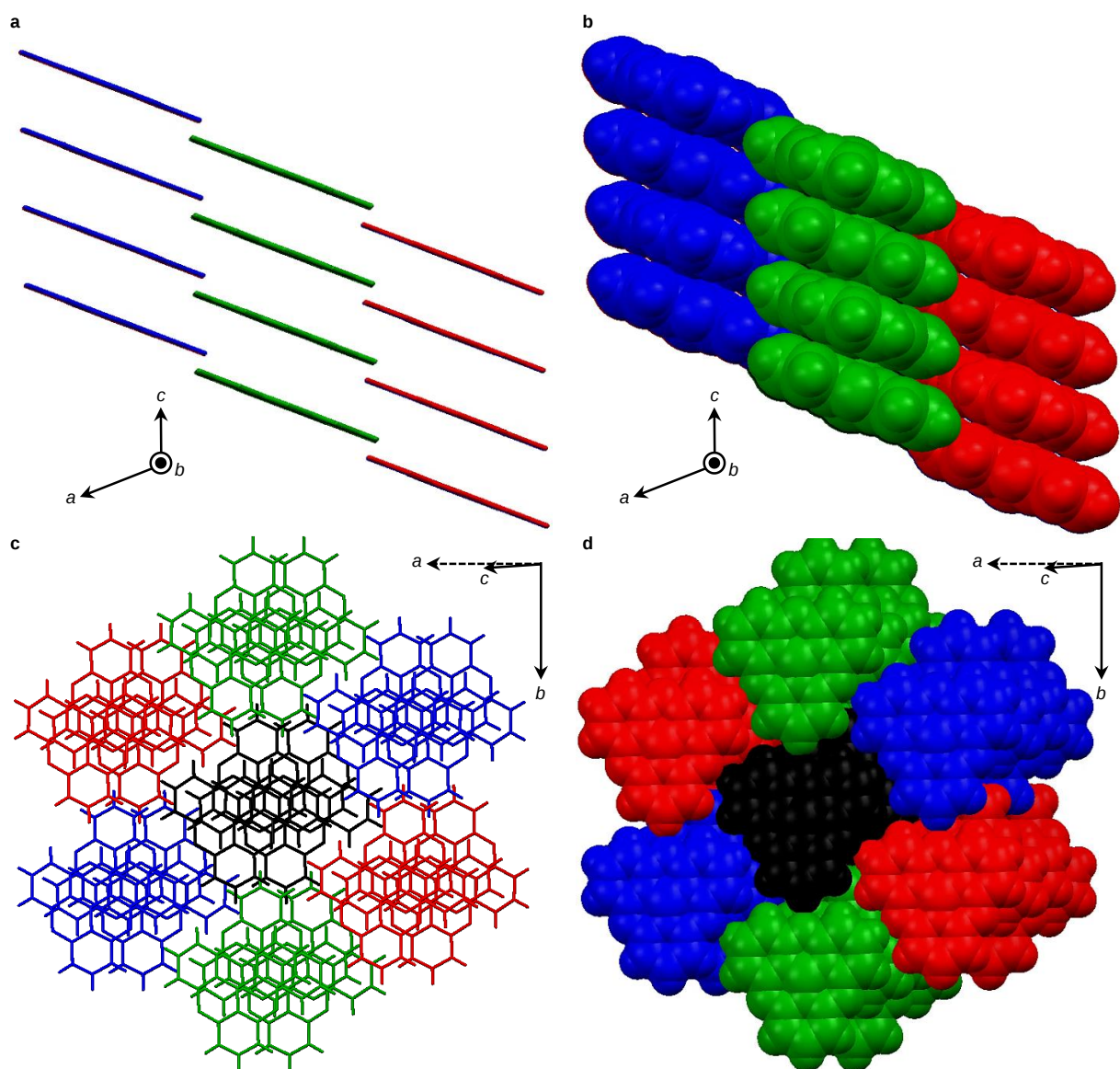


Figure S4. Crystal packing structure of compound **1** of (a, b) side and (c, d) top views depicted in spacefill and capped sticks models. Each color shows a rod unit arranged by a π -interaction along the c -axis.

4. Photoluminescence spectra and transient photoluminescence decay

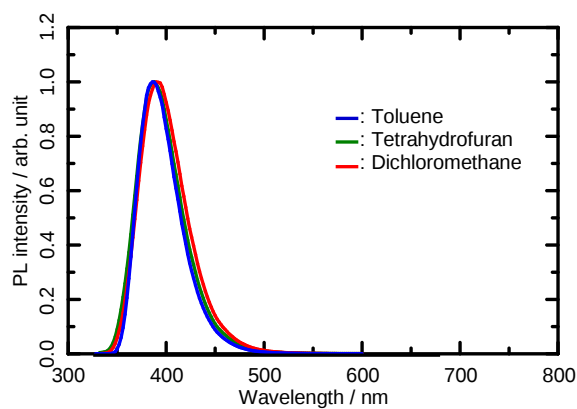


Figure S5. Fluorescence spectra of compound **1** in various solvents (1×10^{-5} M, ex. 320 nm) at 296 K. Blue, green, and red lines represent fluorescence spectra of **1** in toluene, tetrahydrofuran, and dichloromethane, respectively.

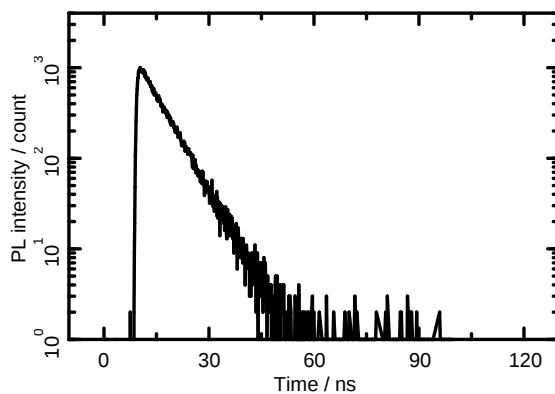


Figure S6. Transient photoluminescence decay of toluene solution of compound **1** [1×10^{-5} M, LED light source ($\lambda_{\text{ex.}} = 340$ nm)] at 296 K.

5. Theoretical calculation

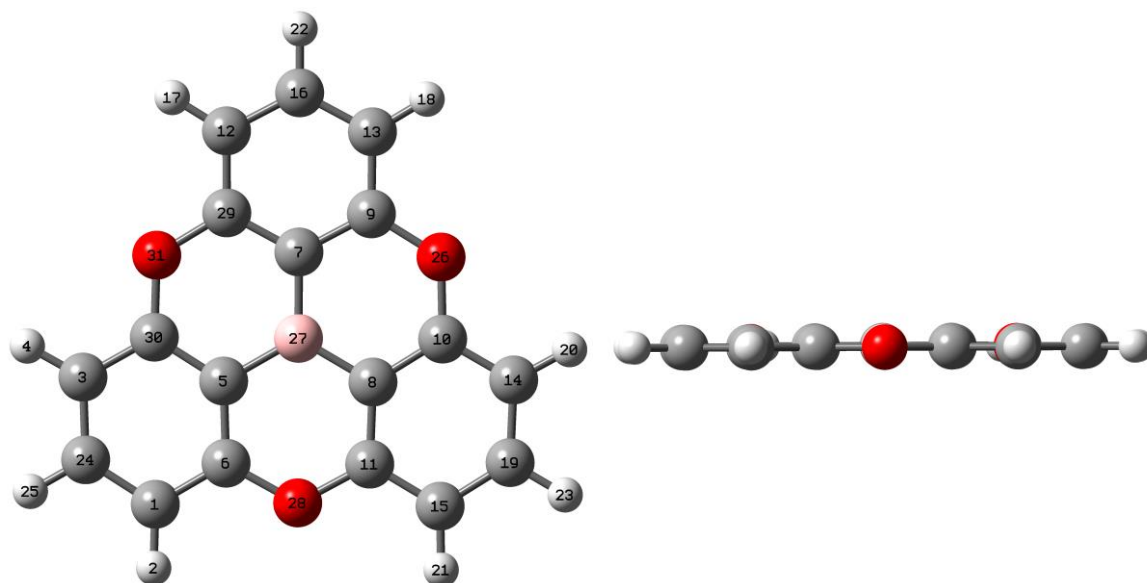
Theoretical calculations to determine the HOMO and LUMO of compound **1** were carried out using the Gaussian 09 package^{S11} at the B3LYP/6-311G(d,p) level (in toluene, PCM model). After the optimization, the TD-DFT calculations were also conducted at the B3LYP/6-311G(d,p) level (in toluene, PCM model). The output views of compound **1** were obtained by the GaussView version 5.0.^{S12}

Table S3. Calculated excitation energy (E , λ) and oscillator strength (f) of compound **1** by DFT and TD-DFT at the B3LYP/6-311G(d,p) level (in toluene, PCM model).

Electron transitions	E / eV	λ / nm	f	Composition	CI ^a
S ₀ →S ₁	3.84	323	0.1124	HOMO→LUMO	0.6941
	3.84	323	0.1129	HOMO-1→LUMO	0.6942
S ₀ →S ₂	4.66	266	0.0049	HOMO-2→LUMO-1	−0.2396
				HOMO-1→LUMO-1	0.4623
				HOMO→LUMO-2	0.4596
	4.66	266	0.0049	HOMO-3→LUMO	−0.2394
				HOMO-1→LUMO-2	−0.4604
				HOMO→LUMO-1	0.4615

^a Coefficient of the wave function for each excitations. The CI coefficients are in absolute values.

Table S4. Optimization structure and selected bond lengths of compound **1** by DFT at the B3LYP/6-311G(d,p) level (in toluene, PCM model).



