Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Methylated Chromenoquinoline Dyes: Synthesis, Optical Properties, and Application for Mitochondrial Labeling

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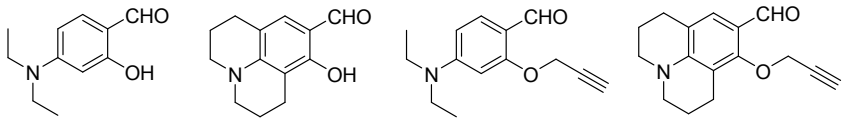
Materials and instruments

All reagents were purchased from commercial suppliers and used without further purification. Solvents were purified by standard methods prior to use. NMR spectra were recorded on Bruker 400/500 spectrometers with TMS as an internal standard. HRMS analysis was performed on a micrOTOF-Q II mass spectrometer (Bruker Daltonik, Germany). The melting point was determined using a WRX-4 melting point meter. Absorption and emission spectra were measured at 25 °C using a Shimadzu UV-2450 spectrophotometer and a HITACHI FL7000 fluorescence spectrophotometer respectively. Cell imaging experiments were performed with a FL microscope (BX41 Microscope) and a confocal laser scanning microscope (CLSM) (LSM710, Carl Zeiss). Silica gel plates and silica gel (mesh 200-300) for TLC analysis and column chromatography were supplied by Qingdao Ocean Chemicals (China).

Structures of compounds 1a, 1b, 2a and 2b



1a **1b** **2a** **2b**

Synthesis of compound 2a

Compound **2a** was prepared according to a literature method (Tetrahedron Lett., 2014, 55, 116-119).

Synthesis of compound 2b

To a solution of compound **1b** (0.2173 g, 1.0 mmol) and 3-bromoprop-1-yne (0.2380 g, 2.0 mmol) in acetone (10.0 mL) was added potassium carbonate (0.2764 g, 2.0 mmol). The resulting suspension was refluxed for 12 h with stirring. Next, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was further purified using flash silica gel chromatography (eluent: ethyl acetate/petroleum ether as eluent, v/v = 1/3) to afford compound **2b** as a yellow solid (0.2002 g, yield 78.4%). MP: 97.2-99.5 °C. HRMS (ESI) m/z: calcd for $C_{16}H_{18}NO_2$ $[M+H]^+$ 256.1338, found 256.1327. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 10.03 (s, 1H), 7.34 (s, 1H), 4.63 (d, J = 2.4 Hz, 2H),

3.52 - 3.05 (m, 4H), 2.81 (t, J = 6.3 Hz, 2H), 2.73 (t, J = 6.3 Hz, 2H), 2.55 (t, J = 2.4 Hz, 1H), 2.01 - 1.82 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C: 187.9, 157.8, 148.9, 127.6, 117.6, 117.1, 112.7, 78.7, 76.1, 62.1, 50.0, 49.7, 27.4, 21.4, 21.3, 20.7.

General procedure for synthesis of dye 3a-f

To a solution of compound **2** (**2a**/**2b**) (1.0 mmol) and the corresponding anilines (1.0 mmol) in dry DMF (5.0 mL) was added CuI (0.3 mmol) as a catalyst. Under nitrogen atmosphere, the resulting mixture was stirred at 110 °C for 5 h. Cool the reaction mixture to room temerature and then pour it into cold water (40.0 mL) with stirring. Next, the mixture was extracted with ethyl acetate (40.0 mL × 4). The obtained organic layer was succcesssively washed with distilled water and brine, and was subsequently dried over anhydrous sodium sulphate. After removal of the solvent, the obtained residue was purified by column chromatography over silica gel (eluent: ethyl acetate/petroleum ether, v/v, 1/20 to 1/4) to give the desrired products.

3a: yellow solid, yield 15.7%. MP: 159.2-160.8 °C. HRMS (ESI) m/z: calcd for $C_{21}H_{23}N_2O$ $[M+H]^+$ 319.1810, found 319.1802. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.30 (s, 1H), 7.98 (s, 1H), 7.68 (s, 1H), 7.47 (d, J = 7.0 Hz, 2H), 6.51 (d, J = 9.0 Hz, 1H), 6.24 (d, J = 2.0 Hz,1H), 5.26 (s, 2H), 3.41 (q, J = 7.5 Hz, 4H), 2.50 (s, 3H), 1.21 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C: 159.0, 150.9, 149.2, 147.0, 134.7, 131.4, 129.7, 128.4, 126.8, 126.6, 126.4, 124.5, 111.1, 106.9, 98.3, 68.7, 44.2, 21.5, 12.7.

3b: yellow solid, yield 25.0%. MP: 141.5-143.1 °C. HRMS (ESI) m/z: calcd for $C_{21}H_{23}N_2O_2$ $[M+H]^+$ 335.1760, found 256.1757. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.27 (s, 1H), 8.00 (s, 1H), 7.68 (s, 1H), 7.32 (dd, J = 9.0, 3.0 Hz, 1H), 7.02 (d, J = 3.0 Hz, 1H), 6.52 (dd, J = 9.0, 3.0 Hz, 1H), 6.26 (d, J = 2.5 Hz 1H), 5.28 (s, 2H), 3.93 (s, 3H), 3.42 (q, J = 7.1 Hz, 4H), 1.23 (t, J = 7.0 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_H: 158.7, 156.8, 150.7, 147.9, 144.5, 130.2, 129.2, 127.6, 126.3, 124.8, 121.4, 111.2, 106.9, 105.6, 98.4, 68.7, 55.5, 44.6, 12.7.

3c: yellow solid, yield 12.0%. MP: 180.7-182.5 °C. HRMS (ESI) m/z: calcd for $C_{21}H_{20}N_3O$ $[M+H]^+$ 330.1606, found 330.1559. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.26 (d, J = 9.0 Hz, 1H), 8.08 - 8.05 (m, 2H), 7.75 (d, J = 10.5 Hz, 2H), 6.52

(dd, J = 9.0 Hz, J = 2.5 Hz,1H), 6.22 (s, 1H), 5.28 (s, 2H), 3.44 (q, J = 7.0 Hz, 4H), 1.24 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C: 159.8, 152.5, 152.0, 149.7, 133.3, 130.2, 129.7, 127.4, 126.2, 126.0, 119.2, 110.0, 107.8, 107.5, 107.3, 98.0, 68.3, 44.7, 12.7.

3d: yellow solid, yield 17.5%. MP: 148.5-150.2 °C. HRMS (ESI) m/z: calcd for $C_{23}H_{23}N_2O$ $[M+H]^+$ 343.1810, found 343.1806. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.97 - 7.91 (m, 2H), 7.66 (s, 1H), 7.47 (d, J = 6.8 Hz, 2H), 5.24 (s, 2H), 3.23 (q, J = 6.4 Hz, 4H), 2.86 (t, J = 6.0 Hz, 2H), 2.75 (t, J = 6.4 Hz, 2H), 2.52 (s, 3H), 2.08 - 1.90 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C: 153.9, 149.7, 147.1, 145.8, 134.5, 131.3, 129.5, 128.4, 126.8, 126.4, 124.8, 122.8, 116.1, 111.0, 107.8, 68.6, 50.2, 49.6, 27.5, 22.1, 21.5, 21.3, 21.0.

3e: yellow solid, yield 22.3%. MP: 163.2-165.0 °C. HRMS (ESI) m/z: calcd for $C_{23}H_{23}N_2O_2$ $[M+H]^+$ 359.1760, found 359.1745. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.00-7.89 (m, 2H), 7.68 (s, 1H), 7.31 (dd, J = 9.2, 2.8 Hz, 1H), 7.03 (d, J = 2.8 Hz, 1H), 5.24 (s, 2H), 3.93 (s, 3H), 3.23 (q, J = 6.4 Hz, 4H), 2.86 (t, J = 6.4 Hz, 2H), 2.75 (t, J = 6.4 Hz, 2H), 2.04 - 1.97 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C: 156.8, 153.7, 148.4, 145.6, 144.4, 130.1, 129.0, 127.5, 125.1, 122.5, 121.2, 116.2, 111.0, 107.9, 105.6, 68.6, 55.5, 50.2, 49.6, 27.5, 22.1, 21.3, 21.0.

3f: yellow solid, yield 8.5%. MP: 271.0-273.2 °C. HRMS (ESI) m/z: calcd for $C_{23}H_{23}N_3O$ $[M]^+$ 353.1528, found 353.1509. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.09 - 8.00 (m, 2H), 7.89 (s, 1H), 7.76 - 7.34 (m, 2H), 5.25 (s, 2H), 3.29 - 3.25 (m, 4H), 2.84 (t, J = 6.5Hz, 2H), 2.73 (t, J = 6.5 Hz, 2H), 2.03 - 1.97 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 154.6, 153.1, 149.9, 147.0, 133.3, 130.1, 129.9, 129.7, 126.5, 126.1, 123.3, 119.3, 116.6, 109.7, 107.5, 107.4, 68.2, 50.2, 49.6, 27.5, 21.9, 21.1, 20.8.

General synthetic procedure for dyes 4a-f

To a 10.0 mL thick-wall pressure tube were added dye **3** (**3a-f**) (1.0 mmol), CH_3I (4.0 mmol) and anhydrous dichloromethane (2.0 mL). The resulting solution was stirred at 100 °C for 12 h under dark. Next, cool the mixture to room temperature and then remove the solvent in vacuum to give a crude product, which was further purified using flash silica gel chromatography (eluent: acetone/dichloromethane, v/v = 1:1) to afford compounds **4a-f**.

4a: red solid, yield 65.0%. MP: 213.1-215.6 °C. HRMS (ESI) m/z: calcd for $C_{22}H_{25}N_2O$ $[M\text{-}I]^+$ 333.1961, found 333.1956. ^1H NMR (500 MHz, DMSO-d_6) δ_H: 8.58 (s, 1H), 8.22 (d, J = 8.5 Hz, 1H), 7.98 (s, 1H), 7.92 (d, J = 9.0 Hz, 2H), 6.77 (d, J = 8.5 Hz, 1H), 6.49 (s, 1H), 5.30 (s, 2H), 4.42 (s, 3H), 3.54 (q,J = 7.0 Hz, 4H), 2.57 (s, 3H), 1.19 (t, J = 7.0 Hz, 6H). ^{13}C NMR(125 MHz, DMSO-d_6) δ_C: 163.2, 154.1, 149.2, 139.2, 138.2, 136.8, 135.8, 133.7, 130.0, 128.7, 126.3, 119.5, 108.4, 103.9, 98.5, 68.0, 44.8, 44.5, 21.0, 13.0.

4b: red solid, yield 73.5%. MP: 231.2-233.5 °C. HRMS (ESI) m/z: calcd for $C_{22}H_{25}N_2O_2$ $[M\text{-}I]^+$ 349.1911, found 349.1913. ^1H NMR (500 MHz, DMSO-d_6) δ_H: 8.55 (s, 1H), 8.23 (d, J = 9.5 Hz, 1H), 7.89 (d, J = 9.5 Hz, 1H), 7.66 (dd, J = 9.5, 3.0 Hz, 1H), 7.63 (d, J = 3.0 Hz, 1H), 6.75 (dd, J = 9.5,2.5 Hz, 1H), 6.44 (d, J = 2.5 Hz, 1H), 5.26 (s, 2H), 4.41 (s, 3H), 3.94 (s, 3H), 3.52 (q, J = 7.0 Hz, 4H), 1.28 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ_C: 163.0, 158.5, 153.8, 147.9, 136.2, 135.8, 133.3, 130.5, 127.9, 124.7, 121.3, 108.9, 108.2, 103.8, 98.6, 68.0, 56.7, 44.9, 44.7, 13.0.

4c: red solid, yield 15.1%. MP: 247.2-249.9 °C. HRMS (ESI) m/z: calcd for $C_{22}H_{22}N_3O$ $[M\text{-}I]^+$ 344.1757, found 344.1753. ^1H NMR (500 MHz, $CDCl_3$+CD_3OD) δ_H: 8.36 (d, J = 2.0 Hz, 1H), 8.34 (s, 1H), 8.19 (d, J = 9.0 Hz, 1H), 8.09 (dd, J = 9.0, 2.0 Hz, 1H), 7.78 (d, J = 9.5 Hz, 1H), 6.71 (dd, J = 9.5, 2.5 Hz, 1H), 6.34 (d, J = 2.5 Hz, 1H), 5.17 (s, 2H), 4.38 (s, 3H), 3.50 (q, J = 7.0 Hz, 4H), 1.22 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$+CD_3OD) δ_C: 164.4, 155.7, 151.6, 142.6, 135.2, 135.0, 134.2, 133.2, 131.8, 125.8, 120.0, 116.9, 111.1, 109.6, 103.9, 98.5, 67.6, 45.4, 44.5, 12.2.

4d: red solid, yield 62.0%. MP: 247.1-249.2 °C. HRMS (ESI) m/z: calcd for $C_{24}H_{25}N_2O$ $[M\text{-}I]^+$ 357.1961, found 357.1961. ^1H NMR (500 MHz, DMSO-d_6) δ_H: 8.48 (s, 1H), 8.13 (d, J = 9.0 Hz, 1H), 7.92 (s, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.53 (s, 1H), 5.23 (s, 2H), 4.36 (s, 3H), 3.42 - 3.38 (m, 4H), 2.78 (t, J = 6.0 Hz, 2H), 2.68 (t, J = 6.0 Hz, 2H), 2.54 (s,3H), 1.94 - 1.88 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6) δ_C: 157.8, 149.7, 149.3, 139.2, 138.0, 135.8, 135.6, 130.3, 128.9, 128.6, 126.0, 119.2, 117.5, 107.5, 103.4, 67.8, 50.2, 49.6, 44.6, 27.3, 21.2, 21.0, 20.6, 20.2.

4e: red solid, yield 66.2%. MP: 180.2-182.2 °C. HRMS (ESI) m/z: calcd for

$C_{24}H_{25}N_2O_2$ $[M\text{-}I]^+$ 373.1911, found 373.1913. ^1H NMR (500 MHz, DMSO-d_6) δ_H: 8.48 (s, 1H), 8.18 (d, J = 9.5 Hz, 1H), 7.67 (dd, J = 9.5, 3.0 Hz, 1H), 7.63 (d, J = 3.0 Hz, 1H), 7.50 (s, 1H), 5.24 (s, 2H), 4.37 (s, 3H), 3.96 (s, 3H), 3.41 - 3.37 (m, 4H), 2.77 (t, J = 6.0 Hz, 2H), 2.68 (t, J = 6.0 Hz, 2H), 1.94 - 1.88 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 158.3, 157.5, 149.4, 148.2, 135.9, 135.3, 130.7, 128.7, 127.5, 124.1, 121.0, 117.3, 109.0, 107.4, 103.3, 67.9, 56.6, 50.2, 49.5, 44.6, 27.3, 21.2, 20.6, 20.2.

4f: red solid, yield 10.1%. MP: 222.3-224.0 °C. HRMS (ESI) m/z: calcd for $C_{24}H_{22}N_3O$ $[M\text{-}I]^+$ 368.1757, found 368.1750. ^1H NMR (500 MHz, DMSO-d_6) δ_H: 8.70 (s, 1H), 8.43 (s, 1H), 8.34 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H), 7.53 (s, 1H), 5.28 (s, 2H), 4.31 (s, 3H), 3.48 - 3.43 (m, 4H), 2.78 (t, J = 5.5 Hz, 2H), 2.68 (t, J = 5.5 Hz, 2H), 1.95 - 1.89 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6) δ_C: 158.5, 151.0, 151.0, 143.0, 134.9, 134.6, 134.5, 132.2, 129.1, 125.6, 120.8, 118.7, 118.2, 109.7, 107.3, 103.8, 67.5, 50.6, 49.9, 45.1, 27.2, 21.1, 20.4, 20.0.

Synthesis of compound 5

Compound **5** was prepared according to a literature method (Mol. Divers., 2013, 17, 721-730).

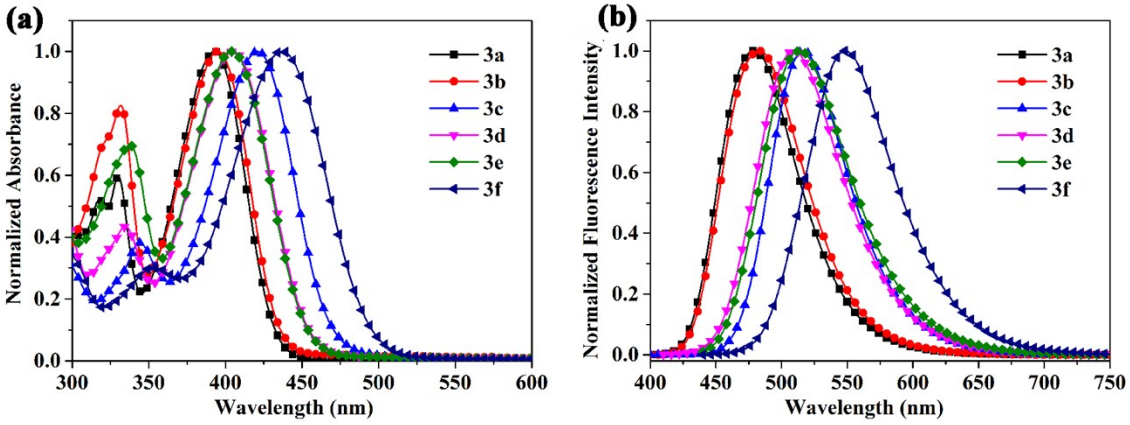


Figure S1. Normalized absorption (a) and emission (b) spectra of dyes **3a-f** in EtOH.

