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Supplementary Information

Synthesis of Near-Infrared Fluorescent Rhodamines via an S_NAr^H Reaction and Their Biological Applications

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General methods

Starting materials and reagents of AR grade were purchased from Tokyo Kasei Kogyo (TCI: Tokyo, Japan). Dry solvents were purchased from Alfa-Aesar, and used without further purification. Reactions were carried out in oven dried glass ware with magnetic stirring. NMR chemical shifts were reported in ppm downfield from internal Me4Si (^{1}H and ^{13}C NMR). High resolution mass spectra (HRMS) were acquired on an Agilent 6510Q-TOF LC/MS instrument (Agilent Technologies, Palo Alto, CA) equipped with an electro-spray ionization (ESI) source. Melting points were recorded on Boethius Block apparatus. All absorption spectra were recorded using a Shimadzu UV-2550 UV/Vis spectrophotometer with a 1 cm quartz cell. In a similar manner, fluorescence spectra were recorded on a Hitachi F-4600 spectrofluorophotometer with a 1 cm quartz cell. Cell imaging was performed with FV-1000 Olympus confocal fluorescence microscopy. Deionized water was used to prepare all aqueous solutions.

Single crystal X-ray diffraction structure of RE1 and table of crystal data

Single crystals of **RE1** suitable for X-ray crystallographic studies were obtained by slow evaporation of solvent mixture (MeOH/CH_2Cl_2 = 2:1, v/v) at ambient temperature. The single-crystal X-ray diffraction data of **RE1** was collected on a Rigaku SCX-mini diffractometer at 293(2) K. The structure was solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL. The solvent of two molecules of methanol contribution were subtracted using SQUEEZE facility of PLATON.

Relative fluorescence quantum yield measurement

Nile Blue in ethanol (Φ= 0.27)[1] was chosen as the standard. The fluorescence quantum yields were calculated according to the following equation: $\Phi_x = \Phi_{st}[n_x^2/n_{st}^2][G_x/G_{st}]$, where Φ is the fluorescence quantum yield, G is the gradient from the plot of integrated fluorescence intensity versus absorbance, n is the refractive index of different solvents. The subscript "st" and "x" refer to the standard and dye, respectively. The excitation wavelengths (λ_{ex}) for QY measurement were 540 nm for **RE1** and **RE4**, 570 nm for **RE3**, and 600 nm for **RE2**, **RE5-RE7**, respectively. The absorbance values of all dyes were below 0.08.

Cells imaging experiment

Cell culture

HeLa cells and L929 cells were grown in medium RPMI 1640 supplemented with 10% FBS (fetal bovine serum) under atmosphere of 5% CO_2 and 95% air at 37 °C. The cells were seeded at a density of 1×10^6 cells per mL for imaging on 24-well plates and allowed to adhere for 12 h.

Live-cell imagings with RE1, RE3, RE4 and DAPI

Before the experiments, the cells were incubated with 5 μg mL^{-1} DAPI for 15 h firstly then washed with phosphate-buffered saline (PBS) buffer. Subsequently, dye **RE1** (2 μM) was added to the medium (containing 0.1% DMSO as a cosolvent) over 30 min at 37 °C, and finally washed with PBS three times. The cell imaging of dyes **RE3** and **RE4** followed the same operation steps. The Cell imaging was performed on a FV-1000 Olympus confocal fluorescence microscopy. DAPI was excited at 405 nm and fluorescence in the green channel (425 nm-475 nm) was acquired. Dyes **RE1**, **RE3** and **RE4** were excited at 635 nm and fluorescence in the NIR channel (650 nm-750 nm for dyes) was acquired.

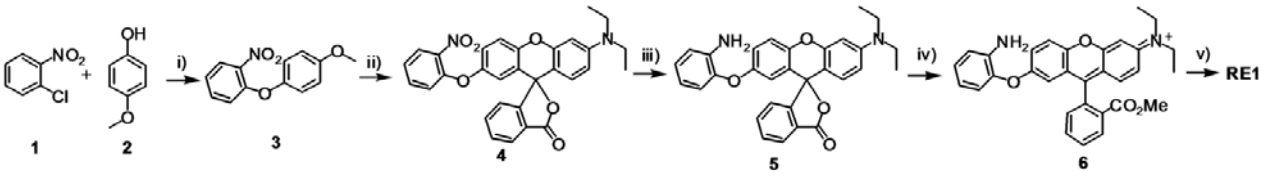
Subcellular localization experiment

To observe the subcellular distributions of **RE1**, **RE3**, and **RE4**, L929 cells were treated with commercial subcellular organelle markers, namely, LysoTracker Green DND-26 (200 nM), ER-Tracker Green (500 nM), MitoTracker Green (200 nM), and Golgi-Tracker Green (200 nM) for 30 min, respectively, then treated with a dye for additional 30 min. The media was removed and the cells were rinsed three times with PBS buffer (pH 7.4). Fluorescence images were collected by sequentially line scanning with an Olympus FV1000 confocal laser-scanning microscope. Commercial subcellular organelle markers were excited at 488 nm and their green emission were collected in the range of 510-540 nm for Lyso-TG, 510-550 nm for ER-TG, 510-520 nm for both Golgi-TG and Mito-TG, respectively. Dyes **RE1**, **RE3**, and **RE4** were excited at 635 nm and NIR emissions were collected in the range of 656-756 nm.

Cytotoxicity assays

The cytotoxicity studies of dyes **RE1, RE3** and **RE4** were examined by MTT ([3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium) assay. L929 cells were cultured in a 96-well plate for 12 h, and then the cell medium was exchanged with fresh medium, and the dyes were then added to achieve final concentrations at 50, 100, 150, 200, 250 nM. After a 24 h incubation at 37 °C in 5% CO2, the cell medium were exchanged with fresh medium (100 uL), and then 20 uL of the MTT (5 mg/mL) solution was added to each well. After incubation at 37 °C in 5% CO2 for 4 h, 100 μL of DMSO was added after the culture medium had been discarded. The absorbance for all the wells with cell medium was measured at 570 nm, and the cell viability of untreated cells was set to 100% as a reference.

Synthesis of dyes RE1-RE7 and probe RE1-Cu



Scheme S1. Synthesis of **RE1**. Reagents and conditions: (i) DMF, Na_2CO_3, 100 °C, 85%. (ii) 2-(4-(*N,N*-diethylamino)-2-hydroxybenzoyl)benzoic acid, CH_3SO_3H, 85 °C, 76%. (iii) $SnCl_2$, EtOH, 85 °C, 76%. (iv) MeOH, H_2SO_4 (98 wt%), reflux, 90%. (v) Na_2CO_3, EtOAc, 50 °C, 52%.

Preparation of 3. To a suspension of *o*-chloronitro-benzene **1** (3.746 g, 23.77 mmol) and Na_2CO_3 (2.646 g, 24.9 mmol) in anhydrous DMF (25 mL) under argon atmosphere was added *p*-hydroxyanisole **2** (2.517 g, 20.3 mmol). After being stirred for 14 h at 100 °C, the reaction mixture was poured into water (100 mL) and extracted with dichloromethane (30 mL × 3). Removal of solvent under reduced pressure and purification by silica gel column chromatography with ethyl acetate/petroleum ether (20:1) as the eluent generated **3** as a white solid (4.231 g) in 85% yield; mp. 79-80 °C; HRMS: m/z [M + H$^+$] = 246.0766; Calcd for [$C_{13}H_{11}NO_4$ + H$^+$]: 246.0761; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.81 (s, 3H, OCH_3), 6.91 (m, 3H, Ar-H), 7.01 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.12 (td, 1H, *J* = 7.6 Hz, 1.2 Hz, Ar-H), 7.44 (td, 1H, *J* = 8.8 Hz, 1.6 Hz, Ar-H), 7.91 (dd, 1H, *J* = 8.0 Hz, 1.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 55.9, 115.4, 119.3, 121.3, 122.6, 125.9, 134.3, 141.1, 149.0, 152.2, 157.1.

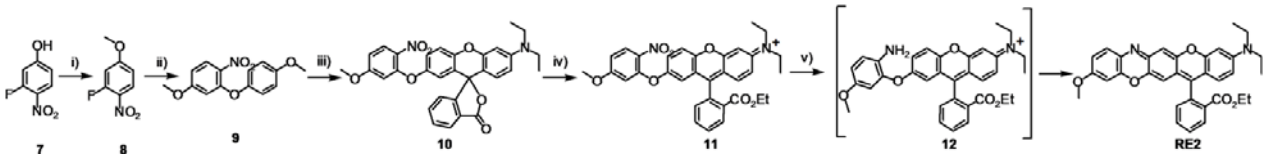
Preparation of 4. To a solution of **3** (2.452 g, 10 mmol) in CH_3SO_3H (10 mL) under argon atmosphere was added 2-(4-*N*,*N*-diethylamino-2-hydroxybenzoyl)-benzoic acid (3.227 g, 10.3 mmol). After being stirred for 3 d at 85 °C, the red reaction mixture was poured onto ice (100 g) with vigorous stirring. The aqueous phase was adjusted to ca. pH = 7.0 with Na_2CO_3, and then extracted with dichloromethane (30 mL × 3). Removal of solvent under reduced pressure and purification by column chromatography (SiO_2) with ethyl acetate/petroleum ether (1:3) as the eluent generated **4** as a pink powder (3.868 g) in 76% yield; mp. 215-216 °C; HRMS: m/z [M + H$^+$] = 509.1736; Calcd for [$C_{30}H_{24}N_2O_6$ + H$^+$]: 509.1707; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.18 (t, 6 H, *J* = 7.2 Hz, CH_3), 3.36 (q, 4H, *J* = 7.2 Hz, CH_2), 6.38 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz, Ar-H), 6.47 (d, 1H, *J* = 2.4 Hz, Ar-H), 6.54 (d, 1H, *J* = 2.4 Hz, Ar-H), 6.57 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.85 (dd, 1H, *J* = 8.4 Hz, 1.2 Hz, Ar-H), 7.06 (dd, 1H, *J* = 9.2 Hz, 2.8 Hz, Ar-H), 7.11 (td, 1H, *J* = 7.8 Hz, 0.8 Hz, Ar-H), 7.21 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.29 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.42 (td, 1H, *J* = 8.0 Hz, 1.6 Hz, Ar-H), 7.59 (td, 1H, *J* = 7.6 Hz, 0.8 Hz, Ar-H), 7.65 (td, 1H, *J* = 8.8 Hz, 0.8 Hz, Ar-H), 7.87 (dd, 1H, *J* = 8.0 Hz, 1.6 Hz, Ar-H), 7.97 (d, 1H, *J* = 7.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 13.4, 45.1, 83.9, 97.6, 104.4, 108.7, 118.8, 118.9, 119.0, 120.9, 122.2, 122.6, 123.9, 124.9, 125.5, 126.6, 128.6, 129.6, 134.03, 134.85, 140.2, 148.6, 149.3, 149.7, 150.7, 152.2, 152.4, 168.8.

Preparation of 5. A mixture of of **4** (1.526 g, 3 mmol) and $SnCl_2.2H_2O$ (6.311 g, 27.9 mmol) in ethanol (50 ml) was stirred for 10 h at 85 °C. After being cooled to room temperature, the reaction mixture was poured into water (30 mL) under vigorous stirring. The pH was adjusted to ca. 7.0 with Na_2CO_3 and the solid was filtered and washed with dichloromethane. The aqueous filtrate was extracted with dichloromethane (30 mL × 3). After removal of the solvent, the residue was purified by column chromatography (SiO_2) with ethyl acetate/petroleum ether (2:5) as the eluent generated **5** as a pink powder (1.091 g) in 76% yield; mp. 199-210 °C; HRMS: m/z [M + 2H$^+$]/2 = 240.1038, [M + H$^+$] = 479.1979; Calcd for[$C_{30}H_{26}N_2O_4$ + 2H$^+$]/2 = 240.1019; [$C_{30}H_{26}N_2O_4$ + H$^+$] = 479.1965; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.18 (t, 6H, *J* = 7.2 Hz, CH_3), 3.36 (q, 4H, *J* = 7.2 Hz, CH_2), 3.74 (bs, 2H, NH_2), 6.37 (dd, 1H, *J* = 8.9 Hz, 2.4 Hz, Ar-H), 6.46 (d, 1H, *J* = 1.2 Hz, Ar-H), 6.49 (d, 1H, *J* = 2.8 Hz, Ar-H), 6.58 (d, 1H, *J* = 9.2 Hz, Ar-H), 6.62 (td, 1H, *J* = 7.2 Hz, 1.6 Hz, Ar-H), 6.68 (dd, 1H, *J* = 8.0 Hz, 2.4 Hz, Ar-H), 6.75 (dd, 1H, *J* = 8.0 Hz, 1.6 Hz, Ar-H), 6.90 (td, 1H, *J* = 7.6 Hz, 1.6 Hz, Ar-H), 7.15 (dd, 1H, *J* = 8.4 Hz, 2.8 Hz, Ar-H), 7.19 (d, 1H, *J* = 9.2 Hz, Ar-H), 7.23 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.60 (td, 1H, *J* = 7.6 Hz, 1.2 Hz, Ar-H), 7.67 (td, 1H, *J* = 7.6 Hz, 1.2 Hz, Ar-H), 8.00 (d, 1H, *J* = 7.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 12.8, 44.9, 84.3, 98.0, 104.9, 108.8, 116.7, 117.2, 118.4, 118.9, 119.0, 120.1, 120.9, 124.3, 124.8, 125.3, 127.4, 129.2, 129.9, 135.2, 138.4, 143.9, 149.9, 150.0, 152.6, 153.2, 153.3, 169.8.

Preparation of 6. To a solution of concentrated sulfuric acid (98 wt%, 6.0 mL) in methanol (30 mL) at 25 °C was added **5** (0.402 g, 0.840 mmol). After refluxing for 24 h, the reaction mixture was poured onto ice (100 g) with vigorous stirring. The pH of the aqueous phase was

adjusted to ca. 7.0 with Na_2CO_3. Then, solid NaCl (5 g) was added and stirred for 30 min at room temperature. The aqueous mixture was extracted with dichloromethane (30 mL × 3). After removal of the solvent, the residue was purified by column chromatography (SiO_2) with dichloromethane/methanol (10:1) as the eluent generated **6** as a red powder (0.375 g) in 90% yield; mp. 139-140 °C; HRMS: m/z [M - Cl^-] = 493.2129; Calcd for $C_{31}H_{29}N_2O_4^+$ = 493.2127; ^{1}H NMR (400 MHz, CD_3OD, ppm): δ 1.05 (t, 3H, *J* = 7.2 Hz, CH_3), 1.14 (t, 3H, *J* = 7.2 Hz, CH_3), 3.38 (s, 3H, CH_3), 3.55-3.65 (m, 4H, CH_2), 6.58-6.60 (m, 2H, Ar-H), 6.88 (td, 1H, *J* = 7.6 Hz, 1.2 Hz, Ar-H), 6.93 (td, 1H, *J* = 7.6 Hz, 1.6 Hz, Ar-H), 6.98 (d, 1H, *J* = 2.0 Hz, Ar-H), 7.07 (d, 1H, *J* = 9.6 Hz, Ar-H), 7.10 (dd, 1H, *J* = 7.6 Hz, 1.6 Hz, Ar-H), 7.15 (dd, 1H, *J* = 9.6 Hz, 2.0 Hz, Ar-H), 7.24 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.49 (dd, 1H, *J* = 7.6 Hz, 1.6 Hz, Ar-H), 7.53 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.61 (t, 1H, *J* = 7.2 Hz, Ar-H), 7.69 (d, 1H, *J* = 9.2 Hz, Ar-H), 8.01 (d, 1H, *J* = 7.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 13.4, 14.6, 48.2, 53.2, 54.9, 96.8, 116.2, 118.7, 119.0, 119.5, 119.6, 122.4, 125.0, 125.1, 128.4, 129.5, 130.5, 130.7, 131.3, 132.5, 132.8, 133.4, 146.4, 149.7, 153.7, 158.2, 159.1, 160.0, 164.9.

Preparation of dye RE1 *via* the intramolecular S_NAr^H reaction. To a red-coloured solution of compound **6** (0.201 g, 0.38 mmol) in ethyl acetate (20 mL) was added Na_2CO_3 (0.201 g, 1.90 mmol). After stirring for 20 min at 50 °C, the blue-coloured solution was poured into ice water (100 mL) under vigorous stirring. The water phase was extracted with dichloromethane (30 mL × 3). After removal of the solvent, the residue was purified by column chromatography (SiO_2) with dichloromethane/methanol (20:1) as the eluent generated the product **RE1** as a blue powder (97 mg) in 52% yield; mp. 259- 260°C; HRMS: m/z [M + H^+] = 491.1966; Calcd for [$C_{31}H_{26}N_2O_4$ + H^+] = 491.1965; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.18 (t, 6H, *J* = 7.2 Hz, CH_3), 3.36 (q, 4H, *J* = 7.2 Hz, CH_2), 3.68 (s, 3H, CH_3), 5.60 (s, 1H, Ar-H), 6.23 (s, 1H, Ar-H), 6.29 (dd, 1H, *J* = 9.2 Hz, 2.4 Hz, Ar-H), 6.40 (d, 1H, *J* = 2.0 Hz, Ar-H), 6.49 (d, 1H, *J* = 9.2 Hz, Ar-H), 6.57 (d, 1H, *J* = 7.6 Hz, Ar-H), 6.81 (td, 1H, *J* = 8.4 Hz, 1.6 Hz, Ar-H), 6.90 (td, 1H, *J* = 7.6 Hz, 0.8 Hz, Ar-H), 7.05 (dd, 1H, *J* = 7.6 Hz, 1.6 Hz, Ar-H), 7.25 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.55 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.66 (t, 1H, *J* = 7.6 Hz, Ar-H), 8.14 (d, 1H, *J* = 7.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 12.7, 45.0, 52.6, 97.5, 103.2, 103.5, 109.0, 112.6, 114.6, 120.2, 124.3, 125.8, 126.0, 127.2, 129.0, 131.1, 131.3, 131.4, 133.0, 136.2, 137.1, 145.0, 145.6, 150.0, 154.7, 156.6, 166.6.



Scheme S2. Synthesis of dye **RE2.** Reagents and conditions: (i) Dimethyl sulfate, K_2CO_3, acetonitrile, room temperature, 89%. (ii) *p*-hydroxyanisole, DMF, Na_2CO_3, 100 °C, 82%. (iii) 2-(4-(*N*,*N*-diethylamino)-2-hydroxybenzoyl)benzoic acid, CH_3SO_3H, 85 °C, 67%. (iv) EtOH, H_2SO_4 (98 wt%), reflux, NaCl, 88%. (v) $SnCl_2$, EtOH, 85 °C, Na_2CO_3, 82%.

Preparation of 3-fluoro-4-nitroanisole 8[6]. Dimethyl sulfate (6.698 g, 53.1 mmol) was dissolved in acetonitrile (20 mL) and added dropwise to the suspension of 3-fluoro-4-nitrophenol **7** (4.162 g, 26.5 mmol) and K_2CO_3 (7.397 g, 53.5 mmol) in acetonitrile (20 mL) at room temperature. After stirred overnight, the suspension was poured into mixture of water (200 mL) and extracted with ethyl acetate (50 mL × 3). The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (SiO_2) with petroleum ether/dichloromethane (5:1) as the eluent generated the product 3-fluoro-4-nitroanisole **8** as white solid (4.032 g) in 89% yield.

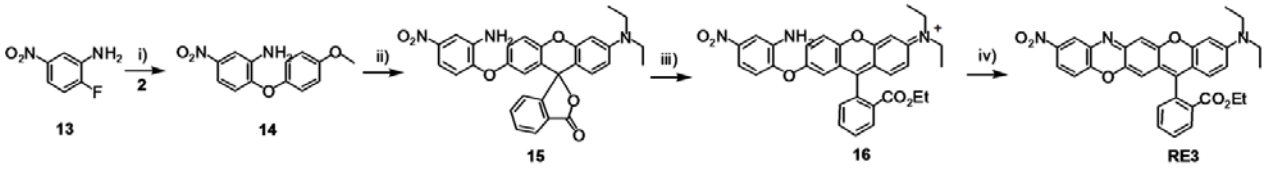
Preparation of 9. The reaction of 3-fluoro-4-nitroanisole **8** (4.231 g, 24.7 mmol), *p*-hydroxyanisole **2** (4.591 g, 37.0 mmol) and Na_2CO_3 (4.251 g, 40.1 mmol) yielded compound **9** as a yellow solid (5.571 g) in 82% yield by the method for the preparation of **3**; mp. 75-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.75 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.32 (d, 1H, *J* = 2.8 Hz, Ar-H), 6.60 (dd, 1H, *J* = 9.2 Hz, 2.8 Hz, Ar-H), 6.91 (d, 2H, *J* = 9.0 Hz, Ar-H), 7.01 (d, 2H, *J* = 9.0 Hz, Ar-H), 8.03 (d, 1H, *J* = 9.2 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 54.8, 55.0, 103.2, 106.7, 114.3, 120.3, 127.3, 132.8, 147.4, 153.7, 156.0, 163.5.

Preparation of 10. Compound **10** was synthesized as a pink powder (6.591 g) in 67% yield by the reaction of compound **9** (5.033 g, 18.3 mmol) with 2-(4-*N*,*N*-diethylamino-2-hydroxybenzoyl)benzoic acid (8.597 g, 27.4 mol) by the method for the preparation of **4**; m.p. 151-153 °C; HRMS: m/z [M + H^+] = 539.1813; Calcd for $C_{31}H_{27}N_2O_7^+$: 539.1818; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.17 (t, 6H, *J* = 7.0 Hz, CH_3), 3.36 (q, 4H, *J* = 7.0 Hz, CH_2), 3.73 (s, 3H, OCH_3), 6.26 (d, 1H, *J* = 2.4 Hz, Ar-H), 6.38 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz, Ar-H), 6.46 (d, 1H, *J* = 2.4 Hz,

Ar-H), 6.55 (d, 1H, *J* = 2.4 Hz, Ar-H), 6.57 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.59 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz, Ar-H), 7.07 (dd, 1H, *J* = 9.2 Hz, 2.4 Hz, Ar-H), 7.21 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.30 (d, 1H, *J* = 9.2 Hz, Ar-H), 7.60 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.68 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.98 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.99 (d, 1H, *J* = 9.2 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 12.6, 44.6, 56.1, 83.7, 97.7, 103.9, 104.4, 108.7, 108.8, 118.9, 119.1, 121.2, 122.4, 124.1, 125.1, 126.9, 128.3, 128.9, 129.9, 133.7, 135.2, 149.0, 149.9, 150.0, 152.8, 152.9, 153.8, 164.6, 169.5.

Preparation of 11. To a solution of concentrated sulfuric acid (98 wt%, 6.0 mL) in ethanol (30 mL) at room temperature was added **10** (6.113 g, 11.35 mmol). After refluxing for 24 h, the reaction mixture was poured onto ice (150 g) with vigorous stirring. The pH of the aqueous phase was adjusted to ca. 7.0 with Na_2CO_3. Then, solid NaCl (5 g) was added and stirred for 30 min at room temperature. The aqueous mixture was extracted with dichloromethane (50 mL × 3). After removal of the solvent, the residue was purified by column chromatography (SiO_2) using dichloromethane/ethanol (10:1) as the eluent generated **11** as a red powder (6.211 g) in 88% yield; m.p. 130-132 °C; HRMS: m/z [M] = 567.2139; Calcd for $C_{33}H_{31}N_2O_7^+$ = 567.2131; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.11 (t, 3H, *J* = 7.0 Hz, CH_3), 1.19 (t, 3H, *J* = 7.0 Hz, from solvent EtOH), 1.35 (t, 3H, *J* = 7.0 Hz, CH_3), 1.40 (t, 3H, *J* = 7.0 Hz, CH_3), 3.79 (s, 3H, OCH_3), 3.80 (q, 2H, *J* = 7.0 Hz, CH_2), 3.88 (q, 2H, *J* = 7.0 Hz, CH_2), 4.03 (q, 4H, *J* = 7.0 Hz, CH_2, overlapped with solvent EtOH), 6.38-6.40 (m, 1H, Ar-H), 6.72 (dd, 1H, *J* = 9.2 Hz, 2.4 Hz, Ar-H), 6.70-6.85 (m, 1H, Ar-H), 7.00 (s, 1H, Ar-H), 7.28 (dd, 1H, *J* = 9.2 Hz, 4.8 Hz, Ar-H), 7.36 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.43-7.45 (m, 2H, Ar-H), 7.72 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.78 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.82 (d, 1H, *J* = 9.2 Hz, Ar-H), 8.03 (dd, 1H, *J* = 9.2 Hz, 4.8 Hz, Ar-H), 8.26 (dd, 1H, *J* = 7.6 Hz, 3.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 12.4, 13.7 (from solvent EtOH), 13.8, 15.3, 47.7, 56.5, 61.9 (from solvent EtOH), 62.9, 96.7, 106.7, 110.3, 116.3, 119.2, 119.9, 120.0, 122.7, 127.1, 128.5, 130.0, 130.4, 131.0, 131.5, 132.7, 132.8, 133.5, 134.3, 150.0, 151.4, 153.4, 158.8, 159.4, 159.6, 164.8, 164.9.

One step preparation of dye RE2 via the reduction of 11 with $SnCl_2.2H_2O$, followed by intramolecular S_NAr^H reaction of ester 12. The reaction of **11** (5.801 g, 9.6 mmol) and $SnCl_2.2H_2O$ (17.368 g, 7.7 mmol) in ethanol (70 ml) for 10 h at 85 °C yielded compound **12** by the method of preparing **5**. However, **12** was gradually converted to the final product **RE2** during the neutralization by Na_2CO_3. The pure product of **12** cannot be obtained when we try to purify it by silica gel column chromatography. **RE2** was obtained as blue solid in 82% yield from the one pot synthesis; m.p. 211-213 °C; HRMS: m/z [M + H$^+$] = 535.2239; Calcd for $C_{33}H_{31}N_2O_5^+$ = 535.2233; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.04 (t, 3H, *J* = 7.2 Hz, CH_3), 1.18 (t, 6H, *J* = 7.2 Hz, CH_3), 3.36 (q, 4H, *J* = 7.2 Hz, CH_2), 3.72 (s, 3H, OCH_3), 4.10 (q, 2H, *J* = 7.2 Hz, CH_2), 5.60 (s, 1H, Ar-H), 6.19-6.21 (m, 2H, Ar-H), 6.27 (dd, 1H, *J* = 8.8 Hz, 1.6 Hz, Ar-H), 6.38 (d, 1H, *J* = 1.6 Hz, Ar-H), 6.40-6.49 (m, 2H, Ar-H), 7.01 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.25 (d, 1H, *J* = 7.6 Hz, 1.0 Hz, Ar-H), 7.55 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.65 (t, 1H, *J* = 7.6 Hz, Ar-H), 8.14 (d, 1H, *J* = 7.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 12.8, 13.8, 44.8, 55.6, 61.2, 97.3, 100.7, 103.0, 103.2, 108.6, 109.4, 112.6, 120.3, 126.2, 126.9, 128.7, 130.8, 131.1, 131.5, 132.6, 135.8, 136.6, 136.7, 144.4, 145.9, 149.7, 152.4, 154.0, 155.8, 158.1, 166.4.



Scheme S3. Synthesis of dye **RE3**. Reagents and conditions: (i) *p*-hydroxyanisole, DMF, Na_2CO_3, 80 °C, 86%. (ii) 2-(4-(*N,N*-diethylamino)-2-hydroxybenzoyl)benzoic acid, CH_3SO_3H, 85 °C, 56.8%. (iii) EtOH, H_2SO_4 (98 wt%), reflux, 87%. (iv) Na_2CO_3, EtOAc, 50 °C, 76%.

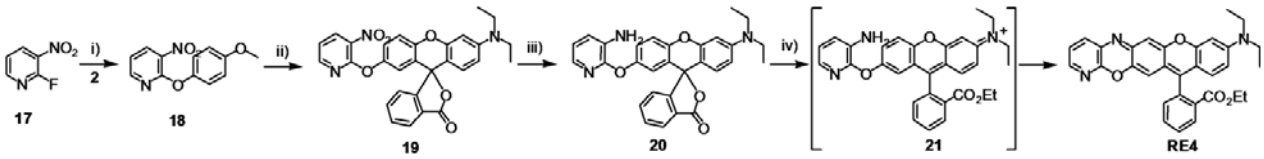
Preparation of 14. By the method for preparing **3**, the yellow compound **14** (4.470 g) was obtained in 86.0% yield by reaction of 2-fluoro-5-nitroaniline **13** (3.12 g, 20 mmol), 4-methoxyphenol (2.73 g, 22 mmol) and K_2CO_3 (3.0 g, 22 mmol) in DMF (20 mL) at 80 °C for 48 h under argon; m.p. 76-78 °C; HRMS: m/z [M + H$^+$] = 261.0890, Calcd for [$C_{13}H_{12}N_2O_4$ + H$^+$] = 261.0875; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.83 (s, 3H, CH_3), 4.23 (s, 2H, NH_2), 6.62 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.93 (d, 2H, *J* = 9.2 Hz, Ar-H), 7.01 (d, 2H, *J* = 9.2 Hz, Ar-H), 7.51 (dd, 1H, *J* = 8.8 Hz, 2.8 Hz, Ar-H), 7.64 (d, 1H, *J* = 2.8 Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 55.8, 110.1, 114.3, 114.6, 115.3, 121.3, 137.6, 143.2, 148.3, 151.1, 157.0.

Preparation of 15. Following the procedures for the preparation of **4**, the reaction of **13** (2.610 g, 10 mmol) and 2-(4-(diethylamino)-2-hydroxybenzoyl)benzoic acid (3.130 g, 10 mmol) in $MeSO_3H$ (10 mL) produced **15** (2.940 g) as a pink solid in 56.8% yield after a silica gel

chromatography (dichloromethane:ethanol = 50:1) purification; m.p. 124-126 °C, HRMS: m/z [M – Cl^-] = 524.1825, calcd for [$C_{30}H_{26}N_3O_6^+$] = 524.1822; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.18 (t, 6H, *J* = 7.0 Hz, CH_3), 3.37 (q, 4H, *J* = 7.0 Hz, CH_2), 4.14 (s, 2H, NH_2), 6.38 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz, Ar-H), 6.47 (d, 1H, *J* = 2.4 Hz, Ar-H), 6.53 (d, 1H, *J* = 2.8 Hz, Ar-H), 6.53 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.58 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.06 (dd, 1H, *J* = 8.8 Hz, 2.8 Hz, Ar-H), 7.23 (d, 1H, 7.6 Hz, Ar-H), 7.30 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.46 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz, Ar-H), 7.58 (d, 1H, *J* = 2.4 Hz, Ar-H), 7.61 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.68 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.99 (d, 1H, *J* = 7.6 Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 12.6, 44.6, 83.8, 97.6, 104.3, 108.8, 110.3, 114.2, 114.9, 118.9, 119.1, 121.3, 122.3, 124.0, 125.2, 127.0, 128.9, 129.9, 135.1, 137.7, 143.5, 149.0, 149.9, 145.0, 152.8, 152.9, 169.5.

Preparation of 16. Following the procedures for the preparation of **11**, the black solid of **16** (2.010 g) was obtained in 87% yield by the reaction of **15** (2.10 g, 4 mmol) and ethanol (20 mL) in the presence of concentrated H_2SO_4 (2 mL); m.p. 98-100 °C; HRMS: m/z [M - Cl^-] = 552.2146, calcd for [$C_{32}H_{30}N_3O_6^+$] = 552.2129; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.13 (t, 3H, *J* = 7.2 Hz, CH_3), 1.19 (t, 3H, *J* = 7.2 Hz, from solvent EtOH), 1.36 (t, 3H, *J* = 7.2 Hz, CH_3), 1.43 (t, 3H, *J* = 7.2 Hz, CH_3), 3.81 (q, 2H, *J* = 7.2 Hz, CH_2), 3.87 (q, 2H, *J* = 7.2 Hz, CH_2), 4.03 (q, 2H, *J* = 7.2 Hz, CH_2), 4.07 (q, 2H, *J* = 7.2 Hz, from solvent EtOH), 4.65 (s, 2H, NH_2), 6.61 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.80 (d, 1H, *J* = 2.8 Hz, Ar-H), 7.02 (d, 1H, *J* = 2.4 Hz, Ar-H), 7.29 (d, 1H, *J* = 9.2 Hz, Ar-H), 7.35 (dd, 1H, *J* = 8.8 Hz, 2.8 Hz, Ar-H), 7.37 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.39 (dd, 1H, *J* = 9.2 Hz, 2.4 Hz, Ar-H), 7.51 (dd, 1H, *J* = 9.2 Hz, 2.4 Hz, Ar-H), 7.63 (d, 1H, *J* = 2.4 Hz, Ar-H), 7.72 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.82 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.83 (d, 1H, *J* = 9.2 Hz, Ar-H), 8.28 (d, 1H, *J* = 7.6 Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 12.4, 13.7 (from solvent EtOH), 13.9, 15.3, 47.6, 47.7, 61.8 (from solvent EtOH), 62.9, 96.7, 110.9, 112.6, 116.7, 116.8, 119.1, 119.8, 120.0, 122.7, 128.0, 129.9, 130.4, 131.0, 131.6, 132.6, 132.7, 133.6, 139.6, 144.6, 147.6, 150.1, 152.9, 158.7, 159.4, 159.8, 164.9.

Preparation of RE3. The dye **RE3** (1.26 g) was obtained as blue powder in 76% yield by the intramolecular S_NAr^H reaction of ester **16** (1.660 g, 3 mmol) in acetic ether (50 mL) at 50 °C for 2 h following the preparation of the dye **RE1**; m.p. 253-255 °C. HRMS: m/z [M + H^+] = 550.1981, calcd for [$C_{32}H_{27}N_3O_6$ + H^+] = 550.1978; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.04 (t, 3H, *J* = 7.2 Hz, CH_3), 1.20 (t, 6H, *J* = 7.2 Hz, CH_3), 3.40 (q, 4H, *J* = 7.2 Hz, CH_2), 4.14-4.06 (m, 2H, CH_2), 5.71 (s, 1H, Ar-H), 6.24 (s, 1H, Ar-H), 6.36 (dd, 1H, *J* = 9.2, 2.4, Ar-H), 6.43 (d, 1H, *J* = 2.4 Hz, Ar-H), 6.55 (d, 1H, *J* = 9.2 Hz, Ar-H), 6.56 (d, 1H, *J* = 9.2 Hz, Ar-H), 7.28 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.60 (td, 1H, *J* = 7.6 Hz, 1.2 Hz, Ar-H), 7.64 (dd, 1H, *J* = 8.7 Hz, 2.4 Hz, Ar-H), 7.69 (td, 1H, *J* = 7.6 Hz, 1.2 Hz, Ar-H), 7.80 (d, 1H, *J* = 2.4 Hz, Ar-H), 8.18 (dd, 1H, *J* = 7.6 Hz, 1.2 Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 13.4, 14.4, 45.3, 61.5, 97.1, 103.1, 104.6, 109.4, 112.2, 114.0, 119.1, 120.0, 120.4, 127.3, 128.7, 130.4, 130.8, 131.0, 132.2, 134.7, 137.5, 141.1, 143.5, 144.1, 149.9, 150.2, 153.9, 154.9, 156.5, 165.2.



Scheme S4. Synthesis of dye **RE4.** Reagents and conditions: (i) *p*-hydroxyanisole, DMF, Na_2CO_3, 100 °C, 85%. (ii) 2-(4-(*N,N*-diethylamino)-2-hydroxybenzoyl)benzoic acid, CH_3SO_3H, 85 °C, 20%. (iii) $NaBH_4$, $Ni(OAc)_2{\cdot}4H_2O$, MeOH and THF, room temperature, 20%. (iv) EtOH, H_2SO_4 (98 wt%), reflux, Na_2CO_3, 55%.

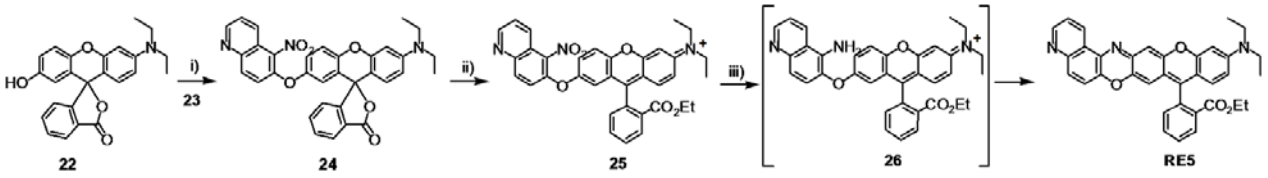
Preparation of 18. The reaction of 2-chloro-3-notropyridine **17** (3.746 g, 23.6 mmol) and *p*-hydroxyanisole **2** (4.781 g, 38.5 mmol) yielded compound **18** as a white solid (4.939 g) in 85% yield by the method of preparation of **3**; m.p. 115-116 °C; HRMS: m/z [M + H^+] = 247.0729; Calcd for [$C_{12}H_{10}N_2O_4$ + H^+] = 247.0719; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.82 (s, 3H, OCH_3), 6.95 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.12 (dd, 1H, *J* = 8.0 Hz, 2.8 Hz, Py-H), 7.11 (d, 2H, *J* = 8.4 Hz, Ar-H), 8.33-8.35 (m, 2H, Py-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 55.9, 115.0, 118.3, 123.0, 134.8, 135.7, 146.2, 152.1, 156.6, 157.6.

Preparation of 19. Compound **19** was synthesized as a pink powder (0.509 g) in 20% yield by the reaction of compound **18** (1.231 g, 5 mmol) with 2-(4-*N*,*N*-diethylamino-2-hydroxy-benzoyl) benzoic acid (1.880 g, 6 mmol) by the method of preparing **4**; m.p. 209-210 °C; HRMS: m/z [M + H^+] = 510.1678; Calcd for [$C_{29}H_{23}N_3O_6$ + H^+] = 510.1665; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.18 (t, 6H, *J* = 7.2 Hz, CH_3), 3.36 (q, 4H, *J* = 7.2 Hz, CH_2), 6.37 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz, Ar-H), 6.47 (d, 1H, *J* = 2.4 Hz, Ar-H), 6.57 (d, 1H, *J* = 9.2 Hz, Ar-H), 6.59 (d, 1H, *J*

= 2.8 Hz, Ar-H), 7.10 (dd, 1H, *J* = 8.0 Hz, 4.8 Hz, Py-H), 7.20 (dd, 1H, *J* = 9.2 Hz, 2.8 Hz, Ar-H), 7.23 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.33 (d, 1H, *J* = 9.2 Hz, Ar-H), 7.60 (td, 1H, *J* = 7.6 Hz, 0.8 Hz, Ar-H), 7.66 (td, 1H, *J* = 7.6 Hz, 0.8 Hz, Ar-H), 7.98 (d, 1H, *J* = 7.6 Hz, Ar-H), 8.24 (dd, 1H, *J* = 4.8 Hz, 1.6 Hz, Py-H) 8.30 (dd, 1H, *J* = 8.0 Hz, 1.6 Hz, Py-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 13.5, 45.2, 83.9, 98.0, 104.9, 108.8, 118.1, 118.3, 120.6, 124.0, 124.2, 124.9, 126.9, 128.6, 129.5, 134.2, 134.7, 135.1, 147.3, 149.1, 149.5, 151.2, 152.5, 152.6, 155.2, 168.8.

Preparation of 20. To a solution of $NaBH_4$ (0.085 g, 2.25 mmol) in MeOH (10 mL) was added $Ni(OAc)_2{\cdot}4H_2O$ (0.187 g, 0.75 mmol) in one portion. After stirring for 15 min at room temperature, a THF (10 mL) solution of compound **19** (0.381 g, 0.75 mmol) was added. After stirring for 30 min, more $NaBH_4$ (0.301 g) was carefully added in three portions within 1 h. When all starting material was consumed as indicated by TLC, the reaction mixture was filtered, washed with THF and CH_2Cl_2, then evaporated to dryness. Purification the residue by silica gel column chromatography with dichloromethane/methanol (5:1) as the eluent generated the product **20** as a red powder (71 mg) in 20% yield; m.p. 89-90 °C; HRMS: m/z [M + 2H$^+$]/2 = 240.6010, [M + H$^+$] = 480.1929; Calcd for [M + 2H$^+$]/2 = 240.5996; [$C_{29}H_{25}N_3O_4$ + H$^+$] = 480.1918; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.00 (t, 6H, *J* = 6.8 Hz, CH_3), 3.19 (q, 4H, *J* = 6.8 Hz, CH_2), 6.20 (dd, 1H, *J* = 8.8 Hz, 1.8 Hz, Ar-H), 6.29 (s, 1H, Ar-H), 6.35 (d, 1H, *J* = 2.4 Hz, Ar-H), 6.37 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.59 (dd, 1H, *J* = 7.2 Hz, 4.8 Hz, Ar-H), 6.65 (d, 1H, *J* = 9.2 Hz, NH_2), 6.76 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.81 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.00 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz, Ar-H), 7.06 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.10 (d, 1H, *J* = 9.2 Hz, NH_2), 7.20 (d, 1H, *J* = 2.4 Hz, Ar-H), 7.42 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.49 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.77 (d, 1H, *J* = 7.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm):δ 13.0, 44.7, 77.6, 97.4, 104.4, 108.2, 115.6, 117.3, 118.4, 118.9, 119.1, 119.6, 121.0, 121.3, 121.4, 123.0, 123.7, 124.2, 126.4, 128.1, 129.1, 131.5, 134.0, 134.2, 134.5, 147.5, 148.6, 149.0, 150.4, 151.9, 152.2, 153.1, 168.3.

One step preparation of dye RE4 via the esterification of 20, followed by intramolecular S_NAr^H reaction of ester 21. To a solution of concentrated sulfuric acid (98 wt%, 6.0 mL) in ethanol (30 mL) was added **20** (0.041 g, 0.085 mmol). After refluxing for 24 h and cooled to room temperature, the reaction mixture was poured into the mixture of water (20 mL) and dichloromethane (20 mL) under vigorous stirring. The pH of the aqueous phase was adjusted to ca. 7.0 with Na_2CO_3. After the addition of excessive Na_2CO_3, the colour of the solution changed from red to blue gradually. Then, the aqueous mixture was extracted with dichloromethane (30 mL ×3). After removal of the solvent, purification of the blue solid residue by silica gel column chromatography using dichloromethane/ethanol (15:1) as the eluent generated **RE4** as a blue powder (23.7 mg) in 55% yield; m.p. 227-228 °C; HRMS: m/z [M + H$^+$] = 506.2080; Calcd for [$C_{31}H_{27}N_3O_4$ + H$^+$] = 506.2074; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.91 (t, 3H, *J* = 7.2 Hz, CH_3), 1.10 (t, 6H, *J* = 7.2 Hz, CH_3), 3.36 (q, 4H, *J* = 7.2 Hz, CH_2), 3.92 (q, 2H, *J* = 7.2 Hz, CH_3), 5.92 (s, 1H, Ar-H), 6.48 (d, 1H, *J* = 8.4 Hz, Ar-H), 6.50 (s, 1H, Ar-H), 6.64-6.71 (m, 3H, Ar-H), 7.10 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.12 (s, 1H, Ar-H), 7.44 (d, 1H, *J* = 4.0 Hz, Ar-H), 7.52 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.58 (t, 1H, *J* = 7.6 Hz, Ar-H), 8.07 (d, 1H, *J* = 7.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 13.2, 14.3, 45.8, 61.4, 96.5, 100.8, 108.1, 112.3, 113.3, 117.6, 120.8, 126.9, 128.9, 129.3, 129.7, 130.2, 130.7, 132.1, 133.5, 141.4, 143.8, 147.9, 150.3, 152.5, 155.5, 155.7, 164.3.



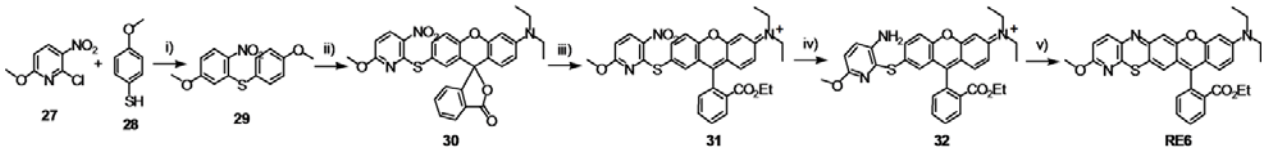
Scheme S5. Synthesis of dye **RE5**. Reagents and conditions: (i) 6-chloro-5-nitroquinoline, DMF, Na_2CO_3, 120 °C, 86%. (ii) EtOH, H_2SO_4 (98 wt%), reflux, 91%. (iii) $SnCl_2$, EtOH, 85 °C, Na_2CO_3, 56%.

Preparation of 24. The reaction of rhodol isomer **22** [2] (1.937 g, 5.00 mmol) with 6-chloro-5-nitroquinoline (1.564 g, 7.50 mmol) **23** in anhydrous DMF at 120°C for 24 h yielded compound **24** as a pink solid (2.403 g) in 86% yield using the similar method as preparation of **3**; m.p. 141-142 °C; HRMS: m/z [M + H$^+$] = 560.1822; Calcd for [$C_{33}H_{25}N_3O_6$ + H$^+$] = 560.1835; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.18 (t, 6H, *J* = 7.0 Hz, CH_3), 3.37 (q, 4H, *J* = 7.0 Hz, CH_2), 6.39 (d, 1H, *J* = 8.7 Hz, Ar-H), 6.48 (s, 1H, Ar-H), 6.58 (d, 1H, *J* = 8.7 Hz, Ar-H), 6.61 (d, 1H, *J* = 2.0 Hz, Ar-H), 7.09 (dd, 1H, *J* = 8.8 Hz, 2.0 Hz, Ar-H), 7.23 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.25 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.30 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.54 (dd, 1H, *J* = 8.8 Hz, 4.4 Hz, Ar-H), 7.59 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.68 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.97 (d, 1H, *J* = 7.6 Hz, Ar-H), 8.11 (d, 1H, *J*

= 5.6 Hz, Ar-H), 8.13 (d, 1H, *J* = 8.8 Hz, Ar-H), 8.92 (d, 1H, *J* = 4.4 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 12.6, 44.6, 83.6, 97.6, 104.3, 108.8, 119.1, 119.2, 120.5, 121.3, 121.4, 122.2, 123.7, 124.1, 125.2, 126.9, 128.9, 129.7, 129.9, 134.4, 135.2, 136.5, 143.8, 147.3, 149.2, 149.8, 150.1, 150.5, 152.7, 152.8, 169.4.

Preparation of 25. The reaction of **24** (2.132 g, 3.81 mmol) with sulfuric acid (98 wt%, 5.0 mL) in ethanol (25 mL) yielded compound **25** as a red solid (2.162g) in 91% yield using the similar method as preparation of **11**; m.p. 93-94 °C; HRMS: $[M - Cl]^+$ = 588.2168; Calcd for $[C_{35}H_{30}N3O_6]^+$ = 588.2168; ^{1}H NMR (400 MHz, $CDCl_3$, ppm, contain one molecular of ethanol): δ 1.13 (t, 3H, *J* = 7.1 Hz, CH_3), 1.18 (t, 3H, *J* = 7.1 Hz, CH_3), 1.36 (t, 3H, *J* = 7.1 Hz, CH_3), 1.43 (t, 3H, *J* = 7.1 Hz, CH_3), 3.82 (q, 2H, *J* = 7.1 Hz, CH_2), 3.89 (q, 2H, *J* = 7.1 Hz, CH_2), 4.01 (q, 2H, *J* = 7.1 Hz, CH_2), 4.08 (q, 2H, *J* = 7.1 Hz, CH_2), 6.88 (d, 1H, *J* = 2.8 Hz, Ar-H), 7.04 (d, 1H, *J* = 2.0 Hz, Ar-H), 7.29 (d, 1H, *J* = 9.6 Hz, Ar-H), 7.31 (d, 1H, *J* = 9.2 Hz, Ar-H), 7.38 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.45 (d, 1H, *J* = 9.6 Hz, Ar-H), 7.52 (dd, 1H, *J* = 9.2 Hz, 2.8 Hz, Ar-H), 7.59 (dd, 1H, *J* = 8.8 Hz, 4.4 Hz, Ar-H), 7.68 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.79 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.86 (d, 1H, *J* = 9.6 Hz, Ar-H), 8.11 (d, 1H, *J* = 8.8 Hz, Ar-H), 8.18 (d, 1H, *J* = 9.6 Hz, Ar-H), 8.24 (d, 1H, *J* = 7.6 Hz, Ar-H), 8.95 (d, 1H, *J* = 4.4 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, contain ethanol): δ 12.5, 13.7, 13.9, 15.3, 47.8, 47.8, 61.9, 62.9, 96.9, 117.2, 119.4, 120.2, 120.3, 121.1, 121.3, 122.8, 124.1, 127.3, 129.9, 129.9, 130.4, 131.0, 131.6, 132.6, 132.8, 133.6, 134.8, 137.5, 144.3, 145.8, 150.3, 151.1, 152.7, 158.9, 159.2, 159.3, 164.8.

