Supporting Information for

Transition-Metal-Free Regioselective Cross-Dehydrogenative Coupling of BODIPYs with Thiols

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1. General information

Reagents and solvents were used as received from commercial suppliers (Energy Chemicals, Shanghai, China) unless noted otherwise. All reactions were performed in oven-dried or flame-dried glassware unless stated otherwise and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). ^{1}H and ^{13}C NMR spectra were recorded on a 300 or 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ (7.26 ppm for ^{1}H and 77 ppm for ^{13}C) or to internal TMS. High-resolution mass spectra (HRMS) were obtained using APCI-TOF in positive mode.

UV-visible absorption and fluorescence emission spectra were recorded on commercial spectrophotometers (Shimadzu UV-2450 and Edinburgh FS5 spectrometers). All measurements were made at 25 ^{o}C, using 5 × 10 mm cuvettes. Relative fluorescence quantum efficiencies of BODIPY derivatives were obtained by comparing the areas under the corrected emission spectrum of the test sample in various solvents with Rhodamine B (Φ = 0.49 in ethanol)[1] and fluorescein (Φ = 0.90 in 0.1 N NaOH aqueous solution.[2] Non-degassed, spectroscopic grade solvents and a 10 mm quartz cuvette were used. Dilute solutions ($0.01<A<0.05$) were used to minimize the reabsorption effects. Quantum yields were determined using the following equation[3]:

$$\Phi_X = \Phi_S (I_X/I_S) (A_S/A_X) (n_X/n_S)^2$$

Where Φ_S stands for the reported quantum yield of the standard, I stands for the integrated emission spectra, A stands for the absorbance at the excitation wavelength and n stands for the refractive index of the solvent being used. X subscript stands for the test sample, and S subscript stands for the standard.

Crystals of compounds **3a**, **4m** and **5a** suitable for X-ray analysis were obtained *via* the slow diffusion of petroleum ether into their dichloromethane solutions. The vial containing this solution was placed, loosely capped, to promote the crystallization. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were collected using a diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. Cell parameters were retrieved using SMART[4] software and refined using SAINT on all observed reflections. The determination of unit cell parameters and data collections were

performed with Mo Kα radiation (λ) at 0.71073 Å. Data reduction was performed using the SAINT software,[5] which corrects for Lp and decay. The structure was solved by the direct method using the SHELXS-974 program and refined by least squares method on F^2, SHELXL-97,[6] incorporated in SHELXTL V5.10.[7] CCDC-1871715 (**3a**), CCDC-1871714 (**4m**), CCDC-1871716 (**5a**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

2. Figure S1

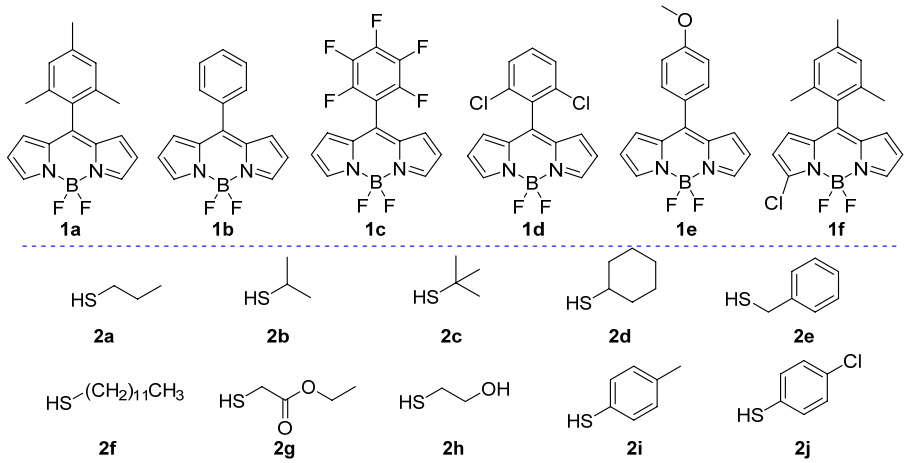
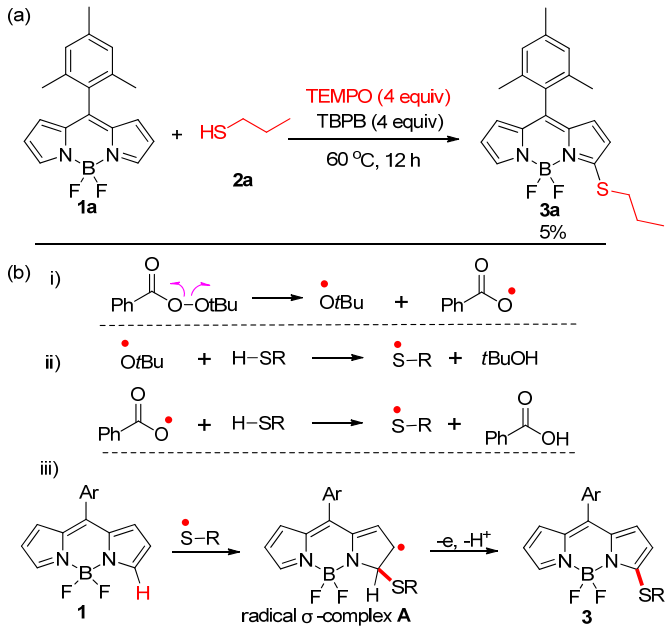
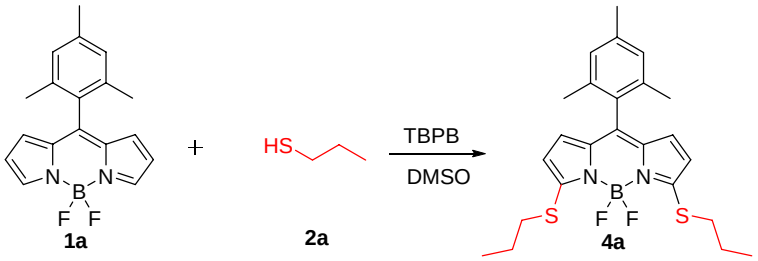


Figure S1. Chemical structure of BODIPYs **1a-f** and various thioalcohols **2a-j.**



Scheme S1. (a) The influence of TEMPO to this thiolation reaction, (b) proposed reaction mechanism.

3. Table S1. Optimization of the reaction conditions[a].

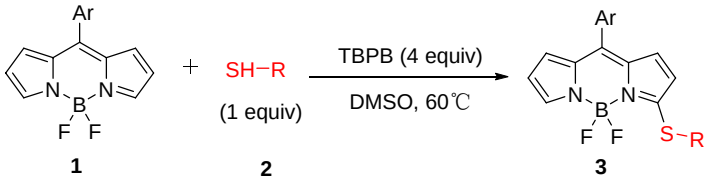


entry	temp (°C)	**2a** (equiv)	yield[b] (%)
1[c]	60	1	<5
2	70	1	<5
3	80	1	trace
4	**60**	**2**	**88**
5	60	3	56[d]
6	60	4	54
7	60	5	32
8	60	6	trace

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), oxidant (0.4 mmol), DMSO (1 mL), 4 h. [b]Isolated yield. [c]The reaction time extended to 24 h. [d]3 equiv **2a** was used and trithiolation of BODIPY **5a** was isolated in 23% yield.

4. Synthesis and characterization

BODIPYs **1a-f** were synthesized according to literatures.[8] Compounds **2**a-**j** are commercially available reagents.



General radical C–H monothiolization procedure: BODIPY **1** (1 equiv, 0.2 mmol), **2** (1 equiv, 0.2 mmol), the oxidant *tert*-butylperoxy benzoate (TBPB, 4 equiv, 0.8 mmol) were dissolved in dimethyl sulfoxide (DMSO, 2 mL). The reaction mixture

was stirred at 60 ^{o}C and the reaction was followed by TLC. Upon completion, the reaction mixture was cooled to room temperature and was poured into dichloromethane (100 mL), washed three times with water (100 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatographically (silica; petroleum ether/ethyl acetate; 50:1-20:1 v/v).

3a was prepared in 73 % yield (56 mg) from **1a** (60 mg, 0.2 mmol) and **2a** (0.020 mL, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 6.93 (s, 2H), 6.66 (d, J = 4.5 Hz, 1H), 6.45 (d, J = 3.8 Hz, 1H), 6.41 (d, J = 4.5 Hz, 1H), 6.38 – 6.37 (m, 1H), 3.09 (t, J = 7.3 Hz, 2H), 2.35 (s, 3H), 2.09 (s, 6H), 1.89 – 1.82 (m, 2H), 1.11 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.01, 140.81, 139.66, 138.48, 137.18, 136.68, 133.97, 131.08, 129.80, 128.07, 126.04, 117.47, 116.69, 34.54, 22.56, 21.10, 19.94, 13.42. HRMS calcd. for $C_{21}H_{23}BF_2N_2S$, $[M\text{-}F]^+$: 365.1659, found: 365.1654.

3b was prepared in 61 % yield (41 mg) from **1b** (54 mg, 0.2 mmol) and **2a** (0.020 mL, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.53 – 7.49 (m, 5H), 6.93 (d, J = 4.4 Hz, 1H), 6.71 (d, J = 3.1 Hz, 1H), 6.49 (d, J = 4.5 Hz, 1H), 6.45 (s, 1H), 3.10 (t, J = 7.3 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.11 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.56, 141.49, 140.06, 137.26, 134.37, 134.22, 132.91, 130.79, 130.51, 128.73, 127.81, 117.99, 117.15, 34.99, 22.98, 13.83. HRMS calcd. For $C_{18}H_{17}BF_2N_2S$, $[M\text{-}F]^+$: 323.1190, found: 323.1194.

3c was prepared in 72 % yield (62 mg) from **1c** (71 mg, 0.2 mmol) and **2a** (0.020 mL, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 6.79 (d, J = 4.6 Hz, 1H), 6.56 (d, J = 5.2 Hz, 1H), 6.54 (s, 1H), 6.46 – 6.45 (m, 1H), 3.13 (t, J = 7.3 Hz, 2H), 1.91–1.83 (m, 2H), 1.12 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.38, 159.25, 149.80, 146.12, 141.50, 141.35, 137.59, 133.48, 131.42, 126.10, 122.81, 119.40, 117.88, 35.15, 23.01, 13.73. HRMS calcd. For $C_{18}H_{12}BF_7N_2S$, $[M\text{-}F]^+$: 413.0718, found: 413.0719.

3d was prepared in 68 % yield (56 mg) from **1d** (67 mg, 0.2 mmol) and **2a** (0.020 mL, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.46 – 7.45 (m, 2H), 7.40 – 7.37 (m, 1H), 6.68 (d, J = 4.6 Hz, 1H), 6.47 (d, J = 4.7 Hz, 1H), 6.46 (s, 1H), 6.41 – 6.40 (m, 1H), 3.11 (t, J = 7.3 Hz, 2H), 1.90 – 1.83 (m, 2H), 1.11 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.36, 140.65, 137.25, 135.99, 134.48, 133.53,

131.99, 131.34, 131.24, 128.56, 125.88, 118.58, 117.39, 35.04, 22.97, 13.81. HRMS calcd. For $C_{18}H_{15}BCl_2F_2N_2S$, $[M\text{-}F]^+$: 391.1410, found: 391.1409.

3e was prepared in 62 % yield (46 mg) from **1e** (59 mg, 0.2 mmol) and **2a** (0.020 mL, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.47 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 4.5 Hz, 1H), 6.75 (d, J = 3.7 Hz, 1H), 6.48 (d, J = 4.5 Hz, 1H), 6.46 – 6.45 (m, 1H), 3.89 (s, 3H), 3.09 (t, J = 7.3 Hz, 2H), 189 – 1.81 (m, 2H), 1.11 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.85, 161.66, 141.65, 139.68, 137.18, 134.23 132.71, 132.46, 127.68, 126.82, 117.77, 116.98, 114.31, 55.86, 35.01, 22.98, 13.82. HRMS calcd. For $C_{19}H_{19}BF_2N_2OS$, $[M\text{-}F]^+$: 353.1295, found: 353.1283.

3f was prepared in 70 % yield (54 mg) from **1a** (60 mg, 0.2 mmol) and **2b** (0.022 mL, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 6.94 (s, 2H), 6.67 (d, J = 4.5 Hz, 1H), 6.45 (d, J = 4.3 Hz, 2H), 6.38 – 6.36 (m, 1H), 3.71 – 3.62 (m, 1H), 2.35 (s, 3H), 2.10 (s, 6H), 1.52 (d, J = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.48, 140.89, 139.76, 138.52, 137.01, 136.74, 134.03, 131.15, 129.88, 128.11, 126.07, 117.95, 116.71, 37.71, 23.59, 21.13, 19.99. HRMS calcd. For $C_{21}H_{23}BF_2N_2S$, $[M\text{-}F]^+$: 365.1659, found: 365.1651.

3g was prepared in 66 % yield (53 mg) from **1a** (60 mg, 0.2 mmol) and **2c** (0.024 mL, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 6.94 (s, 2H), 6.65 (d, J = 4.4 Hz, 1H), 6.61 (d, J = 4.4 Hz, 1H), 6.50 (d, J = 3.8 Hz, 1H), 6.40 – 6.39 (m, 1H), 2.36 (s, 3H), 2.10 (s, 6H), 1.60 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.70, 142.56, 141.64, 138.97, 137.04, 136.78, 134.77, 130.75, 130.23, 128.49, 127.45, 121.83, 117.73, 49.34, 32.00, 21.50, 20.38. HRMS calcd. For $C_{22}H_{25}BF_2N_2S$, $[M\text{-}F]^+$: 379.1816, found: 379.1818.

3h was prepared in 68 % yield (58 mg) from **1a** (60 mg, 0.2 mmol) and **2d** (0.020 mL, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 6.93 (s, 2H), 6.65 (d, J = 4.5 Hz, 1H), 6.43 (d, J = 4.5 Hz, 2H), 6.37 – 6.36 (m, 1H), 3.47 – 3,41 (m, 1H), 2.35 (s, 3H), 2.17 – 2.14 (m, 2H), 2.09 (s, 6H), 1.88 – 1.84 (m, 2H), 1.69 – 1.62 (m, 3H), 1.47 – 1.33 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.69, 140.52, 139.46, 138.47, 137.05, 136.73, 133.92, 131.11, 129.88, 128.09, 125.81, 117.95, 116.56, 45.78, 33.51, 25.74, 25.40, 21.13, 19.99. HRMS calcd. For $C_{24}H_{27}BF_2N_2S$, $[M\text{-}F]^+$: 405.1972, found: 405.1976.

3i was prepared in 66 % yield (53 mg) from **1a** (60 mg, 0.2 mmol) and **2e** (0.020 mL, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.46 – 7.44 (m, 2H), 7.37 – 7.34 (m, 2H), 7.32 – 7.30 (m, 1H), 6.93 (s, 1H), 6.62 (d, J = 4.5 Hz, 1H), 6.48 (d, J = 3.8 Hz, 1H), 6.41 (d, J = 4.5 Hz, 1H), 6.39 – 6.38 (m, 1H), 4.35 (s, 2H), 2.34 (s, 3H), 2.08 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.57, 141.60, 140.63, 140.37, 138.55, 136.63, 134.91, 134.20, 130.99, 129.72, 128.90, 128.87, 128.08, 127.95, 126.64, 117.88, 117.02, 37.22, 21.09, 19.94. HRMS calcd. For $C_{25}H_{23}BF_2N_2S$, $[M\text{-}F]^+$: 413.1659, found: 413.1658.

3j was prepared in 65 % yield (65 mg) from **1a** (60 mg, 0.2 mmol) and **2f** (0.047 mL, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 6.93 (s, 2H), 6.66 (d, J = 4.5 Hz, 1H), 6.45 (d, J = 3.8 Hz, 1H), 6.41 (d, J = 4.5 Hz, 1H), 6.38 – 6.36 (m, 1H), 3.10 (t, J = 7.4 Hz, 2H), 2.35 (s, 3H), 2.09 (s, 6H), 1.83 – 1.81 (m, 2H), 1.52 – 1.45 (m, 2H), 1.37 – 1.26 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.17, 140.82, 139.67, 138.52, 137.22, 136.73, 134.02, 131.11, 129.87, 128.11, 126.04, 117.50, 116.69, 32.69, 31.92, 31.45, 29.71, 29.63, 29.56, 29.44, 29.34, 29.11, 28.84, 22.69, 21.12, 19.97, 14.11. HRMS calcd. For $C_{30}H_{41}BF_2N_2S$, $[M\text{-}F]^+$: 491.3068, found: 491.3068.

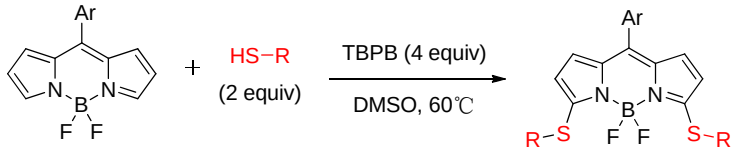
3k was prepared in 62 % yield (53 mg) from **1a** (60 mg, 0.2 mmol) and **2g** (0.022 mL, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 6.94 (s, 2H), 6.66 (d, J = 4.5 Hz, 1H), 6.52 (d, J = 4.0 Hz, 1H), 6.50 (d, J = 4.5 Hz, 1H), 6.41 – 6.40 (m, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.82 (s, 2H), 2.35 (s, 3H), 2.09 (s, 6H), 1.28 (d, J = 3.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.18, 158.20, 142.59, 141.29, 138.70, 137.09, 136.62, 134.47, 130.98, 129.61, 128.16, 127.46, 118.03, 117.48, 62.26, 34.70, 21.13, 19.97, 14.05. HRMS calcd. For $C_{22}H_{23}BF_2N_2O_2S$, $[M\text{-}F]^+$: 409.1557, found: 409.1555.

3l was prepared in 60 % yield (48 mg) from **1a** (60 mg, 0.2 mmol) and **2h** (0.014mL, 0.2 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 6.94 (s, 2H), 6.67 (d, J = 4.4 Hz, 1H), 6.51 (d, J = 3.8 Hz, 1H), 6.48 (d, J = 4.5 Hz, 1H), 6.41 – 6.40 (m, 1H), 3.94 (t, J = 5.9 Hz, 2H), 3.30 (t, J = 6.0 Hz, 2H), 2.35 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.59, 141.66, 141.33, 139.06, 137.45, 137.01, 134.75, 131.33, 128.53, 128.43, 127.54, 118.54, 117.70, 61.47, 36.43, 21.50, 20.35. HRMS calcd. For $C_{20}H_{21}BF_2N_2OS$, $[M\text{-}2F\text{-}H]^+$: 347.1389, found: 347.1388.

3m was prepared in 54 % yield (46 mg) from **1a** (60 mg, 0.2 mmol) and **2i** (24 mg, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.92 (s, 2H), 6.49 (d, J = 4.5 Hz, 1H), 6.46 (d, J = 3.9 Hz, 1H), 6.39 – 6.38 (m, 1H), 5.79 (d, J = 4.5 Hz, 1H), 2.41 (s, 3H), 2.33 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.05, 141.35, 140.70, 139.65, 138.48, 137.53, 136.64, 135.38, 133.99, 130.60, 130.54, 129.75, 128.06, 126.11, 125.08, 119.14, 116.67, 21.33, 21.08, 19.93. HRMS calcd. For $C_{25}H_{23}BF_2N_2S$, $[M\text{-}F]^+$: 413.1659, found: 413.1662.

3n was prepared in 43 % yield (39 mg) from **1a** (60 mg, 0.2 mmol) and **2j** (28 mg, 0.2 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.63 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 6.93 (s, 2H), 6.52 (d, J = 3.9 Hz, 1H), 6.50 (s, 1H), 6.41 (m, 1H), 5.80 (d, J = 4.5 Hz, 1H), 2.34 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.81, 142.74, 141.12, 139.04, 137.74, 136.99, 136.91, 134.71, 130.93, 130.50, 130.00, 128.52, 127.88, 127.44, 119.24, 117.61, 105.38, 21.49, 20.34. HRMS calcd. For $C_{24}H_{20}BClF_2N_2S$, $[M\text{-}F]^+$: 433.1113, found: 433.1109.

3o was prepared in 80 % yield (54 mg) from **1f** (68 mg, 0.2 mmol) and **2a** (28 mg, 0.2 mmol**)**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 2H), 6.64 (d, J = 4.4 Hz, 1H), 6.43 (d, J = 4.5 Hz, 1H), 6.37 (d, J = 3.7 Hz, 1H), 6.24 (d, J = 3.9 Hz, 1H), 3.09 (t, J = 7.3 Hz, 2H), 2.35 (s, 3H), 2.09 (s, 6H), 1.90 – 1.81 (m, 2H), 1.11 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.90, 139.01, 138.94, 138.70, 137.01, 136.83, 133.02, 130.97, 129.02, 128.15, 126.06, 118.08, 116.42, 34.62, 22.49, 21.13, 19.94, 13.41. HRMS calcd. For $C_{21}H_{22}BClF_2N_2S$, $[M\text{-}F]^+$: 399.1269, found:399.1262.



General radical C–H dithiolization procedure: BODIPY **1** (1 equiv, 0.2 mmol), **2** (2 equiv, 0.4 mmol), the oxidant *tert*-butylperoxy benzoate (TBPB), (4 equiv, 0.8 mmol) were dissolved in dimethyl sulfoxide (2 mL). The reaction mixture was stirred at 60 ^{o}C and the reaction was followed by TLC. Upon completion, the reaction mixture was cooled to room temperature and was poured into dichloromethane (100 mL), washed three times with water (100 mL), dried over Na_2SO_4, filtered, and

evaporated to dryness. The crude product was purified by column chromatographically (silica; petroleum ether/ethyl acetate; 30:1-15:1 v/v).

4a was prepared in 88 % yield (79 mg) from **1a** (60 mg, 0.2 mmol) and **2a** (0.040 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (s, 2H), 6.46 (d, J = 4.2 Hz, 2H), 6.30 (d, J = 4.2 Hz, 2H), 3.09 – 2.99 (m, 4H), 2.34 (s, 3H), 2.09 (s, 6H), 1.86 – 1.79 (m, 4H), 1.09 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.54, 138.26, 136.95, 136.51, 135.82, 129.79, 128.00, 127.82, 116.15, 34.72, 22.45, 21.09, 19.92, 13.44. HRMS calcd. For $C_{24}H_{29}BF_2N_2S_2$, $[M\text{-}F]^+$: 439.1849, found:439.1847.

4b was prepared in 75 % yield (61 mg) from **1b** (54 mg, 0.2 mmol) and **2a** (0.040 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 5H), 6.71 (d, J = 4.3 Hz, 2H), 6.38 (d, J = 4.3 Hz, 2H). 3.04 (t, J = 7.3 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.08 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.56, 141.49, 140.06, 137.26, 134.37, 134.22, 132.91, 130.79, 130.51, 128.73, 127.81, 117.99, 117.15, 34.99, 22.98, 13.83. HRMS calcd. For $C_{21}H_{23}BF_2N_2S_2$, $[M\text{-}F]^+$: 397.1380, found: 397.1375.

4c was prepared in 83 % yield (80 mg) from **1c** (71 mg, 0.2 mmol) and **2a** (0.040 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 (d, J = 4.2 Hz, 1H), 6.40 (d, J = 4.4 Hz, 1H), 3.07 (t, J = 7.3 Hz, 2H), 1.87 – 1.79 (m, 2H), 1.09 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.76, 146.20, 144.26, 144.16, 139.08, 135.80, 127.88, 118.63, 117.53, 35.21, 22.87, 13.76. HRMS calcd. For $C_{21}H_{18}BF_7N_2S_2$, $[M\text{-}F]^+$: 487.0909, found: 487.0900.

4d was prepared in 80 % yield (76 mg) from **1d** (67 mg, 0.2 mmol) and **2a** (0.040 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.43 (m, 2H), 7.38 – 7.34 (m, 1H), 6.47 (d, J = 4.3 Hz, 2H), 6.34 (d, J = 4.3 Hz, 2H), 3.05 (t, J = 7.3 Hz, 4H), 1.86 – 1.79 (m, 4H), 1.09 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.27, 136.30, 135.64, 132.08, 131.13, 130.49, 128.49, 127.75, 116.97, 35.18, 22.85, 13.82. $C_{21}H_{21}BCl_2F_2N_2S_2$, $[M+H]^+$: 485.0657, found: 485.0656.

4e was prepared in 73 % yield (64 mg) from **1e** (59 mg, 0.2 mmol) and **2a** (0.040 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 9.7 Hz, 2H), 6.99 (d, J = 7.0 Hz, 2H), 6.75 (d, J = 4.0 Hz, 2H), 6.38 (d, J = 4.1 Hz, 2H), 3.88 (s, 3H), 3.04 (t, J = 7.2 Hz, 4H), 1.85 – 1.78 (m, 4H), 1.08 (t, J = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.45, 156.51, 137.78, 136.14, 132.28, 129.46, 126.79, 116.69, 114.18,

55.83, 35.26, 22.89, 13.82. HRMS calcd. For $C_{22}H_{25}BF_2N_2OS_2$, $[M-F]^+$: 427.1485, found: 427.1480.

4f was prepared in 82 % yield (74 mg) from **1a** (60 mg, 0.2 mmol) and **2b** (0.044 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (s, 2H), 6.47 (d, J = 4.2 Hz, 2H), 6.35 (d, J = 4.3 Hz, 2H), 3.64 – 3.56 (m, 2H), 2.34 (s, 3H), 2.09 (s, 6H), 1.47 (d, J = 6.7 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.26, 138.69, 137.37, 137.19, 136.11, 130.24, 128.42, 128.27, 117.73, 38.19, 23.91, 21.51, 20.38. HRMS calcd. For $C_{24}H_{29}BF_2N_2S_2$, $[M-F]^+$: 439.1849, found: 439.1848.

4g was prepared in 78 % yield (74 mg) from **1a** (60 mg, 0.2 mmol) and **2c** (0.048 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.55 (d, J = 4.2 Hz, 1H), 6.49 (d, J = 4.2 Hz, 1H), 2.35 (s, 1H), 2.09 (s, 3H), 1.55 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.20, 138.44, 136.89, 135.76, 129.88, 128.08, 127.71, 122.01, 48.82, 31.62, 21.13, 20.03. HRMS calcd. For $C_{26}H_{33}BF_2N_2S_2$, $[M-F]^+$: 467.2162, found: 467.2158.

4h was prepared in 75 % yield (79 mg) from **1a** (60 mg, 0.2 mmol) and **2d** (0.040 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (s, 2H), 6.44 (d, J = 4.2 Hz, 2H), 6.33 (d, J = 3.3 Hz, 2H), 3.40 – 3.36 (m, 2H), 2.34 (s, 3H), 2.13 – 2.11 (m, 4H), 2.09 (s, 6H), 1.85 – 1.81 (m, 4H), 1.64 – 1.57 (m, 6H), 1.43 – 1.33 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.74, 138.26, 137.02 136.39, 135.70, 129.91, 128.02, 127.71, 117.15, 45.89, 33.45, 25.75, 25.55, 21.13, 20.00. HRMS calcd. For $C_{30}H_{37}BF_2N_2S_2$, $[M-F]^+$: 519.2475, found: 519.2472.

4i was prepared in 72 % yield (79 mg) from **1a** (60 mg, 0.2 mmol) and **2e** (0.040 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.2 Hz, 4H), 7.33 – 7.30 (m, 4H), 7.28 (s, 1H), 7.25 (s, 1H), 6.90 (s, 2H), 6.43 (d, J = 4.3 Hz, 2H), 6.29 (d, J = 4.3 Hz, 2H), 4.29 (s, 4H), 2.33 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.78, 138.39, 137.61, 136.86, 135.93, 135.50, 129.63, 128.92, 128.70, 128.11, 128.03, 127.68, 117.31, 37.57, 21.08, 19.91. HRMS calcd. For $C_{32}H_{29}BF_2N_2S_2$, $[M-F]^+$: 535.1849, found: 535.1848.

4j was prepared in 73 % yield (98 mg) from **1a** (60 mg, 0.2 mmol) and **2f** (0.094 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (s, 2H), 6.45 (d, J = 4.2 Hz, 2H), 6.29 (d, J = 4.3 Hz, 2H), 3.05 (t, J = 7.4 Hz, 4H), 2.34 (s, 3H), 2.09 (s, 6H), 1.80 – 1.75 (m, 4H), 1.49 – 1.43 (m, 4H), 1.33 – 1.26 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR

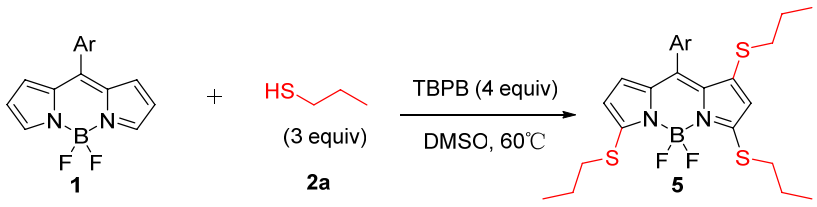
(126 MHz, $CDCl_3$) δ 157.06, 138.66, 137.38, 136.86, 136.24, 130.24, 128.41, 128.20, 116.51, 33.21, 32.30, 30.01, 30.00, 29.95, 29.84, 29.72, 29.52, 29.38, 29.23, 23.07, 21.49, 20.33, 14.49. HRMS calcd. For $C_{42}H_{65}BF_2N_2S_2$, $[M-F]^+$: 691.4666, found: 691.4659.

4k was prepared in 74 % yield (77 mg) from **1a** (60 mg, 0.2 mmol) and **2g** (0.44 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (s, 2H), 6.51 (d, J = 4.3 Hz, 2H), 6.44 (d, J = 4.3 Hz, 2H), 4.23 (q, J = 7.1 Hz, 4H), 3.79 (s, 4H), 2.34 (s, 3H), 2.08 (s, 6H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.82, 154.82, 139.30, 139.00, 137.21, 136.69, 129.76, 129.05, 128.51, 118.21, 62.47, 35.59, 21.49, 20.32, 14.43. HRMS calcd. For $C_{26}H_{29}BF_2N_2O_4S_2$, $[M-F]^+$: 527.1646, found: 527.1645.

4l was prepared in 62 % yield (57 mg) from **1a** (60 mg, 0.2 mmol) and **2h** (0.28 mL, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 2H), 6.52 (d, J = 4.2 Hz, 2H), 6.42 (d, J = 4.3 Hz, 2H), 3.90 (t, J = 5.8 Hz, 4H), 3.26 (t, J = 5.9 Hz, 4H), 2.35 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.28, 137.21, 136.56, 128.89, 128.53, 127.82, 121.43, 118.47, 117.99, 61.34, 37.16, 21.49, 20.35. HRMS calcd. For $C_{22}H_{25}BF_2N_2O_2S_2$, $[M-2F-H]^+$: 423.1372, found: 423.1376.

4m was prepared in 43 % yield (47 mg) from **1a** (60 mg, 0.2 mmol) and **2i** (48mg, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.1 Hz, 4H), 7.23 (d, J = 8.0 Hz, 4H), 6.89 (s, 2H), 6.31 (d, J = 4.3 Hz, 2H), 5.75 (d, J = 3.8 Hz, 2H), 2.39 (s, 6H), 2.31 (s, 3H), 2.08 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.41, 140.05, 138.31, 137.52, 136.93, 136.18, 135.16, 130.43, 129.72, 128.03, 127.53, 126.40, 117.90, 21.33, 21.10, 19.96. HRMS calcd. For $C_{32}H_{29}BF_2N_2S_2$, $[M-F]^+$: 535.1849, found: 535.1853.

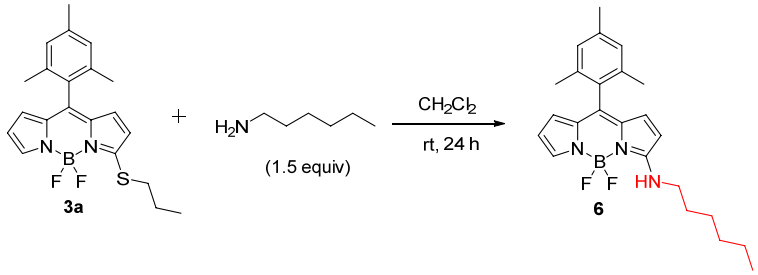
4n was prepared in 41 % yield (48 mg) from **1a** (60 mg, 0.2 mmol) and **2j** (56mg, 0.4 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.4 Hz, 4H), 7.40 (d, J = 8.4 Hz, 4H), 6.90 (s, 2H), 6.38 (d, J = 4.3 Hz, 2H), 5.81 (d, J = 4.4 Hz, 2H), 2.32 (s, 3H), 2.08 (s, 16H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.91, 138.77, 138.60, 136.80, 136.40, 136.11, 136.03, 129.94, 129.39, 128.73, 128.14, 128.08, 118.47 , 21.11, 19.97. HRMS calcd. For $C_{30}H_{23}BCl_2F_2N_2S_2$, $[M-F]^+$: 575.0757, found: 575.0759.



General radical C–H trithiolation procedure: BODIPY **1** (1 equiv, 0.2 mmol), **2** (3 equiv, 0.6 mmol), the oxidant *tert*-butylperoxy benzoate (TBPB), (4 equiv, 0.8 mmol) were dissolved in solvent (2 mL). The reaction mixture was stirred at 60 ^{o}C for 4 h. Upon completion, the reaction mixture was cooled to room temperature and was poured into dichloromethane (100 mL), washed three times with water (100 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatographically (silica; petroleum ether/ethyl acetate; 30:1-15:1 v/v).

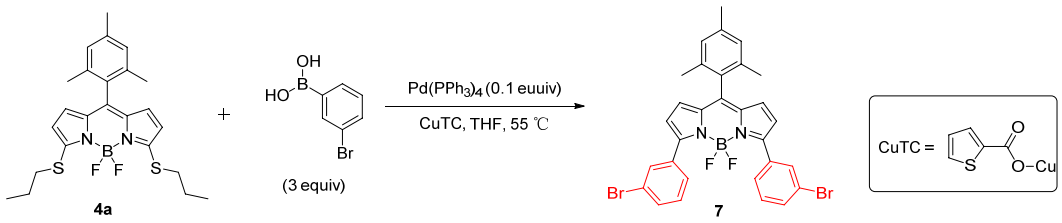
5a was prepared in 25 % yield (24 mg) from **1a** (60 mg, 0.2 mmol) and **2a** (0.060 mL, 0.6 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.30 (d, J = 4.1 Hz, 1H), 6.23 (d, J = 4.2 Hz, 1H), 6.02 (s, 1H), 3.04 – 2.99 (m, 4H), 2.68 (t, J = 7.3 Hz, 2H), 2.35 (s, 3H), 2.03 (s, 6H), 1.87 – 1.76 (m, 4H), 1.62 – 1.55 (m, 2H), 1.12 – 1.05 (m, 6H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.50, 152.19, 145.81, 139.19, 136.93, 135.35, 134.98, 132.48, 129.81, 129.05, 126.02, 115.66, 110.94, 35.38, 35.23, 34.97, 22.87, 22.69, 21.99, 21.68, 20.03, 13.89, 13.77. HRMS calcd. For $C_{27}H_{35}BF_2N_2S_3$, $[M\text{-}F]^+$: 513.2039, found: 513.2040.

5b was prepared in 27 % yield (26 mg) from **1b** (60 mg, 0.2 mmol) and **2a** (0.060 mL, 0.6 mmol**)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 3H), 7.30 – 7.28 (m, 2H), 6.33 (d, J = 4.3 Hz, 1H), 6.27 (d, J = 3.8 Hz, 1H), 6.07 (s, 1H), 3.04 – 2.99 (m, 4H), 2.67 (t, J = 7.2 Hz, 2H), 1.85 – 1.77 (m, 4H), 1.57 – 1.53 (m, 2H), 1.11 – 1.05 (m, 6H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.30, 152.41, 145.65, 136.33, 135.35, 133.38, 132.26, 129.52, 129.42, 128.64, 127.13, 115.66, 111.67, 35.52, 35.13, 34.69, 29.71, 22.56, 22.40, 21.53, 13.44. HRMS calcd. For $C_{24}H_{29}BF_2N_2S_3$, $[M+H]^+$: 491.1626, found: 491.1625.



BODIPY **3a** (38 mg, 0.1 mmol) and hexylamine (0.020 mL, 0.15 mmol) were dissolved in dichloromethane (2 mL) at room temperature for 24 h. Upon completion, the reaction mixture was poured into dichloromethane (100 mL), washed three times

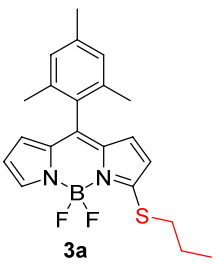
with water (100 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatographically (silica; petroleum ether/ethyl acetate; 20:1 v/v) to provide **6** in 45 % yield (18 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (s, 1H), 6.92 (s, 2H), 6.66 (d, J = 4.9 Hz, 1H), 6.27 – 6.25 (m, 2H), 6.12 (s, 1H), 6.11 (s, 1H), 3.39 (q, J = 6.8 Hz, 2H), 2.34 (s, 3H), 2.10 (s, 6H), 1.73 – 1.67 (m, 2H), 1.45 – 1.40 (m, 2H), 1.34 – 1.32 (m, 4H), 0.90 (t, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.09, 138.23, 137.67, 135.30, 134.06, 132.83, 132.12, 131.15, 130.78, 128.36, 118.96, 113.66, 110.64, 45.15, 31.75, 30.51, 26.68, 22.90, 21.52, 20.38, 14.38. HRMS calcd. For $C_{24}H_{30}BF_2N_3$, $[M]^+$: 409.2500, found: 409.2499.



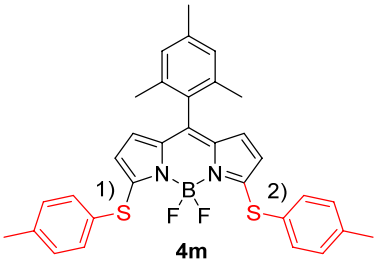
BODIPY **4a** (45 mg, 0.1 mmol), 3-bromophenylboronic acid (60 mg, 0.3 mmol), copper(I) thiophene-2-carboxylate (CuTC, 76 mg, 0.4 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) were dissolved in THF (2 mL). The mixture was monitored by TLC and was stirred at 55 °C for 16 h under nitrogen. Upon completion, the reaction mixture was cooled to room temperature and was poured into dichloromethane (100 mL), washed three times with water (100 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatographically (silica; petroleum ether/ethyl acetate; 30:1 v/v) to provide **7** in 65 % yield (35 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 2H), 7.91 (d, J = 7.9 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.9 Hz, 2H), 6.99 (s, 2H), 6.68 (d, J = 4.2 Hz, 2H), 6.55 (d, J = 4.1 Hz, 2H). 2.38 (s, 3H), 2.18 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.54, 145.54, 139.21, 137.19, 137.08, 134.80, 132.86, 132.51, 130.40, 130.23, 128.61, 128.53,128.49, 122.59, 121.36, 21.56, 20.49. HRMS calcd. For $C_{30}H_{23}BBr^{79}Br^{81}F_2N_2$, $[M\text{-}F]^+$: 601.0305, found: 601.0317.

5. Crystal data

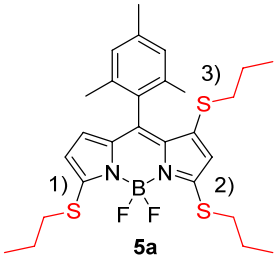
Table S2. Selected Geometrical Parameters of 3a, 4m, and 5a obtained from crystallography



3a



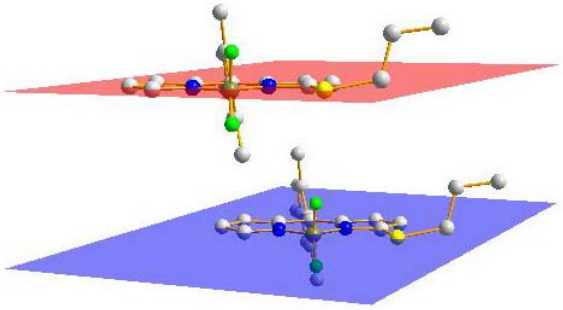
4m



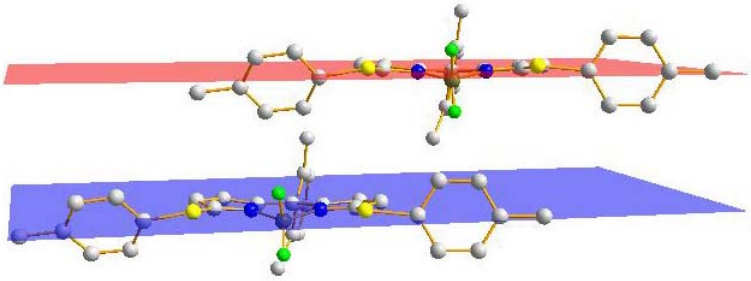
5a

	3a	**4m**	**5a**
B-N bond lengths (Å)	1.5375(27)	1.5506(29)	1.5380(48)
	1.5548(25)	1.5480(22)	1.5501(42)
C-S bond lengths (Å)	1.7329(19)	1.7345(31) (1)	1.7139(130) (1)
		1.7534(47) (2)	1.7215(34) (2)
			1.7355(33) (3)
dihedral angles between *meso*-mesityl group and dipyyrin core (deg)	82.035(43)	81.020(42)	88.342(79)
dihedral angles of two pyrrole rings in dipyyrin core (deg)	2.391(65)	10.774(62)	4.090(142)

3a



4m



5a

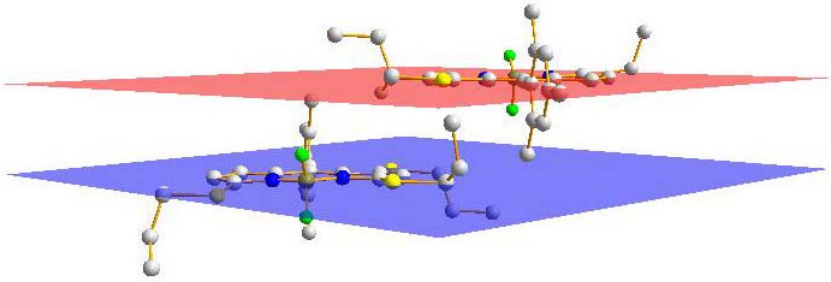


Figure S2 Intermolecular crystal packing of **3a**, **4m**, and **5a**: front view showing intermolecular distances.

6. Photophysical properties

6.1. Table S3: Photophysical properties of BODIPYs 3a-n, 4a-n, 2, 5a, 5b, 6 and 7 in CH_2Cl_2 at room temperature.

dyes	λ_{abs}^{max} (nm)	$\varepsilon_{abs}^{max\ a}$	λ_{em}^{max} (nm)	Φ	Stokes shift (cm^{-1})[d]
1a	500	54600	522	0.84[c]	840
3a	536	61300	551	0.81[b]	510
3b	537	64200	556	0.07[b]	640
3c	551	57400	573	0.77[b]	680
3d	546	73100	562	0.68[b]	520
3e	536	67600	553	0.05[b]	570
3f	536	66400	551	0.77[b]	510
3g	537	72100	552	0.82[b]	510
3h	537	68000	552	0.84[b]	510
3i	536	80200	550	0.84[b]	480
3j	537	67100	548	0.75[b]	470
3k	532	74800	546	0.77[b]	480
3l	534	57600	548	0.79[b]	480
3m	536	91100	557	0.02[b]	700
3n	535	52900	554	0.39[b]	640
3o	545	75700	556	0.61[b]	463
4a	577	64400	592	0.74[b]	440
4b	578	86700	597	0.46[b]	550
4c	559	85200	620	0.45[b]	570
4d	592	112400	609	0.58[b]	470
4e	576	91700	594	0.51[b]	530
4f	578	98000	593	0.82[b]	440
4g	564	68400	593	0.75[b]	760
4h	582	84700	596	0.78[b]	400
4i	578	103300	593	0.84[b]	440

4j	579	110900	594	0.76[b]	440
4k	568	89900	581	0.77[b]	400
4l	572	75200	588	0.71[b]	480
4m	581	105000	600	0.71[b]	550
4n	578	99100	597	0.61[b]	550
5a	575	87800	593	0.68[b]	530
5b	577	78600	598	0.11[b]	610
6	493	93500	522	0.89[c]	1130
7	553	53600	589	0.76[b]	1100

[a]Molar absorption coefficient values rounded to the nearest 100 M^{-1} cm^{-1}. [b]Fluorescence quantum yields determined using Rhodamine B ($\Phi = 0.49$ in ethanol) as reference. [c]Fluorescence quantum yields determined using fluorescein ($\Phi = 0.90$ in 0.1 N NaOH aqueous solution) as references. [d]Stokes shift values rounded to nearest 10 cm^{-1}.

