Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Modulating Photorelease to Singlet Oxygen Generation by Oxygen Functionalization of Phenothiazine Photocages

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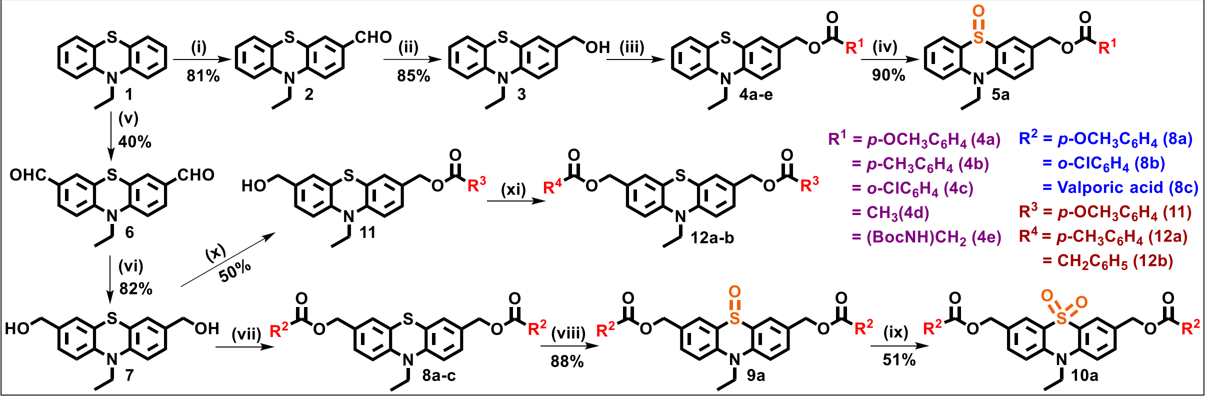
1. General procedure and materials:

^{1}H NMR (500 MHz and 400 MHz) spectra were recorded on a BRUKER-AC 500 MHz and a BRUKER-AC 400 MHz spectrometer, respectively. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, DMSO-d_6: 3.313 ppm and 2.484 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant *J* (Hz). ^{13}C NMR (150 MHz and 100 MHz) spectra were recorded on BRUKER-AC 500 MHz and 400 MHz spectrometers with complete proton decoupling. Chemical shifts (δ) are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 77.23 ppm, DMSO-d_6: 39.96 ppm). UV/vis absorption spectra were recorded on a Shimadzu UV-2450 UV/vis spectrophotometer, fluorescence emission spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer, and HRMS spectra were recorded on a JEOL-Accu TOF JMS-T100L mass spectrometer. Photolysis of all the caged ester was carried out using a 125 W medium pressure mercury lamp supplied by SAIC (India). RP-HPLC was recorded using mobile phase Acetonitrile/water at a flow rate of 1 mL min^{-1} (detection: UV 310 nm). Chromatographic purification was done with 60–120 mesh silica gel (Merck). Precoated silica gel 60 F254 TLC sheets (Merck) were used for reaction monitoring.

Anhydrous solvents dimethylformamide (DMF) was used without distillation. Dichloromethane was distilled from CaH_2 before use. Solvents for workup and column chromatography, such as petroleum ether (PE), ethyl acetate (EtOAc), and other chemicals, were obtained from commercial vendors and used without further purification. All reagents were purchased from Sigma Aldrich and used without further purification. HPLC grade acetonitrile and water were used for photolysis and HPLC.

2. Synthesis of phenothiazine caged ester:

Scheme 1. Synthesis of single and dual (same and different) arm caged esters and oxidized caged ester of phenothiazine.



Reagents and Conditions:

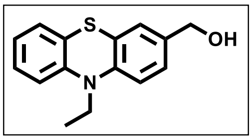
$POCl_3$ (1.1 equiv), DMF, 60ºC, 12 h; (ii) $NaBH_4$, MeOH, rt, 3 h; (iii) EDC (1 eq.), R_1COOH (1 eq.), DMAP, dry DCM, 3 h; (iv) mCPBA, CH_2Cl_2 ; (v) $POCl_3$ (10 equiv), DMF, Chlobenzene, 110ºC, 6 h; (vi) $NaBH_4$, MeOH, rt, 3 h; (vii) EDC (3 eq.), R_2COOH (3 eq.), DMAP, dry DCM, 3 h; (viii) mCPBA, CH_2Cl_2 ; (ix) H_2O_2, Acetic Acid ; (x) EDC (1 eq.), R_3COOH (1 eq.), DMAP, dry DCM, 30 min; (xi) EDC (1 eq.), R_4COOH (1 eq.), DMAP, dry DCM, 3 h.

3. Experimental Procedure and spectroscopic data:

Synthesis of 10-ethyl-10*H*-phenothiazine (1): The compound **1** was synthesized according to the literature procedure.[1]

Synthesis of 10-ethyl-10*H*-phenothiazine-3-carbaldehyde (2): The compound was synthesized according to the literature procedure.[2]

Synthesis of (10-ethyl-10*H*-phenothiazin-3-yl)methanol[3] (3):

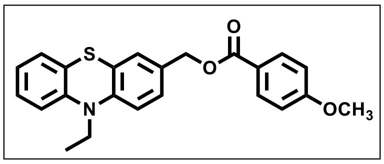


To a stirred solution of the formyl derivative (256 mg, 1 mmol, 1 equiv) in dry methanol (10 ml), $NaBH_4$ (76 mg, 2 mmol, 2 equiv) was added portionwise at 0ºC and the resulting mixture was stirred further at room temperature for 1 hr. The mixture was concentrated in vacuo & the residue was diluted with ethyl acetate. The organic layers was washed with water & then brine, dried over anhydrous Na_2SO_4 and give the colourless solid. (Yield 235 mg, 91%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 4H), 6.92 – 6.88 (m, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 4.55 (s, 2H), 3.91 (q, *J* = 7.0 Hz, 2H), 1.41 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.0, 144.6, 135.1, 127.5, 127.4, 126.4, 126.3, 124.8, 124.3, 122.5, 115.2, 115.2, 64.8, 42.0, 13.1.

General procedure for the synthesis of single-arm caged esters (4a-e):

1.2 equiv of the corresponding acid and EDC-HCl (1.2 equiv) was dissolved in dry DCM and cooled to 0°C. After 5 min compound, **3** (50 mg, 0.19 mmol) and DMAP (cat.) were added to the reaction mixture. The reaction was allowed to stir at room temperature for 3 h. After completion of the reaction, it was extracted with DCM, washed with saturated $NaHCO_3$ solution, and dried over Na_2SO_4. The solvent was removed in rotary evaporation under reduced pressure, and the crude residue was purified by column chromatography using EtOAc in hexane.

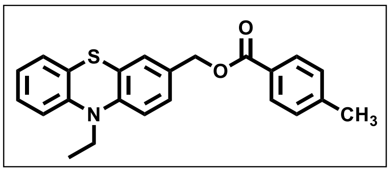
Synthesis of (10-ethyl-10*H*-phenothiazin-3-yl)methyl 4-methoxybenzoate (4a):



4-Methoxybenzoic acid was treated with compound **3** as aforementioned procedure, and the crude residue was purified by chromatography on silica gel using 20% EtOAc in pet ether to give the pale greenish coloured gel product. (Yield 69 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.22 (dd, J = 4.3, 2.3 Hz, 2H), 7.16 – 7.11 (m, 2H), 6.93 – 6.90 (m, 2H), 6.90 (s, 1H), 6.85 (t, J = 7.8 Hz, 2H), 5.22 (s, 2H), 3.92 (q, J = 6.9 Hz, 2H), 3.84 (s, 3H), 1.41 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 163.6, 145.2, 144.9, 131.9, 130.5, 127.8, 127.4, 124.3, 122.8, 122.6, 115.2, 115.1, 113.8, 7.96, 55.6, 42.0, 13.1. HRMS (ESI^{+}) calcd for $C_{23}H_{22}NO_3S$ [M+H]$^{+}$, 392.1320; found: 392.1330.

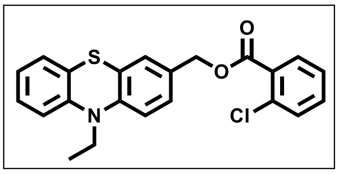
Synthesis of (10-ethyl-10*H*-phenothiazin-3-yl)methyl 4-methylbenzoate (4b):



Toluic acid was treated with compound **3** using the aforementioned procedure, and the crude residue was purified by chromatography on silica gel using 20% EtOAc in pet ether to give the pale yellow coloured gel product. (Yield 65 mg, 90%).

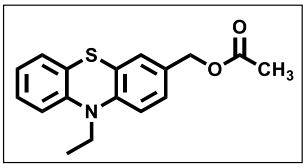
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.9 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.14 (dd, J = 16.1, 7.7 Hz, 2H), 6.91 (s, 1H), 6.86 (t, J = 7.1 Hz, 2H), 5.22 (s, 2H), 3.93 (q, 2H), 2.60 (s, 3H), 1.42 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 145.1, 140.4, 132.2, 131.8, 130.9, 129.6, 127.8, 127.5, 125.8, 124.8, 124.1, 122.7, 115.3, 115.1, 65.6, 42.0, 22.1, 13.2. HRMS (ESI^{+}) calcd for $C_{23}H_{22}NO_2S$ [M+H]$^{+}$, 376.1371; found: 376.1382.

Synthesis of (10-ethyl-10*H*-phenothiazin-3-yl)methyl 2-chlorobenzoate (4c):



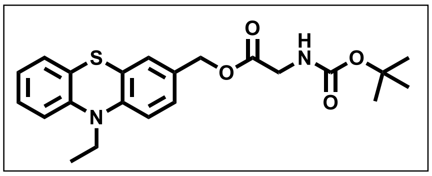
o-chloro benzoic acid was treated with compound **3** as aforementioned procedure and the crude residue was purified by chromatography on silica gel using 20% EtOAc in pet ether to give the pale yellow coloured gel product. (Yield 67 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 7.7, 1.5 Hz, 1H), 7.42 (m, 2H), 7.31 – 7.28 (m, 1H), 7.25 – 7.21 (m, 2H), 7.18 – 7.09 (m, 2H), 6.91 (m, 1H), 6.86 (dd, J = 8.0, 5.1 Hz, 2H), 5.24 (s, 2H), 3.92 (q, J = 6.9 Hz, 2H), 1.41 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 145.3, 144.8, 133.9, 132.6, 131.6, 131.2, 130.1, 129.7, 128.0, 127.8, 127.5, 127.4, 126.6, 124.8, 124.2, 122.6, 115.2, 115.0, 66.8, 42.0, 13.1. HRMS (ESI^{+}) calcd for $C_{22}H_{19}ClNO_2S$ [M+H]$^{+}$, 396.0825; found: 396.0832.

Synthesis of (10-ethyl-10*H*-phenothiazin-3-yl)methyl acetate (4d):



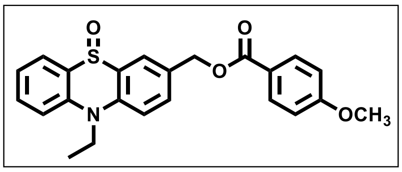
Acetic acid was treated with compound **3** as aforementioned procedure and the crude residue was purified by chromatography on silica gel using 20% EtOAc in pet ether to give the pale yellow coloured gel product. (Yield 48 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.08 (m, 4H), 6.90 (s, 1H), 6.84 (dd, J = 12.3, 8.5 Hz, 2H), 4.98 (s, 2H), 3.91 (q, 2H), 2.08 (s, 3H), 1.41 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 145.2, 144.8, 130.1, 127.8, 127.7, 127.5, 127.4, 124.8, 124.2, 122.6, 115.2, 115.0, 65.8, 42.0, 21.1, 13.1. HRMS calcd for $C_{17}H_{18}NO_2S$ [M+H]$^{+}$, 300.1058, found: 300.1063.

Synthesis of (10-ethyl-10*H*-phenothiazin-3-yl)methyl (tert-butoxycarbonyl)glycinate (4e):



(tert-butoxycarbonyl)glycine was treated with compound **3** as aforementioned procedure and the crude residue was purified by chromatography on silica gel using 20% EtOAc in pet ether to give the pale yellow coloured gel product. (Yield 64 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.08 (m, 4H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.84 (dd, *J* = 17.8, 8.2 Hz, 2H), 5.05 (s, 2H), 4.98 (s, 1H), 3.92 (m, 4H), 1.44 (s, 9H), 1.41 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 155.8, 145.4, 144.8, 129.4, 128.0, 127.9, 127.5, 127.4, 124.9, 124.2, 122.7, 115.3, 115.1, 66.6, 42.7, 42.0, 28.4, 13.1. HRMS (ESI$^+$) calcd for $C_{22}H_{26}N_2NaO_4S$ [M+Na]$^+$, 437.1511; found: 437.1488.

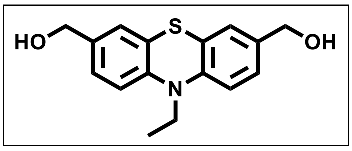
(10-ethyl-5-oxido-10*H*-phenothiazin-3-yl)methyl 4-methoxybenzoate (5a):



Treatment of **4a** (50 mg, 0.127 mmol) with mCPBA (22 mg, 0.127 mmol) in dry DCM (4 ml) at 0 ºC to room temperature for a period of 4 h afforded the conjugate. The crude conjugate was washed with water & $NaHCO_3$, dried over anhydrous Na_2SO_4. Then the solvent was removed in rotary evaporation under reduced pressure and the crude residue was purified by column chromatography using 40% EtOAC in hexane to give the white solid. (Yield 47 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 3H), 7.95 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.72 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.47 (dd, *J* = 8.6, 2.2 Hz, 2H), 7.29 – 7.23 (m, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.39 (s, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.58 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 163.7, 138.1, 138.1, 133.4, 133.2, 132.0, 131.9, 130.0, 122.5, 122.1, 115.9, 115.7, 113.8, 65.5, 55.6, 43.0, 12.2. HRMS (ESI$^+$) calcd for $C_{23}H_{22}NO_4S$ [M+H]$^+$, 408.1270; found: 408.1282.

Synthesis of 10-ethyl-10*H*-phenothiazine-3,7-dicarbaldehyde (6): Same as described procedure.[4]

Synthesis of (10-ethyl-10*H*-phenothiazine-3,7-diyl)dimethanol[5] (7):

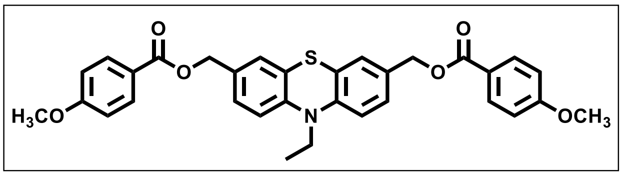


To a stirred solution of the formyl derivative (285 mg, 1 mmol, 1 equiv) in dry methanol (10 ml), $NaBH_4$ (95 mg, 2.5 mmol, 2.5 equiv) was added portion-wise at 0ºC, and the resulting mixture was stirred further at room temperature for 1 hr. The mixture was concentrated in vacuo & the residue was diluted with ethyl acetate. The organic layer was washed with water & then brine, dried over anhydrous Na_2SO_4. Then the solvent was removed in rotary evaporation under reduced pressure, and the crude residue was purified by column chromatography using 40% EtOAc in hexane to give the pale yellow gel. (Yield 230 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.0, 1H), 7.20 (d, *J* = 6.0 Hz, 1H), 7.12 (s, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.56 (s, 4H), 3.90 (s, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 135.2, 126.4, 124.6, 115.2, 64.8, 42.1, 13.1.

General procedure for the synthesis of dual-arm caged esters (8a-c):

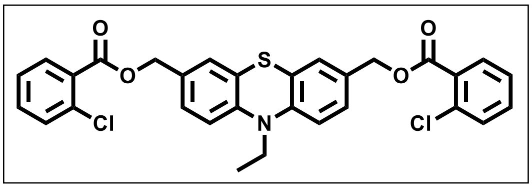
2.2 equiv of the corresponding acid and EDC-HCl (2.2 equiv) was dissolved in dry DCM and cooled to 0°C. After 5 min compound, **7** (50 mg, 0.17 mmol) and DMAP (cat.) were added to the reaction mixture. The reaction was allowed to stir at room temperature for 3 h. After completion of the reaction, it was extracted with DCM, washed with saturated $NaHCO_3$ solution, and dried over Na_2SO_4. The solvent was removed in rotary evaporation under reduced pressure, and the crude residue was purified by column chromatography using EtOAc in hexane.

Synthesis of (10-ethyl-10*H*-phenothiazine-3,7-diyl)bis(methylene) bis(4-methoxybenzoate) (8a):



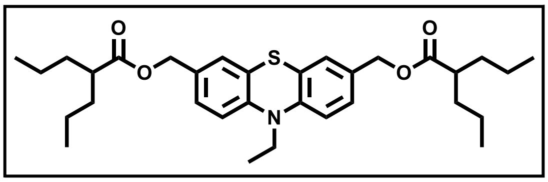
4-Methoxybenzoic acid was treated with compound **7** as aforementioned procedure, and the crude residue was purified by chromatography on silica gel using 30% EtOAc in pet ether to give the pale greenish coloured gel product. (Yield 67 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.6 Hz, 4H), 7.21 (m, 4H), 6.90 (d, *J* = 8.5 Hz, 4H), 6.84 (d, *J* = 8.0 Hz, 2H), 5.20 (s, 4H), 3.92 (m, 2H), 3.85 (s, 6H), 1.41 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 163.6, 144.9, 131.9, 130.7, 127.9, 127.7, 124.5, 122.8, 115.1, 113.8, 65.9, 55.6, 42.1, 13.1. HRMS (ESI$^+$) calcd for $C_{32}H_{30}NO_6S$ $[M+H]^+$, 556.1794; found: 556.1778.

Synthesis of (10-ethyl-10H-phenothiazine-3,7-diyl)bis(methylene) bis(2-chlorobenzoate) (8b):



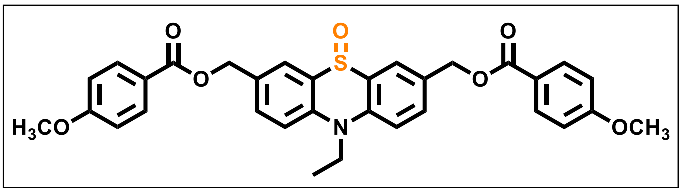
p-Chloro benzoic acid was treated with compound **7** as aforementioned procedure, and the crude residue was purified by chromatography on silica gel using 30% EtOAc in pet ether to give the pale greenish coloured gel product. (Yield 64 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.42 (m, 7.6 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.19 (m, 4H), 6.85 (d, *J* = 8.2 Hz, 2H), 5.24 (s, 4H), 3.92 (q, *J* = 6.9 Hz, 2H), 1.41 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 145.0, 134.0, 132.7, 131.7, 131.2, 130.1, 129.9, 128.2, 127.9, 126.7, 124.5, 115.1, 66.8, 42.1, 13.0. HRMS (ESI$^+$) calcd for $C_{30}H_{24}Cl_2NO_4S$ $[M+H]^+$, 564.0803; found: 564.0788.

Synthesis of (10-ethyl-10*H*-phenothiazine-3,7-diyl)bis(methylene) bis(2 propylpentanoate) (8c):



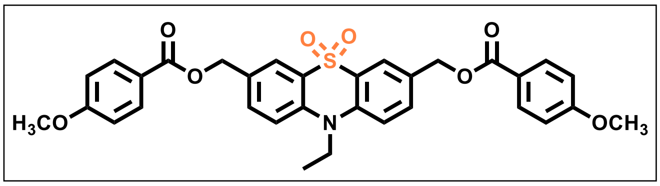
Valproic acid was treated with compound **7** as aforementioned procedure and the crude residue was purified by chromatography on silica gel using 25% EtOAc in pet ether to give the pale yellow coloured gel product. (Yield 66 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 – 6.95 (m, 4H), 6.72 (d, *J* = 8.1 Hz, 2H), 4.88 (s, 4H), 3.81 (q, *J* = 6.7 Hz, 2H), 2.30 (dd, *J* = 11.4, 6.4 Hz, 2H), 1.57 – 1.45 (m, 7H), 1.31 (d, *J* = 6.6 Hz, 7H), 1.20 – 1.16 (m, 8H), 0.78 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 144.8, 135.2, 130.5, 127.5, 126.4, 124.4, 115.0, 65.3, 45.4, 42.0, 34.7, 20.7, 14.1, 13.0. HRMS (ESI$^+$) calcd for $C_{32}H_{46}NO_4S$ $[M+H]^+$, 540.3148; found: 540.3133.

Synthesis of (10-ethyl-5-oxido-10*H*-phenothiazine-3,7-diyl)bis(methylene) bis(4-methoxybenzoate) (9a):



Treatment of **8a** (50 mg, 0.089 mmol) with mCPBA (16 mg, 0.089 mmol) in dry DCM (4 ml) at 0 °C to room temperature for a period of 4 h afforded the conjugate. The crude conjugate was washed with water & $NaHCO_3$, dried over anhydrous Na_2SO_4. Then the solvent was removed in rotary evaporation under reduced pressure, and the crude residue was purified by column chromatography using 50% EtOAc in hexane to give the white solid. (Yield 44 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 6H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 4H), 5.39 (s, 4H), 4.37 (q, *J* = 6.8 Hz, 2H), 3.85 (s, 6H), 1.57 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 163.7, 137.9, 133.4, 131.9, 130.2, 124.1, 122.5, 115.9, 113.8, 65.4, 55.6, 43.0, 12.2. HRMS (ESI$^+$) calcd for $C_{32}H_{30}NO_7S$ $[M+H]^+$, 572.1743; found: 572.1715.