One step preparation of dye RE5 via the reduction of 25 with $SnCl_2.2H_2O$, followed by intramolecular S_NAr^H reaction of ester 26. A mixture of of **25** (1.831 g, 2.93 mmol) and $SnCl_2.2H_2O$ (5.307 g, 23.52 mmol) in ethanol (30 ml) was stirred for 10 h at 85 °C. After being cooled to room temperature, the reaction mixture was poured into the mixture of water (50 mL) and dichloromethane (50 mL) under vigorous stirring. The pH of the aqueous phase was adjusted to ca. 7.0 with Na_2CO_3. The solid was filtered and washed with dichloromethane. Then, the aqueous filtrate was extracted with dichloromethane (50 mL × 3). Because the colour of the solution changed from red to blue gradually after the addition of excessive Na_2CO_3, the pure product of **26** cannot be obtained when we try to purify the red solid by silica gel column chromatography. So without further purification, the crude product **26** was used for preparing **RE5** by the method of preparation of dye **RE1.** Purification of the blue solid residue by silica gel column chromatography using dichloromethane/ethanol (15:1) as the eluent generated **RE5** as a blue solid (0.911 g) in 56% yield; m.p. 221-222 °C; HRMS: m/z $[M + H^+]$ = 556.2266; Calcd for $[C_{35}H_{29}N_3O_4 + H^+]$ = 556.2236; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.05 (t, 3H, *J* = 7.0 Hz, CH_3), 1.18 (t, 3H, *J* = 7.0 Hz, CH_3), 3.36 (q, 4H, *J* = 7.0 Hz, CH_2), 4.11 (q, 2H, *J* = 7.0 Hz, CH_2), 5.64 (s, 1H, Ar-H), 6.27 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.32 (s, 1H, Ar-H), 6.39 (s, 1H, Ar-H), 6.48 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.99 (d, 1H, *J* = 9.2 Hz, Ar-H), 7.29-7.32 (m, 2H, Ar-H), 7.54 (d, 1H, *J* = 9.2 Hz, Ar-H), 7.58 (t, 1H, *J* = 8.0 Hz, Ar-H), 7.67 (t, 1H, *J* = 7.6 Hz, Ar-H), 8.16 (d, 1H, *J* = 8.0 Hz, Ar-H), 8.71 (d, 1H, *J* = 2.4 Hz, Ar-H), 8.84 (d, 1H, *J* = 7.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 12.7, 13.8, 44.8, 61.2, 97.0, 103.23, 103.26, 103.29, 103.5, 109.3, 112.8, 118.6, 120.5, 120.9, 125.9, 126.0, 127.2, 128.9, 131.0, 131.2, 131.3, 131.6, 132.7, 135.5, 141.7, 145.3, 145.93, 145.94, 149.1, 150.0, 154.2, 157.0, 166.2.



Scheme S6. Synthesis of dye **RE6.** Reagents and conditions: (i) DMF, Na_2CO_3, 100 °C, 80%. (ii) 2-(4-(*N,N*-diethylamino)-2-hydroxybenzoyl)benzoic acid, CH_3SO_3H, 85 °C, 28%. (iii) EtOH, H_2SO_4 (98 wt%), reflux, NaCl, 86%. (iv) $SnCl_2$, EtOH, 85 °C, 81%. (v) Na_2CO_3, EtOAc, 50°C, 39%.

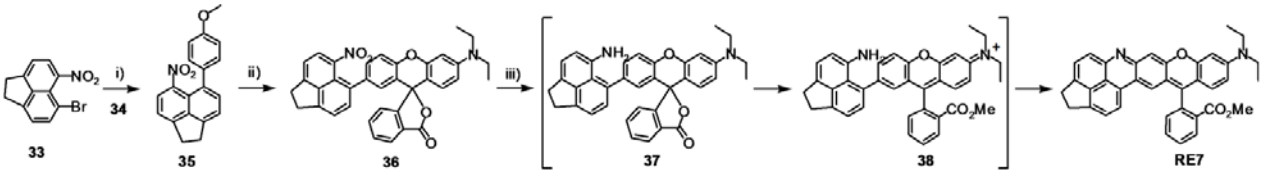
Preparation of 29. Following the procedures for the preparation of **3**, the reaction of 4-methoxybenzenethiol (1.830 g, 13.1 mmol) and 2-chloro-6-methoxy-3-nitropyridine (2.251 g, 11.9 mmol) at 100 °C for 12 h under argon atmosphere yielded **29** (2.743 g) as yellow powder in 80% yield; m.p. 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.42 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.45 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.94 (d, 2H, *J* = 11.6 Hz, Ar-H), 7.43 (d, 2H, *J* = 11.6 Hz, Ar-H), 8.36 (d, 1H, *J* = 8.8 Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 54.6, 55.8, 106.7, 109.6, 114.3, 120.4, 136.0, 137.4, 159.2, 160.2, 163.6.

Preparation of 30. Following the procedures for the preparation of **4**, the product **30** (1.070 g) was obtained in 28% yield by reaction of **29** (2.012 g, 6.88 mmol) and 2-(4-diethylamino-2-hydroxybenzoyl)benzoic acid (3.168 g, 10.11 mmol) in $MeSO_3H$ (10 mL); m.p. 174-176 °C; HRMS: m/z [M + H^+] = 556.1555; Calcd: 556.1542; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.18 (t, 6H, *J* = 7.0 Hz, CH_3), 3.37 (q, 4H, *J* = 7.0 Hz, CH_2), 3.43 (s, 3H, OCH_3), 6.39 (d, 1H, *J* = 8.4 Hz, Ar-H), 6.45 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.48 (s, 1H, Ar-H), 6.57 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.98 (d, 1H, *J* = 1.2 Hz, Ar-H), 7.19 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.33 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.52 (dd, 1H, *J* = 8.8 Hz, 1.2 Hz, Ar-H), 7.61 (t, *J* = 7.6 Hz, Ar-H), 7.68 (t, *J* = 7.6 Hz, Ar-H), 7.98 (d, 1H, *J* = 7.6 Hz, Ar-H), 8.34 (d, 1H, *J* = 8.8 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 12.6, 44.7, 54.7, 83.5, 97.7, 107.5, 108.9, 117.9, 120.7, 124.0, 125.2, 127.1, 129.0, 129.9, 135.1, 135.2, 135.4, 135.5, 136.5, 136.8, 138.4, 149.9, 152.6, 152.7, 152.8, 158.9, 164.5, 169.4.

Preparation of 31. Compound **31** was synthesized as red solid (0.799 g) in 86% yield by the reaction of compound **30** (0.832 g, 1.50 mmol) with ethanol (20 mL) in the presence of concentrated sulfuric acid (4.0 mL); m.p. 130-133 °C; HRMS: m/z [M - Cl^-] = 584.1864; Calcd: 584.1855; ^{1}H NMR (400 MHz, CD_3OD, ppm): δ 1.05 (t, 3H, *J* = 6.1 Hz, CH_3), 1.25 (t, 3H, *J* = 6.1 Hz, CH_3), 1.36 (t, 3H, *J* = 7.2 Hz, from solvent EtOH), 1.44 (t, 3H, *J* = 7.2 Hz, CH_3), 3.36 (s, 3H, OCH_3), 3.86-3.92 (m, 4H, CH_2), 4.00-4.04 (m, 4H, overlapped with EtOH), 6.51-6.58 (m, 1H, Ar-H), 7.31 (d, 1H, *J* = 2.0 Hz, Ar-H), 7.35 (d, 1H, *J* = 10.0 Hz, Ar-H), 7.42 (s, 1H, Ar-H), 7.43 (d, 1H, *J* = 9.2 Hz, Ar-H), 7.53 (d, 1H, *J* = 6.8 Hz, Ar-H), 7.76-7.79 (m, 1H, Ar-H), 7.85 (t, 1H, *J* = 7.2 Hz, Ar-H), 7.98 (d, 1H, *J* = 8.8 Hz, Ar-H), 8.05-8.08 (m, 1H, Ar-H), 8.28-8.32 (m, 2H, Ar-H). ^{13}C NMR (100MHz, CD_3OD, ppm) δ 12.6, 13.7, 14.2, 15.4 (from EtOH), 55.3, 62.7 (from EtOH), 64.8, 98.2, 108.9, 119.7, 120.6, 120.7, 123.6, 129.7, 131.6, 131.7, 132.2, 132.5, 134.0, 134.1, 134.5, 136.7, 137.9, 145.6, 155.4, 158.3, 160.5, 60.8, 165.9, 166.3.

Preparation of 32. Following the procedures for the preparation of **5**, the reduction of **31** (0.612 g, 0.99 mmol) by $SnCl_2.2H_2O$ (1.696 g, 7.89 mmol) in ethanol (30 mL) yielded the compound **32** (0. 473 g) as red powder in 81% yield; m.p. 132-135 °C; HRMS: m/z [M + H^+ - Cl^-] = 277.6111, [M - Cl^-] = 554.2104; Calcd for [M + H^+ - Cl^-] = 277.6096, [M - Cl^-] = 554.2114; ^{1}H NMR (400 MHz, CD_3OD, ppm): δ 0.99 (t, 3H, *J* = 7.2 Hz, CH_3), 1.33 (t, 3H, *J* = 7.2 Hz, CH_3), 1.41 (t, 3H, *J* = 7.2 Hz, CH_3), 3.55 (s, 3H, OCH_3), 3.85 (q, 4H, *J* = 7.2 Hz, CH_2), 3.99 (q, 2H, *J* = 7.2 Hz, CH_2), 4.89 (s, 2H, NH_2 overlapped with H_2O), 6.56 (dd, 1H, *J* = 8.8 Hz, 1.0 Hz, Ar-H), 6.82 (d, 1H, *J* = 2.0 Hz, Ar-H), 7.13 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.22 (s, 1H, Ar-H), 7.35 (d, 1H, *J* = 10.0 Hz, Ar-H), 7.37-7.41 (m, 2H, Ar-H), 7.79-7.85 (m, 3H, Ar-H), 7.88 (td, 1H, *J* = 8.8 Hz, 1.6 Hz, Ar-H), 8.27 (dd, 1H, *J* = 7.2 Hz, 1.2 Hz, Ar-H). ^{13}C NMR (100 MHz, CD_3OD, ppm) δ 12.5, 13.6, 14.0, 54.0, 62.7, 97.8, 113.5, 119.1, 120.2, 120.4, 123.4, 128.3, 129.6, 131.3, 131.4, 131.5, 132.0, 132.4, 133.8, 134.0, 134.3, 135.6, 138.7, 141.4, 153.6, 158.0, 160.2, 160.8, 161.0, 166.1.

Preparation of RE6. The dye **RE6** (0.175 g) was obtained as blue powder in 39 % yield by the intramolecular S_NAr^H reaction of **32** (0.478 g, 0.81 mmol) in acetic ether (50 mL) at 50 °C for 2 h following the preparation of the dye **RE1**. m.p. 192-194 °C; HRMS: m/z [M + H^+] = 552.1954; Calcd: 552.1957; ^{1}H NMR (400 MHz, $CDCl_3$ with 20 % CD_3OD and 1% CF_3CO_2D, ppm): δ 0.91 (s, 3H, CH_3), 1.03 (s, 6H, CH_3), 3.24 (s, 4H, CH_2), 3.54 (s, 3H, CH_3), 3.92 (s, 2H, CH_2), 5.87 (s, 1H, Ar-H), 6.12 (s, 2H, Ar-H), 6.27 (s, 2H, Ar-H), 6.43 (d, 1H, *J* = 7.5 Hz, Ar-H), 6.88 (d, 1H, *J* = 6.9 Hz, Ar-H), 7.09 (d, 1H, *J* = 5.6 Hz, Ar-H), 7.47 (s, 1H, Ar-H), 7.53 (s, 1H, Ar-H), 8.01 (d, 1H, *J* = 6.2 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 12.4, 13.5, 45.0, 53.8, 61.3, 96.7, 102.2, 108.6, 110.6, 112.8, 118.9, 119.2, 124.7, 128.4, 129.3, 130.6, 130.8, 131.1, 131.7, 132.7, 133.7, 134.3, 140.0, 143.3, 151.6, 151.8, 155.2, 157.3, 160.4, 165.8.

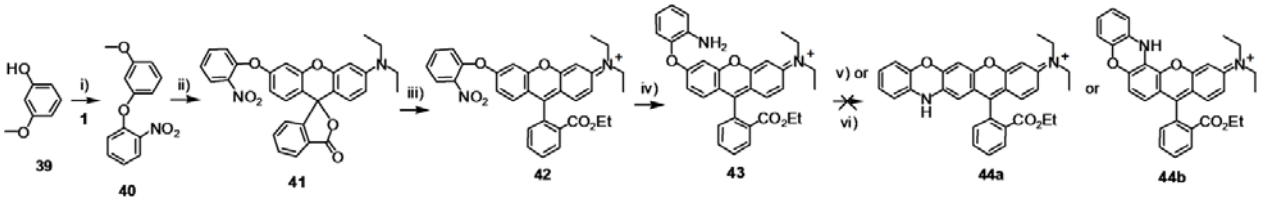


Scheme S7. Synthesis of dye **RE7.** Reagents and conditions: (i) 4-methoxyphenylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, 1,4-dioxane (30 mL) and water, 100 °C, argon atmosphere, 84%. (ii) 2-(4-(*N,N*-diethylamino)-2-hydroxybenzoyl)benzoic acid, CH_3SO_3H, 85 °C, 21%. (iii) $SnCl_2{\cdot}2H_2O$, MeOH, 90 °C, Na_2CO_3, 26%.

Preparation of 35. 4-Bromo-5-nitroacenaphthene **33** (0.557 g, 2.0 mmol), 4-methoxyphenylboronic acid **34** (0.335 g, 2.2 mmol), Na_2CO_3 (0.636 g, 6.0 mmol) were added to a solvent mixture of 1,4-dioxane (30 mL) and water (10 mL) and stirred for 30 min under argon flow. Then $Pd(PPh_3)_4$ (0.070 g, 0.06 mmol) was added and stirred for another 15 min at room temperature under argon flow. The reaction mixture was heated at 100 °C overnight. After the completion of the reaction, the dark solid was removed by filtration and washed with EtOAc (5 mL × 3). The combined filtrate was poured into water (50 mL) with vigorous stirring and the aqueous mixture was extracted with EtOAc (30 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, purification of the residue by column chromatography (SiO_2) using dichloromethane/ethanol (10:1) as the eluent generated **35** as a white solid (0.510 g) in 84% yield; m.p. 195-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.50 (m, 4H, CH_2), 3.85 (s, 3H, OCH_3), 6.94 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.25 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.30 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.47 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.54 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.85 (d, 1H, *J* = 7.2 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 30.4, 30.8, 55.3, 113.9, 118.1, 121.3, 126.0, 128.7, 133.6, 133.8, 133.9, 140.9, 145.4, 145.5, 152.3, 159.1.

Preparation of 36. Following the procedures for the preparation of **4**, the compound **36** (0.120 g) was obtained in 21% yield by the reaction of **35** (0.306 g, 1 mmol) and 2-(4-(diethylamino)-2-hydroxybenzoyl)benzoic acid (0.344 g, 1.1 mmol) in $MeSO_3H$ (5 mL) at 85 °C for 24 h; m.p. 280-282 °C; HRMS: m/z [M + H$^+$] = 569.2095; Calcd for [$C_{36}H_{28}N_2O_5$ + H$^+$] = 569.2076; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.19 (t, 6H, *J* = 7.0 Hz, CH_3), 3.37 (q, 4H, *J* = 7.0 Hz, CH_2), 3.40-3.46 (m, 4H, CH_2), 6.37 (dd, 1H, *J* = 8.8 Hz, 2.0 Hz, Ar-H), 6.50 (d, 1H, *J* = 2.0 Hz, Ar-H), 6.56 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.62 (s, 1H, Ar-H), 7.23 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.31 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.34 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.40-7.44 (m, 3H, Ar-H), 7.54 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.71 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.72 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.91 (d, 1H, *J* = 7.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 12.7, 30.4, 30.7, 44.7, 97.9, 105.5, 105.6, 108.5, 108.6, 117.3, 118.1, 121.1, 121.2, 124.7, 125.0, 126.0, 127.1, 127.2, 129.0, 129.5, 130.1, 132.7, 134.3, 135.1, 135.2, 136.2, 140.6, 145.0, 146.0, 149.7, 149.8, 151.4, 152.4, 153.1.

One step preparation of dye RE7 via the reduction of 36 with $SnCl_2.2H_2O$, followed by intramolecular S_NAr^H reaction. Following the procedures the preparation of **5**, the reduction of **36** (0.082 mg, 0.144 mmol) with $SnCl_2.2H_2O$ (0.261 g, 1.15 mmol) was carried out in methanol (20 mL) in the presence of concentrated HCl (100 μL) at 90 °C for 12 h. Then, the reaction mixture was poured onto ice and neutralized with saturated Na_2CO_3 solution. During the neutralization, the color of the solution was changed from red to blue gradually, suggested that the reduction product **37** was converted to its ester **38** during the reduction process. The ester **38** proceeded the S_NAr^H reaction to form the product **RE7** during the neutralization procedure. Finally, the dye **RE7** (0.022 g) was obtained in 26% yield after silica gel chromatography (CH_2Cl_2:MeOH = 10:1); m.p. > 300 °C; HRMS: m/z [M + H$^+$] = 551.2344; Calcd for [$C_{37}H_{30}N_2O_3$ + H$^+$] = 551.2335; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.25 (t, 6H, *J* = 7.2 Hz, CH_3), 3.16-3.21 (m, 4H, CH_2), 3.45 (q, 4H, *J* = 7.2 Hz, CH_2), 3.62 (s, 3H, CH_3), 6.56 (d, 1H, *J* = 2.0 Hz, Ar-H), 6.66 (dd, 1H, *J* = 9.6 Hz, 2.0 Hz, Ar-H), 6.92 (d, 1H, *J* = 9.6 Hz, Ar-H), 6.94 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.00 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.06 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.08 (s, 1H, Ar-H), 7.18 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.42 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.56 (s, 1H, Ar-H), 7.77 (t, 1H, *J* = 7.2 Hz, Ar-H), 7.88 (t, 1H, *J* = 7.2 Hz, Ar-H), 8.30 (d, 1H, *J* = 7.2 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 12.8, 30.6, 31.3, 45.9, 52.7, 96.7, 101.2, 112.9, 113.4, 114.1, 117.7, 118.5, 120.0, 120.6, 121.2, 121.4, 124.2, 124.3, 130.3, 130.4, 130.5, 130.9, 131.4, 132.4, 133.3, 133.9, 139.5, 140.2, 146.4, 152.2, 154.2, 154.6, 157.0, 157.8, 165.7.



Scheme S8. Control experiment of synthesis of dye **43**. Reagents and conditions: (i) DMF, Na_2CO_3, 100 °C for 14 h, 89%; (ii) 2-(4-(*N*,*N*-diethylamino)-2-hydroxybenzoyl)benzoic acid, CH_3SO_3H, 85 °C for 3 d, 40%; (iii) EtOH, H_2SO_4, refluxed for 24 h, 92%; (iv) $SnCl_2{\cdot}2H_2O$, EtOH, refluxed for 10 h, 70%; (v) Na_2CO_3, EtOAc, 50 °C for 4 h; (vi) Na_2CO_3, toluene, 110 °C for 4 h.

Preparation of 40. Compound **40** was synthesized as a light yellow solid (4.365 g) in 89% yield by the reaction of **1** (3.138 g, 19.99 mmol) with *m*-hydroxyanisole **39** (2.480 g, 20.0 mmol) by the method of preparation of **3**; m.p. 55-56 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.79 (s, 3H, OCH_3), 6.60 (dd, 1H, *J* = 7.6 Hz, 2.4 Hz, Ar-H), 6.61 (d, 1H, *J* = 2.8 Hz, Ar-H), 6.73 (dd, 1H, *J* = 8.4 Hz, 2.4 Hz, Ar-H), 7.05 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.20 (td, 1H, *J* = 7.6 Hz, 0.8 Hz, Ar-H), 7.26 (t, 1H, *J* = 8.4 Hz, Ar-H), 7.50 (td, 1H, *J* = 7.6 Hz, 1.6 Hz, Ar-H), 7.94 (dd, 1H, *J* = 8.0 Hz, 1.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 56.0, 105.4, 109.8, 110.3, 111.1, 120.7, 123.2, 125.5, 130.2, 133.8, 150.1, 156.6, 160.8.

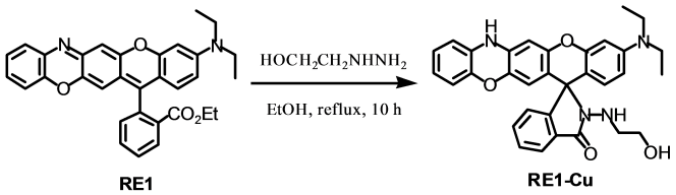
Preparation of 41. Compound **41** was synthesized as a red powder (3.016 g) in 40% yield by the reaction of compound **40** (3.722 g, 15.178 mmol) with 2-(4-*N*,*N*-diethylamino-2-hydroxy-benzoyl) benzoic acid (4.646 g, 14.827 mmol) by the method of preparation of **4**; m.p. 119-120 °C; HRMS: m/z [M + H^+] = 509.1717; Calcd for [$C_{30}H_{24}N_2O_6$ + H^+]: 509.1713; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.16 (t, 6H, *J* = 7.0 Hz, CH_3), 3.34 (q, 4H, *J* = 7.0 Hz, CH_2), 6.36 (dd, 1H, *J* = 8.8 Hz, 2.0 Hz, Ar-H), 6.41 (d, 1H, *J* = 2.0 Hz, Ar-H), 6.57 (d, H, *J* = 8.8 Hz, Ar-H), 6.68 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz, Ar-H), 6.76 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.85 (d, 1H, *J* = 2.4 Hz, Ar-H), 7.15 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.22 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.29 (t, 1H, *J* = 8.0 Hz, Ar-H), 7.58 (td, 1H, *J* = 8.0 Hz, 1.6 Hz, Ar-H), 7.62 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.68 (td, 1H, *J* = 7.5 Hz, 1.2 Hz, Ar-H), 7.98 (dd, 1H, *J* = 8.4 Hz, 1.6 Hz, Ar-H), 8.01 (d, 1H, *J* = 7.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ13.4, 45.2, 84.0, 98.0, 105.4, 106.3, 108.9, 113.8, 115.6, 122.0, 124.0, 124.3, 124.8, 125.6, 127.1, 128.7, 129.4, 129.6, 134.1, 134.6, 141.8, 149.0, 149.4, 152.4, 152.6, 157.4, 168.8.

Preparation of 42. To a solution of concentrated sulfuric acid (98 wt%, 6.0 mL) in ethanol (30 mL) at 25 °C was added **41** (1.420 g, 2.79 mmol). After refluxing for 24h, the reaction mixture was poured onto ice (150 g) with vigorous stirring. The pH of the aqueous phase was adjusted to ca. 7.0 with Na_2CO_3. Then, solid NaCl (5 g) was added and stirred for 30 min at room temperature. The aqueous mixture was extracted with dichloromethane (30 mL × 3), and the combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, purification of the red residue by column chromatography (SiO_2) with dichloromethane/ethanol (10:1) as the eluent generated **42** as a red powder (1.472 g) in 92% yield; m.p. 149-150 °C; HRMS: m/z [M - Cl^-] = 537.2025; Calcd for $C_{32}H_{29}N_2O_6^+$ = 537.2026; ^{1}H NMR (400 MHz, CD_3OD, ppm contain ethanol): δ 1.05 (t, 3H, *J* = 7.2 Hz, CH_3), 1.26 (t, 3H, *J* = 7.1 Hz, CH_3), 1.35 (t, 3H, *J* = 7.2 Hz, CH_3), 1.43 (t, 3H, *J* = 7.2 Hz, CH_3), 3.85 (q, 4H, *J* = 7.2 Hz, CH_2), 4.08 (q, 2H, *J* = 7.2 Hz, CH_2), 7.15 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz, Ar-H), 7.21 (d, 1H, *J* = 2.4 Hz, Ar-H), 7.33-7.40 (m, 4H, Ar-H), 7.53 (d, 2H, *J* = 8.4Hz, Ar-H), 7.63 (td, 1H, *J* = 8.0 Hz, 1.2 Hz, CH_2), 7.86-7.90 (m, 2H, Ar-H), 7.92 (td, 1H, *J* = 7.2 Hz, 1.2 Hz, Ar-H), 8.20 (dd, 1H, *J* = 8.4 Hz, 1.6 Hz, Ar-H), 8.39 (dd, 1H, *J* = 7.6 Hz, 0.8 Hz, Ar-H). ^{13}C NMR (100 MHz, CD_3OD, ppm): 11.2, 12.2, 12.8, 14.1, 56.2, 61.4, 61.5, 63.6, 96.5, 100.2, 103.8, 116.3, 117.7, 118.2, 124.3, 126.2, 127.2, 130.3, 130.4, 130.8, 131.2, 131.2, 132.5, 133.1, 135.5, 142.5, 146.5, 155.7, 158.6, 159.6, 160.7, 164.8, 165.1, 168.1.

Preparation of 43. A suspension of **42** (1.031 g, 1.80 mmol) and $SnCl_2.2H_2O$ (6.311 g, 27.9 mmol) in ethanol (20 ml) was refluxed for 10 h. After being cooled to room temperature, the reaction mixture was poured into water (100 mL) with vigorous stirring. The pH was adjusted to ca. 7.0 with Na_2CO_3. The solid was filtered and washed with dichloromethane. The aqueous filtrate was extracted with dichloromethane (30 mL × 3). After removal of the solvent, the red residue was purified by column chromatography (SiO_2) with ethyl acetate/petroleum ether (1:5) as the eluent. Compound **43** was obtained as a red powder (0.684 g) in 70% yield; m.p. 127-128 °C; HRMS: m/z [M - Cl^-] = 507.2296; Calcd for $C_{32}H_{31}N_2O_4^+$ = 507.2284; ^{1}H NMR (400 MHz, $CDCl_3$, contain ethanol, ppm): δ1.04 (t, 6H, *J* = 7.2 Hz, CH_3), 1.24 (t, 3H, *J* = 7.2 Hz, CH_3), 1.28 (t, 6H, *J* = 7.2 Hz, CH_3), 3.55 (q, 4H, *J* = 7.2 Hz, CH_2), 4.05 (q, 2H, *J* = 7.2 Hz, CH_2), 3.55 (q, 4H, *J* = 7.1 Hz, CH_2), 6.69 (d, 1H, *J* = 2.0 Hz, Ar-H), 6.80 (dd, 1H, *J* = 9.6 Hz, 2.4 Hz, Ar-H), 6.84 (t, 1H, *J* = 7.2 Hz, Ar-H), 6.97 (d, 1H, *J* = 9.6 Hz, Ar-H), 7.02-7.12 (m, 4H, Ar-H), 7.20 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.25 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.70 (td, 1H, *J* = 7.6 Hz, 0.8 Hz, Ar-H), 7.75 (td, 1H, *J* = 7.6 Hz, 1.2 Hz, Ar-H), 8.27 (d, 1H, *J* = 7.2 Hz, Ar-H), 8.6 (s, 1H, Ar-H), 9.6 (s, 1H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 13.2, 13.5, 14.7, 16.0, 46.5, 61.8, 63.9, 95.9,

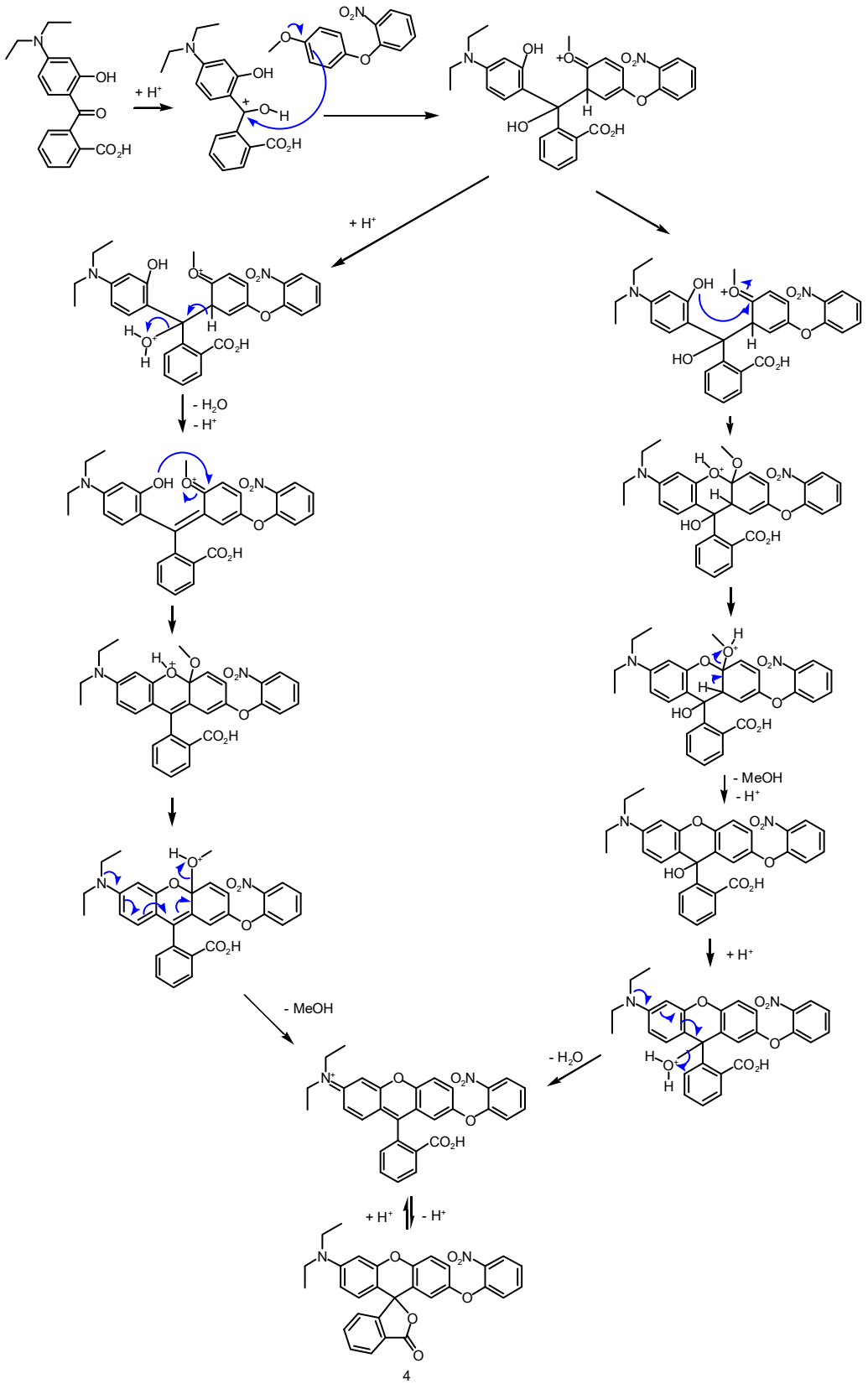
96.2, 98.0, 113.4, 114.1, 114.6, 118.2, 119.8, 124.9, 125.6, 128.0, 129.6, 129.8, 129.9, 130.5, 130.7, 131.0, 132.5, 133.1, 151.3, 154.7, 156.5, 157.1, 157.3, 158.5, 164.3.

Attempt to prepare of 44a or 44b *via* intramolecular S_NAr^H reaction. Protocol A. A suspension of **43** (0.121 g, 0.22 mmol) and Na_2CO_3 (0.201 g, 1.90 mmol) in ethyl acetate (20 ml) was stirred at 50 °C for 2 h. However, no color change of the solution was observed and no new product formed as indicated by TLC. Then, air was bumped in the reaction mixture and stirred at 50 °C for another 2 h. There was also no S_NAr^H reaction proceeded, as monitored by TLC. **Protocol B**. A suspension of **43** (0.121 g, 0.22 mmol) and Na_2CO_3 (0.201 g, 1.90 mmol) in toluene (20 ml) was stirred at 110 °C for 2 h. There was no new product formed, as monitored by TLC. The S_NAr^H reaction did not proceed even with air bumped at 110 °C for another 2 h.



Scheme S9. Synthesis of the probe **RE1-Cu**. Reagents and conditions: 2-hydroxyethylhydrazine, EtOH, nitrogen atmosphere, refluxed for 10 h, 44%.

To a solution of dye **RE1** (0.101 g, 0.2 mmol) in ethanol (20 mL), 2-hydroxyethylhydrazine (0.046 g, 0.6 mmol) was added at room temperature, and then the mixture was refluxing for 10 h under nitrogen atmosphere. The solvent was removed and the residue was purified by column chromatography (SiO_2) with dichloromethane/ethyl acetate (4/1) as the eluent generated **RE1-Cu** as a white solid (0.047 g) in 44% yield; m.p. 260-262 °C; HRMS: m/z [M + H^+] = 535.2350, [M + Na^+] = 557.2164, [2M + Na^+] = 1091.4432; Calcd for [$C_{32}H_{30}N_4O_4$ + H^+] = 535.2345, [$C_{32}H_{30}N_4O_4$ + Na^+] = 557.2165, [2 $C_{32}H_{30}N_4O_4$ + Na^+] = 1091.4421; ^{1}H NMR (400 MHz, DMSO-d_6 and $CDCl_3$, contain H_2O, ppm): δ 1.09 (t, 6H, *J* = 6.8 Hz, CH_3), 3.25-3.30 (m, 14H, CH_2 and H_2O), 5.65 (s, 1H, Ar-H), 6.22 (m, 2H, Ar-H), 6.27 (s, 1H, Ar-H), 6.29 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.36 (d, 1H, *J* = 7.2 Hz, Ar-H), 6.38 (d, 1H, *J* = 7.2 Hz, Ar-H), 6.45 (t, 1H, *J* = 7.2 Hz, Ar-H), 6.60 (t, 1H, *J* = 7.2 Hz, Ar-H), 7.04 (d, 1H, *J* = 6.8 Hz, Ar-H), 7.45 (t, 1H, *J* = 6.8 Hz, Ar-H), 7.49 (t, 1H, *J* = 6.8 Hz, Ar-H), 7.78 (d, 1H, *J* = 6.8 Hz, Ar-H), 8.18 (s, 1H, N-H). ^{13}C NMR (100 MHz, DMSO-d_6 and $CDCl_3$, ppm): δ12.0, 44.1, 52.3, 58.7, 65.0, 100.1, 107.8, 109.0, 111.7, 113.0, 114.5, 120.2, 122.2, 123.1, 123.3, 127.9, 128.1, 128.2, 129.5, 129.6, 130.7, 132.5, 133.5, 133.6, 138.8, 142.4, 148.4, 150.3, 152.8, 166.2.



Scheme S10. Proposed two possible ways to form **4**.

Table S1. Crystal data and structure refinement for dye **RE1**.

Item analys	Data	
Empirical formula	$C_{31}H_{26}N_2O_4$	
Formula weight	490.54	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	*P*2(1)/c	
Unit cell dimensions	*a* = 16.190(2) Å	α = 90°
	b = 19.621(3) Å	β = 95.873(13)°
b, Å	*c* = 8.6624(15) Å	γ = 90°
Volume	2737.3(7) Å3	
Z	4	
Density (calculated)	1.19 Mg/m^3	
Absorption coefficient	0.079	
F(000)	1032	
Theta range for data collection	2.431° to 25.009°	
No of data collected	8419	
No of reflections unique data	2520	
Data/restraints/parameters	8419/0/337	
Goodness-of-fit on F^2	0.918	
Final R indices	R = 0.057, ωR_2 = 0.1378	
R indices (all data)	R = 0.1093, ωR_2 = 0.1599	

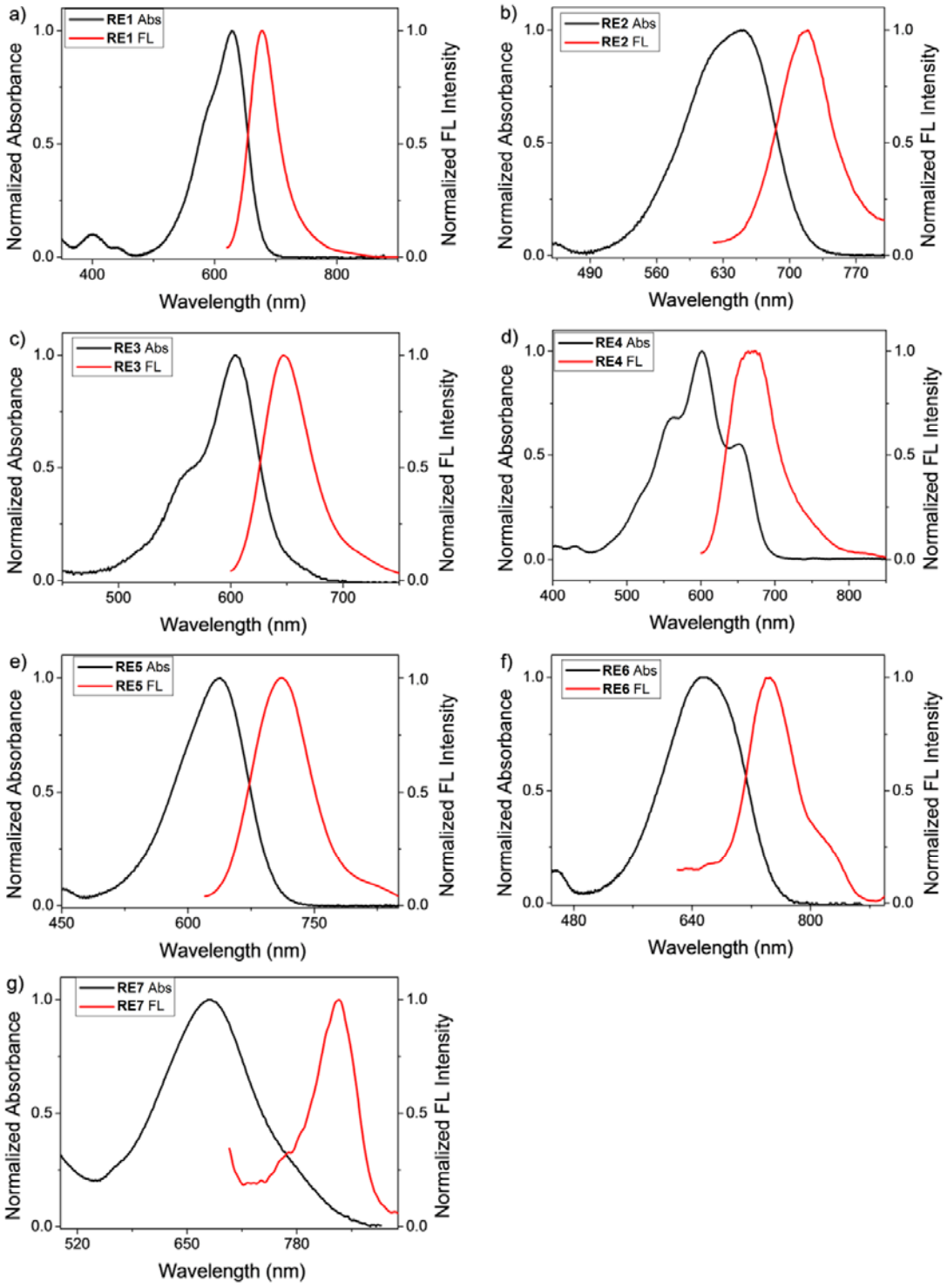


Fig. S1. Normalized absorption and fluorescence spectra of the dyes in ethanol, a) **RE1**, b) **RE2**, c) **RE3**, d) **RE4**, e) **RE5**, f) **RE6** and g) **RE7**.

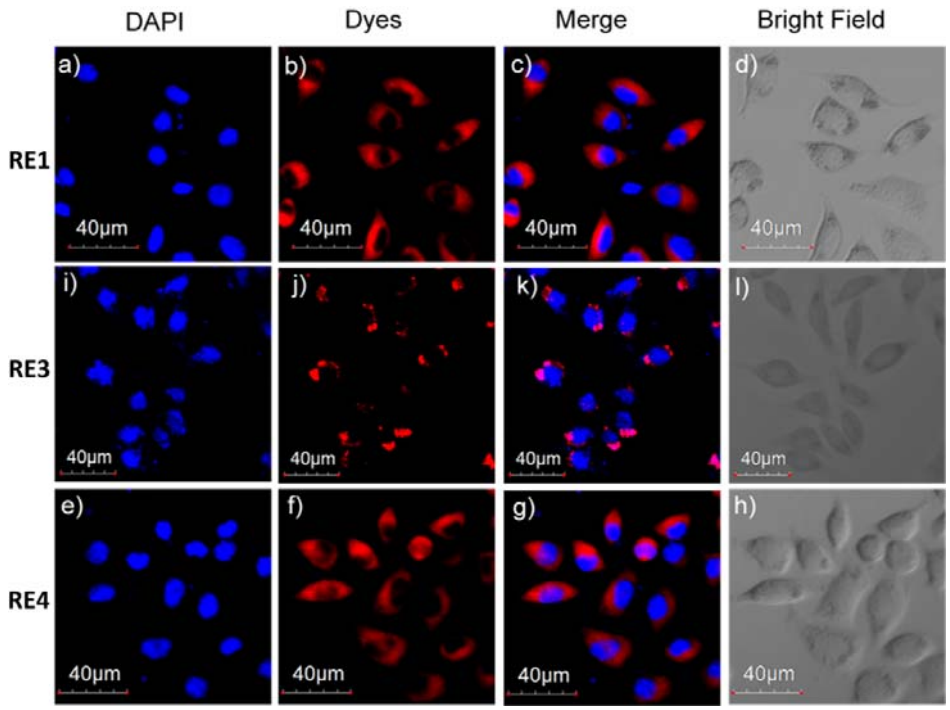


Fig. S2. Confocal fluorescence microscopy images of HeLa cells incubated with DAPI (5 μg mL^{-1}) and 2 μM dyes **RE1** (top row), **RE3** (middle row) and **RE4** (bottom row). (a), (d) and (g) 5 μg mL^{-1} of DAPI; (b), (e) and (h) 2 μM of **RE1**, **RE3** and **RE4**, respectively; (c) overlay of (a) and (b) and its bright imaging; (f) overlay of (d) and (e) and its bright imaging; (i) overlay of (c) and (f) and its bright imaging.

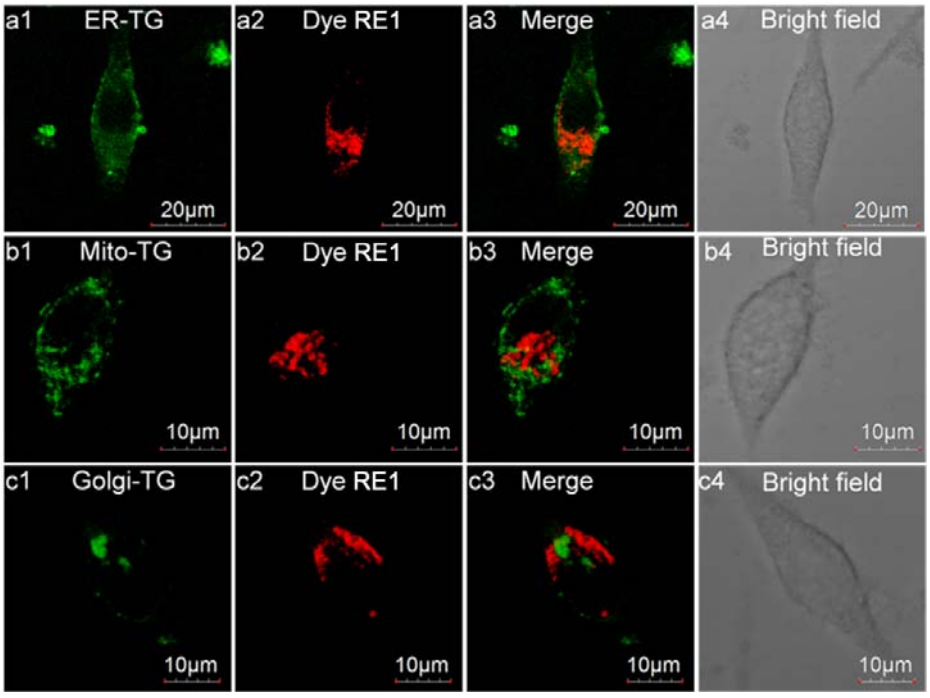


Fig. S3. Colocalization of **RE1** (50 nM) with commercially organelle markers. (a1, b1, c1) fluorescence images from the ER-TG (500 nM), Mito-TG (200 nM), and Golgi-TG (200 nM) in L929 cells, respectively; (a2, b2, c2) fluorescence images from **RE1** (50 nM); (a3, b3, c3) merged images from respective green and NIR channels; (a4, b4, c4) bright-field images**.**

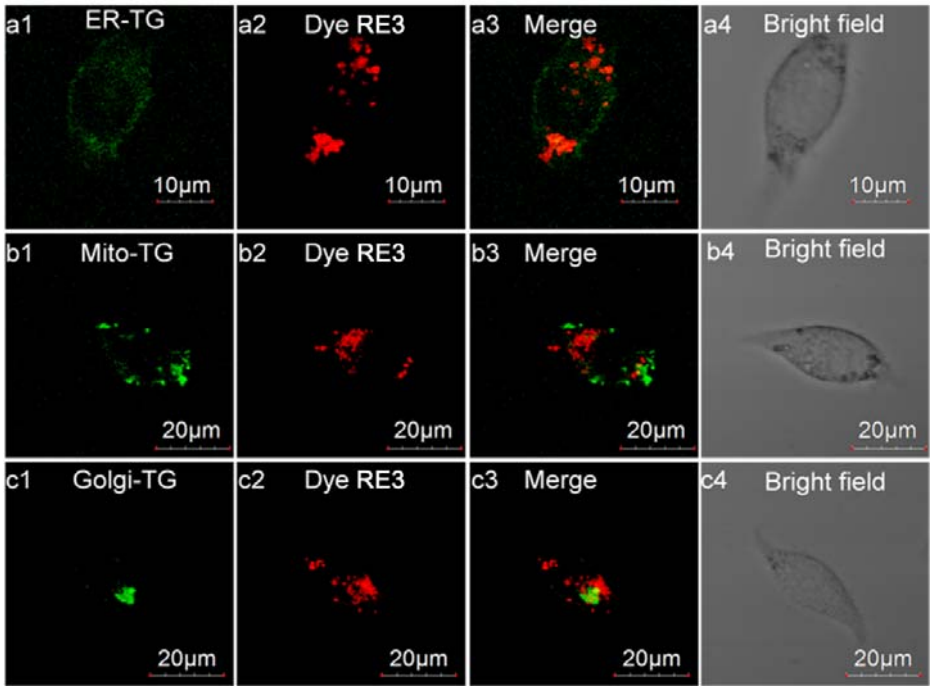


Fig. S4. Colocalization of **RE3** (50 nM) with commercially organelle markers. (a1, b1, c1) fluorescence images from the ER-TG (500 nM), Mito-TG (200 nM), and Golgi-TG (200 nM) in L929 cells, respectively; (a2, b2, c2) fluorescence images from **RE3** (50 nM); (a3, b3, c3) merged images from respective green and NIR channels; (a4, b4, c4) bright-field images

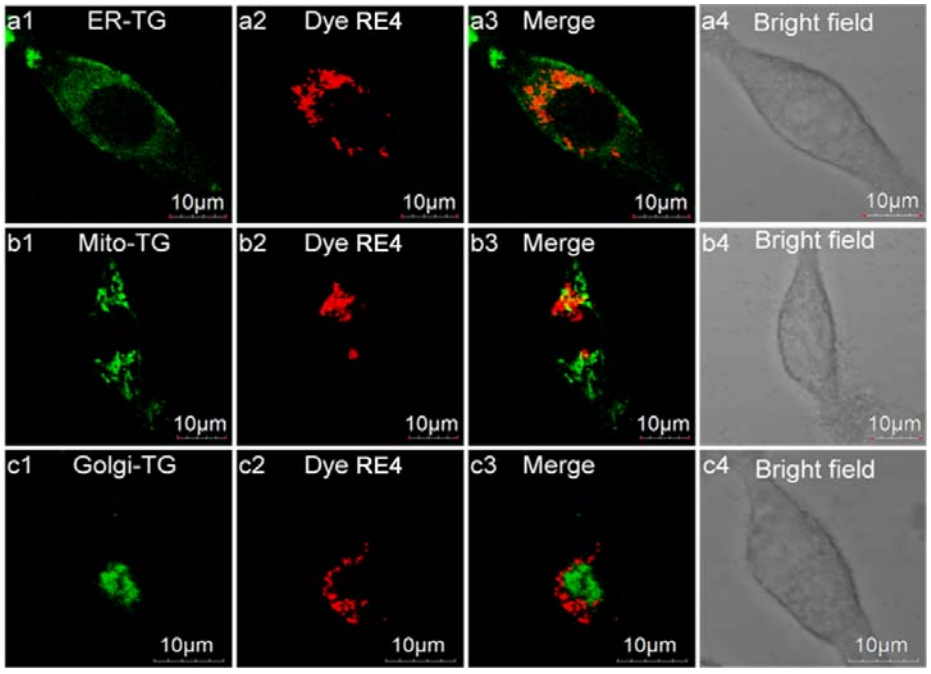


Fig. S5. Colocalization of **RE4** (50 nM) with commercially organelle markers. (a1, b1, c1) fluorescence images from the ER-TG (500 nM), Mito-TG (200 nM), and Golgi-TG (200 nM) in L929 cells, respectively; (a2, b2, c2) fluorescence images from **RE4** (50 nM); (a3, b3, c3) merged images from respective green and NIR channels; (a4, b4, c4) bright-field images

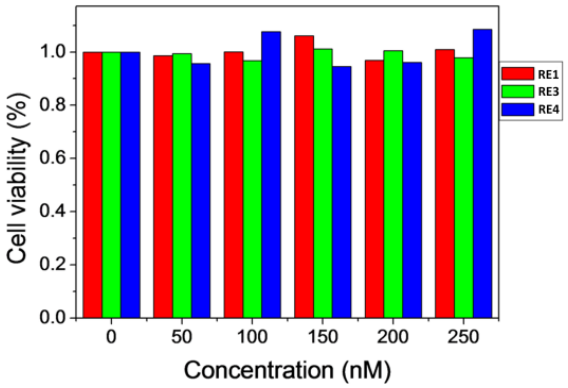


Fig. S6. Cytotoxicity of dyes **RE1, RE3,** and **RE4** in L929 cells. Cell viability values (%) estimated by MTT assays using L929 cells, cultured in the presence of 50-250 nM of **RE1, RE3,** and **RE4** for 24 h at 37 °C, respectively.

