

Electronic supplementary information

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

Fumika Ohashi,^a Hideaki Takano^{*a,b} and Hiroshi Shinokubo^{*a}

^a Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan

^b Institute for Advanced Research, Nagoya University. Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8601, Japan.

E-mail: htakano@chembio.nagoya-u.ac.jp, hshino@chembio.nagoya-u.ac.jp

Table of Contents

1.	Instrumentation and materials	3
2.	Experimental procedures and compound data	4
3.	NMR spectra	15
4.	Mass spectra	78
5.	Crystal data.....	98
6.	Temperature-dependent ^{19}F NMR spectra	102
7.	Fluorescence decay profiles	104
8.	Photophysical properties in the different solvents	108
9.	Electrochemistry	110
10.	DFT calculations	118
11.	References	123

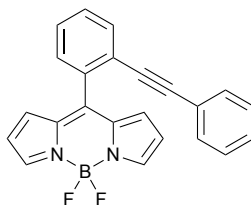
1. Instrumentation and materials

^1H 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 ^1H 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)BODIPY⁵ 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

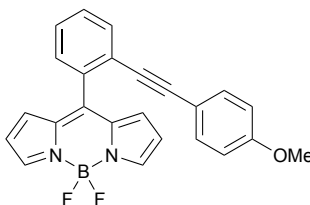
4,4-Difluoro-8-(2-(phenylethynyl)phenyl)-4-bora-3a,4a-diaza-s-indacene (1a)



In a Schlenk tube, 8-(2-iodophenyl)BODIPY (100 mg, 0.25 mmol), PdCl₂(PPh₃)₂ (3.5 mg, 5 μmol), phenylacetylene (70 μL, 0.64 mmol), Et₃N (70 μL, 0.50 mmol) and THF (0.8 mL) were added under N₂. 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 CH₂Cl₂. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/CH₂Cl₂ (v/v = 1/1) to afford **1a** as an orange solid (89.4 mg, 96%).

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 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); ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 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); ¹⁹F NMR (376 MHz, CDCl₃, 298 K) δ = –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 C₂₃H₁₅¹⁰BFN₂ 348.1343; Found 348.1345.

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

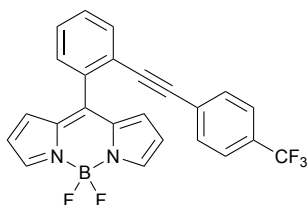


In a Schlenk tube, 8-(2-iodophenyl)BODIPY (100 mg, 0.25 mmol), PdCl₂(PPh₃)₂ (3.5 mg, 5 μmol), 1-ethynyl-4-methoxybenzene (54 mg, 0.41 mmol), Et₃N (70 μL, 0.50 mmol) and THF (0.8 mL) were added under N₂. The mixture was stirred for 5 min, and CuI (4.8 mg, 25 μmol) was added. After stirring at room temperature for 20 h, the mixture was filtered through Celite[®] with CH₂Cl₂. The solvent was evaporated, and the crude product was purified by column

chromatography on silica gel using hexane/CH₂Cl₂ (v/v = 1/1) to afford **1b** as an orange solid (91.0 mg, 90%).

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 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); ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 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); ¹⁹F NMR (376 MHz, CDCl₃, 298 K) δ = –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 C₂₄H₁₇¹⁰BFN₂O 348.1449; Found 348.1441.

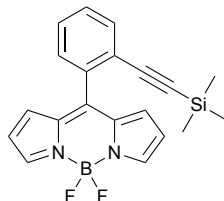
4,4-Difluoro-8-(2-((4-trifluoromethylphenyl)ethynyl)phenyl)-4-bora-3a,4a-diaza-s-indacene (**1c**)



In a Schlenk tube, 8-(2-iodophenyl)BODIPY (100 mg, 0.25 mmol), PdCl₂(PPh₃)₂ (3.6 mg, 5 μmol), 1-ethynyl-4-(trifluoromethyl)benzene (70 μL, 0.49 mmol), Et₃N (70 μL, 0.50 mmol) and THF (0.8 mL) were added under N₂. 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 CH₂Cl₂. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/CH₂Cl₂ (v/v = 1/1) to afford **1c** as an orange solid (59.1 mg, 54%).

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 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); ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 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; ¹⁹F NMR (376 MHz, CDCl₃, 298 K) δ = –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 C₂₄H₁₄¹⁰BF₄N₂ 416.1217; Found 416.1198.

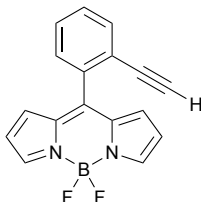
4,4-Difluoro-8-(2-(trimethylsilylethynyl)phenyl)-4-bora-3a,4a-diaza-s-indacene (**S1**)



In a Schlenk tube, 8-(2-iodophenyl)BODIPY (256 mg, 0.65 mmol), PdCl₂(PPh₃)₂ (23 mg, 33 μmol), trimethylsilylacetylene (0.22 mL, 1.6 mmol), Et₃N (0.26 mL, 1.9 mmol) and THF (2 mL) were added under N₂. 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 CH₂Cl₂. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/CH₂Cl₂ (v/v = 1/1) to provide **S1** as a red solid (226 mg, 96%).

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 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); ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 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; ¹⁹F NMR (376 MHz, CDCl₃, 298 K) δ = –146.0– –146.8 (m, 2F) ppm; HRMS (APCI): [M–F]⁺ Calcd for C₂₀H₁₉¹⁰BFN₂Si 344.1425; Found 344.1420.

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

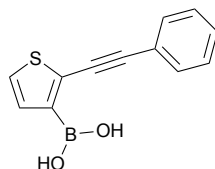


BODIPY **S1** (51 mg, 0.14 mmol) was dissolved in THF (2.7 mL) under N₂. TBAF (tetrabutylammonium fluoride) (1 M solution in THF; 0.14 mL, 0.14 mmol) was added and the mixture was stirred for 45 minutes at room temperature. The mixture was quenched with aqueous NH₄Cl, extracted with Et₂O, dried over Na₂SO₄, filtered, and concentrated. The crude product was purified by silica gel short pad using CH₂Cl₂ to afford the desired product **1d** as a brown solid (29.0 mg, 71%).

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 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); ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 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; ¹⁹F NMR (376 MHz, CDCl₃, 298 K) δ = –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 C₁₇H₁₁¹⁰BFN₂

272.1030; Found 272.1017.

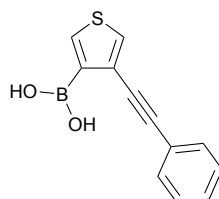
(2-(Phenylethynyl)thiophen-3-yl)boronic acid (S2)



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 Et₂O under N₂ 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 Na₂SO₄, 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%).

¹H NMR (500 MHz, acetone-*d*₆, 298 K): δ = 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); ¹³C NMR (126 MHz, acetone-*d*₆, 298 K): δ = 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 C₁₂H₁₀¹⁰BO₂S 228.0525; Found 228.0522.

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

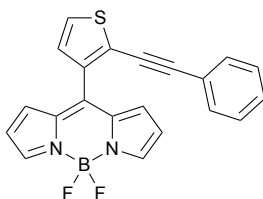


In a two-necked round bottom flask, 1.6 M solution of *n*-BuLi (12 mL, 1.6 M in hexane, 19 mmol) was added dropwise to a solution of 3-bromo-4-(phenylethynyl)thiophene (3.3 g, 13 mmol) in 100 mL of Et₂O under N₂ at -78 °C. The mixture was stirred at -40 °C for 1 h and then cooled back to -78 °C. Then, 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 Na₂SO₄, 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%).

^1H NMR (500 MHz, acetone- d_6 , 298 K): δ = 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): δ = 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): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{10}^{10}\text{BO}_2\text{S}$ 228.0525; Found 228.0519.

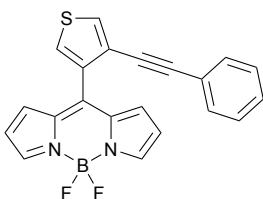
4,4-Difluoro-8-(2-(phenylethynyl)thiophen-3-yl)-4-bora-3a,4a-diaza-s-indacene (**1e**)



In a Schlenk tube, **S2** (144 mg, 0.63 mmol), 8-thiomethylBODIPY (50 mg, 0.21 mmol), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (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 $^\circ\text{C}$ 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%).

^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 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): δ = 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) δ = -145.5 (qd, J = 28.8, 105.8 Hz, 1F), -147.1 (qd, J = 28.8, 105.8 Hz, 1F) ppm; HRMS (APCI): $[\text{M}-\text{F}]^+$ Calcd for $\text{C}_{21}\text{H}_{13}^{10}\text{BFN}_2\text{S}$ 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) $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (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 $^\circ\text{C}$ for 12 h. It was

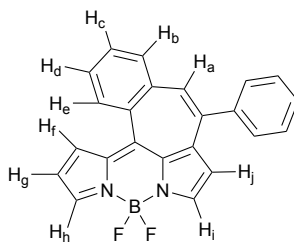
then cooled to room temperature and filtered through Celite[®] with CH₂Cl₂. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/CH₂Cl₂ (v/v = 1/1) to afford **1f** as an orange solid (61.3 mg, 76%).

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 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); ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 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; ¹⁹F NMR (376 MHz, CDCl₃, 298 K) δ = -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 C₂₁H₁₃¹⁰BFN₂S 354.0907; Found 354.0895.

General procedure for synthesis of 2a–f

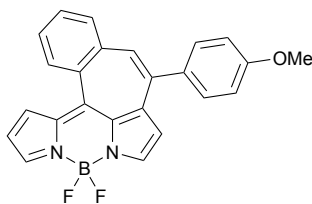
In a Schlenk tube, BODIPYs **1a–f** (0.10 mmol, 1.0 equiv), chloro[tris(2,4-di-*tert*-butylphenyl)phosphite]gold (0.01 mol, 0.10 equiv) AgPF₆ (0.01 mmol, 0.10 eq) were dissolved in CH₂Cl₂ (5 mL) under N₂. The reaction was stirred at room temperature for 1–2 h. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/CH₂Cl₂ (v/v = 1/1) to yield **2a–f**.

9,9-Difluoro-6-phenyl-9*H*-8a,9aλ⁴-diazia-9λ⁴-borabenzocyclohepta[1,2,3-*kl*]-s-indacene (**2a**)



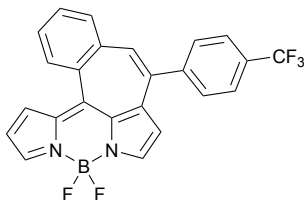
Red solid; ¹H NMR (500 MHz, CDCl₃, 298 K): δ = 8.84 (br d, J = 8.3 Hz, H_e), 8.18 (br, H_i), 7.99 (d, J = 8.3 Hz, H_b), 7.87 (ddd, J = 1.4, 7.1, 8.3 Hz, H_c), 7.82 (br, H_h), 7.75 (ddd, J = 1.4, 7.1, 8.3 Hz, H_d), 7.64 (s, H_a), 7.55–7.49 (m, 5H on Ph group), 7.12 (d, J = 3.9 Hz, H_f), 6.73 (d, J = 2.4 Hz, H_j), 6.59 (dd, J = 2.4, 3.9 Hz, H_g); ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 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); ¹⁹F NMR (376 MHz, CDCl₃, 298 K) δ = -147.2 (br, 2F) ppm; ¹¹B NMR (160 MHz, CDCl₃, 298 K) δ = 0.63 (t, J = 27.9 Hz) ppm; HRMS (APCI): [M-F]⁺ Calcd for C₂₃H₁₅¹⁰BFN₂ 348.1343; Found 348.1329.

9,9-Difluoro-6-(4-methoxyphenyl)-9*H*-8a,9a λ^4 -diaz-9 λ^4 -borabenz[6,7]cyclohepta[1,2,3-*kl*]-*s*-indacene (2b)



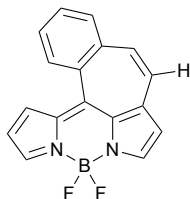
Red solid; ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 8.83 (br d, J = 8.2 Hz, 1H), 8.18 (d, J = 2.3 Hz, 1H), 7.98 (br d, J = 8.2 Hz, 1H), 7.86 (ddd, J = 1.4, 7.1, 8.2 Hz, 1H), 7.81 (br, 1H), 7.73 (ddd, J = 1.4, 7.1, 8.2 Hz, 1H), 7.64 (s, 1H), 7.48 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 3.9 Hz, 1H), 7.05 (d, J = 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): δ = 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) δ = -147.9 (br, 2F) ppm; ^{11}B NMR (160 MHz, CDCl_3 , 298 K) δ = 0.63 (t, J = 28.4 Hz) ppm; HRMS (APCI): $[\text{M}-\text{F}]^+$ Calcd for $\text{C}_{24}\text{H}_{17}^{10}\text{BFN}_2\text{O}$ 348.1449; Found 348.1449.

9,9-Difluoro-6-(4-trifluoromethylphenyl)-9*H*-8a,9a λ^4 -diaz-9 λ^4 -borabenz[6,7]cyclohepta[1,2,3-*kl*]-*s*-indacene (2c)



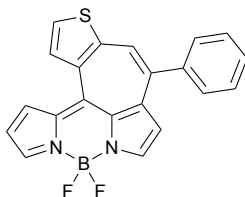
Red solid; ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 8.82 (br d, J = 8.0 Hz, 1H), 8.17 (br, 1H), 7.98 (br d, J = 8.0 Hz, 1H), 7.90 (ddd, J = 1.3, 7.1, 8.0 Hz, 1H), 7.85 (br, 1H), 7.80–7.77 (m, 3H), 7.67 (d, J = 8.0 Hz, 2H), 7.58 (s, 1H), 7.13 (d, J = 3.9 Hz, 1H), 6.63 (d, J = 2.4 Hz, 1H), 6.61 (dd, J = 2.4, 3.9 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3 , 298 K): δ = 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) δ = -63.7 (s, 3F), -147.7 (br, 2F) ppm; ^{11}B NMR (160 MHz, CDCl_3 , 298 K) δ = 0.58 (t, J = 27.9 Hz) ppm; HRMS (APCI): $[\text{M}-\text{F}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}^{10}\text{BF}_4\text{N}_2$ 416.1217; Found 416.1204

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



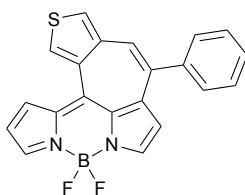
Red solid; ^1H NMR (500 MHz, CDCl_3 , 298 K): $\delta = 8.84$ (br d, $J = 8.3$ Hz, 1H), 8.22 (br, 1H), 7.99 (br d, $J = 8.3$ Hz, 1H), 7.87 (ddd, $J = 1.4, 7.0, 8.3$ Hz, 1H), 7.81 (br, 1H), 7.76 (d, $J = 11.0$ Hz, 1H), 7.75 (ddd, $J = 1.4, 7.0, 8.3$ Hz, 1H), 7.62 (d, $J = 11.0$ Hz, 1H), 7.10 (d, $J = 3.8$ 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): $[\text{M}-\text{F}]^+$ Calcd for $\text{C}_{17}\text{H}_{11}^{10}\text{BFN}_2$ 272.1030; Found 272.1018.

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



Orange solid; ^1H 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): $[\text{M}-\text{F}]^+$ Calcd for $\text{C}_{21}\text{H}_{13}^{10}\text{BFN}_2\text{S}$ 354.0907; Found 354.0896.

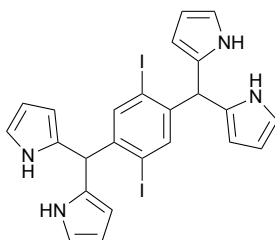
4,4-Difluoro-7-phenyl-10*H*-10-thia-3a,4a λ^4 -diaz-4 λ^4 -boraazuleno[6,5,4-*ij*]-s-indacene (2f)



Purple solid; ^1H 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): $[\text{M}-\text{F}]^+$ Calcd for $\text{C}_{21}\text{H}_{13}^{10}\text{BFN}_2\text{S}$ 354.0907; Found 354.0893.

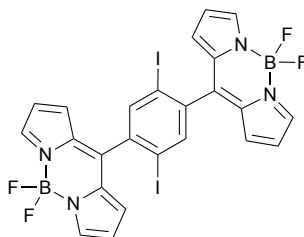
2,5-Diiodo-1,4-bis(dipyrromethan-5-yl)benzene (S4)



2,5-Diiodoterephthalaldehyde (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%).

^1H 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): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{21}\text{I}_2\text{N}_4$ 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)

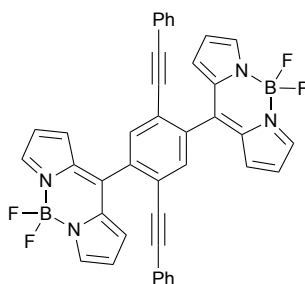


Dipyrromethane **S4** (62 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (10 mL) under N_2 . Chloranil (63 mg, 0.26 mmol) was added, and the mixture was stirred for 18 h at room temperature. The reaction mixture was filtered through alumina with CH_2Cl_2 , and the solvent was

evaporated. To a solution of the dipyrin intermediate in CH₂Cl₂ (10 mL), *N,N*-diisopropylethylamine (0.26 mL, 1.5 mmol) was added under N₂, and the mixture was stirred at room temperature for 20 min. BF₃•OEt₂ (0.26 mL, 2.1 mmol) was added dropwise, and stirring was continued for 6 h. The reaction was quenched by NaHCO₃ and extracted with CH₂Cl₂. The combined organic solution was dried over Na₂SO₄, filtered and concentrated. The crude product was purified by column chromatography on silica gel using hexane/ CH₂Cl₂ (v/v = 1/3) to provide **S5** as a red solid (16.7 mg, 23%).

¹H NMR (500 MHz, acetone-*d*₆, 298 K): δ = 8.25 (s, 2H), 8.10 (br, 4H), 7.11 (d, *J* = 4.3 Hz, 4H), 6.68 (d, *J* = 4.3 Hz, 4H); ¹³C NMR (126 MHz, acetone-*d*₆, 298 K): δ = 146.7, 146.3, 142.1, 140.9, 135.9, 132.4, 120.2, 97.6 ppm; ¹⁹F NMR (376 MHz, CDCl₃, 298 K) δ = -146.3– -146.6 (m, 4F) ppm; HRMS (APCI): [M-F]⁺ Calcd for C₂₄H₁₄¹⁰B₂F₃I₂N₄ 688.9513; Found 688.9490.

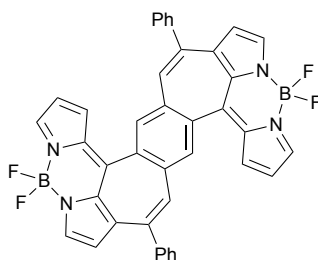
4,4-Difluoro-8-(4-(4,4-difluoro-4-bora-3a,4a-diaza-s-indacen-8-yl)-2,5-bis(phenylethynyl)phenyl)-4-bora-3a,4a-diaza-s-indacene (3)



In a Schlenk tube, **S5** (85 mg, 0.12 mmol), PdCl₂(PPh₃)₂ (11 mg, 15 μmol), phenylacetylene (70 μL, 0.64 mmol), Et₃N (0.20 mL, 1.4 mmol) and THF (5 mL) were added under N₂ 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 CH₂Cl₂. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using hexane/CH₂Cl₂ (v/v = 1/3) to provide **3** as an orange solid (67.7 mg, 86%).

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 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); ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 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; ¹⁹F NMR (376 MHz, CDCl₃, 298 K) δ = -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 C₄₀H₂₄O¹⁰B₂F₃N₄ 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 μ mol) and AgPF₆ (2.5 mg, 10 μ mol) were dissolved in CH₂Cl₂ (2.5 mL) under N₂. 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/CH₂Cl₂ (v/v = 1/1) to yield **4** as a purple solid (32.4 mg, 98%).

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 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); ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 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); ¹⁹F NMR (376 MHz, CDCl₃, 298 K) δ = -146.9 ppm (br, 4F); ¹¹B NMR (160 MHz, CDCl₃, 298 K) δ = 0.58 (t, J = 28.0 Hz) ppm; HRMS (APCI): [M-F]⁺ Calcd for C₄₀H₂₄O¹⁰B₂F₃N₄ 637.2206; Found 637.2175.

3. NMR spectra

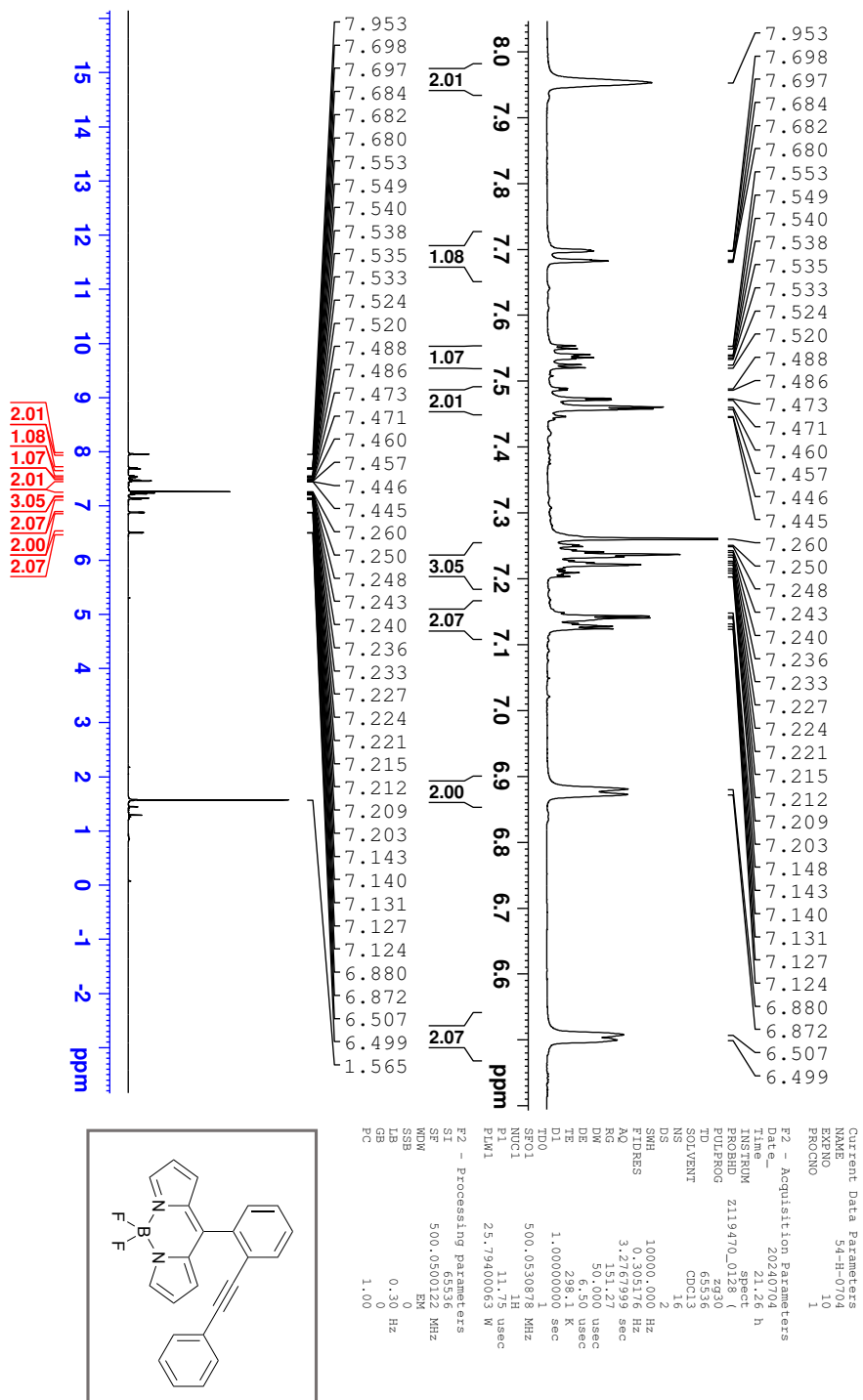
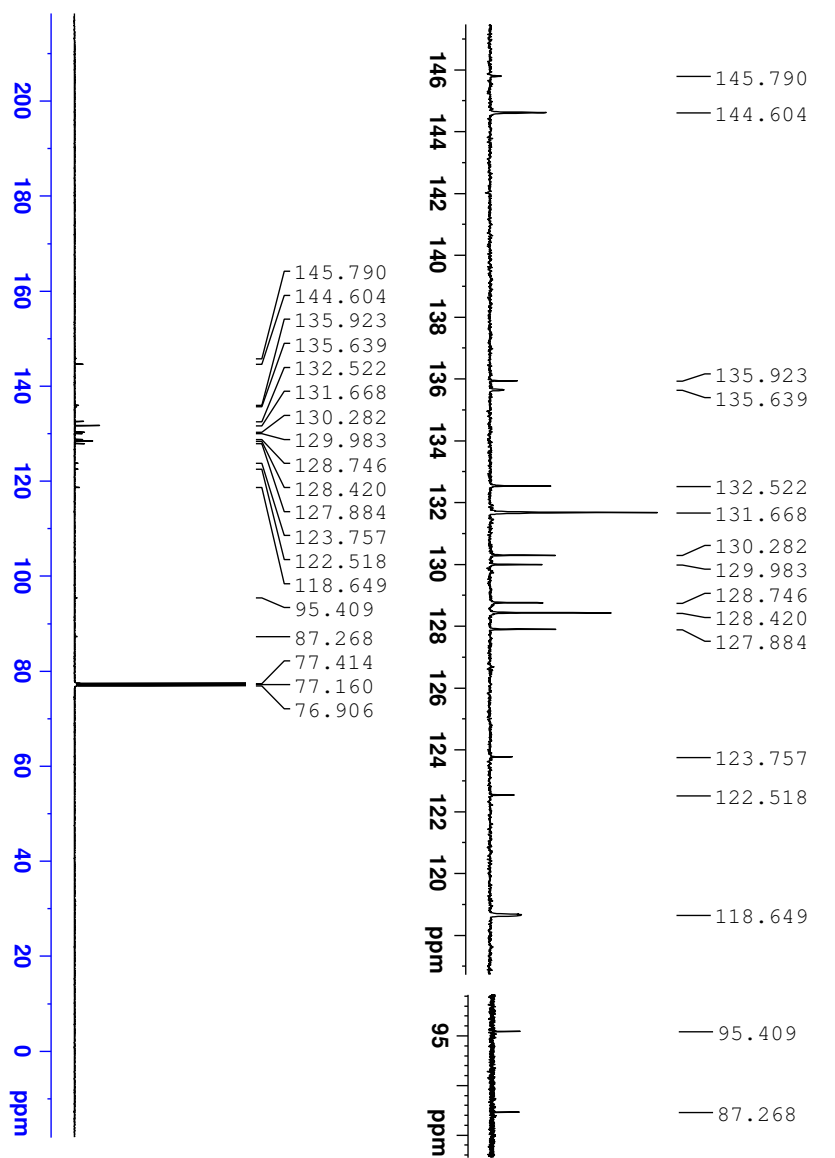


Figure S1. ¹H NMR spectrum of **1a** in CDCl₃ at 25 °C.



```

Current Data Parameters
EXNO          1
PROCNO       10
PROCNO       1
F2 - Acquisition Parameters
Date_         20240705
Time         4.51 h
INSTRUM      spect
PROBHD       Z119470_018
PULPROG      zgpg30
TD           65536
SFO1         4096
NS           4096
DS           2
SWH          29961.904 Hz
AQ           1.1010048 sec
RG           190.44
DM           16.800 usec
DE           0.200 usec
TE           299.0 K
D11          2.00000000 sec
D12          0.03000000 sec
SFO2         125.7502463 MHz
NUC1         13C
NUC2         13C
F1A1         93.8130034 MHz
SFO2         500.0520002 MHz
NUC2         1H
PCPD2        waltz16
PCPD2        80.70 usec
PLM12        25.7940063 MHz
PLM12        0.55844000 M
PLM13        0.73581929 M
F2 - Processing parameters
SI           125.737465 MHz
WDW          RM
SSB          0
GB           1.0 Hz
PC           1.40
  
```

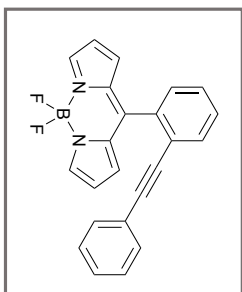
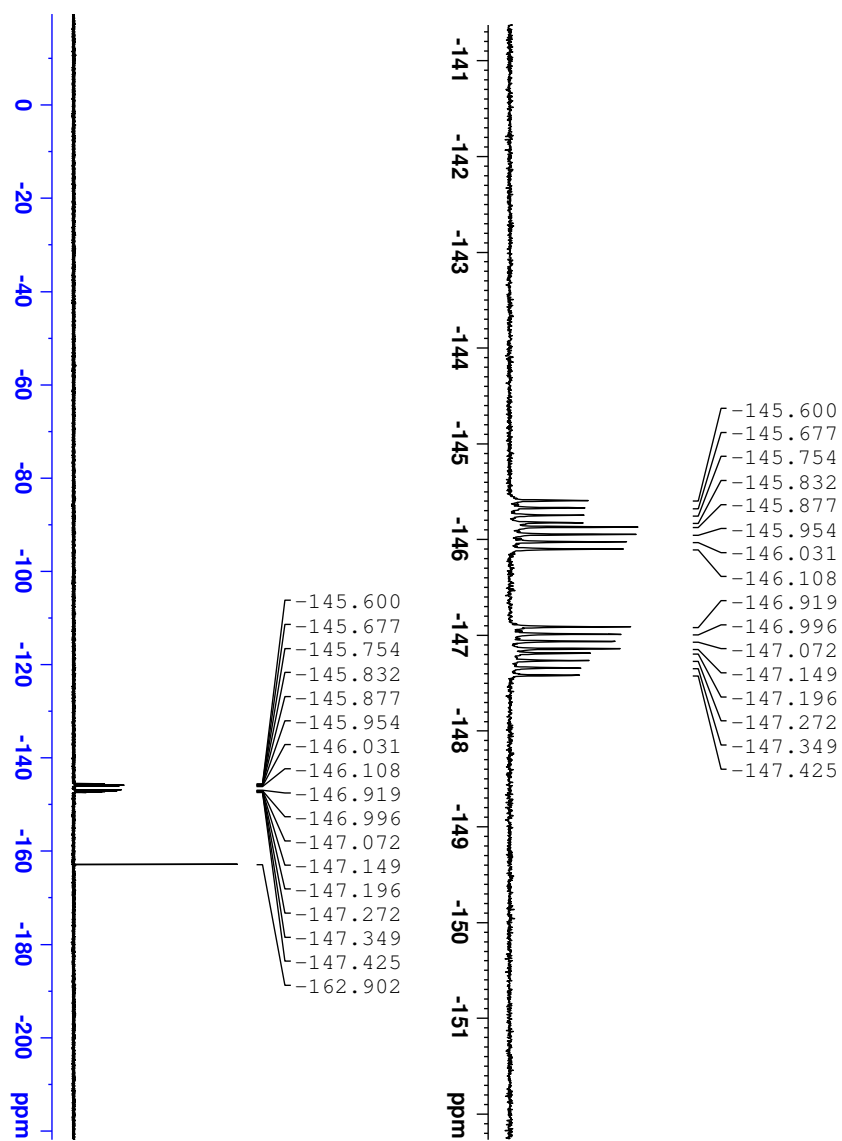


Figure S2. ^{13}C NMR spectrum of **1a** in CDCl_3 at 25°C .



```

Current Data Parameters
NAME          1a
EXPNO        10
PROCNO       1
F2 - Acquisition Parameters
Date_         20240807
Time          10.22 h
INSTRUM      Avance
PROBHD       Z163739_002419
PULPROG      zgpg30
TD           131072
SOLVENT      CDCl3
NS           4
DS           4
SWH          90909.094 Hz
FIDRES      1.387163 Hz
AQ          0.1268101 sec
RG          101
DE          5.500 usec
DELTA       6.500 usec
TE          298.2 K
D1          1.00000000 sec
d11         0.03000000 sec
TD0         1
NUC1         19F
NUC2         13C
P1          17.60 usec
PL1         15.6399981 W
PL2         400.1316911 MHz
CDEPRG12    waltz16
PCPD2       15.10000000 usec
PLM12       0.17904000 W
F2 - Processing parameters
SF          376.498890 MHz
WDW         EM
SSB         0
GB          0
PC          1.00

```

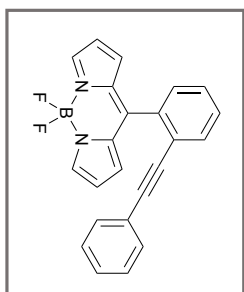


Figure S3. ^{19}F NMR spectrum of **1a** in CDCl_3 at 25°C .

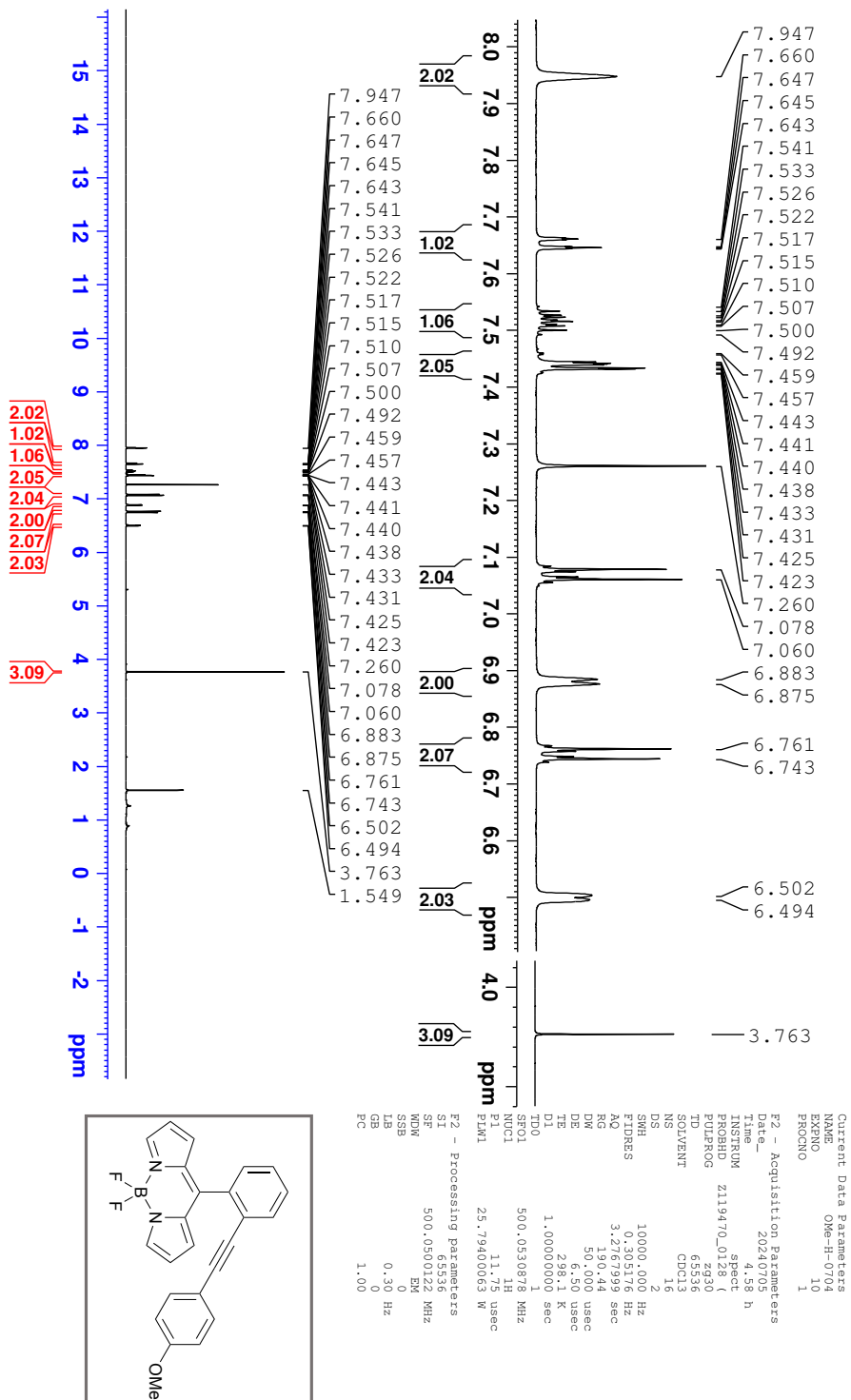
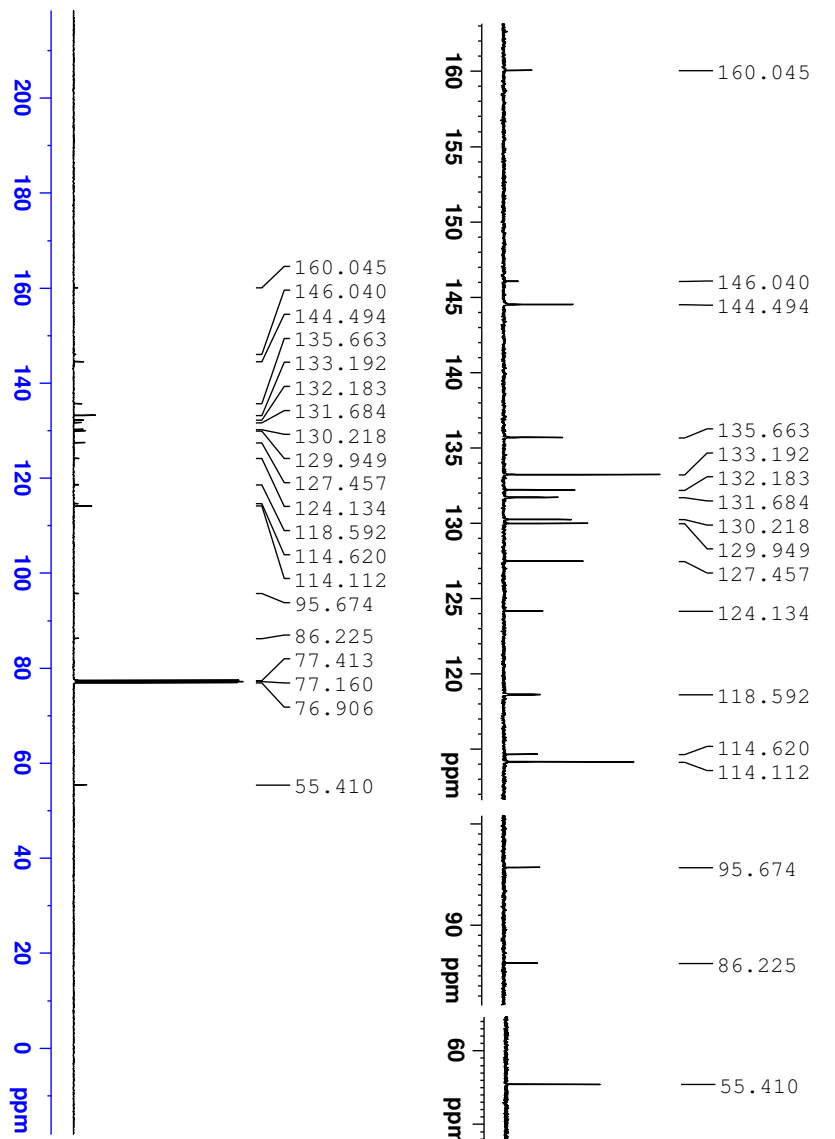


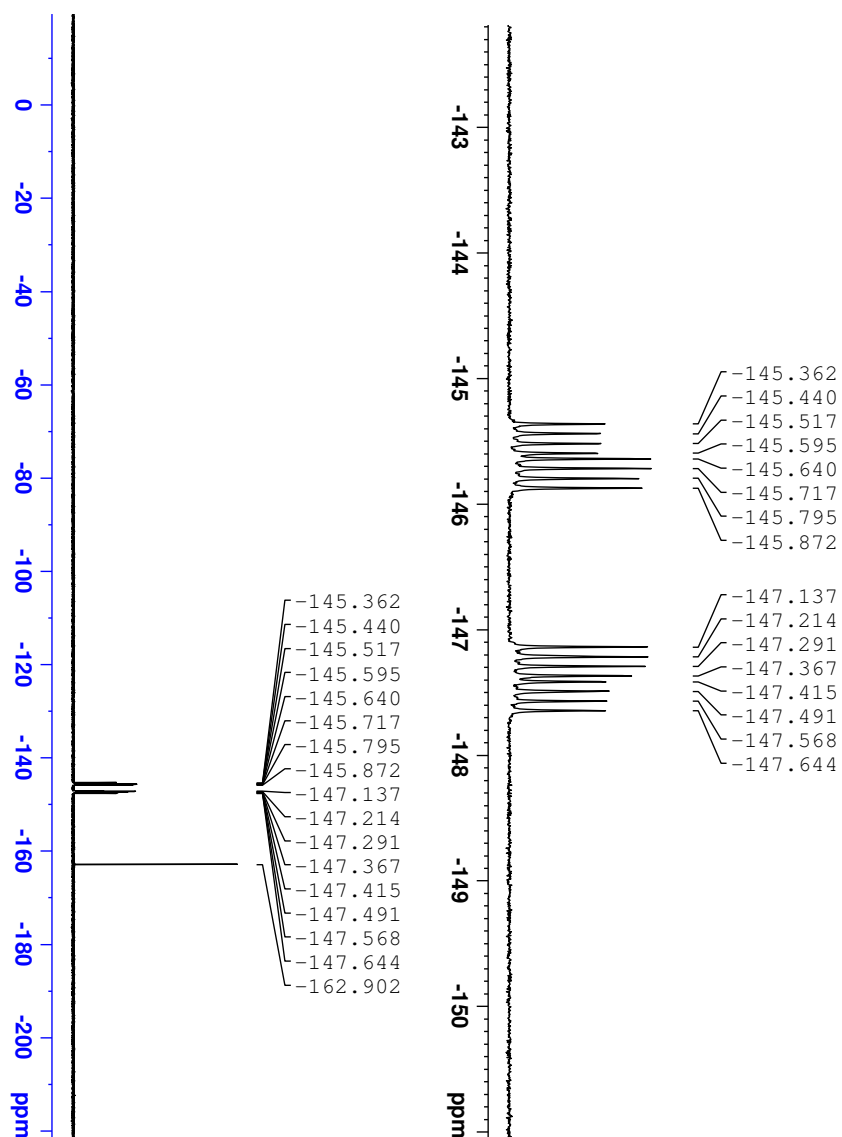
Figure S4. ^1H NMR spectrum of **1b** in CDCl_3 at $25\text{ }^\circ\text{C}$.



```

Current Data Parameters
EXNO          1
PROCNO       10
F2 - Acquisition Parameters
Date_         20240705
Time         8:35 h
INSTRUM      spect
PROBHD       Z119470_018
PULPROG      zgpg30
TD           65536
ID           4096
NS           4096
DS           2
SOLVENT      CDCl3
SWH          29961.904 Hz
AQ           1.1010048 sec
RG           190.444
DM           16.800 usec
DE           0.0000000 usec
TE           298.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TDO         125.7502463 MHz
SF01        125.7502463 MHz
NUC01       13C
F1A1        93.8130034 MHz
SF02        500.0520002 MHz
NUC02       1H
PCPD2       1H
PCPD1       1H
P1M12      25.79400063 M
P1M13      0.35844000 M
F1M13      0.72981929 M
F2 - Processing parameters
SI           125.737465 MHz
WDW          SM
SSB          0
GB           1.0 Hz
PC           1.40
  
```

Figure S5. ¹³C NMR spectrum of **1b** in CDCl₃ at 25 °C.



```

Current Data Parameters
EXPNO          10
PROCNO         1
F2 - Acquisition Parameters
Date_          20240807
Time           10.26 h
INSTRUM       Avance
PROBHD        zgpg30
PULPROG       zgpg30
TD            131072
SOLVENT       CDCl3
NS            1
DS            4
SWH           90909.094 Hz
FIDRES       1.387163 Hz
AQ           0.1268101 sec
RG           101
DE           5.500 usec
DELTA        6.500 usec
TE           299.2 K
D1           1.00000000 sec
d11          0.03000000 sec
TD0          376.4607161 MHz
NUC1         19F
NUC2
P1           17.60 usec
PL1         15.6393981 W
PL2         400.316691 MHz
CDEPRG12     waltz16
PCPD2        15.1000000 usec
PLM12        0.1790400 W
F2 - Processing parameters
SF           376.498089 MHz
WDW          EM
SSB          0
GB           0.3 Hz
PC           1.00
  
```

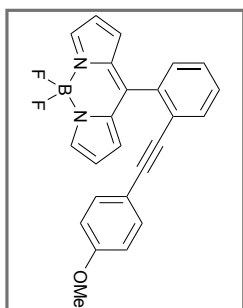
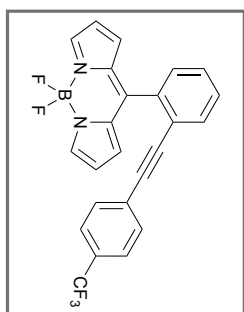
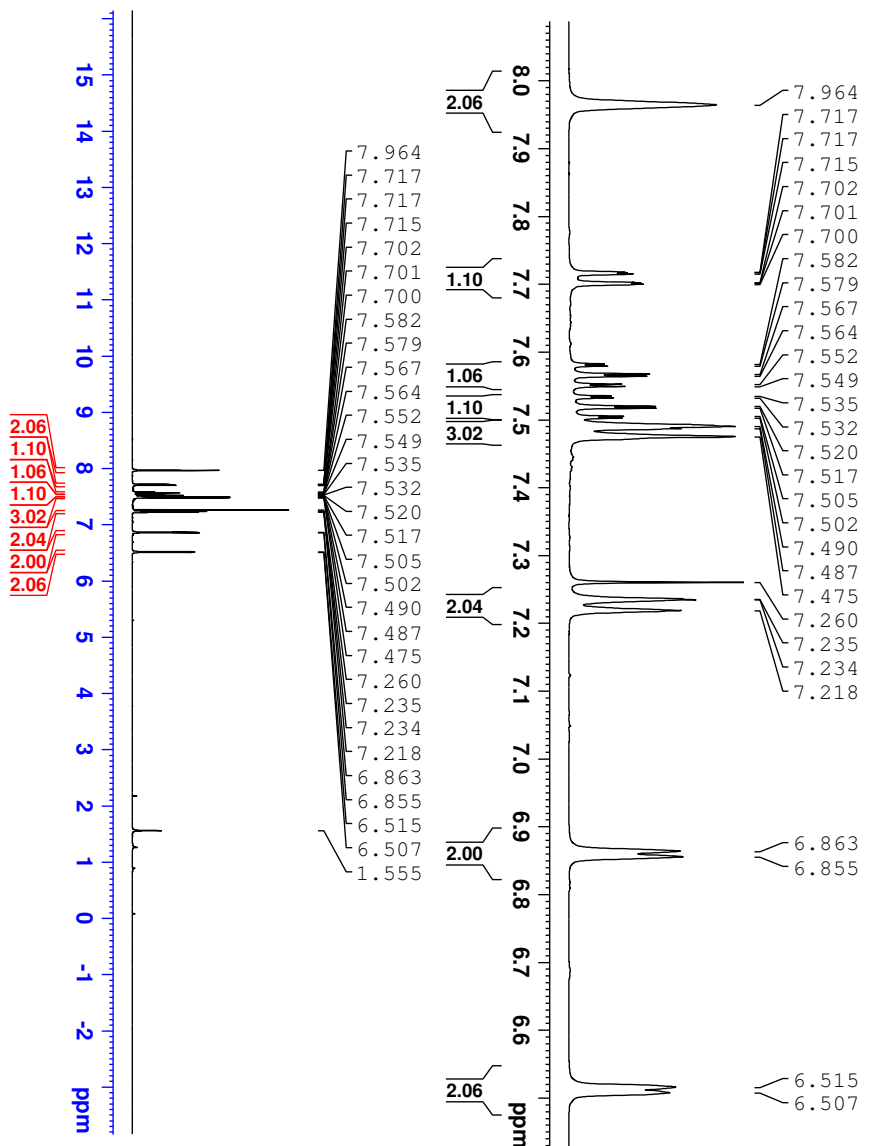


Figure S6. ^{19}F NMR spectrum of **1b** in CDCl_3 at $25\text{ }^\circ\text{C}$.



Current Data Parameters
 NAME CF3-H-0705
 EXNO 10
 FRCNO 1

F2 - Acquisition Parameters
 Date_ 20240706
 Time_ 1.30 h
 INSTRUM spect
 PROBH0 Z930
 PULPROG zg30
 TD 65536
 N0 SOLVENT CDCl3
 N1 2
 DS 1

SWH 10000.000 Hz
 FIDRES 0.305176 Hz
 AQ 3.2767999 sec
 RG 138.28
 DM 50.000 usec
 DE 6.30 usec
 TE 300.2 K
 D1 1.000000 sec
 TD0 1

SEOI 500.0530878 MHz
 NU01 1H
 P1 11.75 usec
 PLW1 25.79400063 W

F2 - Processing parameters
 S2 500.0530878 MHz
 SF 500.0500121 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S7. ¹H NMR spectrum of 1c in CDCl₃ at 25 °C.

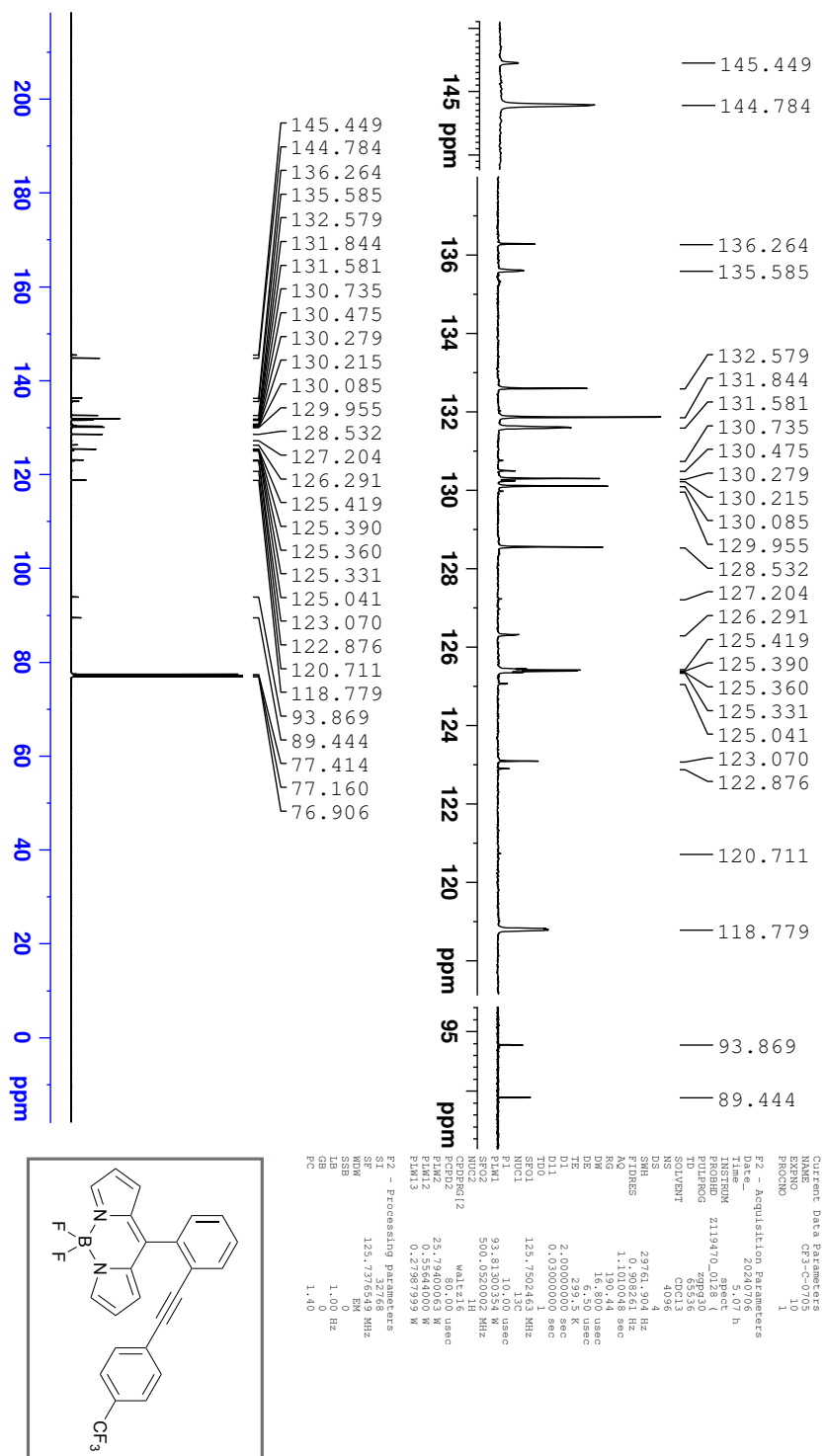


Figure S8. ¹³C NMR spectrum of **1c** in CDCl₃ at 25 °C.

