# Electronic supplementary information

# Zig-zag-fused π-extended BODIPYs via gold-catalysed cycloisomerisation

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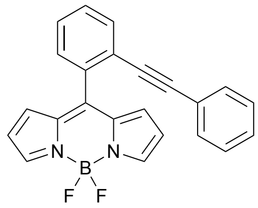
## 1. Instrumentation and materials

$^{1}H$ NMR (500 MHz), $^{13}C$ NMR (126 MHz) and $^{11}B$ NMR (160 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer. $^{19}F$ NMR (376 MHz) spectra were recorded on a Bruker AVANCE NEO spectrometer. Chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ ($\delta$ = 7.26 ppm) or acetone-$d_6$ ($\delta$ = 2.05 ppm) for $^{1}H$ NMR, $CDCl_3$ ($\delta$ = 77.16 ppm) or acetone-$d_6$ ($\delta$ = 29.84 ppm) for $^{13}C$ NMR and $C_6F_6$ ($\delta$ = 162.9 ppm) for $^{19}F$ NMR. UV/vis/NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V 670 spectrometer. High-resolution atmospheric pressure chemical ionization time-of-flight (APCI-TOF) mass spectra were taken on a Bruker micrOTOF instrument using a positive ionization mode. X-ray data were obtained using a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics and a Rigaku CCD diffractometer (HyPix-6000 with PhotonJet-R, DW) with XtaLAB Synergy-R, DW.

Copper(I) 2-thiophenecarboxylate (CuTC),[1] 8-thiomethylBODIPY,[2] 3-bromo-2-(phenylethynyl)thiophene,[3] 3-bromo-4-(phenylethynyl)thiophene,[4] and 8-(2-iodophenyl)BODIPY[5] were prepared according to the literature. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

## 2. Experimental procedures and compound data

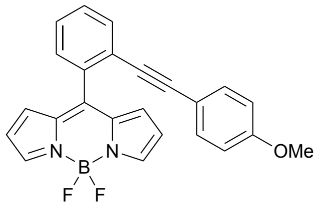
**4,4-Difluoro-8-(2-(phenylethynyl)phenyl)-4-bora-3a,4a-diaza-*s*-indacene (1a)**




In a Schlenk tube, 8-(2-iodophenyl)BODIPY (100 mg, 0.25 mmol), $PdCl_2(PPh_3)_2$ (3.5 mg, 5 μmol), phenylacetylene (70 μL, 0.64 mmol), $Et_3N$ (70 μL, 0.50 mmol) and THF (0.8 mL) were added under $N_2$. The mixture was stirred for 5 min, and CuI (5.2 mg, 27 μmol) was added. After stirring at room temperature for 12 h, the mixture was filtered through Celite® with $CH_2Cl_2$. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/$CH_2Cl_2$ (v/v = 1/1) to afford **1a** as an orange solid (89.4 mg, 96%).

$^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 7.95 (br, 2H), 7.69 (br d, $J$ = 8.1 Hz, 1H), 7.55–7.52 (m, 1H), 7.49–7.45 (m, 2H), 7.25–7.20 (m, 3H), 7.15–7.12 (m, 2H), 6.88 (d, $J$ = 4.2 Hz, 2H), 6.50 (d, $J$ = 4.2 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 145.8, 144.6, 135.9, 135.6, 132.5, 131.7, 130.3, 130.0, 128.7, 128.4, 127.9, 123.8, 122.5, 118.6, 95.4, 87.3 ppm (a pair of peaks in the aromatic region was overlapped); $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = −145.9 (qd, $J$ = 29.0, 104.2 Hz, 1F), –147.2 (qd, $J$ = 29.0, 104.2 Hz, 1F) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{23}H_{15}{}^{10}BFN_2$ 348.1343; Found 348.1345.

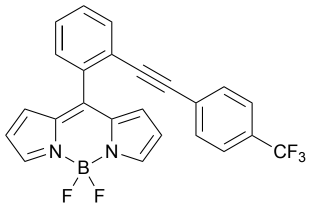
**4,4-Difluoro-8-(2-((4-methoxyphenyl)ethynyl)phenyl)-4-bora-3a,4a-diaza-*s*-indacene (1b)**




In a Schlenk tube, 8-(2-iodophenyl)BODIPY (100 mg, 0.25 mmol), $PdCl_2(PPh_3)_2$ (3.5 mg, 5 μmol), 1-ethynyl-4-methoxybenzene (54 mg, 0.41 mmol), $Et_3N$ (70 μL, 0.50 mmol) and THF (0.8 mL) were added under $N_2$. The mixture was stirred for 5 min, and CuI (4.8 mg, 25 μmol) was added. After stirring at room temperature for 20 h, the mixture was filtered through Celite® with $CH_2Cl_2$. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/$CH_2Cl_2$ (v/v = 1/1) to afford **1b** as an orange solid (91.0 mg, 90%).

$^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 7.95 (br, 2H), 7.65 (br d, $J$ = 7.7 Hz, 1H), 7.54–7.49 (m, 1H), 7.46–7.42 (m, 2H), 7.07 (d, $J$ = 8.9 Hz, 2H), 6.88 (d, $J$ = 3.9 Hz, 2H), 6.75 (d, $J$ = 8.9 Hz, 2H), 6.50 (d, $J$ = 3.9 Hz, 2H), 3.76 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 160.0, 146.0, 144.5, 135.7, 133.2, 132.2, 131.7, 130.2, 129.9, 127.5, 124.1, 118.6, 114.6, 114.1, 95.7, 86.2, 55.4 ppm (a pair of peaks in the aromatic region was overlapped); $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = −145.6 (qd, $J$ = 29.1, 104.8 Hz, 1F), –147.4 (qd, $J$ = 29.1, 104.8 Hz, 1F) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{24}H_{17}{}^{10}BFN_2O$ 348.1449; Found 348.1441.

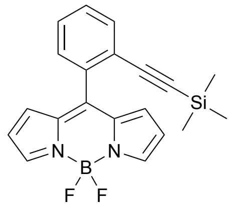
**4,4-Difluoro-8-(2-((4-trifluoromethylphenyl)ethynyl)phenyl)-4-bora-3a,4a-diaza-*s*-indacene (1c)**




In a Schlenk tube, 8-(2-iodophenyl)BODIPY (100 mg, 0.25 mmol), $PdCl_2(PPh_3)_2$ (3.6 mg, 5 μmol), 1-ethynyl-4-(trifluoromethyl)benzene (70 μL, 0.49 mmol), $Et_3N$ (70 μL, 0.50 mmol) and THF (0.8 mL) were added under $N_2$. The mixture was stirred for 5 min, and CuI (5.1 mg, 27 μmol) was added. After stirring at room temperature for 20 h, the mixture was filtered through Celite® with $CH_2Cl_2$. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/$CH_2Cl_2$ (v/v = 1/1) to afford **1c** as an orange solid (59.1 mg, 54%).

$^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 7.96 (br, 2H), 7.71 (br d, $J$ = 7.6 Hz, 1H), 7.57 (ddd, $J$ = 1.5, 7.5, 7.5 Hz, 1H), 7.52 (ddd, $J$ = 1.5, 7.5, 7.5 Hz, 1H), 7.49–7.48 (m, 3H), 7.23 (d, $J$ = 7.8 Hz, 2H), 6.86 (d, $J$ = 4.2 Hz, 2H), 6.51 (d, $J$ = 4.1 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 145.4, 144.8, 136.3, 135.6, 132.6, 131.8, 131.6, 130.3 (q, $J$ = 32.7 Hz), 130.3, 130.1, 128.5, 126.3, 125.4 (q, $J$ = 3.8 Hz), 124.0 (q, $J$ = 272.1 Hz), 123.1, 118.8 (q, $J$ = 2.6 Hz), 93.9, 89.4 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –64.1 (s, 3F), –144.9 (qd, $J$ = 29.0, 103.2 Hz, 1F), –148.1 (qd, $J$ = 29.0, 103.2 Hz, 1F) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{24}H_{14}{}^{10}BF_4N_2$ 416.1217; Found 416.1198.

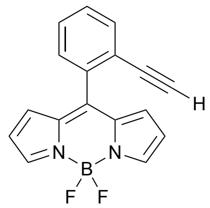
**4,4-Difluoro-8-(2-(trimethylsilylethynyl)phenyl)-4-bora-3a,4a-diaza-*s*-indacene (S1)**



In a Schlenk tube, 8-(2-iodophenyl)BODIPY (256 mg, 0.65 mmol), $PdCl_2(PPh_3)_2$ (23 mg, 33 µmol), trimethylsilylacetylene (0.22 mL, 1.6 mmol), $Et_3N$ (0.26 mL, 1.9 mmol) and THF (2 mL) were added under $N_2$. The mixture was stirred for 5 min, and CuI (12.4 mg, 65 µmol) was added. After stirring at room temperature for 30 h, the mixture was filtered through Celite® with $CH_2Cl_2$. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/$CH_2Cl_2$ (v/v = 1/1) to provide **S1** as a red solid (226 mg, 96%).

$^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 7.92 (br, 2H), 7.61 (br d, $J$ = 7.7 Hz, 1H), 7.50–7.43 (m, 2H), 7.41–7.40 (m, 1H), 6.80 (d, $J$ = 4.1 Hz, 2H), 6.49 (d, $J$ = 4.1 Hz, 2H), –0.02 (s, 9H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 145.7, 144.5, 136.5, 135.6, 132.7, 131.6, 130.1, 129.8, 128.1, 123.6, 118.4, 102.4, 101.1, –0.4 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –146.0– –146.8 (m, 2F) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{20}H_{19}{}^{10}BFN_2Si$ 344.1425; Found 344.1420.

**4,4-Difluoro-8-(2-ethynylphenyl)-4-bora-3a,4a-diaza-*s*-indacene (1d)**

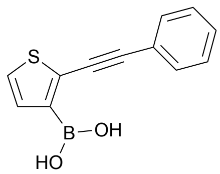


BODIPY **S1** (51 mg, 0.14 mmol) was dissolved in THF (2.7 mL) under $N_2$. TBAF (tetrabutylammonium fluoride) (1 M solution in THF; 0.14 mL, 0.14 mmol) was added and the mixture was stirred for 45 minutes at room temperature. The mixture was quenched with aqueous $NH_4Cl$, extracted with $Et_2O$, dried over $Na_2SO_4$, filtered, and concentrated. The crude product was purified by silica gel short pad using $CH_2Cl_2$ to afford the desired product **1d** as a brown solid (29.0 mg, 71%).

$^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 7.93 (br, 2H), 7.68–7.66 (m,1H), 7.53–7.47 (m, 2H), 7.42–7.40 (m, 1H), 6.79 (d, $J$ = 4.2 Hz, 2H), 6.50 (d, $J$ = 4.2 Hz, 2H), 3.03 (s, 1H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 145.2, 144.8, 136.2, 135.6, 133.6, 131.5, 130.3, 129.9, 128.5, 122.4, 118.7, 82.7, 81.0 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –145.8 (qd, $J$ = 29.1, 105.1 Hz, 1F), –147.1 (qd, $J$ = 29.1, 105.1 Hz, 1F) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{17}H_{11}{}^{10}BFN_2$

272.1030; Found 272.1017.

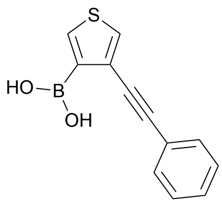
**(2-(Phenylethynyl)thiophen-3-yl)boronic acid (S2)**




In a two-necked round bottom flask, 1.6 M solution of *n*-BuLi (6.5 mL, 1.6 M in hexane, 10 mmol) was added dropwise to a solution of 3-bromo-2-(phenylethynyl)thiophene (1.8 g, 6.9 mmol) in 53 mL of $Et_2O$ under $N_2$ at –78 °C. The mixture was stirred at –40 °C for 1 h and then cooled back to –78 °C. Then, triisopropyl borate (2.4 mL, 10 mmol) was added. After stirring at room temperature for 17 h, the reaction was quenched with 1 M HCl for 30 min and extracted with EtOAc. The combined organic solution was dried over $Na_2SO_4$, filtered and concentrated. The crude product was purified by column chromatography on silica gel using hexane/EtOAc (v/v = 3/1) to afford **S2** as a white solid (915 mg, 58%).

$^1$H NMR (500 MHz, acetone-$d_6$, 298 K): $\delta$ = 7.58–7.55 (m, 2H), 7.50 (d, $J$ = 5.1 Hz, 1H), 7.45–7.42 (m, 3H), 7.39 (d, $J$ = 5.1 Hz, 1H), 7.07 (s, 2H); $^{13}$C NMR (126 MHz, acetone-$d_6$, 298 K): $\delta$ = 133.9, 132.1, 129.7, 129.5, 129.5, 127.8, 123.5, 96.2, 84.4 ppm (pairs of peaks in the aromatic region were overlapped); HRMS (APCI): $[M+H]^+$ Calcd for $C_{12}H_{10}{}^{10}BO_2S$ 228.0525; Found 228.0522.

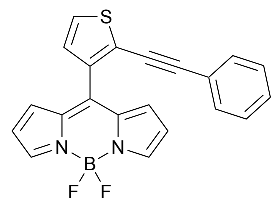
**(4-(Phenylethynyl)thiophen-3-yl)boronic acid (S3)**




In a two-necked round bottom flask, 1.6 M solution of *n*-BuLi (12 mL, 1.6 M in hexane, 19 mmol) was added dropwise to a solution of 3-bromo-4-(phenylethynyl)thiophene (3.3 g, 13 mmol) in 100 mL of $Et_2O$ under $N_2$ at –78 °C. The mixture was stirred at –40 °C for 1 h and then cooled back to –78 °C. Then, triisopropyl borate (4.4 mL, 19 mmol) was added. After stirring at room temperature for 17 h, the reaction was quenched with 1 M HCl for 30 min and extracted with EtOAc. The combined organic solution was dried over $Na_2SO_4$, filtered and concentrated. The crude product was purified by column chromatography on silica gel using hexane/EtOAc (v/v = 3/1) to afford **S3** as a white solid (1.37 g, 48%).

$^{1}$H NMR (500 MHz, acetone-$d_6$, 298 K): $\delta$ = 8.00 (d, $J$ = 3.0 Hz, 1H), 7.77 (d, $J$ = 3.0 Hz, 1H), 7.56–7.54 (m, 2H), 7.45–7.40 (m, 3H), 7.01 (s, 2H); $^{13}$C NMR (126 MHz, acetone-$d_6$, 298 K): $\delta$ = 136.7, 132.2, 131.1, 129.5, 129.5, 126.3, 123.8, 91.1, 86.4 ppm (a pair of peaks in the aromatic region was overlapped); HRMS (APCI): $[M+H]^+$ Calcd for $C_{12}H_{10}{}^{10}BO_2S$ 228.0525; Found 228.0519.

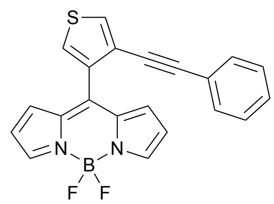
**4,4-Difluoro-8-(2-(phenylethynyl)thiophen-3-yl)-4-bora-3a,4a-diaza-*s*-indacene (1e)**



In a Schlenk tube, **S2** (144 mg, 0.63 mmol), 8-thiomethylBODIPY (50 mg, 0.21 mmol), $Pd_2(dba)_3$•$CHCl_3$ (11 mg, 11 µmol), $PPh_3$ (9.0 mg, 34 µmol), CuTC (123 mg, 0.64 mmol) and chlorobenzene (6 mL) were added under $N_2$. The mixture was stirred at 100 °C for 12 h. It was then cooled to room temperature and filtered through Celite® with $CH_2Cl_2$. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/$CH_2Cl_2$ (v/v = 1/1) to provide **1e** as an orange solid (61.6 mg, 78%).

$^{1}$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 7.93 (br, 2H), 7.43 (d, $J$ = 5.2 Hz, 1H), 7.30–7.23 (m, 5H), 7.21 (d, $J$ = 5.2 Hz, 1H), 7.15 (d, $J$ = 4.0 Hz, 2H), 6.54 (d, $J$ = 4.0 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 144.4, 140.4, 137.2, 134.8, 131.9, 131.5, 130.6, 129.1, 128.5, 127.1, 125.3, 122.1, 118.4, 98.1, 81.0 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –145.5 (qd, $J$ = 28.8, 105.8 Hz, 1F), –147.1 (qd, $J$ = 28.8, 105.8 Hz, 1F) ppm; HRMS (APCI): $[M-F]^+$ Calcd for $C_{21}H_{13}{}^{10}BFN_2S$ 354.0907; Found 354.0893.

**4,4-Difluoro-8-(4-(phenylethynyl)thiophen-3-yl)-4-bora-3a,4a-diaza-*s*-indacene (1f)**



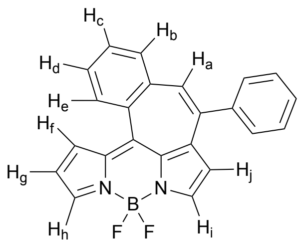
In a Schlenk tube, **S3** (65 mg, 0.29 mmol), 8-thiomethylBODIPY (52 mg, 0.22 mmol) $Pd_2(dba)_3$•$CHCl_3$ (11 mg, 11 µmol), $PPh_3$ (8.8 mg, 34 µmol), CuTC (119 mg, 0.62 mmol) and chlorobenzene (6 mL) were added under $N_2$. The mixture was stirred at 100 °C for 12 h. It was then cooled to room temperature and filtered through Celite® with $CH_2Cl_2$. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/$CH_2Cl_2$ (v/v = 1/1) to afford **1f** as an orange solid (61.3 mg, 76%).

$^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 7.94 (br, 2H), 7.70 (d, $J$ = 3.3 Hz, 1H), 7.59 (d, $J$ = 3.3 Hz, 1H), 7.27–7.22 (m, 3H), 7.19–7.17 (m, 2H), 7.09 (d, $J$ = 4.1 Hz, 2H), 6.54 (d, $J$ = 4.1 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 144.5, 140.2, 135.8, 135.2, 132.0, 131.5, 130.3, 129.4, 128.7, 128.4, 123.6, 122.5, 118.4, 92.9, 83.0 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –145.7 (qd, $J$ = 28.9, 105.5 Hz, 1F), –147.1 (qd, $J$ = 28.9, 105.5 Hz, 1F) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{21}H_{13}{}^{10}BFN_2S$ 354.0907; Found 354.0895.

**General procedure for synthesis of 2a–f**

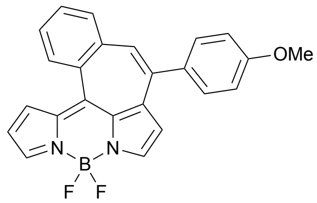
In a Schlenk tube, BODIPYs **1a–f** (0.10 mmol, 1.0 equiv), chloro[tris(2,4-di-*tert*-butylphenyl)phosphite]gold (0.01 mol, 0.10 equiv) $AgPF_6$ (0.01 mmol, 0.10 eq) were dissolved in $CH_2Cl_2$ (5 mL) under $N_2$. The reaction was stirred at room temperature for 1–2 h. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/$CH_2Cl_2$ (v/v = 1/1) to yield **2a–f**.

**9,9-Difluoro-6-phenyl-9*H*-8a,9aλ$^4$-diaza-9λ$^4$-borabenzo[6,7]cyclohepta[1,2,3-*kl*]-*s*-indacene (2a)**



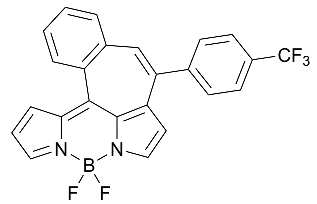

Red solid; $^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 8.84 (br d, $J$ = 8.3 Hz, $H_e$), 8.18 (br, $H_i$), 7.99 (d, $J$ = 8.3 Hz, $H_b$), 7.87 (ddd, $J$ = 1.4, 7.1, 8.3 Hz, $H_c$), 7.82 (br, $H_h$), 7.75 (ddd, $J$ = 1.4, 7.1, 8.3 Hz, $H_d$), 7.64 (s, $H_a$), 7.55–7.49 (m, 5H on Ph group), 7.12 (d, $J$ = 3.9 Hz, $H_f$), 6.73 (d, $J$ = 2.4 Hz, $H_j$), 6.59 (dd, $J$ = 2.4, 3.9 Hz, $H_g$); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 144.3, 142.3, 142.2, 140.8, 140.5, 138.9, 137.3, 135.9, 135.6, 134.3, 134.1, 133.4, 132.0, 130.8, 130.6, 129.3, 128.7, 128.5, 116.2, 114.9 ppm (a pair of peaks in the aromatic region was overlapped); $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –147.2 (br, 2F) ppm; $^{11}$B NMR (160 MHz, $CDCl_3$, 298 K) $\delta$ = 0.63 (t, $J$ = 27.9 Hz) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{23}H_{15}{}^{10}BFN_2$ 348.1343; Found 348.1329.

**9,9-Difluoro-6-(4-methoxyphenyl)-9*H*-8a,9a$\lambda^4$-diaza-9$\lambda^4$-borabenzo[6,7]cyclohepta[1,2,3-*kl*]-*s*-indacene (2b)**



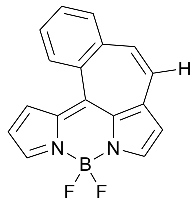
Red solid; $^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 8.83 (br d, $J$ = 8.2 Hz, 1H), 8.18 (d, $J$ = 2.3 Hz, 1H), 7.98 (br d, $J$ = 8.2 Hz, 1H), 7.86 (ddd, $J$ = 1.4, 7.1, 8.2 Hz, 1H), 7.81 (br, 1H), 7.73 (ddd, $J$ = 1.4, 7.1, 8.2 Hz, 1H), 7.64 (s, 1H), 7.48 (d, $J$ = 8.7 Hz, 2H), 7.11 (d, $J$ = 3.9 Hz, 1H), 7.05 (d, $J$ = 8.7 Hz, 2H), 6.77 (d, $J$ = 2.3 Hz, 1H), 6.59 (dd, $J$ = 2.3, 3.9 Hz, 1H), 3.91 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 159.9, 144.2, 142.1, 141.1, 140.5, 139.0, 137.1, 135.9, 135.5, 134.7, 134.3, 134.1, 133.3, 132.0, 130.7, 130.6, 130.4, 128.6, 116.1, 114.9, 114.1, 55.6 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –147.9 (br, 2F) ppm; $^{11}$B NMR (160 MHz, $CDCl_3$, 298 K) $\delta$ = 0.63 (t, $J$ = 28.4 Hz) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{24}H_{17}{}^{10}BFN_2O$ 348.1449; Found 348.1449.

**9,9-Difluoro-6-(4-trifluoromethylphenyl)-9*H*-8a,9a$\lambda^4$-diaza-9$\lambda^4$-borabenzo[6,7]cyclohepta[1,2,3-*kl*]-*s*-indacene (2c)**



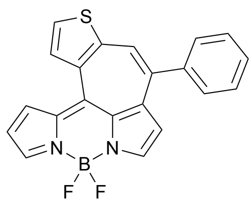
Red solid; $^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 8.82 (br d, $J$ = 8.0 Hz, 1H), 8.17 (br, 1H), 7.98 (br d, $J$ = 8.0 Hz, 1H), 7.90 (ddd, $J$ = 1.3, 7.1, 8.0 Hz, 1H), 7.85 (br, 1H), 7.80–7.77 (m, 3H), 7.67 (d, $J$ = 8.0 Hz, 2H), 7.58 (s, 1H), 7.13 (d, $J$ = 3.9 Hz, 1H), 6.63 (d, $J$ = 2.4 Hz, 1H), 6.61 (dd, $J$ = 2.4, 3.9 Hz, 1H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 145.8, 144.5, 140.5, 140.5, 139.8, 138.6, 138.2, 135.8, 135.7, 134.6, 133.9, 133.5, 132.2, 131.2, 130.9, 130.7 (q, $J$ = 32.8 Hz), 129.7, 129.1, 125.8 (q, $J$ = 3.6 Hz) 124.1 (q, $J$ = 282.8 Hz), 116.6, 114.6 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –63.7 (s, 3F), –147.7 (br, 2F) ppm; $^{11}$B NMR (160 MHz, $CDCl_3$, 298 K) $\delta$ = 0.58 (t, $J$ = 27.9 Hz) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{24}H_{14}{}^{10}BF_4N_2$ 416.1217; Found 416.1204

**9,9-Difluoro-9*H*-8a,9aλ$^4$-diaza-9λ$^4$-borabenzo[6,7]cyclohepta[1,2,3-*kl*]-*s*-indacene (2d)**



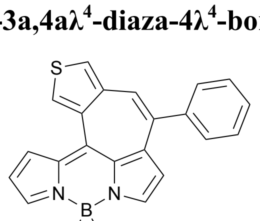

Red solid; $^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 8.84 (br d, $J$ = 8.3 Hz, 1H), 8.22 (br, 1H), 7.99 (br d, $J$ = 8.3 Hz, 1H), 7.87 (ddd, $J$ = 1.4, 7.0, 8.3 Hz, 1H), 7.81 (br, 1H), 7.76 (d, $J$ = 11.0 Hz, 1H), 7.75 (ddd, $J$ = 1.4, 7.0, 8.3 Hz, 1H), 7.62 (d, $J$ = 11.0 Hz, 1H), 7.10 (d, $J$ = 3.8 Hz, 1H), 6.95 (d, $J$ = 2.2 Hz, 1H), 6.58 (dd, $J$ = 2.2, 3.8 Hz, 1H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 144.2, 141.3, 140.7, 139.4, 137.5, 136.0, 135.8, 134.4, 133.0, 132.9, 132.0, 131.4, 130.6, 128.8, 128.2, 116.2, 114.3 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –148.1 (br, 2F) ppm; $^{11}$B NMR (160 MHz, $CDCl_3$, 298 K) $\delta$ = 0.57 (t, $J$ = 27.9 Hz) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{17}H_{11}{}^{10}BFN_2$ 272.1030; Found 272.1018.

**4,4-Difluoro-7-phenyl-9*H*-9-thia-3a,4aλ$^4$-diaza-4λ$^4$-boraazuleno[6,5,4-*ij*]-*s*-indacene (2e)**



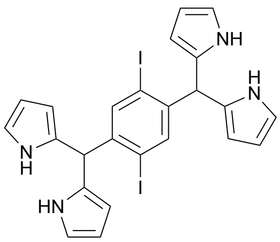

Orange solid; $^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 8.48 (br d, $J$ = 5.7 Hz, 1H), 8.22 (d, $J$ = 2.4 Hz, 1H), 7.97 (s, 1H), 7.83 (d, $J$ = 5.7 Hz, 1H), 7.77 (br, 1H), 7.57–7.51 (m, 5H), 7.42 (d, $J$ = 3.9 Hz, 1H), 6.86 (d, $J$ = 2.4 Hz, 1H), 6.61 (dd, $J$ = 2.4, 3.9 Hz, 1H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 151.7, 143.0, 141.5, 140.3, 138.8, 137.3, 135.8, 135.0, 134.9, 133.0, 131.8, 129.4, 129.2, 128.9, 128.8, 126.2, 125.9, 115.3, 114.3 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –147.2 (q, $J$ = 28.3 Hz, 2F) ppm; $^{11}$B NMR (160 MHz, $CDCl_3$, 298 K) $\delta$ = 0.75 (t, $J$ = 28.3 Hz) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{21}H_{13}{}^{10}BFN_2S$ 354.0907; Found 354.0896.

**4,4-Difluoro-7-phenyl-10*H*-10-thia-3a,4aλ$^4$-diaza-4λ$^4$-boraazuleno[6,5,4-*ij*]-*s*-indacene (2f)**




Purple solid; $^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 8.88 (dd, $J$ = 0.7, 3.7 Hz, 1H), 8.06 (br, 1H), 7.95 (dd, $J$ = 0.7, 3.7 Hz, 1H), 7.84 (br, 1H), 7.49–7.45 (m, 7H), 6.58 (dd, $J$ = 2.3, 4.0 Hz, 1H), 6.55 (d, $J$ = 2.3 Hz, 1H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 142.2, 141.7, 141.2, 140.9, 138.6, 138.0, 137.1, 135.2, 133.8, 133.1, 132.7, 129.3, 128.7, 128.2, 128.0, 127.9, 127.0, 116.3, 116.1 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –148.5 (q, $J$ = 28.2 Hz, 2F) ppm; $^{11}$B NMR (160 MHz, $CDCl_3$, 298 K) $\delta$ = 0.49 (t, $J$ = 28.0 Hz) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{21}H_{13}{}^{10}BFN_2S$ 354.0907; Found 354.0893.

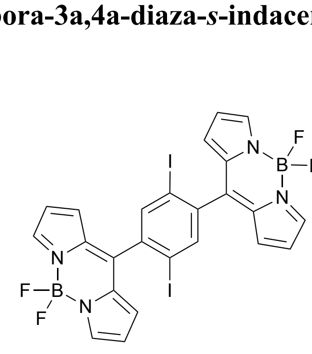
**2,5-Diiodo-1,4-bis(dipyrromethan-5-yl)benzene (S4)**




2,5-Diiodoterephthaladehyde (683 mg, 1.8 mmol) was dissolved in dry pyrrole (14 mL, 200 mmol) under $N_2$. Trifluoroacetic acid (90 µL, 1.2 mmol) was added, and the mixture was stirred for 30 min at room temperature. The reaction mixture was concentrated under reduced pressure to remove excess pyrrole. The crude product was purified by column chromatography on silica gel using hexane/$CH_2Cl_2$ (v/v = 2/3) to provide **S4** as a white solid (767 mg, 70%).

$^1$H NMR (500 MHz, acetone-$d_6$, 298 K): $\delta$ = 9.88 (br, 4H), 7.51 (s, 2H), 6.72–6.71 (m, 4H), 6.00–5.98 (m, 4H), 5.67–5.65 (m, 4H), 5.60 (s, 2H); $^{13}$C NMR (126 MHz, acetone-$d_6$, 298 K): $\delta$ = 146.7, 140.7, 132.3, 118.4, 108.3, 101.6, 48.7 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{24}H_{21}I_2N_4$ 618.9850; Found 618.9840.

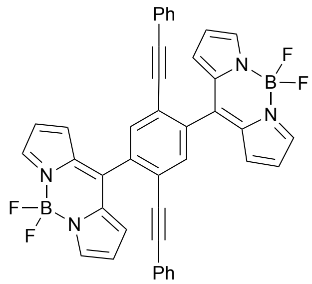
**4,4-Difluoro-8-(4-(4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacen-8-yl)-2,5-diiodophenyl)-4-bora-3a,4a-diaza-*s*-indacene (S5)**




Dipyrromethane **S4** (62 mg, 0.10 mmol) was dissolved in $CH_2Cl_2$ (10 mL) under $N_2$. Chloranil (63 mg, 0.26 mmol) was added, and the mixture was stirred for 18 h at room temperature. The reaction mixture was filtered through alumina with $CH_2Cl_2$, and the solvent was evaporated. To a solution of the dipyrrin intermediate in $CH_2Cl_2$ (10 mL), *N*,*N*-diisopropylethylamine (0.26 mL, 1.5 mmol) was added under $N_2$, and the mixture was stirred at room temperature for 20 min. $BF_3$•$OEt_2$ (0.26 mL, 2.1 mmol) was added dropwise, and stirring was continued for 6 h. The reaction was quenched by $NaHCO_3$ and extracted with $CH_2Cl_2$. The combined organic solution was dried over $Na_2SO_4$, filtered and concentrated. The crude product was purified by column chromatography on silica gel using hexane/ $CH_2Cl_2$ (v/v = 1/3) to provide **S5** as a red solid (16.7 mg, 23%).

$^1$H NMR (500 MHz, acetone-$d_6$, 298 K): $\delta$ = 8.25 (s, 2H), 8.10 (br, 4H), 711 (d, $J$ = 4.3 Hz, 4H), 6.68 (d, $J$ = 4.3 Hz, 4H); $^{13}$C NMR (126 MHz, acetone-$d_6$, 298 K): $\delta$ = 146.7, 146.3, 142.1, 140.9, 135.9, 132.4, 120.2, 97.6 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –146.3– –146.6 (m, 4F) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{24}H_{14}{}^{10}B_2F_3I_2N_4$ 688.9513; Found 688.9490.

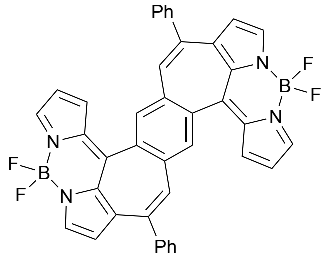
**4,4-Difluoro-8-(4-(4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacen-8-yl)-2,5-bis(phenylethynyl)phenyl)-4-bora-3a,4a-diaza-*s*-indacene (3)**



In a Schlenk tube, **S5** (85 mg, 0.12 mmol), $PdCl_2(PPh_3)_2$ (11 mg, 15 µmol), phenylacetylene (70 µL, 0.64 mmol), $Et_3N$ (0.20 mL, 1.4 mmol) and THF (5 mL) were added under $N_2$ at room temperature. The mixture was stirred for 5 min, and CuI (7.8 mg, 41 µmol) was added. After stirring at room temperature for 24 h, the mixture was filtered through Celite® with $CH_2Cl_2$. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/$CH_2Cl_2$ (v/v = 1/3) to provide **3** as an orange solid (67.7 mg, 86%).

$^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 8.02 (br, 4H), 7.79 (s, 2H), 7.29–7.23 (m, 6H), 7.16–7.14 (m, 4H), 7.00 (d, $J$ = 4.0 Hz, 4H), 6.59 (d, $J$ = 4.0 Hz, 4H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 145.4, 143.4, 137.2, 135.3, 133.7, 131.8, 131.5, 129.4, 128.6, 123.3, 121.8, 119.2, 98.5, 86.2 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –145.5 (qd, $J$ = 28.7, 103.3 Hz, 2F), –147.4 (qd, $J$ = 28.7, 103.3 Hz, 2F) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{40}H_{24}O^{10}B_2F_3N_4$ 637.2206; Found 637.2176.

**BODIPY dimer 4**



In a Schlenk tube, **3** (32.9 mg, 0.05 mmol), chloro[tris(2,4-di-*tert*-butylphenyl)phosphite]gold (8.8 mg, 10 μmol) and $AgPF_6$ (2.5 mg, 10 μmol) were dissolved in $CH_2Cl_2$ (2.5 mL) under $N_2$. The reaction was stirred at room temperature for 1 h. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/$CH_2Cl_2$ (v/v = 1/1) to yield **4** as a purple solid (32.4 mg, 98%).

$^1$H NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ = 9.29 (s, 2H), 8.23 (d, $J$ = 2.4 Hz, 2H), 7.93 (br, 2H), 7.71 (s, 2H), 7.56–7.50 (m, 10H), 7.17 (d, $J$ = 4.0 Hz, 2H), 6.78 (d, $J$ = 2.4 Hz, 2H), 6.66 (dd, $J$ = 2.4, 4.0 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K): $\delta$ = 143.0, 142.7, 142.1, 141.8, 141.2, 140.8, 139.6, 136.8, 135.7, 135.2, 133.1, 132.5, 131.4, 129.3, 128.9, 117.7, 116.5 ppm (a pair of peaks in the aromatic region was overlapped); $^{19}$F NMR (376 MHz, $CDCl_3$, 298 K) $\delta$ = –146.9 ppm (br, 4F); $^{11}$B NMR (160 MHz, $CDCl_3$, 298 K) $\delta$ = 0.58 (t, $J$ = 28.0 Hz) ppm; HRMS (APCI): $[M–F]^+$ Calcd for $C_{40}H_{24}O^{10}B_2F_3N_4$ 637.2206; Found 637.2175.

