

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 N₂ atmosphere unless otherwise noted. Compounds **1a**, **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 F₂₅₄, Merck). Detection was conducted using UV-light ($\lambda_{\text{ex}} = 254$ 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: ¹H NMR (400 MHz) spectra were recorded on a Bruker AVANCE NEO spectrometer. ¹H NMR (500 MHz), ¹³C NMR (126 MHz) and ¹¹B 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 ($\delta = 0$ ppm) for ¹H NMR and CDCl₃ ($\delta = 77.16$ ppm) for ¹³C NMR. The following abbreviations were used to describe the multiplicities: s = singlet, d = doublet, m = multiplet, ps = pseudo singlet, pd = pseudo doublet.

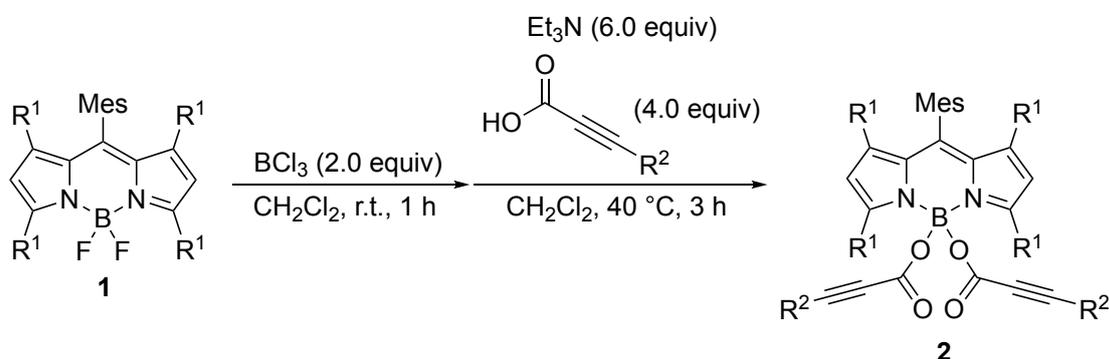
Mass spectrometry (MS): High-resolution electrospray ionisation time-of-flight (ESI-TOF) mass spectra were taken on a Bruker micrOTOF instrument using a positive ionisation mode.

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 Quantaaurus-Tau

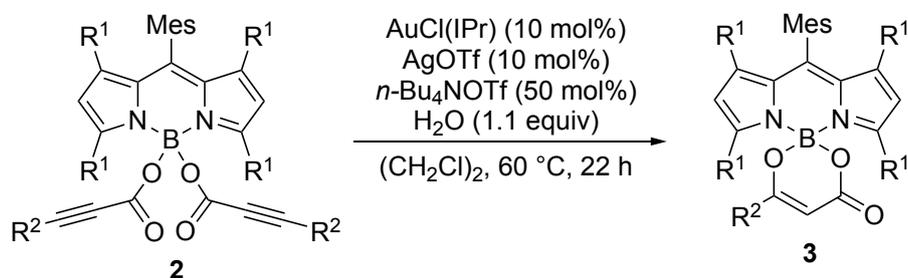
spectrometer. Fourier transform infrared (FT-IR) spectroscopic analysis was performed on a JASCO FT/IR-4200 spectrometer using a Sealed Liquid Cell with CaF₂ windows and a path length of 1 mm.

2. Experimental procedures and compound data



General procedure A²

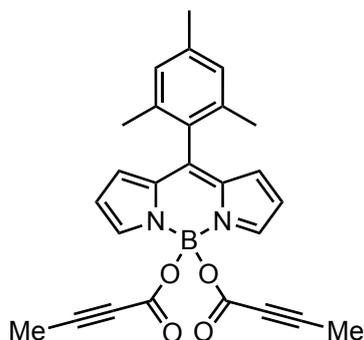
1 (1.0 eq.), CH₂Cl₂, and BCl₃ (2.0 eq.) were placed in a two-necked round-bottom flask. After the mixture was stirred at room temperature for 1 h under N₂, Et₃N (6.0 eq.) and carboxylic acid (4.0 eq.) was added. The mixture was stirred at room temperature for 3 h. The reaction mixture was washed with water, and the organic phase was separated. The organic phase was dried over Na₂SO₄, 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*-Bu₄NOTf (19.6 mg, 50 μmol), dichloroethane (0.20 mL), and H₂O (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 (SiO₂).

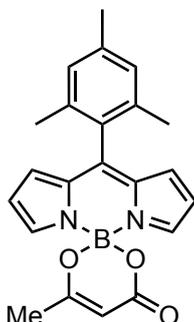
COO-BODIPY 2a



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. $R_f = 0.28$ (hexane/ CH_2Cl_2 1:5).

^1H NMR (500 MHz, CDCl_3 , 298 K): $\delta = 7.88$ (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): $\delta = 153.5, 148.7, 144.0, 138.8, 137.0, 136.6, 130.2, 129.9, 128.1, 118.7, 83.1, 74.8, 21.3, 20.0, 3.8$ ppm; ^{11}B NMR (160 MHz, CDCl_3 , 298 K) $\delta = -0.61$ (s, 1B) ppm; HR-MS (ESI-TOF): $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{23}^{11}\text{BN}_2\text{O}_4\text{Na}$ 461.1648; Found 461.1643.

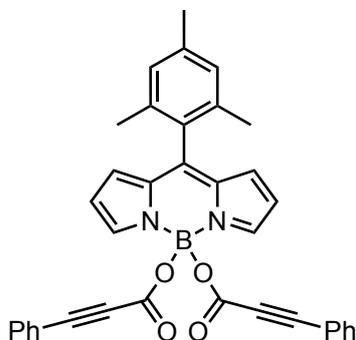
***B*-spiroBODIPY 3a**



According to the described general procedure B, **2a** (44 mg, 0.10 mmol) was reacted with AuCl(IPr) (6.2 mg, 10 μ mol), AgOTf (2.6 mg, 10 μ mol), *n*-Bu₄NOTf (19.6 mg, 50 μ mol), dichloroethane (0.30 mL), and H₂O (0.11 mmol, 2.0 μ L). The crude product was purified by pTLC (SiO₂, hexane/ethyl acetate = 5/4) to obtain **3a** (29.7 mg, 80%) as an orange solid. R_f = 0.16 (hexane/ethyl acetate = 1/1).

¹H NMR (500 MHz, CDCl₃, 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; ¹³C NMR (126 MHz, CDCl₃, 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; ¹¹B NMR (160 MHz, CDCl₃, 298 K) δ = 1.81 (s, 1B) ppm; HR-MS (ESI-TOF): [M+H]⁺ Calcd for C₂₂H₂₂¹¹BN₂O₃ 373.1722; Found 373.1707.

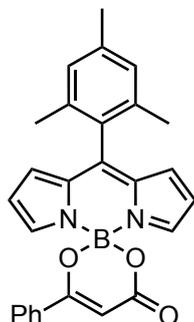
COO-BODIPY 2b



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), phenylpropionic 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. $R_f = 0.36$ (hexane/ CH_2Cl_2 1:2).

^1H NMR (500 MHz, CDCl_3 , 298 K): $\delta = 7.95$ (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): $\delta = 153.8, 148.9, 143.8, 138.8, 137.0, 136.8, 133.0, 130.3, 130.3, 129.9, 128.6, 128.1, 120.3, 118.8, 84.1, 83.0, 21.3, 20.0$ ppm; ^{11}B NMR (160 MHz, CDCl_3 , 298 K) $\delta = -0.38$ (s, 1B) ppm; HR-MS (ESI-TOF): $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{36}\text{H}_{27}^{11}\text{BN}_2\text{O}_4\text{Na}$ 585.1962; Found 585.1939.

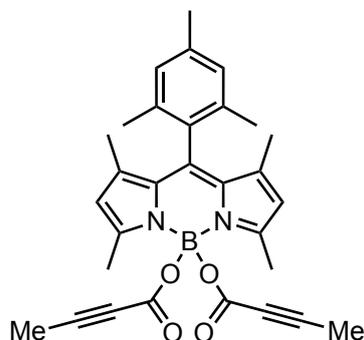
***B*-spiroBODIPY 3b**



According to the described **general procedure B**, **2b** (56 mg, 0.10 mmol) was reacted with AuCl(IPr) (6.2 mg, 10 μ mol), AgOTf (2.6 mg, 10 μ mol), *n*-Bu₄NOTf (19.6 mg, 50 μ mol), dichloroethane (0.30 mL), and H₂O (0.11 mmol, 2.0 μ L). The crude product was purified by pTLC (SiO₂, hexane/ethyl acetate = 5/4) to obtain **3b** (39.9 mg, 92%) as an orange solid. R_f = 0.32 (hexane/ethyl acetate = 2/3).

¹H NMR (500 MHz, CDCl₃, 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; ¹³C NMR (126 MHz, CDCl₃, 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; ¹¹B NMR (160 MHz, CDCl₃, 298 K) δ = 2.14 (s, 1B) ppm; HR-MS (ESI-TOF): [M+Na]⁺ Calcd for C₂₇H₂₃¹¹BN₂O₃Na 457.1699; Found 457.1678.

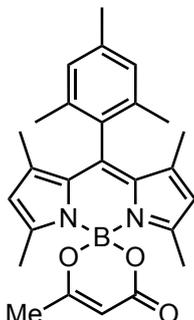
COO-BODIPY 2c



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. $R_f = 0.28$ (hexane/ethyl acetate = 4:1).

^1H NMR (500 MHz, CDCl_3 , 298 K): $\delta = 6.94$ (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): $\delta = 153.4$, 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) $\delta = -0.24$ (s, 1B) ppm; HR-MS (ESI-TOF): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{32}^{11}\text{BN}_2\text{O}_4$ 495.2455; Found 495.2473.

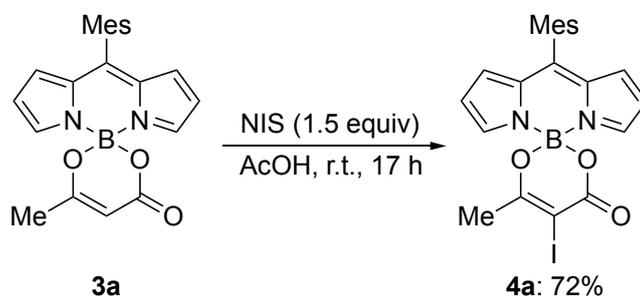
***B*-spiroBODIPY 3c**



According to the described general procedure B, **2c** (99 mg, 0.20 mmol) was reacted with Au(IPr) (6.2 mg, 10 μ mol), AgOTf (2.6 mg, 10 μ mol), *n*-Bu₄NOTf (19.6 mg, 50 μ mol), dichloroethane (0.40 mL), and H₂O (0.22 mmol, 4.0 μ L). The crude product was purified by pTLC (SiO₂, hexane/ethyl acetate = 5/4) to obtain **3c** (63.9 mg, 75%) as an orange solid. R_f = 0.20 (hexane/ethyl acetate = 1/1).

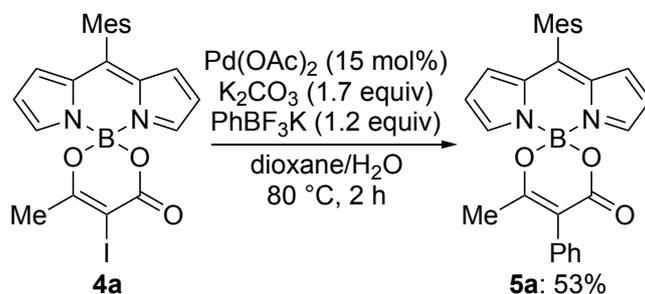
¹H NMR (500 MHz, CDCl₃, 298 K): δ = 6.95 (s, 2H), 5.96 (s, 2H), 5.33 (s, 1H), 2.34 (s, 3H), 2.32 (s, 6H), 2.13 (s, 3H), 2.08 (s, 3H), 1.99 (s, 3H), 1.38 (s, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 170.3, 165.5, 155.8, 143.0, 142.1, 138.9, 135.2, 134.8, 131.1, 129.3, 129.1, 121.9, 95.2, 21.8, 21.3, 19.7, 19.7, 15.0, 13.7 ppm (a pair of peaks was overlapped); ¹¹B NMR (160 MHz, CDCl₃, 298 K) δ = 2.21 (s, 1B) ppm; HR-MS (ESI-TOF): [M+Na]⁺ Calcd for C₂₆H₂₉¹¹BN₂O₃Na 451.2168; Found 451.2189.

4a



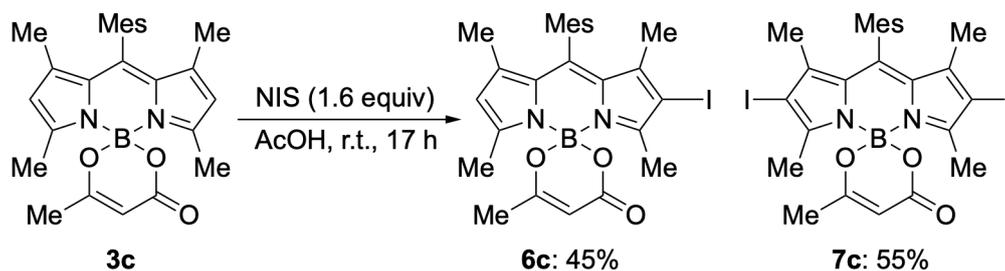
In a Schlenk tube, **3a** (18.6 mg, 0.050 mmol), NIS (16.9 mg, 0.075 mmol), and AcOH (1 mL) were added under N₂. After stirring at room temperature for 17 h in the dark, H₂O (5.0 mL) was added to the reaction mixture. The crude products were extracted with CH₂Cl₂ (× 3). The organic layer was washed with saturated aqueous NaHCO₃, 10% aqueous Na₂S₂O₃, brine, and dried with Na₂SO₄. The organic layer was concentrated under reduced pressure. The crude product was purified by pTLC (SiO₂, hexane/ethyl acetate = 2/1) to obtain **4a** (18.0 mg, 72%) as an orange solid. R_f = 0.52 (hexane/ethyl acetate = 1/1).

¹H NMR (500 MHz, CDCl₃, 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; ¹³C NMR (126 MHz, CDCl₃, 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; ¹¹B NMR (160 MHz, CDCl₃, 298 K) δ = 1.66 (s, 1B) ppm; HR-MS (ESI-TOF): [M+H]⁺ Calcd for C₂₂H₂₁¹¹BN₂O₃I 499.0688; Found 499.0667.

5a

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 $^\circ\text{C}$ and stirred for 2 h. The crude products were extracted with EtOAc ($\times 3$). 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. $R_f = 0.40$ (hexane/ethyl acetate = 1/1).

$^1\text{H NMR}$ (500 MHz, CDCl_3 , 298 K): $\delta = 7.90$ (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; $^{13}\text{C NMR}$ (126 MHz, CDCl_3 , 298 K): $\delta = 167.5, 164.7, 148.2, 144.8, 139.1, 136.7, 136.3, 135.5, 135.4, 131.2, 130.7, 129.6, 128.4, 128.3, 128.3, 127.1, 118.9, 108.3, 21.3, 20.9, 20.3, 20.2$ ppm; $^{11}\text{B NMR}$ (160 MHz, CDCl_3 , 298 K) $\delta = 1.54$ (s, 1B) ppm; HR-MS (ESI-TOF): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{26}^{11}\text{BN}_2\text{O}_3$ 449.2036; Found 449.2046.



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 ($\times 3$). The organic layer was washed with saturated aqueous NaHCO_3 , 10% aqueous $\text{Na}_2\text{S}_2\text{O}_3$, 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). ^1H 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): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{29}^{11}\text{BN}_2\text{O}_3\text{I}$ 555.1315; Found 555.1327.

7c

Rf = 0.60 (hexane/ethyl acetate = 2/3). ^1H 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): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{28}^{11}\text{BN}_2\text{O}_3\text{I}_2$ 681.0282; Found 681.0286.

3. NMR spectra

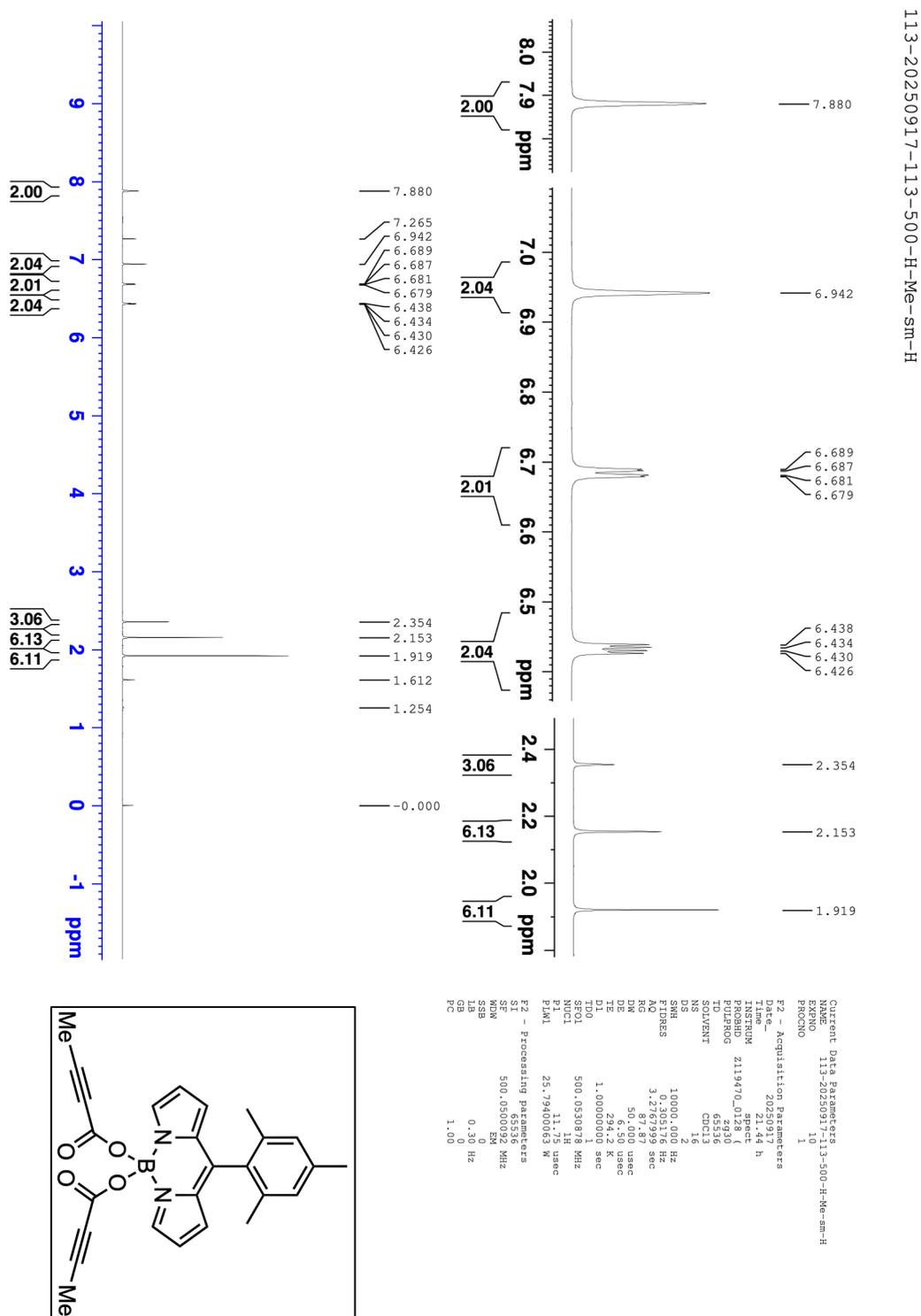


Figure S1. ¹H NMR spectrum of **2a** in CDCl₃ at 25 °C.