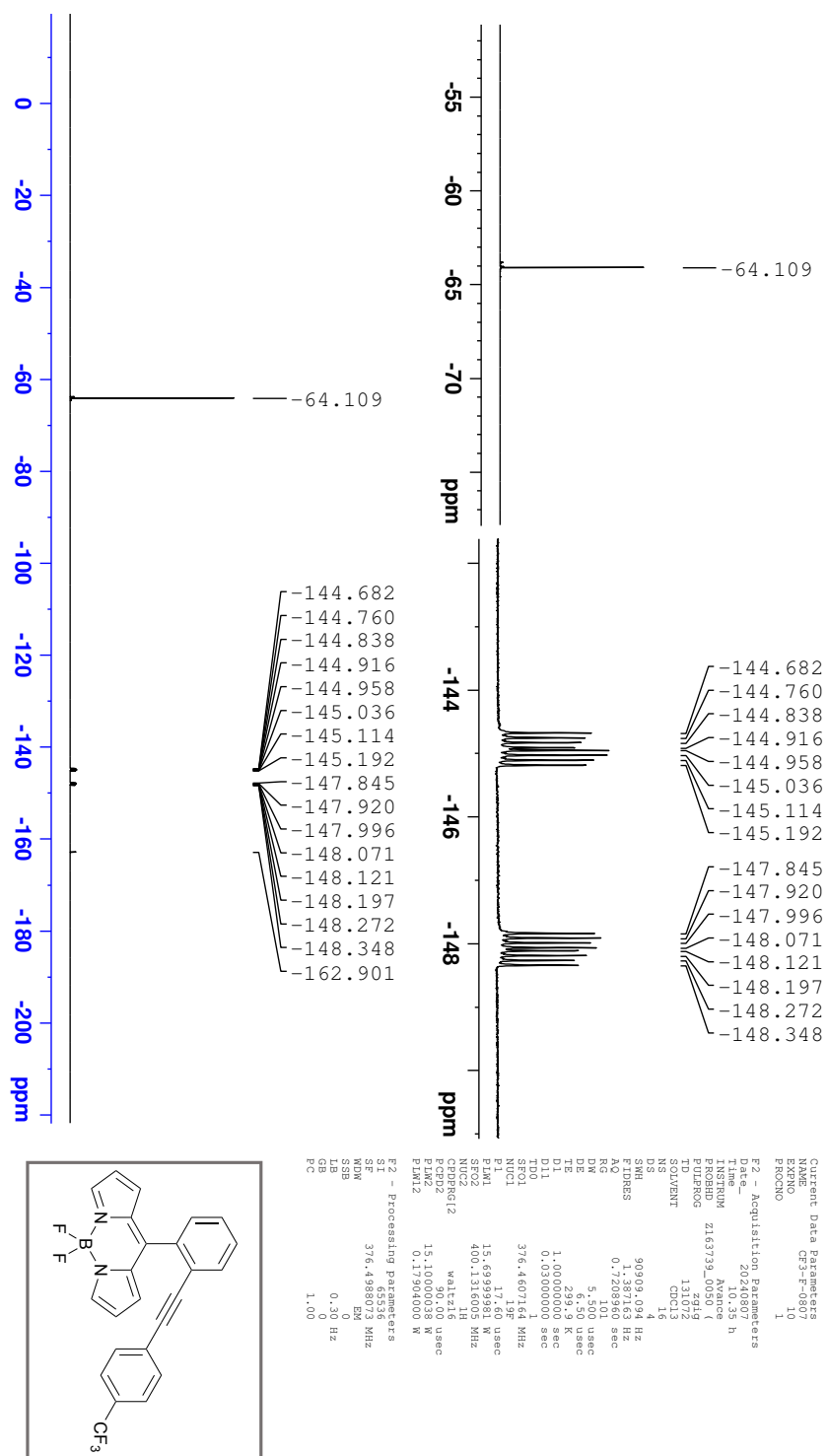
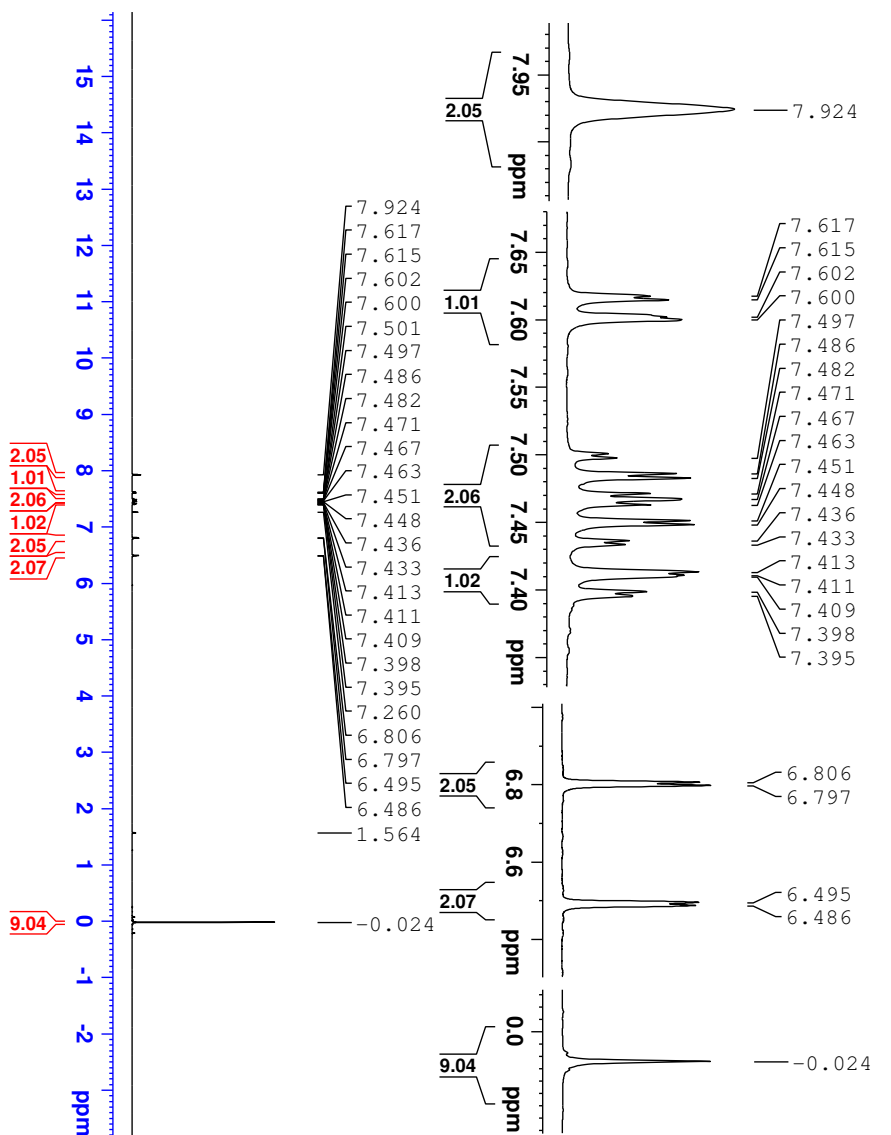


Figure S9. ^{19}F NMR spectrum of **1c** in CDCl_3 at $25\text{ }^\circ\text{C}$.



```

Current Data Parameters
NAME          TMS-H-NMR
EXPNO         10
PROCNO        1
F2 - Acquisition Parameters
Date_         20240422
Time          22.21 h
INSTRUM      spect - Copy
PROBHD       zg30
PULPROG      zg30
TD           65536
SOLVENT      CDCl3
NUC1          13
DS            19
SFO1          10000.000 Hz
FIDRES       0.305176 Hz
AQ           3.2767999 sec
RG           194.99
DE           50.000 usec
TE           298.15 K
D1           1.00000000 sec
TDO
SFO1          500.1130882 MHz
NUC1          1H
P1           11.82 usec
PLM1         18.00000000 W
F2 - Processing parameters
SI            500.1100122 MHz
WDW          EM
SSB          0
GB           0.30 Hz
LB           0
GB           0
PC           1.00

```

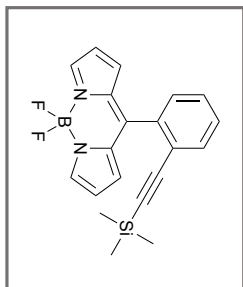
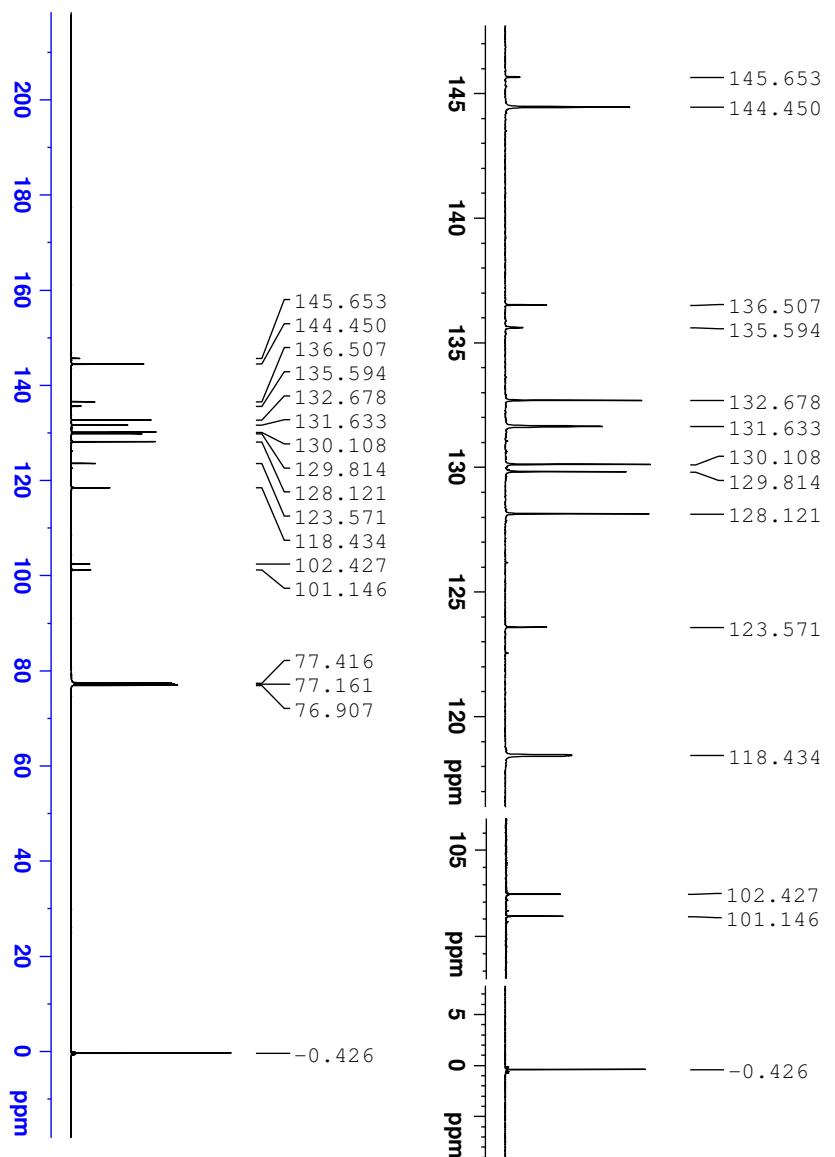


Figure S10. ¹H NMR spectrum of S1 in CDCl₃ at 25 °C.



```

Current Data Parameters
NAME          S1
EXPNO         10
PROCNO        1
F2 - Acquisition Parameters
Date_         20240423
Time         5.35 h
INSTRUM       spect
PROBHD        5mm QNP 1H/13
PULPROG       zgpg30
TD            65536
SFO          125.76348
AQ            8192
RG            327.612904 Hz
SI            1.010048 sec
RG            194.99
DM            16.800 usec
DE            4.000 usec
TE            298.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TDO           1.1
SFO1          125.765348 MHz
NUC1           13C
PLM1          130.0000000 M
SFO2          500.1120004 MHz
NUC2           1H
PLM2          18.0000000 M
PCPD2        80.00 usec
PLM12         0.39294001 M
PLM13         0.13765800 M
F2 - Processing parameters
SI            327.612904 Hz
SF            125.76348 MHz
WDW           EM
SSB           0
GB            1.00 Hz
PC            1.40
  
```

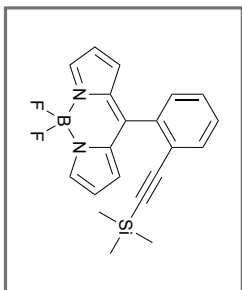
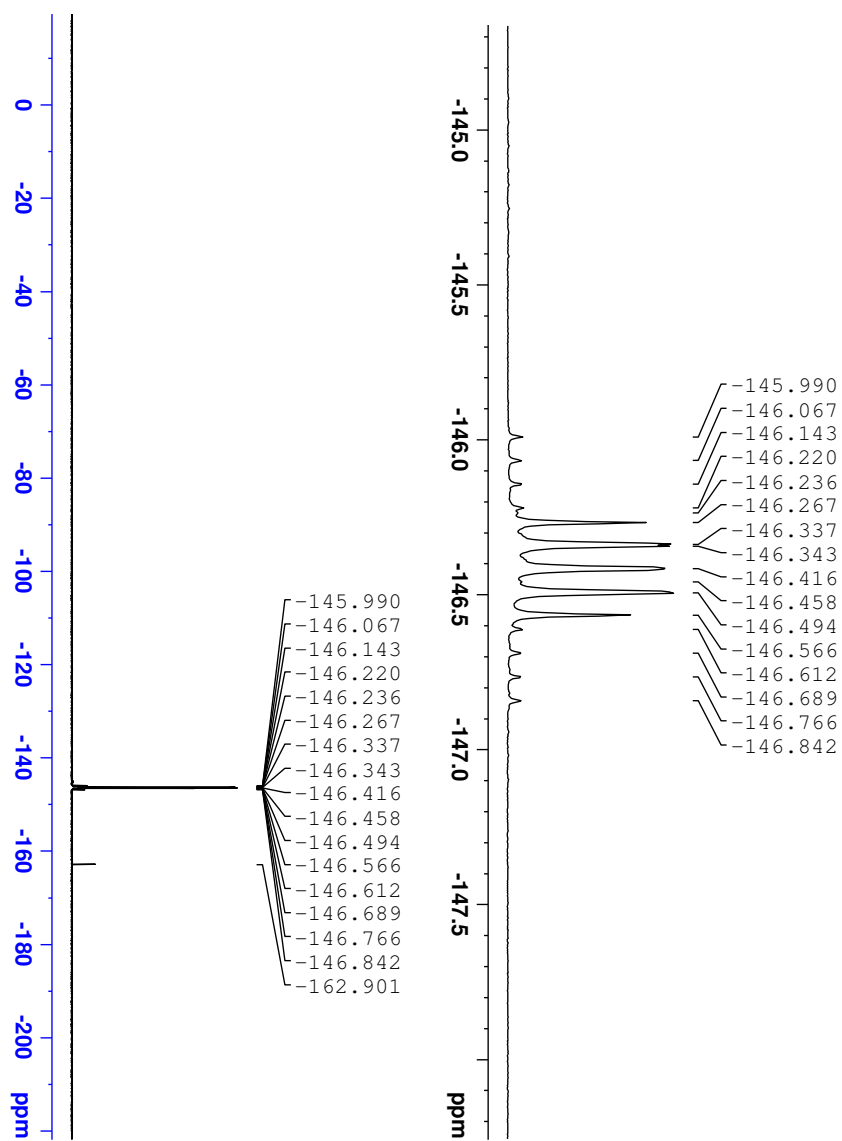


Figure S11. ^{13}C NMR spectrum of S1 in CDCl_3 at 25 °C.



```

Current Data Parameters
NAME          S1
EXPNO        10
PROCNO       1
F2 - Acquisition Parameters
Date_         20240807
Time         10.43 h
INSTRUM      Avance
PROBHD       Z163739_02249
PULPROG      zgpg30
TD           131072
SOLVENT      CDCl3
NS           1
DS           4
SWH          90909.094 Hz
FIDRES       1.387163 Hz
AQ           0.1268101 sec
RG           101
DE           5.500 usec
DELTA        2.0000000 sec
D1           1.00000000 sec
D11          0.03000000 sec
TDO         376.4607161 MHz
TDC1        198 MHz
NUC1         19F
P1           17.60 usec
PLM1        15.6399981 W
PCPD2       400.1316911 MHz
NUC2         1H
CPDPRG12    waltz16
PCPD2       15.1000000 usec
PLM2        0.17904000 W
F2 - Processing parameters
SF           376.4980775 MHz
WDW          EM
SSB          0
GB           0.3 Hz
PC           1.00
  
```

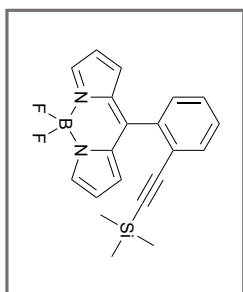
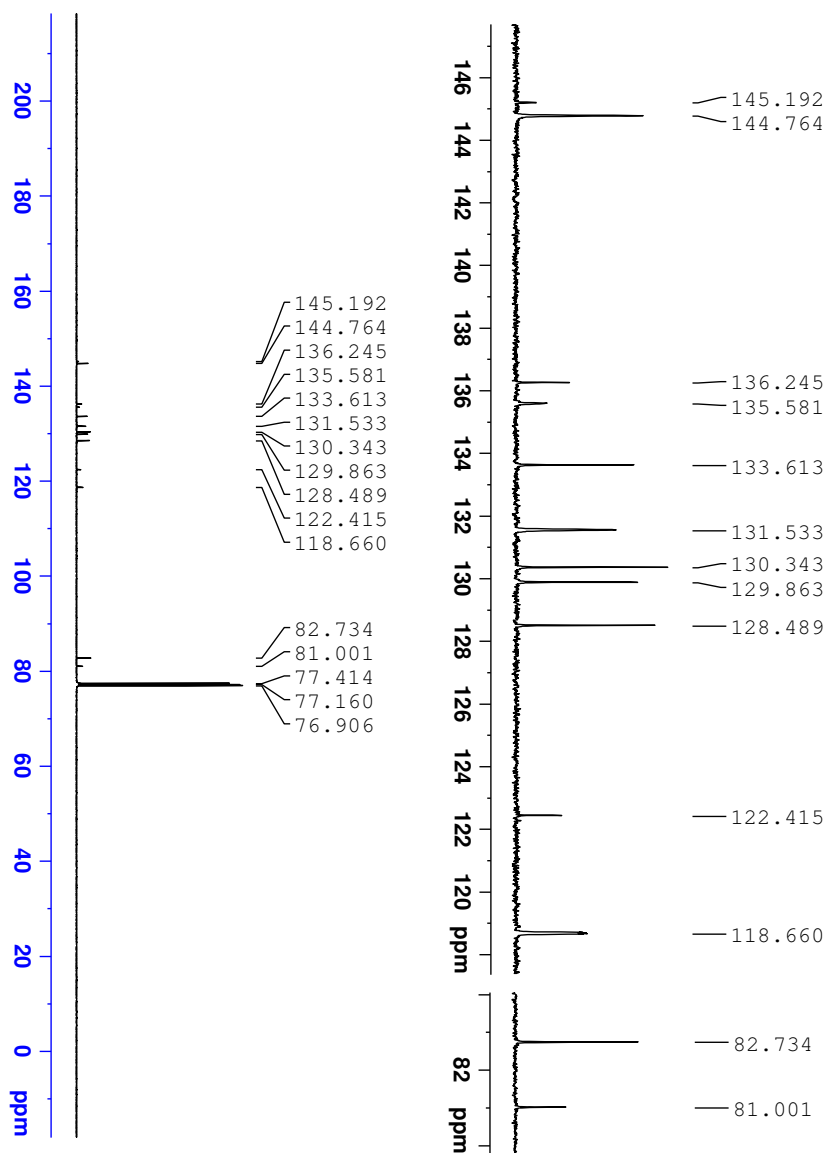


Figure S12. ^{19}F NMR spectrum of S1 in CDCl_3 at 25 °C.



```

Current Data Parameters
EXNO          1
PROCNO       1
F2 - Acquisition Parameters
Date_         20240706
Time         16:19 h
INSTRUM      spect
PROBHD       Z119470_019
PULPROG      zgpg30
TD           65536
SFO2         4076
DS           2
SWH          29961.904 Hz
AQ           1.1010048 sec
RG           190.44
DM           16.800 usec
DE           4.200 usec
TE           300.5 K
D11          2.00000000 sec
D12          0.03000000 sec
D13          0.03000000 sec
SFO1         125.7502463 MHz
NUC1         13C
F1A1         93.8130034 MHz
SFO2         500.0520002 MHz
NUC2         1H
PCPD2        waltz16
PULPROG      zgpg30
PCPD2        80.70 usec
P1M12        25.79400063 M
P1M13        0.55844000 M
P1M14        0.7391929 M
F2 - Processing parameters
SI           32768
WDW          EM
SSB          0
GB           0
PC           1.40
  
```

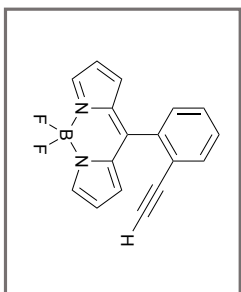
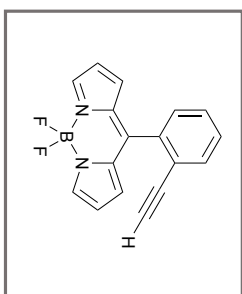
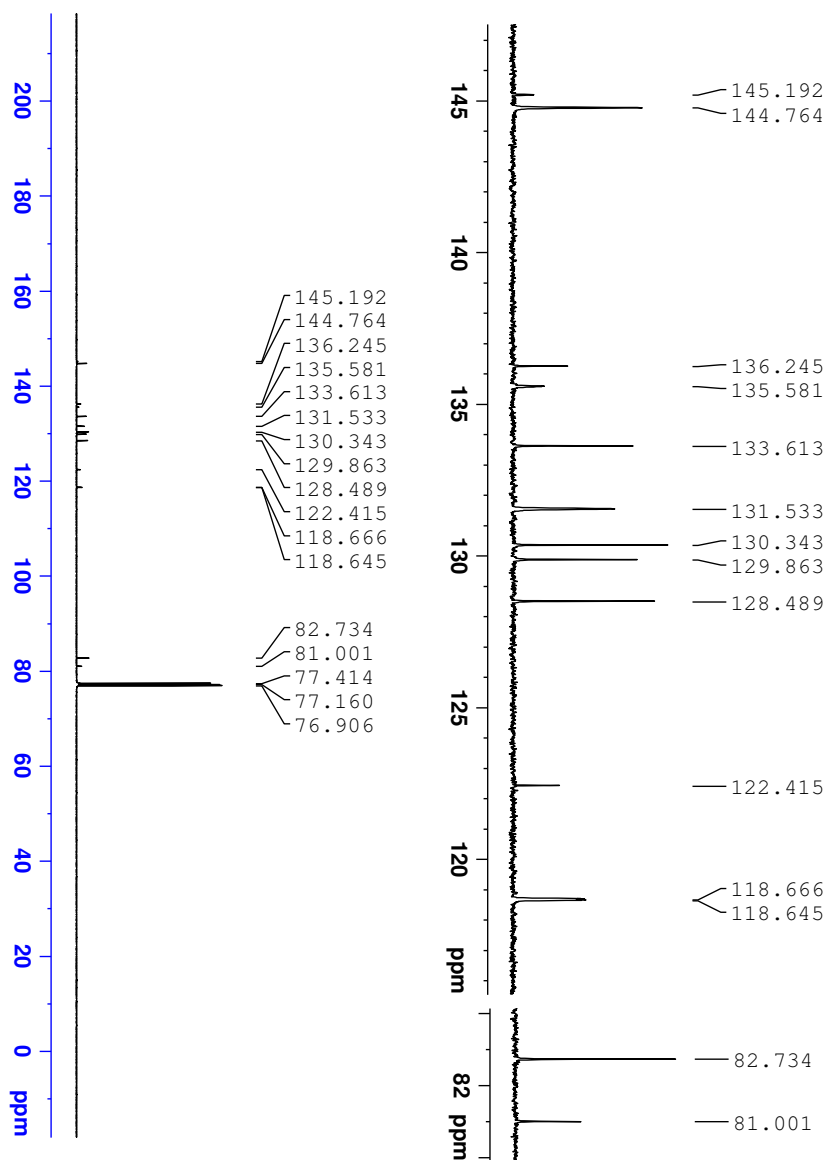


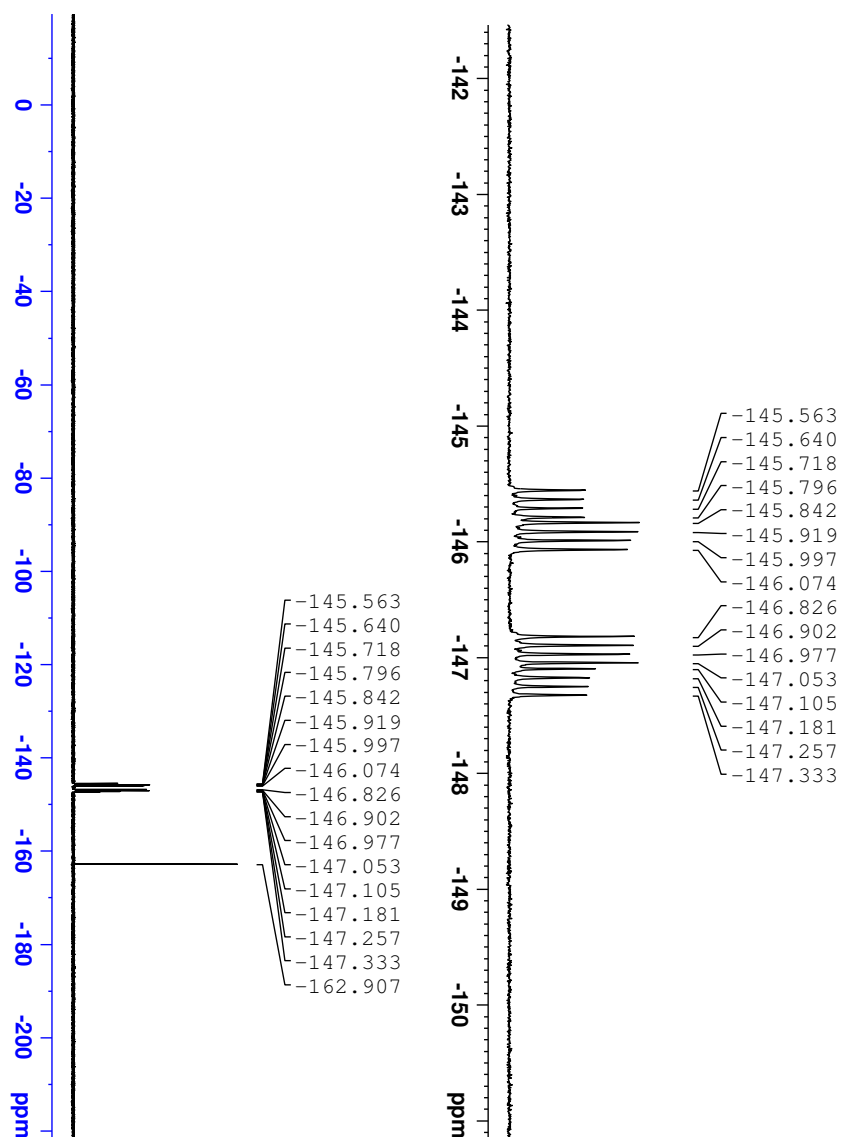
Figure S13. ¹H NMR spectrum of **1d** in CDCl₃ at 25 °C.



```

Current Data Parameters
EXNO          1
PROCNO        1
F2 - Acquisition Parameters
Date_          20240706
Time          16:19 h
INSTRUM       spect
PROBHD        Z119470_019
PULPROG       zgpg30
TD            65536
ID            4096
NS            4096
DS            2
SOLVENT       CDCl3
SWH           29961.904 Hz
AQ            1.1010048 sec
RG            190.444
DM            16.800 usec
DE            4.000 usec
TE            300.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TDO           125.7502463 MHz
SF01          125.7502463 MHz
NUC01         13C
F1L1          93.8130034 MHz
SF02          500.0520002 MHz
NUC02         1H
PCPD2         1H
PCPD1         1H
P1M12        25.79400063 M
P1M13        0.55844000 M
P1M14        0.73981929 M
F2 - Processing parameters
SI            125.737468 MHz
WDW           EM
SSB           0
GB            1.0 Hz
PC            1.40
  
```

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



```

Current Data Parameters
EXPNO          10
PROCNO         1
F2 - Acquisition Parameters
Date_          20240807
Time           10.51 h
INSTRUM       Avance
PROBHD        Z163739_002419
PULPROG       zgpg30
TD             131072
SOLVENT       CDCl3
NS             4
DS             1
SWH            90909.094 Hz
FIDRES        1.387163 Hz
AQ            0.1268101 sec
RG            101
WDW            5.500 usec
DE            2.000 usec
TE            298.2 K
D1            1.00000000 sec
d11           0.03000000 sec
TDO          376.4607161 MHz
NUC1          19F
NUC2          1H
P1            17.60 usec
PLM1          15.6393981 W
PLM2          400.1316911 MHz
CDEPRG12     waltz16
PCPD2        15.1000000 usec
PLM12        0.17904000 W
F2 - Processing parameters
SF            376.498109 MHz
WDW           EM
SSB           0
GB            0
PC            1.00
  
```

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

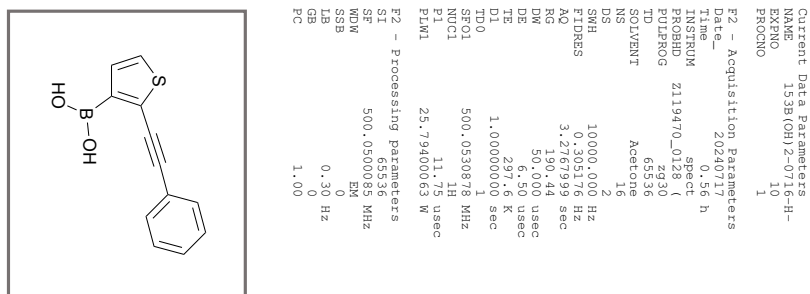
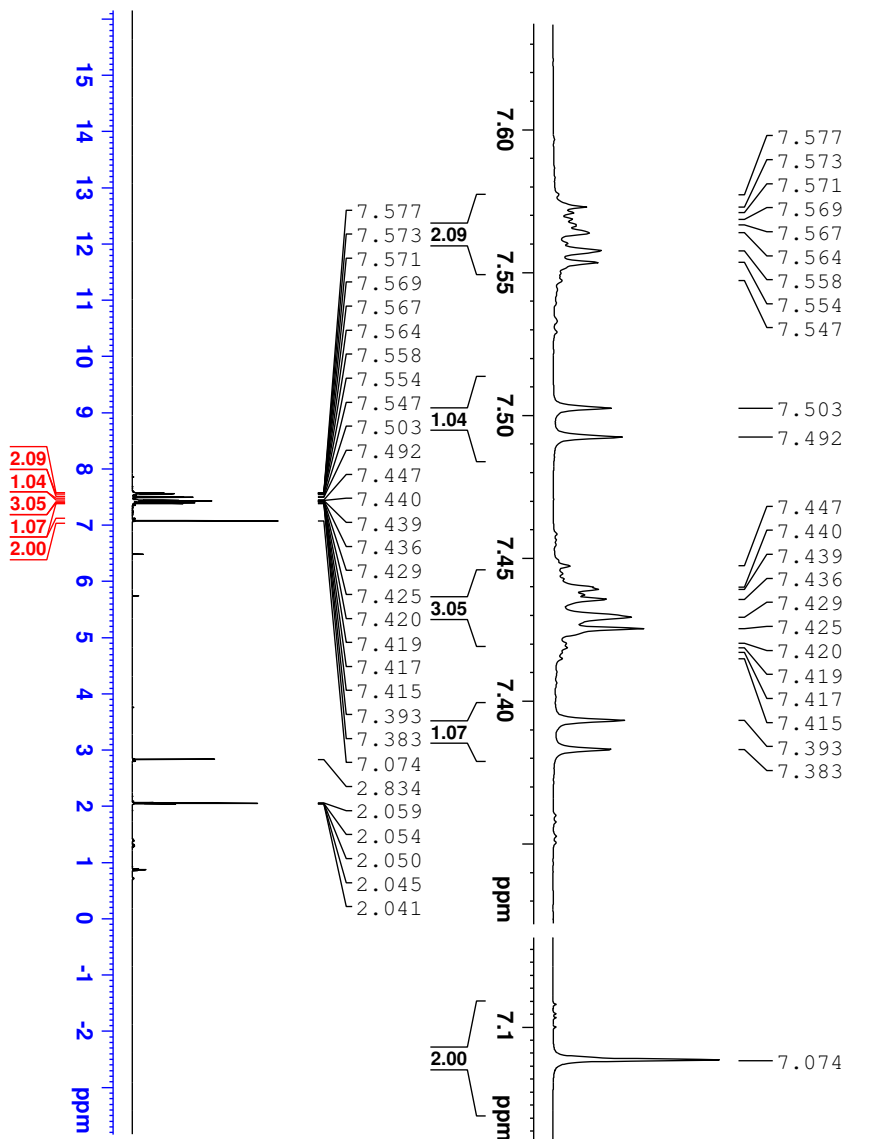
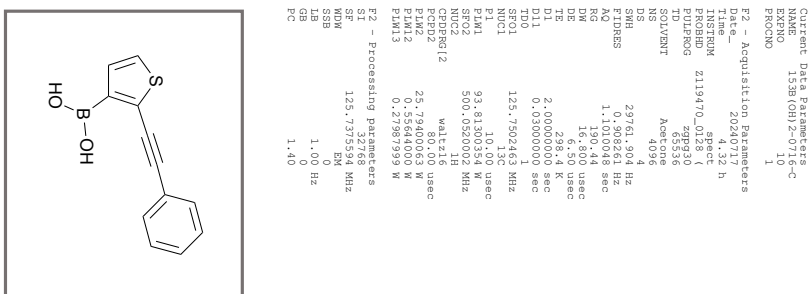
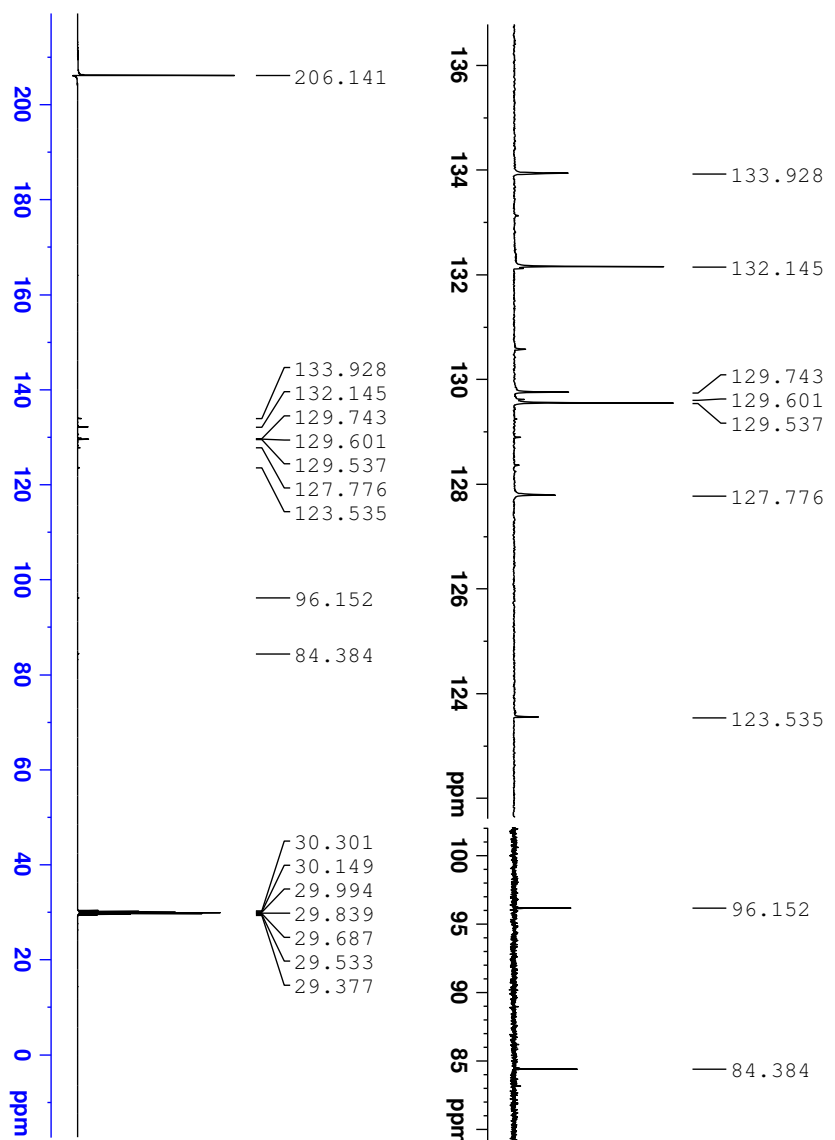


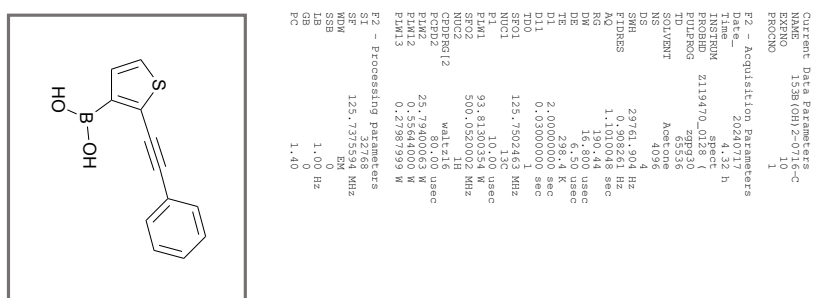
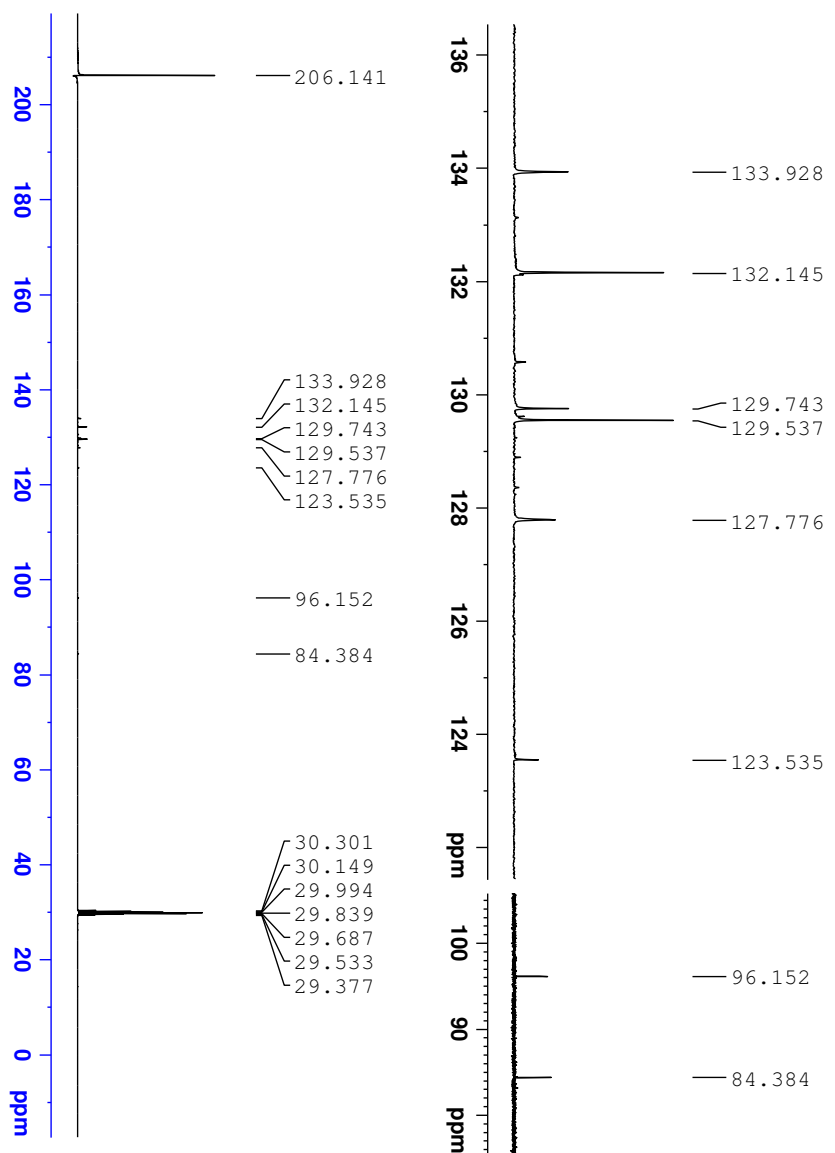
Figure S16. ^1H NMR spectrum of S2 in acetone- d_6 at 25 °C.



```

Current Data Parameters
EXNO      1539
PROCNO    1
F2 - Acquisition Parameters
Date_     20240717
Time      4.32 h
INSTRUM   spect
PROBHD    Z119470_019
PULPROG   zgpg30
TD        65536
SI        32768
SF        40096
DS        4
SOLVENTS  Acetone-d6
AQ        1.1010048 sec
RG        190.44
DM        16.800 usec
DE        4.20 usec
TE        298.4 K
D11       2.0000000 sec
TDO       0.0300000 sec
SF01      125.7502463 MHz
NUC01     13C
F1L1      93.8130034 MHz
SF02      500.0520002 MHz
NUC02     1H
PCPD2     1H
PCPD1     1H
P1M12     25.79400063 M
P1M13     0.55844000 M
F1M12     0.72591929 M
F2 - Processing parameters
SI        32768
SF        125.737549 MHz
WDW       EM
SSB       0
GB        1.0
PC        1.40
  
```

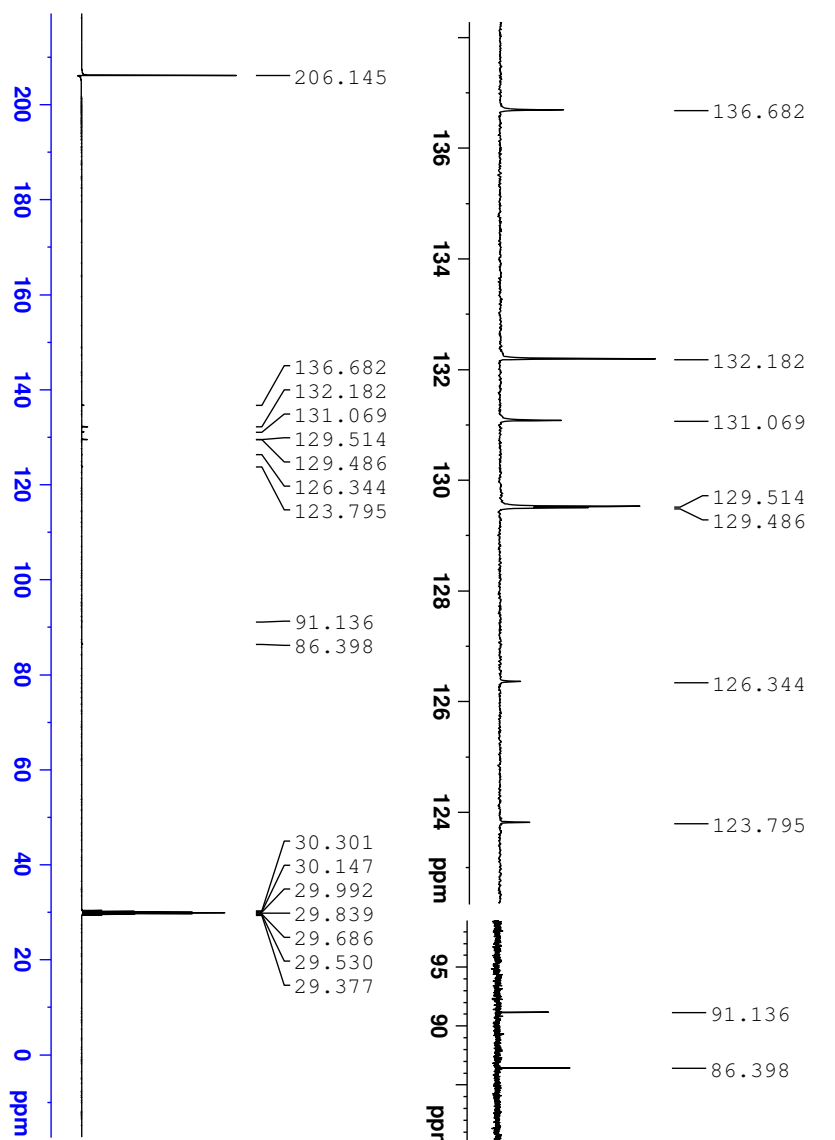
Figure S17. ¹³C NMR spectrum of S2 in acetone-*d*₆ at 25 °C.



```

Current Data Parameters
EXNO      1539
PROCNO    1
F2 - Acquisition Parameters
Date_      20240717
Time       4.32 h
INSTRUM   spect
PROBHD    Z119470_019
PULPROG   zgpg30
TD         65536
SI         Acq4096
DS         4
SMB       29961.904 Hz
AQ         1.1010048 sec
RG         190.44
DM         16.800 usec
DE         4.20 usec
TE         298.4 K
D1         2.00000000 sec
TDO        0.03000000 sec
NUC1       125.7502463 MHz
NUC2       13C
P1         1.00 usec
PL1        93.81300354 W
SFO2       500.0520002 MHz
NUC3
NUC4
PCPD2/2   waltz16
PLM12     25.79400063 W
PLM13     0.55844000 W
PLM14     0.72591929 W
F2 - Processing parameters
SI         125.737549 MHz
WDW        EM
SSB        0
GB         1.00 Hz
PC         1.40
  
```

Figure S18. ^{13}C NMR spectrum of S3 in acetone- d_6 at 25 °C.



Current Data Parameters
 EXNO 1
 F2 - Acquisition Parameters
 Date_ 20240717
 Time 8:13 h
 INSTR spect
 PULPROG zgpg30
 ID 65536
 NS 4096
 DS 4
 SWH 29961.904 Hz
 AQ 1.1010048 sec
 RG 190.444
 DM 16.800 usec
 DE 4.000 usec
 TE 298.3 K
 D1 2.0000000 sec
 TDO 0.0300000 sec
 SF01 125.7502463 MHz
 NU01 13C
 FWH 93.8130034 M
 SF02 500.0520002 MHz
 NUC2 1H
 WALTZ16
 PCPD2 80.00 usec
 PULP2 25.7940063 M
 FWH2 0.5584400 M
 FWH3 0.7391929 M

F2 - Processing parameters
 SI 32768
 WDW EM
 SSB 0
 GB 1.0 Hz
 DB 0
 PC 1.40

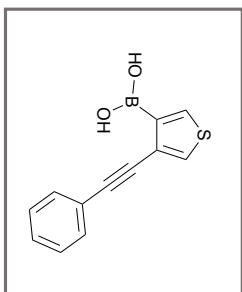


Figure S19. ^{13}C NMR spectrum of S3 in acetone- d_6 at 25 °C.