6.2. UV-Vis absorption and fluorescence emission spectra in CH_2Cl_2.

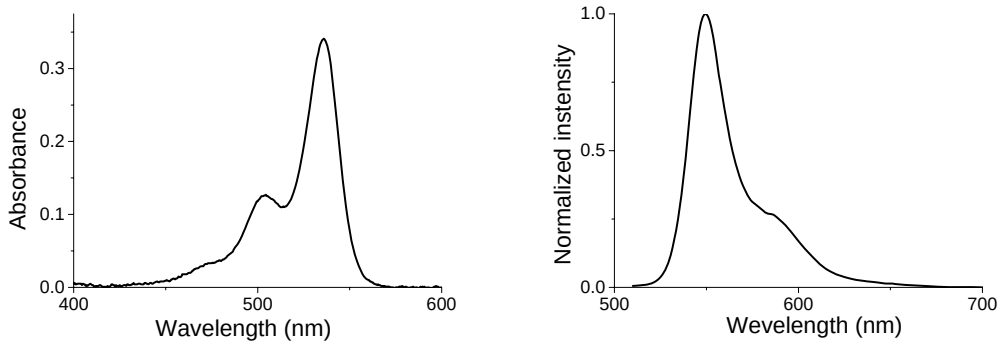


Figure S3. Absorption (left) and fluorescence emission (right) spectra of **3a** recorded in CH_2Cl_2 (excitation at 500 nm).

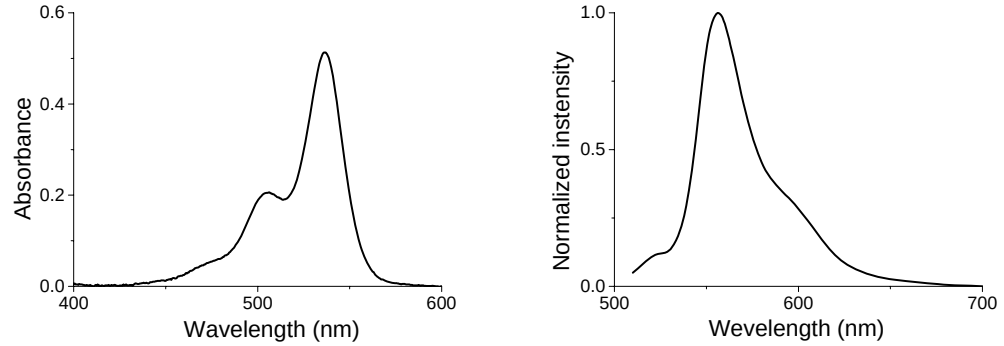


Figure S4. Absorption (left) and fluorescence emission (right) spectra of **3b** recorded in CH_2Cl_2 (excitation at 500 nm).

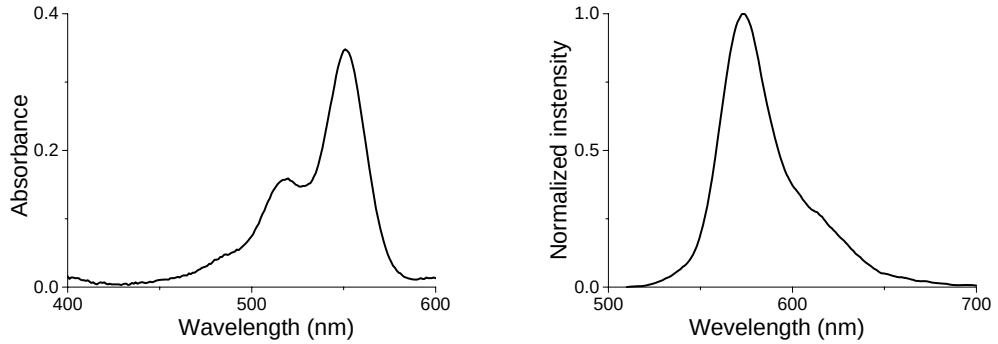


Figure S5. Absorption (left) and fluorescence emission (right) spectra of **3c** recorded in CH_2Cl_2 (excitation at 520 nm).

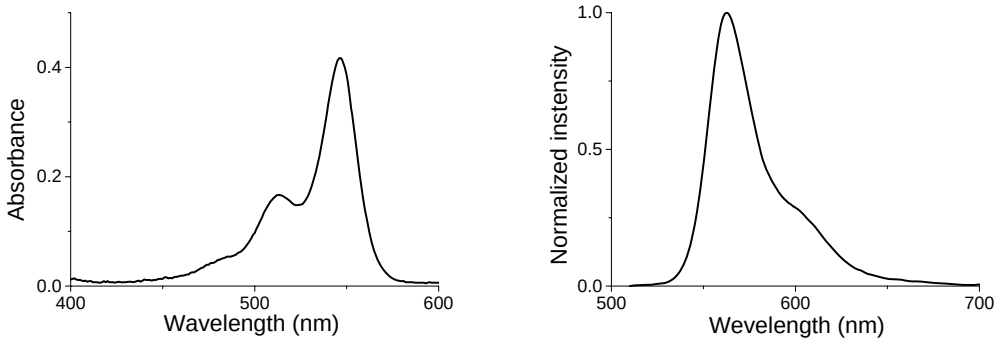


Figure S6. Absorption (left) and fluorescence emission (right) spectra of 3**d** recorded in CH_2Cl_2 (excitation at 500 nm).

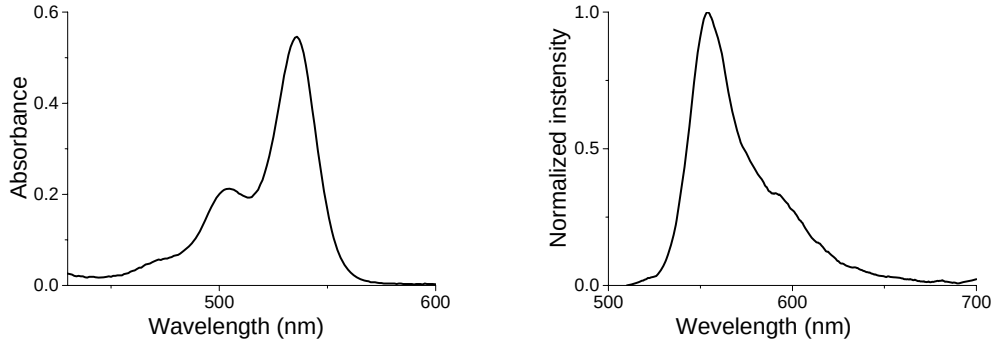


Figure S7. Absorption (left) and fluorescence emission (right) spectra of **3e** recorded in CH_2Cl_2 (excitation at 500 nm).

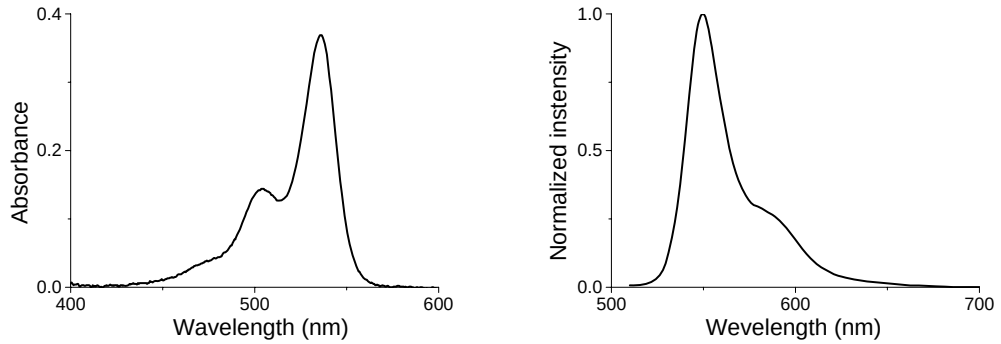


Figure S8. Absorption (left) and fluorescence emission (right) spectra of **3f** recorded in CH_2Cl_2 ($_2$ (excitation at 500 nm).

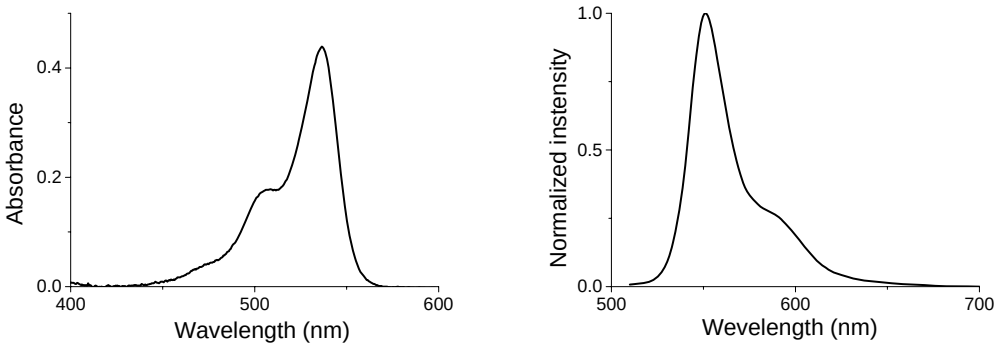


Figure S9. Absorption (left) and fluorescence emission (right) spectra of **3g** recorded in CH_2Cl_2 (excitation at 500 nm).

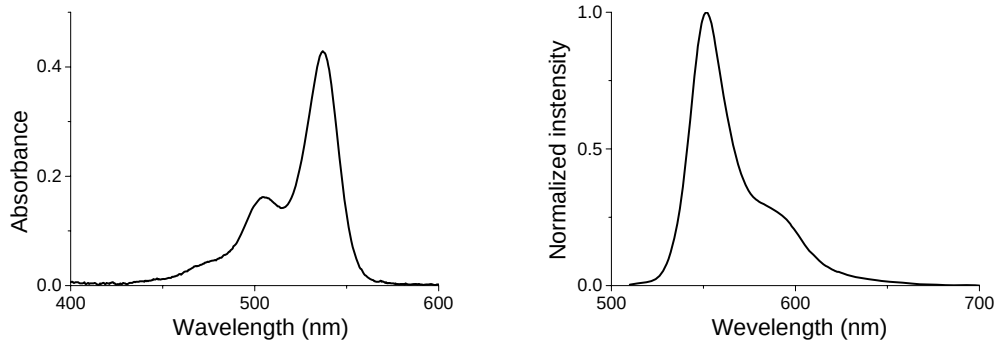


Figure S10. Absorption (left) and fluorescence emission (right) spectra of **3h** recorded in CH_2Cl_2 (excitation at 500 nm).

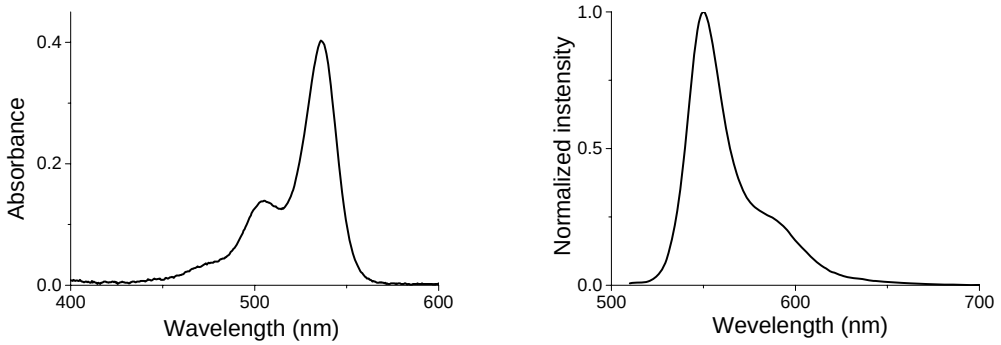


Figure S11. Absorption (left) and fluorescence emission (light) spectra of **3i** recorded in CH_2Cl_2 (excitation at 500 nm).

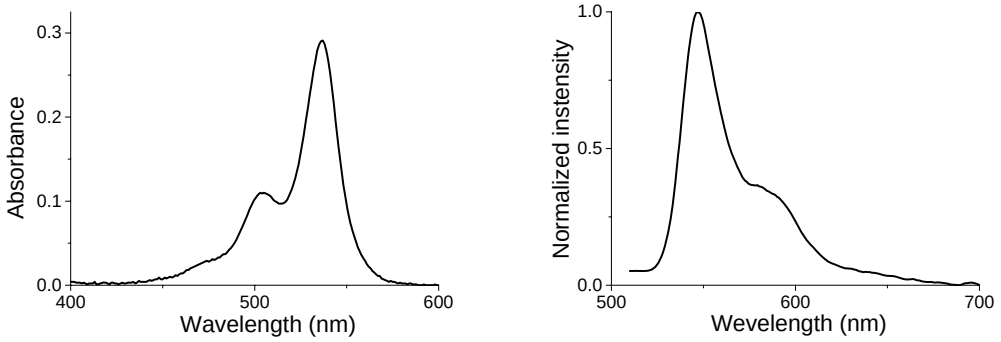


Figure S12. Absorption (left) and fluorescence emission (right) spectra of **3j** recorded in CH_2Cl_2 (excitation at 500 nm).

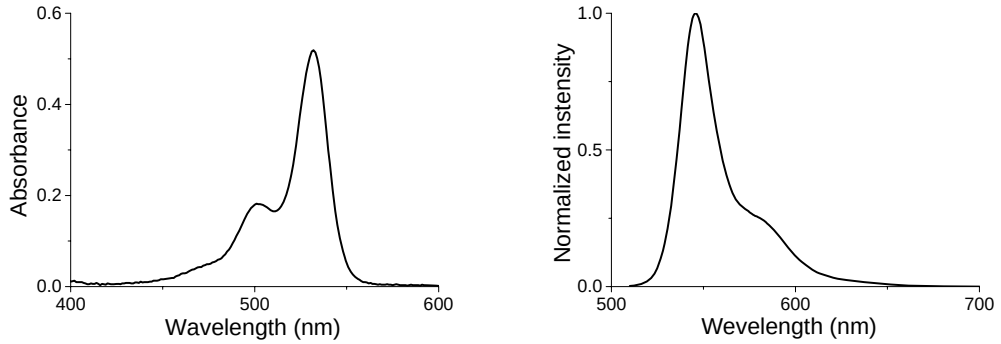


Figure S13. Absorption (left) and fluorescence emission (right) spectra of **3k** recorded in CH_2Cl_2 (excitation at 500 nm).

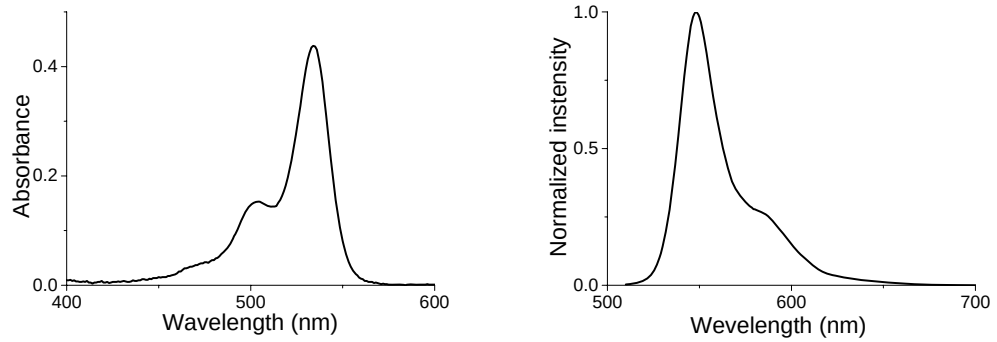


Figure S14. Absorption (left) and fluorescence emission (right) spectra of **3l** recorded in CH_2Cl_2 (excitation at 500 nm).

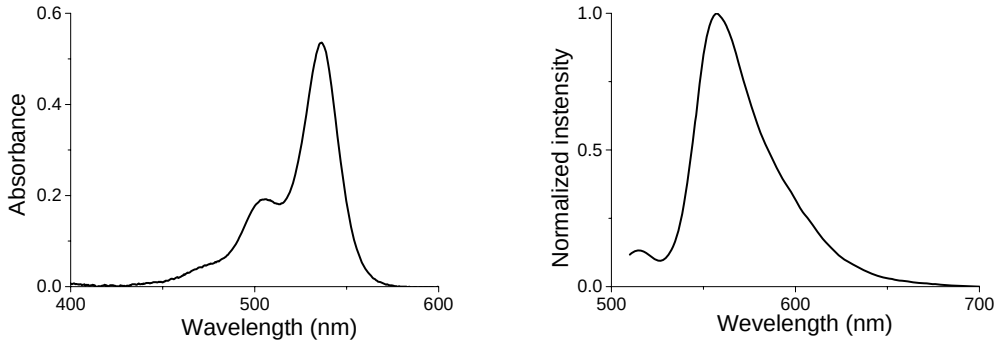


Figure S15. Absorption (left) and fluorescence emission (right) spectra of 3**m** recorded in CH_2Cl_2 (excitation at 500 nm).

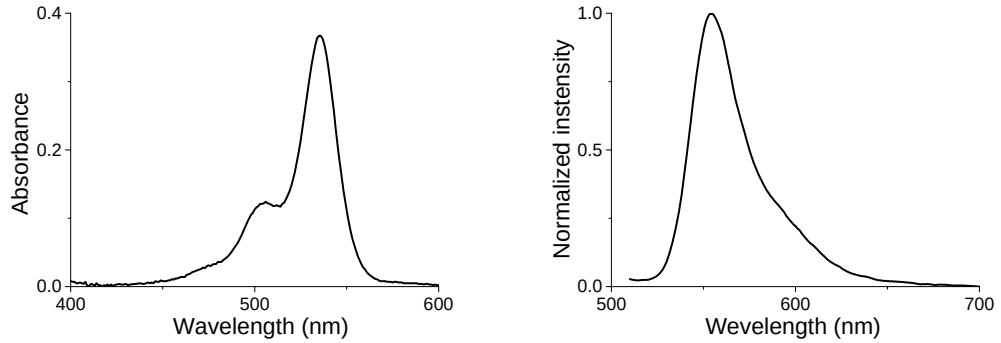


Figure S16. Absorption (left) and fluorescence emission (right) spectra of 3**n** recorded in CH_2Cl_2 (excitation at 500 nm).

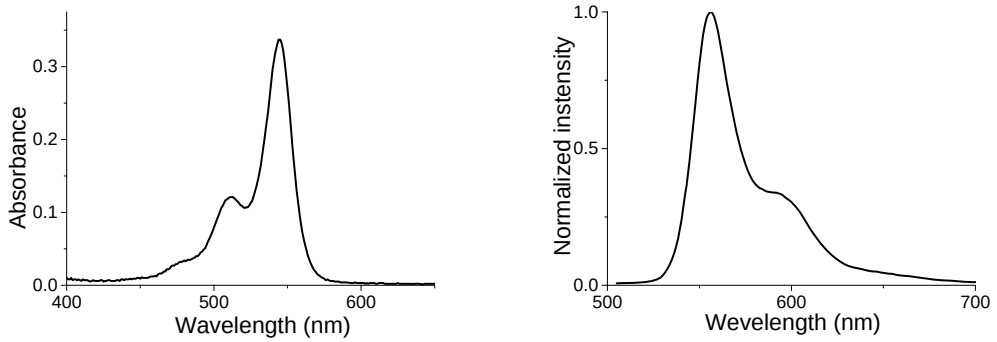


Figure S17. Absorption (left) and fluorescence emission (right) spectra of 3**o** recorded in CH_2Cl_2 (excitation at 500 nm).

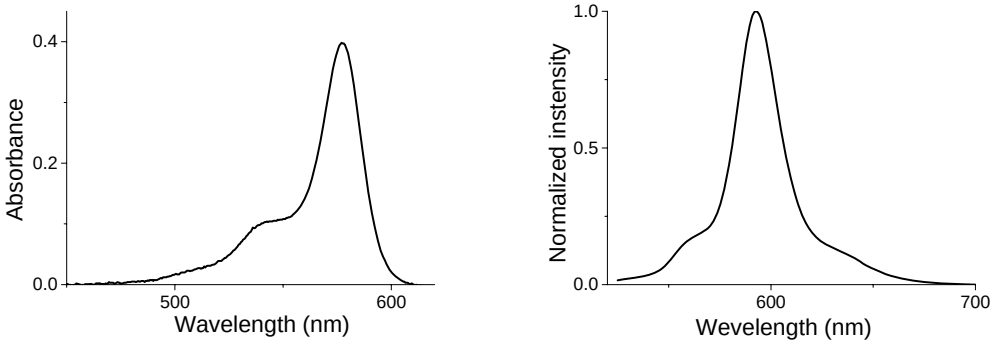


Figure S18. Absorption (left) and fluorescence emission (right) spectra of **4a** recorded in CH_2Cl_2 (excitation at 520 nm).

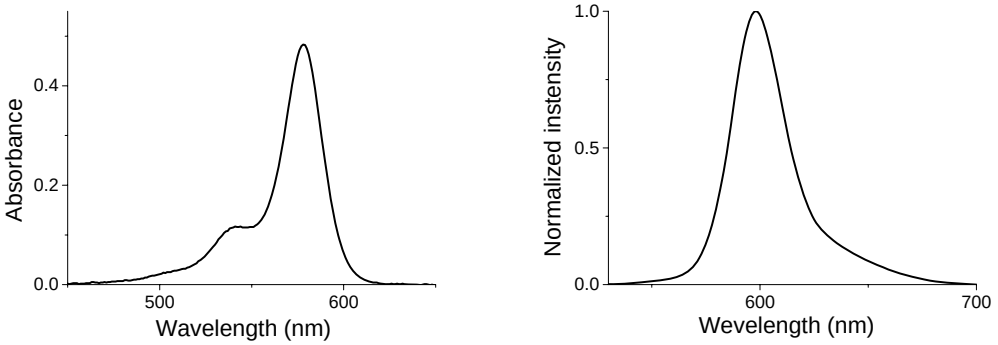


Figure S19. Absorption (left) and fluorescence emission (right) spectra of **4b** recorded in CH_2Cl_2 (excitation at 520 nm).

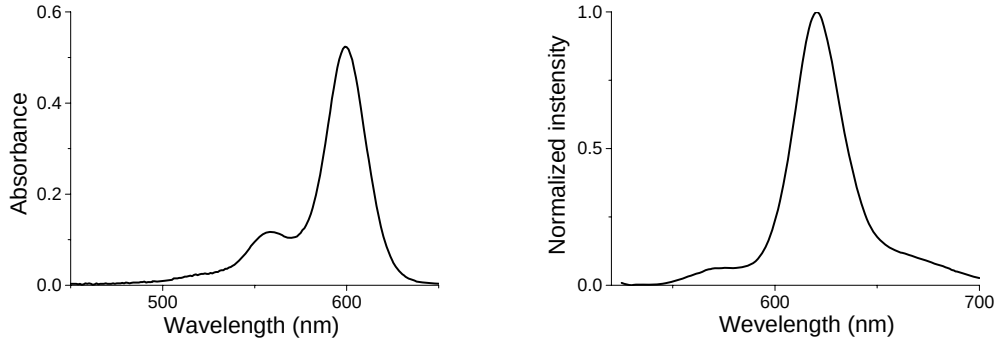


Figure S20. Absorption (left) and fluorescence emission (right) spectra of **4c** recorded in CH_2Cl_2 (excitation at 520 nm).

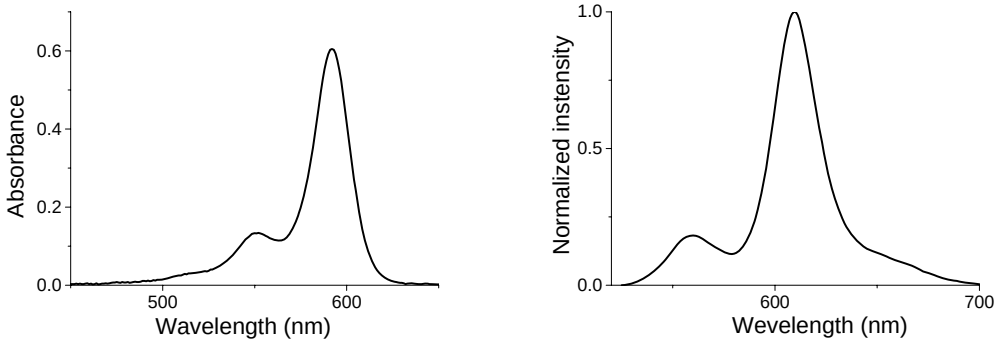


Figure S21. Absorption (left) and fluorescence emission (right) spectra of **4d** recorded in CH_2Cl_2 (excitation at 520 nm).

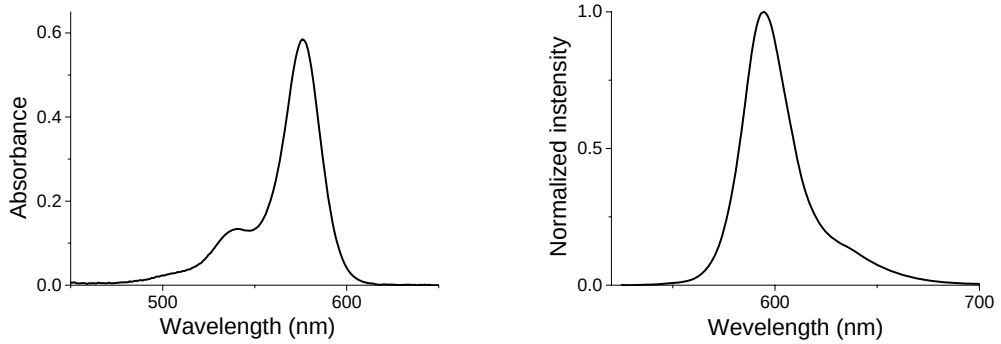


Figure S22. Absorption (left) and fluorescence emission (right) spectra of **4e** recorded in CH_2Cl_2 (excitation at 520 nm).

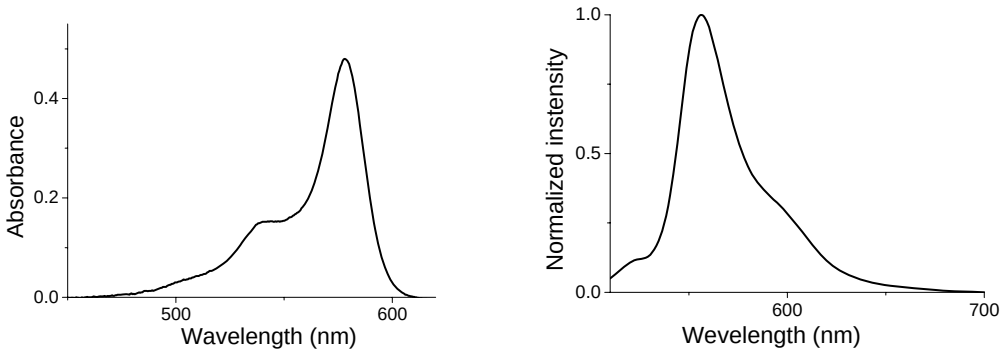


Figure S23. Absorption (left) and fluorescence emission (right) spectra of **4f** recorded in CH_2Cl_2 (excitation at 520 nm).

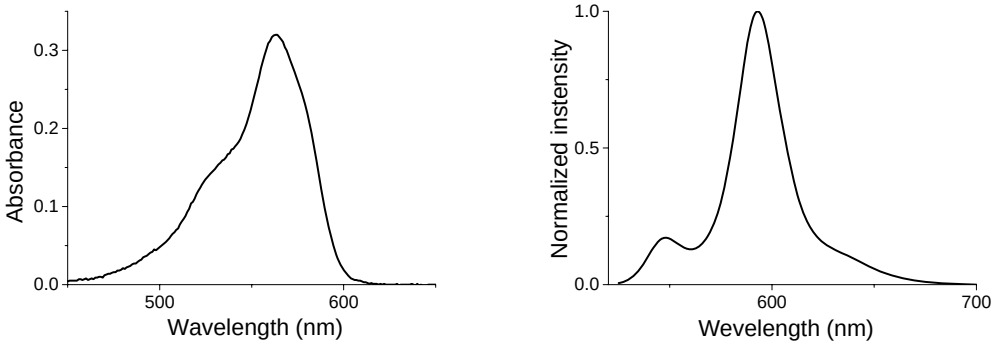


Figure S24. Absorption (left) and fluorescence emission (right) spectra of **4g** recorded in CH_2Cl_2 (excitation at 520 nm).

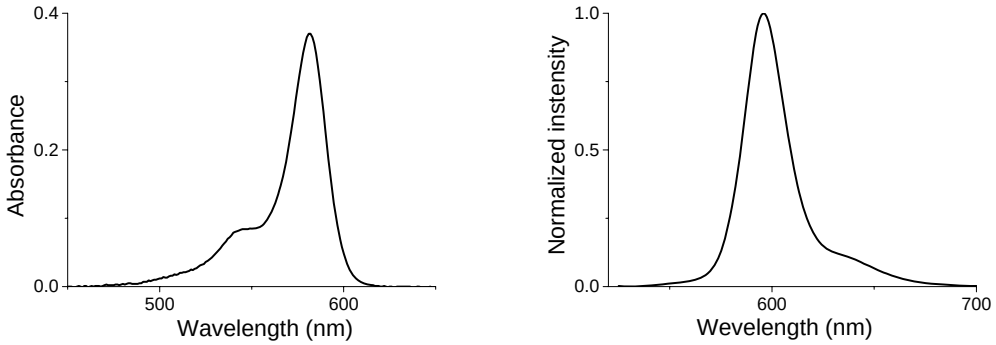


Figure S25. Absorption (left) and fluorescence emission (right) spectra of **4h** recorded in CH_2Cl_2 (excitation at 520 nm).

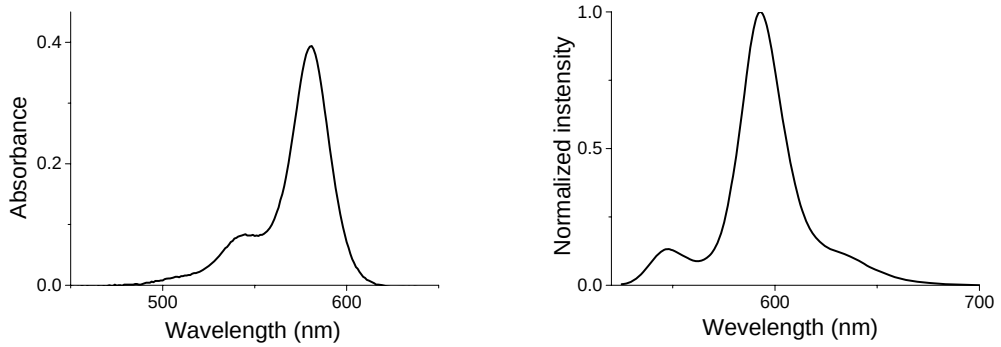


Figure S26. Absorption (left) and fluorescence emission (right) spectra of **4i** recorded in CH_2Cl_2 (excitation at 520 nm).

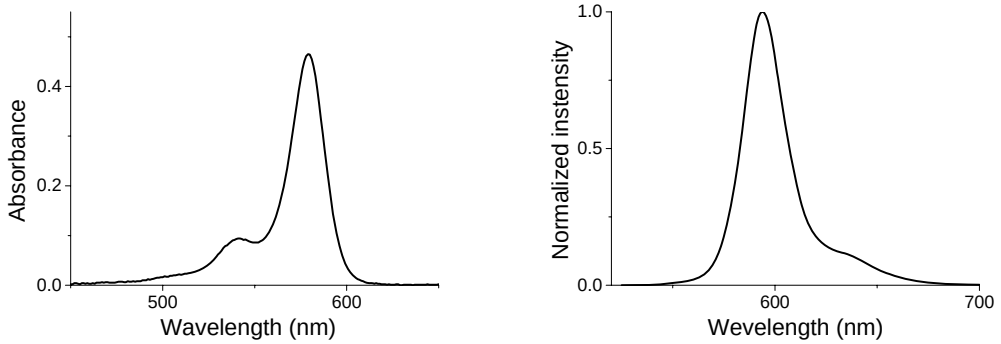


Figure S27. Absorption (left) and fluorescence emission (right) spectra of **4j** recorded in CH_2Cl_2 (excitation at 520 nm).

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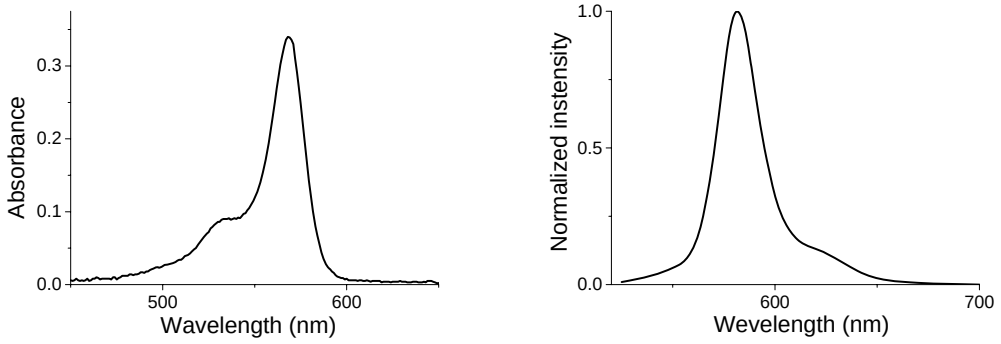


Figure S28. Absorption (left) and fluorescence emission (right) spectra of **4k** recorded in CH_2Cl_2 (excitation at 520 nm).

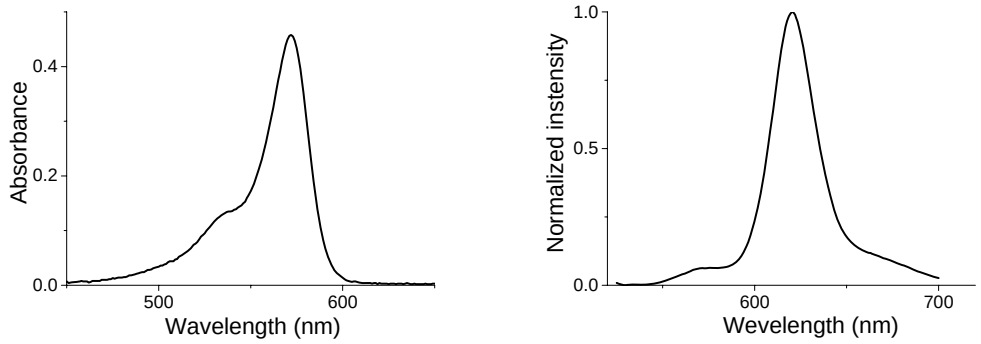


Figure S29. Absorption (left) and fluorescence emission (right) spectra of **4l** recorded in CH_2Cl_2 (excitation at 520 nm).

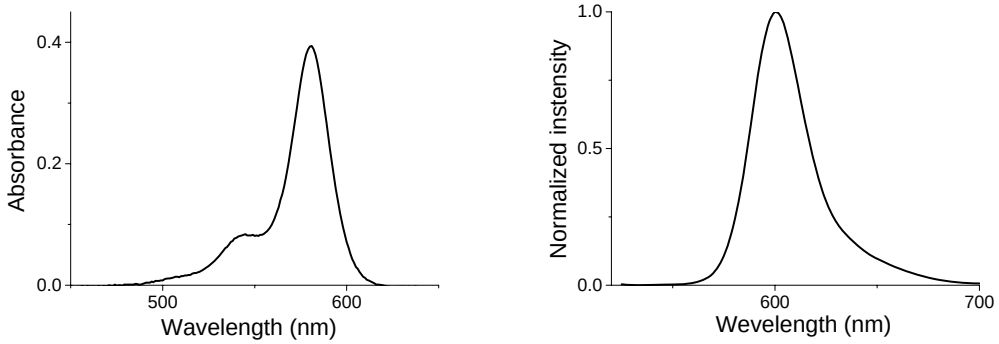


Figure S30. Absorption (left) and fluorescence emission (right) spectra of **4m** recorded in CH_2Cl_2 (excitation at 520 nm).

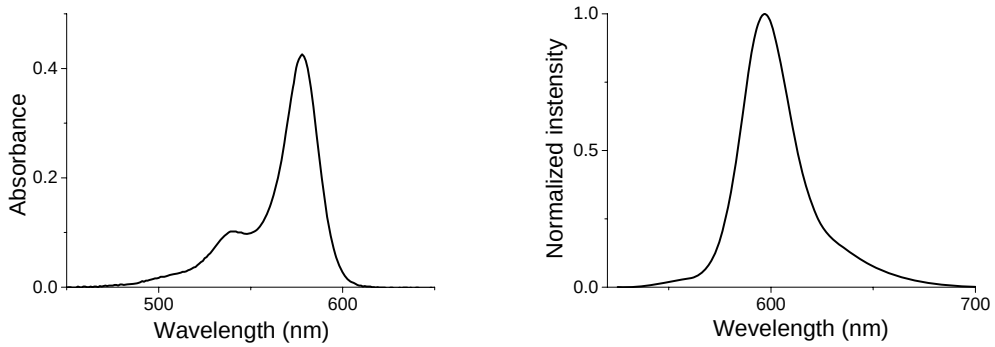


Figure S31. Absorption (left) and fluorescence emission (right) spectra of **4n** recorded in CH_2Cl_2 (excitation at 520 nm).

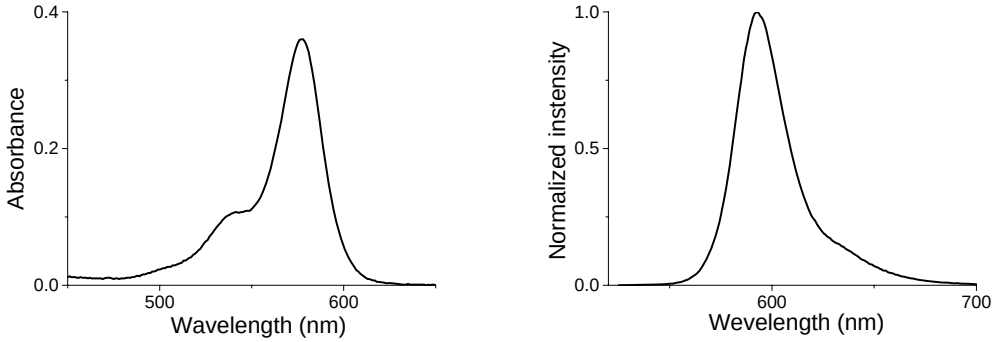


Figure S32. Absorption (left) and fluorescence emission (right) spectra of **5a** recorded in CH_2Cl_2 (excitation at 520 nm).

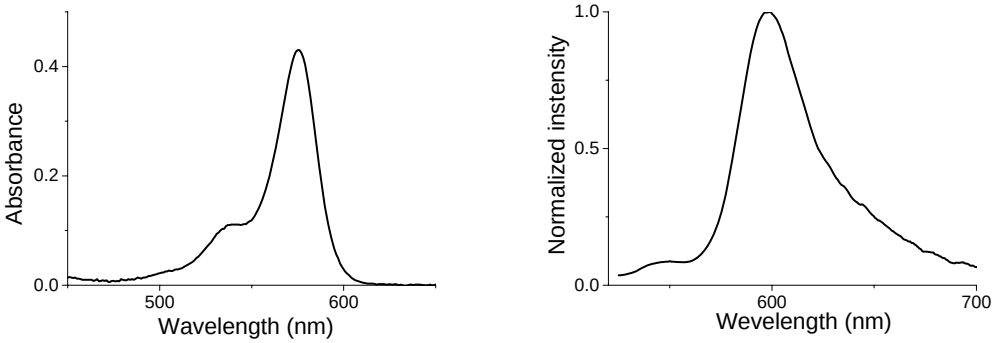


Figure S33. Absorption (left) and fluorescence emission (right) spectra of **5b** recorded in CH_2Cl_2 (excitation at 520 nm).

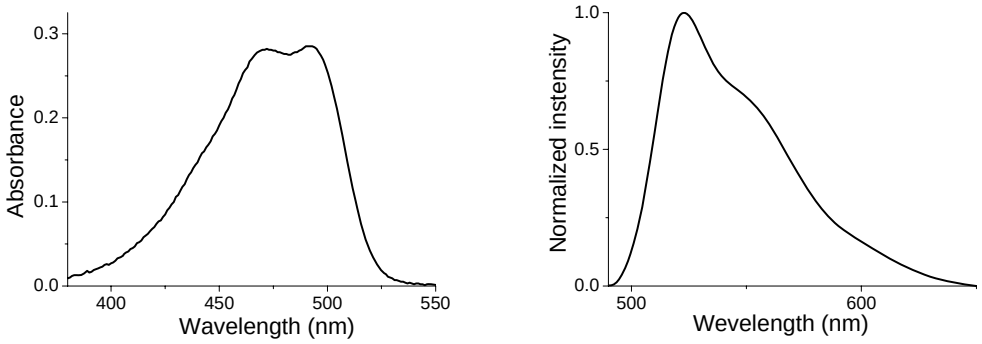


Figure S34. Absorption (left) and fluorescence emission (right) spectra of **6** recorded in CH_2Cl_2 (excitation at 480 nm).