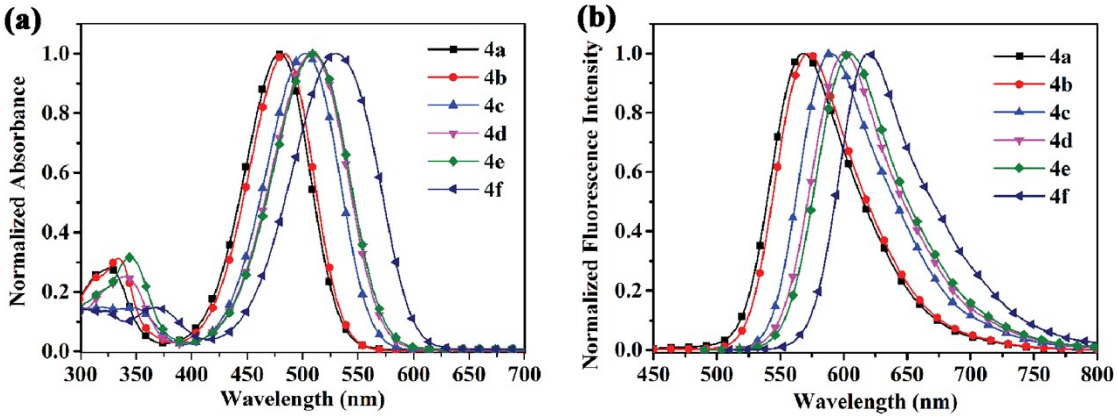


Figure S2. Normalized absorption (a) and emission (b) spectra of dyes **4a-f** in EtOH.

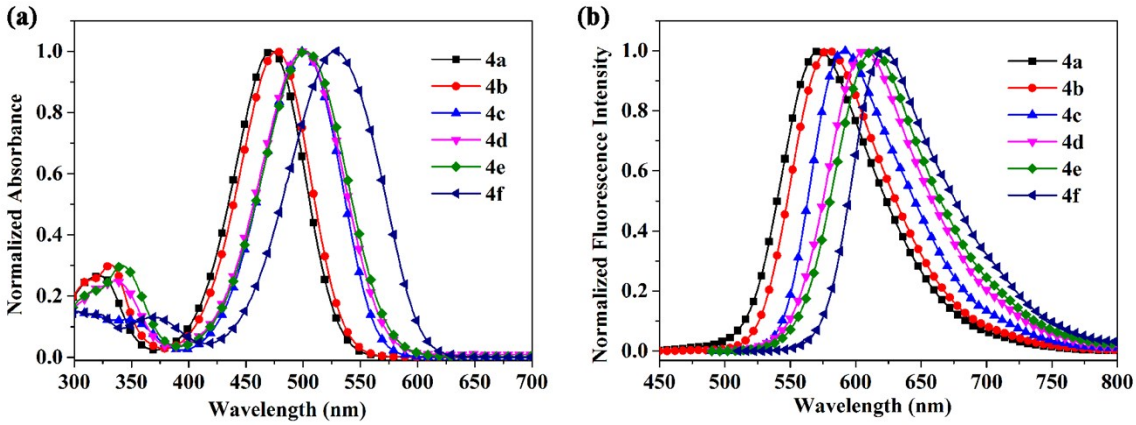


Figure S3. Normalized absorption (a) and emission (b) spectra of dyes **4a-f** in H_2O.

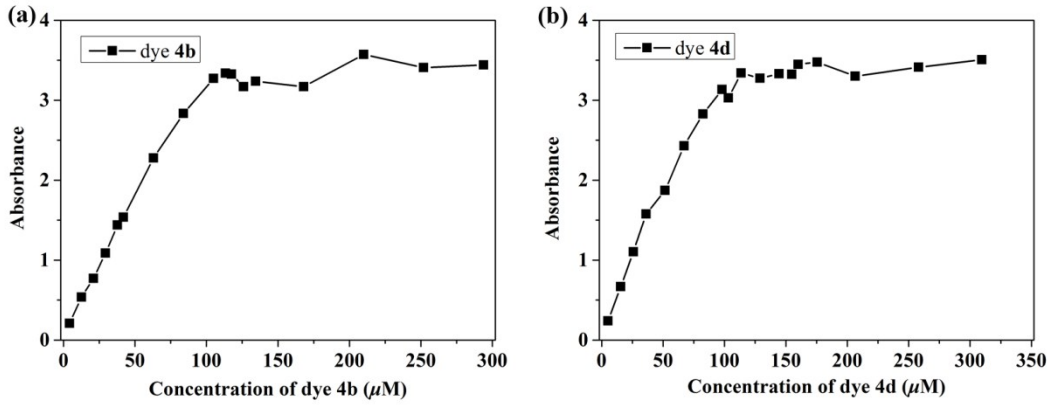


Figure S4. Plots of the absorbance verus the concentration in H_2O for dye **4b** (a) and dye **4d** (b).

Cell viability via MTT assay

HeLa cells were seeded in 96-well plates at a density of 5000 cells/well and allowed to adhere for 24 hours. Cells were incubated with the solution of dye **4b/4d** (0.0, 1.0, 2.0, 5.0, 10.0, and 20.0 μM), respectively, in DMEM with 10% FBS culture media under dark for 24 h at 37 °C. Then, wash cells with PBS buffer and incubate them in MTT (0.5 mg/mL, 200.0 μL) for another 4 h at 37 °C. Next, the MTT medium solution was discarded to obtain formazan crystals. DMSO (200.0 μL) was added to each well to dissolve the formazan crystals. Finally, the absorbance at 570 nm was recorded with a microplate reader (Genios Tecan). The viability for untreated cells was set as control.

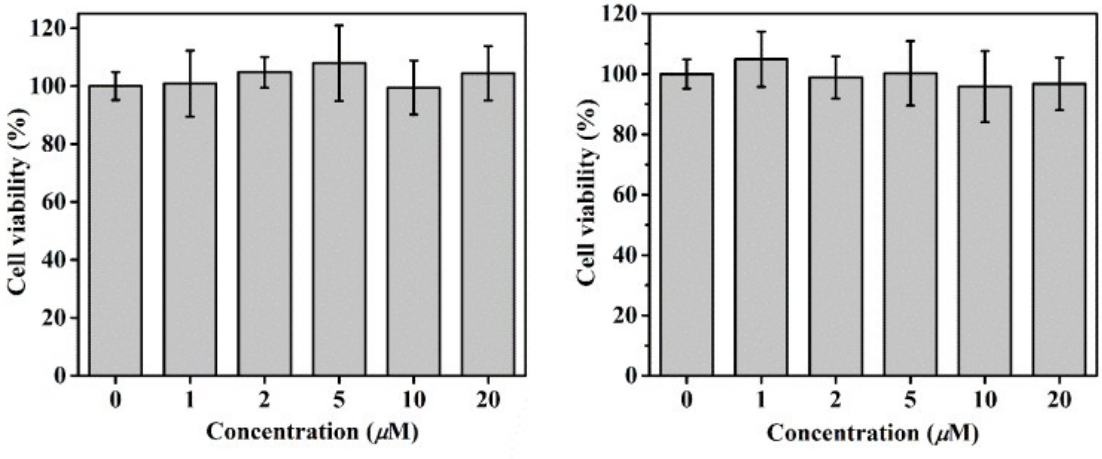


Figure S5. Cytotoxicity assay of dye **4b** (left) and **4**d (right) at different concentrations for HeLa cells.

Preparation of bacteria solution and fluorescence imaging experiments

E. coli and S. epidermidison in solid Luria Broth (LB) agar plates were respectively transferred to liquid LB culture medium (2.0 mL), and were allowed to incubate at 37 ^{o}C for 12 h. The bacteria were obtained through centrifuging for 3 min at 8000 rpm and washing with PBS buffer. Then, discard the supernatant and suspend the obtained bacteria in PBS buffer. Next, based on OD600 1.0 ≈ 1×10^{9} CFU/mL, the bacteria solution was diluted. The prepared bacteria solutions were incubated with dyes **4b**/**4d** (5.0 μM) under dark (shaking tables, 200 r/min) for 10 min at 37 ^{o}C after dispersion with vortex. Then, the soluiton (10.0 μL) was spotted on polylysine with

glass slides and immobilized by the coverslips. Finally, fluorescence imaging experiments were carried out on a FL microscope (BX41 Microscope) using 100 × objective.

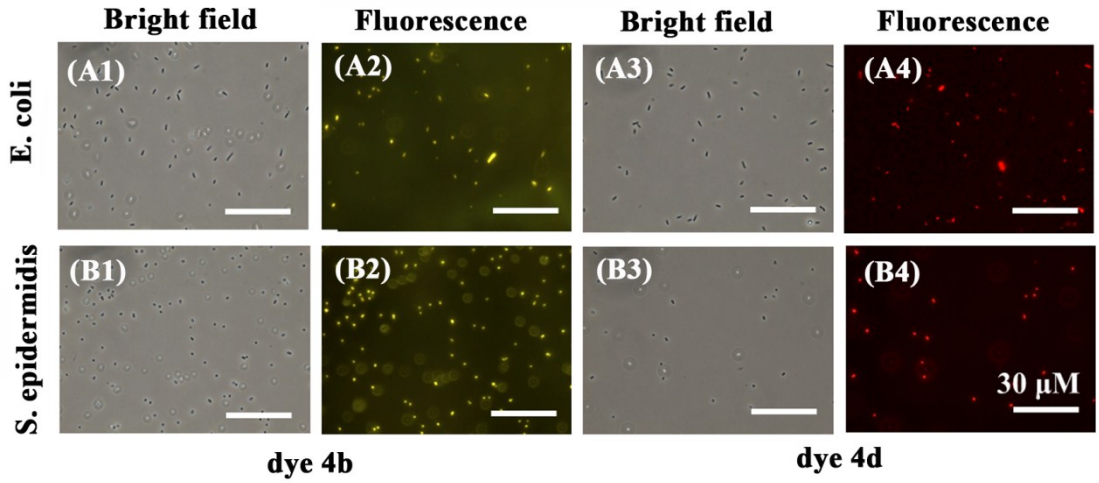


Figure S6. Images of E. coli (A1-A4) and S. epidermidis (B1-B4) after incubation with dye **4b** (5.0 μM, A1-A2, B1-B2) and dye **4d** (5.0 μM, A3-A4, B3-B4) for 10 min at 37 °C, repectively. For **4b**, excitation filter: band pass 460-490 nm; emission filter: long pass 515 nm. For **4d**, excitation filter: band pass 510-550 nm; emission filter: long pass 590 nm.

Cell culture and fluorescence imaging experiments

HeLa cells were grown in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% fetal bovine serum (FBS) and 1% penicillinG (P) (100 U mL^{-1}), and streptomycin (S) (100 U mL^{-1}). The cells were cultured in a humidified incubator at 37 °C with 5% CO_2 humidified atmosphere and the medium was changed every 3 days. The cells were plated on culture dishes and allowed to adhere for 24 hours. Before use, the cells were washed with PBS buffer. Living cells were incubated with dye **4b**/**4d** (5.0 μM) for 15 min at 37 °C. Next, the cells were washed three times with PBS buffer and cell imaging experiments were performed on a BX41 Microscope.

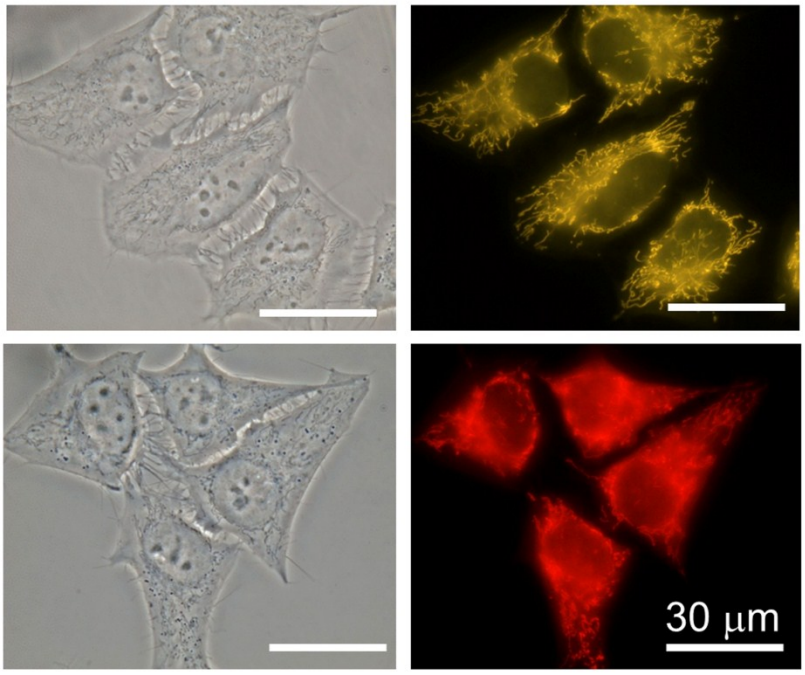


Figure S7. Bright field (left) and fluorescence (right) images of living HeLa cells. Cells were respectively incubated with dye **4b** (5.0 μM, top row) and dye **4d** (5.0 μM, bottom row) for 15 min at 37 °C. Images were collected using 100 × objective. For **4b**, excitation filter: band pass 460-490 nm; emission filter: long pass 515 nm. For **4d**, excitation filter: band pass 510-550 nm; emission filter: long pass 590 nm.

For co-localization experiments, **Hoechst 33258** was used to stain nucleus, and **MitoTracker®Green FM** was used to stain mitochondria. Living HeLa cells were incubated with dye **4b**/**4d** (5.0μM), **MitoTracker®Green FM** (0.2 μM) and Hoechst 33258 (0.2 μM) at 37 °C for 15 min. After washing the cells with PBS buffer and adding 300 μL PBS, cell imaging experimwents were performed on a confocal laser scanning microscope (CLSM) (LSM710, Carl Zeiss).

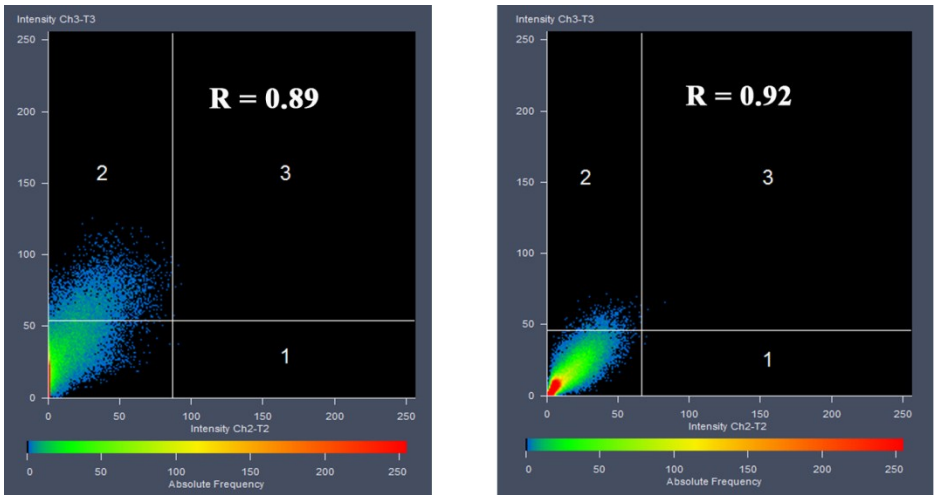


Figure S8. Co-localization scatter plots of Mito-Tracker Green FM and dye **4b** (left), and Mito-Tracker Green FM and dye **4d** (right) in mitochondria of HeLa Cells.

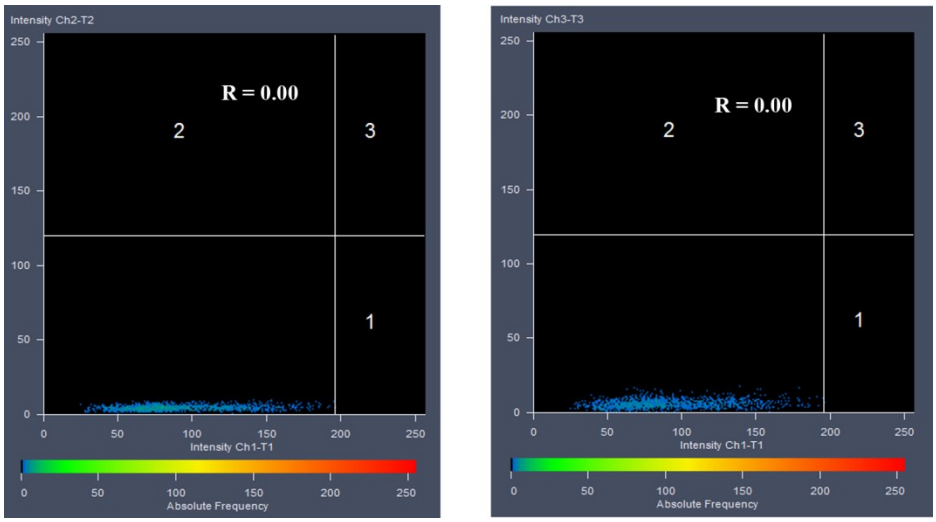


Figure S9. Co-localization scatter plots of Hoechst 33258 and dye **4b** (left), and Hoechst 33258 and dye **4d** (right) in HeLa Cells.

