Supporting information

B-spiroBODIPYs as a fluorophore responsive to hydrogen bond donors

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1. Instrumentation and materials

Materials: All used reagents, solvents, and materials were purchased from Tokyo Chemical Industry (TCI), FUJIFILM Wako Pure Chemical Corporation, Sigma-Aldrich, Kanto Chemical, Nacalai Tesque, BLDpharm, or Alfa Aesar. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Dry toluene, dichloromethane, THF, 1,4-dioxane, and diethyl ether were supplied from the Glass Countor solvent purification system. All reactions were performed under N_2 atmosphere unless otherwise noted. Compounds **1a**,[1] **1c**[2] and **2**[3] were prepared according to the literature.

Chromatography: Analytical thin-layer chromatography was performed using fluorescent-labelled silica-coated plates (TLC silica gel 60 F_{254}, Merck). Detection was conducted using UV-light (λ_{ex} = 254 nm). Flash column chromatography was performed using silica gel (Wakogel 60N (particle size: 63–212 μm), C-300 (particle size: 45–75 μm). Recycle GPC was conducted using a JAI LabACE LC-7080 plus preparative HPLC with a GPC column (JAIGEL-2HR Plus).

Nuclear magnetic resonance (NMR) spectroscopy: ^{1}H NMR (400 MHz) spectra were recorded on a Bruker AVANCE NEO spectrometer. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{11}B NMR (160 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer. Chemical shifts were reported as the delta scale in ppm relative to TMS (δ = 0 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.16 ppm) for ^{13}C NMR. The following abbreviations were used to describe the multiplicities: s = singlet, d = doublet, m = multiplet, ps = pseudo singlet, pd = pseudo doublet.

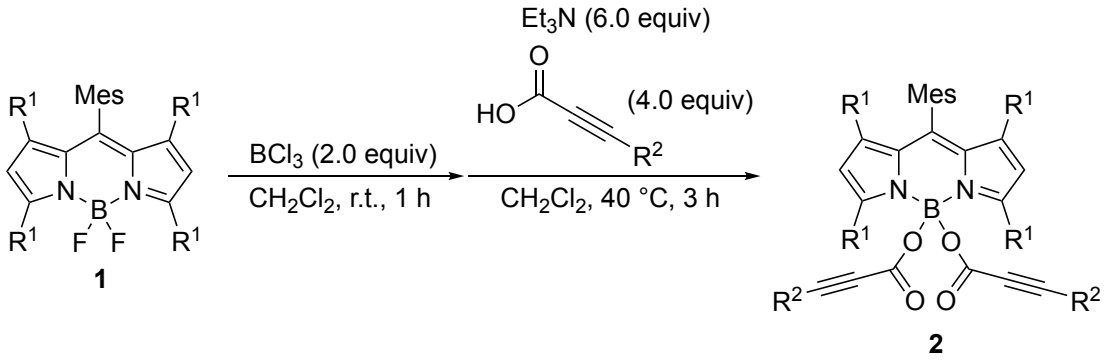
Mass spectrometry (MS): High-resolution electrospray ionisation time-of-flight (ESI-TOF) mass spectra were taken on a Bruker micrOTOF instrument using a positive ionisation mode.

X-ray diffraction analysis: X-ray data were obtained using a Rigaku XtaLAB Synergy-R/NLN diffractometer with a MicroMax007HFMR X-ray generator and a HyPix-6000HE detector, or obtained using a Rigaku CCD diffractometer (Saturn 724 with MicroMax007) with Varimax Mo optics. The structures were solved using a direct method (SHELXT) and refined by a full-matrix least-squares method on F^2 for all reflections using the programs of SHELXL-2014. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in idealised positions and refined as riding models with the relative isotropic displacement parameters.

Photophysical measurements: UV/vis/NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V 670 spectrometer. Emission spectra were recorded on a JASCO FP-8550 spectrometer. Fluorescence lifetimes were recorded on a HAMAMATSU Quantaurus-Tau

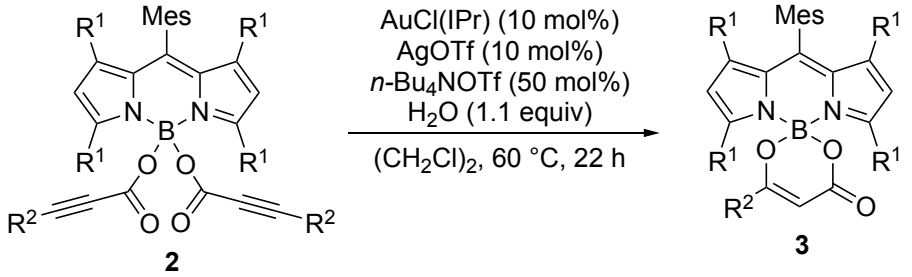
spectrometer. Fourier transform infrared (FT-IR) spectroscopic analysis was performed on a JASCO FT/IR-4200 spectrometer using a Sealed Liquid Cell with CaF_2 windows and a path length of 1 mm.

2. Experimental procedures and compound data



General procedure A[2]

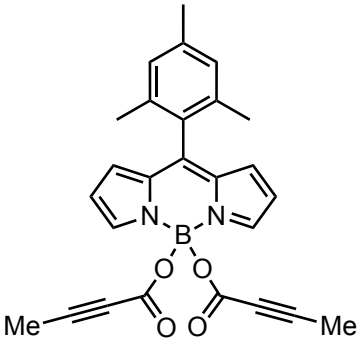
1 (1.0 eq.), CH_2Cl_2, and BCl_3 (2.0 eq.) were placed in a two-necked round-bottom flask. After the mixture was stirred at room temperature for 1 h under N_2, Et_3N (6.0 eq.) and carboxylic acid (4.0 eq.) was added. The mixture was stirred at room temperature for 3 h. The reaction mixture was washed with water, and the organic phase was separated. The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel.



General procedure B

In an 8 mL vial, **2** (0.10 mmol), AuCl(IPr) (6.2 mg, 10 μmol), AgOTf (2.6 mg, 10 μmol), *n*-Bu_4NOTf (19.6 mg, 50 μmol), dichloroethane (0.20 mL), and H_2O (0.11 mmol, 2.0 μL) were added under air. After stirring at 60 °C for 24 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by pTLC (SiO_2).

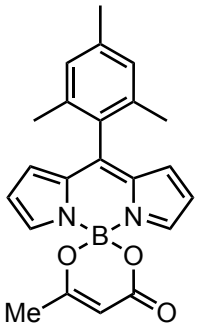
***COO*-BODIPY 2a**



According to the described general procedure A, **1a** (310 mg, 1.0 mmol) was reacted with BCl_3 (2.0 mL, 2.0 mmol), Et_3N (0.83 mL, 6.0 mmol), and 2-butynoic acid (336 mg, 4.0 mmol) in CH_2Cl_2 (25 mL). The crude product was purified by flash chromatography (hexane/CH_2Cl_2 1:4) to obtain **2a** (332 mg, 76%) as a red solid. Rf = 0.28 (hexane/CH_2Cl_2 1:5).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.88 (ps, 2H), 6.94 (s, 2H), 6.68 (dd, *J* = 1.0, 4.2 Hz, 2H), 6.43 (dd, *J* = 2.0, 4.2 Hz, 2H), 2.35 (s, 3H), 2.15 (s, 6H), 1.92 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 153.5, 148.7, 144.0, 138.8, 137.0, 136.6, 130.2, 129.9, 128.1, 118.7, 83.1, 74.8, 21.3, 20.0, 3.8 ppm; ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) δ = –0.61 (s, 1B) ppm; HR-MS (ESI-TOF): $[M+Na]^+$ Calcd for $C_{26}H_{23}{}^{11}BN_2O_4Na$ 461.1648; Found 461.1643.

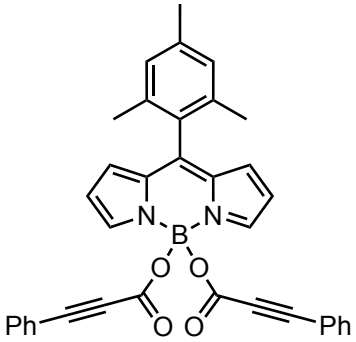
***B*-spiroBODIPY 3a**



According to the described general procedure B, **2a** (44 mg, 0.10 mmol) was reacted with AuCl(IPr) (6.2 mg, 10 μmol), AgOTf (2.6 mg, 10 μmol), *n*-Bu_4NOTf (19.6 mg, 50 μmol), dichloroethane (0.30 mL), and H_2O (0.11 mmol, 2.0 μL). The crude product was purified by pTLC (SiO_2, hexane/ethyl acetate = 5/4) to obtain **3a** (29.7 mg, 80%) as an orange solid. Rf = 0.16 (hexane/ethyl acetate = 1/1).

^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.78 (ps, 2H), 6.96 (s, 2H), 6.70 (dd, *J* = 0.9, 4.2 Hz, 2H), 6.44 (dd, *J* = 1.9, 4.2 Hz, 2H), 5.26 (s, 1H), 2.36 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 2.02 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 171.0, 165.1, 148.1, 144.8, 139.1, 136.6, 136.2, 135.3, 130.7, 129.6, 128.4, 128.2, 118.9, 94.2, 22.0, 21.2, 20.2, 20.2 ppm; ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) δ = 1.81 (s, 1B) ppm; HR-MS (ESI-TOF): $[M+H]^+$ Calcd for $C_{22}H_{22}{}^{11}BN_2O_3$ 373.1722; Found 373.1707.

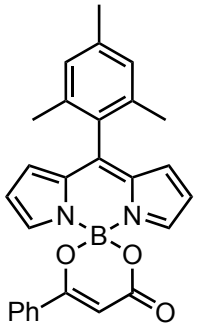
***COO*-BODIPY 2b**



According to the described **general procedure A**, **1a** (310 mg, 1.0 mmol) was reacted with BCl_3 (2.0 mL, 2.0 mmol), Et_3N (0.90 mL, 6.0 mmol), phenylpropiolic acid (585 mg, 4.0 mmol), and CH_2Cl_2 (25 mL). The crude product was purified by flash chromatography (hexane/CH_2Cl_2 1:4) to obtain **2b** (390 mg, 69%) as a red solid. Rf = 0.36 (hexane/CH_2Cl_2 1:2).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.95 (ps, 2H), 7.56-7.54 (m, 4H), 7.43-7.39 (m, 2H), 7.36-7.32 (m, 4H), 6.97 (s, 2H), 6.74 (dd, *J* = 1.1, 4.2 Hz, 2H), 6.48 (dd, *J* = 2.0, 4.2 Hz, 2H), 2.36 (s, 3H), 2.21 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 153.8, 148.9, 143.8, 138.8, 137.0, 136.8, 133.0, 130.3, 130.3, 129.9, 128.6, 128.1, 120.3, 118.8, 84.1, 83.0, 21.3, 20.0 ppm; ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) δ = –0.38 (s, 1B) ppm; HR-MS (ESI-TOF): $[M+Na]^+$ Calcd for $C_{36}H_{27}{}^{11}BN_2O_4Na$ 585.1962; Found 585.1939.

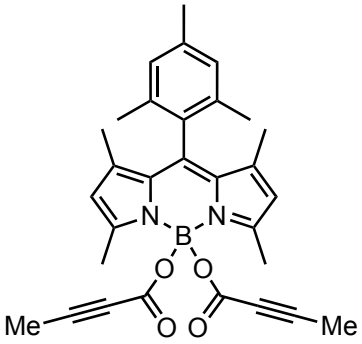
***B*-spiroBODIPY 3b**



According to the described **general procedure B**, **2b** (56 mg, 0.10 mmol) was reacted with AuCl(IPr) (6.2 mg, 10 μmol), AgOTf (2.6 mg, 10 μmol), *n*-Bu_4NOTf (19.6 mg, 50 μmol), dichloroethane (0.30 mL), and H_2O (0.11 mmol, 2.0 μL). The crude product was purified by pTLC (SiO_2, hexane/ethyl acetate = 5/4) to obtain **3b** (39.9 mg, 92%) as an orange solid. Rf = 0.32 (hexane/ethyl acetate = 2/3).

^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.80 (ps, 2H), 7.80-7.79 (m, 2H), 7.47-7.39 (m, 3H), 6.98 (s, 2H), 6.73 (dd, *J* = 0.9, 4.2 Hz, 2H), 6.43 (dd, *J* = 1.9, 4.2 Hz, 2H), 5.97 (s, 1H), 2.38 (s, 3H), 2.18 (s, 3H), 2.05 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 166.9, 165.6, 148.2, 144.9, 139.1, 136.7, 136.2 135.4, 134.2, 131.1, 130.8, 129.6, 128.6, 128.4, 128.3, 126.4, 119.0, 91.8, 21.3, 20.2, 20.1 ppm; ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) δ = 2.14 (s, 1B) ppm; HR-MS (ESI-TOF): $[M+Na]^+$ Calcd for $C_{27}H_{23}{}^{11}BN_2O_3Na$ 457.1699; Found 457.1678.

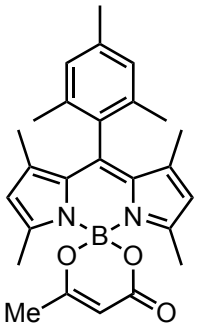
***COO*-BODIPY 2c**



According to the described general procedure A, **1c** (148 mg, 0.30 mmol) was reacted with BCl_3 (0.60 mL, 0.60 mmol), Et_3N (0.27 mL, 1.8 mmol), 2-butynoic acid (101 mg, 1.2 mmol), and CH_2Cl_2 (7.5 mL). The crude product was purified by flash chromatography (hexane/CH_2Cl_2 1:4) to obtain **2c** (110 mg, 74%) as a red solid. Rf = 0.28 (hexane/ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 6.94 (s, 2H), 5.93 (s, 2H), 2.48 (s, 6H), 2.32 (s, 3H), 2.17 (s, 6H), 1.91 (s, 6H), 1.39 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 153.4, 153.2, 143.2, 142.6, 138.5, 135.6, 132.3, 131.3, 128.9, 121.1, 82.5, 74.7, 21.4, 19.3, 14.8, 13.7, 3.8 ppm; ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) δ = –0.24 (s, 1B) ppm; HR-MS (ESI-TOF): $[M+H]^+$ Calcd for $C_{30}H_{32}{}^{11}BN_2O_4$ 495.2455; Found 495.2473.

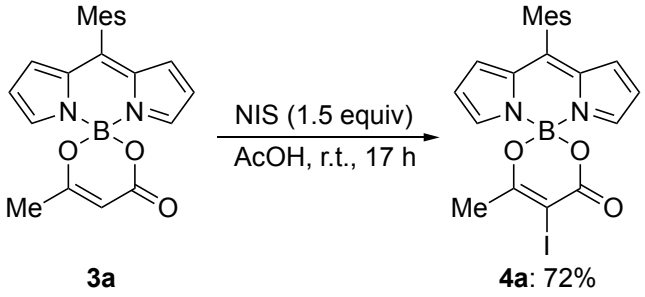
***B*-spiroBODIPY 3c**



According to the described general procedure B, **2c** (99 mg, 0.20 mmol) was reacted with Au(IPr) (6.2 mg, 10 μmol), AgOTf (2.6 mg, 10 μmol), *n*-Bu_4NOTf (19.6 mg, 50 μmol), dichloroethane (0.40 mL), and H_2O (0.22 mmol, 4.0 μL). The crude product was purified by pTLC (SiO_2, hexane/ethyl acetate = 5/4) to obtain **3c** (63.9 mg, 75%) as an orange solid. Rf = 0.20 (hexane/ethyl acetate = 1/1).

^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 6.95 (s, 2H), 5.96 (s, 2H), 5.33 (s, 1H), 2.34 (s, 3H), 2.32 (s, 6H), 2.13 (s, 3H), 2.08 (s, 3H), 1.99 (s, 3H), 1.38 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 170.3, 165.5, 155.8, 143.0, 142.1, 138.9, 135.2, 134.8, 131.1, 129.3, 129.1, 121.9, 95.2, 21.8, 21.3, 19.7, 19.7, 15.0, 13.7 ppm (a pair of peaks was overlapped); ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) δ = 2.21 (s, 1B) ppm; HR-MS (ESI-TOF): $[M+Na]^+$ Calcd for $C_{26}H_{29}{}^{11}BN_2O_3Na$ 451.2168; Found 451.2189.

4a

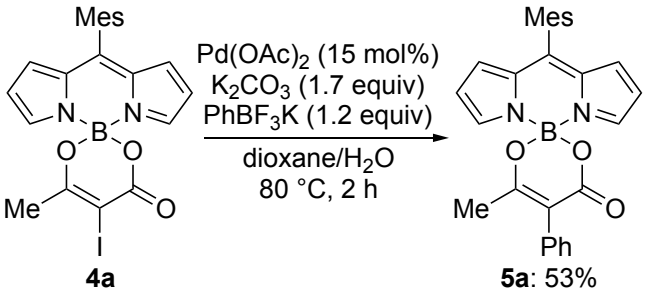


3a **4a**: 72%

In a Schlenk tube, **3a** (18.6 mg, 0.050 mmol), NIS (16.9 mg, 0.075 mmol), and AcOH (1 mL) were added under N_2. After stirring at room temperature for 17 h in the dark, H_2O (5.0 mL) was added to the reaction mixture. The crude products were extracted with CH_2Cl_2 (× 3). The organic layer was washed with saturated aqueous $NaHCO_3$, 10% aqueous $Na_2S_2O_3$, brine, and dried with Na_2SO_4. The organic layer was concentrated under reduced pressure. The crude product was purified by pTLC (SiO_2, hexane/ethyl acetate = 2/1) to obtain **4a** (18.0 mg, 72%) as an orange solid. Rf = 0.52 (hexane/ethyl acetate = 1/1).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.76 (ps, 2H), 6.96 (s, 2H), 6.71 (dd, *J* = 1.1, 4.2 Hz, 2H), 6.46 (dd, *J* = 2.0, 4.2 Hz, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 2.13 (s, 3H), 2.08 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 171.7, 161.4, 148.3, 144.8, 139.2, 136.6, 136.2, 135.3, 131.0, 129.4, 128.5, 128.3, 119.1, 64.6, 26.5, 21.3, 20.2, 20.2 ppm; ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) δ = 1.66 (s, 1B) ppm; HR-MS (ESI-TOF): $[M+H]^+$ Calcd for $C_{22}H_{21}{}^{11}BN_2O_3I$ 499.0688; Found 499.0667.

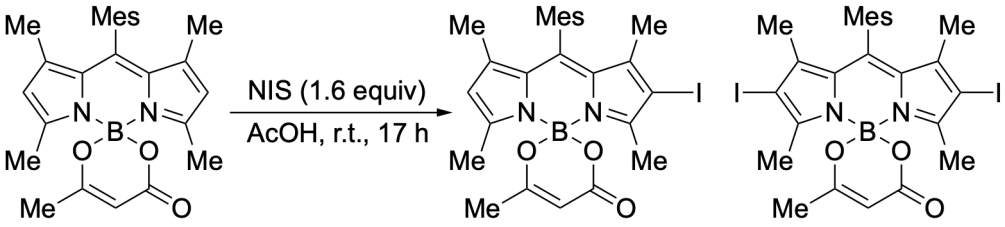
5a



4a **5a**: 53%

In a Schlenk tube, potassium phenyltrifluoroborate (6.37 mg, 0.035 mmol), K_2CO_3 (7.03 mg, 0.051 mmol), water (1 mL), and 1,4-dioxane (0.5 mL) were added under N_2. After stirring at room temperature for 2 min, $Pd(OAc)_2$ (1.03 mg, 4.6 μmol) and **4a** (14.8 mg, 0.030 mmol) were added to the reaction mixture. The reaction mixture was heated at 80 °C and stirred for 2 h. The crude products were extracted with EtOAc (× 3). The organic layer was dried with Na_2SO_4. The organic layer was concentrated under reduced pressure. The crude product was purified by pTLC (SiO_2, hexane/ethyl acetate = 5/4) to obtain **5a** (7.16 mg, 53%) as an orange solid. Rf = 0.40 (hexane/ethyl acetate = 1/1).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.90 (ps, 2H), 7.42-7.36 (m, 4H), 7.32-7.29 (m, 1H), 6.97 (s, 2H), 6.72 (dd, *J* = 0.9, 4.2 Hz, 2H), 6.48 (dd, *J* = 1.9, 4.2 Hz, 2H), 2.37 (s, 3H), 2.16 (s, 3H), 2.11 (s, 3H), 2.00 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 167.5, 164.7, 148.2, 144.8, 139.1, 136.7, 136.3, 135.5, 135.4, 131.2, 130.7, 129.6, 128.4, 128.3, 128.3, 127.1, 118.9, 108.3, 21.3, 20.9, 20.3, 20.2 ppm; ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) δ = 1.54 (s, 1B) ppm; HR-MS (ESI-TOF): $[M+H]^+$ Calcd for $C_{28}H_{26}{}^{11}BN_2O_3$ 449.2036; Found 449.2046.



3c **6c**: 45% **7c**: 55%

In a Schlenk tube, **3c** (21.4 mg, 0.050 mmol), NIS (17.4 mg, 0.077 mmol), and AcOH (1 mL) were added under N_2. After stirring at room temperature for 17 h in the dark, H_2O (5.0 mL) was added to the reaction mixture. The crude products were extracted with CH_2Cl_2 (× 3). The organic layer was washed with saturated aqueous $NaHCO_3$, 10% aqueous $Na_2S_2O_3$, brine, and dried with Na_2SO_4. The organic layer was concentrated under reduced pressure. The crude product was purified by pTLC (SiO_2, hexane/ethyl acetate = 2/1) to obtain **6c** (12.6 mg, 45%) and **7c** (18.6 mg, 55%) as red solids.

6c

Rf = 0.34 (hexane/ethyl acetate = 2/3). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 6.97 (s, 1H), 6.97 (s, 1H), 6.03 (s, 1H), 5.35 (pd, *J* = 0.6 Hz, 1H), 2.42 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 1.99 (d, *J* = 0.6 Hz, 3H), 1.41 (s, 3H), 1.38 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 170.4, 165.2, 158.0, 154.7, 145.1, 143.3, 142.1 139.2, 135.1, 134.8, 131.6, 131.0, 130.6, 129.5, 129.3, 123.1, 95.5, 85.6, 21.7, 21.4, 19.7, 19.7, 16.1, 16.0, 15.2, 13.9 ppm; ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) δ = 2.22 (s, 1B) ppm; HR-MS (ESI-TOF): $[M+H]^+$ Calcd for $C_{26}H_{29}{}^{11}BN_2O_3I$ 555.1315; Found 555.1327.

