Electronic Supplementary Information (ESI)

New Journal of Chemistry

BODIPY Derivatives Incorporating Dithiacrown Ether Substituents Showing Combined Environmental Polarity and Heavy Metal Cation Sensing Functionality

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1. Experimental Methods and Synthetic Procedures

All chemicals were reagent grade, and used without further purification. All reactions were performed under nitrogen atmosphere unless stated otherwise. 2-methyl-4,5-dimethoxyphenylboronic acid,[1] 2,8-dibromoBODIPY[2] and 3,12-dioxa-6,9-dithiatetradecane-1,14-diyl bis(4-methylbenzenesulfonate)[3] were prepared according to the literature procedures.

Column chromatography was performed using Kanto Chemical silica gel 60 N (spherical, neutral) or Wako Chemical alumina (activated, about 200 mesh). Gel-permeation chromatography (GPC) was performed at room temperature using columns JAIGEL 2H-1H on a Ja[1]pan Analytical Industry LC-908 recycling preparative HPLC system equipped with a variable-wavelength UV-vis detector. ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz, or a Bruker Avance 600 spectrometer at 600 MHz. 13C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 100 MHz. In both NMR measurements, tetramethylsilane was used as an internal standard. UV-Vis spectra were recorded using a JASCO V-660 spectrophotometer. Fluorescence spectra were recorded using a Jasco FP-8600 spectrofluorometer. Absolute quantum yields were measured using a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-02. Mass spectra (ESI-TOF, positive mode) were recorded on an Applied Biosystems QStar Pulsar *i* spectrometer. MALDI-TOF spectra were recorded on a Bruker BIFLES III with dithranol as matrix. Elemental analyses were performed at the Chemical Analysis Center, University of Tsukuba.

X-ray Crystallography

X-ray diffraction measurements were performed using a Bruker APEXII ULTRA. The X-ray diffraction intensities were collected on a CCD diffractometer at 120 K using MoKα (graphite-monochromated, λ = 0.71073 Å) radiation. The data were integrated with SAINT (Bruker, 2004), and an empirical absorption correction (SADABS) was applied. The structure was solved by the direct method of SHELXS-97 and refined using the SHELXL-2014 program. All of the positional parameters and thermal parameters of non-hydrogen atoms were anisotropically refined on F^2 by

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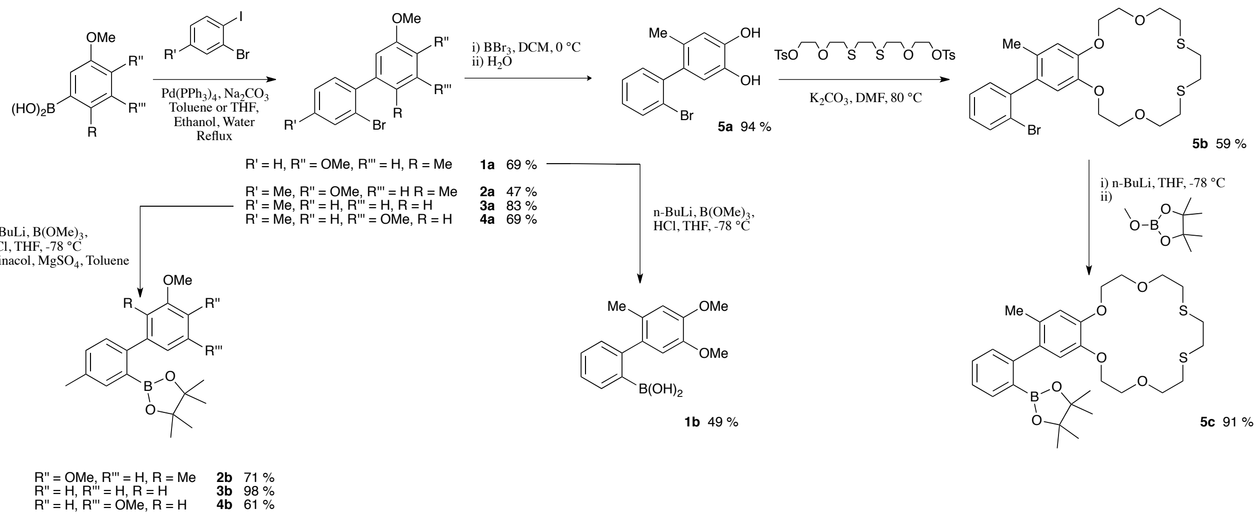
[1] F. Dinnino *et al.*, PCT. Int. Appl., 207139729, 2007.

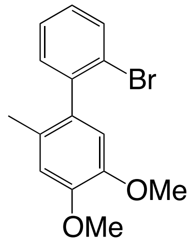
[2] Y. Hayashi *et al.*, *Org. Lett.*, 2008, 13, 2992.

[3] H. J. Kim *et al.*, *Bull. Korean Chem. Soc.*, 2008, **29**, 1831.

the full-matrix least-squares method. Hydrogen atoms were placed at the calculated positions and refined riding on their corresponding carbon atoms. The crystallographic data were deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 1026064 and 1026065. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).



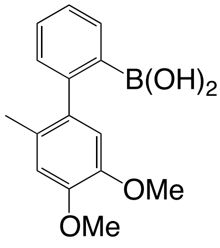
Scheme S1 Synthesis of the boronic acids and boronic acid esters **1-4b**, **5c**.



1a

*2-Methyl-4,5-dimethoxy-2'-bromo-1,1'-biphenyl (**1a**)*

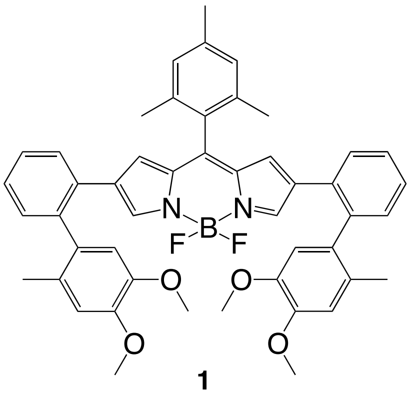
A mixture of 1-bromo-2-iodobenzene (2.0 g, 7.07 mmol) and tetrakistriphenylphosphinepalladium (0) (100 mg, 0.8 mmol) in toluene (60 mL) was sparged with N_2 for 10 minutes. A solution of 2-methyl-4,5-dimethoxyphenylboronic acid (1.39 g, 7.07 mmol) in ethanol (10 mL) was added followed by a solution of sodium carbonate (2.2 g, 21 mmol) in water (10 mL) and the entire mixture sparged with N_2 for a further 10 minutes. The mixture was heated under reflux under a N_2 atmosphere for 48 hours. Ethyl acetate (30 mL) and water (20 mL) were added and the organic layer separated, washed with water, brine, dried over magnesium sulphate, filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography [silica gel, ethyl acetate-hexane 4:1] twice to give **1a** as a viscous oil which slowly crystallised on standing. Yield 1.5 g (69 %) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, J = 7.6 Hz, 1H), 7.37 (m, 1H), 7.25 (m, 2H), 6.80 (s, 1H), 6.67 (s, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 2.08 (s, 3H) ppm; ESI-MS for $C_{15}H_{15}BrO_2Na$ calculated m/z = 329.02; found = 329.01 $[M+Na]^+$



1b

*2-Methyl-4,5-dimethoxy-1,1'-biphenyl-2'-boronic acid (**1b**)*

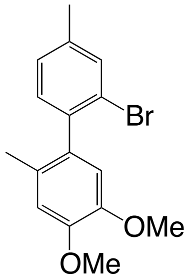
A solution of **1a** (1.5 g, 4.9 mmol) in dry THF (25 mL) was cooled to -78 °C under an argon atmosphere. n-BuLi (1.64 M in hexane, 3.71 mL, 6.08 mmol) was slowly added and the mixture stirred at -78 °C for 1 hour. Trimethylborate (0.9 mL, 6.1 mmol) was added and the mixture stirred for a further 2 hours at -78 °C. Dilute hydrochloric acid (2N, 9 mL) was added and the solution allowed to warm to room temperature overnight. Ethyl acetate (10 mL) and water (10 mL) were added and the organic layer separated, washed with water, saturated sodium bicarbonate solution, brine, dried over sodium carbonate, filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography [silica gel, ethyl acetate-hexane 1:3 eluting to 1:1] to give the product as a white solid. Used immediately in the following step. Yield 0.65 g (49%)



1

*Compound **1***

A mixture of 2,8-dibromo-BODIPY (232 mg, 0.5 mmol), boronic acid **1b** (325 mg, 1.2 mmol), cesium carbonate (650 mg, 2.0 mmol), tri-*t*-butylphosphonium tetrafluoroborate (58 mg, 0.2 mmol) and tris(dibenzylideneacetone)dipalladium (0) (52 mg, 5.7×10^{-5} mol) in THF (120 mL) and water (0.8 mL) was sparged with N_2 for 10 minutes. The mixture was stirred at room temperature overnight and the solvent removed under reduced pressure. The crude product was purified by column chromatography [silica gel, dichloromethane eluting to 3 % ethyl acetate in dichloromethane] and again [silica gel, dichloromethane eluting to 1 % ethyl acetate in dichloromethane] to give **1** as a purple solid. Yield 289 mg (76 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.00 (s, 2H), 7.70 (m, 2H), 7.35 (m, 4H), 7.16 (m, 2H), 6.84 (s, 2H), 6.69 (s, 2H), 6.56 (s, 2H), 5.86 (s, 2H), 3.76 (s, 6H), 3.52 (s, 6H), 2.33 (s, 3H), 1.75 (s, 6H), 1.70 (s, 6H) ppm; ^{13}C NMR (150 MHz, DMSO) δ = 148.24, 146.77, 145.38, 143.97, 139.13, 138.06, 134.85, 134.56, 132.98, 132.36, 131.12, 131.09, 130.48, 128.37, 127.70, 128.50, 127.45, 127.34, 126.79, 126.43, 113.57, 113.24, 55.74, 55.31, 20.65, 19.03, 18.91, 18.78, 18.74 ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ = 0.01 (t, J_{BF} = 25 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -145.92 (mult) ppm; HIRES ESI-MS for $C_{48}H_{45}BF_2N_2O_4Na$ m/z = 785.3333; found = 785.3326 $[M+Na]^+$.

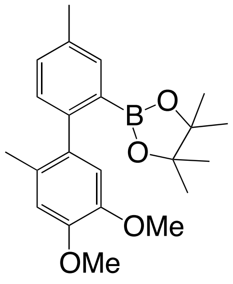


2a

2-Bromo-2’,4-dimethyl-4’,5’-dimethoxy-2,2’-biphenyl (**2a**)

A 100 mL three-neck flask was charged with 2-methyl-4,5-dimethyoxyphenylboronic acid (0.96 g, 4.88 mmol), 3-bromo-4-iodotoluene (1.82 g, 6.13 mmol), sodium carbonate (2.29 g, 21.6 mmol), tetrakis(triphenylphosphine)palladium (0) (152 mg, 0.132 mmol). The flask was evacuated then refilled with argon. Degassed tetrahydrofuran (45 mL), and degassed water (15 mL) were added and the mixture stirred at 80 °C for 2 days under argon. After cooling, water (50 mL) was added and extracted with dichloromethane. The combined organic layers were washed with brine (100 mL), dried over sodium sulphate, and evaporated. The resulting oil was purified by column chromatography [silica gel, chloroform-hexane 1:1] to give **2a** as a brown oil. Yield 0.73g (47 %). ^{1}H

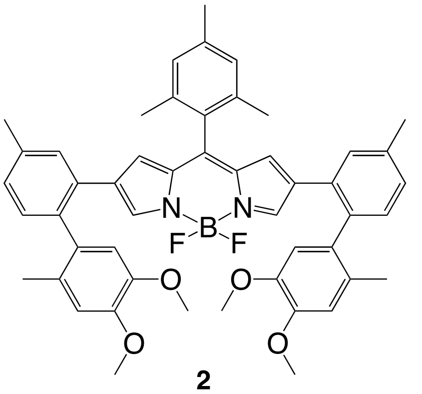
NMR (400 MHz, $CDCl_3$) δ = 7.49 (s, 1H), 7.15 (d, J = 7.7 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 6.76 (s, 1H), 6.63 (s, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 2.38 (s, 3H), 2.06 (s, 3H) ppm. ESI-MS observed *m/z* 343.03 ($[M+Na]^+$).



2b

2-(4',5'-dimethoxy-2',4-dimethyl-1,1'-biphenyl-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***2b***

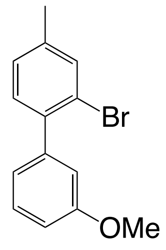
A 50 mL two-neck flask was charged with **2a** (380 mg, 1.18 mmol). The flask was evacuated then refilled with argon. Dry THF (10 mL) was added. To the stirred solution was added n-butyllithium (1.60 M in hexane, 0.82 mL, 1.3 mmol) at -78 °C. After stirring for 30 min. at -78°C, trimethyl borate (0.48 mL, 4.34 mmol) was added dropwise at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 20 h. Dilute hydrochloric acid (1 M) was added to make the aqueous layer acidic (pH = 3). The solution was extracted with ethyl acetate (3 × 20 mL) and the combined organic layers were washed with brine (50 mL), dried over sodium sulphate and evaporated to give a yellow oil. The obtained crude boronic acid was dissolved in toluene (10 mL), pinacol (136 mg, 1.15 mmol) and magnesium sulphate (288 mg, 2.39 mmol) were added and the mixture heated under reflux for 15 h. After cooling to room temperature, the solution was filtered to remove excess magnesium sulphate. The solvent was removed by evaporation and the residue was purified by column chromatography [silica gel, ethyl acetate-hexane 1:4] to give **2b** as a colourless oil. Yield 308 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (s, 1H), 7.52 (s, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.70 (s, 1H), 6.68 (s, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 2.38 (s, 3H), 2.05 (s, 3H), 1.10 (s, 12H) ppm.