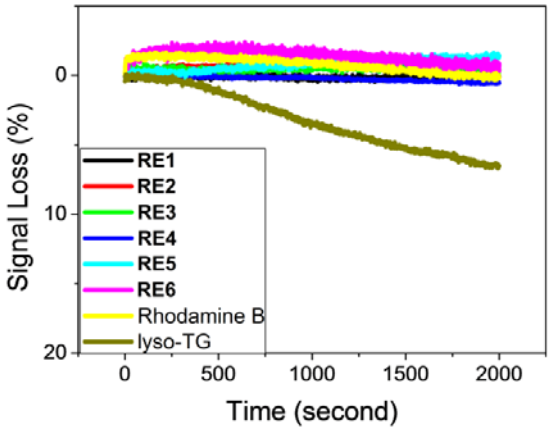


Fig. S7. Photostabilities[3] of dyes **RE1-RE6, Rhodamine B** and Lyso-TG in PBS buffer (pH = 5.5, containing 5 % DMSO) under xenon lamp irradiation using fluorescence spectrometer.

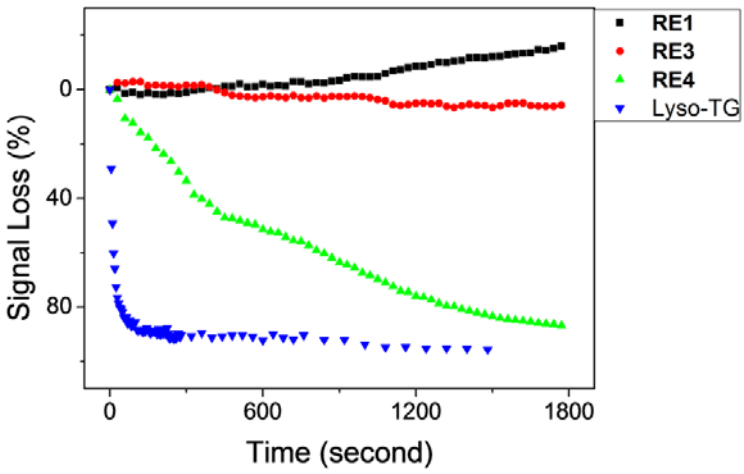


Fig. S8. Photostabilities of dyes **RE1**, **RE3**, **RE4**, and Lyso-TG in L929 cells. Confocal fluorescence images of L929 cells cultured with dyes and Lyso-TG with increasing number of irradiation time, respectively.

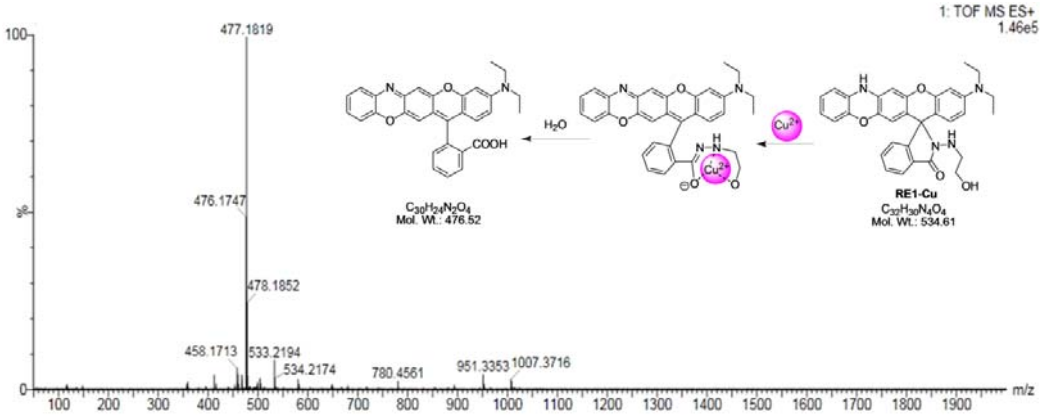


Fig. S9. HRMS spectra of **RE1-Cu** upon addition of Cu^{2+} (2.0 equiv.). The peak at m/z = 477.1819 (calcd: 477.1814) was assigned to the mass of [**RE1**].

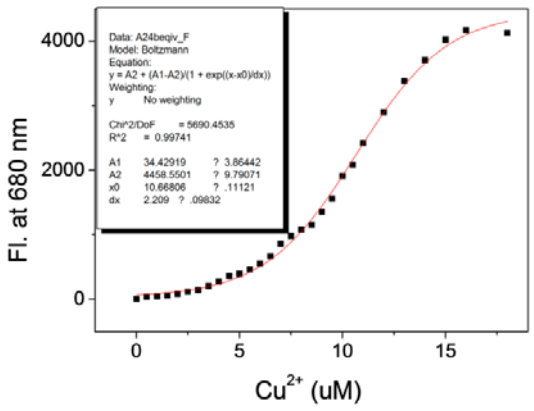


Fig. S10. Measurement of the fluorescence turn-on constant ($K_{turn\text{-}on}$)[4] of **RE1-Cu** (5 μM).

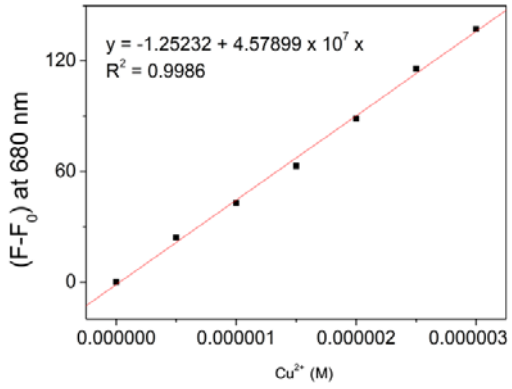


Fig. S11. The detection limit[5] of **RE1-Cu** towards Cu^{2+} by signal-to-noise ratio of three method (3σ/k) in PBS buffer (0.01 M, pH 7.4, containing 25% CH_3CN as a cosolvent). Detection limit = 3σ/k. σ is the standard deviation of blank measurement (n = 11, σ = 0.139), k is the slope between the fluorescence intensity versus Cu^{2+} ions concentration (k = 4.57899 × 10^7). The detection limit is 9.1 nM.

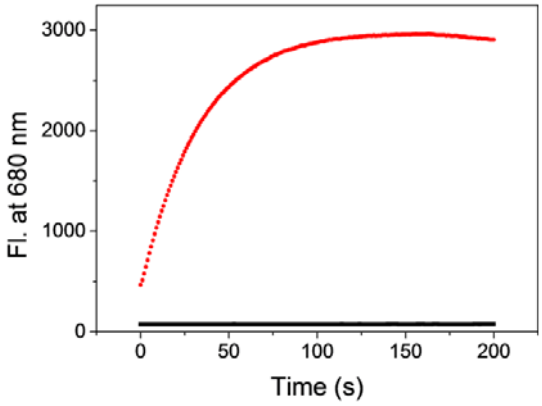


Fig. S12. Time-dependent fluorescence change (at 680 nm) of probe **RE1-Cu** (7 μM) with the addition of Cu^{2+} ions (2 equiv) in PBS buffer (0.01 M, pH 7.4, containing 25% CH_3CN as a cosolvent).

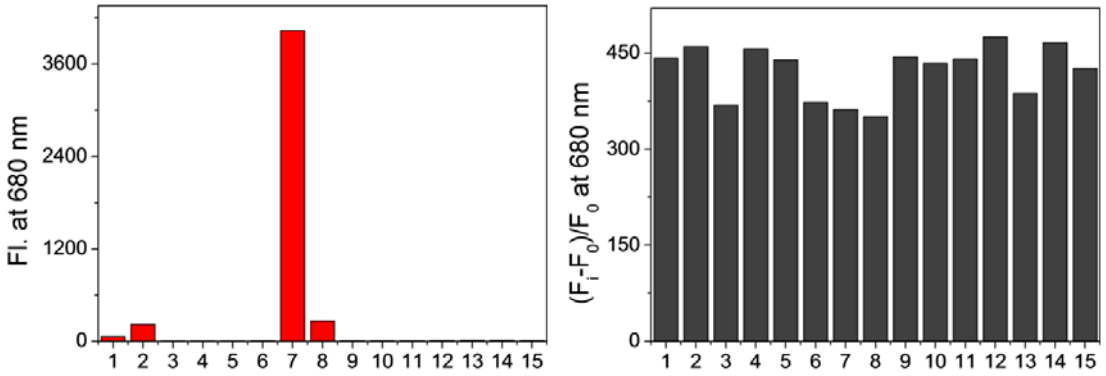


Fig. S13. a) Fluorescence intensity (at 680 nm) of **RE1-Cu** (5 μM) with excitation at 600 nm in the presence of various species (20 μM). b) Change ratio (($F_i - F_0$)/F_0)) of fluorescence intensity at 680 nm of **RE1-Cu** (5 μM) upon addition of each metal ion (20 μM) followed by Cu^{2+} (20 μM) in PBS buffer (0.01 M, pH 7.4, containing 25% CH_3CN as a cosolvent). 1, Ag^+; 2, Al^{3+}; 3, Ca^{2+}; 4, Cd^{2+}; 5, Co^{2+}; 6, Cr^{3+}; 7, Cu^{2+}; 8, Hg^{2+}; 9, K^+; 10, Mg^{2+}; 11, Na^+; 12, NH_4^+; 13, Ni^{2+}; 14, Pb^{2+}; 15, Zn^{2+}.

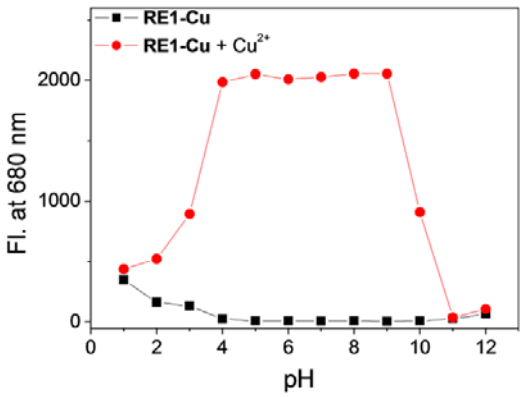


Fig. S14. a) Profile of pH dependence of the fluorescence intensity of **RE1-Cu** (2.5 μM) at 680 nm in the absence and presence of Cu^{2+} ions (4 equiv) in CH_3CN-H_2O (v/v, 1/3).

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[6] (a) M. Mąkosza, T. Lemek, A. Kwast, F. Terrier, *J. Org. Chem.* **2002**, *67*, 394; (b) N. Zhang, S. Ayral-Kaloustian, J. T. Anderson, T. Nguyen, S. Das, A. M. Venkatesan, N. Brooijmans, J. Lucas, K. Yu, I. Hollander, R. Mallon, *Bioorg. Med. Chem. Lett.* **2010**, *20*, 3526.

^{1}H NMR, ^{13}C NMR and HRMS Spectra

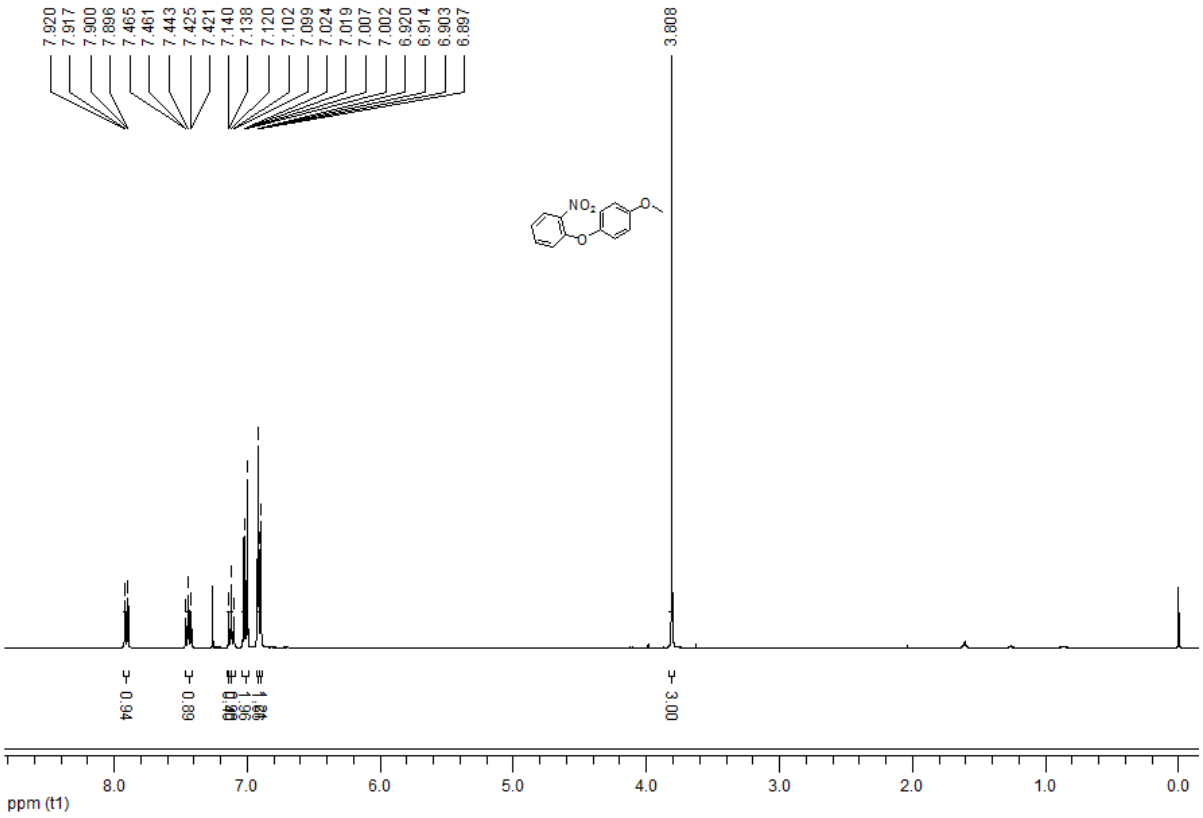

Fig. S15 ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$).

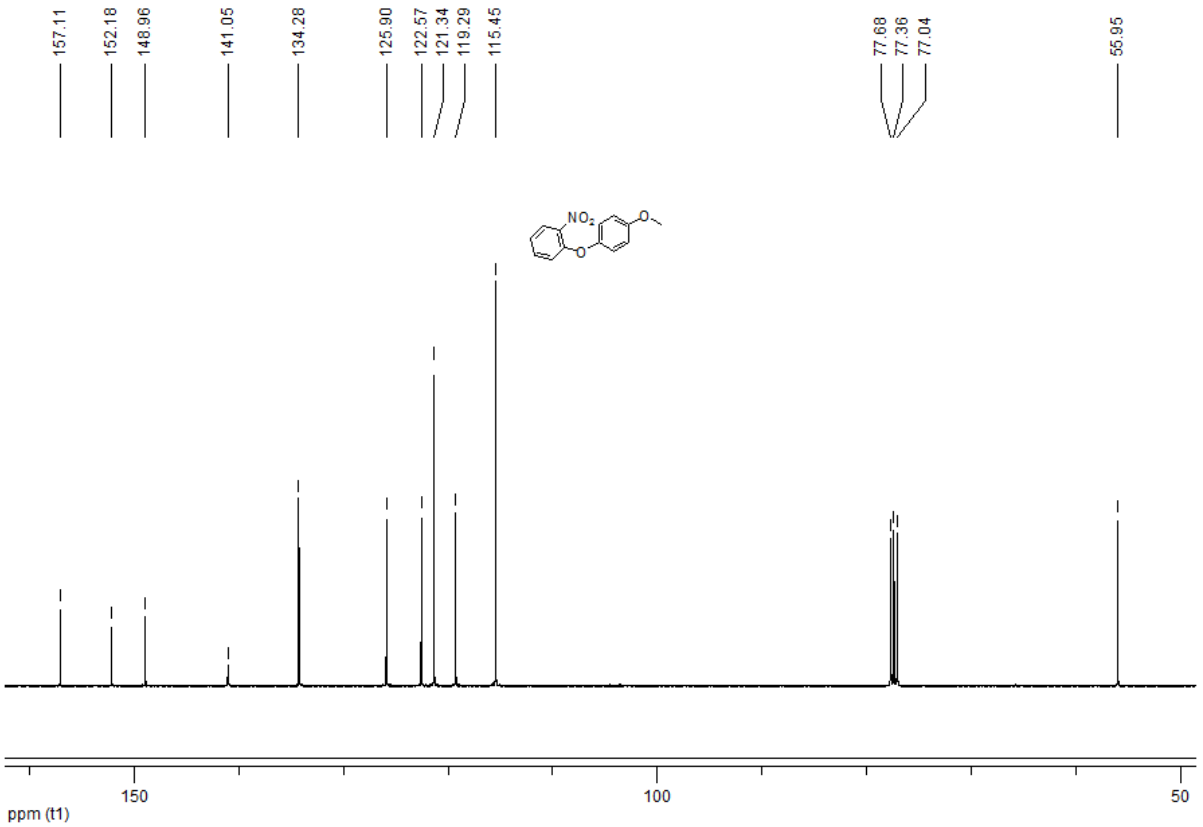

Fig. S16 ^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$).

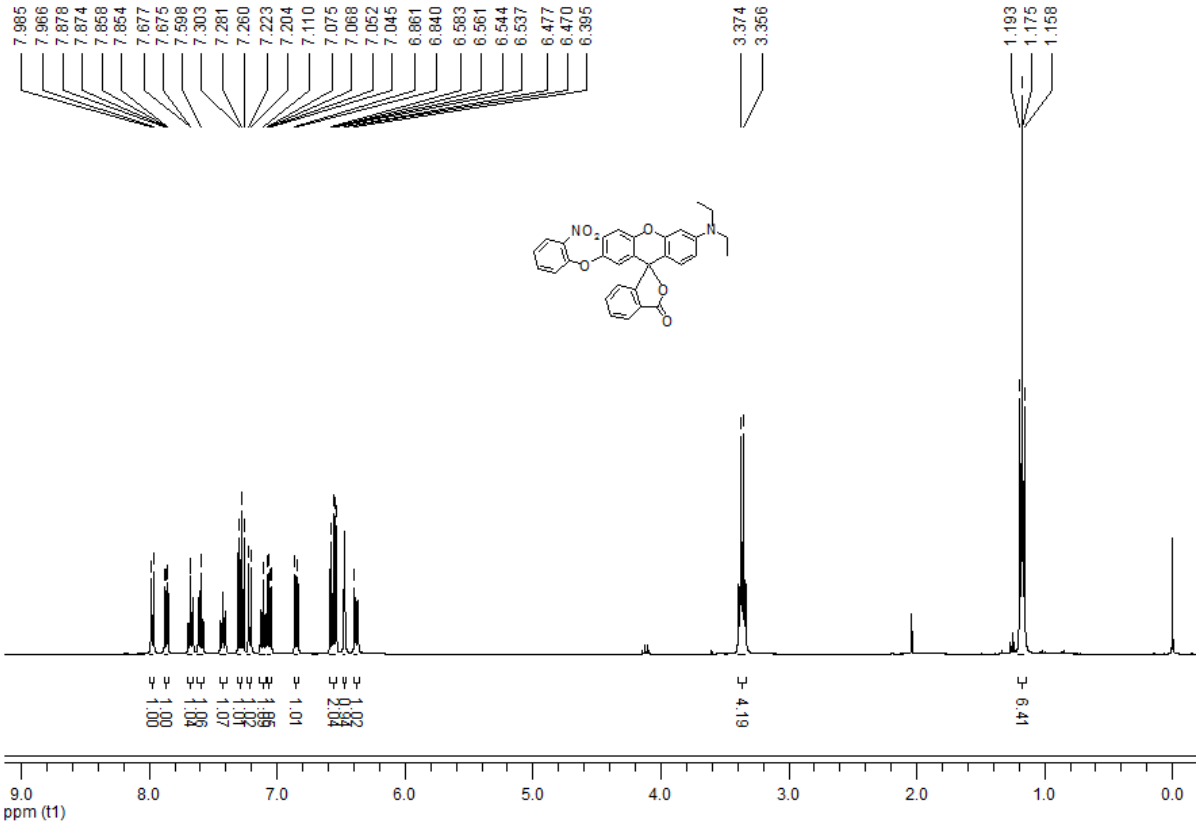

Fig. S17 ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$).

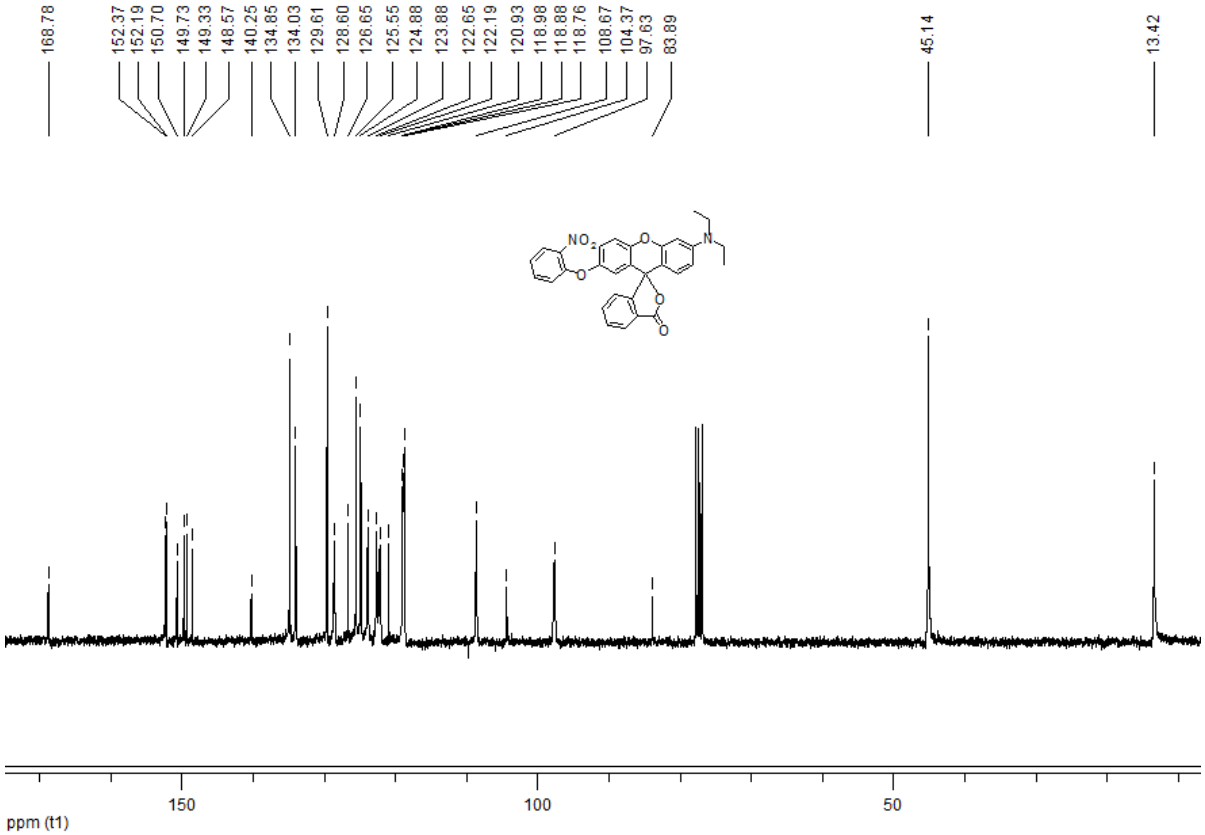

Fig. S18 ^{13}C NMR spectrum of **4** (100 MHz, $CDCl_3$).

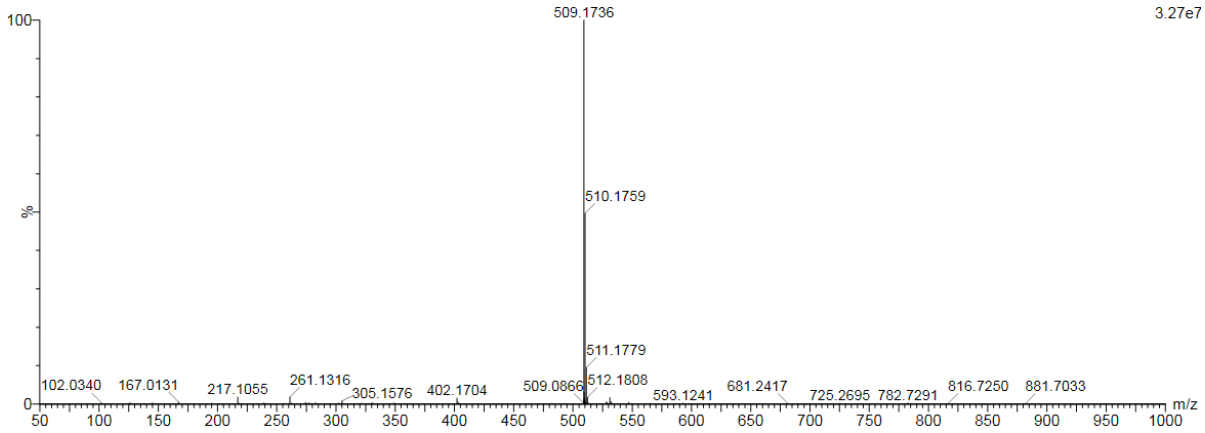

Fig. S19 HRMS of **4**. HRMS: m/z [M + H^+] = 509.1736; Calcd for [$C_{30}H_{24}N_2O_6$ + H^+]: 509.1707.

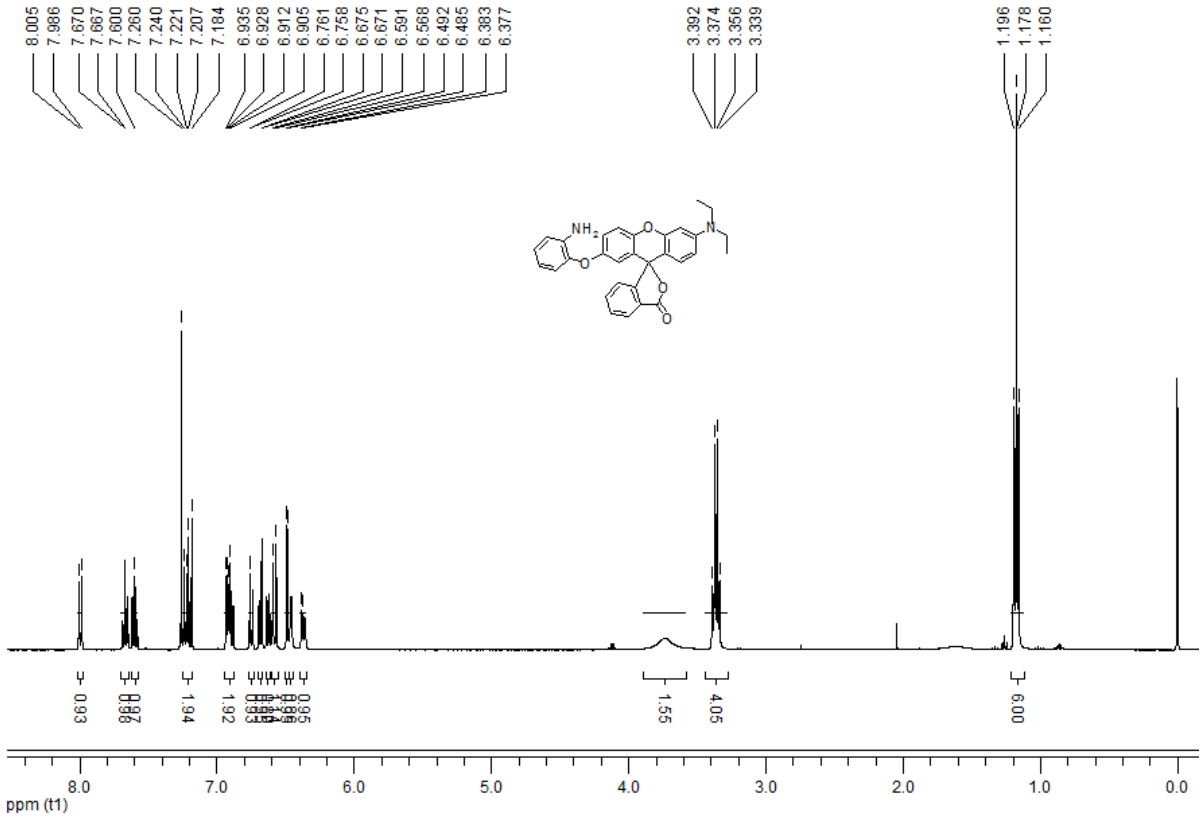

Fig. S20 ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$).

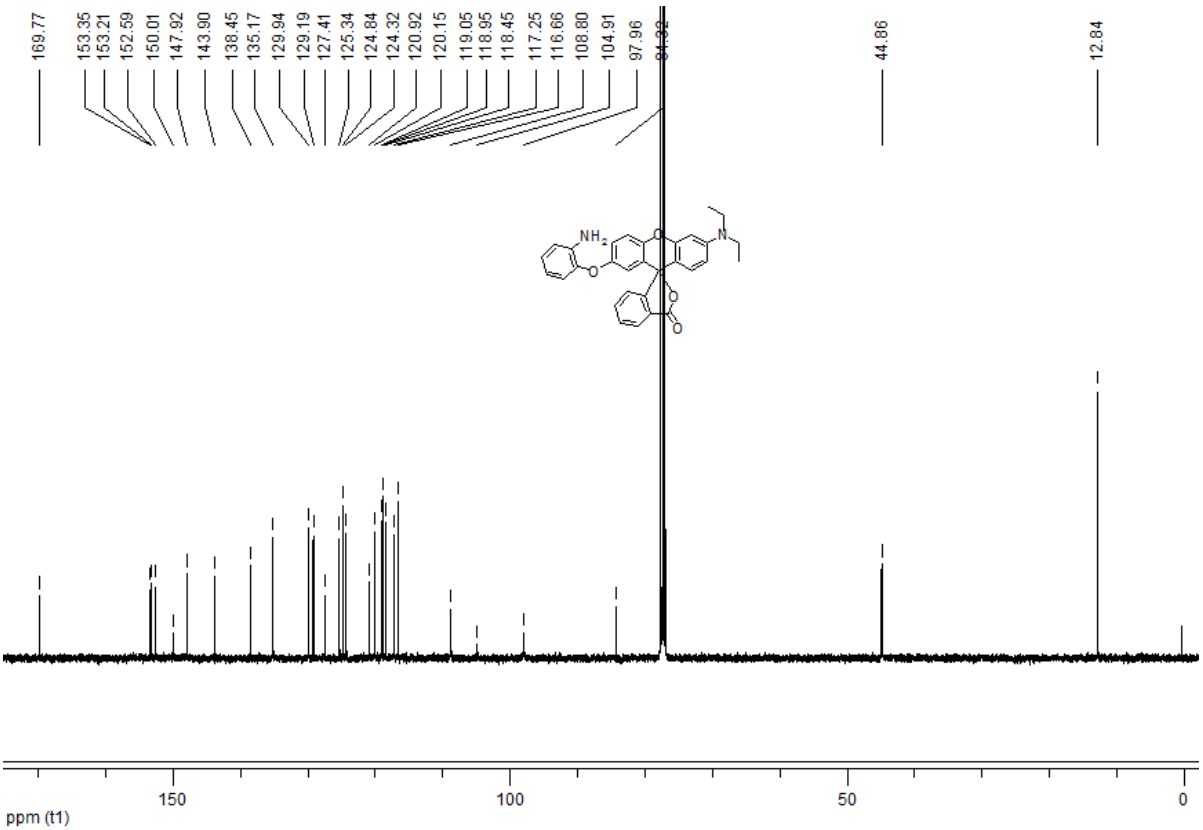

Fig. S21 ^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$).

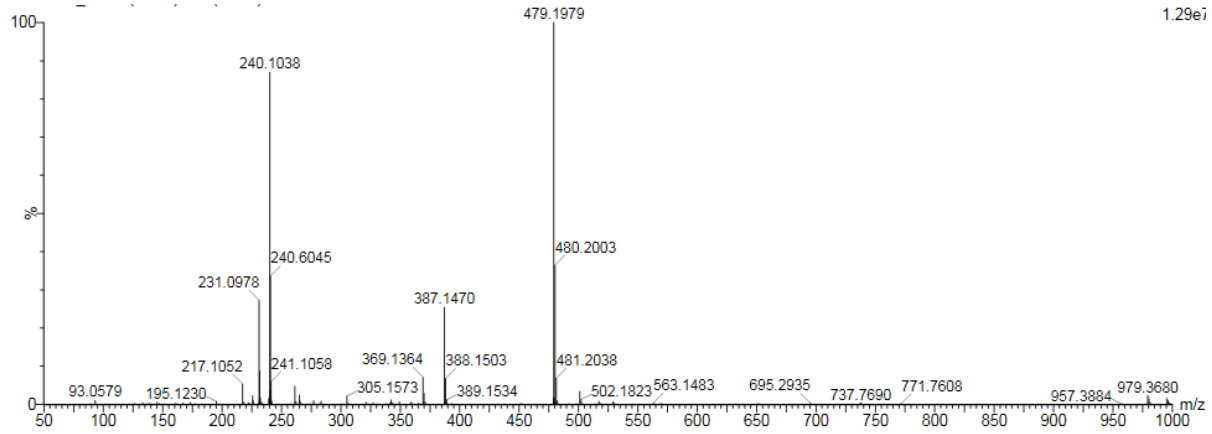

Fig. S22 HRMS of **5**. HRMS: m/z [M + 2H$^+$]/2 = 240.1038, [M + H$^+$] = 479.1979; Calcd for [$C_{30}H_{26}N_2O_4$ + 2H$^+$]/2 = 240.1019; [$C_{30}H_{26}N_2O_4$ + H$^+$] = 479.1965.

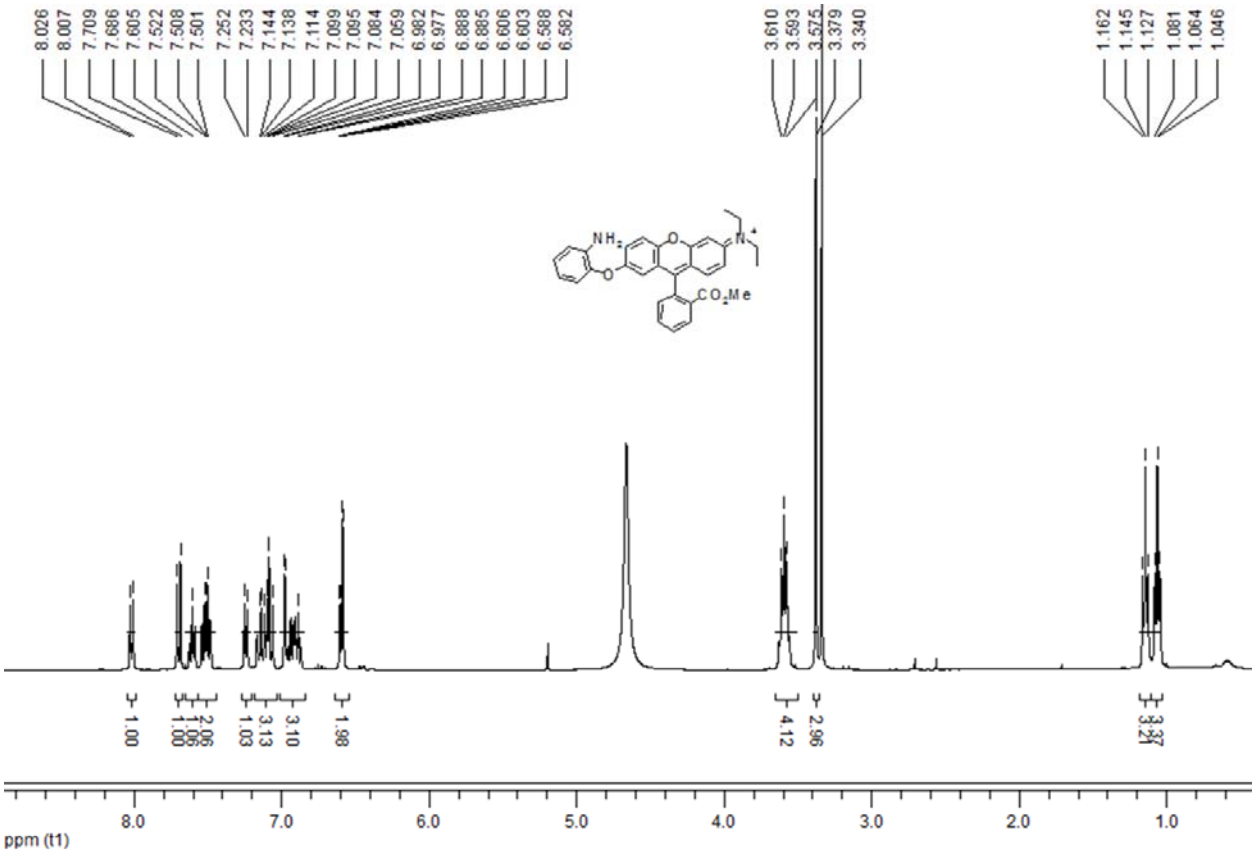

Fig. S23 ^{1}H NMR spectrum of **6** (400 MHz, CD_3OD).

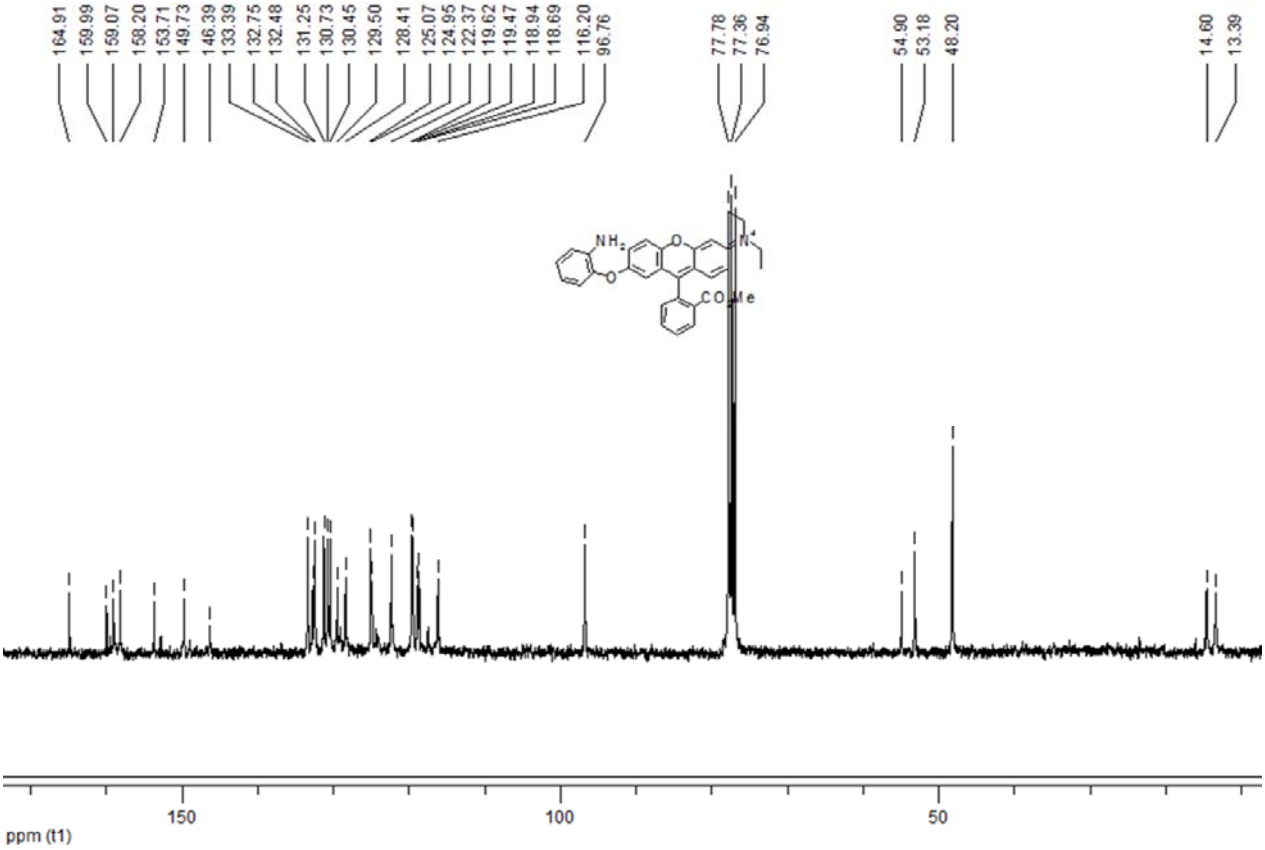

Fig. S24 ^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$).

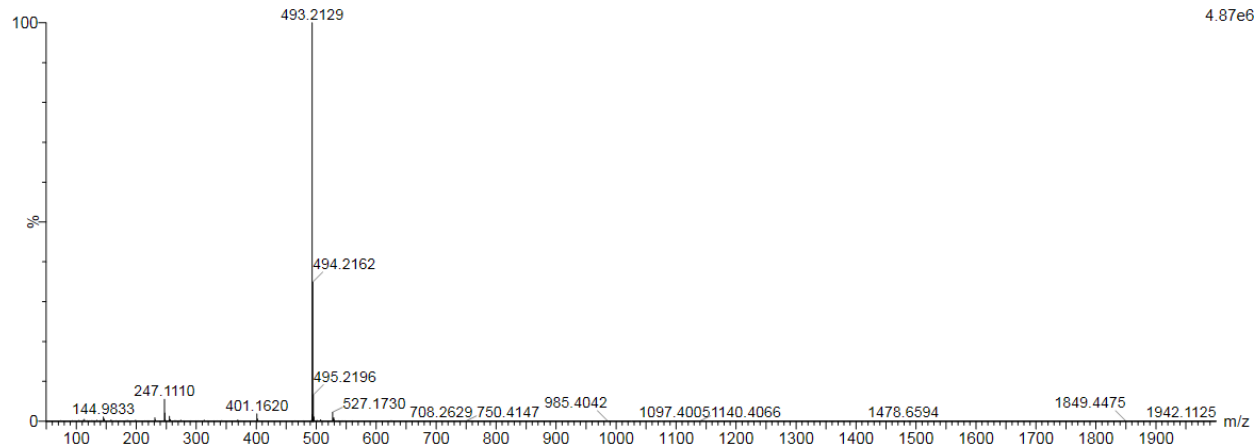

Fig. S25 HRMS of **6**. HRMS: m/z [M - Cl^-] = 493.2129; Calcd for $C_{31}H_{29}N_2O_4^+$ = 493.2127.

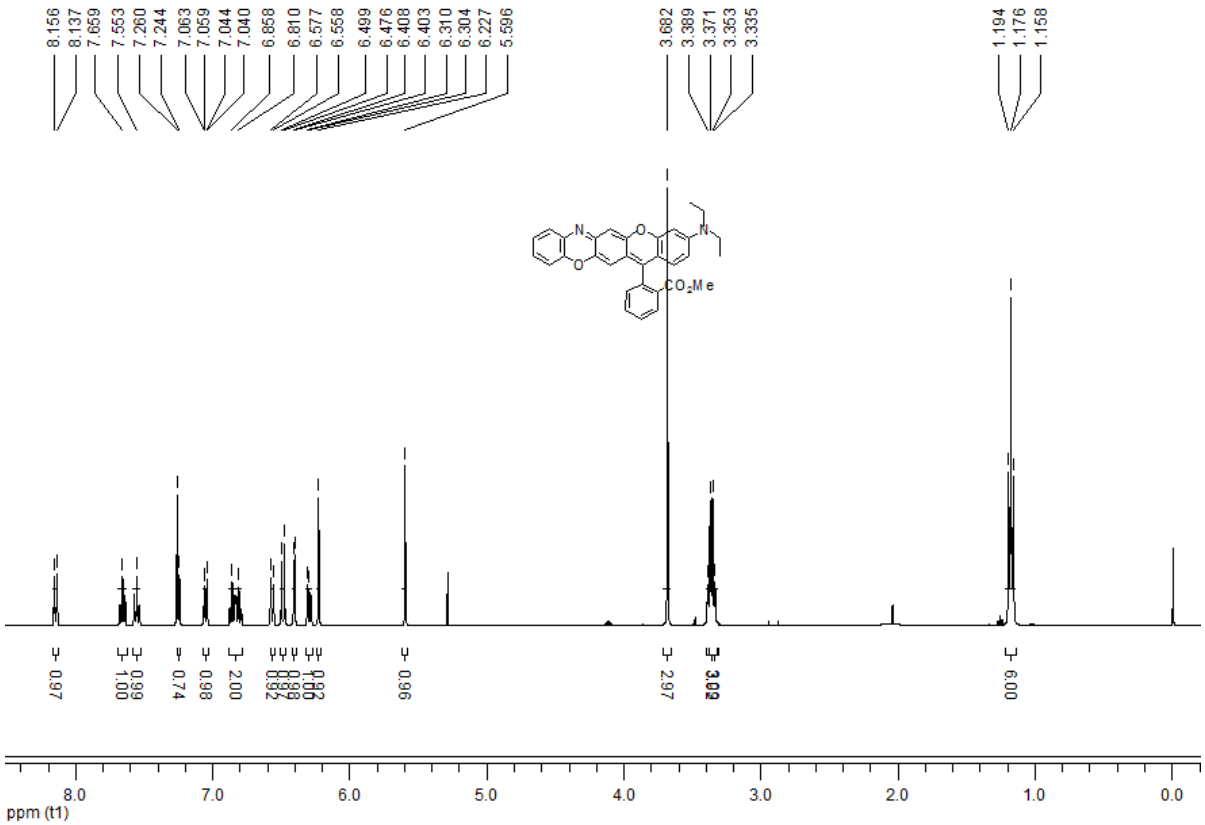

Fig. S26 ^{1}H NMR spectrum of **RE1** (400 MHz, $CDCl_3$).