7c

Rf = 0.60 (hexane/ethyl acetate = 2/3). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 6.98 (s, 2H), 5.38 (pd, *J* = 0.6 Hz, 1H), 2.44 (s, 6H), 2.36 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 1.99 (s, 3H), 1.42 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 170.5, 164.8, 156.9, 145.4, 142.1, 139.6, 135.1, 134.7, 131.0, 131.0, 129.6, 129.4, 95.7, 87.1, 21.7, 21.4, 19.7, 19.7, 16.4, 16.4 ppm; ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) δ = 2.25 (s, 1B) ppm; HR-MS (ESI-TOF): $[M+H]^+$ Calcd for $C_{26}H_{28}{}^{11}BN_2O_3I_2$ 681.0282; Found 681.0286.

3. NMR spectra

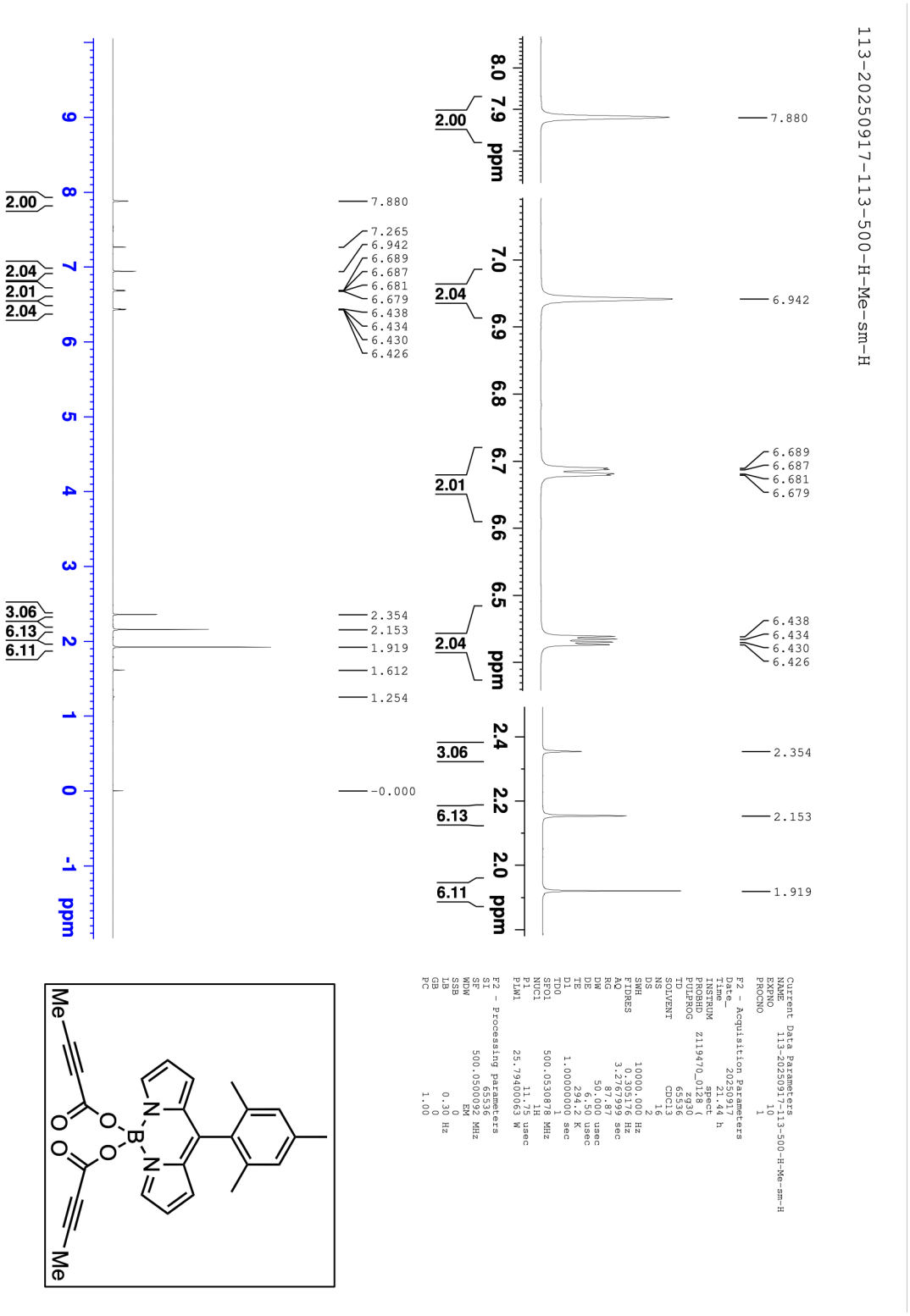


Figure S1. ^{1}H NMR spectrum of **2a** in $CDCl_3$ at 25 °C.

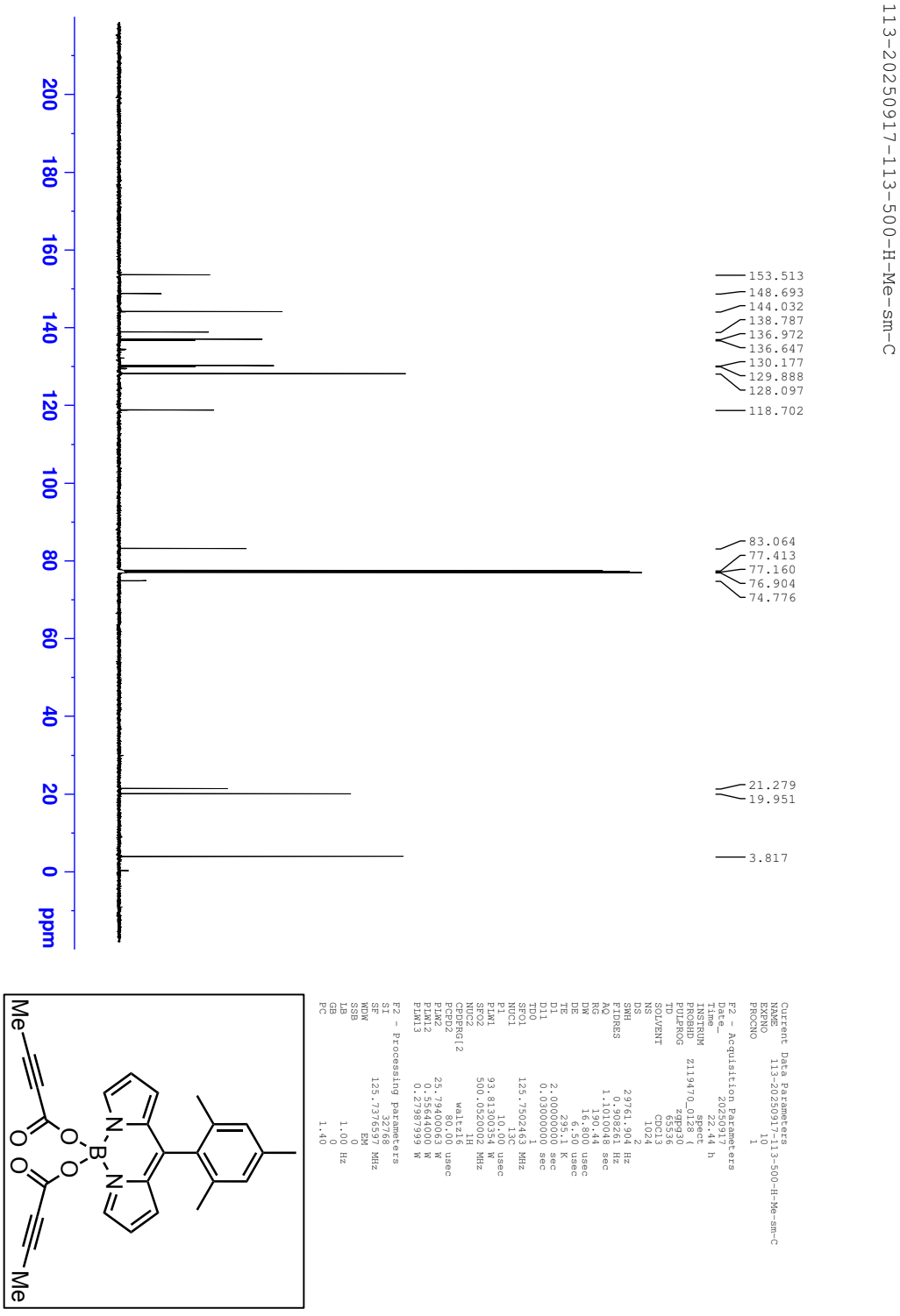


Figure S2. ^{13}C NMR spectrum of **2a** in $CDCl_3$ at 25 °C.

Figure S3. ^{11}B NMR spectrum of **2a** in $CDCl_3$ at 25 °C.

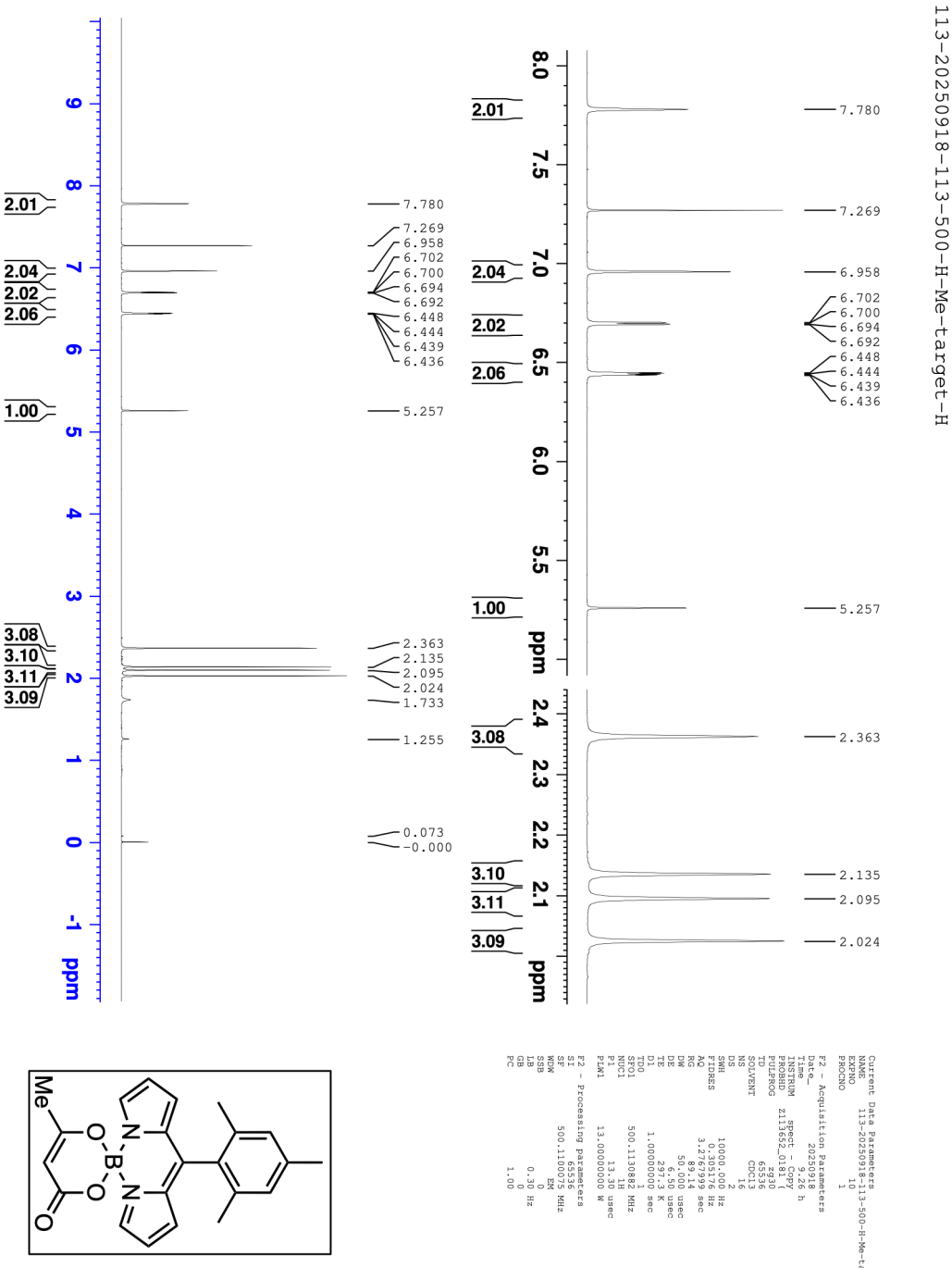


Figure S4. ^{1}H NMR spectrum of **3a** in $CDCl_3$ at 25 °C.

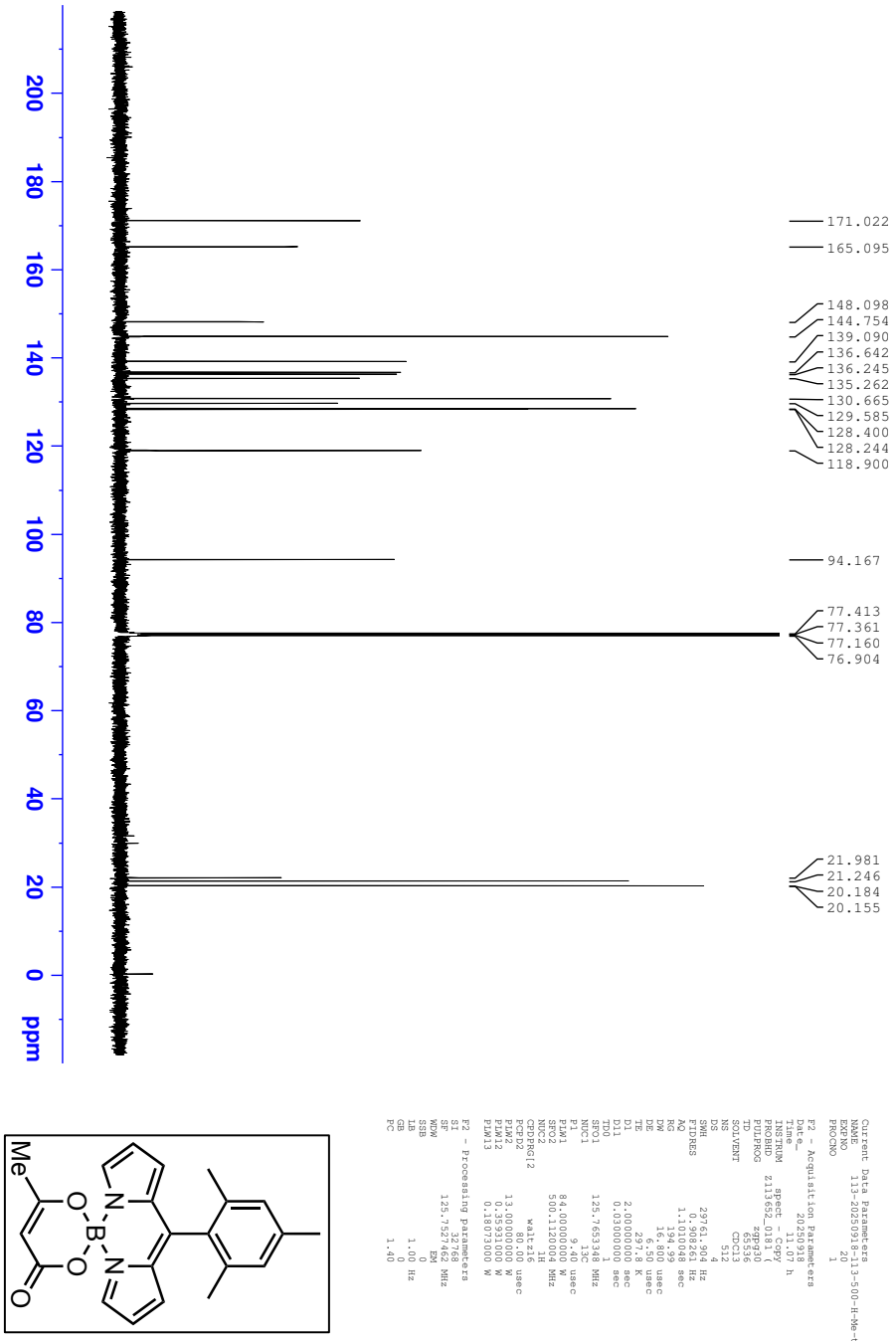


Figure S5. ^{13}C NMR spectrum of **3a** in $CDCl_3$ at 25 °C.

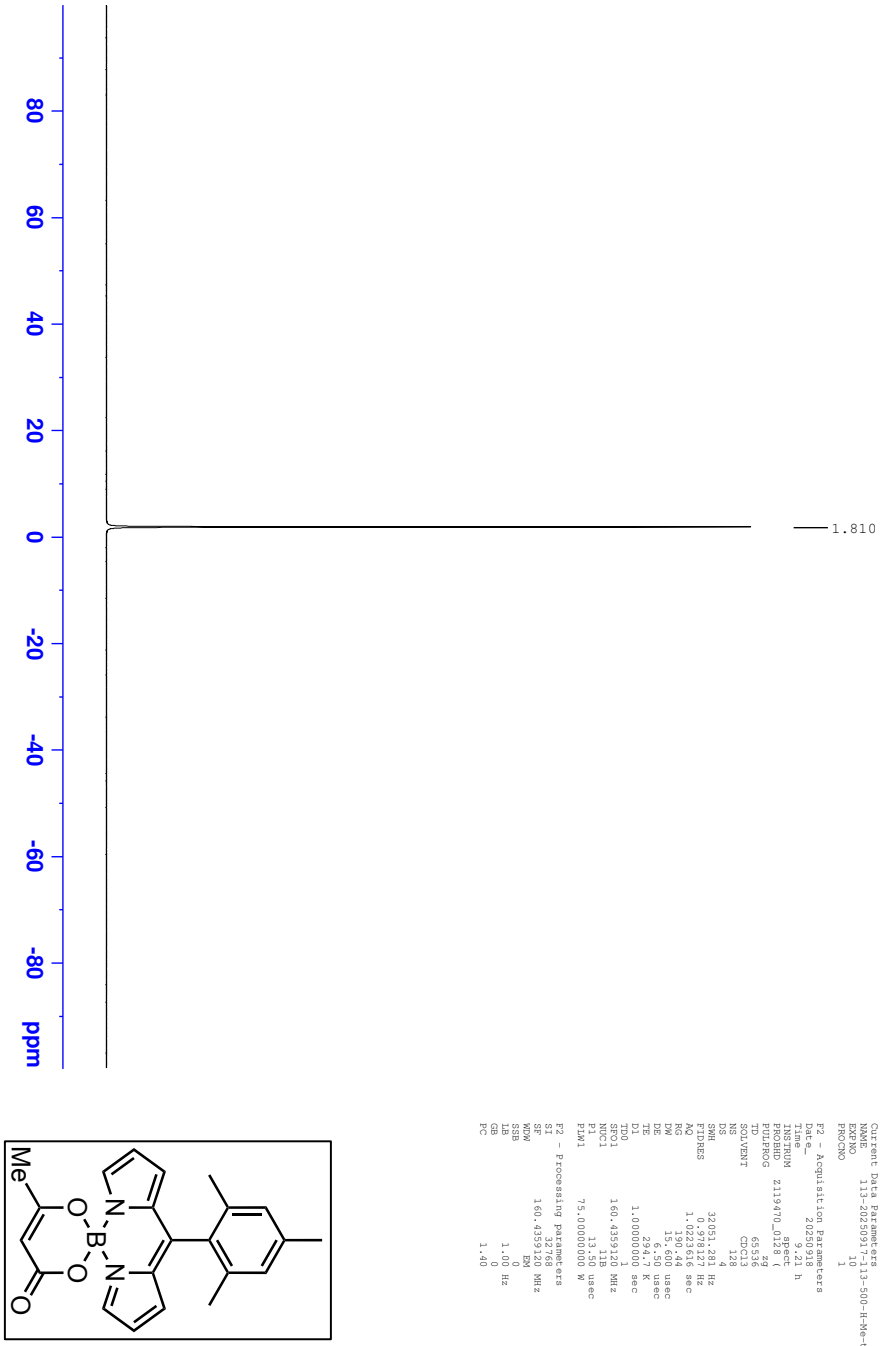


Figure S6. ^{11}B NMR spectrum of **3a** in $CDCl_3$ at 25 °C.

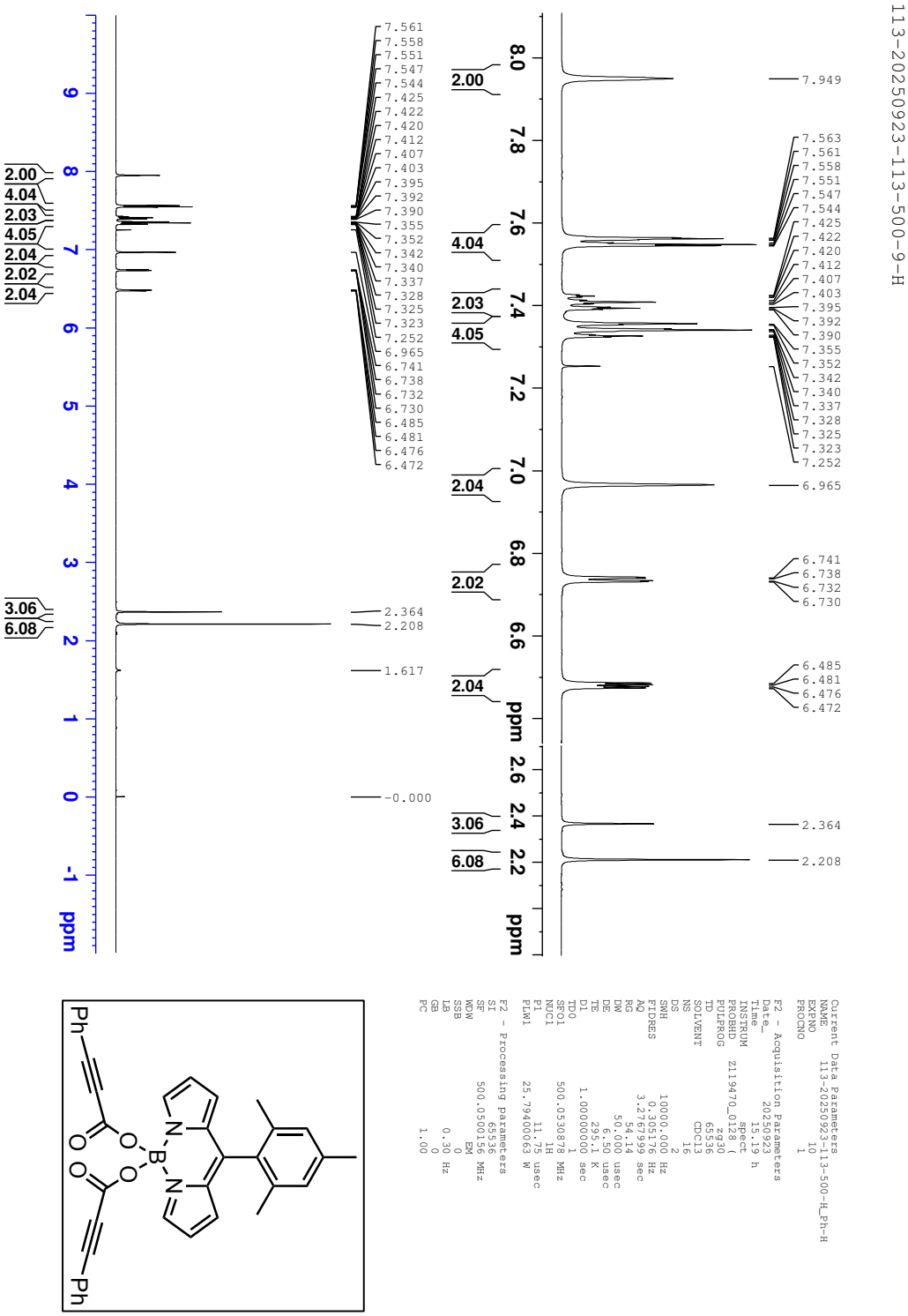


Figure S7. ^{1}H NMR spectrum of **2b** in $CDCl_3$ at 25 °C.