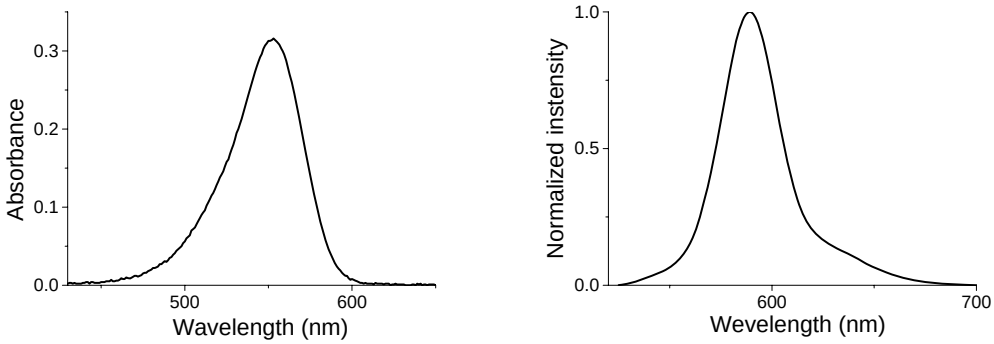
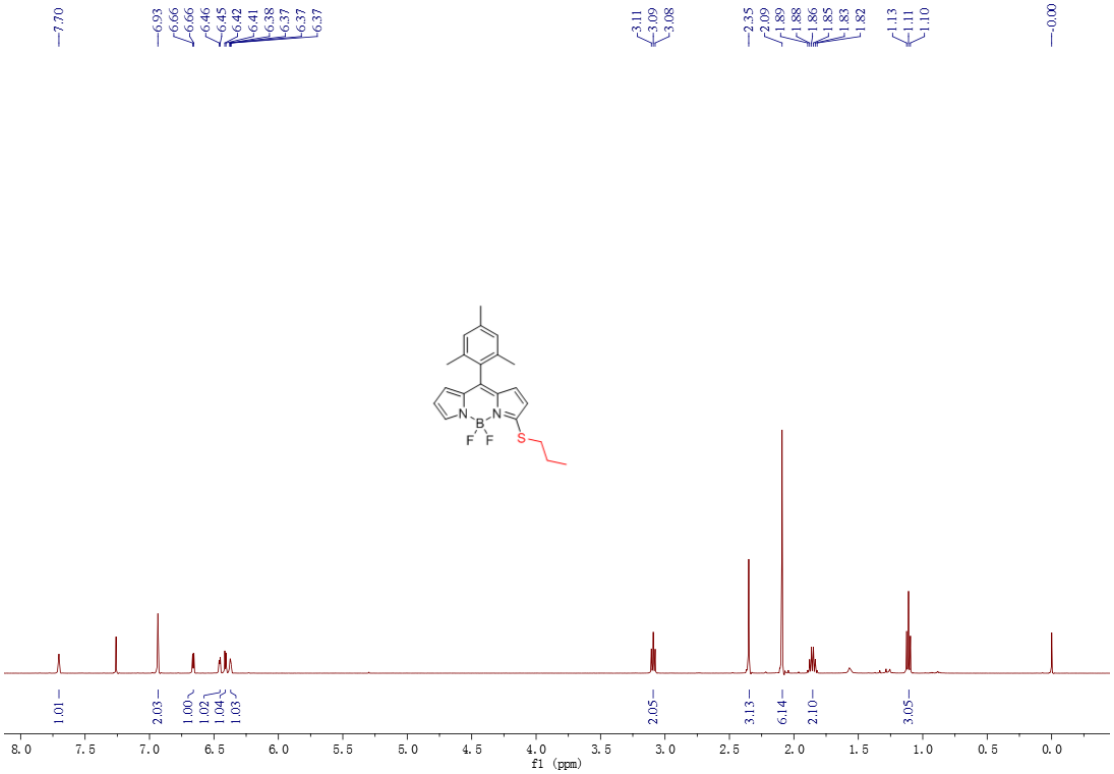


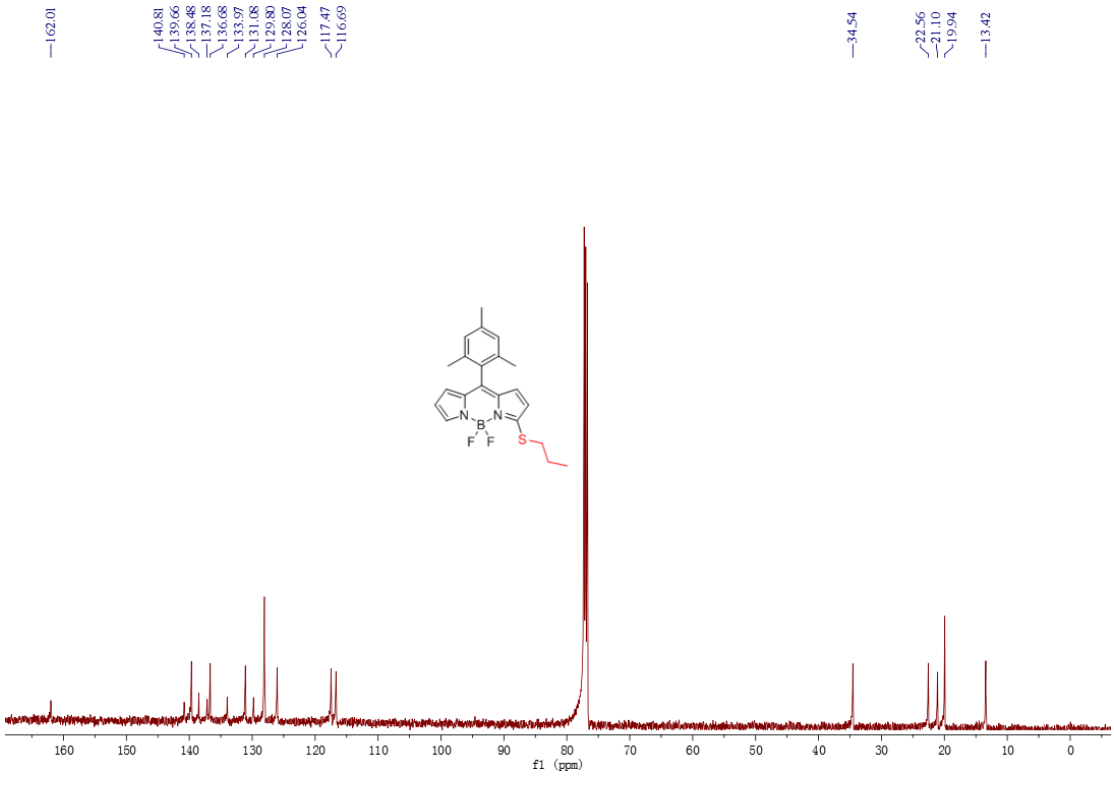
Figure S35. Absorption (left) and fluorescence emission (right) spectra of **7** recorded in CH_2Cl_2 (excitation at 520 nm).

7. NMR and HRMS spectra of all new compounds

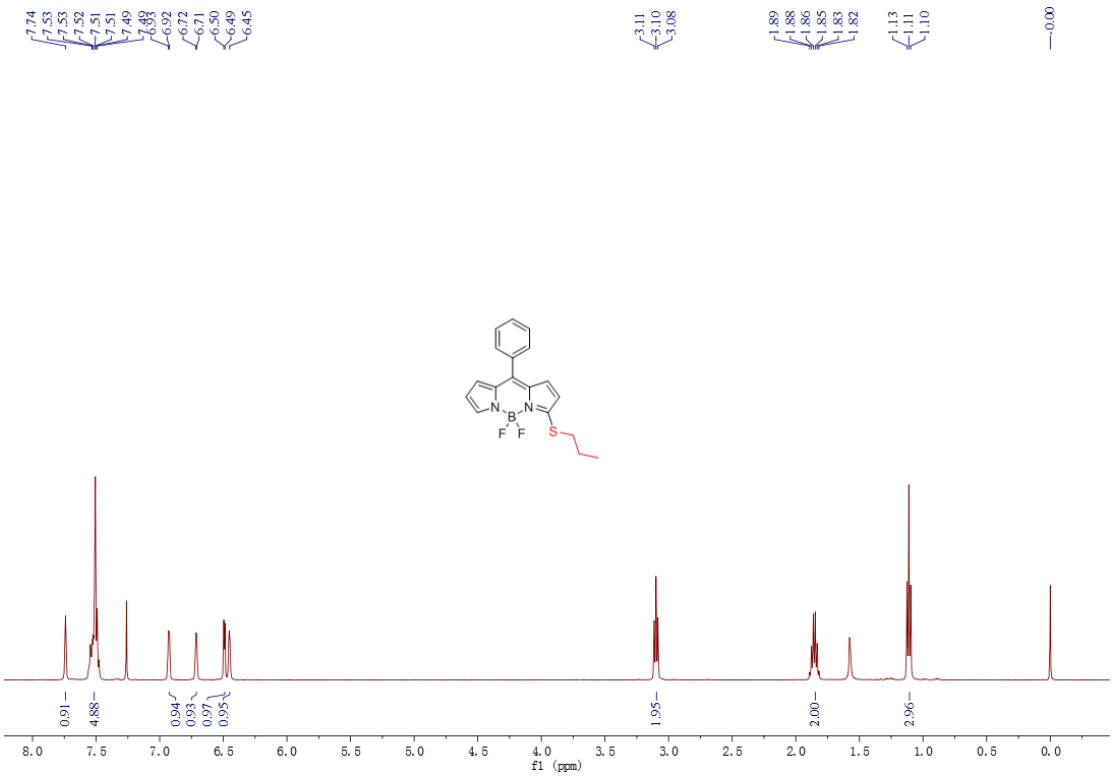
^{1}H NMR spectrum of **3a** in $CDCl_3$



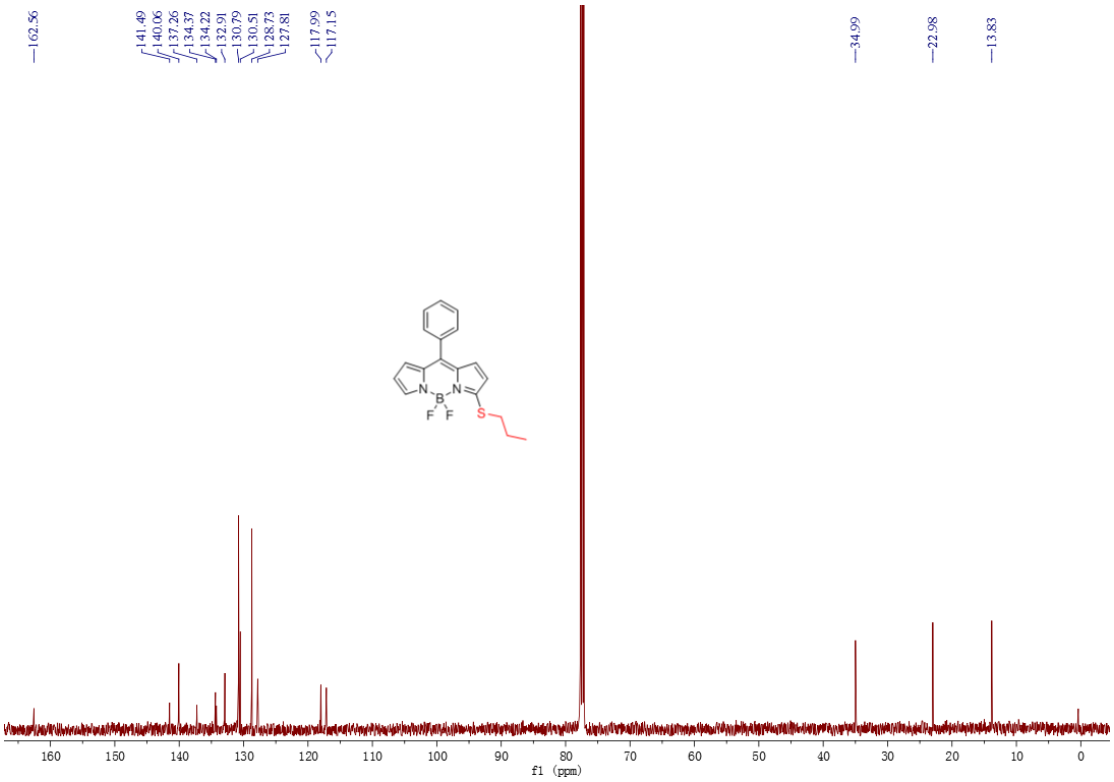
^{13}C NMR spectrum of **3a** in $CDCl_3$



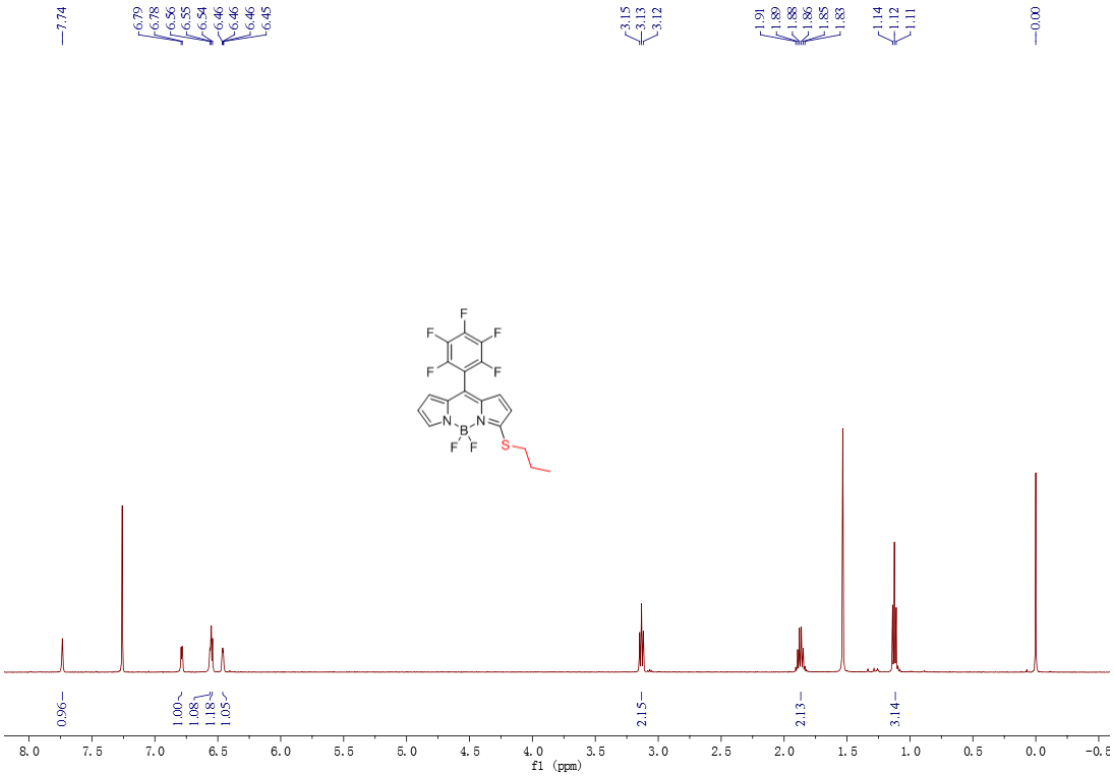
^{1}H NMR spectrum of **3b** in $CDCl_3$



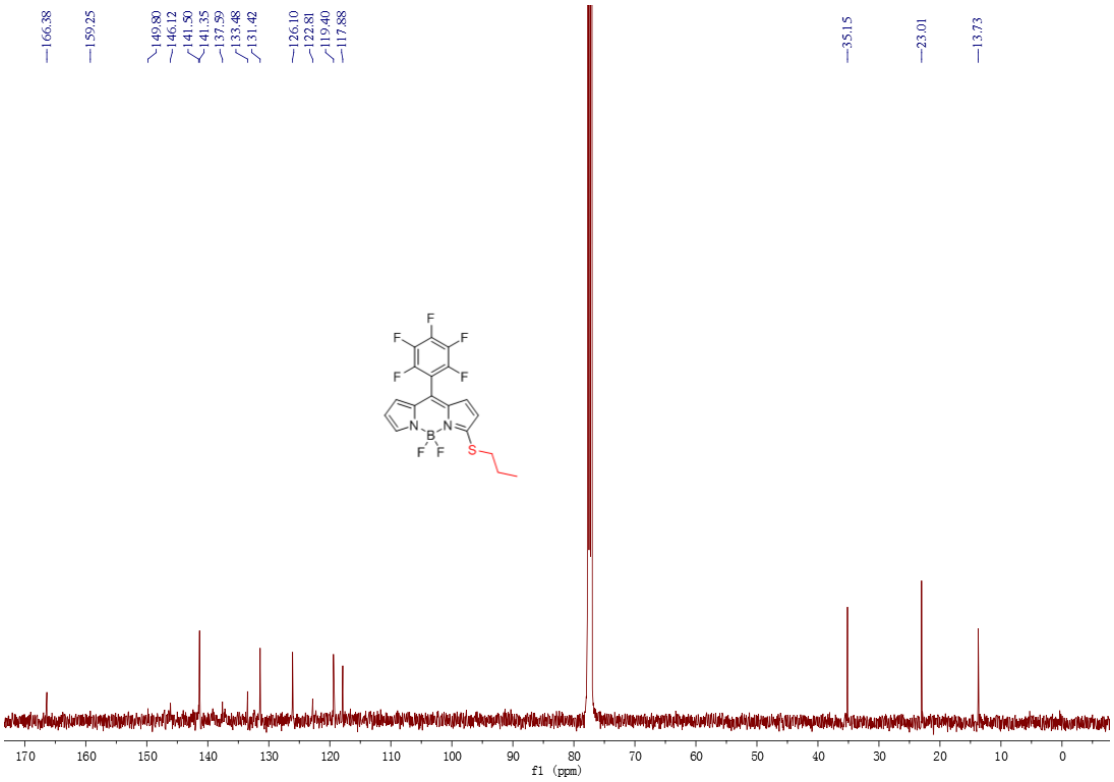
^{13}C NMR spectrum of **3b** in $CDCl_3$



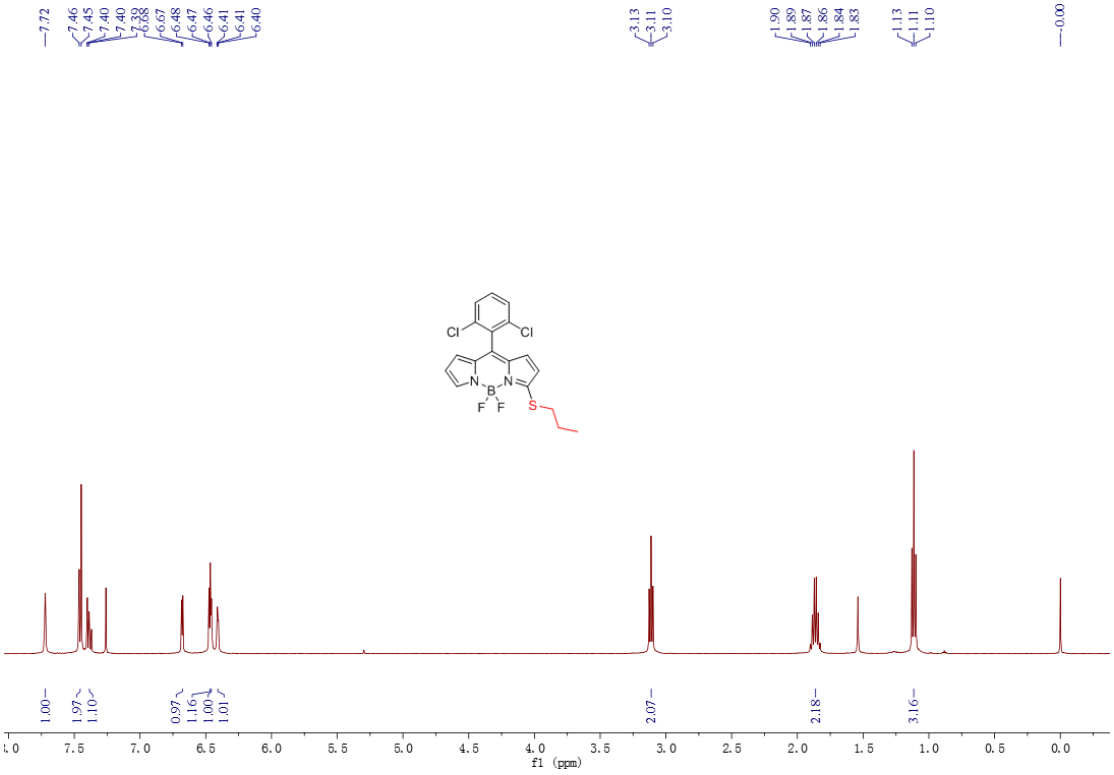
^{1}H NMR spectrum of **3c** in $CDCl_3$



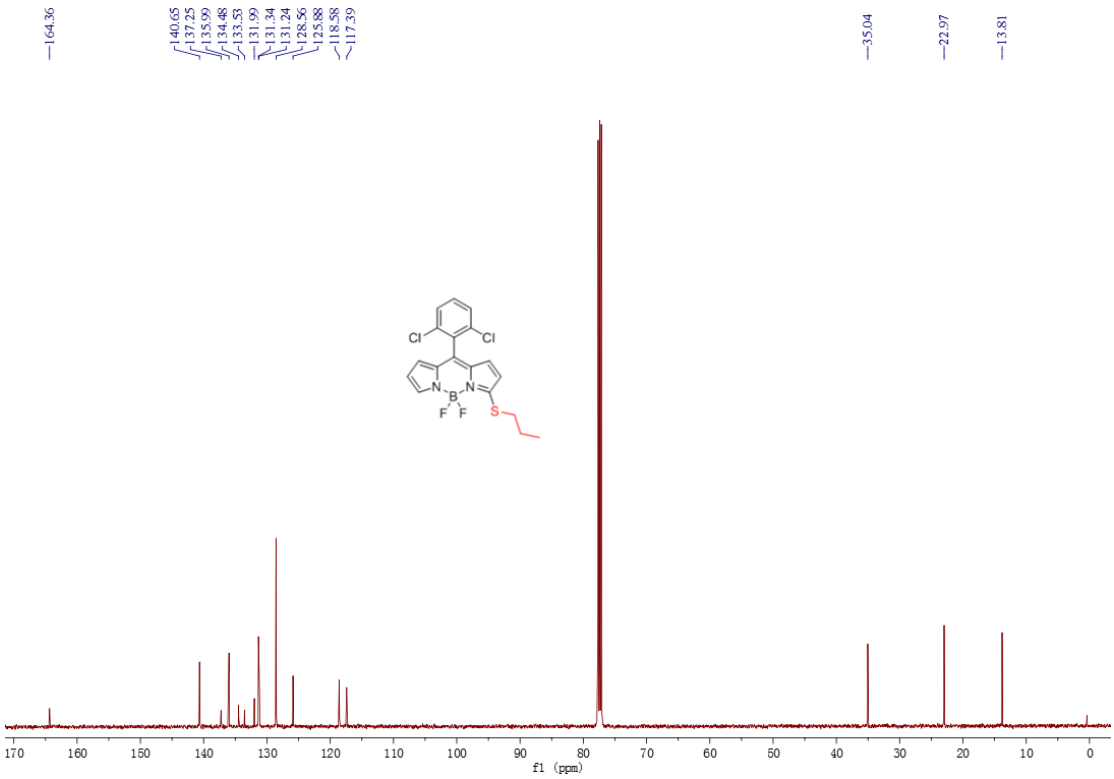
^{13}C NMR spectrum of **3c** in $CDCl_3$



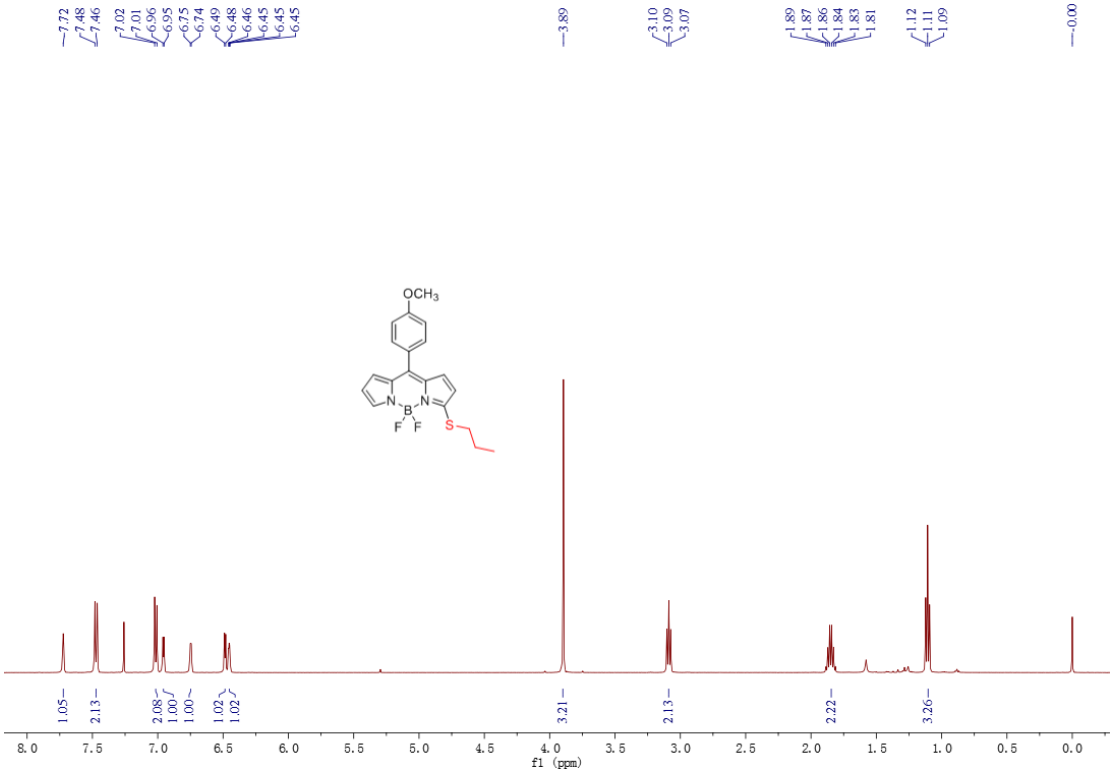
^{1}H NMR spectrum of **3d** in $CDCl_3$



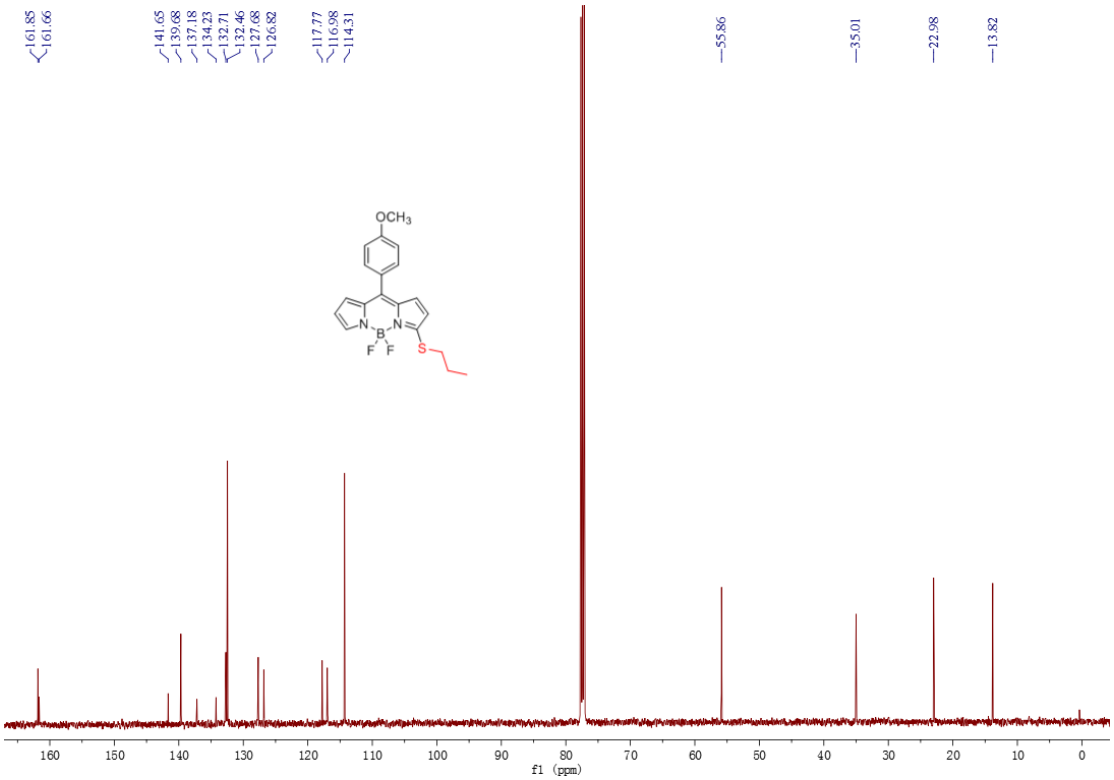
^{13}C NMR spectrum of **3d** in $CDCl_3$



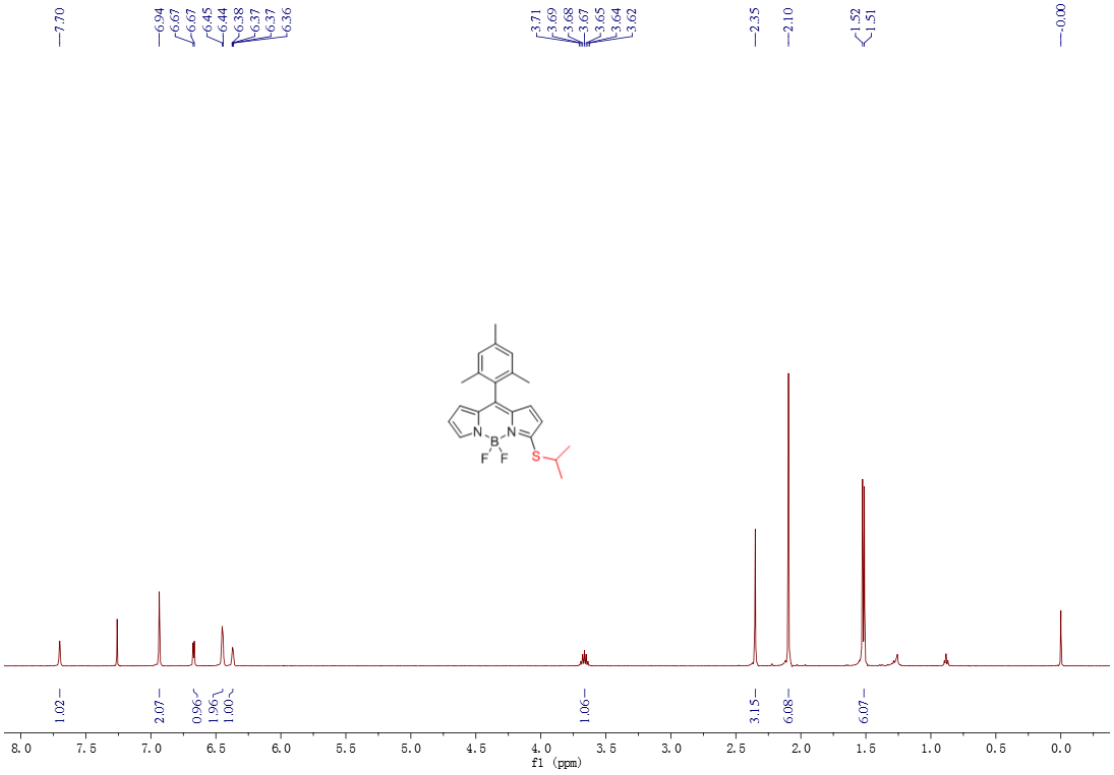
^{1}H NMR spectrum of **3e** in $CDCl_3$



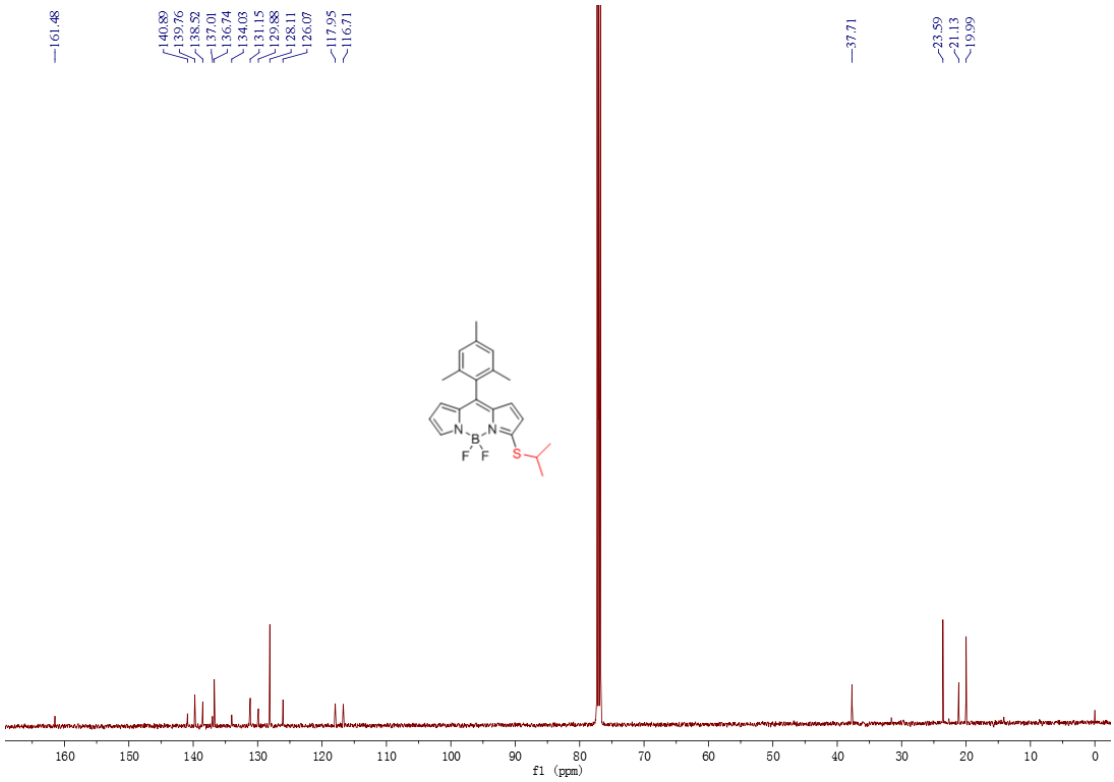
^{13}C NMR spectrum of **3e** in $CDCl_3$



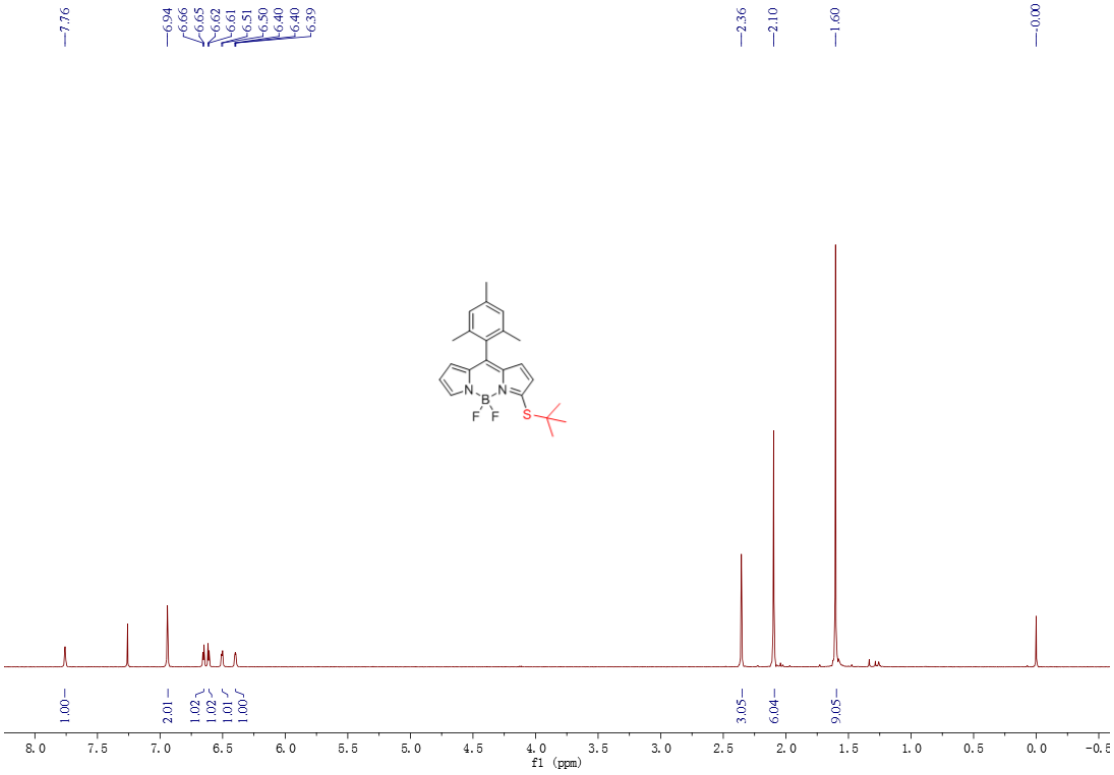
^{1}H NMR spectrum of **3f** in $CDCl_3$



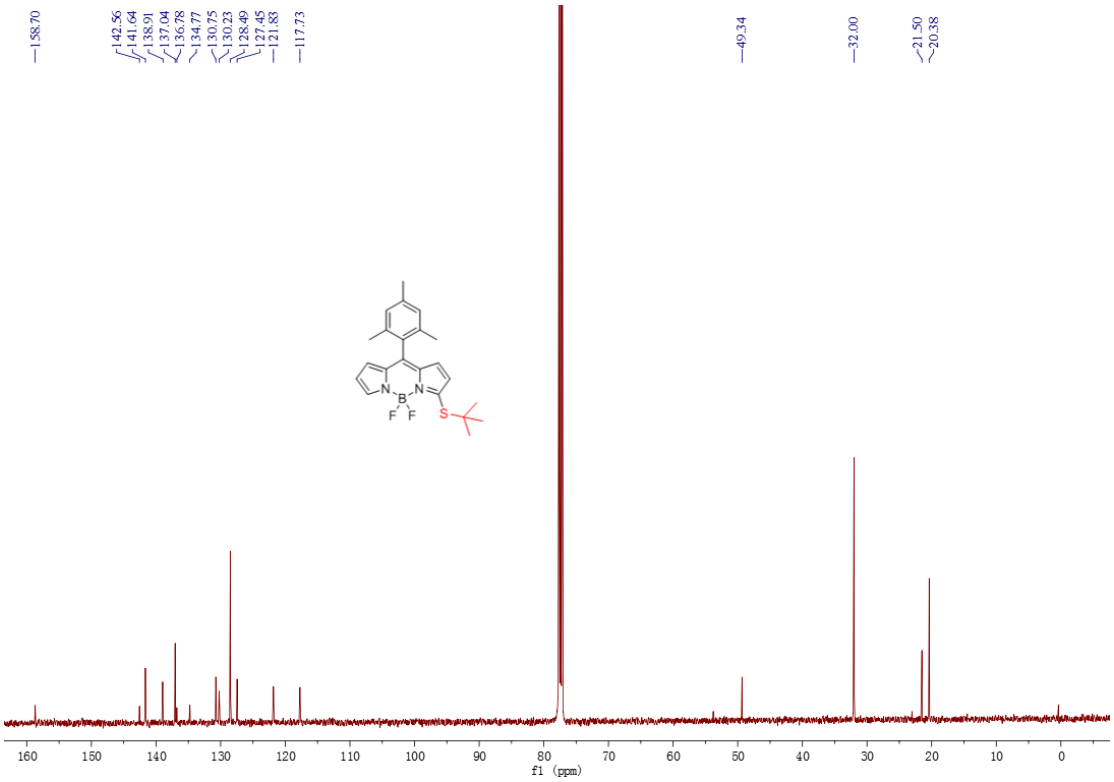
^{13}C NMR spectrum of **3f** in $CDCl_3$



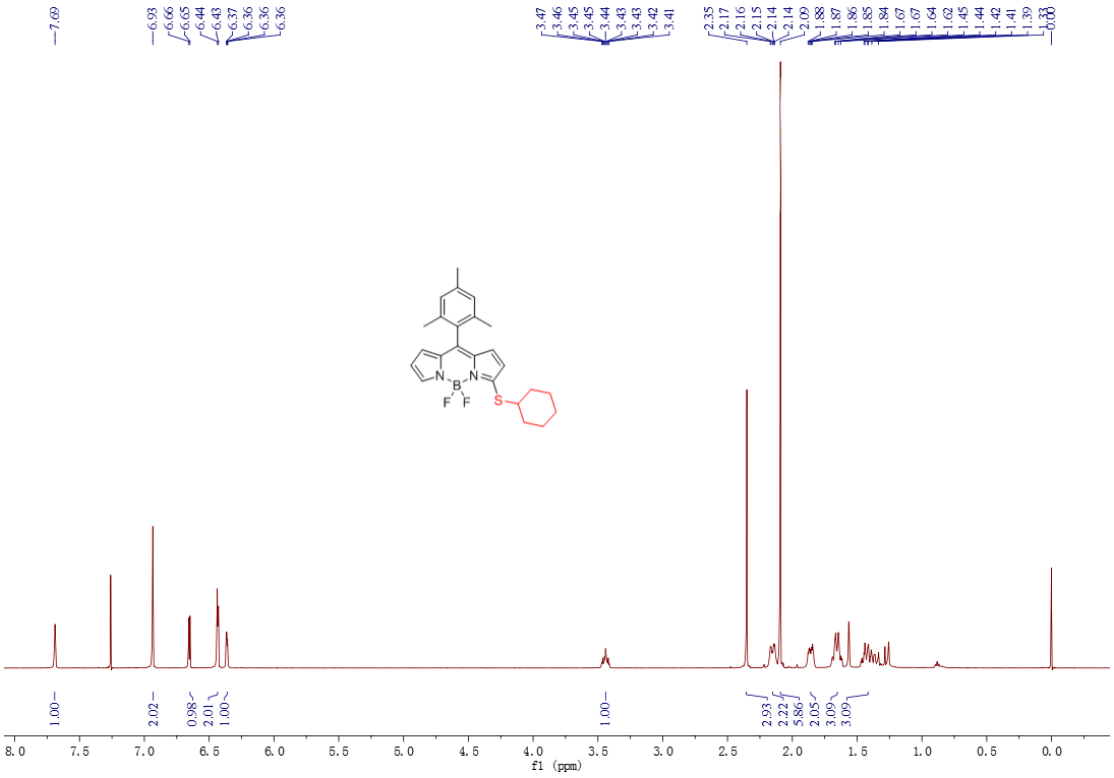
^{1}H NMR spectrum of **3g** in $CDCl_3$



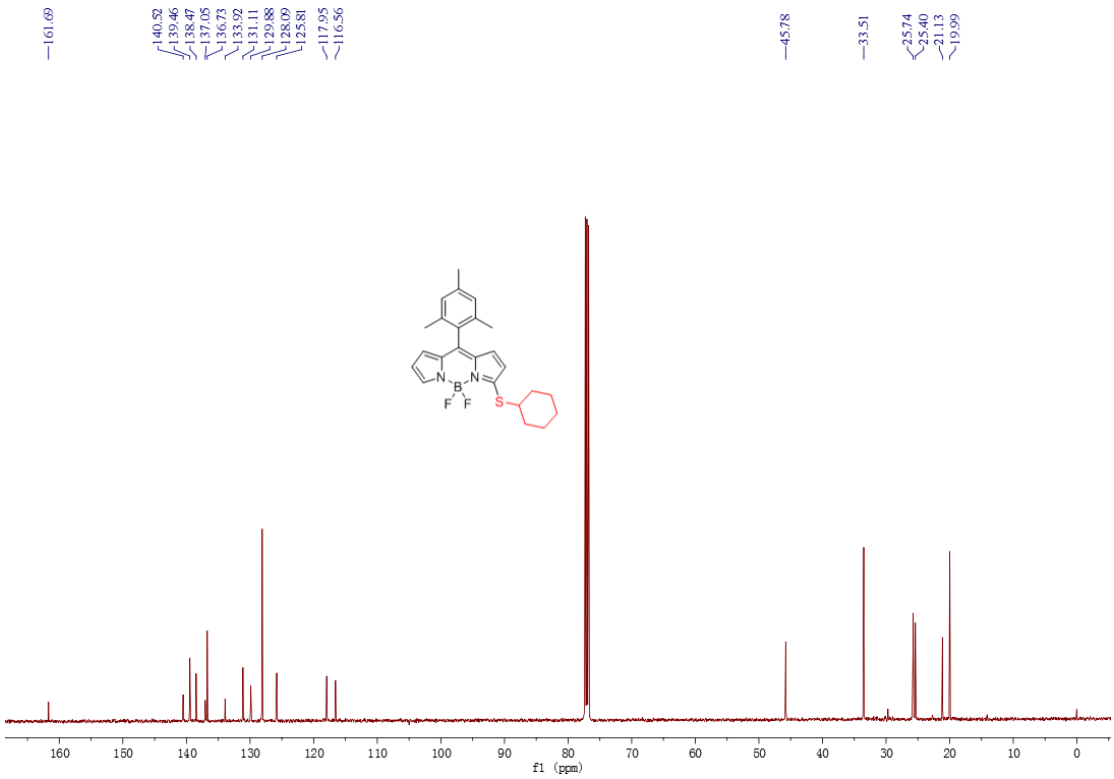
^{13}C NMR spectrum of **3g** in $CDCl_3$



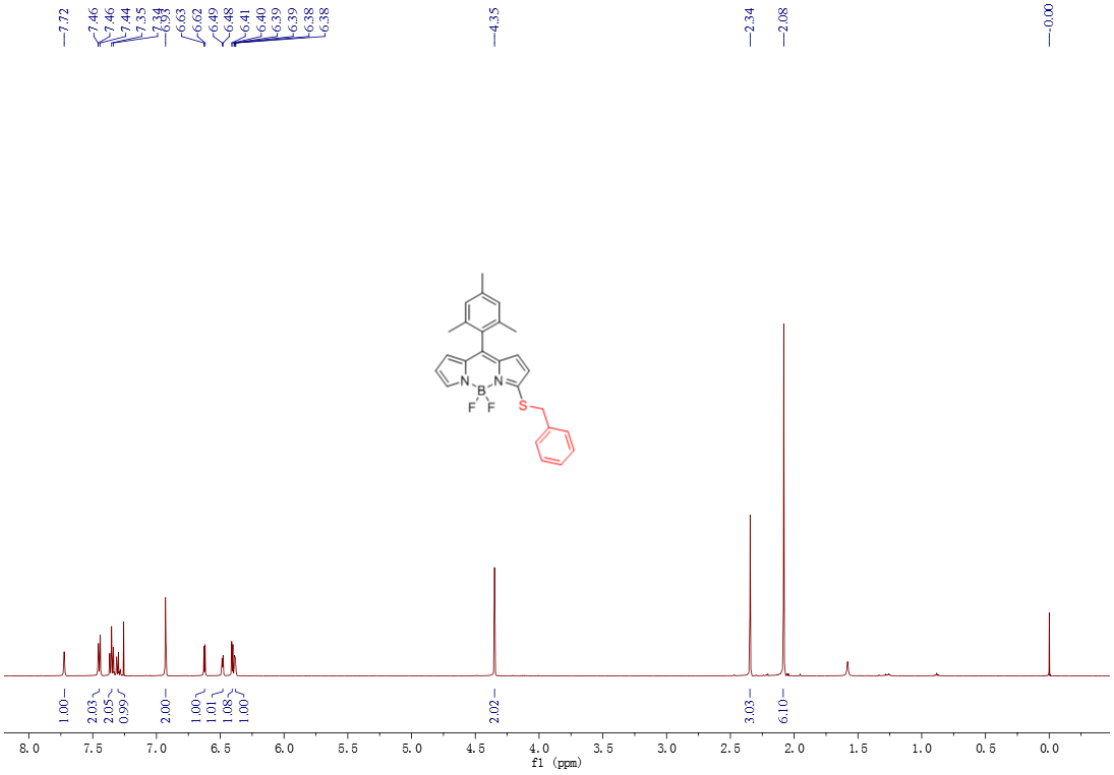
^{1}H NMR spectrum of **3h** in $CDCl_3$