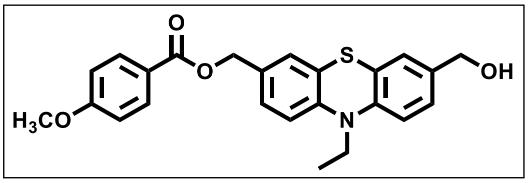
Synthesis of (10-ethyl-5,5-dioxido-10*H*-phenothiazine-3,7-diyl)bis(methylene) bis(4-methoxybenzoate) (10a):



Oxidation of **9a** (50 mg, 0.085 mmol) with H_2O_2 (0.05 ml) in the presence of acetic acid (0.25 ml) at 50°C for a period of 2 h afforded compound **10a.** The crude conjugate was extracted with DCM and washed with water, dried over anhydrous Na_2SO_4. Then the solvent was removed in rotary evaporation under reduced pressure and the crude residue was purified by column chromatography using 80% EtOAc in hexane to give the white solid. (Yield 23 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 2H), 8.01 (d, *J* = 8.7 Hz, 4H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 4H), 5.38 (s, 4H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 6H), 1.55 (t, *J*

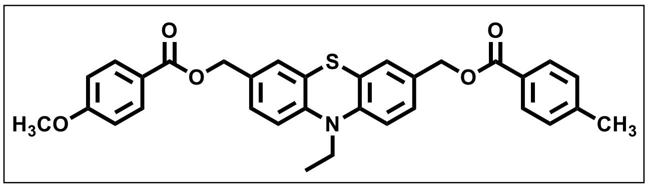
= 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 163.7, 140.3, 133.6, 131.9, 130.5, 124.1, 123.7, 122.3, 116.1, 113.8, 65.2, 55.5, 43.4, 12.6. HRMS (ESI$^+$) calcd for $C_{32}H_{33}N_2O_8S$ [M+NH$_4$]$^+$, 605.1958; found: 605.1947.

Synthesis of (10-ethyl-7-(hydroxymethyl)-10*H*-phenothiazin-3-yl)methyl 4-methoxybenzoate (11):



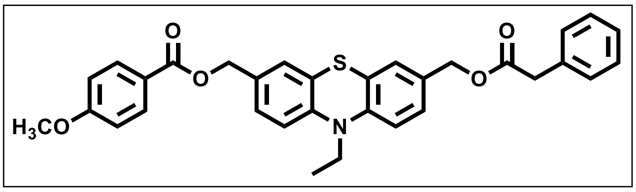
Anisic acid (0.9 equiv,) and EDC-HCl (1.0 equiv,) was dissolved in dry DCM and cooled to 0 °C. After 5 min compound **7** (200 mg, 0.97 mmol) and DMAP (cat.) was added to the reaction mixture. The reaction was allowed to stir at room temperature for 3 h. After completion of the reaction it was extracted with DCM and washed with saturated $NaHCO_3$ solution and dried over Na_2SO_4. The solvent was removed in rotary evaporation under reduced pressure and the crude residue was purified by column chromatography using 30% EtOAc in hexane. (Yield 148 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.12 (s, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 5.5 Hz, 2H), 5.20 (s, 2H), 4.57 (s, 2H), 3.91 (m, 2H), 3.85 (s, 3H), 1.41 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 163.6, 135.4, 131.9, 130.6, 127.9, 127.7, 126.4, 124.6, 122.8, 115.2, 115.0, 113.8, 65.93 (s), 55.6, 42.1, 13.1. HRMS (ESI$^+$) calcd for $C_{24}H_{24}NO_4S$ [M+H]$^+$, 422.1426; found: 422.1409.

Synthesis of (10-ethyl-7-(((4-methoxybenzoyl)oxy)methyl)-10H-phenothiazin-3-yl)methyl 4-methylbenzoate (12a):



Toluic acid (0.9 equiv,) and EDC-HCl (1.0 equiv,) was dissolved in dry DCM and cooled to 0 °C. After 5 min compound **11** (50 mg, 0.12 mmol) and DMAP (cat.) was added to the reaction mixture. The reaction was allowed to stir at room temperature for 3 h. After completion of the reaction it was extracted with DCM and washed with saturated $NaHCO_3$ solution and dried over Na_2SO_4. The solvent was removed in rotary evaporation under reduced pressure and the crude residue was purified by column chromatography using 20% EtOAc in hexane. (Yield 49 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.17 (m, 6H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 2H), 5.21 (s, 4H), 3.92 (q, 2H), 3.85 (s, 3H), 2.59 (s, 3H), 1.41 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 166.2, 163.7, 140.6, 132.4, 131.9, 131.7, 130.6, 129.6, 127.8, 127.6, 126.0, 122.3 115.1, 113.8, 65.9, 55.6, 43.4, 41.8, 22.0. HRMS (ESI$^+$) calcd for $C_{32}H_{30}NO_5S$ [M+H]$^+$, 540.1845; found: 540.1829.

Synthesis of (10-ethyl-7-((2-phenylacetoxy)methyl)-10H-phenothiazin-3-yl)methyl 4-methoxybenzoate (12b):



Phenyl acetic acid (0.9 equiv,) and EDC-HCl (1.0 equiv,) was dissolved in dry DCM and cooled to 0 °C. After 5 min compound **11** (50 mg, 0.12 mmol) and DMAP (cat.) was added to the reaction mixture. The reaction was allowed to stir at room temperature for 3 h. After completion of the reaction it was extracted with DCM and washed with saturated $NaHCO_3$ solution and dried over Na_2SO_4. The solvent was removed in rotary evaporation under reduced pressure and the crude residue was purified by column chromatography using 20% EtOAc in hexane. (Yield 45 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.27 (d, *J* = 7.5 Hz, 4H), 7.21 (d, *J* = 9.4 Hz, 2H), 7.08 (d, *J* = 11.8 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 5.20 (s, 2H), 5.00 (s, 2H), 3.91 (q, *J* = 6.9 Hz, 2H), 3.85 (s, 3H), 3.63 (s, 2H), 1.40 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 166.2, 163.5, 144.7, 133.9, 131.7, 130.5, 130.1, 129.3, 128.6 127.6, 127.1, 124.3, 122.6, 114.9, 113.6, 65.9, 65.7, 55.4, 41.9, 41.4, 12.8. HRMS (ESI$^+$) calcd for $C_{32}H_{30}NO_5S$ $[M+H]^+$, 540.1845; found: 540.1833.

4. ^{1}H and ^{13}C NMR of the caged compounds:

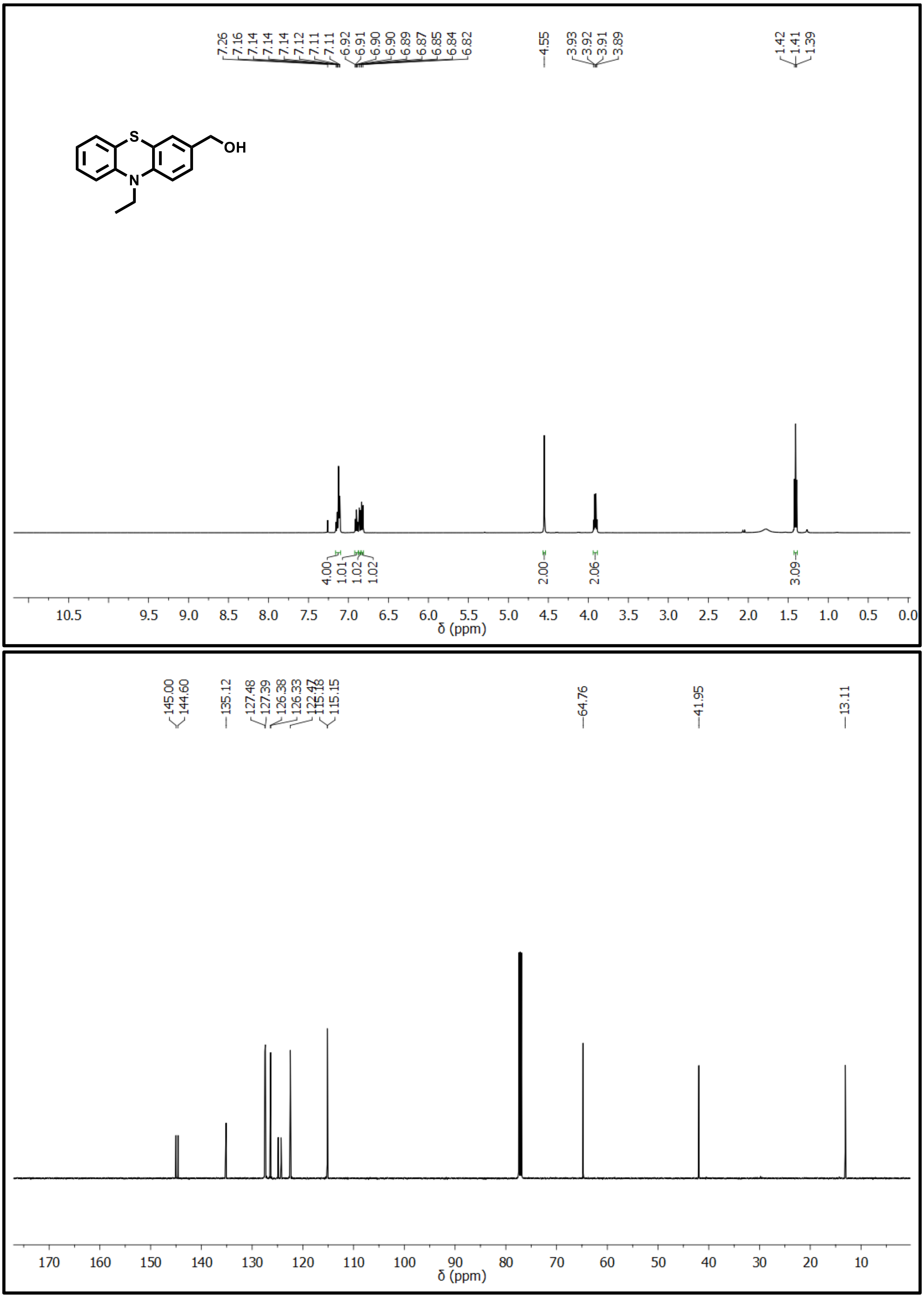


Fig. S1 ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR spectra of **3**.

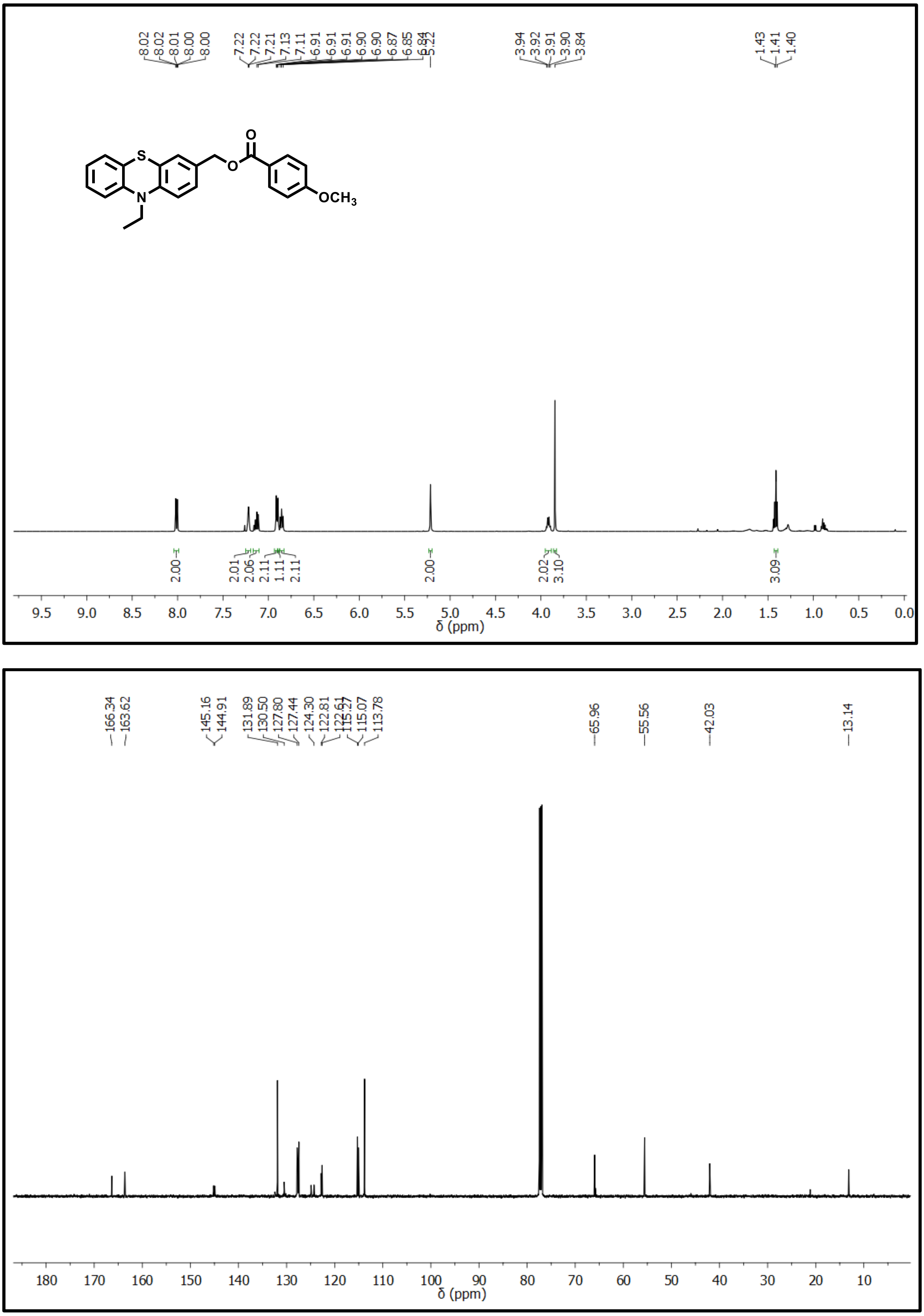


Fig. S2 ^{1}H (500 MHz, CDCl$_3$) and ^{13}C (126 MHz, CDCl$_3$) NMR spectra of **4a**.

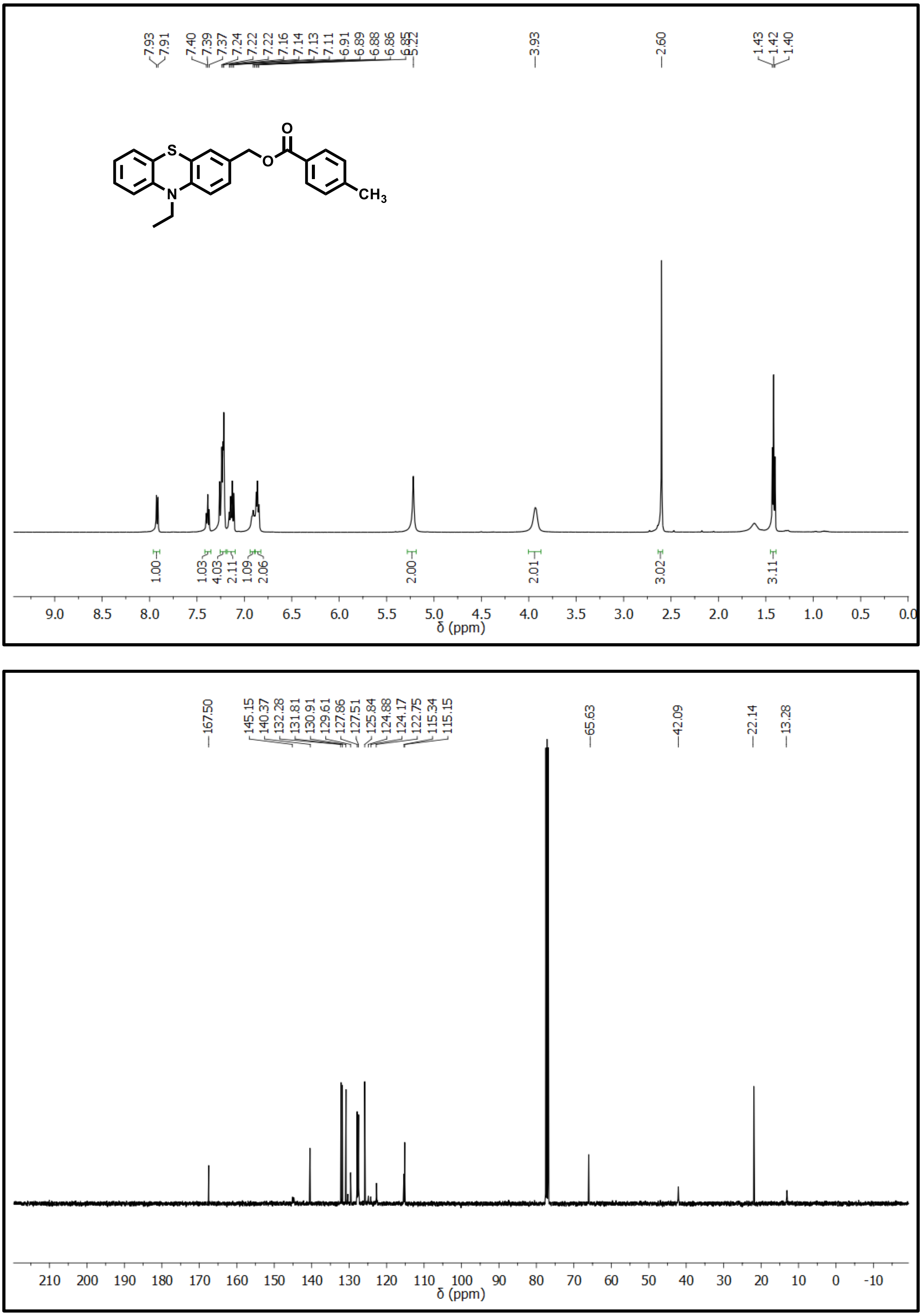


Fig. S3 ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (101 MHz, $CDCl_3$) NMR spectra of **4b**.

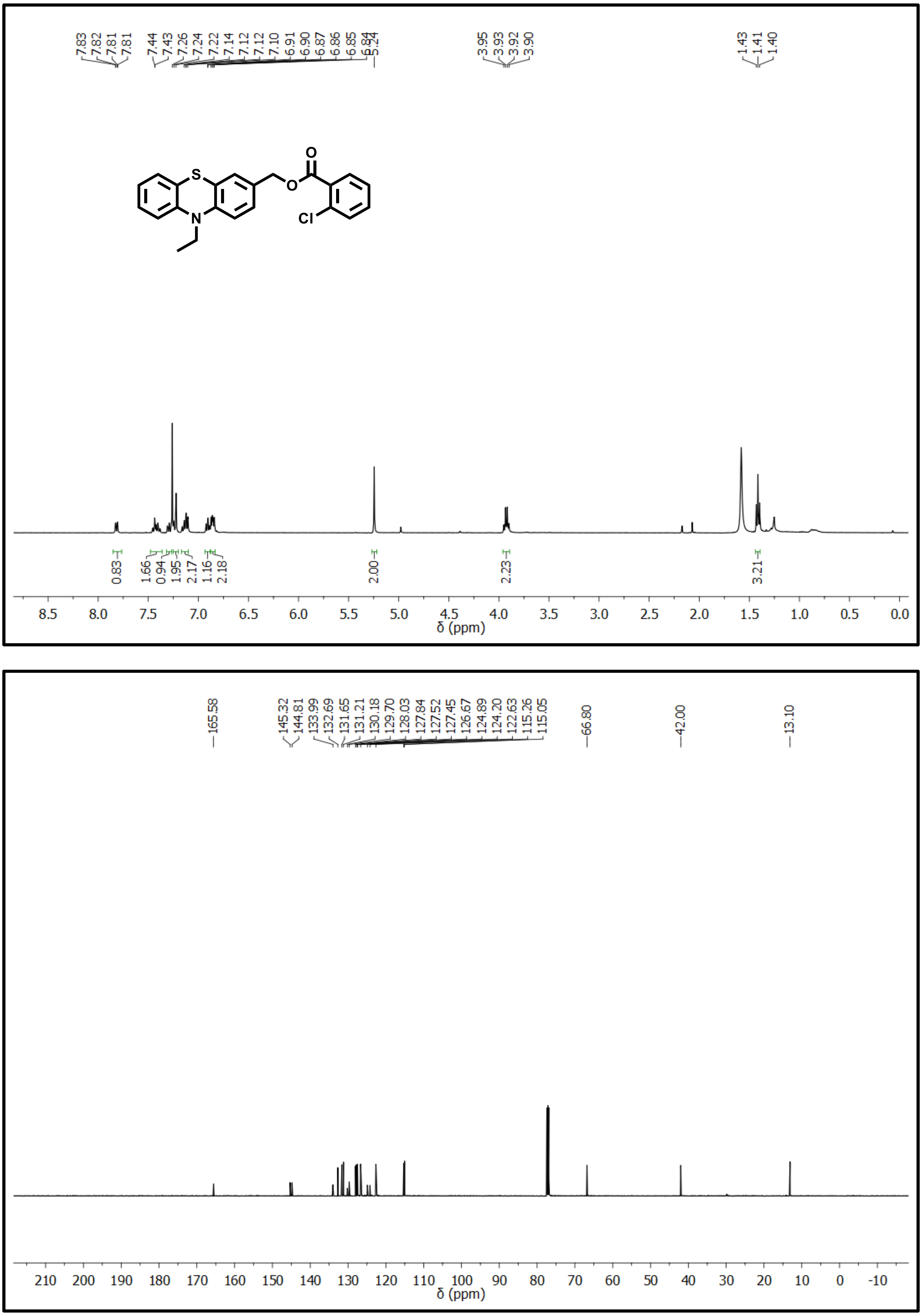


Fig. S4 ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR spectra of **4c**.