Length / Å		Angle / °	
C7–B27	1.467	C5–B27–C7	120
C5–B27	1.467	C5–B27–C8	120
C8–B27	1.467	C7–B27–C8	120
C9–O26	1.393		
C10–O26	1.392		
C6–O28	1.392		
C11–O28	1.392		
C29–O31	1.393		
C30–O31	1.392		

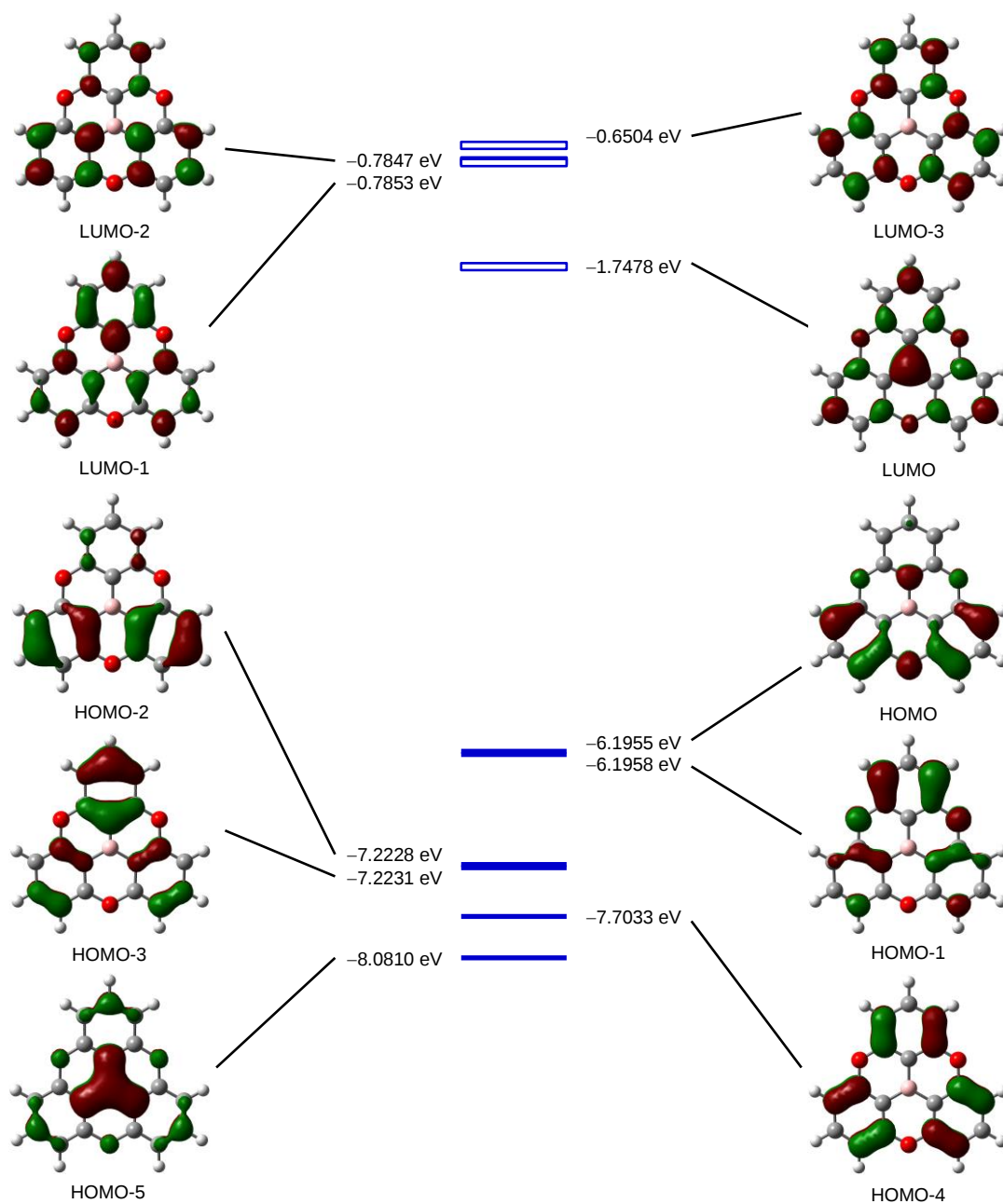


Figure S7. HOMO and LUMO levels for compound **1** at the B3LYP/6-311G(d,p) level theory (in toluene, PCM model).

Table S5 The energy and coordinates of **1** in ground state optimized at B3LYP/6-311G(d,p) (in toluene, PCM model).

Energy = -942.1139087 Hartrees

	Coordinates (Angstroms)		
	X	Y	Z
C	-0.000379139	-2.833067672	2.423206809
H	-0.000684627	-3.915334888	2.445965005
C	-0.00037304	-0.68203244	3.664976512
H	-0.000676318	-0.16058148	4.613618869
C	0.000566057	-0.733496363	1.270272155
C	0.000158481	-2.127127977	1.222750447
C	0.000566094	1.466888473	0
C	0.000566057	-0.733496363	-1.270272155
C	0.00016502	2.122541575	-1.230728992
C	0.000163791	0.004589776	-2.453372339
C	0.000158481	-2.127127977	-1.222750447
C	-0.000372862	3.515114181	1.241867246
C	-0.000372862	3.515114181	-1.241867246
C	-0.00037304	-0.68203244	-3.664976512
C	-0.000379139	-2.833067672	-2.423206809
C	-0.000587394	4.170021847	0
H	-0.000677222	4.076003258	2.167741097
H	-0.000677222	4.076003258	-2.167741097
C	-0.000591191	-2.084943623	-3.611276519
H	-0.000676318	-0.160581481	-4.613618869

H	−0.000684627	−3.915334888	−2.445965005
H	−0.001019954	5.254348352	0
H	−0.001026258	−2.627057898	−4.550362006
C	−0.000591191	−2.084943623	3.611276519
H	−0.001026258	−2.627057898	4.550362006
O	0.000215642	1.39660515	−2.419068466
B	0.000858035	5.12104E-05	0
O	0.000206513	−2.7933617	0
C	0.00016502	2.122541575	1.230728992
C	0.000163791	0.004589776	2.453372339
O	0.000215642	1.39660515	2.419068466

6. References

- (S1) CrystalClear (1998–2014): Data Collection and Processing Software, Rigaku Corporation, Tokyo, Japan.
- (S2) SIR2008: M. C. Burla, R. Cailandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi and R. Spagna, *J. Appl. Cryst.*, 2007, **40**, 609.
- (S3) Least Squares function minimized: (SHELXL2013)
- $$\sum w (Fo^2 - Fc^2)^2 \quad \text{where } w = \text{Least Squares weights.}$$
- (S4) Goodness of fit is defined as:
- $$[\sum w (Fo^2 - Fc^2)^2 / (No - Nv)]^{1/2}$$
- where No = number of observations
 Nv = number of variables
- (S5) *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, Netherlands, 1992, Vol. C, pp 572, Table 6.1.1.4.
- (S6) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.
- (S7) D. C. Creagh and W. J. McAuley, *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, 1992, Vol. C, pp 219–222, Table 4.2.6.8.
- (S8) D. C. Creagh and J. H. Hubbell, *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, 1992, Vol. C, pp 200–206, Table 4.2.4.3.
- (S9) CrystalStructure 4.1 (2000–2014): Crystal Structure Analysis Package, Rigaku Corporation, Tokyo, Japan.
- (S10) SHELXL2013: G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
- (S11) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, M. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09 (Revision D.01), Gaussian, Inc., Wallingford CT, 2009.

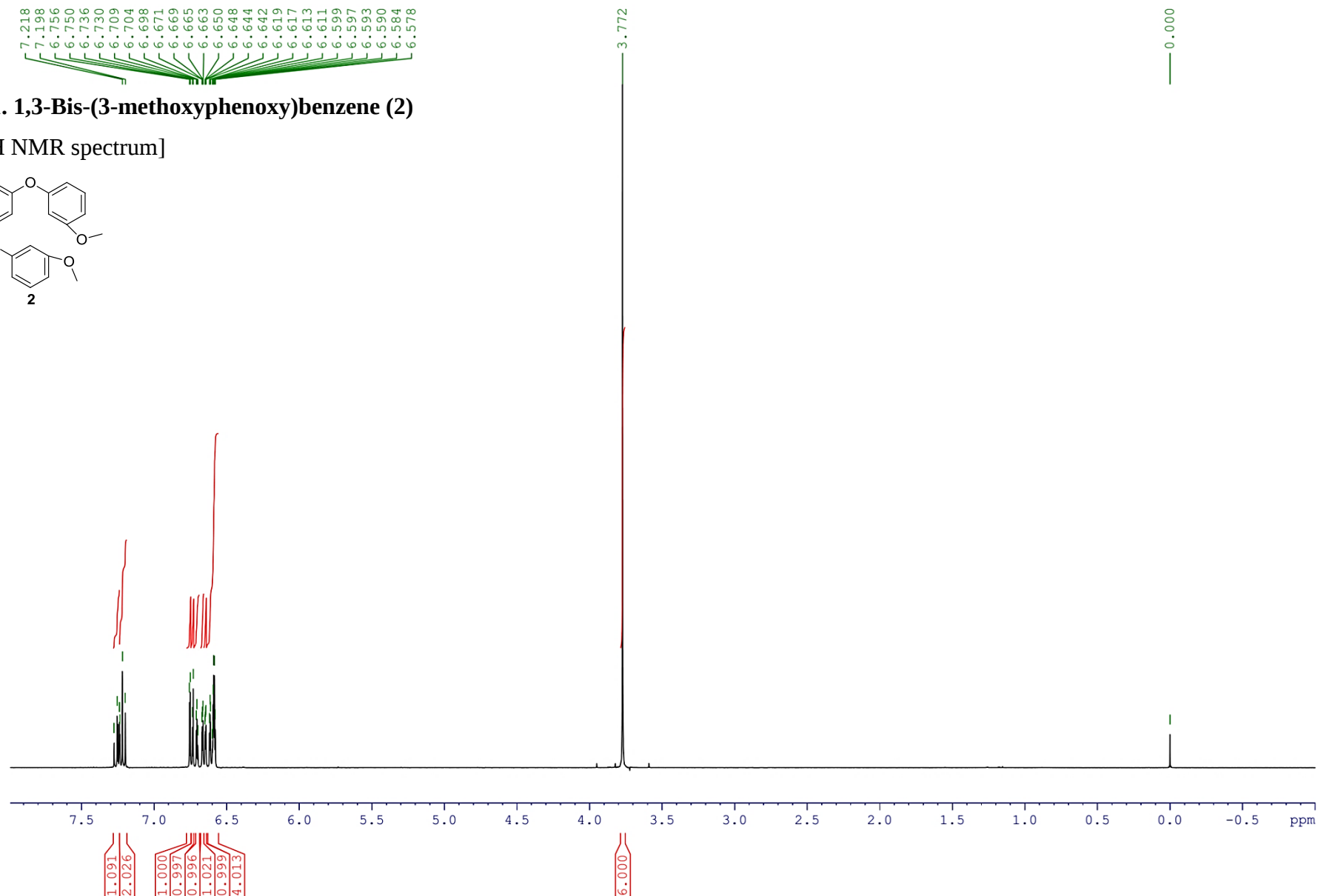
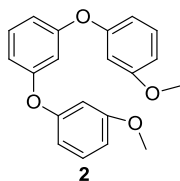
(S12) R. Dennington, T. Keith and J. Millam, Gauss View (Version 5), Semichem, Inc., Shawnee Mission, KS, 2009.