## 3. NMR spectra

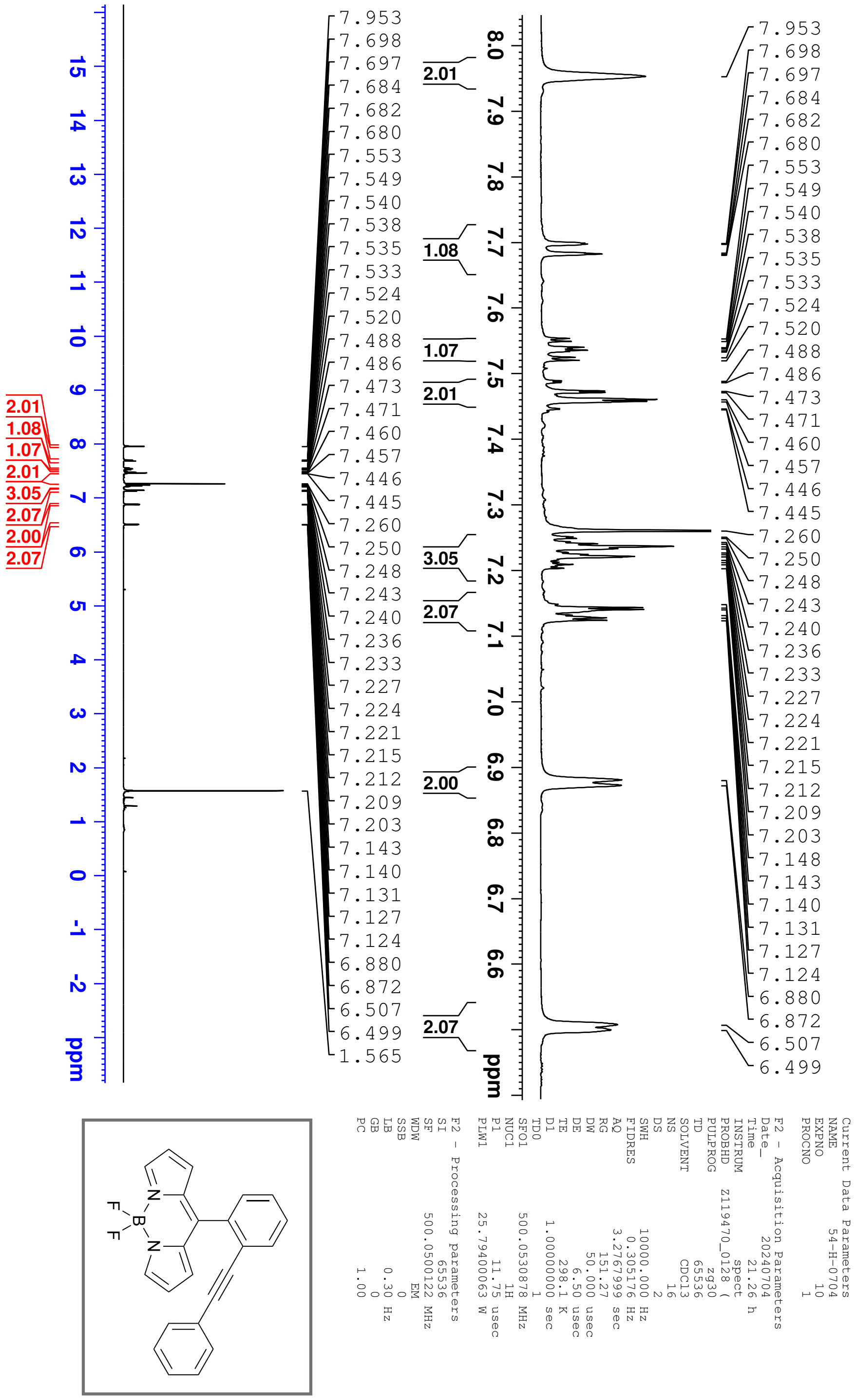


**Figure S1.** $^{1}H$ NMR spectrum of **1a** in $CDCl_3$ at 25 °C.

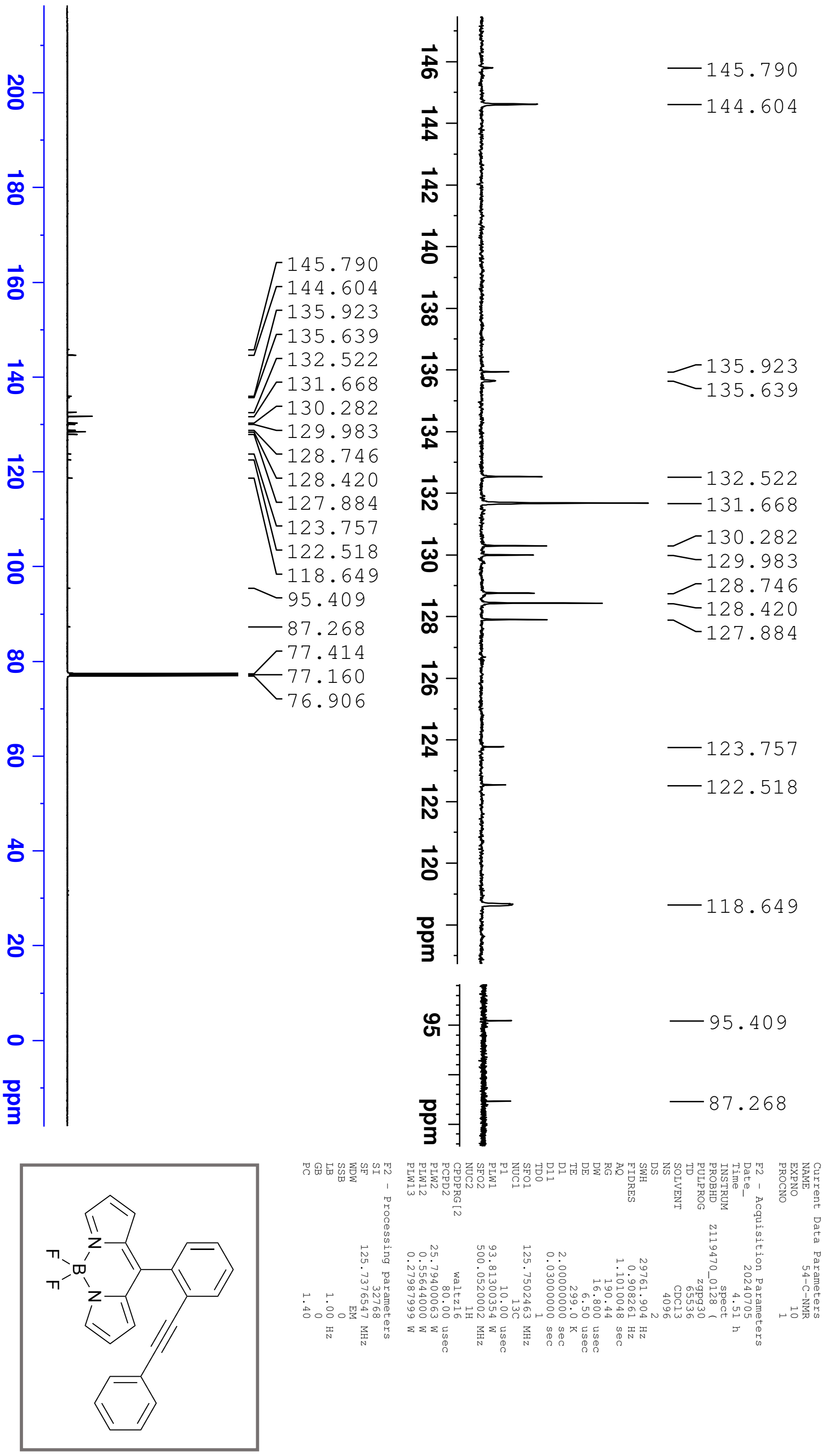



**Figure S2.** $^{13}$C NMR spectrum of **1a** in $CDCl_3$ at 25 °C.

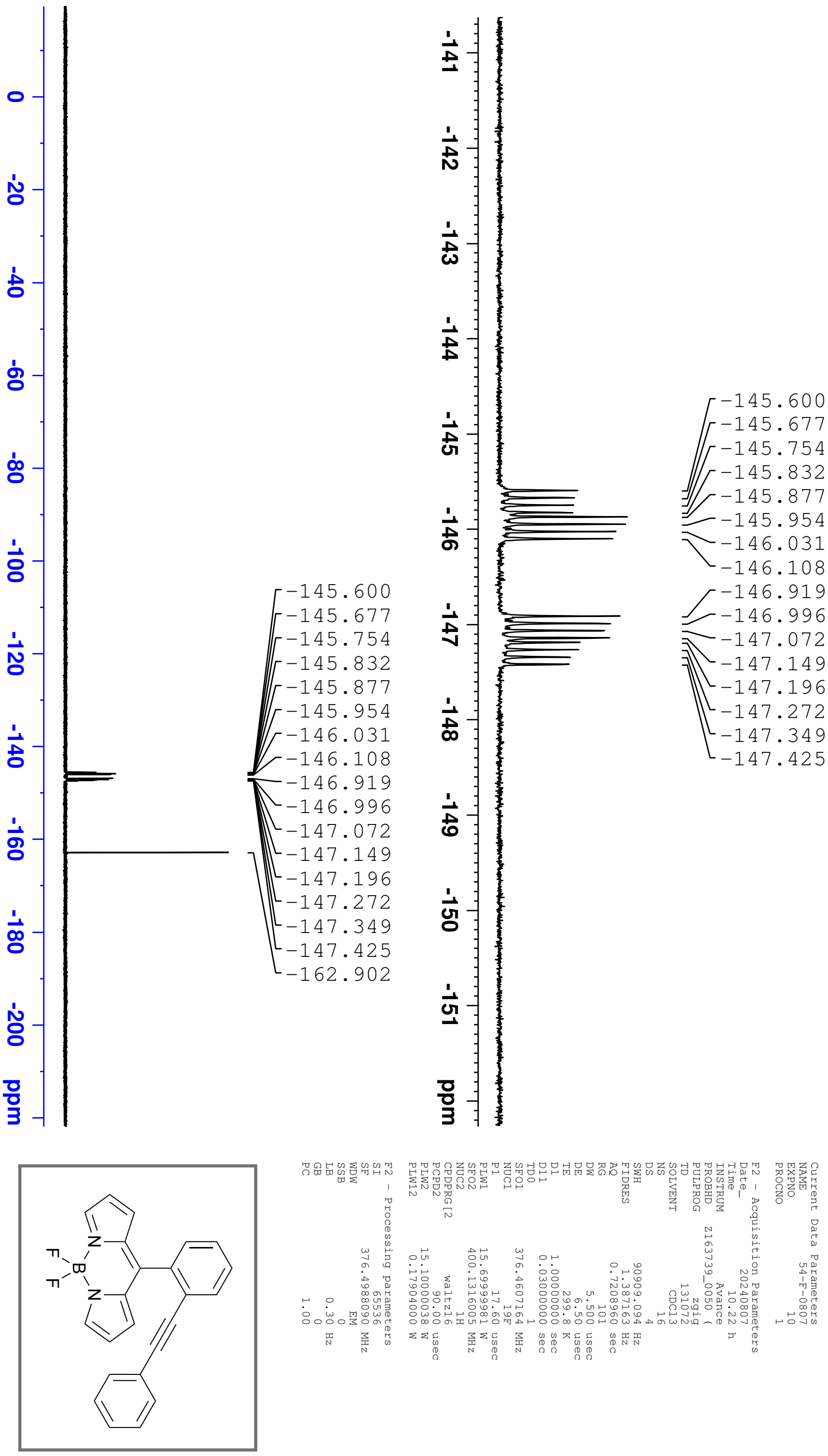



**Figure S3.** ${}^{19}$F NMR spectrum of **1a** in $CDCl_3$ at 25 °C.

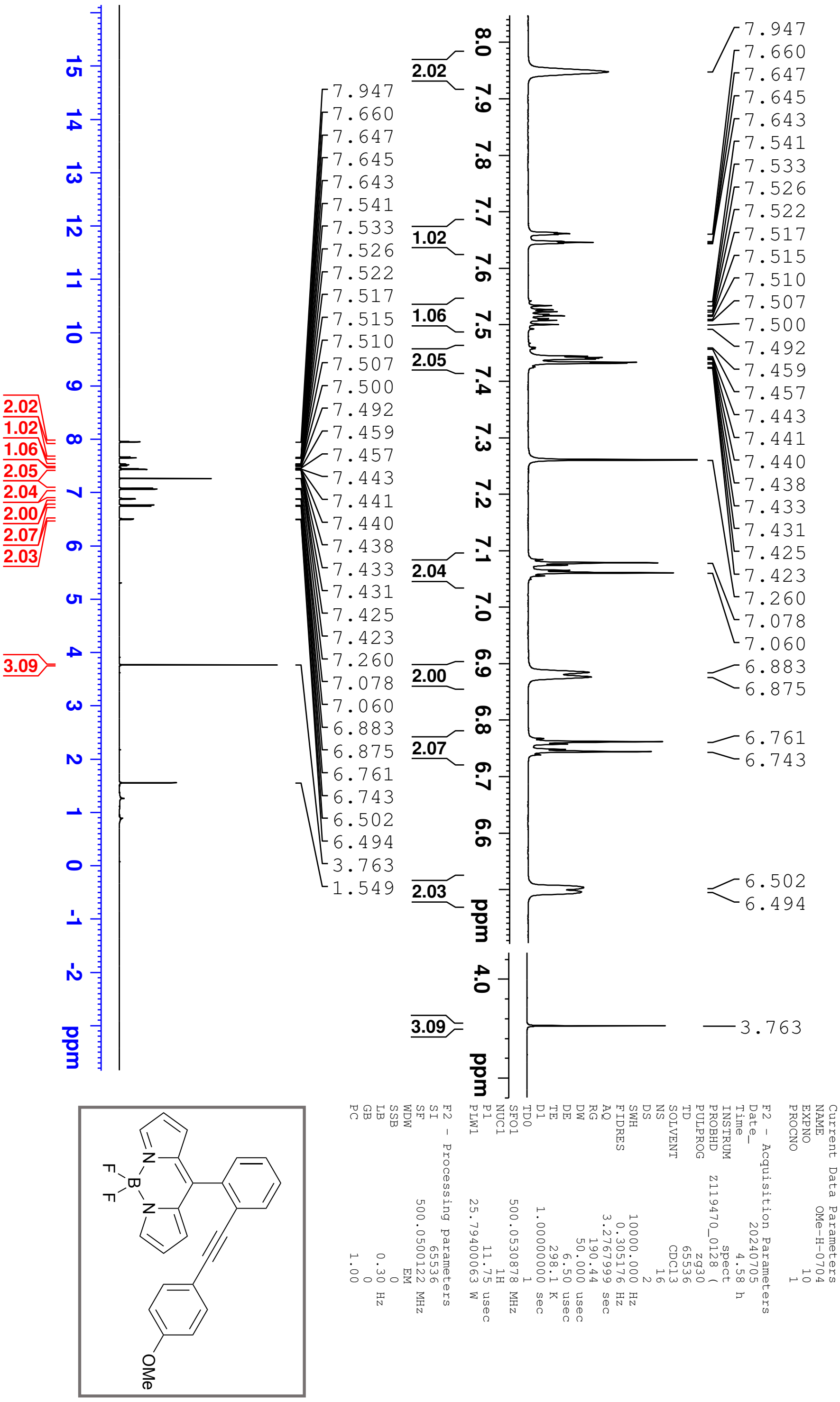


**Figure S4.** [1]H NMR spectrum of **1b** in $CDCl_3$ at 25 °C.

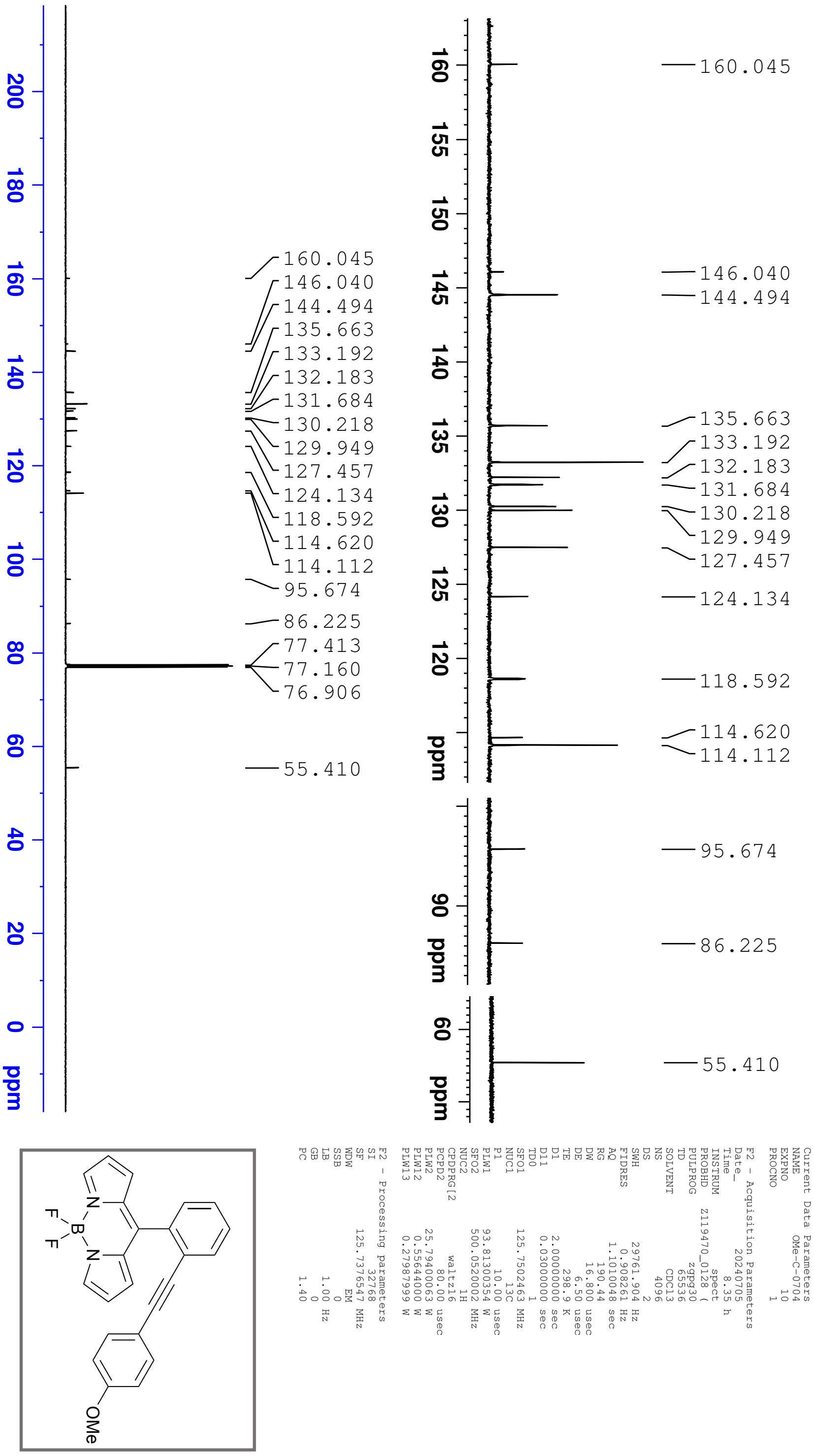



**Figure S5.** $^{13}$C NMR spectrum of **1b** in $CDCl_3$ at 25 °C.

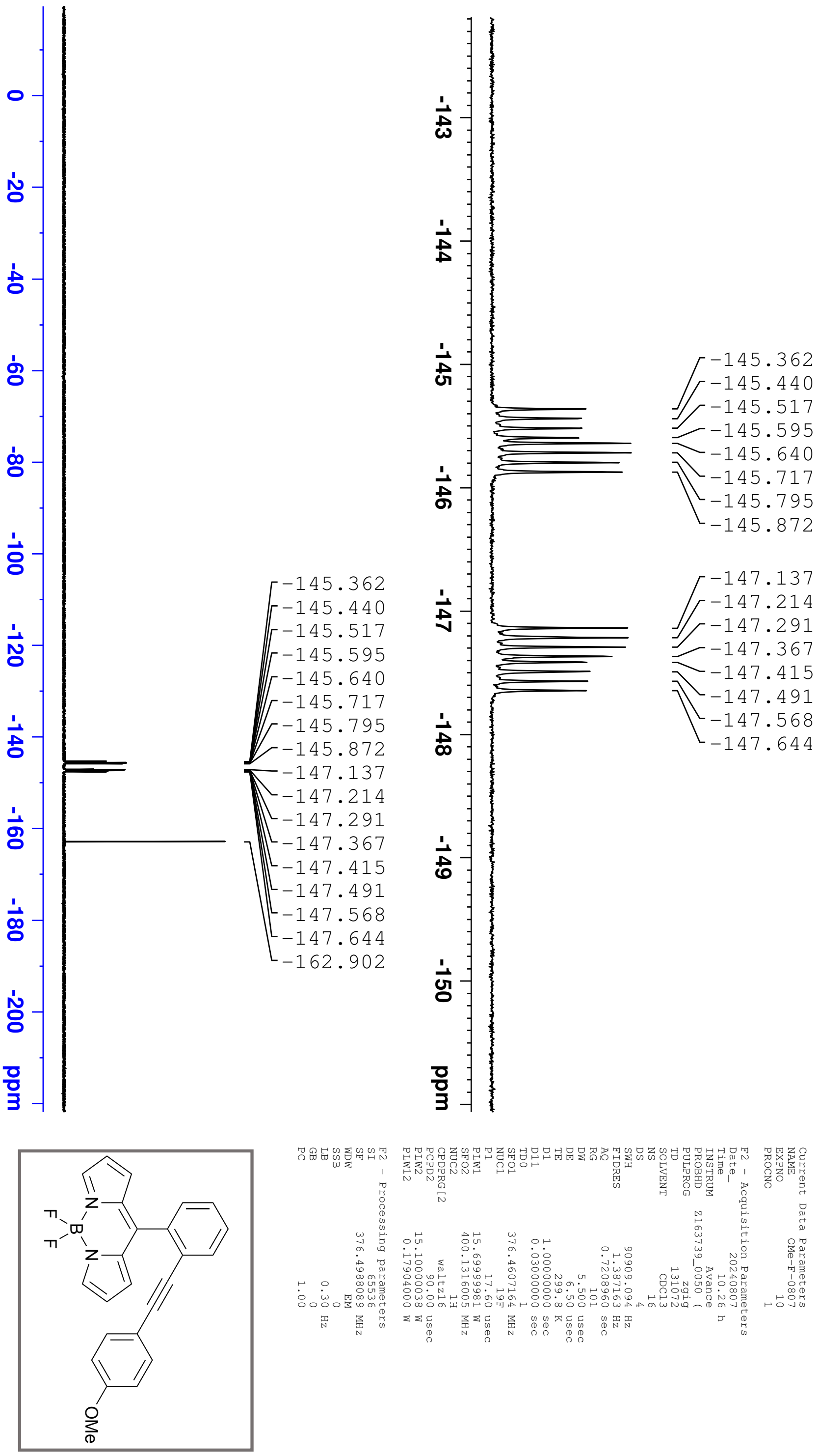



**Figure S6.** [19]F NMR spectrum of **1b** in $CDCl_3$ at 25 °C.

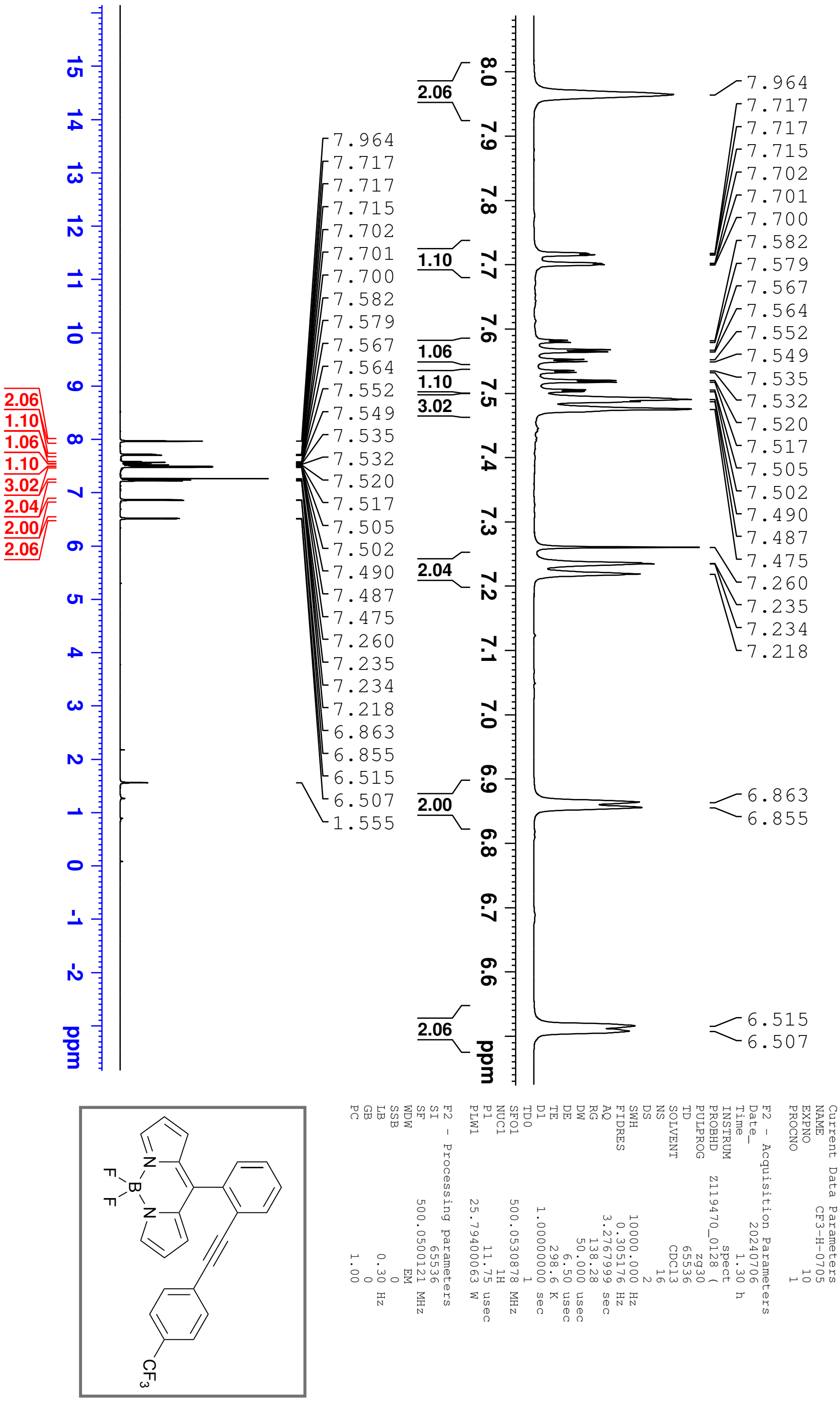


Figure S7. $^{1}$H NMR spectrum of 1c in $CDCl_3$ at 25 °C.