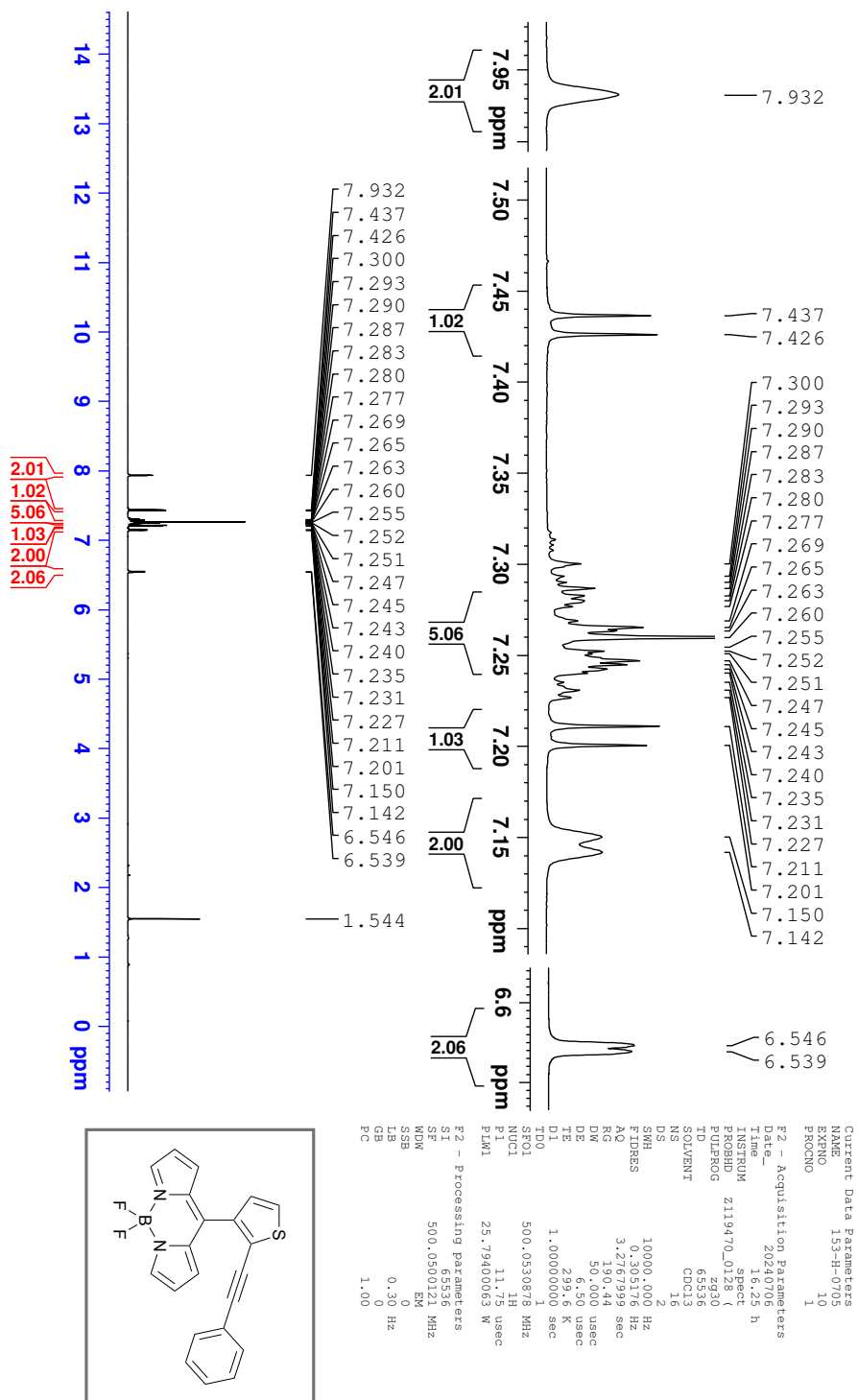
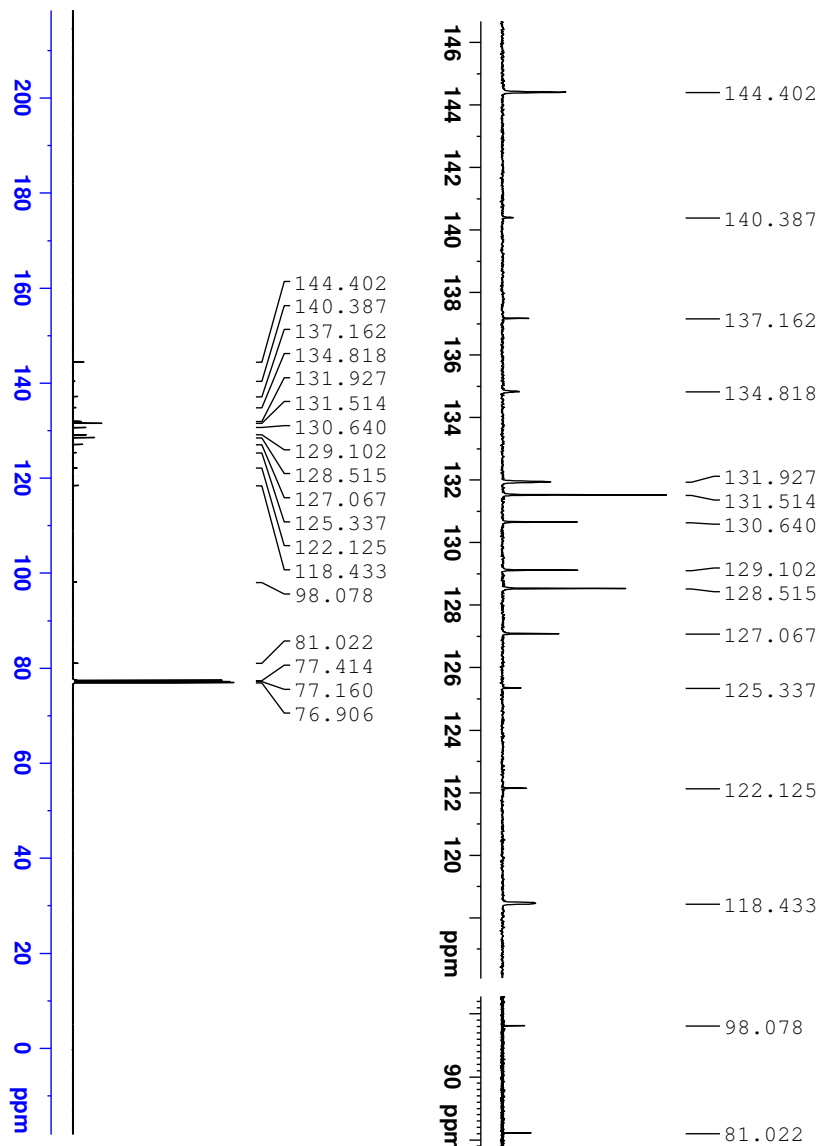


Figure S20. ¹H NMR spectrum of **1e** in CDCl₃ at 25 °C.



```

Current Data Parameters
EXNO      1
PROCNO    1
F2 - Acquisition Parameters
Date_      20240706
Time       20.02 h
INSTRUM    spect
PROBHD     Z119470_018
PULPROG    zgpg30
TD         65536
SFO1       125.7502463 MHz
SF02       500.0520002 MHz
NUC1        13C
NUC2        1H
PCPD2      80.00 usec
PL1         1.00 usec
PL12        0.55844000 M
PL13        0.725819259 M
F2 - Processing parameters
SI          32768
WDW         EM
SSB         0
GB          0
PC          1.40
  
```

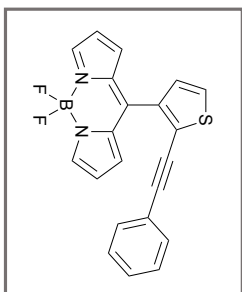
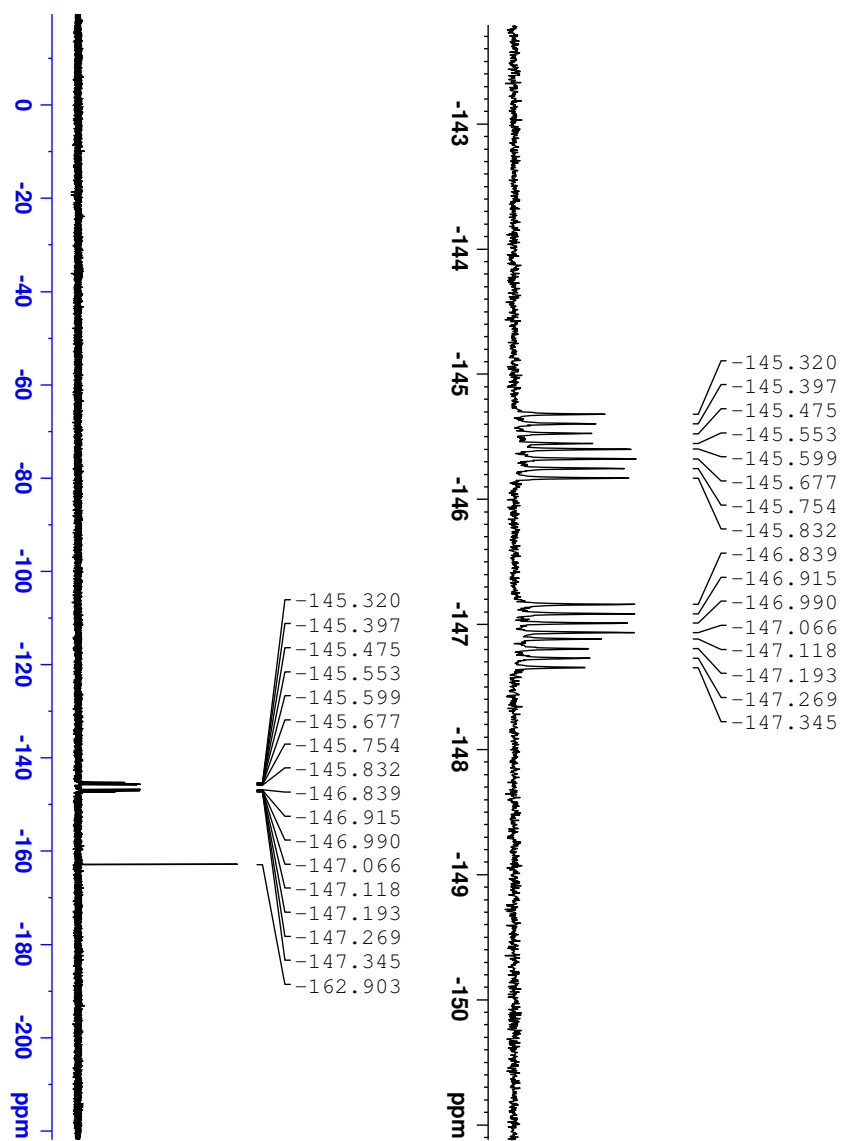


Figure S21. ^{13}C NMR spectrum of **1e** in CDCl_3 at 25°C .



```

Current Data Parameters
NAME          1e
EXPNO        10
PROCNO       1
F2 - Acquisition Parameters
Date_         20240807
Time         10.59 h
INSTRUM      Z163739_002419
PROBHD       5mm QNP1H
PULPROG      zgpg30
TD           131072
SOLVENT      CDCl3
NS           4
DS           4
SWH          90909.094 Hz
FIDRES      1.387163 Hz
AQ          0.1268101 sec
RG          101
WDW          EM
SSB          0
GB          0
PC          1.00
F2 - Processing parameters
SI          376.498089 MHz
SF          376.498089 MHz
WDW          EM
SSB          0
GB          0
PC          1.00
P1          17.60 usec
P2          15.6399981 usec
P3          400.1316011 Hz
PCPD2      waltz16
NUC2        1H
NUC1        19F
P1M1       0.17904000 usec
P1M2       0.17904000 usec

```

Figure S22. ^{19}F NMR spectrum of **1e** in CDCl_3 at 25°C .

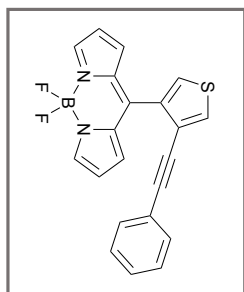
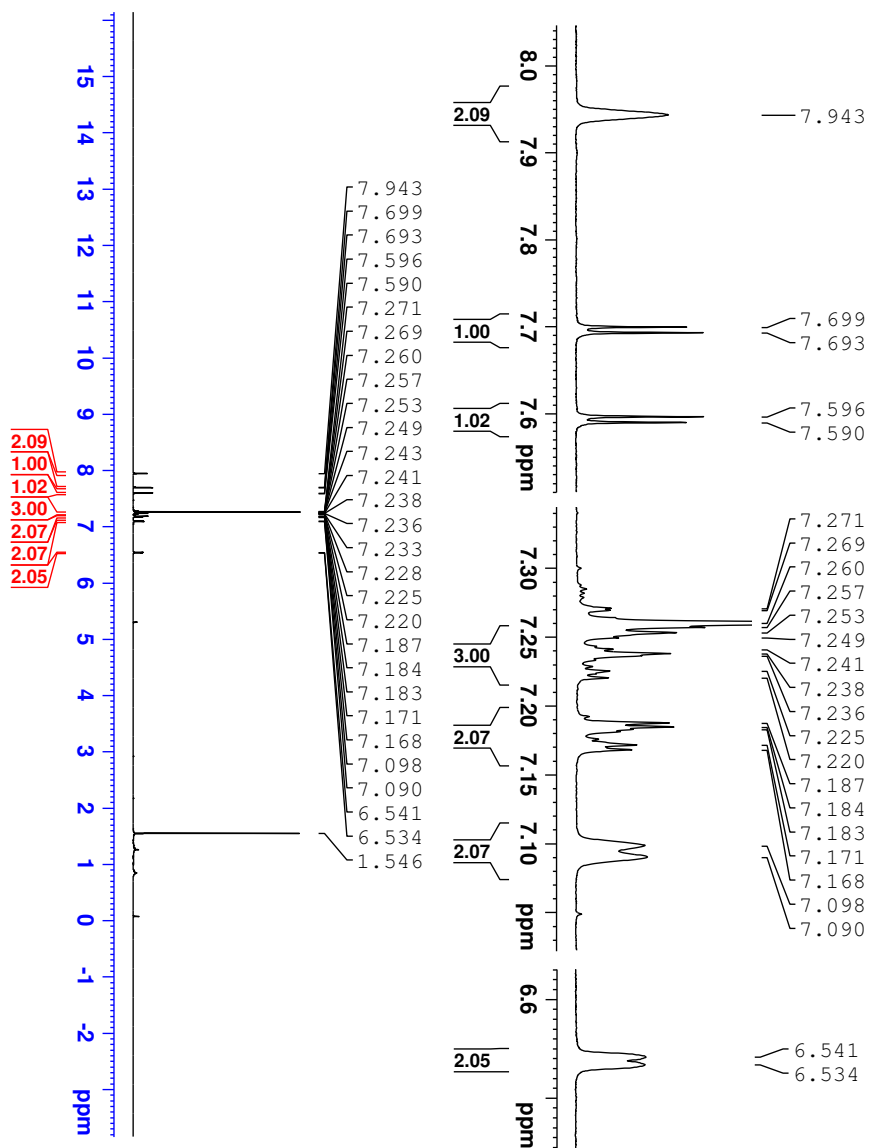
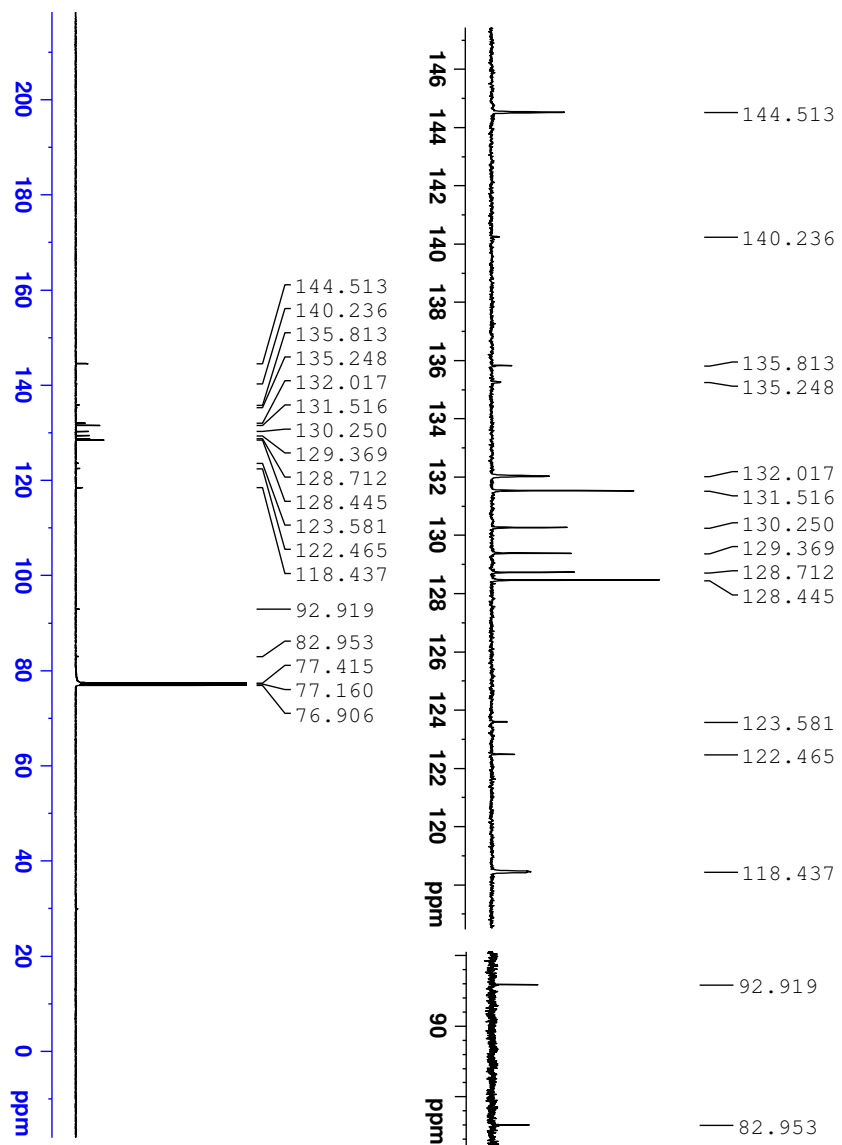


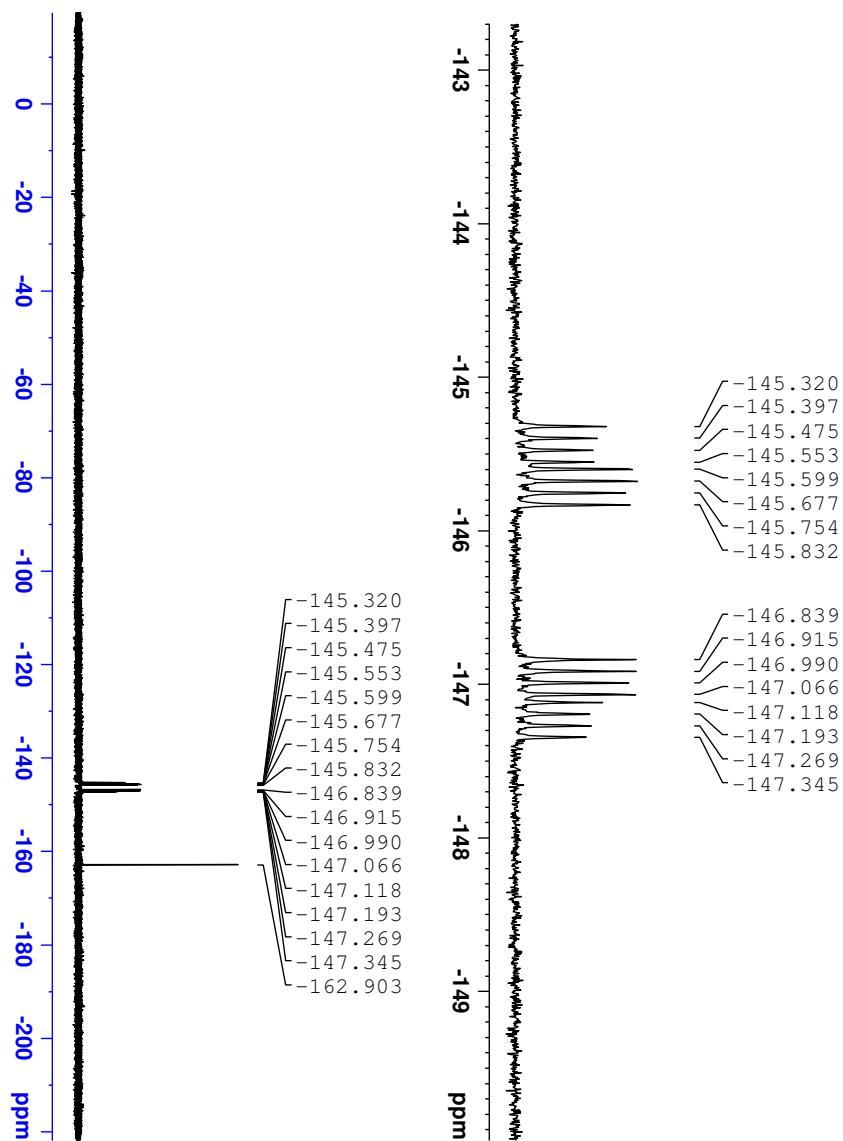
Figure S23. ^1H NMR spectrum of **1f** in CDCl_3 at 25°C .



```

Current Data Parameters
NAME      1f
EXPNO    10
PROCNO   1
F2 - Acquisition Parameters
Date_    20240502
Time     4.16 h
INSTRUM  spect
PROBHD   5mm QNP 1H/13
PULPROG  zgpg30
TD        65536
SFO      125.763348 MHz
AQ        1.1010048 sec
RG         194.99
DM         16.800 usec
DE         4.50 usec
TE        298.5 K
D1         2.00000000 sec
D11        1.11
TDO        0.03000000 sec
SFO1      125.765348 MHz
NUC1       13C
PLM1      13C
PLM2      13C
PLM3      13C
F1M1      130.00000000 MHz
F1M2      500.1120004 MHz
NOC2      NO2
PCPD2     waltz16
PCPD1     80.00 usec
PLM2      18.00000000 MHz
PLM3      0.3929001 MHz
F1M3      0.19745000 MHz
F2 - Processing parameters
SI         32768
SF         125.762741 MHz
WDW        EM
SSB         0
GB          1.00
PC          1.40
  
```

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



```

Current Data Parameters
Name          139f-F0910
EXPNO        10
PROCNO       1
F2 - Acquisition Parameters
Date_         20240807
Time         10.59 h
INSTRUM      Avance
PROBHD       Z163739_092414
PULPROG      zgpg30
TD           131072
SOLVENT      CDCl3
NS           14
DS           4
SWH          90909.094 Hz
FIDRES      1.26263 Hz
AQ          0.726493 sec
RG           101
DM           5.500 usec
DE           2.500 usec
TE           293.2 K
D1           1.00000000 sec
d11          0.03000000 sec
DDO         376.4607164 MHz
SFO1        199.613 MHz
NUC1         19F
P1           17.60 usec
SFO2        15.6393981 MHz
SFO3        400.338981 MHz
NUC2         1H
CPDPRG12    waltz16
PCPDZ       15.10000000 usec
PLM12       0.17904000 N
F2 - Processing parameters
SF          376.4980889 MHz
WDW         EM
SSB         0
GB          0.30 Hz
PC          1.00
  
```

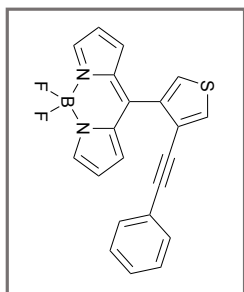


Figure S25. ^{19}F NMR spectrum of **1f** in CDCl_3 at 25°C .

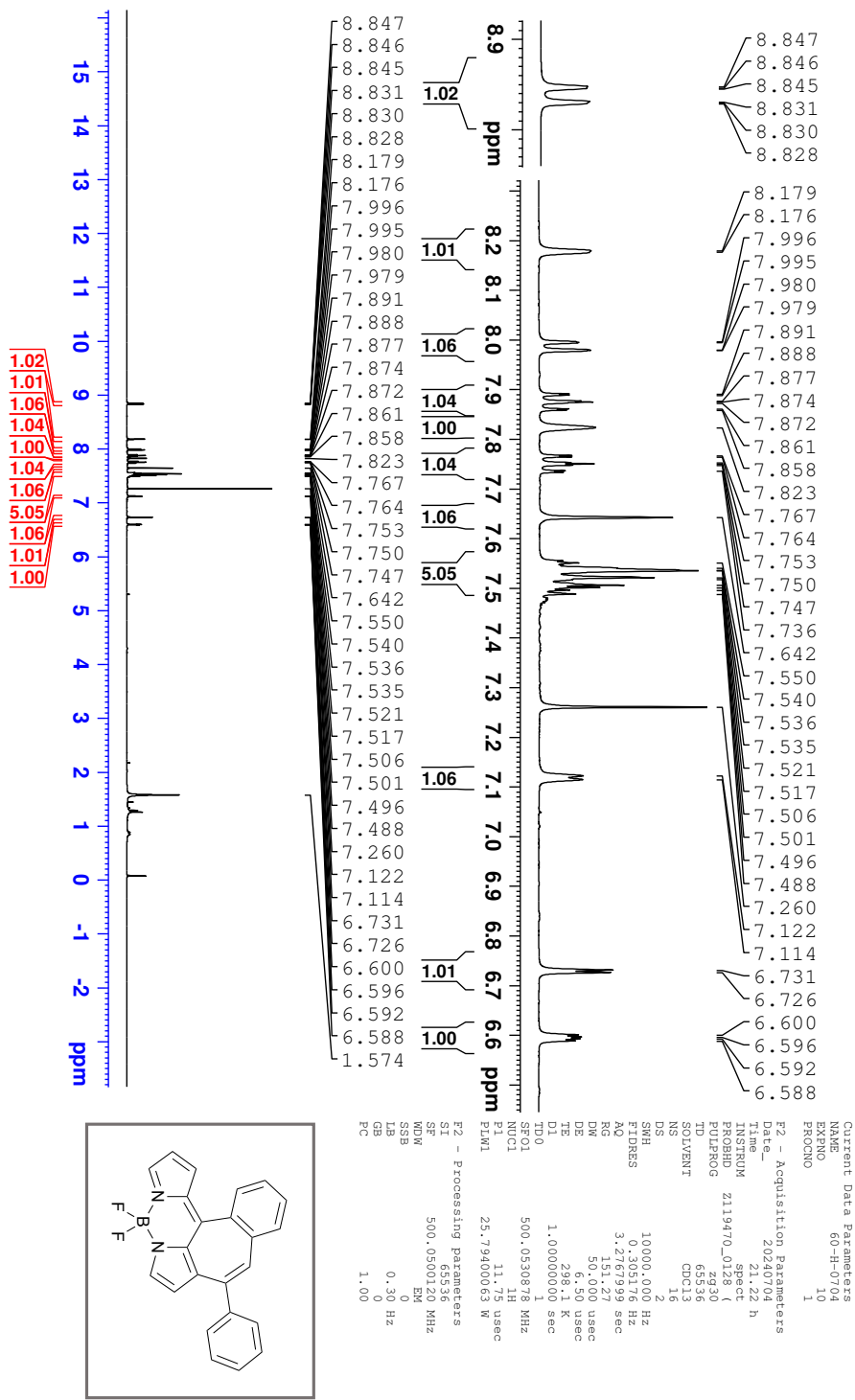
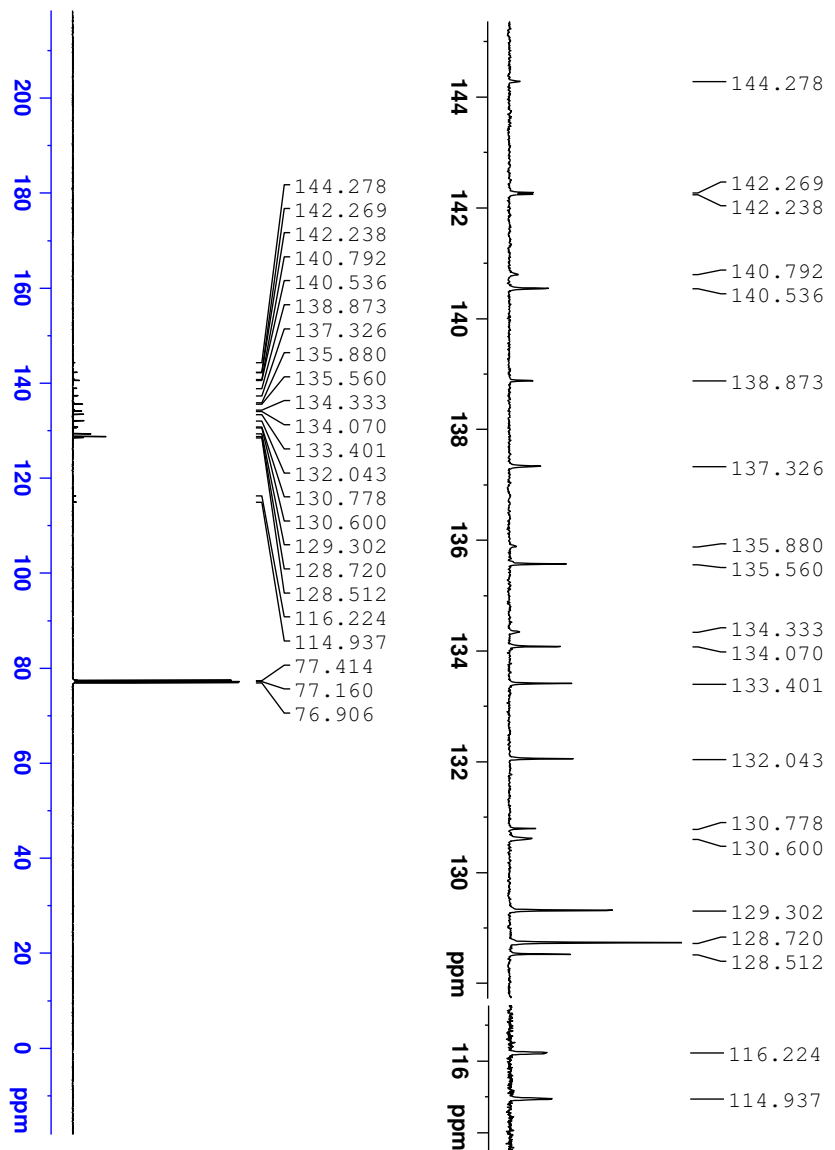


Figure S26. ¹H NMR spectrum of 2a in CDCl₃ at 25 °C.



Current Data Parameters
 EXNO 00-CM10
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20240705
 Time 1.10 h
 Day 18 Dec
 PROBHD Z119470_018
 PULPROG zgpg30
 ID_ 65536
 NS 4096
 DS 2
 SWH 29961.904 Hz
 FWHM 32.250 Hz
 AQ 1.1010048 sec
 RG 190.44
 DM 16.800 usec
 DE 4.200 usec
 TE 299.0 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 125.750243 MHz
 SF01 125.750243 MHz
 NU01 13C
 FL01 93.8130034 M
 SF02 500.0520002 MHz
 NU02 1H
 FL02 500.136099 M
 F2 - Processing parameters
 SI 25.7940063 M
 PCPD2 80.70 usec
 FWH2 0.3584400 M
 FWH3 0.42581929 M
 F2 - Processing parameters
 SF 125.737448 MHz
 WDM 0
 SSB 0
 GB 1.0 Hz
 DB 0
 PC 1.40

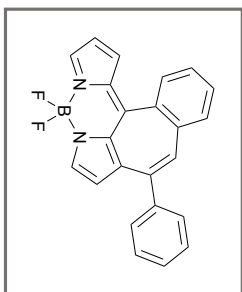


Figure S27. ^{13}C NMR spectrum of **2a** in CDCl_3 at 25 °C.

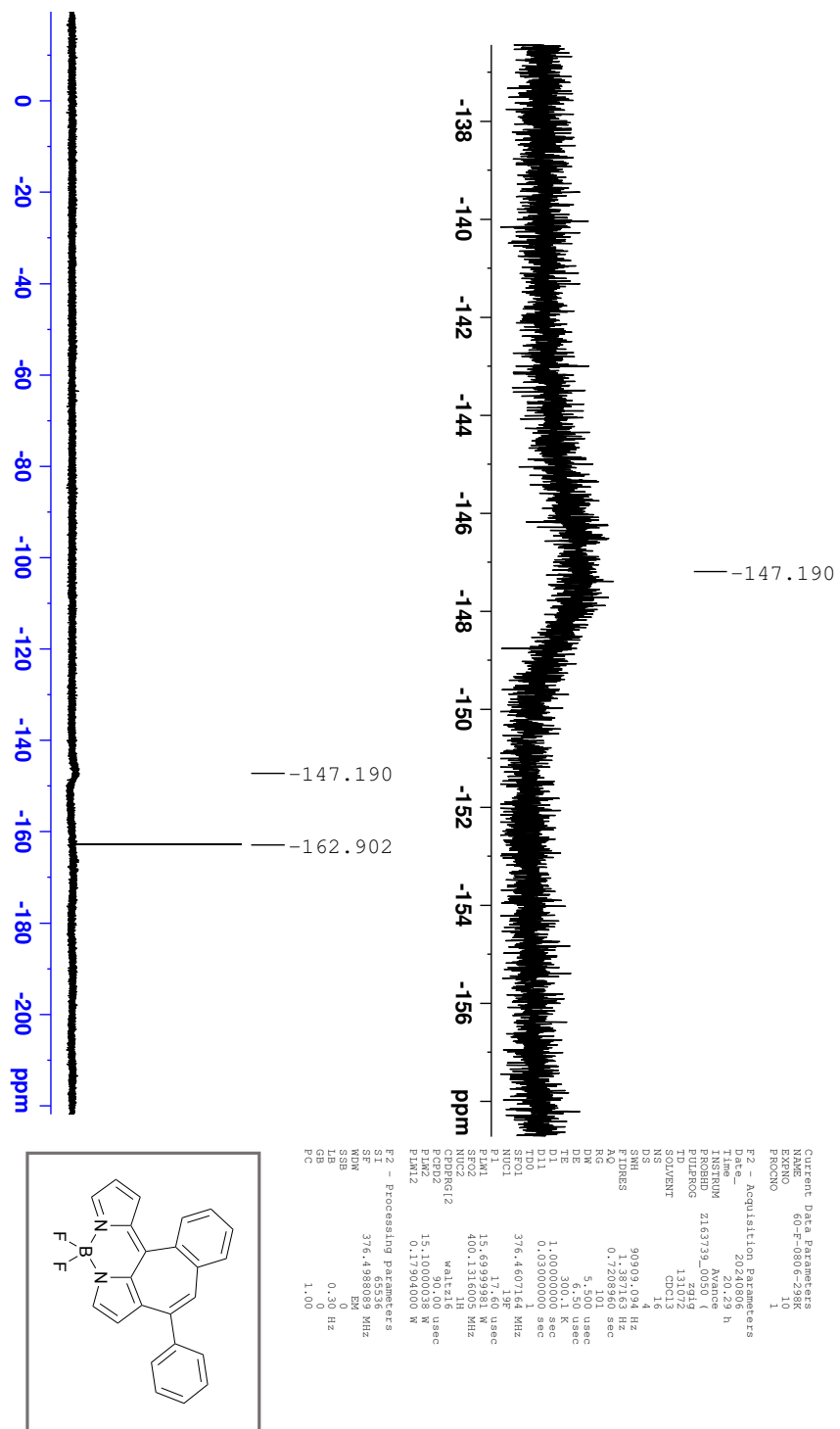
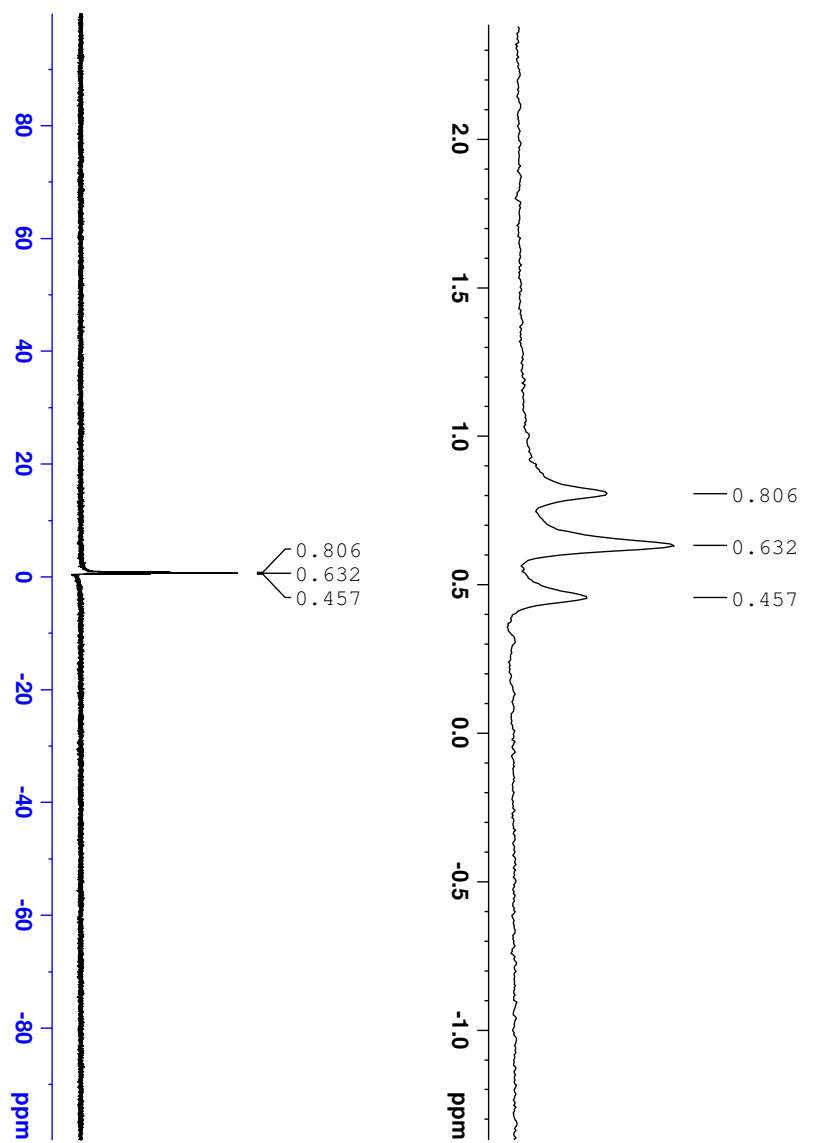


Figure S28. ^{19}F NMR spectrum of **2a** in CDCl_3 at $25\text{ }^\circ\text{C}$.



Current Data Parameters
 NAME 60-B-0926-2
 EXNO 10
 F2PROCNO 1

F2 - Acquisition Parameters
 Date_ 20240926
 Time 17.33 h
 INSTRUM spect
 PROBHD Z119470_0128 (z9
 PULPROG zgpg30
 TD 65536
 NS 128
 DS 4
 SWH 32051.281 Hz
 FIDRES 0.978127 Hz
 AQ 1.0223616 sec
 RG 190.44
 DW 15.600 usec
 DE 25.54 usec
 TE 300.2 K
 D1 1.0000000 sec
 TDO 1
 SFO1 160.4359120 MHz
 NUC1 11B
 P1 13.50 usec
 PL1 75.00000000 W
 PLM1

F2 - Processing Parameters
 SI 32768
 SF 160.4359120 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

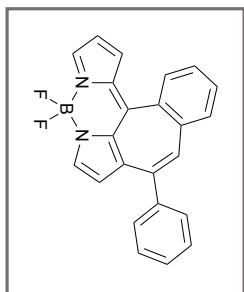


Figure S29 ^{11}B NMR spectrum of **2a** in CDCl_3 at 25°C .

cosy-60-0919

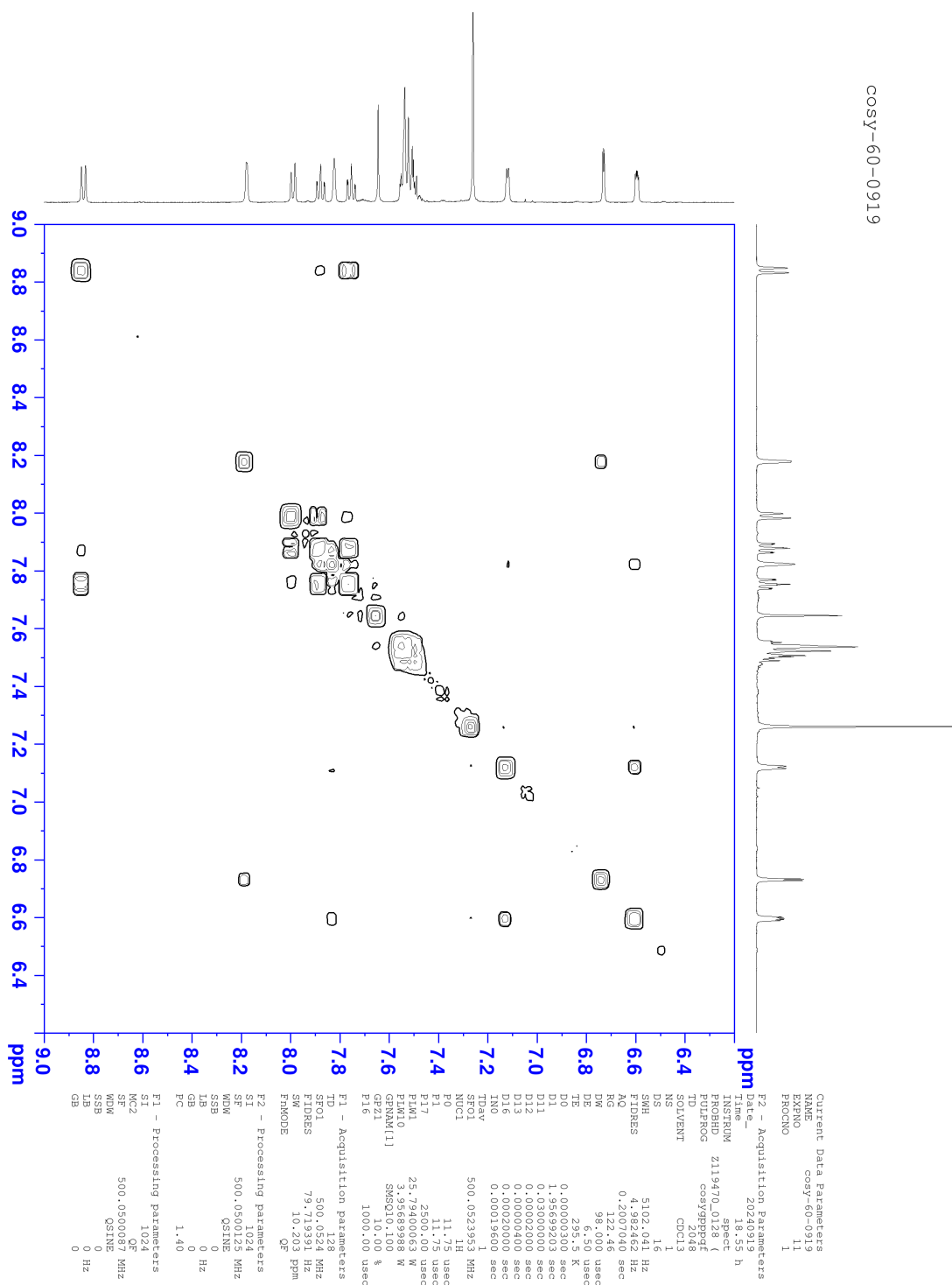
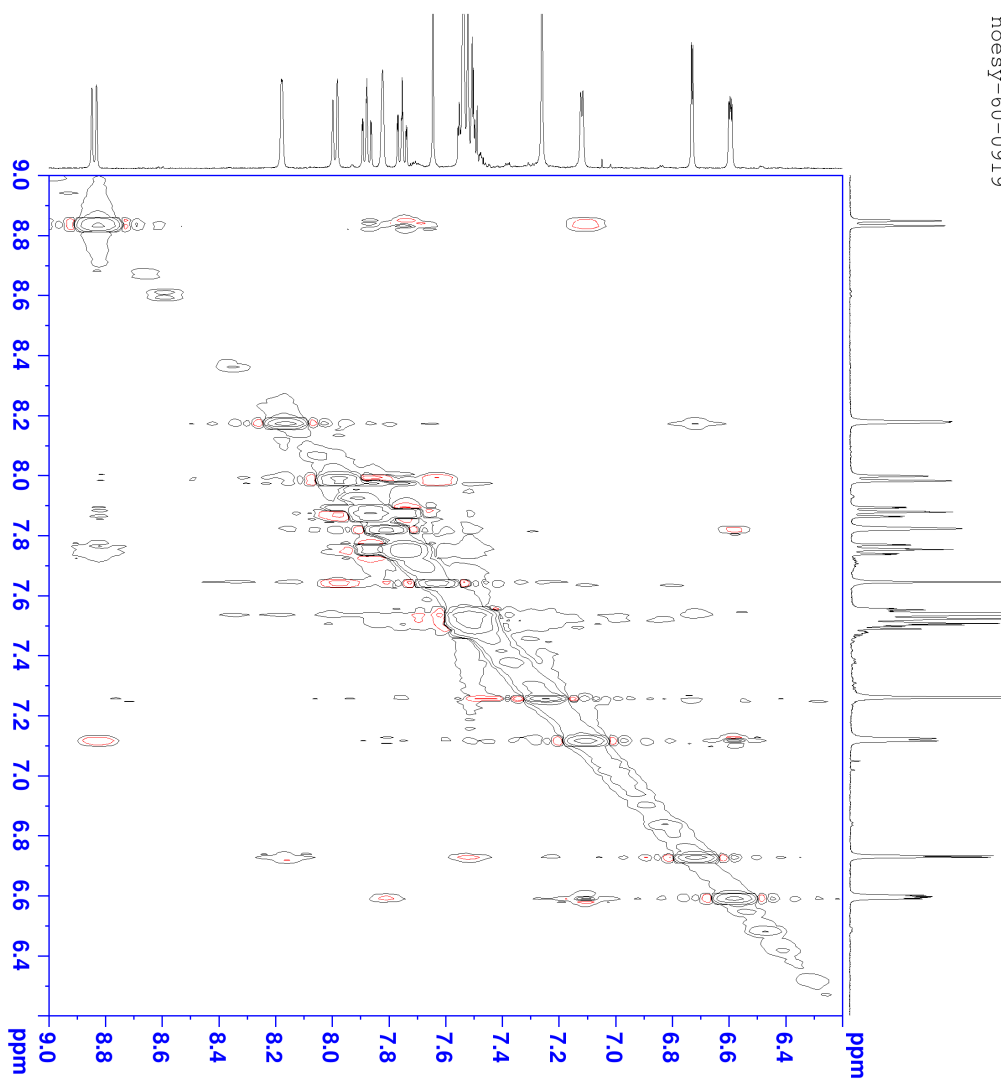


Figure S30. COSY spectrum of **2a** in CDCl₃ at 25 °C.

noesy-60-0919

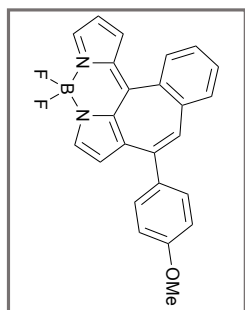
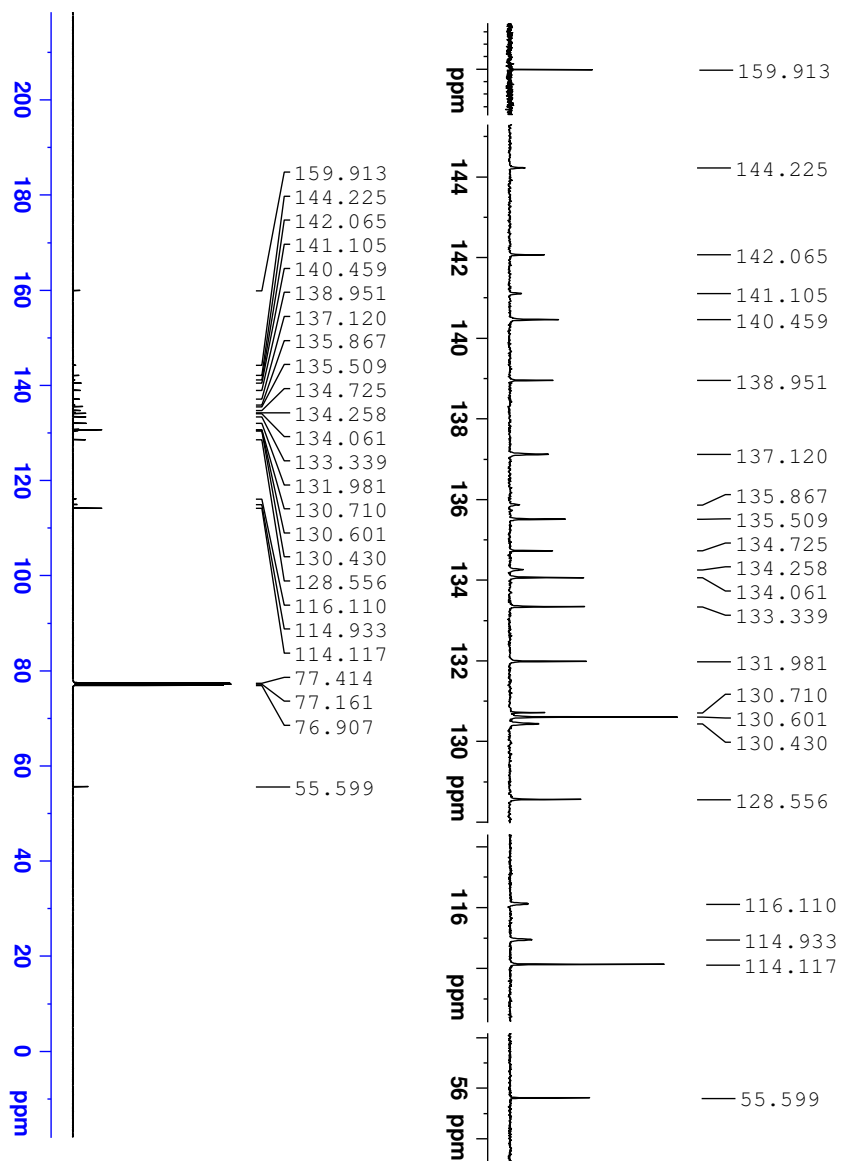


```

Current Data Parameters
NAME      noesy-60-0919
EXPNO    11
PROCNO   11
-----
F2 - Acquisition Parameters
Date_    20240919
Time     18.10 h
INSTRUM  spect
PROBHD   Z119q70.0128 (
PULPROG  noesygpphnp
TD       2048
SOLVENT  CDCl3
NS       32
DS       2
SWH      5102.041 Hz
FIDRES   4.982462 Hz
AQ       0.2007040 sec
RG       388.28
AQ       6.50 usec
DE       235.5 K
TE       293.5 K
D0       0.00008304 sec
D1       2.00409603 sec
D2       0.03000001 sec
D3       0.03000001 sec
D12      0.00020000 sec
D16      0.00020000 sec
IN0      0.00019600 sec
TDAY     500.0523971 MHz
N1       1H
N2       1H
N3       N
P1       11.75 usec
P2       23.50 usec
P17      2500.00 usec
PL1      25.2500083 W
PL12     25.2500083 W
PL16     40.00 %
GENAM(1) GPCZ1
P16      1000.00 usec
-----
F1 - Acquisition parameters
TD       2048
SFOL     500.0524 MHz
FIDRES   39.859695 Hz
SW       10.203 ppm
FMODE    States-TPsi
-----
F2 - Processing parameters
SI       1024
SF       500.0500139 MHz
WDW      COSYSE
SSB      2
GB       0
PC       1.00
-----
F1 - Processing parameters
SI       1024
SF       500.0500116 MHz
WDW      COSYSE
SSB      2
GB       0
PC       1.00

```

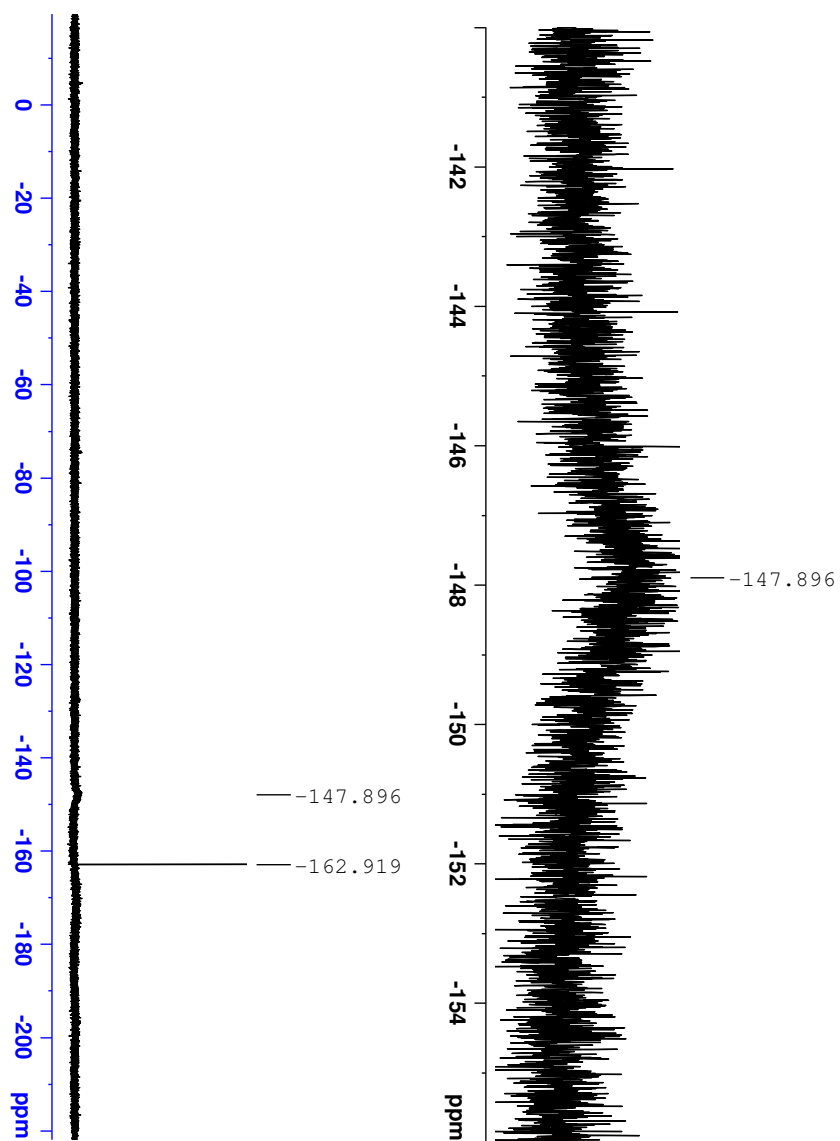
Figure S31. NOESY spectrum of **2a** in CDCl₃ at 25 °C.



```

Current Data Parameters
NAME 20240706
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20240706
Time 1.23 h
INSTRUM z119470_012sec
PROBHD 5mm QNP 1H/13
PULPROG zgpg30
TD 65536
SFO 409.6
AQ 2.97612904 Hz
RG 190.44
DM 16.800 usec
DE 4.000 usec
TE 299.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TDO 1
SFO1 125.7502463 MHz
NUC1 13C
PLM1 93.81300354 M
SFO2 500.0520002 MHz
NUC2 1H
PCPD2 1.00000000 usec
PLM2 25.79400063 M
PCPD1 0.35844000 M
PLM13 0.121591992 M
F2 - Processing parameters
SI 8
SF 125.732648 MHz
WDW EM
SSB 0
GB 1.00 Hz
PC 1.40
  
```

Figure S33. ^{13}C NMR spectrum of **2b** in CDCl_3 at 25°C .



```

Current Data Parameters
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20240807
Time 10:30 h
INSTRUM Z163739_002419
PROBHD1 5mm QNP 1H/13
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
DS 4
SWH 90909.094 Hz
FIDRES 1.387163 Hz
RG 0.1260101 sec
AQ 0.0200000 sec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
d11 0.03000000 sec
TD0 1
FID1 19F
NUC1 19F
P1 17.60 usec
PL1 15.6399981 W
PC12 100.000000 W
NUC2 1H
CPDPRG12 waltz16
PCPD2 15.1000000 usec
PCPD3 15.1000000 usec
PLM12 0.17904000 W
F2 - Processing parameters
SI 0
SF 376.498152 MHz
WDW EM
SSB 0
GB 0
PC 1.00

```

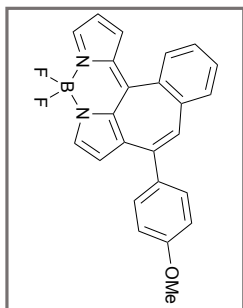
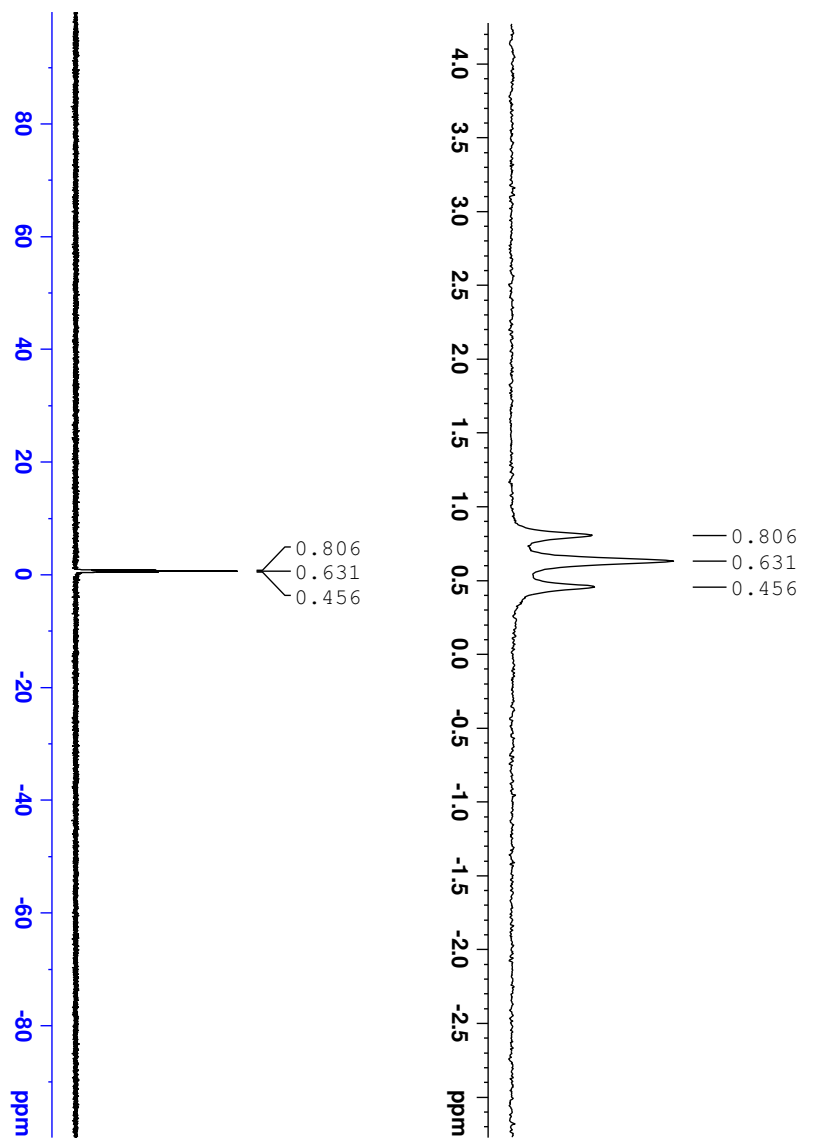


Figure S34. ^{19}F NMR spectrum of **2b** in CDCl_3 at $25\text{ }^\circ\text{C}$.