7. ^1H , ^{13}C , and ^{11}B NMR spectra of synthesized compounds

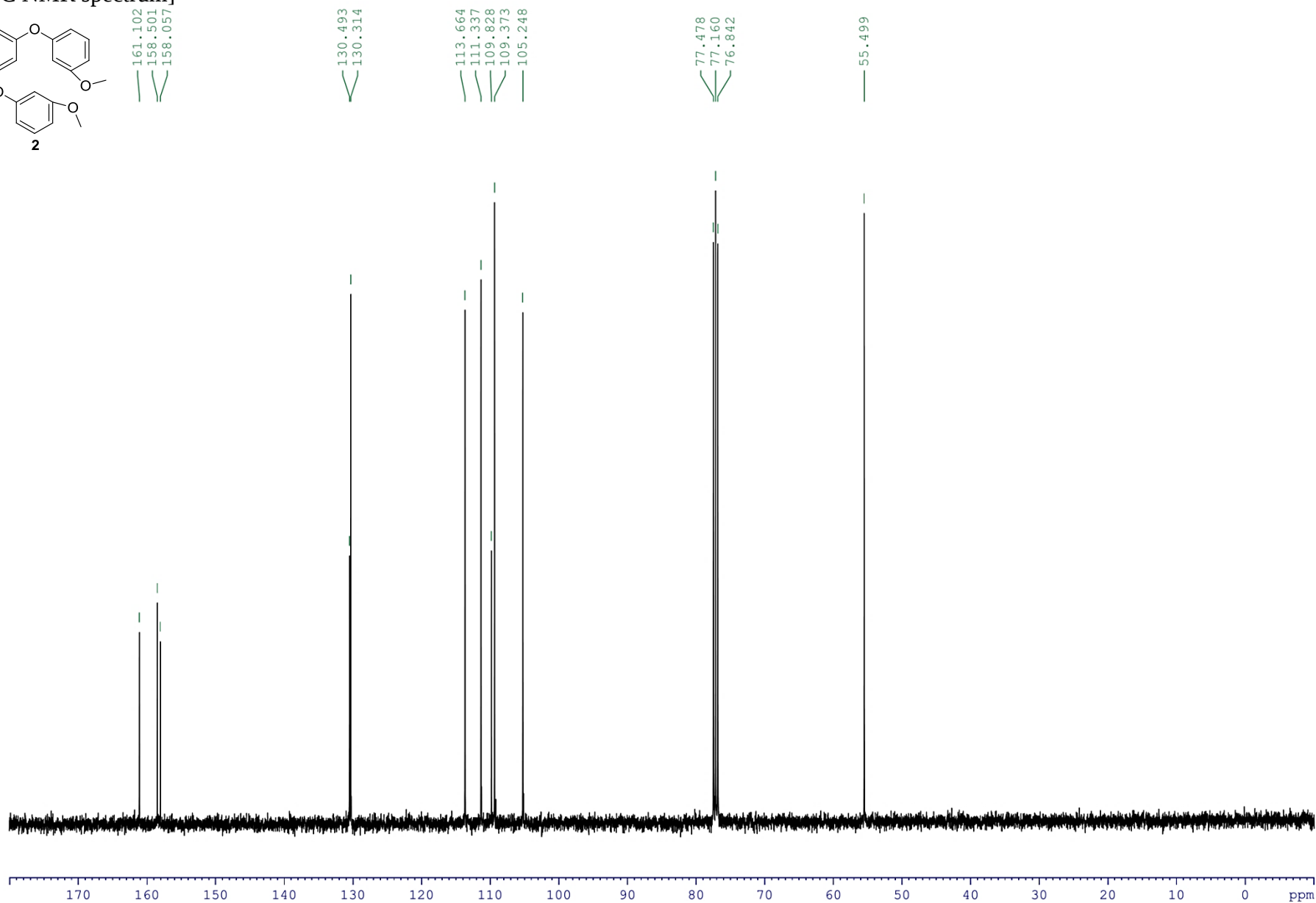
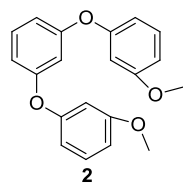


7.1. 1,3-Bis-(3-methoxyphenoxy)benzene (2)

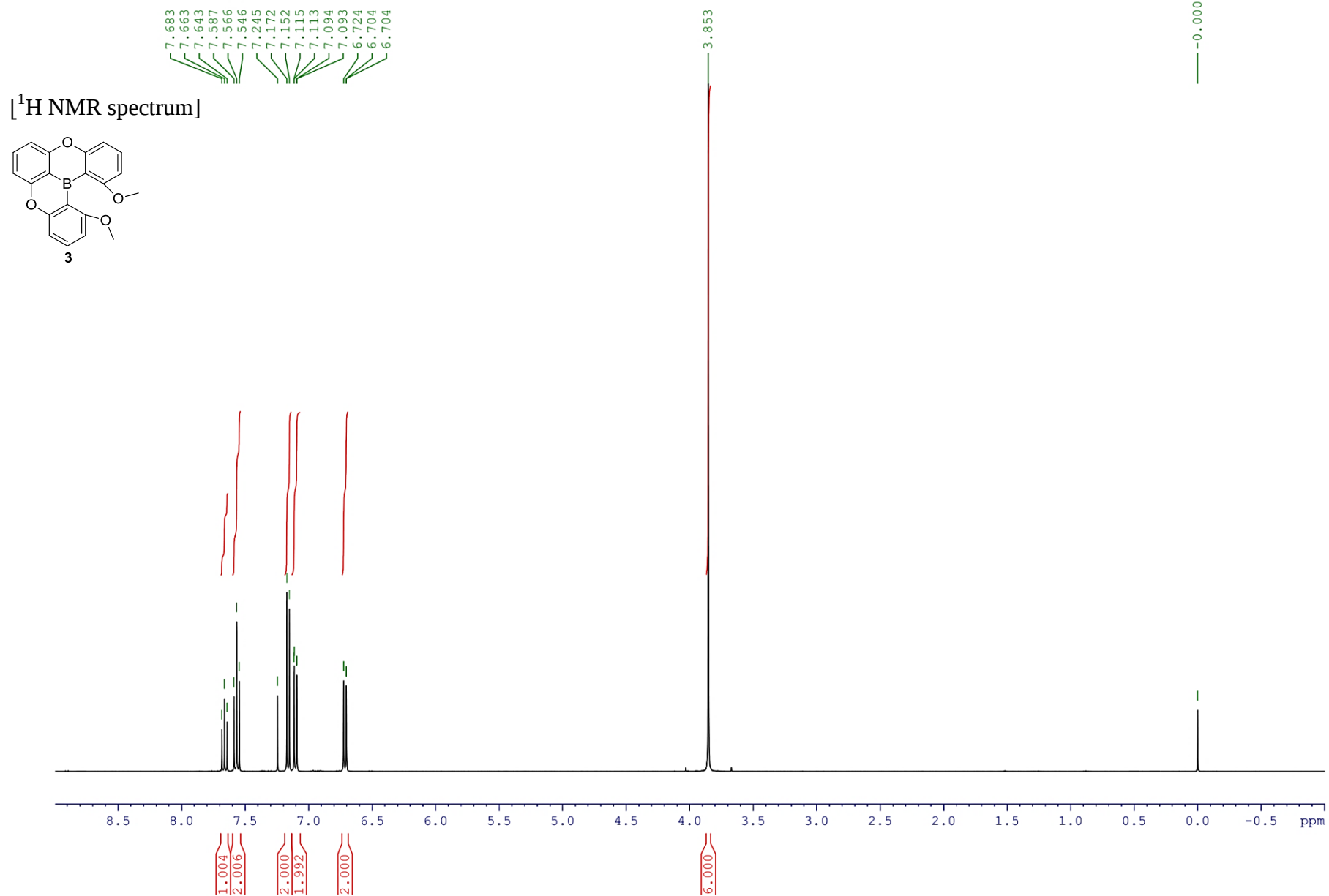
[^1H NMR spectrum]