2

Compound **2**

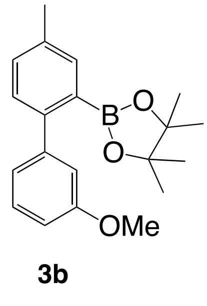
A 200 mL three-neck flask was cherged with **2b** (308 mg, 0.836 mmol), 2,8-dibromo-BODIPY (163 mg, 0.348 mmol), tri-t-butylphosphonium tetrafluoroborate (40.8 mg, 0.141 mmol), cesium carbonate (452 mg, 1.39 mmol) and tris(dibenzylideneacetone)dipalladium (0) (32.5 mg, 0.0348 mmol). The flask was evacuated then refilled with argon. Degassed THF (75 mL) and degassed H_2O (0.50 mL) were added and the mixture was stirred at room temperature for 13 h. The reaction mixture was filtered through a pad of Celite eluting with dichloromethane. After removal of solvents under reduced pressure, the residue was purified by column chromatography [silica gel, ethyl acetate-hexane 1:2] to give **154** as a purple solid. Yield 245 mg, 0.310 mmol, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (s, 2H), 7.28 (s, 2H), 7.11 (d, J = 7.6 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 6.84 (s, 2H), 6.57 (s, 2H), 6.54 (s, 2H), 6.01 (s, 2H), 3.88 (s, 6H), 3.67 (s, 6H), 2.38 (s, 6H), 2.36 (s, 3H), 1.85 (s, 6H), 1.79 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.30, 146.96, 145.96, 143.51, 138.47, 137.19, 136.88, 136.08, 135.98, 135.90, 135.19, 133.54, 132.88, 131.91, 131.89, 130.72, 129.33, 128.27, 128.10, 127.98, 127.79, 127.73, 127.69, 127.03, 113.41, 112.96, 77.35, 77.23, 77.03, 76.71, 56.06, 55.85, 21.17, 21.13, 19.67, 19.58, 19.50, 19.31 ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ = -0.03 (t, J_{BF} = 29 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -146.08 (mult) ppm; MALDI-TOF MS for $C_{50}H_{49}BF_2N_2O_4$ calculated m/z = 790.38; found = 790.43; Elemental analysis for $C_{50}H_{49}N_2O_4BF_2{\bullet}2.5H_2O$: calculated C, 71.85; H, 6.51; N, 3.35; Found C, 72.01; H, 6.02; N, 3.20.



3a

2-Bromo-4-methyl-3’-methoxy-2,2’-biphenyl (**3a**)

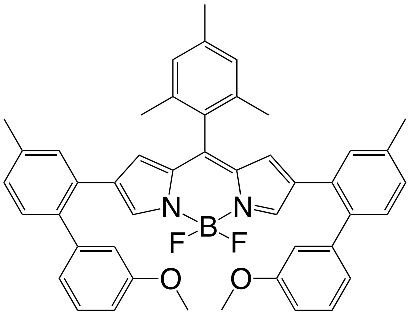
A 200 mL three-neck flask was charged with 3-methoxyphenylboronic acid (2.01 g, 13.2 mmol), 3-bromo-4-iodotoluene (4.32 g, 14.6 mmol), sodium carbonate (5.60 g, 52.7 mmol), tetrakis(triphenylphosphine)palladium (0) (306 mg, 0.265 mmol). The flask was evacuated then refilled with argon. Degassed toluene (45 mL), degassed ethanol (30 mL), and degassed water (15 mL) were added and the mixture was stirred at 80 °C for 3 days under argon. After cooling, water (100 mL) was added and extracted with dichloromethane. The combined organic layers were washed with brine (100 mL), dried over sodium sulphate, and evaporated. The resulting oil was purified by column chromatography [silica gel, chloroform-hexane 1:3] to give **3a** as a colourless oil. Yield 3.04 g (83 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (s, 1H), 7.32 (dd, J = 8.4 Hz, 8.4 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 6.93-6.90 (m, 2H), 3.84 (s, 3H), 2.37 (s, 3H) ppm.



3b

*2-(3’-methoxy-4-methyl-1,1’-biphenyl-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**)*

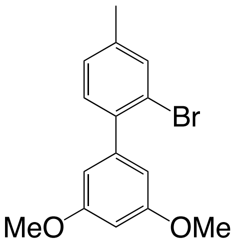
A 100 mL three-neck flask was charged with **3a** (1.02 g, 3.68 mmol). The flask was evacuated then refilled with argon. Dry THF (25 mL) was added. To the stirred solution was added n-butyllithium (1.60 M in hexane, 2.50 mL, 4.00 mmol) at -78 °C. After stirring for 30 min. at -78 °C, trimethyl borate (1.50 mL, 10.1 mmol) was added dropwise at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 20 h. Dilute hydrochloric acid (1 M) was added to make the aqueous layer acidic (pH = 2). The solution was extracted with ethyl acetate (3 × 30 mL) and the combined organic layers were washed with brine (80 mL), dried over sodium sulphate and evaporated to give a yellow oil. The obtained crude boronic acid was dissolved in toluene (25 mL), pinacol (434 mg, 3.67 mmol) and magnesium sulphate (860 mg, 7.14 mmol) were added and the mixture heated under reflux for 22.5 h. After cooling to room temperature, the solution was filtered to remove excess magnesium sulphate. The solvent was removed by evaporation and the residue was purified by column chromatography [silica gel, ethyl acetate-hexane 1:9] to give **3b** as a yellow oil. Yield 1.17 g (98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.50 (s, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.25-7.26 (m, 2H), 6.96 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 1.8 Hz, 1H), 6.86 (dd, J = 1.8 Hz, 7.5 Hz, 1H), 3.83 (s, 3H), 2.38 (s, 3H), 1.21 (s, 12H) ppm.



3

Compound **3**

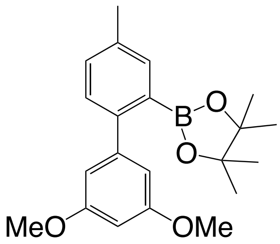
A 500 mL three-neck flask was charged with **3b** (1.17 g, 3.30 mmol), 2,8-dibromo-BODIPY (643 mg, 1.37 mmol), tri-t-butylphosphonium tetrafluoroborate (159 mg, 0.548 mmol), cesium carbonate (1.78 g, 5.46 mmol) and tris(dibenzylideneacetone)dipalladium (0) (128 mg, 0.140 mmol). The flask was evacuated then refilled with argon. Degassed THF (300 mL) and degassed H_2O (2.0 mL) were added and the mixture stirred at room temperature for 3 days. The reaction mixture was filtered through a Celite pad eluting with dichloromethane. After removal of solvents under reduced pressure, the residue was purified by column chromatography [silica gel, ethyl acetate – hexane 1:6] to give **3** as a purple solid. Yield 941 mg (98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.58 (s, 2H), 7.24 (s, 2H), 7.20 (d, J = 5.2 Hz, 2H), 7.16 (t, J = 7.8 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 6.83 (s, 2H), 6.79 (d, J =7.8 Hz, 2H), 6.72 (d, J = 7.8 Hz, 2H), 6.68 (s, 2H), 6.12 (s, 2H), 3.69 (s, 6H), 2.38 (s, 6H), 2.34 (s, 3H), 1.91 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 19.8, 21.0, 21.1, 55.1, 112.9, 114.9, 121.9, 127.5, 127.8, 128.3, 129.1, 129.2, 129.4, 130.3, 131.3, 133.6, 135.2, 136.1, 137.4, 137.5, 138.4, 142.8, 144.0, 146.1, 159.4 ppm ; ^{11}B NMR (128 MHz, $CDCl_3$) δ = 0.00 (t, J_{BF} = 29 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -146.10 (q, J_{BF} = 29 Hz) ppm; MALDI-TOF MS for $C_{46}H_{41}BF_2N_2O_2$ calculated m/z = 702.6; found: 702.4 [M^+]; Elemental Analysis for $C_{46}H_{41}N_2O_2BF_2$: calculated C, 78.63; H, 5.88; N, 3.99; Found C, 78.55; H, 6.11; N, 3.96.



4a

2-Bromo-4-methyl-3’,5’-dimethoxy-2,2’-biphenyl (**4a**)

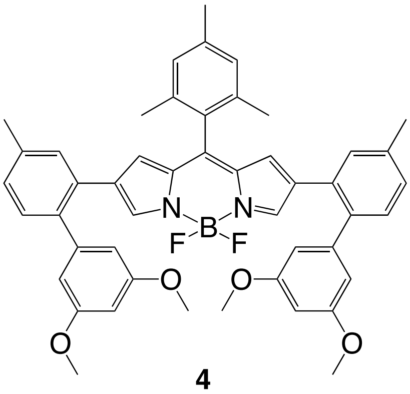
A 100 mL three-neck flask was charged with 3,5-dimethoxyphenylboronic acid (100 mg, 0.555 mmol), 3-bromo-4-iodotoluene (205 mg, 0.690 mmol), sodium carbonate (232 mg, 2.19 mmol), tetrakis(triphenylphosphine palladium (0) (31 mg, 0.026 mmol). The flask was evacuated then refilled with argon. Degassed toluene (3.0 mL), degassed ethanol (2.0 mL), and degassed water (1.0 mL) were added and the mixture stirred at 80 °C for 2 days under argon. After cooling, water (20 mL) was added and extracted with dichloromethane. The combined organic layer was washed with brine (60 mL), dried over sodium sulphate, and evaporated. The resulting oil was purified by column chromatography [silica gel, chloroform-hexane 1:1] to give **4a** as a colourless oil. Yield 117 mg, (69 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.49 (s, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.53 (d, J = 2.2 Hz, 2H), 6.48 (dd, J = 2.2 Hz, 2.2 H, 1H), 3.82 (s, 6H), 2.37 (s, 3H) ppm; ESI-MS observed m/z 307.032 ($[M+H]^+$).



4b

2-(3’,5’-dimethoxy-4-methyl-1,1’-biphenyl-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4b**)

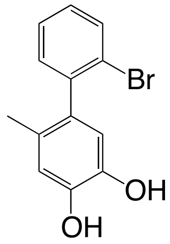
A 100 mL three-neck flask was charged with **4a** (505 mg, 1.64 mmol). The flask was evacuated then refilled with argon. Dry THF (20 mL) was added. To the stirred solution was added n-butyllithium (1.60 M hexane solution 1.10 mL, 1.76 mmol) at -78 °C. After stirring for 30 min. at -78°C, trimethyl borate (0.65 mL, 5.9 mmol) was added dropwise at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 20 h. Dilute hydrochloric acid (1 M) was added to make the aqueous layer acidic (pH = 3). The solution was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over sodium sulphate and evaporated to give a yellow oil. The obtained crude boronic acid was dissolved in toluene (20 mL), pinacol (194 mg, 1.64 mmol) and magnesium sulphate (568 mg, 4.72 mmol) were added and the mixture heated under reflux for 25 h. After cooling to room temperature, the solution was filtered to remove excess magnesium sulphate. The solvent was removed by evaporation and the residue was purified by column chromatography [silica gel, ethyl acetate-hexane 1:9] to give **4b** as a colourless oil. Yield 353 mg, (61%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.48 (s, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 6.53 (d, J = 2.2 Hz, 2H), 6.43 (dd, J = 2.2 Hz, 2.2 H, 1H), 3.81 (s, 6H), 2.38 (s, 3H), 1.22 (s, 12H) ppm.