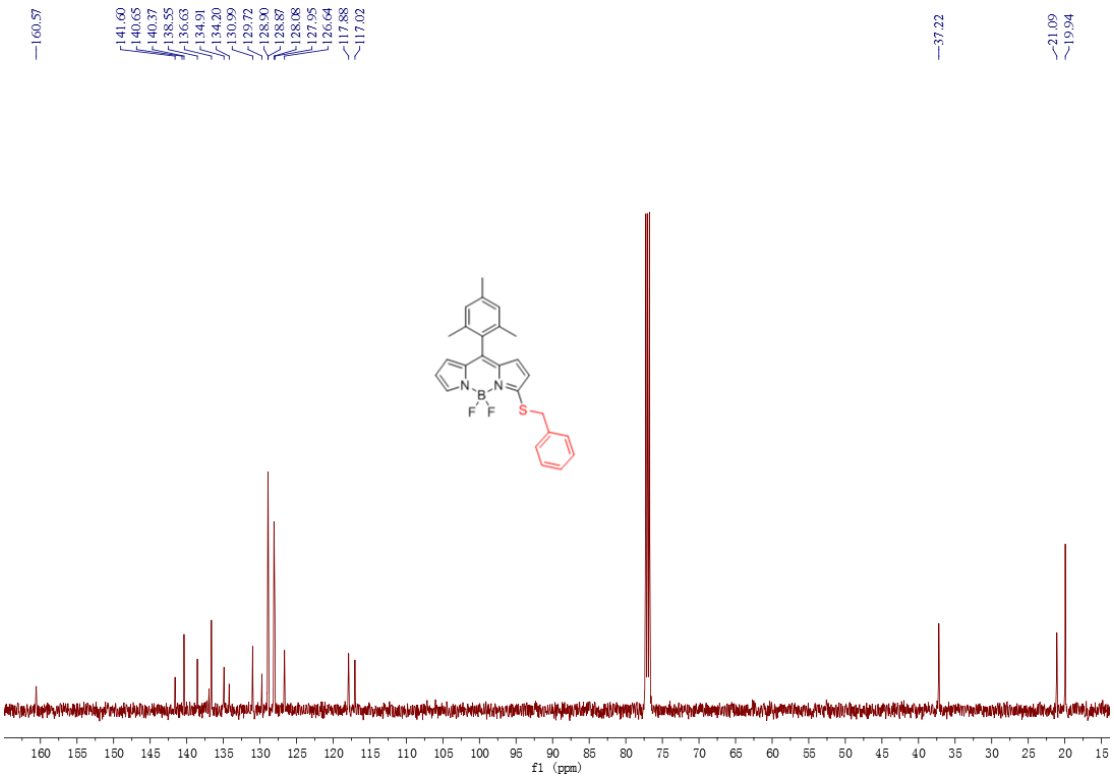
^{13}C NMR spectrum of **3h** in $CDCl_3$



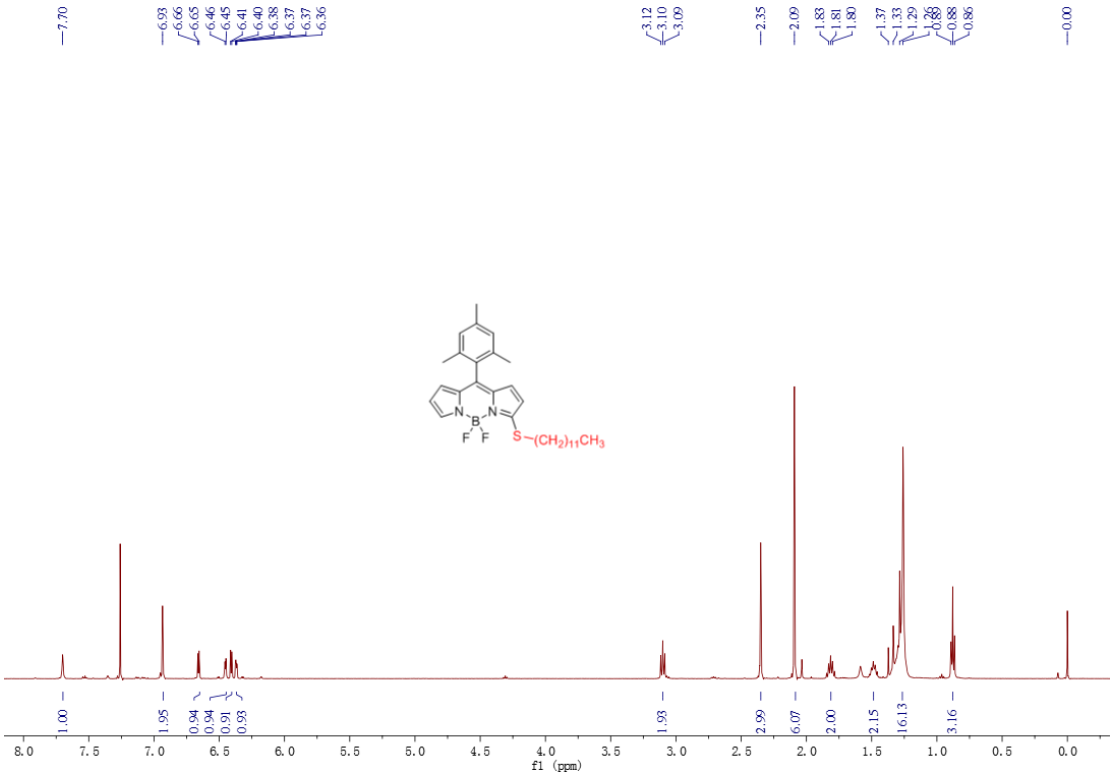
^{1}H NMR spectrum of **3i** in $CDCl_3$



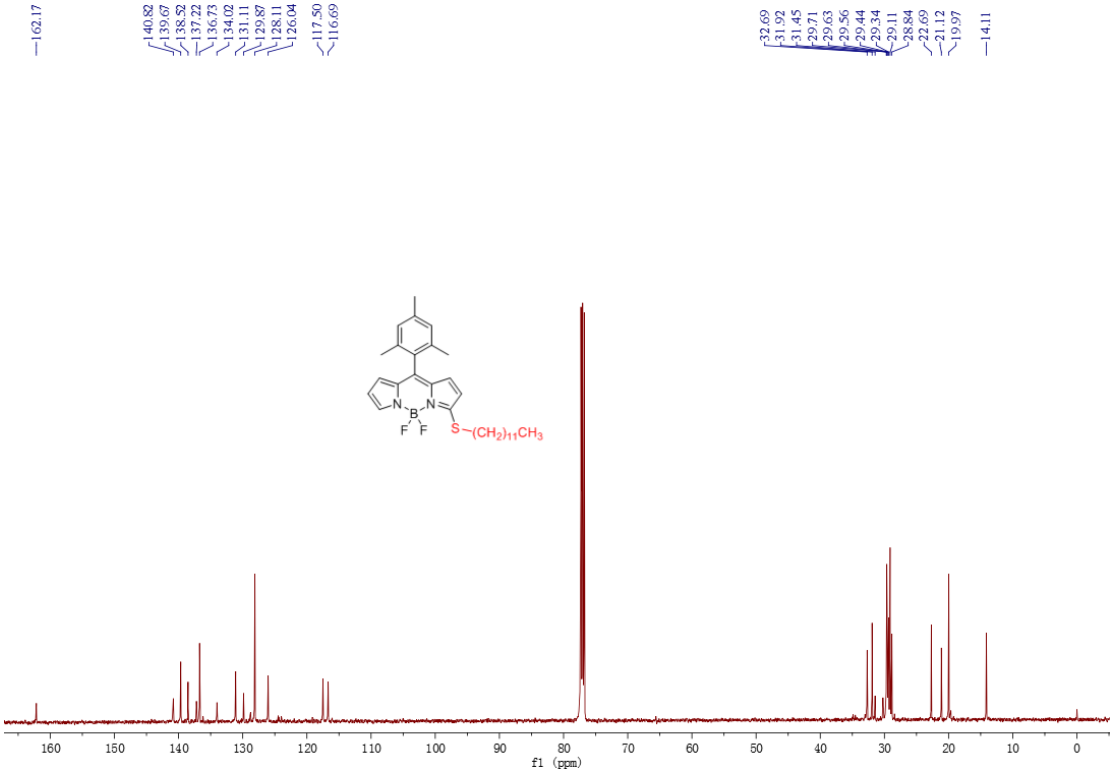
^{13}C NMR spectrum of **3i** in $CDCl_3$



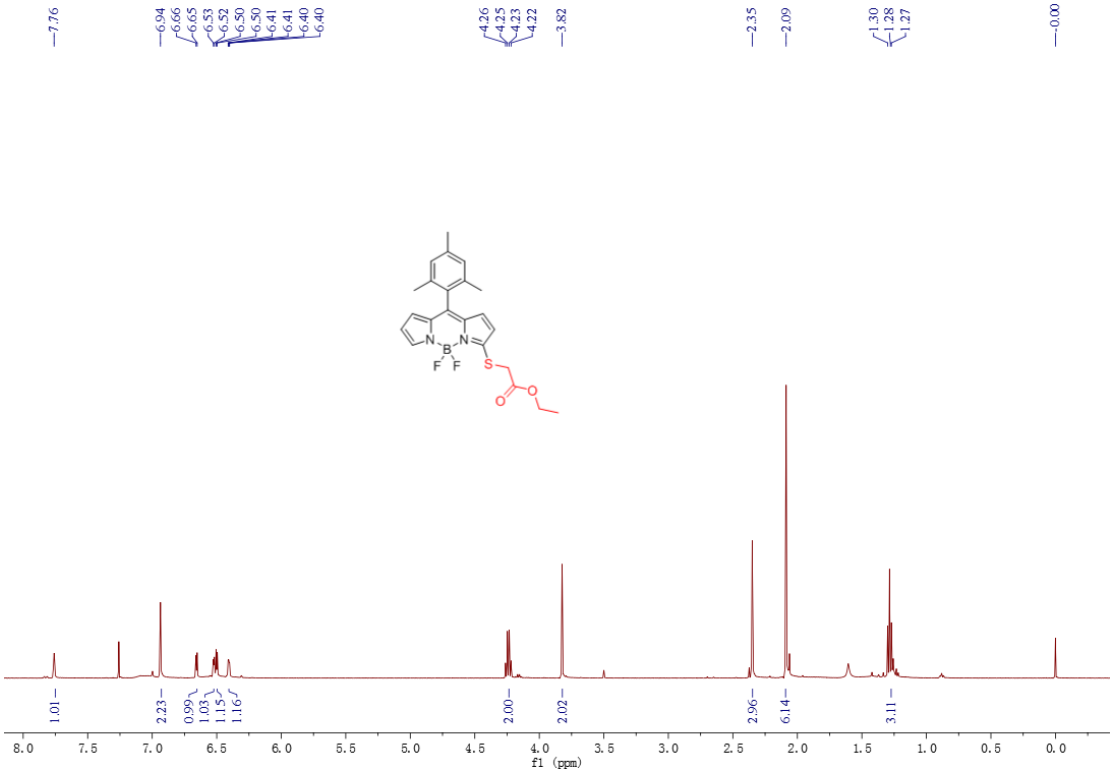
^{1}H NMR spectrum of **3j** in $CDCl_3$



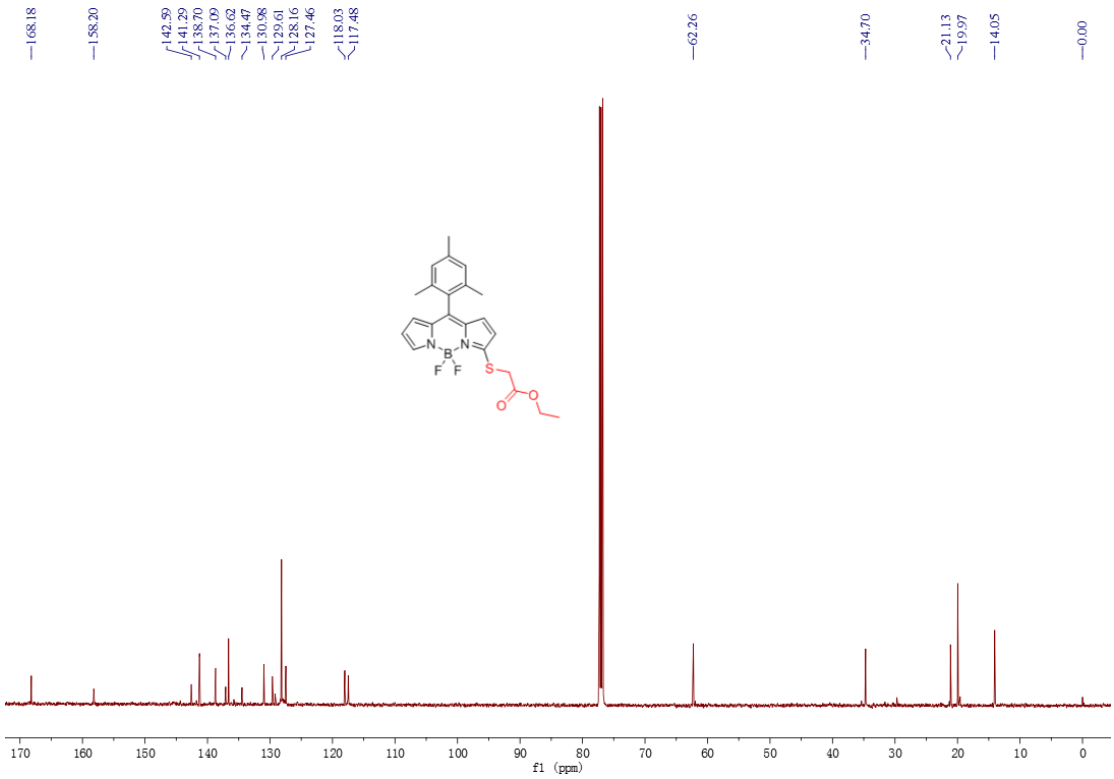
^{13}C NMR spectrum of **3j** in $CDCl_3$



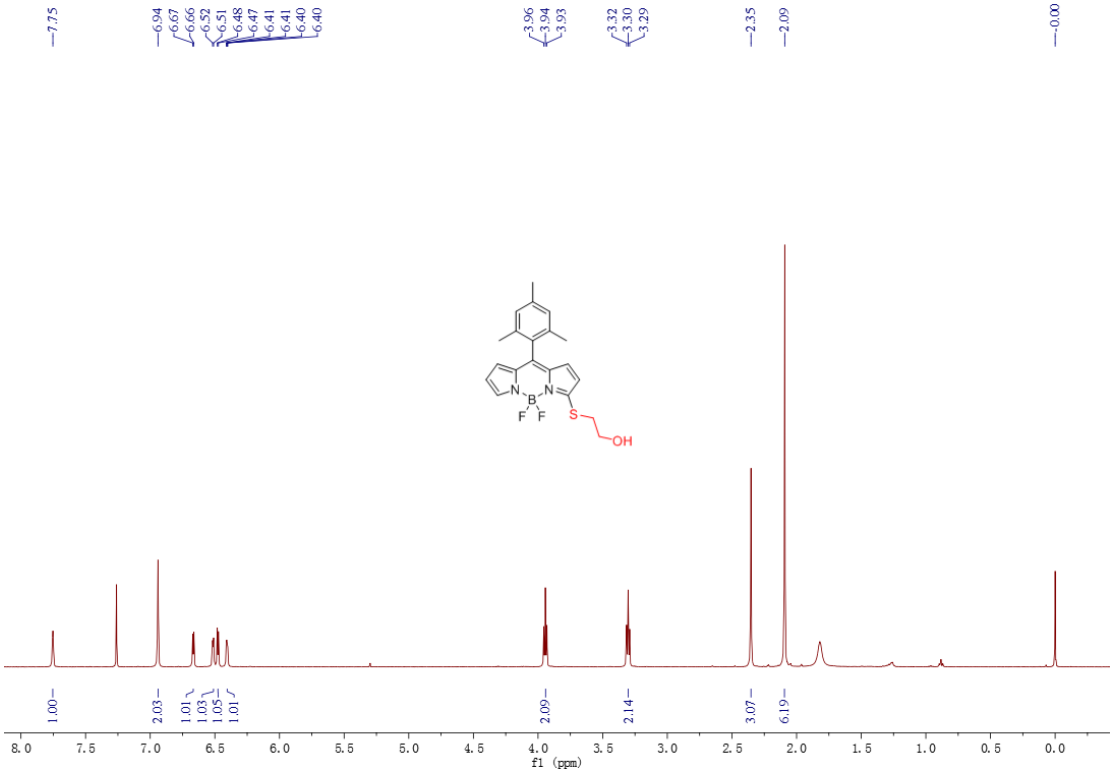
^{1}H NMR spectrum of **3k** in $CDCl_3$



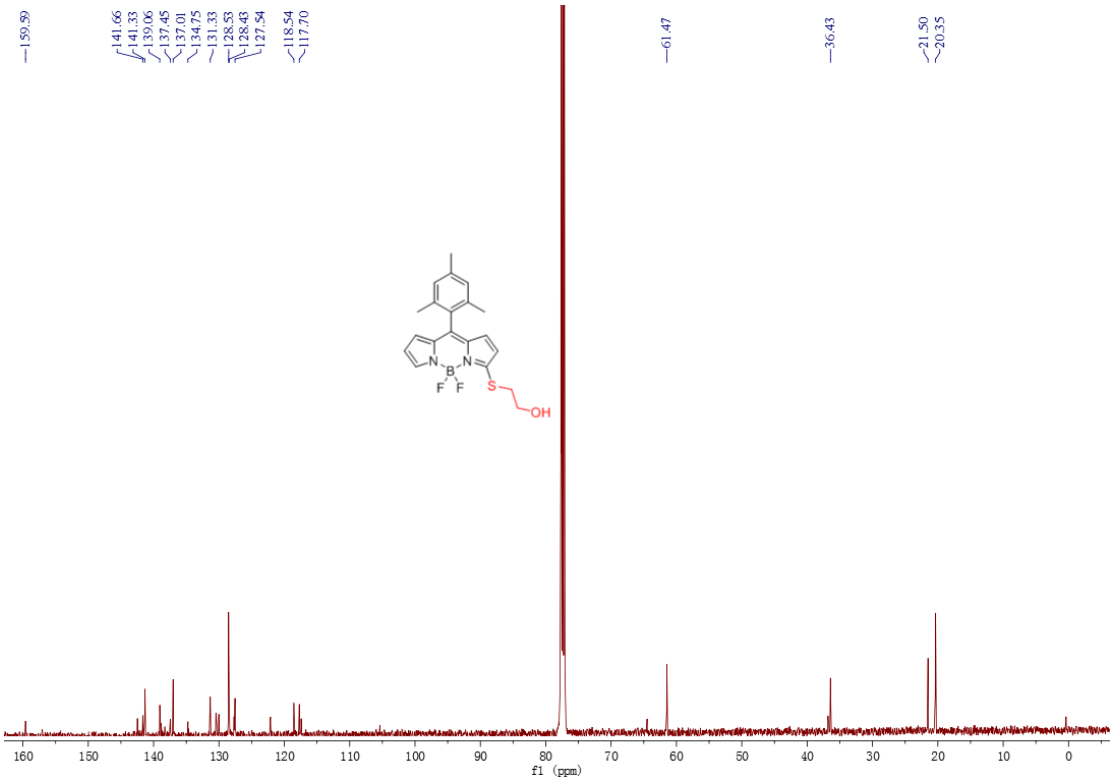
^{13}C NMR spectrum of **3k** in $CDCl_3$



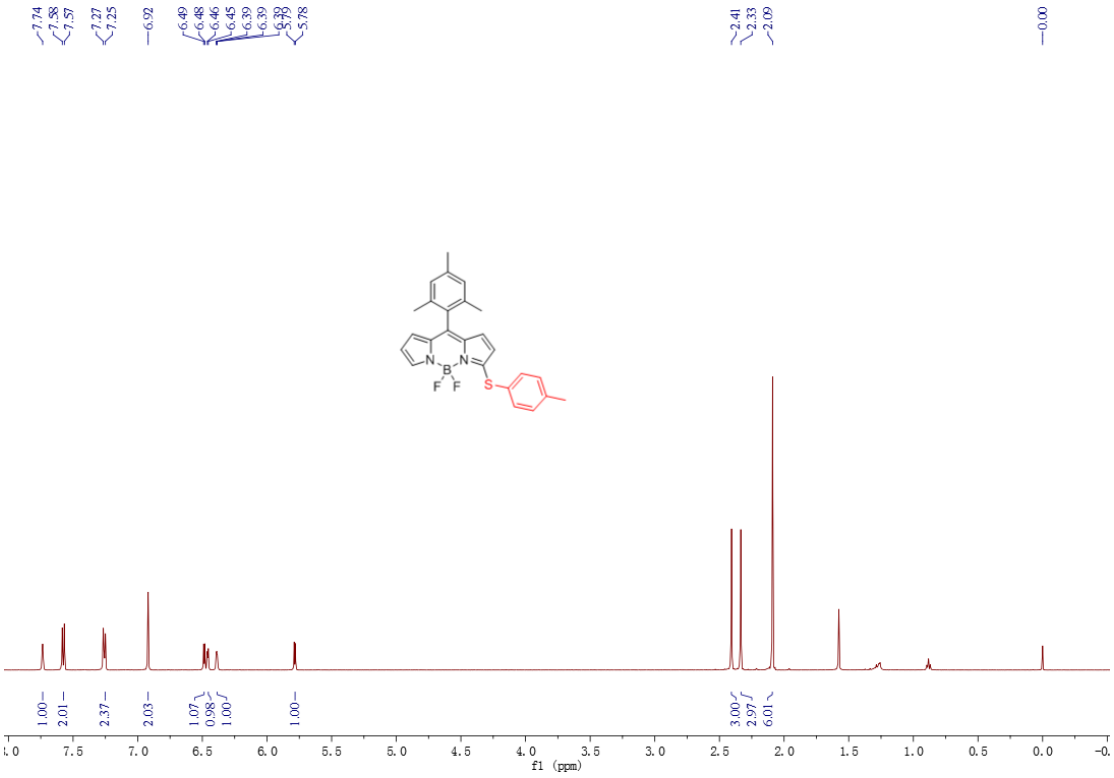
^{1}H NMR spectrum of **3l** in $CDCl_3$



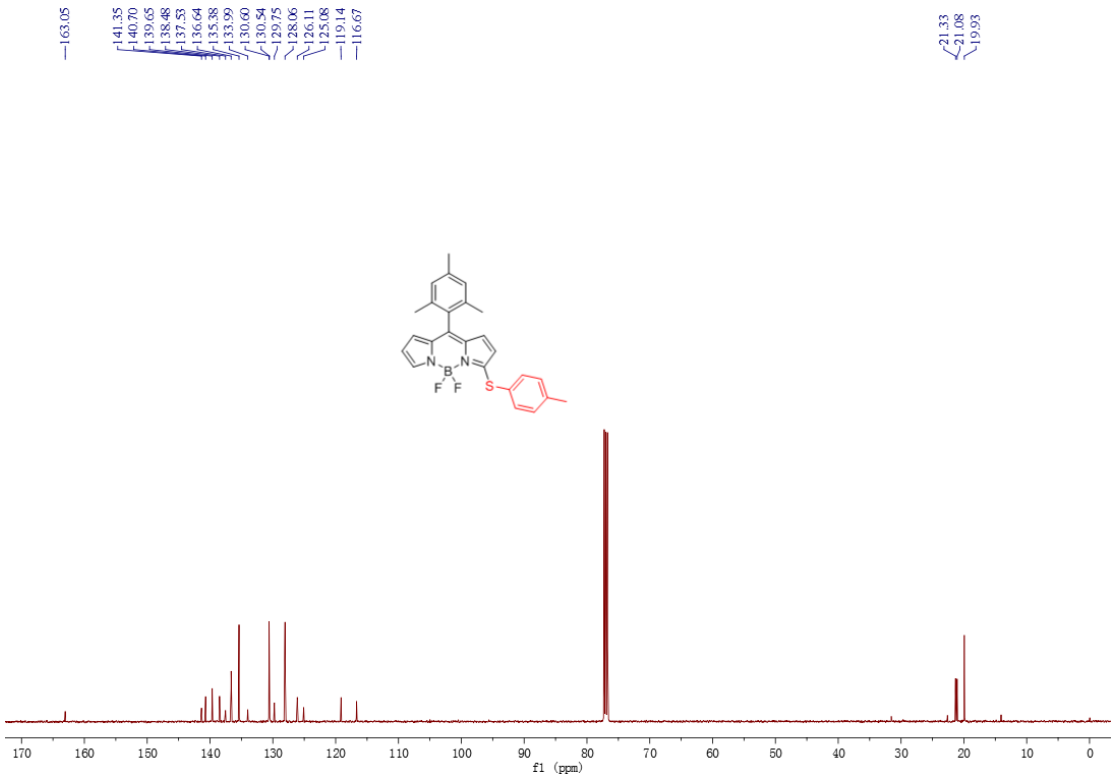
^{13}C NMR spectrum of **3l** in $CDCl_3$



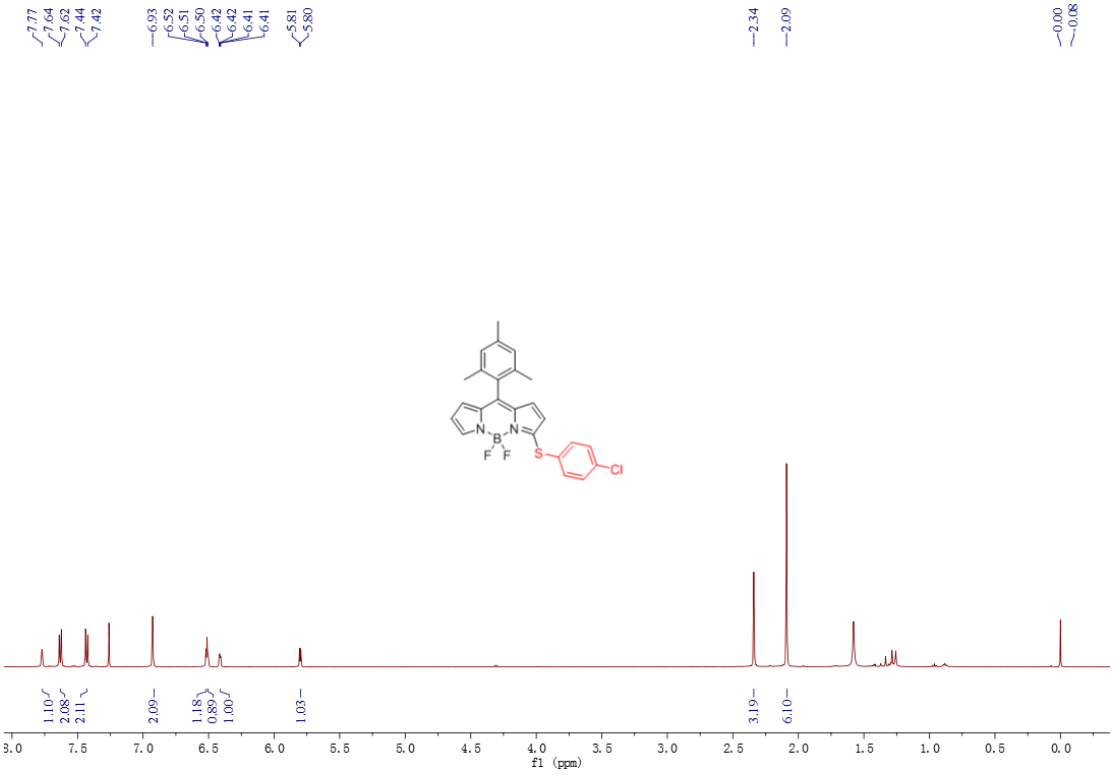
^{1}H NMR spectrum of **3m** in $CDCl_3$



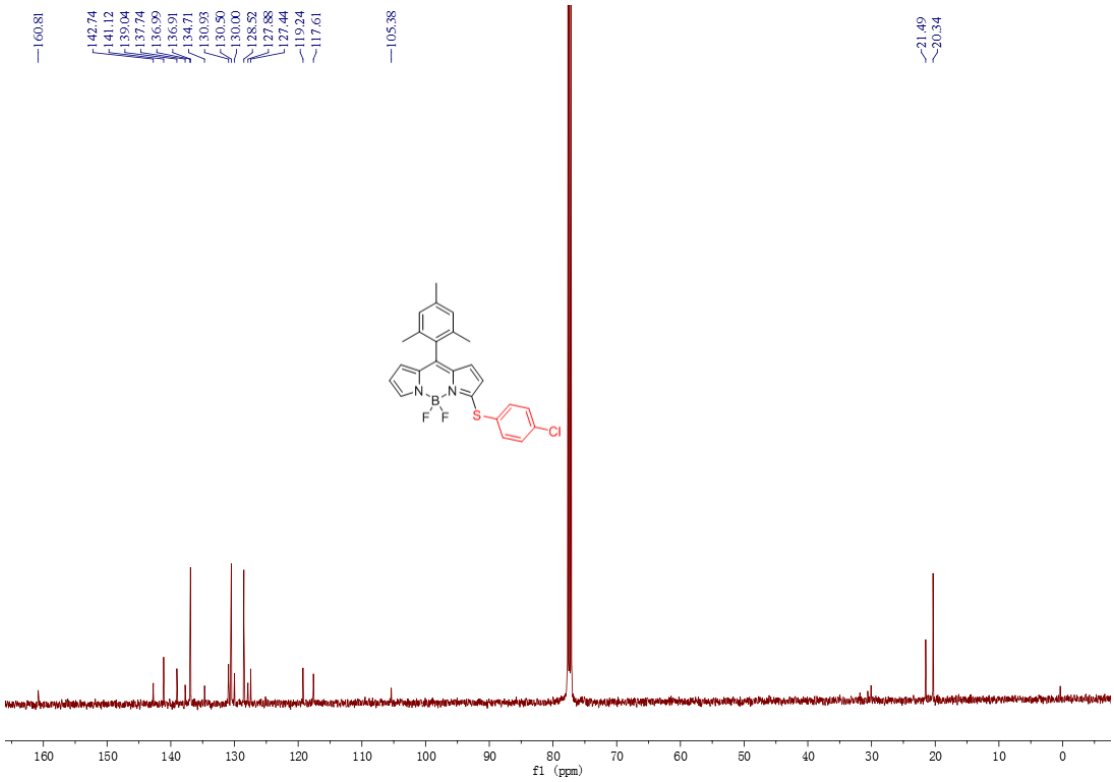
^{13}C NMR spectrum of **3m** in $CDCl_3$



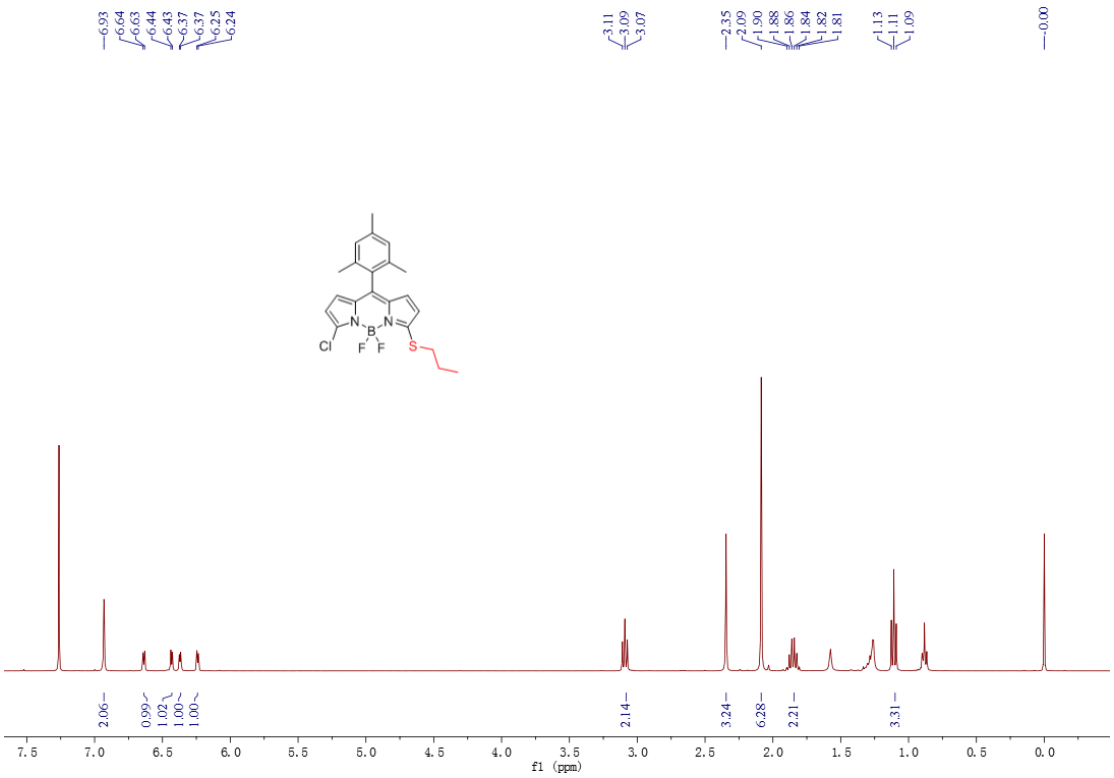
^{1}H NMR spectrum of **3n** in $CDCl_3$



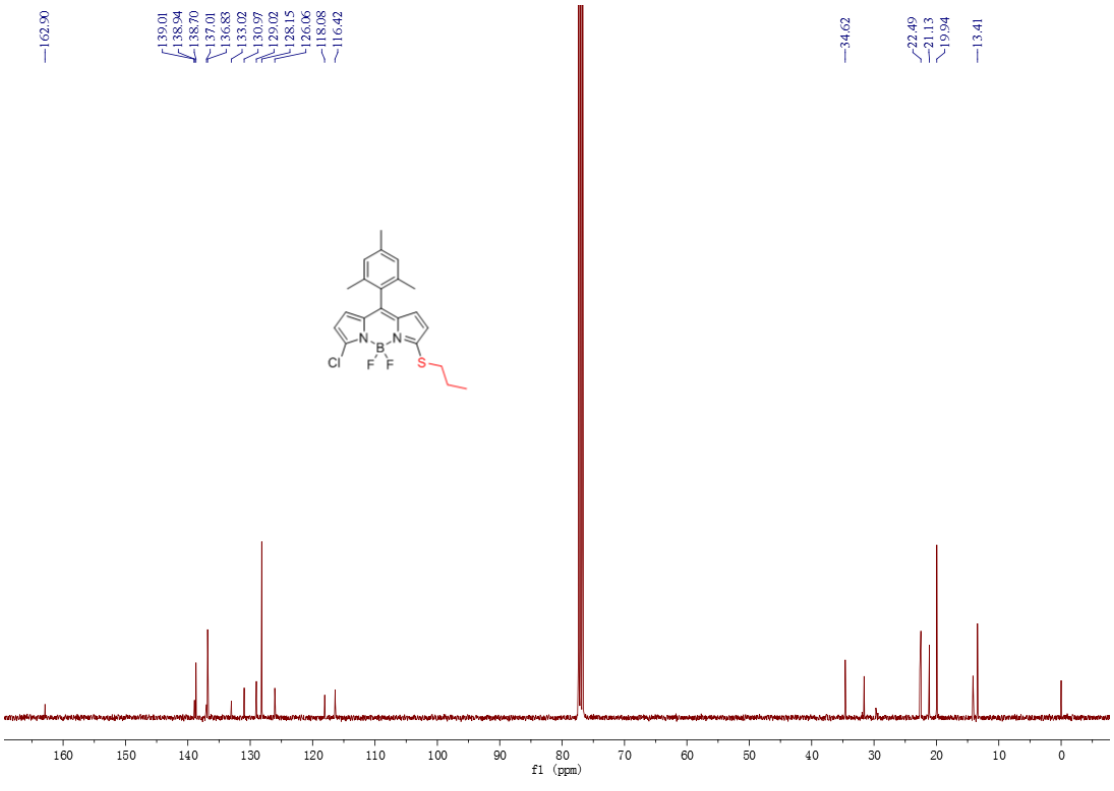
^{13}C NMR spectrum of **3n** in $CDCl_3$



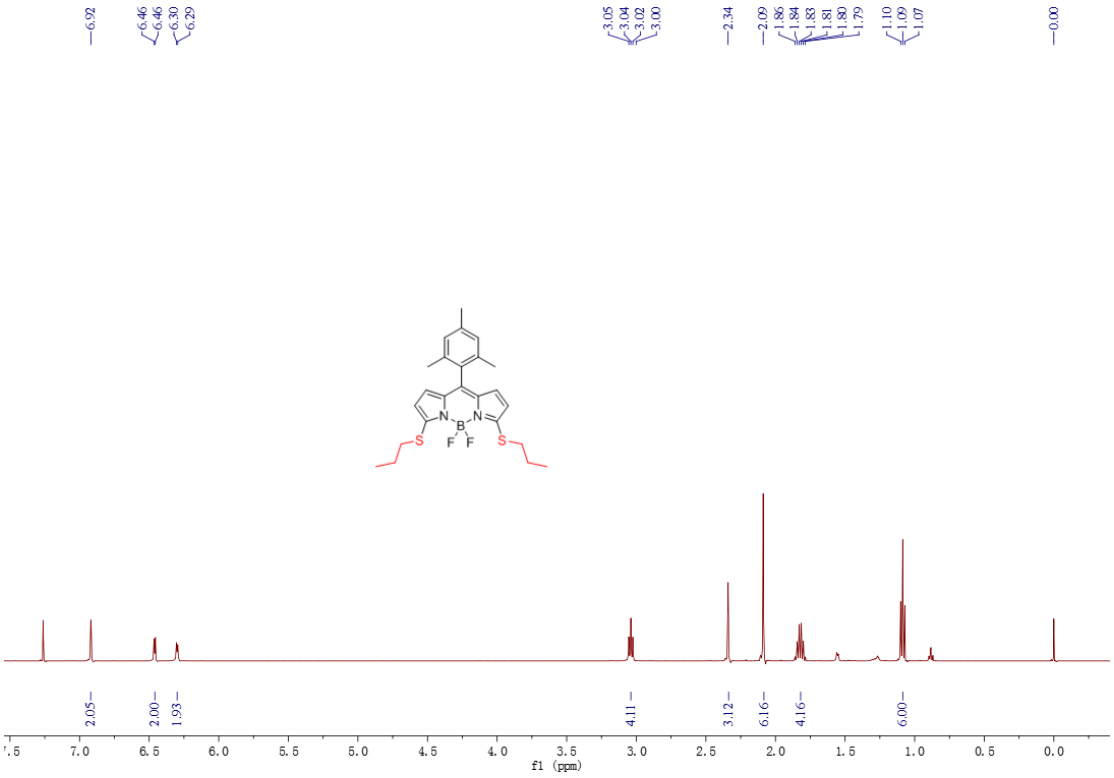
^{1}H NMR spectrum of **3o** in $CDCl_3$



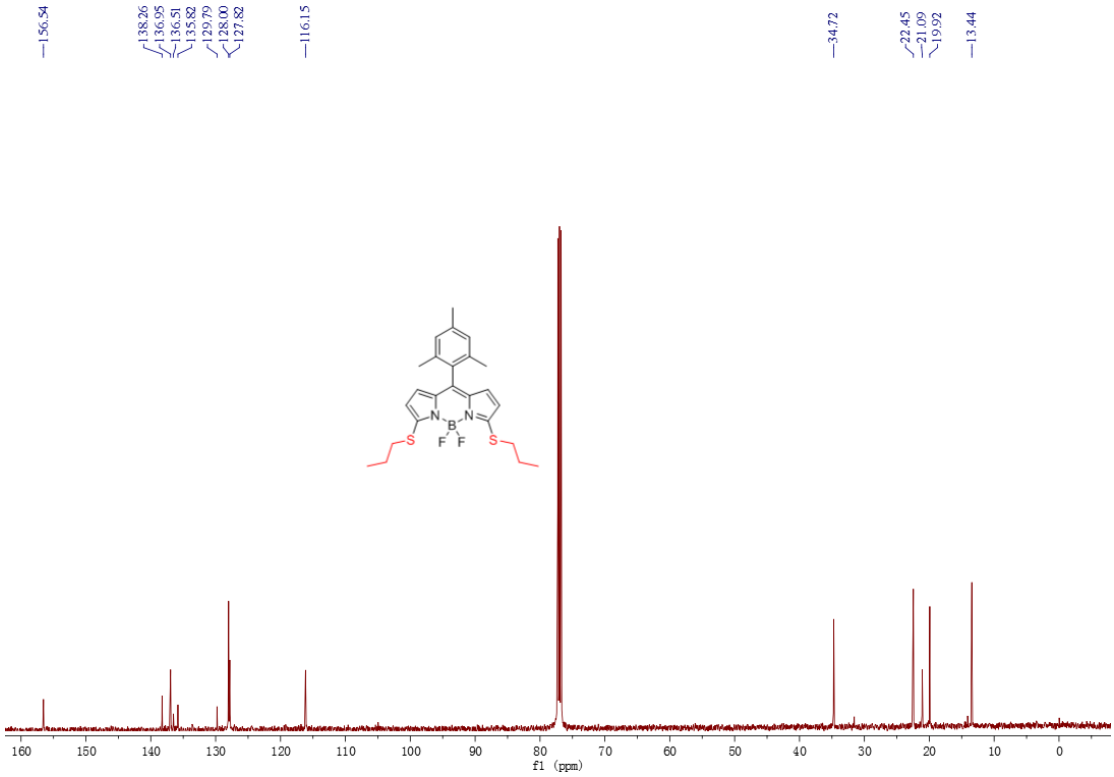
^{13}C NMR spectrum of **3o** in $CDCl_3$



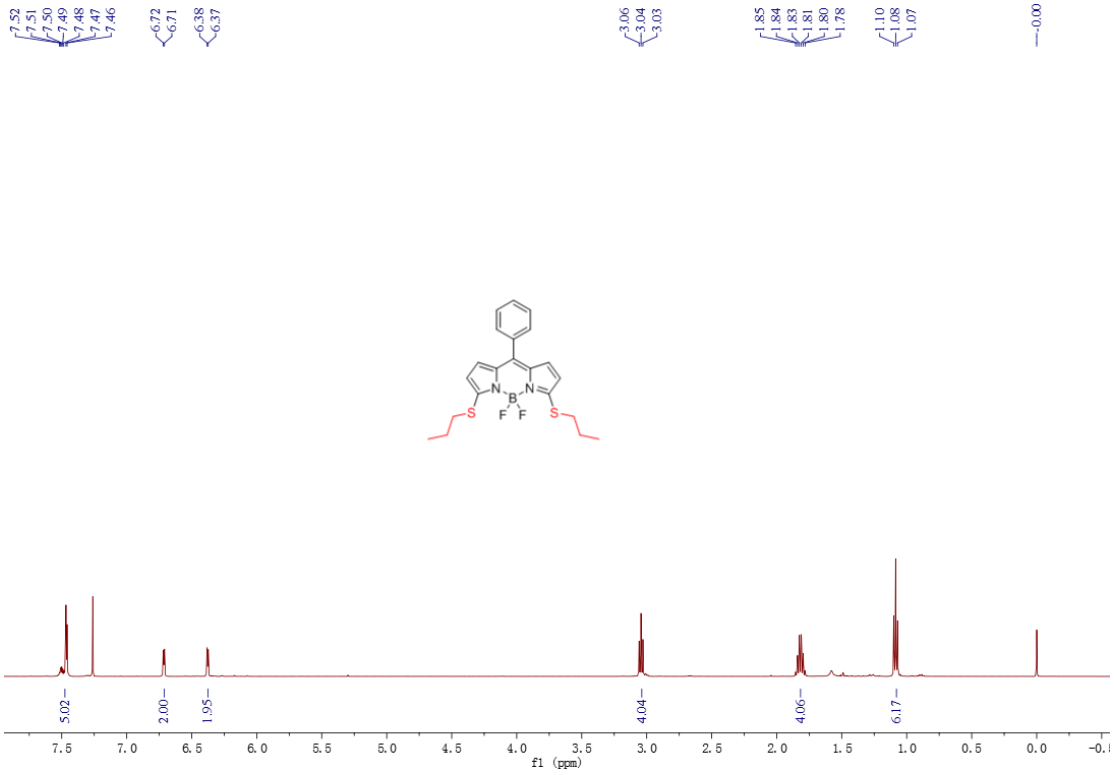
^{1}H NMR spectrum of **4a** in $CDCl_3$