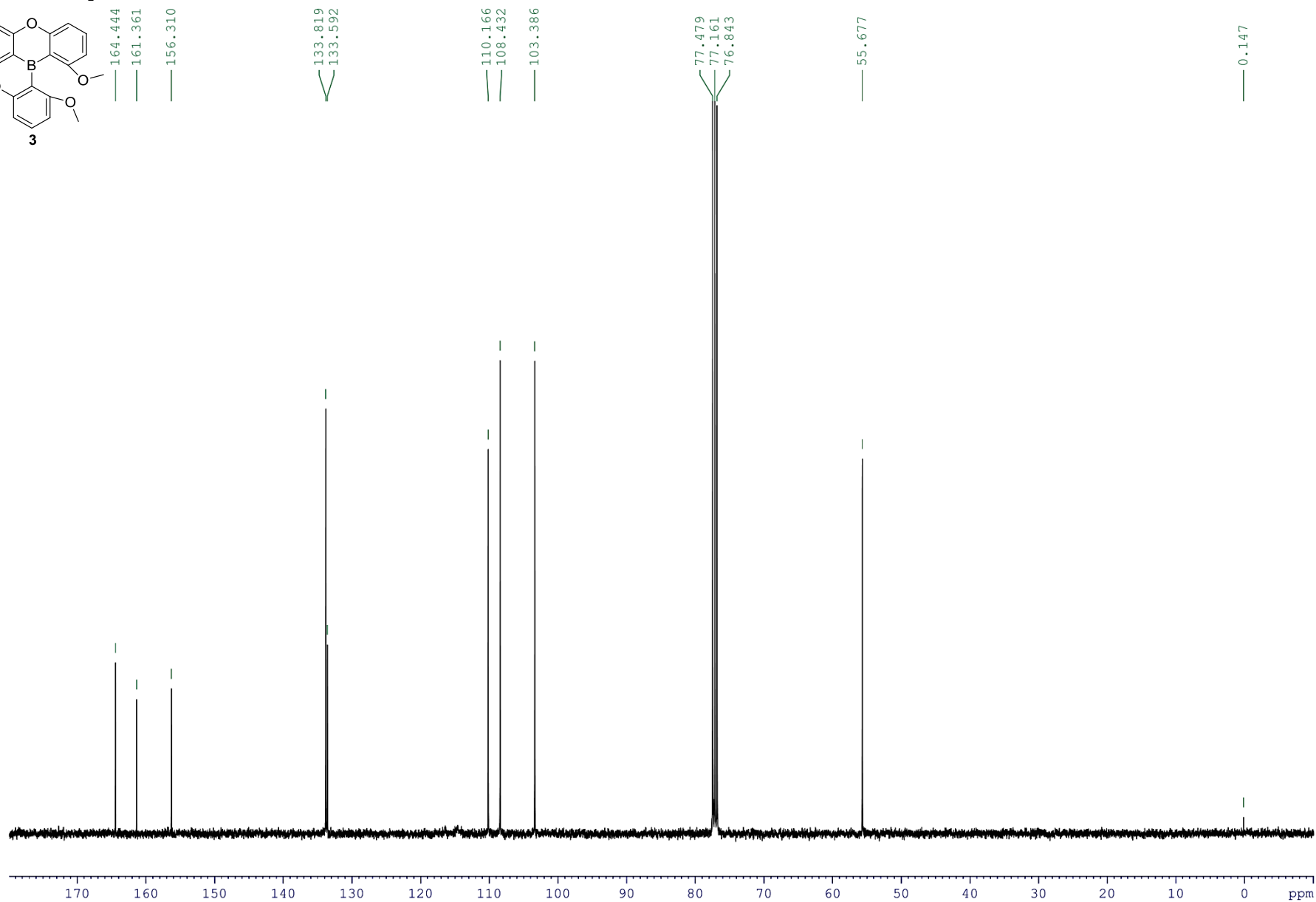
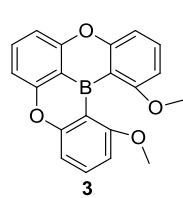
[¹³C NMR spectrum]



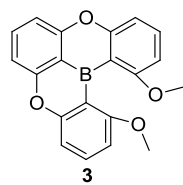
7.2. 1,13-Dimethoxy-5,9-dioxa-13b-boranaphtho[3,2,1-*de*]anthracene (3)



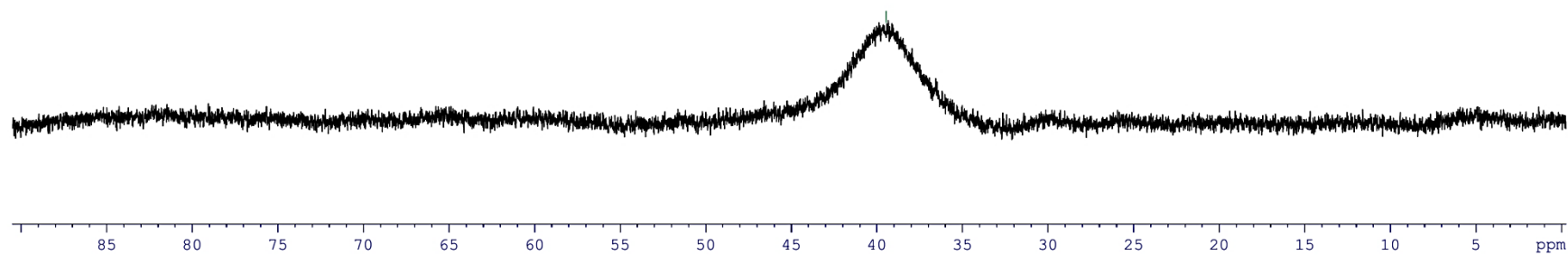
[¹³C NMR spectrum]



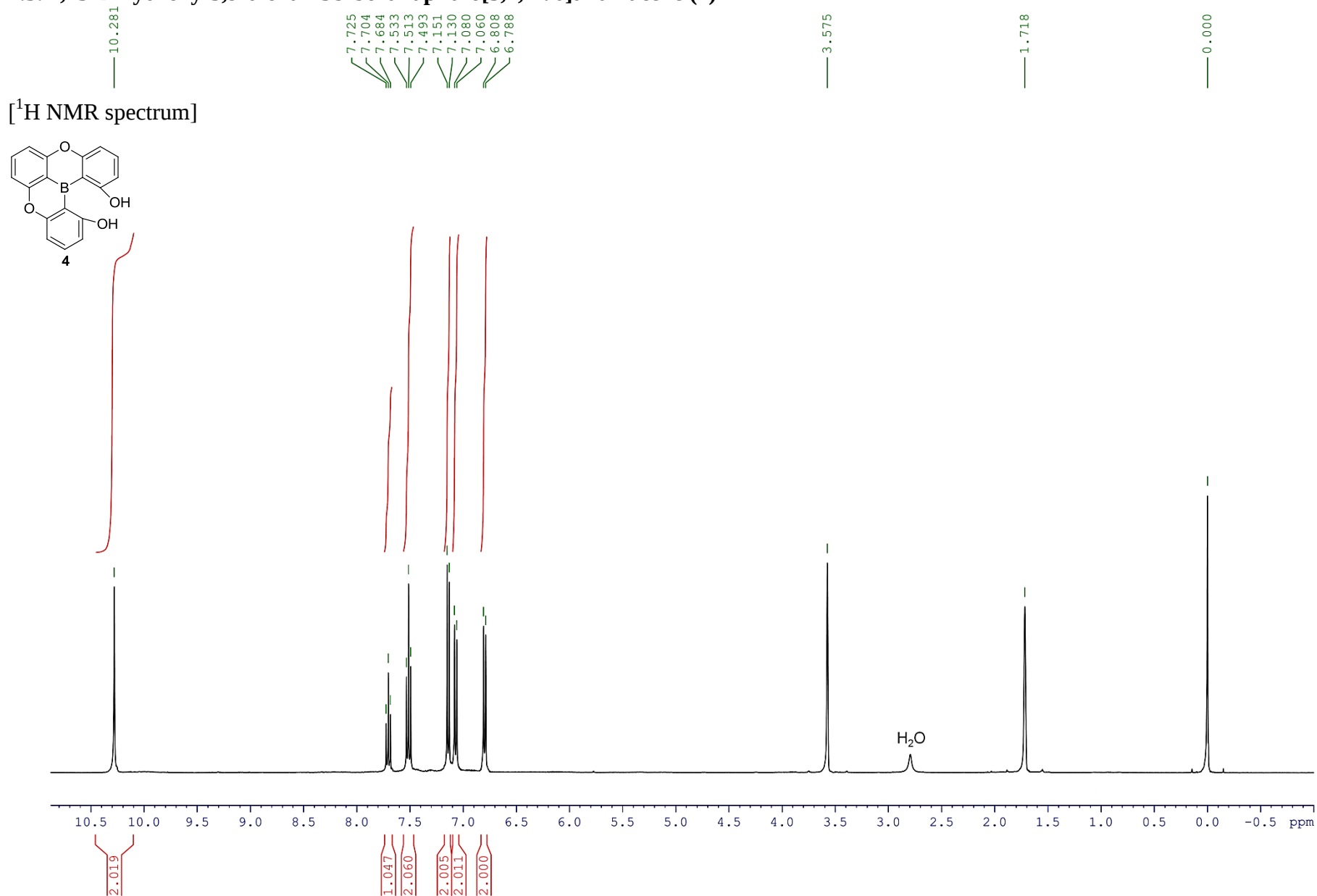
[^{11}B NMR spectrum]