Current Data Parameters
 NAME OMe-B-0926-2
 EXNO 10
 F2PROCNO 1

F2 - Acquisition Parameters
 Date_ 20240926
 Time_ 18.46 h
 INSTRUM spect
 PROBHID Z119470_0128 (z9
 PULPROG zgpg30
 TD 65536
 CH13 CDCl3
 NS 128
 DS 4
 SWH 32051.281 Hz
 FIDRES 0.978127 Hz
 AQ 1.0223616 sec
 RG 190.44
 DW 15.600 usec
 DE 6.50 usec
 HE 2.50 K
 D1 1.00000001 sec
 TDO 1
 SFO1 160.4359120 MHz
 NUC1 11B
 P1 13.50 usec
 PLW1 75.00000000 W

F2 - Processing parameters
 S 512
 SF 160.4359120 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

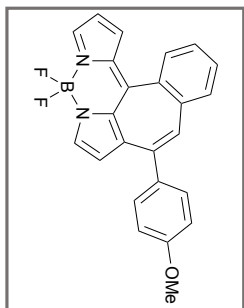


Figure S35 ^{11}B NMR spectrum of **2b** in CDCl_3 at 25°C .

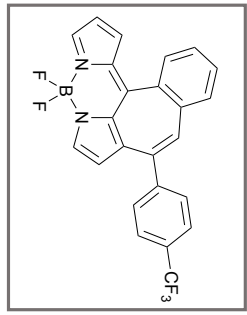
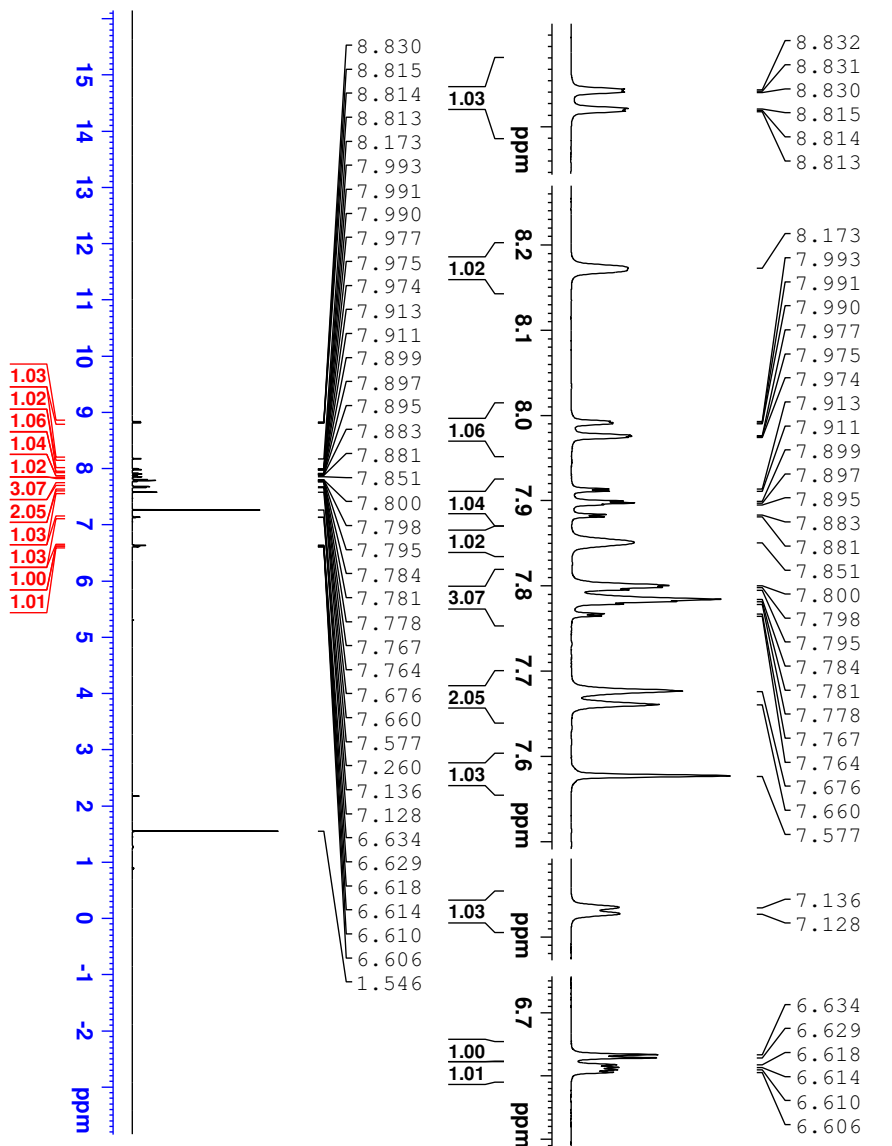


Figure S36. ¹H NMR spectrum of 2c in CDCl₃ at 25 °C.

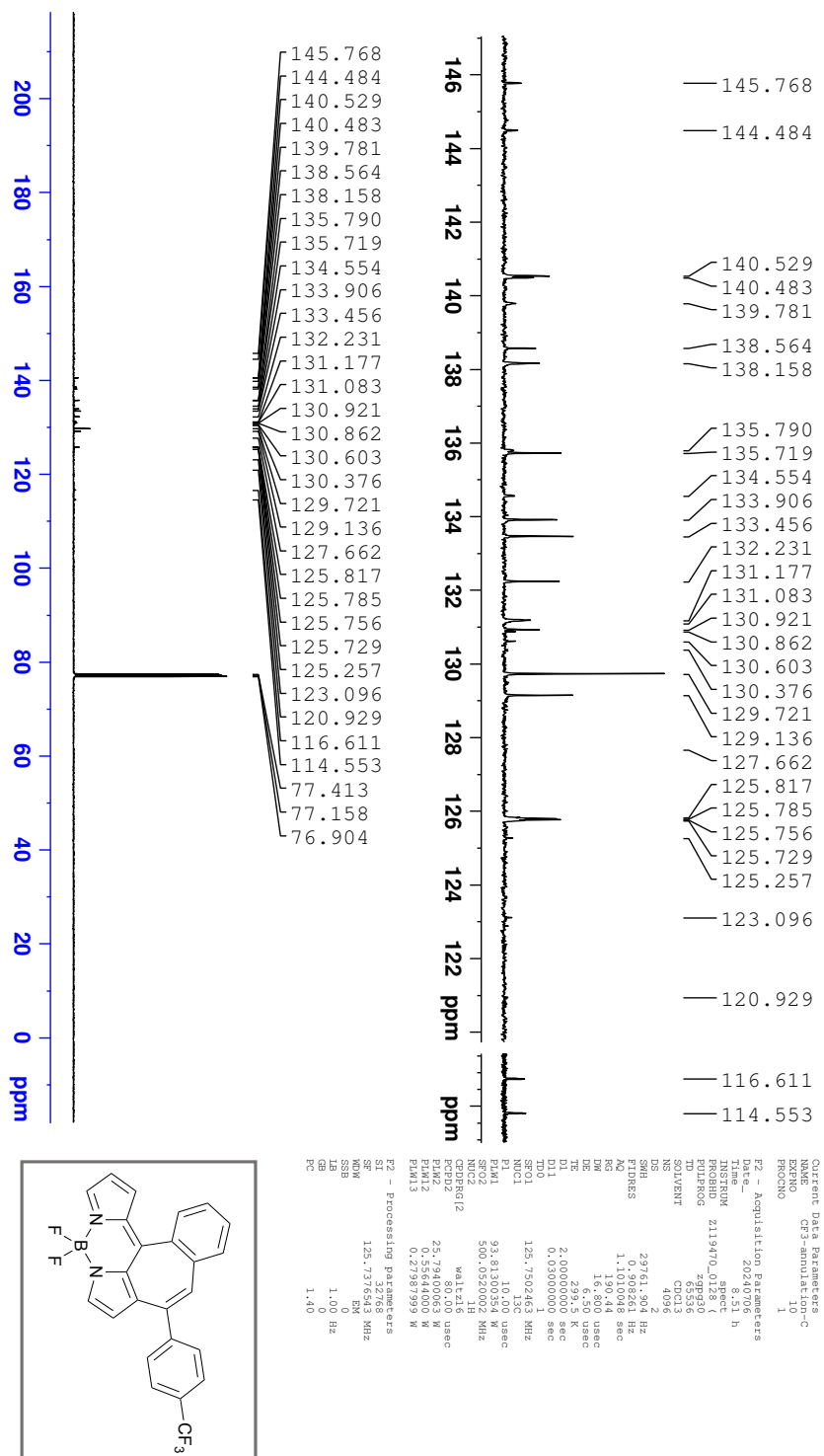
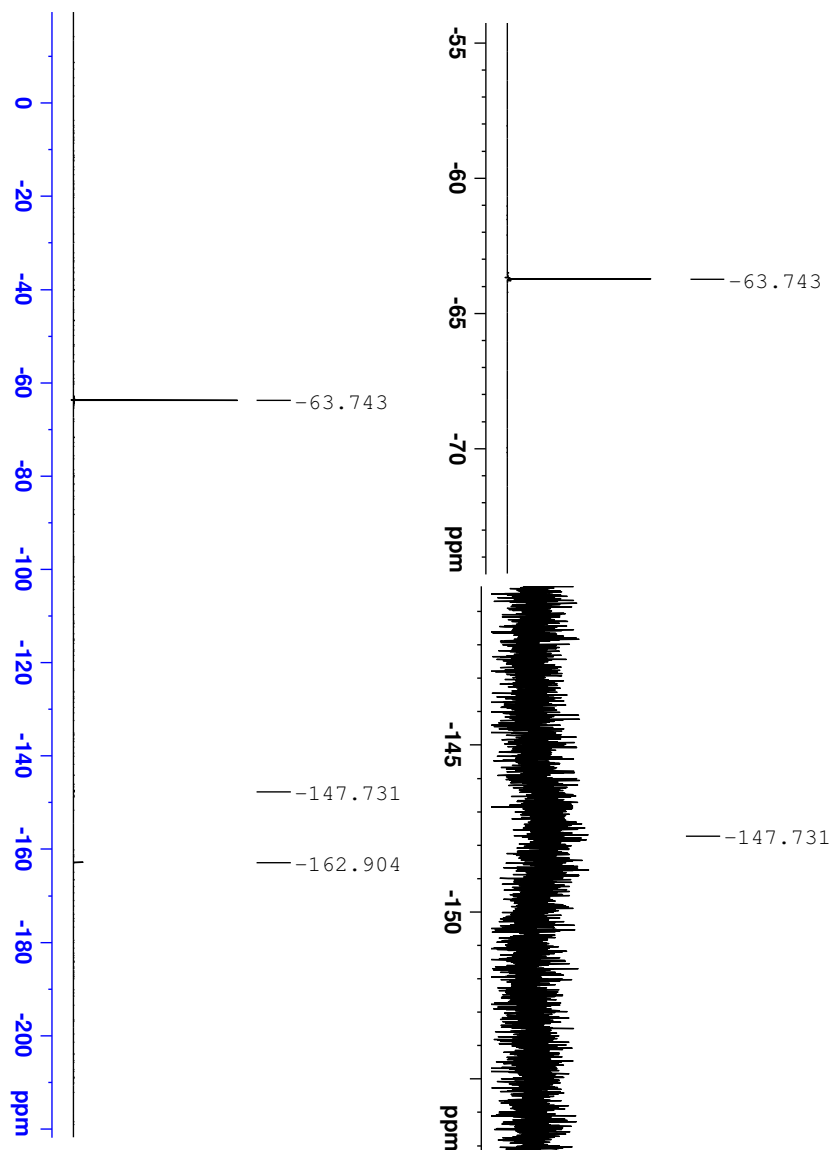


Figure S37. ^{13}C NMR spectrum of **2c** in CDCl_3 at 25 °C.



```

Current Data Parameters
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20240807
Time 10.39 h
INSTRUM zgpg30
PROBHD 5mmQNP1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
DS 4
SWH 90909.094 Hz
FIDRES 1.387163 Hz
AQ 0.126101 sec
RG 101
DE 5.500 usec
DELTA 6.500 usec
D1 1.00000000 sec
D11 0.03000000 sec
TDO 1
TDC1 1
NUC1 19F
P1 17.60 usec
PL1 15.6393981 W
PCPD2 400.1316011 MHz
CDEPRG12 waltz16
NUC2 15N
PCPD2 15.1000000 usec
PLM12 0.17904000 W
F2 - Processing parameters
SF 376.498083 MHz
WDW EM
SSB 0
GB 0
PC 1.00

```

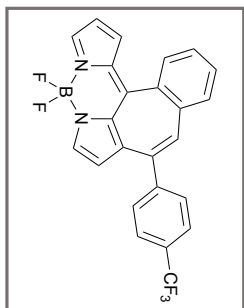


Figure S38. ^{19}F NMR spectrum of **2c** in CDCl_3 at $25\text{ }^\circ\text{C}$.

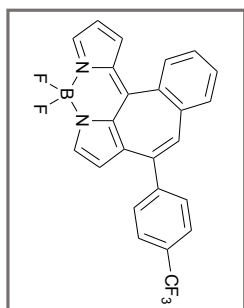
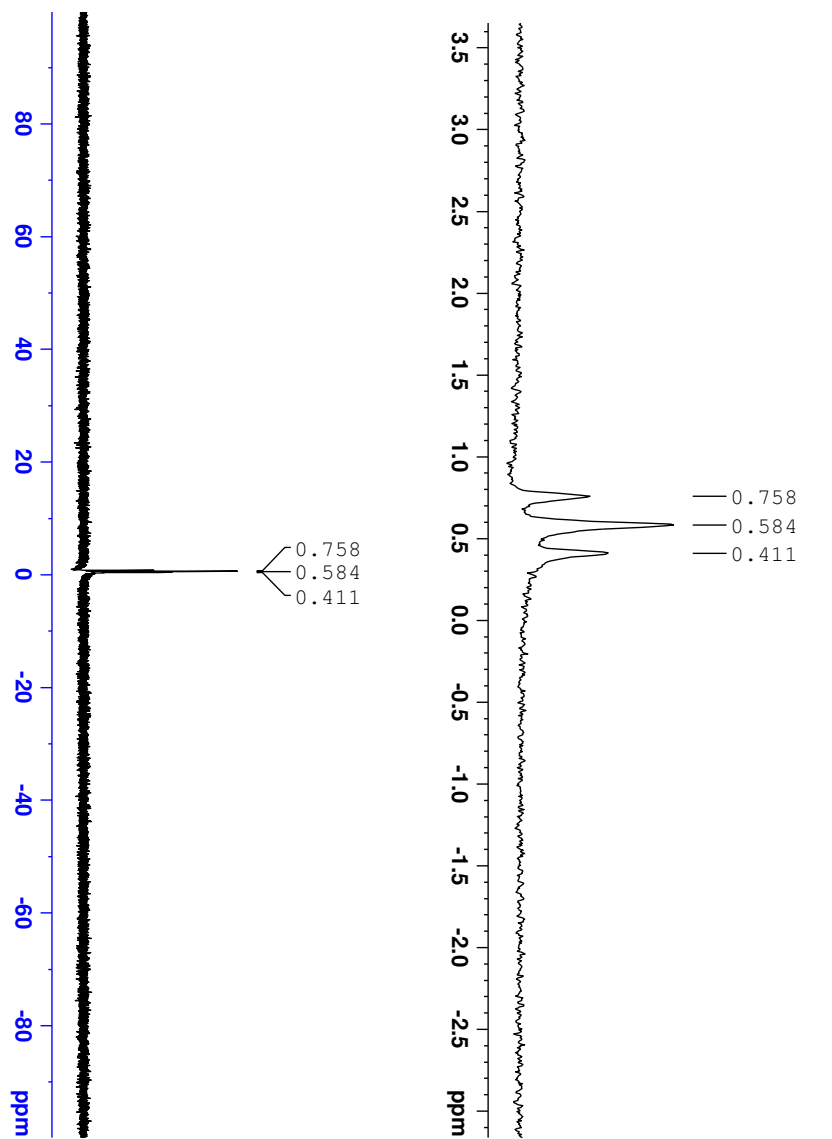
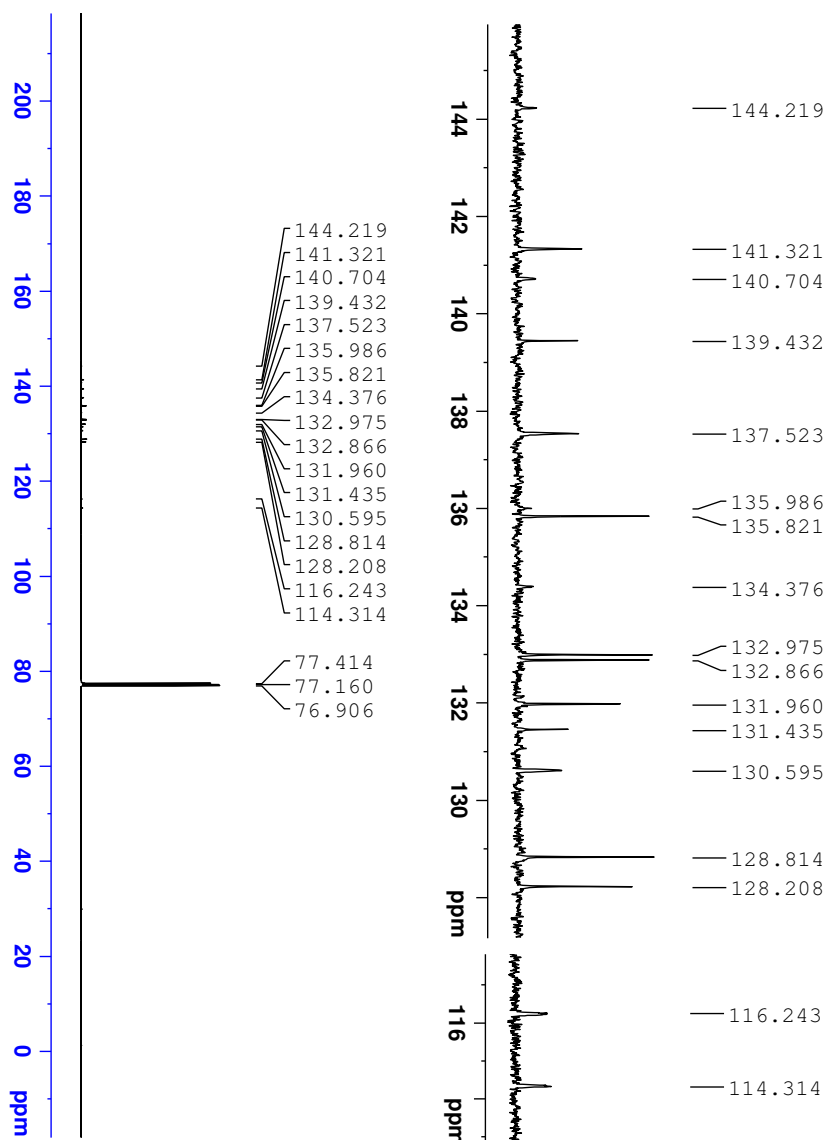


Figure S39 ¹¹B NMR spectrum of 2c in CDCl₃ at 25 °C.



```

Current Data Parameters
EXPNO      1
PROCNO     1
F2 - Acquisition Parameters
Date_      20240706
Time      12.35 h
INSTRUM    zgpg30
PROBHD     zgpg30
PULPROG    zgpg30
TD         65536
SFO2       4096
DS         2
SWH        29961.904 Hz
AQ         1.1010048 sec
RG         190.44
DM         16.800 usec
DE         4.200 usec
TE         299.7 K
D1         2.00000000 sec
D11        0.03000000 sec
SFO1       125.7502463 MHz
NUC1       13C
F1A1       93.8130034 MHz
SFO2       500.0520002 MHz
NUC2       1H
wALT       1H
PCPD2      80.70 usec
PLM12     25.79400063 M
PLM13     0.55644000 M
PLM14     0.72591929 M
F2 - Processing parameters
SI         32768
SF         125.737466 MHz
WDW        EM
SSB        0
GB         1.0 Hz
PC         1.40
  
```

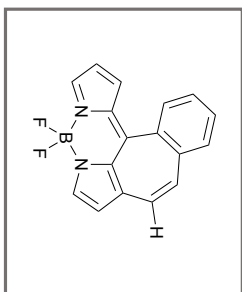
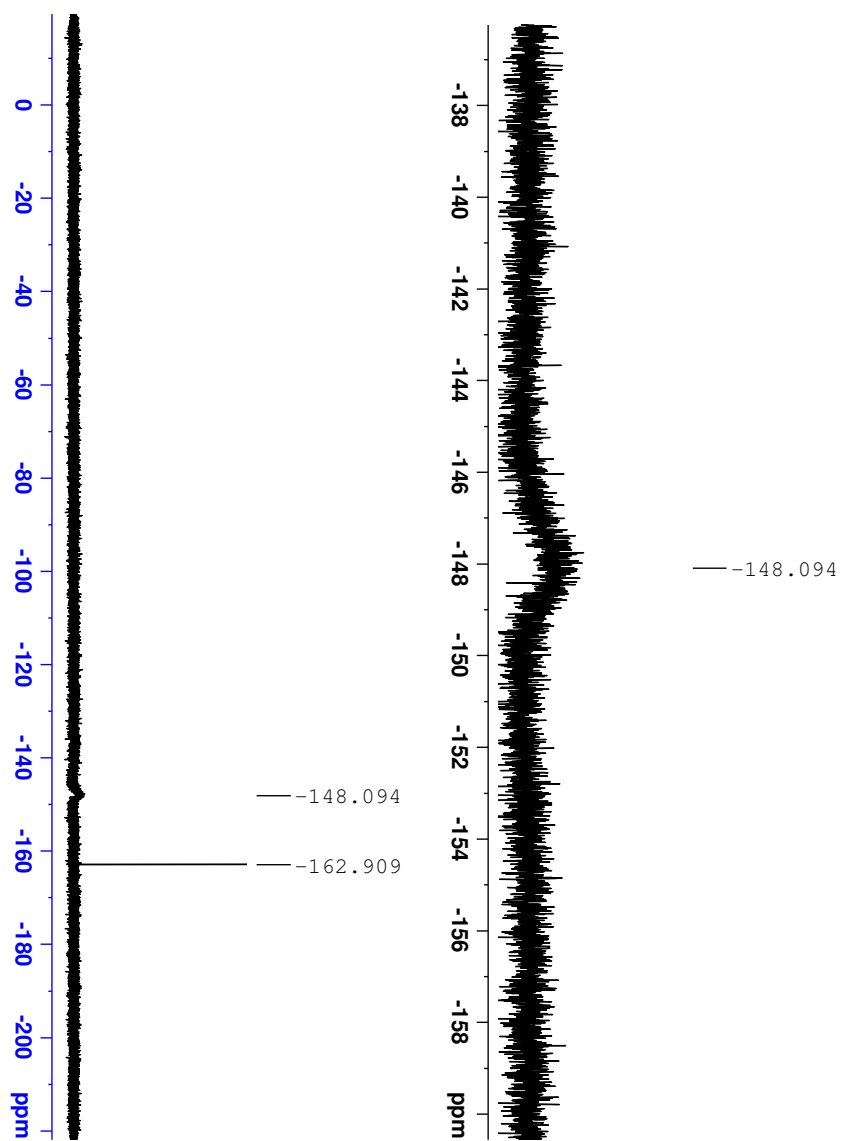


Figure S41. ^{13}C NMR spectrum of **2d** in CDCl_3 at 25°C .



Current Data Parameters -0907
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20240807
 Time 10:47 h
 INSTRUM Avance
 PULPROG zgpg30
 TD 131072
 SOLVENT CDCl3
 DS 4
 SWH 90909.094 Hz
 FIDRES 1.387163 Hz
 RG 0.126101 sec
 DW 5.500 usec
 DE 6.50 usec
 TE 300.2 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TDO 1.00000000 sec
 TDF1 1.00000000 sec
 NUCL1 19F
 P1 17.60 usec
 P11 15.6399981 W
 P12 400.1316918 MHz
 CDEPRG12 waltz16
 NUCC 15.10000000 usec
 P1M1 0.17904000 W
 P1M2 0.17904000 W

F2 - Processing parameters
 SF 376.498814 MHz
 WDM EM
 SSB 0
 GB 0.33 Hz
 PC 1.00

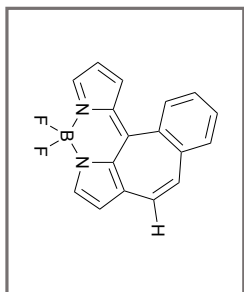
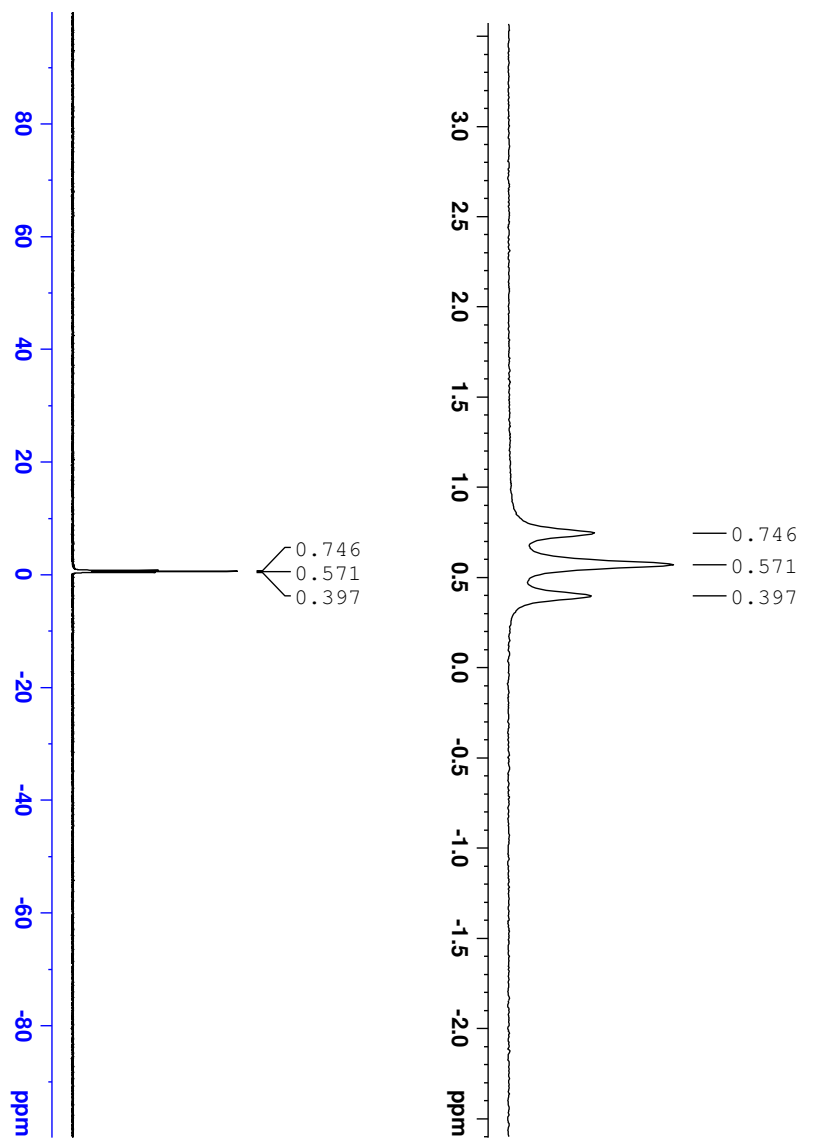


Figure S42. ^{19}F NMR spectrum of **2d** in CDCl_3 at $25\text{ }^\circ\text{C}$.



Current Data Parameters
 NAME H-B-0926
 EXNO 10
 F2 - Acquisition Parameters
 Date_ 20240926
 Time 19.01 h
 INSTRUM spect
 PROBH1 2119470_0128 (z9
 PULPROG zgpg30
 TD 65536
 NUC1 11B
 SOLVENT CDCl3
 NS 128
 DS 4
 SWH 32051.281 Hz
 FIDRES 0.978127 Hz
 AQ 1.0223616 sec
 RG 190.44
 DW 15.600 usec
 DE 6.50 usec
 TE 300.2 K
 D1 2.00000000 sec
 TDO 1.00000000 sec
 SFO1 160.4359120 MHz
 NUC1 11B
 P1 13.50 usec
 PLW1 75.00000000 W

F2 - Processing parameters
 S 512
 SF 160.4359120 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

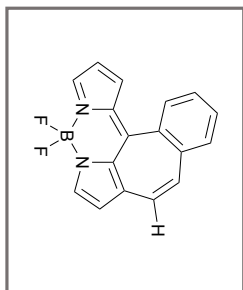


Figure S43 ^{11}B NMR spectrum of **2d** in CDCl_3 at 25°C .

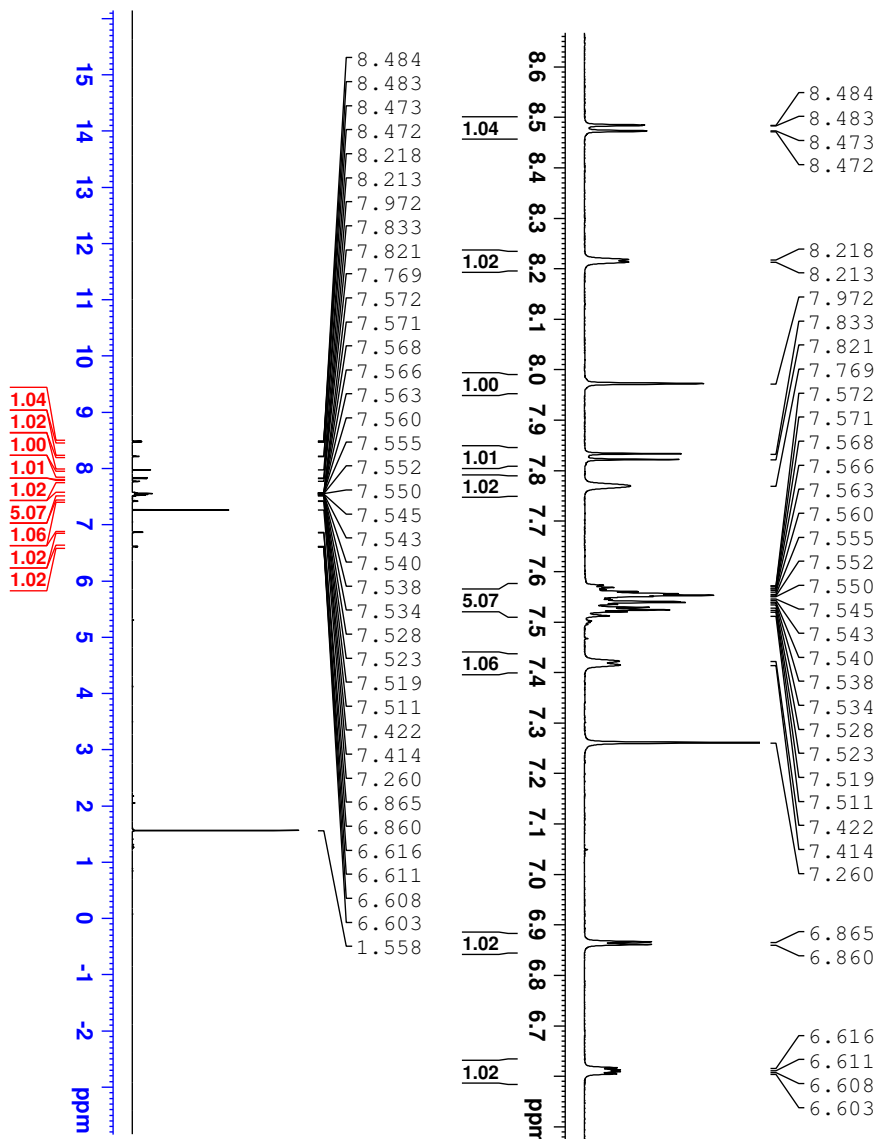
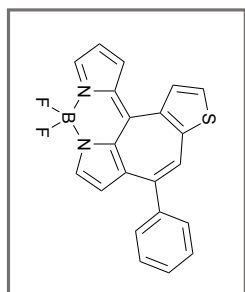
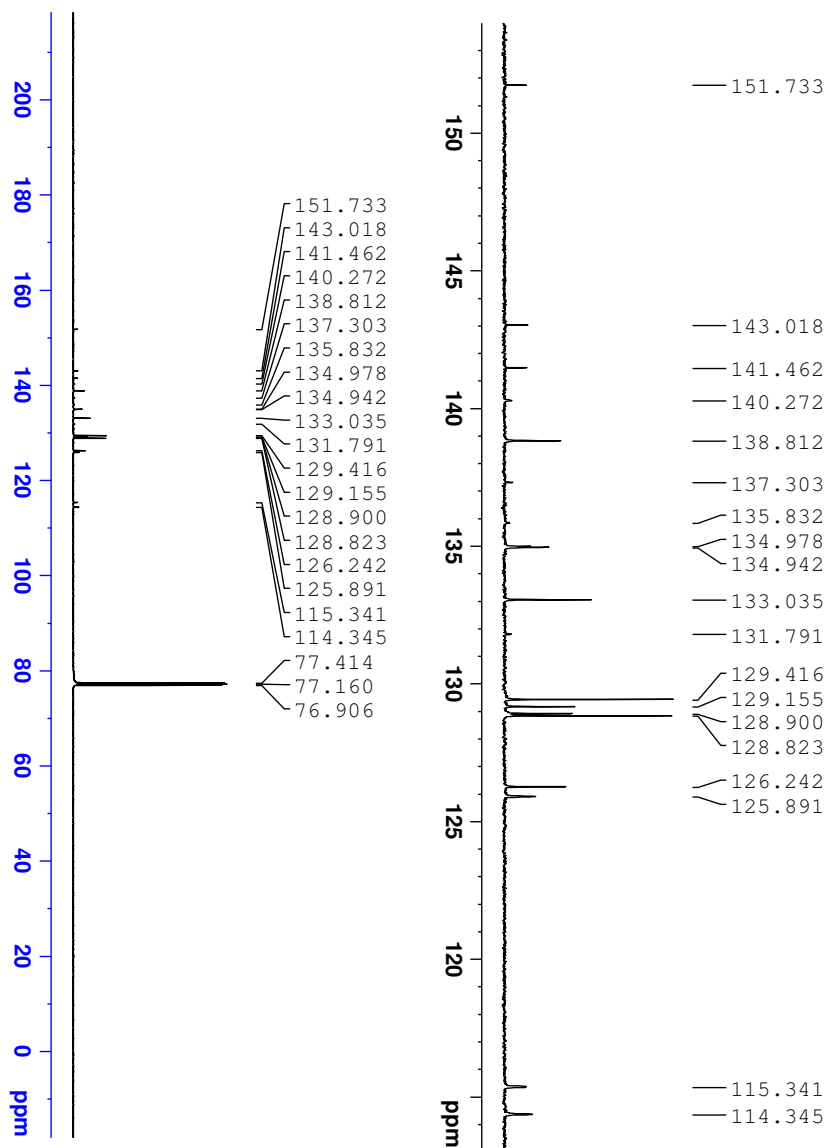


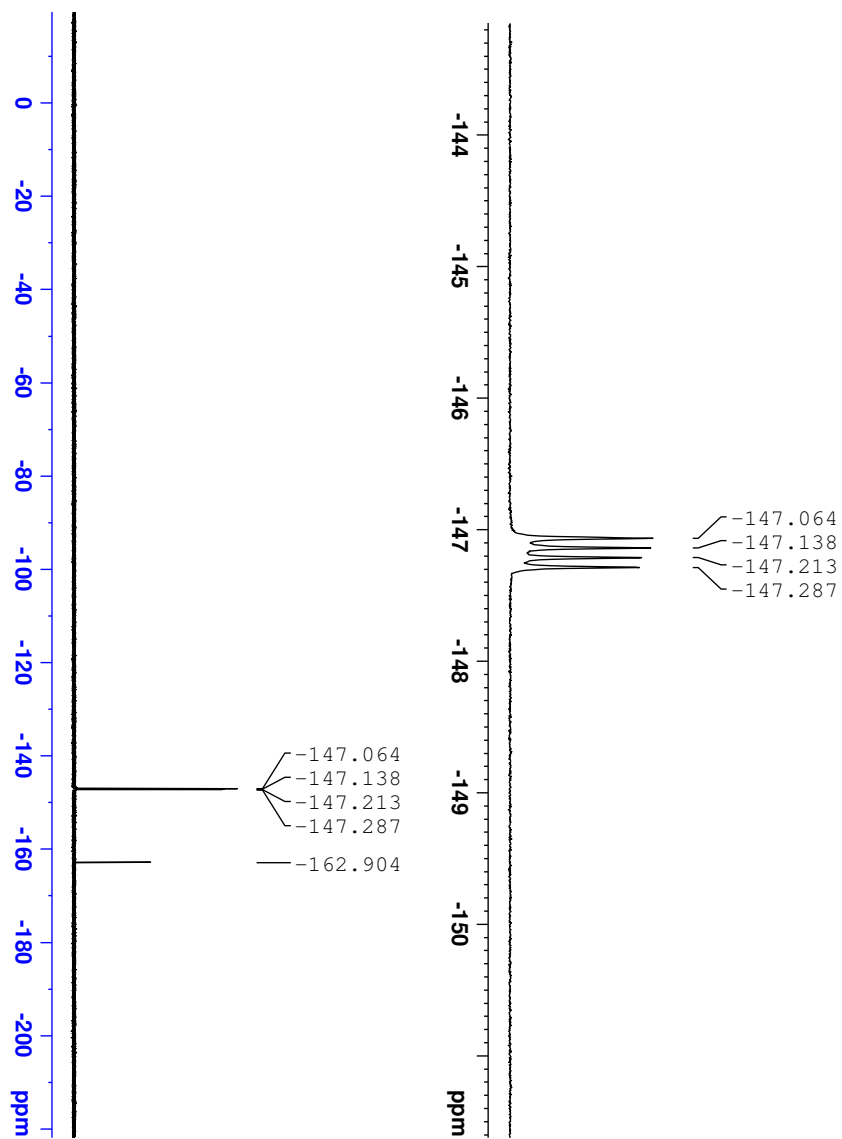
Figure S44. ¹H NMR spectrum of 2e in CDCl₃ at 25 °C.



```

Current Data Parameters
NAME          20240605
EXPNO        111-01_125-010
PROCNO       1
F2 - Acquisition Parameters
Date_        20240605
Time         3.44 h
INSTRUM      spect
PROBHD       5mm QNP 1H/13
PULPROG      zgpg30
TD           65536
SFO          125.76348
AQ           8192
RG           29761.904
DS           4
SWH          29761.904
FIDRES       0.2314
AQ           1.1010048
RG           194.99
DM           16.800
DE           6.000
TE           298.1
D1           2.00000000
D11          0.03000000
D12          0.03000000
D13          0.03000000
SFO1         125.765348
SFO2         133.035
SFO3         130.000000
SFO4         500.1120004
NUC1          13C
NUC2          13C
WALT16       walt16
PCPD2        80.00
PLM1         18.00000000
PLM2         0.39294001
PLM3         0.19765800
F2 - Processing parameters
SI           32768
SF           125.7627428
WDW          EM
SSB          1.00
GB           0
PC           1.40
  
```

Figure S45. ¹³C NMR spectrum of **2e** in CDCl₃ at 25 °C.



```

Current Data Parameters
EXPNO      10
PROCNO     1
F2 - Acquisition Parameters
Date_      20240807
Time       11.03 h
INSTRUM    Avance
PROBHD     zgpg30
PULPROG    zgpg30
TD         131072
SOLVENT    CDCl3
NS         4
DS         4
SWH        90909.094 Hz
FIDRES     1.387163 Hz
AQ         0.726101 sec
RG         101
DE         5.500 usec
TE         300.2 K
D1         1.00000000 sec
d11        0.03000000 sec
TD0        1
NUC1       19F
NUC1F1    376.4607161 MHz
P1         17.60 usec
PLM1       15.6399981 W
PRG2       waltz16
NUC2       1H
CPDPRG12  waltz16
PCPD2      15.1000000 usec
PLM2       0.17904000 W
F2 - Processing parameters
SF         376.498108 MHz
WDW        EM
SSB        0
GB         0.3 Hz
PC         1.00
  
```

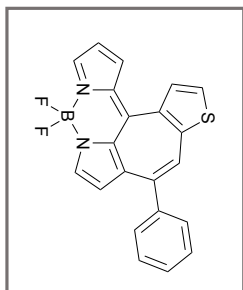


Figure S46. ^{19}F NMR spectrum of **2e** in CDCl_3 at 25°C .

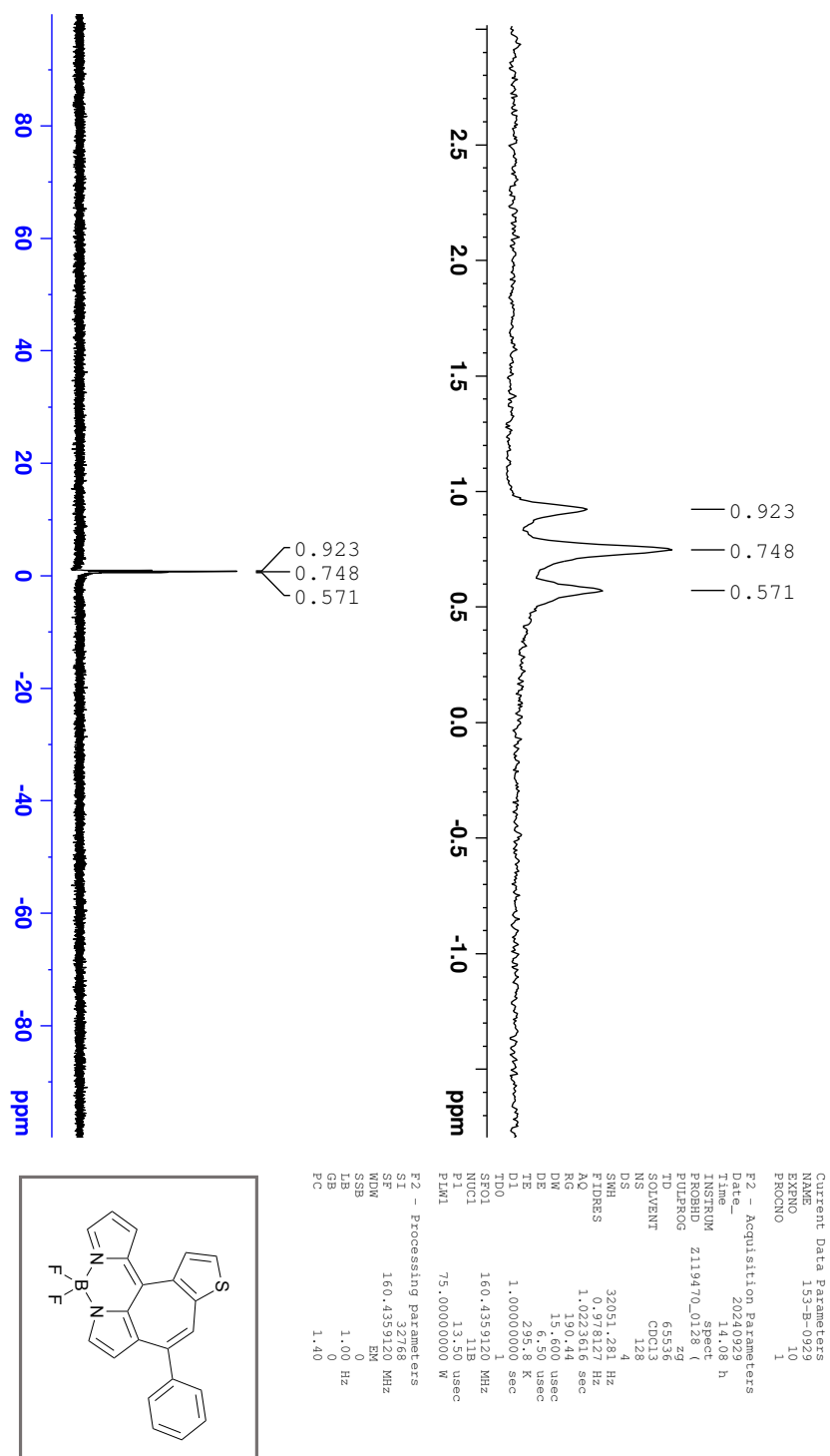


Figure S47 ^{11}B NMR spectrum of **2e** in CDCl_3 at $25\text{ }^\circ\text{C}$.

