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Supporting Information

Improving Quantum Yields of Fluorophores by Inhibiting Twisted Intramolecular Charge Transfer Using Electron-Withdrawing Group-Functionalized Piperidine Auxochromes

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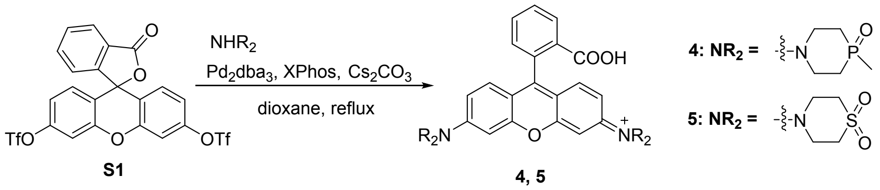
1. General Information

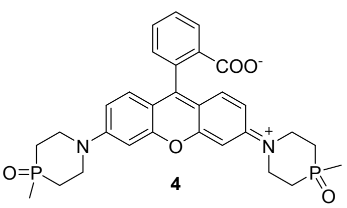
All reagents and solvents of the highest grade were purchased from commercial suppliers and used without further purification unless otherwise stated. All reactions were magnetically stirred and monitored by thin–layer chromatography (TLC). Flash chromatography was performed using silica gel 60 (200–300 mesh). The ^{1}H NMR and ^{13}C NMR spectra were measured on Bruker 600 Hz spectrometer (600 MHz for ^{1}H, 150 MHz for ^{13}C) and Bruker 400 Hz (400 MHz for ^{1}H, 100 MHz for ^{13}C) spectrometer. The chemical shifts in ^{1}H NMR spectra are reported in δ ppm using TMS as an internal standard unless otherwise stated. The following abbreviations were used to explain the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiple; br = broad. High resolution mass spectra were obtained on a Varian QFT-ESI mass spectrometer. Absorption spectra were taken on Varian Carry 4000 spectrophotometer. Fluorescence spectra were taken on Hitachi F–7000 fluorescence spectrometer. The fluorescence lifetimes of all samples were measured using steady-stead fluorimeter Edinburgh FLS1000 and monitored at their respective peak emission wavelengths. The stock solutions of dyes **1-17** were prepared in DMSO and diluted with phosphate buffer (PBS) such that the DMSO concentration did not exceed 1% (v/v).

2. Synthetic materials and methods

Compounds **1**,[1] **S1**,[1] **3**,[2] **S6**,[3] **S9**,[4] **10**,[5] **S20**,[2] **S22**,[6] **S23**,[2] and 4-methyl-1,4-azaphosphinane 4-oxide[7] were known compounds and synthesized according to literature procedures. Compounds **2**, **12**, **14**, and thiomorpholine 1,1-dioxide were purchased from Innochem reagent company.

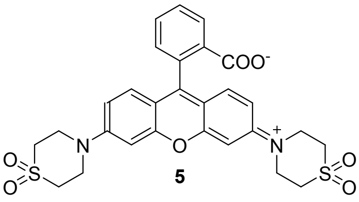
*2.1 Synthesis of Rhodamine dyes **4** and **5***





4

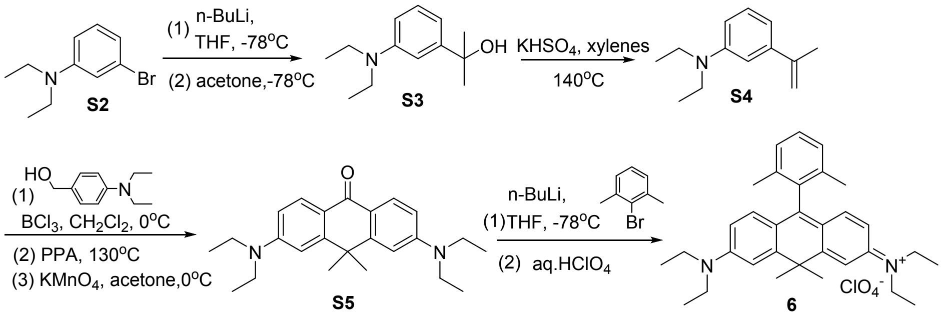
A vial was charged with fluorescein ditriflate **S1** (200 mg, 0.34 mmol), Pd_2dba_3 (31 mg, 0.034 mmol, 0.1 eq), XPhos (48 mg, 0.10 mmol, 0.3 eq), and Cs_2CO_3 (306 mg, 0.94 mmol, 2.8 eq). The vial was sealed and evacuated/backfilled with nitrogen (3×). 4-methyl [1,4] azaphosphinane-4-oxide (134 mg, 1.00 mmol, 3.0 eq) dissolved in dioxane (20 mL) was added and the reaction was refluxed for 18 h. It was subsequently cooled to room temperature and diluted with MeOH. Silica gel (~2 g) was added and the mixture was concentrated to dryness. Purification by silica gel chromatography (CH_2Cl_2/MeOH =20:1) afforded **4** as a pink solid (132 mg, 70%). ^{1}H NMR (600 MHz, D_2O) δ (ppm): 7.97 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 5.4 Hz, 2H), 7.48 (d, J = 6.0 Hz, 1H), 7.43 (d, J = 9.0 Hz, 2H), 7.15 (d, J = 9.0 Hz, 2H), 6.85 (s, 2H), 4.00-3.97 (m, 8H), 2.18-2.07 (m, 8H), 1.68 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (150 MHz, D_2O): 174.2, 161.7, 157.8, 155.4, 139.3, 132.1, 130.4, 129.9, 129.7, 128.9, 111.5, 111.4, 97.7, 44.0, 27.0, 26.9, 26.6, 26.5, 13.0, 12.5. HRMS (ESI) calcd for $C_{30}H_{33}N_2O_5P_2$ $[M+H]^+$ 563.1859; found 563.1861.

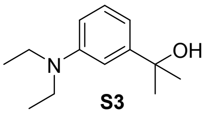


5

A vial was charged with fluorescein ditriflate **S1** (200 mg, 0.34 mmol), Pd_2dba_3 (31 mg, 0.034 mmol, 0.1 eq), XPhos (48 mg, 0.10 mmol, 0.3 eq), and Cs_2CO_3 (306 mg, 0.94 mmol, 2.8 eq). The vial was sealed and evacuated/backfilled with nitrogen (3×). Thiomorpholine-1,1-dioxide (108 mg, 0.81 mmol, 2.4 eq) in dioxane (20 mL) was added and the reaction was refluxed for 18 h. After cooling to room temperature, water (50 mL) was added and CH_2Cl_2 (50 mL × 4) was used to extract organic compounds. The combined organic phase was dried over Na_2SO_4 and then concentrated to dryness. Purification by silica gel chromatography (PE/EA =1:1) afforded **5** as a white solid (161 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.03 (s, 1H), 7.69 (d, J = 4.8 Hz, 1H), 7.64 (d, J = 5.4 Hz, 1H), 7.19 (d, J = 6.0 Hz, 1H), 6.70 (d, J = 3.0 Hz, 4H), 6.58 (s, 2H), 3.92 (s, 8H) , 3.09 (s, 8H). ^{13}C NMR (150 MHz, $CDCl_3$): 169.3, 152.8, 152.6, 148.9, 135.0, 129.8, 129.7, 126.8, 125.1, 123.9, 111.6, 110.6, 102.4, 50.3. 46.7. HRMS (ESI) calcd for $C_{28}H_{27}N_2O_7S_2$ $[M+H]^+$ 567.1254; found 567.1259.

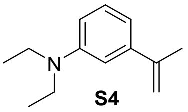
*2.2 Synthesis of Carborhodamine dye **6***





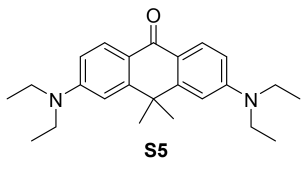
S3

3-bromo-N, N-diethyl aniline **S2** (4.56 g, 20.0 mmol) was dissolved in dry THF (100 mL) under dry N_2 atmosphere and cooled to −78 °C. n-BuLi (2.5 M solution in hexane, 10.0 mL, 25.0 mmol) was added dropwise to the solution and the reaction mixture was stirred for 30 min. Then, dry acetone (2.21 mL, 30.0 mmol) was added dropwise at −78 °C. The reaction mixture was stirred continue for another 15 min at this temperature, and then warmed to room temperature. The reaction was quenched by dropwise addition of 2 M HCl (10 mL) and the solution was neutralized to pH 7 with sat aq $NaHCO_3$. The reaction mixture was then extracted with CH_2Cl_2 (3×) and the combined organic layers were dried over Na_2SO_4, filtered, and evaporated to dryness. Purification by silica gel chromatography (EA / PE= 1:5, v/v) gave the pure product **S3** as colorless oil (3.32 g, 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.59 (q, *J* = 2.0 Hz, 1H), 3.39 (q, *J* = 7.2 Hz, 4H), 1.57 (s, 6H), 1.18 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 129.0, 111.6, 110.3, 108.0, 72.7, 44.4, 31.6, 12.6. HRMS (ESI) calcd for $C_{13}H_{22}NO$ [M+H] $^+$ 208.1696, found 208.1694.



S4

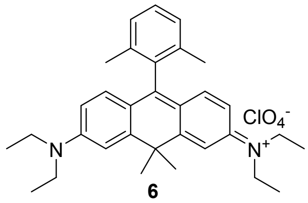
A suspension of 2-(3(diethylamino)phenyl) propan-2-ol **S3** (3.11 g, 15.0 mmol) and $KHSO_4$ (2.04 g, 15.0 mmol) in xylenes (20 mL) was stirred in a pressure tube at 140 °C for 2 h. The reaction mixture was cooled to room temperature, water (30 mL) was added, and the mixture was stirred until an inorganic precipitate was dissolved. The reaction mixture was neutralized to pH~8 by dropwise addition of aq NaOH (20%, w/w), and the organic material was extracted with CH_2Cl_2 (3 ×). The combined organic layers were dried over Na_2SO_4, filtered, and evaporated to dryness. Purification by silica gel chromatography (EA/PE= 1:20, v/v) gave the pure product **S4** as light- yellow oil (2.18 g, 77%).^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.0 Hz, 1H), 6.76 (s, 2H), 6.62 (d, *J* = 6.4 Hz, 1H), 5.31 (s, 1H), 5.04 (s, 1H), 3.38 (q, *J* = 7.2 Hz, 4H), 2.14 (q, *J* = 0.8 Hz, 3H), 1.84 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 144.4, 142.6, 129.0, 113.2, 111.9, 111.3, 109.4, 44.5, 22.0, 12.5. HRMS (ESI) calcd for $C_{13}H_{20}N$ [M+H] $^+$ 190.1590, found 190.1588.



S5

Boron trichloride (1 M solution in CH_2Cl_2, 23 mL, 23.0 mmol) was added dropwise to a solution of (4-(diethylamino)phenyl)methanol

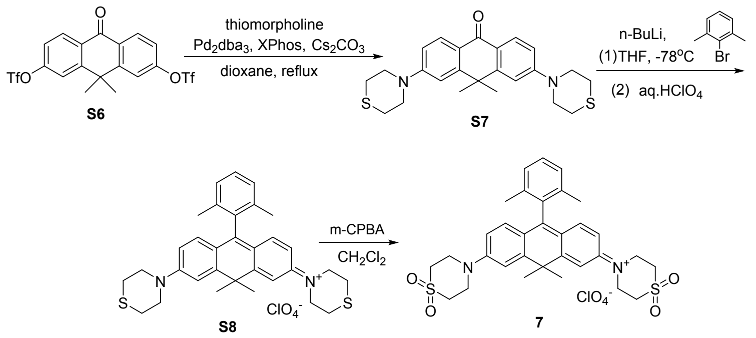
(3.58 g, 20.0 mmol) and N,N-diethyl-3-(prop-1en-2-yl)aniline **S4** (3.78 g, 20.0 mmol) in dry CH_2Cl_2 (100 mL) at 0 °C under N_2 atmosphere over 15 min. The reaction mixture was stirred overnight and was allowed to warm to room temperature. Polyphosphoric acid (≥83% phosphate (as P_2O_5), 50 g) was then added to the reaction mixture. The mixture was warmed to 40 °C, and CH_2Cl_2 was allowed to slowly evaporate through a thick cannula under slow flow of N_2. The reaction mixture was then heated to 130 °C, and the viscous material was stirred for an additional 3 h. The reaction mixture was allowed to cool to 20 °C, poured onto ice in a beaker, neutralized with cold aq NaOH (20%, w/w), and extracted with CH_2Cl_2 (4 ×). The combined organic layers were washed with aq $Na_2S_2O_3$ (100 mL, 10%). The organic layer was then separated, dried over Na_2SO_4, and the solvent was removed under reduced pressure to give a yellow viscous residue. The above-described viscous residue was dissolved in acetone (150 mL) and $KMnO_4$ (6.80 g, 43.0 mmol) was added portion wise at 0 °C over 2 h. When no starting material was observed (the reaction progress was monitored by TLC), the reaction mixture was filtered to remove MnO_2, and the pad was thoroughly washed with CH_2Cl_2. The filtrate was collected, and the solvents were evaporated to give a green powder. Purification by silica gel chromatography (EA / PE= 1:5, v/v) gave the product **S5** as light- yellow solid (1.48 g, 20%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 6.72 (m, 4H), 3.49 (q, *J* = 6.8 Hz, 4H), 1.70 (s, 6H), 1.26 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 152.4, 150.7, 129.3, 119.3, 110.3, 107.2, 44.6, 37.9, 33.6, 12.6. HRMS (ESI) calcd for $C_{24}H_{33}N_2O$ $[M+H]^+$ 365.2587, found 365.2585.

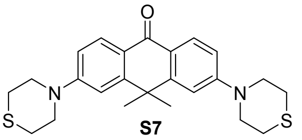


6

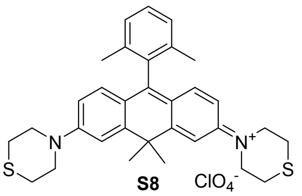
To a flame-dried flask flushed with argon, 2,6-dimethylbromobenzene (0.925 g, 5.0 mmol) and anhydrous THF (10 mL) were added. The solution was cooled to – 78 °C, and then n-BuLi (2.5 M in hexanes, 1.20 mL, 3.0 mmol) was added dropwise. After stirring 30 min at – 78 °C, C-xanthone **S5** (364 mg, 1.0 mmol) dissolved in anhydrous THF (20 mL) was added dropwise, and the mixture was warmed to room temperature then stirred for 2 h. The reaction was quenched by aq NH_4Cl and then acidified with 2 N $HClO_4$. The reaction mixture was diluted with water and the whole was extracted with CH_2Cl_2 (3×). The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by silica gel column chromatography (DCM / EtOH = 50:1) to afford desired product **6** as blue solid (120 mg, 25%).^{1}H NMR (600 MHz, CD_3CN) δ 7.40 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.14 (s, 2H), 6.99 (d, *J* = 9.6 Hz, 2H), 6.77 (d, *J* = 9.6 Hz, 2H), 3.67 (q, *J* = 7.2 Hz, 8H), 1.95 (s, 6H), 1.78 (s, 6H), 1.27 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, CD_3CN) δ 157.9, 155.7, 136.9, 136.5, 129.8, 128.3, 120.1, 118.2, 114.2, 111.9, 46.5, 42.3, 33.9, 19.7, 12.8. HRMS (ESI) calcd for $C_{32}H_{41}N_2$ $[M]^+$ 453.3264, found 453.3264.

2.3 Synthesis of Carborhodamine dye 7



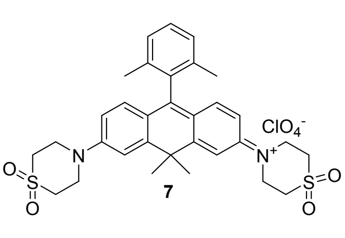

S7

A Schlenk bottle filled with dry nitrogen, compound **S6**[4] (518 mg, 1.00 mmol), Pd_2dba_3 (91.5 mg, 0.10 mmol, 0.1 eq.), XPhOS (143 mg, 0.30 mmol, 0.3 eq.), and Cs_2CO_3 (912 mg, 2.80 mmol, 2.8 eq.) were mixed. A suspension of thiomorpholine (247 mg, 2.40 mmol, 2.4 eq.) in anhydrous dioxane (20 mL) was added dropwise and stirred at 100 °C for 4 h. It was then cooled to room temperature, diluted with dichloromethane. The combined organic phase was washed with water and brine, dried over Na_2SO_4, filtered and evaporated. Purification by silica gel chromatography (EA/PE =1:5, v/v) afforded compound **S7** as an pale yellow solid (297 mg, 74%).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, J = 7.8 Hz, 2H), 6.95 (s, 2H), 6.91 (d, J = 7.8 Hz, 2H), 3.80 (s, 8H), 2.76 (s, 8H), 1.69 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 181.0, 152.3, 129.4, 114.2, 51.0, 38.1, 33.4, 26.1. HRMS (ESI) calcd for $C_{24}H_{28}N_2OS_2$ $[M+H]^+$ 425.1716, found 425.1715.


S8

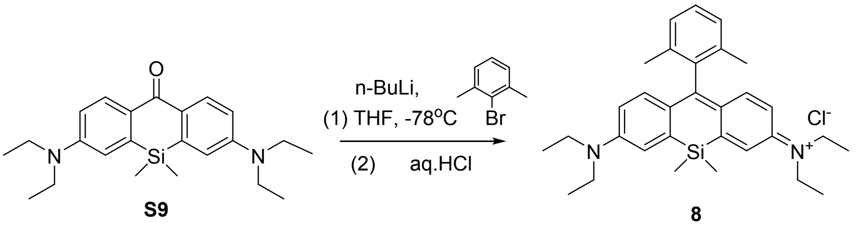
To a flame-dried flask flushed with argon, 2,6-dimethylbromobenzene (0.925 g, 5.00 mmol) and anhydrous THF (10 mL) were added. The solution was cooled to - 78 °C, n-BuLi (2.5 M in hexanes, 1.20 mL, 3.0 mmol) was added, and the mixture was stirred for 30 min. At the same temperature, C-xanthone **S7** (424 mg, 1.00 mmol) dissolved in anhydrous THF (20 mL) was added dropwise, and the mixture was warmed to room temperature and stirred for another 4h. The reaction was quenched by water, acidified with 2 N $HClO_4$ and then stirred for 30 min. The reaction mixture was diluted with water and the whole was extracted with CH_2Cl_2 (3×). The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by silica gel column chromatography (DCM / EtOH = 50:1) to afford desired product **S8** as dark red solid (0.411 g, 67%).^{1}H NMR (600 MHz, CD_3CN) δ (ppm): 7.41 (t, J = 7.8 Hz, 1H), 7.30 (d, J = 1.8 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 9.0 Hz, 2H), 6.89 (dd, J_1 = 1.8 Hz, J_2 = 7.8 Hz, 2H), 4.10 (t, J = 4.8 Hz, 8H), 2.79 (t, J = 4.8 Hz, 8H), 1.95 (s, 6H), 1.77 (s, 6H). ^{13}C NMR (150 MHz, CD_3CN) δ 165.0, 157.8, 155.6, 136.5, 135.5, 129.1, 127.5, 120.2, 117.3, 114.2, 112.1, 50.8, 41.9, 32.8, 26.8, 18.9. HRMS (ESI) calcd for $C_{32}H_{37}N_2S_2$ $[M]^+$ 531.2387, found 531.2393.

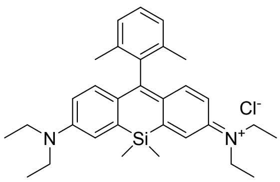
A solution of 3-chloroperozybenzoic acid (138 mg, 0.81 mmol)


7

in CH_2Cl_2 (10 mL) was added dropwise to a solution of **S8** (61.3 mg, 0.10 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, then allowed to warm to room temperature and stirred for another 4 h. The mixture was washed successively with aq. $NaHSO_3$, and 2N $HClO_4$. The organic layer was collected and dried over Na_2SO_4. The solvent was filtered off and evaporated to dryness. The residue was purified by silica gel column chromatography (DCM / EtOH = 50:1) and further recrystallized by portion wise addition of Et_2O to the solution of product in CH_2Cl_2 with frequent sonication. The product was dried under vacuum to give **7** as dark red solid (20 mg, 30%).^{1}H NMR (600 MHz, CD_3CN) δ (ppm): 7.44 (t, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 9.6 Hz, 2H), 7.02-7.00 (dd, *J* = 2.4 Hz, 2H), 4.23 (t, *J* = 4.8 Hz, 8H), 3.23 (t, *J* = 4.8 Hz, 8H), 1.95 (s, 6H), 1.81 (s, 6H). ^{13}C NMR (150 MHz, CD_3CN) δ 169.0, 159.8, 157.0, 138.2, 136.3, 135.4, 130.3, 128.5, 122.1, 118.2, 115.7, 113.5, 52.2, 47.0, 43.2, 33.4, 19.8. HRMS (ESI) calcd for $C_{32}H_{37}N_2O_4S_2$ $[M]^+$ 577.2189, found 577.2185.

*2.4 Synthesis of Silicon-Rhodamine dye **8***

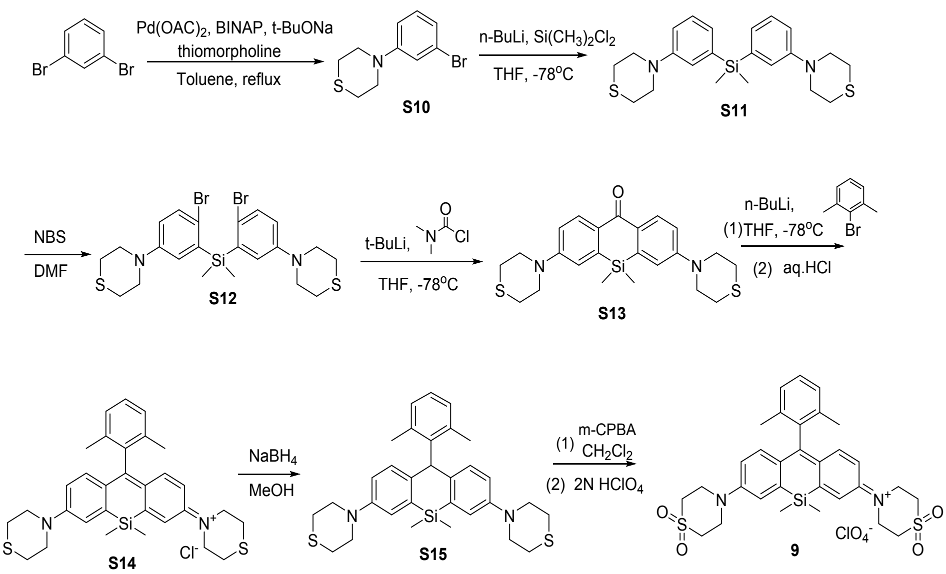


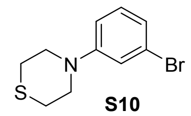


8

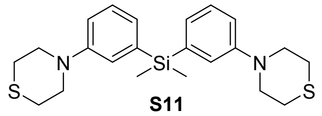
To a flame-dried flask flushed with argon, 2,6-dimethylbromobenzene (0.925 g, 5.00 mmol) and anhydrous THF (10 mL) were added. The solution was cooled to – 78 °C, and then n-BuLi (2.5 M in hexanes, 1.20 mL, 3.00 mmol) was added dropwise. After stirring 30 min at – 78 °C, Si-xanthone **S9**[5](380 mg, 1.00 mmol) dissolved in anhydrous THF (20 mL) was added dropwise, and the mixture was warmed to room temperature then stirred for 2 h. The reaction was quenched by aq NH_4Cl and then acidified with 2 N HCl. The reaction mixture was diluted with water and the whole was extracted with CH_2Cl_2 (3×). The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by silica gel column chromatography (DCM / MeOH = 30:1) to afford desired product **8** as blue solid (207 mg, 41%).^{1}H NMR (600 MHz, DMSO-d_6) δ 7.41 (s, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 9.6 Hz, 2H), 6.85 (d, *J* = 9.6 Hz, 2H), 3.67 (m, 8H), 1.94 (s, 6H), 1.19 (s, 12H), 0.65 (s, 6H). ^{13}C NMR (DMSO-d_6, 150 MHz) δ 167.3, 152.7, 147.8, 139.5, 138.6, 135.4, 128.9, 127.9, 126.1, 121.6, 115.1, 45.6, 19.7, 13.2, -0.88. HRMS (ESI) calcd for $C_{31}H_{41}N_2Si$ $[M]^+$ 469.3034, found 469.3039.

*2.5 Synthesis of silicon-rhodamine dye **9***

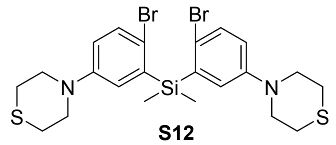



S10

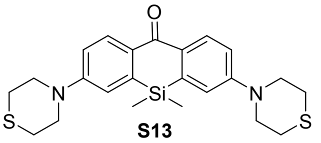
A vial was charged with 1,3-dibromobenzene (9.44 g, 40.0 mmol), thiomorpholine (4.12 g, 40.0 mmol), Pd(OAc)$_2$ (449 mg, 2.00 mmol), BINAP (1.92 g, 3.00 mmol) and t-BuONa (4.62 g, 48 mmol). The vial was sealed and evacuated/backfilled with nitrogen (3×) followed by addition of toluene (50 mL) by a syringe. The reaction mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with CH$_2$Cl$_2$ and filtered through a celite pad. The combined filtrate and washings were concentrated. The residue was purified by silica gel column chromatography (PE / EA = 20: 1) to afford desired product **S10** as colorless oil (6.41 g, 62%).^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.11 (t, J = 7.8 Hz, 1H), 7.00 (s, 1H), 6.95 (d, J = 7.8 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 3.56-3.54 (m, 4H), 2.72-2.70 (m, 4H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 152.1, 130.5, 123.3, 122.3, 119.6, 115.2, 51.7, 26.4. HRMS (ESI) calcd for $C_{10}H_{13}BrNS$ $[M+H]^+$ 257.9947, found 257.9945.


S11

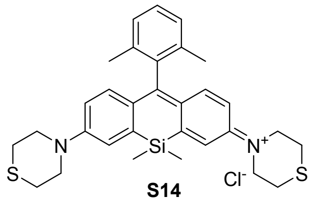
Compound **S10** (5.16 g, 20.0 mmol, 2.4 eq) was dissolved in THF (100 mL) and cooled to -78 °C with dry ice bath under nitrogen. n-BuLi (2.5 M in hexanes, 8.00 mL, 20.0 mmol, 2.4 eq) was added dropwise to the solution, and the reaction was stirred at -78 °C for 30 min. Dichlorodimethylsilane (1.1 mL, 8.33 mmol) in THF (10 mL) was then added dropwise over 30 min. The dry ice bath was removed, and the reaction was stirred at room temperature for 3 h. It was subsequently quenched with saturated NH$_4$Cl, diluted with water, and extracted with EtOAc. The organic phase was collected and washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE / EA = 20:1) to afford desired product **S11** as white solid (2.77 g, 80%).^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.27 (t, J = 7.8 Hz, 2H), 7.05 (d, J = 2.4 Hz, 2H), 7.03 (d, J = 7.2 Hz, 2H), 6.92 (d, J = 2.4 Hz, 2H), 3.49 (t, J = 4.8 Hz, 8H), 2.75 (m, 8H), 0.52 (s, 6H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 151.0, 139.2, 128.7, 126.0, 123.2, 118.2, 52.4, 27.0, -2.2. HRMS (ESI) calcd for $C_{22}H_{31}N_2S_2Si$ $[M+H]^+$ 415.1692, found 415.1691.


S12

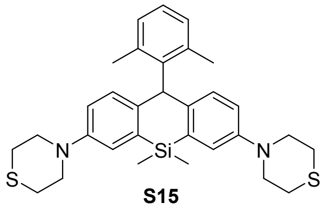
Compound **S11** (2.07 g, 5.00 mmol) was taken up in DMF (50 mL). N-Bromosuccinimide (1.77 g, 10.0 mmol, 2 eq) was added portion-wise over 5 min, and the reaction was then stirred at room temperature for 24 h. The reaction mixture was concentrated in vacuo and the resulting residue was diluted with water and extracted with EtOAc (2×). The combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Silica gel chromatography (PE / DCM = 2:1) afforded **S12** as a white solid (2.72 g, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.38 (d, *J* = 9.0 Hz, 2H), 6.97 (s, 2H), 6.76 (d, *J* = 7.2 Hz, 2H), 3.47-3.45 (t, *J* = 4.8 Hz, 8H), 2.72-2.71 (m, 8H), 0.74 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 138.1, 132.3, 125.3, 118.9, 51.0, 25.6, -2.0. HRMS (ESI) calcd for $C_{22}H_{29}Br_2N_2S_2Si$ $[M+H]^+$ 572.9882, found 572.9880.


S13

A solution of **S12** (1.90 g, 3.31 mmol) in anhydrous THF (50 mL) was cooled to -78 °C, and tert-Butyllithium (10.2 mL of 1.3 M in hexanes, 13.2 mmol, 4 eq) was added quickly dropwise. The resulting dark yellow solution was stirred at -78 °C for 1 h. Neat N, N-dimethylcarbamoyl chloride (0.62 mL, 6.62 mmol, 2 eq) was then injected dropwise (the color of the reaction mixture changed to light yellow). The resulting mixture was stirred at -78 °C for 30 min, then allowed to warm to rt. and left stirring overnight. It was then quenched with sat. aq. NH_4Cl, and diluted with water. The mixture was extracted with ethyl acetate (3×). The combined extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was isolated by silica gel chromatography (PE / DCM = 1:1) to give the ketone **S13** as bright yellow solid (1.21 g, 82%).^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.38 (d, *J* = 8.4 Hz, 2H), 6.99 (s, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 3.82 (s, 8H), 2.74 (s, 8H), 0.46 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.0, 151.5, 140.7, 131.1, 117.6, 116.4, 50.5, 26.1, -1.0. HRMS (ESI) calcd for $C_{23}H_{29}N_2OS_2Si$ $[M+H]^+$ 441.1485, found 441.1484.

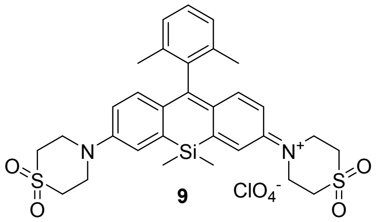

S14

To a flame-dried flask flushed with argon, 2,6-dimethylbromobenzene (0.925 g, 5.00 mmol) and anhydrous THF (10 mL) were added. The solution was cooled to – 78 °C, *n*-BuLi (2.5 M in hexanes, 1.20 mL, 3.00 mmol) was added, and the mixture was stirred for 30 min. At the same temperature, Si-xanthone **S13** (0.44 g, 1.00 mmol) dissolved in anhydrous THF (20 mL) was slowly added, and the mixture was warmed to r.t. then stirred for 2 h. The reaction was quenched by addition of 2 N HCl and the mixture was stirred at r.t. for 10 min. Saturated $NaHCO_3$ was added, and the whole was extracted with CH_2Cl_2 (3×). The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by silica gel column chromatography (DCM / MeOH = 20:1) to afford desired product **S14** as green solid (0.42 g, 74%).^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.63 (d, *J* = 3.0 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 9.6 Hz, 2H), 6.75 – 6.73 (dd, *J* = 2.4 Hz, 2H), 4.24 (t, *J* = 4.2 Hz, 8H), 2.88 (t, *J* = 4.2 Hz, 8H), 1.98 (s, 6H), 0.77 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 153.1, 149.7, 140.8, 138.0, 135.5, 128.6, 127.8, 127.6, 122.2, 114.9, 51.2, 27.7, 19.8, -0.75. HRMS (ESI) calcd for $C_{31}H_{37}N_2S_2Si$ $[M]^+$ 529.2162, found 529.2164.



S15

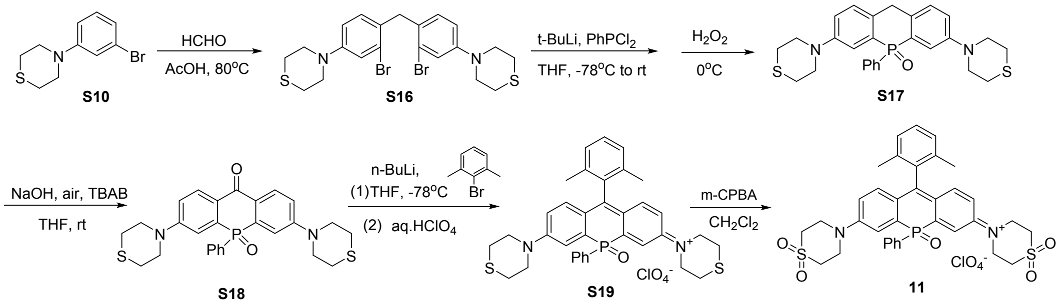
To a solution of **S14** (0.565 g, 1.00 mmol) in MeOH (30 mL) was added $NaBH_4$ (76.2 mg, 2.00 mmol). The reaction mixture was stirred for 30 min at 50°C. The mixture was diluted with H_2O and then extracted with CH_2Cl_2 (3×). The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by silica gel column chromatography (PE / EA = 20:1) to afford **S15** as white solid (0.191 g, 36%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.16 -7.12 (m, 4H), 6.93 (s, 1H), 6.75 (d, *J* = 7.8 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 5.74 (s, 1H), 3.49 (s, 8H), 2.77 (s, 8H), 2.53 (s, 3H), 1.48 (s, 3H), 0.56 (s, 3H), 0.39 (s, 3H). ^{13}C NMR (150 MHz $CDCl_3$) δ 148.8, 143.5, 139.7, 137.0, 134.0, 130.3, 128.6, 127.7, 126.4, 121.3, 118.9, 52.4, 45.8, 27.2, 21.3, 20.8, 0.07, -1.84. HRMS (ESI) calcd for $C_{31}H_{39}N_2S_2Si$ $[M+H]^+$ 531.2318, found 531.2319.