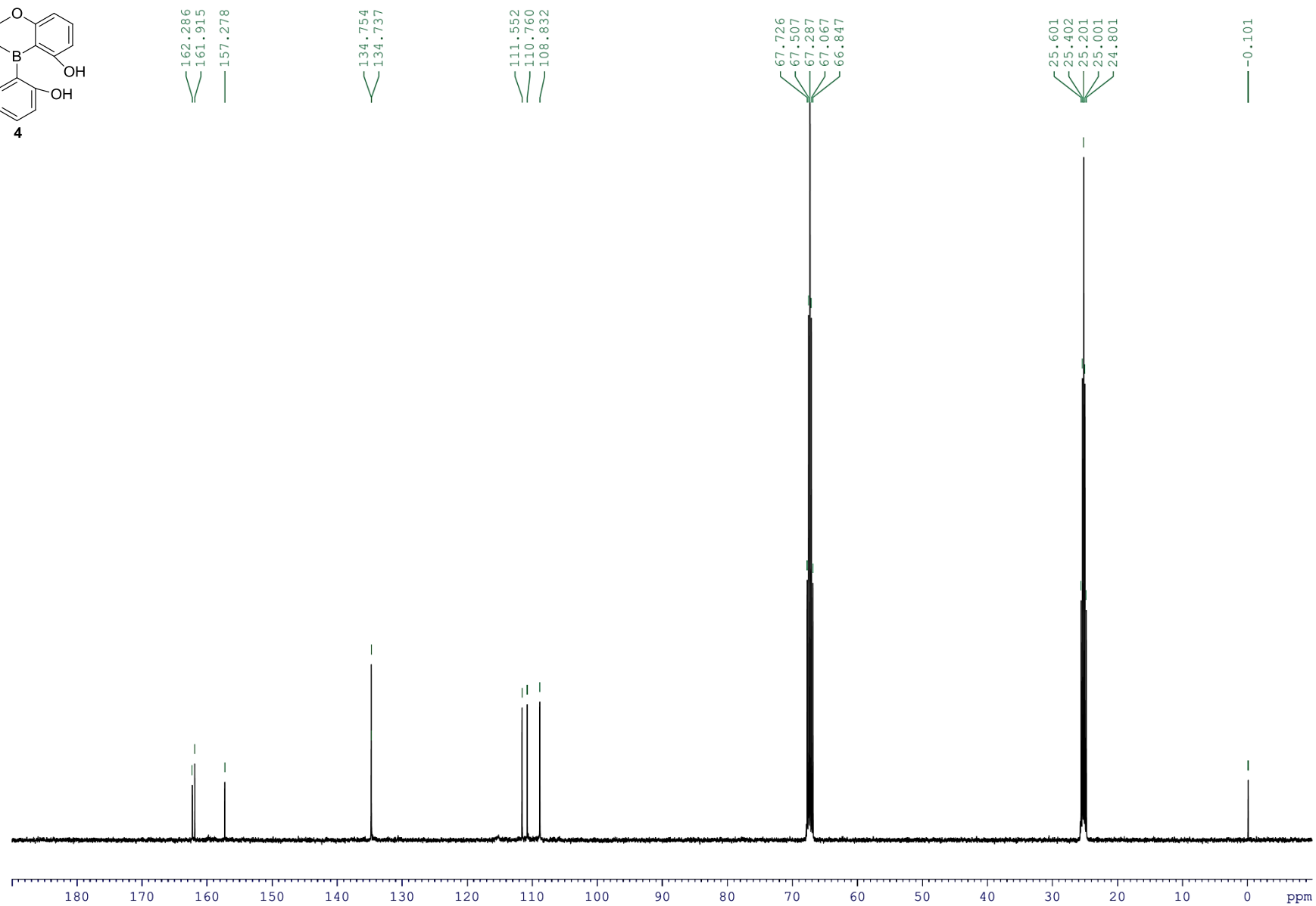
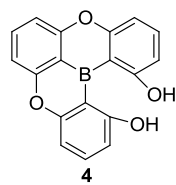
— 39.469



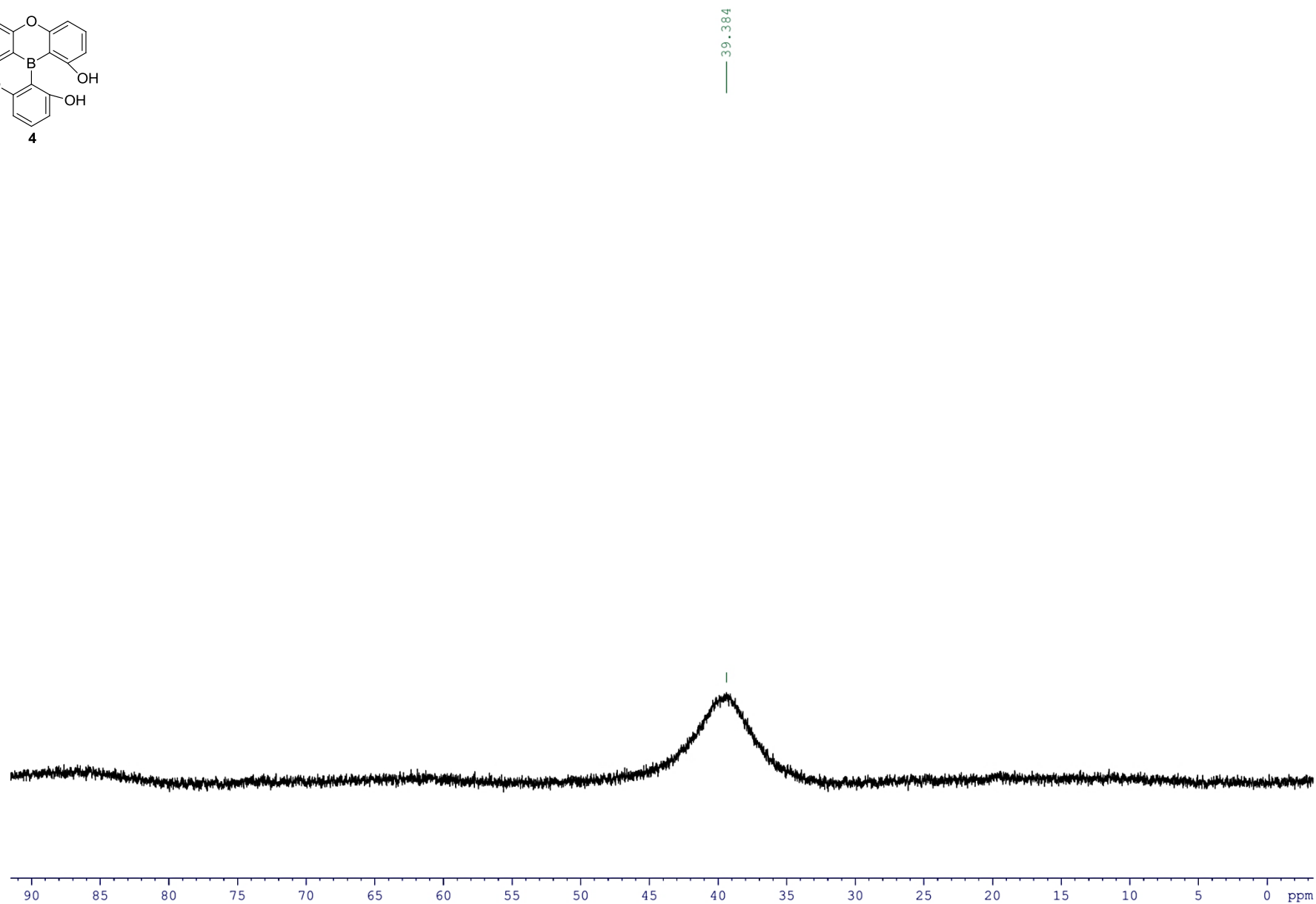
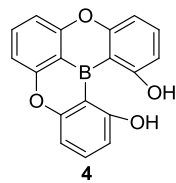
7.3. 1,13-Dihydroxy-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (4)



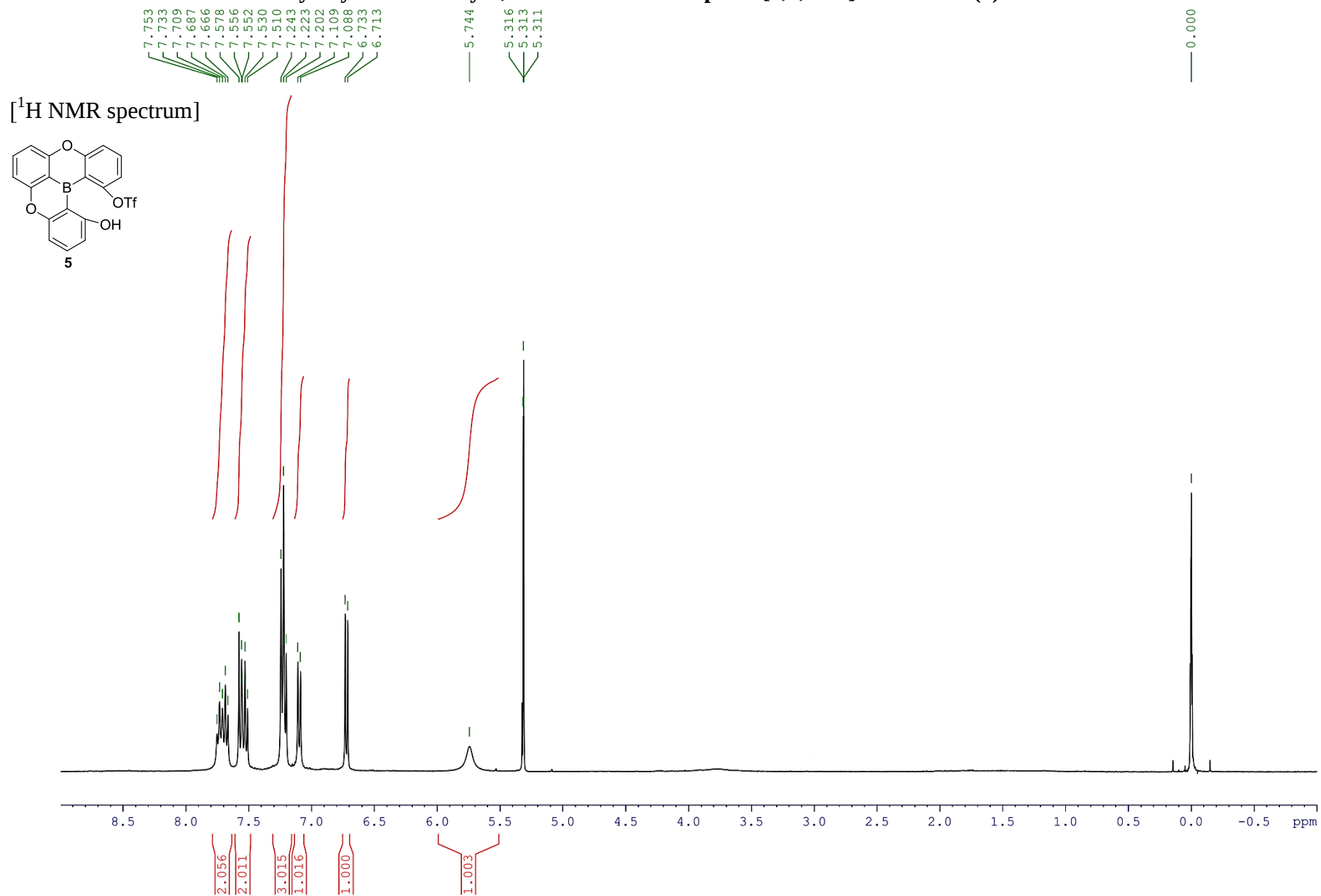
[^{13}C NMR spectrum]