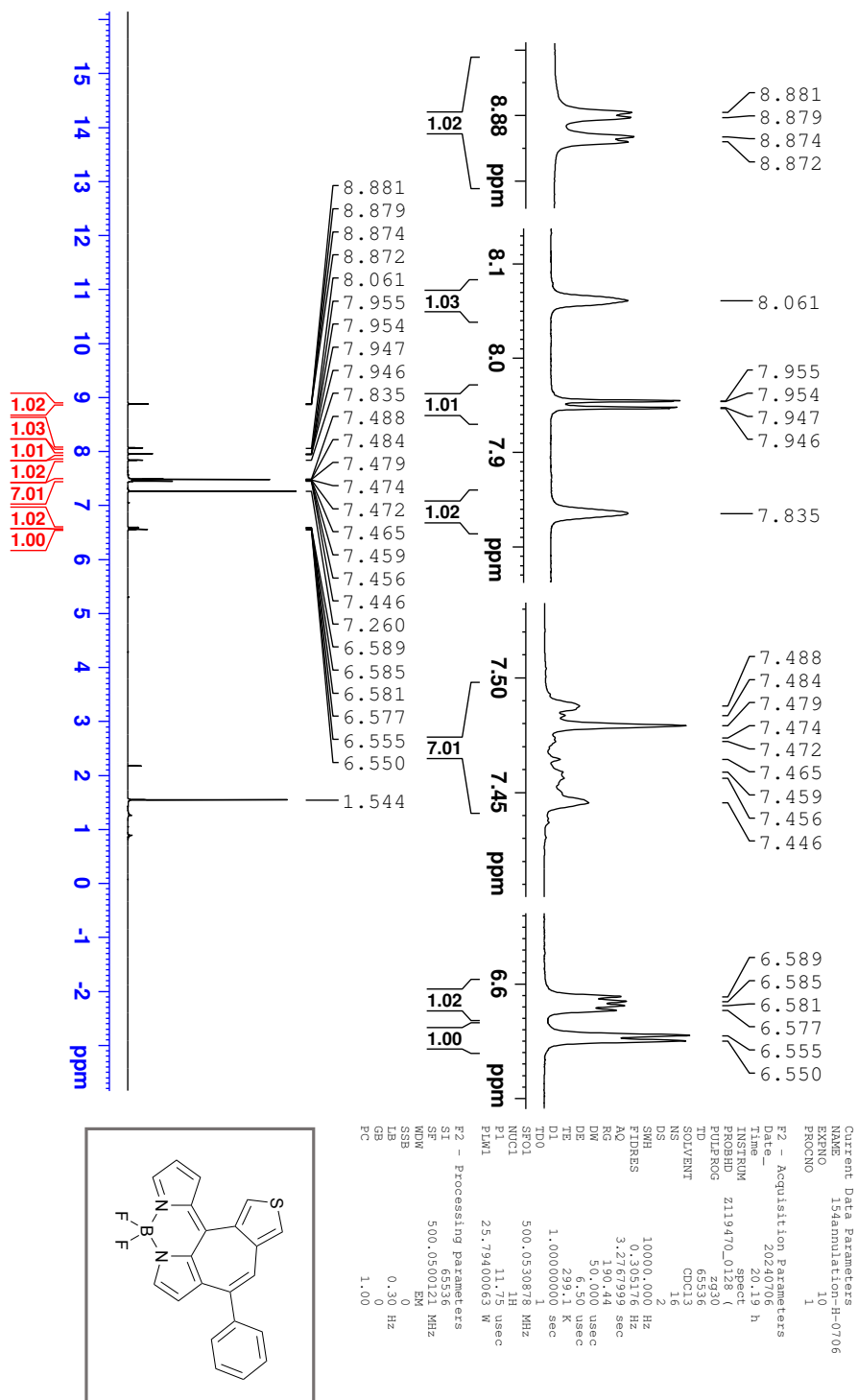
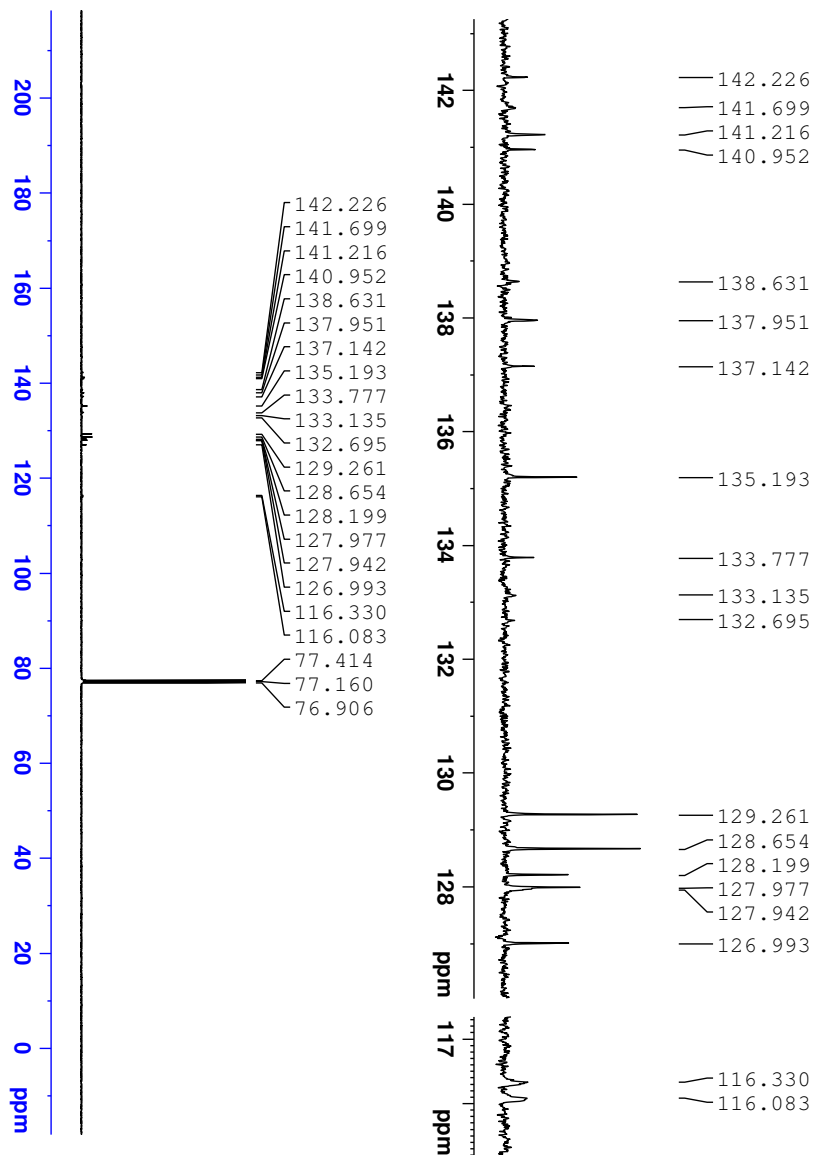


Figure S48. ¹H NMR spectrum of 2f in CDCl₃ at 25 °C.



```

Current Data Parameters
EXNO          1
PROCNO       10
F2 - Acquisition Parameters
Date_         20240706
Time         22.08 h
INSTRUM      spect
PROBHD       Z119470_019
PULPROG      zgpg30
TD           65536
ID           2048
NS           2048
DS           2
SMB          29961.904 Hz
AQ           1.1010048 sec
RG           190.44
DM           16.800 usec
DE           4.200 usec
TE           300.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TDO         125.7502463 MHz
SF01        125.7502463 MHz
NUC01       13C
F1L1        93.8130034 MHz
F1L2        500.0520002 MHz
SF02
NUC02
PCPD2       80.70 usec
PCPD1       1.40
PCPD2       1.40
PCPD1       1.40
PCPD2       1.40
F2 - Processing parameters
SI           125.737488 MHz
WDW          EM
SSB          0
GB           1.0 Hz
PC           1.40
  
```

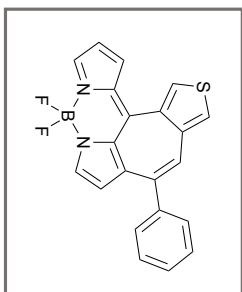
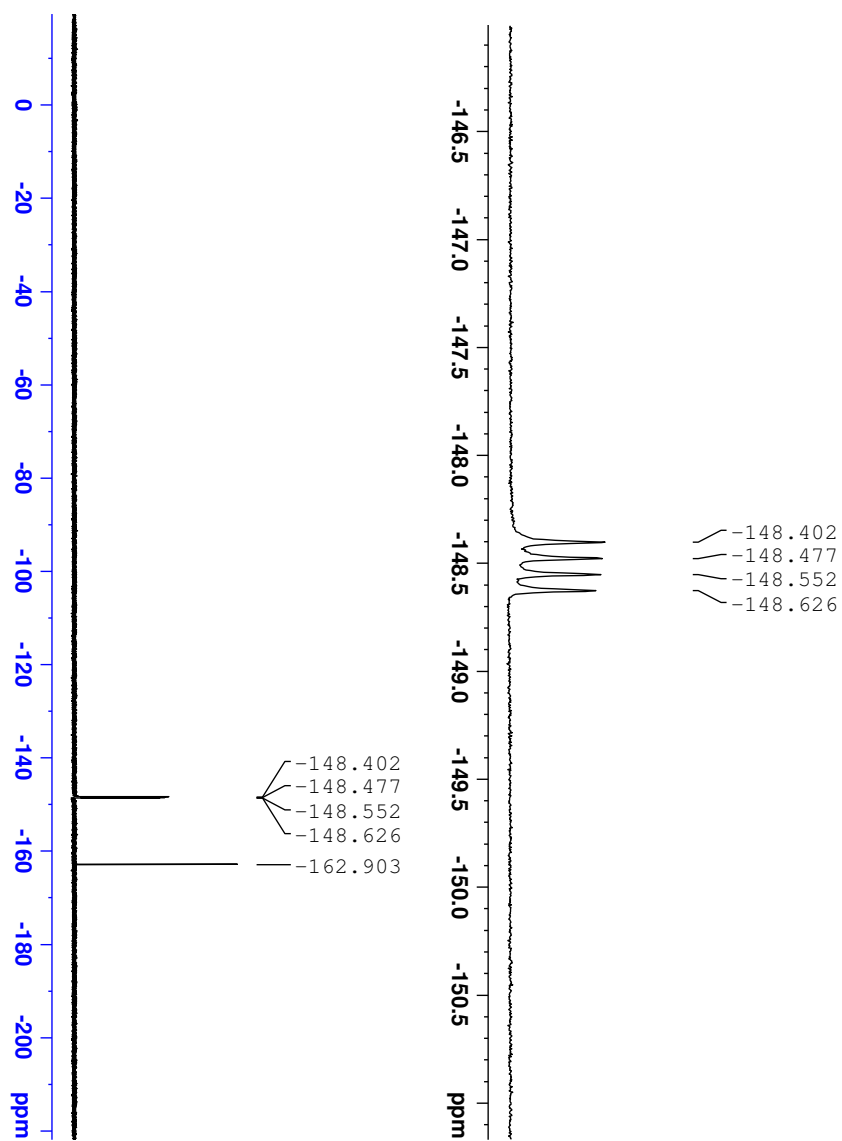


Figure S49. ^{13}C NMR spectrum of **2f** in CDCl_3 at 25°C .



Current Data Parameters
 EXPNO 1
 F2 - Acquisition Parameters
 Date_ 20240807
 Time 12:23 h
 INSTRUM Avance
 PULPROG zgpg30
 TD 65536
 SFO 400.141854
 AQ 1.00
 SOLVENT CDCl3
 NS 4
 DS 4
 SWH 90909.094 Hz
 FIDRES 1.387163 Hz
 AQRES 0.1286101 sec
 RG 327.5
 DW 5.500 usec
 DE 2.000 usec
 TE 300.2 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TDD 1
 TDC1 19f
 NU1 376.4607161 MHz
 P1 17.60 usec
 PL1 15.6393981 W
 PR2 15.6393981 W
 NU2 400.141854 MHz
 CEPRG12 waltz16
 PCPD2 15.1000000 usec
 PLM12 0.17904000 W
 F2 - Processing parameters
 SF 376.498892 MHz
 WDM 0
 SSB 0
 GB 0
 PC 1.00

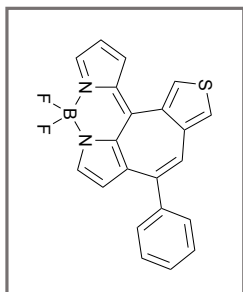
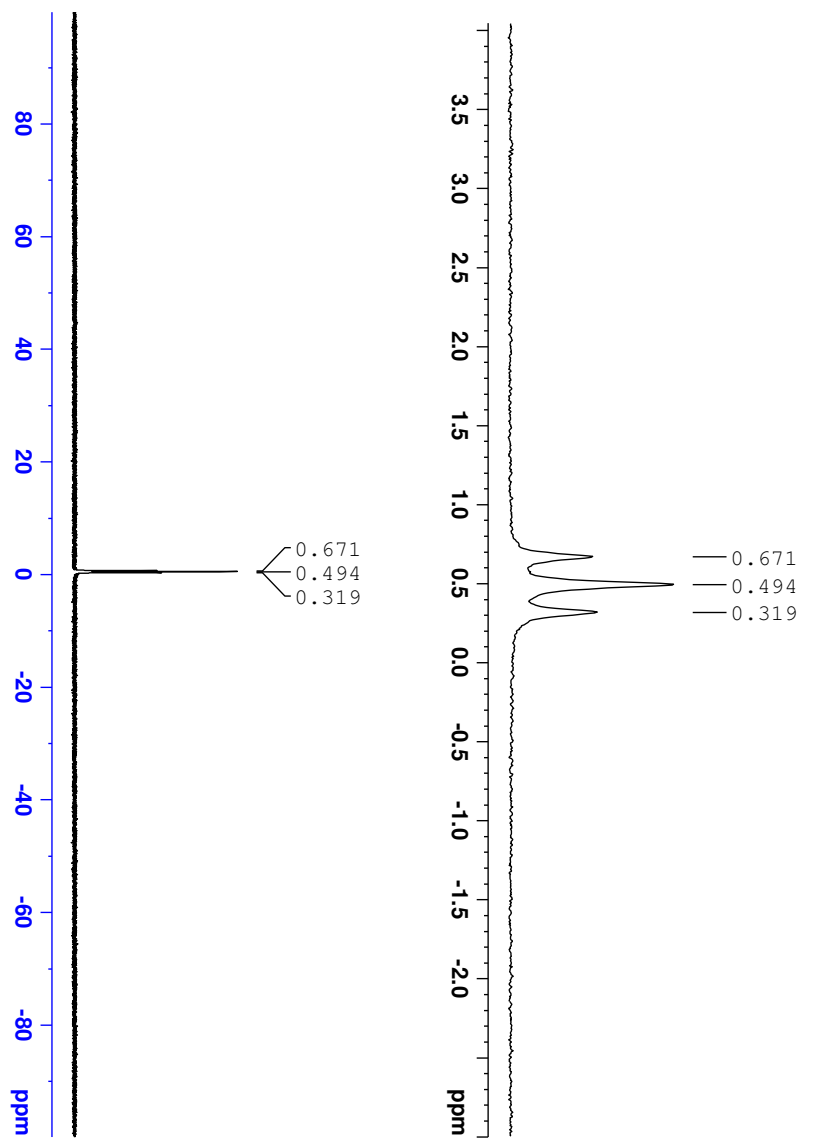


Figure S50. ^{19}F NMR spectrum of **2f** in CDCl_3 at 25 °C.



Current Data Parameters
 NAME 154-B-0926
 EXNO 10
 F2 - Acquisition Parameters
 Date_ 20240926
 Time 18.54 h
 INSTRUM spect
 PROBH1 2119470_0128 (PULPROG zg)
 TD 65536
 CD13
 NOVENT 124
 DS 4
 SWH 32051.281 Hz
 FIDRES 0.9778127 Hz
 AQ 1.0223616 sec
 RG 190.44
 DW 15.600 usec
 DE 6.50 usec
 TE 29.50 K
 D1 1.00000000 sec
 TD0 1
 SFO1 160.4359120 MHz
 NUC1 11B
 P1 13.50 usec
 PLW1 75.00000000 W

F2 - Processing parameters
 SI 512
 SF 160.4359120 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

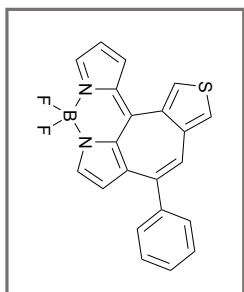
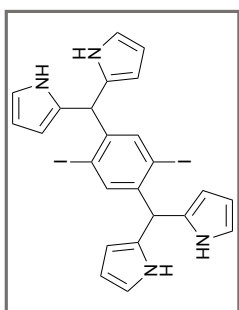
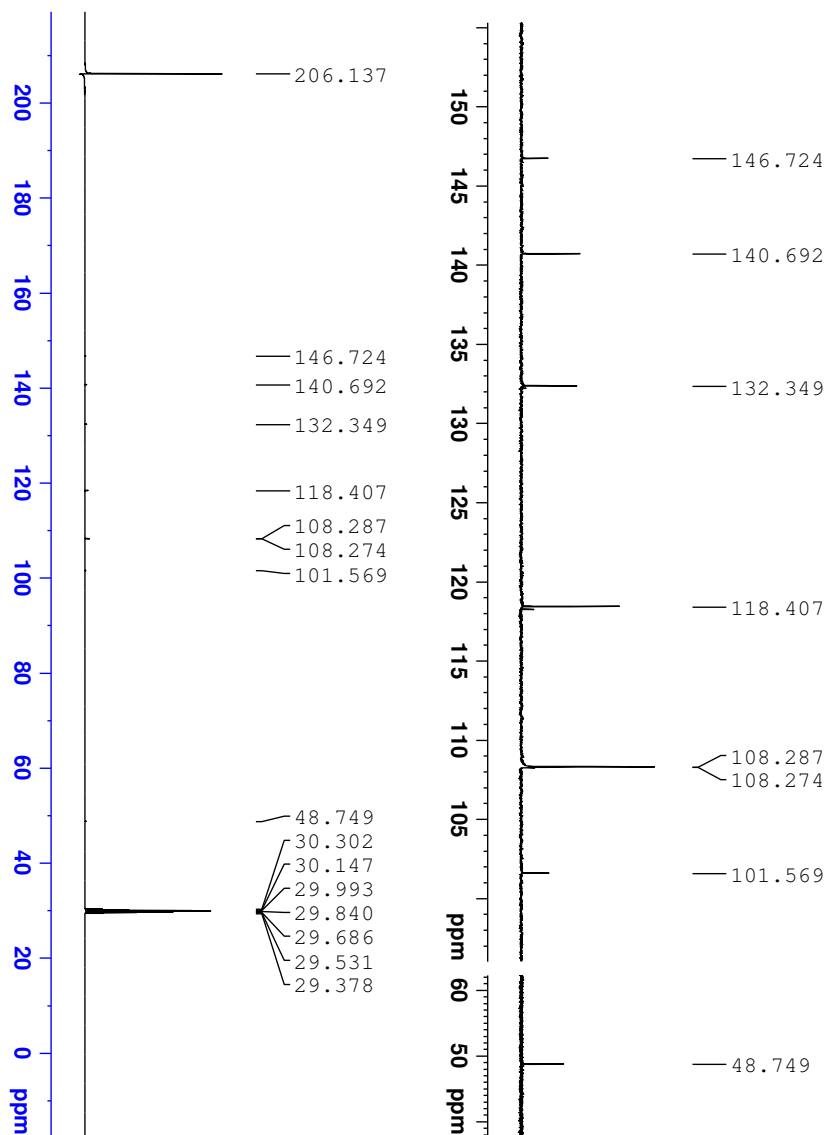


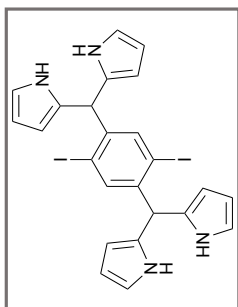
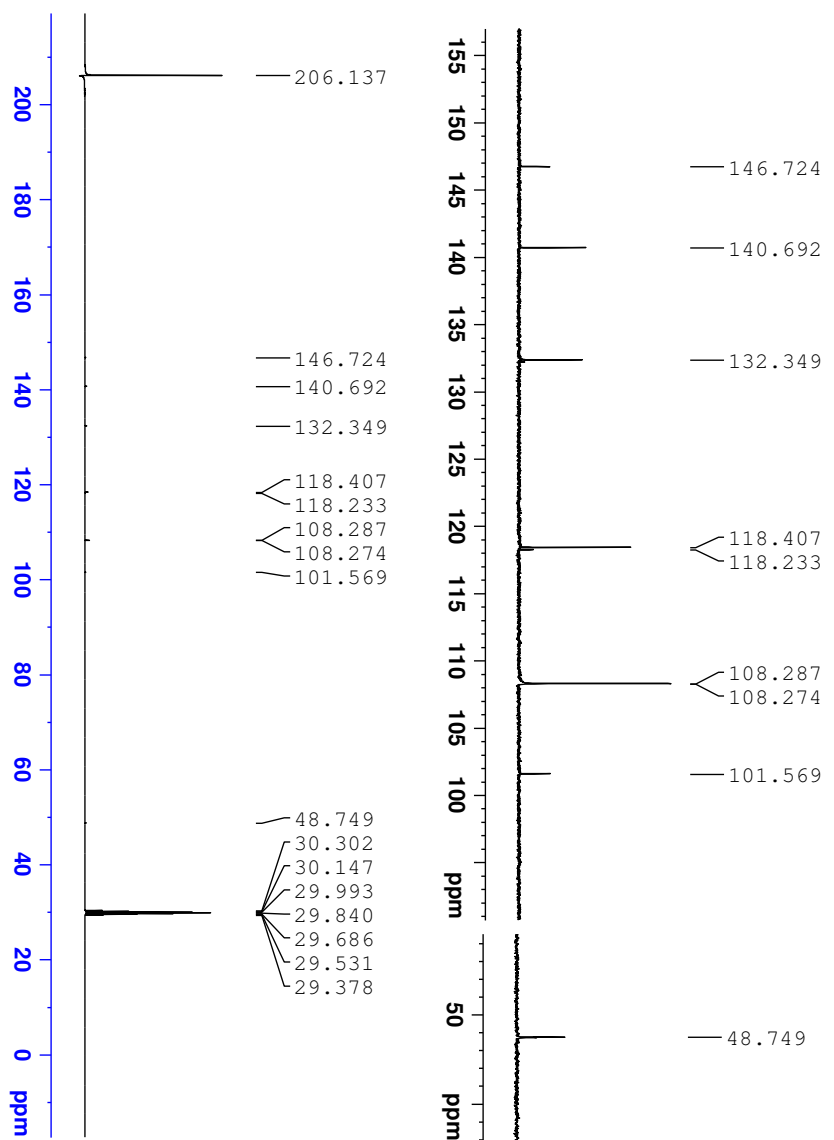
Figure S51 ^{11}B NMR spectrum of **2f** in CDCl_3 at 25 °C.



```

Current Data Parameters
Name: 20240717-0110
ExpNo: 1
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20240717
Time: 0.52 h
INSTRUM: spect
PROBHD: 5mm
PULPROG: zgpg30
TD: 65536
SOLVENT: Acetone
NS: 4096
DS: 4
SWH: 29761.904 Hz
AQ: 1.1010048 sec
RG: 190.44
FM: 16.400 usec
TM: 2.98
TE: 298.4 K
D1: 2.00000000 sec
D11: 0.03000000 sec
D10: 125.7502463 MHz
SFO1: 13C
N1C1: 1.3C usec
F1M1: 93.8130054 MHz
SFO2: 500.0520002 MHz
N1C2: 13C
PCPD12: waltz16
PCPD2: 30.00 usec
PLW2: 25.79400063 W
PLW1: 0.35844009 W
FM13: 0.81957593 M
F2 - Processing parameters
SI: 32768
SF: 125.73549 MHz
WDW: EM
SSB: 0
GB: 1.40
PC: 1.40
  
```

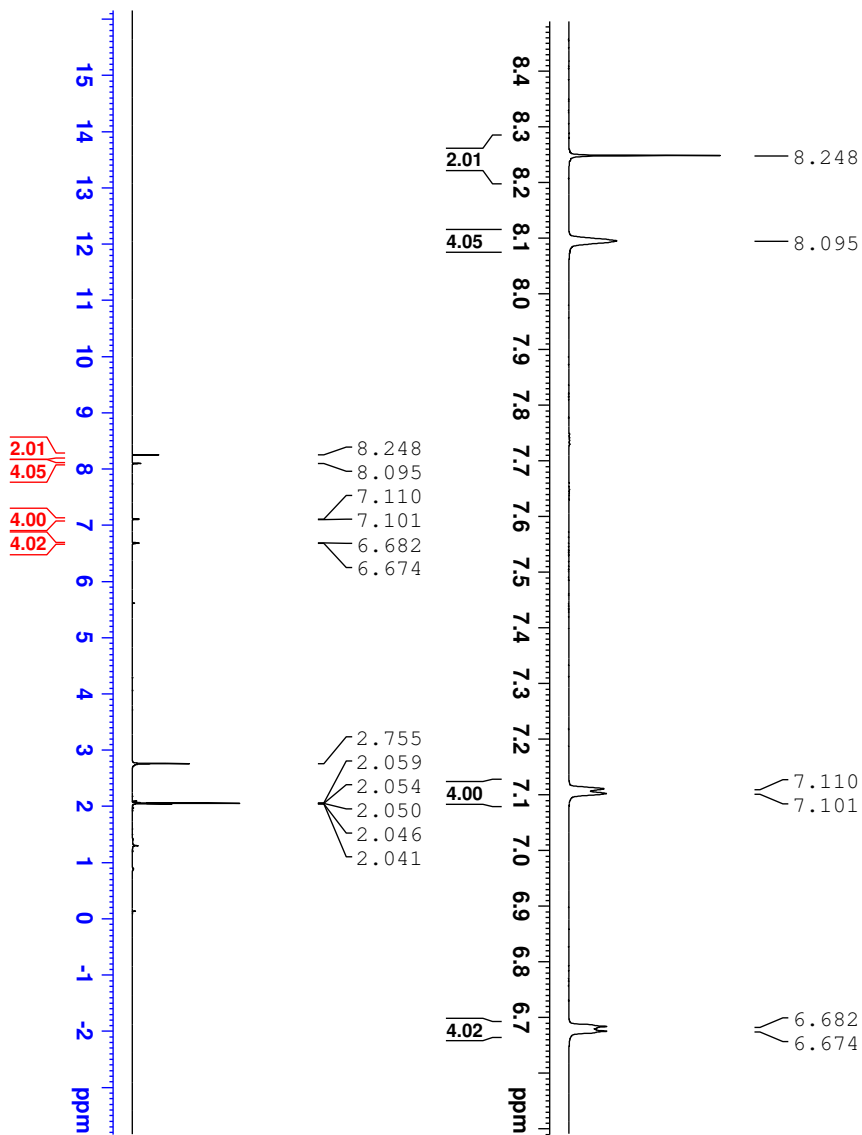
Figure S52. ¹H NMR spectrum of S4 in acetone-*d*₆ at 25 °C.



```

Current Data Parameters
EXNO          01
PROCNO        10
F2 - Acquisition Parameters
Date_         20240717
Time         0.52 h
INSTRUM      spect
PROBHD       Z119470_018
PULPROG      zgpg30
TD           65536
SI           Acq4096
AQ           4.096
RG           299.61, 904 Hz
AQ           1.1010048 sec
RG           190.44
DM           16, 800 usec
DE           1.0000000 sec
TE           298.4 K
D11          0.0300000 sec
TDO          0.0300000 sec
SF01         125.7502463 MHz
NUC01        13C
F1A1         93.8130034 MHz
SF02         500.0520002 MHz
NUC02        1H
PCPD2/2      waltz16
PULPROG      zgpg30
PCPD2/2      80.70 usec
PLM12        25.79400063 W
PLM13        0.55844000 W
PLM14        0.75917929 W
F2 - Processing parameters
SI           125.737548 MHz
WDW          EM
SSB          0
GB           1.0 Hz
PC           1.40
  
```

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



```

Current Data Parameters
NAME      W-I-H-0802
EXNO     10
PROCNO   1
-----
F2 - Acquisition Parameters
Date_    20240802
Time     21.10 h
INSTRUM  spect
PROBHD   Z119470_0128 (
PULPROG  zg30
TD        65536
SOLVENT  Acetone
NS        2
DS        1
SWH       10000.000 Hz
FIDRES   0.305176 Hz
AQ        3.2767999 sec
RG        151.27
DM        50.000 usec
DE        6.90 usec
TE        306.2 K
D1        1.0000001 sec
TDO       1
SFO1     500.0530878 MHz
NUC1     1H
P1        11.75 usec
PLM1     25.79400063 W
-----
F2 - Processing parameters
SI        32768
SF        500.0500082 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
  
```

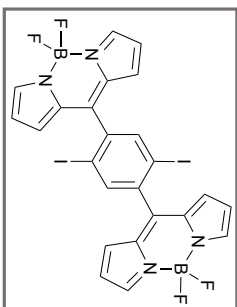
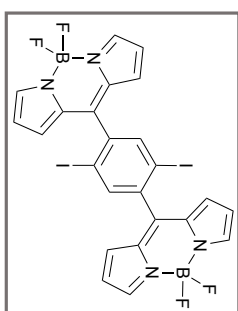
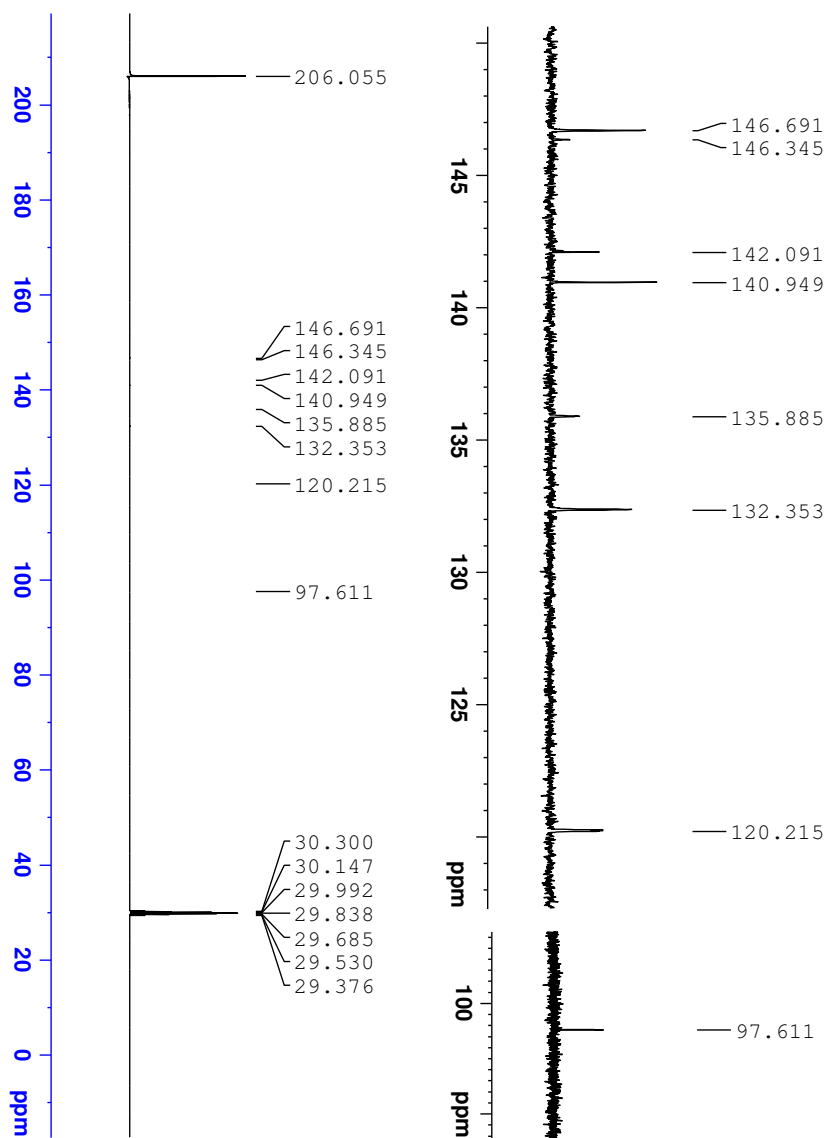


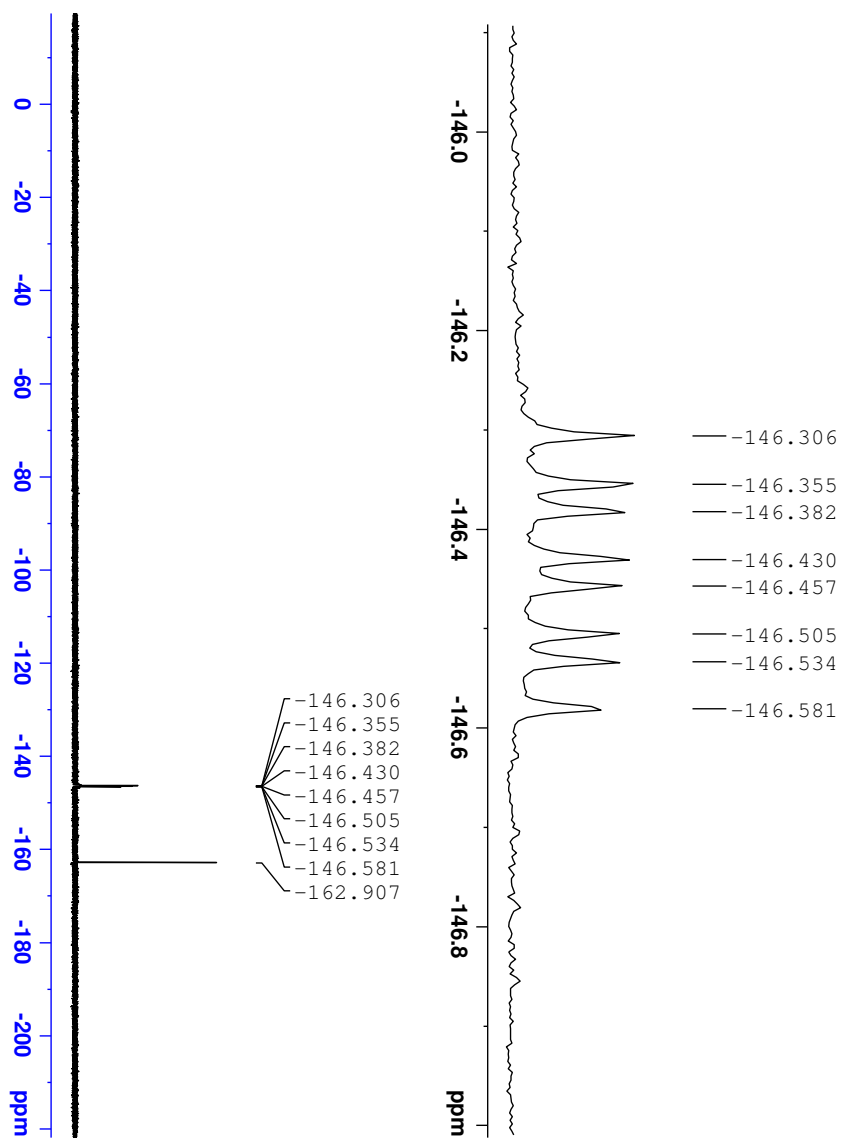
Figure S54. ^1H NMR spectrum of S5 in acetone- d_6 at 25 °C.



```

Current Data Parameters
EXNO          M-1-C-09-10
PROCNO        1
F2 - Acquisition Parameters
Date_         20240803
Time         4.29 h
INSTRUM      spect
PROBHD       Z119470_019
PULPROG      zgpg30
TD           65536
SI           Acq8192
SF           125.750243 MHz
DS           4
SOLVENT      acetone-d6
NS           256
DSB          29961.904 Hz
AQ           1.4010048 sec
RG           190.444
DM           16.800 usec
DE           4.420 usec
TE           307.8 K
D11          2.0000000 sec
D12          0.0300000 sec
D13          307.8 K
SF01         125.750243 MHz
NUC01        13C
F1A1         93.8130034 MHz
SF02         500.0520002 MHz
NUC02        1H
N1A1         1H
PCPD2/G2    waltz16
P1M12       25.79400063 W
P1M13       0.55844000 W
F1M12       0.72591929 W
F1M13       0.72591929 W
F2 - Processing parameters
SI           242483 MHz
SF           125.737543 MHz
WDW          EM
SSB          0
GB           1.0 Hz
PC           1.40
  
```

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



```

Current Data Parameters
EXPNO      10
PROCNO     1
P2 - Acquisition Parameters
Date_      20240807
Time       12.27 h
INSTRUM    Avance
PULPROG    zgpg30
TD         131072
SOLVENT    CDCl3
DS         4
SWH        90909.094 Hz
FIDRES     1.387463 Hz
RG         0.72809101
DM         5.500 usec
DE         6.550 usec
D1         1.00000000 sec
D11        0.03000000 sec
TDO       376.460714 MHz
NUC1       19F
NUC2       17.60 usec
P1         15.69999881 M
PCPD2     400.131818 MHz
CPCPD2    waltz16
PCPD2     15.10000000 usec
PMT12     0.17904000 M
F2 - Processing parameters
SF         376.4988096 MHz
WDW        EM
SSB        0
GB         0.0 Hz
PC         1.00
  
```

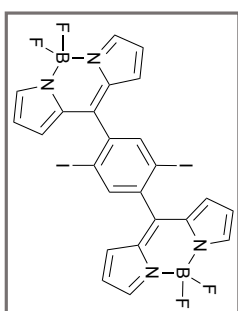


Figure S56. ^{19}F NMR spectrum of S5 in CDCl_3 at 25 °C.

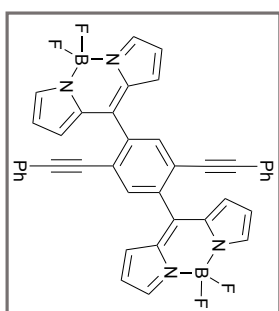
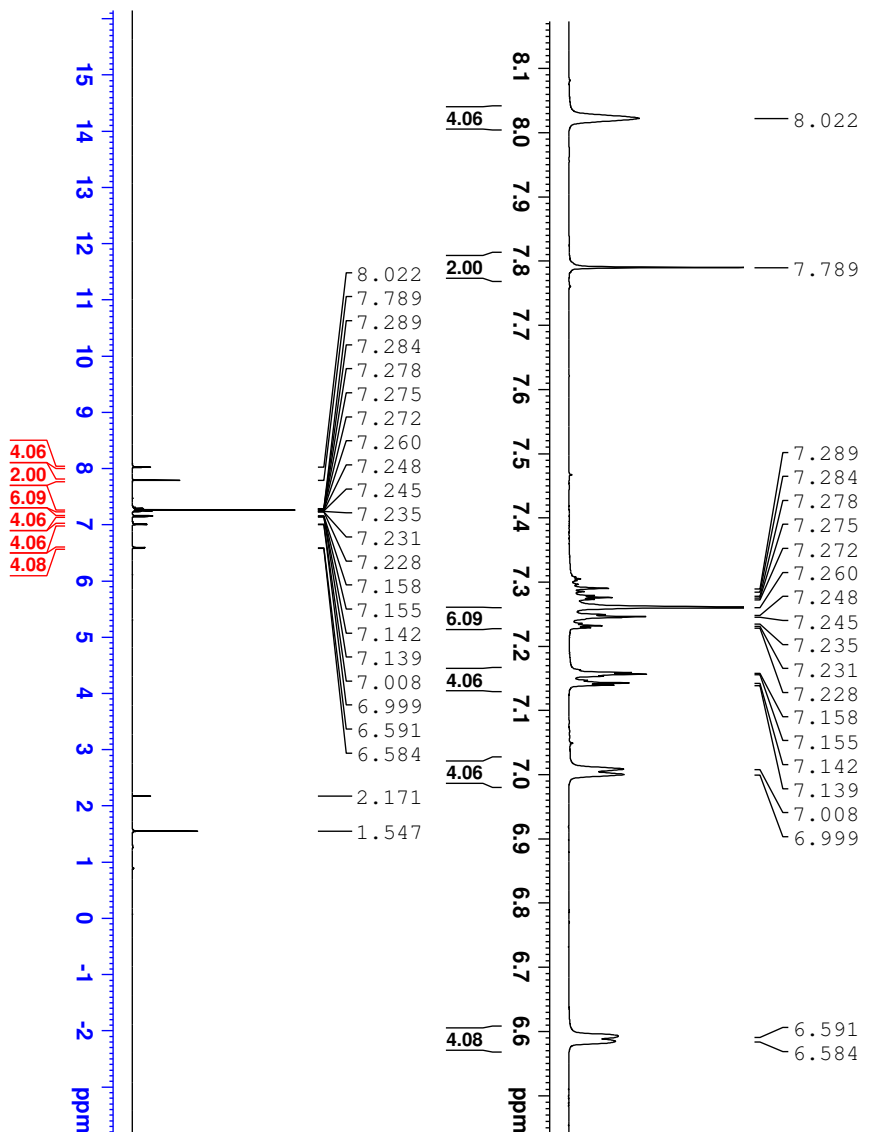


Figure S57. ¹H NMR spectrum of **3** in CDCl₃ at 25 °C.

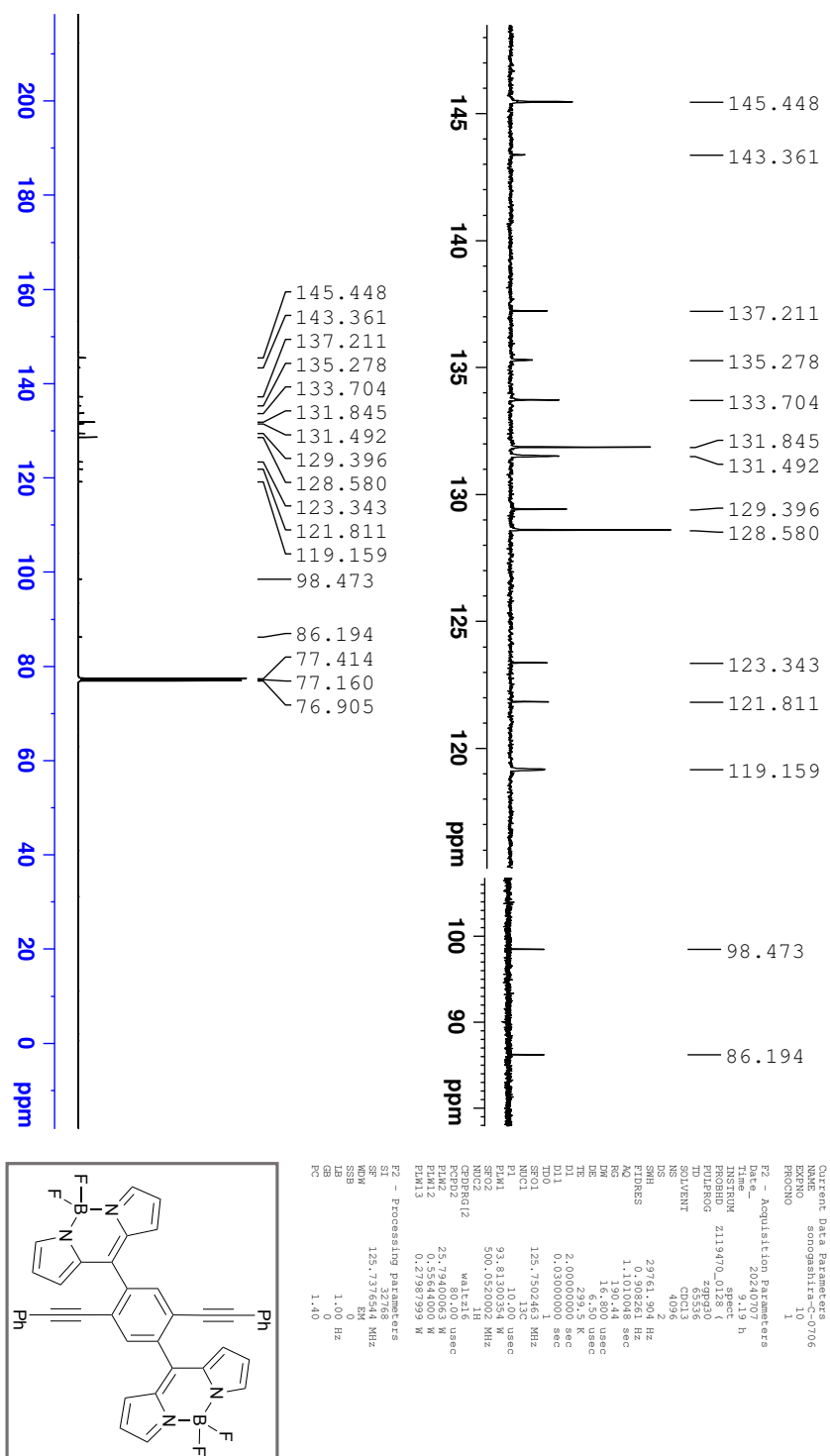


Figure S58. ^{13}C NMR spectrum of **3** in CDCl_3 at 25°C .

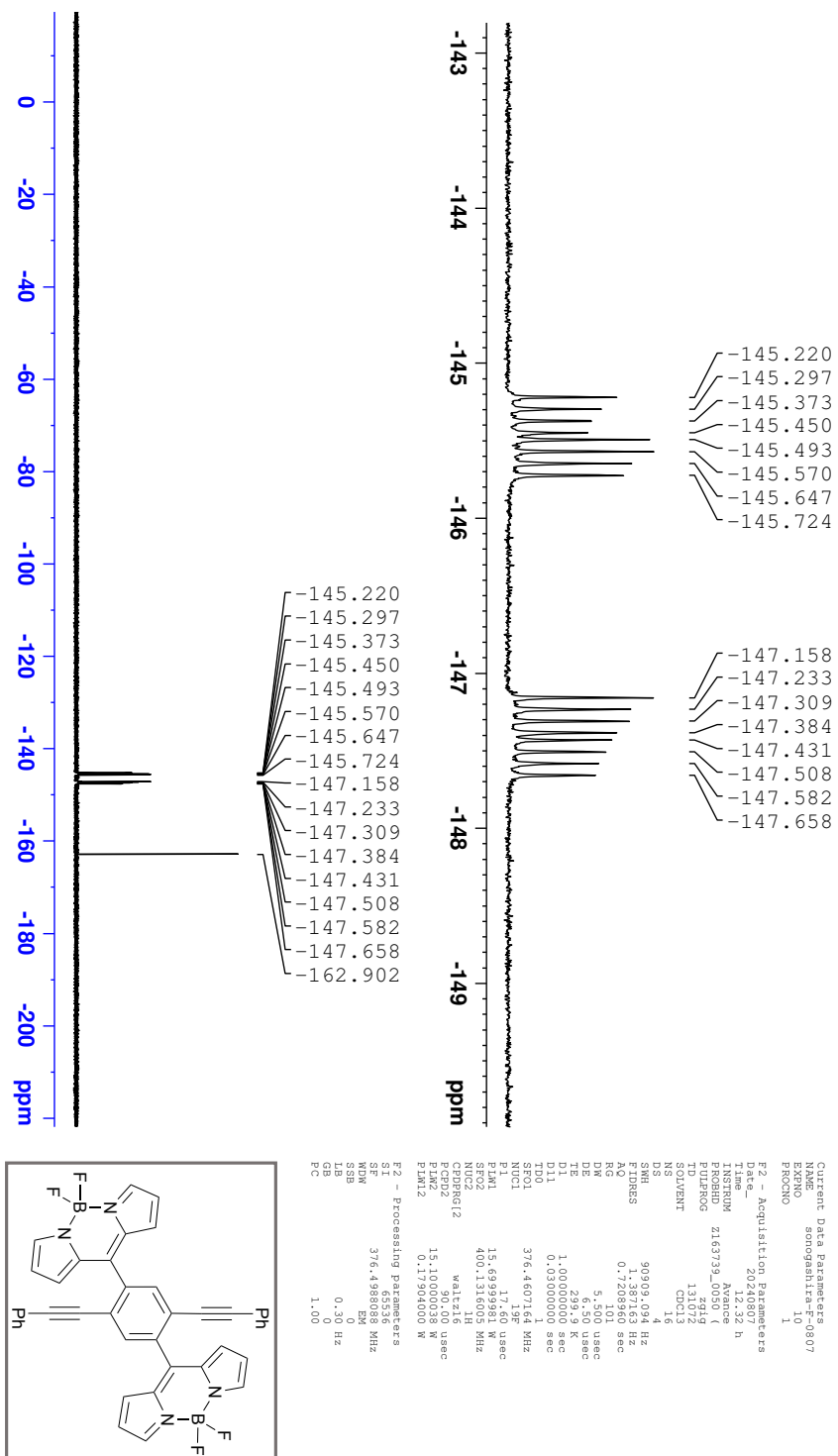
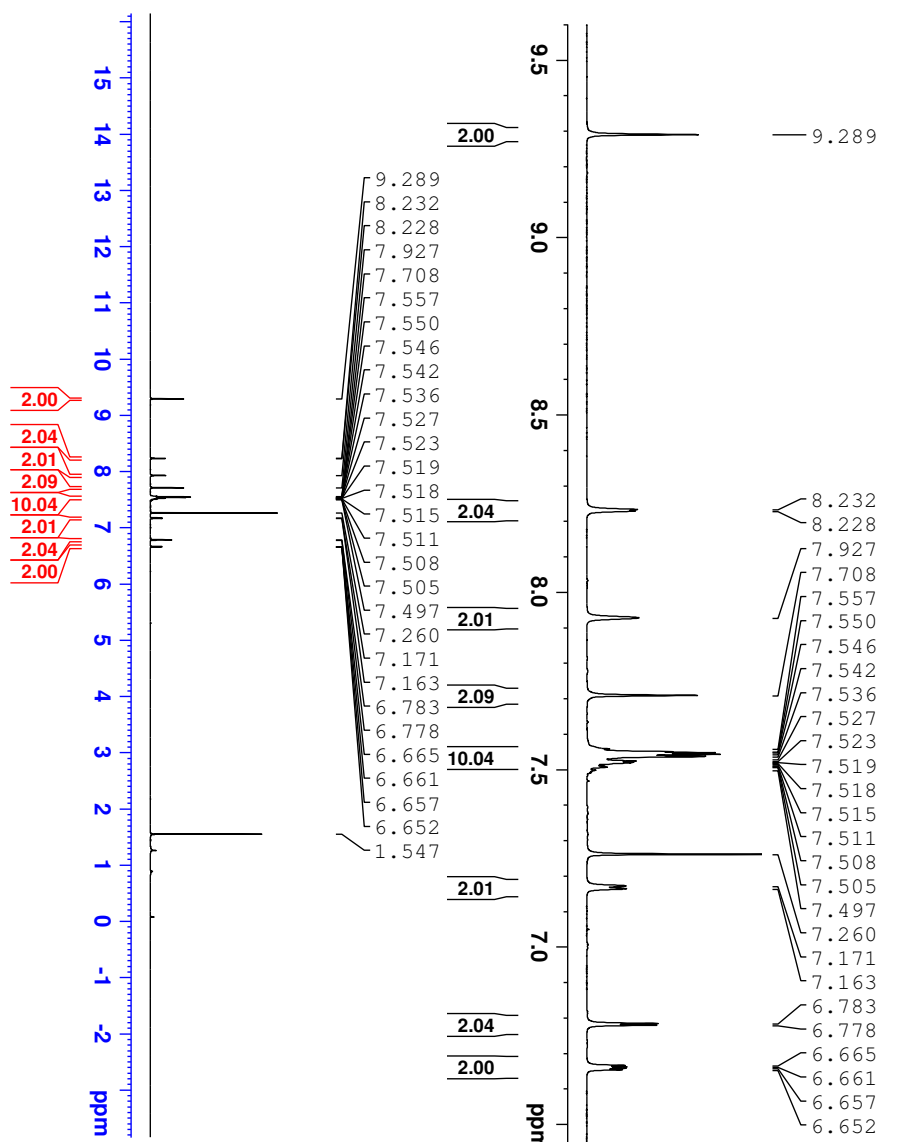


Figure S59. ^{19}F NMR spectrum of **3** in CDCl_3 at 25°C .