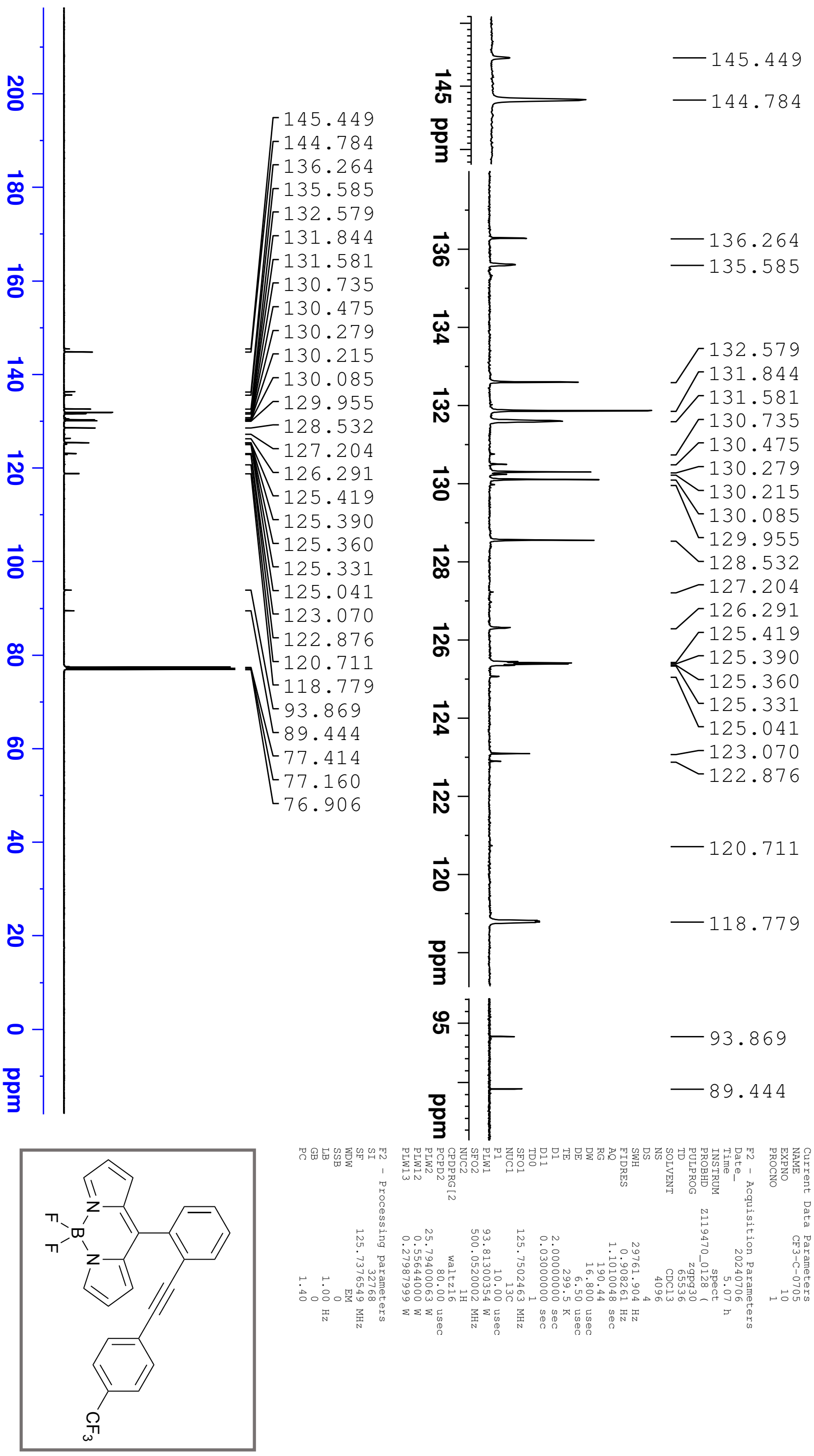



**Figure S8.** $^{13}C$ NMR spectrum of **1c** in $CDCl_3$ at 25 °C.

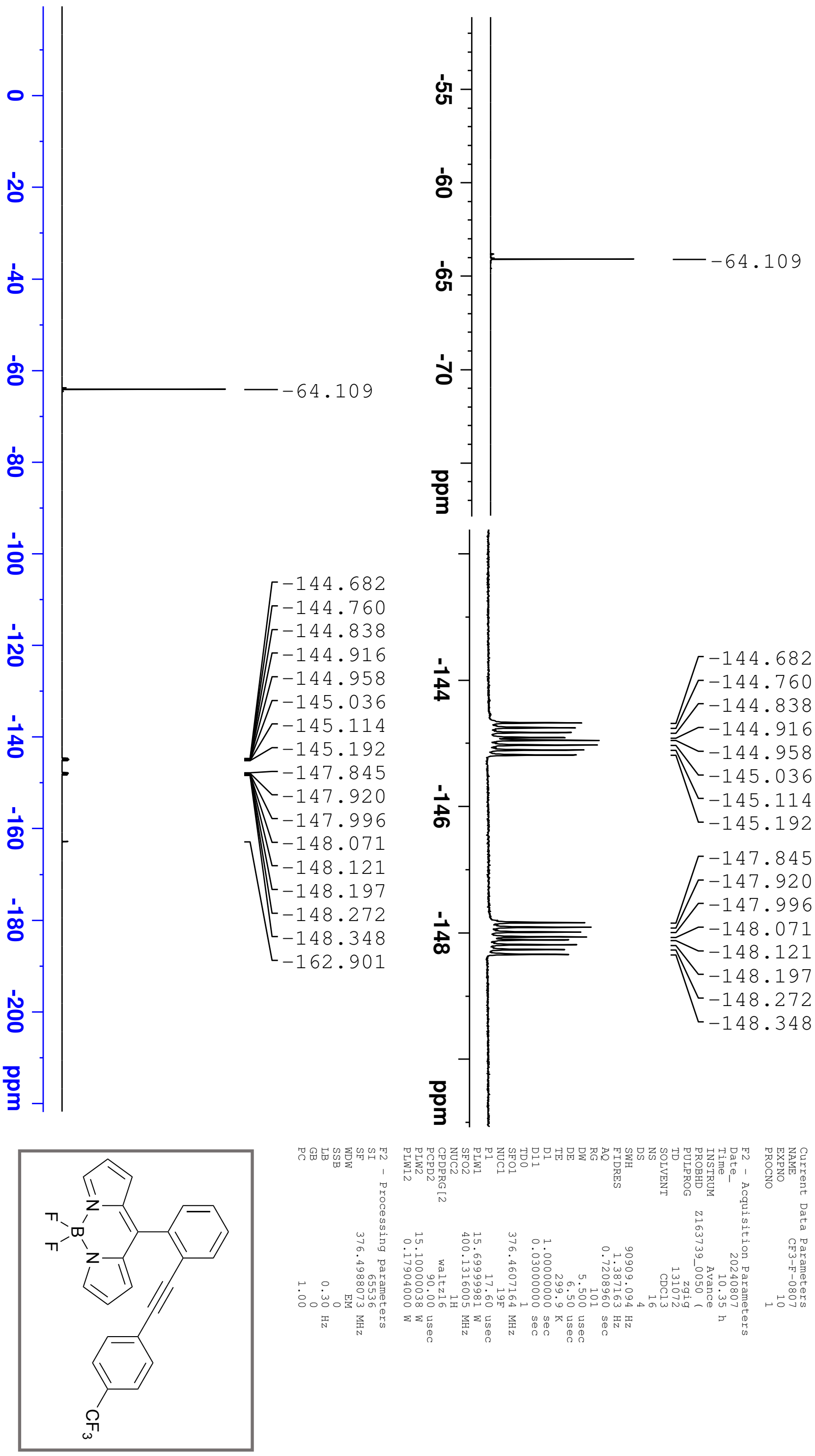



**Figure S9.** ${}^{19}F$ NMR spectrum of **1c** in $CDCl_3$ at 25 °C.

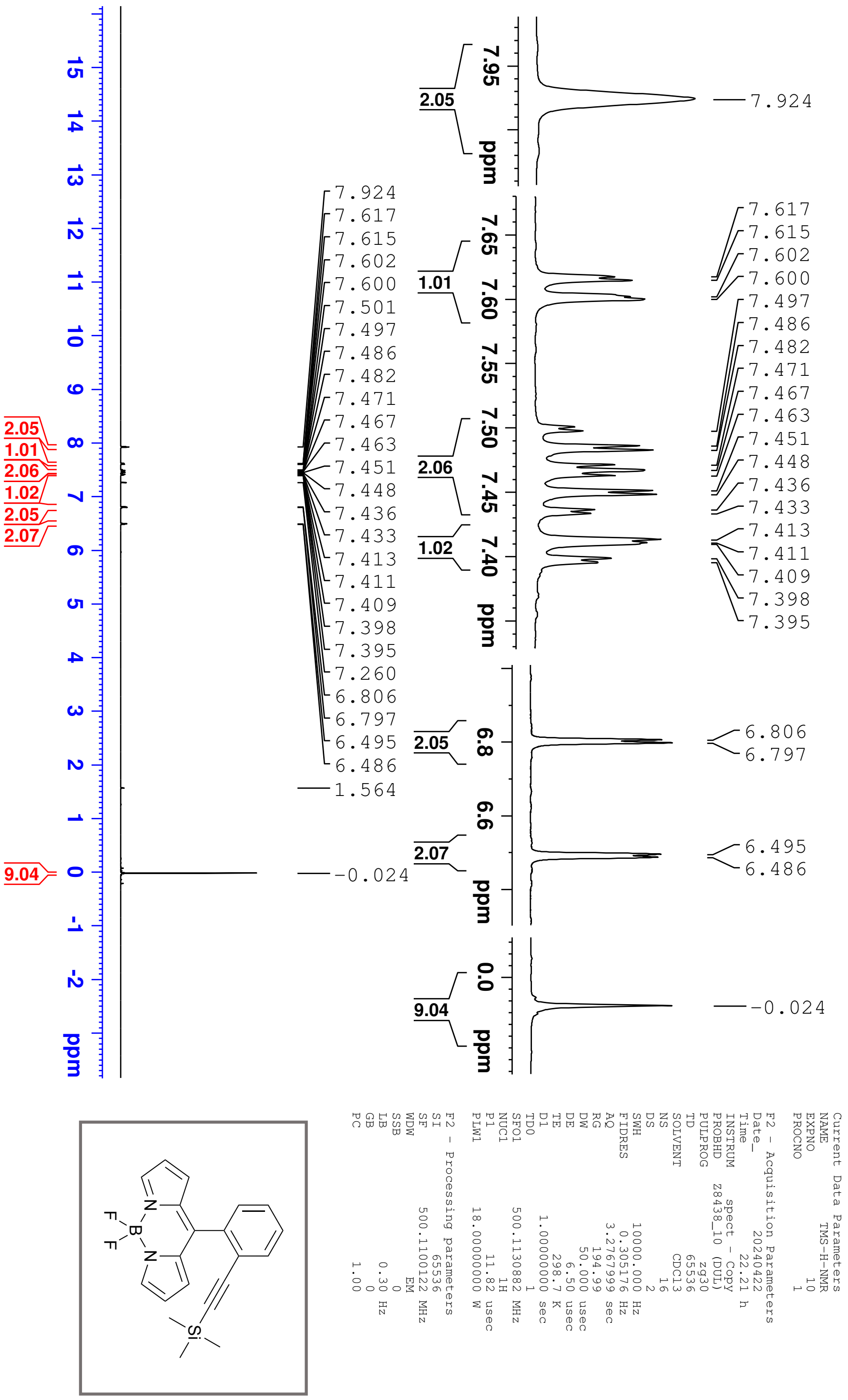



**Figure S10.** [1]H NMR spectrum of **S1** in $CDCl_3$ at 25 °C.

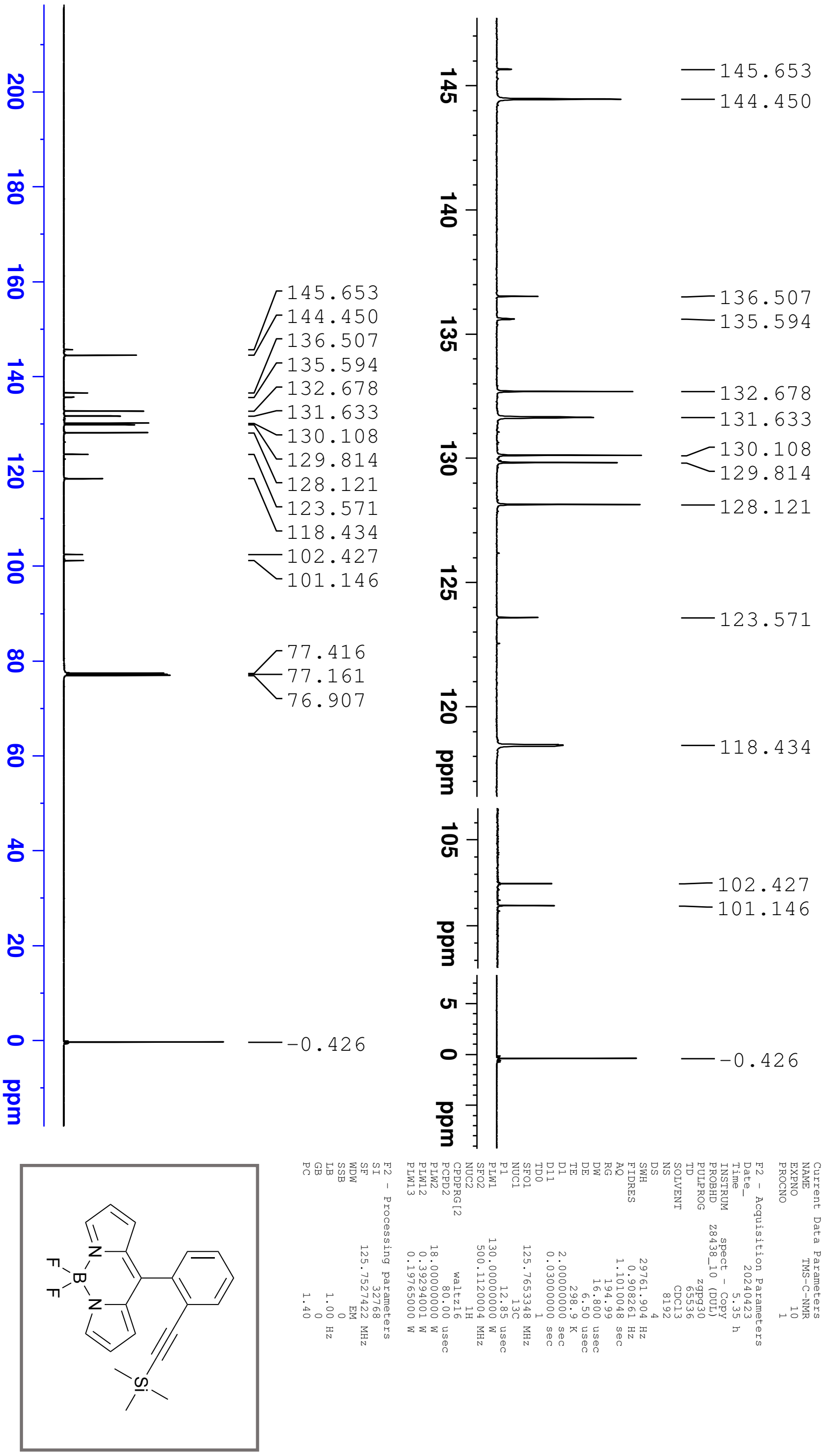



**Figure S11.** ^13^C NMR spectrum of **S1** in $CDCl_3$ at 25 °C.

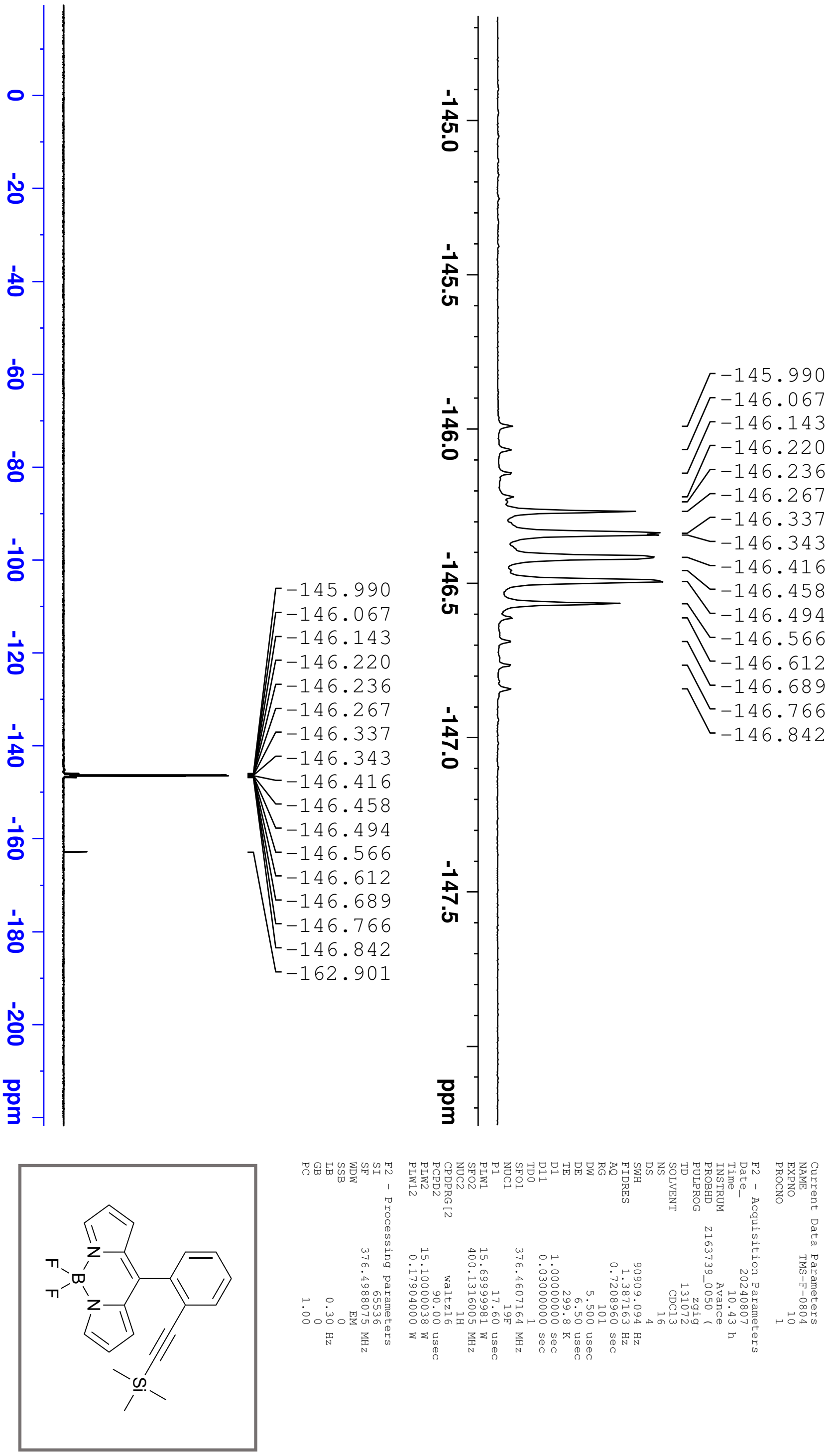



**Figure S12.** $^{19}$F NMR spectrum of **S1** in $CDCl_3$ at 25 °C.

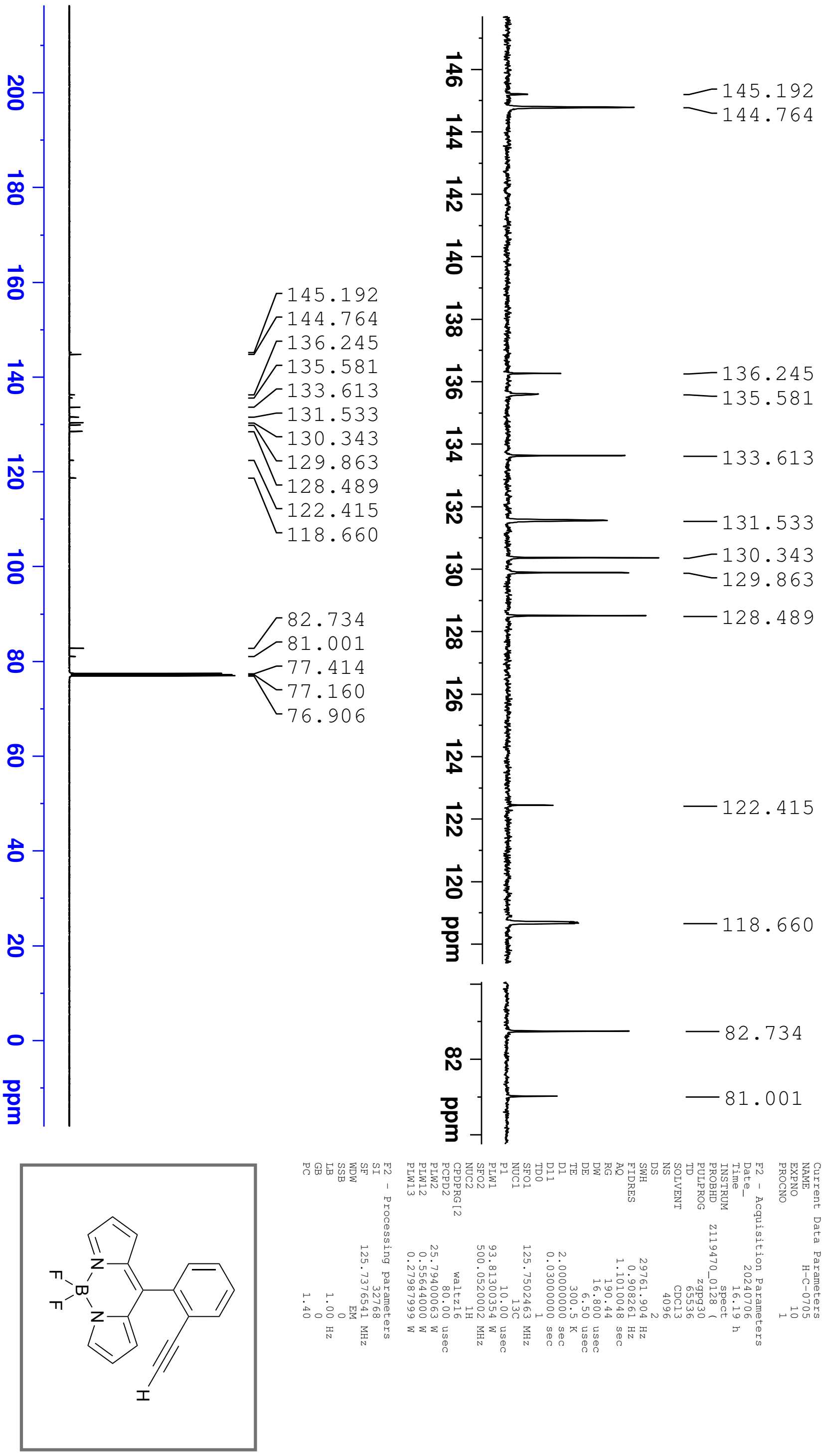



**Figure S13.** $^{1}$H NMR spectrum of **1d** in $CDCl_3$ at 25 °C.

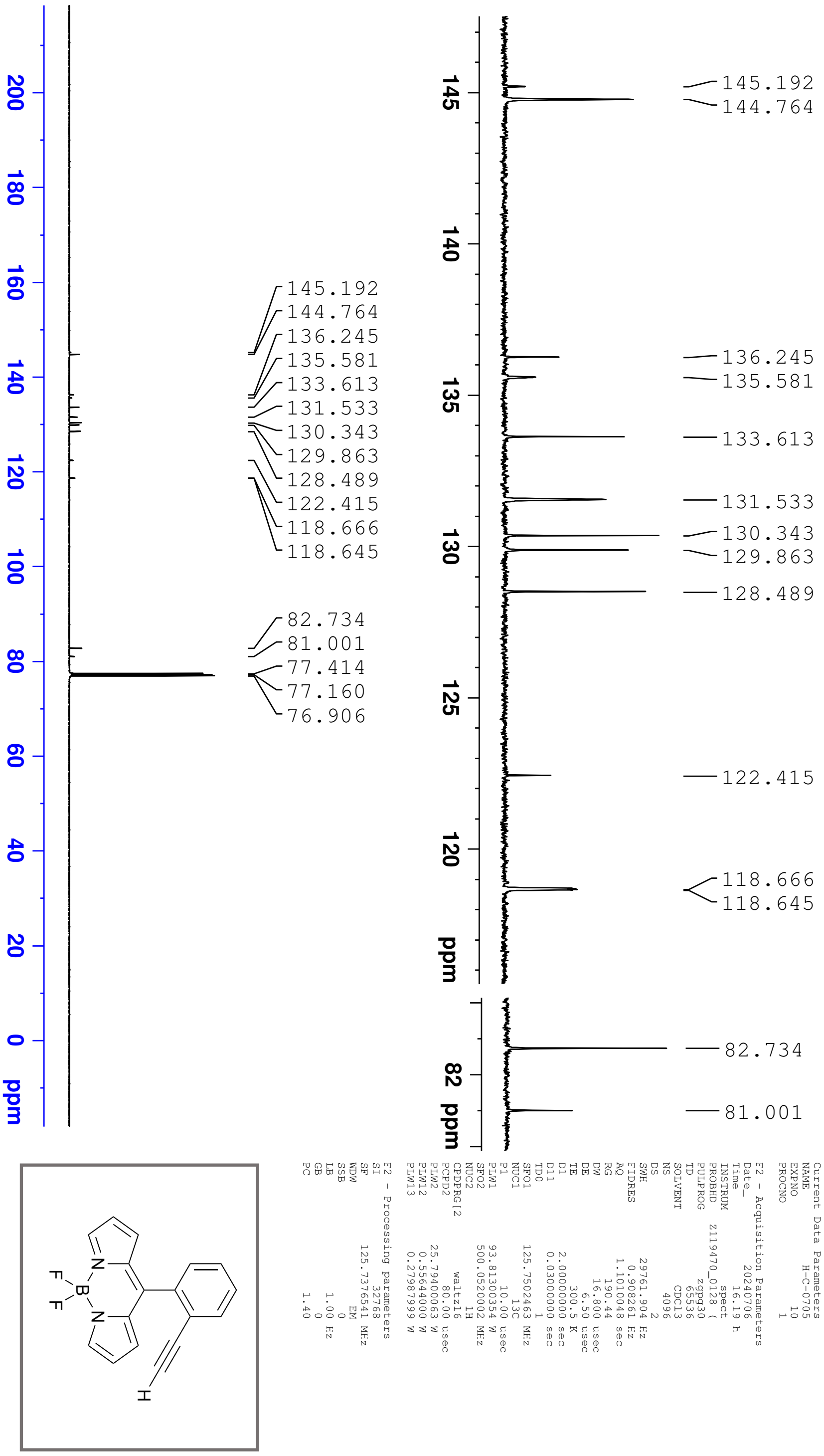


**Figure S14.** $^{13}$C NMR spectrum of **1d** in $CDCl_3$ at 25 °C.

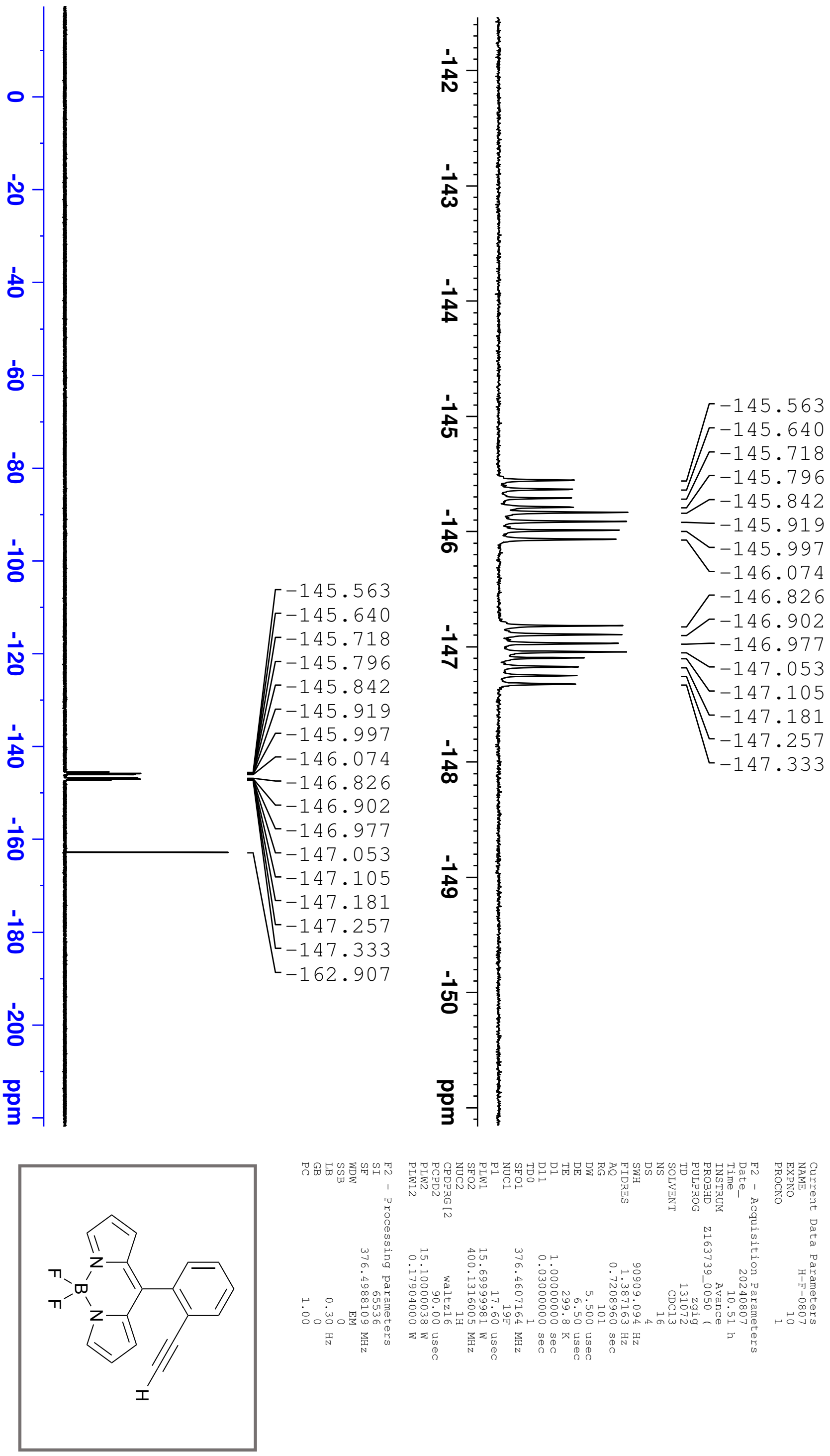


**Figure S15.** $^{19}$F NMR spectrum of **1d** in $CDCl_3$ at 25 °C.

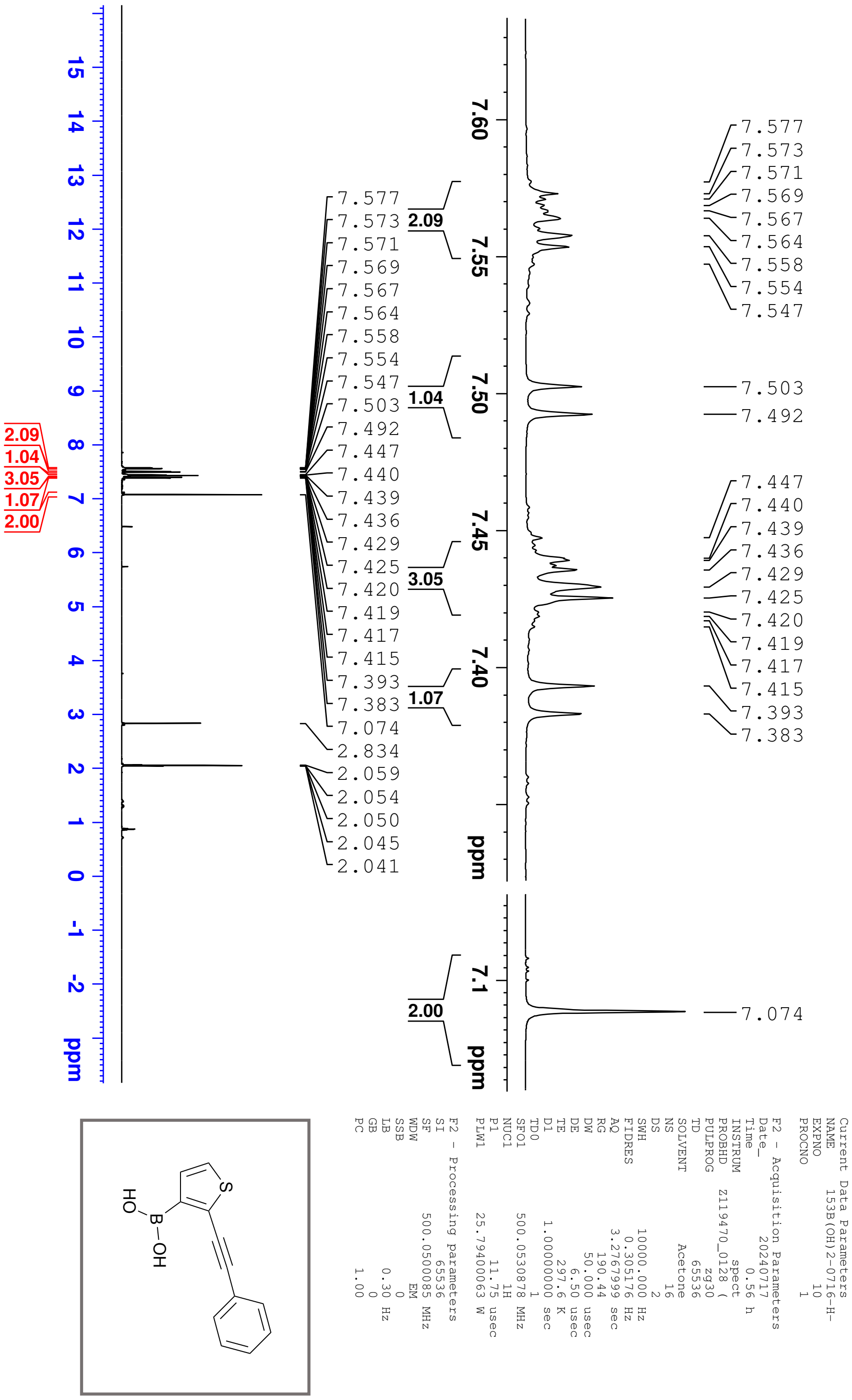



**Figure S16.** $^{1}$H NMR spectrum of **S2** in acetone-$d_6$ at 25 °C.

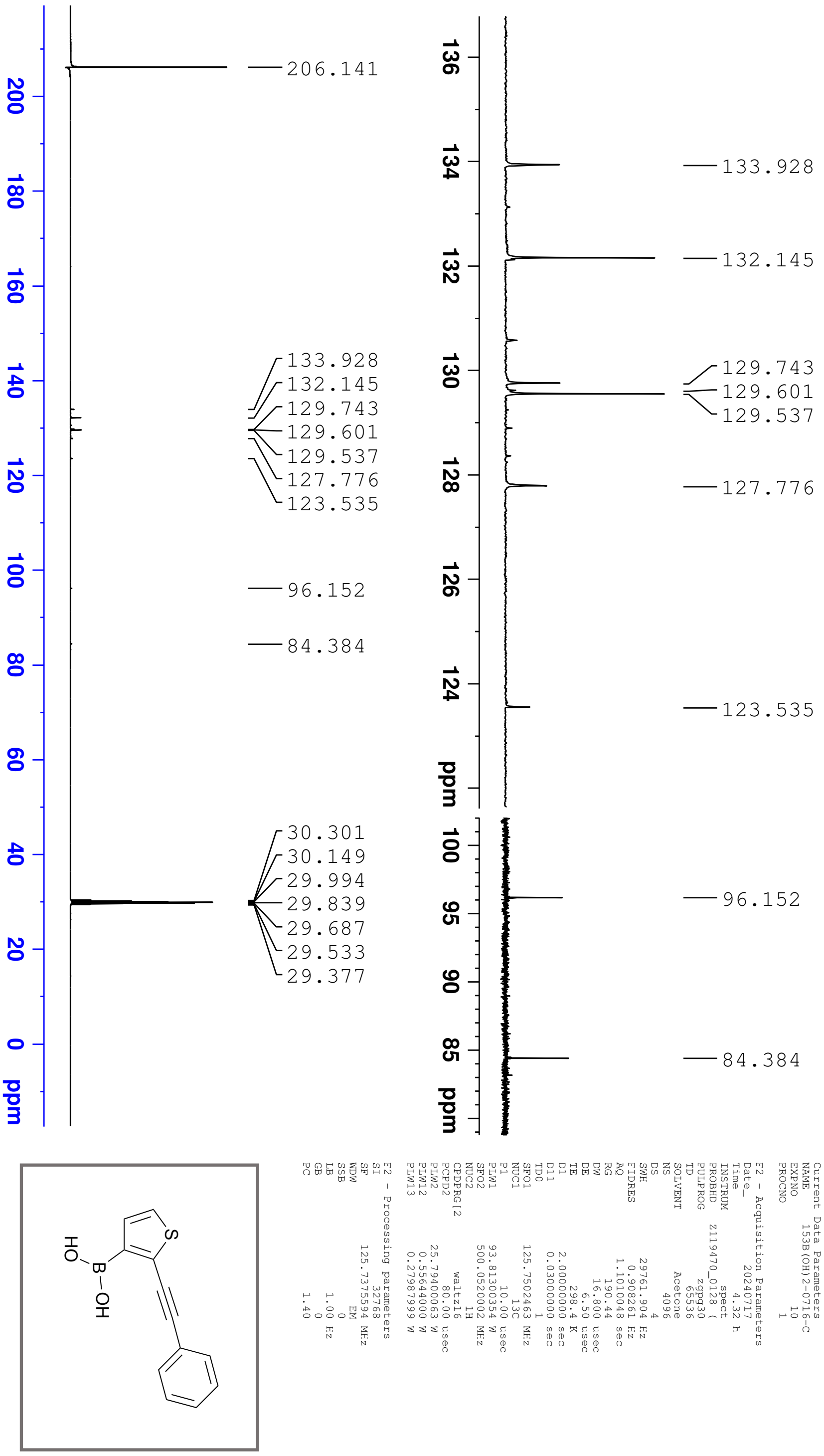



**Figure S17.** $^{13}$C NMR spectrum of **S2** in acetone-$d_6$ at 25 °C.

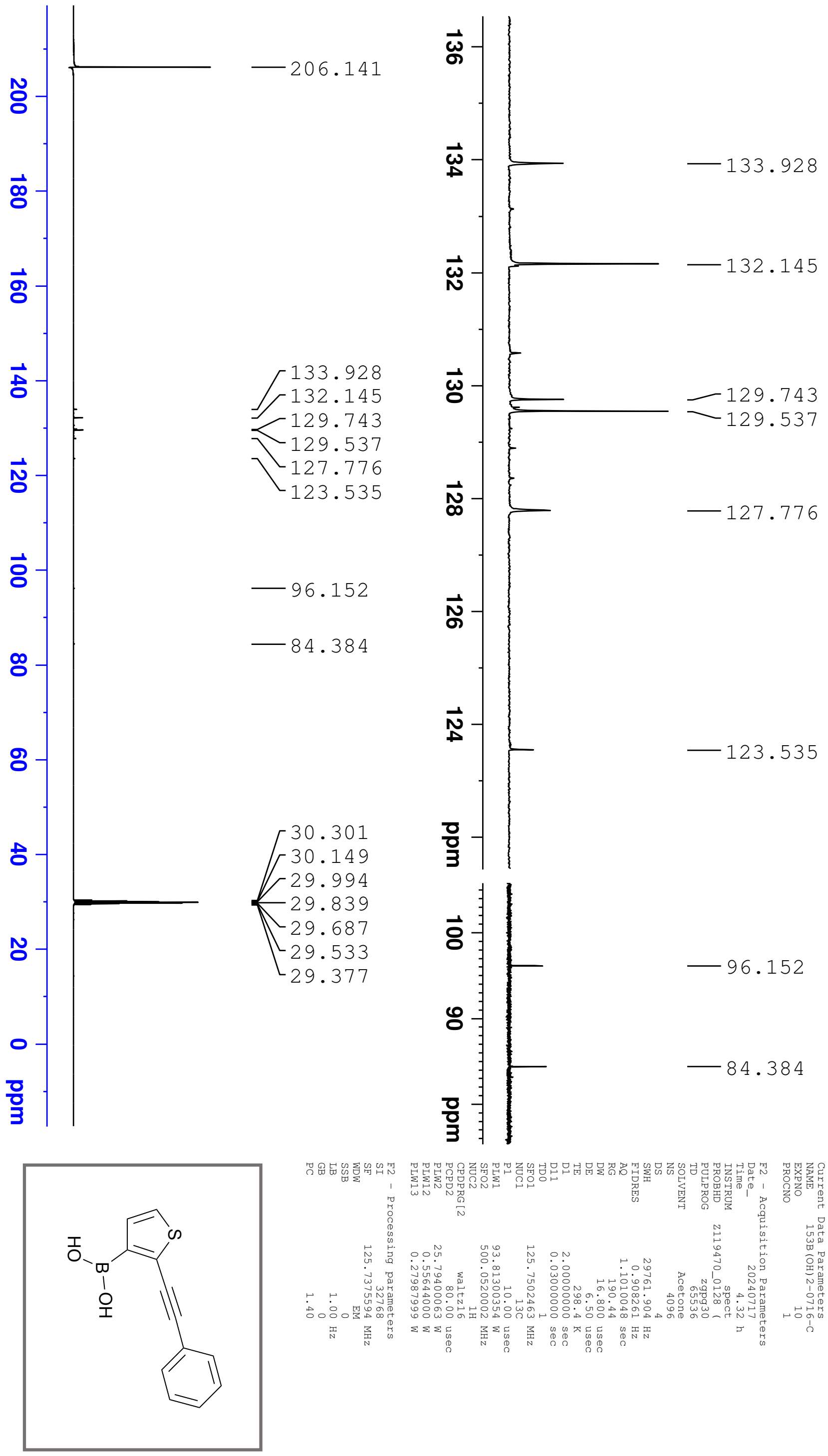



**Figure S18.** $^{1}$H NMR spectrum of **S3** in acetone-$d_6$ at 25 °C.

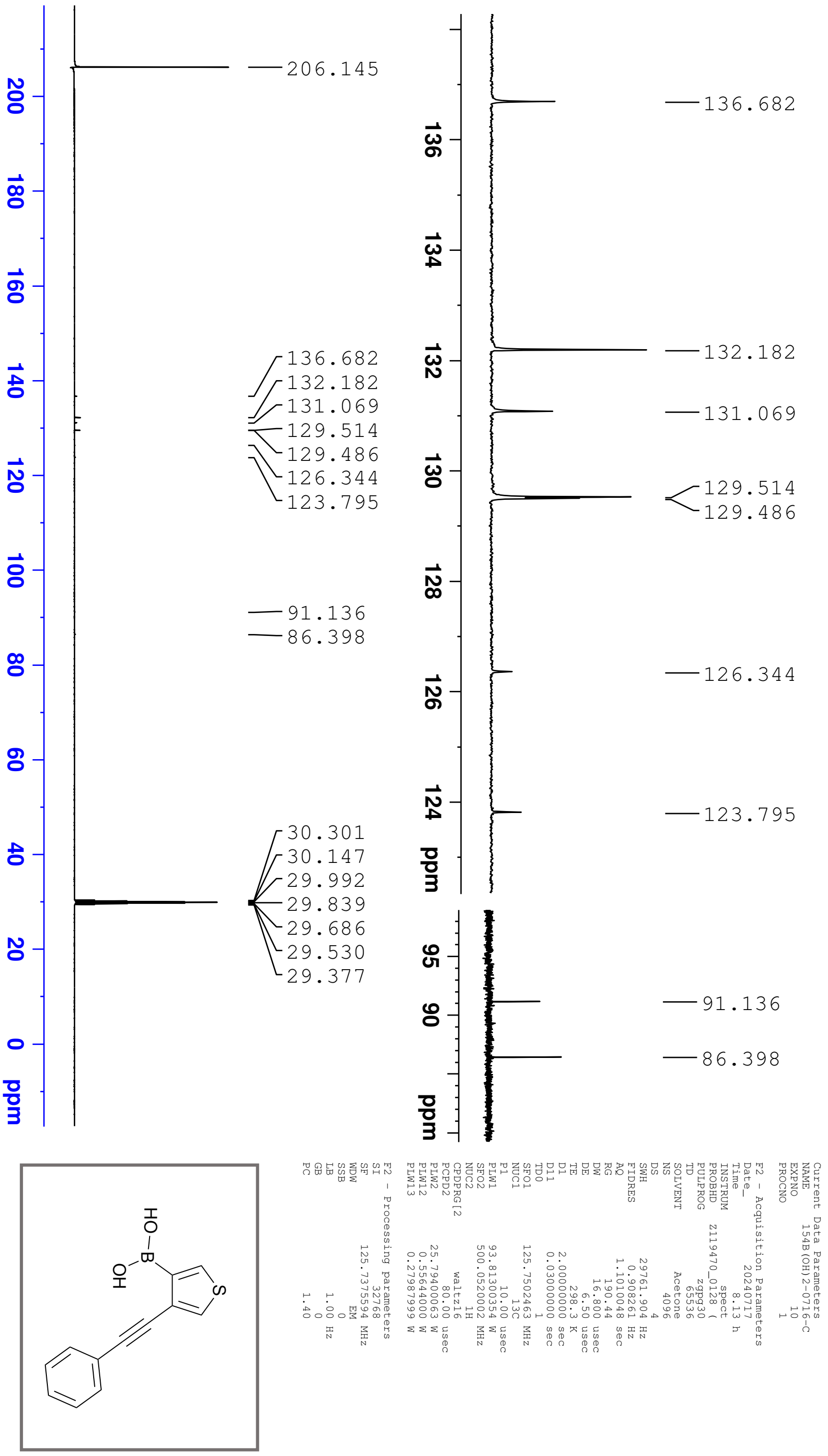



**Figure S19.** $^{13}C$ NMR spectrum of **S3** in acetone-$d_6$ at 25 °C.

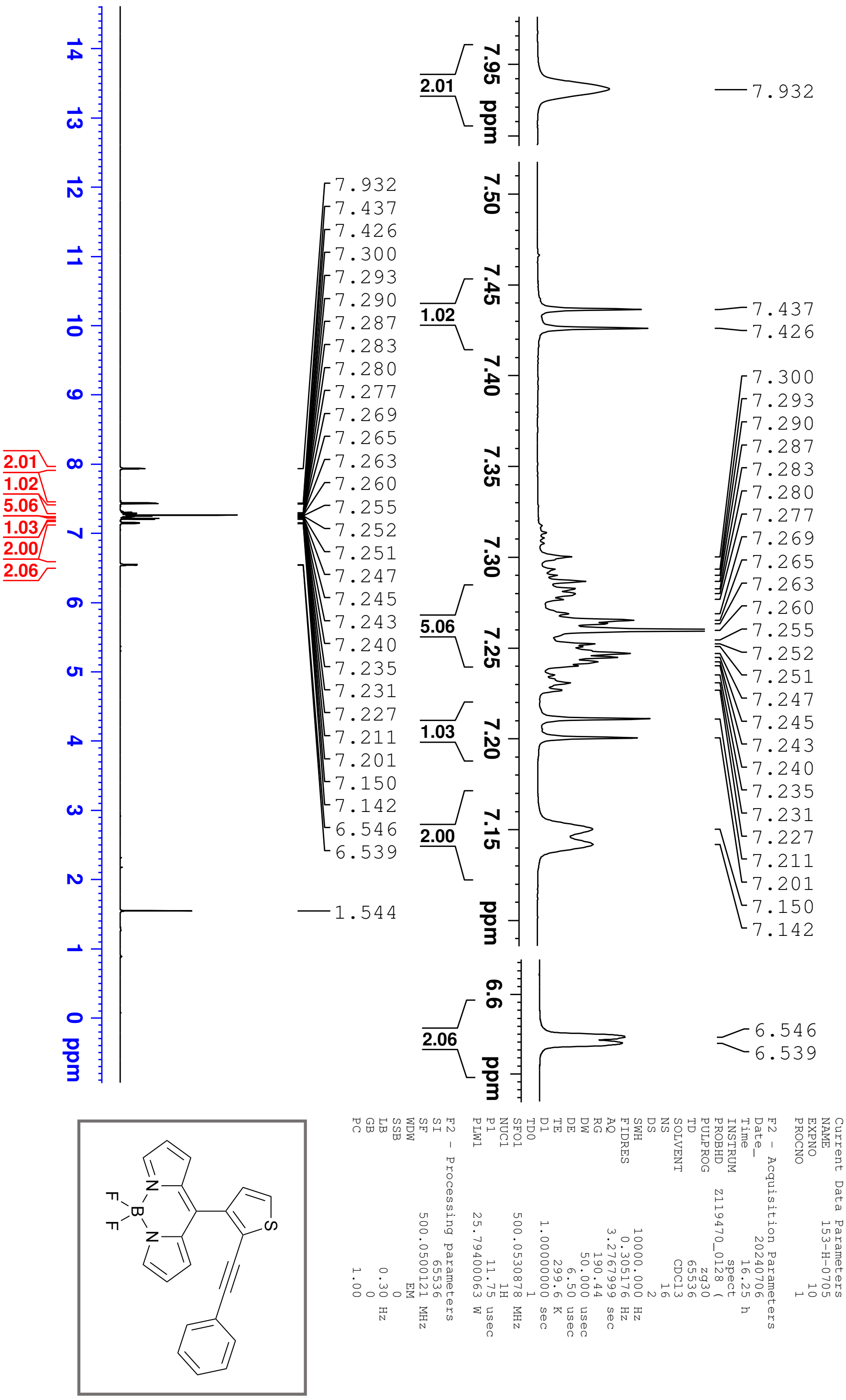


**Figure S20.** $^{1}$H NMR spectrum of **1e** in $CDCl_3$ at 25 °C.

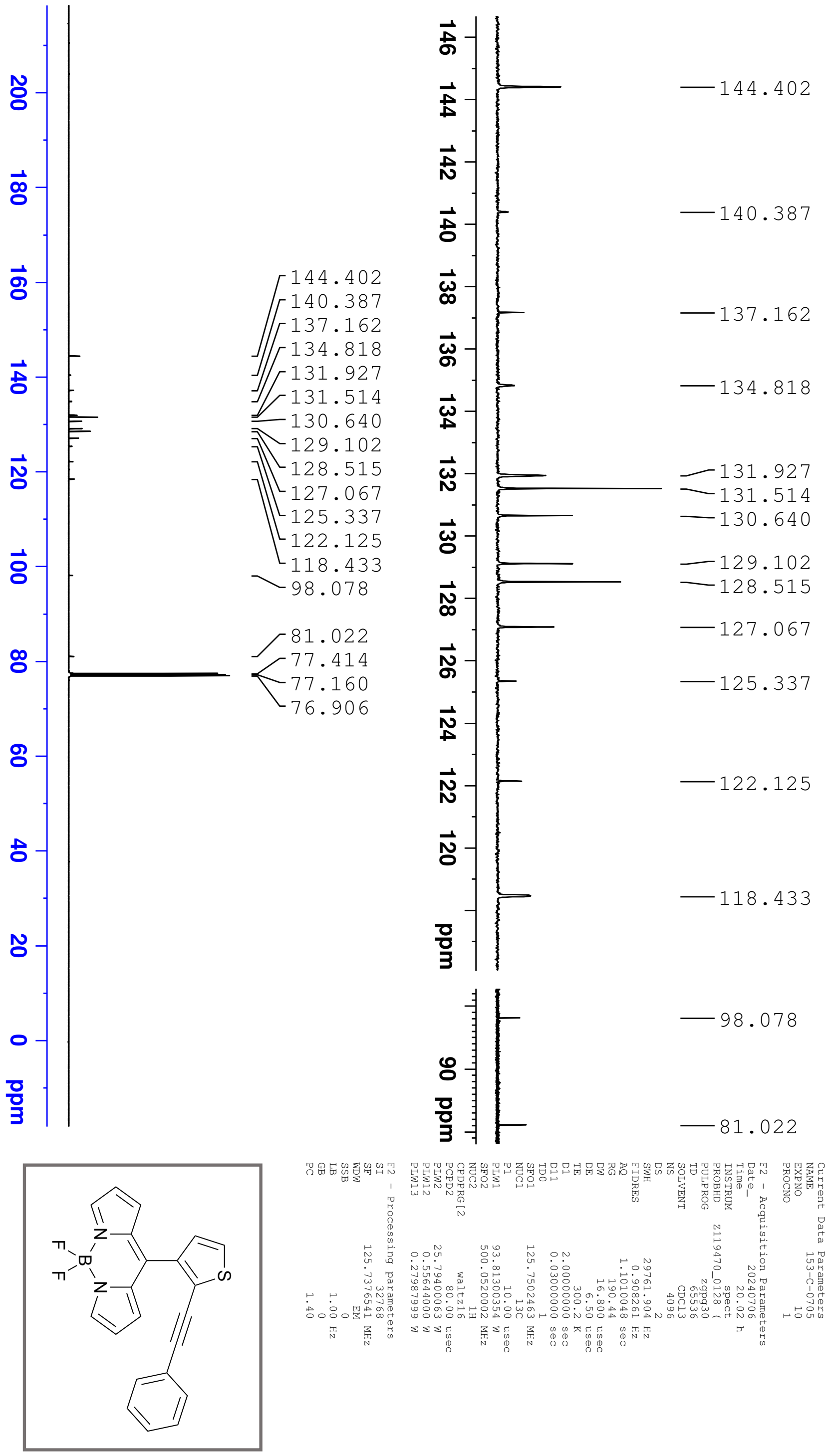



**Figure S21.** $^{13}$C NMR spectrum of **1e** in $CDCl_3$ at 25 °C.

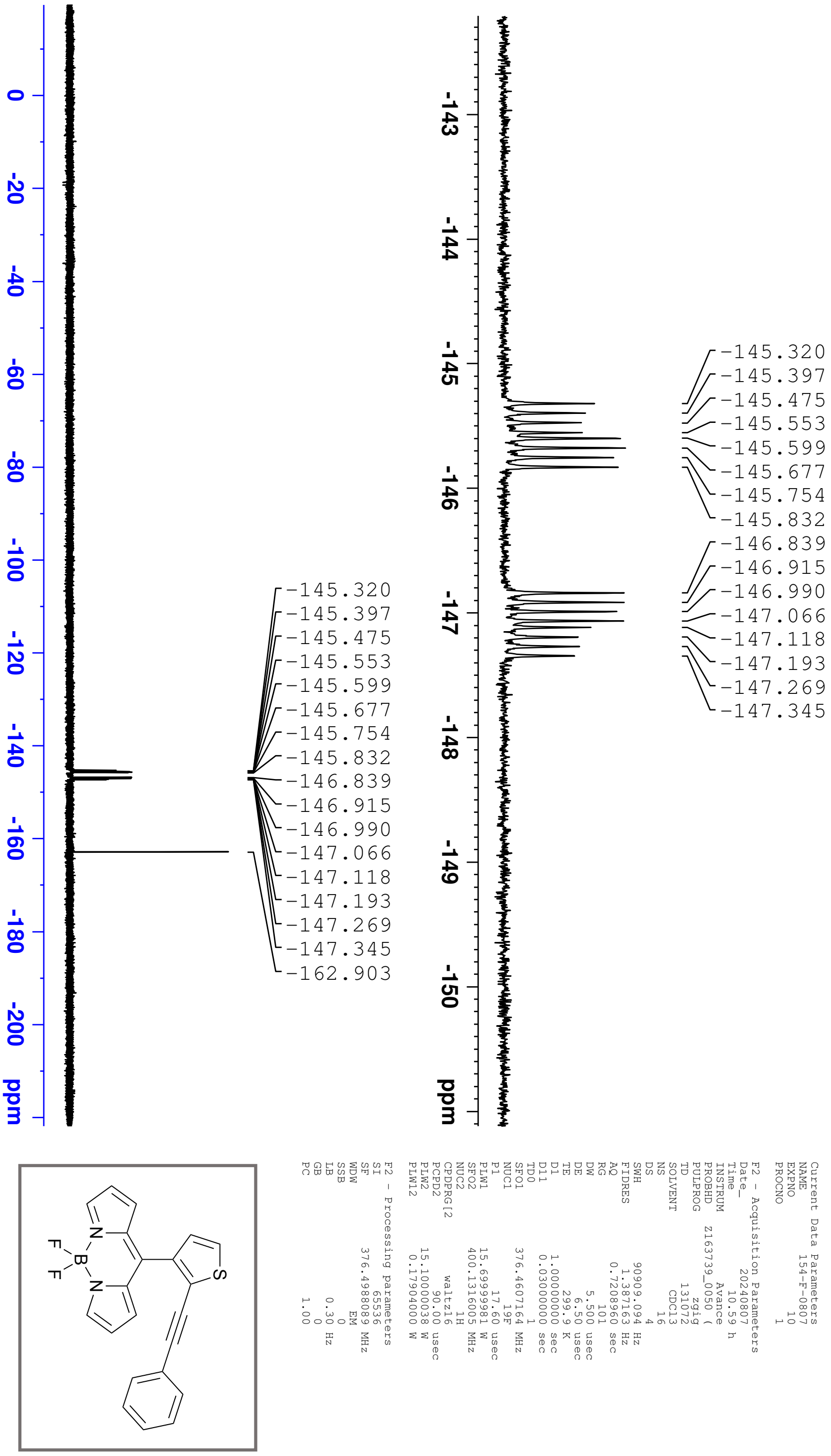



**Figure S22.** [19]F NMR spectrum of **1e** in $CDCl_3$ at 25 °C.

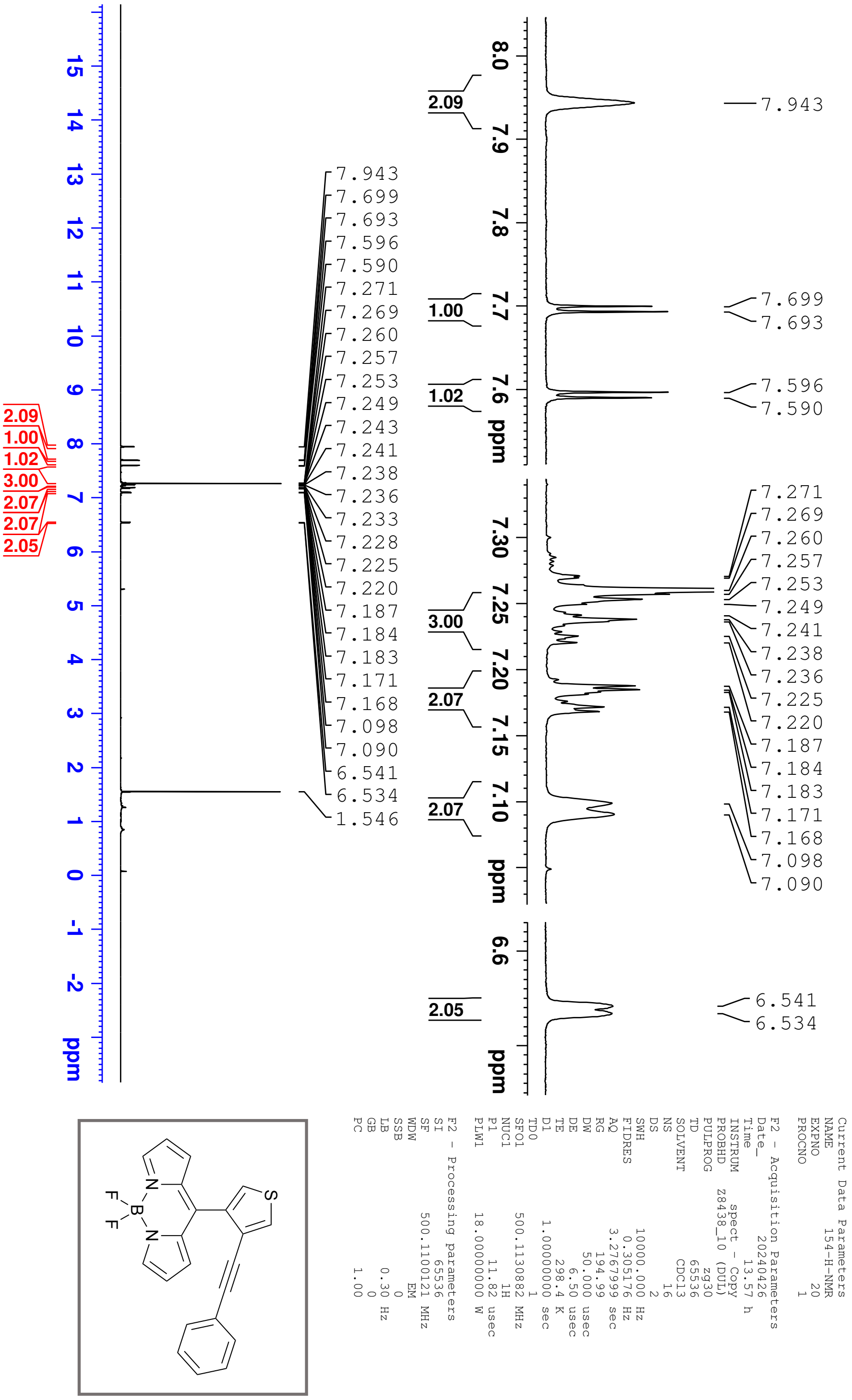


**Figure S23**. [1]H NMR spectrum of **1f** in $CDCl_3$ at 25 °C.

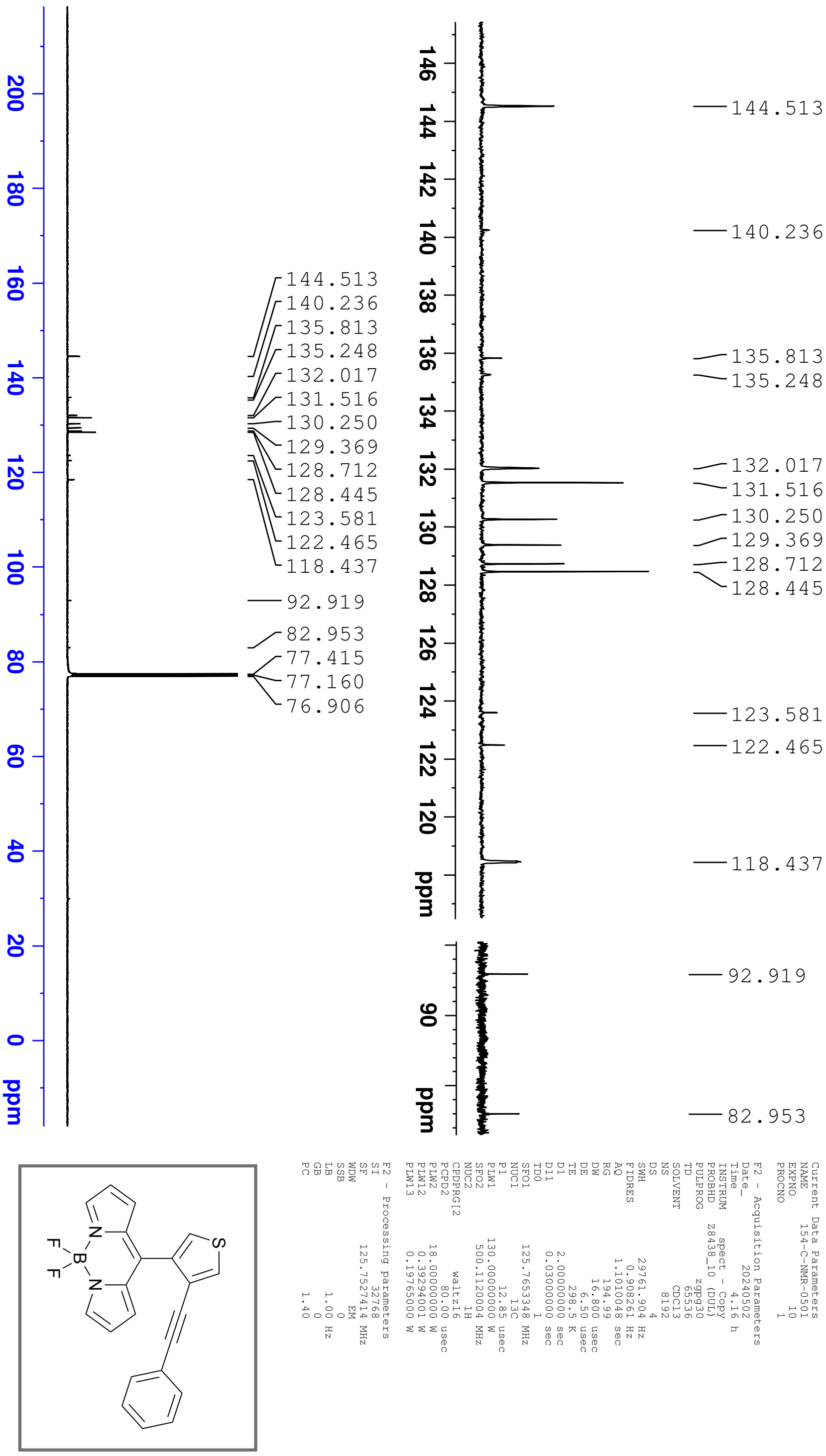



**Figure S24**. $^{13}$C NMR spectrum of **1f** in $CDCl_3$ at 25 °C.

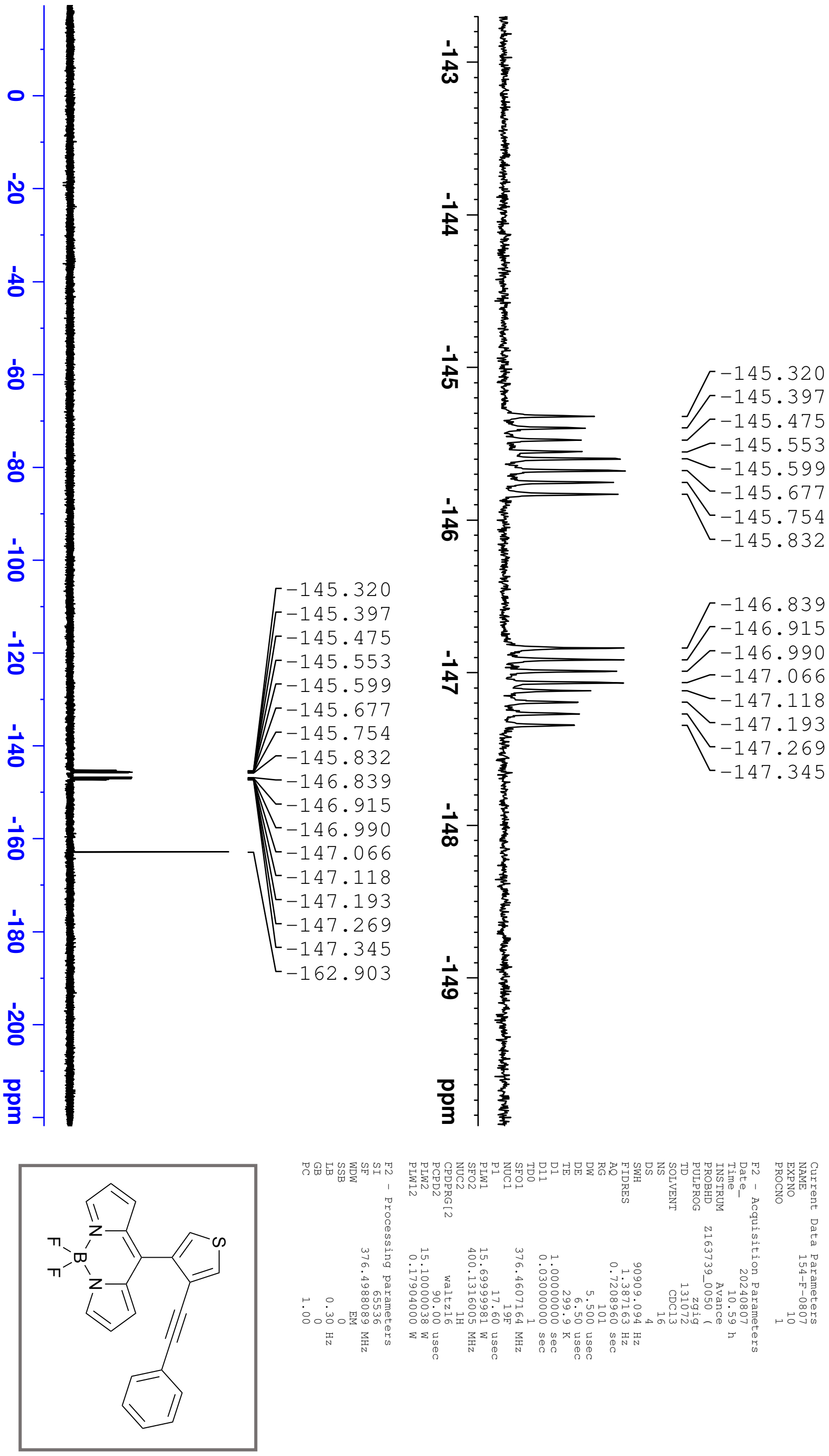



**Figure S25**. [19]F NMR spectrum of **1f** in $CDCl_3$ at 25 °C.

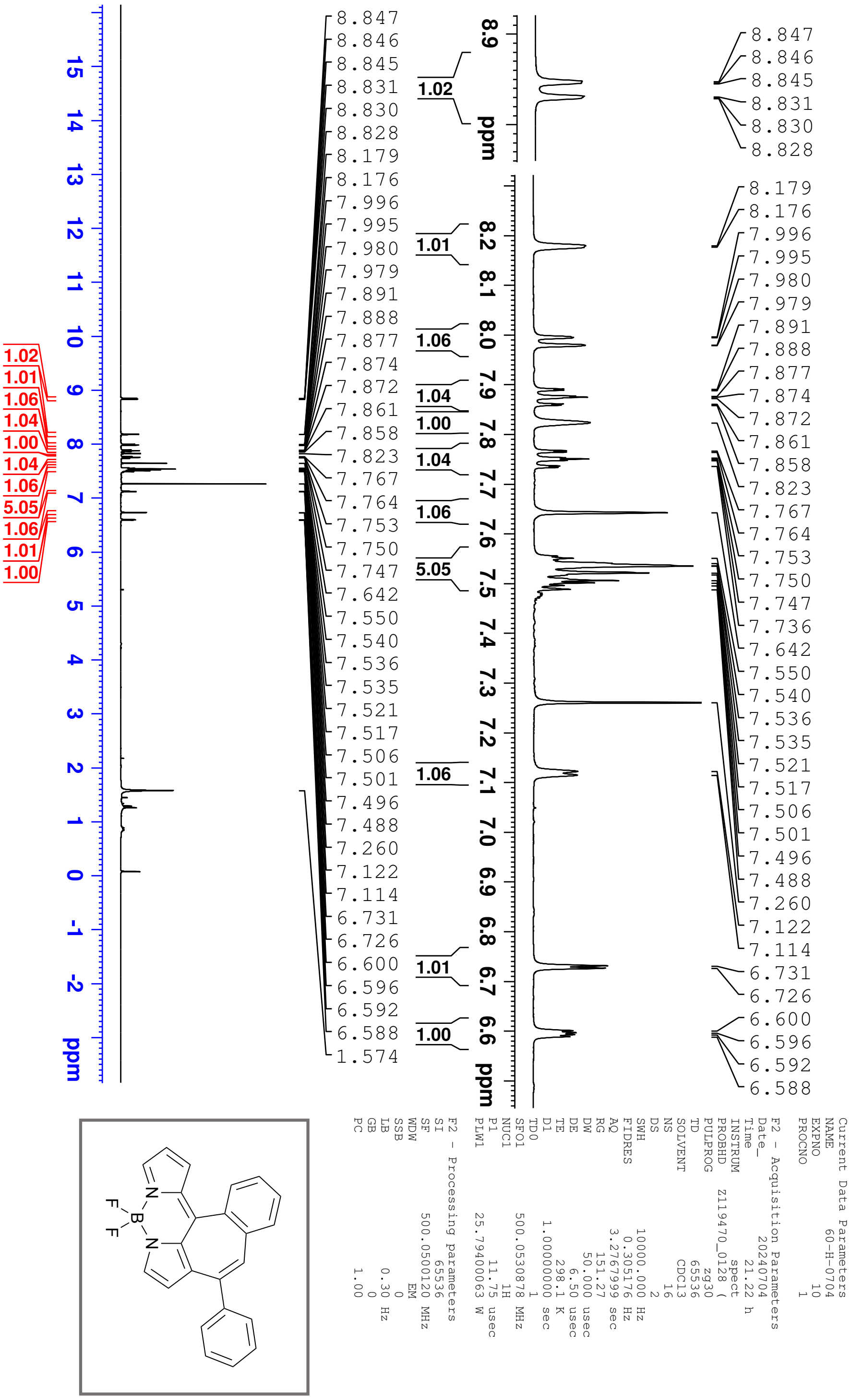


**Figure S26**. $^{1}H$ NMR spectrum of **2a** in $CDCl_3$ at 25 °C.

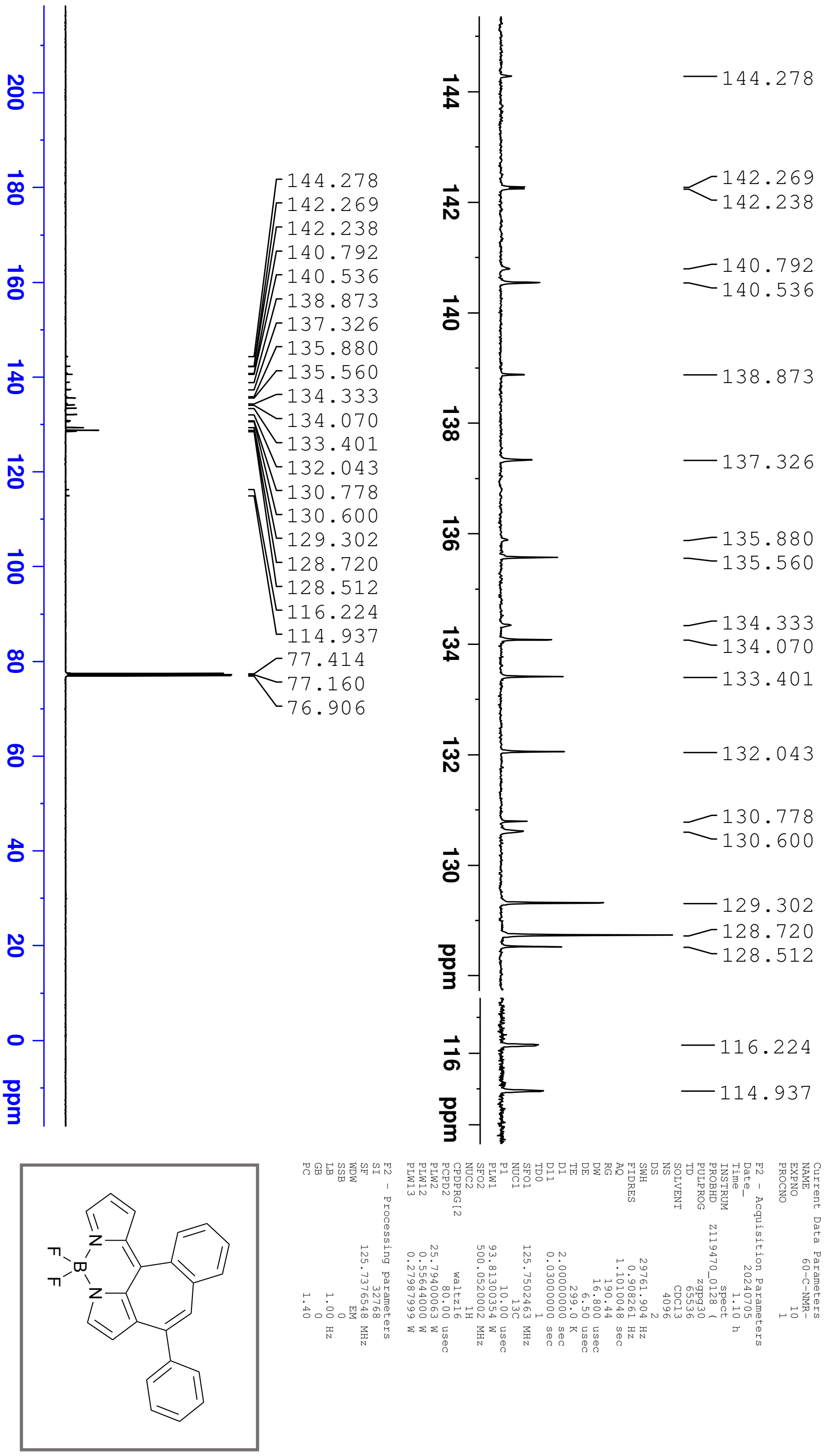