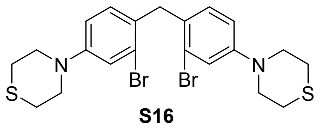


9

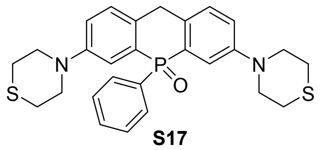
A solution of 3-chloroperozybenzoic acid (0.641 g, 2.80 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of **S15** (0.191 g, 0.36 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, then allowed to warm to room temperature overnight. The mixture was washed with aq. $NaHSO_3$, and water. The collected organic layers were dried over Na_2SO_4 and evaporated. The residue was again dissolved in CH_2Cl_2 (20 mL), and DDQ (80 mg, 0.36 mmol) was added in one portion. The mixture was stirred for 2 h, and then washed with 2N $HClO_4$. The organic layer was collected, dried over Na_2SO_4, filtered, and concentrated. The residual crude product was purified by column chromatography (DCM / MeOH = 30:1) and further recrystallized by portion wise addition of Et_2O to the solution of product in MeOH with frequent sonication. The product was dried under vacuum to give **9** as blue crystalline solid (0.15 g, 61%).^{1}H NMR (600 MHz, CD_3CN) δ (ppm): 7.51 (s, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 9.6 Hz, 2H), 6.94 (d, *J* = 9.6 Hz, 2H), 4.22 (s, 8H), 3.22 (s, 8H), 1.96 (s, 6H), 0.61 (s, 6H). ^{13}C NMR (150 MHz, CD_3CN) δ 153.8, 150.0, 141.4, 137.8, 135.4, 129.0, 128.4, 127.5, 122.1, 115.8, 51.3, 45.9, 18.8, -2.4. HRMS (ESI) calcd for $C_{31}H_{37}N_2O_4S_2Si$ $[M]^+$ 593.1959, found 593.1956.

*2.6 Synthesis of phospha-rhodamine dye **11***

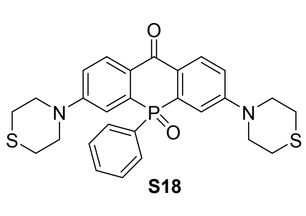



S16

4-(3-bromophenyl)thiomorpholine **S10** (5.16 g, 20.0 mmol) and formaldehyde (37 wt. % in H_2O, 3.01 g, 100 mmol) were dissolved in acetic acid (100 mL) and the mixture was stirred at 80 ºC for 8 h. Solvent was removed by evaporation and saturated $NaHCO_3$ aqueous was added. The resulting mixture was extracted by CH_2Cl_2 (3×). The organic layer was collected, dried over Na_2SO_4, and filtered. Solvent was removed by evaporation and the residue was purified by column chromatography (DCM / PE = 1:3) to yield product **S16** as a white solid (4.02 g, 76%).^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.10 (d, *J* = 2.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 4.00 (s, 2H), 3.52 (t, *J* = 4.8 Hz, 8H), 2.73 (t, *J* = 4.8 Hz, 8H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 150.5, 130.9, 125.5, 120.7, 116.1, 51.8, 40.1, 26.6. HRMS (ESI) calcd for $C_{21}H_{25}Br_2N_2S_2$ $[M+H]^+$ 528.9800, found 528.9806.

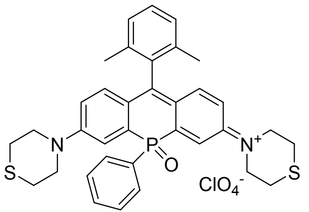

S17

To a solution of bis(2-bromo-4-thiomorpholinophenyl)methane **S16** (3.01 g, 5.70 mmol) in anhydrous THF (50 mL) was added tert-Butyllithium (17.5 mL of 1.3 M in hexanes, 22.8 mmol, 4 eq) at -78 °C, and the mixture was stirred for 1 hour at -78 °C. P, P-dichlorophenylphosphine (0.86 mL, 6.27 mmol) was then added dropwise at -78 °C for 20 min and the resulting solution was warmed up to room temperature overnight. After it was cooled to 0 ºC, 35% aqueous H_2O_2 (2.5 mL) was added. The mixture was stirred for 30 min at 0 °C and quenched with the solution of Na_2SO_3. The mixture was diluted with water and extracted with CH_2Cl_2 (3×). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The residual crude product was purified by column chromatography (PE / EA = 1:1) to give **S17** as white solid (2.51 g, 89%).^{1}H NMR (600MHz, $CDCl_3$) δ (ppm): 7.68 (d, *J* = 12.6 Hz, 2H), 7.45-7.41(m, 3H), 7.34-7.32 (dd, *J* = 6.0 Hz, 2H), 7.28 (s, 2H), 7.02 (s, 2H), 3.90 (d, *J* = 18 Hz, 1H), 3.73 (d, *J* = 18 Hz, 1H), 3.62 (t, *J* = 4.2 Hz, 8H), 2.75 (s, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.7, 131.4, 130.5, 130.4, 129.2, 129.1, 128.5, 128.4, 120.0, 118.2, 51.8, 35.6, 26.4. HRMS (ESI) calcd for $C_{27}H_{30}N_2OPS_2$ $[M+H]^+$ 493.1532, found 493.1536.


S18

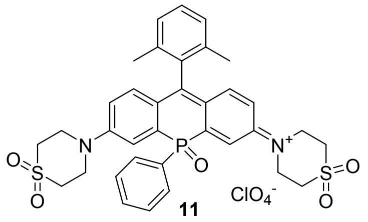
Compound **S17** (2.31 g, 4.70 mmol) was dissolved in dry THF (100 mL), followed by the addition of powdered NaOH (0.56 g, 14.1

mmol) and tetrabutylammonium bromide (TBAB, 77 mg, 0.24 mmol). The resulting suspension was vigorously stirred for 5 h at room temperature under the flow of dry air. The mixture was diluted with water, acidified with 2M HCl aq and extracted with CH_2Cl_2 (3×). The organic layers were combined and dried over Na_2SO_4. The drying agent was filtered off and the solvent was removed under reduced pressure. The residual was purified by column chromatography (DCM / MeOH = 100:1) to give **S18** as yellow solid (1.31 g, 55%).^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.34 (t, *J* = 6.0 Hz, 2H), 7.61-7.57 (dd, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 14.4 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 8H), 2.70 (s, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.0, 152.2, 152.1, 135.3, 134.6, 131.6, 130.4, 130.3, 128.8, 125.7, 117.2, 114.4, 50.0, 26.0. HRMS (ESI) calcd for $C_{27}H_{27}N_2NaO_2PS_2$ $[M+Na]^+$ 529.1144, found 529.1148.



S19

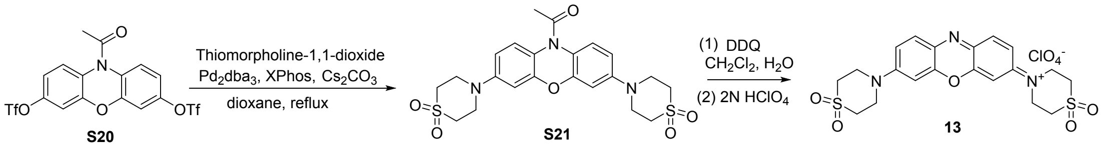
To a flame-dried flask flushed with argon, 2,6-dimethylbromobenzene (0.925 g, 5.00 mmol) and anhydrous THF (10 mL) were added. The solution was cooled to - 78 °C, n-BuLi (2.5 M in hexanes, 1.20 mL, 3.0 mmol) was added, and the mixture was stirred for 30 min. At the same temperature, P-xanthone **S18** (506 mg, 1.00 mmol) dissolved in anhydrous THF (20 mL) was added dropwise, and the mixture was warmed to room temperature then stirred overnight. The reaction was quenched by water, acidified with 2 N $HClO_4$ and then stirred for 30 min. The reaction mixture was diluted with water and the whole was extracted with CH_2Cl_2 (3×). The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by silica gel column chromatography (DCM / MeOH = 30:1) to afford desired product **S19** as dark green solid (0.27 g, 38%).^{1}H NMR (600 MHz, CD_3CN) δ (ppm): 7.69 (s, 1H), 7.66 (s, 1H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.46 (s, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.24 (m, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 1.8 Hz, 2H), 6.59 (d, *J* = 7.8 Hz, 1H), 4.06 (s, 8H), 2.76 (s, 8H), 1.89 (s, 6H). ^{13}C NMR (150 MHz, CD_3CN) δ 154.4, 154.3, 148.0., 139.7, 139.5, 132.8, 130.3, 130.2, 129.4, 129.2, 129.1, 129.0, 127.8, 127.6, 127.7, 120.0, 114.3, 51.4, 27.4, 18.9, 18.8. HRMS (ESI) calcd for $C_{35}H_{36}N_2OPS_2$ $[M]^+$ 595.2001, found 595.1997.

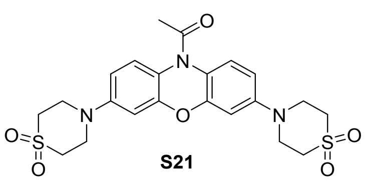


11

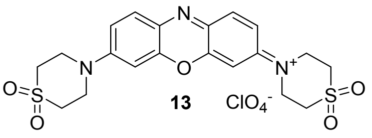
A solution of 3-chloroperozybenzoic acid (138 mg, 0.81 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **S19** (69.6 mg, 0.10 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, then allowed to warm to room temperature and stirred for another 4h. The mixture was washed successively with aq. $NaHSO_3$, and 2N $HClO_4$. The organic layer was collected and dried over Na_2SO_4. The solvent was filtered off and evaporated to dryness. The residue was purified by silica gel column chromatography (DCM / MeOH = 30:1) and further recrystallized by portion wise addition of Et_2O to the solution of product in CH_2Cl_2 with frequent sonication. The product was dried under vacuum to give **11** as dark green solid (30 mg, 39%).^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 7.81 (s, J = 2.4 Hz, 1H), 7.80 (s, J = 2.4 Hz, 1H), 7.70-7.60 (m, 3H), 7.54-7.49 (m, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.30-7.25 (dd, J = 7.6 Hz, 2H), 7.21-7.17 (dd, J = 5.6 Hz, 2H), 7.07-7.05 (dd, J = 2.0 Hz, 2H), 4.24 (t, J = 4.2 Hz, 8H), 3.24 (s, 8H), 1.99 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ 155.9, 155.7, 141.4, 141.3, 136.7, 135.8, 135.4, 133.8, 131.2, 131.1, 130.2, 129.9, 129.8, 128.4, 128.3, 125.0, 124.9, 121.3, 121.2, 117.9, 51.8, 47.2, 19.5, 19.4. HRMS (ESI) calcd for $C_{35}H_{36}N_2O_5PS_2$ $[M]^+$ 659.1798, found 659.1795.

*2.7 Synthesis of oxazine dye **13***



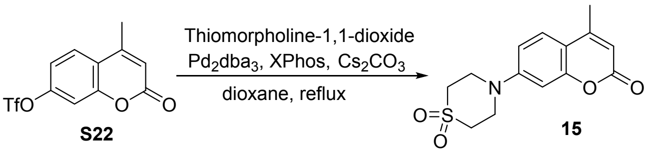


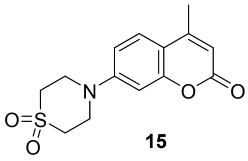
A Schlenk bottle filled with dry nitrogen, compound **S20** (300 mg, 0.57 mmol), Pd_2dba_3 (52.2 mg, 0.057 mmol, 0.1 eq.), XPhOS (81.5 mg, 0.17 mmol, 0.3 eq.), and Cs_2CO_3 (524 mg, 1.6 mmol, 2.8 eq.) were mixed. A suspension of thiomorpholine-1,1-dioxide (186 mg, 1.37 mmol, 2.4 eq) in anhydrous dioxane (20 mL) was added dropwise and stirred at 100 °C for 4 h. It was then cooled to room temperature, diluted with dichloromethane. The combined organic phase was washed with water and brine, dried over Na_2SO_4, filtered and evaporated. Purification by silica gel chromatography (EA / PE =1 : 1, v/v) afforded compound **S21** as an pale yellow solid (156 mg, 56%).^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.44 (d, J = 6.4 Hz, 2H), 6.81 (d, J = 4.4 Hz, 4H), 3.80 (s, 8H), 3.11 (s, 8H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.5, 146.6, 126.1, 121.3, 110.6, 103.8, 50.1, 47.0, 23.0. HRMS (ESI) calcd for $C_{22}H_{26}N_3O_6S_2$ $[M+H]^+$ 492.1258, found 492.1254.



The intermediate **S21** (49 mg, 0.10 mmol) was taken up in a mixture of CH_2Cl_2 (10 mL) and water (0.5 mL) and then cooled to 0 °C. DDQ (25 mg, 0.11 mmol, 1.1 eq) was added, and the reaction was stirred at room temperature for 3 h. A second portion of DDQ (12 mg, 0.05 mmol, 0.5 eq) was added, and the reaction was stirred for an additional 1 h. The mixture was filtered and solid was collected. The collected solid was dissolved in CH_3CN (10 mL), then 2 N $HClO_4$ (20 mL) was added and stirred for 30 min. The insoluble solid was collected by filtration and washed with CH_2Cl_2 and MeOH successively. After drying in vacuum, compound **13** was obtained as a blue-purple solid. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.00 (d, J = 6.4 Hz, 2H), 7.77 (dd, J_1 = 1.2 Hz, J_2 = 6.4 Hz, 2H), 7.44 (s, 2H), 4.36 (s, 8H), 3.42 (s, 8H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.6, 149.6, 135.5, 134.8, 119.4, 98.4, 51.6, 47.1. HRMS (ESI) calcd for $C_{20}H_{22}N_3O_5S_2$ $[M]^+$ 448.0995, found 448.0995.

*2.8 Synthesis of coumarin dye **15**.*

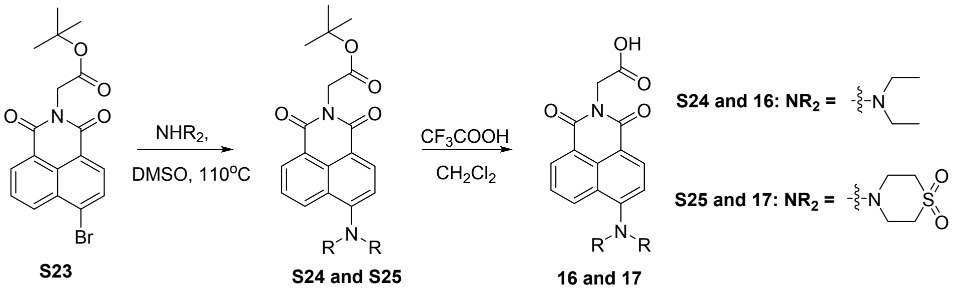


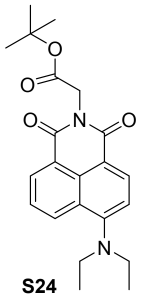


15

A vial was charged with 4-methylumbelliferone triflate **S22** (314 mg, 1.02 mmol), Pd_2dba_3 (93.4 mg, 0.102 mmol, 0.1 eq), XPhos (145 mg, 0.306 mmol, 0.3 eq), and Cs_2CO_3 (926 mg, 2.85 mmol, 2.8 eq). The vial was sealed and evacuated/backfilled with nitrogen (3×). Dioxane (20 mL) was added, and the reaction was flushed again with nitrogen (3×). Following the addition of thiomorpholine-1,1-dioxide (331 mg, 2.45 mmol, 2.4 eq), the reaction was refluxed for 8 h. After cooling to room temperature, water (50 mL) was added and CH_2Cl_2 (50 mL × 3) was used to extract organic compounds. The combined organic phase was dried over Na_2SO_4 and then concentrated to dryness. Purification by silica gel chromatography (PE / EA =1: 1) afforded **15** as a white solid (180 mg, 60%).^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.51 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 2.4 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 6.11 (s, 1H), 4.00 (t, *J* = 4.8 Hz, 4H), 3.12 (t, *J* = 4.8 Hz, 4H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): 161.1, 155.5, 152.1, 149.6, 126.2, 112.7, 111.9, 111.1, 102.0, 50.4. 46.5, 18.5. HRMS (ESI) calcd for $C_{14}H_{16}NO_4S$ $[M+H]^+$ 294.0795, found 294.0791.

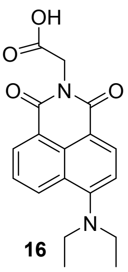
*2.9 Synthesis of 1,8-naphthalimide dyes **16** and **17***





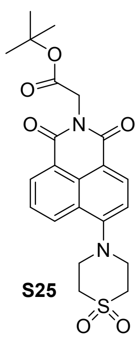
S24

Diethylamine (731 mg, 10. 0 mmol, 10.0 eq) was added to the solution of tert - Butyl 2-(6-bromo-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl) acetate **S23** (390 mg, 1.00 mmol) in DMSO (10 mL). The mixture was heated to 110℃ for 8 h. It was then diluted with water and extracted with EtOAc (3×). The combined organics were washed with brine, dried with Na_2SO_4 and then concentrated to dryness. The residue was purified by column chromatography (DCM / MeOH = 100:1) to give **S24** as a light yellow powder (268 mg, 70%).^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.58 (dd, *J* = 1.2 Hz, 1H), 8.50 (d, *J* =8.4 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 4.83 (s, 2H), 3.42 (q, *J* = 7.2 Hz, 4H), 1.48 (s, 9H), 1.18 (t, *J* = 7.2 Hz, 6H) . ^{13}C NMR (150 MHz, $CDCl_3$): 167.3, 164.3, 163.7, 132.4, 132.4, 131.2, 130.4, 127.3, 125.1, 122.6, 116.7, 82.0, 47.4. 41.9, 28.0, 12.2. HRMS (ESI) calcd for $C_{22}H_{26}N_2O_4Na$ $[M+Na]^+$ 405.1785, found 405.1784



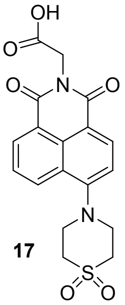
16

Ester **S24** (191 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (10 mL), and trifluoroacetic acid (2.0 mL) was added. The reaction was stirred at room temperature for 4 h and then concentrated to dryness. The residue was purified by column chromatography (DCM / MeOH = 100:1) to give **16** as a light yellow solid (150 mg, 92%). ^1H NMR (600 MHz, DMSO-d_6) δ (ppm): 13.01 (s, 1H), 8.50 (t, J = 3.6 Hz, 2H), 8.40 (d, J = 8.4 Hz, 1H), 7.82 (t, J = 7.8Hz, 1H), 7.37 (d, J = 7.8 Hz, 1H), 4.71 (s, 2H), 3.45 (q, J = 7.2 Hz, 4H), 1.15 (t, J = 7.2 Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d_6): 169.9, 163.8, 163.1, 155.5, 132.6, 131.8, 131.4, 130.1, 126.7, 126.0, 122.4, 116.9, 114.1, 47.3, 41.4, 12.5. HRMS (ESI) calcd for $C_{18}H_{17}N_2O_4$ $[M-H]^-$ 325.1194, found 325.1197.



S25

Thiomorpholine-1,1-dioxide (676 mg, 5.00 mmol, 5.0 eq) was added to the solution of tert -Butyl 2-(6-bromo-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl) acetate **S23** (390 mg, 1.00 mmol) in DMSO (10 mL). The mixture was heated to 110°C for 6 h. It was then diluted with water and extracted with EtOAc (3×). The combined organics were washed with brine, dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography (DCM / MeOH = 200:1) to give **S25** as a light-yellow powder (223 mg, 50%). ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.47 (d, J = 7.2 Hz, 1H), 8.45 (d, J =8.4 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.25(d, J = 7.8Hz, 1H), 4.80 (s, 2H), 3.71 (s, 4H), 3.40 (s, 4H), 1.51 (s, 9H). ^{13}C-NMR (150 MHz, $CDCl_3$): 167.3, 163.7, 163.2, 154.2, 132.1, 132.1, 129.5, 129.4, 126.7, 126.0, 122.8, 117.9, 116.6, 82.3, 52.0. 51.5, 42.0, 28.1. HRMS (ESI) calcd for $C_{22}H_{24}N_2O_6SNa$ $[M+Na]^+$ 467.1247, found 467.1249.



17

Ester **S25** (222 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (20 mL), and trifluoroacetic acid (2.5 mL) was added. The reaction was stirred at room temperature for 4 h and then concentrated to dryness. The residue was washed with Et_2O to afford **17** as a light yellow solid (190 mg, 98%). ^1H NMR (600 MHz, DMSO-d_6) δ (ppm): 8.65 (dd, J = 3.0 Hz, 1H), 8.54 (m, 1H), 8.44 (dd, J = 4.2 Hz, 3.6Hz, 1H), 7.89 (dd, J = 8.4Hz, 4.8 Hz, 1H), 7.54 (dd, J = 3.6 Hz, 4.2Hz, 1H), 4.72 (s, 2H), 3.68 (s, 4H), 3.52 (s, 4H). ^{13}C NMR (150 MHz, DMSO-d_6): 169.8, 163.7, 163.1, 155.3, 132.6, 131.6, 131.5, 129.5, 127.1, 126.1, 122.5, 117.6, 116.6, 51.8. 51.6, 41.5. HRMS (ESI) calcd for $C_{18}H_{15}N_2O_6S$ $[M-H]^-$ 387.0656, found 387.0655.

3. Computational methods for vertical ionization potentials

All theoretical calculations were performed using a suite of Gaussian 09. To compute the vertical ionization potential (IP) of various amino moieties in vacuo, we employed the benzene as the basis to simulate the fluorophore. All of the molecular structures were firstly optimized and conducted frequency checks using B3LYP/6-311G(d). Based on these optimized molecular structures, the electronic energies of ionized molecules were calculated using B3LYP/6-311G(d) by removing one electron in each molecule. The difference of the electronic energies in their neutral and ionized states is the vertical ionization potential of these amino moieties.

4. Determination of Quantum Yields

Fluorescence quantum yields of all samples in PBS buffer (10 mM, pH 7.4) were determined via the relative determination method. The quantum yields were calculated using the following Equation:

$$\Phi_u = [(A_s FA_u \eta^2)/(A_u FA_s \eta_0^2)]\Phi_s$$

Where A_s and A_u are the absorbance of the reference and sample solution at the reference excitation wavelength, FA_s and FA_u are the corresponding integrated fluorescence intensity, and η and η_0 are the solvent refractive indexes of sample and reference, respectively. Absorbance of sample and reference at their respective excitation wavelengths was controlled to be lower than 0.05. Reported values are averages (n = 3). For rhodamine dyes **1**, **3**, **4** and **5**, their quantum yields were determined with Rhodamine B ($\Phi = 0.31$, in H_2O) as a reference. For Carborhodamines **6** and **7**, silicon-rhodamines **8** and **9**, and oxazines **12** and **13**, their quantum yields were determined with Cresyl Violet ($\Phi = 0.53$, in CH_3OH) as a reference. For phospha-rhodamines **10** and **11**, their quantum yields were determined with Cy5.5 ($\Phi = 0.23$, in PBS) as a reference. For coumarins **14** and **15** and naphthalimides **16** and **17**, their quantum yields were determined with quinine sulphate ($\Phi = 0.58$, in 0.1M H_2SO_4) as a reference.

5. Photostability assays of Rhodamines 1–5

Photostability of Rhodamine dyes **1-5** were tested using CXE-350 xenon lamp illumination system. The solutions of **1-5** (10 mM PBS, with 0.1% DMSO) were subjected to irradiation by the xenon lamp with an optical *density* 200 mW/cm^2. The solution temperature was maintained steady by air-cooling. The fluorescence intensities of the solution were monitored every 2 minutes.

6. Supplementary Spectra

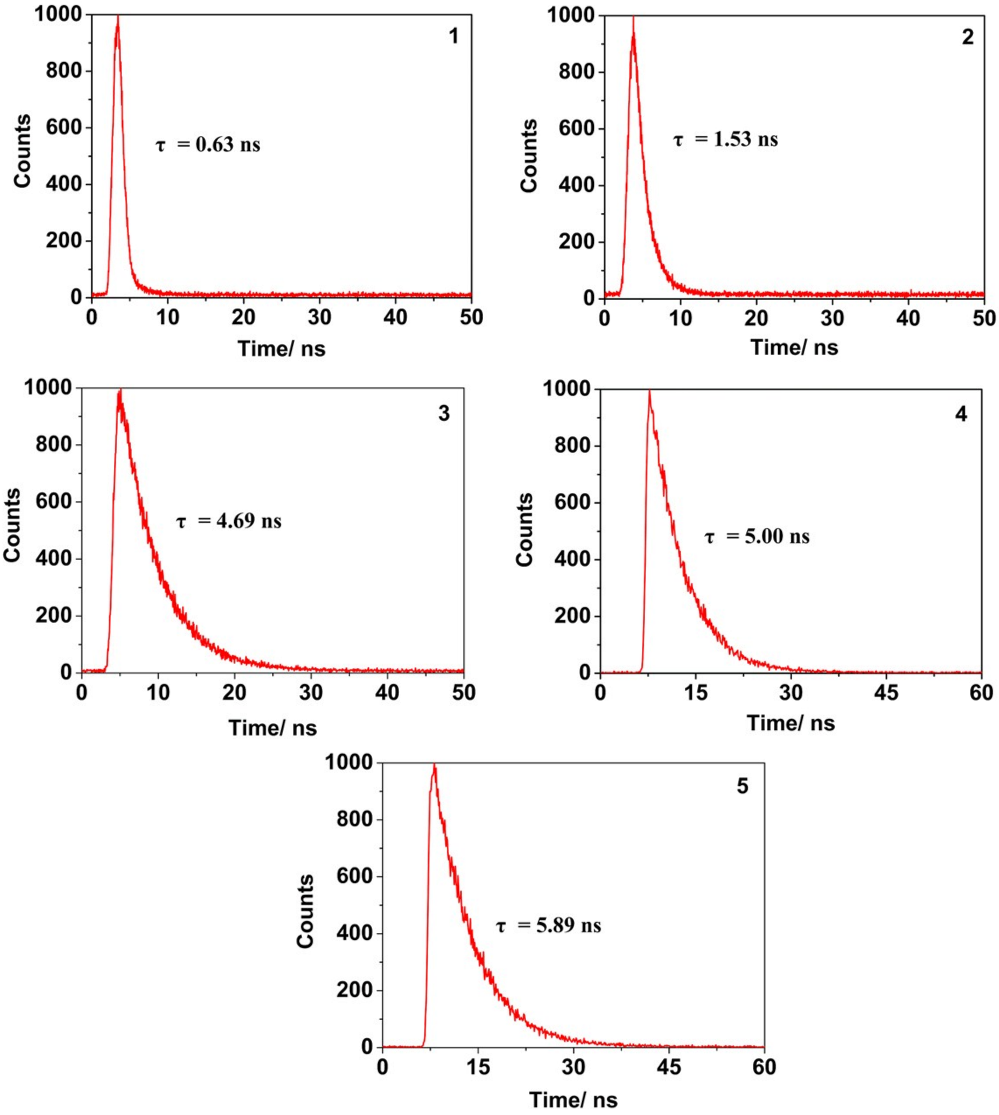


Figure S1. Fluorescence lifetime spectra for dyes **1-5**.

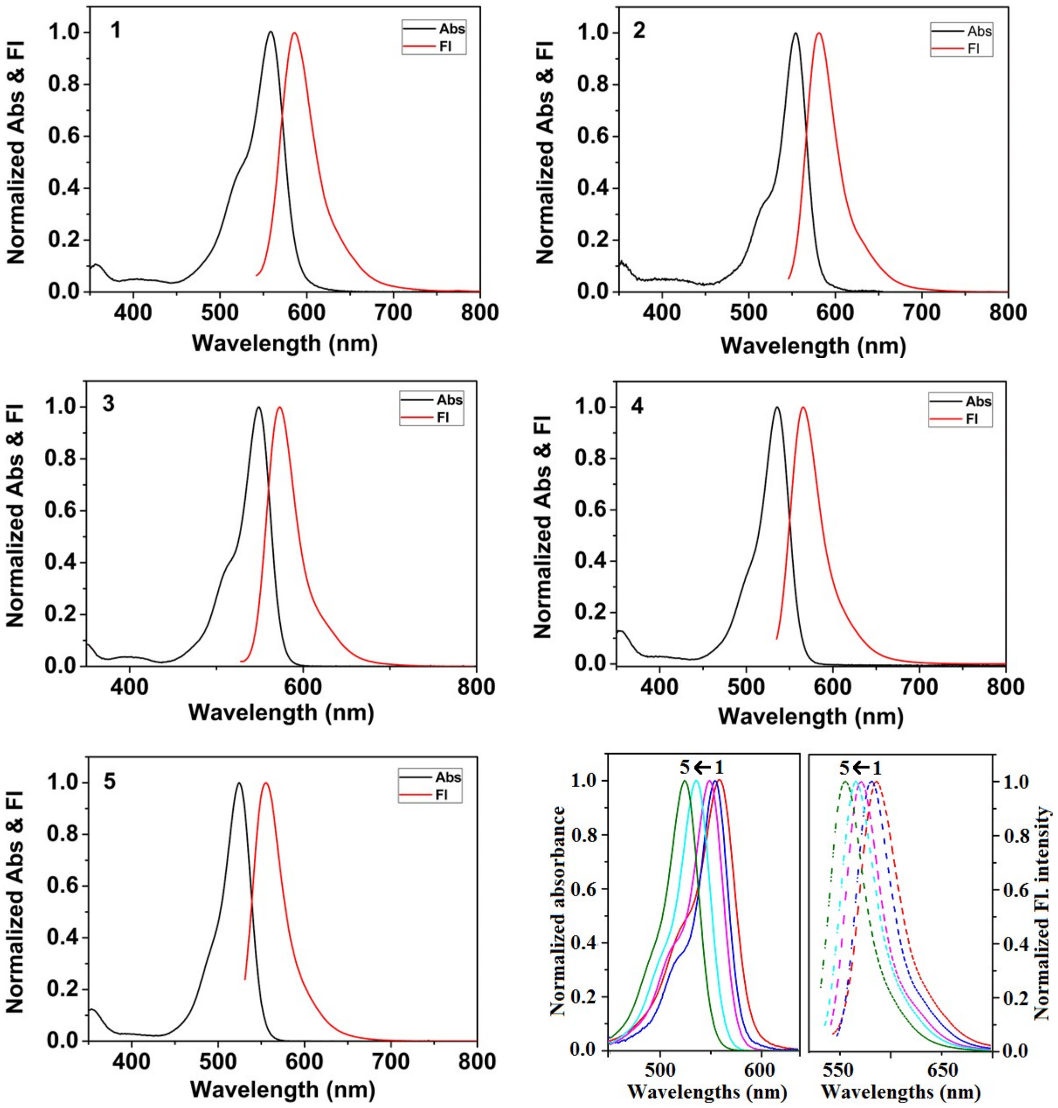


Figure S2. Normalized absorption and emission spectra for dyes **1-5** in PBS.

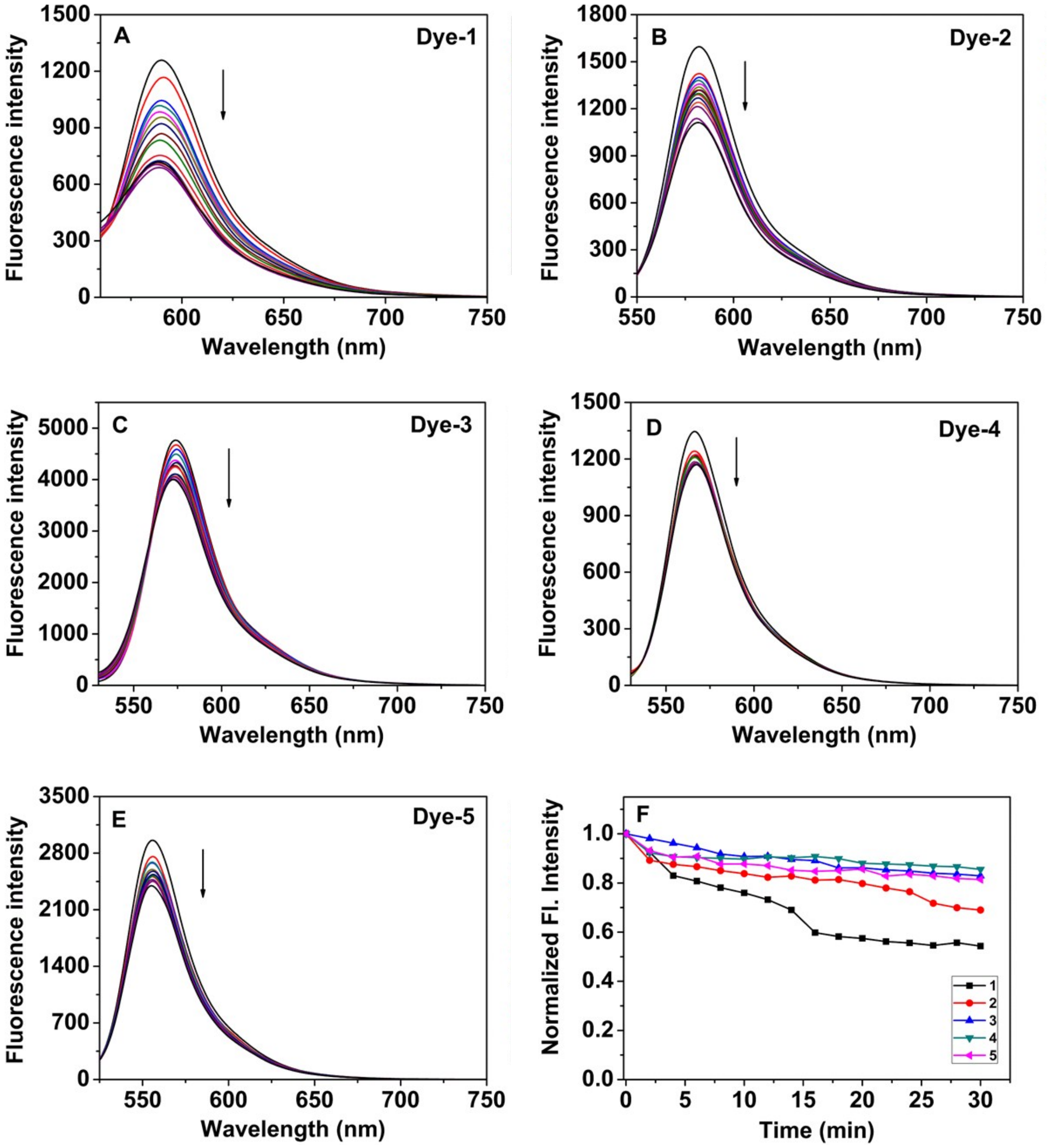


Figure S3. (A-E) The fluorescence emission spectra changes of rhodamine dyes **1-5** (2 μM) under the irradiation of a Xe lamp. (F) Photostability comparison of Rhodamine dyes **1-5** (2 μM). Condition: PBS (10 mM, pH = 7.4).

