Supporting Information for

Silver-Mediated, Direct Phosphorylation of BODIPY dyes at the 3- or 3,5-positions with H-Phosphonates

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1. Experimental details

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 and ESI in positive mode.

Absorption and emission measurements. 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 fluorescein (Φ = 0.90 in 0.1 M NaOH aqueous solution.[1] 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[2]:

$$\Phi_x = \Phi_r \times \frac{F_x}{F_r} \times \frac{1 - 10^{-A_r(\lambda_{ex})}}{1 - 10^{-A_x(\lambda_{ex})}} \times \frac{n_x^2}{n_r^2}$$

The subscripts *x* and *r* refer respectively to our sample *x* and reference (standard) fluorophore *r* with known quantum yield Φ_r in a specific solvent, F stands for the spectrally corrected, integrated fluorescence spectra, $A(\lambda_{ex})$ denotes the absorbance at the used excitation wavelength λ_{ex}, and *n* represents the refractive index of the solvent (in principle at the average emission wavelength).

X-ray structure analysis. Crystals of compounds **4a** suitable for X-ray analysis were obtained *via* the slow diffusion of methanol 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[3] 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,[4] 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,[5] incorporated in SHELXTL V5.10.[6] CCDC-2084364 (**4a**), 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.

Theoretical calculations. The ground state geometry was optimized by using DFT method at B3LYP/6-31G(d) level. The same method was used for vibrational analysis to verify that the optimized structures correspond to local minima on the energy surface. The calculated molecules in dichloromethane were done using the Self-Consistent Reaction Field (SCRF) method and Polarizable Continuum Model (PCM). All of the calculations were carried out by the methods implemented in Gaussian 09 package.[7]

2. Chemical structures of 1a-d and 2a-g

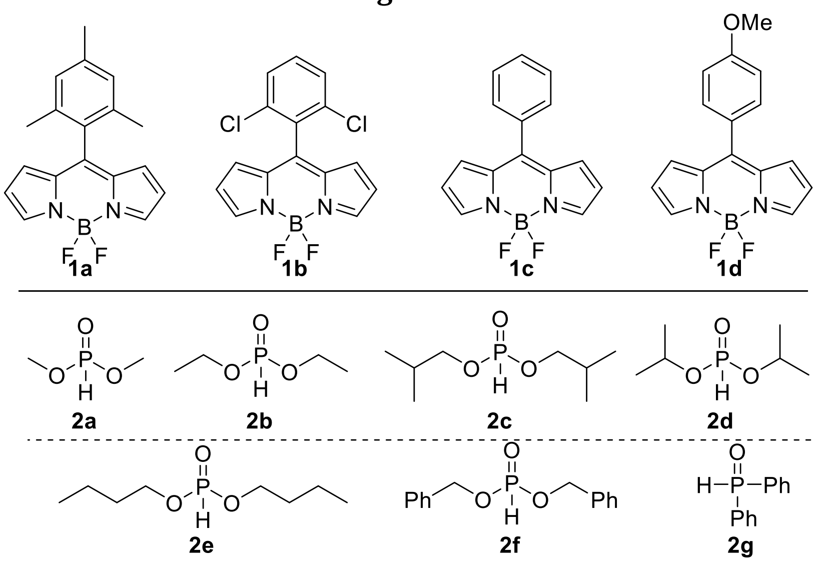
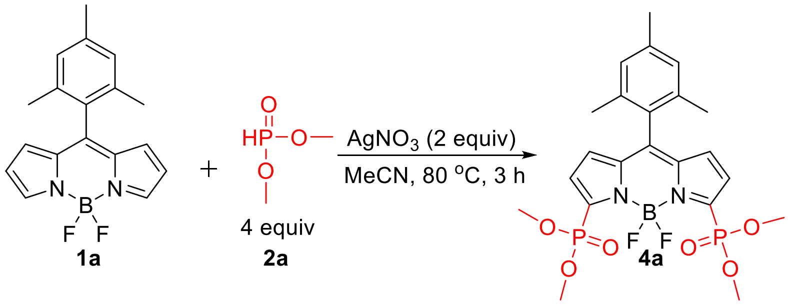


Figure S1. Chemical structure of BODIPYs **1a-d** and various H-phosphonates **2a-g**.

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

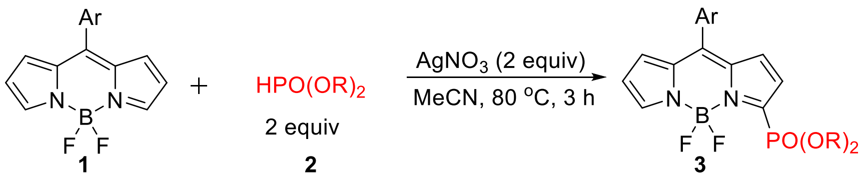


entry	**2a** (equiv)	yield (%)[b]
1	2.0	0[c]
2	3.0	34
3	**4.0**	**65**
4	5.0	64

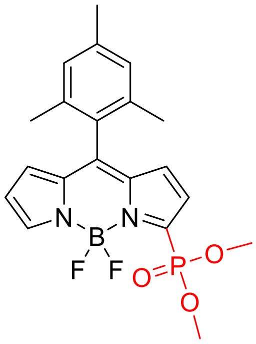
[a]Reaction condition: **1a** (0.1 mmol), $AgNO_3$ (0.4 mmol), MeCN (1 mL). [b]Isolated yields based on **1a**. [c]The reaction time was extended to 6 h.

4. Synthesis and characterization

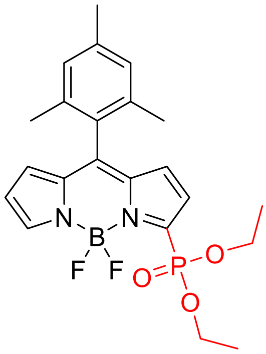
4.1 Synthesis of mono-phosphonation of BODIPYs



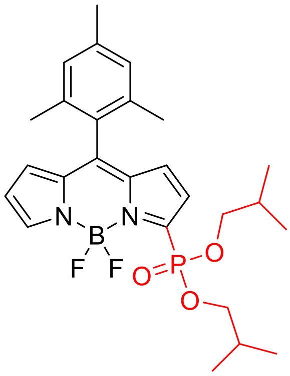
We are using **3a** (R = methoxyl, Ar = mesityl) as an example to show the **general procedure for the preparation of mono-phosphonation of BODIPYs 3a-i:** BODIPY **1a** (60 mg, 0.2 mmol), dimethyl phosphonate **2a** (0.036 mL, 0.4 mmol), $AgNO_3$ (67 mg, 0.4 mmol) were dissolved in 2 mL acetonitrile. The reaction mixture was stirred at 80 °C for 3 h under argon. 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; 5:1-3:1, v/v).



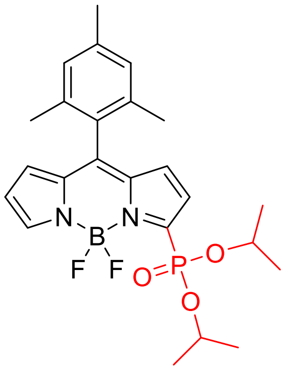
BODIPY **3a** was prepared in 56% yield (46 mg) from **1a** (60 mg, 0.2 mmol) and **2a** (0.036 mL, 0.4 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 6.99 (s, 1H), 6.97 (s, 2H), 6.87 (d, J = 4.4 Hz, 1H), 6.62 (d, J = 4.4 Hz, 1H), 6.58 – 6.56 (m, 1H), 3.93 (d, J = 11.4 Hz, 6H), 3.91 (s, 3H), 2.37 (s, 3H), 2.09 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1, 149.5, 140.6 (d, J = 216.1 Hz), 139.3, 138.7 (d, J = 17.2 Hz), 137.5, 136.2, 133.4, 129.4, 128.4, 126.9 (d, J = 14.1 Hz), 126.6 (d, J = 16.2 Hz), 121.8, 53.6 (d, J = 5.6 Hz), 21.2, 20.1; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 9.76; **HRMS** (ESI) m/z calcd for $C_{20}H_{23}BF_2N_2O_3P^+$ $(M+H)^+$ 419.1507, found 419.1505.



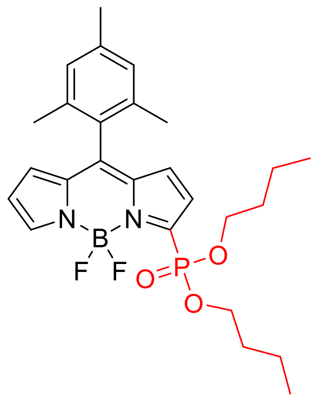
BODIPY **3b** was prepared in 60% yield (53 mg) from **1a** (60 mg, 0.2 mmol) and **2b** (0.051 mL, 0.4 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 6.97 (s, 1H), 6.96 (s, 2H), 6.84 (d, J = 4.3 Hz, 1H), 6.60 (d, J = 4.2 Hz, 1H), 6.57 – 6.55 (m, 1H), 4.37 – 4.23 (m, 4H), 2.36 (s, 3H), 2.09 (s, 6H), 1.42 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.7, 149.4, 142.4 (d, J = 214.1 Hz), 139.3, 138.7 (d, J = 14.1 Hz), 137.3, 136.2, 133.1, 129.5, 128.3, 127.0 (d, J = 13.1 Hz), 126.4 (d, J = 18.2 Hz), 121.5, 63.1 (d, J = 5.6 Hz), 21.2, 20.1, 16.3 (d, J = 6.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 6. 77; **HRMS** (APCI) m/z calcd for $C_{22}H_{27}BF_2N_2O_3P^+$ $(M+H)^+$ 447.1820, found 447.1806.



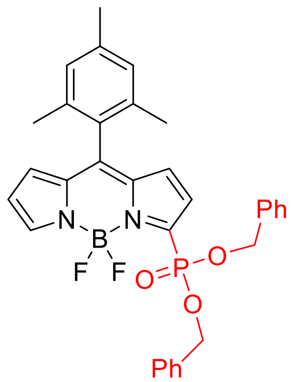
BODIPY **3c** was prepared in 59% yield (59 mg) from **1a** (60 mg, 0.2 mmol) and **2c** (0.079 mL, 0.4 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$) *δ* 8.13 (s, 1H), 6.96 (s, 2H), 6.94 (s, 1H), 6.83 (d, *J* = 4.4 Hz, 1H), 6.59 (d, *J* = 4.3 Hz, 1H), 6.57 – 6.55 (m, 1H), 4.05 – 3.94 (m, 4H), 2.36 (s, 3H), 2.09 (s, 6H), 2.07 – 2.03 (m, 2H), 1.00 – 0.97 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 149.6, 149.2, 142.6 (d, *J* = 214.1 Hz), 139.2, 138.6 (d, *J* = 15.2 Hz), 137.3, 136.2, 132.9, 129.5, 128.4, 127.0 (d, *J* = 12.1 Hz), 126.2 (d, *J* = 20.2 Hz), 121.4, 72.9 (d, *J* = 6.3 Hz), 29.3 (d, *J* = 6.5 Hz), 21.1, 20.1, 18.8 (d, *J* = 2.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 6.75; **HRMS** (APCI) m/z calcd for $C_{26}H_{35}BF_2N_2O_3P^+$ $(M+H)^+$ 503.2446, found 503.2429.



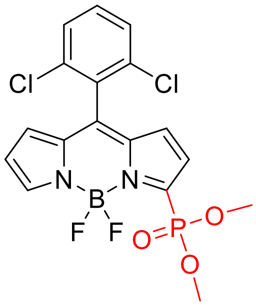
BODIPY **3d** was prepared in 62% yield (58 mg) from **1a** (60 mg, 0.2 mmol) and **2d** (0.067 mL, 0.4 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.11 (s, 1H), 6.96 (s, 2H), 6.94 (s, 1H), 6.81 (d, *J* = 4.3 Hz, 1H), 6.58 (d, *J* = 4.3 Hz, 1H), 6.55 – 6.54 (m, 1H), 4.95 – 4.87 (m, 2H), 2.36 (s, 3H), 2.08 (s, 6H), 1.45 (d, *J* = 6.2 Hz, 6H), 1.36 (d, *J* = 6.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 149.3, 149.2, 144.4 (d, *J* = 214.1 Hz), 139.2, 138.6 (d, *J* = 14.1 Hz), 137.1, 136.2, 132.7, 129.6, 128.3, 127.0 (d, *J* = 11.1 Hz), 126.0 (d, *J* = 18.2 Hz), 121.2, 72.0 (d, *J* = 5.9 Hz), 24.2 (d, *J* = 4.2 Hz), 23.7 (d, *J* = 5.2 Hz), 21.1, 20.0; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 4. 26; **HRMS** (APCI) m/z calcd for $C_{24}H_{31}BF_2N_2O_3P^+$ $(M+H)^+$ 475.2133, found 475.2119.



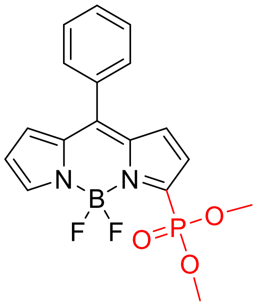
BODIPY **3e** was prepared in 58% yield (58 mg) from **1a** (60 mg, 0.2 mmol) and **2e** (0.081 mL, 0.4 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.04 (s, 1H), 6.88 (s, 3H), 6.75 (d, *J* = 4.3 Hz, 1H), 6.52 (d, *J* = 4.3 Hz, 1H), 6.49 – 6.47 (m, 1H), 4.21 – 4.07 (m, 4H), 2.28 (s, 3H), 2.01 (s, 6H), 1.71 – 1.64 (m, 4H), 1.41 – 1.32 m, 4H), 0.85 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 149.6, 149.3, 142.7 (d, *J* = 214.1 Hz), 139.2, 138.6 (d, *J* = 15.2 Hz), 137.3, 136.2, 132.9, 129.5, 128.3, 127.0 (d, *J* = 12.1 Hz), 126.3 (d, *J* = 18.2 Hz), 121.4, 66.8 (d, *J* = 5.9 Hz), 32.5 (d, *J* = 6.4 Hz), 21.1, 20.0, 18.7, 13.6; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 6.78; **HRMS** (APCI) m/z calcd for $C_{26}H_{35}BF_2N_2O_3P^+$ $(M+H)^+$ 503.2446, found 503.2440.



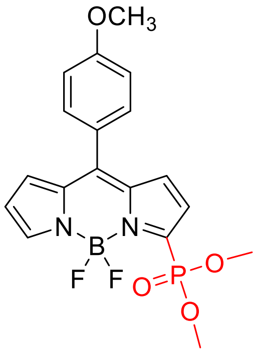
BODIPY **3f** was prepared in 61% yield (69 mg) from **1a** (60 mg, 0.2 mmol) and **2f** （0.088 mL, 0.4 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.16 (s, 1H), 7.43 – 7.41 (m, 4H), 7.34 – 7.26 (m, 6H), 6.95 (s, 2H), 6.87 (s, 1H), 6.83 (d, *J* = 4.4 Hz, 1H), 6.60 (d, *J* = 4.3 Hz, 1H), 6.52 – 6.50 (m, 1H), 5.27 – 5.17 (m, 4H), 2.35 (s, 3H), 2.07 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 150.1, 149.3, 141.6 (d, *J* = 218.2 Hz), 139.3, 138.7 (d, *J* = 16.2 Hz), 137.5, 136.3 (d, *J* = 6.1 Hz), 136.2, 133.2, 129.4, 128.5, 128.4, 128.3, 128.2, 126.8 (d, *J* = 13.1 Hz), 126.1 (d, *J* = 17.2 Hz), 121.7, 68.5 (d, *J* = 5.5 Hz), 21.2, 20.1; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 7.49; **HRMS** (APCI) m/z calcd for $C_{32}H_{31}BF_2N_2O_3P^+$ $(M+H)^+$ 571.2133, found 571.2136.



BODIPY **3g** was prepared in 51% yield (44 mg) from **1b** (67 mg, 0.2 mmol) and **2a** (0.036 mL, 0.4 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.19 (s, 1H), 7.51-7.43 (m, 3H), 7.02 – 7.01 (m, 1H), 6.88 (d, *J* = 4.5 Hz, 1H), 6.67 (d, *J* = 4.5 Hz, 1H), 6.59-6.57 (m, 1H), 3.92 (d, *J* = 11.5 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 151.7, 142.2, 141.5 (d, *J* = 215.1 Hz), 137.7 (d, *J* = 17.2 Hz), 137.3, 135.0, 133.2, 131.7, 130.9, 128.4, 126.9 (d, *J* = 21.2 Hz), 126.6 (d, *J* = 12.1 Hz), 122.5, 53.6 (d, *J* = 5.1 Hz); ; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 9.30; **HRMS** (APCI) m/z calcd for $C_{17}H_{15}BCl_2F_2N_2O_3P^+$ $(M+H)^+$ 445.0258, found 445.0244.

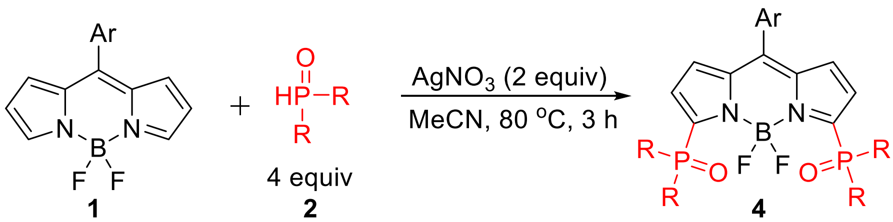


BODIPY **3h** was prepared in 53% yield (36 mg) from **1c** (54 mg, 0.2 mmol) and **2a** (0.036 mL, 0.4 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.17 (s, 1H), 7.64 – 7.55 (m, 5H), 7.10 (s, 2H), 6.87 – 6.85 (m, 1H), 6.70 (d, *J* = 4.2 Hz, 1H), 3.91 (d, *J* = 11.5 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 149.8, 148.8, 140.5 (d, *J* = 215.1 Hz), 138.6, 136.8, 134.8, 133.5, 131.3, 130.6, 128.6, 128.4 (d, *J* = 13.1 Hz), 127.0 (d, *J* = 20.2 Hz), 121.6, 53.5 (d, *J* = 5.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 9.79; **HRMS** (APCI) m/z calcd for $C_{17}H_{17}BF_2N_2O_3P^+$ $(M+H)^+$ 377.1038, found 377.1039.

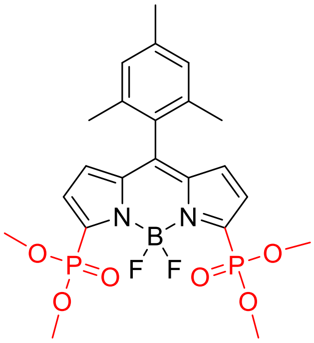


BODIPY **3i** was prepared in 58% yield (46 mg) from **1d** (59 mg, 0.2 mmol) and **2a** (0.036 mL, 0.4 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.13 (s, 1H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 3.8 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.92 – 6.90 (m, 1H), 6.69 (d, *J* = 4.4 Hz, 1H), 3.92 (d, *J* = 3.8 Hz, 6H), 3.89 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 162.6, 148.9, 148.8, 139.6 (d, *J* = 230.3 Hz), 137.6 (d, *J* = 214.1 Hz), 134.5, 132.7, 131.4, 128.2 (d, *J* = 13.1 Hz), 127.0 (d, *J* = 18.2 Hz), 126.1, 121.3, 114.3, 55.6, 53.5 (d, *J* = 5.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 10.11; **HRMS** (APCI) m/z calcd for $C_{18}H_{19}BF_2N_2O_4P^+$ $(M+H)^+$ 407.1144, found 407.1169.

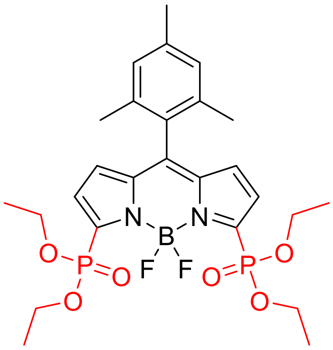
4.2 Synthesis of di-phosphonation of BODIPYs



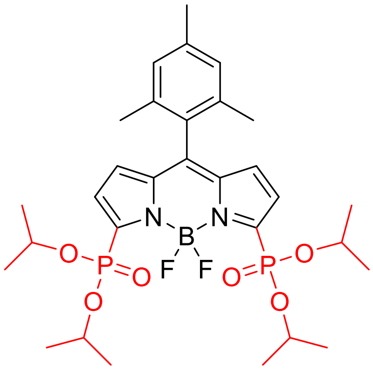
We are using **4a** (R = methoxyl, Ar = mesityl) as an example to show the **general procedure for the preparation of di-phosphonation of BODIPYs 4a-g:** BODIPY **1a** (60 mg, 0.2 mmol), dimethyl phosphonate **2a** (0.072 mL, 0.8 mmol) and $AgNO_3$ (67 mg, 0.4 mmol) were dissolved in 2 mL acetonitrile. The reaction mixture was stirred at 80 °C for 3 h under argon. Upon completion, the reaction mixture was cooled to room temperature and was poured into dichloromethane (100 mL), washed three times with water (100 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatographically (silica; petroleum ether/ethyl acetate; 1:1-1:2, v/v)



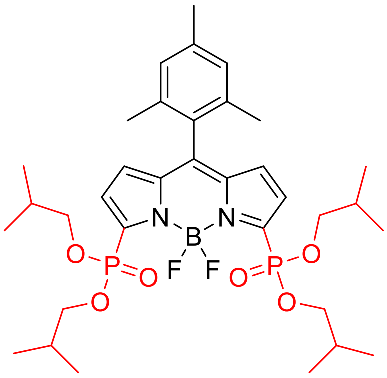
BODIPY **4a** was prepared in 65% yield (68 mg) from **1a** (60 mg, 0.2 mmol) and **2a** (0.072 mL, 0.8 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.04 (d, *J* = 2.9 Hz, 2H), 6.97 (s, 2H), 6.77 – 6.75 (m, 2H), 3.95 (d, *J* = 11.5 Hz, 12H), 2.37 (s, 3H), 2.08 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 153.1, 147.6 (d, *J* = 212.1 Hz), 139.9 (d, *J* = 17.2 Hz), 139.7, 136.1, 130.6 (d, *J* = 11.1 Hz), 129.4, 128.4, 128.0 (d, *J* = 18.2 Hz), 53.9 (d, *J* = 5.9 Hz), 21.1, 20.1; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 7. 68; **HRMS** (APCI) m/z calcd for $C_{22}H_{28}BF_2N_2O_6P_2^+$ $(M+H)^+$ 527.1484, found 527.1499.



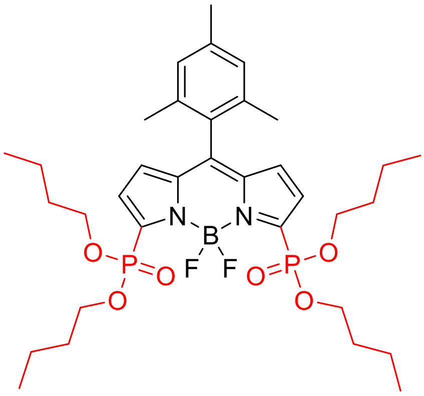
BODIPY **4b** was prepared in 67% yield (77 mg) from **1a** (60 mg, 0.2 mmol) and **2b** (0.102 mL, 0.8 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.02 (d, *J* = 4.0 Hz, 2H), 6.96 (s, 2H), 6.74 – 6.72 (m, 2H), 4.38 – 4.27 (m, 8H), 2.36 (s, 3H), 2.08 (s, 6H), 1.42 (t, *J* = 7.1 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 152.6, 148.7 (d, *J* = 212.1 Hz), 139.8 (d, *J* = 16.2 Hz), 139.6, 136.1, 130.3 (d, *J* = 11.1 Hz), 129.5, 128.4, 127.8 (d, *J* = 19.2 Hz), 63.6 (d, *J* = 5.8 Hz), 21.1, 20.1, 16.3 (d, *J* = 6.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 4.87; **HRMS** (APCI) m/z calcd for $C_{26}H_{36}BF_2N_2O_6P_2^+$ $(M+H)^+$ 583.2110, found 583.2094.



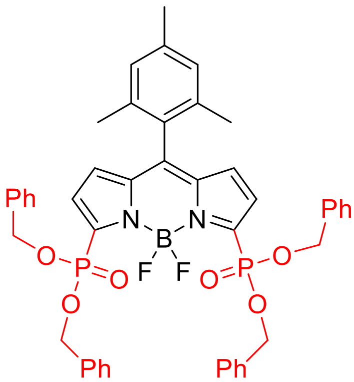
BODIPY **4c** was prepared in 68% yield (86 mg) from **1a** (60 mg, 0.2 mmol) and **2d** (0.134 mL, 0.8 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (d, J = 4.1 Hz, 2H), 6.95 (s, 2H), 6.70 – 6.68 (m, 2H), 4.98 – 4.90 (m, 4H), 2.36 (s, 3H), 2.07 (s, 6H), 1.45 (d, J = 6.2 Hz, 12H), 1.39 (d, J = 6.2 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.2, 150.0 (d, J = 213.1 Hz), 139.9 (d, J = 16.2 Hz), 139.4, 136.2, 130.0 (d, J = 11.1 Hz), 129.7, 128.3, 127.6 (d, J = 17.2 Hz), 72.5 (d, J = 6.3 Hz), 24.1 (d, J = 4.5 Hz), 23.8 (d, J = 5.1 Hz), 21.1, 20.1; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 2.67; **HRMS** (APCI) m/z calcd for $C_{30}H_{44}BF_2N_2O_6P_2^+$ $(M+H)^+$ 639.2736, found 639.2743.



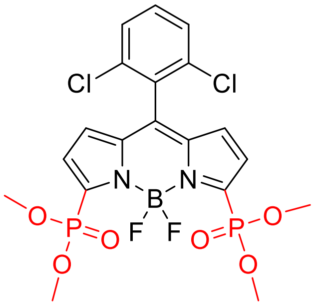
BODIPY **4d** was prepared in 62% yield (86 mg) from **1a** (60 mg, 0.2 mmol) and **2c** (0.158 mL, 0.8 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 – 7.01 (m, 2H), 6.96 (s, 2H), 6.72 (s, 2H), 4.08 – 3.95 (m, 8H), 2.36 (s, 3H), 2.07 (s, 6H), 2.05 – 2.00 (m, 4H), 0.98 (d, J = 6.7 Hz, 24H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.4, 148.7 (d, J = 212.1 Hz), 139.8 (d, J = 16.2 Hz), 139.5, 136.2, 130.2 (d, J = 11.1 Hz), 129.6, 128.3, 127.9 (d, J = 18.2 Hz), 73.3 (d, J = 6.6 Hz), 29.2 (d, J = 6.5 Hz), 21.1, 20.1, 18.8; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 4.95; **HRMS** (APCI) m/z calcd for $C_{34}H_{52}BF_2N_2O_6P_2^+$ $(M+H)^+$ 695.3362, found 695.3321.



BODIPY **4e** was prepared in 65% yield (90 mg) from **1a** (60 mg, 0.2 mmol) and **2e** (0.160 mL, 0.8 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.02 (d, *J* = 3.0 Hz, 2H), 6.96 (s, 2H), 6.73 – 6.71 (m, 2H), 4.32 – 4.19 (m, 8H), 2.36 (s, 3H), 2.08 (s, 6H), 1.79 – 1.72 (m, 8H), 1.50 – 1.41 (m, 8H), 0.94 (t, *J* = 7.4 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 152.4, 148.7 (d, *J* = 211.1 Hz), 139.8 (d, *J* = 16.2 Hz), 139.5, 136.1, 130.2 (d, *J* = 11.1 Hz), 129.6, 128.4, 127.9 (d, *J* = 17.2 Hz), 67.2 (d, *J* = 6.2 Hz), 32.5 (d, *J* = 6.4 Hz), 21.1, 20.1, 18.7, 13.6; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 5.01; **HRMS** (APCI) m/z calcd for $C_{34}H_{52}BF_2N_2O_6P_2^+$ $(M+H)^+$ 695.3362, found 695.3382.

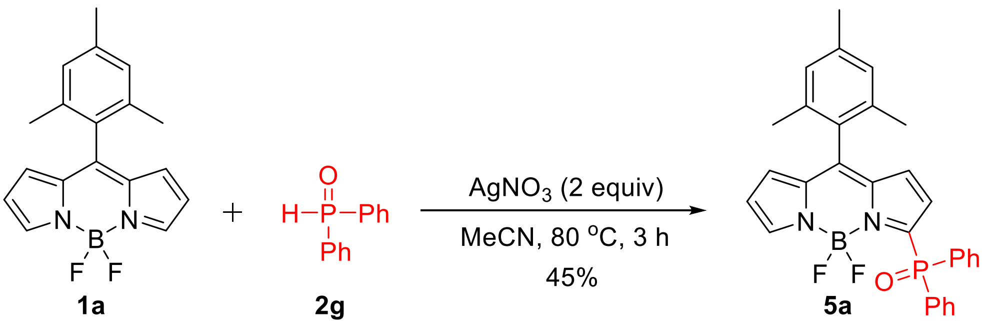


BODIPY **4f** was prepared in 63% yield (104 mg) from **1a** (60 mg, 0.2 mmol) and **2f** (0.176 mL, 0.8 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.38 – 7.26 (m, 20H), 6.95 (s, 4H), 6.69 (s, 2H), 5.26 – 5.15 (m, 8H), 2.35 (s, 3H), 2.07 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 152.8, 148.3 (d, *J* = 213.1 Hz), 139.9 (d, *J* = 16.2 Hz), 139.6, 136.2, 136.1, 130.4 (d, *J* = 11.1 Hz), 129.5, 128.5, 128.4, 128.3, 128.2, 127.8 (d, *J* = 18.2 Hz), 68.9 (d, *J* = 5.1 Hz), 21.2, 20.2; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 5.59; **HRMS** (APCI) m/z calcd for $C_{46}H_{44}BF_2N_2O_6P_2^+$ $(M+H)^+$ 831.2736, found 831.2741.

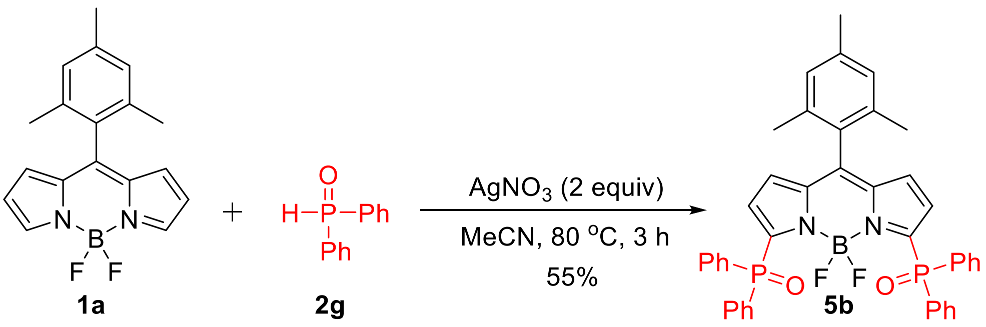


BODIPY **4g** was prepared in 57% yield (62 mg) from **1b** (67 mg, 0.2 mmol) and **2a** (0.072 mL, 0.8 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 3H), 7.07 (d, J = 4.3 Hz, 2H), 6.78 – 6.76 (m, 2H), 3.96 (d, J = 11.5 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1, 146.6 (d, J = 289.9 Hz), 139.3 (d, J = 17.2 Hz), 134.9, 131.9, 130.8, 130.4 (d, J = 11.1 Hz), 128.5 (d, J = 10.1 Hz), 128.4, 54.0 (d, J = 5.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 7. 17; **HRMS** (APCI) m/z calcd for $C_{19}H_{20}BCl_2F_2N_2O_6P_2^+$ $(M+H)^+$ 553.0235, found 553.0247.

4.3 Synthesis of phosphorylated BODIPYs 5a and 5b

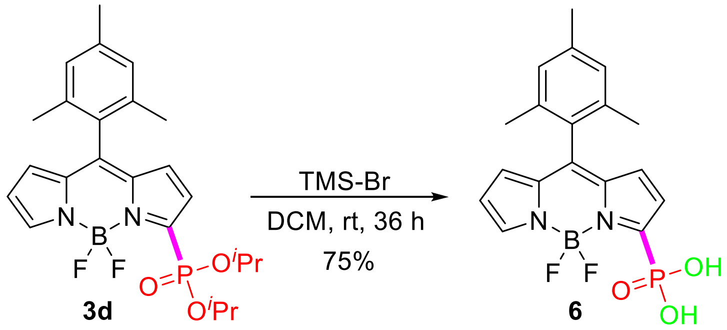


BODIPY **1a** (60 mg, 0.2 mmol), dimethyl phosphonate **2g** (80 mg, 0.4 mmol), $AgNO_3$ (67 mg, 0.4 mmol) were dissolved in 2 mL acetonitrile. The reaction mixture was stirred at 80 °C for 3 h under argon. Upon completion, the reaction mixture was cooled to room temperature and was poured into dichloromethane (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; 3:1, v/v) to obtained BODIPY **5a** in 45% yield (45 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.84 – 7.79 (m, 4H), 7.58 – 7.46 (m, 6H), 6.96 (s, 2H), 6.80 (d, J = 4.3 Hz, 1H), 6.54 (d, J = 4.4 Hz, 1H), 6.49 – 6.48 (m, 1H), 6.30 – 6.28 (m, 1H), 2.36 (s, 3H), 2.08 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 148.9, 139.5, 139.3, 137.6, 136.2, 133.1, 132.8, 132.1 (d, J = 10.1 Hz), 132.0 (d, J = 3.3 Hz), 131.7, 129.4, 128.3 128.2, 126.7 (d, J = 19.2 Hz), 126.1 (d, J = 12.1 Hz), 121.7, 21.2, 20.1; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 19.80; **HRMS** (APCI) m/z calcd for $C_{30}H_{27}BF_2N_2OP^+$ $(M+H)^+$ 511.1922, found 511.1924.



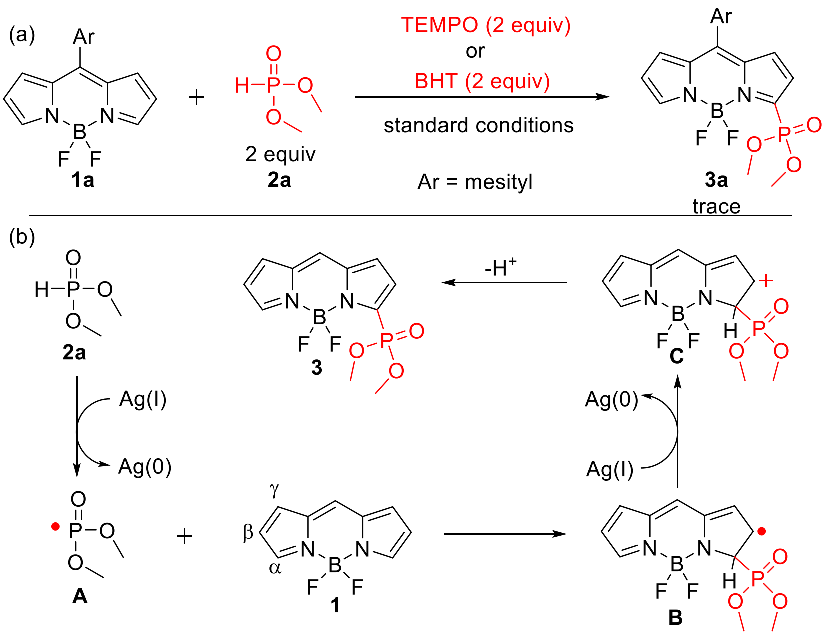
BODIPY **1a** (60 mg, 0.2 mmol), dimethyl phosphonate **2g** (160 mg, 0.8 mmol), $AgNO_3$ (67 mg, 0.4 mmol) were dissolved in 2 mL acetonitrile. The reaction mixture was stirred at 80 °C for 3 h under argon. Upon completion, the reaction mixture was cooled to room temperature and was poured into dichloromethane (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; 1:1, v/v) to obtain BODIPY **5b** in 55% yield (78 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 8H), 7.53 – 7.50 (m, 4H), 7.42 – 7.38 (m, 8H), 6.95 (s, 2H), 6.69 (s, 4H), 2.35 (s, 3H), 2.07 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.6 (d, J = 105.0 Hz), 152.46, 140.8 (d, J = 10.1 Hz), 139.7, 136.2, 132.3, 132.2, 131.7 (d, J = 10.1 Hz), 131.2, 130.1 (d, J = 9.1 Hz), 129.3, 128.7 (d, J = 13.1 Hz), 128.4, 128.3 (d, J = 13.1 Hz), 128.2, 21.1, 20.3; **^{31}P NMR** (162 MHz, $CDCl_3$, δ ppm): 20.72; **HRMS** (APCI) m/z calcd for $C_{42}H_{35}BF_2N_2O_2P_2^+$ $(M+H)^+$ 711.2313, found 711.2316.

4.4 Synthesis of phosphoric acid 6



BODIPY **3d** (47 mg, 0.1 mmol) and bromotrimethylsilane (0.026 mL, 0.2 mmol) were dissolved in 3 mL dry dichloromethane at room temperature and the resulting mixture was stirred for 36 h. Upon completion, the reaction mixture was evaporated to dryness, and the residue was purified by column chromatographically (silica; dichloromethane/ methanol; 10:1, v/v) to obtain BODIPY **6** in 75% yield (29 mg). **^{1}H NMR** (400 MHz, D_2O) δ 8.14 (s, 1H), 7.08 (s, 2H), 6.90 (d, J = 3.7 Hz, 1H), 6.83 – 6.79 (m, 1H), 6.68 (dd, J = 11.5, 4.4 Hz, 2H), 2.32 (s, 3H), 2.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 137.3, 134.9 (d, J = 14.7 Hz), 134.7 (d, J = 12.5 Hz), 134.6, 130.6, 130.1, 129.9, 129.1, 127.8 (d, J = 4.9 Hz), 127.7, 124.9, 116.9, 12.1, 9.4; **^{31}P NMR** (162 MHz, D_2O, δ ppm): 1.09; **HRMS** (ESI) m/z calcd for $C_{18}H_{19}BF_2N_2O_3P^+$ $(M+H)^+$ 391.1189, found 391.1187.