**Figure S27**. [13]C NMR spectrum of **2a** in $CDCl_3$ at 25 °C.

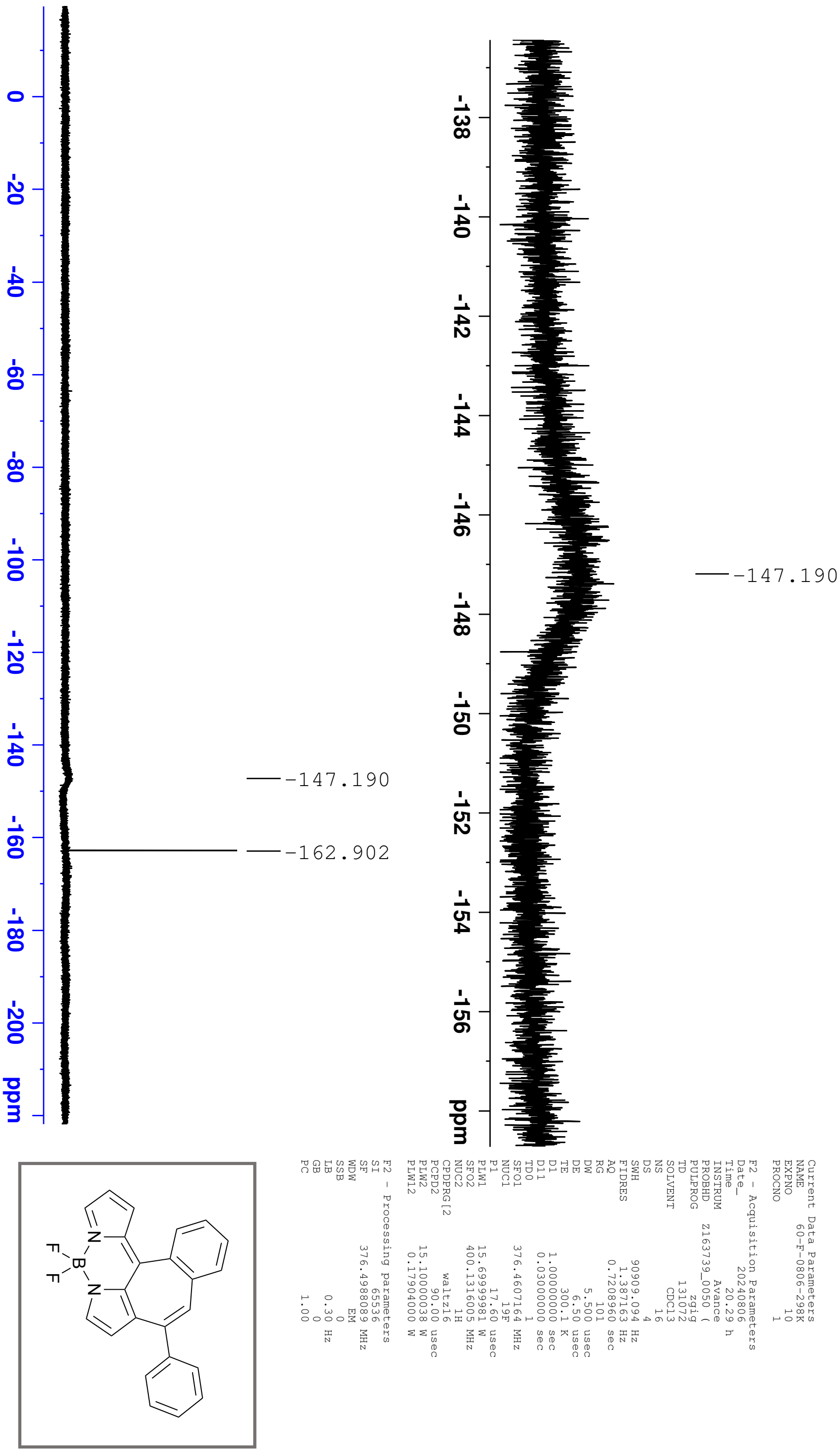



**Figure S28**. [19]F NMR spectrum of **2a** in $CDCl_3$ at 25 °C.

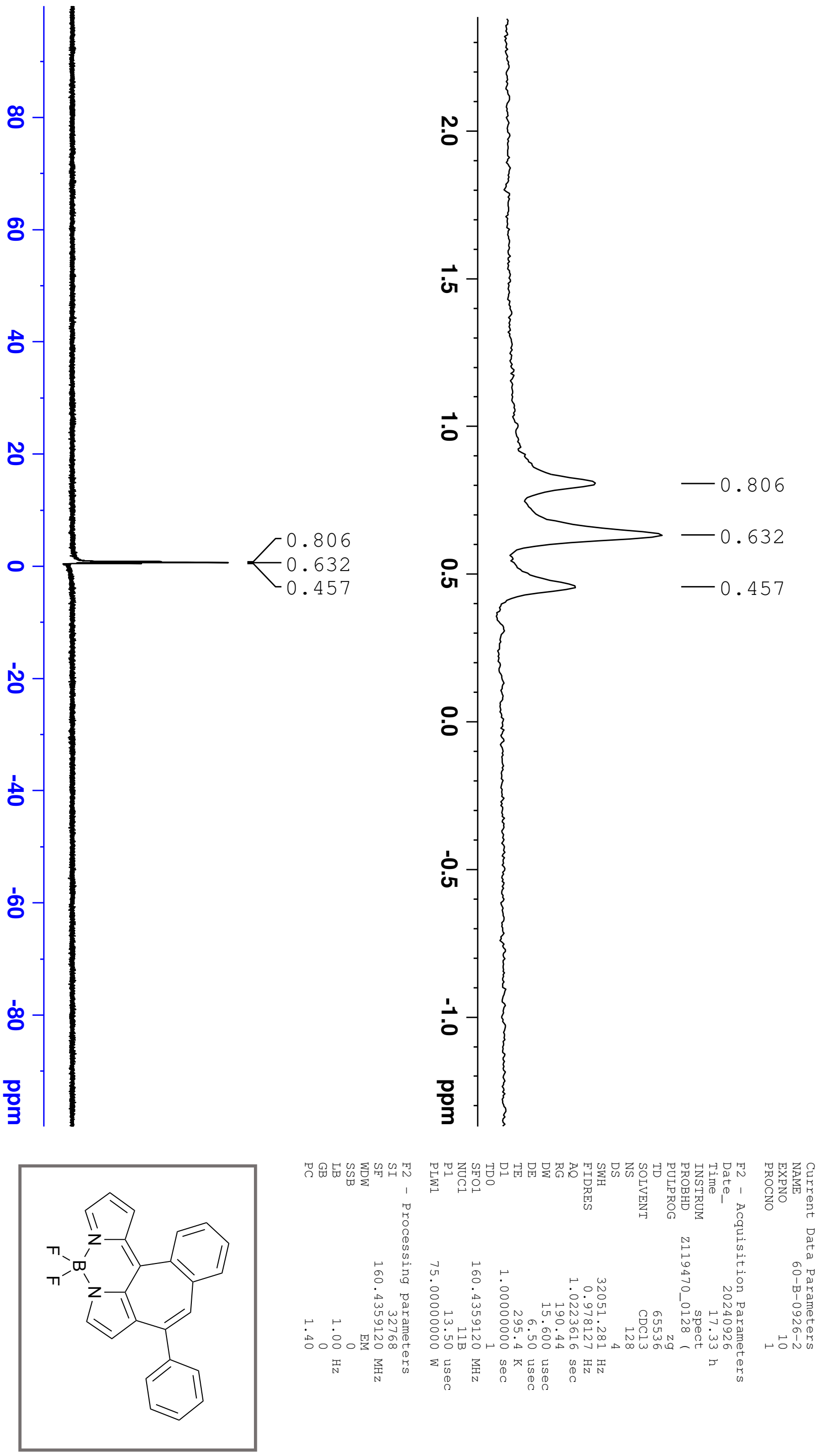



**Figure S29** $^{11}$B NMR spectrum of **2a** in $CDCl_3$ at 25 °C.

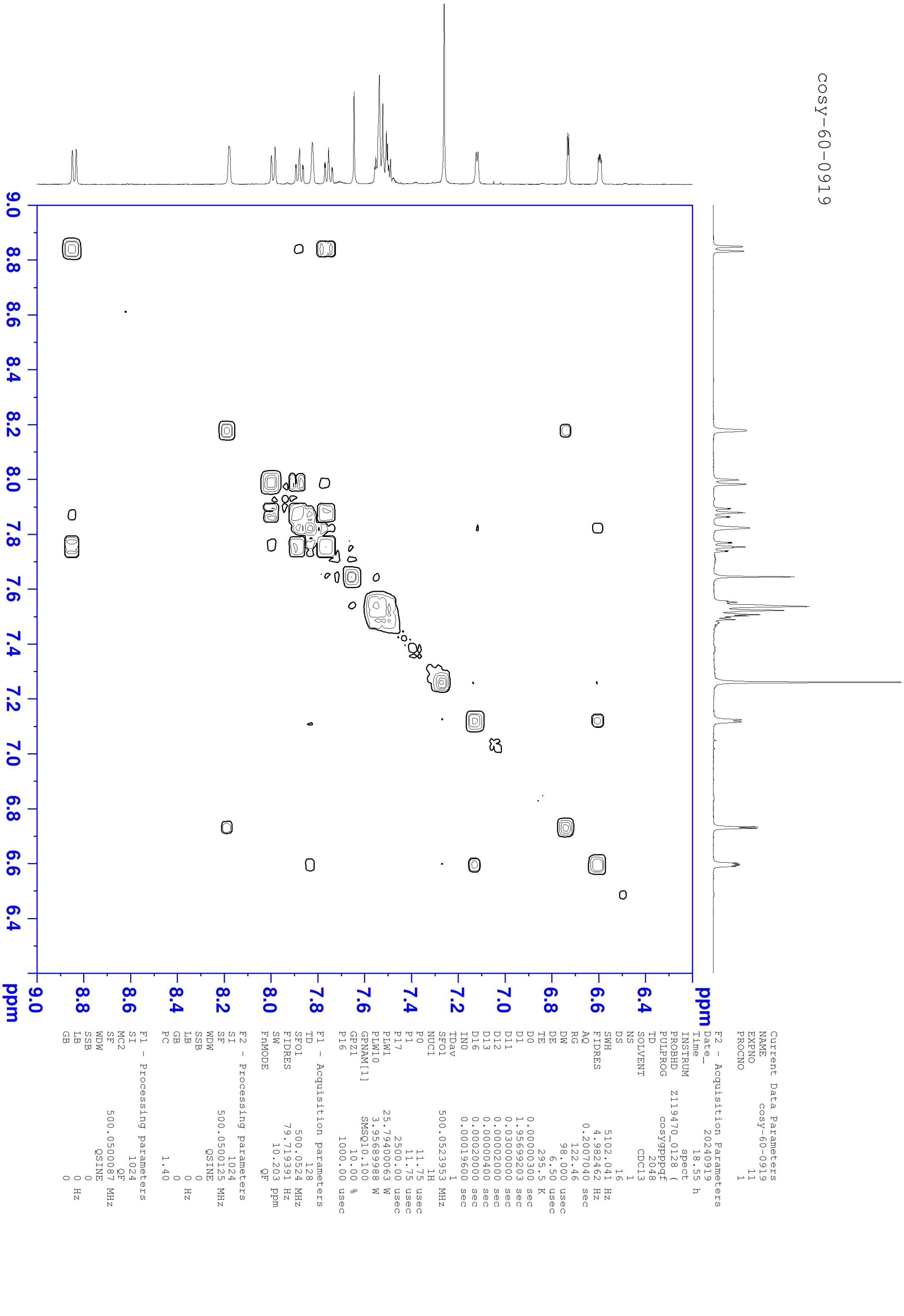



**Figure S30**. COSY spectrum of **2a** in $CDCl_3$ at 25 °C.

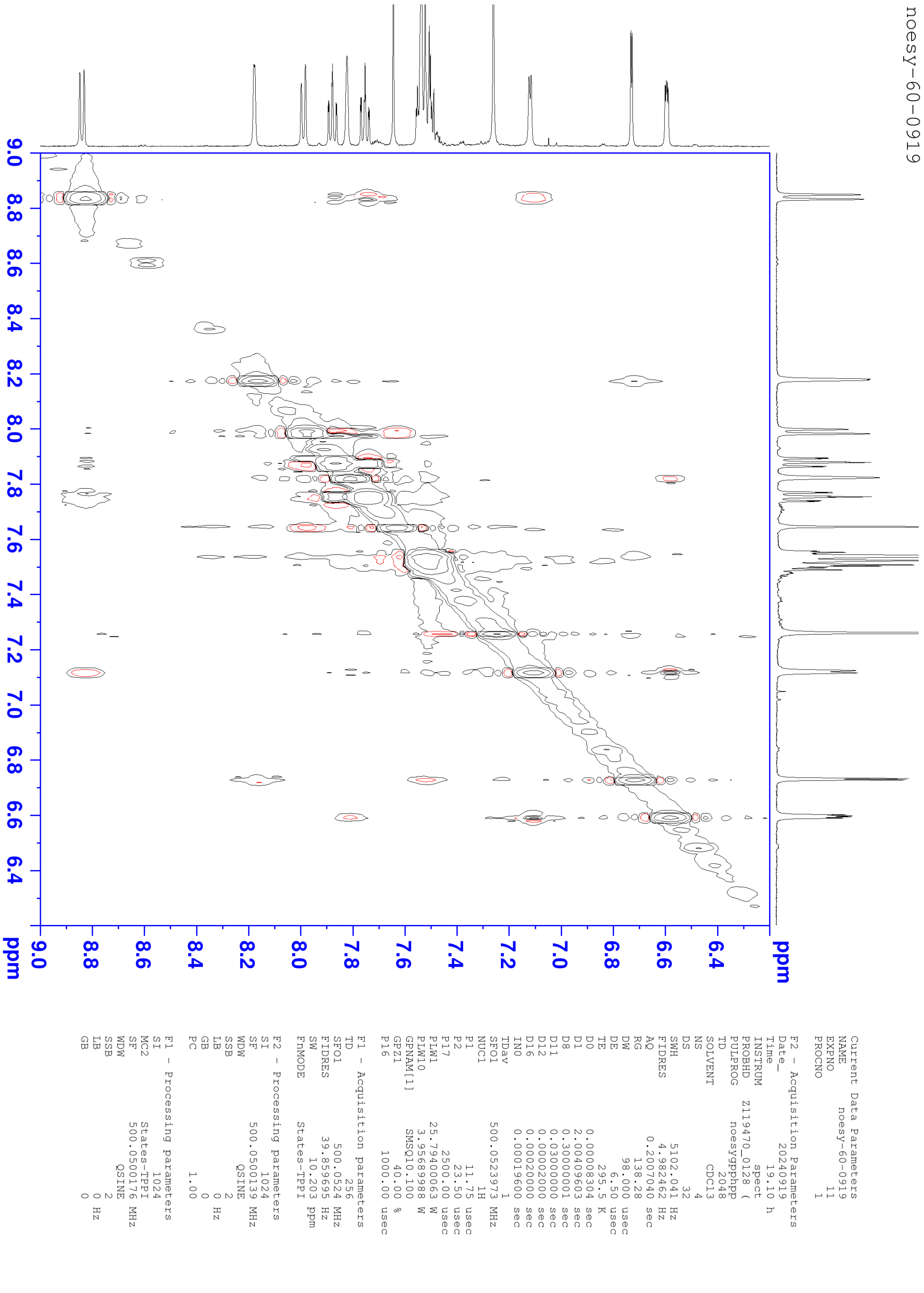



**Figure S31**. NOESY spectrum of **2a** in $CDCl_3$ at 25 °C.

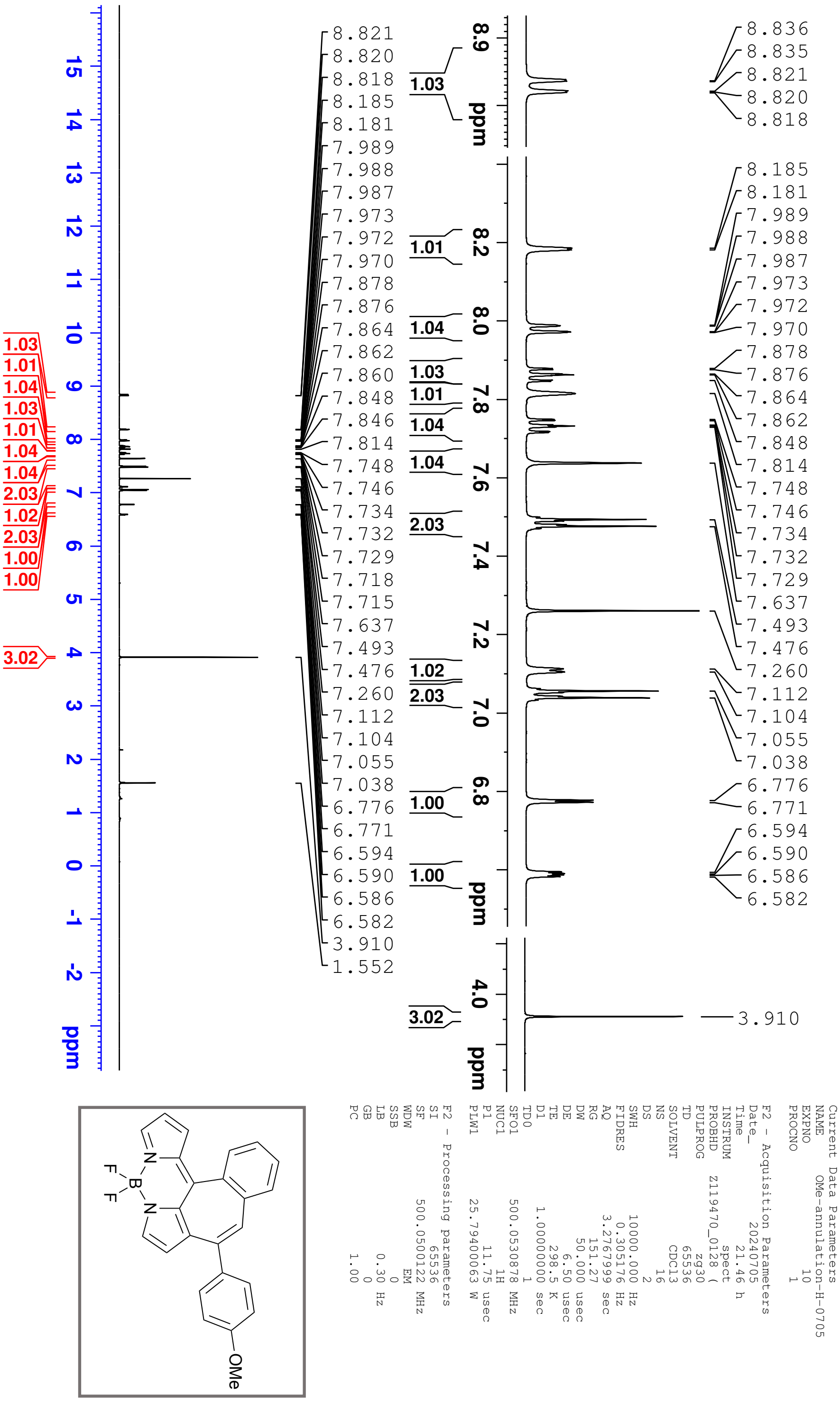


**Figure S32**. [1]H NMR spectrum of **2b** in $CDCl_3$ at 25 °C.

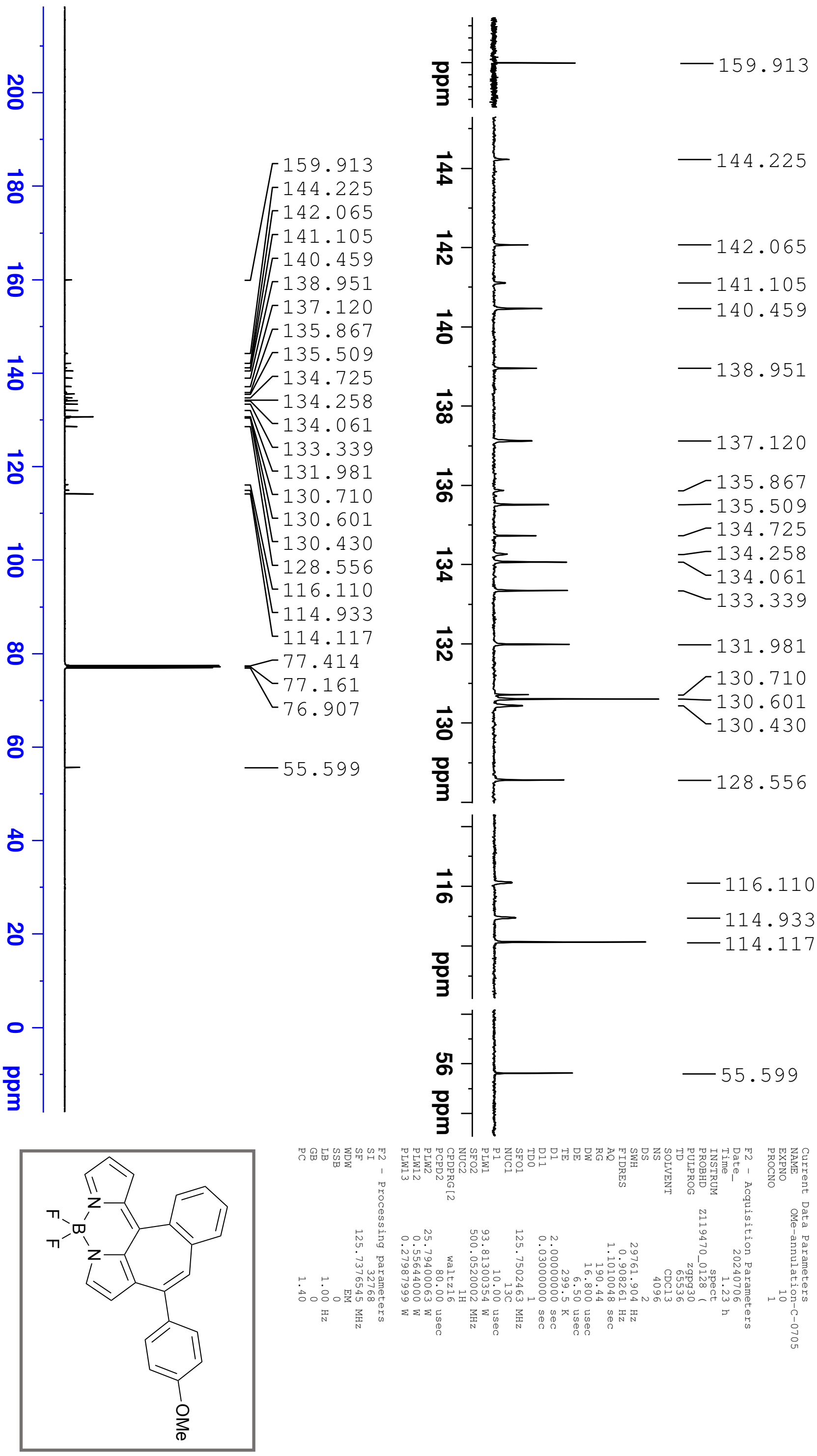



**Figure S33**. [13]C NMR spectrum of **2b** in $CDCl_3$ at 25 °C.

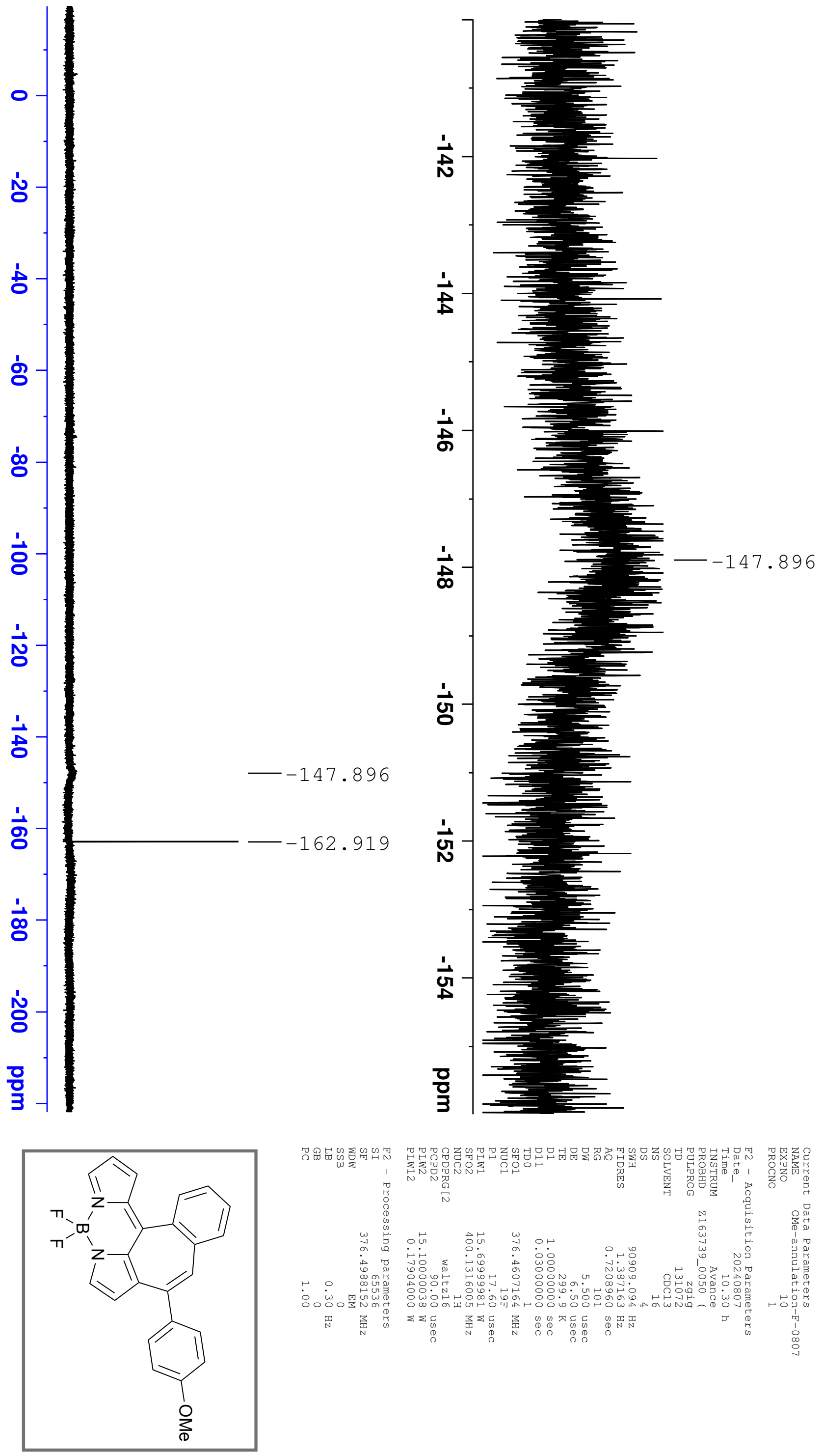



**Figure S34**. $^{19}$F NMR spectrum of **2b** in $CDCl_3$ at 25 °C.

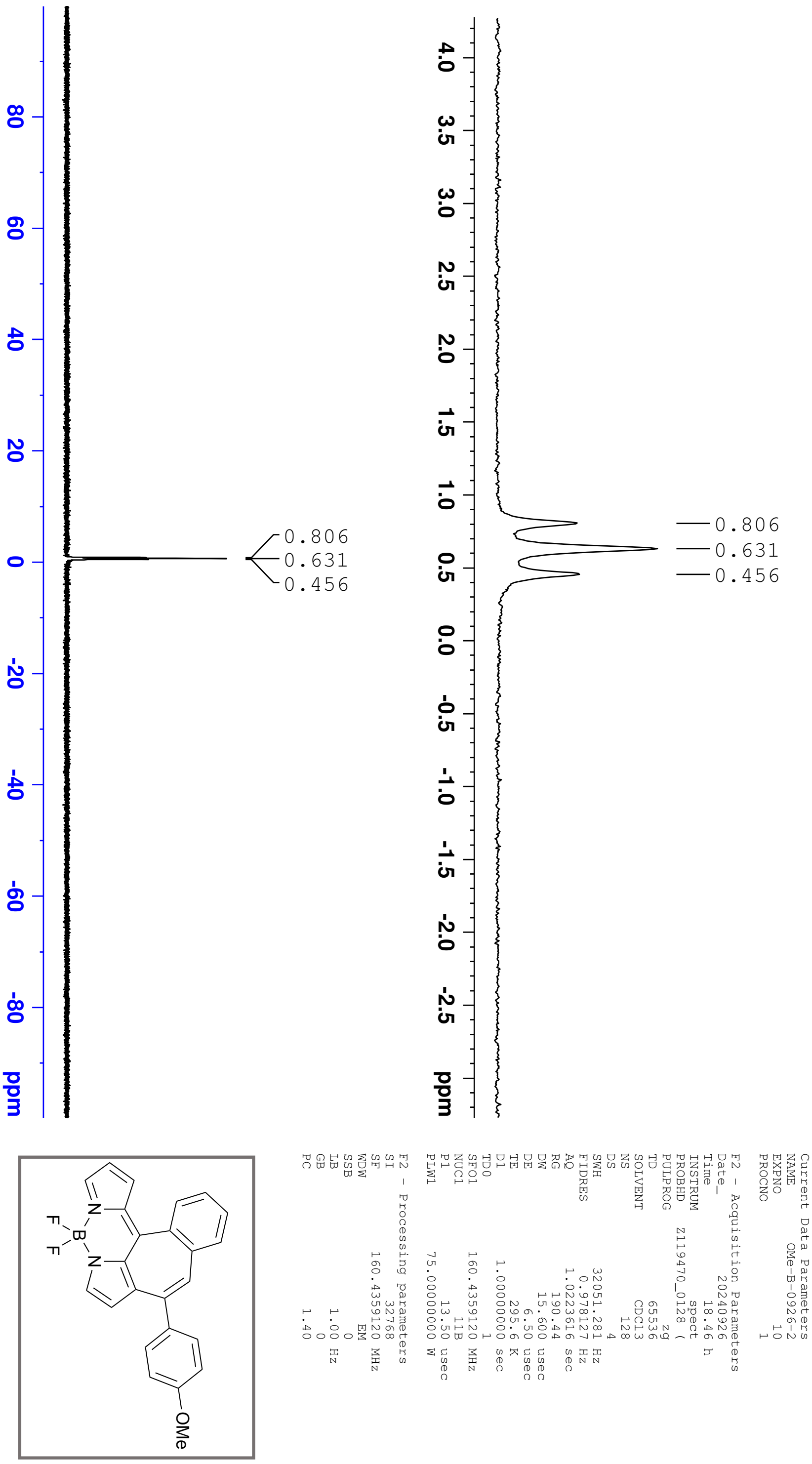



**Figure S35** $^{11}$B NMR spectrum of **2b** in $CDCl_3$ at 25 °C.

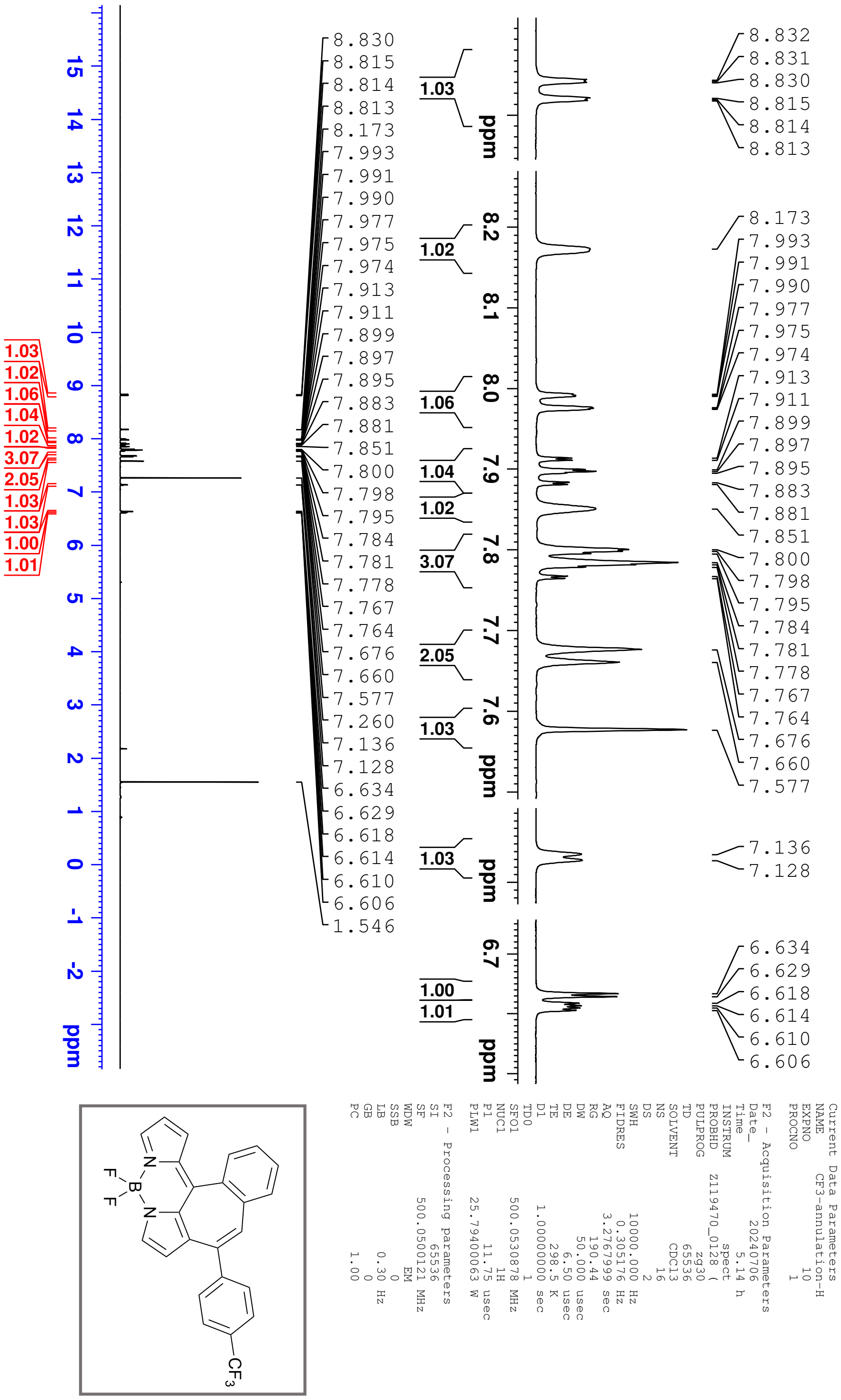


**Figure S36**. [1]H NMR spectrum of **2c** in $CDCl_3$ at 25 °C.

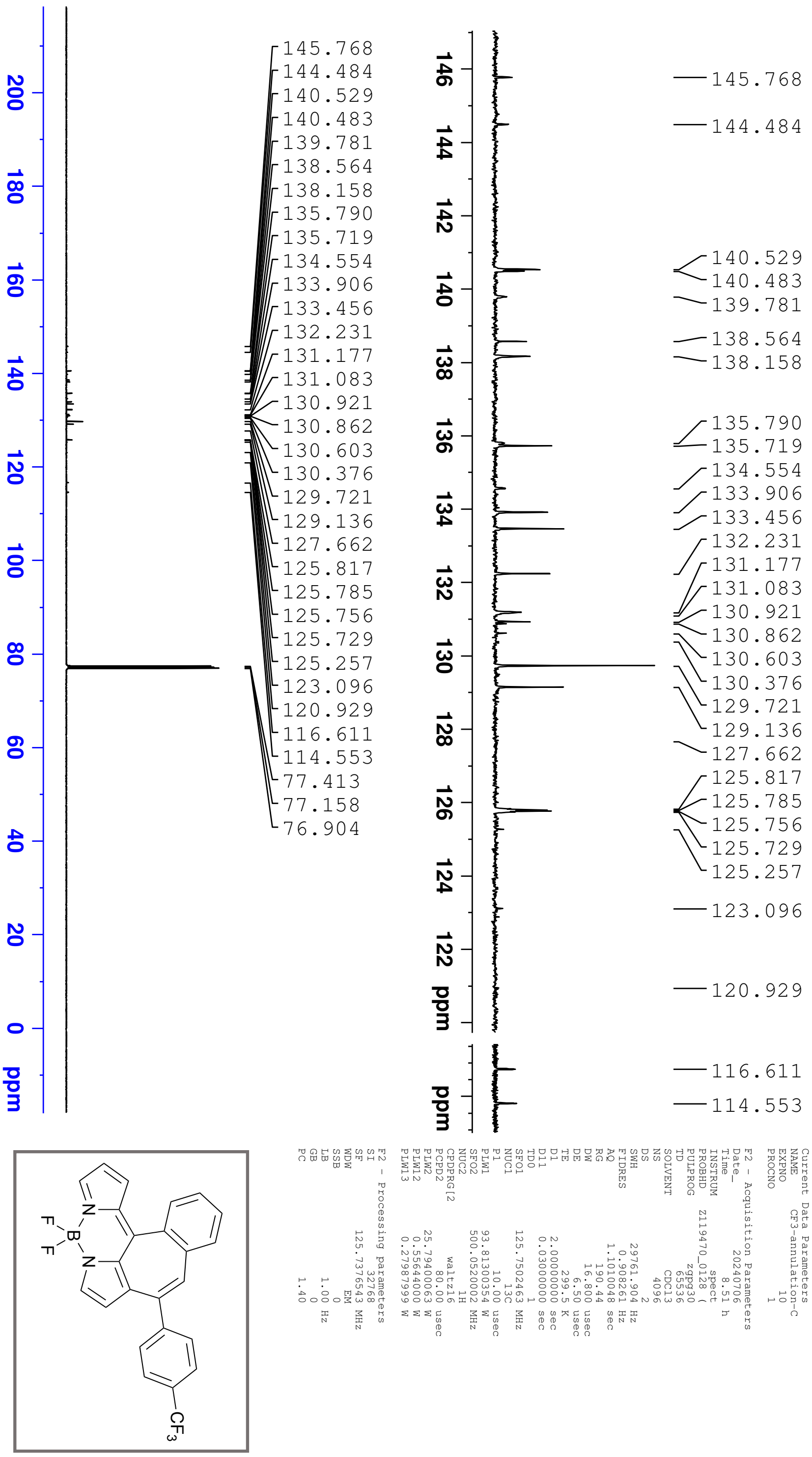



**Figure S37**. [13]C NMR spectrum of **2c** in $CDCl_3$ at 25 °C.

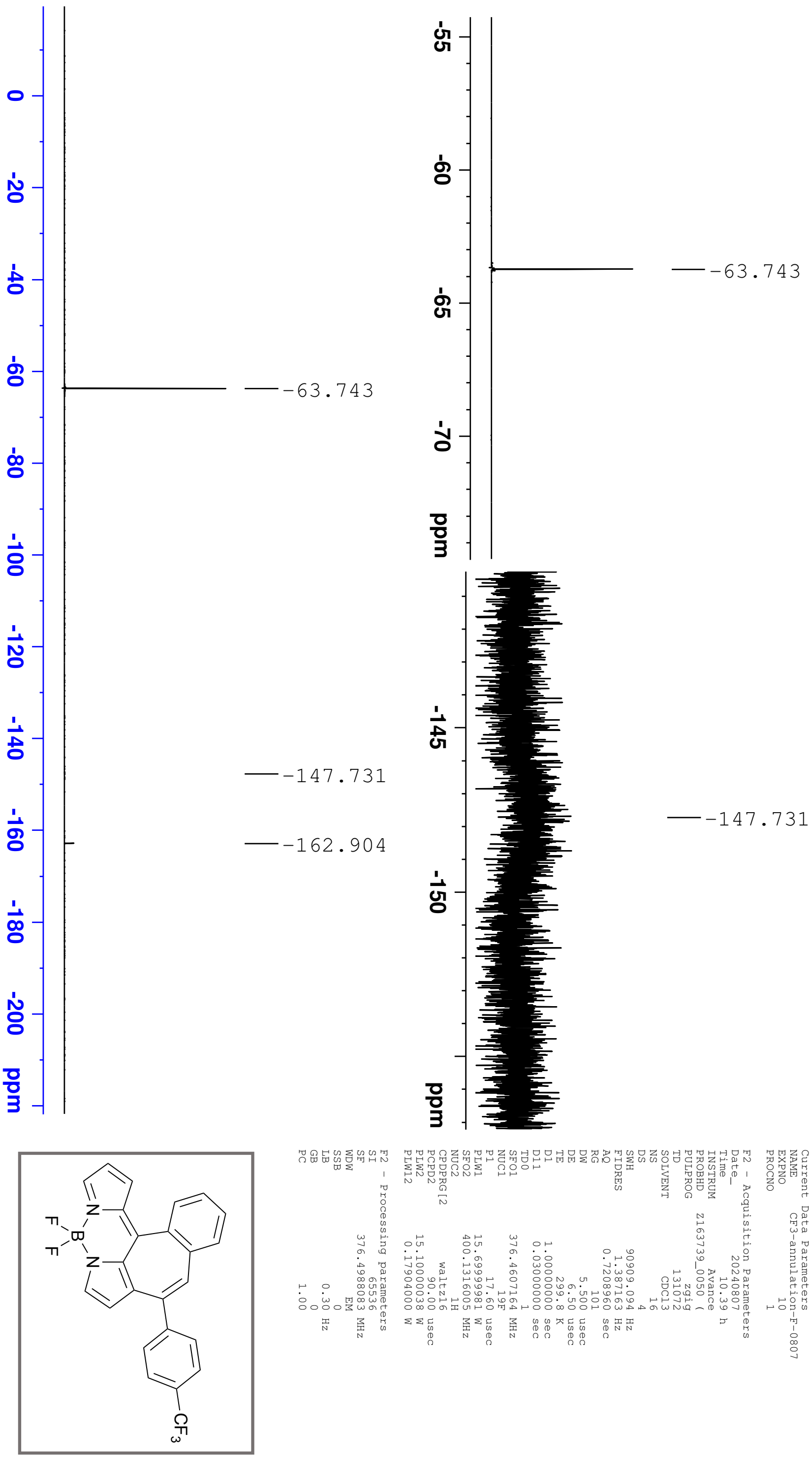



**Figure S38**. $^{19}F$ NMR spectrum of **2c** in $CDCl_3$ at 25 °C.

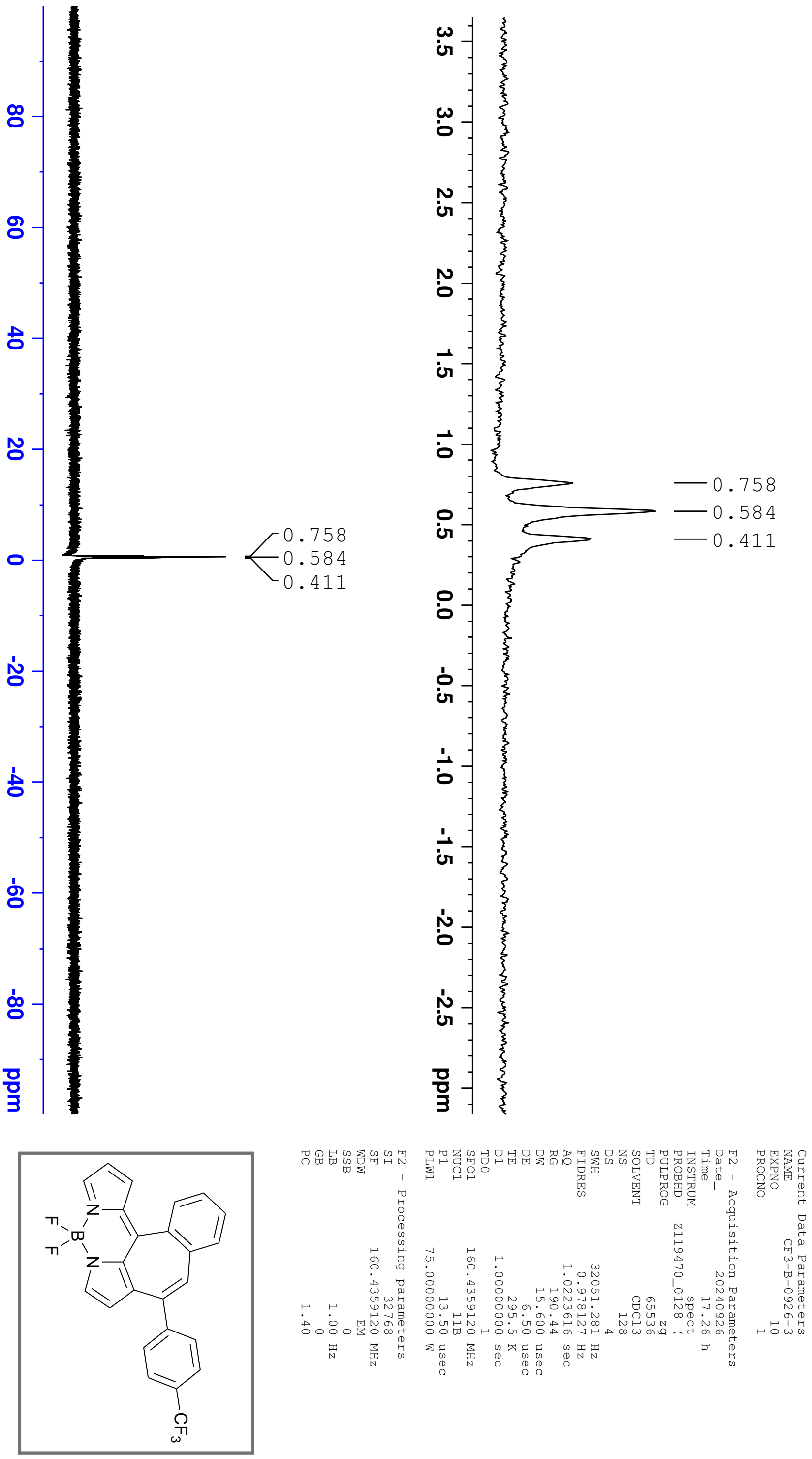



**Figure S39** $^{11}$B NMR spectrum of **2c** in $CDCl_3$ at 25 °C.

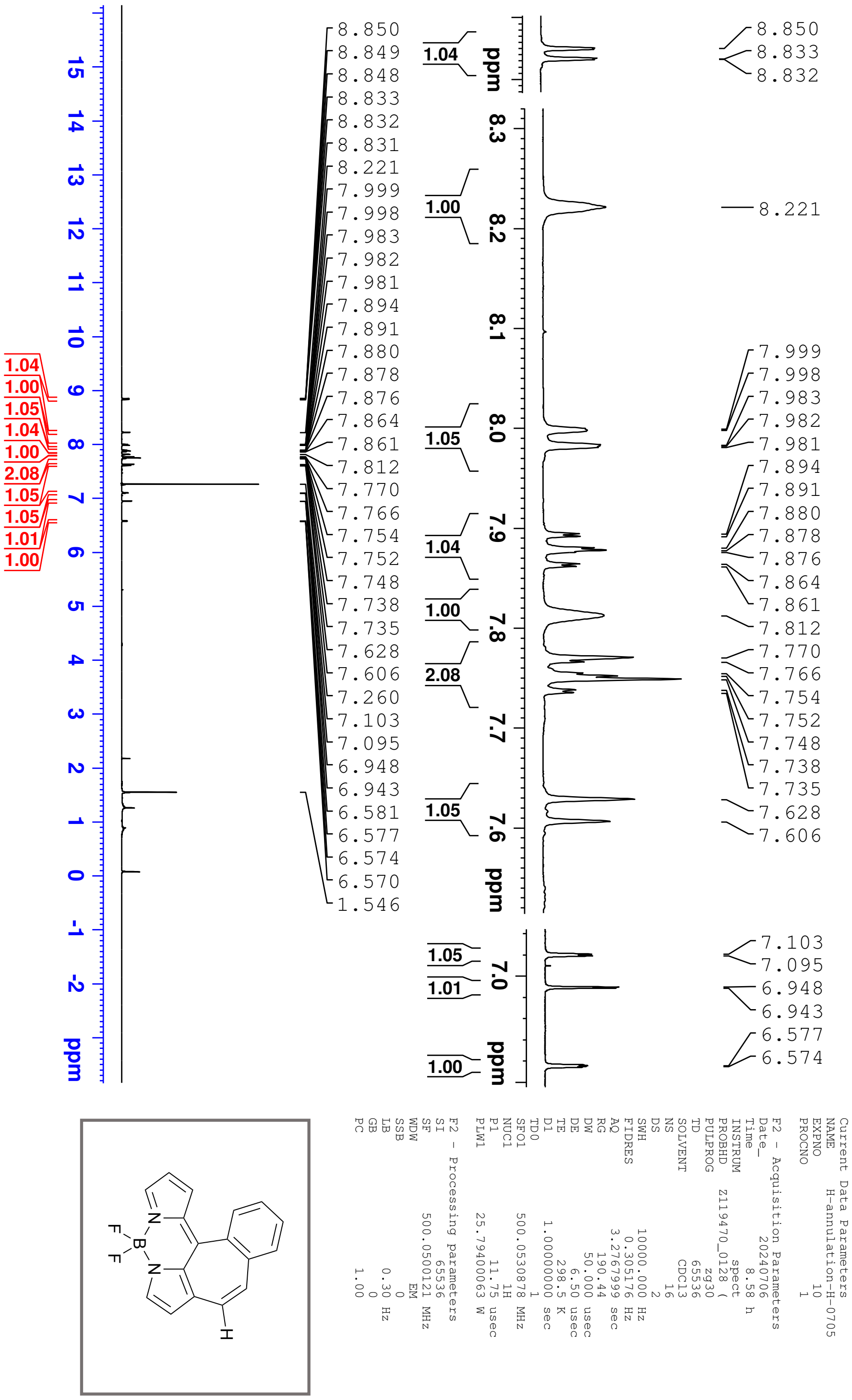



**Figure S40**. [1]H NMR spectrum of **2d** in $CDCl_3$ at 25 °C.

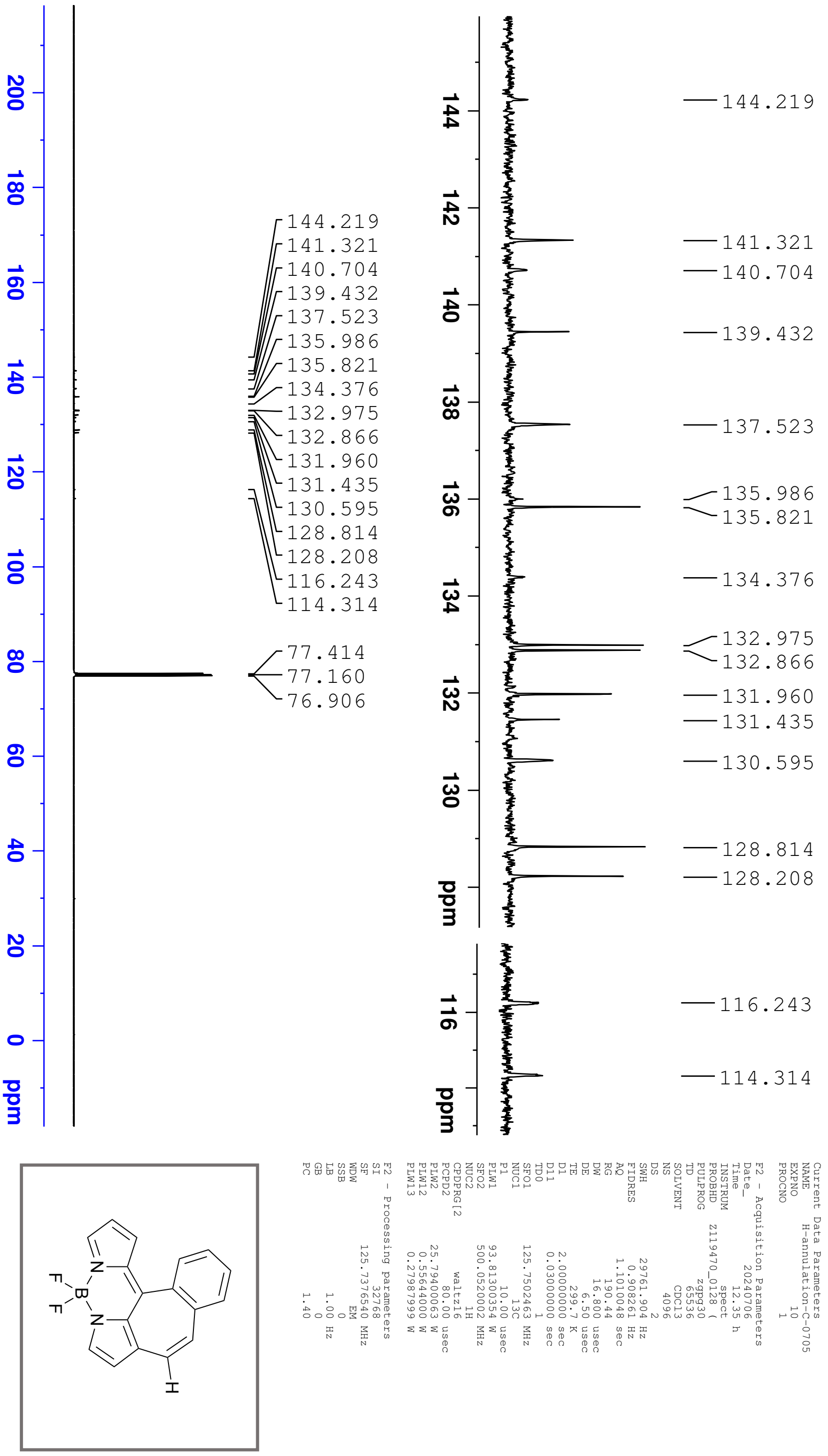



**Figure S41**. [13]C NMR spectrum of **2d** in $CDCl_3$ at 25 °C.

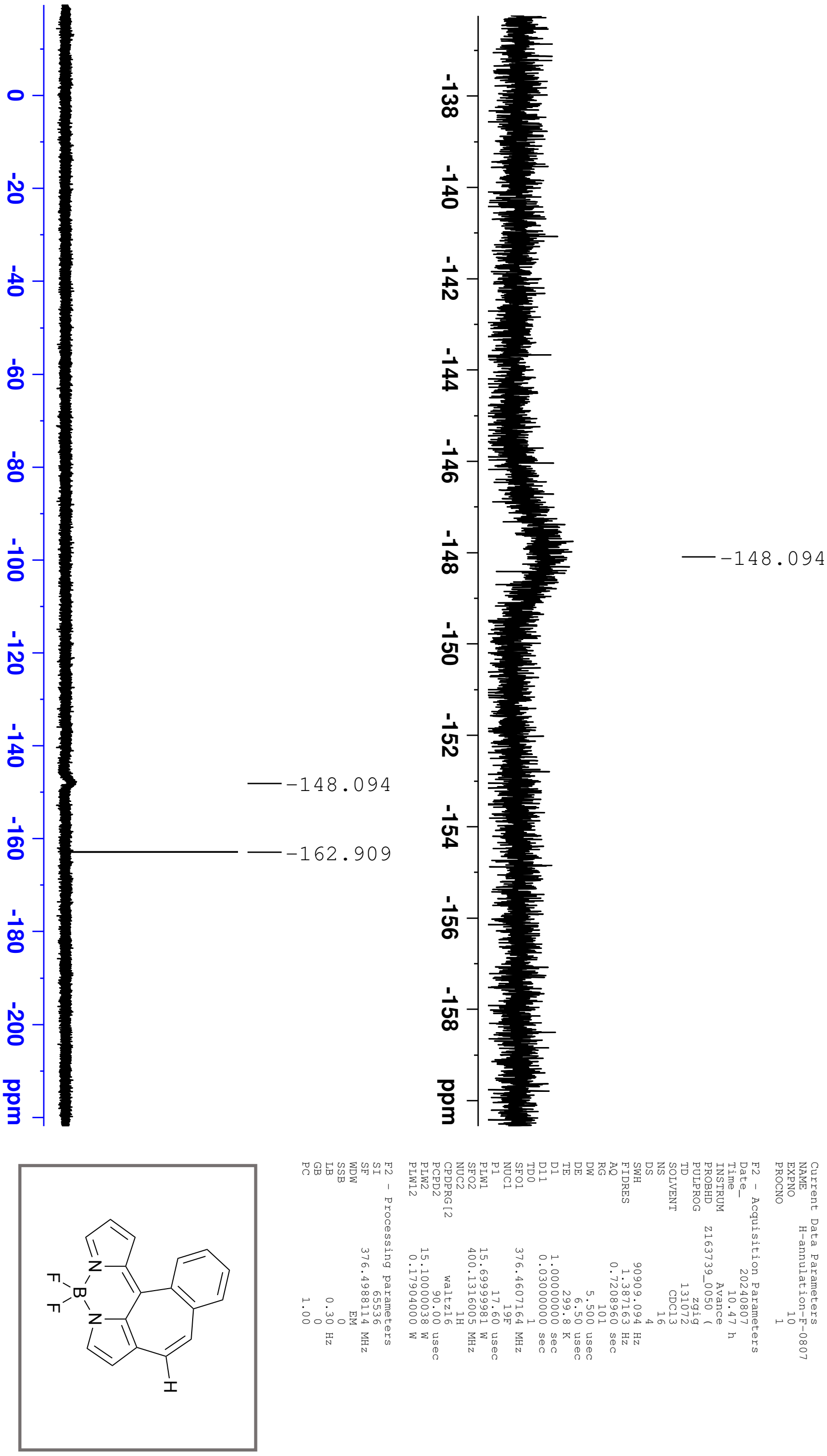



**Figure S42**. [19]F NMR spectrum of **2d** in $CDCl_3$ at 25 °C.

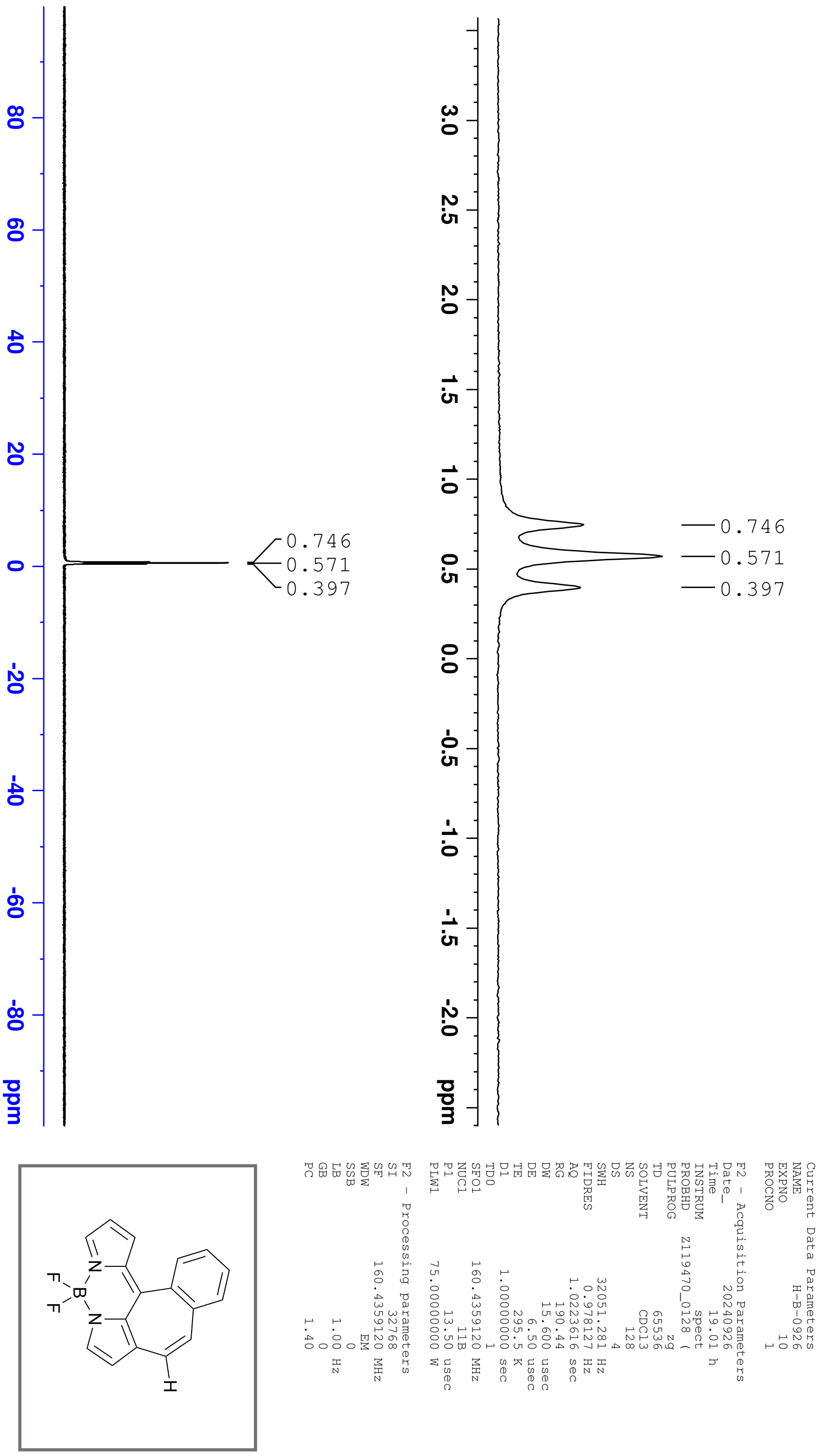



**Figure S43** $^{11}$B NMR spectrum of **2d** in $CDCl_3$ at 25 °C.

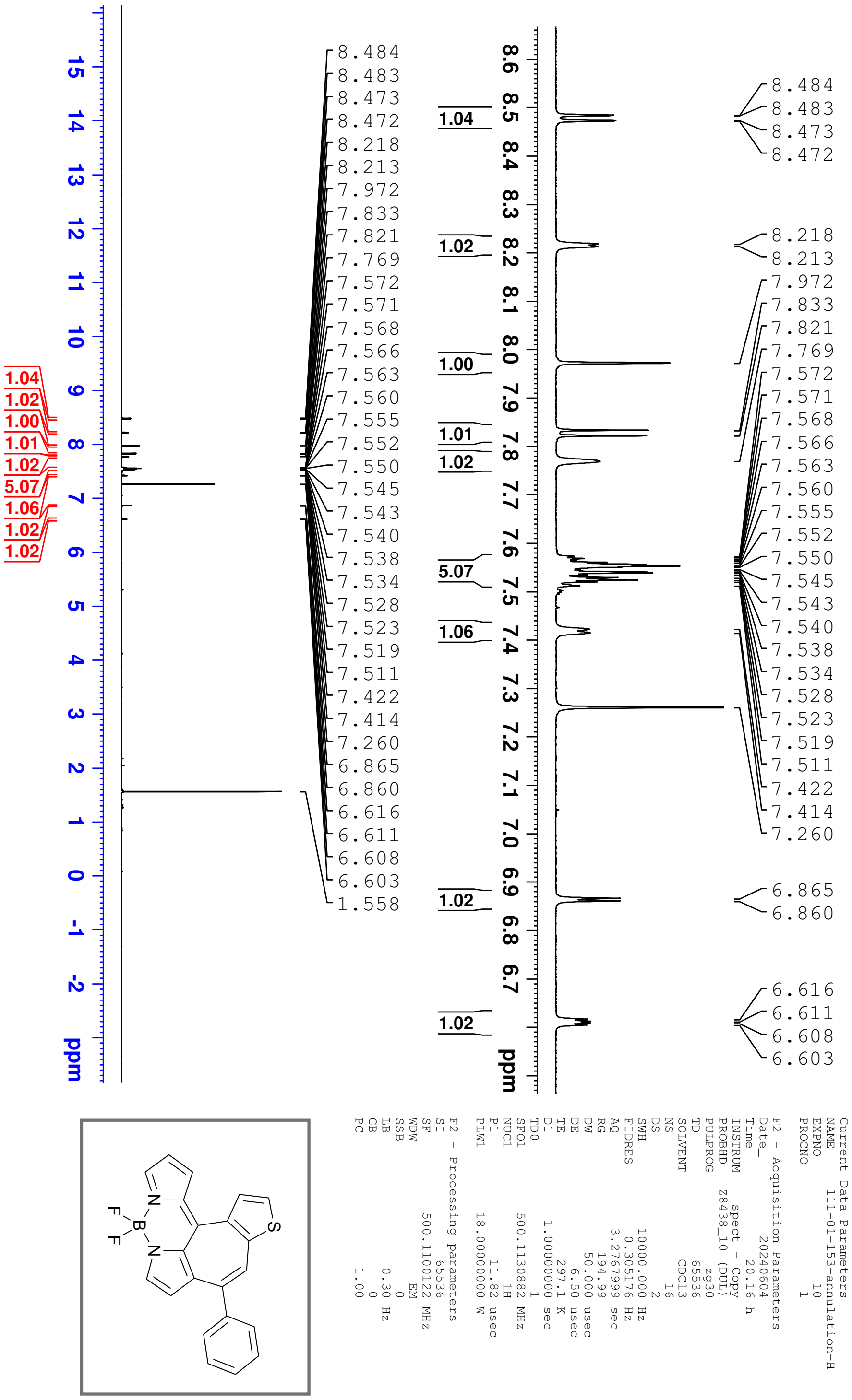


**Figure S44.** $^{1}H$ NMR spectrum of **2e** in $CDCl_3$ at 25 °C.

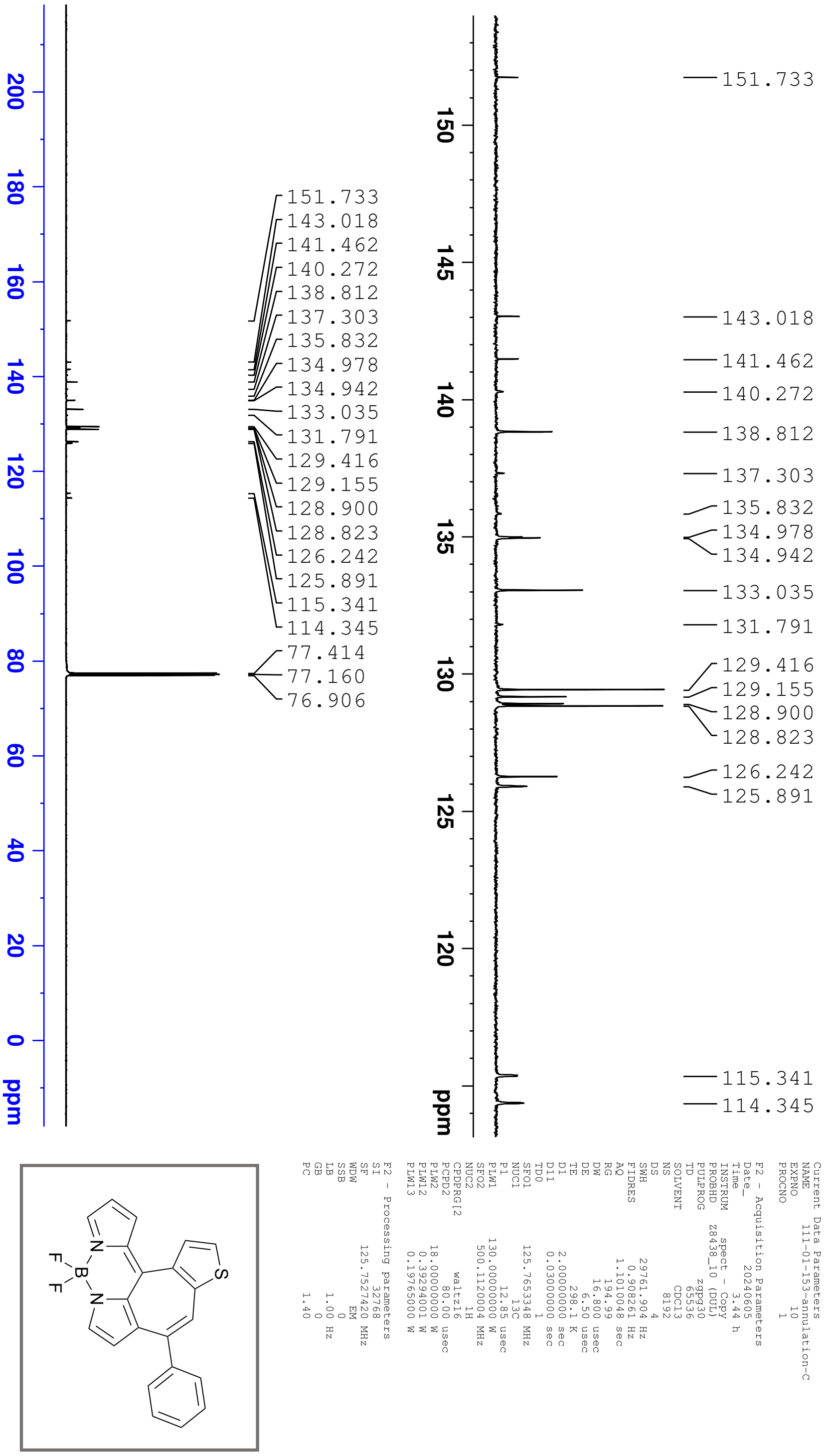



**Figure S45**. [13]C NMR spectrum of **2e** in $CDCl_3$ at 25 °C.

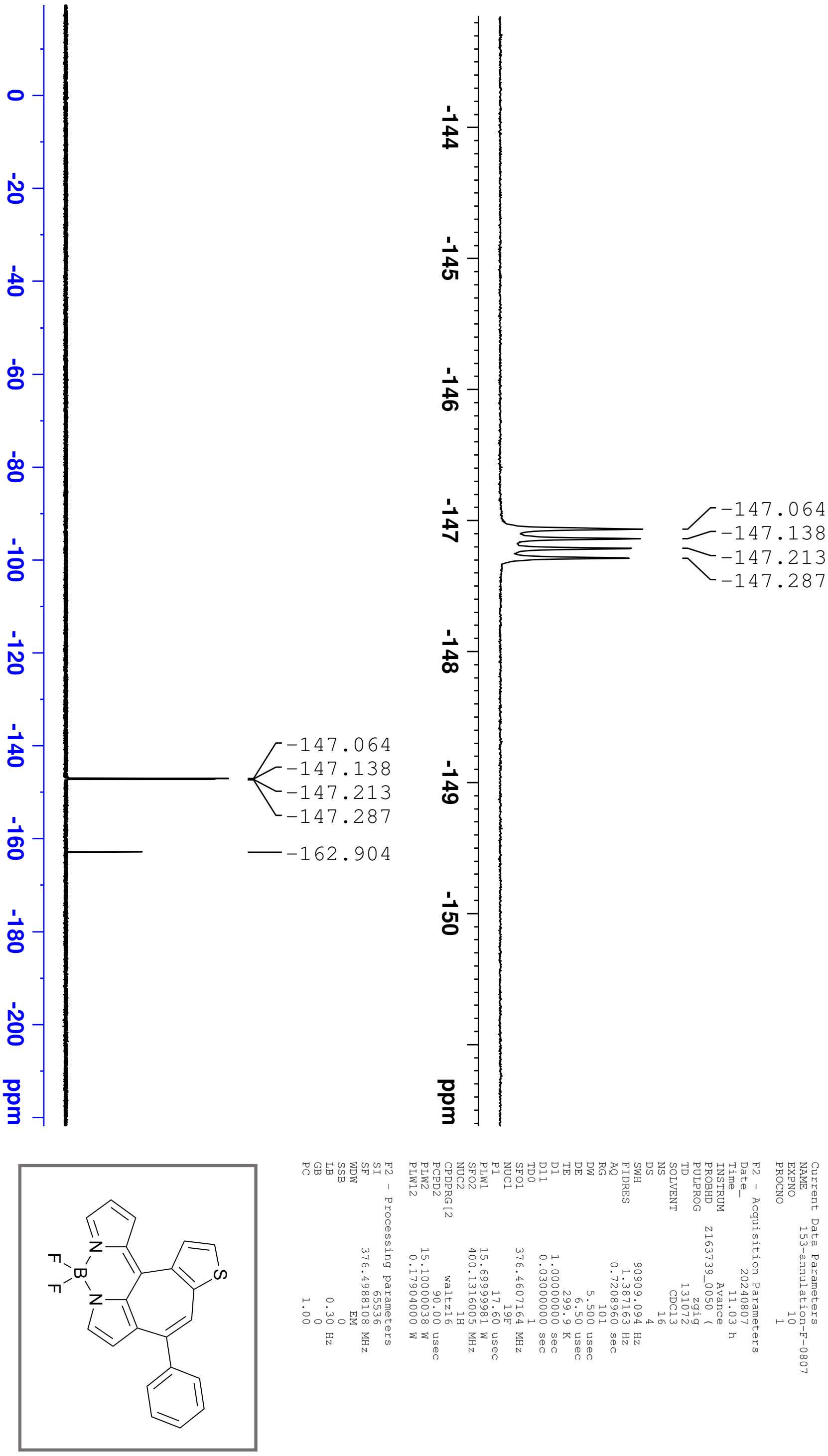
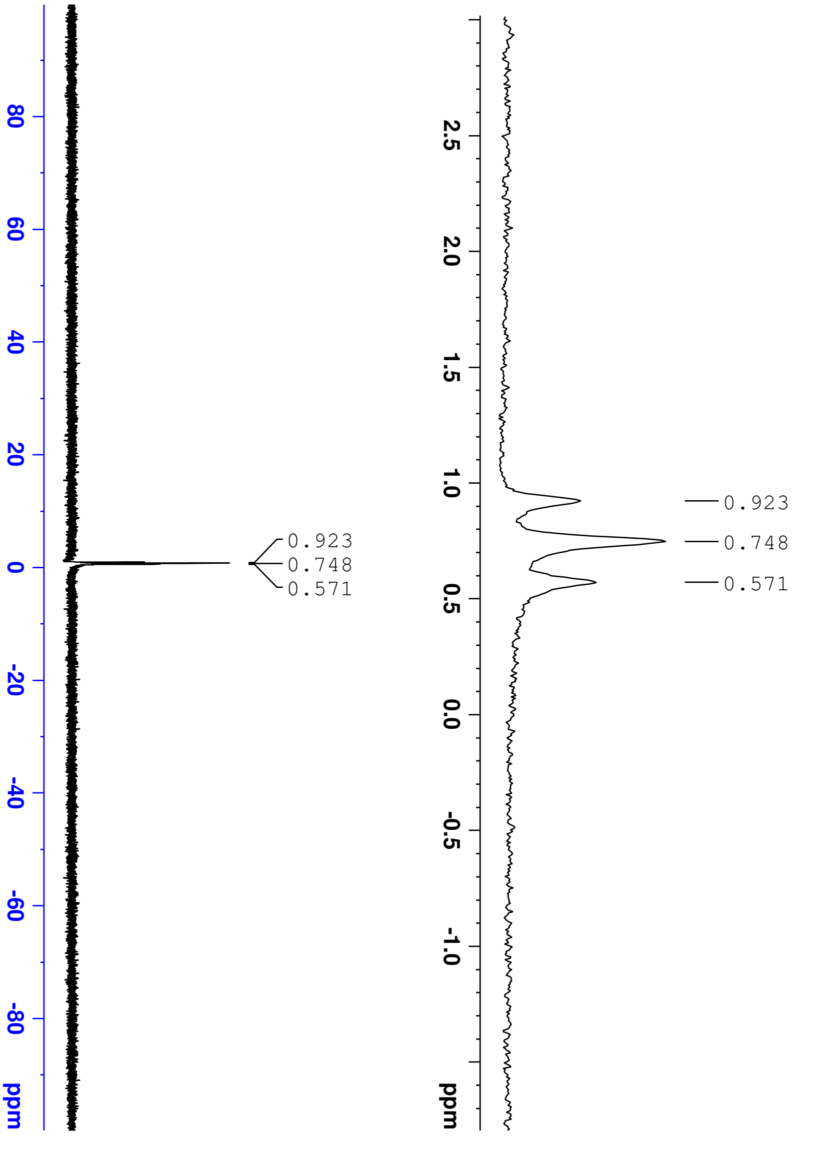



