

Synthesis of an azadioxa-planar triphenylborane and investigation of its structural and photophysical properties

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Supplementary Information

Contents:

1. Experimental Section	S2
2. Synthesis	S4
3. ¹¹ B NMR study	S5
4. X-ray crystallographic analysis	S6
5. Photophysical data	S10
6. Theoretical calculation	S11
7. References	S21
8. NMR spectra of synthesized compounds	S22
9. HRMS spectra of synthesized compounds	S28

1. Experimental Section

General: ^1H , ^{13}C and ^{11}B NMR were recorded using a Bruker Biospin AVANCE III 400 spectrometer. The ^1H NMR chemical shifts were reported in ppm (δ) with reference to protons of tetramethylsilane singlet at 0.00 ppm. The ^{13}C NMR chemical shifts were reported in ppm (δ) with reference to residual carbons (CHCl_3) in CDCl_3 at 77.16 ppm. Interaction of the boron-bonded carbon atoms with the quadrupole moment of the boron nucleus causes line broadening. Therefore, the carbon atoms are not observed in the ^{13}C NMR spectrum. The ^{11}B NMR chemical shifts were reported in ppm (δ) with reference to the chemical shift of $\text{BF}_3\cdot\text{OEt}$ at 0.00 ppm as an external standard. The multiplicities were presented as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. IR spectra were recorded on a JASCO FT/IR-350 Fourier-transform infrared spectrometer. Characteristic IR absorptions were reported in cm^{-1} . High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-700 spectrometer using the electron impact (EI) method at Technical Division, School of Engineering, Tohoku University. Melting points were obtained using a Stuart melting point apparatus SMP3. UV-vis absorption spectra were recorded on a Shimadzu UV-2500 spectrophotometer. The photoluminescence spectra in toluene were recorded on a Hitachi High-Tech F-7000 Spectrophotometer. The absolute photoluminescence quantum yield was measured using Hamamatsu Photonics Quantaaurus-QY C11347. The transient photoluminescence decay was recorded using Hamamatsu Photonics Quantaaurus-Tau C11367 equipped with YAG laser ($\lambda = 355 \text{ nm}$) as an excitation source. Spectrophotometric grade toluene solvent was purchased from Kanto Chemical Co., Inc. The solution for UV-vis and photoluminescence experiments was bubbled with N_2 .

Reaction: All reactions were carried out under a positive pressure of nitrogen in egg-plant shaped flasks or Biotage 20 mL vials sealed with crimp caps unless noted otherwise. Column chromatography was performed using spherical silica gel (63–200 μm , Kanto Chemical).

Materials: All solvents using in reactions, UV-vis, and photoluminescence experiments were purchased and used as received. Commercially available reagents were used without purification unless noted otherwise. Aniline was dried with KOH and distilled at reduced pressure, and then stored under N_2 atmosphere before using. 1,13-Dihydroxy-5,9-dioxa-13b-boranaphtho[3,2,1-*de*]anthracene (dihydroxy-triphenylborane **6**) was prepared according to the literature.^{S1}

X-ray Crystallographic analysis: Single crystal of compound **1** was obtained by crystallizing the synthesized **1** from chloroform–hexane as a colorless crystal. Single-crystal X-ray diffraction data were collected with a Bruker APEX II CCD diffractometer equipped with a Helios multi-layered confocal mirror and a TXS fine-focus rotating anode using Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by least-squares method on F^2 with SHELXL-97.^{S2} X-ray analysis was undertaken using the free GUI software of Yadokari-XG 2009.^{S3,S4} Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (deposition number: CCDC 1570941). The crystal data are summarized in Table S1.

2. Synthesis

5,9-Dioxa-13b-boranaphtho[3,2,1-*de*]anthracene-1,13-diyl bis(trifluoromethanesulfonate) (7).

A 300 mL two necked and egg-plant shaped flask equipped with a Teflon coated magnetic stirring bar was charged with **6** (1.362 g, 4.51 mmol), and then evacuated by heating and refilled with N₂. *N,N*-Diisopropylethylamine (2.3 mL, 3.0 equiv., 13.5 mmol) and 200 mL of dry dichloromethane were added, and then dry dichloromethane (10 mL) solution of trifluoromethanesulfonic anhydride (1.63 mL, 2.2 equiv., 9.92 mmol) was added to the stirred solution using syringe driver at -78 °C for 2.0 h. The reaction mixture was gradually warmed to room temperature overnight, and then stirred at room temperature for 3 h. The resulting mixture was washed successively with sat. NH₄Cl aq., 1N HCl aq., and brine, and the extracts were dried over MgSO₄. After filtration, volatiles were evaporated under reduced pressure. The residue was purified by silica gel chromatography using hexane–dichloromethane (2:1) as an eluent to give the product **7** (2.28 g, 89%) as colorless powder. Colorless powder; Mp: 159.3–159.8 °C; IR (KBr, cm⁻¹): 3436, 1617, 1582, 1471, 1418, 1332, 1297, 1214, 1139, 1027, 968, 863, 838, 801, 754; ¹H NMR (400 MHz, CDCl₃): δ(ppm) 7.85 (t, *J* = 8.2 Hz, 1H), 7.78 (t, *J* = 8.2 Hz, 2H), 7.64 (dd, *J* = 8.2, 0.8 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ(ppm) 160.5, 156.1, 151.7, 135.8, 134.2, 118.7, 118.6 (q, *J* = 319.1 Hz), 116.1, 109.5, two signals for the carbon atoms bonded to the boron atom were not observed due to the quadrupolar relaxation; ¹¹B NMR (128 MHz, CDCl₃): δ(ppm) 40.2; HRMS (EI) *m/z* [M]⁺: calcd for C₂₀H₉BF₆O₈S₂, 565.9736; found, 565.9738.

12-Phenyl-12*H*-4,8-dioxa-12-aza-3a²-boradibenzo[*cd,mn*]pyrene (1).

A Biotage 20 mL vial equipped with a Teflon coated magnetic stirring bar was charged with **7** (0.566 g, 1.00 mmol) and sealed with a crimp cap, and then evacuated by heating and refilled with N₂. 9.0 mL of dry 1,4-dioxane and aniline (364 μL, 4.0 equiv., 4.00 mmol) was added, and then lithium hexamethyldisilazide (LiHMDS) (1.5 mL, 1.5 equiv., 1.50 mmol, 1.0 mol/L in tetrahydrofuran) was added dropwise to the solution at ca. 10 °C. The reaction mixture was stirred at 150 °C for 20 h. After the reaction mixture was diluted with chloroform, the resulting mixture was washed successively with 1N HCl aq. and brine, and the extracts were dried over MgSO₄. After filtration, volatiles were evaporated under reduced pressure. The residue was purified by recrystallization from methanol–pentane (1:1) at 0 °C. The crude precipitate was purified by silica gel chromatography using hexane–dichloromethane (1:1) as an eluent to give the product **1** (0.127 g, 35%) as colorless powder.

Colorless powder; Mp: 306.6–307.1 °C; IR (KBr, cm^{-1}): 3449, 3067, 1622, 1606, 1487, 1446, 1312, 1269, 1227, 1209, 1160, 1057, 984, 855, 784, 741; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.67–7.71 (m, 3H), 7.60 (tt, $J = 7.4, 1.5$ Hz, 1H), 7.53 (t, $J = 8.2$ Hz, 2H), 7.43–7.45 (m, 2H), 7.19 (d, $J = 8.2$ Hz, 2H), 7.06 (d, $J = 8.2$ Hz, 2H), 6.38 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.7, 158.7, 147.6, 140.8, 134.8, 134.7, 131.0, 130.2, 129.0, 109.8, 109.1, 107.2, two signals for the carbon atoms bonded to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 33.9; HRMS (EI) m/z $[\text{M}]^+$: calcd for $\text{C}_{24}\text{H}_{14}\text{BNO}_2$, 359.1118; found, 359.1117.

