Electronic Supporting Information for

A Cascade Strategy for Vinyl Chloride-Substituted BODIPYs with Tunable Photophysical Properties

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Contents

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 400 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 **3c** and **3i** 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-2418848 (**3c**) and CCDC-2010636 (**3i**), 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

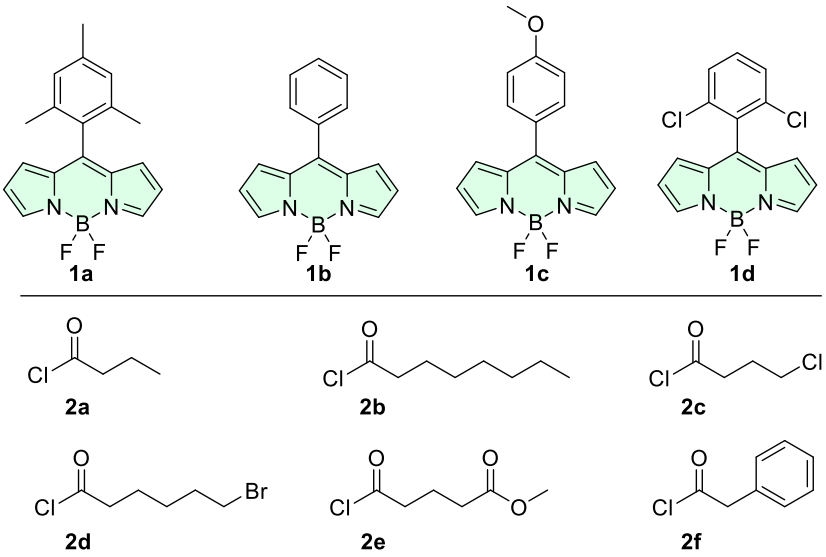
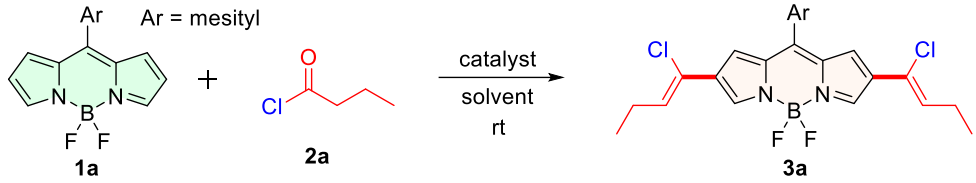


Figure S1. Chemical structure of BODIPYs **1a-d** and various acyl chlorides **2a-f.**

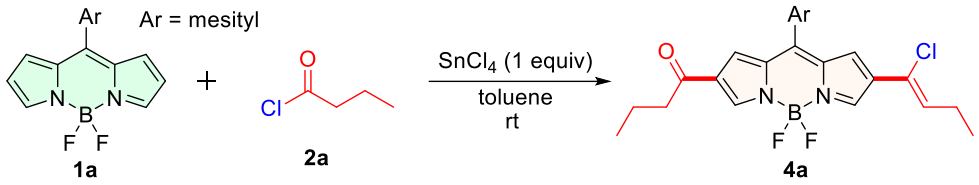
3. Table S1. Optimization of the Reaction Conditions for 3a.[a]



entry	catalyst	**2a** (equiv.)	solvent	yields [%)][b]
1	$BF_3{\cdot}OEt_2$	10	toluene	25
2	TFA	10	toluene	NR
3	$FeCl_3$	10	toluene	45
4	$ZnBr_2$	10	toluene	26
5	$ZnCl_2$	10	toluene	31
6	**$SnCl_4$**	**10**	**toluene**	**58**
7	$SnCl_4$	10	DCM	15
8	$SnCl_4$	10	DCE	17
9	$SnCl_4$	10	CH_3CN	32
10	$SnCl_4$	10	DMF	NR
11	$SnCl_4$	10	DMSO	NR
12[c]	$SnCl_4$	10	toluene	55
13[d]	$SnCl_4$	10	toluene	56
14[e]	$SnCl_4$	10	toluene	33
15[f]	$SnCl_4$	10	toluene	56
16	$SnCl_4$	12	toluene	57
17[g]	$SnCl_4$	8	toluene	31

[a]Reaction condition: **1a** (0.1 mmol), **2a** (1.0 mmol), catalyst (0.1 mmol), toluene (1 mL), rt, 3 h. [b]Isolated yields based on **1a**. [c]The reaction temperature was raised to 80 °C. [d]The reaction time extended to 12 h. [e]0.5 equiv. Of $SnCl_4$ was used. [f]1.5 equiv. of SnCl4 was used. [g]The β-vinyl chloride-β'-acyl-BODIPY **4a** was isolated in 27% yield. NR = no reaction.

Table S2. Optimization of the reaction conditions for 4a[a].



entry	**2a** (equiv)	yield[b] (%)
1	9	11
2	8	27
3	7	45
4	***6***	***65***
5	5	56

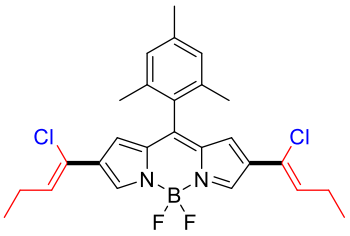
[a]Reaction condition: **1a** (0.1 mmol), **2a** (0.6 mmol), catalyst (0.1 mmol), toluene (1 mL), rt, 3 h.

[b]Isolated yields based on **1a**.

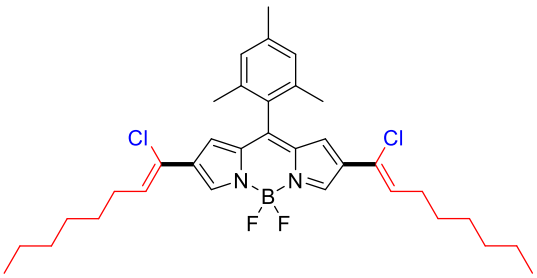
4. Synthesis and characterization

General procedure for the synthesis of 3a-g

BODIPY **1** (1 equiv, 0.2 mmol), **2** (10 equiv, 2 mmol), $SnCl_4$ (1 equiv, 0.2 mmol), were dissolved in toluene (2 mL). The reaction mixture was stirred at room temperature and the reaction was followed by TLC. After completion of the reaction, the reaction mixture was poured into dichloromethane (100 mL), and saturated aqueous $NaHCO_3$ solution (25 mL) was added to remove excess acyl chloride. The organic layer was collected and was 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; 30:1-10:1 v/v).

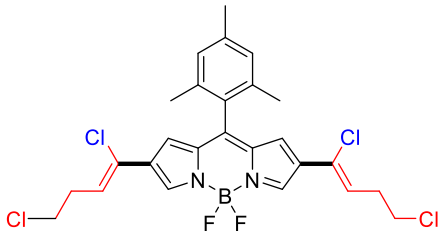


3a was prepared in 58% yield (red solid, 56 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2a** (0.21 mL, 2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 2H), 6.99 (s, 2H), 6.64 (s, 2H), 6.06 (t, J = 7.1 Hz, 2H), 2.39 (s, 3H), 2.35-2.29 (m, 4H), 2.12 (s, 6H), 1.05 (t, J = 7.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 142.0, 139.2, 136.3, 135.5, 132.9, 129.2, 128.4, 128.3, 124.5, 124.4, 22.4, 21.2, 20.0, 13.01. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.06 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.68 (q, J = 30.1 Hz). HRMS calcd for $C_{26}H_{27}BCl_2FN_2$ $(M\text{-}F)^+$ 467.1628, found 467.1605.

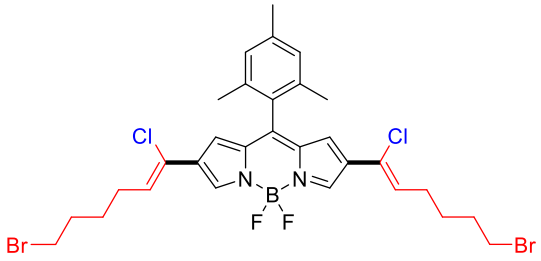


3b was prepared in 62% yield (red solid, 74 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2b** (0.34 mL, 2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 6.99 (s, 2H), 6.63 (s, 2H), 6.06 (t, J

= 7.2 Hz, 2H), 2.39 (s, 3H), 2.33-2.28 (m, 4H), 2.12 (s, 6H), 1.47-1.40 (m, 4H), 1.37-1.26 (m, 12H), 0.88 (t, J = 8.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 142.4, 139.5, 136.7, 135.8, 133.3, 129.6, 128.8, 127.5, 125.3, 124.8, 32.0, 29.5, 29.4, 28.9, 23.0, 21.6, 20.5, 14.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.06 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.88 (q, J = 26.3 Hz). HRMS calcd for $C_{34}H_{44}BCl_2F_2N_2$ $(M+H)^+$ 599.2943, found 599.2933.

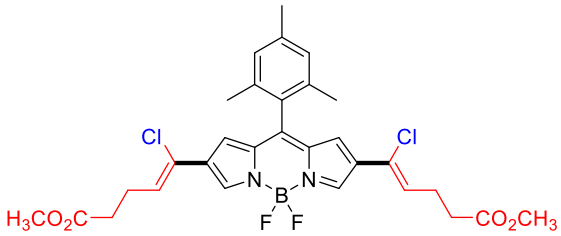


3c was prepared in 55% yield (red solid, 60 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2c** (0.22 mL, 2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.00 (s, 2H), 6.69 (s, 2H), 6.13 (t, J = 6.9 Hz, 2H), 3.61 (t, J = 6.6 Hz, 4H), 2.82-2.78 (m, 4H), 2.39 (s, 3H), 2.12 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 142.7, 139.8, 136.6, 136.0, 132.7, 129.3, 128.9, 127.9, 125.3, 122.5, 43.3, 32.6, 21.6, 20.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.05 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.77 (q, J = 30.1 Hz). HRMS calcd for $C_{26}H_{25}BCl_4FN_2$ $(M-F)^+$ 535.0849, found 535.0845.

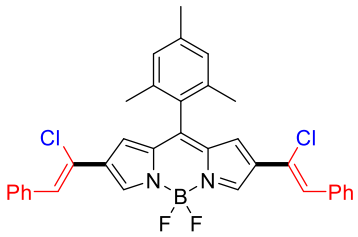


3d was prepared in 60% yield (red solid, 83 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2d** (0.31 mL, 2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 6.99 (s, 2H), 6.64 (s, 2H), 6.05 (t, J = 7.2 Hz, 2H), 3.42 (t, J = 6.7 Hz, 4H), 2.39 (s, 3H), 2.37-2.33 (m, 4H), 2.12 (s, 6H), 1.93-1.86 (m, 4H), 1.65-1.57 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 142.5, 139.6, 136.7, 135.9, 133.1, 129.5, 128.8, 126.3, 126.1, 124.9, 33.8, 32.5, 28.5, 27.4, 21.6, 20.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.06 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz,

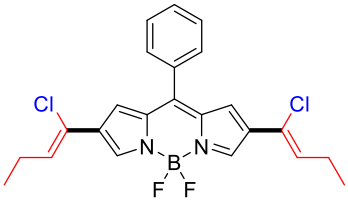
$CDCl_3$) δ -145.77 (q, J = 26.3 Hz). HRMS calcd for $C_{30}H_{33}BBr_2Cl_2FN_2$ $(M\text{-}F)^+$ 679.0464, found 679.0473.



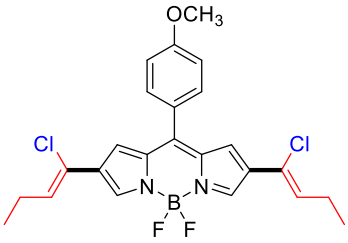
3e was prepared in 53% yield (red solid, 64 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2e** (0.26 mL, 2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 6.99 (s, 2H), 6.65 (s, 2H), 6.09 (t, J = 7.0 Hz, 2H), 3.69 (s, 6H), 2.66-2.60 (m, 4H), 2.47 (t, J = 7.2 Hz, 4H), 2.39 (s, 3H), 2.11 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 148.3, 142.2, 139.3, 136.2, 135.5, 132.5, 129.0, 128.5, 126.4, 124.7, 124.4, 51.8, 32.6, 24.4, 21.2, 20.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.04 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.84 (q, J = 30.1 Hz). HRMS calcd for $C_{30}H_{31}BCl_2FN_2O_4$ $(M\text{-}F)^+$ 583.1738, found 583.1737.



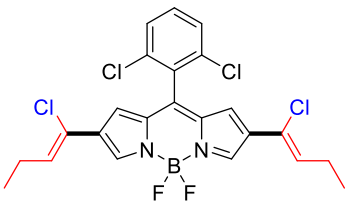
3f was prepared in 68% yield (violet solid, 79 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2f** (0.26 mL, 2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 2H), 7.69 (d, J = 8.1 Hz, 4H), 7.40-7.36 (m, 4H), 7.32-7.28 (m, 2H), 7.04 (s, 2H), 7.01 (s, 2H), 6.81 (s, 2H), 2.41 (s, 3H), 2.18 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 142.6, 139.4, 136.4, 135.8, 134.5, 133.9, 129.5, 129.1, 128.5, 128.4, 128.3, 124.8, 124.4, 124.1, 21.2, 20.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.13 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.71 (q, J = 26.3 Hz). HRMS calcd for $C_{34}H_{27}BCl_2FN_2$ $(M\text{-}F)^+$ 563.1628, found 563.1609.



3g was prepared in 56% yield (red solid, 49 mg) from BODIPY **1b** (54 mg, 0.2 mmol) and **2a** (0.21 mL, 2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 2H), 7.67-7.59 (m, 5H), 6.93 (s, 2H), 6.11 (t, J = 7.1 Hz, 2H), 2.41-2.33 (m, 4H), 1.09 (t, J = 7.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3, 141.8, 134.9, 133.4, 132.9, 131.1, 130.4, 128.7, 128.4, 126.1, 124.5, 22.5, 13.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.03 (t, J = 46.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.33 (q, J = 26.3 Hz). HRMS calcd for $C_{23}H_{21}BCl_2FN_2$ $(M\text{-}F)^+$ 425.1159, found 425.1183.



3h was prepared in 52% yield (red solid, 49 mg) from BODIPY **1b** (60 mg, 0.2 mmol) and **2a** (0.21 mL, 2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 7.56 (d, J = 8.7 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H), 6.95 (s, 2H), 6.09 (t, J = 7.1 Hz, 2H), 3.93 (s, 3H), 2.35 (q, J = 7.5 Hz, 4H), 1.07 (t, J = 7.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 147.4, 140.9, 134.8, 132.6, 132.4, 128.2, 125.9, 125.8, 124.7, 114.4, 55.6, 22.5, 13.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.04 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.36 (q, J = 30.1 Hz). HRMS calcd for $C_{24}H_{23}BCl_2FN_2O$ $(M\text{-}F)^+$ 455.1265, found 455.1269.

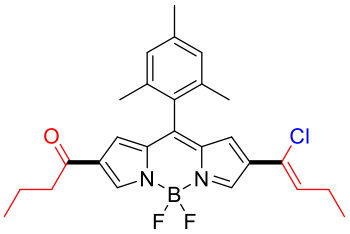


3i was prepared in 61% yield (red solid, 62 mg) from BODIPY **1b** (67 mg, 0.2 mmol) and **2a** (0.21 mL, 2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.52-7.44 (m, 3H), 6.63 (s, 2H),

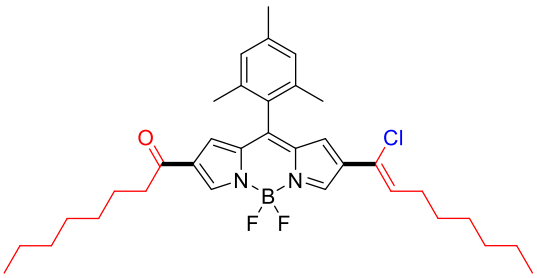
6.09 (t, J = 7.1 Hz, 2H), 2.37-2.31 (m, 4H), 1.06 (t, J = 7.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 140.9, 135.5, 135.2, 133.8, 131.9, 131.2, 129.3, 128.8, 124.8, 124.4, 22.9, 13.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.04 (t, J = 26.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.69 (q, J = 30.1 Hz). HRMS calcd for $C_{23}H_{19}BCl_4FN_2$ $(M\text{-}F)^+$ 493.0379, found 493.0363.

General procedure for the synthesis of 4a-g

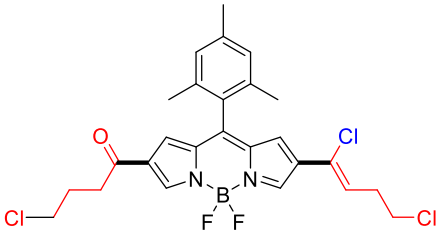
BODIPY **1** (1 equiv, 0.2 mmol), **2** (6 equiv, 1.2 mmol), $SnCl_4$ (1 equiv, 0.2 mmol), were dissolved in toluene (2 mL). The reaction mixture was stirred at room temperature and the reaction was followed by TLC. After completion of the reaction, the reaction mixture was poured into dichloromethane (100 mL), and saturated aqueous $NaHCO_3$ (25 mL) was added to remove excess acyl chloride. The organic layer was collected, and was 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; 10:1-5:1 v/v).



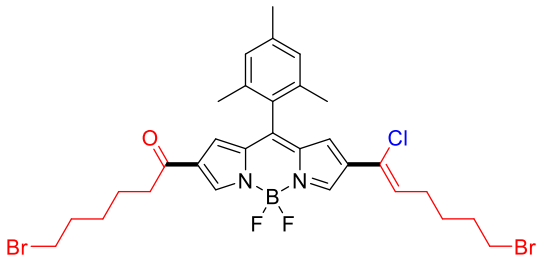
4a was prepared in 65% yield (red solid, 60 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2a** (0.12 mL, 1.2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 2H), 6.99 (s, 3H), 6.77 (s, 1H), 6.15 (t, J = 7.1 Hz, 1H), 2.70 (t, J = 7.3 Hz, 2H), 2.39 (s, 3H), 2.39-2.31 (m, 2H), 2.10 (s, 6H), 1.75-1.66 (m, 2H), 1.06 (t, J = 7.5 Hz, 3H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 149.9, 145.7, 142.7, 139.5, 136.9, 136.2, 135.0, 134.8, 132.3, 130.0, 128.7, 128.5, 127.8, 126.2, 124.1, 41.8, 22.6, 21.2, 20.0, 17.8, 13.8, 12.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.10 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.57 (q, J = 26.3 Hz). HRMS calcd for $C_{26}H_{29}BClF_2N_2O$ $(M+H)^+$ 469.2029, found 469.1992.



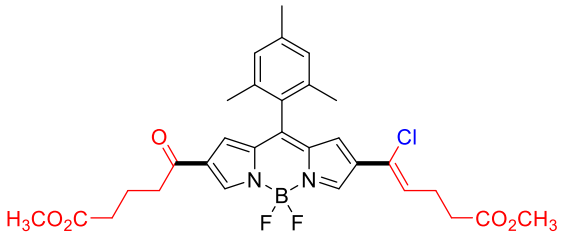
4b was prepared in 66% yield (red solid, 76 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2b** (0.21 mL, 1.2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 2H), 6.99 (s, 3H), 6.77 (s, 1H), 6.16 (t, J = 7.2 Hz, 1H), 2.71 (t, J = 7.5 Hz, 2H), 2.39 (s, 3H), 2.39-2.33 (m, 2H), 2.10 (s, 6H), 1.70-1.64 (m, 2H), 1.48-1.42 (m, 2H), 1.34-1.26 (m, 14H), 0.90-0.86 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1, 149.9, 145.7, 142.7, 139.5, 136.9, 136.2, 135.0, 134.9, 134.8, 132.2, 128.8, 128.5, 127.8, 126.2, 124.6, 39.9, 31.7, 31.6, 29.7, 29.3, 29.2, 29.1, 28.9, 28.4, 24.3, 22.6, 22.5, 21.2, 20.0, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.10 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.55 (q, J = 30.1 Hz). HRMS calcd for $C_{34}H_{45}BClF_2N_2O$ $(M+H)^+$ 581.3282, found 581.3280.



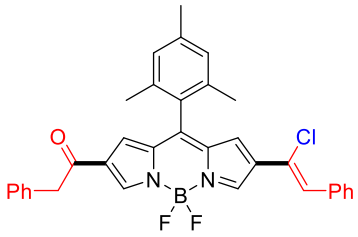
4c was prepared in 56% yield (red solid, 53 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2c** (0.13 mL, 1.2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.28 (s, 1H), 7.03 (s, 1H), 7.01 (s, 2H), 6.82 (s, 1H), 6.23 (t, J = 6.9 Hz, 1H), 3.64-3.61 (m, 4H), 2.94 (t, J = 7.1 Hz, 2H), 2.85-2.81 (m, 2H), 2.40 (s, 3H), 2.19-2.14 (m, 2H), 2.11 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 151.0, 146.0, 143.4, 140.1, 137.3, 136.5, 135.6, 134.4, 132.5, 132.5, 129.0, 128.5, 127.5, 127.0, 124.0, 44.9, 43.2, 36.9, 32.6, 26.9, 21.6, 20.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.10 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.47 (q, J = 30.1 Hz). HRMS calcd for $C_{26}H_{27}BCl_3F_2N_2O$ $(M+H)^+$ 537.1250, found 537.1239.



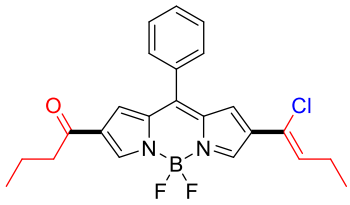
4d was prepared in 60% yield (red solid, 81 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2d** (0.18 mL, 1.2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.25 (s, 1H), 7.00 (s, 3H), 6.78 (s, 1H), 6.14 (t, J = 7.2 Hz, 1H), 3.44-3.39 (m, 4H), 2.75 (d, J = 7.4 Hz, 2H), 2.39 (s, 3H), 2.38 (d, J = 10.0 Hz, 2H), 2.10 (s, 6H), 1.94-1.85 (m, 4H), 1.74-1.68 (m, 2H), 1.66-1.60 (m, 2H), 1.51-1.47 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 150.2, 145.6, 142.8, 139.6, 136.9, 136.1, 135.1, 134.5, 132.2, 128.7, 128.5, 127.9, 127.5, 126.3, 125.3, 39.6, 33.5, 33.3, 32.5, 32.1, 28.2, 27.8, 27.0, 23.2, 21.2, 20.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.09 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.51 (q, J = 30.1 Hz). HRMS calcd for $C_{30}H_{35}BBr_2ClF_2N_2O$ $(M+H)^+$ 681.0866, found 681.0863.



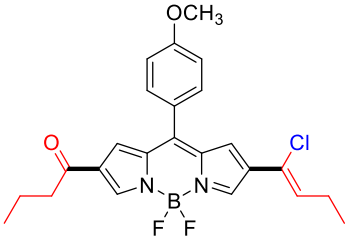
4e was prepared in 54% yield (red solid, 64 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2e** (0.19 mL, 1.2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.25 (s, 1H), 7.00 (s, 3H), 6.79 (s, 1H), 6.19 (t, J = 7.1 Hz, 1H), 3.70-3.69 (m, 3H), 3.67-3.66 (m, 3H), 2.81 (t, J = 7.2 Hz, 2H), 2.68-2.63 (m, 2H), 2.49 (t, J = 7.1 Hz, 2H), 2.39 (s, 3H), 2.41-2.38 (m, 2H), 2.10 (s, 6H), 2.02-1.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 173.6, 172.9, 150.3, 145.6, 142.9, 139.6, 136.9, 136.1, 135.1, 134.3, 132.0, 128.6, 128.6, 128.0, 126.5, 126.0, 125.9, 51.8, 51.6, 38.7, 33.0, 32.5, 24.4, 21.2, 20.0, 19.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.08 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.53 (q, J = 30.1 Hz). HRMS calcd for $C_{30}H_{33}BClF_2N_2O_5$ $(M+H)^+$ 585.2139, found 585.2130.



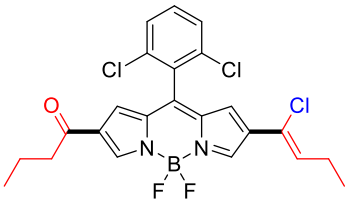
4f was prepared in 70% yield (violet solid, 79 mg) from BODIPY **1a** (62 mg, 0.2 mmol) and **2f** (0.16 mL, 1.2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.29 (s, 1H), 7.70 (d, J = 7.4 Hz, 2H), 7.41-7.38 (m, 2H), 7.33-7.30 (m, 4H), 7.24-7.22 (m, 2H), 7.06 (s, 1H), 7.04 (s, 1H), 7.01 (s, 2H), 6.92 (s, 1H), 4.03 (s, 2H), 2.40 (s, 3H), 2.10 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 150.3, 145.9, 143.4, 139.7, 137.0, 136.2, 13.0, 135.7, 135.2, 134.2, 134.1, 131.8, 129.6, 129.4, 128.8, 128.6, 128.6, 128.6, 128.5, 127.1, 126.5, 125.6, 123.5, 47.0, 21.2, 20.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.11 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.42 (q, J = 30.1 Hz). HRMS calcd for $C_{34}H_{28}BClF_2N_2O$ $(M+H)^+$ 565.2029, found 565.2001.



4g was prepared in 63% yield (red solid, 53 mg) from BODIPY **1b** (54 mg, 0.2 mmol) and **2a** (0.12 mL, 1.2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.27 (s, 1H), 7.67 -7.58 (m, 5H), 7.27 (s, 1H), 7.04 (s, 1H), 6.18 (t, J = 7.1 Hz, 1H), 2.75 (t, J = 7.3 Hz, 2H), 2.41-2.33 (m, 2H), 1.76-1.70 (m, 2H), 1.08 (t, J = 7.5 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 149.2, 145.3, 142.6, 136.1, 134.6, 132.9, 132.3, 132.2, 131.5, 130.5, 129.9, 129.5, 128.9, 127.8, 124.1, 41.9, 22.6, 17.8, 13.9, 12.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.07 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.03 (q, J = 26.3 Hz). HRMS calcd for $C_{23}H_{23}BClF_2N_2O$ $(M+H)^+$ 427.1555, found 427.1574.

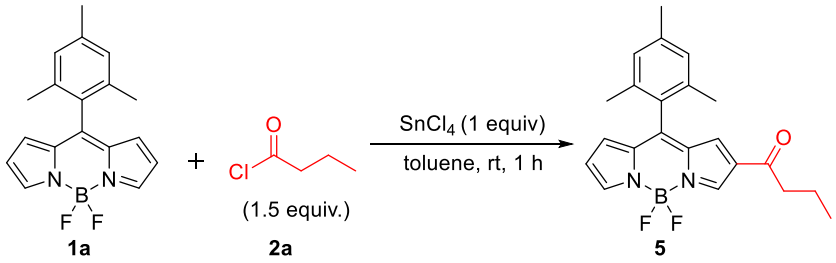


4h was prepared in 58% yield (red solid, 52 mg) from BODIPY **1b** (67 mg, 0.2 mmol) and **2a** (0.12 mL, 1.2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.23 (s, 1H), 7.58 (d, J = 8.7 Hz, 2H), 7.32 (s, 1H), 7.09 (d, J = 8.7 Hz, 2H), 6.17 (t, J = 7.1 Hz, 1H), 3.94 (s, 3H), 2.75 (t, J = 7.3 Hz, 2H), 2.41-2.34 (m, 2H), 1.78-1.69 (m, 2H), 1.08 (t, J = 7.5 Hz, 3H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.01, 162.8, 149.3, 144.2, 141.9, 135.8, 134.5, 134.3, 132.6, 132.1, 129.6, 129.2, 127.7, 125.5, 124.3, 114.6, 55.7, 41.9, 22.6, 17.9, 13.9, 13.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.06 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.08 (q, J = 30.1 Hz). HRMS calcd for $C_{24}H_{25}BClF_2N_2O_2$ $[M+H]^+$: 457.1660, found 457.1667.



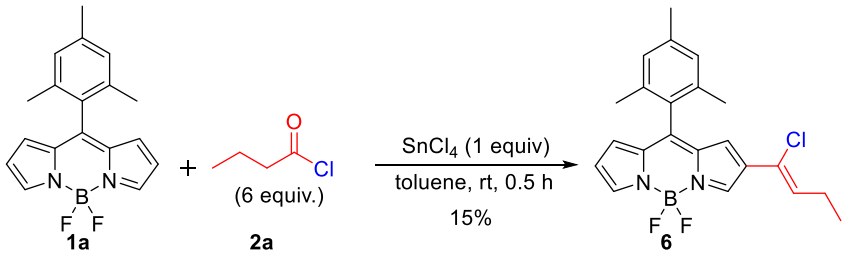
4i was prepared in 64% yield (red solid, 63 mg) from BODIPY **1b** (67 mg, 0.2 mmol) and **2a** (0.12 mL, 1.2 mmol), $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in toluene (2 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.27 (s, 1H), 7.54-7.46 (m, 3H), 7.01 (s, 1H), 6.77 (s, 1H), 6.19 (t, J = 7.1 Hz, 1H), 2.72 (t, J = 8.0 Hz, 2H), 2.40-2.33 (m, 2H), 1.76-1.67 (m, 2H), 1.08 (t, J = 7.5 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.1, 147.6, 143.8, 142.9, 137.0, 135.8, 135.3, 134.5, 132.8, 132.2, 131.1, 130.7, 128.9, 127.8, 126.2, 124.4, 42.3, 23.0, 18.1, 14.2, 13.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.08 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.31 (q, J = 26.3 Hz). HRMS calcd for $C_{23}H_{21}BCl_3F_2N_2O$ $(M+H)^+$ 495.0781, found 495.0762.

synthesis of 5



BODIPY **1a** (60 mg, 0.2 mmol), butyryl chloride **2a** (0.031 mL, 0.3 mmol), and $SnCl_4$ (0.026 mL, 0.2 mmol) were dissolved in dichloromethane (2 mL). The reaction mixture was stirred at room temperature and the reaction was followed by TLC. After completion of the reaction, the reaction mixture was poured into dichloromethane (100 mL), and statured aqueous $NaHCO_3$ (25 mL) was added to remove excess butyryl chloride. The organic layer was collected, and was 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; 5:1 v/v) to provide **5** in 56 % yield (orange oil, 42 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.10 (s, 1H), 7.02 (s, 1H), 6.98 (s, 2H), 6.86 (d, J = 4.3 Hz, 1H), 6.61 (d, J = 4.3 Hz, 1H), 2.71 (t, J = 7.4 Hz, 2H), 2.38 (s, 3H), 2.09 (s, 6H), 1.76-1.64 (m, 2H), 0.96 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1, 149.9, 148.6, 142.4, 139.4, 137.3, 136.1, 134.7, 132.9, 132.1, 128.9, 128.4, 127.6, 120.9, 41.8, 21.2, 19.9, 17.8, 13.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.21 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.52 (q, J = 30.1 Hz). HRMS calcd for $C_{22}H_{24}BF_2N_2O$ [M+H]+:381.1944, found 381.1958.

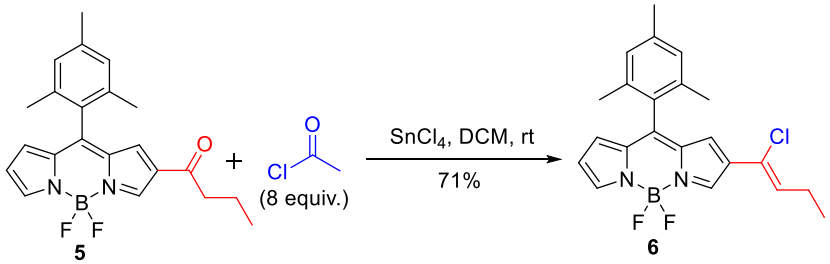
synthesis of 6



BODIPY **1** (1 equiv, 0.2 mmol), **2a** (6 equiv, 1.2 mmol), $SnCl_4$ (1 equiv, 0.2 mmol), were dissolved in toluene (2 mL). The reaction mixture was stirred at room temperature for o.5 h. The reaction mixture was poured into dichloromethane (100 mL), and statured aqueous $NaHCO_3$ (25 mL) was added to remove excess acyl

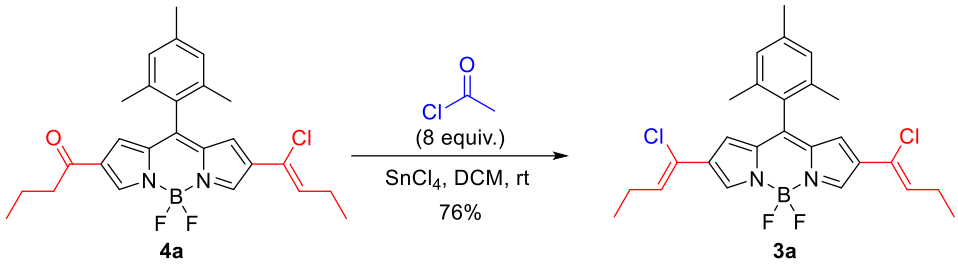
chloride. The organic layer was collected, and was washed three times with water (100 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatographically (silica; petroleum ether/ethyl acetate; 50:1 v/v) to provide **5** in 15 % yield (red solid, 11 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.92 (s, 1H), 6.97 (s, 2H), 6.68 (d, J = 4.2 Hz, 1H), 6.64 (s, 1H), 6.48 (d, J = 3.4 Hz, 1H), 6.05 (t, J = 7.1 Hz, 1H), 2.37 (s, 3H), 2.36-2.29 (m, 2H), 2.11 (s, 6H), 1.05 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 144.9, 141.3, 139.0, 136.3, 135.9, 135.0, 132.6, 130.5, 129.4, 128.3, 128.1, 124.6, 124.2, 118.9, 22.4, 21.2, 20.0, 13.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.19 (t, J = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.78 (q, J = 30.1 Hz). HRMS calcd for $C_{22}H_{22}BClFN_2$ $(M-F)^+$ 379.1549, found 379.1530.

synthesis of 6 from 5



BODIPY **5** (38 mg, 0.1 mmol), acetyl chloride (0.056 mL, 0.8 mmol), $SnCl_4$ (0.013 mL, 0.1 mmol), were dissolved in dichloromethane (2 mL). The reaction mixture was stirred at room temperature and the reaction was followed by TLC. After completion of the reaction, the reaction mixture was poured into dichloromethane (100 mL), and saturated aqueous $NaHCO_3$ (25 mL) was added to remove excess acetyl chloride. The organic layer was collected, and was 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 71% yield (red solid, 26 mg).

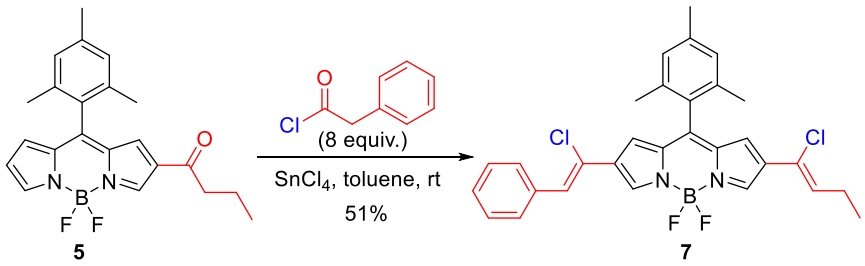
synthesis of 3a form 4a



4a 3a

BODIPY **4a** (47 mg, 0.1 mmol), acetyl chloride (0.056 mL, 0.8 mmol), $SnCl_4$ (0.013 mL, 0.1 mmol), were dissolved in dichloromethane (2 mL). The reaction mixture was stirred at room temperature and the reaction was followed by TLC. After completion of the reaction, the reaction mixture was poured into dichloromethane (100 mL), and saturated aqueous $NaHCO_3$ (25 mL) was added to remove excess acetyl chloride. The organic layer was collected, and was 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 **3a** in 76 % yield (red solid, 36 mg).

synthesis of 7 from 5

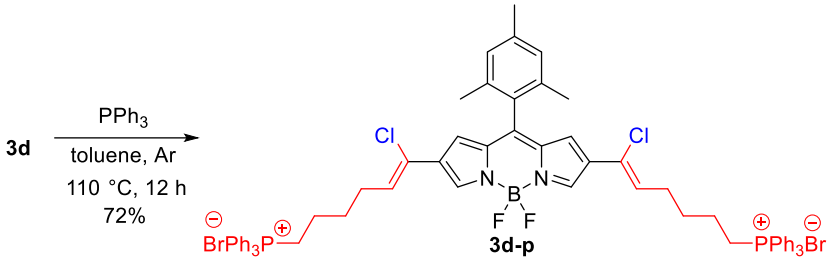


5 7

BODIPY **5** (38 mg, 0.1 mmol), phenylacetyl chloride (0.11 mL, 0.8 mmol), $SnCl_4$ (0.013 mL, 0.1 mmol), were dissolved in toluene (1 mL). The reaction mixture was stirred at room temperature and the reaction was followed by TLC. After completion of the reaction, the reaction mixture was poured into dichloromethane (100 mL), and saturated aqueous $NaHCO_3$ (25 mL) was added to remove excess phenylacetyl chloride. The organic layer was collected, and was 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 55 % yield (violet solid, 54 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.12 (s, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.39-7.35 (m, 2H), 7.31-7.29 (m,

1H), 7.01 (s, 2H), 6.98 (s, 1H), 6.77 (s, 1H), 6.67 (s, 1H), 6.08 (t, *J* = 7.1 Hz, 1H), 2.40 (s, 3H), 2.37-2.30 (m, 2H), 2.15 (s, 6H), 1.06 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 142.8, 141.9, 139.3, 136.3, 135.8, 135.5, 134.6, 133.6, 133.3, 129.5, 129.1, 128.7, 128.4, 128.3, 128.2, 124.8, 124.5, 124.4, 124.2, 124.1, 22.5, 21.2, 20.1, 13.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.09 (t, *J* = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.81 (q, *J* = 30.1 Hz). HRMS calcd for $C_{30}H_{27}BCl_2FN_2$ $(M\text{-}F)^+$ 515.1628, found 515.1653.

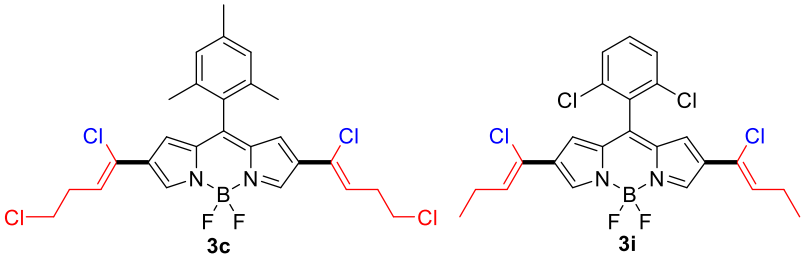
synthesis of 3d-p from 3d



BODIPY **3d** (70 mg, 0.1 mmol) and triphenylphosphine (263.0 mg, 1.0 mmol) were dissolved in 5 mL toluene. The mixture was heated at 110 ℃ for 12 h under argon atmosphere. Upon completion, the mixture was then cooled to room temperature. The precipitate was collected and was washed with toluene until the triphenylphosphine was completely removed. The crude product was dissolved in a 1 mL dichloromethane solution and was layered with petroleum ether to give brown powder **3d-p** in 60% yield (violet solid, 73 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.82 -7.67 (m, 30H), 7.01 (s, 2H), 6.61 (s, 2H), 5.99 (t, *J* = 7.2 Hz, 2H), 3.87-3.80 (m, 4H), 2.38 (s, 3H), 2.36 -2.32 (m, 4H), 2.11 (s, 6H), 1.94 -1.87 (m, 4H), 1.69-1.58 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 142.2, 139.4, 135.1, 135.0, 133.7, 133.6, 130.6, 130.4, 128.6, 126.0, 125.5, 124.5, 118.7, 117.8, 22.6, 22.1, 22.0, 21.9, 21.2, 20.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.06 (t, *J* = 28.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.71 (q, *J* = 30.1 Hz). HRMS (ESI) m/z calcd for $C_{66}H_{63}BBrCl_2F_2N_2P_2^+$ $(M\text{-}Br)^+$ 1145.30621, found 1145.30835.

5. Crystal data

Table S3. Selected Geometrical Parameters of 3c and 3i obtained from crystallography



	3c	3i
B-N bond lengths (Å)	1.5462 (42) 1.5462 (42)	1.5466 (36) 1.5466 (36)
C=C bond lengths of alkenyl units (Å)	1.3201 (71) 1.3201 (71)	1.3048 (47) 1.3048 (47)
C-Cl bond lengths of alkenyl units (Å)	1.7575 (42) 1.7575 (42)	1.7425 (403) 1.7403 (402)
dihedral angles of two pyrrole rings in dipyyrin core (deg)	4.705(156)	2.995(117)
dihedral angles of alkenyl units and dipyyrin core (deg)	20.048(141) 20.048(160)	21.114(66) 20.964(745)

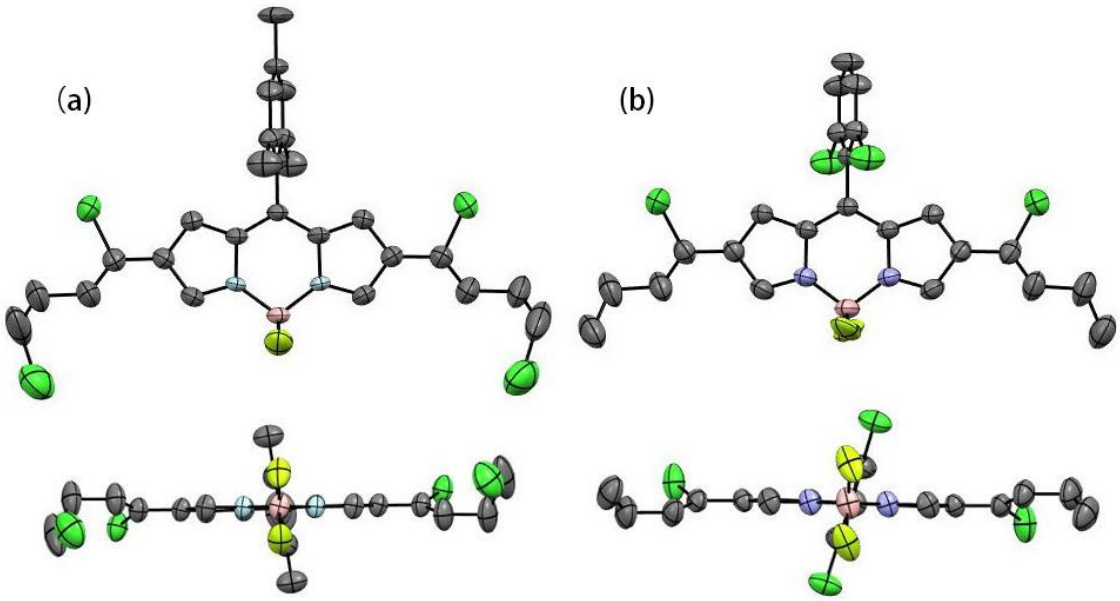


Figure S2. Top and front views of X-Ray structures of **3c** (a) and **3i** (b)**.**

Compound name	**3c**
CCDC number	2418848
Empirical formula	$C_{26}H_{25}BCl_4F_2N_2$
Formula weight	556.09
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbcn
a/Å	16.744
b/Å	17.965
c/Å	9.147
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2751.6
Z	4
ρ_{calc}g/cm^3	1.342
μ/mm^{-1}	0.462
F(000)	1144.0
Crystal size/mm^3	0.22 × 0.21 × 0.2
Radiation	MoKα (λ = 0.71076)
2Θ range for data collection/°	6.358 to 50.698
Index ranges	$-20 \leq h \leq 20$, $-21 \leq k \leq 21$, $-11 \leq l \leq 11$
Reflections collected	109216
Independent reflections	2508 [R_{int} = 0.0361, R_{sigma} = 0.0080]
Data/restraints/parameters	2508/16/163
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0875, wR_2 = 0.2541
Final R indexes [all data]	R_1 = 0.1007, wR_2 = 0.2792
Largest diff. peak/hole / e Å^{-3}	1.49/-0.65

Compound name	**3i**	
CCDC number	2010636	
Empirical formula	$C_{23}H_{19}BCl_4F_2N_2$	
Formula weight	514.01	
Temperature	293.15 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 14.694(3) Å	α= 90 °
	b = 16.305(3) Å	β= 90 °
	c = 9.870(2) Å	γ= 90 °
Volume	2364.7(8) $Å^3$	
Z	4	
Density (calculated)	1.444 Mg/m^3	
Absorption coefficient	0.531 mm^{-1}	
F(000)	1048	
Crystal size	0.05 x 0.04 x 0.03 mm^3	
Theta range for data collection	3.241 to 27.489 °	
Index ranges	-18<=h<=18, -21<=k<=20, -11<=l<=12	
Reflections collected	37155	
Independent reflections	2682 [R(int) = 0.0807]	
Completeness to theta = 25.242?	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6813	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2682 / 2 / 161	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0574, wR2 = 0.1491	
R indices (all data)	R1 = 0.0900, wR2 = 0.1680	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.920 and -0.687 e $Å^{-3}$	

6. Spectroscopic properties

6.1. Table S4: Selected Photophysical Data of BODIPYs in Dichloromethane.

BODIPYs	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	ε_{abs}^{max} [M^{-1} cm^{-1}][a]	$\Phi^{b,c}$	Stokes Shift (cm^{-1})[c]
1a	500	522	54100	0.74[c]	840
3a	584	619	39500	0.26[b]	970
3b	576	609	48600	0.35[b]	960
3c	581	616	36000	0.24[b]	1060
3d	581	616	47600	0.26[b]	980
3e	587	622	37200	0.23[b]	960
3f	609	662	48300	0.06[b]	1310
3g	583	625	36300	0.09[b]	1150
3h	579	619	30300	0.08[b]	1120
3i	605	642	37200	0.29[b]	1020
4a	536	593	34000	0.28[b]	1130
4b	544	579	43000	0.38[b]	1110
4c	535	588	25800	0.34[b]	1150
4d	535	586	26800	0.37[b]	1120
4e	537	593	32100	0.33[b]	1020
4f	552	647	46700	0.08[b]	1330
4g	535	604	36400	0.12[b]	1270
4h	532	600	34900	0.09[b]	1140
4i	546	611	27700	0.36[b]	1380
5	501	514	64300	0.76[c]	760
6	539	586	32200	0.35[b]	1180
7	594	643	46400	0.09[b]	1260
3d-p	580	611	42100	0.24[b]	960

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

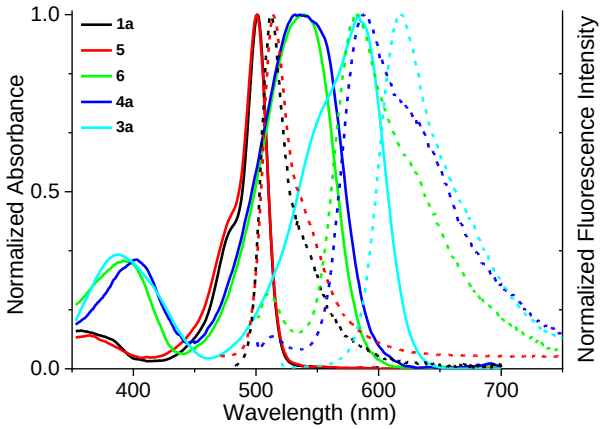


Figure S3. Overlaid normalized absorption (solid lines) and fluorescence (dashed lines) spectra of dyes in dichloromethane.

6.2. Table S5: Photophysical properties of BODIPY 3d-p in different solvents at room temperature

solvent	λ_{abs}^{max} (nm)	ε_{abs}^{max} $[M^{-1}\ cm^{-1}]^a$	λ_{em}^{max} (nm)	Φ^b	Stokes shift $(cm^{-1})^c$
cyclohexane	595	36000	633	0.16	1000
CH_3CN	570	42700	613	0.22	1230
THF	578	41900	617	0.18	1090
toluene	584	45300	622	0.20	1150
MeOH	572	40700	611	0.19	1120
DMSO	582	47700	623	0.23	1110

[a]Molar absorption coefficient values rounded to the nearest 100 $M^{-1}\ cm^{-1}$.

[b]Fluorescence quantum yields determined using Rhodamine B (Φ = 0.49 in ethanol) as reference.

[c]Stokes shift values rounded to nearest 10 cm^{-1}.