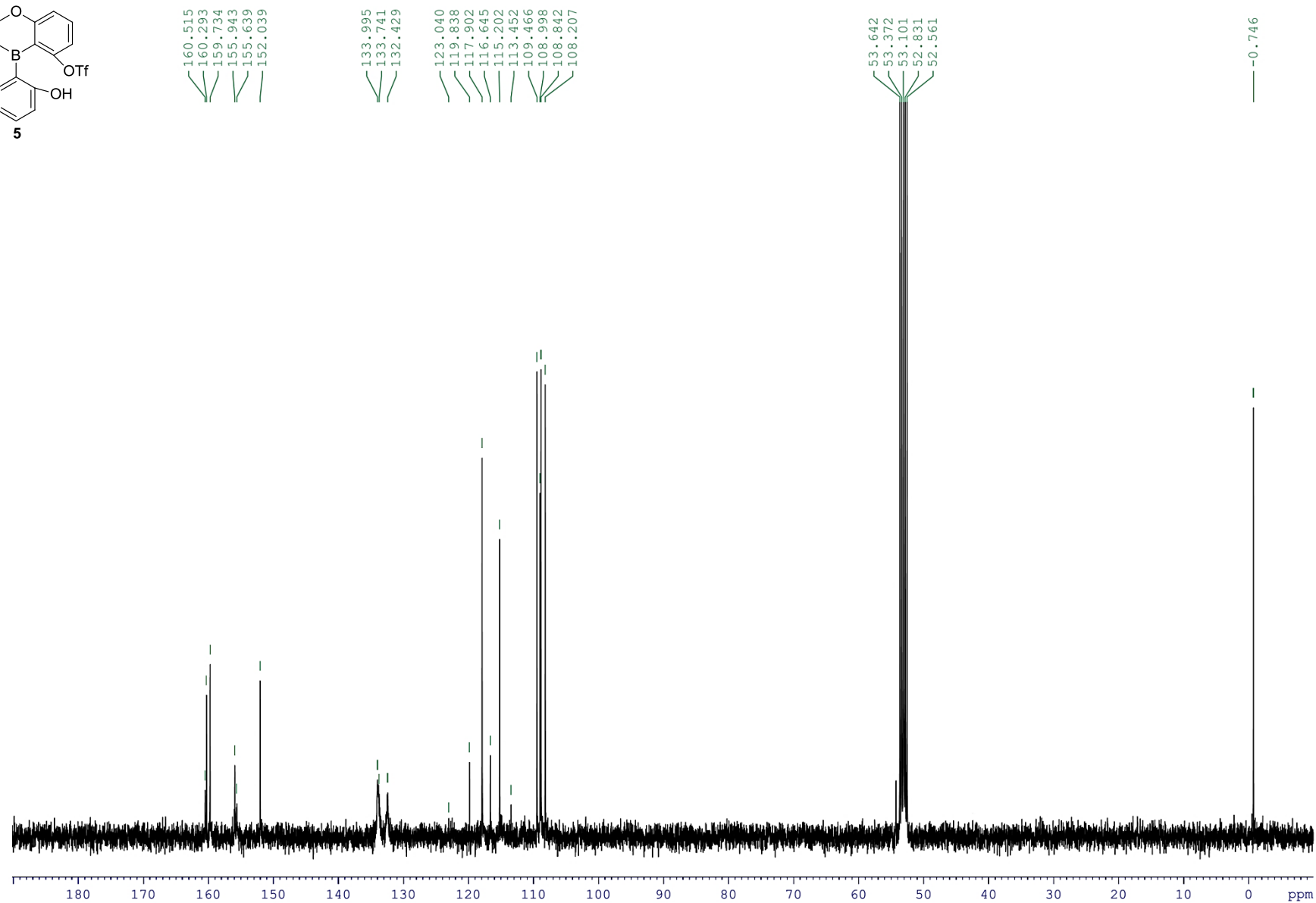
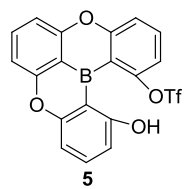
[^{11}B NMR spectrum]



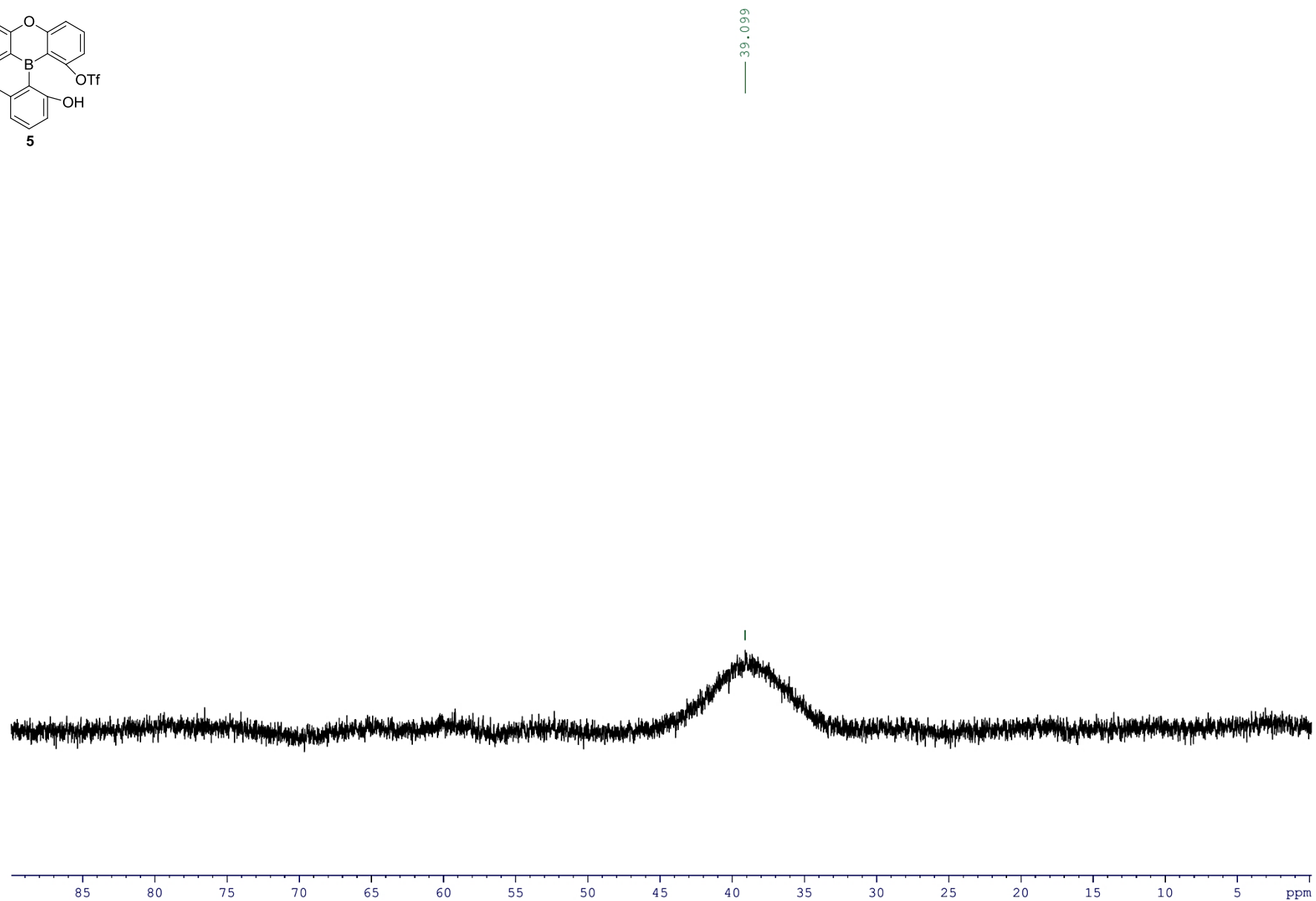
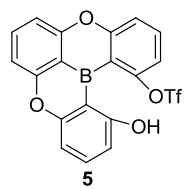
7.4. 1-Trifluoromethansulfonyloxy-13b-hidroxy-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (5)