113-20250917-113-500-H-Me-sm-C

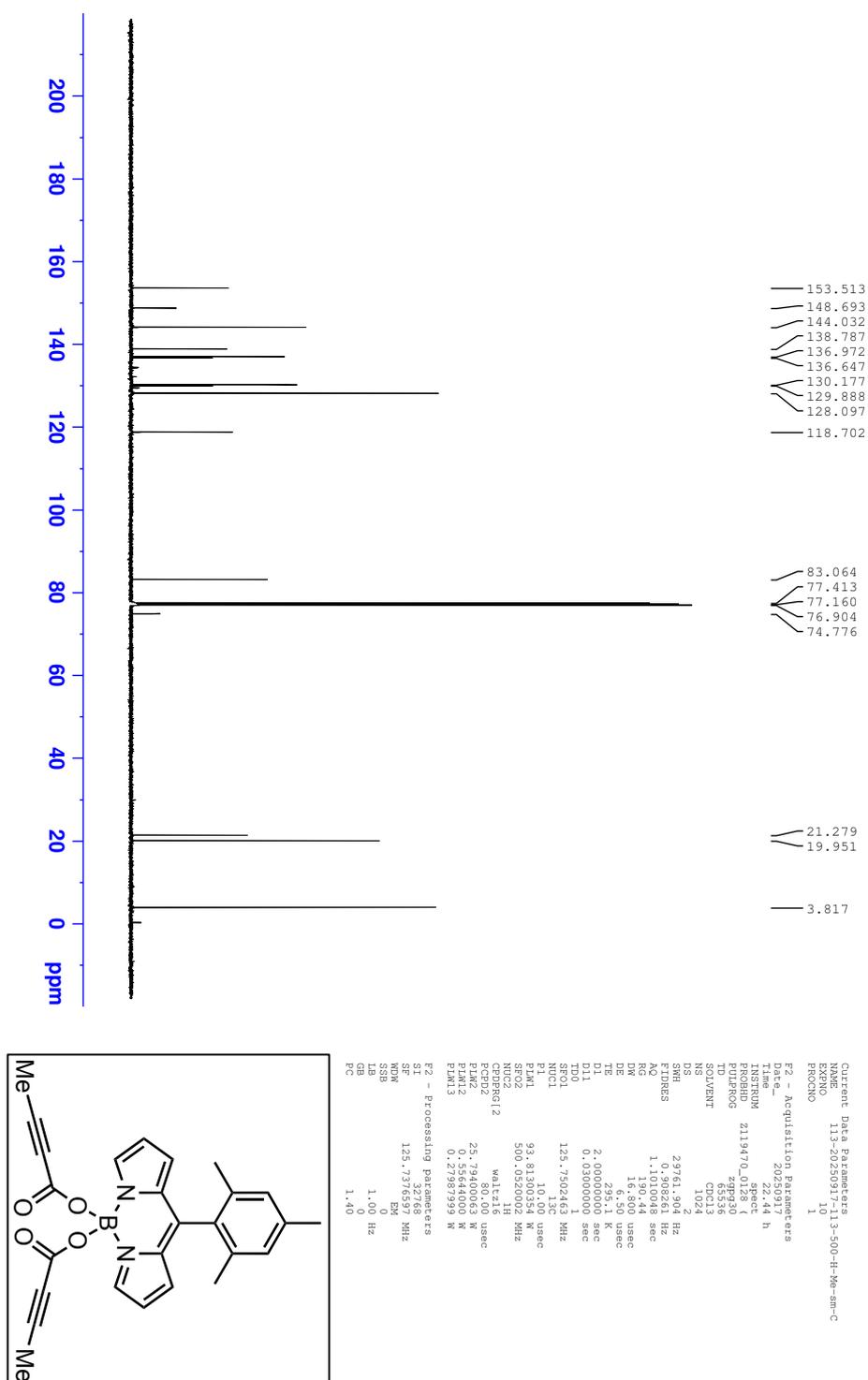
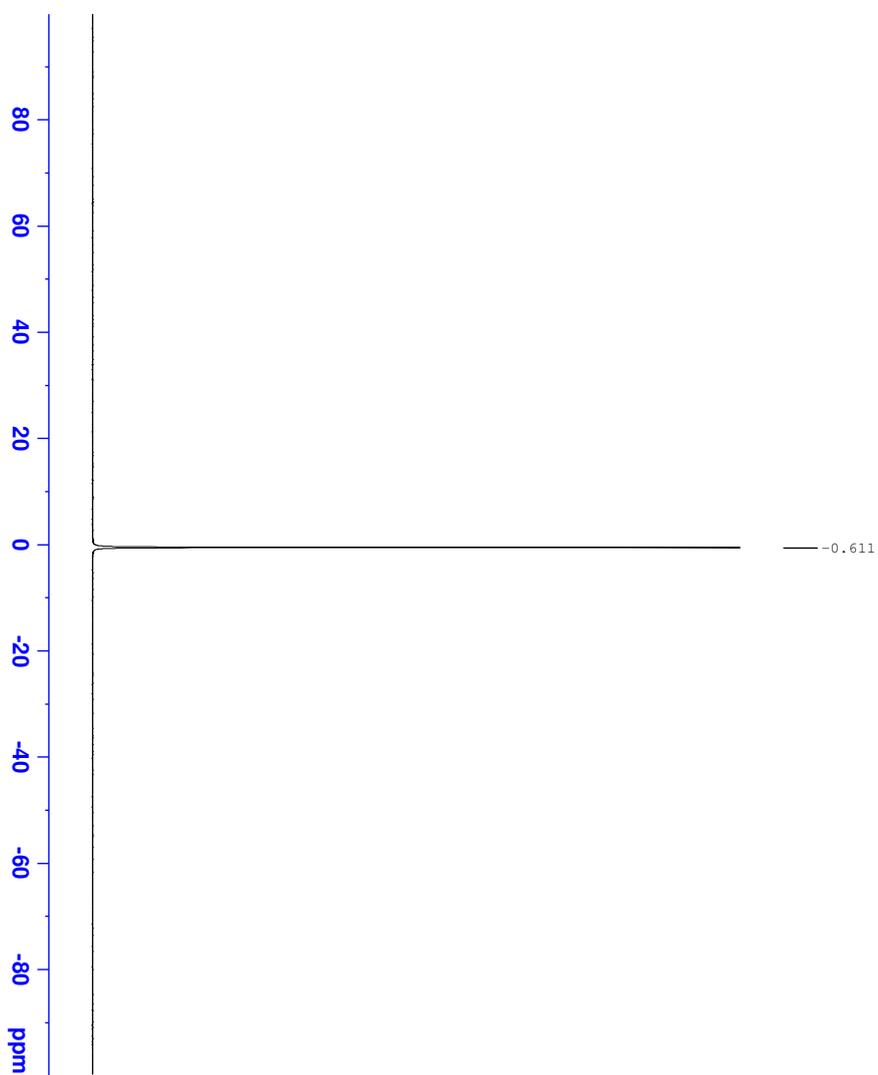


Figure S2. ¹³C NMR spectrum of 2a in CDCl₃ at 25 °C.

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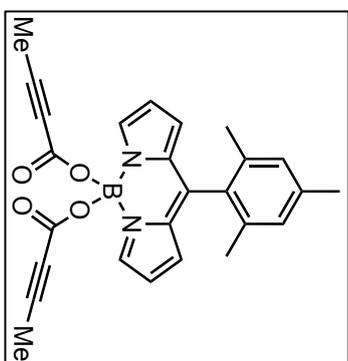
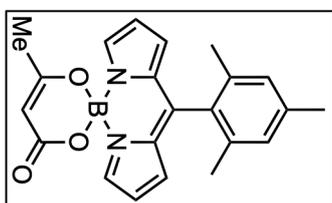
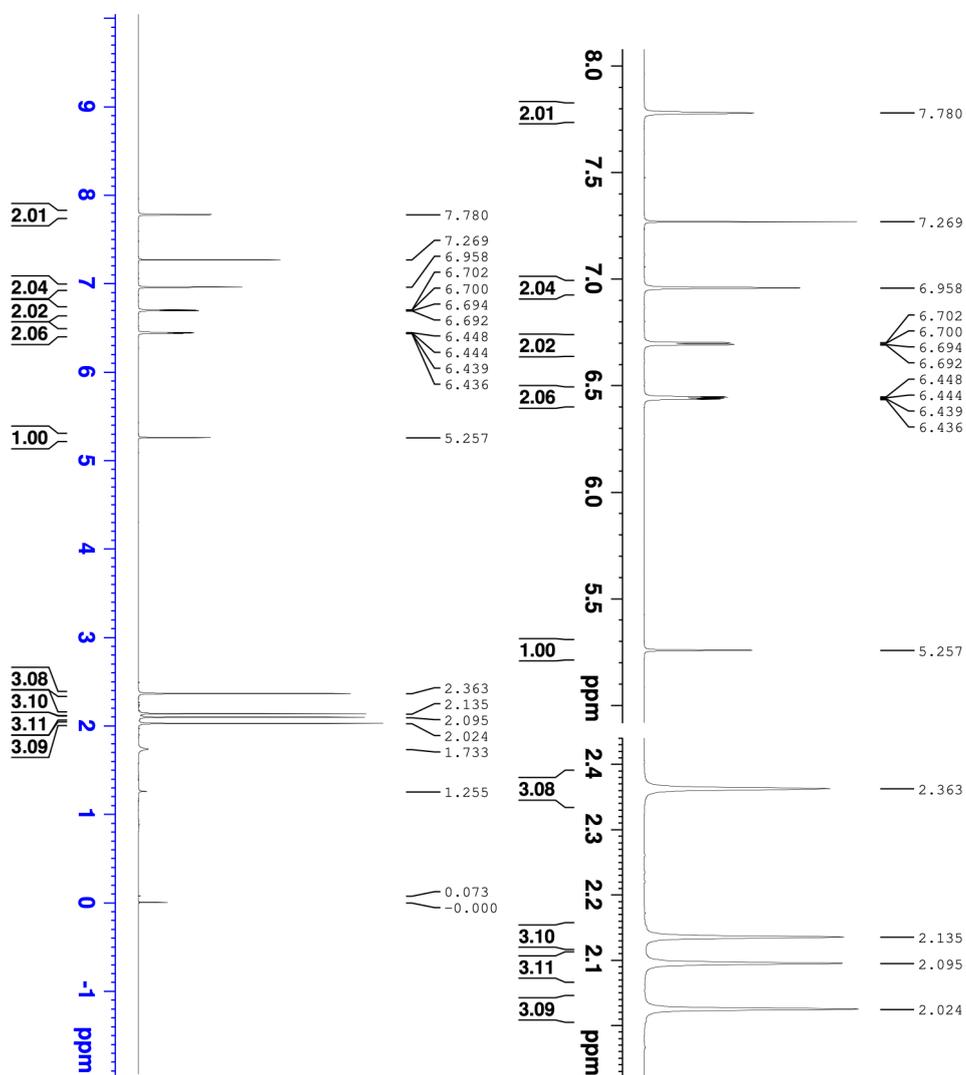


Figure S3. ^{11}B NMR spectrum of **2a** in CDCl_3 at 25°C .

113-20250918-113-500-H-Me-target-H

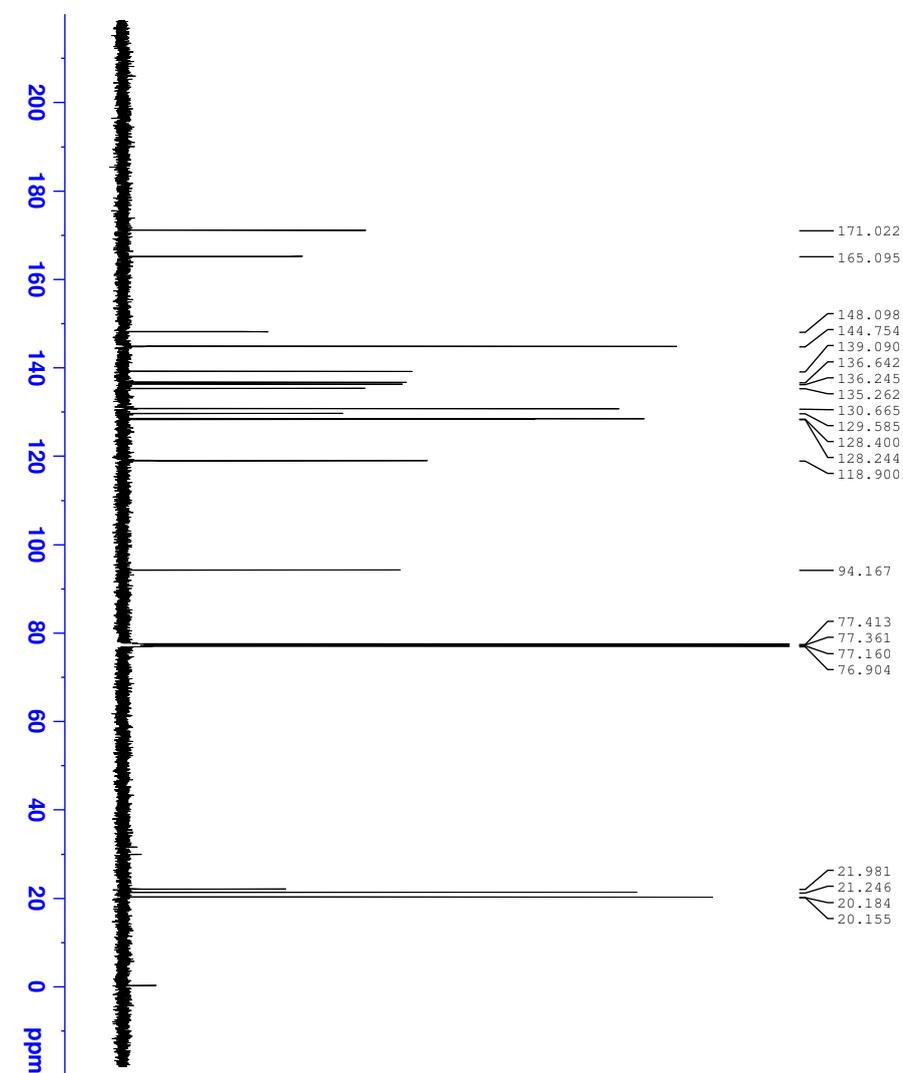


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NAME      113-20250918-113-500-H-Me-target-H
EXPNO    10
PROCNO   1
F2 - Acquisition Parameters
Date_    20250918
Time     10:29:28
INSTRUM  spect - Copy
PROBHD   Z13852-0181 (
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
DS        2
AQ        1.00000000 sec
RG        10000.000 Hz
AQ        1.00000000 sec
RG        89.14
DI        50.00 usec
DE        3.2767989 sec
TE        297.3 K
TD0       1.00000000 sec
SFO1      500.1130882 MHz
NUC1       13
NUC2       13
PC        1.00
F2 - Processing parameters
SI
SF        500.1100715 MHz
AQ        1.00000000 sec
RG        10000.000 Hz
DI        50.00 usec
DE        3.2767989 sec
TE        297.3 K
TD0       1.00000000 sec
SFO1      500.1130882 MHz
NUC1       13
NUC2       13
PC        1.00
  
```

Figure S4. ¹H NMR spectrum of 3a in CDCl₃ at 25 °C.

113-20250918-113-500-H-Me-target-C



```

Current Data Parameters
NAME      113-20250918-113-500-H-Me-target-C
EXPNO    20
PROCNO   1
F2 - Acquisition Parameters
Time     20251107 h
INSTRUM  spect - CQY
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
DS        4
SI        32
SM       297.61304 Hz
SFO1     101.25304 MHz
AQ       1.1010048 sec
RG       194.499
DE       6.50 usec
TE       297.8 K
D1       2.00000000 sec
D11      0.03000000 sec
TDO      125.1653241 MHz
NUC1     13C
P1       9.40 usec
PL1      0.10000000 MHz
SFO2     500.1250004 MHz
NUC2     1H
CPDPRG2  waltz16
CDEPRG   1H
F1M1     13.00000000 W
F1M2     0.38931000 W
F1M3     0.58101000 W
F2 - Processing parameters
SI        32
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
  
```

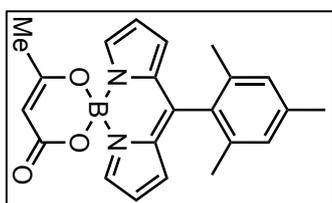


Figure S5. ^{13}C NMR spectrum of **3a** in CDCl_3 at 25°C .

113-20250917-113-500-H-Me-target-B

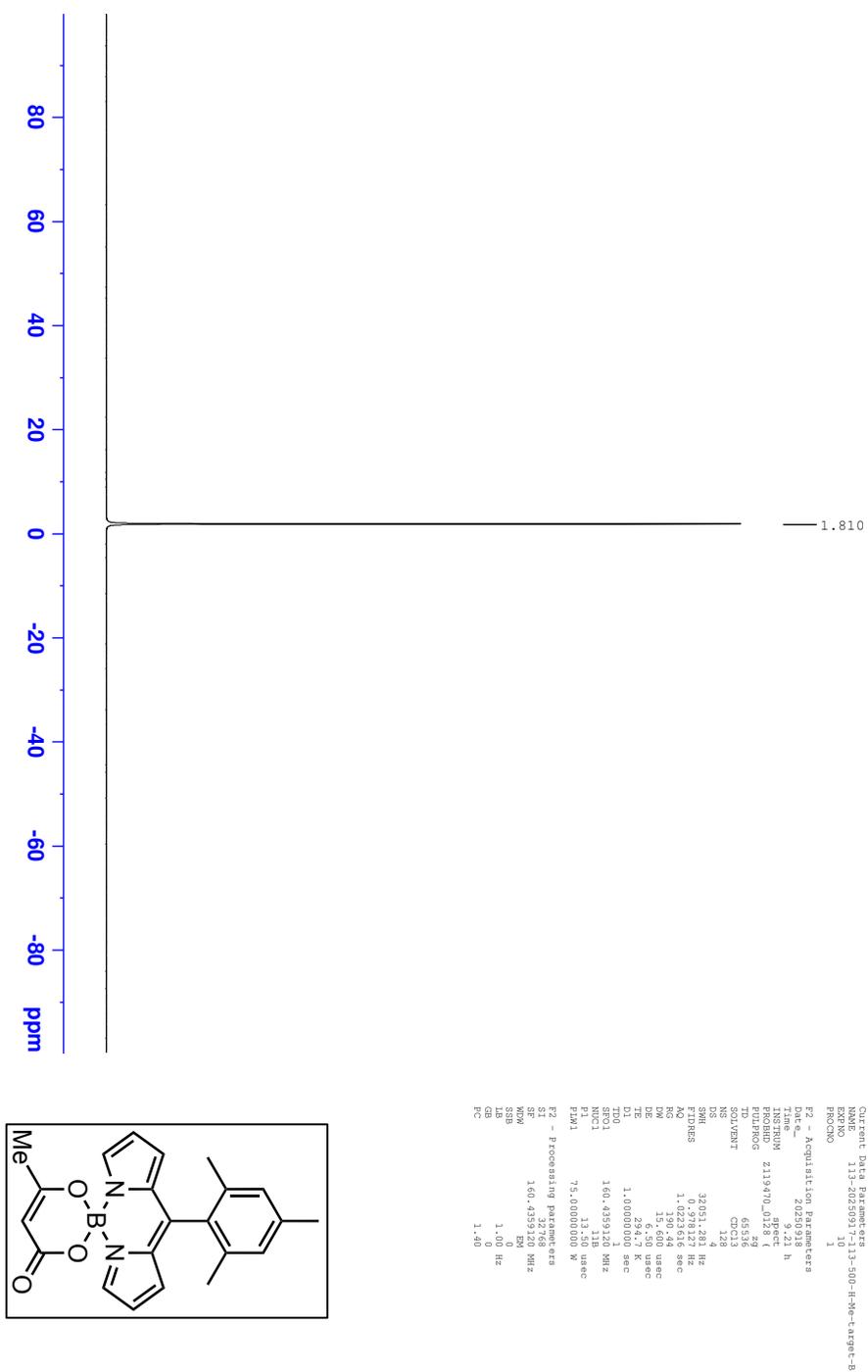
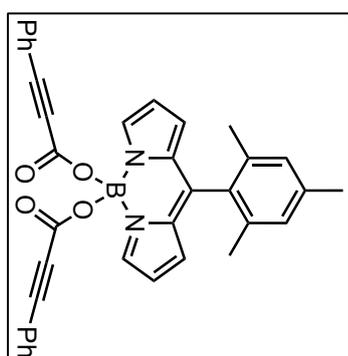
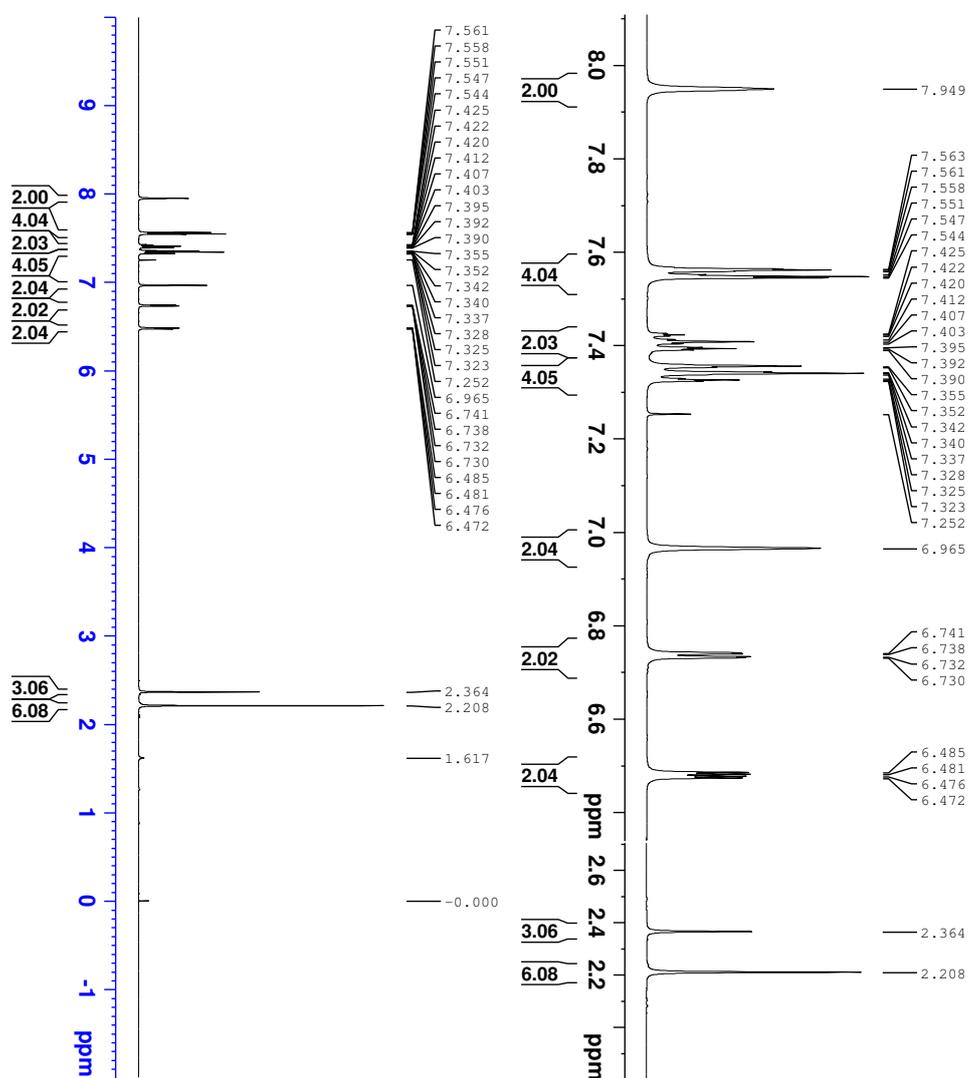


Figure S6. ¹¹B NMR spectrum of **3a** in CDCl₃ at 25 °C.

113-20250923-113-500-9-H