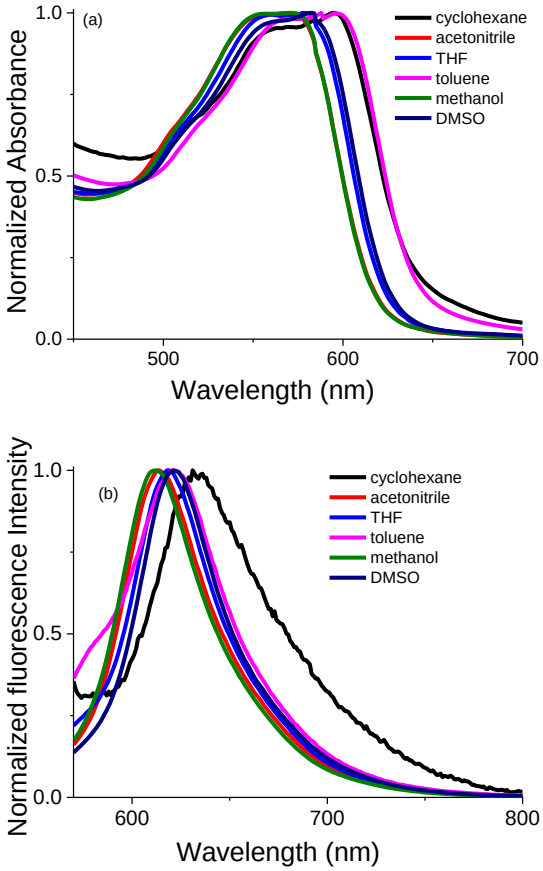


Figure S4. Overlaid normalized absorption (a) and fluorescence emission (b) spectra of BODIPYs **3d-p** recorded in different solvents (excitation at 550 nm).

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

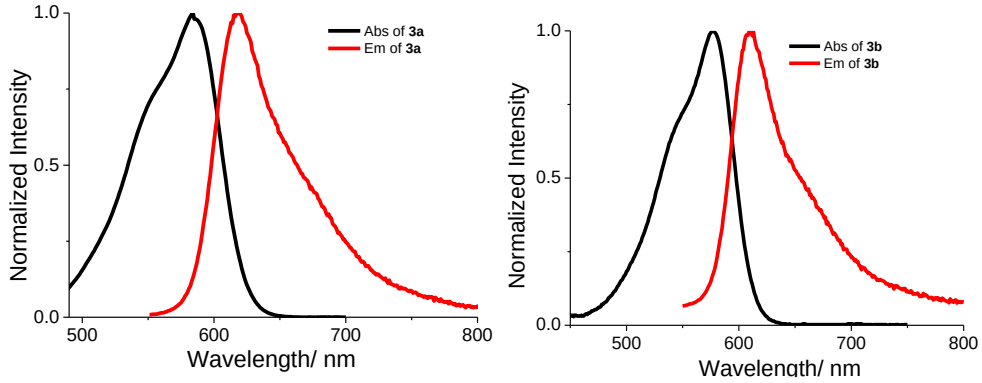


Figure **S5.** Absorption and fluorescence emission (right) spectra of **3a** (left) and **3b** (right) recorded in dichloromethane (excitation at 550 nm).

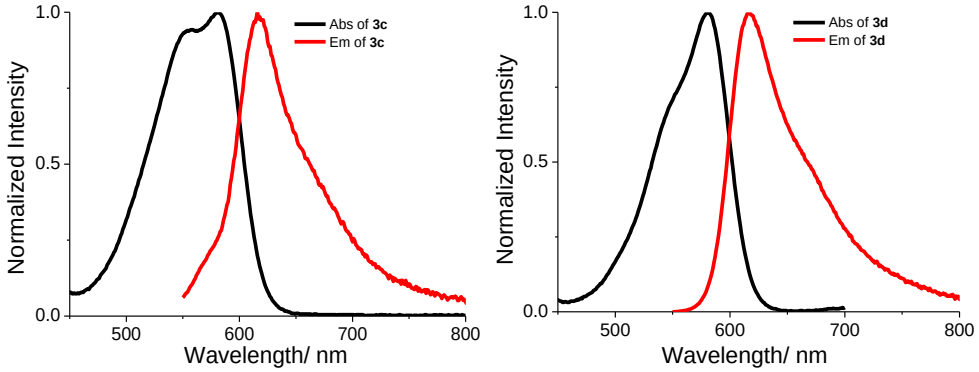


Figure **S6.** Absorption and fluorescence emission (right) spectra of **3c** (left) and **3d** (right) recorded in dichloromethane (excitation at 550 nm).

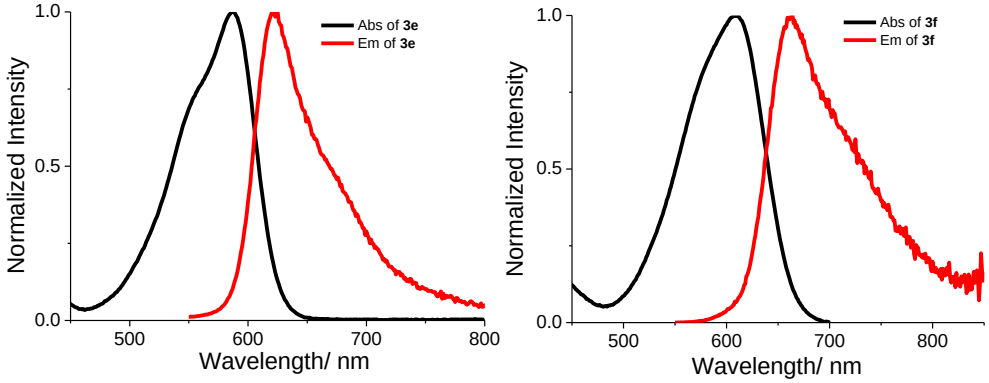


Figure **S7.** Absorption and fluorescence emission (right) spectra of **3e** (left) and **3f** (right) recorded in dichloromethane (excitation at 550 nm).

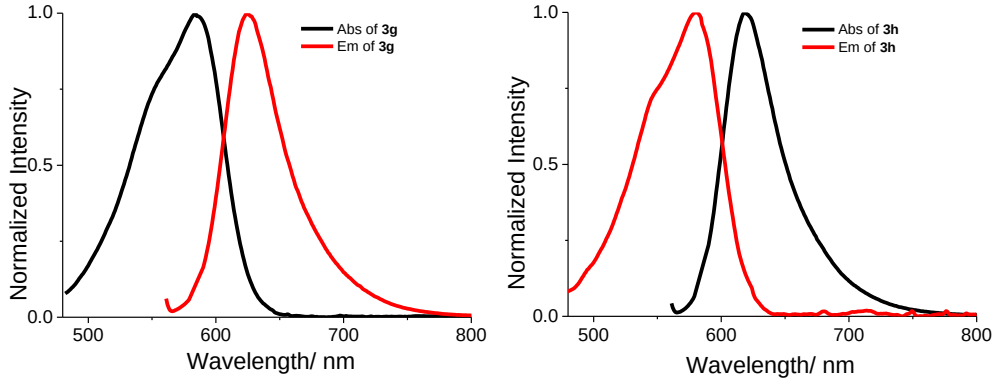


Figure **S8.** Absorption and fluorescence emission (right) spectra of **3g** (left) and **3h** (right) recorded in dichloromethane (excitation at 550 nm).

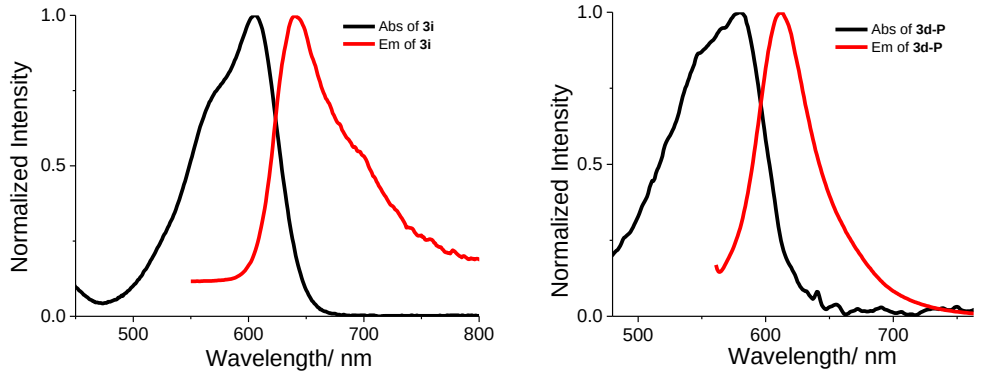


Figure **S9.** Absorption and fluorescence emission (right) spectra of **3i** (left) and **3d-p** (right) recorded in dichloromethane (excitation at 550 nm).

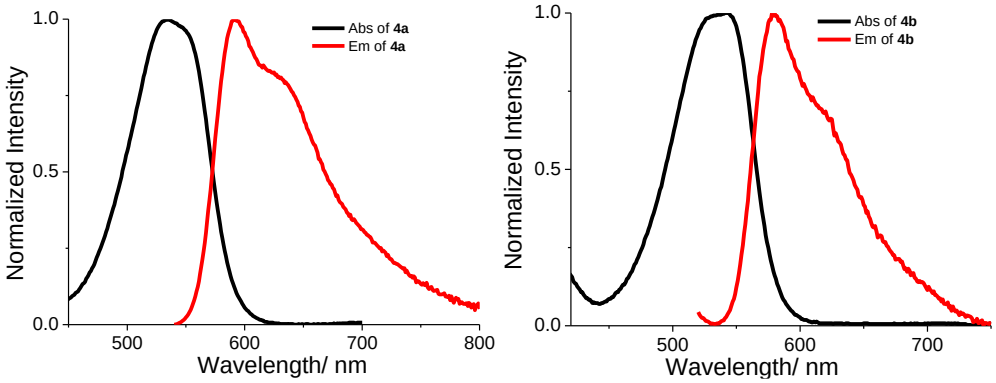


Figure **S10.** Absorption and fluorescence emission (right) spectra of **4a** (left) and **4b** (right) recorded in dichloromethane (excitation at 520 nm).

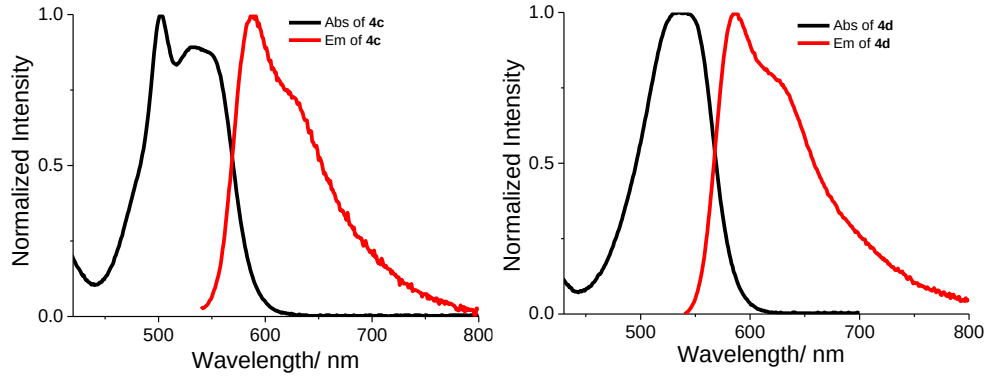


Figure **S11.** Absorption and fluorescence emission (right) spectra of **4c** (left) and **4d** (right) recorded in dichloromethane (excitation at 520 nm).

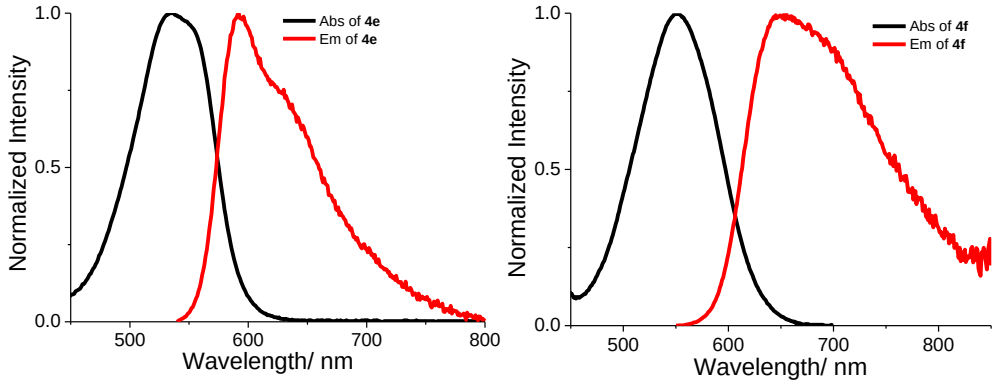


Figure **S12.** Absorption and fluorescence emission (right) spectra of **4e** (left) and **4f** (right) recorded in dichloromethane (excitation at 520 nm).

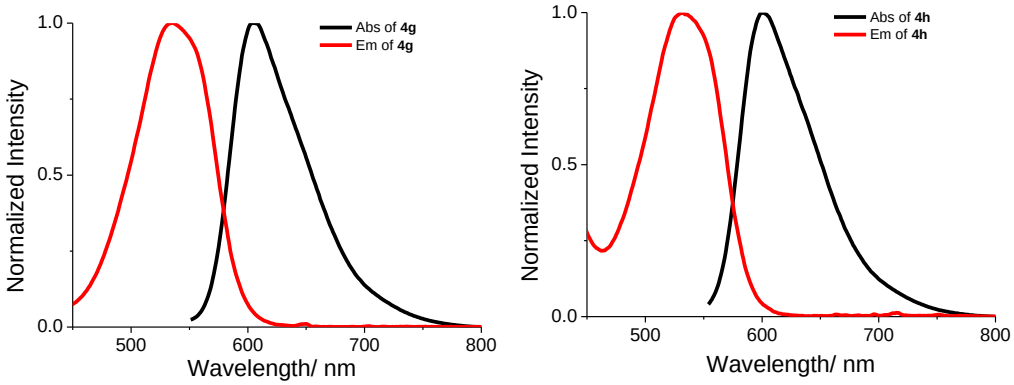


Figure **S13.** Absorption and fluorescence emission (right) spectra of **4g** (left) and **4h** (right) recorded in dichloromethane (excitation at 520 nm).

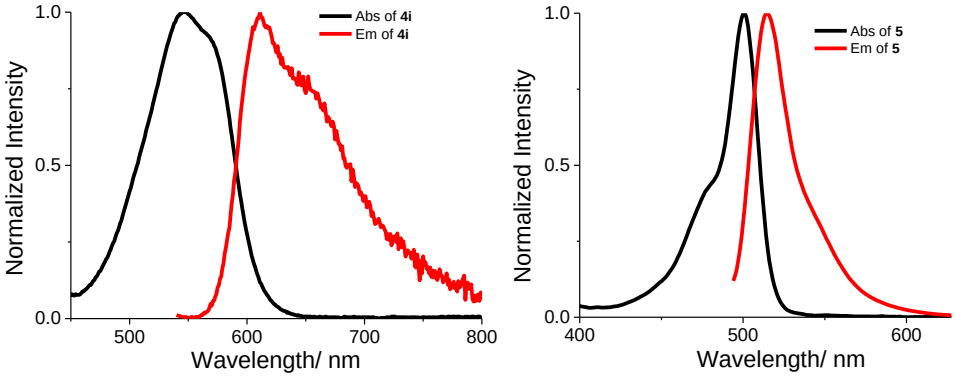


Figure **S14.** Absorption and fluorescence emission (right) spectra of **4i** (left, excitation at 520 nm) and **5** (right, excitation at 480 nm) recorded in dichloromethane.

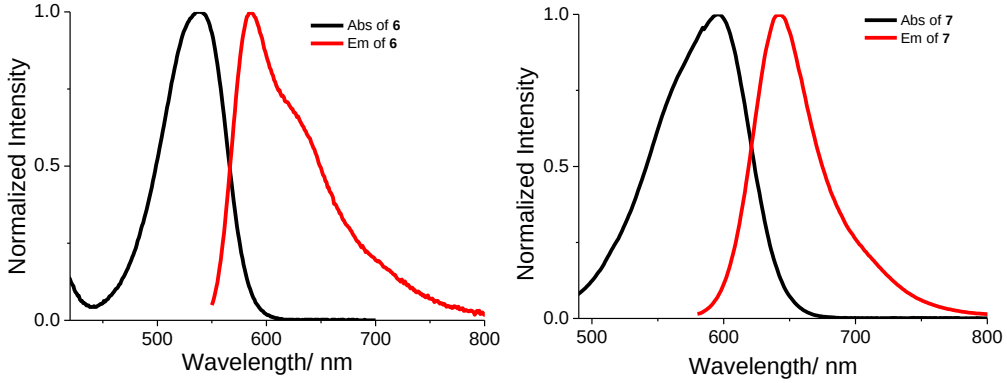


Figure **S15.** Absorption and fluorescence emission spectra of **6** (left, (excitation at 520 nm) and **7** (right, (excitation at 550 nm) recorded in dichloromethane.

8. Cellular studies

8.1 Cell culture

HeLa cells (human cervical cancer cells) were cultured in culture media (RPMI-1640, supplemented with 10% FBS and 1% penicillin/streptomycin solution) at 37 ℃ in an atmosphere of 5% CO_2 and 95% humidified atmosphere for 24 h.

8.2 Cytotoxicity determined by the CCK-8 method

The cytotoxicity of the **3d-p** was evaluated on Hela cells. These cells were seeded into 96-well plates with a density of 5000 cells per well and cultured overnight. Then, **3d-p** solutions with serious concentrations were added and incubated with cells for 24 h. Every experiment was performed for at least three times. The working solutions were then removed, and the cells were washed with PBS buffer for two times. A total of 10 μL of CCK-8 (Cell Counting Kit-8, BIOMIKY) was added into each well, and the cells were further incubated at 37 ℃ for 2 h. Then the plate was shaken for 5 min (protect from light), and the absorbance at 450 nm was measured with a microplate reader (Multiskan Sky).

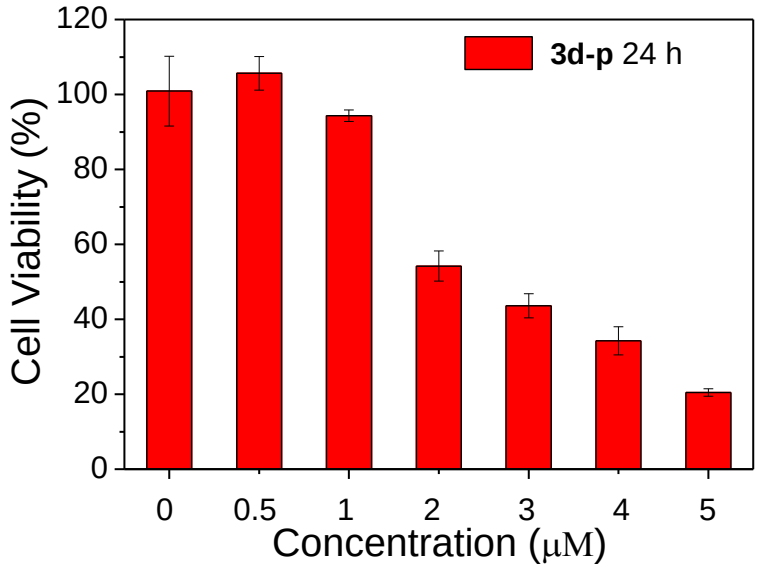


Figure S16. Viability of HeLa cells treated with 0.0, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 μM of **3d-p** for 24 h as demonstrated by CCK-8 assay.

8.2 Cellular uptake

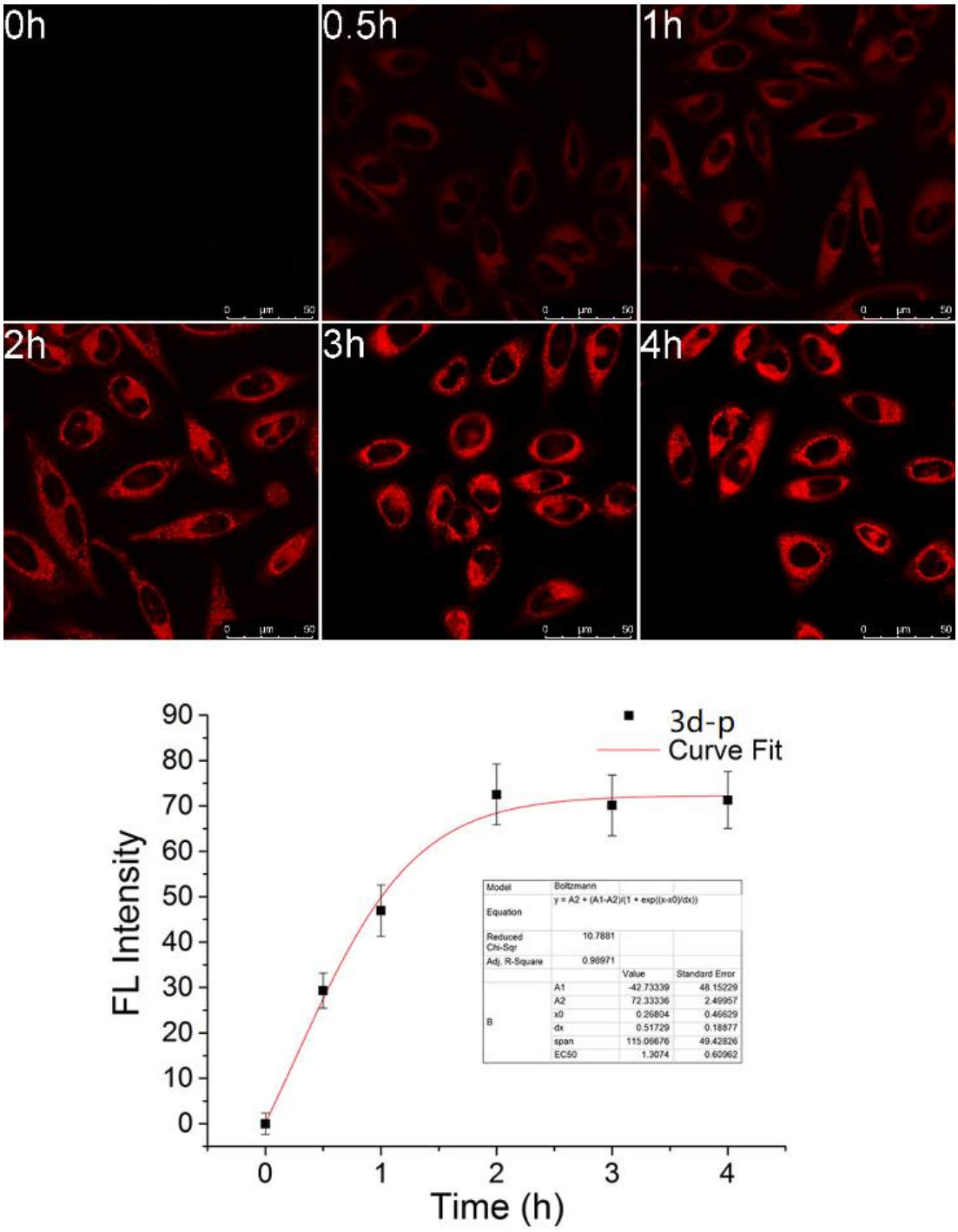


Figure S17. (a) Fluorescence microscopy images of time-dependent uptake of **3d-p** at 1.0 μM by Hela cells (human cervical cells). (b) Fluorescence intensity quantitation was analyzed by the images.

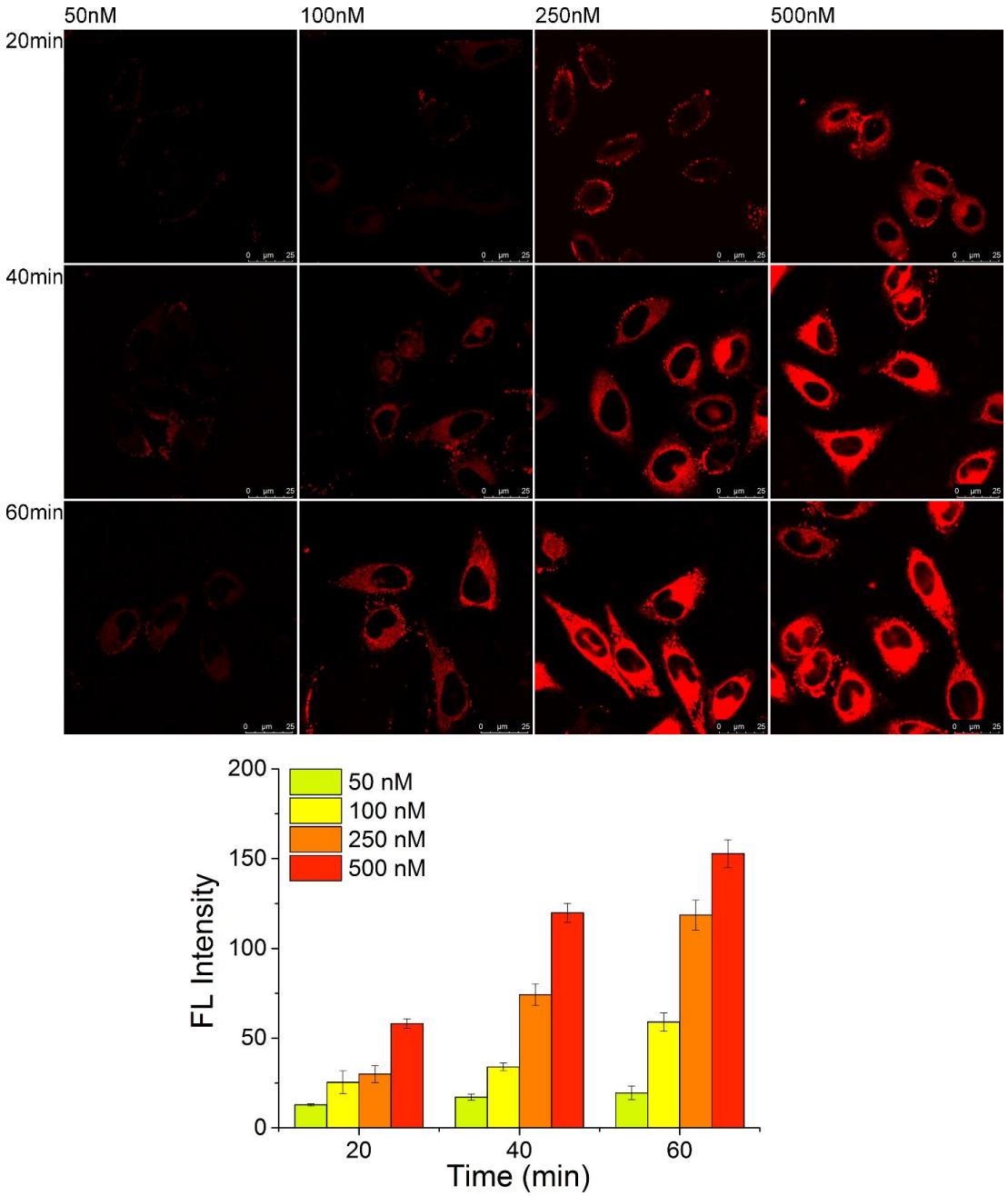


Figure S18. (a) Fluorescence microscopy images of HeLa cells with **3d-p** (50, 100, 250, 500 nM) for 20, 40 and 60 min at 37 ^{o}C. (b) Fluorescence intensity quantitation was analyzed by these images.

8.3 Two-photon fluorescence imaging

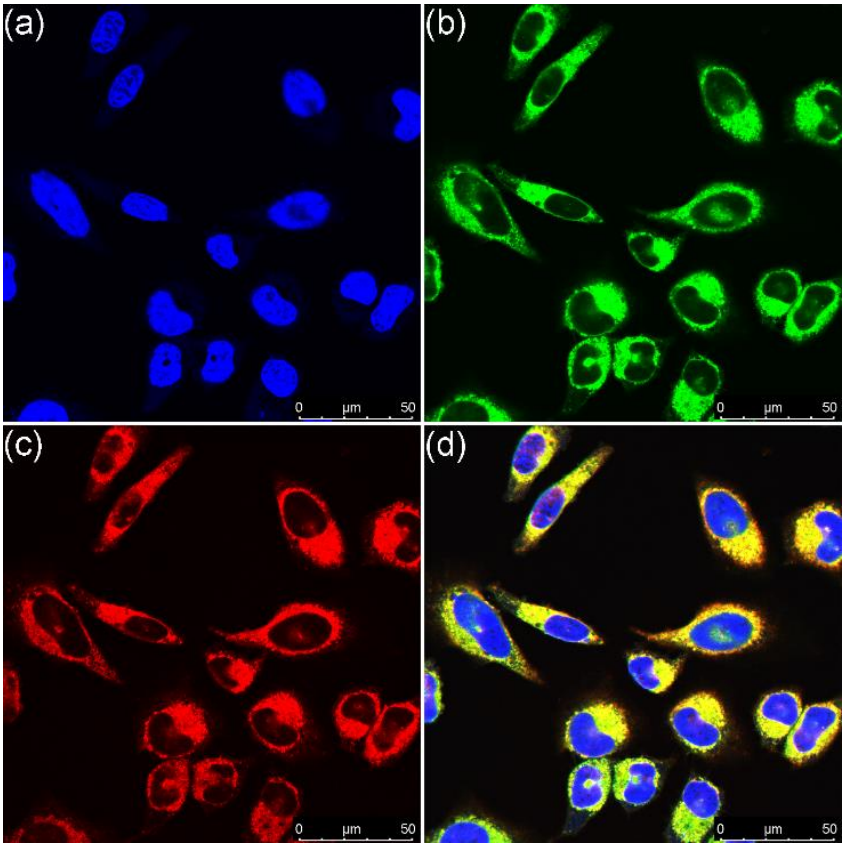


Figure S19. Fluorescence images using **3d-p** in HeLa cells. The cells were incubated with **3d-p** (1.0 μM) for 1 h at 37 ºC. Images for **3d-p** were then recorded using excitation wavelengths of 550 nm (single photon) and 900 nm (two-photon), and recording over the 590-720 nm spectral regions, respectively. (a) DAPI fluorescence, (b) single photon fluorescence of **3d-p**, (c) two-photon fluorescence of **3d-p** and (d) merged images of parts a, b and c. Scale bars = 50 μm.

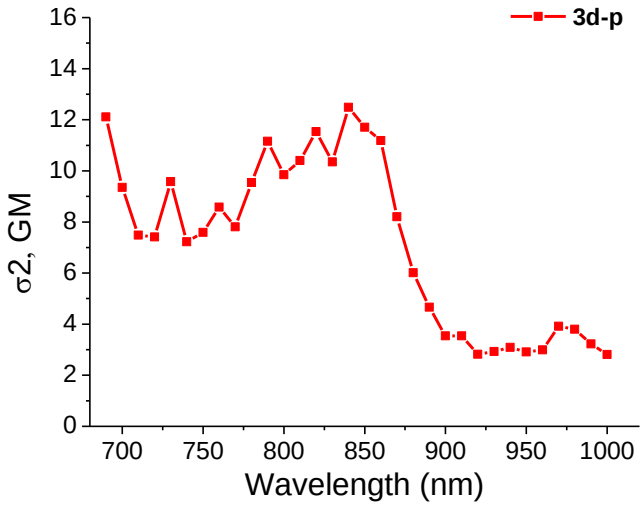


Figure S20. Two photon excitation spectra of **3d-p** in ethanol.

9. Electrochemical data

Table S6. Electrochemical data acquired at 100 mV/s, and HOMO-LUMO Gaps determined from spectroscopy of dyes 1a, 5, 6, 4a and 3a[a]

dyes	$E_{1/2}^{red}$ (V)	E_{pa}^{red} (V)	E_{red}^{onest} (V)	E_{pa}^{ox} (V)	E_{ox}^{onest} (V)	LUMO (eV)	HOMO (eV)	E_g^e (eV)	E_g^o (eV)
1a	-0.96	-	-0.87	1.79	1.48	-3.53	-5.88	2.35	2.38
5	-0.77	-	-0.69	-	1.65	-3.71	-6.05	2.34	2.28
6	-0.82	-	-0.61	1.46	1.33	-3.79	-5.73	1.94	2.02
4a	-0.68	-1.85	-0.60	1.63	1.51	-3.80	-5.91	2.11	2.04
3a	-0.76	-	-0.62	1.42	1.28	-3.78	-5.68	1.90	1.96

[a] $E_{1/2}^{red}$ = half wave potentials of reversible reduction potential; E_{pa}^{red} = irreversible reduction peak potentials; E_{red}^{onest} = the onset reduction potentials; E_{pa}^{ox} = irreversible oxidation peak potentials; E_{ox}^{onest} = the onset oxidation potentials; E_{LUMO} = -e(E_{red}^{onest} + 4.4); E_{HOMO} = -e(E_{ox}^{onest} + 4.4); E_g^e = bandgap, obtained from the intercept of the electrochemical data; E_g^e = E_{LUMO} - E_{HOMO}; E_g^o = bandgap, obtained from the intercept of the absorption spectra.

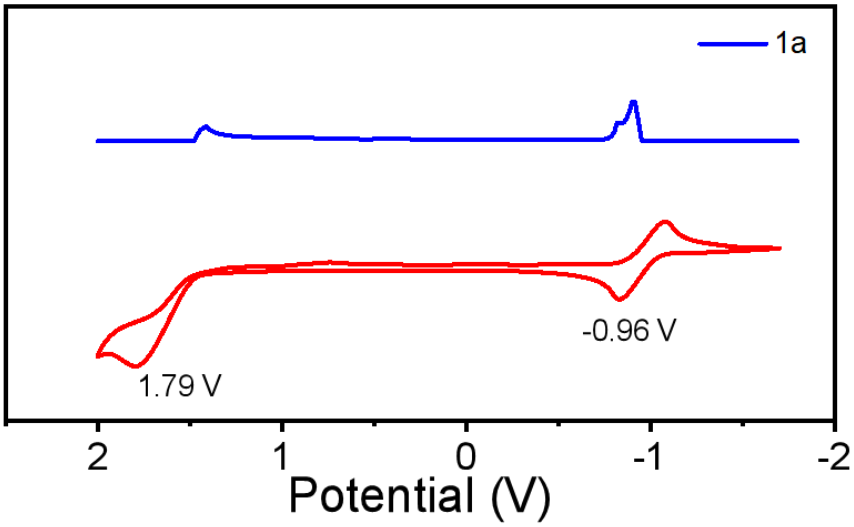


Figure **S21.** Differential pulse voltammogram and cyclic voltammogram of **1a** recorded in dichloromethane containing 0.1 M $TBAPF_6$ at room temperature.

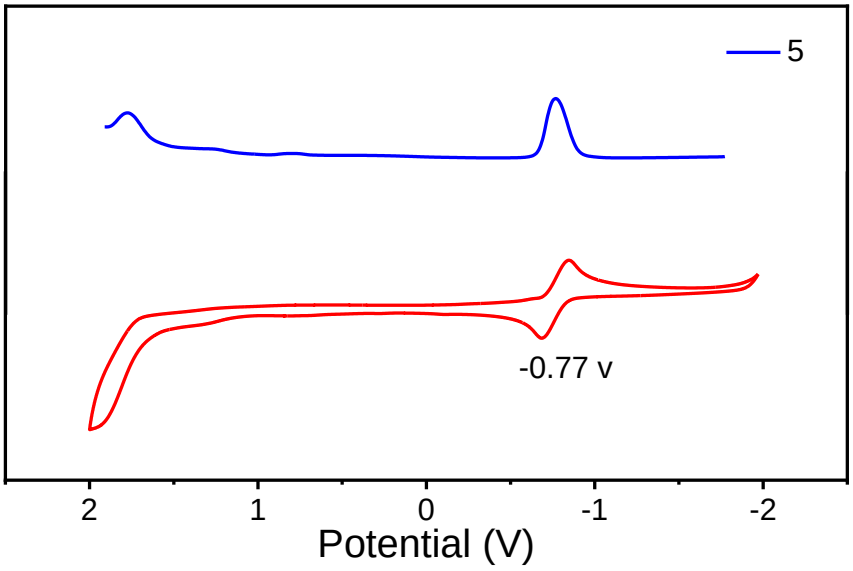


Figure **S22.** Differential pulse voltammogram and cyclic voltammogram of **5** recorded in dichloromethane containing 0.1 M $TBAPF_6$ at room temperature.

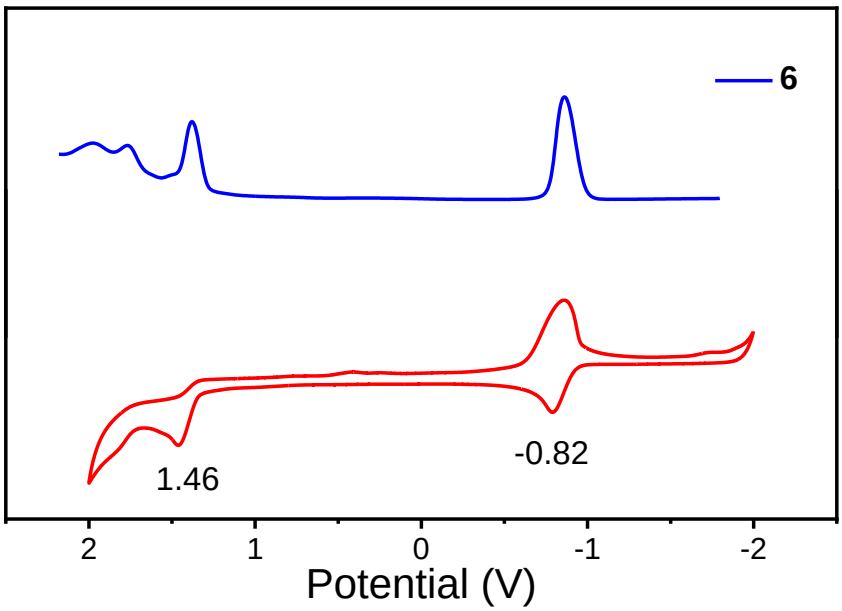


Figure **S23.** Differential pulse voltammogram and cyclic voltammogram of **6** recorded in dichloromethane containing 0.1 M $TBAPF_6$ at room temperature.

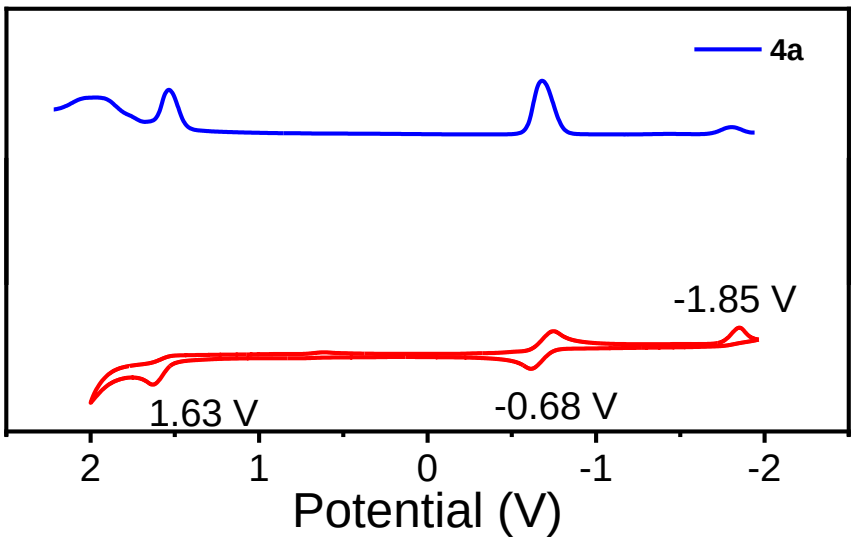


Figure **S24.** Differential pulse voltammogram and cyclic voltammogram of **4a** recorded in dichloromethane containing 0.1 M $TBAPF_6$ at room temperature.

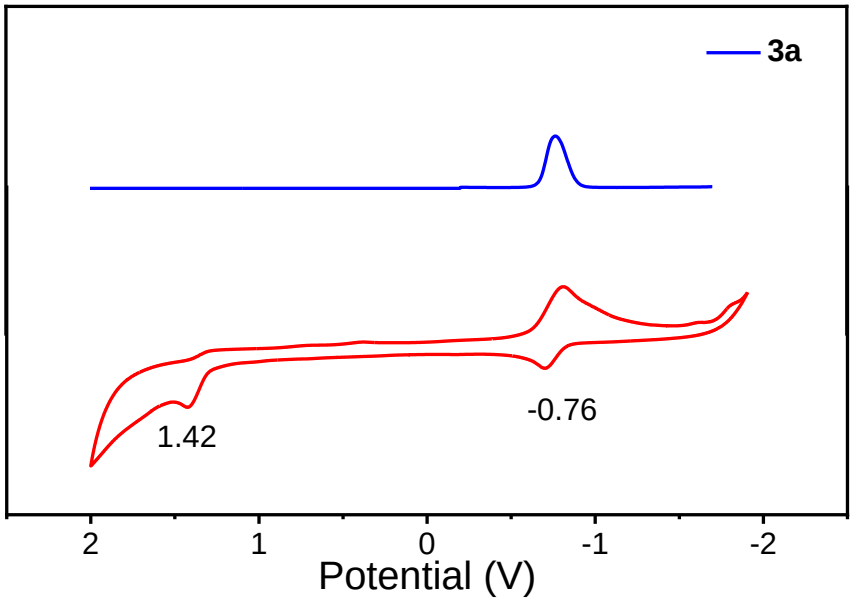
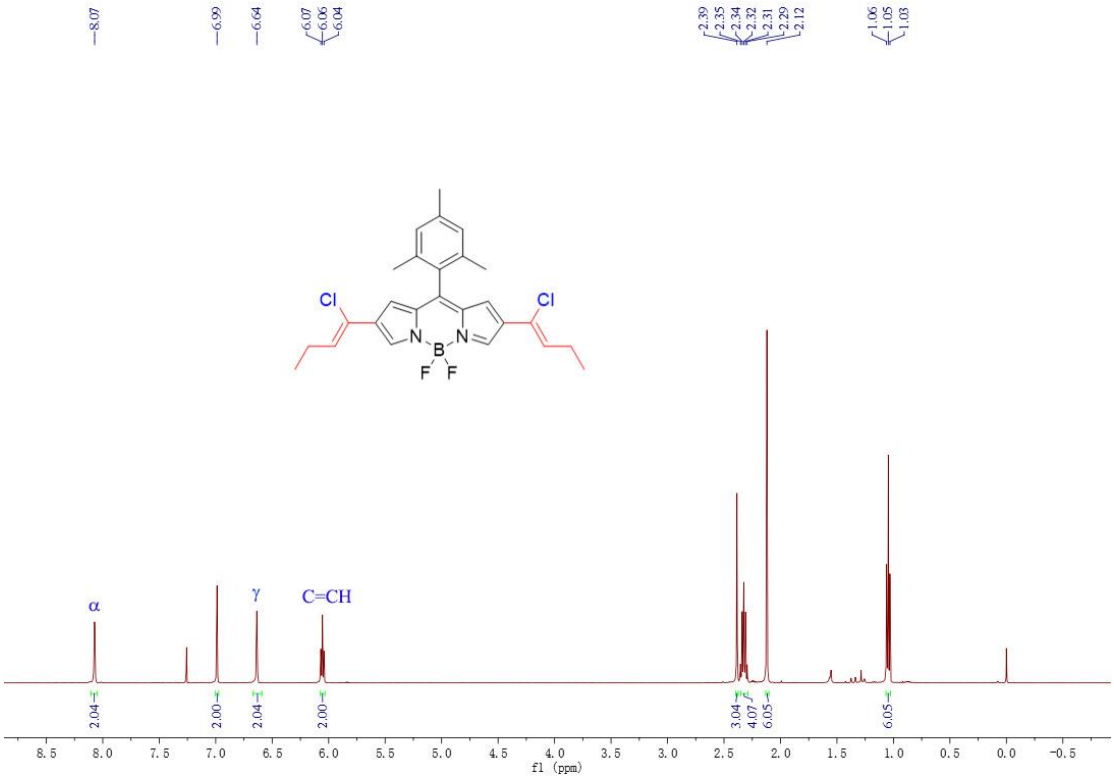


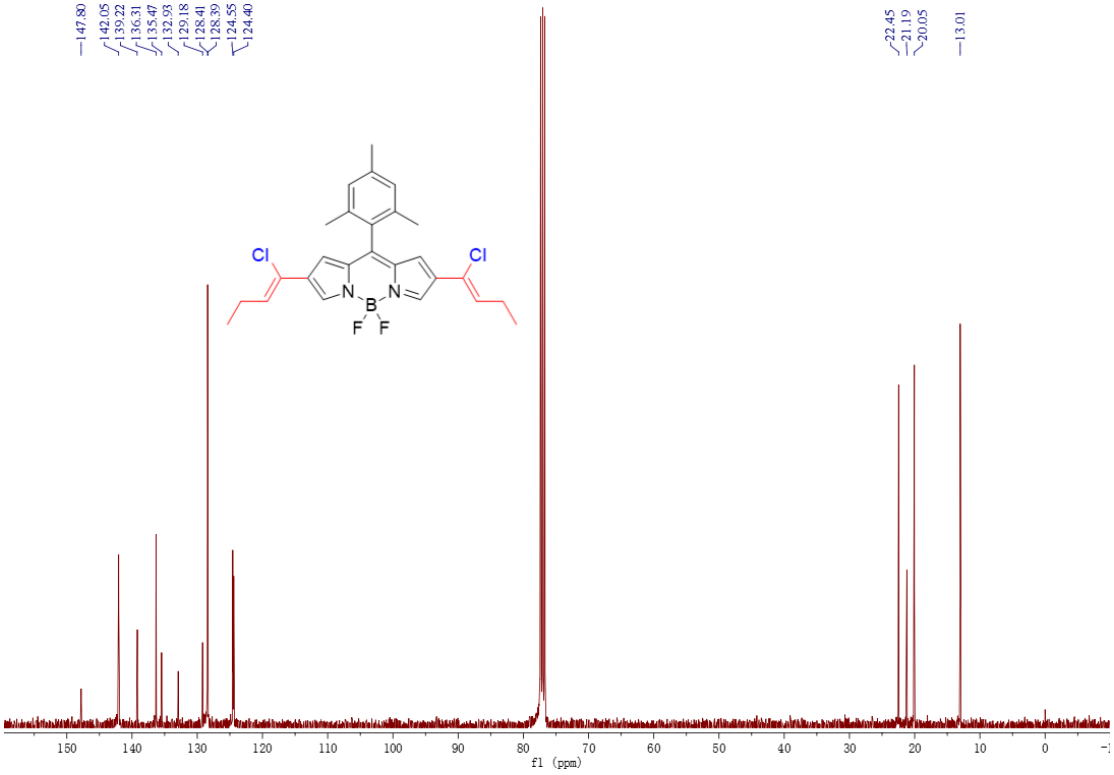
Figure **S25.** Differential pulse voltammogram and cyclic voltammogram of **3a** recorded in dichloromethane containing 0.1 M $TBAPF_6$ at room temperature.