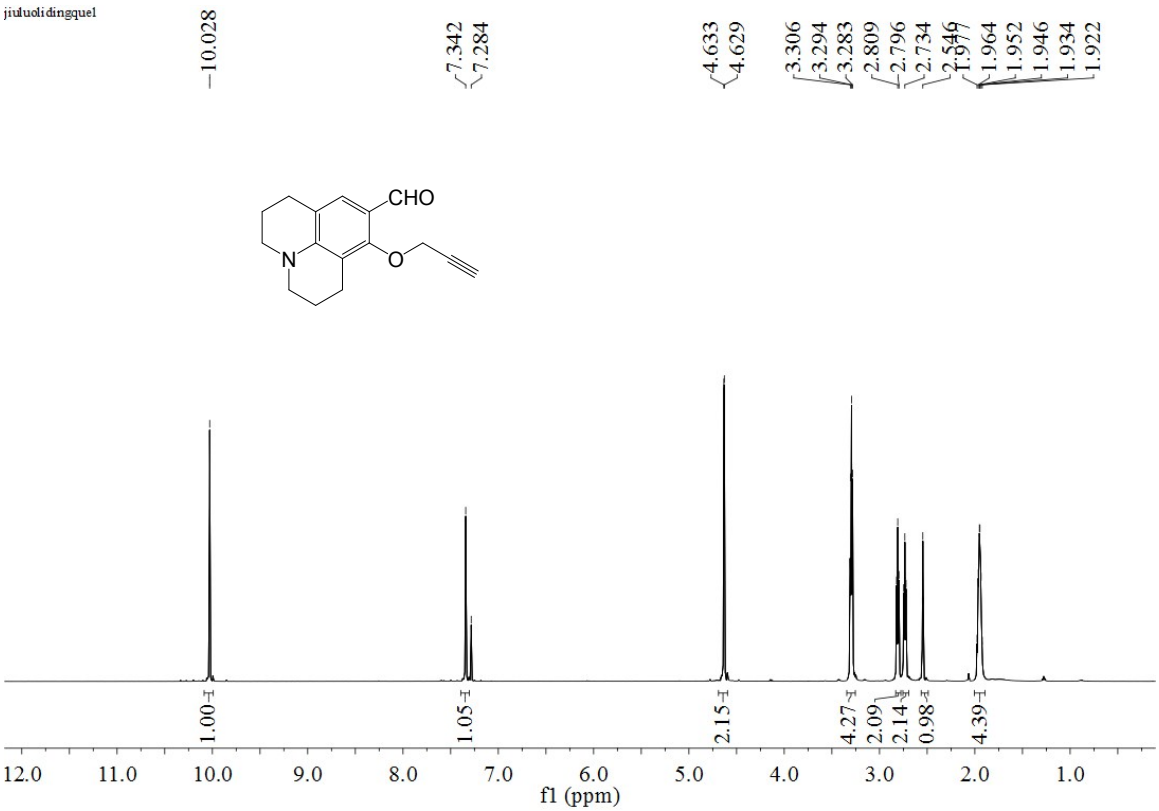


Figure S10. ^{1}H NMR spectrum of compound **2b** in $CDCl_3$.

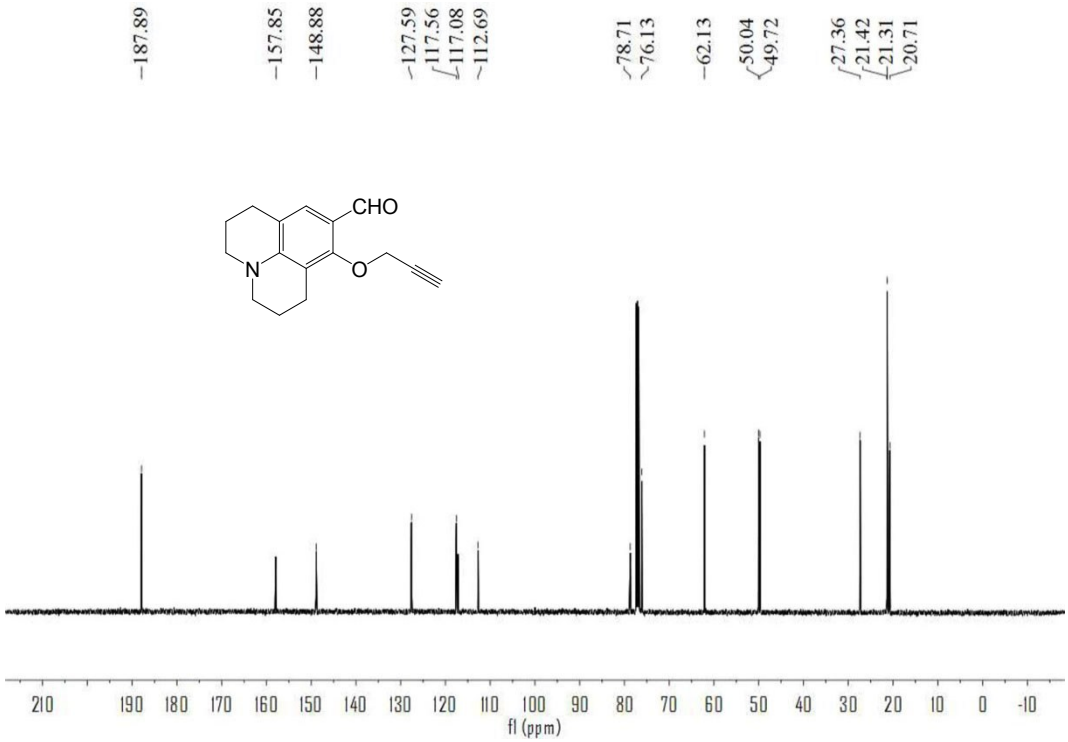


Figure S11. ^{13}C NMR spectrum of compound **2b** in $CDCl_3$.

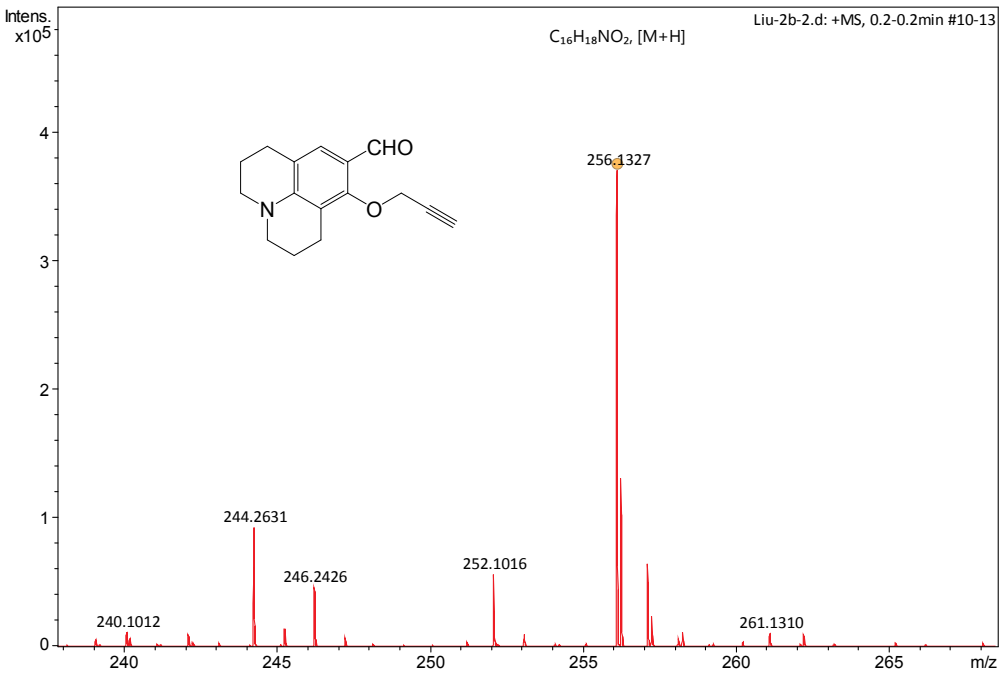


Figure S12. HRMS spectrum of compound **2b** in $CDCl_3$.

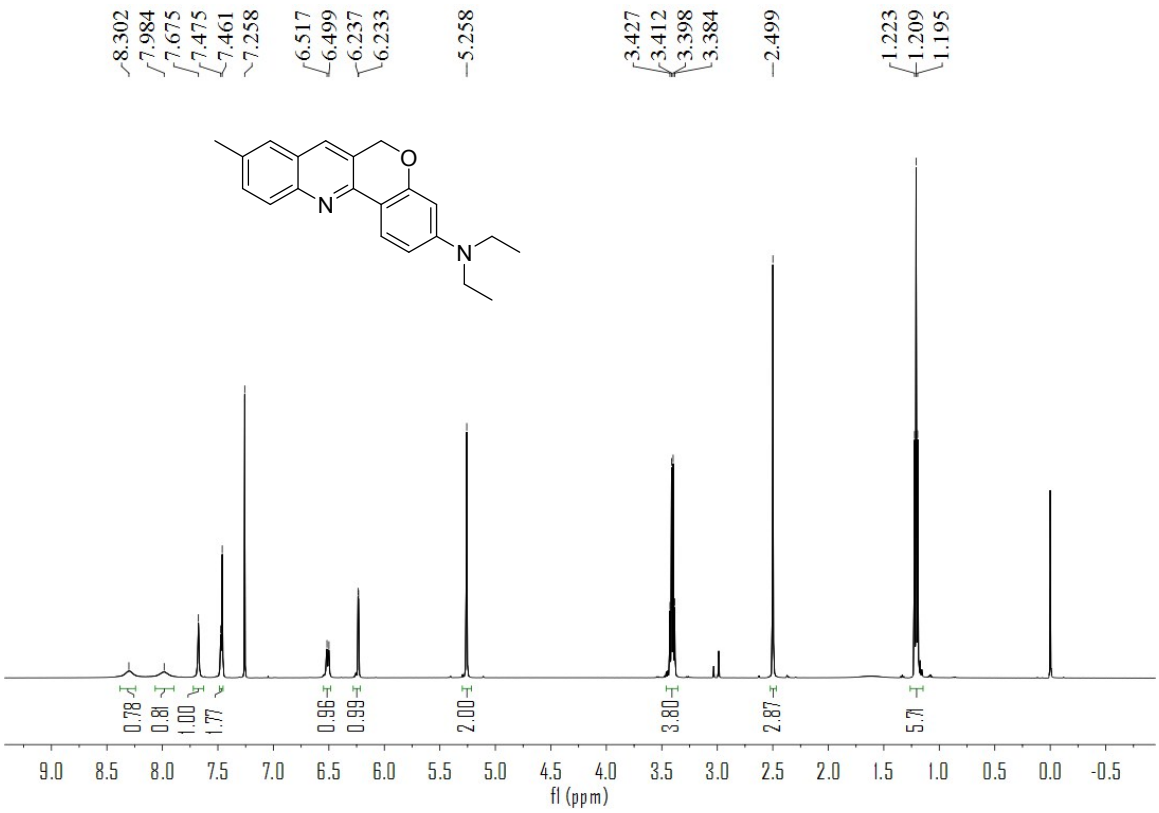


Figure S13. ^1H NMR spectrum of dye **3a** in $CDCl_3$.

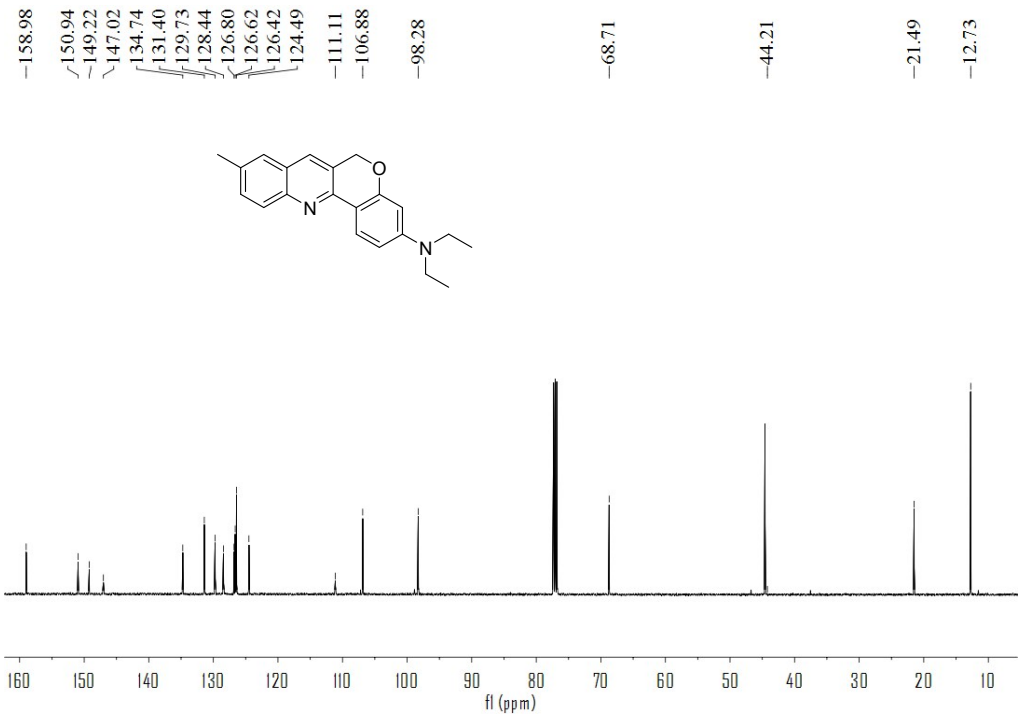


Figure S14. ^{13}C NMR spectrum of dye **3a** in $CDCl_3$.

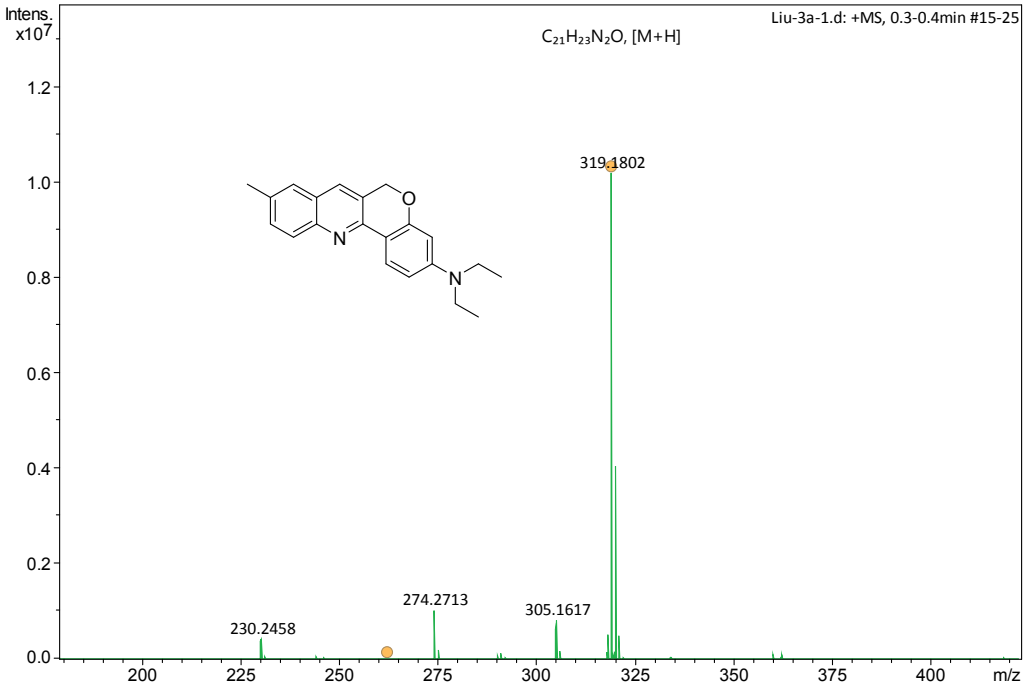


Figure S15. HRMS spectrum of dye **3a** in $CDCl_3$.

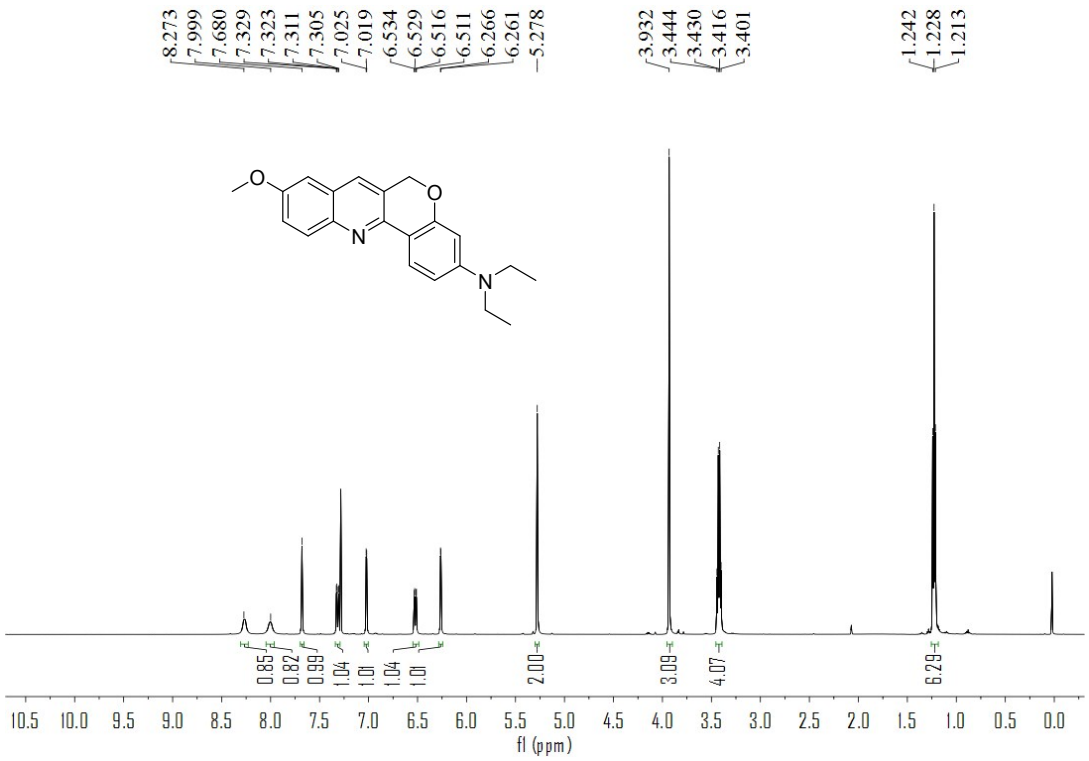


Figure S16. ^{1}H NMR spectrum of dye **3b** in $CDCl_3$.