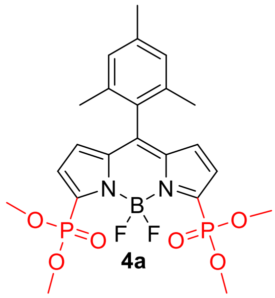
5. Reaction mechanism



Scheme S1. Proposed reaction mechanism.

6. Crystal data

Table S2. Selected Geometrical Parameters of **4a** obtained from crystallography



4a

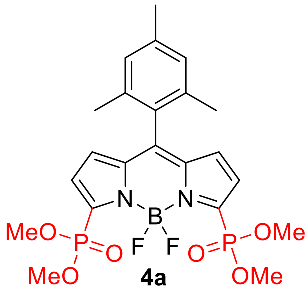
	4a
B-N bond distances (Å)	1.5757(25) 1.5783(24)
C-P bond distances (Å)	1.8052(19) 1.7965(20)
dihedral angles between *meso*-mesityl group and dipyrrin core (deg)	88.147(55)
dihedral angles of two pyrrole rings in dipyrrin core (deg)	5.435(35)

Table S3. Selected Geometrical Parameters of **4a** obtained from crystallography

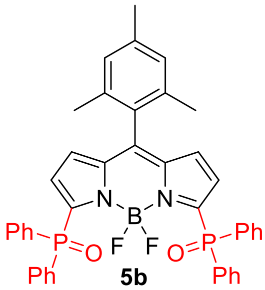
Empirical formula	$C_{22}H_{27}BF_2N_2O_6P_2$
Formula weight	526.20
Temperature/K	298.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.4985(5)
b/Å	15.0627(5)
c/Å	11.9448(4)
α/°	90
β/°	107.7800(10)
γ/°	90
Volume/Å^3	2483.99(15)
Z	4
ρ_{calc}g/cm^3	1.407
μ/mm^{-1}	0.231
F(000)	1096.0
Crystal size/mm^3	0.21 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.942 to 55.12
Index ranges	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -15 ≤ l ≤ 15
Reflections collected	119295
Independent reflections	5704 [R_{int} = 0.0726, R_{sigma} = 0.0207]
Data/restraints/parameters	5704/0/323
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1305
Final R indexes [all data]	R_1 = 0.0589, wR_2 = 0.1404
Largest diff. peak/hole / e Å^{-3}	0.84/-0.57

7. Photophysical properties

7.1 Table S4: Photophysical properties of 4a and 5b in different solvents at room temperature.



4a



5b

dyes	Solvent	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	$\log\varepsilon_{max}$ [a]	Φ[b]	Stokes shift (cm^{-1})
4a	cyclohexane	520	535	4.83	0.61	540
	toluene	522	537	4.81	0.55	570
	CH_3CN	516	531	4.79	0.48	620
	MeOH	516	529	5.08	0.08	550
	DMSO	519	532	4.78	0.01	570
5b	cyclohexane	534	549	4.63	0.37	510
	toluene	536	550	4.59	0.33	470
	CH_3CN	528	542	4.74	0.29	490
	MeOH	528	543	5.01	0.09	420
	DMSO	530	542	4.66	0.06	450

[a]Molar absorption coefficient at λ_{bs}^{max}. [b]Fluorescence quantum yields determined using fluorescein (Φ = 0.90 in 0.1 M NaOH aqueous solution) as standard. [c]Stokes shift values rounded to nearest 10 cm^{-1}. λ_{em}= 500 nm.

7.2 UV-vis absorption and fluorescence emission spectra of 4a and 5b recorded in various solvents.

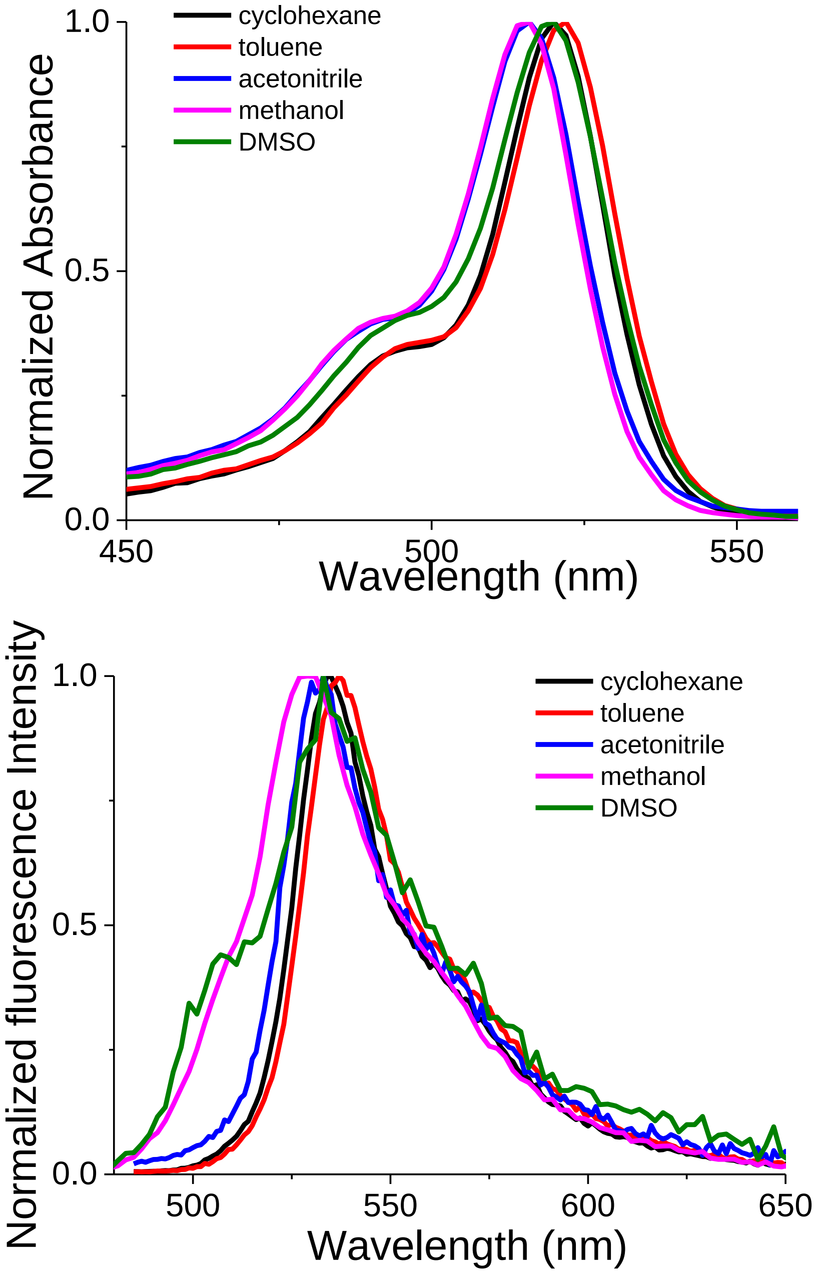
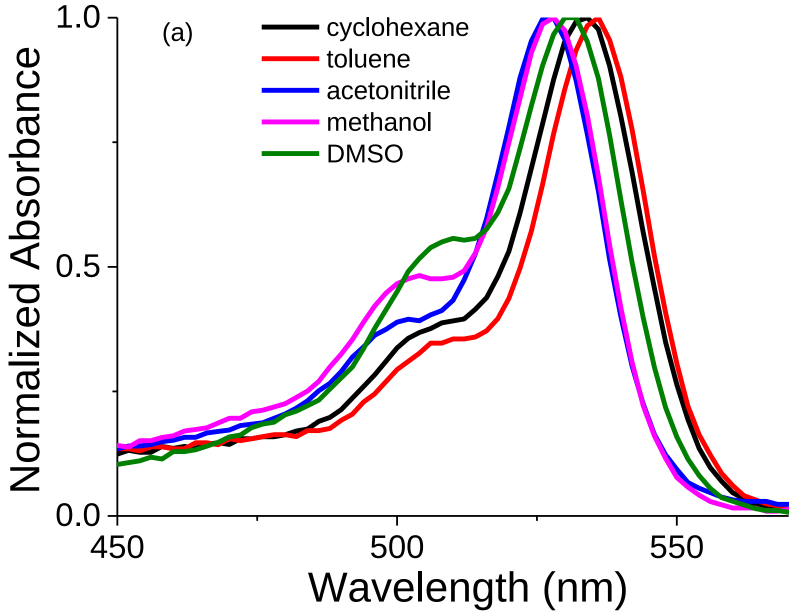


Figure S2. Absorption (a) and fluorescence emission (b) spectra of **4a** recorded in different solvents (excitation at 500 nm).



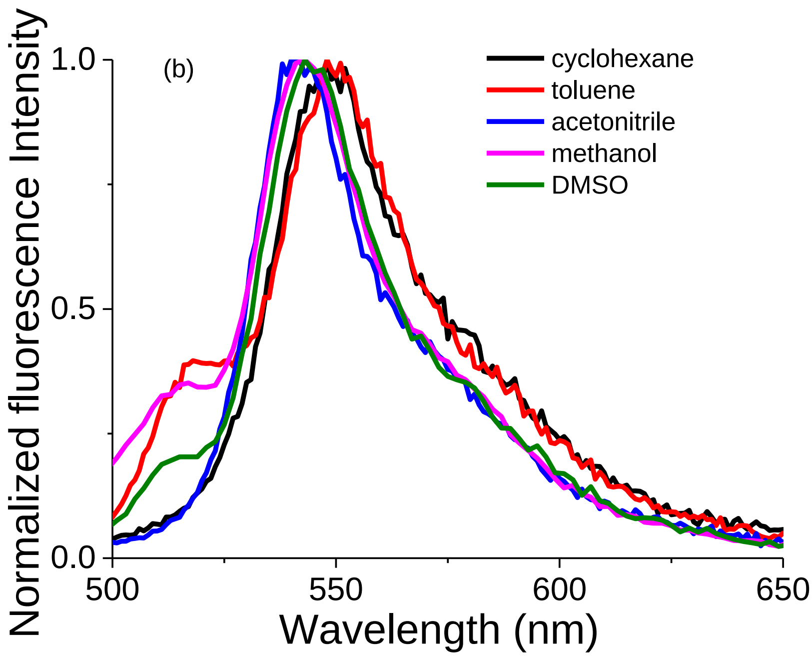


Figure S3. Absorption (a) and fluorescence emission (b) spectra of **5b** recorded in different solvents (excitation at 500 nm).

7.3 UV-Vis absorption and fluorescence emission spectra in CH_2Cl_2

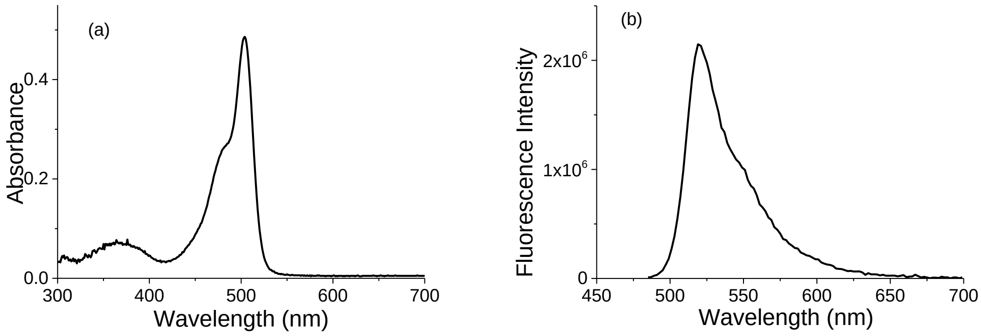


Figure S4. Absorption (a) and fluorescence emission (b) spectra of **3a** recorded in CH_2Cl_2 (excitation at 480 nm).

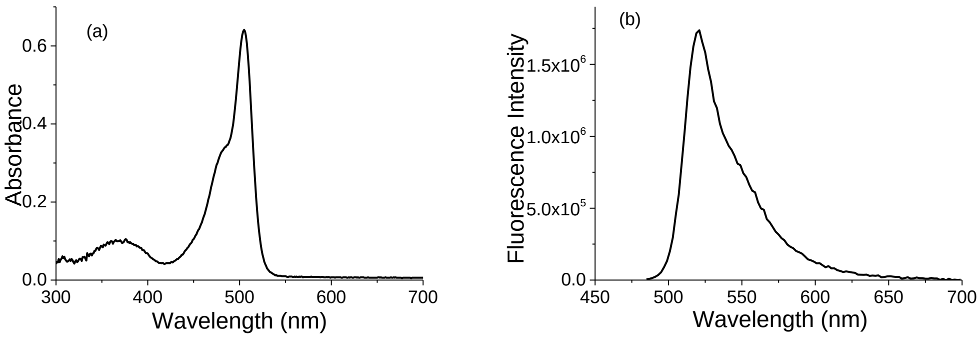


Figure S5. Absorption (a) and fluorescence emission (b) spectra of **3b** recorded in CH_2Cl_2 (excitation at 480 nm).

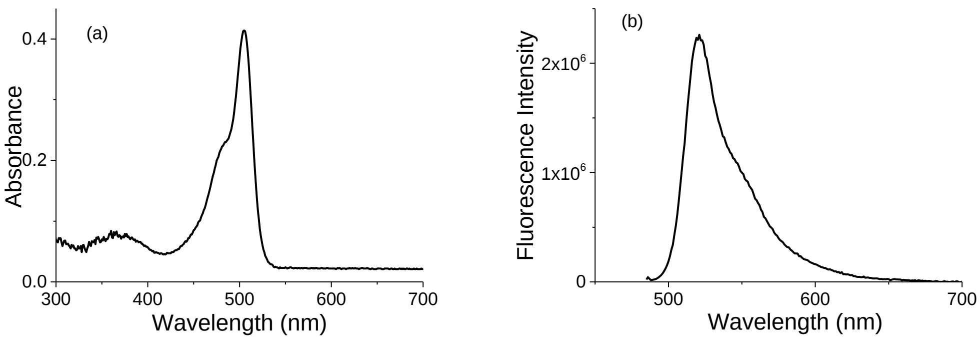


Figure S6. Absorption (a) and fluorescence emission (b) spectra of **3c** recorded in CH_2Cl_2 (excitation at 480 nm).

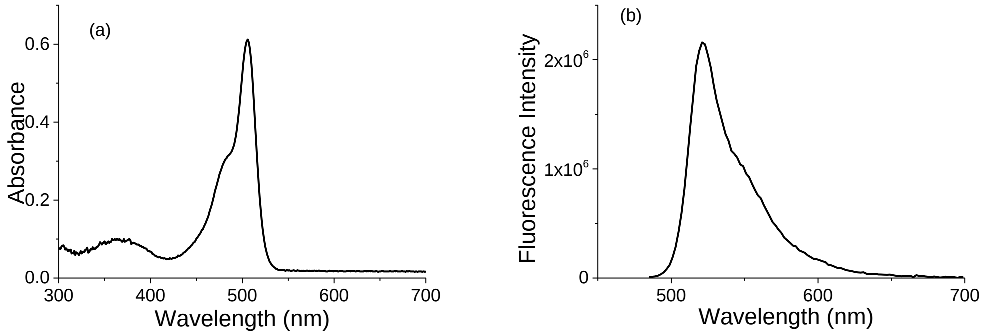


Figure S7. Absorption (a) and fluorescence emission (b) spectra of **3d** recorded in CH_2Cl_2 (excitation at 480 nm).

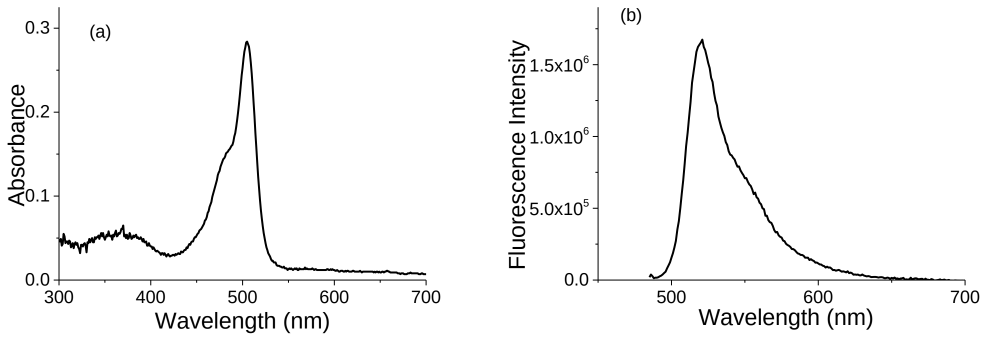


Figure S8. Absorption (a) and fluorescence emission (b) spectra of **3e** recorded in CH_2Cl_2 (excitation at 480 nm).

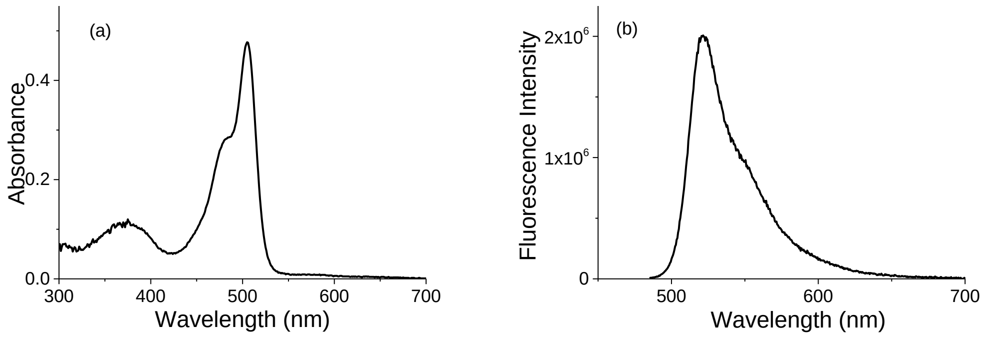


Figure S9. Absorption (a) and fluorescence emission (b) spectra of **3f** recorded in CH_2Cl_2 (excitation at 480 nm).

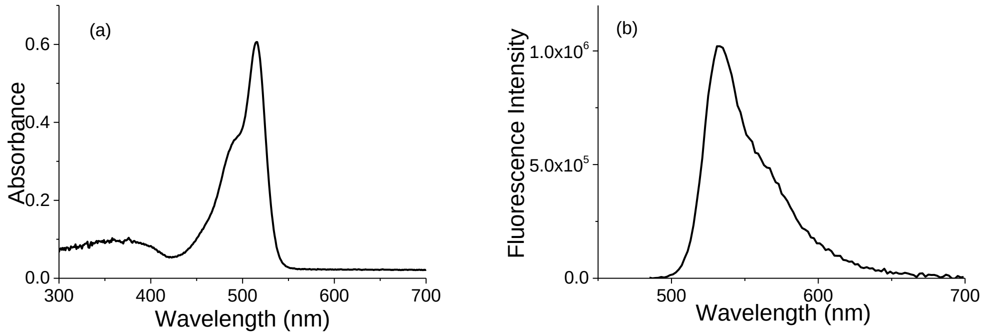


Figure S10. Absorption (a) and fluorescence emission (b) spectra of **3g** recorded in CH_2Cl_2 (excitation at 480 nm).

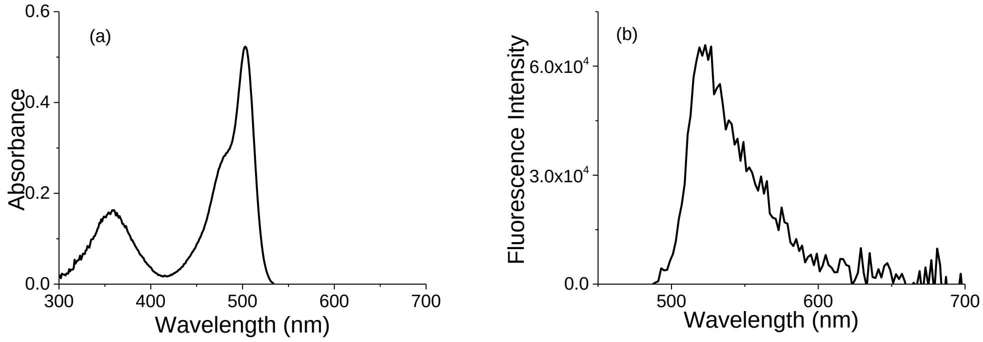


Figure S11. Absorption (a) and fluorescence emission (b) spectra of **3h** recorded in CH_2Cl_2 (excitation at 480 nm).

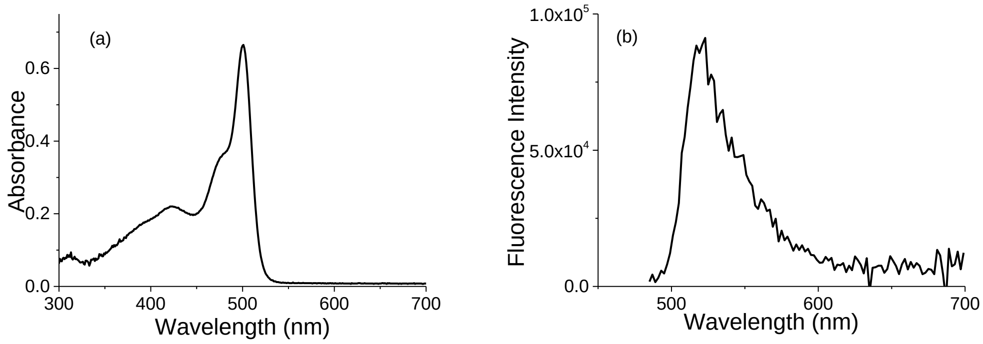


Figure S12. Absorption (a) and fluorescence emission (b) spectra of **3i** recorded in CH_2Cl_2 (excitation at 480 nm).

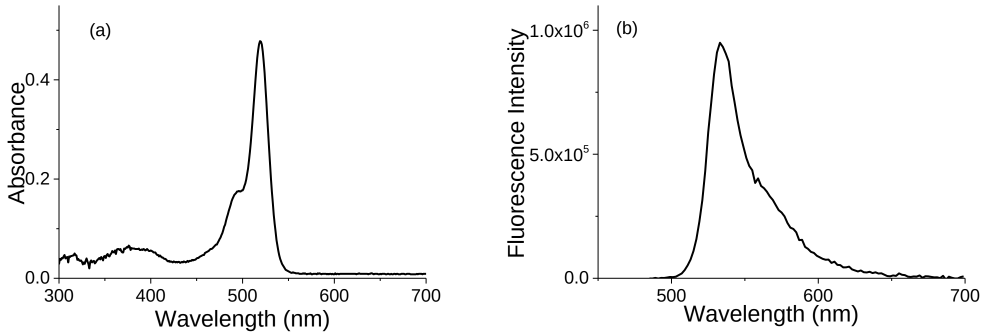


Figure S13. Absorption (a) and fluorescence emission (b) spectra of **4a** recorded in CH_2Cl_2 (excitation at 500 nm).

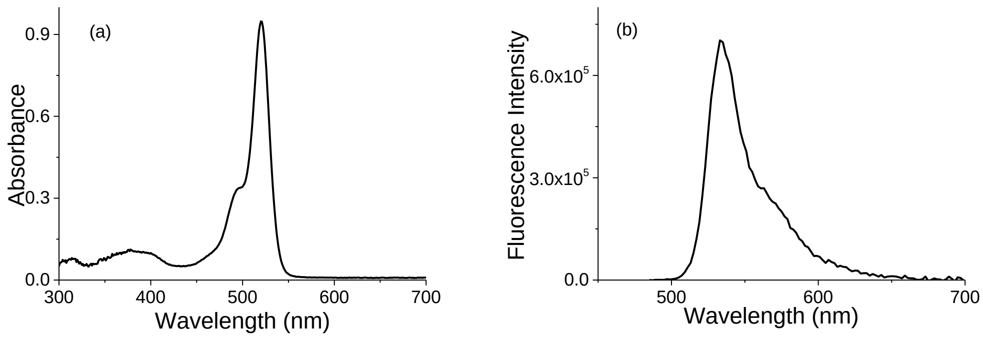


Figure S14. Absorption (a) and fluorescence emission (b) spectra of **4b** recorded in CH_2Cl_2 (excitation at 500 nm).

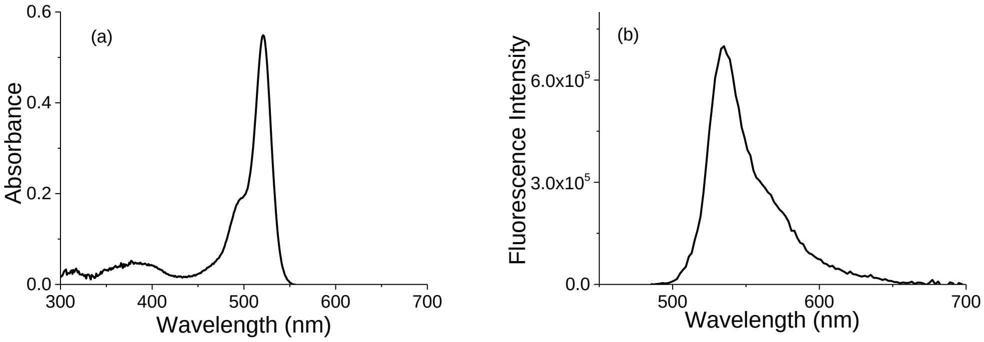


Figure S15. Absorption (a) and fluorescence emission (b) spectra of **4c** recorded in CH_2Cl_2 (excitation at 500 nm).

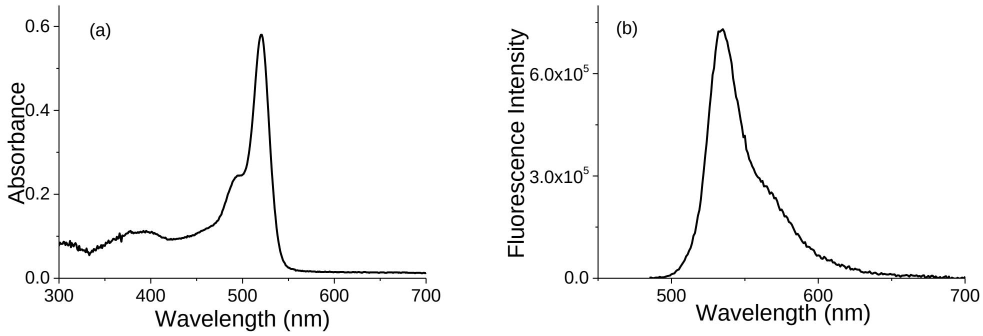


Figure S16. Absorption (a) and fluorescence emission (b) spectra of **4d** recorded in CH_2Cl_2 (excitation at 500 nm).

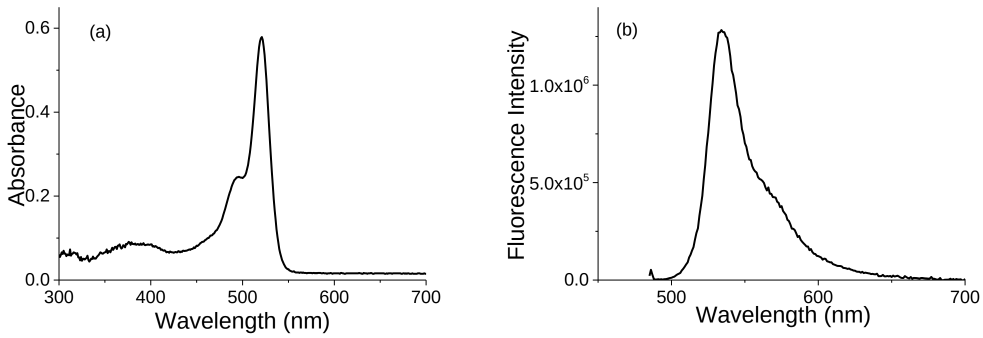


Figure S17. Absorption (a) and fluorescence emission (b) spectra of **4e** recorded in CH_2Cl_2 (excitation at 500 nm).

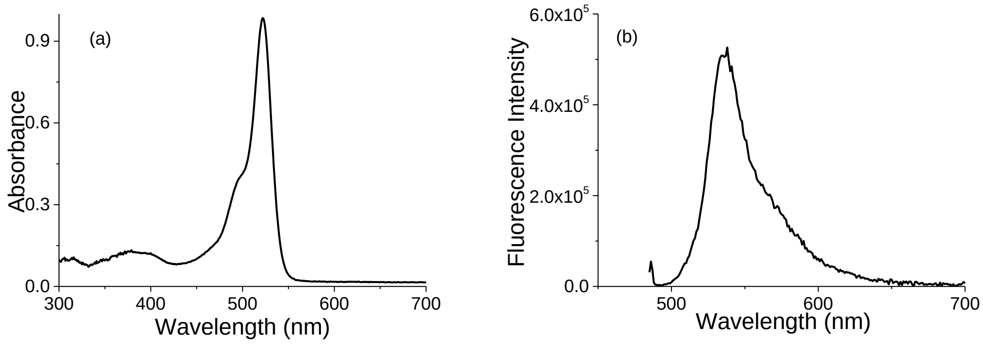


Figure S18. Absorption (a) and fluorescence emission (b) spectra of **4f** recorded in CH_2Cl_2 (excitation at 500 nm).

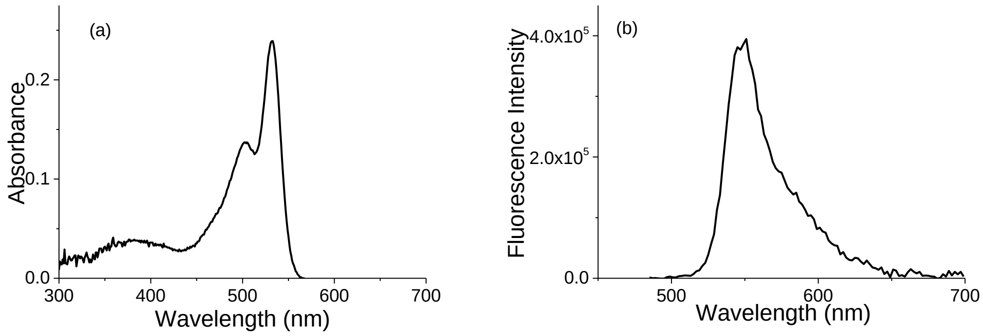


Figure S19. Absorption (a) and fluorescence emission (b) spectra of **4g** recorded in CH_2Cl_2 (excitation at 500 nm).

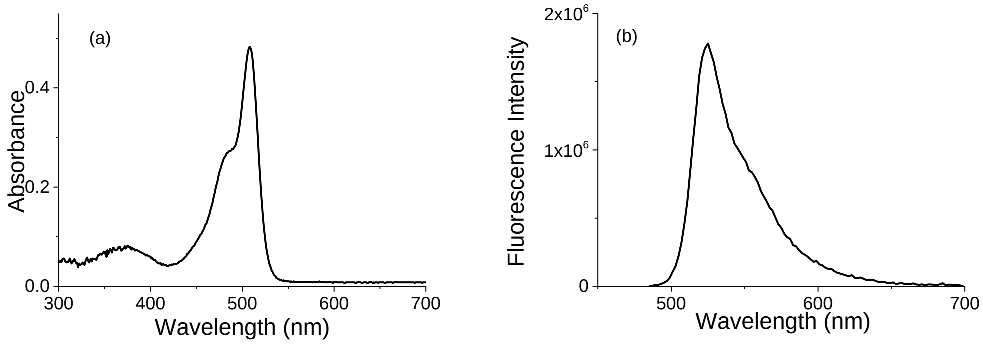


Figure S20. Absorption (a) and fluorescence emission (b) spectra of **5a** recorded in CH_2Cl_2 (excitation at 500 nm).

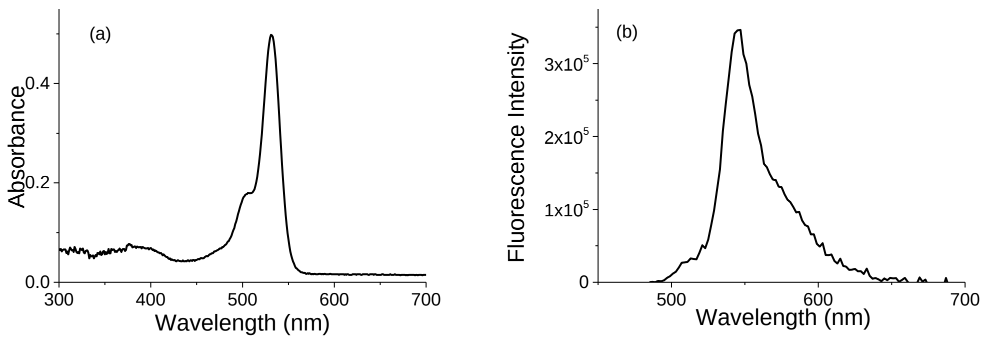


Figure S21. Absorption (a) and fluorescence emission (b) spectra of **5b** recorded in CH_2Cl_2 (excitation at 500 nm).

8. **DFT calculation**

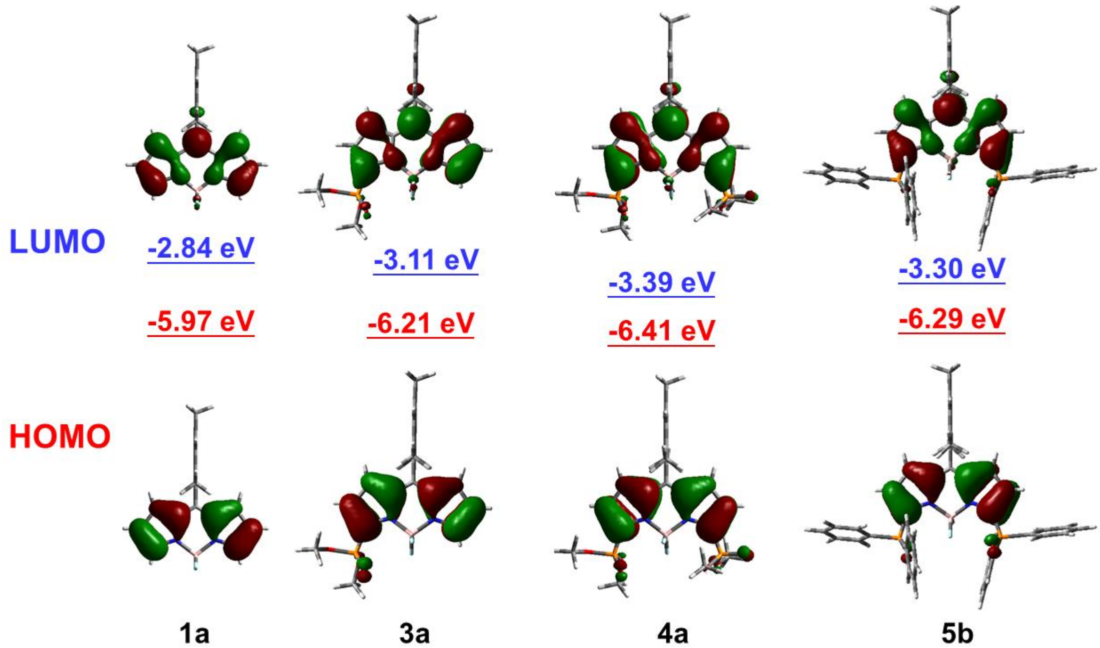


Figure S22. HOMO and LUMO energy levels for **1a**, **3a**, **4a** and **5b** obtained from DFT calculations.

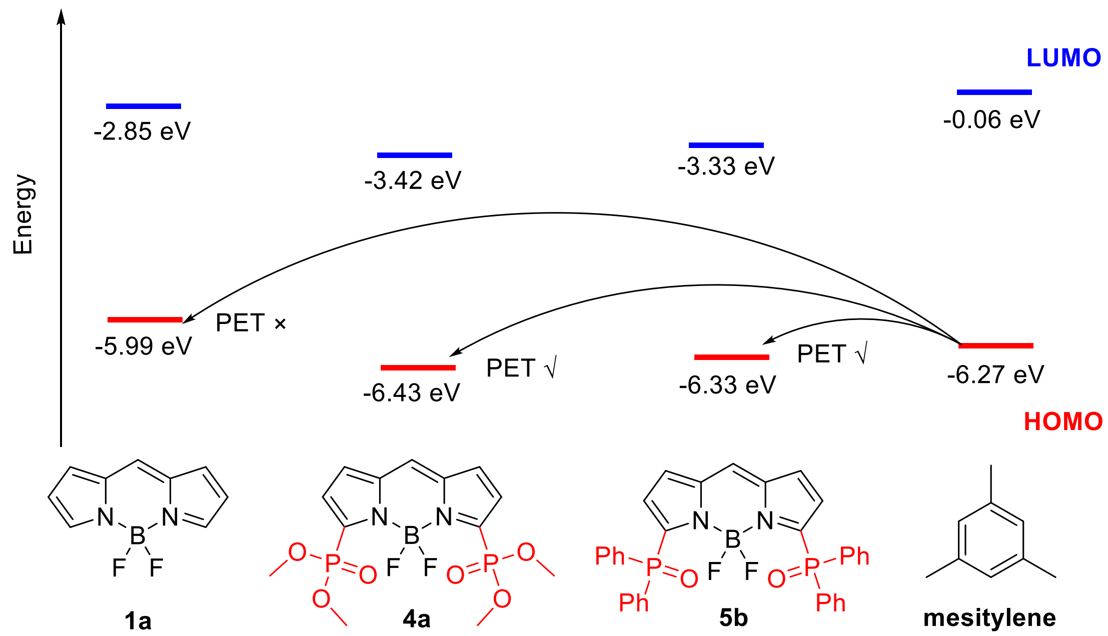


Figure S23. Schematic illustration of intramolecular PeT.