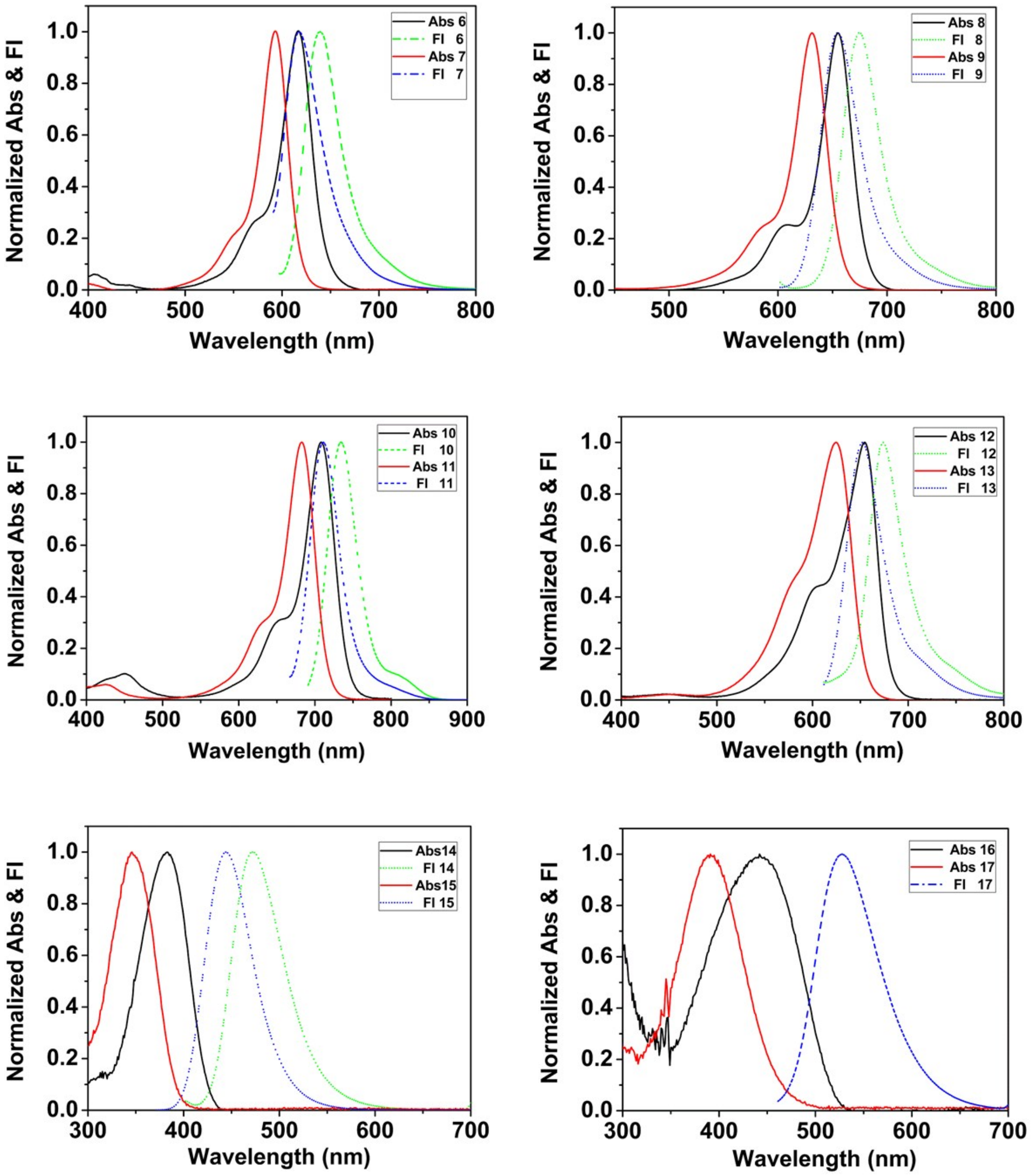
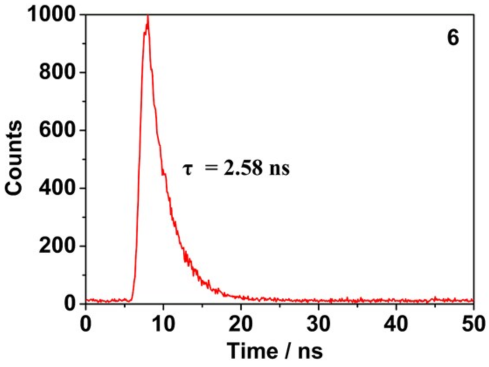


Figure S4. Normalized absorption and emission spectra of dyes **6-17.**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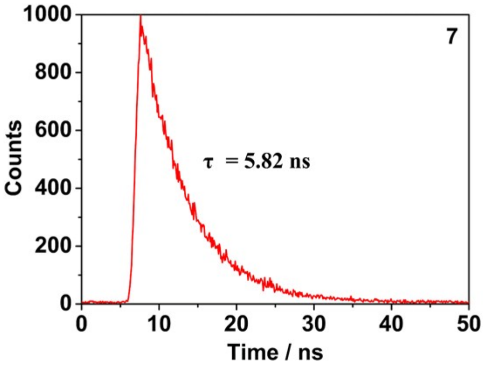
600
800
1000
0
10
20
30
40
50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τ = 5.82 ns
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Time / ns
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1000
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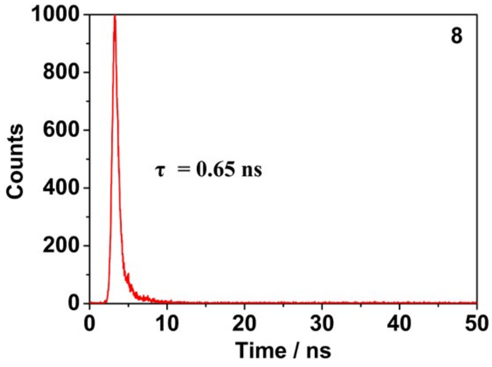
10
20
30
40
50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Counts
Time / ns
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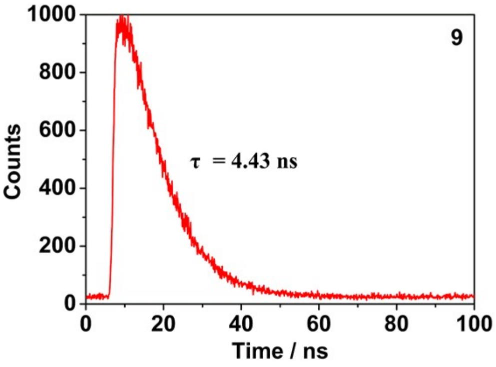
600
800
1000
0
10
20
30
40
50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τ = 4.43 ns
Counts
Time / ns
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1000
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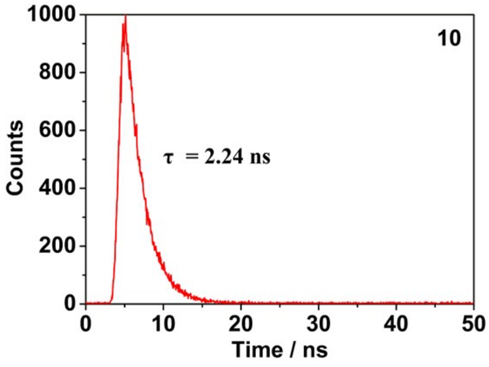
20
40
60
80
100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τ = 2.24 ns
Counts
Time / ns
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400
600
800
1000
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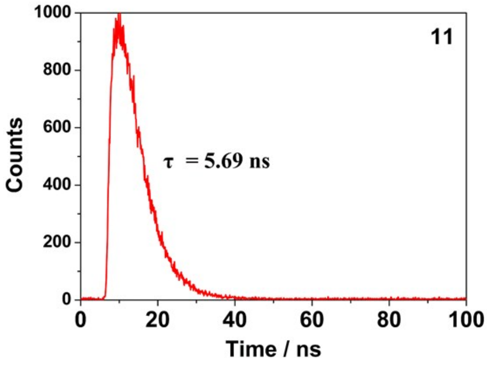
20
30
40
50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τ = 5.69 ns
Counts
Time / ns
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400
600
800
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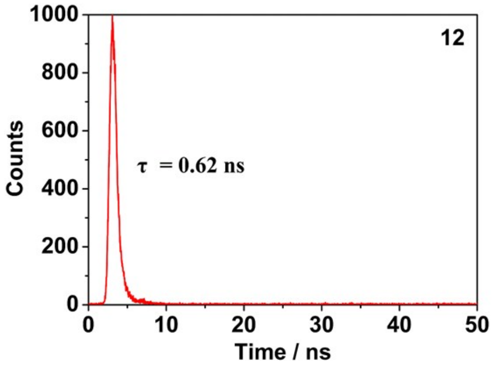
0
20
40
60
80
100


12
τ = 0.62 ns
Counts
Time / ns
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400
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800
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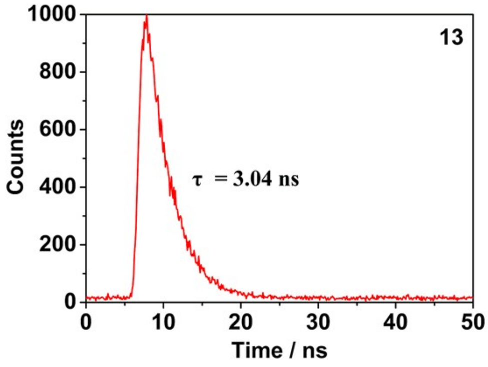
20
30
40
50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τ = 3.04 ns
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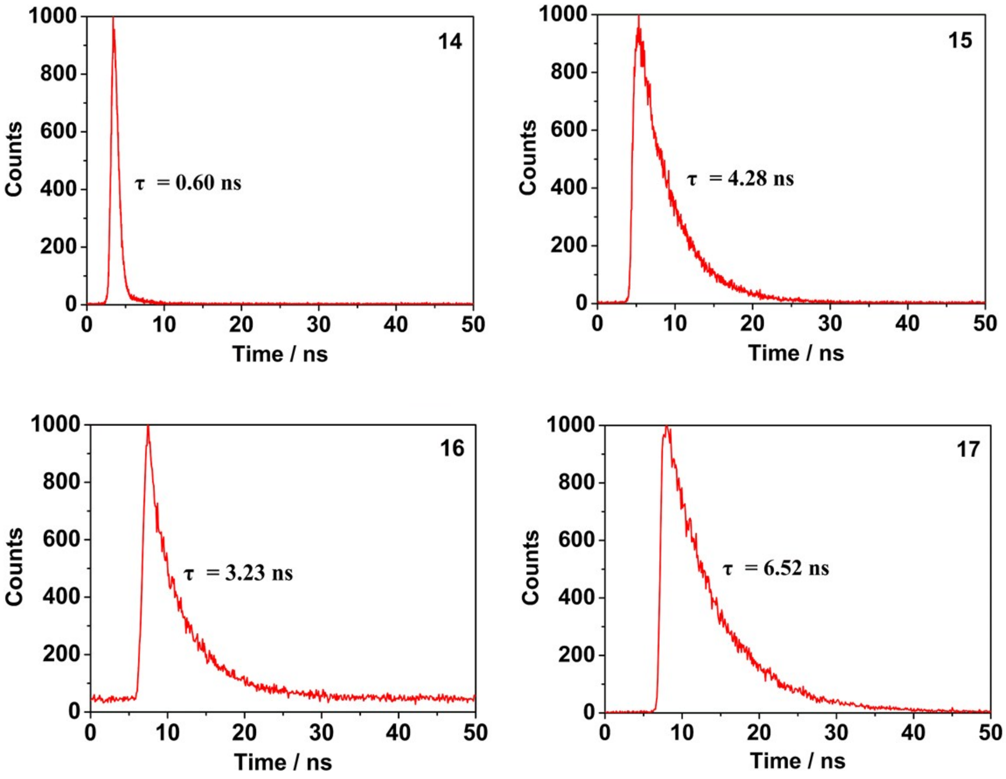


Figure S5. Fluorescence lifetime spectra for dyes **6-17**. (For **16**, the lifetime decay data were fit to a double exponential decay function τ_1= 3.23 (51.52%), τ_2=7.87 (48.48%), χ^2=1.069. As for others, the lifetime decay data were fit to a single exponential decay function).

7. References

1 J. Grimm, L. Lavis, Synthesis of rhodamines from fluoresceins using Pd-catalyzed C–N cross-coupling, Org. Lett. 13 (2011) 6354–6357.

2 J. Grimm, B. English, J. Chen, J. Slaughter, Z. Zhang, A. Revyakin, R. Patel, J. Macklin, D. Normanno, R. Singer, T. Lionnet, L. Lavis, A general method to improve fluorophores for live-cell and single-molecule microscopy, Nature methods 12 (2015) 244–250.

3 S. Jia, K. M. Ramos-Torres, S. Kolemen, M. Ackerman, C. J. Chang, Tuning the color palette of fluorescent copper sensors through systematic heteroatom substitution at Rhodol cores, ACS Chem. Biol. 13 (2018) 1844−1852.

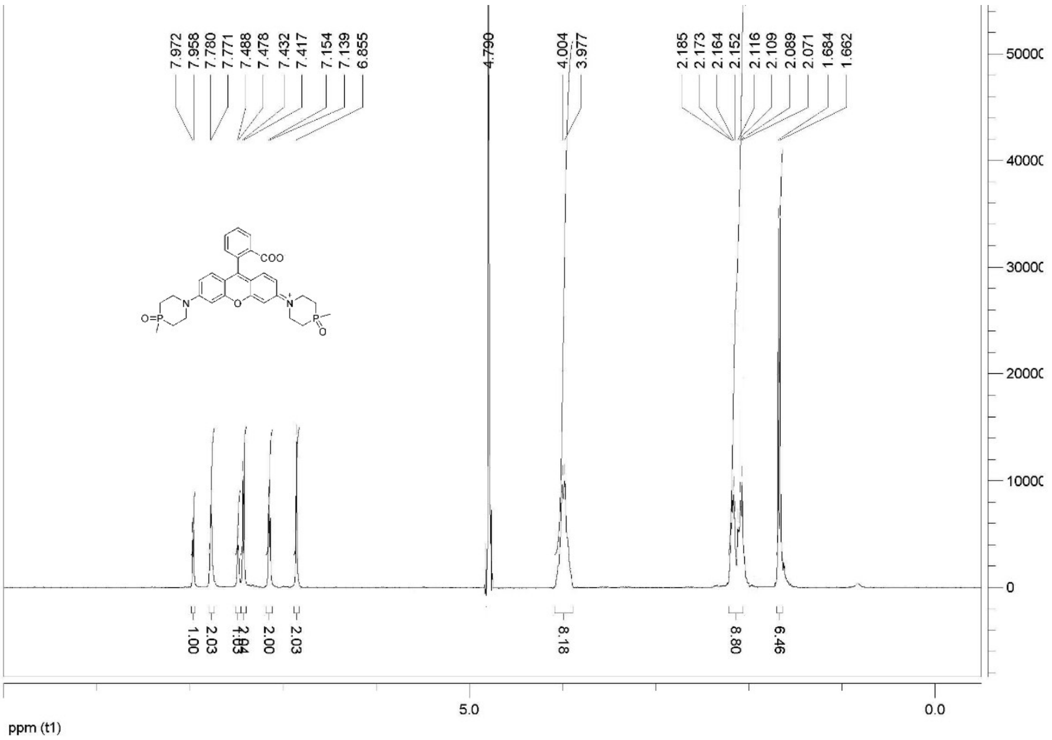
4 T. Wang, Q. Zhao, H. Hu, S. Yu, X. Liu, L. Liu, Q. Wu, Spirolactonized Si-rhodamine: a novel NIR fluorophore utilized as a platform to construct Si-rhodamine-based probes, Chem. Commun. 48 (2012) 8781–8783.

5 M. Grzybowski, M. Taki, K. Senda, Y. Sato, T. Ariyoshi, Y. Okada, R. Kawakami, T. Imamura, S. Yamaguchi, A highly photostable near-infrared labeling agent based on a phospha-rhodamine for long-term and deep imaging, Angew. Chem. Int. Ed. 57 (2018) 10137–10141.

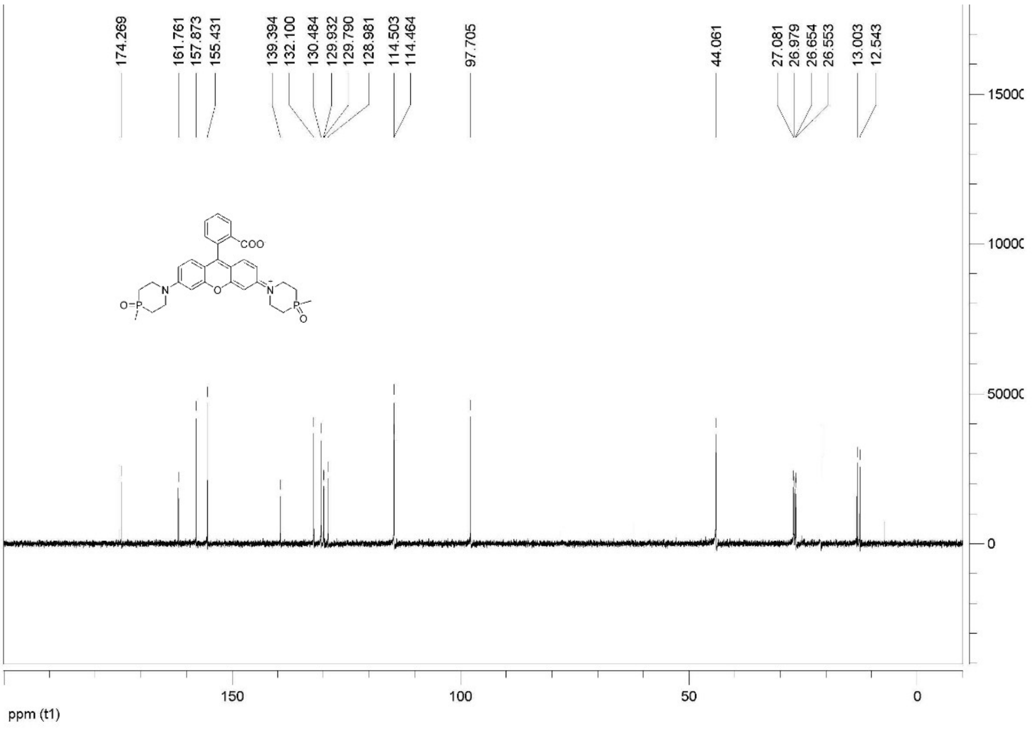
6 J. Kövér, S. Antus, Facile deoxygenation of hydroxylated flavonoids by palladium-catalysed reduction of its triflate derivatives, Z. Naturforsch., B: J. Chem. Sci. 60 (2005) 792–796.

7 Y. Wang, W.-S. Huang, S. Liu, W.C. Shakespeare, R.M. Thomas, J. Qi, F. Li, X. Zhu, A. Kohlmann, D.C. Dalgarno, J.C. Romero, D. Zou, Heterocyclic phosphine oxide derivatives as kinase inhibitors, US Patent 20140066406, 2014.

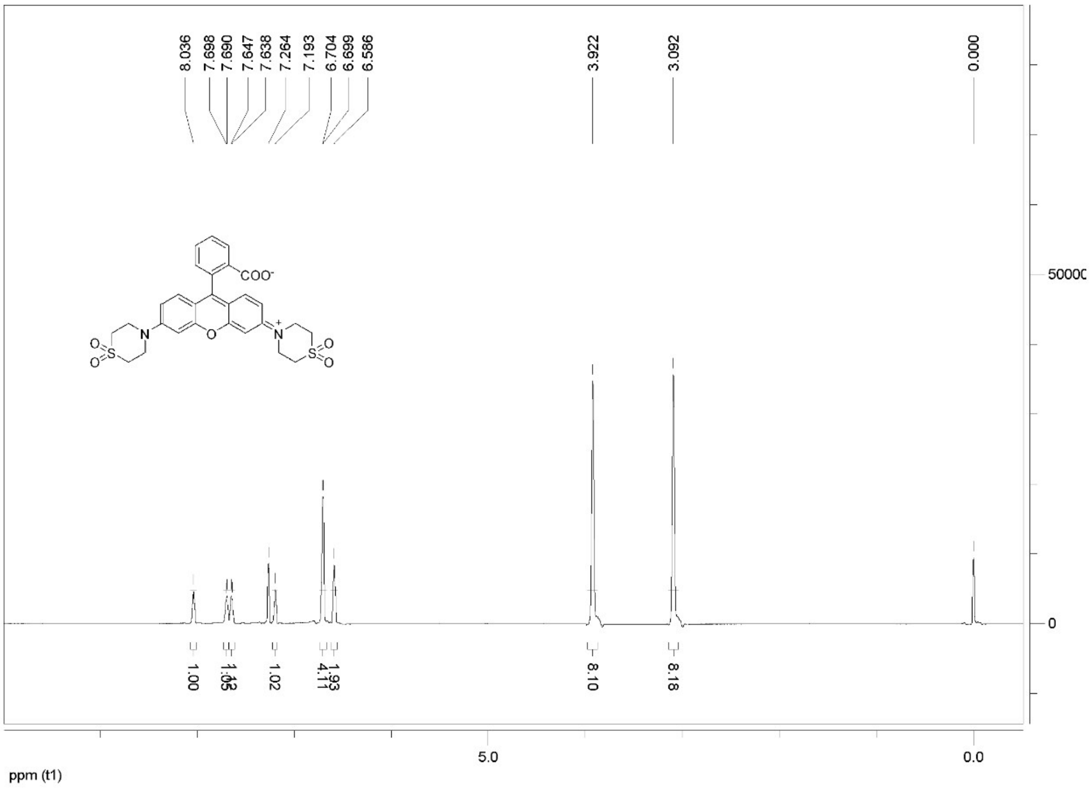
8. NMR spectra



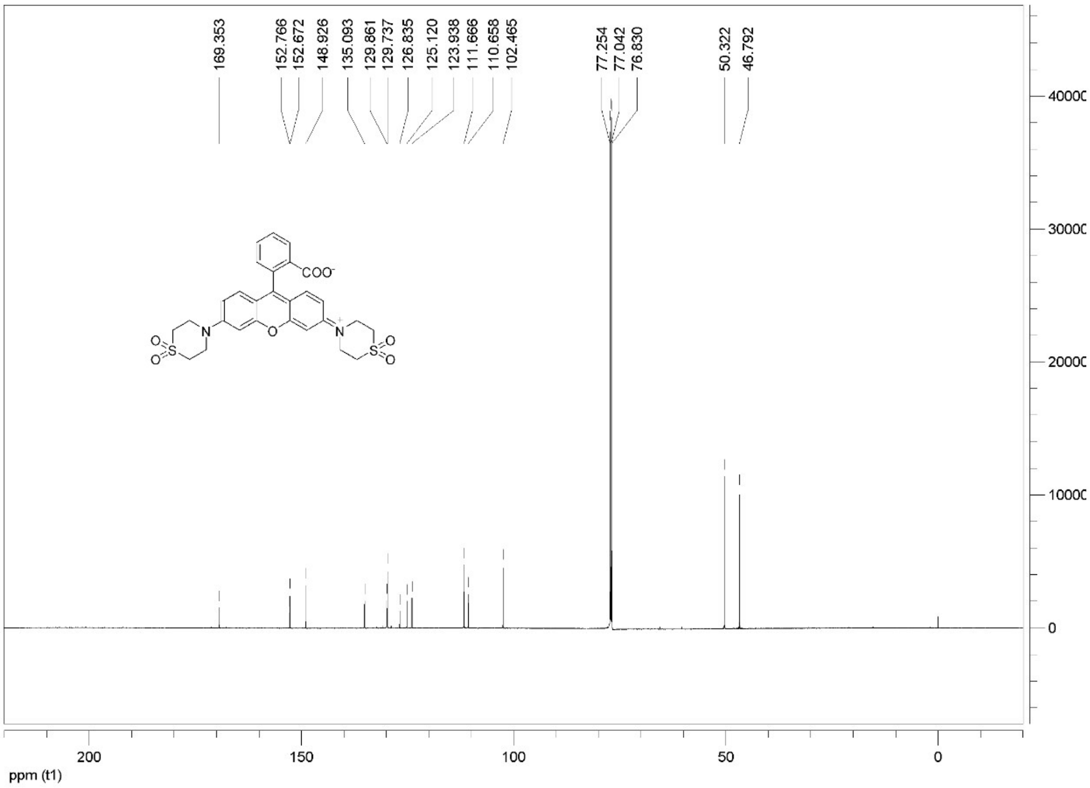
^{1}H NMR spectrum of **4**



^{13}C NMR spectrum of **4**



^{1}H NMR spectrum of **5**



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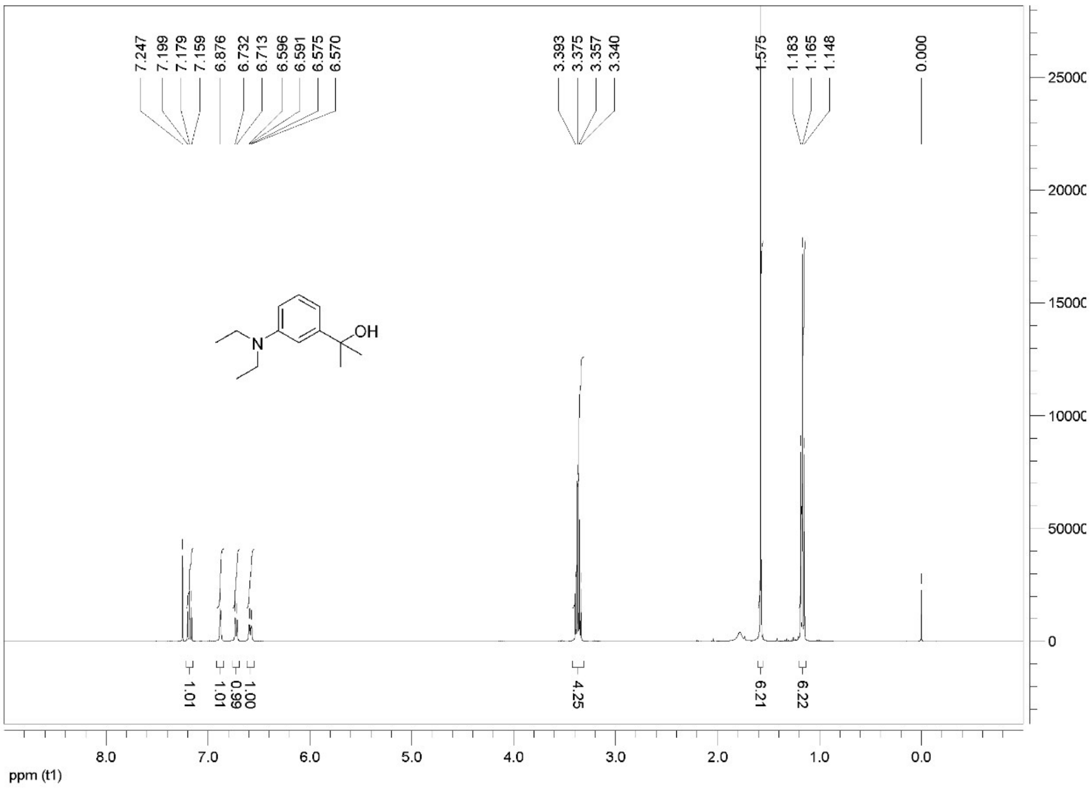
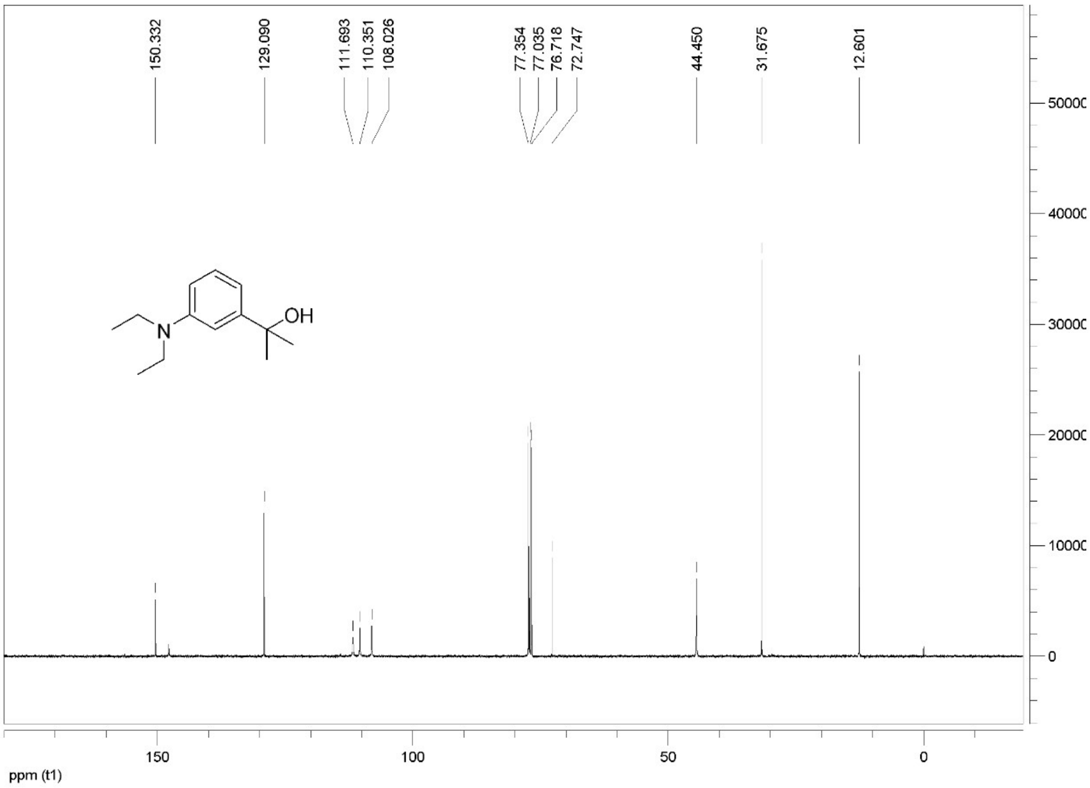
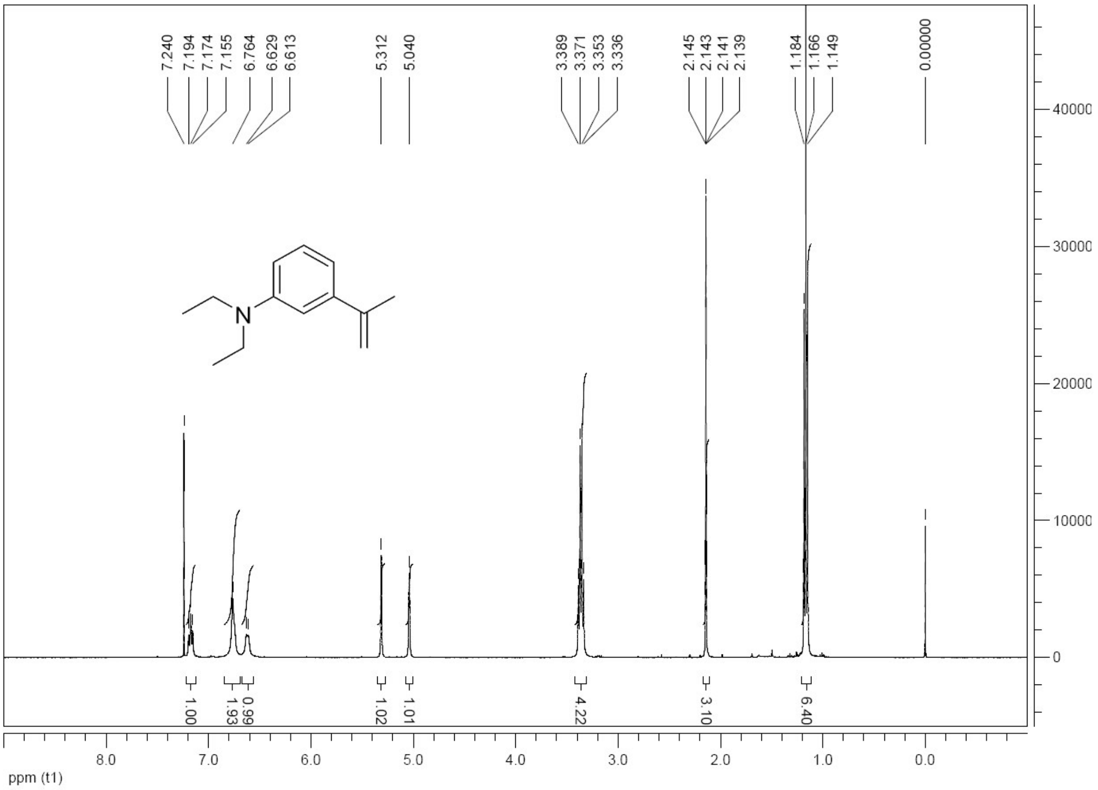