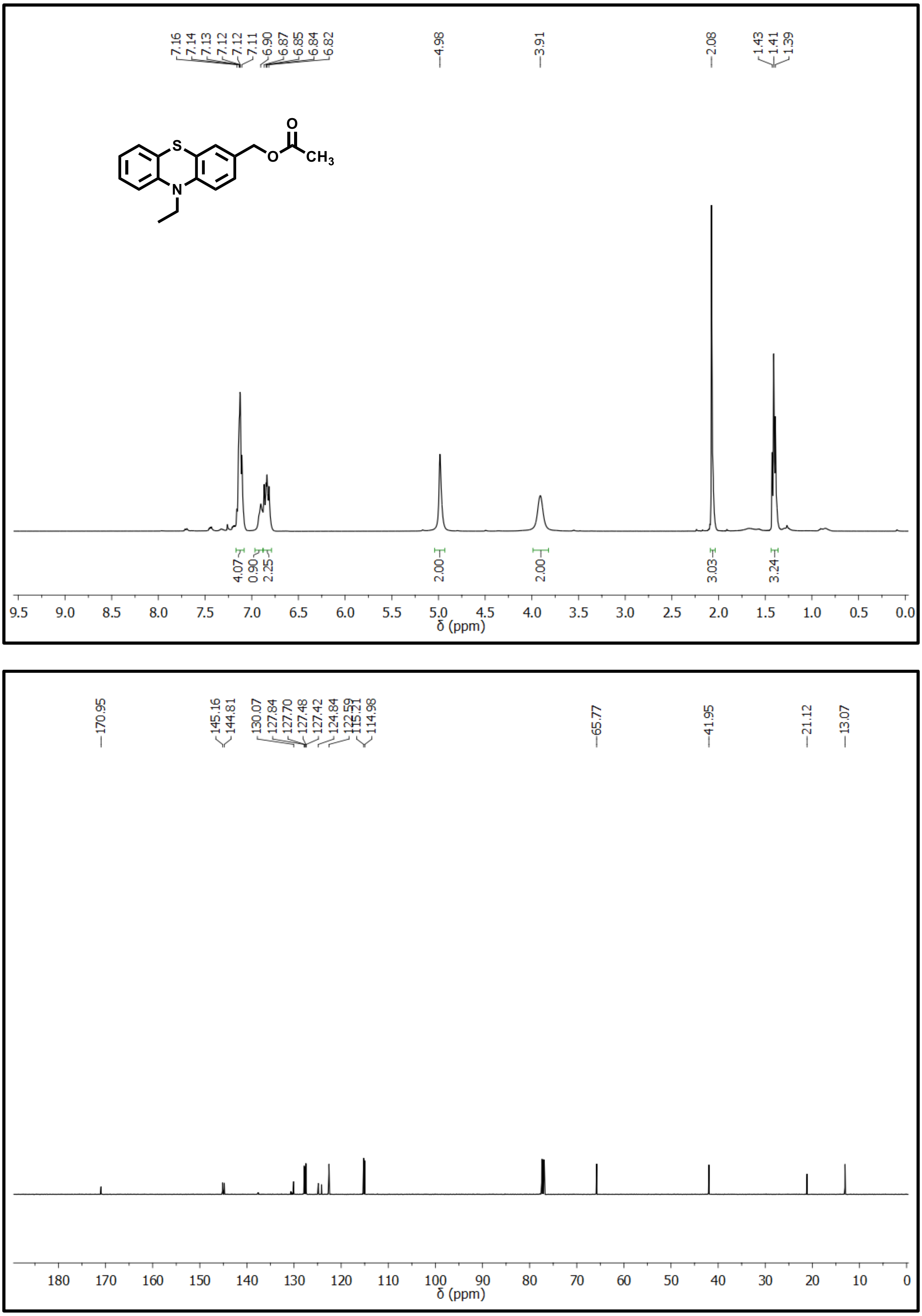


Fig. S5 ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (126 MHz, CDCl$_3$) NMR spectra of **4d**.

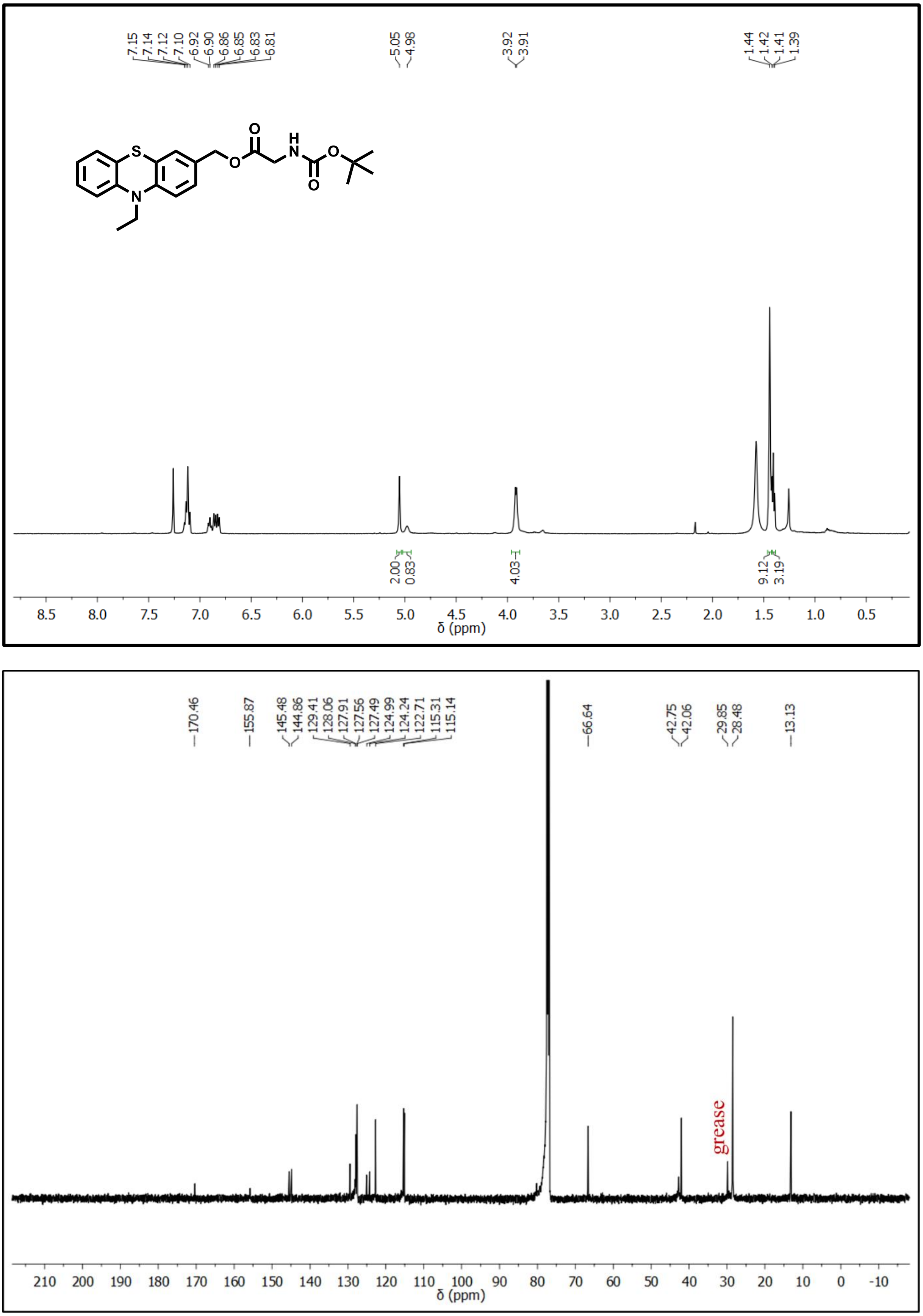


Fig. S6 ^{1}H (500 MHz, CDCl$_3$) and ^{13}C (126 MHz, CDCl$_3$) NMR spectra of **4e**.

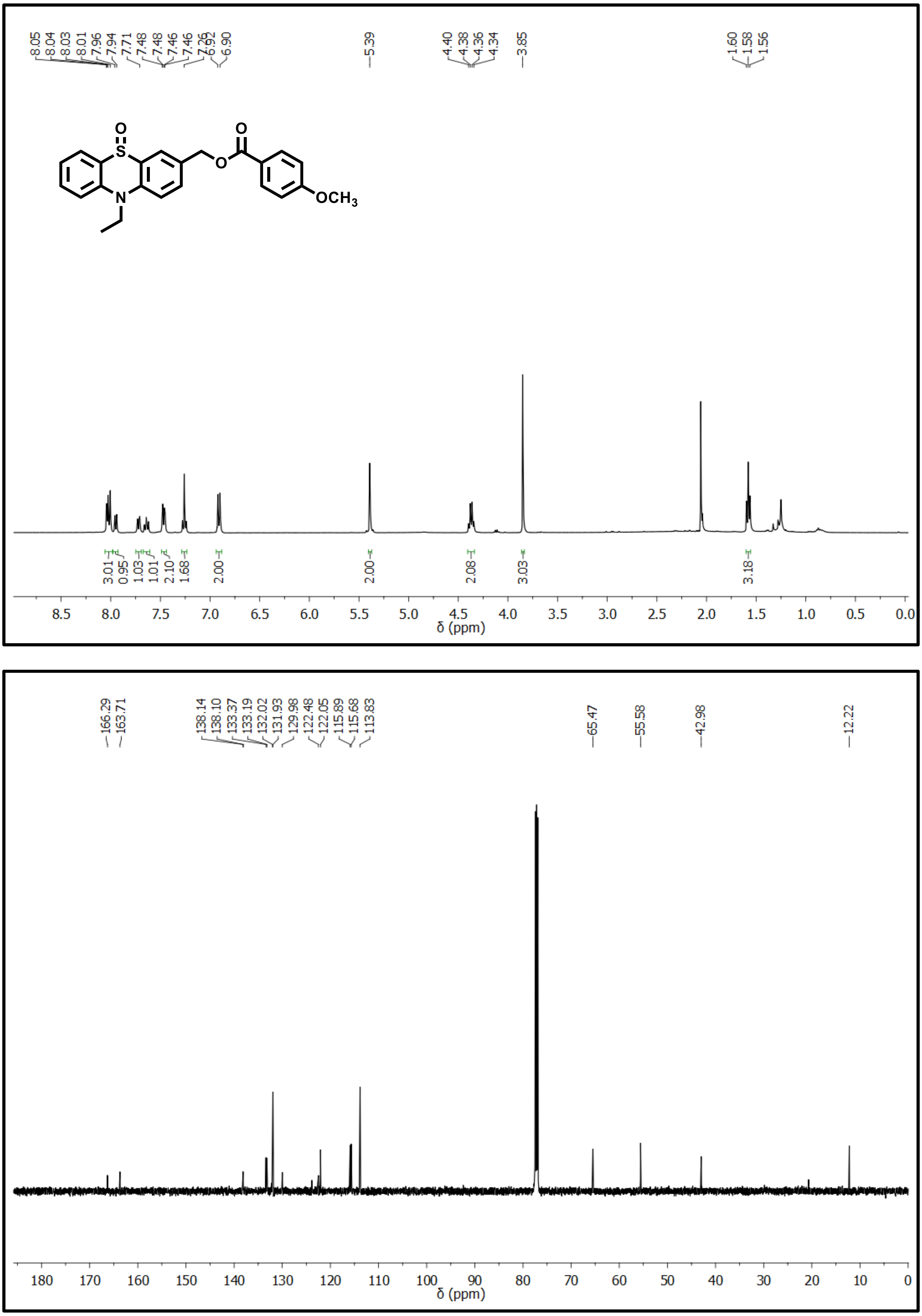


Fig. S7 ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (126 MHz, CDCl$_3$) NMR spectra of **5a**.

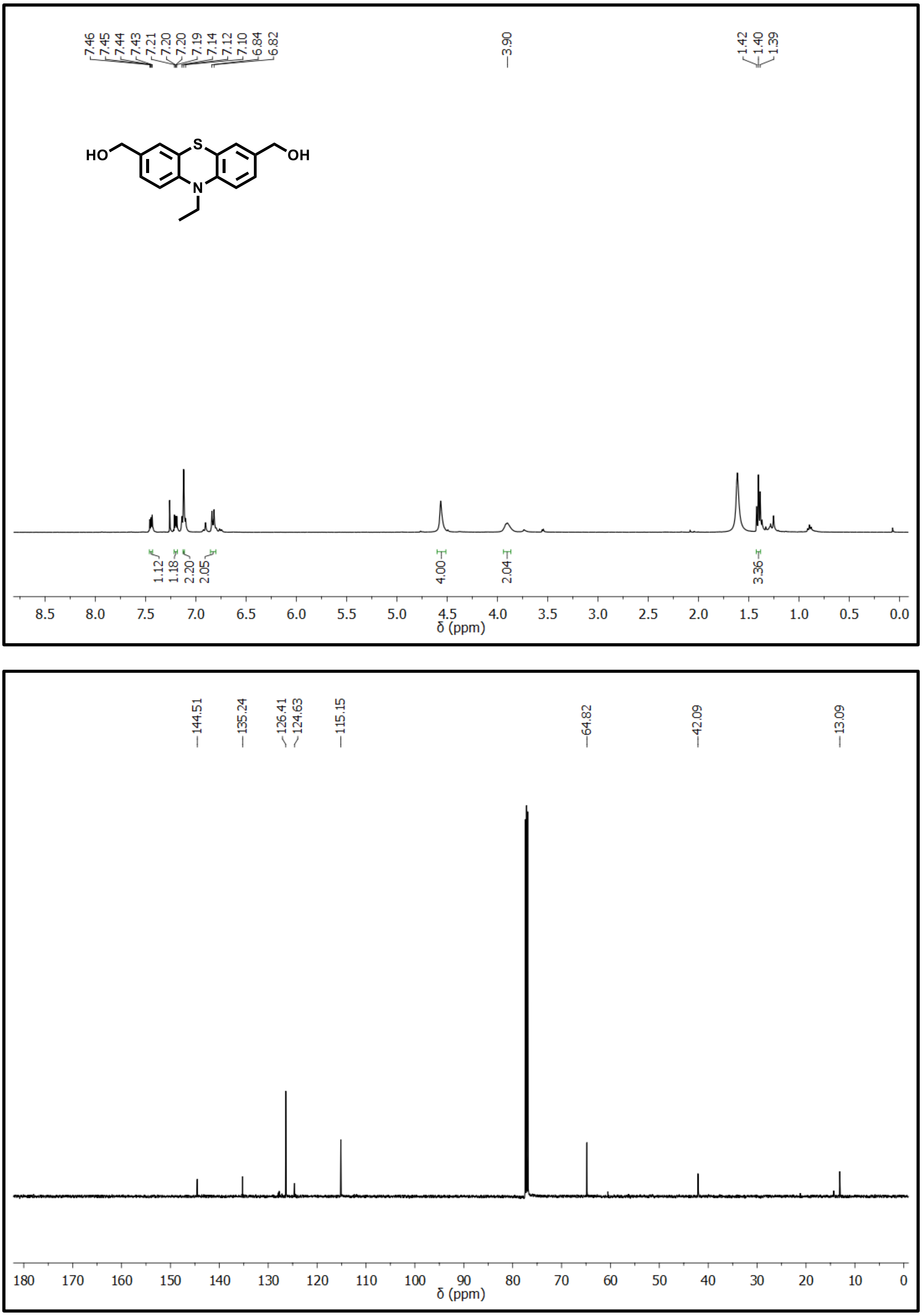


Fig. S8 ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (126 MHz, CDCl$_3$) NMR spectra of **7**.

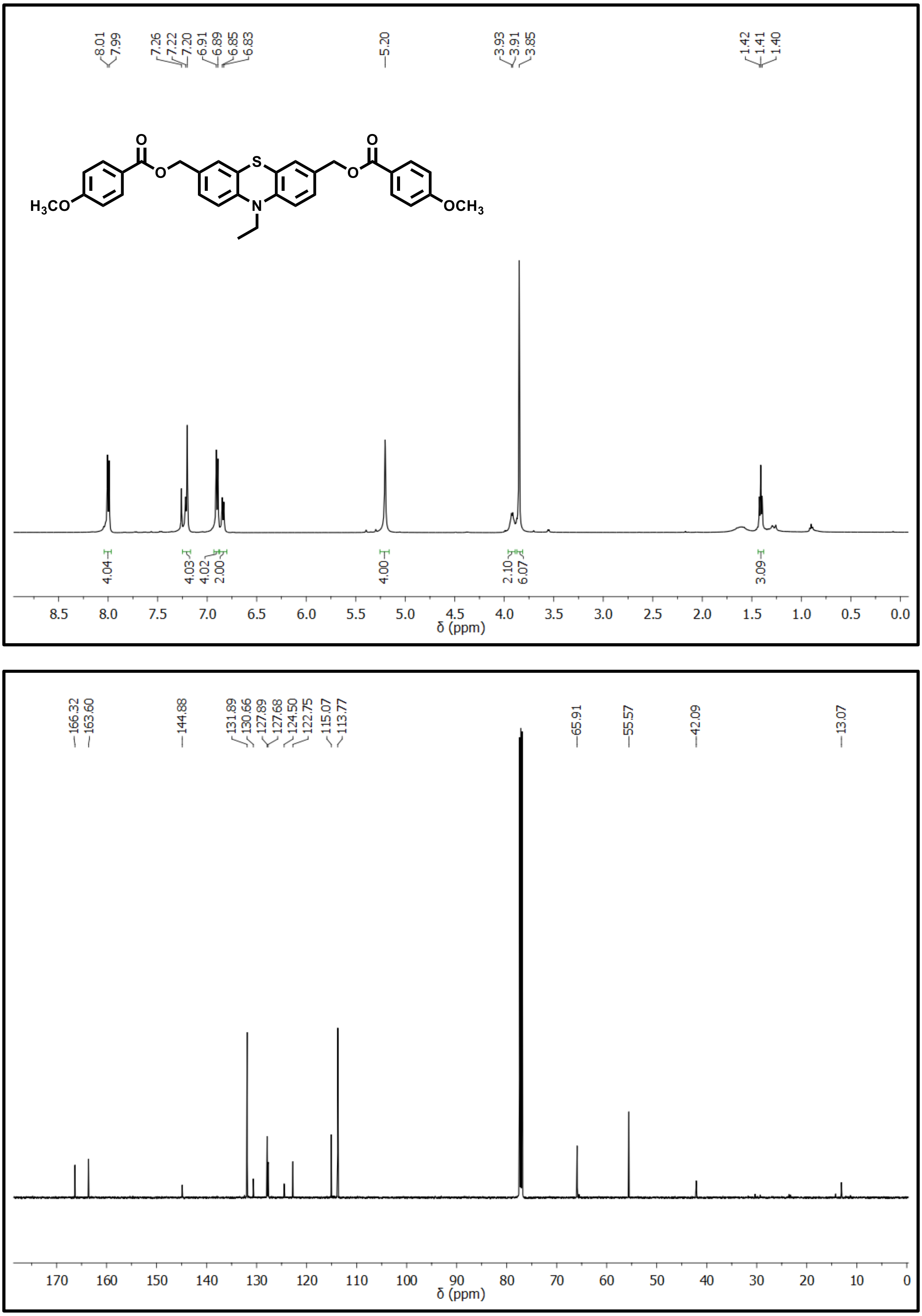


Fig. S9 ^{1}H (500 MHz, CDCl$_3$) and ^{13}C (126 MHz, CDCl$_3$) NMR spectra of **8a**.