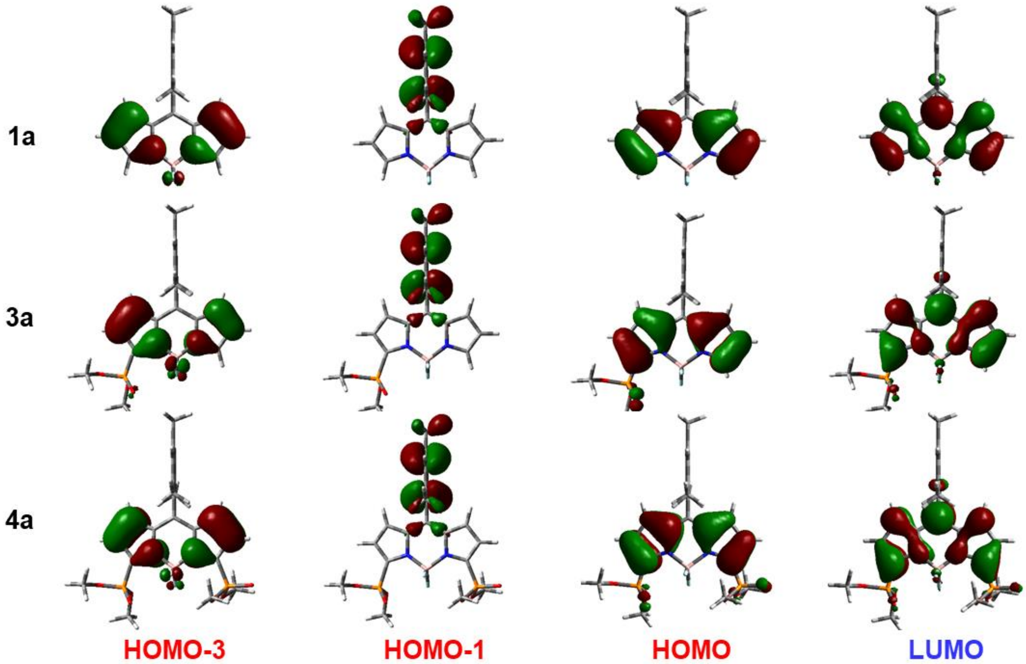


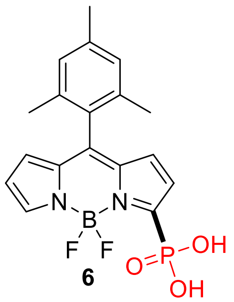
Figure S24. Frontier orbitals in ground state for **1a**, **3a** and **4a**.

Table S5. Selected electronic excitation energies (eV) and oscillator strengths (f), configurations of the low-lying excited states of the **1a**, **3a**, **4a** and **5b** calculated by TDDFT//M062X/6-31G(d,p), based on the optimized ground state geometries. The TDDFT of all the molecules in dichloromethane were using the Self Consistent Reaction Field (SCRF) method and the Polarizable Continuum Model (PCM).

	Electronic transition	TD//M062X/6-31G(d, p)			
		Energy/ eV [a]	*f* [b]	Composition [c]	CI [d]
1a	S0→S1	3.0035 eV 412.80 nm	0.5288	HOMO → LUMO	0.6980
	S0→S2	3.5670 eV 347.59 nm	0.0000	HOMO -1 → LUMO	0.6935
	S0→S3	3.9582 eV 313.23 nm	0.0000	HOMO -2 → LUMO	0.7018
3a	S0→S1	2.9428 eV 421.31 nm	0.5449	HOMO → LUMO	0.6959
				HOMO -3 → LUMO	0.1054
	S0→S2	3.3322 eV 372.07 nm	0.0009	HOMO -1 → LUMO	0.6927
	S0→S3	3.6946 eV 335.58 nm	0.0001	HOMO -2 → LUMO	0.7030
4a	S0→S1	2.8605 eV 433.44 nm	0.5464	HOMO → LUMO	0.6958
				HOMO -3 → LUMO	0.1068
	S0→S2	3.1276 eV 396.42 nm	0.0062	HOMO -1 → LUMO	0.6933
	S0→S3	3.4892 eV 355.34 nm	0.0006	HOMO -2 → LUMO	0.7034
5b	S0→S1	2.7884 eV 444.65 nm	0.6498	HOMO → LUMO	0.6946
	S0→S2	3.1868 eV 389.05 nm	0.0075	HOMO -1 → LUMO	0.6940
	S0→S3	3.5535 eV 348.91 nm	0.0005	HOMO -2→ LUMO	0.7041

[a] Only the selected low-lying excited states are presented. [b] Oscillator strength. [c] Only the main configurations are presented. [d] The CI coefficients are in absolute values.

9. Table S6. Selected optical data measured in water, DMSO and different pH aqueous solution



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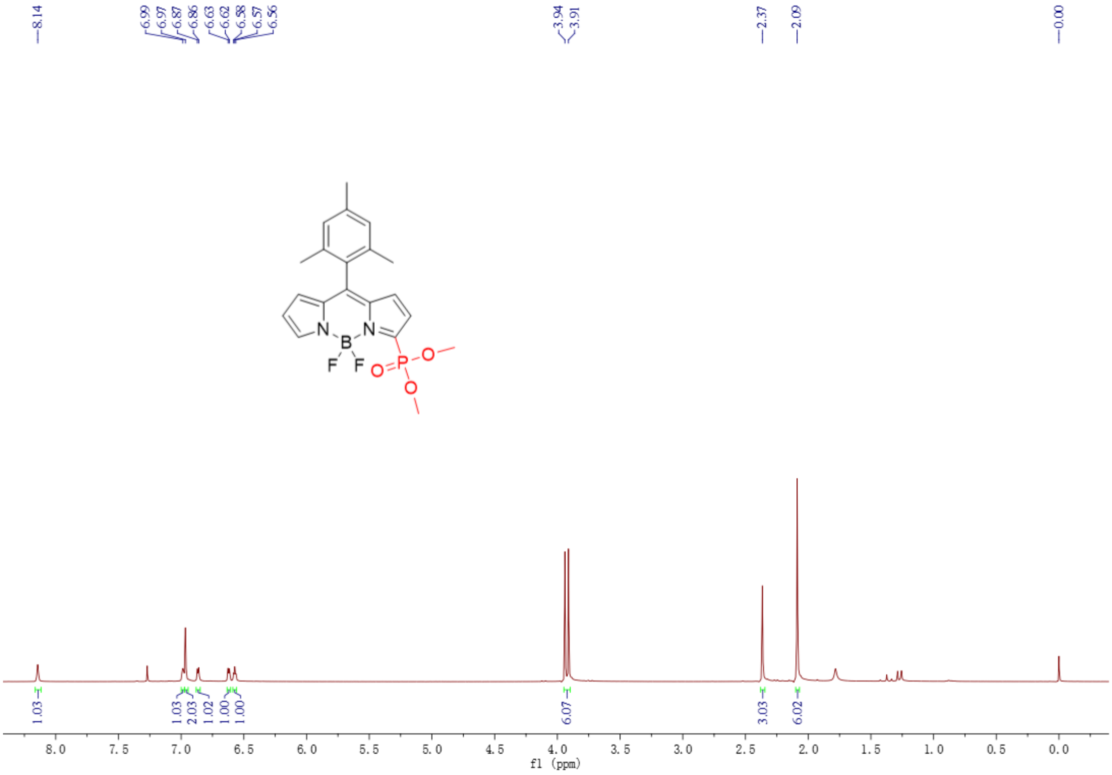
solvent	λ_{abs}^{max} [nm]	λ_{em}^{max} [nm]	log ε [a]	Φ [b]	Stokes shift [cm^{-1}] [c]
DMSO	516	527	4.12	0.71	400
H_2O	506	519	4.05	0.83	490
H_2O (pH = 6)	506	519	4.16	0.79	490
H_2O (pH = 8)	506	519	4.15	0.68	490

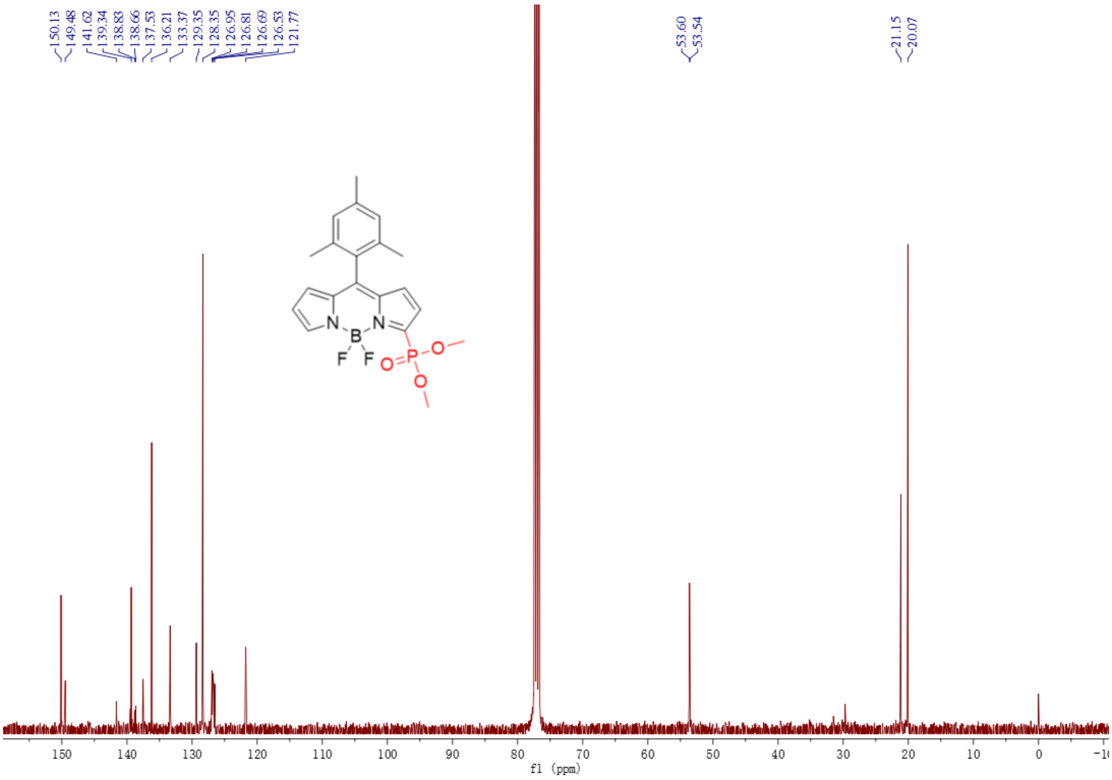
[a] Molar absorption coefficient at λ_{abs}^{max}. [b] Fluorescence quantum yields determined using fluorescein (Φ = 0.90 in 0.1 M NaOH aqueous solution) as standard. [c] Stokes shift values rounded to nearest 10 cm^{-1}. λ_{em}= 480 nm.

10. ^{1}H、^{13}C and ^{31}P NMR spectra of all new compounds

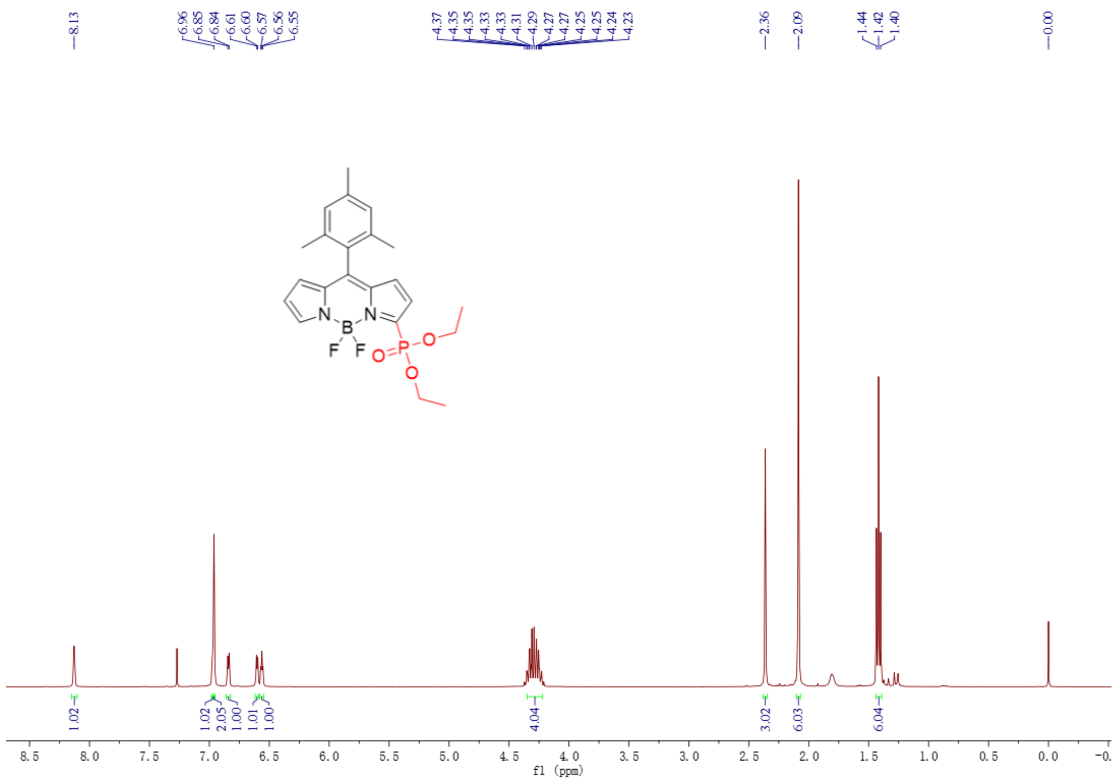
^{1}H NMR spectrum of **3a** in $CDCl_3$



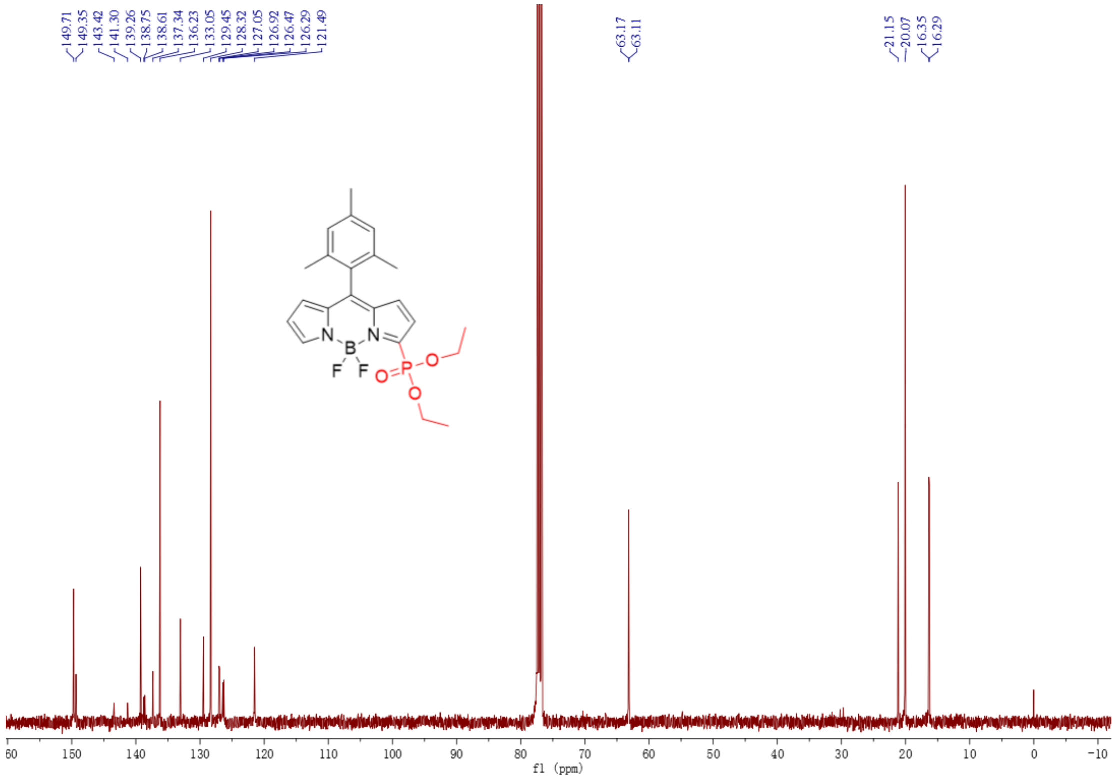
^{13}C NMR spectrum of **3a** in $CDCl_3$



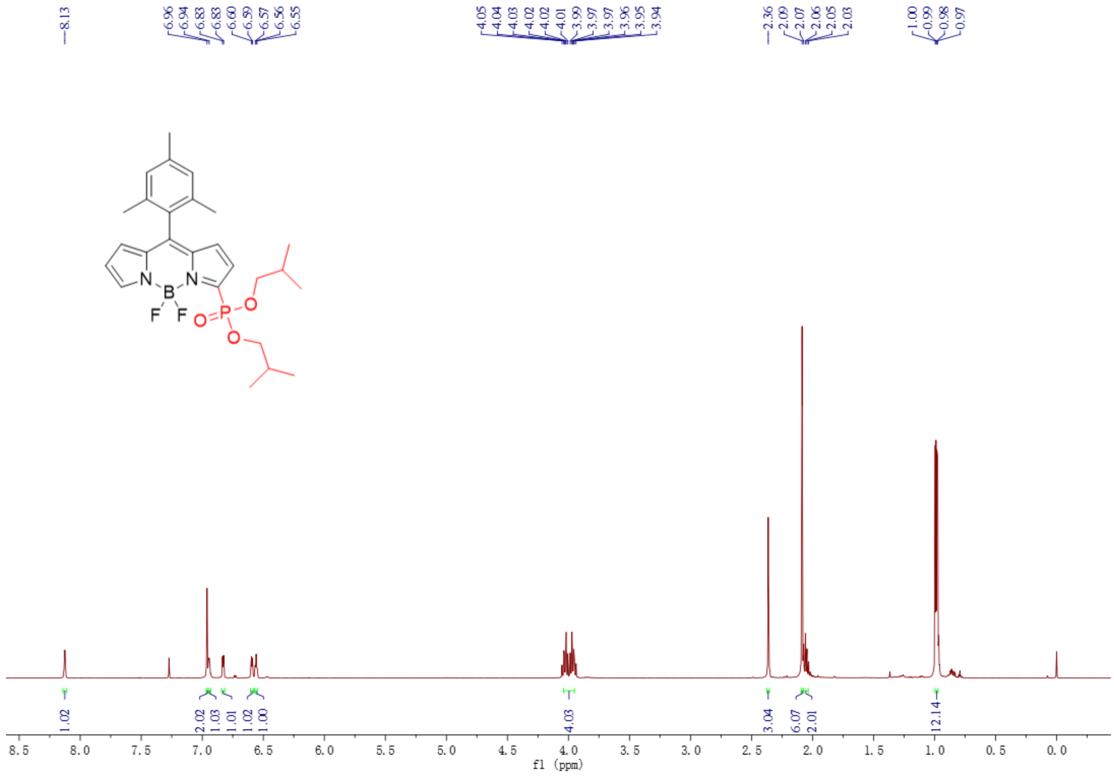
[1]H NMR spectrum of **3b** in $CDCl_3$



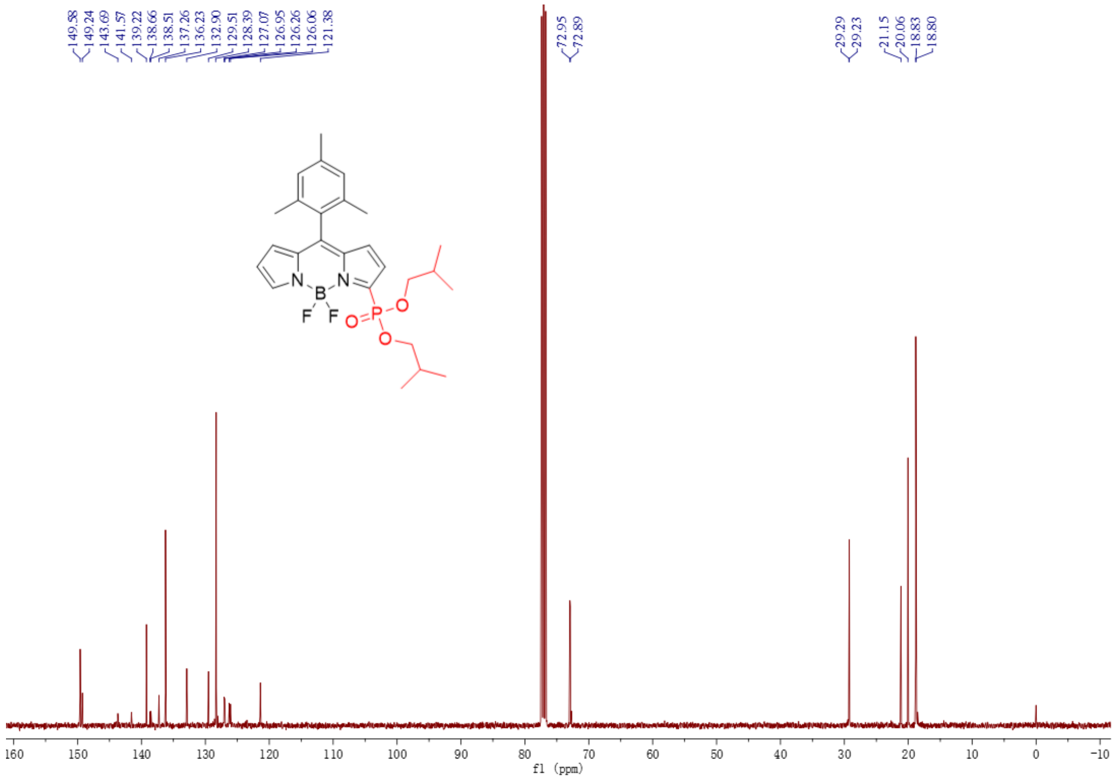
[13]C NMR spectrum of **3b** in $CDCl_3$



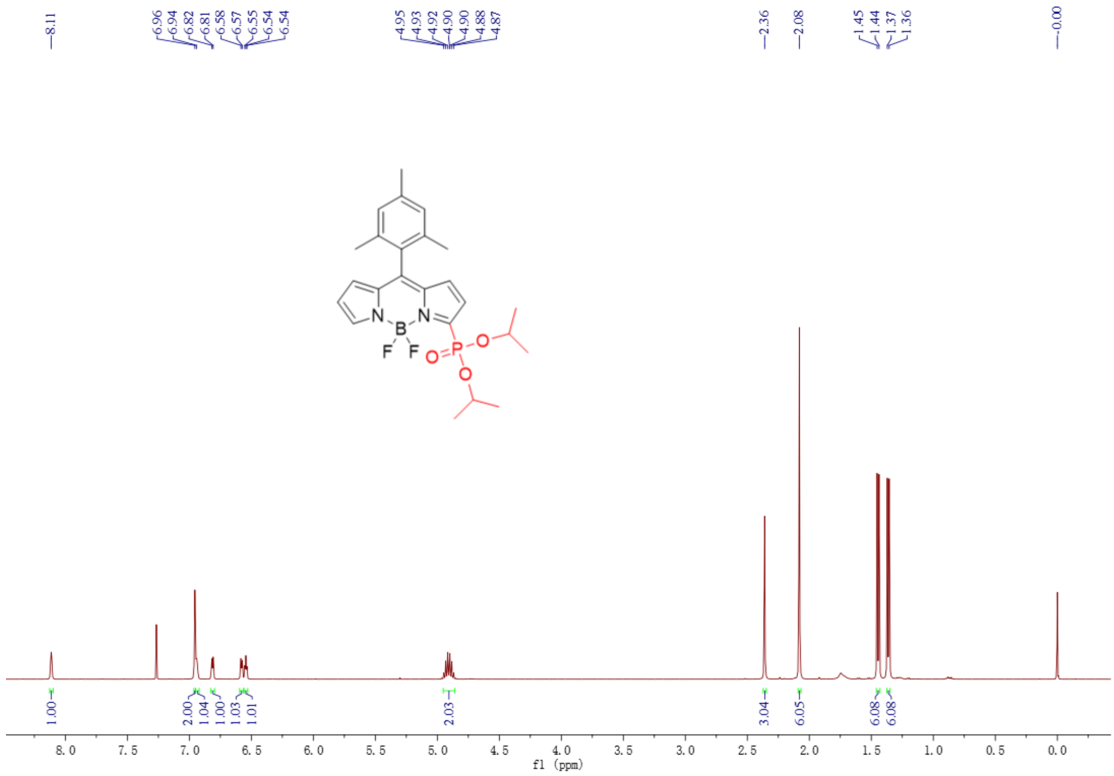
^{1}H NMR spectrum of **3c** in $CDCl_3$



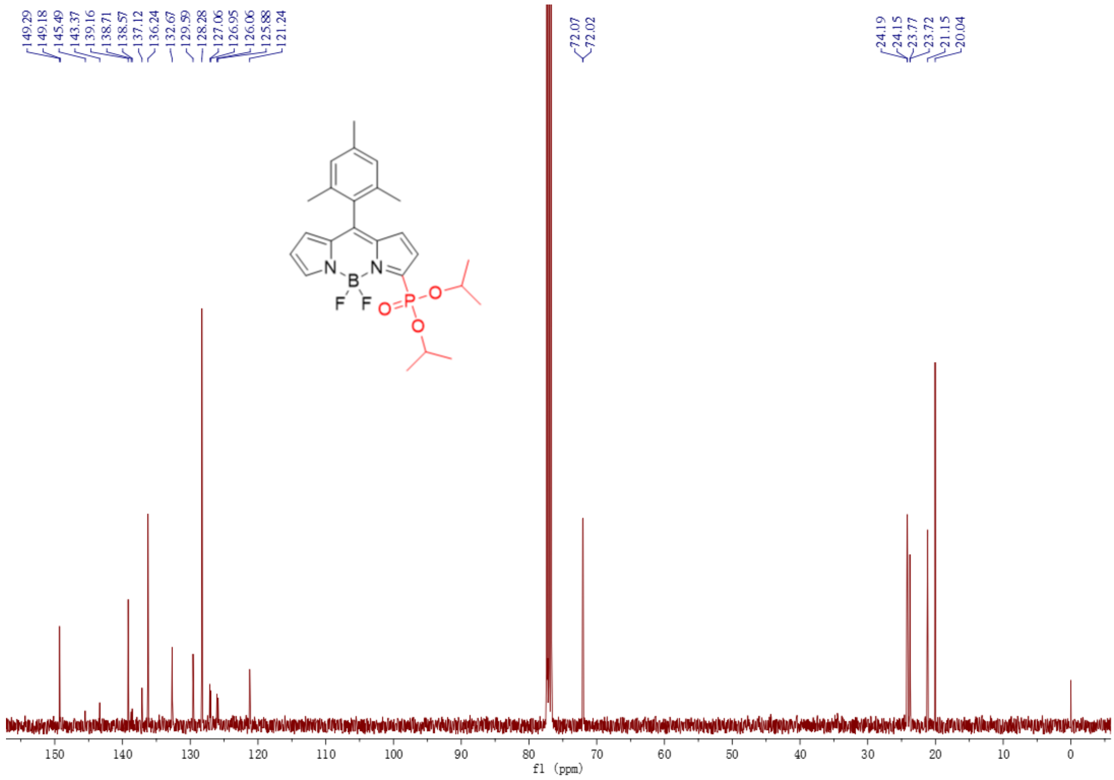
^{13}C NMR spectrum of **3c** in $CDCl_3$



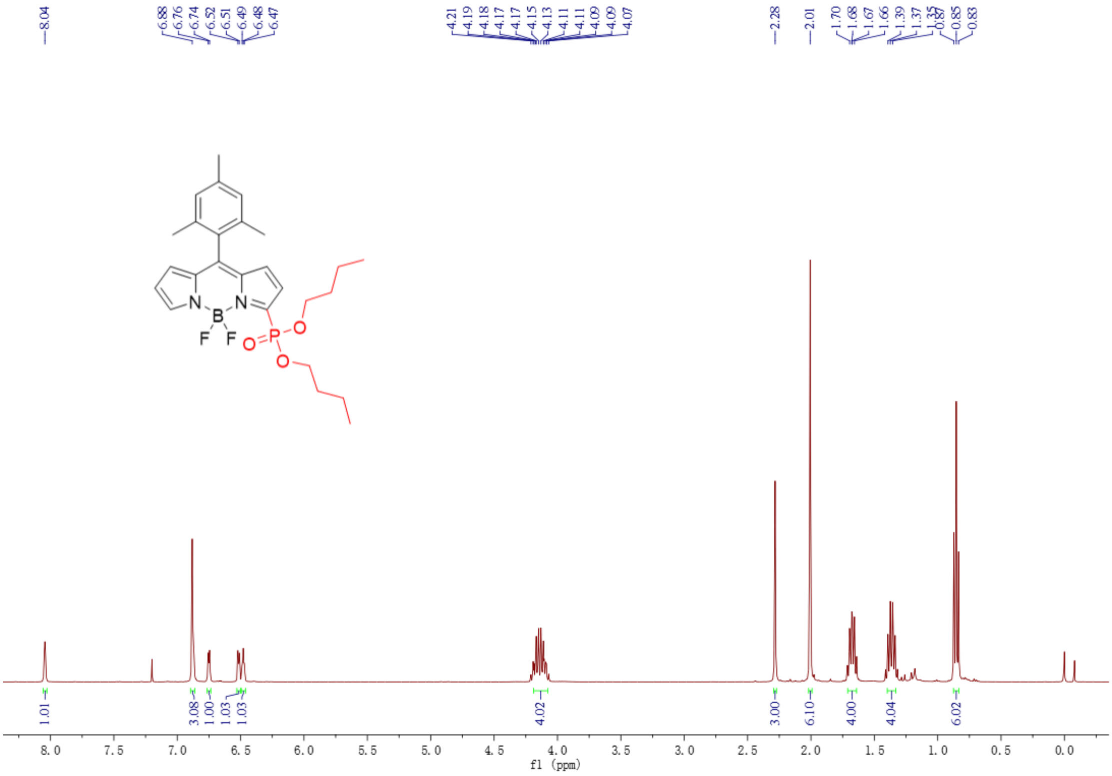
^{1}H NMR spectrum of **3d** in $CDCl_3$



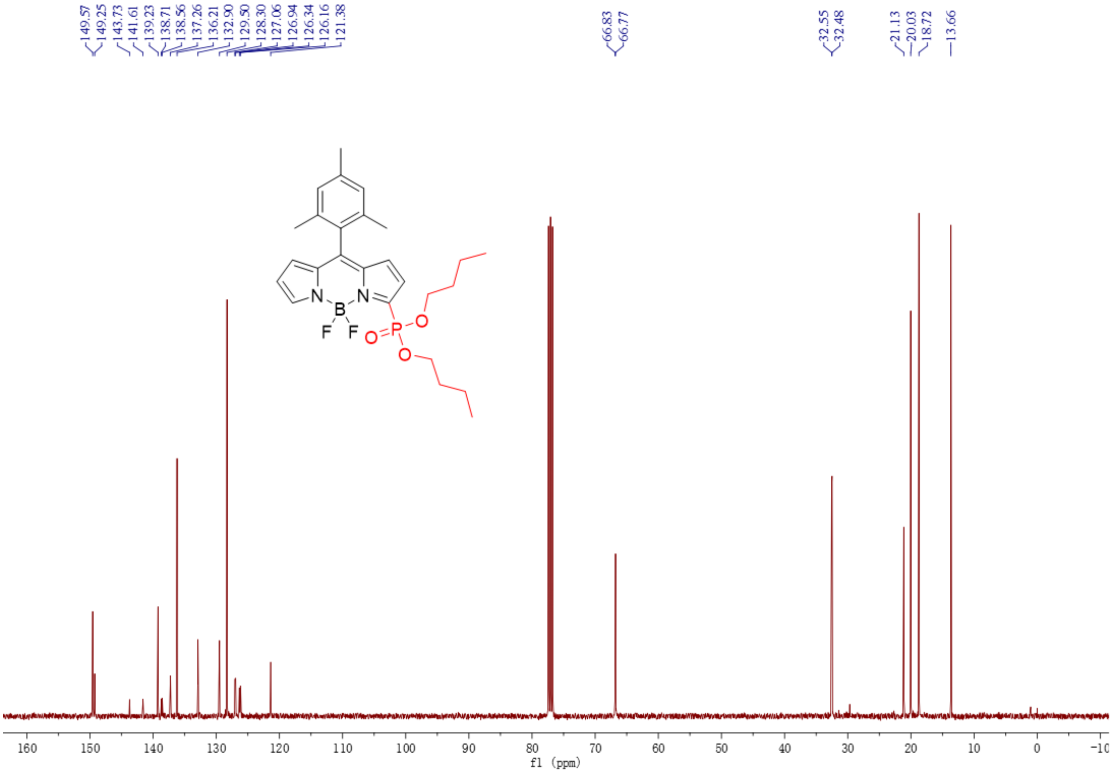
^{13}C NMR spectrum of **3d** in $CDCl_3$



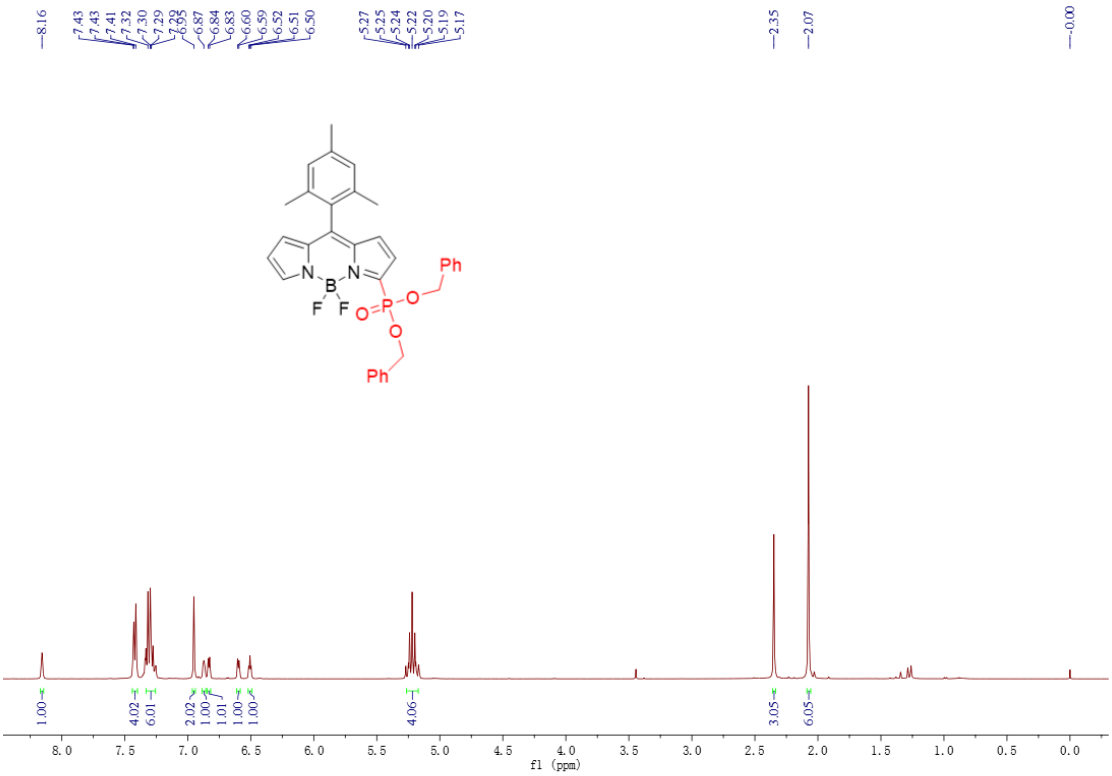
^{1}H NMR spectrum of **3e** in $CDCl_3$



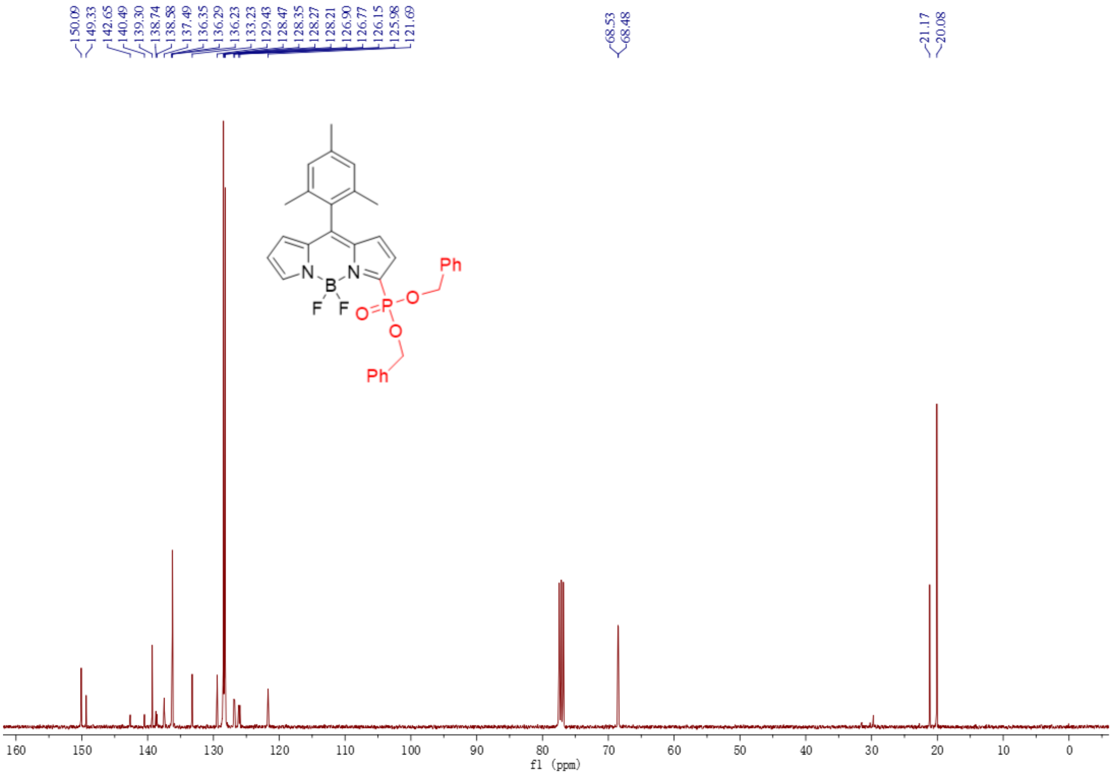
^{13}C NMR spectrum of **3e** in $CDCl_3$