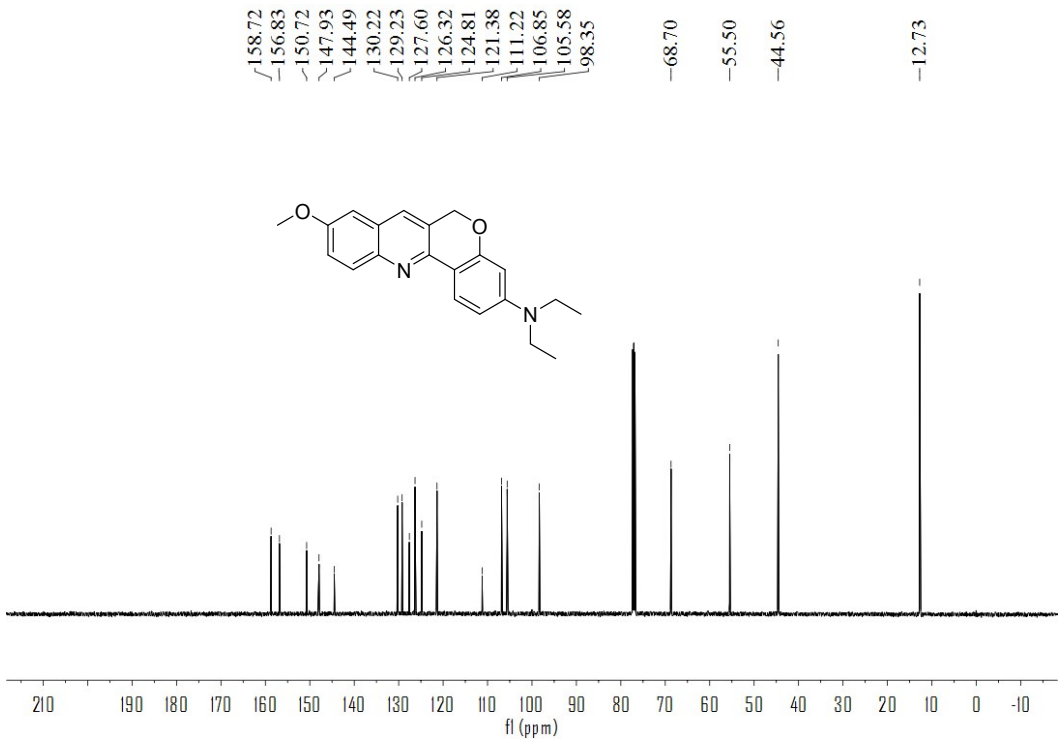


Figure S17. ^{13}C NMR spectrum of dye **3b** in $CDCl_3$.

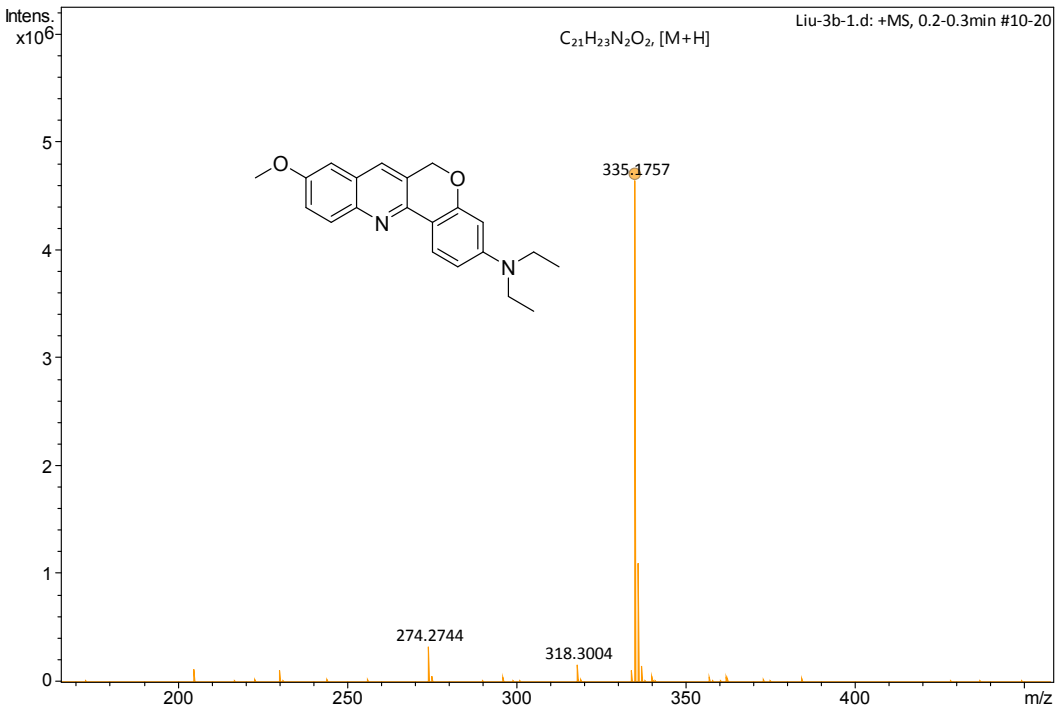


Figure S18. HRMS spectrum of dye **3b** in $CDCl_3$.

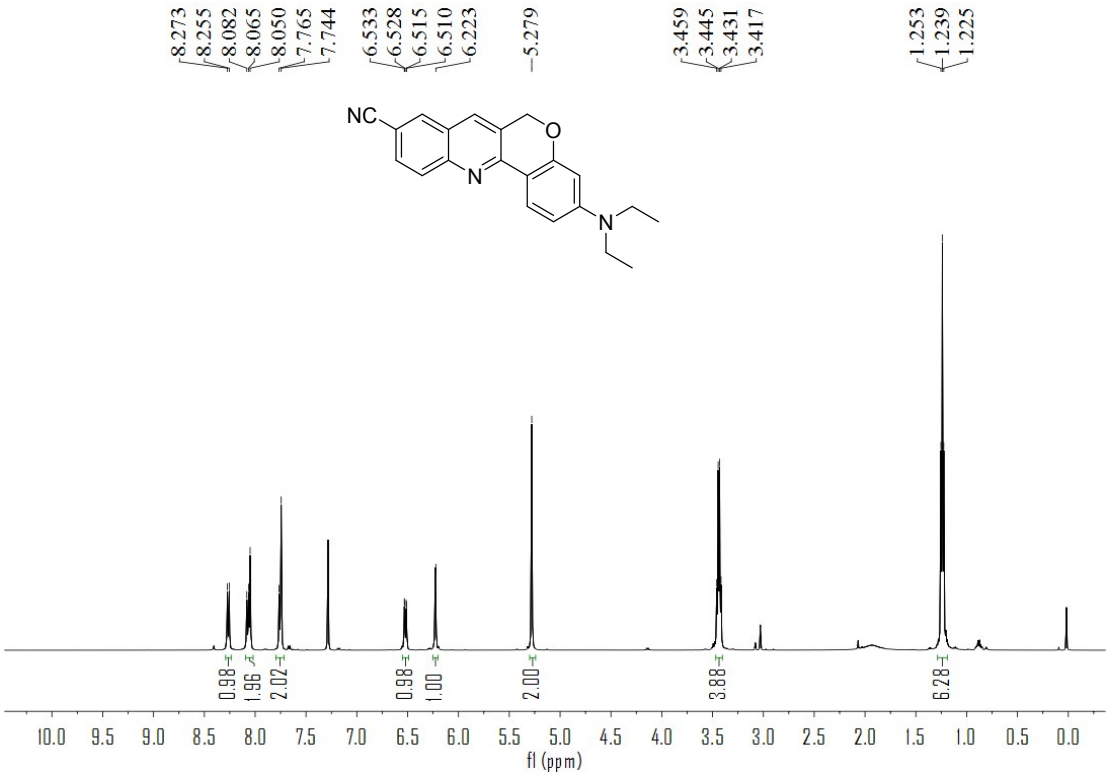


Figure S19. ^1H NMR spectrum of dye **3c** in $CDCl_3$.

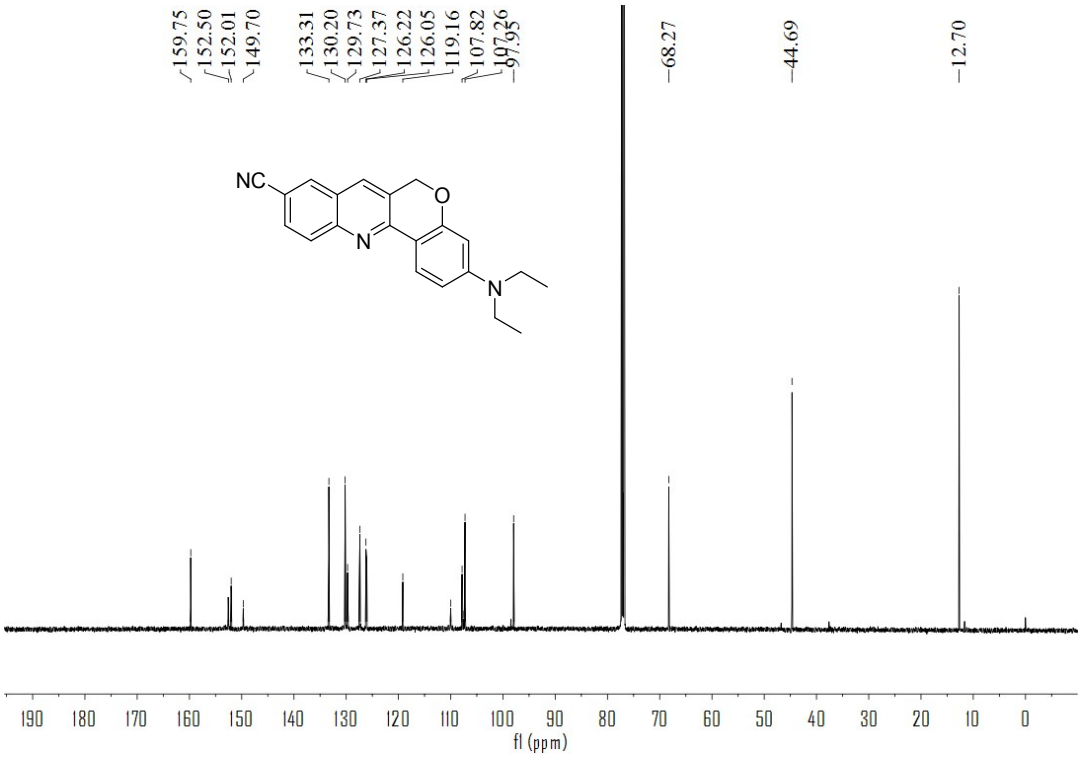


Figure S20. ^{13}C NMR spectrum of dye **3c** in $CDCl_3$.

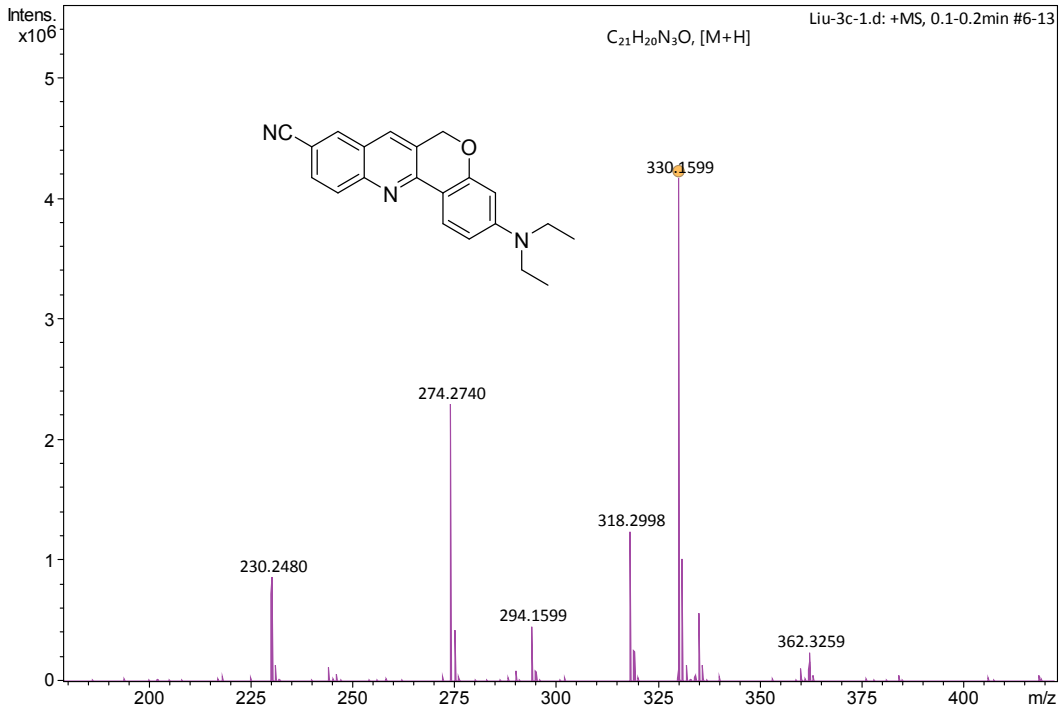


Figure S21. HRMS spectrum of dye **3c** in $CDCl_3$.

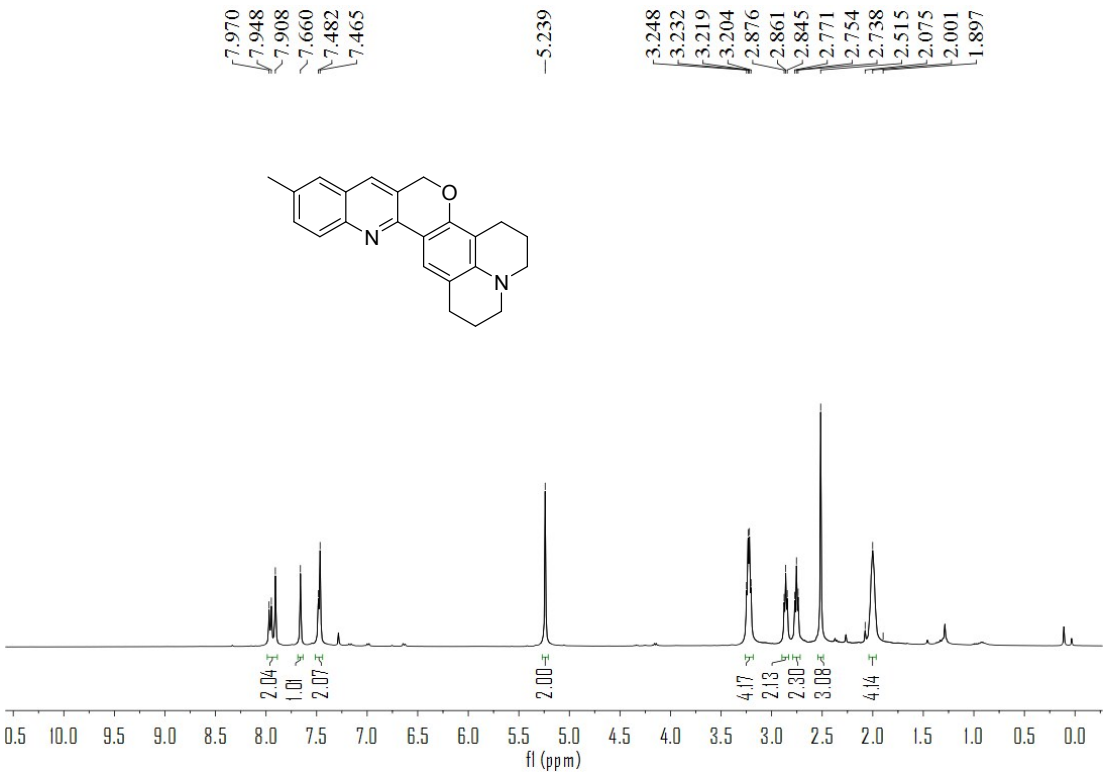


Figure S22. ^{1}H NMR spectrum of dye **3d** in $CDCl_3$.

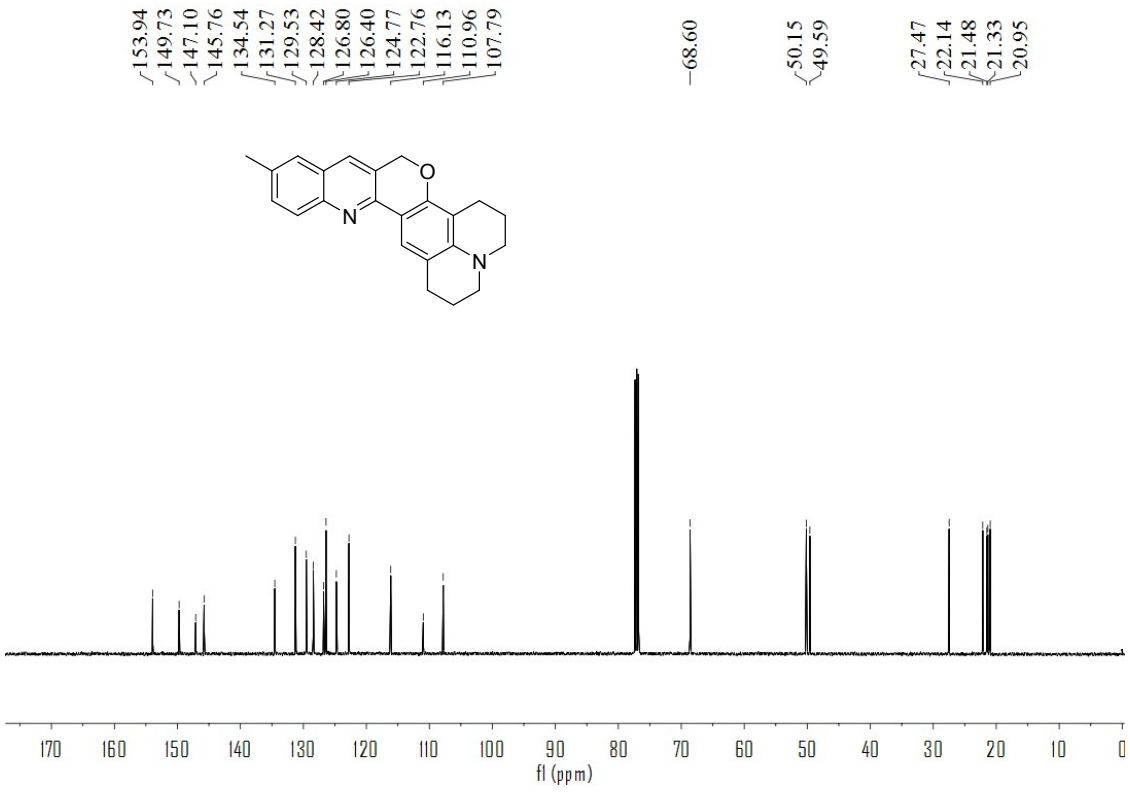


Figure S23. ^{13}C NMR spectrum of dye **3d** in $CDCl_3$.