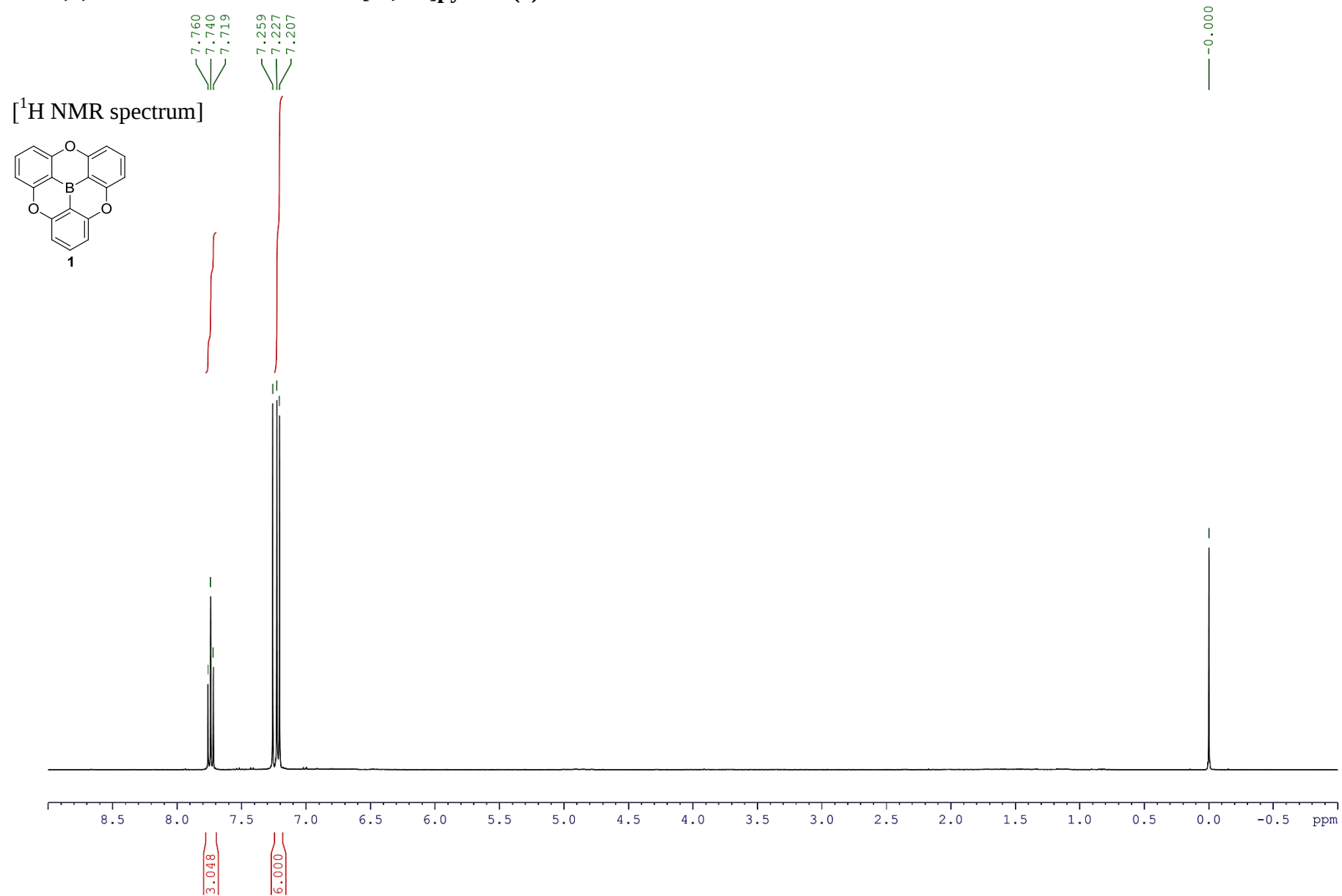
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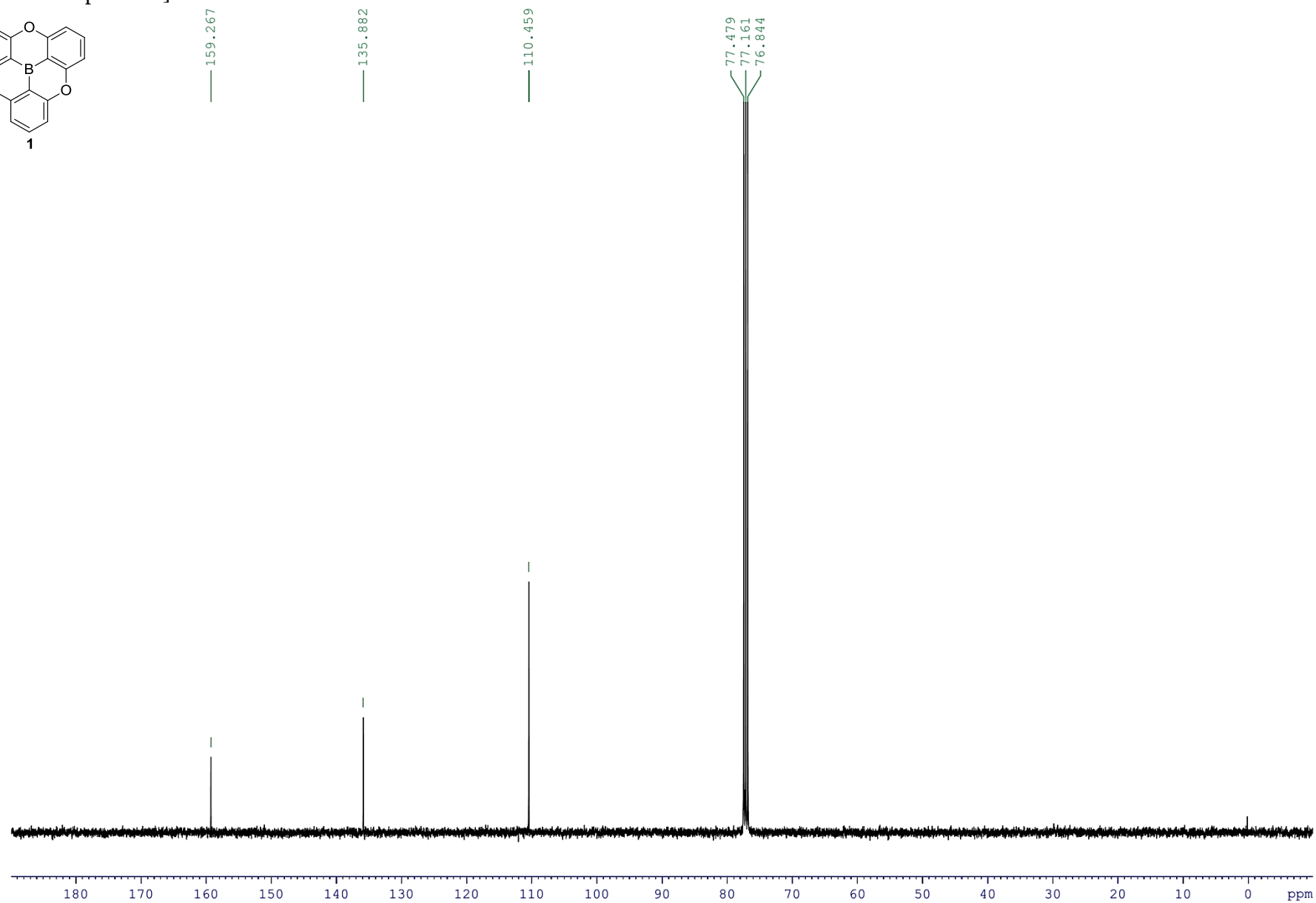
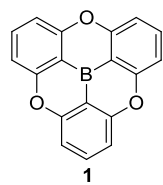
[^{11}B NMR spectrum]