3. ^{11}B NMR study

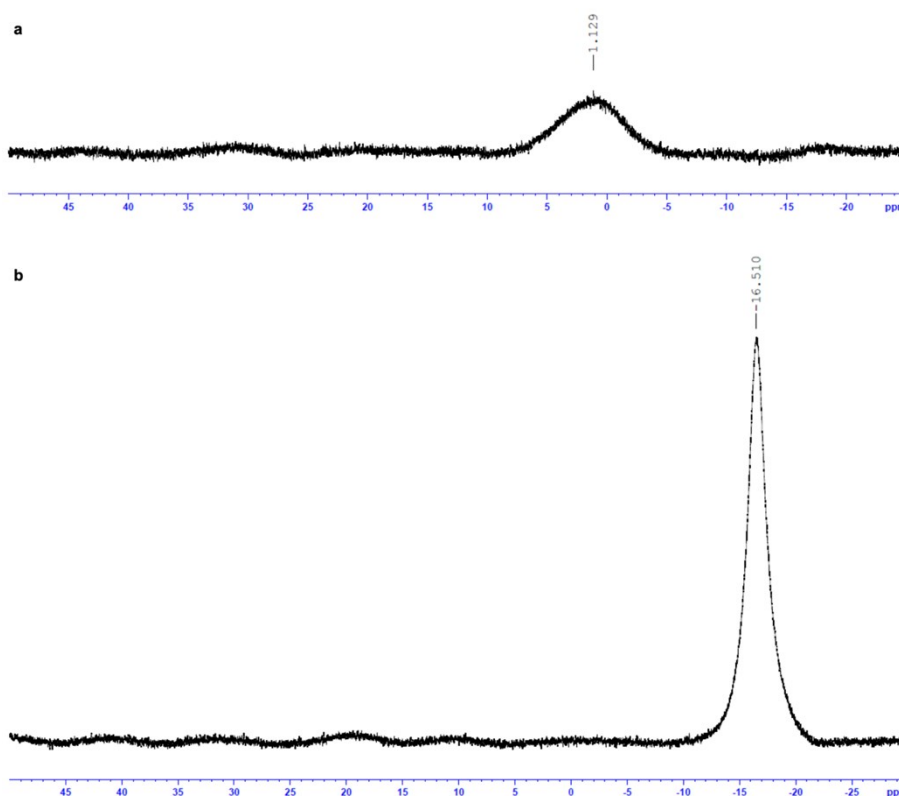


Figure S1 ^{11}B NMR spectra of **7** in the presence of aniline (a) and the presence of aniline and LiHMDS (b) at 23 °C in dioxane- d_8 . Conditions: **7** (6.71×10^{-2} mmol), aniline (4.0 equiv., 2.68×10^{-1} M), LiHMDS (1.5 equiv., 1.01×10^{-1} mmol), 1,4-dioxane- d_8 (0.7 mL).

4. X-ray crystallographic analysis

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

Empirical formula	C ₂₄ H ₁₄ BNO ₂
Formula weight	359.17
Temperature	100 K
Wavelength (Mo K α)	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 10.9490(12)$ Å $\alpha = 90^\circ$ $b = 19.966(2)$ Å $\beta = 99.4220(10)^\circ$ $c = 7.4024(8)$ Å $\gamma = 90^\circ$
Volume	1596.4(3) Å ³
Z	4
Density (calculated)	1.494 g·cm ⁻³
μ (Mo K α)	0.094 mm ⁻¹
$F(000)$	744
Crystal dimensions	0.2×0.1×0.1 mm ³
Theta range for data collection	2.04 to 27.89°
Reflections collected	4595
Independent reflections	1866 [$R(\text{int}) = 0.0146$]
Refinement method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	1866 / 0 / 130
Goodness-of fit on F^2	1.045
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0407$, $wR_2 = 0.1214$
R indices (all data)	$R_1 = 0.0445$, $wR_2 = 0.1255$
Largest diff. peak and hole	0.358 and -0.320 e ⁻ ·Å ⁻³

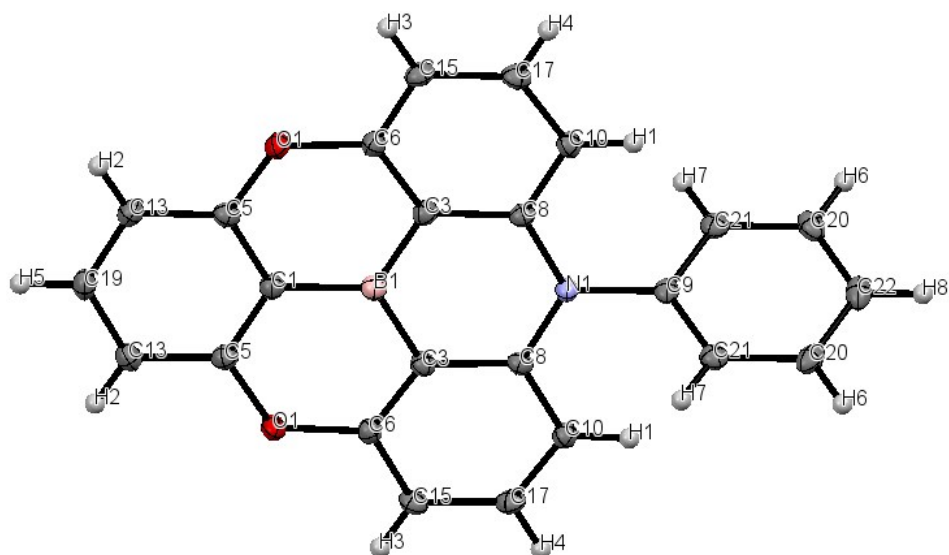


Figure S2 Thermal ellipsoid drawing of **1** with thermal ellipsoids at 50% probability.

Table S2 Selected bond lengths and angles of **1**.

	Length / Å		Angle / °
C1–B1	1.472(2)	C3–B1–C3 ^{#1}	121.03(14)
C3–B1	1.4699(13)	C3 ^{#1} –B1–C1	119.49(7)
C3 ^{#1} –B1	1.4699(13)	C3–B1–C1	119.48(7)
O1–C6	1.3951(12)		
O1–C5	1.3971(12)		
N1–C8	1.4200(11)		
N1–C8 ^{#1}	1.4200(11)		

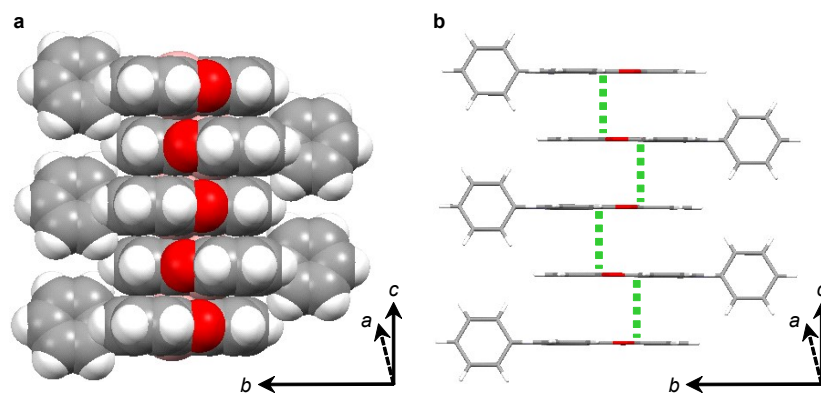


Figure S3 π - π Stacking structure of **1** depicted in spacefill (a) and capped sticks models (b). Green dotted lines indicate π - π interaction (interplanar distance = 3.446 Å).