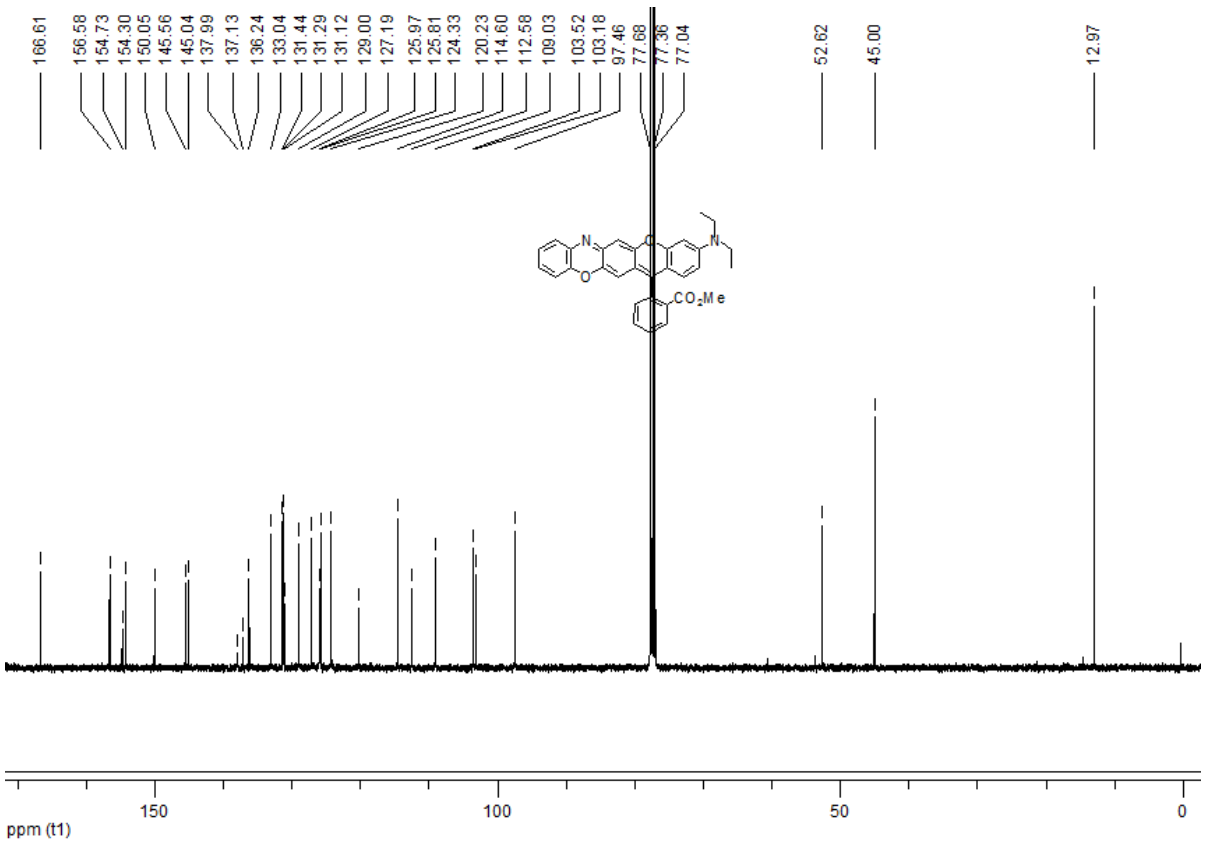

Fig. S27 ^{13}C NMR spectrum of **RE1** (100 MHz, $CDCl_3$).

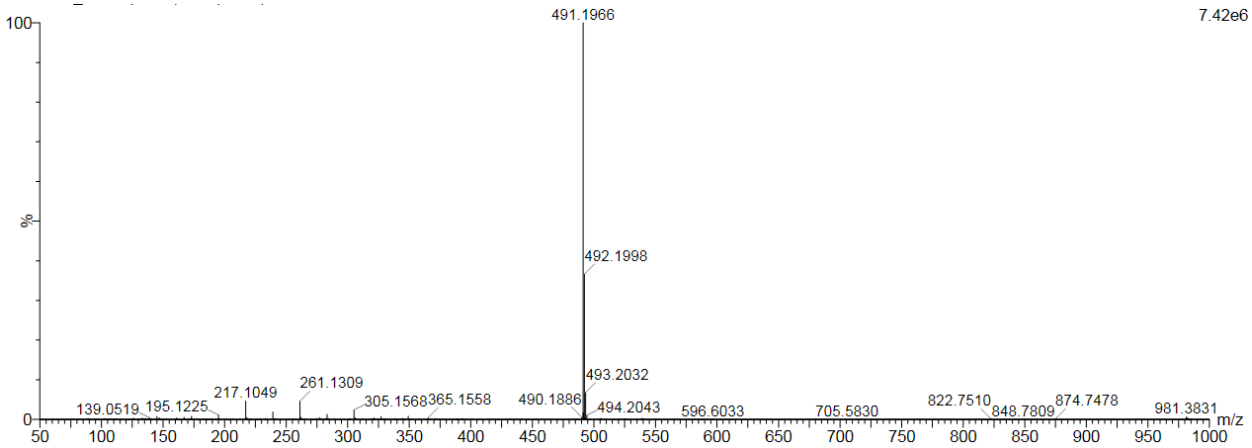

Fig. S28 HRMS of **RE1**. HRMS: m/z [M + H$^+$] = 491.1966; Calcd for [$C_{31}H_{26}N_2O_4$ + H$^+$] = 491.1965.

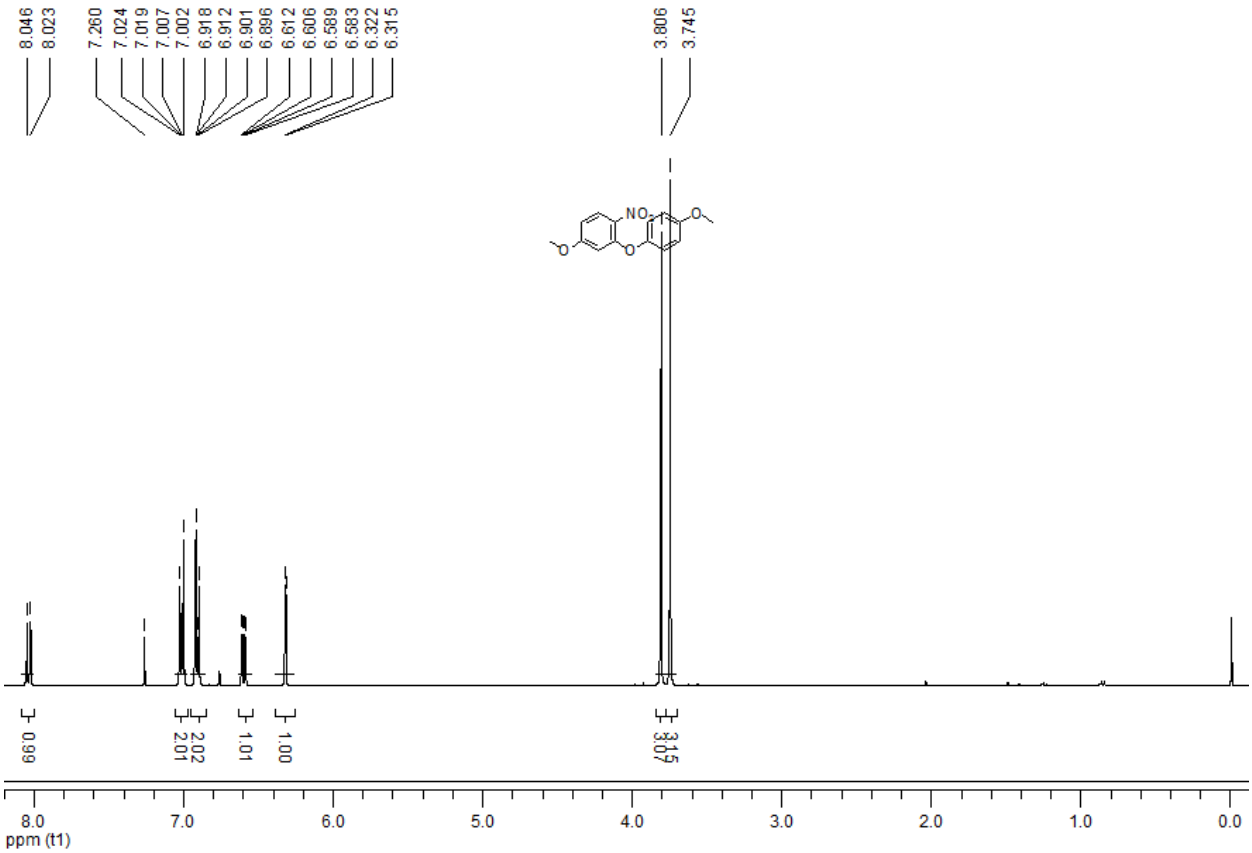

Fig. S29 ^{1}H NMR spectrum of **9** (400 MHz, $CDCl_3$).

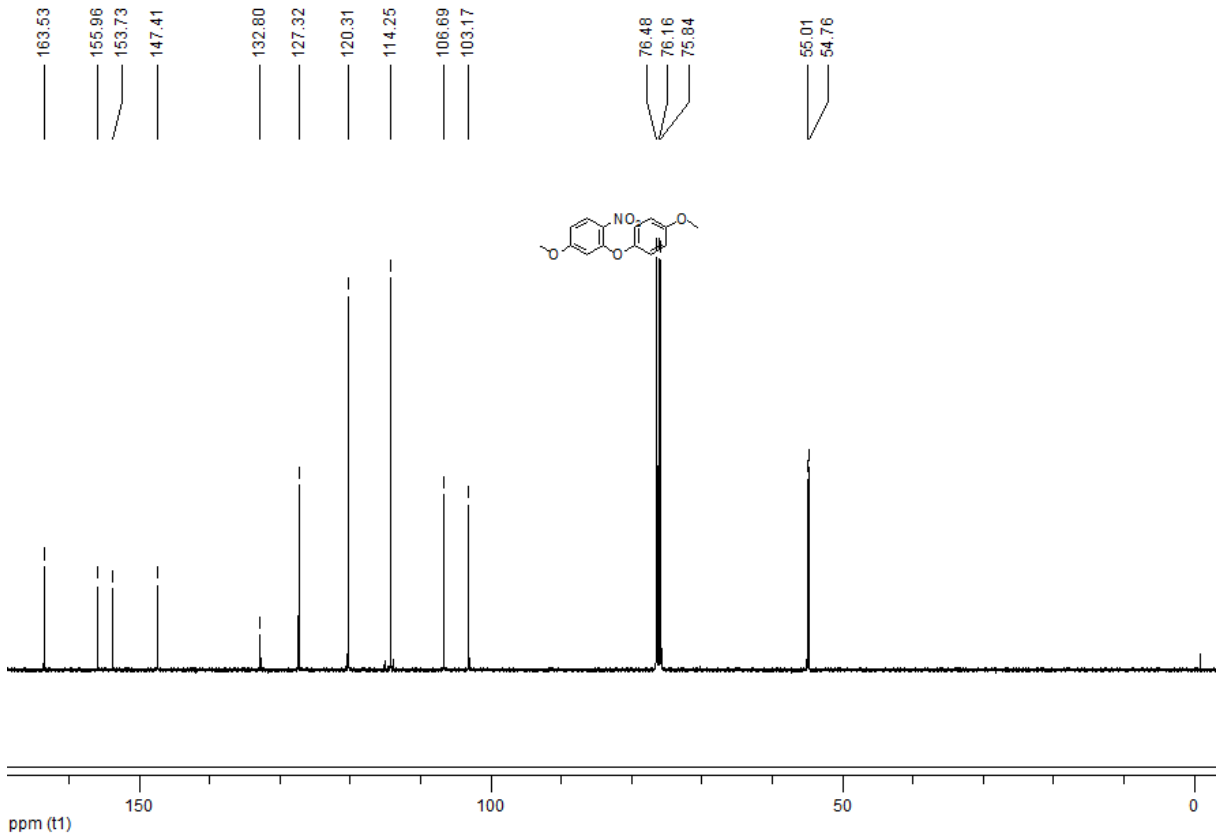

Fig. S30 ^{13}C NMR spectrum of **9** (100 MHz, $CDCl_3$).

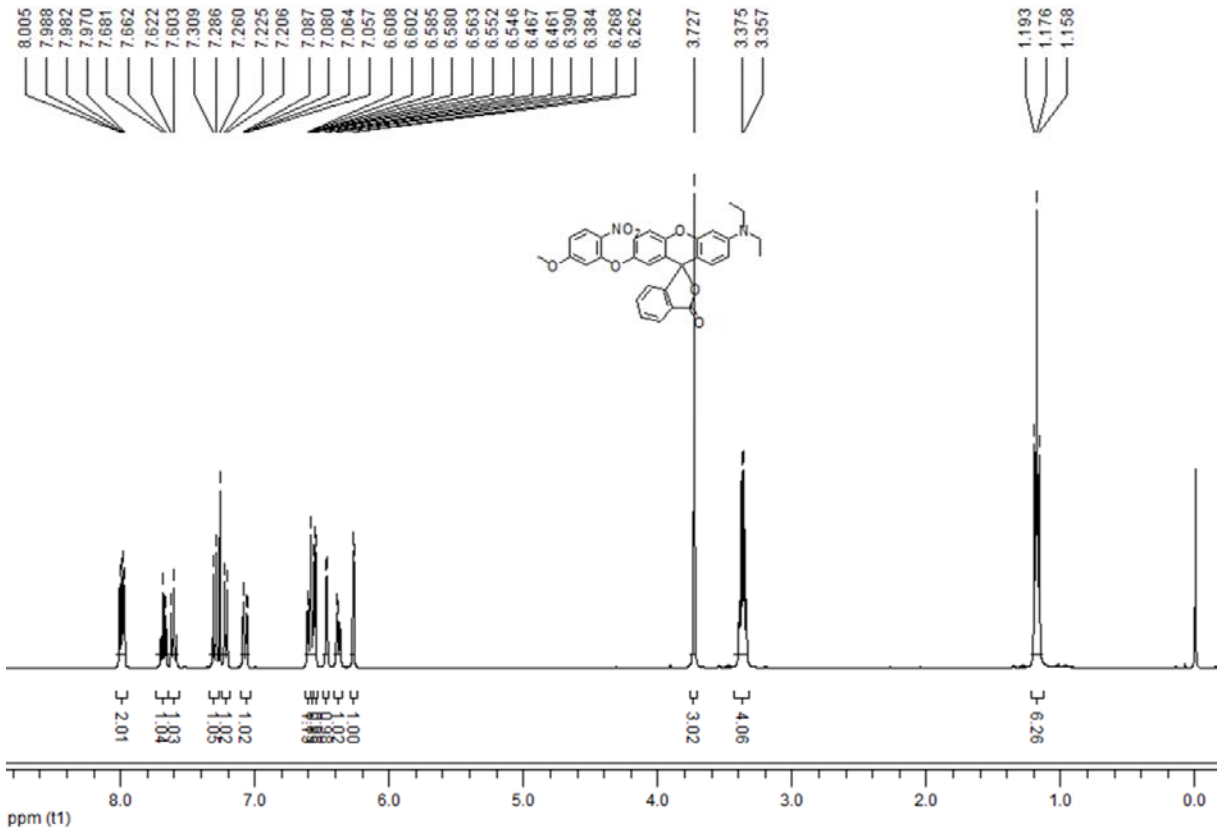

Fig. S31 ^{1}H NMR spectrum of **10** (400 MHz, $CDCl_3$).

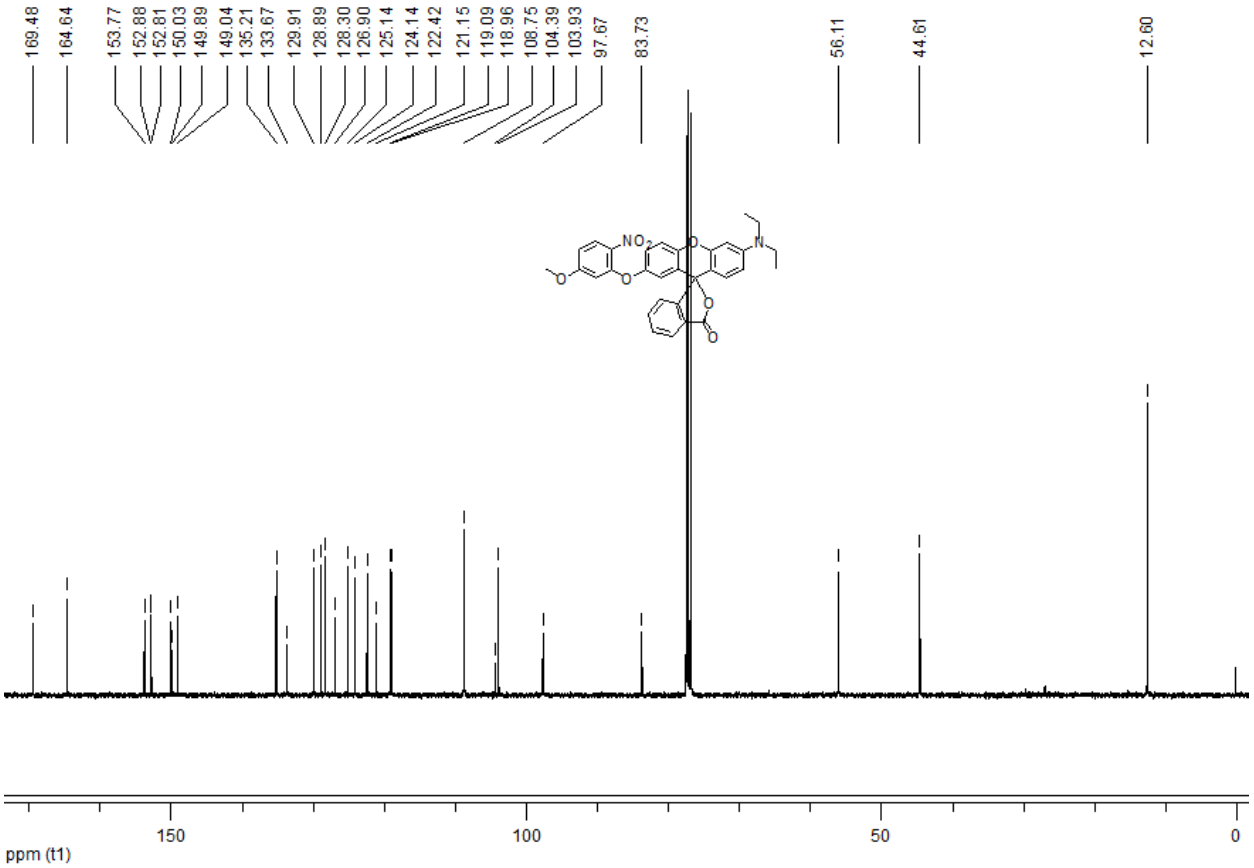

Fig. S32 ^{13}C NMR spectrum of **10** (100 MHz, $CDCl_3$).

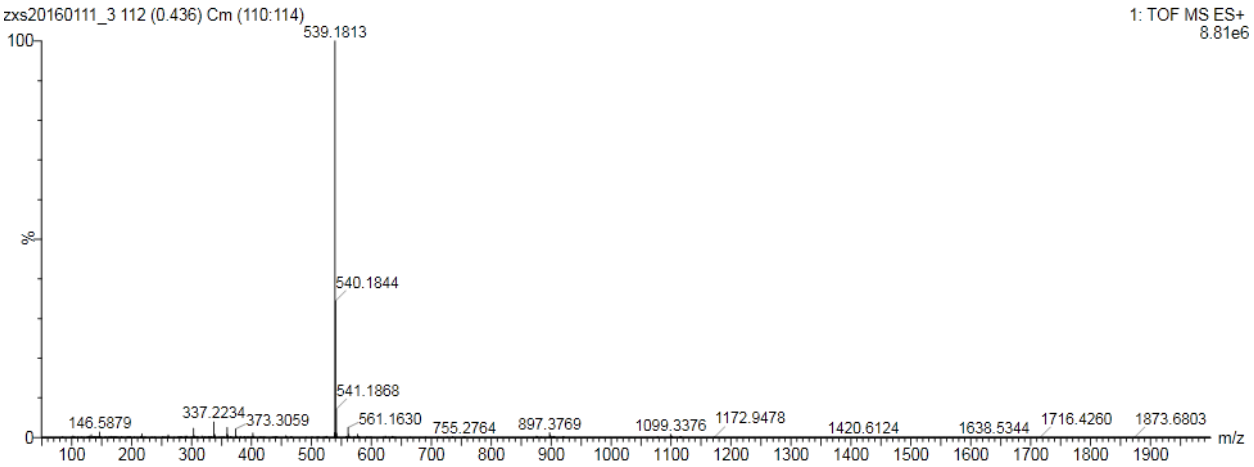

Fig. S33 HRMS of **10**. HRMS: m/z [M + H^+] = 539.1813; Calcd for [$C_{31}H_{26}N_2O_7$ + H^+] = 539.1818.

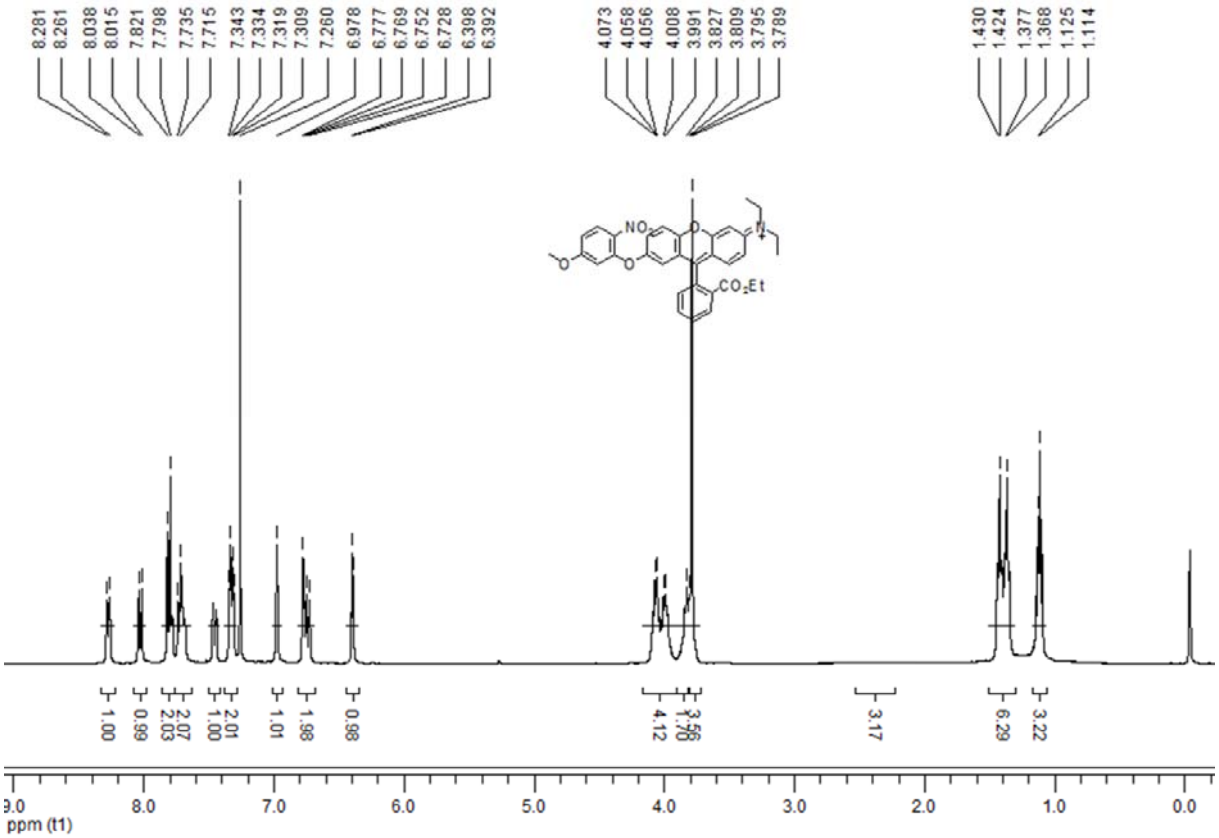

Fig. S34 ^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$). * solvent (EtOH).

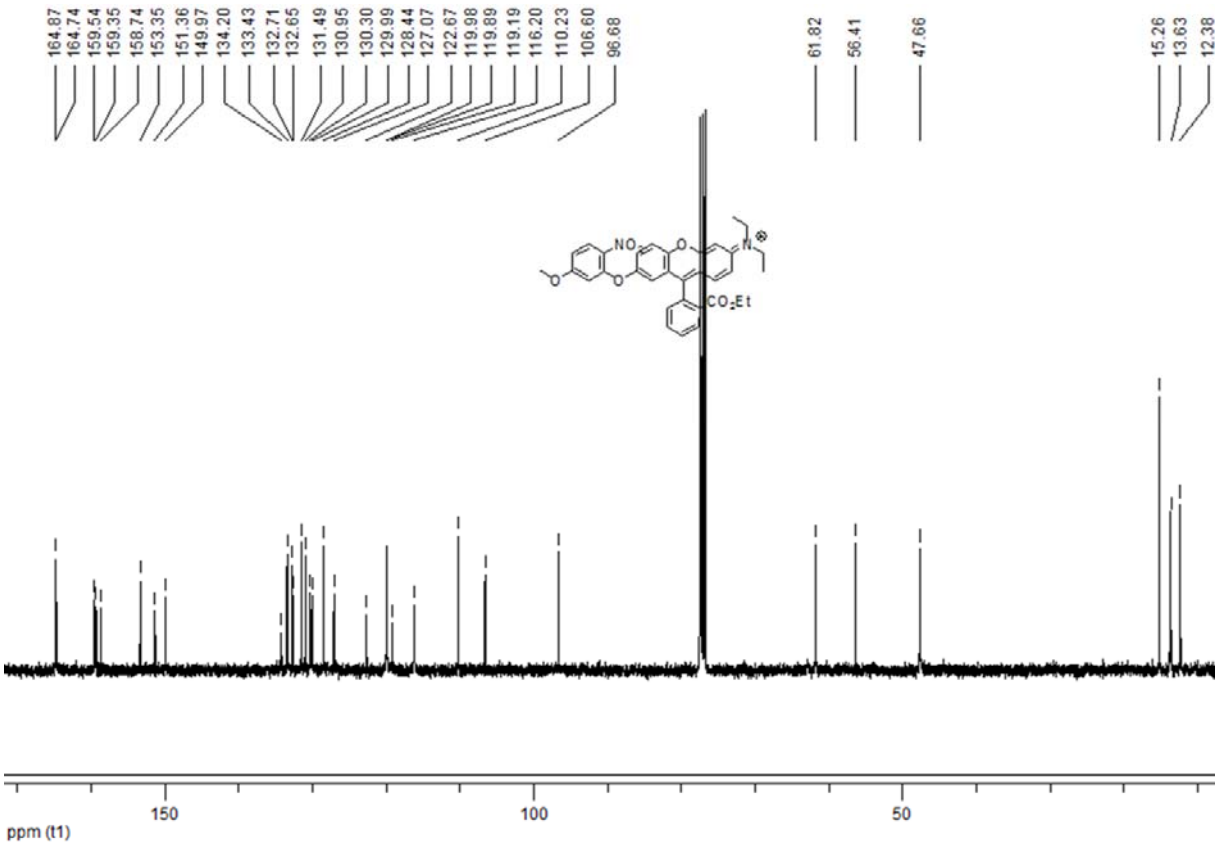

Fig. S35 ^{13}C NMR spectrum of **11** (100 MHz, $CDCl_3$). * solvent (EtOH).

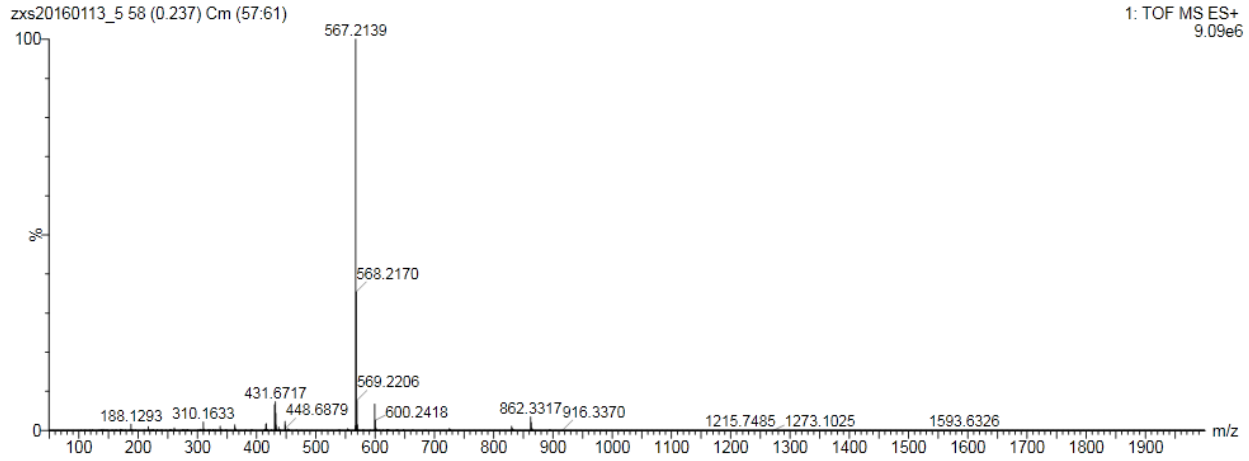

Fig. S36 HRMS of **11**. HRMS: m/z [M – Cl^-] = 567.2139; Calcd for [$C_{33}H_{21}N_2O_7^+$] = 567.2131.

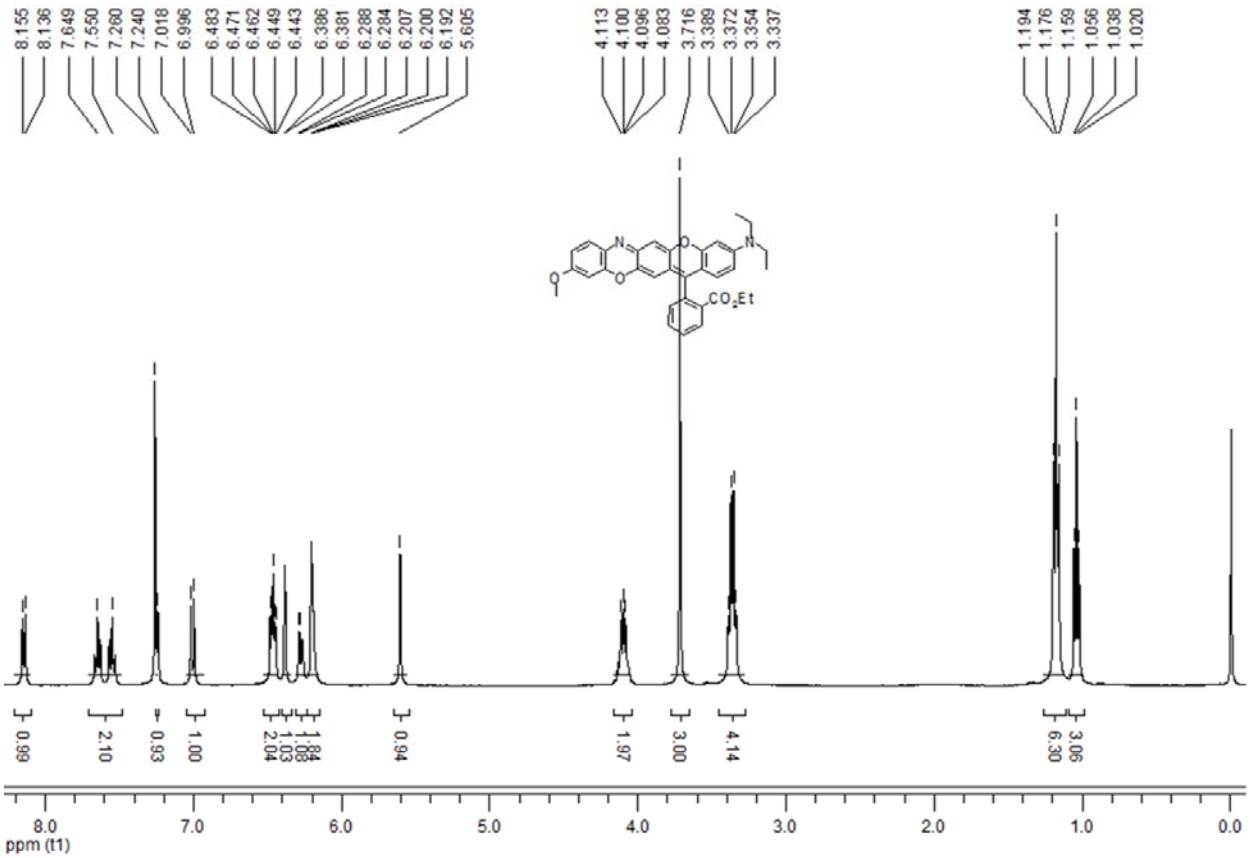

Fig. S37 ^{1}H NMR spectrum of **RE2** (400 MHz, $CDCl_3$).

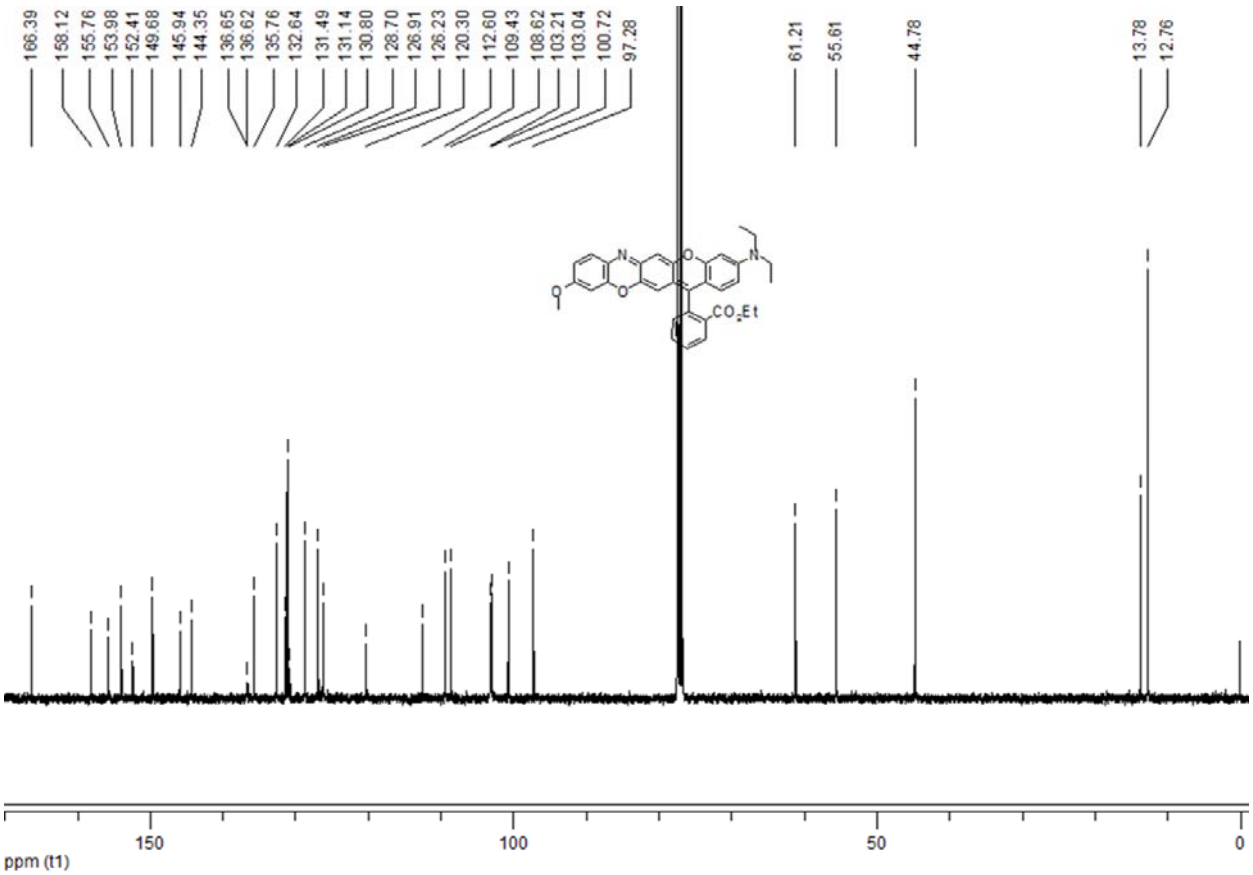

Fig. S38 ^{13}C NMR spectrum of **RE2** (100 MHz, $CDCl_3$).

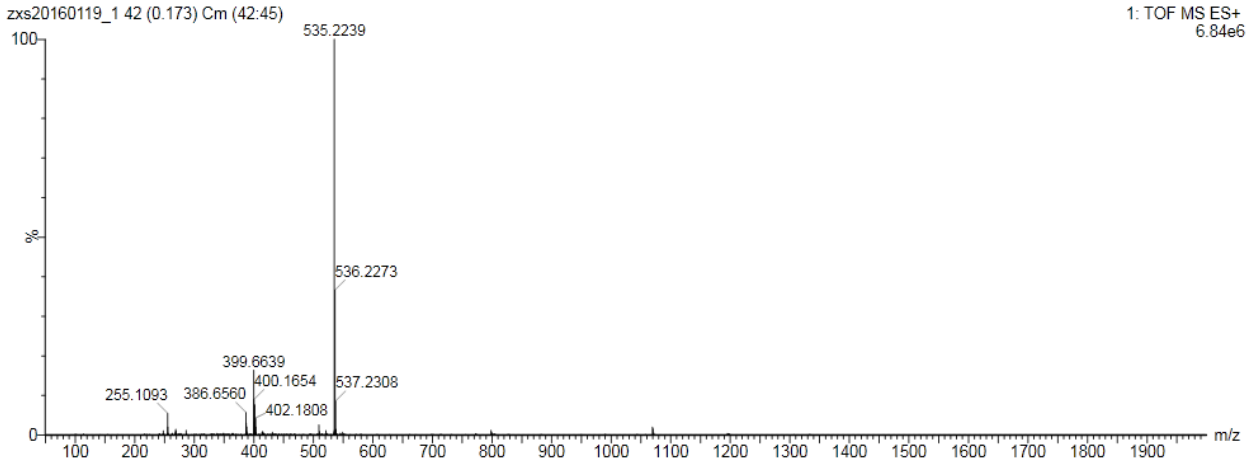

Fig. S39 HRMS of **RE2**. HRMS: m/z [M + H^+] = 535.2239; Calcd for [$C_{33}H_{30}N_2O_5$ + H^+] = 535.2233.

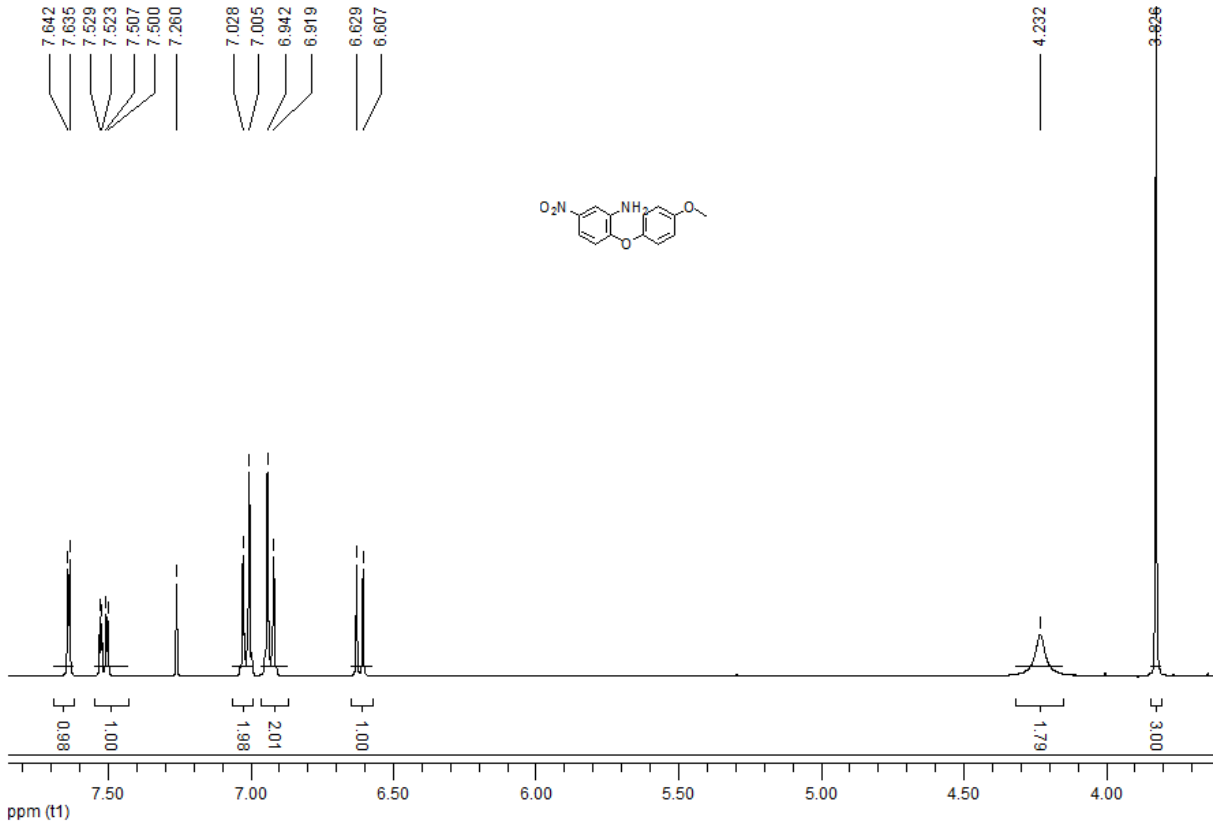

Fig. S40 ^{1}H NMR spectrum of **14** (400 MHz, $CDCl_3$).

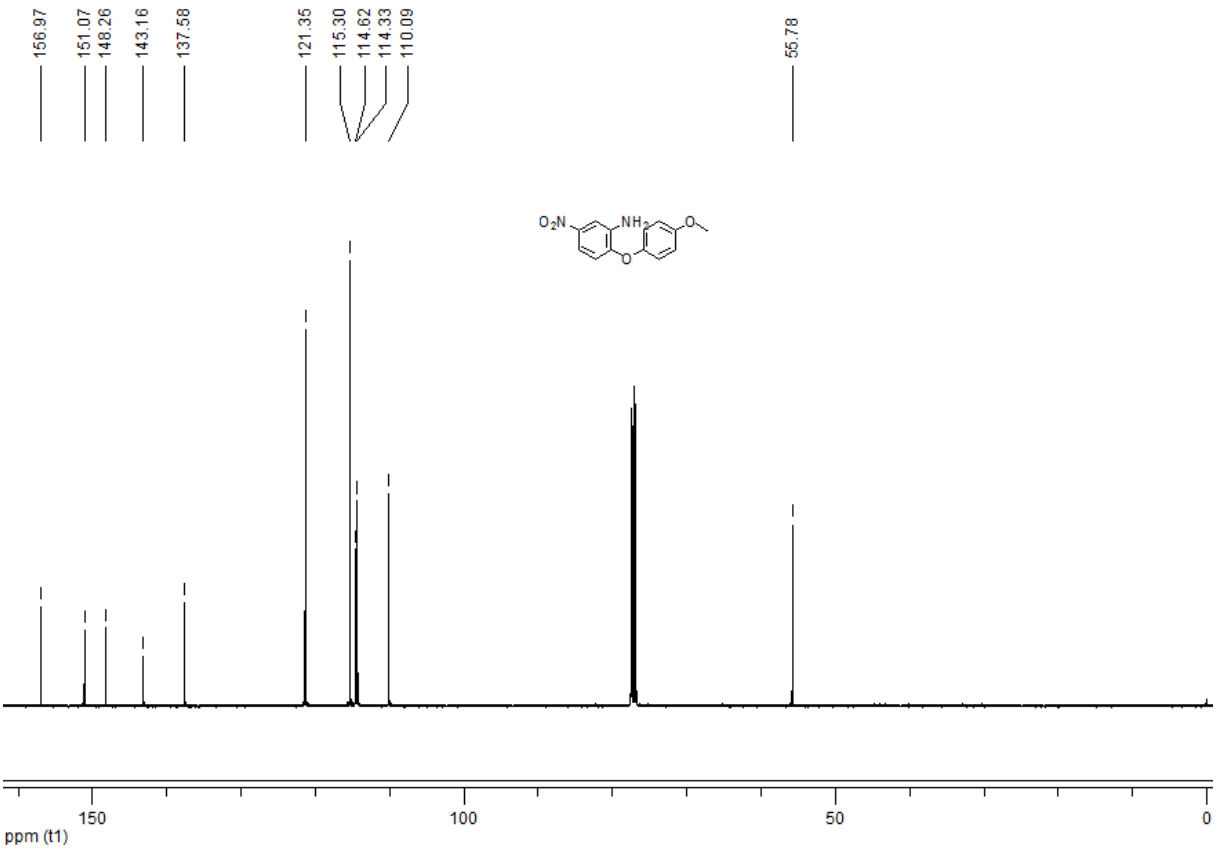

Fig. S41 ^{13}C NMR spectrum of **14** (100 MHz, $CDCl_3$).

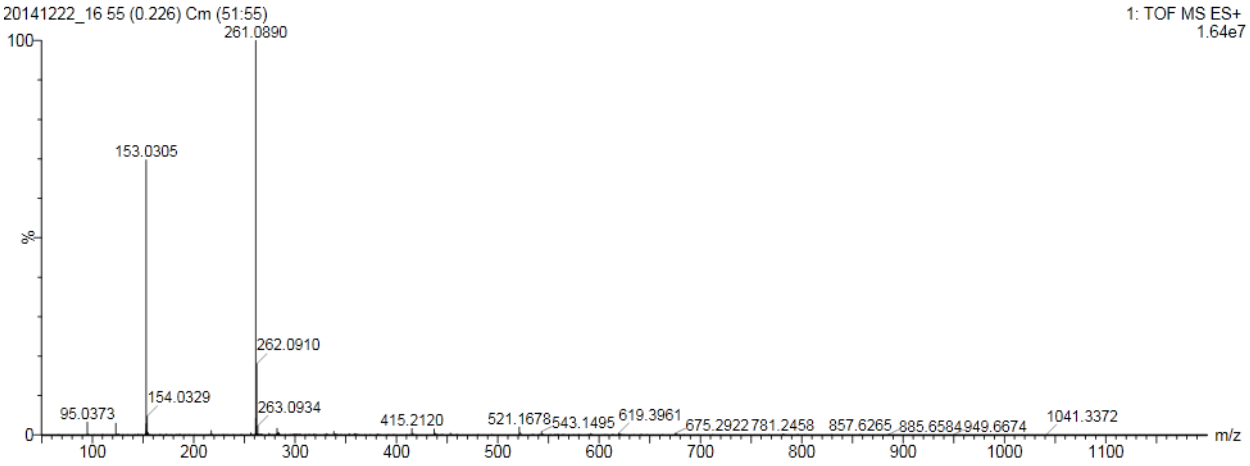

Fig. S42 HRMS of **14**. HRMS: m/z [M+H$^+$] = 261.0890, Calcd for [$C_{13}H_{12}N_2O_4$ + H$^+$] = 261.0875.

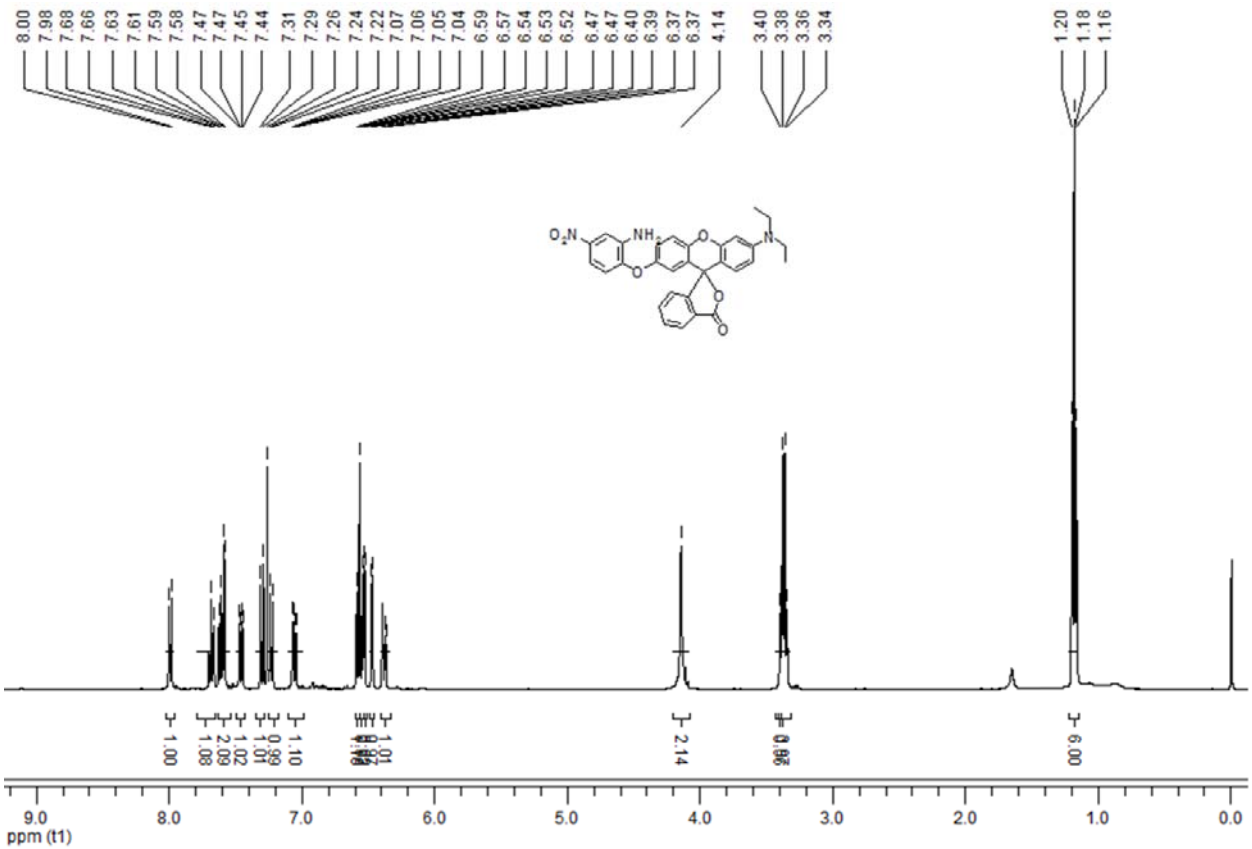

Fig. S43 ^{1}H NMR spectrum of **15** (400 MHz, $CDCl_3$).