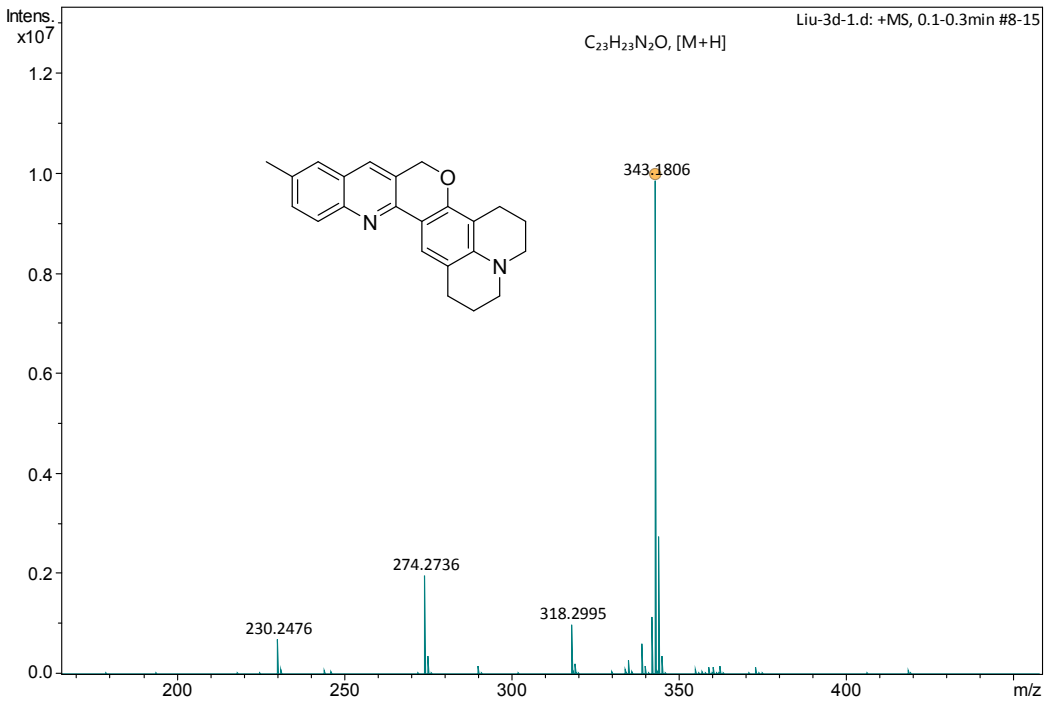


Figure S24. HRMS spectrum of dye **3d**.

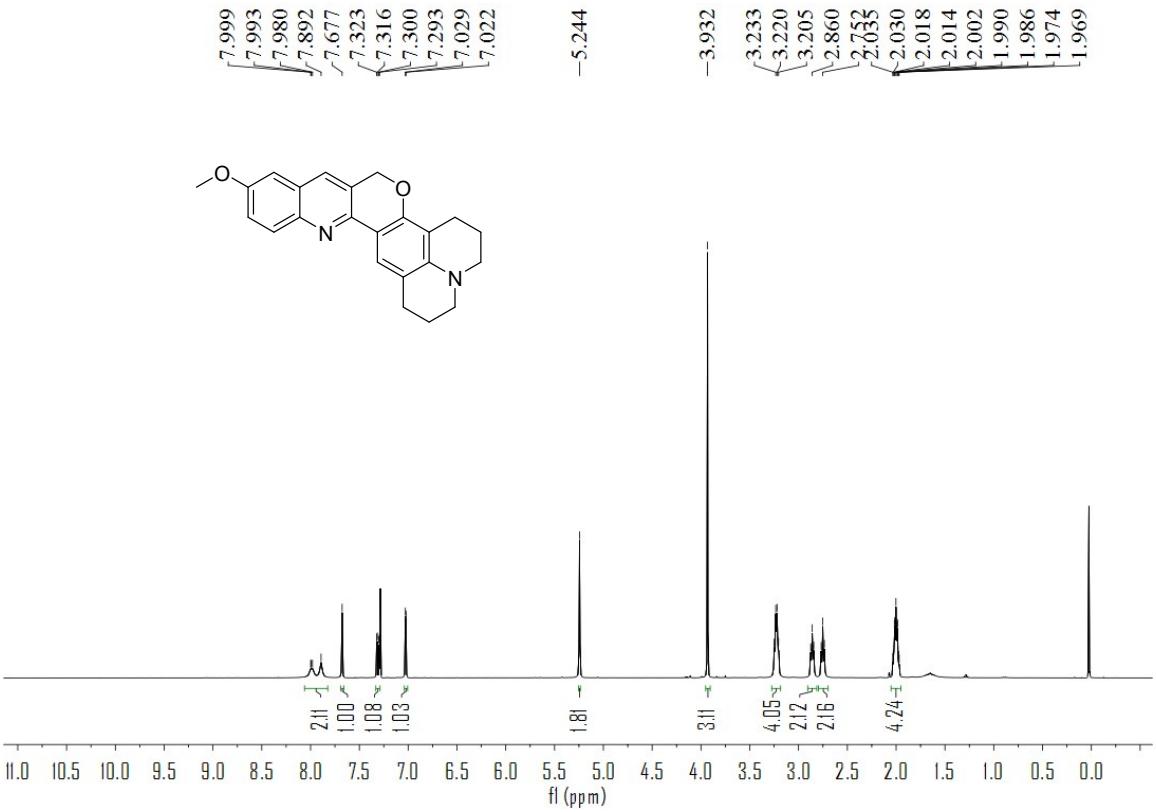


Figure S25. ^{1}H NMR spectrum of dye **3e** in $CDCl_3$.

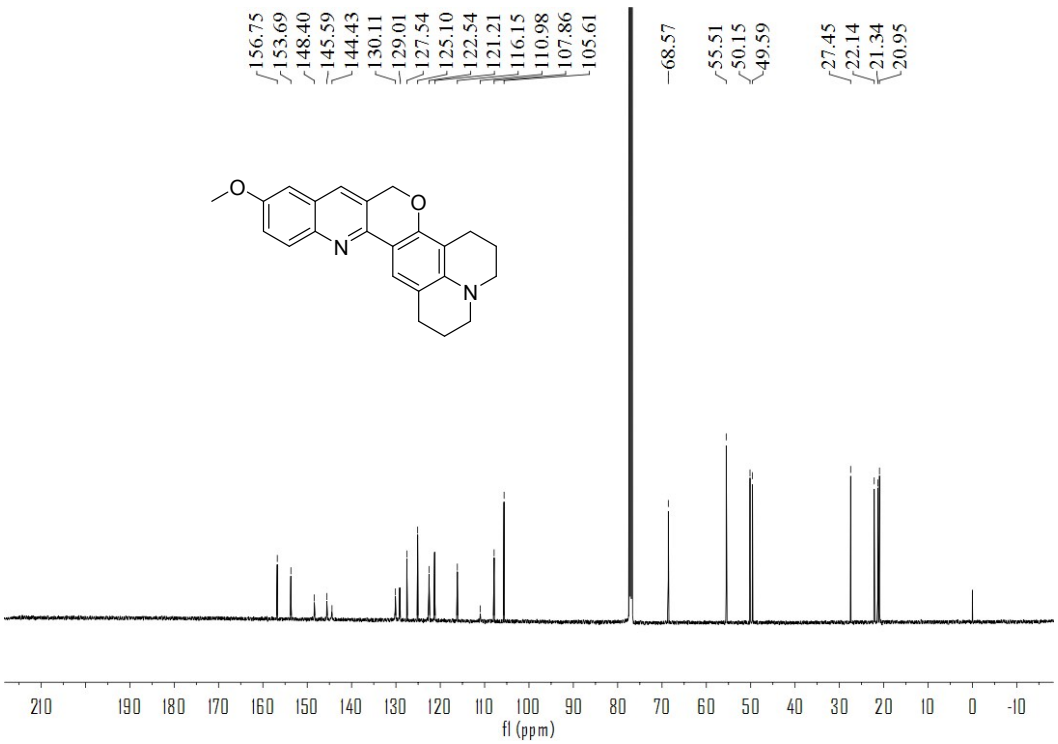


Figure S26. ^{13}C NMR spectrum of dye **3e** in $CDCl_3$.

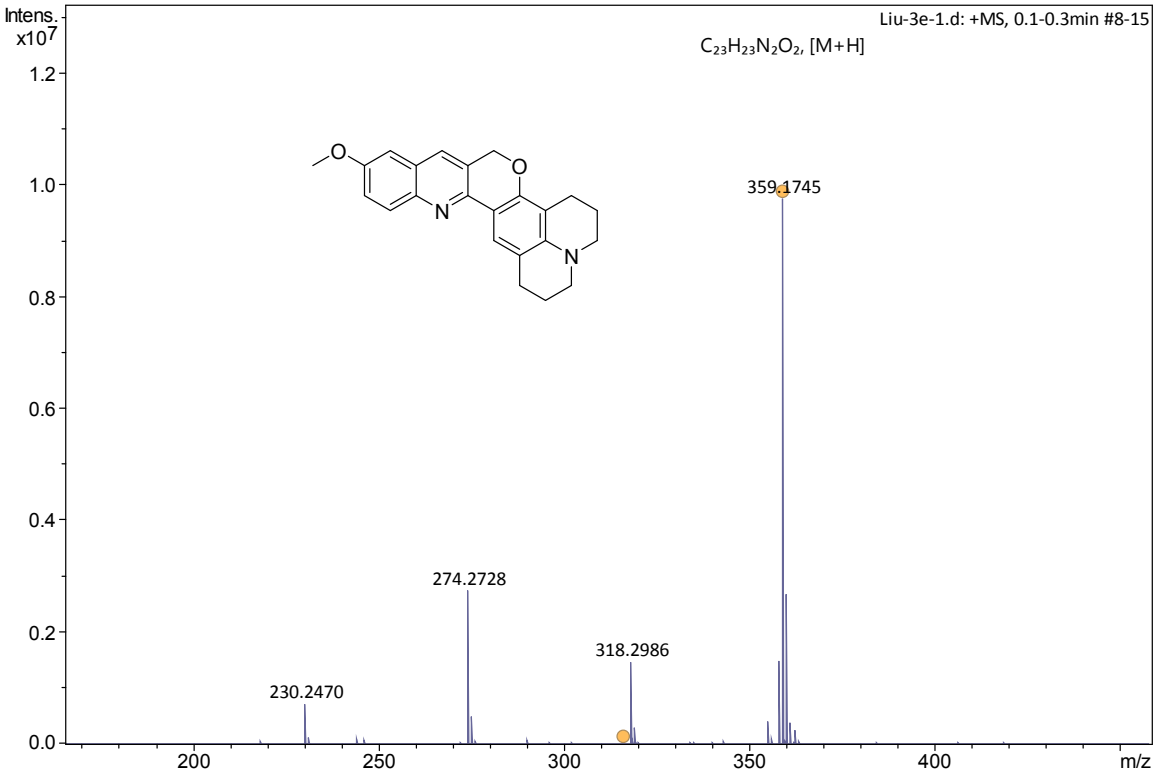


Figure S27. HRMS spectrum of dye **3e**.

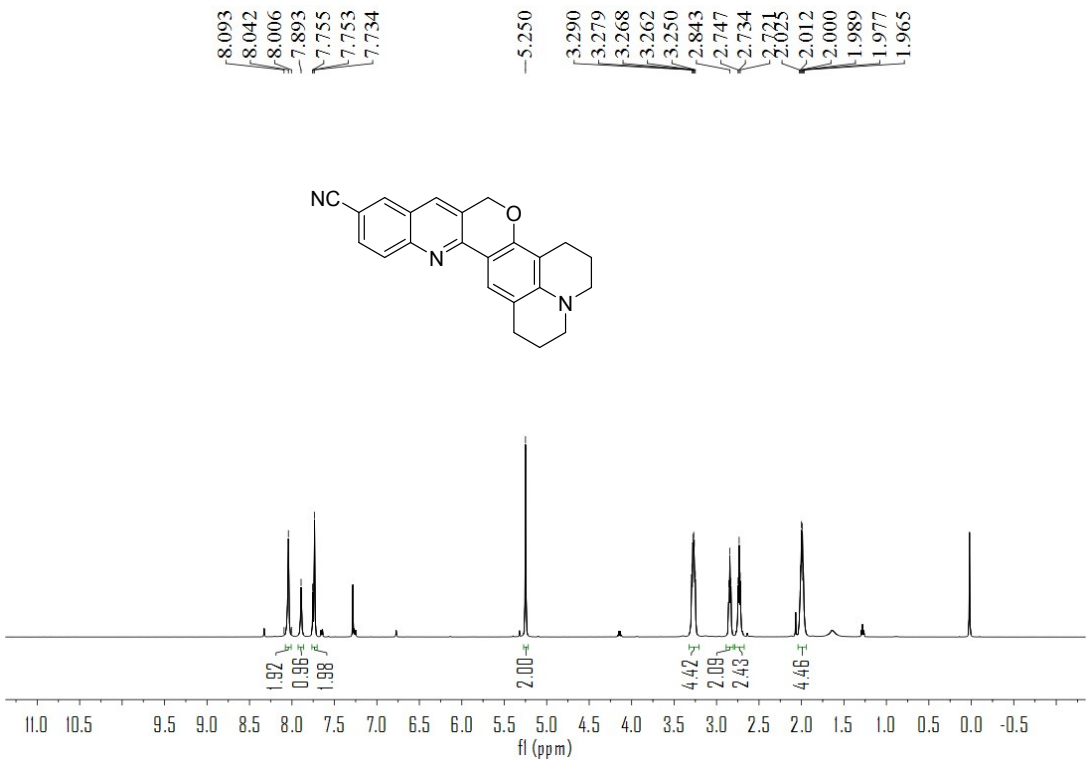


Figure S28. ^{1}H NMR spectrum of dye **3f** in $CDCl_3$.

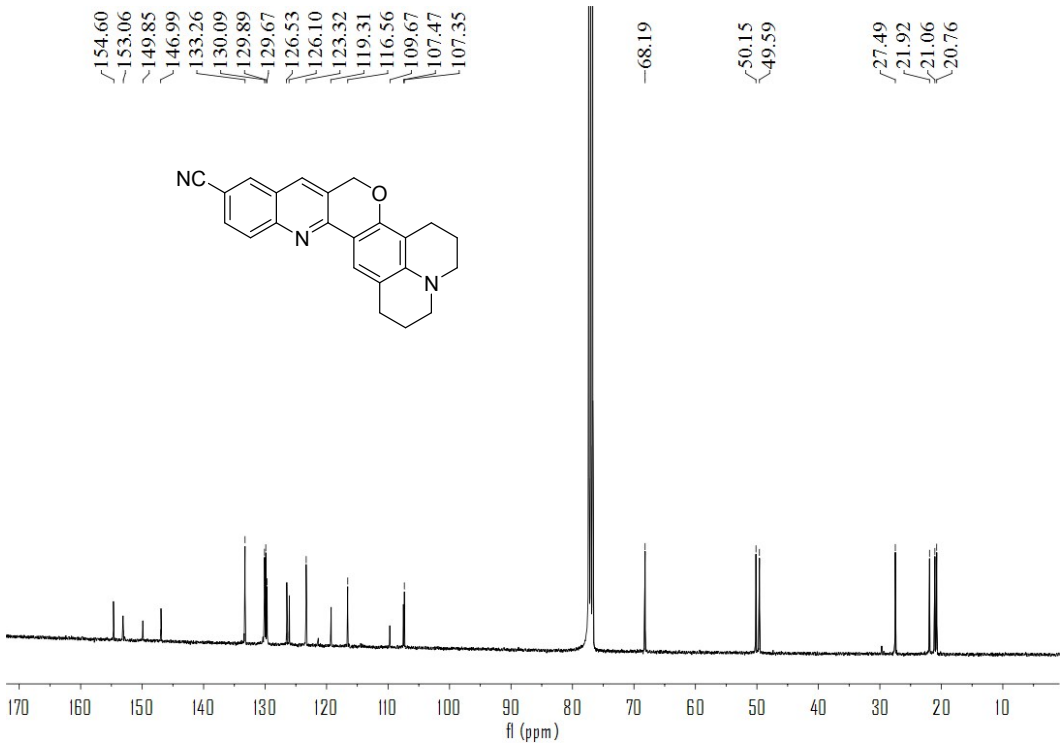


Figure S29. ^{13}C NMR spectrum of dye **3f** in $CDCl_3$.