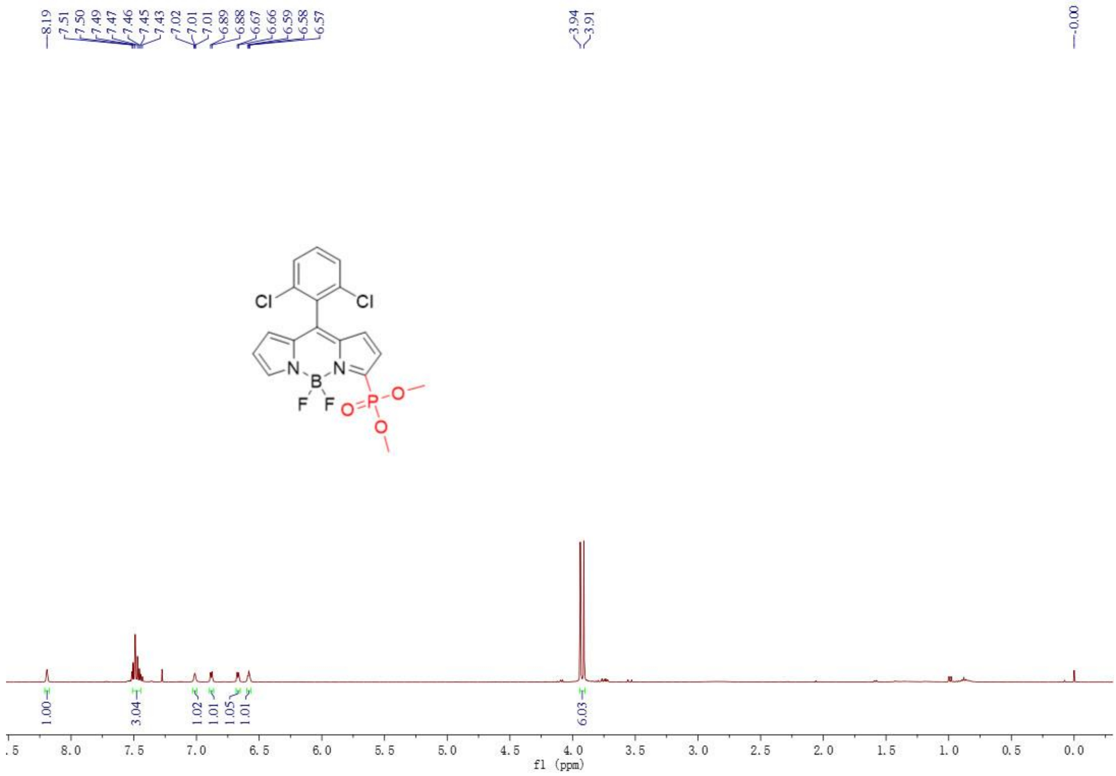
^{1}H NMR spectrum of **3f** in $CDCl_3$



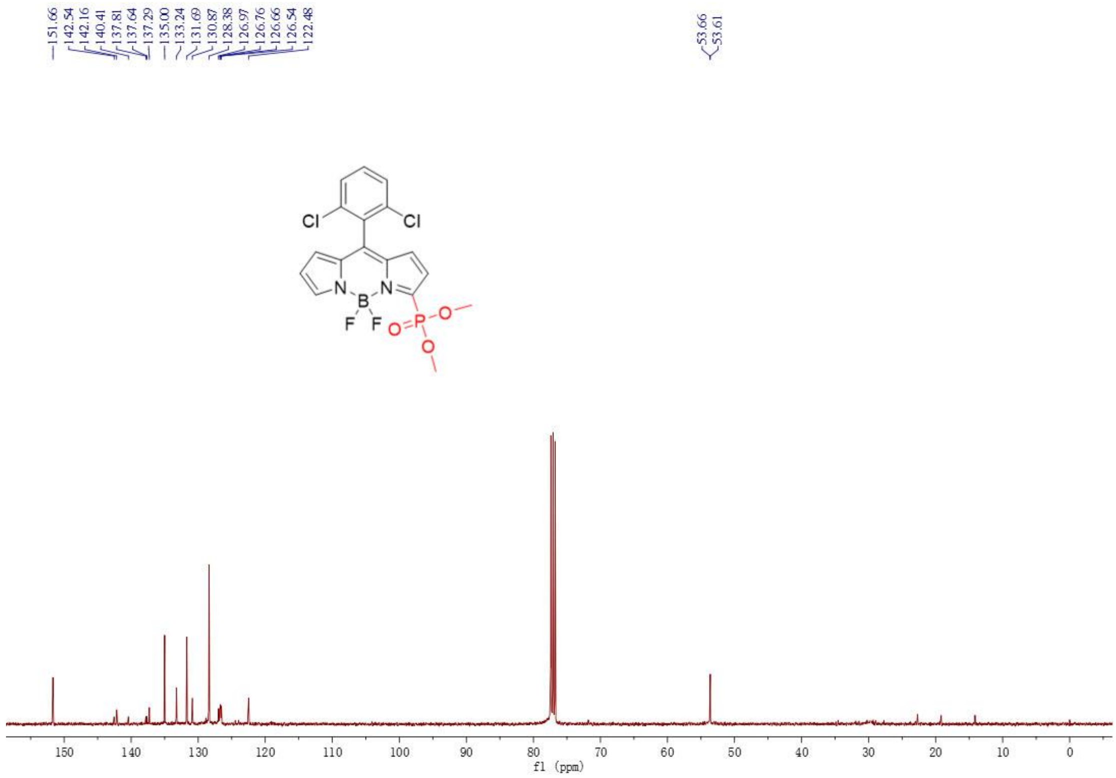
^{13}C NMR spectrum of **3f** in $CDCl_3$



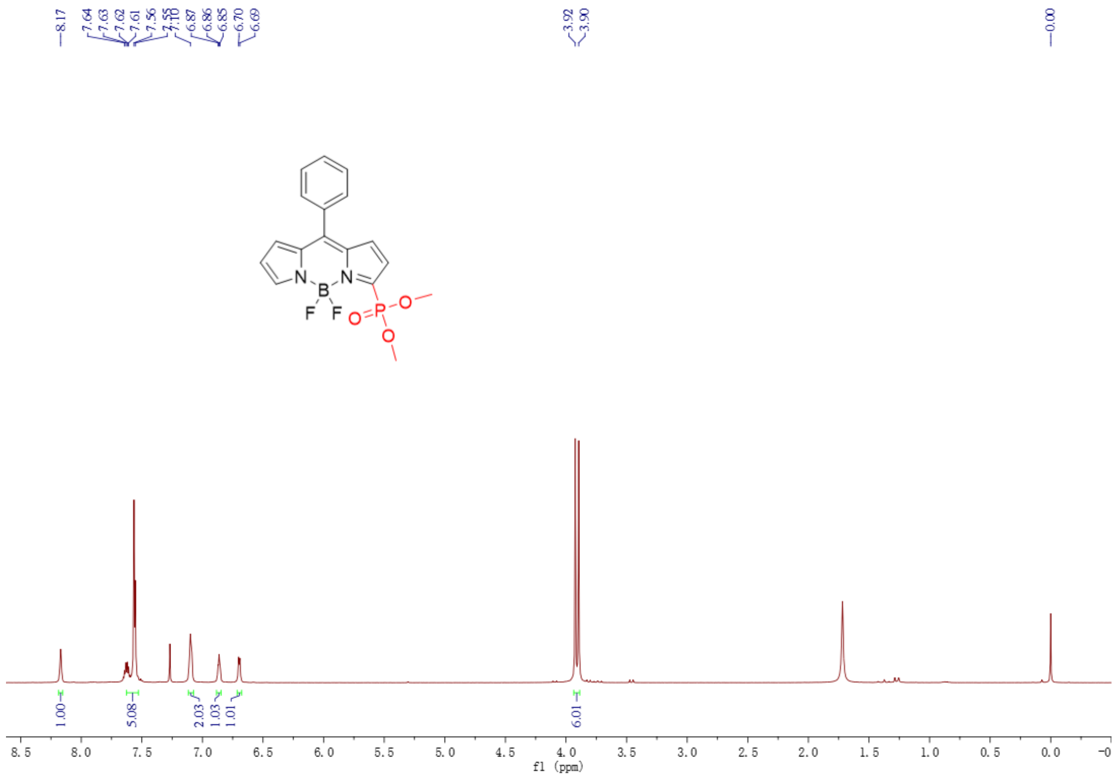
^{1}H NMR spectrum of **3g** in $CDCl_3$



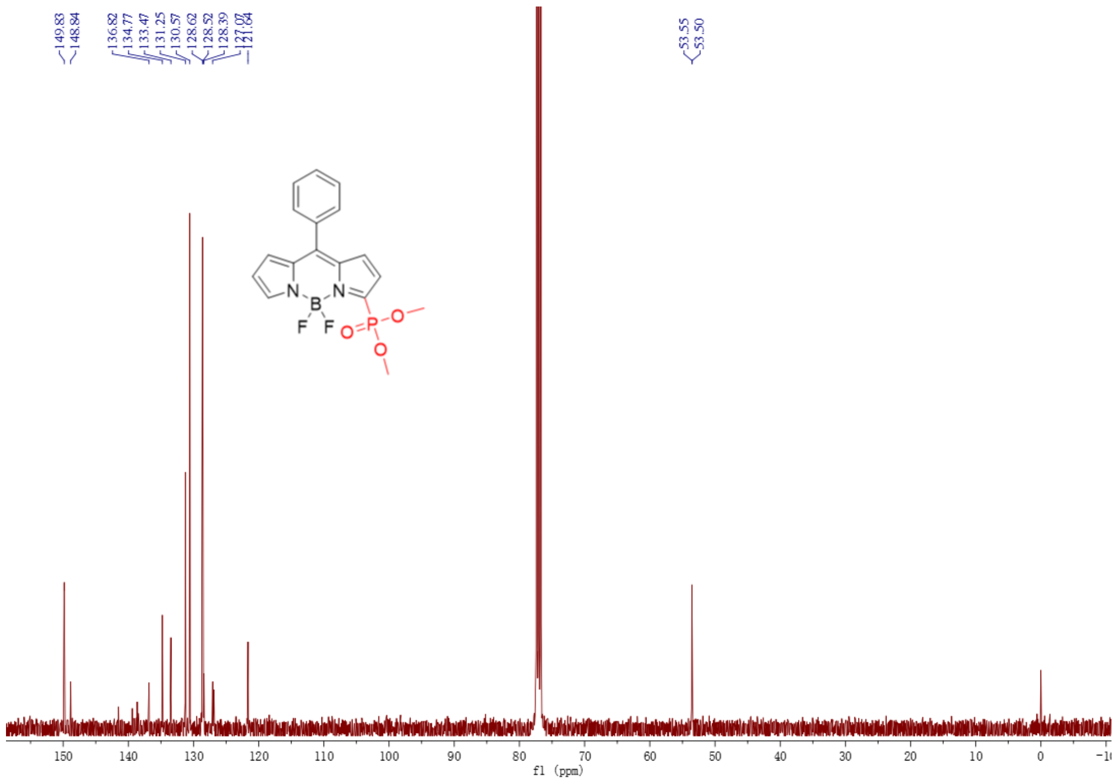
^{13}C NMR spectrum of **3g** in $CDCl_3$



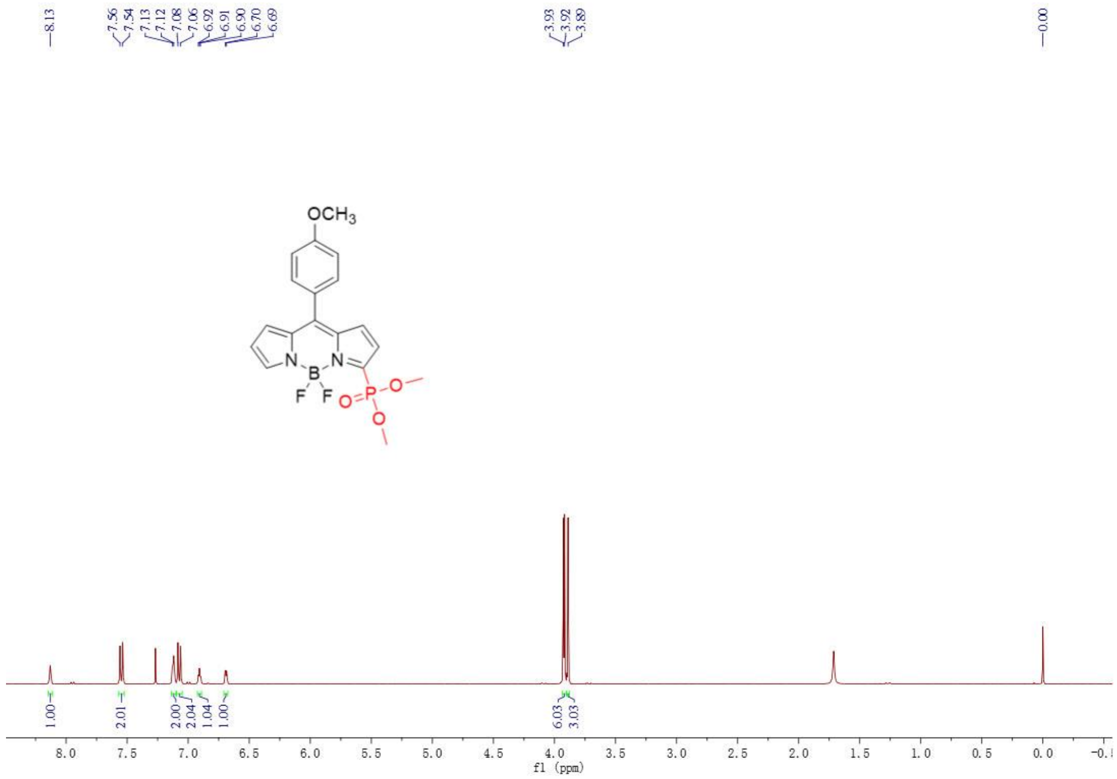
^{1}H NMR spectrum of **3h** in $CDCl_3$



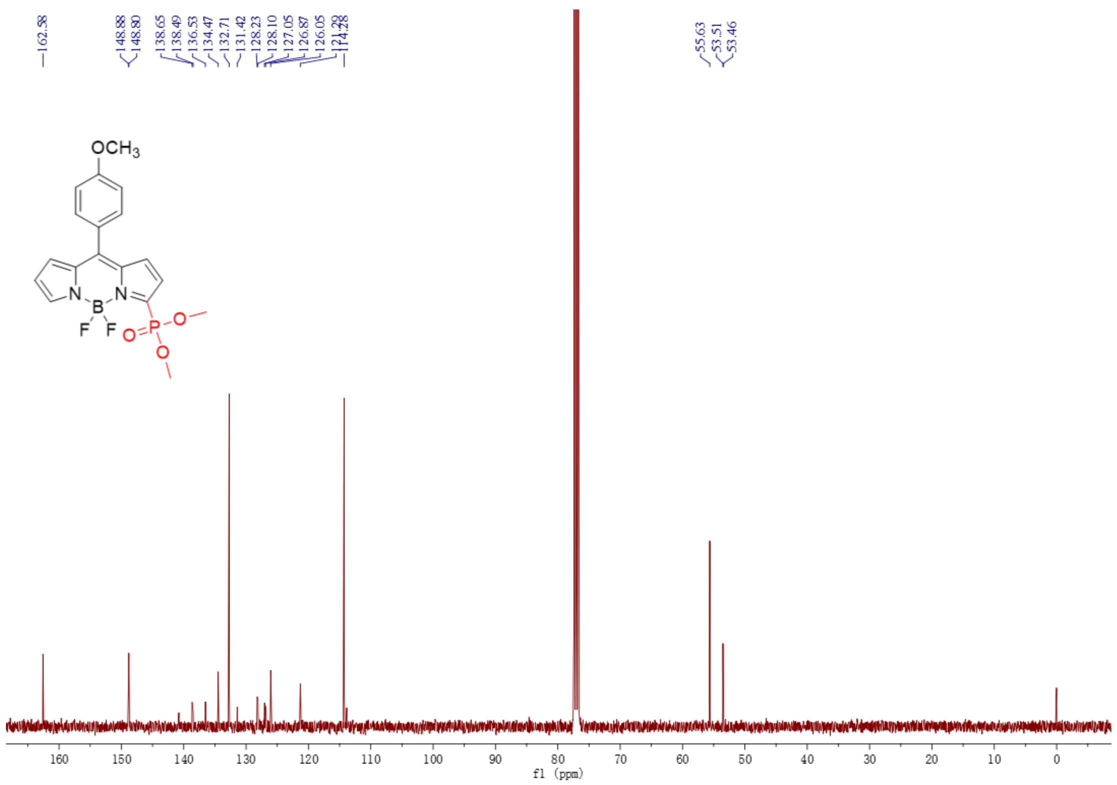
^{13}C NMR spectrum of **3h** in $CDCl_3$



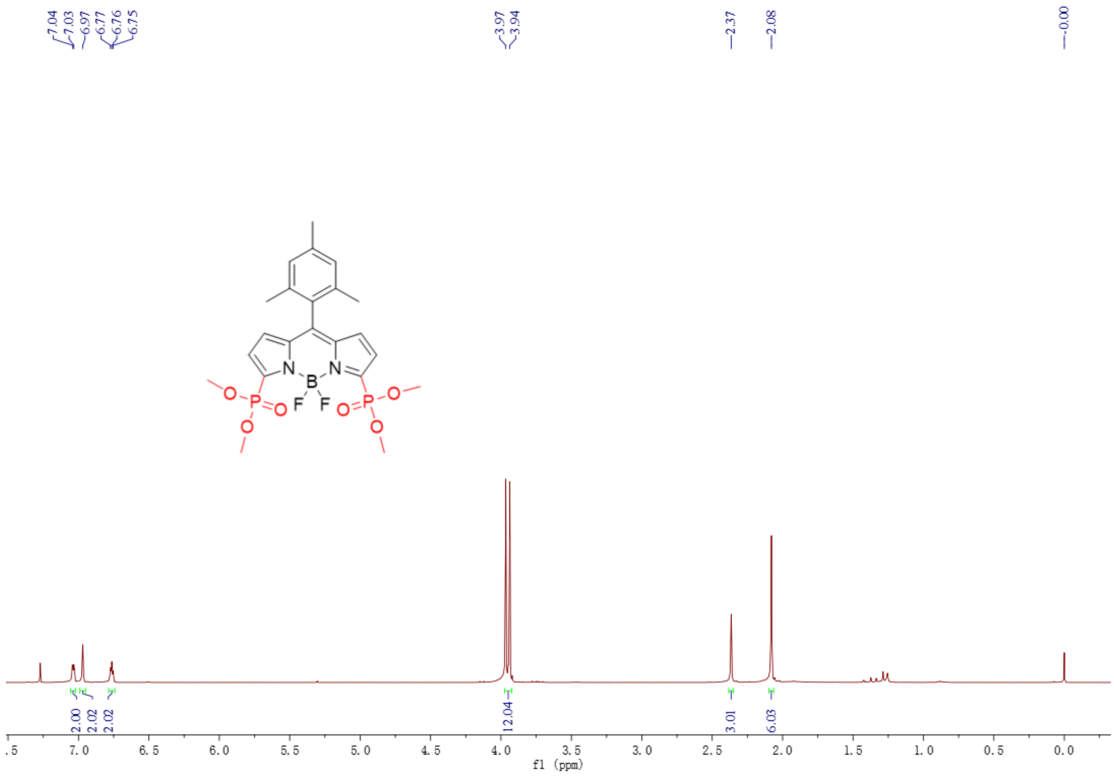
^{1}H NMR spectrum of **3i** in $CDCl_3$



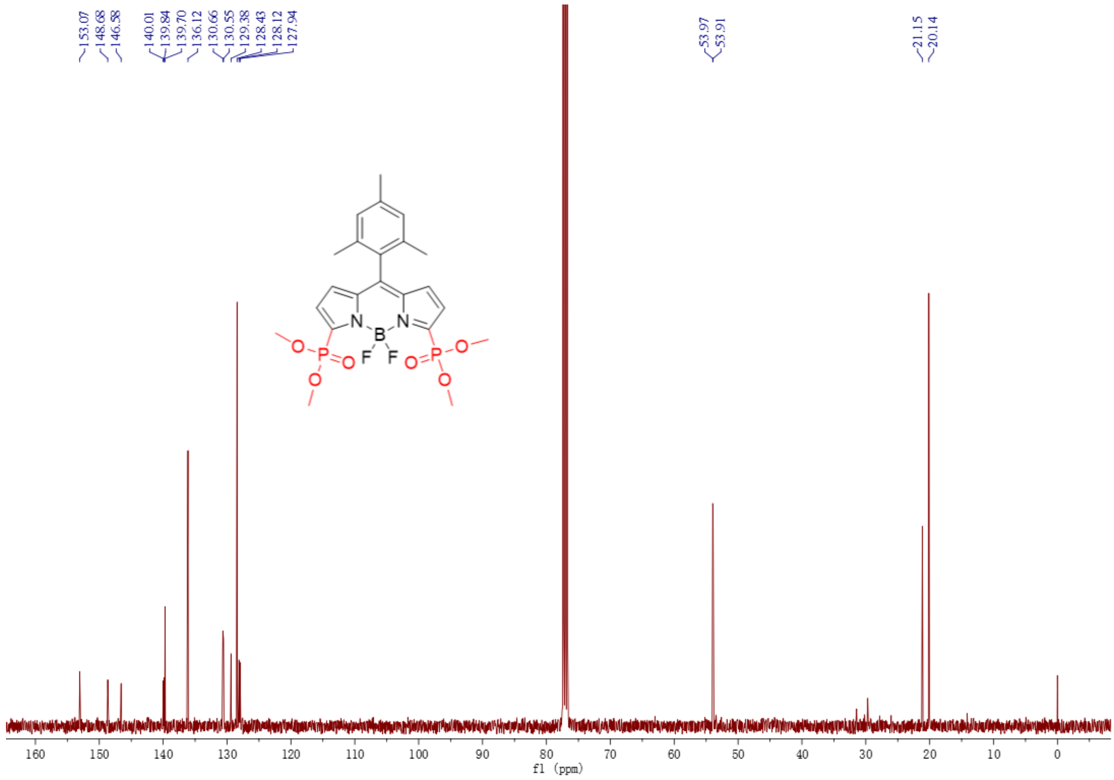
^{13}C NMR spectrum of **3i** in $CDCl_3$



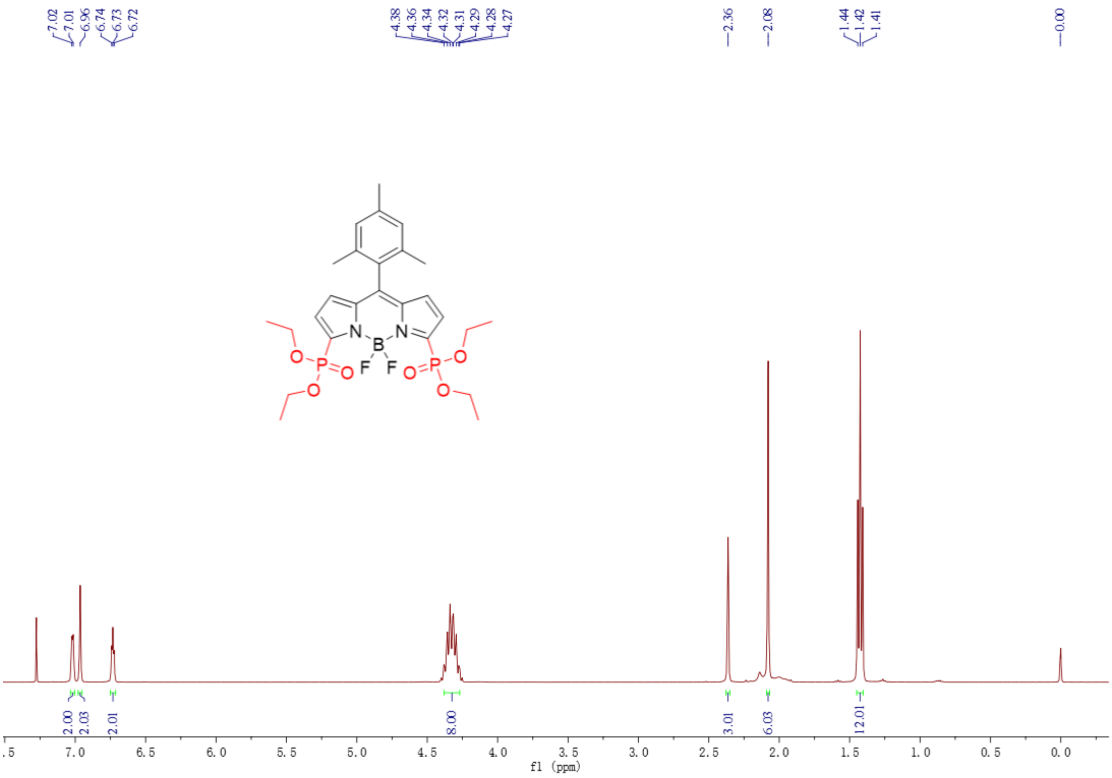
^{1}H NMR spectrum of **4a** in $CDCl_3$



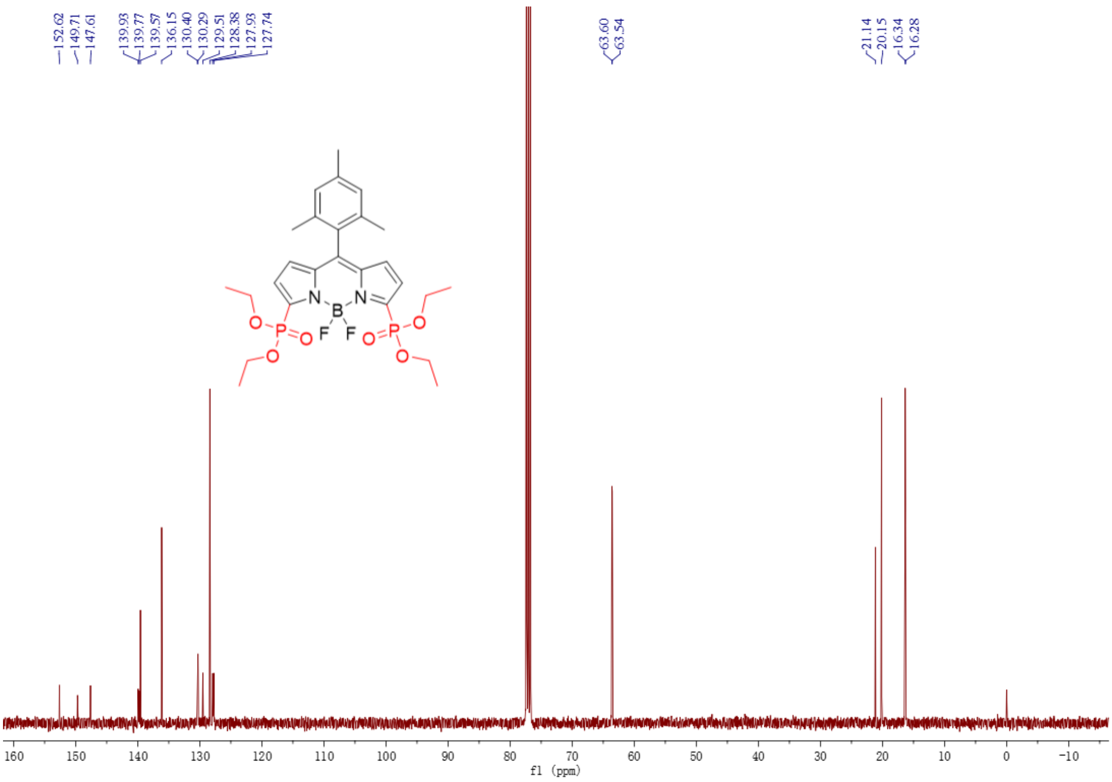
^{13}C NMR spectrum of **4a** in $CDCl_3$



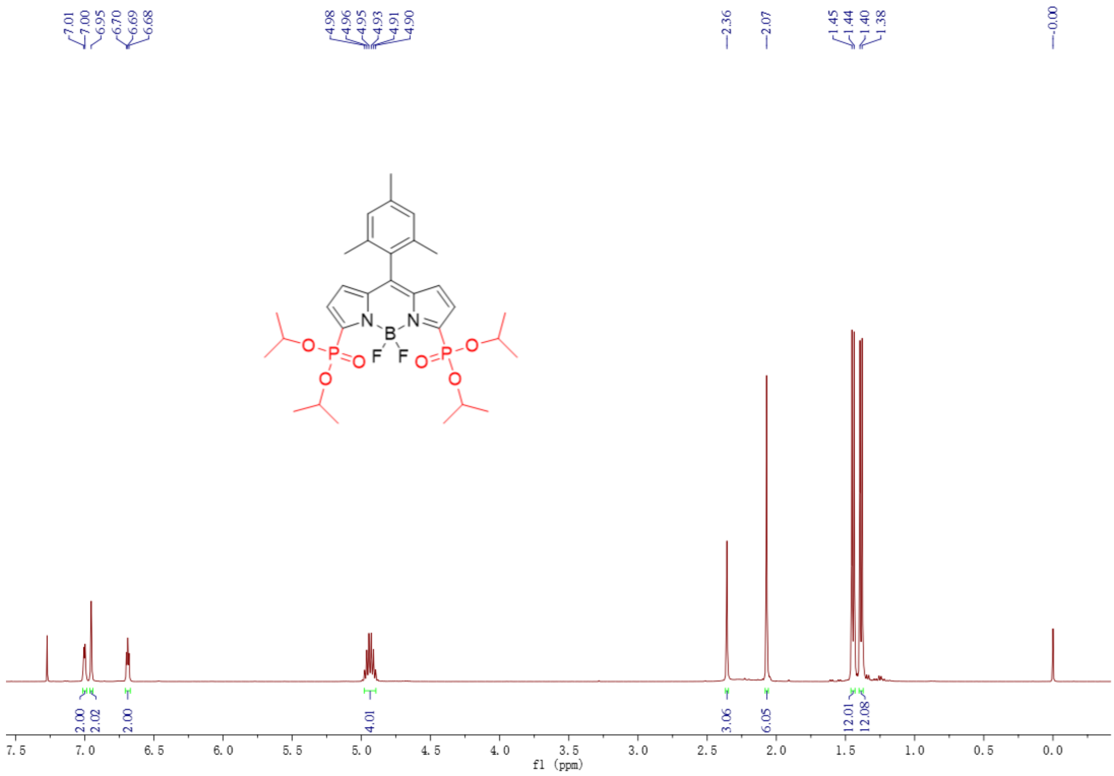
^{1}H NMR spectrum of **4b** in $CDCl_3$



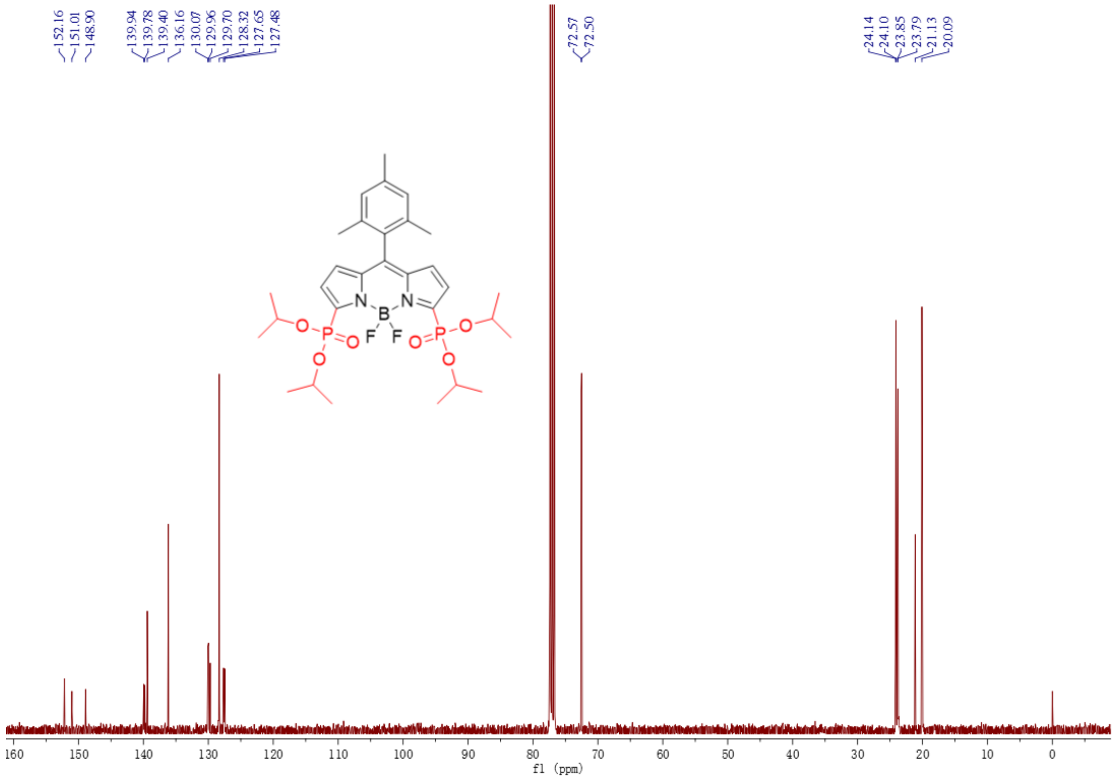
^{13}C NMR spectrum of **4b** in $CDCl_3$



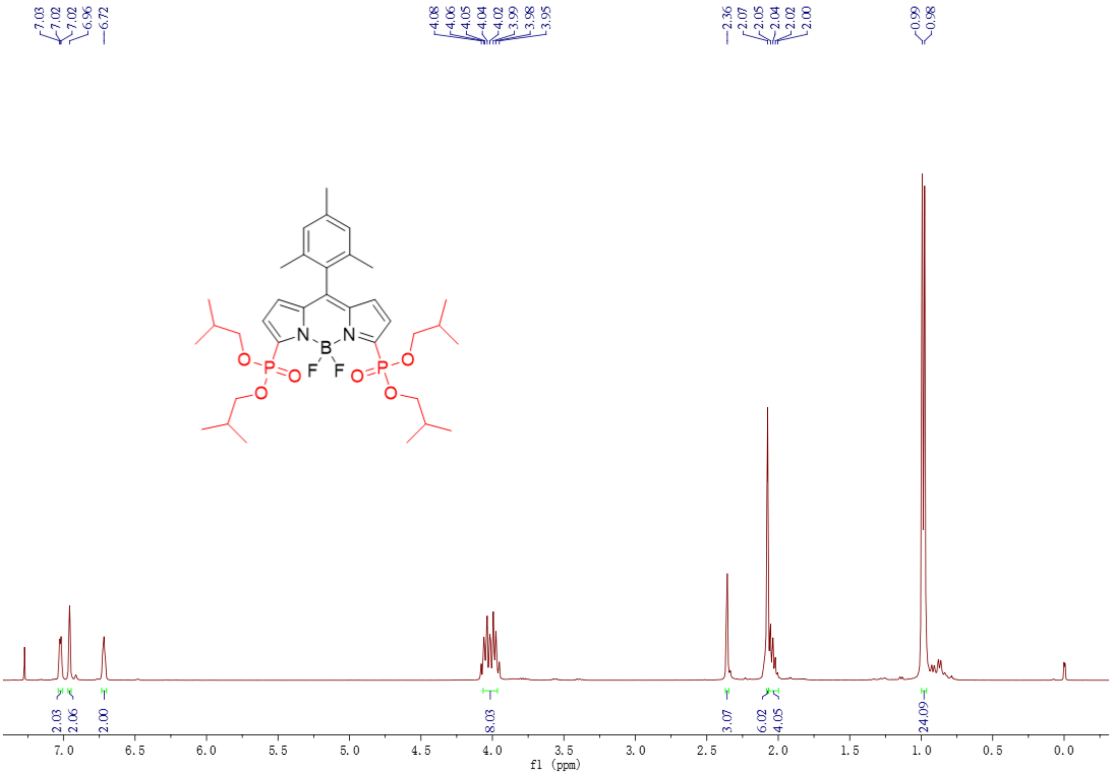
[1]H NMR spectrum of **4c** in $CDCl_3$



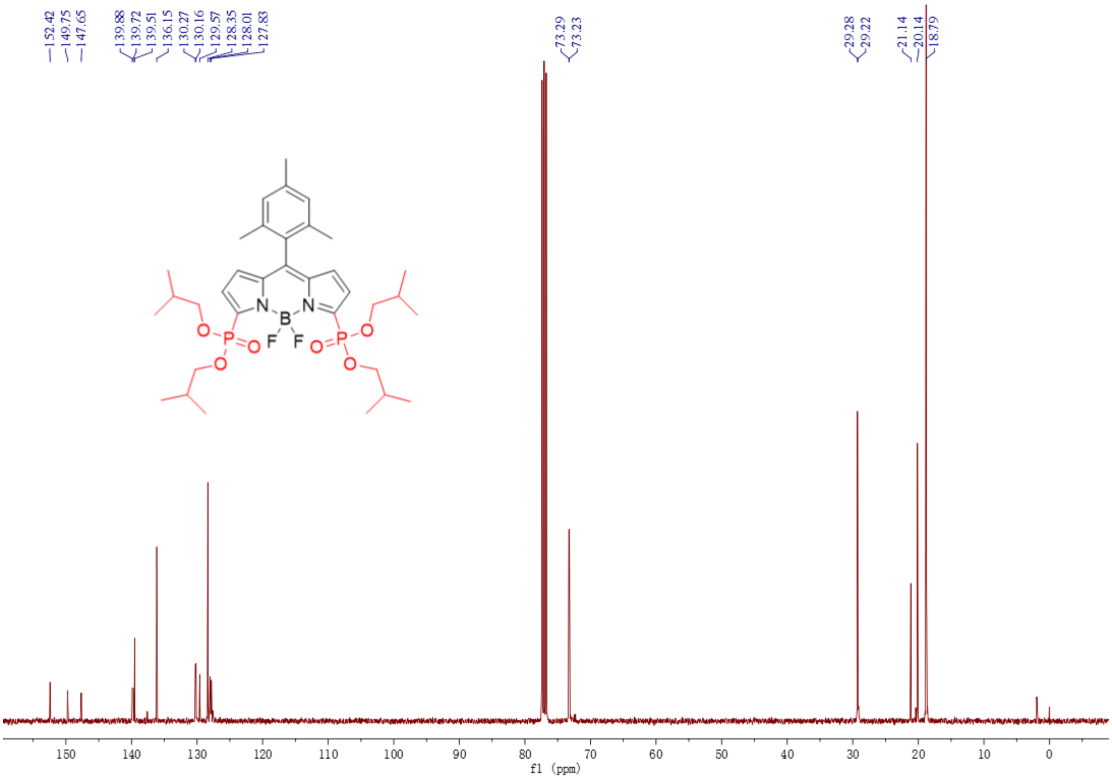
[13]C NMR spectrum of **4c** in $CDCl_3$