4

Compound **4**

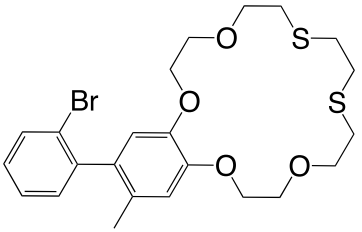
A 500 mL three-neck flask was cherged with **4b** (678 mg, 1.91 mmol), 2,8-dibromo-BODIPY (373 mg, 0.797 mmol), tri-t-butylphosphonium tetrafluoroborate (92.4 mg, 0.318 mmol), cesium carbonate (1.04 g, 3.19 mmol) and tris(dibenzylideneacetone)dipalladium (0) (72.8 mg, 0.0795 mmol). The flask was evacuated then refilled with argon. Degassed THF (170 mL) and degassed H_2O (1.1 mL) were added and the mixture was stirred at room temperature for 24 h. The reaction mixture was filtered through a Celite pad eluting with dichloromethane. After removal of solvents under reduced pressure, the residue was purified by column chromatography [silica gel, ethyl acetate-hexane 5:1 eluting to 3:1] to give **4** as a purple solid. Yield 525 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (s, 2H), 7.24 (s, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 6.86 (s, 2H), 6.36 (dd, J = 2.4 Hz, 2.4 Hz, 2H), 6.29 (d, J = 2.4 Hz, 4H), 3.66 (s, 12H), 6.18 (s, 2H), 2.38 (s, 6H), 2.35 (s, 3H), 1.92 (s, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 19.6, 21.1, 21.1, 55.2, 99.5, 107.7, 127.4, 127.9, 128.3, 129.1, 129.5, 130.2, 131.2, 133.6, 135.2, 136.1, 137.5, 137.6, 138.5, 143.3, 144.1, 145.9, 160.6 ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ = 0.03 (t, J_{BF} = 29 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -146.04 (q, J_{BF} = 29 Hz) ppm; MALDI-TOF MS for $C_{48}H_{45}BF_2N_2O_4$ calculated m/z = 762.34; found = 762.45 $[M]^-$; Elemental analysis for $C_{48}H_{45}N_2O_4BF_2{\bullet}0.5H_2O$: calculated C, 74.71; H,6.01; N,3.63; Found C, 74.92; H, 6.01; N, 3.63.



5a

*2-Methyl-4,5-dihydroxy-2'-bromo-1,1'-biphenyl (**5a**)*

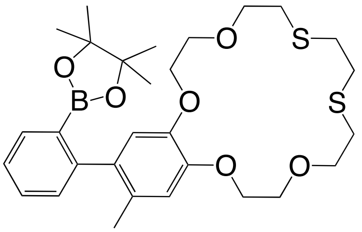
A solution of **1a** (0.27 g, 0.88 mmol) in dichloromethane was cooled to 0 °C under an argon atmosphere. Boron tribromide (0.5 g, 5.27 mmol) was added and the solution stirred at 0 °C for 4 hours after which ice-water (15 mL) was added. The organic layer was separated, washed with water, saturated aqueous sodium bicarbonate solution, brine, dried over sodium sulphate, filtered and the solvent removed under reduced pressure to give a colourless oil. Yield 0.23 g (94 %) ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.65 (m, 1H), 7.35 (m, 1H), 7.24 (m, 2H), 6.81 (s, 1H), 6.67 (s, 1H), 5.23 (s, 1H), 5.05 (s, 1H), 2.01 (s, 3H) ppm. ESI-MS for $C_{13}H_{11}BrO_2Na$ calculated *m/z* = 300.98; found = 300.96 [M+Na]$^+$



5b

*18-(2-bromophenyl)-19-methyl-2,3,5,6,8,9,11,12,14,15-decahydrobenzo[e][1,4,7,10,13,16]tetraoxadithiacyclooctadecine (**5b**)*

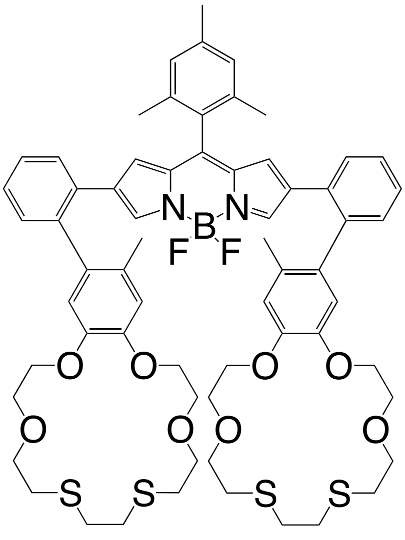
A mixture of catechol **5a** (0.46 g, 1.66 mmol), 3,12-dioxa-6,9-dithiatetradecane-1,14-diyl bis(4-methylbenzenesulfonate) (970 mg, 1.68 mmol) and potassium carbonate (464 mg, 3.36 mmol) in dimethylformamide (50 mL) was heated at 80 °C overnight. The mixture was allowed to cool to room temperature and then diethyl ether (60 mL) and water (60 mL) added. The water layer was separated and washed with two portions of diethyl ether. The organic extracts were combined, washed with water, brine, dried over sodium sulphate, filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography [silica gel, ethyl acetate-hexane 1:2] to give a **5b** as a colourless oil which crystallised on standing. Yield 0.5 g (59 %) ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.66 (m, 1H), 7.36 (m, 1H), 7.23 (m, 2H), 6.79 (s, 1H), 6.68 (s, 1H), 4.34 (t, J = 2.8 Hz, 2H), 4.17 (t, J = 3.2 Hz, 2H), 3.93, (t, J = 4.4 Hz, 2H) 3.88 (m, 6H), 2.92 (s, 4H), 2.79 (m, 4H) 2.05 (s, 3H) ppm; ESI-MS for $C_{23}H_{29}BrO_4S_2Na$ calculated *m/z* = 537.06; found = 537.06 [M+Na]$^+$



5c

*4,4,5,5-tetramethyl-2-(2-(19-methyl-2,3,5,6,8,9,11,12,14,15-decahydrobenzo[e][1,4,7,10,13,16]tetraoxadithiacyclooctadecin-18-yl)phenyl)-1,3,2-dioxaborolane (**5c**)*

A solution of crown ether **5b** (152 mg, 0.30 mmol) in THF (14 mL) was cooled to -78 °C under an argon atmosphere. n-BuLi (1.64 M in hexane, 0.50 mL, 0.80 mmol) was added and the solution stirred at -78 °C for 1 hour. 2-Methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.40 mL, 2.30 mmol) was added and the reaction mixture allowed to warm slowly to room temperature. Saturated aqueous ammonium chloride (25 mL) and diethyl ether (20 mL) were added and the organic layer was separated, washed with brine, dried over sodium sulphate, filtered and the solvent removed under reduced pressure to give a **5c** as a colourless oil. Used immediately in the following step. Yield 150 mg (91 % as crude material).



5

*Compound **5***

A mixture of the crude borolane **5c** (150 mg, 0.27 mmol) and 2,8-dibromo-BODIPY (42 mg, 8.9 × 10^{-5} mol) was dissolved in THF (27 mL) and thoroughly degassed (freeze-pump-thaw). Tri-*t*-butylphosphonium tetrafluoroborate (32 mg, 0.11 mmol), tris(dibenzylideneacetone)dipalladium (0) (48 mg, 5.2 × 10^{-5} mol) and degassed water (180 μl) were added and the mixture heated at 50 °C for 3 days in the dark. The cooled mixture was filtered through a pad of silica and the solvent removed under reduced pressure. The crude product was purified by preparative GPC twice followed by column chromatography [silica gel, dichloromethane-ethyl acetate 4:1] to give **5** as a purple solid. Yield 10 mg (9 %). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.73 (s, 2H), 7.58 (d, *J* = 6.8 Hz, 2H), 7.38 (m, 4H), 7.22 (d, *J* = 6.9 Hz, 2H), 6.94 (s, 2H), 6.73 (s, 2H), 6.62 (s, 2H), 6.08 (s, 2H), 4.17 (m, 4H), 3.92 (m, 8H), 3.85 (m, 4H), 3.76 (m, 8H), 2.90 (s, 8H), 2.83 (t, *J* = 6.3 Hz, 4H), 2.76 (t, *J* = 6.3 Hz, 4H), 2.41 (s, 3H), 1.89 (s, 6H), 1.81 (s, 6H) ppm; ^{13}C NMR (150 MHz, CD_3CN) δ = 148.66, 146.93, 146.58, 143.72, 139.67, 138.83, 135.86, 135.28, 133.64, 131.95, 130.72, 129.07, 128.50, 127.89, 127.80, 127.59, 127.42, 127.16, 116.66, 115.70, 72.00, 69.51, 68.91, 32.59, 32.56, 31.06, 20.51, 18.87, 18.30 ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ = -0.12 (t, J_{BF} = 27 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -145.69 (mult) ppm; HIRES-MS for $C_{64}H_{73}BF_2N_2O_8S_4Na$ calculated *m/z* = 1197.4203; found = 1197.4163 $[M+Na]^+$.

2. Summary of Optical Properties

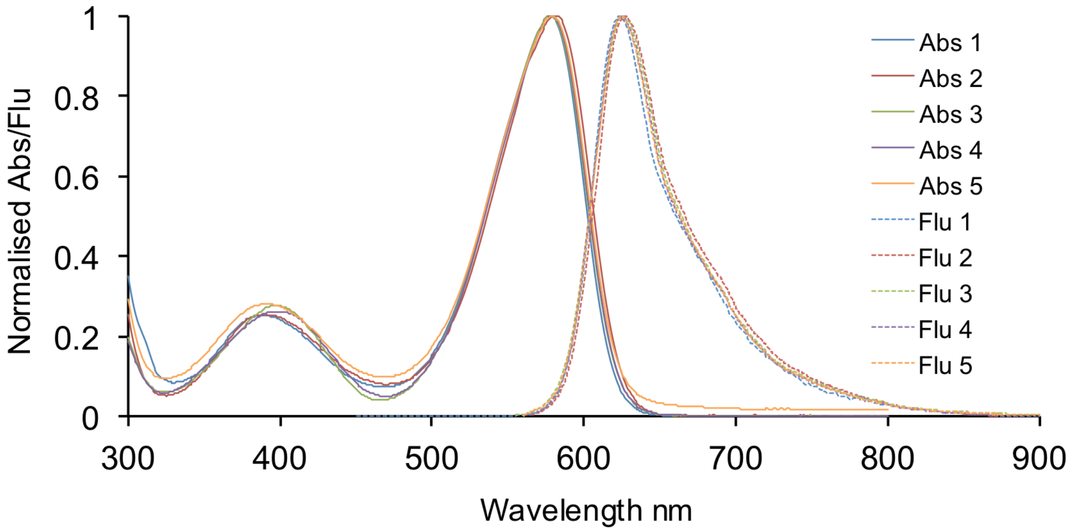


Figure S1 Normalised UV/Vis absorption and photoluminescence spectra for compounds **1-5** in chloroform 10^{-5} M.

	Fluorescence Quantum Yield, Φ			
Compound	Hexane	$CHCl_3$	MeCN	DMSO
1	0.69	0.63	0.00	0.00
2	0.70	0.58	0.01	0.01
3	0.66	0.57	0.29	0.31
4	0.70	0.60	0.34	0.33
5	0.48	0.47	0.00	0.00

Table S1 Fluorescence quantum yields of solutions of compounds **1-5** (10^{-5} M) in various solvents.

3. Job's Plot for Mercury (II) Binding.

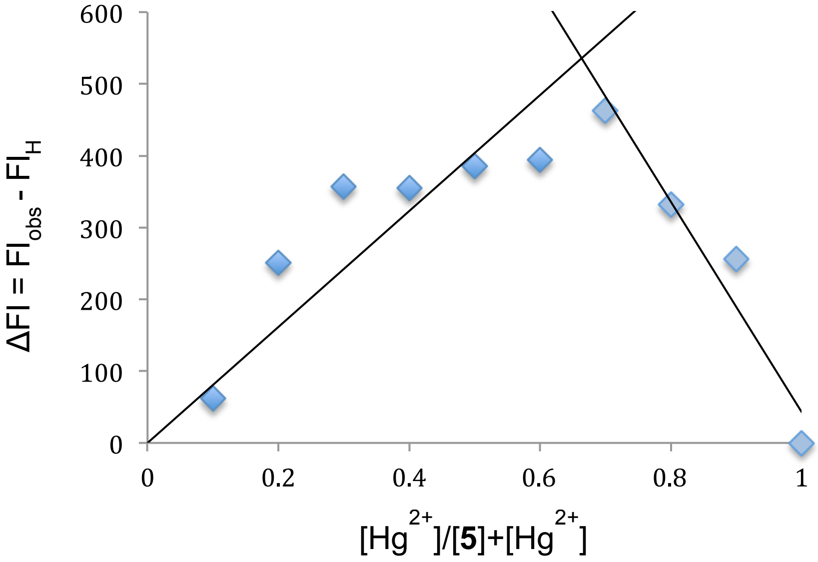


Figure S2 Job's plot for Mercury (II) binding with compound **5** based on fluorescence at 624 nm in CH_2Cl_2. [**5**]+[Hg^{2+}] = 10^{-5} M.

4. Ion Interference

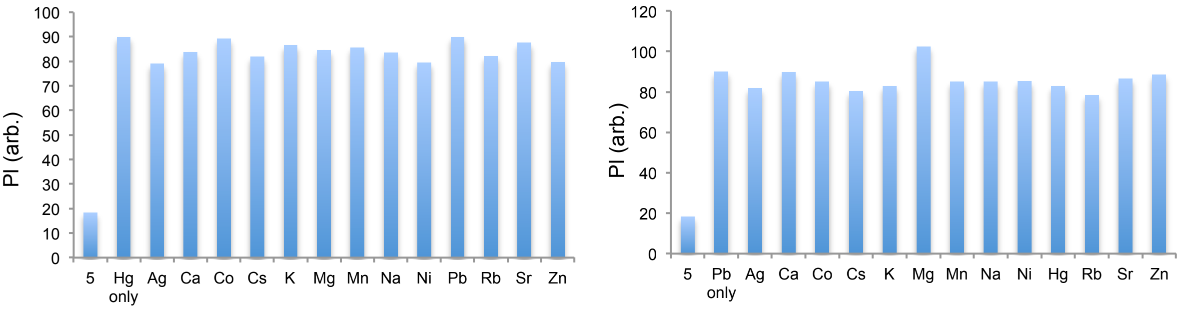


Figure S3 Ion interference of 20 equivalents of various metal cations with (a) 4 eq Hg^{2+} and (b) 6 eq of Pb^{2+} in 10^{-5} M solutions of **5** in 5:1 DCM:MeCN.