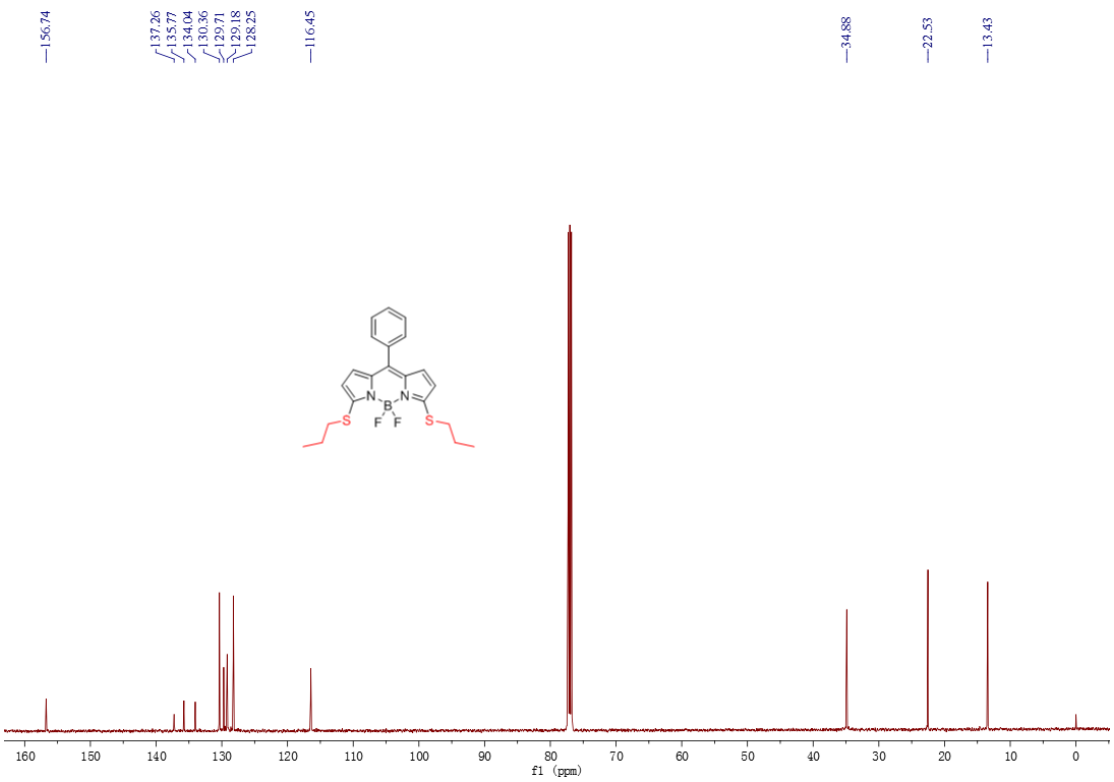
^{13}C NMR spectrum of **4a** in $CDCl_3$



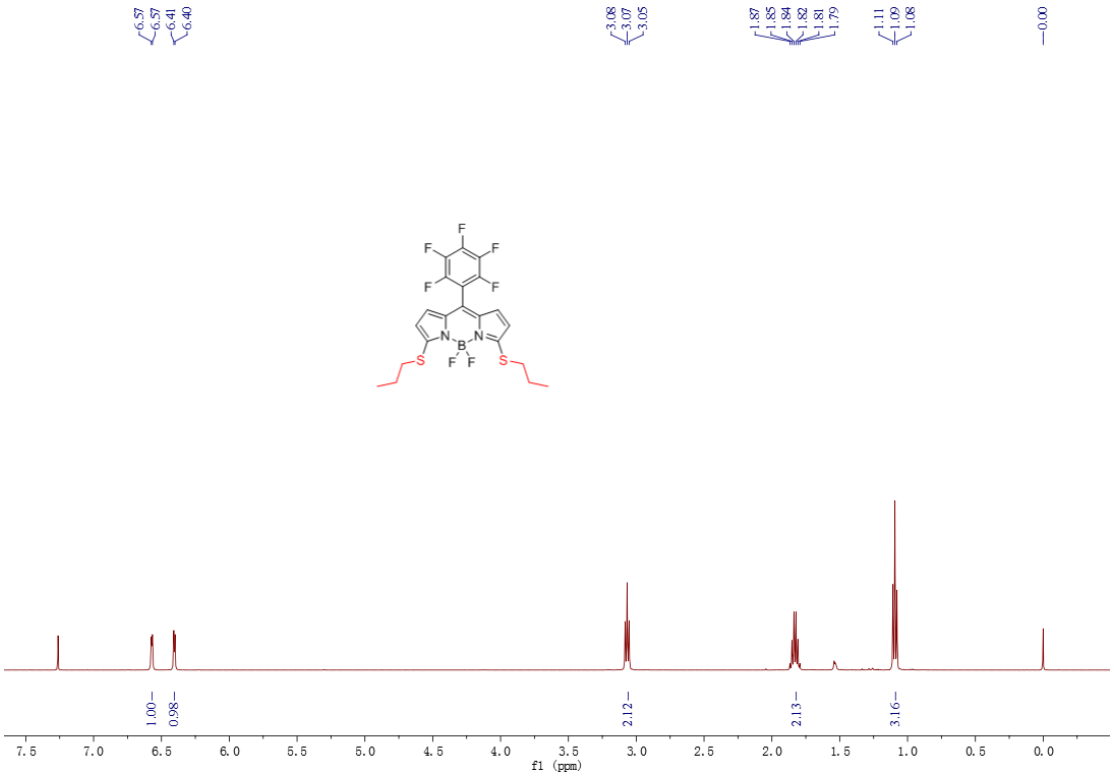
^{1}H NMR spectrum of **4b** in $CDCl_3$



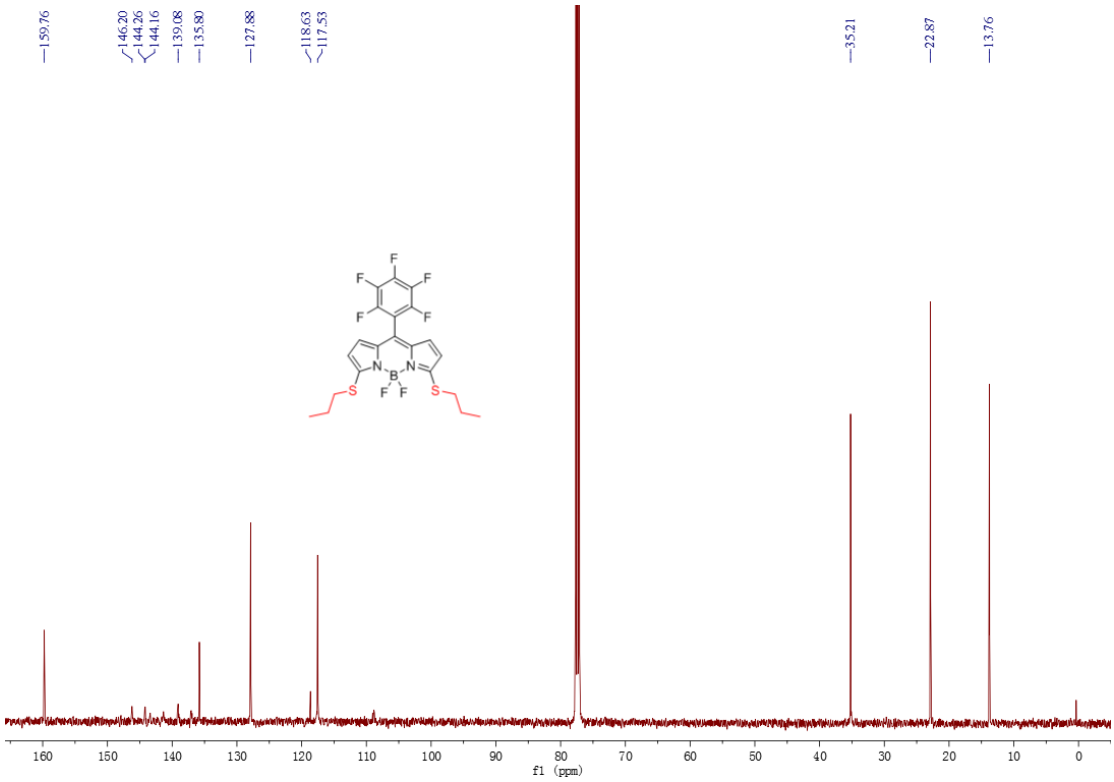
^{13}C NMR spectrum of **4b** in $CDCl_3$



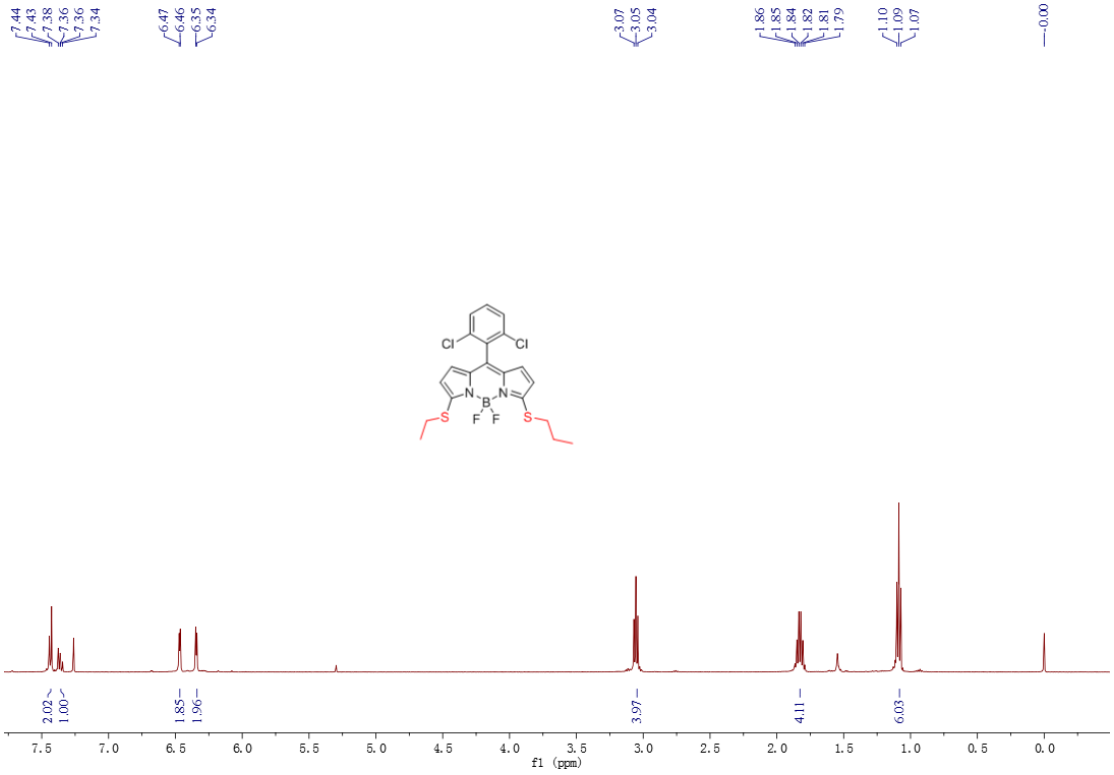
^{1}H NMR spectrum of **4c** in $CDCl_3$



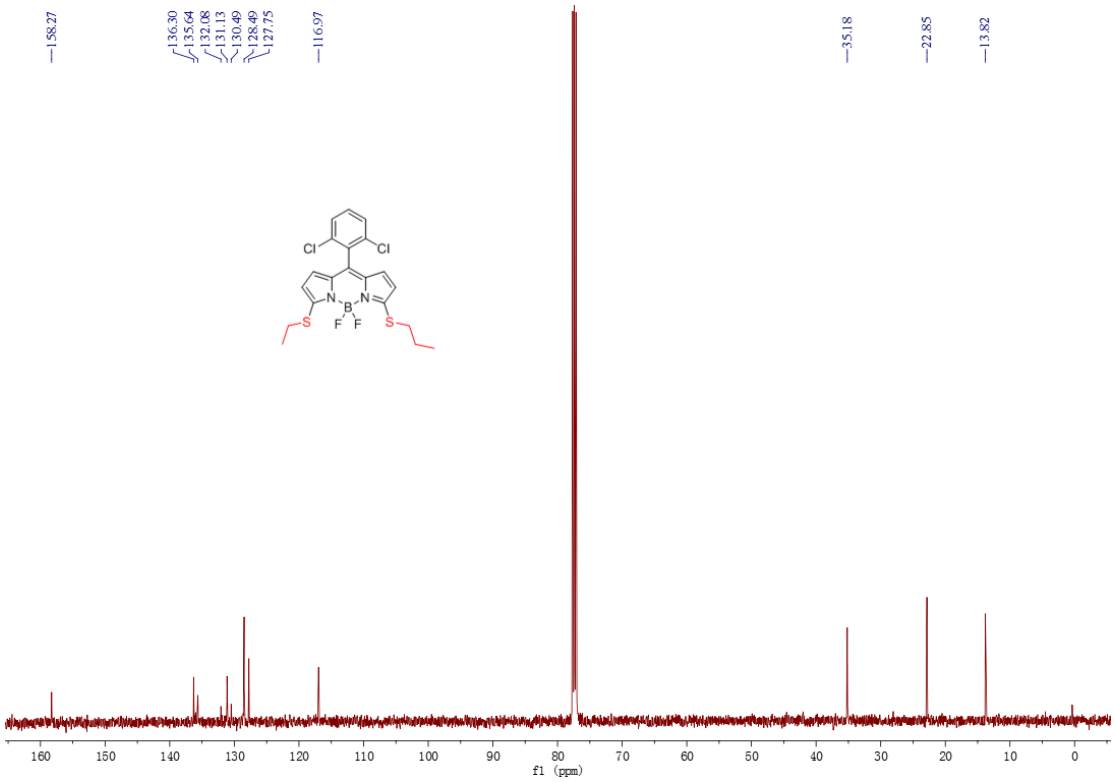
^{13}C NMR spectrum of **4c** in $CDCl_3$



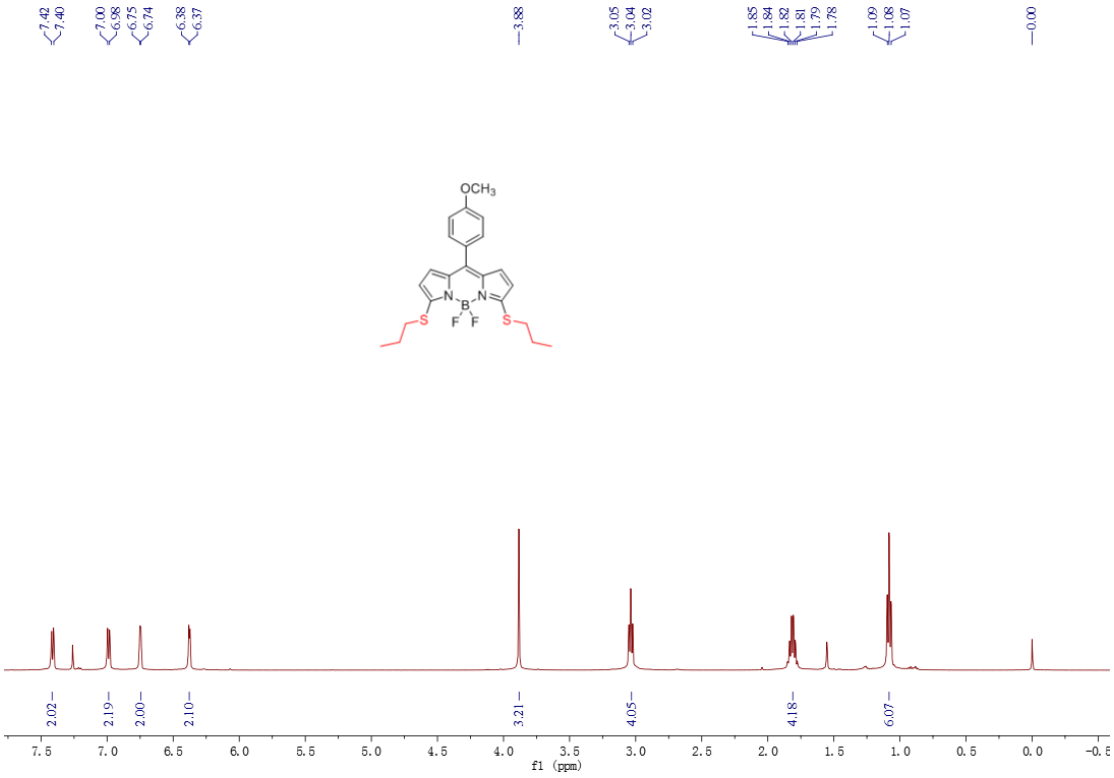
^{1}H NMR spectrum of **4d** in $CDCl_3$



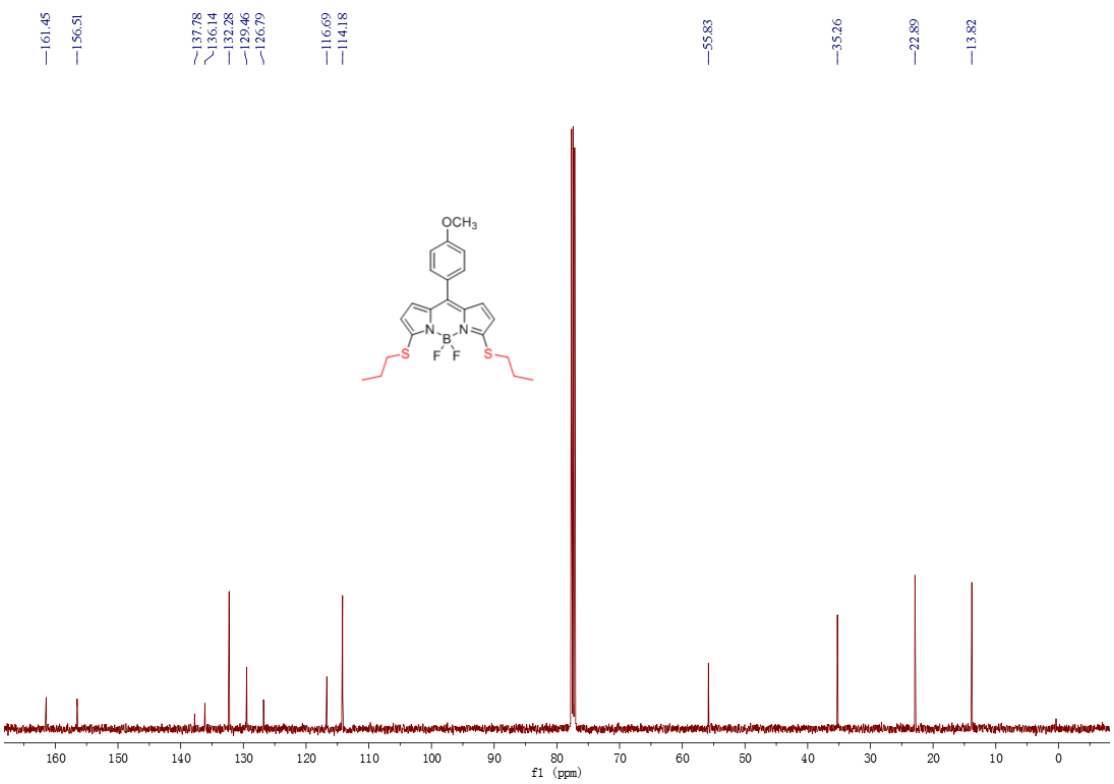
^{13}C NMR spectrum of **4d** in $CDCl_3$



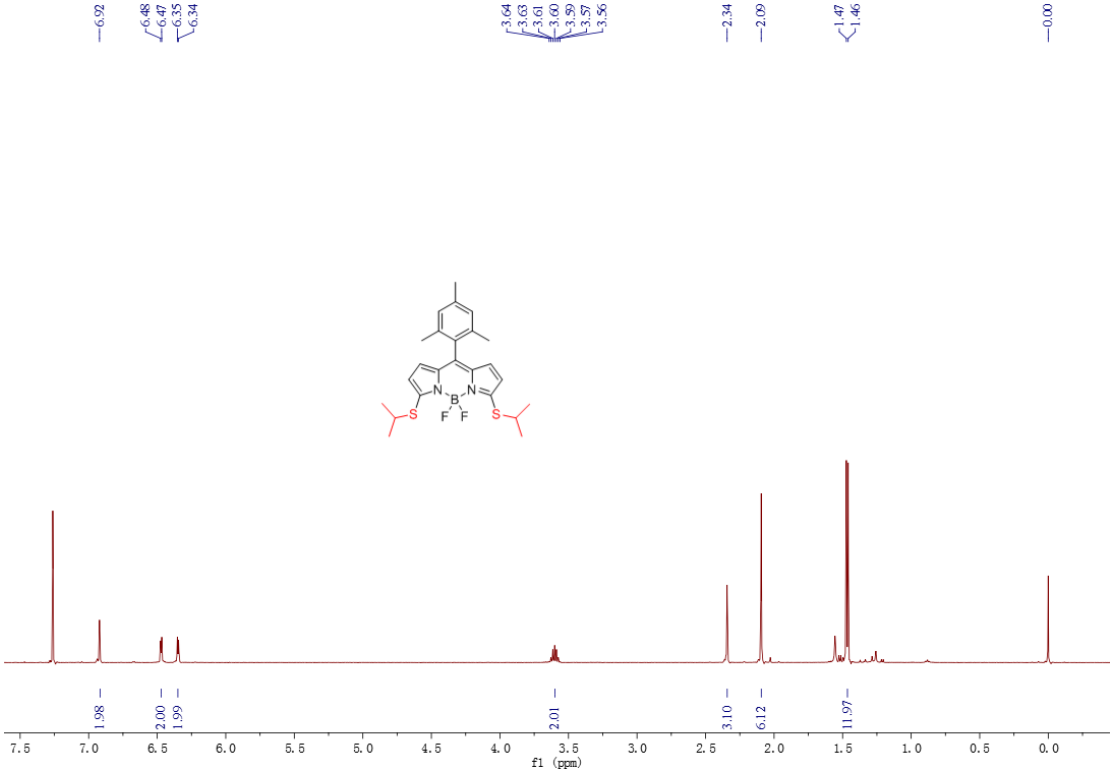
^{1}H NMR spectrum of **4e** in $CDCl_3$



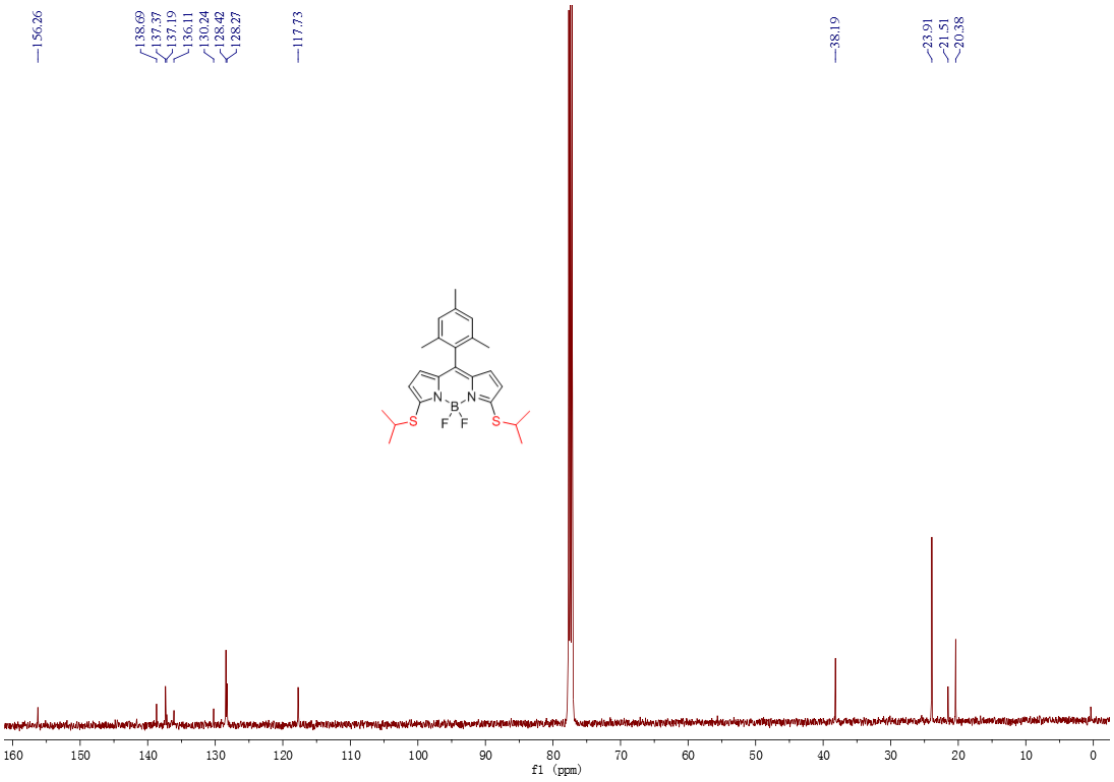
^{13}C NMR spectrum of **4e** in $CDCl_3$



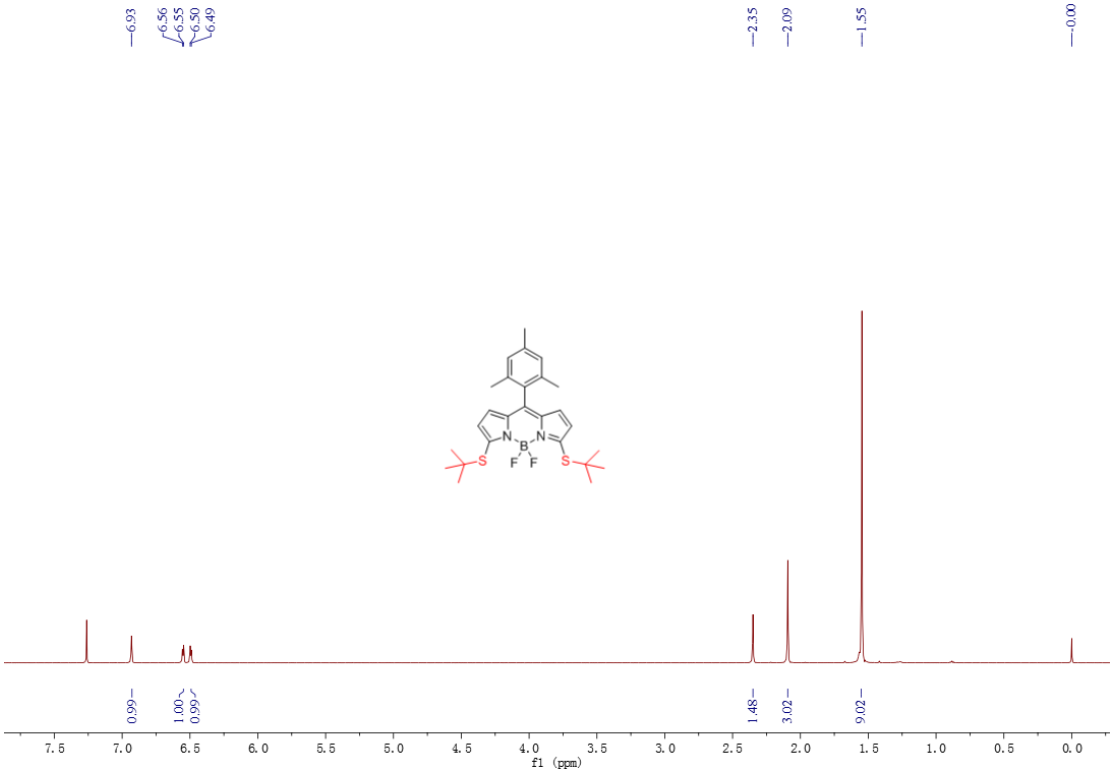
^{1}H NMR spectrum of **4f** in $CDCl_3$



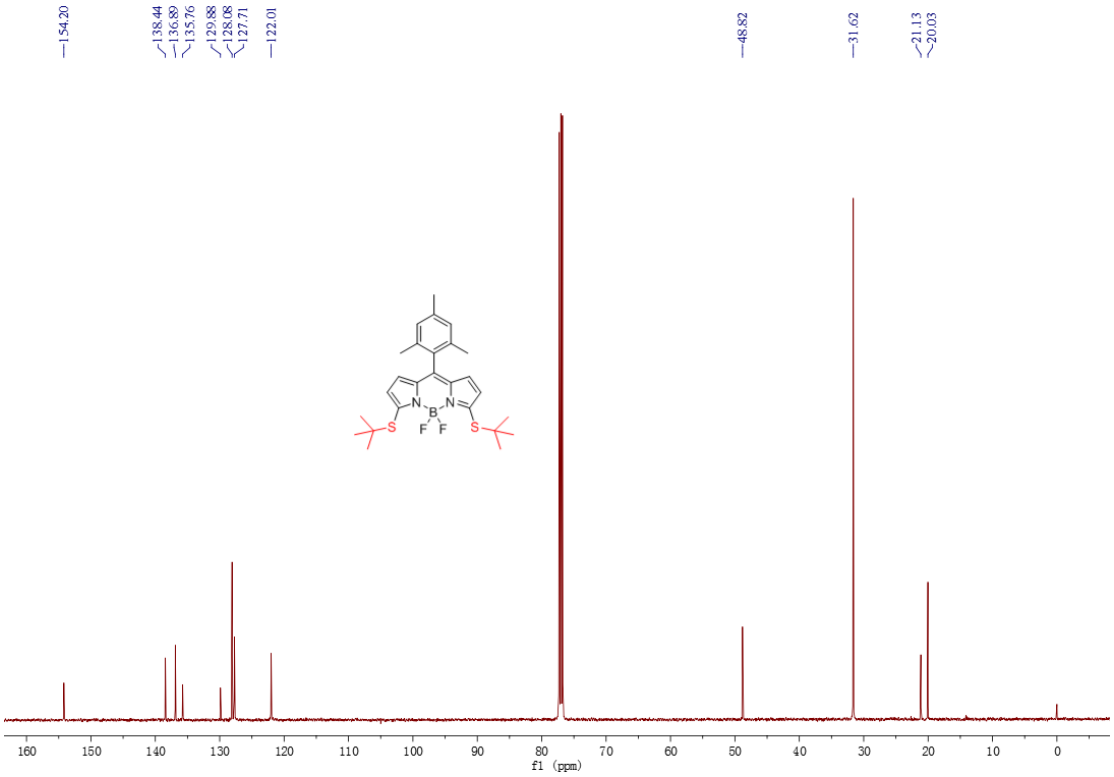
^{13}C NMR spectrum of **4f** in $CDCl_3$



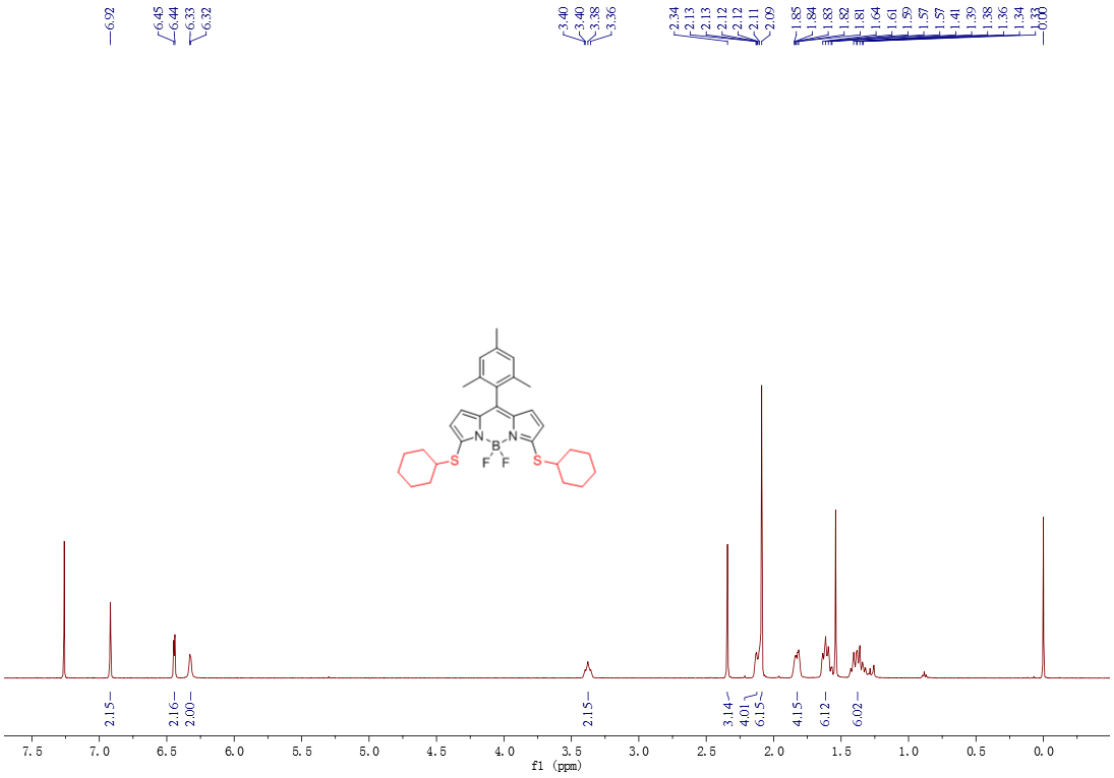
^{1}H NMR spectrum of **4g** in $CDCl_3$



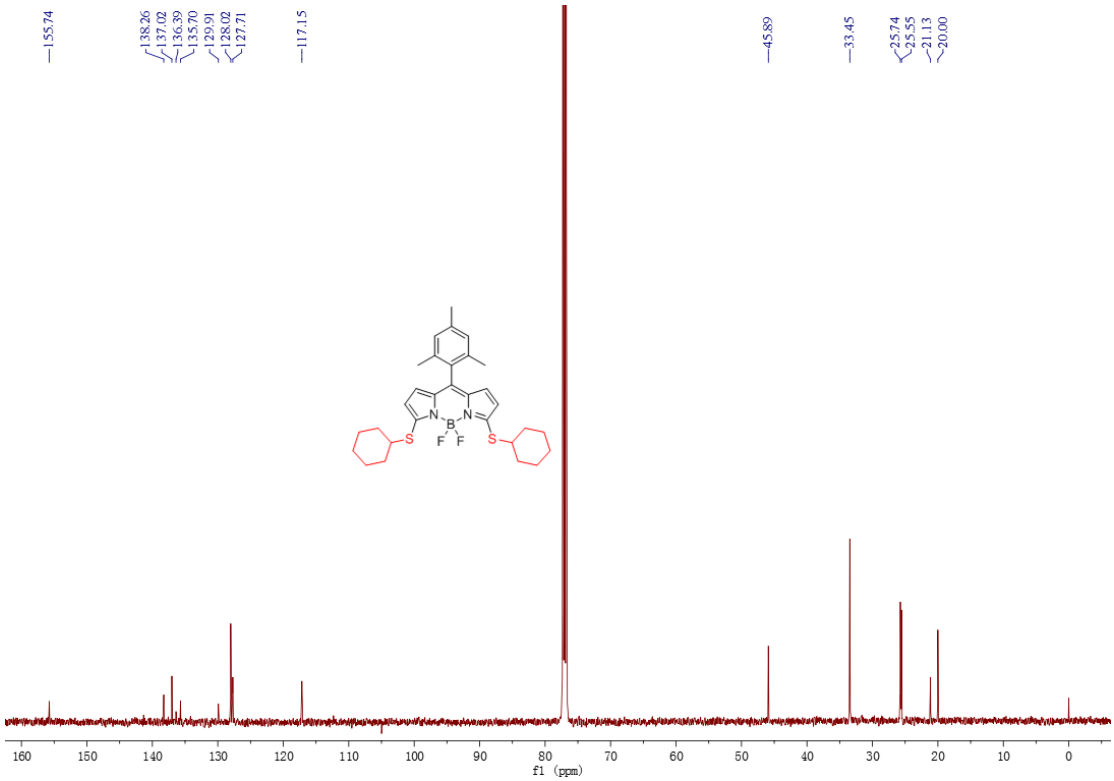
^{13}C NMR spectrum of **4g** in $CDCl_3$



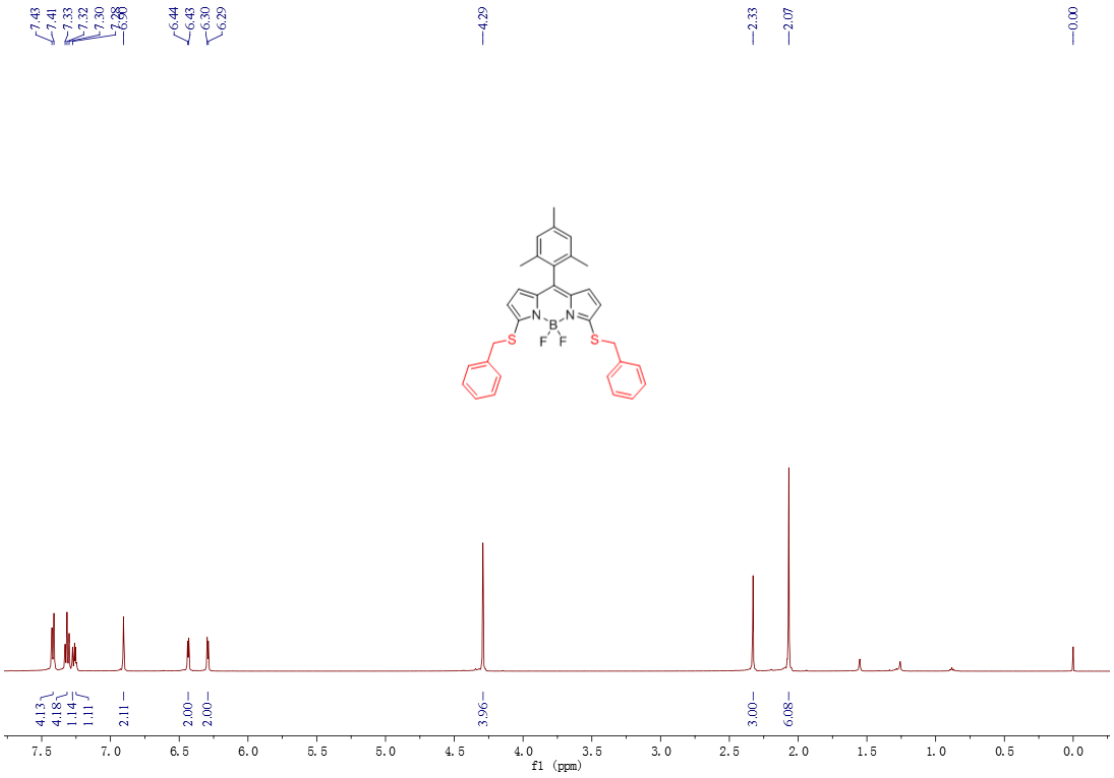
^{1}H NMR spectrum of **4h** in $CDCl_3$



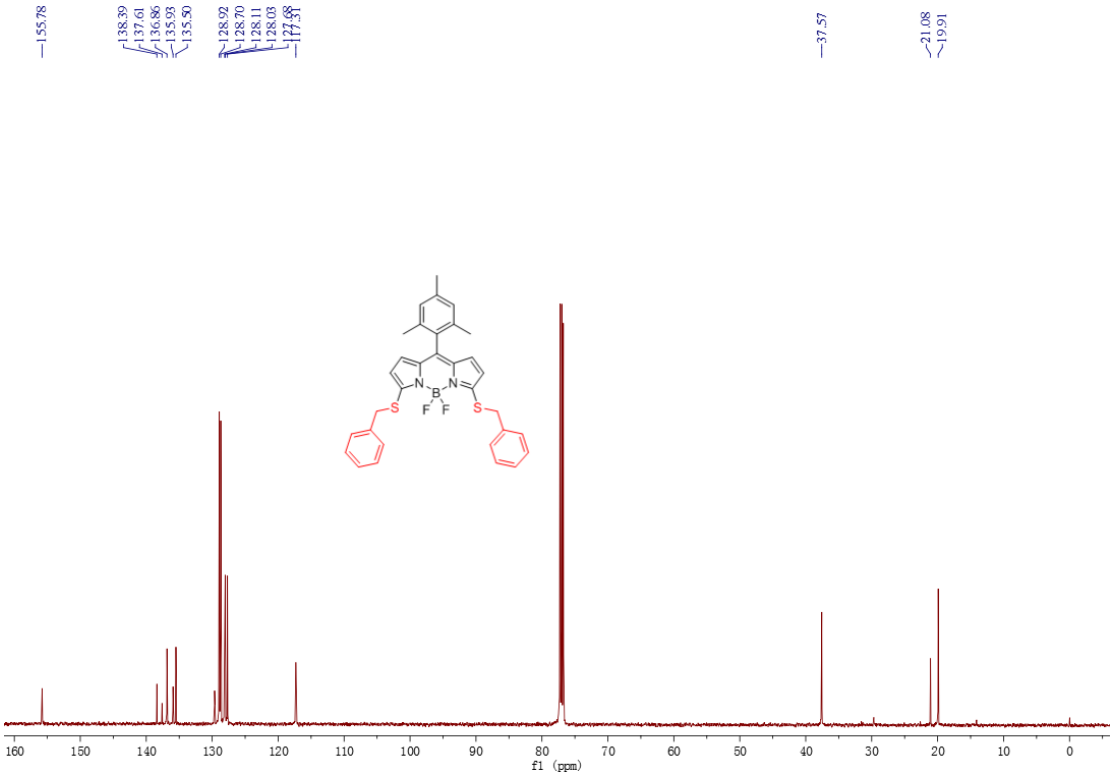
^{13}C NMR spectrum of **4h** in $CDCl_3$



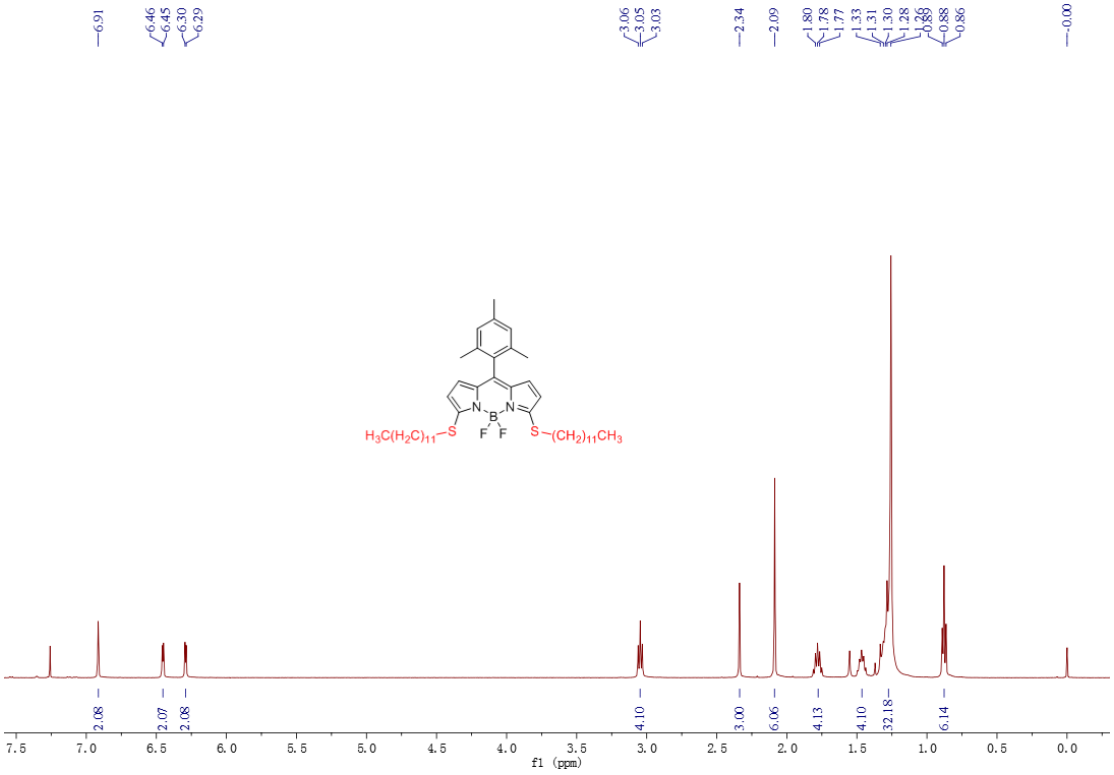
^{1}H NMR spectrum of **4i** in $CDCl_3$