10. NMR and HRMS spectra of all new compounds

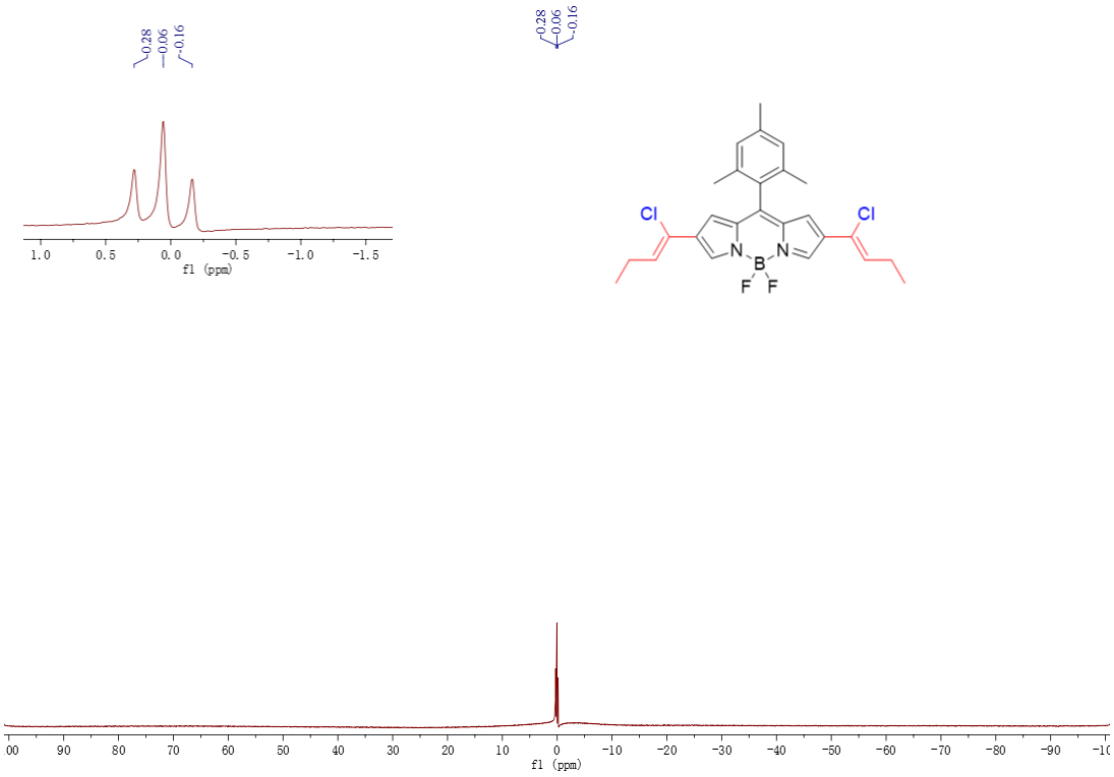
^{1}H NMR spectrum of **3a** in $CDCl_3$



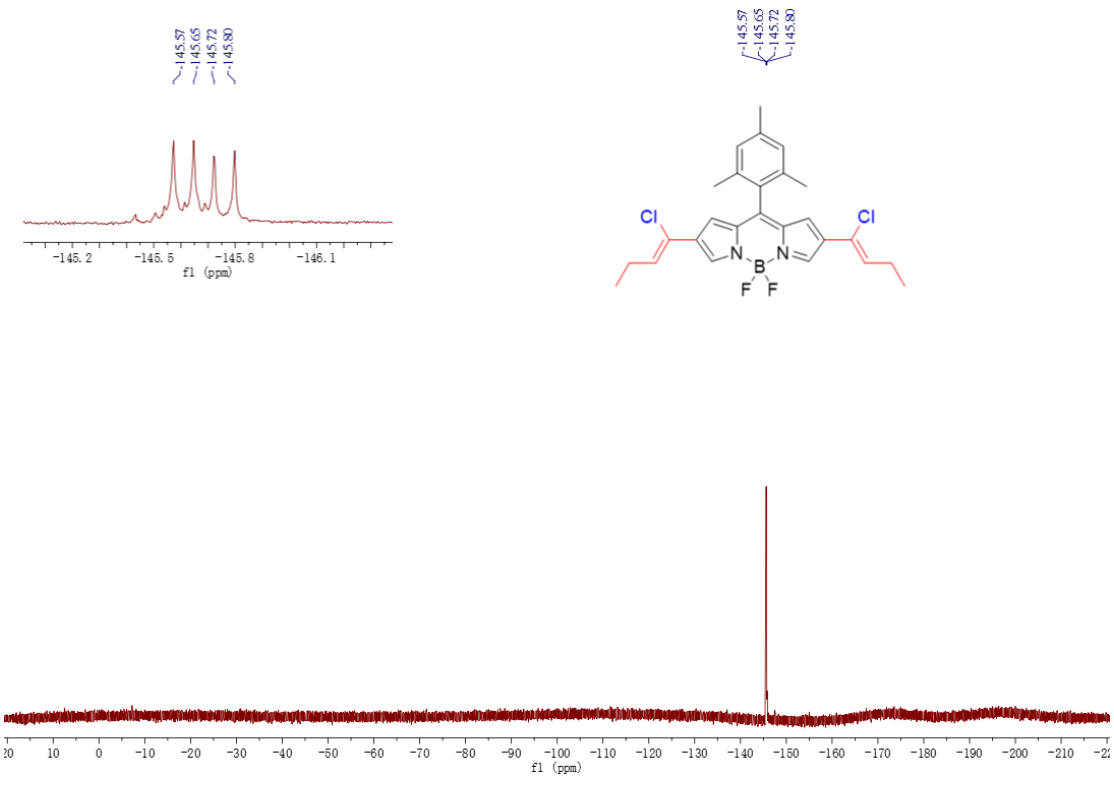
^{13}C NMR spectrum of **3a** in $CDCl_3$



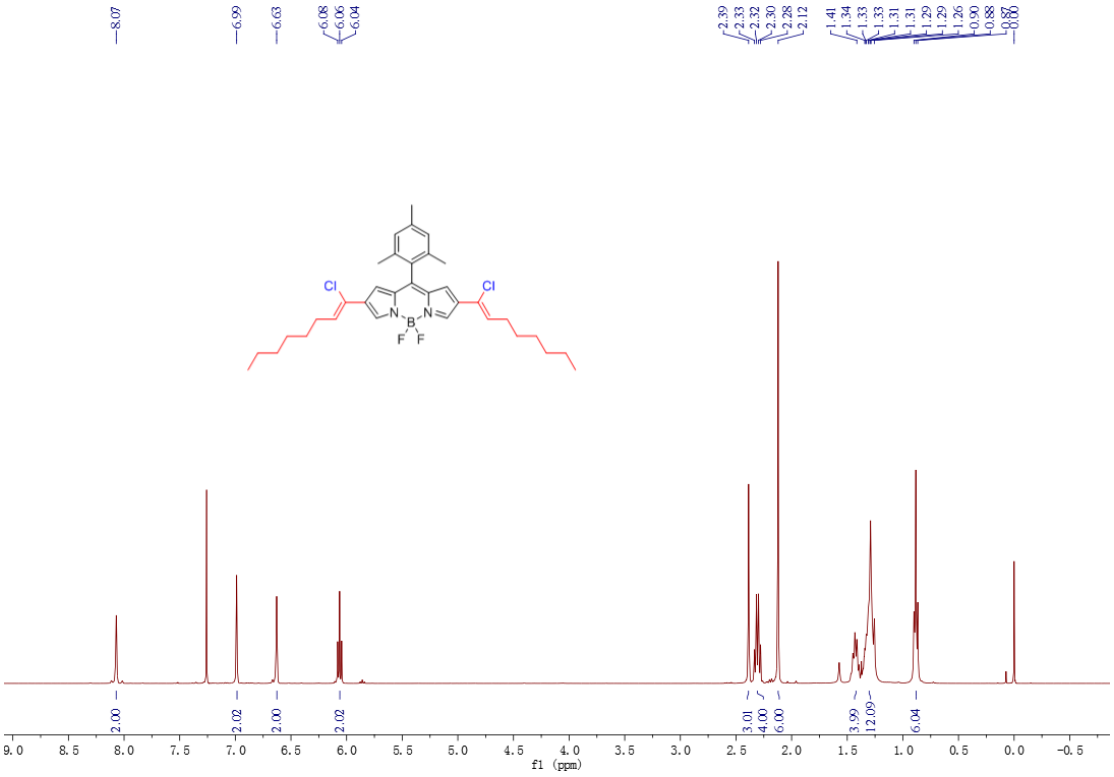
^{11}B NMR spectrum of **3a** in $CDCl_3$



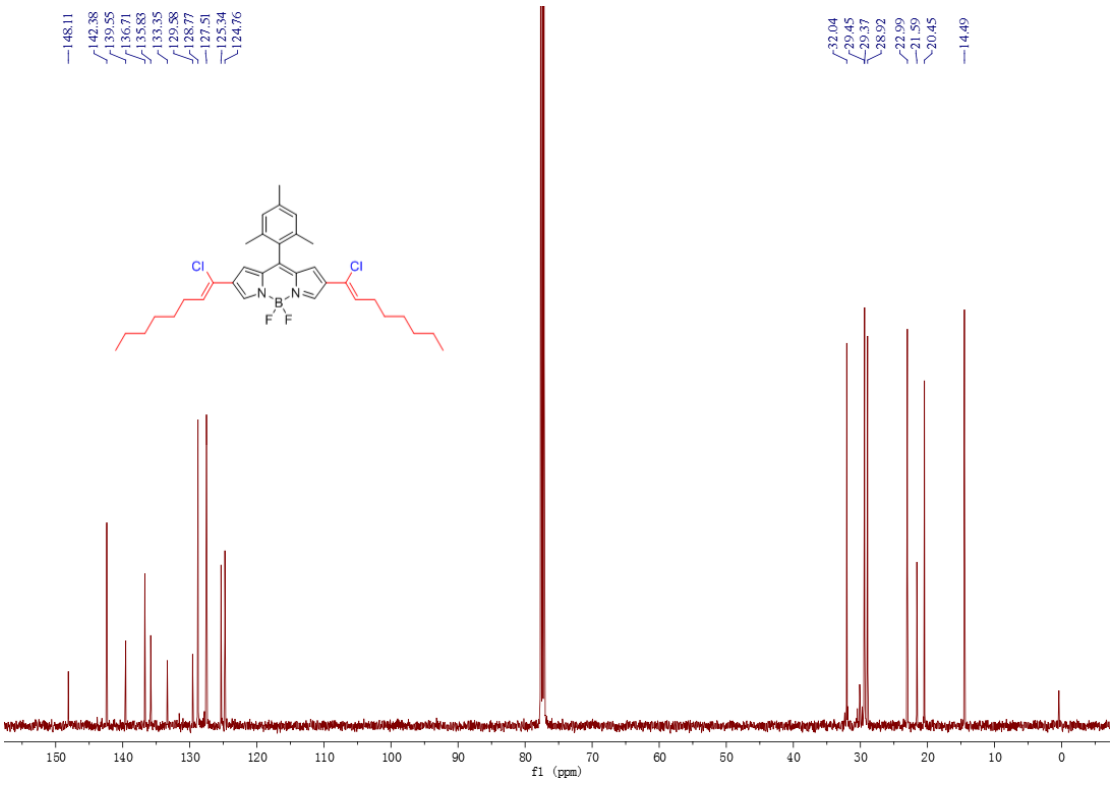
^{19}F NMR spectrum of **3a** in $CDCl_3$



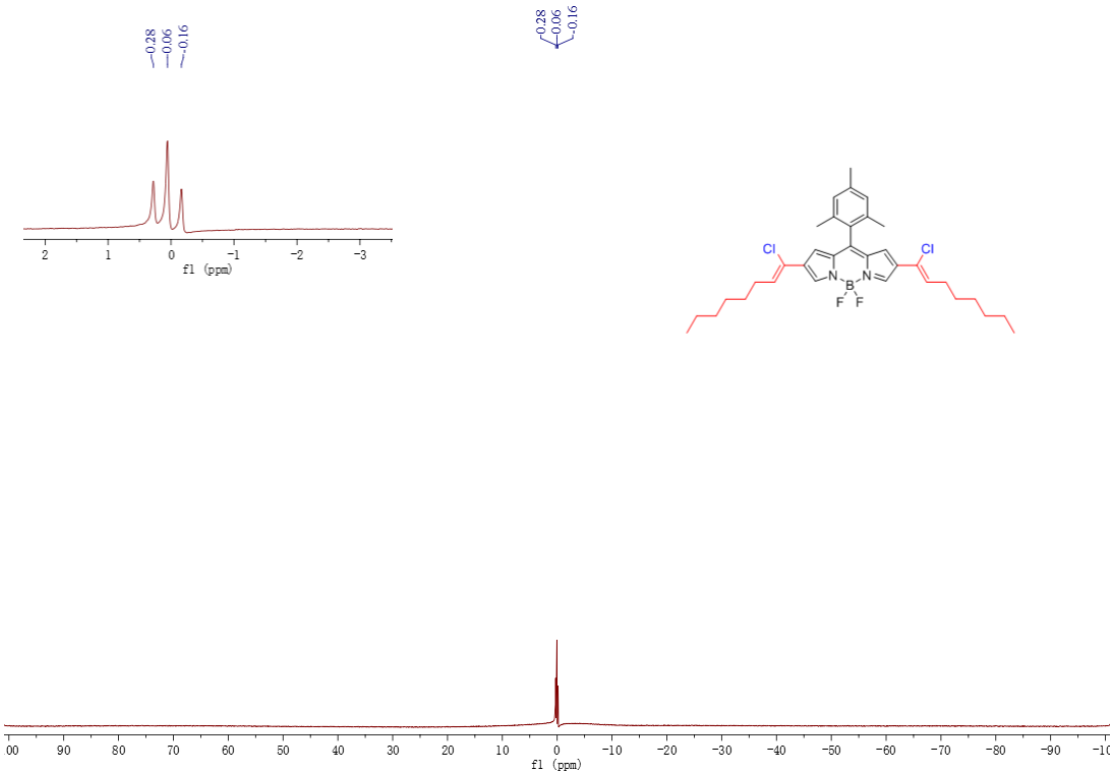
^{1}H NMR spectrum of **3b** in $CDCl_3$



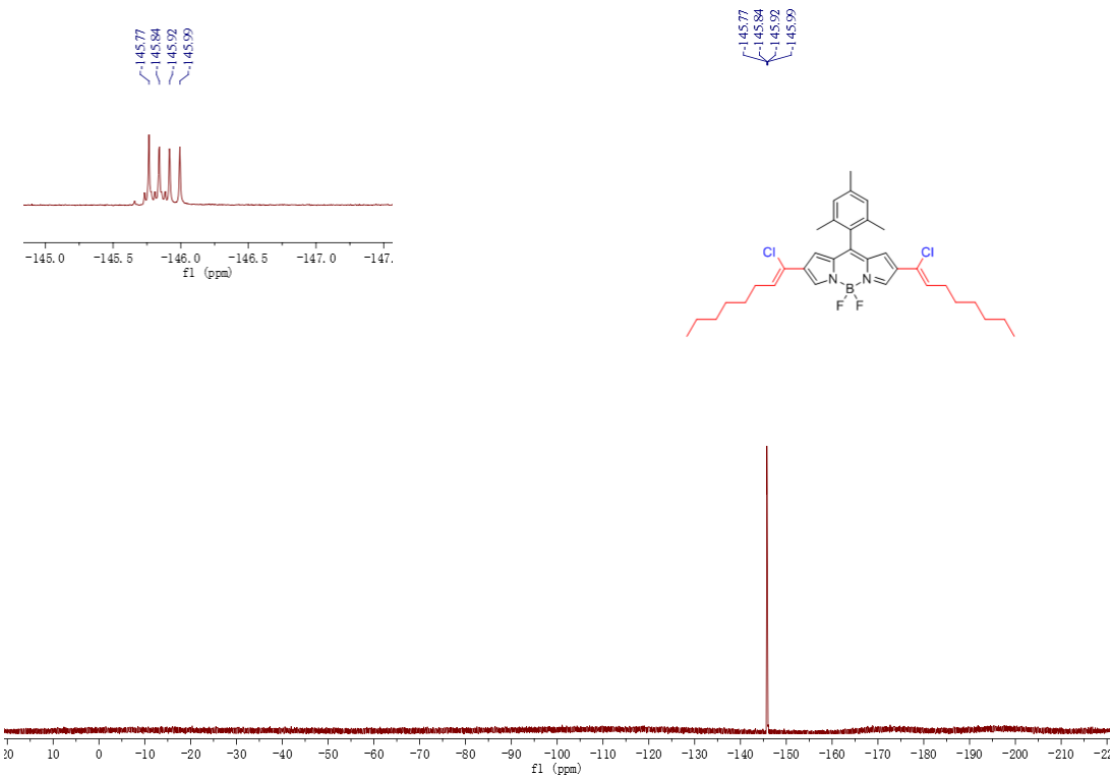
^{13}C NMR spectrum of **3b** in $CDCl_3$



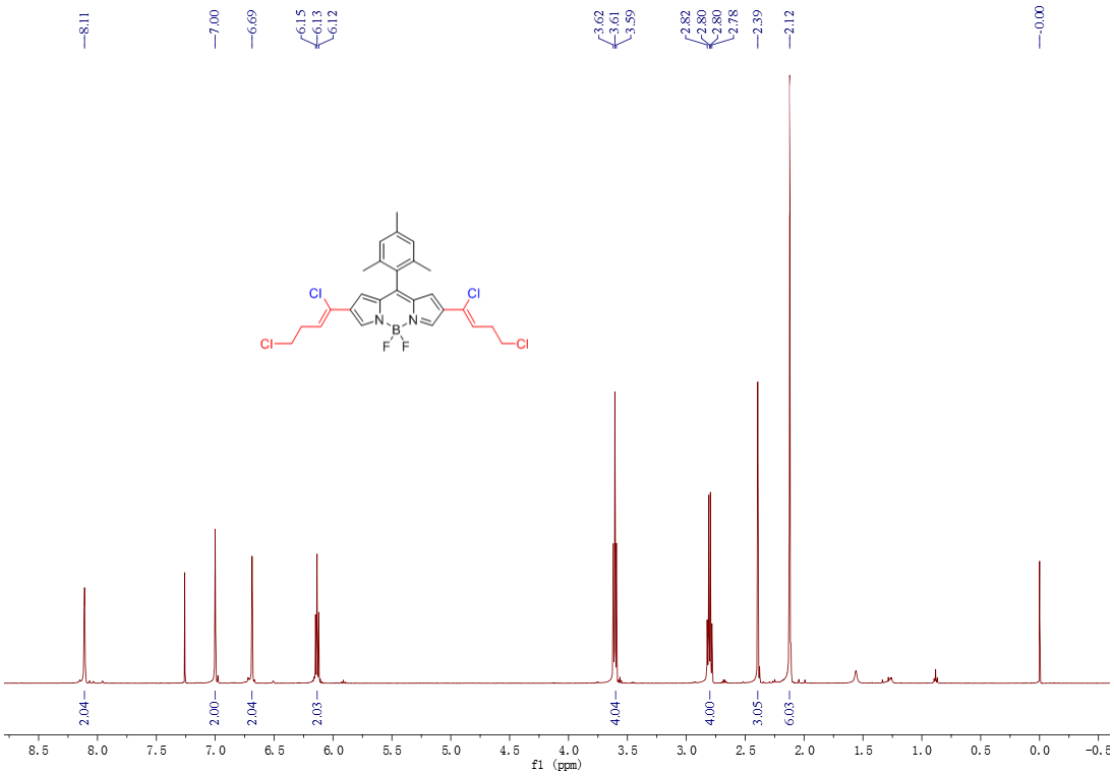
^{11}B NMR spectrum of **3b** in $CDCl_3$



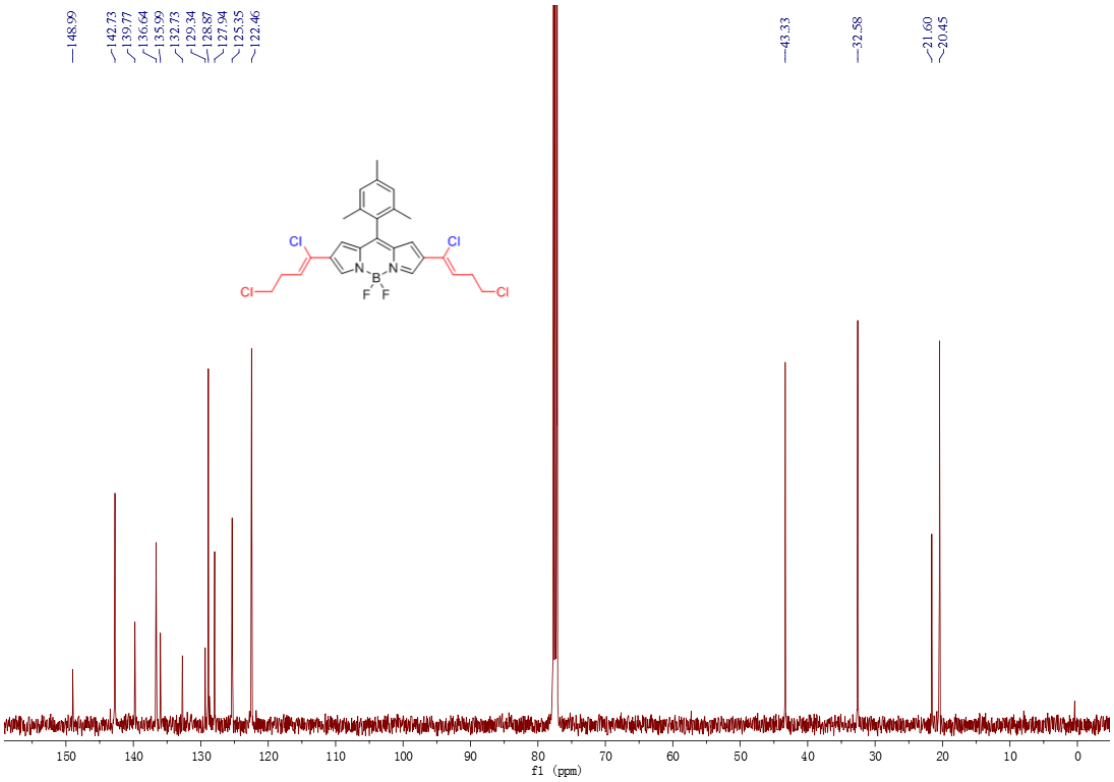
^{19}F NMR spectrum of **3b** in $CDCl_3$



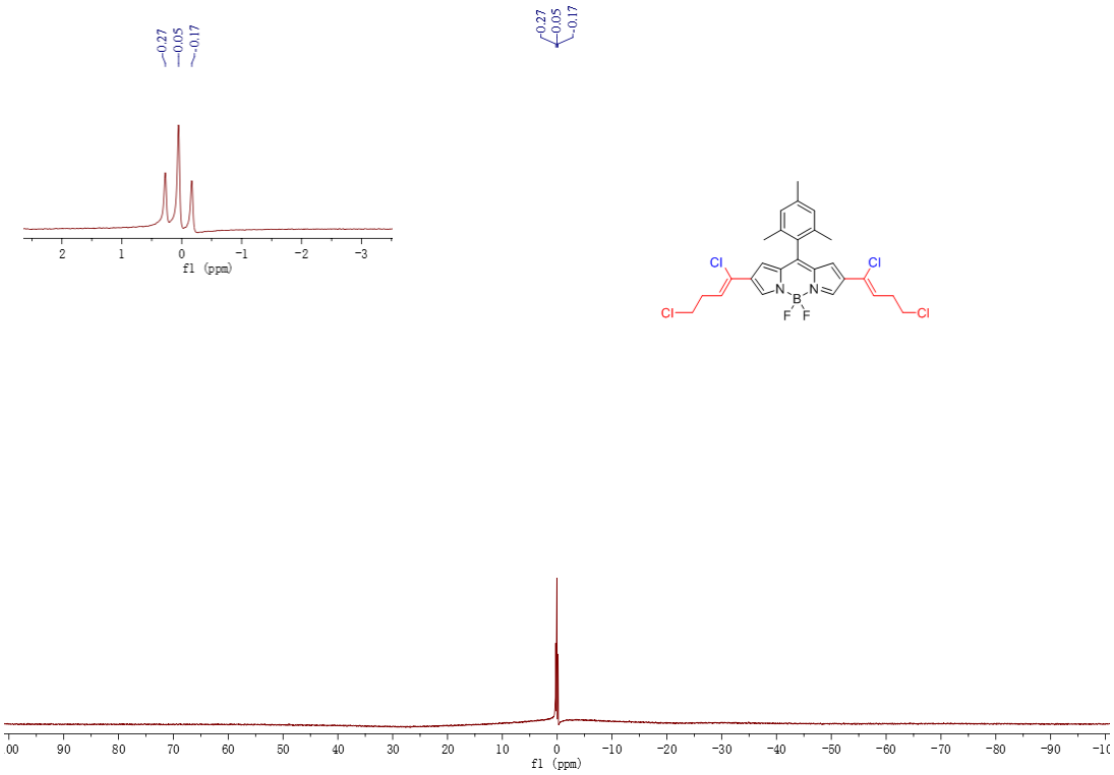
^{1}H NMR spectrum of **3c** in $CDCl_3$



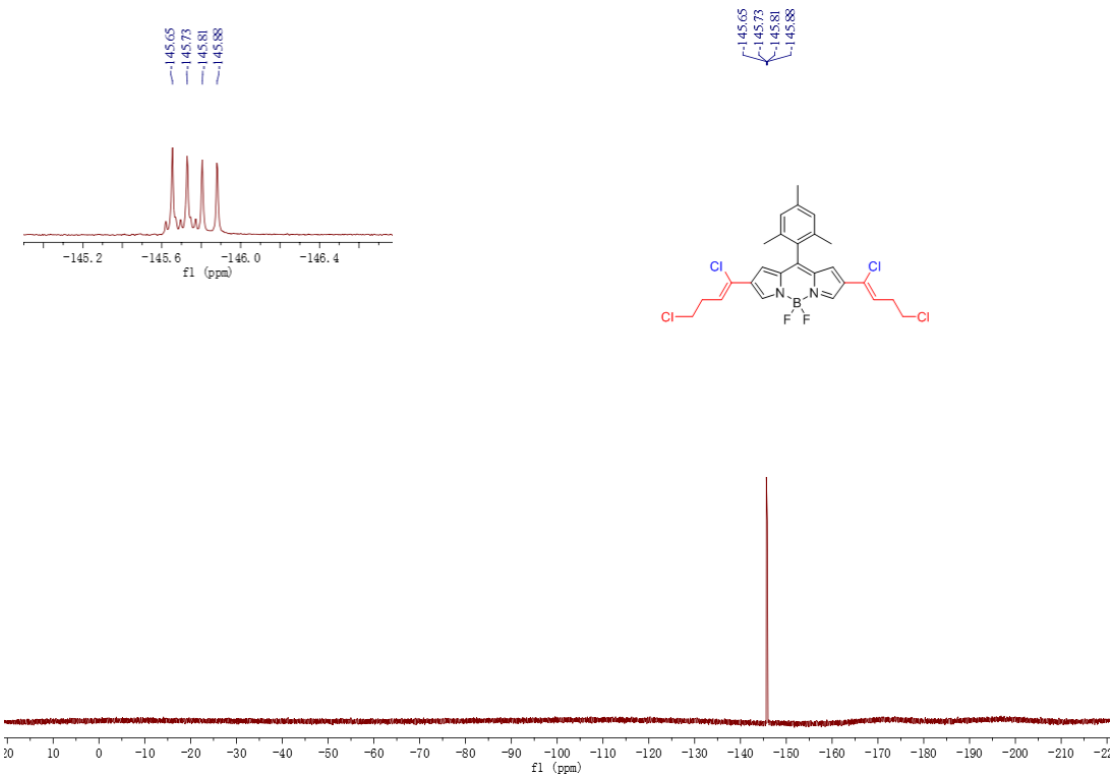
^{13}C NMR spectrum of **3c** in $CDCl_3$



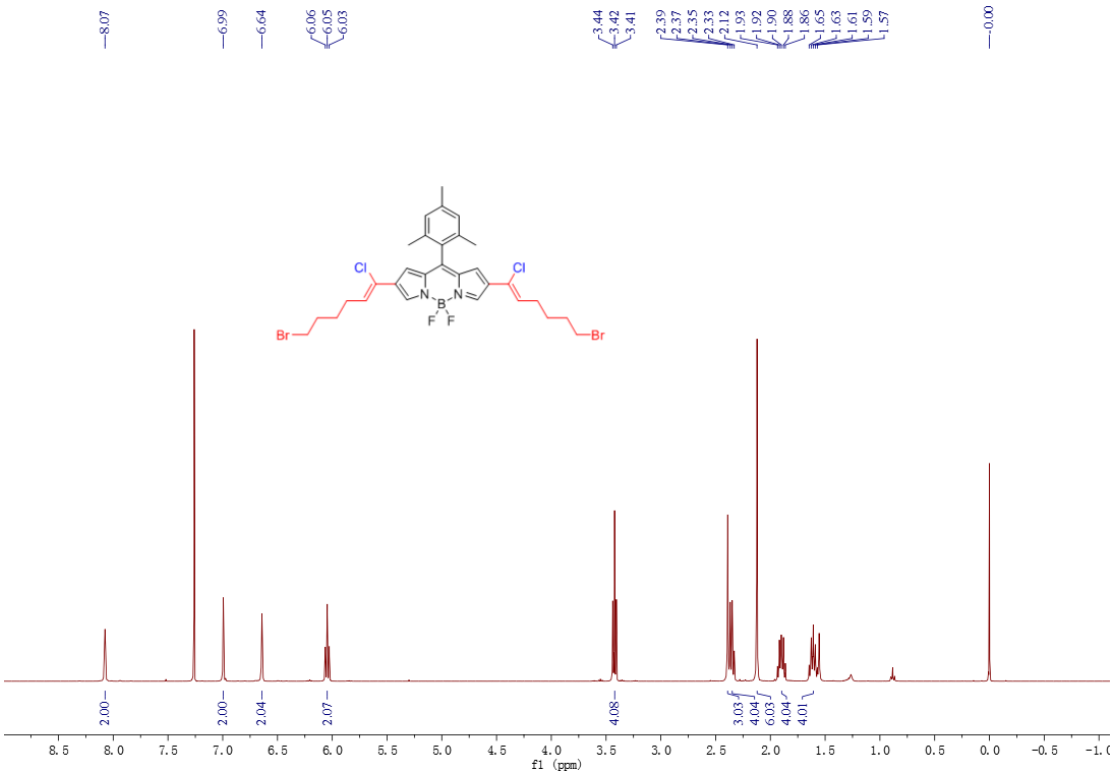
^{11}B NMR spectrum of **3c** in $CDCl_3$



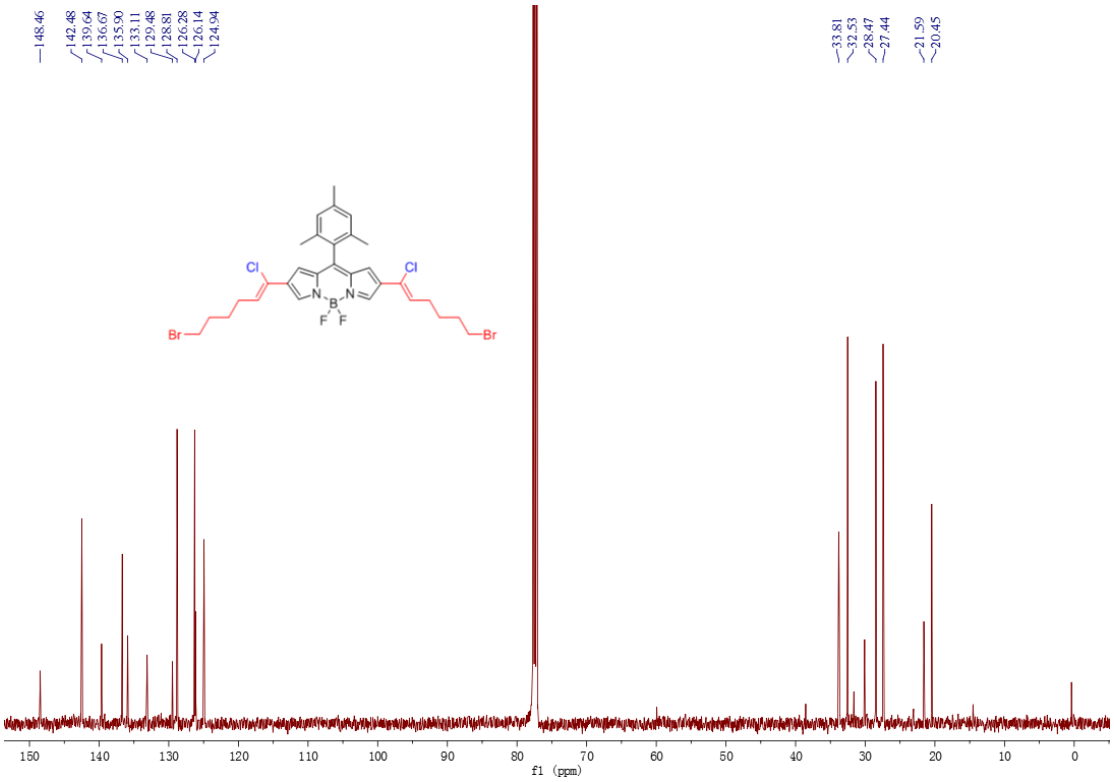
^{19}F NMR spectrum of **3c** in $CDCl_3$



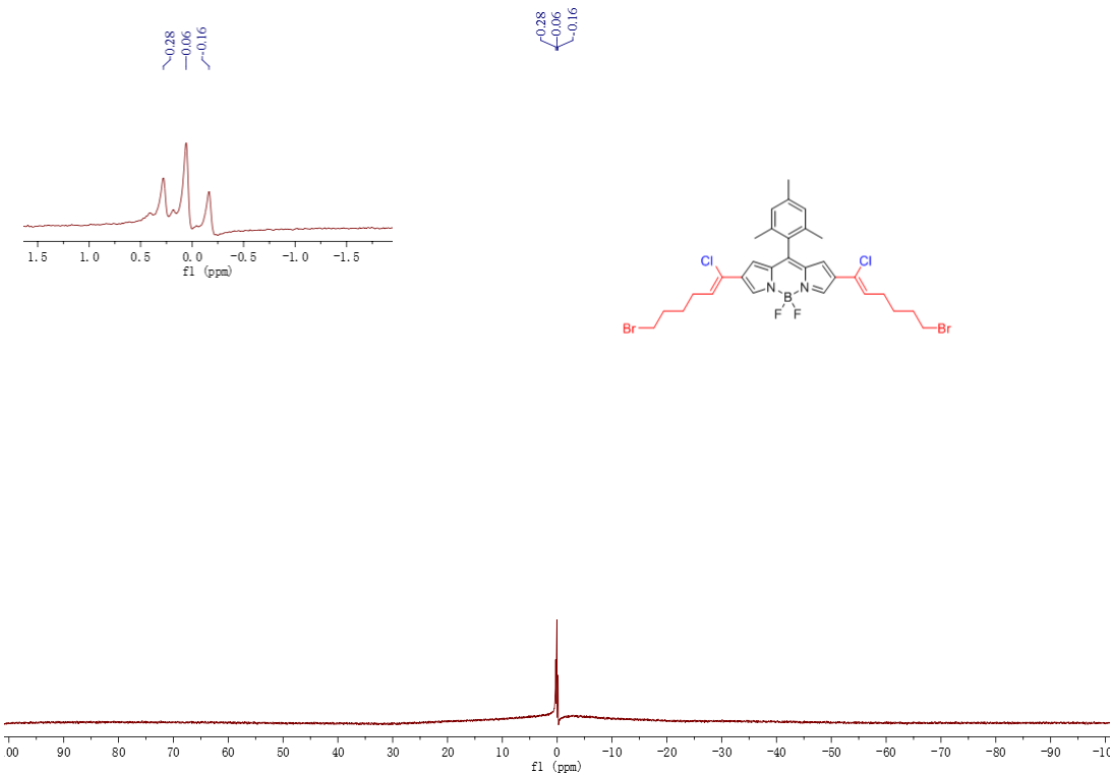
^{1}H NMR spectrum of **3d** in $CDCl_3$



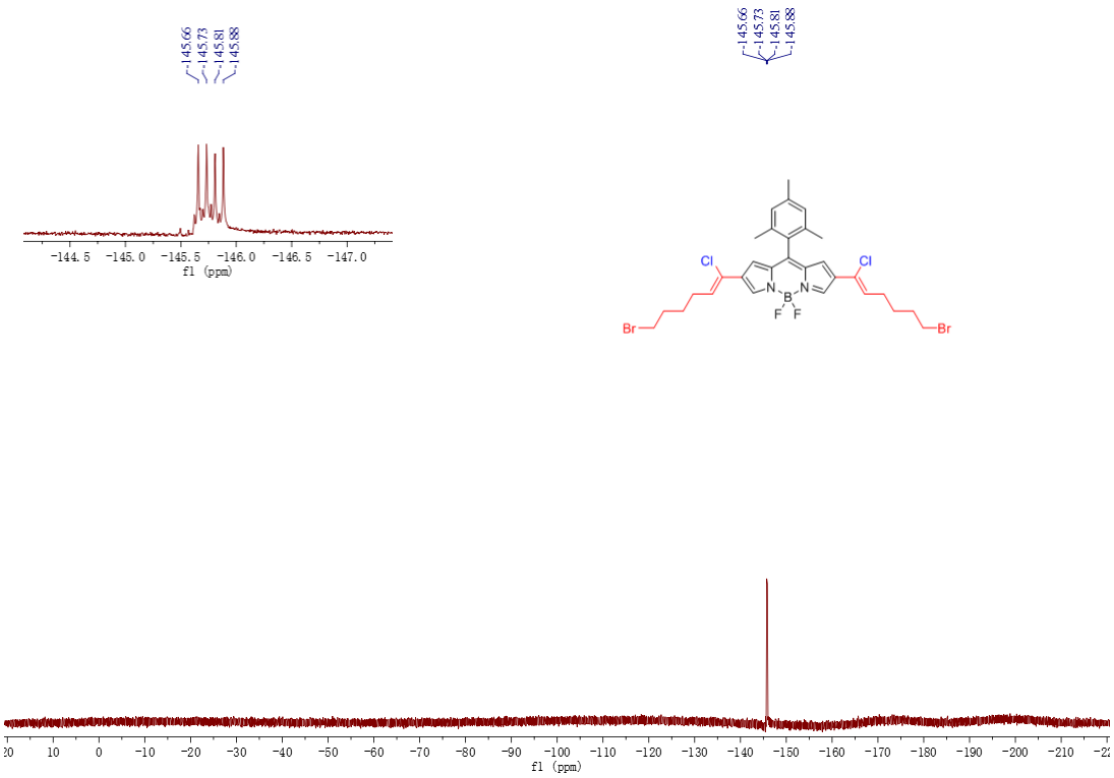
^{13}C NMR spectrum of **3d** in $CDCl_3$



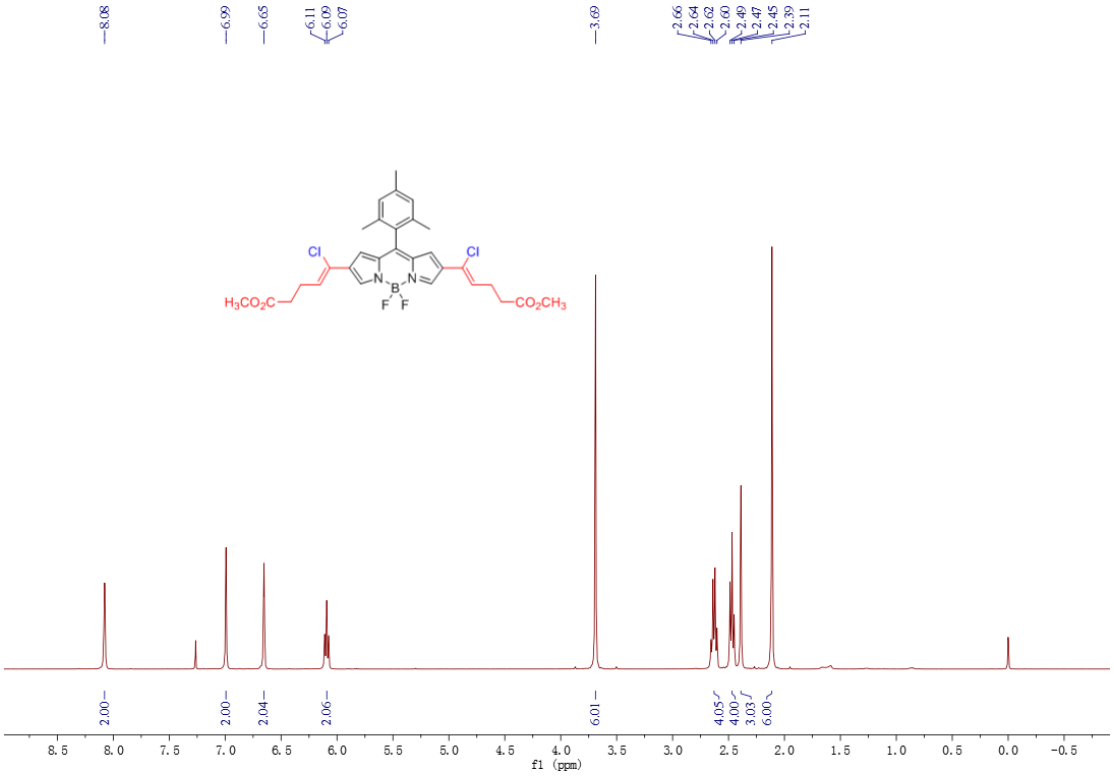
^{11}B NMR spectrum of **3d** in $CDCl_3$



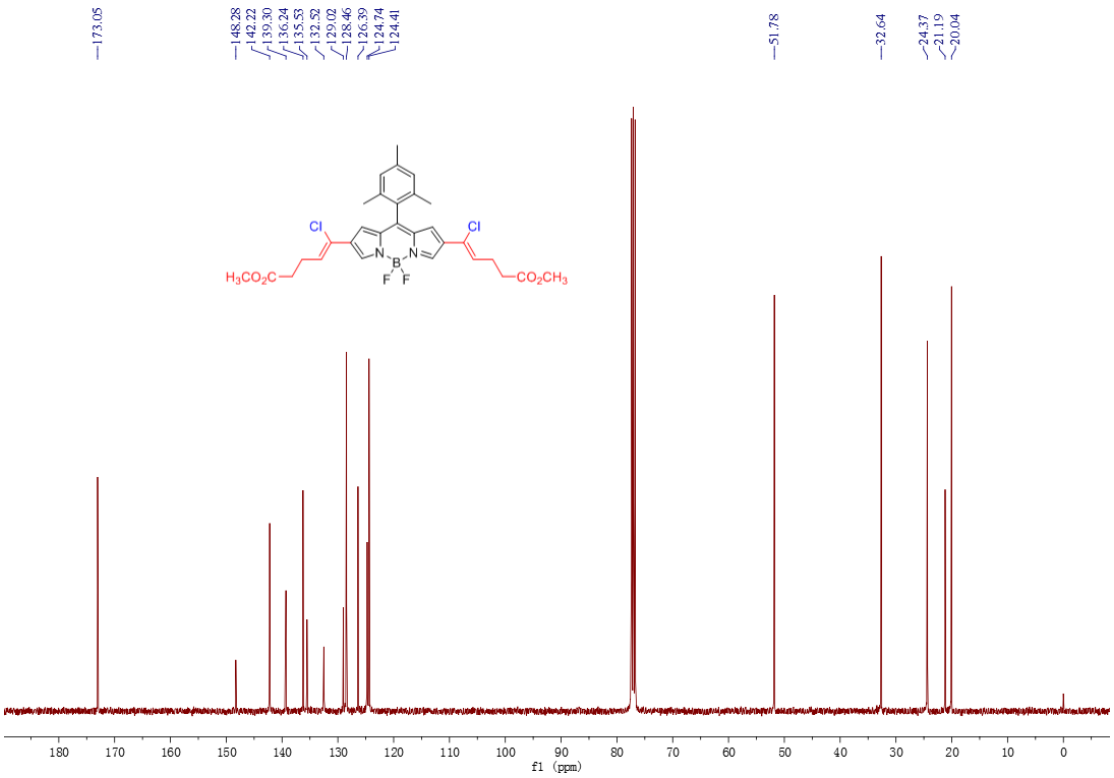
^{19}F NMR spectrum of **3d** in $CDCl_3$



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



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



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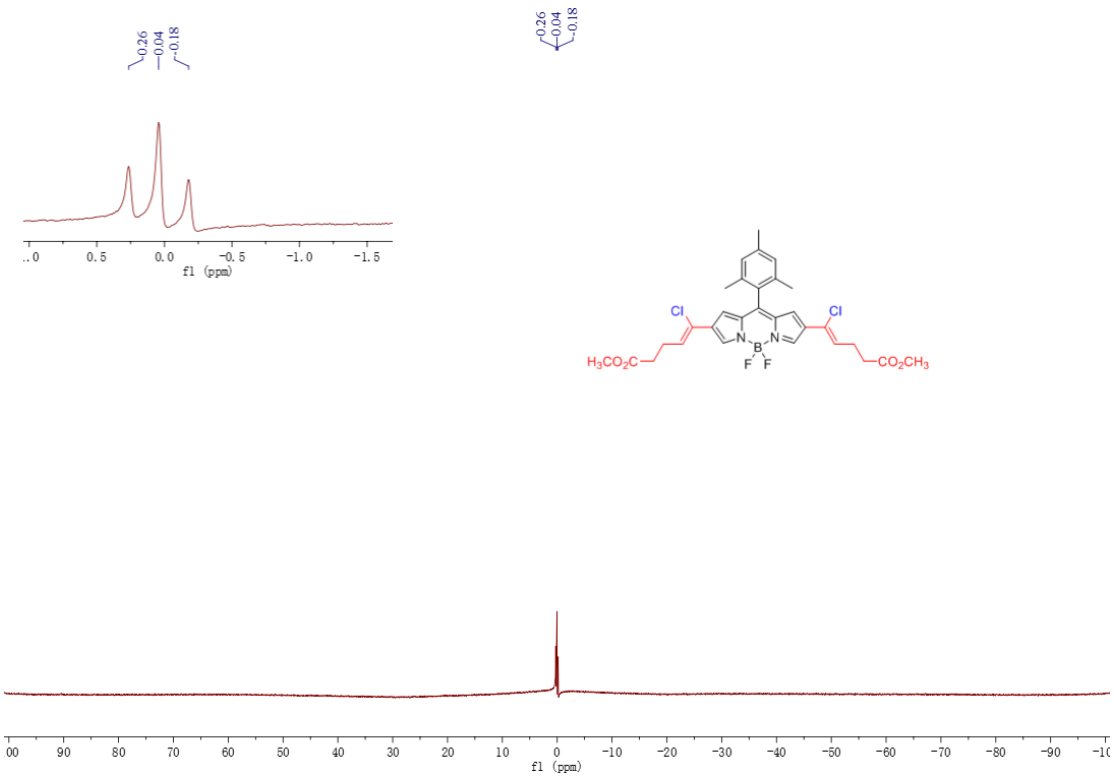
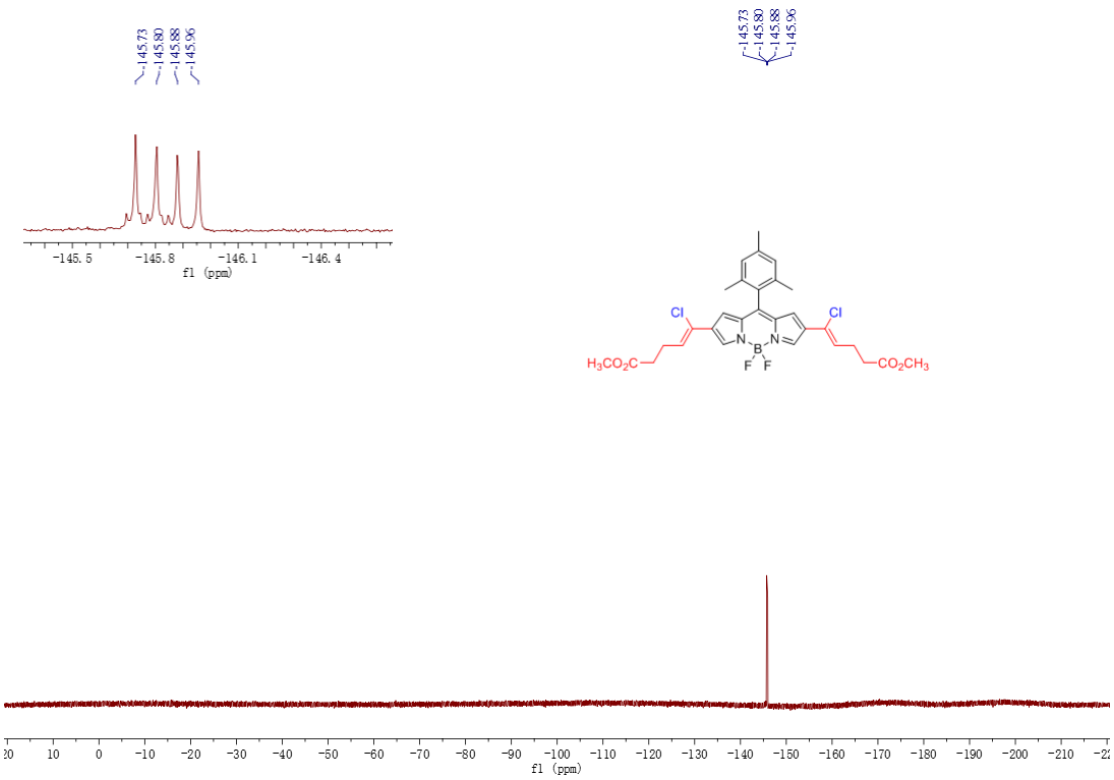
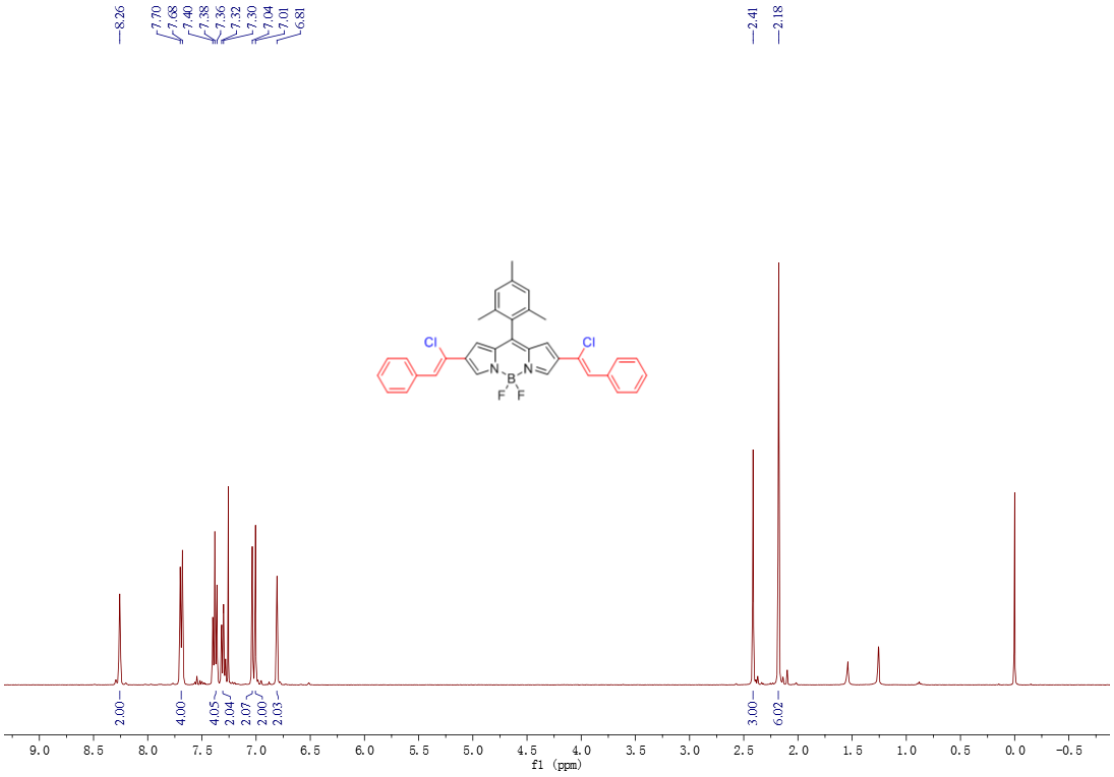