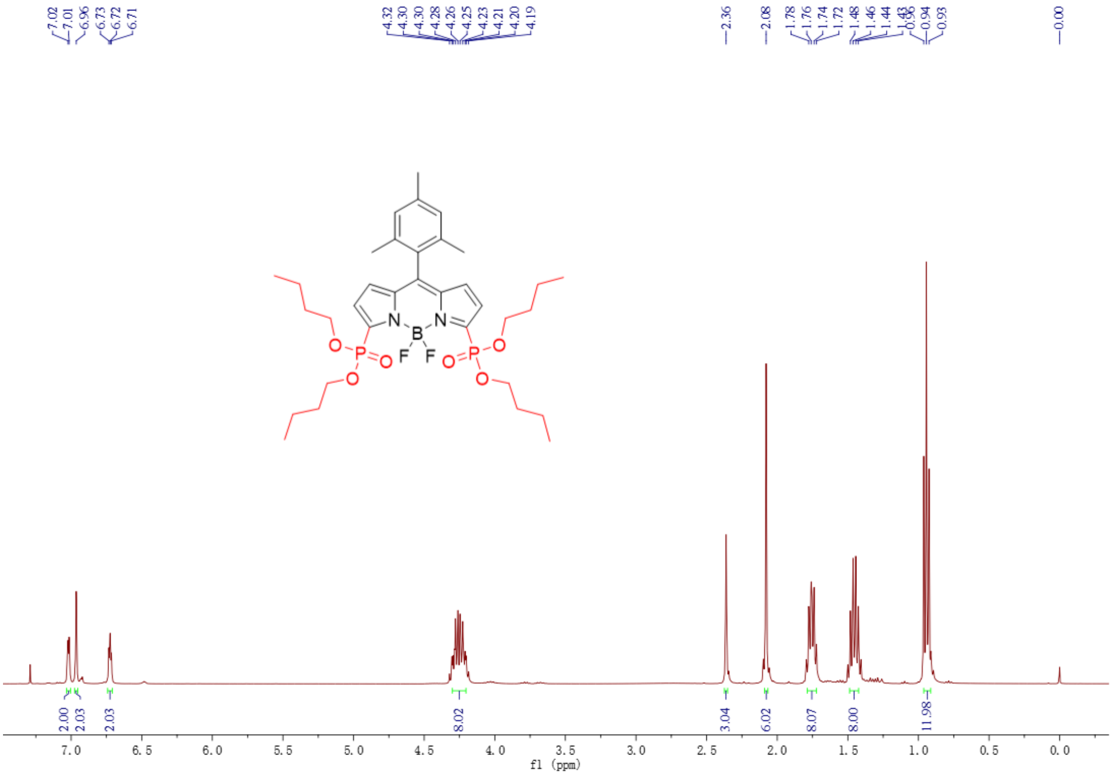
^{1}H NMR spectrum of **4d** in $CDCl_3$



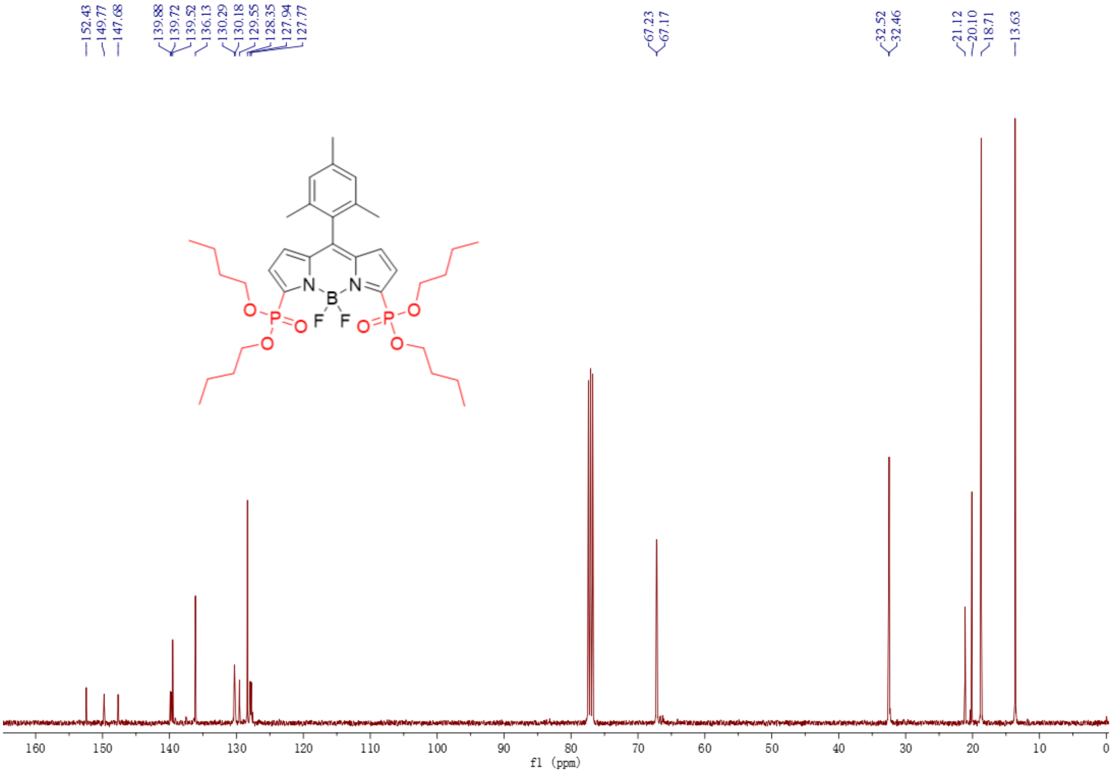
^{13}C NMR spectrum of **4d** in $CDCl_3$



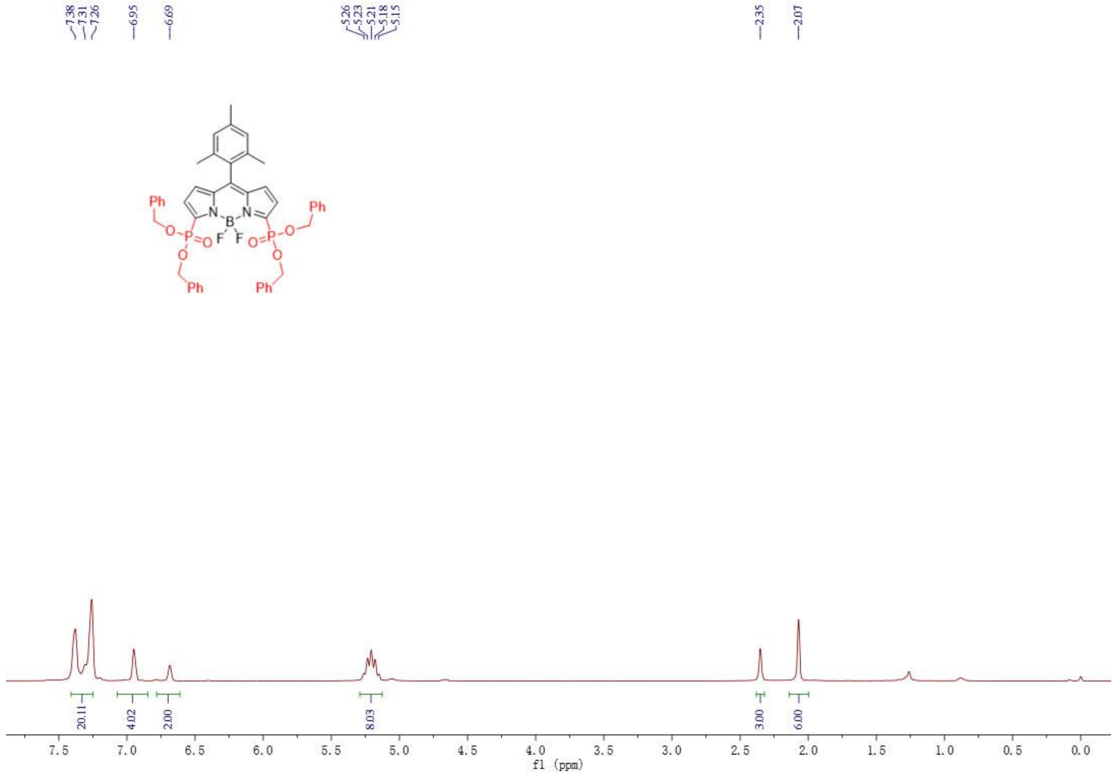
^{1}H NMR spectrum of **4e** in $CDCl_3$



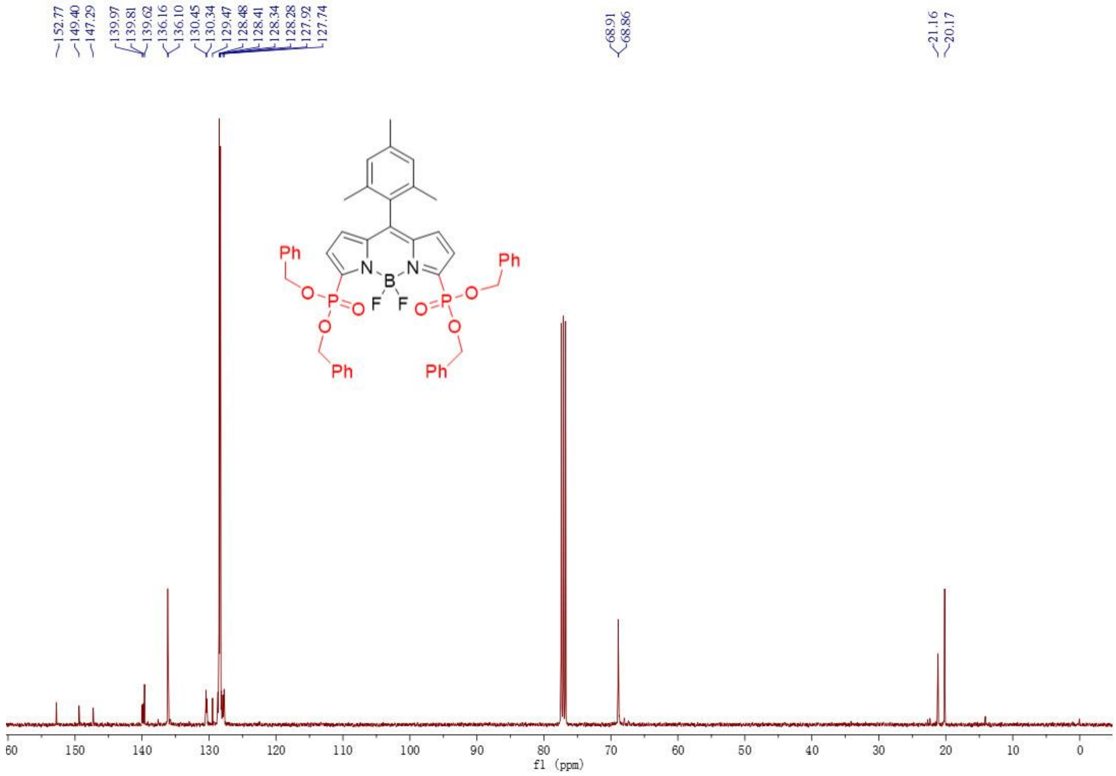
^{13}C NMR spectrum of **4e** in $CDCl_3$



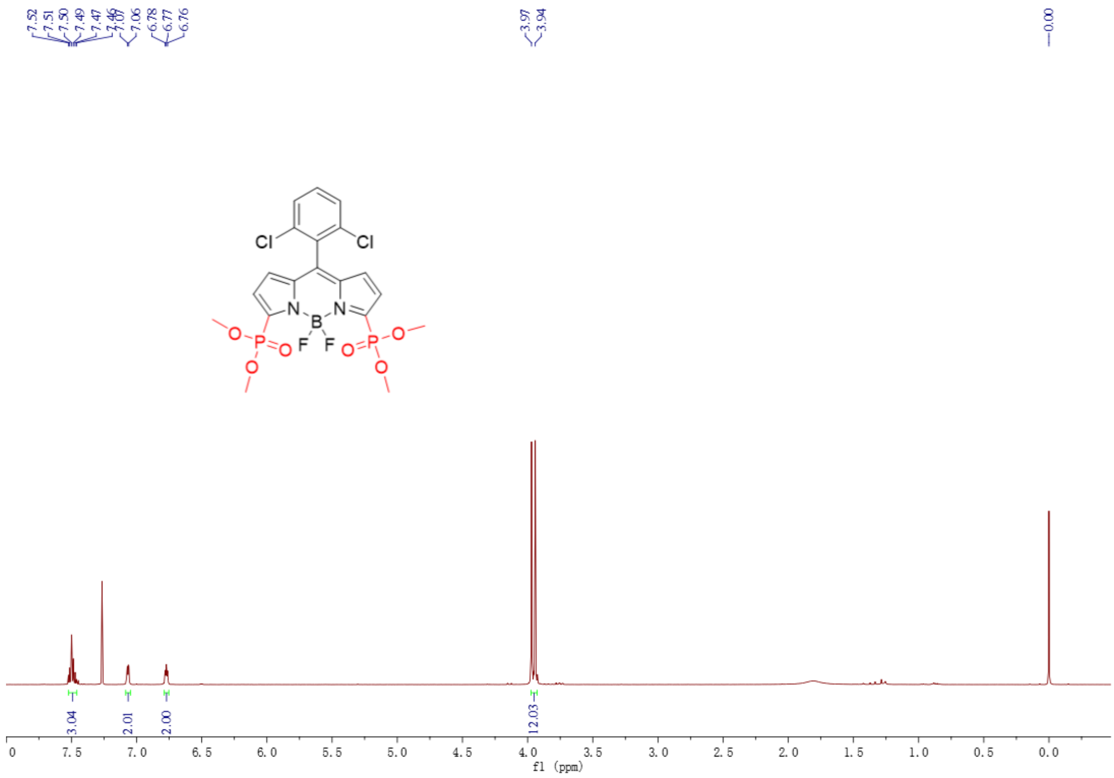
^{1}H NMR spectrum of **4f** in $CDCl_3$



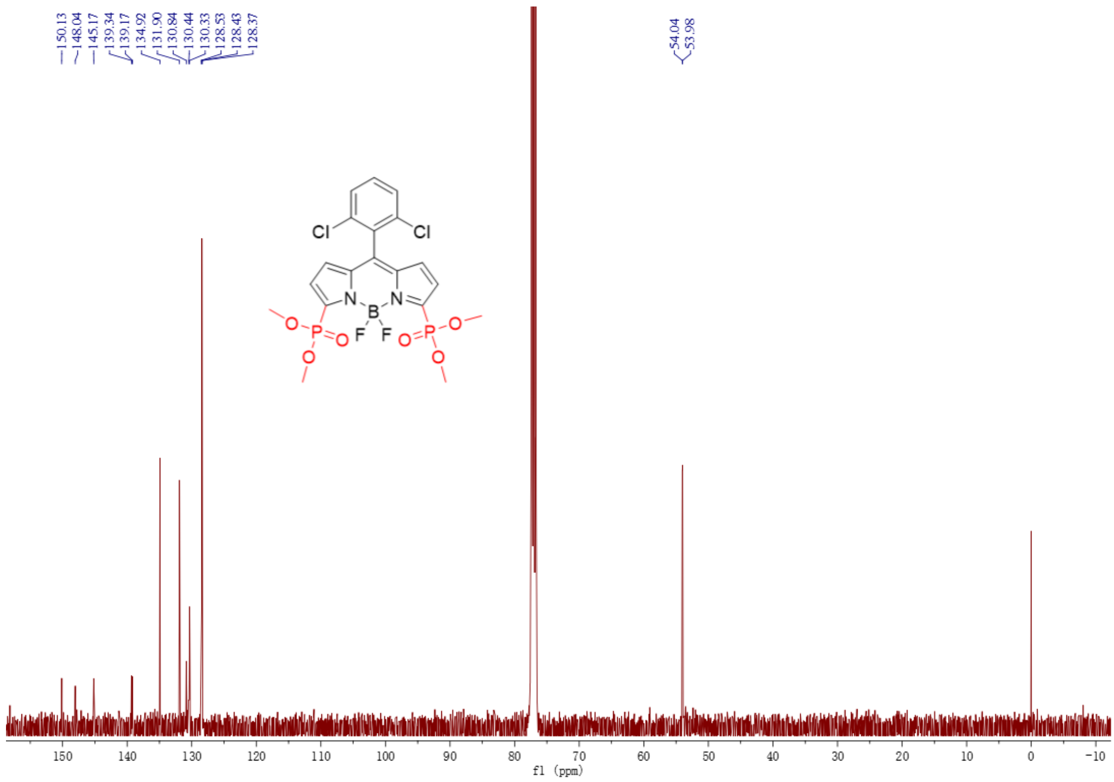
^{13}C NMR spectrum of **4f** in $CDCl_3$



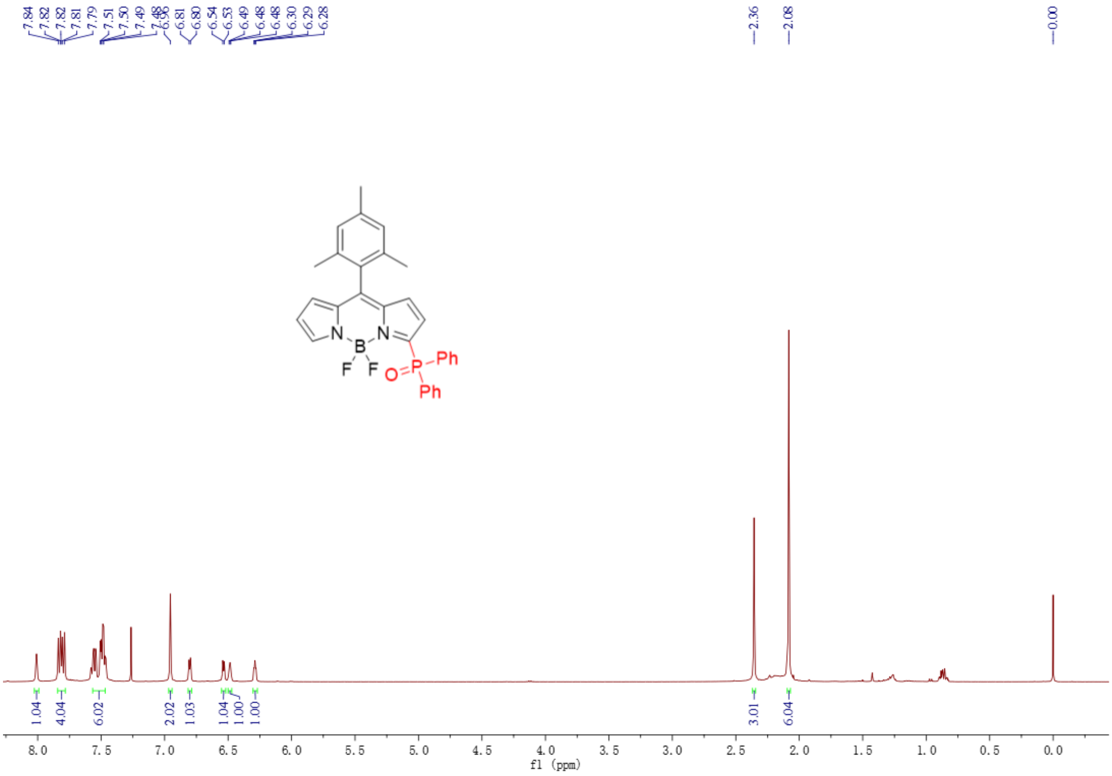
^{1}H NMR spectrum of **4g** in $CDCl_3$



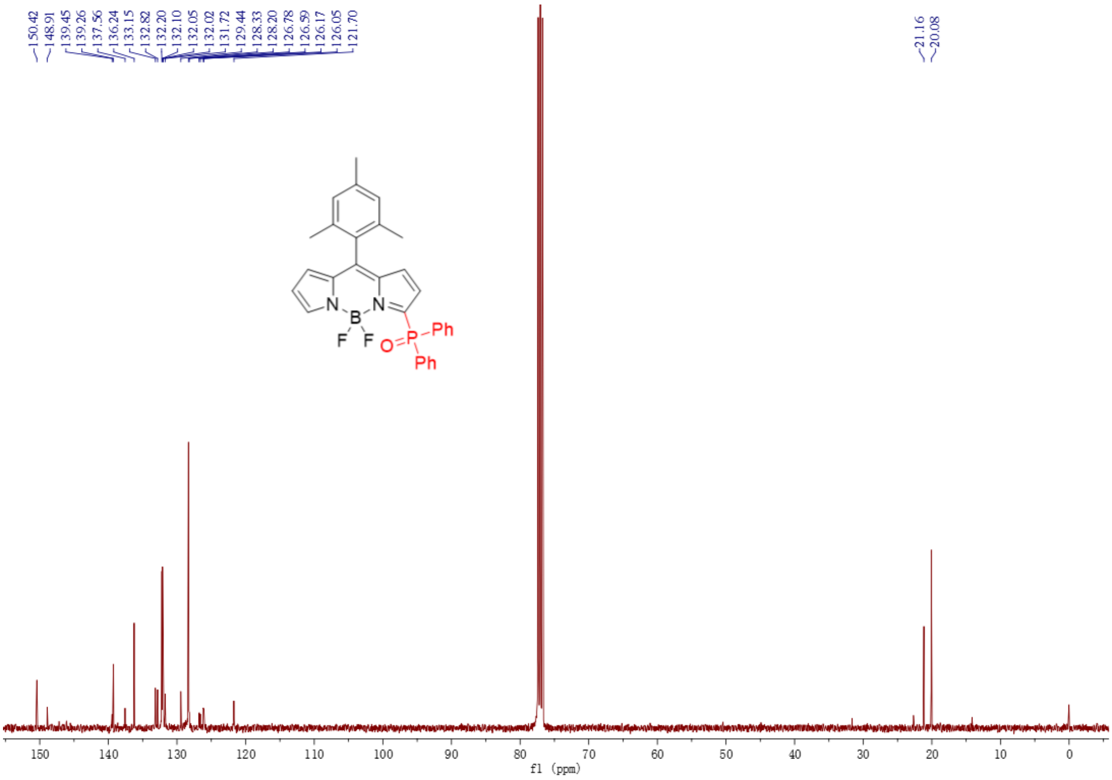
^{13}C NMR spectrum of **4g** in $CDCl_3$



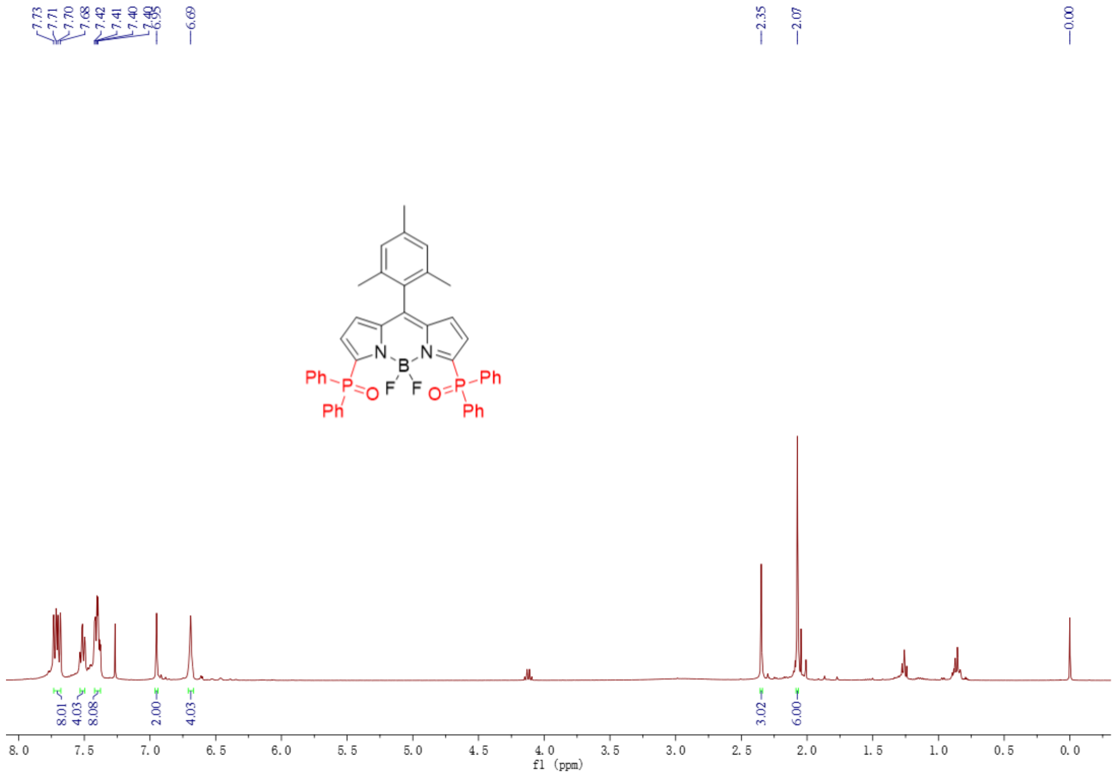
^{1}H NMR spectrum of **5a** in $CDCl_3$



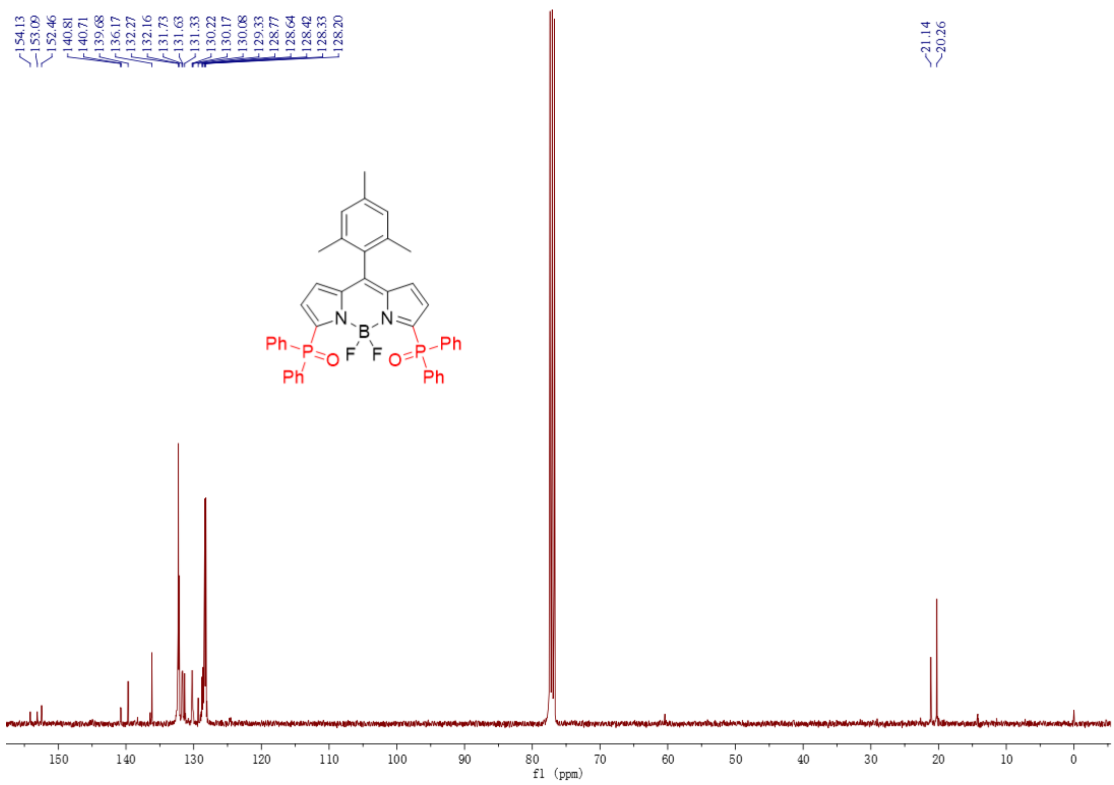
^{13}C NMR spectrum of **5a** in $CDCl_3$



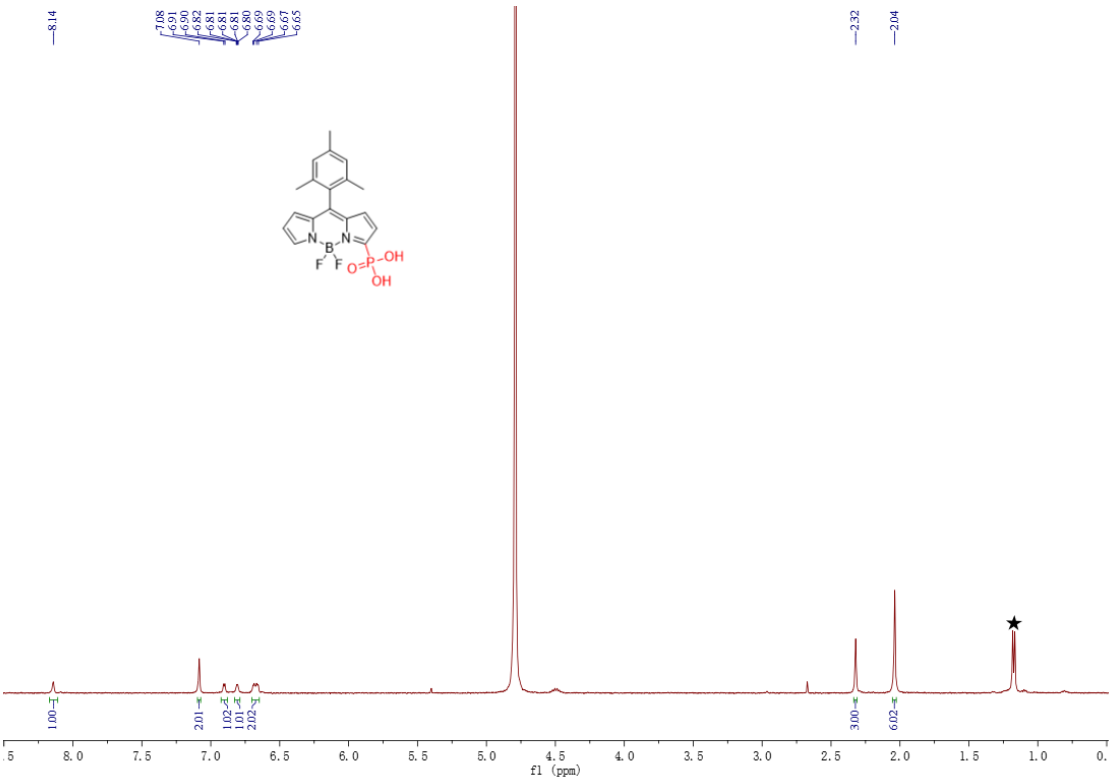
^{1}H NMR spectrum of **5b** in $CDCl_3$



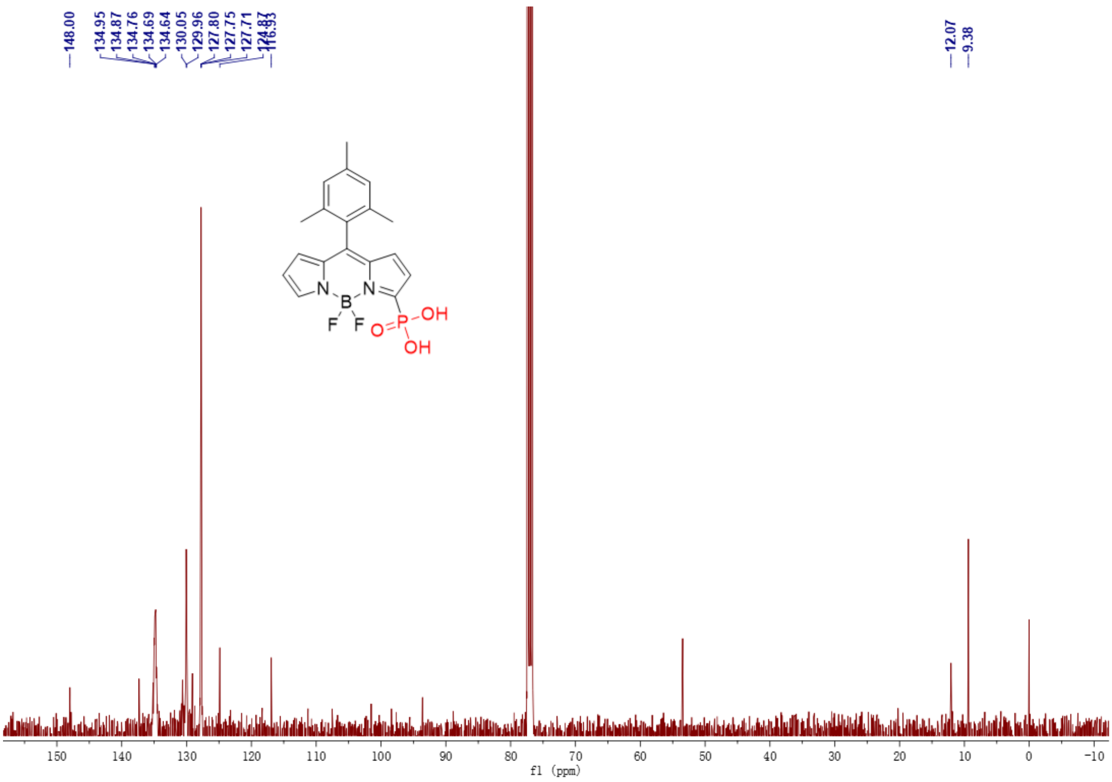
^{13}C NMR spectrum of **5b** in $CDCl_3$



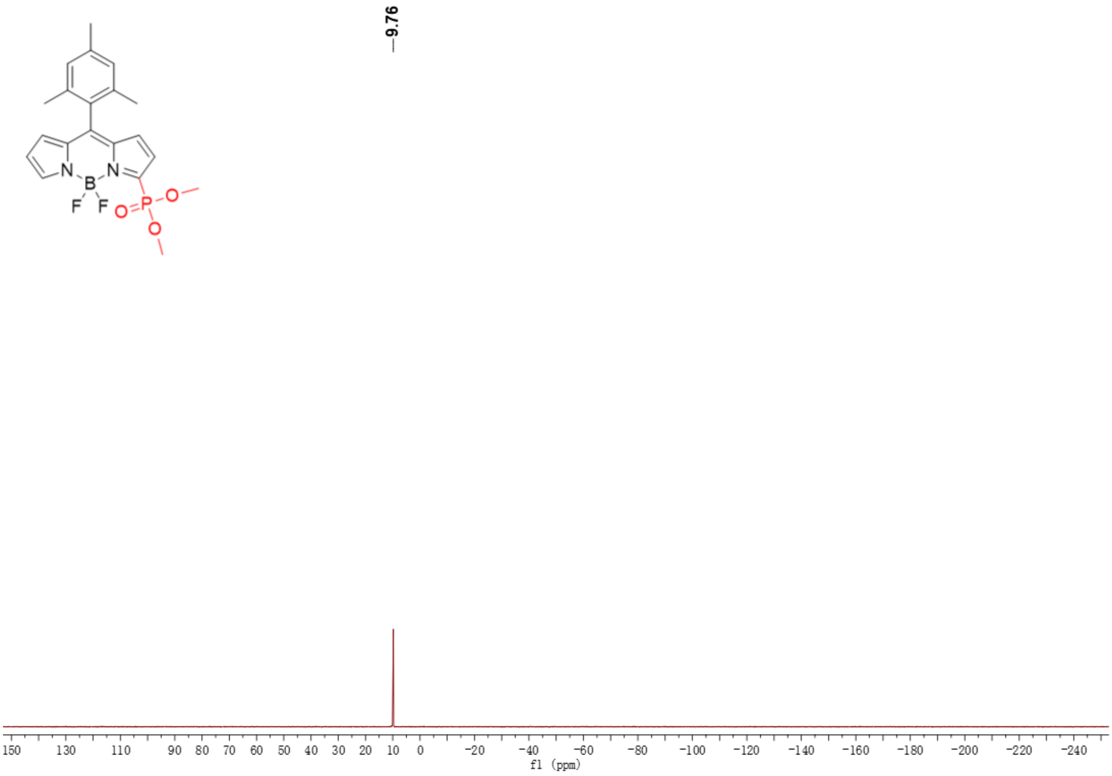
^{1}H NMR spectrum of **6** in D_2O



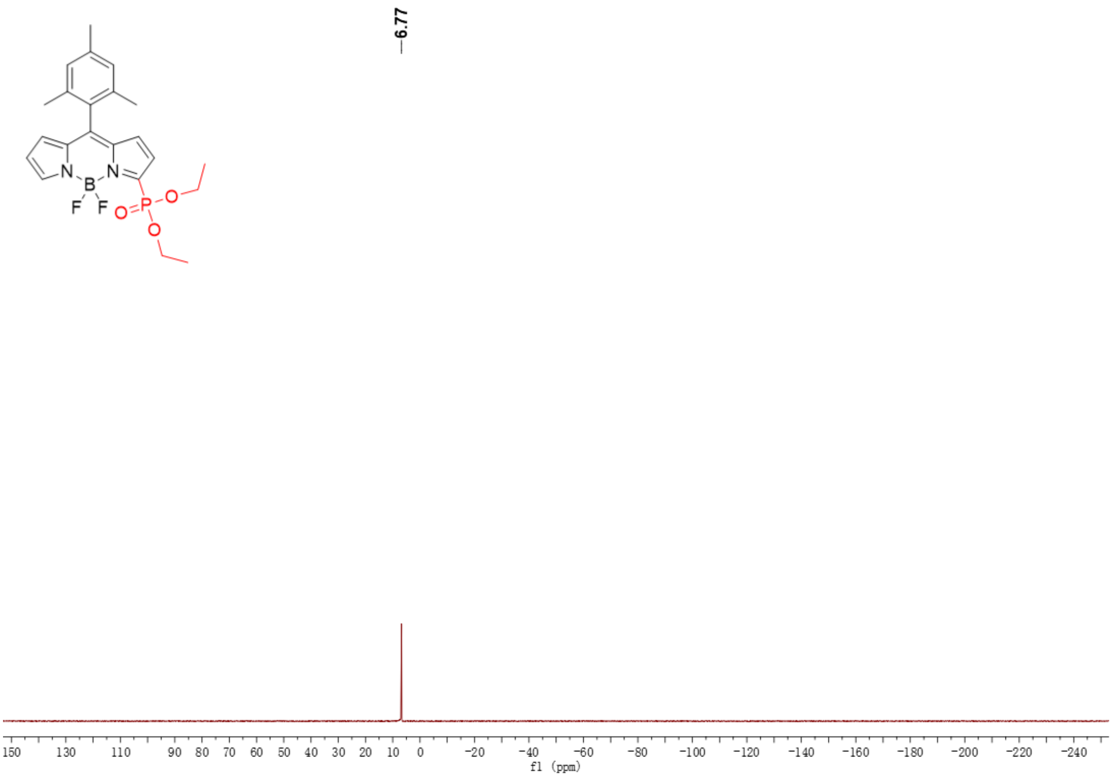
^{13}C NMR spectrum of **6** in $CDCl_3$