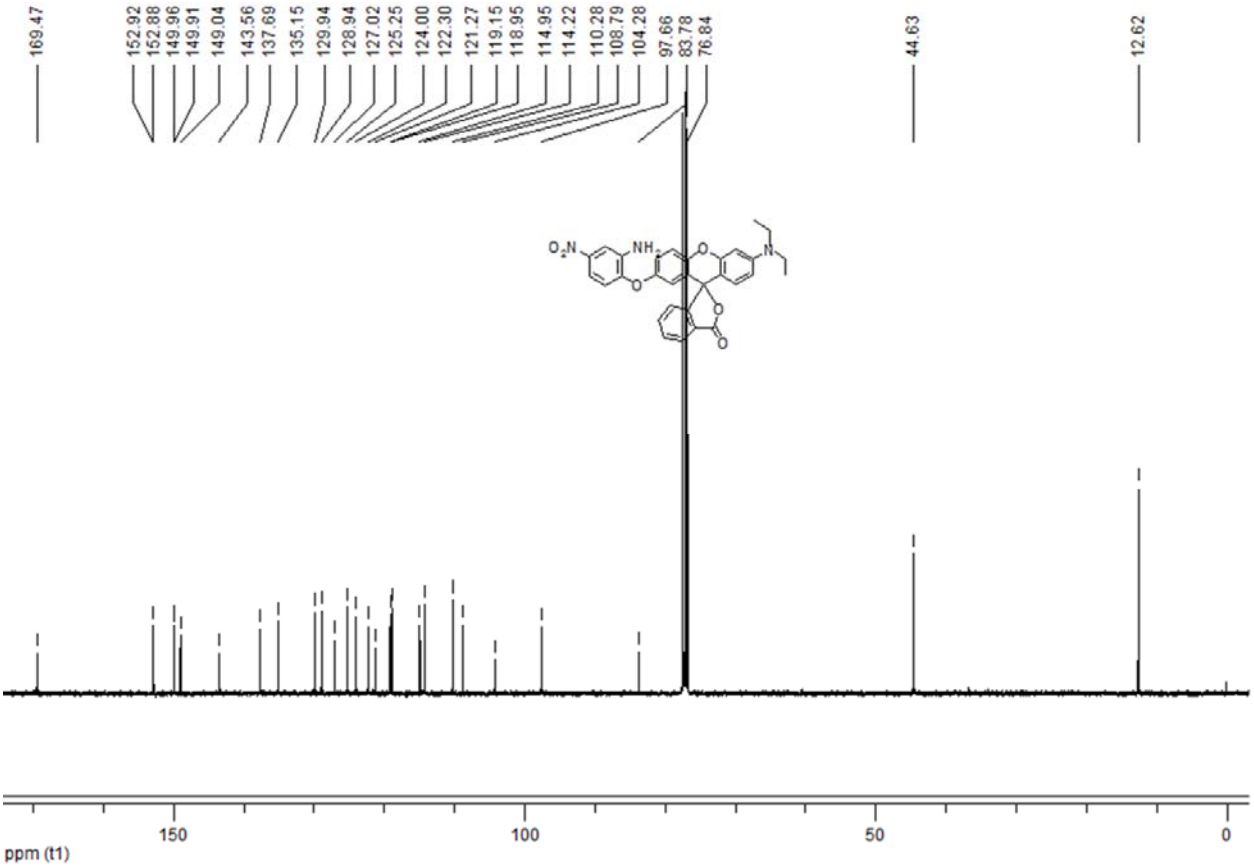

Fig. S44 ^{13}C NMR spectrum of **15** (100 MHz, $CDCl_3$).

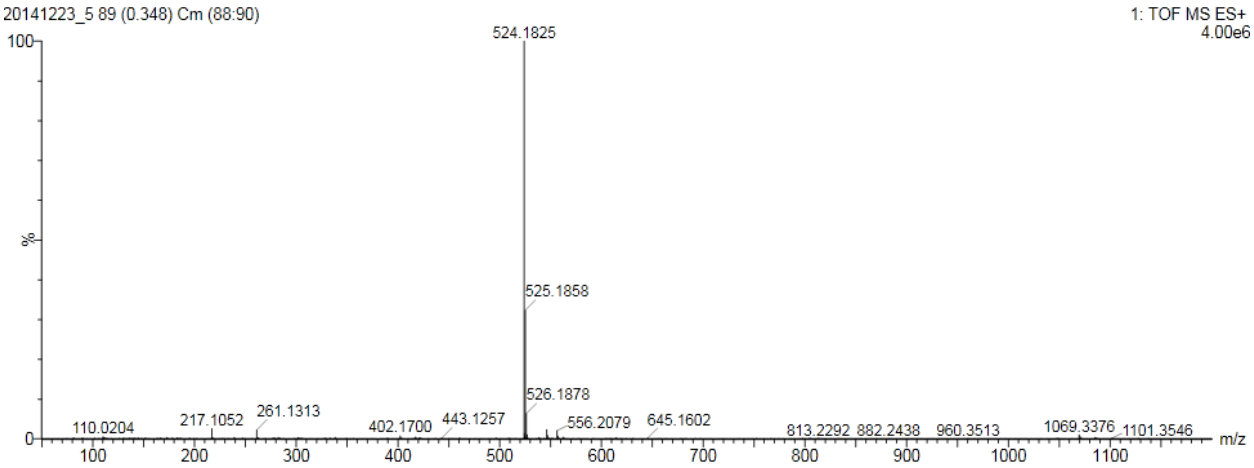

Fig. S45 HRMS of **15**. HRMS: m/z [M – Cl^-] = 524.1825, calcd for [$C_{30}H_{26}N_3O_6^+$] = 524.1822.

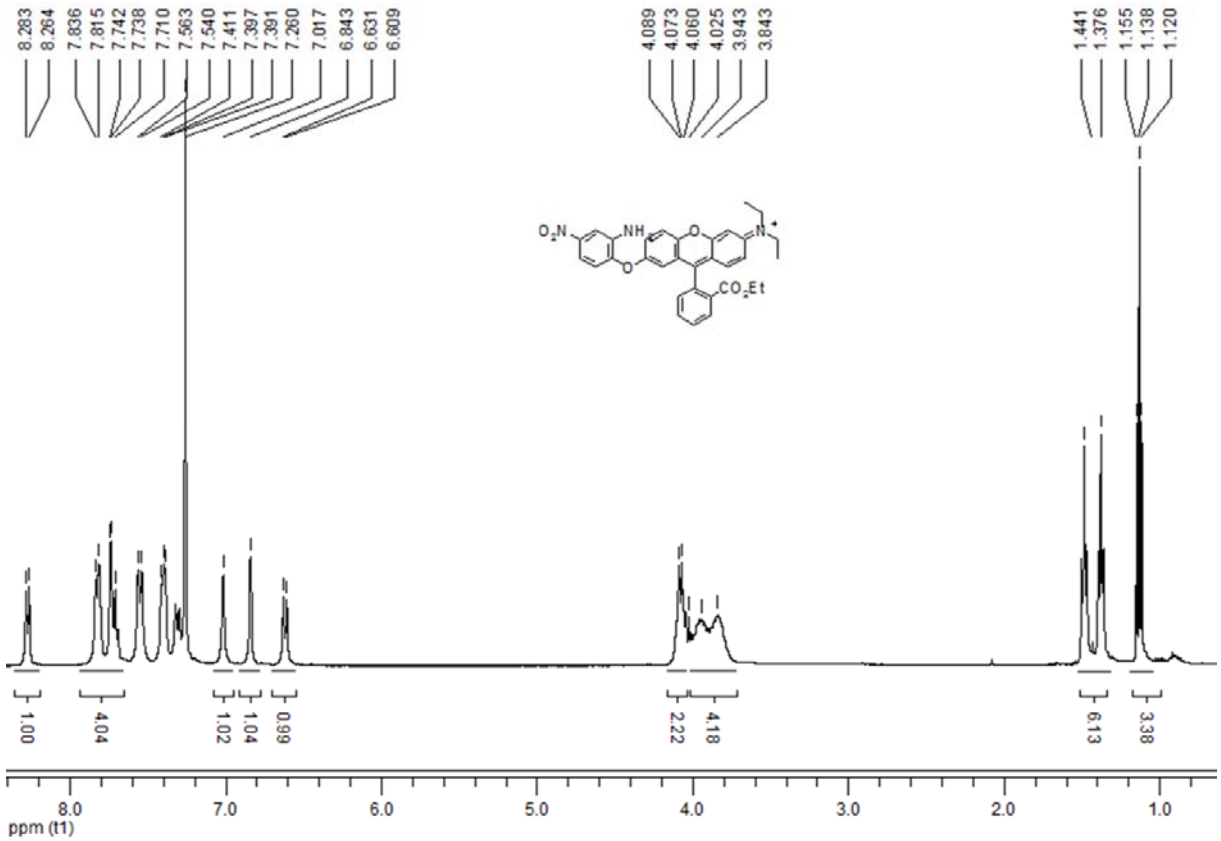

Fig. S46 ^{1}H NMR spectrum of **16** (400 MHz, $CDCl_3$).

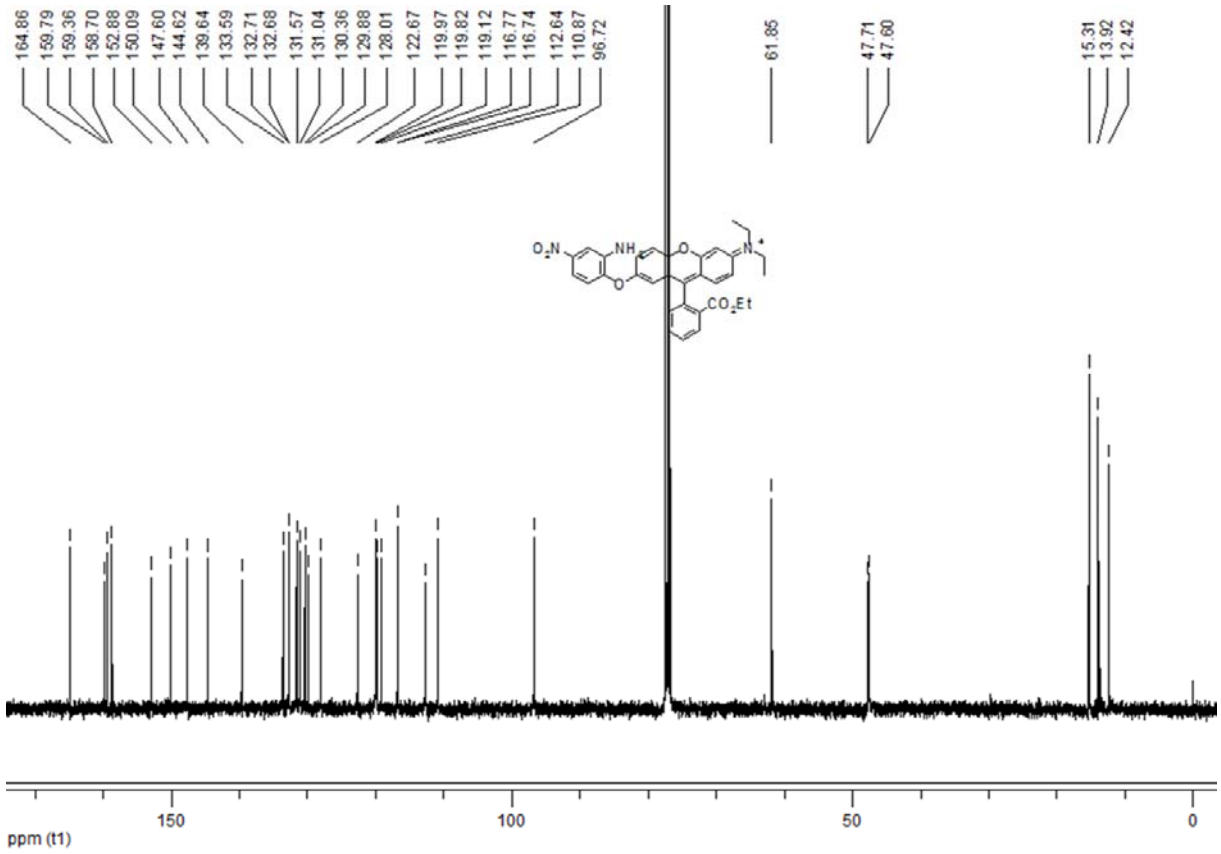

Fig. S47 ^{13}C NMR spectrum of **16** (100 MHz, $CDCl_3$).

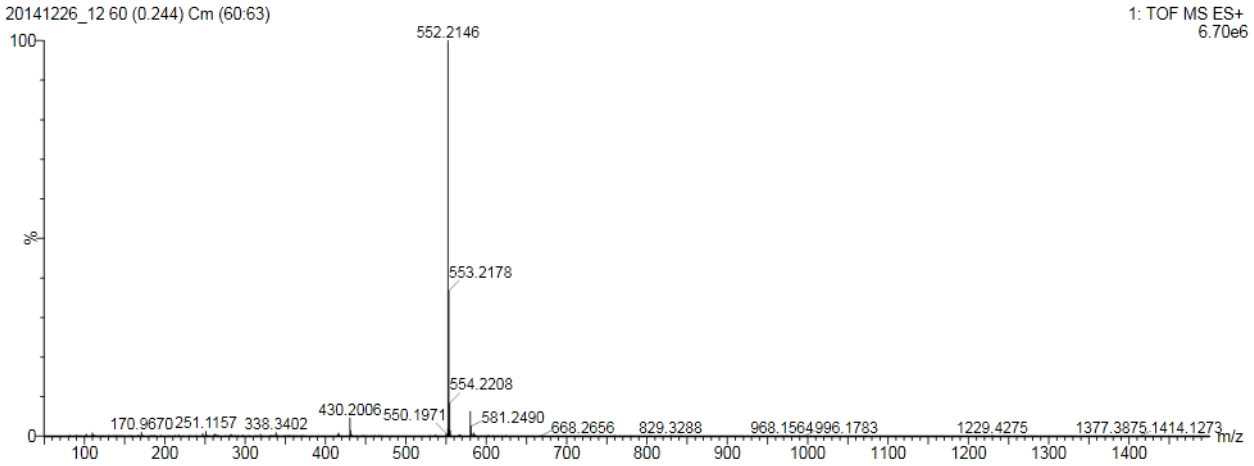

Fig. S48 HRMS of **16**. HRMS: m/z [M + H^+] = 552.2146, calcd for [$C_{30}H_{25}N_3O_6$ + H^+] = 552.2129.

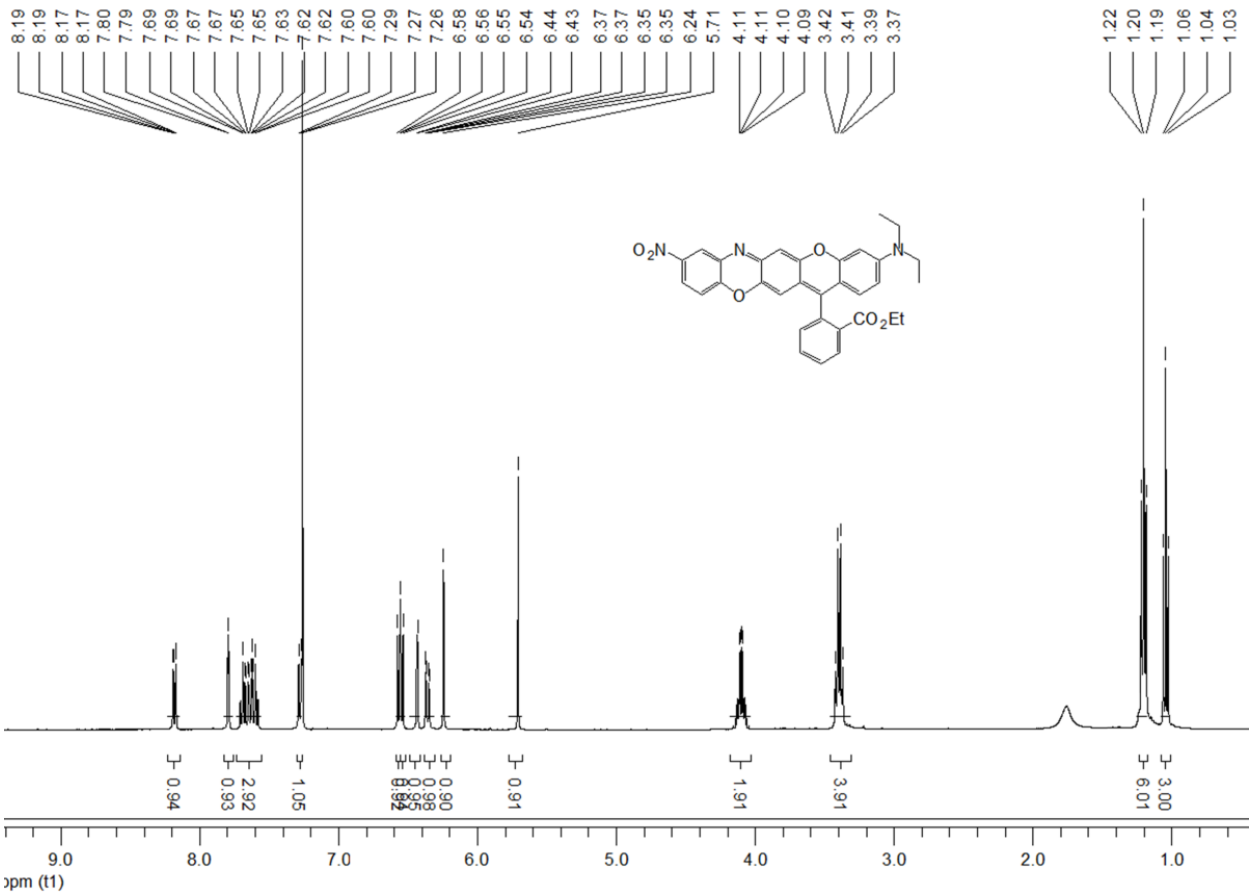

Fig. S49 ^{1}H NMR spectrum of **RE3** (400 MHz, $CDCl_3$).

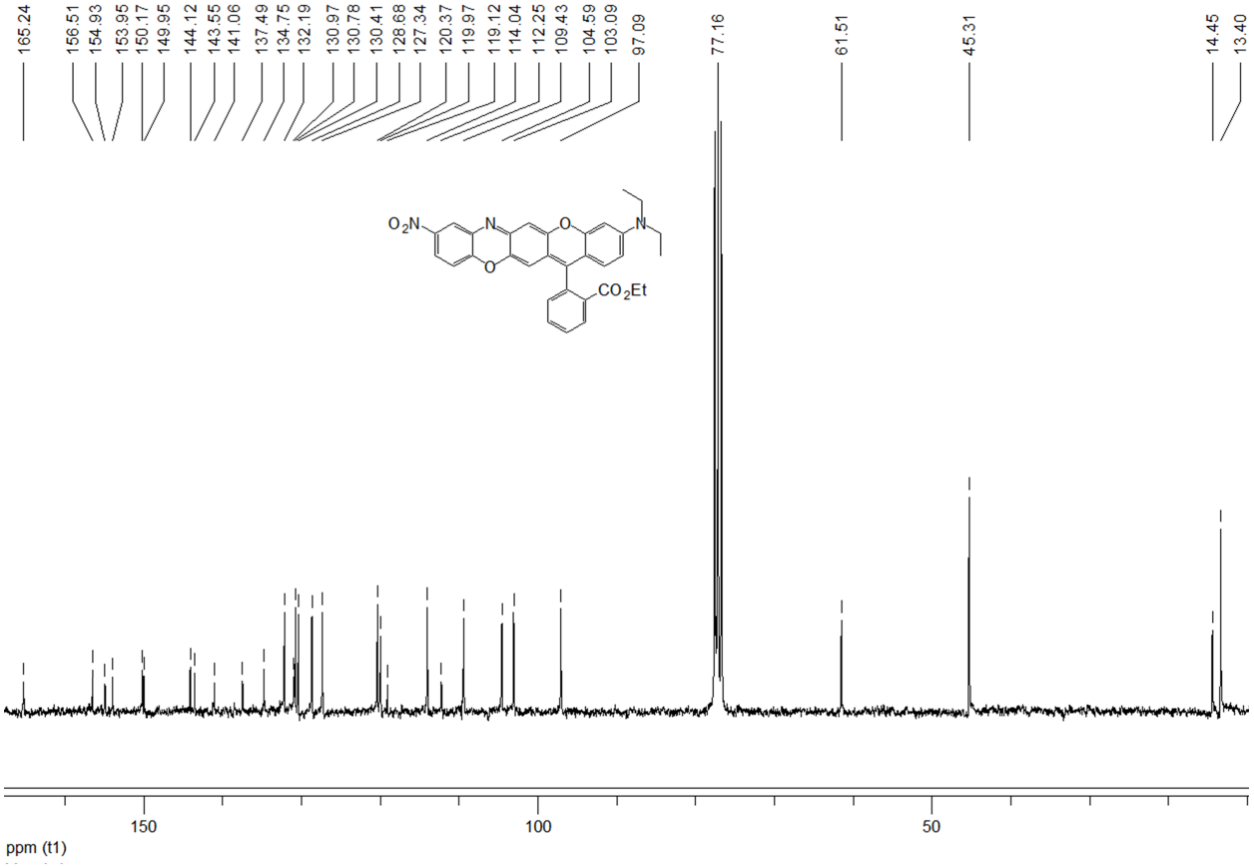

Fig. S50 ^{13}C NMR spectrum of **RE3** (75 MHz, $CDCl_3$).

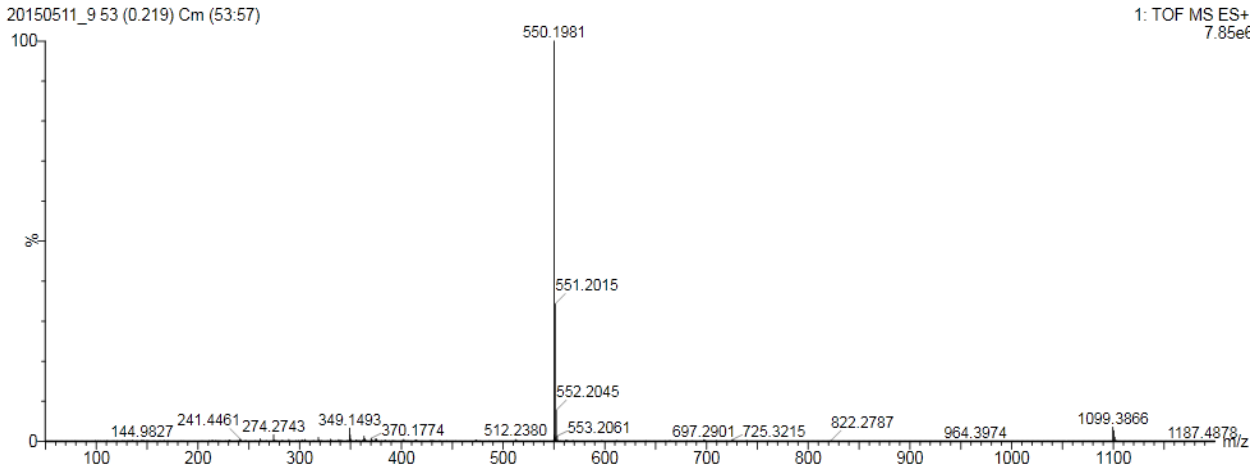

Fig. S51 HRMS of **RE3**. m/z [M + H^+] = 550.1981, calcd for [$C_{32}H_{27}N_3O_6$ + H^+] = 550.1978.

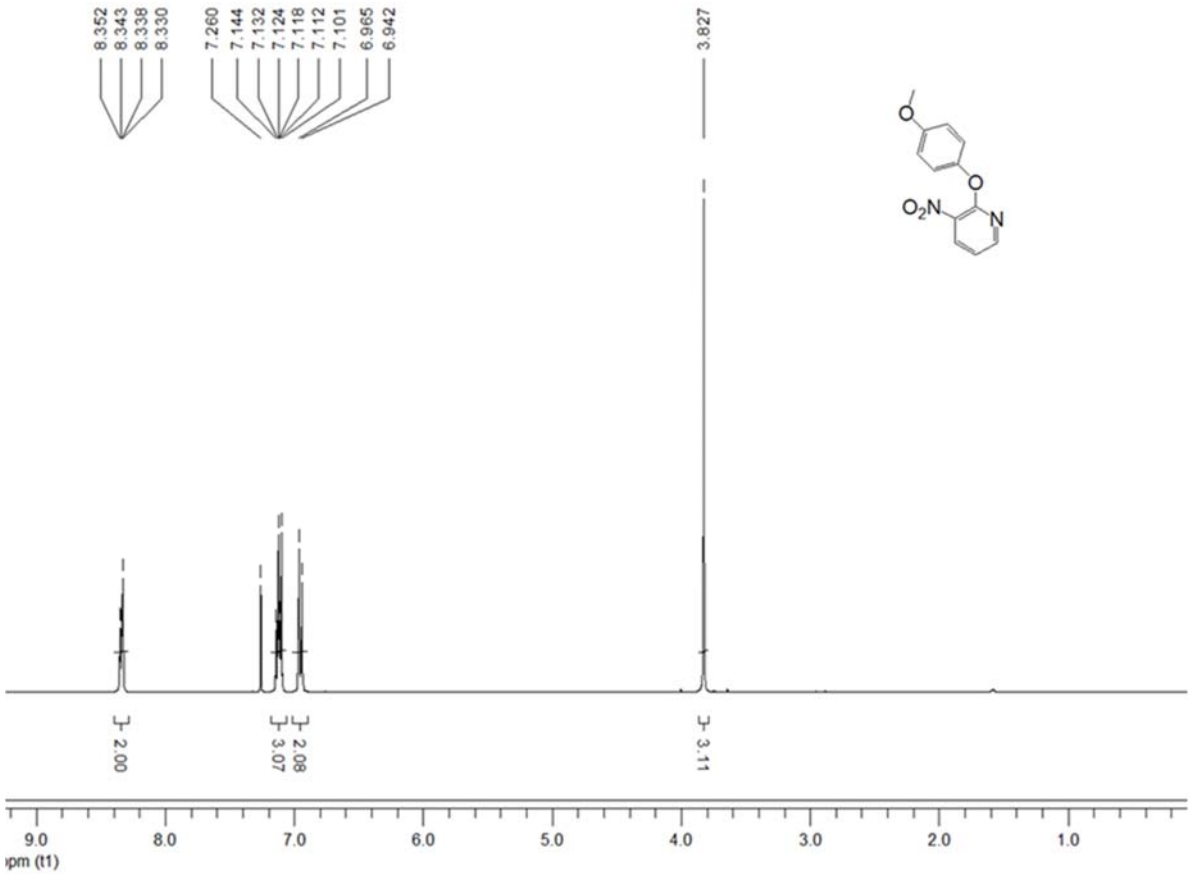

Fig. S52 ^{1}H NMR spectrum of **18** (400 MHz, $CDCl_3$).

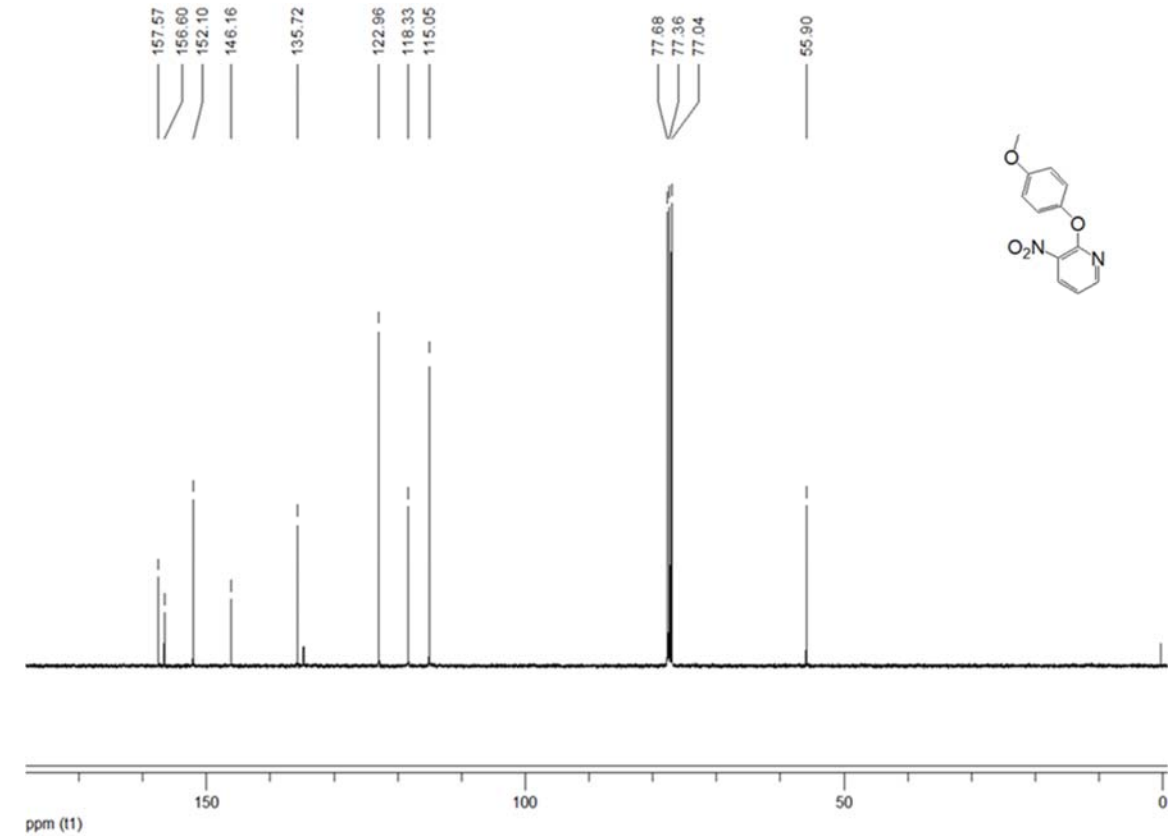

Fig. S53 ^{13}C NMR spectrum of **18** (100 MHz, $CDCl_3$).

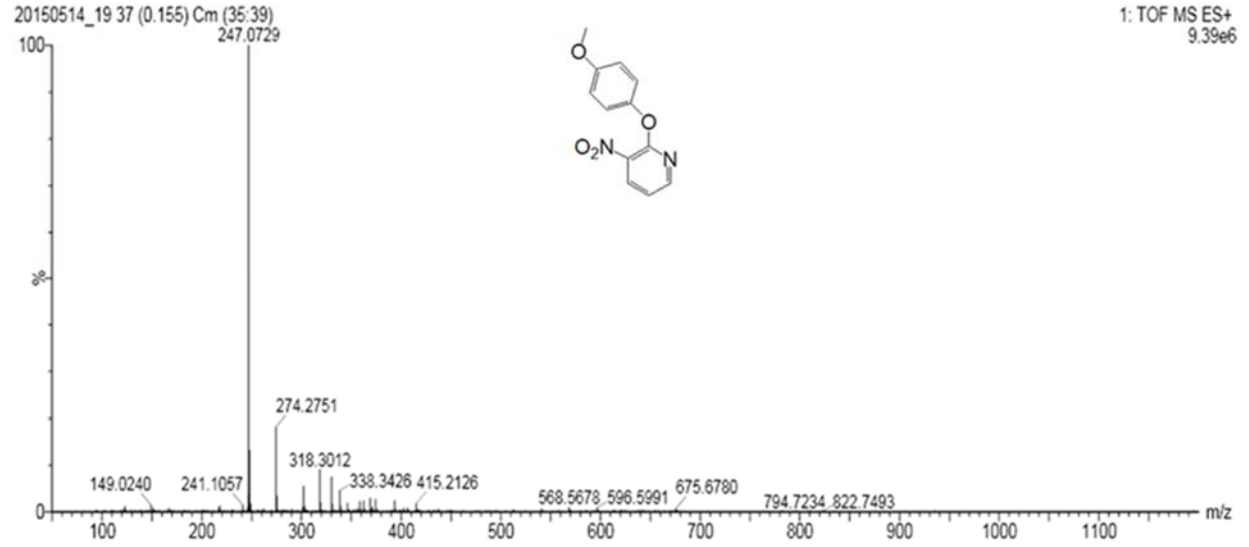

Fig. S54 HRMS of **18**. m/z [M + H$^+$] = 247.0729; Calcd for [$C_{12}H_{10}N_2O_4$ + H$^+$] = 247.0719.

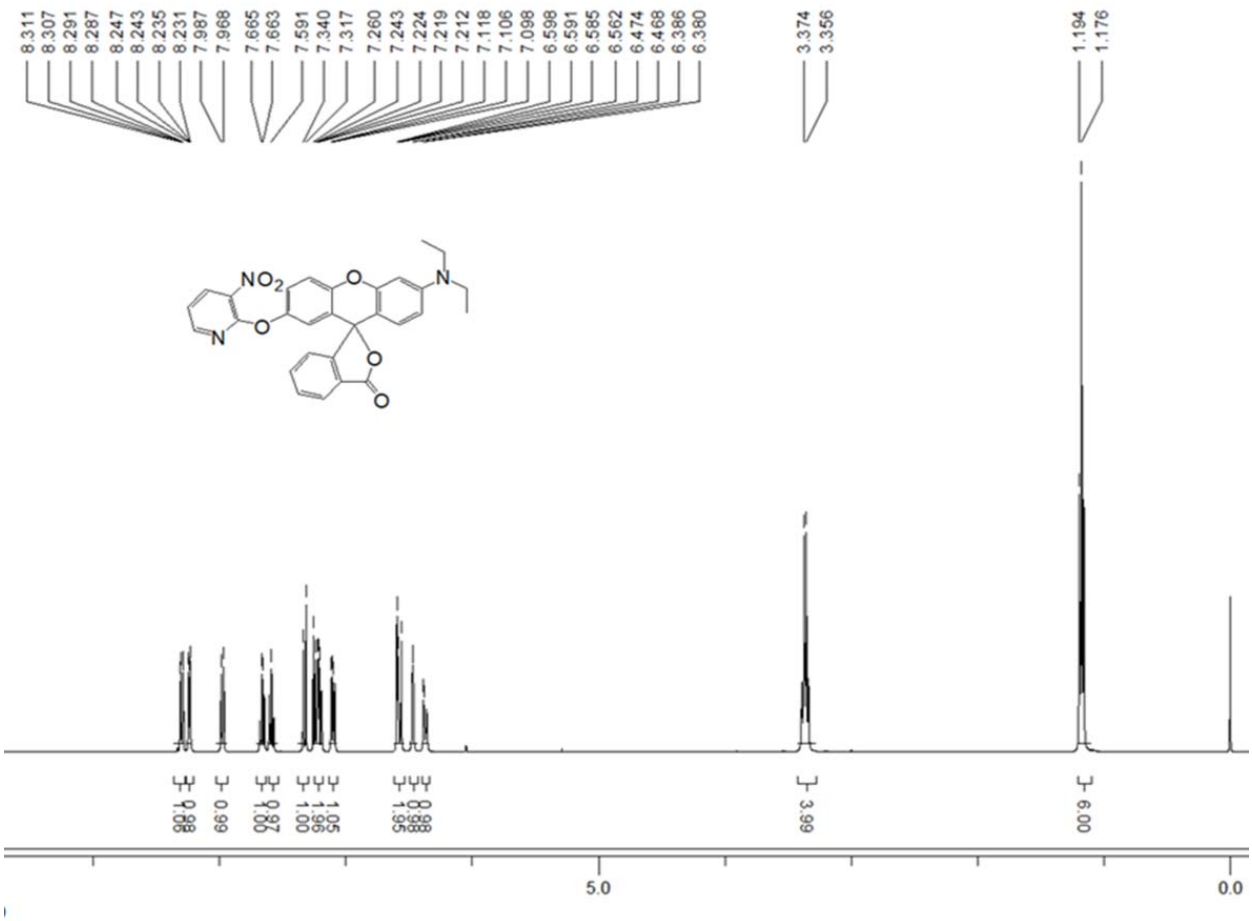

Fig. S55 ^{1}H NMR spectrum of **19** (400 MHz, $CDCl_3$).

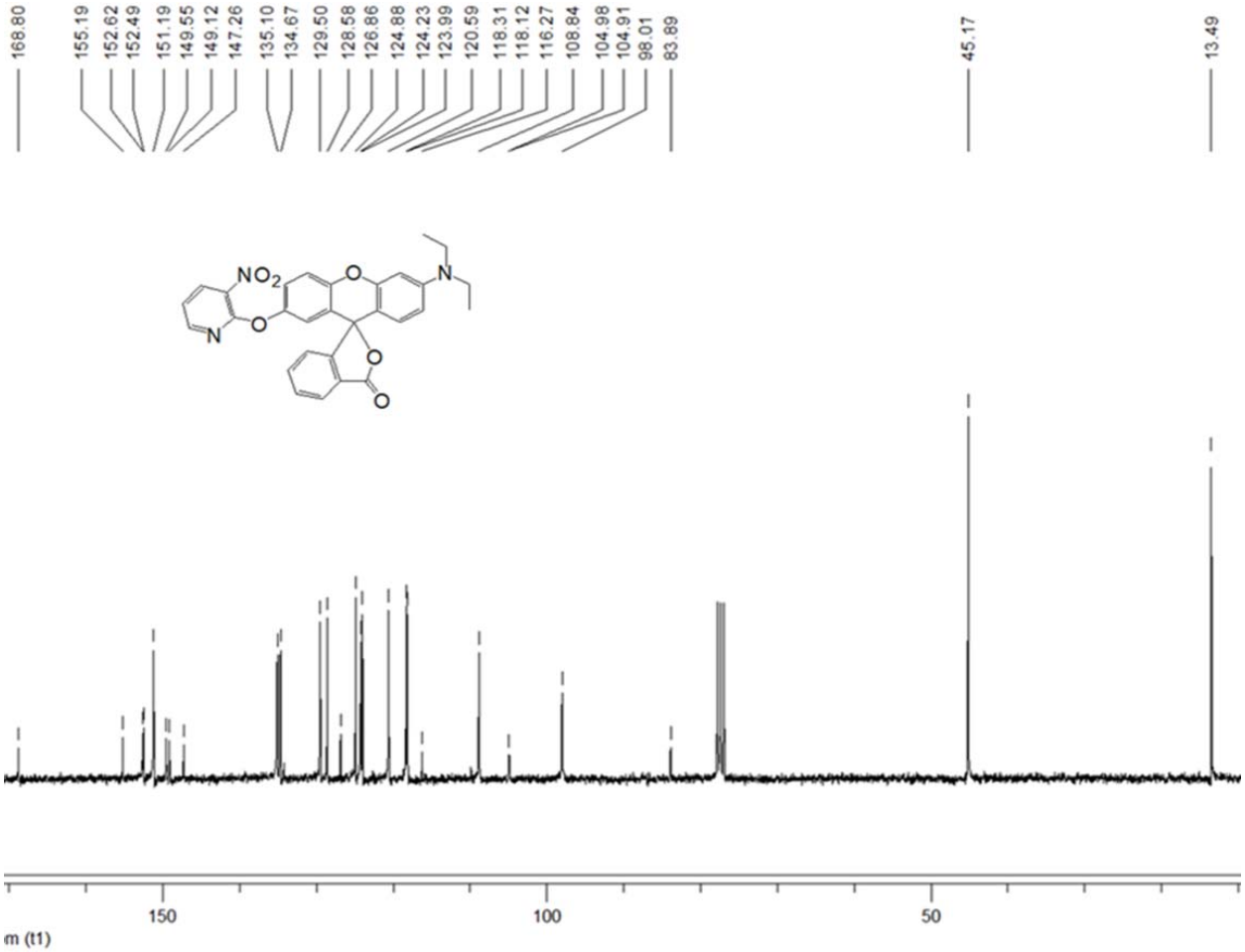

Fig. S56 ^{13}C NMR spectrum of **19** (100 MHz, $CDCl_3$).

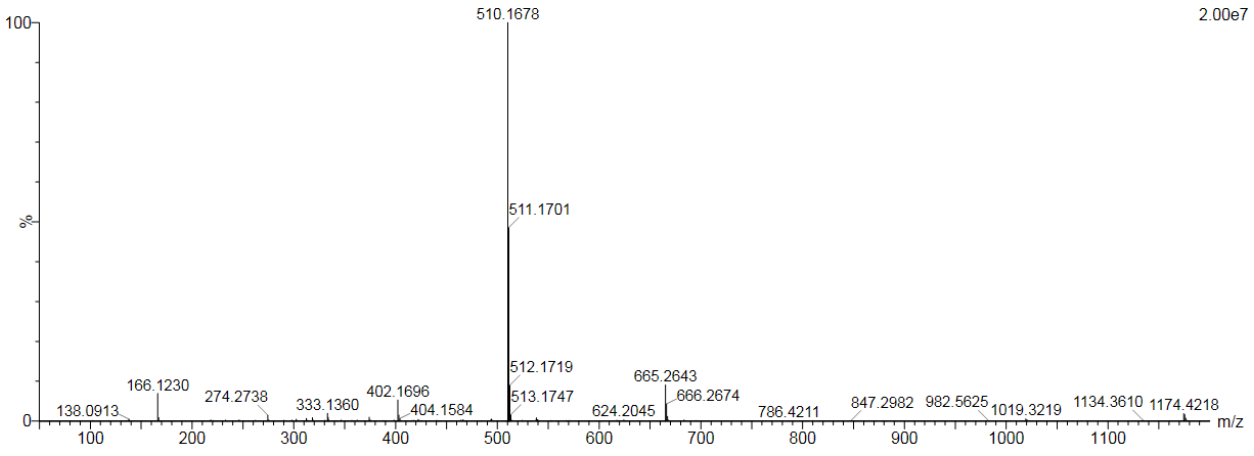

Fig. S57 HRMS of **19**. HRMS: m/z [M + H^+] = 510.1678; Calcd for [$C_{29}H_{23}N_3O_6$ + H^+] = 510.1665.

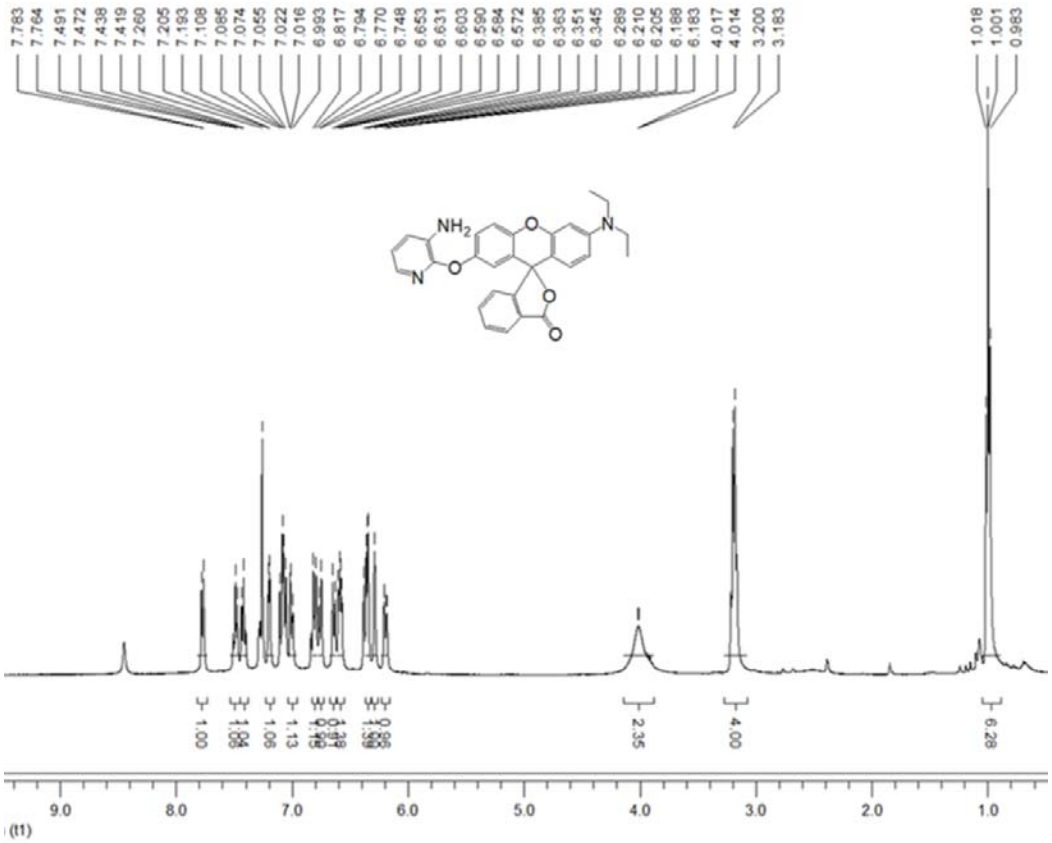

Fig. S58 ^{1}H NMR spectrum of **20** (400 MHz, $CDCl_3$).

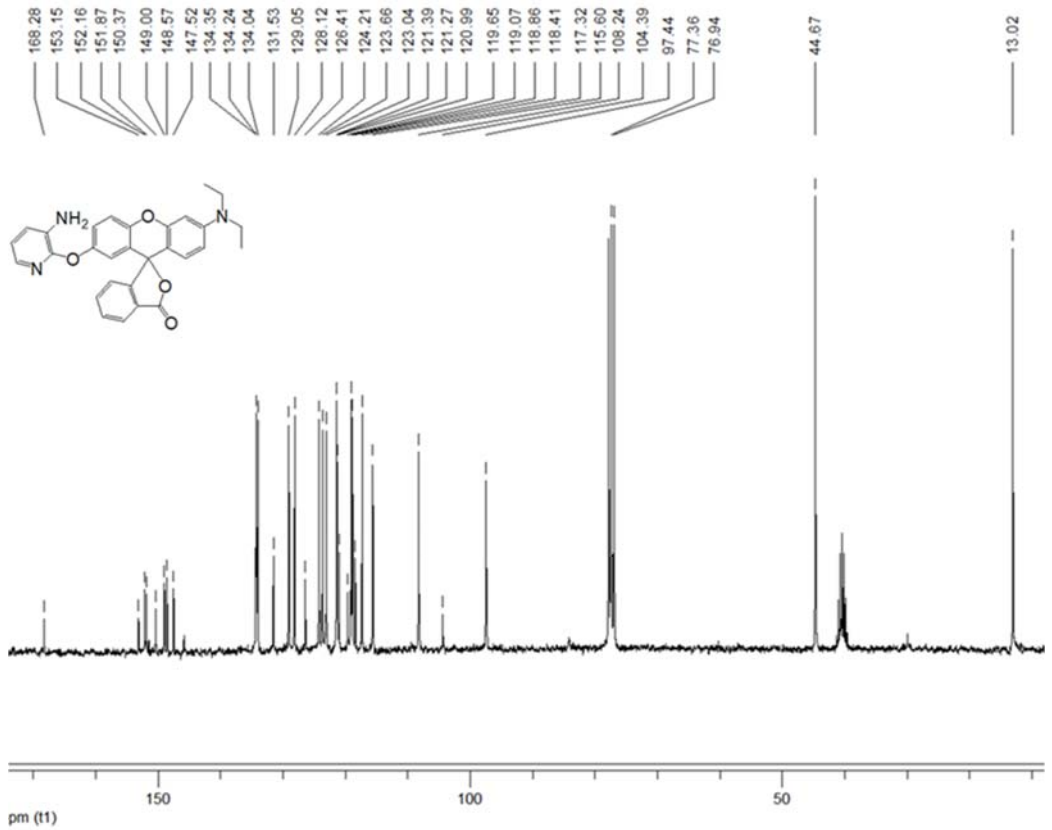

Fig. S59 ^{13}C NMR spectrum of **20** (100 MHz, $CDCl_3$).