```

Current Data Parameters
NAME      113-20250923-113-500-H-Ph-H
EXPNO    10
PROCNO   1
F2 - Acquisition Parameters
Date_    20250923
Time     15.19 h
INSTRUM  spect
PROBHD   Z119470_012830
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        16
DS        4
SWH       10000.000 Hz
FIDRES    0.305176 Hz
AQ         3.275799 sec
RG         54.14
DM         50.000 usec
DE         2.000 usec
TE         29.50 usec
D1         1.00000000 sec
TD0        1
SFO1      500.0530878 MHz
NUC1       11B
P1         11.70 usec
PL1        0.00 dB
PL12       25.7940063 W
F2 - Processing parameters
SI        65536
SF         500.0500136 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
  
```

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

113-20250923-113-500-9-13C

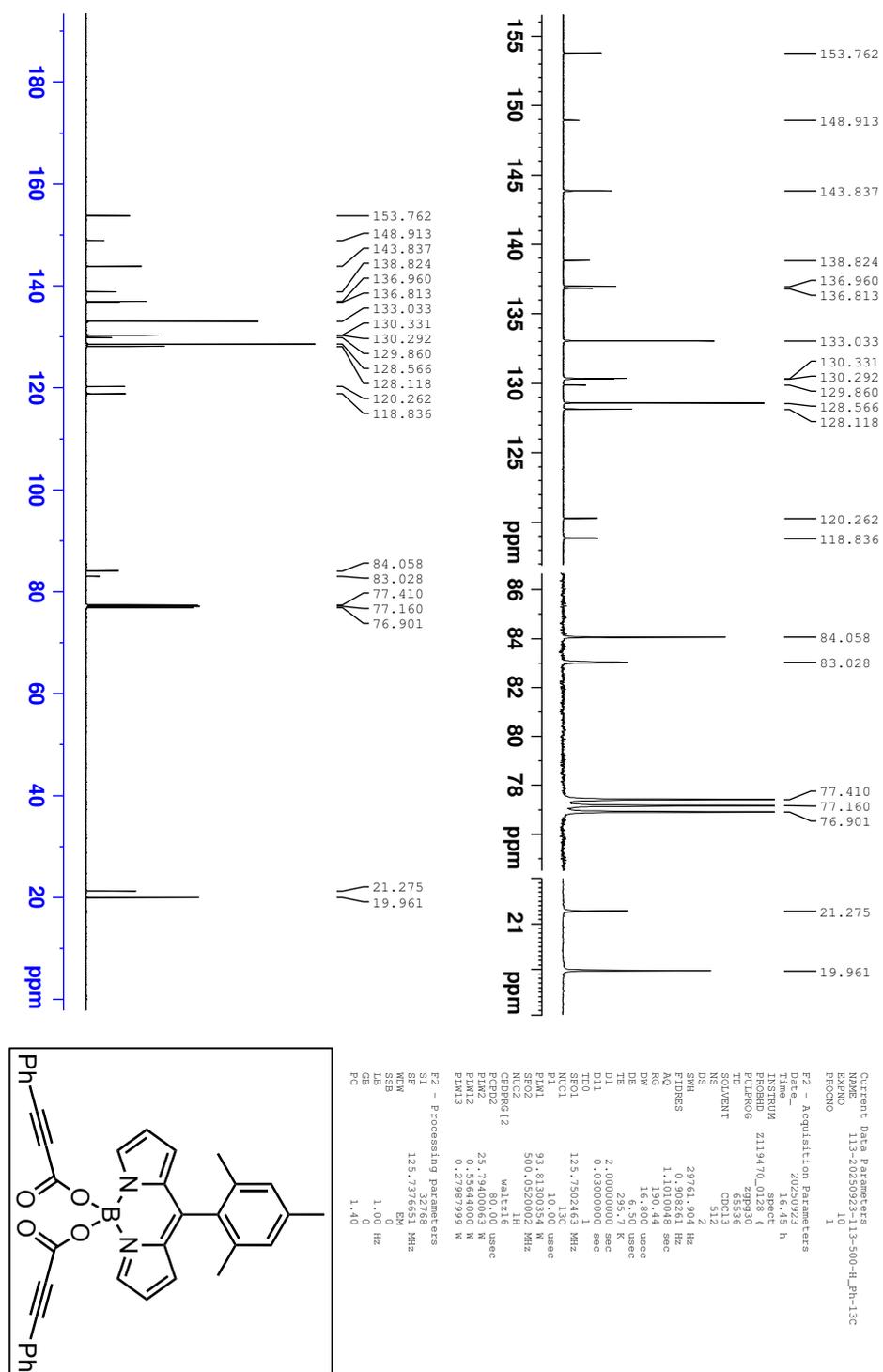
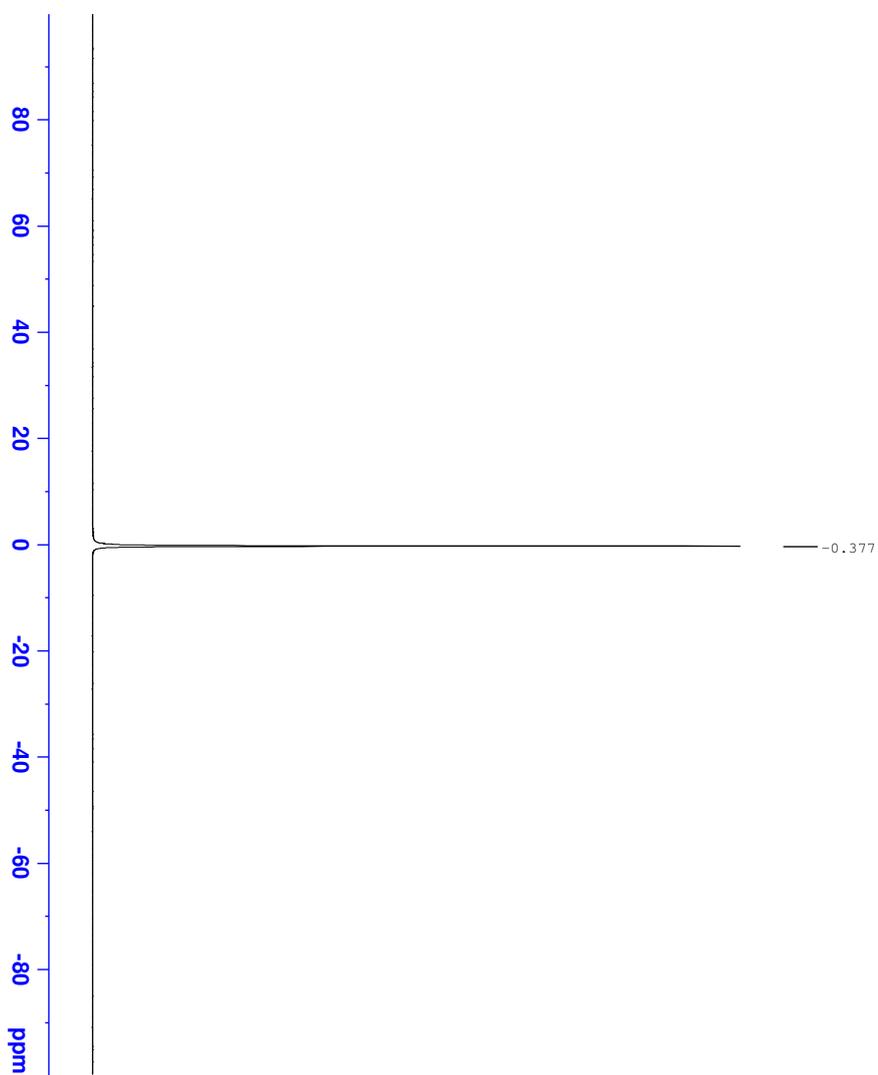


Figure S8. ¹³C NMR spectrum of **2b** in CDCl₃ at 25 °C.

113-20251008-113-500-H_Ph-sm-B



Current Data Parameters
NAME 113-20251008-113-500-H_Ph-sm-B
EXNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20251008
Time 11:08 h
INSTRUM spect
PROBHD Z119470.0128 (65428
PULPROG zgpg30
SOLVENT CDCl3
NS 128
DS 4
SS 32051.248 Hz
FIDRES 0.9781227 Hz
AQ 1.0223616 sec
RG 190.44 usec
DE 19.450 usec
TE 295.5 K
D1 1.00000000 sec
SFO1 160.4359120 MHz
NUC1 11B
P1 13.50 usec
PL1 75.00000000 W
F2 - Processing parameters
SI 32768
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

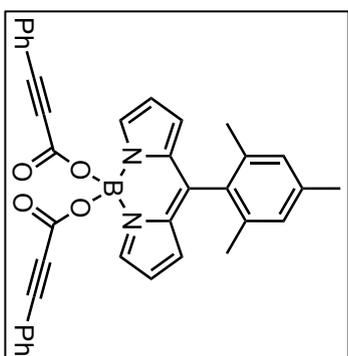


Figure S9. ^{11}B NMR spectrum of **2b** in CDCl_3 at 25°C .

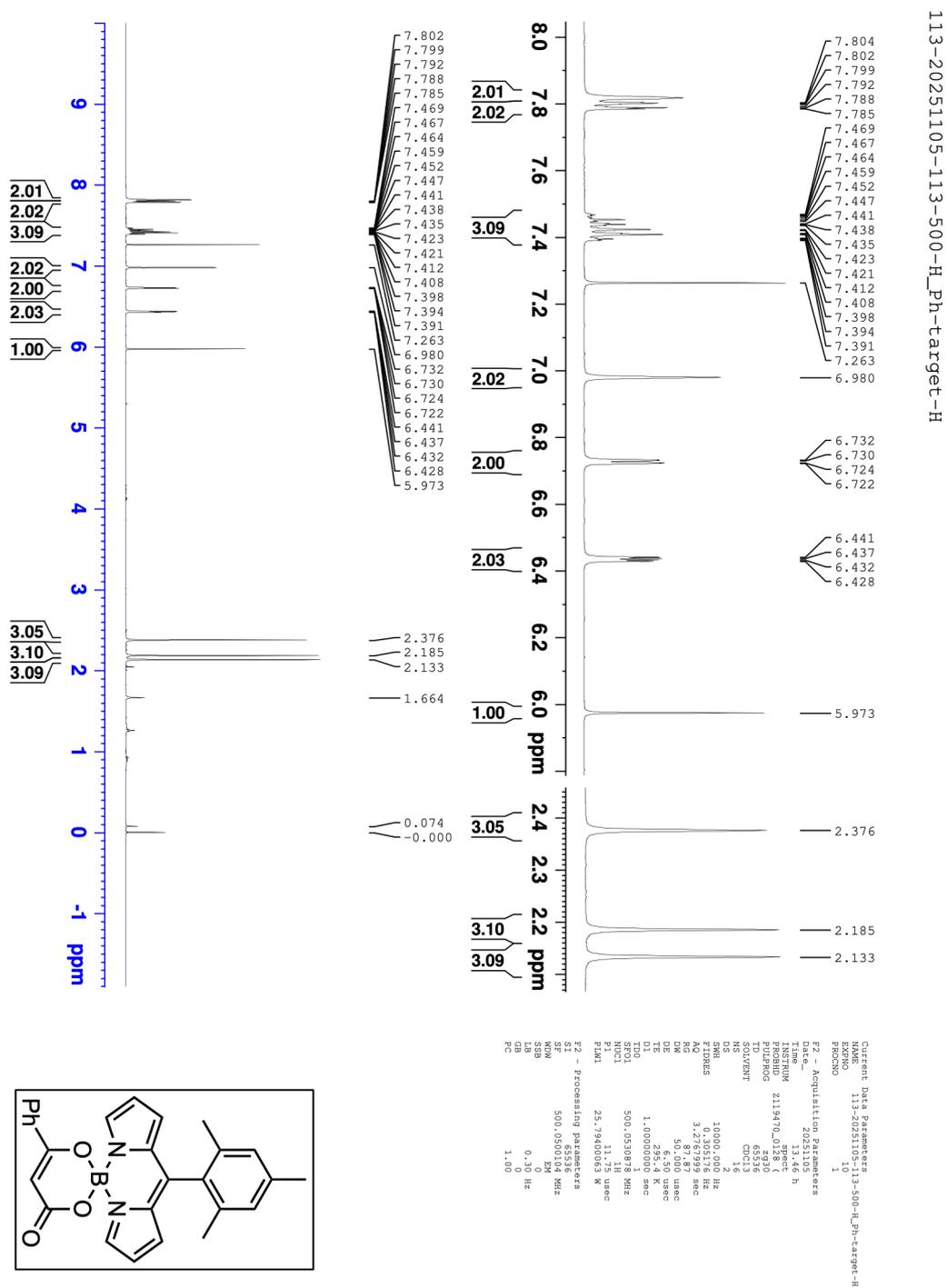
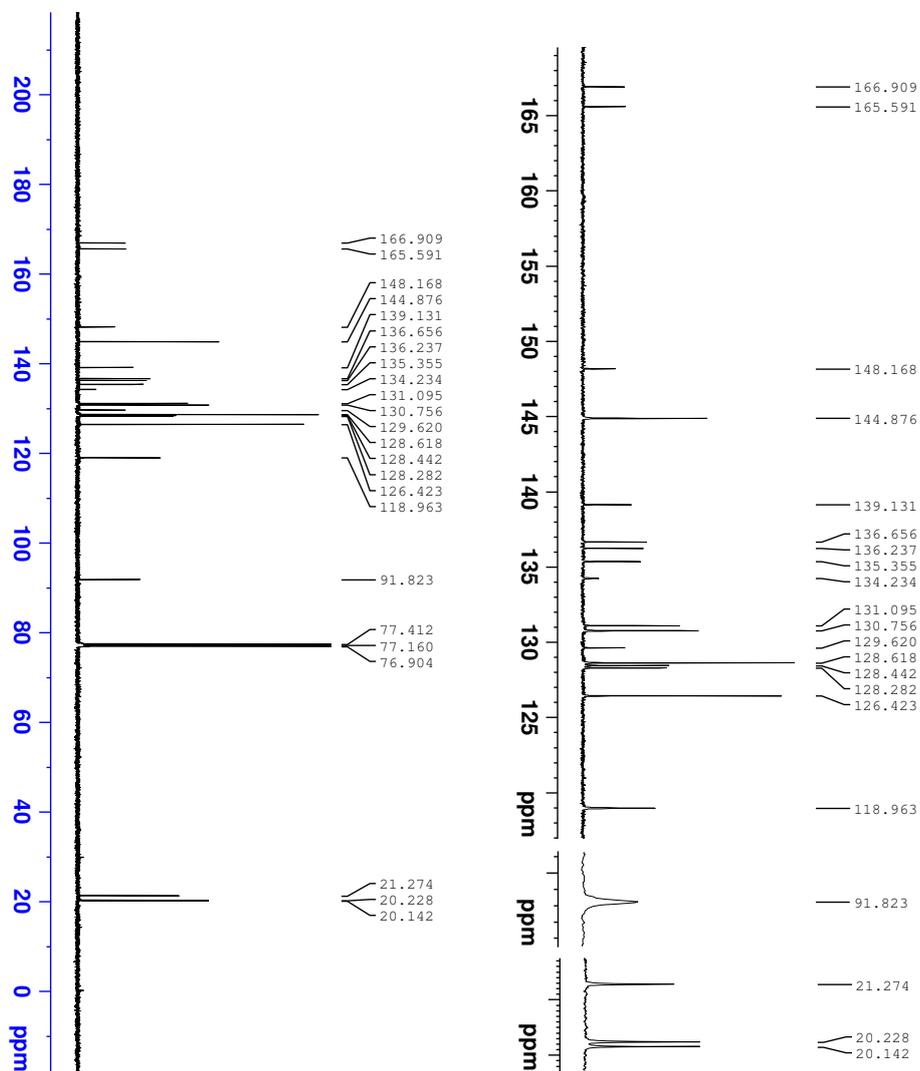


Figure S10. ¹H NMR spectrum of **3b** in CDCl₃ at 25 °C.

113-20251107-113-500-H_Ph-sm-C