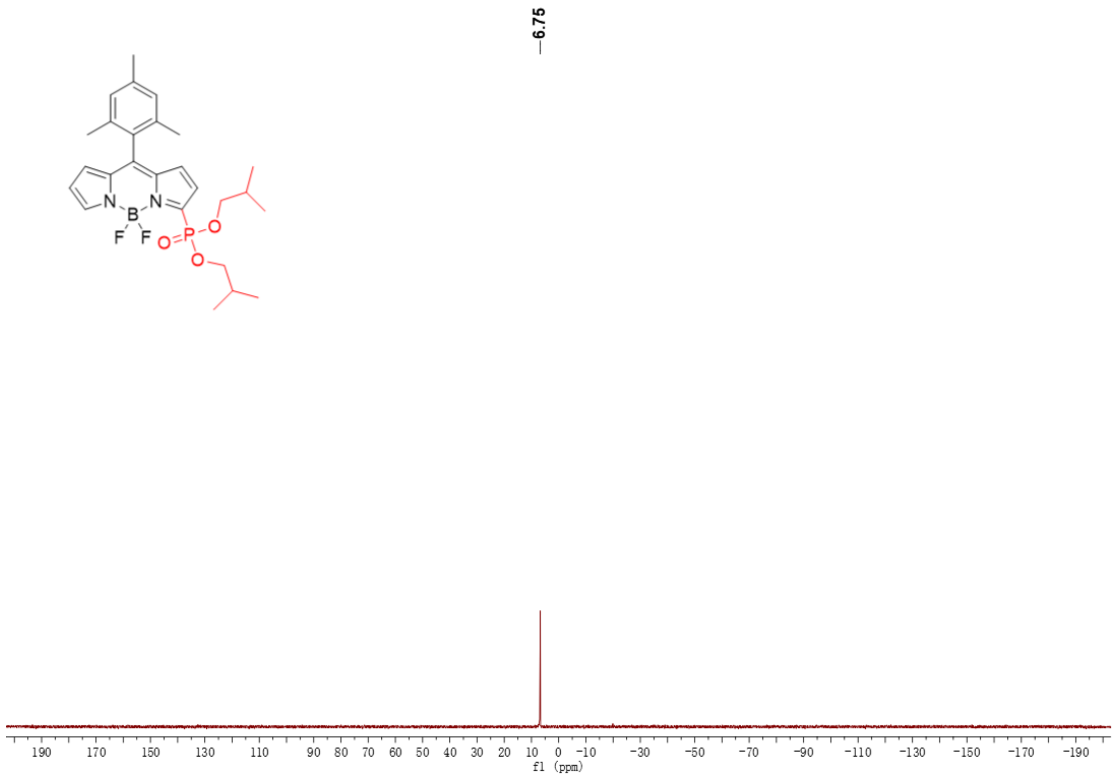
^{31}P NMR spectrum of **3a** in $CDCl_3$



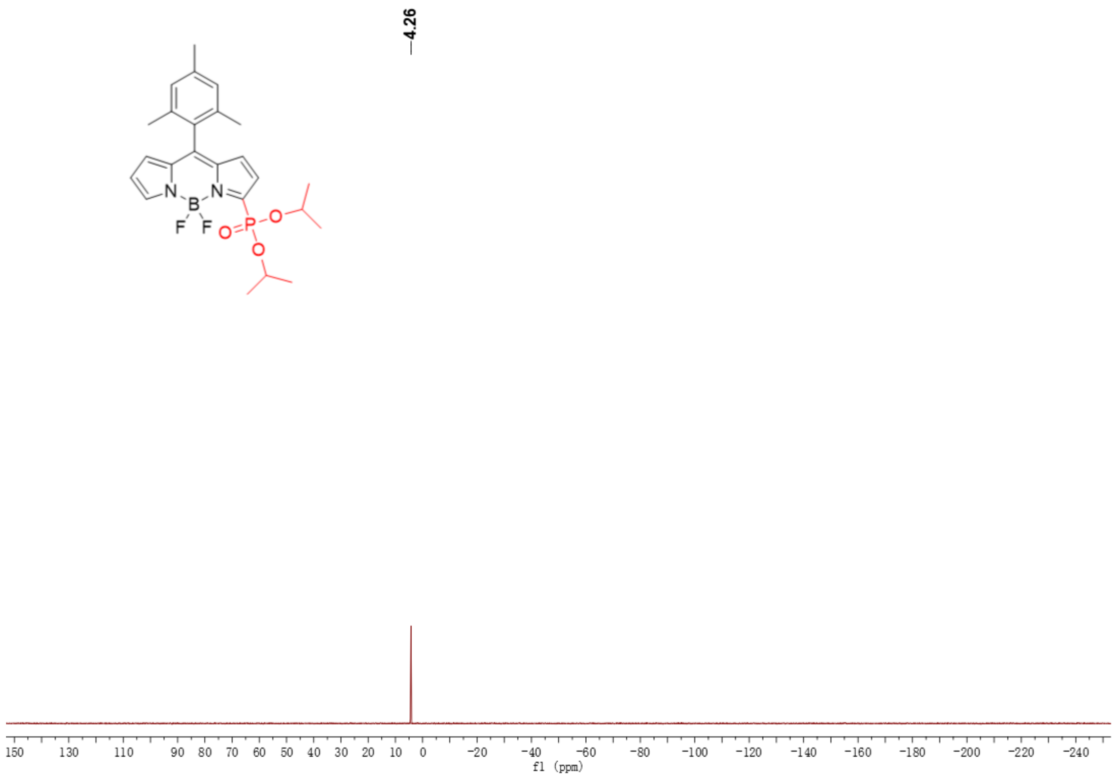
^{31}P NMR spectrum of **3b** in $CDCl_3$



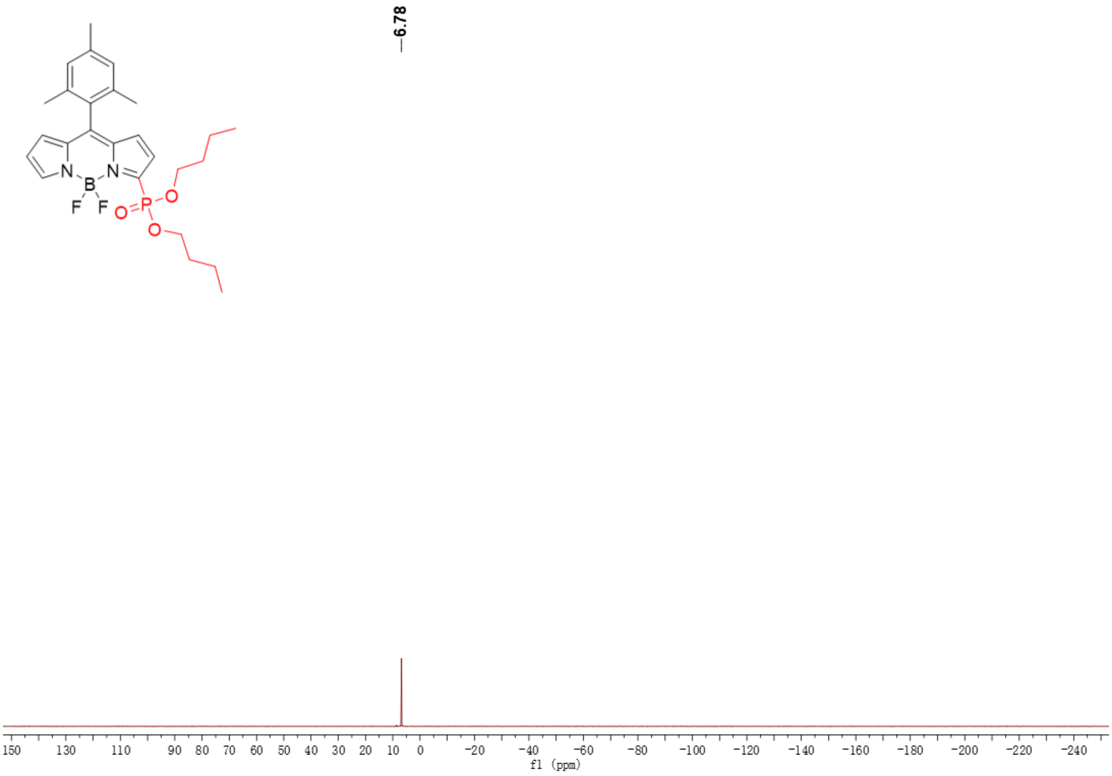
^{31}P NMR spectrum of **3c** in $CDCl_3$



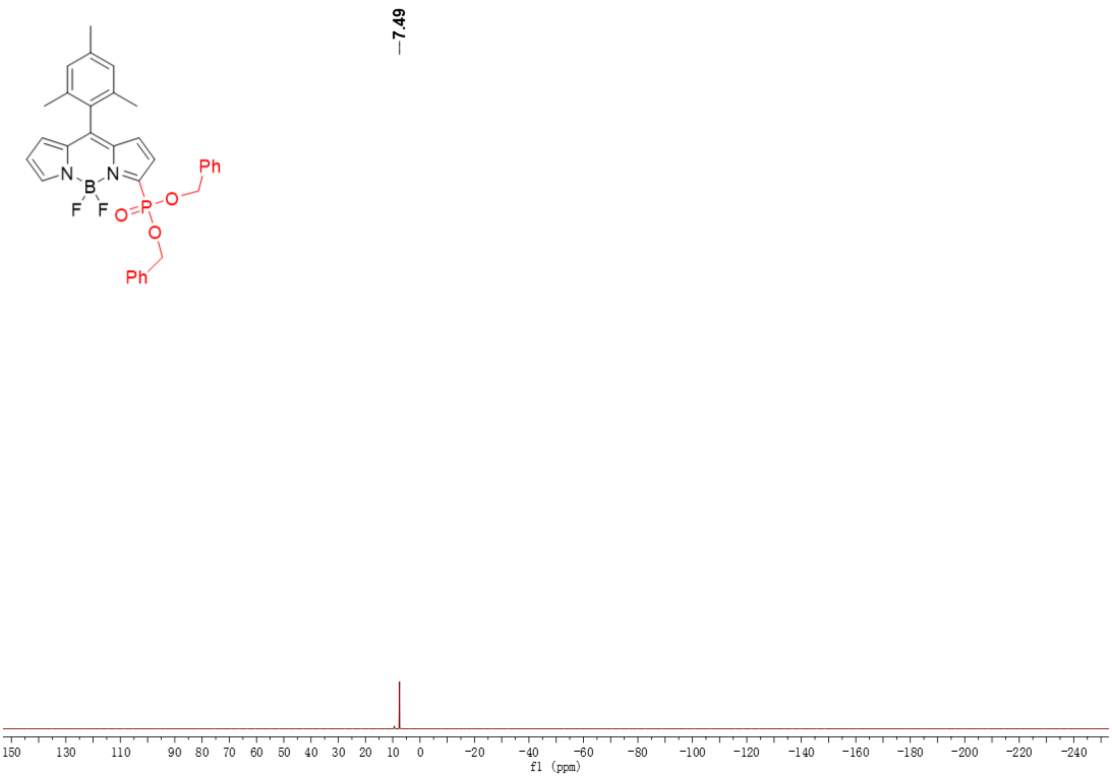
^{31}P NMR spectrum of **3d** in $CDCl_3$



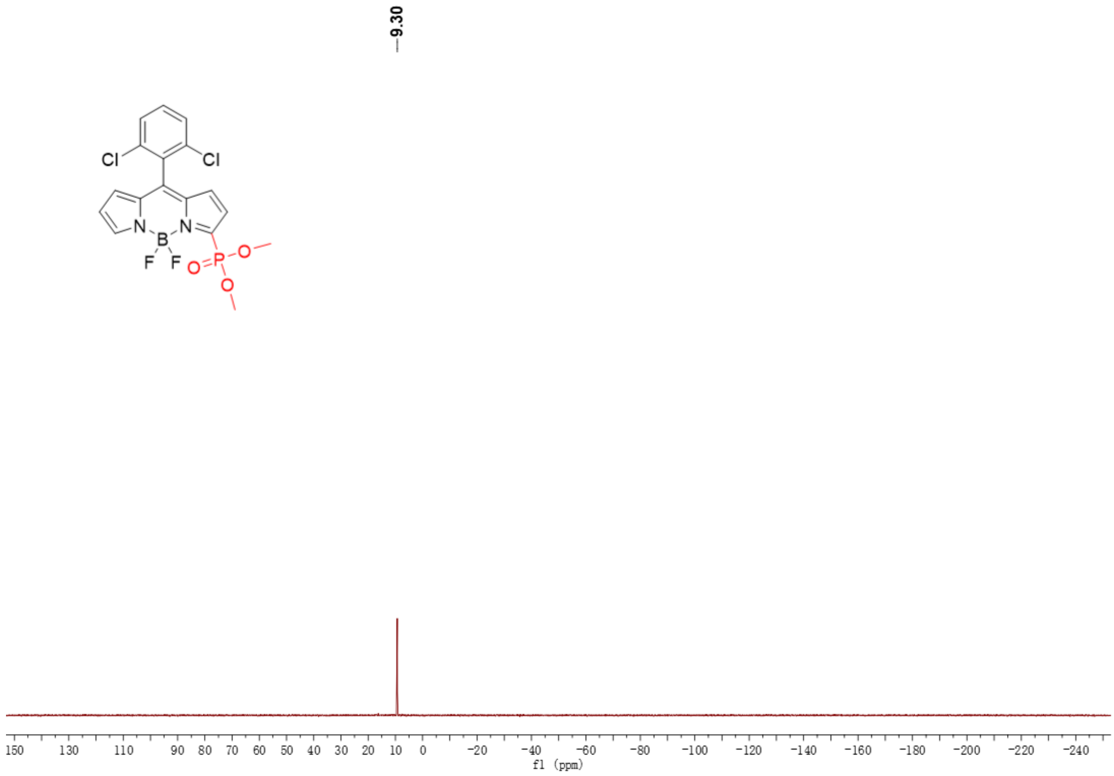
^{31}P NMR spectrum of **3e** in $CDCl_3$



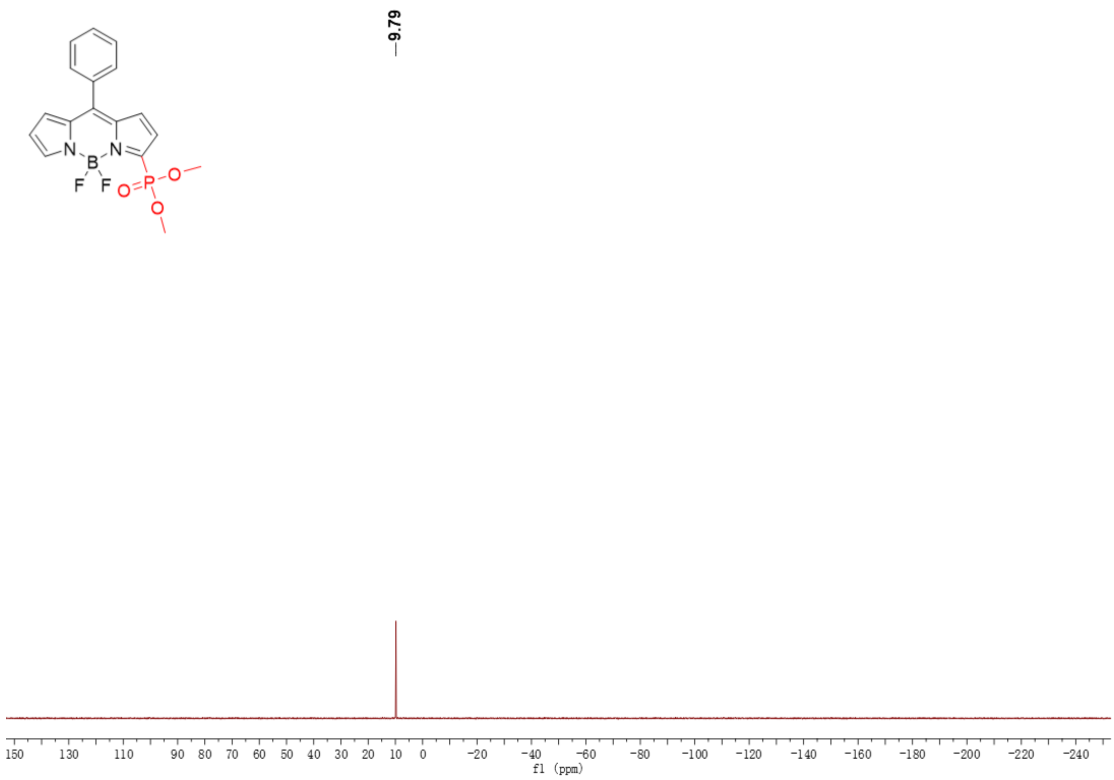
^{31}P NMR spectrum of **3f** in $CDCl_3$



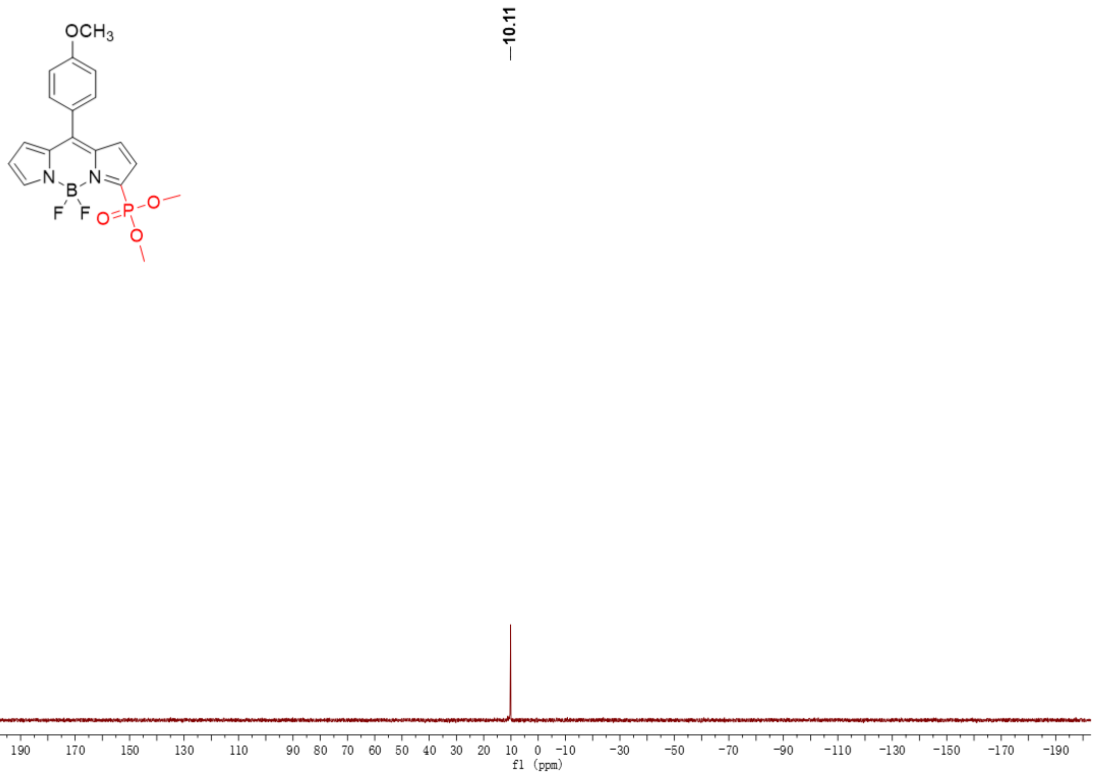
^{31}P NMR spectrum of **3g** in $CDCl_3$



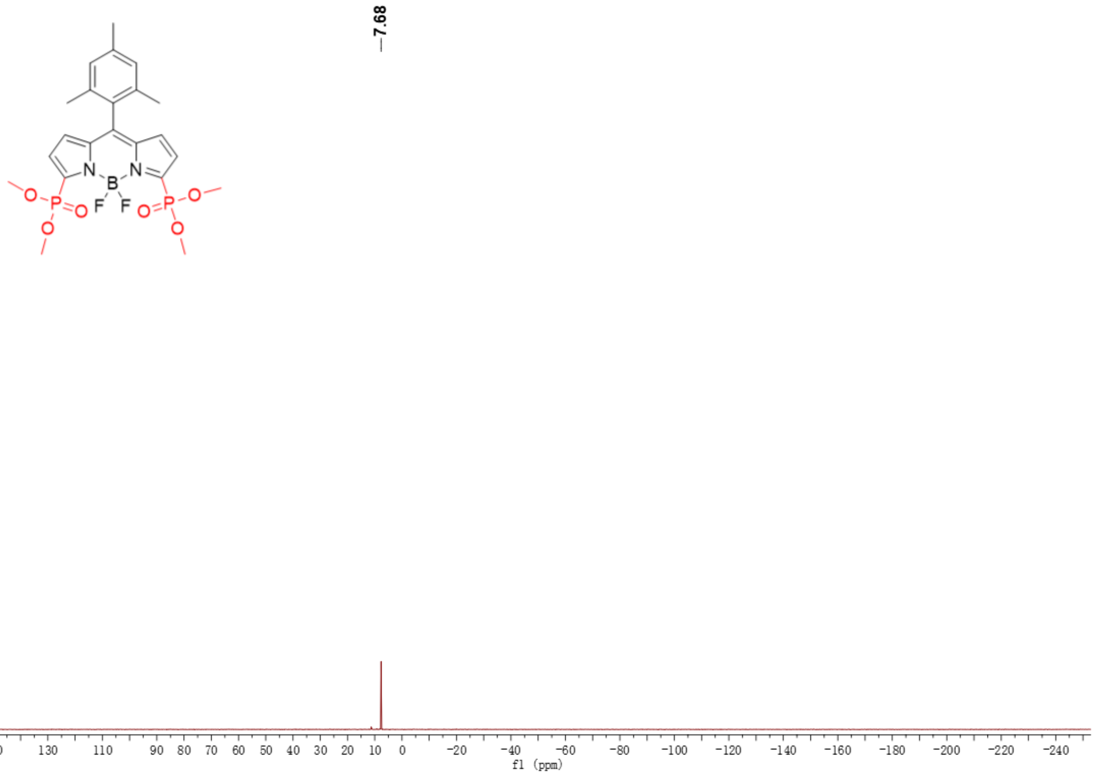
^{31}P NMR spectrum of **3h** in $CDCl_3$



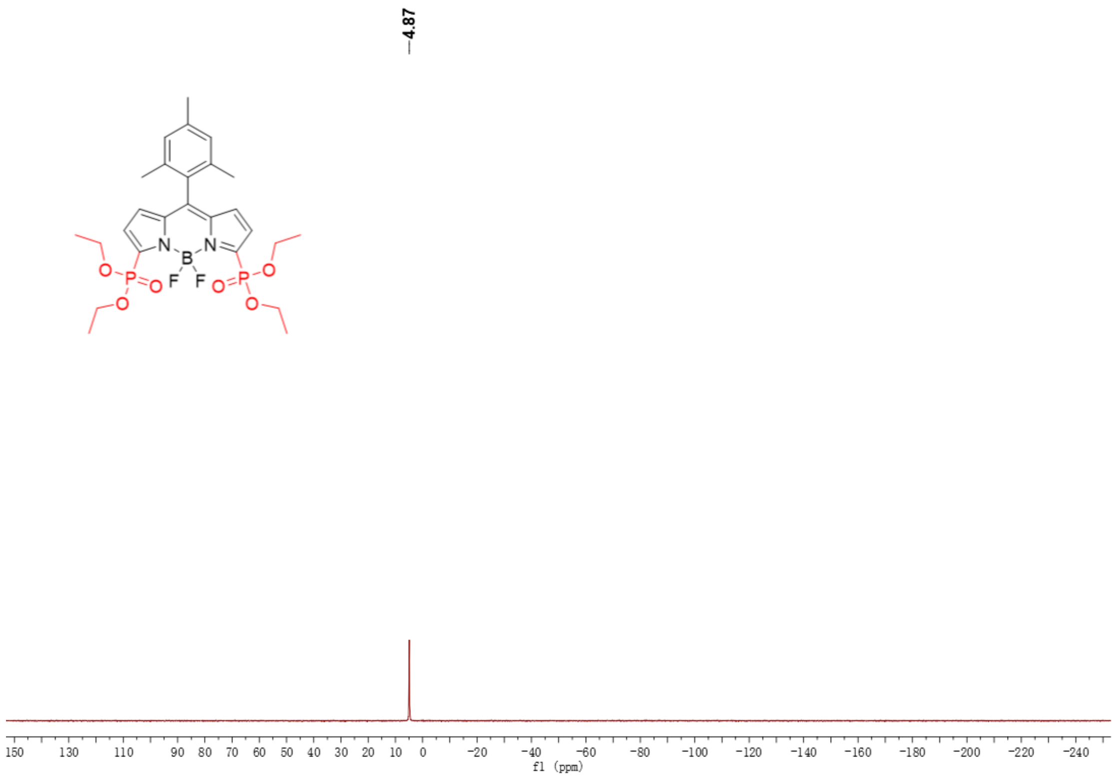
^{31}P NMR spectrum of **3i** in $CDCl_3$



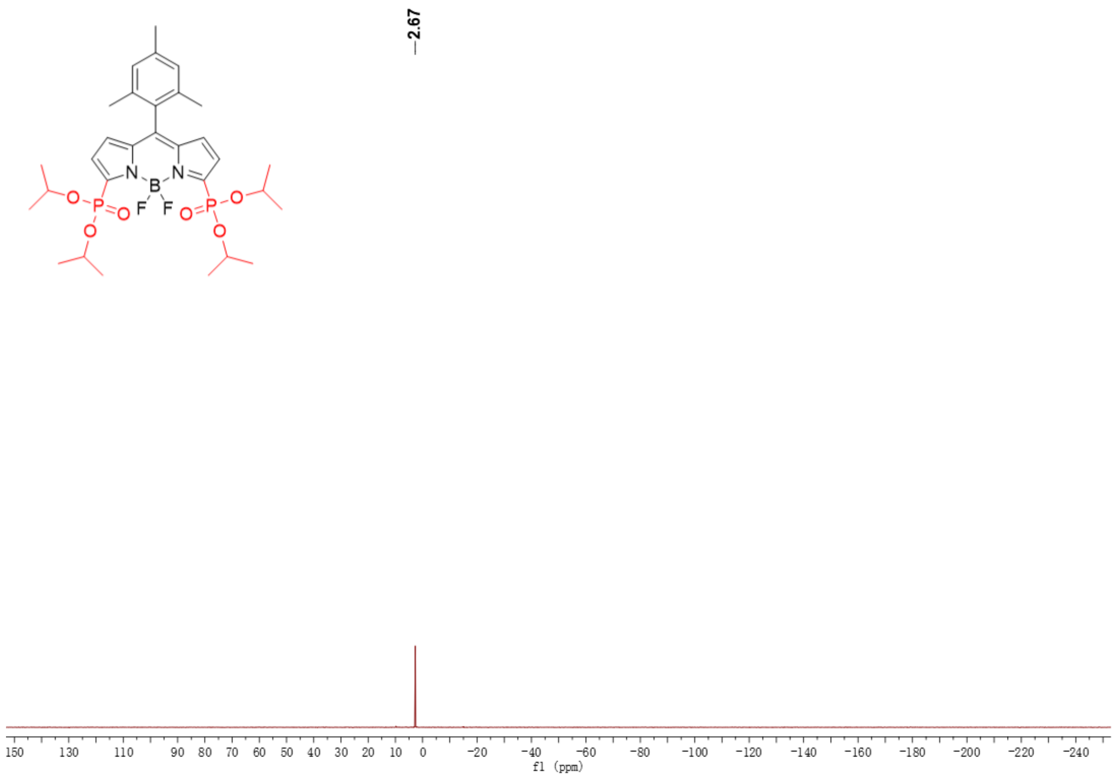
^{31}P NMR spectrum of **4a** in $CDCl_3$



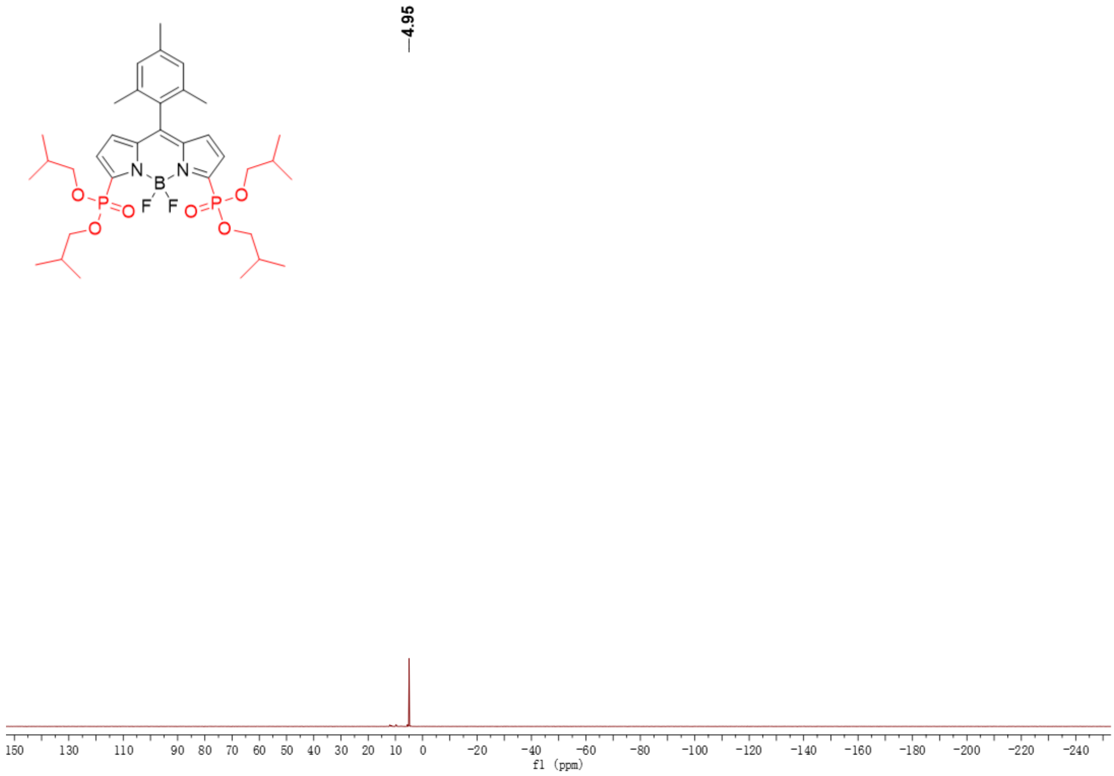
^{31}P NMR spectrum of **4b** in $CDCl_3$



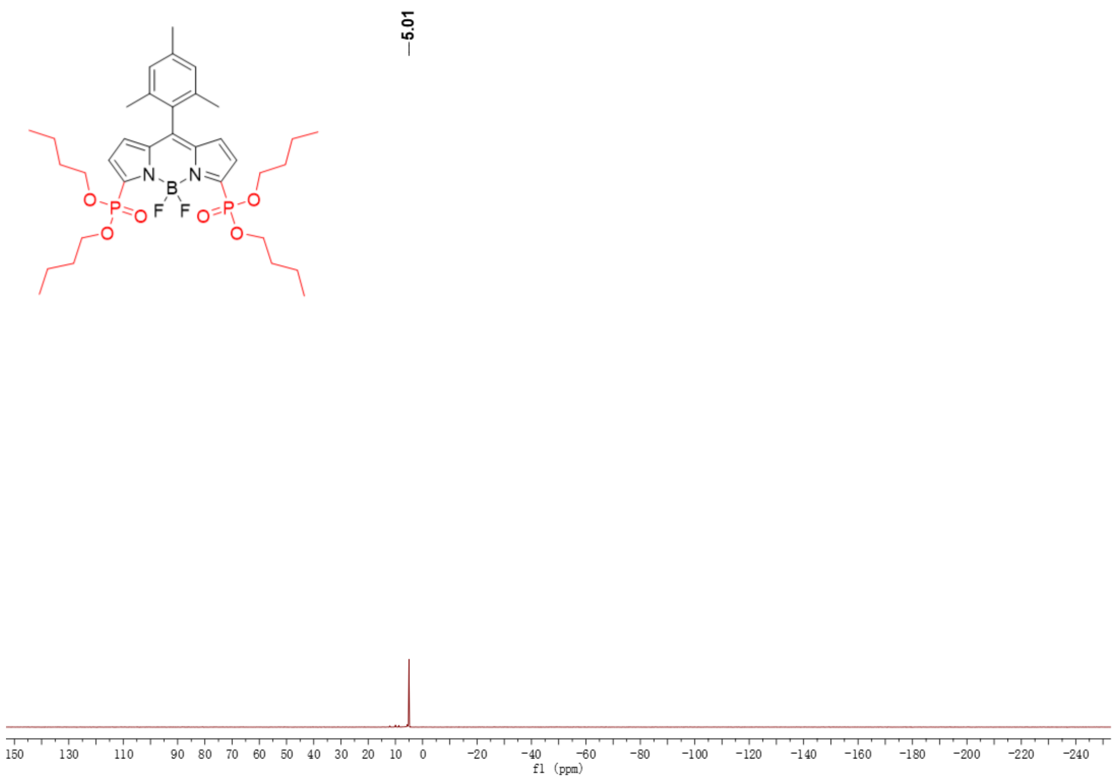
^{31}P NMR spectrum of **4c** in $CDCl_3$



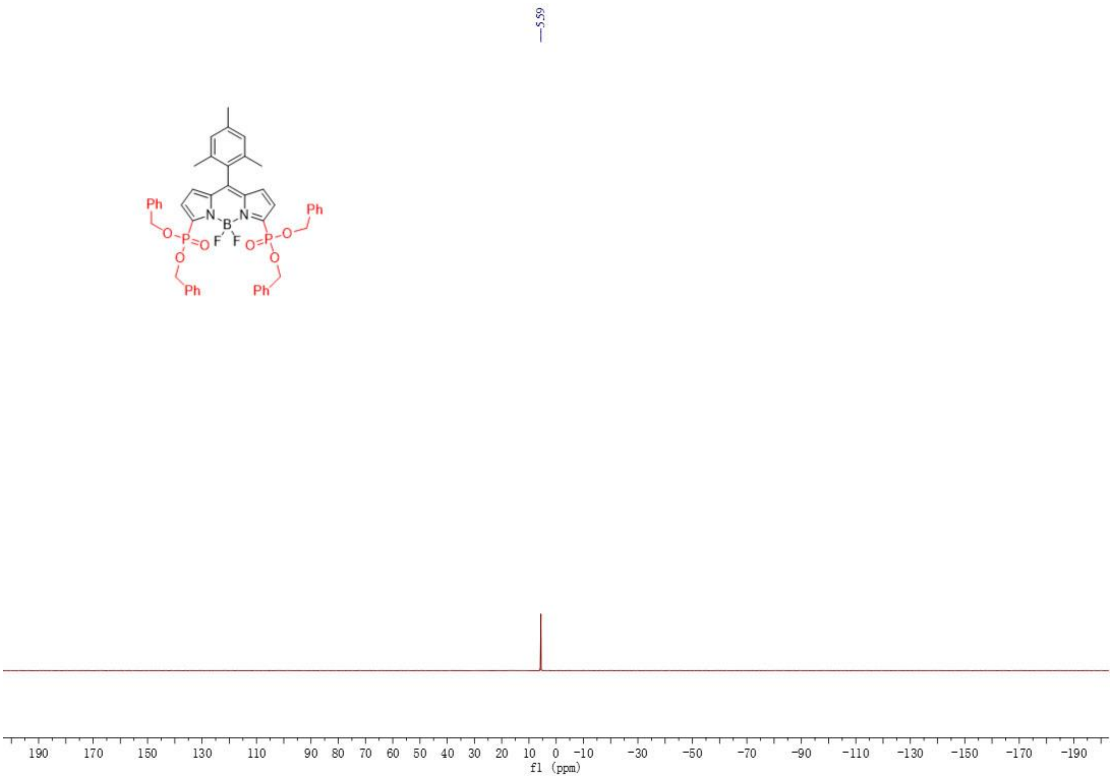
^{31}P NMR spectrum of **4d** in $CDCl_3$