^{1}H NMR spectrum of **S3**



^{13}C NMR spectrum of **S3**



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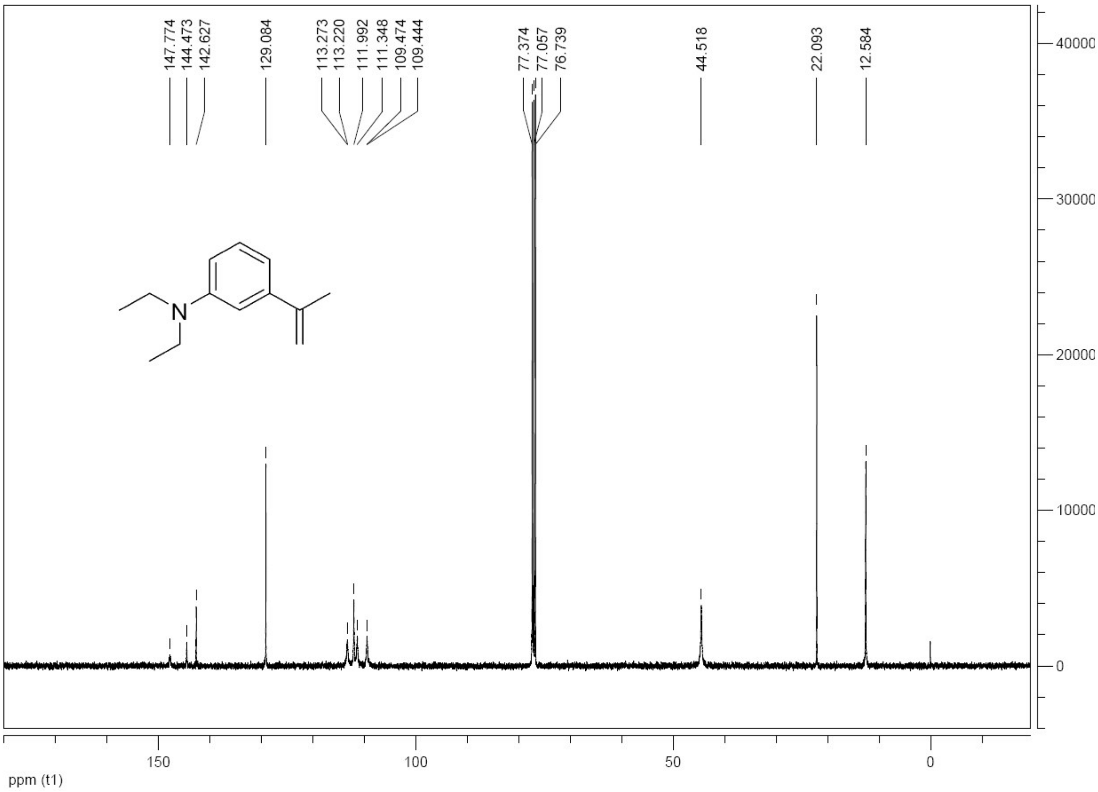
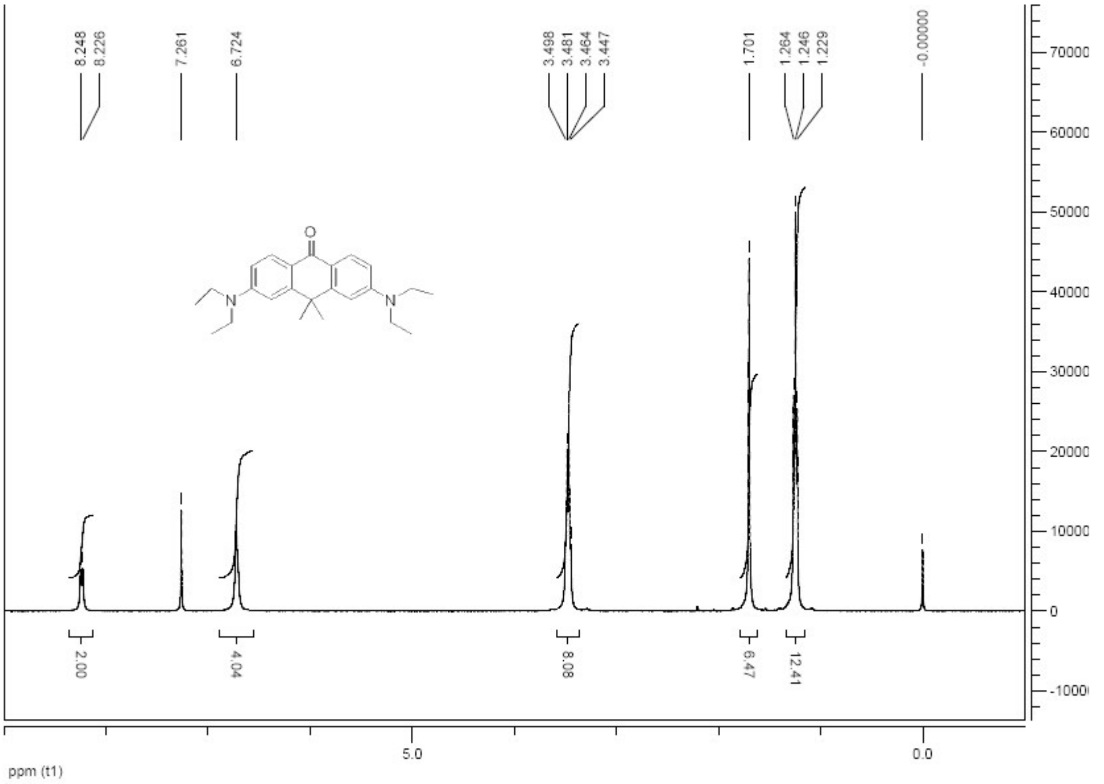
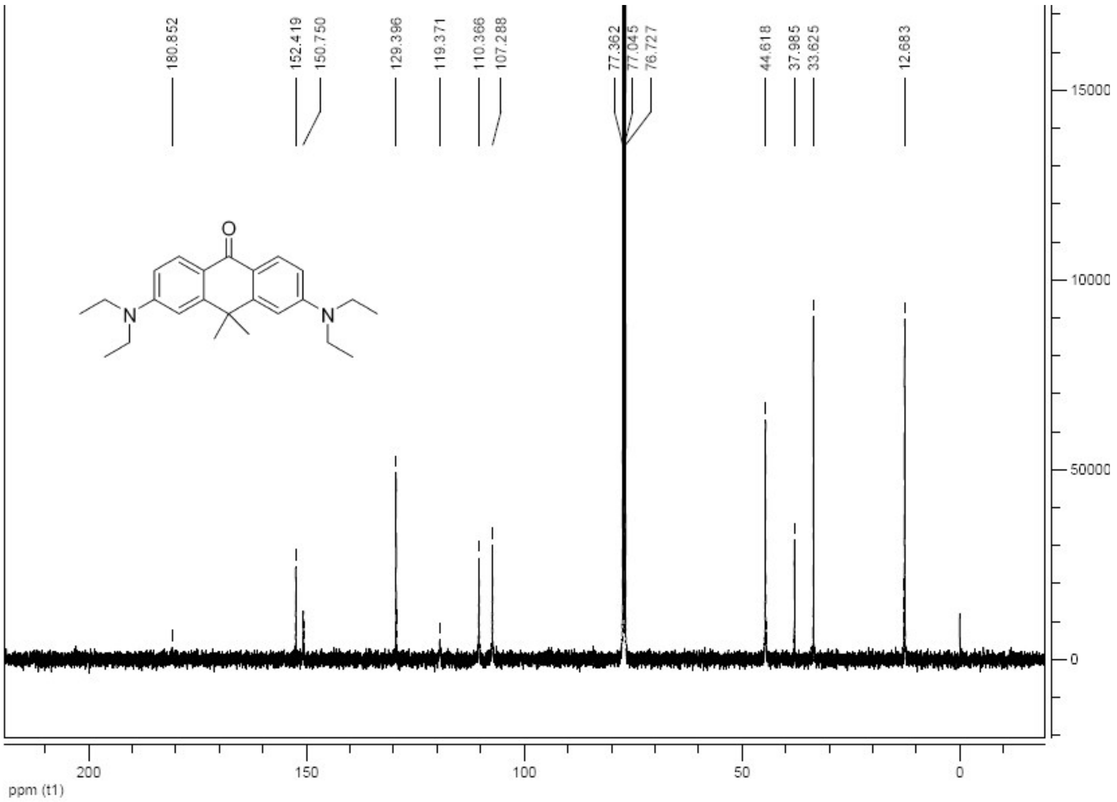


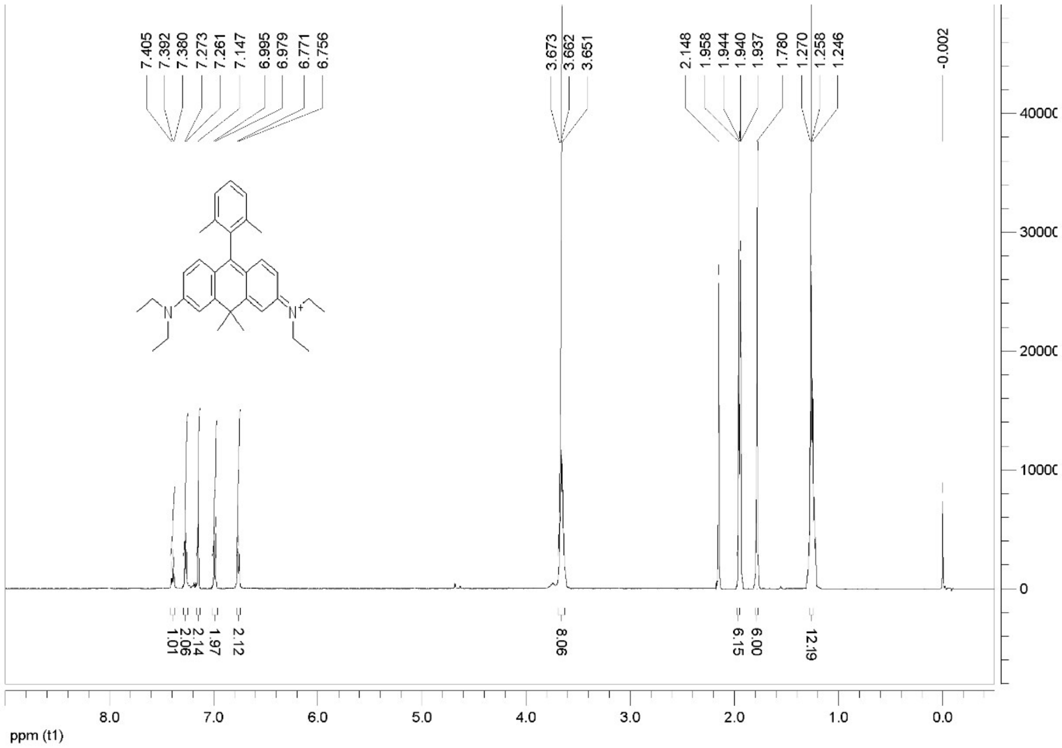
^{13}C NMR spectrum of **S4**



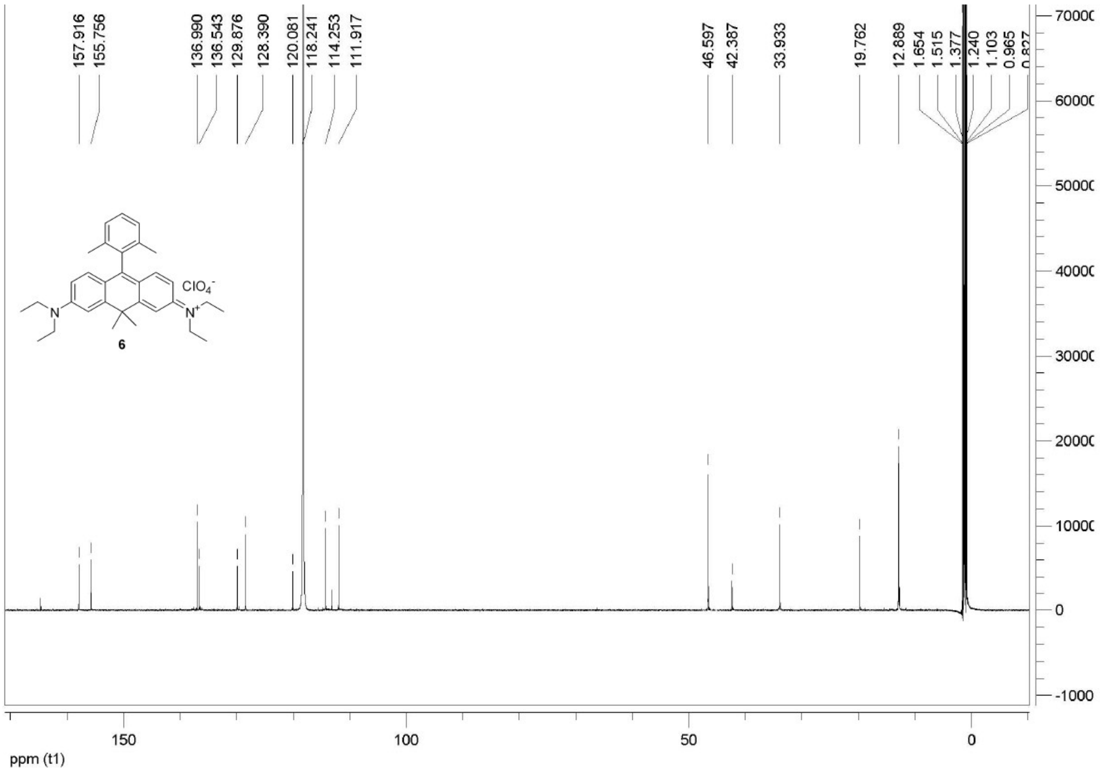
^{1}H NMR spectrum of **S5**



^{13}C NMR spectrum of **S5**



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



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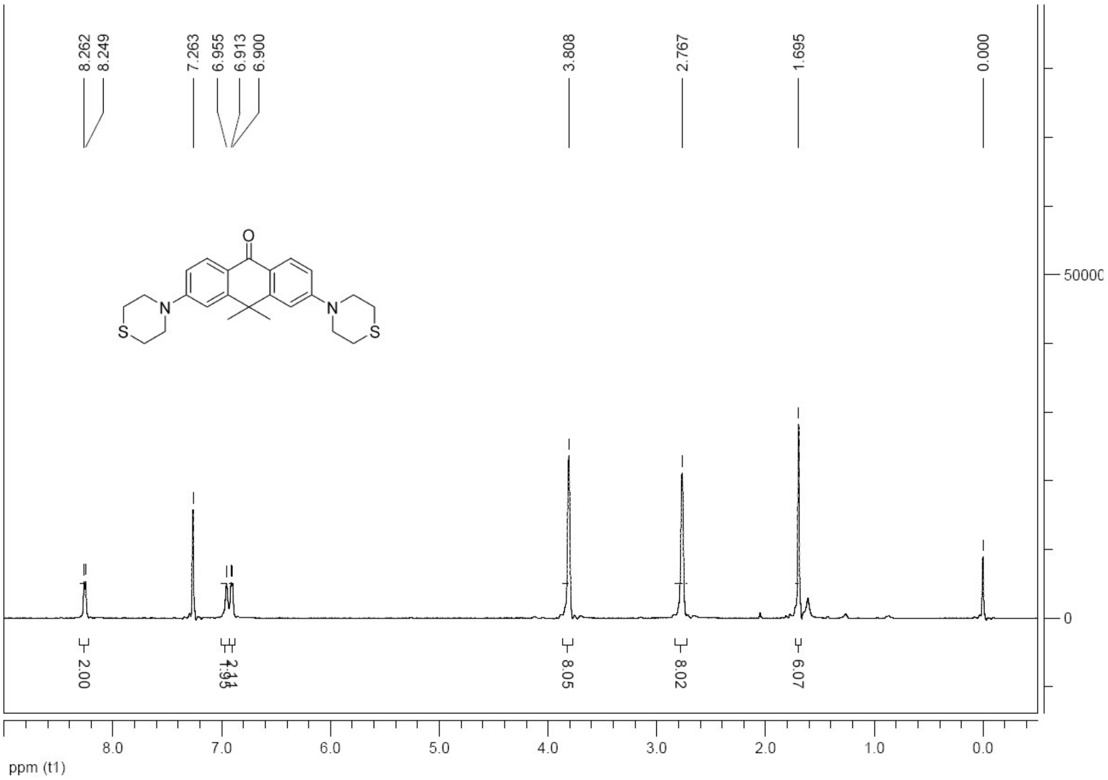
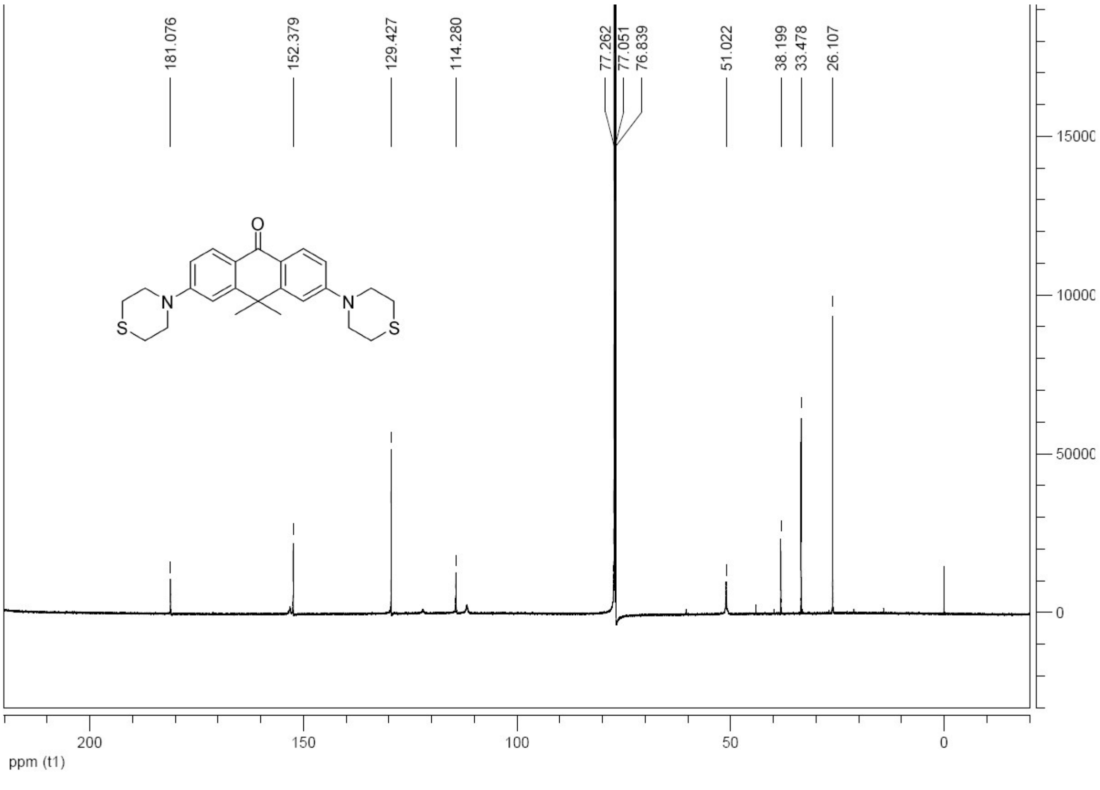
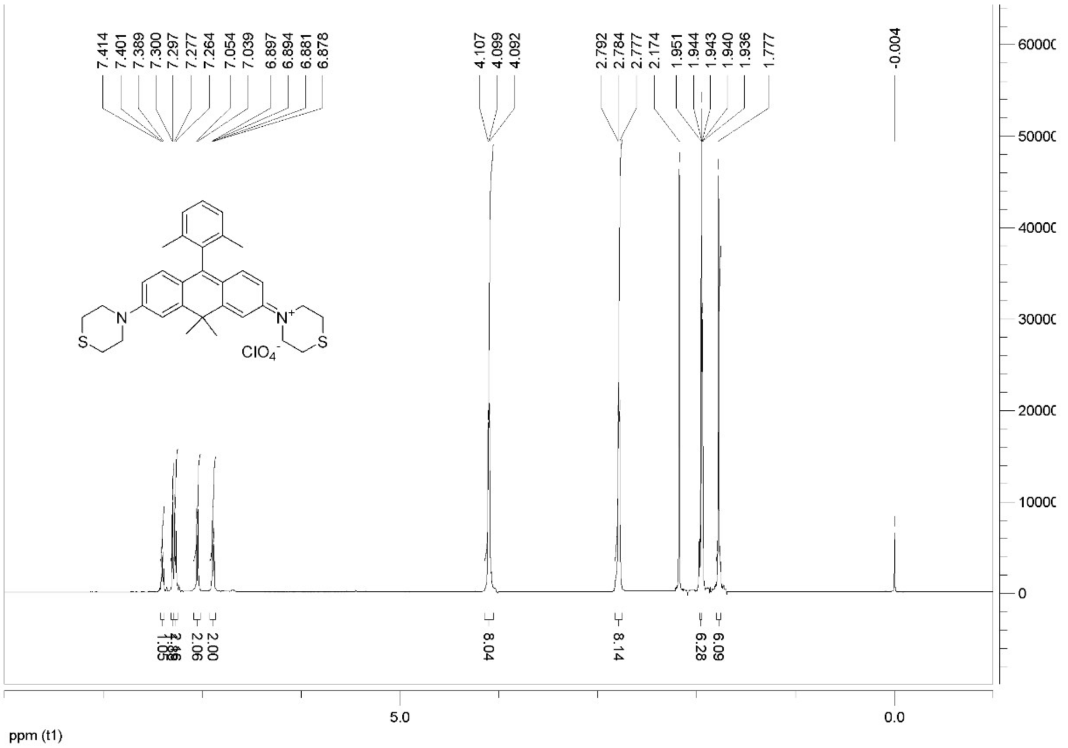


^{1}H NMR spectrum of **S7**



^{13}C NMR spectrum of **S7**



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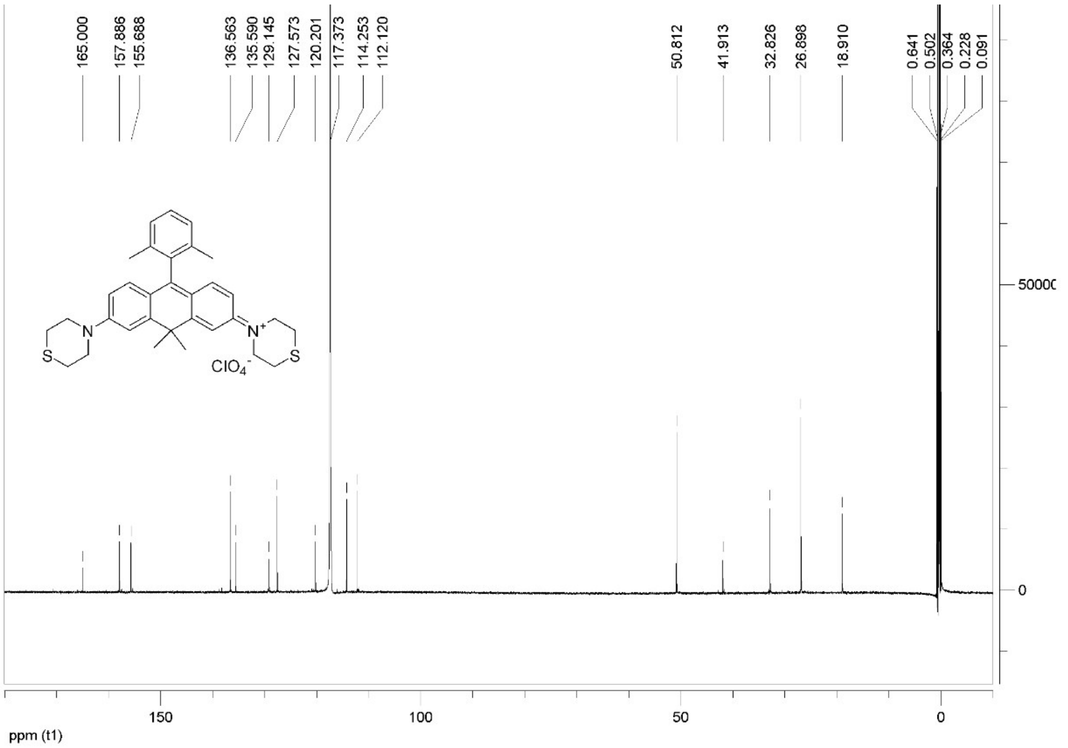
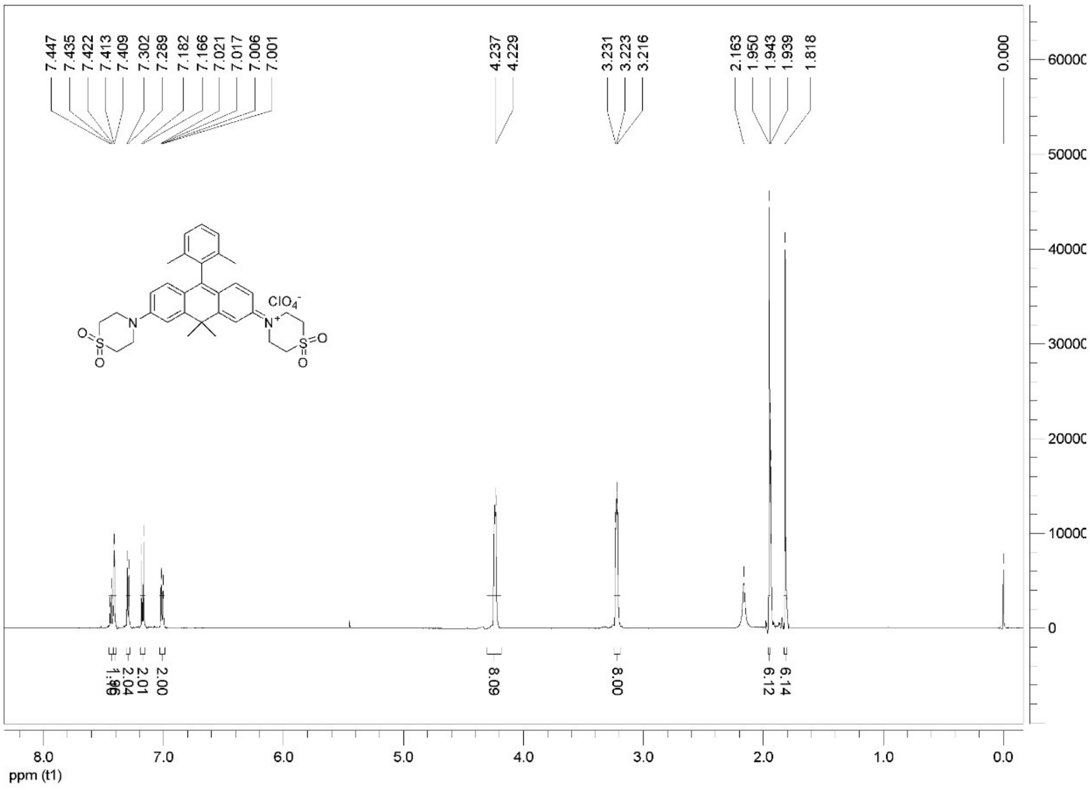
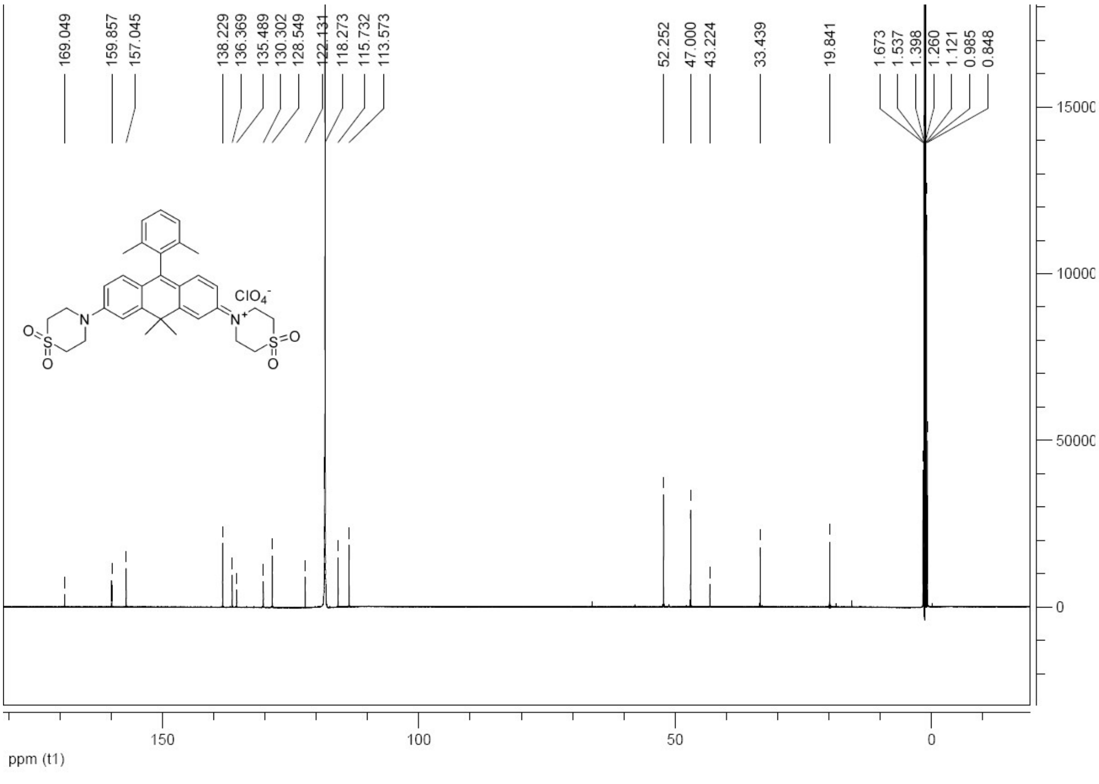