**Figure S46**. $^{19}F$ NMR spectrum of **2e** in $CDCl_3$ at 25 °C.



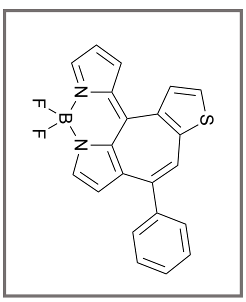



**Figure S47** $^{11}$B NMR spectrum of **2e** in $CDCl_3$ at 25 °C.

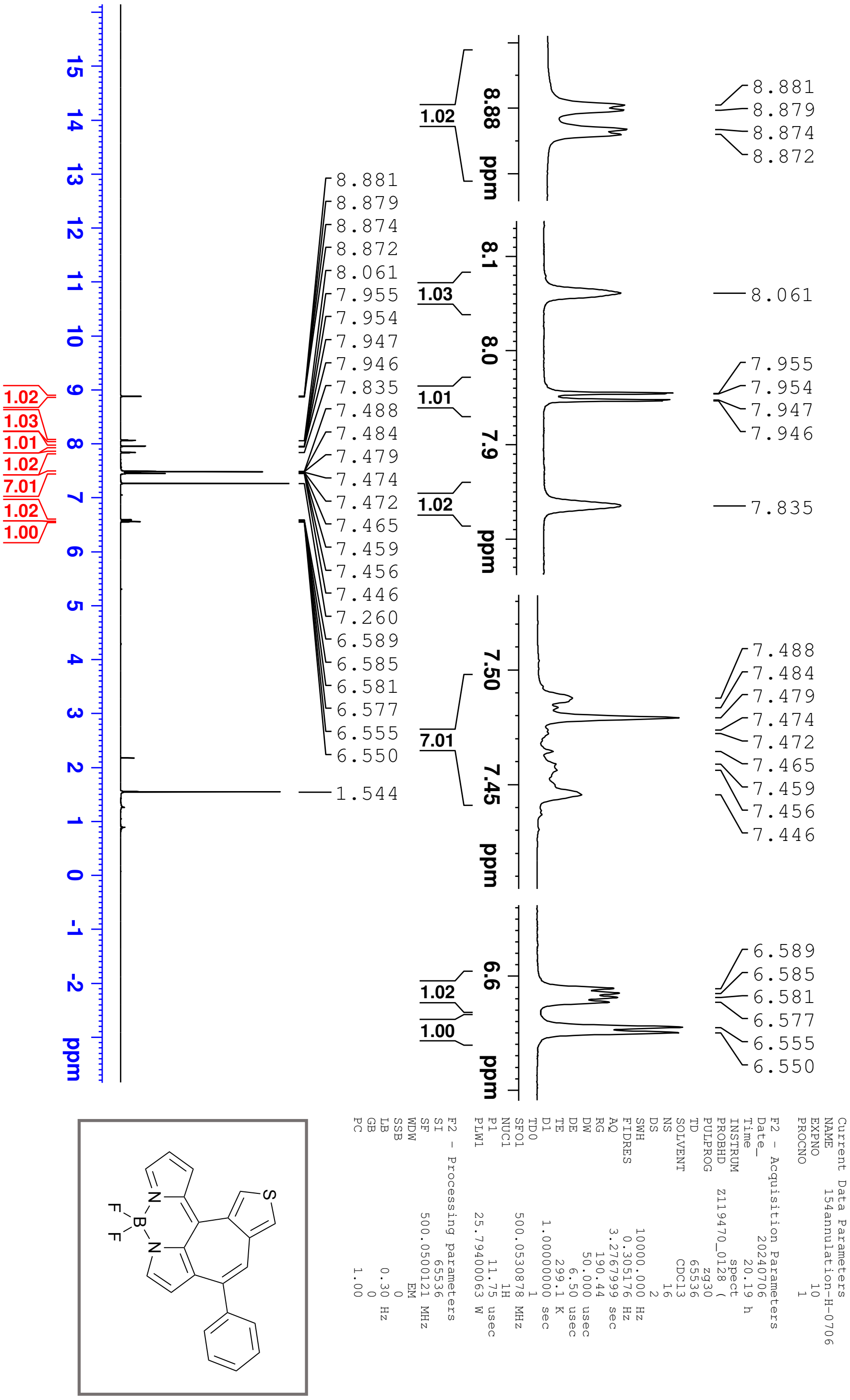



**Figure S48**. [1]H NMR spectrum of **2f** in $CDCl_3$ at 25 °C.

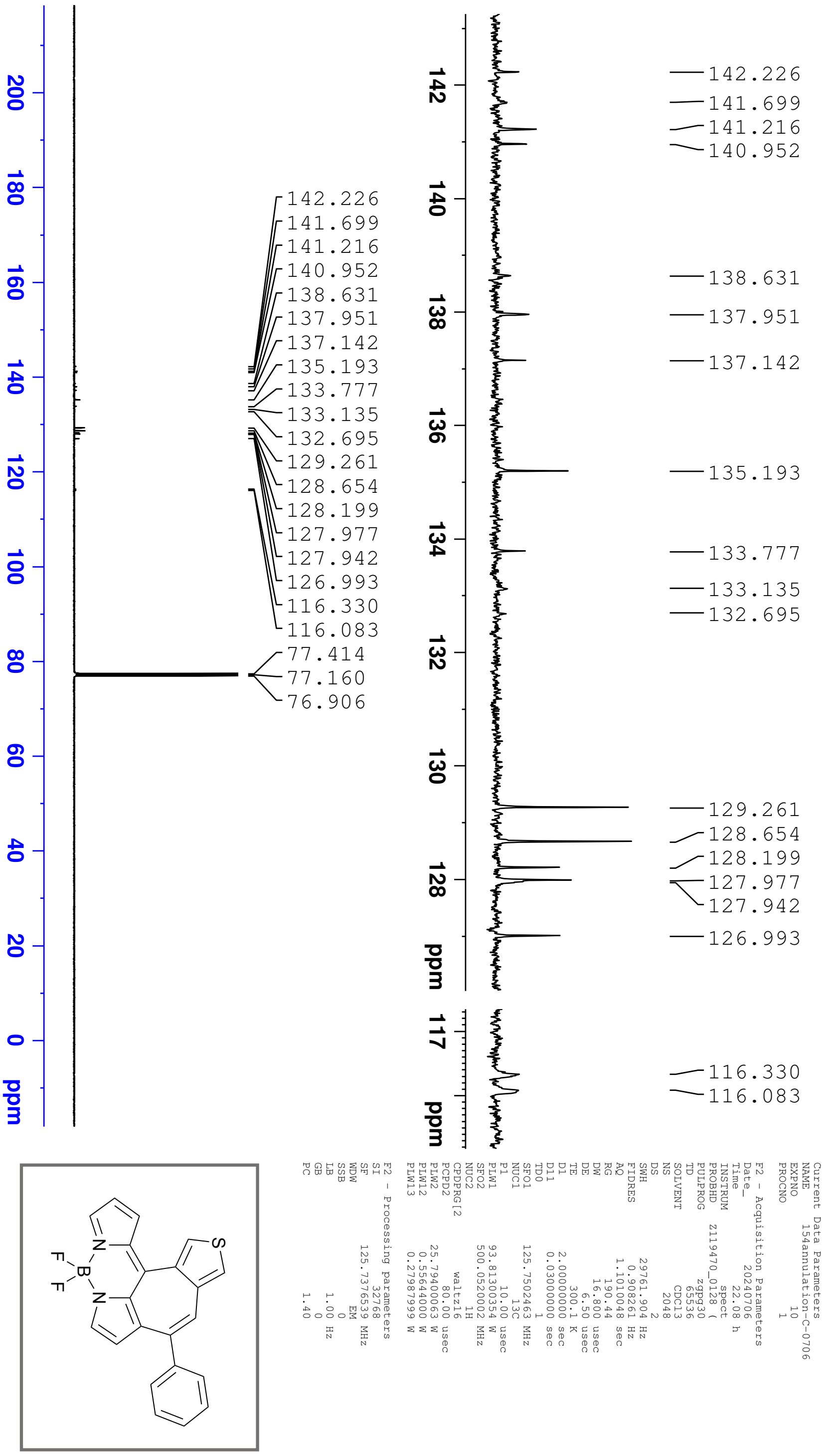



**Figure S49**. [13]C NMR spectrum of **2f** in $CDCl_3$ at 25 °C.

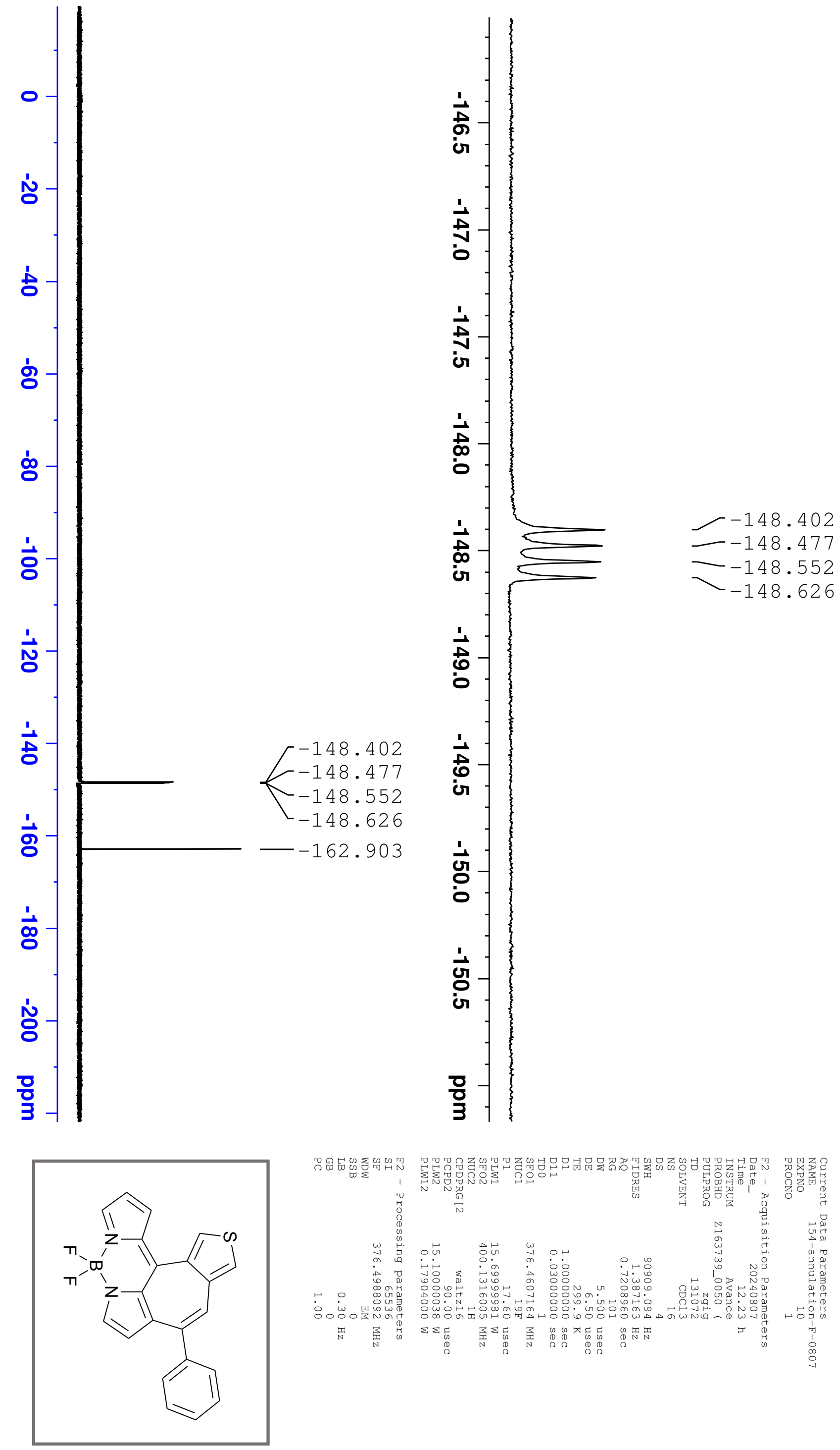



**Figure S50**. $^{19}$F NMR spectrum of **2f** in $CDCl_3$ at 25 °C.

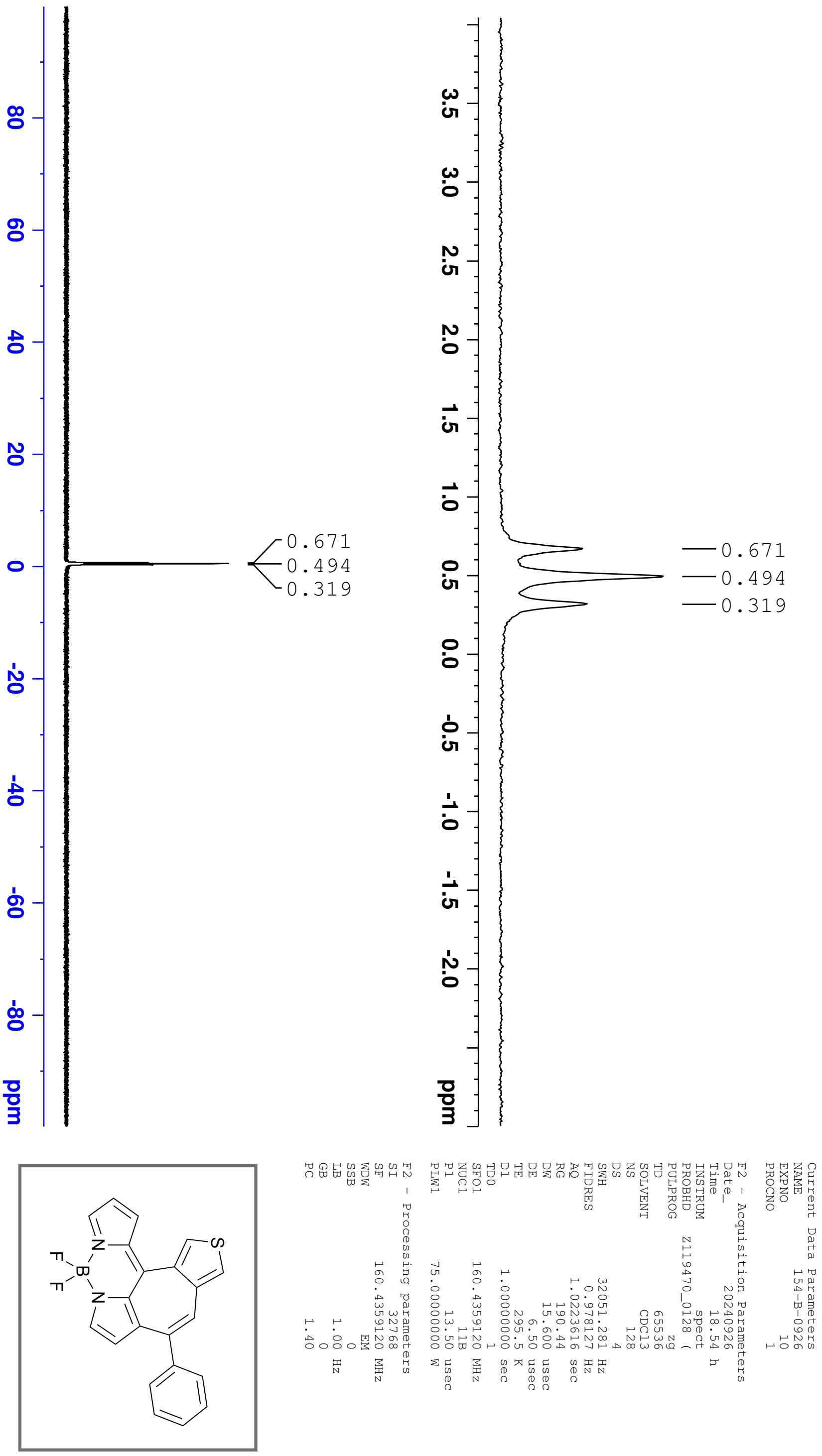



**Figure S51** $^{11}B$ NMR spectrum of **2f** in $CDCl_3$ at 25 °C.

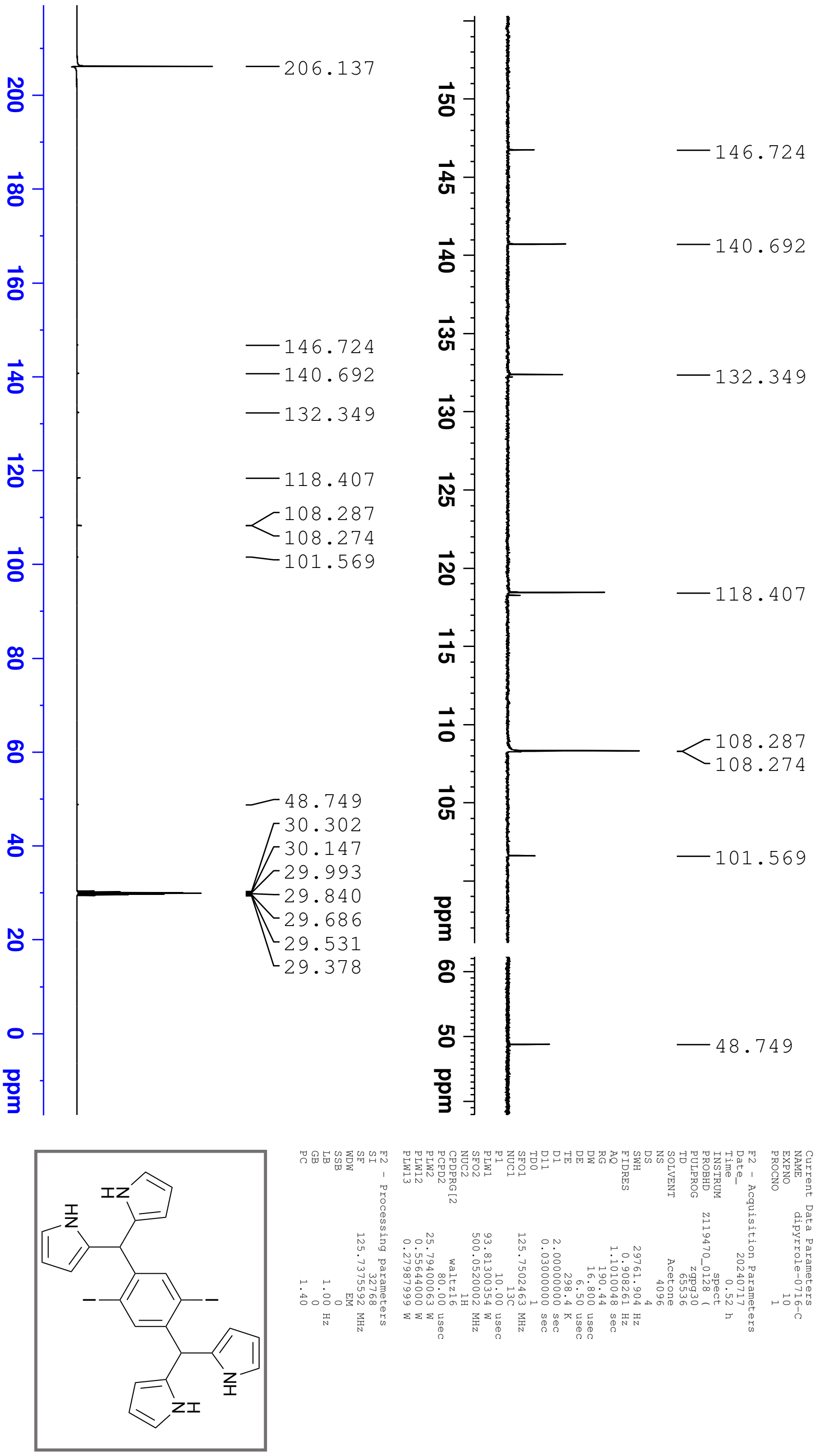



**Figure S52**. [1]H NMR spectrum of **S4** in acetone-$d_6$ at 25 °C.

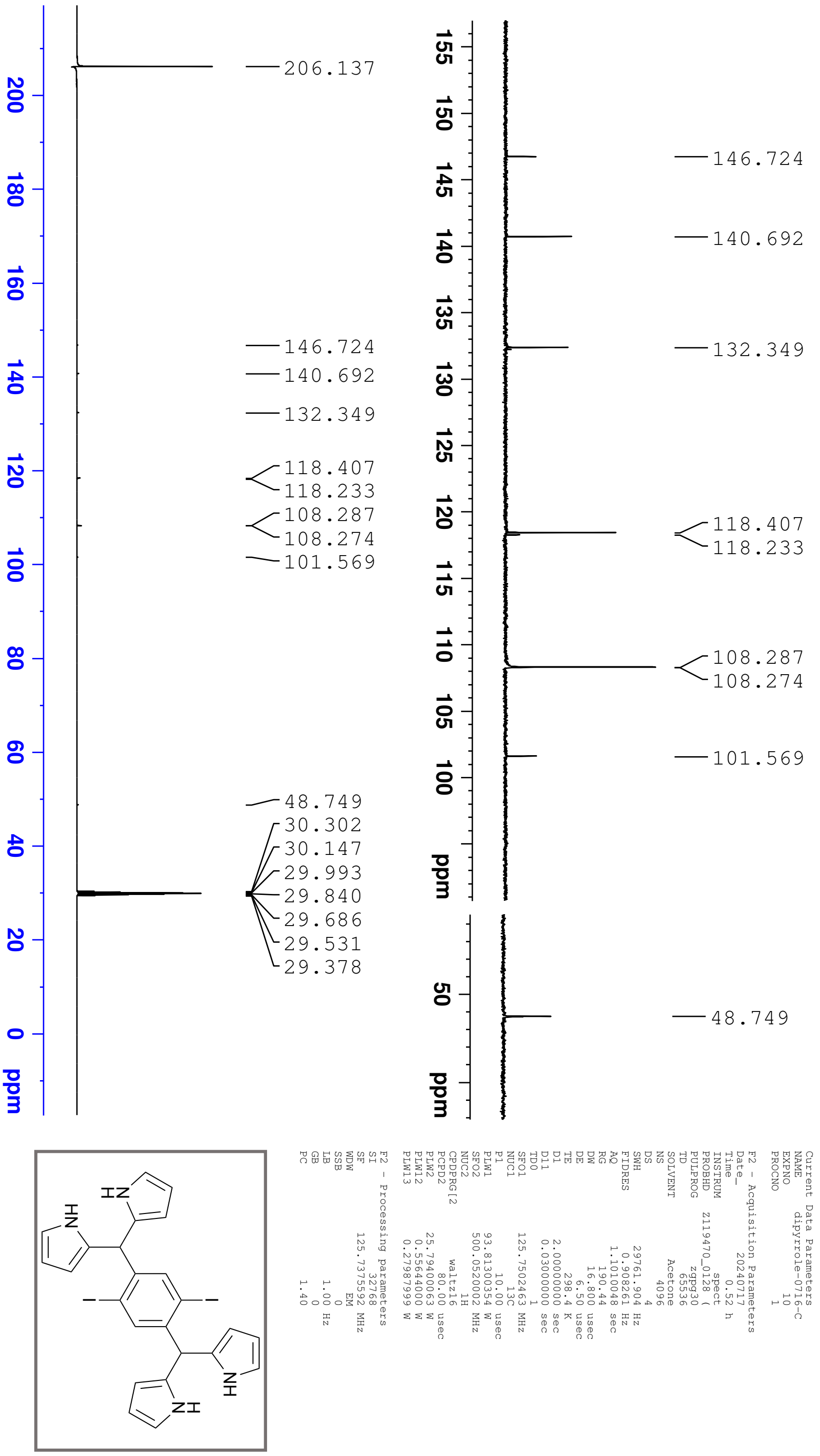



**Figure S53**. $^{13}C$ NMR spectrum of **S4** in acetone-$d_6$ at 25 °C.

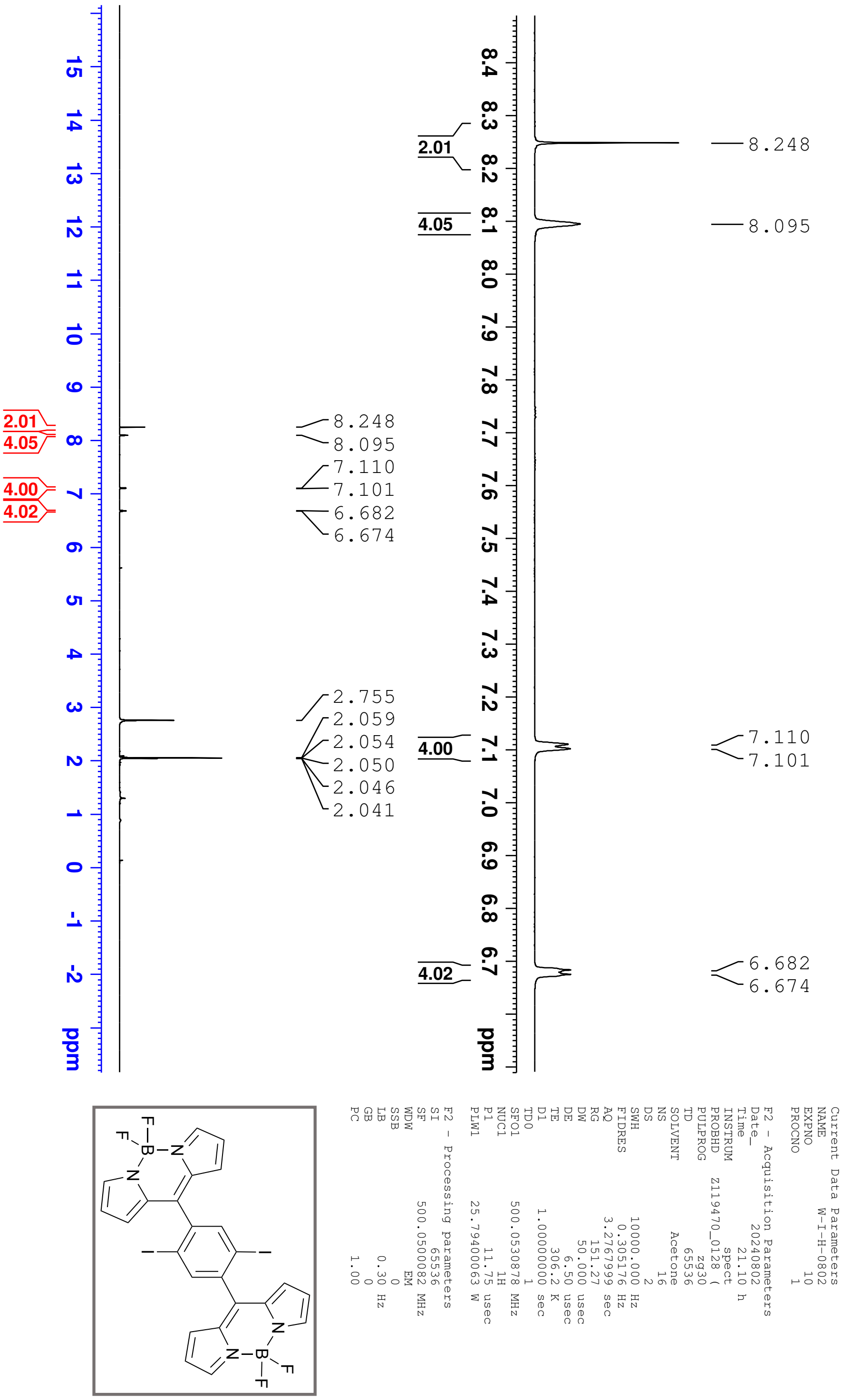



**Figure S54**. [1]H NMR spectrum of **S5** in acetone-$d_6$ at 25 °C.

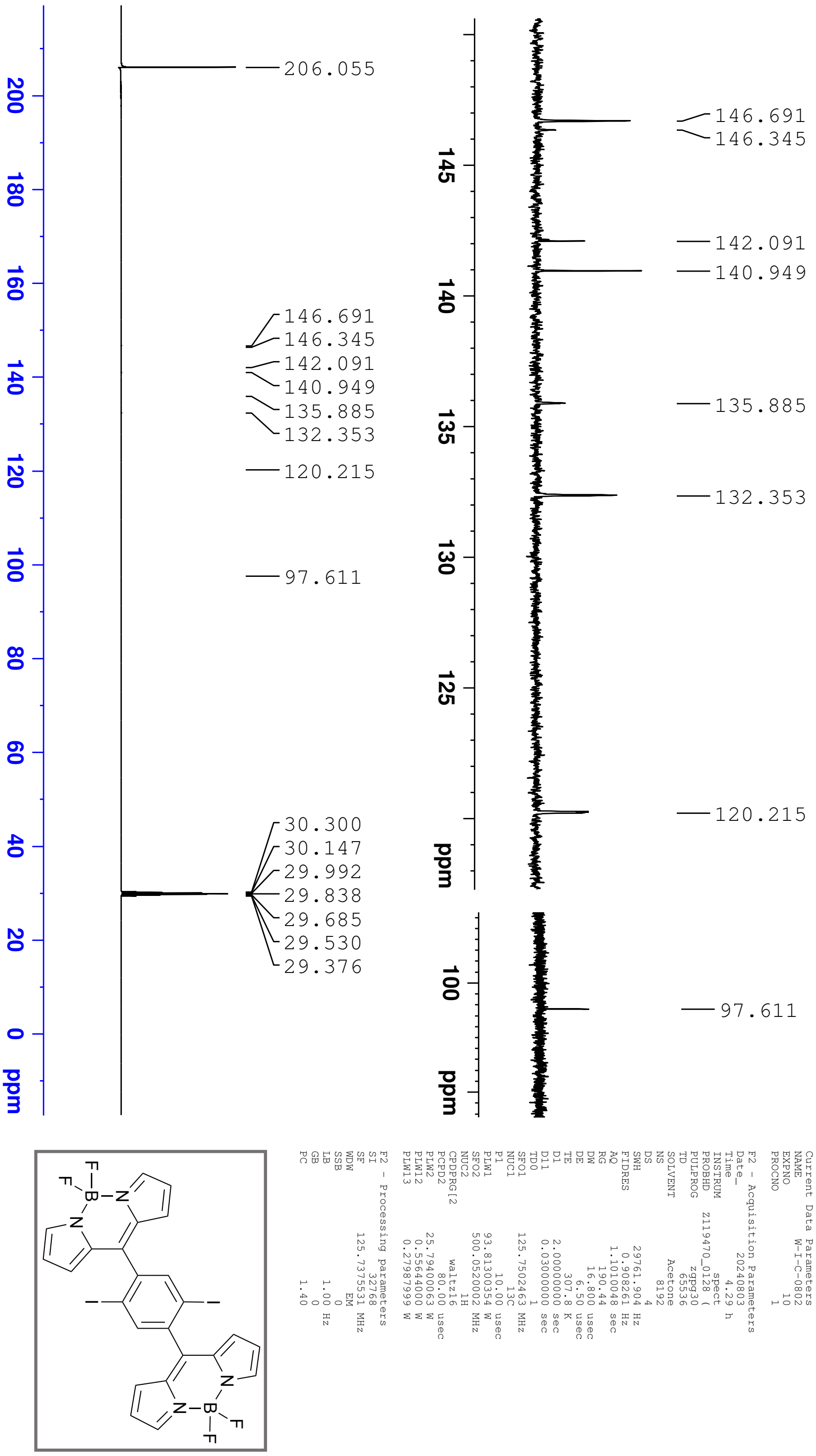



**Figure S55**. ${}^{13}C$ NMR spectrum of **S5** in acetone-$d_6$ at 25 °C.

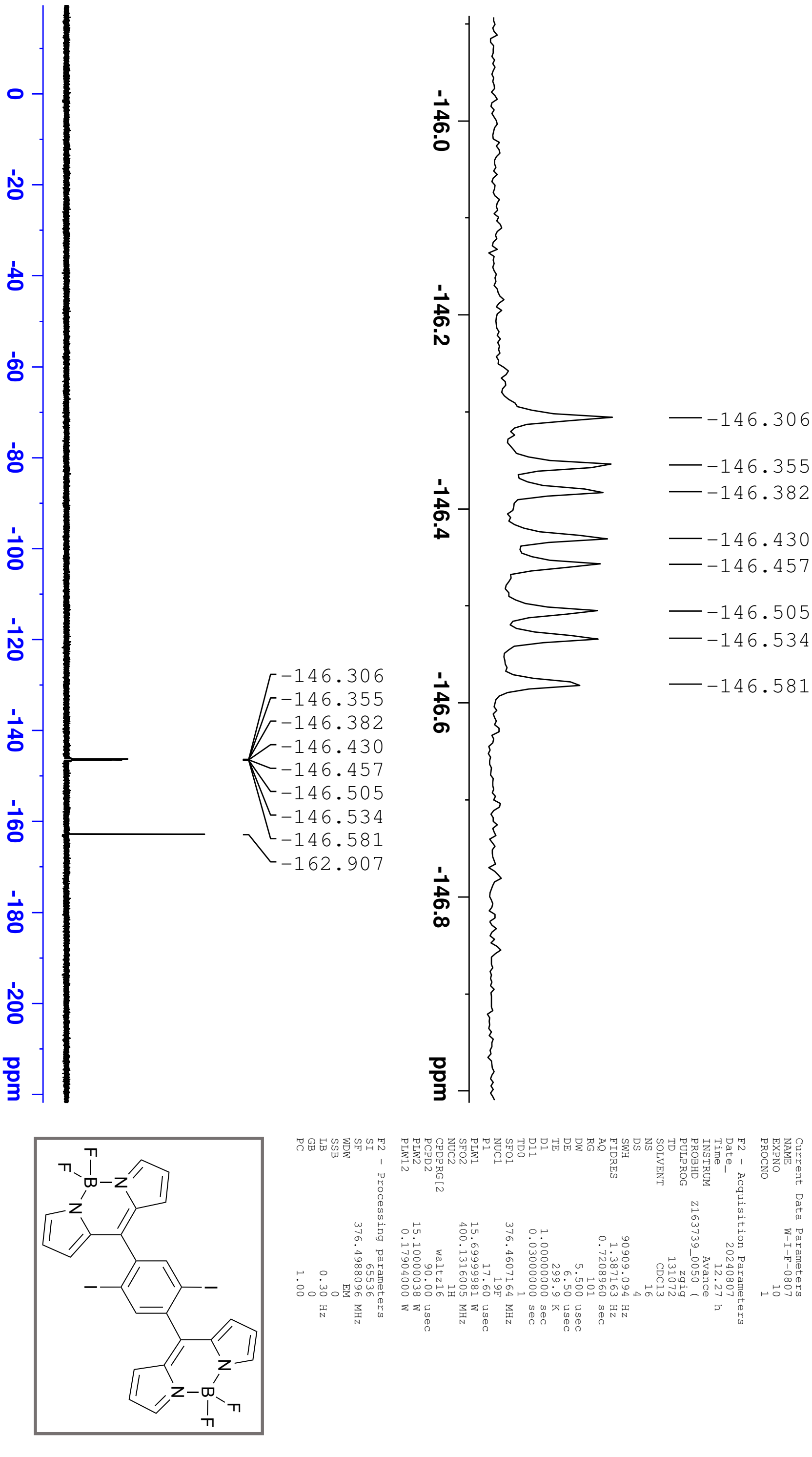



**Figure S56**. [19]F NMR spectrum of **S5** in $CDCl_3$ at 25 °C.

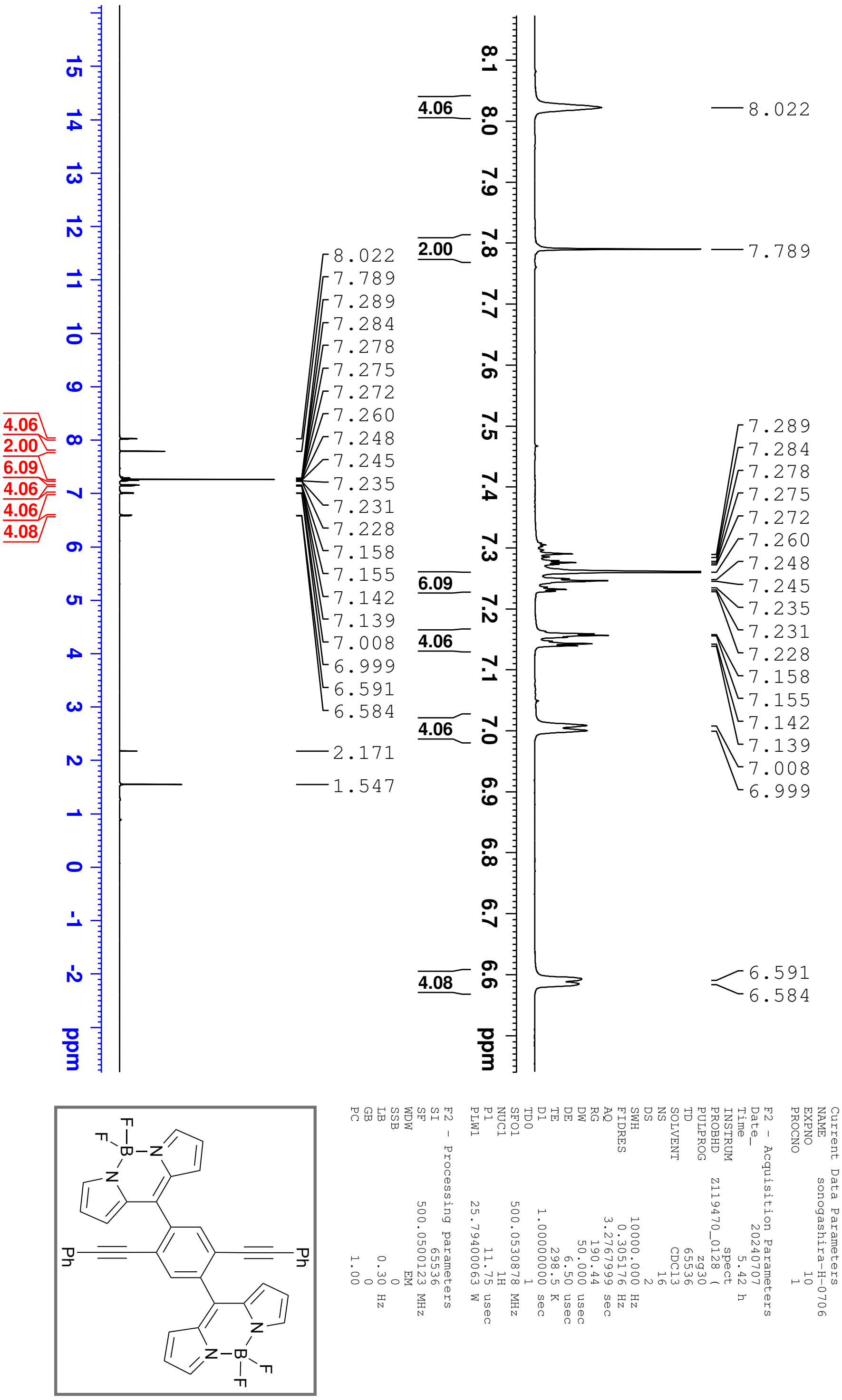


**Figure S57**. $^{1}$H NMR spectrum of **3** in $CDCl_3$ at 25 °C.

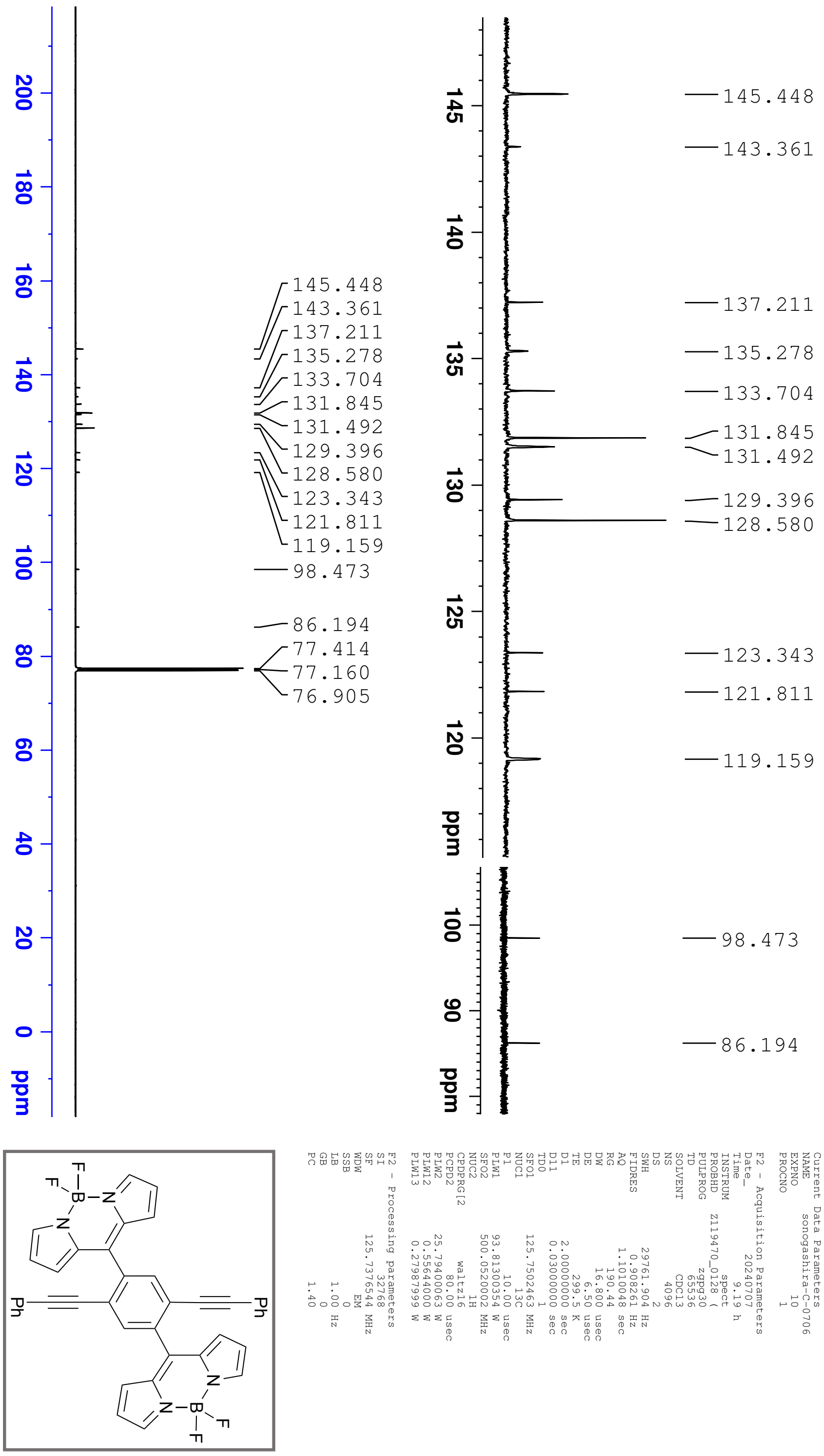



**Figure S58**. $^{13}C$ NMR spectrum of **3** in $CDCl_3$ at 25 °C.

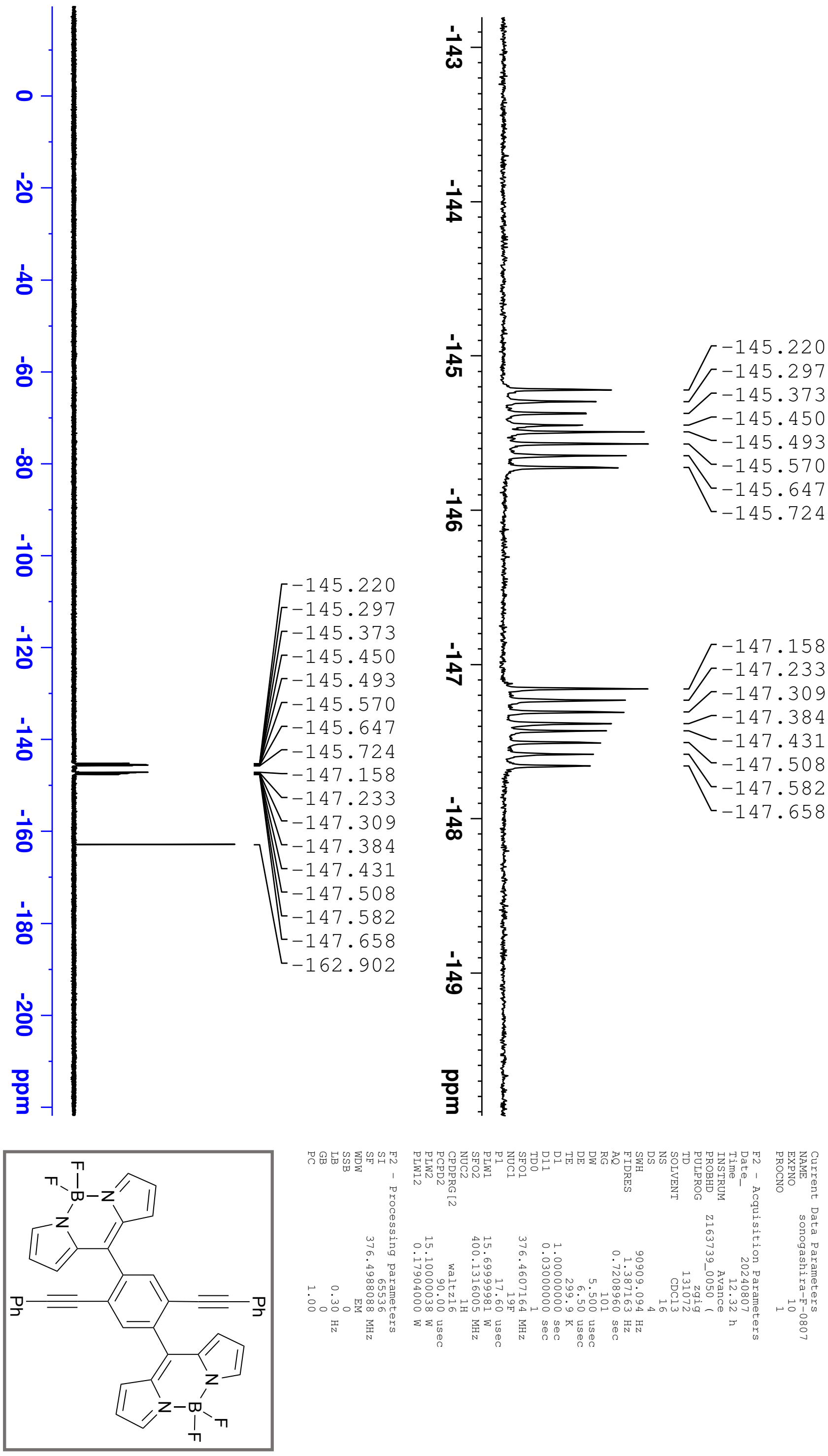



**Figure S59**. [19]F NMR spectrum of **3** in $CDCl_3$ at 25 °C.

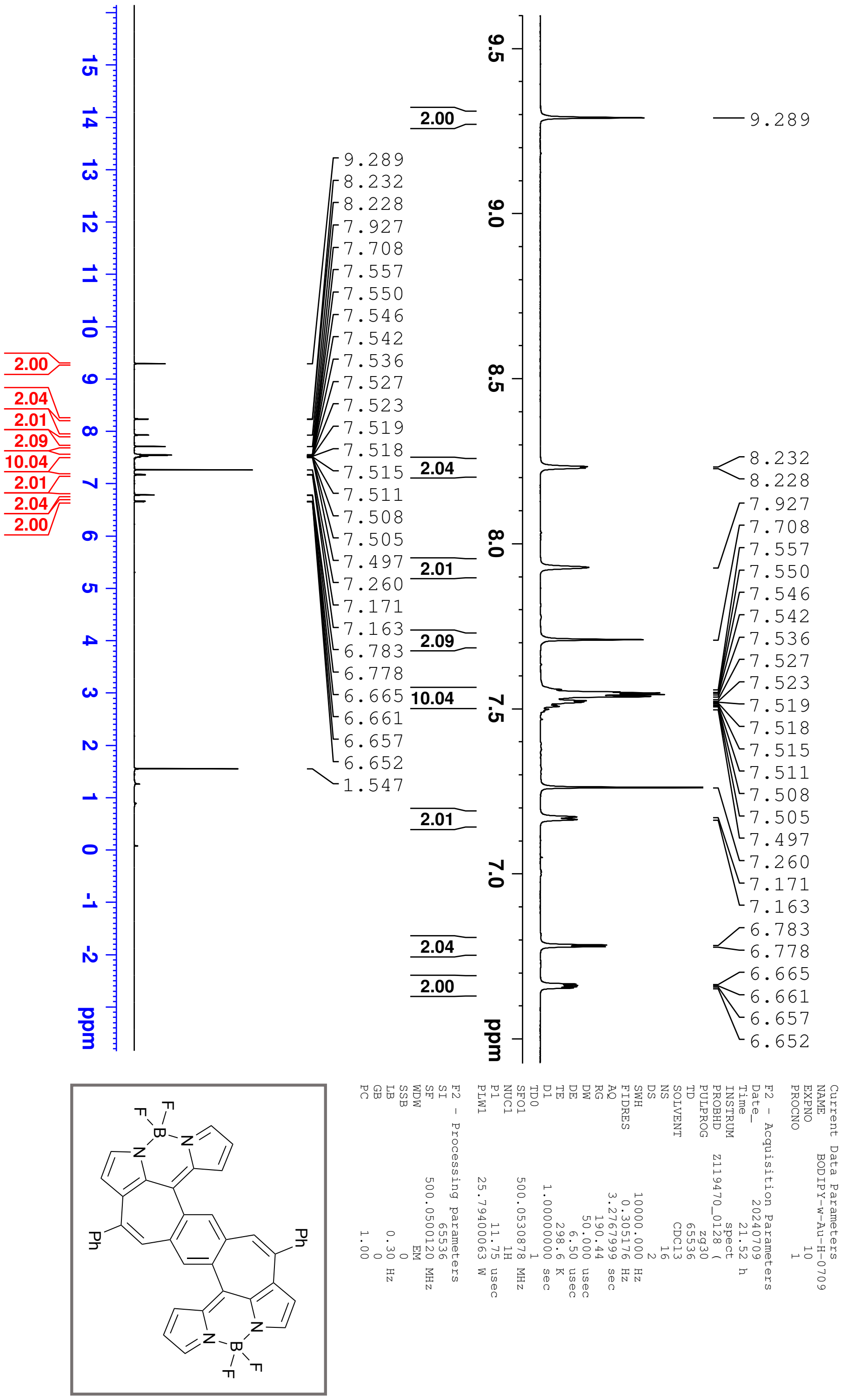


**Figure S60**. $^{1}$H NMR spectrum of **4** in $CDCl_3$ at 25 °C.

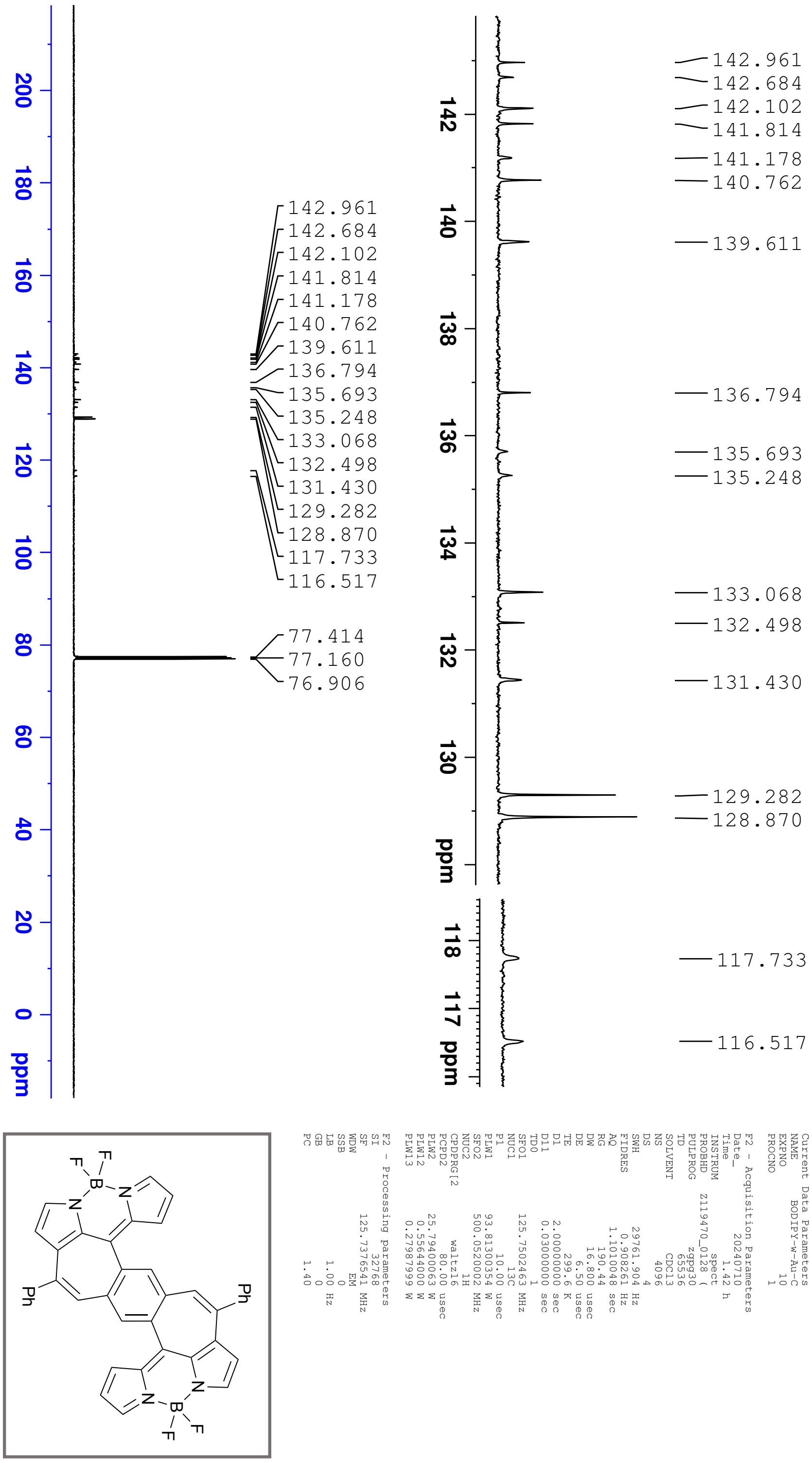



**Figure S61**. [13]C NMR spectrum of **4** in $CDCl_3$ at 25 °C.

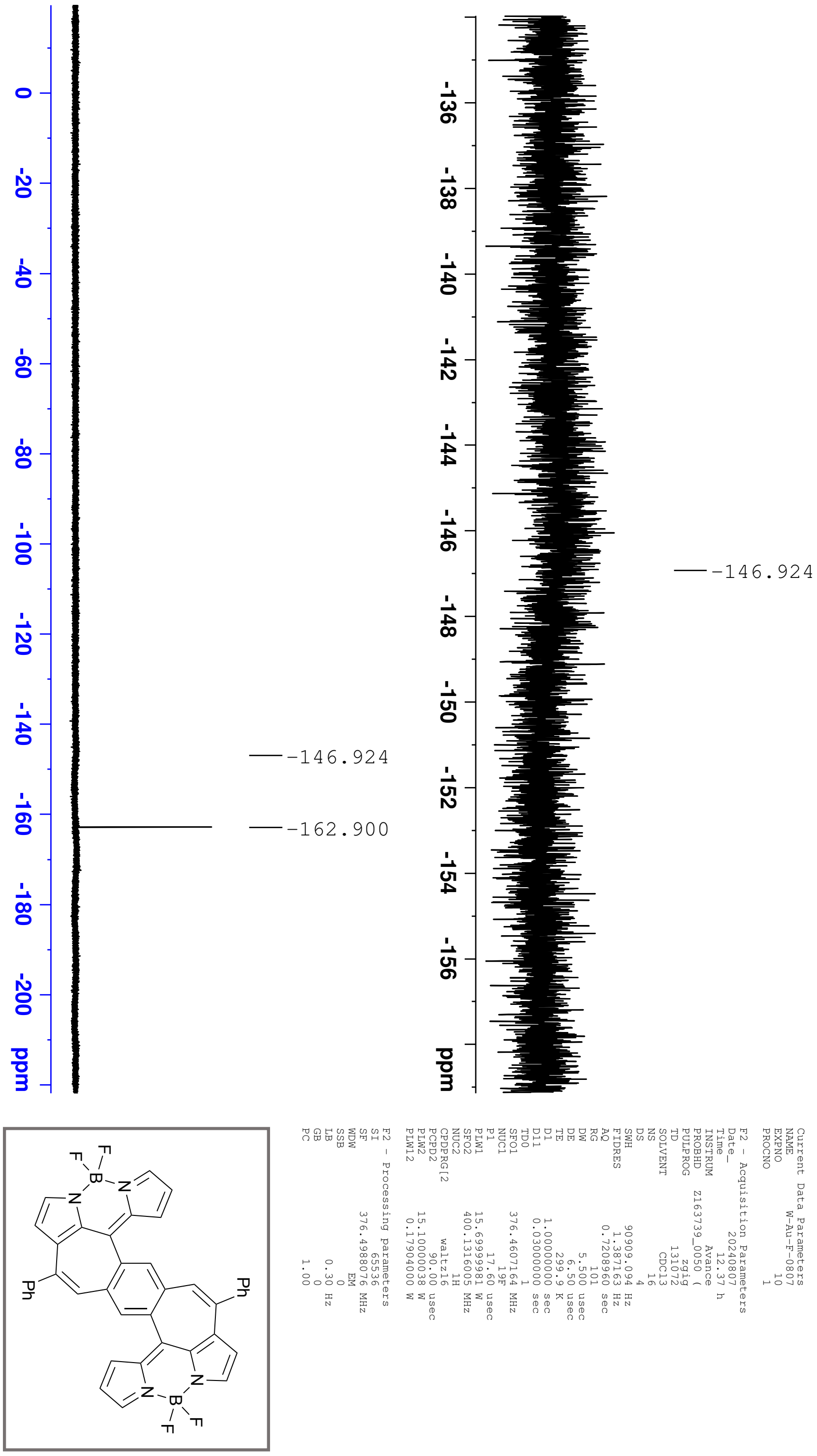



**Figure S62**. $^{19}$F NMR spectrum of **4** in $CDCl_3$ at 25 °C.

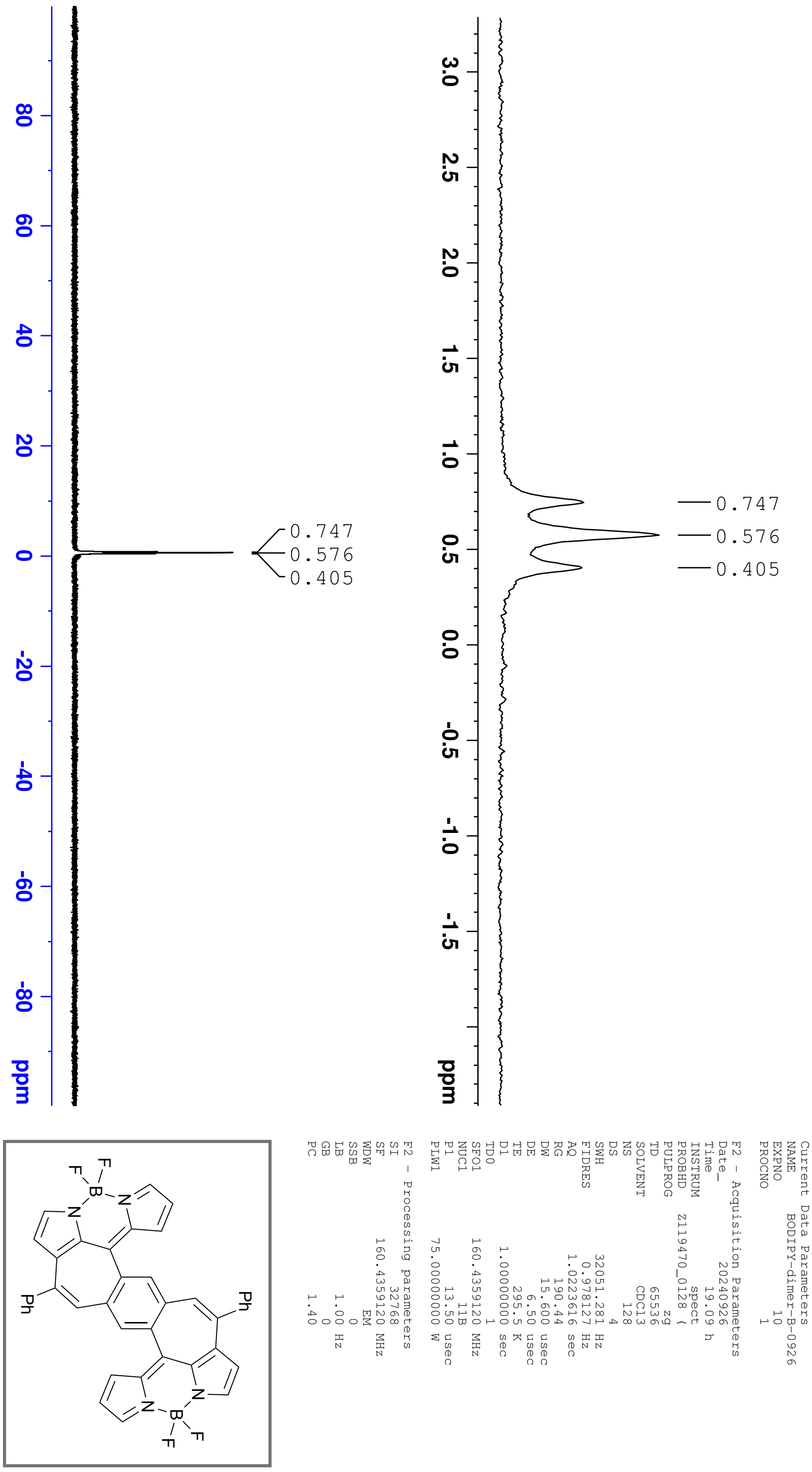



**Figure S63** $^{11}$B NMR spectrum of **4** in $CDCl_3$ at 25 °C.

# 4. Mass spectra

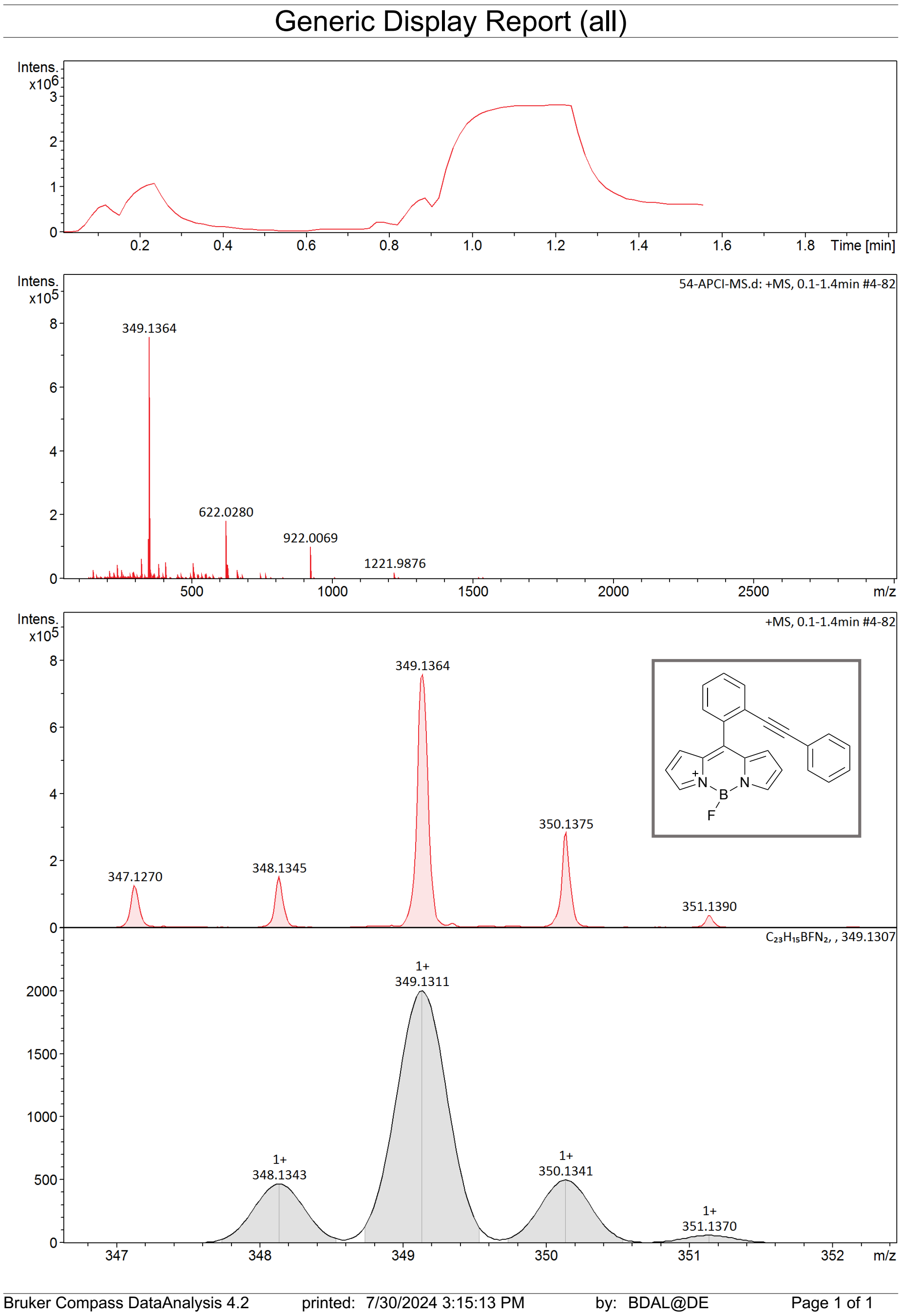



**Figure S64.** APCI-TOF mass spectrum of **1a**.

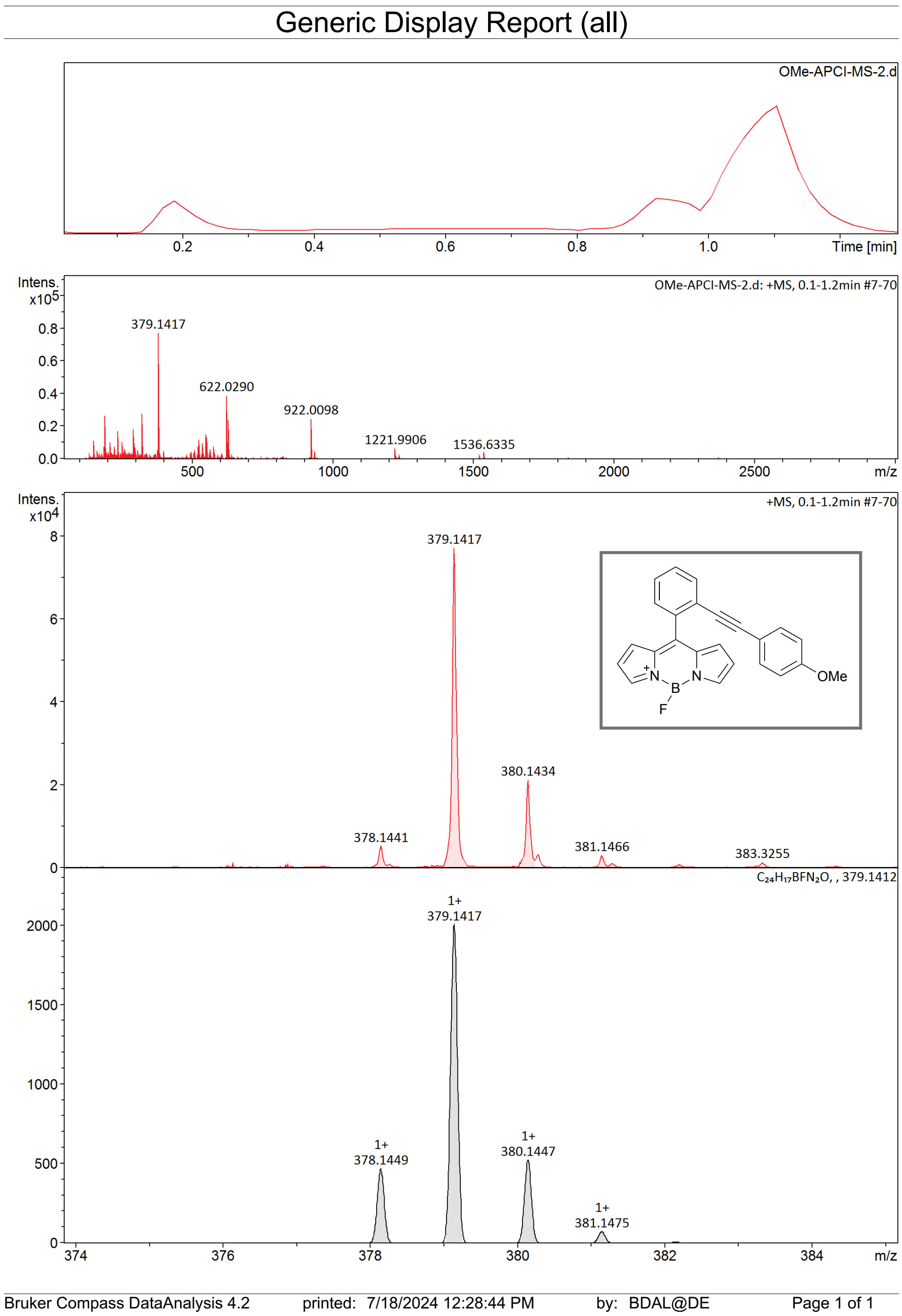



**Figure S65.** APCI-TOF mass spectrum of **1b**.

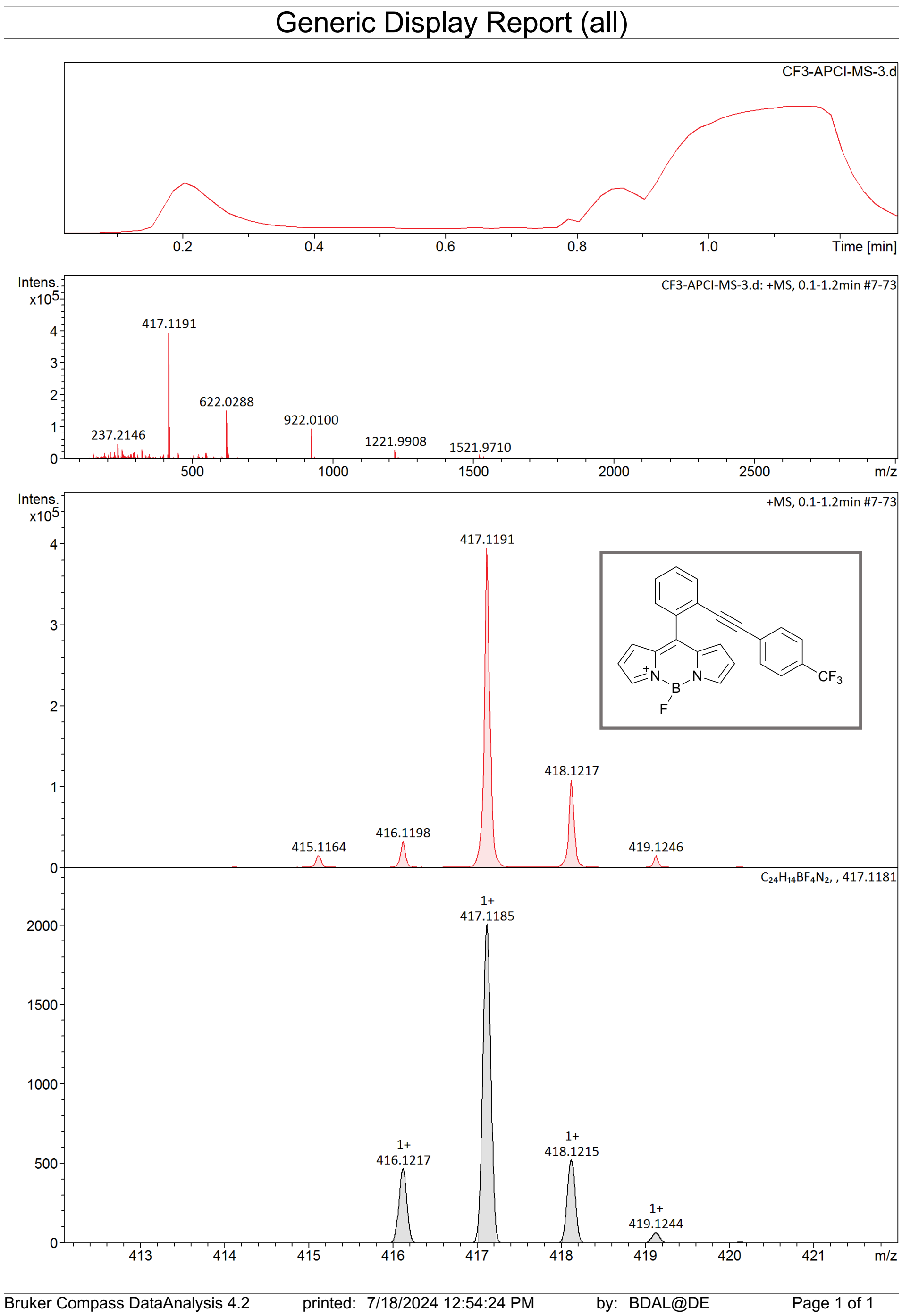



**Figure S66.** APCI-TOF mass spectrum of **1c**.

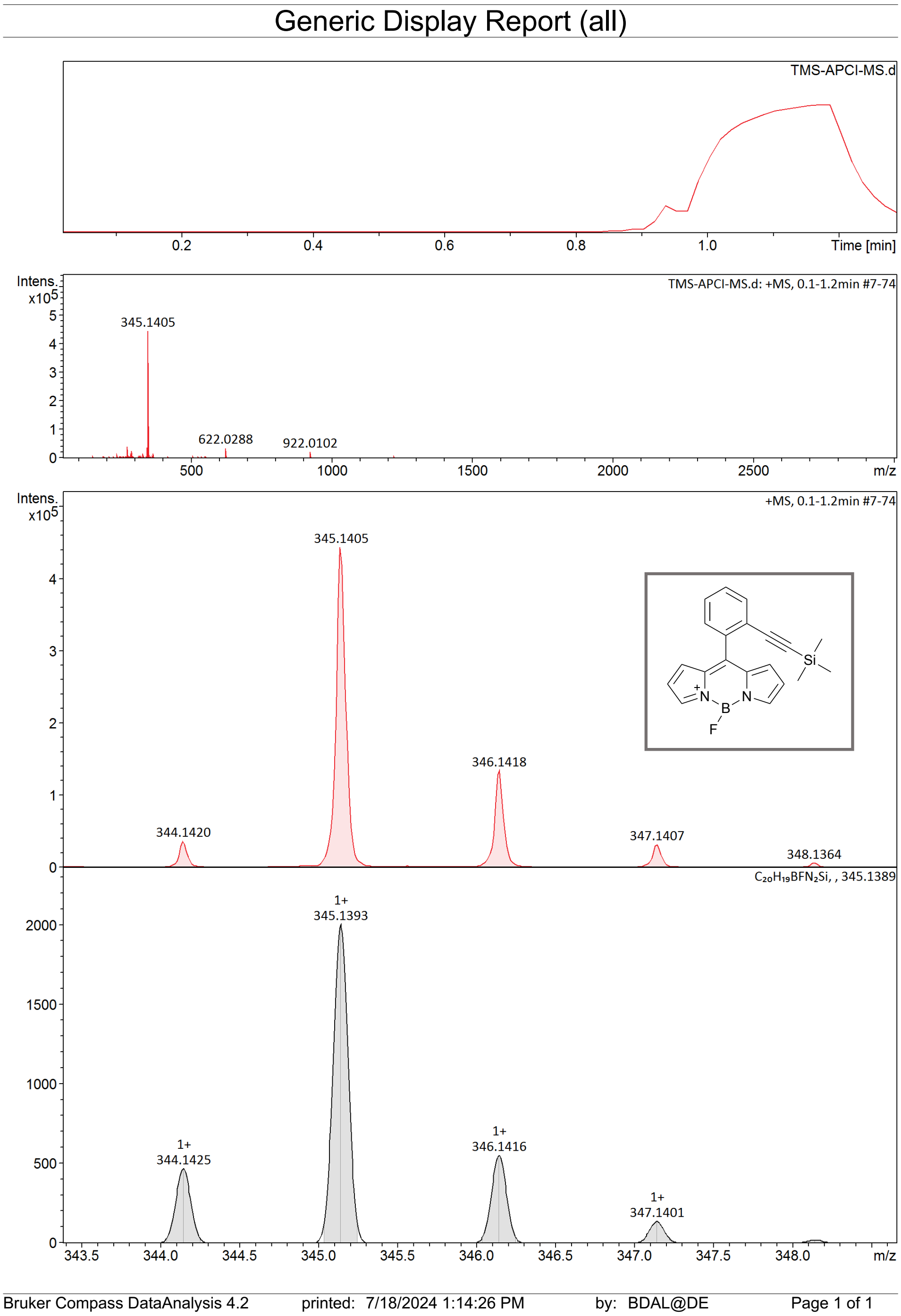



**Figure S67.** APCI-TOF mass spectrum of **S1**.

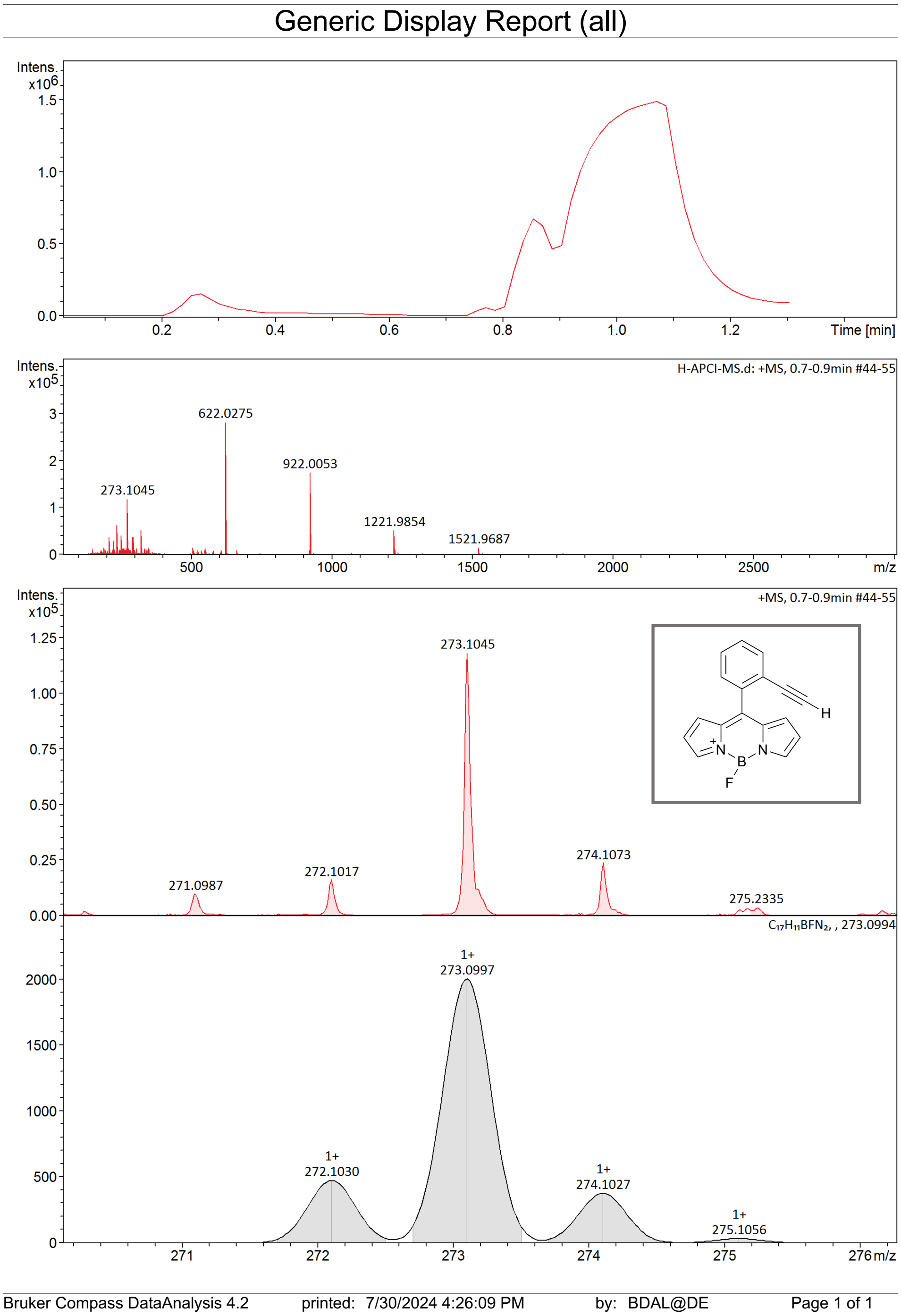



**Figure S68.** APCI-TOF mass spectrum of **1d**.

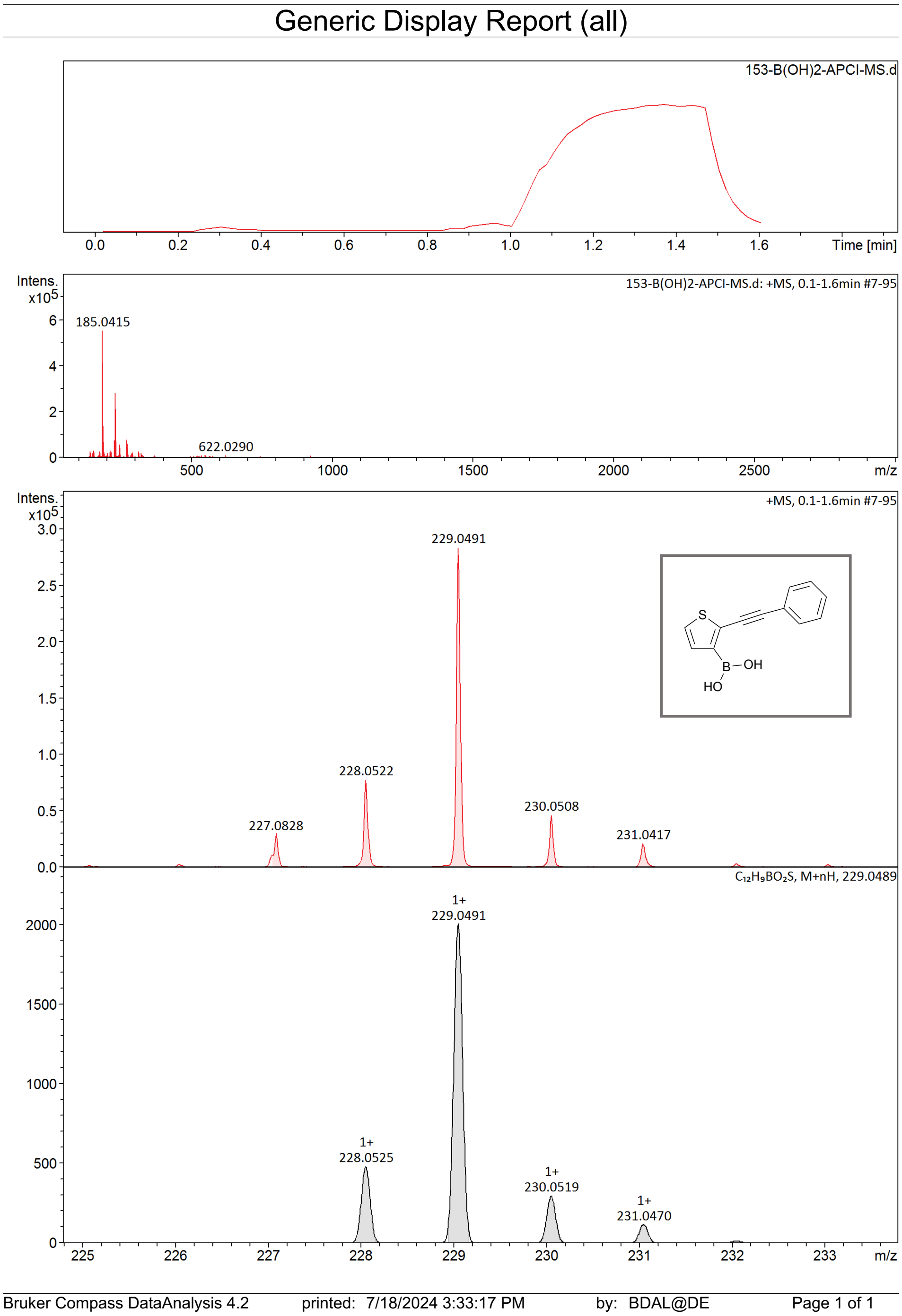