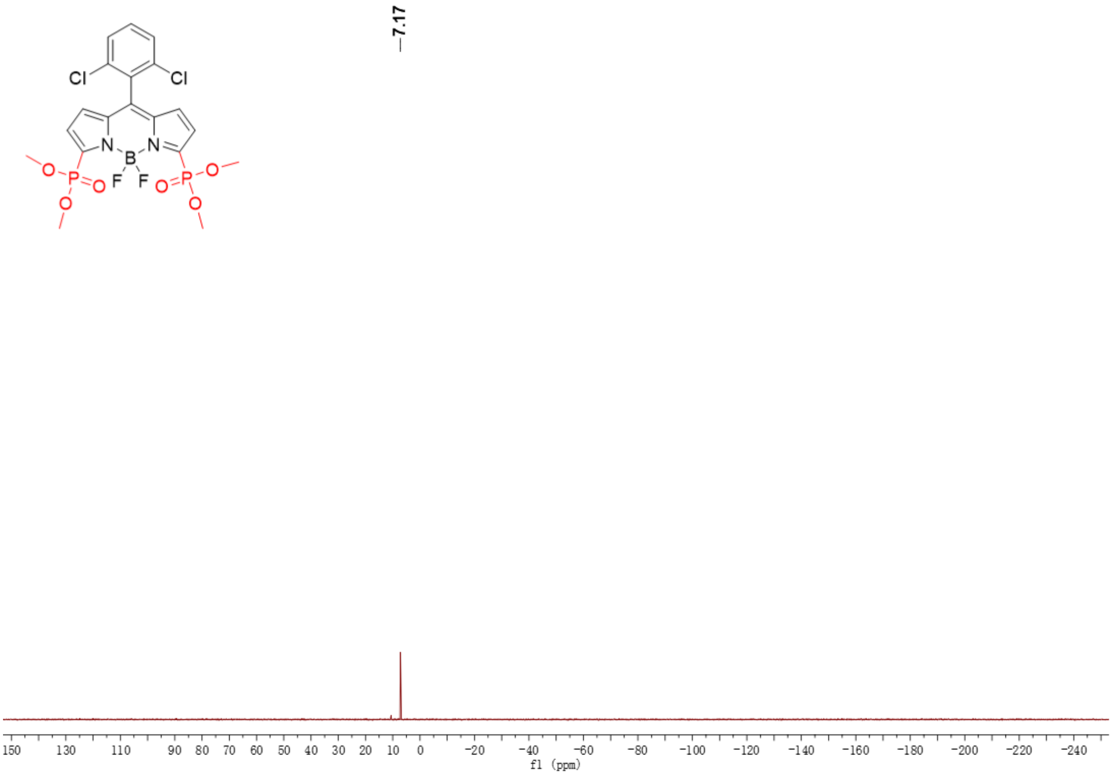
^{31}P NMR spectrum of **4e** in $CDCl_3$



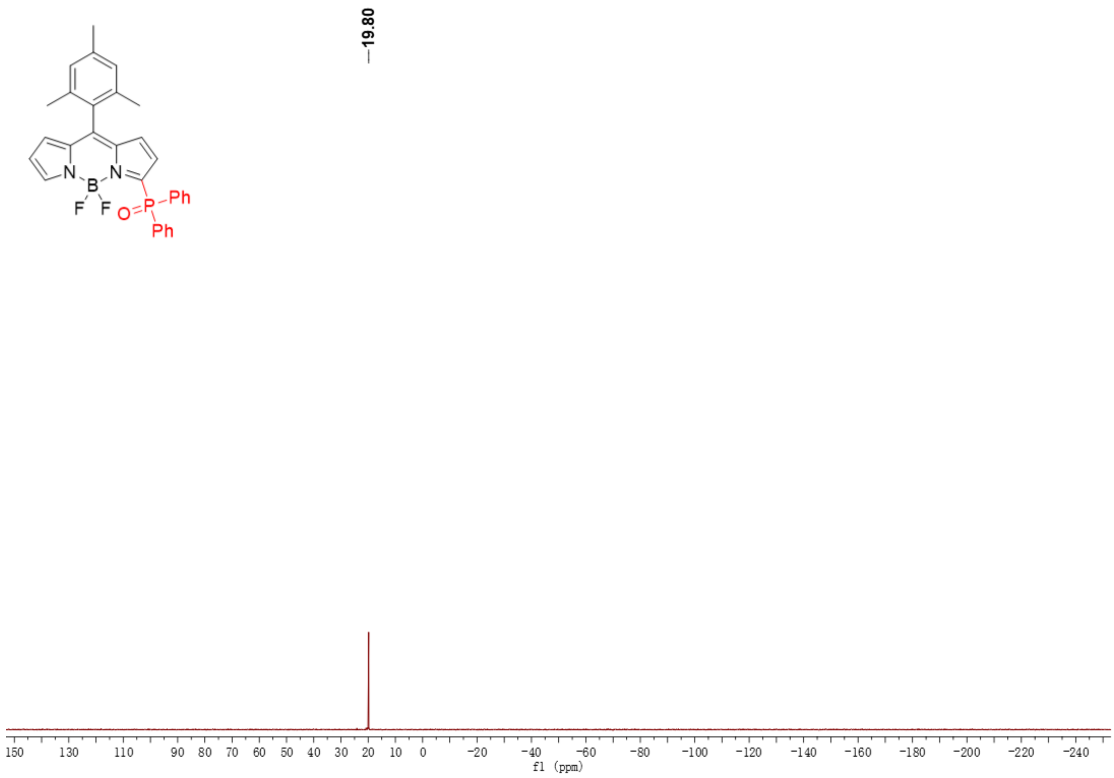
^{31}P NMR spectrum of **4f** in $CDCl_3$



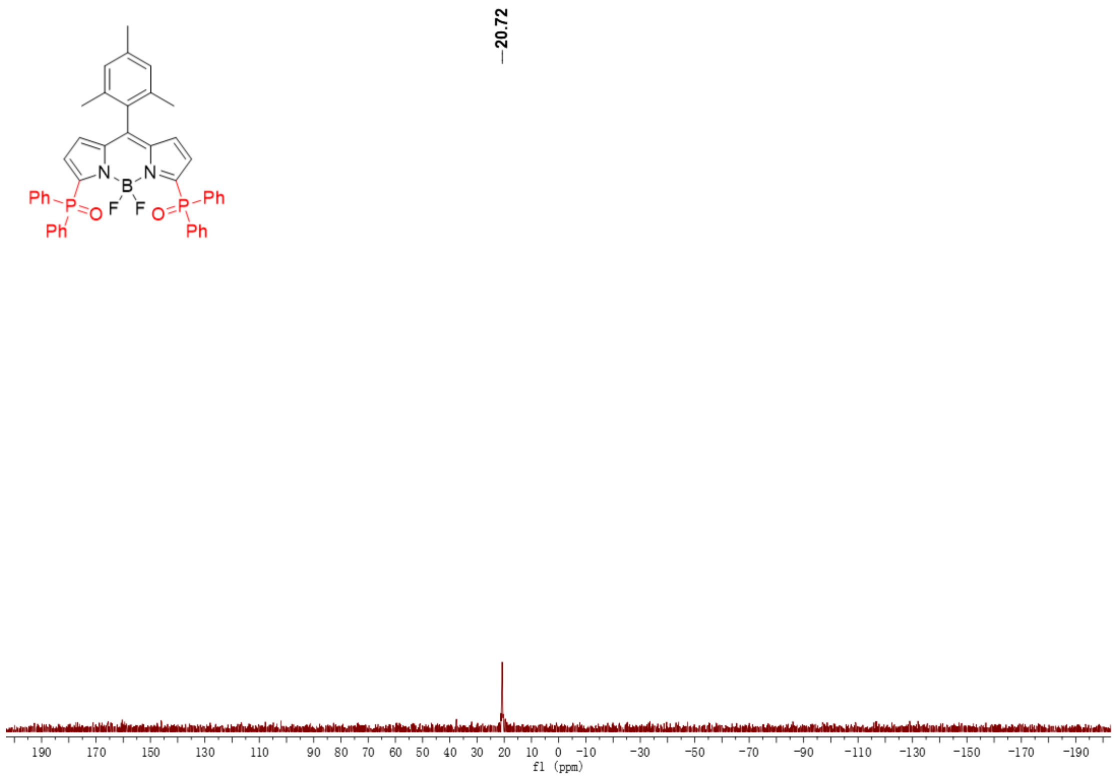
^{31}P NMR spectrum of **4g** in $CDCl_3$



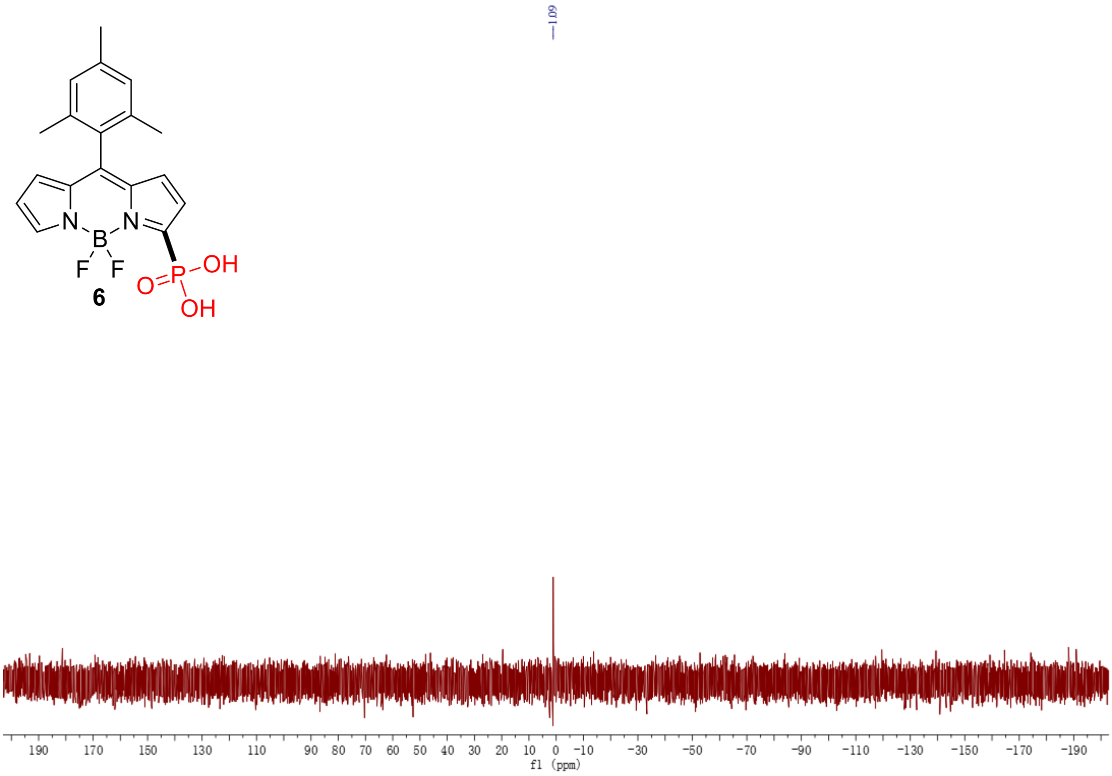
^{31}P NMR spectrum of **5a** in $CDCl_3$



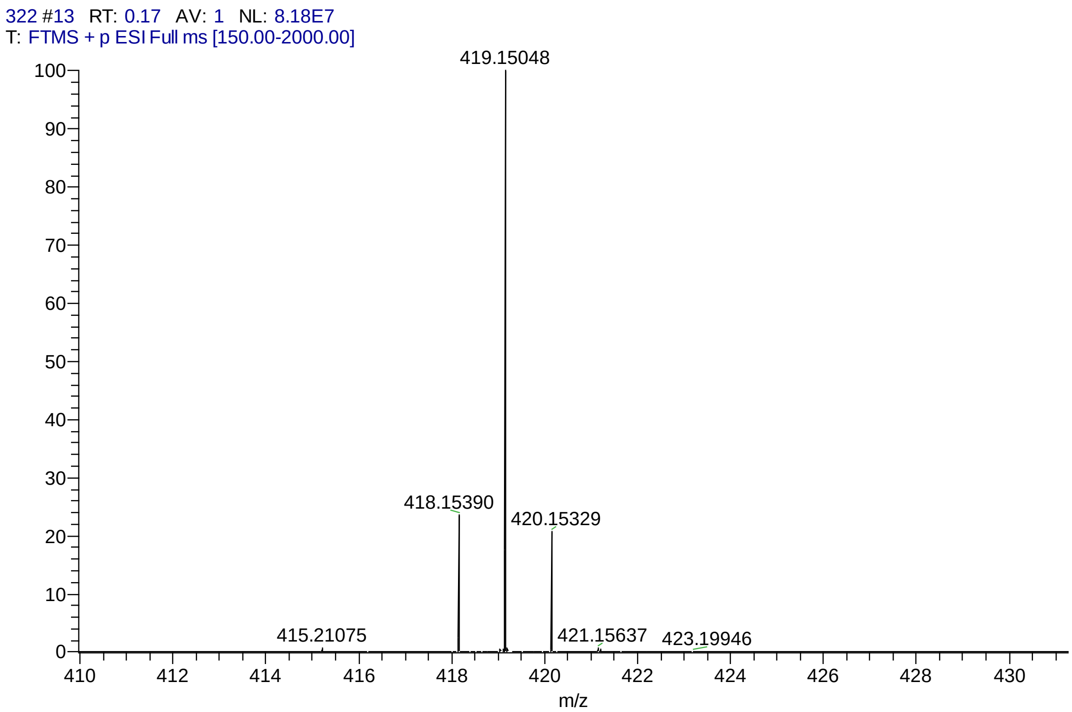
^{31}P NMR spectrum of **5b** in $CDCl_3$