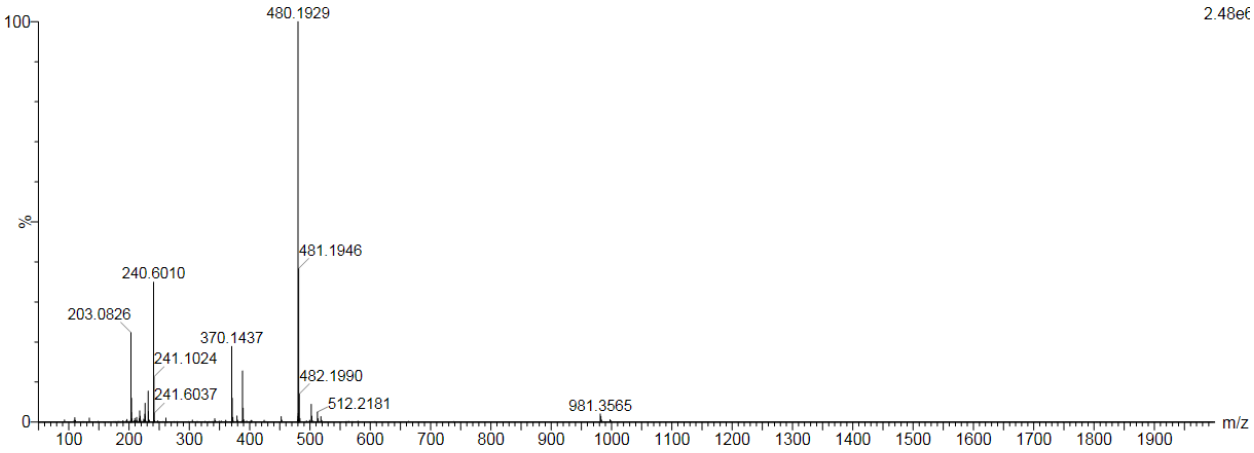

Fig. S60 HRMS of **20**. The peak at 480.1929 (m/z) corresponds to [M + H^+], Calcd for [$C_{31}H_{27}N_3O_4$ + H^+] = 480.1923; The peak at 240.6010 corresponds to [M + 2H^+]/2, Calcd for [M + 2H^+]/2 = 240.5996.

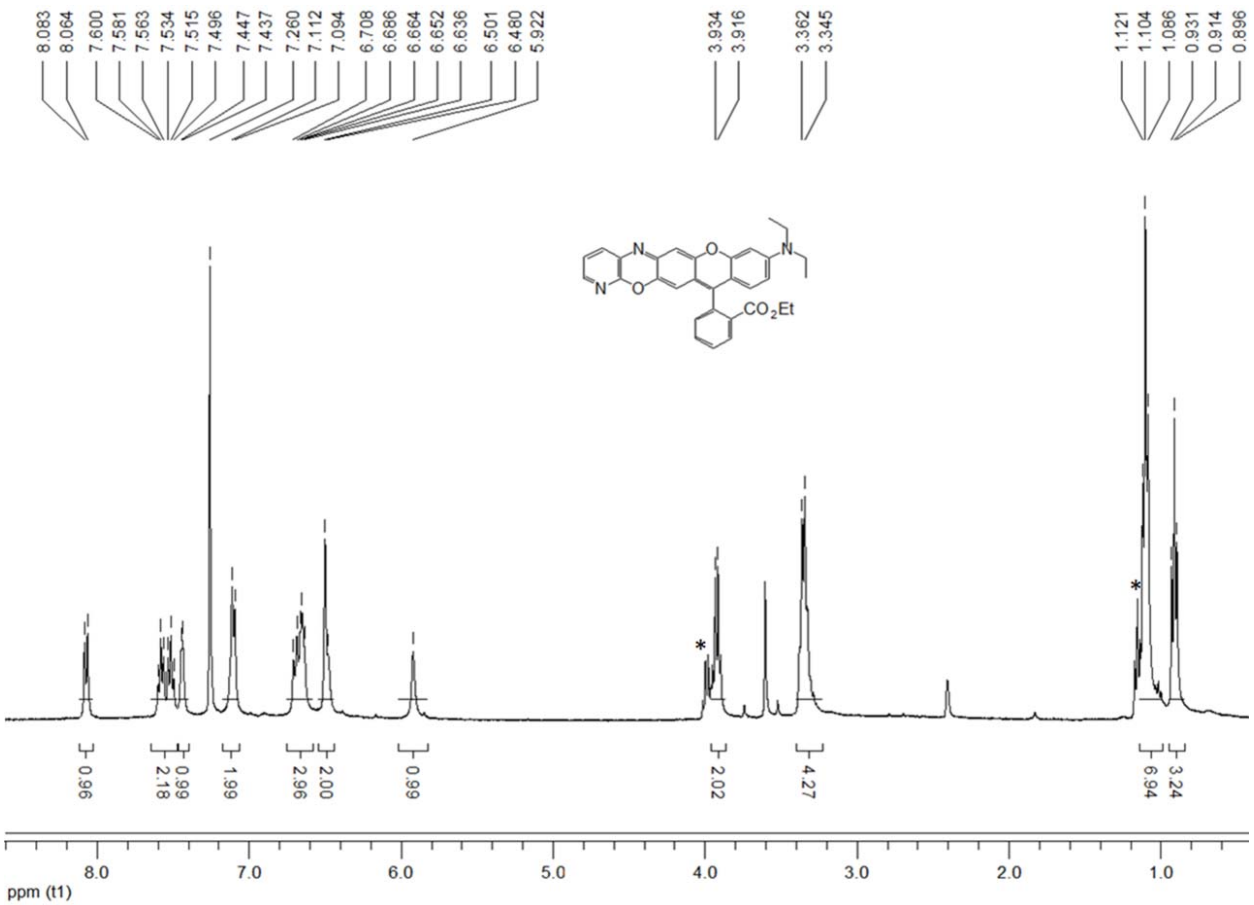

Fig. S61 ^{1}H NMR spectrum of **RE4** (400 MHz, $CDCl_3$). * solvent (EtOH).

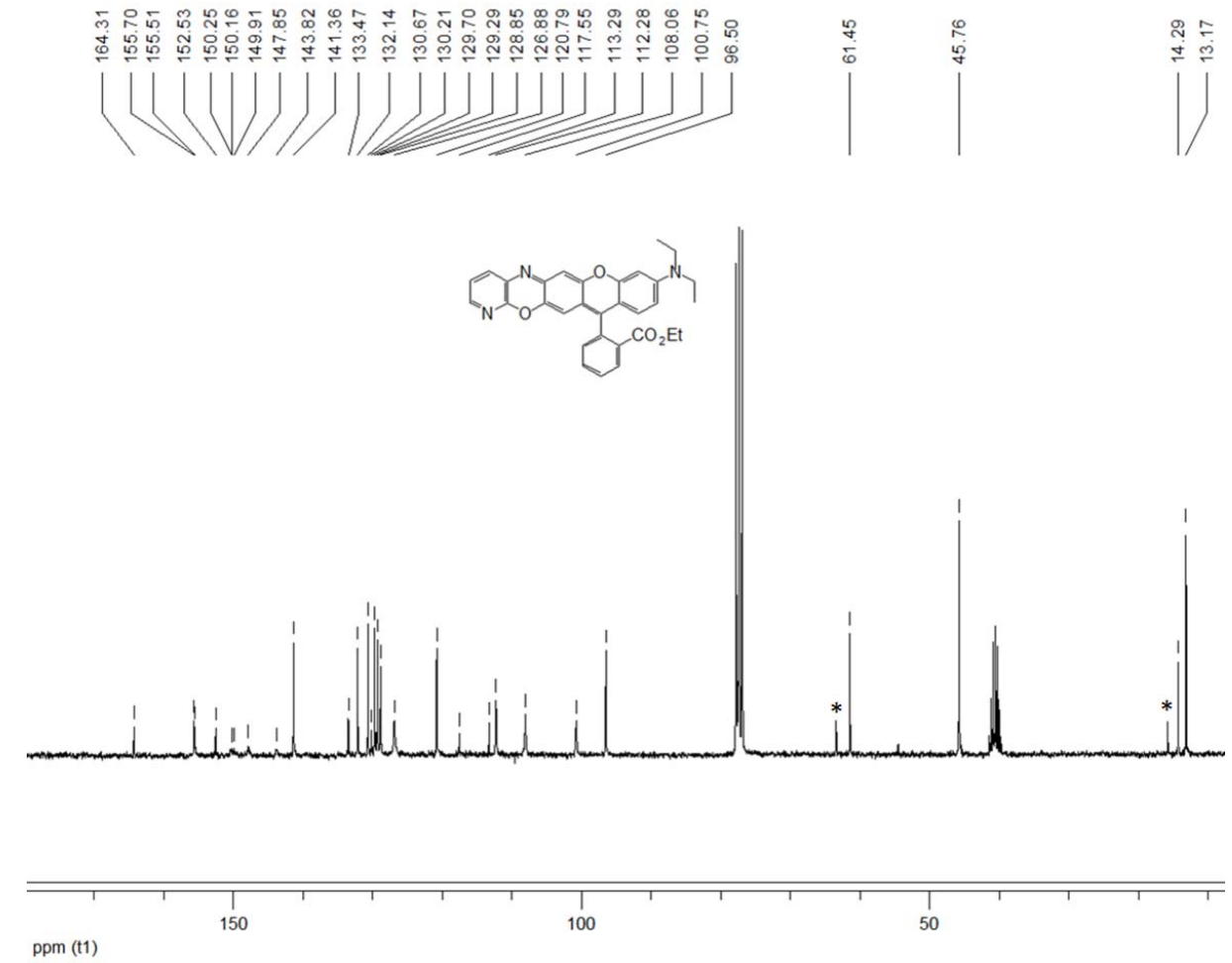

Fig. S62 ^{13}C NMR spectrum of **RE4** (100 MHz, $CDCl_3$). * solvent (EtOH)

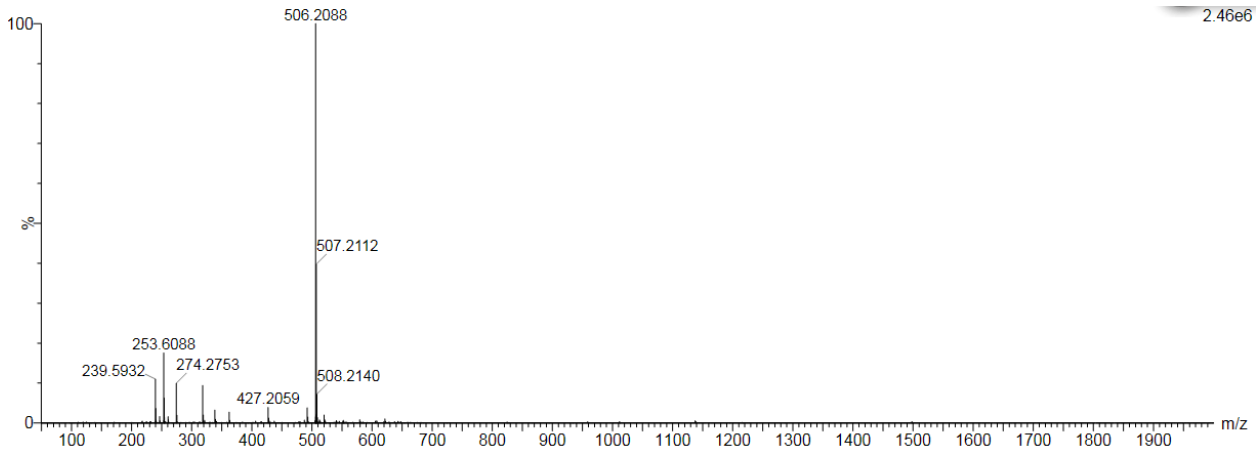

Fig. S63 HRMS of **RE4**. The peak at 506.2088 (m/z) corespond to [M + H^+], Calcd for [$C_{31}H_{27}N_3O_4$ + H^+] = 506.2080.

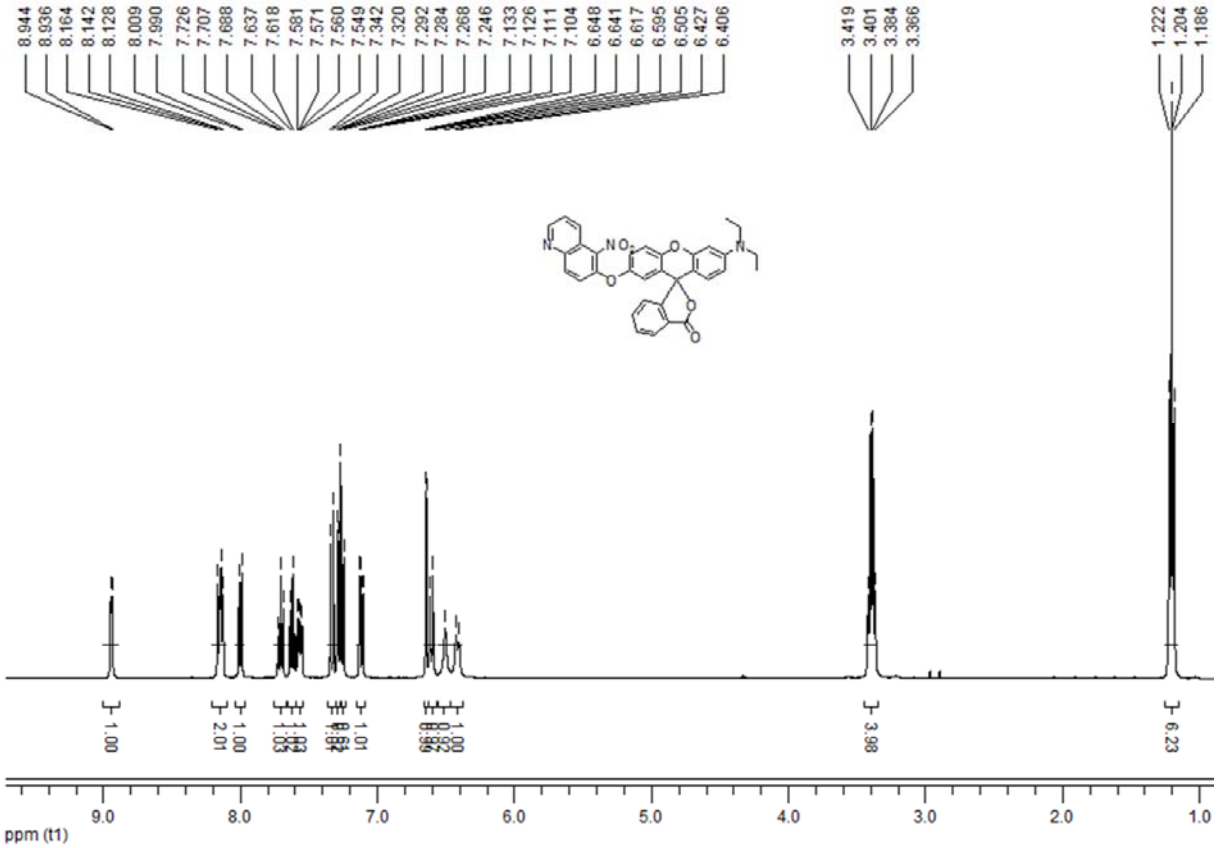

Fig. S64 ^{1}H NMR spectrum of **24** (400 MHz, $CDCl_3$).

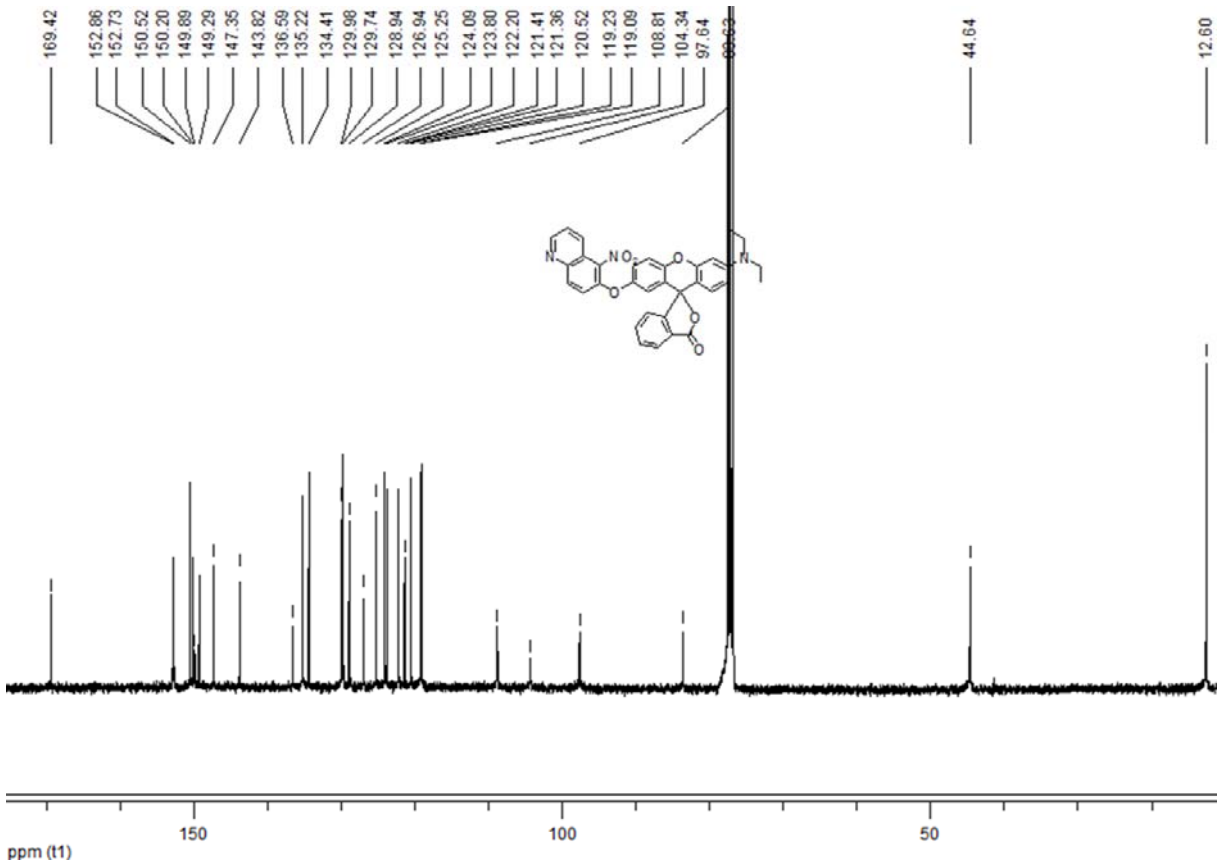

Fig. S65 ^{13}C NMR spectrum of **24** (100 MHz, $CDCl_3$).

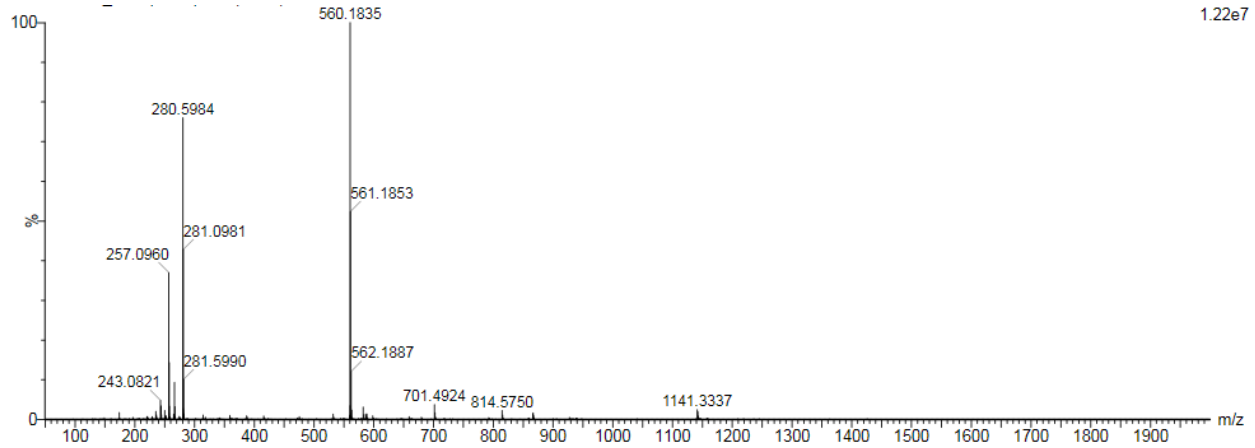

Fig. S66 HRMS of **24**. HRMS: m/z [M + H^+] = 560.1822; Calcd for [$C_{33}H_{25}N_3O_6$ + H^+] = 560.1835.

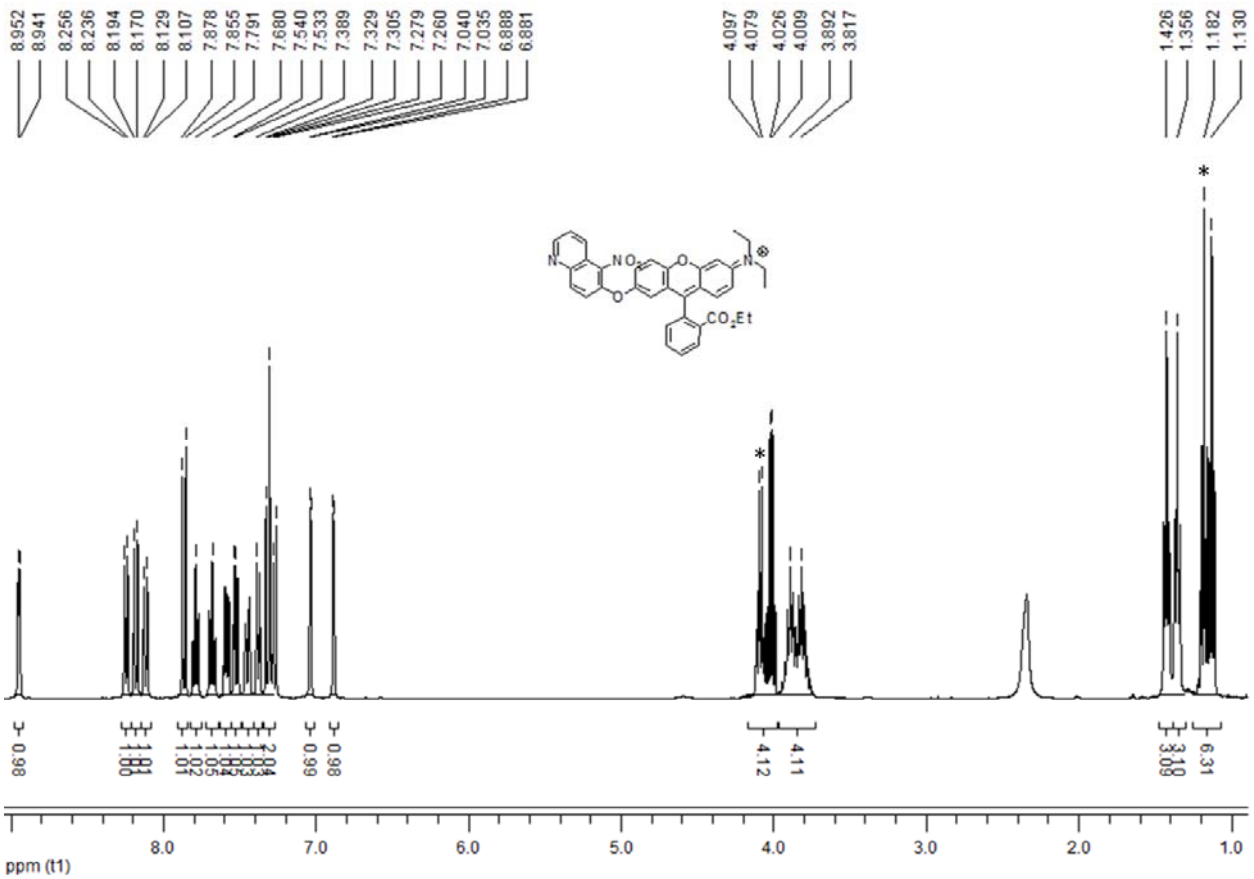

Fig. S67 ^{1}H NMR spectrum of **25** (400 MHz, $CDCl_3$). * solvent (EtOH).

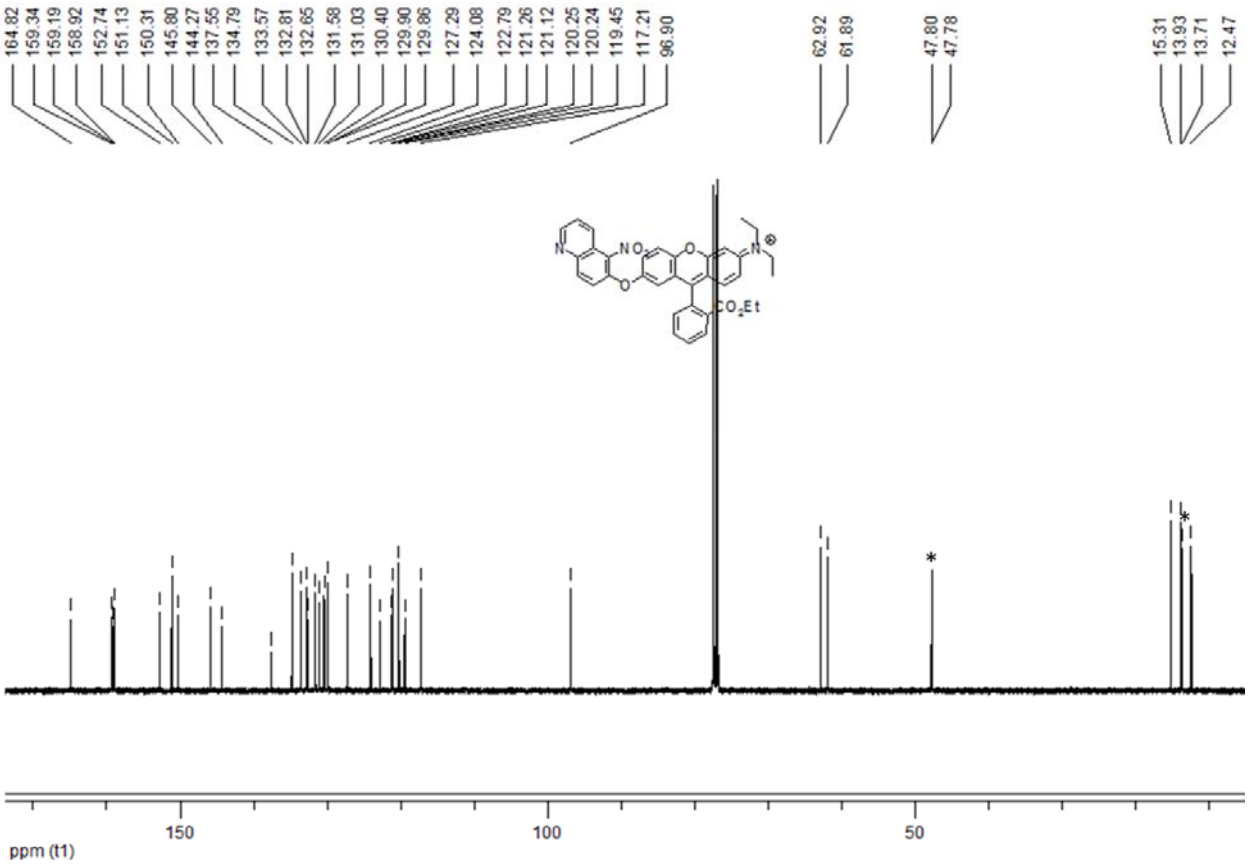

Fig. S68 ^{13}C NMR spectrum of **25** (100 MHz, $CDCl_3$). * solvent (EtOH).

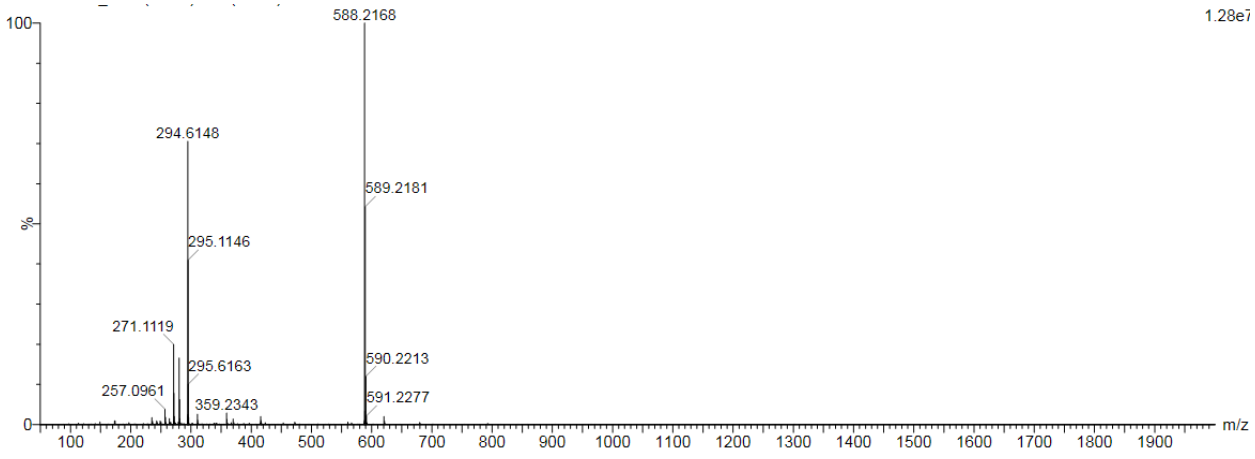

Fig. S69 HRMS of **25**. HRMS: $[M - Cl]^+$ = 588.2168; Calcd for $[C_{35}H_{30}N3O_6]^+$ = 588.2168.

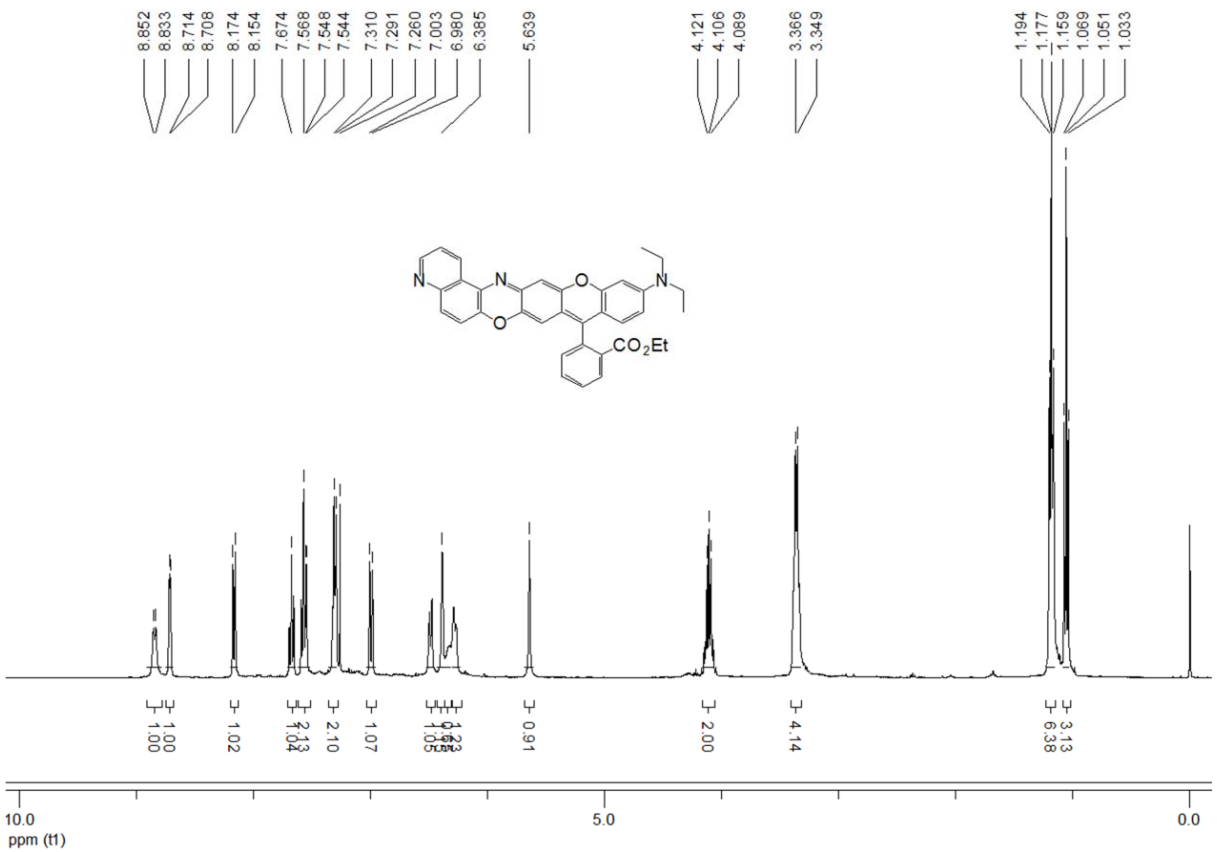

Fig. S70 ^{1}H NMR spectrum of dye **RE5** (400 MHz, $CDCl_3$).

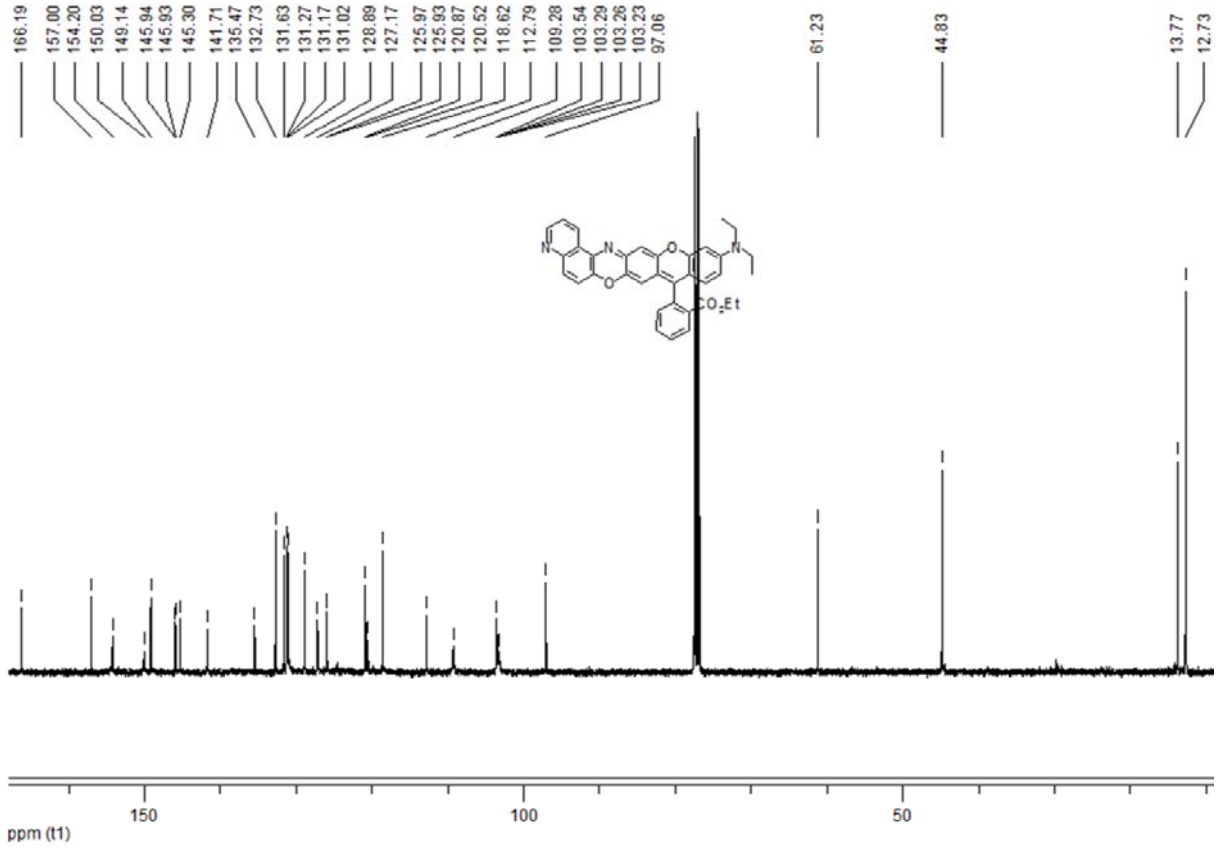

Fig. S71 ^{13}C NMR spectrum of dye **RE5** (100 MHz, $CDCl_3$).

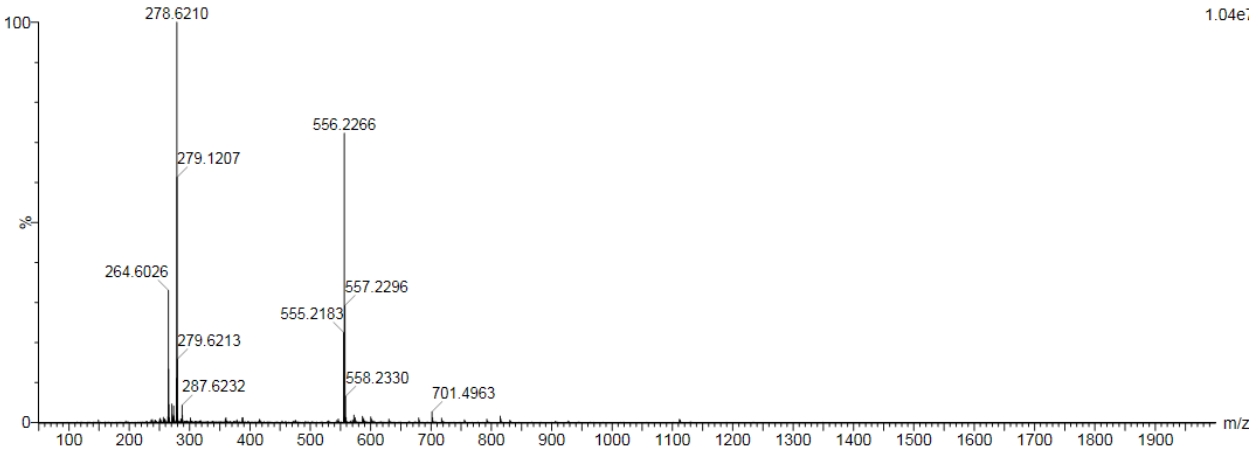

Fig. S72 HRMS of dye **RE5**. HRMS: m/z [M + H^+] = 556.2266; Calcd for [$C_{35}H_{29}N_3O_4$ + H^+] = 556.2236.

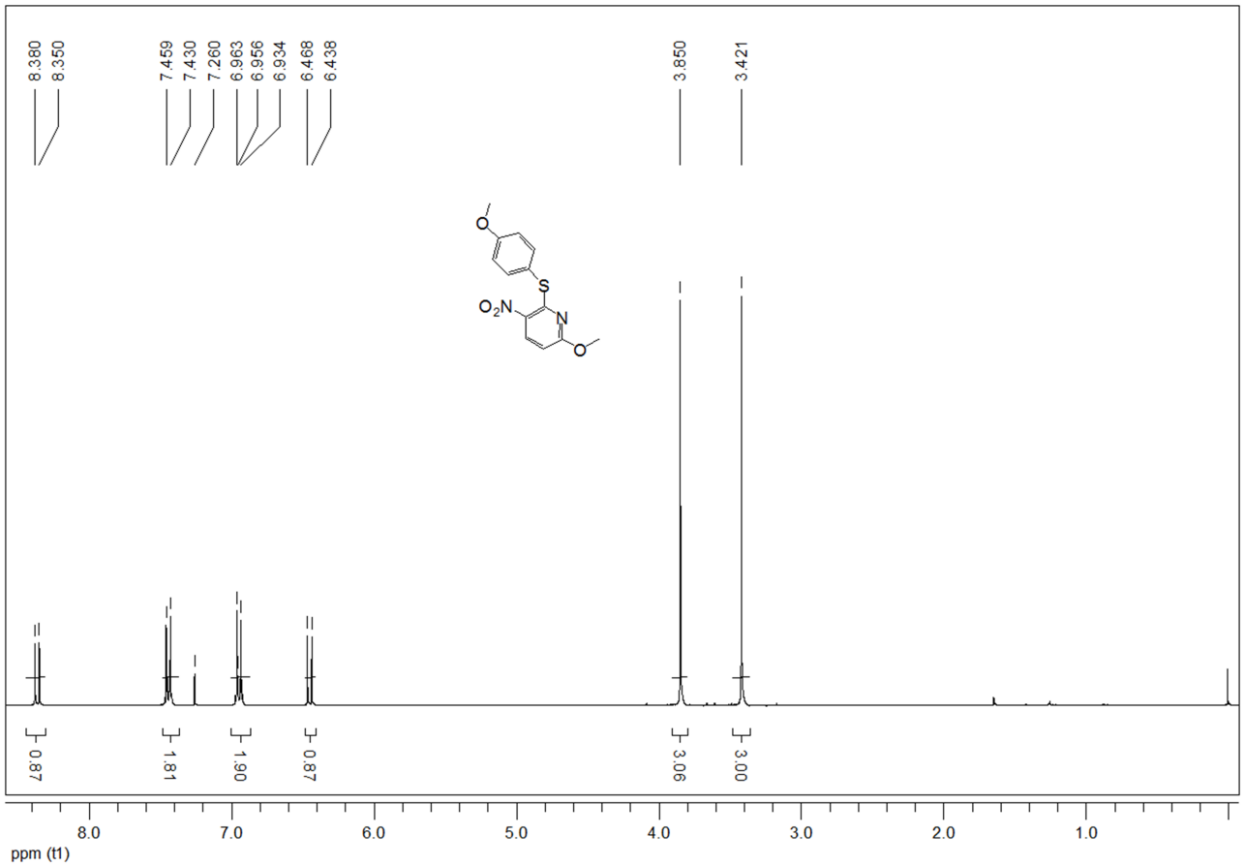

Fig. S73 ^{1}H NMR spectrum of **29** (400 MHz, $CDCl_3$).

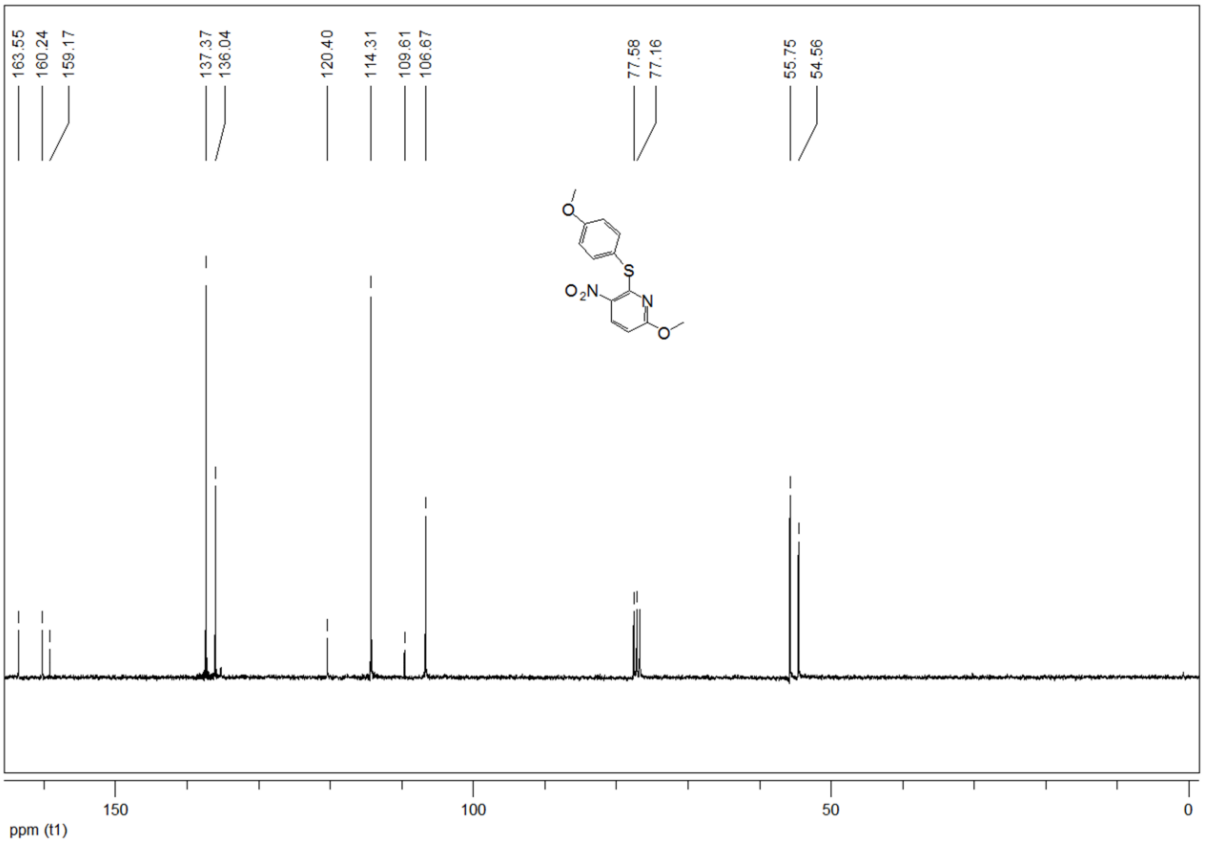

Fig. S74 ^{13}C NMR spectrum of **29** (100 MHz, $CDCl_3$).

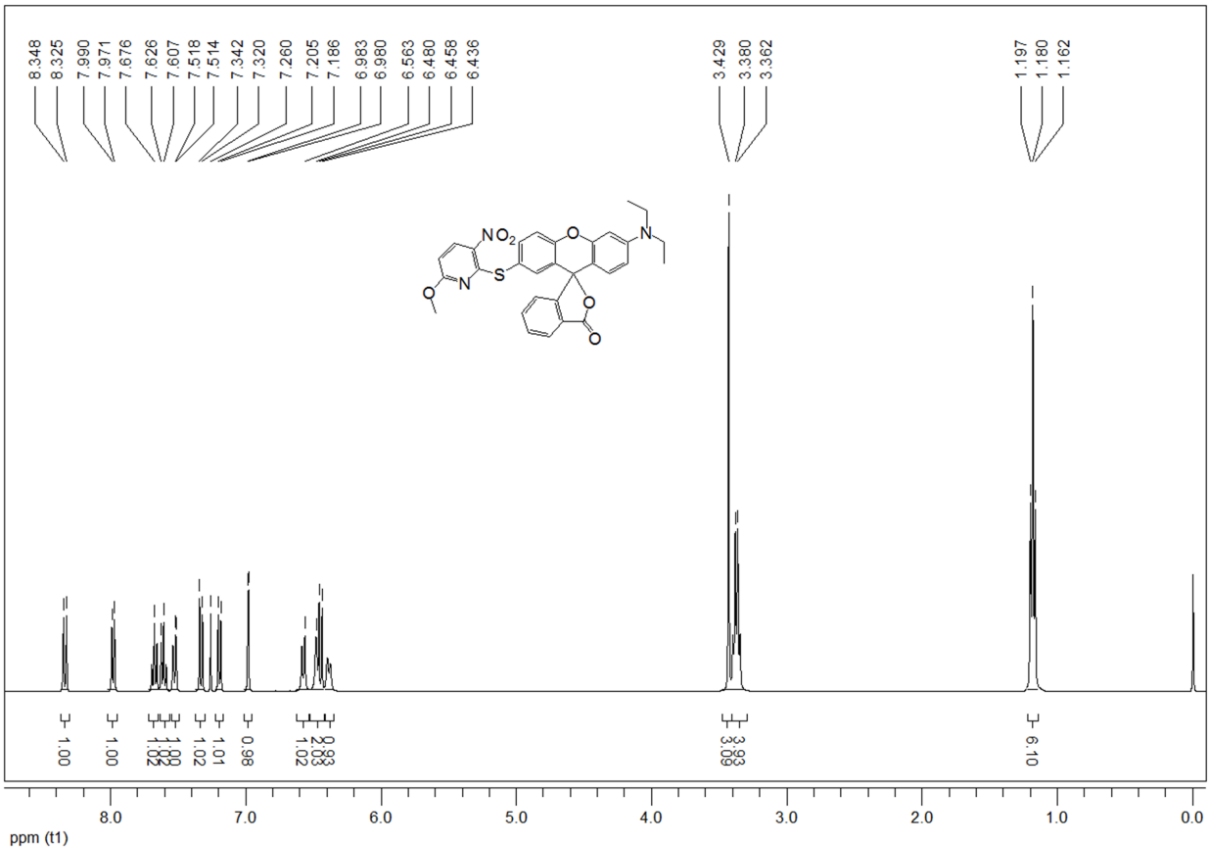

Fig. S75 ^{1}H NMR spectrum of **30** (400 MHz, $CDCl_3$).