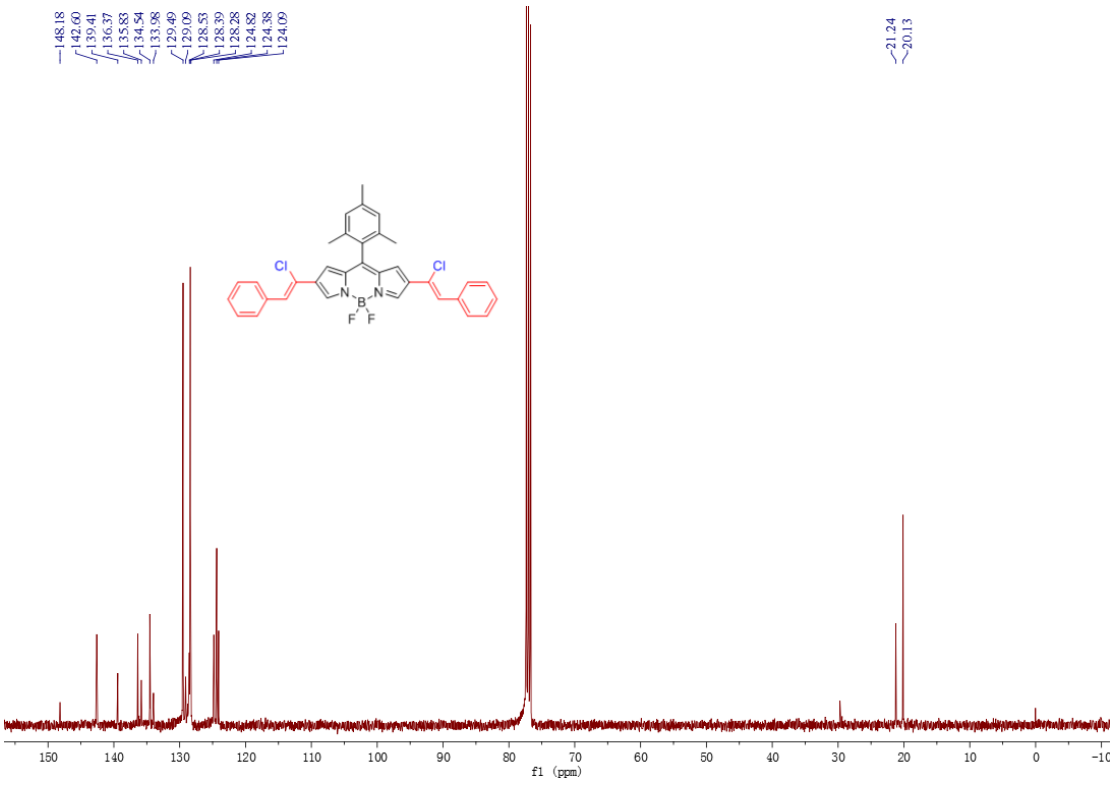
^{19}F NMR spectrum of **3e** in $CDCl_3$



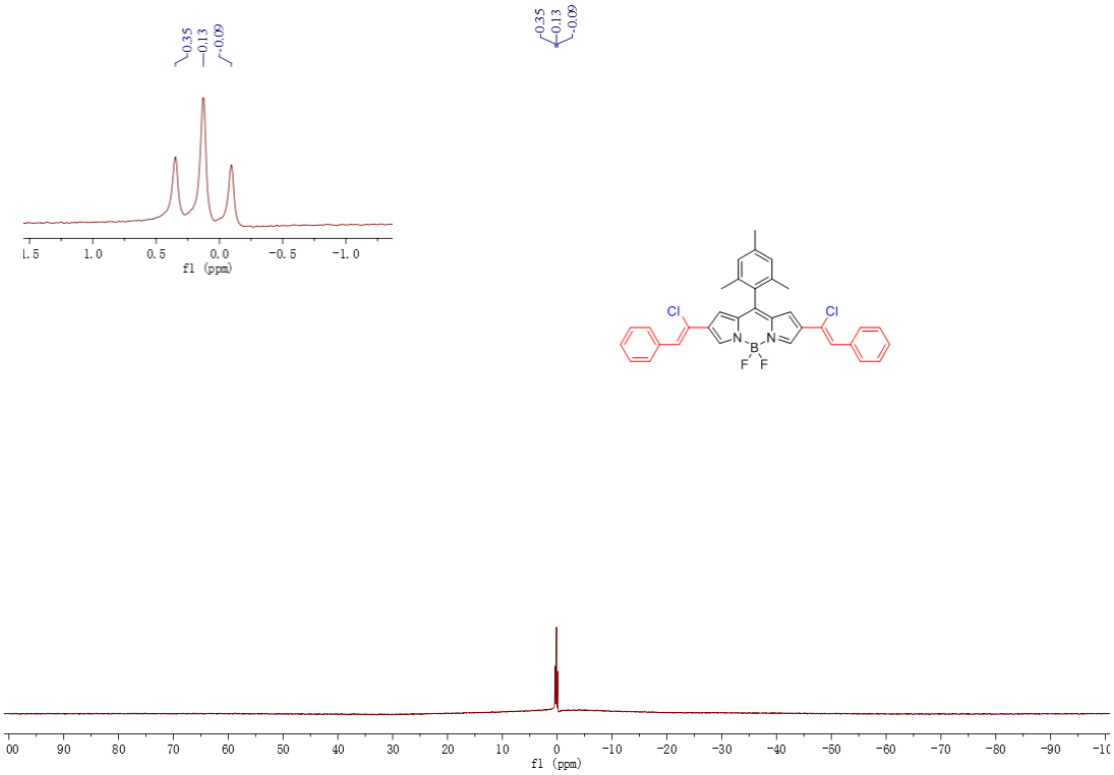
^{1}H NMR spectrum of **3f** in $CDCl_3$



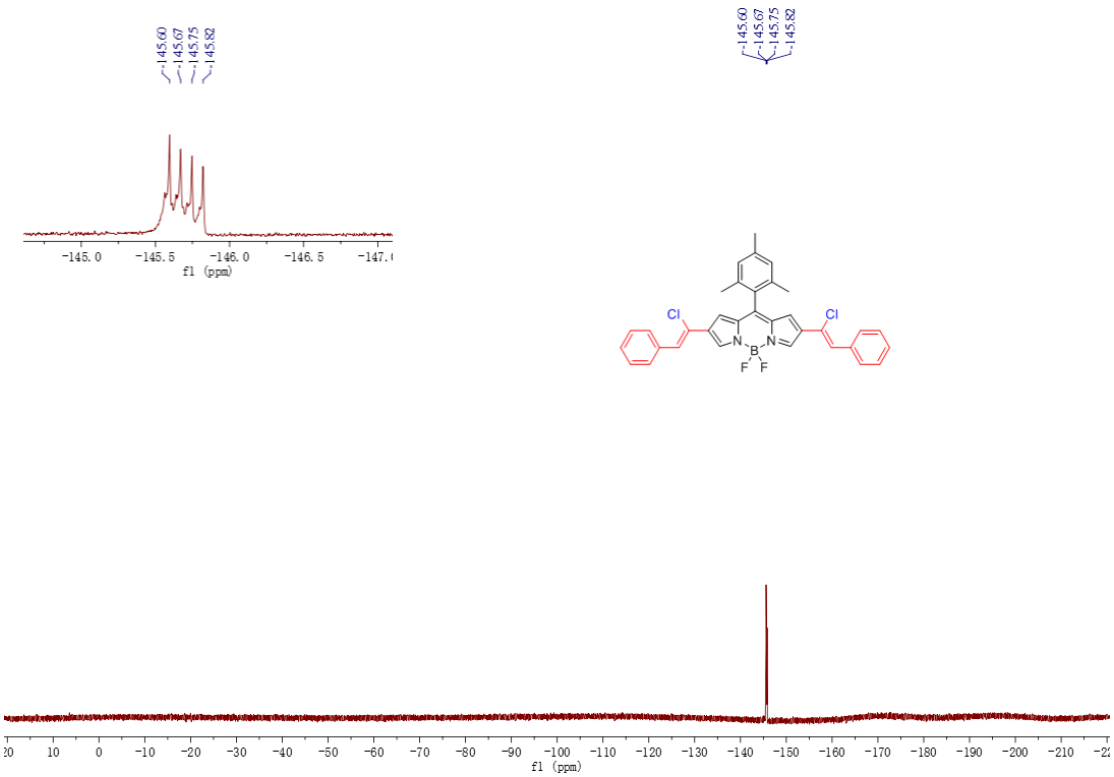
^{13}C NMR spectrum of **3f** in $CDCl_3$



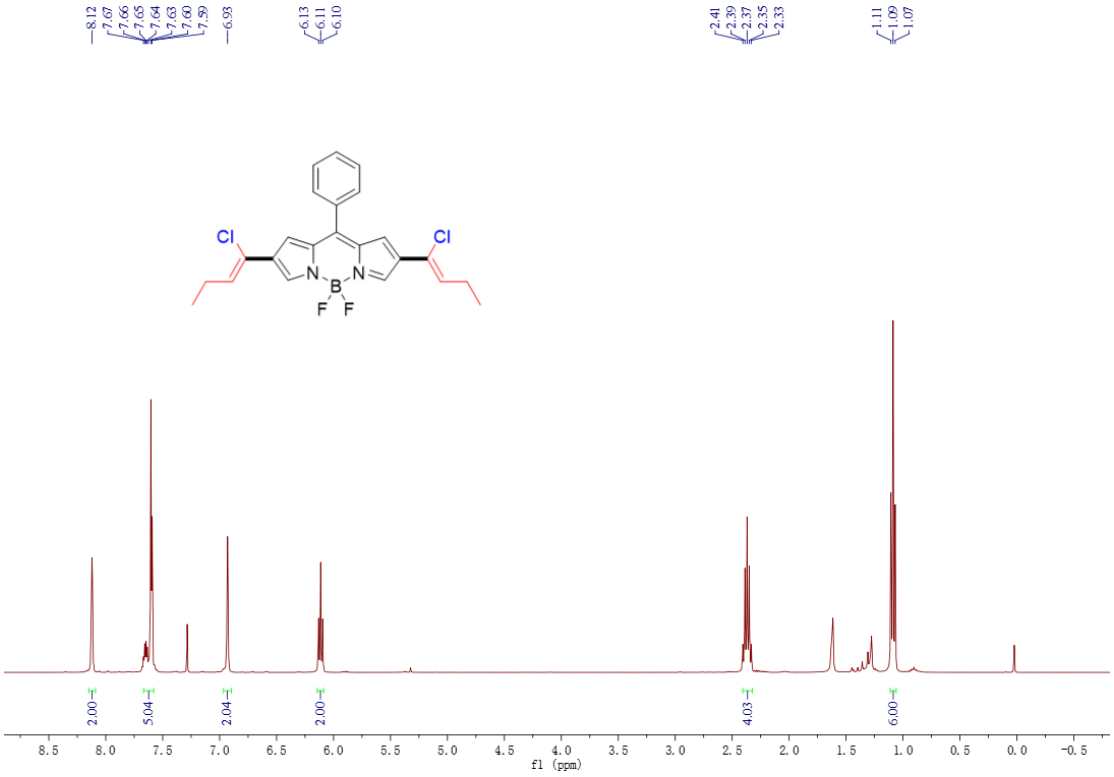
^{11}B NMR spectrum of **3f** in $CDCl_3$



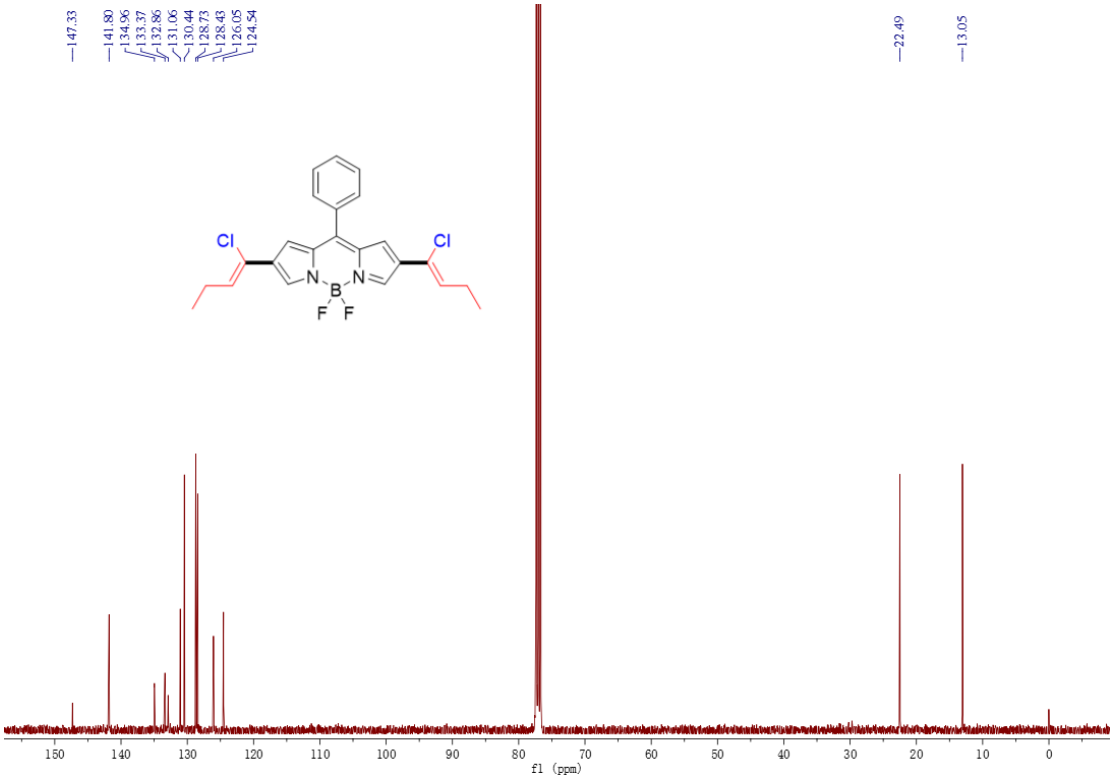
^{19}F NMR spectrum of **3f** in $CDCl_3$



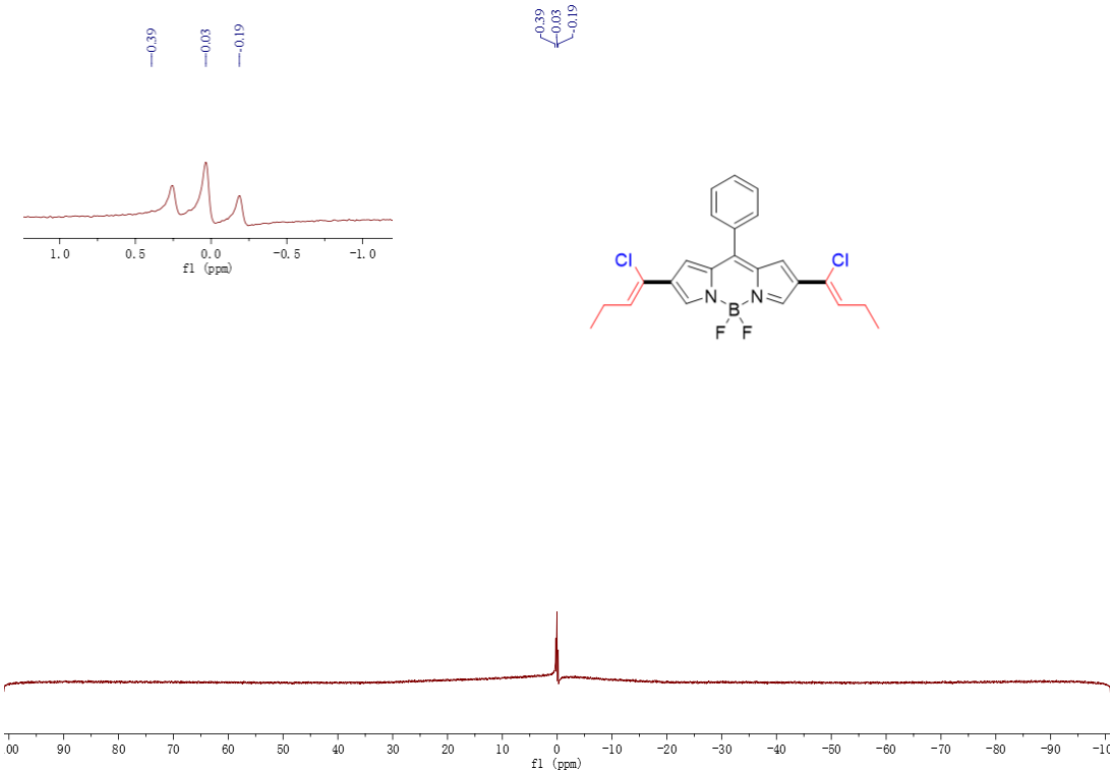
^{1}H NMR spectrum of **3g** in $CDCl_3$



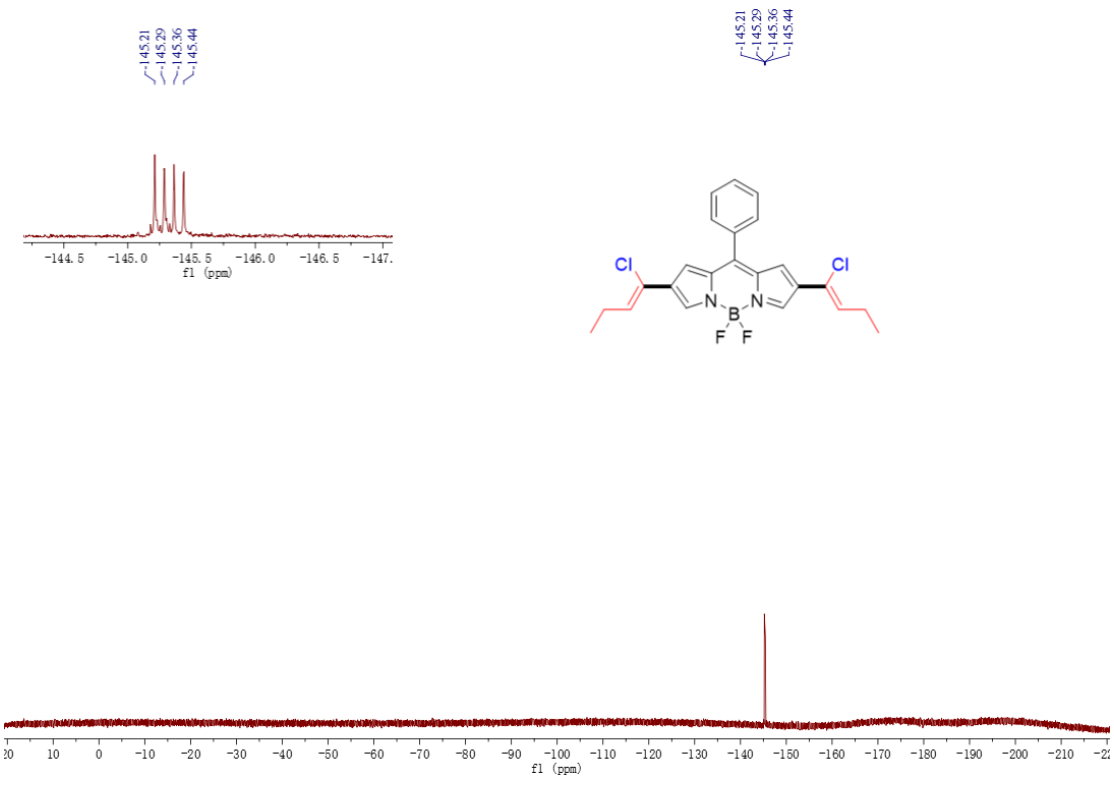
^{13}C NMR spectrum of **3g** in $CDCl_3$



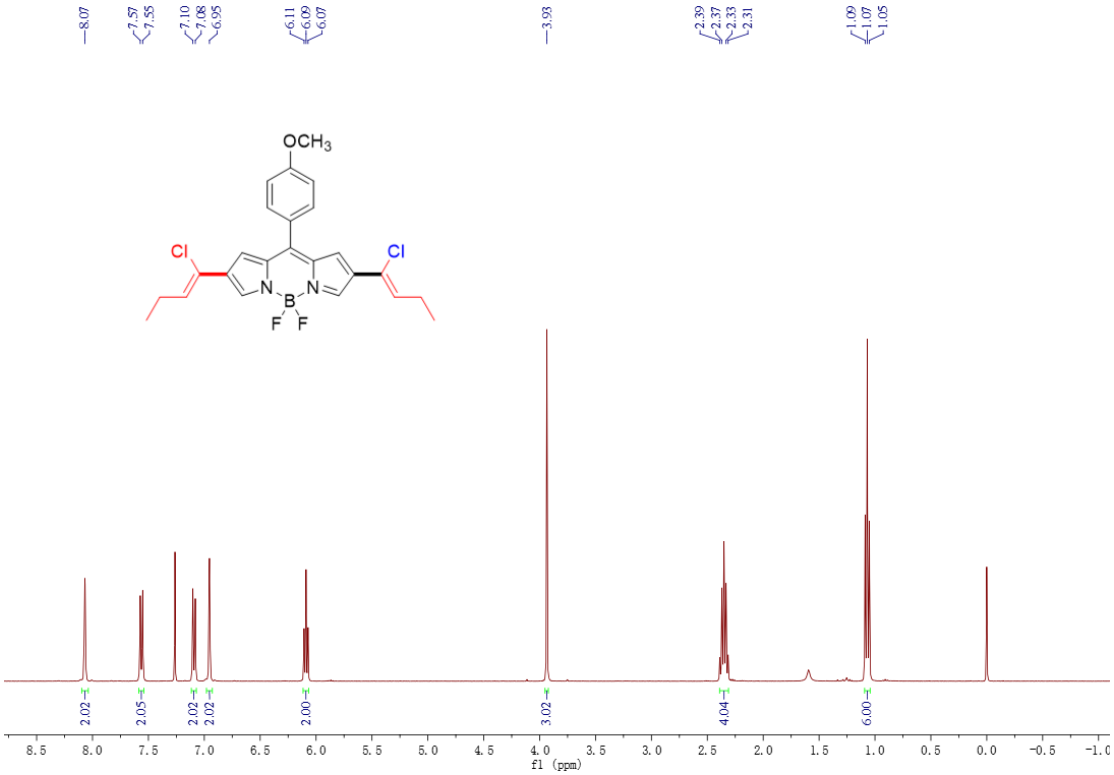
^{11}B NMR spectrum of **3g** in $CDCl_3$



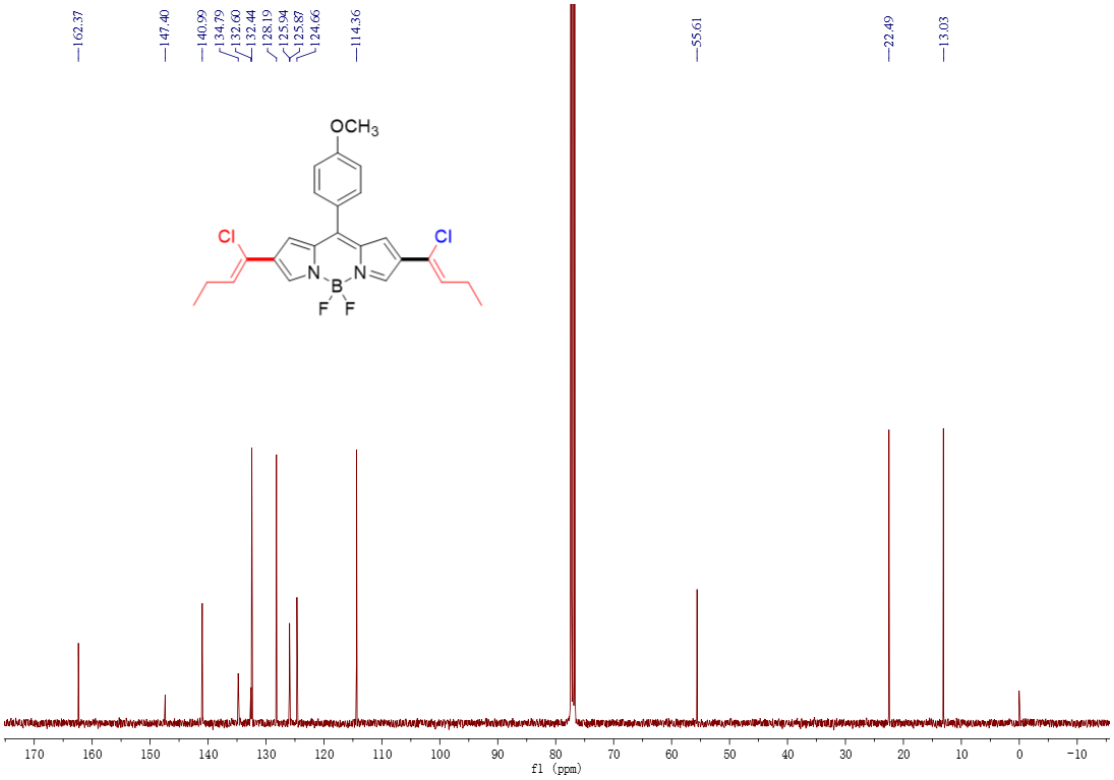
^{19}F NMR spectrum of **3g** in $CDCl_3$



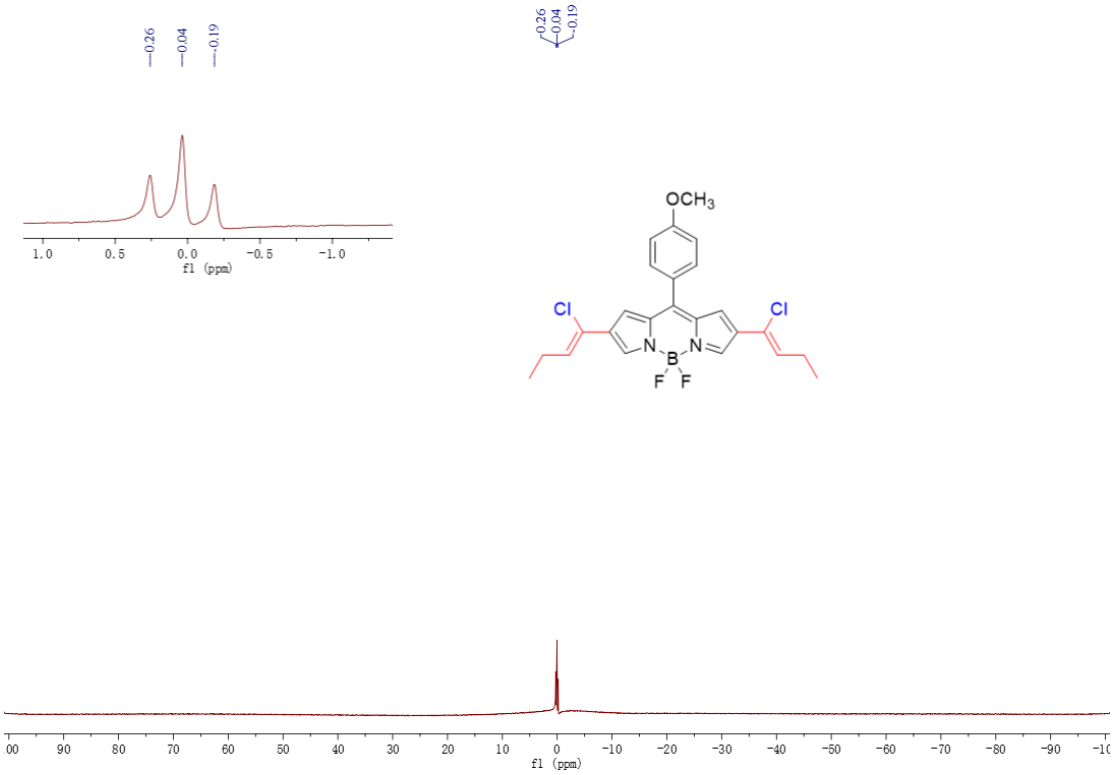
^{1}H NMR spectrum of **3h** in $CDCl_3$



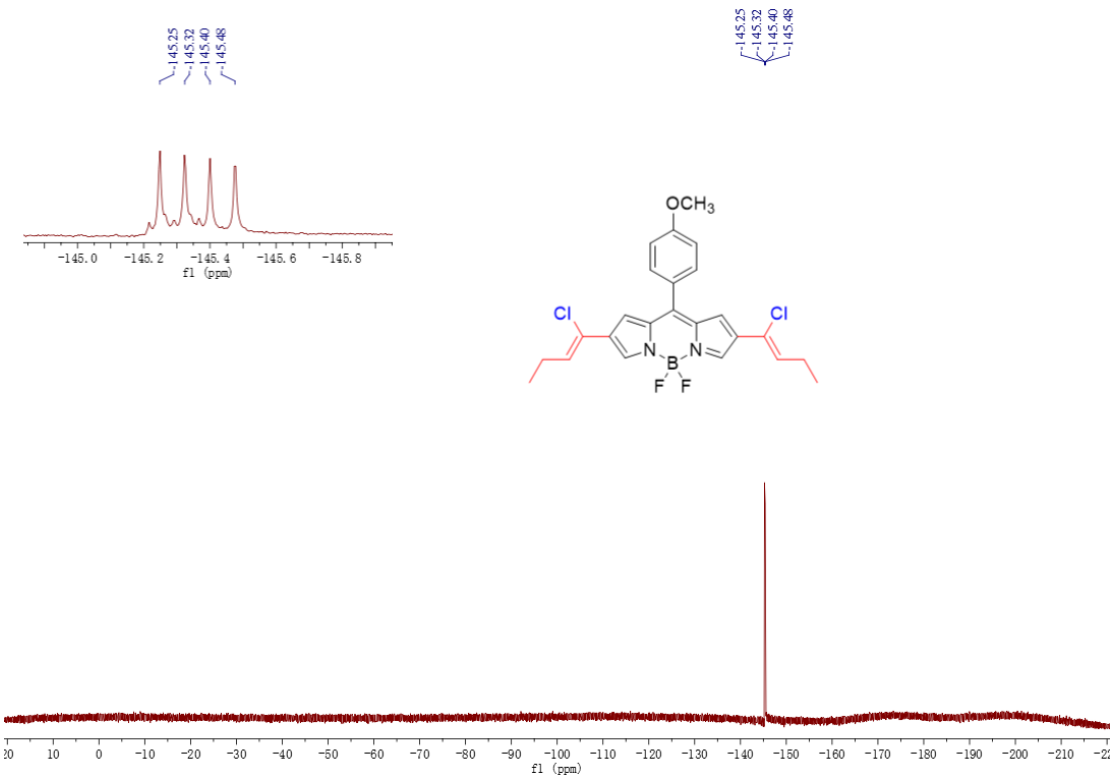
^{13}C NMR spectrum of **3h** in $CDCl_3$



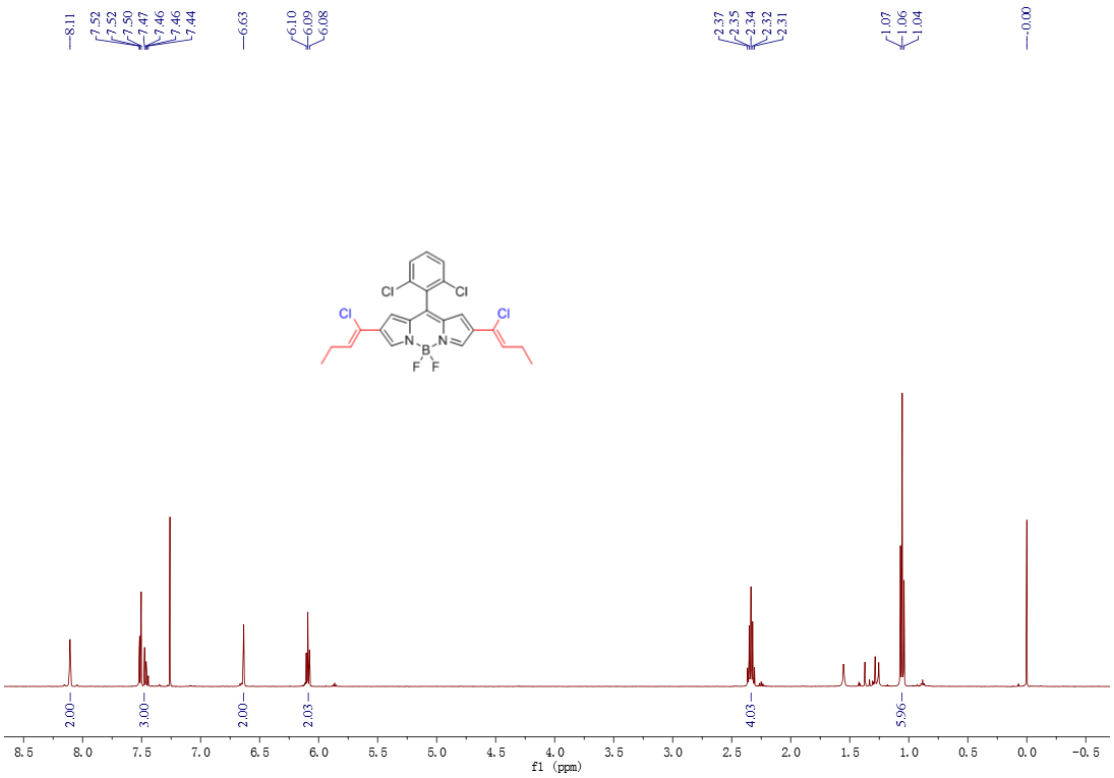
^{11}B NMR spectrum of **3h** in $CDCl_3$



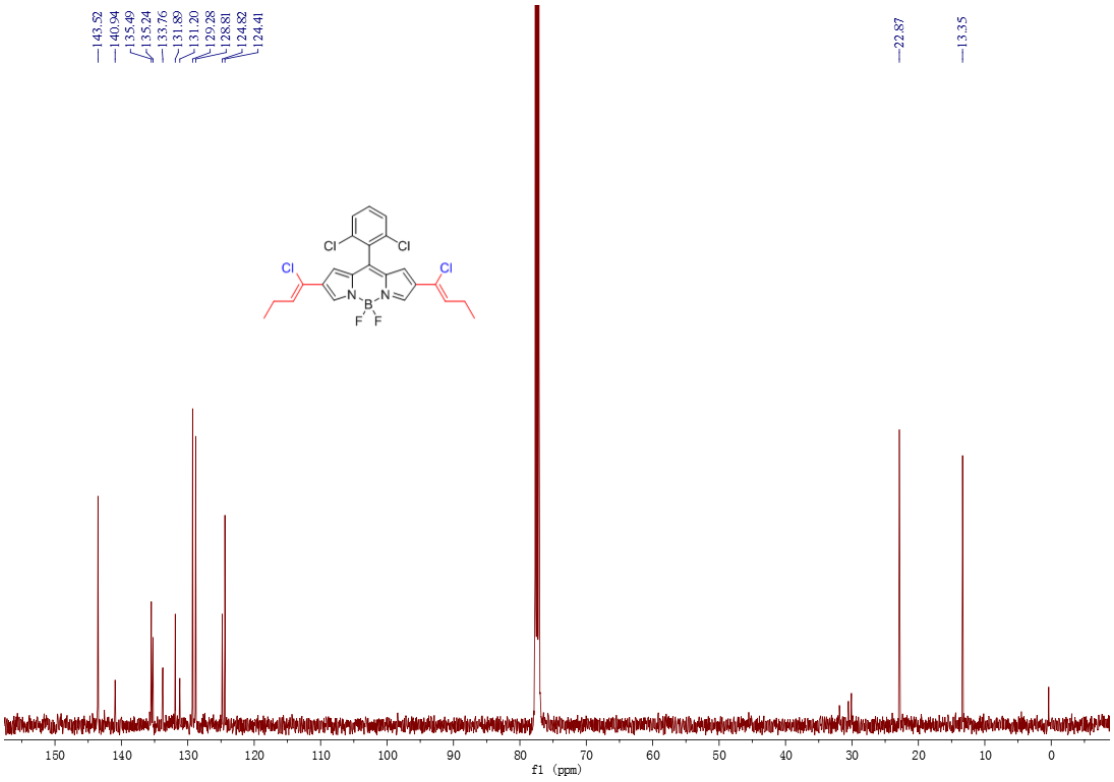
^{19}F NMR spectrum of **3h** in $CDCl_3$



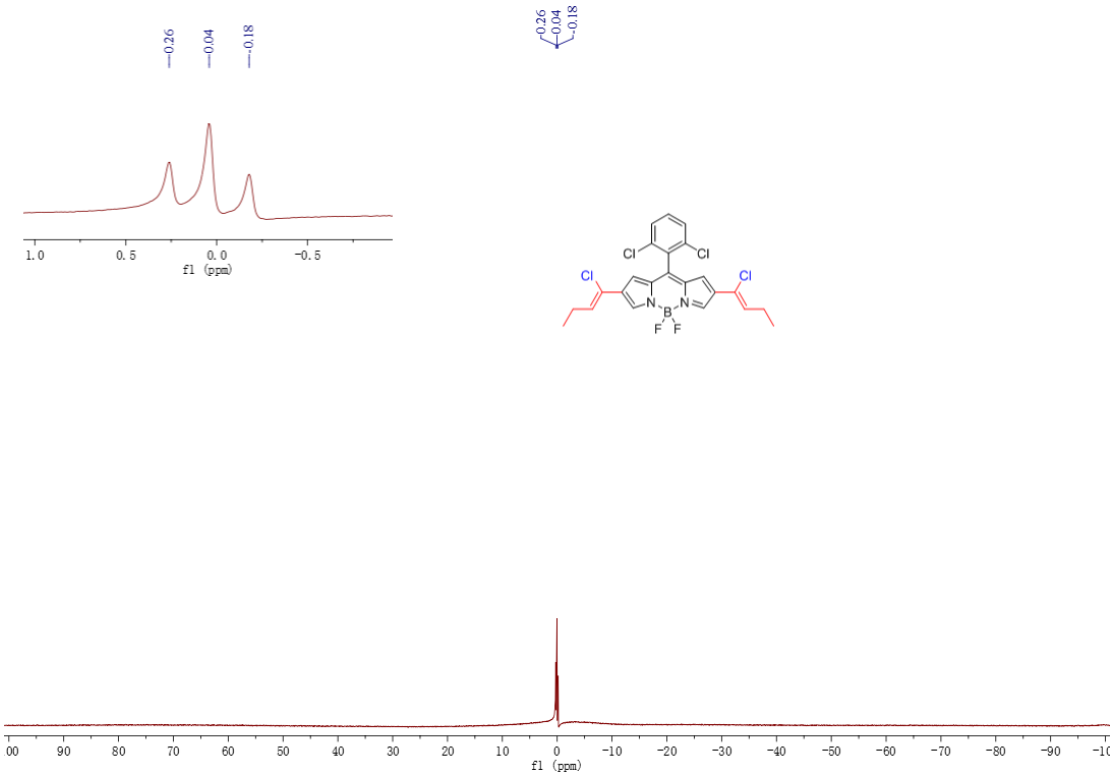
^{1}H NMR spectrum of **3i** in $CDCl_3$



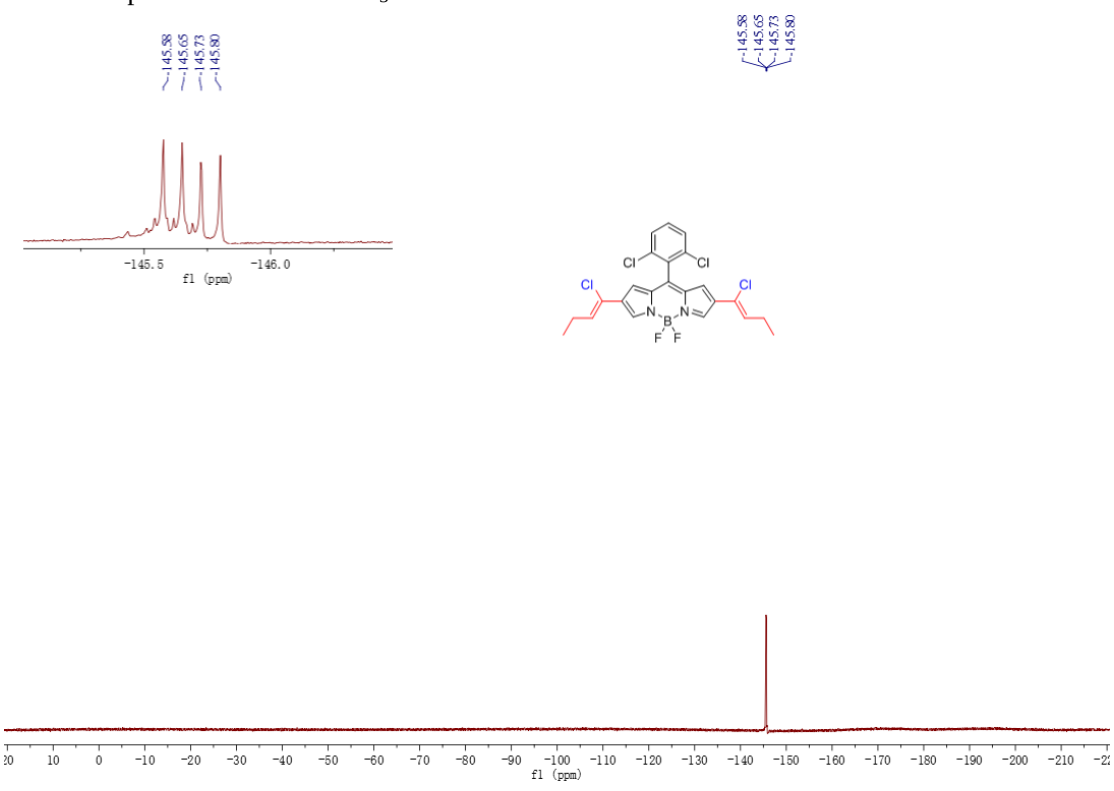
^{13}C NMR spectrum of **3i** in $CDCl_3$



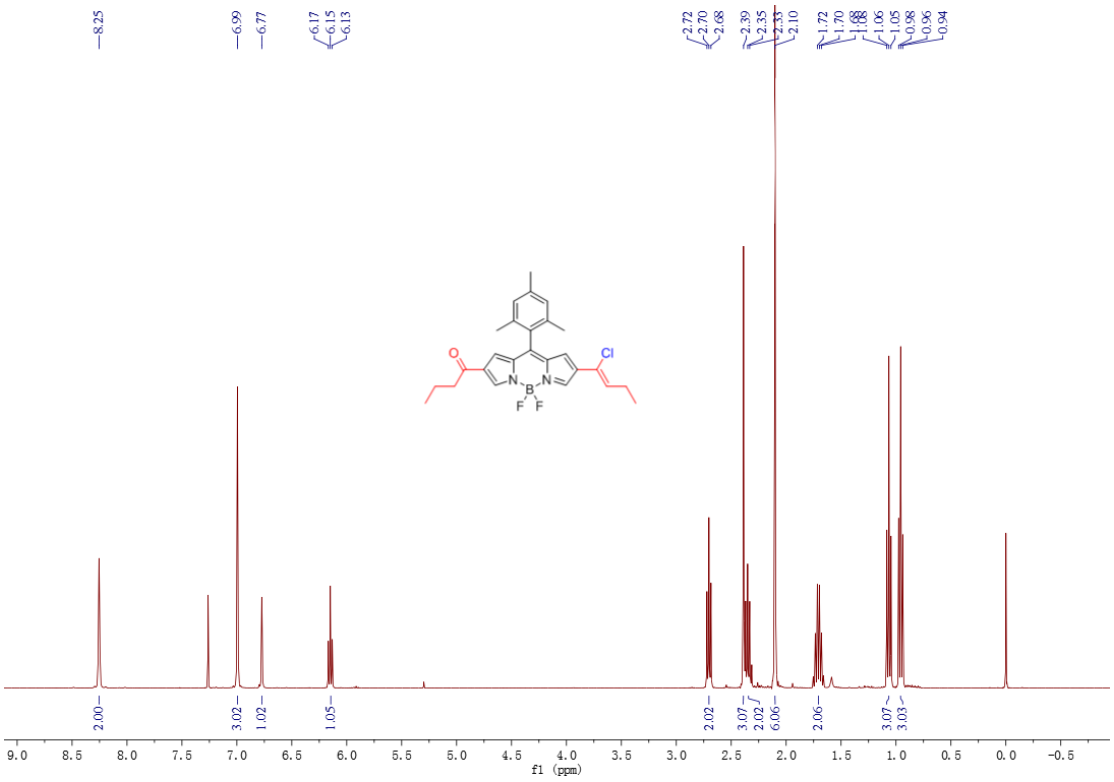
^{11}B NMR spectrum of **3i** in $CDCl_3$



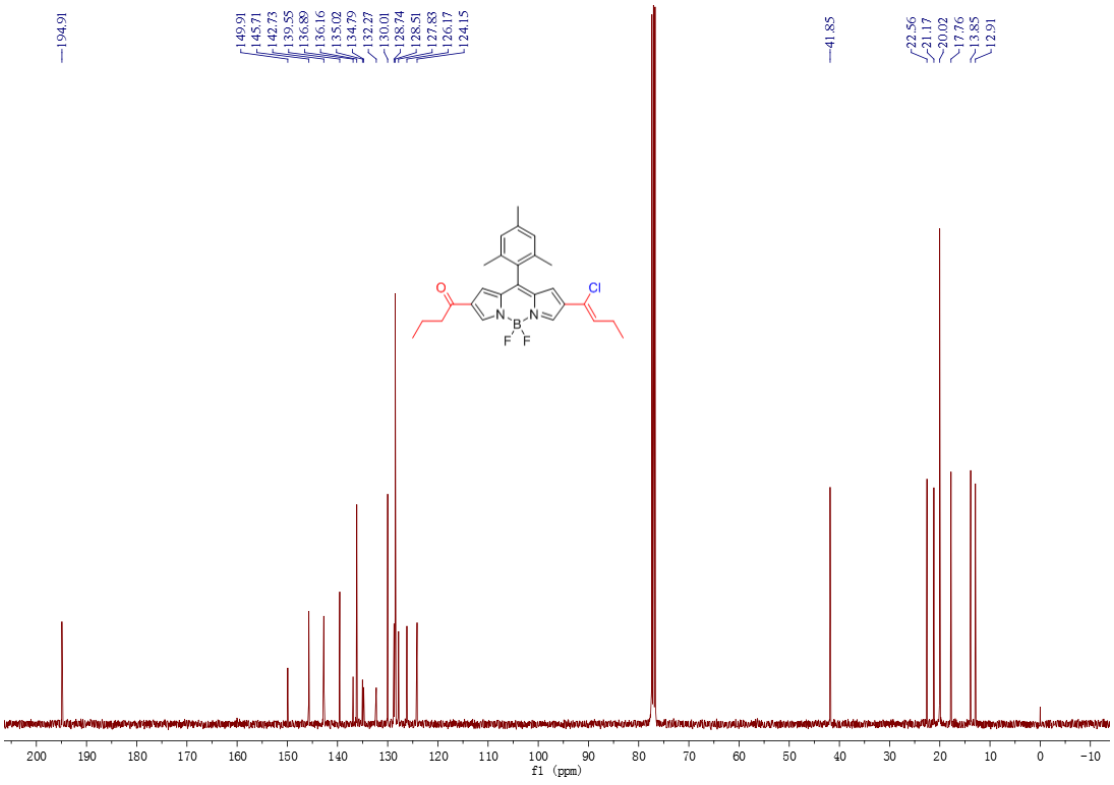
^{19}F NMR spectrum of **3i** in $CDCl_3$