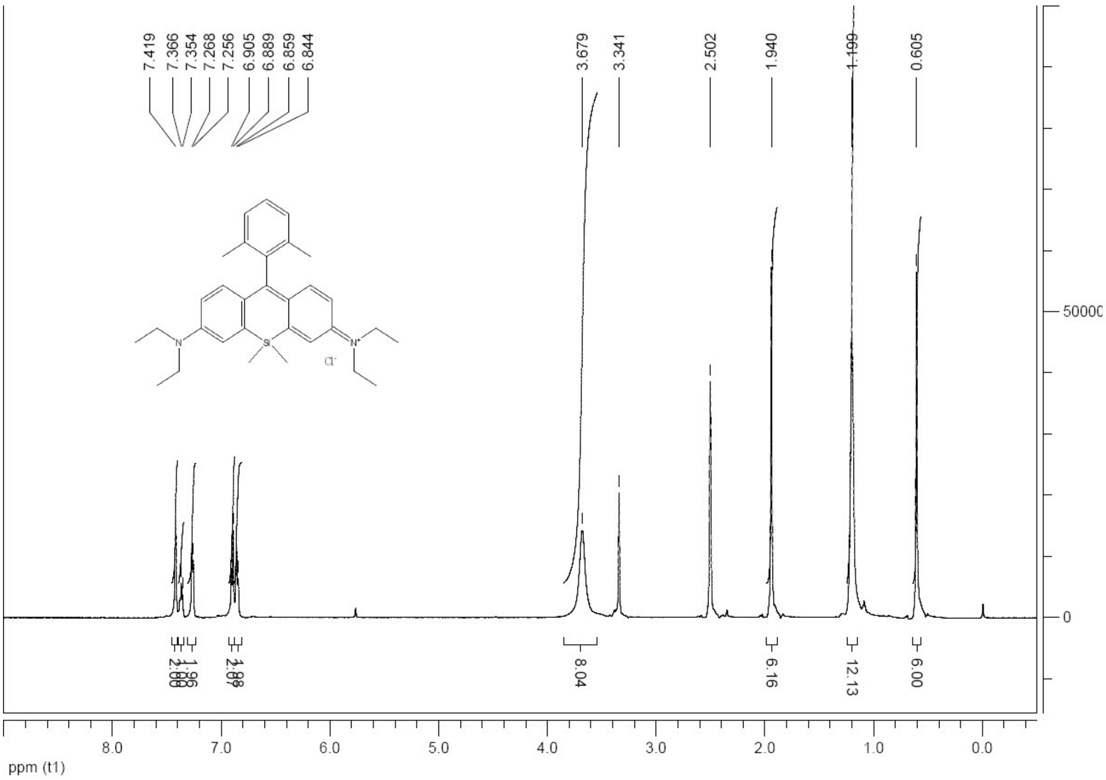
^{13}C NMR spectrum of **S8**



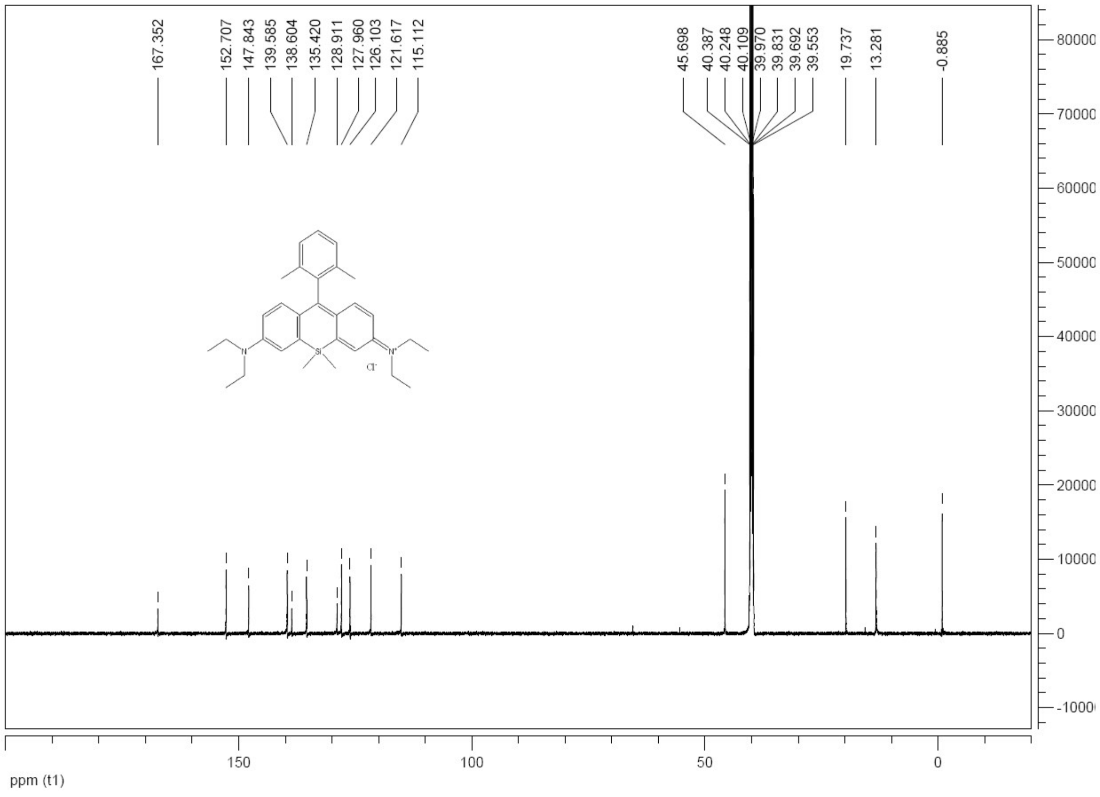
^{1}H NMR spectrum of **7**



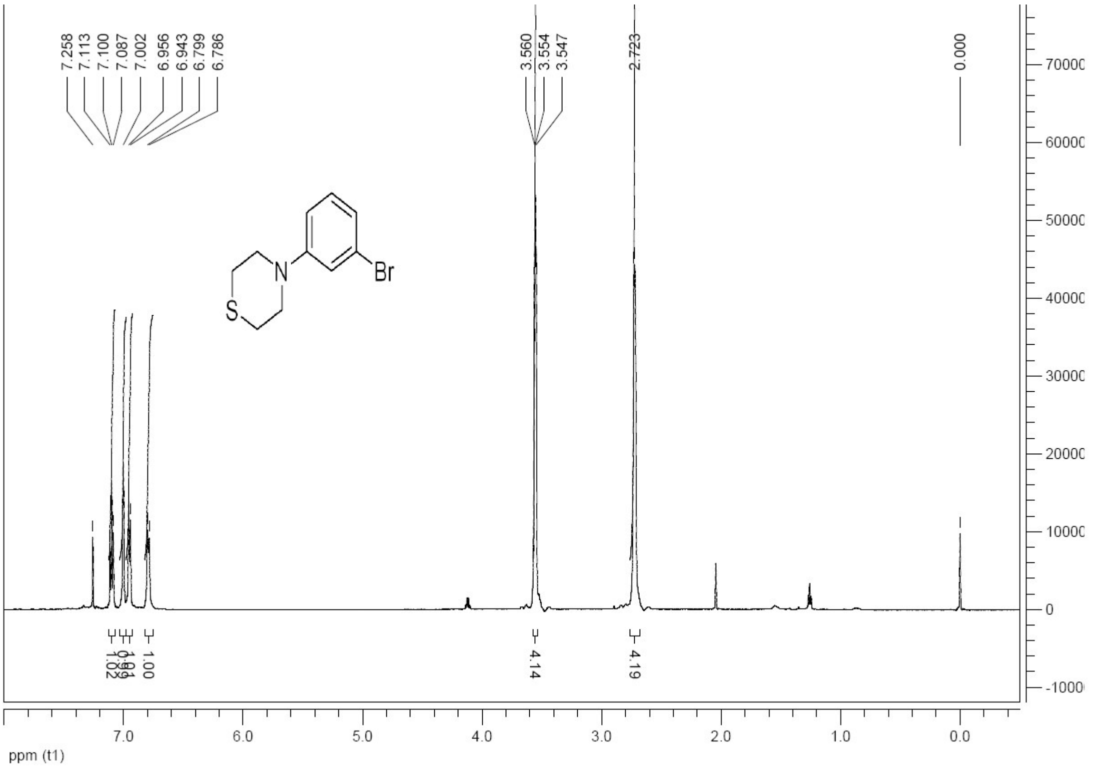
^{13}C NMR spectrum of **7**



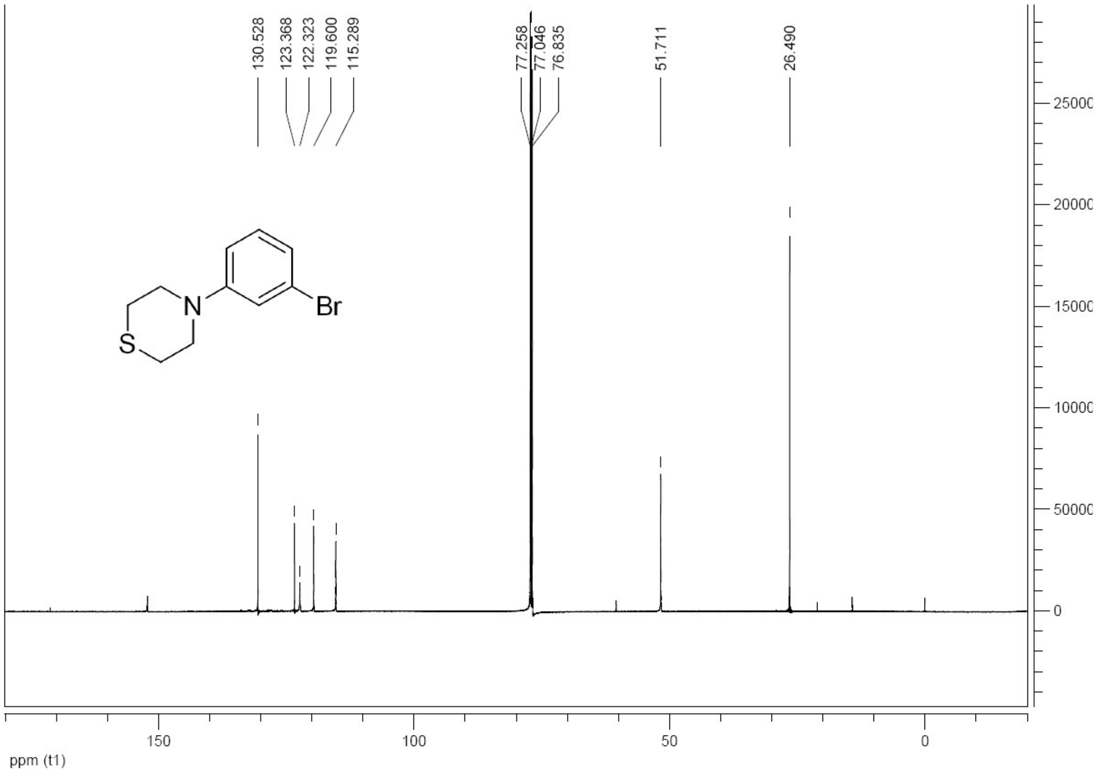
^{1}H NMR spectrum of **8**



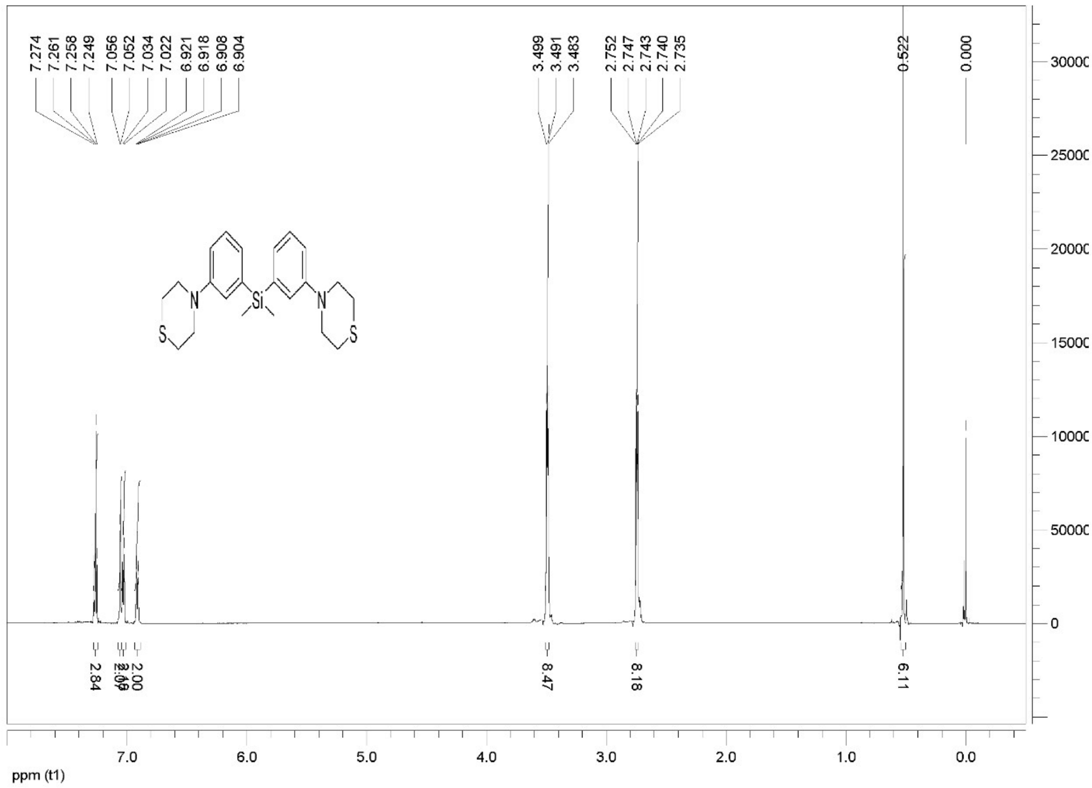
^{13}C NMR spectrum of **8**



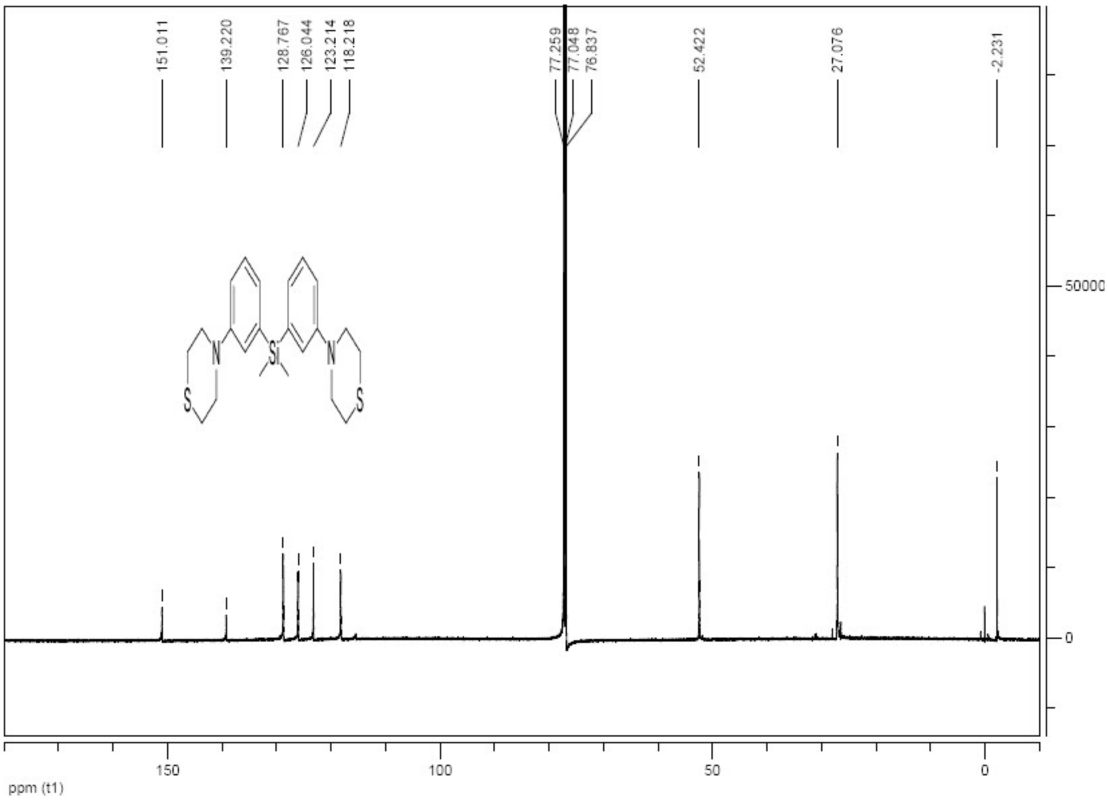
^{1}H NMR spectrum of **S10**



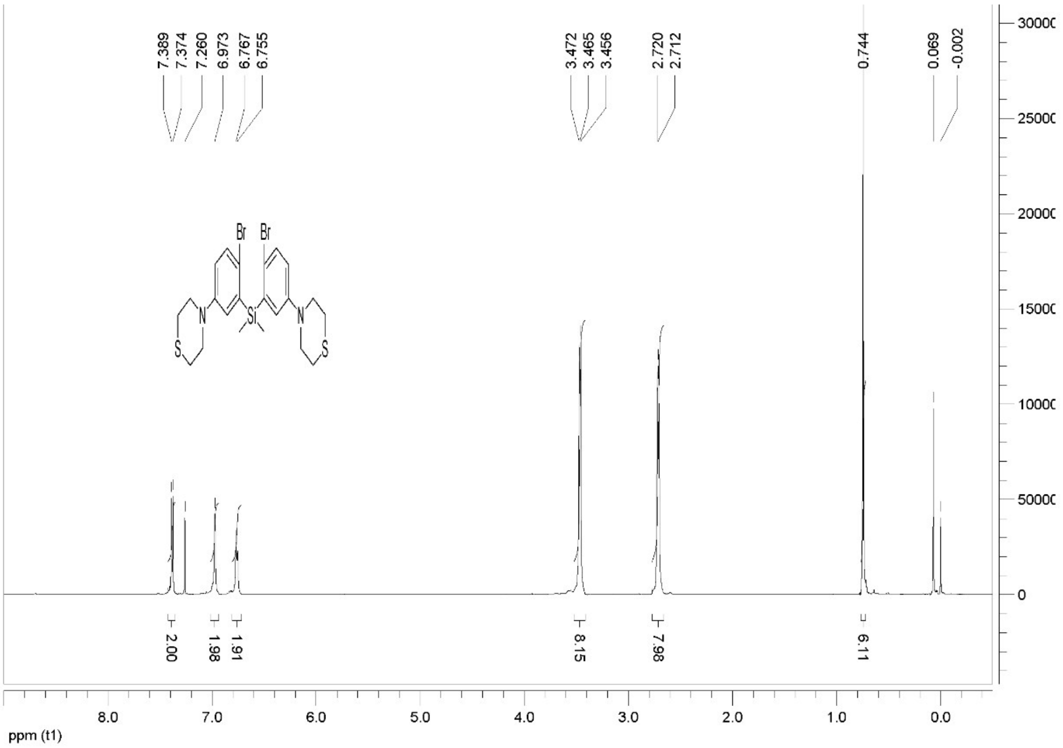
^{13}C NMR spectrum of **S10**



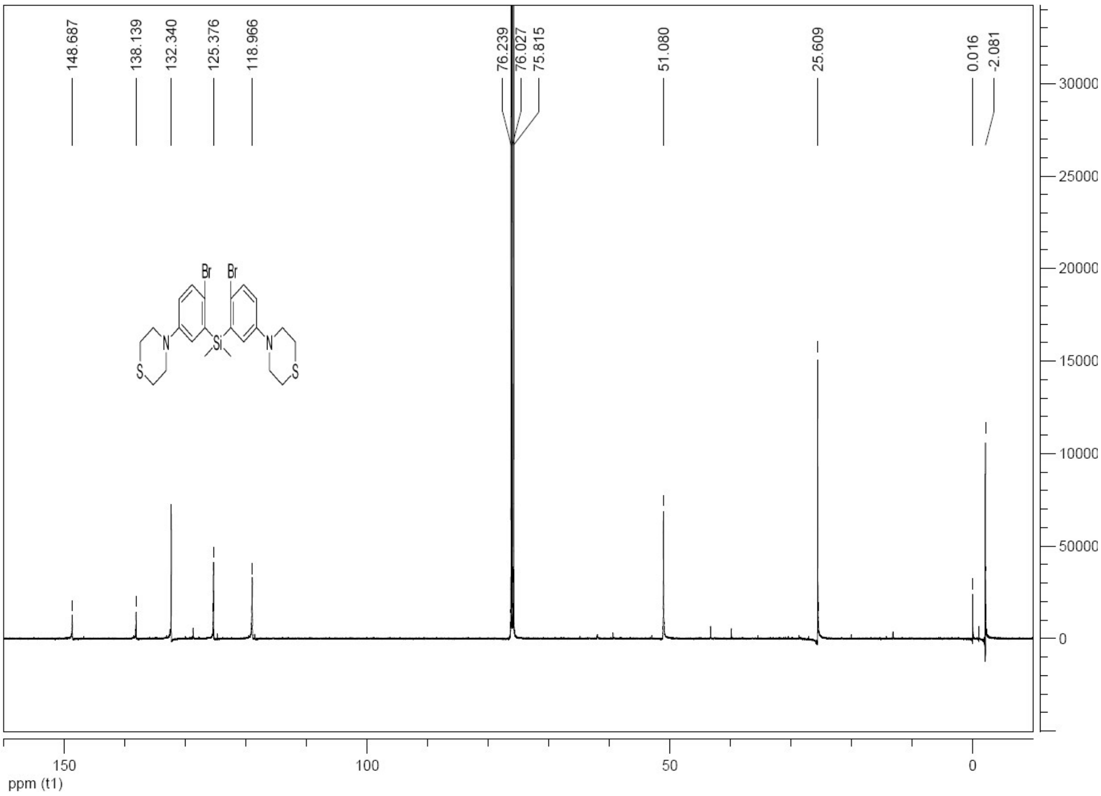
^{1}H NMR spectrum of **S11**



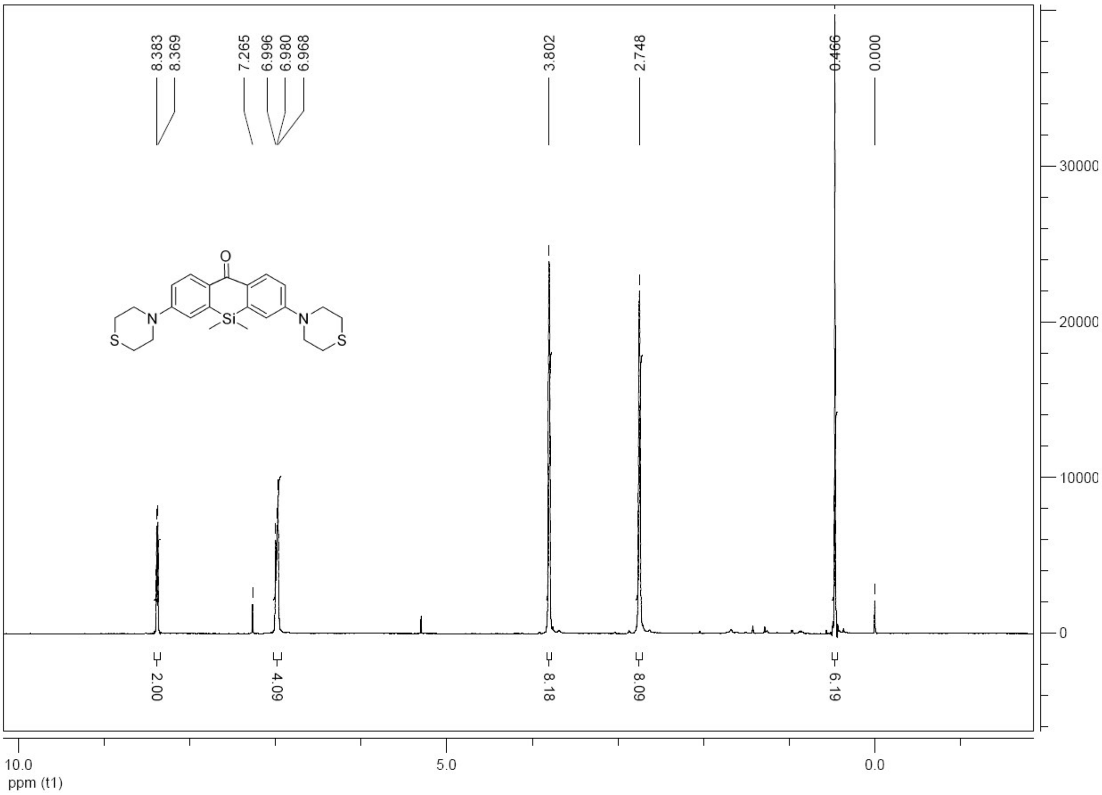
^{13}C NMR spectrum of **S11**



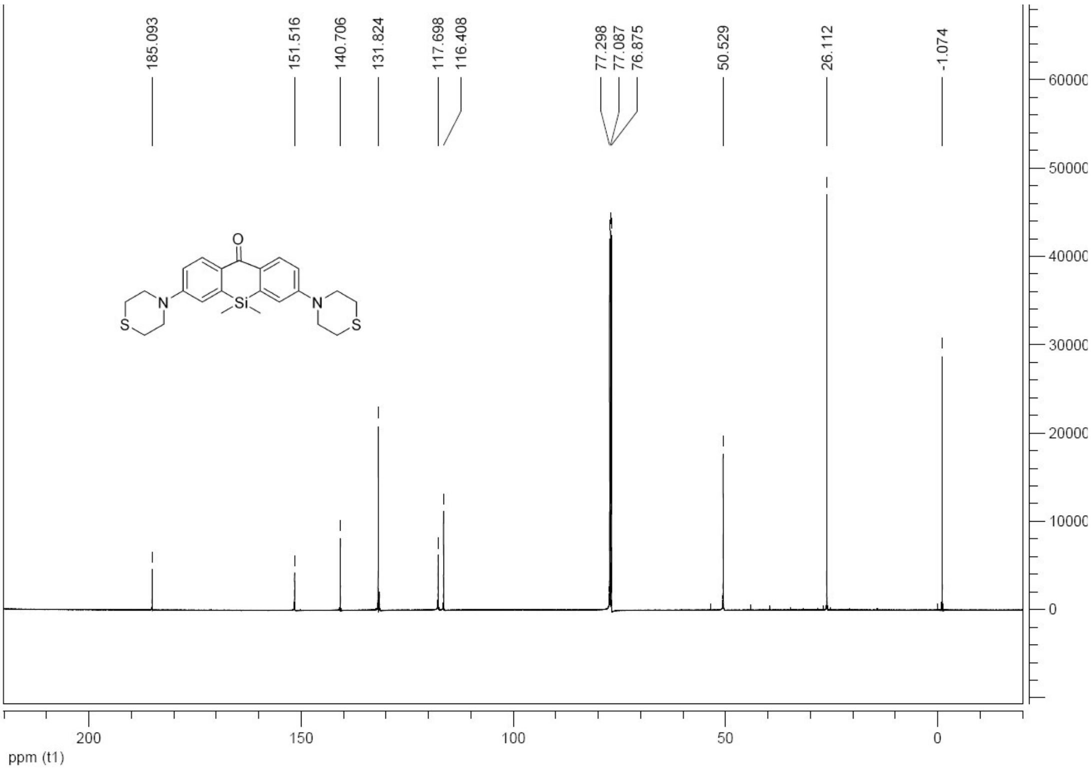
^{1}H NMR spectrum of **S12**



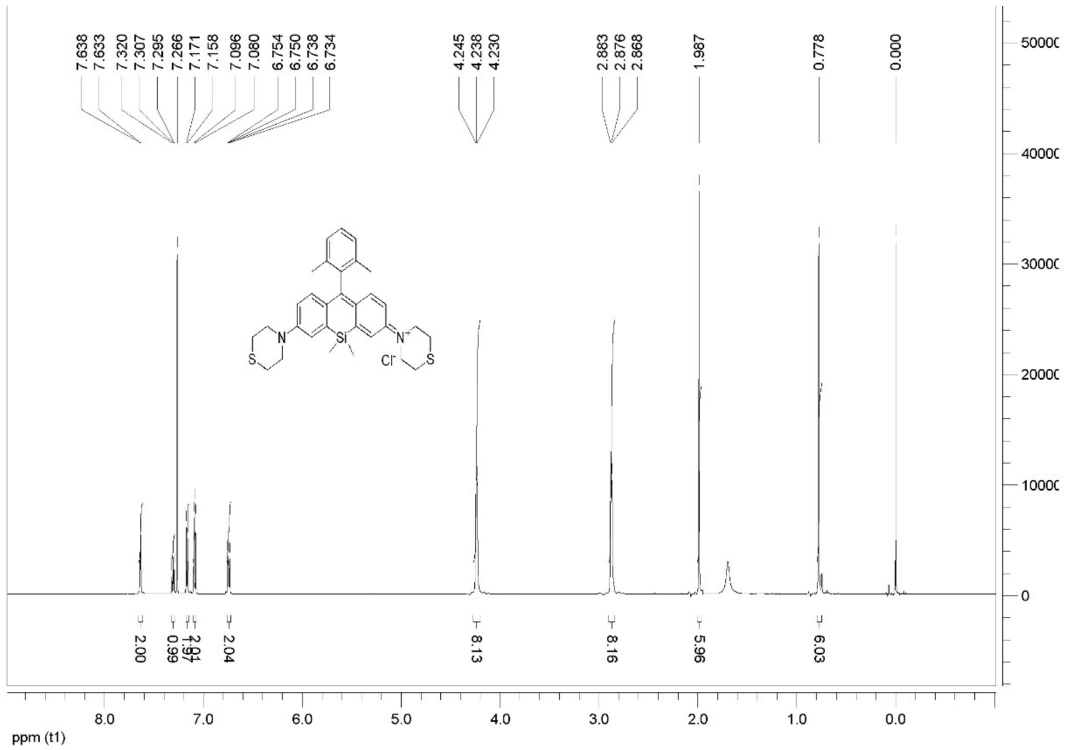
^{13}C NMR spectrum of **S12**



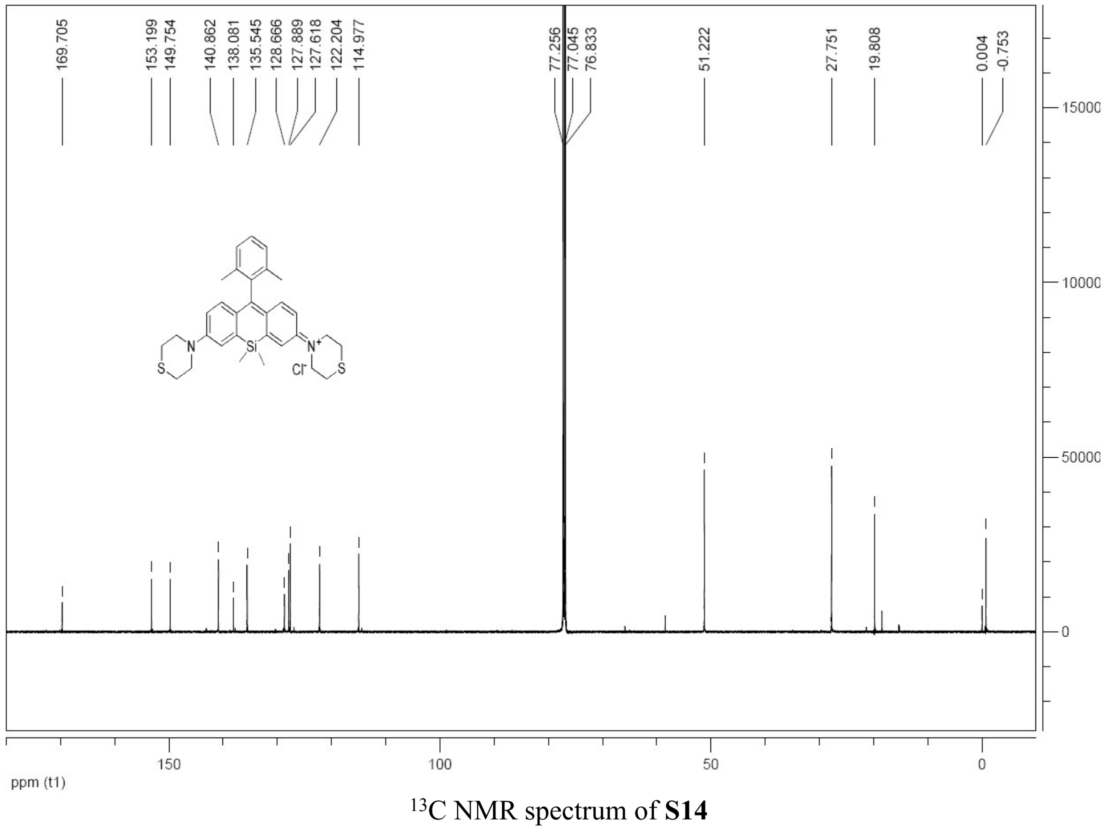
^{1}H NMR spectrum of **S13**



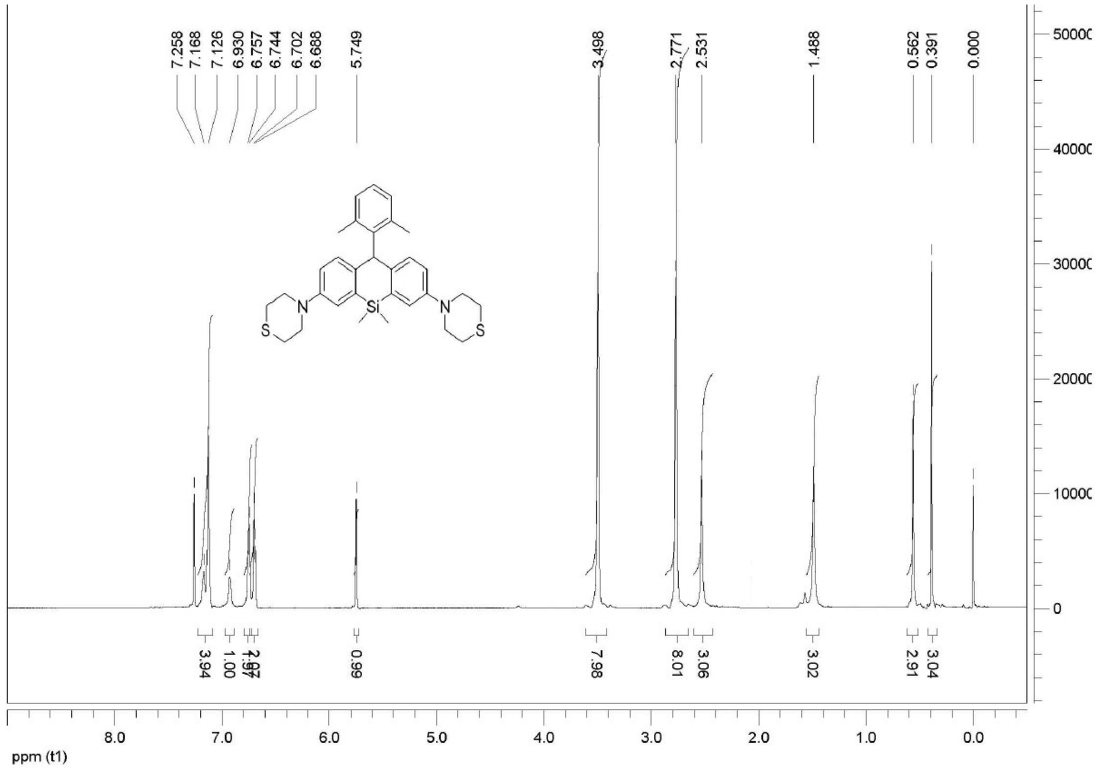
^{13}C NMR spectrum of **S13**



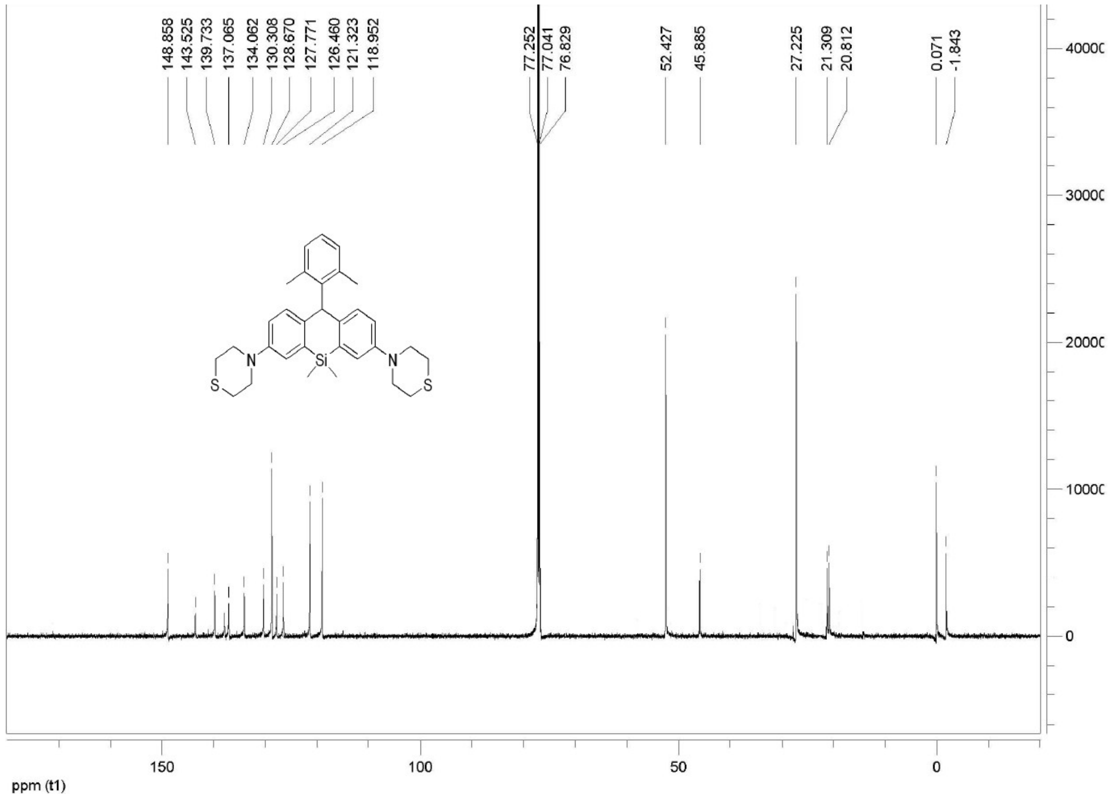
^{1}H NMR spectrum of **S14**