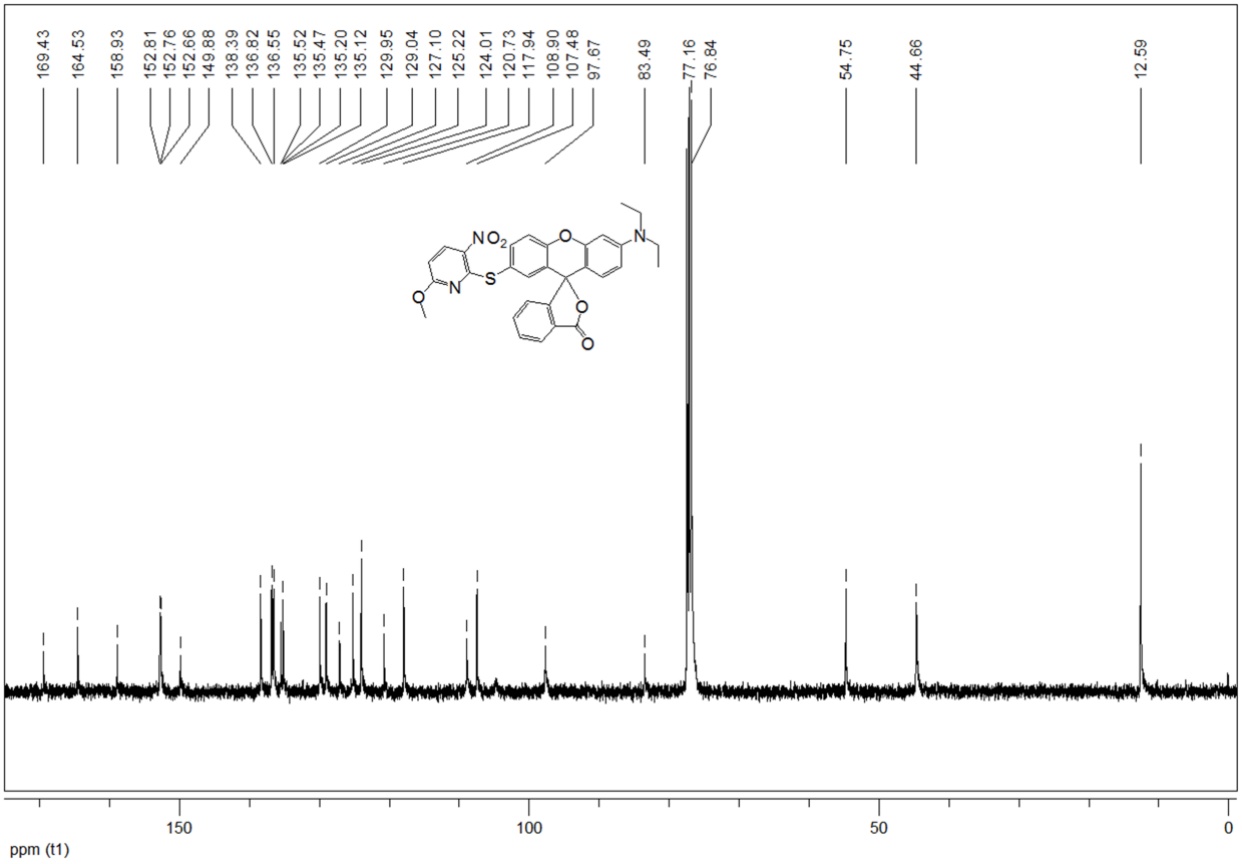

Fig. S76 ^{13}C NMR spectrum of **30** (100 MHz, $CDCl_3$).

Fig. S77 HRMS of **30**. HRMS: m/z [M + H^+] = 556.1555; Calcd for [$C_{30}H_{25}N_3O_6S$ + H^+]: 556.1542.

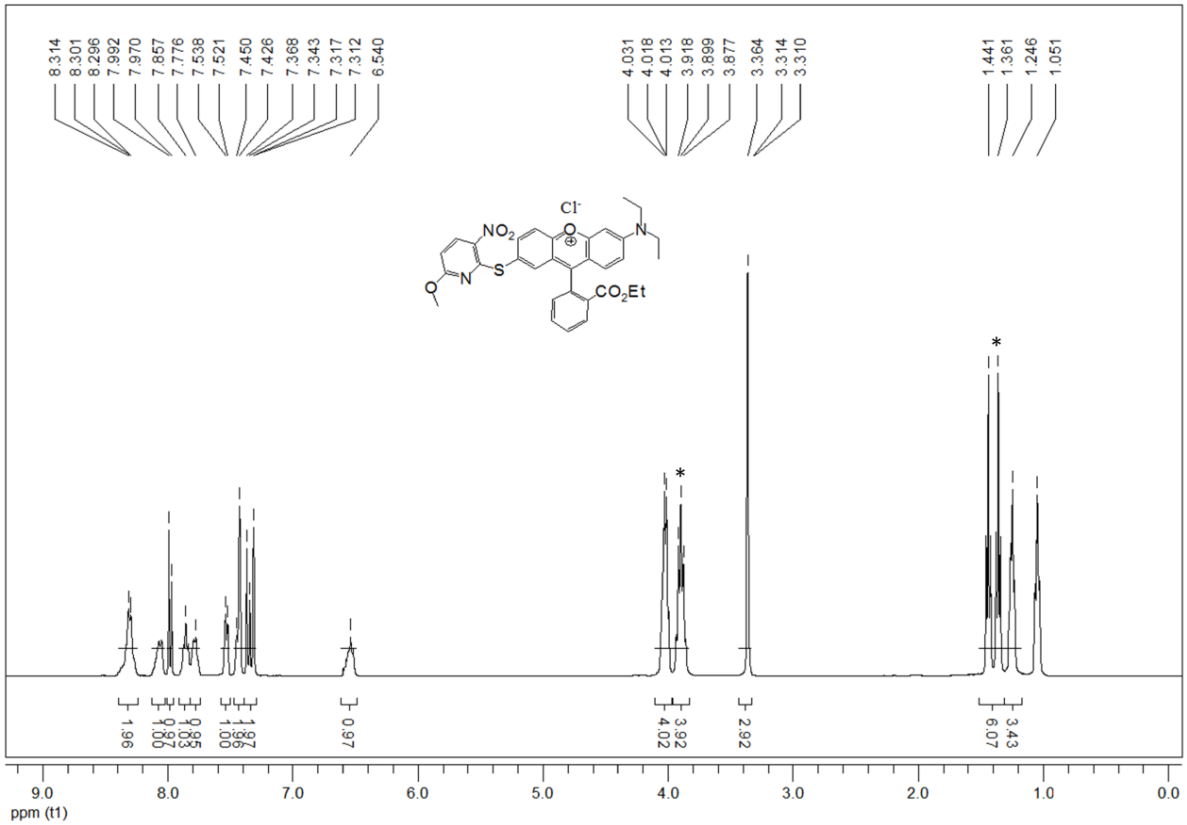

Fig. S78. ^{1}H NMR spectrum of **31** (400 MHz, CD_3OD). * solvent (EtOH).

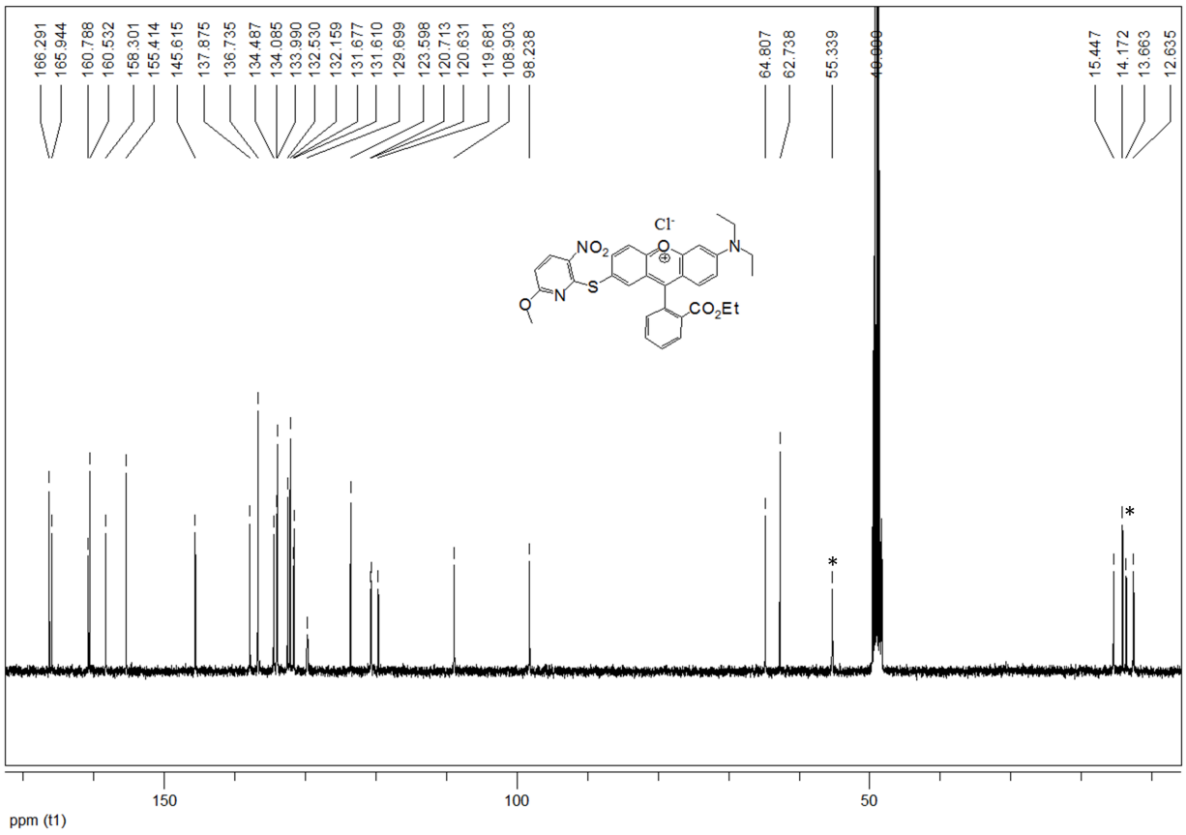

Fig. S79 ^{13}C NMR spectrum of **31** (100 MHz, CD_3OD). * solvent (EtOH).

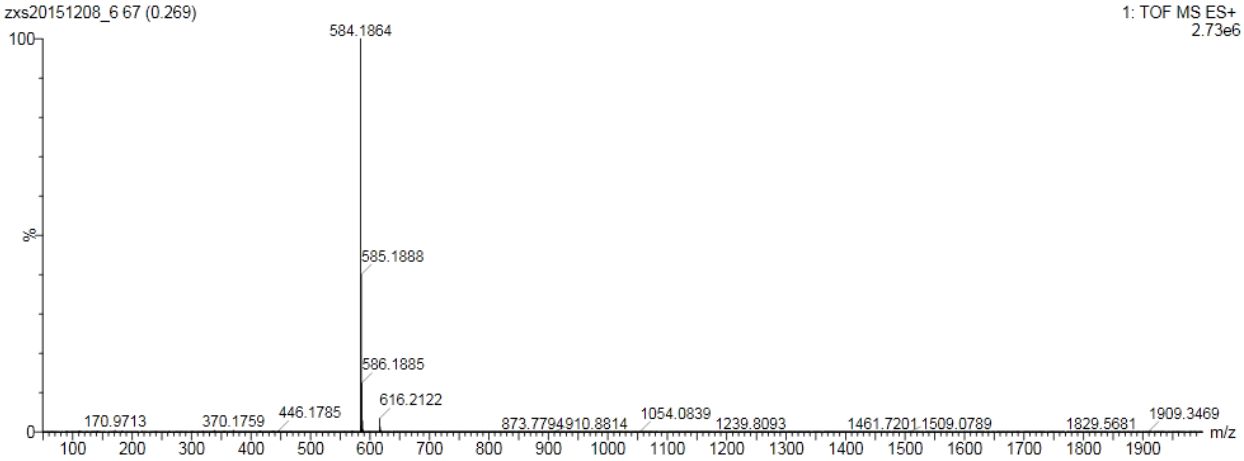

Fig. S80 HRMS of **31**. HRMS: m/z [M – Cl^-] = 584.1864; Calcd for [$C_{32}H_{30}N_3O_6S^+$]: 584.1855.

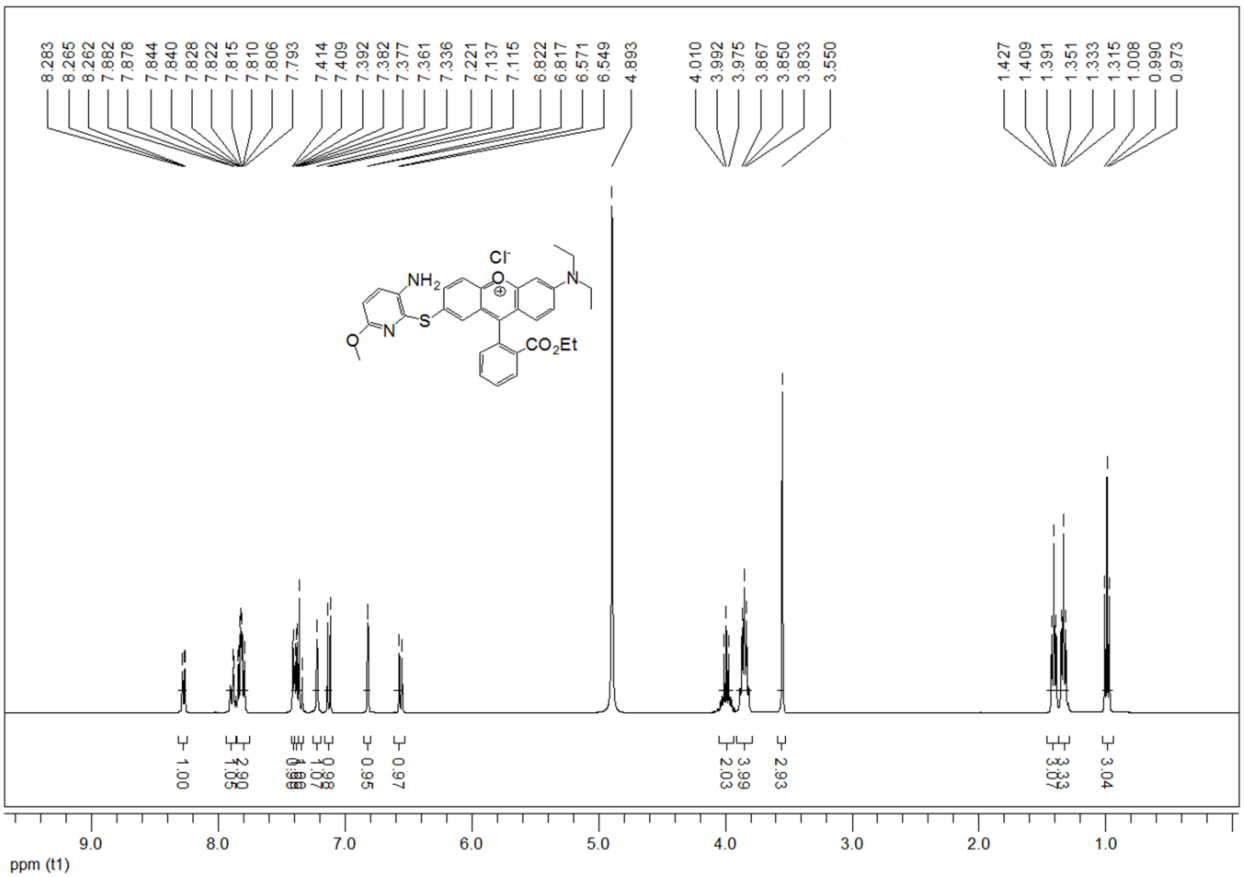

Fig. S81 ^{1}H NMR spectrum of **32** (400 MHz, CD_3OD).

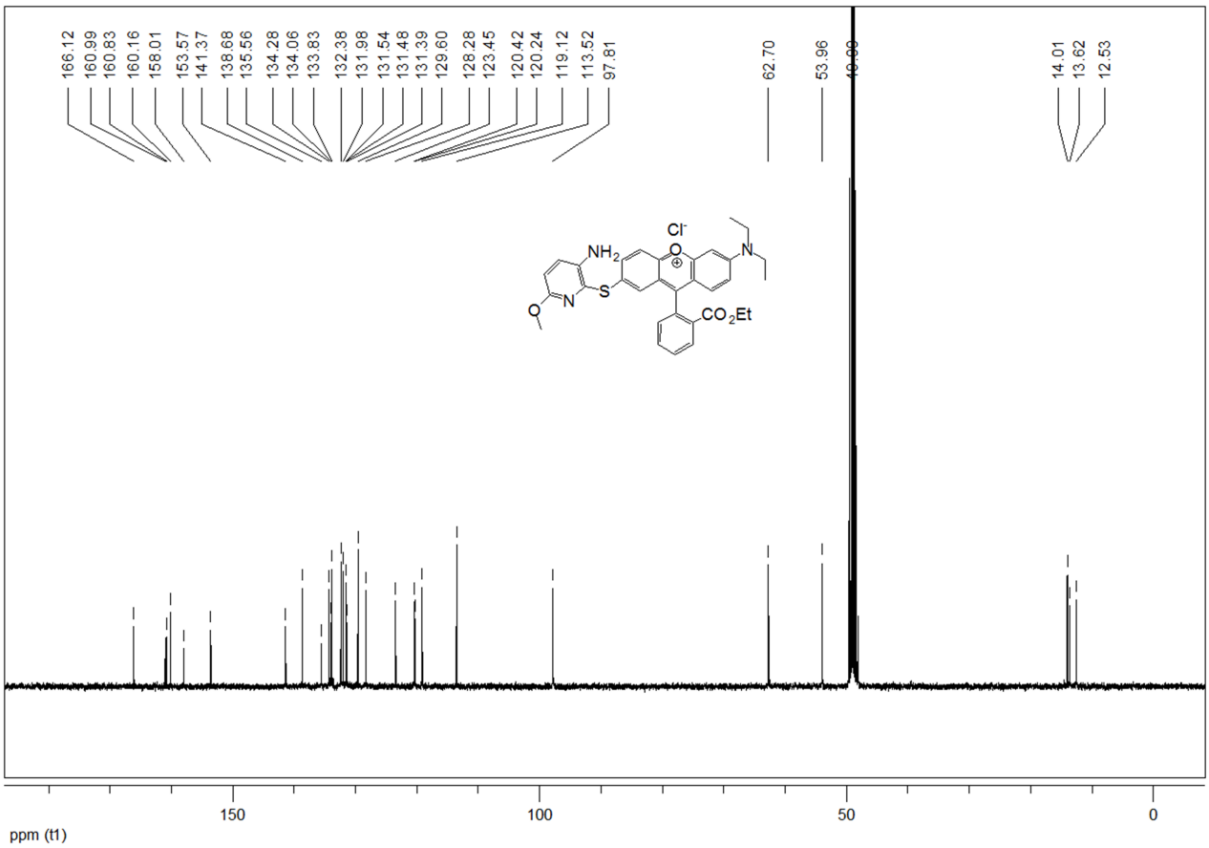

Fig. S82 ^{13}C NMR spectrum of **32** (100 MHz, CD_3OD).

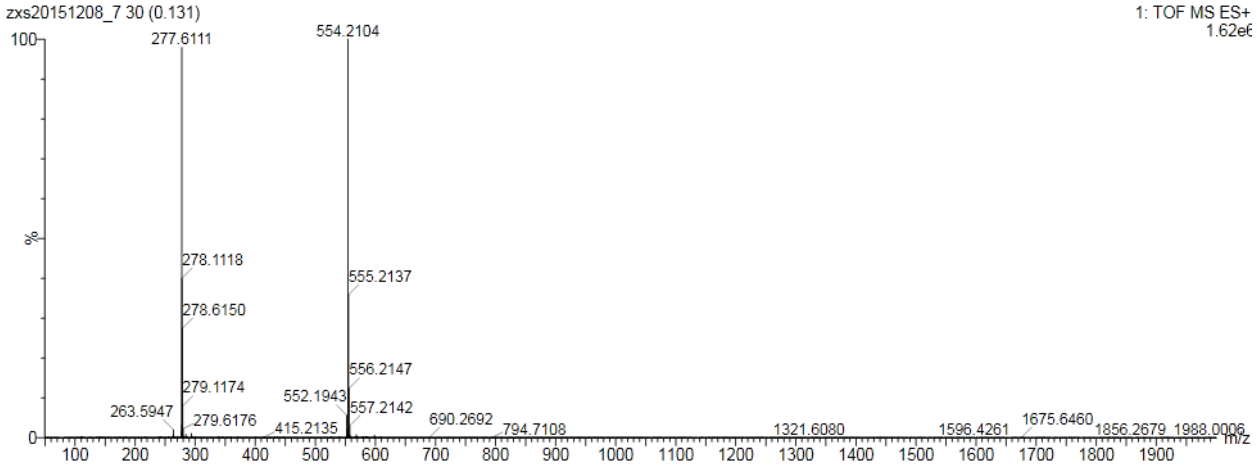

Fig. S83 HRMS of **32**. HRMS: m/z [M + H^+ - Cl^-] = 277.6111, [M - Cl^-] = 554.2104; Calcd for [M + H^+ - Cl^-] = 277.6096, [M - Cl^-] = 554.2114.

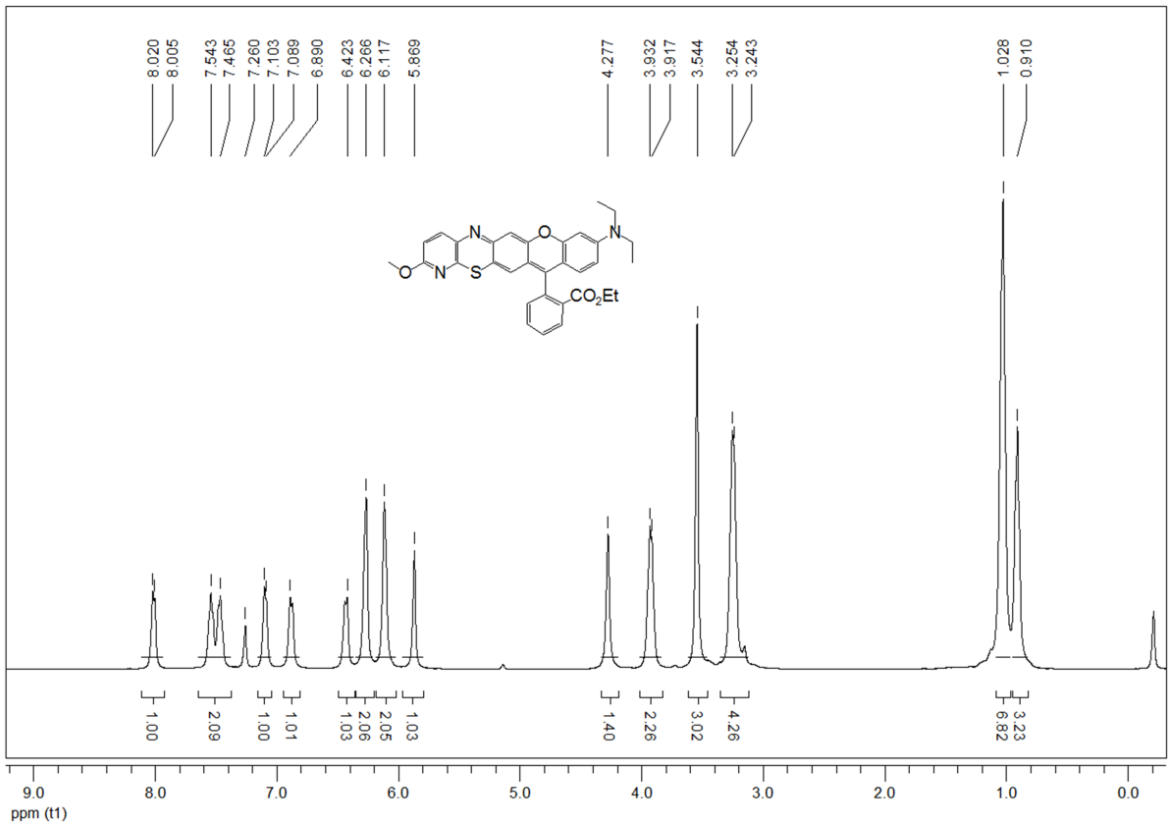

Fig. S84 ^{1}H NMR spectrum of **RE6** (400 MHz, $CDCl_3$ with 20 % CD3OD and 1% CF_3COOD).

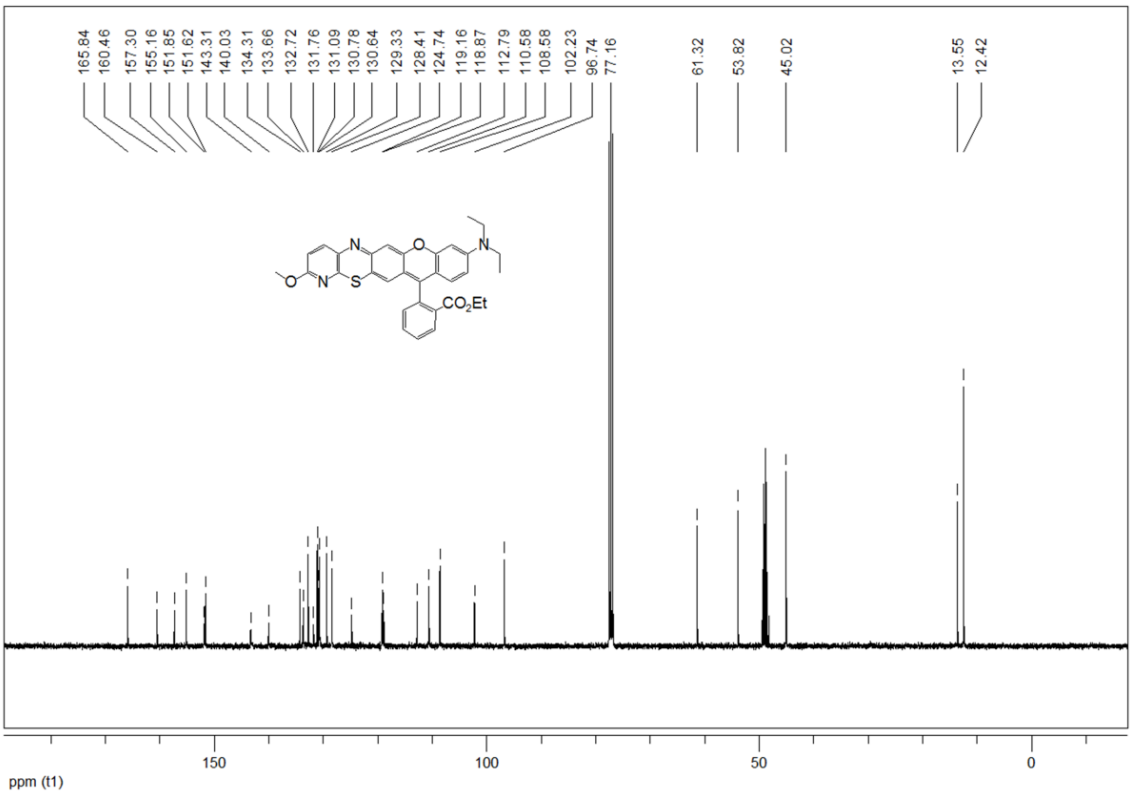

Fig. S85 ^{13}C NMR spectrum of **RE6** (100 MHz, $CDCl_3$ with 20 % CD3OD and 1% CF_3COOD).

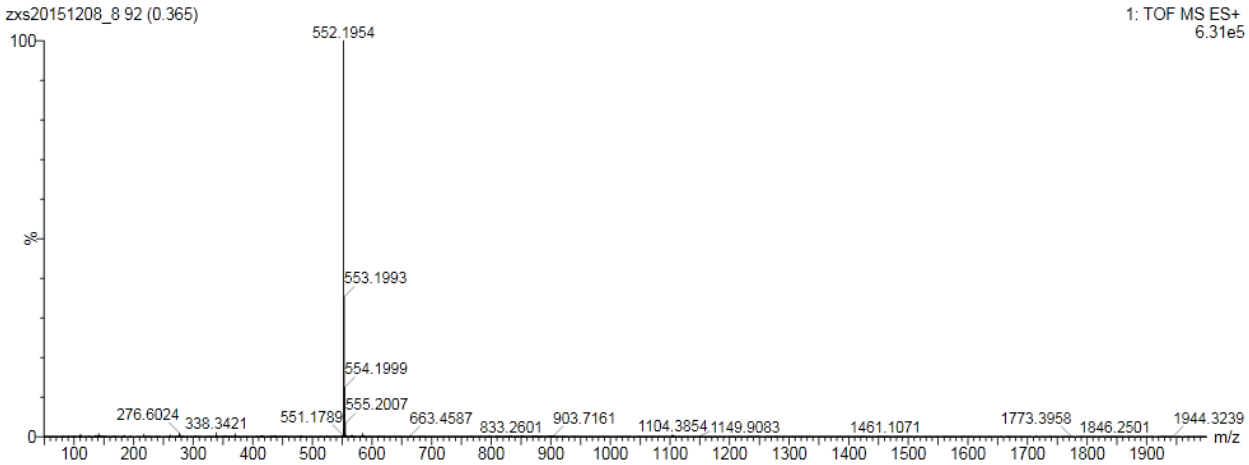

Fig. S86 HRMS of **RE6**. HRMS: m/z [M + H^+] = 552.1954; Calcd for [$C_{32}H_{29}N_3O_4S$ + H^+]: 552.1957.

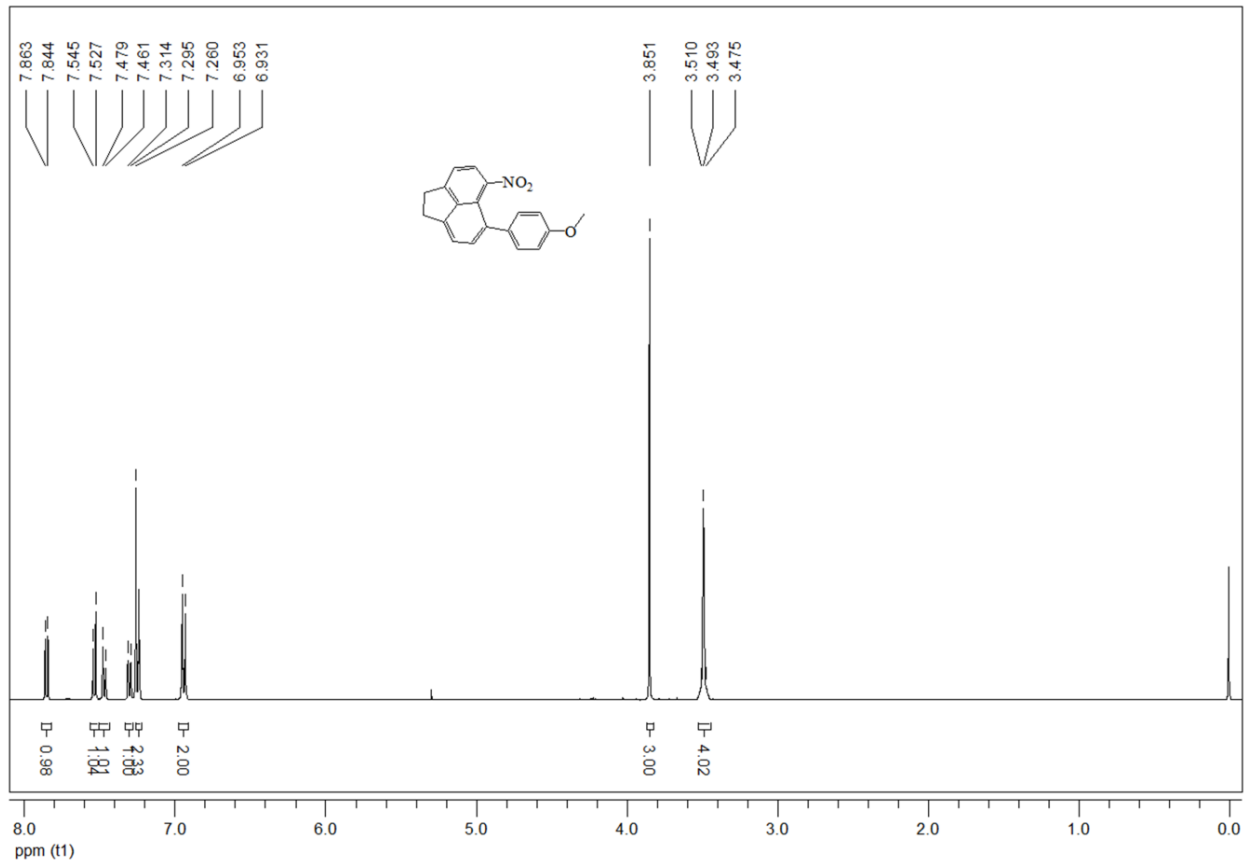

Fig. S87 ^{1}H NMR spectrum of **35** (400 MHz, $CDCl_3$).

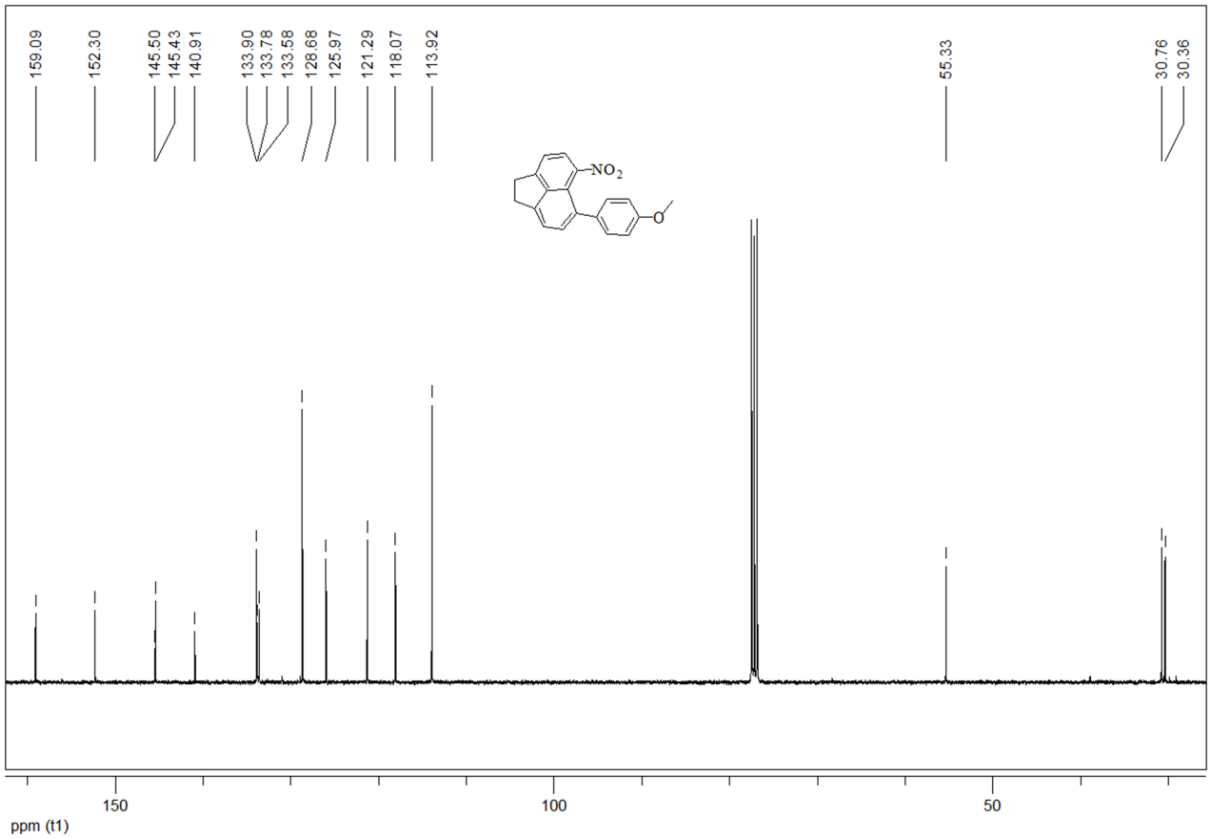

Fig. S88 ^{13}C NMR spectrum of **35** (100 MHz, $CDCl_3$).

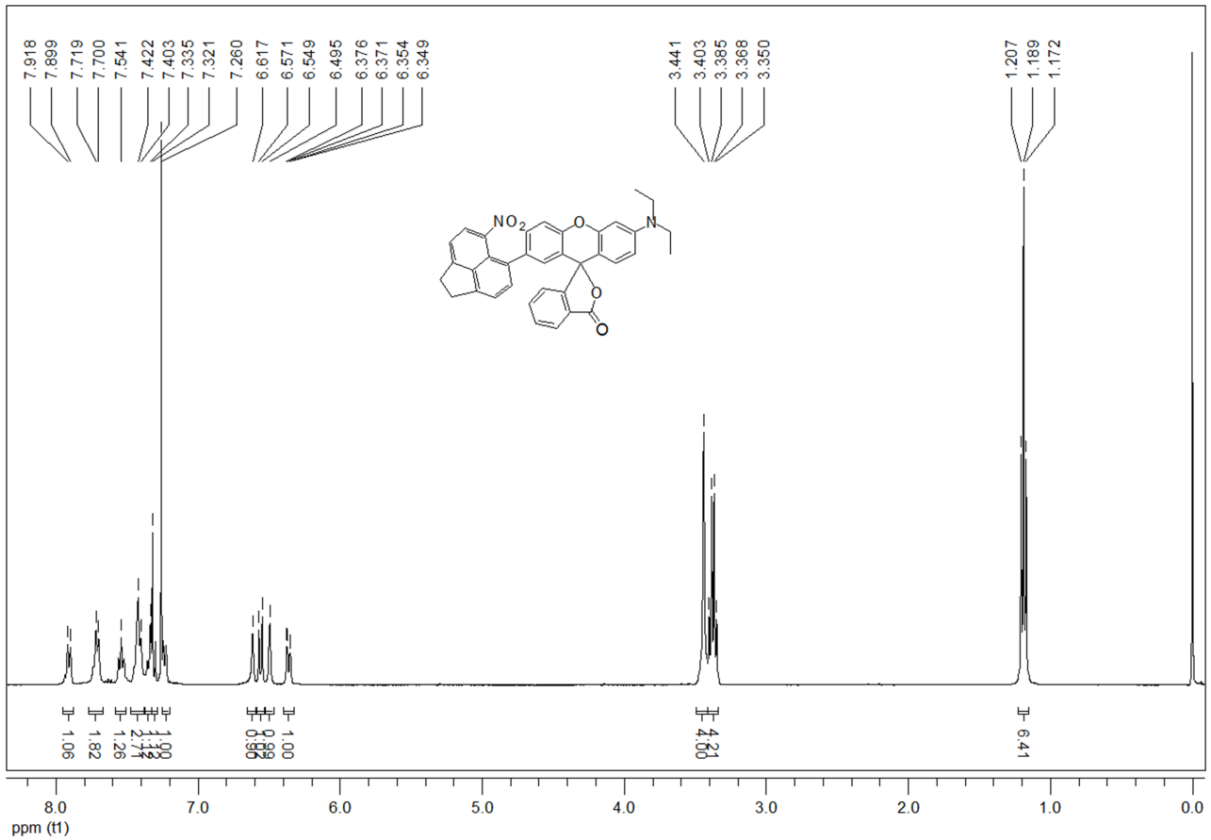

Fig. S89 ^{1}H NMR spectrum of **36** (400 MHz, $CDCl_3$).

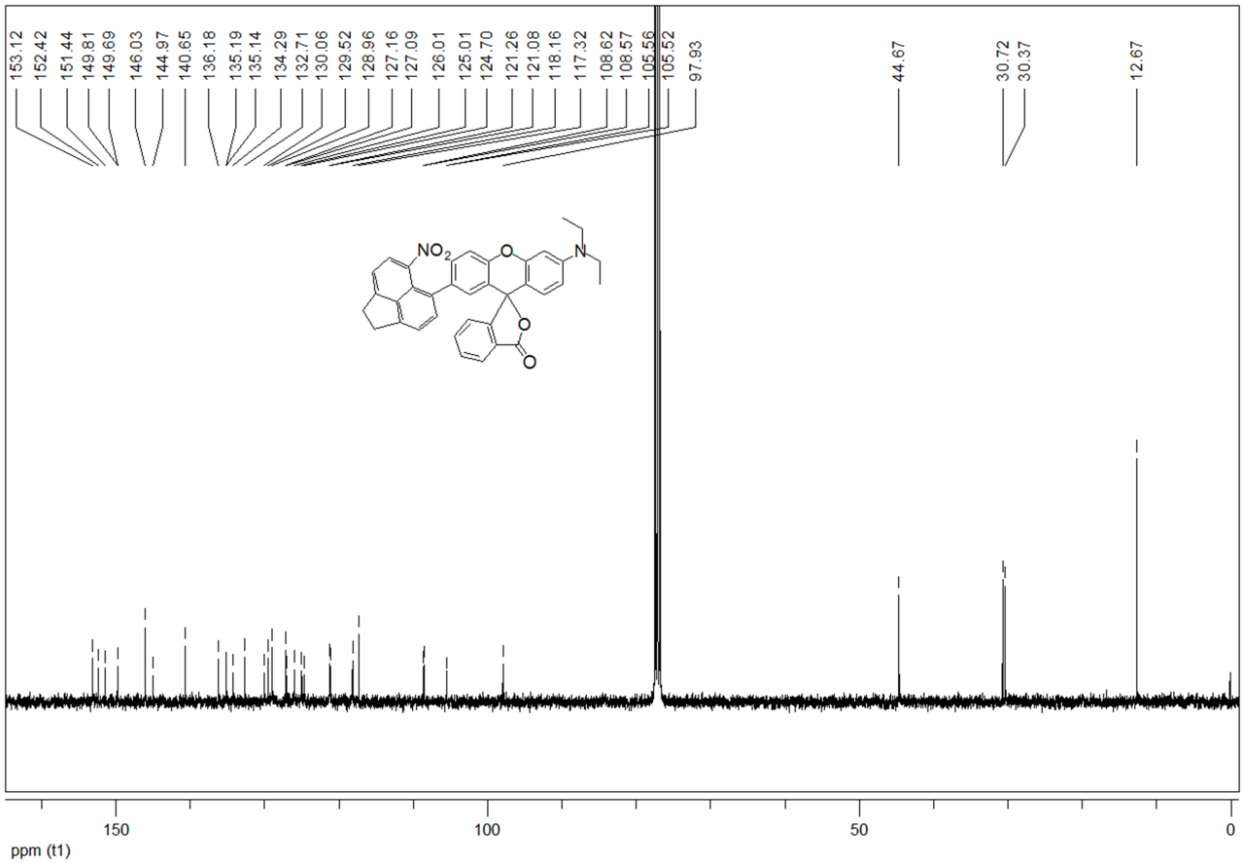

Fig. S90 ^{13}C NMR spectrum of **36** (100 MHz, $CDCl_3$).

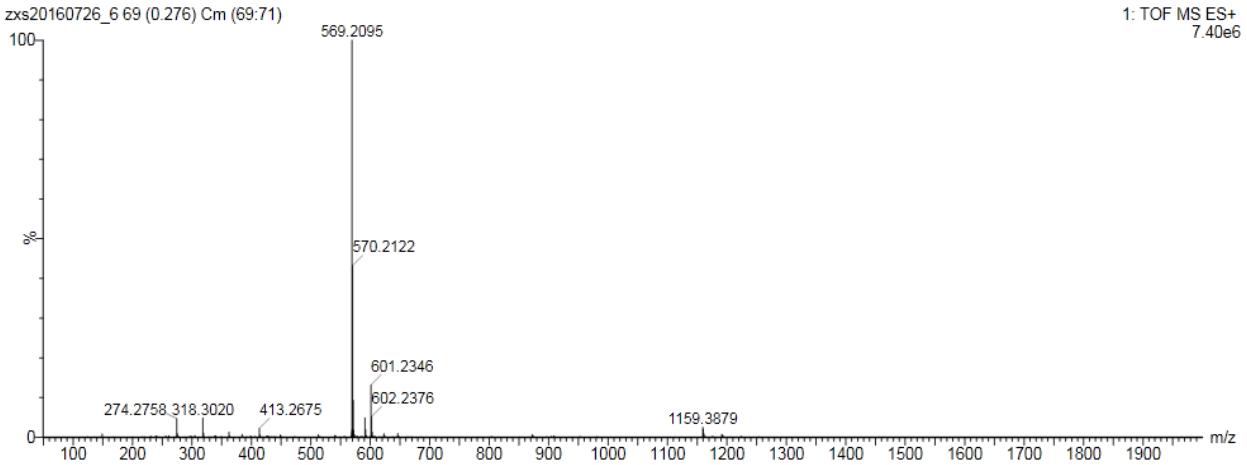

Fig. S91 HRMS of **36**. HRMS: m/z [M + H^+] = 569.2095; Calcd for [$C_{36}H_{28}N_2O_5$ + H^+]: 569.2076.

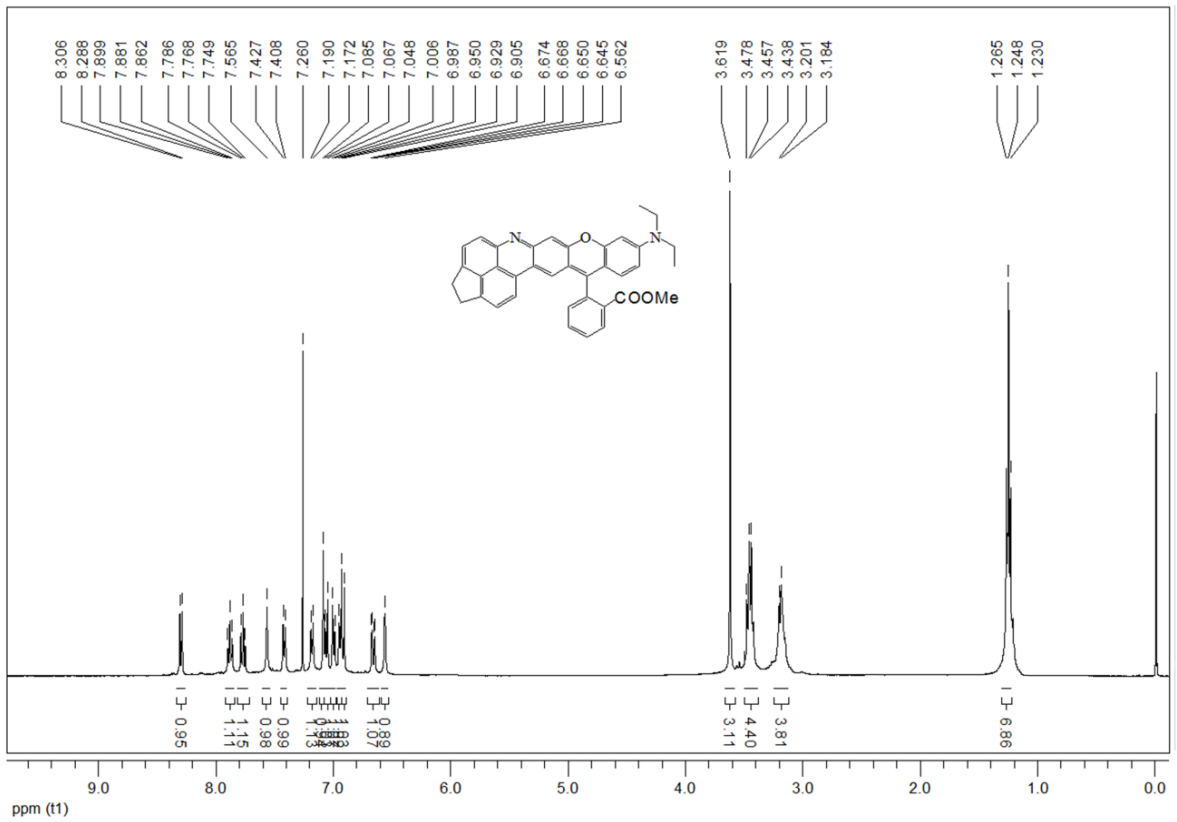

Fig. S92 ^{1}H NMR spectrum of **RE7** (400 MHz, $CDCl_3$).