5. Dihedral Angles in Compounds 3 and 4

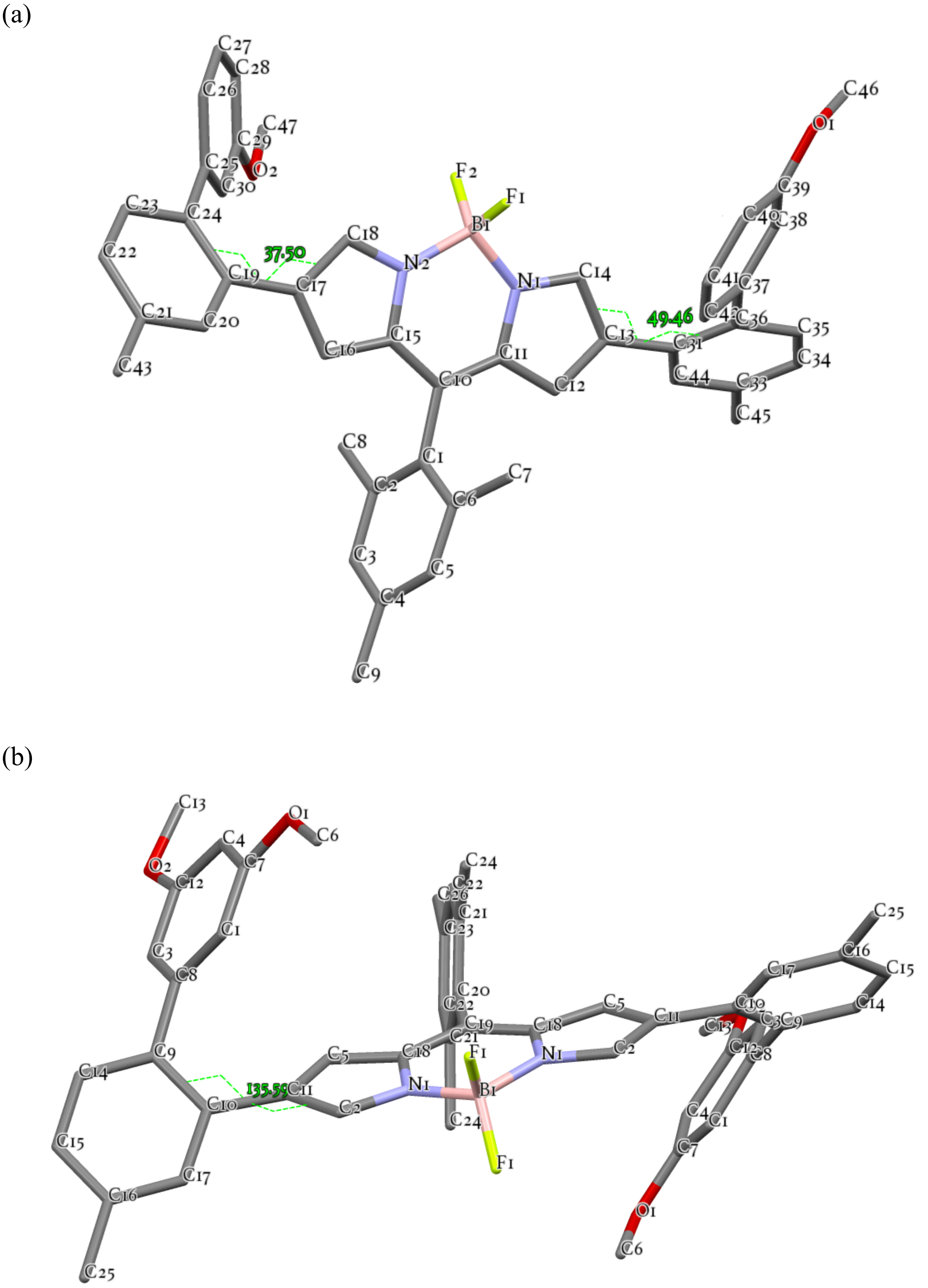
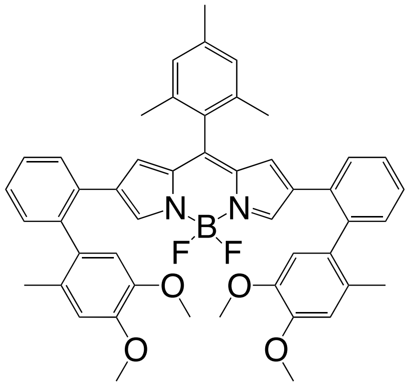


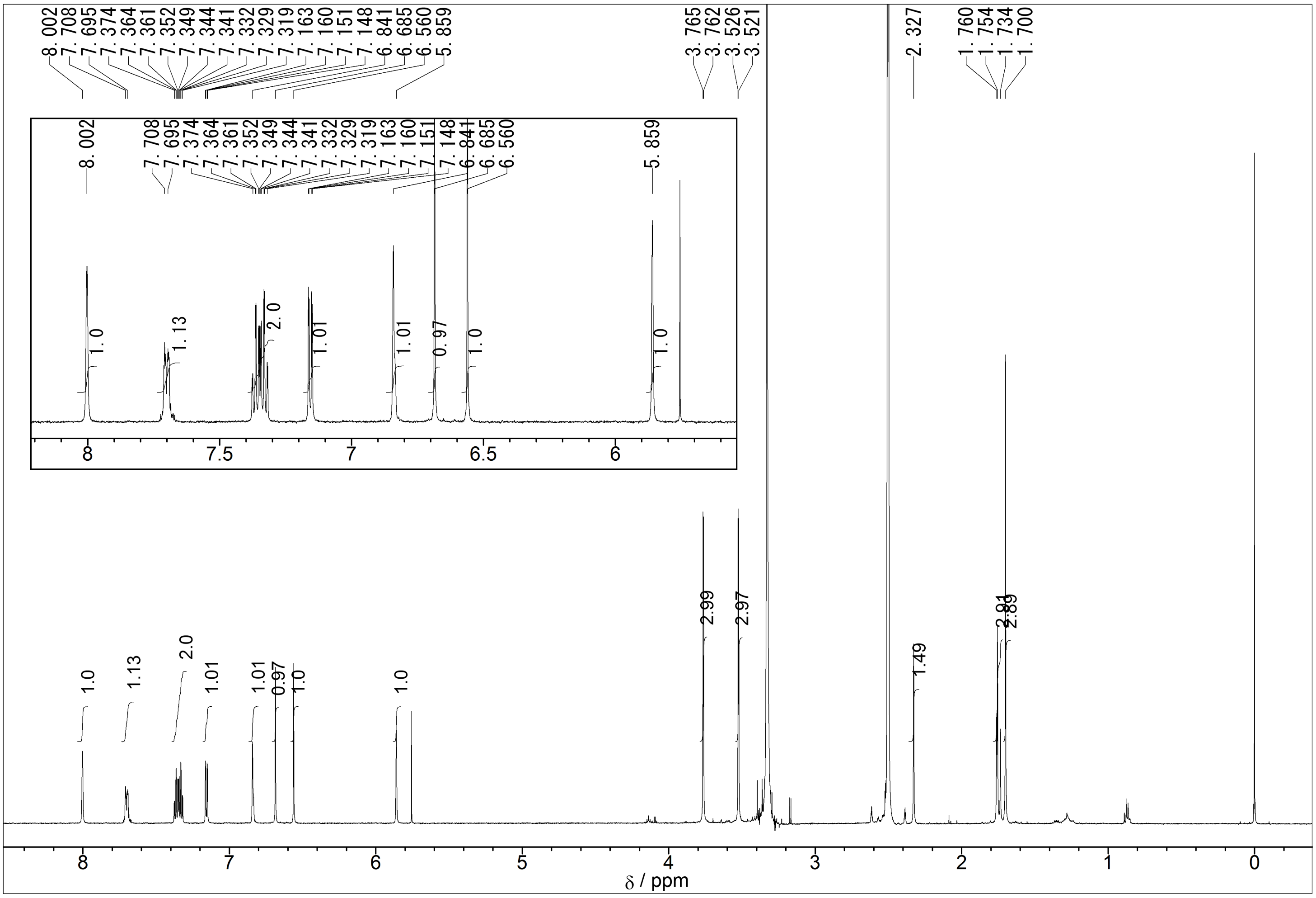
Figure S4 Dihedral angles in (a) compound **3** and (b) compound **4** (hydrogens omitted for clarity).

6. ^{1}H NMR, ^{13}C NMR Spectra for Compounds 1-5.