Current Data Parameters
 NAME BODIPY-w-Av-H-0709
 EXNO 10
 FPCNO 1

F2 - Acquisition Parameters
 Date_ 20240709
 Time_ 21.52 h
 INSTRUM spect
 PROBH1 219470_0128 (z930
 PULPROG zgpg30
 TD 65536
 N1 SOLVENT CDCl3
 N2 12
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.305176 Hz
 AQ 3.2767999 sec
 RG 190.44
 DM 50.000 usec
 DE 6.90 usec
 TE 300.2 K
 D1 1.000000 sec
 TD0 1
 SFO1 500.0530878 MHz
 NUOC1 1H
 P1 11.75 usec
 PLW1 25.79400063 W

F2 - Processing parameters
 SI 32768
 SF 500.0500120 MHz
 WDWW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

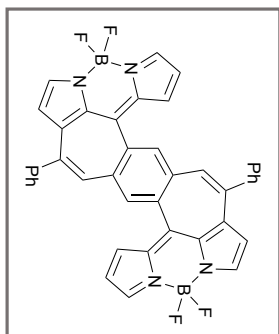
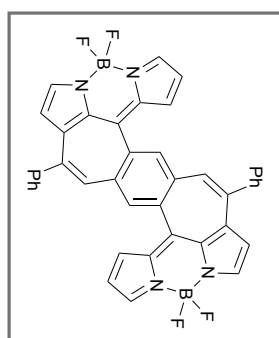
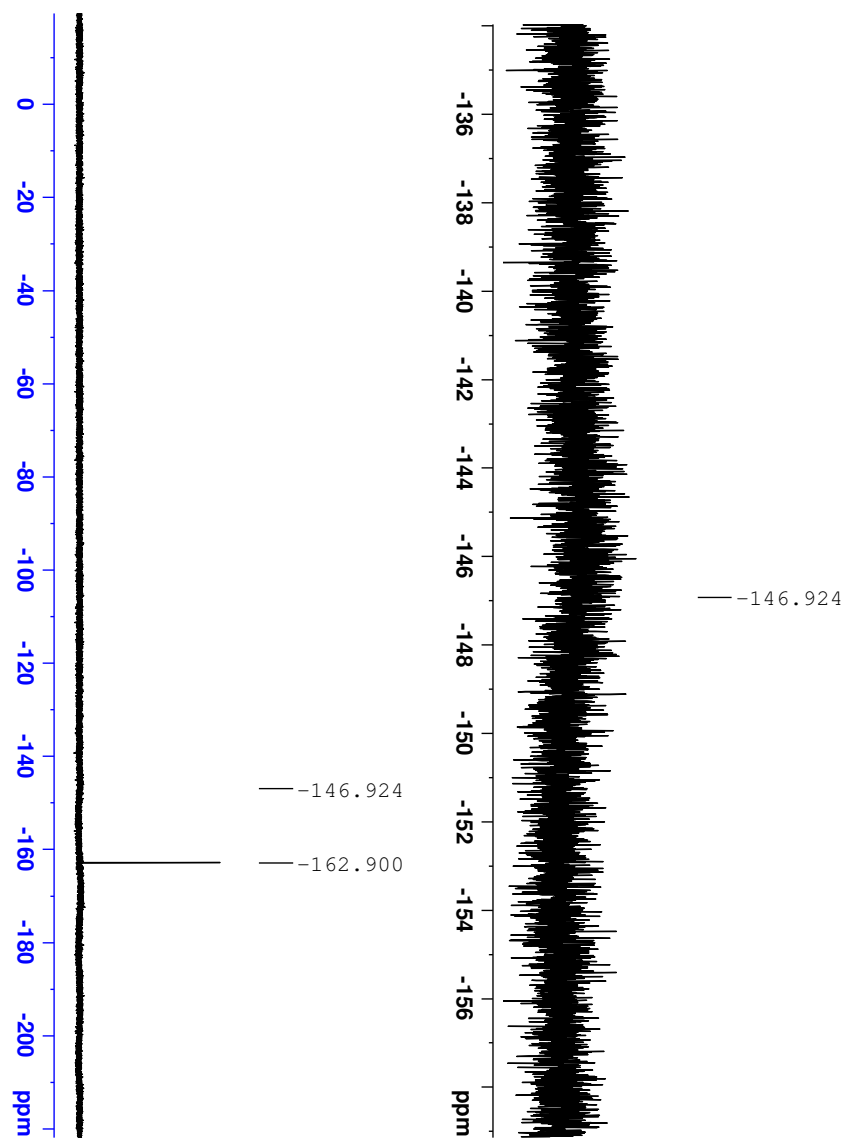


Figure S60. ^1H NMR spectrum of **4** in CDCl_3 at 25°C .



```

Current Data Parameters
EXPNO          1
PROCNO         1
Date_          20240807
Time_         12.37 h
INSTRUM       215739_Avance
PULPROG       zgpg30
TD            131672
SOLVENT       CDCl3
DS            4
SWH           90909.094 Hz
FIDRES       1.387463 Hz
RG            0.72809301
DM           5.500 usec
DE           3.50 usec
D1           1.00000000 sec
D11          0.03000000 sec
TD0          376.460714 MHz
NUC1         19F
NUC2          17.60 usec
P1           15.6999981 MHz
P2           400.1318018 MHz
PCPD2        waltz16
CPCPD2       90.00 usec
PMT12        0.17904000 W
F2 - Processing parameters
SE           376.4988076 MHz
WDW          EM
SSB          0 Hz
GB           0.0
PC           1.00

```

Figure S62. ¹⁹F NMR spectrum of **4** in CDCl₃ at 25 °C.

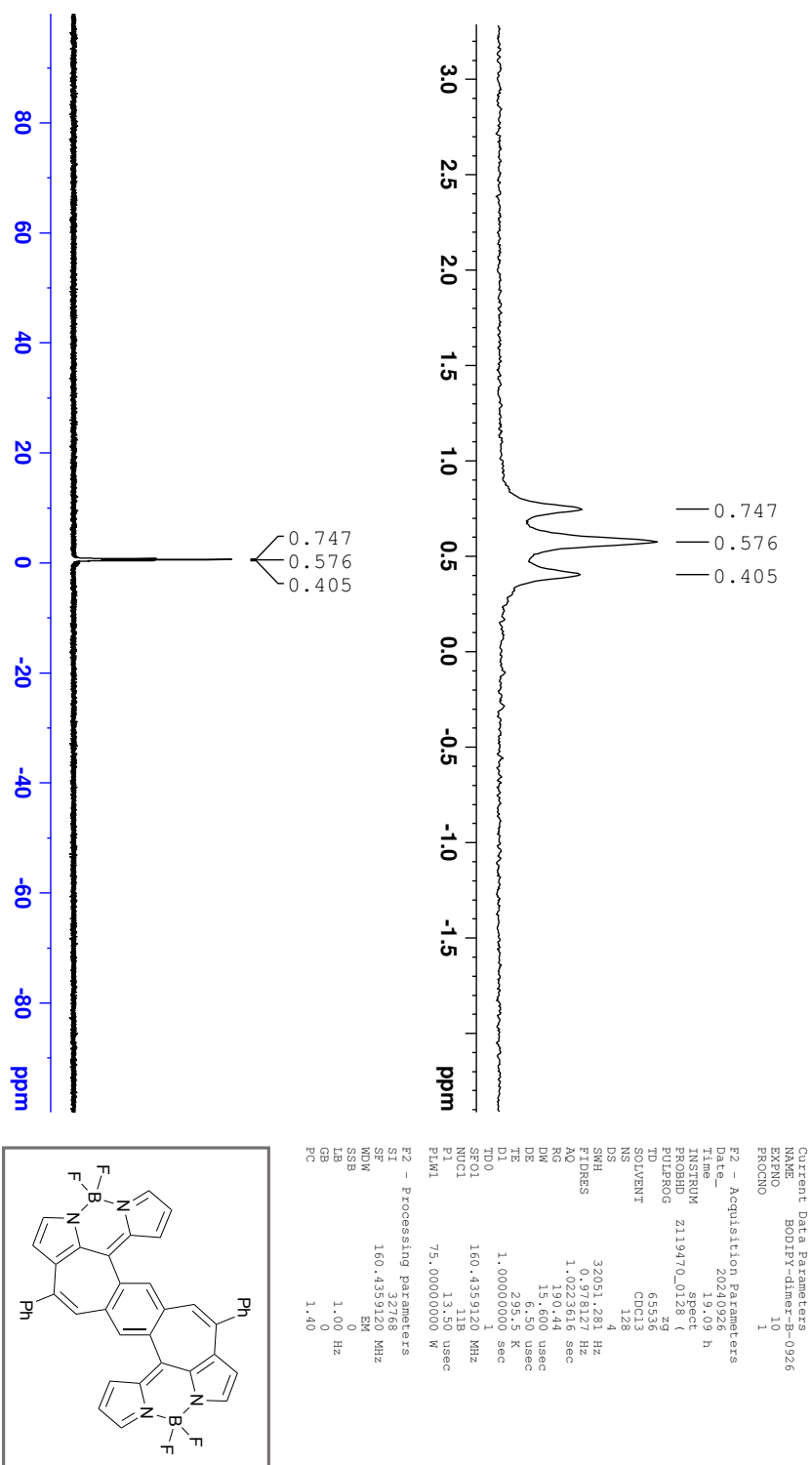


Figure S63 ^{11}B NMR spectrum of **4** in CDCl_3 at 25 °C.

4. Mass spectra

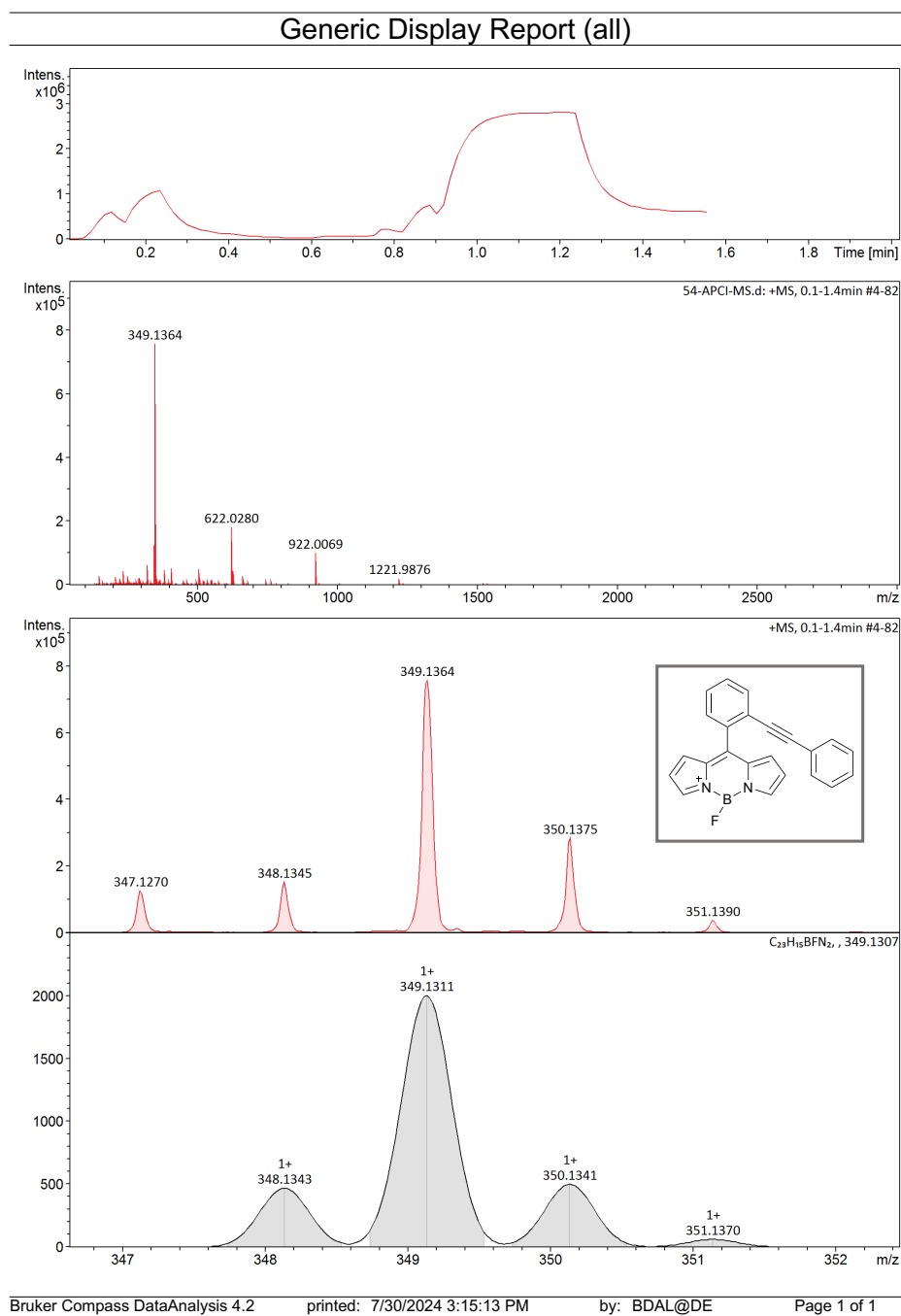


Figure S64. APCI-TOF mass spectrum of **1a**.

Generic Display Report (all)

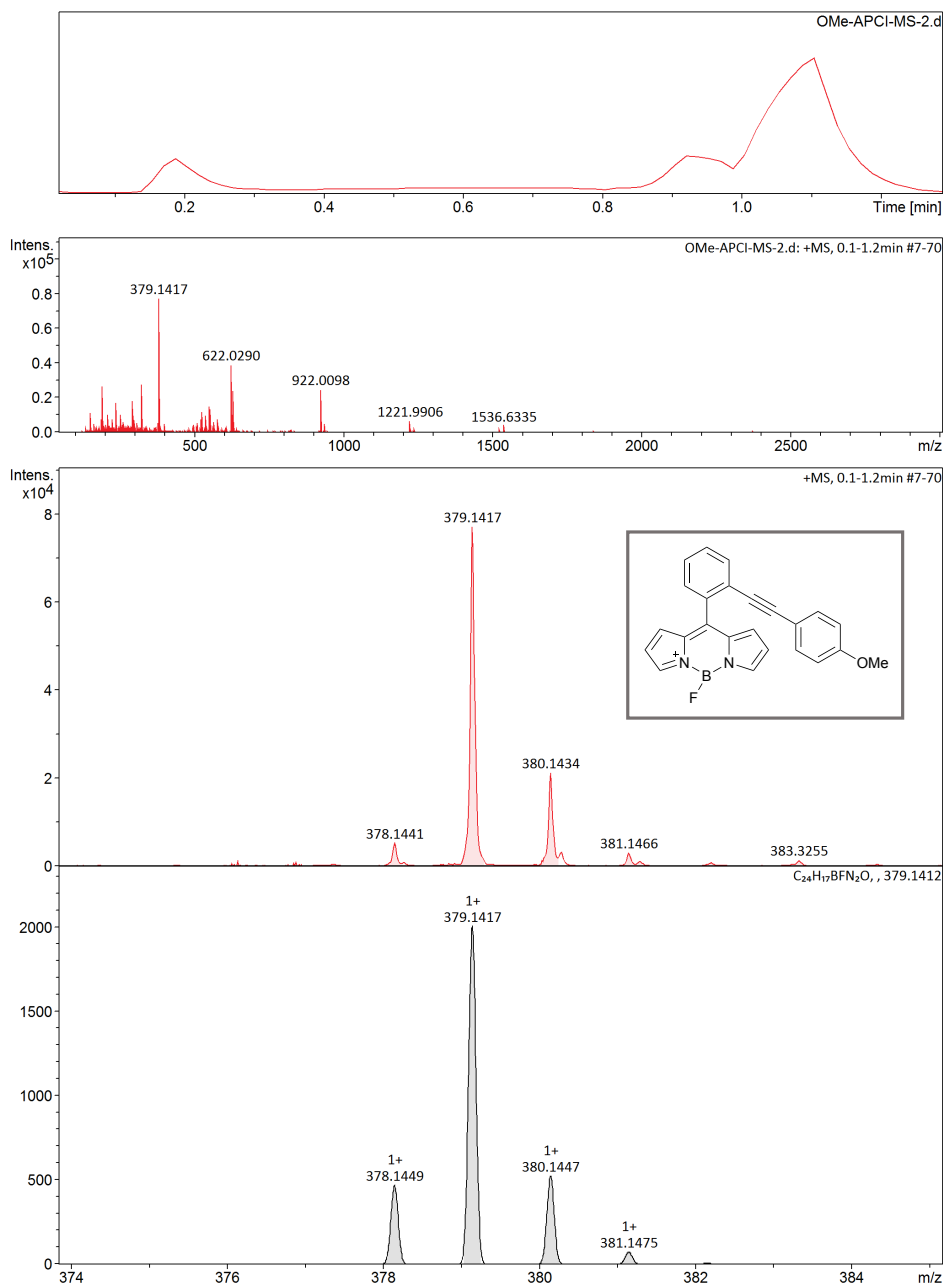
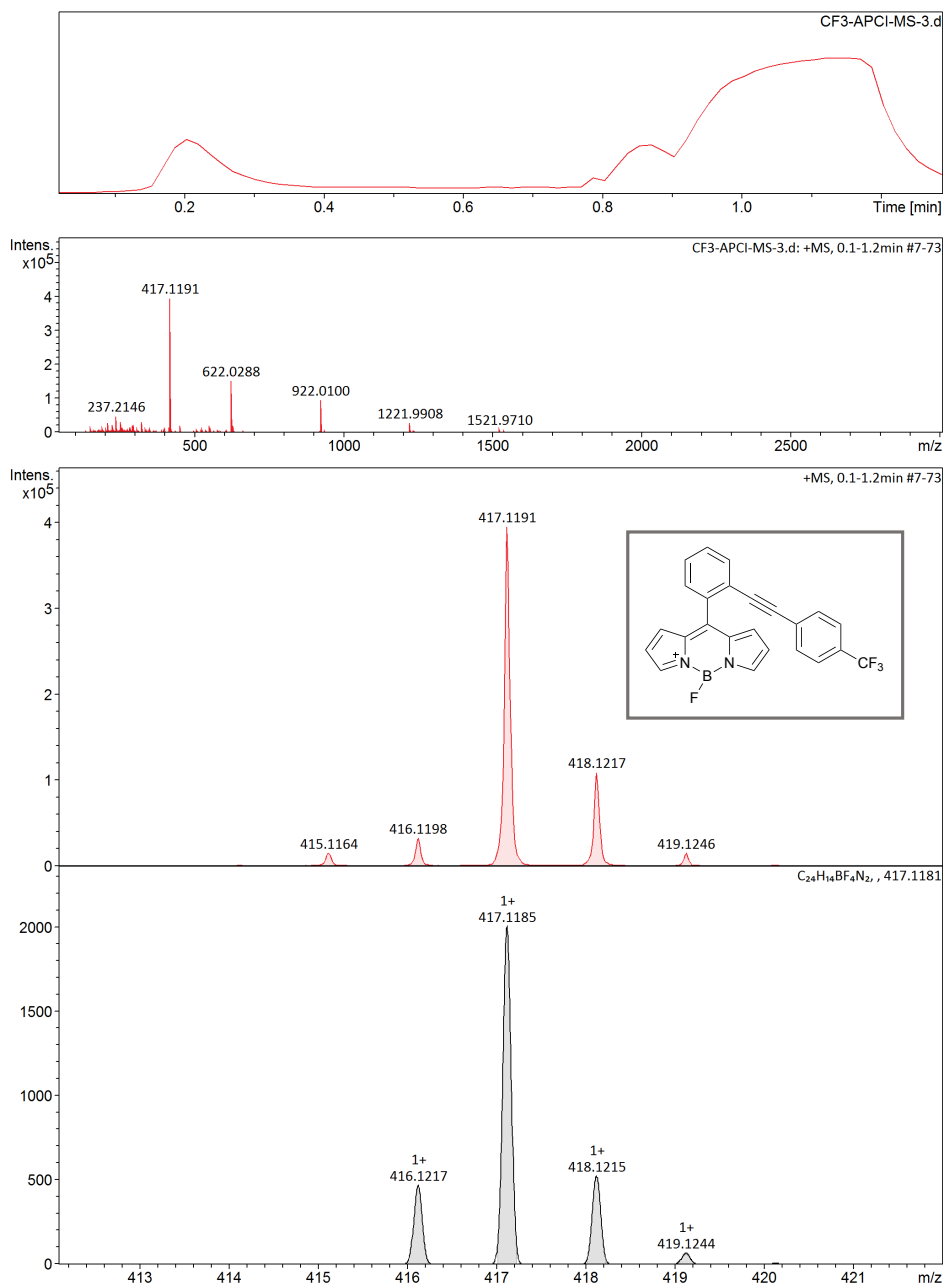


Figure S65. APCI-TOF mass spectrum of **1b**.

Generic Display Report (all)



Bruker Compass DataAnalysis 4.2

printed: 7/18/2024 12:54:24 PM

by: BDAL@DE

Page 1 of 1

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

Generic Display Report (all)

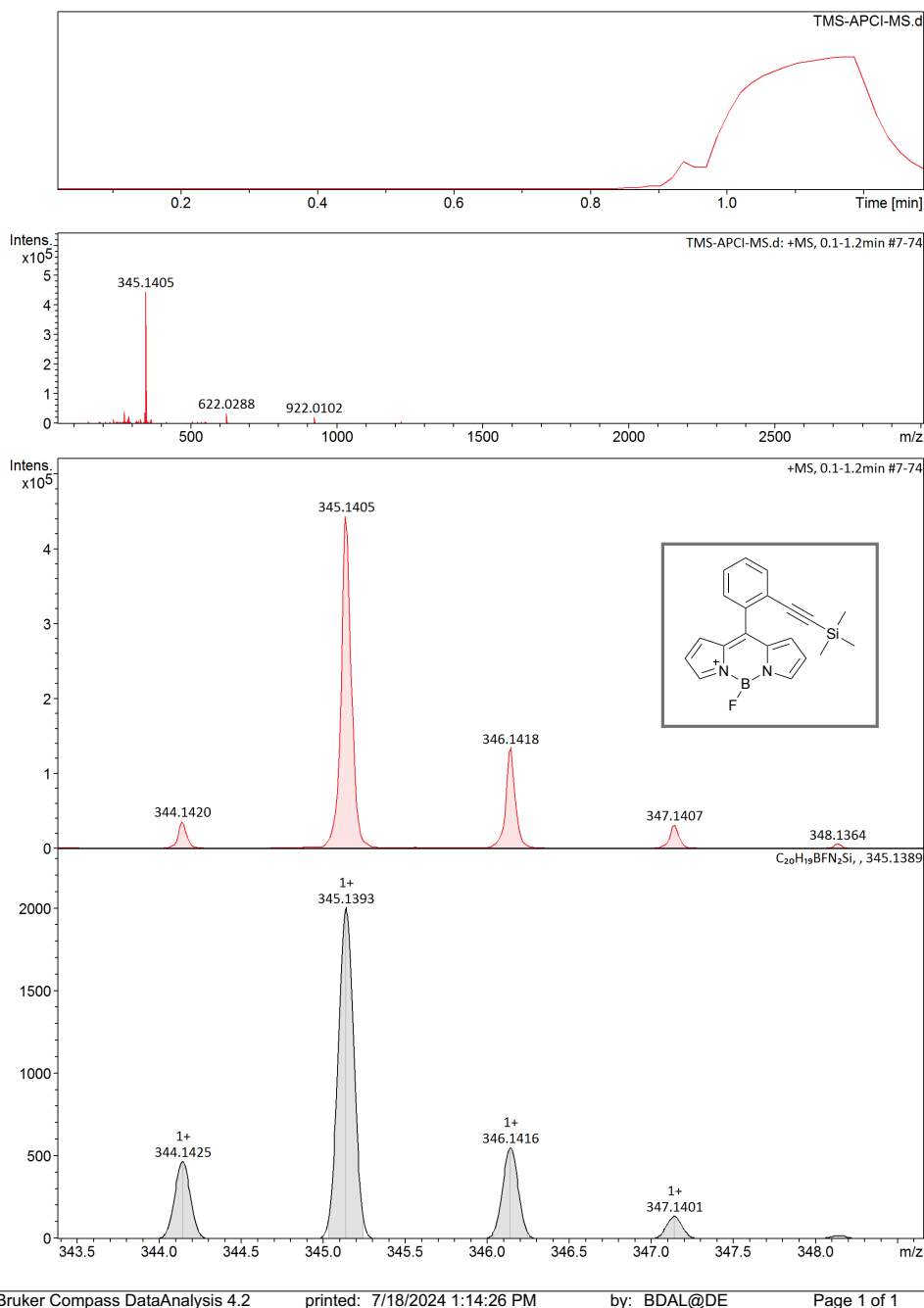


Figure S67. APCI-TOF mass spectrum of S1.

Generic Display Report (all)

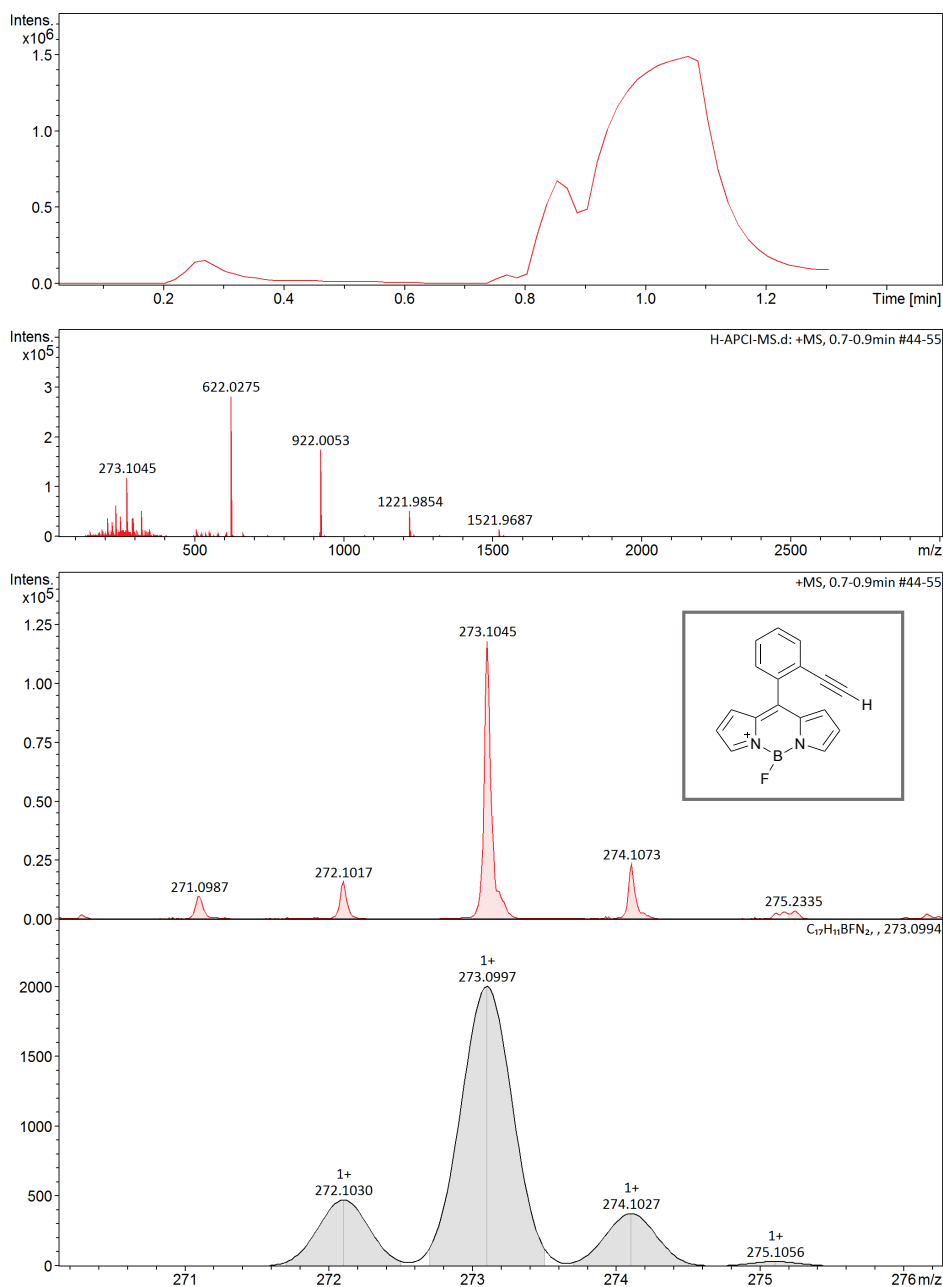


Figure S68. APCI-TOF mass spectrum of **1d**.

Generic Display Report (all)

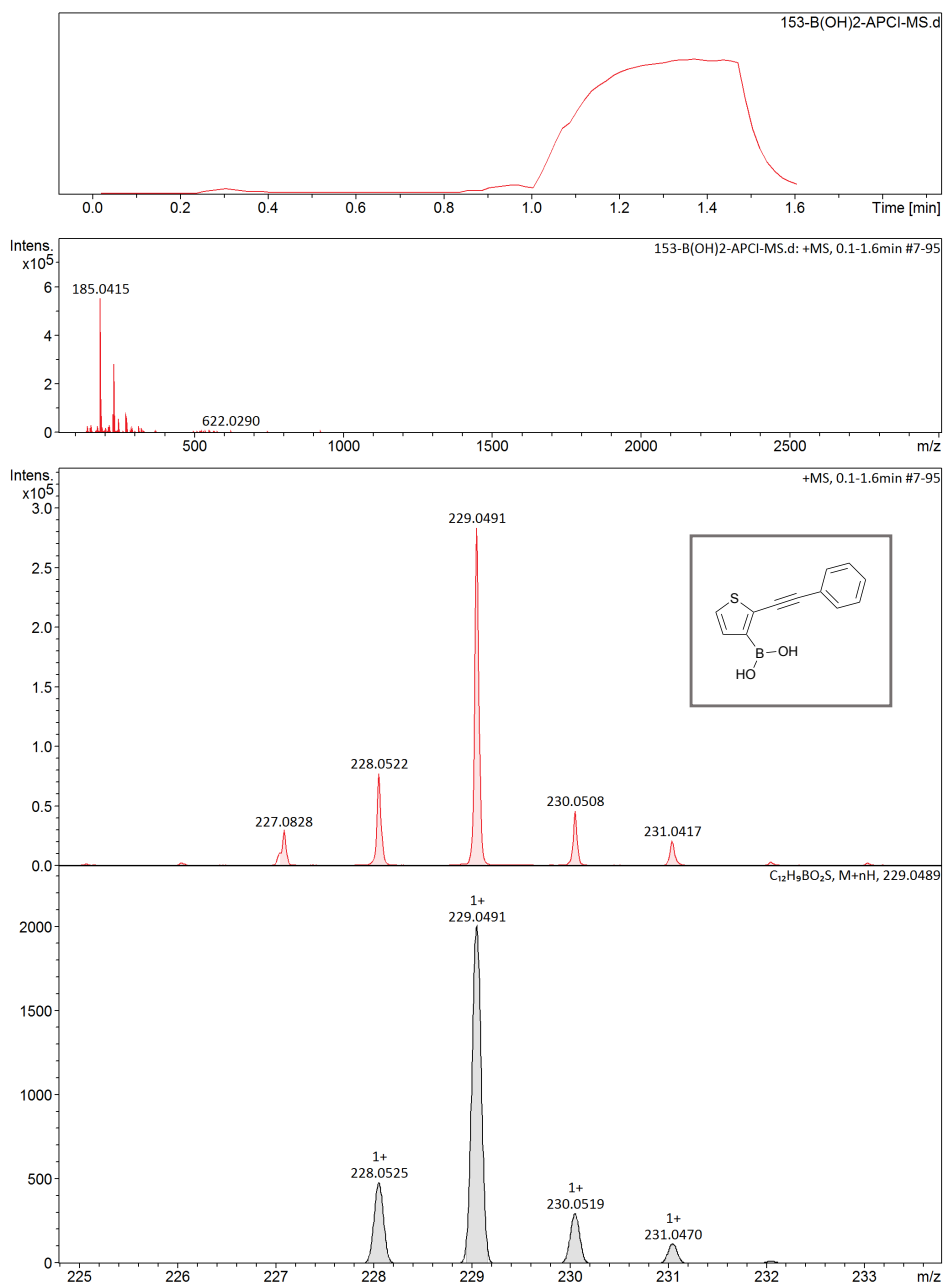


Figure S69. APCI-TOF mass spectrum of S2.

Generic Display Report (all)

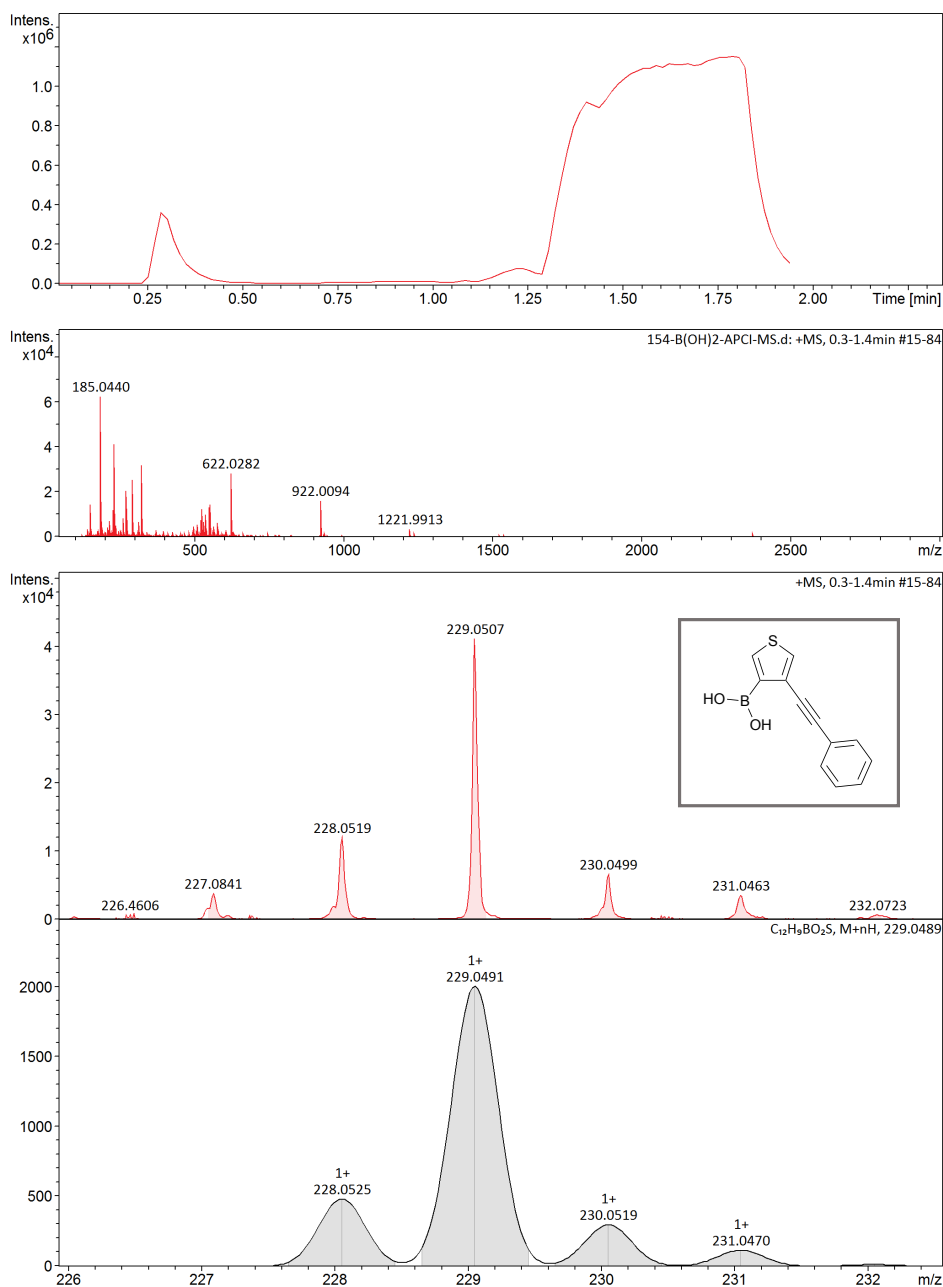


Figure S70. APCI-TOF mass spectrum of S3.

Generic Display Report (all)

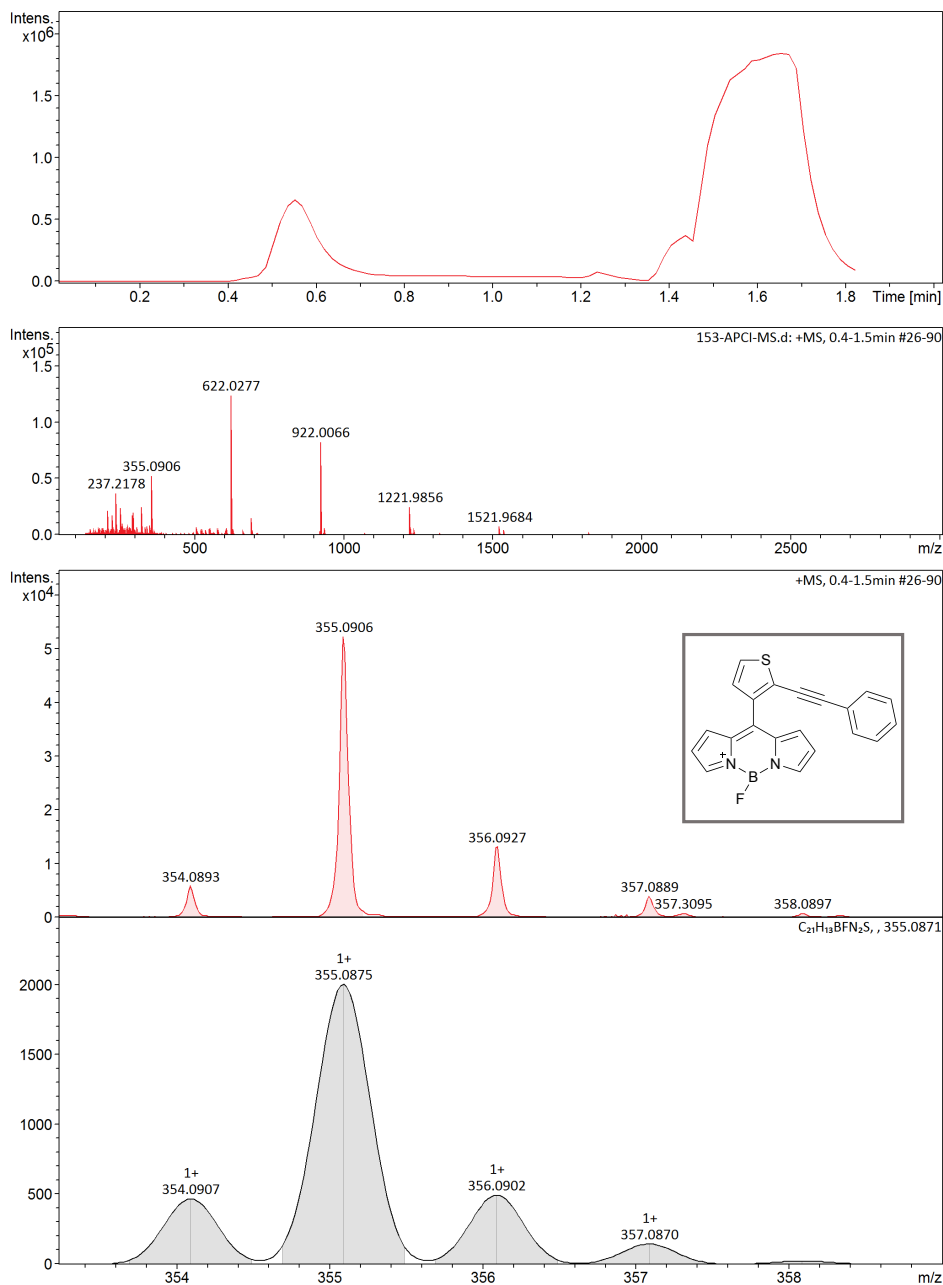
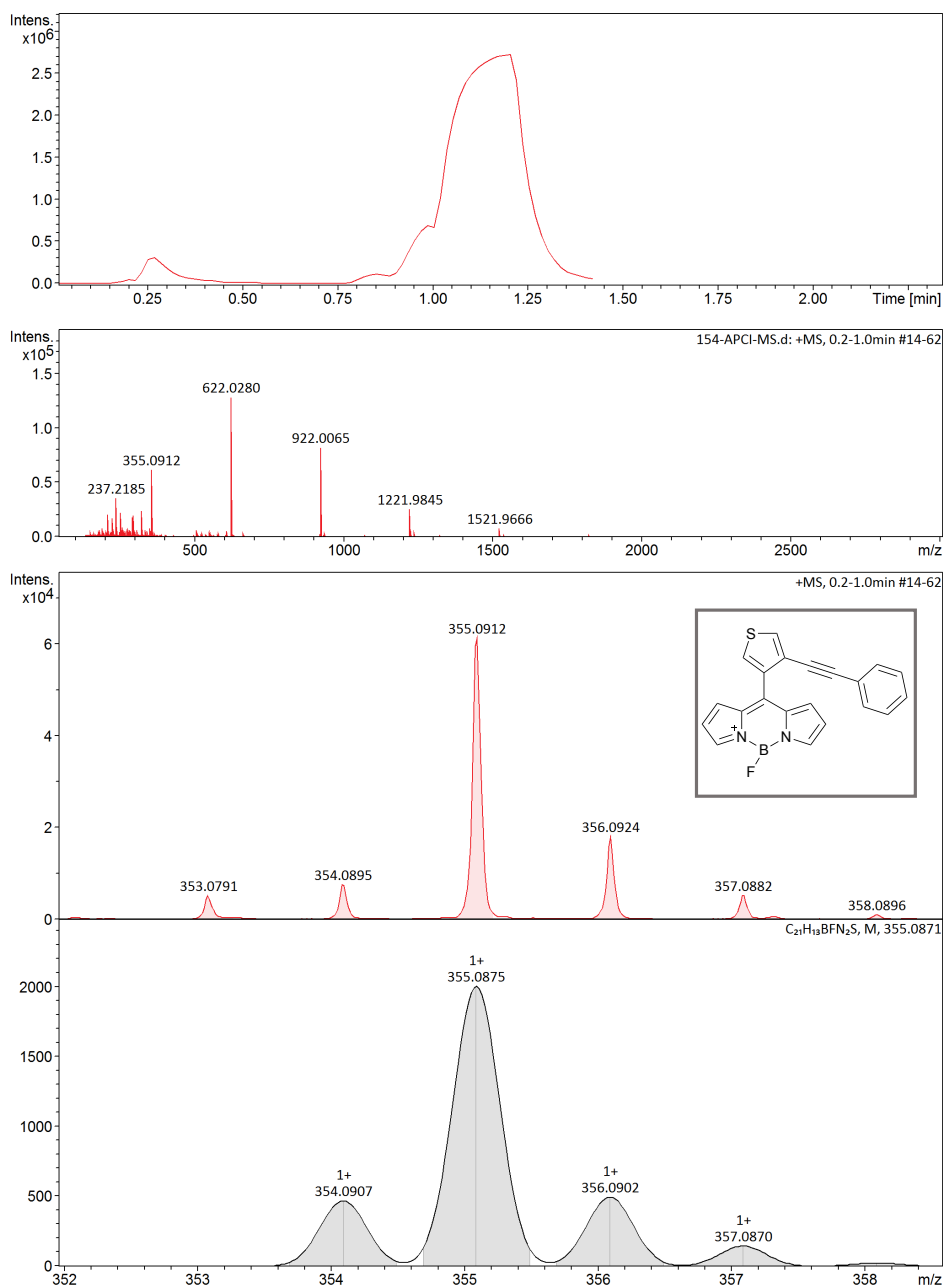


Figure S71 APCI-TOF mass spectrum of 1e.

Generic Display Report (all)



Bruker Compass DataAnalysis 4.2

printed: 7/30/2024 4:05:32 PM

by: BDAL@DE

Page 1 of 1

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

Generic Display Report (all)

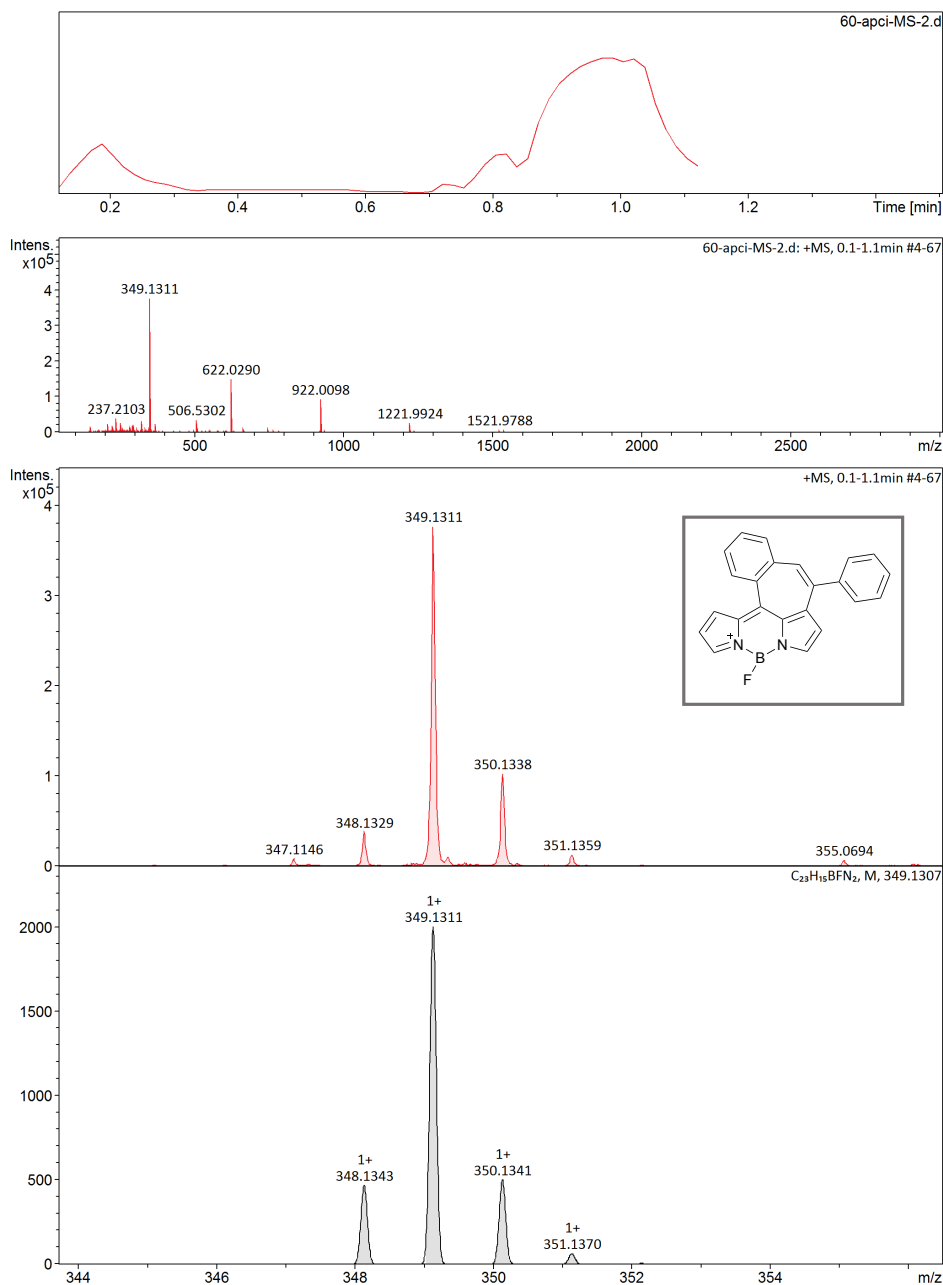


Figure S73. APCI-TOF mass spectrum of **2a**.

Generic Display Report (all)

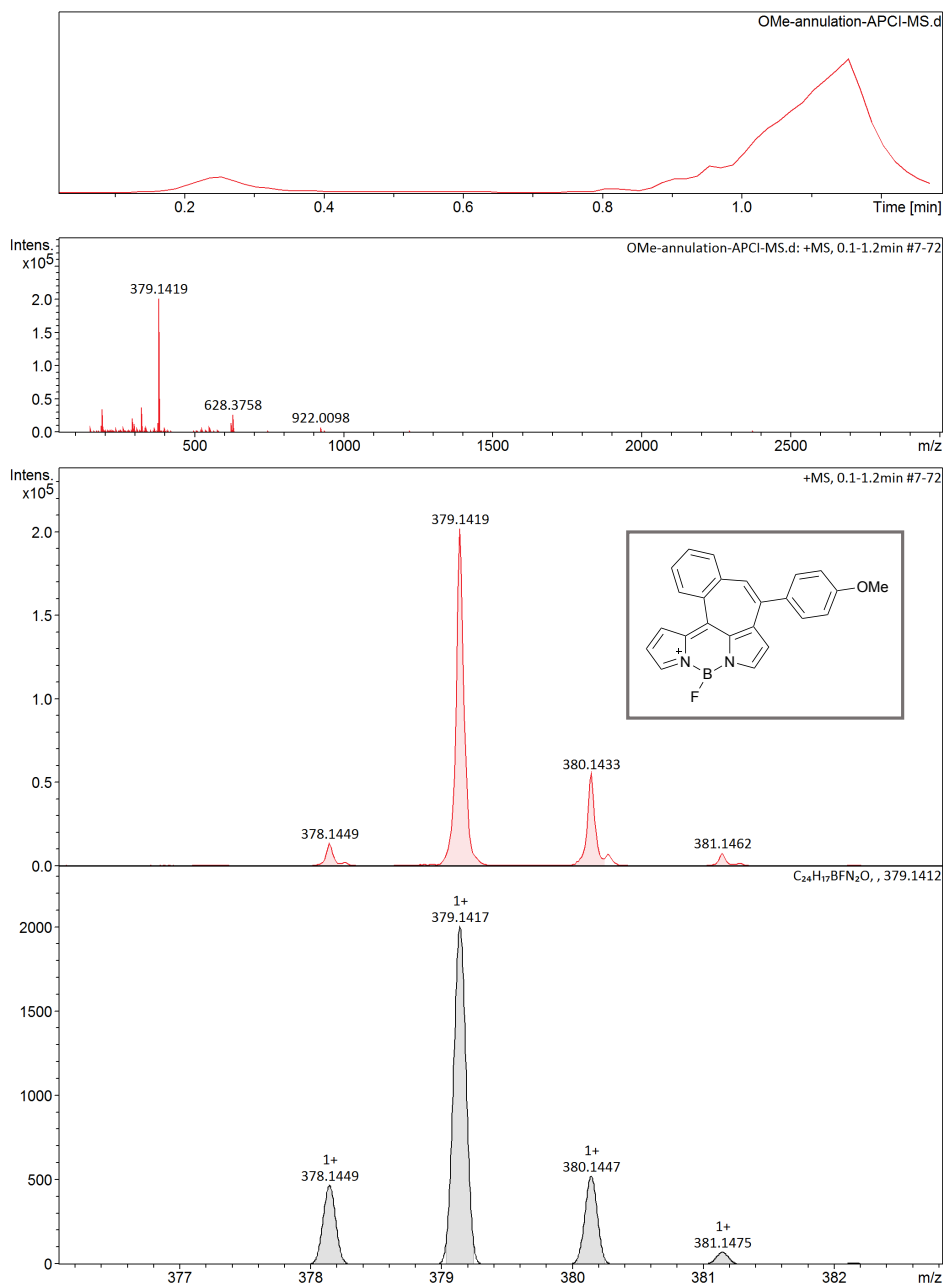


Figure S74. APCI-TOF mass spectrum of **2b**.