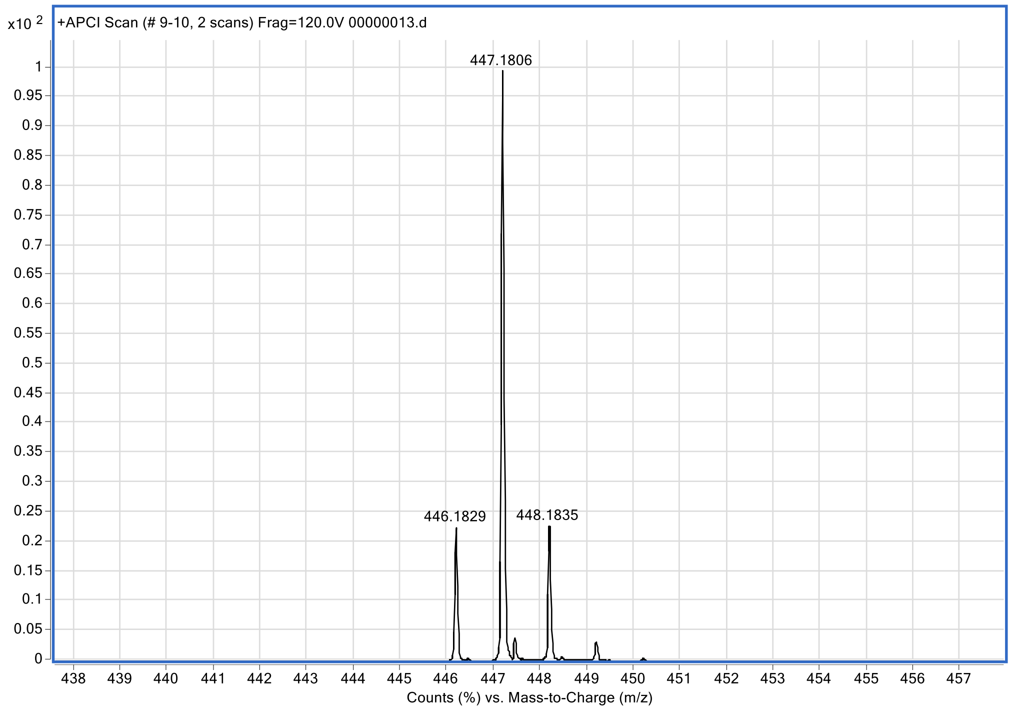
^{31}P NMR spectrum of **6** in D_2O



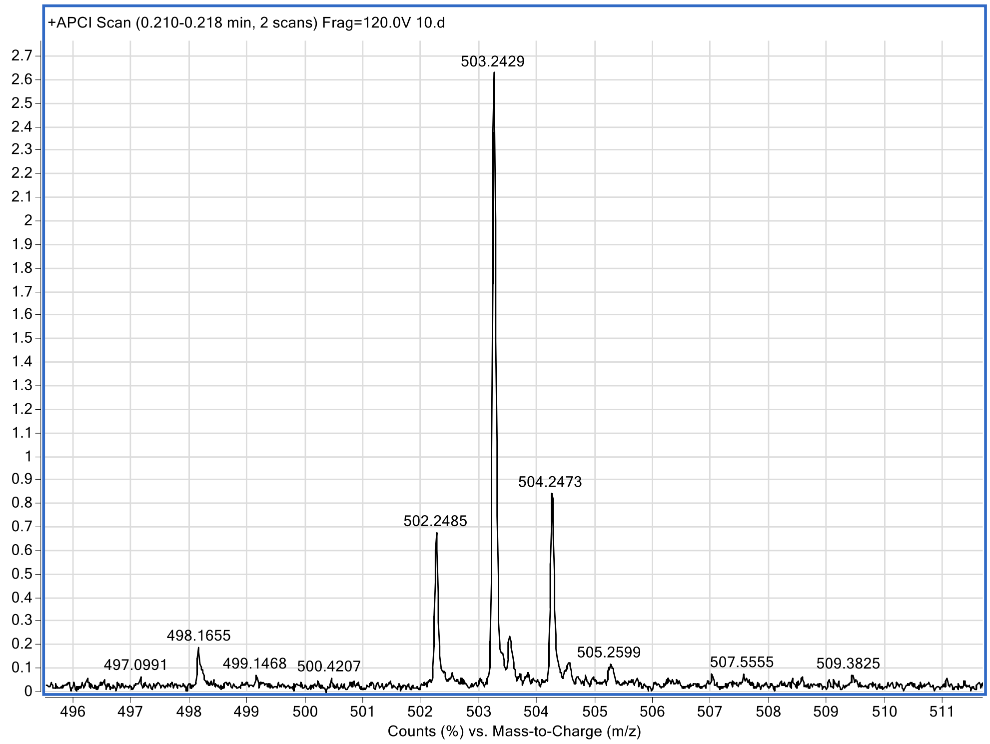
HRMS for **3a**



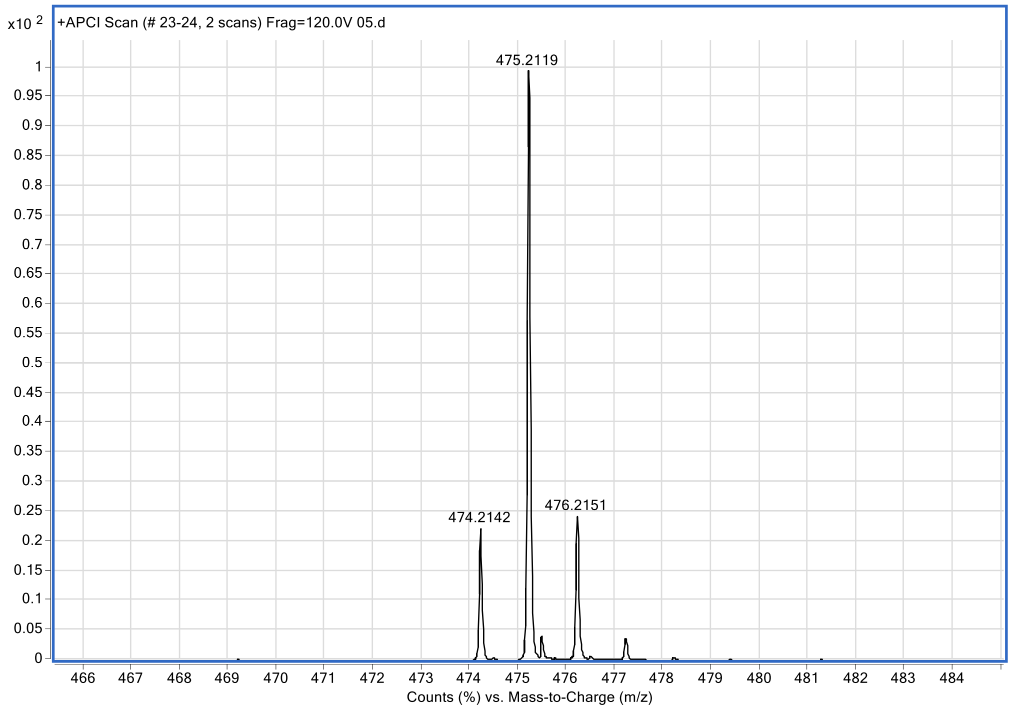
HRMS for **3b**



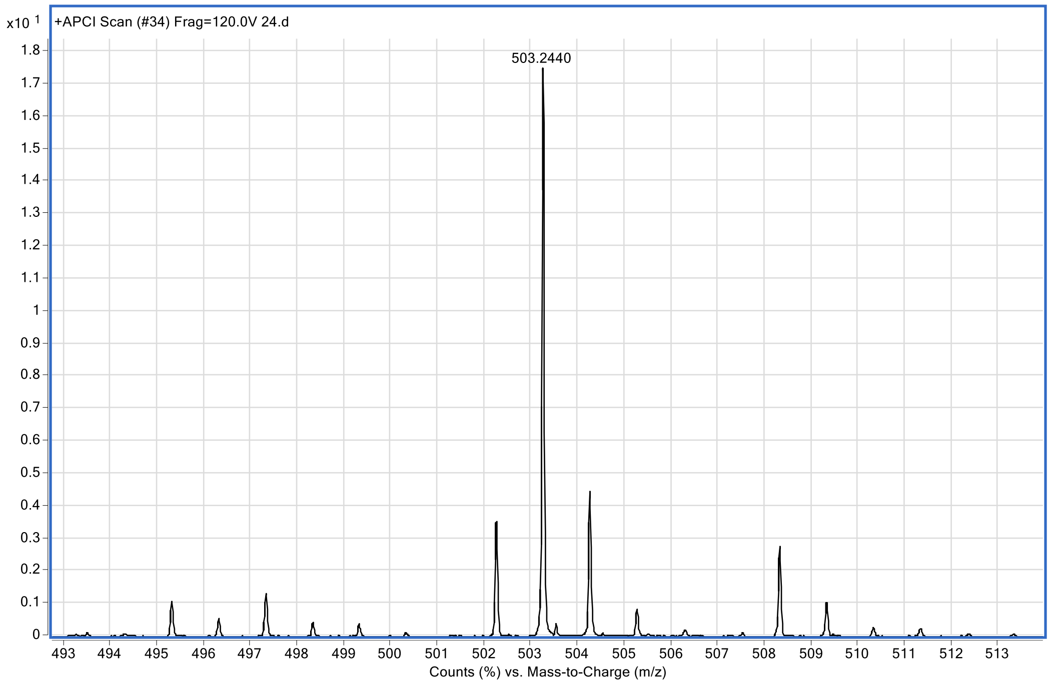
HRMS for **3c**



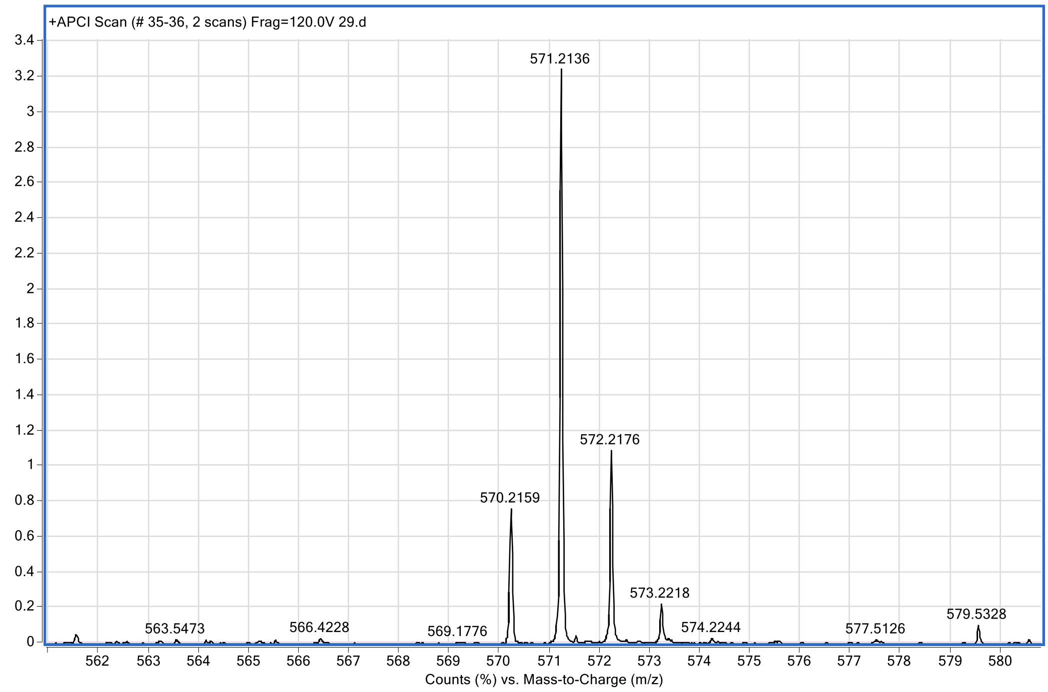
HRMS for **3d**



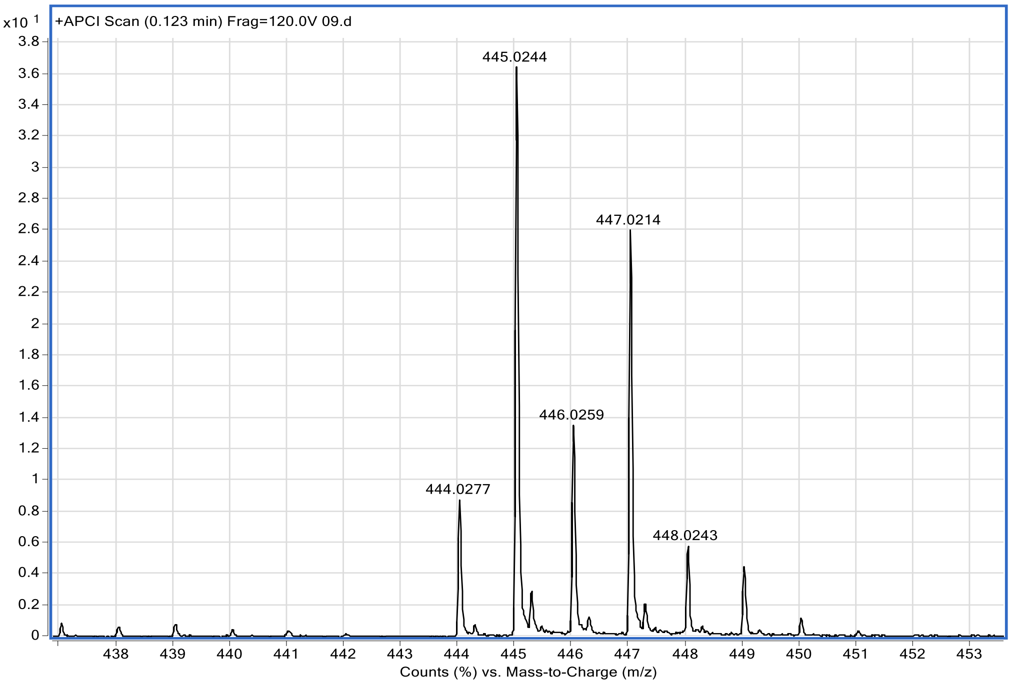
HRMS for **3e**



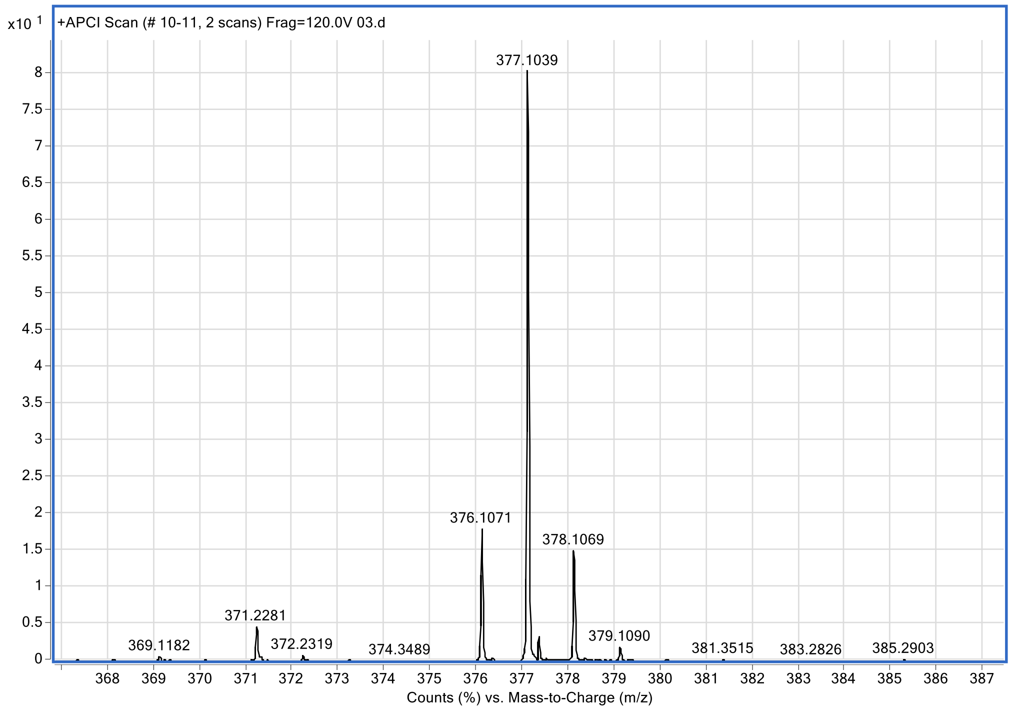
HRMS for **3f**



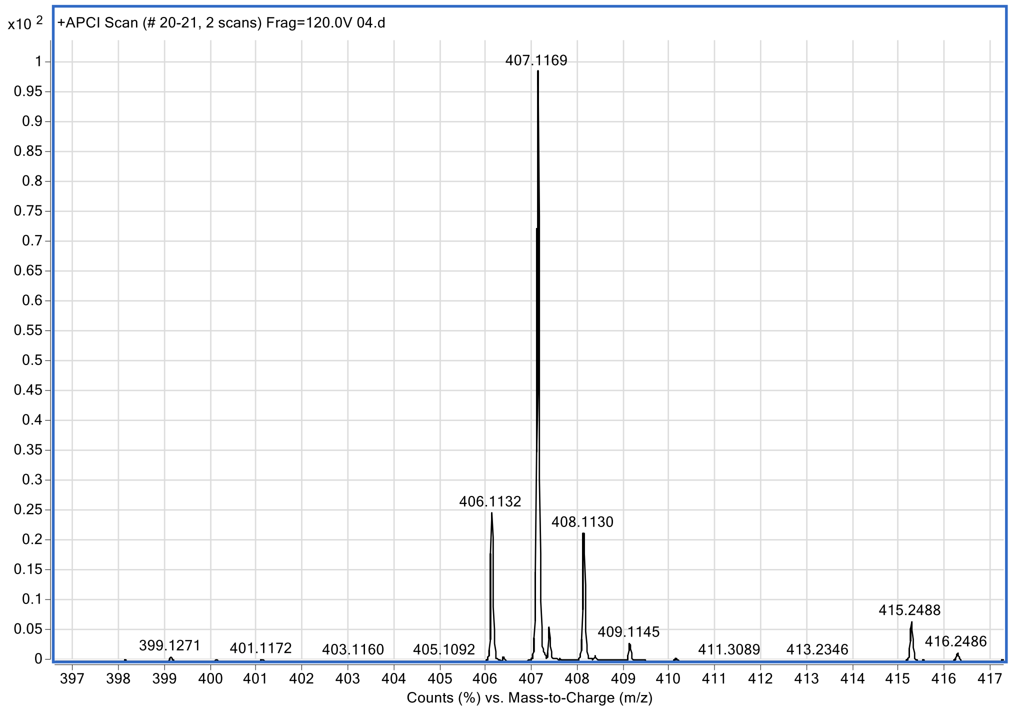
HRMS for **3g**



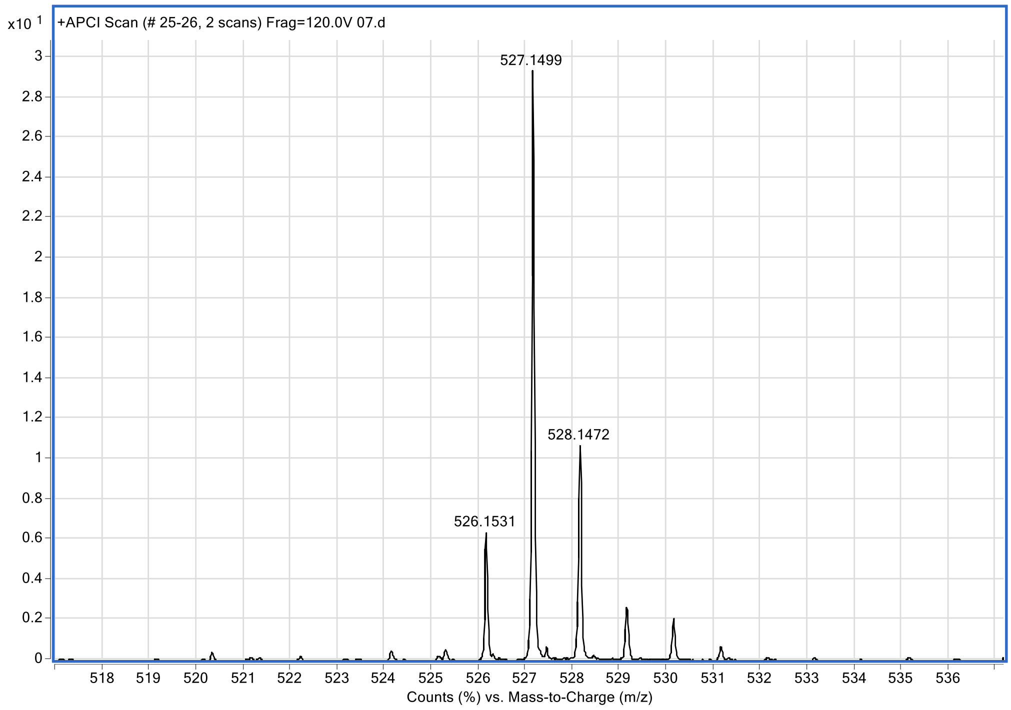
HRMS for **3h**



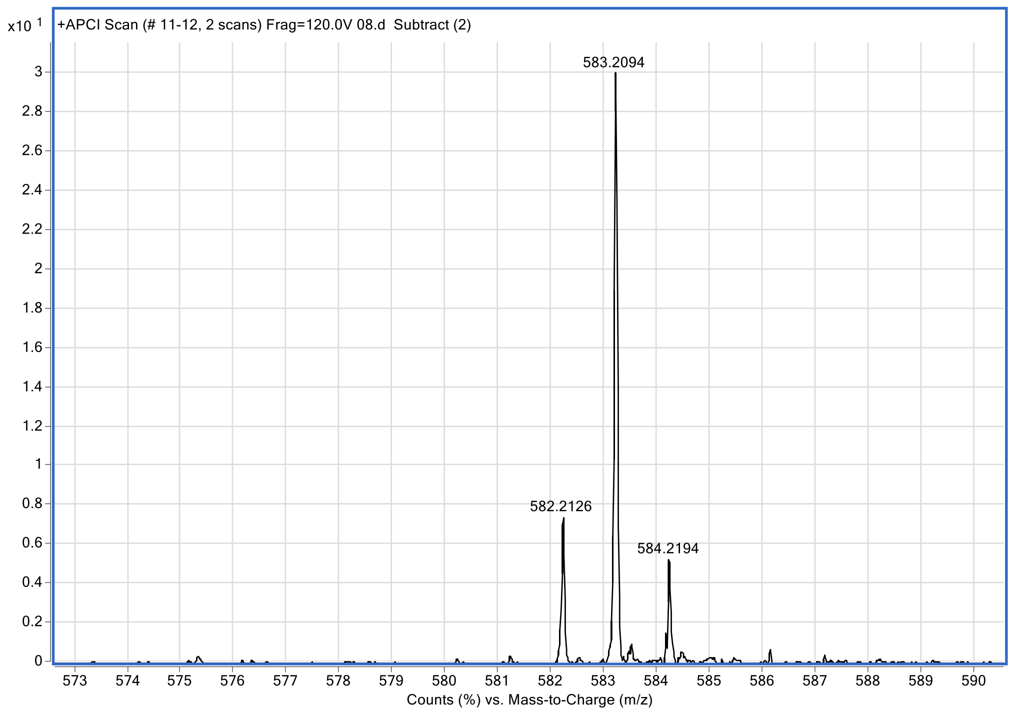
HRMS for **3i**



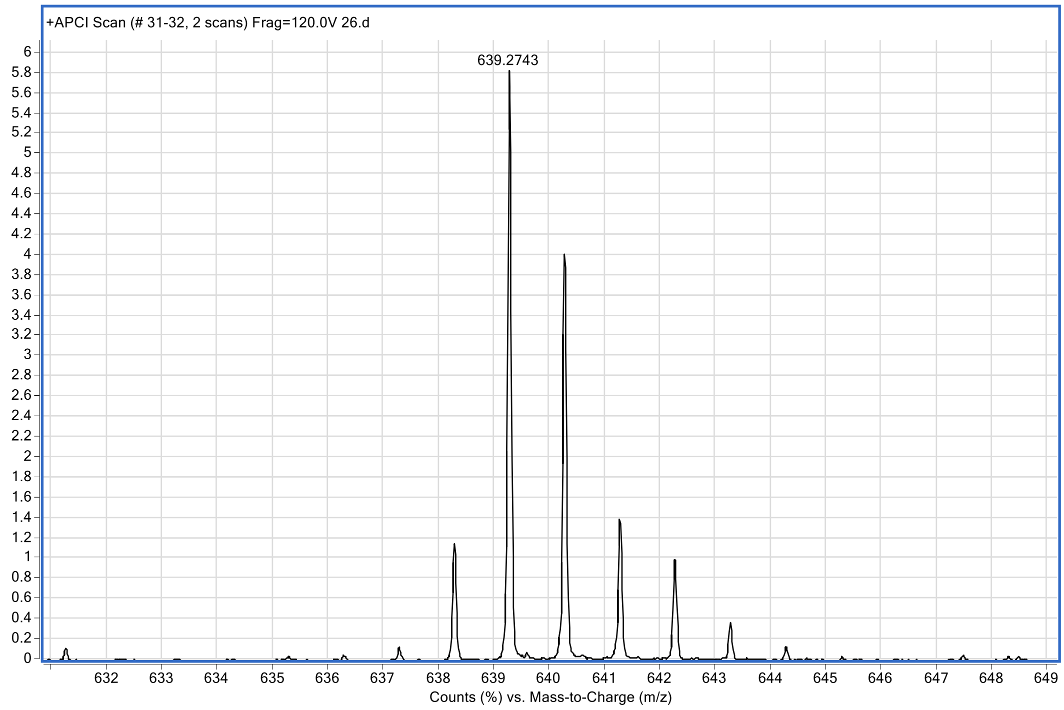
HRMS for **4a**



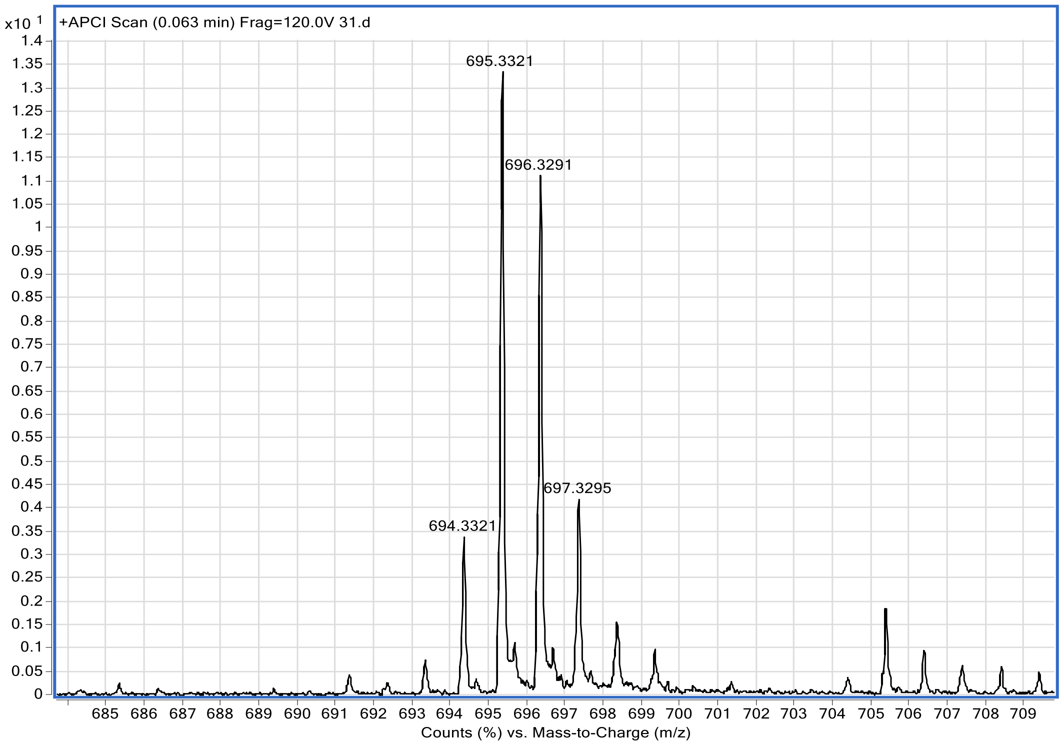
HRMS for **4b**



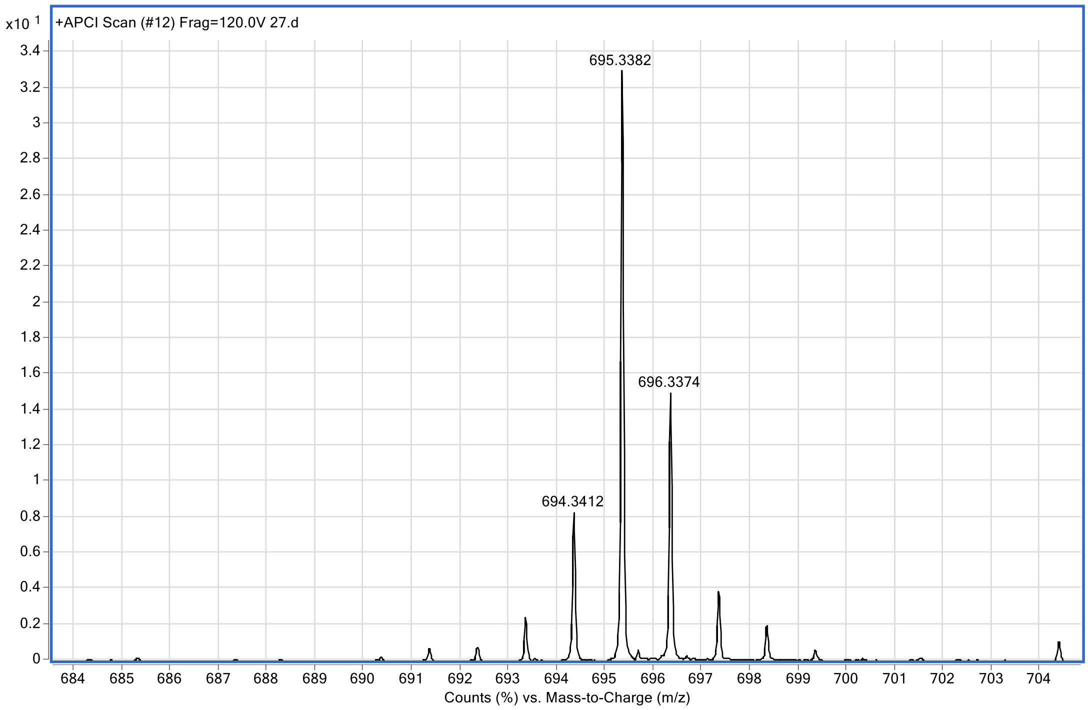
HRMS for **4c**



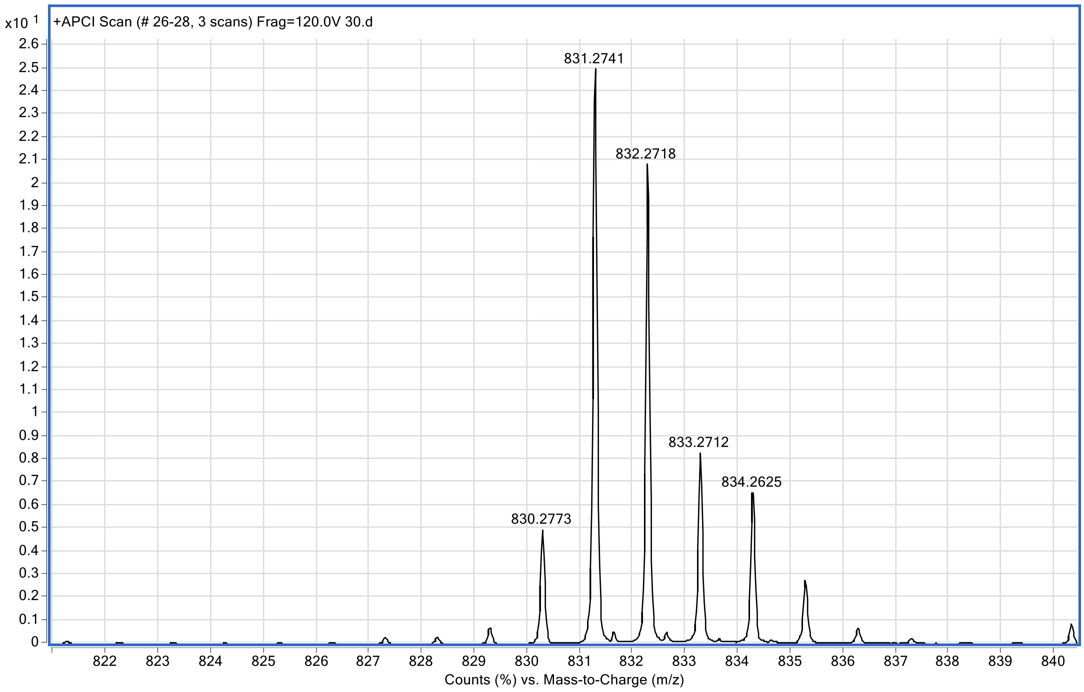
HRMS for **4d**



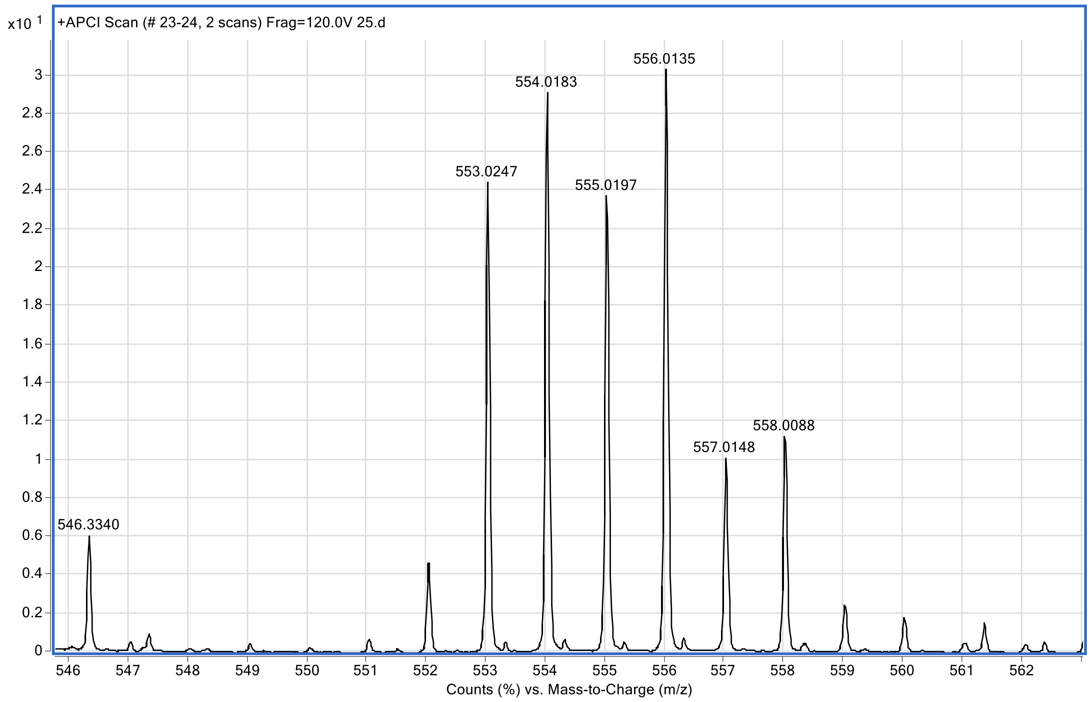
HRMS for **4e**



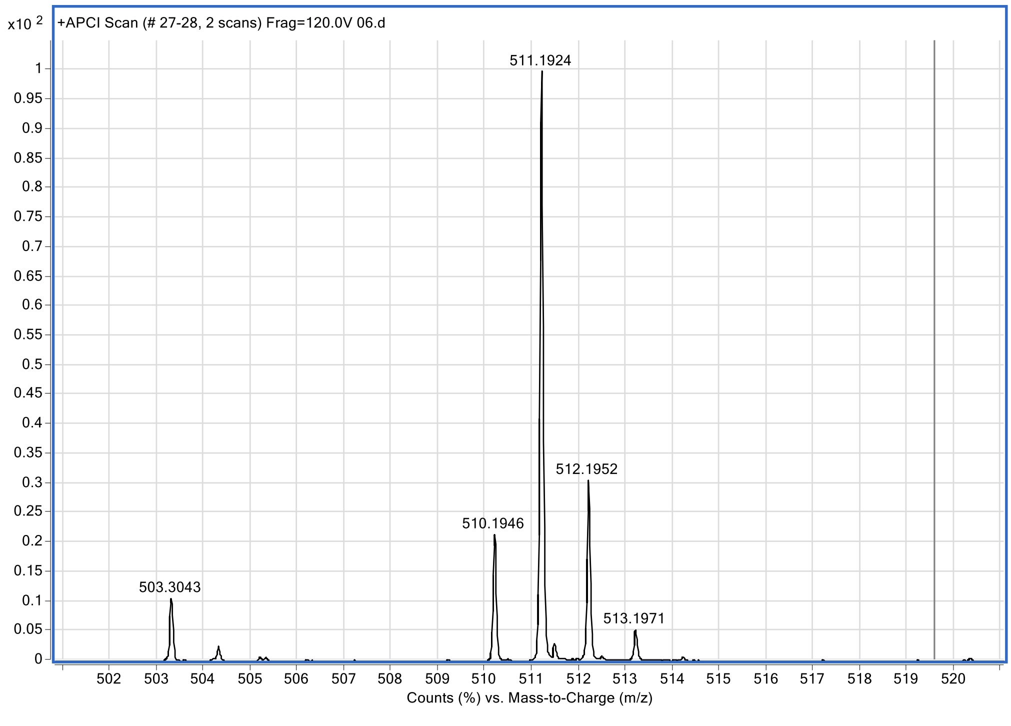
HRMS for **4f**



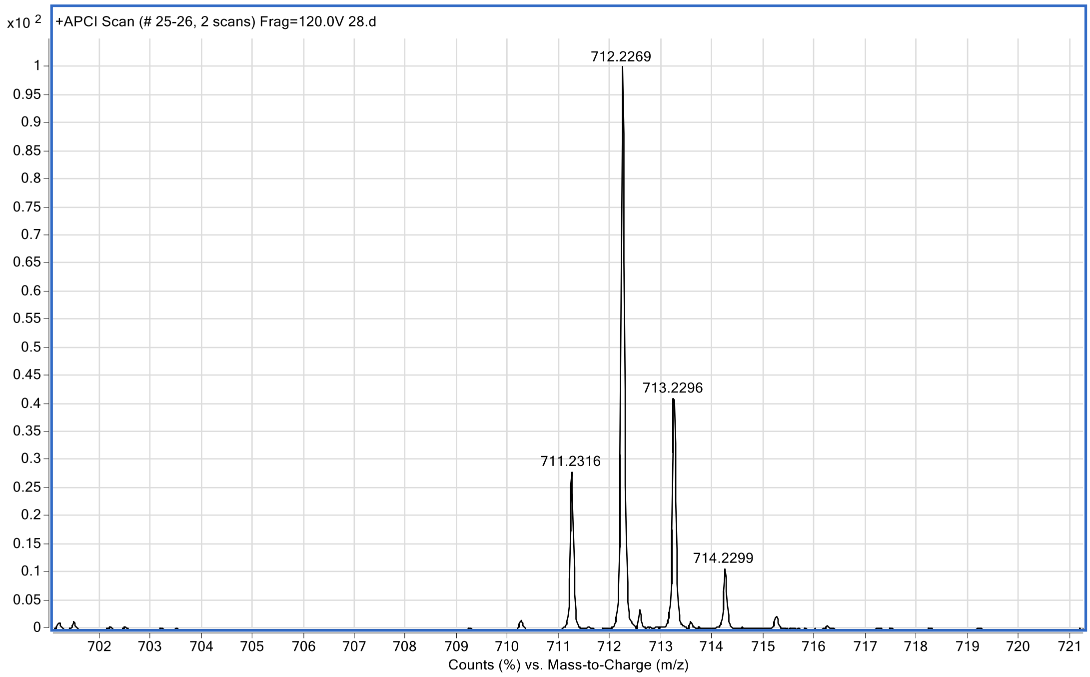
HRMS for **4g**



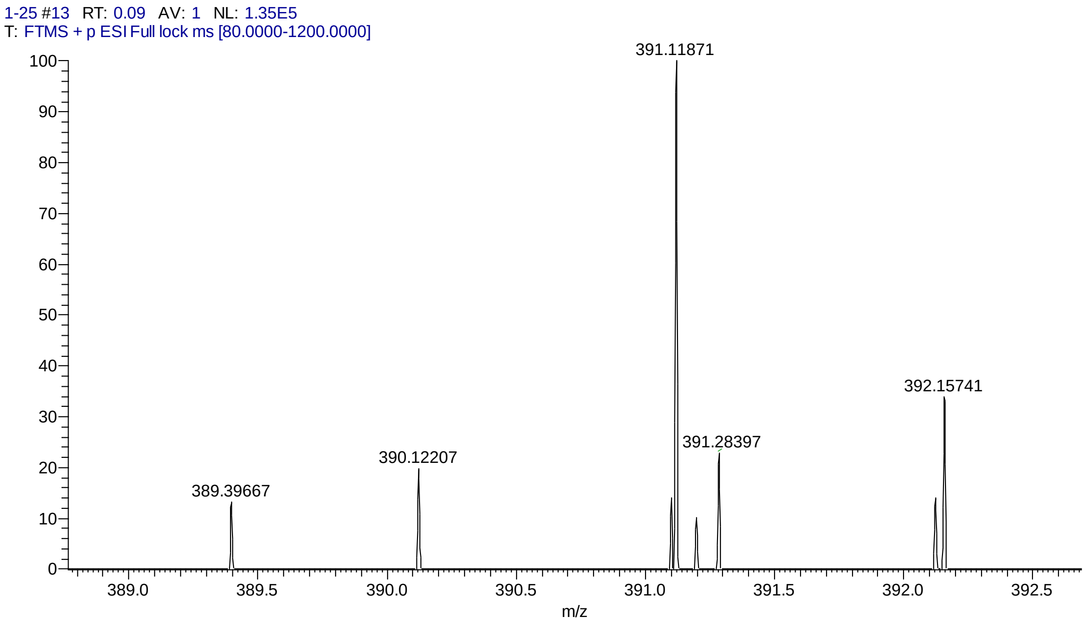
HRMS for **5a**



HRMS for **5b**



HRMS for **6**



11. Optimized geometries of the compounds

1a, optimized S_0 state Geometry.

F	3.81379800	0.00260500	1.23028900
F	3.96371500	0.00274600	-1.04023900
N	2.16108300	-1.24074800	-0.01851700
N	2.15960200	1.24406300	-0.01832400
C	1.41360800	-3.36640200	-0.06455300
C	0.77237100	-1.20893400	-0.00815100
C	2.54099400	-2.52050800	-0.05237300
H	3.59093400	-2.78380600	-0.06623100
C	0.29967100	-2.54228200	-0.03578400
H	-0.74371300	-2.82915000	-0.03880300
C	0.07372800	0.00044500	0.00043100
C	0.77091500	1.21065900	-0.00807400
B	3.10519500	0.00221100	0.04235100
C	2.53804500	2.52428200	-0.05139200
H	3.58768600	2.78878300	-0.06502200
C	0.29669900	2.54346200	-0.03500500
H	-0.74699700	2.82912700	-0.03797900
C	1.40969100	3.36888500	-0.06307700
H	1.43133200	4.44841400	-0.09128800
H	1.43648600	-4.44588900	-0.09343200
C	-1.41643800	-0.00050000	0.00534000
C	-2.11030000	-0.00298500	-1.21506000
C	-2.10070600	-0.00411300	1.22988800
C	-3.50404100	-0.00817200	-1.18579500
C	-3.49555000	-0.00925400	1.21125400
C	-4.21356200	-0.00835600	0.01580200
H	-4.04981600	-0.01381500	-2.12704500
H	-4.03378200	-0.01580200	2.15670500
C	-5.72078400	0.01639800	0.01811900
H	-6.09203700	1.04236900	-0.08186300
H	-6.12700000	-0.56151100	-0.81659800
H	-6.12228100	-0.39140200	0.94930100
C	-1.36626900	-0.00458800	-2.52697200
H	-0.72012300	0.87551500	-2.61468000
H	-0.72332100	-0.88706600	-2.61463800
H	-2.06259000	-0.00333300	-3.36822100
C	-1.34691400	-0.00680400	2.53621100
H	-0.70295600	-0.88906800	2.61801200
H	-0.70043100	0.87343500	2.61980400
H	-2.03672600	-0.00663100	3.38280000

SCF done: -1030.39132503 Hartree

No imaginary Frequency.

1a (mesitylene was omited), optimized S_0 state Geometry.

F	0.00000000	1.98087400	1.18556500
F	-0.00000200	2.05753500	-1.09722800
N	1.24991800	0.28543300	-0.01269900
N	-1.24991800	0.28543200	-0.01269700
C	3.38149500	-0.47248200	-0.03109600
C	1.21591400	-1.11075000	0.01059500
C	2.53993500	0.65979600	-0.03787200
H	2.81281800	1.70667600	-0.05930300
C	2.55231500	-1.58674700	0.00020800
H	2.84213600	-2.62923300	0.01121100
C	0.00000100	-1.78827400	0.02488500
C	-1.21591300	-1.11075000	0.01059700
B	-0.00000200	1.22722900	0.01688500
C	-2.53993600	0.65979500	-0.03787100
H	-2.81281900	1.70667400	-0.05930600
C	-2.55231300	-1.58674900	0.00022300
H	-2.84213400	-2.62923400	0.01123500
C	-3.38149400	-0.47248300	-0.03110800
H	-4.46235900	-0.45365700	-0.04896400
H	4.46236000	-0.45365300	-0.04894000
H	0.00000100	-2.87358800	0.04100200

SCF done: -681.38491004 Hartree

No imaginary Frequency.

3a, optimized S_0 state Geometry.

P	-3.70793400	-0.70337500	-0.01535000
F	-2.27741300	2.15756400	0.41498200
F	-1.61982000	1.81669600	-1.75613000
N	-1.01512200	0.14359100	-0.10437500
O	-4.29260800	0.12307400	-1.10467400
N	0.06147700	2.39418100	-0.13509600
O	-4.01598000	-0.26780700	1.49984800
O	-4.21620100	-2.24273000	-0.00737400
C	1.42602600	0.39094700	-0.03303700
C	1.31385700	1.77757200	-0.06838200
C	0.25854000	-0.40992900	-0.03064900
C	2.77168800	-0.25778700	0.03904900
C	0.25330800	3.71702100	-0.08601900
C	-1.90948200	-0.87444200	0.01217900
C	3.42577400	-0.62897200	-1.15472300
C	1.63432300	4.01310600	0.01580800
H	2.06167000	5.00383600	0.08237400
C	0.13766000	-1.80845600	0.12708700

H	0.96255100	-2.50021000	0.22517500
C	2.30226200	2.80087900	0.02196400
H	3.36728400	2.63064600	0.09781600
C	4.68145000	-1.23873100	-1.06765100
H	5.18588300	-1.52790600	-1.98709800
C	3.37039900	-0.49977600	1.29367200
C	-1.22161100	-2.09722400	0.15943600
H	-1.68812400	-3.06273600	0.28941800
C	5.30149100	-1.48757500	0.16060500
C	4.62663100	-1.11400000	1.32689600
H	5.08783400	-1.30603700	2.29332700
B	-1.29072000	1.65657500	-0.41823200
C	2.68381000	-0.11673500	2.58607200
H	2.51374100	0.96445700	2.64863500
H	3.28986200	-0.41073800	3.44750000
H	1.70453100	-0.59989600	2.68283000
C	2.79787600	-0.38351200	-2.50883600
H	1.83878000	-0.90492200	-2.61026400
H	3.45558900	-0.73252500	-3.30974000
H	2.60060500	0.68190700	-2.67595500
C	6.67153100	-2.12091800	0.22581400
H	6.85160900	-2.77496100	-0.63352500
H	6.79586300	-2.71195400	1.13911900
H	7.45984300	-1.35645500	0.22377000
C	-5.37185100	0.06277900	1.88176900
H	-5.31948100	0.40151300	2.91660600
H	-6.01064100	-0.82190100	1.81147200
H	-5.76247300	0.86095200	1.24609100
C	-4.49869500	-2.91191700	-1.25571800
H	-5.03118800	-3.82799000	-0.99714900
H	-3.56671500	-3.16154200	-1.77227500
H	-5.12061400	-2.28314400	-1.89622700
H	-0.58478600	4.40032200	-0.12829400

SCF done: -1676.69565204 Hartree

No imaginary Frequency.

4a, optimized S_0 state Geometry.

P	-2.04460200	3.47402800	-0.03230600
P	-2.61117900	-2.78514500	0.00874100
F	-2.25284200	0.25516100	0.42651900
F	-1.51813500	0.24117700	-1.75317600
O	-2.95411700	2.68724600	-1.06701400
N	-0.36815800	-1.12532200	-0.12886300
O	-2.77495200	3.03040500	1.31168300
O	-3.44229700	-2.18783000	-1.05578200

N	-0.16330800	1.36489100	-0.11666400
O	-1.86848800	4.92957100	-0.23576400
O	-3.00558400	-2.48687600	1.52074400
O	-2.57842800	-4.39210500	-0.00545400
C	1.80822400	-0.06089600	-0.06094100
C	1.21201900	1.20593000	-0.06483600
C	1.01170100	-1.21072200	-0.07752600
C	3.28909800	-0.18670000	0.01768700
C	-0.41812500	2.68369800	-0.04353500
C	-0.85561900	-2.36876100	-0.00460900
C	4.04599700	-0.13422100	-1.16318500
C	0.79057600	3.40600200	0.06739000
H	0.85768300	4.48152500	0.14585500
C	1.37990000	-2.56904100	0.06757900
H	2.39556200	-2.93355100	0.14545100
C	1.81693300	2.47908600	0.05326900
H	2.88174700	2.65560900	0.12741700
C	5.43037200	-0.26976900	-1.06801700
H	6.02436900	-0.23965800	-1.97885000
C	3.89984200	-0.36482300	1.26931400
C	0.20434300	-3.29608800	0.12032600
H	0.08406400	-4.36229600	0.24902000
C	6.06882100	-0.44540800	0.15988800
C	5.28763700	-0.49075000	1.31505800
H	5.76951600	-0.62943000	2.28041500
B	-1.17311600	0.19517500	-0.41872900
C	3.08111900	-0.42061800	2.53518500
H	2.42205700	0.45001300	2.62013100
H	3.73008900	-0.44461400	3.41294600
H	2.44480900	-1.31193800	2.55813900
C	3.37854200	0.05594500	-2.50232800
H	2.60856900	-0.70404900	-2.67292300
H	4.10890100	-0.01038300	-3.31134800
H	2.88834500	1.03366400	-2.56502900
C	7.56965000	-0.55770100	0.23953600
H	7.98306600	-0.98952600	-0.67556200
H	7.87534100	-1.17857700	1.08568800
H	8.02455500	0.42992700	0.37354300
C	-2.66652500	2.84155800	-2.46694600
H	-2.88282400	3.86503400	-2.77894400
H	-3.31376900	2.13786600	-2.98611500
H	-1.62356400	2.58889600	-2.67360000
C	-4.39107400	-2.61731900	1.89014500
H	-4.45728100	-2.31200200	2.93271000
H	-4.70974700	-3.65715000	1.78433500
H	-5.00728100	-1.96684700	1.26704100

C	-2.30678700	3.60957100	2.53950200
H	-2.94404000	3.21107600	3.32672400
H	-2.38986700	4.69761800	2.50214200
H	-1.26787700	3.31939800	2.72460700
C	-2.55496900	-5.04855100	-1.28288600
H	-2.61490600	-6.11690400	-1.08109100
H	-1.62064000	-4.82461100	-1.80692700
H	-3.40466800	-4.72807900	-1.88779000

SCF done: -2322.99829906 Hartree

No imaginary Frequency.

4a (mesitylene was omited), optimized S_0 state Geometry.

P	3.38424700	-0.96436500	0.10746500
P	-3.09242400	-0.79667400	0.04283000
F	0.08100100	-0.87690400	-0.32853300
F	0.10932600	0.12583300	1.74679600
O	2.57378800	-1.76221300	1.23078900
N	-1.10357600	1.21091700	-0.04264600
O	2.85312200	-1.79350700	-1.16016300
O	-2.65526300	-1.56882100	1.23514400
N	1.42257500	1.12678500	-0.01078600
O	4.86200500	-0.87265300	0.26965100
O	-2.80094000	-1.41195300	-1.40897100
O	-4.68863000	-0.53683700	-0.02897800
C	0.22579200	3.21780900	-0.27755600
C	1.42083500	2.50887100	-0.18493000
C	-1.01433300	2.58667200	-0.23168000
C	2.71814200	0.72293400	-0.01796300
C	-2.41169200	0.87458200	-0.13910600
C	3.56735000	1.84310800	-0.20515400
H	4.64496100	1.79212200	-0.25636600
C	-2.31531300	3.10785400	-0.44163400
H	-2.54992200	4.14715300	-0.62863100
C	2.75855200	2.96138800	-0.30712900
H	3.05876600	3.98890900	-0.46350300
C	-3.18829600	2.03416200	-0.38950000
H	-4.25932600	2.04509000	-0.52771400
B	0.12482600	0.30971400	0.37052300
C	2.74361300	-1.42855500	2.62901100
H	3.79320600	-1.22361000	2.85436500
H	2.41181200	-2.30400100	3.18768200
H	2.11458200	-0.57202500	2.87530200
C	-3.12451500	-2.79851300	-1.67348700
H	-2.76958500	-3.00201700	-2.68366400
H	-4.20593700	-2.95002000	-1.62001000

H	-2.61529400	-3.44927700	-0.95908600
C	3.44955100	-1.57218400	-2.45688900
H	3.05210600	-2.35202000	-3.10659400
H	4.53786100	-1.65174900	-2.40015400
H	3.16441700	-0.58988300	-2.84582100
C	-5.45675200	-0.41999200	1.19019100
H	-6.50439300	-0.49860800	0.89783900
H	-5.27688400	0.55170700	1.66003800
H	-5.19731800	-1.22144900	1.88452500
H	0.26326100	4.29146700	-0.43039200

SCF done: -2322.99829906 Hartree

No imaginary Frequency.

5b, optimized S_0 state Geometry.

P	-3.02405300	-1.66952900	-0.38144100
F	0.02442600	-1.51216500	0.13801200
F	0.19446200	-0.51959200	-1.92647300
O	-2.47905400	-2.44034800	-1.54337900
N	1.23764800	0.56684800	-0.04968600
N	-1.24722100	0.50427200	-0.30774100
C	-0.06162800	2.61640400	-0.13270700
C	-1.25078100	1.88745000	-0.25161000
C	1.16302400	1.94987400	-0.01853200
C	-0.10956300	4.10225000	-0.05544800
C	-2.52610600	0.08927000	-0.32091800
C	2.50731400	0.21796100	0.22482200
C	-0.14430800	4.84883100	-1.24417100
C	-3.39024400	1.20957300	-0.26756300
H	-4.46976000	1.16645600	-0.25456100
C	2.44471300	2.46910900	0.27574500
H	2.68197600	3.51997500	0.37658600
C	-2.59020100	2.33796700	-0.22589300
H	-2.89795000	3.37343100	-0.16570000
C	-0.18390500	6.23887500	-1.15169700
H	-0.20268700	6.82604600	-2.06737100
C	-0.11902300	4.72871100	1.20022000
C	3.28501200	1.38328400	0.43650400
H	4.33574800	1.39283200	0.68916500
C	-0.19940400	6.89280900	0.08101700
C	-0.16555000	6.12214000	1.24296600
H	-0.17585800	6.61710700	2.21171800
B	0.05602500	-0.33403600	-0.56794900
C	-0.07810800	3.92341300	2.47548500
H	-0.84195100	3.13845600	2.47580100

H	-0.24825400	4.56623000	3.34178900
H	0.89194300	3.43078000	2.60355900
C	-0.13476000	4.16344600	-2.58763700
H	0.70868200	3.47004300	-2.67363100
H	-0.06005000	4.89490200	-3.39500300
H	-1.04932800	3.57984800	-2.73976200
C	-0.27949700	8.39612400	0.15238400
H	0.26413500	8.86116300	-0.67438300
H	0.13268100	8.77091500	1.09268300
H	-1.32091200	8.73087300	0.09017800
P	3.09620200	-1.49473300	0.49344800
O	2.61177400	-2.12151900	1.76566400
C	-4.83605700	-1.55503300	-0.42679100
C	-5.46061400	-1.77869200	-1.65622800
C	-5.60244500	-1.24203900	0.70067000
C	-6.84598600	-1.67956400	-1.76066700
H	-4.85582000	-2.03820800	-2.52008500
C	-6.98588300	-1.13951200	0.59118800
H	-5.12306900	-1.08426300	1.66360300
C	-7.60648700	-1.35684900	-0.63896200
H	-7.33046500	-1.85520600	-2.71586600
H	-7.58032900	-0.89579500	1.46590200
H	-8.68632600	-1.27925700	-0.72048900
C	-2.59606000	-2.33441500	1.24498200
C	-2.38374500	-3.71162900	1.33602600
C	-2.50345100	-1.53236100	2.38531000
C	-2.09153500	-4.28705600	2.56915100
H	-2.43088400	-4.32022500	0.43741400
C	-2.21380700	-2.11281600	3.61693200
H	-2.64559200	-0.45605200	2.31512300
C	-2.01015100	-3.48847400	3.70843600
H	-1.92109200	-5.35657600	2.64024000
H	-2.13962400	-1.49065200	4.50314400
H	-1.78030300	-3.93813800	4.66946200
C	2.70450000	-2.42799700	-1.00111100
C	2.41863700	-3.78633100	-0.84678100
C	2.73368500	-1.85728900	-2.27579900
C	2.17979800	-4.57507800	-1.96806200
H	2.37205900	-4.21139300	0.15171700
C	2.49728900	-2.64991100	-3.39444000
H	2.90741100	-0.79104600	-2.39866300
C	2.22495500	-4.00792400	-3.24025600
H	1.95243900	-5.62961200	-1.84893500
H	2.51320700	-2.20571800	-4.38453300

H	2.03438900	-4.62320200	-4.11425900
C	4.90034900	-1.26910000	0.51628400
C	5.64267900	-0.93571100	-0.62141000
C	5.54188900	-1.41988500	1.74763100
C	7.01713900	-0.74606000	-0.52157700
H	5.15462800	-0.82721600	-1.58616700
C	6.91915800	-1.23178400	1.84347000
H	4.95426900	-1.68893500	2.62012400
C	7.65481200	-0.89290800	0.71065900
H	7.59211300	-0.48727200	-1.40492000
H	7.41557200	-1.35161100	2.80121800
H	8.72797200	-0.74610600	0.78466800

SCF done: -2788.99940195 Hartree

No imaginary Frequency.

5b (mesitylene was omited), optimized S_0 state Geometry.

P	-3.18158300	-0.38812900	-0.41396500
F	-0.02616500	-0.34080000	0.14913200
F	0.16614400	0.73491600	-1.87824300
O	-2.68576100	-1.08459700	-1.65362600
N	1.24893800	1.72413700	0.03178600
N	-1.26988400	1.71746200	-0.20766400
C	-0.02604100	3.78340400	0.02229400
C	-1.23623500	3.10601300	-0.10569400
C	1.19122500	3.11368500	0.11057600
C	-2.57411800	1.34050800	-0.22798800
C	2.53655300	1.35556600	0.25475100
C	-3.39771700	2.49362600	-0.13855600
H	-4.47724400	2.48840500	-0.12295900
C	2.48721900	3.61393600	0.38652100
H	2.74150900	4.65753500	0.51545300
C	-2.56377000	3.59661200	-0.06611800
H	-2.84457600	4.63741100	0.02525000
C	3.32377200	2.51618400	0.48414200
H	4.38007600	2.51697800	0.70783900
B	0.03028300	0.87180700	-0.50521000
P	3.15472900	-0.36278400	0.49566600
O	2.66151200	-0.99471100	1.77191000
C	-5.00099700	-0.18800900	-0.44929600
C	-5.63281600	-0.29943800	-1.69663900
C	-5.77398900	0.04686400	0.69824200
C	-7.01853700	-0.16512800	-1.79663000
H	-5.03396000	-0.50216700	-2.57902400
C	-7.15865000	0.18369600	0.59422400

H	-5.30218300	0.11561800	1.67410800
C	-7.78142700	0.07936700	-0.65268700
H	-7.50124200	-0.25479900	-2.76572200
H	-7.75125400	0.36427900	1.48661200
H	-8.86029400	0.18199400	-0.73026700
C	-2.79407500	-1.24573600	1.14576900
C	-2.69540000	-2.64398800	1.10071200
C	-2.63746600	-0.57898900	2.36928900
C	-2.44993000	-3.36647300	2.26848100
H	-2.79607600	-3.15951600	0.15028900
C	-2.39404900	-1.30586500	3.53567400
H	-2.69255300	0.50501000	2.41678700
C	-2.30169400	-2.69867400	3.48648100
H	-2.36929400	-4.44895300	2.22623400
H	-2.26829600	-0.78356300	4.47980700
H	-2.10780500	-3.26195800	4.39502500
C	2.79656900	-1.32230900	-1.00666400
C	2.60156600	-2.70268000	-0.85236000
C	2.78682600	-0.75951100	-2.29082500
C	2.40824000	-3.51131500	-1.97243600
H	2.58961600	-3.13390900	0.14401100
C	2.59858100	-1.57286600	-3.40873700
H	2.89928200	0.31217500	-2.42331400
C	2.41216600	-2.94806300	-3.25081800
H	2.25139400	-4.57886500	-1.84671400
H	2.58631200	-1.13082800	-4.40087200
H	2.26137300	-3.57853300	-4.12271600
C	4.97320900	-0.14095500	0.53650500
C	5.74524800	0.13122200	-0.60342700
C	5.60454900	-0.26952600	1.78221300
C	7.12737900	0.28456800	-0.49366500
H	5.27616100	0.21550400	-1.57908900
C	6.98836700	-0.11772200	1.88837900
H	5.00581000	-0.49681200	2.65856700
C	7.74984700	0.16183200	0.75190000
H	7.71858300	0.49393700	-1.38068900
H	7.47013400	-0.22077500	2.85664300
H	8.82698700	0.27841300	0.83382000
H	-0.03668200	4.86529800	0.10666700

SCF done: -2439.99280213 Hartree

No imaginary Frequency.

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