```

Current Data Parameters
NAME      113-20251107-113-500-H_Ph-sm-C
PROCNO    1
F2 - Acquisition Parameters
Date_      20251107
Time       15:40 h
INSTRUM    spect
PROBHD     5mm QNP 1H/13
PULPROG    zgpg30
SFOVENT    C2513
NS          512
DS          4
SWH         23761.904 Hz
FIDRES     0.368261 Hz
AQ         1.13499 sec
RG         16.800 us/c
DW         16.800 us/c
TE         297.2 K
D1         2.00000000 sec
T1         0.03000000 sec
T1R1       125.765348 MHz
SFO1       125.765348 MHz
NUC1       13C
P1         9.20 us/c
PLM1       84.0000000 W
PLM2       500.1120014 MHz
NDC2
CPDPRG2   waltz16
PCPD2     13.0000000 us/c
PLM3       0.33931000 W
PLM4       0.18013000 W
F2 - Processing parameters
SI         32768
SF         125.762688 MHz
WDW        EM
SSB        0
GB         0
PC         1.40
  
```

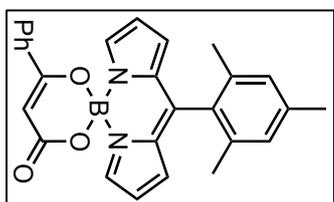


Figure S11. ^{13}C NMR spectrum of **3b** in CDCl_3 at 25°C .

113-20251105-113-500-H_Ph-target-B

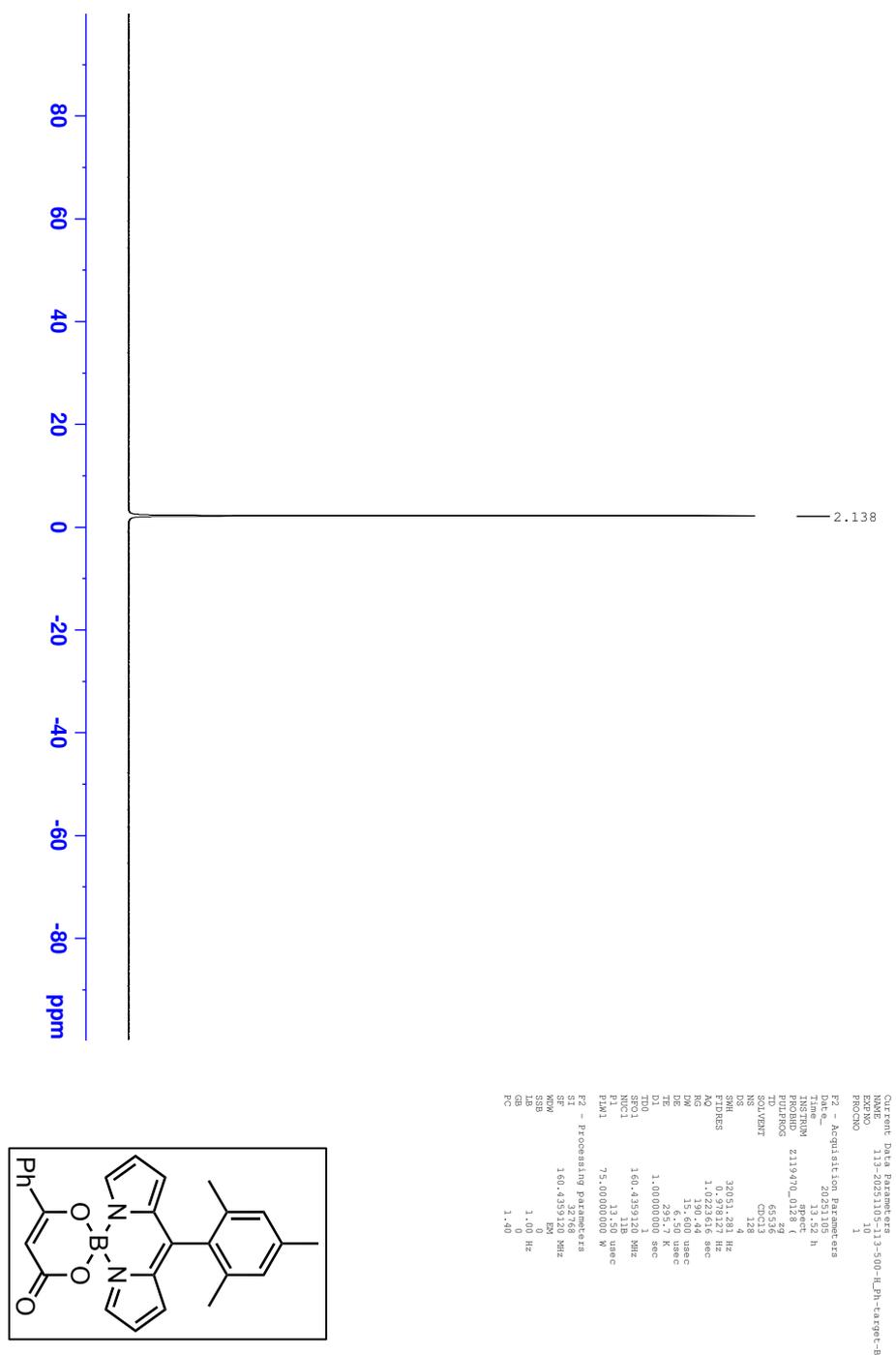
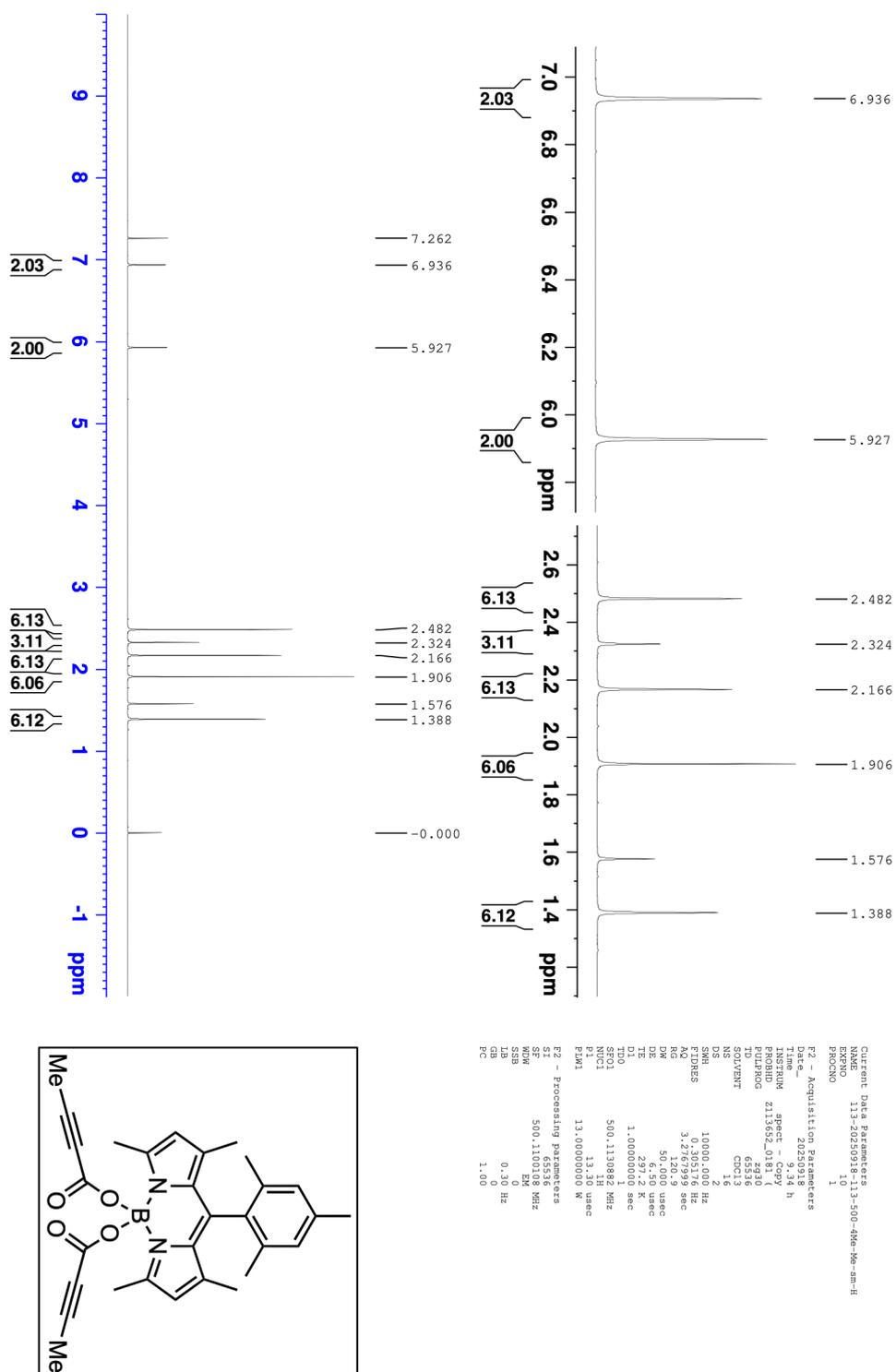
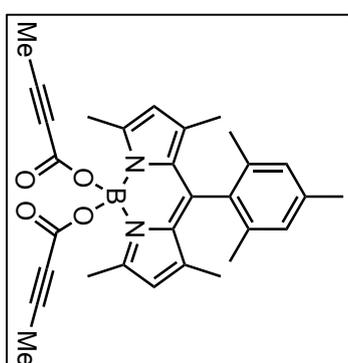
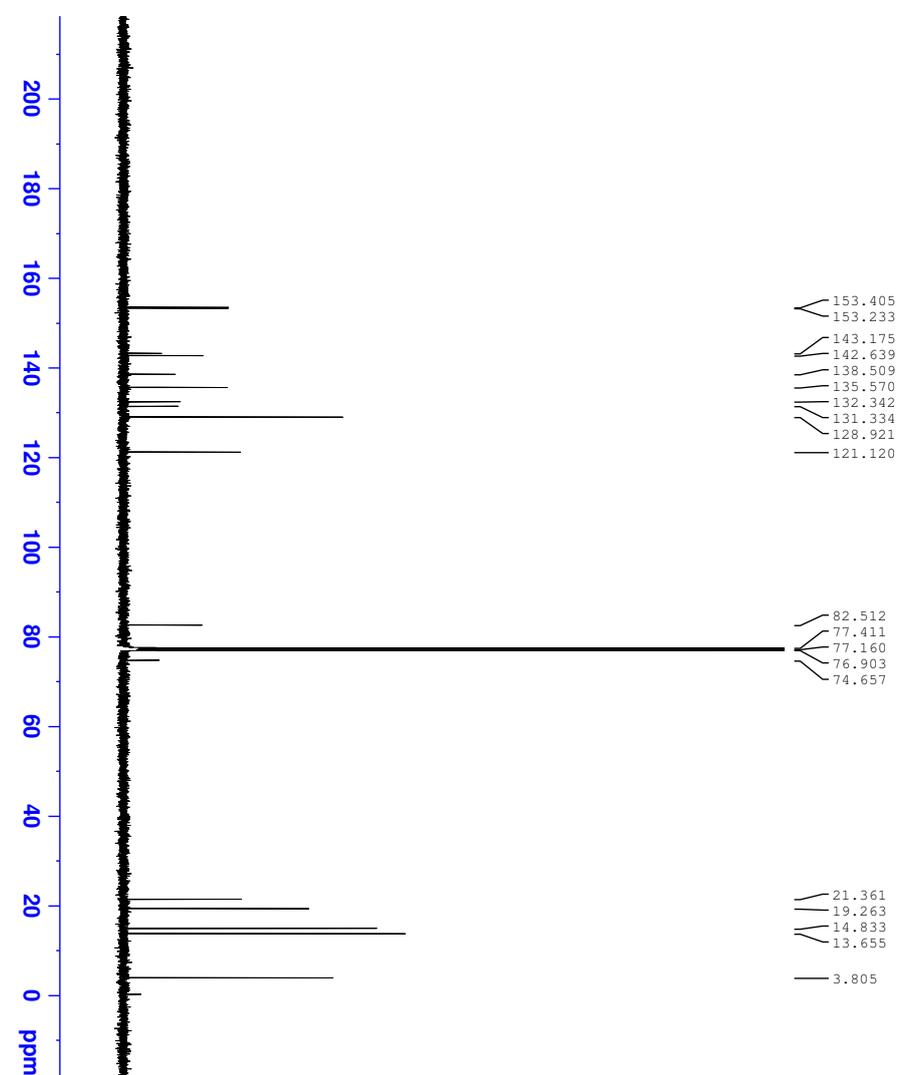


Figure S12. ^{11}B NMR spectrum of **3b** in CDCl_3 at 25 °C.

Figure S13. ¹H NMR spectrum of 2c in CDCl₃ at 25 °C.

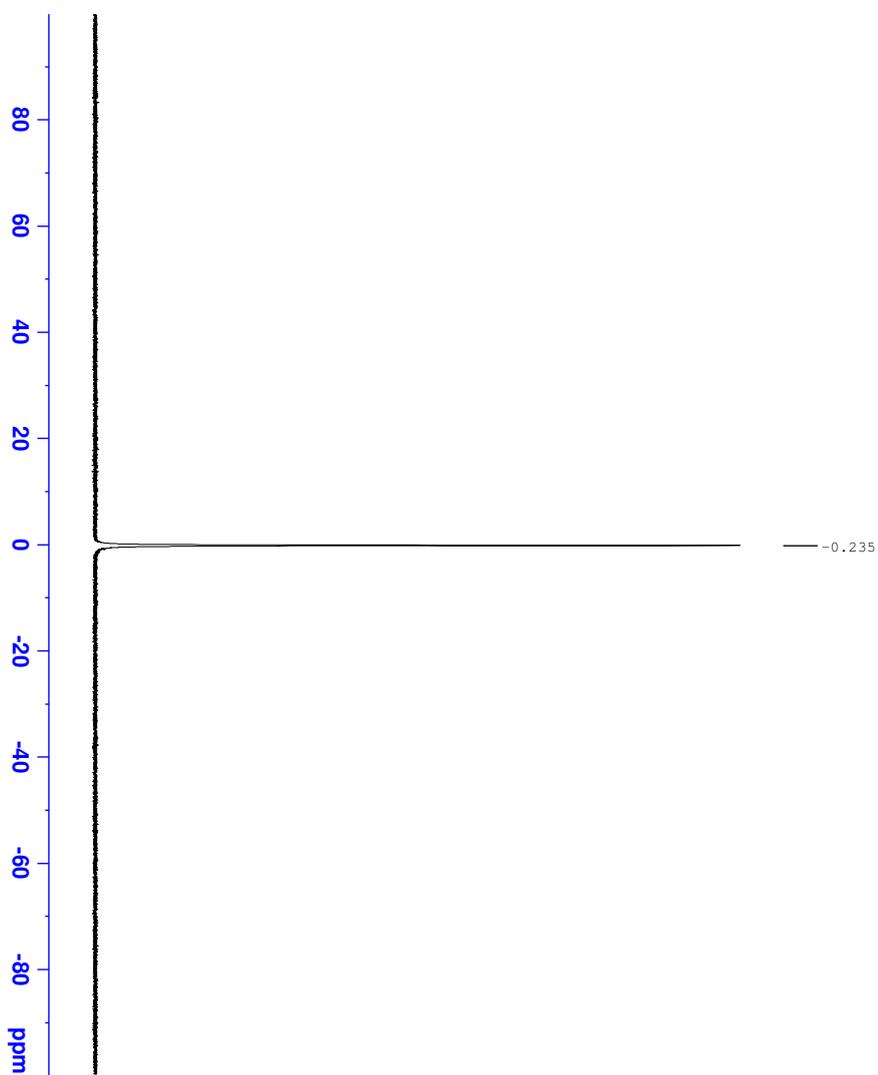
113-20250918-113-500-4Me-Me-sm-C



```
Current Data Parameters:
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PROCNO    1
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Time      20.10.02 h
INSTRUM   spect - Copy
PULPROG   zgpg30
TD         65536
SOLVENT    CDCl3
DS         4
SWH        239761.904 Hz
AQ         0.10100048 sec
RG         1194.99
WDW        EM
SS         16.800 usec
TE         297.8 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        125.765348 MHz
SFO1       125.765348 MHz
NUC1       13C
P1         13.00000000 usec
F1M1       84.00000000 MHz
SFO2       500.1120004 MHz
PROBHD1   5mm QNP1H1
PULPROG2  waltz16
CPCORRG2  1
PCPDPR2   13.00000000 MHz
PCPDPR3   13.00000000 MHz
PCPDPR4   0.18073000 MHz
F1M3       0.18073000 MHz
F2 - Processing parameters
SF         125.7627435 MHz
WDW        EM
SS         1.00 Hz
LB         0
GB         0
PC         1.40
```

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

113-20250917-113-500-4Me-Me-sm-B



```

=====
Date_      20250918
Time      09:29 h
INSTRUM   spect
PROBHD    2139470_0128 (
PULPROG   zgpg30
SOLVENT   CDCl3
NS        128
DS        4
AQ        32051.281 Hz
FIDRES    0.978827 Hz
DE        1.0228515 sec
DM        15.400 usec
DI        6.50 usec
TE        298.1 K
TD        1.00000000
TDC1      13.50 usec
PL1       75.00000000 W
PLM1
=====
F2 - Acquisition Parameters
Date_      20250918
Time      09:29 h
INSTRUM   spect
PROBHD    2139470_0128 (
PULPROG   zgpg30
SOLVENT   CDCl3
NS        128
DS        4
AQ        32051.281 Hz
FIDRES    0.978827 Hz
DE        1.0228515 sec
DM        15.400 usec
DI        6.50 usec
TE        298.1 K
TD        1.00000000
TDC1      13.50 usec
PL1       75.00000000 W
PLM1
=====
F2 - Processing parameters
SI        32768
SF        160.4359120 MHz
RG        655
SSB       0
GB        1.00 Hz
GB        0
PC        1.40
=====

```

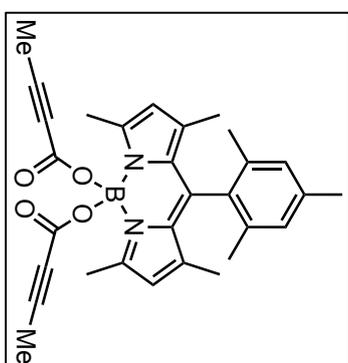


Figure S15. ^{11}B NMR spectrum of **2c** in CDCl_3 at 25°C .

113-20250918-113-500-4Me-Me-target-H

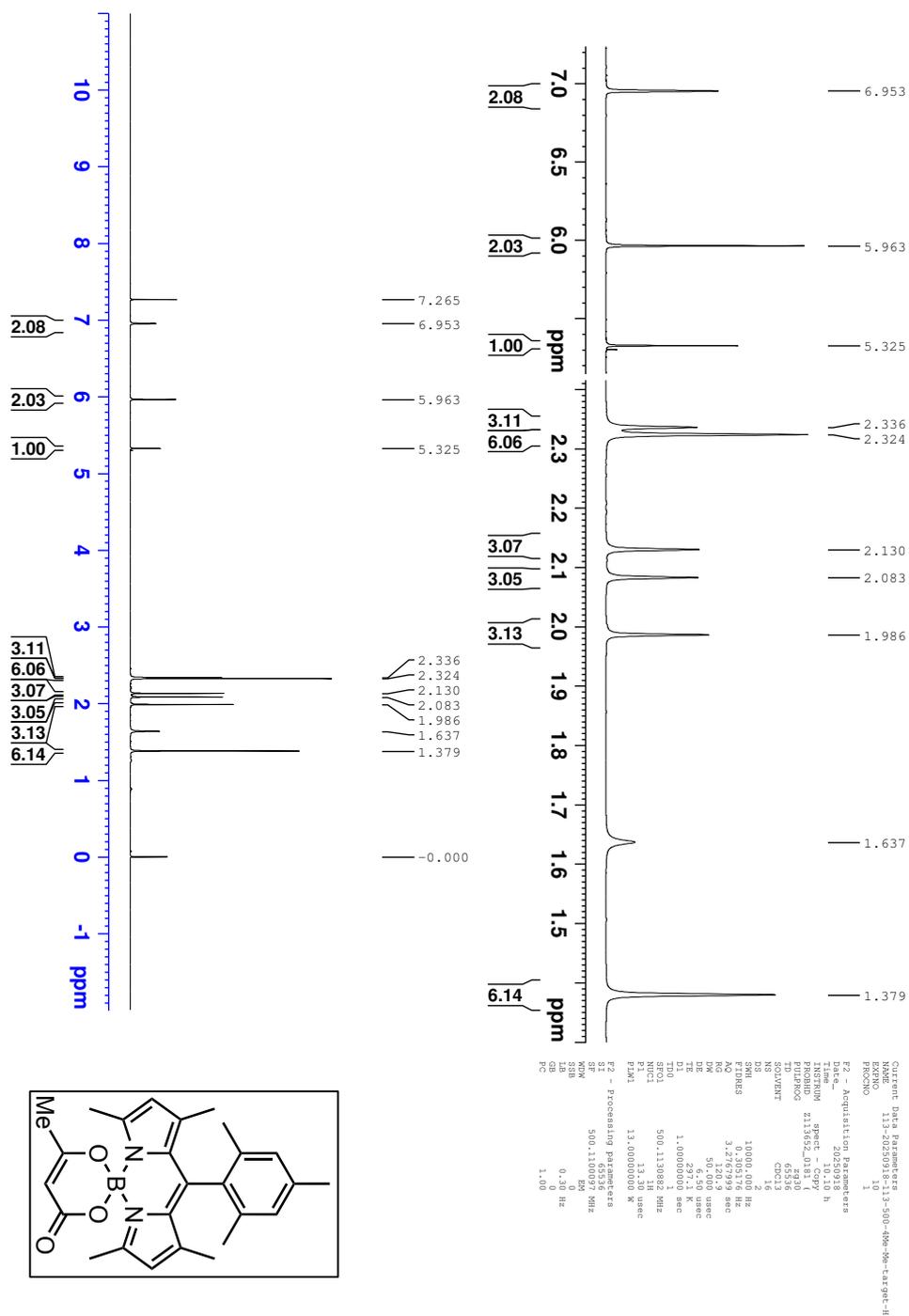


Figure S16. ¹H NMR spectrum of 3c in CDCl₃ at 25 °C.

113-20250918-113-500-4Me-Ne-target-C

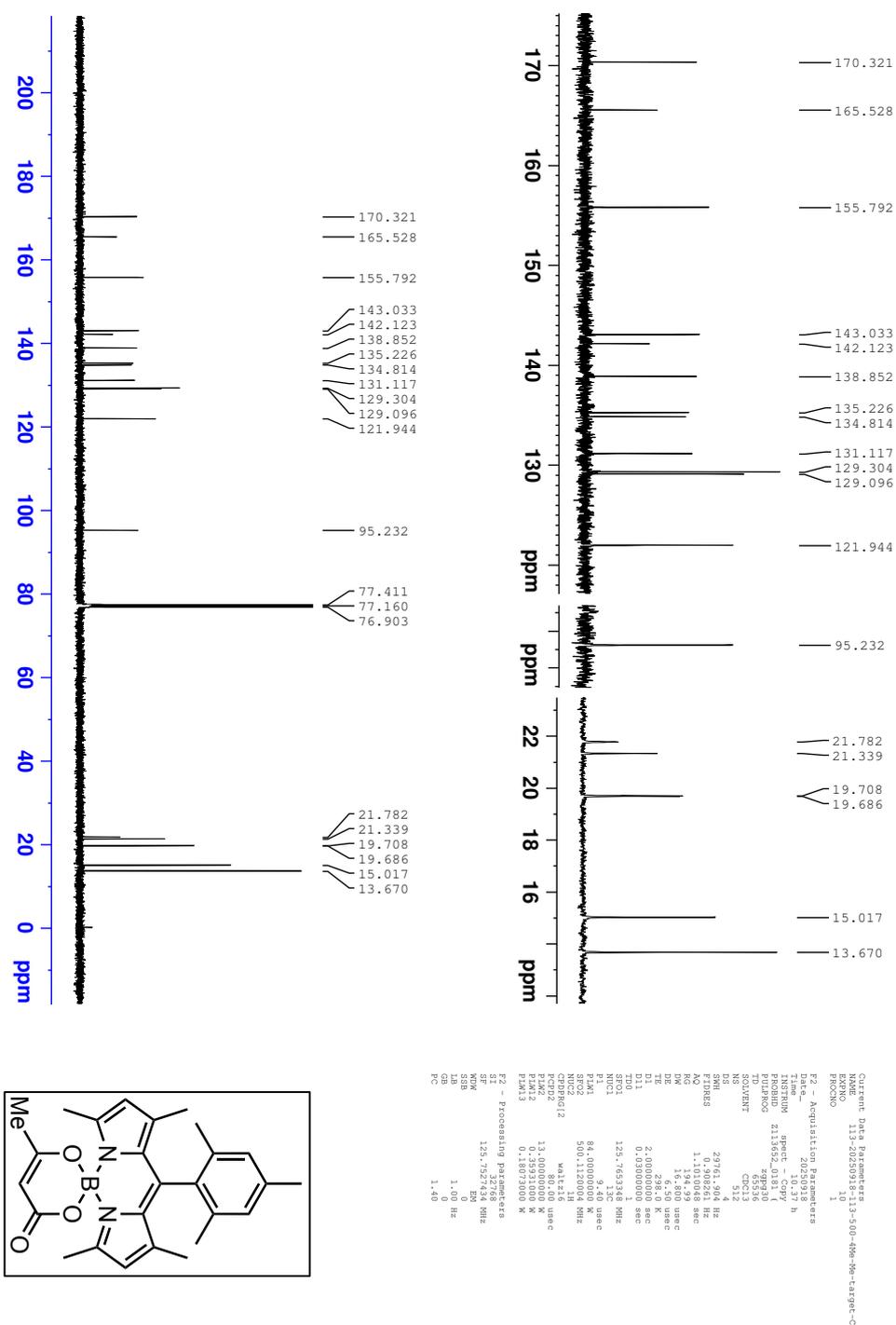


Figure S17. ¹³C NMR spectrum of 3c in CDCl₃ at 25 °C.

113-20250917-113-500-4Me-Me-target-B

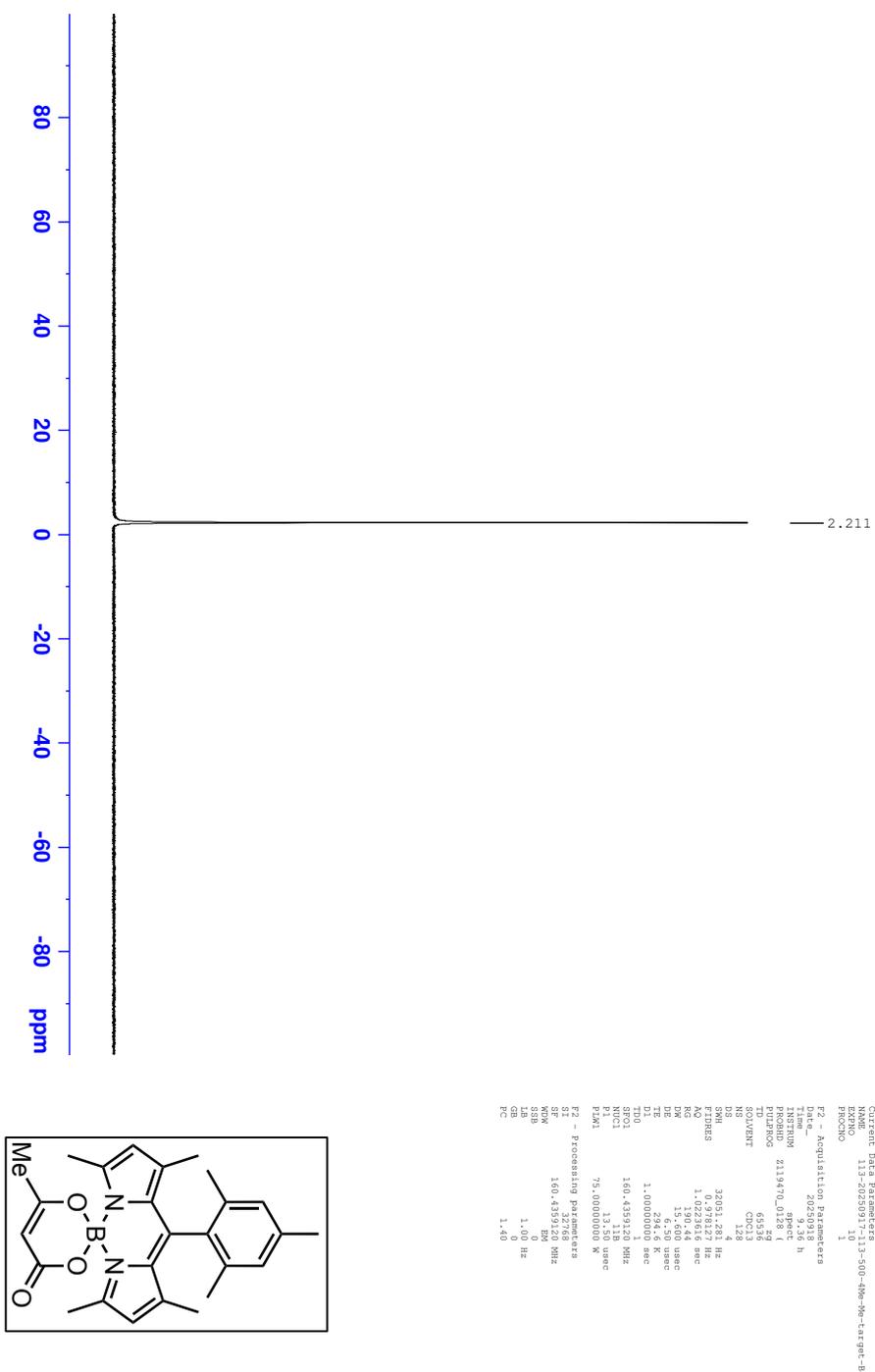
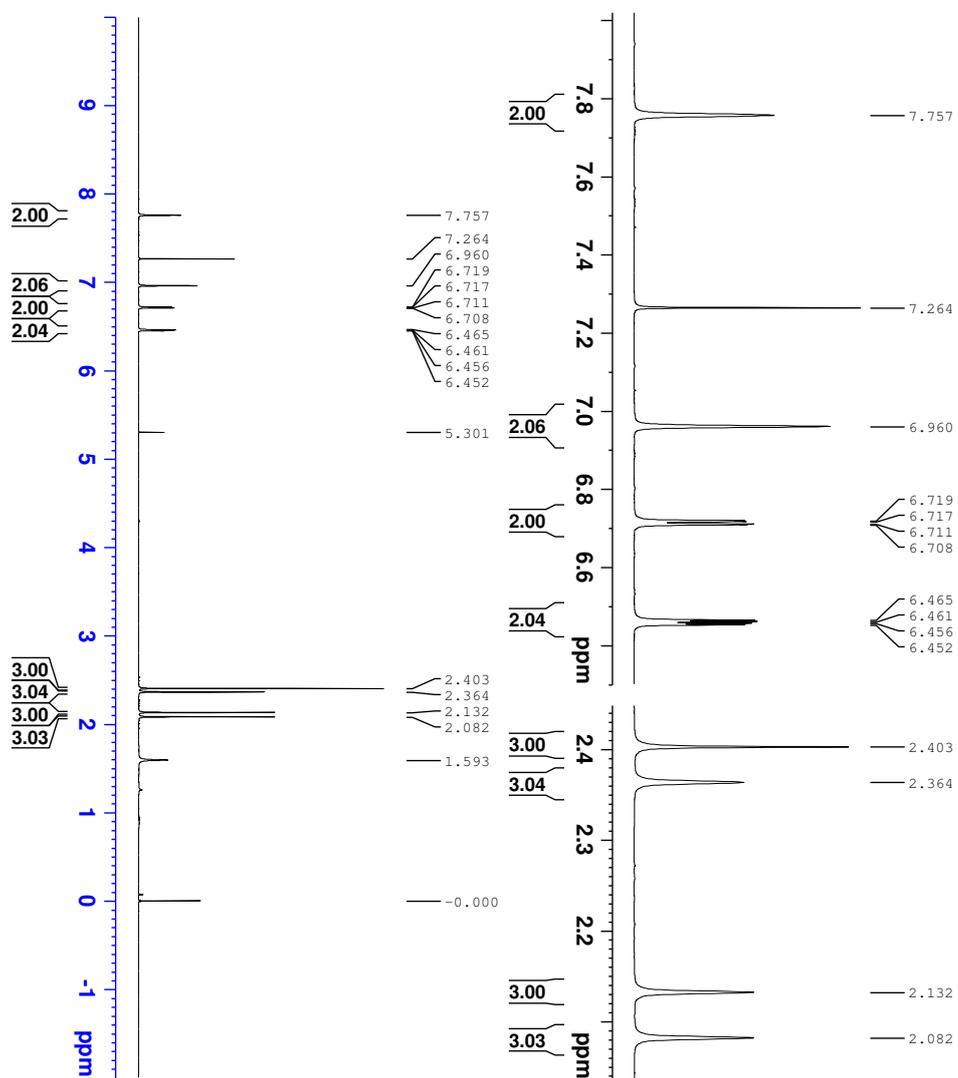


Figure S18. ^{11}B NMR spectrum of **3c** in CDCl_3 at 25 °C.