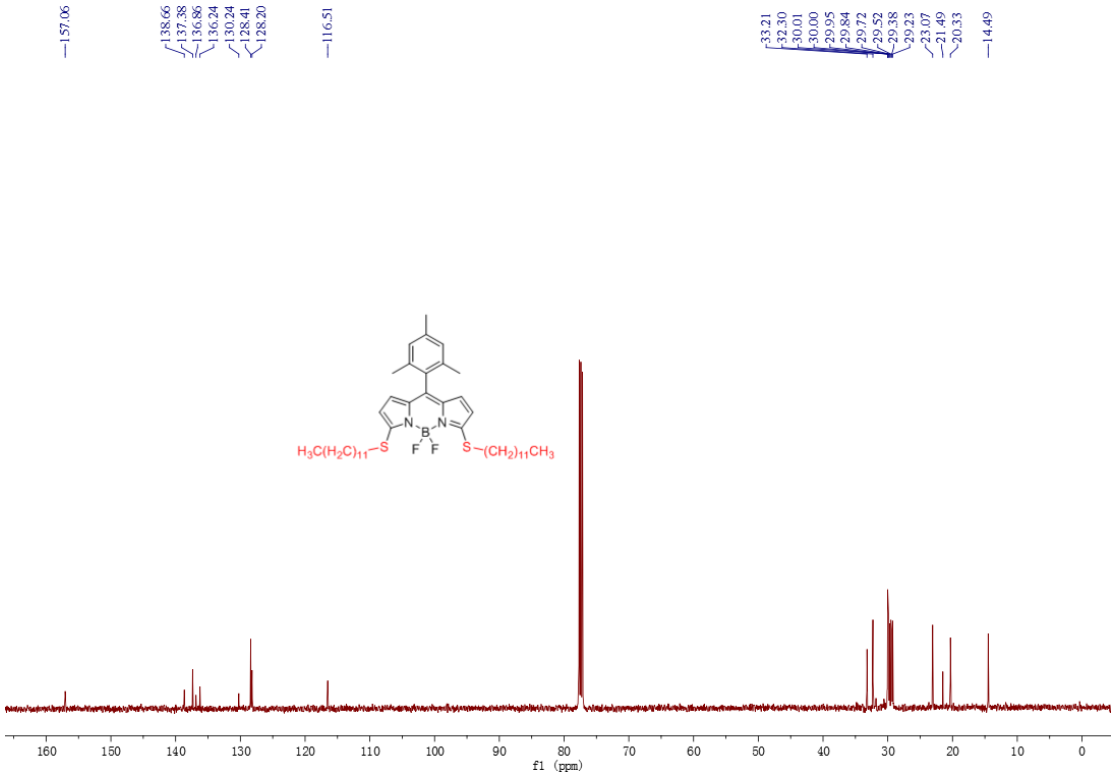
^{13}C NMR spectrum of **4i** in $CDCl_3$



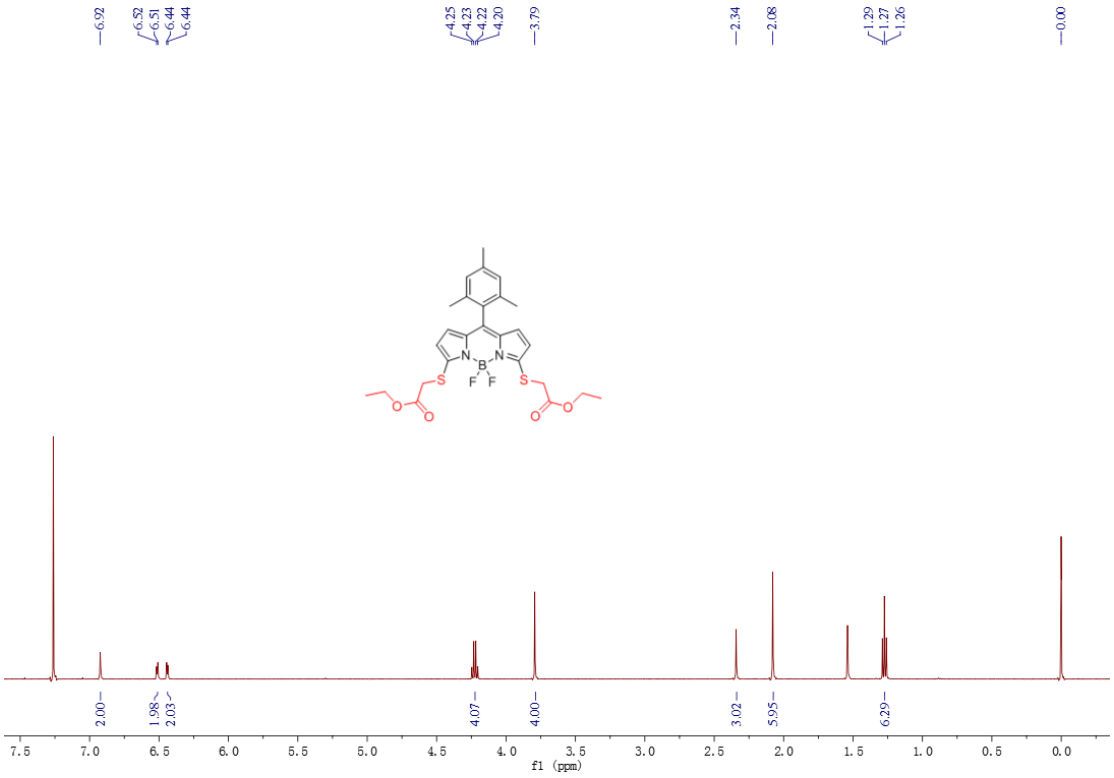
^{1}H NMR spectrum of **4j** in $CDCl_3$



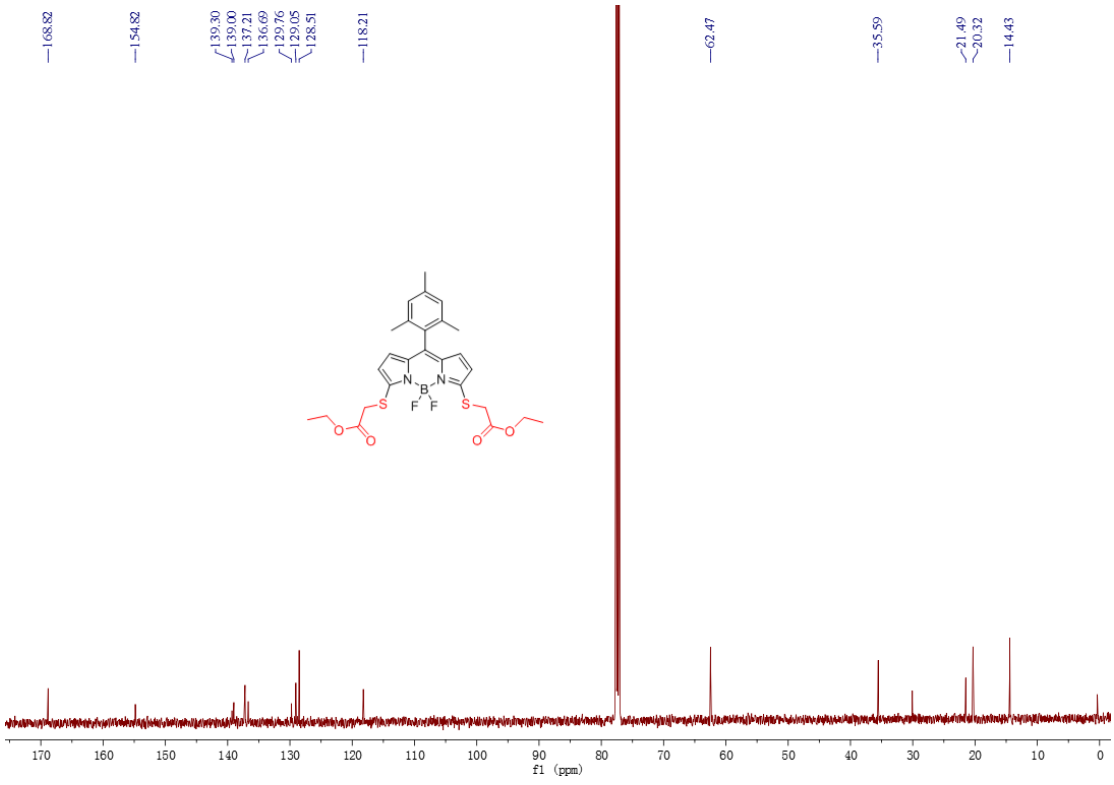
^{13}C NMR spectrum of **4j** in $CDCl_3$



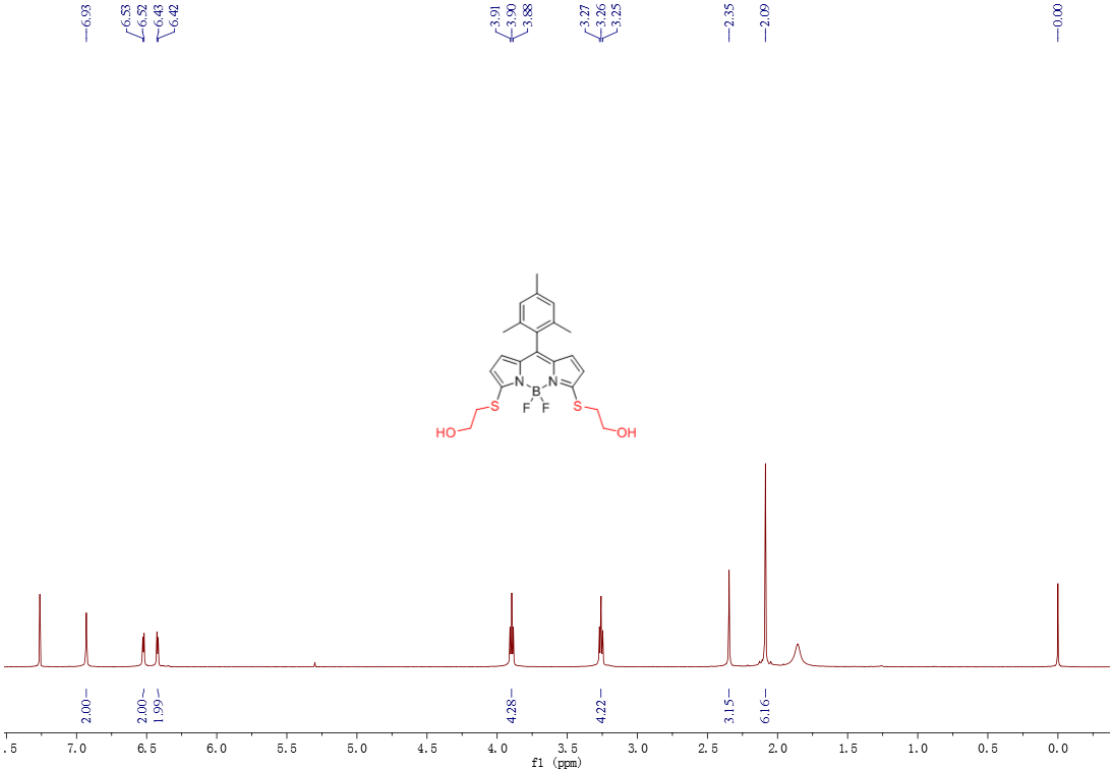
^{1}H NMR spectrum of **4k** in $CDCl_3$



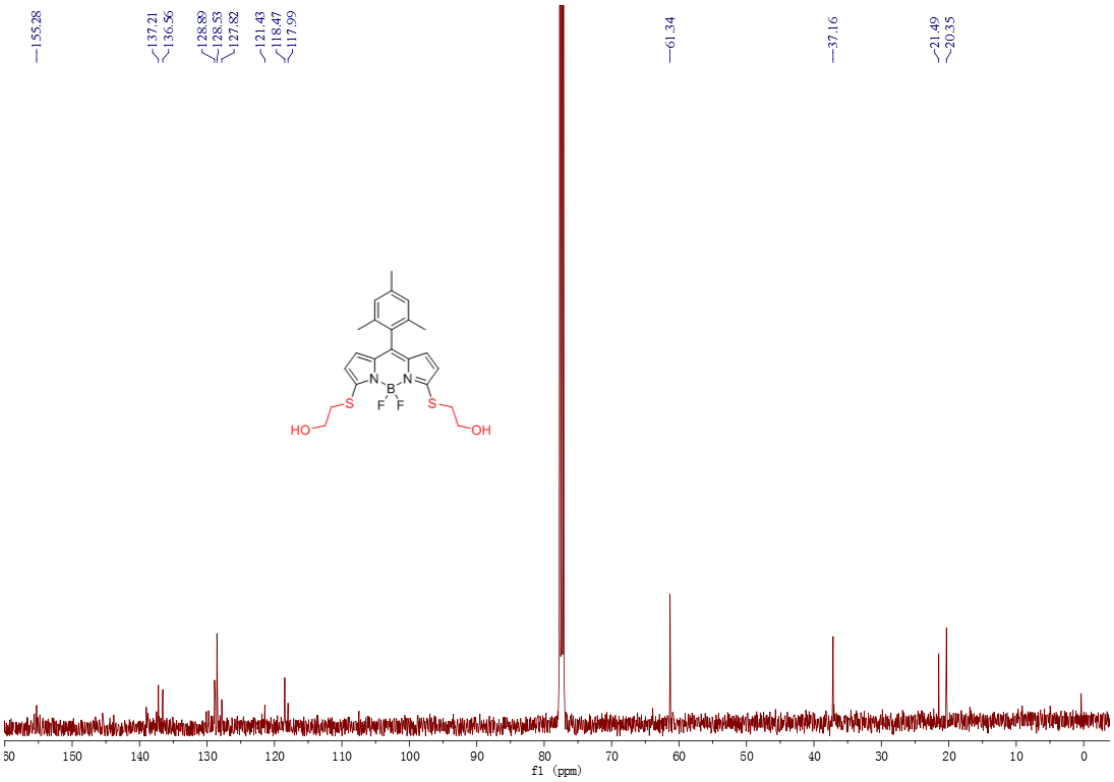
^{13}C NMR spectrum of **4k** in $CDCl_3$



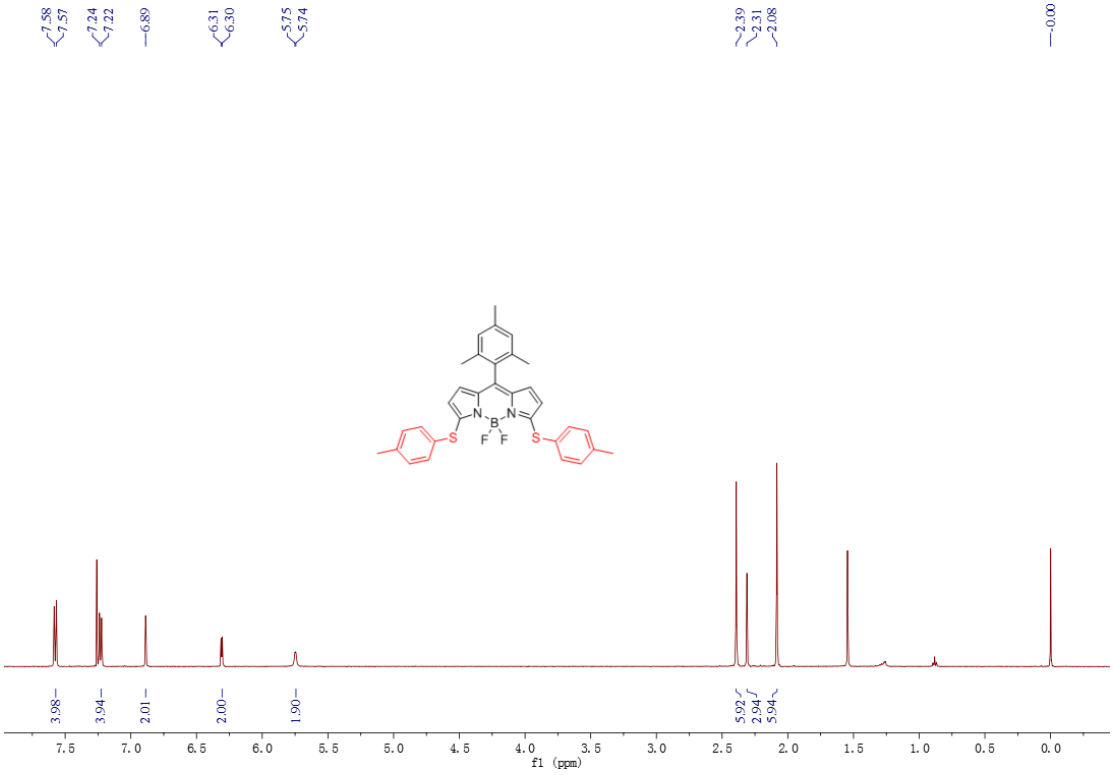
^{1}H NMR spectrum of **4l** in $CDCl_3$



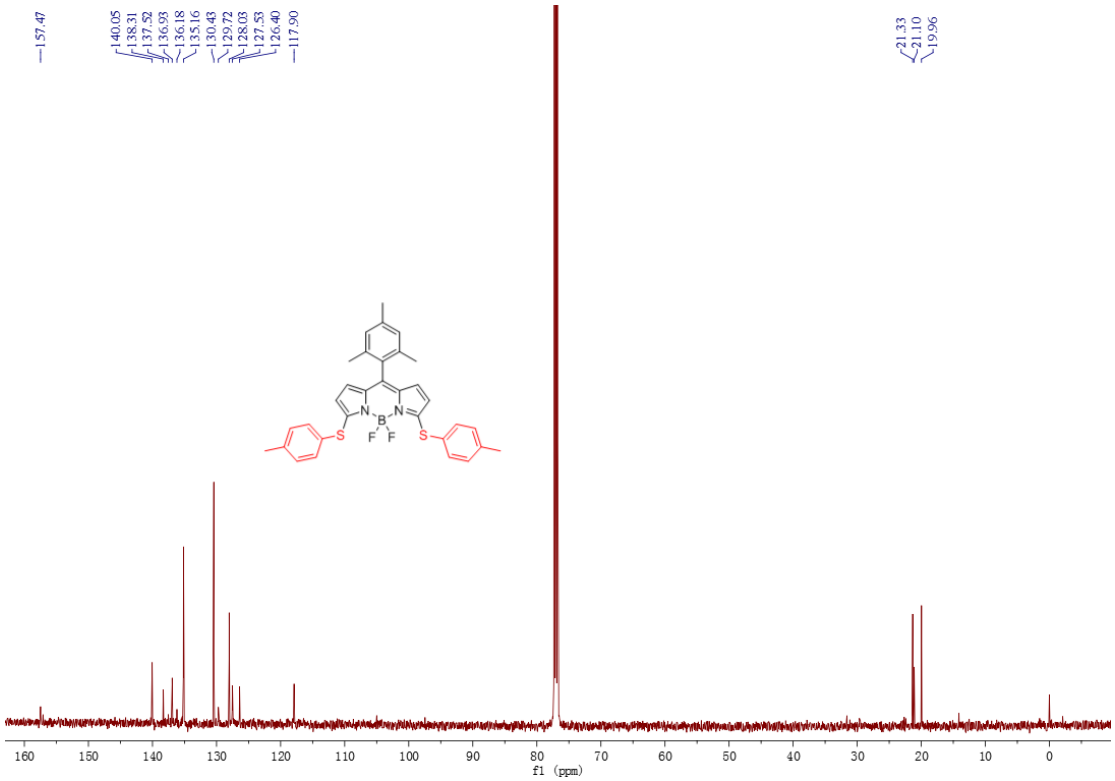
^{13}C NMR spectrum of **4l** in $CDCl_3$



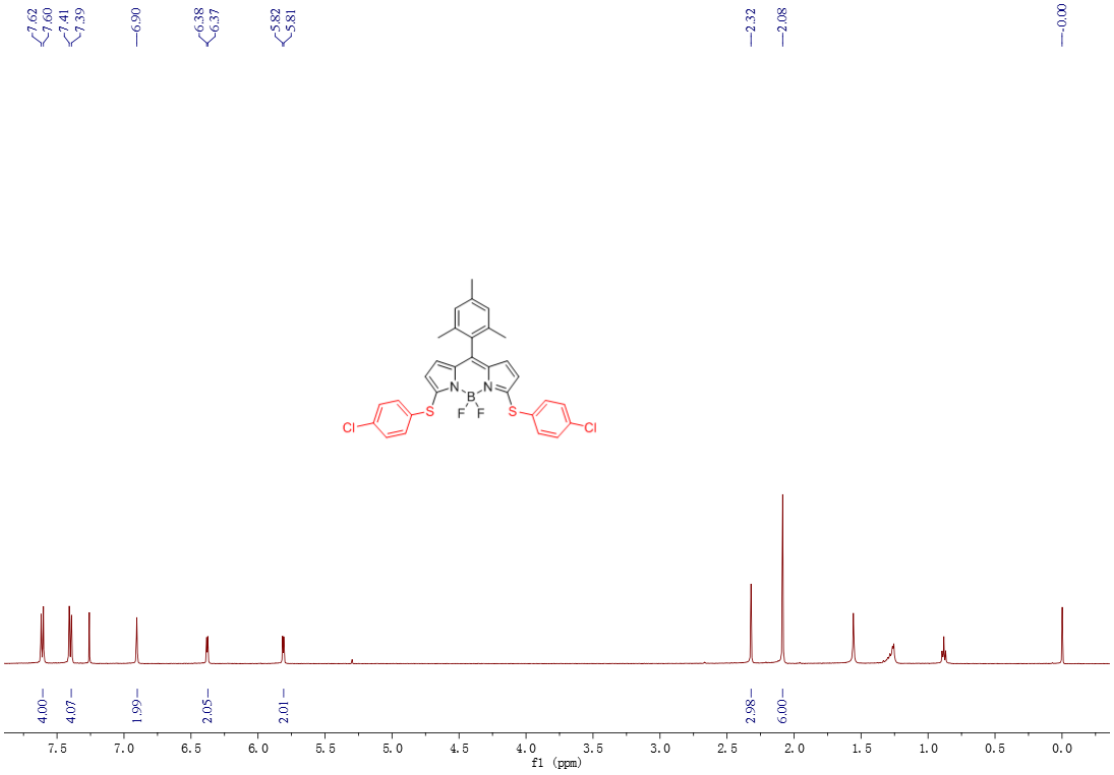
^{1}H NMR spectrum of **4m** in $CDCl_3$



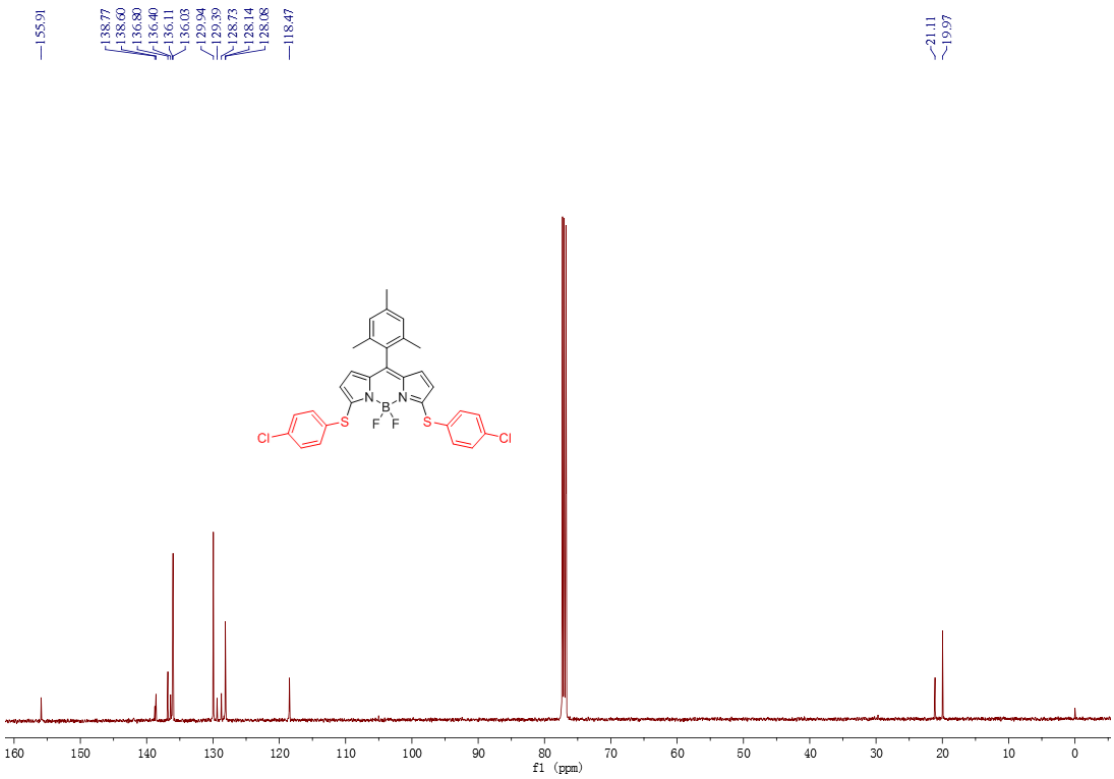
^{13}C NMR spectrum of **4m** in $CDCl_3$



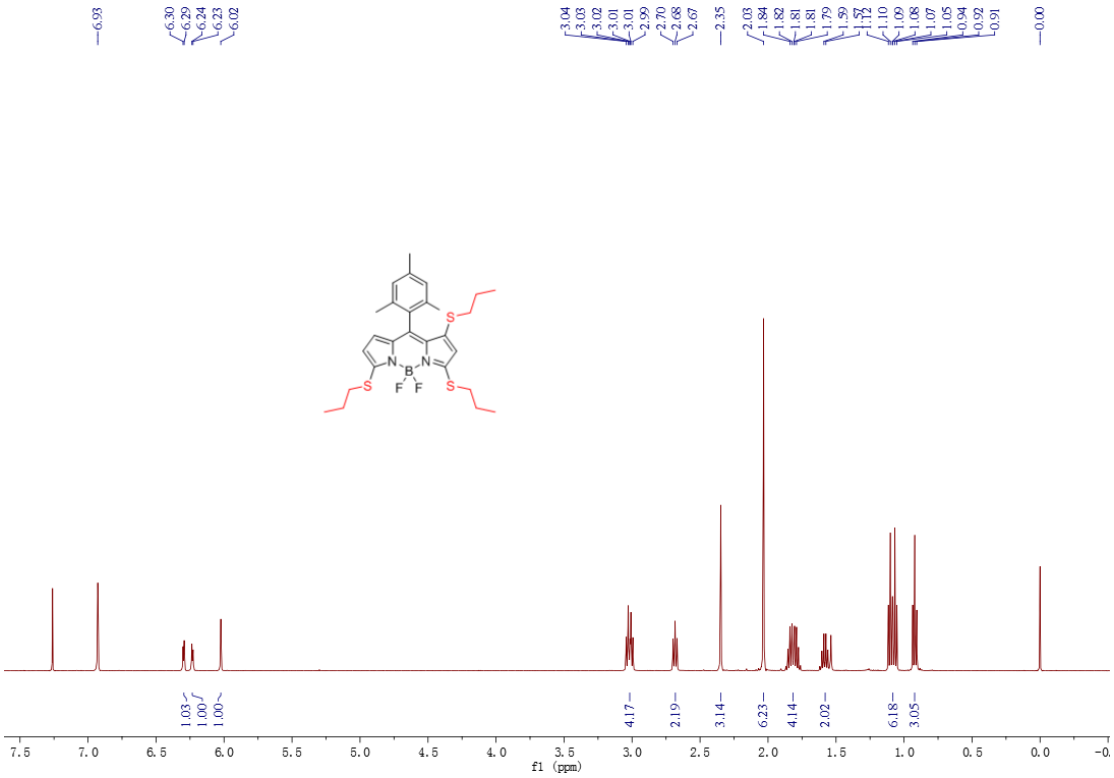
^{1}H NMR spectrum of **4n** in $CDCl_3$



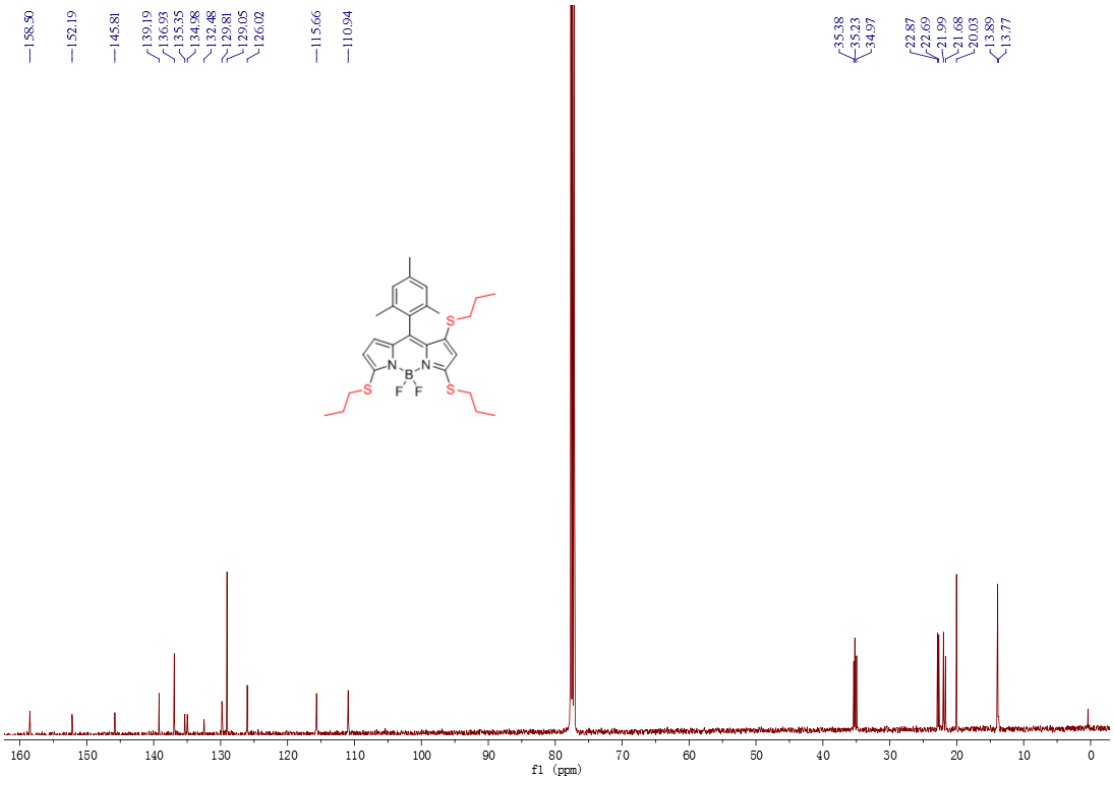
^{13}C NMR spectrum of **4n** in $CDCl_3$



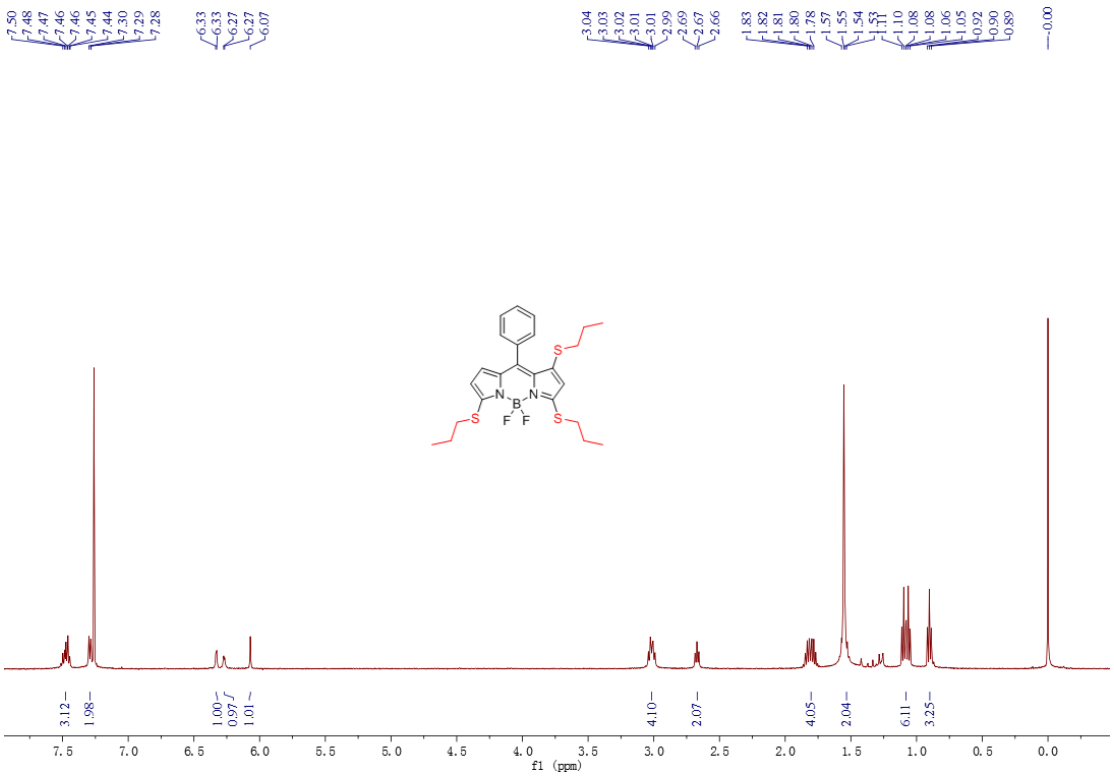
^{1}H NMR spectrum of **5a** in $CDCl_3$



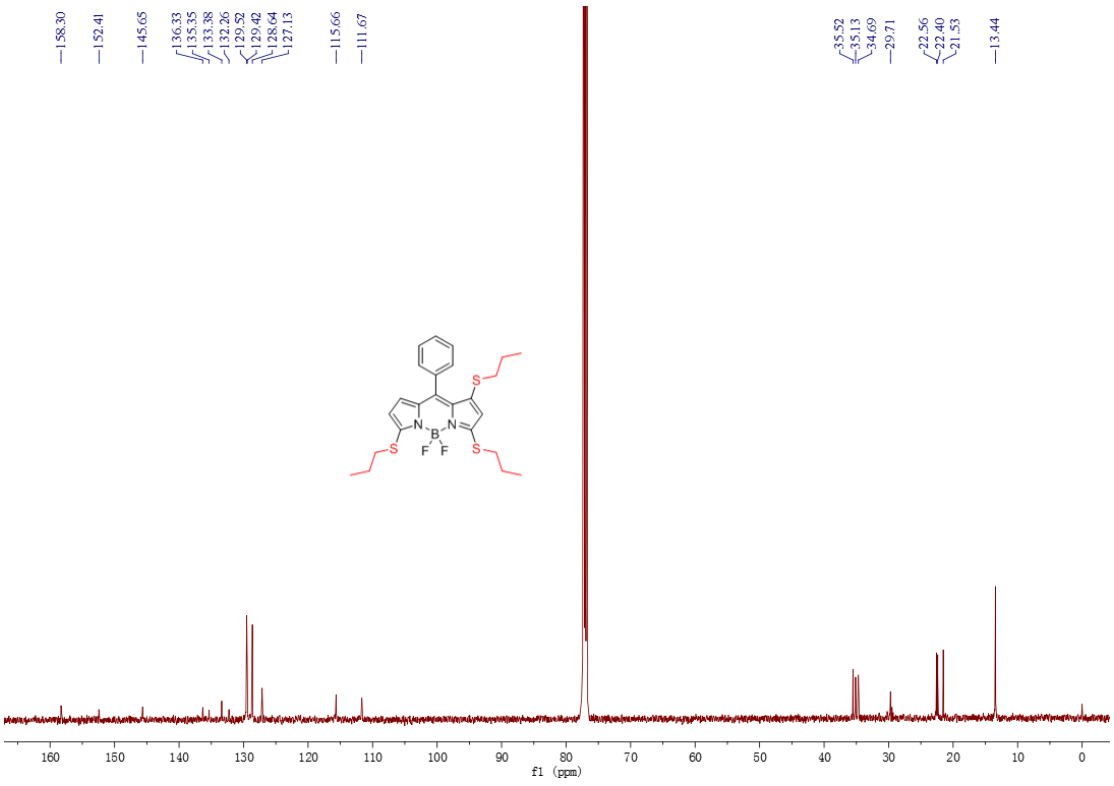
^{13}C NMR spectrum of **5a** in $CDCl_3$



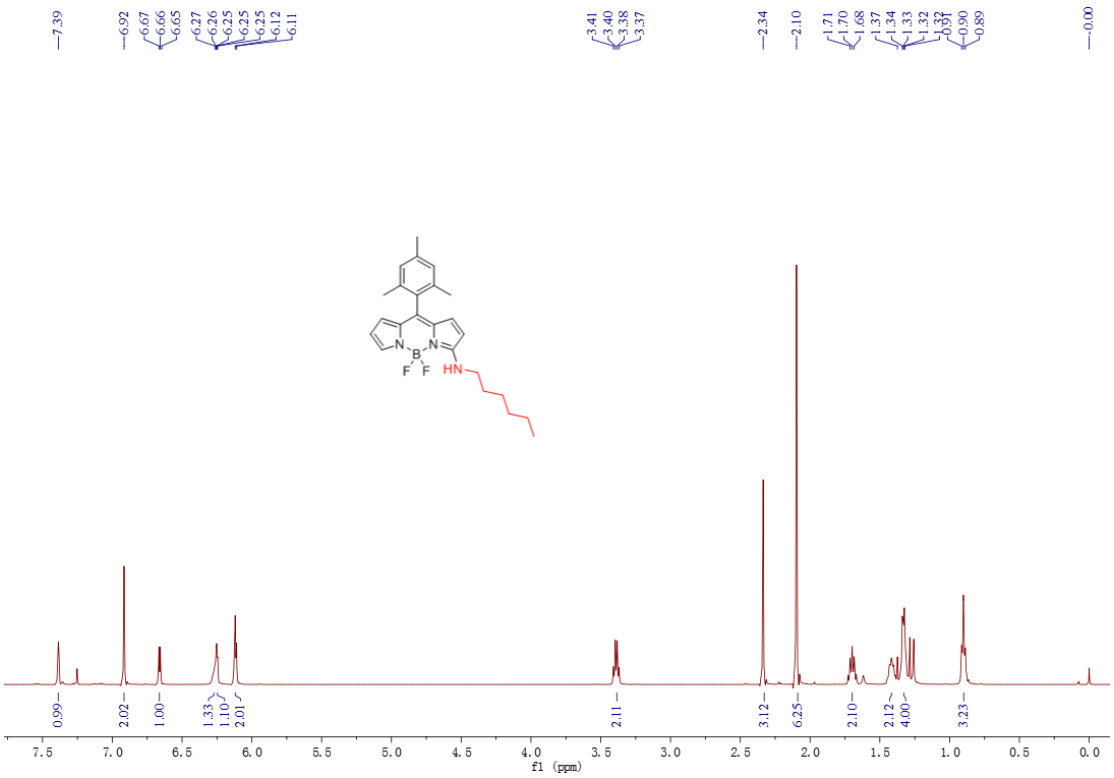
^{1}H NMR spectrum of **5b** in $CDCl_3$



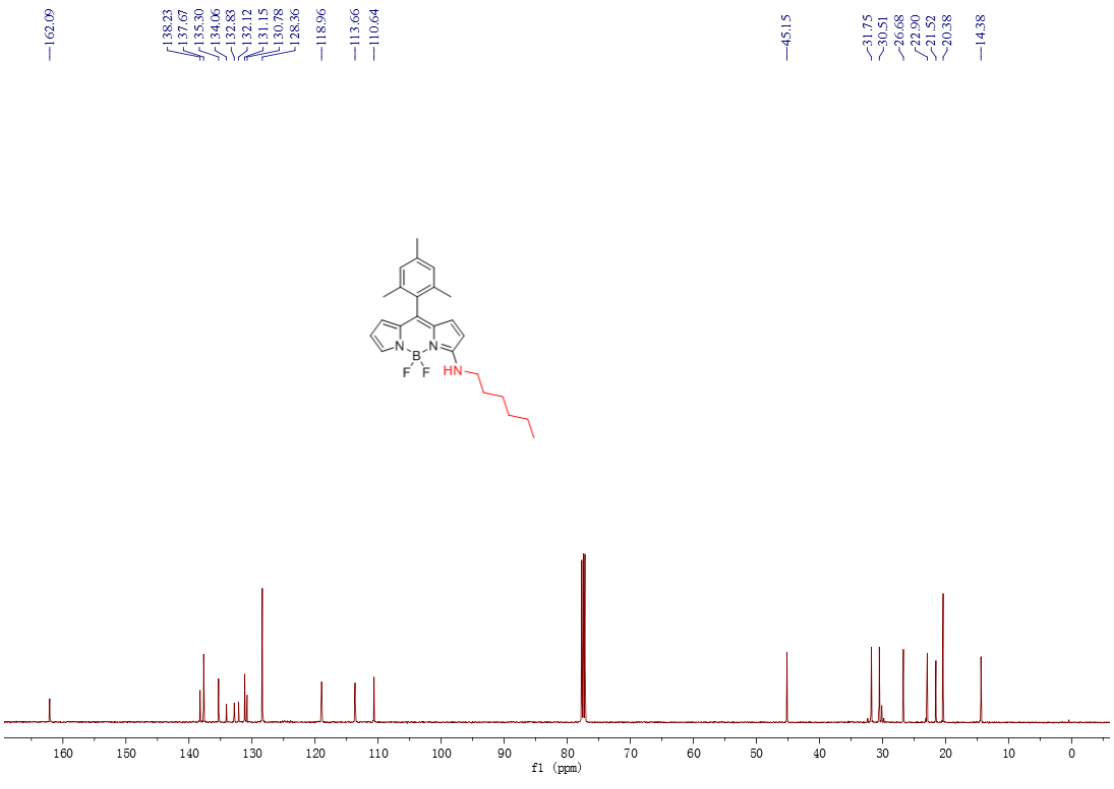
^{13}C NMR spectrum of **5b** in $CDCl_3$