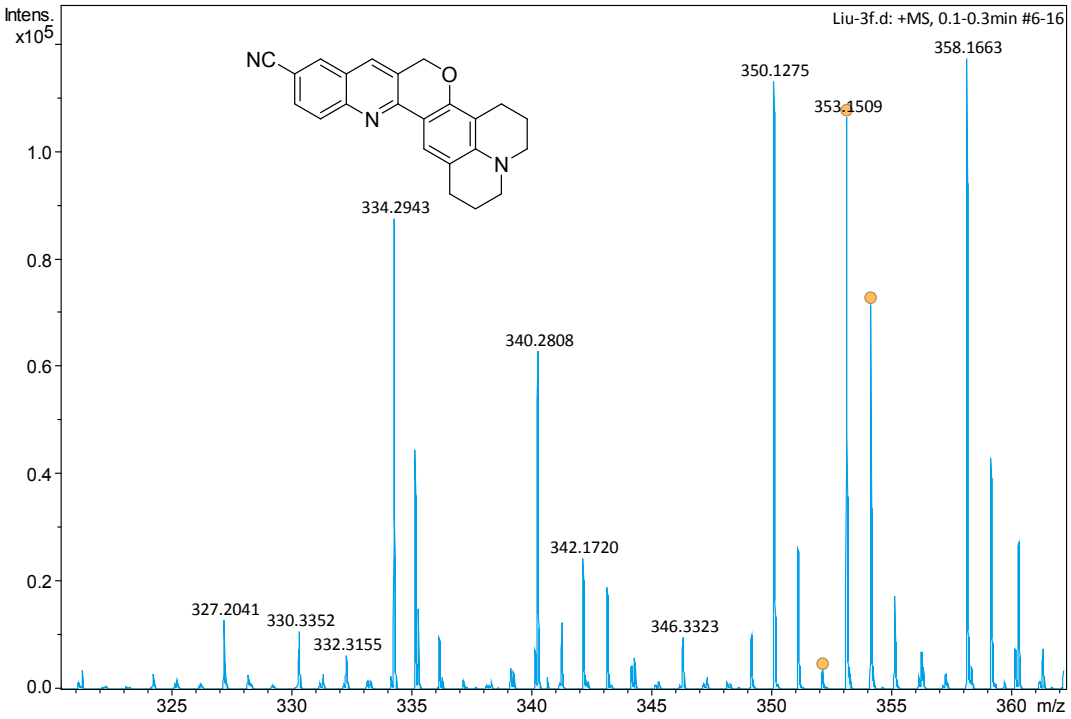


Figure S30. HRMS spectrum of dye **3f**.

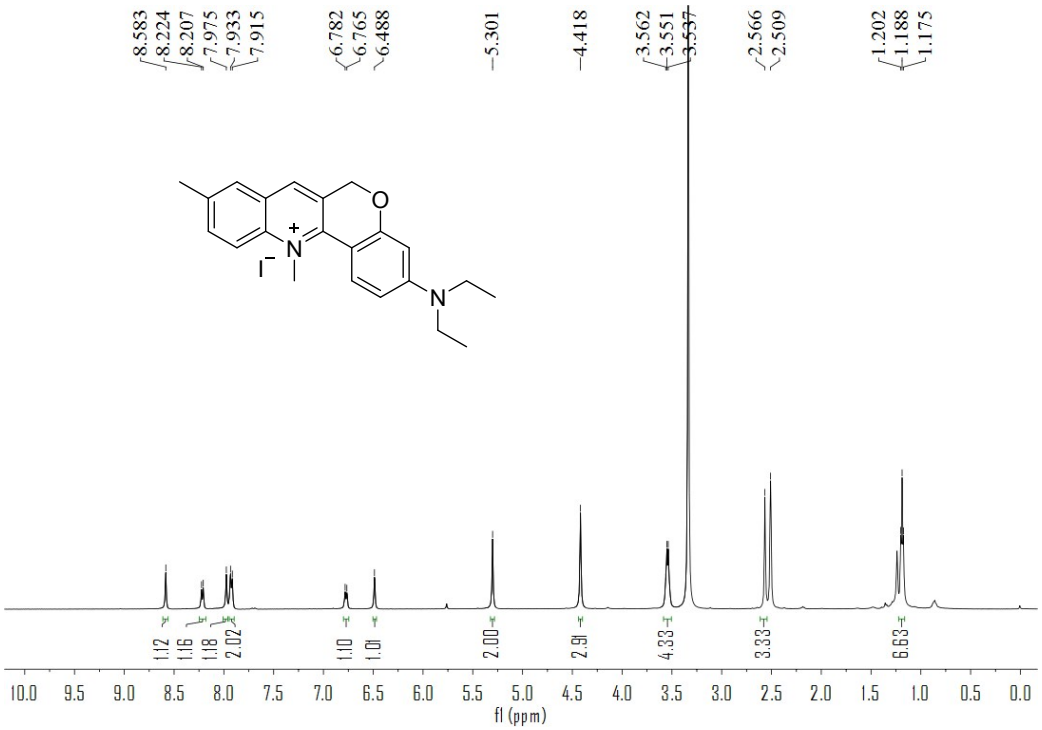


Figure S31. ^{1}H NMR spectrum of dye **4a** in DMSO-d_6.

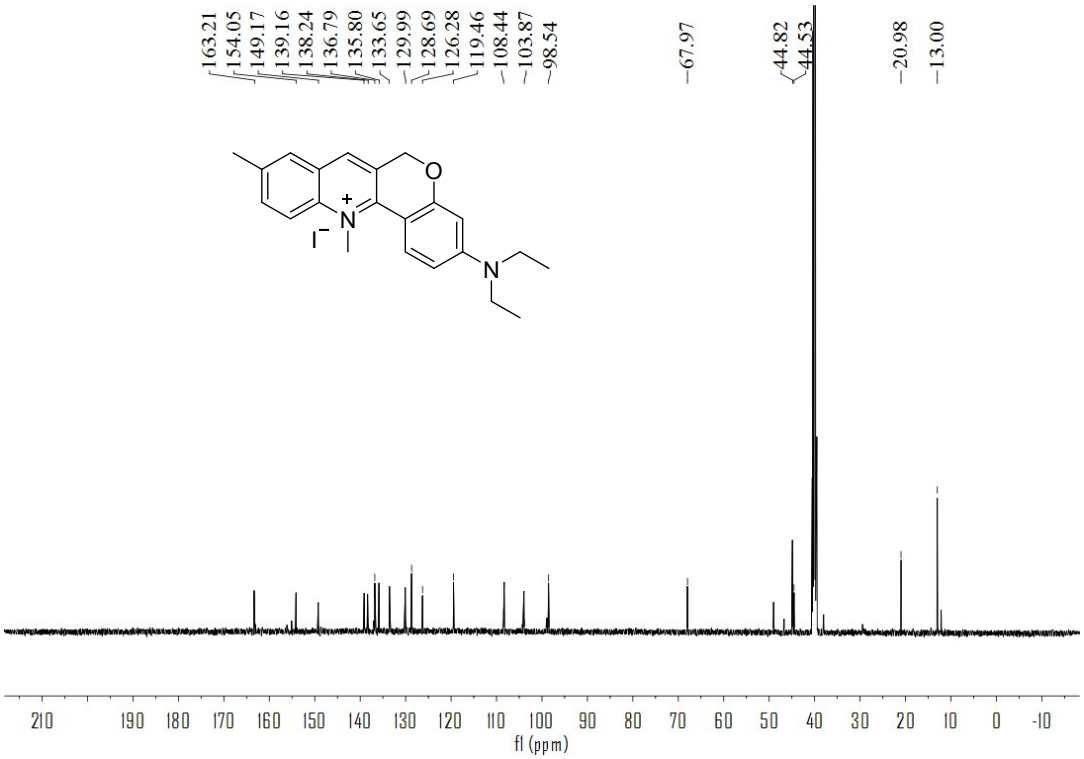


Figure S32. ^{13}C NMR spectrum of dye **4a** in DMSO-d_6.

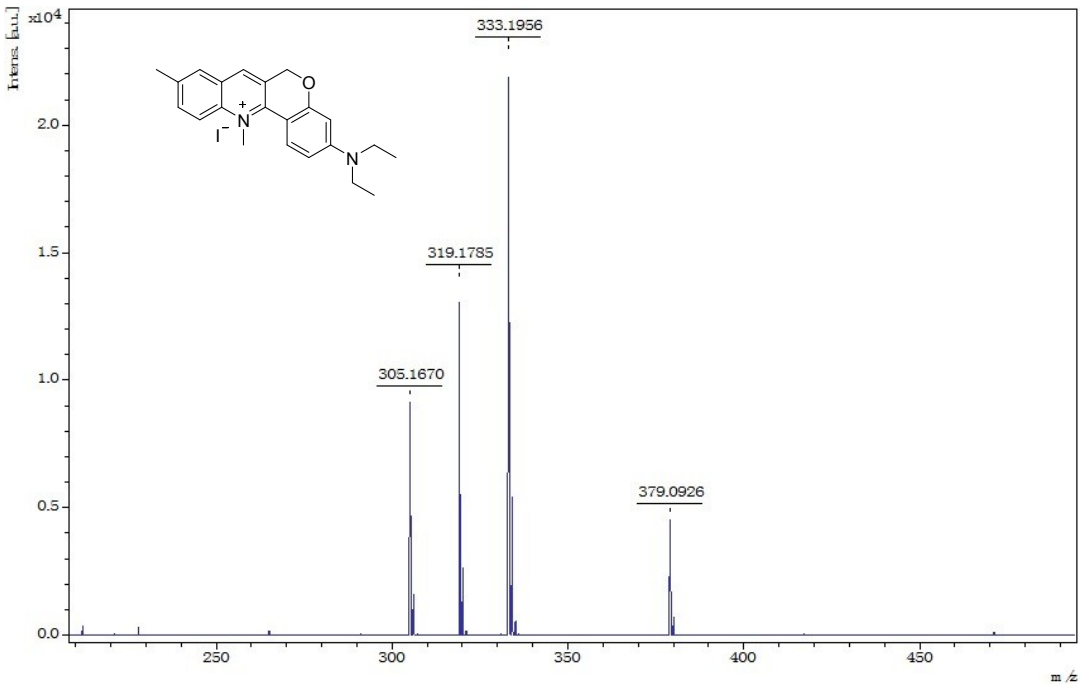


Figure S33. HRMS spectrum of dye **4a**.

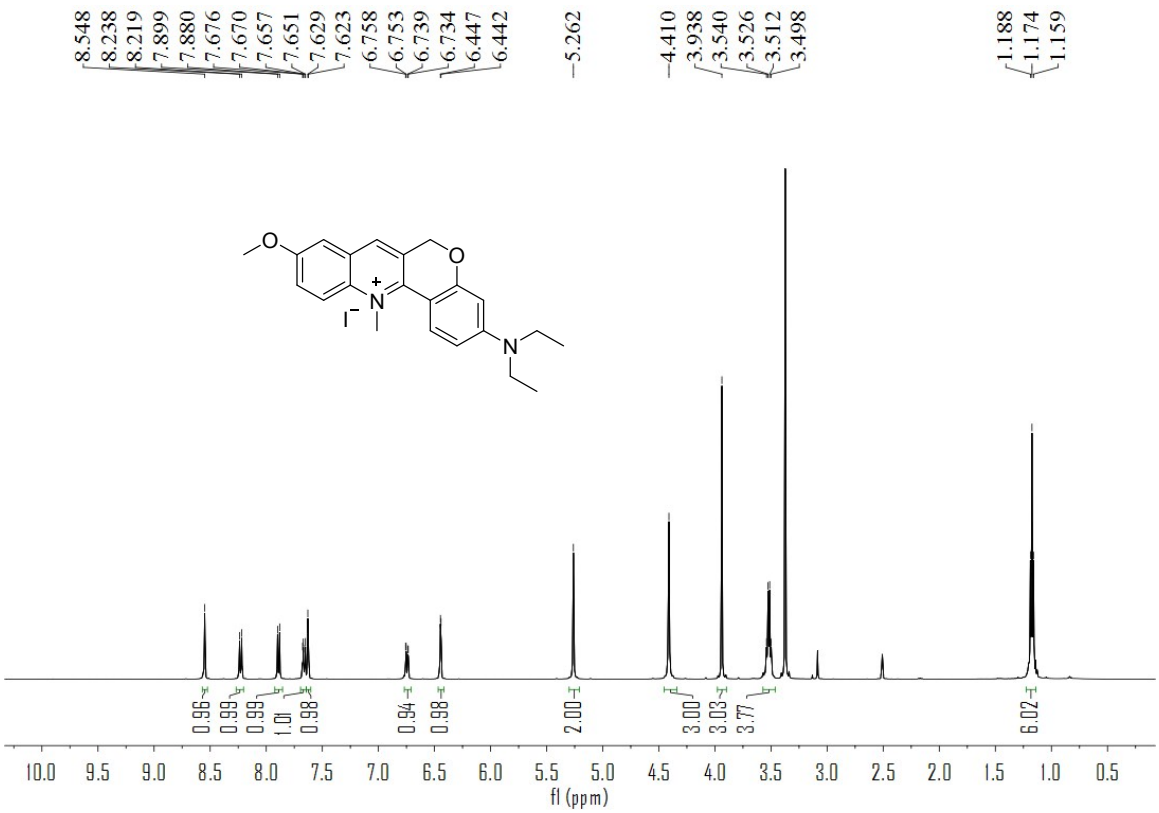


Figure S34. ^{1}H NMR spectrum of dye **4b** in DMSO-d_6.

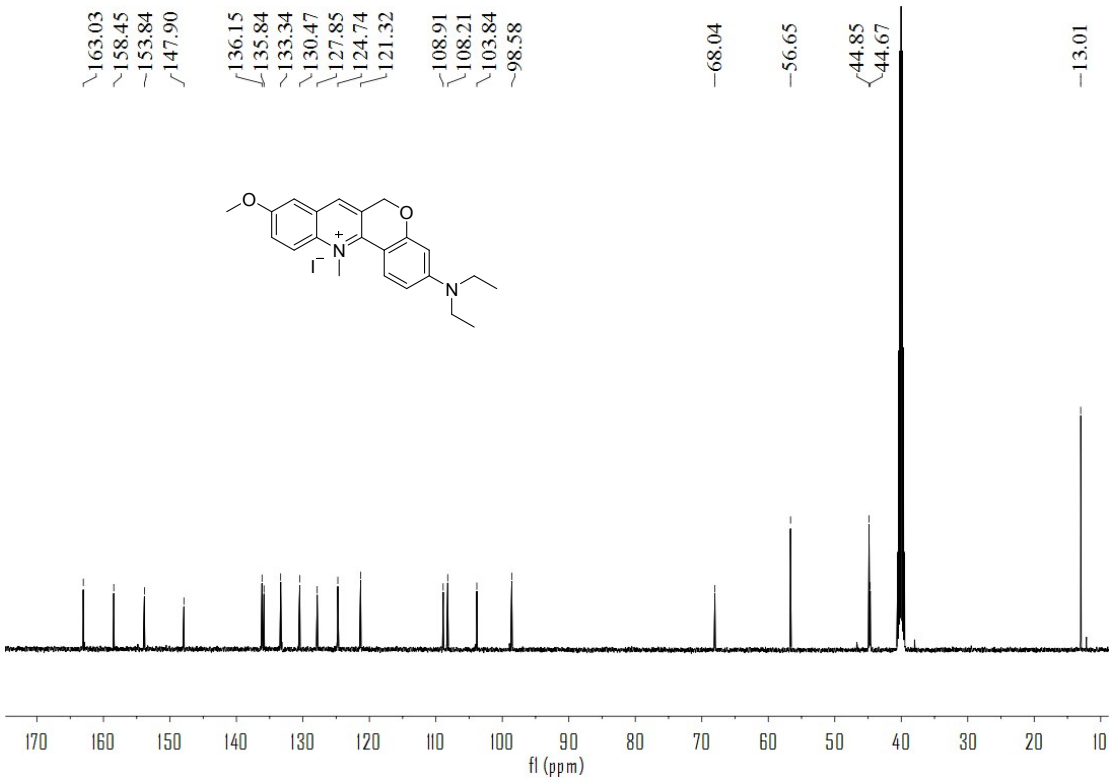


Figure S35. ^{13}C NMR spectrum of dye **4b** in DMSO-d_6.

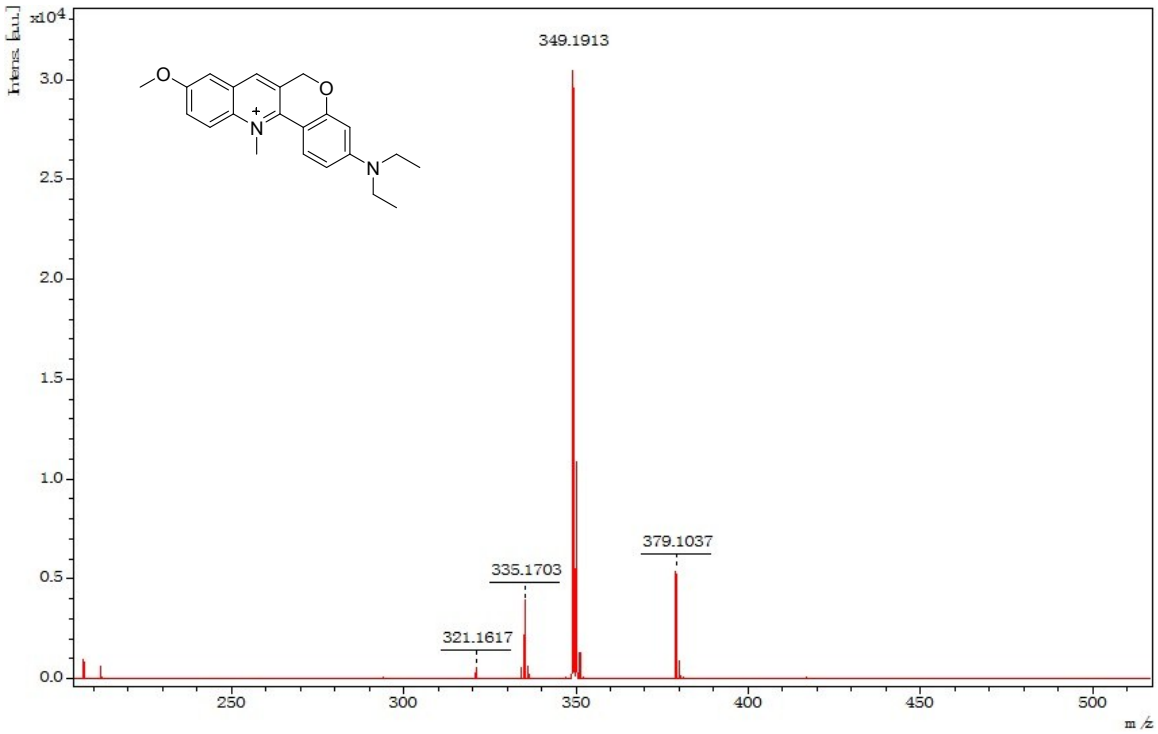


Figure S36. HRMS spectrum of dye **4b**.