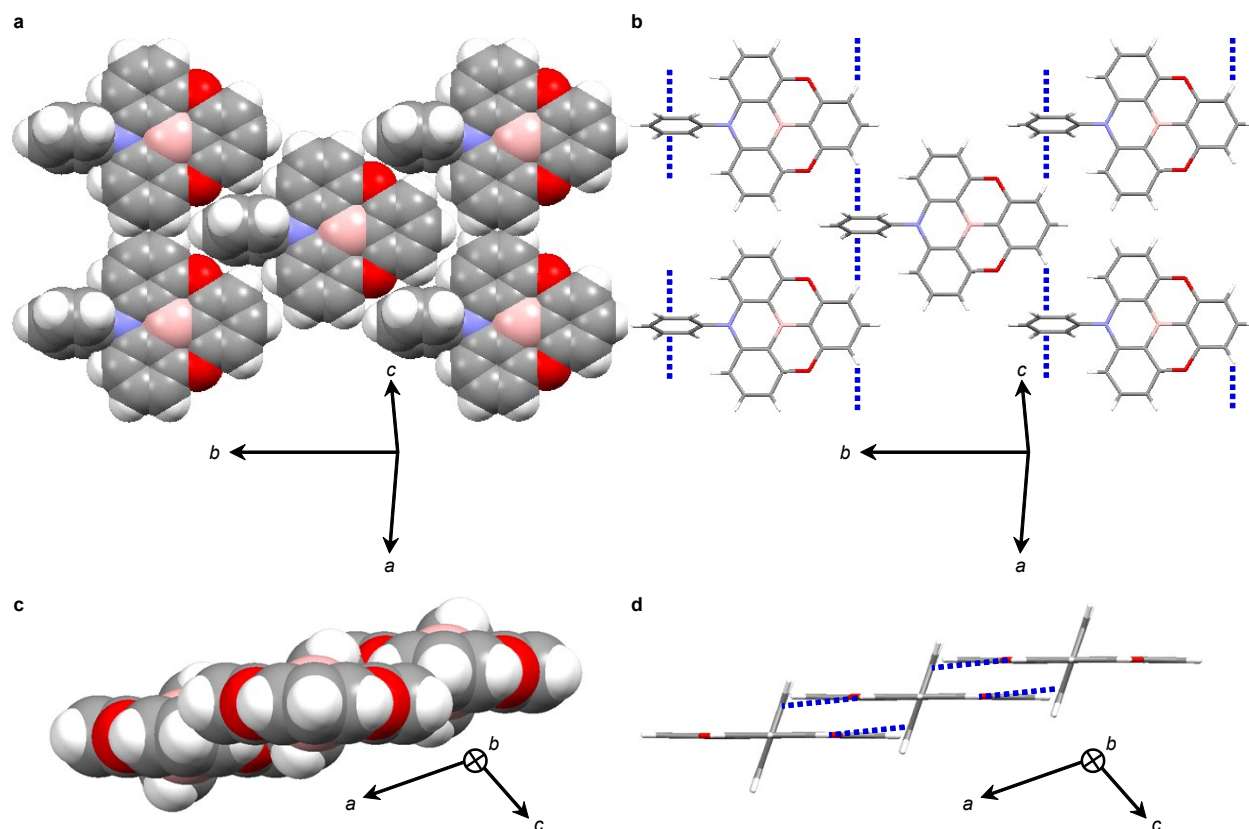


Figure S4 The motif of intermolecular CH- π hydrogen bonds of **1** from the top (a, b) and the side (c, d). The molecules in (a, c) and (b, d) are depicted in spacefill and capped sticks models, respectively. Blue dotted lines indicate CH- π hydrogen bond (intermolecular distance = 2.662 Å).

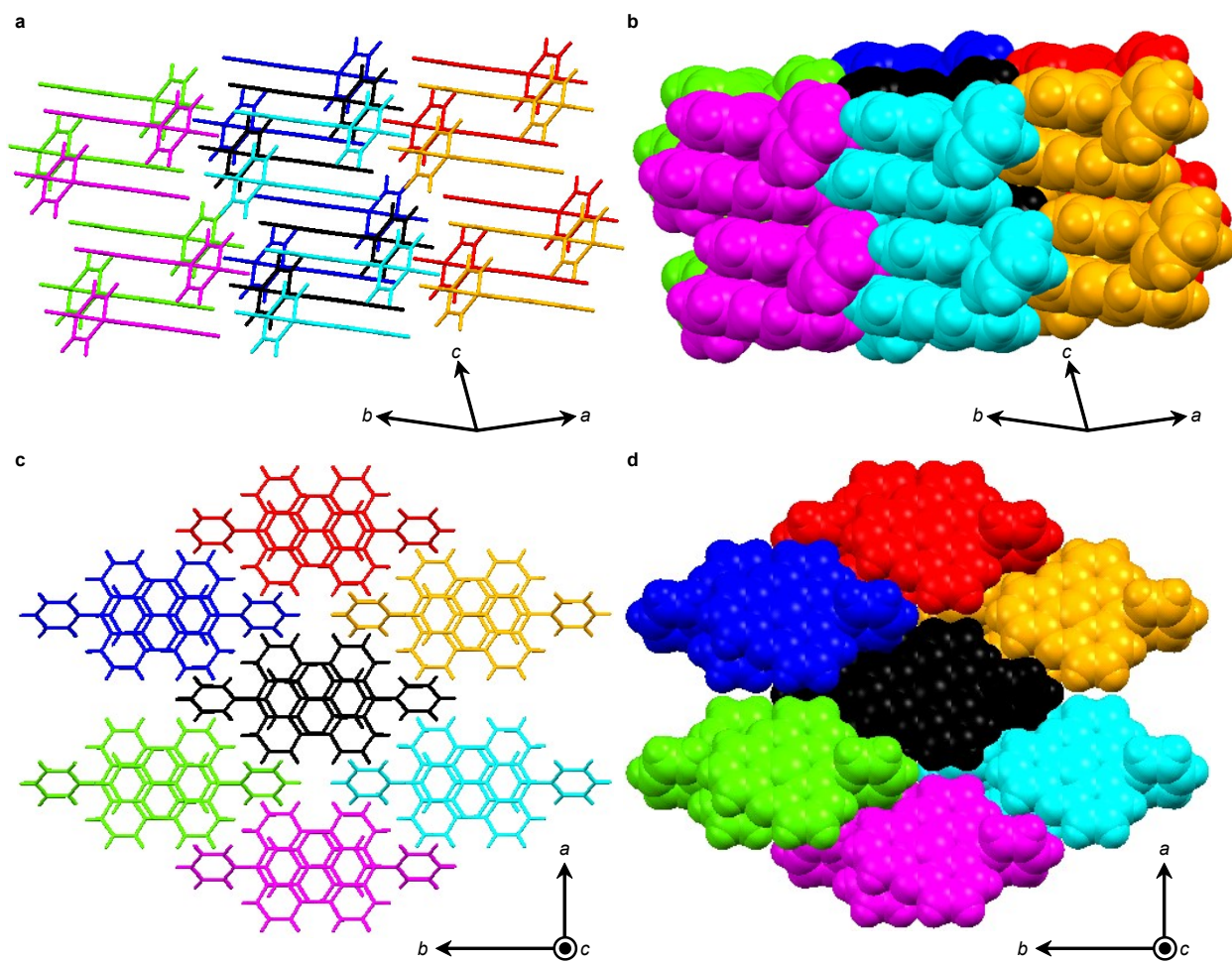
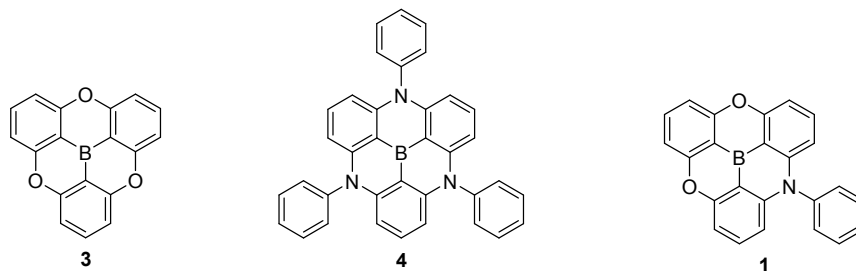


Figure S5 Crystal packing structure of **1** from the side (a, b) and the top (c, d). The molecules in (a, c) and (b, d) are depicted in capped sticks and spacefill models, respectively. Each color shows a rod unit arranged by π - π stacking interaction along the *c*-axis.

5. Photophysical data

Table S3 Comparison of photophysical data of **3**,^{S1} **4**,^{S5} and **1**.