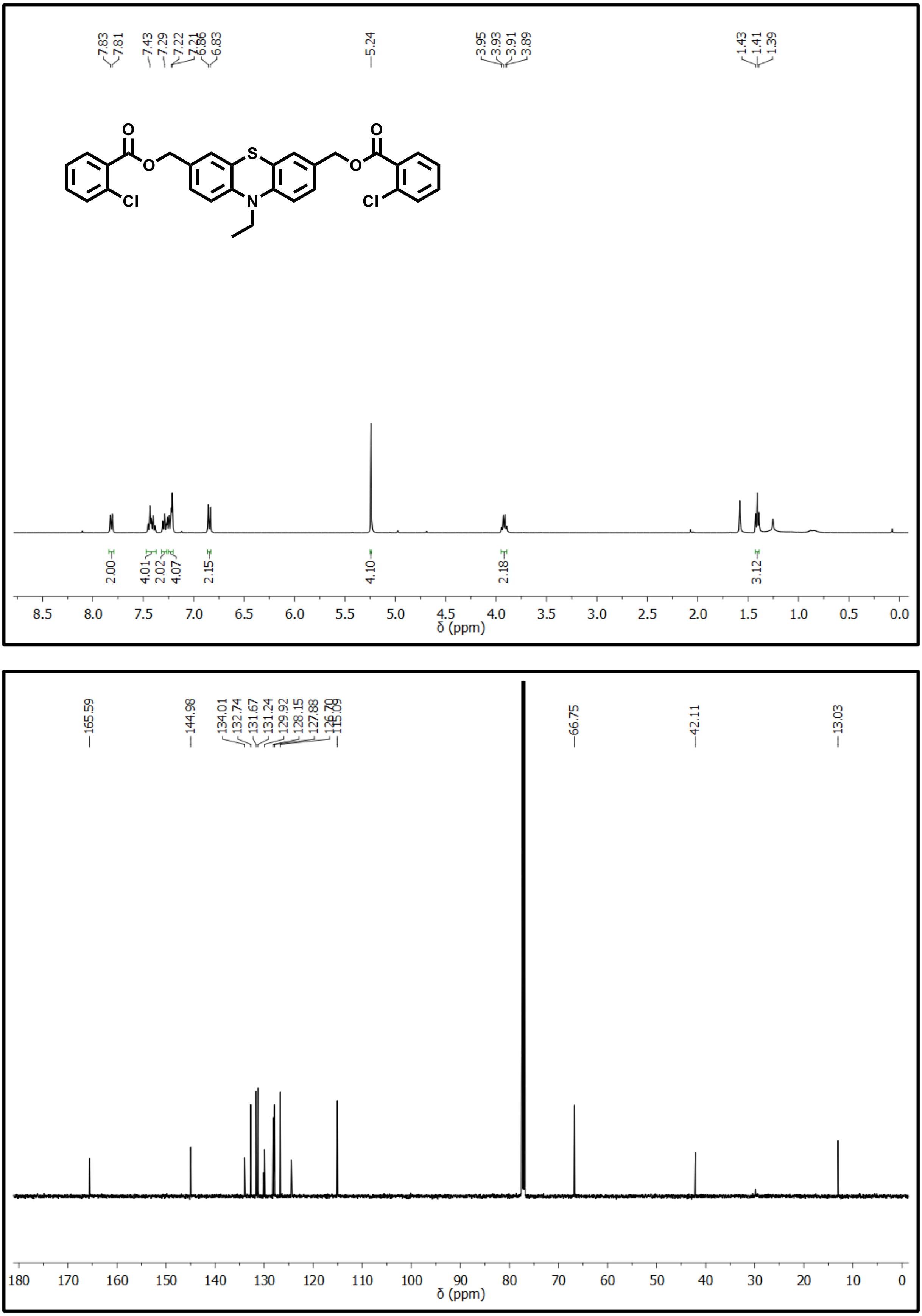


Fig. S10 ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR spectra of **8b**.

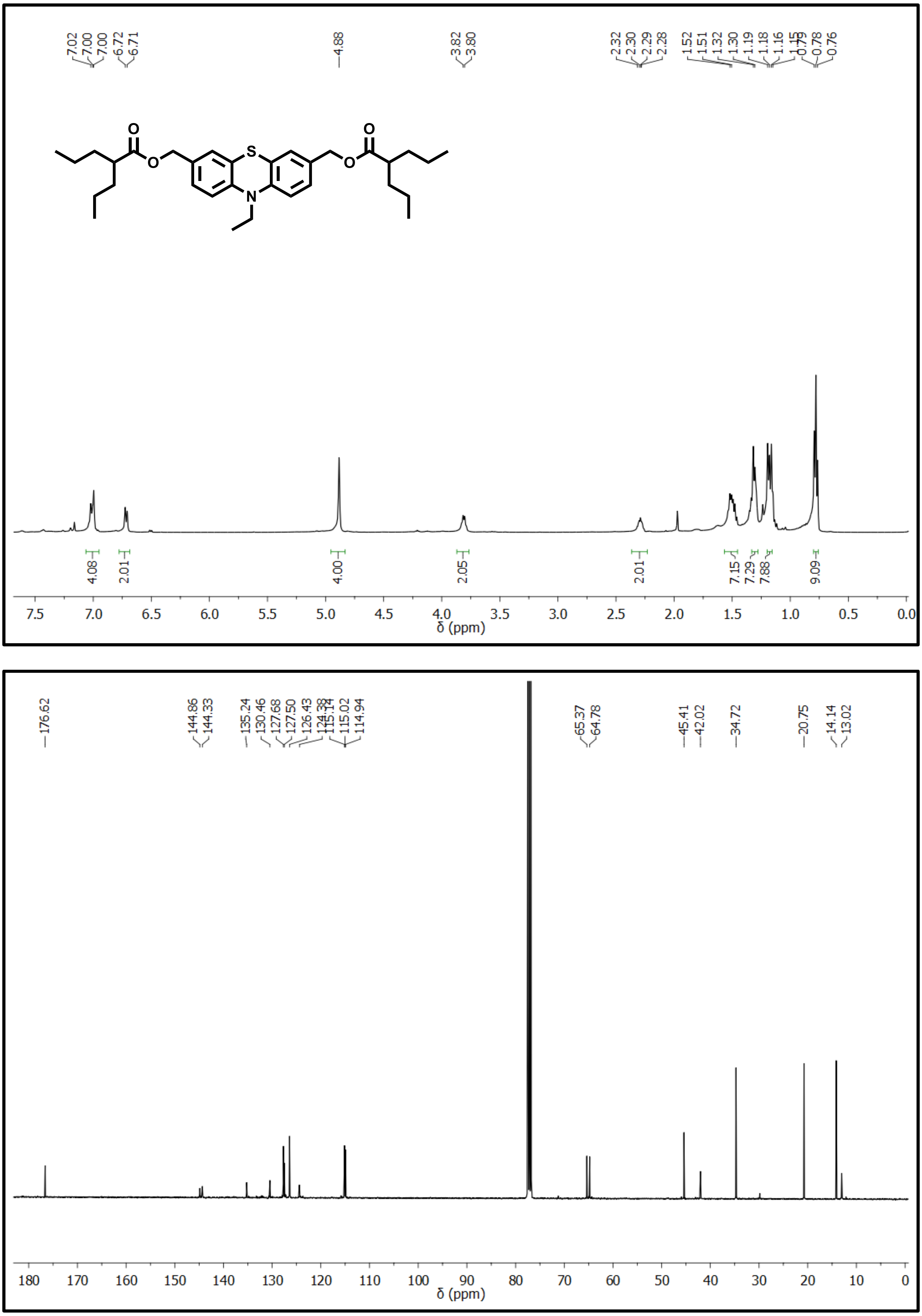


Fig. S11 ^{1}H (500 MHz, CDCl$_3$) and ^{13}C (101 MHz, CDCl$_3$) NMR spectra of **8c**.

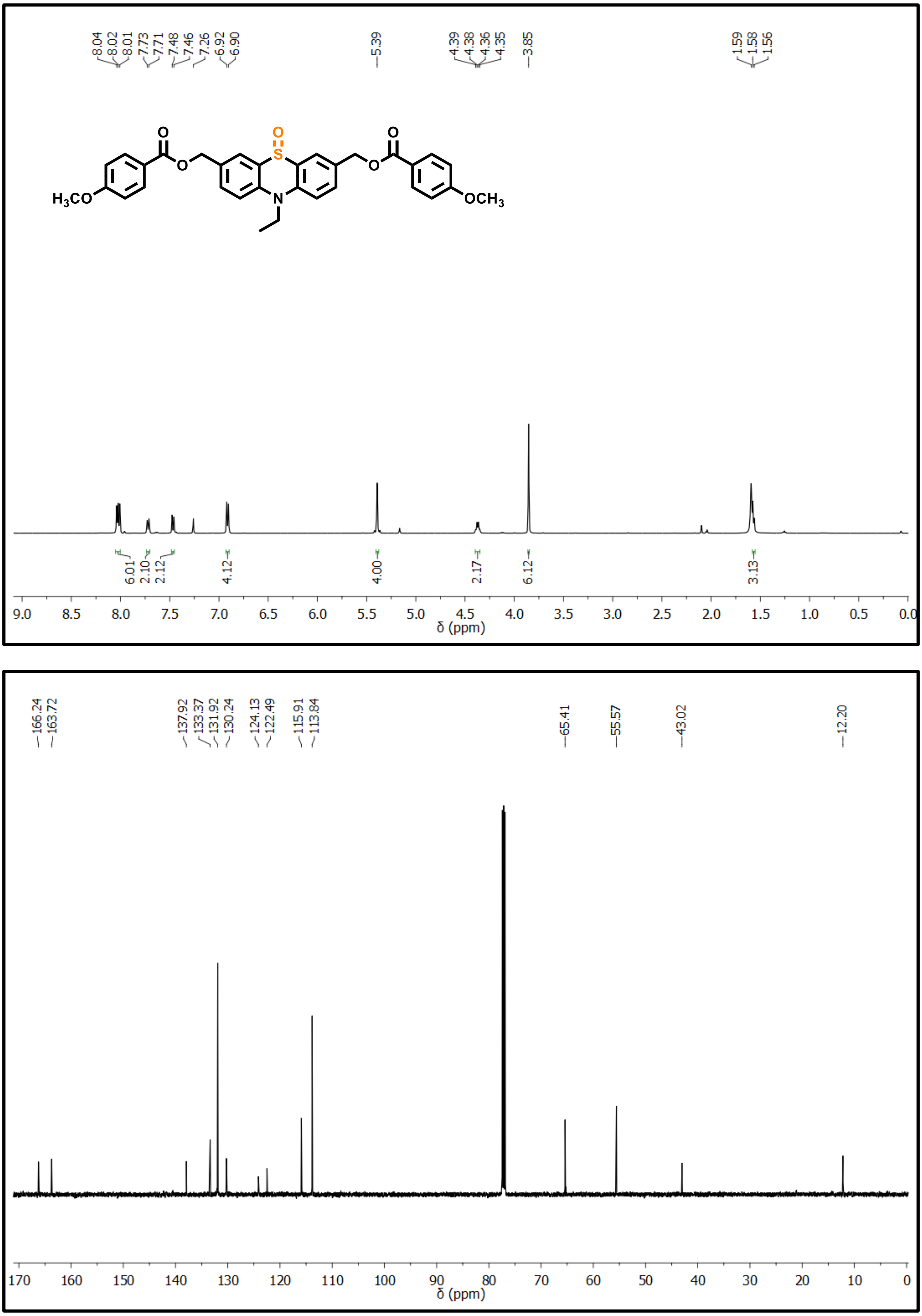
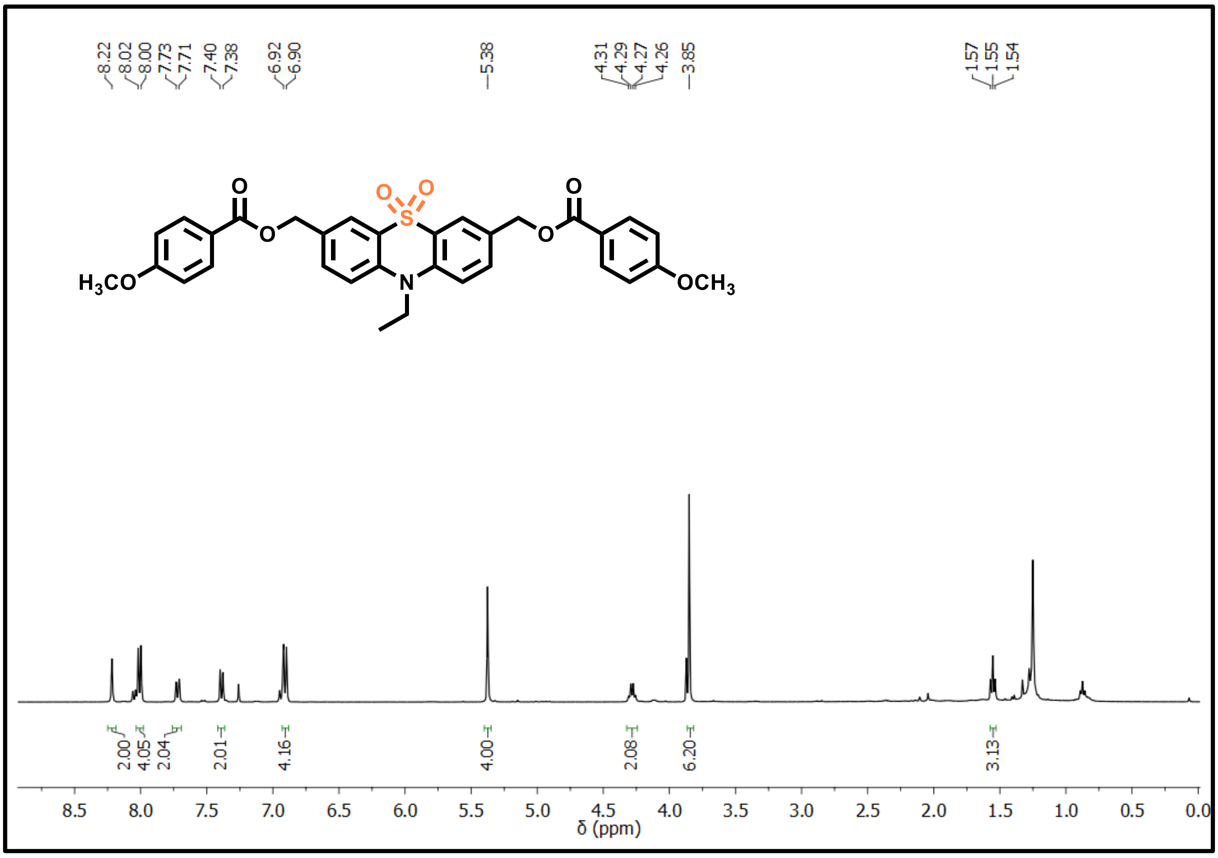


Fig. S12 ^{1}H (500 MHz, CDCl$_3$) and ^{13}C (126 MHz, CDCl$_3$) NMR spectra of **9a**.



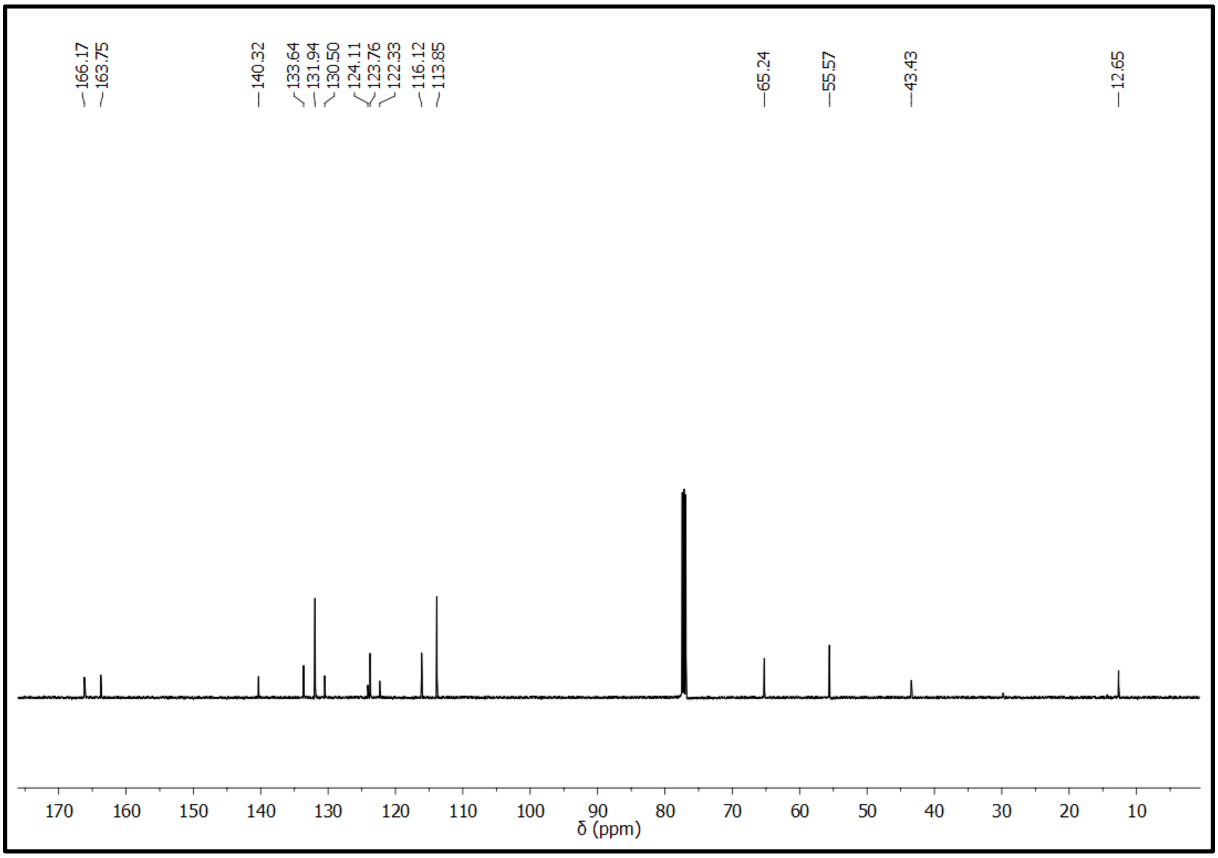


Fig. S13 ^1H (400 MHz, $CDCl_3$) and ^{13}C (101 MHz, $CDCl_3$) NMR spectra of **10a**.

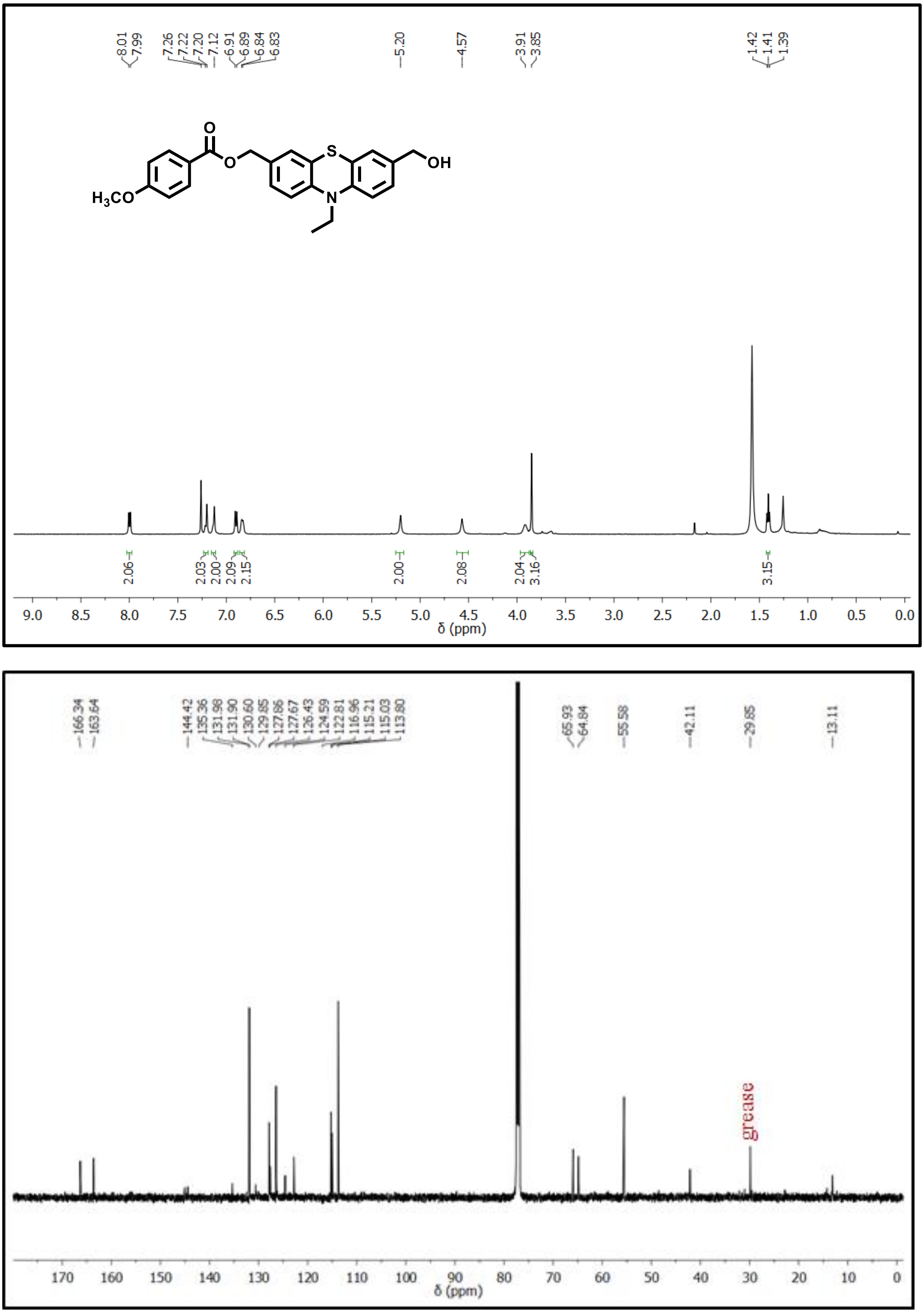


Fig. S14 ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR spectra of **11**.