Generic Display Report (all)

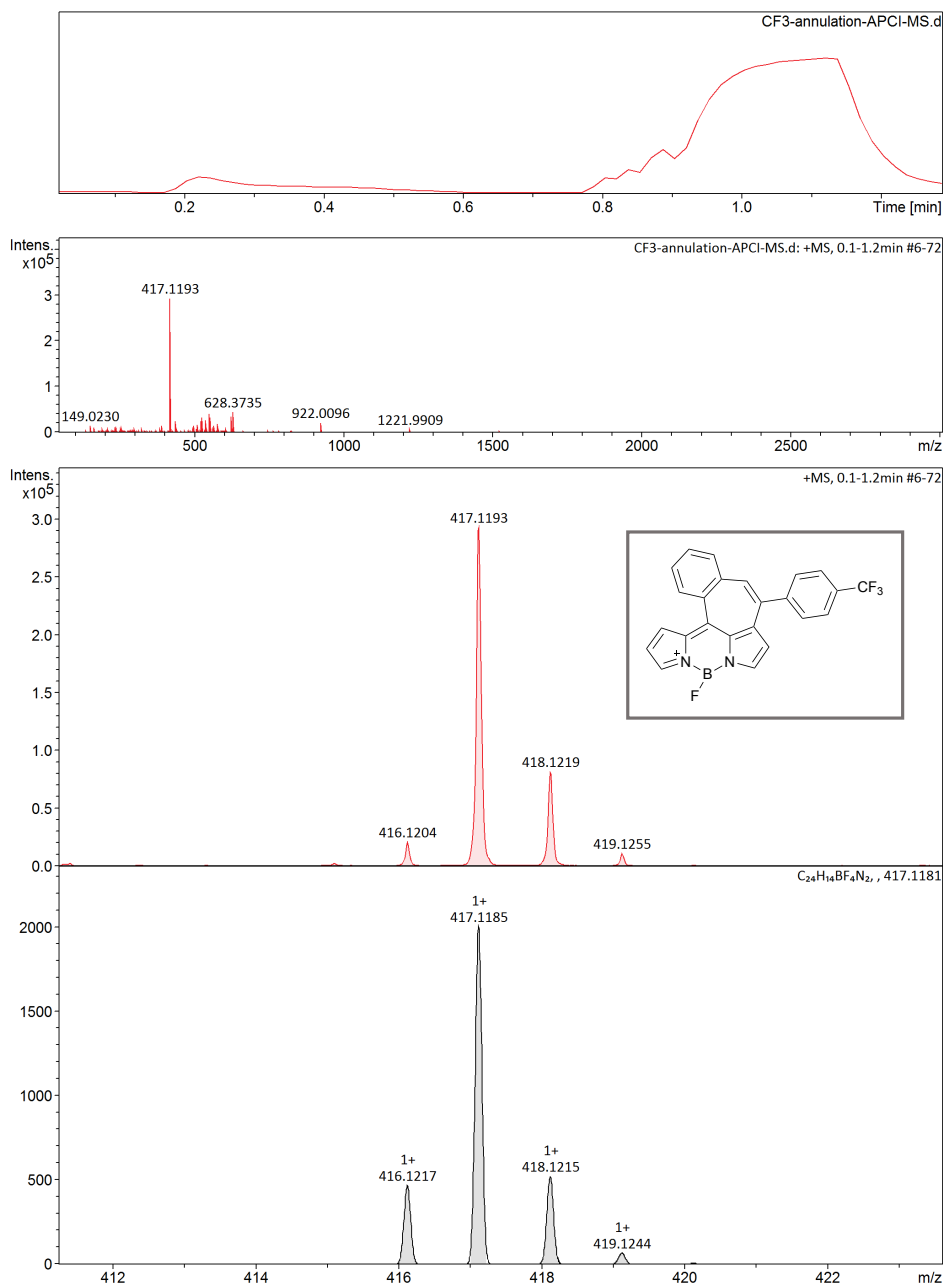


Figure S75. APCI-TOF mass spectrum of **2c**.

Generic Display Report (all)

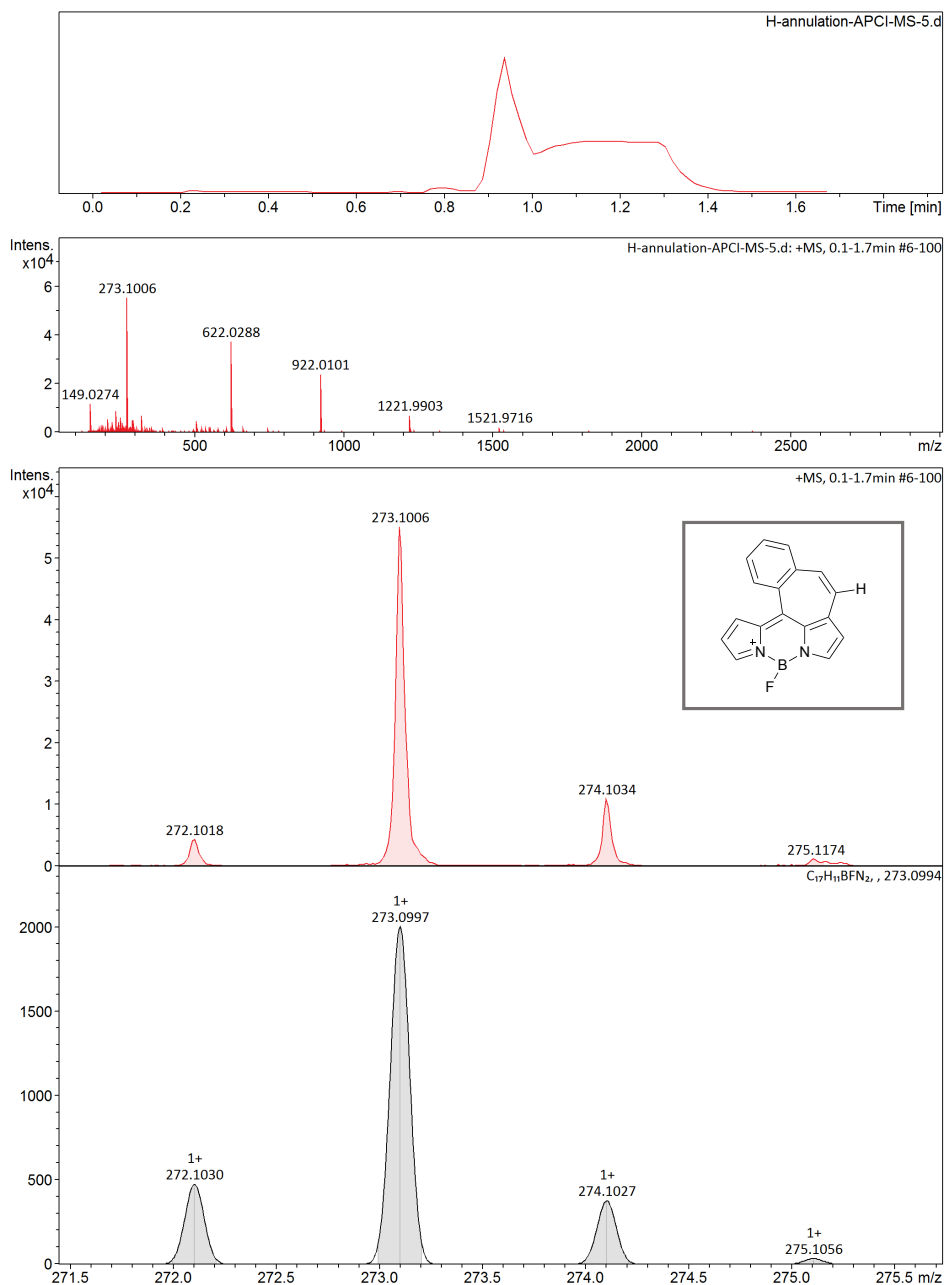
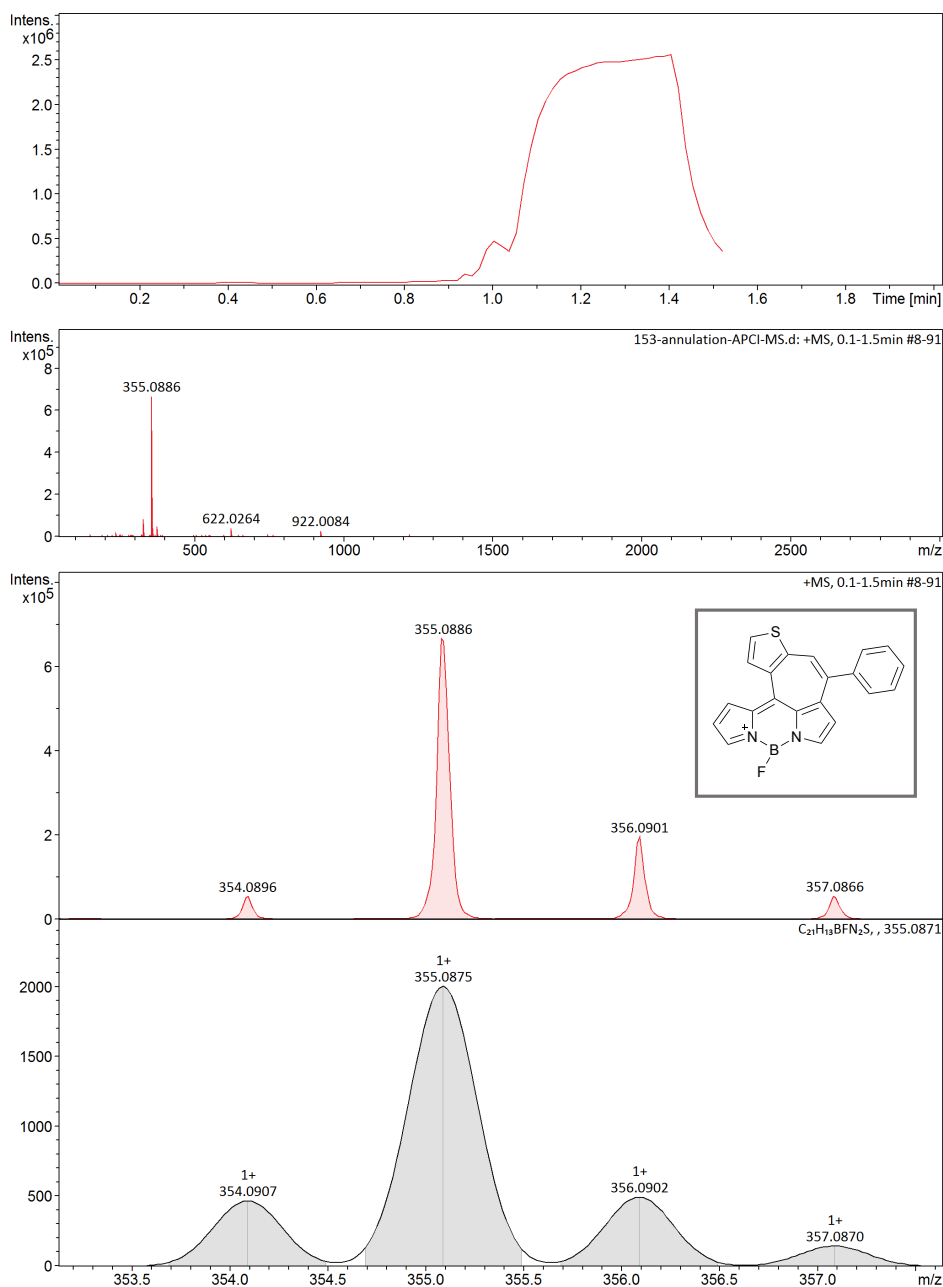


Figure S76. APCI-TOF mass spectrum of **2d**.

Generic Display Report (all)



Bruker Compass DataAnalysis 4.2

printed: 7/30/2024 3:35:06 PM

by: BDAL@DE

Page 1 of 1

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

Generic Display Report (all)

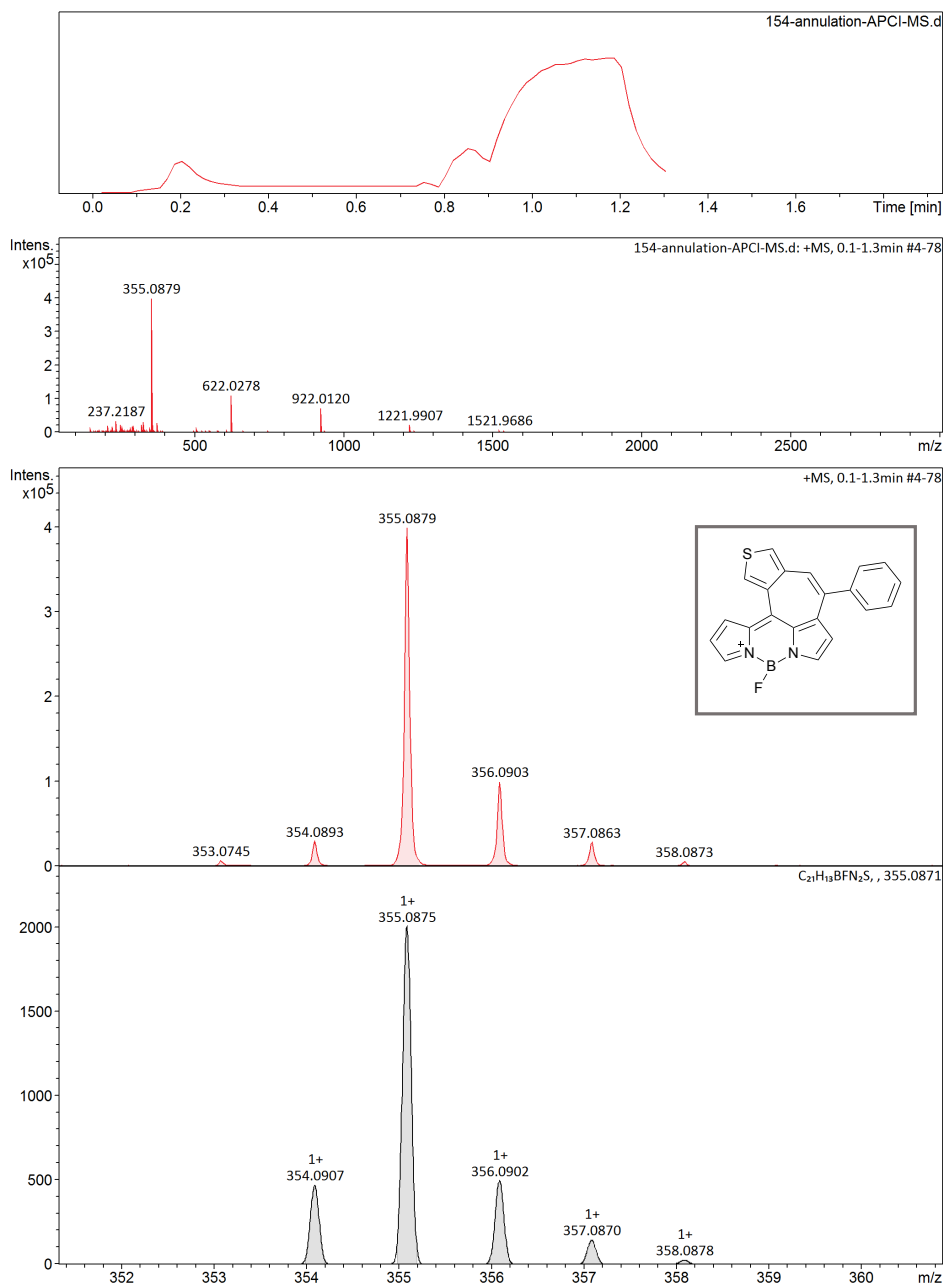
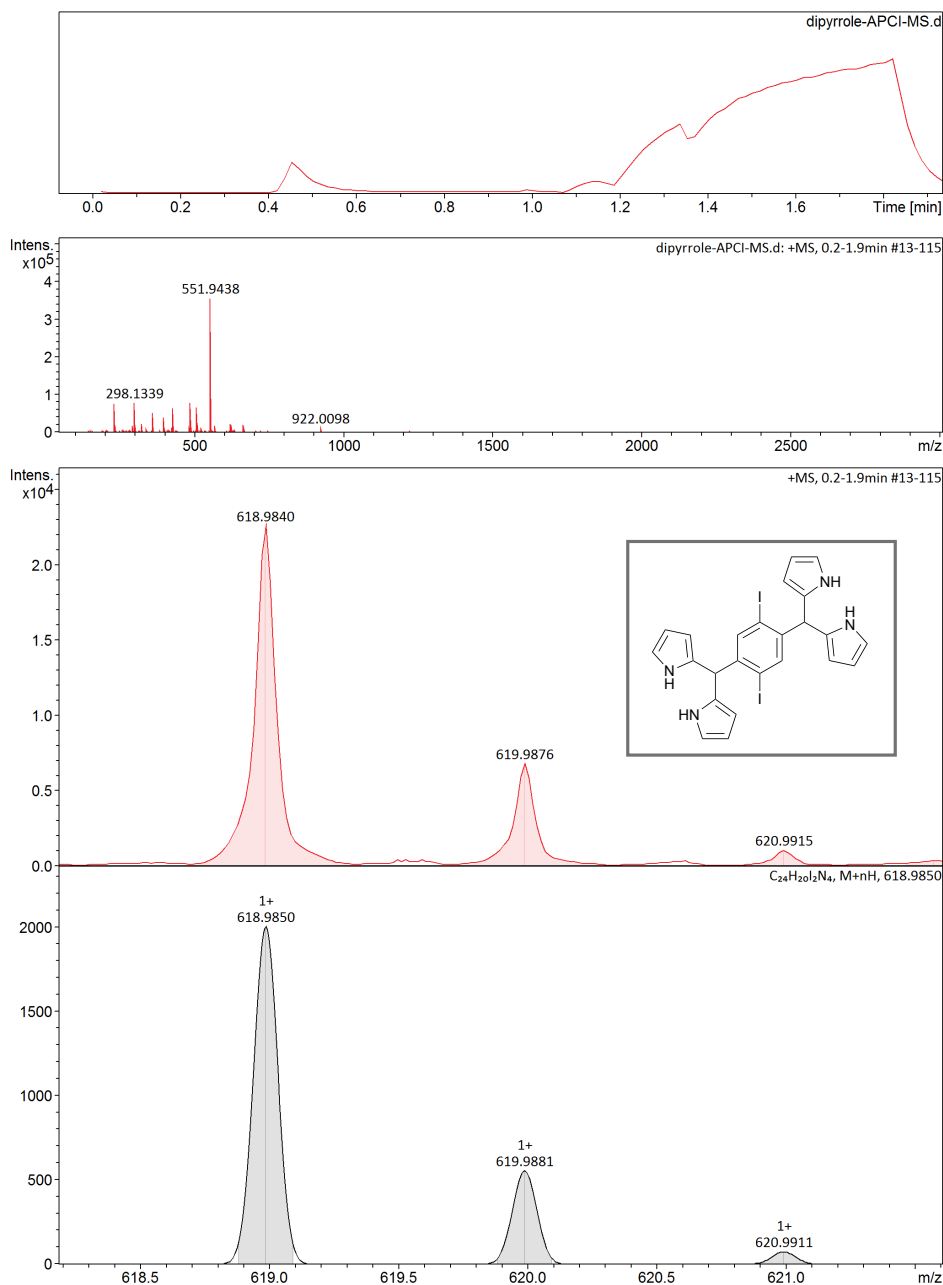


Figure S78. APCI-TOF mass spectrum of **2f**.

Generic Display Report (all)



Bruker Compass DataAnalysis 4.2

printed: 7/18/2024 3:16:24 PM

by: BDAL@DE

Page 1 of 1

Figure S79. APCI-TOF mass spectrum of S4.

Generic Display Report (all)

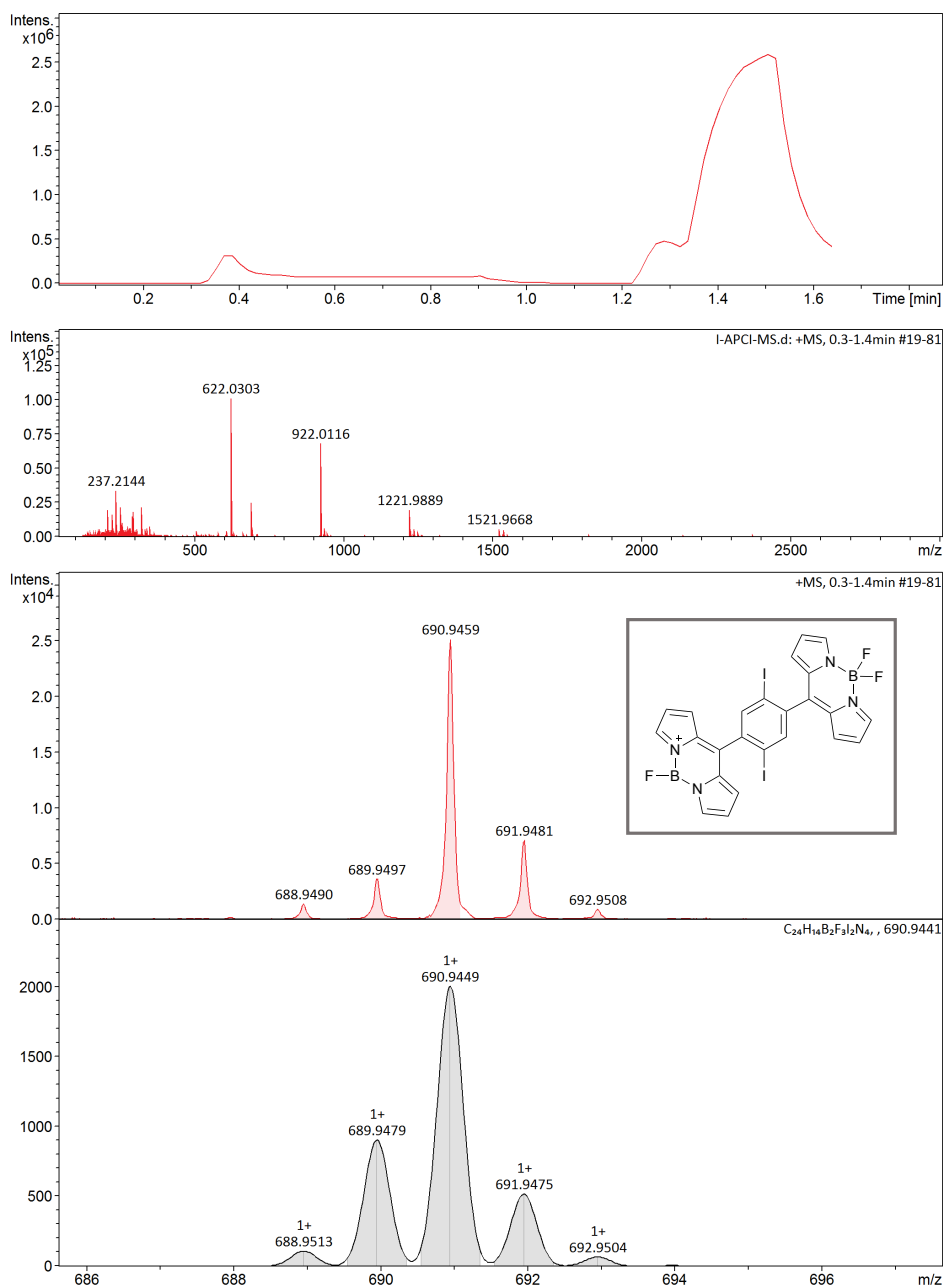


Figure S80. APCI-TOF mass spectrum of S5.

Generic Display Report (all)

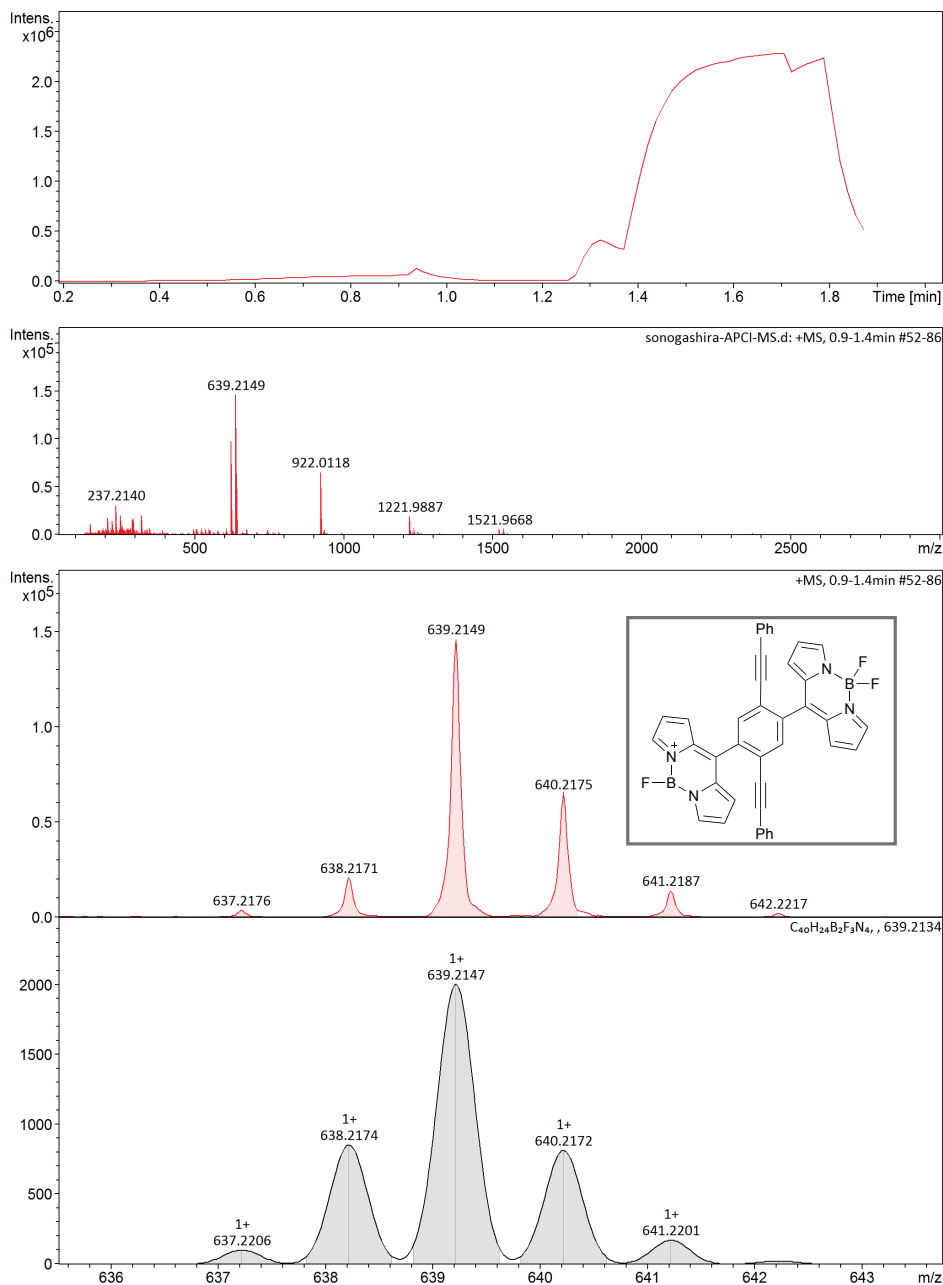


Figure S81. APCI-TOF mass spectrum of 3.

Generic Display Report (all)

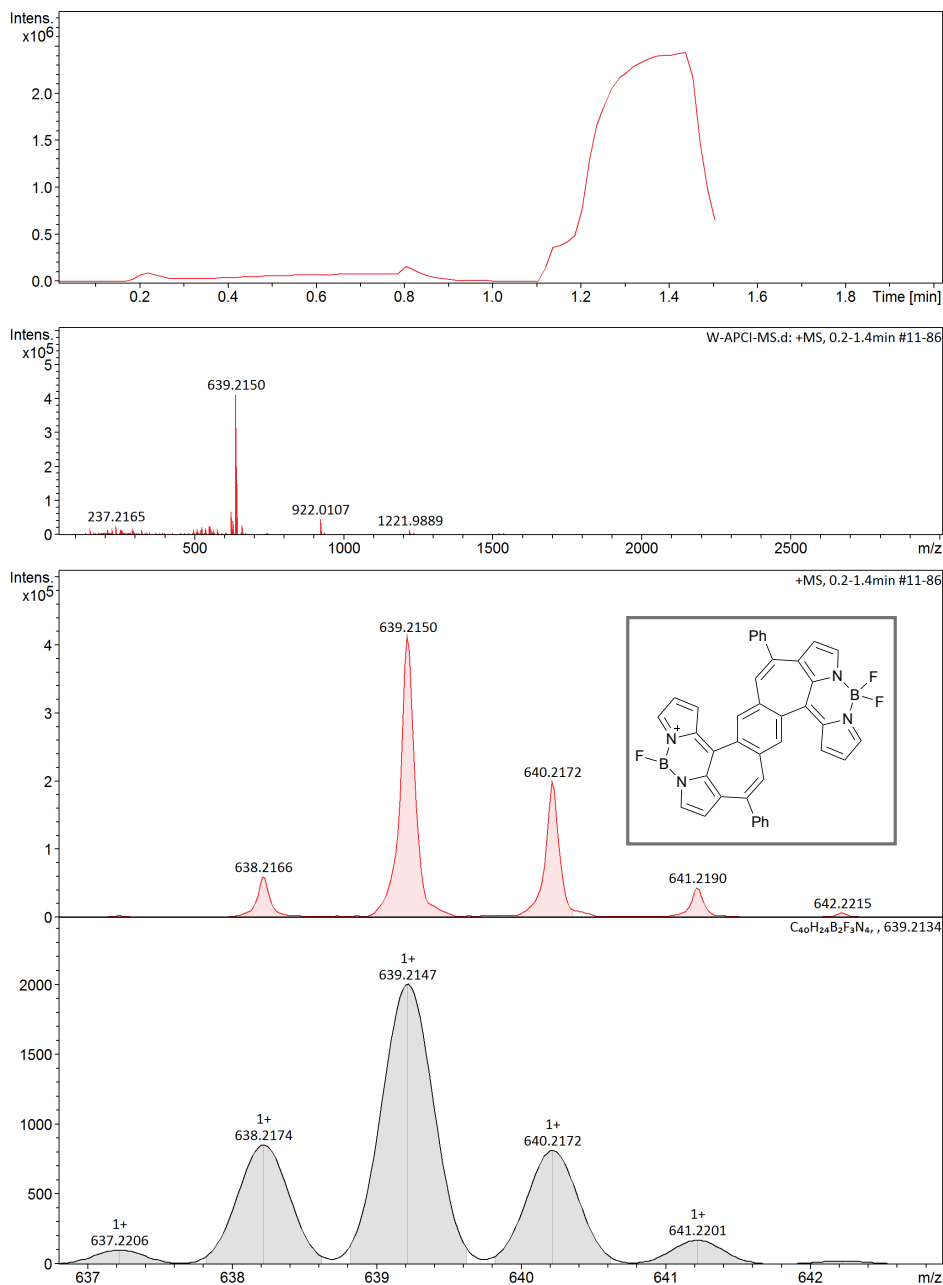


Figure S82. APCI-TOF mass spectrum of **4**.

Generic Display Report (all)

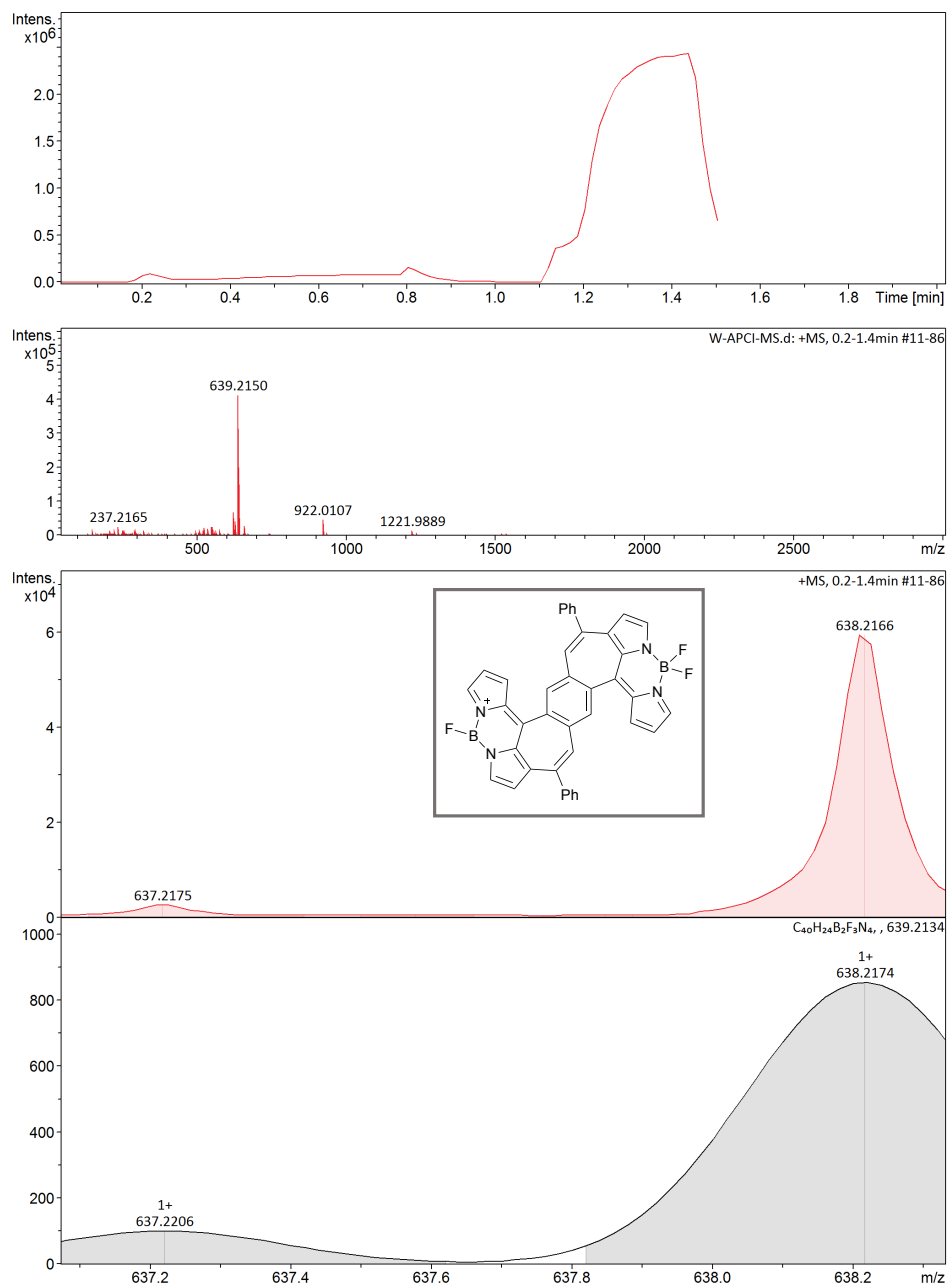


Figure S83. APCI-TOF mass spectrum of **4** (enlarged).

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.

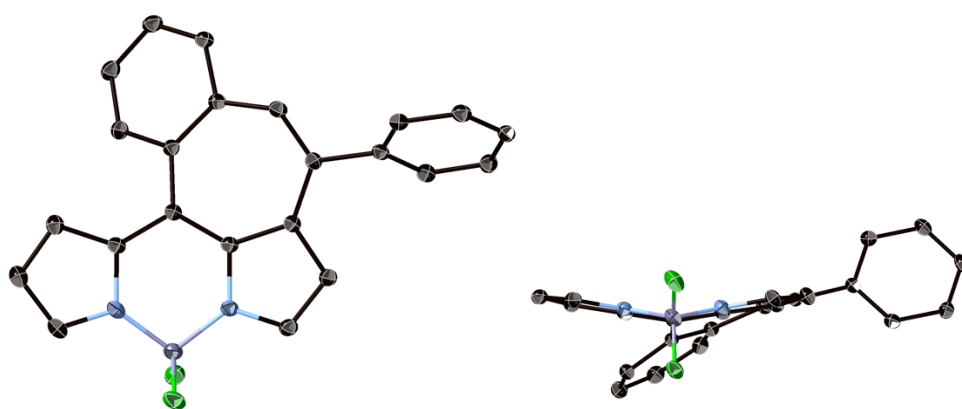


Figure S84. X-ray crystal structure of **2a** (C; black, N; sky blue, B; gray, F; green). Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

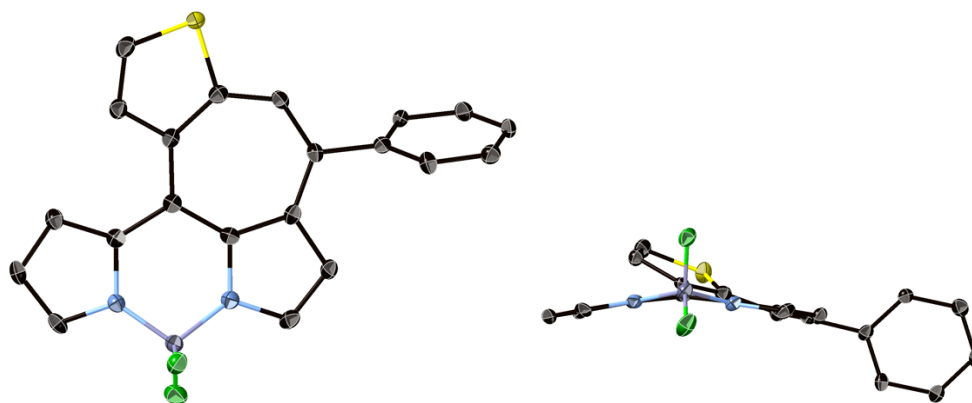


Figure S85. X-ray crystal structure of **2e** (C; black, N; sky blue, B; gray, F; green, S; yellow). Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.



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.

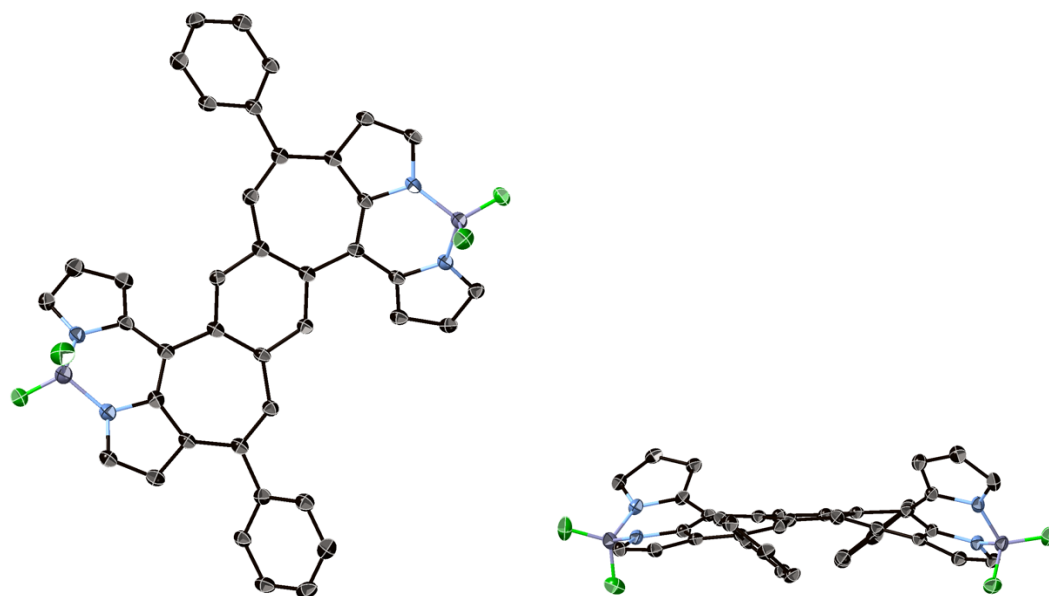


Figure S87. X-ray crystal structure of **4** (C; black, N; sky blue, B; gray, F; green). Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

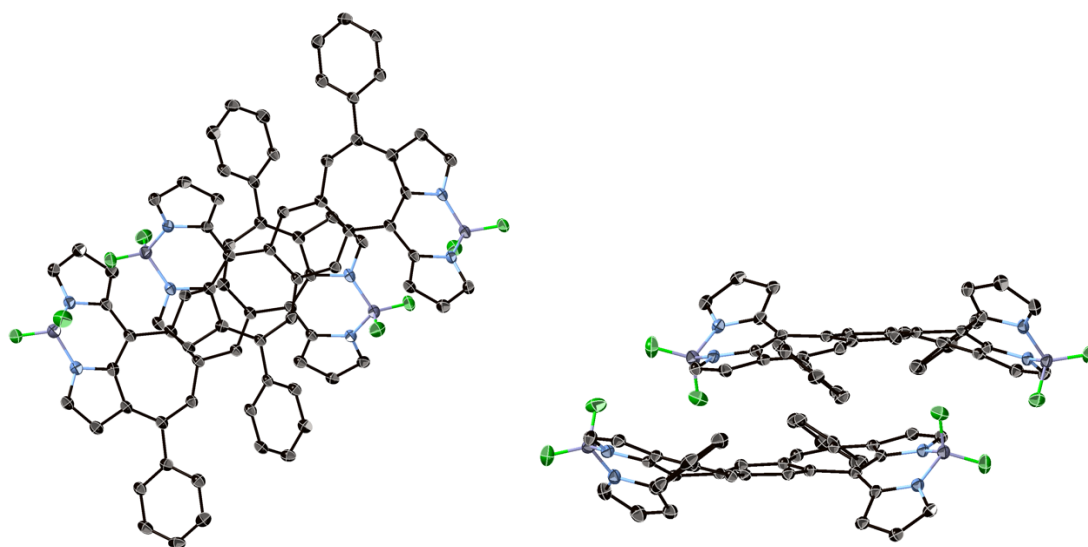


Figure S88. Crystal packing structure of **4** in the solid state (C; black, N; sky blue, B; gray, F; green).

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

compound	2a	2e	2f	4
Formula	C ₂₃ H ₁₅ BF ₂ N ₂	C ₂₁ H ₁₃ BF ₂ N ₂ S	C ₂₁ H ₁₃ BF ₂ N ₂ S	C ₄₀ H ₂₄ B ₂ F ₄ N ₄
Formula weight	368.18	374.20	374.20	658.25
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> , (No. 14)	<i>P</i> 2 ₁ / <i>c</i> , (No. 14)	<i>P</i> 2 ₁ / <i>c</i> , (No. 14)	<i>P</i> -1 (No. 2)
Crystal color	dark red	red	red	black
Crystal description	plate	plate	plate	block
<i>a</i> [Å]	5.8694(2)	5.9057(1)	11.6699(2)	11.2443(2)
<i>b</i> [Å]	16.1821(4)	15.6724(4)	10.8486(2)	12.5476(3)
<i>c</i> [Å]	17.7533(4)	17.7952(5)	14.0687(3)	23.0507(4)
α [°]	—	—	—	94.375(2)
β [°]	97.915(3)	97.537(2)	111.763(2)	92.406(1)
γ [°]	—	—	—	112.285(2)
<i>V</i> [Å ³]	1670.13(8)	1632.83(7)	1654.18(6)	2991.64(11)
<i>Z</i>	4	4	4	4
<i>d</i> _{calcd} [g cm ⁻³]	1.464	1.522	1.503	1.461
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0449	0.0644	0.0320	0.0609
<i>wR</i> 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

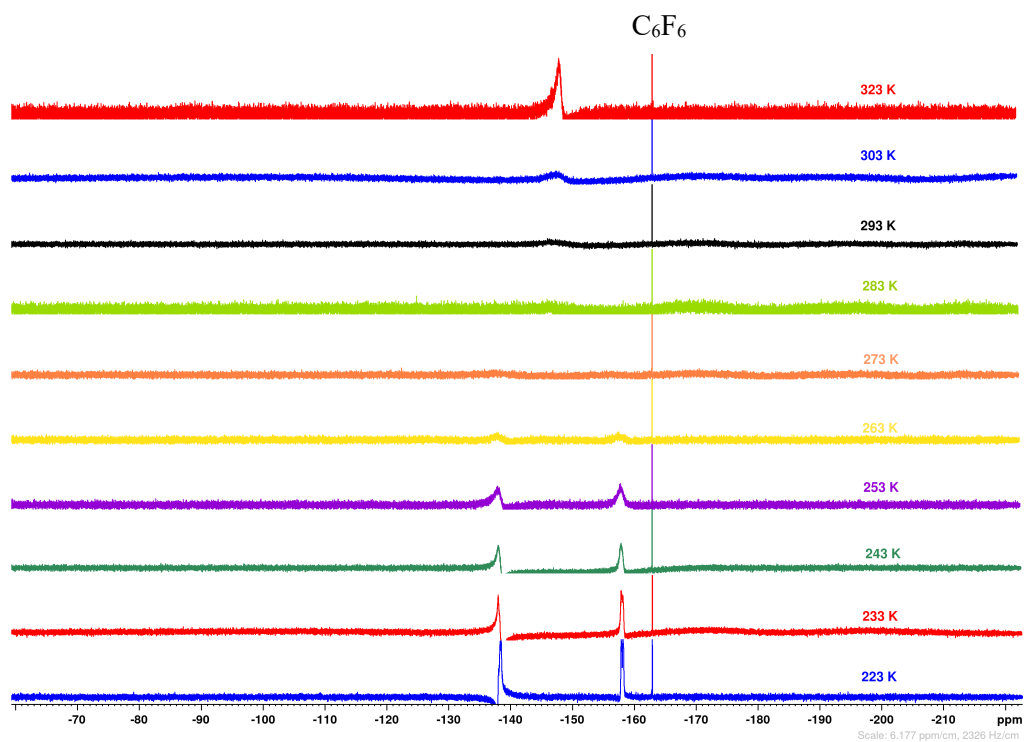


Figure S89. Temperature-dependent ^{19}F NMR spectra of **2a** in CDCl_3 . C_6F_6 was added as an internal standard.

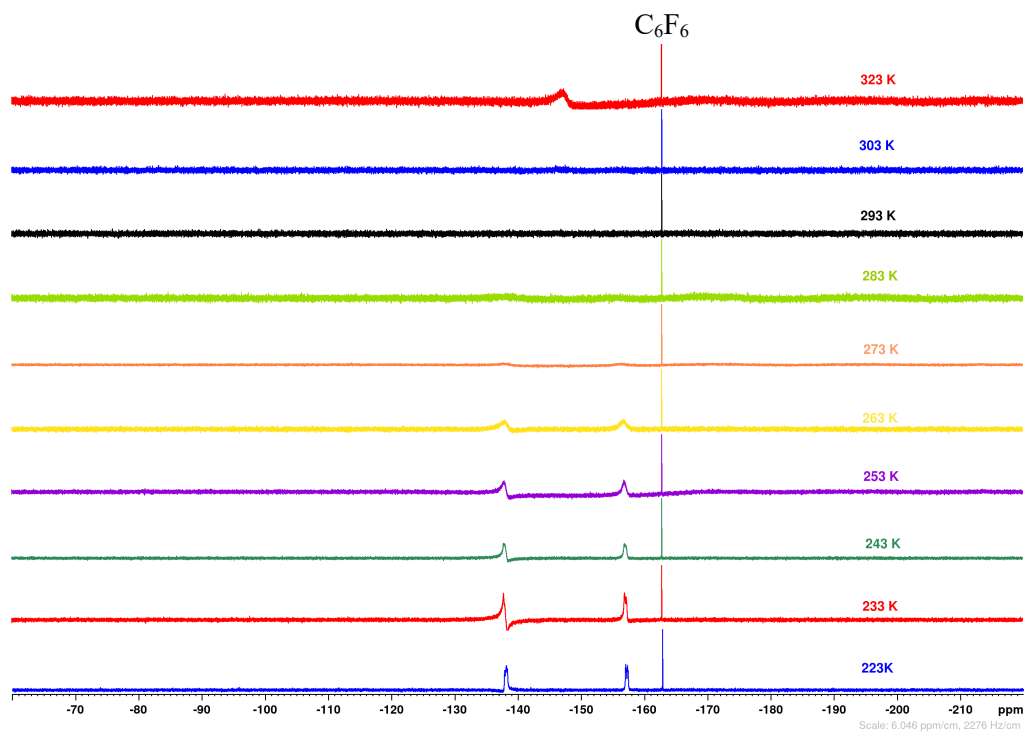


Figure S90. Temperature-dependent ^{19}F NMR spectra of **4** in CDCl_3 . C_6F_6 was added as an internal standard.