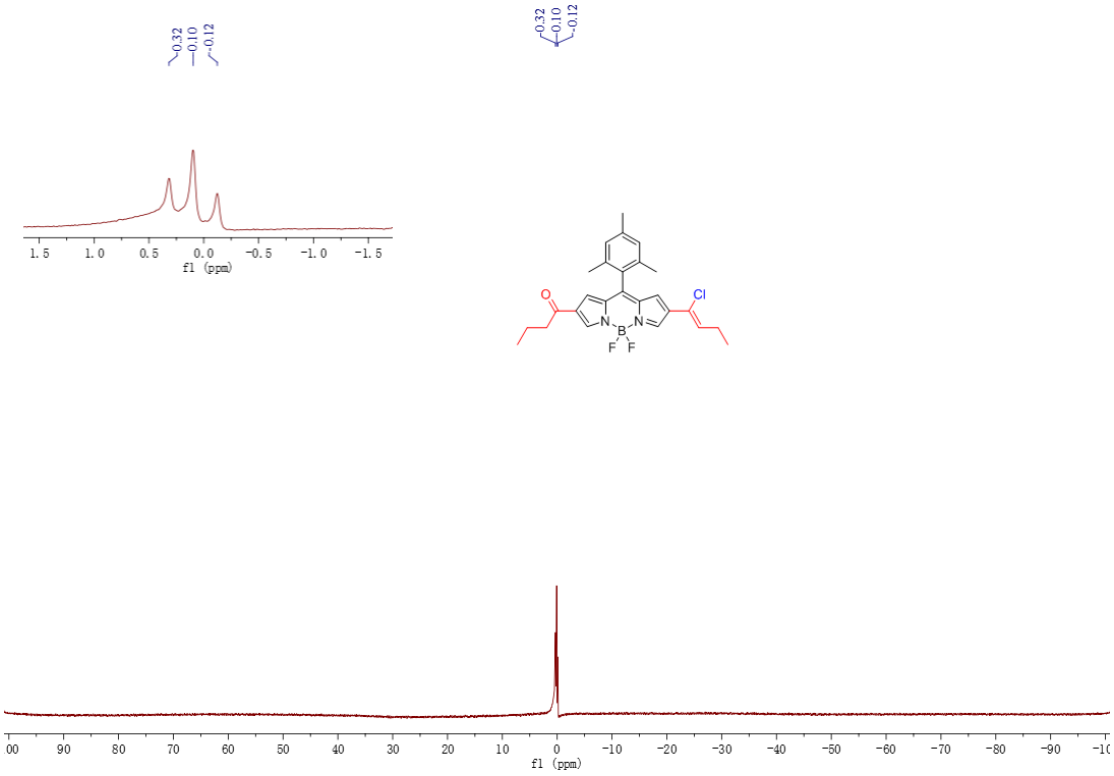
^{1}H NMR spectrum of **4a** in $CDCl_3$



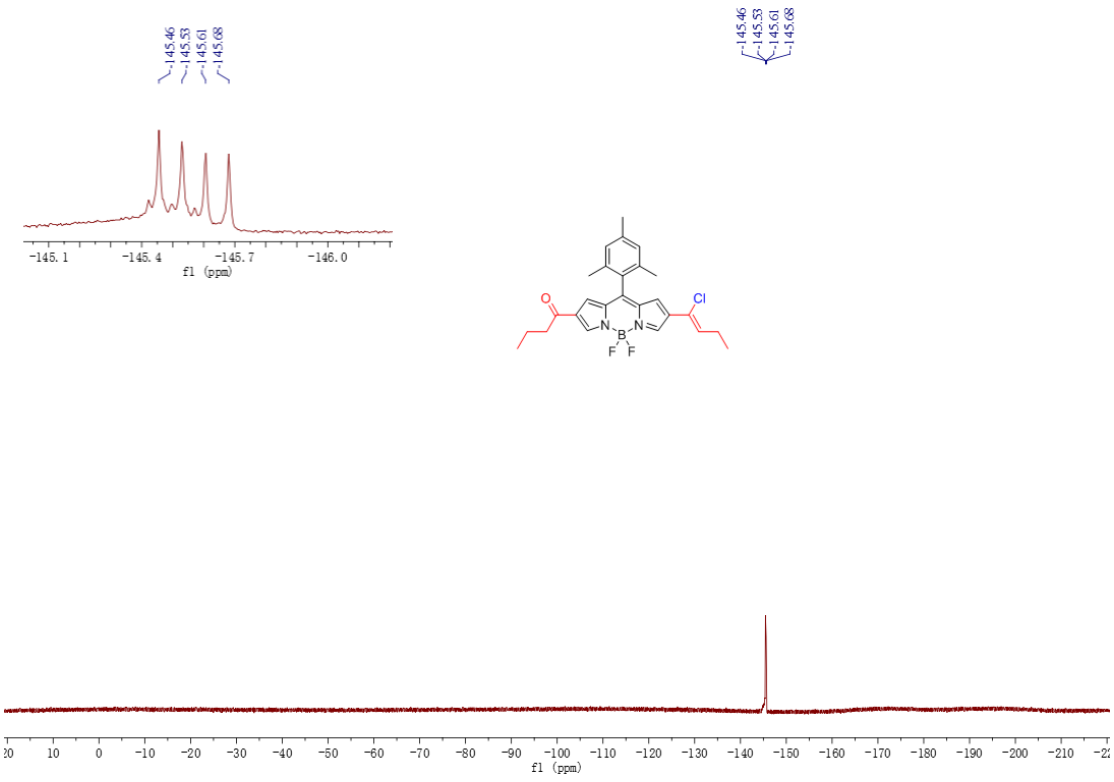
^{13}C NMR spectrum of **4a** in $CDCl_3$



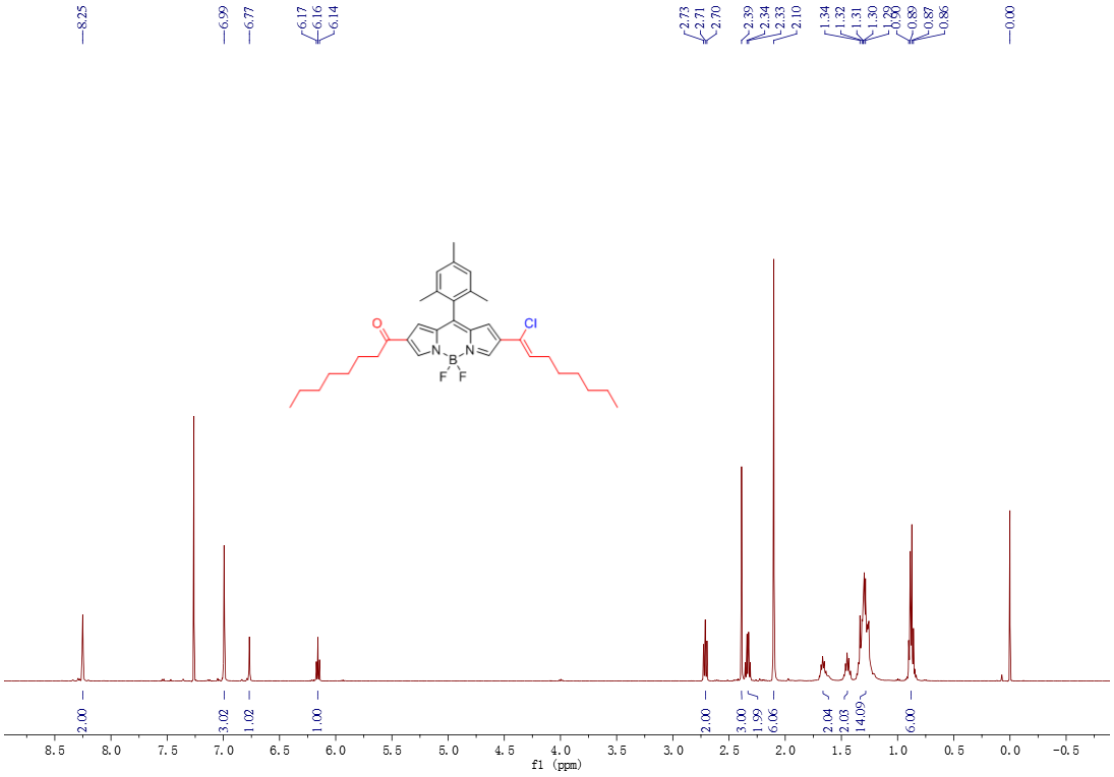
^{11}B NMR spectrum of **4a** in $CDCl_3$



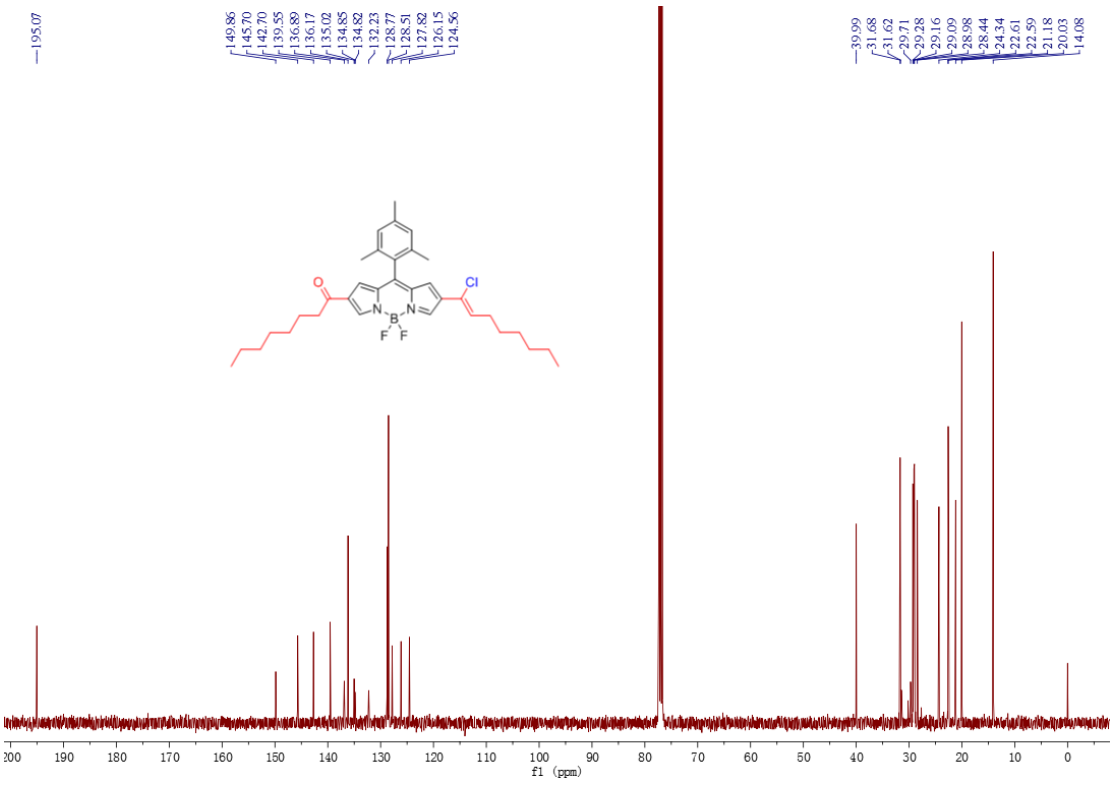
^{19}F NMR spectrum of **4a** in $CDCl_3$



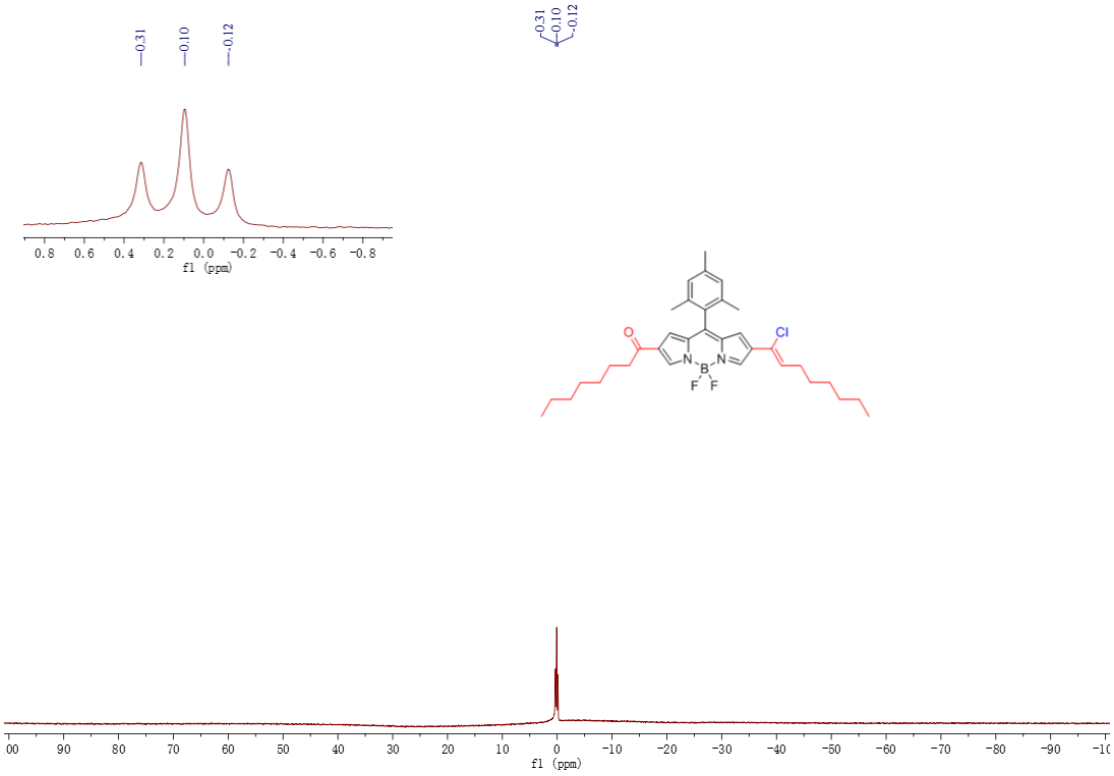
^{1}H NMR spectrum of **4b** in $CDCl_3$



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



^{11}B NMR spectrum of **4b** in $CDCl_3$



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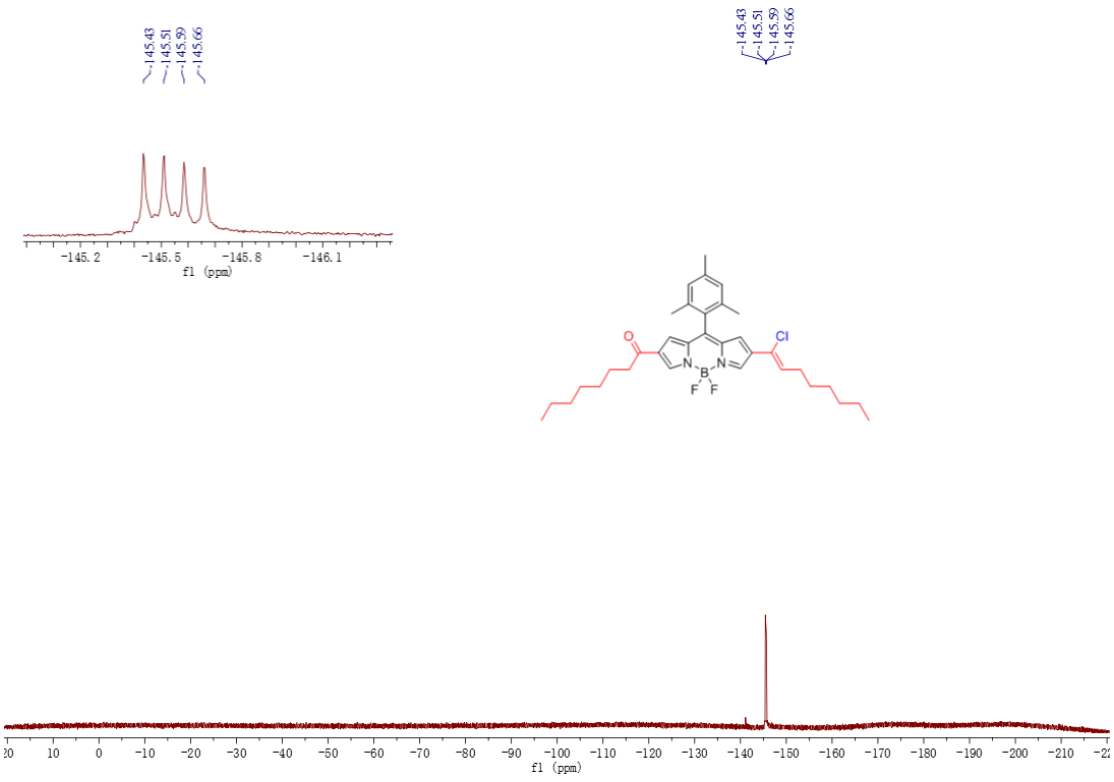

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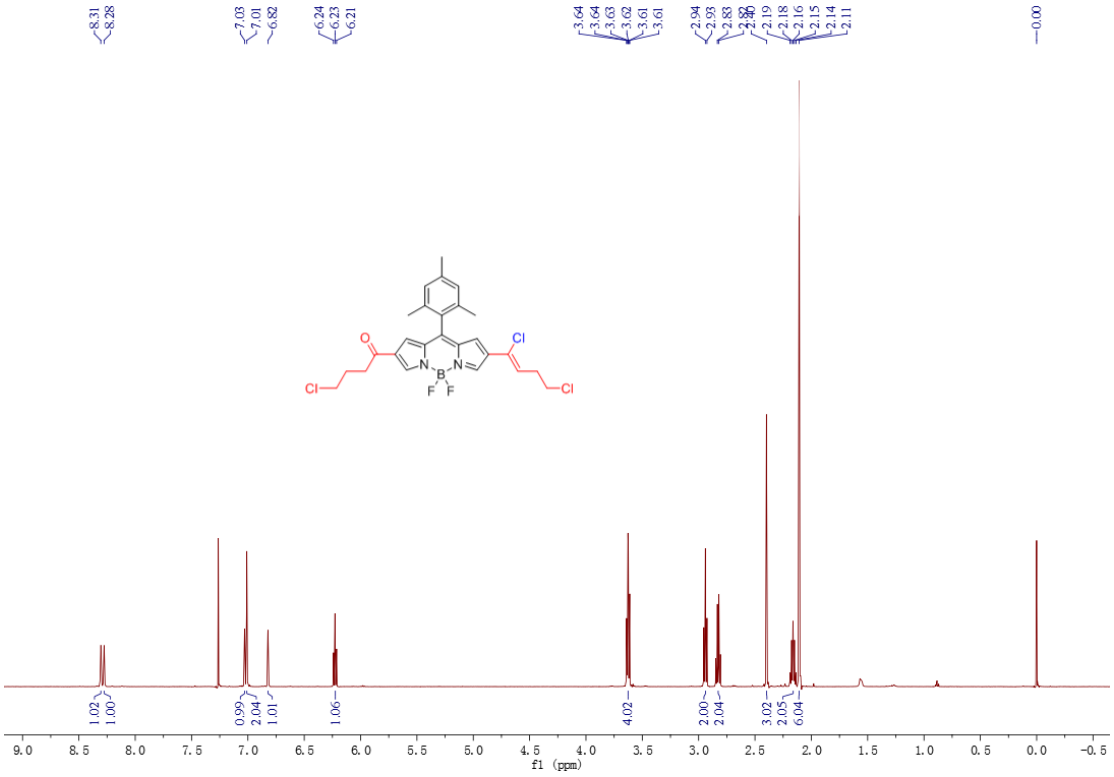
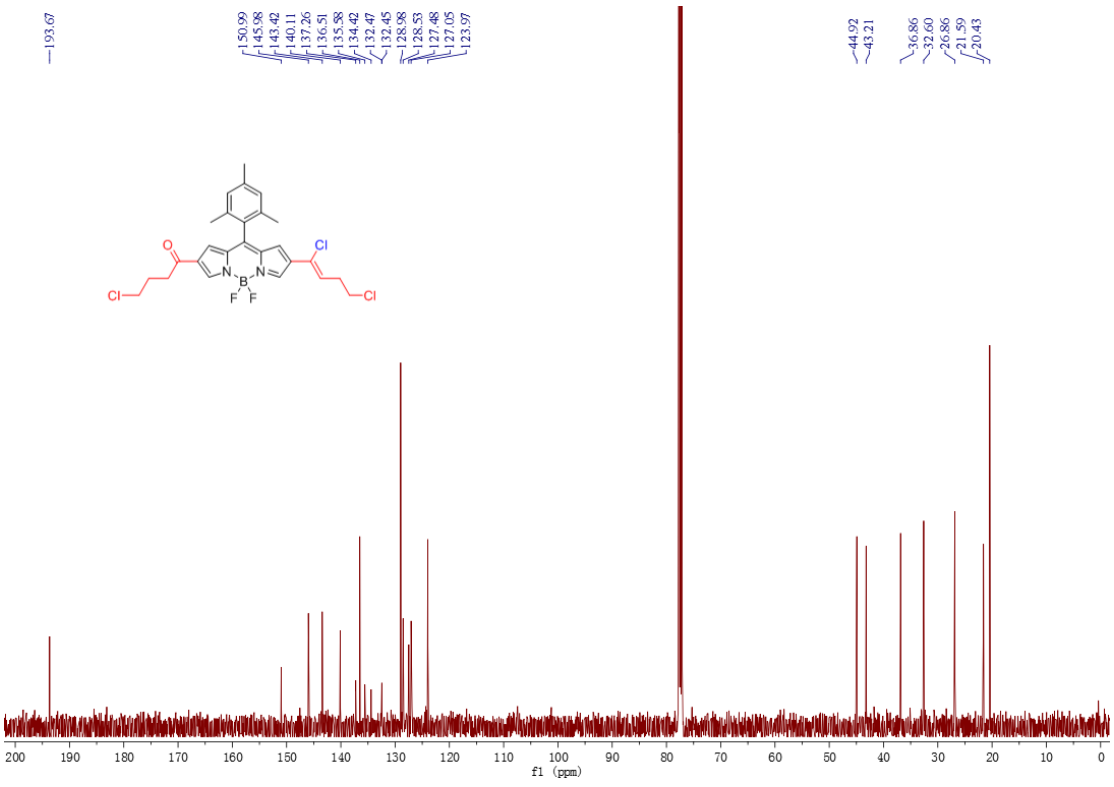
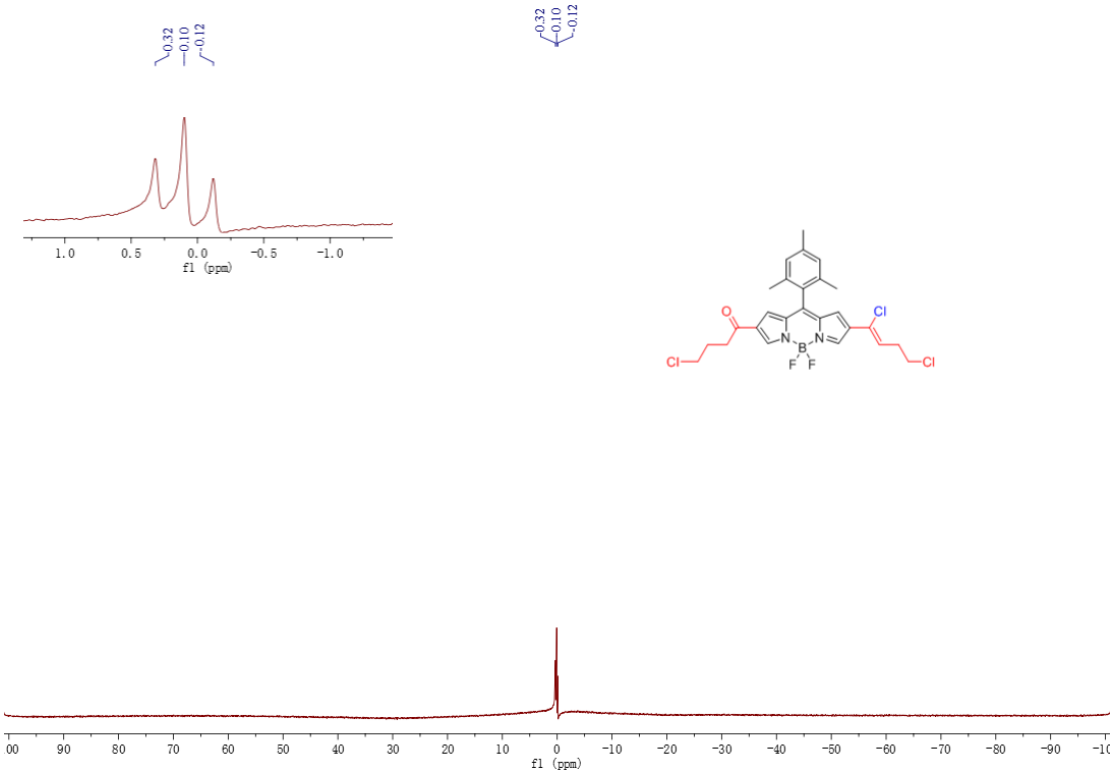


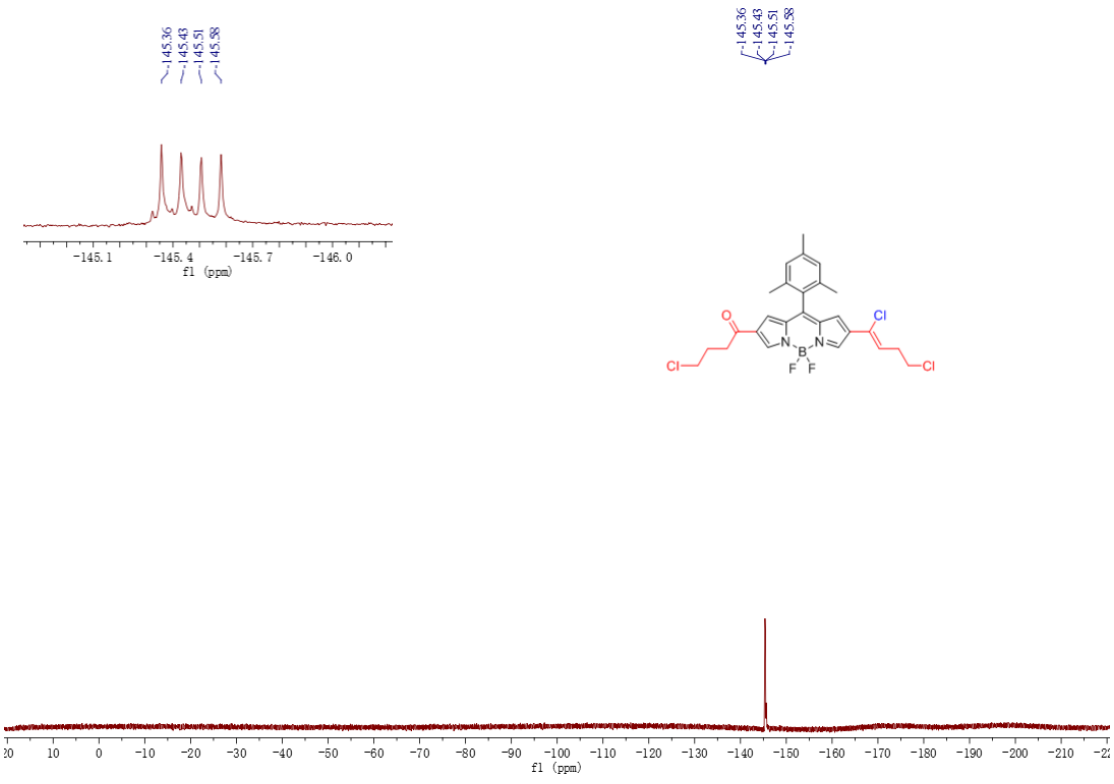
^{13}C NMR spectrum of **4c** in $CDCl_3$



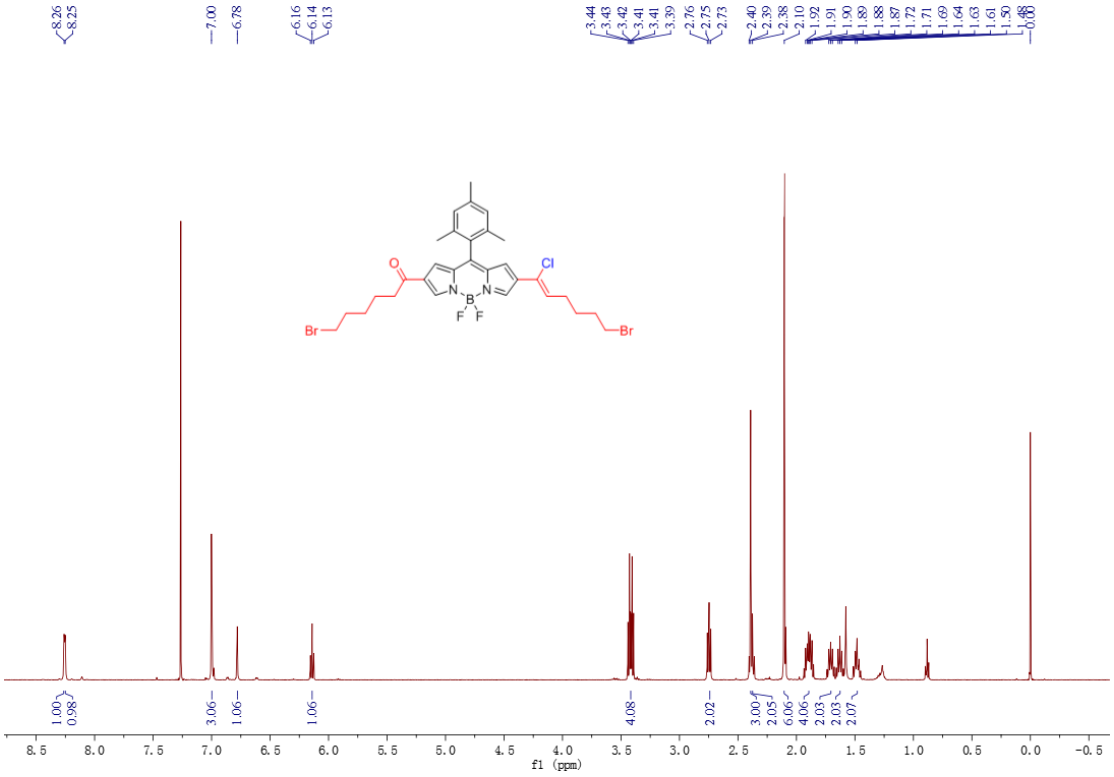
^{11}B NMR spectrum of **4c** in $CDCl_3$



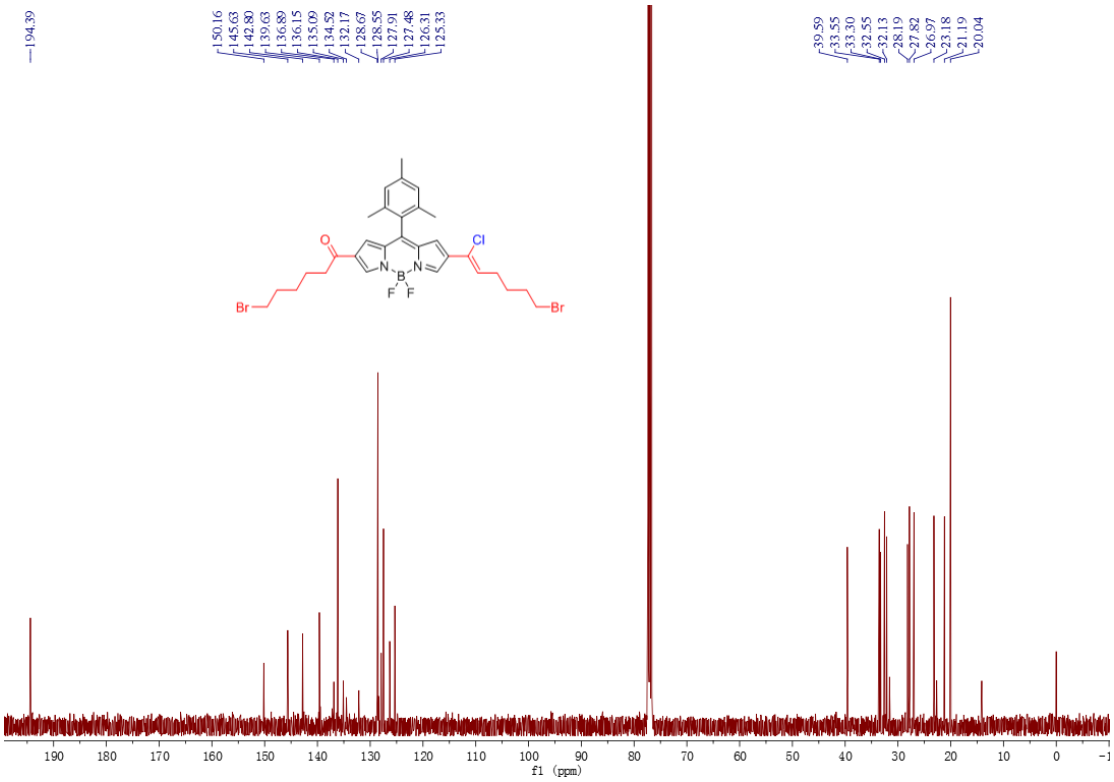
^{19}F NMR spectrum of **4c** in $CDCl_3$



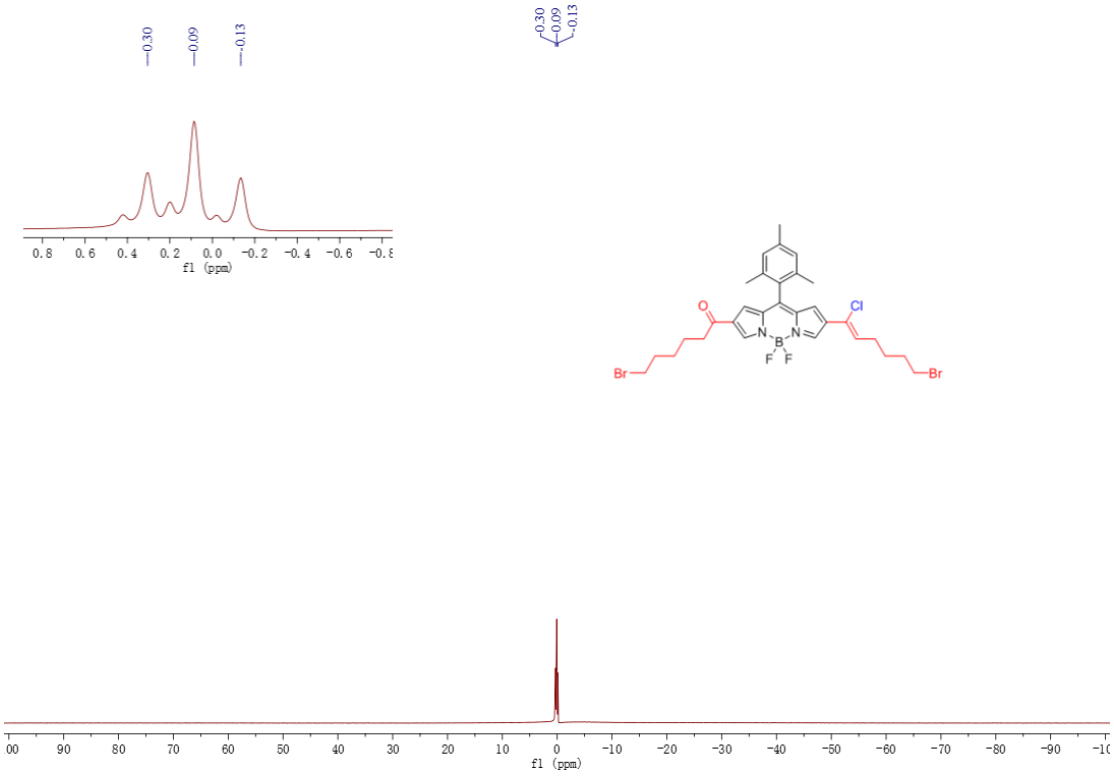
^{1}H NMR spectrum of **4d** in $CDCl_3$



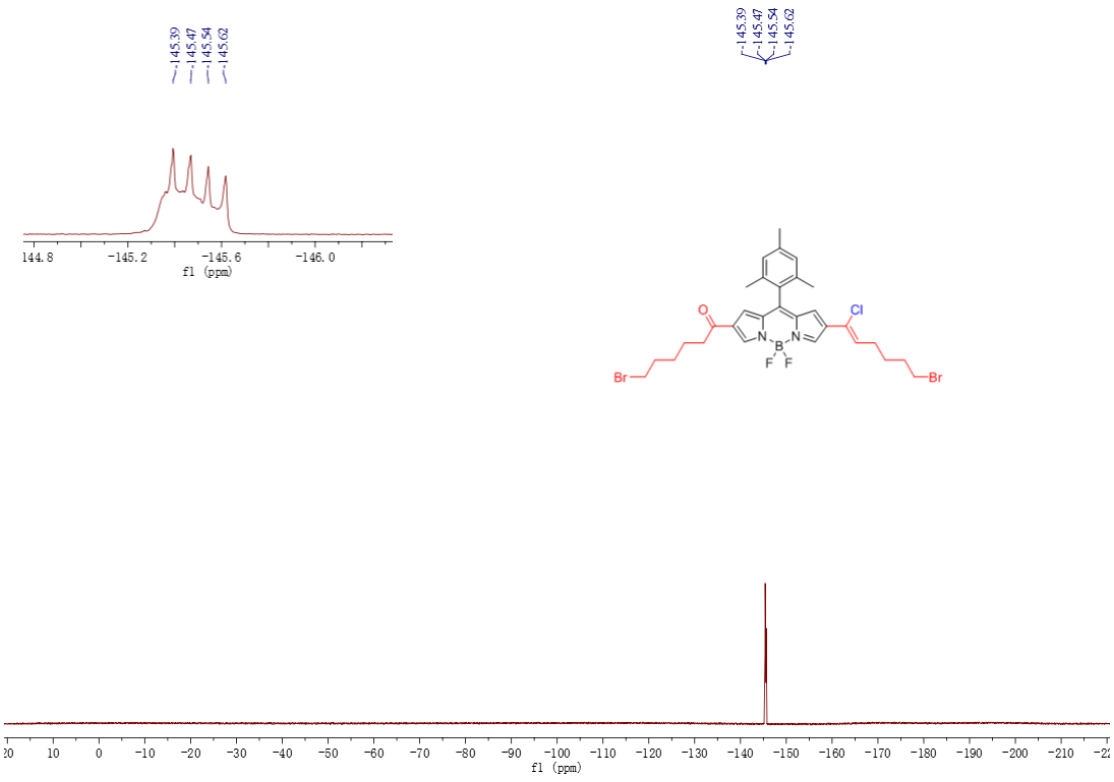
^{13}C NMR spectrum of **4d** in $CDCl_3$



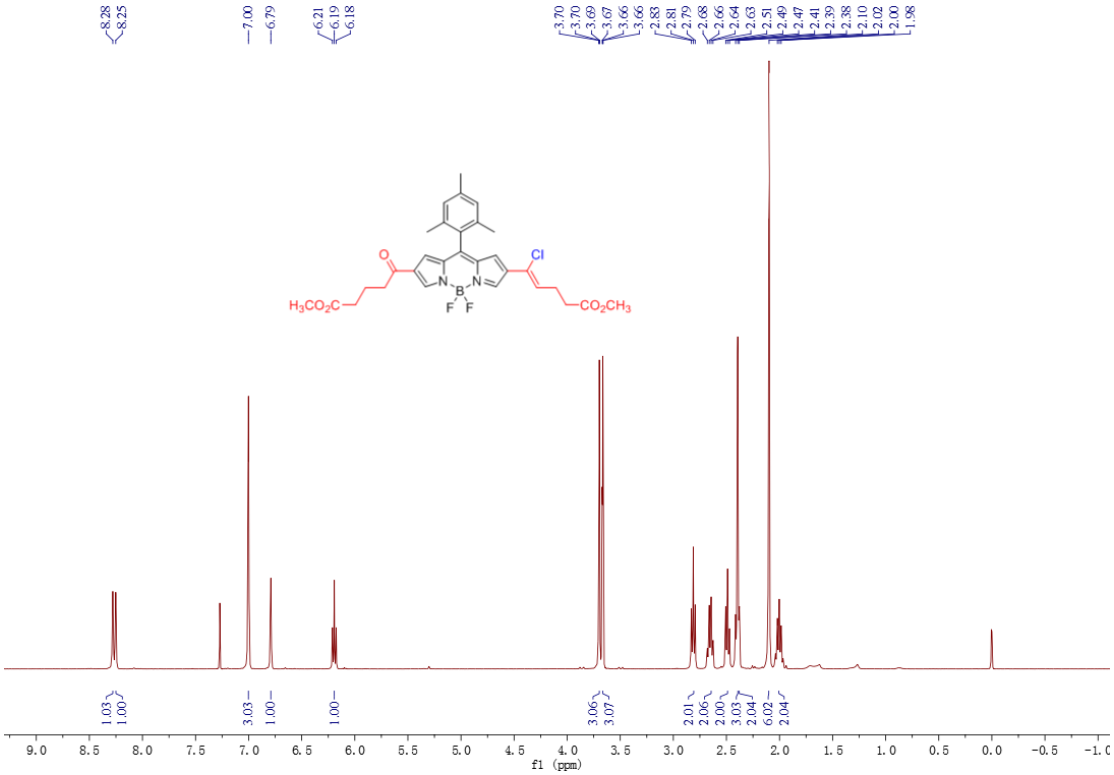
^{11}B NMR spectrum of **4d** in $CDCl_3$



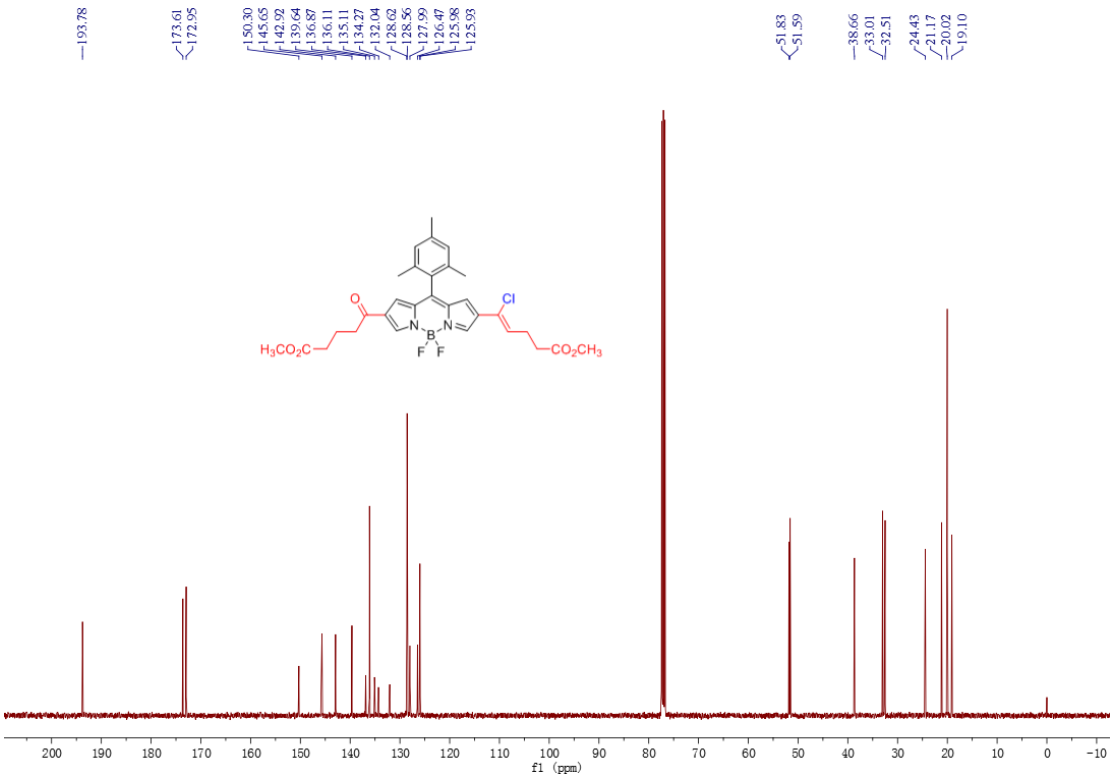
^{19}F NMR spectrum of **4d** in $CDCl_3$



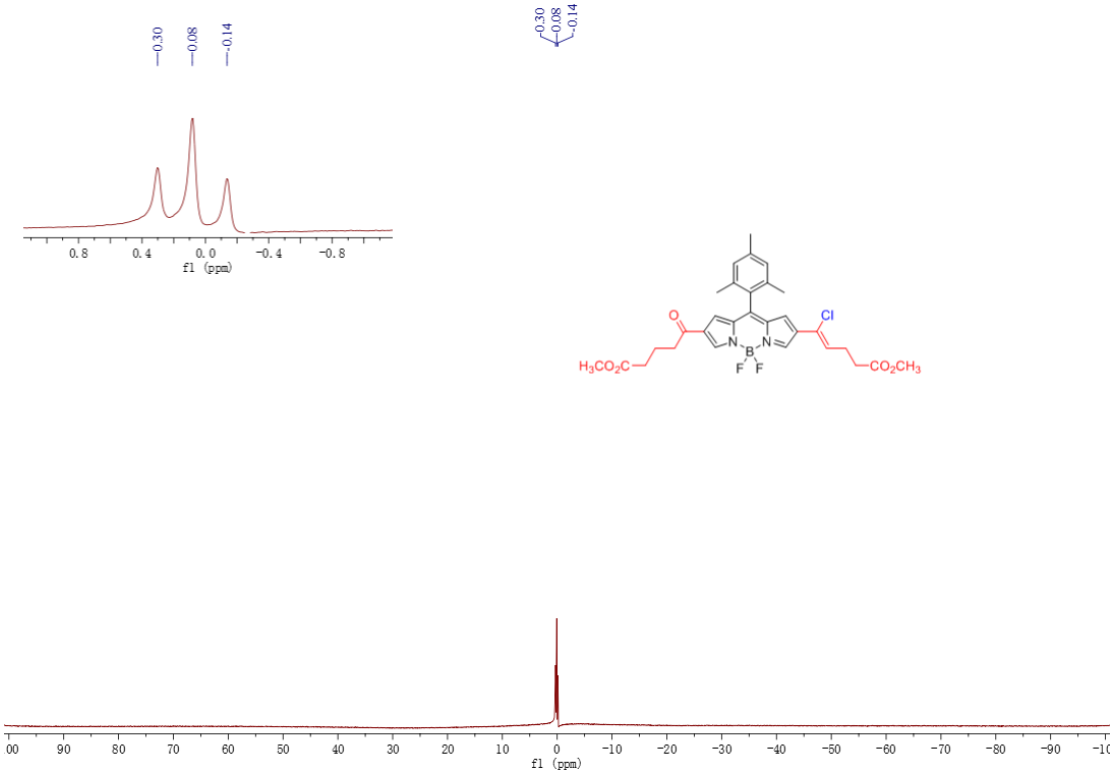
^{1}H NMR spectrum of **4e** in $CDCl_3$