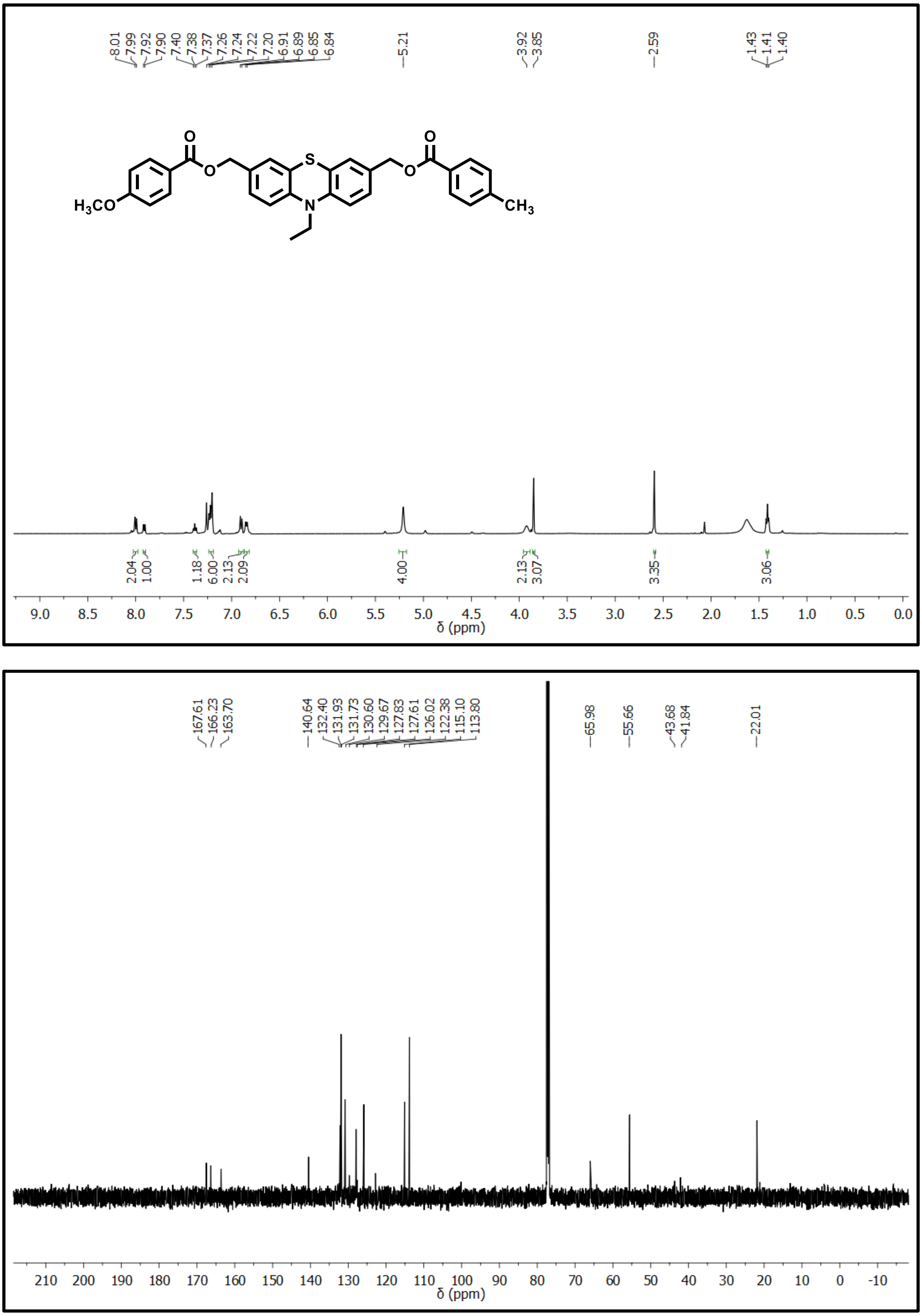


Fig. S15 ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR spectra of **12a**.

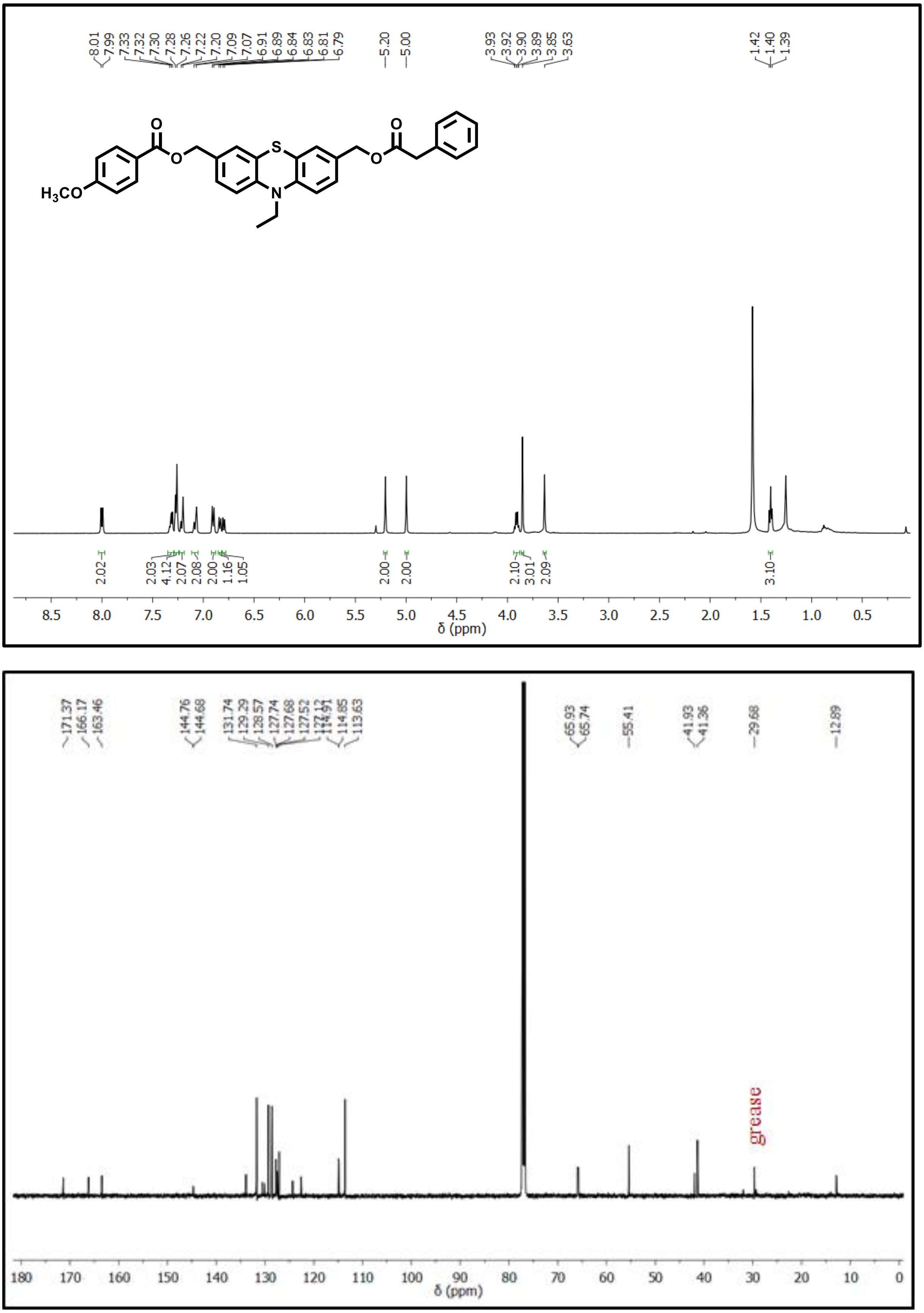


Fig. S16 ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR spectra of **12b**.

5. HRMS spectra of caged compounds:

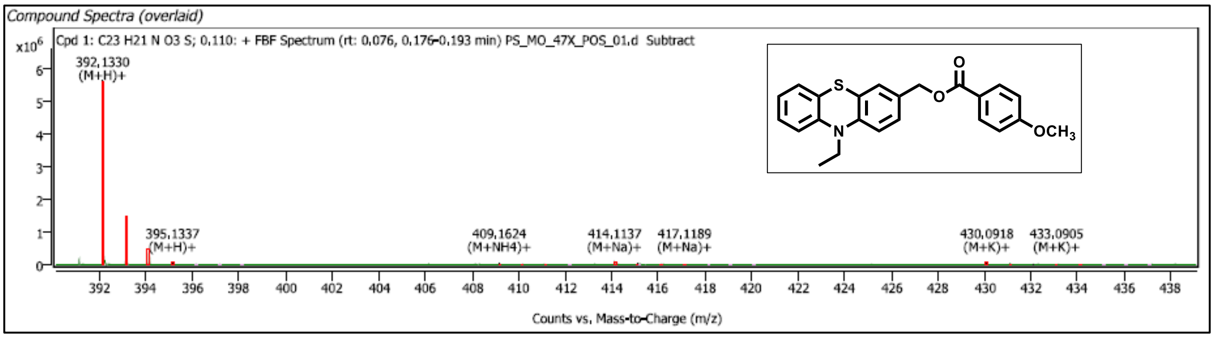


Fig. S17 HRMS spectrum of **4a**.

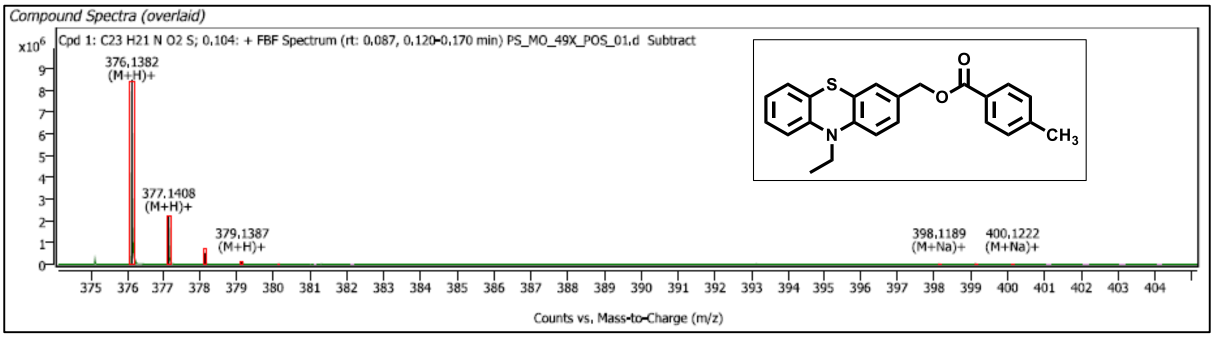


Fig. S18 HRMS spectrum of **4b**.

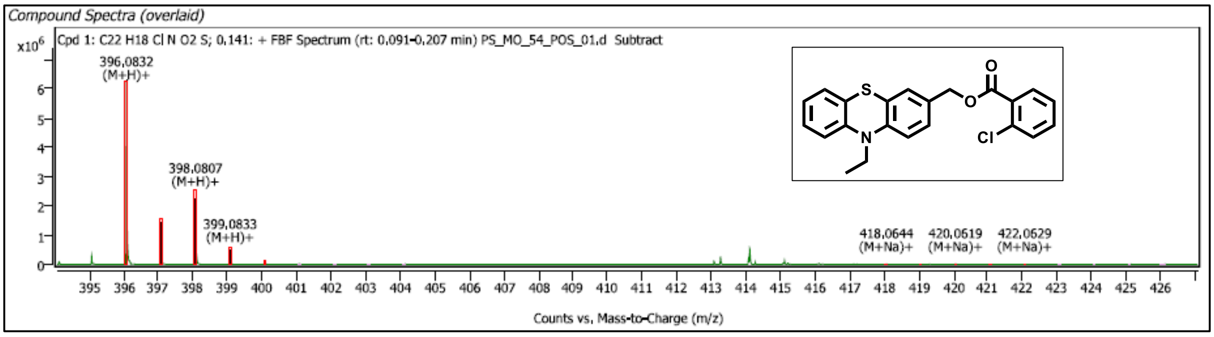


Fig. S19 HRMS spectrum of **4c**.

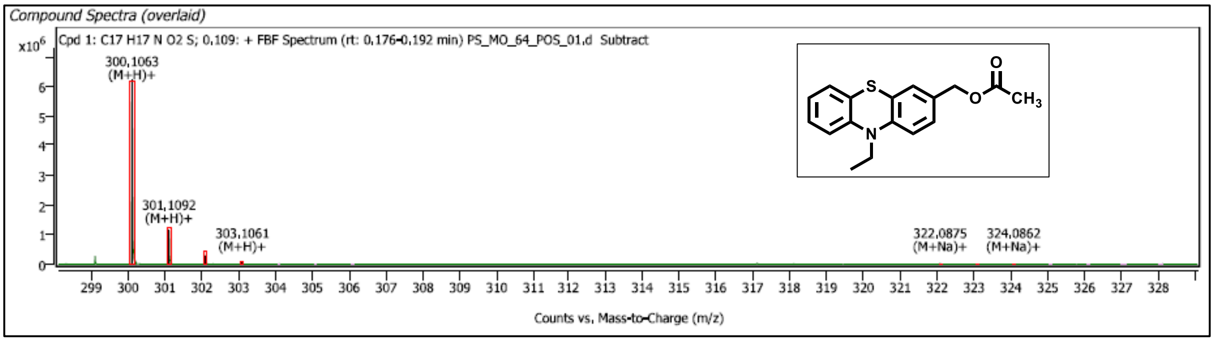


Fig. S20 HRMS spectrum of **4d**.

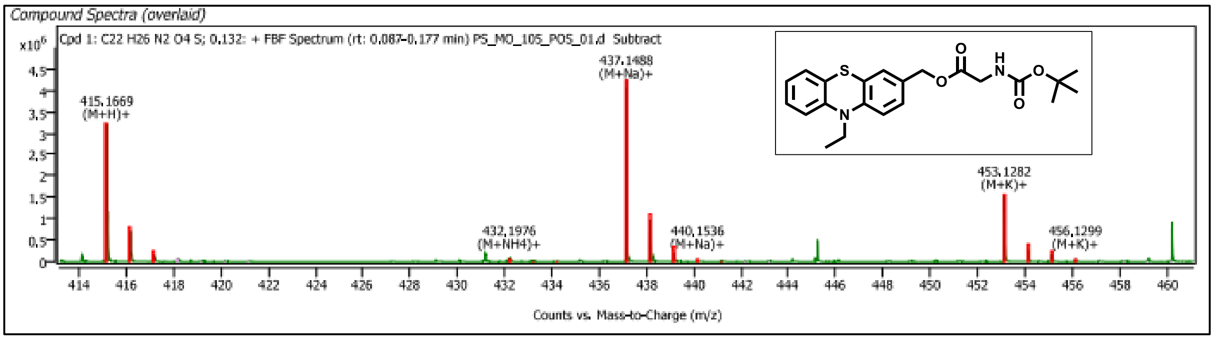


Fig. S21 HRMS spectrum of **4e**.

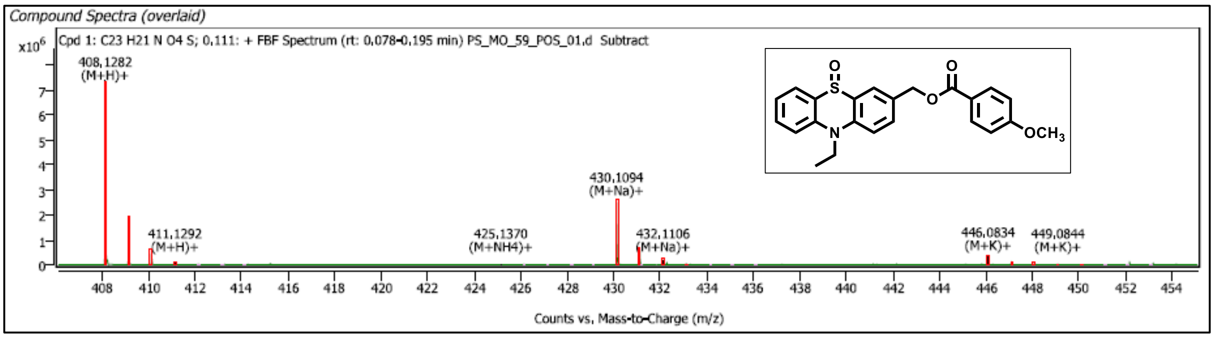


Fig. S22 HRMS spectrum of **5a**.

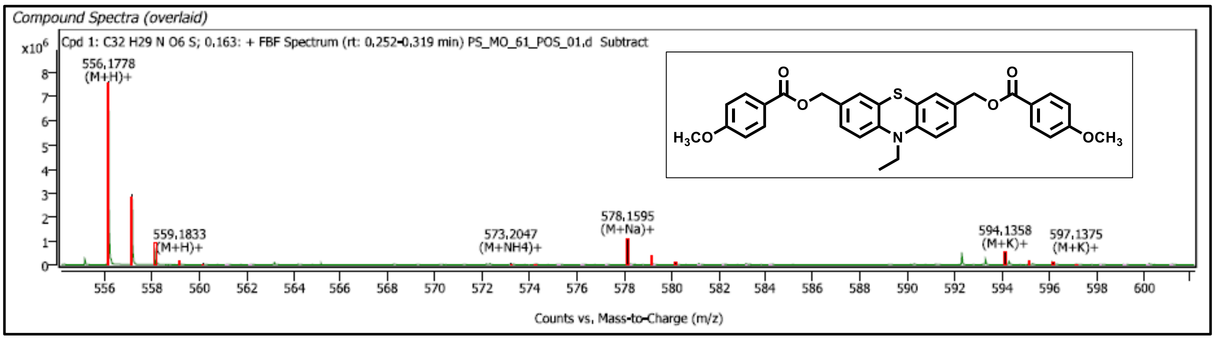


Fig. S23 HRMS spectrum of **8a**.

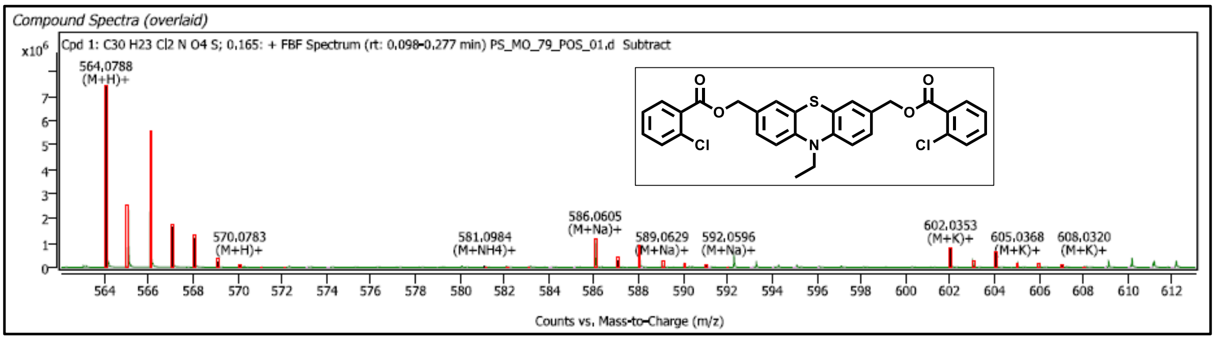


Fig. S24 HRMS spectrum of **8b**.

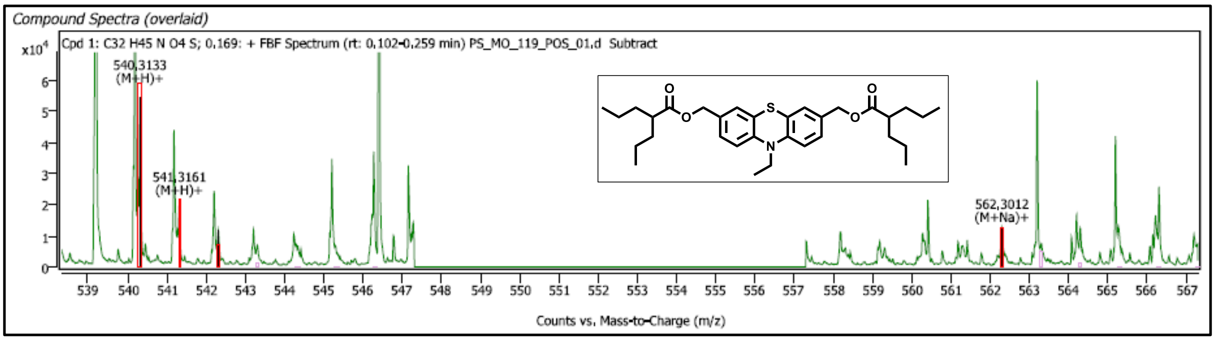


Fig. S25 HRMS spectrum of **8c**.

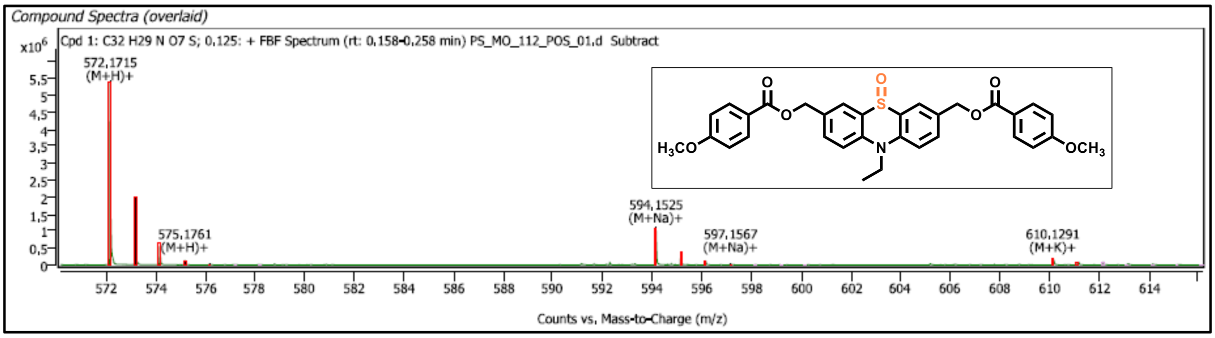


Fig. S26 HRMS spectrum of **9a**.