7. Fluorescence decay profiles

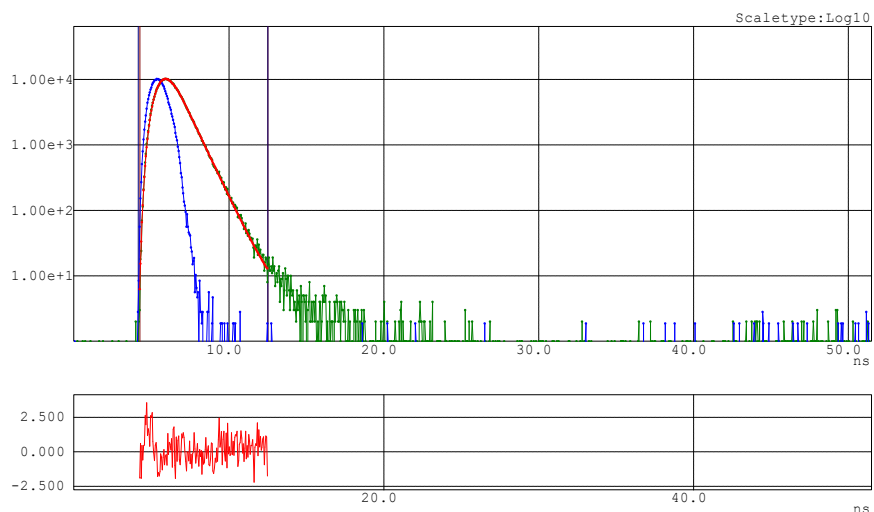


Figure S91. Time-correlated single photon counting (TCSPC) data of **1a** in CH_2Cl_2 . Top: simulated decay profile (red line) and IRF (blue line). Bottom: residuals.

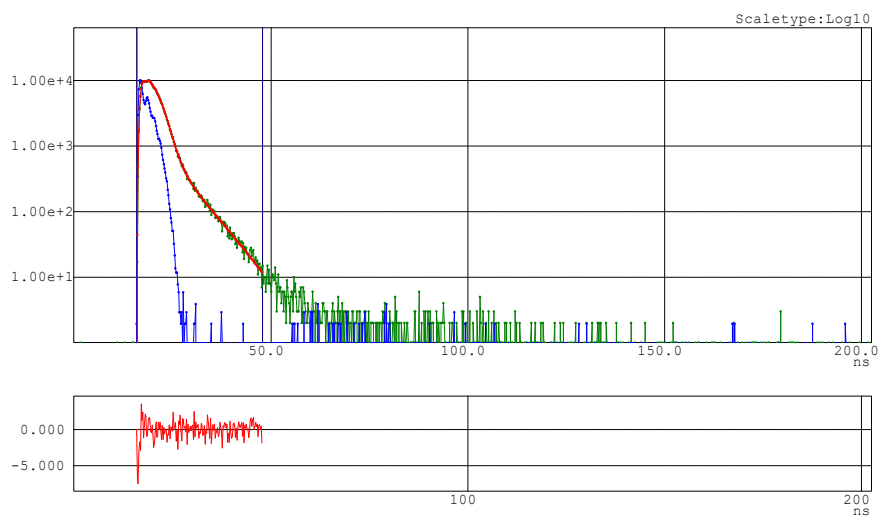


Figure S92. Time-correlated single photon counting (TCSPC) data of **1e** in CH_2Cl_2 .

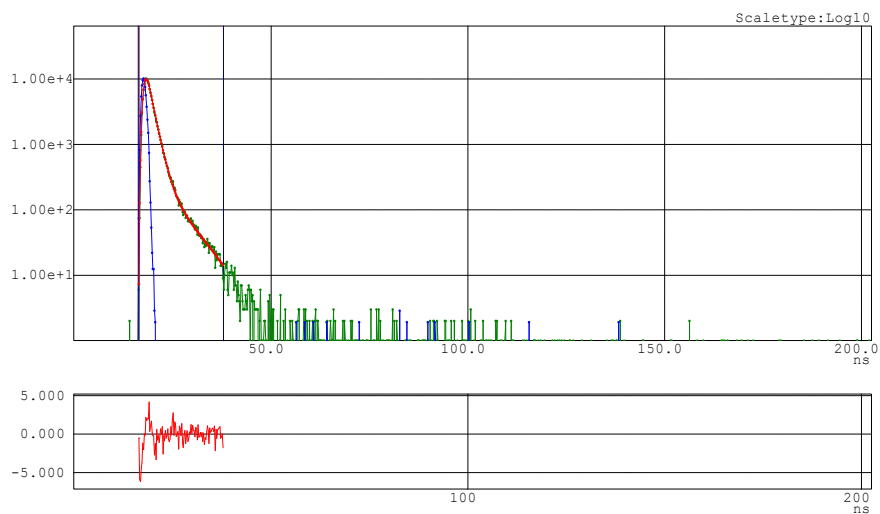


Figure S93. Time-correlated single photon counting (TCSPC) data of **1f** in CH_2Cl_2 .

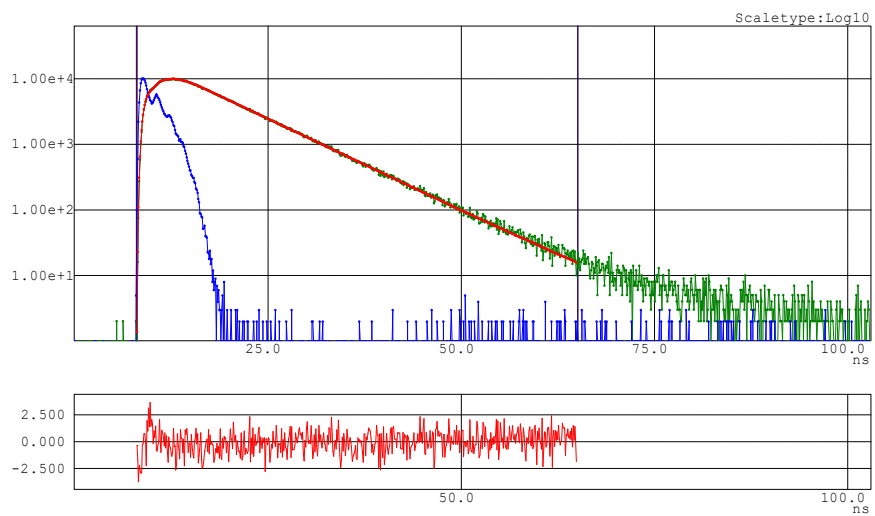


Figure S94. Time-correlated single photon counting (TCSPC) data of **2a** in CH_2Cl_2 .

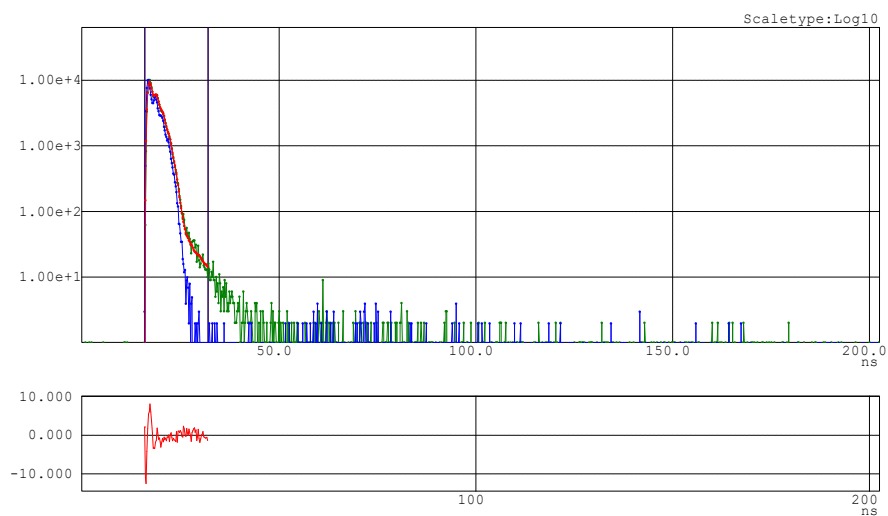


Figure S95. Time-correlated single photon counting (TCSPC) data of **2e** in CH_2Cl_2 .

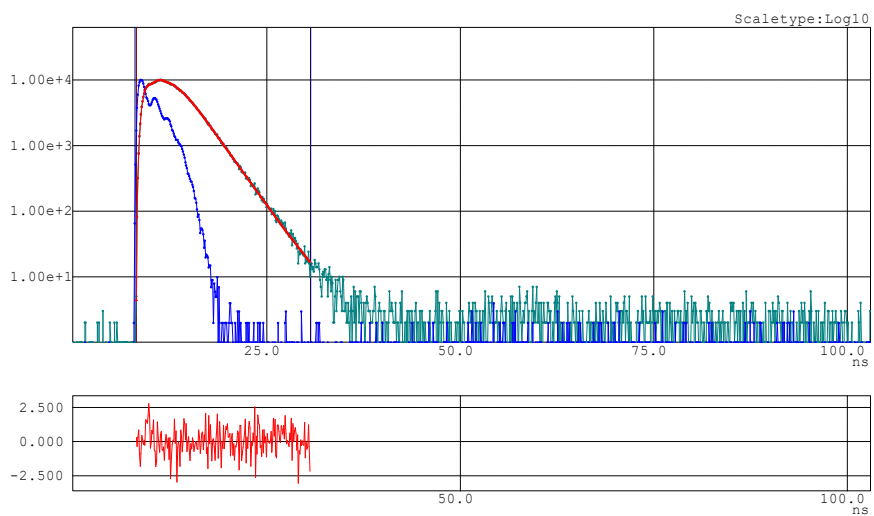


Figure S96. Time-correlated single photon counting (TCSPC) data of **2f** in CH_2Cl_2 .

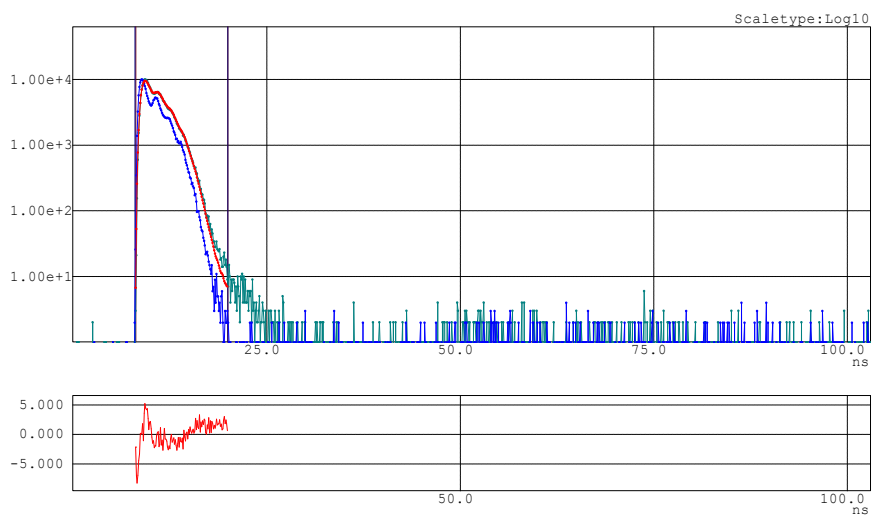


Figure S97. Time-correlated single photon counting (TCSPC) data of **3** in CH_2Cl_2 .

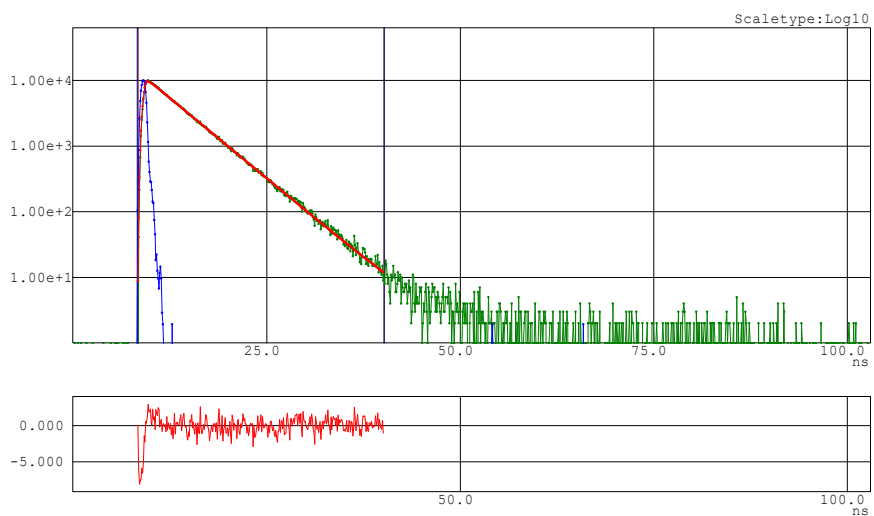


Figure S98. Time-correlated single photon counting (TCSPC) data of **4** in CH_2Cl_2 .

8. Photophysical properties in the different solvents

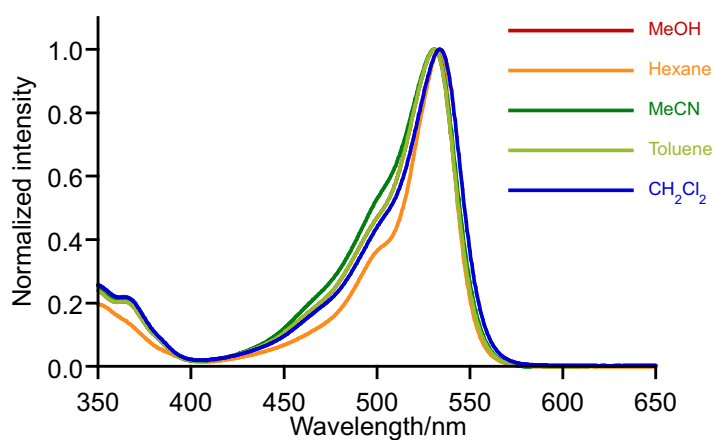


Figure S99. UV/vis absorption spectra of **2a** in different solvents.

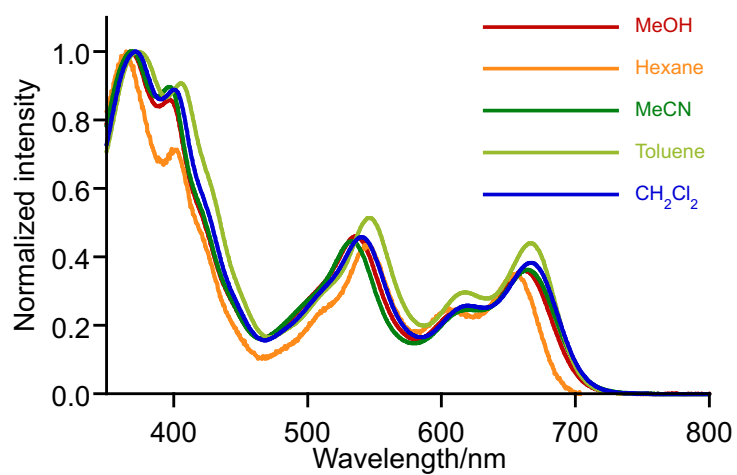


Figure S100. UV/vis absorption spectra of **4** in different solvents.

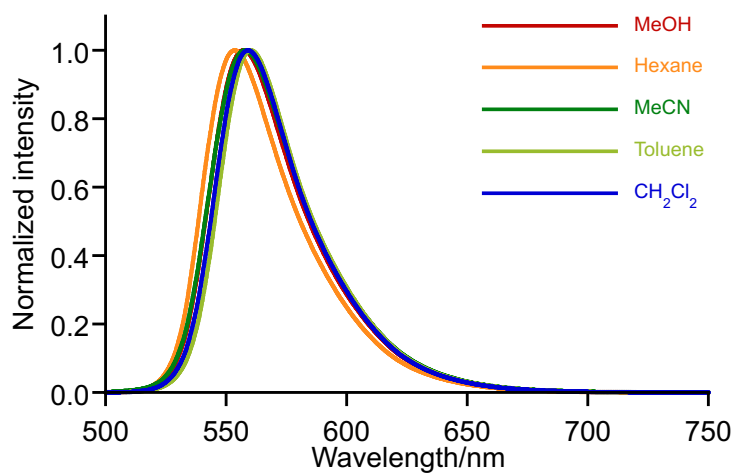


Figure S101. Emission spectra of **2a** in different solvents.

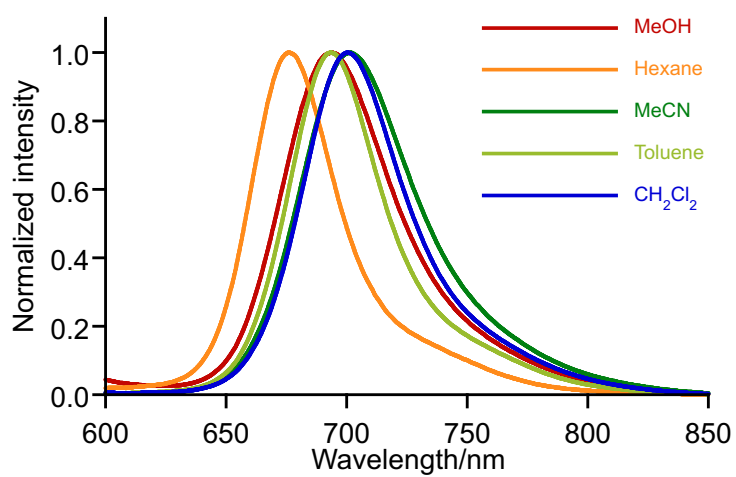


Figure S102. Emission spectra of **4** in different solvents.

9. Electrochemistry

Cyclic voltammograms and differential pulse voltammograms of **1a**, **2a** and **4** were measured in 0.1 M solution of Bu₄NPF₆ as a supporting electrolyte in acetonitrile (working electrode: Pt, counter electrode: Pt, reference electrode: Ag/AgNO₃, scan rate: 100 mVs⁻¹).

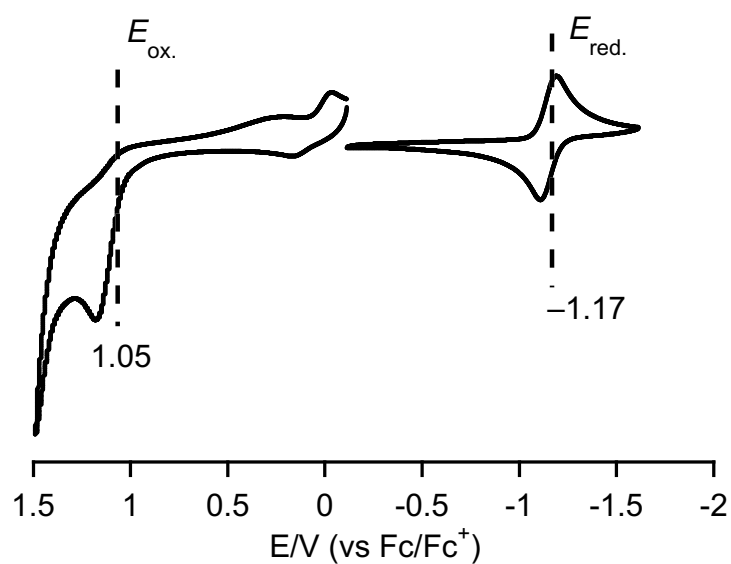


Figure S103. Cyclic voltammograms of **1a**.

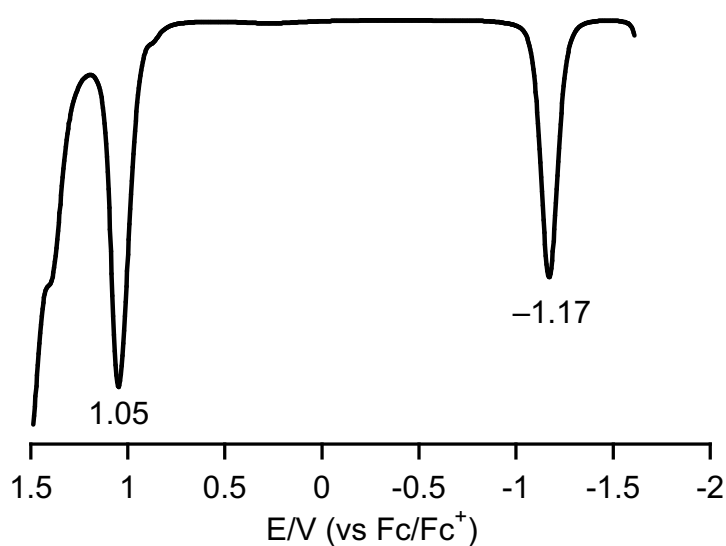


Figure S104. Differential pulse voltammogram of **1a**.

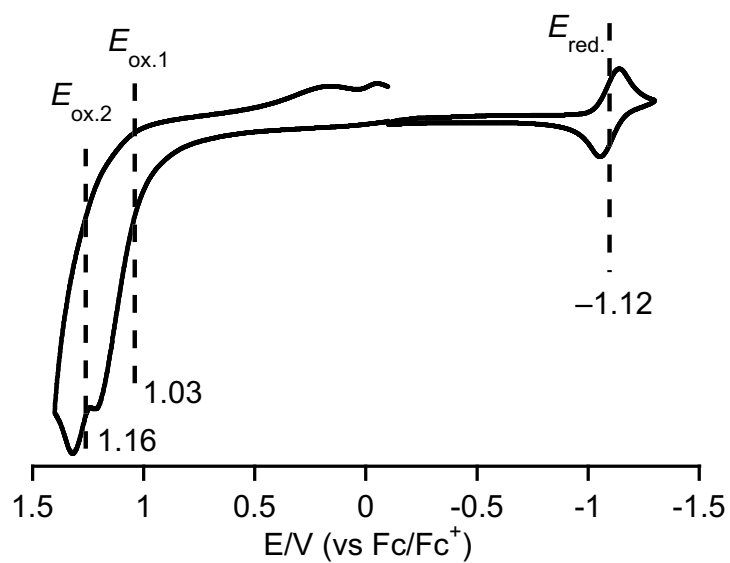


Figure S105. Cyclic voltammograms of **1e**.

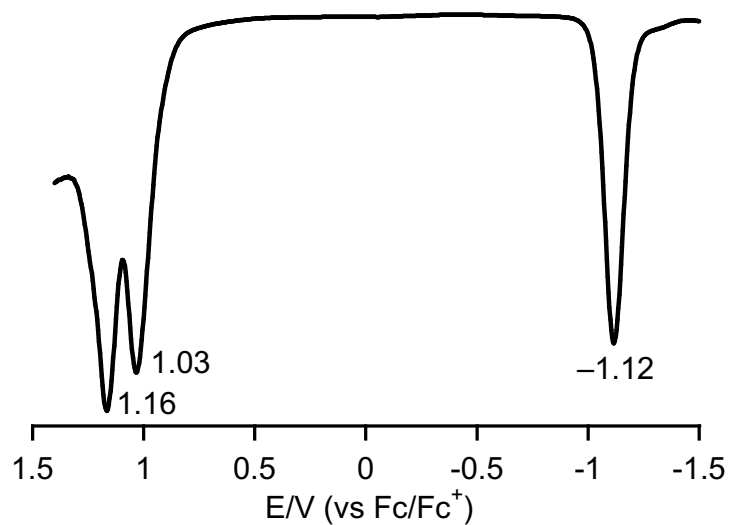


Figure S106. Differential pulse voltammogram of **1e**.

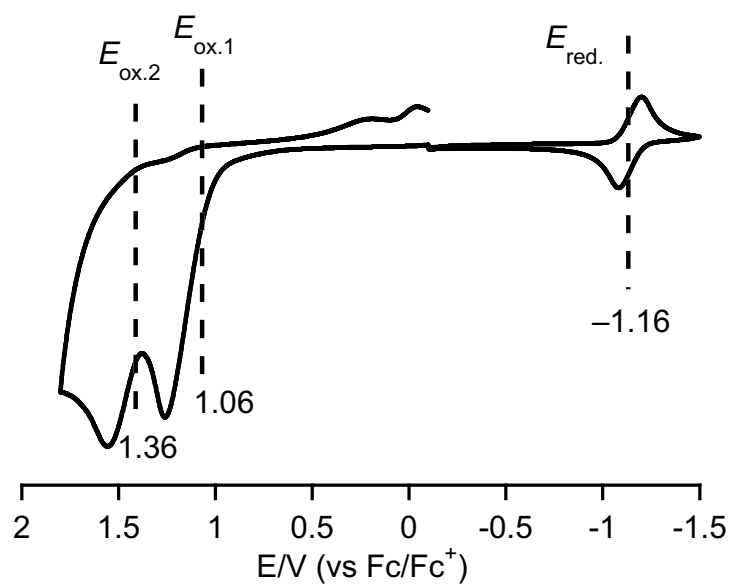


Figure S107. Cyclic voltammograms of **1f**.

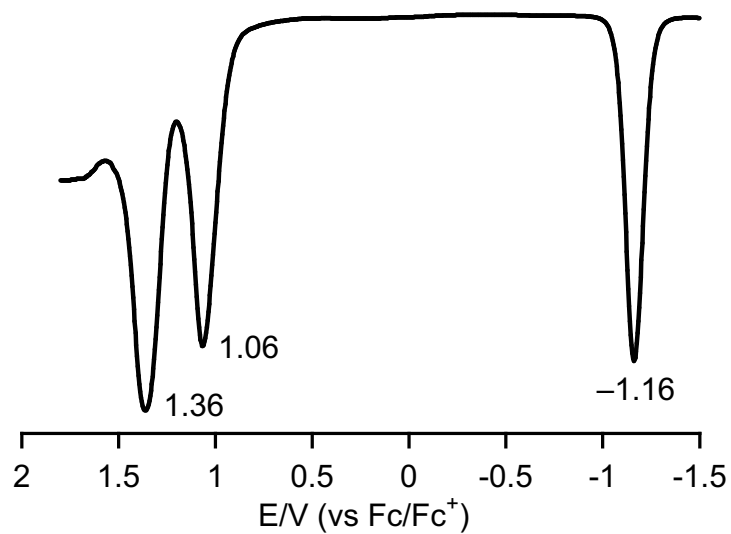


Figure S108. Differential pulse voltammogram of **1f**.

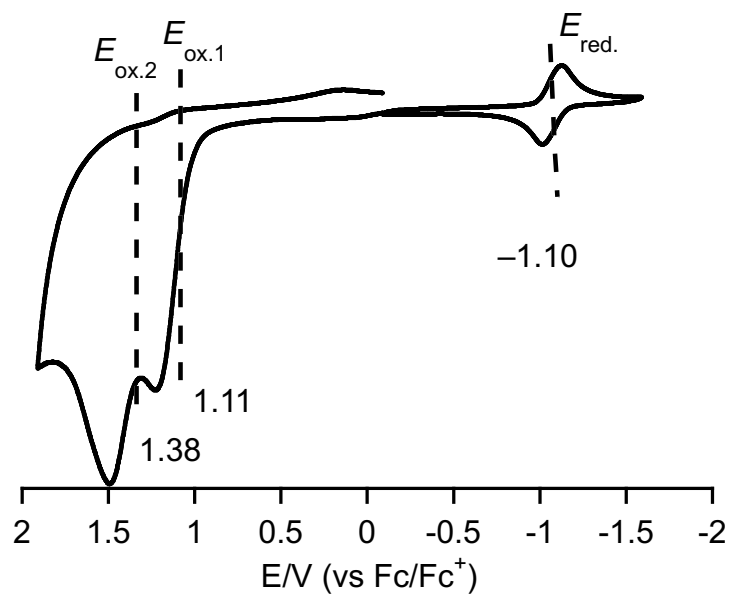


Figure S109. Cyclic voltammograms of **3**.

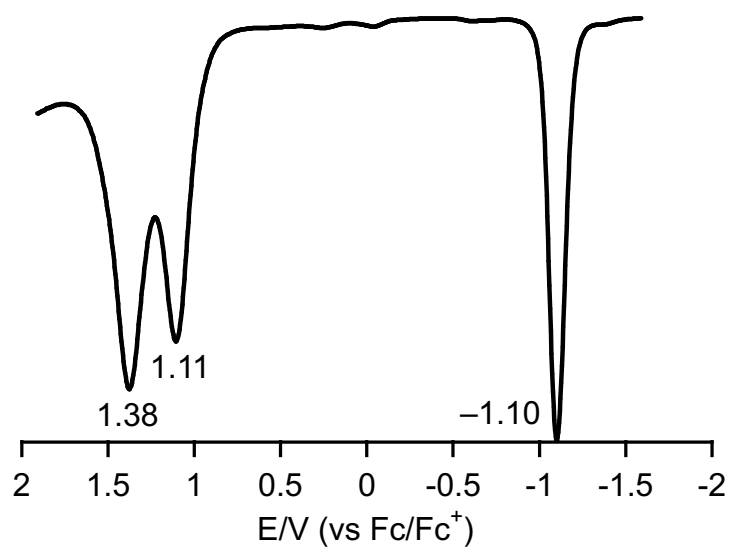


Figure S110. Differential pulse voltammogram of **3**.

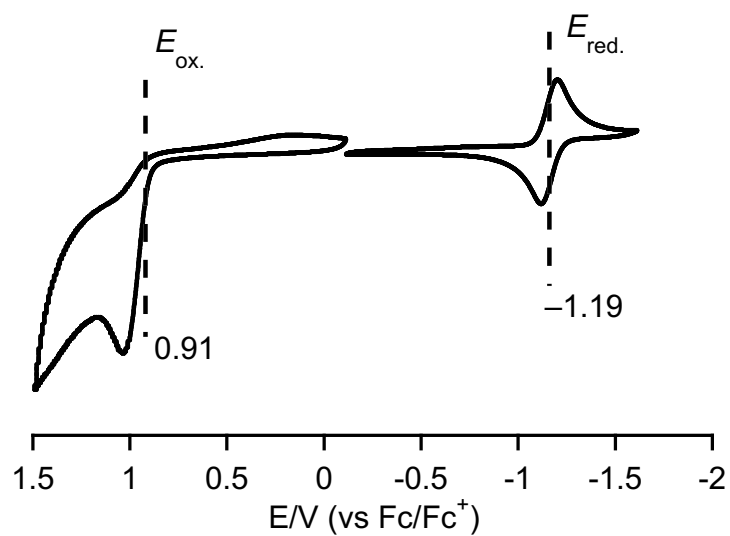


Figure S111. Cyclic voltammograms of **2a**.

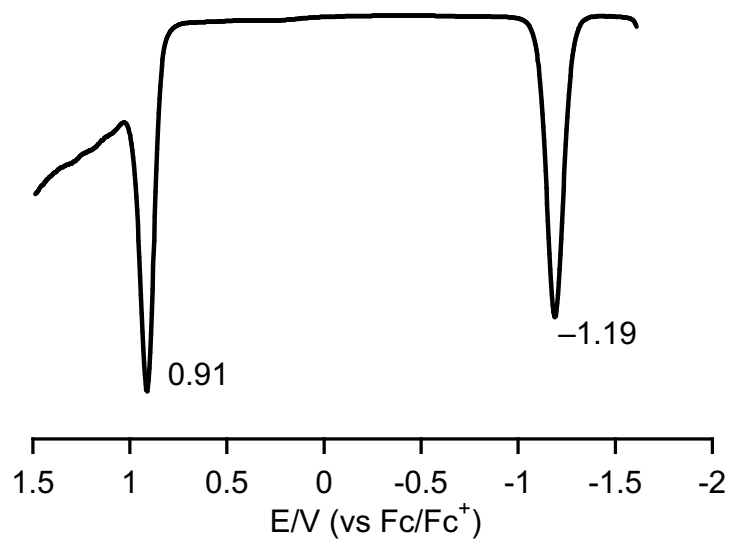


Figure S112. Differential pulse voltammogram of **2a**.

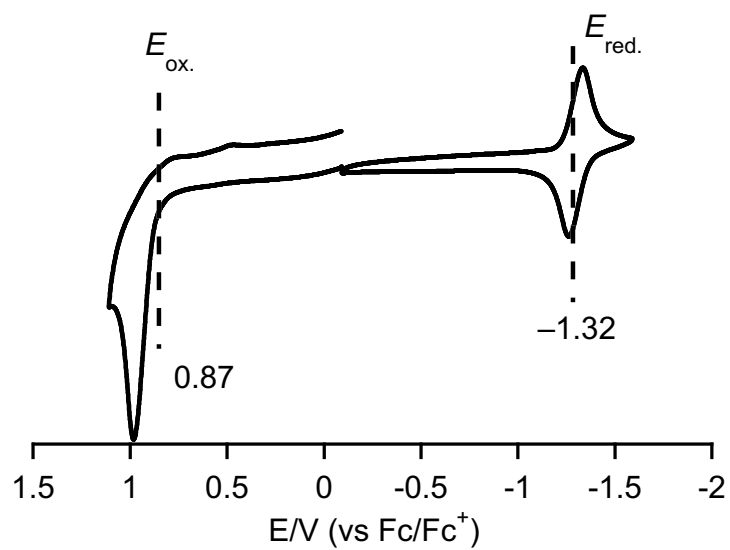


Figure S113. Cyclic voltammograms of **2e**.

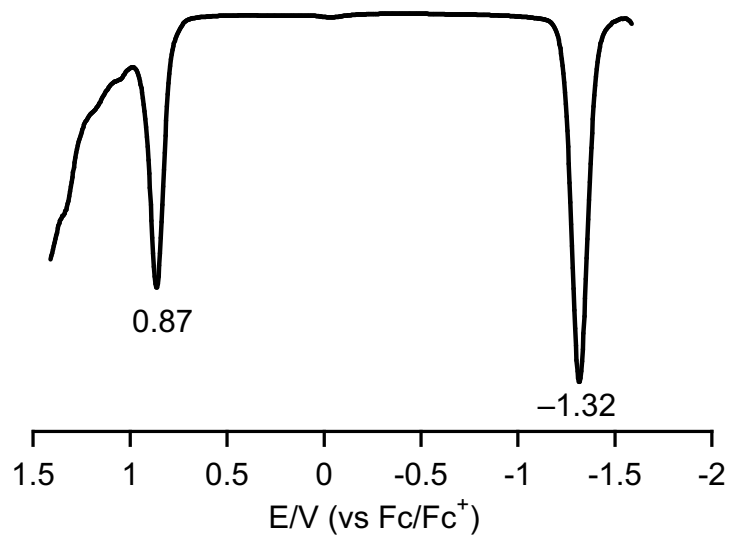


Figure S114. Differential pulse voltammogram of **2e**.

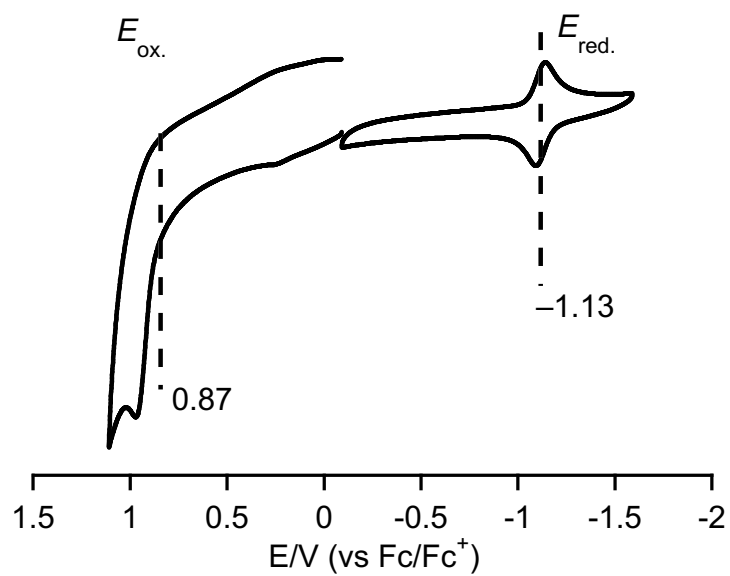


Figure S115. Cyclic voltammograms of **2f**.

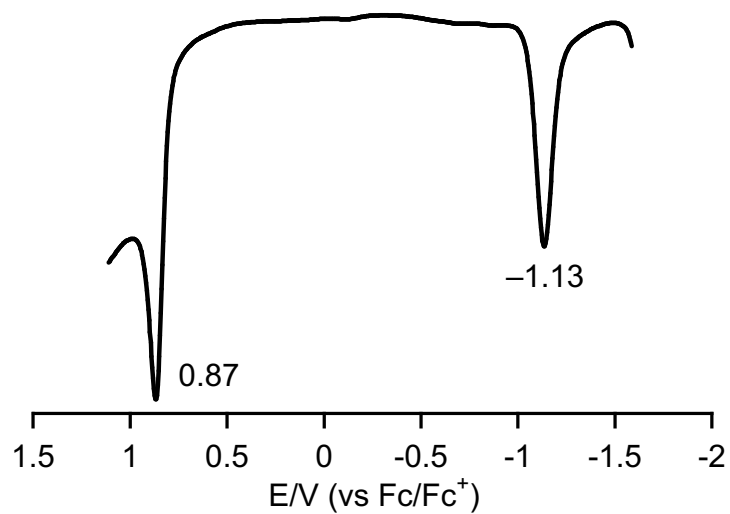


Figure S116. Differential pulse voltammogram of **2f**.

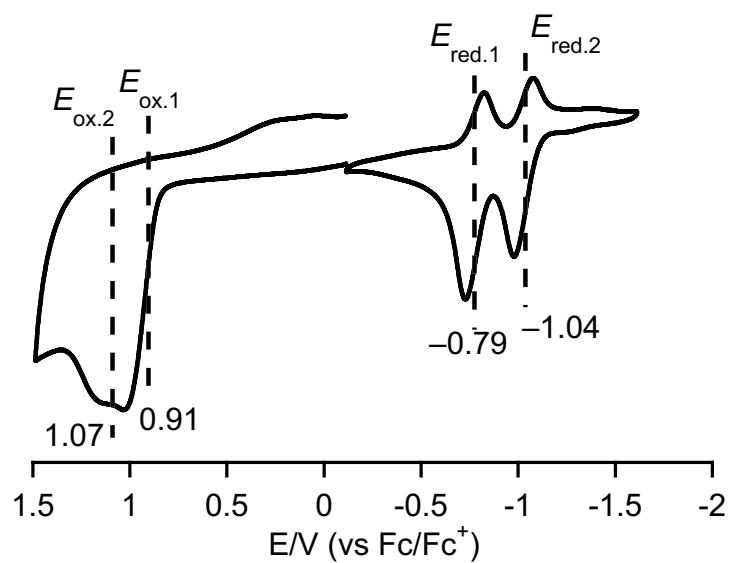


Figure S117. Cyclic voltammograms of **4**.

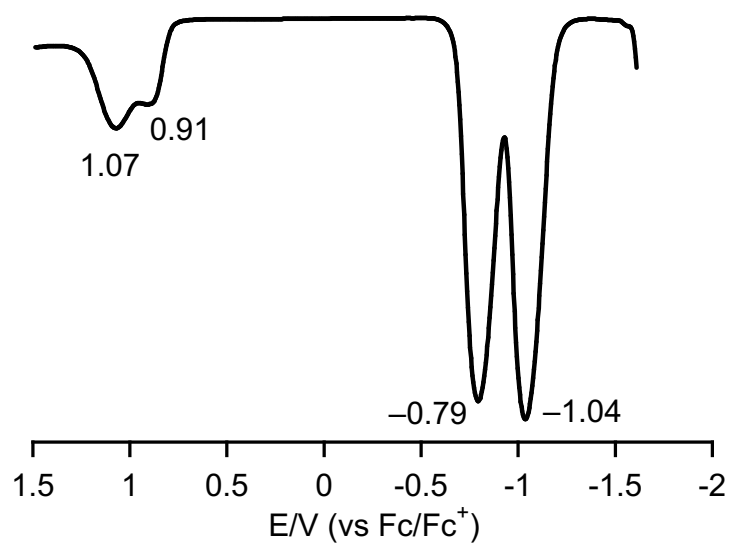


Figure S118. Differential pulse voltammogram of **4**.

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

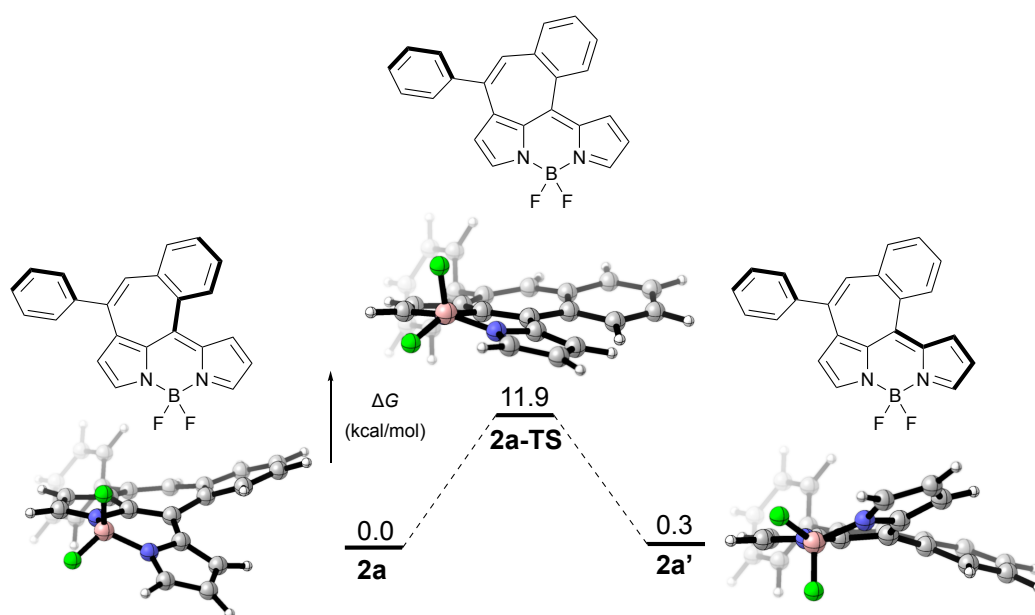


Figure S119. Inversion of helical structure of **2a**.

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	-1.760723	1.577836	-0.113608	
C	1.582500	-2.459972	-2.344195	C	-3.072409	1.021859	-0.183411
C	2.012883	-1.411163	-3.185169	C	-4.207924	1.857754	-0.210095
C	2.046972	-0.260461	-2.405062	C	-3.245672	-0.378203	-0.228566
C	1.646600	-0.633304	-1.094203	C	-5.485167	1.304704	-0.279566
N	1.368701	-2.000877	-1.100804	H	-4.075845	2.934588	-0.175886
H	1.417134	-3.502286	-2.581472	C	-4.528380	-0.919226	-0.298266
H	2.263203	-1.504008	-4.232348	H	-2.378096	-1.030348	-0.209674
H	2.330857	0.736569	-2.710469	C	-5.649883	-0.083748	-0.323871
C	1.202001	-0.506388	1.293002	H	-6.353144	1.957347	-0.299507
C	1.139431	0.001755	2.617699	H	-4.649882	-1.997752	-0.332987
N	0.911528	-1.870321	1.340113	H	-6.646656	-0.511691	-0.378358
C	0.814708	-1.064167	3.449099				
H	1.325461	1.028003	2.900938	2a			
C	0.677856	-2.199081	2.620643	F	-2.833927	-3.427304	0.051138
H	0.689997	-1.047589	4.522412	F	-2.994825	-2.135704	-1.847037
H	0.424391	-3.215582	2.889971	N	-1.034547	-1.883476	-0.442222
C	1.541248	0.118698	0.084801	N	-3.208738	-1.046596	0.312005
B	0.738102	-2.790249	0.090798	C	-0.476272	-0.638087	-0.240570
F	1.389081	-4.004727	0.277452	C	-1.302779	0.477869	0.045528
F	-0.628271	-2.989714	-0.154121	C	-0.855656	1.860070	-0.128900
C	1.801145	1.588073	0.055796	C	-2.643766	0.214545	0.464283
C	3.112240	2.074757	0.079057	C	0.497620	2.324979	-0.005731
C	0.713536	2.498207	0.001636	C	0.954588	-0.783613	-0.309133
C	3.365511	3.448459	0.060939	C	1.947588	0.205880	0.002041
H	3.936897	1.369293	0.119555	C	1.695606	1.542628	0.171893
C	0.987531	3.881387	-0.018067	H	2.567292	2.143368	0.417858
C	2.298446	4.350260	0.013691	C	1.194891	-2.147587	-0.598533
H	4.389117	3.809344	0.084488	H	2.157914	-2.619282	-0.718251
H	0.155335	4.576301	-0.062343	C	3.369235	-0.240837	0.151476
H	2.487790	5.419422	-0.001112	C	3.727186	-1.207172	1.107021
C	-0.628445	2.021629	-0.054344	H	2.958699	-1.650994	1.732681

C	4.379906	0.328942	-0.639565	C	0.815732	1.918073	-0.082411
H	4.115085	1.064759	-1.393584	C	2.805032	0.278285	-0.231012
C	-4.660232	0.195096	1.504222	C	-0.547853	2.306817	0.212605
H	-5.532999	0.464430	2.081948	C	-0.931875	-0.783192	-0.051234
C	6.058453	-1.013037	0.476091	C	-1.969790	0.191408	0.016416
H	7.095003	-1.311875	0.601477	C	-1.749268	1.522637	0.223588
C	5.713526	-0.056499	-0.481471	H	-2.649048	2.117642	0.348187
H	6.480046	0.388207	-1.109577	C	-1.180313	-2.173695	-0.039959
C	-1.849568	2.817689	-0.473934	H	-2.147428	-2.650121	-0.053278
H	-2.849394	2.463323	-0.685773	C	-3.394702	-0.260092	-0.066922
C	-0.040722	-2.772142	-0.685869	C	-3.881612	-0.885346	-1.226975
H	-0.278135	-3.803159	-0.907588	H	-3.209066	-1.064360	-2.060774
C	-3.554889	0.998210	1.220782	C	-4.280887	-0.027348	0.996536
H	-3.383303	2.005714	1.569334	H	-3.913273	0.441075	1.905223
C	-1.577531	4.167783	-0.597996	C	5.083519	0.216073	-0.550188
H	-2.367574	4.853573	-0.887666	H	6.104164	0.503360	-0.758233
C	0.724850	3.727888	-0.075171	C	-6.096320	-1.028472	-0.255226
H	1.740862	4.083353	0.068268	H	-7.138242	-1.325884	-0.328187
C	-4.413921	-1.054911	0.913813	C	-5.620943	-0.412072	0.904620
H	-5.028442	-1.944117	0.895601	H	-6.290227	-0.233336	1.741197
C	-0.276301	4.636156	-0.357675	C	1.697963	3.011038	-0.302717
H	-0.048140	5.695584	-0.425094	H	2.688678	2.810815	-0.639378
C	5.060804	-1.584798	1.271600	C	0.045373	-2.802062	0.047320
H	5.320644	-2.324196	2.023674	H	0.284503	-3.854198	0.111966
B	-2.564300	-2.185085	-0.518783	C	3.973254	1.054507	-0.528359
				H	4.073328	2.101546	-0.739977
2a-TS				C	1.376649	4.342504	-0.133383
F	2.871007	-3.395425	-0.350872	H	2.129601	5.100570	-0.325682
F	2.654880	-2.488489	1.746985	C	-0.837036	3.690464	0.427554
N	1.037511	-1.884981	0.066139	H	-1.858497	3.947319	0.689064
N	3.288055	-1.030534	-0.077245	C	4.618224	-1.065823	-0.256793
C	0.513219	-0.607109	-0.005078	H	5.154014	-1.999531	-0.161251
C	1.369957	0.539682	-0.116199	C	0.088267	4.697439	0.286738

H	-0.186141	5.732994	0.461488	H	2.831242	2.445539	-0.869380
C	-5.222548	-1.261680	-1.321529	C	0.044610	-2.850817	-0.309384
H	-5.584954	-1.734822	-2.229594	H	0.284061	-3.899585	-0.379032
B	2.497281	-2.260294	0.373523	C	3.617999	1.083531	1.055838
2a'				H	3.468531	2.115383	1.329842
F	2.940304	-2.327791	-1.732554	C	1.557144	4.151825	-0.799821
F	2.861118	-3.439598	0.320442	H	2.334079	4.830634	-1.134221
N	1.042214	-1.922364	-0.244722	C	-0.733159	3.722484	-0.204428
N	3.235937	-1.029392	0.323733	H	-1.747743	4.076930	-0.053991
C	0.482450	-0.650527	-0.177823	C	4.467549	-1.002262	0.892078
C	1.316181	0.484102	-0.005405	H	5.071263	-1.894463	0.935796
C	0.857008	1.855623	-0.230899	C	0.258751	4.624793	-0.541046
C	2.672555	0.253032	0.388845	H	0.026722	5.680036	-0.638354
C	-0.497533	2.320427	-0.086878	C	-5.377278	-1.265607	-0.796368
C	-0.953312	-0.817851	-0.182552	H	-5.862147	-1.788689	-1.614503
C	-1.949059	0.195695	0.021464	B	2.555882	-2.226636	-0.359798
C	-1.693728	1.542286	0.120916	4			
H	-2.574496	2.157260	0.284505	F	5.986035	-3.734679	0.791014
C	-1.190108	-2.217242	-0.257268	F	4.553029	-4.032934	-0.985360
H	-2.151421	-2.701319	-0.241883	N	4.859142	-1.792467	-0.116207
C	-3.382710	-0.226325	0.142935	N	3.608405	-3.459563	1.173742
C	-4.027799	-0.915416	-0.902224	C	3.785919	-0.924086	-0.062405
H	-3.474518	-1.160343	-1.802962	C	2.553709	-1.354604	0.482780
C	-4.123821	0.103689	1.292589	C	1.302799	-0.612278	0.302634
H	-3.634042	0.625268	2.109017	C	2.533158	-2.579388	1.214607
C	4.732681	0.294883	1.366138	C	1.183045	0.812675	0.150226
H	5.621353	0.609199	1.890819	C	4.239839	0.362519	-0.532467
C	-6.103386	-0.937307	0.354941	C	3.530370	1.613222	-0.501567
H	-7.149876	-1.212733	0.436620	C	2.220229	1.772001	-0.130256
C	-5.472540	-0.251705	1.398880	H	1.861429	2.797601	-0.148481
H	-6.026759	0.002654	2.296774	C	5.603304	0.194635	-0.864820
C	1.838255	2.805391	-0.639552	H	6.278458	0.958224	-1.217668

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

11. References

1. W. P. Gallagher and R. E. Maleczka, *J. Org. Chem.*, 2003, **68**, 6775.
2. (a) T. V. Goud, A. Tutar and J.-F. Biellmann, *Tetrahedron*, 2006, **62**, 5084. (b) N. R. Treich, J. D. Wimpenny, I. A. Kieffer and Z. M. Heiden, *New J. Chem.*, 2017, **41**, 14370.
3. K. Hirano, Y. Inaba, T. Watanabe, S. Oishi, N. Fujii and H. Ohno, *Adv. Synth. Catal.*, 2010, **352**, 368
4. A. Konishi, T. Fujiwara, N. Ogawa, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, C. Kitamura and T. Kawase, *Chem. Lett.*, 2010, **39**, 300.
5. S. Feng, Z. Qu, Z. Zhou, J. Chen, L. Gai and H. Lu, *Chem. Commun.*, 2021, **57**, 11689.
6. S. Seo and T. J. Marks, *Chem. Eur. J.*, 2010, **16**, 5148.
7. 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.
8. (a) S. Maeda, Y. Harabuchi, Y. Sumiya, M. Takagi, K. Suzuki, M. Hatanaka, Y. Osada, T. Taketsugu, K. Morokuma, K. Ohno, GRRM17, see http://iqce.jp/GRRM/index_e.shtml (accessed date: 23th Aug., 2024). (b) S. Maeda, K. Ohno and K. Morokuma, *Phys. Chem. Chem. Phys.*, 2013, **15**, 3683.
9. (a) K. Fukui, *J. Phys. Chem.*, 1970, **74**, 4161. (b) K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363.