**Figure S69.** APCI-TOF mass spectrum of **S2**.

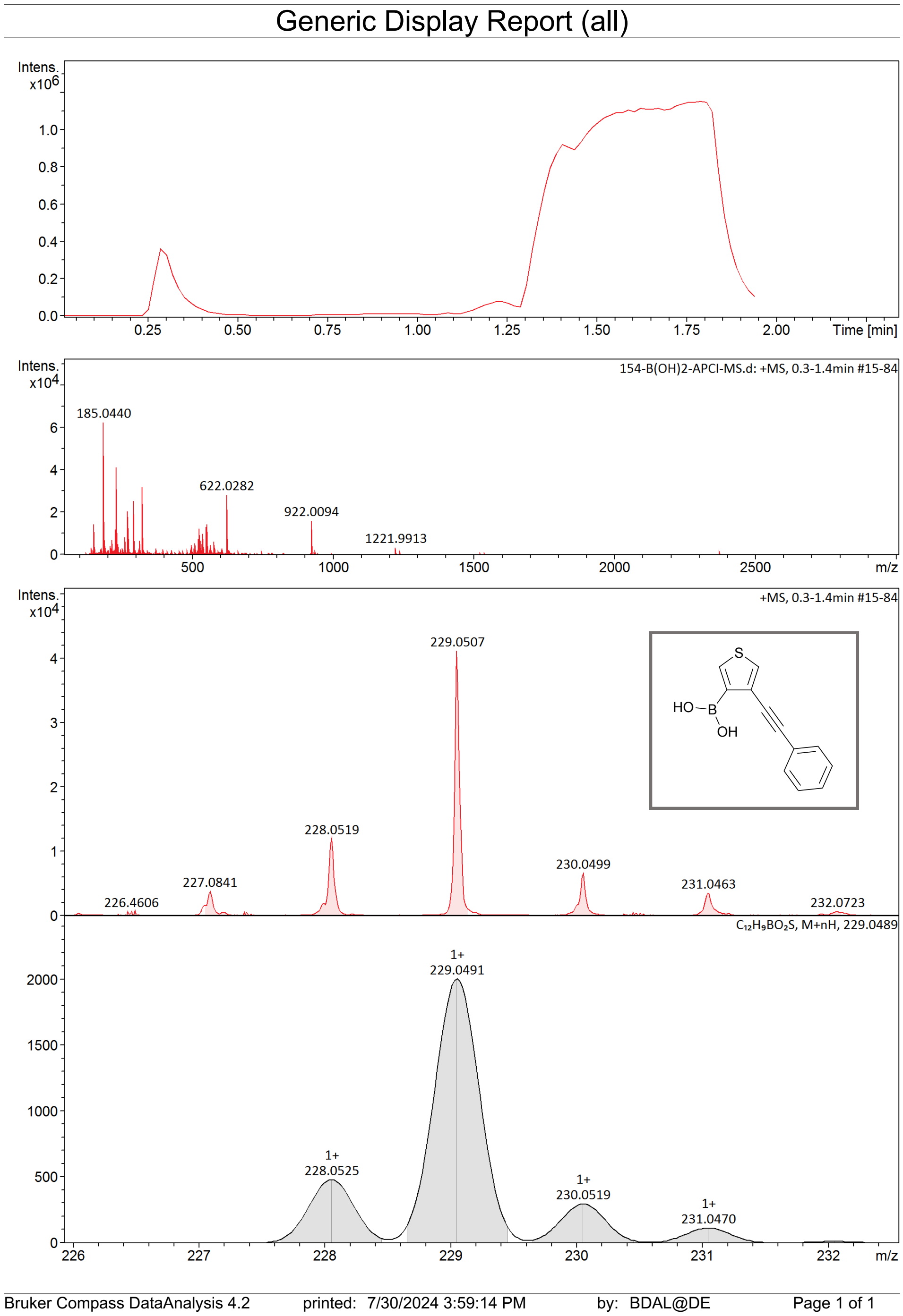



**Figure S70.** APCI-TOF mass spectrum of **S3**.

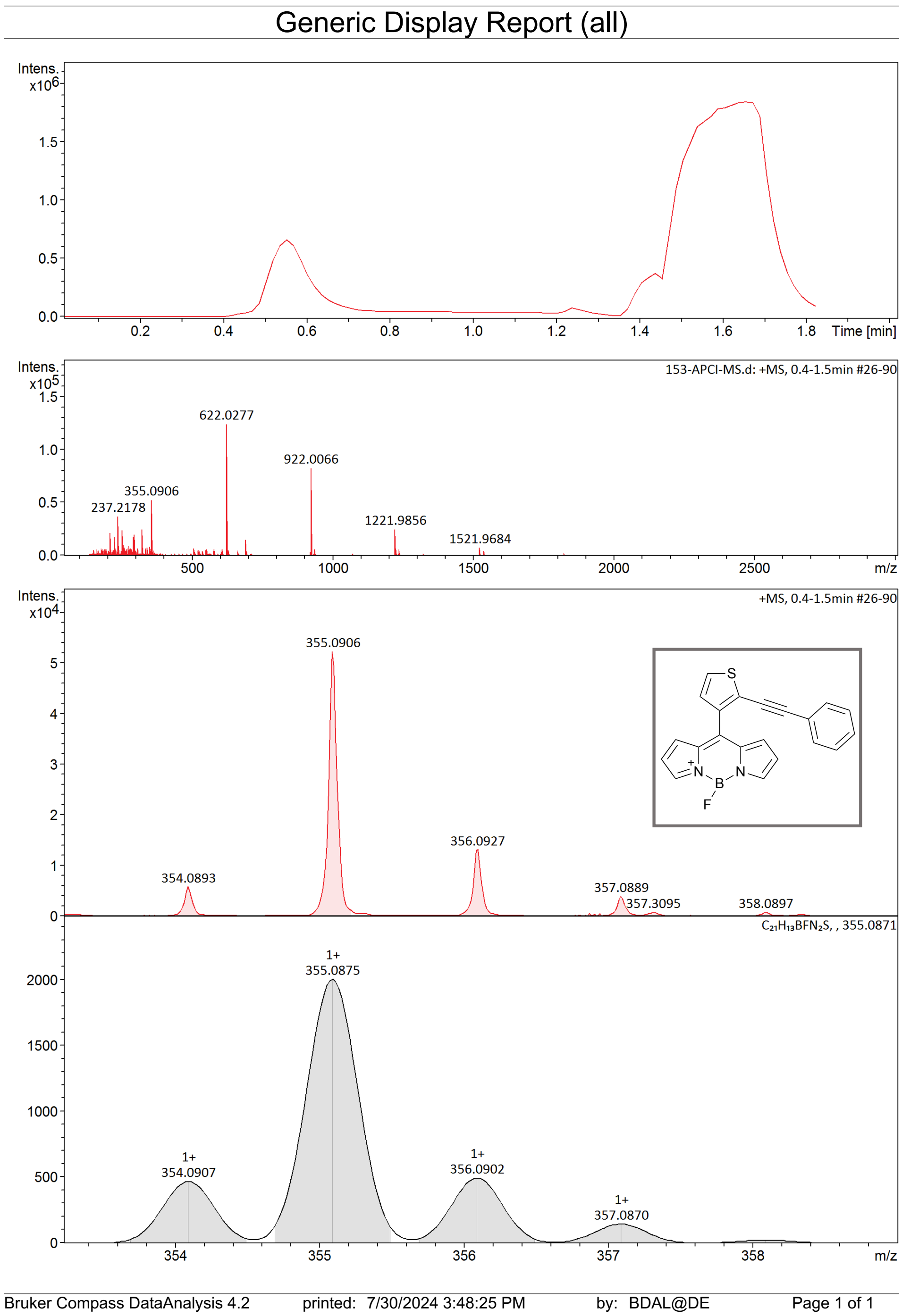



**Figure S71** APCI-TOF mass spectrum of **1e**.

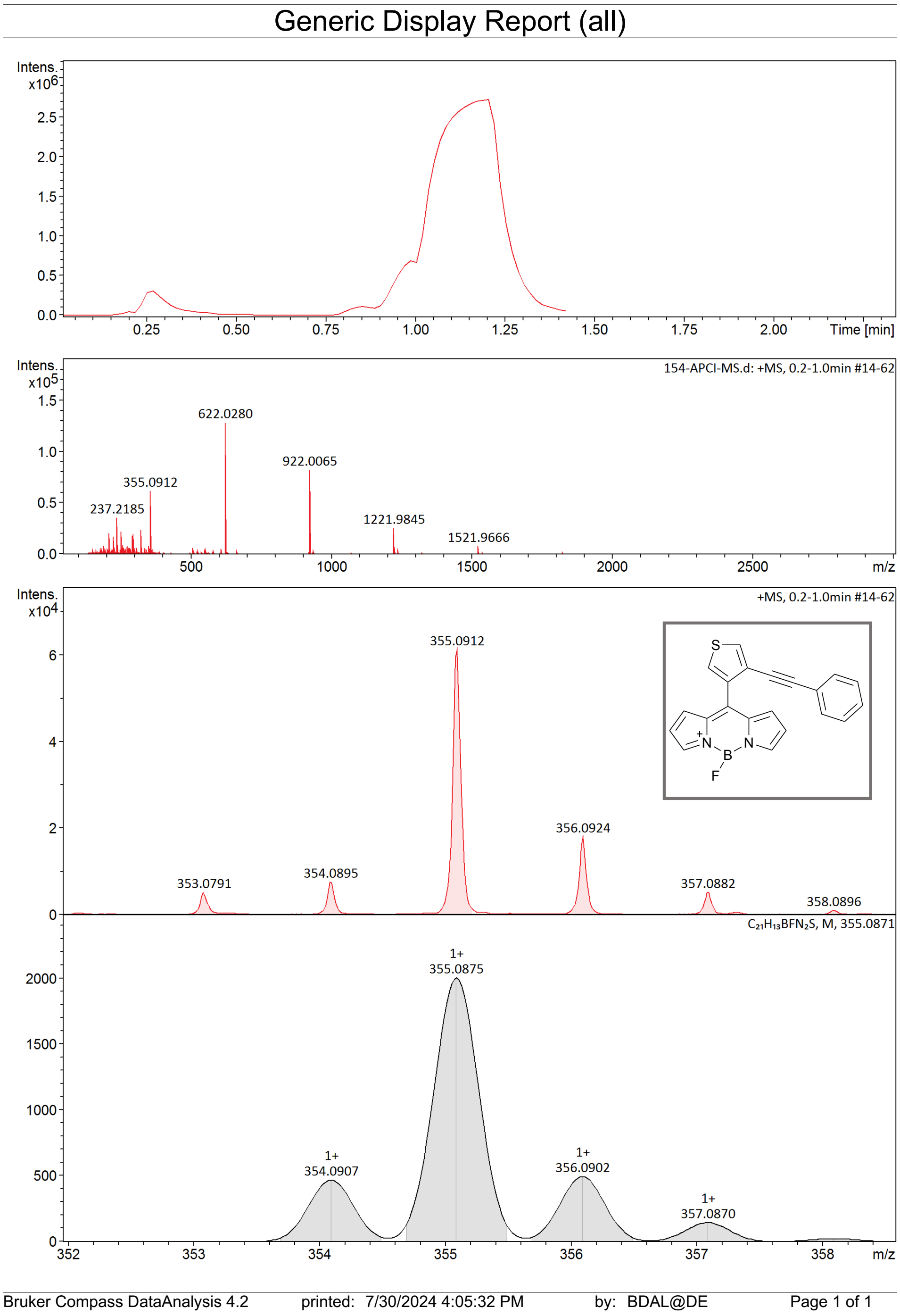



**Figure S72.** APCI-TOF mass spectrum of **1f**.

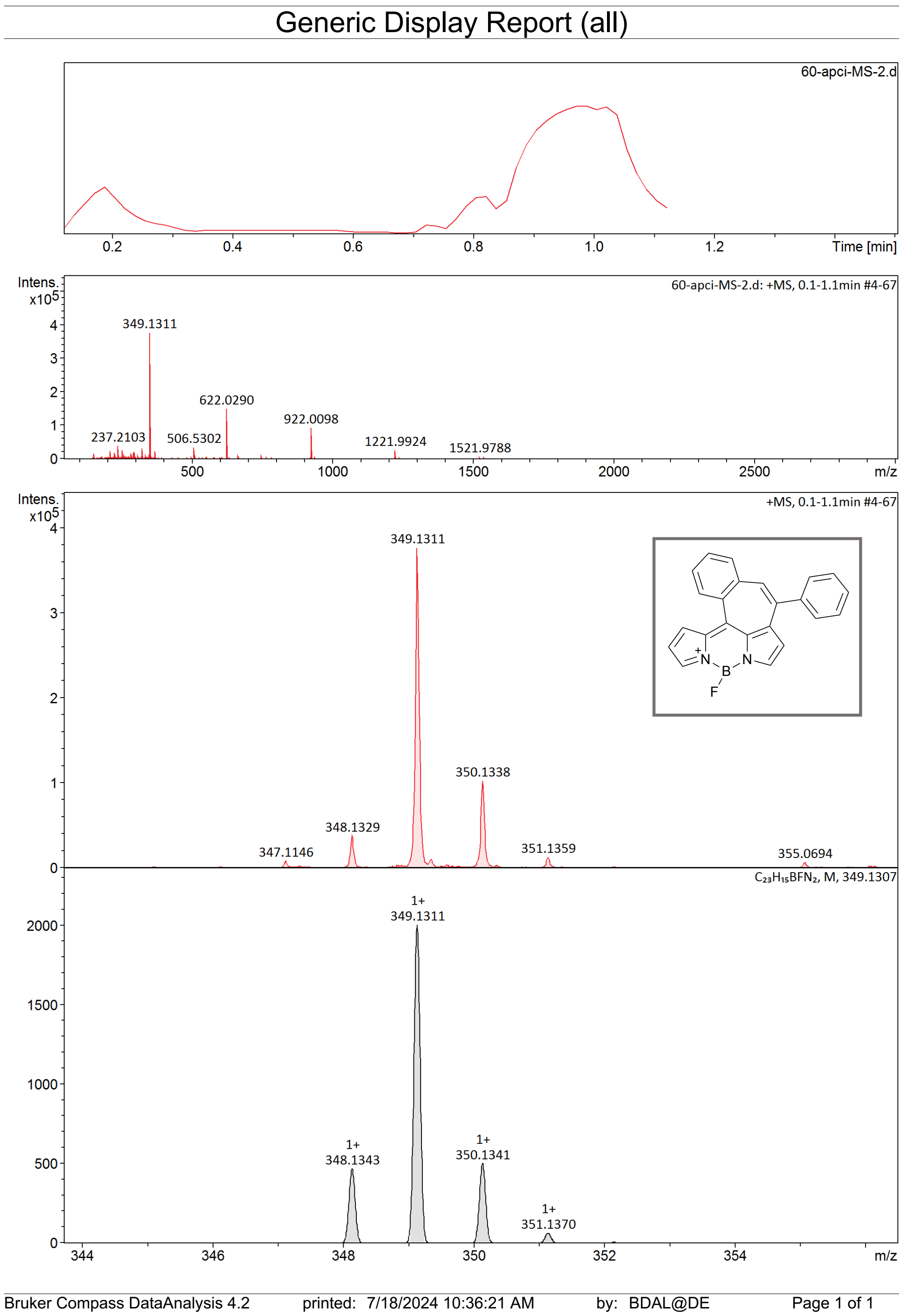



**Figure S73**. APCI-TOF mass spectrum of **2a**.

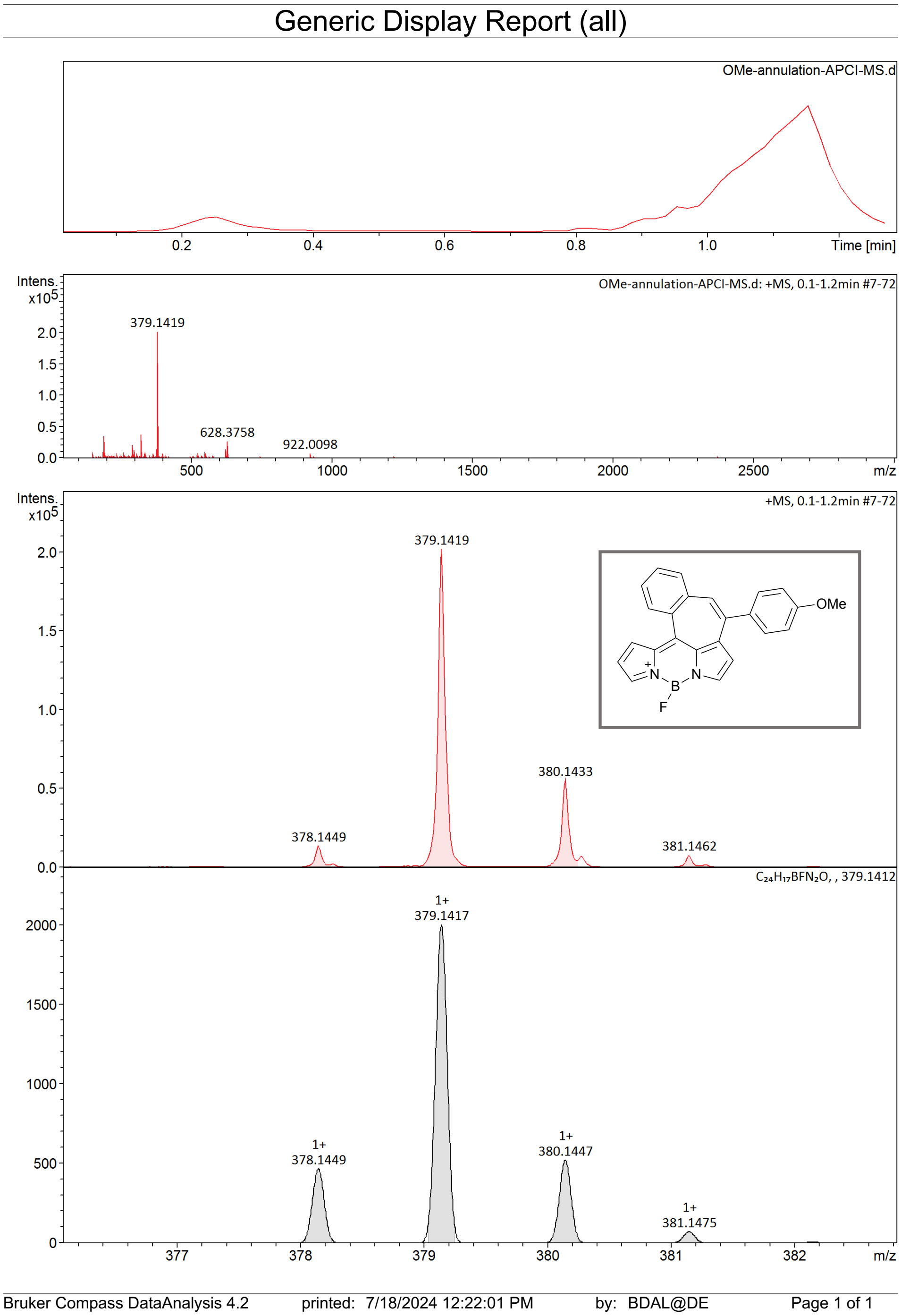



**Figure S74**. APCI-TOF mass spectrum of **2b**.

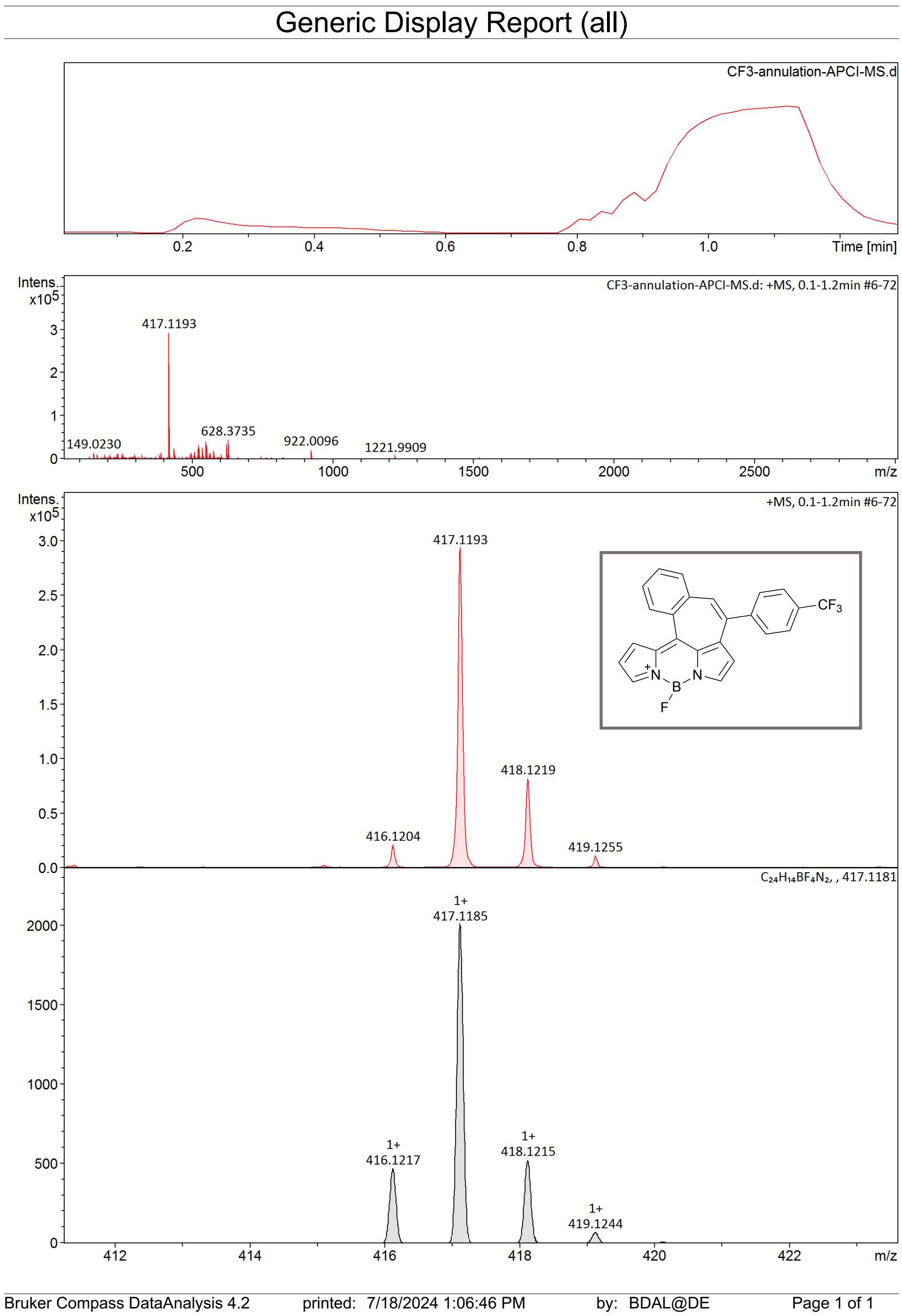



**Figure S75**. APCI-TOF mass spectrum of **2c**.

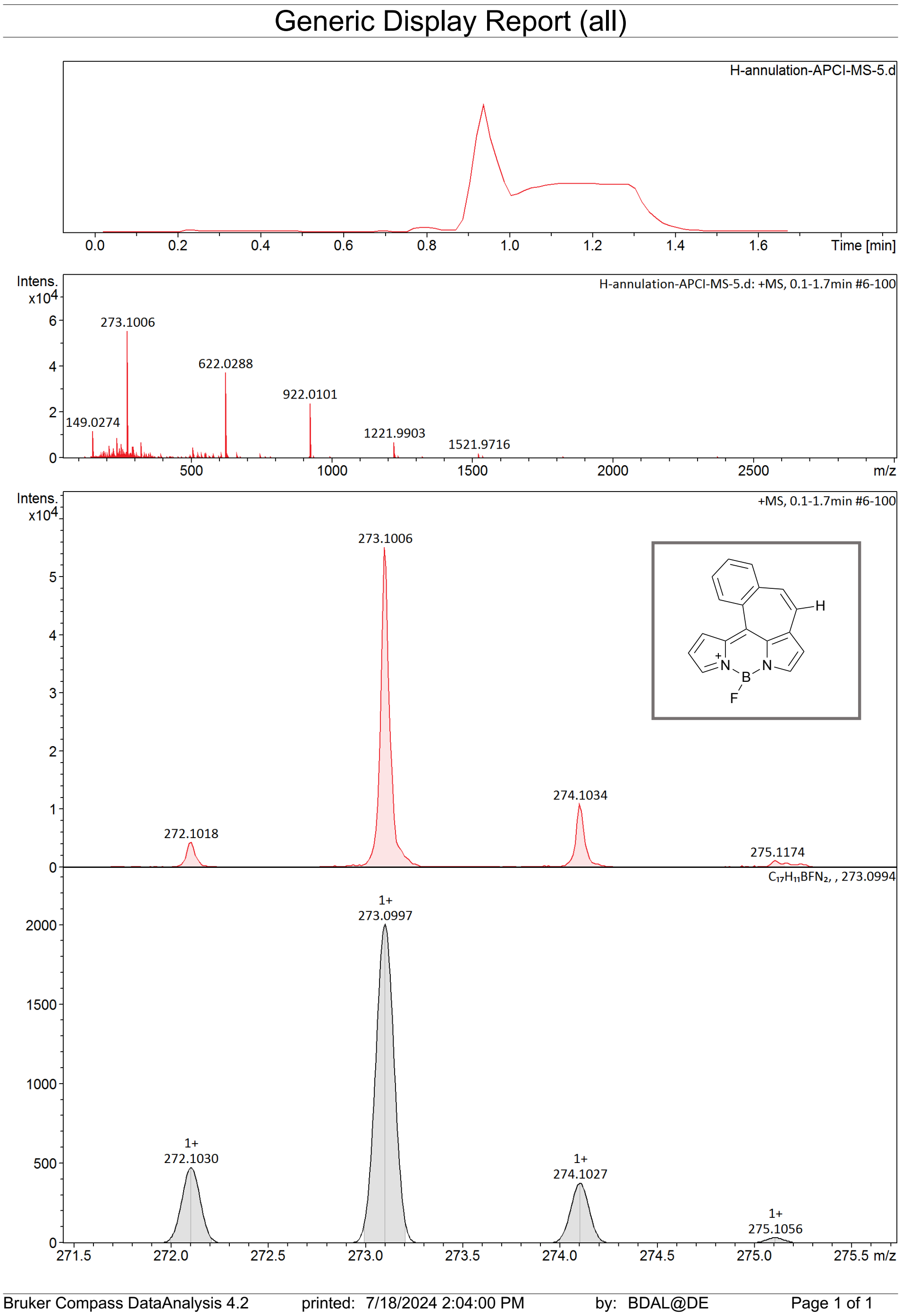



**Figure S76**. APCI-TOF mass spectrum of **2d**.

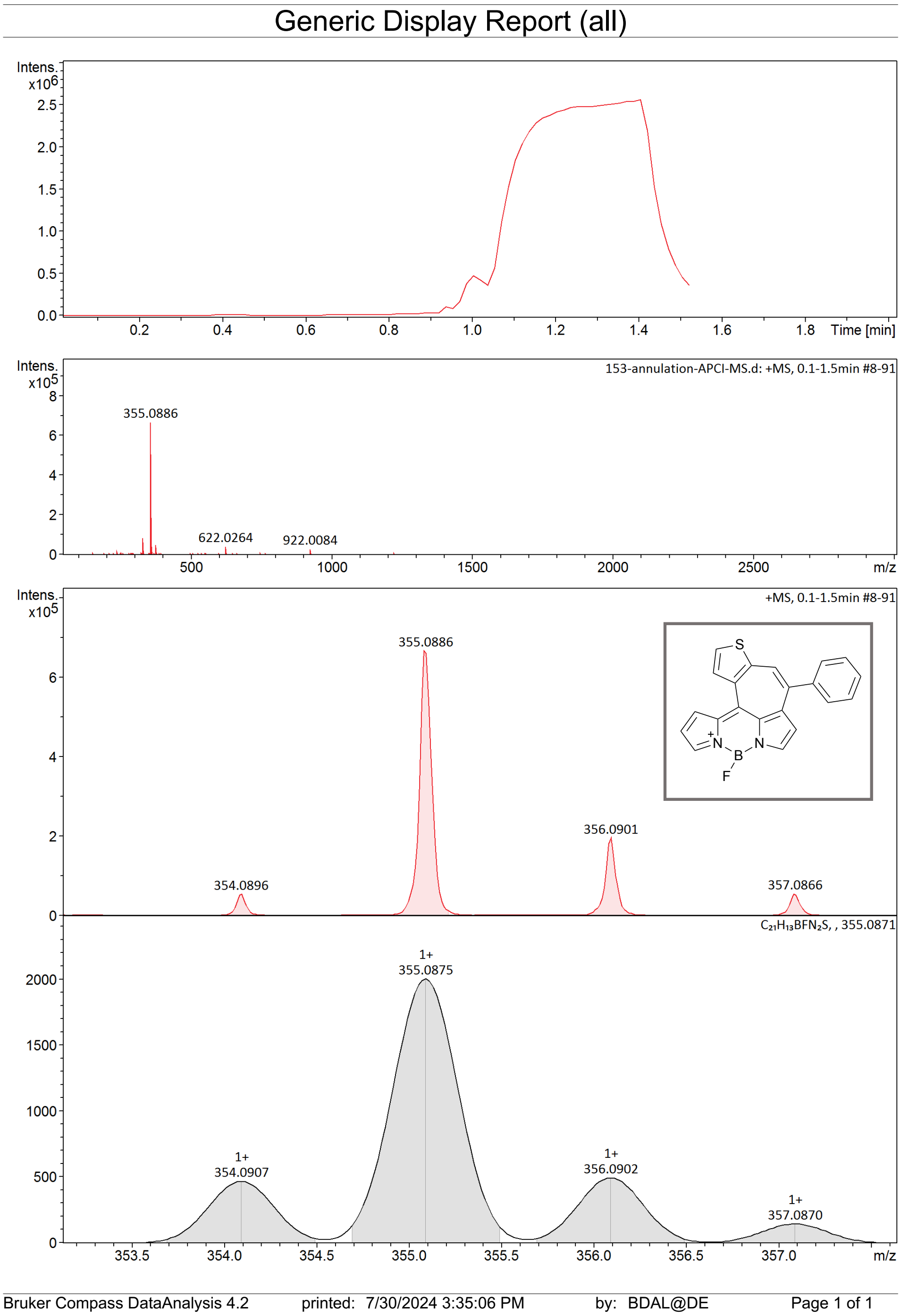



**Figure S77**. APCI-TOF mass spectrum of **2e**.

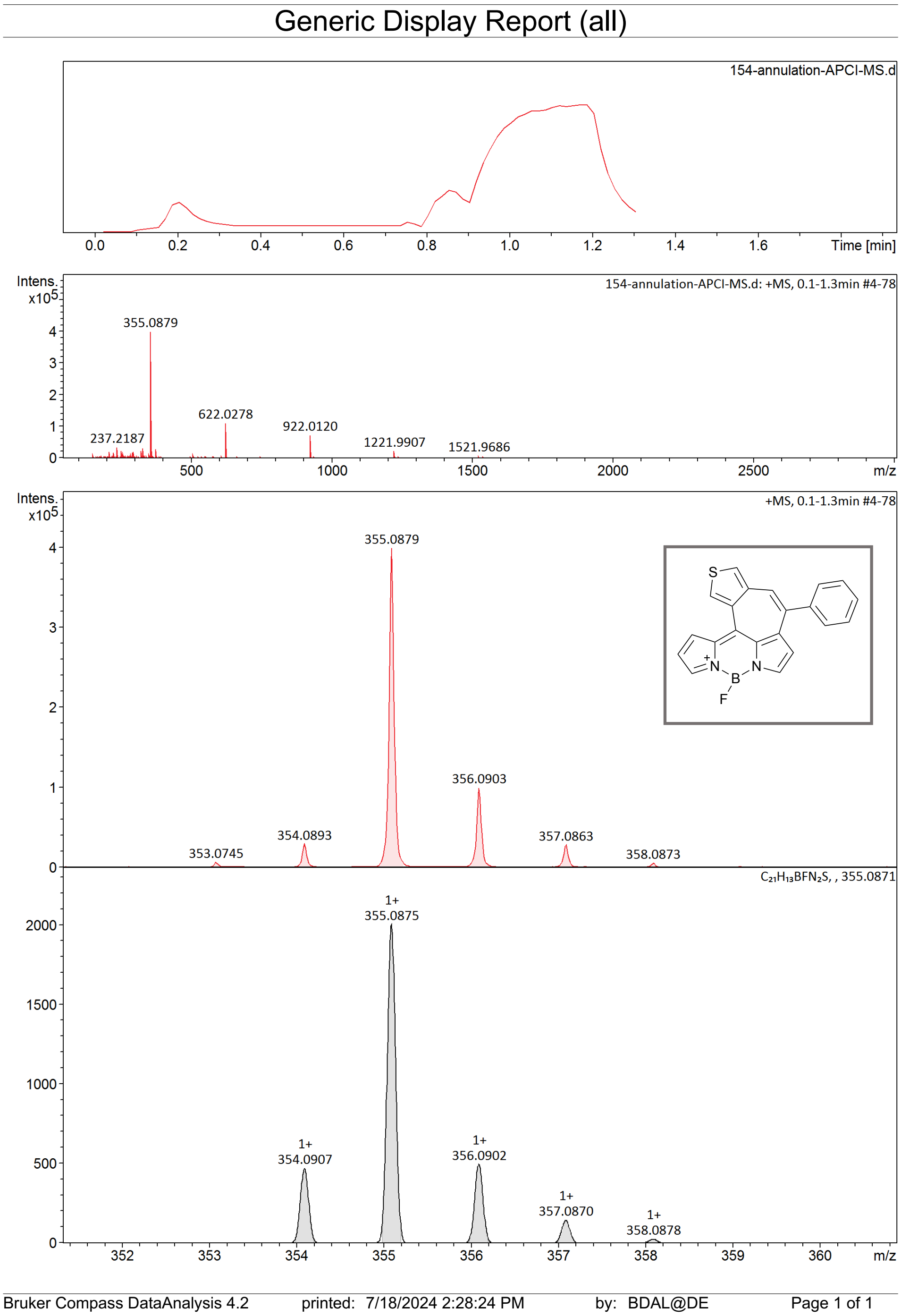



**Figure S78**. APCI-TOF mass spectrum of **2f**.

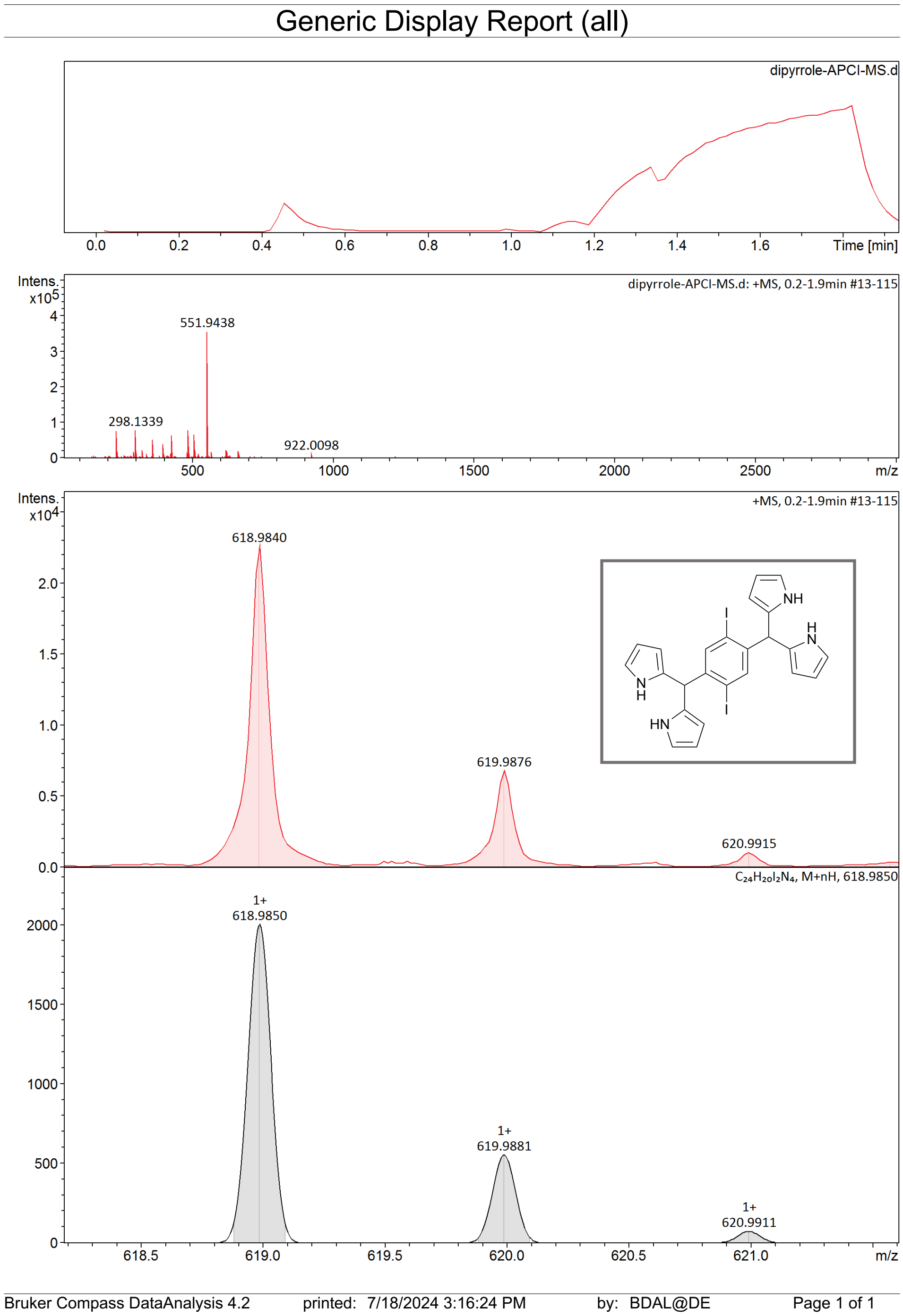



**Figure S79**. APCI-TOF mass spectrum of **S4**.

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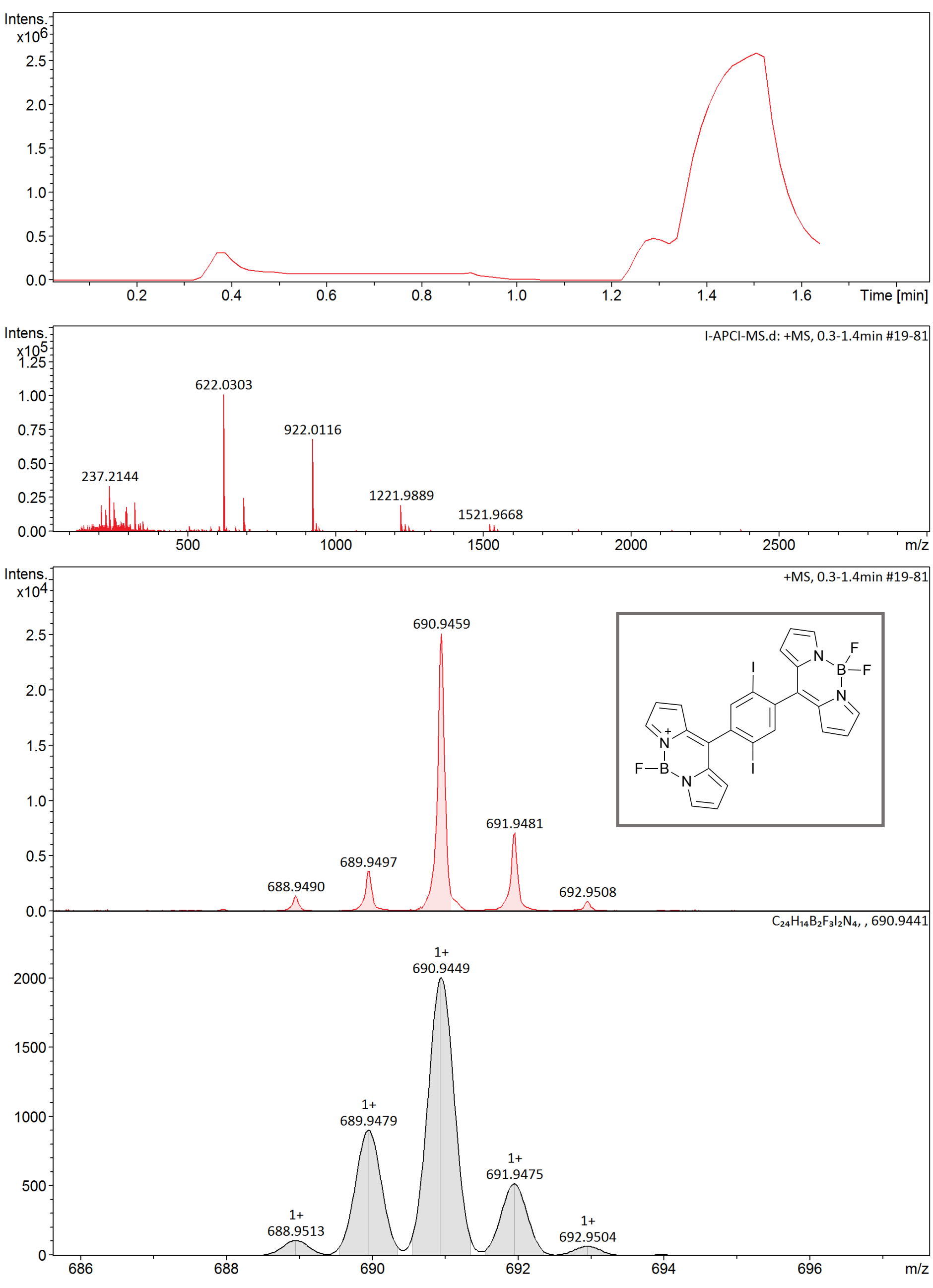


Bruker Compass DataAnalysis 4.2 printed: 7/30/2024 4:37:44 PM by: BDAL@DE Page 1 of 1

**Figure S80**. APCI-TOF mass spectrum of **S5**.

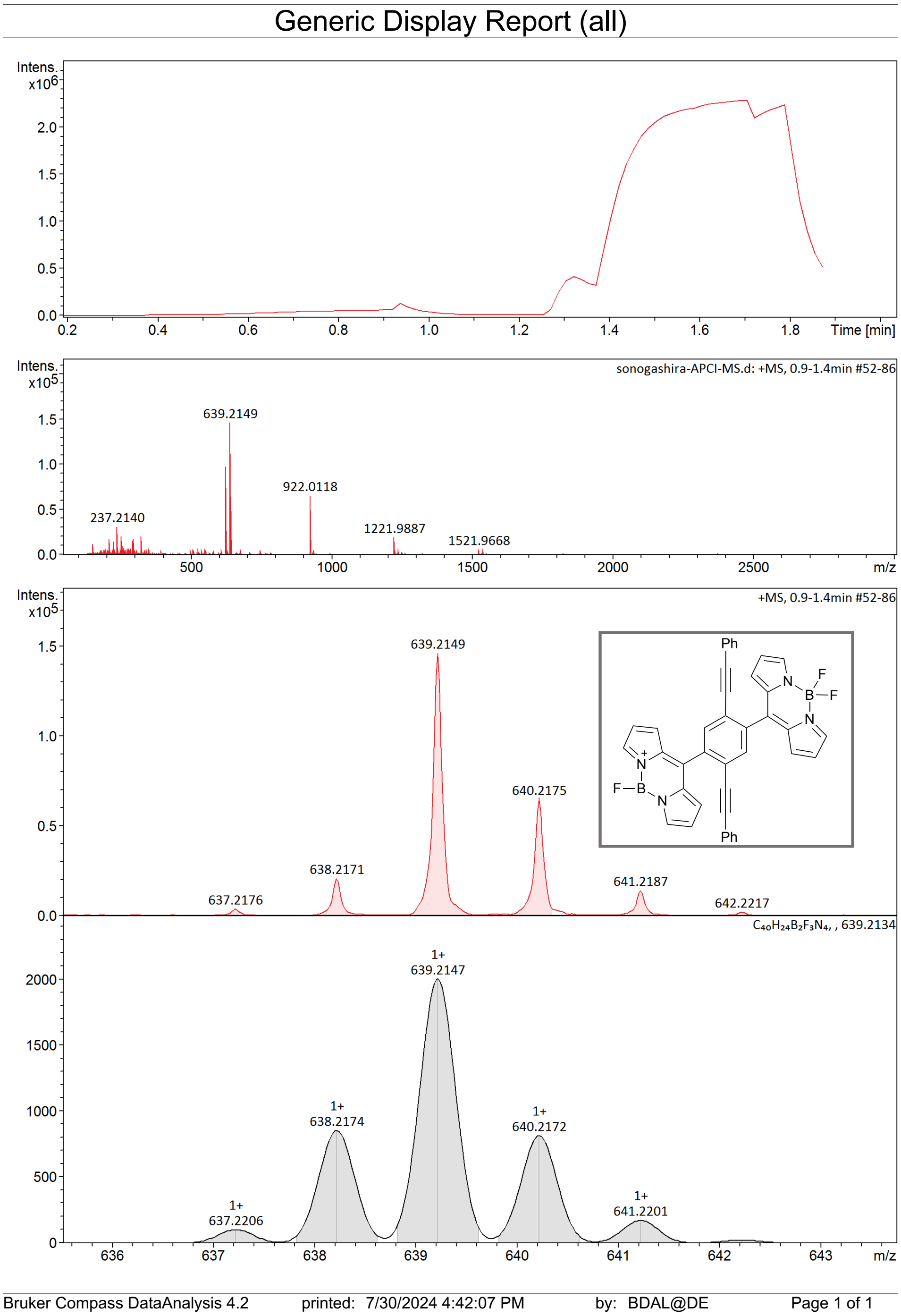


**Figure S81**. APCI-TOF mass spectrum of **3**.

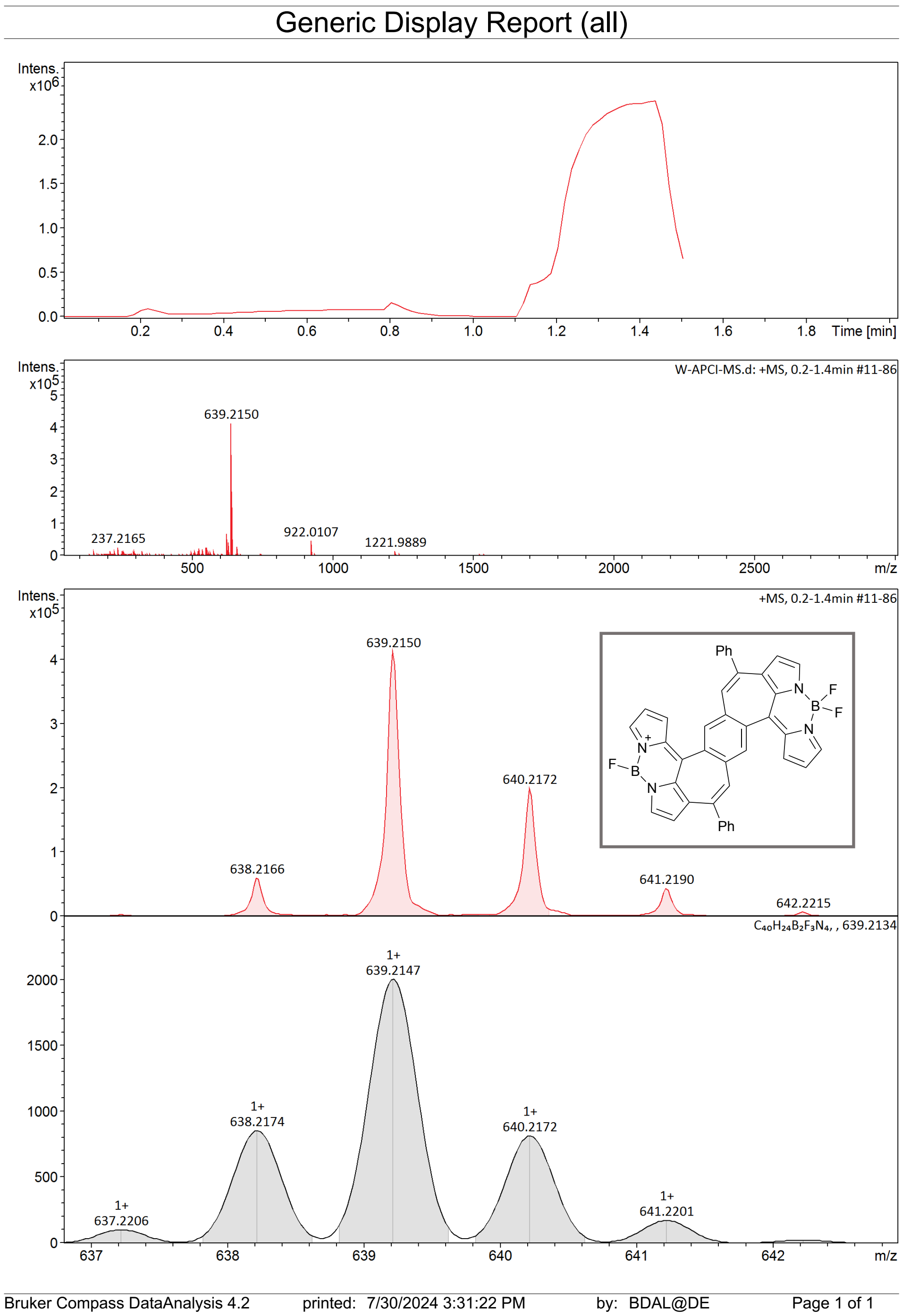


**Figure S82**. APCI-TOF mass spectrum of **4**.

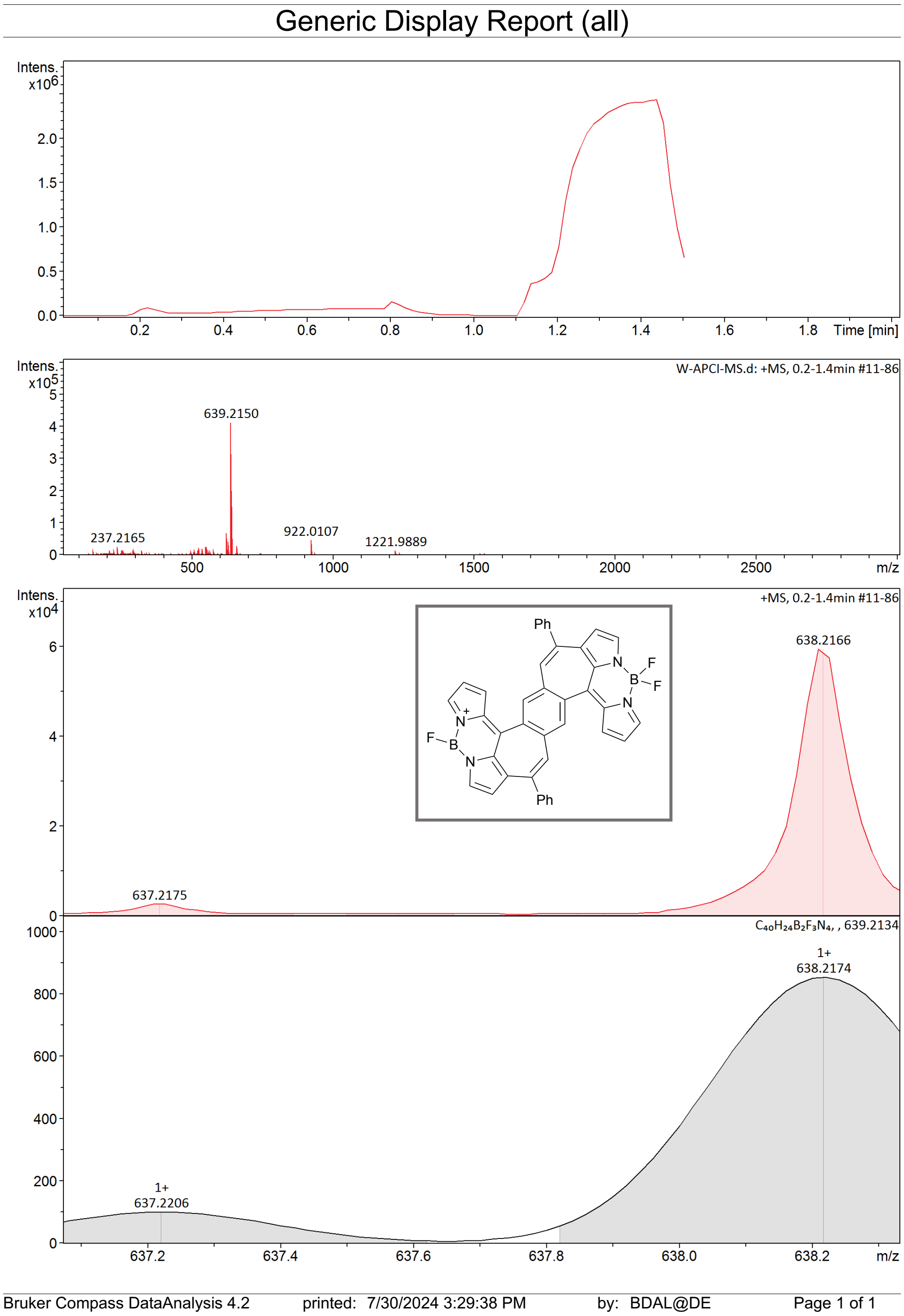


**Figure S83**. APCI-TOF mass spectrum of **4** (enlarged).

## 5. Crystal data

X-ray data of **2a** was obtained using a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics. X-ray data of **2e**, **2f** and **4** were obtained using a Rigaku CCD diffractometer (HyPix-6000 with PhotonJet-R, DW) with XtaLAB Synergy-R, DW. Fine crystals of **2a**, **2e**, **2f** and **4** suitable for the X-ray diffraction analysis were obtained by the liquid diffusion heptane into its dichloromethane solution. Crystallographic data for **2a**, **2e**, **2f** and **4** have been deposited with the Cambridge Crystallographic Data Centre.

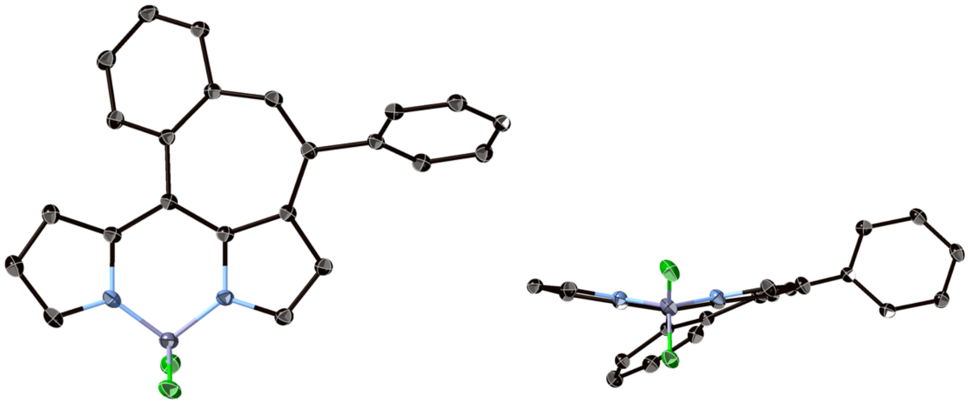

**Figure S84.** X-ray crystal structure of **2a** (C; black, N; sky blue, B; gray, F; green). Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

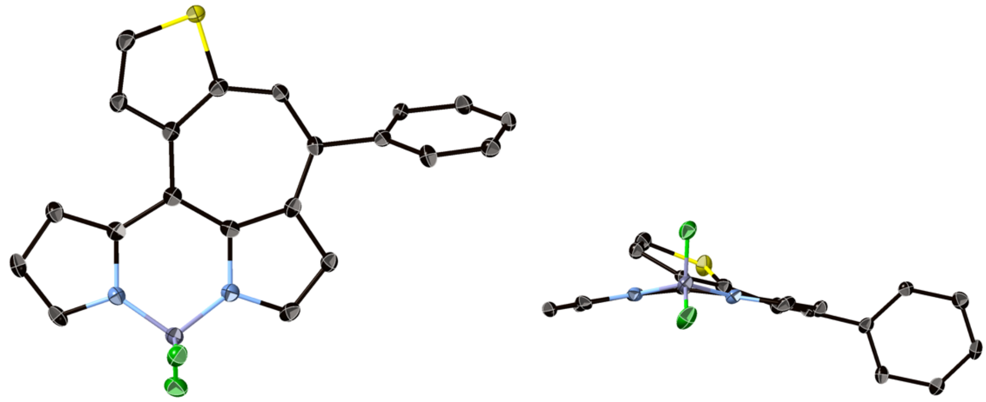

**Figure S85.** X-ray crystal structure of **2e** (C; black, N; sky blue, B; gray, F; green, S; yellow). Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

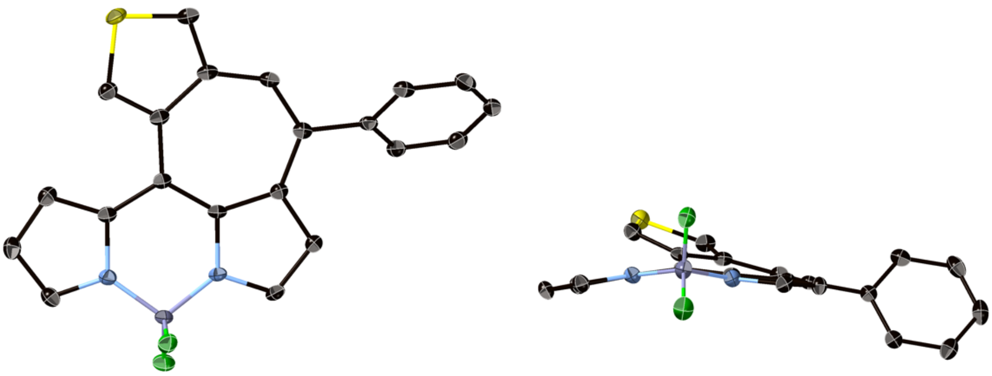