	Absorption		Fluorescence			Phosphorescence ^f
	λ_{\max} / nm	$\log_{10} \varepsilon$	λ_{\max} / nm	k_r / s ⁻¹	k_{nr} / s ⁻¹	λ_{\max} / nm
3 ^{a,h}	338	4.39	386 ($\Phi_{\text{PL}} = 0.63$) ^{c,d}	1.02×10^8	0.59×10^8	400–414
4 ^{b,h}	384	4.51	403 ($\Phi_{\text{PL}} = 0.36$) ^c	0.75×10^8	1.32×10^8	427 ^g
1 ^a	380	4.34	406 ($\Phi_{\text{PL}} = 0.84$) ^{c,e}	0.98×10^8	0.19×10^8	426

^a 1×10^{-5} M, toluene solution. ^b 2×10^{-5} M, dichloromethane solution. ^c Absolute PL quantum yield.

^d $\lambda_{\text{ex}} = 320$ nm. ^e $\lambda_{\text{ex}} = 360$ nm. ^f at 77 K. ^g A poly(methyl methacrylate) film of **4** (1 wt%).

^h Photophysical data of **3** and **4** are referenced from refs. S1 and S5, respectively.

6. Theoretical calculation

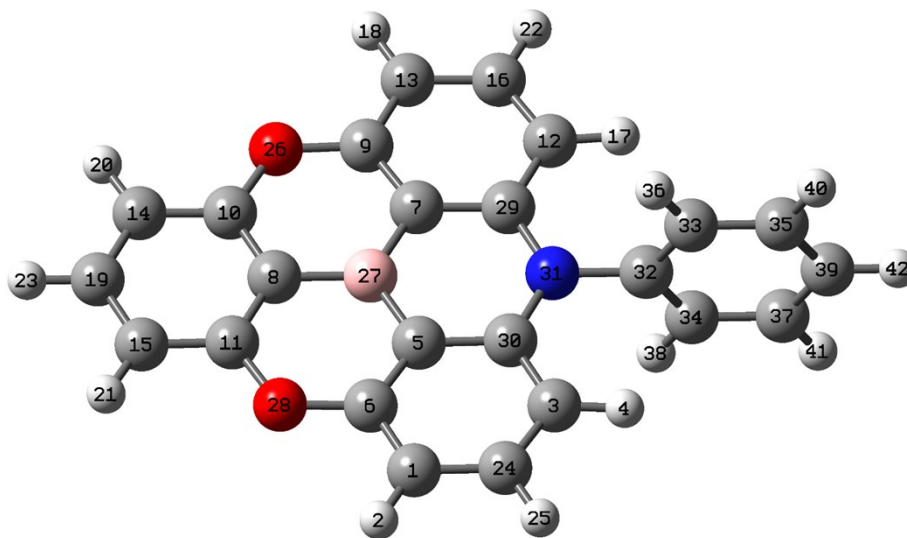
Theoretical calculations of **1** and **4** were carried out using the Gaussian 09 package^{S6} at the B3LYP/6-311G(d,p) level (in toluene, PCM model). After the optimization, the TD-DFT calculations were also conducted at the B3LYP/6-311G(d,p) level (in toluene, PCM model). The output views were obtained by the GaussView version 5.0.^{S7}

Table S4 Calculated excitation energy (E , λ) and oscillator strength (f) of **1** by DFT and TD-DFT at the B3LYP/6-311G(d,p) level (in toluene, PCM model).

Excited state	E / eV	λ / nm	f^a	Main CI coefficient ^b	
1	3.519	352	0.1961	HOMO→LUMO	0.69723
2	3.897	318	0.0639	HOMO-1→LUMO	0.68701
3	4.053	306	0.0233	HOMO→LUMO+1	0.69711
5	4.377	283	0.0118	HOMO-1→LUMO+1	0.27452
				HOMO→LUMO+3	0.62135
6	4.417	281	0.0967	HOMO→LUMO+4	0.57830
				HOMO→LUMO+5	0.36443
7	4.602	269	0.1163	HOMO-1→LUMO+3	0.25433
				HOMO→LUMO+4	-0.29088
				HOMO→LUMO+5	0.55479

^a Oscillator strength. ^b Coefficient of the wave function for each excitation.

Table S5 Optimized structure and selected bond lengths of **1** by DFT at the B3LYP/6-311G(d,p) level (in toluene, PCM model).



	Length / Å		Angle / °
C5–B27	1.47071	C5–B27–C7	120.750
C7–B27	1.47071	C5–B27–C8	119.625
C8–B27	1.47508	C7–B27–C8	119.625
C9–O26	1.39228		
C10–O26	1.38843		
C6–O28	1.39228		
C11–O28	1.38843		
C29–N31	1.41926		
C30–N31	1.41926		

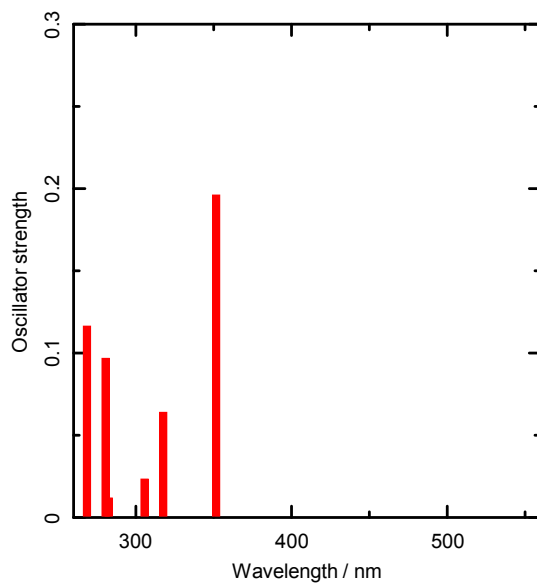


Figure S6 The theoretical excitation (oscillator strength vs. wavelength) of **1** obtained by TD-DFT calculation at the B3LYP/6-311G(d,p) level (in toluene, PCM model). The values of the oscillator strength are shown in Table S4.