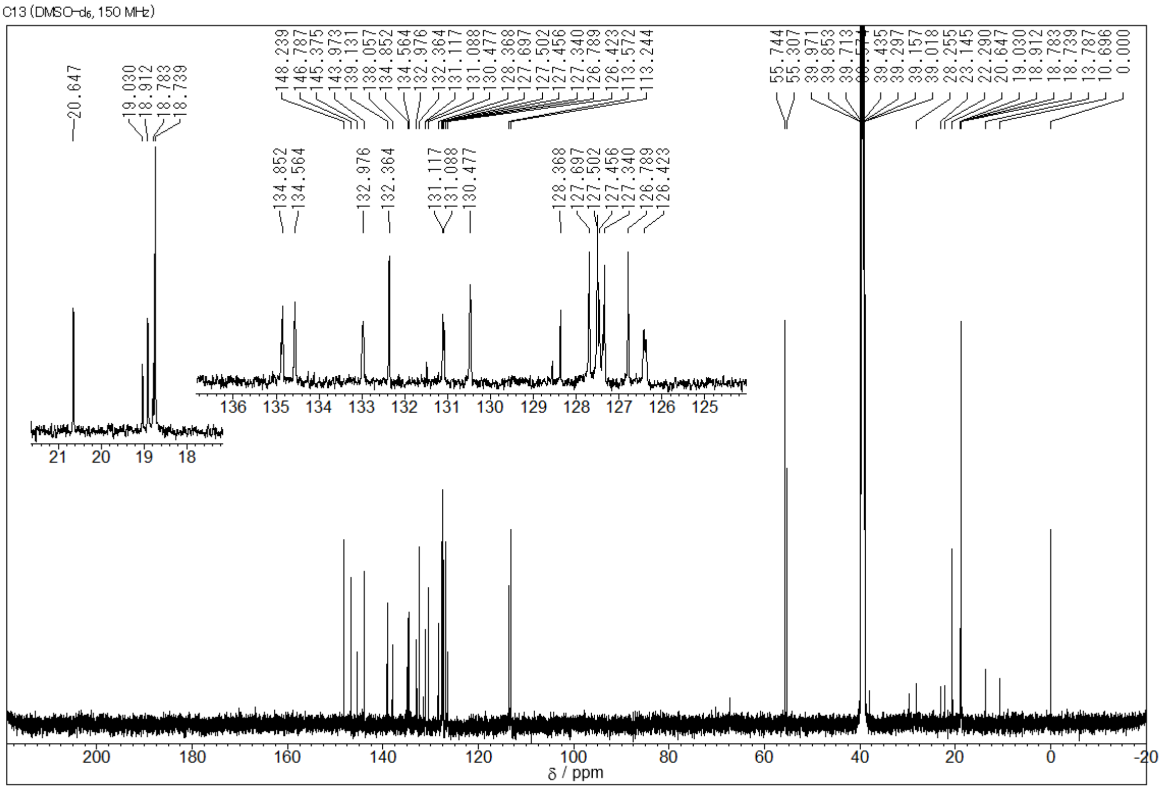
Compound **1**



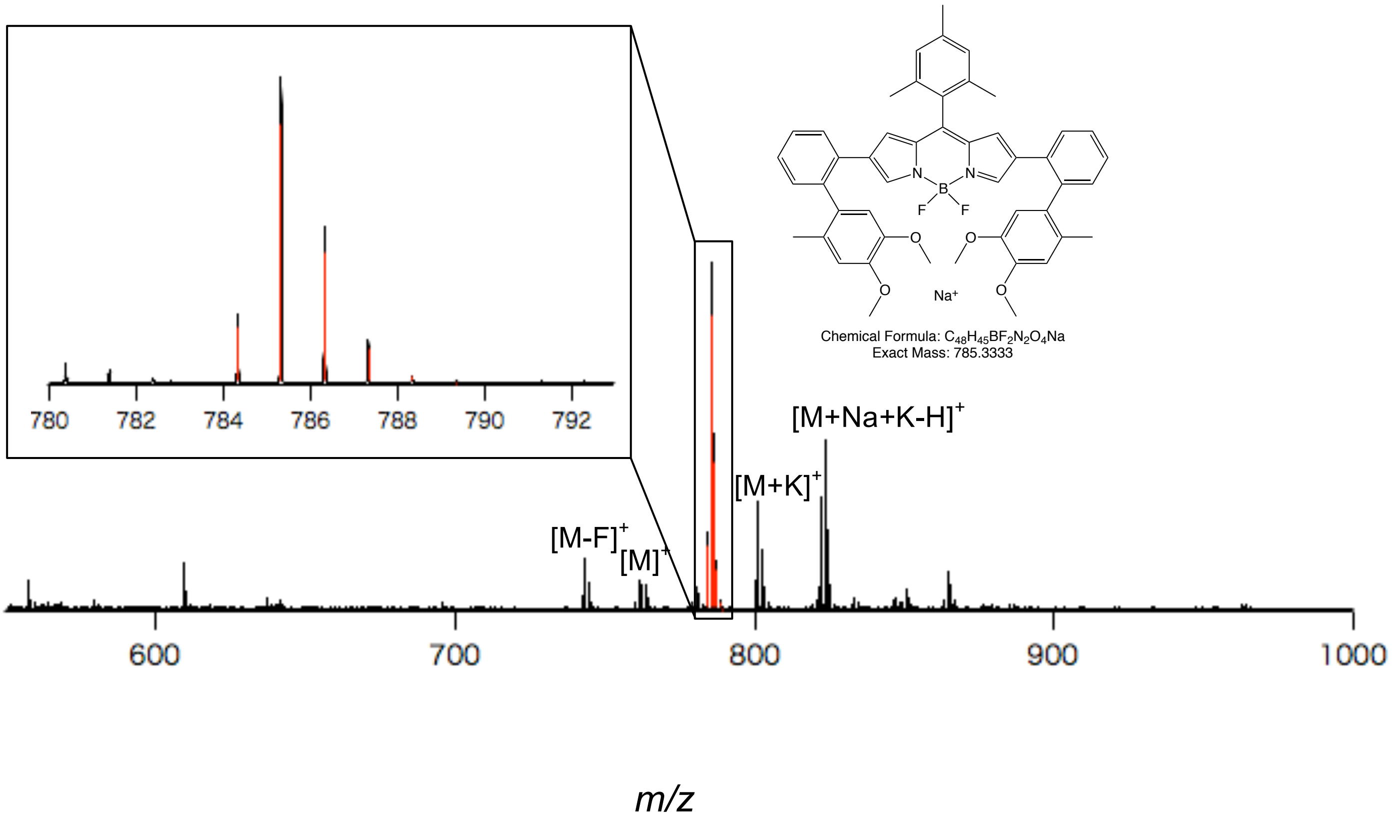
^{1}H NMR (400 MHz, DMSO) of compound **1**



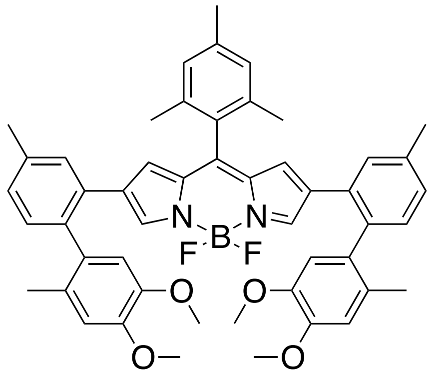
^{13}C NMR (150 MHz, DMSO) of compound **1**



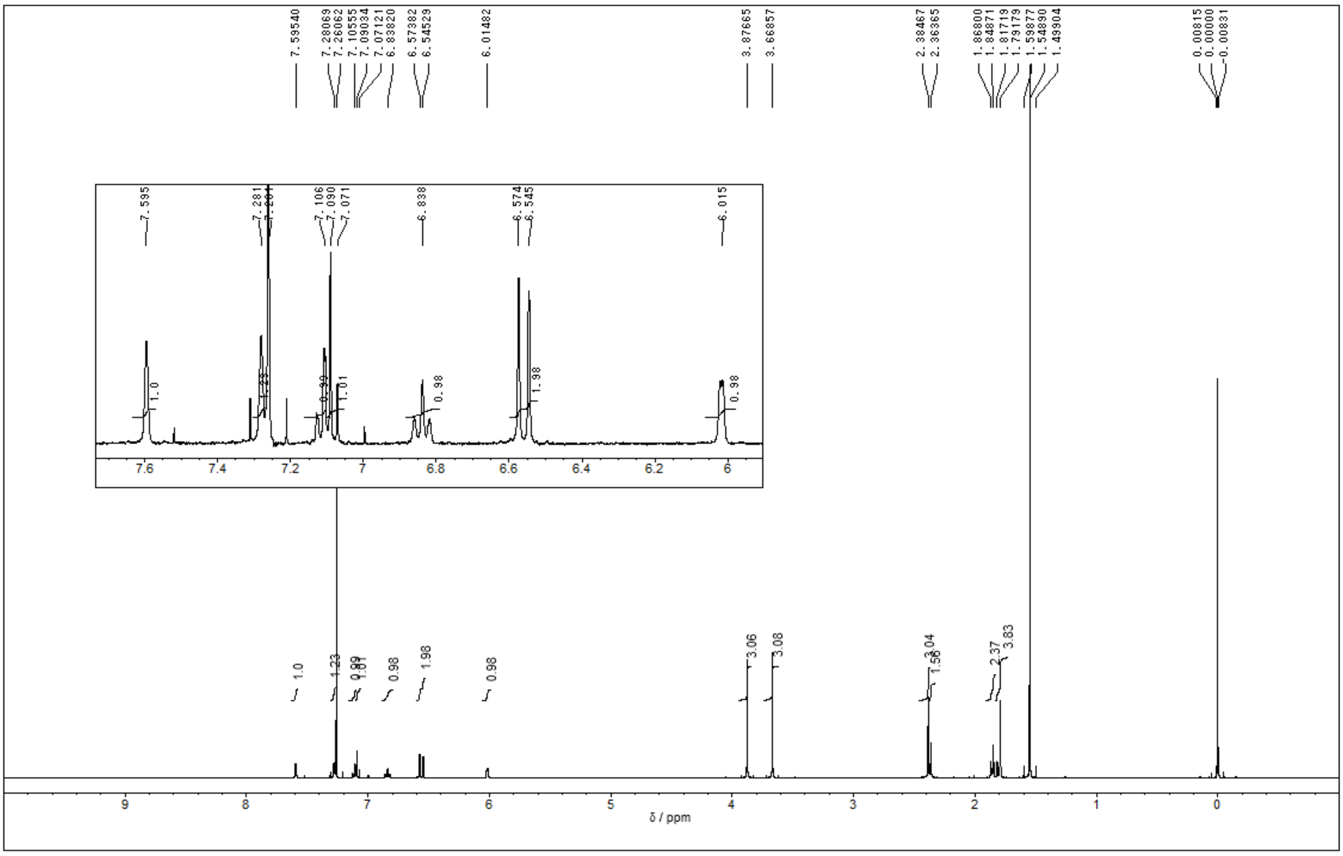
HIRES-MS (ESI-TOF, positive mode)



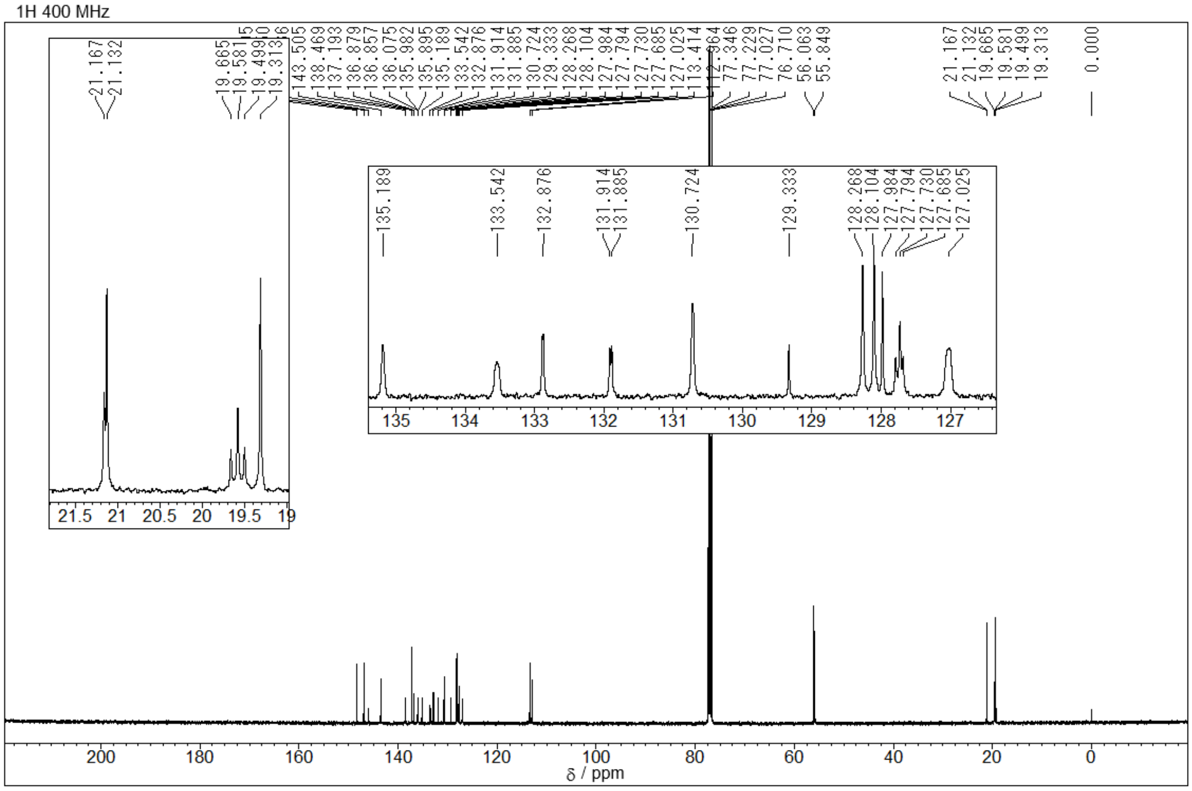
Compound **2**



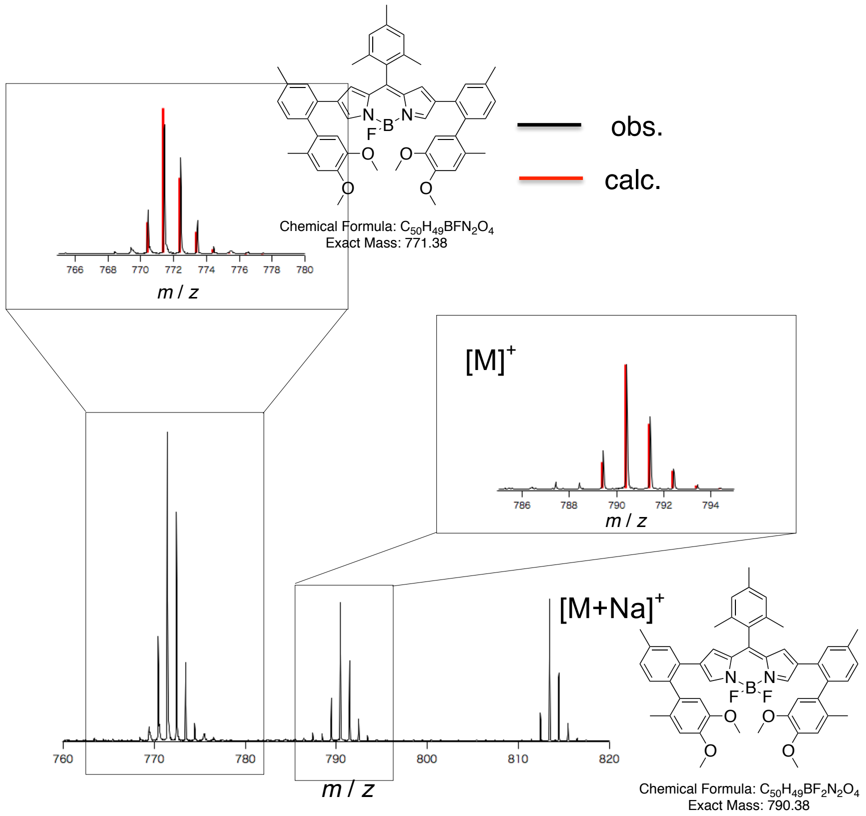
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2**



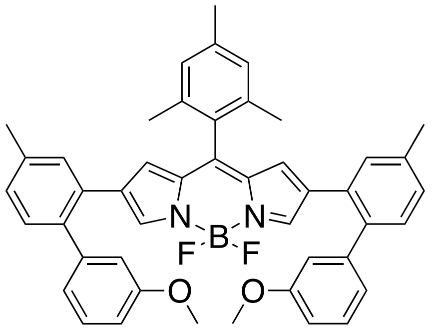
^{13}C NMR (100 MHz, CDCl$_3$) of compound **2**



MALDI-TOF MS (negative mode, Dithranol)