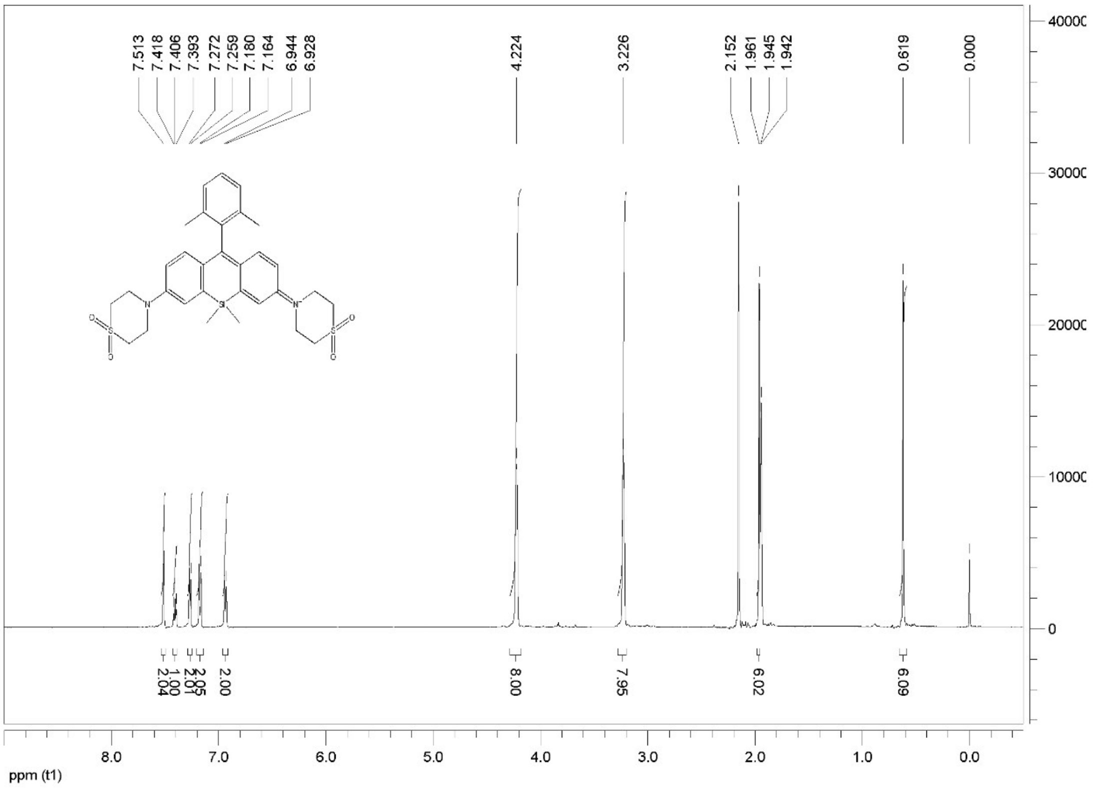
^{13}C NMR spectrum of **S14**



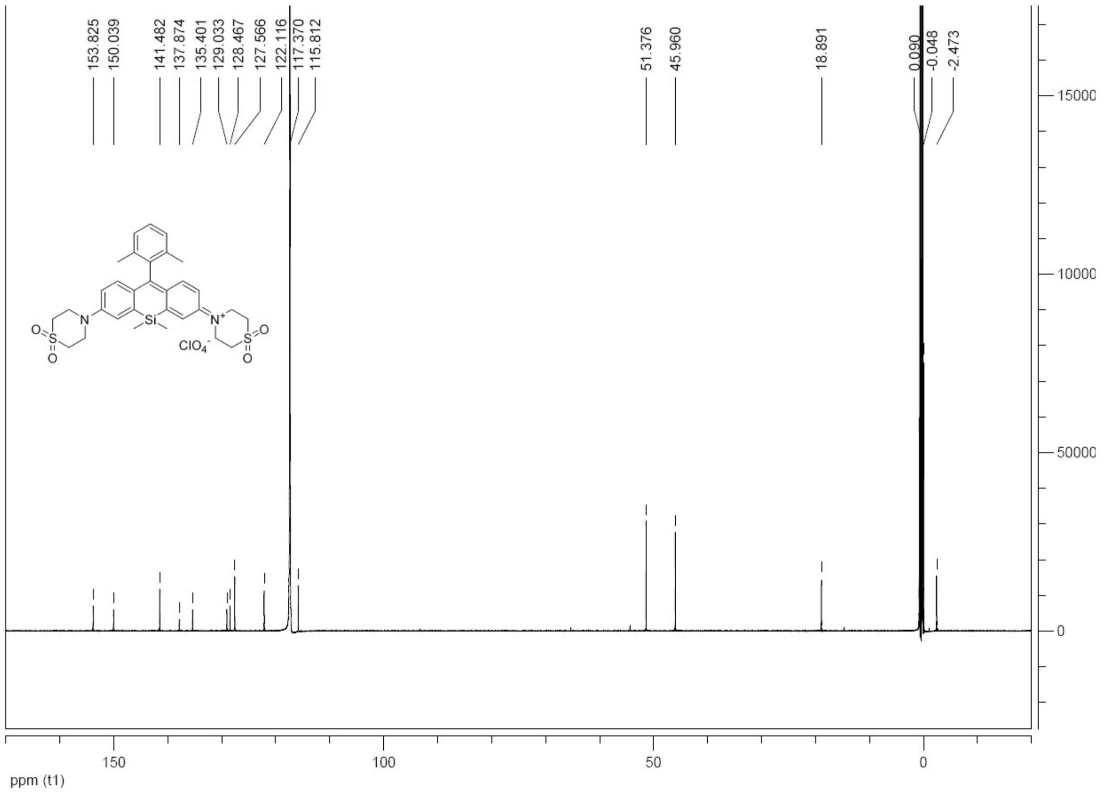
^{1}H NMR spectrum of **S15**



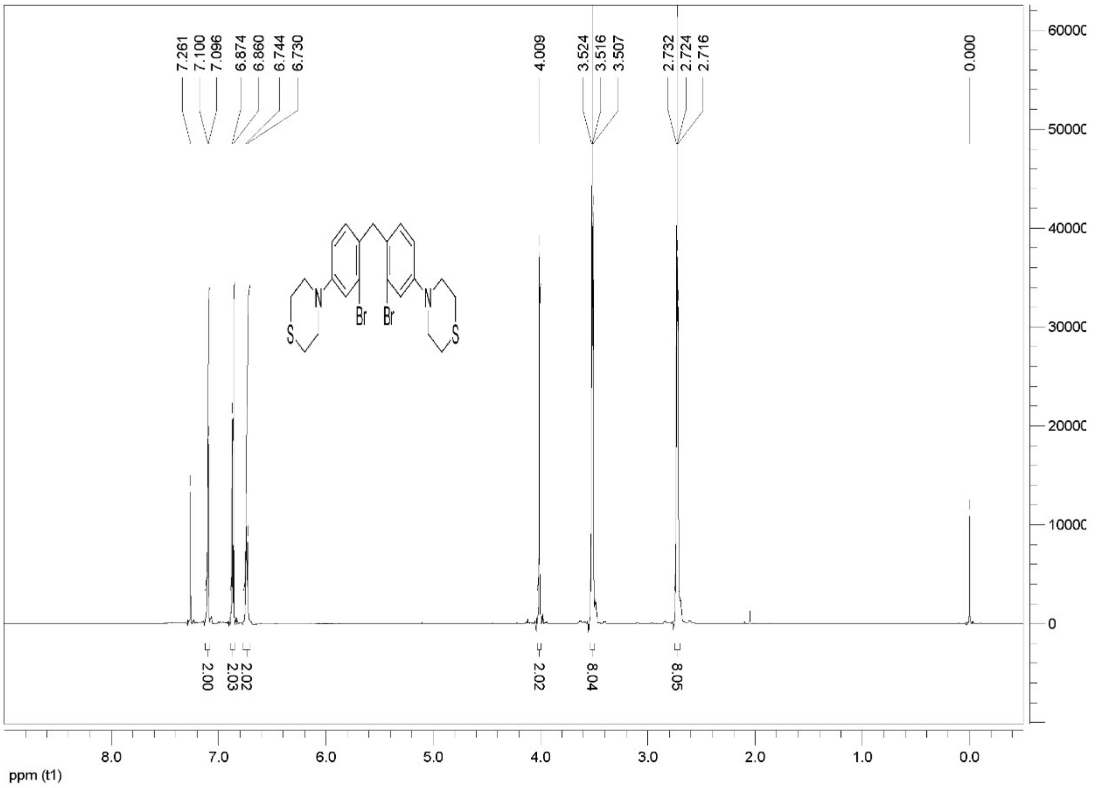
^{13}C NMR spectrum of **S15**



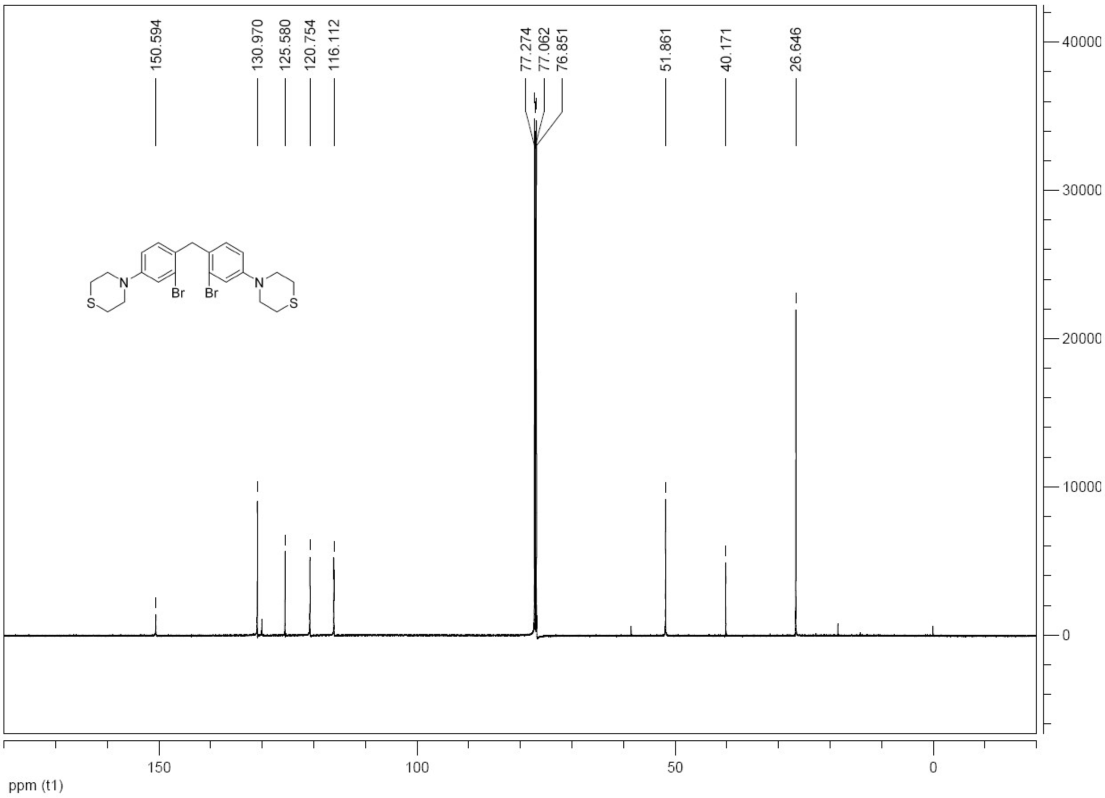
^{1}H NMR spectrum of **9**



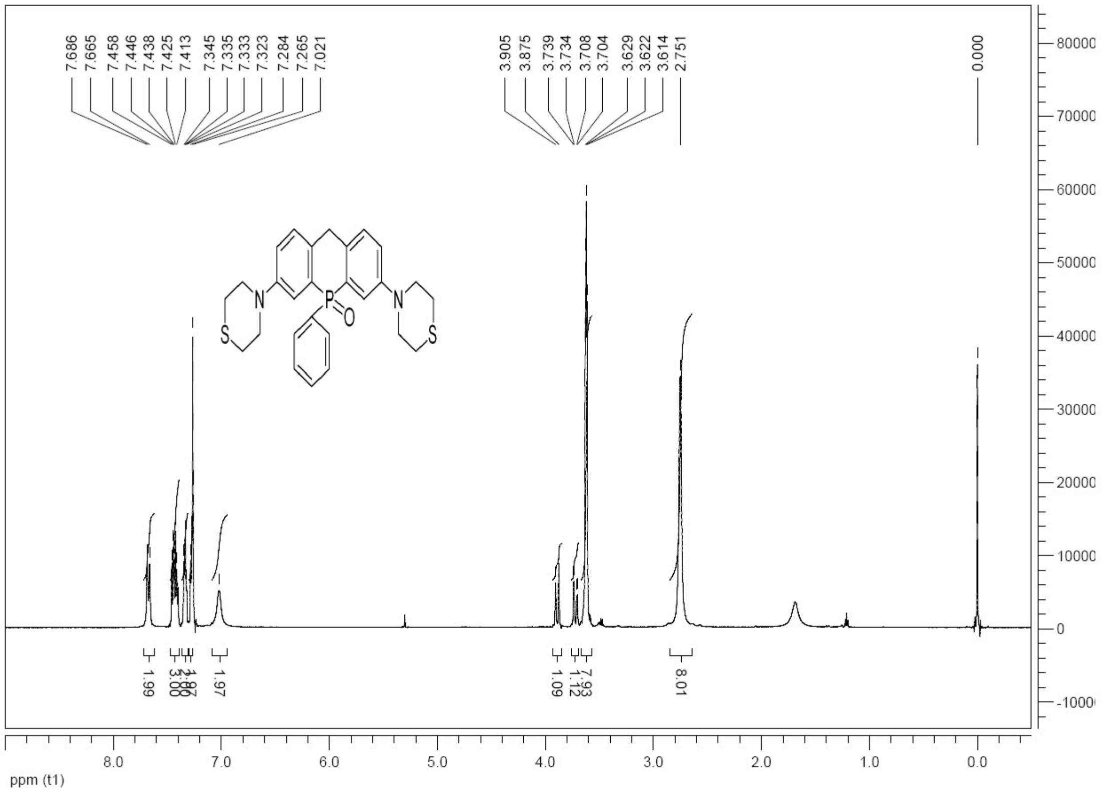
^{13}C NMR spectrum of **9**



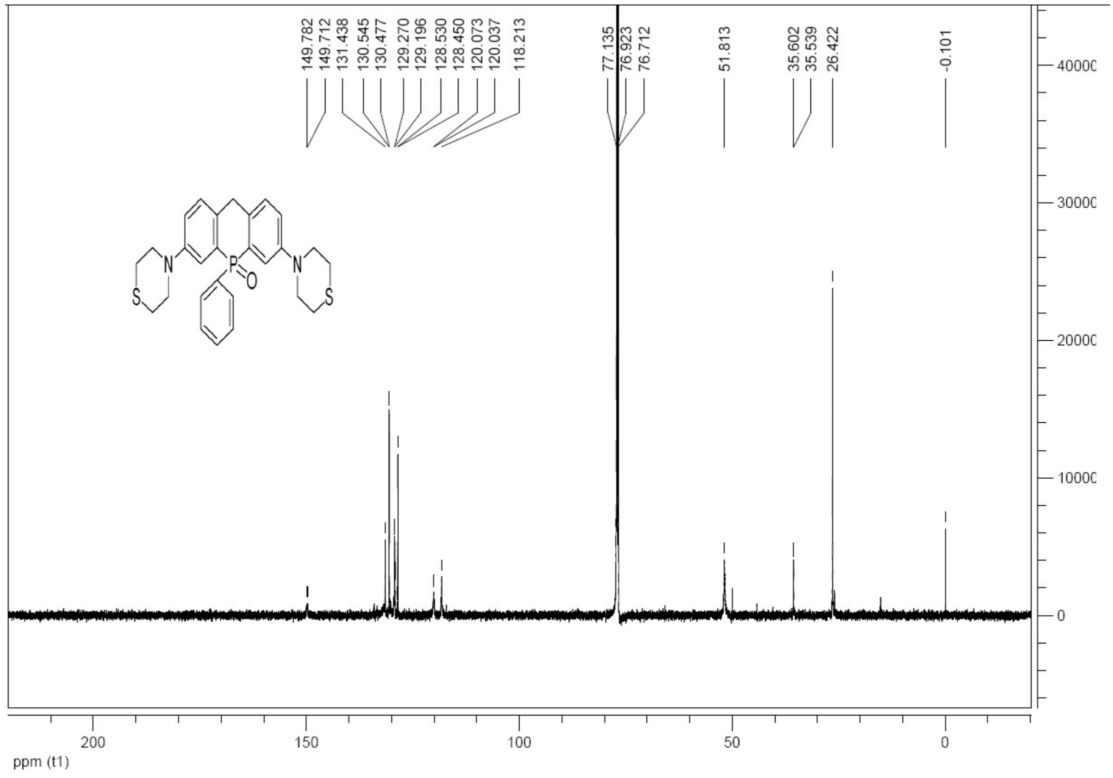
^{1}H NMR spectrum of **S16**



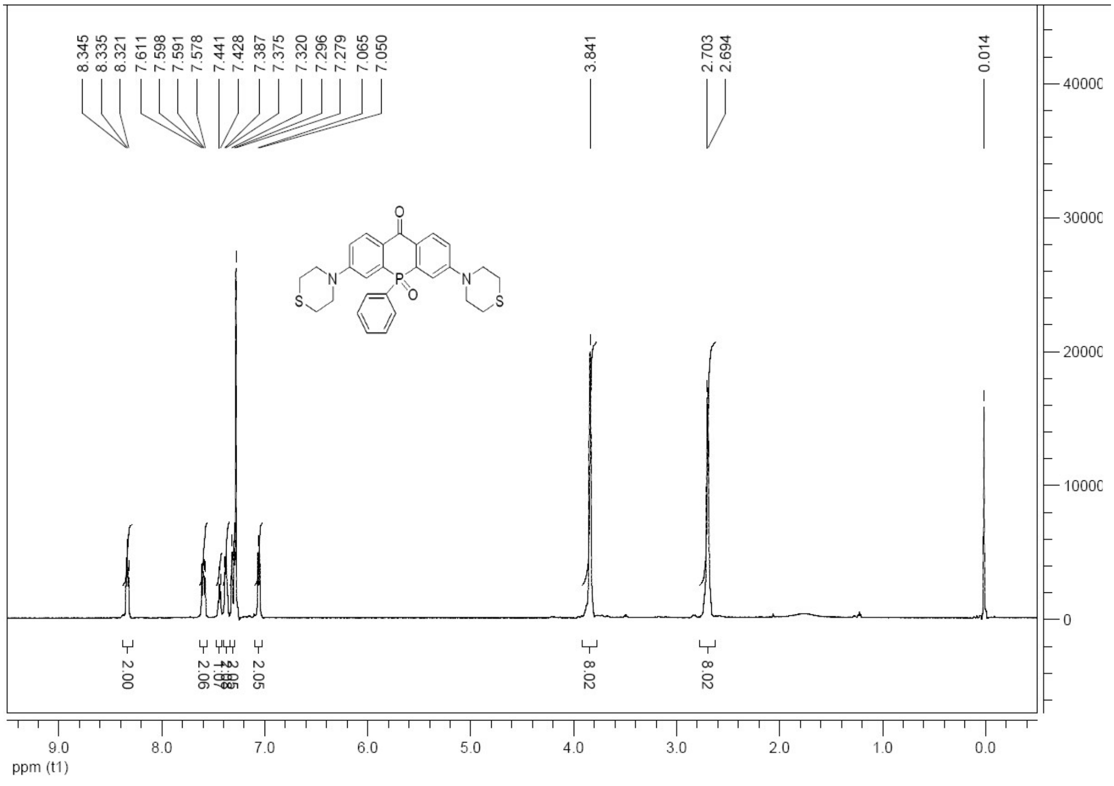
^{13}C NMR spectrum of **S16**



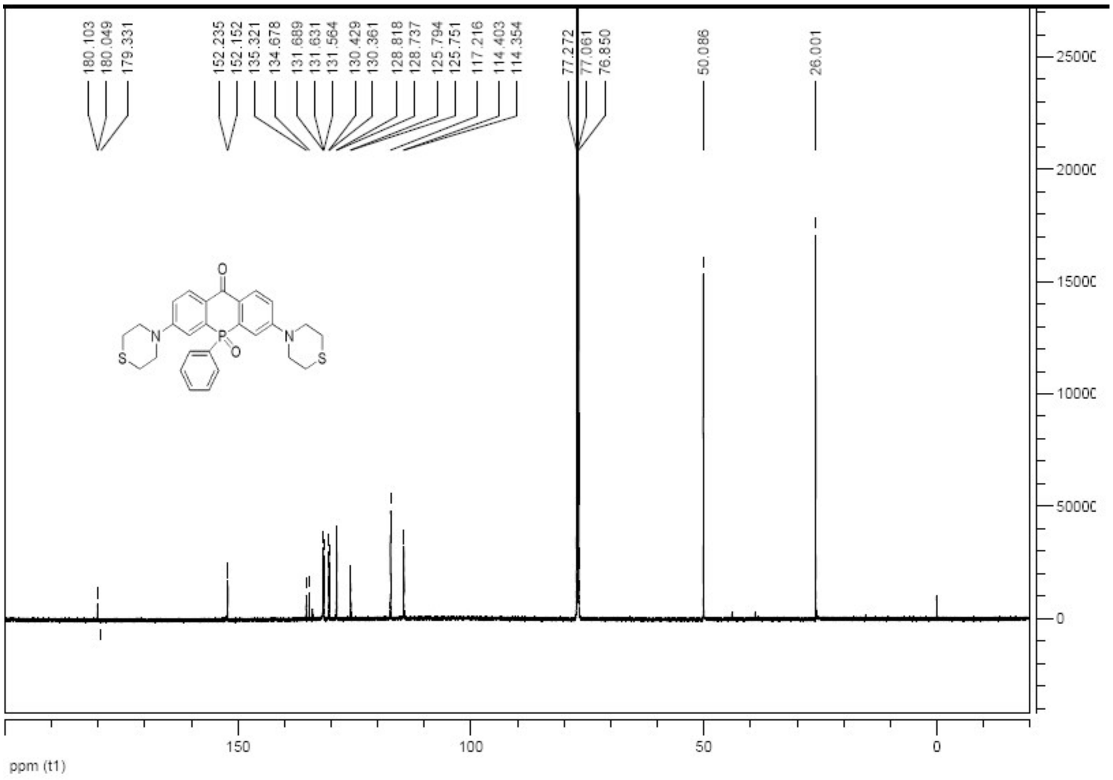
^{1}H NMR spectrum of **S17**



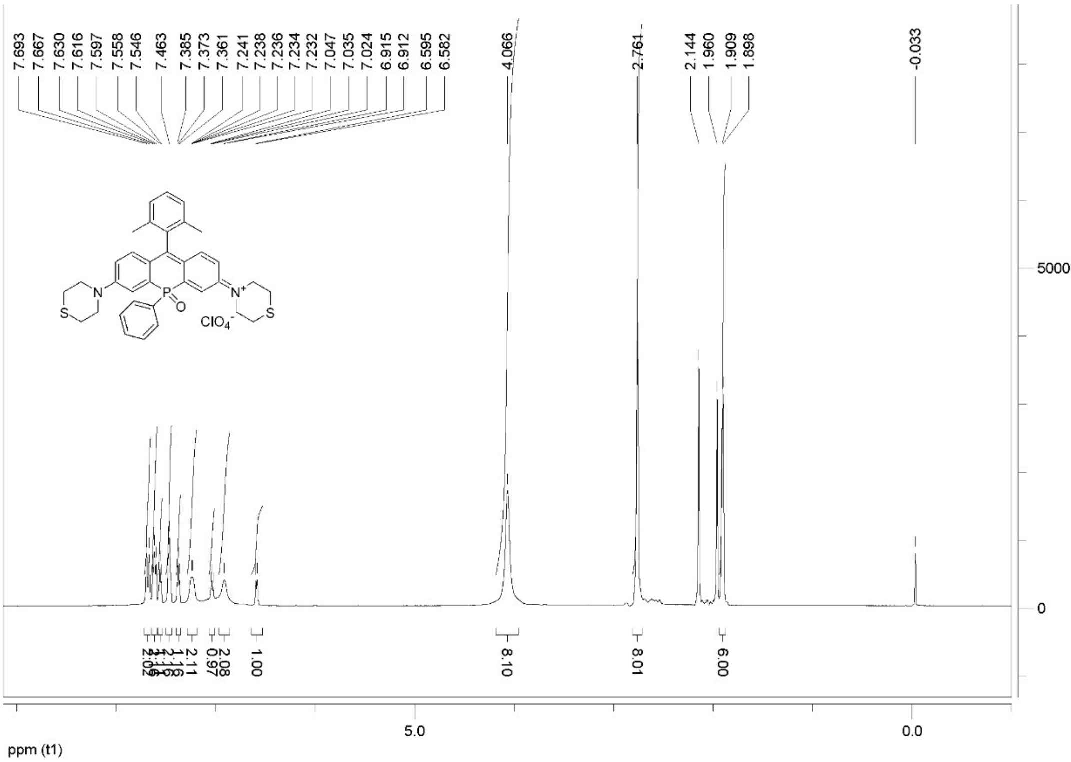
^{13}C NMR spectrum of **S17**



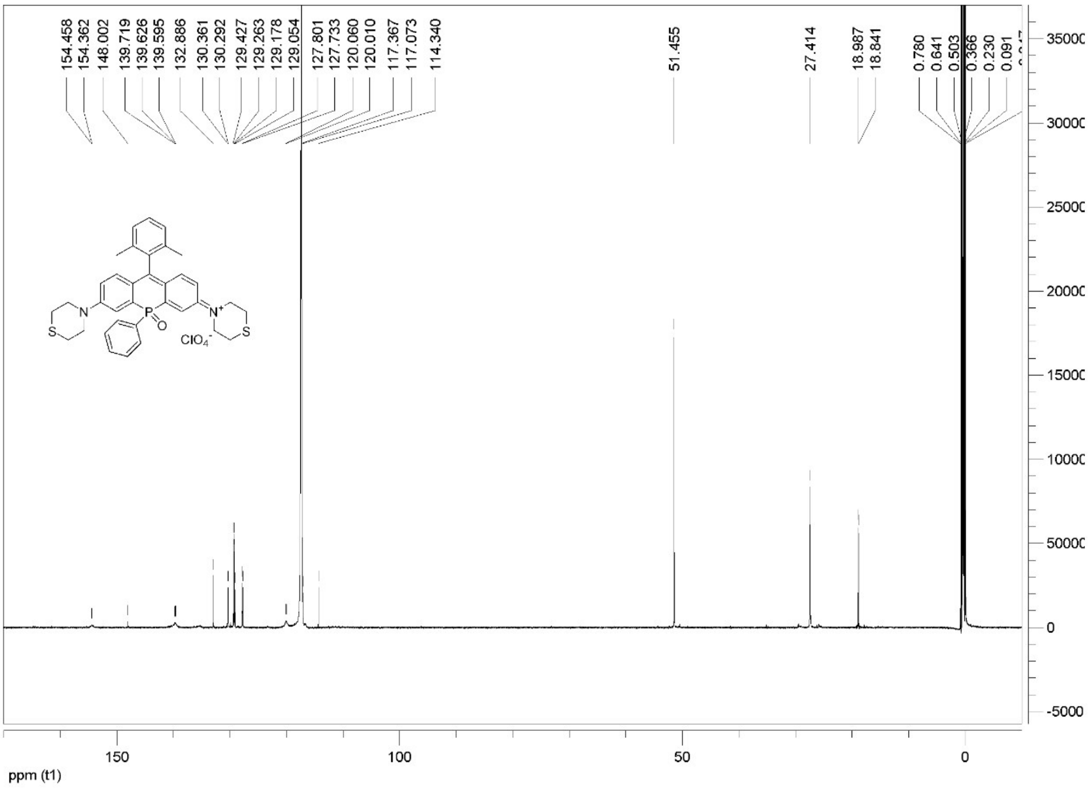
^{1}H NMR spectrum of **S18**



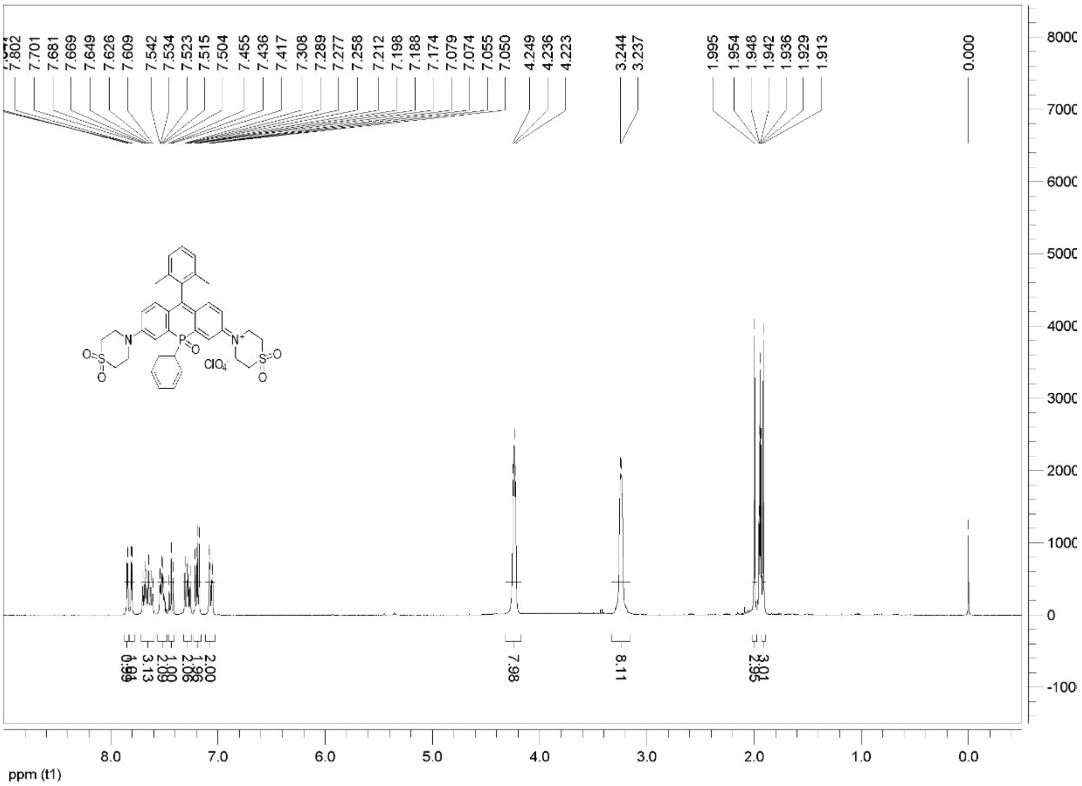
^{13}C NMR spectrum of **S18**



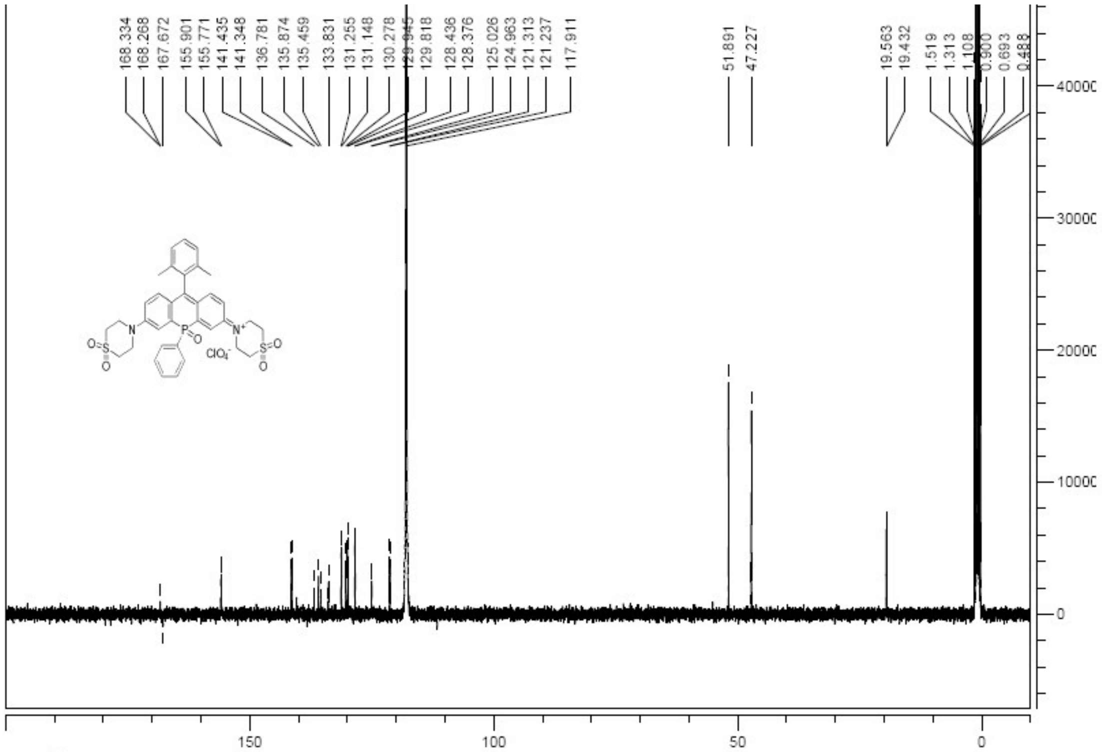
^{1}H NMR spectrum of **S19**



^{13}C NMR spectrum of **S19**



^{1}H NMR spectrum of **11**



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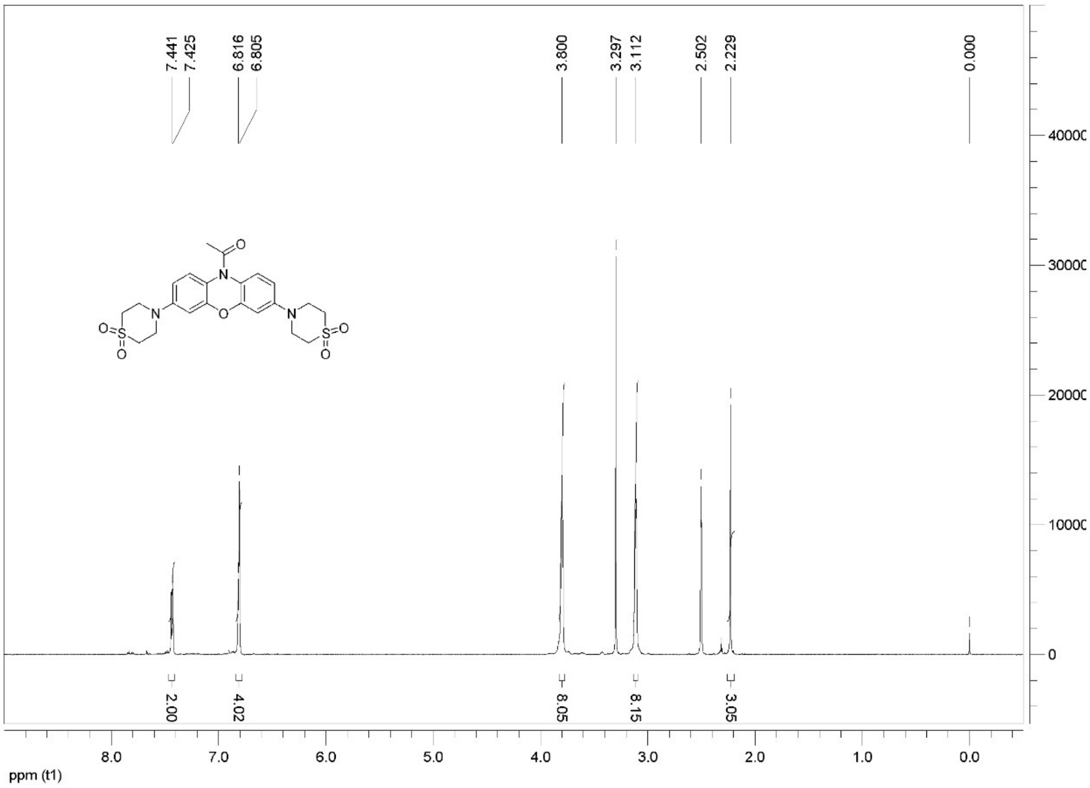