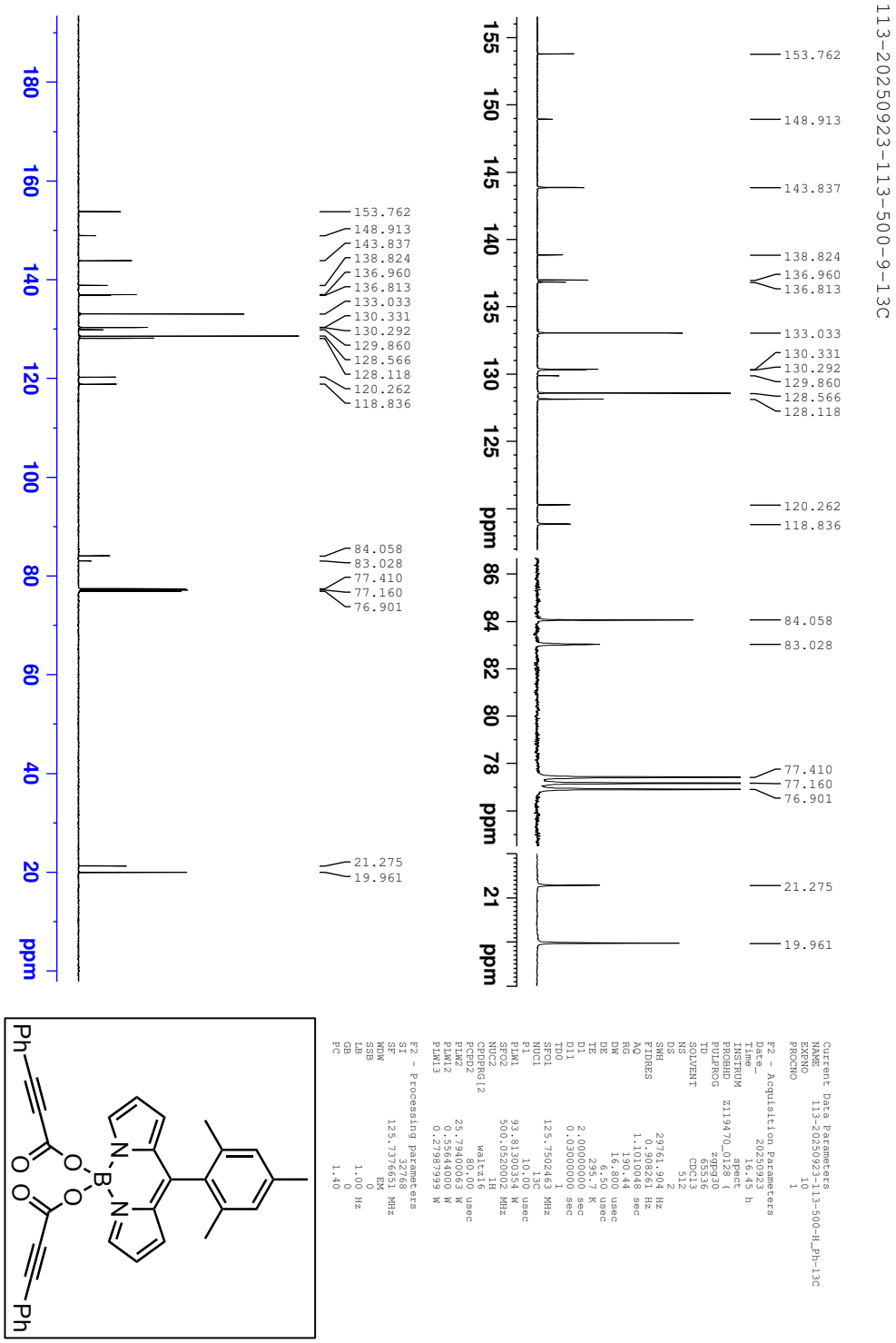


Figure S8. ^{13}C NMR spectrum of **2b** in $CDCl_3$ at 25 °C.

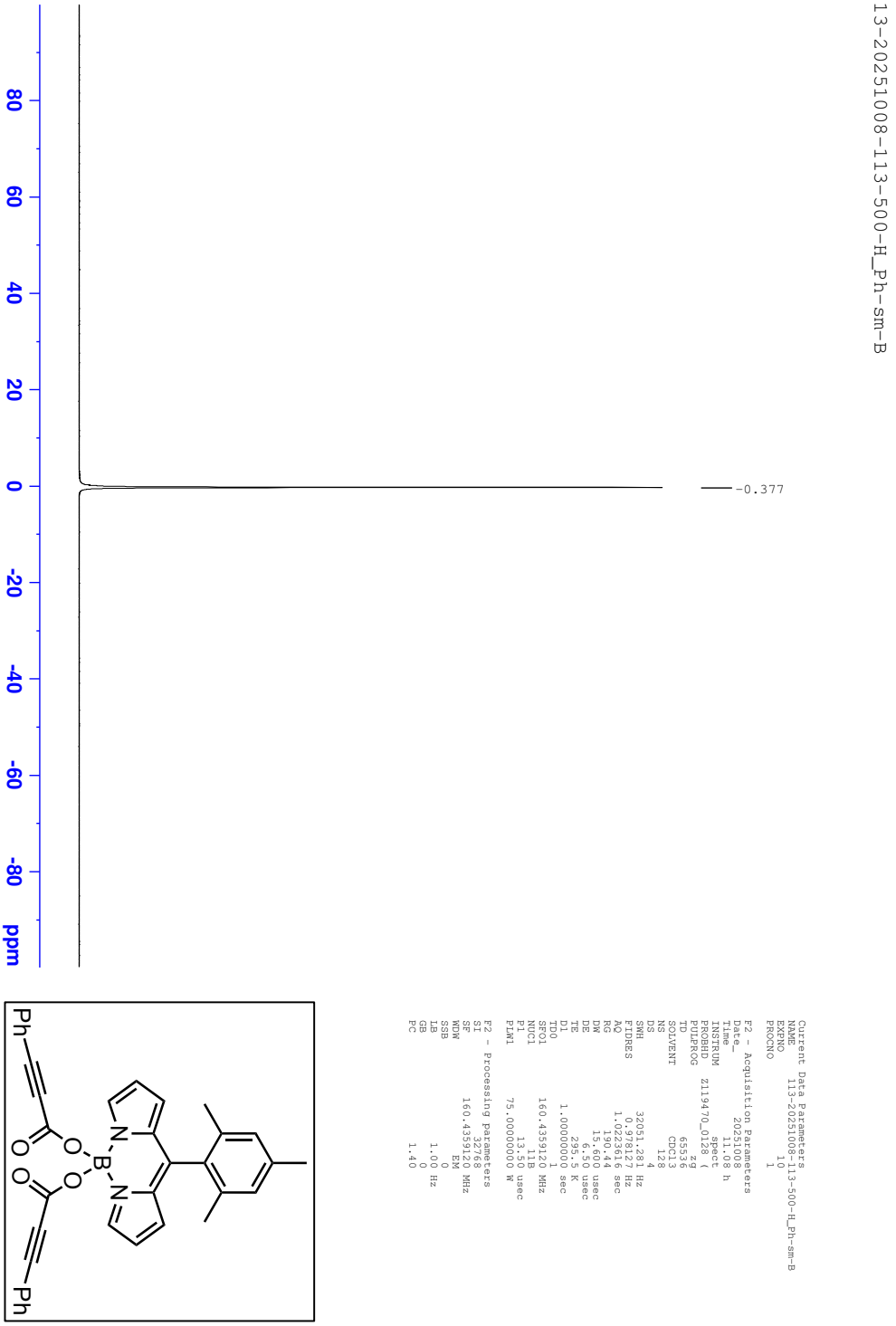


Figure S9. ^{11}B NMR spectrum of **2b** in $CDCl_3$ at 25 °C.

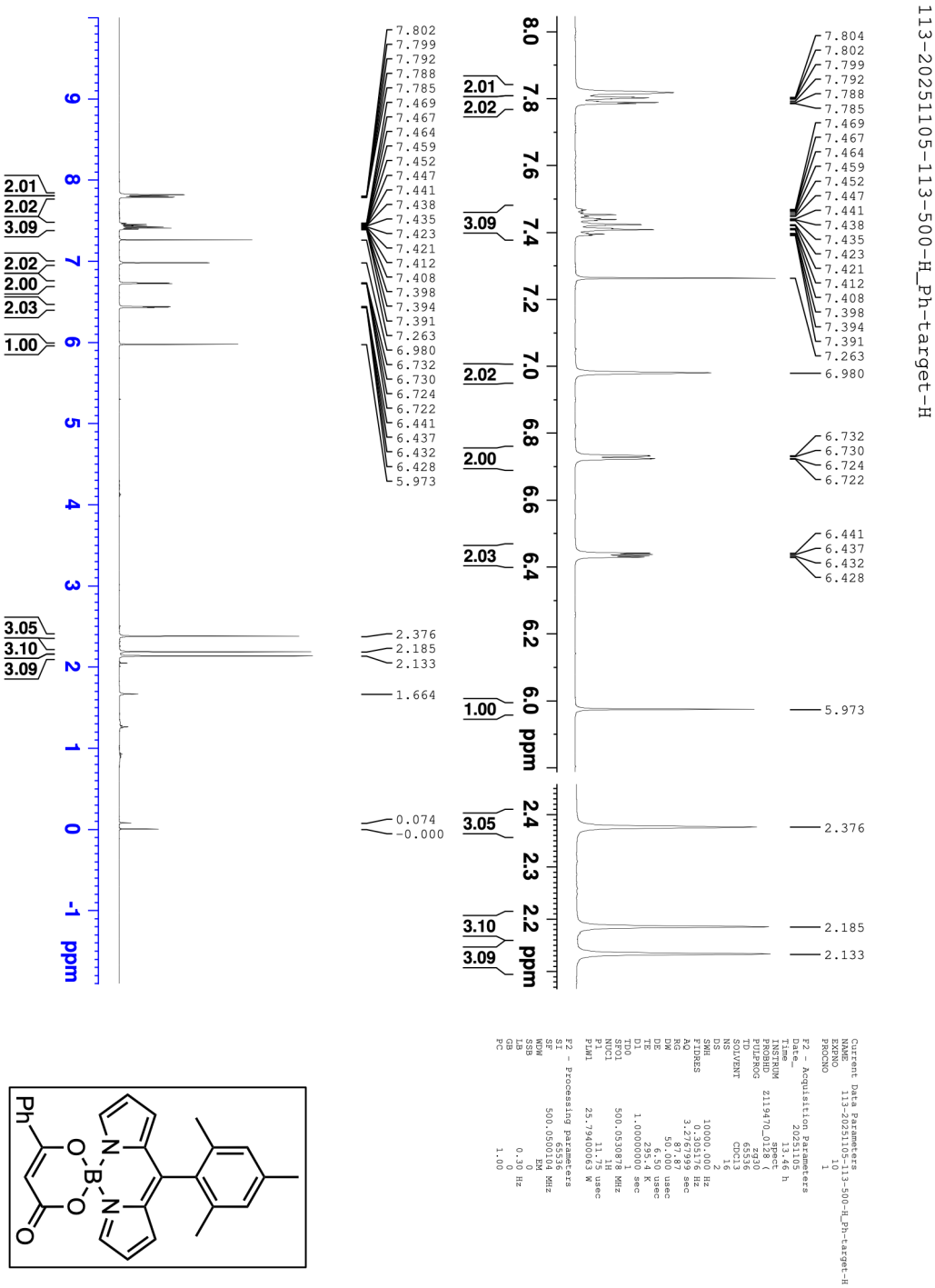


Figure S10. ^{1}H NMR spectrum of **3b** in $CDCl_3$ at 25 °C.

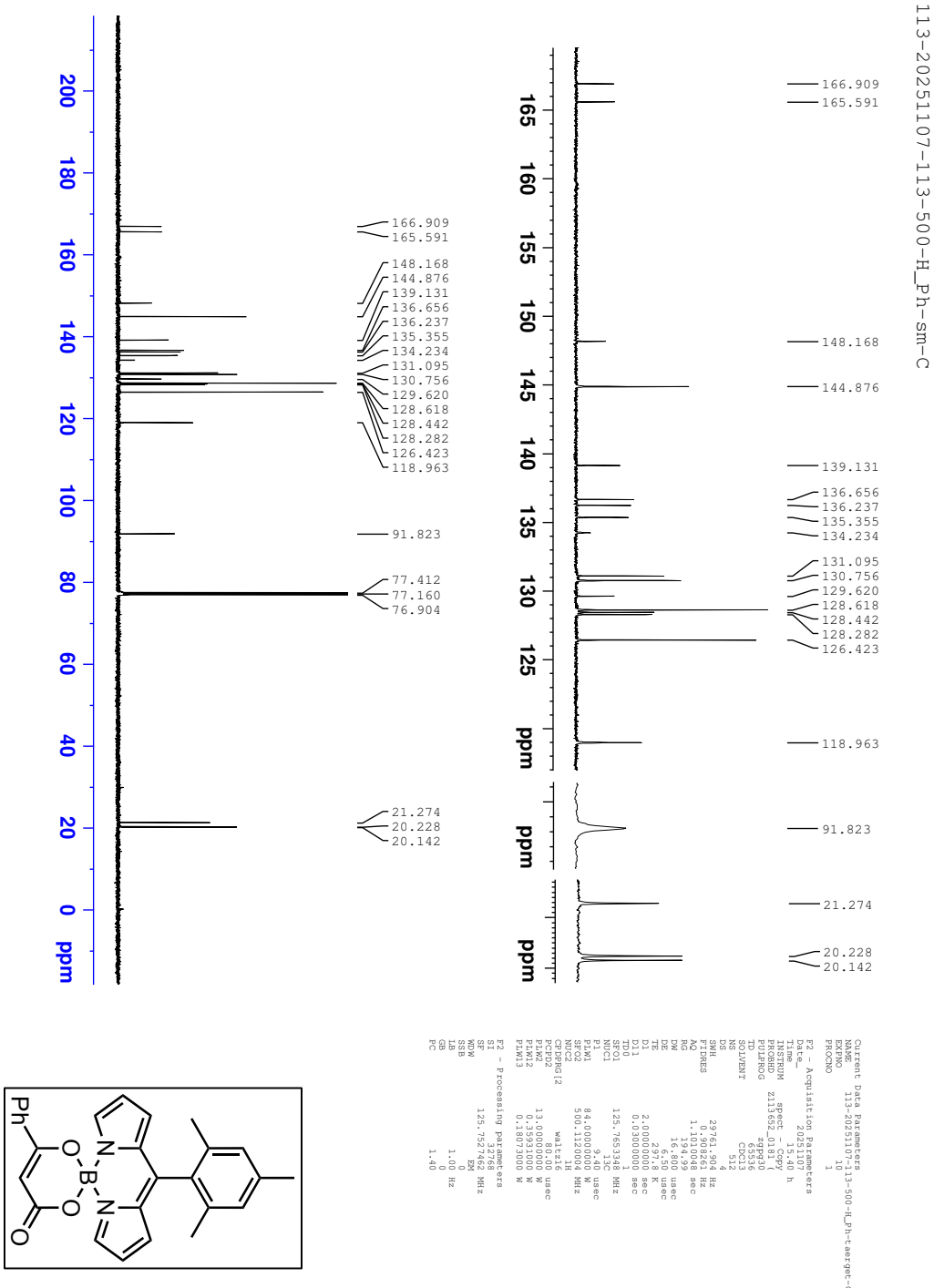


Figure S11. ^{13}C NMR spectrum of **3b** in $CDCl_3$ at 25 °C.

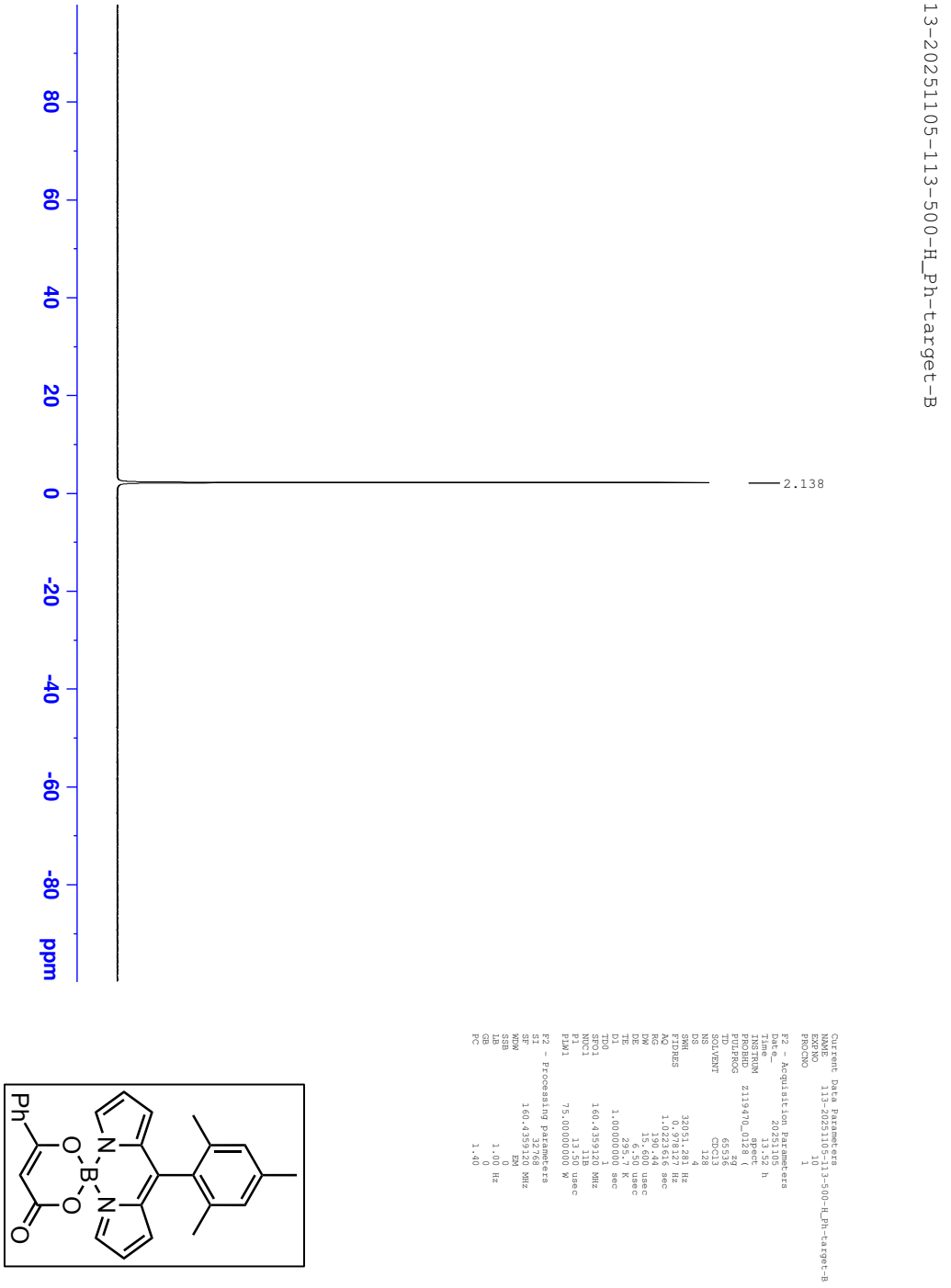


Figure S12. ^{11}B NMR spectrum of **3b** in $CDCl_3$ at 25 °C.

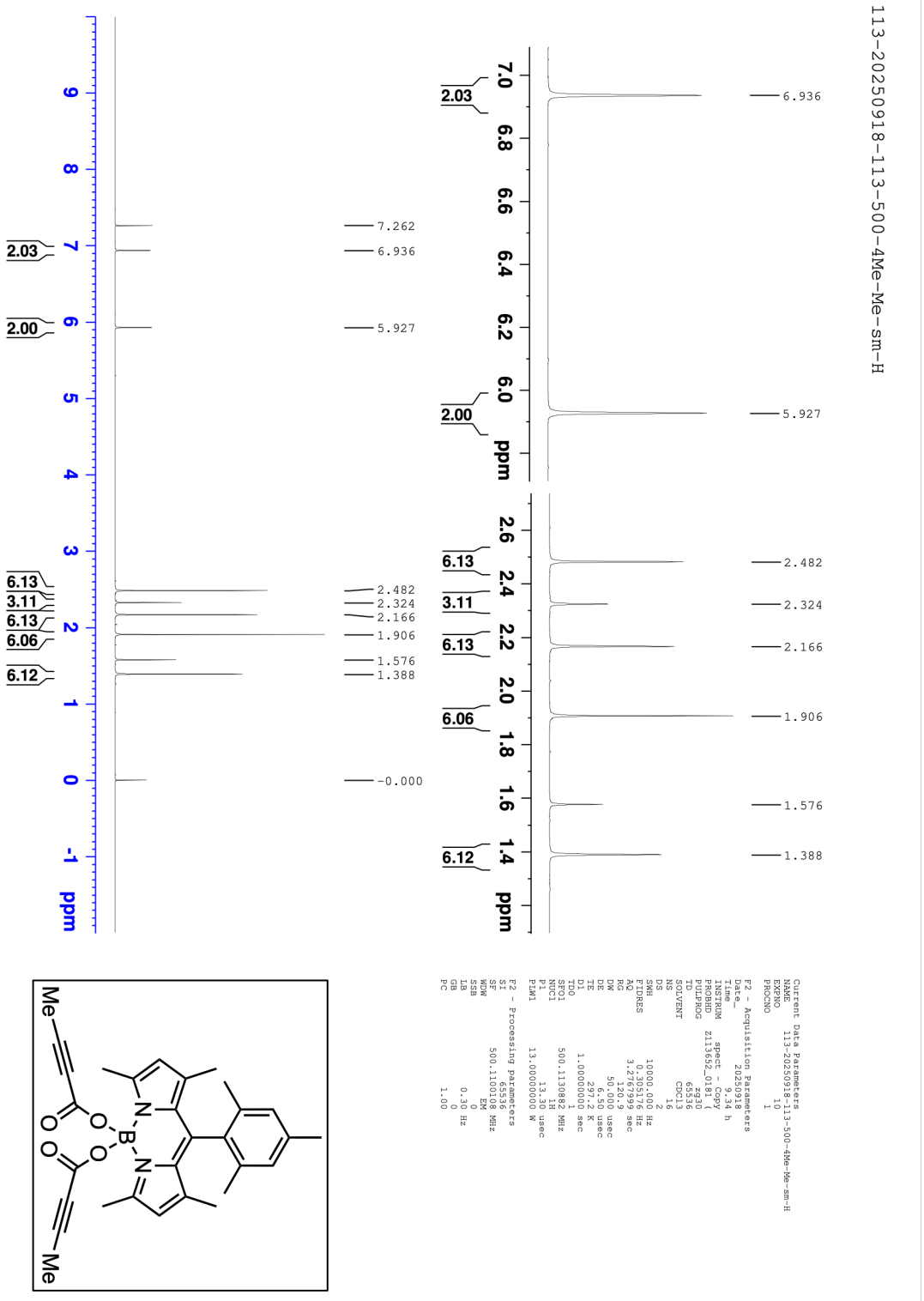


Figure S13. ^{1}H NMR spectrum of **2c** in $CDCl_3$ at 25 °C.