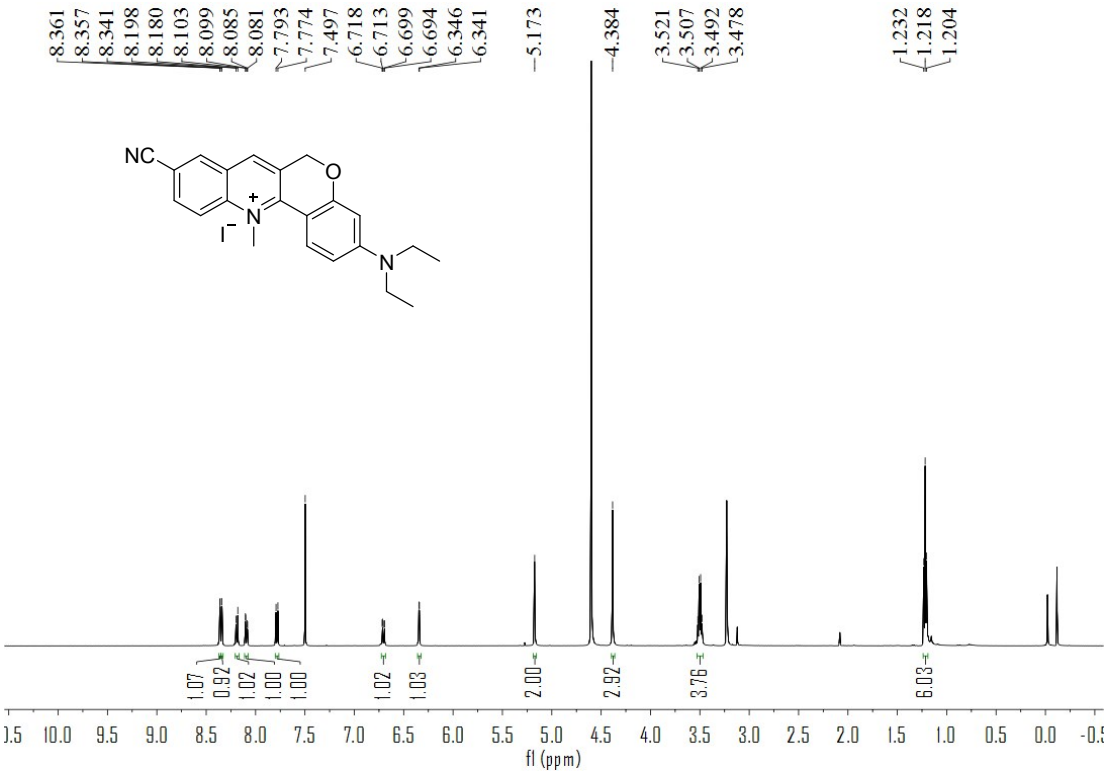


Figure S37. ^{1}H NMR spectrum of dye **4c** in $CDCl_3$ and CD_3OD.

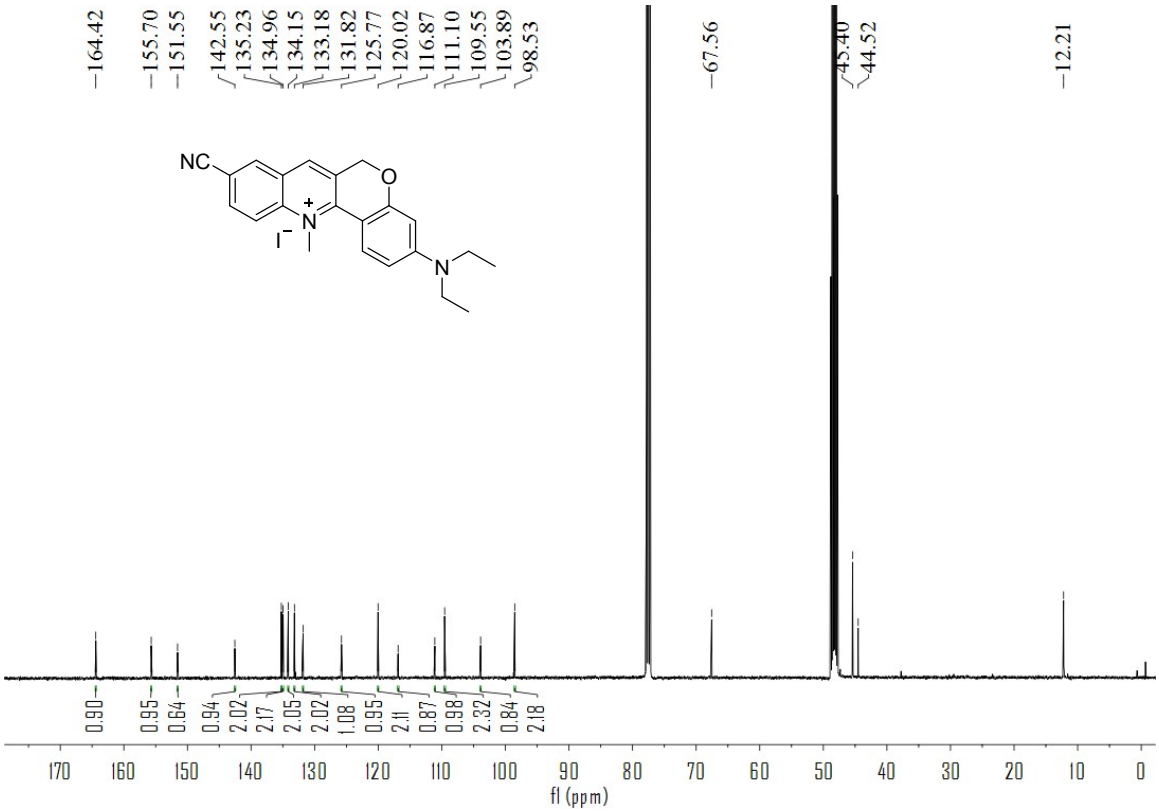


Figure S38. ^{13}C NMR spectrum of dye **4c** in $CDCl_3$ and CD_3OD.

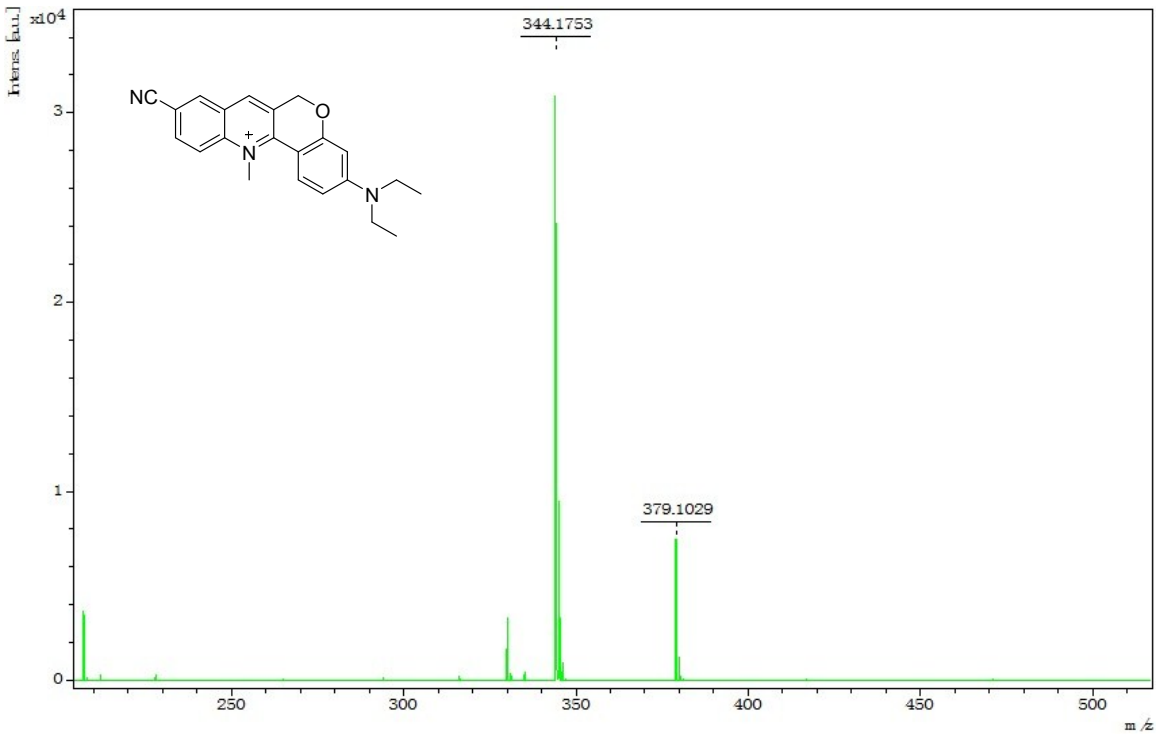


Figure S39. HRMS spectrum of dye **4c**.

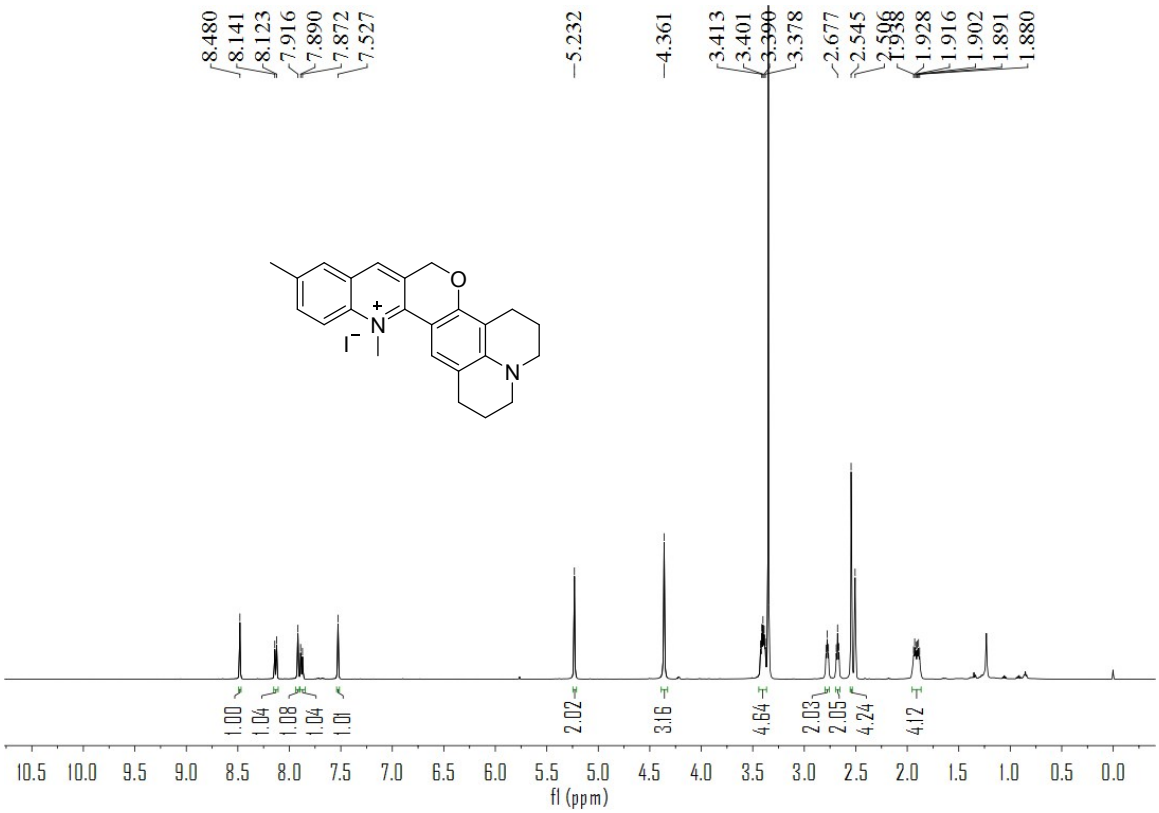


Figure S40. ^{1}H NMR spectrum of dye **4d** in DMSO-d_6.

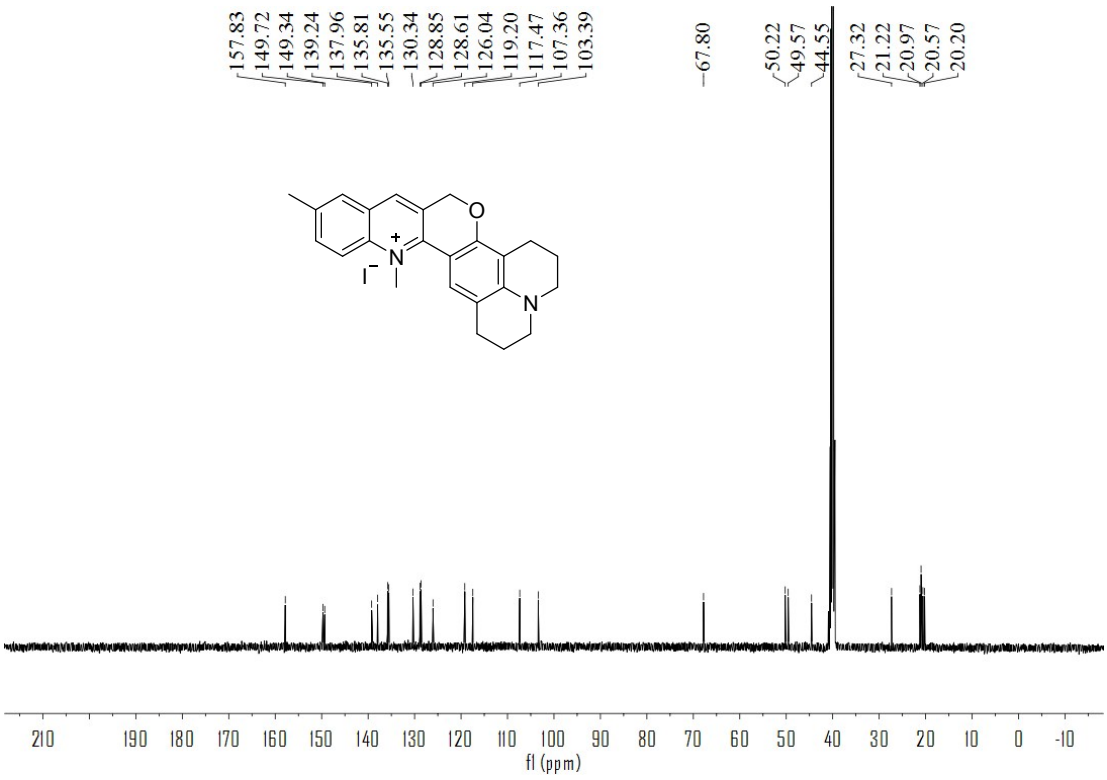


Figure S41. ^{13}C NMR spectrum of dye **4d** in DMSO-d_6.

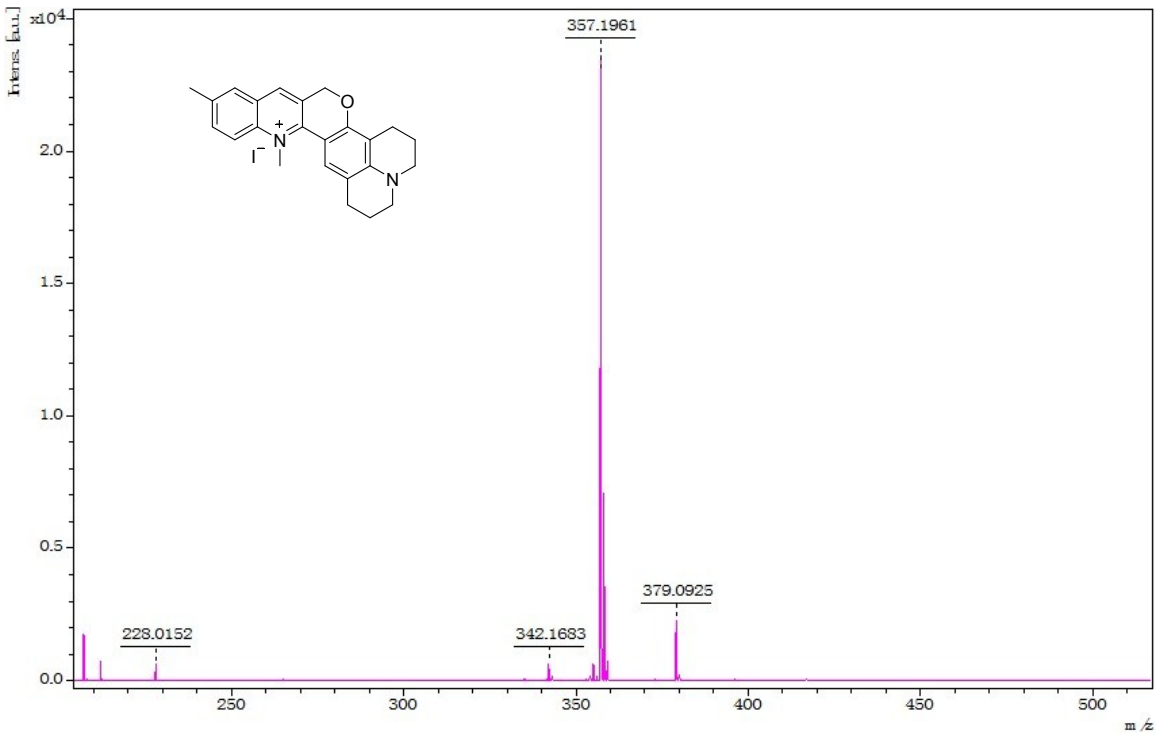


Figure S42. HRMS spectrum of dye **4d**.