```

Current Data Parameters
Name: 113-20251003-113-500-H_Me-I-H
EXPNO: 1
PROCNO: 1
F2 - Acquisition Parameters
Date_ : 20250310
Time: 23:06 h
INSTRUM: spect
PROBHD: 2119470.01283 (
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 16
DS: 2
AQ: 10000.000 Hz
FIDRES: 0.305176 Hz
RG: 3.2767999 sec
DE: 151.27 usec
TE: 300.2 K
D1: 296.00 K
D11: 1.00000000 sec
SFO1: 500.0530878 MHz
NUC1: 1H
P1: 11.75 usec
PL1: 25.79400063 W
F2 - Processing parameters
SI: 65536
SF: 500.0500096 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00
  
```

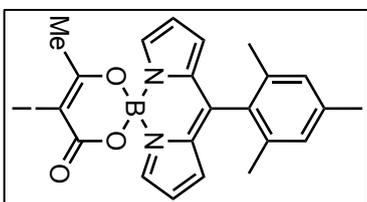
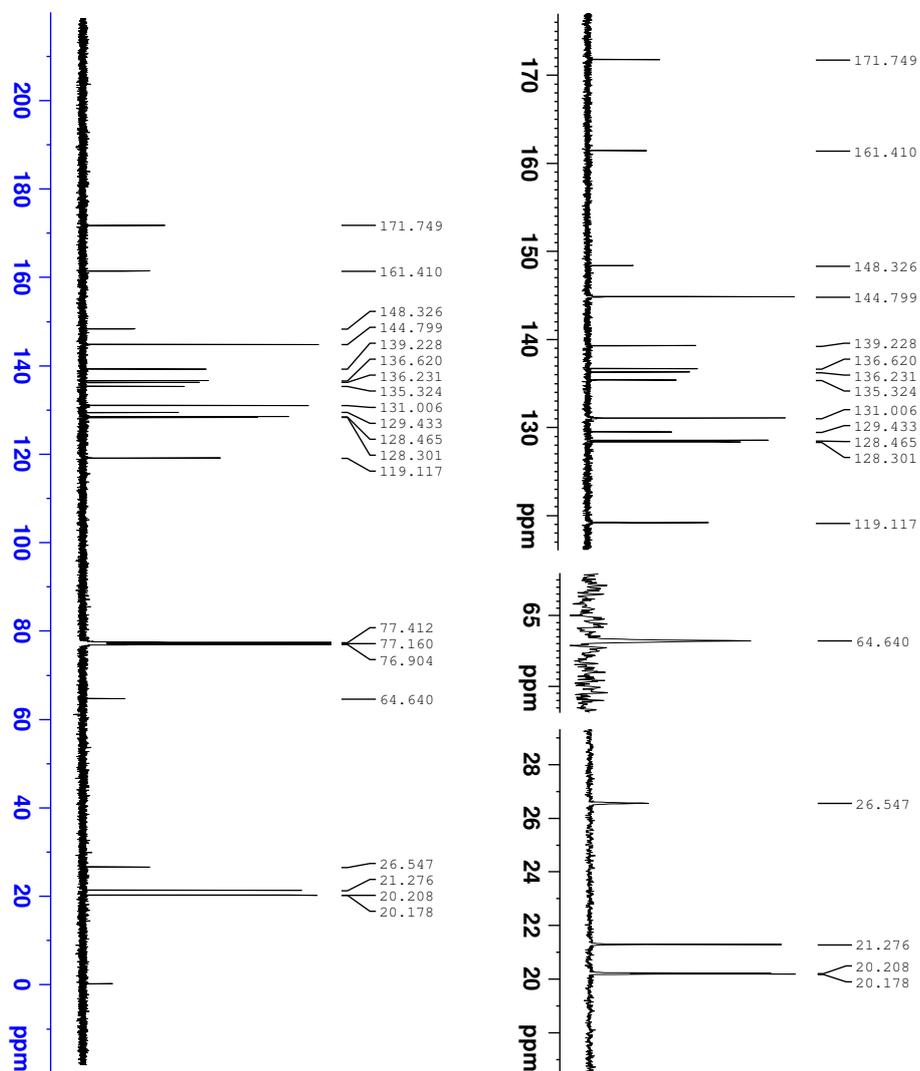


Figure S19. ^1H NMR spectrum of **4a** in CDCl_3 at 25°C .

113-20251003-113-500-H_Me-I-C