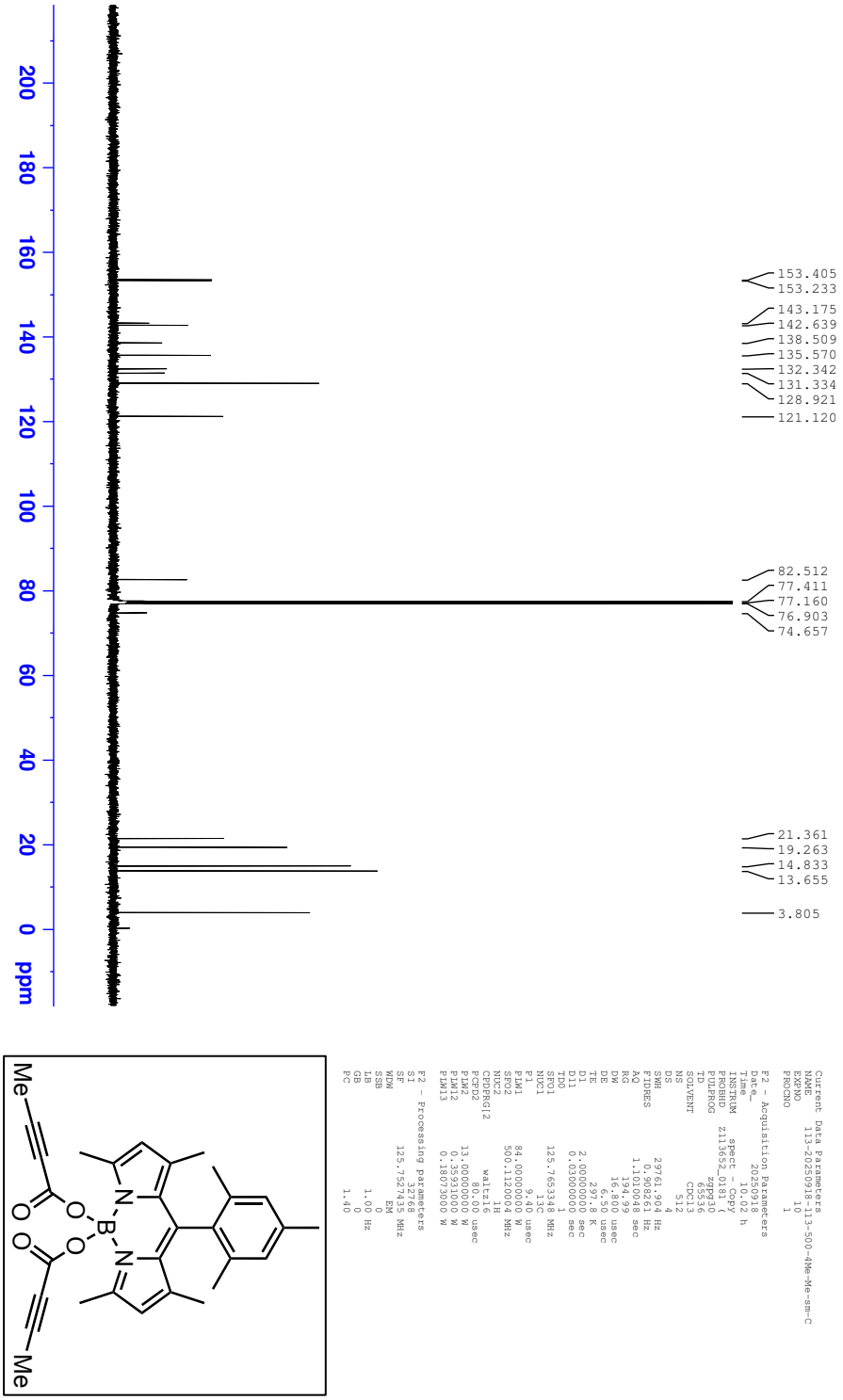


Figure S14. ^{13}C NMR spectrum of **2c** in $CDCl_3$ at 25 °C.

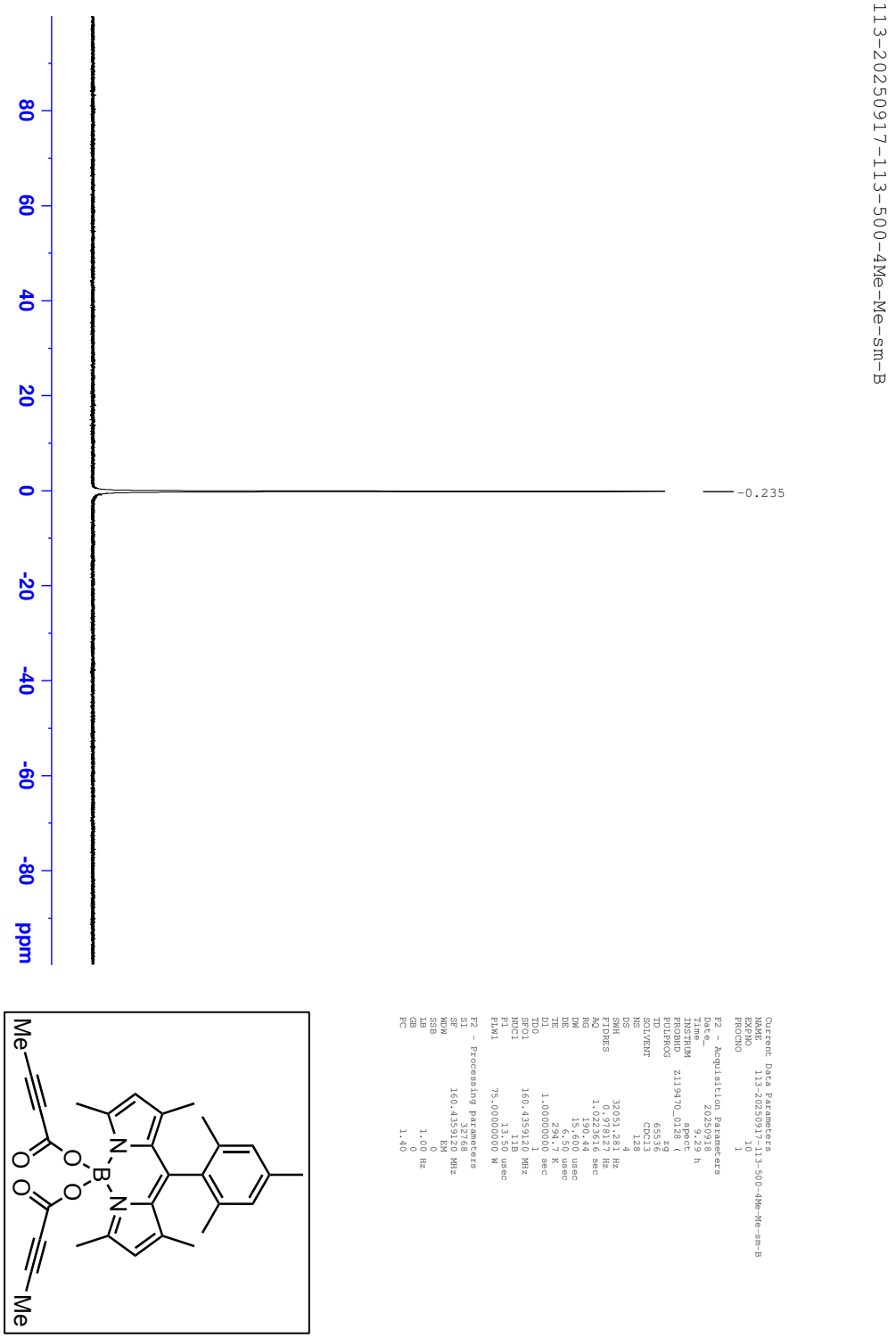


Figure S15. ^{11}B NMR spectrum of **2c** in $CDCl_3$ at 25 °C.

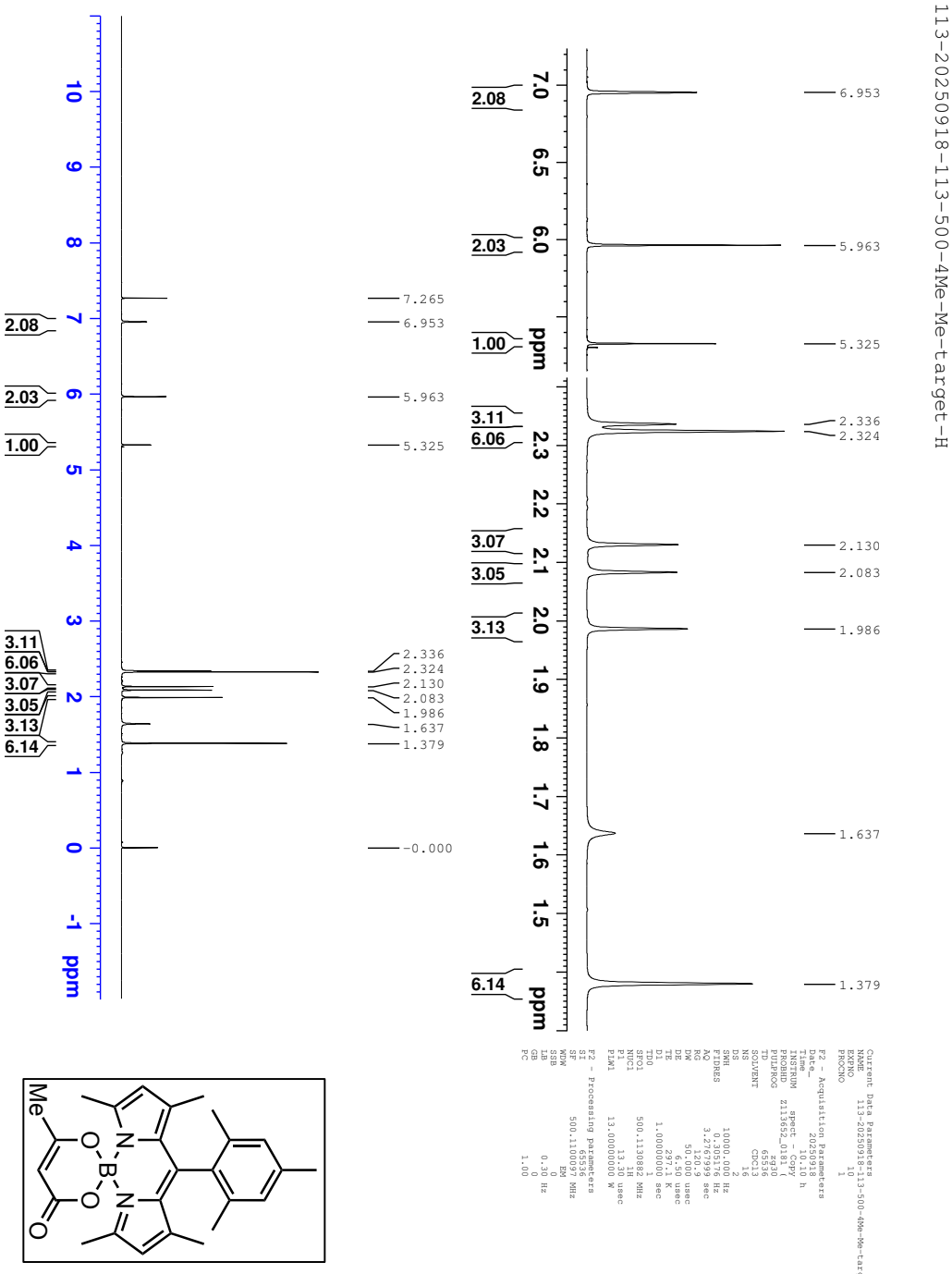


Figure S16. ^{1}H NMR spectrum of **3c** in $CDCl_3$ at 25 °C.

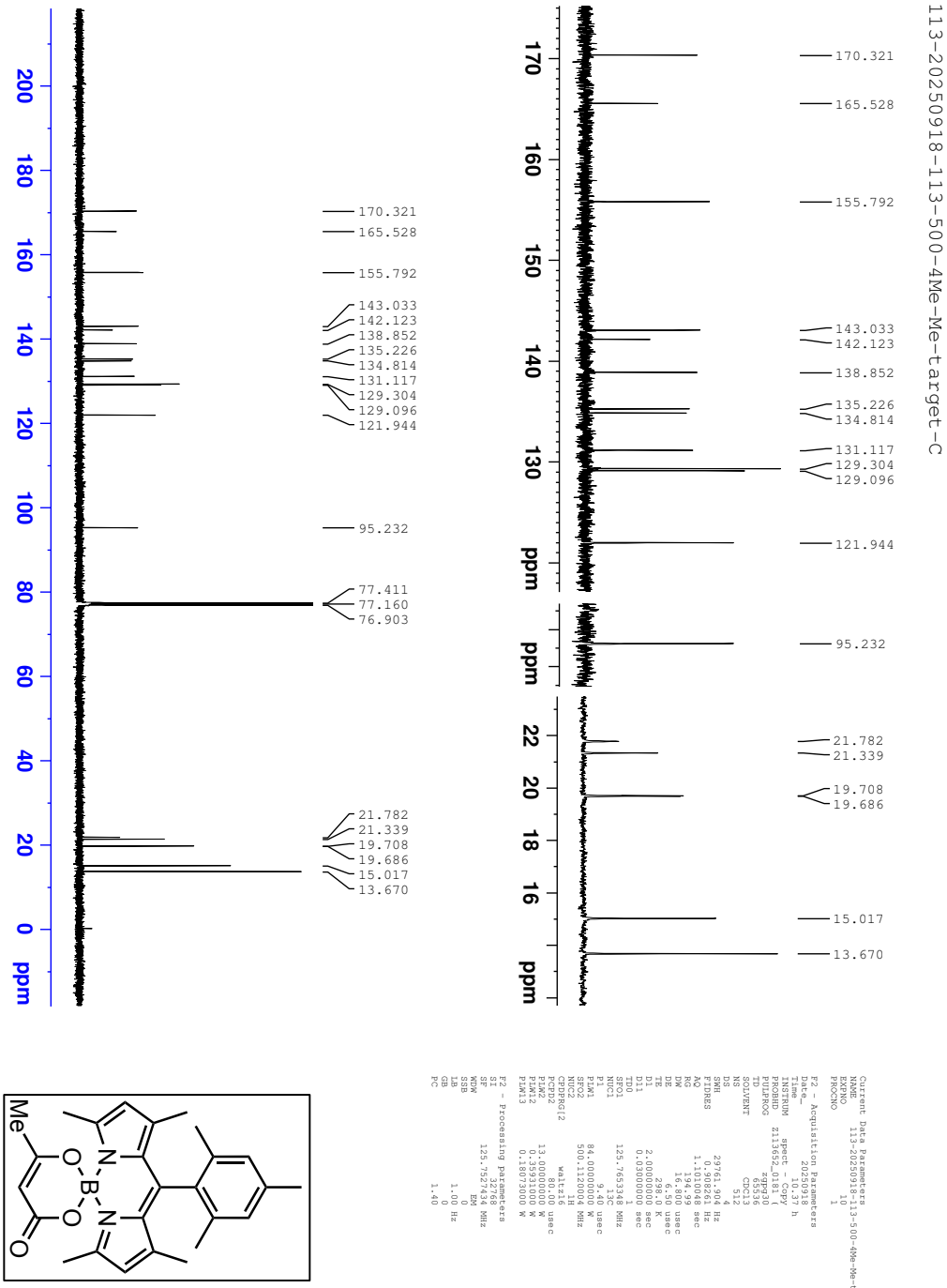


Figure S17. ^{13}C NMR spectrum of **3c** in $CDCl_3$ at 25 °C.

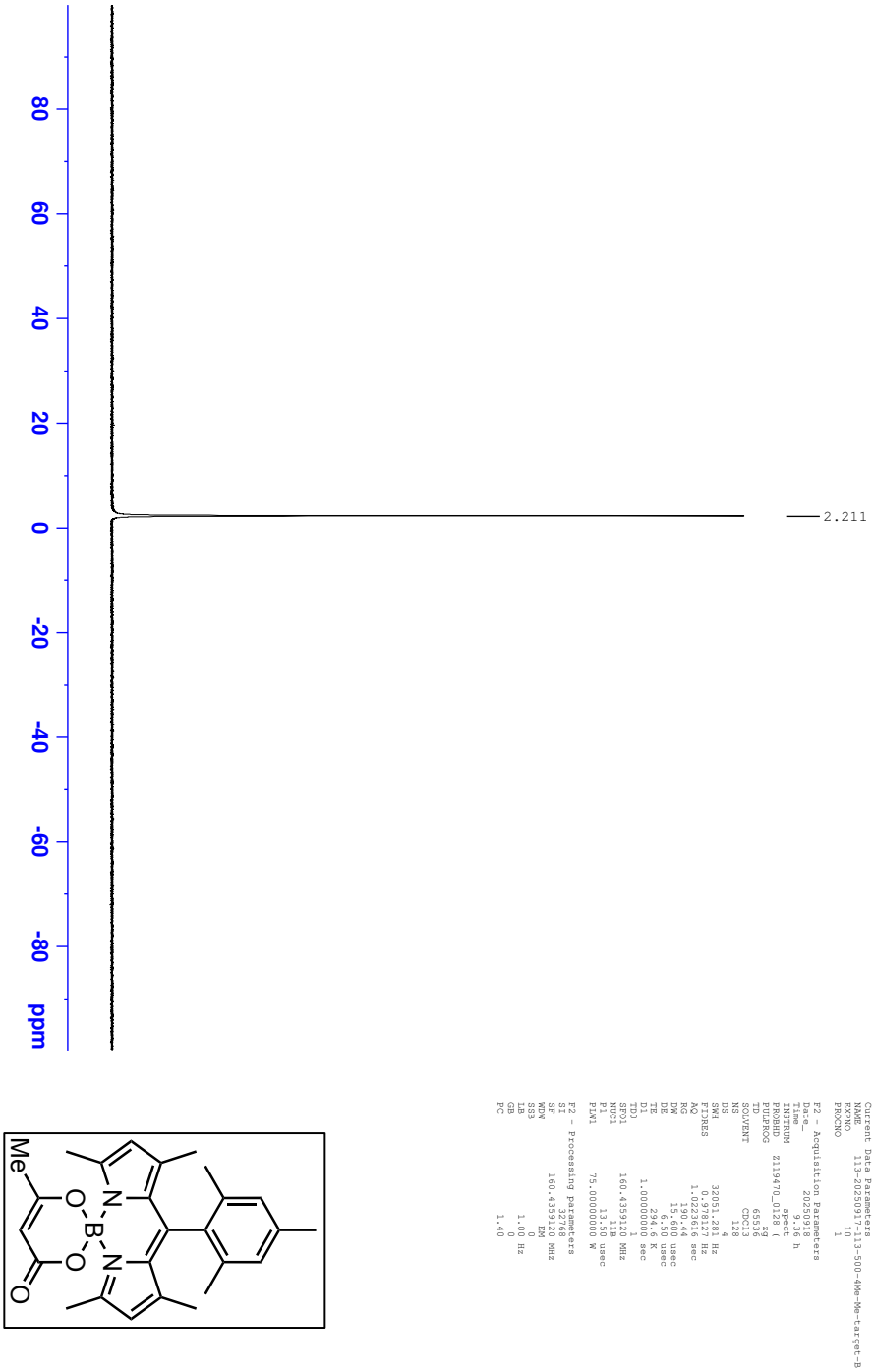


Figure S18. ^{11}B NMR spectrum of **3c** in $CDCl_3$ at 25 °C.