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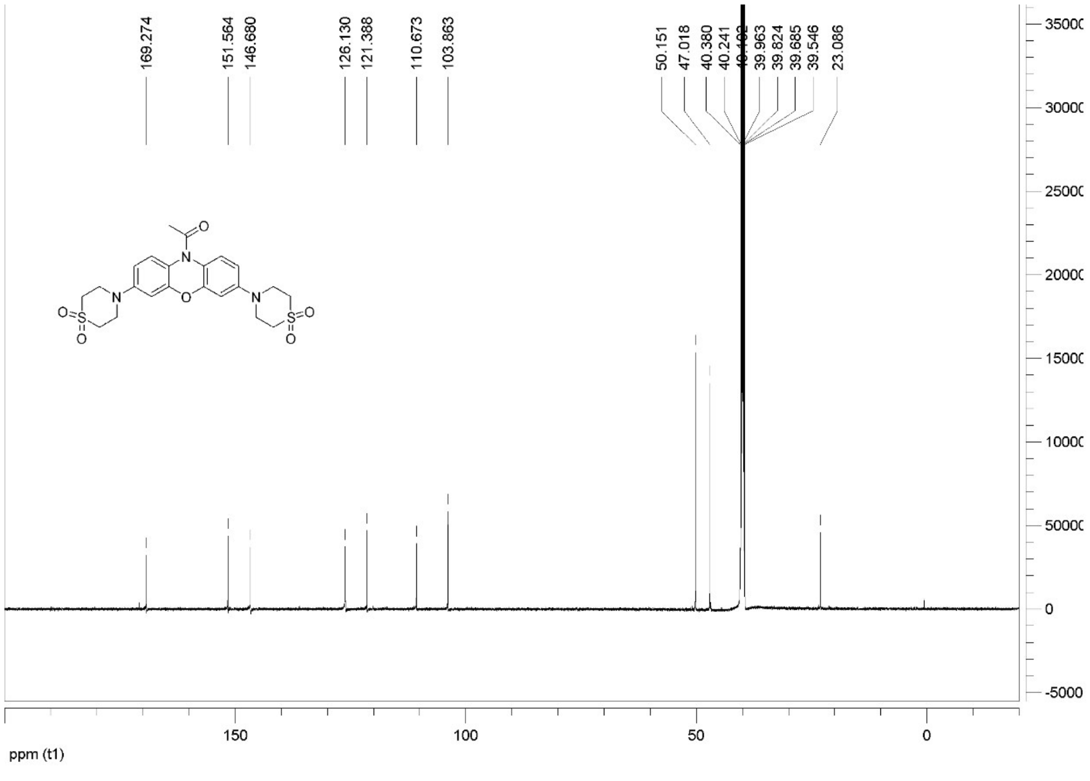
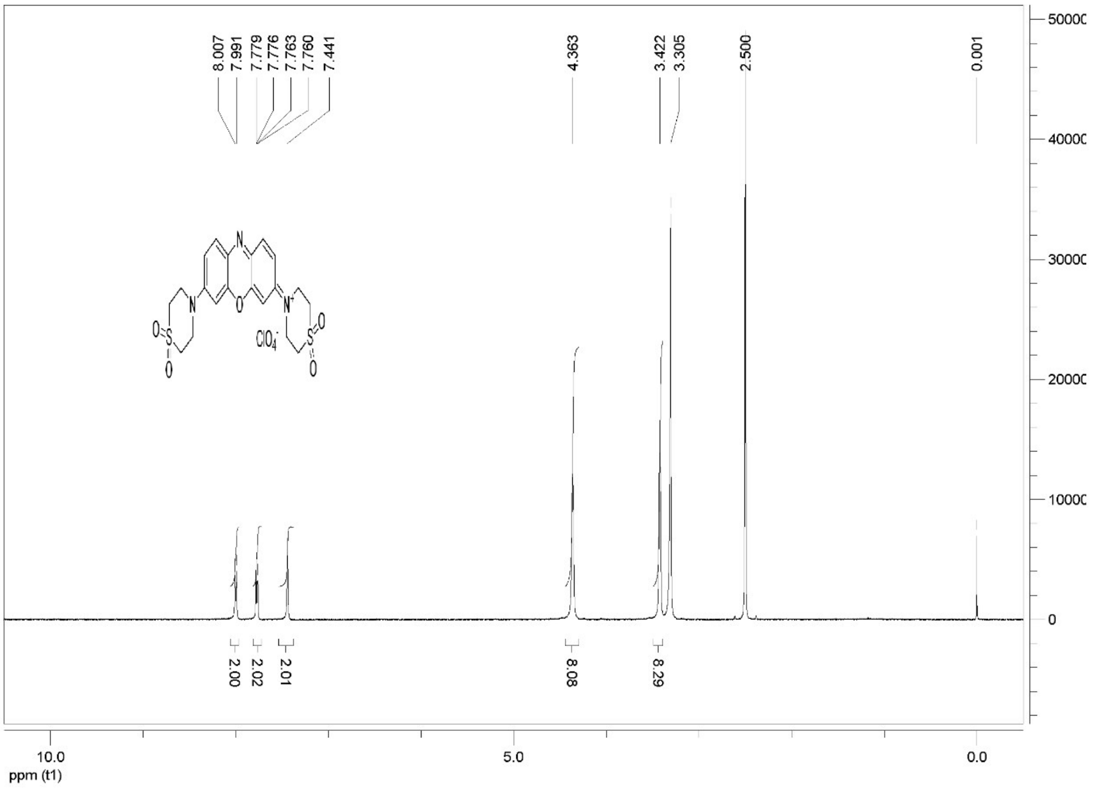
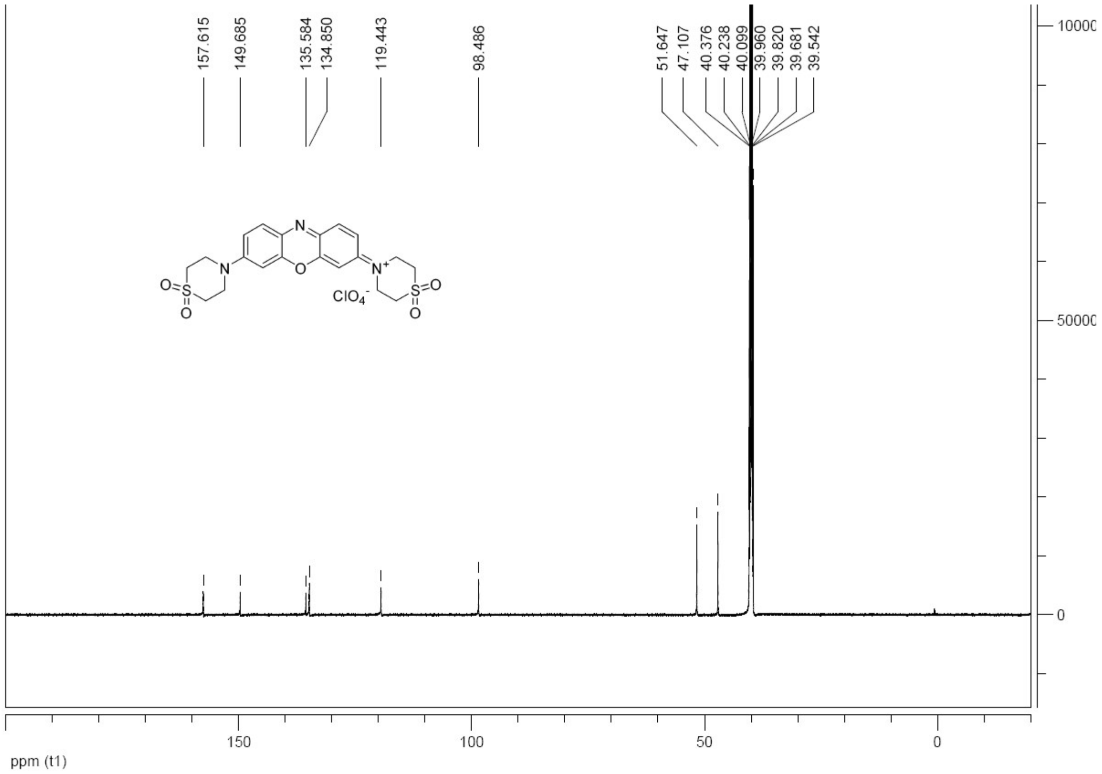


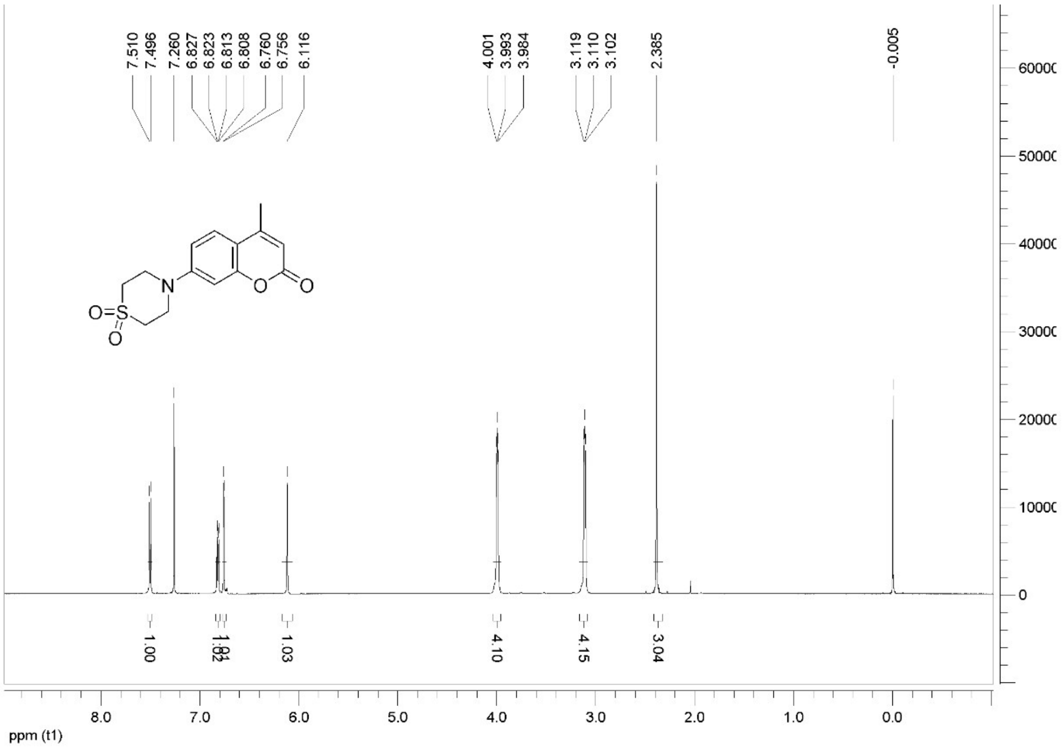
^{13}C NMR spectrum of **S21**



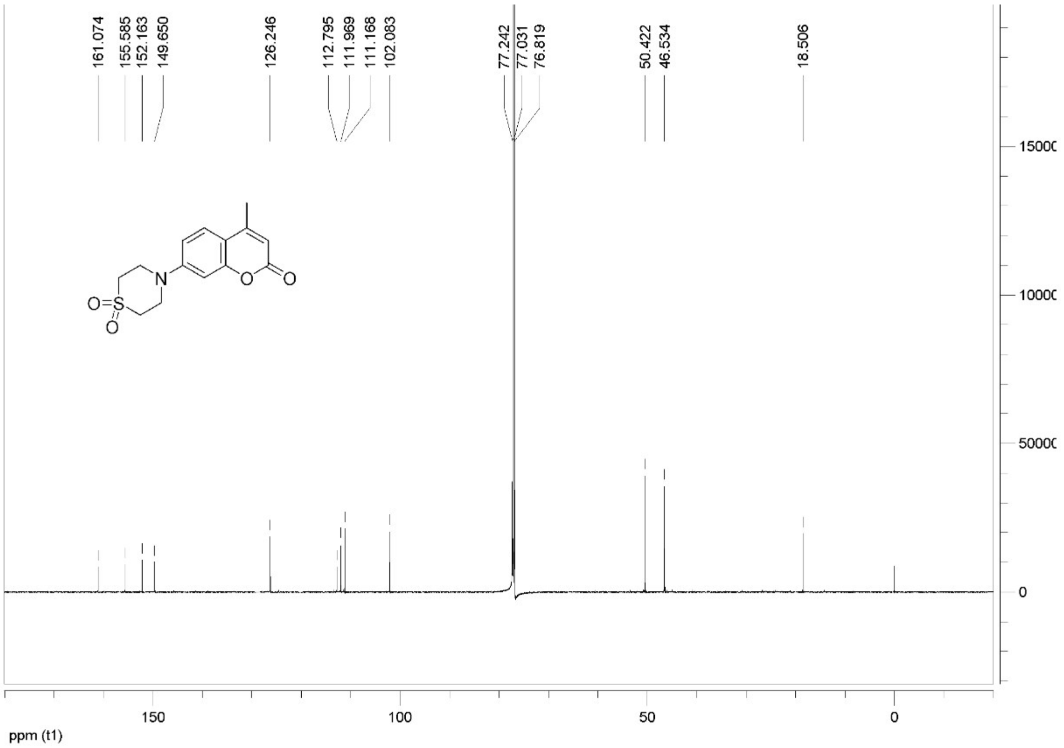
^{1}H NMR spectrum of **13**



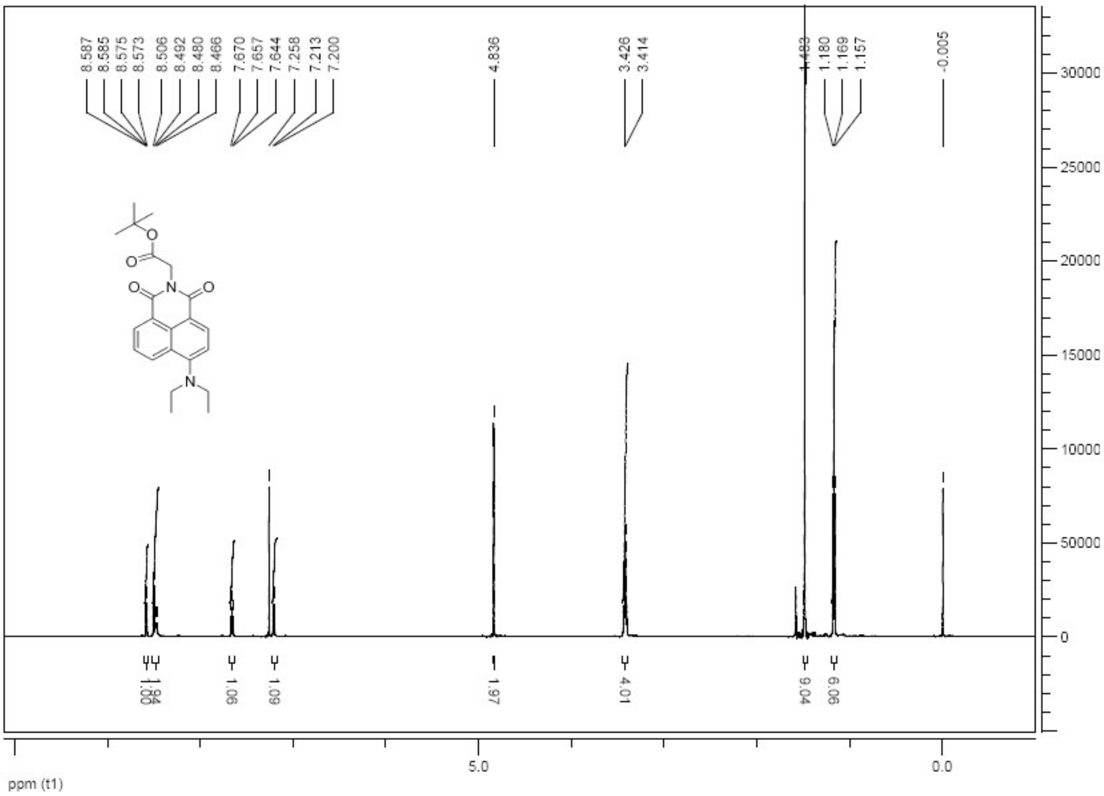
^{13}C NMR spectrum of **13**



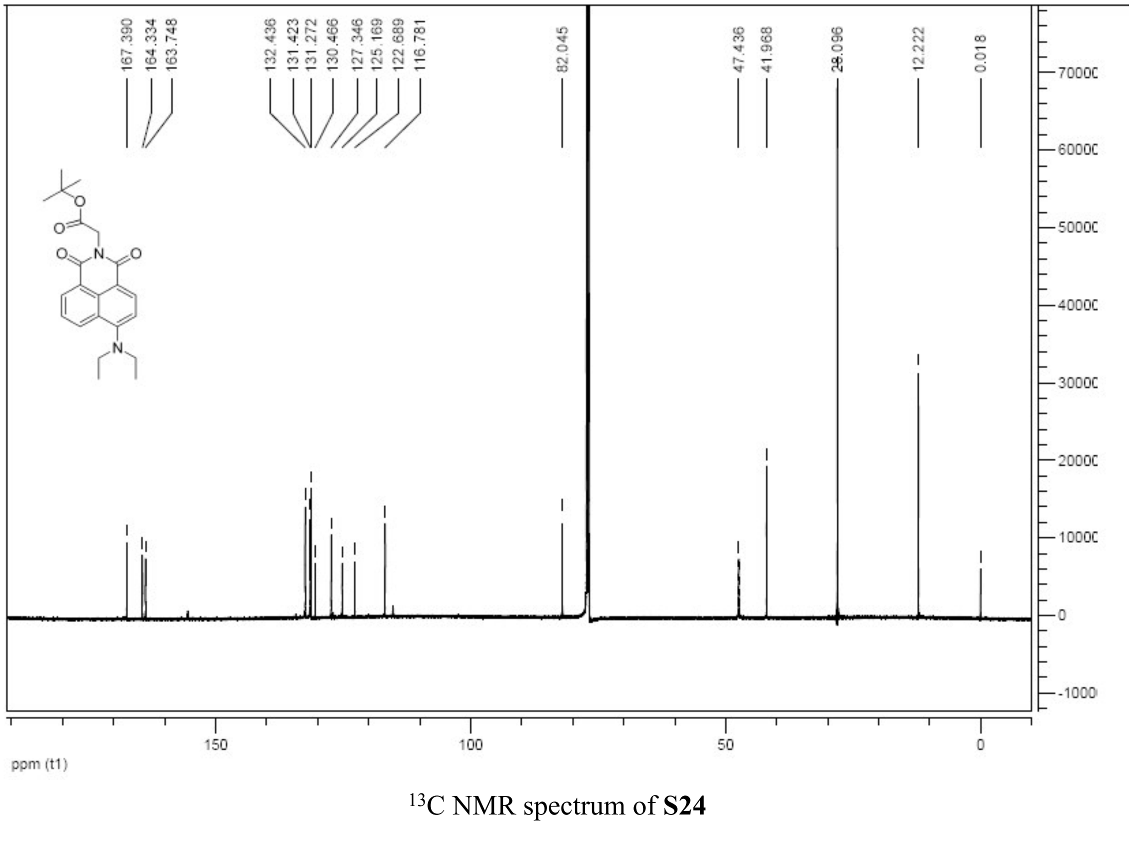
^{1}H NMR spectrum of **15**



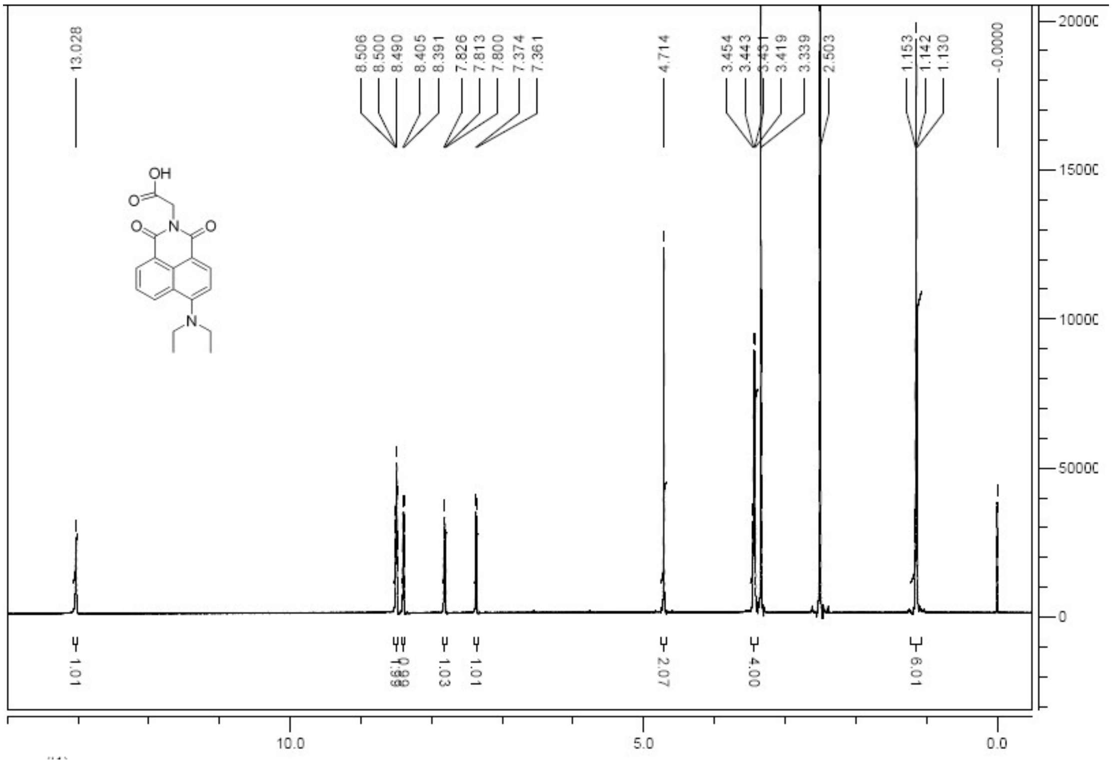
^{13}C NMR spectrum of **15**



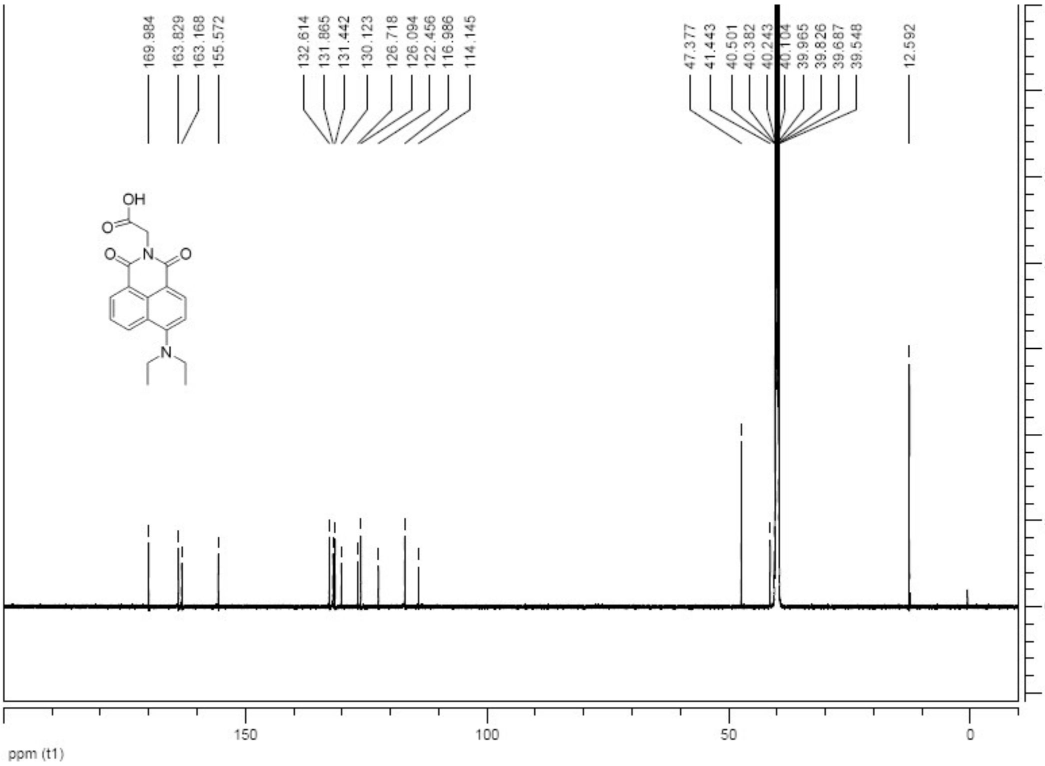
^{1}H NMR spectrum of **S24**



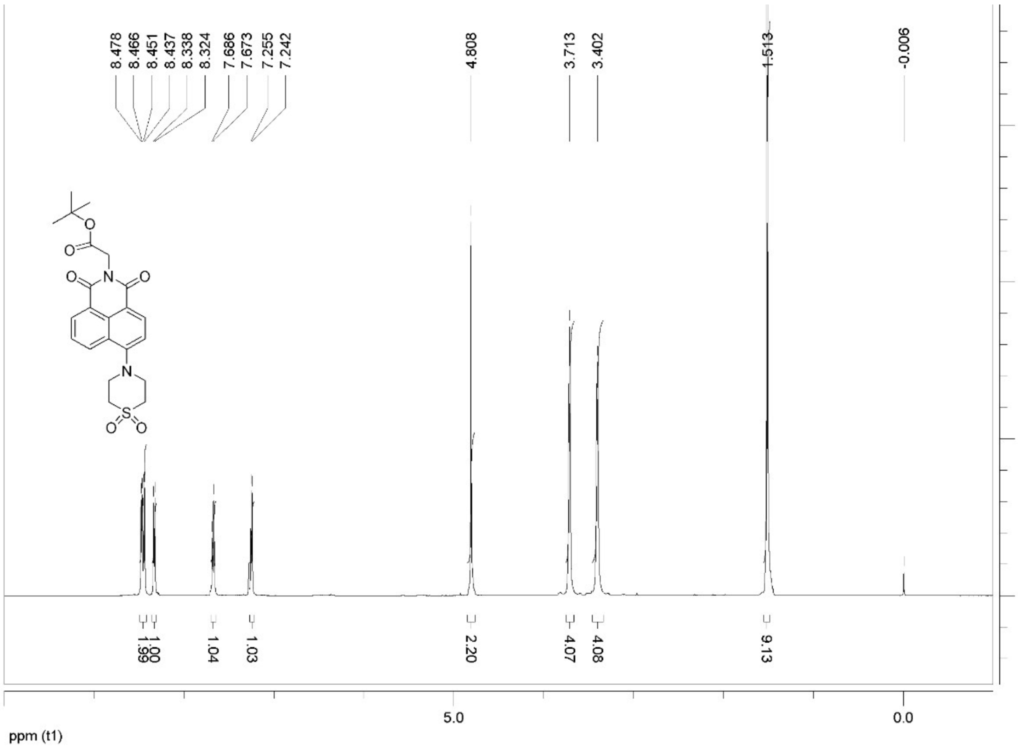
^{13}C NMR spectrum of **S24**



^{1}H NMR spectrum of **16**



^{13}C NMR spectrum of **16**



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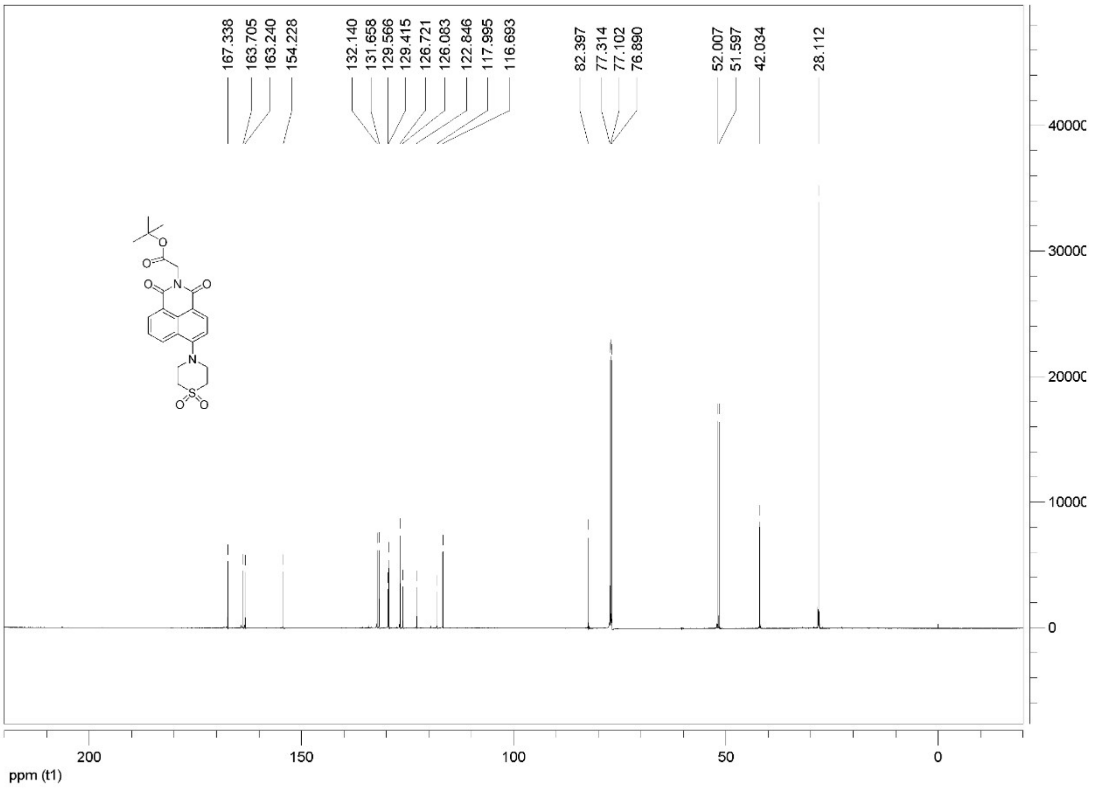
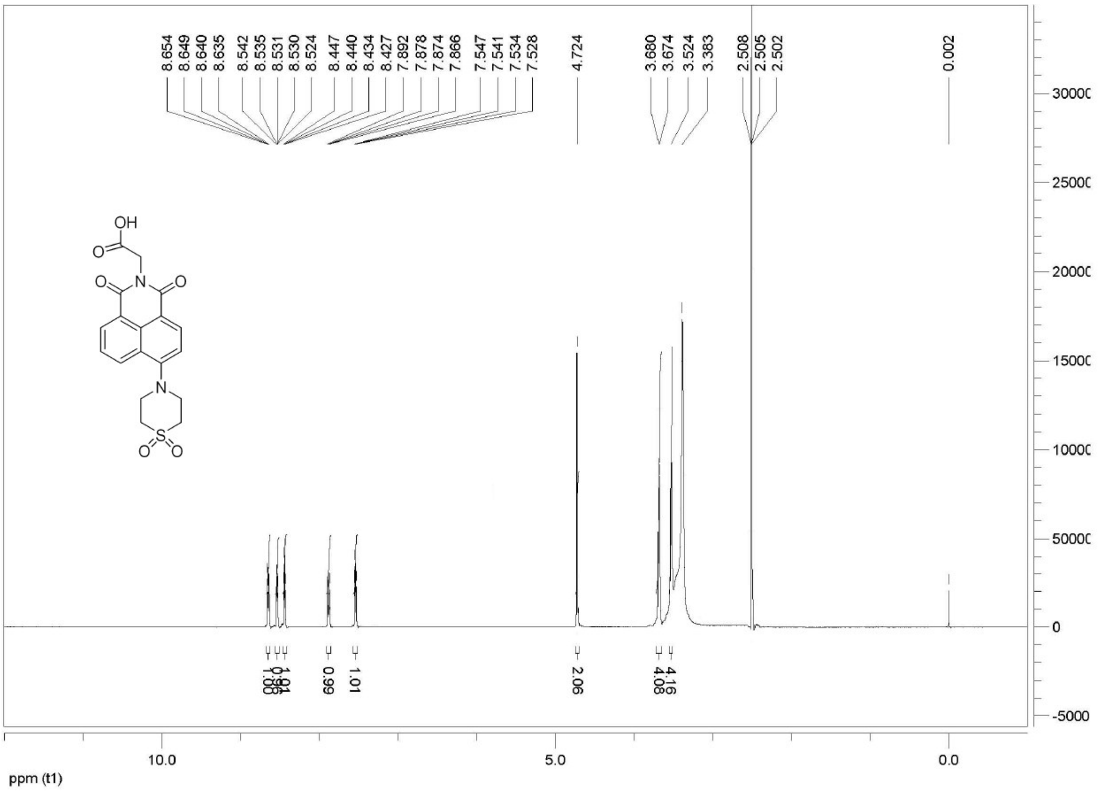
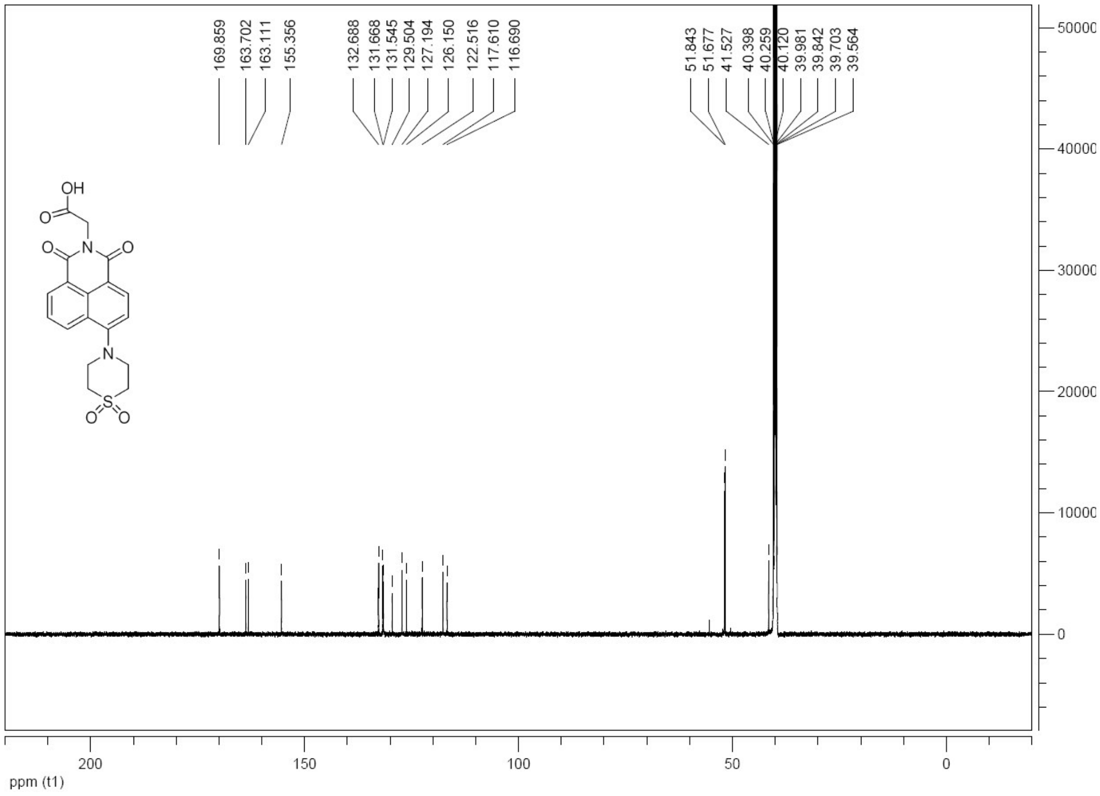