```

Current Data Parameters
NAME      113-20251003-113-500-H_Me-I-C
EXPNO    10
PROCNO   1
F2 - Acquisition Parameters
Date_    20251004
Time     11:27:00
INSTRUM  spect
PROBHD   Z119470.0128 (
PULPROG  zgpg30
SOLVENT  CDCl3
NS       2048
DS       2
SWH      29761.3094 Hz
FIDRES   0.00012294 Hz
AQ       1.1010048 sec
RG       190.44
DM       16.800 usec
TE       295.2 K
D1       2.00000000 sec
D11      0.03000000 sec
D12      0.03000000 sec
D13      0.03000000 sec
NUC1     13C
NUC2     13C
P1       10.00 usec
PL1      0.00 dB
PL2      0.00 dB
PL3      0.00 dB
PL4      0.00 dB
PL5      0.00 dB
PL6      0.00 dB
PL7      0.00 dB
PL8      0.00 dB
PL9      0.00 dB
PL10     0.00 dB
PL11     0.00 dB
PL12     0.00 dB
PL13     0.00 dB
PL14     0.00 dB
PL15     0.00 dB
PL16     0.00 dB
PL17     0.00 dB
PL18     0.00 dB
PL19     0.00 dB
PL20     0.00 dB
PC       1.40
=====
F2 - Processing parameters
SI       32768
SF       125.7376570 MHz
WDW      EM
SSB      0 Hz
GB       0
PC       1.40
  
```

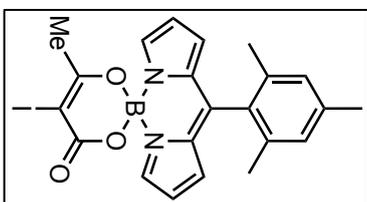
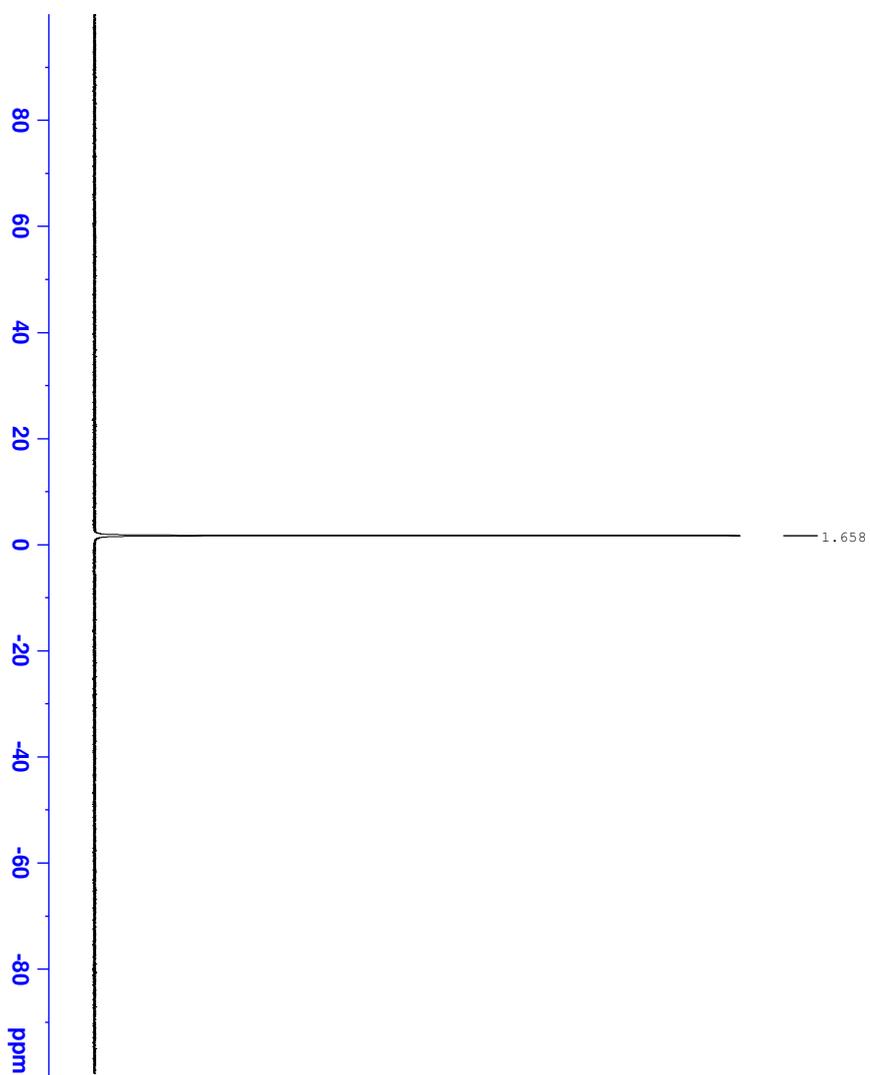


Figure S20. ¹³C NMR spectrum of **4a** in CDCl₃ at 25 °C.

113-20251008-113-500-H_Me-I-B



Current Data Parameters
NAME 113-20251008-113-500-H_Me-I-B
EXNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20251008
Time 11:13 h
INSTRUM spect
PROBHD Z113470_0128 (2g
PULPROG zgpg30
TD 65536
FIDRES 0.228
AQ 1.228
RG 190.44
DE 6.50 usec
TE 29.50 usec
D1 1.0000000 sec
TDO 1
SFO1 160.4359120 MHz
NUC1 11B
P1 13.18 usec
PL1 75.0000000 W
F2 - Processing parameters
SI 32051.281 Hz
SF 160.4359120 MHz
WDW EM
SSB 0
GB 0
PC 1.40

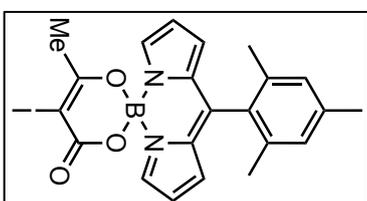


Figure S21. ^{11}B NMR spectrum of **4a** in CDCl_3 at 25 °C.

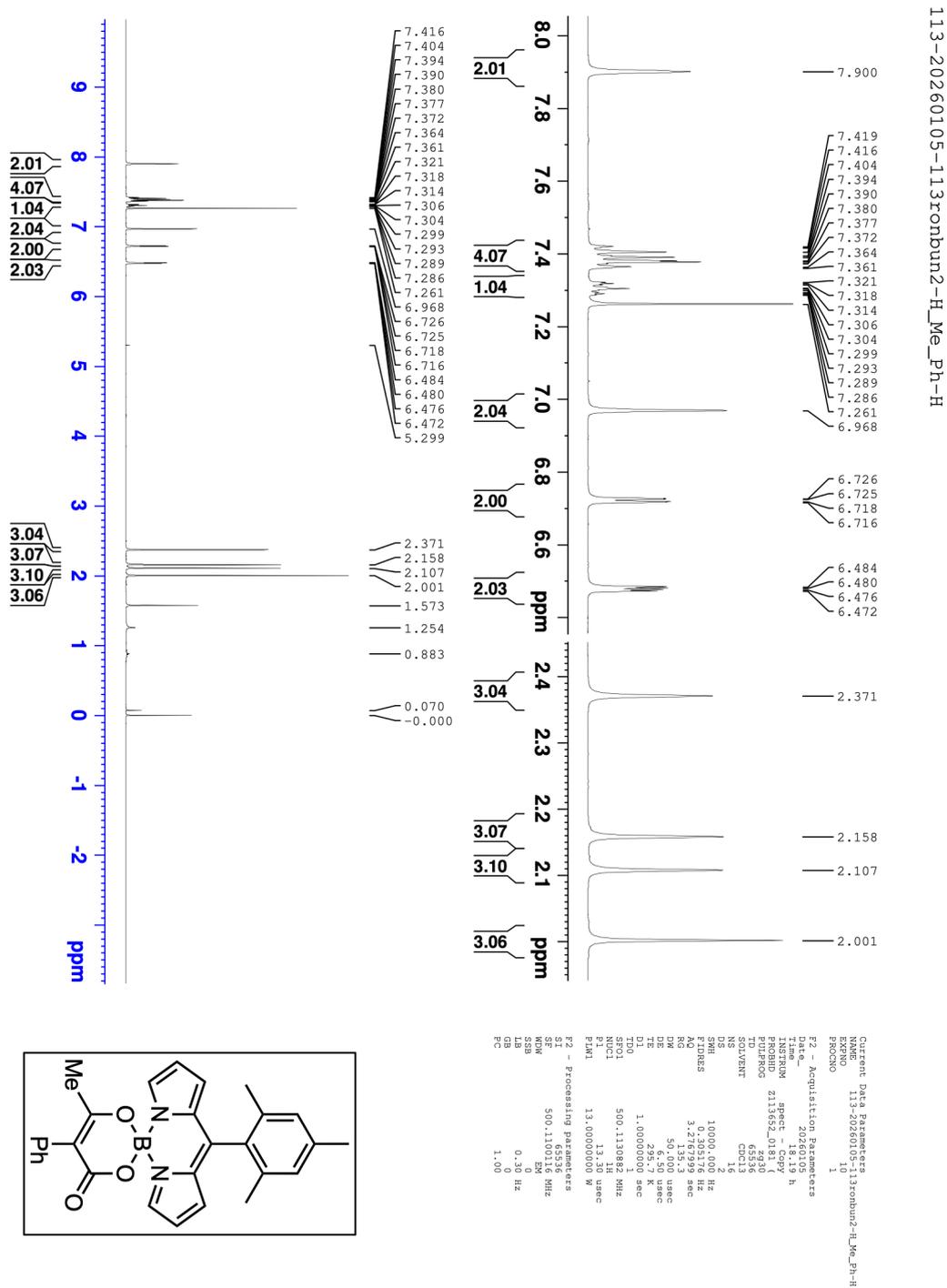


Figure S22. ¹H NMR spectrum of **5a** in CDCl₃ at 25 °C.

113-20260105-113ronbun2-H_Me_Ph-H

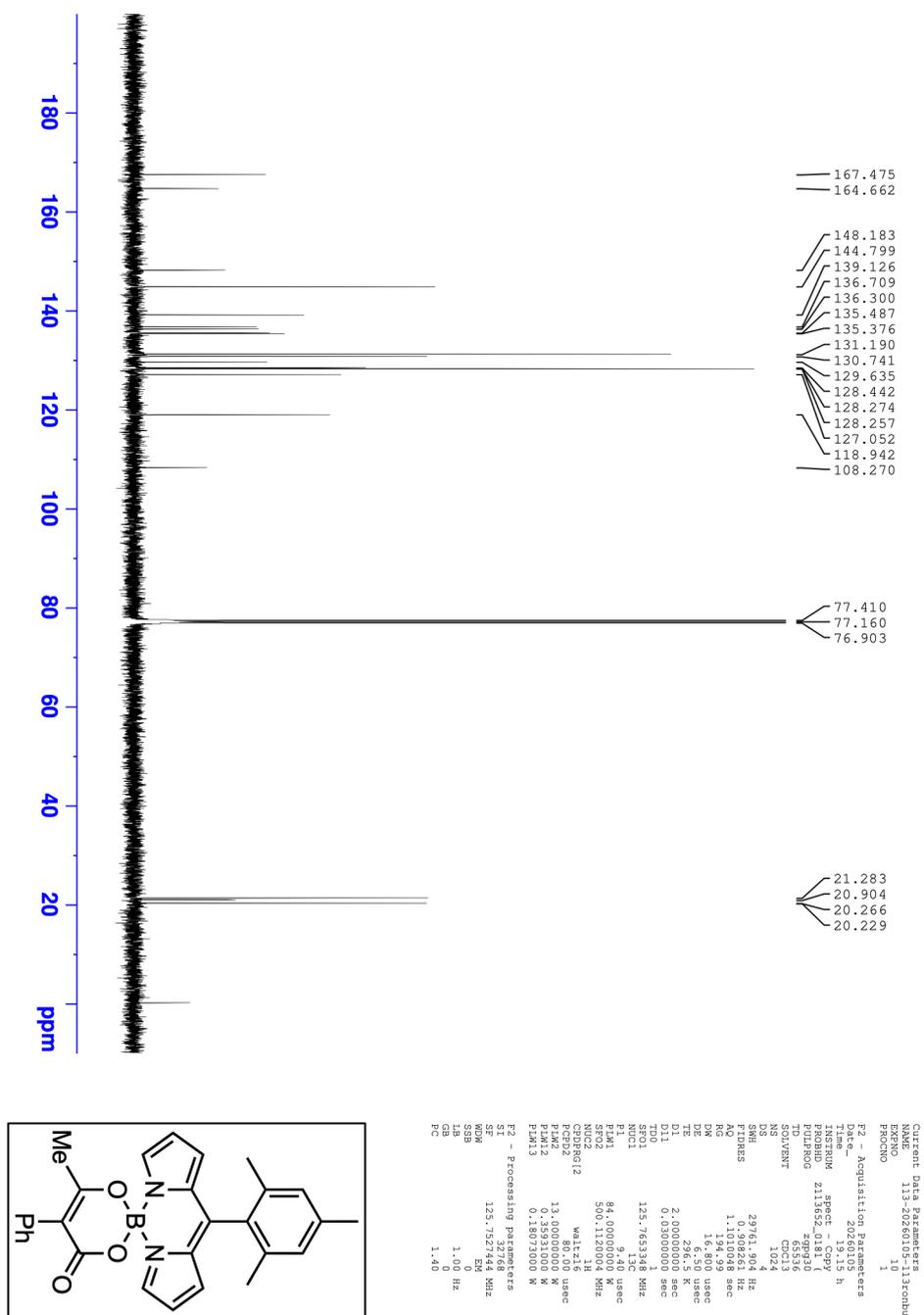


Figure S23. ¹³C NMR spectrum of 5a in CDCl₃ at 25 °C.

113-20260105-113ronbun2-H_Me_Ph-B

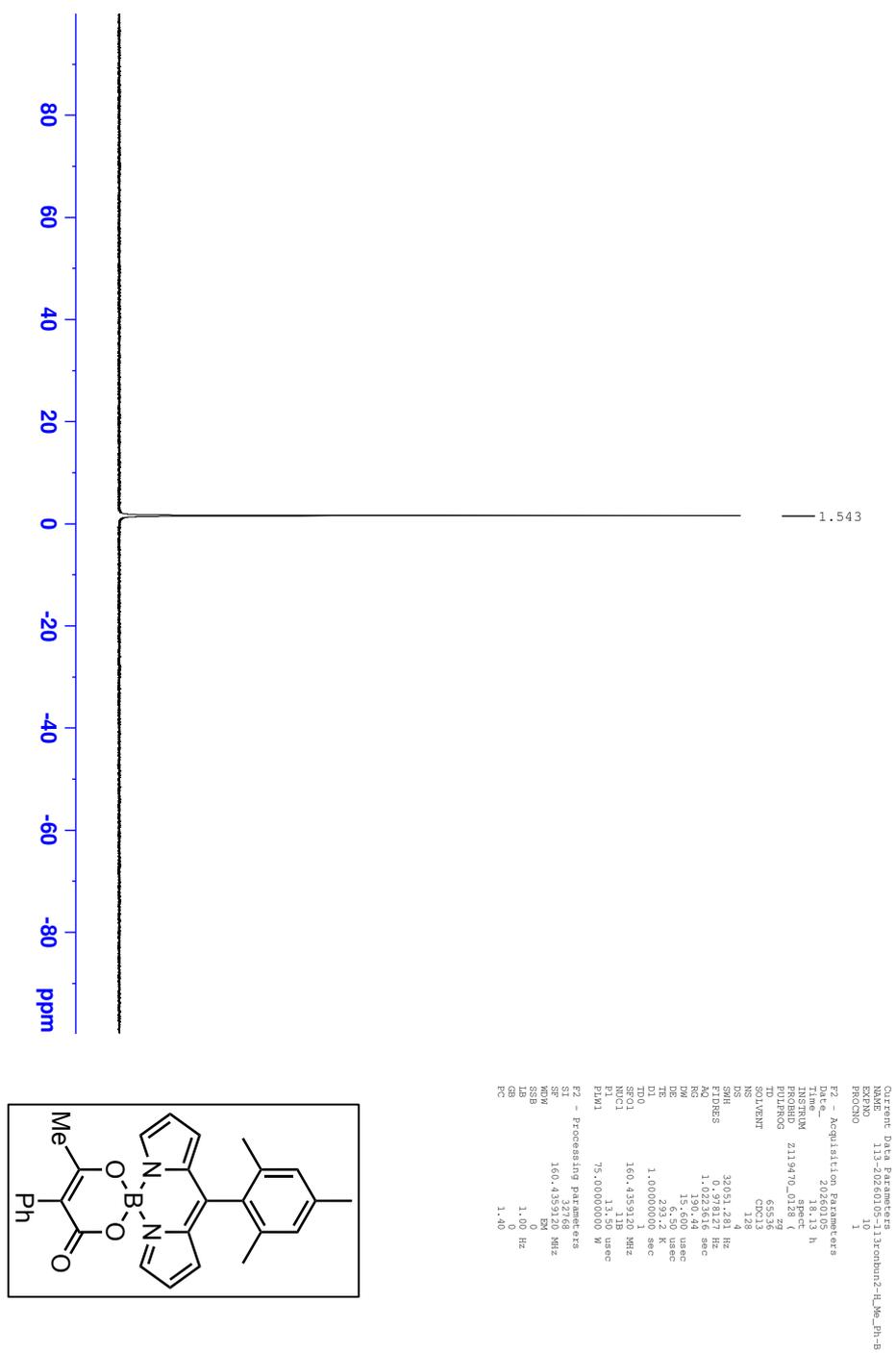
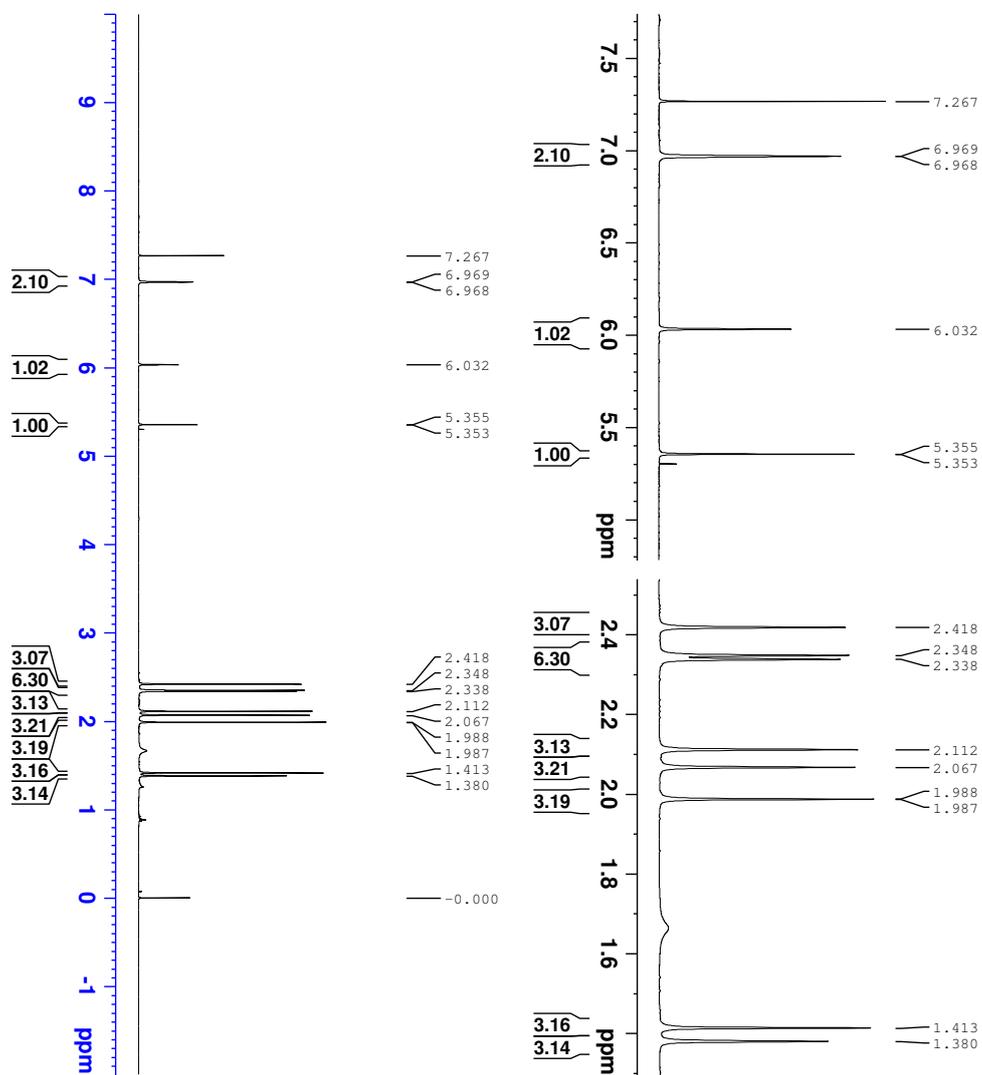


Figure S24. ^{11}B NMR spectrum of **5a** in CDCl_3 at 25 °C.

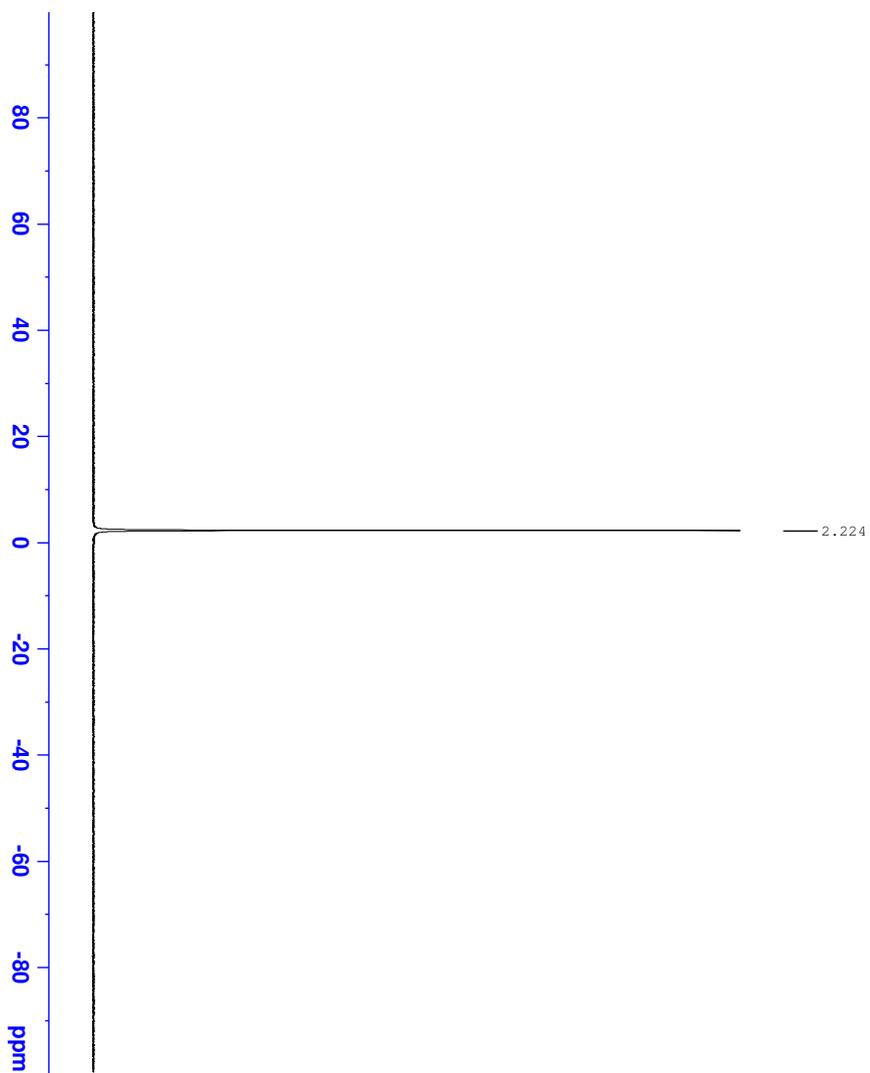
113-20251003-113-500-4Me_Me_mono1-H



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Current Data Parameters
NAME      113-20251003-113-500-4Me_Me_mono1-H
EXPNO    10
PROCNO   1
F2 - Acquisition Parameters
Time     0.57 h
INSTRUM  spect
PULPROG  zgpg30
TD       65536
SFO      400.146
AQ       1.16
RG        320
NS       16
DS       4
SWH       10000.000 Hz
FIDRES   0.305176 Hz
AQ       3.275929 sec
RG        320
WDW       EM
SSB       0
LB        50.0000 usec
GB        0
PC        1.00000000 sec
D1        500.0350823 MHz
D11       1H
D12       1H
D13       1H
E1        25.79400000 N
F2 - Processing parameters
SI        32768
SF        500.0350885 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
  
```

Figure S25. ¹H NMR spectrum of 6c in CDCl₃ at 25 °C.



Current Data Parameters
 NAME: 113-20231009-113-500-40s_36_mnnc1-B
 EXPNO: 10
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_ 20231009
 Time 12:56 h
 INSTRUM spect
 PULPROG zgpg30
 TD 65536
 TO 0.00000000
 NS 128
 DS 4
 SFO 32051.281 Hz
 EQ 0.00000000
 FIDRES 1.0223616 sec
 AQ 0.00000000
 DQ 0.00000000
 DW 8.50 usec
 DE 15.600 usec
 DI 1.00000000 sec
 TDO 0.00000000
 TDC 160.4359221 MHz
 NUC1 11B
 P1 13.50 usec
 F1 75.0000000 MHz
 F2 - Processing parameters
 SI 32768
 SF 160.4359120 MHz
 EX 0
 MW 0
 LB 1.00 Hz
 GB 0
 PC 1.40

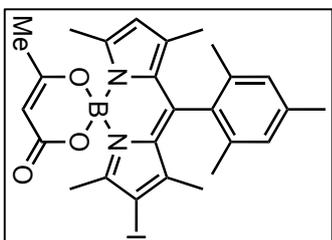
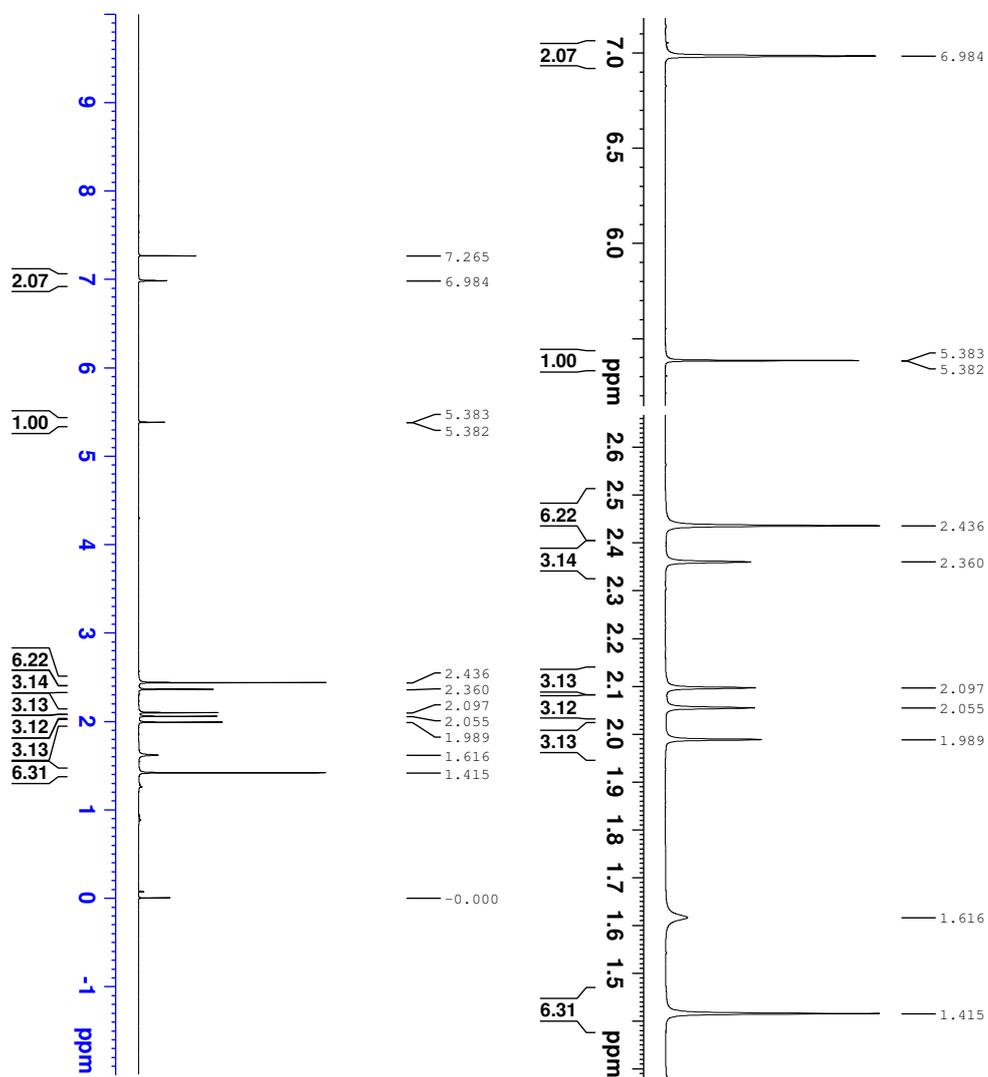


Figure S27. ^{11}B NMR spectrum of **6c** in CDCl_3 at 25°C .

113-20251003-113-500-4Me_Me_d11-H



Current Data Parameters
 NAME 113-20251003-113-500-4Me_Me_d11-H
 EXPNO 10
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20251003
 Time 20:25:51 h
 INSTRUM spect
 PULPROG zgpg30
 TD 65536
 SFO 500.136260
 SOLVENT CDCl3
 NS 2
 DS 2
 SM 10000.000 Hz
 SFO50 500.136260 MHz
 AQ 3.217939 sec
 RG 138.428
 DE 50.450 usec
 TE 295.6 K
 D1 1.00000000 sec
 D11 500.0530878 MHz
 SFO1 NUC1 13
 NUC1 1H
 FWH 25.7940063 W
 P2 - Processing parameters
 SI 65536
 SF 500.0500936 MHz
 KW EX
 SFO 500.136260 MHz
 DE 50.450 usec
 TE 295.6 K
 GE 1.00

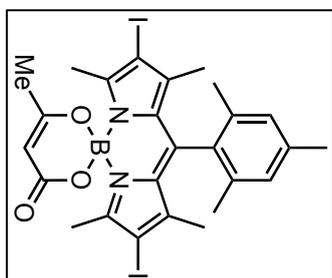
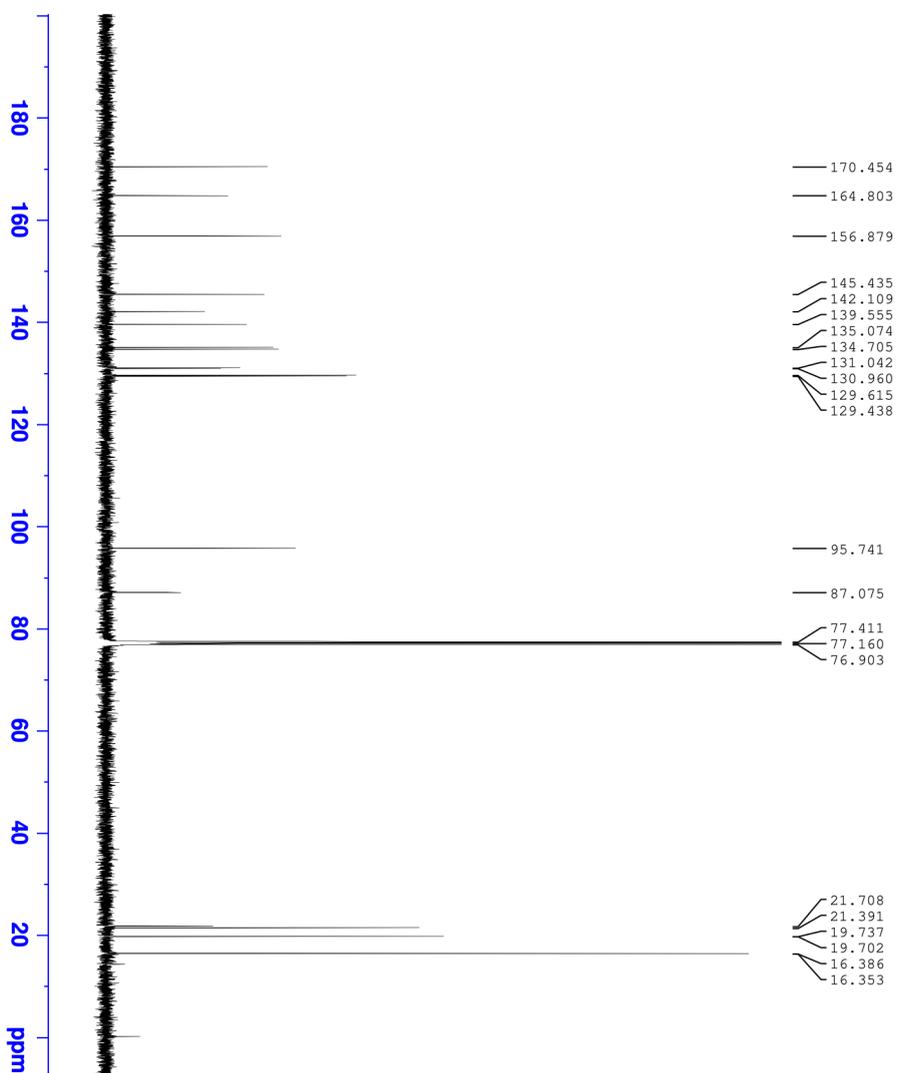


Figure S28. ¹H NMR spectrum of 7c in CDCl₃ at 25 °C.