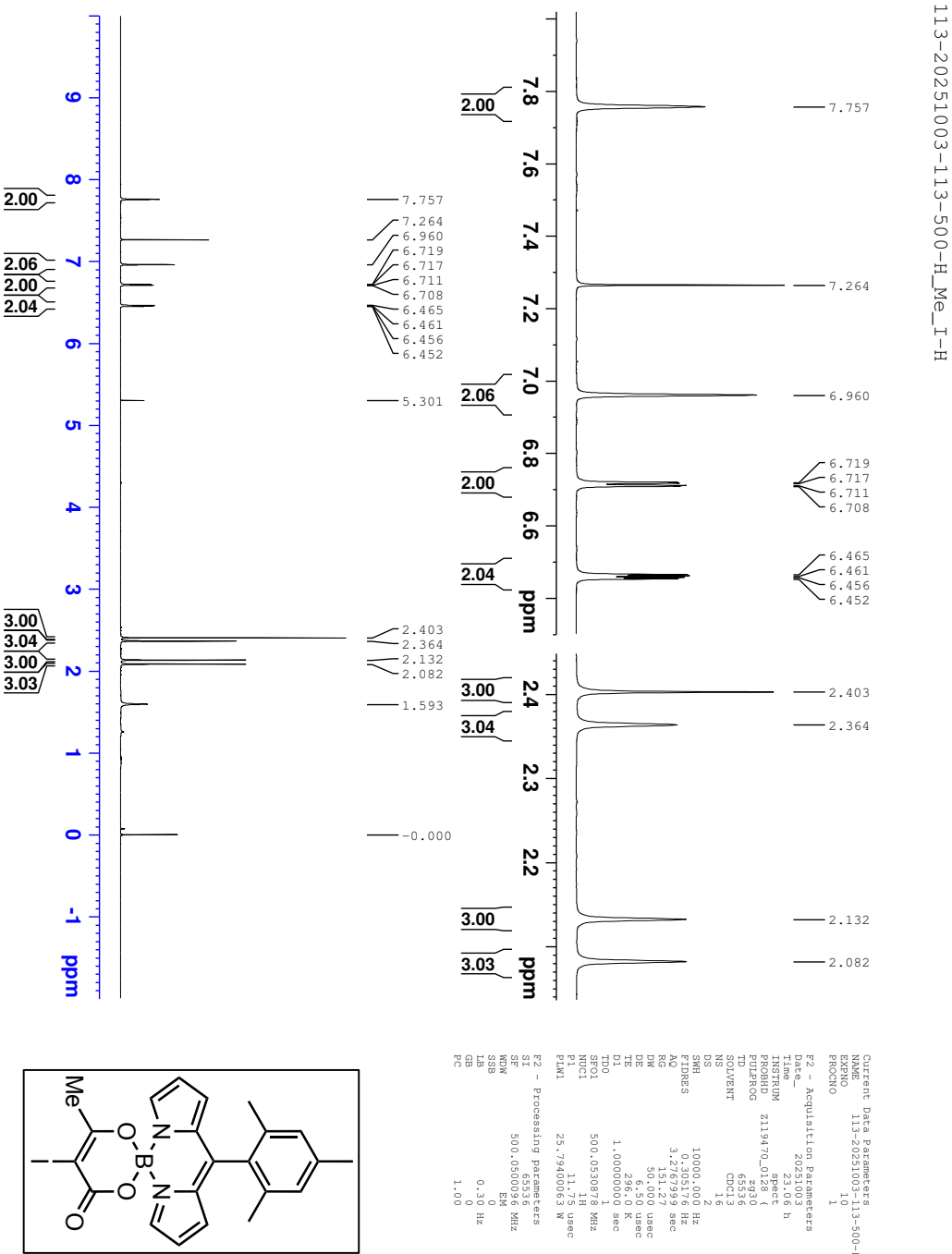


Figure S19. ^{1}H NMR spectrum of **4a** in $CDCl_3$ at 25 °C.

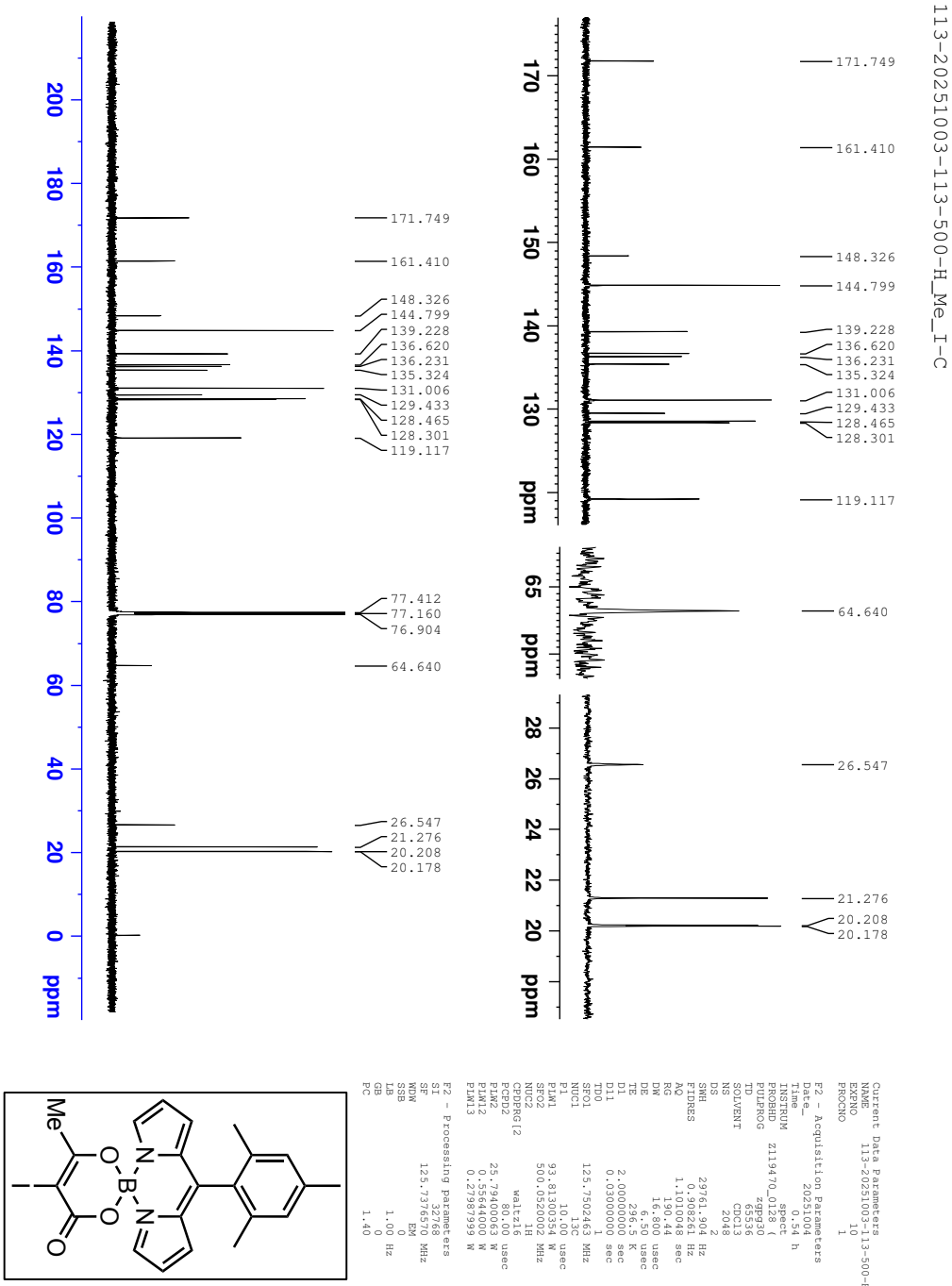


Figure S20. ^{13}C NMR spectrum of **4a** in $CDCl_3$ at 25 °C.

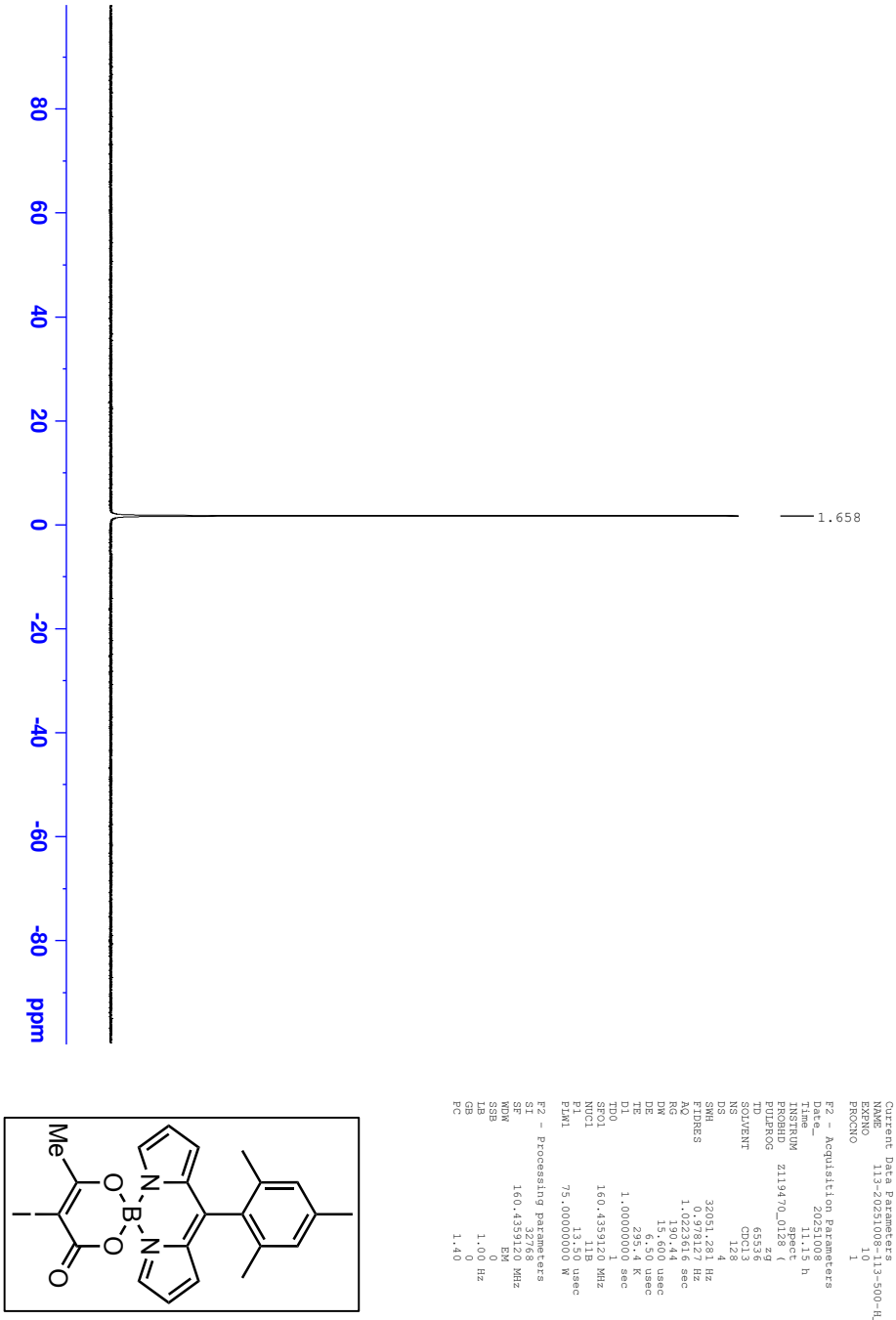


Figure S21. ^{11}B NMR spectrum of **4a** in $CDCl_3$ at 25 °C.

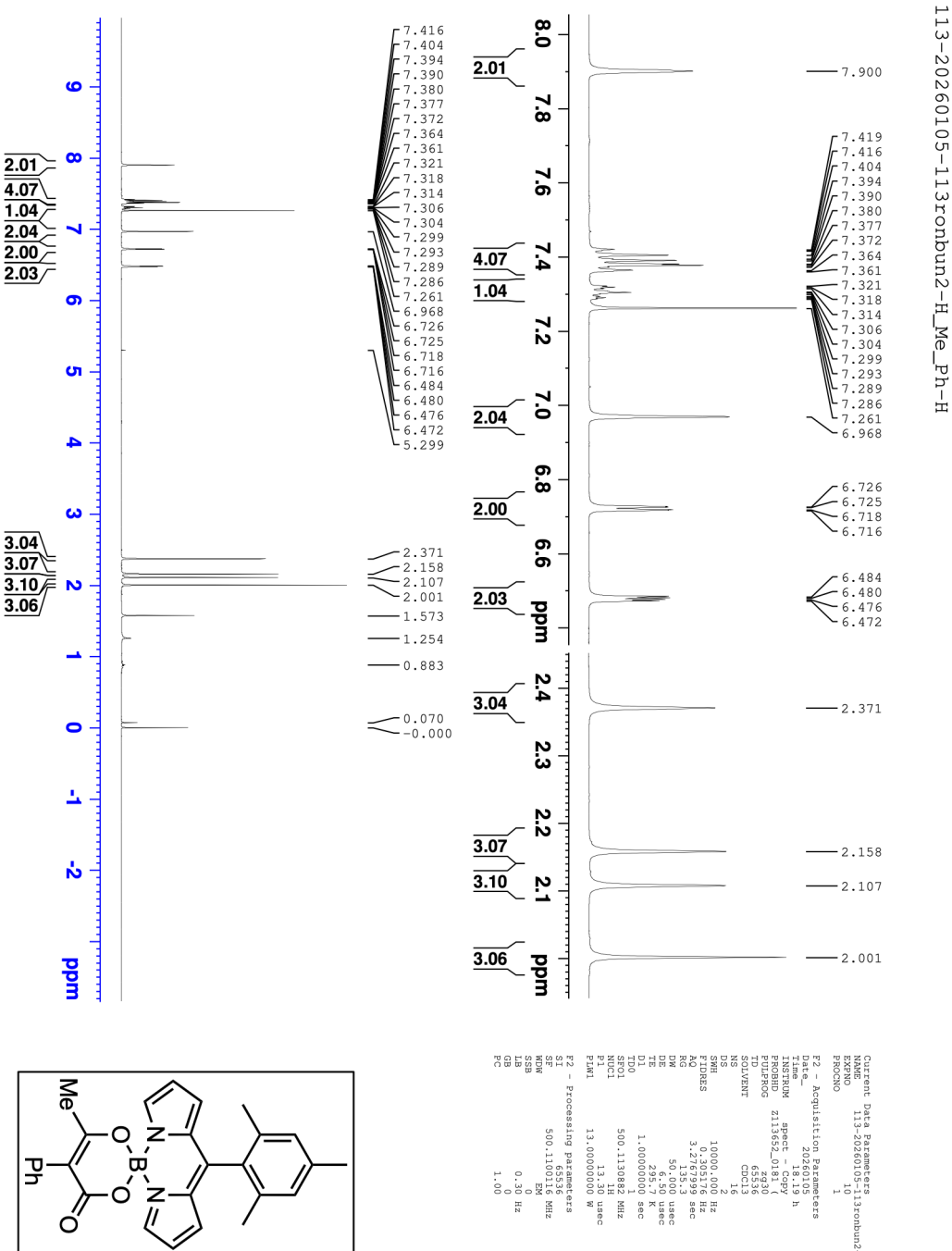


Figure S22. ^{1}H NMR spectrum of **5a** in $CDCl_3$ at 25 °C.

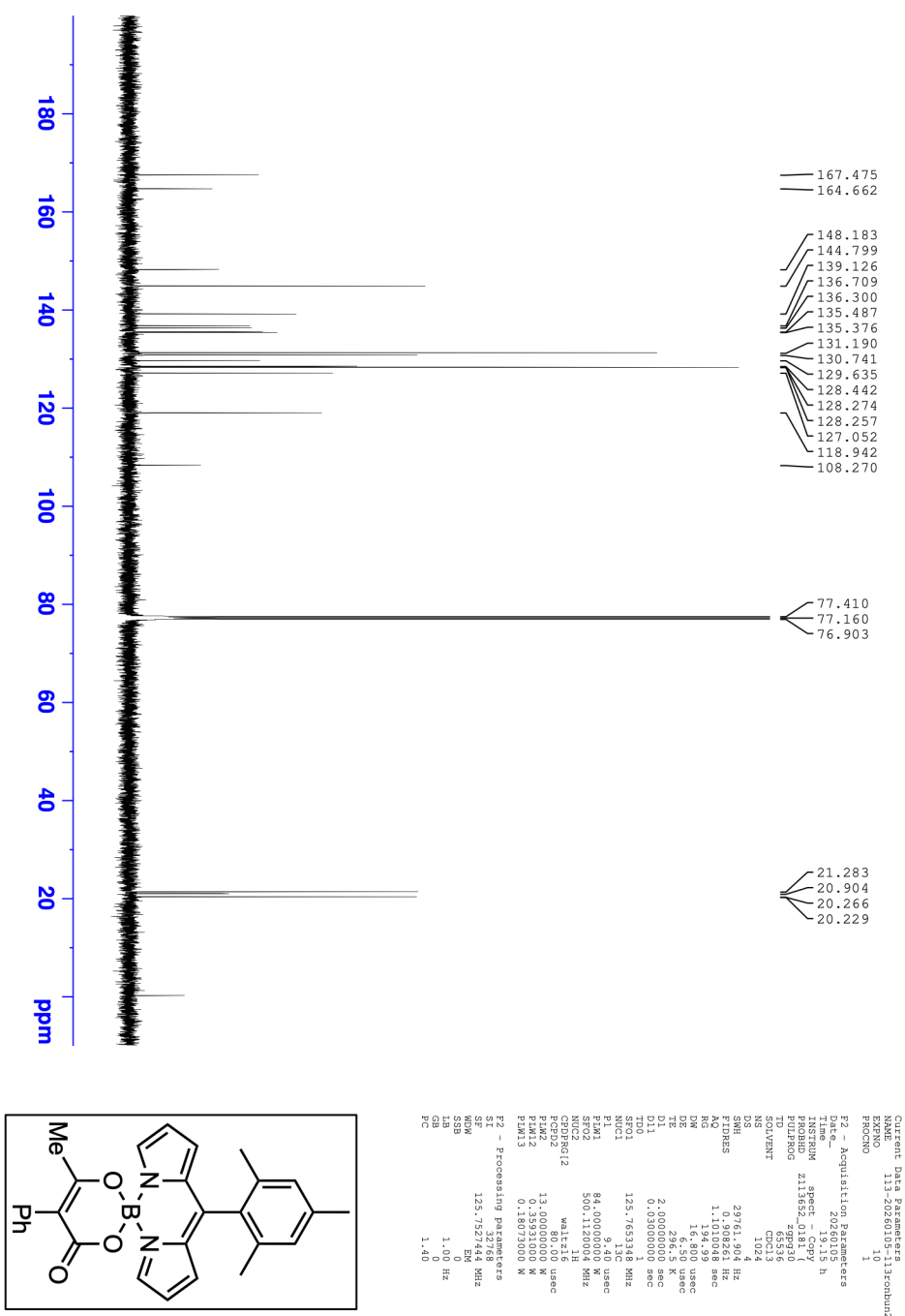


Figure S23. ^{13}C NMR spectrum of **5a** in $CDCl_3$ at 25 °C.

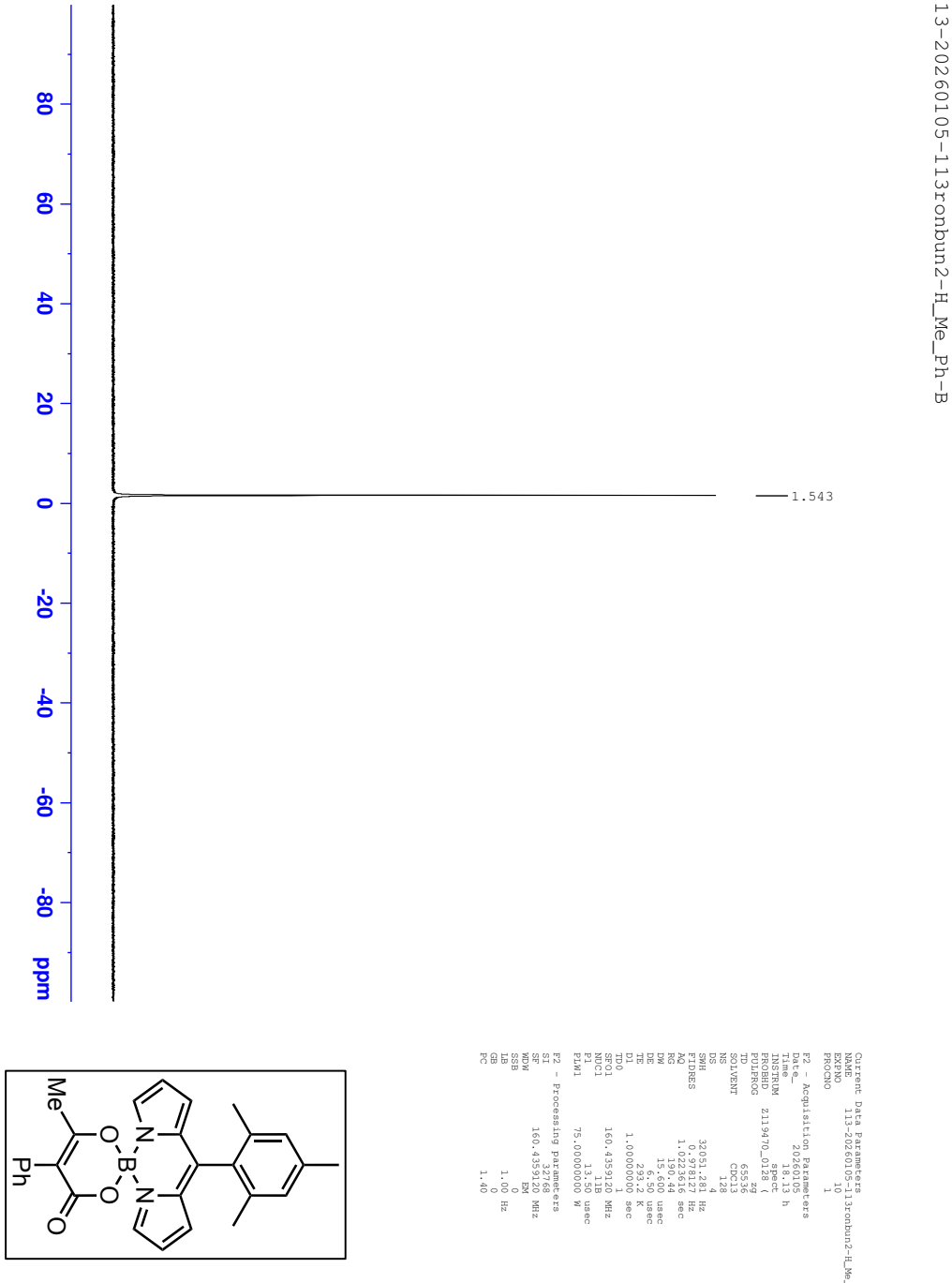


Figure S24. ^{11}B NMR spectrum of **5a** in $CDCl_3$ at 25 °C.