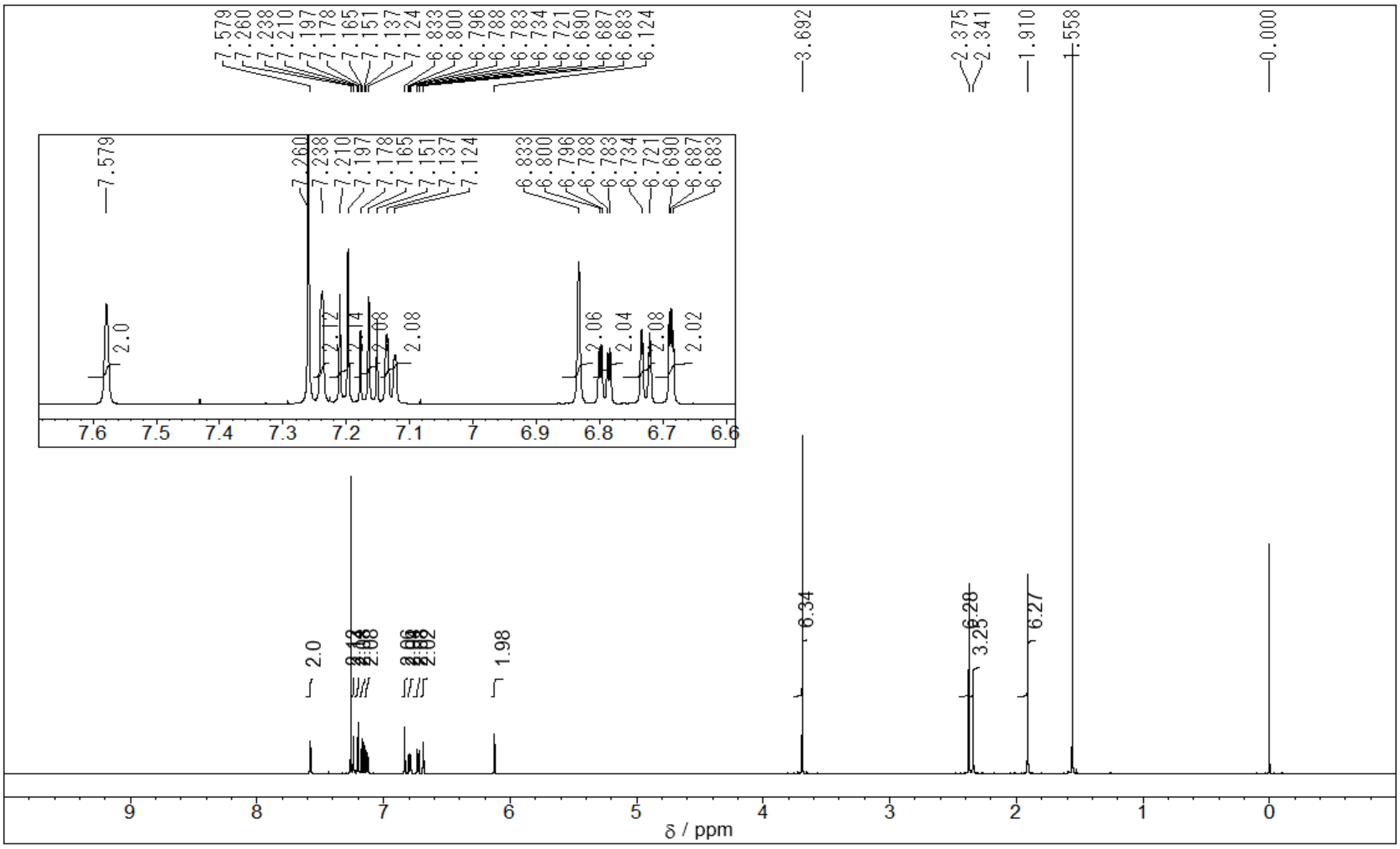


Compound **3**

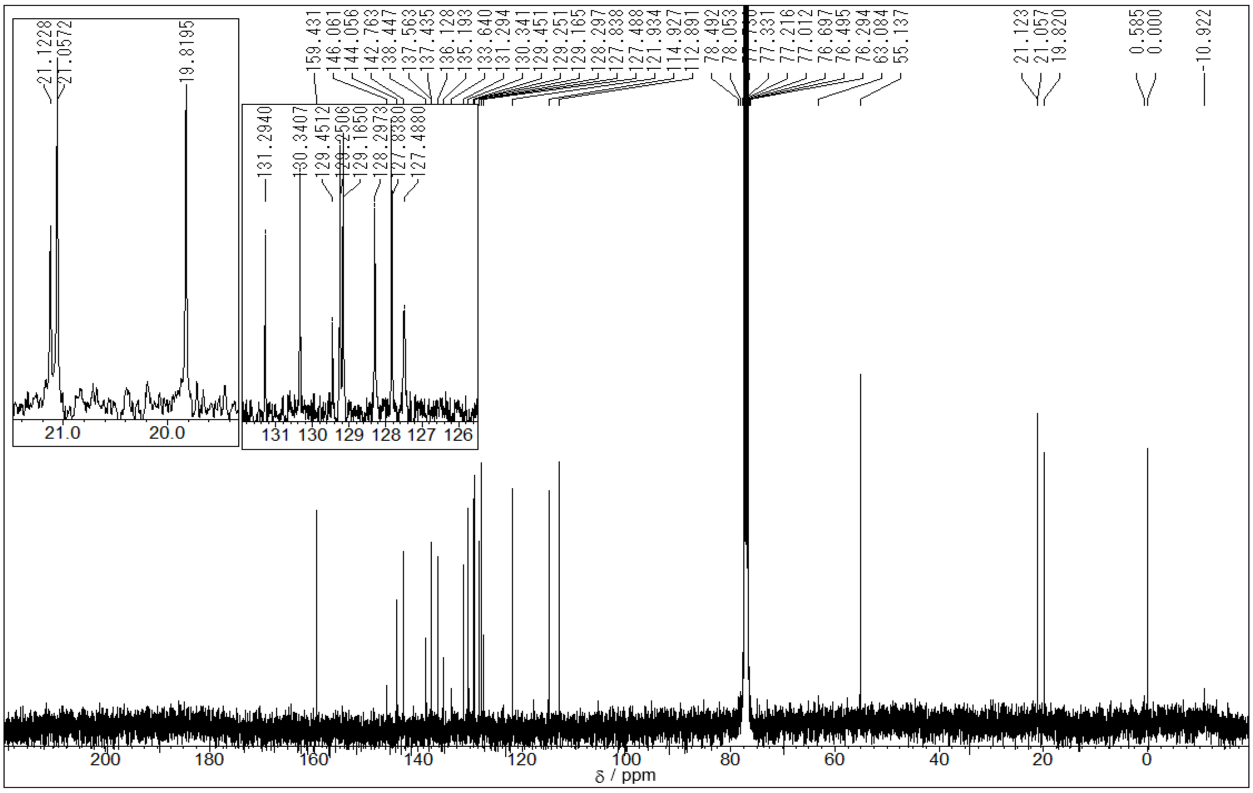


Chemical Formula: $C_{46}H_{41}BF_2N_2O_2$
Exact Mass: 702.32
Molecular Weight: 702.64

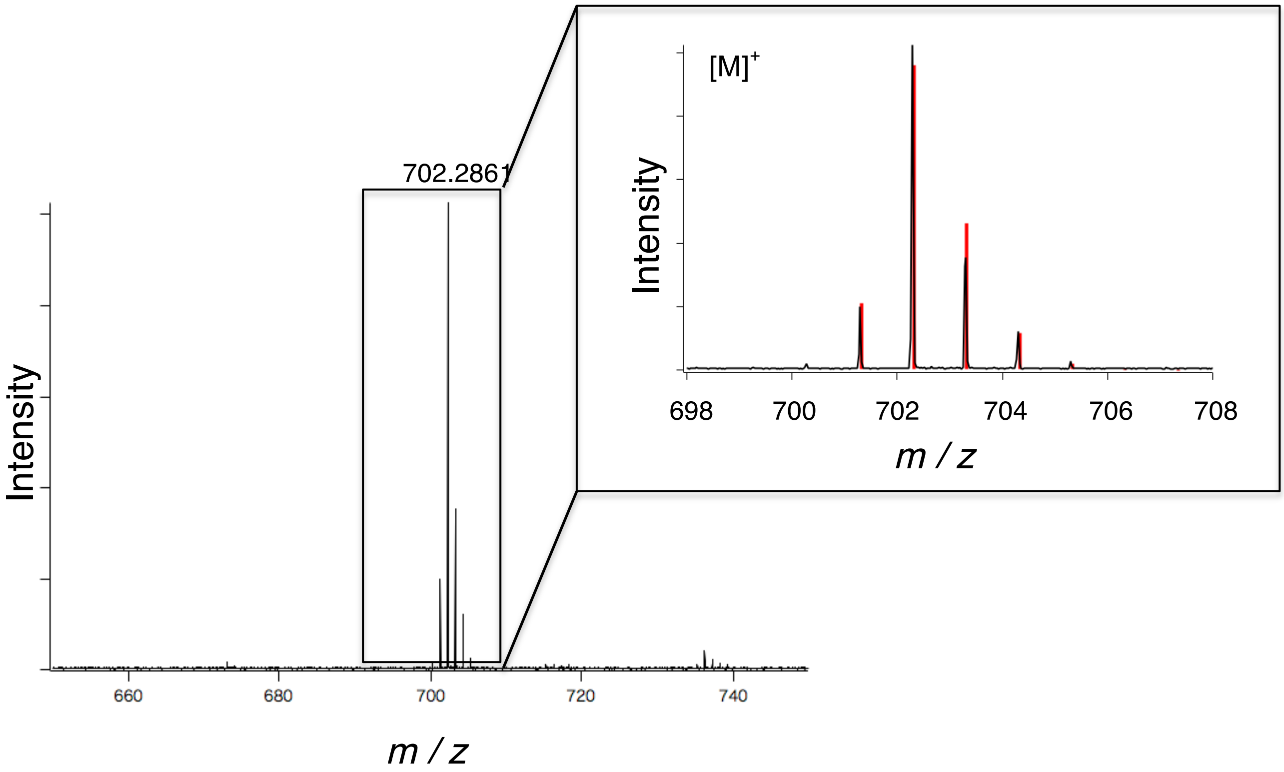
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3**



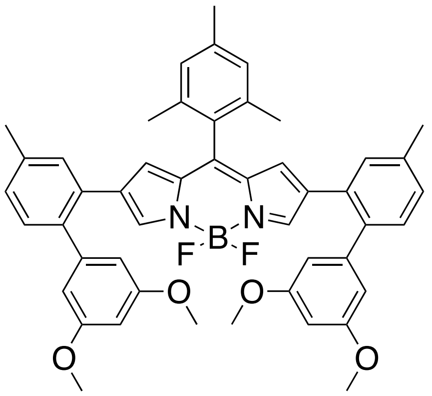
^{13}C NMR (100 MHz, CDCl$_3$) of compound **3**



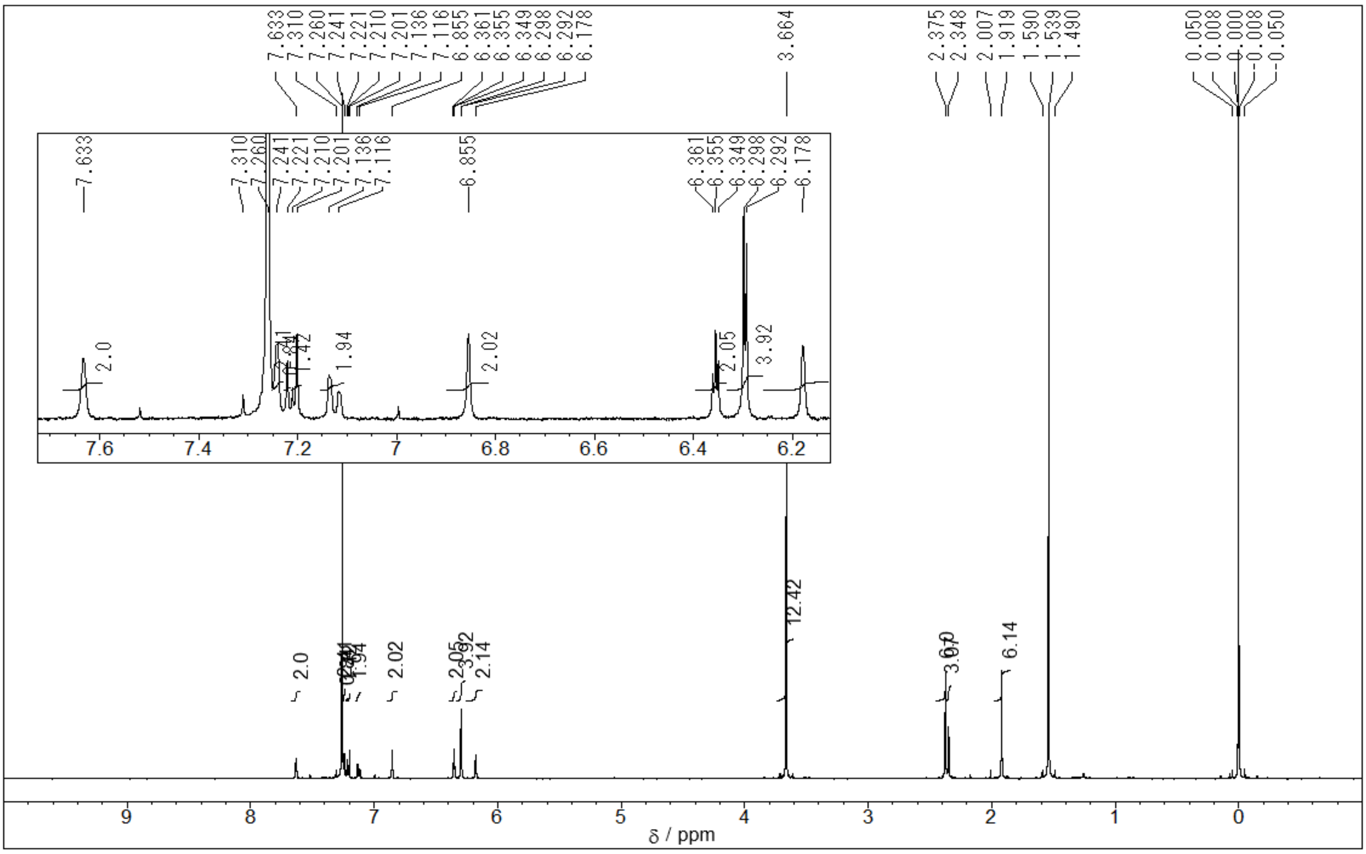
MALDI-TOF MS (negative mode, Dithranol)