113-20251003-113-500-4Me_Me_d11-C



```

Current Data Parameters
NAME      113-20251003-113-500-4Me_Me_d11-C
EXPNO     1
PROCNO    1
F2 - Acquisition Parameters
Time      2023.4.10 h
INSTRUM   spect
PROBHD    zgpg30
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
DS         2
SFO1      297.61,904 Hz
SFO2      0.00000000
AQ        1.00000000
RG         190.44
DM         16.800 usec
DE         0.00000000
TE         296.6 K
D1         2.00000000 sec
D11        0.00000000
D12        0.00000000
D13        1.00000000
D14        0.00000000
SFO1      125.7502463 MHz
SFO2      1.00 usec
P1         93.8100354 W
SFO1      500.0520002 MHz
SFO2      1.00 usec
P1         32758 W
SFO1      125.7376570 MHz
SFO2      1.00 usec
P1         0 W
SFO1      1.00 Hz
SFO2      1.00 Hz
PC         1.40
  
```

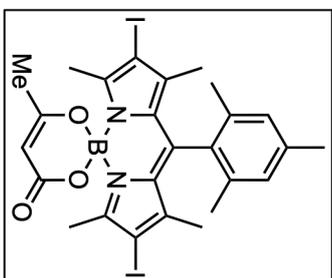
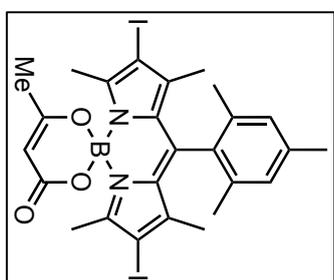
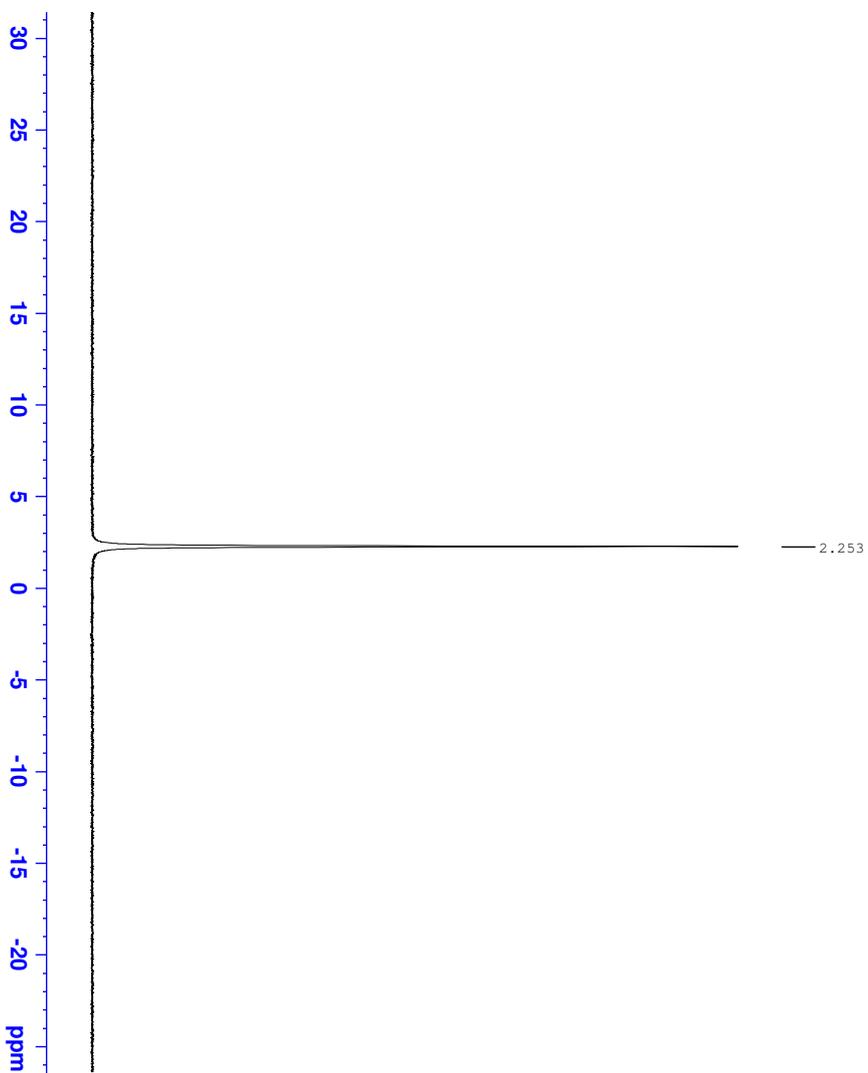