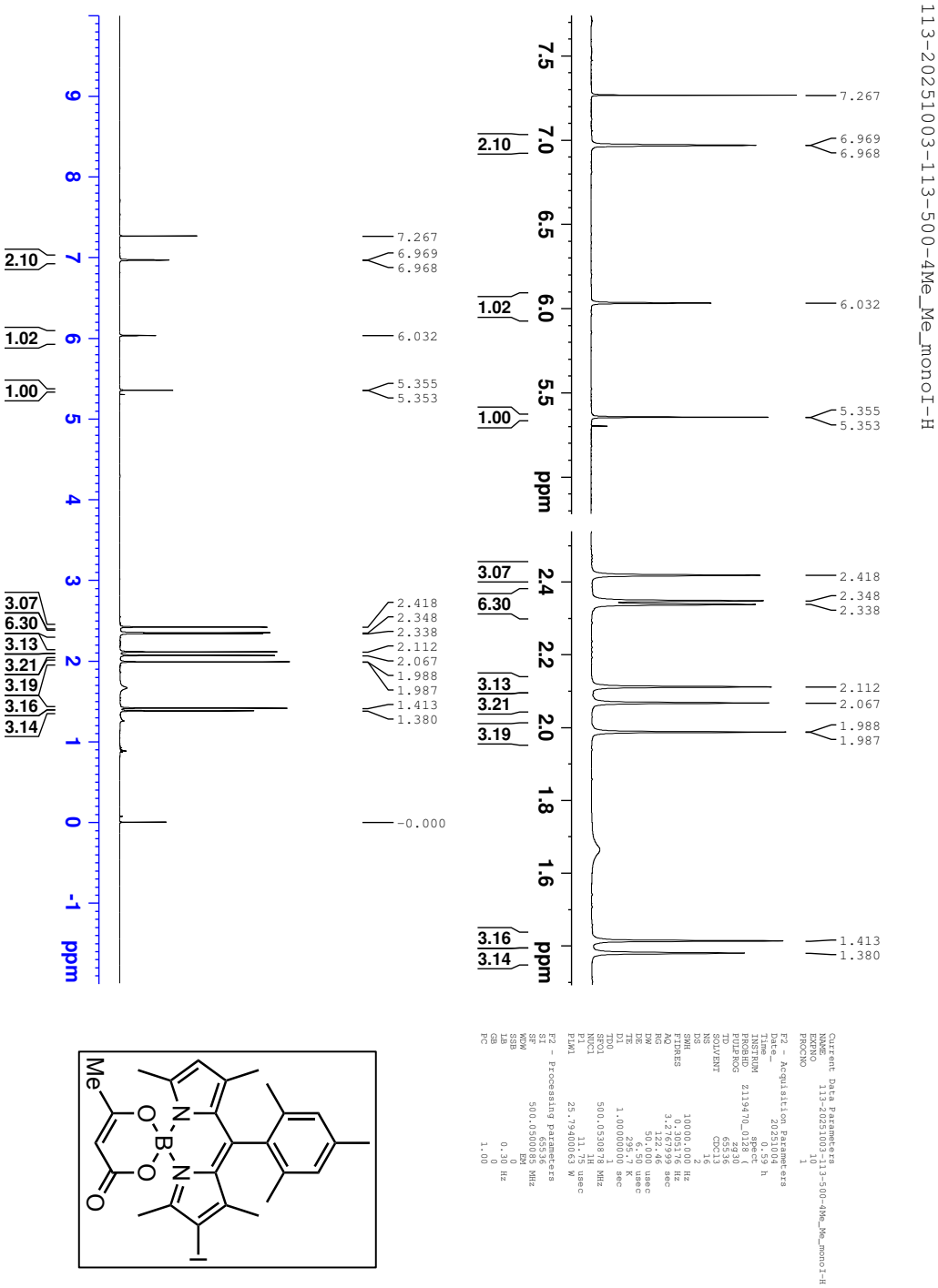


Figure S25. ^{1}H NMR spectrum of **6c** in $CDCl_3$ at 25 °C.

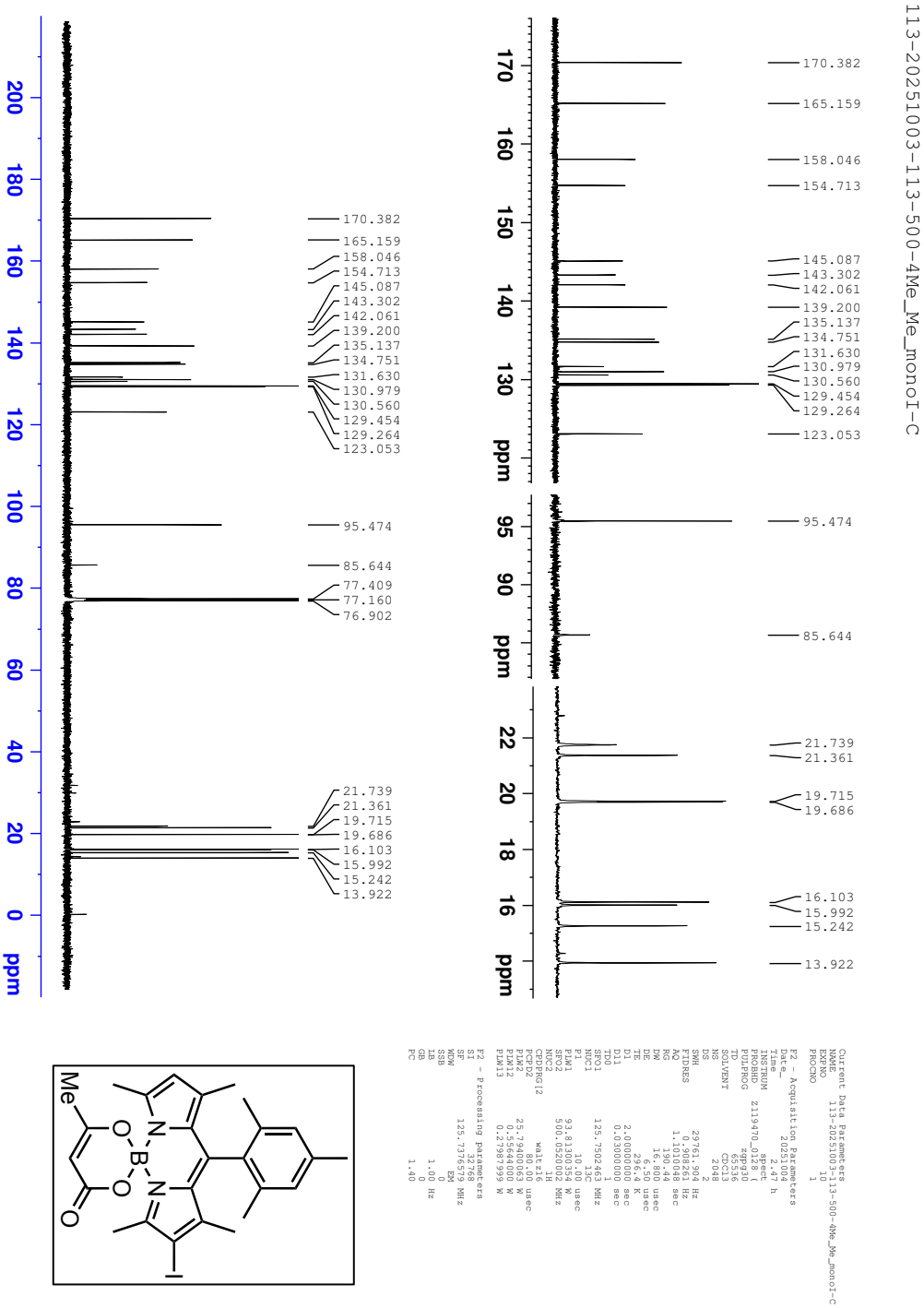


Figure S26. ^{13}C NMR spectrum of **6c** in $CDCl_3$ at 25 °C.

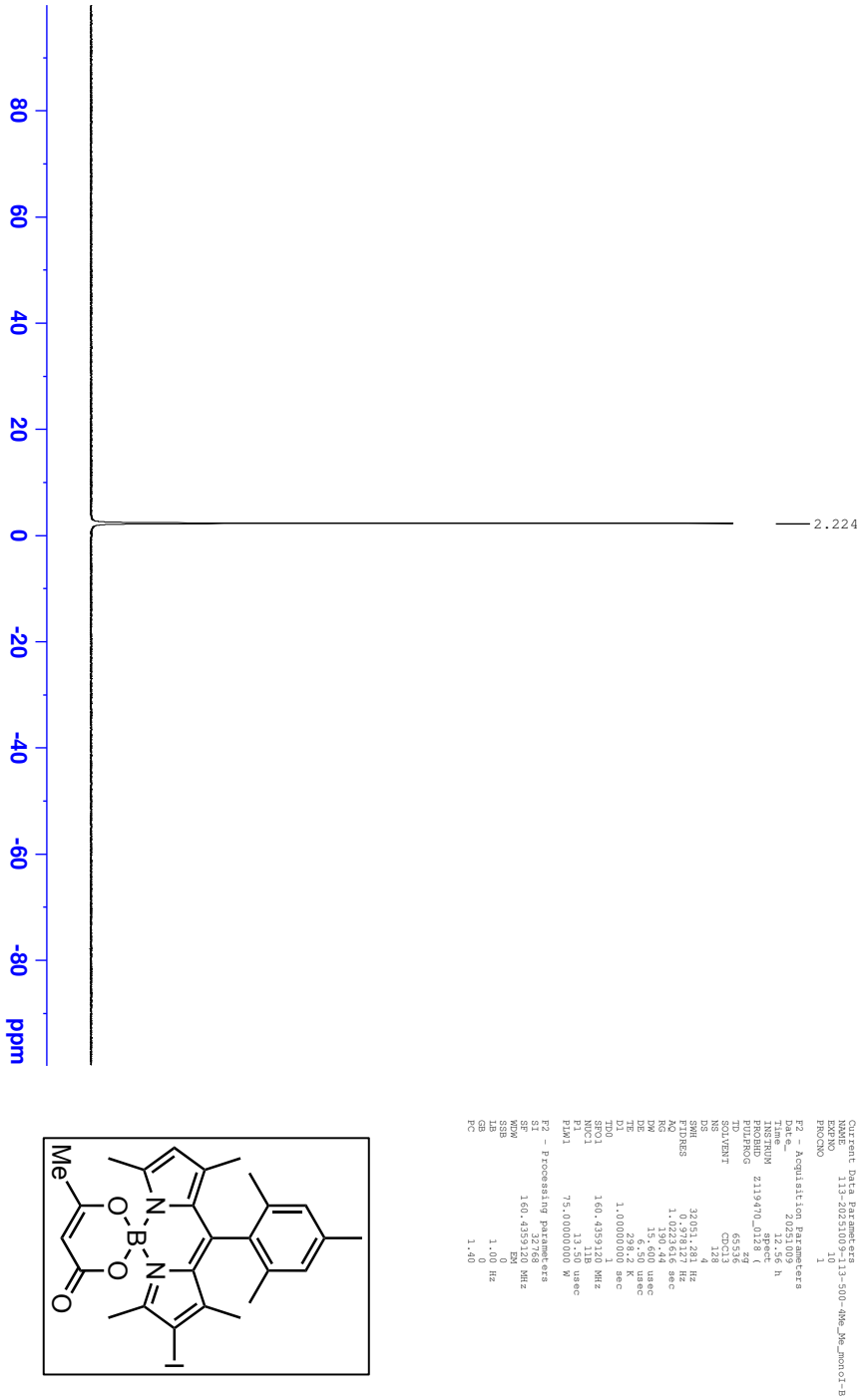


Figure S27. ^{11}B NMR spectrum of **6c** in $CDCl_3$ at 25 °C.

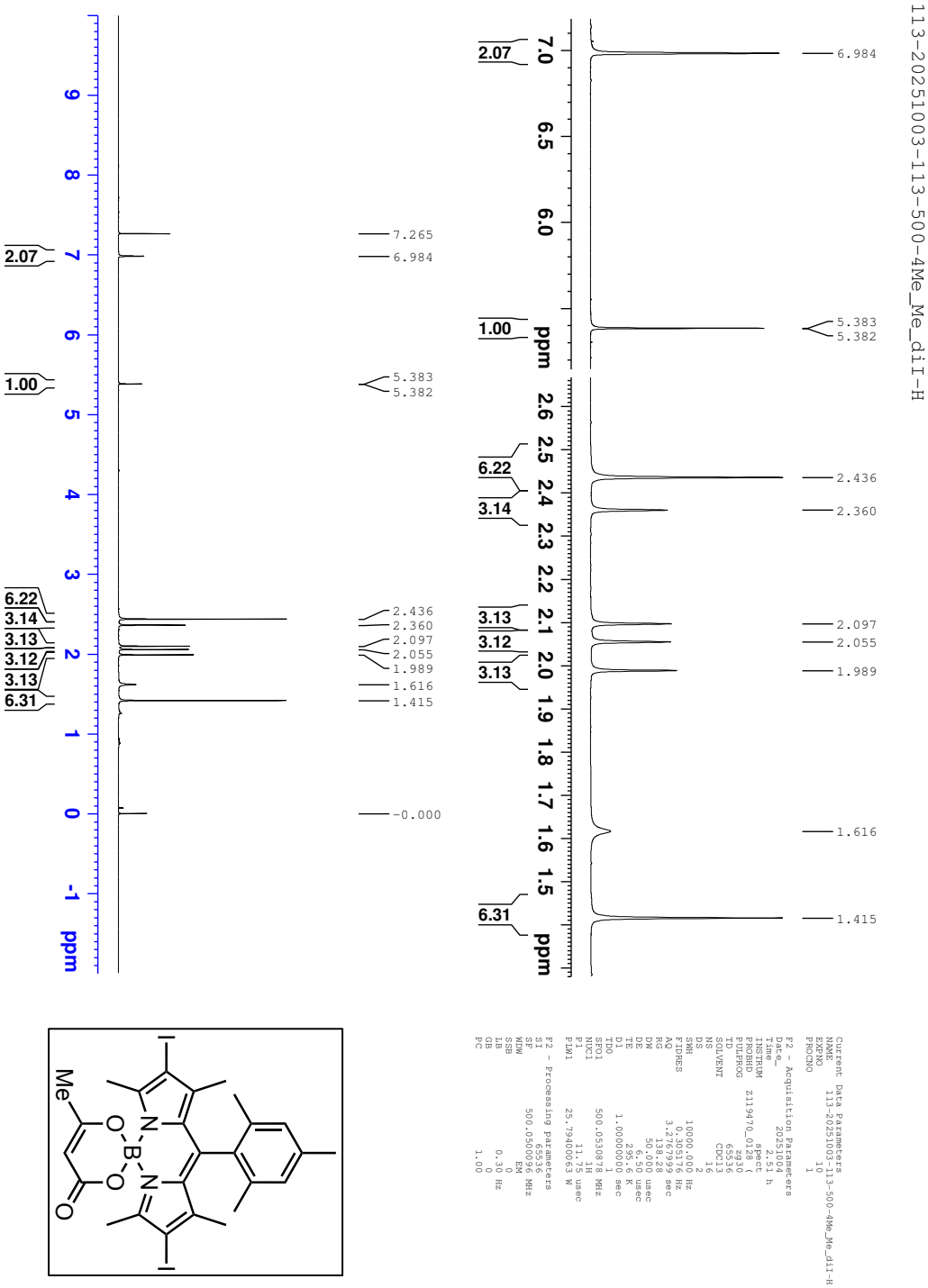


Figure S28. ^{1}H NMR spectrum of **7c** in $CDCl_3$ at 25 °C.

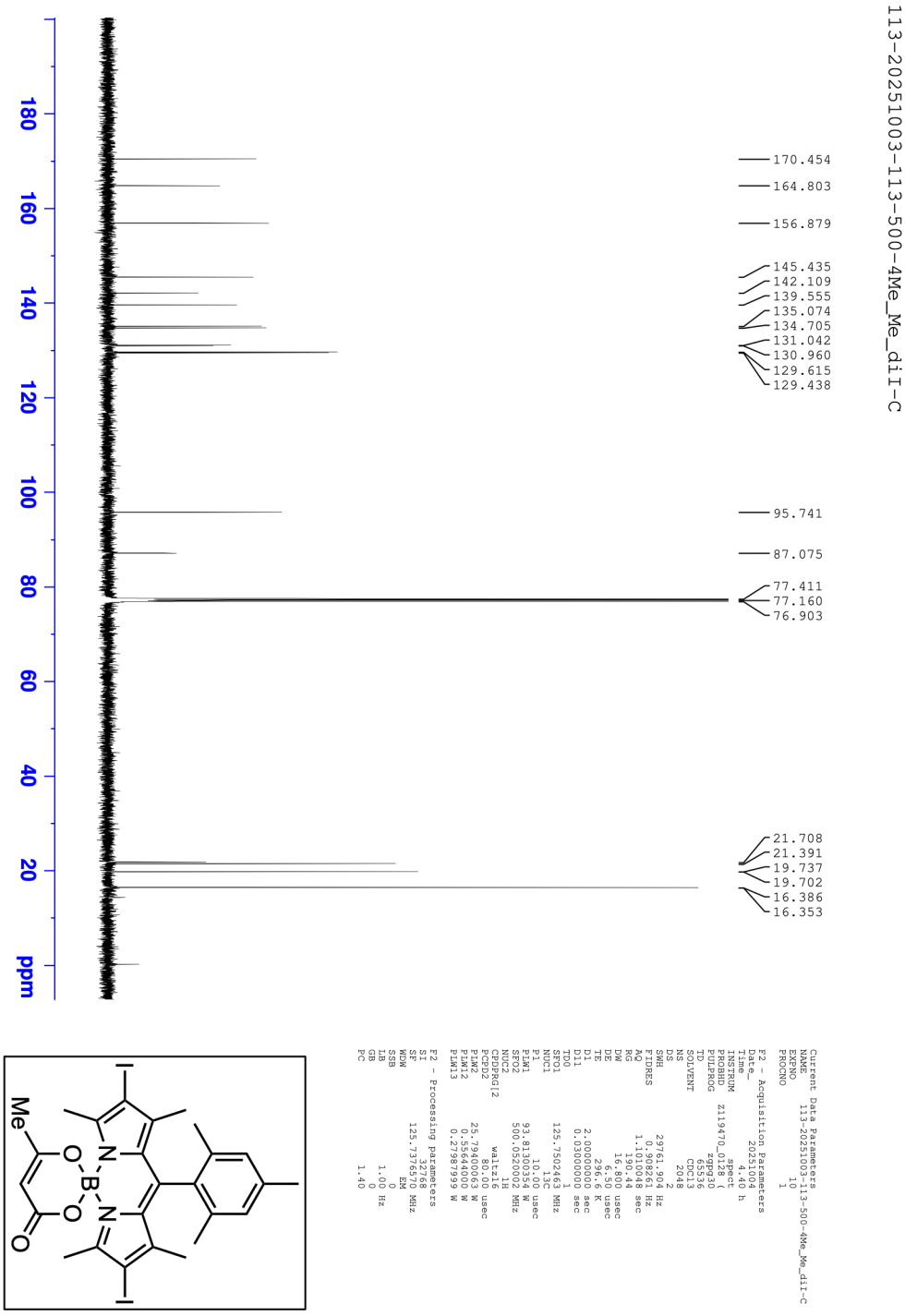


Figure S29. ^{13}C NMR spectrum of **7c** in $CDCl_3$ at 25 °C.

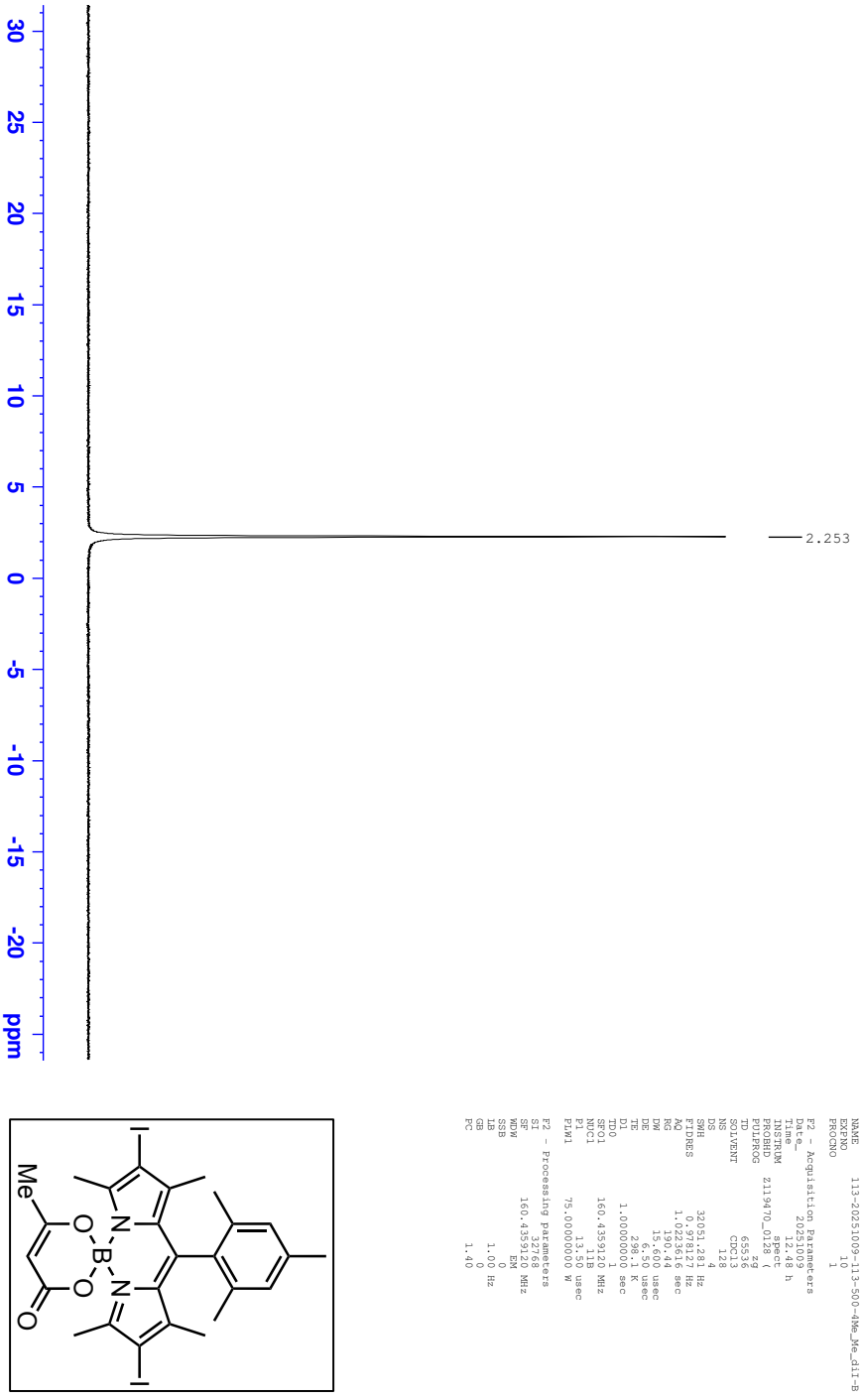


Figure S30. ^{11}B NMR spectrum of **7c** in $CDCl_3$ at 25 °C.