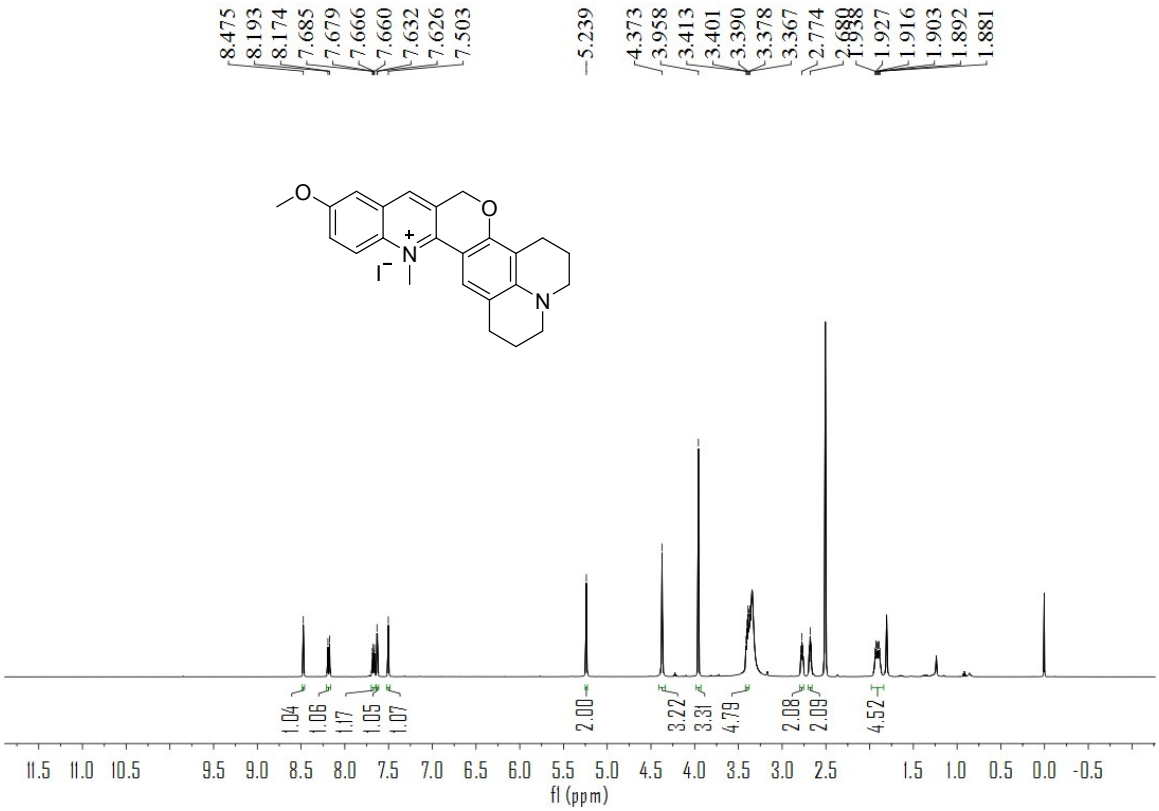


Figure S43. [1]H NMR spectrum of dye **4e** in DMSO-d_6.

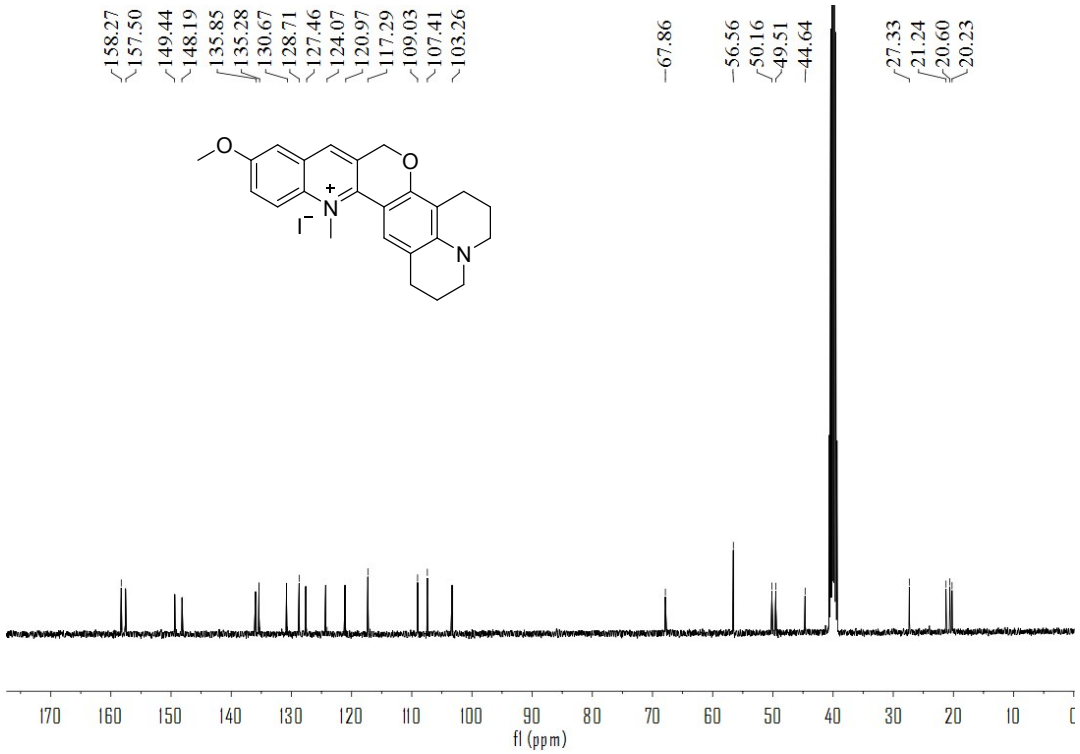


Figure S44. ^{13}C NMR spectrum of dye **4e** in DMSO-d_6.

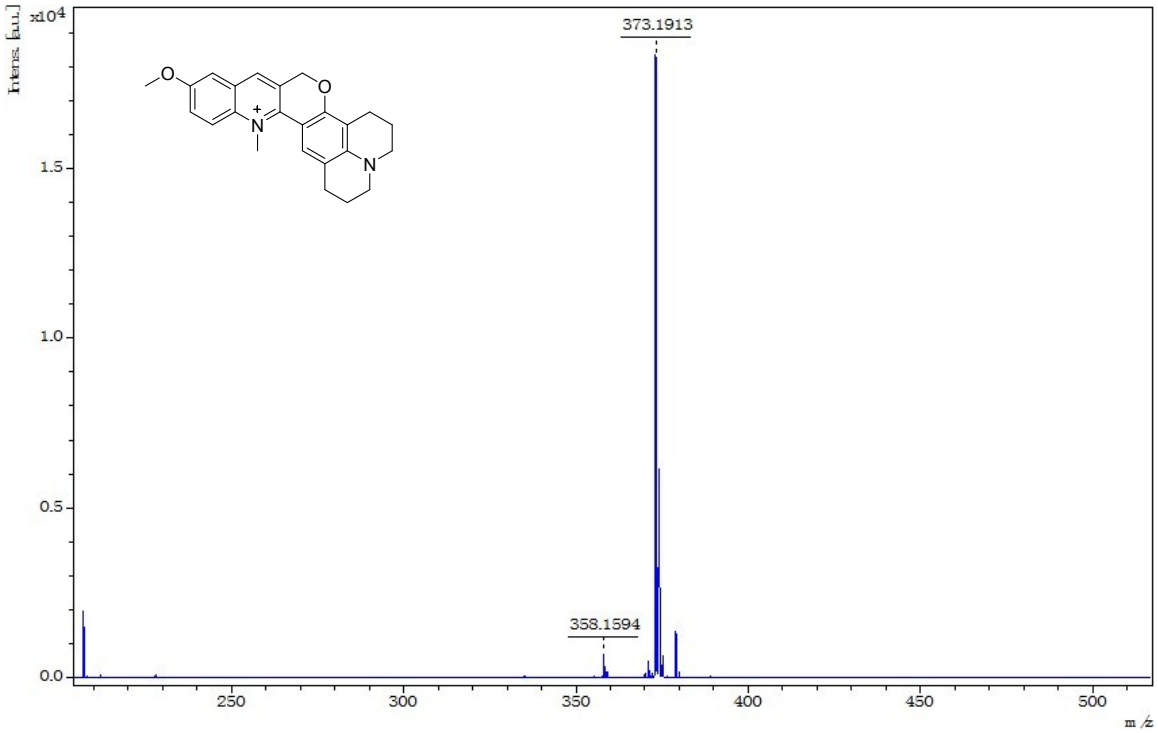


Figure S45. HRMS spectrum of dye **4e**.

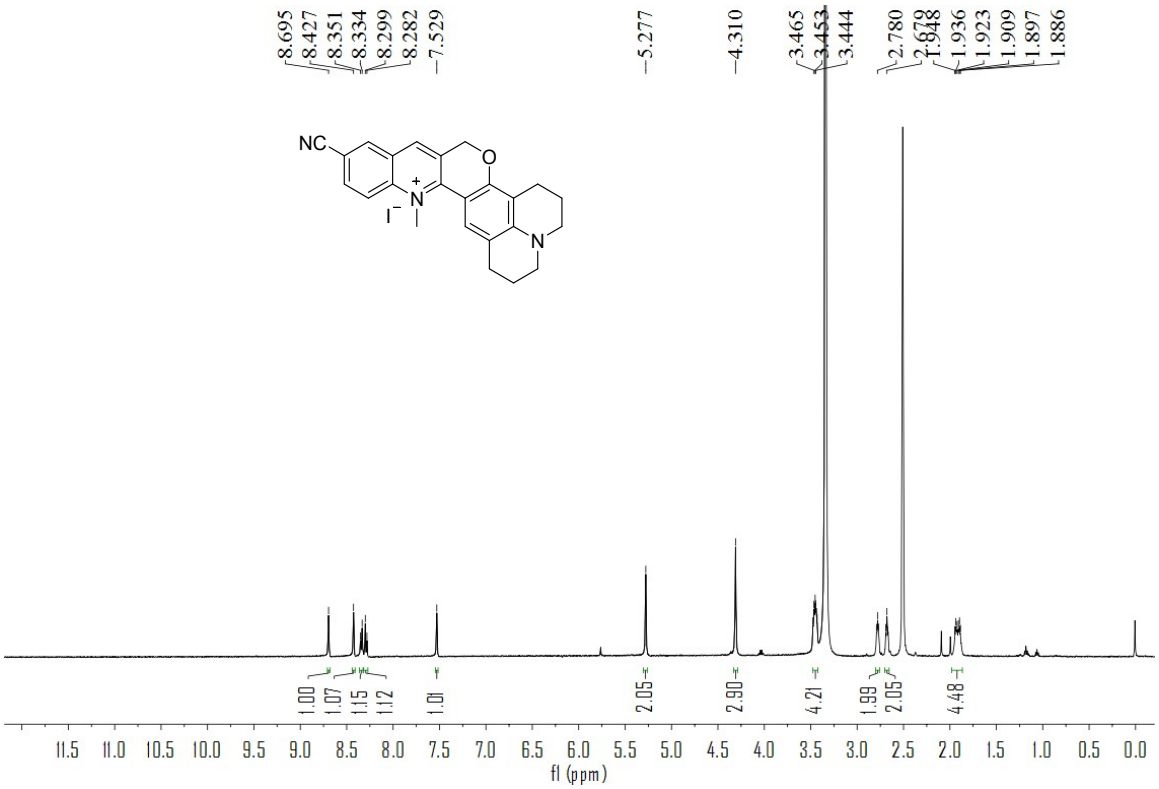


Figure S46. ^{1}H NMR spectrum of dye **4f** in DMSO-d_6.

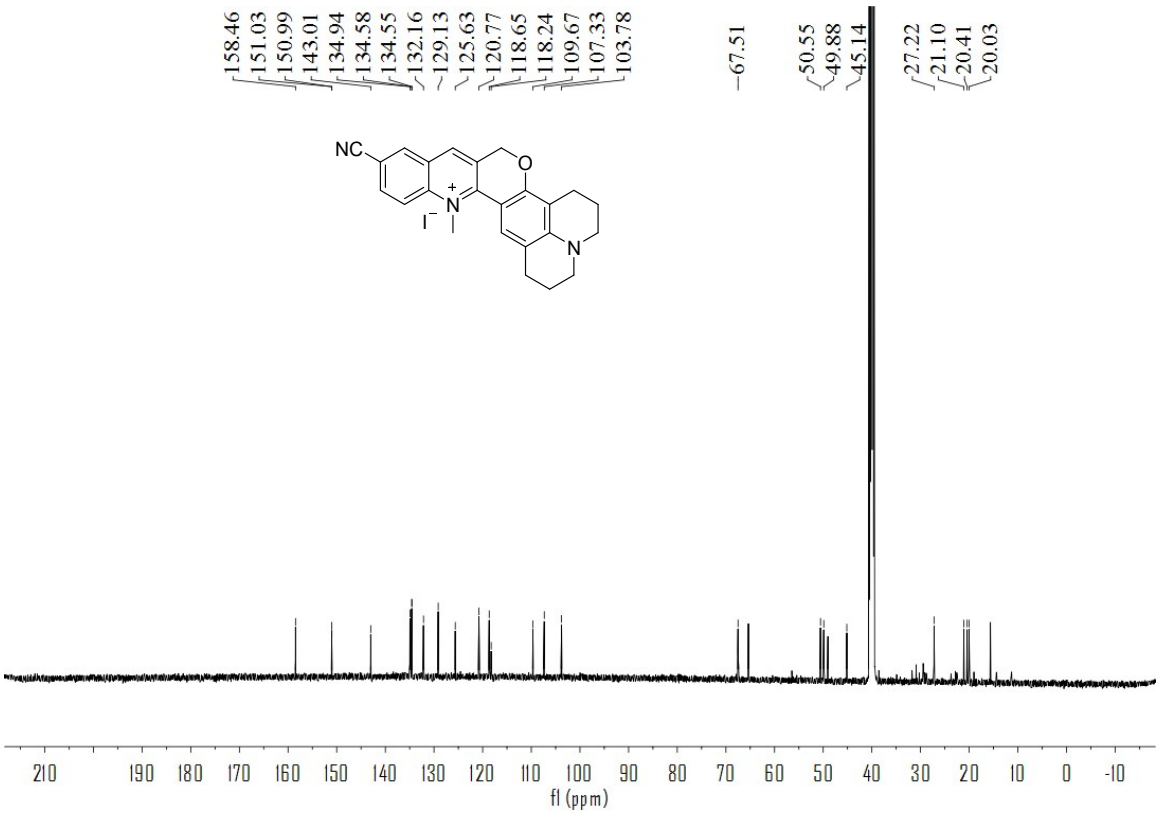


Figure S47. ^{13}C NMR spectrum of dye **4f** in DMSO-d_6.

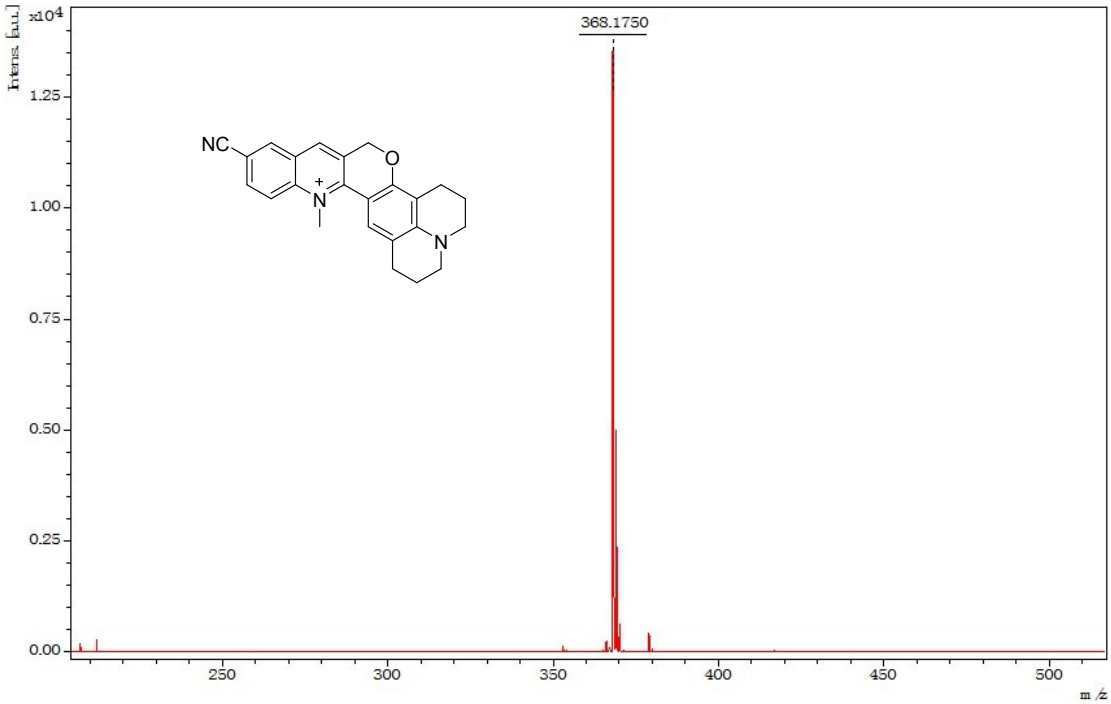


Figure S48. HRMS spectrum of dye **4f**.