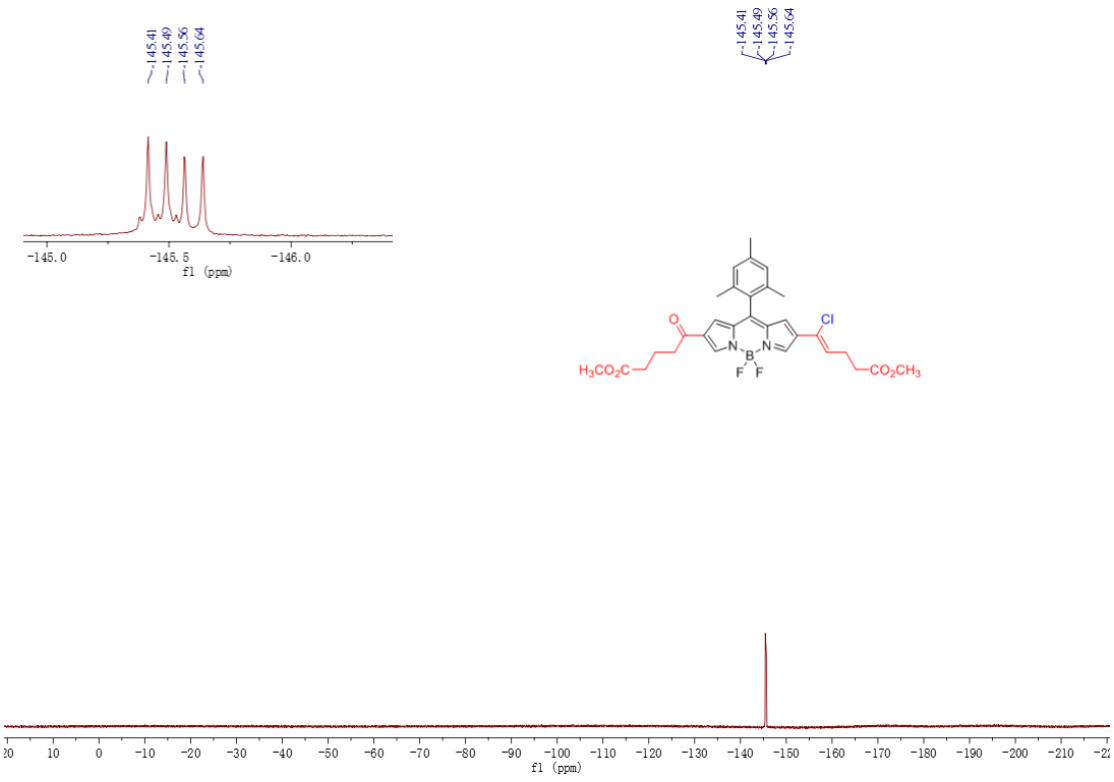
^{13}C NMR spectrum of **4e** in $CDCl_3$



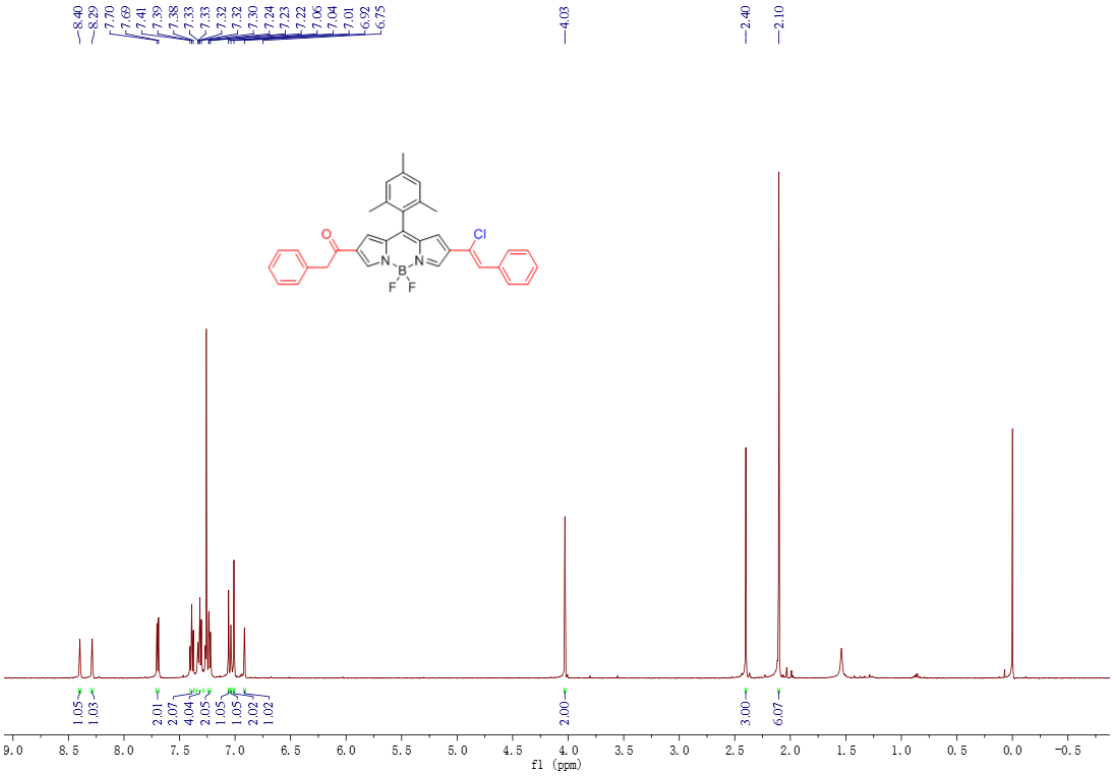
^{11}B NMR spectrum of **4e** in $CDCl_3$



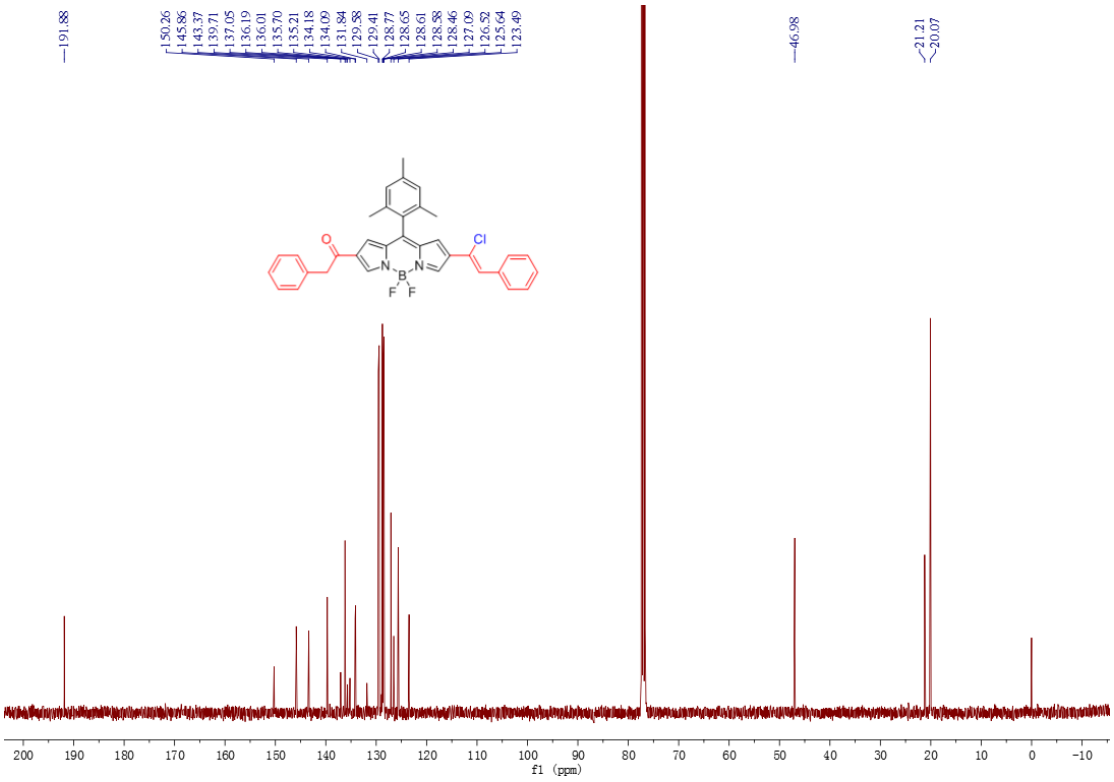
^{19}F NMR spectrum of **4e** in $CDCl_3$



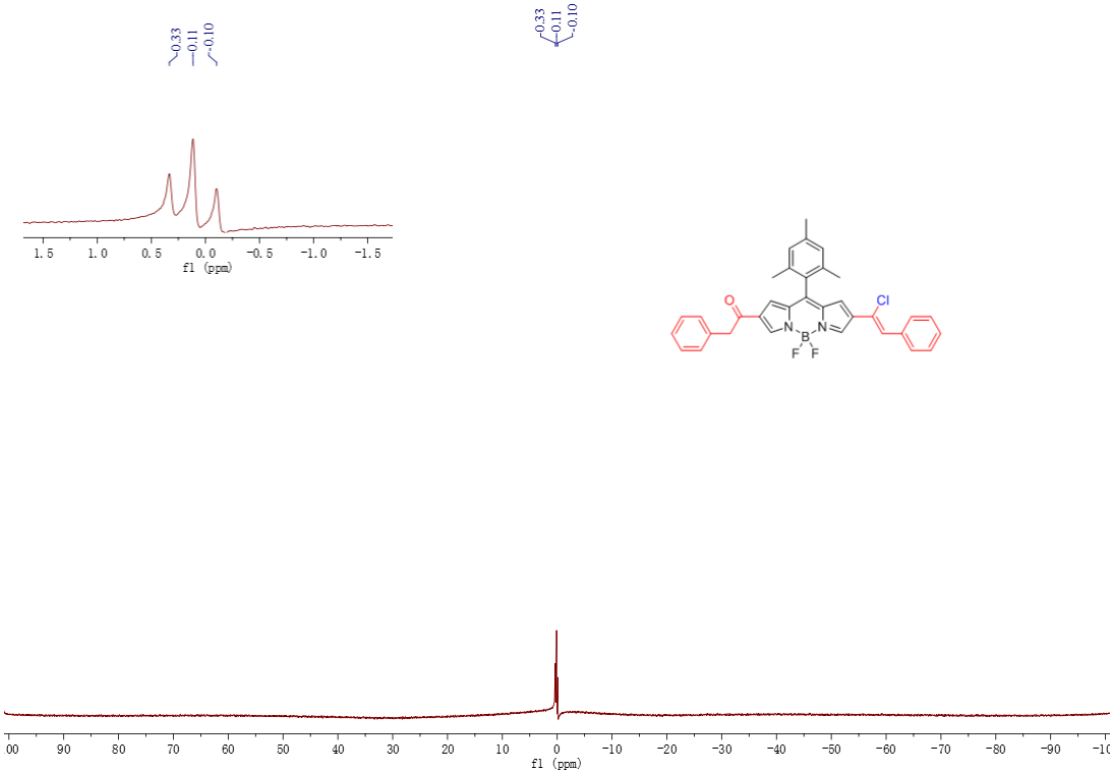
^{1}H NMR spectrum of **4f** in $CDCl_3$



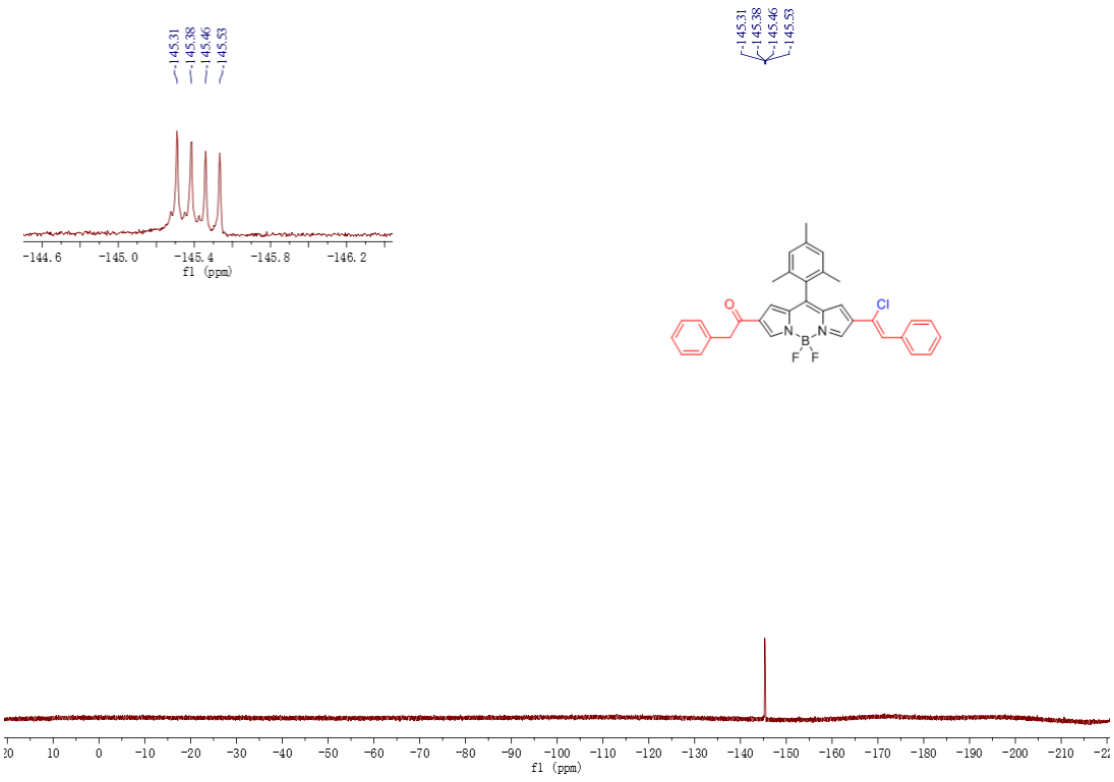
^{13}C NMR spectrum of **4f** in $CDCl_3$



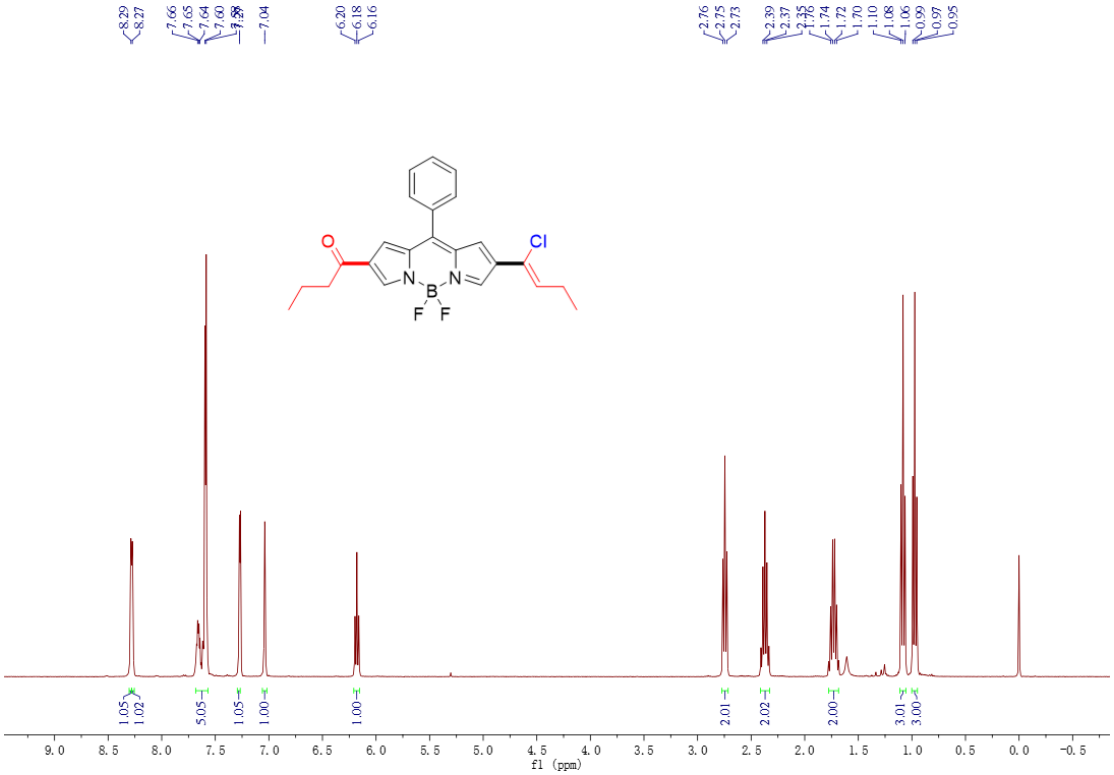
^{11}B NMR spectrum of **4f** in $CDCl_3$



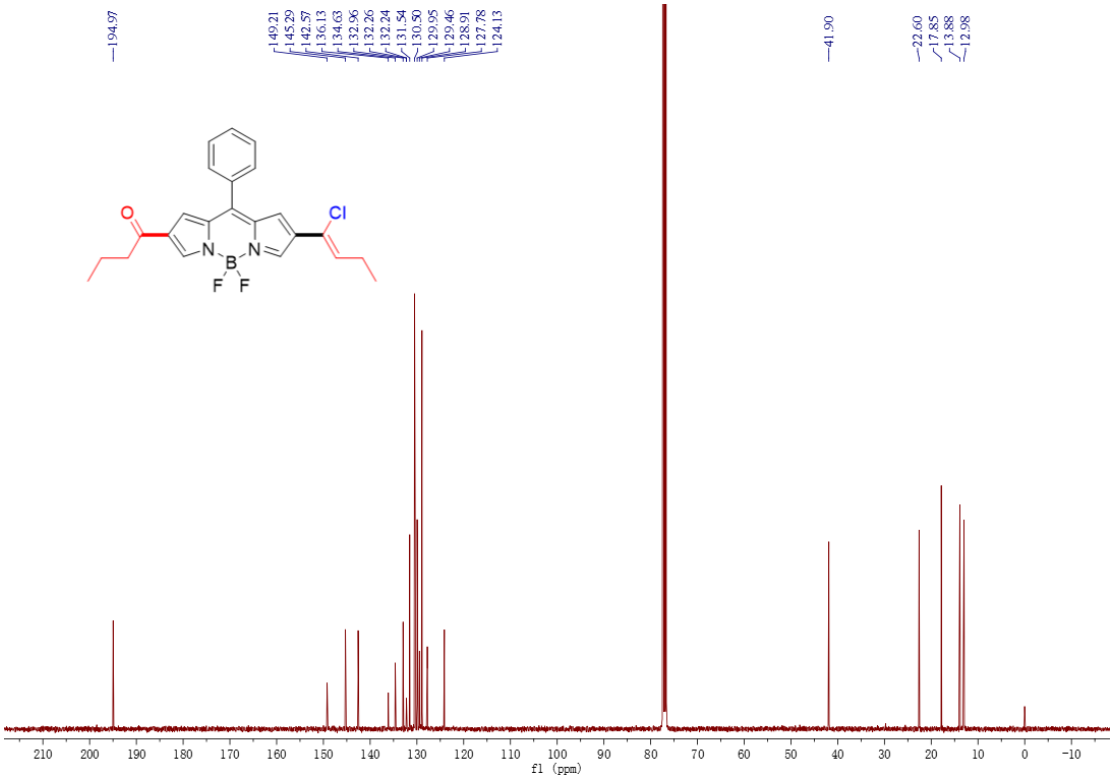
^{19}F NMR spectrum of **4f** in $CDCl_3$



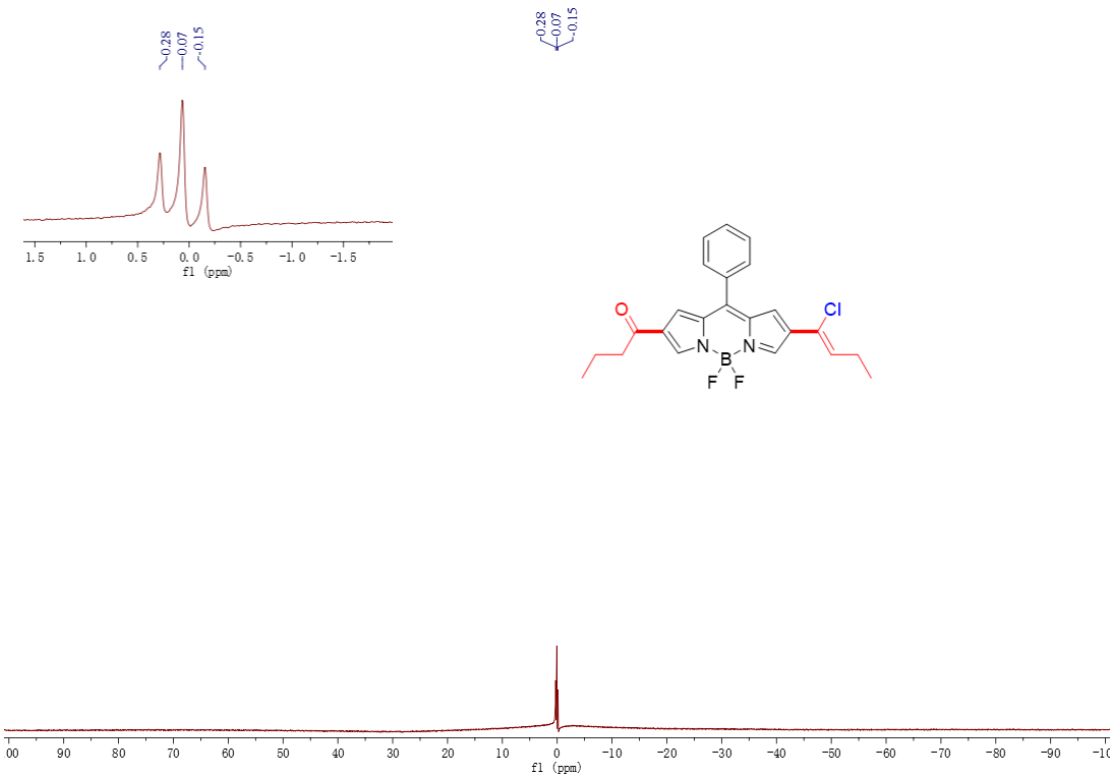
^{1}H NMR spectrum of **4g** in $CDCl_3$



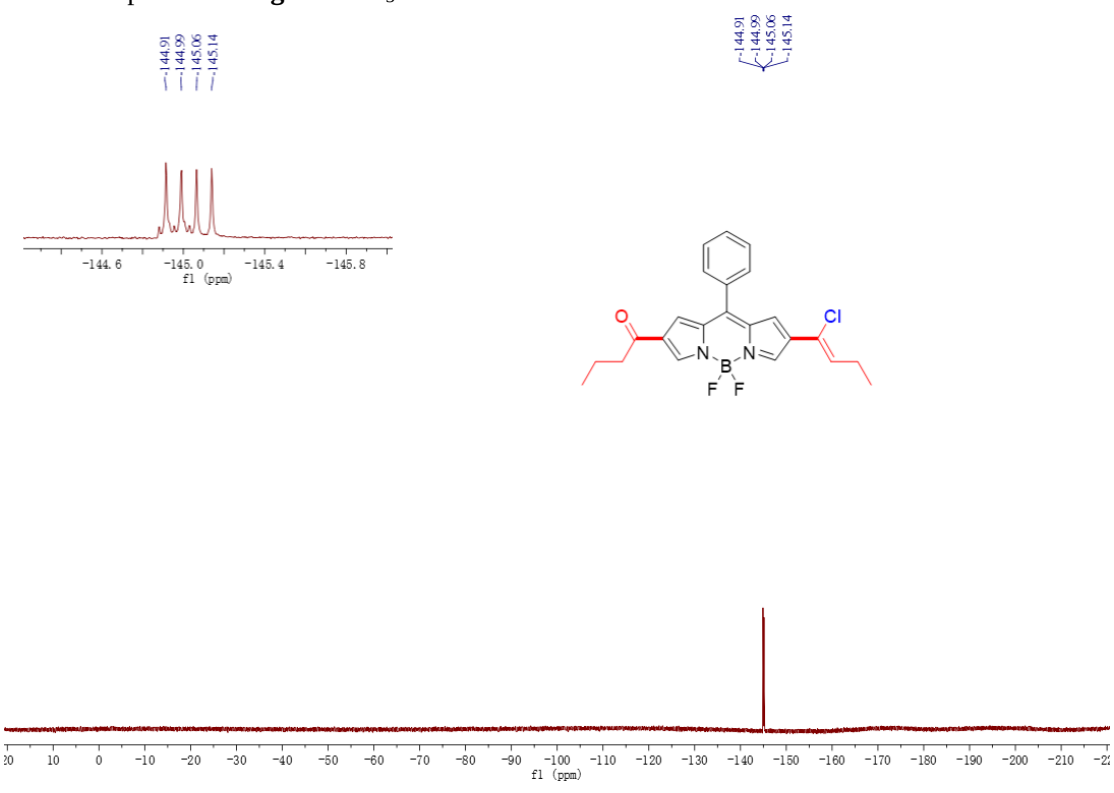
^{13}C NMR spectrum of **4g** in $CDCl_3$



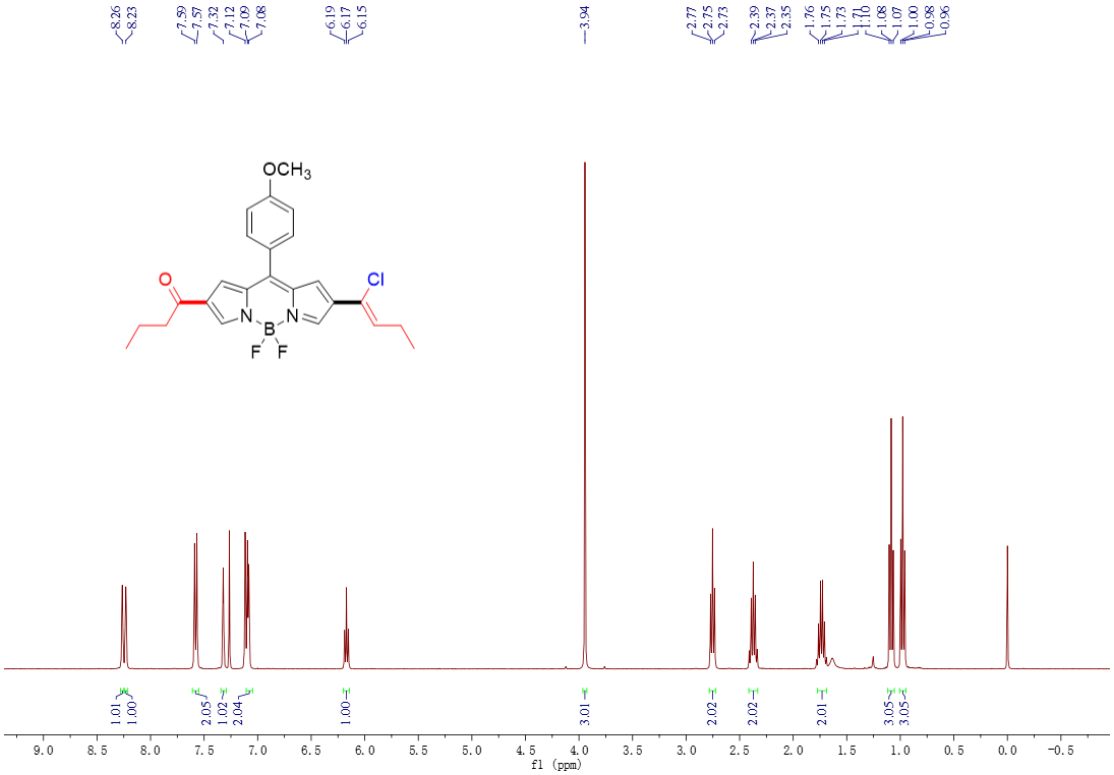
^{11}B NMR spectrum of **4g** in $CDCl_3$



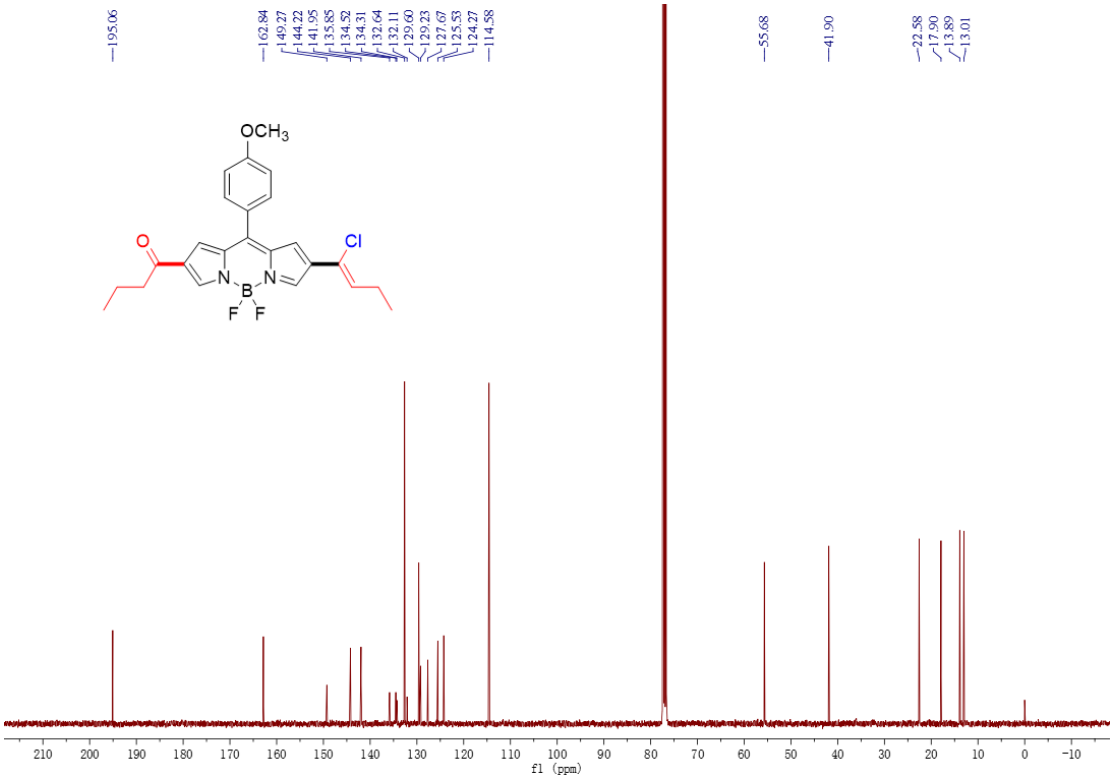
^{19}F NMR spectrum of **4g** in $CDCl_3$



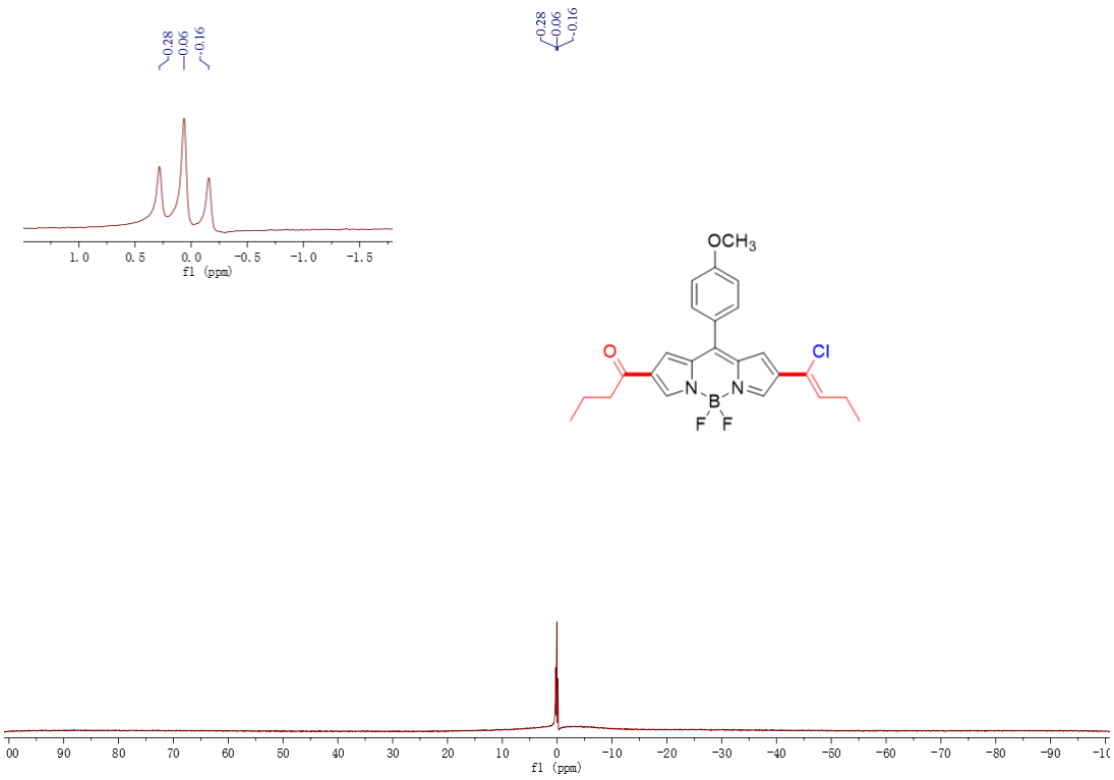
^{1}H NMR spectrum of **4h** in $CDCl_3$



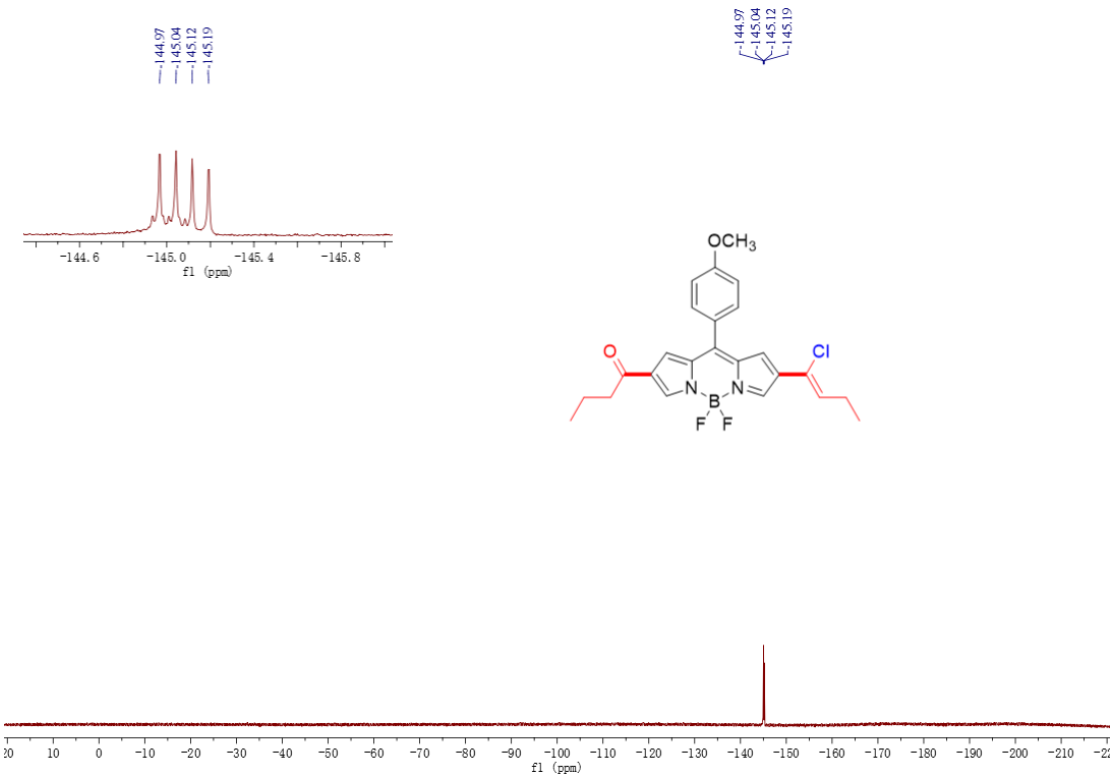
^{13}C NMR spectrum of **4h** in $CDCl_3$



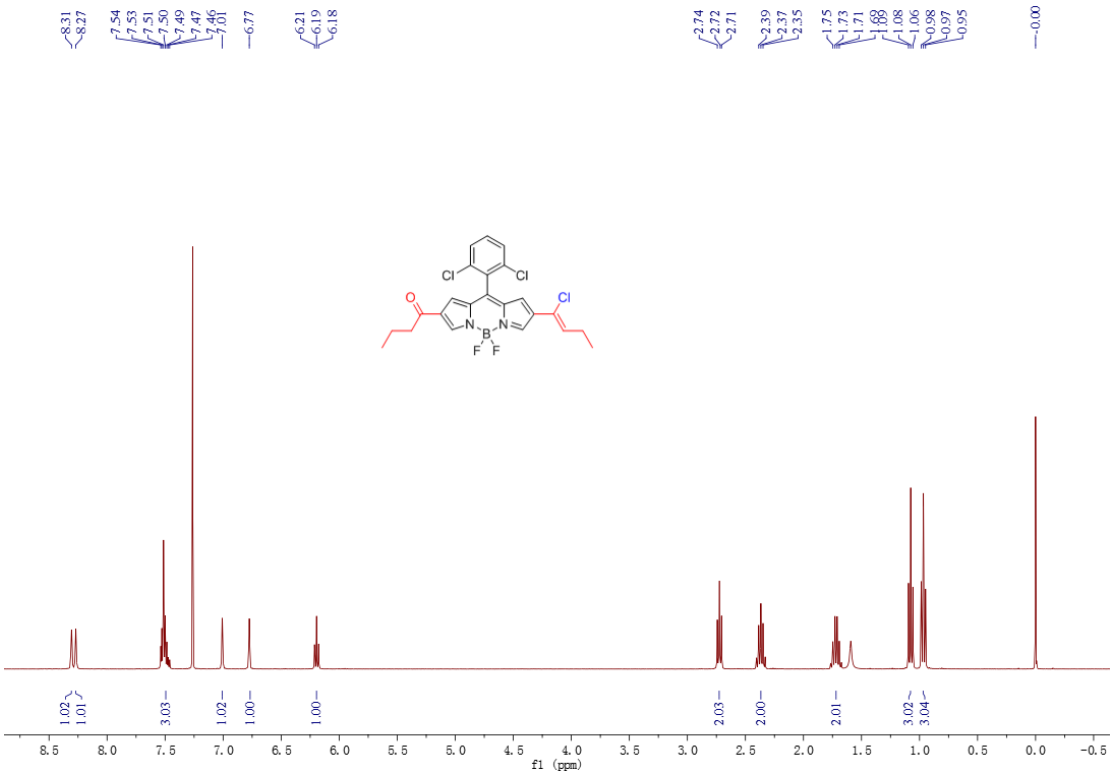
^{11}B NMR spectrum of **4h** in $CDCl_3$



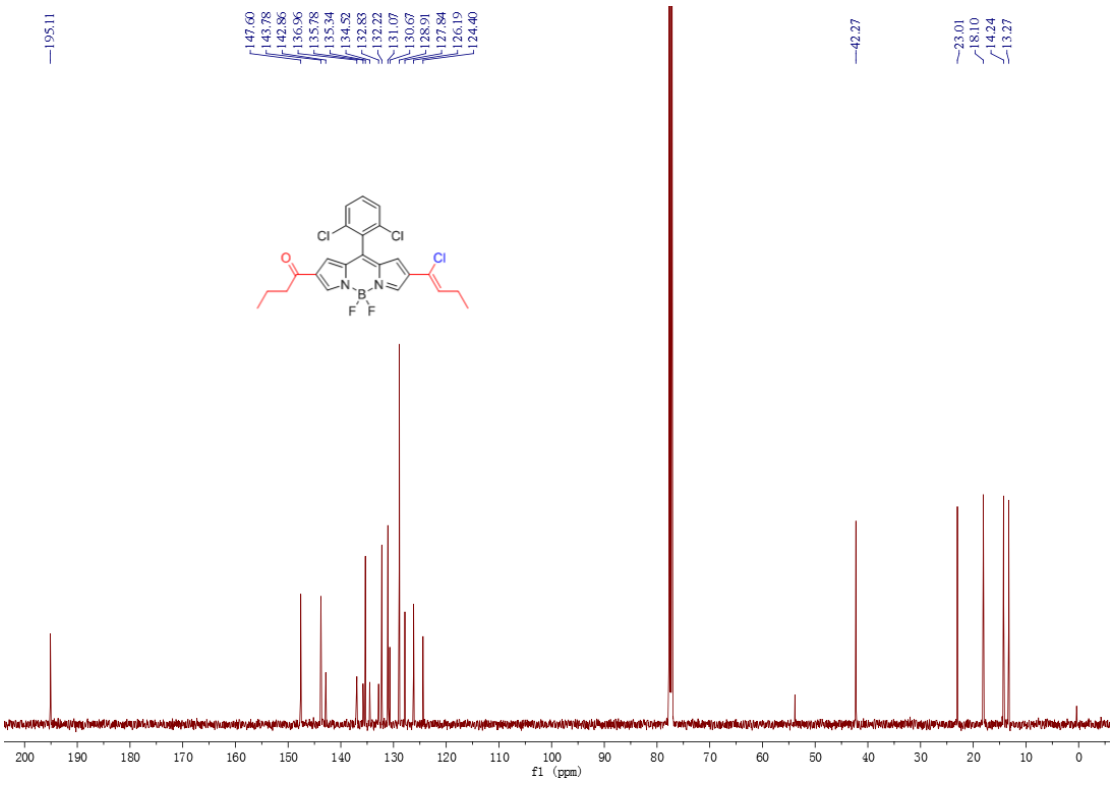
^{19}F NMR spectrum of **4h** in $CDCl_3$



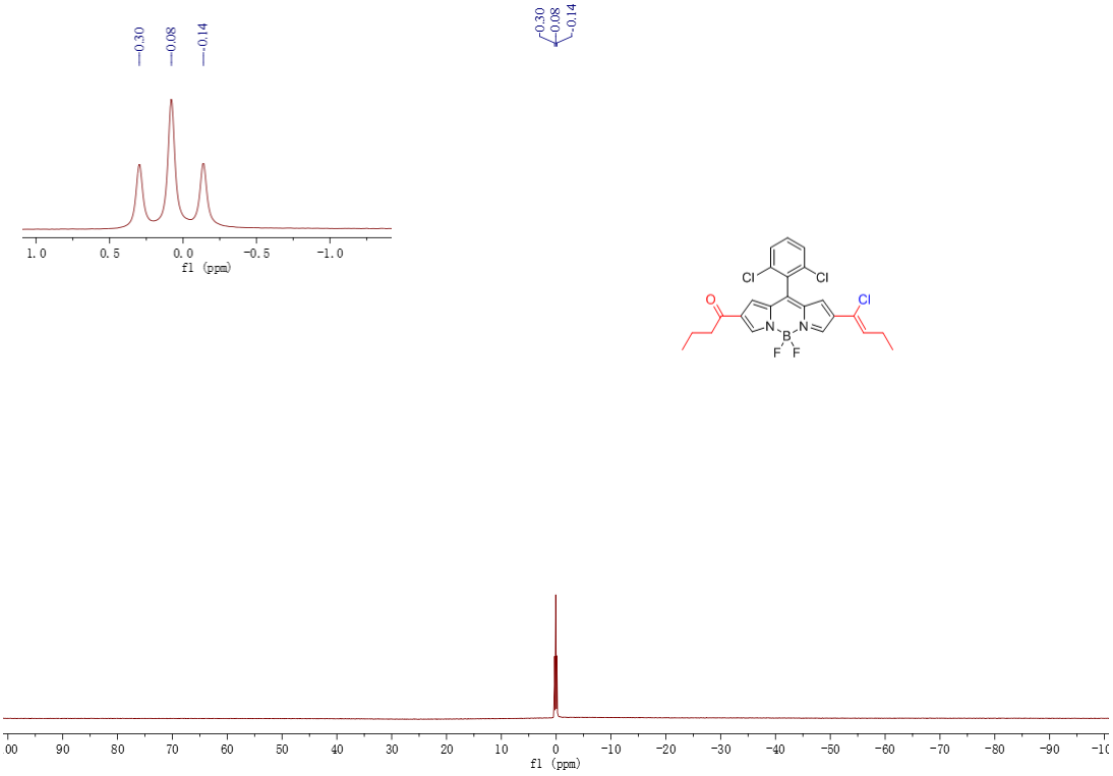
^{1}H NMR spectrum of **4i** in $CDCl_3$



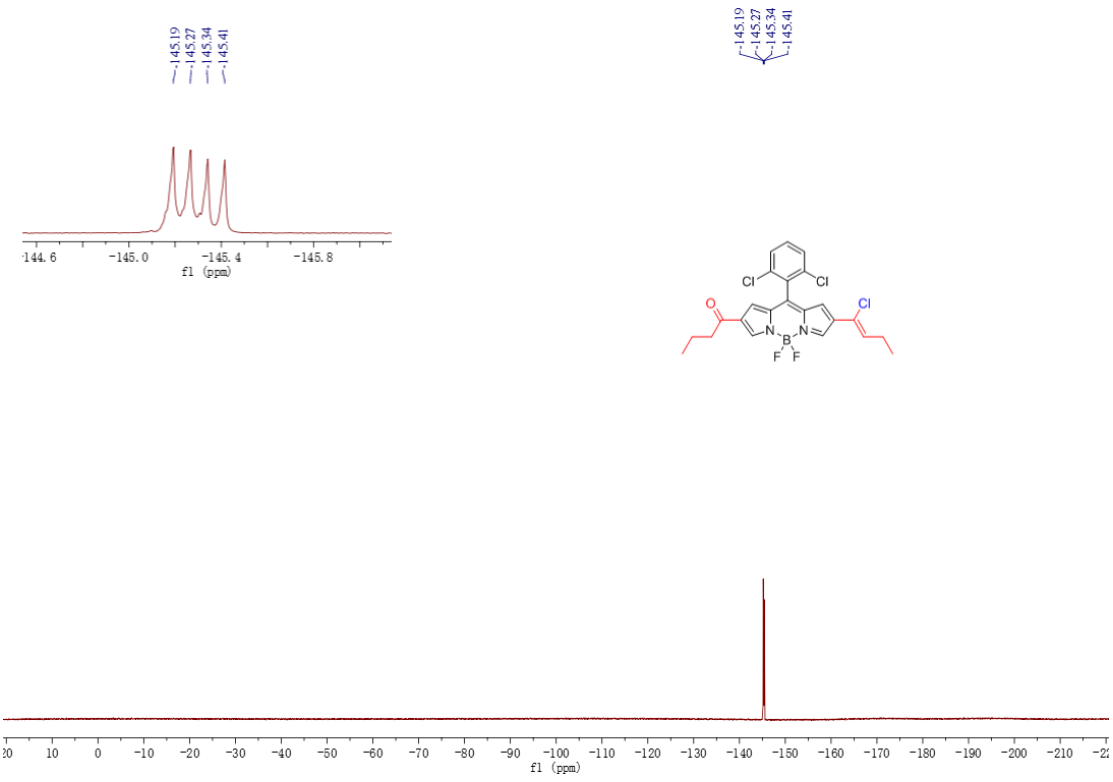
^{13}C NMR spectrum of **4i** in $CDCl_3$



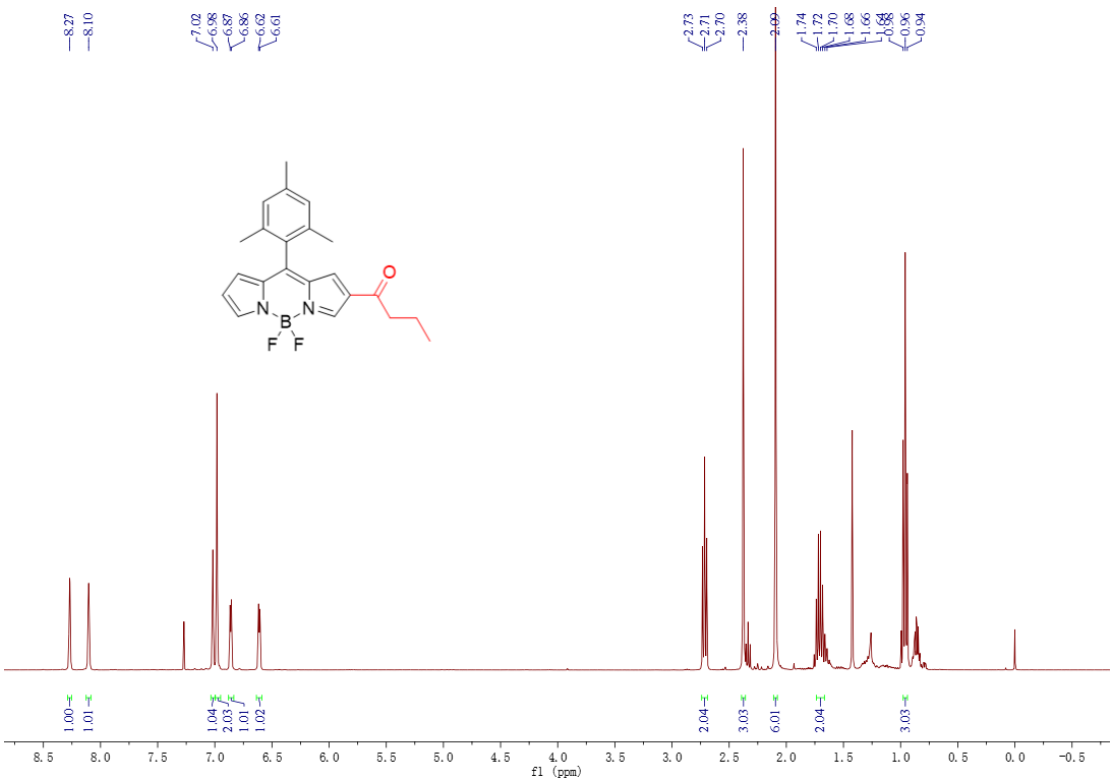
^{11}B NMR spectrum of **4i** in $CDCl_3$