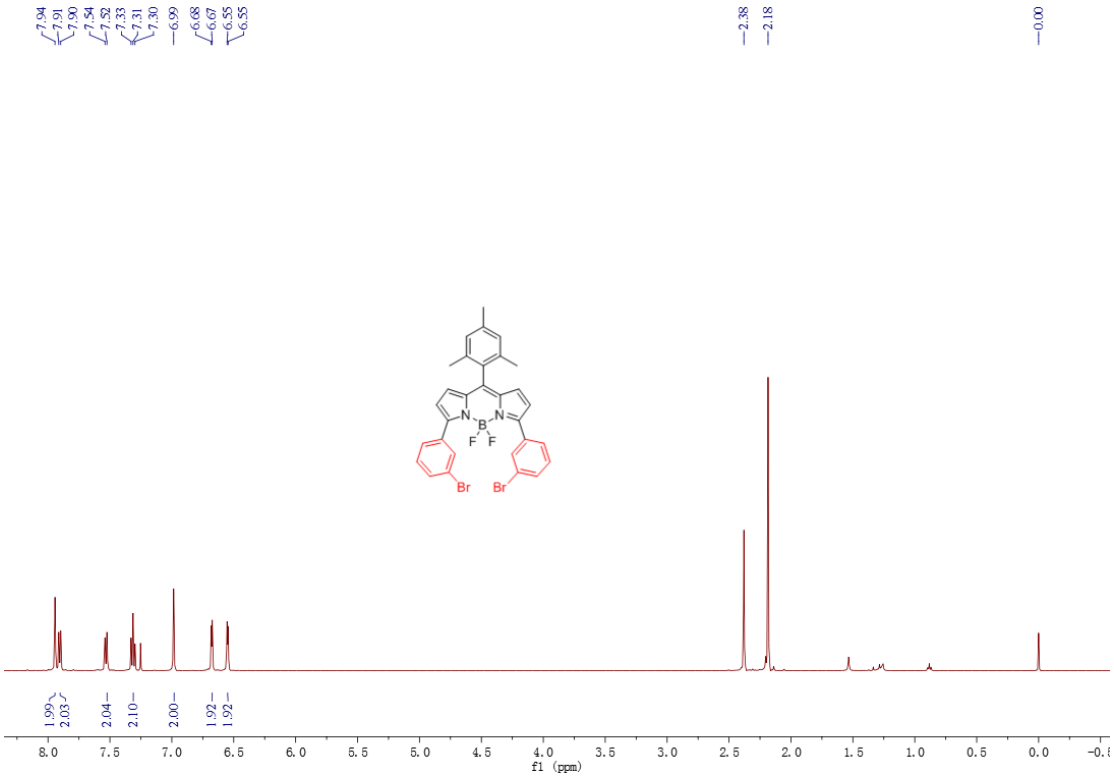
^{1}H NMR spectrum of **6** in $CDCl_3$



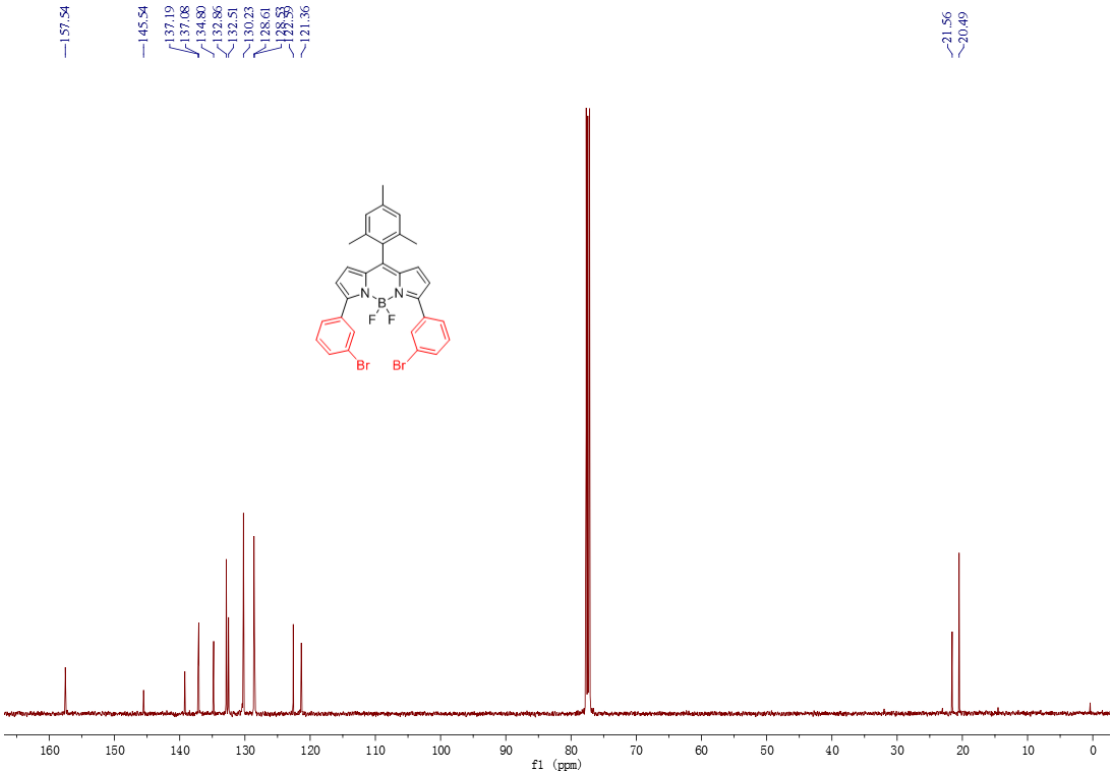
^{13}C NMR spectrum of **6** in $CDCl_3$



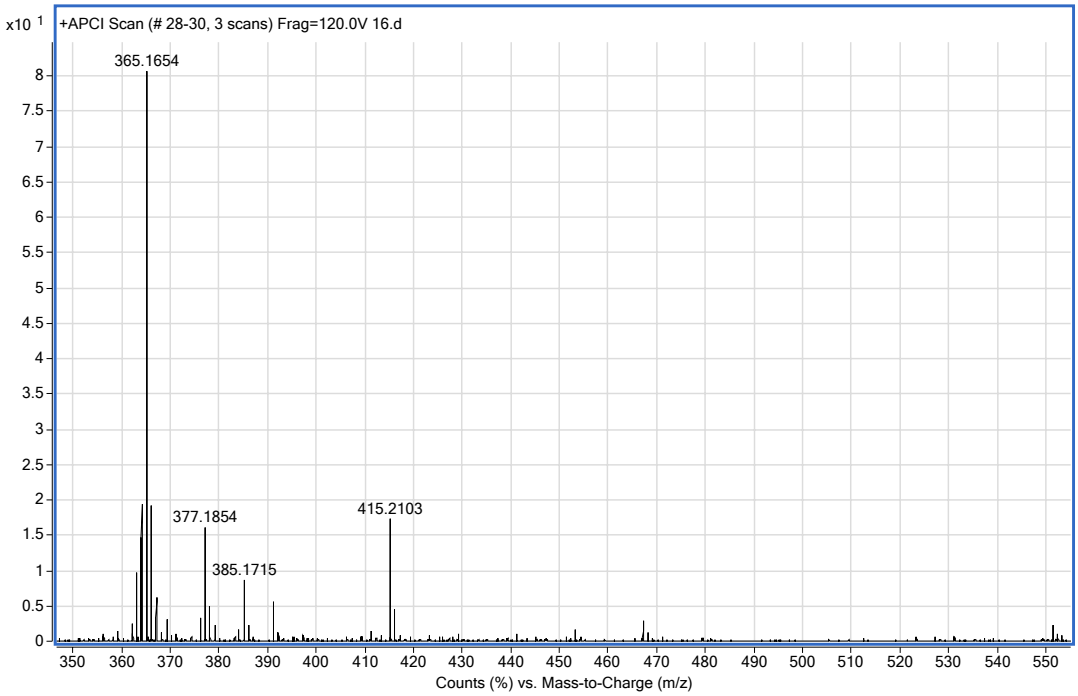
^{1}H NMR spectrum of **7** in $CDCl_3$



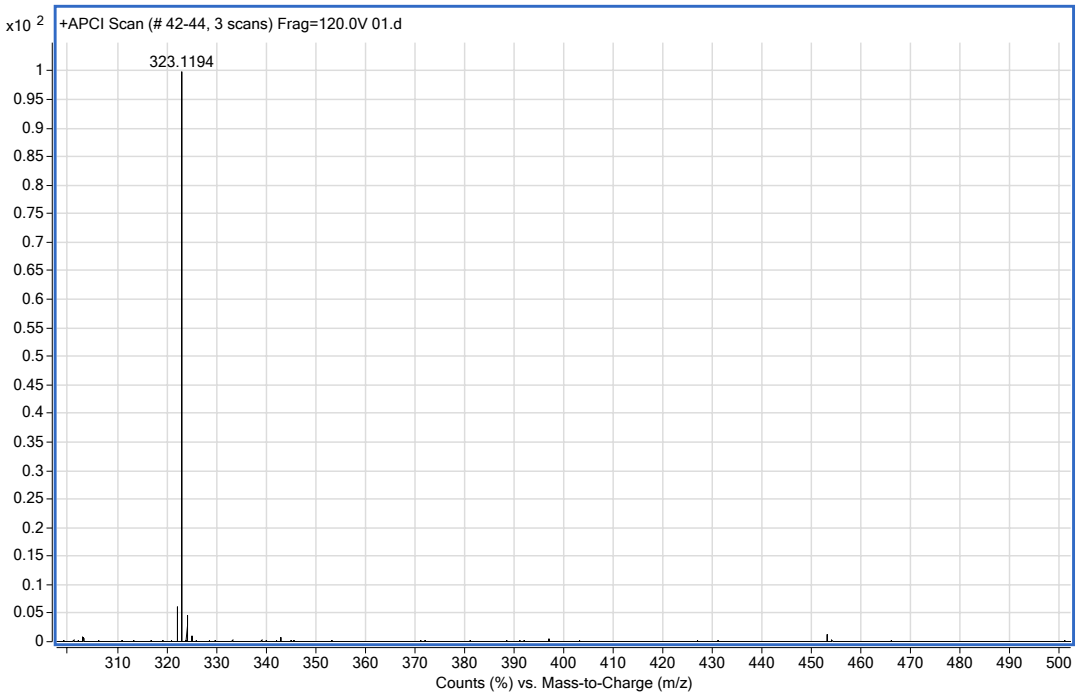
^{13}C NMR spectrum of **7** in $CDCl_3$



HRMS for **3a**



HRMS for **3b**



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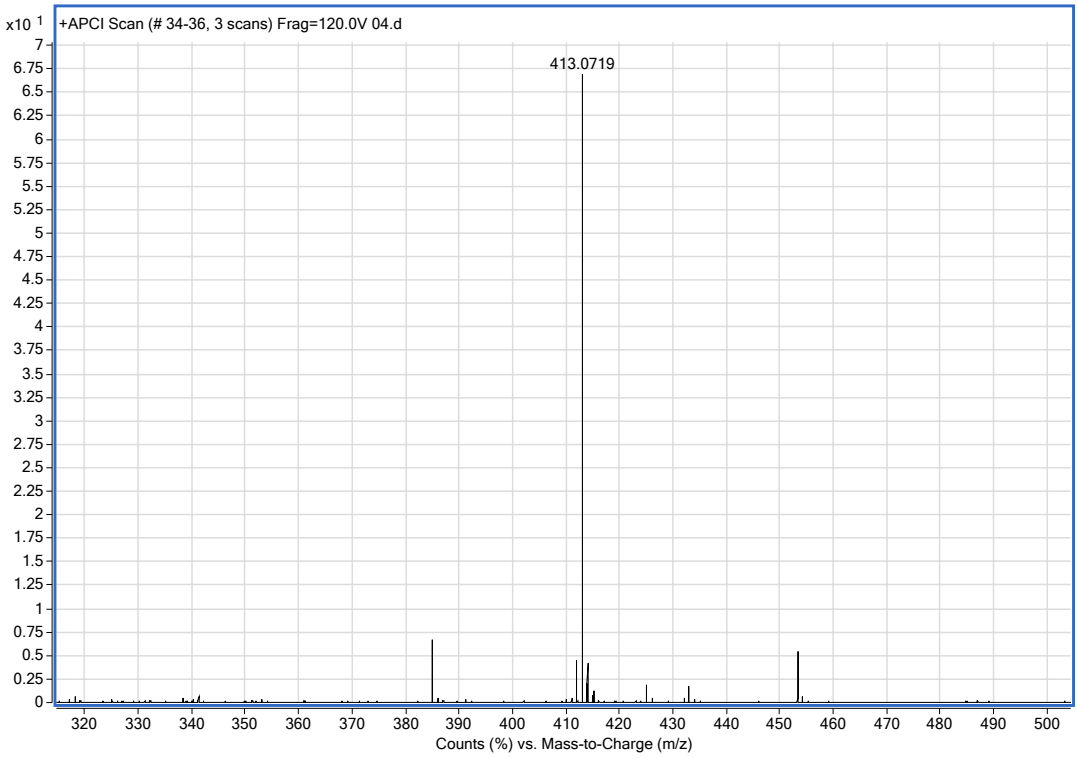
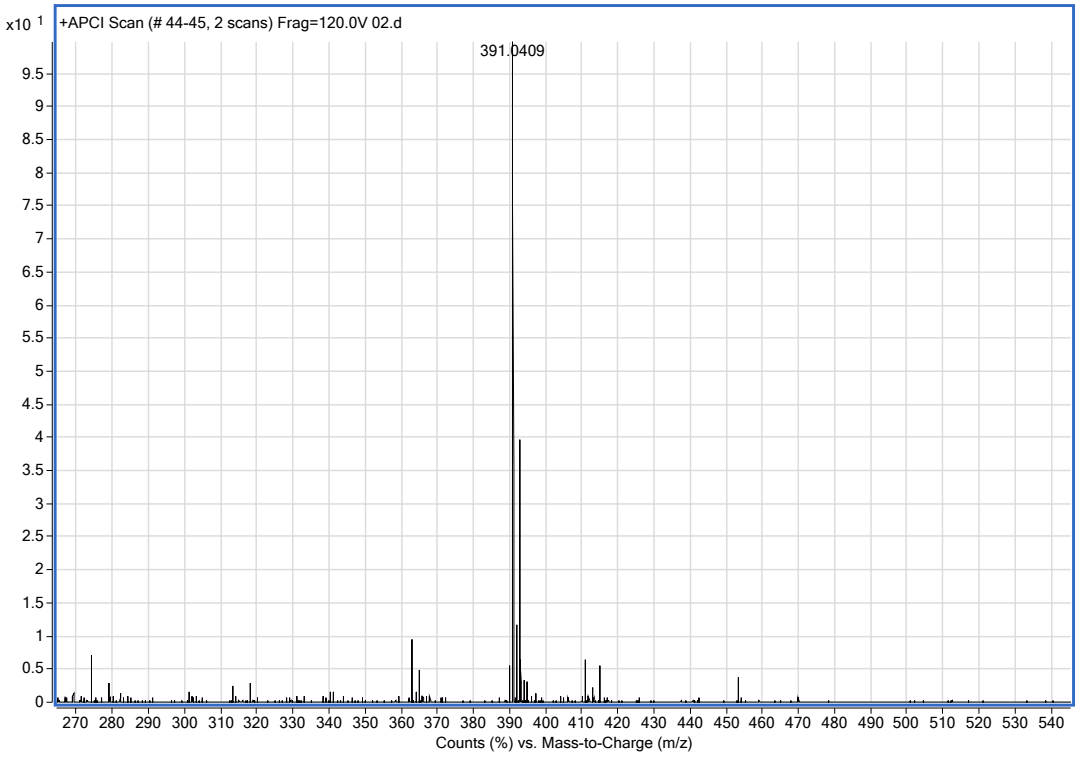
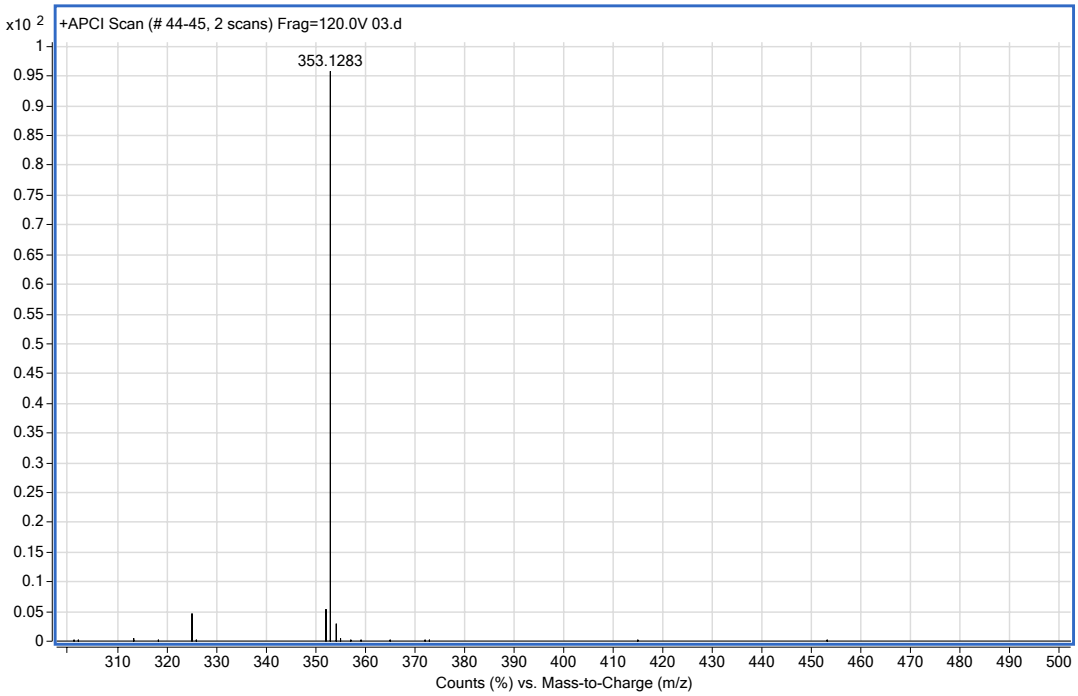