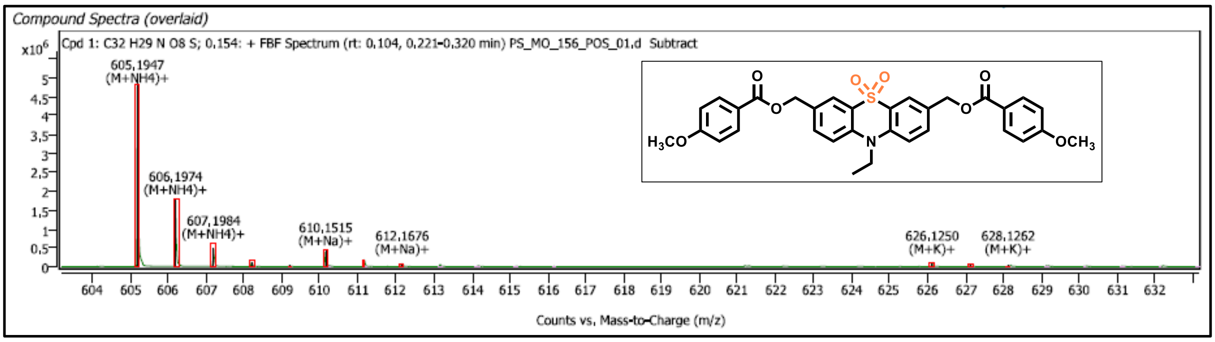


Fig. S27 HRMS spectrum of **10a**.

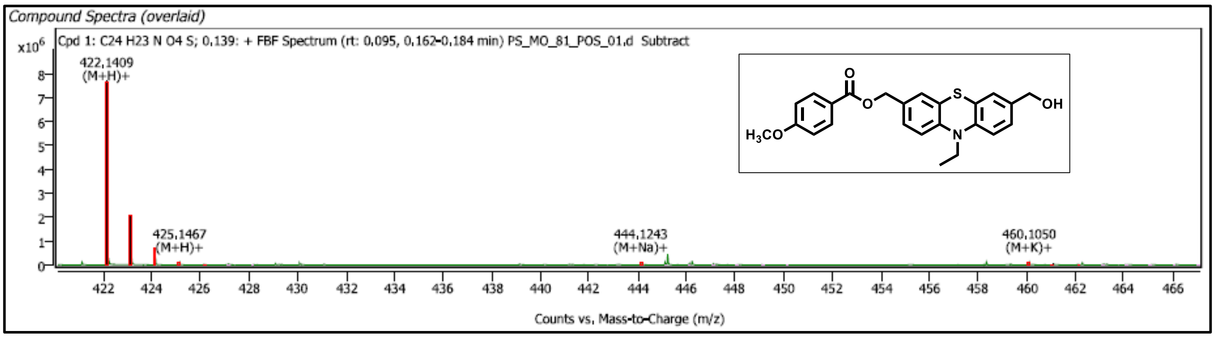


Fig. S28 HRMS spectrum of **11**.

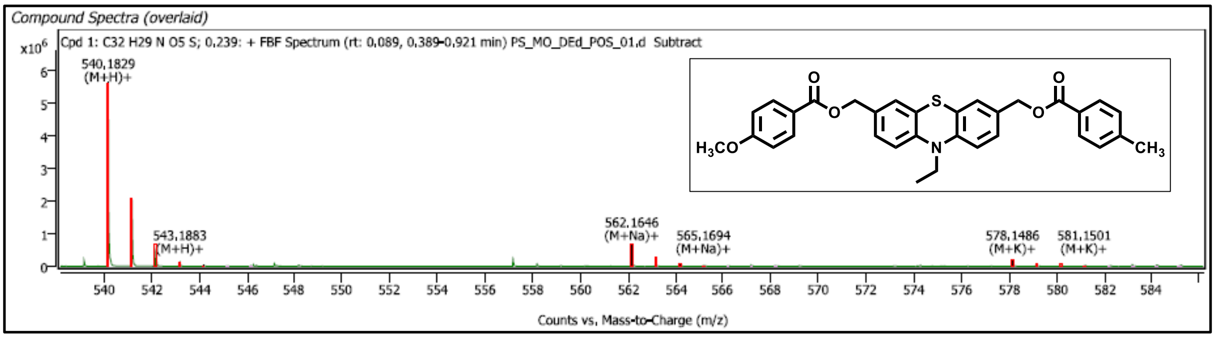


Fig. S29 HRMS spectrum of **12a**.

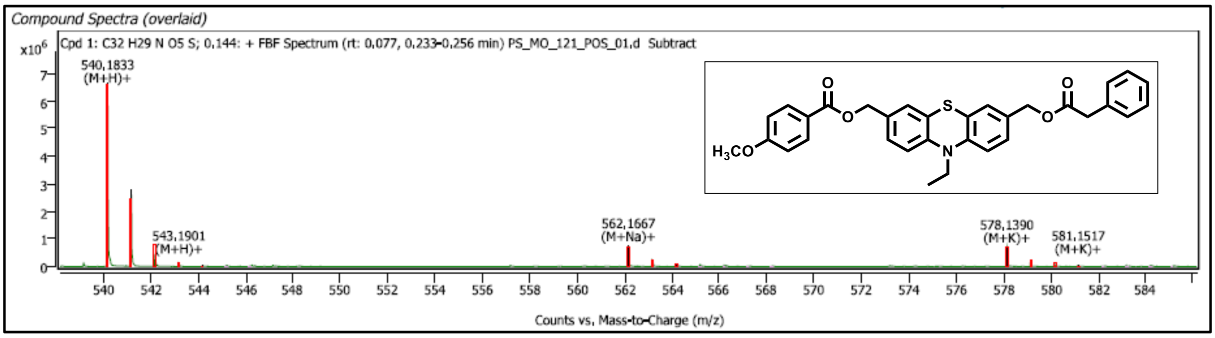


Fig. S30 HRMS spectrum of **12b**.

6. Photophysical properties of caged ester:

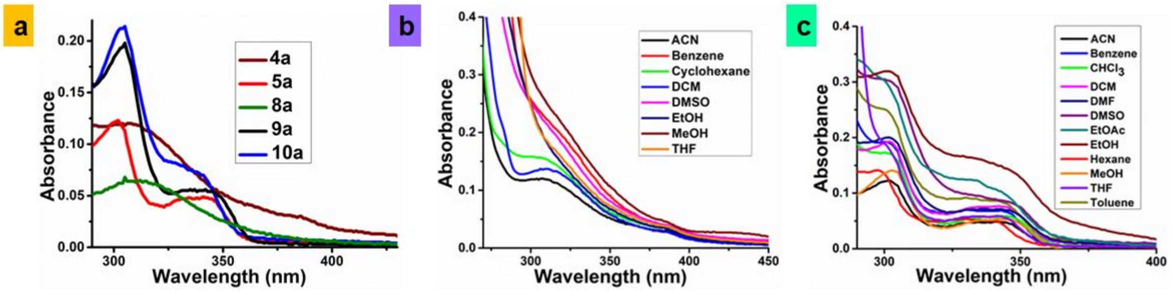


Fig. S31 Absorption spectra of (a) single (**4a**) and dual-arm (**8a**) caged ester, oxidized caged ester **5a** (single-arm mono-OPTZ), **9a** (dual-arm mono-OPTZ), **10a** (dual-arm di-OPTZ) in ACN (10^{-5} M) (b) single-arm caged ester **4a** in different solvents (10^{-5} M) and (C) **5a** (mono-OPTZ) in different solvents (10^{-5} M).

The absorption and emission spectra of a degassed solution of all the caged esters were recorded in acetonitrile (1×10^{-5} M). The absorption, emission maxima, Stokes shift, and fluorescence quantum yield of all the single (**4a-e**) and dual-arm caged ester (**8a-c**, **12a-b**), mono-oxidized caged ester (**5a, 9a**), and di-oxidized caged ester (**10a**) are summarized in Table S1.

Table S1. Photophysical data of all the single (**4a-e**) and dual-arm caged ester (**8a-c, 12a-b**), mono-oxidized caged ester (**5a, 9a**), and di-oxidized caged ester (**10a**).

Caged ester	**Synthetic yield**[a]	**Absorbance**		**Fluorescence**			
		$\lambda_{max.}$ (nm)[b]	**ε_{max} x10^3 (L mol^{-1} cm^{-1})**[c]	**$\lambda_{max.}$ (nm)**[d]	**Stokes shift**[e] **(nm)**	**Stokes shift (cm^{-1})**	**ϕ_f**[h]
4a	92	308	12.0	455	147	10489	0.038
4b	90	307	11.8	456	149	10643	0.035
4c	88	309	11.9	454	145	10336	0.037
4d	85	306	11.5	446	140	10258	0.032
4e	80	307	11.7	449	142	10301	0.034
8a	69	312	6.5	462	150	10406	0.038
8b	65	310	6.6	461	151	10566	0.036
8c	70	309	6.4	459	150	10575	0.035
12a	77	311	6.8	460	149	10415	0.036
12b	70	310	6.7	461	150	10566	0.037
5a	91	344	4.9	456	112	7139	0.033
9a	90	345	5.6	425	80	5456	0.030
10a	47	340	7.4	370	30	2384	0.026

[a]Based on isolated yield, [b]Maximum absorption wavelength, [c]Molar absorption coefficient at maximum absorption wavelength [d]Maximum emission wavelength, [e]Difference between maximum absorption wavelength and maximum emission wavelength in nm, [g]Fluorescence quantum yield (error limit within ± 5%).

7. Measurement of fluorescence quantum yields:

The quantum yield (QY) of the single and dual-arm FPRPG was determined by the reference point method. 9, 10-diphenyl anthracene as standard ($\Phi = 0.95$ in ethanol) was used as a standard sample to calculate the QY of phenothiazine caged esters (**4a-e**, **5a**, **8a-c**, **9a**, **10a,** and **12a-b**) which were dissolved in acetonitrile. The absorbance values of the solutions at the excitation wavelength were measured with a UV–vis spectrophotometer. Photoluminescence (PL) emission spectra of all the sample solutions were recorded by Hitachi F-7000 fluorescence spectrophotometer at an excitation wavelength of 310 nm. Further, the fluorescence quantum yield of caged esters was calculated using equation (1)

$$\frac{\Phi_S}{\Phi_R} = \frac{A_S}{A_R}\ \frac{(Abs)_R}{(Abs)_S}\ \frac{\eta_S^2}{\eta_R^2} \qquad (1)$$

Where **Φ** represents quantum yield, **Abs** represents absorbance, **A** represents the area under the fluorescence curve, and **η** is the refractive index of the medium. The subscripts **S** and **R** denote the corresponding parameters for the sample and reference, respectively.

8. Characterisation of photoproduct for photolysis of single-arm caged ester 4a:

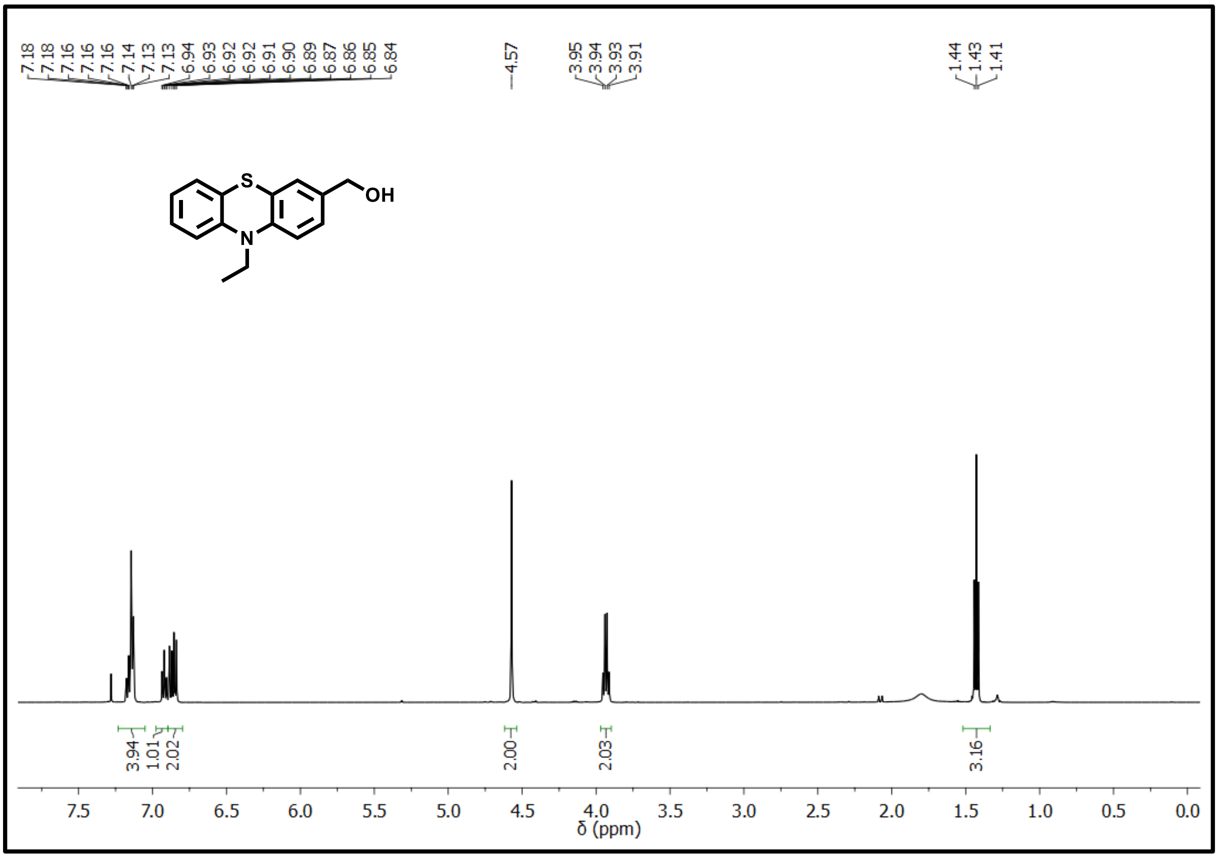


Fig. S32 ^1H NMR (500 MHz) of photoproduct **3** in $CDCl_3$.

9. Characterisation of photoproduct for photolysis of dual-arm (same) caged ester 8a:

a) ^1H NMR study of dual-arm caged ester 8a during photolysis:

Here, we have shown the photorelease of dual caged ester **8a** (1×10^{-4} M) in ACN/H_2O (1:1 v/v) at 365 nm wavelength by ^1H NMR at different irradiation time intervals. With an increase in irradiation time from 0 to 20 min, the intensity of the characteristic ester peaks at 5.20 ppm of **8a** decreases, and three new CH_2 peaks at 5.39 ppm, 4.78 ppm, and 4.57 ppm appeared. Peaks **c** and **d** correspond to the benzylic alcohol protons of photoproducts **11** and **7,** respectively. Peak **b c**orresponds to the benzylic protons of single-arm caged ester. Upon continuation of photolysis for 20 min, we noted a decrease in the intensity of the peak (**a**) at 5.20 ppm and an increase in the intensity of the peak (**d**) at 4.78, indicating the decomposition of dual-arm caged ester **8a** and formation of final photoproduct **7**.

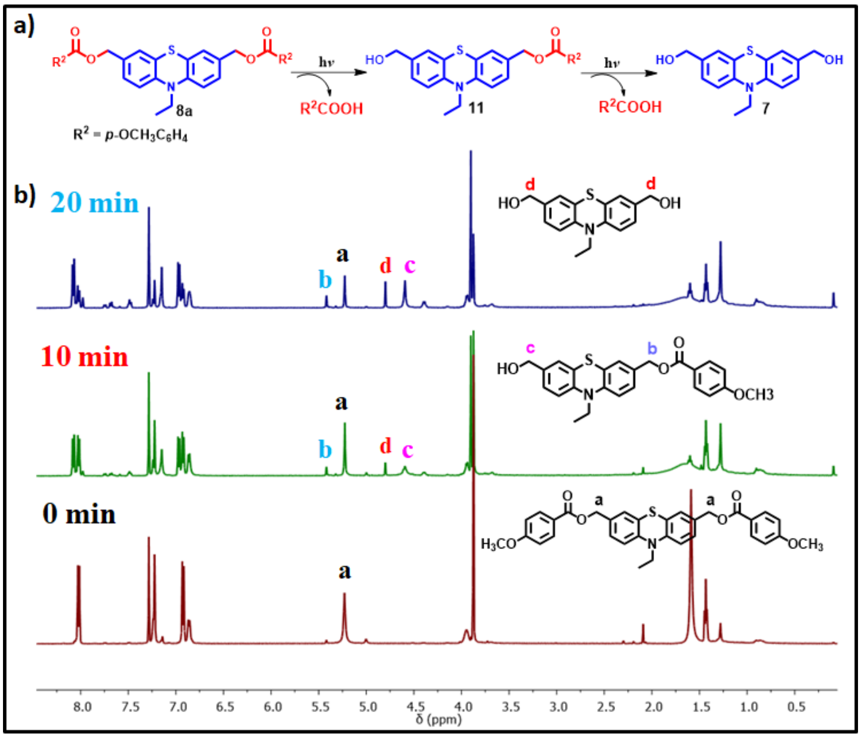


Fig. S33 (a) Stepwise photorelease scheme for dual caged esters **8a** (1×10^{-4} M). (b) ^{1}H NMR study of dual-arm caged ester **8a** in $CDCl_3$ at different time intervals during photolysis (λ ≥365 nm).

b). HRMS spectra of dual-arm (same) caged ester 8a and its photoproducts during photolysis:

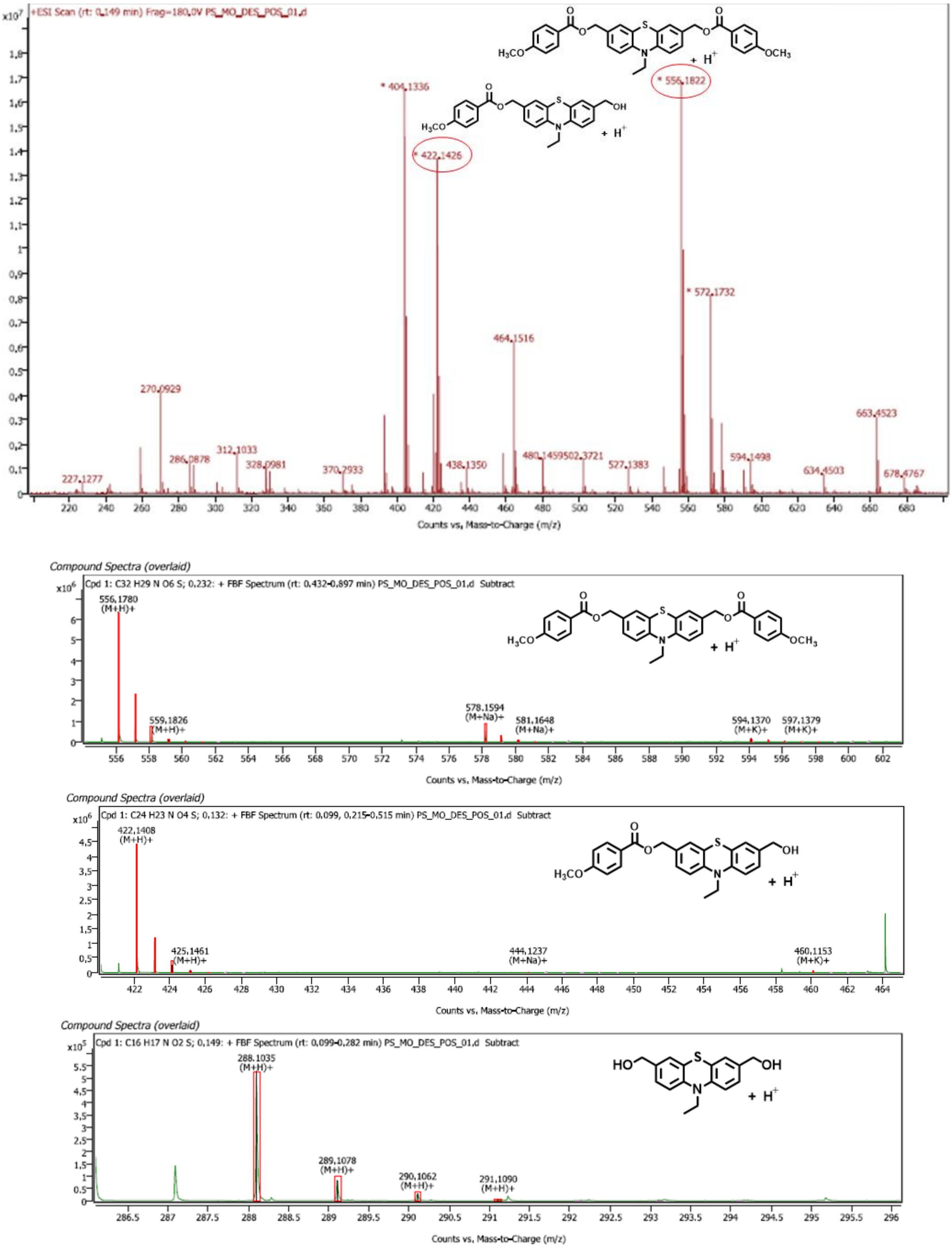
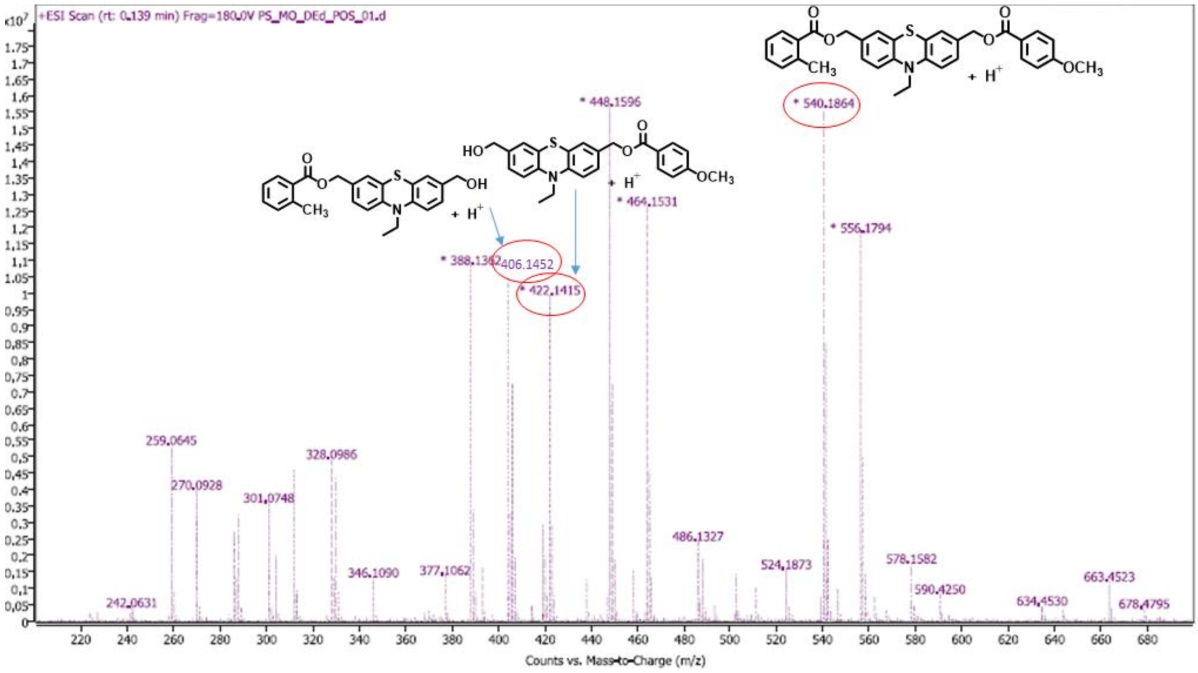
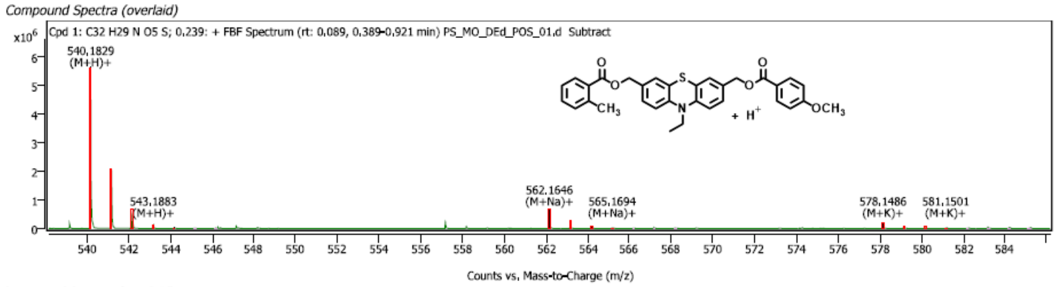
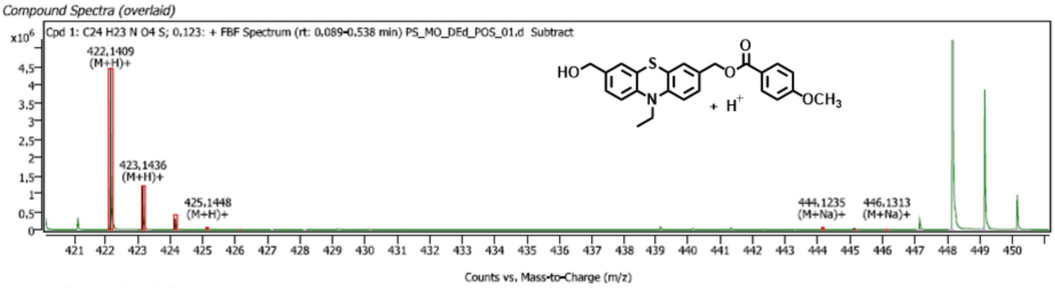


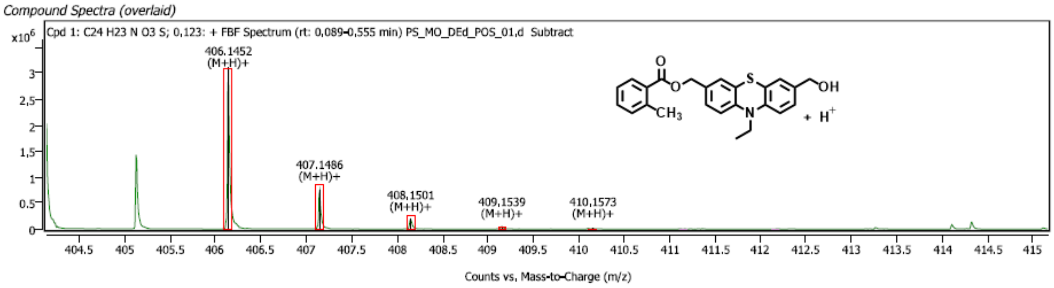
Fig. S34 HRMS spectra of dual-arm (same) caged ester **8a** and its photoproducts.

10. Characterisation of photoproduct for photolysis of dual-arm (different) caged ester 12a by HRMS spectra:


x10^7
+ESI Scan (rt: 0.139 min) Frag=180.0V PS_MO_DEd_POS_01.d
* 540.1864
* 556.1794
* 448.1596
* 464.1531
* 388.1362
406.1452
* 422.1415
259.0645
270.0928
301.0748
328.0986
346.1090
377.1062
486.1327
524.1873
578.1582
590.4250
634.4530
663.4523
678.4795
242.0631
HO
OH
S
N
O
CH3
OCH3
+ H+
Counts vs. Mass-to-Charge (m/z)


Compound Spectra (overlaid)
x10^6
Cpd 1: C32 H29 N O5 S; 0.239: + FBF Spectrum (rt: 0.089, 0.389-0.921 min) PS_MO_DEd_POS_01.d Subtract
540.1829 (M+H)+
543.1883 (M+H)+
562.1646 (M+Na)+
565.1694 (M+Na)+
578.1486 (M+K)+
581.1501 (M+K)+
CH3
OCH3
S
N
O
+ H+
Counts vs. Mass-to-Charge (m/z)


Compound Spectra (overlaid)
x10^6
Cpd 1: C24 H23 N O4 S; 0.123: + FBF Spectrum (rt: 0.089-0.538 min) PS_MO_DEd_POS_01.d Subtract
422.1409 (M+H)+
423.1436 (M+H)+
425.1448 (M+H)+
444.1235 (M+Na)+
446.1313 (M+Na)+
HO
S
N
O
OCH3
+ H+
Counts vs. Mass-to-Charge (m/z)


Compound Spectra (overlaid)
x10^6
Cpd 1: C24 H23 N O3 S; 0.123: + FBF Spectrum (rt: 0.089-0.555 min) PS_MO_DEd_POS_01.d Subtract
406.1452 (M+H)+
407.1486 (M+H)+
408.1501 (M+H)+
409.1539 (M+H)+
410.1573 (M+H)+
CH3
S
N
O
OH
+ H+
Counts vs. Mass-to-Charge (m/z)

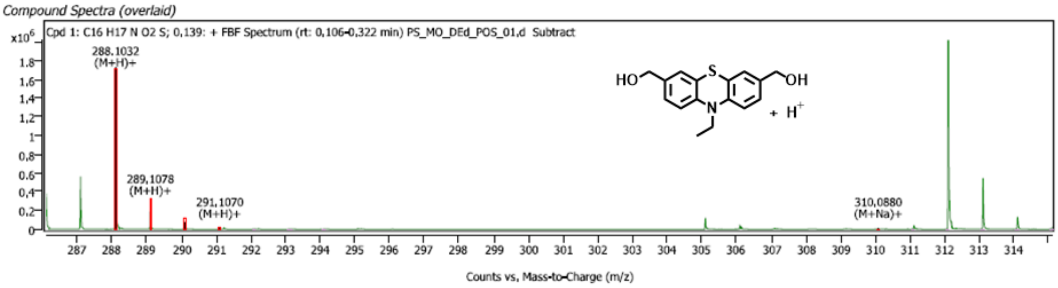

Compound Spectra (overlaid)
x10^6
Cpd 1: C16 H17 N O2 S; 0.139: + FBF Spectrum (rt: 0.106-0.322 min) PS_MO_DEd_POS_01.d Subtract
288.1032 (M+H)+
289.1078 (M+H)+
291.1070 (M+H)+
310.0880 (M+Na)+
HO
OH
S
N
+ H+
Counts vs. Mass-to-Charge (m/z)

Fig. S35 HRMS spectra of dual-arm (different) caged ester **12a** and its photoproducts.

11. Hydrolytic stability of the caged esters under dark:

Caged Esters	% of depleted	Caged Esters	% of depleted
4a	5	8a	6
4b	7	8b	5
4c	6	8c	8
4d	8	12a	6
4e	9	12b	7

Table S2. Hydrolytic stability of the single-arm (**4a-e**) and dual-arm (**8a-c** and **12a-b**) caged esters under dark.

12. Photorelease study of 4a in the presence of singlet and triplet quencher:

Photorelease study of 10^{-4} M compound **4a** was performed in the presence and absence of 1mM triplet and singlet quencher individually and was monitored the course of photolysis by RP-HPLC. Naphthalene and potassium sorbate was used as singlet and triplet quencher, respectively. We observed (fig. S35) that there is no change in photolysis in the presence of triplet quencher, whereas, in the presence of naphthalene, photolysis is quenched.

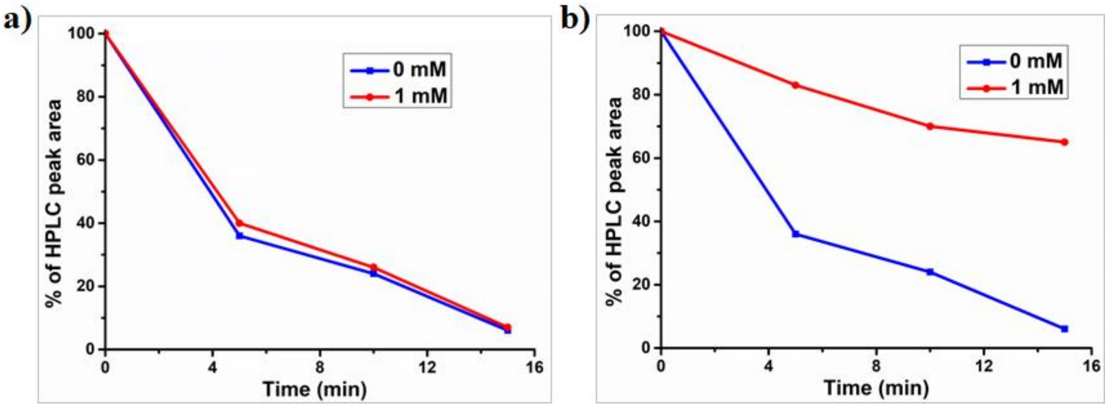


Fig. S36 Photorelease study of single-arm caged ester **4a** (1×10^{-4} M) in the presence of a) triplet quencher and b) singlet quencher.

13. Measurement of singlet oxygen quantum yield of oxidized caged ester 5a (mono-OPTZ) and 10a (di-OPTZ) in acetonitrile:

The Φ_Δ of each solution was calculated by the following equation,

$$\Phi_S = \frac{K_S}{K_R} \times \Phi_R \qquad (2)$$

Where, K is the slope of the photodegradation plot of DPBF against time (s) and the subscripts S and R denote the sample and the reference respectively, and Φ_R is the singlet oxygen quantum yield of the reference (Rose Bengal).[6]

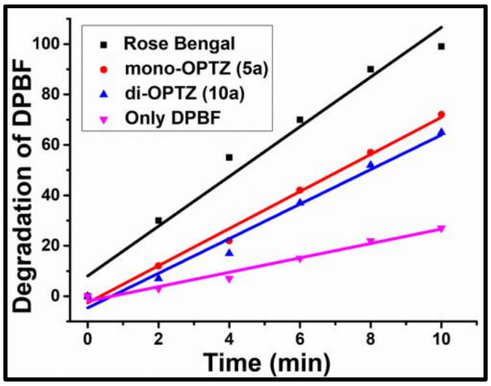


Fig. S37 Photodegradation of DPBF (1×10^{-4}) at 415 nm in the presence of oxidized caged ester **5a** (mono-OPTZ) and **10a** (di-OPTZ) and Rose Bengal (1×10^{-4}) under visible-light irradiation.

14. Determination of incident photon flux (I_0) of the UV lamp by potassium ferrioxalate actinometry:

Potassium ferrioxalate actinometry was used for the determination of incident photon flux (I_0) of the UV lamp used for irradiation. Solution of potassium ferrioxalate, 1, 10-phenanthroline, and the buffer solution was prepared following the literature procedure.[7]

Solution (0.006 M) of potassium ferrioxalate was irradiated using 125W medium pressure Hg lamp as UV light source (≥365 nm) and 1M $CuSO_4$ solution as UV cut-off filter. At a regular interval of time (3 min), 1ml of the aliquots was taken out, and to it, 3 ml of 1,10 phenanthroline solution and 2 ml of the buffer solution were added, and the whole solution was kept in the dark for 30 min. The absorbance of the red phenanthroline-ferrous complex formed was then measured spectrophotometrically at 510 nm. The amount of Fe^{2+} ion was determined from the calibration graph. The calibration graph was plotted by measuring the absorbance of the phenanthroline-ferrous complex at several known concentrations of Fe^{2+} ion in the dark. From the slope of the graph, the **molar absorptivity** of the phenanthroline-ferrous complex was calculated to be $\mathbf{1.11 \times 10^4\ M^{-1}}$ cm^{-1} at 510 nm, which is found to be similar to the reported value.[8] Using the known **quantum yield** (**1.283** ± **0.023**) for potassium ferrioxalate actinometer at 363.8 nm, the number of Fe^{2+} ions formed during photolysis and the fraction of light absorbed by the actinometer, the incident photon flux ($\mathbf{I_0}$) at 365 nm of the 125W Hg lamp was determined as $\mathbf{3.7\times10^{17}}$ photons s^{-1} cm^{-2}.

$$\Phi_{act} = k_{act} / [(I_0 / N_A)\times F] \qquad (3)$$

Where, k is the rate of reaction; I_0 is photon flux; F is fraction of light absorbed (molar absorptivity); N_A is Avogadro's no. From the above equation, we calculated the rate of reaction of actinometer (k_{act}) and we calculated the photochemical quantum yield by putting the value of k_{act} in the **equation 4**.

Similarly, we were determined the incident photon flux (I_0) at 410 nm of the 125W Hg lamp is 2.886 $\times 10^{16}$ photons $s^{-1}cm^{-2}$.[9]

15. Measurement of photochemical quantum yields and photochemical rate constant determination for the photodegradation of single-arm caged ester 4a and dual-arm caged ester 8a:

A solution of 1×10^{-4} M of the caged esters (**4a** and **8a)** was prepared in ACN/H_2O (1:1 v/v). The solution is then irradiated using 125 W medium pressure Hg lamp 1M $CuSO_4$ solution as UV cut–off filter for 30 min and similarly using 125 W medium pressure. At a regular interval of time, 20 μl of the aliquots was taken and analyzed by RP-HPLC using mobile phase acetonitrile-water (9:1 v/v), at a flow rate of 1 mL/min (detection: UV 254 nm). Peak areas were determined by RP-HPLC, which indicated a gradual decrease of the caged ester with time and the average of three runs. The reaction was followed until the consumption of the caged ester was less than 10% of the initial area. Based on HPLC data for caged compounds, the natural logarithm of the concentration of caged compound (lnC) (from HPLC peak area) versus irradiation time was plotted. We observed an exponential correlation for the disappearance of the caged compounds, which suggested a first-order reaction.

Further, the quantum yield for the photolysis of caged esters was calculated using equation (4).

$$(\Phi_p)_{CG} = (\Phi_p)_{act} \quad \frac{(k_p)_{CG}}{(k_p)_{act}} \; \frac{(F_{act})}{(F_{CG})} \qquad (4)$$

Where the subscript 'CG' and 'act' denotes caged ester and actinometer, respectively. Potassium ferrioxalate was used as an actinometer. Φ_p is the photolysis quantum yield, k_p is the photolysis rate constant, and F is the fraction of light absorbed.

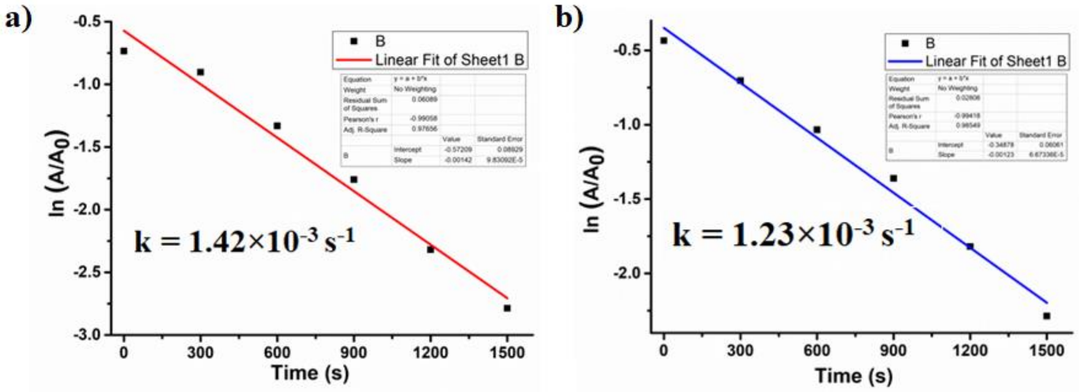


Fig. S38 Rate of release from a) single-arm caged ester **4a** and b) dual-arm caged ester **8a.**

16. Computational Data:

Single-arm phenothiazine caged ester **4d** and momo-OPTZ of **4d** were optimized in the ground state using ORCA5[10] in B3LYP[11-14]/def2-TZVP[15] level of theory along with RIJCOSX[16] approximations and D3BJ[17,18] dispersion correction. We carried out a relaxed surface scan along the pathways for C-O breaking for the leaving groups using PBE/def2-SVP[18,20] level of theory along with RI[21] approximation in the ORCA Package. The singlet and triplet excitation energies were calculated at all these points using CAM-B3LYP/def2-TZVP and RIJCOSX approximation. The maxima from the PES was taken as the guess TS, optimized in CAM-B3LYP/def2-TZVP(D3BJ) level of theory. The TS was corroborated with a negative frequency and intrinsic reaction coordination search in the same level of view. The molecular orbital and the electron density maps were studied using Multiwfn[22] program.

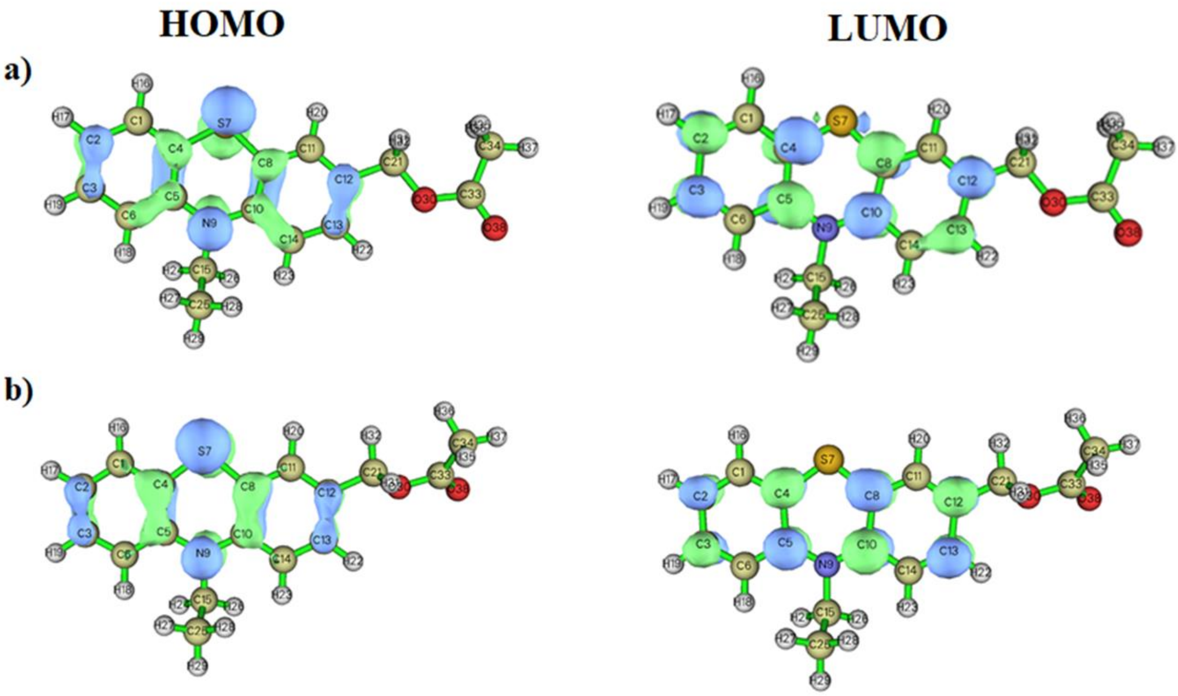


Fig. S39 Orbital picture of HOMO and LUMO involved in the a) S_0 state b) S_1 state of single-arm caged ester **4d**.