4. Mass spectra

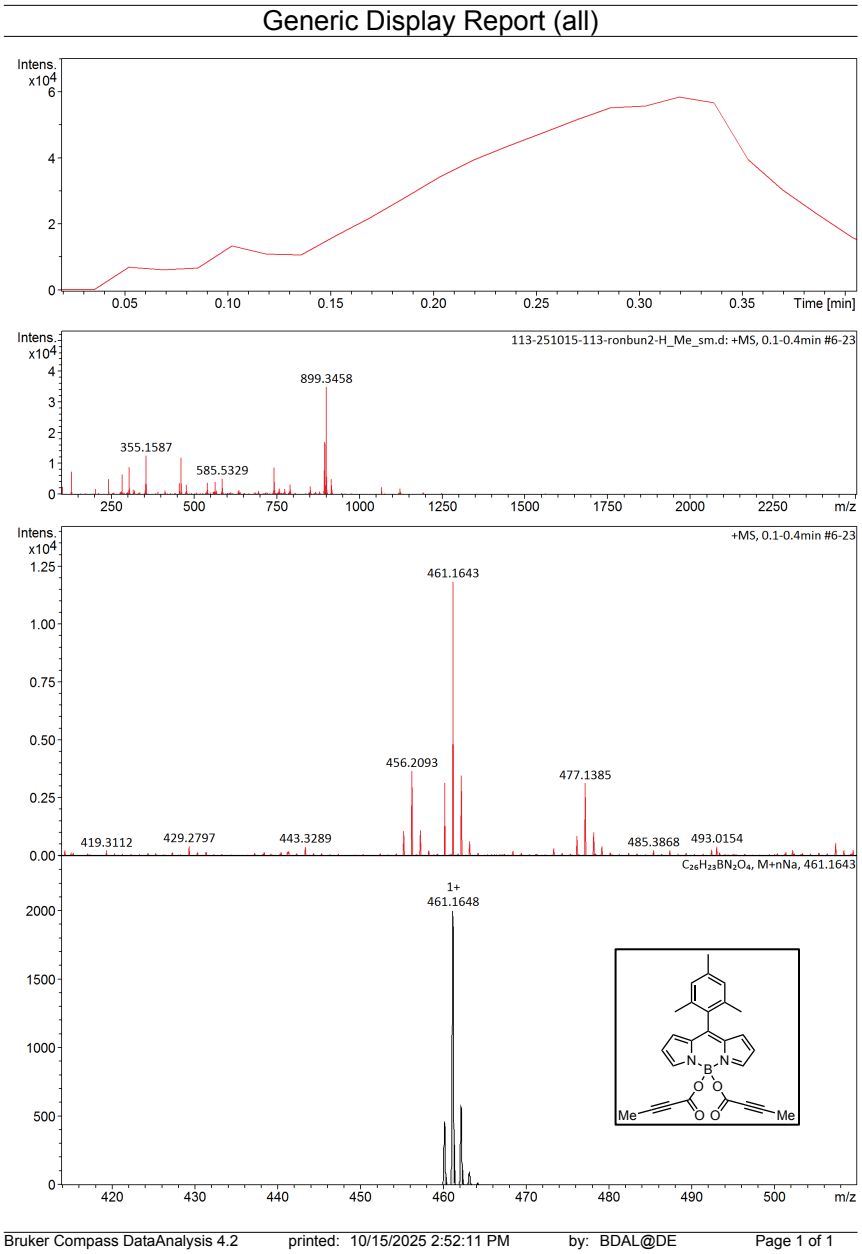


Figure S31. ESI-TOF mass spectrum of **2a**.

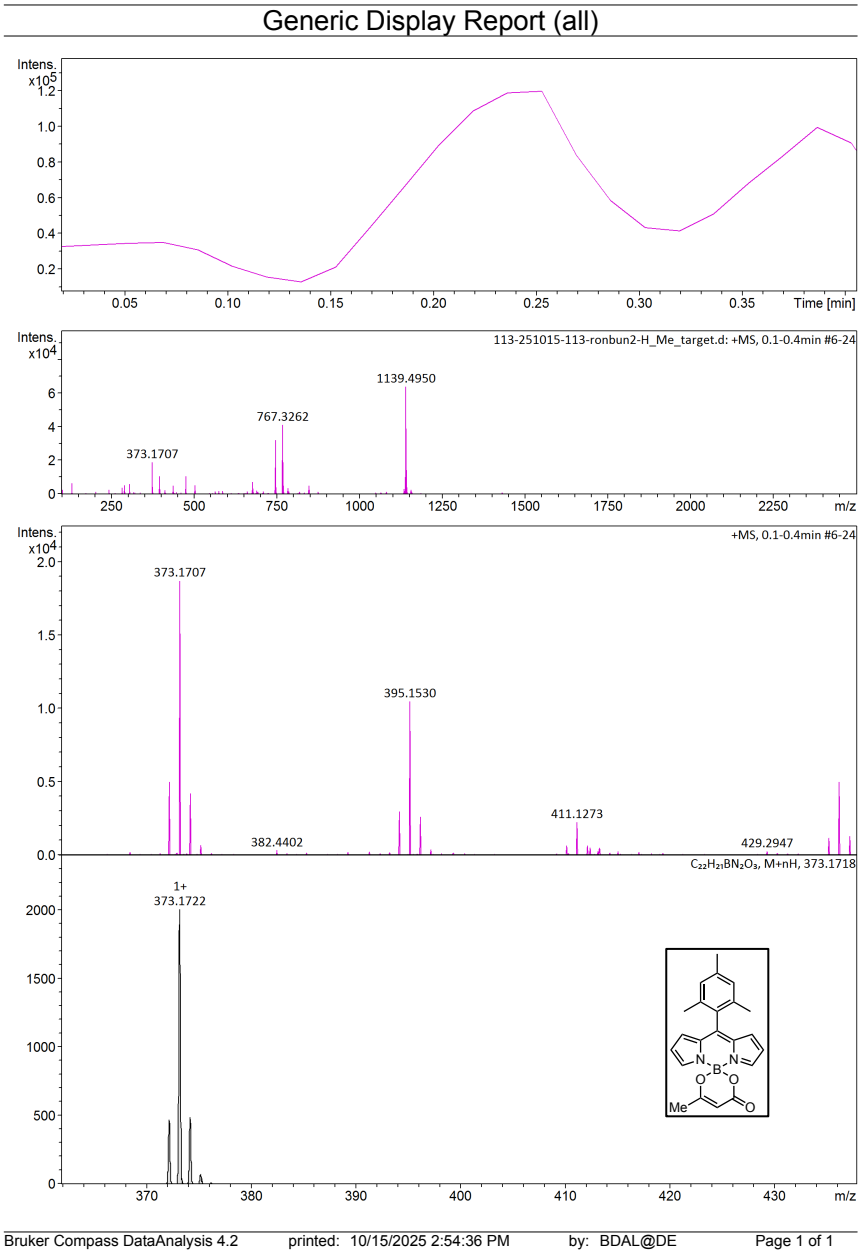


Figure S32. ESI-TOF mass spectrum of **3a**.

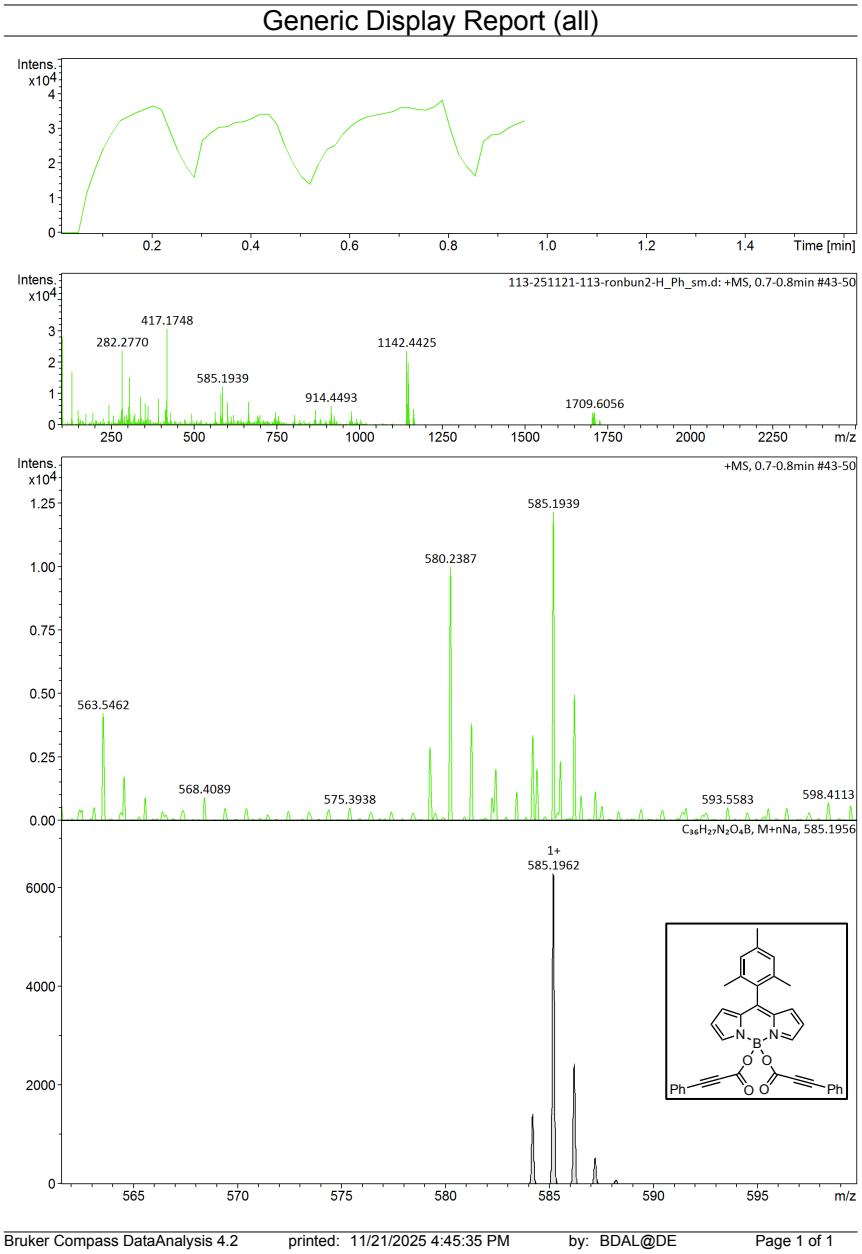


Figure S33. ESI-TOF mass spectrum of **2b**.

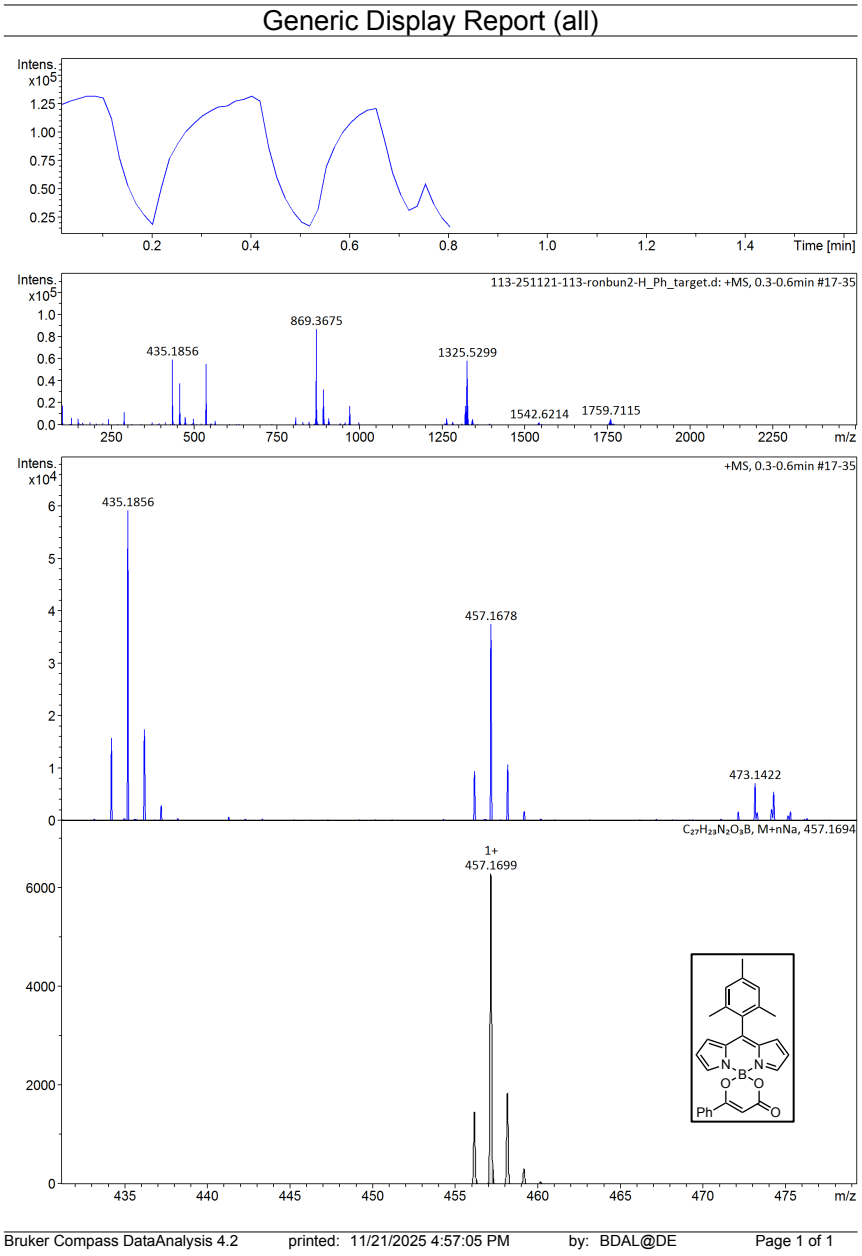


Figure S34. ESI-TOF mass spectrum of **3b**.

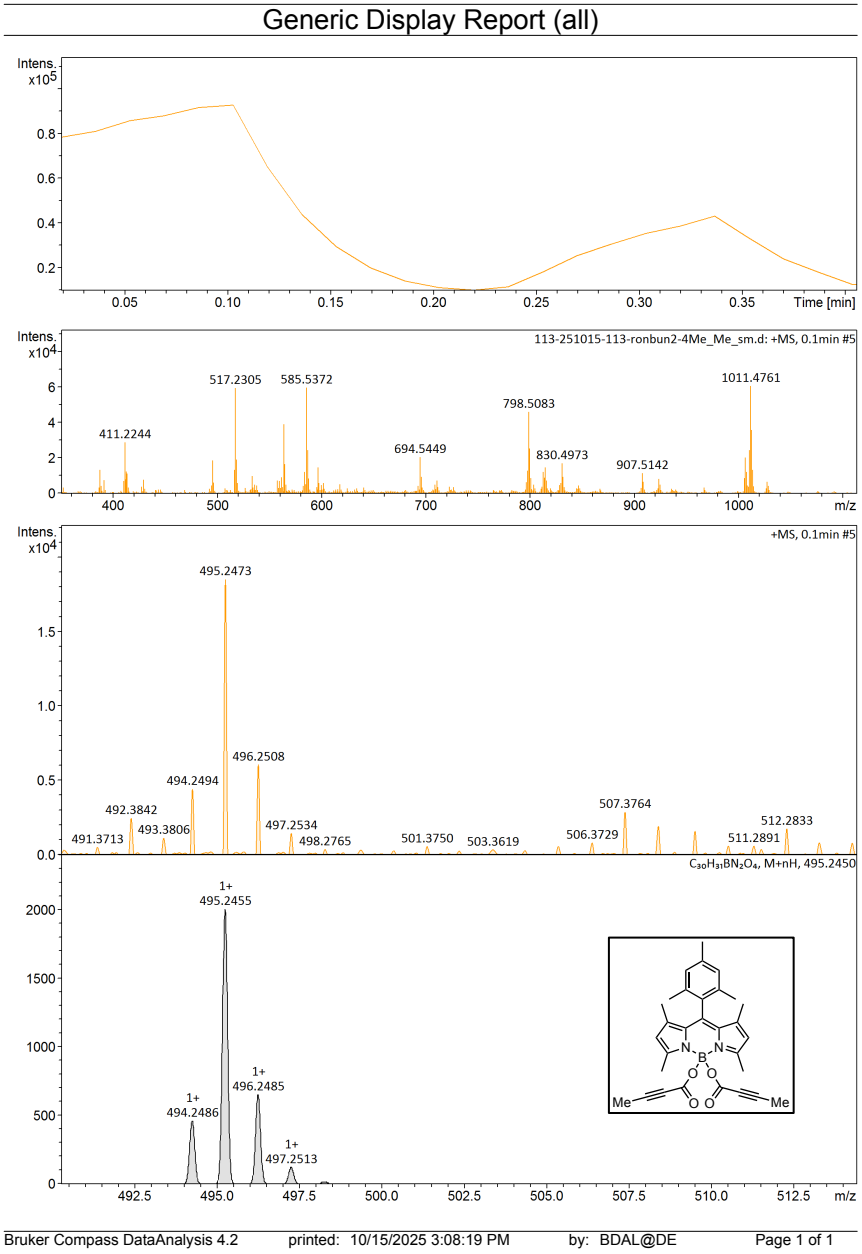


Figure S35. ESI-TOF mass spectrum of **2c**.

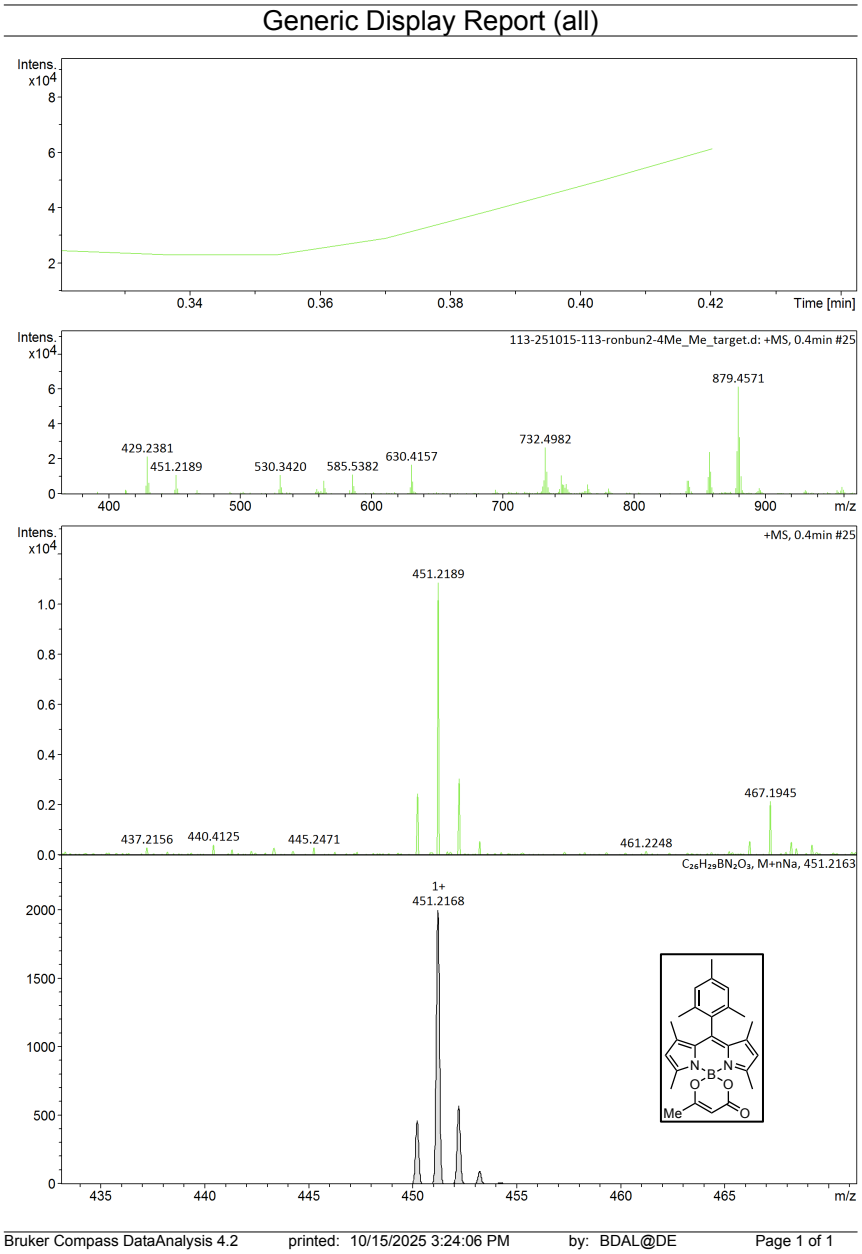


Figure S36. ESI-TOF mass spectrum of **3c**.

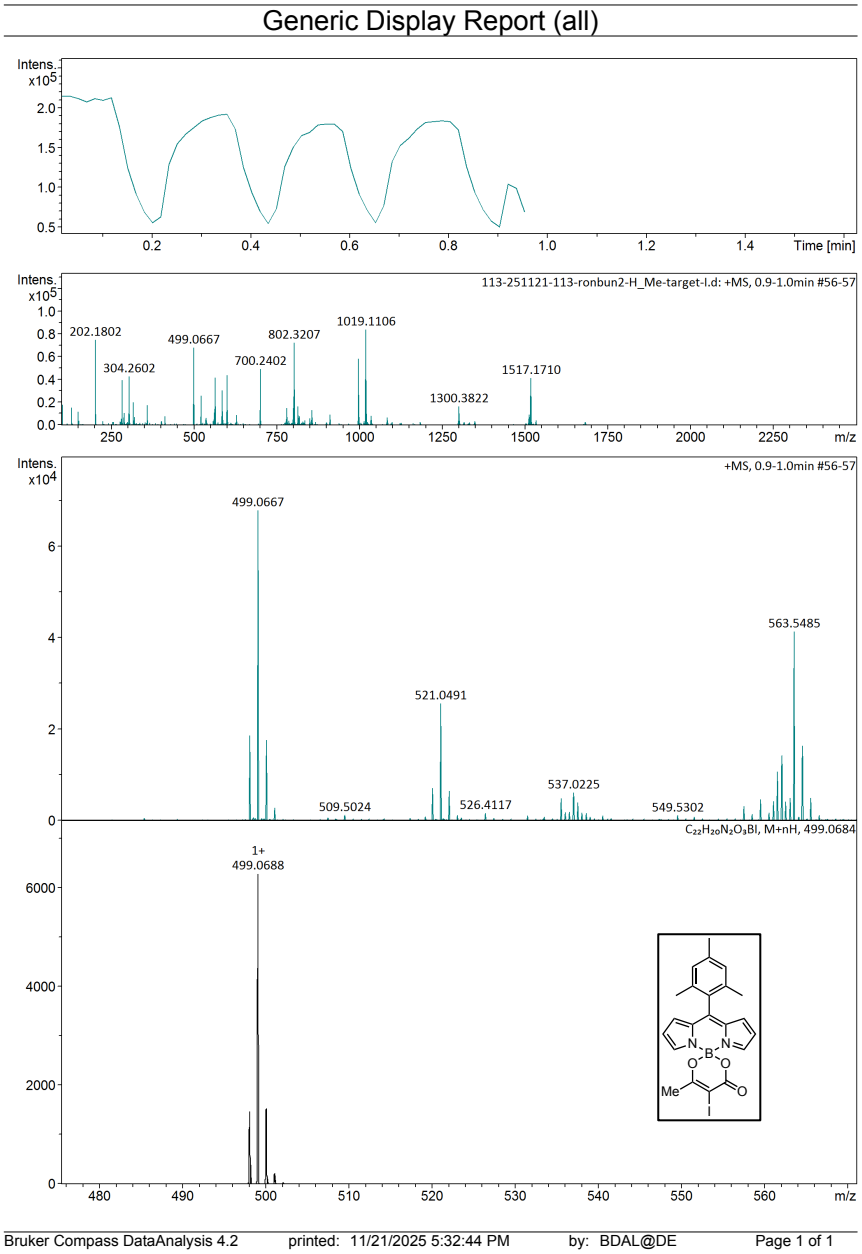


Figure S37. ESI-TOF mass spectrum of **4a**.