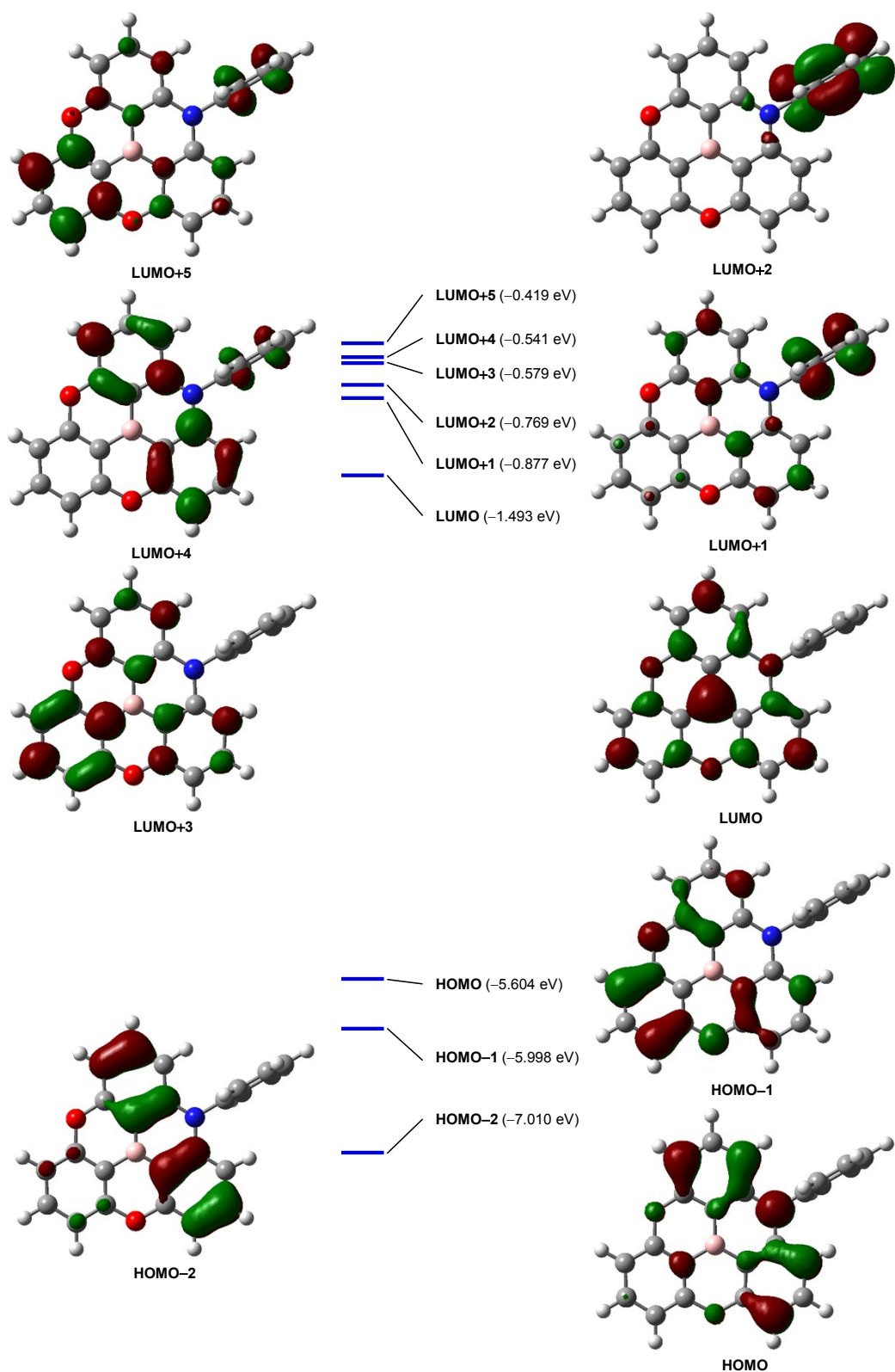


Figure S7 Kohn-Sham molecular orbitals for **1** at the B3LYP/6-311G(d,p) level (in toluene, PCM model).

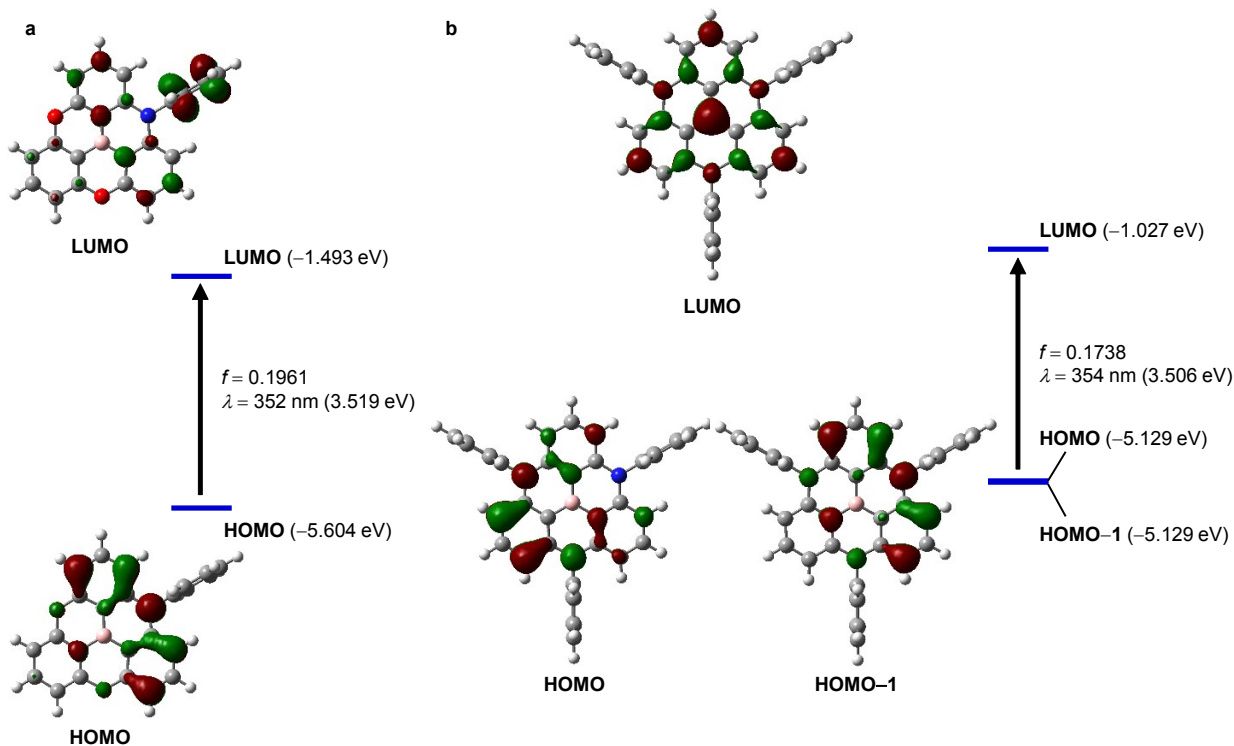


Figure S8 Energy diagram and Kohn-Sham molecular orbitals (HOMOs and LUMOs) for **1** and **4** at the B3LYP/6-311G(d,p) level (in toluene, PCM model). To compare **1**, **3**,^{S1} and **4** at the same method [the B3LYP/6-311G(d,p) level (in toluene, PCM model)], DFT and TD-DFT calculations of **4** were carried out. Hatakeyama et al. reported the result of calculation for **4** at the B3LYP/6-31G(d) level.^{S5}

Table S6 The energy and coordinates of **1** in the ground state optimized at the B3LYP/6-311G(d,p) level (in toluene, PCM model).

Energy = -1153.3570759 Hartrees

	Coordinates (Angstroms)		
	X	Y	Z
C	0.598721827	1.128113221	3.507363628
H	1.149582844	1.413300355	4.394391321
C	-1.574235408	0.764459112	2.377384913
H	-2.653033957	0.786894833	2.447932177
C	0.49200595	0.391843747	1.216933576
C	1.247590723	0.751872869	2.336698829
C	0.492015328	-0.391833057	-1.216916635
C	2.694089851	-3.3384×10 ⁻⁶	1.97494×10 ⁻⁵
C	1.247608729	-0.75186829	-2.3366741
C	3.357979587	-0.37538878	-1.166138014
C	3.357970602	0.37537725	1.166184189
C	-1.574217086	-0.764432969	-2.37738886
C	0.598748853	-1.128103961	-3.507345404
C	4.750778822	-0.379529061	-1.179056185
C	4.750769737	0.379507189	1.179116422
C	-0.803132603	-1.121912038	-3.488791826
H	-2.653015093	-0.786860483	-2.447947066
H	1.149616705	-1.413295563	-4.394367416
C	5.409228251	-1.33949×10 ⁻⁵	0.000033446
H	5.307249198	-0.664036663	-2.063031436

H	5.307233302	0.664010717	2.063097271
H	-1.325631527	-1.412734905	-4.393727112
H	6.493570261	-1.74271×10 ⁻⁵	3.89221×10 ⁻⁵
C	-0.803159486	1.121932038	3.488795796
H	-1.325665381	1.412758691	4.393725841
O	2.639266228	-0.739303556	-2.296960394
B	1.219011513	2.5054×10 ⁻⁶	1.21861×10 ⁻⁵
O	2.639248528	0.739297492	2.296999273
C	-0.915328449	-0.384605034	-1.195549194
C	-0.915337668	0.384626407	1.19555185
N	-1.576406082	1.32528×10 ⁻⁵	-2.0516×10 ⁻⁶
C	-3.018488362	1.87471×10 ⁻⁵	-9.4078×10 ⁻⁶
C	-3.712396077	-1.151273286	0.370645289
C	-3.712383504	1.151316062	-0.370671236
C	-5.105875884	-1.14904702	0.369883775
H	-3.158681037	-2.037957383	0.65611299
C	-5.105863335	1.149100435	-0.369923951
H	-3.158658776	2.037995928	-0.65613329
C	-5.803173128	2.93714×10 ⁻⁵	-2.36404×10 ⁻⁵
H	-5.645165036	-2.043994609	0.657992874
H	-5.645142714	2.044052138	-0.658038562
H	-6.887096206	3.35062×10 ⁻⁵	-2.91826×10 ⁻⁵

Table S7 The energy and coordinates of **4** in the ground state optimized at the B3LYP/6-311G(d,p) level (in toluene, PCM model).