**Figure S86.** X-ray crystal structure of **2f** (C; black, N; sky blue, B; gray, F; green, S; yellow). Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

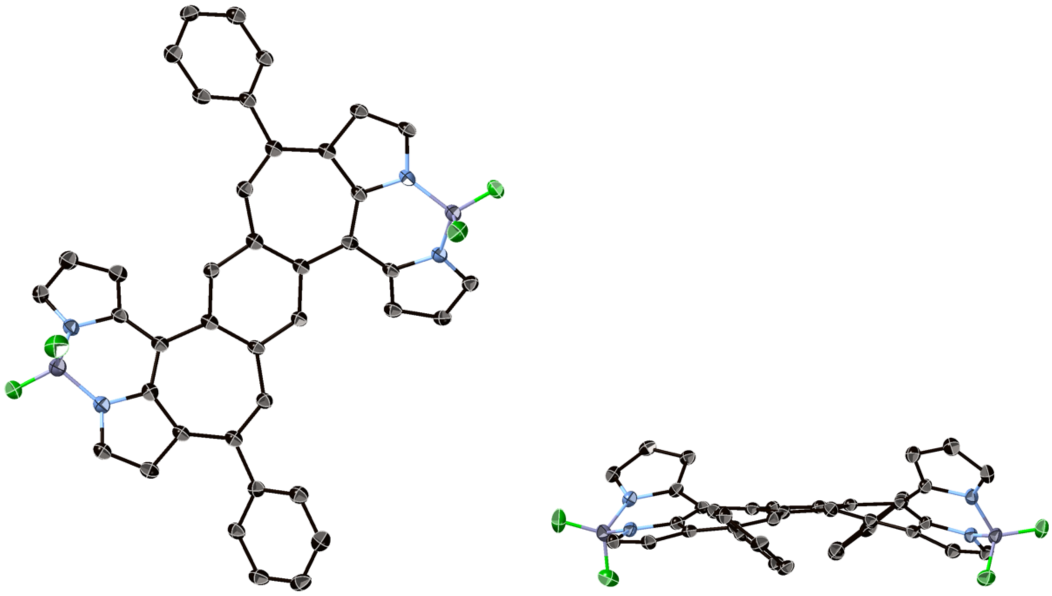

**Figure S87.** X-ray crystal structure of **4** (C; black, N; sky blue, B; gray, F; green). Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

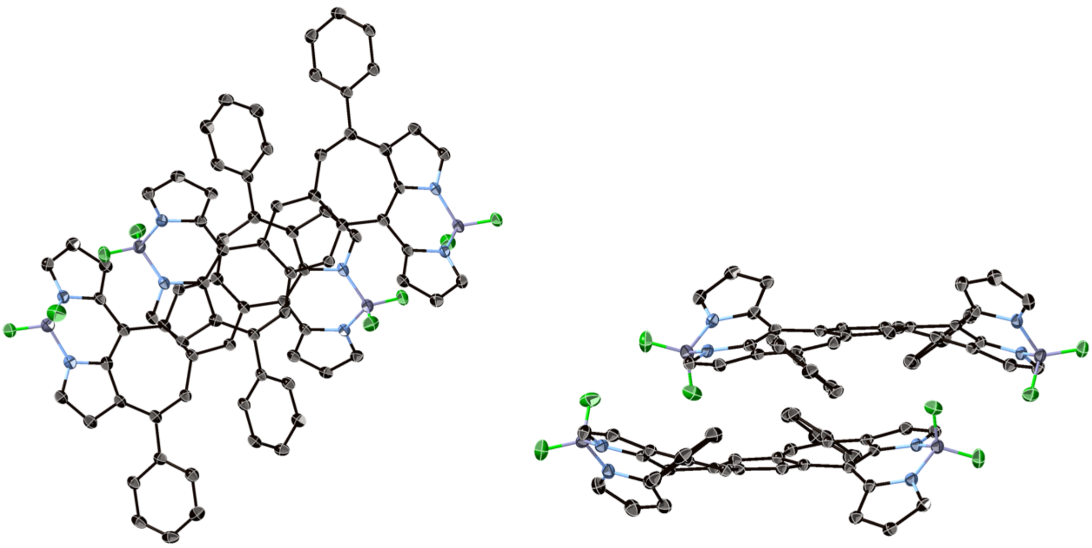

**Figure S88.** Crystal packing structure of **4** in the solid state (C; black, N; sky blue, B; gray, F; green).

**Table S1.** Crystallographic data of **2a, 2e, 2f** and **4**.

| compound | **2a** | **2e** | **2f** | **4** |
|---|---|---|---|---|
| Formula | $C_{23}H_{15}BF_2N_2$ | $C_{21}H_{13}BF_2N_2S$ | $C_{21}H_{13}BF_2N_2S$ | $C_{40}H_{24}B_2F_4N_4$ |
| Formula weight | 368.18 | 374.20 | 374.20 | 658.25 |
| Crystal system | monoclinic | monoclinic | monoclinic | triclinic |
| Space group | $P2_1/c$, (No. 14) | $P2_1/c$, (No. 14) | $P2_1/c$, (No. 14) | $P$-1 (No. 2) |
| Crystal color | dark red | red | red | black |
| Crystal description | plate | plate | plate | block |
| $a$ [Å] | 5.8694(2) | 5.9057(1) | 11.6699(2) | 11.2443(2) |
| $b$ [Å] | 16.1821(4) | 15.6724(4) | 10.8486(2) | 12.5476(3) |
| $c$ [Å] | 17.7533(4) | 17.7952(5) | 14.0687(3) | 23.0507(4) |
| $\alpha$ [°] | — | — | — | 94.375(2) |
| $\beta$ [°] | 97.915(3) | 97.537(2) | 111.763(2) | 92.406(1) |
| $\gamma$ [°] | — | — | — | 112.285(2) |
| $V$ [Å$^3$] | 1670.13(8) | 1632.83(7) | 1654.18(6) | 2991.64(11) |
| $Z$ | 4 | 4 | 4 | 4 |
| $d_{calcd}$ [g cm$^{-3}$] | 1.464 | 1.522 | 1.503 | 1.461 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0449 | 0.0644 | 0.0320 | 0.0609 |
| $wR_2$ (all data) | 0.1497 | 0.1625 | 0.0875 | 0.1666 |
| Goodness-of-fit | 1.136 | 1.205 | 1.043 | 1.111 |
| Temperature [K] | 93(2) | 93(2) | 93(2) | 93(2) |
| CCDC No. | 2371965 | 2371963 | 2371964 | 2371966 |

## 6. Temperature-dependent $^{19}F$ NMR spectra

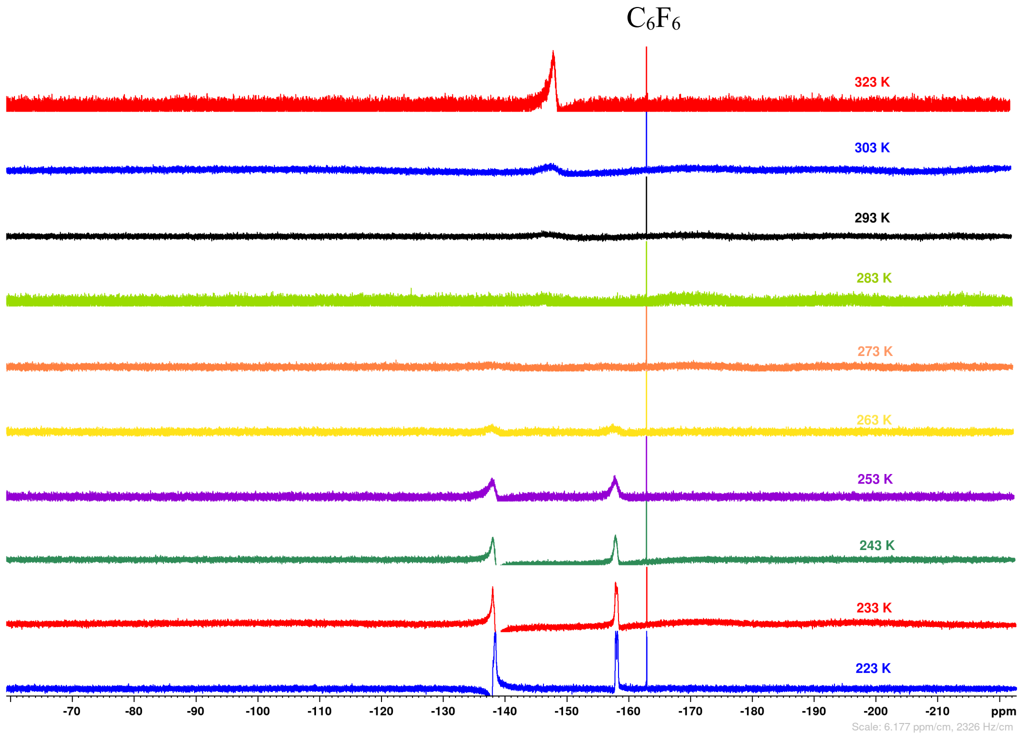


**Figure S89.** Temperature-dependent $^{19}F$ NMR spectra of **2a** in $CDCl_3$. $C_6F_6$ was added as an internal standard.

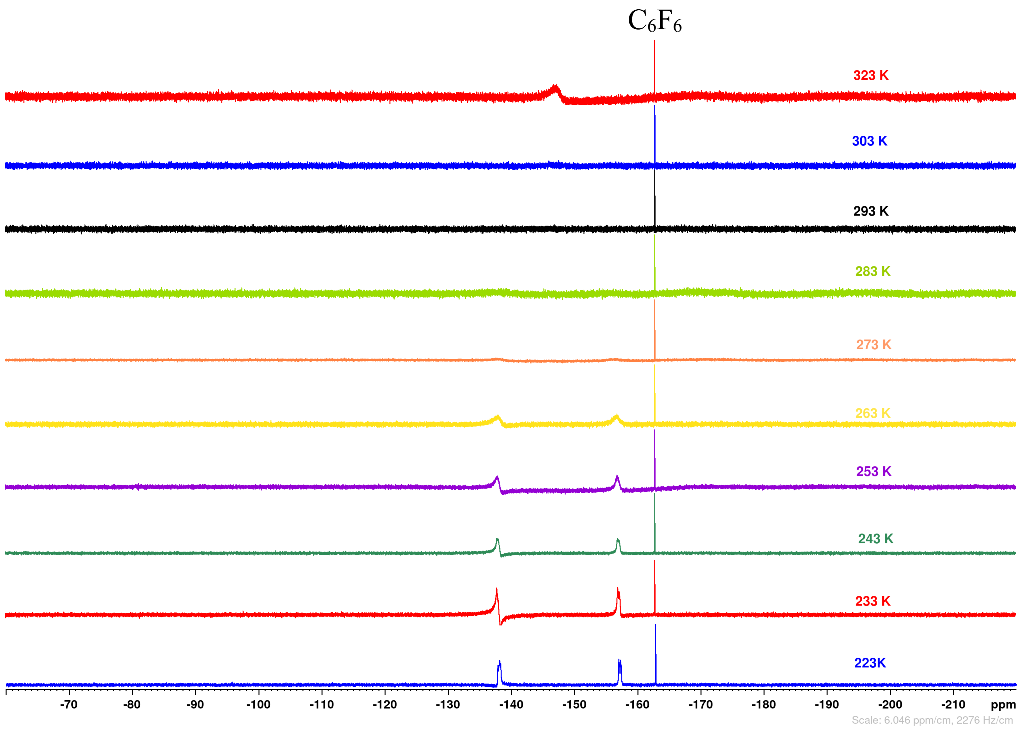


**Figure S90.** Temperature-dependent $^{19}F$ NMR spectra of **4** in $CDCl_3$. $C_6F_6$ was added as an internal standard.

## 7. Fluorescence decay profiles

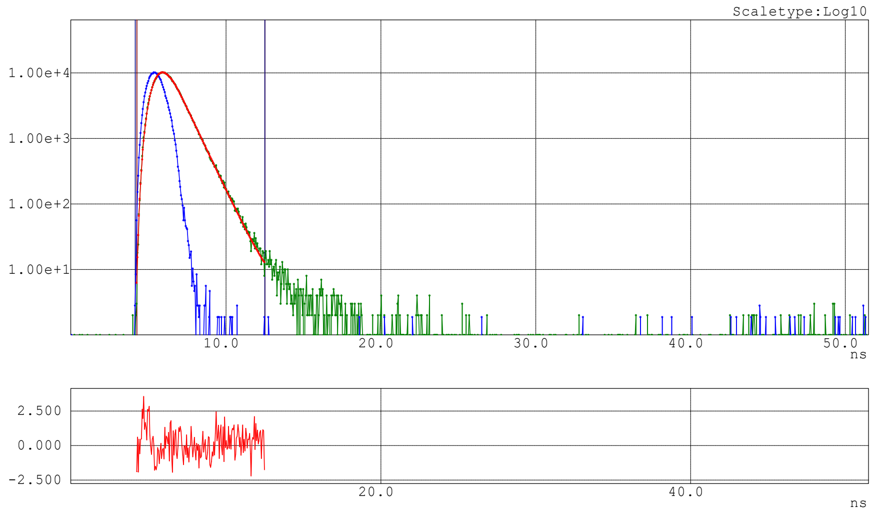


**Figure S91.** Time-correlated single photon counting (TCSPC) data of **1a** in $CH_2Cl_2$. Top: simulated decay profile (red line) and IRF (blue line). Bottom: residuals.