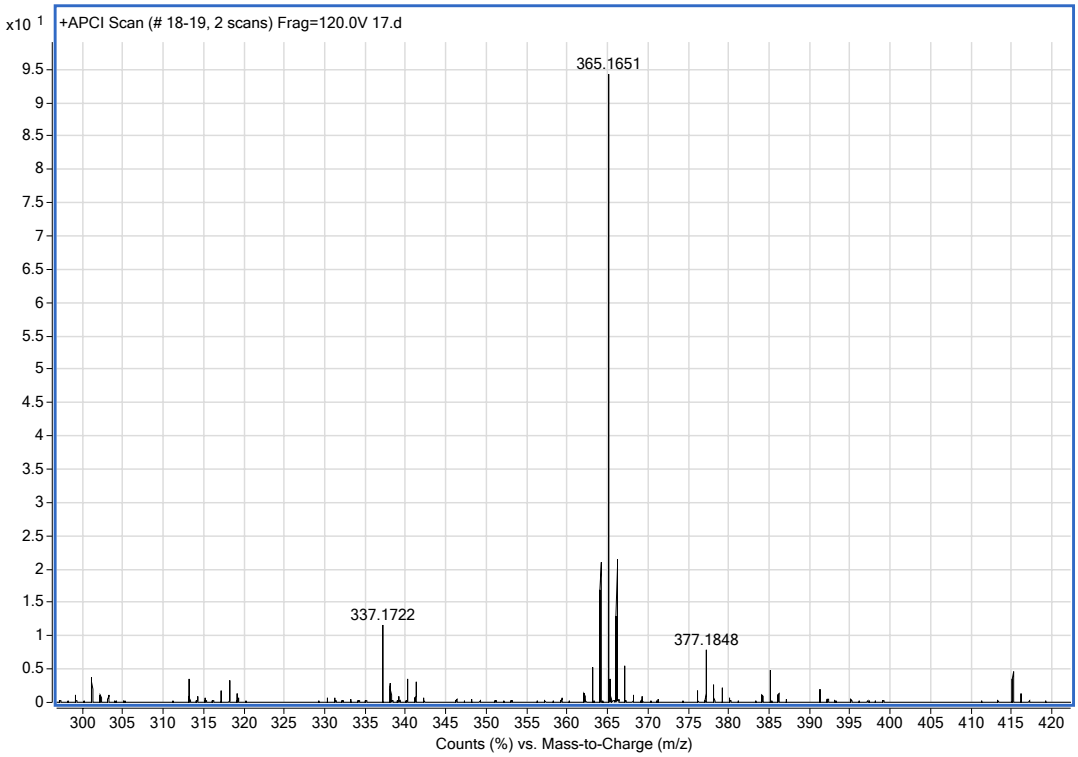
HRMS for **3d**



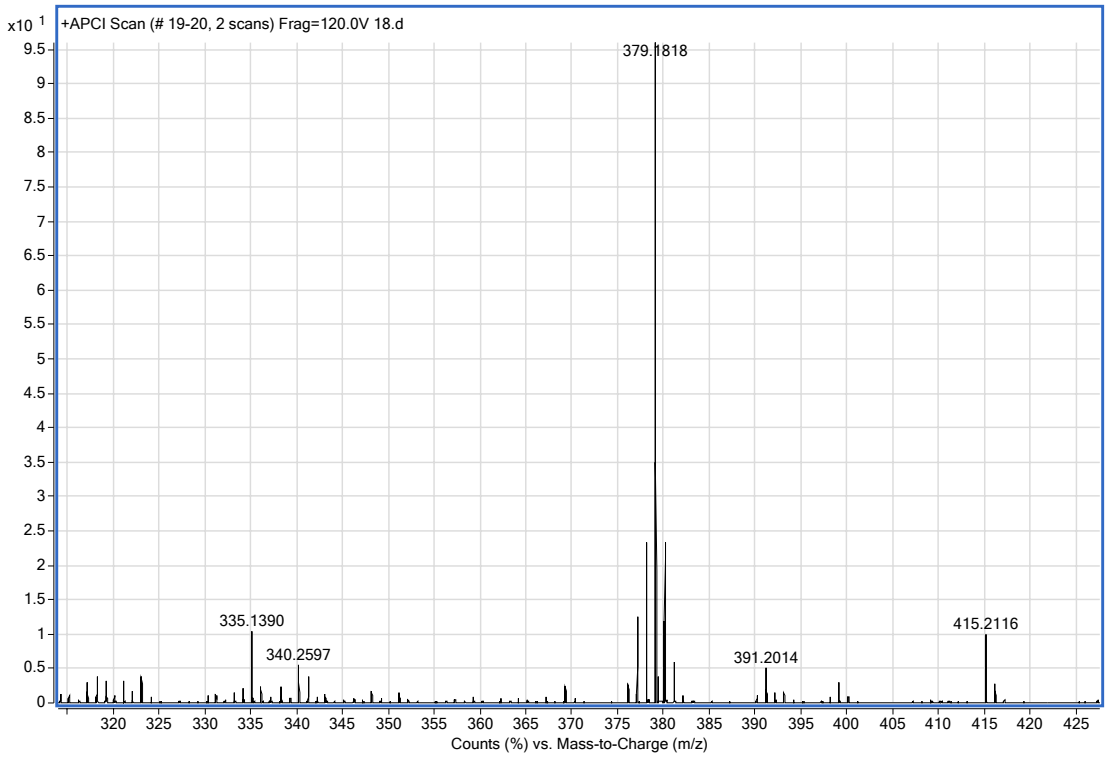
HRMS for **3e**



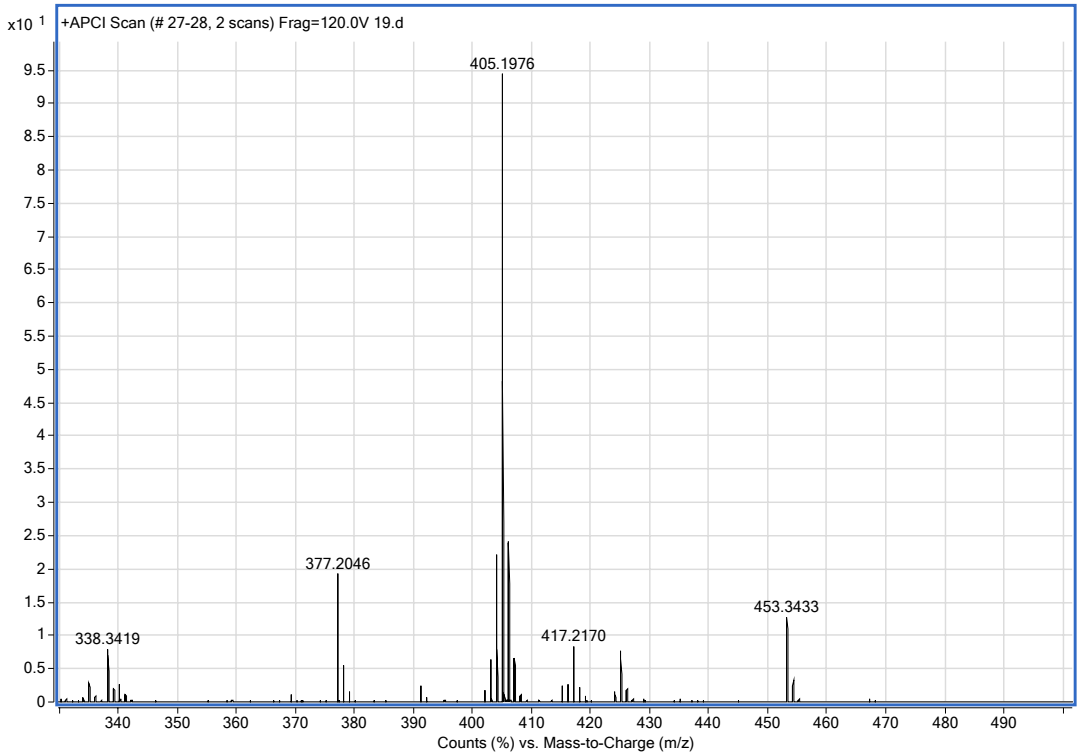
HRMS for **3f**



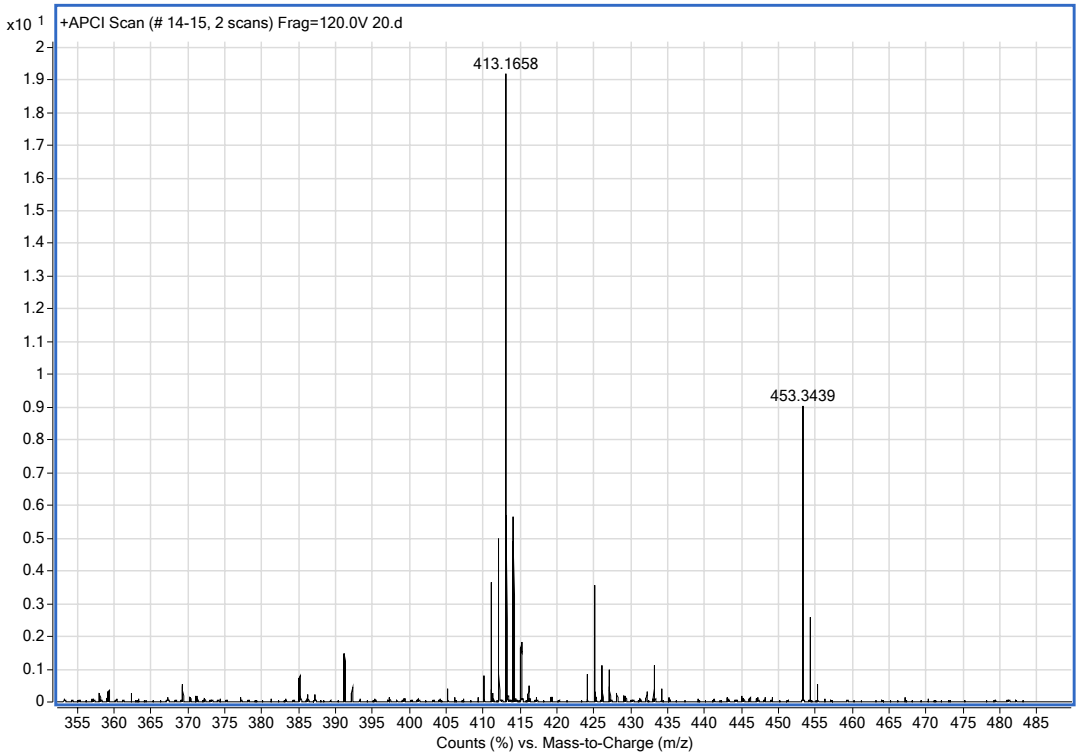
HRMS for **3g**



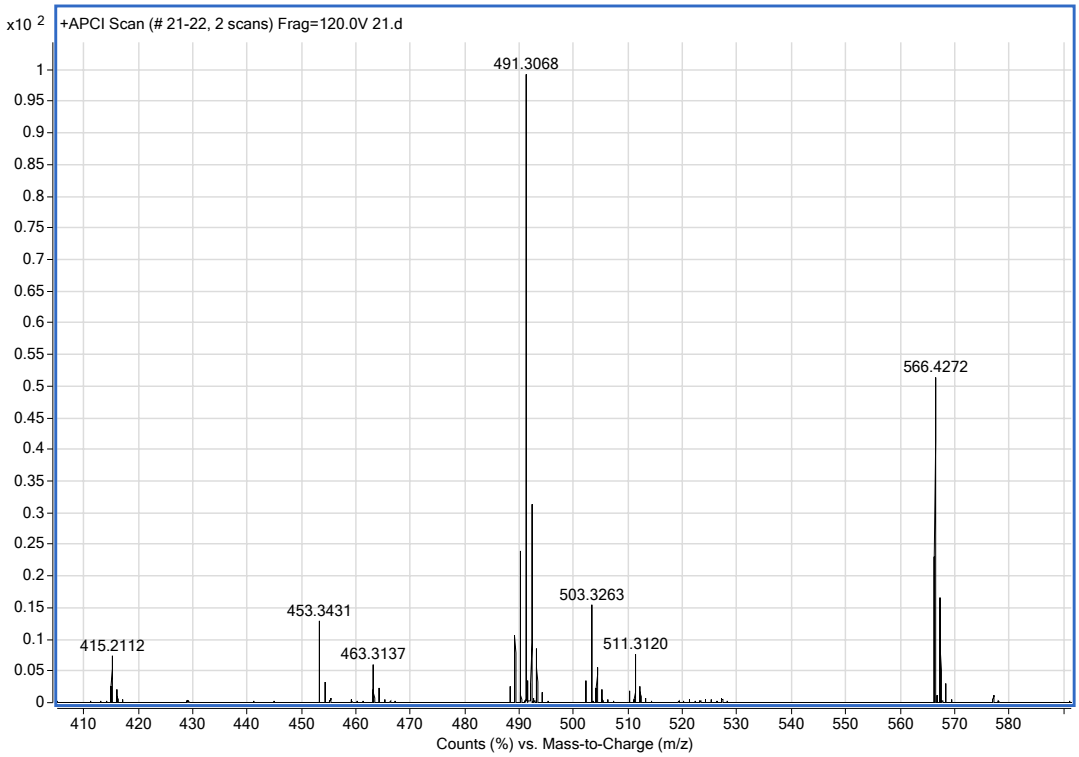
HRMS for **3h**



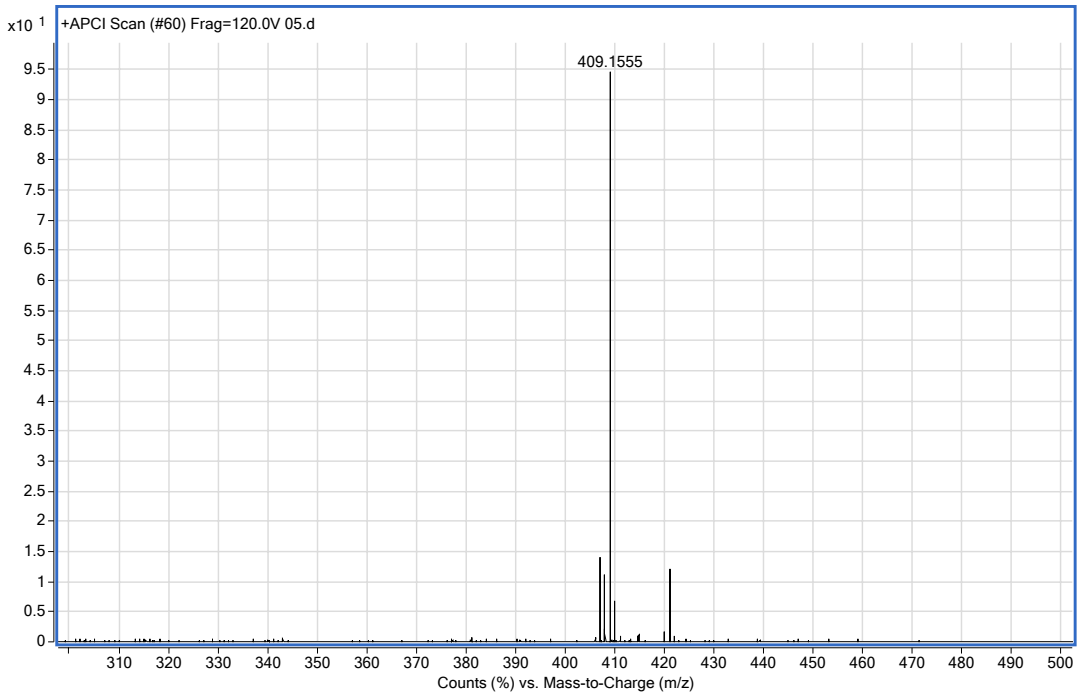
HRMS for **3i**



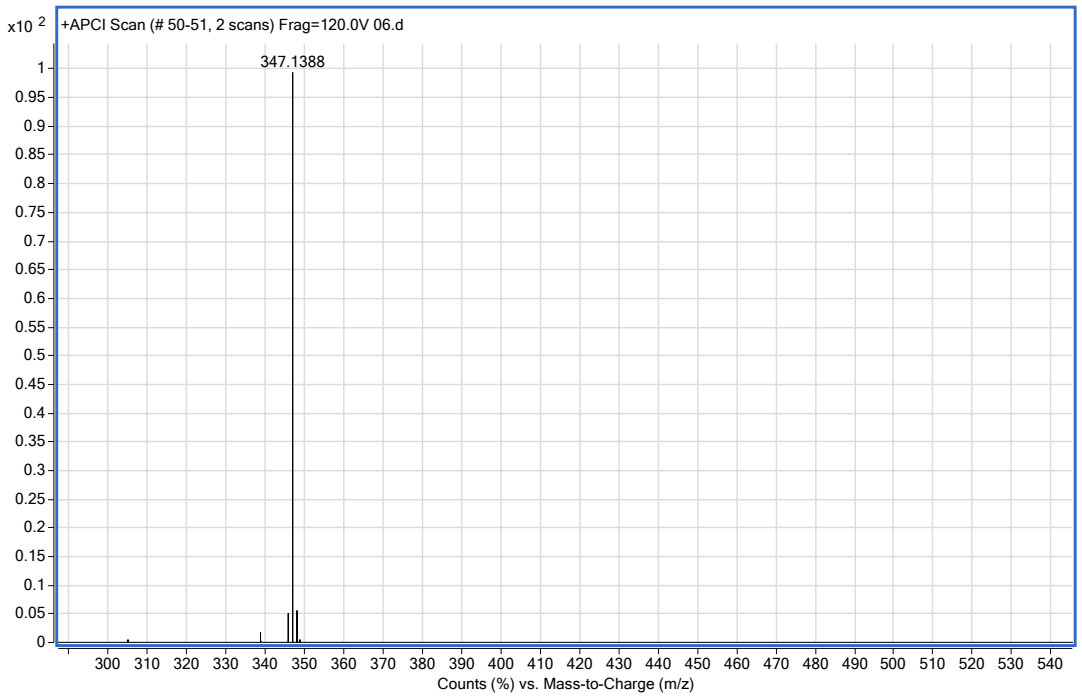
HRMS for **3j**



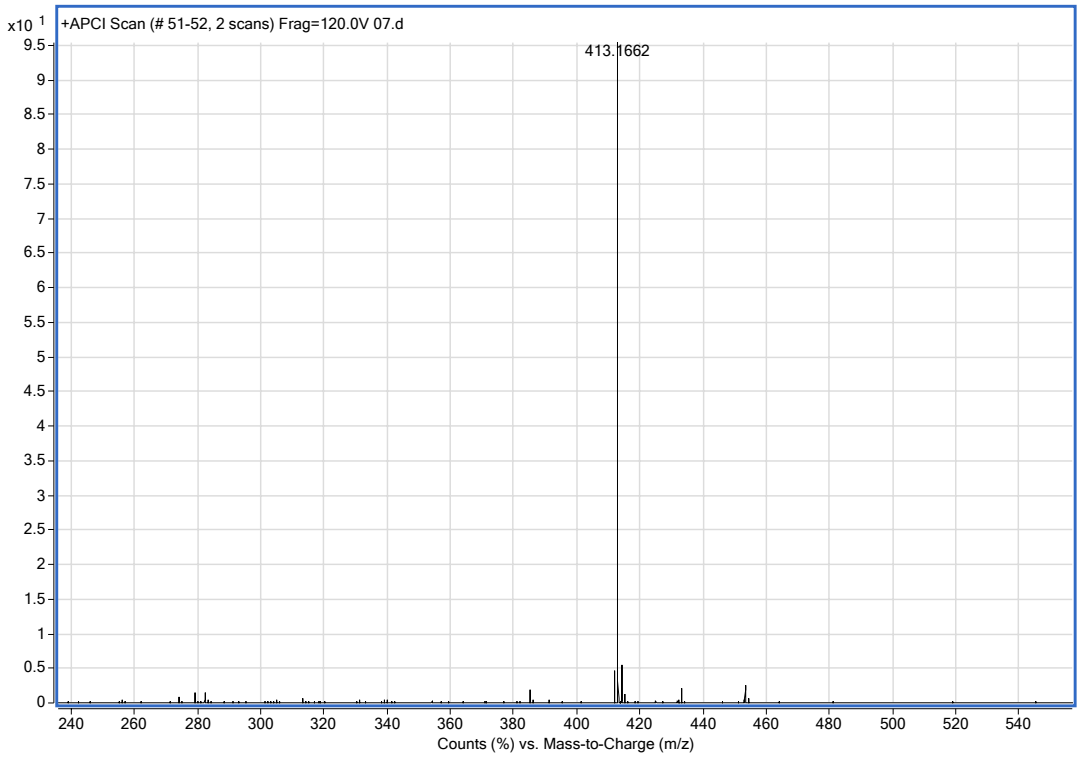
HRMS for **3k**



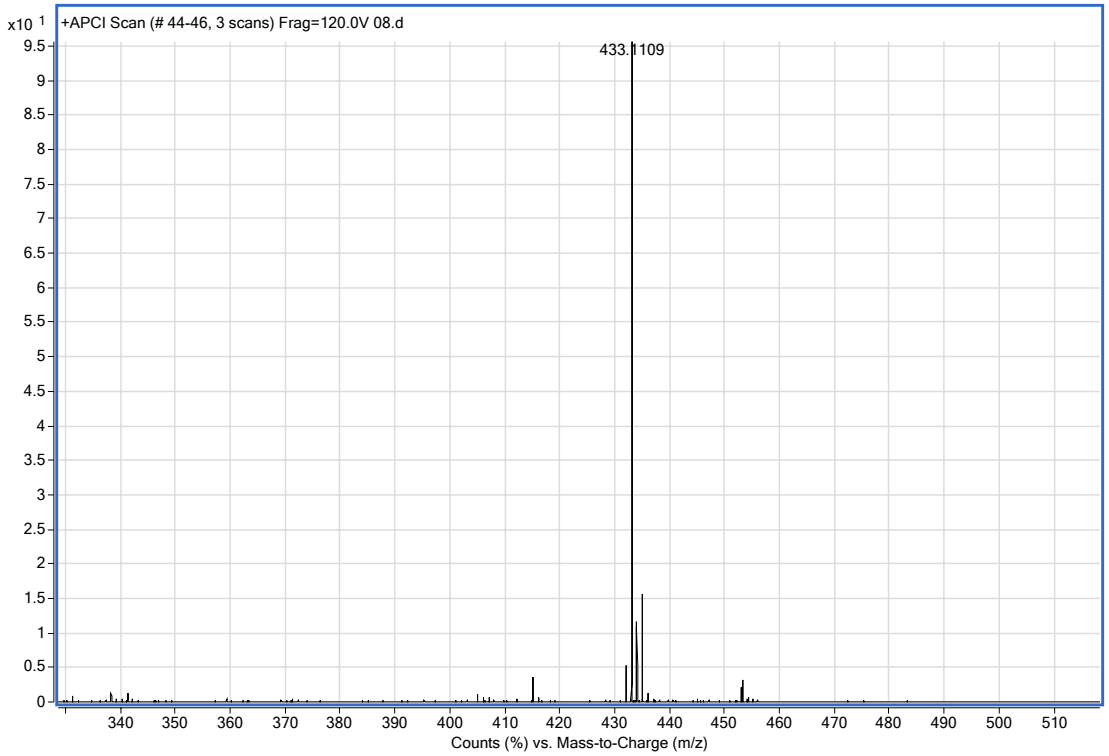
HRMS for **3l**



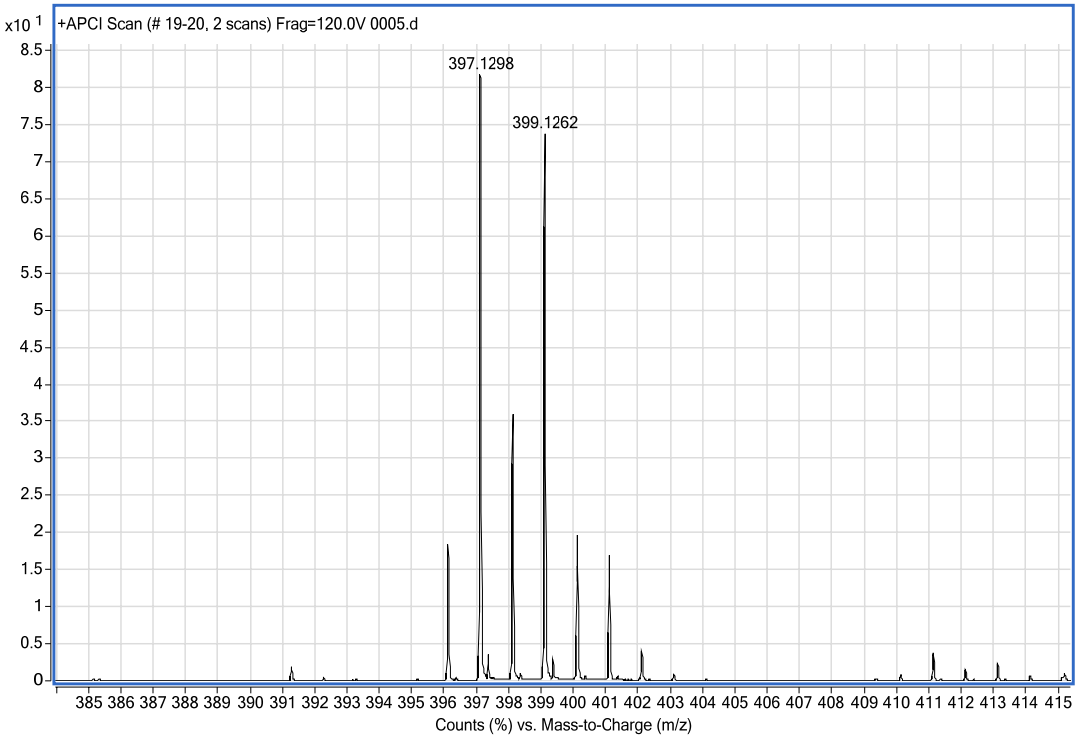
HRMS for **3m**



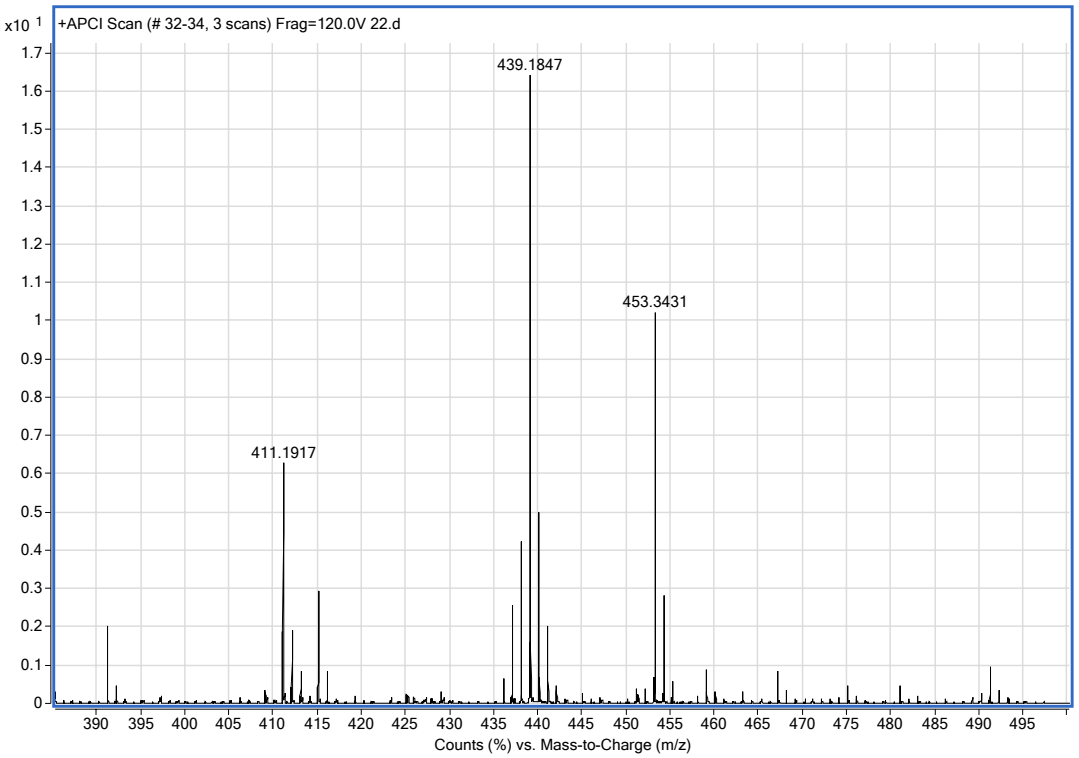
HRMS for **3n**



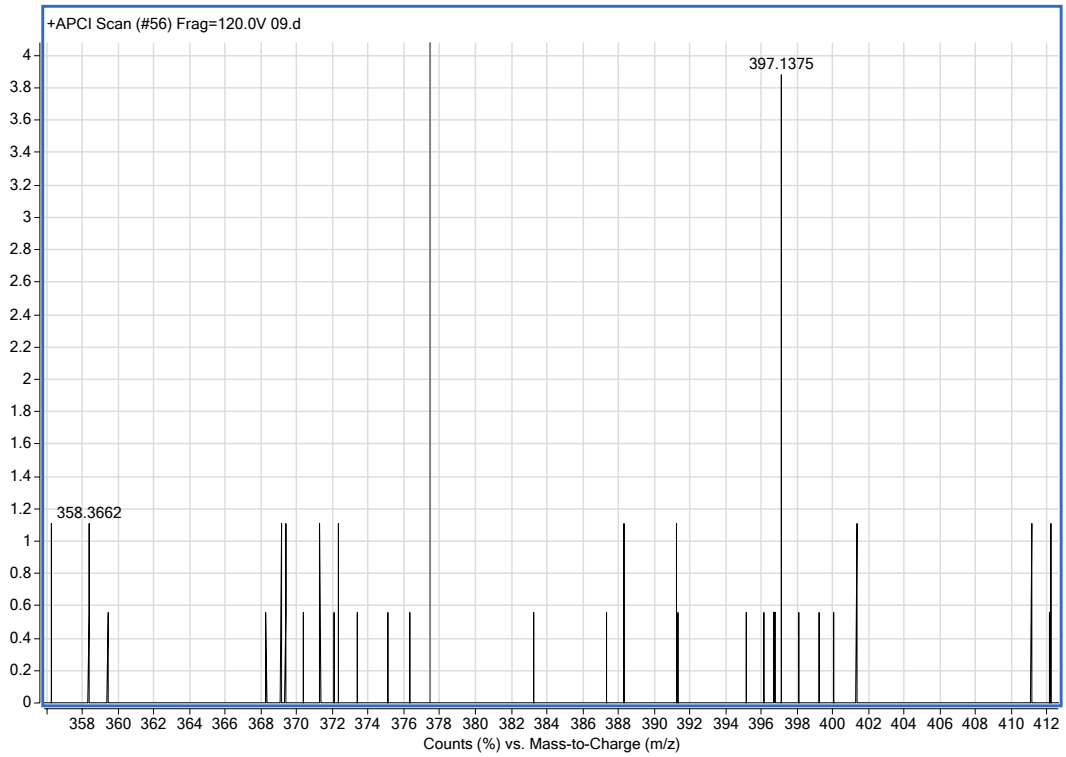
HRMS for **3o**



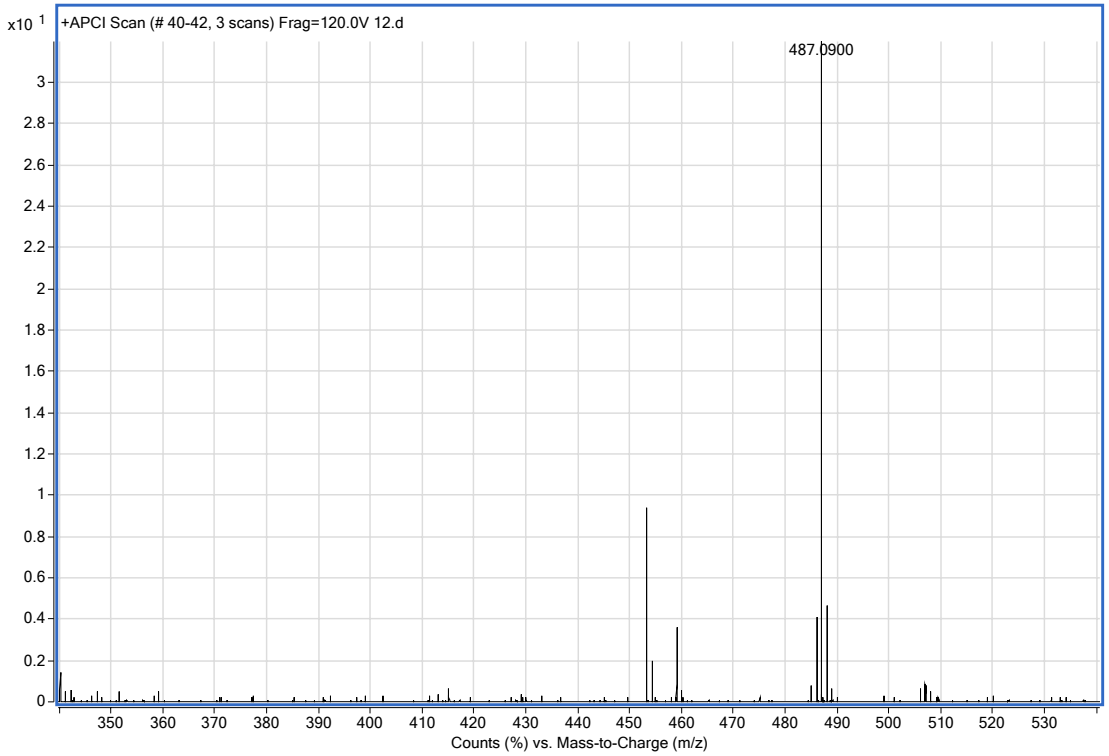
HRMS for **4a**



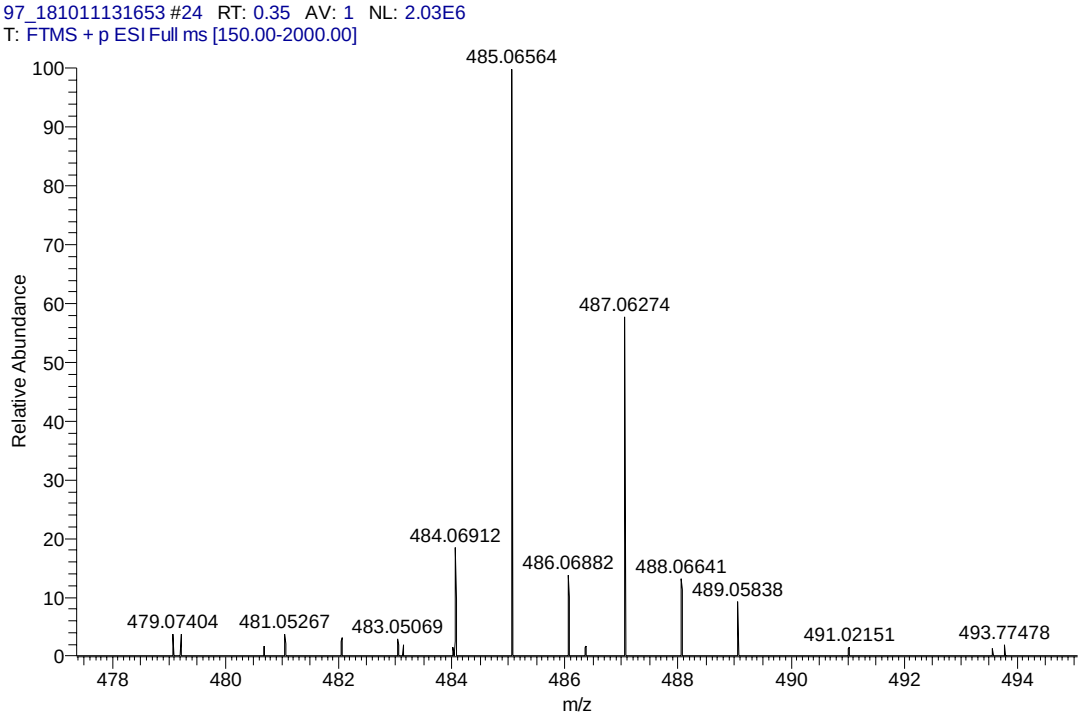
HRMS for **4b**



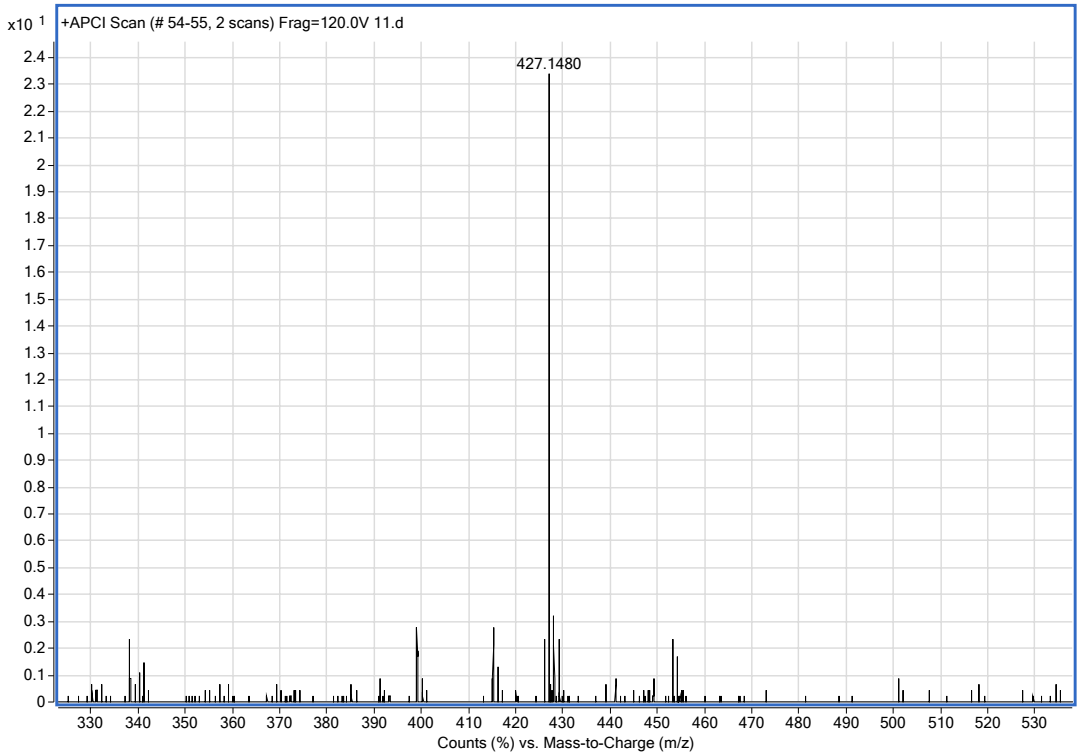
HRMS for **4c**



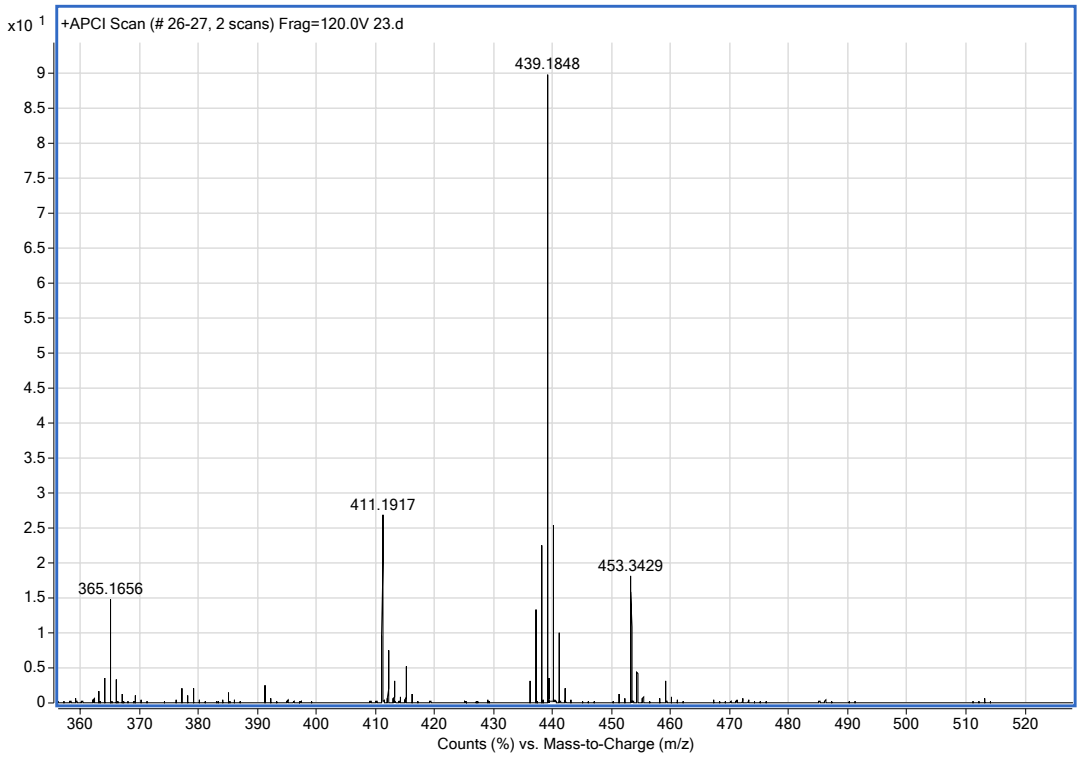
HRMS for **4d**



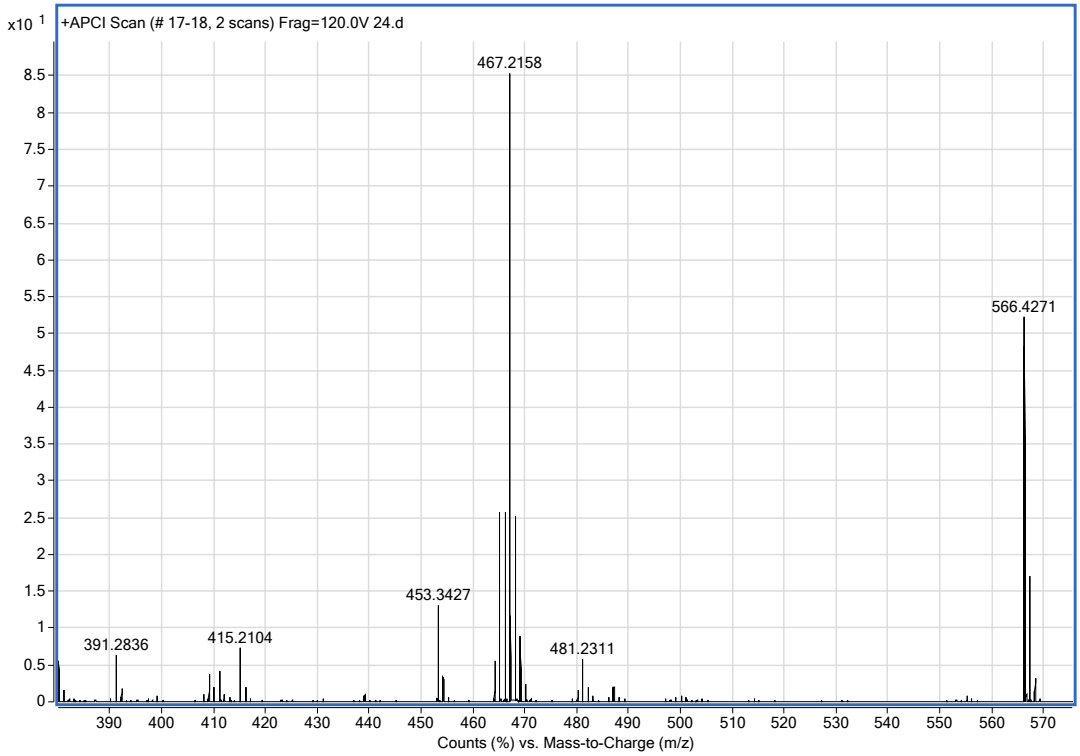
HRMS for **4e**



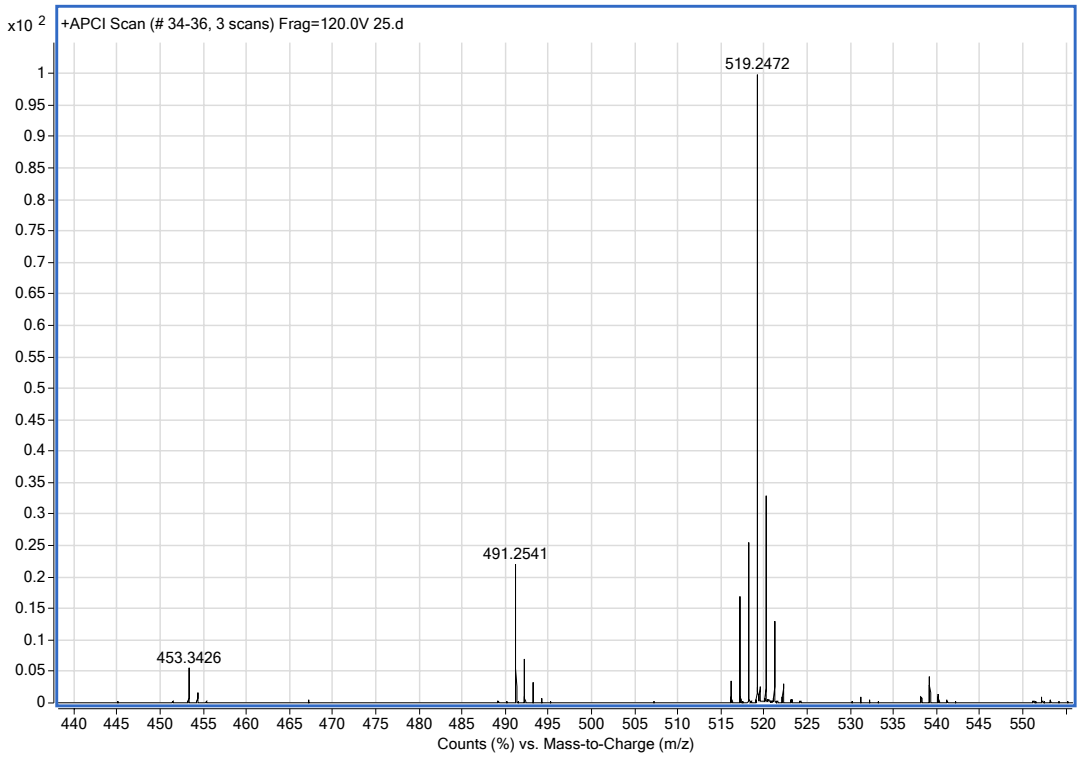
HRMS for **4f**



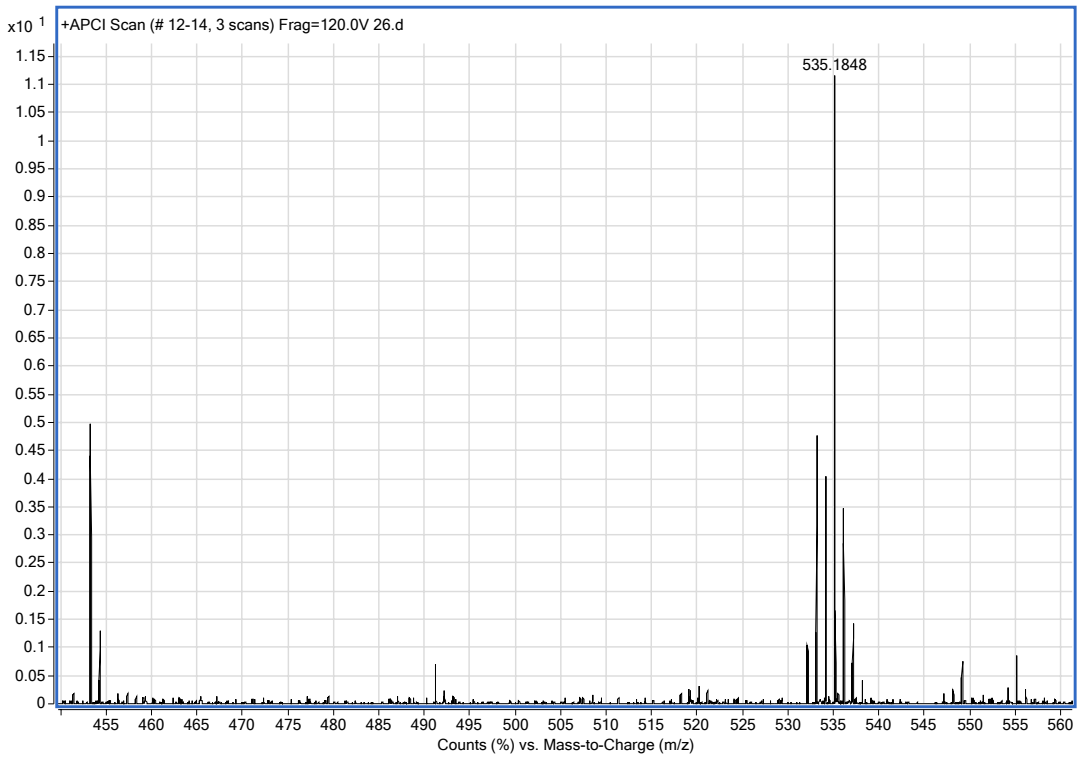
HRMS for **4g**



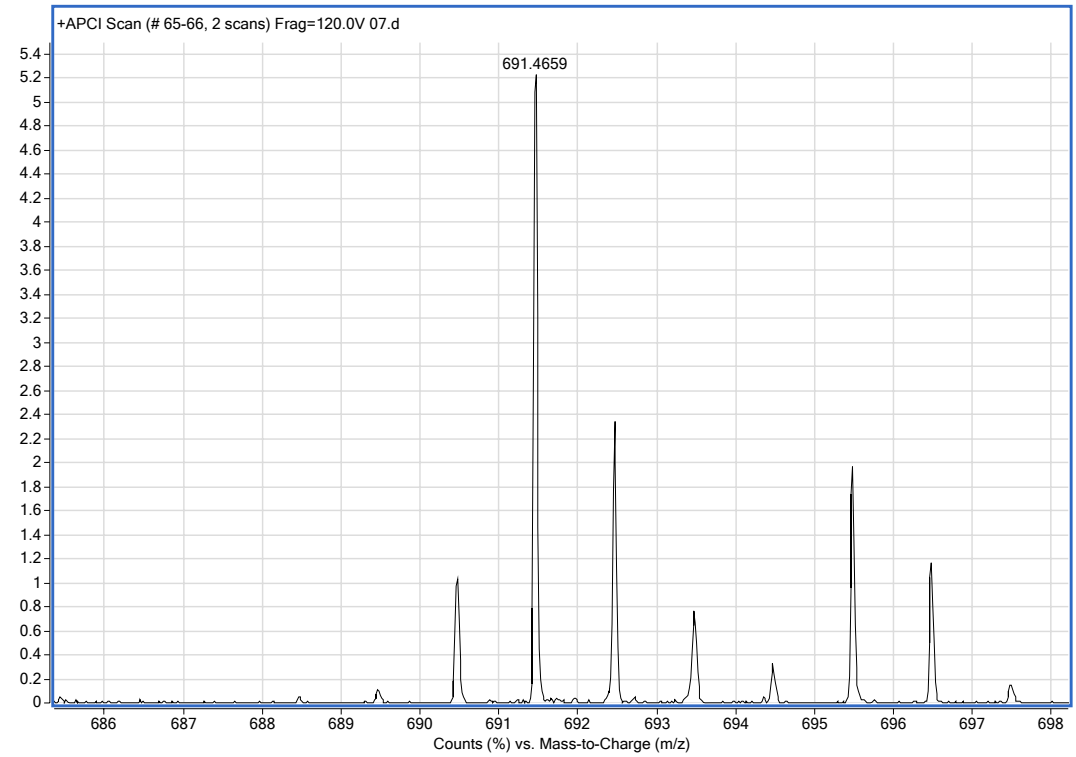
HRMS for **4h**



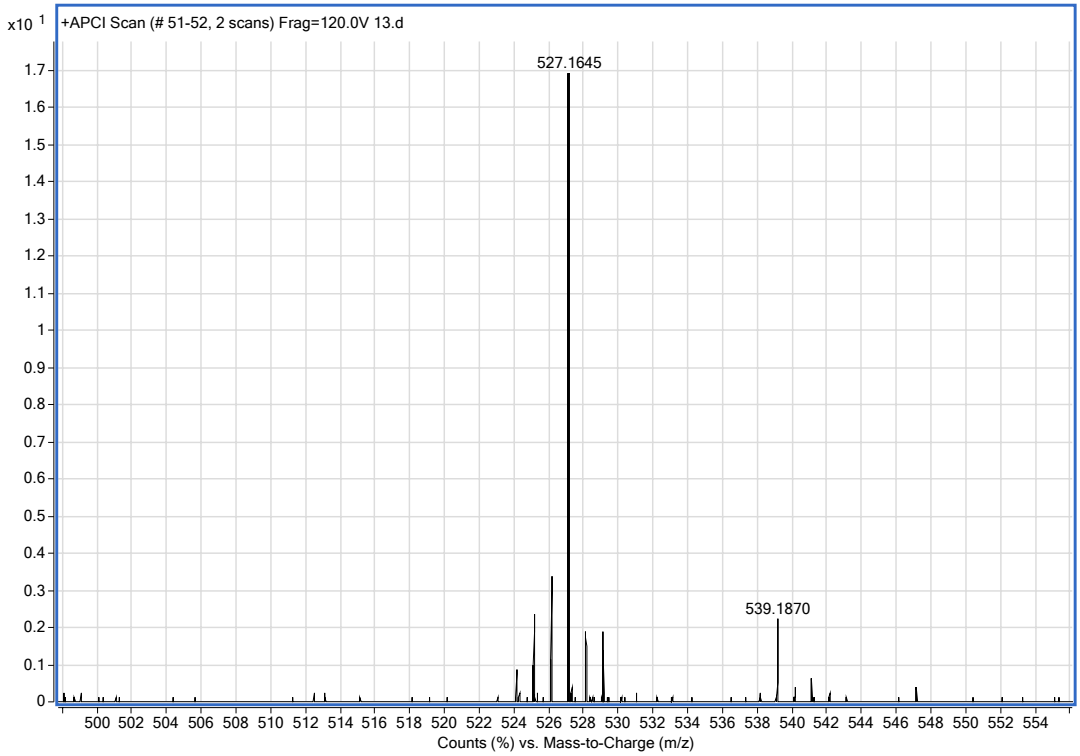
HRMS for **4i**



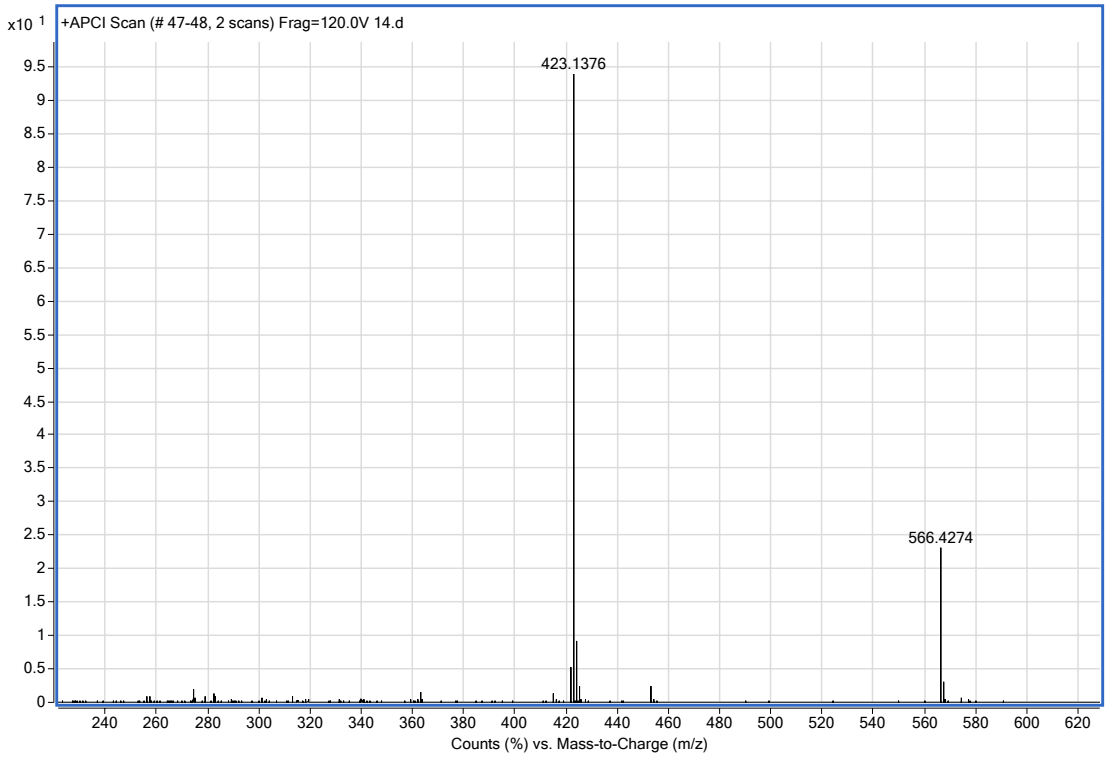
HRMS for **4j**



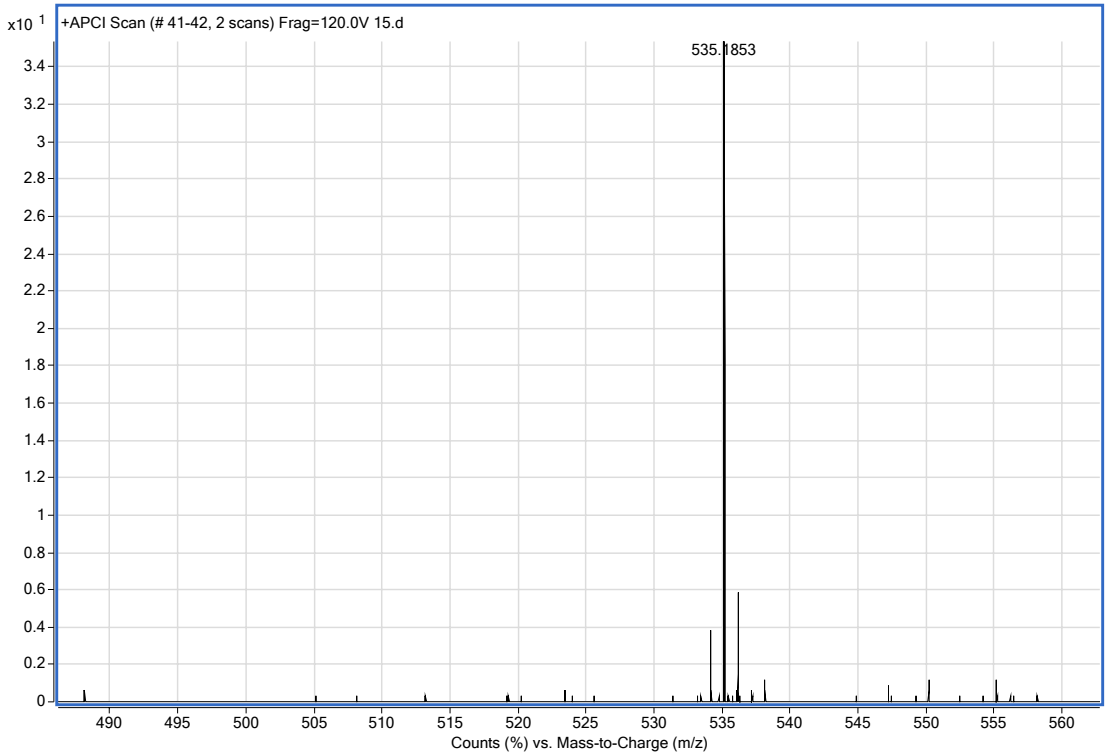
HRMS for **4k**



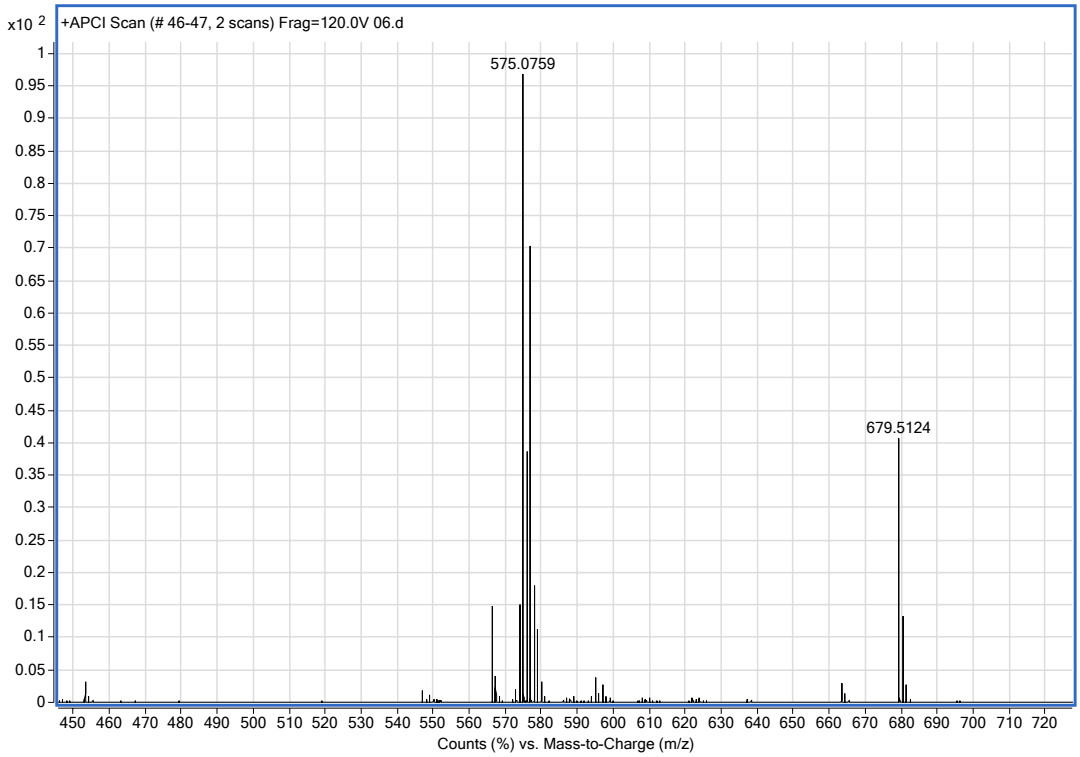
HRMS for **4l**



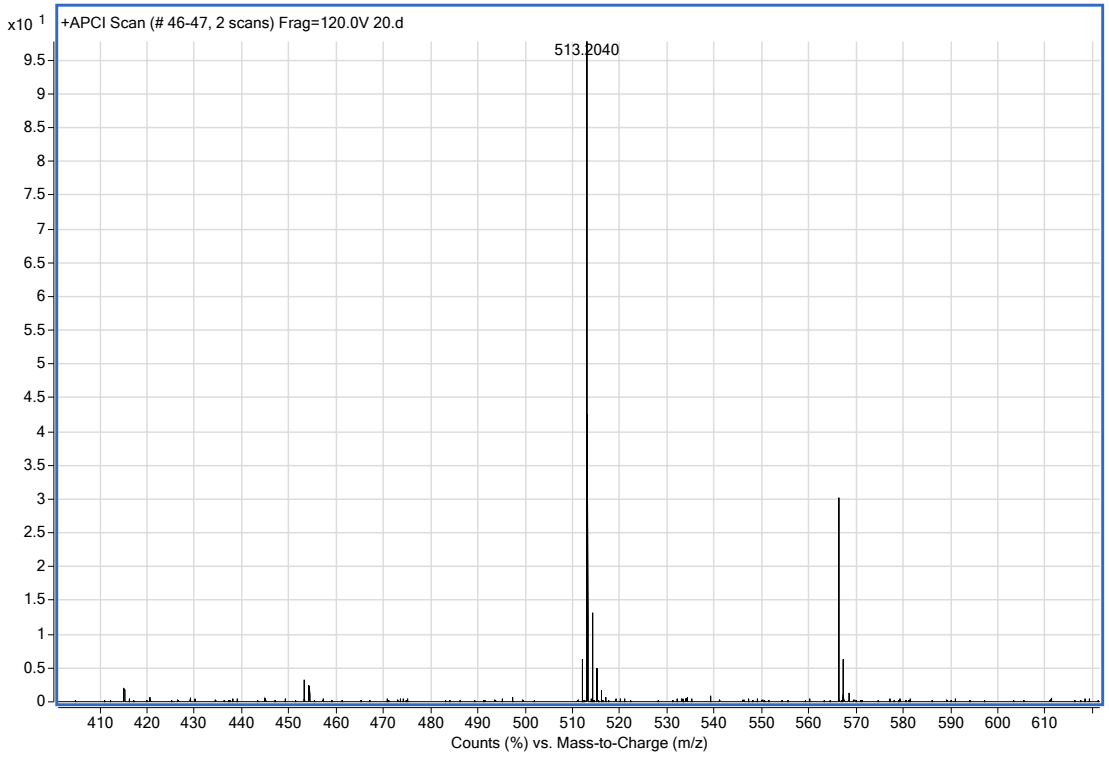
HRMS for **4m**



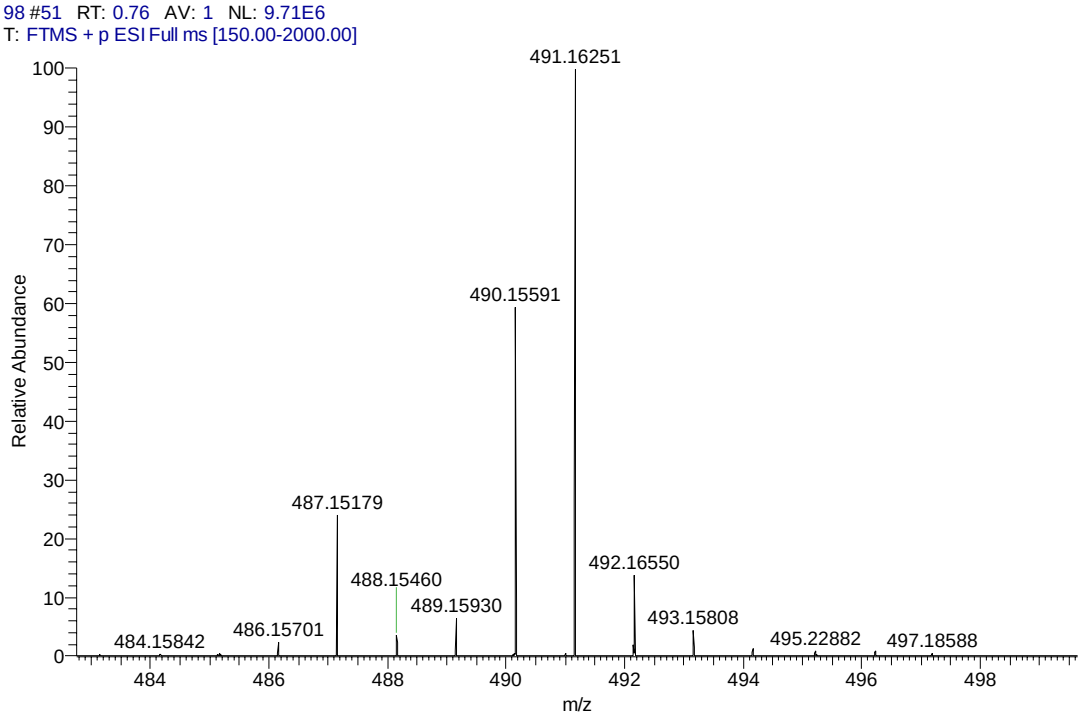
HRMS for **4n**



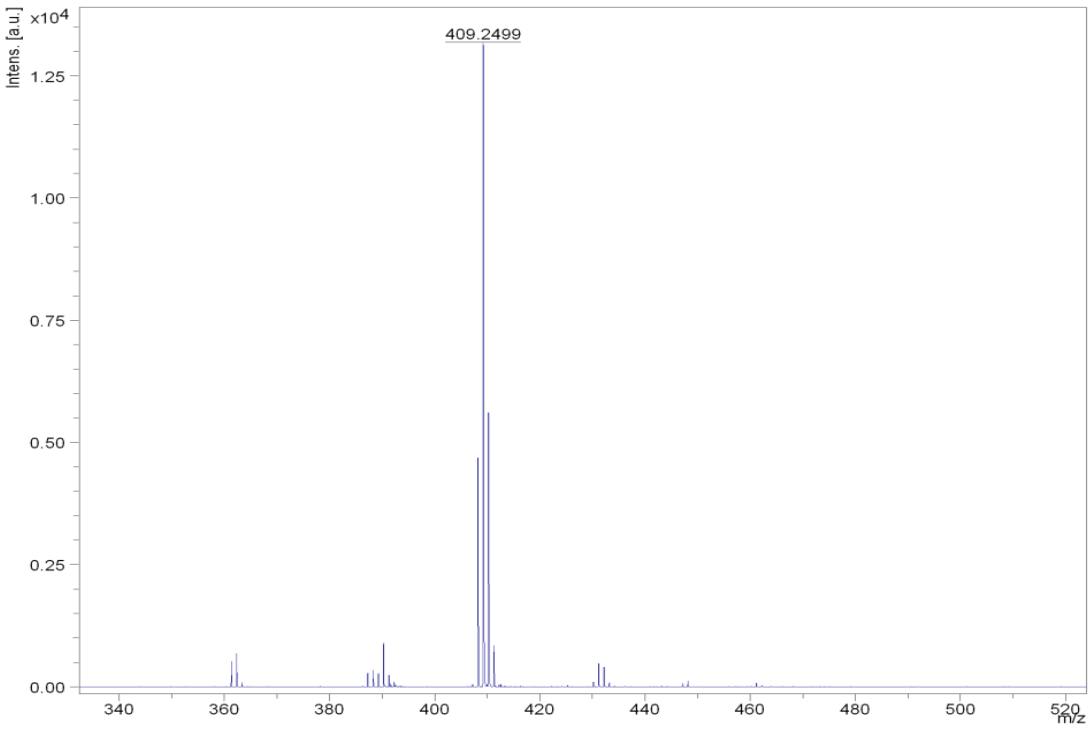
HRMS for **5a**



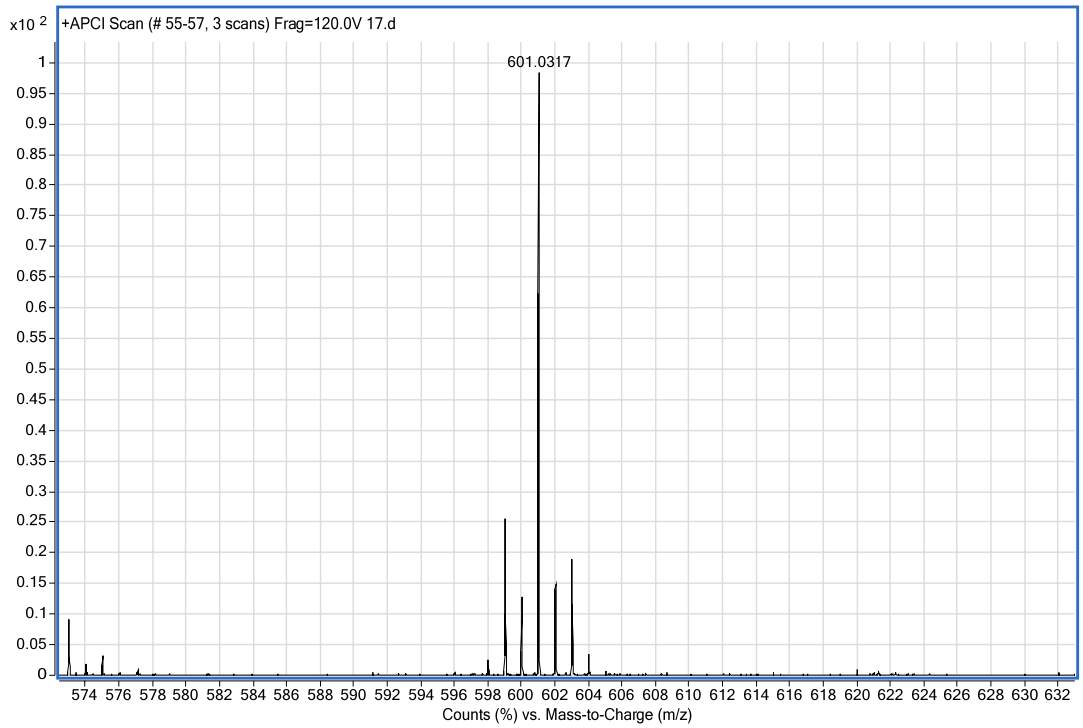
HRMS for **5b**



HRMS for **6**



HRMS for **7**



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