Energy = -1575.8363413 Hartrees

	Coordinates (Angstroms)		
	X	Y	Z
C	2.818282934	2.507363667	-0.000190184
H	3.897743058	2.560240991	-0.000219698
C	0.6714447	3.712014161	-0.000196537
H	0.154090576	4.660892129	-0.000230751
C	0.726188917	1.29432196	-7.87505×10 ⁻⁵
C	2.136826417	1.279693765	-0.000112459
C	-1.484319106	-0.018291929	3.56492×10 ⁻⁵
C	0.757722463	-1.276367285	4.41548E-05
C	-2.146650067	-1.263878901	0.00011073
C	0.039700537	-2.49067342	0.000118965
C	2.167599569	-1.227180502	8.7701×10 ⁻⁶
C	-3.580850271	1.186979801	2.80159×10 ⁻⁵
C	-3.55070672	-1.274596156	0.000144698
C	0.762140609	-3.69466209	0.000160355
C	2.878880293	-2.437812767	5.07525×10 ⁻⁵
C	-4.223211296	-0.051862301	0.000102537
H	-4.166376932	2.0953781	-1.3067×10 ⁻⁶
H	-4.113757931	-2.19709023	0.000202005
C	2.156182753	-3.63156537	0.000125241
H	0.26816432	-4.655920747	0.000217961

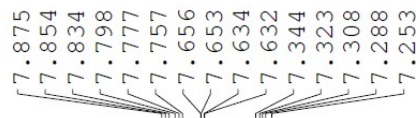
H	3.959308507	-2.464262644	2.70453×10 ⁻⁵
H	-5.308220272	-0.065152441	0.000129128
H	2.710177148	-4.564578955	0.000157471
C	2.066608223	3.683086829	-0.000229912
H	2.597600546	4.629381529	-0.000290023
B	-0.000129782	-0.000119132	0.000000695
C	-2.176948135	1.210707455	-6.5952×10 ⁻⁶
C	-0.021324825	2.490716246	-0.000119335
N	-1.434804408	2.415994369	-8.14027×10 ⁻⁵
C	-2.170587499	3.655141244	-0.000121181
C	-2.52546999	4.252831677	-1.20892153
C	-2.525414479	4.252941653	1.208641071
C	-3.236799972	5.451065136	-1.207135942
H	-2.242517023	3.776122362	-2.140021958
C	-3.236744832	5.451174769	1.206779213
H	-2.242418995	3.776316966	2.139771918
C	-3.592945204	6.051106734	-0.000197466
H	-3.512080194	5.914687915	-2.147504695
H	-3.511982136	5.914882932	2.147118439
H	-4.146235502	6.983282562	-0.000227149
N	-1.375153682	-2.45060641	0.000149207
C	-2.080289535	-3.707463621	0.000222954
C	-2.420275699	-4.313712033	1.209038259

C	-2.420330551	-4.313822893	-1.208521349
C	-3.101971292	-5.529049732	1.207298071
H	-2.149054134	-3.830169724	2.140109019
C	-3.102026106	-5.529160418	-1.206638681
H	-2.149151266	-3.830366058	-2.139648834
C	-3.443302526	-6.137678254	0.000365342
H	-3.365710311	-5.999283292	2.14769564
H	-3.365807944	-5.999480253	-2.146981109
H	-3.973577445	-7.083134446	0.000420714
N	2.809580584	0.034314378	-6.76185×10 ⁻⁵
C	4.250616781	0.052165646	0.000101192
C	4.945732986	0.060979402	1.20865846
C	4.94567825	0.06085814	1.208893152
C	6.339097997	0.0784293	1.206806554
H	4.391455532	0.054141185	2.139791035
C	6.339043357	0.078308349	-1.207106064
H	4.39135866	0.053926662	-2.139999948
C	7.036753288	0.087202897	0.00016601
H	6.878279343	0.085298425	2.147161112
H	6.878182169	0.085083236	-2.147485697
H	8.120686825	0.100824804	-0.000191253

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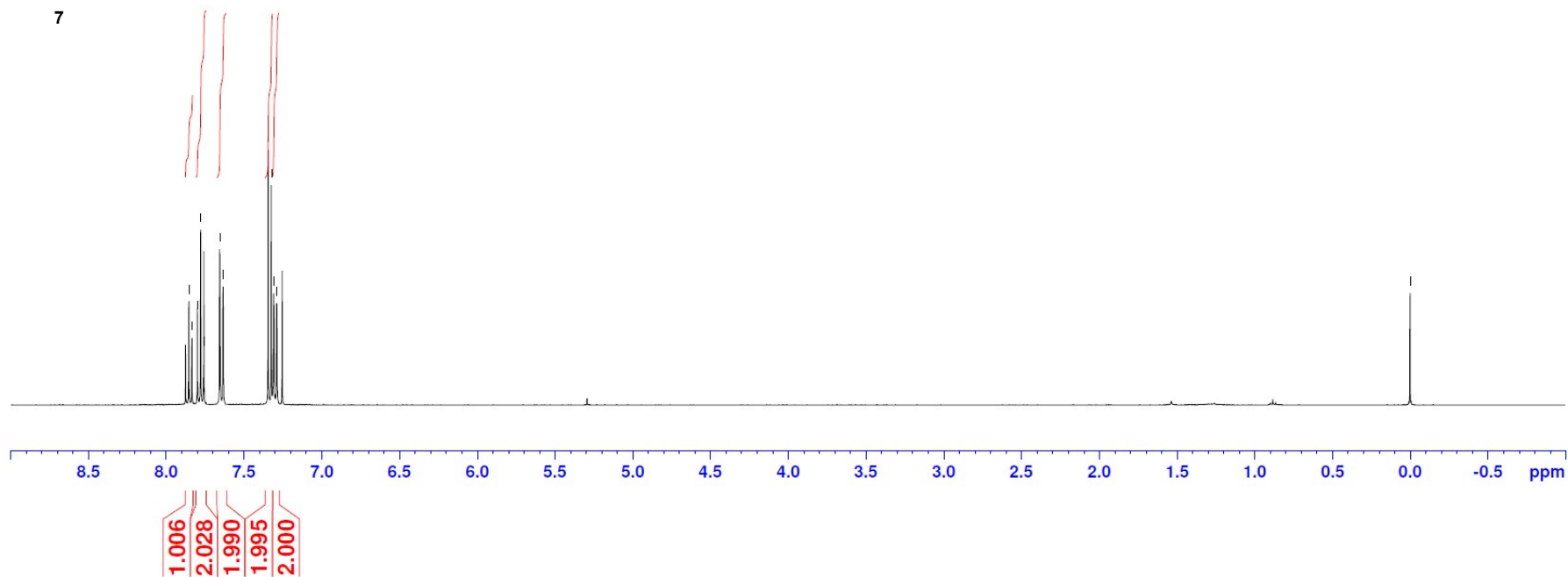
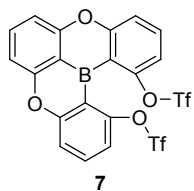
8. ^1H , ^{13}C , and ^{11}B NMR spectra of synthesized compounds



— -0.000

8.1. 5,9-Dioxa-13b-boranaphtho[3,2,1-*de*]anthracene-1,13-diyl bis(trifluoromethanesulfonate) (7).