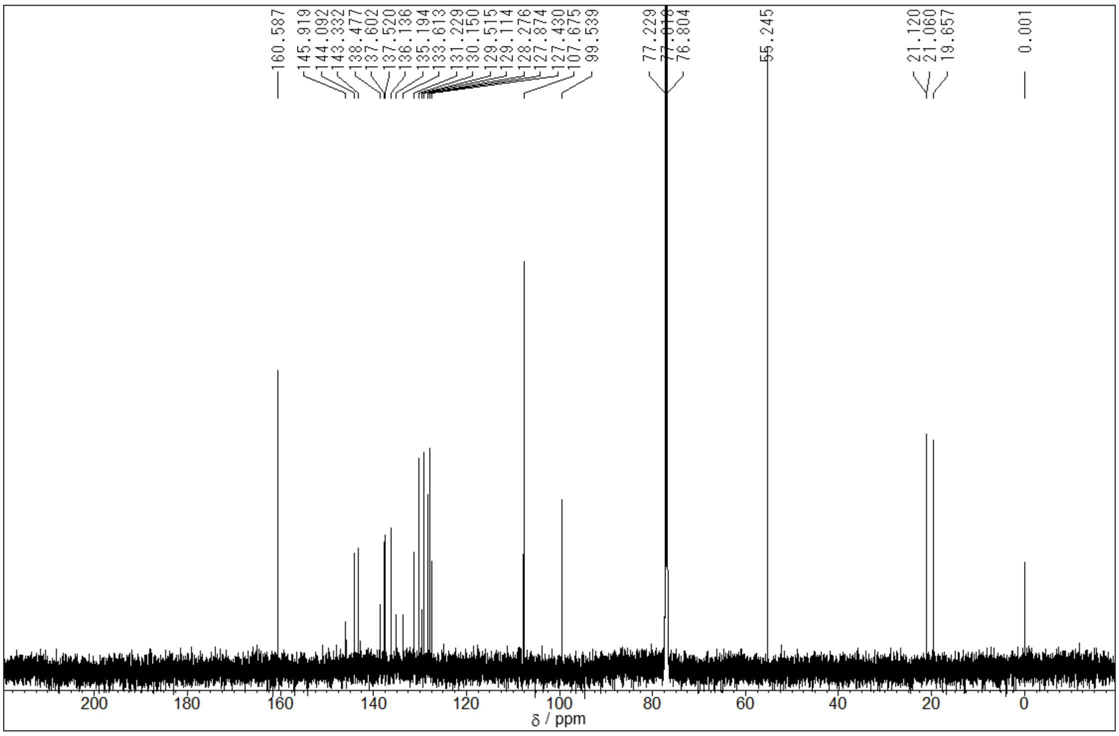
Compound **4**



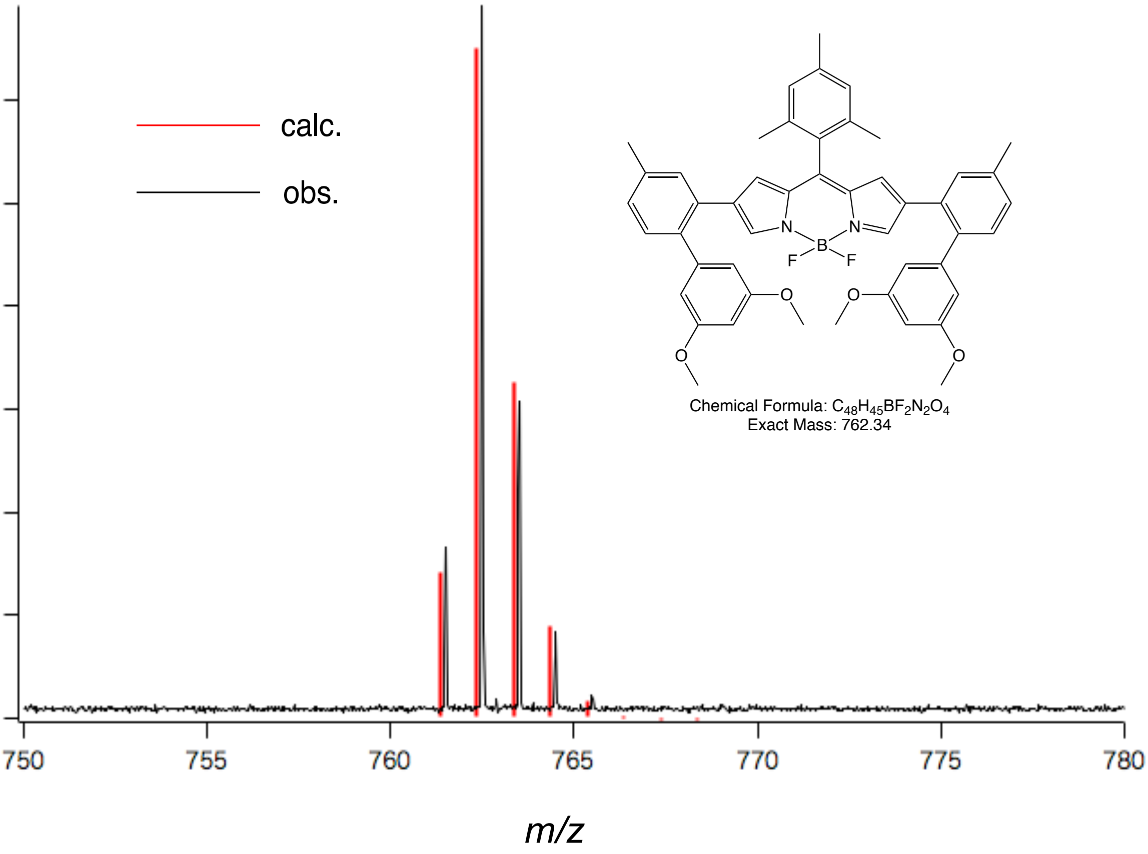
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4**



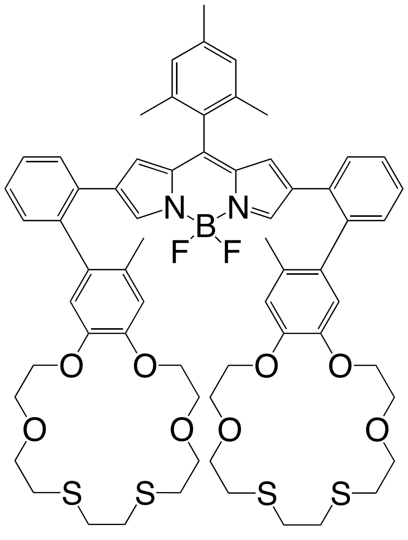
^{13}C NMR (100 MHz, CDCl$_3$) of compound **4**



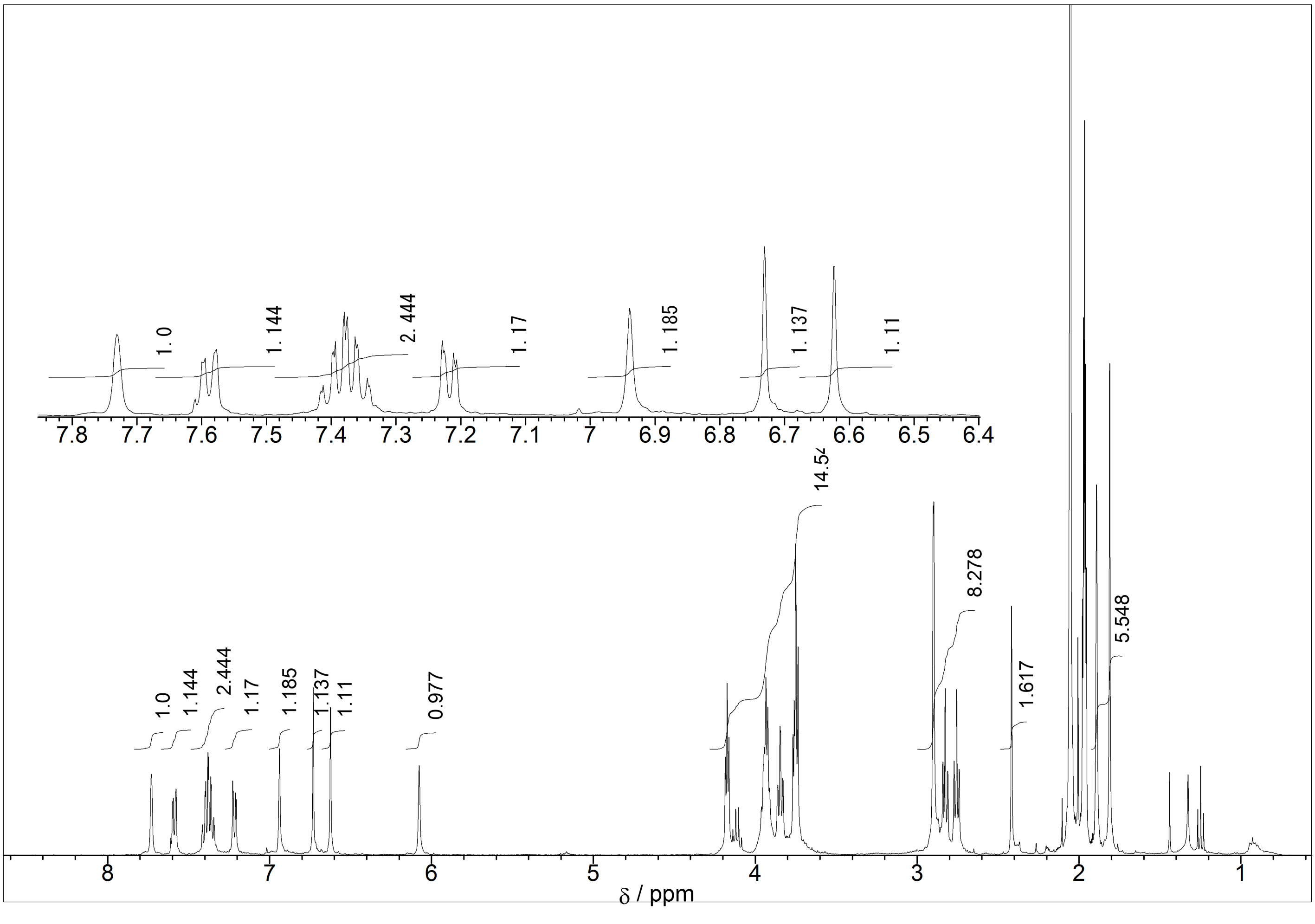
MALDI-TOF MS (negative mode, Dithranol)