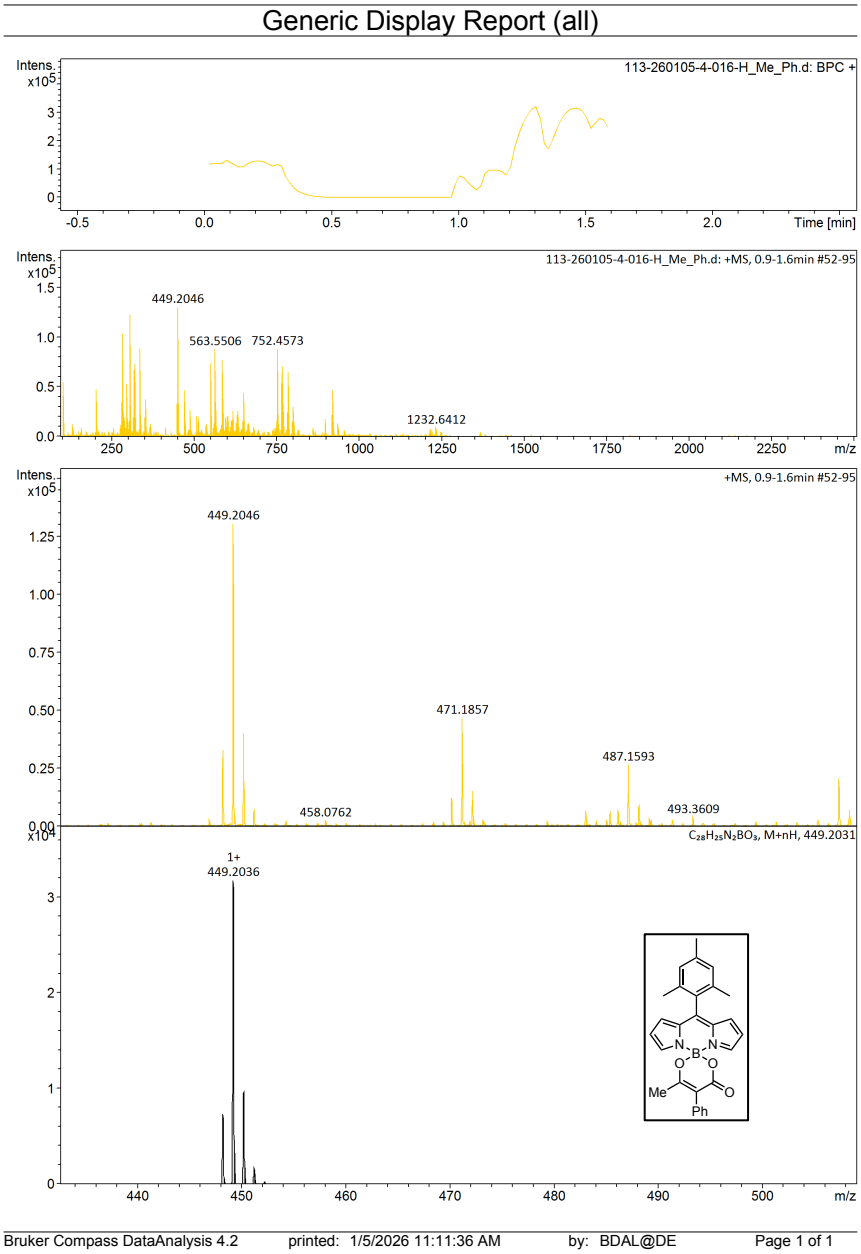


Figure S38. ESI-TOF mass spectrum of **5a**.

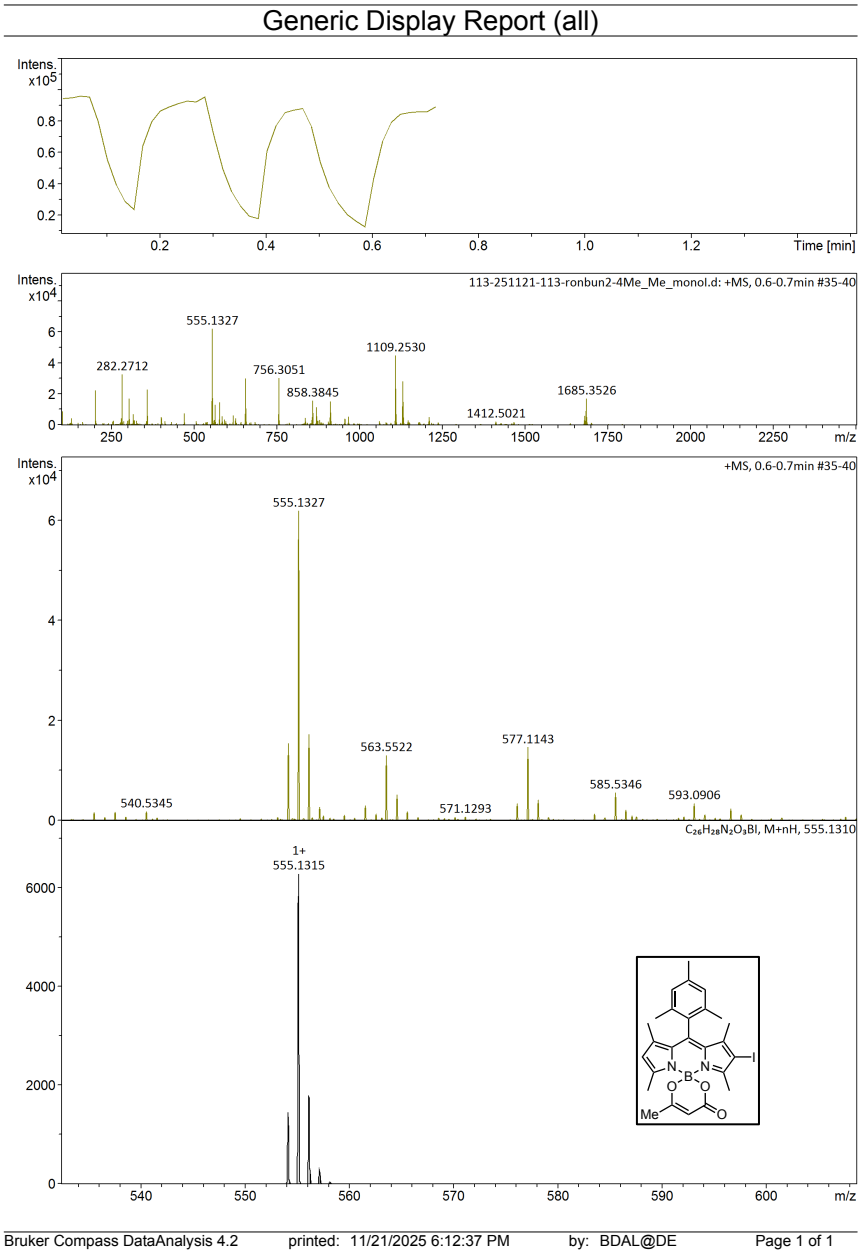


Figure S39. ESI-TOF mass spectrum of **6c**.

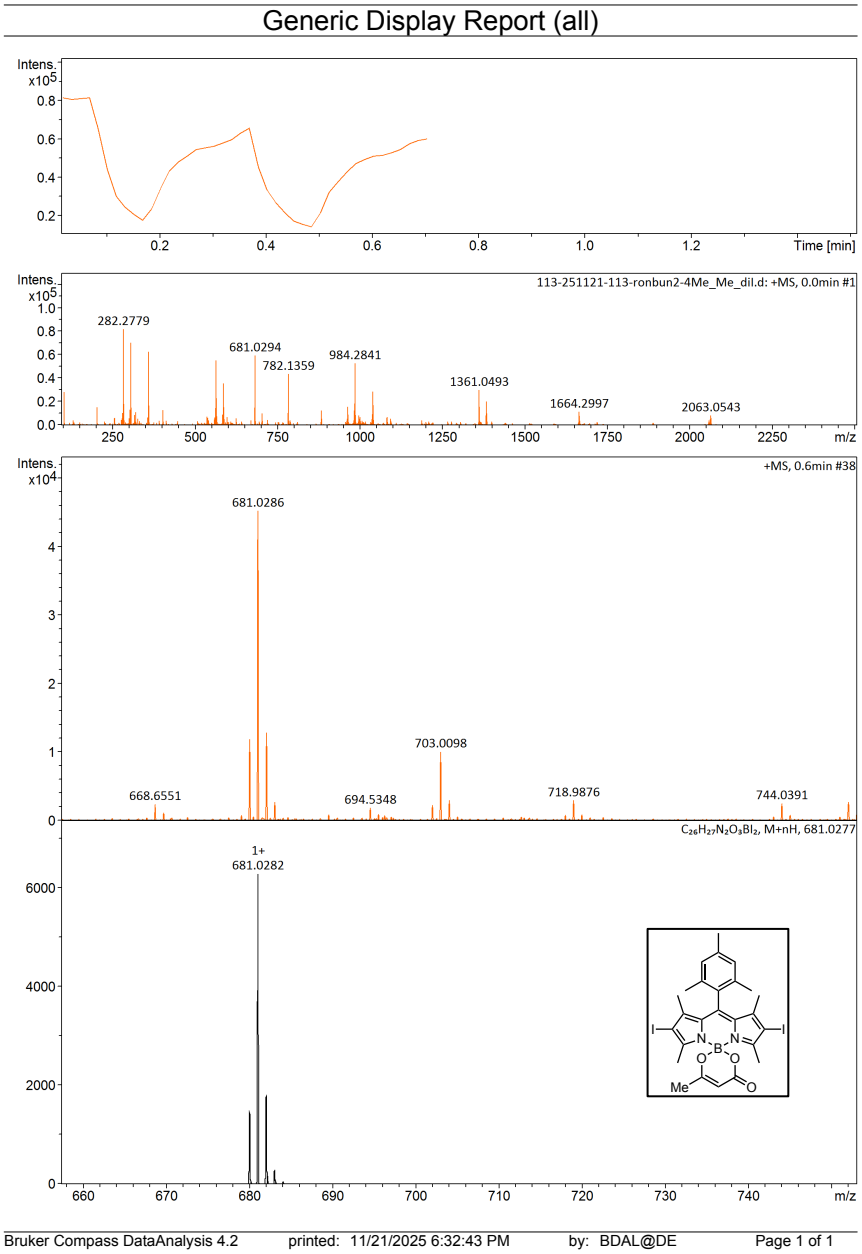


Figure S40. ESI-TOF mass spectrum of **7c**.

5. Crystal data

Table S1. Crystallographic data of **3a** in several solvents.

Compound	**3a•CH_2Cl_2**	**3a•$CHCl_3$**	**3a•HFIP**
CCDC number	2523319	2523317	2523318
Formula	CH_2Cl_2, $C_{22}H_{21}BN_2O_3$	$CHCl_3$, $C_{22}H_{21}BN_2O_3$	$2(C_3H_2F_6O)$, $2(C_{22}H_{21}BN_2O_3)$
Formula weight	457.14	491.58	1079.53
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Crystal colour	Red	Orange	Orange
Crystal description	Plate	Plate	needle
a [Å]	7.3489(2)	7.3143(1)	7.8099(1)
b [Å]	24.0265(6)	24.6211(4)	17.2188(3)
c [Å]	12.8678(4)	13.1796(2)	19.0199(3)
α [°]	90	90	82.063(1)
β [°]	104.907(3)	101.440(2)	80.498(2)
γ [°]	90	90	88.397(2)
V [Å^3]	2195.58(11)	2326.31(6)	2498.45(7)
Z	4	4	2
d_{calcd} [g cm^{-3}]	1.383	1.404	1.435
R_1 ($I > 2\sigma(I)$)	0.0437	0.0690	0.0614
wR_2 (all data)	0.1064	0.1777	0.1760
Goodness-of-fit	1.013	1.060	1.058
Temperature [K]	93	93	93
Solvent	CH_2Cl_2/hexane	$CHCl_3$	HFIP/H_2O

6. Photophysical properties of **3a** in various solvents

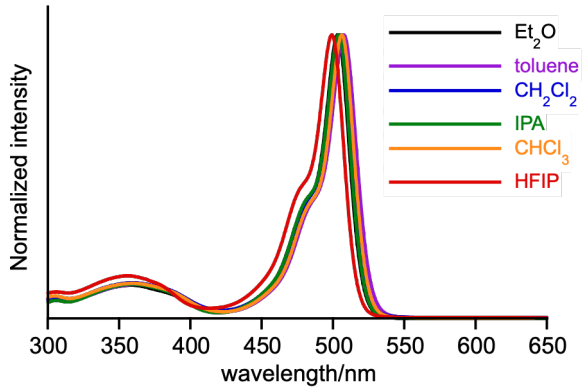


Figure S41. Absorption spectra of **3a** (10^{-5} M solutions).

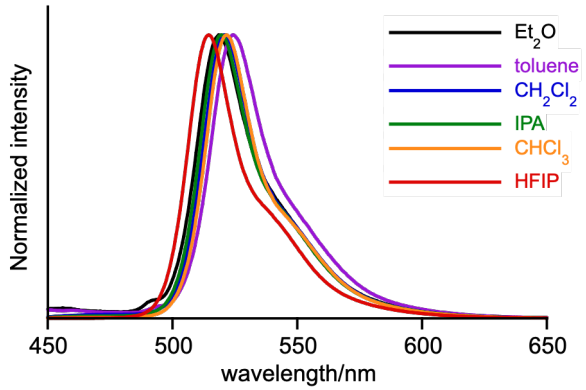
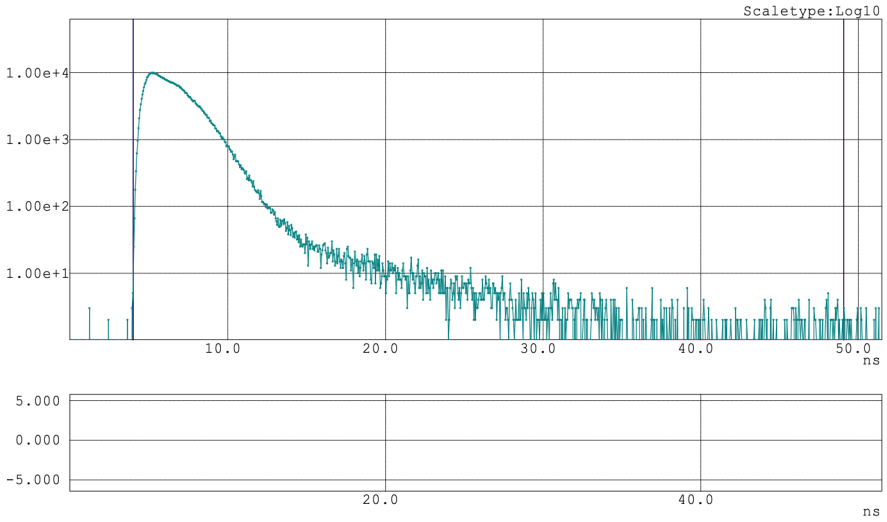


Figure S42. Emission spectra of **3a** (10^{-5} M solutions).

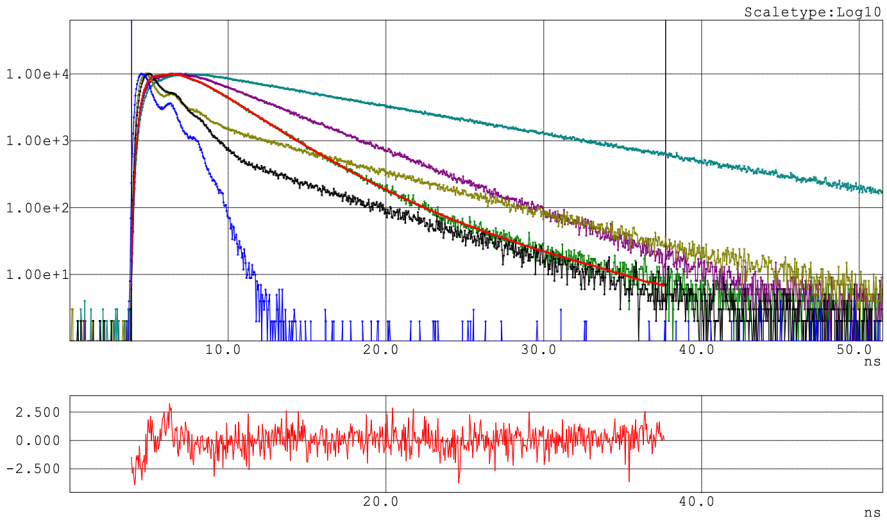


Excitation Wavelength /nm : 470
Time Range /ns : 51 ns
Stop Condtion : Peak 10000
Frequency : 5 MHz

Lifetime

Name	EWL	Ch1	Meas. Time	<τ>	Tau1	Tau2	Tau3	Tau4	Tau5	A1	A2	A3	A4	A5	Background
H_Me-target	515	1.21812	230.5	1.14967	1.01732	8.1038				938.84	2.24302				-2

Figure S43. Time-correlated single photon counting (TCSPC) data of **3a** in CH_2Cl_2.



Excitation Wavelength /nm : 470
Time Range /ns : 51 ns
Stop Condtion : Peak 10000
Frequency : 5 MHz

Lifetime

Name	EWL	Ch1	Meas. Time	<τ>	Tau1	Tau2	Tau3	Tau4	Tau5	A1	A2	A3	A4	A5	Background
IPA	515	1.16568	227.1	3.02439	2.68938	6.62897				578.343	21.807				0
HFIP	515	1.11859	130.1	10.3857	0.625676	10.4774				60.6275	385.676				3
CHCl3	515	1.1983	204.5	4.50903	0.121646	4.56741				241.786	483.976				3
Et2O	515	1.19326	1012.9	3.81912	0.186141	7.02287				2583.43	77.6479				-1
toluene	515	1.34216	764.4	1.70323	0.451476	5.81653				1382.08	32.6463				-1

Figure S44. Time-correlated single photon counting (TCSPC) data of **3a** in various solvents.

7. DFT calculations

All calculations were conducted using the *Gaussian 16*[4]. All geometry optimisations for stationary points were performed by the density functional theory (DFT) method with the B3LYP/6-31+G(d,p) level of theory. The single-point calculations were performed at the B3LYP/6-311+G(d,p) level of theory using the optimised structure or the crystal structure.

Cartesian coordinates of the optimised structures of 2a, 3a, and 3c at B3LYP/6-31+G(d,p) and that of crystal structure of 3a•HFIP

2a

C	0.788643	0.123760	-2.532625
C	-0.347207	0.168926	-3.370138
C	-1.465510	0.112818	-2.543009
C	-0.992947	0.033706	-1.208511
N	0.404117	0.034575	-1.244451
H	1.840322	0.141245	-2.780077
H	-2.508226	0.129506	-2.826875
C	-0.992266	-0.036287	1.209273
C	-1.464201	-0.116030	2.543987
N	0.404833	-0.037157	1.244531
C	-0.345511	-0.172478	3.370516
H	-2.506793	-0.133002	2.828349
C	0.789967	-0.126810	2.532465
C	-1.691963	-0.001158	0.000606
H	-0.328839	0.235471	-4.448322
H	-0.326608	-0.239506	4.448660
B	1.331841	-0.000419	-0.000201
O	2.126550	-1.235769	0.078736
C	4.479926	-3.709029	0.023230
C	3.185614	-1.498534	-0.684456
C	3.866574	-2.708379	-0.276398
O	3.558868	-0.822942	-1.632389
C	-3.181868	-0.000859	0.000969
C	-3.875931	-1.219755	-0.116704
C	-3.875369	1.217948	0.124262
C	-5.274399	-1.196127	-0.108497
C	-5.273722	1.194280	0.123942
C	-5.991199	-0.000692	0.006671
H	-5.814786	-2.135902	-0.192304
H	-5.813634	2.133260	0.219265
C	-3.131234	-2.527602	-0.240947
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H	-2.440150	-2.674142	0.595872
H	-3.826592	-3.370170	-0.260589
C	-3.129996	2.524864	0.254156
H	-2.532752	2.554292	1.171763
H	-2.436608	2.672803	-0.580482
H	-3.824733	3.367943	0.273864
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H	-7.871212	0.118932	-1.048764
H	-7.909030	-0.932937	0.369442
H	-7.908659	0.828415	0.567918
O	2.124081	1.236461	-0.079688
C	3.182494	1.501516	0.683650
C	3.861217	2.712503	0.275316
O	3.556887	0.826899	1.631808
C	4.472379	3.714824	-0.023224

C	5.220187	-4.909790	0.387436
H	6.297612	-4.754816	0.266125
H	5.027406	-5.193361	1.427428
H	4.928114	-5.749536	-0.252910
C	5.212293	4.914196	-0.392526
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H	1.841751	-0.143977	2.779458

3a

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3a•HFIP

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F	1.818553	-1.671875	-0.389705
C	5.427559	-1.665367	0.232392
C	3.036536	-2.233403	-0.270986

8. References

1. C. Yu, L. Jiao, H. Yin, J. Zhou, W. Pang, Y. Wu, Z. Wang, G. Yang and E. Hao, α-/β-Formylated Boron–Dipyrrin (BODIPY) Dyes: Regioselective Syntheses and Photophysical Properties, *Eur. J. Org. Chem.*, 2011, **2011**, 5460–5468.
2. A. B. Nepomnyashchii, M. Bröring, J. Ahrens and A. J. Bard, Synthesis, Photophysical, Electrochemical, and Electrogenerated Chemiluminescence Studies. Multiple Sequential Electron Transfers in BODIPY Monomers, Dimers, Trimers, and Polymer, *J. Am. Chem. Soc.*, 2011, **133**, 8633–8645.
3. C. Ray, C. Schad, F. Moreno, B. L. Maroto, J. Bañuelos, T. Arbeloa, I. García-Moreno, C. Villafuerte, G. Muller and S. de la Moya, BCl_3-Activated Synthesis of COO-BODIPY Laser Dyes: General Scope and High Yields under Mild Conditions, *J. Org. Chem.*, 2020, **85**, 4594–4601.
4. Gaussian 16, Revision C.01, 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, 2016.