[^1H NMR spectrum]

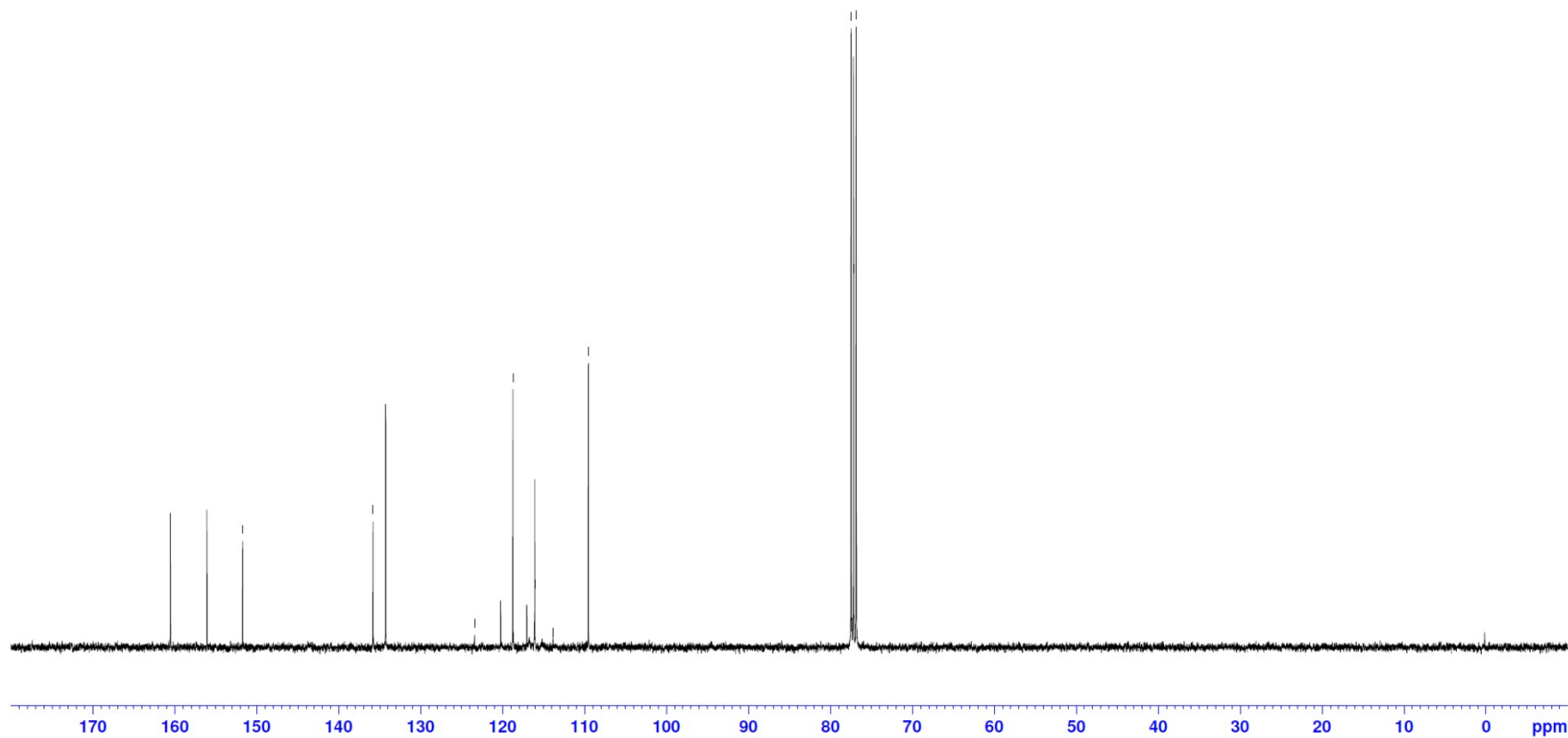
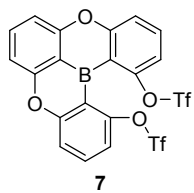


[¹³C NMR spectrum]

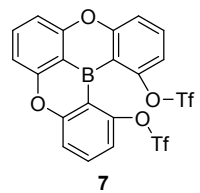
— 160.539
— 156.068
— 151.727

∩ 135.817
∩ 134.273
∩ 123.417
∩ 120.228
∩ 118.744
∩ 117.035
∩ 116.079
∩ 113.842
∩ 109.531

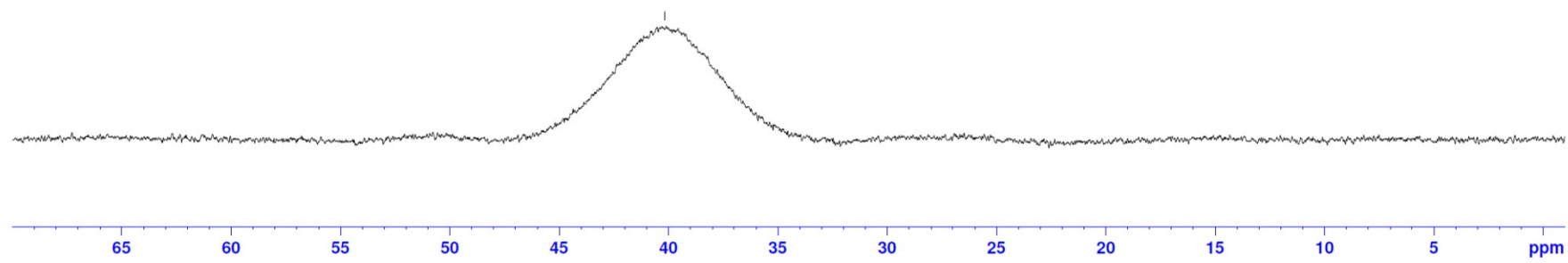
∩ 77.477
∩ 77.160
∩ 76.842



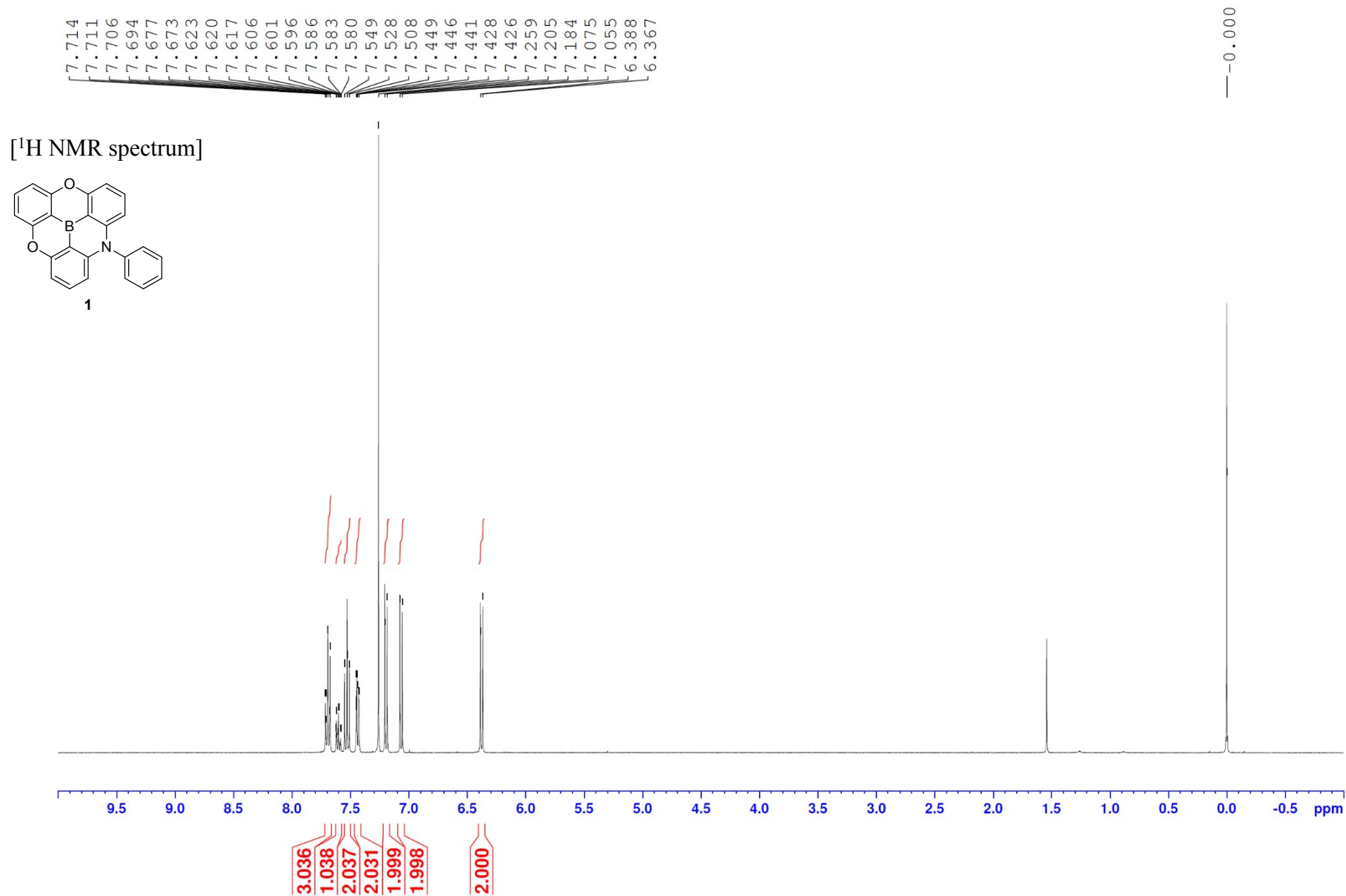
[¹¹B NMR spectrum]