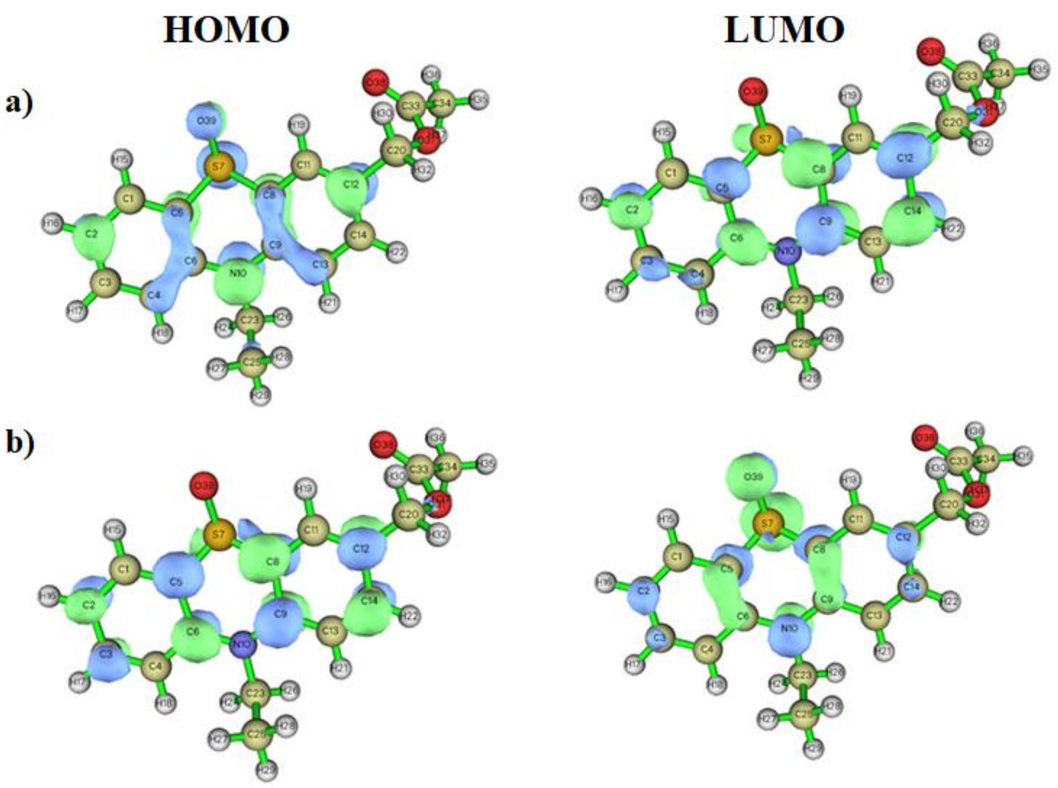
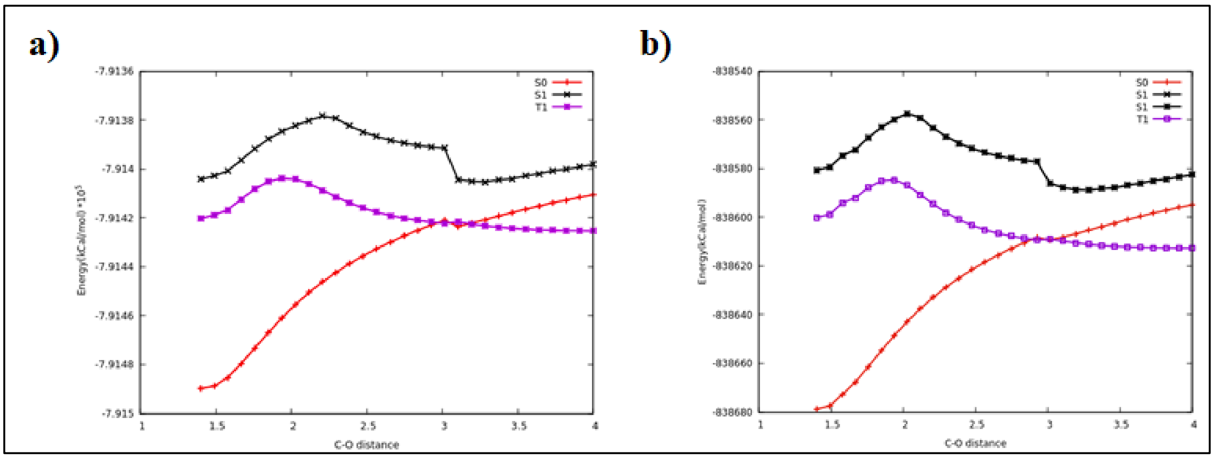


Fig. S40 Orbital picture of HOMO and LUMO involved in the a) S$_0$ state b) S$_1$ state of mono-oxidized caged ester of **4d**.

Table S3. Vertical transition energy (ΔE, eV) and wavelength (λ, nm), oscillator strength (f) calculated at the TDDFT/CAM-B3LYP/def2tzvp level.

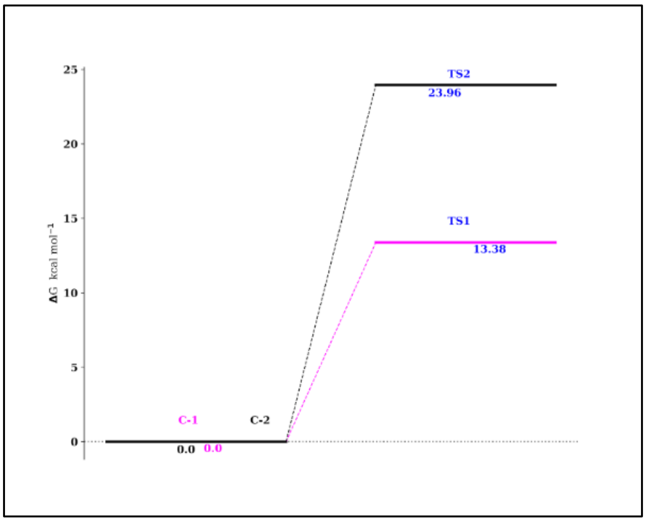
	single-arm caged ester 4d			mono-oxidized caged ester of 4d		
State	**ΔE(eV)**	**λ(nm)**	**f**	**ΔE(eV)**	**λ(nm)**	**f**
S0-S1	3.829	323.8	0.007342253	4.318	287.1	0.063363601
S0-S2	4.414	280.9	0.016539392	4.507	275.1	0.057373094
S0-S3	4.540	273.1	0.011520512	4.955	250.2	0.034002717
S0-T1	3.160	392.4	0	3.525	351.8	0
S0-T2	3.620	342.5	0	3.790	327.2	0
S0-T3	3.863	321.0	0	3.999	310.0	0

S$_0$(red), T$_1$(magenta), S$_1$(black) state PES scan of the C–O fission of positions of a) single-arm caged ester 4d and b) mono-oxidized caged ester of 4d (mono-OPTZ).



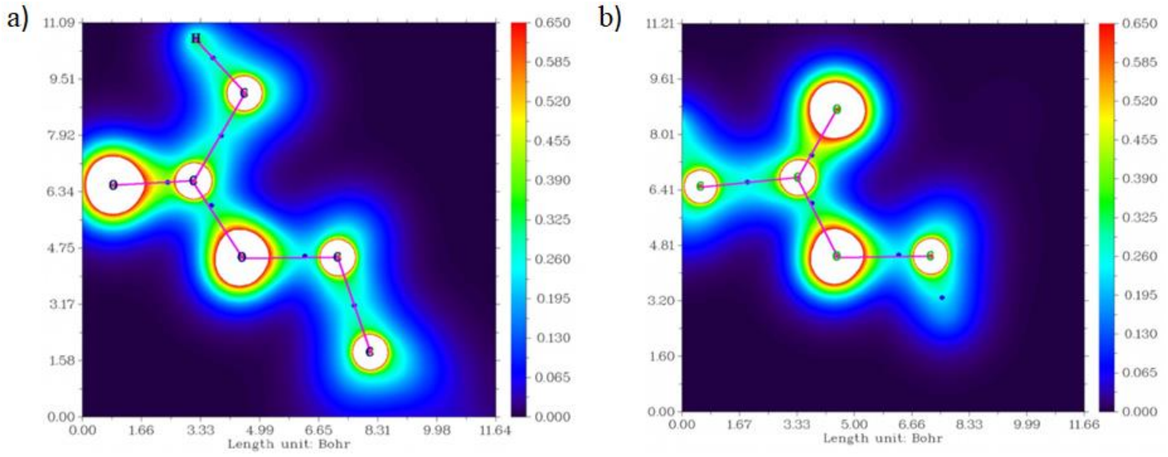
Energy barrier in the photo-release in single-arm caged ester 4d (C-1,magenta) and mono-oxidized caged ester of 4d (mono-OPTZ) (C-2,blue) in the S_1 state

Lower activation energies (ΔG) suggest that the photorelease step is faster in the case of phenothiazine caged ester.



17. Electron density map at the critical point around the C-O cleaved site for 4d (left) and mono-OPTZ of 4d:

Electron density around the C-O site is more for single-arm caged ester **4d** than its oxidized caged ester at the critical point.
(0.2523442822E+00 for **4d** and 0.2451720792E+00 for mono-OPTZ of **4d**. This could be attributed due to the donation of electrons towards the ester group by electron-rich PTZ moiety in **4d**.



18. Cartesian coordinates used in DFT and TDFT Computations:

All coordinates optimised at cam-b3lyp/def2tzvp

a) Single-arm caged ester 4d at S_0
FINAL SINGLE POINT ENERGY -1261.383790479081 Eh
Zero point energy 0.30834825 Eh
Nimag 0

38

C	3.841233	-1.848378	0.137056
C	5.087944	-1.318846	0.419716
C	5.243488	0.052151	0.415255
C	2.771909	-1.024976	-0.165442
C	2.904881	0.367282	-0.135525
C	4.166141	0.883044	0.157061
S	1.281422	-1.765801	-0.727338
C	0.135964	-0.549170	-0.188742
N	1.813271	1.205138	-0.415642
C	0.496090	0.800360	-0.159318
C	-1.162431	-0.943685	0.080991
C	-2.159011	-0.018762	0.337521
C	-1.819335	1.322292	0.332543
C	-0.518107	1.723200	0.101184
C	2.066612	2.615410	-0.671435
H	3.693043	-2.920224	0.122474
H	5.921322	-1.972213	0.635706
H	4.326655	1.947601	0.181876
H	6.207634	0.494036	0.627008
H	-1.397734	-2.000761	0.053607
C	-3.558193	-0.462620	0.626981
H	-2.580343	2.071091	0.504587
H	-0.303799	2.778290	0.118061
H	2.968582	2.677770	-1.278945

C	2.206594	3.508146	0.558220
H	1.256487	2.979605	-1.302032
H	3.041378	3.209450	1.188574
H	1.314345	3.489313	1.180240
H	2.375257	4.538469	0.242380
O	-4.453217	0.306554	-0.179579
H	-3.799471	-0.304708	1.681100
H	-3.665005	-1.525627	0.406493
C	-5.788230	0.124915	-0.125862
C	-6.313399	-0.956371	0.779398
H	-6.016131	-0.785889	1.813849
H	-5.928991	-1.932302	0.482687
H	-7.395761	-0.959102	0.709458
O	-6.491031	0.819966	-0.797886

b) Single-arm caged ester 4d at S_1
FINAL SINGLE POINT ENERGY -1261.260836437680 Eh
Zero point energy ... 0.30598266 Eh
Nimag=0

38

C	3.902596	-1.857720	0.059369
C	5.155029	-1.335422	-0.027629
C	5.307827	0.069833	-0.129921
C	2.757021	-1.037810	0.047290
C	2.895770	0.393380	-0.087323
C	4.220826	0.891279	-0.158310
S	1.261769	-1.813370	0.137157
C	0.136419	-0.557226	0.229407
N	1.802753	1.227070	-0.129383
C	0.497909	0.834439	0.088165
C	-1.211661	-0.917909	0.398303
C	-2.207859	0.008368	0.463832
C	-1.856328	1.384554	0.357799
C	-0.561657	1.767612	0.182389
C	2.042477	2.644570	-0.413590
H	3.762203	-2.928113	0.147763
H	6.020401	-1.981535	-0.006924
H	4.399455	1.952258	-0.210431
H	6.296774	0.503342	-0.177261
H	-1.450338	-1.972491	0.479209
C	-3.624727	-0.390496	0.668264
H	-2.629862	2.137860	0.413967
H	-0.359772	2.824816	0.133944
H	2.884460	2.707158	-1.094241
C	2.287754	3.466943	0.839468
H	1.187860	3.018960	-0.966171
H	3.158482	3.104644	1.383590
H	1.431578	3.425024	1.510849

H	2.460831	4.508856	0.569687
O	-4.374560	-0.059221	-0.514644
H	-4.056020	0.145416	1.518046
H	-3.691385	-1.462129	0.860157
C	-5.703357	-0.260120	-0.585802
C	-6.391842	-0.854214	0.614400
H	-6.293064	-0.202598	1.482580
H	-5.962993	-1.820586	0.878366
H	-7.442515	-0.976772	0.374114
O	-6.282189	0.035999	-1.590206

c) Single-arm caged ester 4d TS at S_1
FINAL SINGLE POINT ENERGY -1261.234634066753 Eh
Zero point energy ... 0.30173106 Eh 189.34 kcal/mol
Nimag=1

38

C	-3.643039	-1.869223	-0.015443
C	-4.867254	-1.342747	0.310998
C	-4.956801	0.021972	0.573893
C	-2.504100	-1.067128	-0.081904
C	-2.576912	0.320474	0.180065
C	-3.849117	0.830383	0.507089
S	-1.020421	-1.887411	-0.406289
C	0.078584	-0.593647	-0.689173
N	-1.471032	1.134710	0.138213
C	-0.239216	0.757065	-0.422763
C	1.319394	-0.966918	-1.174579
C	2.320793	-0.028256	-1.429451
C	1.989554	1.335037	-1.185528
C	0.758476	1.699134	-0.714292
C	-1.580870	2.491843	0.663858
H	-3.541796	-2.926865	-0.223615
H	-5.741848	-1.975029	0.356780
H	-3.976571	1.883181	0.692053
H	-5.911902	0.463297	0.824024
H	1.522250	-2.018055	-1.338738
C	3.605383	-0.436459	-1.800967
H	2.727288	2.095268	-1.388552
H	0.572503	2.749730	-0.565157
H	-2.258687	2.467022	1.514074
C	-2.040186	3.519602	-0.359412
H	-0.607459	2.761699	1.065806
H	-3.032559	3.286471	-0.742417
H	-1.361728	3.562305	-1.209371
H	-2.075277	4.508331	0.098960
O	4.650647	-0.905655	0.020796
H	4.352846	0.295389	-2.058243
H	3.790872	-1.457134	-2.090128

C	4.571303	0.059435	0.814589
C	5.264403	-0.119537	2.164804
H	6.253907	-0.542806	2.005904
H	4.680766	-0.830075	2.750201
H	5.329167	0.824297	2.698674
O	3.978018	1.138563	0.632632

d) Mono-oxidized caged ester of 4d (mono-OPTZ) at S_0
FINAL SINGLE POINT ENERGY -1336.600509851650 Eh
Zero point energy ... 0.31317673 Eh 196.52 kcal/mol
Nimag 0

39

C	-3.402807	-1.992428	-0.394395
C	-4.700983	-1.566248	-0.598532
C	-5.021109	-0.250280	-0.317135
C	-4.056776	0.643888	0.110681
C	-2.445681	-1.107402	0.062179
C	-2.732344	0.240522	0.287225
S	-0.878673	-1.790279	0.551460
C	0.068600	-0.380752	0.024830
C	-0.403717	0.912999	0.255203
N	-1.724371	1.141529	0.656808
C	1.342190	-0.622158	-0.450401
C	2.215494	0.424271	-0.687101
C	0.500589	1.958337	0.050900
C	1.779011	1.710974	-0.406858
H	-3.108591	-3.018006	-0.574045
H	-5.454565	-2.255088	-0.952623
H	-6.036030	0.100660	-0.447730
H	-4.345877	1.667164	0.283164
H	1.653030	-1.647031	-0.605285
C	3.609276	0.178201	-1.175123
H	0.207265	2.980220	0.223405
H	2.449446	2.547471	-0.560640
C	-2.100455	2.470051	1.118945
H	-2.964737	2.352197	1.771055
C	-2.402545	3.498136	0.032728
H	-1.292566	2.829536	1.755073
H	-3.234457	3.194382	-0.598832
H	-1.548726	3.662564	-0.620473
H	-2.661319	4.450749	0.496514
H	3.713429	-0.834405	-1.557361
O	4.581159	0.392587	-0.133117
H	3.888208	0.890367	-1.948530
C	4.762801	-0.620175	0.730654
C	5.727507	-0.241279	1.811568
H	6.632313	0.183482	1.380342
H	5.964086	-1.115933	2.408893

H	5.272966	0.522213	2.443193
O	4.208273	-1.679056	0.634565
O	-0.563171	-2.941558	-0.318224

e) Mono-oxidized caged ester of 4d (mono-OPTZ) at S_1

FINAL SINGLE POINT ENERGY -1336.461082182450 Eh
Zero point energy ... 0.31055873 Eh 194.88 kcal/mol
Nimag 0

39

C	-3.479615	-2.030103	-0.352822
C	-4.782609	-1.641219	-0.308738
C	-5.093539	-0.311096	0.072107
C	-4.112695	0.594084	0.349260
C	-2.451581	-1.114069	-0.079682
C	-2.739276	0.254498	0.262477
S	-0.867702	-1.706602	0.128702
C	0.085689	-0.335597	-0.222811
C	-0.406070	0.963841	0.161007
N	-1.741853	1.188096	0.422863
C	1.420295	-0.530480	-0.600004
C	2.295877	0.512971	-0.647248
C	0.552791	2.006568	0.164210
C	1.840995	1.795652	-0.223849
H	-3.201667	-3.041156	-0.618866
H	-5.571026	-2.334665	-0.562794
H	-6.126640	0.000596	0.135959
H	-4.412439	1.597372	0.603522
H	1.743577	-1.531868	-0.852785
C	3.705709	0.326511	-1.093124
H	0.272378	3.008610	0.444733
H	2.535568	2.625069	-0.213477
C	-2.128509	2.526473	0.878848
H	-2.976116	2.416397	1.546454
C	-2.449571	3.472832	-0.264362
H	-1.320636	2.912163	1.491451
H	-3.278615	3.098809	-0.862916
H	-1.590997	3.599986	-0.921627
H	-2.725831	4.449933	0.132167
H	3.837878	-0.636542	-1.579795
O	4.633737	0.425062	0.012388
H	4.021414	1.122565	-1.765643
C	4.795802	-0.681077	0.753873
C	5.712898	-0.426368	1.911520
H	6.626357	0.058714	1.571982
H	5.941427	-1.365261	2.405883
H	5.222955	0.247831	2.614246
O	4.264474	-1.729249	0.510879
O	-0.556696	-2.898859	-0.661011

f) Mono-oxidized caged ester of 4d (mono-OPTZ) TS at S_1
FINAL SINGLE POINT ENERGY -1336.419614130762 Eh
Zero point energy ... 0.30618190 Eh 192.13 kcal/mol
Nimag=1

39

C	-3.149343	-2.308737	-0.406991
C	-4.461907	-2.032386	-0.140195
C	-4.788954	-0.770939	0.368983
C	-3.837347	0.190540	0.579091
C	-2.168627	-1.337592	-0.201480
C	-2.472923	-0.045151	0.293633
S	-0.530011	-1.840806	-0.395588
C	0.281027	-0.348560	-0.650057
C	-0.223843	0.840270	-0.064676
N	-1.525577	0.921872	0.464202
C	1.544284	-0.452519	-1.186156
C	2.398420	0.661556	-1.229285
C	0.640680	1.944811	-0.113660
C	1.891941	1.861678	-0.664218
H	-2.844957	-3.271568	-0.794054
H	-5.228365	-2.771745	-0.318809
H	-5.820784	-0.536018	0.592810
H	-4.155210	1.152944	0.941995
H	1.887657	-1.411311	-1.540188
C	3.731364	0.466866	-1.568297
H	0.325710	2.900633	0.271838
H	2.528642	2.735945	-0.646035
C	-1.892321	2.151323	1.163604
H	-2.610391	1.893582	1.937712
C	-2.443102	3.235985	0.251616
H	-1.006974	2.500342	1.688010
H	-3.352784	2.909539	-0.250284
H	-1.722448	3.510440	-0.516570
H	-2.676440	4.127049	0.834739
H	4.039888	-0.444157	-2.051562
O	4.686767	-0.140816	0.237655
H	4.424042	1.291950	-1.587234
C	4.022082	-0.899171	0.999757
C	4.549562	-1.033757	2.416940
H	5.632266	-1.146448	2.402088
H	4.085364	-1.877921	2.921415
H	4.317984	-0.118252	2.963176
O	2.983162	-1.510412	0.693327
O	-0.359095	-2.855731	-1.431428

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