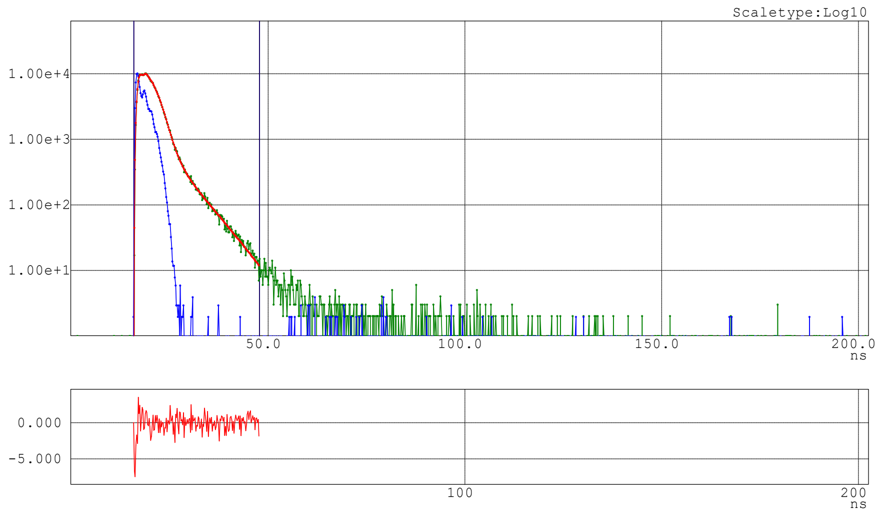


**Figure S92.** Time-correlated single photon counting (TCSPC) data of **1e** in $CH_2Cl_2$.

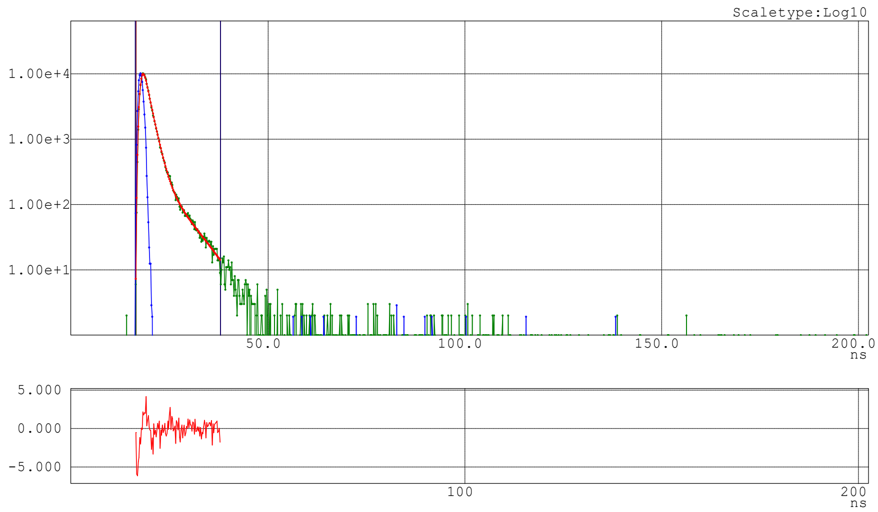


**Figure S93.** Time-correlated single photon counting (TCSPC) data of **1f** in $CH_2Cl_2$.

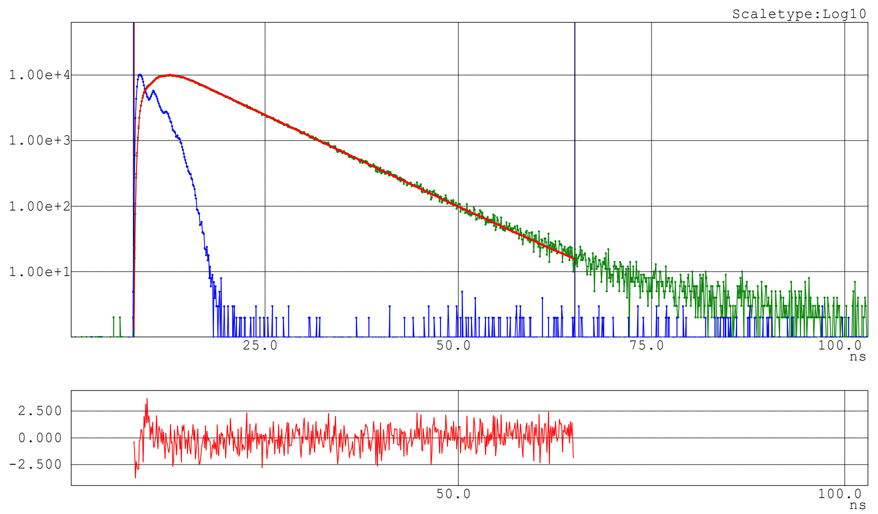


**Figure S94.** Time-correlated single photon counting (TCSPC) data of **2a** in $CH_2Cl_2$.

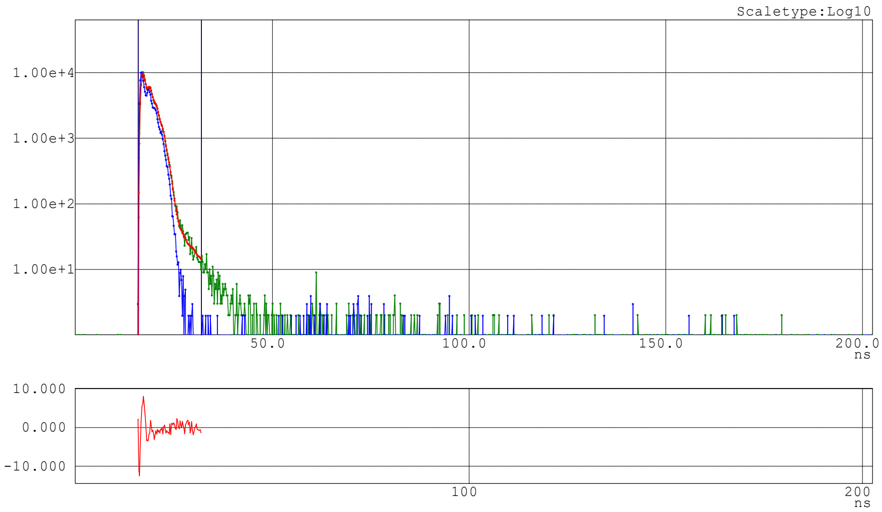


**Figure S95.** Time-correlated single photon counting (TCSPC) data of **2e** in $CH_2Cl_2$.

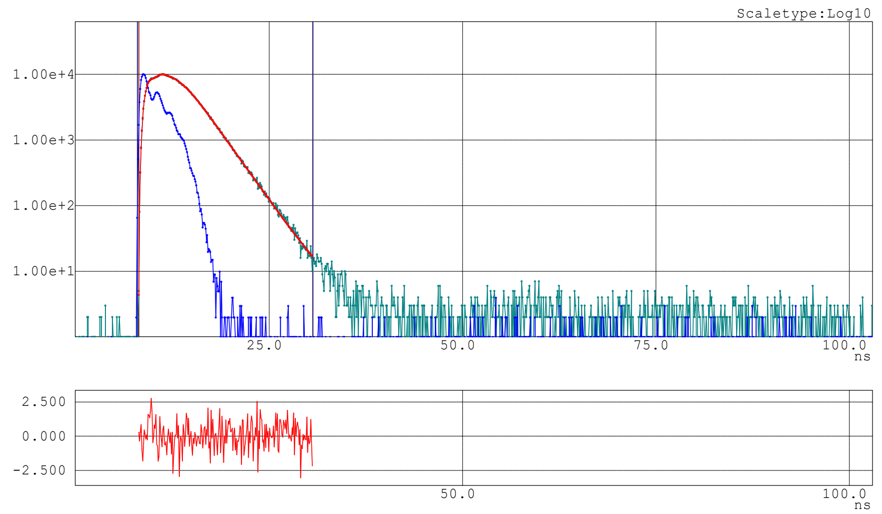


**Figure S96.** Time-correlated single photon counting (TCSPC) data of **2f** in $CH_2Cl_2$.

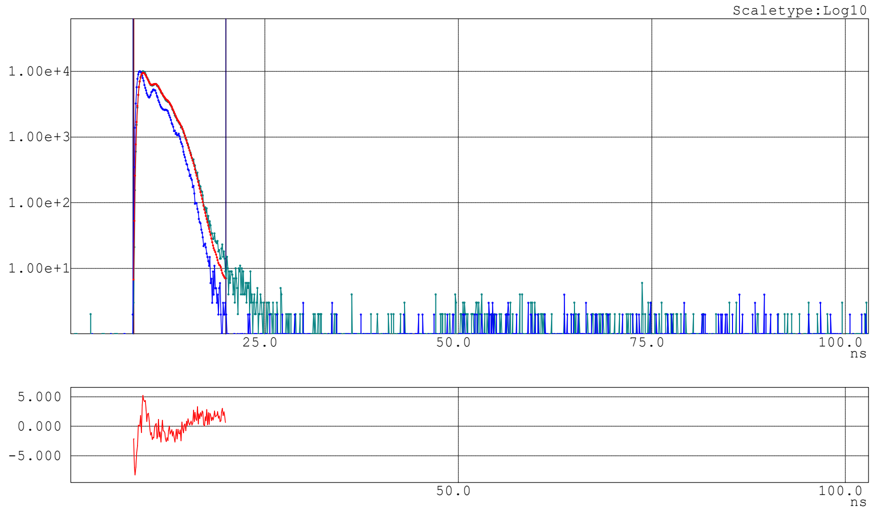


**Figure S97.** Time-correlated single photon counting (TCSPC) data of **3** in $CH_2Cl_2$.

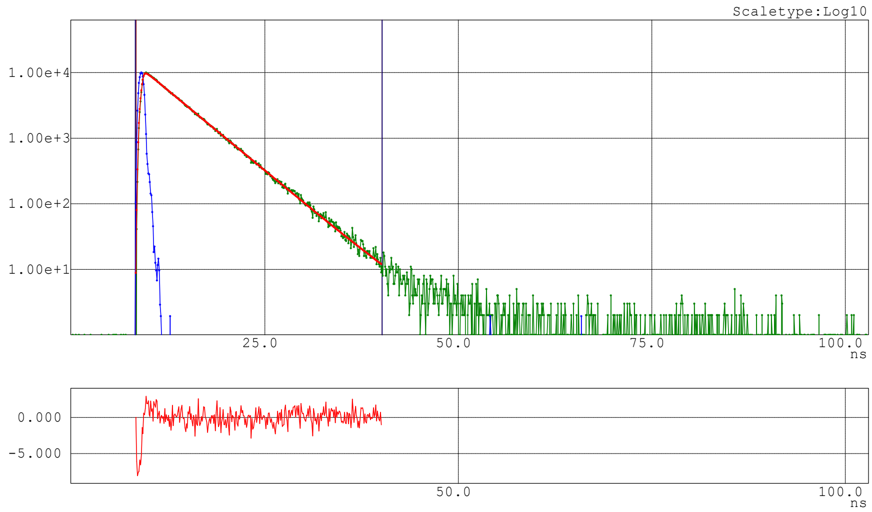


**Figure S98.** Time-correlated single photon counting (TCSPC) data of **4** in $CH_2Cl_2$.

## 8. Photophysical properties in the different solvents

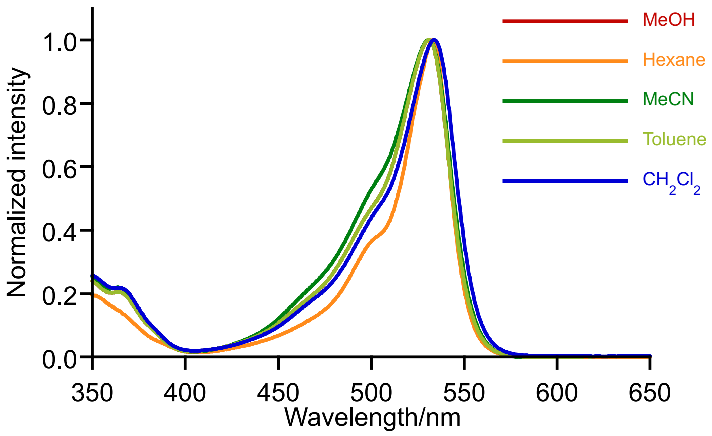


**Figure S99.** UV/vis absorption spectra of **2a** in different solvents.

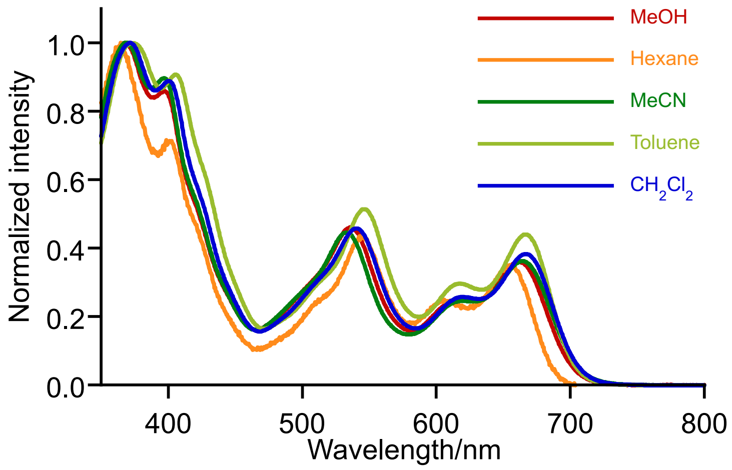


**Figure S100.** UV/vis absorption spectra of **4** in different solvents.

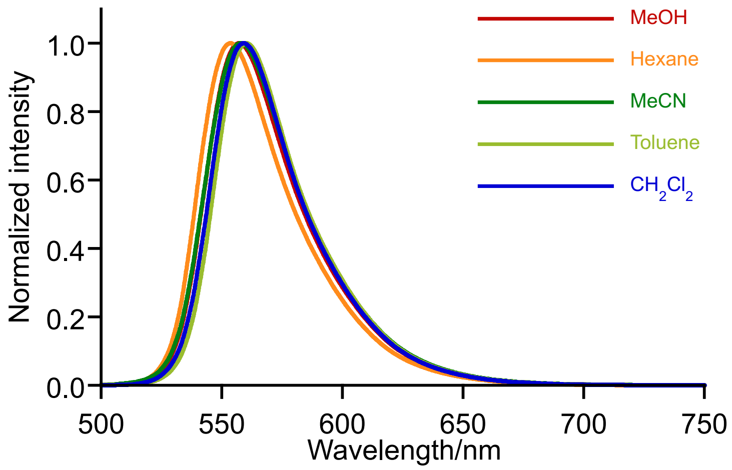


**Figure S101.** Emission spectra of **2a** in different solvents.

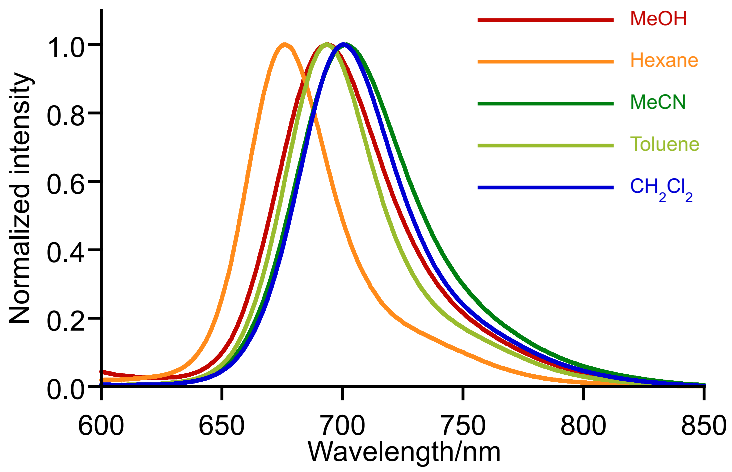


**Figure S102.** Emission spectra of **4** in different solvents.

## 9. Electrochemistry

Cyclic voltammograms and differential pulse voltammograms of **1a**, **2a** and **4** were measured in 0.1 M solution of $Bu_4NPF_6$ as a supporting electrolyte in acetonitrile (working electrode: Pt, counter electrode: Pt, reference electrode: $Ag/AgNO_3$, scan rate: 100 $mVs^{-1}$).

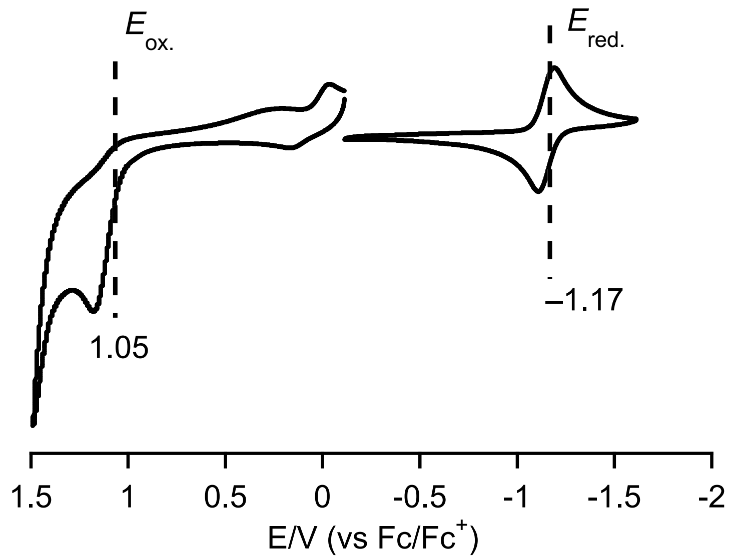


**Figure S103.** Cyclic voltammograms of **1a**.

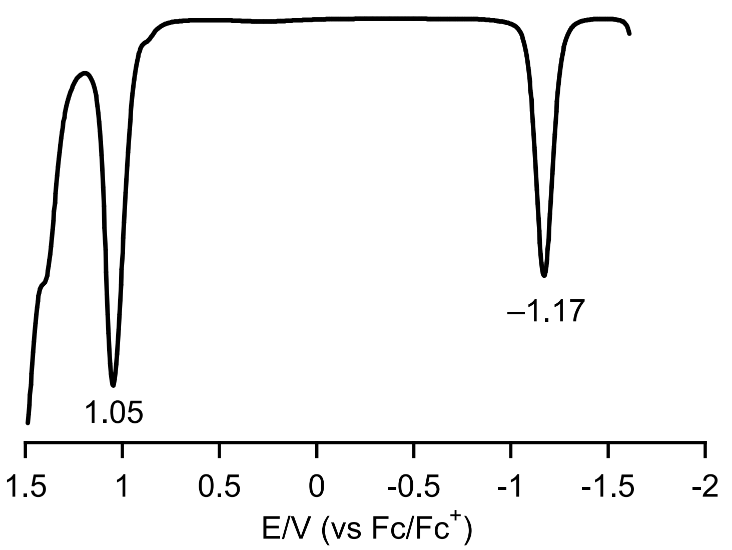


**Figure S104.** Differential pulse voltammogram of **1a**.

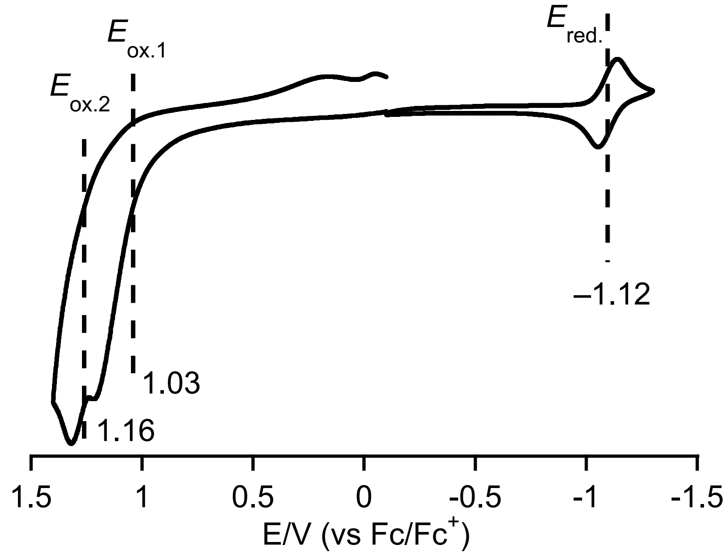


**Figure S105.** Cyclic voltammograms of **1e**.

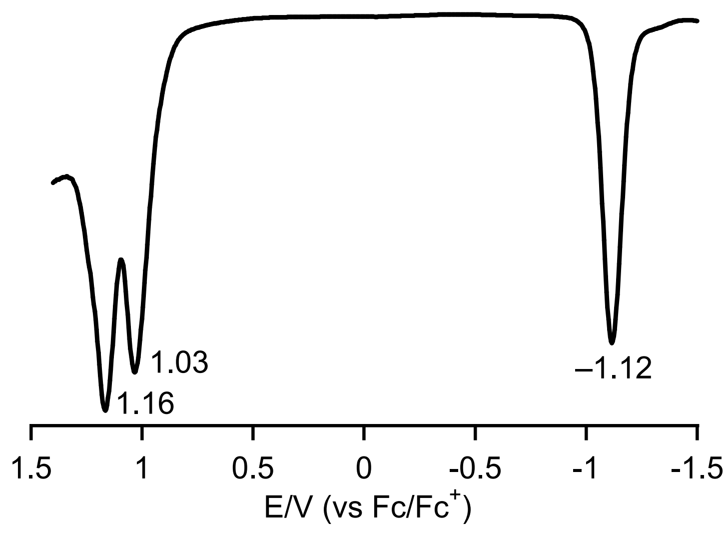


**Figure S106.** Differential pulse voltammogram of **1e**.

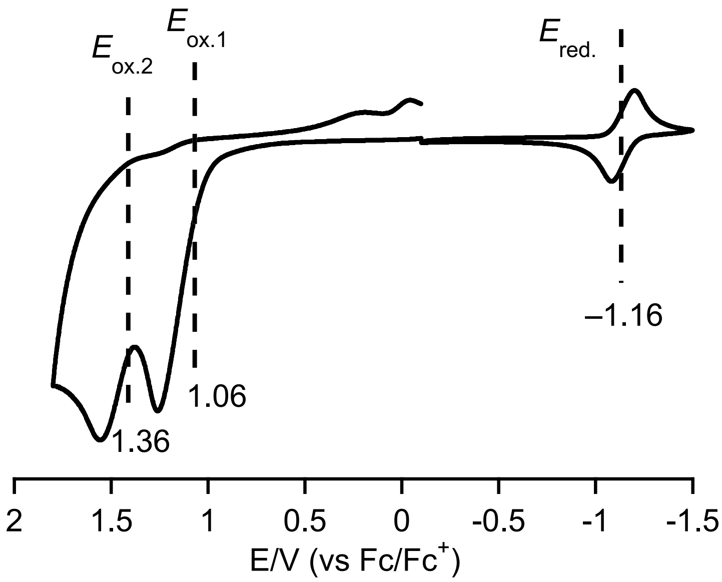


**Figure S107.** Cyclic voltammograms of **1f**.

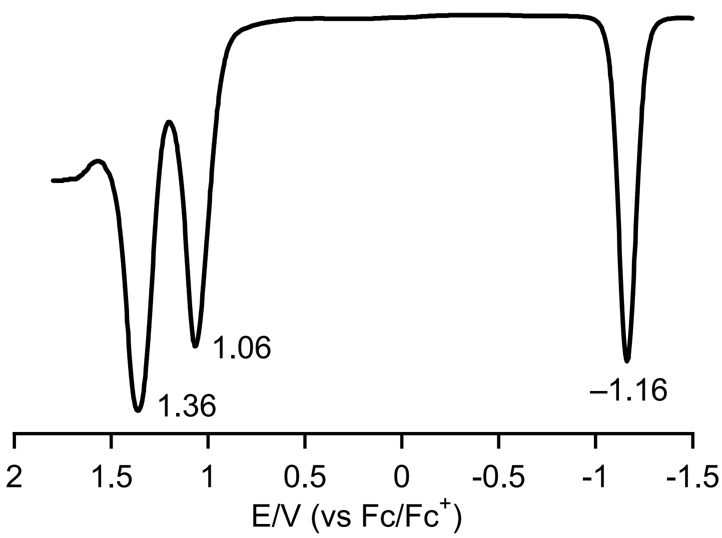


**Figure S108.** Differential pulse voltammogram of **1f**.

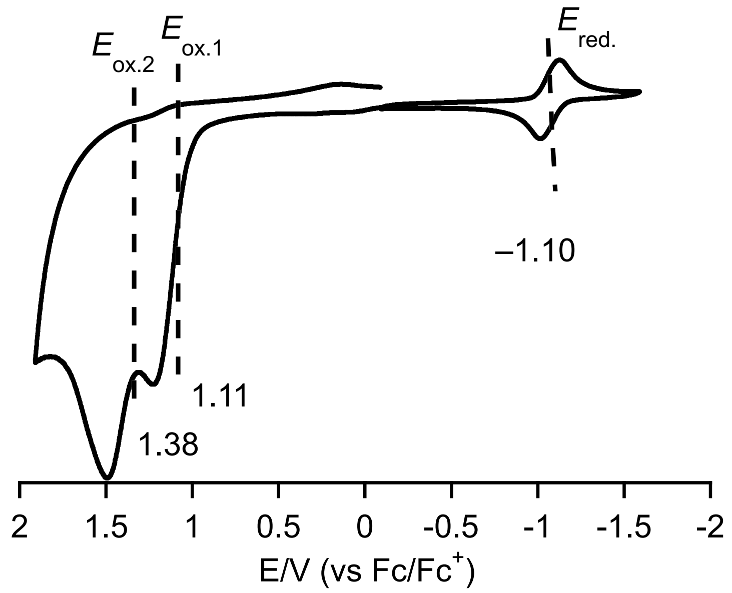


**Figure S109.** Cyclic voltammograms of **3**.

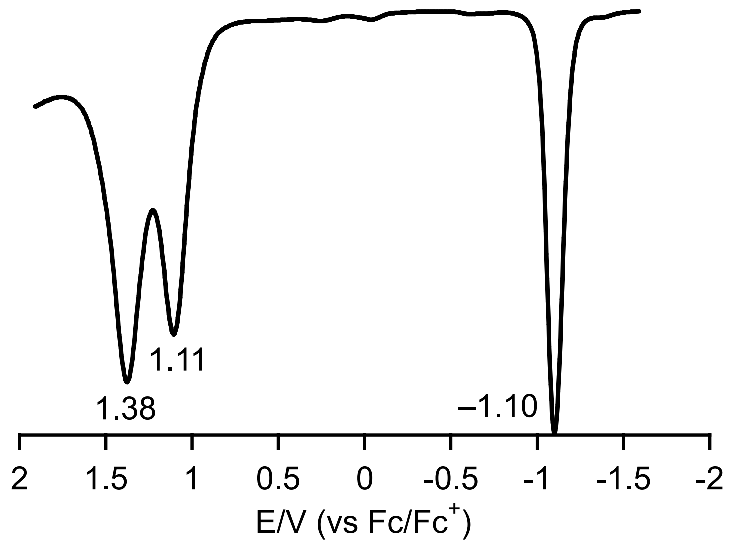


**Figure S110.** Differential pulse voltammogram of **3**.

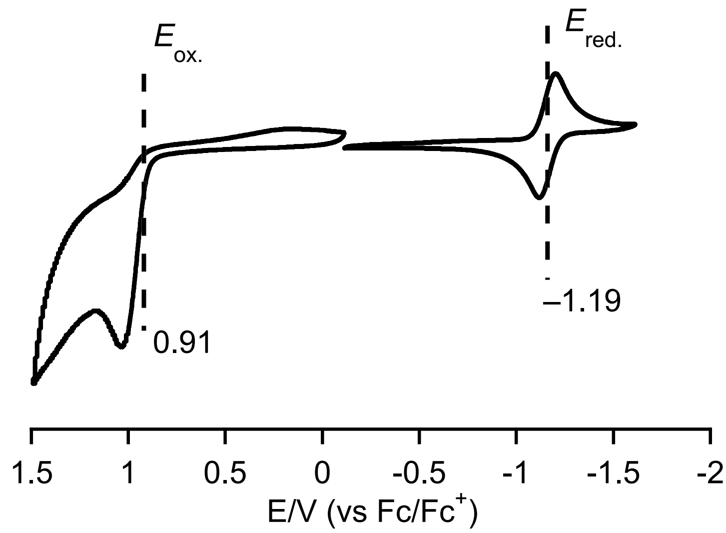


**Figure S111.** Cyclic voltammograms of **2a**.

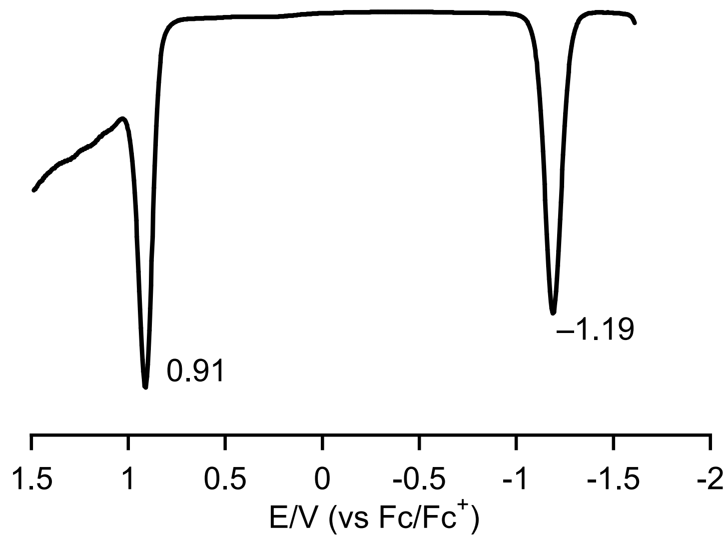


**Figure S112.** Differential pulse voltammogram of **2a**.

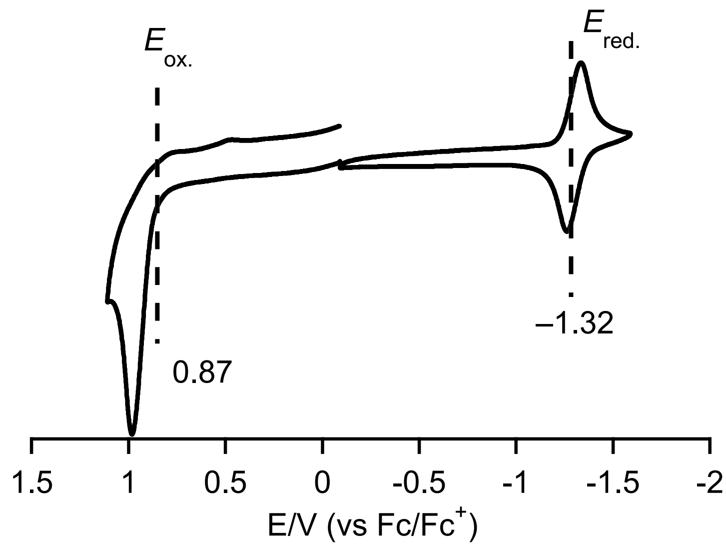


**Figure S113.** Cyclic voltammograms of **2e**.

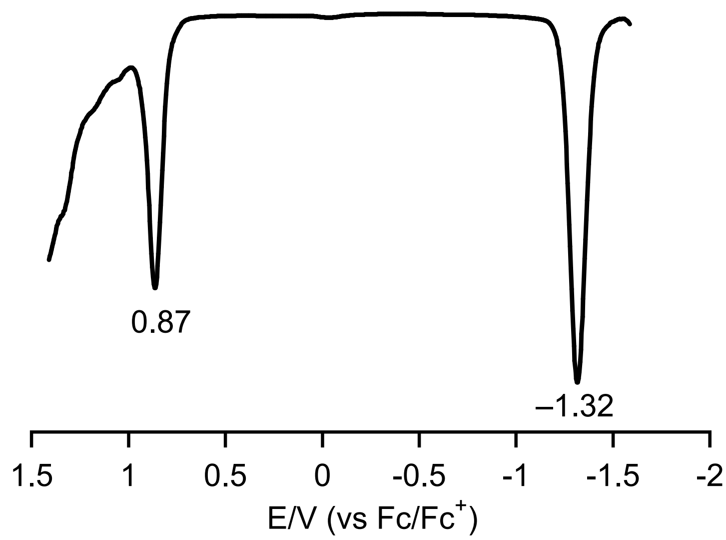


**Figure S114.** Differential pulse voltammogram of **2e**.

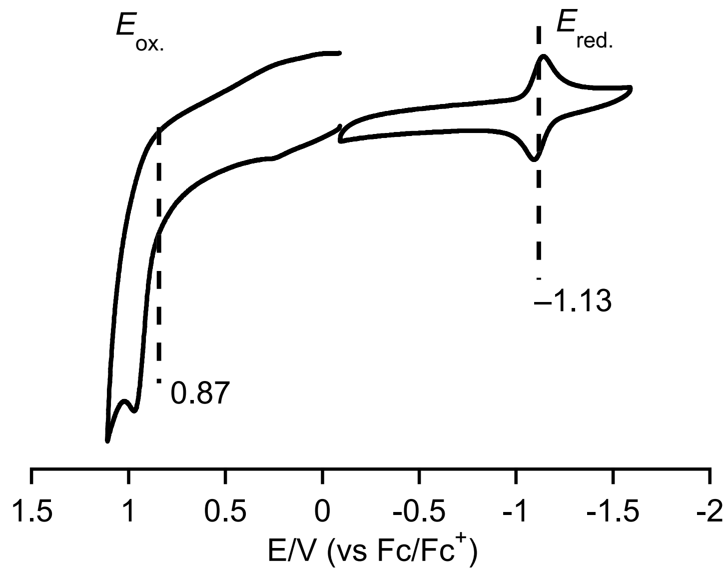


**Figure S115.** Cyclic voltammograms of **2f**.

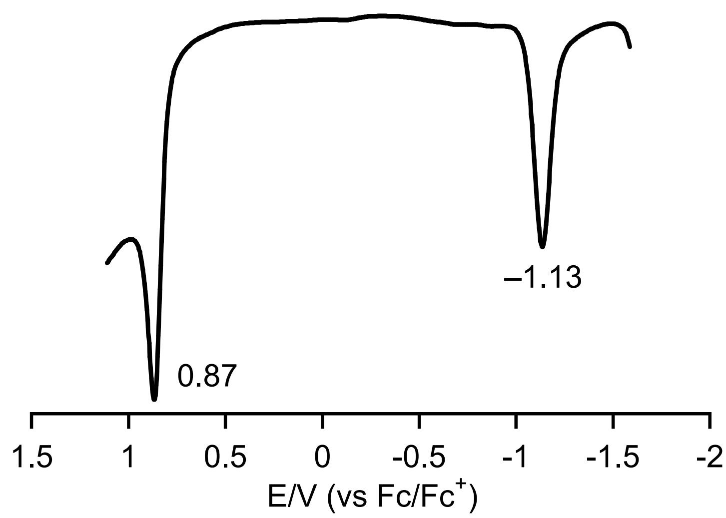


**Figure S116.** Differential pulse voltammogram of **2f**.

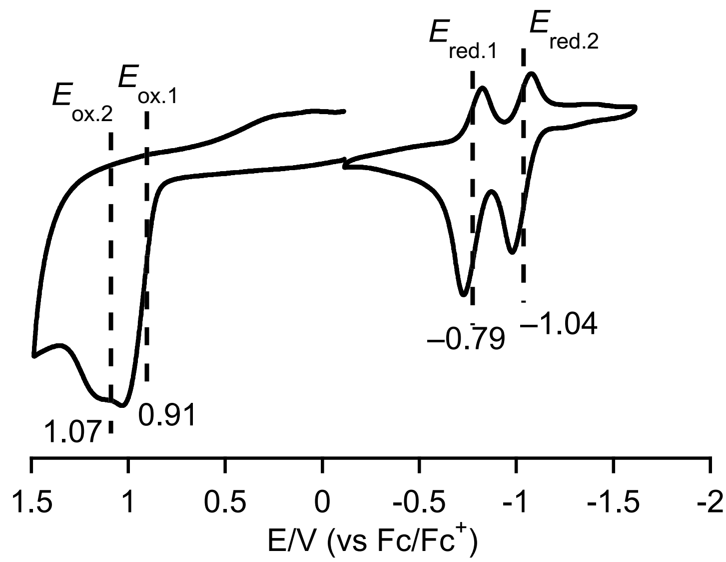


**Figure S117.** Cyclic voltammograms of **4**.

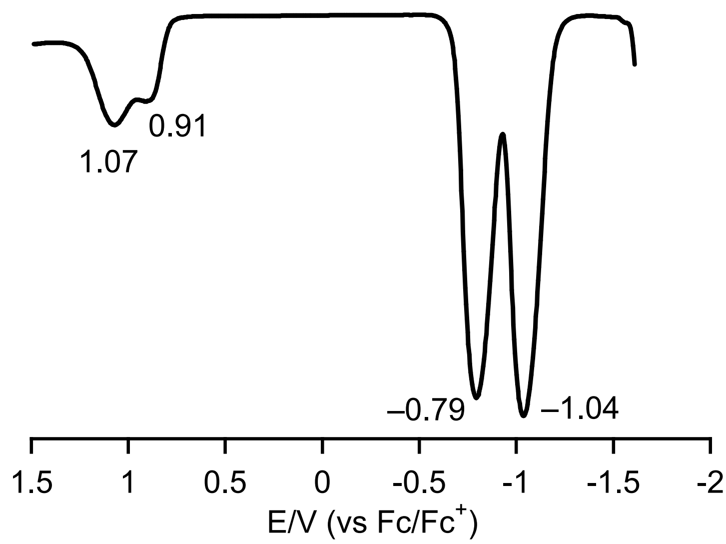


**Figure S118.** Differential pulse voltammogram of **4**.

## 10. DFT calculations

All calculations were conducted using the *Gaussian 16*[7] and *GRRM17*.[8] All geometry optimizations for stationary points were performed by the density functional theory (DFT) method with the B3LYP/6-31G+(d,p) level of theory. Vibration frequencies were also calculated using the same level of theory to confirm whether the stationary point structures are minima or transition states. The transition state of the inversion of the helical structure was confirmed to connect corresponding stable structures by using intrinsic reaction coordination (IRC) calculations.[9]

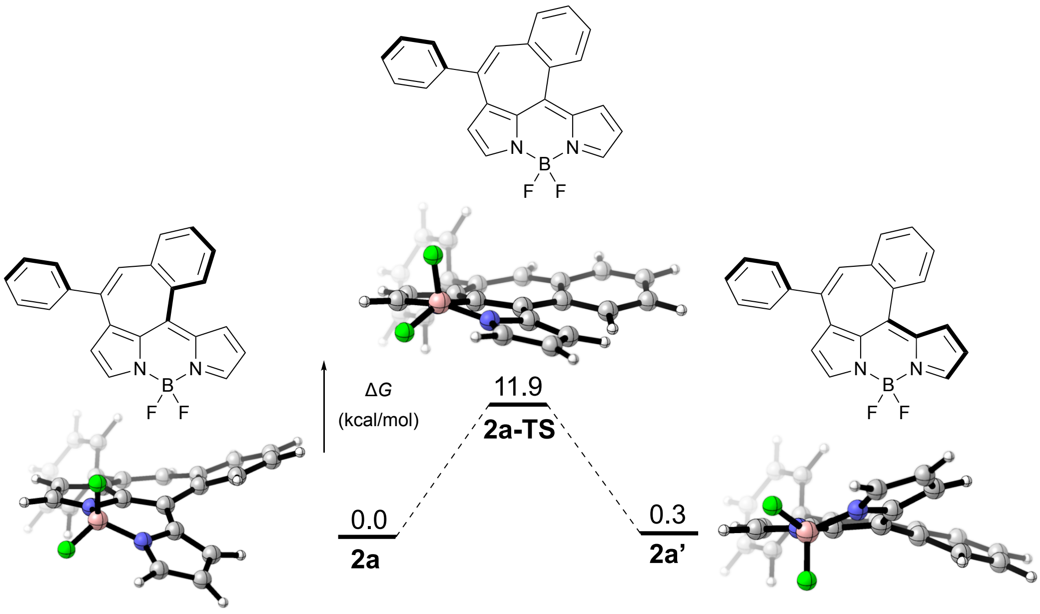


**Figure S119.** Inversion of helical structure of **2a**.

**Table S2.** Electron energies and Gibbs free energies.

| Structure | Electron energy/hartree | Free energy/hartree |
|---|---|---|
| **2a** | –1219.772323 | –1219.494740 |
| **2a-TS** | –1219.7529973 | –1219.475703 |
| **2a'** | –1219.771649 | –1219.494317 |

**Table S2.** Cartesian coordination of optimized structures.

**1a**

| | | | |
|---|---|---|---|
| C | 1.582500 | -2.459972 | -2.344195 |
| C | 2.012883 | -1.411163 | -3.185169 |
| C | 2.046972 | -0.260461 | -2.405062 |
| C | 1.646600 | -0.633304 | -1.094203 |
| N | 1.368701 | -2.000877 | -1.100804 |
| H | 1.417134 | -3.502286 | -2.581472 |
| H | 2.263203 | -1.504008 | -4.232348 |
| H | 2.330857 | 0.736569 | -2.710469 |
| C | 1.202001 | -0.506388 | 1.293002 |
| C | 1.139431 | 0.001755 | 2.617699 |
| N | 0.911528 | -1.870321 | 1.340113 |
| C | 0.814708 | -1.064167 | 3.449099 |
| H | 1.325461 | 1.028003 | 2.900938 |
| C | 0.677856 | -2.199081 | 2.620643 |
| H | 0.689997 | -1.047589 | 4.522412 |
| H | 0.424391 | -3.215582 | 2.889971 |
| C | 1.541248 | 0.118698 | 0.084801 |
| B | 0.738102 | -2.790249 | 0.090798 |
| F | 1.389081 | -4.004727 | 0.277452 |
| F | -0.628271 | -2.989714 | -0.154121 |
| C | 1.801145 | 1.588073 | 0.055796 |
| C | 3.112240 | 2.074757 | 0.079057 |
| C | 0.713536 | 2.498207 | 0.001636 |
| C | 3.365511 | 3.448459 | 0.060939 |
| H | 3.936897 | 1.369293 | 0.119555 |
| C | 0.987531 | 3.881387 | -0.018067 |
| C | 2.298446 | 4.350260 | 0.013691 |
| H | 4.389117 | 3.809344 | 0.084488 |
| H | 0.155335 | 4.576301 | -0.062343 |
| H | 2.487790 | 5.419422 | -0.001112 |
| C | -0.628445 | 2.021629 | -0.054344 |
| C | -1.760723 | 1.577836 | -0.113608 |
| C | -3.072409 | 1.021859 | -0.183411 |
| C | -4.207924 | 1.857754 | -0.210095 |
| C | -3.245672 | -0.378203 | -0.228566 |
| C | -5.485167 | 1.304704 | -0.279566 |
| H | -4.075845 | 2.934588 | -0.175886 |
| C | -4.528380 | -0.919226 | -0.298266 |
| H | -2.378096 | -1.030348 | -0.209674 |
| C | -5.649883 | -0.083748 | -0.323871 |
| H | -6.353144 | 1.957347 | -0.299507 |
| H | -4.649882 | -1.997752 | -0.332987 |
| H | -6.646656 | -0.511691 | -0.378358 |

**2a**

| | | | |
|---|---|---|---|
| F | -2.833927 | -3.427304 | 0.051138 |
| F | -2.994825 | -2.135704 | -1.847037 |
| N | -1.034547 | -1.883476 | -0.442222 |
| N | -3.208738 | -1.046596 | 0.312005 |
| C | -0.476272 | -0.638087 | -0.240570 |
| C | -1.302779 | 0.477869 | 0.045528 |
| C | -0.855656 | 1.860070 | -0.128900 |
| C | -2.643766 | 0.214545 | 0.464283 |
| C | 0.497620 | 2.324979 | -0.005731 |
| C | 0.954588 | -0.783613 | -0.309133 |
| C | 1.947588 | 0.205880 | 0.002041 |
| C | 1.695606 | 1.542628 | 0.171893 |
| H | 2.567292 | 2.143368 | 0.417858 |
| C | 1.194891 | -2.147587 | -0.598533 |
| H | 2.157914 | -2.619282 | -0.718251 |
| C | 3.369235 | -0.240837 | 0.151476 |
| C | 3.727186 | -1.207172 | 1.107021 |
| H | 2.958699 | -1.650994 | 1.732681 |

| | | | |
|---|---|---|---|
| C | 4.379906 | 0.328942 | -0.639565 |
| H | 4.115085 | 1.064759 | -1.393584 |
| C | -4.660232 | 0.195096 | 1.504222 |
| H | -5.532999 | 0.464430 | 2.081948 |
| C | 6.058453 | -1.013037 | 0.476091 |
| H | 7.095003 | -1.311875 | 0.601477 |
| C | 5.713526 | -0.056499 | -0.481471 |
| H | 6.480046 | 0.388207 | -1.109577 |
| C | -1.849568 | 2.817689 | -0.473934 |
| H | -2.849394 | 2.463323 | -0.685773 |
| C | -0.040722 | -2.772142 | -0.685869 |
| H | -0.278135 | -3.803159 | -0.907588 |
| C | -3.554889 | 0.998210 | 1.220782 |
| H | -3.383303 | 2.005714 | 1.569334 |
| C | -1.577531 | 4.167783 | -0.597996 |
| H | -2.367574 | 4.853573 | -0.887666 |
| C | 0.724850 | 3.727888 | -0.075171 |
| H | 1.740862 | 4.083353 | 0.068268 |
| C | -4.413921 | -1.054911 | 0.913813 |
| H | -5.028442 | -1.944117 | 0.895601 |
| C | -0.276301 | 4.636156 | -0.357675 |
| H | -0.048140 | 5.695584 | -0.425094 |
| C | 5.060804 | -1.584798 | 1.271600 |
| H | 5.320644 | -2.324196 | 2.023674 |
| B | -2.564300 | -2.185085 | -0.518783 |

**2a-TS**

| | | | |
|---|---|---|---|
| F | 2.871007 | -3.395425 | -0.350872 |
| F | 2.654880 | -2.488489 | 1.746985 |
| N | 1.037511 | -1.884981 | 0.066139 |
| N | 3.288055 | -1.030534 | -0.077245 |
| C | 0.513219 | -0.607109 | -0.005078 |
| C | 1.369957 | 0.539682 | -0.116199 |
| C | 0.815732 | 1.918073 | -0.082411 |
| C | 2.805032 | 0.278285 | -0.231012 |
| C | -0.547853 | 2.306817 | 0.212605 |
| C | -0.931875 | -0.783192 | -0.051234 |
| C | -1.969790 | 0.191408 | 0.016416 |
| C | -1.749268 | 1.522637 | 0.223588 |
| H | -2.649048 | 2.117642 | 0.348187 |
| C | -1.180313 | -2.173695 | -0.039959 |
| H | -2.147428 | -2.650121 | -0.053278 |
| C | -3.394702 | -0.260092 | -0.066922 |
| C | -3.881612 | -0.885346 | -1.226975 |
| H | -3.209066 | -1.064360 | -2.060774 |
| C | -4.280887 | -0.027348 | 0.996536 |
| H | -3.913273 | 0.441075 | 1.905223 |
| C | 5.083519 | 0.216073 | -0.550188 |
| H | 6.104164 | 0.503360 | -0.758233 |
| C | -6.096320 | -1.028472 | -0.255226 |
| H | -7.138242 | -1.325884 | -0.328187 |
| C | -5.620943 | -0.412072 | 0.904620 |
| H | -6.290227 | -0.233336 | 1.741197 |
| C | 1.697963 | 3.011038 | -0.302717 |
| H | 2.688678 | 2.810815 | -0.639378 |
| C | 0.045373 | -2.802062 | 0.047320 |
| H | 0.284503 | -3.854198 | 0.111966 |
| C | 3.973254 | 1.054507 | -0.528359 |
| H | 4.073328 | 2.101546 | -0.739977 |
| C | 1.376649 | 4.342504 | -0.133383 |
| H | 2.129601 | 5.100570 | -0.325682 |
| C | -0.837036 | 3.690464 | 0.427554 |
| H | -1.858497 | 3.947319 | 0.689064 |
| C | 4.618224 | -1.065823 | -0.256793 |
| H | 5.154014 | -1.999531 | -0.161251 |
| C | 0.088267 | 4.697439 | 0.286738 |

| | | | |
|---|---|---|---|
| H | -0.186141 | 5.732994 | 0.461488 |
| C | -5.222548 | -1.261680 | -1.321529 |
| H | -5.584954 | -1.734822 | -2.229594 |
| B | 2.497281 | -2.260294 | 0.373523 |

**2a'**

| | | | |
|---|---|---|---|
| F | 2.940304 | -2.327791 | -1.732554 |
| F | 2.861118 | -3.439598 | 0.320442 |
| N | 1.042214 | -1.922364 | -0.244722 |
| N | 3.235937 | -1.029392 | 0.323733 |
| C | 0.482450 | -0.650527 | -0.177823 |
| C | 1.316181 | 0.484102 | -0.005405 |
| C | 0.857008 | 1.855623 | -0.230899 |
| C | 2.672555 | 0.253032 | 0.388845 |
| C | -0.497533 | 2.320427 | -0.086878 |
| C | -0.953312 | -0.817851 | -0.182552 |
| C | -1.949059 | 0.195695 | 0.021464 |
| C | -1.693728 | 1.542286 | 0.120916 |
| H | -2.574496 | 2.157260 | 0.284505 |
| C | -1.190108 | -2.217242 | -0.257268 |
| H | -2.151421 | -2.701319 | -0.241883 |
| C | -3.382710 | -0.226325 | 0.142935 |
| C | -4.027799 | -0.915416 | -0.902224 |
| H | -3.474518 | -1.160343 | -1.802962 |
| C | -4.123821 | 0.103689 | 1.292589 |
| H | -3.634042 | 0.625268 | 2.109017 |
| C | 4.732681 | 0.294883 | 1.366138 |
| H | 5.621353 | 0.609199 | 1.890819 |
| C | -6.103386 | -0.937307 | 0.354941 |
| H | -7.149876 | -1.212733 | 0.436620 |
| C | -5.472540 | -0.251705 | 1.398880 |
| H | -6.026759 | 0.002654 | 2.296774 |
| C | 1.838255 | 2.805391 | -0.639552 |
| H | 2.831242 | 2.445539 | -0.869380 |
| C | 0.044610 | -2.850817 | -0.309384 |
| H | 0.284061 | -3.899585 | -0.379032 |
| C | 3.617999 | 1.083531 | 1.055838 |
| H | 3.468531 | 2.115383 | 1.329842 |
| C | 1.557144 | 4.151825 | -0.799821 |
| H | 2.334079 | 4.830634 | -1.134221 |
| C | -0.733159 | 3.722484 | -0.204428 |
| H | -1.747743 | 4.076930 | -0.053991 |
| C | 4.467549 | -1.002262 | 0.892078 |
| H | 5.071263 | -1.894463 | 0.935796 |
| C | 0.258751 | 4.624793 | -0.541046 |
| H | 0.026722 | 5.680036 | -0.638354 |
| C | -5.377278 | -1.265607 | -0.796368 |
| H | -5.862147 | -1.788689 | -1.614503 |
| B | 2.555882 | -2.226636 | -0.359798 |

**4**

| | | | |
|---|---|---|---|
| F | 5.986035 | -3.734679 | 0.791014 |
| F | 4.553029 | -4.032934 | -0.985360 |
| N | 4.859142 | -1.792467 | -0.116207 |
| N | 3.608405 | -3.459563 | 1.173742 |
| C | 3.785919 | -0.924086 | -0.062405 |
| C | 2.553709 | -1.354604 | 0.482780 |
| C | 1.302799 | -0.612278 | 0.302634 |
| C | 2.533158 | -2.579388 | 1.214607 |
| C | 1.183045 | 0.812675 | 0.150226 |
| C | 4.239839 | 0.362519 | -0.532467 |
| C | 3.530370 | 1.613222 | -0.501567 |
| C | 2.220229 | 1.772001 | -0.130256 |
| H | 1.861429 | 2.797601 | -0.148481 |
| C | 5.603304 | 0.194635 | -0.864820 |
| H | 6.278458 | 0.958224 | -1.217668 |

| | | | |
|---|---|---|---|
| C | 4.273964 | 2.853977 | -0.891242 |
| C | 4.452809 | 3.895553 | 0.032461 |
| H | 4.082764 | 3.778406 | 1.047156 |
| C | 4.770053 | 3.015224 | -2.195632 |
| H | 4.625954 | 2.224015 | -2.925638 |
| C | 2.160603 | -4.245056 | 2.709966 |
| H | 1.742224 | -4.868453 | 3.487283 |
| C | 5.602845 | 5.220653 | -1.636612 |
| H | 6.115223 | 6.133677 | -1.924945 |
| C | 5.425520 | 4.191059 | -2.565569 |
| H | 5.792880 | 4.304315 | -3.581419 |
| C | 0.115463 | -1.354418 | 0.229238 |
| H | 0.201998 | -2.431448 | 0.166084 |
| C | 5.929493 | -1.131912 | -0.613491 |
| H | 6.868672 | -1.648555 | -0.754213 |
| C | 1.621531 | -3.069615 | 2.189472 |
| H | 0.715324 | -2.578681 | 2.511328 |
| C | -0.115468 | 1.354410 | 0.229254 |
| H | -0.202004 | 2.431442 | 0.166117 |
| C | 3.382360 | -4.457351 | 2.048590 |
| H | 4.098703 | -5.259195 | 2.161549 |
| C | -1.302803 | 0.612269 | 0.302633 |
| C | 5.115317 | 5.069042 | -0.336491 |
| H | 5.251174 | 5.861973 | 0.393212 |
| B | 4.799855 | -3.322601 | 0.191141 |
| F | -5.986025 | 3.734676 | 0.791054 |
| F | -4.553048 | 4.032935 | -0.985342 |
| N | -4.859145 | 1.792466 | -0.116189 |
| N | -3.608388 | 3.459564 | 1.173744 |
| C | -3.785924 | 0.924082 | -0.062395 |
| C | -2.553711 | 1.354595 | 0.482786 |
| C | -2.533144 | 2.579385 | 1.214600 |
| C | -1.183050 | -0.812682 | 0.150213 |
| C | -4.239849 | -0.362520 | -0.532462 |
| C | -3.530379 | -1.613223 | -0.501576 |
| C | -2.220236 | -1.772006 | -0.130274 |
| H | -1.861436 | -2.797605 | -0.148508 |
| C | -5.603316 | -0.194633 | -0.864801 |
| H | -6.278474 | -0.958220 | -1.217647 |
| C | -4.273975 | -2.853975 | -0.891256 |
| C | -4.452815 | -3.895557 | 0.032441 |
| H | -4.082766 | -3.778418 | 1.047135 |
| C | -4.770069 | -3.015213 | -2.195645 |
| H | -4.625974 | -2.224000 | -2.925646 |
| C | -2.160558 | 4.245060 | 2.709941 |
| H | -1.742163 | 4.868460 | 3.487248 |
| C | -5.602860 | -5.220647 | -1.636636 |
| H | -6.115238 | -6.133668 | -1.924973 |
| C | -5.425538 | -4.191046 | -2.565587 |
| H | -5.792903 | -4.304295 | -3.581436 |
| C | -5.929502 | 1.131914 | -0.613466 |
| H | -6.868680 | 1.648559 | -0.754180 |
| C | -1.621492 | 3.069621 | 2.189436 |
| H | -0.715276 | 2.578691 | 2.511271 |
| C | -3.382326 | 4.457354 | 2.048586 |
| H | -4.098666 | 5.259199 | 2.161554 |
| C | -5.115325 | -5.069044 | -0.336516 |
| H | -5.251179 | -5.861979 | 0.393182 |
| B | -4.799854 | 3.322600 | 0.191162 |

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