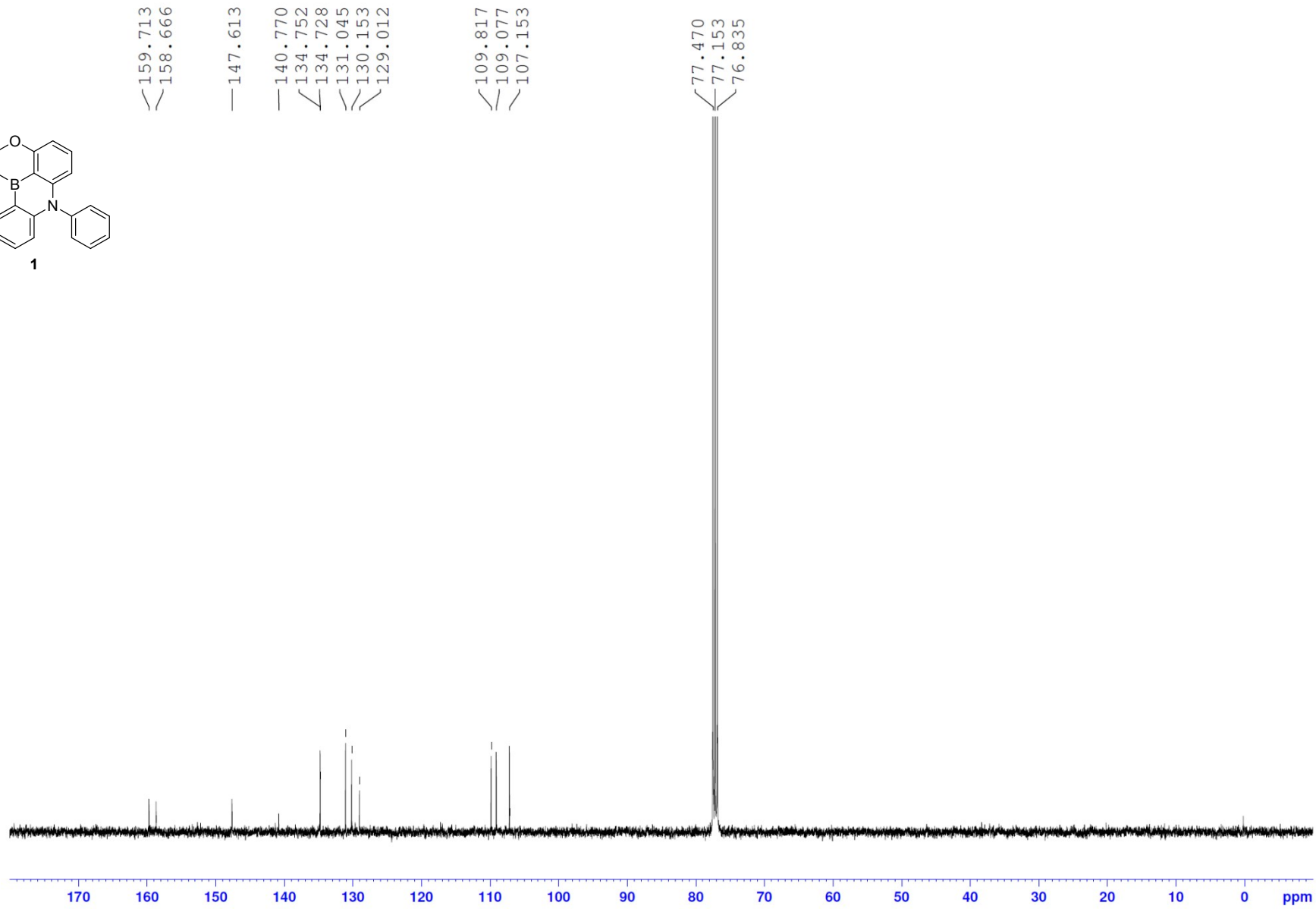
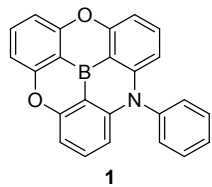
—40.179



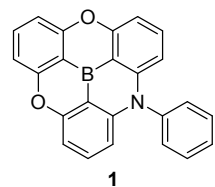
8.2. 12-Phenyl-12*H*-4,8-dioxa-12-aza-3a²-boradibenzo[*cd,mn*]pyrene (1).



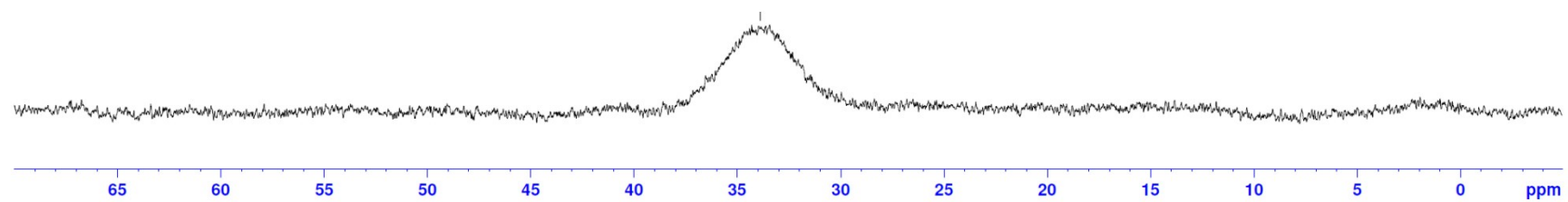
[¹³C NMR spectrum]



[¹¹B NMR spectrum]



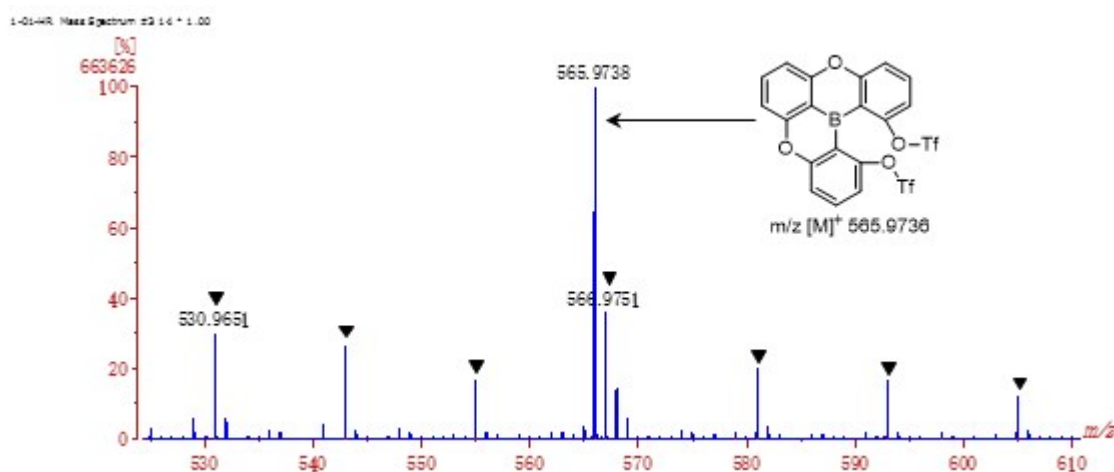
— 33.914



9. HRMS spectra of synthesized compounds

9.1. 5,9-Dioxa-13b-boranaphtho[3,2,1-*de*]anthracene-1,13-diyl bis(trifluoromethanesulfonate) (7).

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



9.2. 12-Phenyl-12*H*-4,8-dioxa-12-aza-3a²-boradibenzo[*cd,mn*]pyrene (1).

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