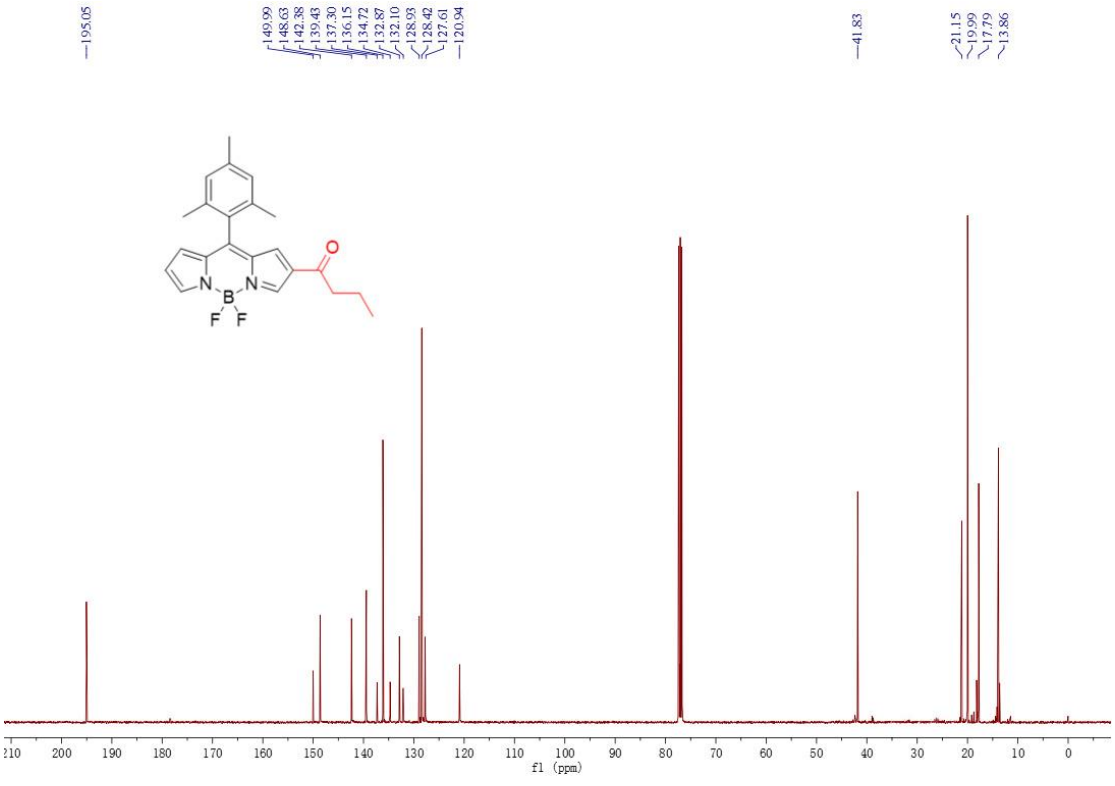
^{19}F NMR spectrum of **4i** in $CDCl_3$



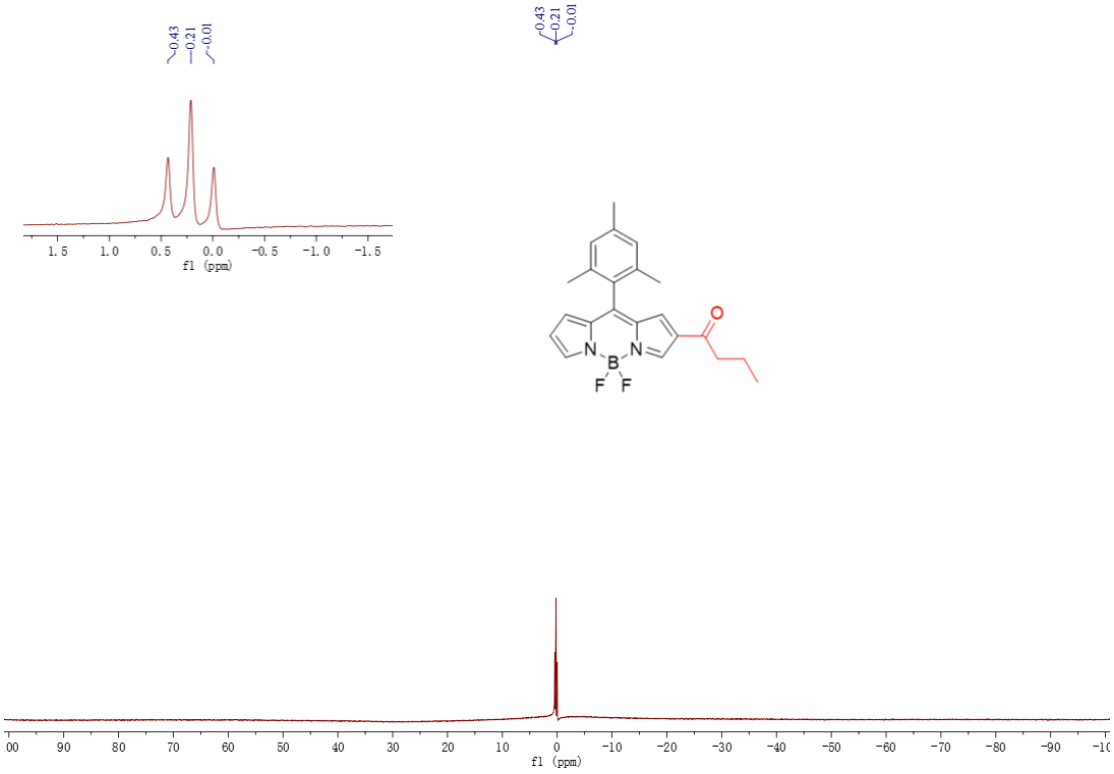
^{1}H NMR spectrum of **5** in $CDCl_3$



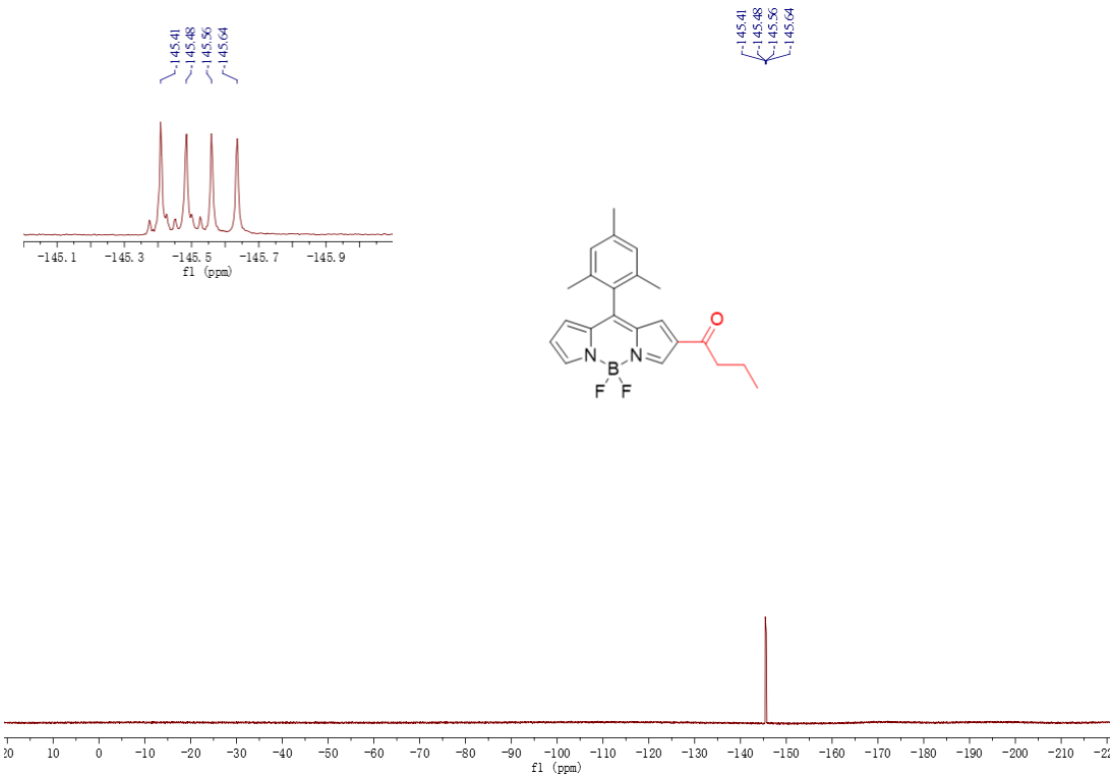
^{13}C NMR spectrum of **5** in $CDCl_3$



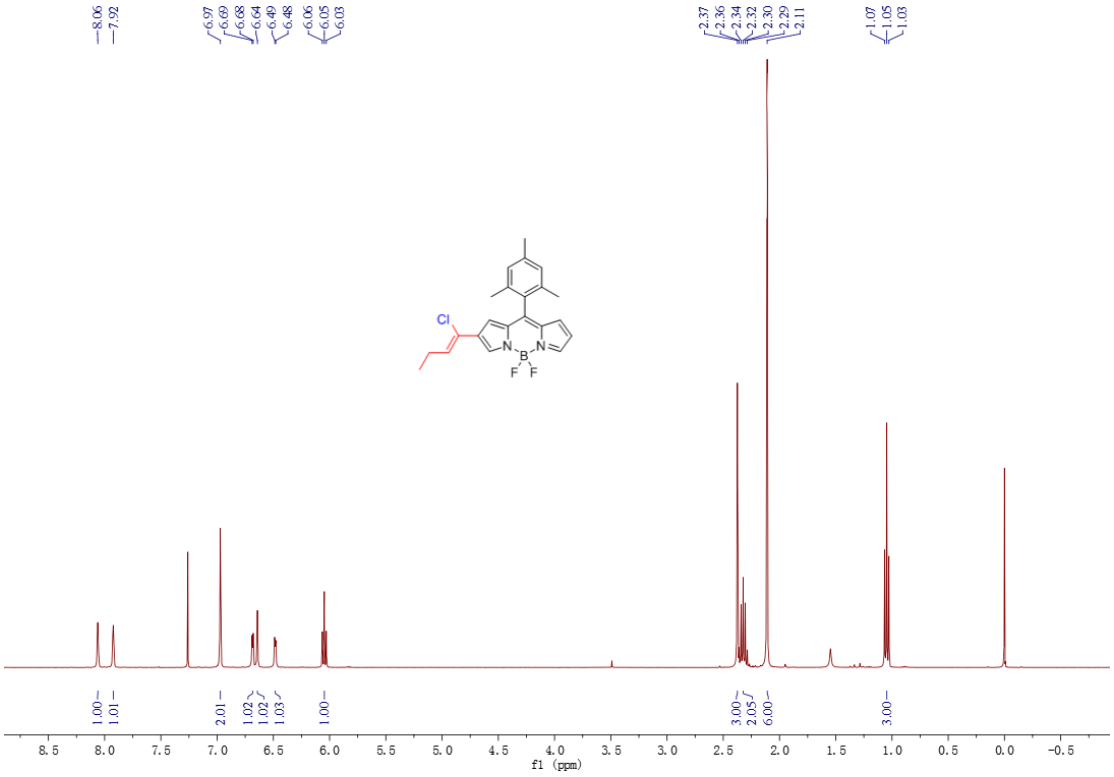
^{11}B NMR spectrum of **5** in $CDCl_3$



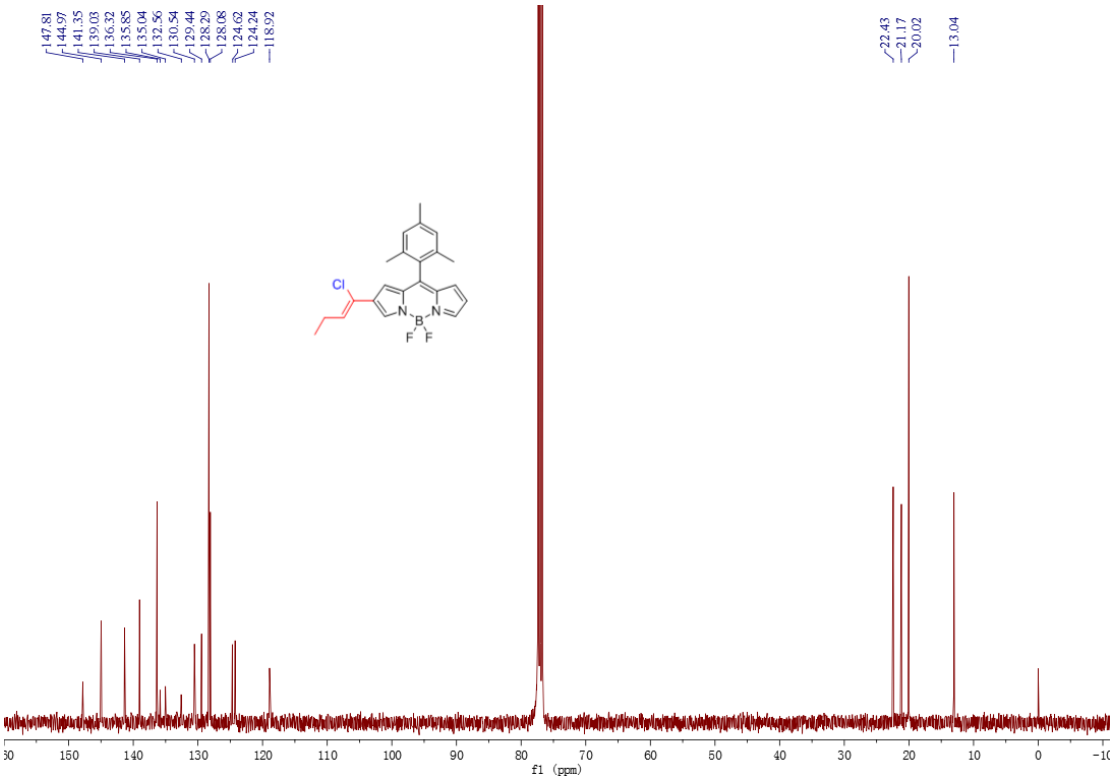
^{19}F NMR spectrum of **5** in $CDCl_3$



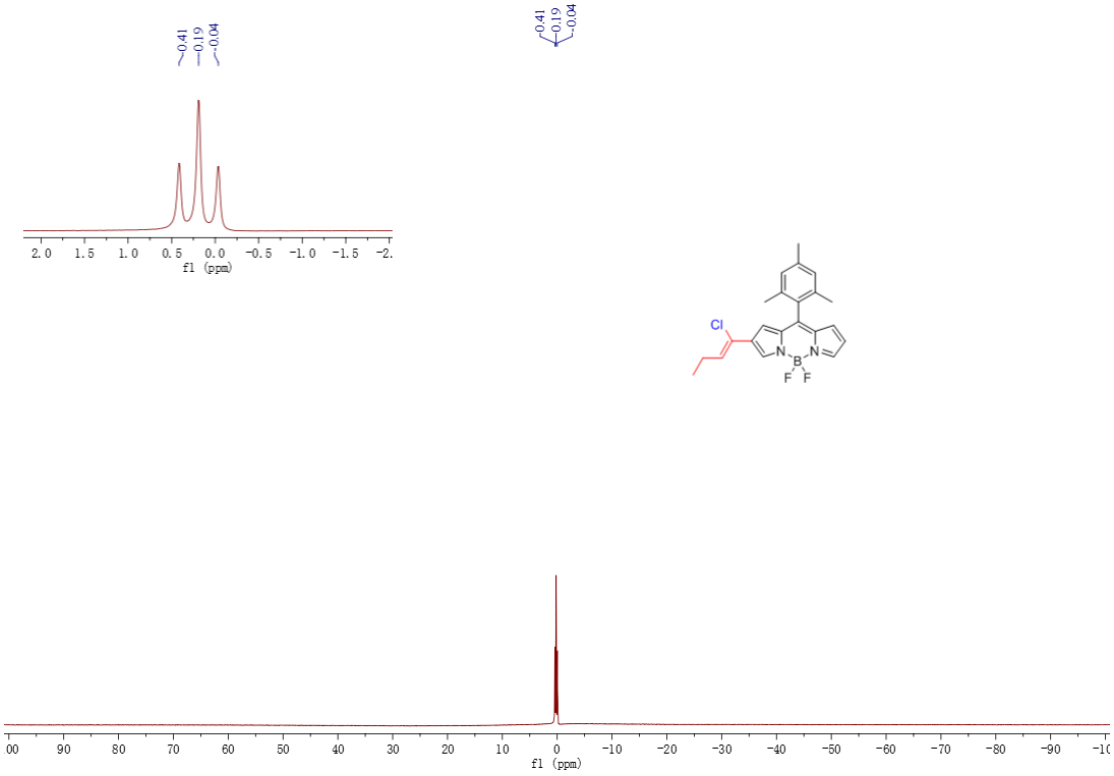
^{1}H NMR spectrum of **6** in $CDCl_3$



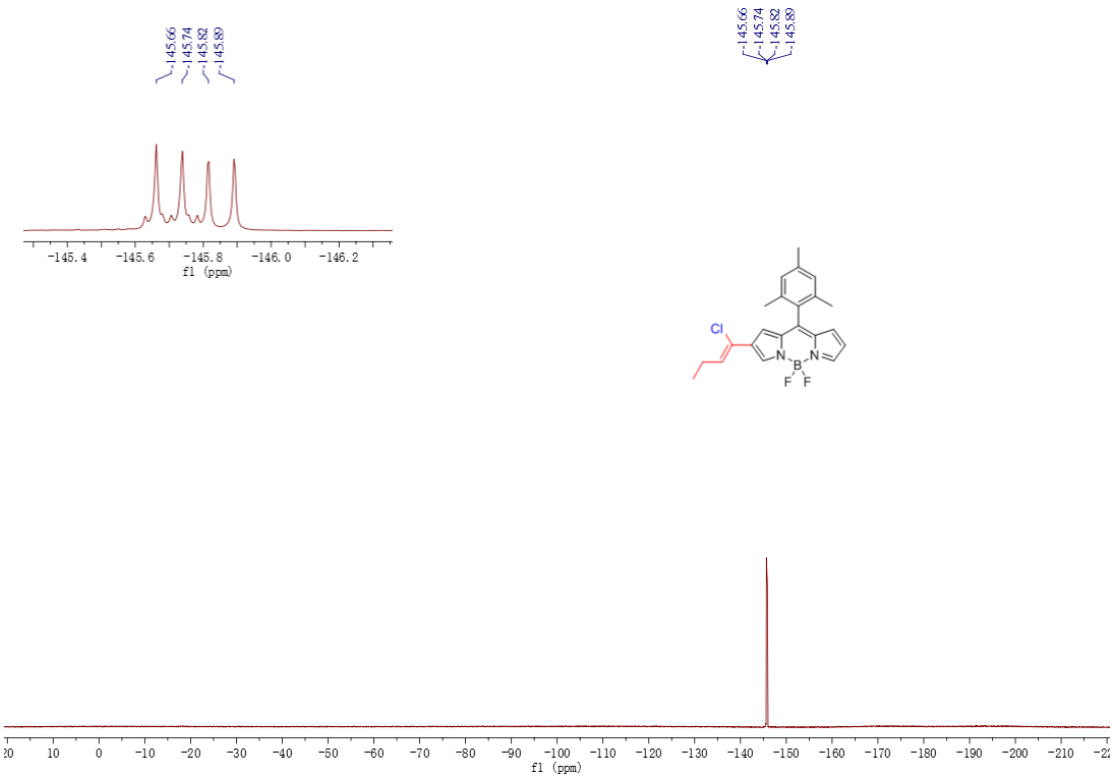
^{13}C NMR spectrum of **6** in $CDCl_3$



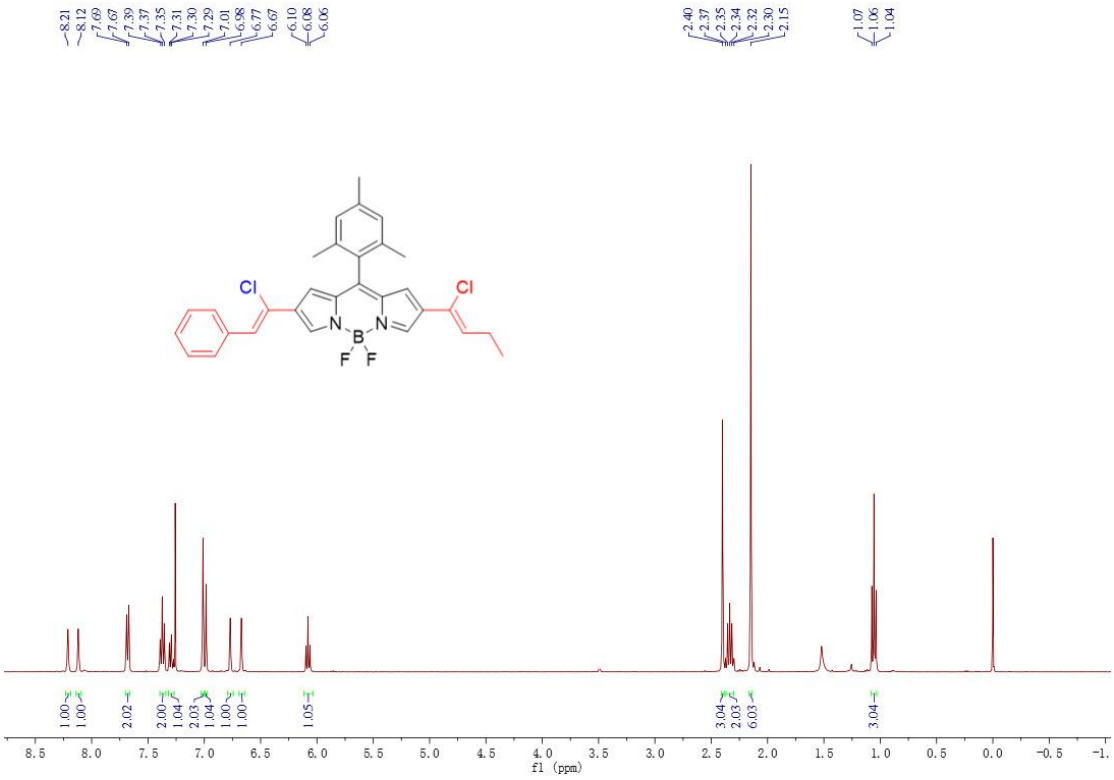
^{11}B NMR spectrum of **6** in $CDCl_3$



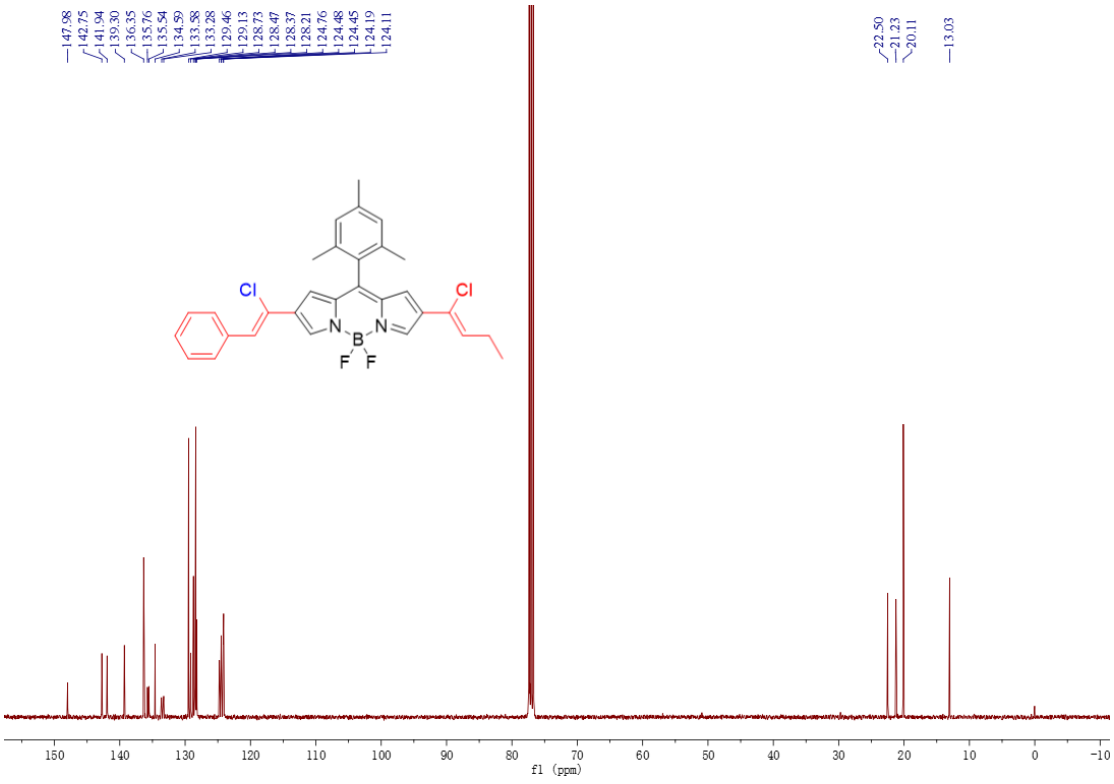
^{19}F NMR spectrum of **6** in $CDCl_3$



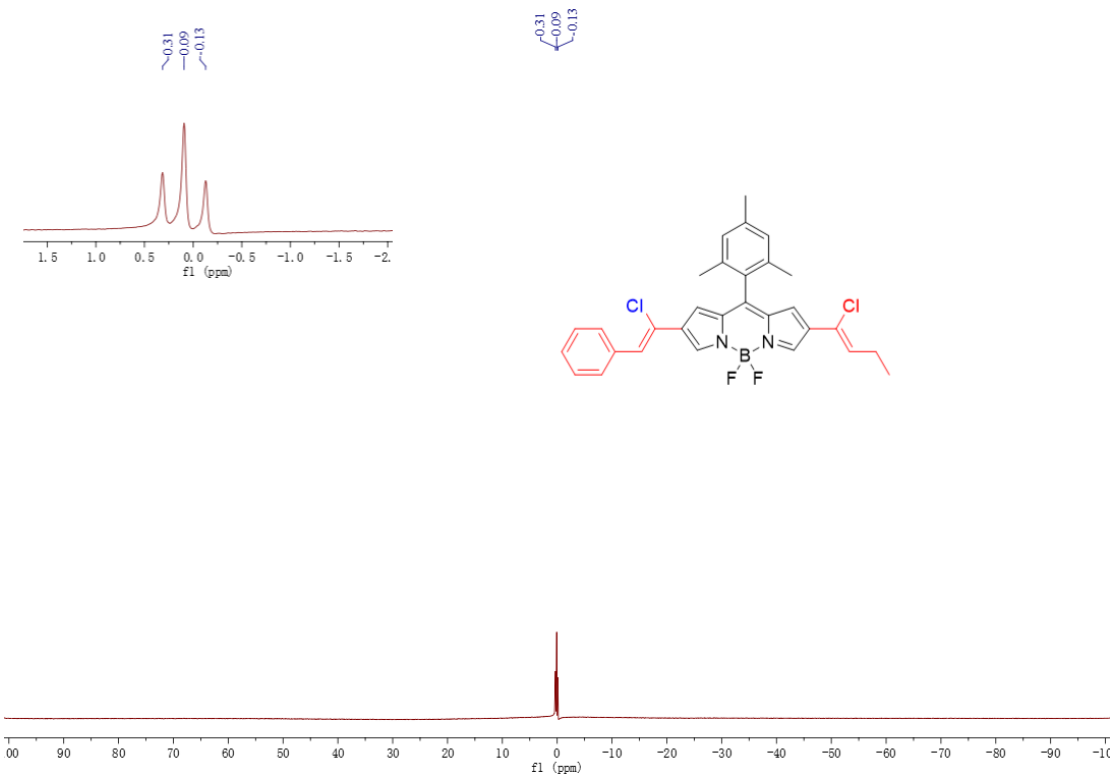
^{1}H NMR spectrum of **7** in $CDCl_3$



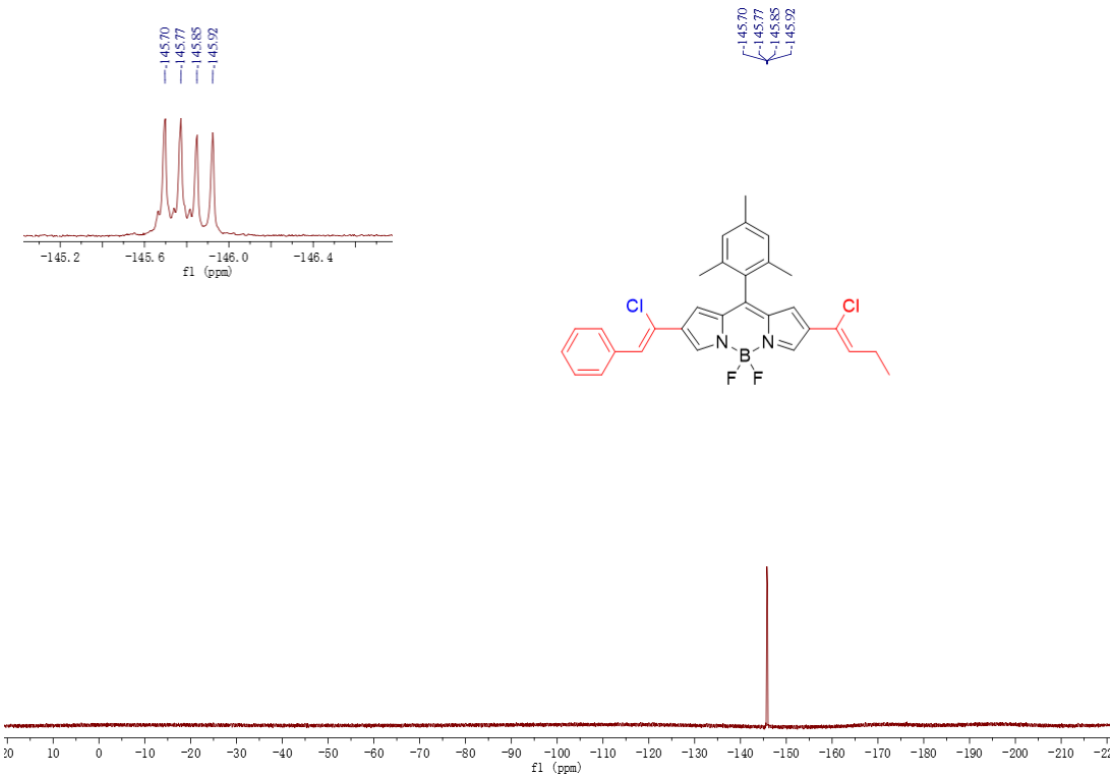
^{13}C NMR spectrum of **7** in $CDCl_3$



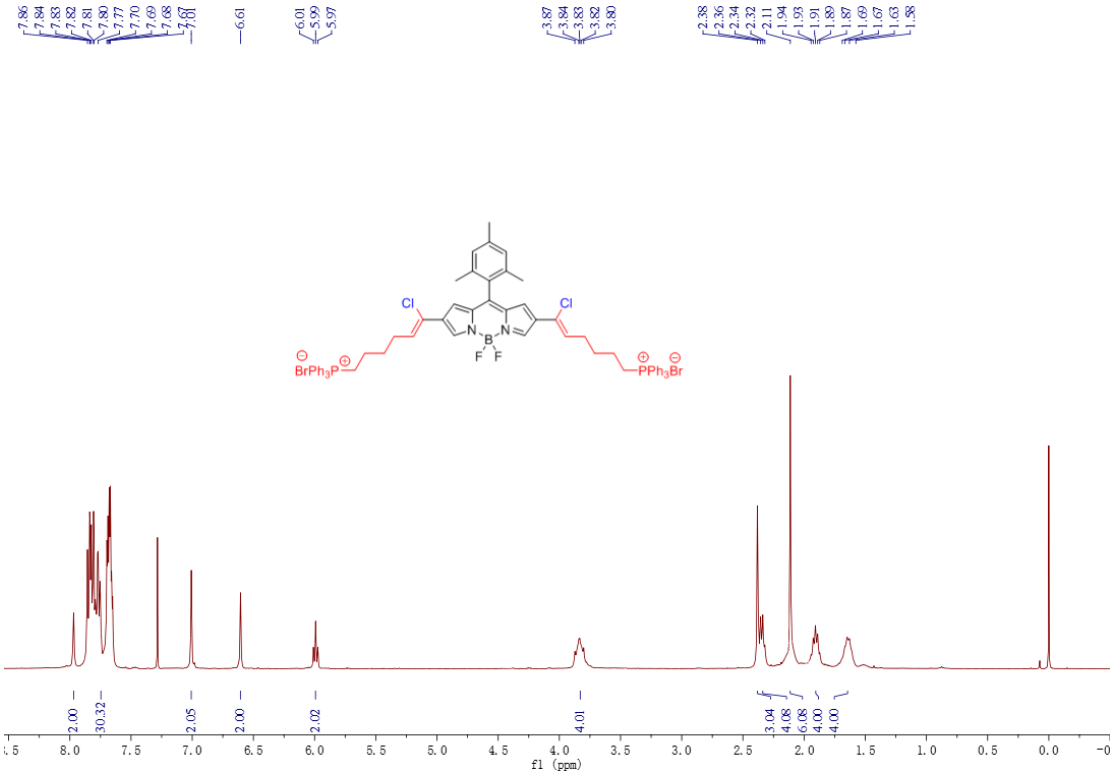
^{11}B NMR spectrum of **7** in $CDCl_3$



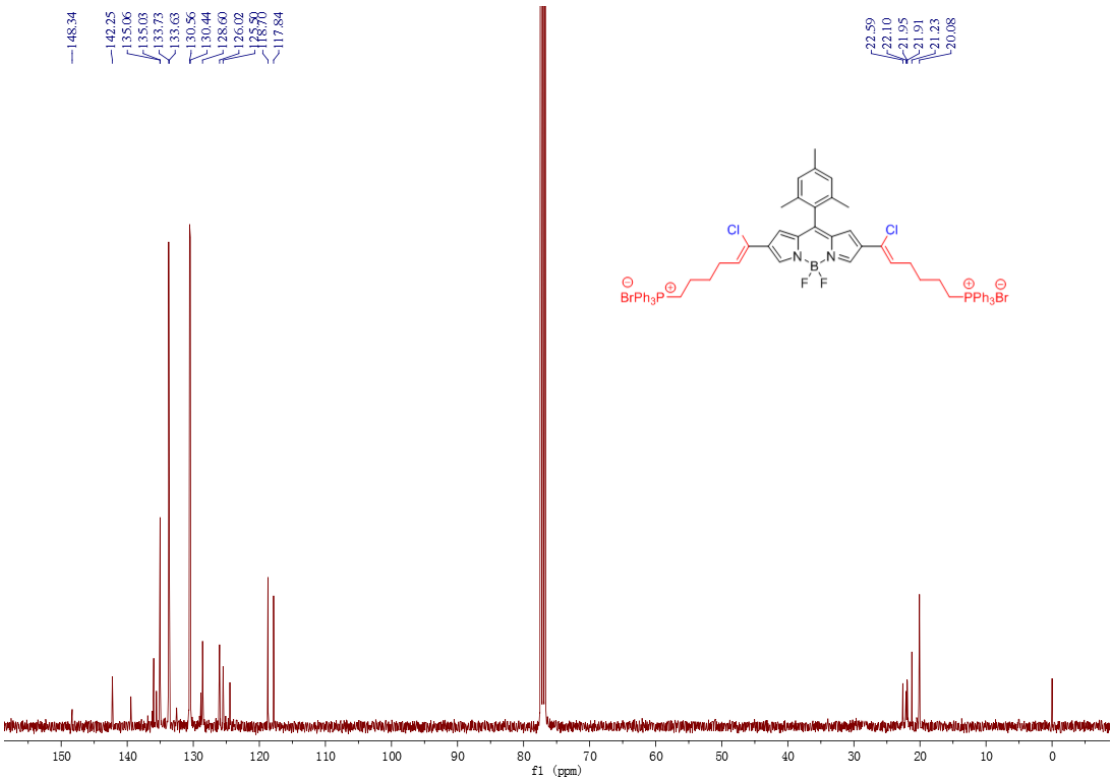
^{19}F NMR spectrum of **7** in $CDCl_3$



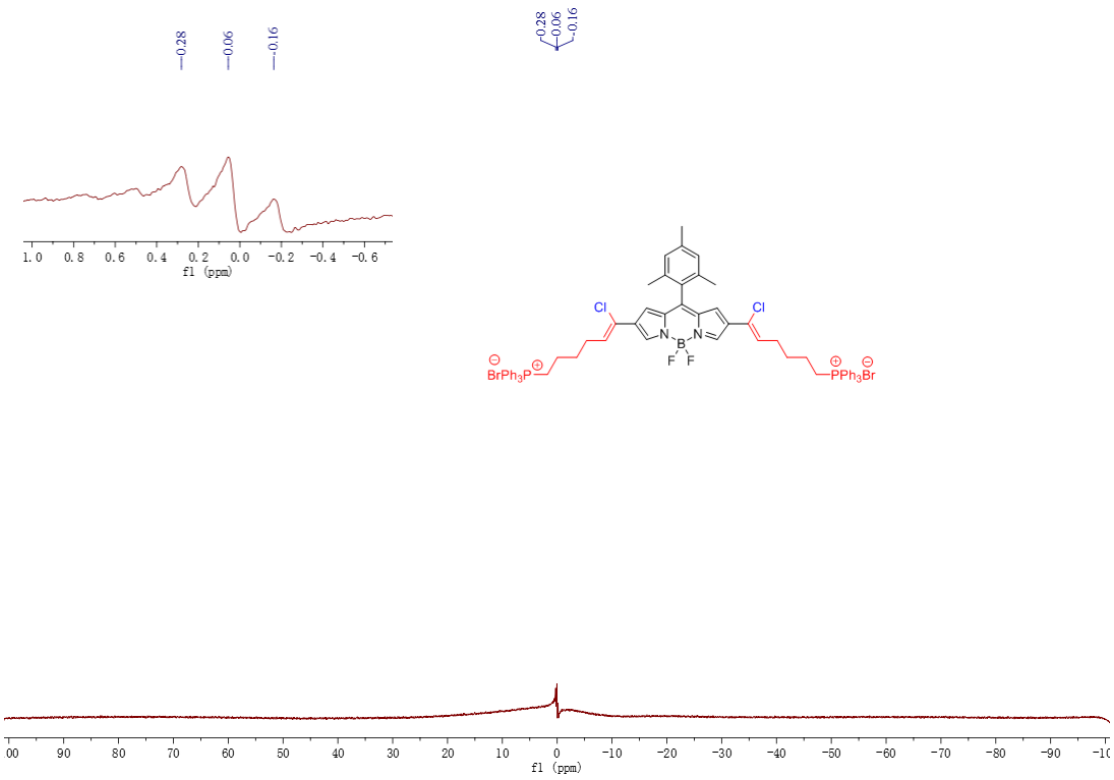
^{1}H NMR spectrum of **3e-p** in $CDCl_3$



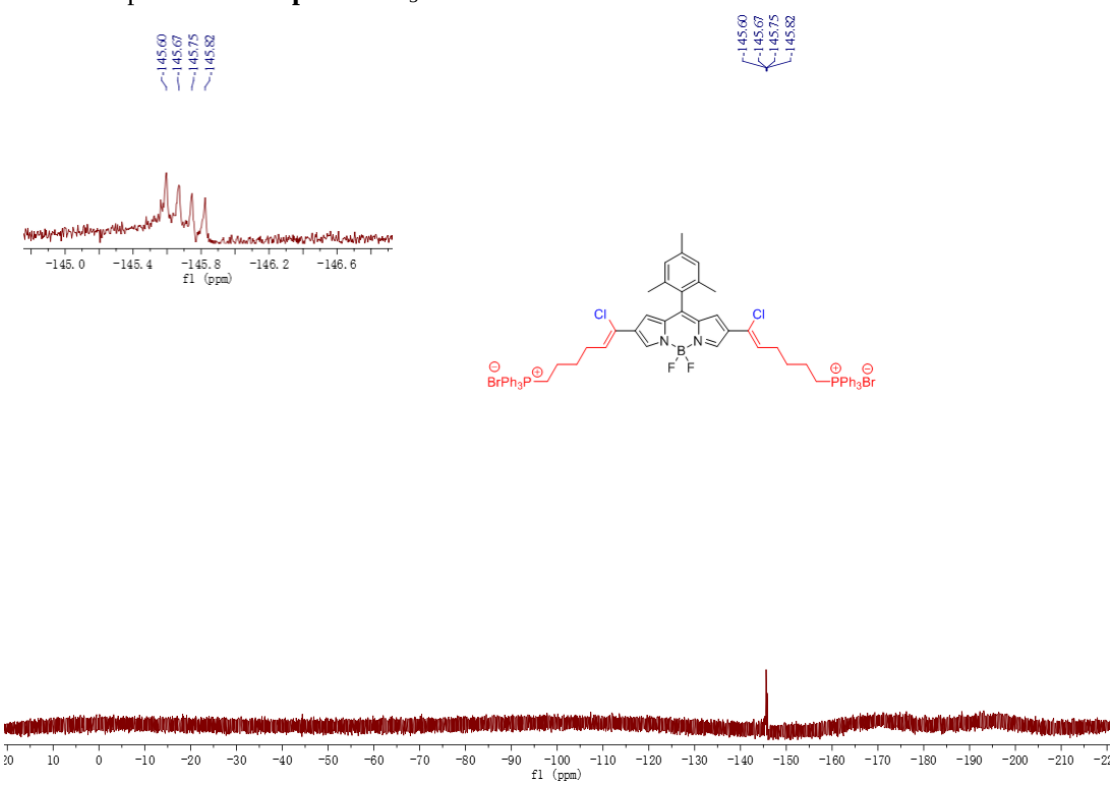
^{13}C NMR spectrum of **3e-p** in $CDCl_3$



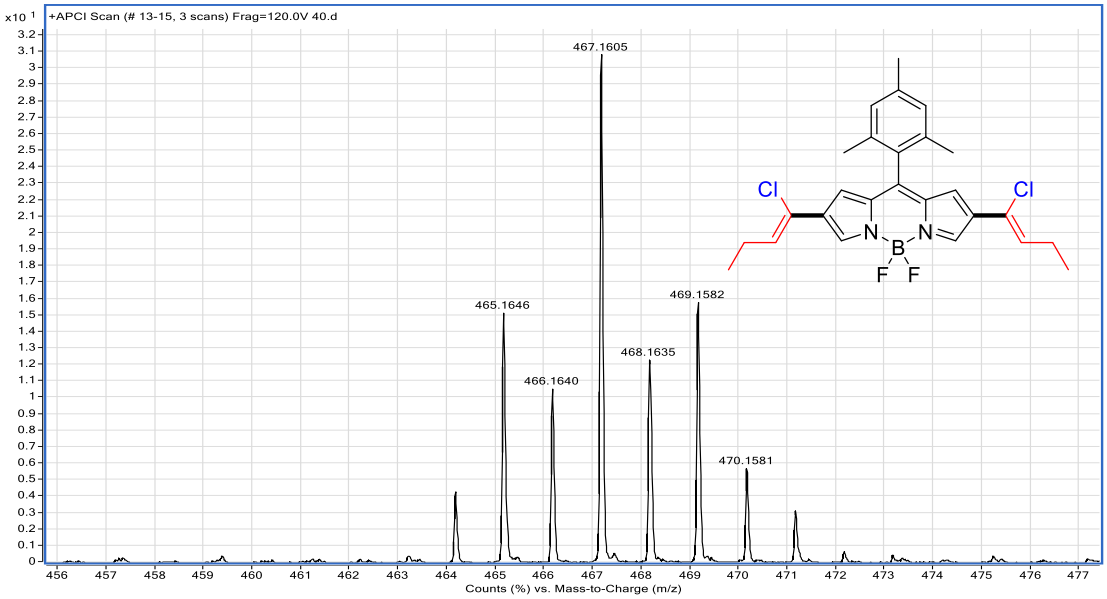
^{11}B NMR spectrum of **3e-p** in $CDCl_3$



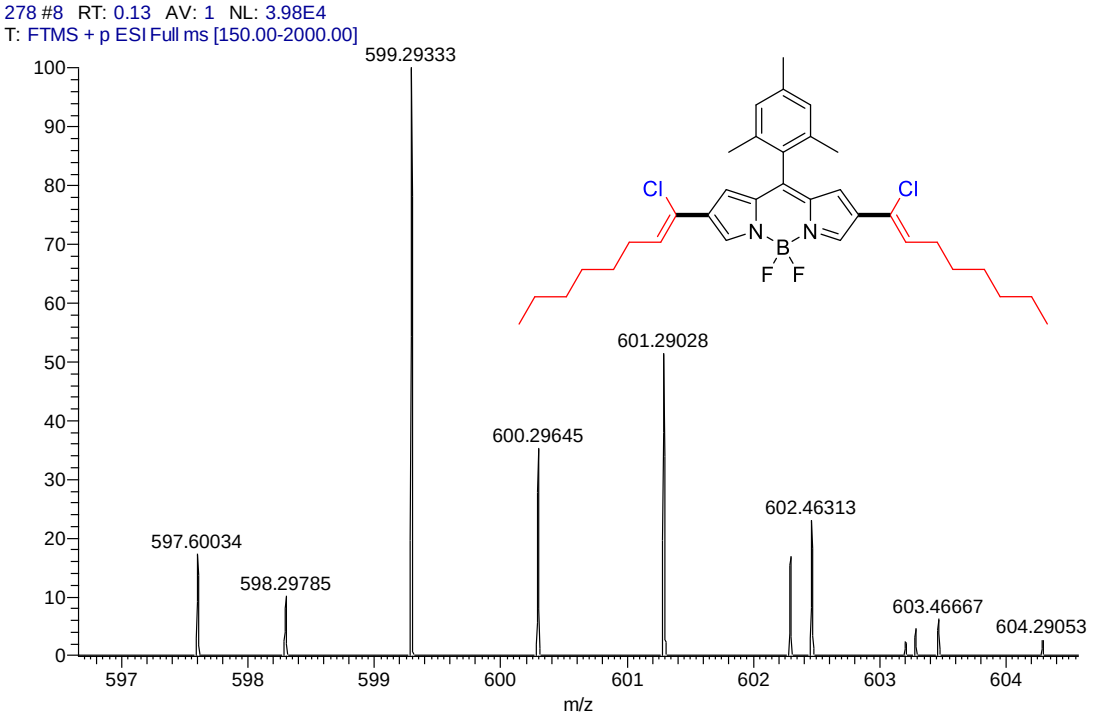
^{19}F NMR spectrum of **3e-p** in $CDCl_3$