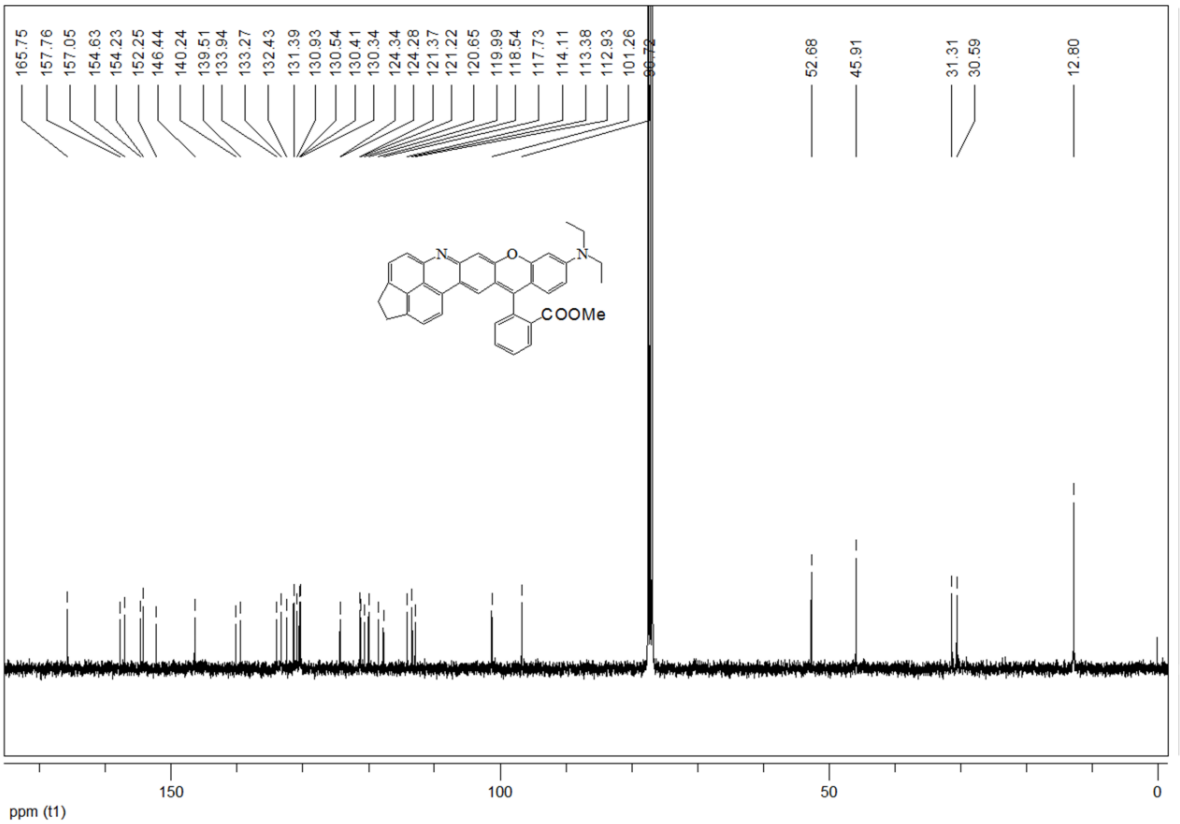

Fig. S93 ^{13}C NMR spectrum of **RE7** (100 MHz, $CDCl_3$).

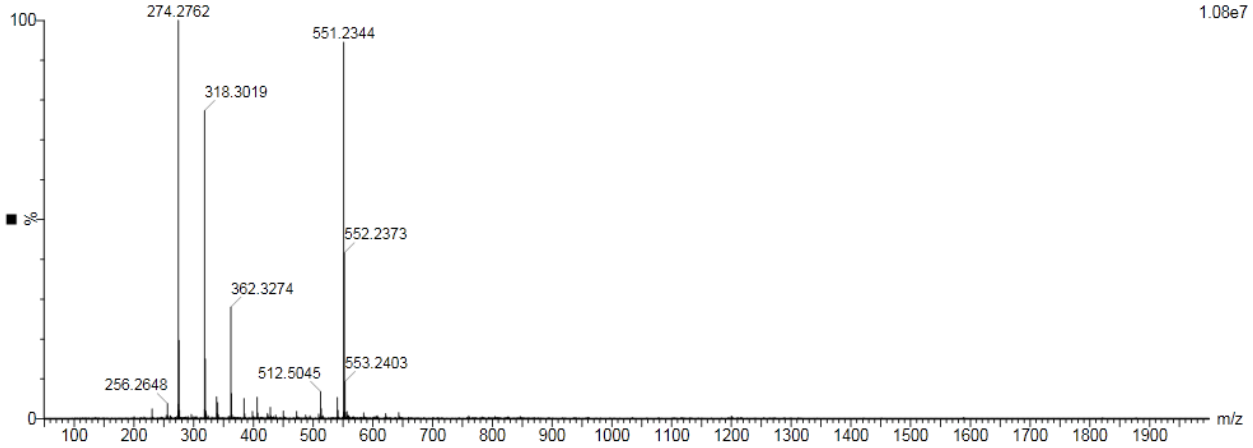

Fig. S94 HRMS of **RE7**. HRMS: m/z [M + H$^+$] = 551.2344; Calcd for [$C_{37}H_{30}N_2O_5$ + H$^+$]: 551.2335.

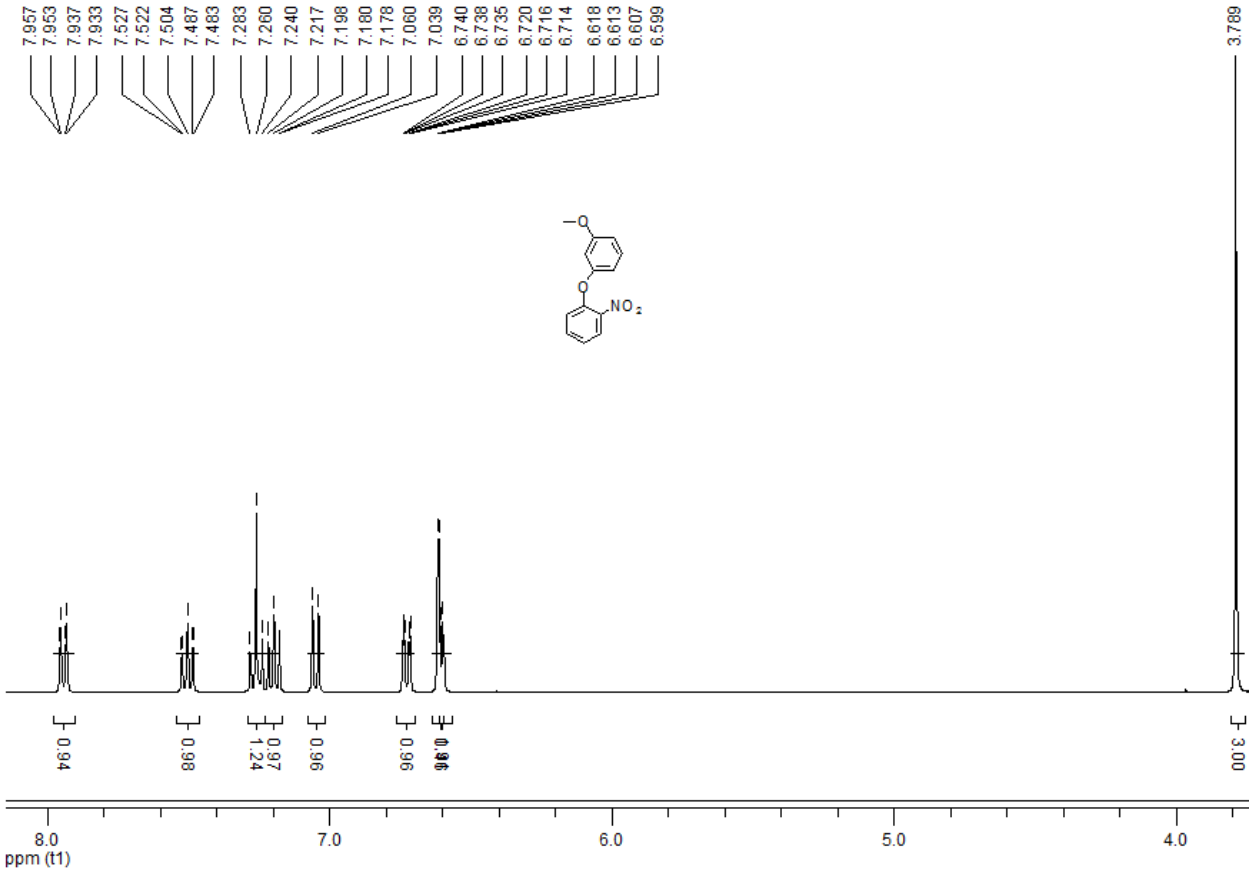

Fig. S95 ^{1}H NMR spectrum of **40** (400 MHz, $CDCl_3$).

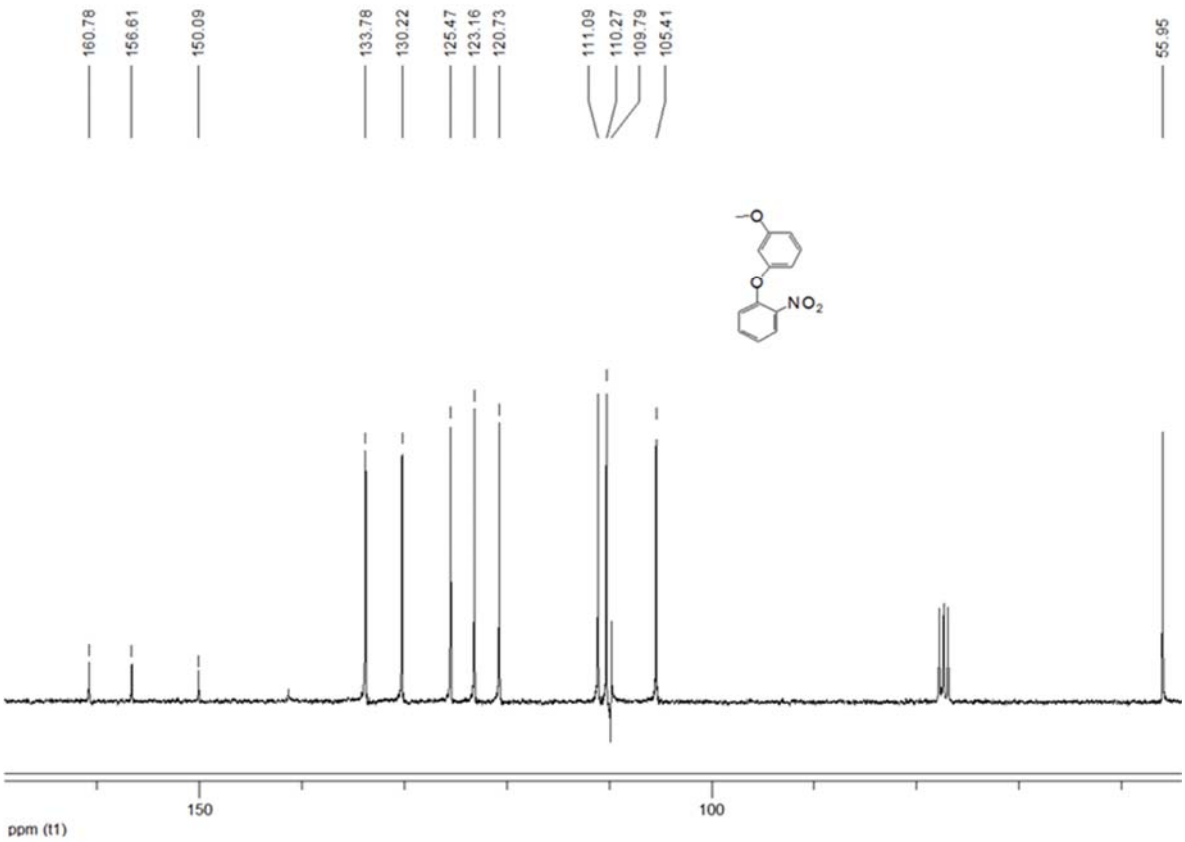

Fig. S96 ^{13}C NMR spectrum of **40** (100 MHz, $CDCl_3$).

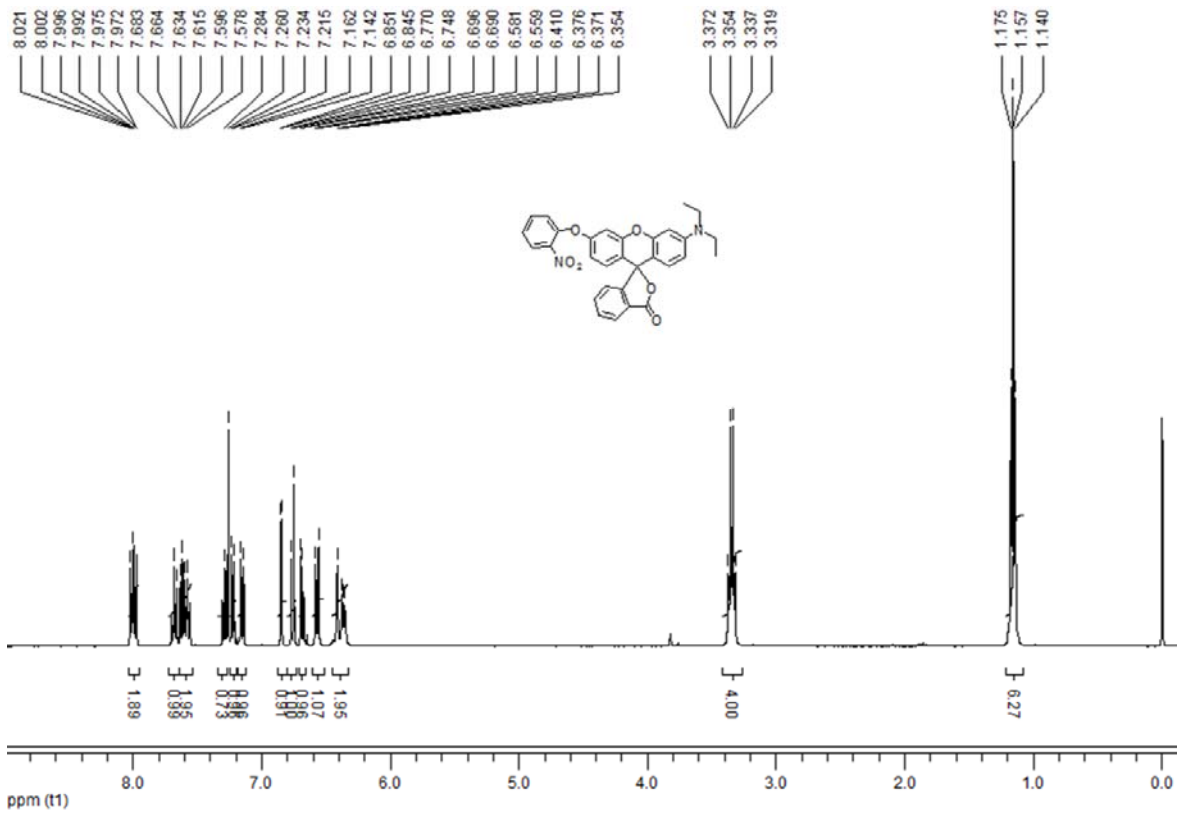

Fig. S97 ^{1}H NMR spectrum of **41** (400 MHz, $CDCl_3$).

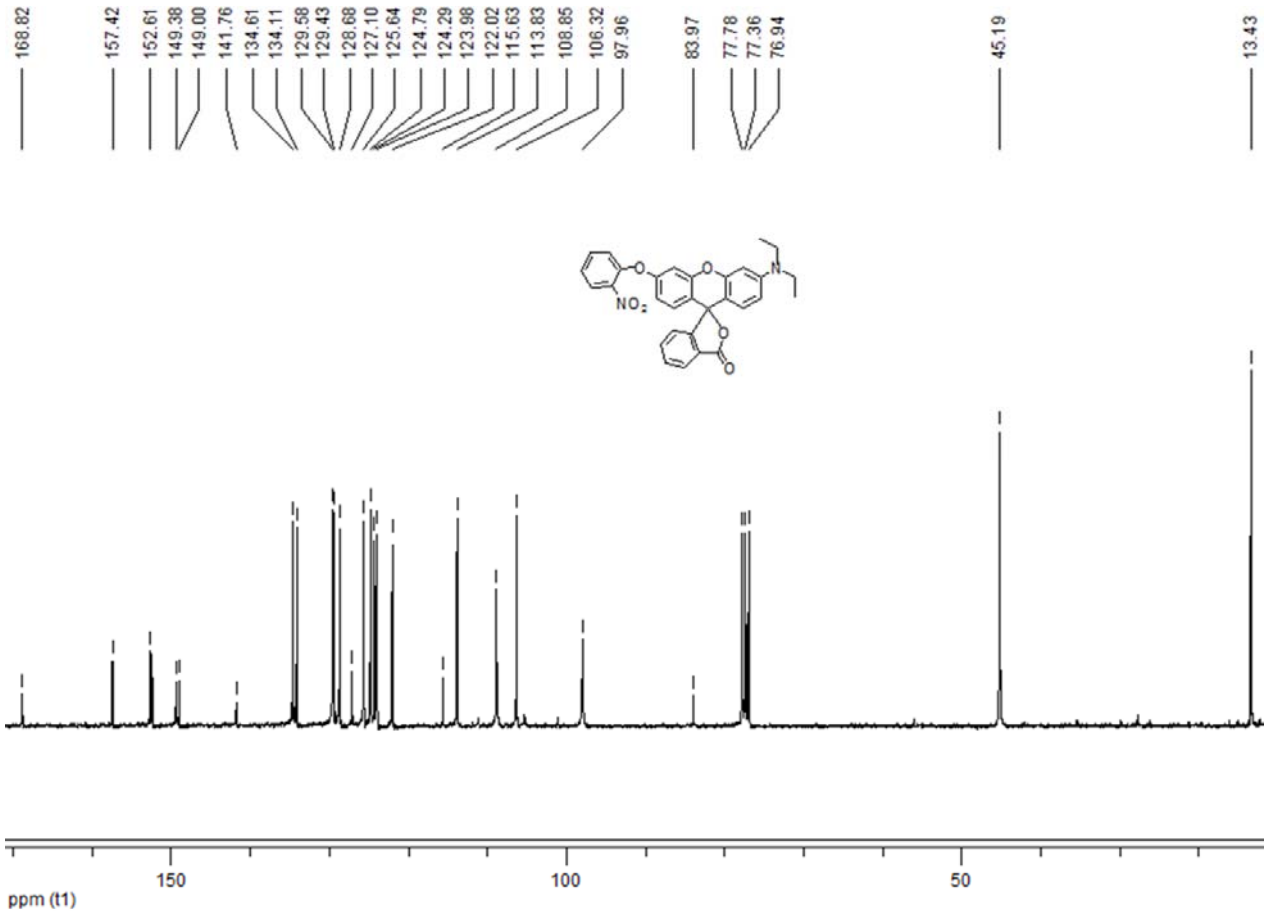

Fig. S98 ^{13}C NMR spectrum of **41** (100 MHz, $CDCl_3$).

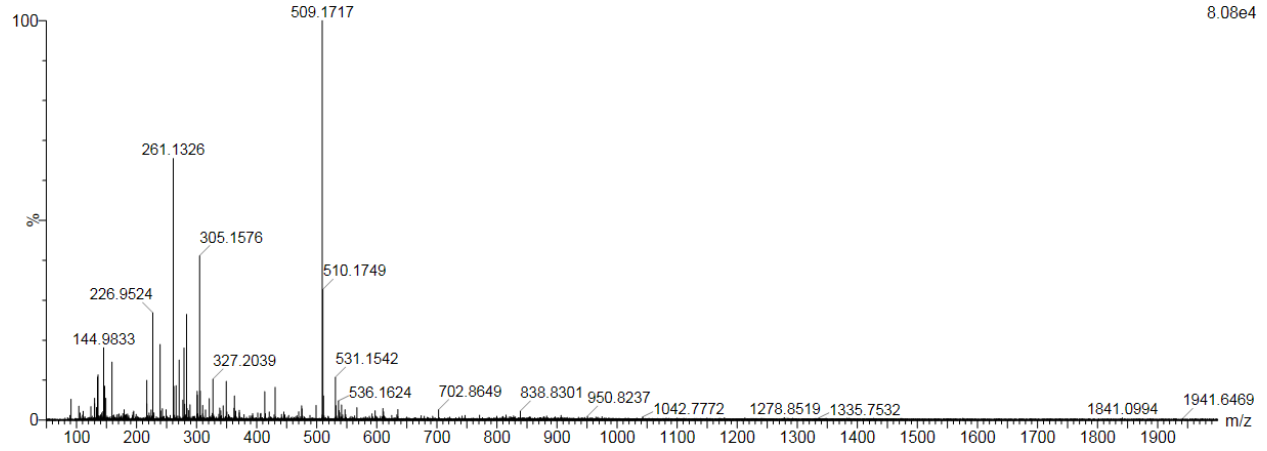

Fig. S99 HRMS of **41**. HRMS: m/z [M + H^+] = 509.1717; Calcd for [$C_{30}H_{24}N_2O_6$ + H^+]: 509.1713.

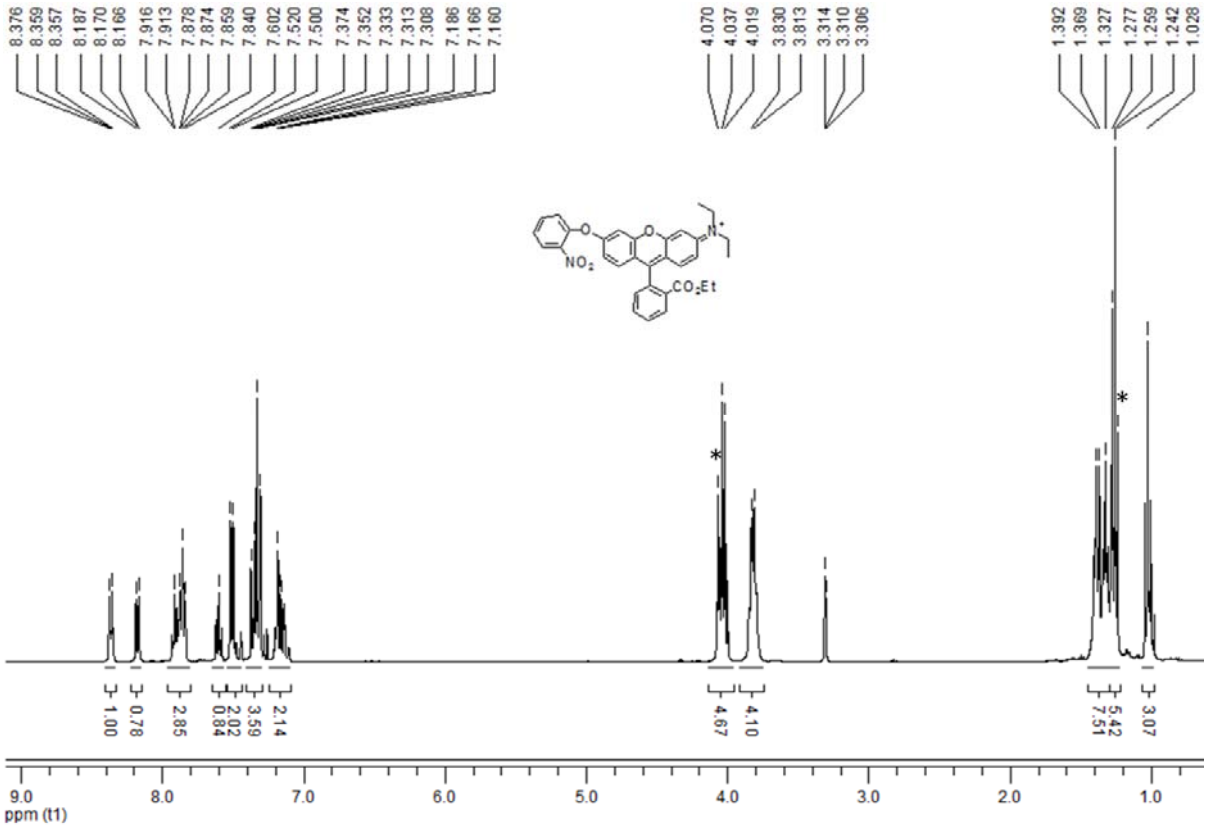

Fig. S100 ^{1}H NMR spectrum of **42** (400 MHz, $CDCl_3$).* solvent (EtOH).

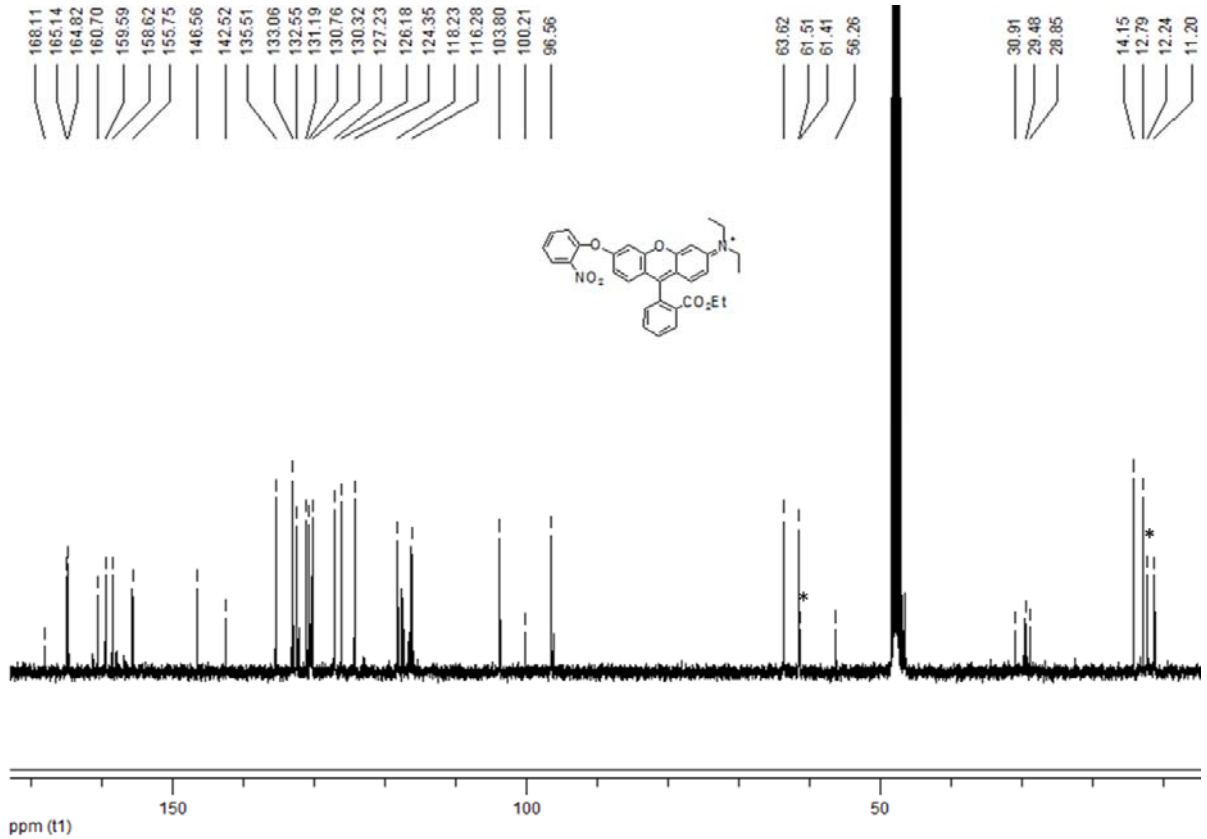

Fig. S101 ^{13}C NMR spectrum of **42** (100 MHz, $CDCl_3$). * solvent (EtOH).

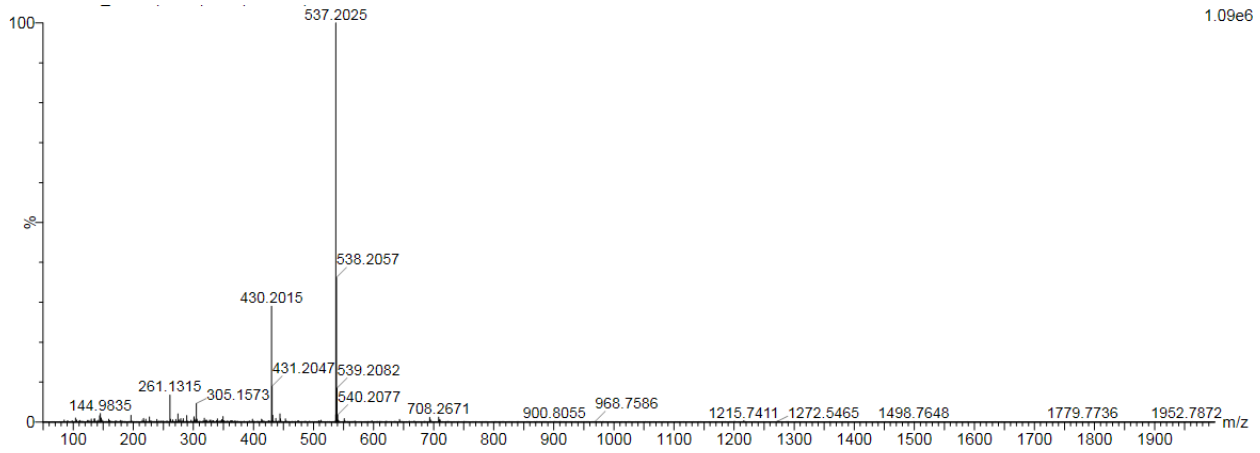

Fig. S102 HRMS of **42**. HRMS: m/z [M - Cl^-] = 537.2025; Calcd for $C_{32}H_{29}N_2O_6^+$ = 537.2026.

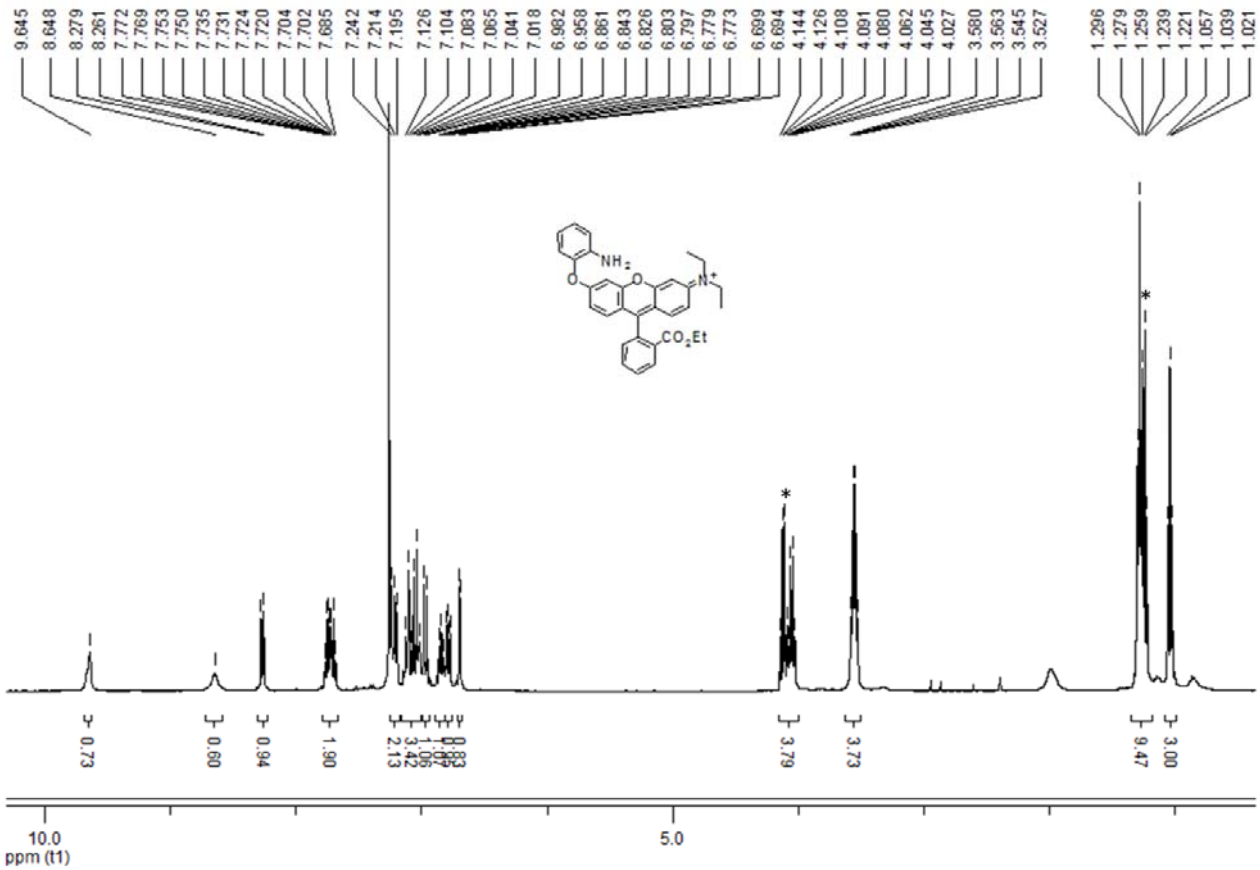

Fig. S103 ^{1}H NMR spectrum of **43** (400 MHz, $CDCl_3$). * solvent (EtOH).

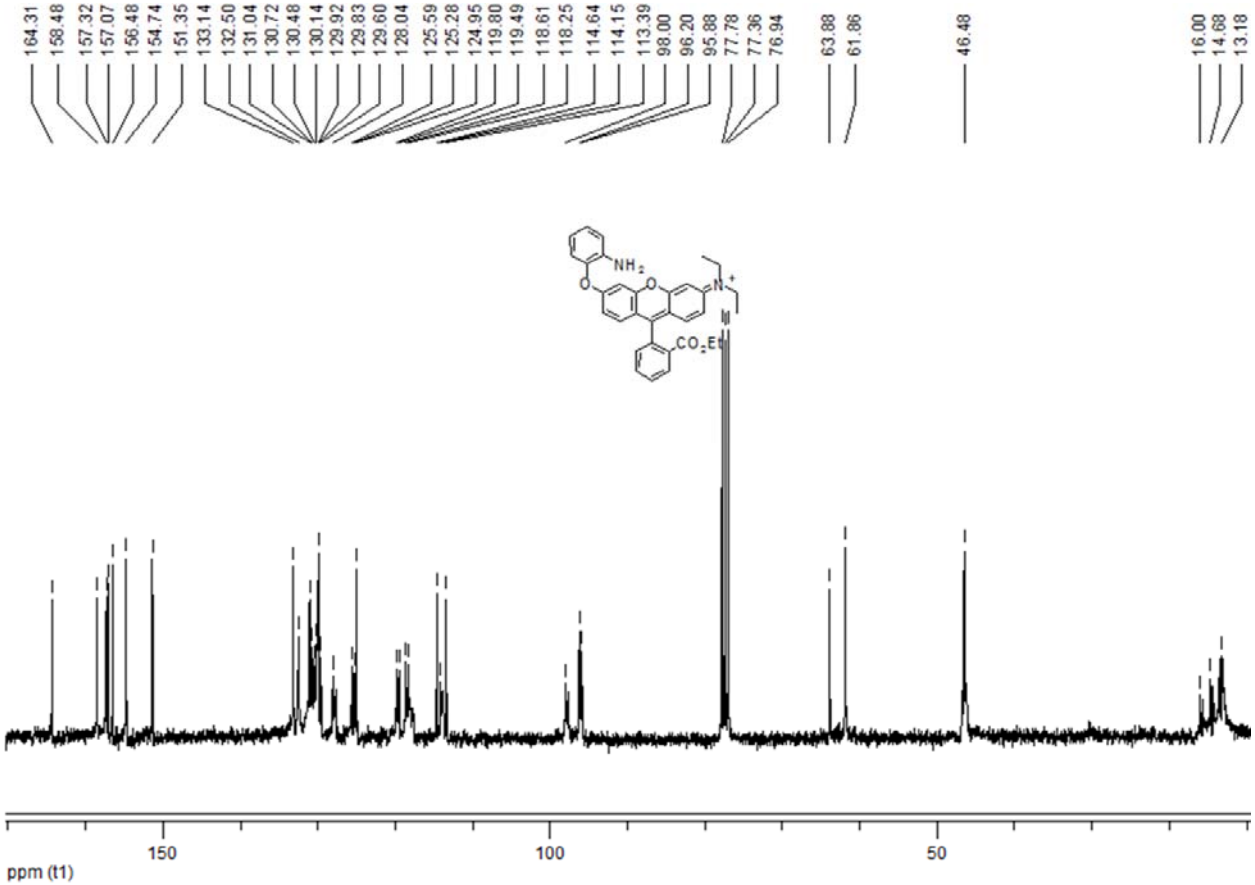

Fig. S104 ^{13}C NMR spectrum of **43** (100 MHz, $CDCl_3$). * solvent (EtOH).

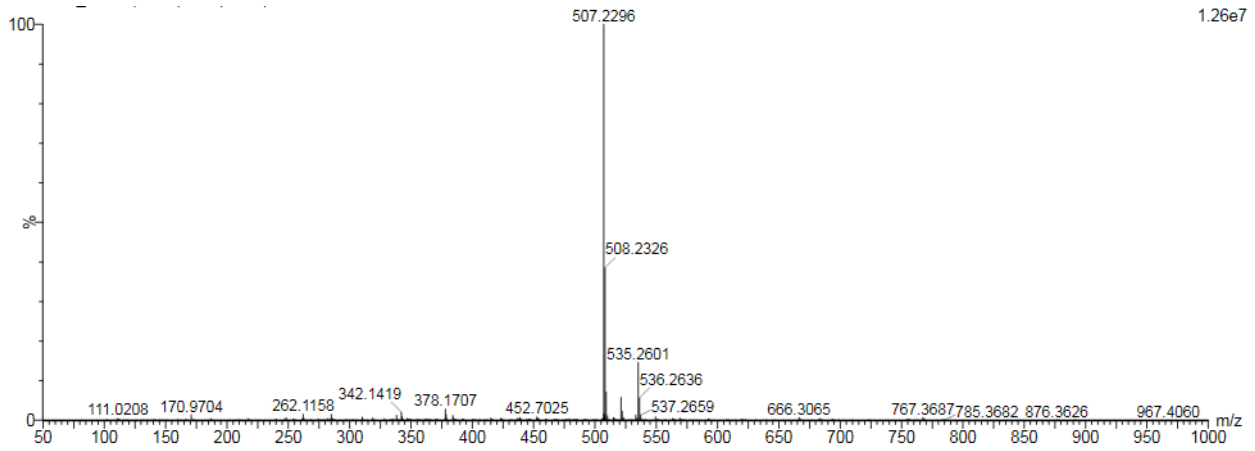

Fig. S105 HRMS of **43**. HRMS: m/z [M - Cl^-] = 507.2296; Calcd for $C_{32}H_{31}N_2O_4^+$ = 507.2284.

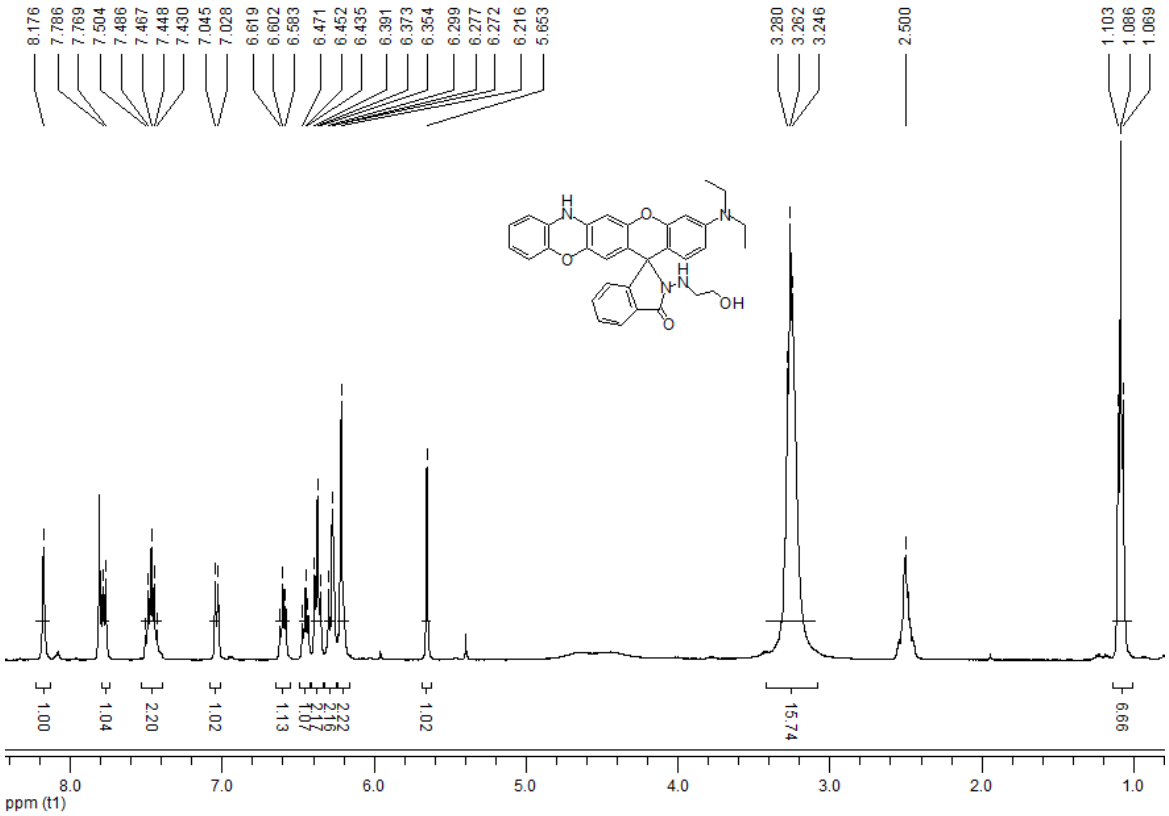

Fig. S107 ^{1}H NMR spectrum of probe **RE1-Cu** (400 MHz, DMSO-d_6 and $CDCl_3$).

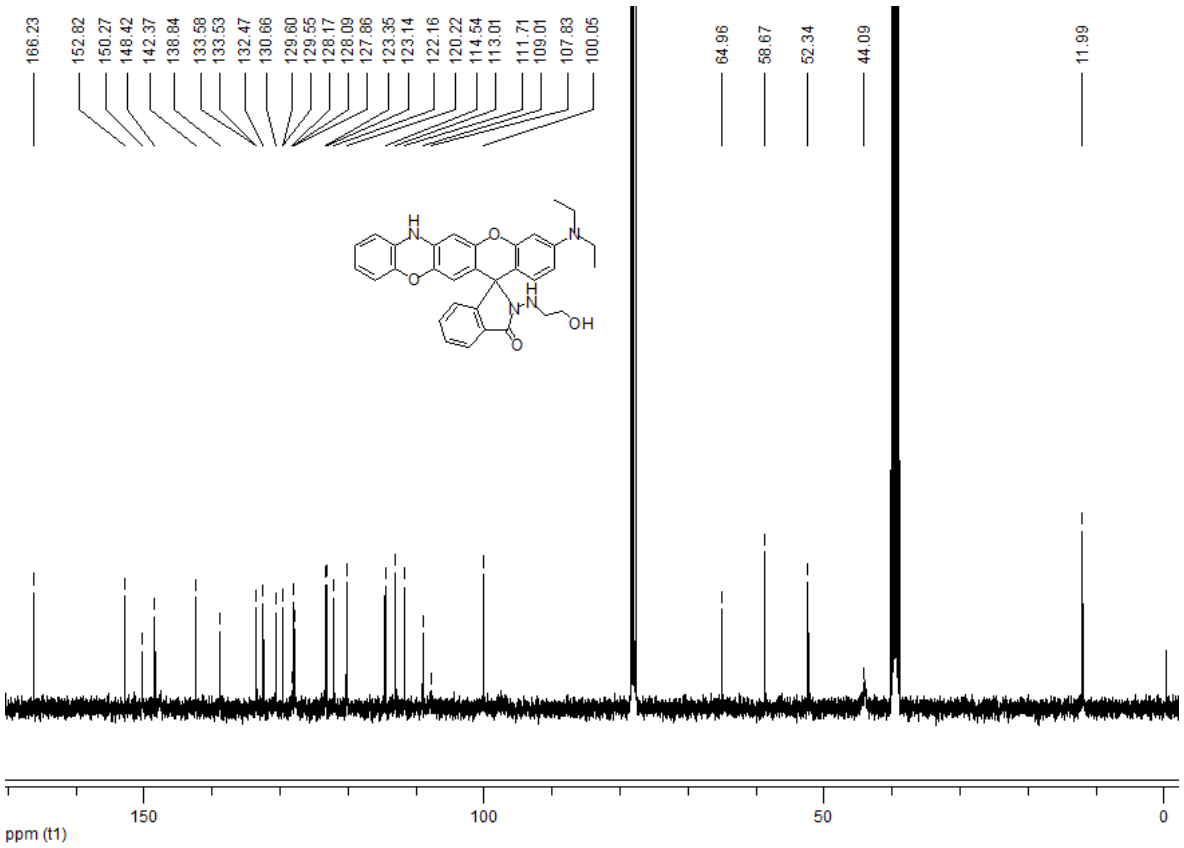

Fig. S108 ^{13}C NMR spectrum of probe **RE1-Cu** (100 MHz, DMSO-d_6 and $CDCl_3$).

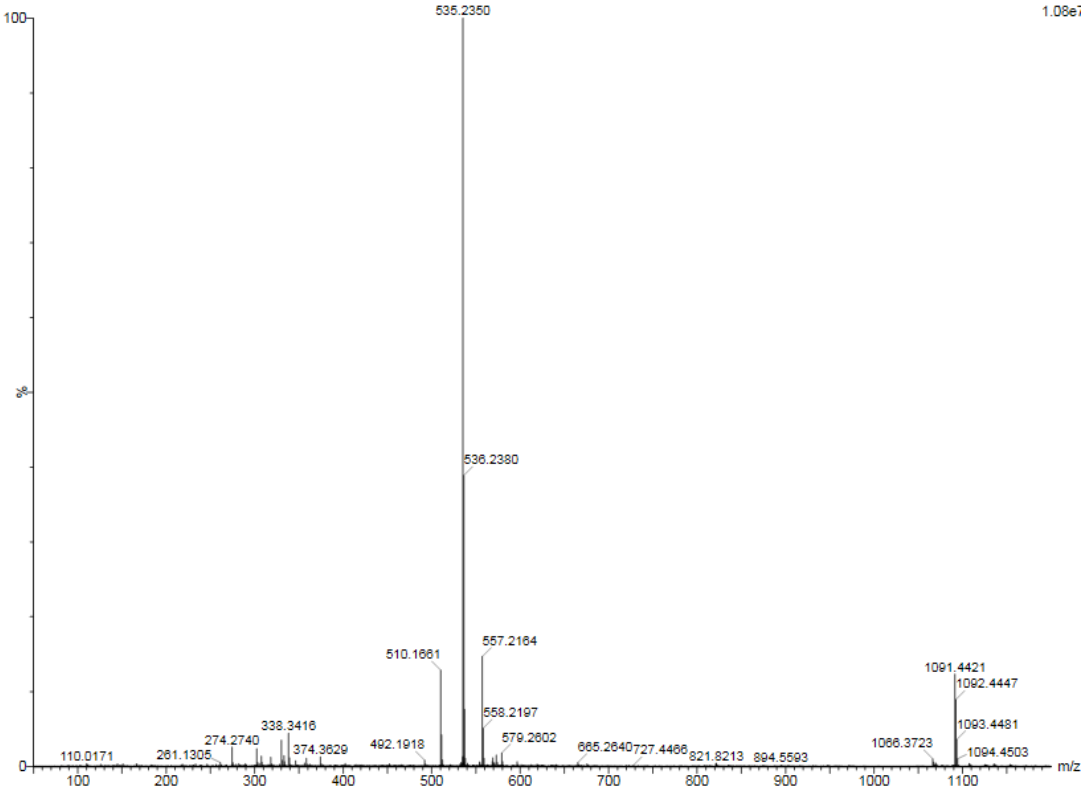

Fig. S109 HRMS of probe **RE1-Cu**. HRMS: m/z [M + H^+] = 535.2350, [M + Na^+] = 557.2164, [2M + Na^+] = 1091.4432; Calcd for [$C_{32}H_{30}N_4O_4$ + H^+] = 535.2345, [$C_{32}H_{30}N_4O_4$ + Na^+] = 557.2165, [2 $C_{32}H_{30}N_4O_4$ + Na^+] = 1091.4421.