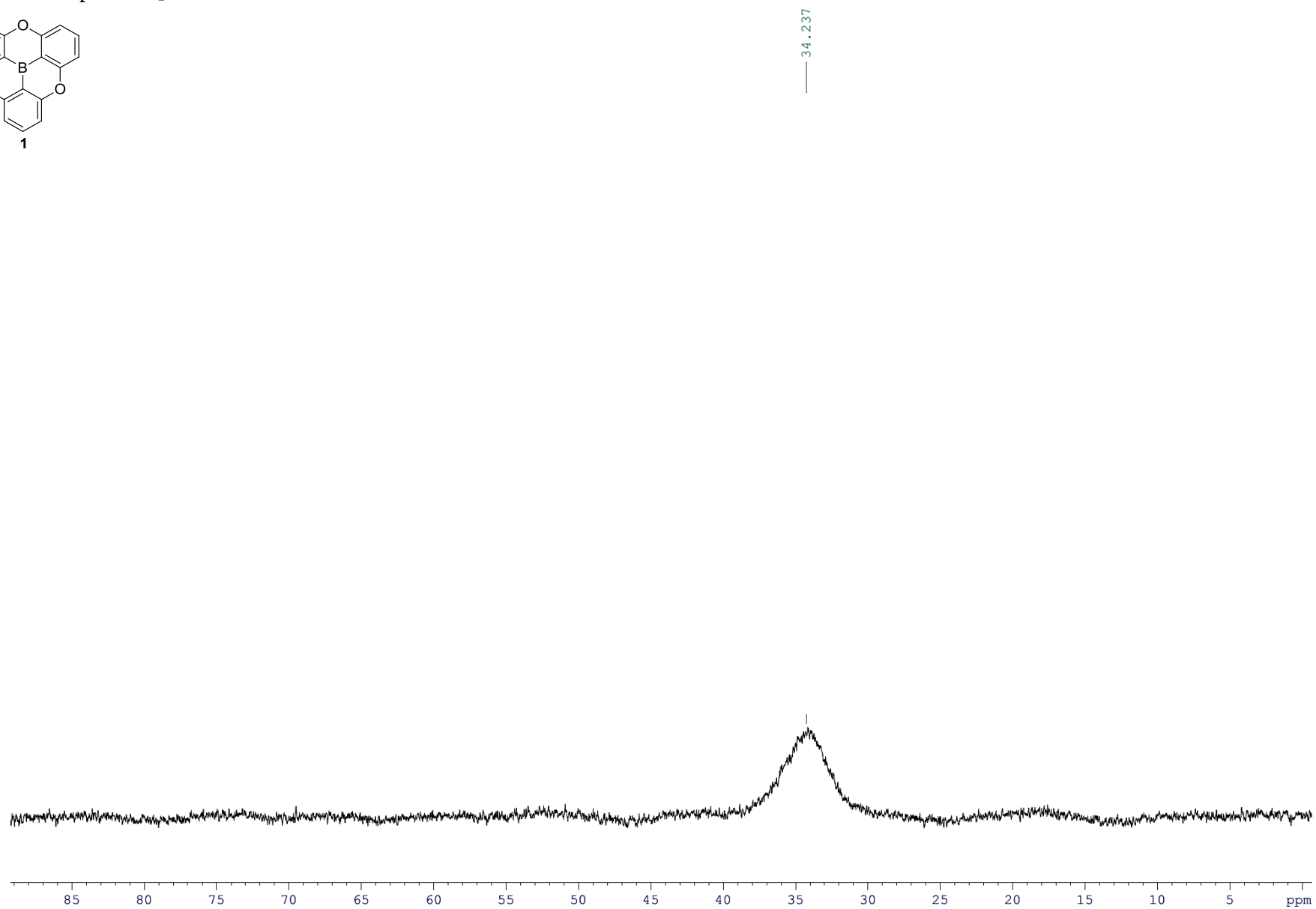
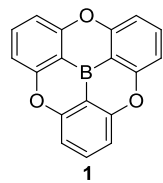
7.5. 4,8,12-Trioxa-12c-boradibenzo[*cd,mn*]pyrene (1)



[^{13}C NMR spectrum]



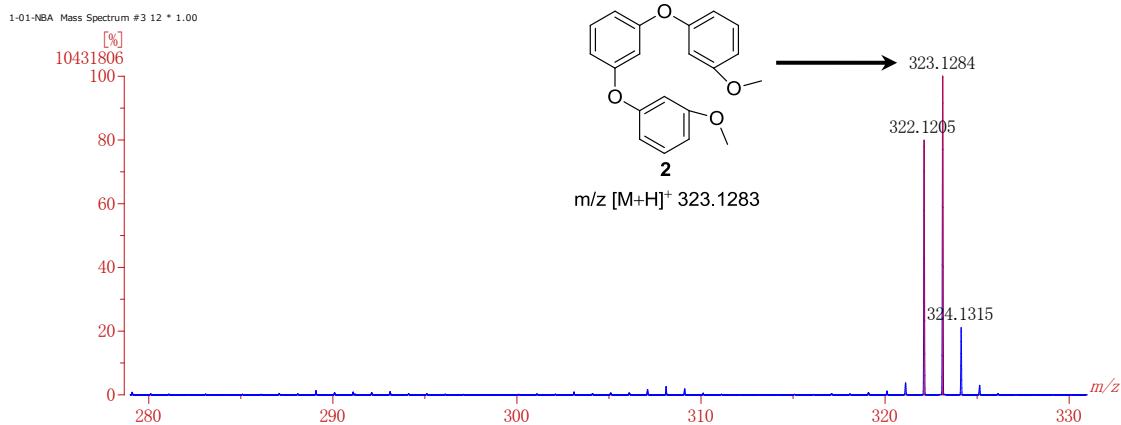
[^{11}B NMR spectrum]



8. HRMS spectra of synthesized compounds

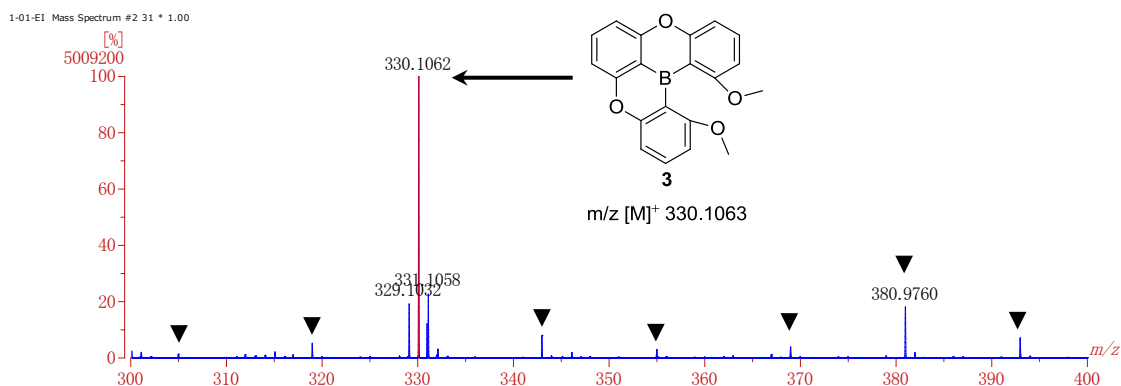
8.1. 1,3-Bis-(3-methoxyphenoxy)benzene (2)

HRMS (FAB), MS standard: PEG200 (external standard)



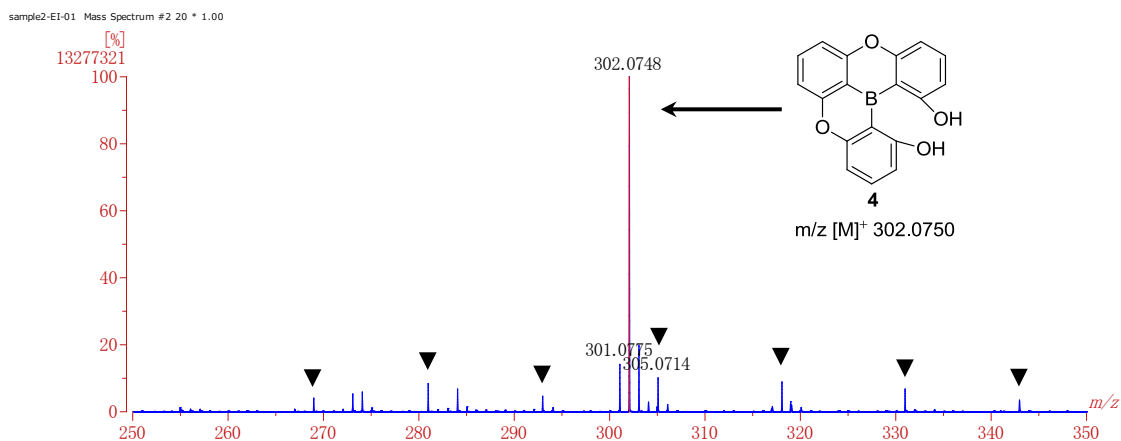
8.2. 1,13-Dimethoxy-5,9-dioxa-13b-boranaphtho[3,2,1-*de*]anthracene (3)

HRMS (EI), MS standard: PFK (internal standard, PFK peaks: ▼)



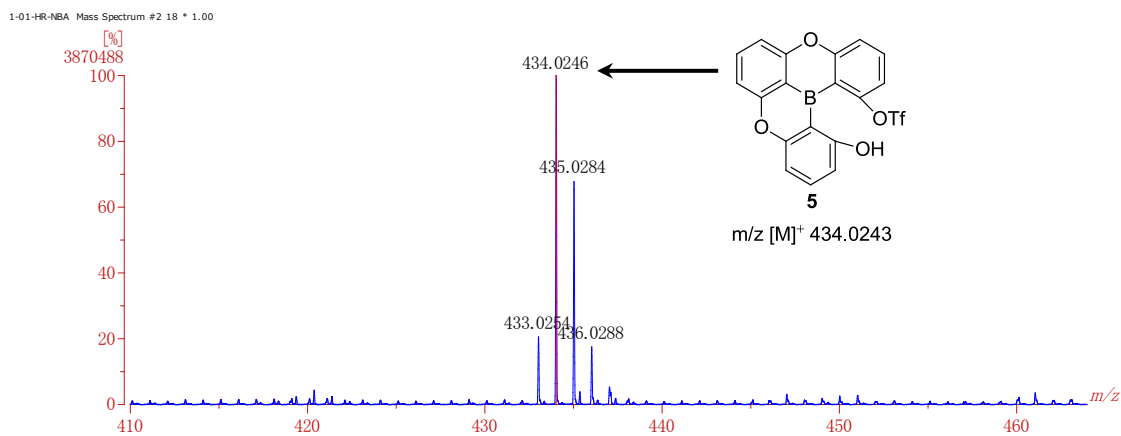
8.3. 1,13-Dihydroxy-5,9-dioxa-13b-boranaphtho[3,2,1-*de*]anthracene (4)

HRMS (EI), MS standard: PFK (internal standard, PFK peaks: ▼)



8.4. 1-Trifluoromethansulfonyloxy-13b-hidroxy-5,9-dioxa-13b-boranaphtho[3,2,1-de]-anthracene (5)

HRMS (FAB), MS standard: PEG200 (external standard)



8.5. 4,8,12-Trioxa-12c-boradibenzo[cd,mn]pyrene (1)

HRMS (EI), MS standard: PFK (internal standard, PFK peaks: ▼)