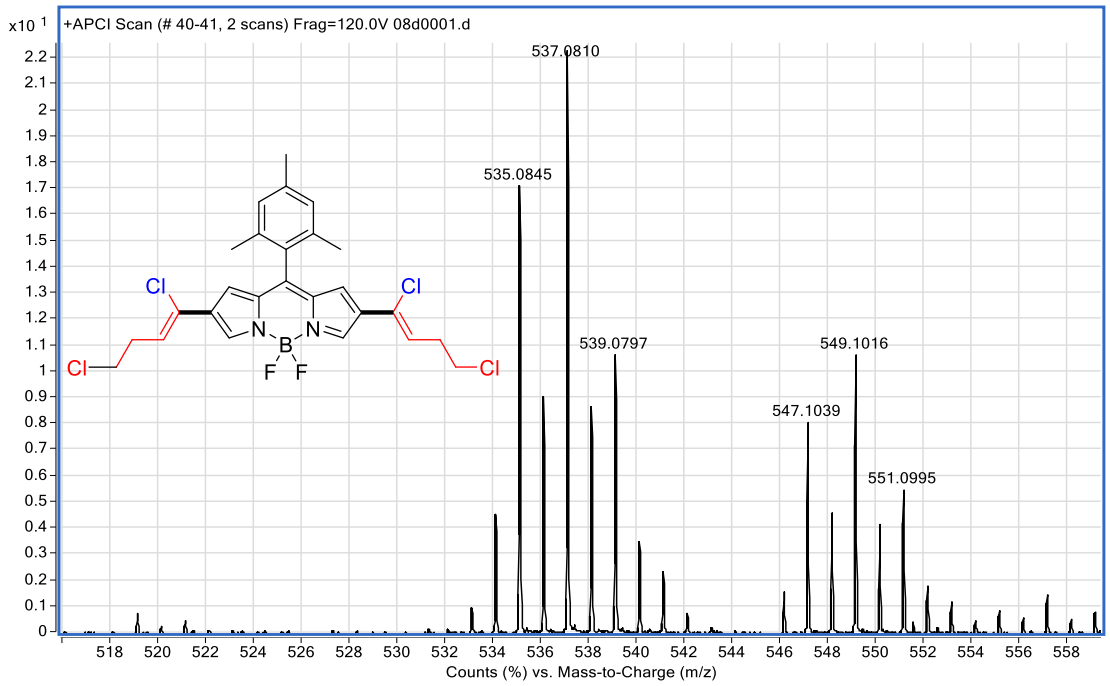
HRMS spectra of **3a**



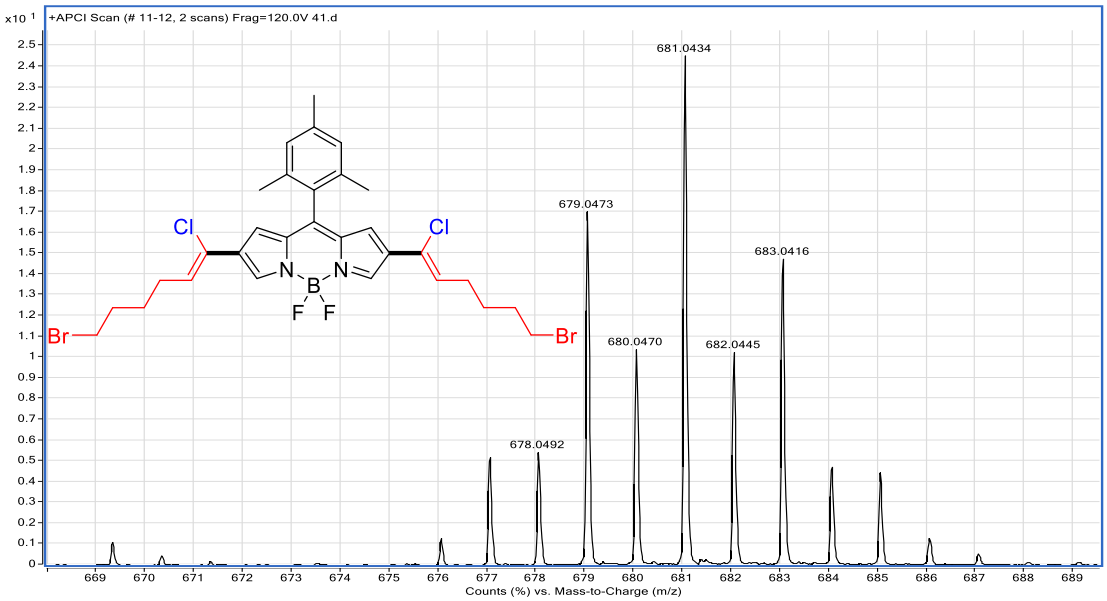
HRMS spectra of **3b**



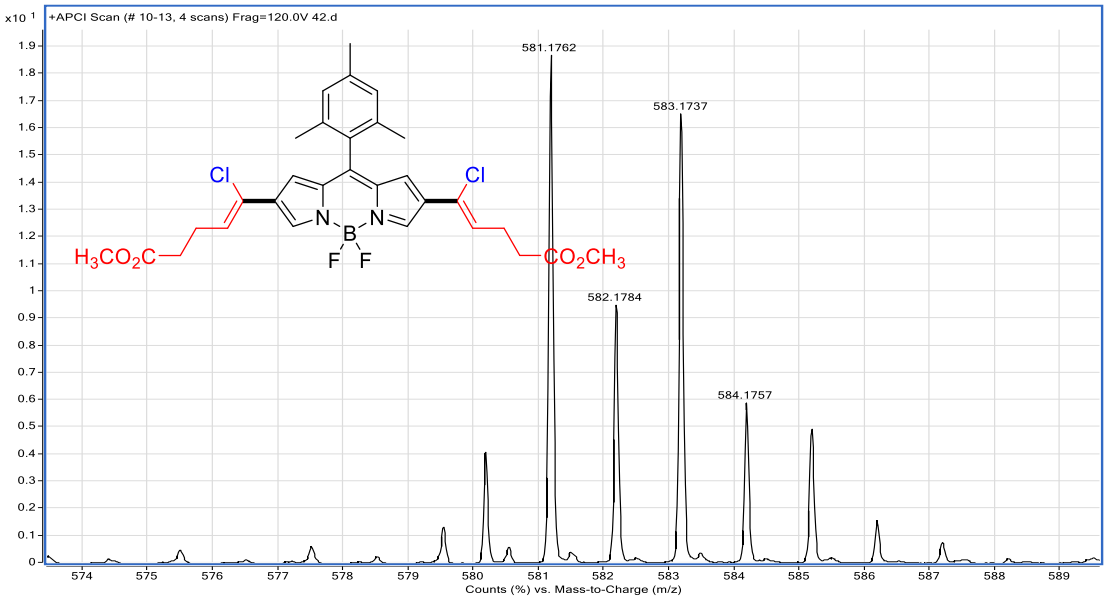
HRMS spectra of **3c**



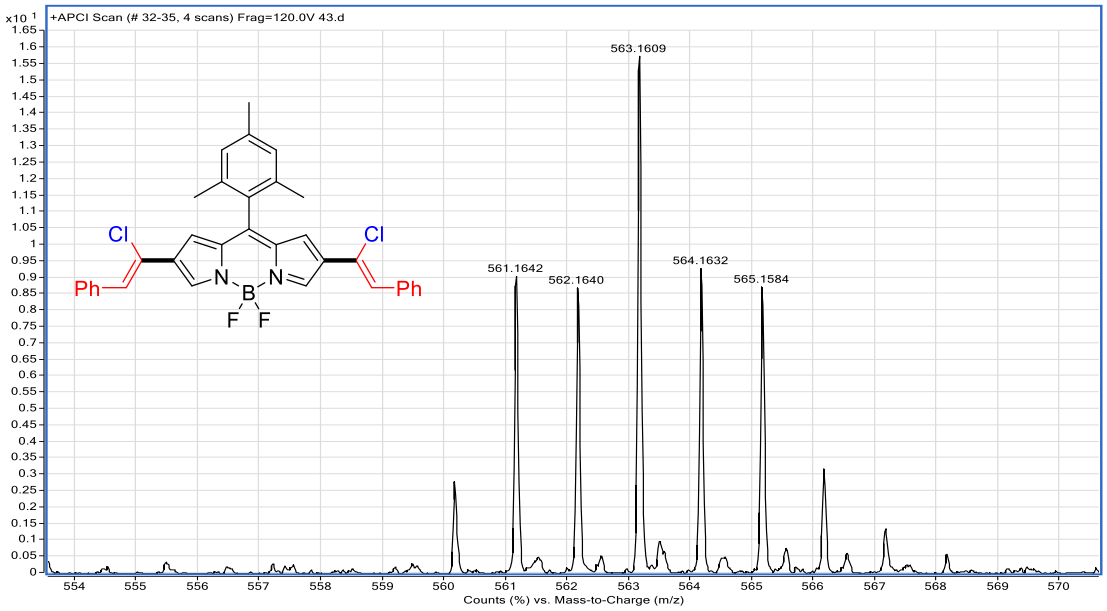
HRMS spectra of **3d**



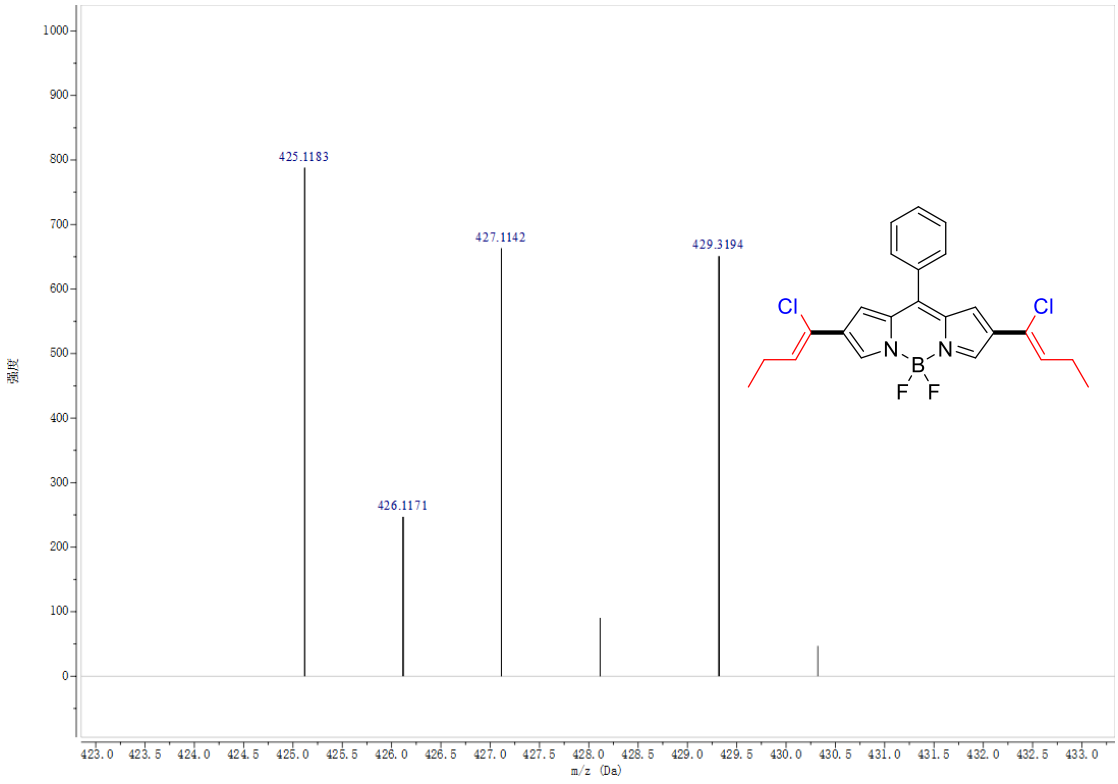
HRMS spectra of **3e**



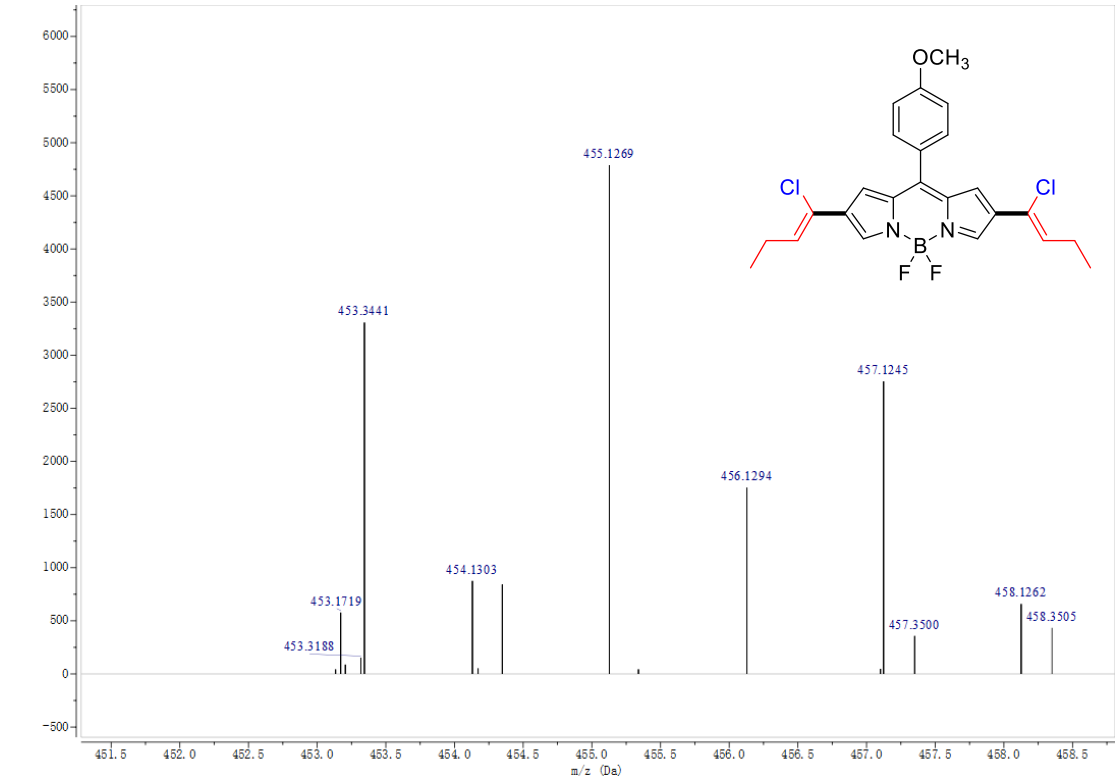
HRMS spectra of **3f**



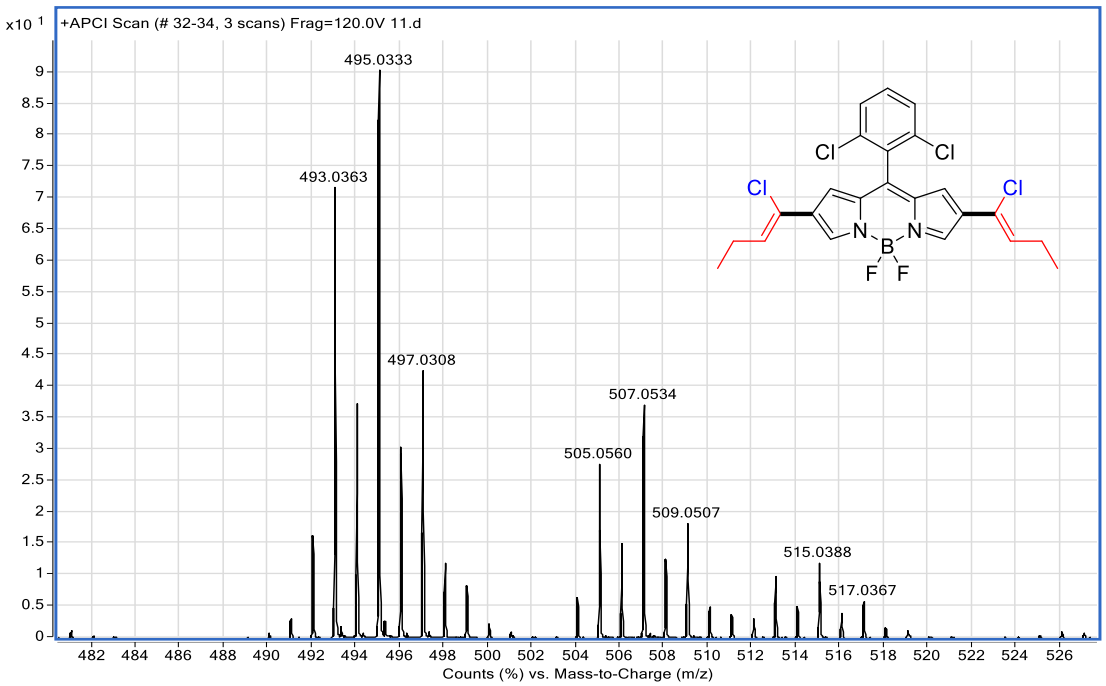
HRMS spectra of **3g**



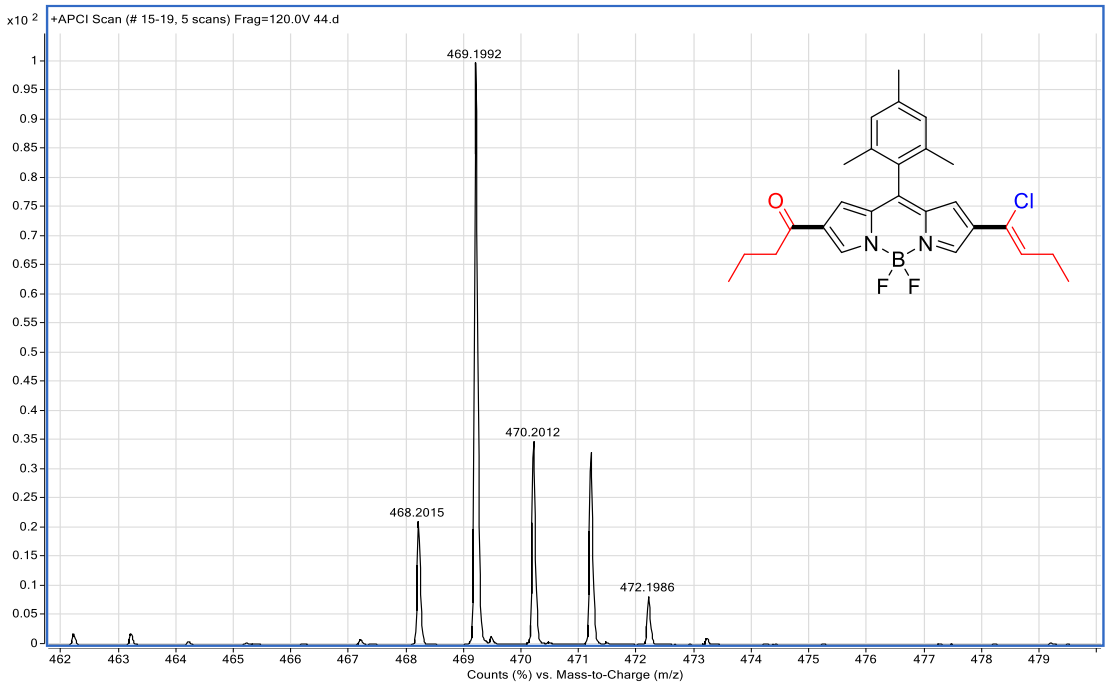
HRMS spectra of **3h**



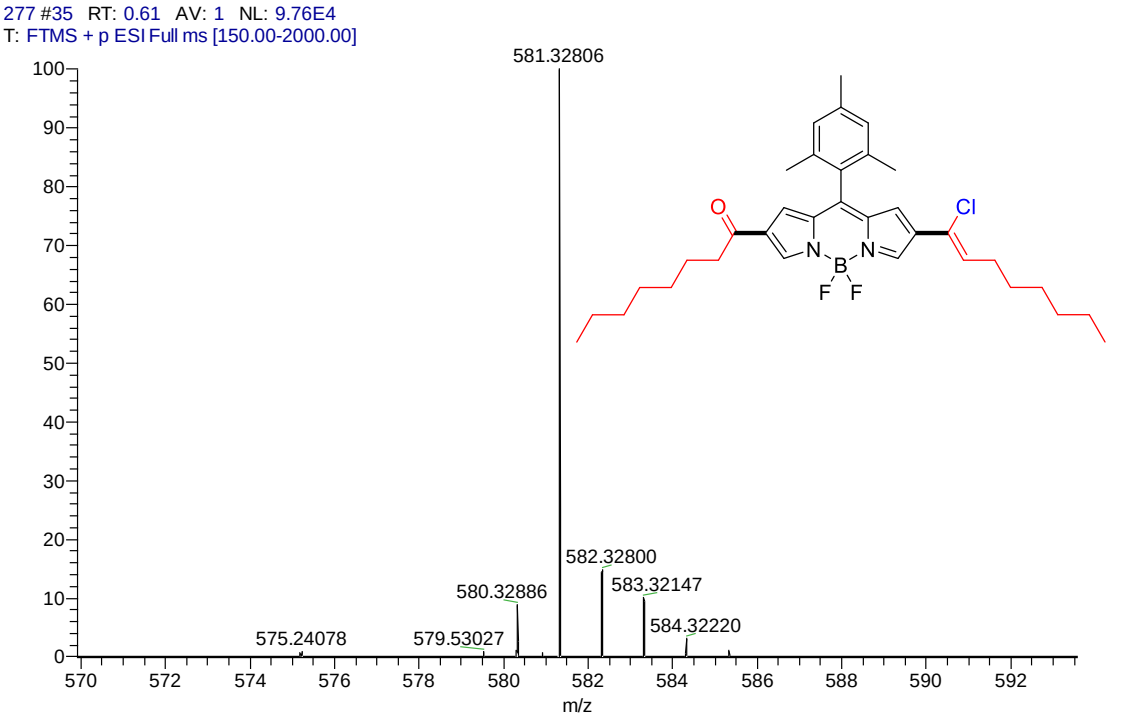
HRMS spectra of **3i**



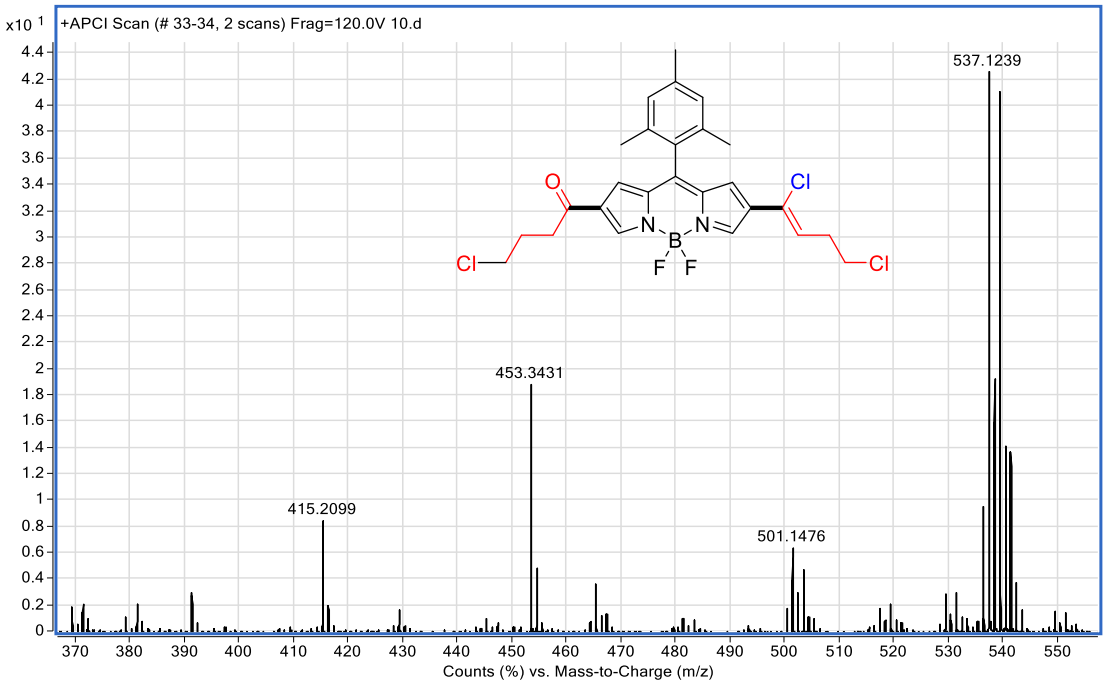
HRMS spectra of **4a**



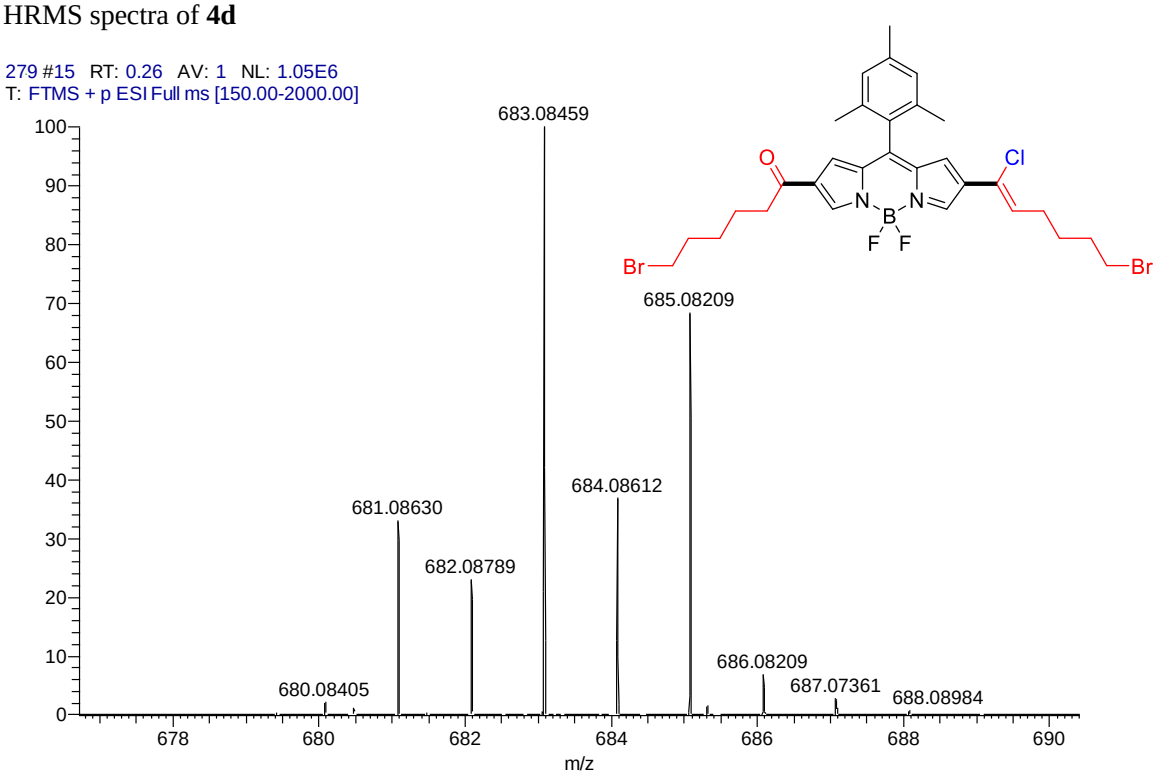
HRMS spectra of **4b**



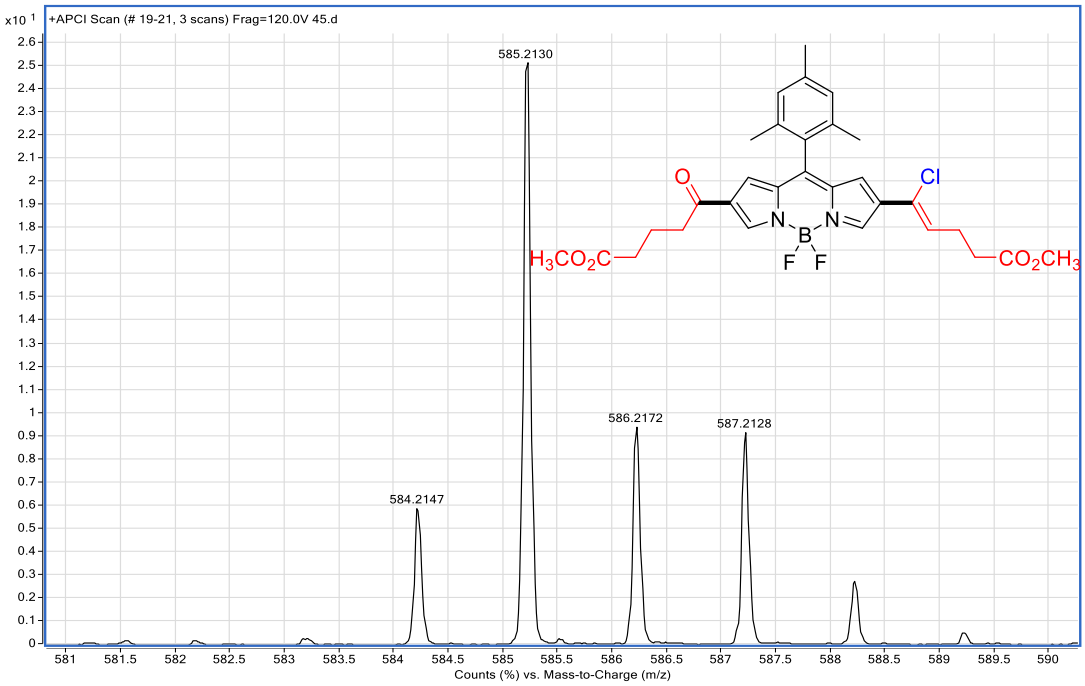
HRMS spectra of **4c**



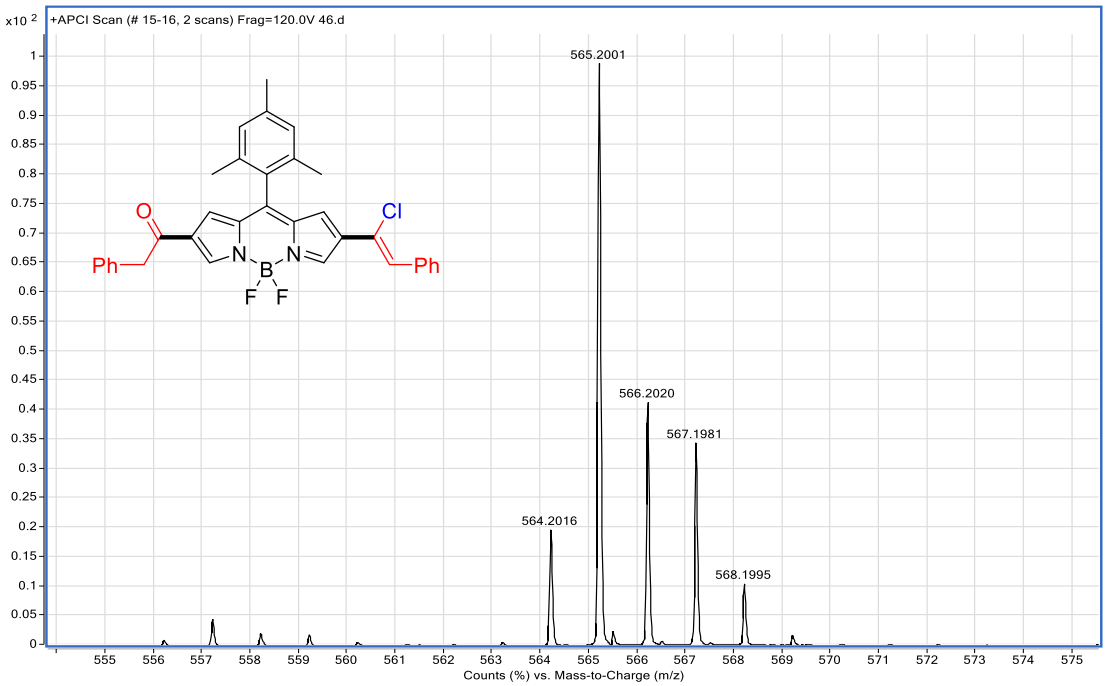
HRMS spectra of **4d**



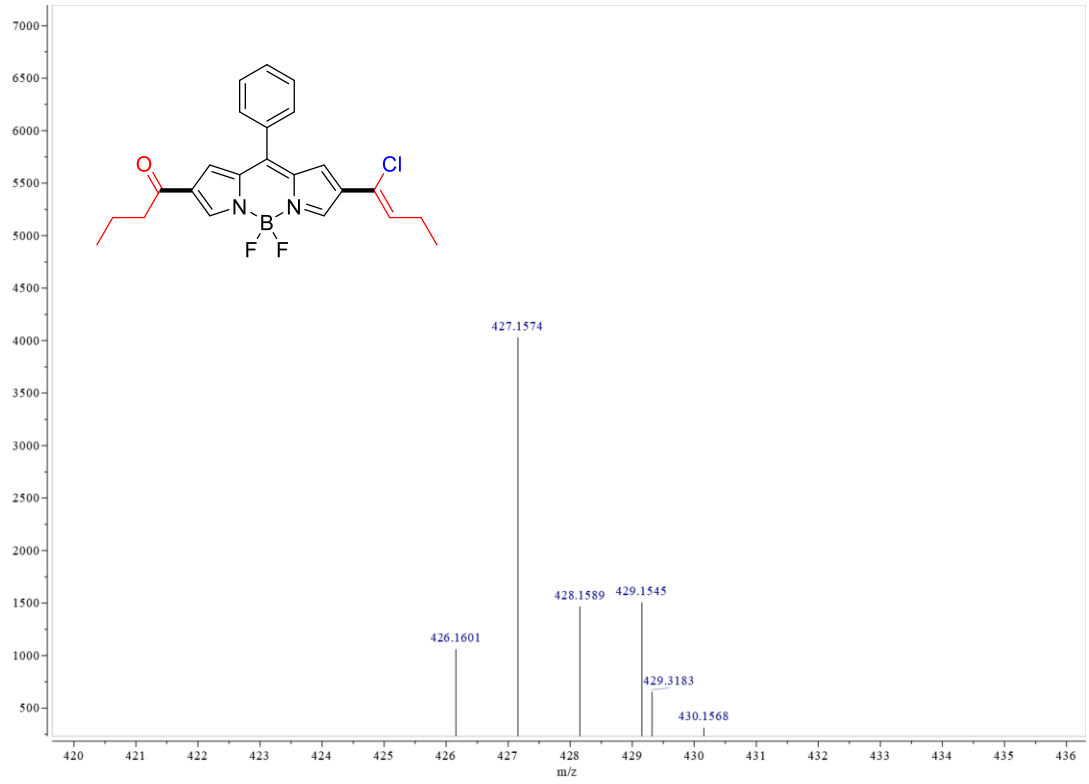
HRMS spectra of **4e**



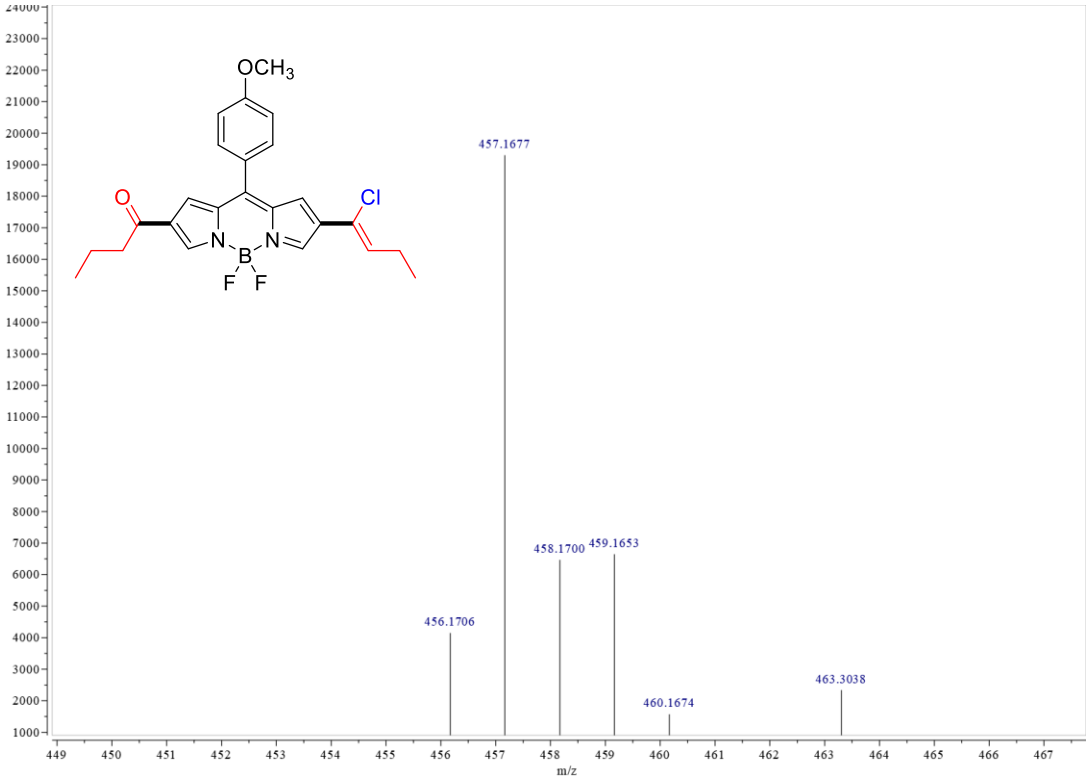
HRMS spectra of **4f**



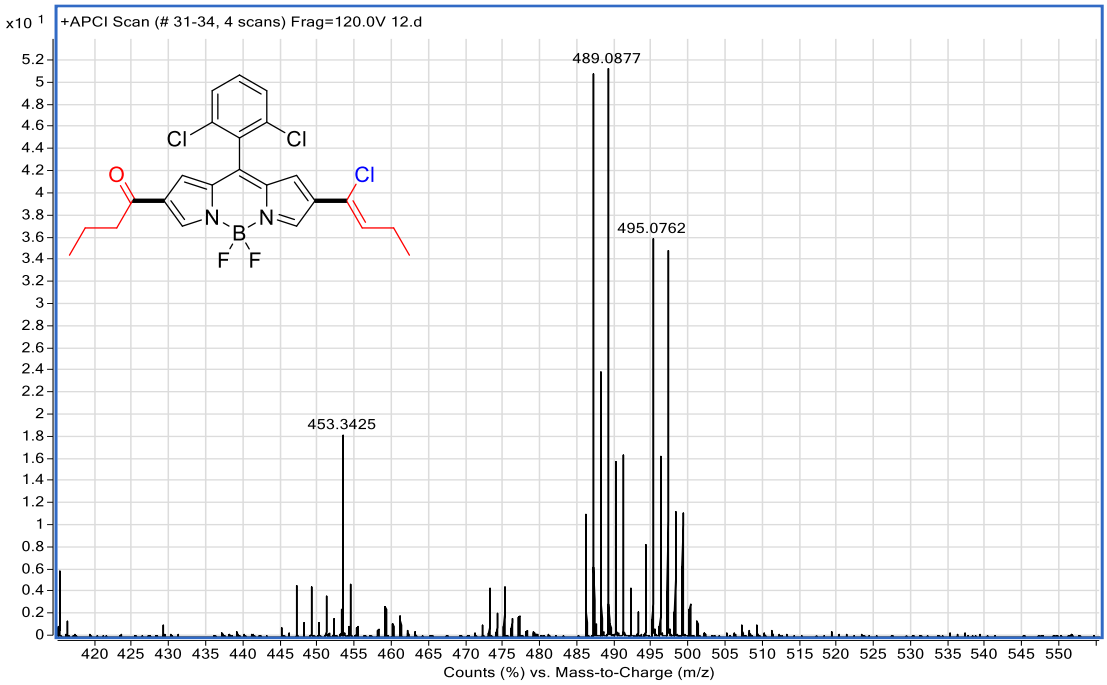
HRMS spectra of **4g**



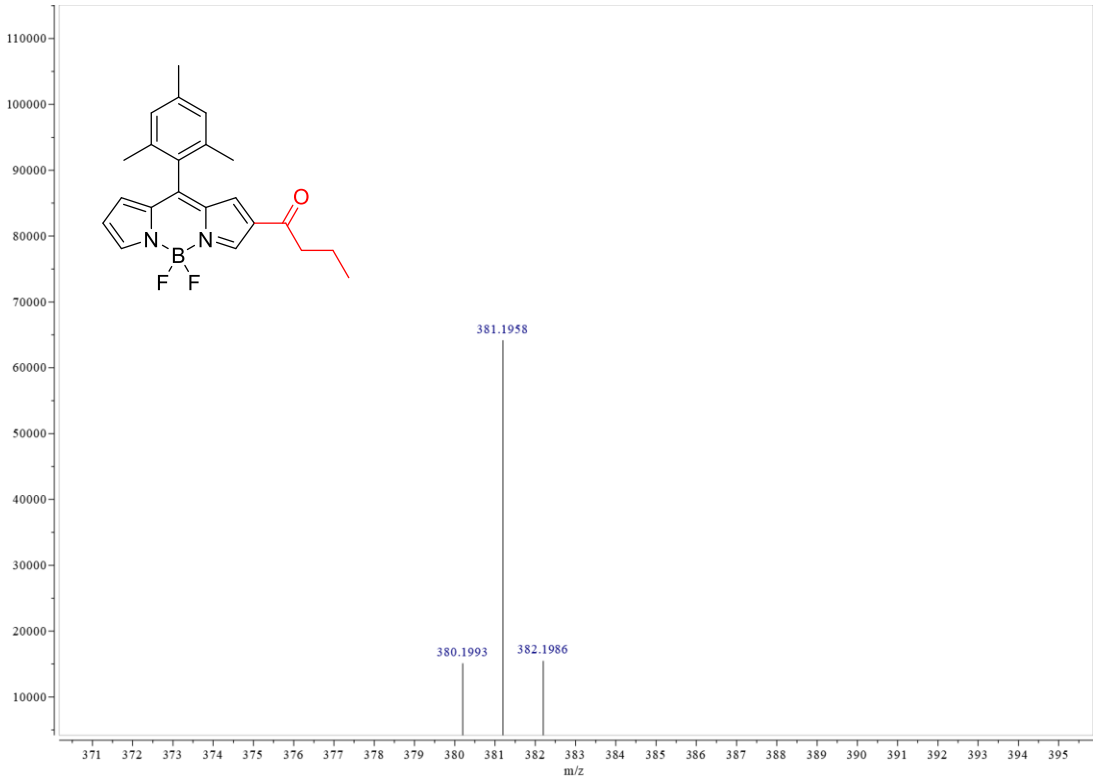
HRMS spectra of **4h**



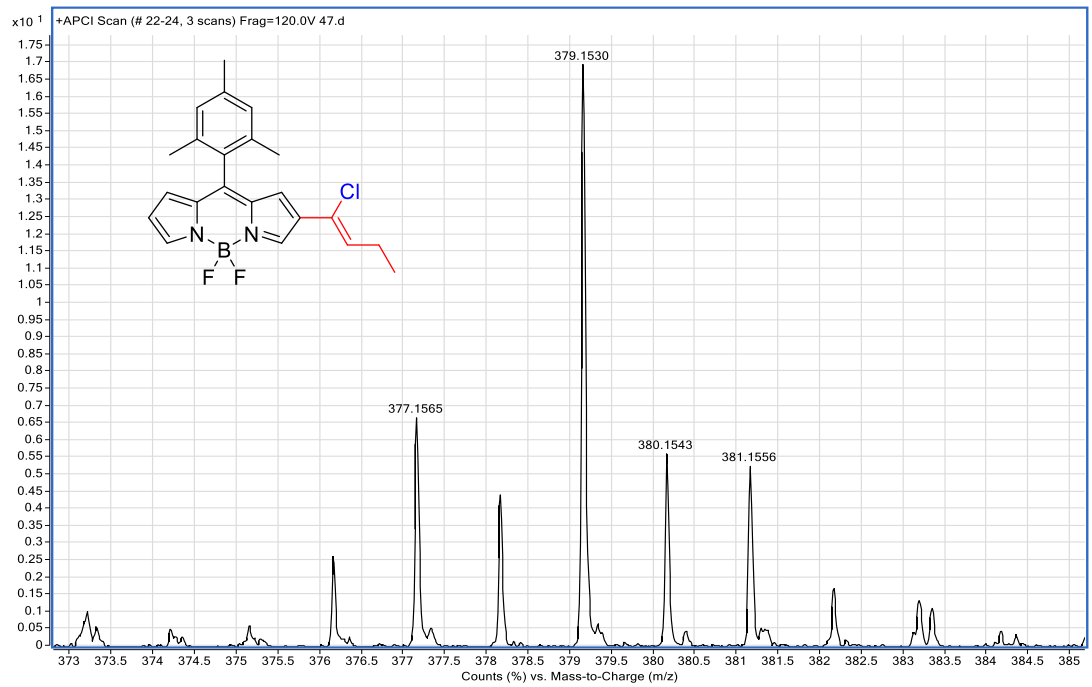
HRMS spectra of **4i**



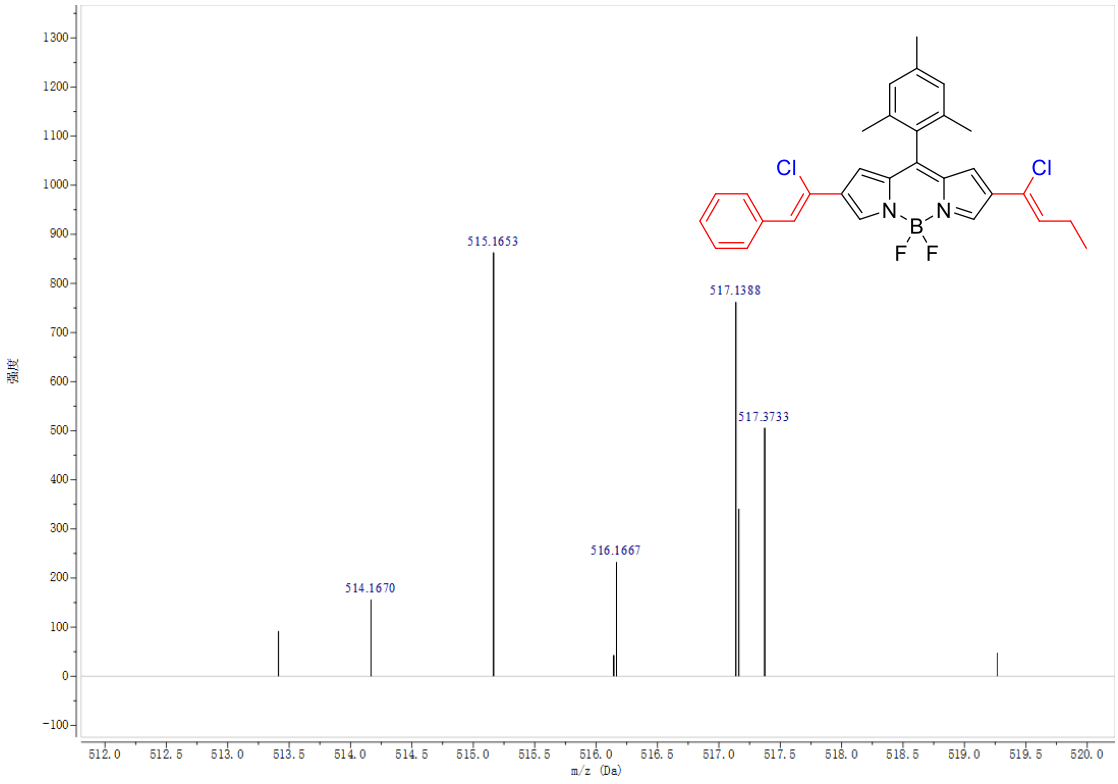
HRMS spectra of **5**



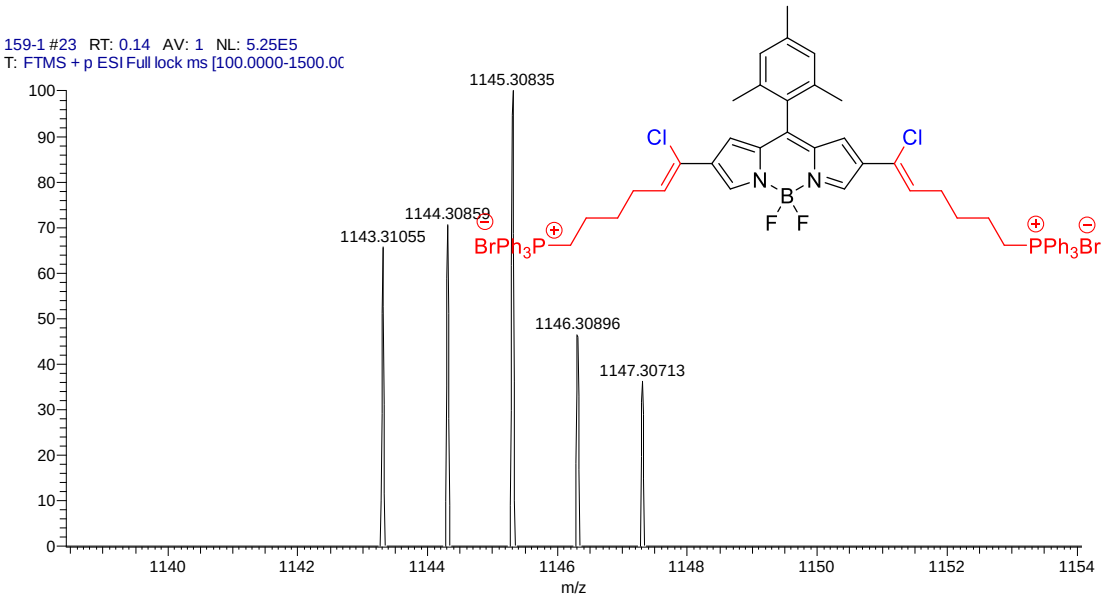
HRMS spectra of **6**



HRMS spectra of **7**



HRMS spectra of **3d-p**



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