Figure S29. ^{13}C NMR spectrum of **7c** in CDCl_3 at $25\text{ }^\circ\text{C}$.



```

Current Data Parameters
NAME      113-20251009-113-500-4Me_Me_d11-B
PROCNO    1
F2 - Acquisition Parameters
Date_     20191218
Time      12:48 h
INSTRUM   spect
PULPROG   zgpg30
TD         65536
AQ         6.50
RG         327.68
DE         1.00
TE         298.15 K
TDO        1.00000000 sec
SFO1      160.4359120 MHz
NUC1       11B
PL1        1.18 usec
PLM1       75.00000000 W
F2 - Processing parameters
SI         32768
SF         160.4359120 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```

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

4. Mass spectra

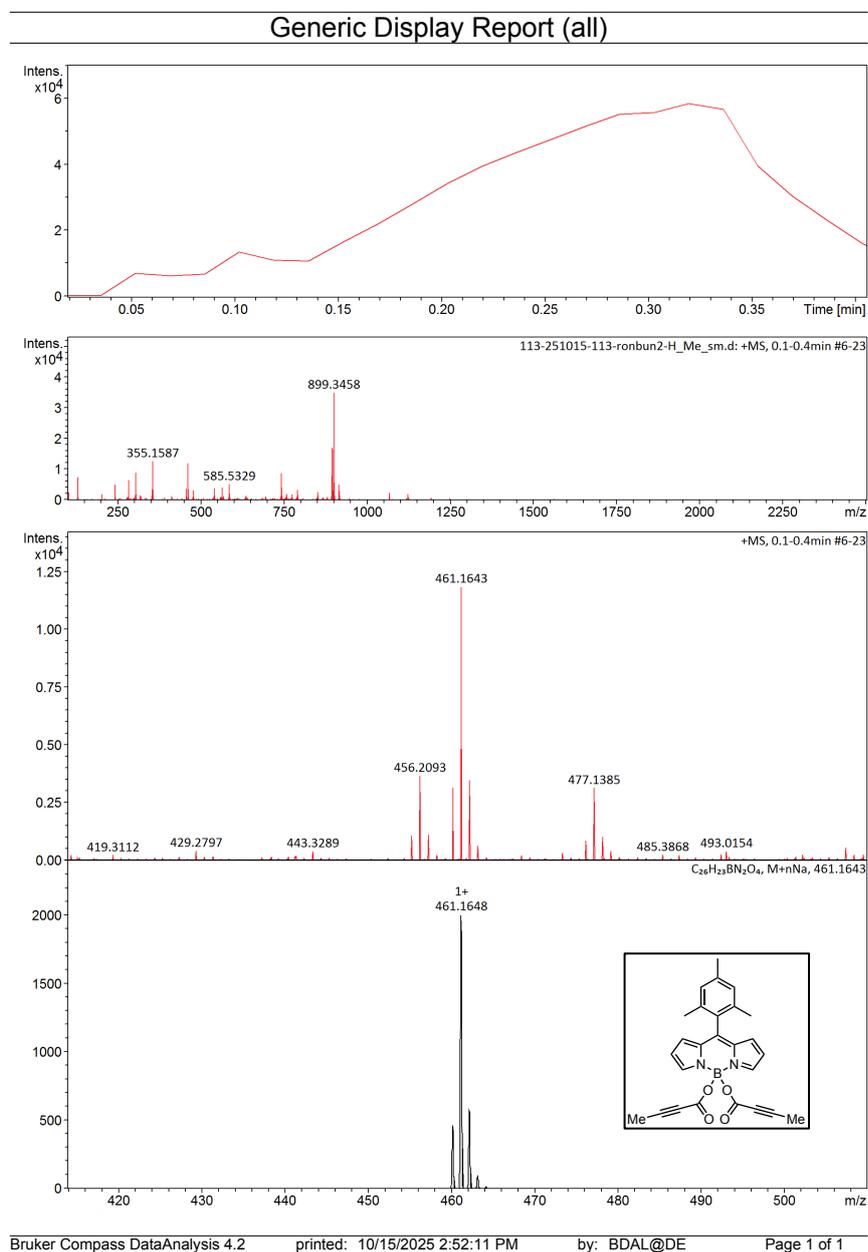
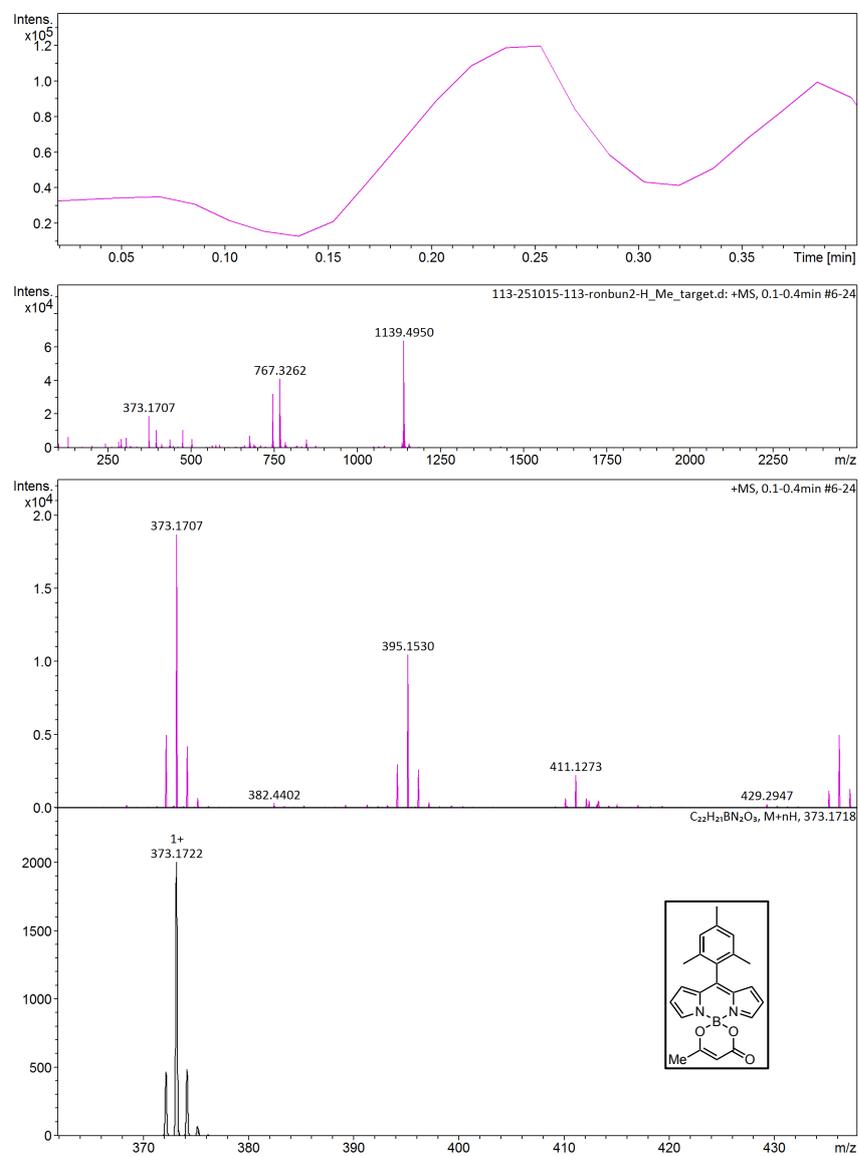


Figure S31. ESI-TOF mass spectrum of **2a**.

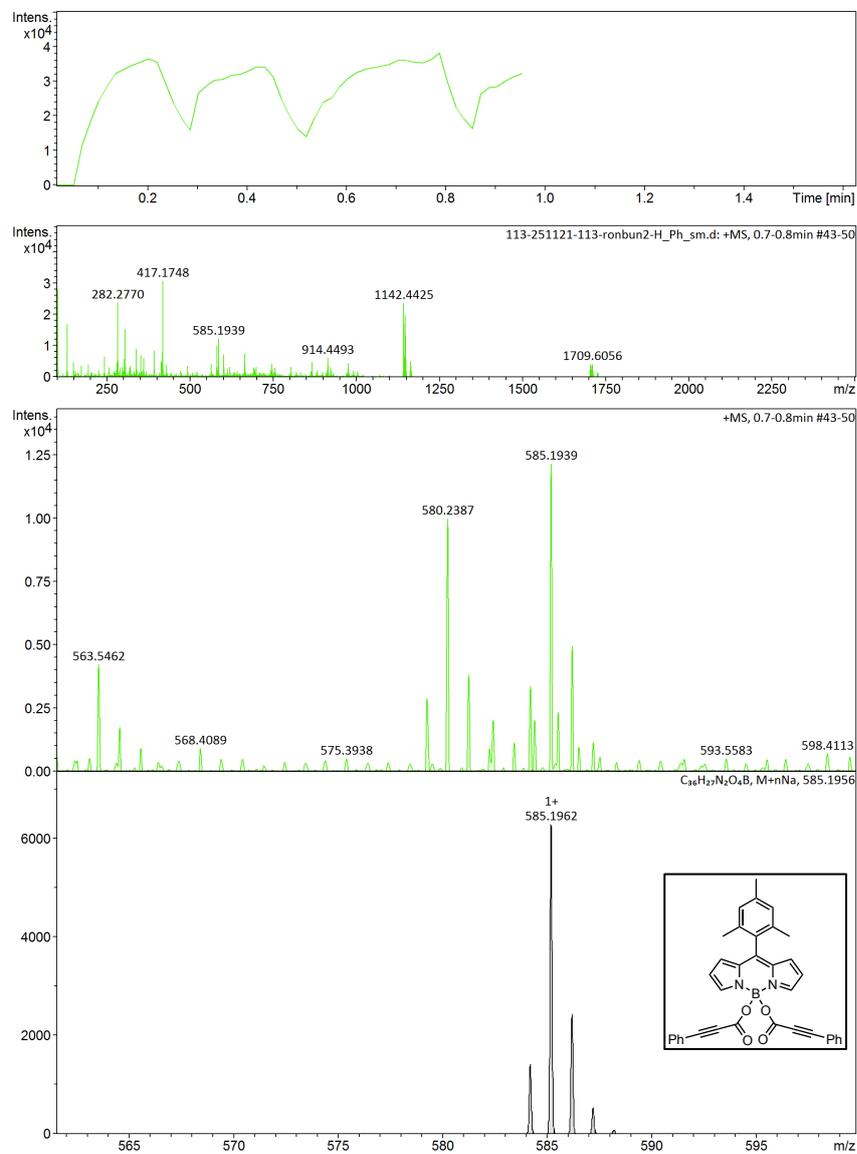
Generic Display Report (all)



Bruker Compass DataAnalysis 4.2 printed: 10/15/2025 2:54:36 PM by: BDAL@DE Page 1 of 1

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

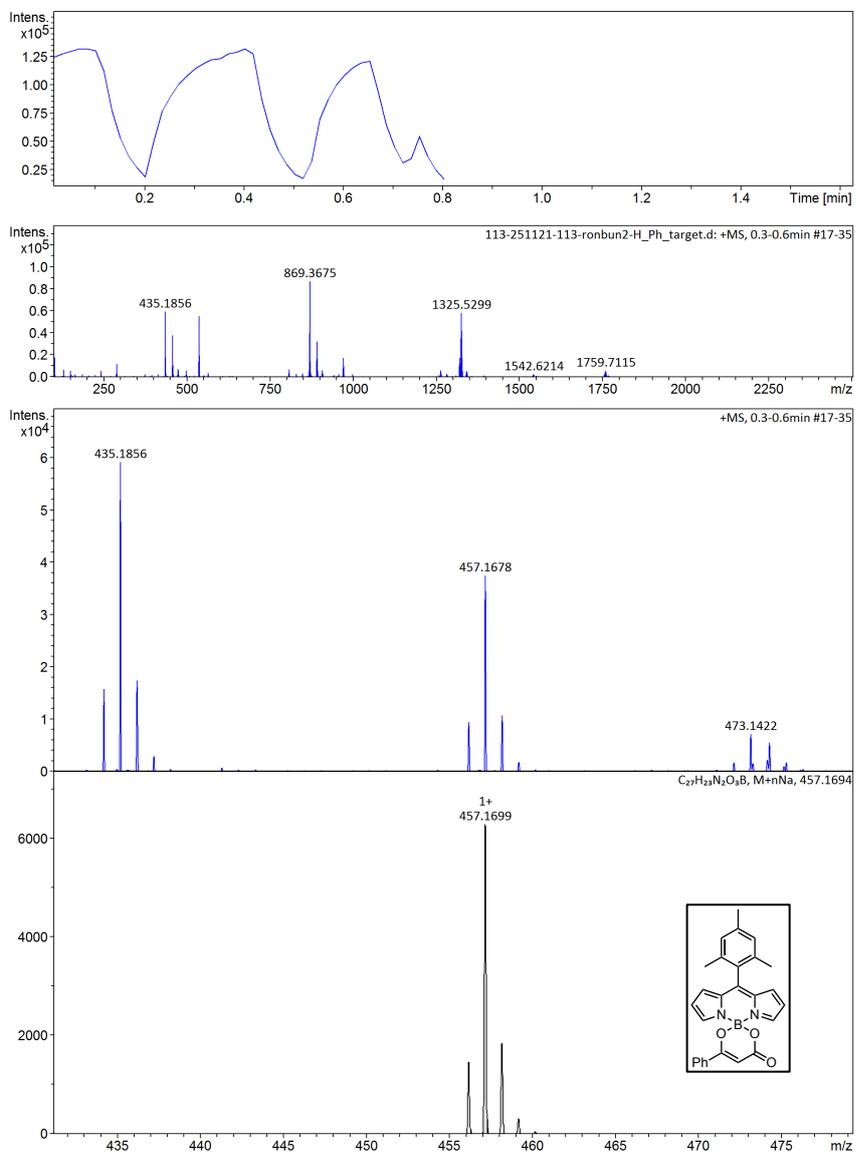
Generic Display Report (all)



Bruker Compass DataAnalysis 4.2 printed: 11/21/2025 4:45:35 PM by: BDAL@DE Page 1 of 1

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

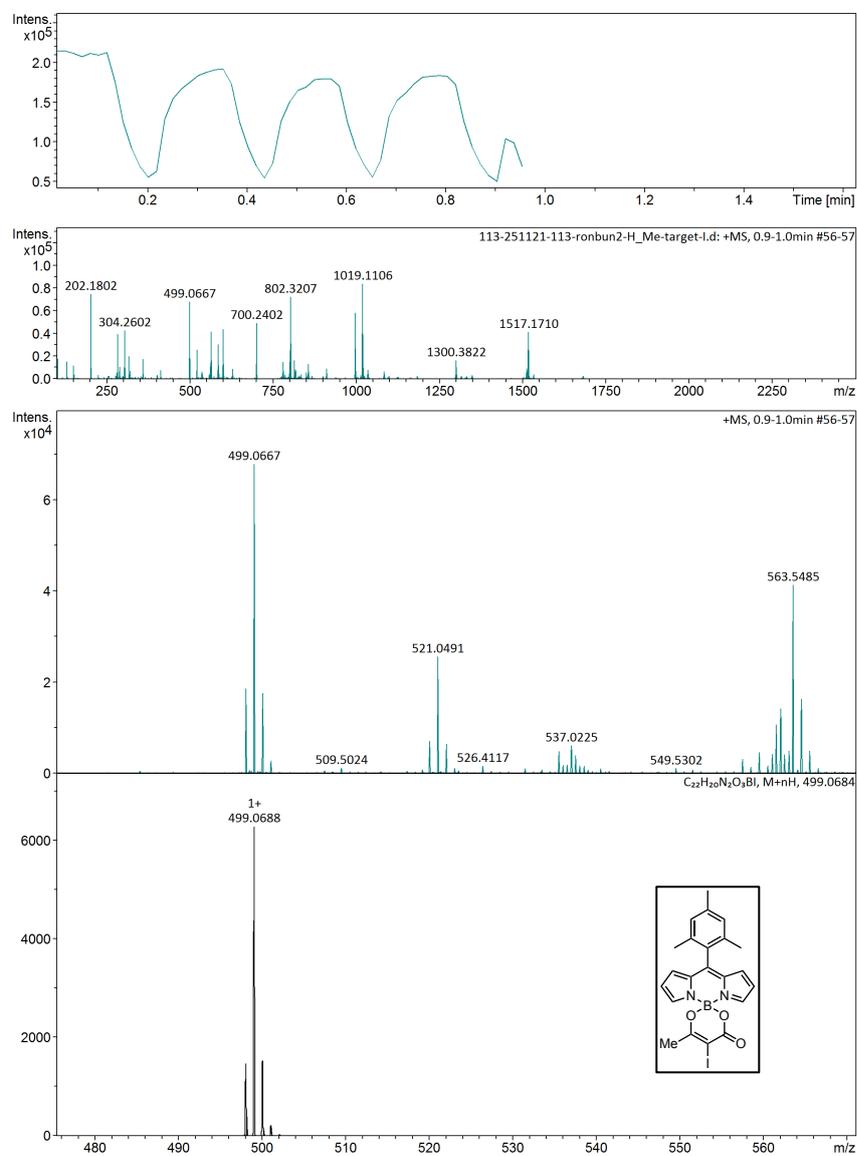
Generic Display Report (all)



Bruker Compass DataAnalysis 4.2 printed: 11/21/2025 4:57:05 PM by: BDAL@DE Page 1 of 1

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

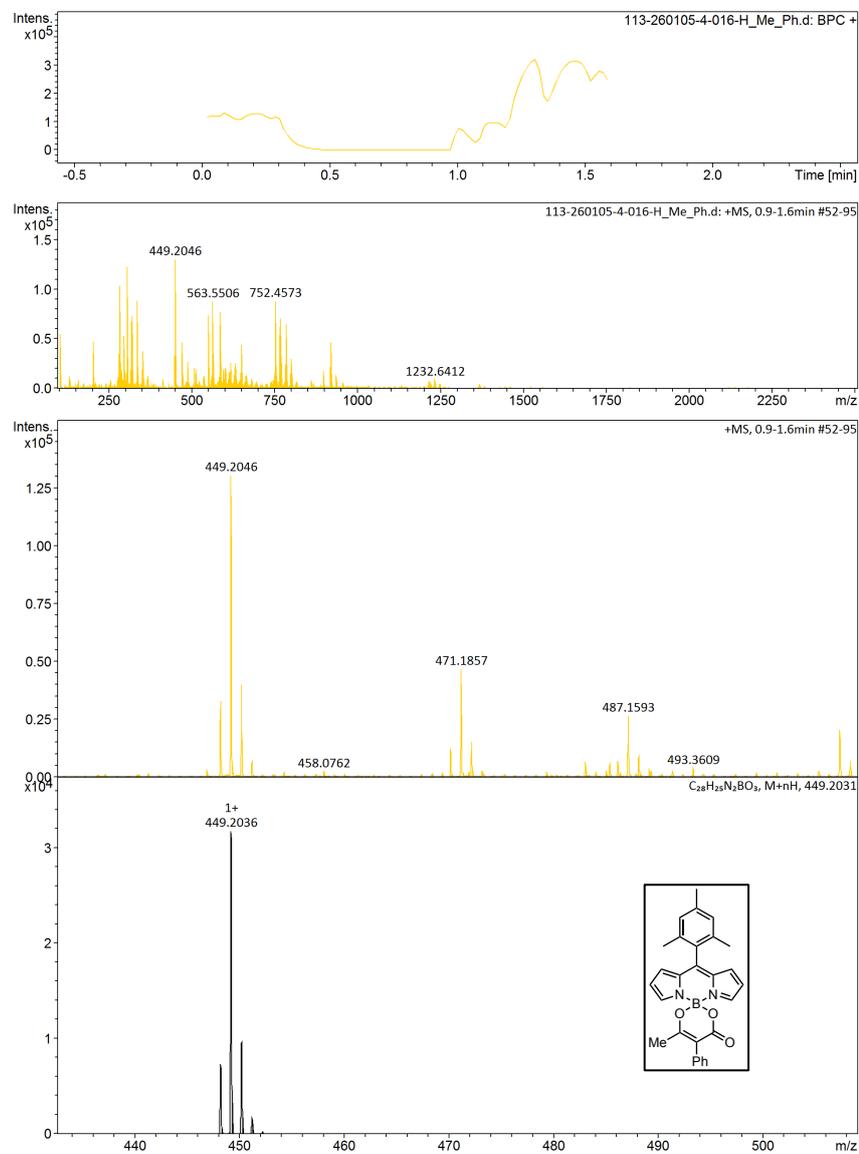
Generic Display Report (all)



Bruker Compass DataAnalysis 4.2 printed: 11/21/2025 5:32:44 PM by: BDAL@DE Page 1 of 1

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

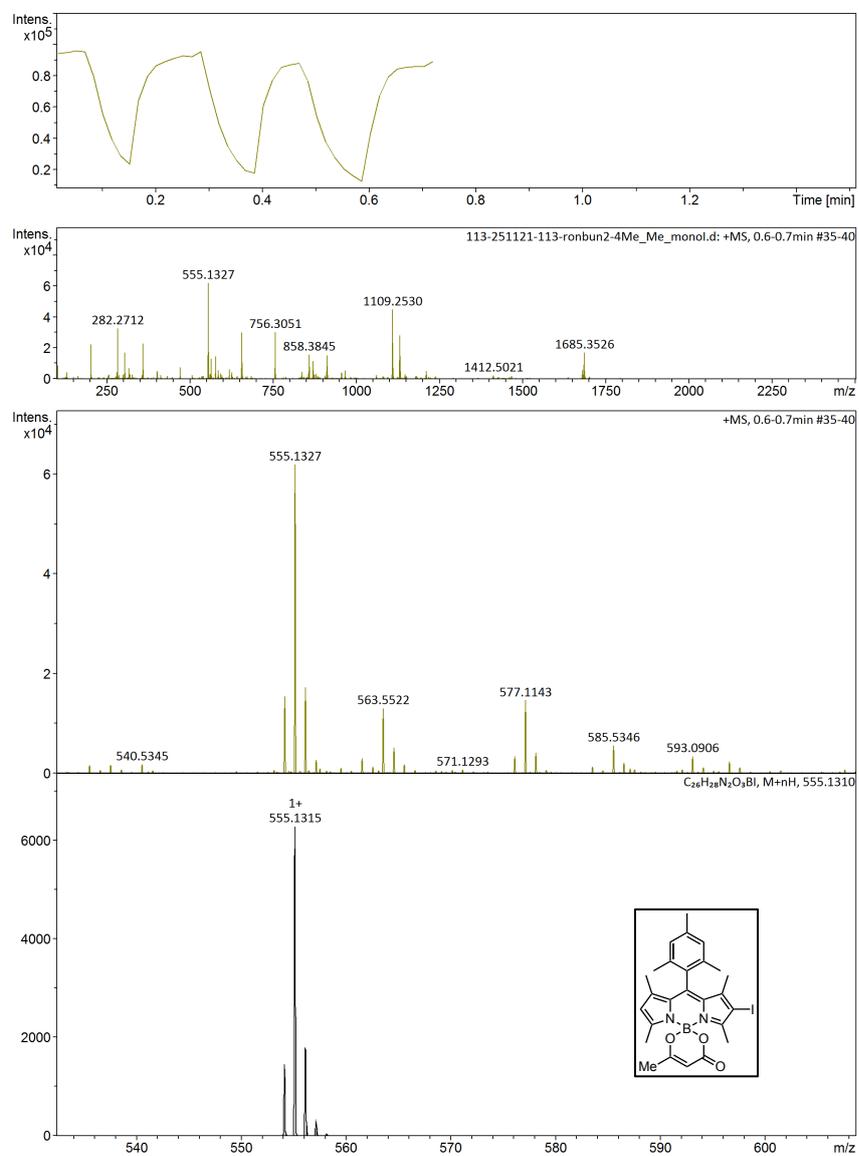
Generic Display Report (all)



Bruker Compass DataAnalysis 4.2 printed: 1/5/2026 11:11:36 AM by: BDAL@DE Page 1 of 1

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

Generic Display Report (all)



Bruker Compass DataAnalysis 4.2 printed: 11/21/2025 6:12:37 PM by: BDAL@DE Page 1 of 1

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

5. Crystal data

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

Compound	3a •CH ₂ Cl ₂	3a •CHCl ₃	3a •HFIP
CCDC number	2523319	2523317	2523318
Formula	CH ₂ Cl ₂ , C ₂₂ H ₂₁ BN ₂ O ₃	CHCl ₃ , C ₂₂ H ₂₁ BN ₂ O ₃	2(C ₃ H ₂ F ₆ O) , 2(C ₂₂ H ₂₁ BN ₂ O ₃)
Formula weight	457.14	491.58	1079.53
Crystal system	monoclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> -1 (No. 2)
Crystal colour	Red	Orange	Orange
Crystal description	Plate	Plate	needle
<i>a</i> [Å]	7.3489(2)	7.3143(1)	7.8099(1)
<i>b</i> [Å]	24.0265(6)	24.6211(4)	17.2188(3)
<i>c</i> [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)
<i>V</i> [Å ³]	2195.58(11)	2326.31(6)	2498.45(7)
<i>Z</i>	4	4	2
<i>d</i> _{calcd} [g cm ⁻³]	1.383	1.404	1.435
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0437	0.0690	0.0614
<i>wR</i> 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 ₂ Cl ₂ /hexane	CHCl ₃	HFIP/H ₂ O

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

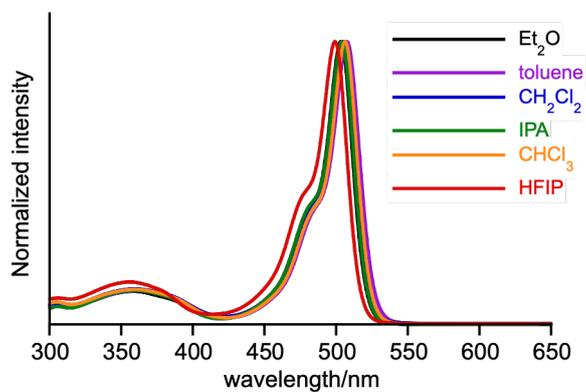


Figure S41. Absorption spectra of **3a** (10^{-5} M solutions).

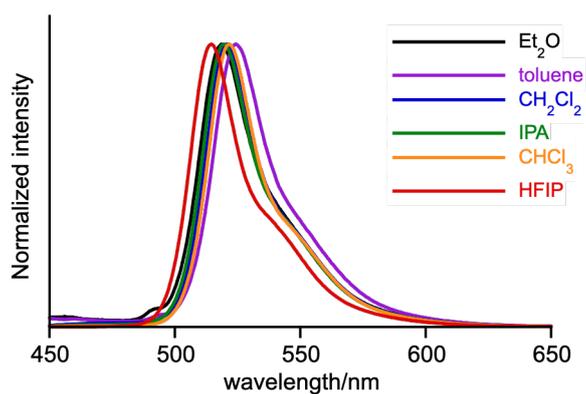
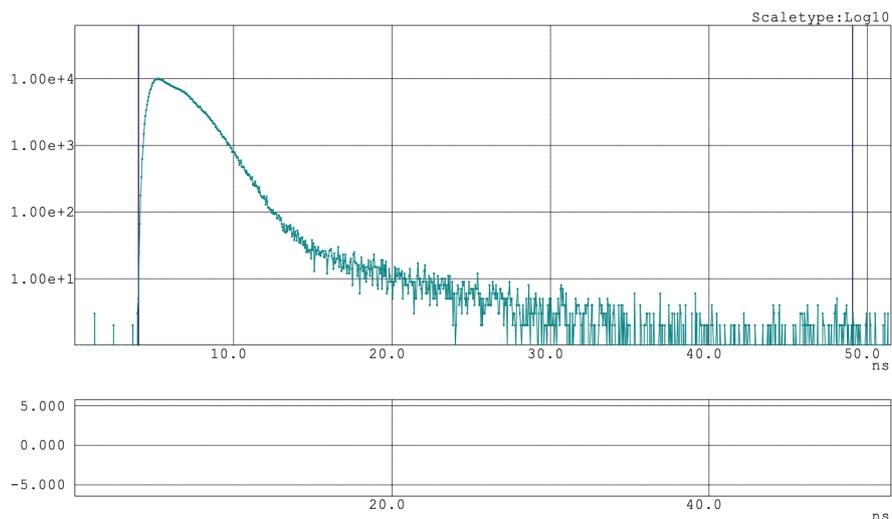


Figure S42. Emission spectra of **3a** (10^{-5} M solutions).

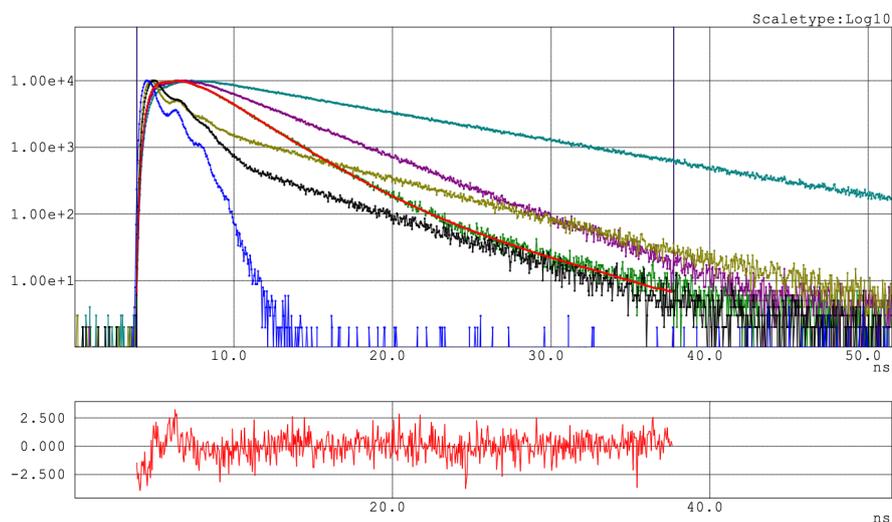


Excitation Wavelength /nm : 470
 Time Range /ns : 51 ns
 Stop Condition : Peak 10000
 Frequency : 5 MHz

Lifetime

Name	EML	CHI	Meas. Time	<χ>	Tau1	Tau2	Tau3	Tau4	Tau5	A1	A2	A3	A4	A5	Background
H.Mu-target	SIS	1.21872	230.5	1.14907	1.01732	0.1038				930.04	2.24002				-2

Figure S43. Time-correlated single photon counting (TCSPC) data of **3a** in CH₂Cl₂.



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

Lifetime

Name	EML	CHI	Meas. Time	<χ>	Tau1	Tau2	Tau3	Tau4	Tau5	A1	A2	A3	A4	A5	Background
IPA	SIS	1.16588	227.1	3.02439	2.68938	6.62897				578.343	21.007				0
HFIP	SIS	1.11899	130.1	10.3807	0.825076	10.4774				60.8275	380.876				3
DMF	SIS	1.11993	204.5	4.59861	0.121666	4.58741				241.706	482.576				3
EtOH	SIS	1.19208	102.9	3.81912	0.188141	7.02037				330.45	77.8478				-1
toluene	SIS	1.34214	764.4	1.70023	0.451476	5.81853				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	-3.875931	-1.219755	-0.116704
C	0.788643	0.123760	-2.532625	C	-3.875369	1.217948	0.124262
C	-0.347207	0.168926	-3.370138	C	-5.274399	-1.196127	-0.108497
C	-1.465510	0.112818	-2.543009	C	-5.273722	1.194280	0.123942
C	-0.992947	0.033706	-1.208511	C	-5.991199	-0.000692	0.006671
N	0.404117	0.034575	-1.244451	H	-5.814786	-2.135902	-0.192304
H	1.840322	0.141245	-2.780077	H	-5.813634	2.133260	0.219265
H	-2.508226	0.129506	-2.826875	C	-3.131234	-2.527602	-0.240947
C	-0.992266	-0.036287	1.209273	H	-2.531613	-2.559646	-1.156897
C	-1.464201	-0.116030	2.543987	H	-2.440150	-2.674142	0.595872
N	0.404833	-0.037157	1.244531	H	-3.826592	-3.370170	-0.260589
C	-0.345511	-0.172478	3.370516	C	-3.129996	2.524864	0.254156
H	-2.506793	-0.133002	2.828349	H	-2.532752	2.554292	1.171763
C	0.789967	-0.126810	2.532465	H	-2.436608	2.672803	-0.580482
C	-1.691963	-0.001158	0.000606	H	-3.824733	3.367943	0.273864
H	-0.328839	0.235471	-4.448322	C	-7.500381	0.002986	-0.022824
H	-0.326608	-0.239506	4.448660	H	-7.871212	0.118932	-1.048764
B	1.331841	-0.000419	-0.000201	H	-7.909030	-0.932937	0.369442
O	2.126550	-1.235769	0.078736	H	-7.908659	0.828415	0.567918
C	4.479926	-3.709029	0.023230	O	2.124081	1.236461	-0.079688
C	3.185614	-1.498534	-0.684456	C	3.182494	1.501516	0.683650
C	3.866574	-2.708379	-0.276398	C	3.861217	2.712503	0.275316
O	3.558868	-0.822942	-1.632389	O	3.556887	0.826899	1.631808
C	-3.181868	-0.000859	0.000969	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
H 4.539802 5.690178 -0.773509
H 5.759169 5.320786 0.464723
H 5.939573 4.684360 -1.179150
H 1.841751 -0.143977 2.779458

3a

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
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C 0.789967 -0.126810 2.532465
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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
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O 3.558868 -0.822942 -1.632389

C -3.181868 -0.000859 0.000969
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C -5.274399 -1.196127 -0.108497
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C -5.991199 -0.000692 0.006671
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C -3.131234 -2.527602 -0.240947
H -2.531613 -2.559646 -1.156897
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
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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
H 4.539802 5.690178 -0.773509
H 5.759169 5.320786 0.464723
H 5.939573 4.684360 -1.179150

H	1.841751	-0.143977	2.779458	C	-5.272000	-0.007219	0.202437
				H	-4.956789	-0.015753	2.331209
3c				H	-5.233098	-0.012432	-1.949187
C	1.505879	-2.533520	-0.316703	C	-2.249484	-0.009485	2.545157
C	0.368423	-3.367827	-0.279615	H	-1.596954	-0.888470	2.588688
C	-0.765094	-2.566726	-0.159030	H	-1.594640	0.867583	2.591963
C	-0.290971	-1.217201	-0.130795	H	-2.885277	-0.010274	3.433816
N	1.108006	-1.244180	-0.227550	C	-2.577300	-0.005326	-2.510454
C	-0.292754	1.215742	-0.130624	H	-1.934910	0.872377	-2.641557
C	-0.768867	2.564532	-0.158619	H	-1.934673	-0.883091	-2.640051
N	1.106165	1.244808	-0.227415	H	-3.322762	-0.006054	-3.309220
C	0.363432	3.367369	-0.279012	C	-6.777998	0.023219	0.299474
C	1.502132	2.534792	-0.316344	H	-7.128732	-0.468288	1.211766
C	-0.980562	-0.001268	-0.073521	H	-7.147777	1.055867	0.319858
H	0.388814	-4.447721	-0.339938	H	-7.242756	-0.474011	-0.557063
H	0.382235	4.447309	-0.339106	C	-2.179862	3.064064	-0.087935
B	2.030167	0.000986	-0.103254	H	-2.781556	2.713832	-0.932262
O	2.620199	0.001119	1.255307	H	-2.690342	2.724414	0.818032
O	3.015938	0.001848	-1.164521	H	-2.184633	4.157218	-0.096247
C	3.944416	0.002833	1.433875	C	2.924203	2.965508	-0.442715
C	4.361883	0.003090	-0.986048	H	3.543953	2.558619	0.361181
C	4.821094	0.003662	0.397702	H	3.355501	2.620334	-1.387593
C	4.343479	0.003528	2.876752	H	2.982694	4.055342	-0.408087
O	5.102670	0.003757	-1.956816	C	-2.175310	-3.068455	-0.088655
H	5.888766	0.004962	0.569447	H	-2.686731	-2.730044	0.817211
H	3.929693	-0.878589	3.378080	H	-2.777567	-2.719009	-0.932917
H	5.429260	0.005121	2.988639	H	-2.178370	-4.161601	-0.097387
H	3.927106	0.884551	3.377863	C	2.928670	-2.961890	-0.442980
C	-2.468225	-0.002080	0.021308	H	3.359501	-2.615962	-1.387798
C	-3.081903	-0.005677	1.285967	H	3.547620	-2.553915	0.360992
C	-3.239536	-0.003799	-1.154131	H	2.989043	-4.051621	-0.408365
C	-4.478460	-0.009344	1.354657				
C	-4.633136	-0.007491	-1.042265				

3a•HFIP

O 1.232038 1.643727 0.391400
O -0.177802 3.537951 -0.241547
O 3.421685 1.834668 0.367523
N -1.047251 1.807201 1.241461
N -0.678442 1.291797 -1.142680
C -1.792428 0.452528 -1.105031
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C -3.661116 -0.695884 0.062102
C -2.525675 0.279121 0.070902
C -4.982292 -0.240151 -0.079393
C -3.377852 -2.067705 0.145031
C -1.936762 1.790038 3.309181
H -2.070130 1.986355 4.228536
C -6.013009 -1.186938 -0.117083
H -6.911811 -0.888676 -0.197205
C -0.910949 2.279310 2.491277
H -0.218230 2.862371 2.778320
C -2.717766 0.968082 2.523820
H -3.489803 0.491642 2.805755
C -4.446891 -2.970730 0.089193
H -4.267951 -3.901739 0.141471
C -5.760664 -2.544506 -0.040621
C 0.940511 4.190694 -0.605716
C -0.182704 1.241619 -2.398288
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C 2.324877 2.337740 0.099431
C -1.962429 -0.105797 -2.382218
H -2.644468 -0.711147 -2.644497
C 2.155789 3.635891 -0.491408
H 2.916512 4.109206 -0.806087
C -1.978119 -2.589776 0.304073

H -1.391809 -2.156384 -0.351329
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H -6.249933 1.335300 -0.420426
H -4.771778 1.589893 -0.978871
C 0.683110 5.573017 -1.089331
H 0.012032 5.549915 -1.804539
H 1.514181 5.959517 -1.434871
H 0.351424 6.122078 -0.348476
C -6.885145 -3.551751 -0.071293
H -7.744265 -3.081609 -0.090955
H -6.840040 -4.116429 0.728644
H -6.800456 -4.111920 -0.871267
B -0.113730 2.108814 0.052073
O 3.646962 -0.615065 1.339951
H 3.453296 0.195045 1.227527
F 3.317178 -2.779816 -1.454438
F 5.873457 -2.239677 -0.880895
F 6.211793 -0.628063 0.494840
C 4.016681 -1.174734 0.123841
H 3.991073 -0.454296 -0.569346
F 2.942168 -3.190356 0.590829
F 5.555957 -2.562073 1.202754
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 Electrogenenerated 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.