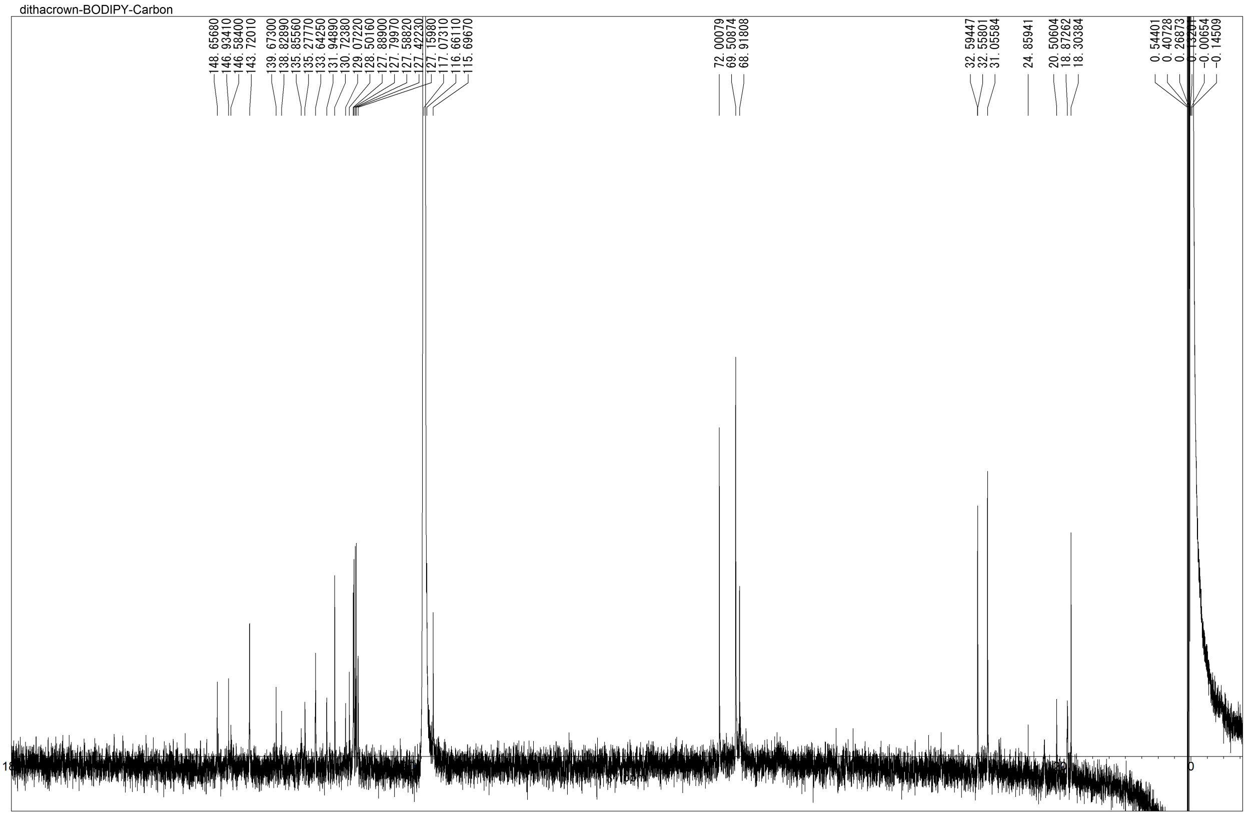
Compound **5**



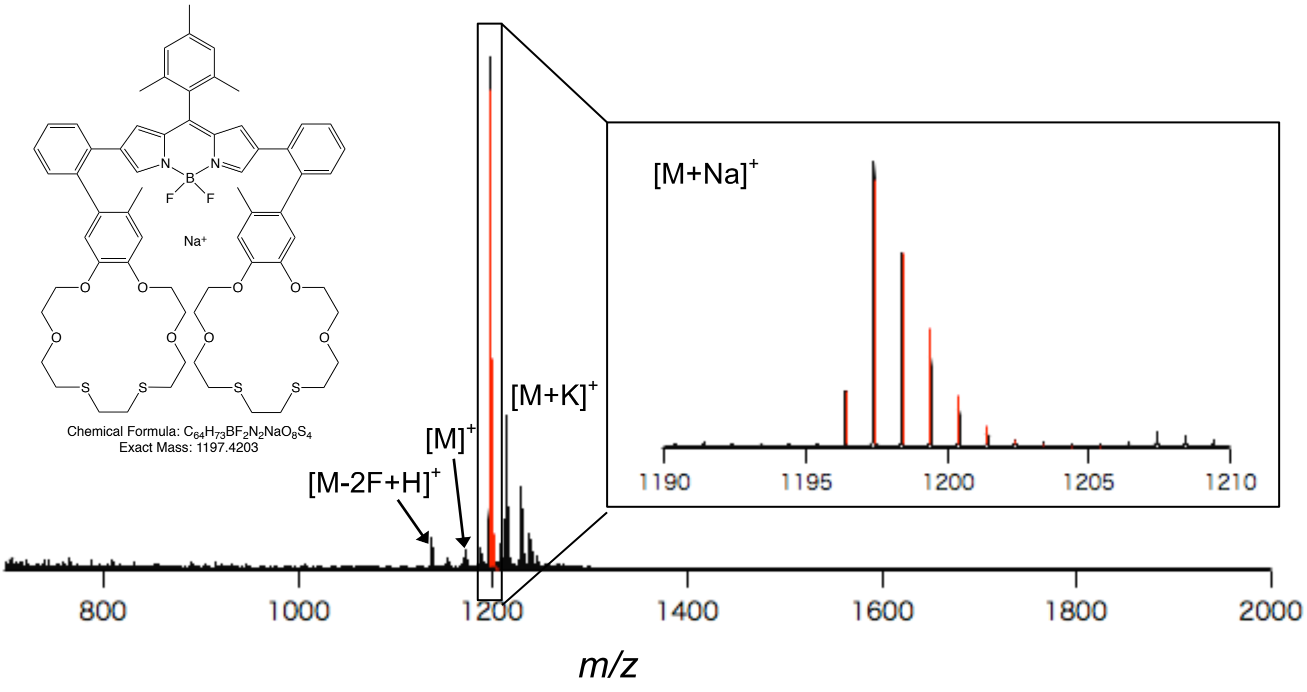
^{1}H NMR (400 MHz, CD_3CN) of compound **5**



^{13}C NMR (100 MHz, CD_3CN) of compound **5**



HIRES-MS (ESI-TOF, positive mode)



ESI MS (positive mode) compound **5** with Hg^{2+}

Found

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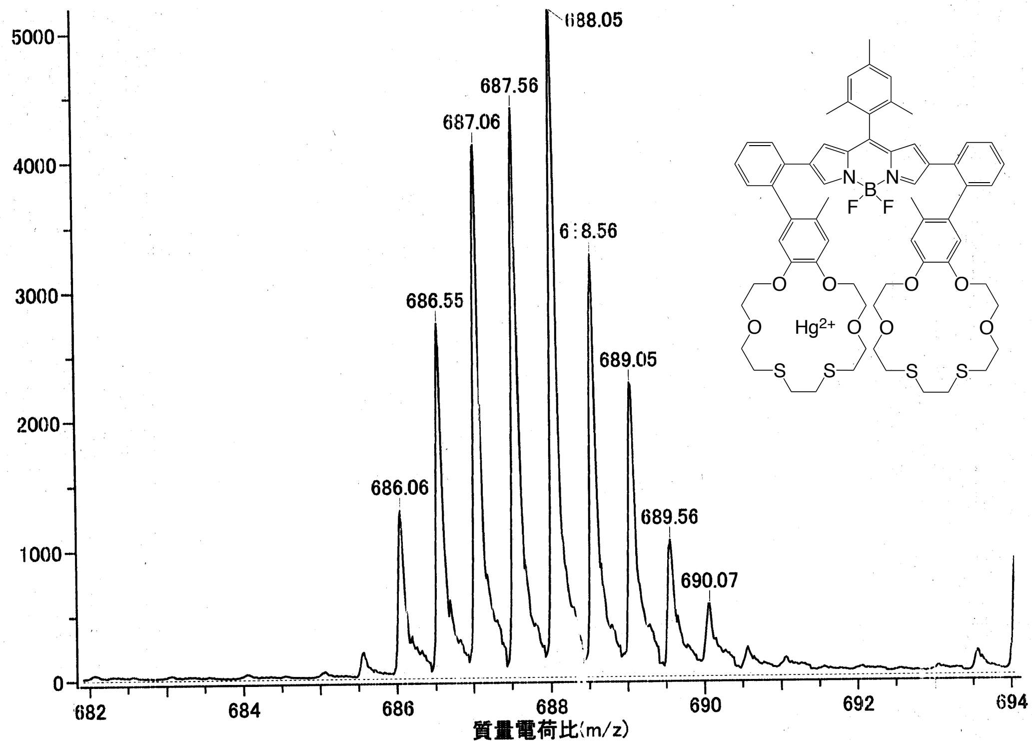

Calculated for $C_{64}H_{73}BF_2N_2O_8S_4Hg/2$

付加/脱離イオン: なし
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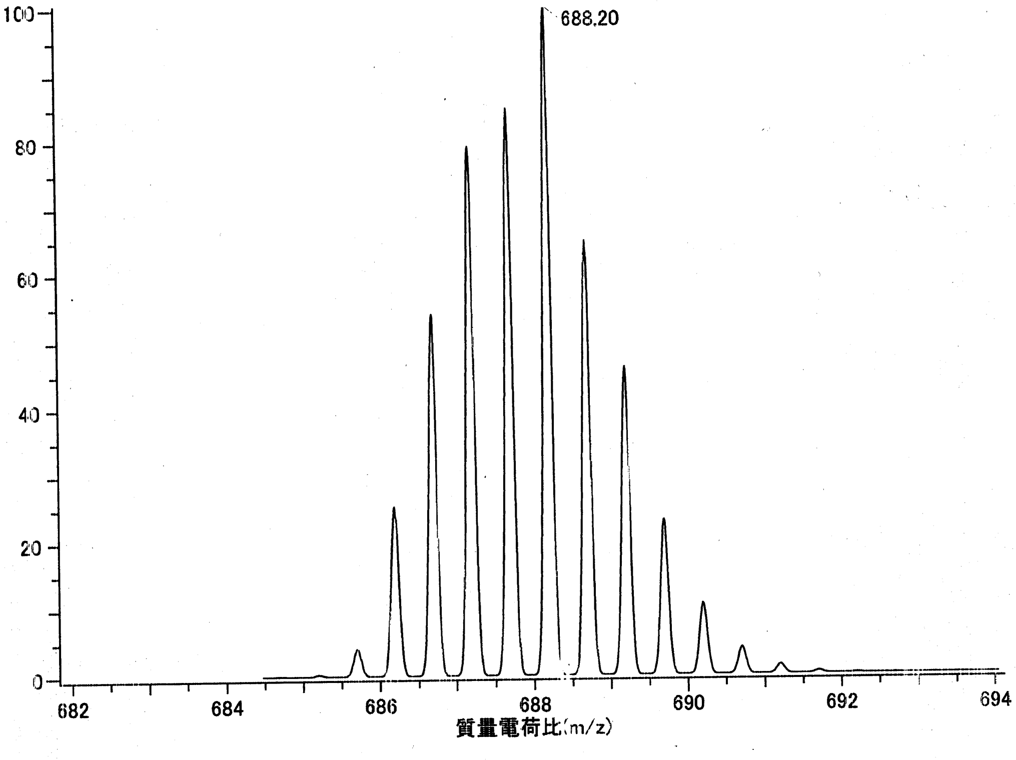
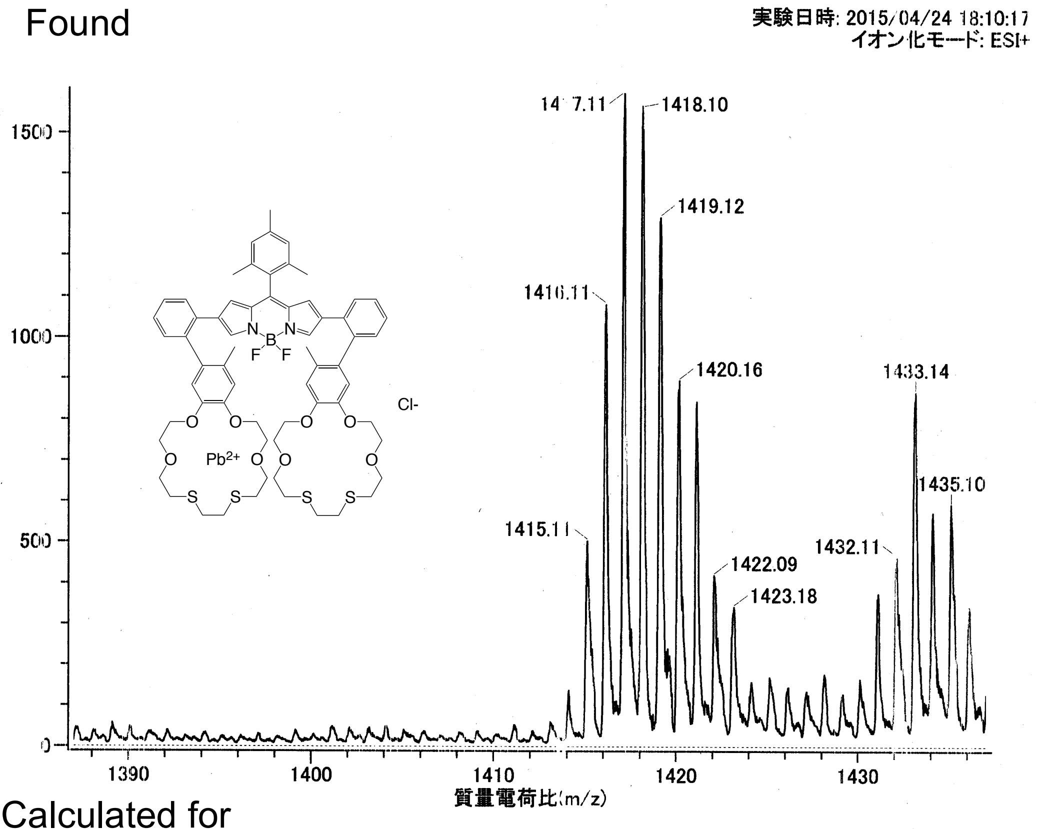


ESI MS (mode) compound **5** with Pb^{2+}

Found



Calculated for
$C_{64}H_{73}BF_2N_2O_8S_4PbCl$