^{13}C NMR spectrum of **S25**

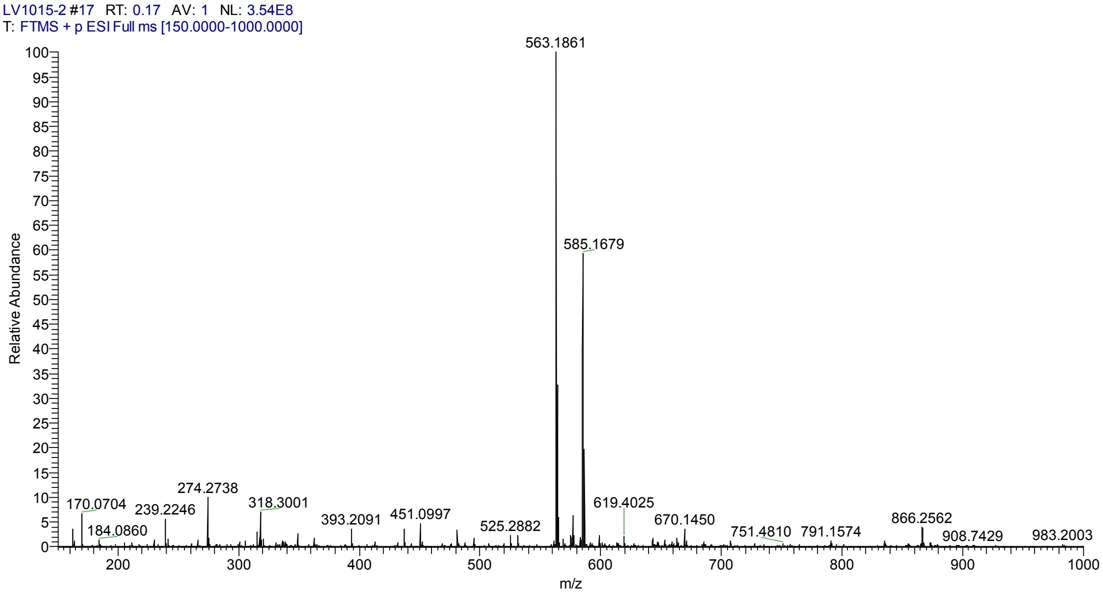


^{1}H NMR spectrum of **17**

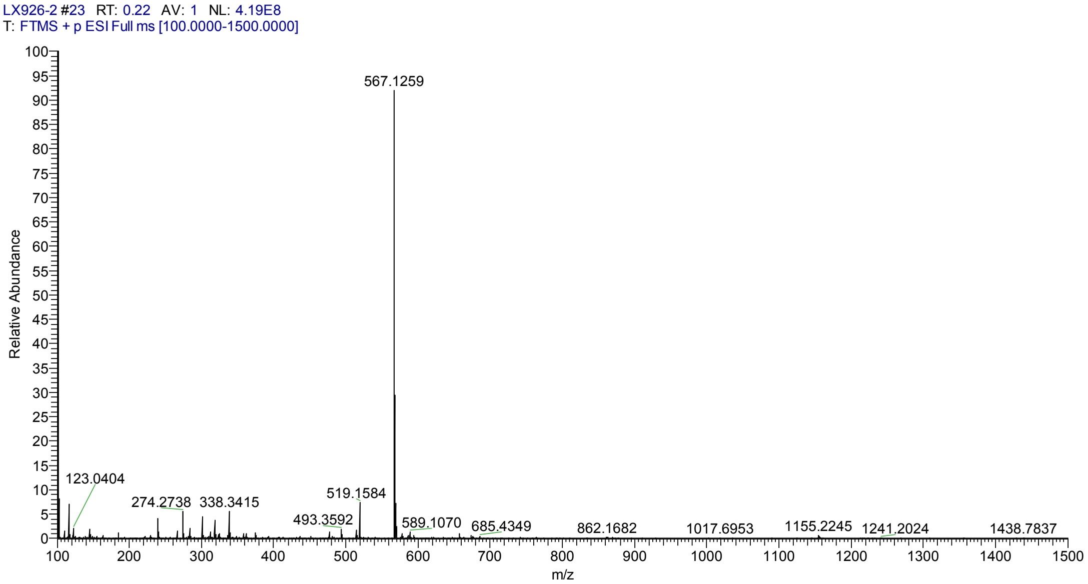


^{13}C NMR spectrum of **17**

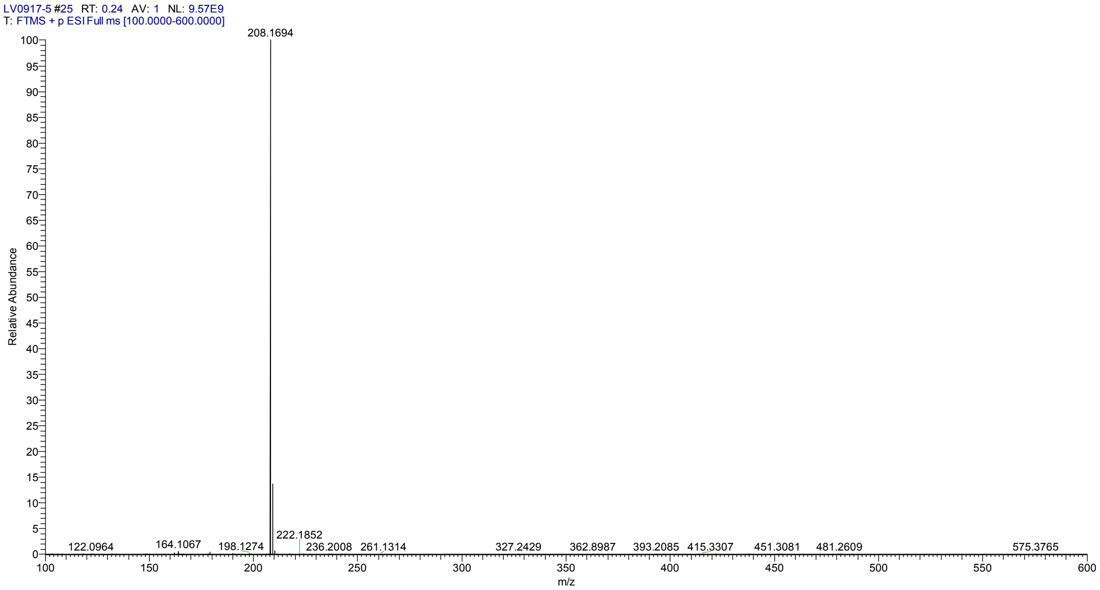
9. HRMS spectra



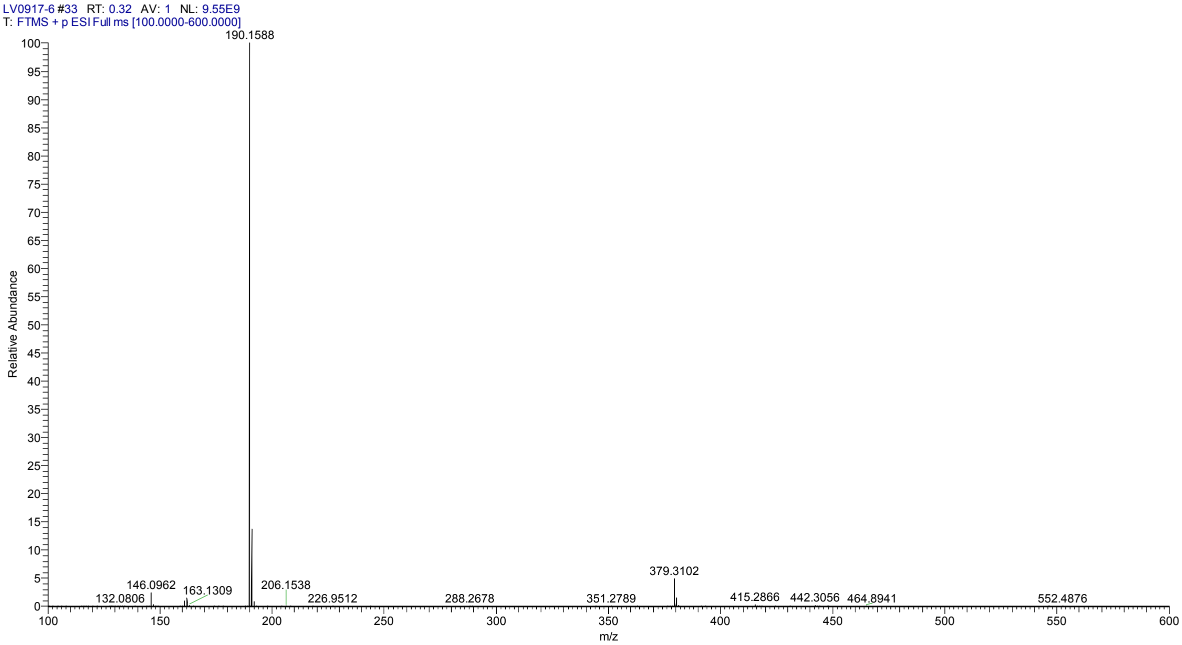
HRMS spectrum of **4**



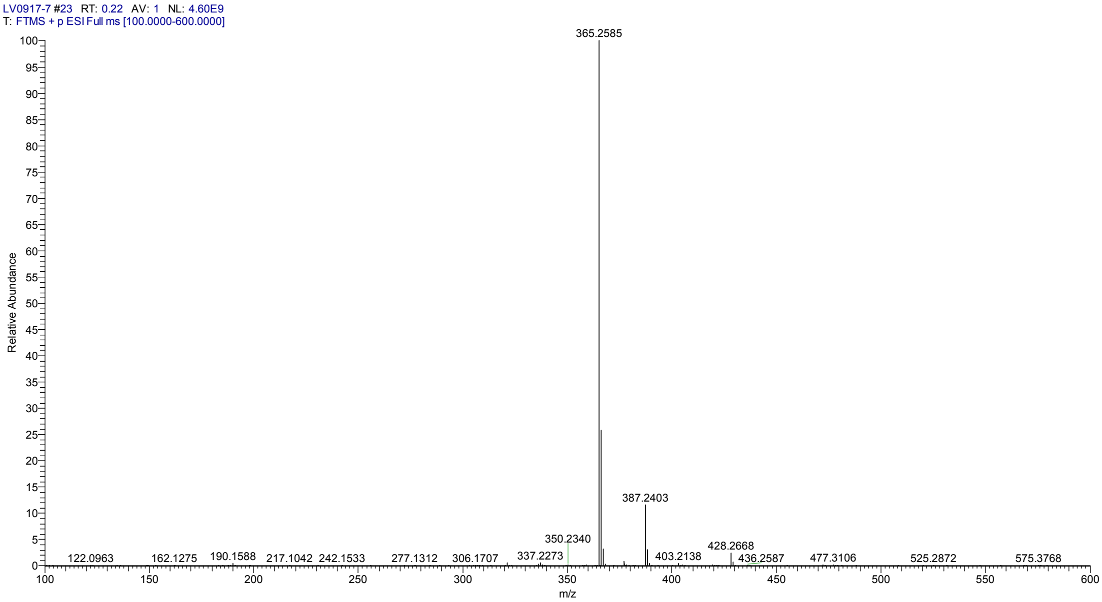
HRMS spectrum of **5**



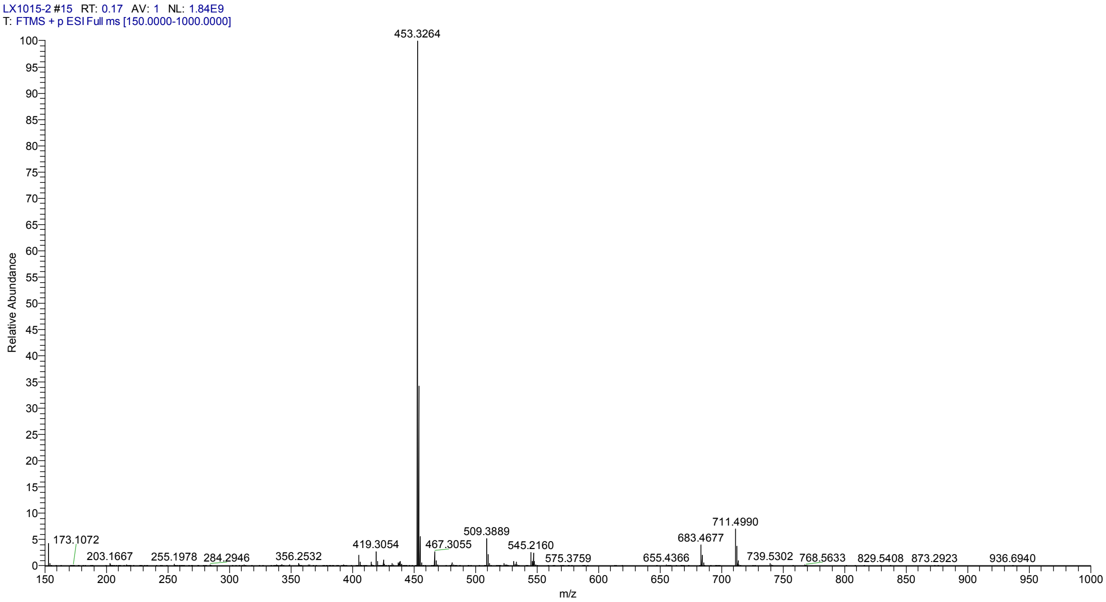
HRMS spectrum of **S3**



HRMS spectrum of **S4**



HRMS spectrum of **S5**



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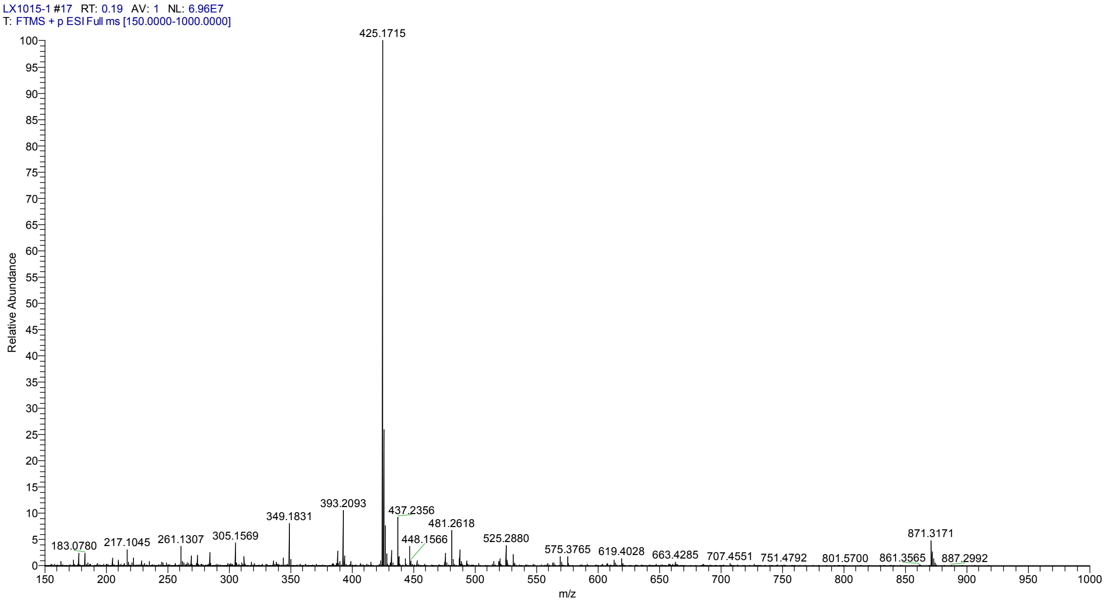
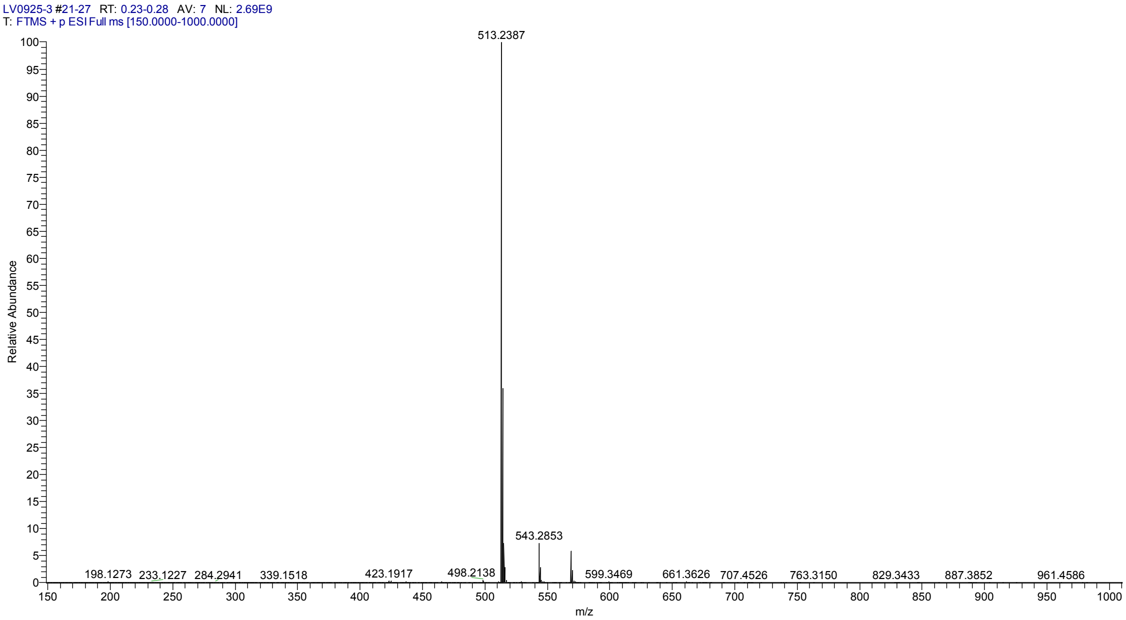
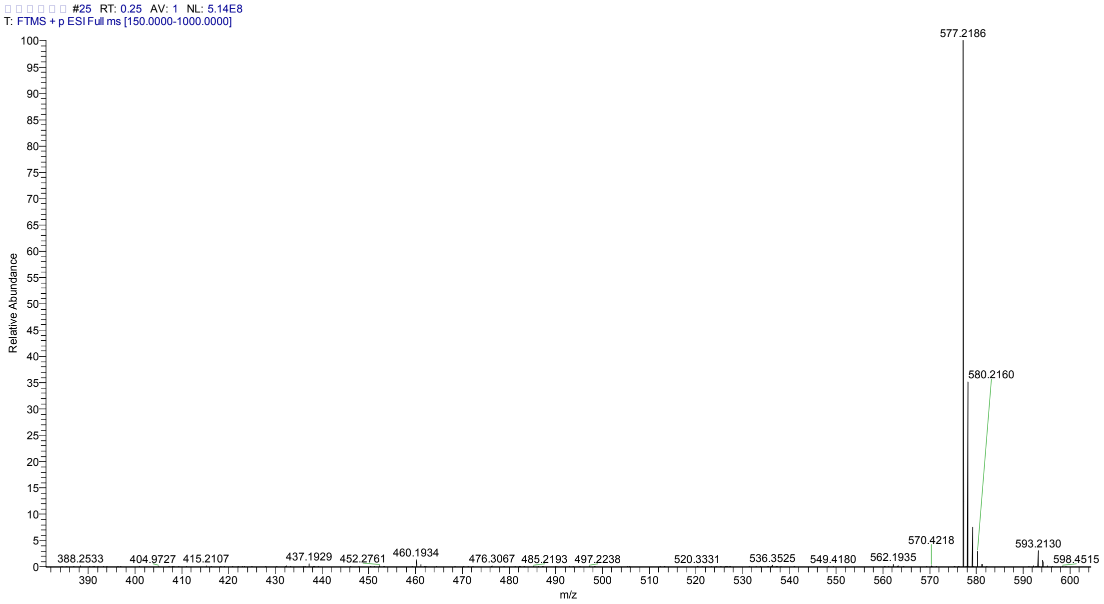


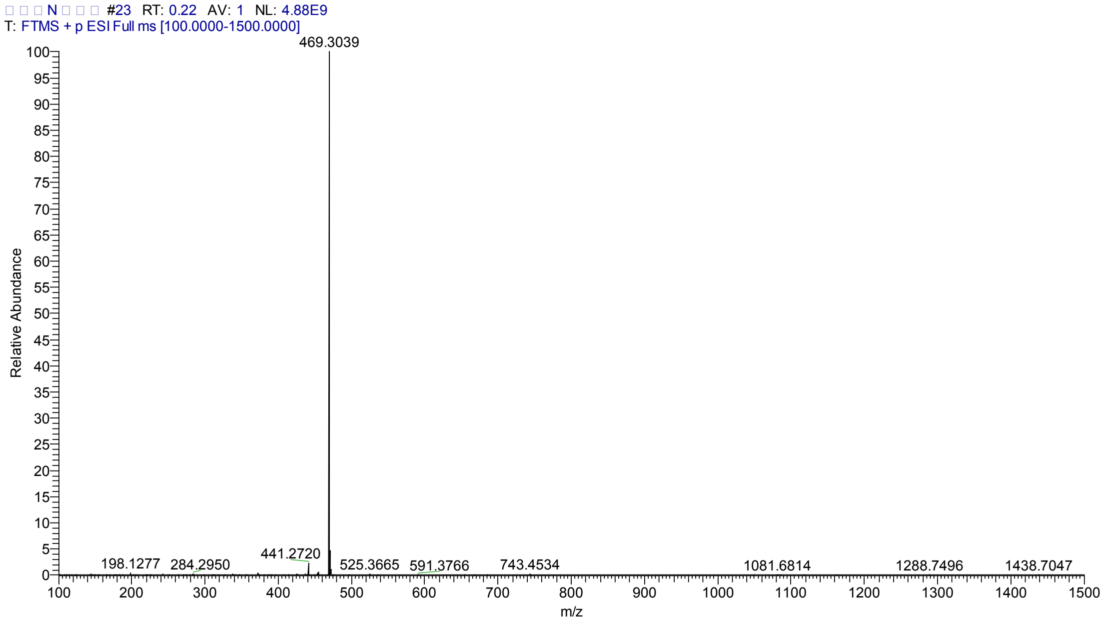
HRMS spectrum of **S7**



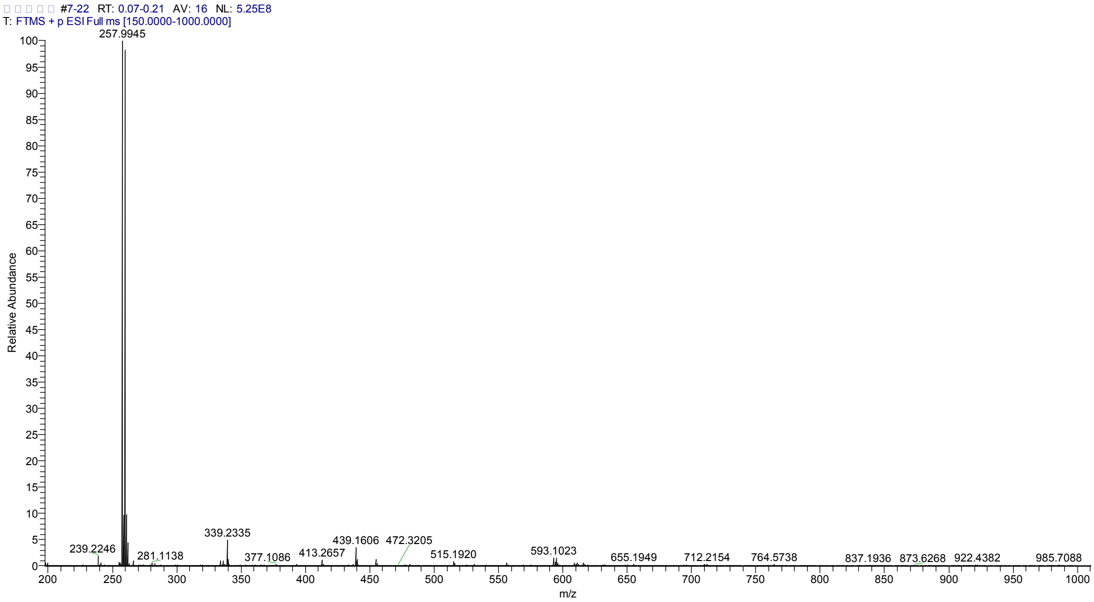
HRMS spectrum of **S8**



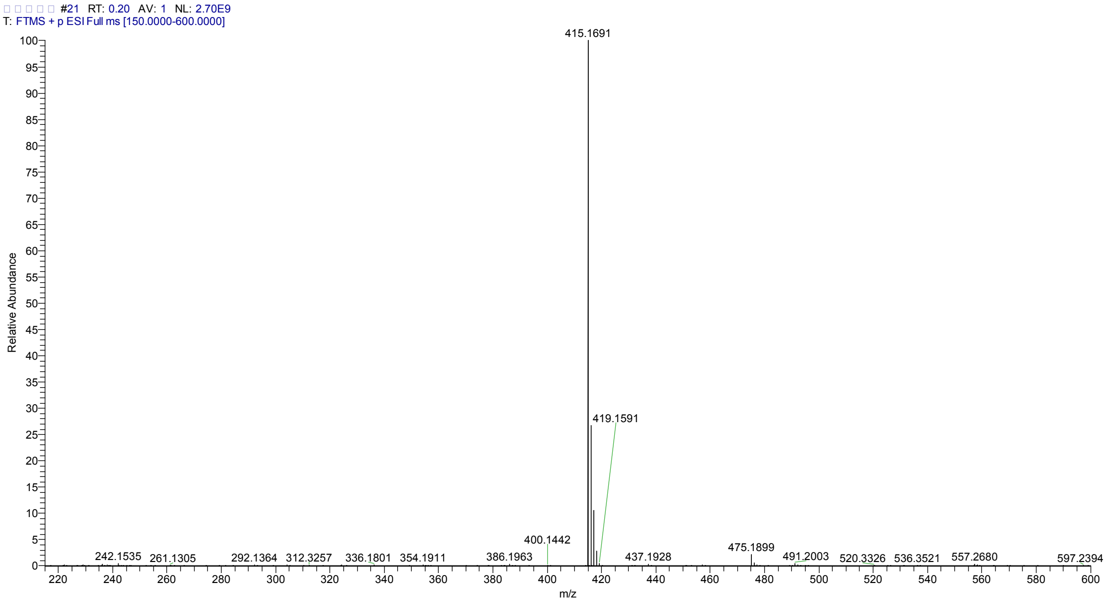
HRMS spectrum of **7**



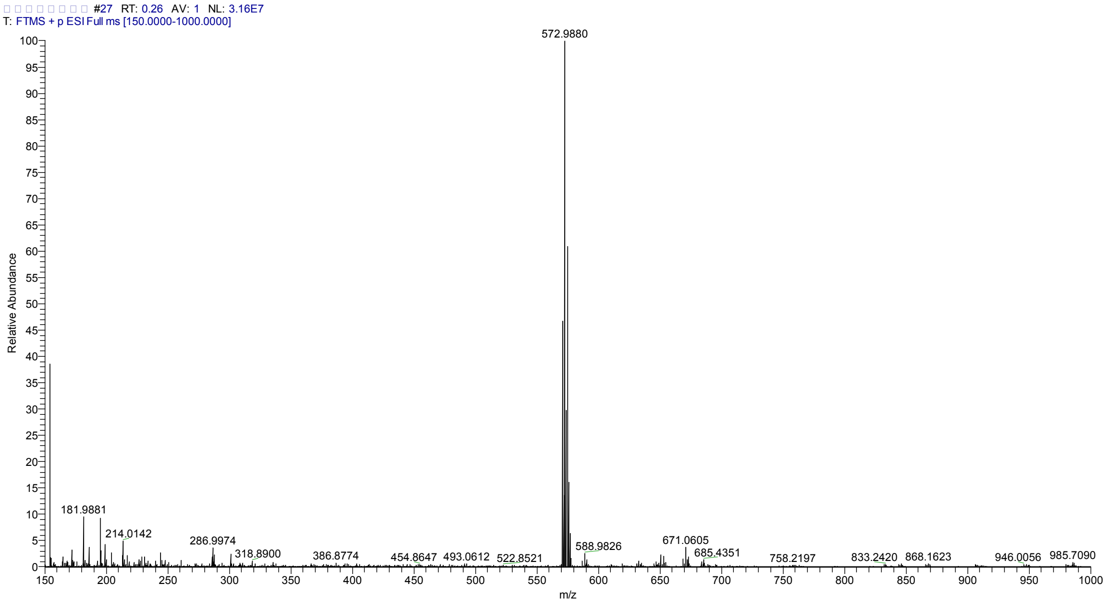
HRMS spectrum of **8**



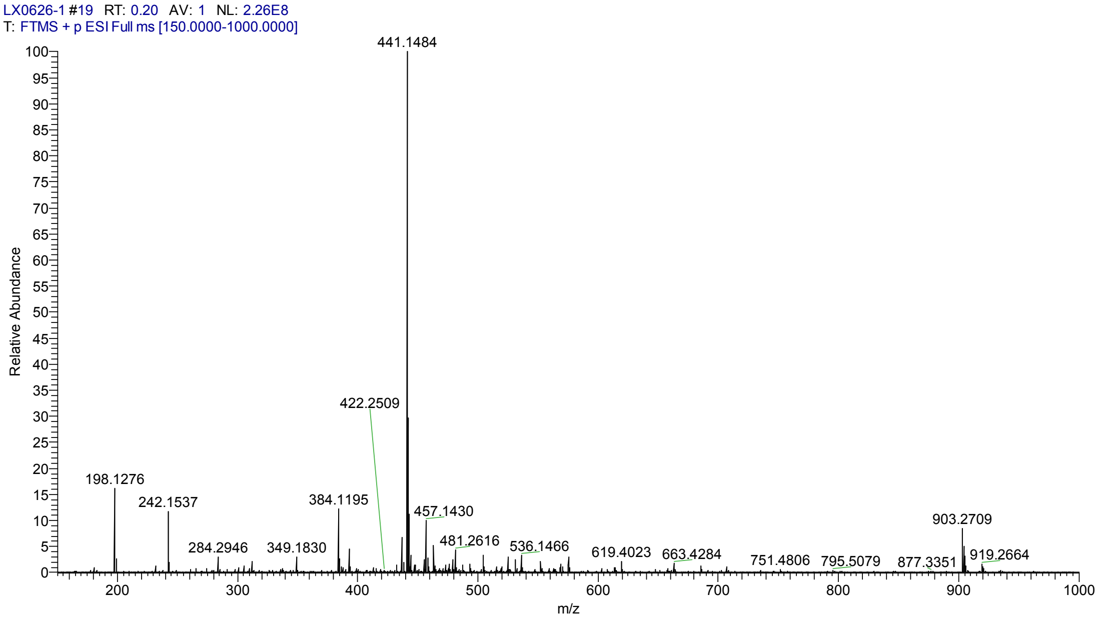
HRMS spectrum of **S10**



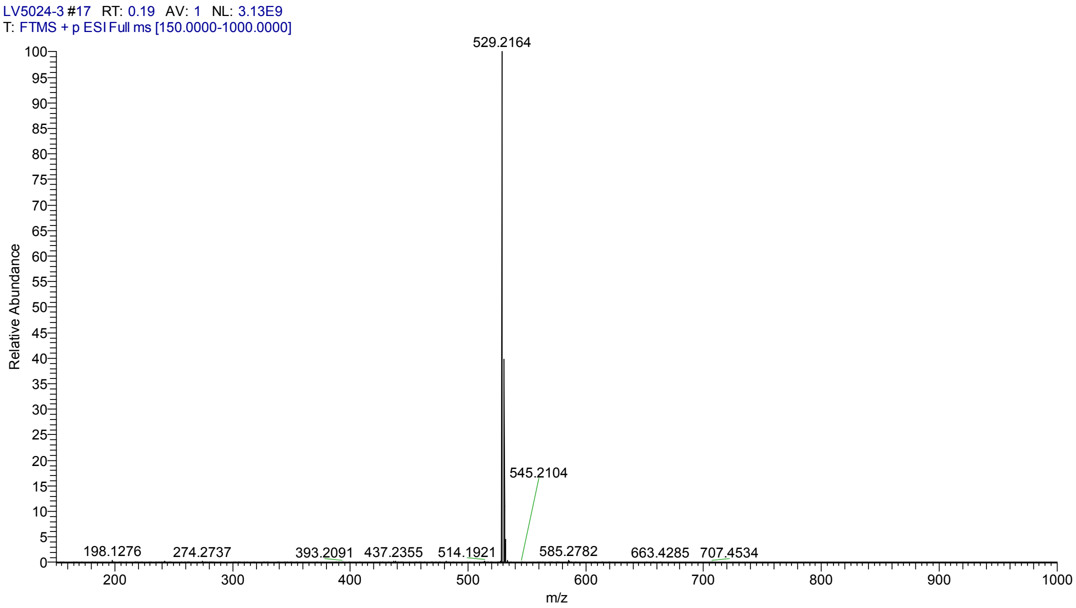
HRMS spectrum of **S11**



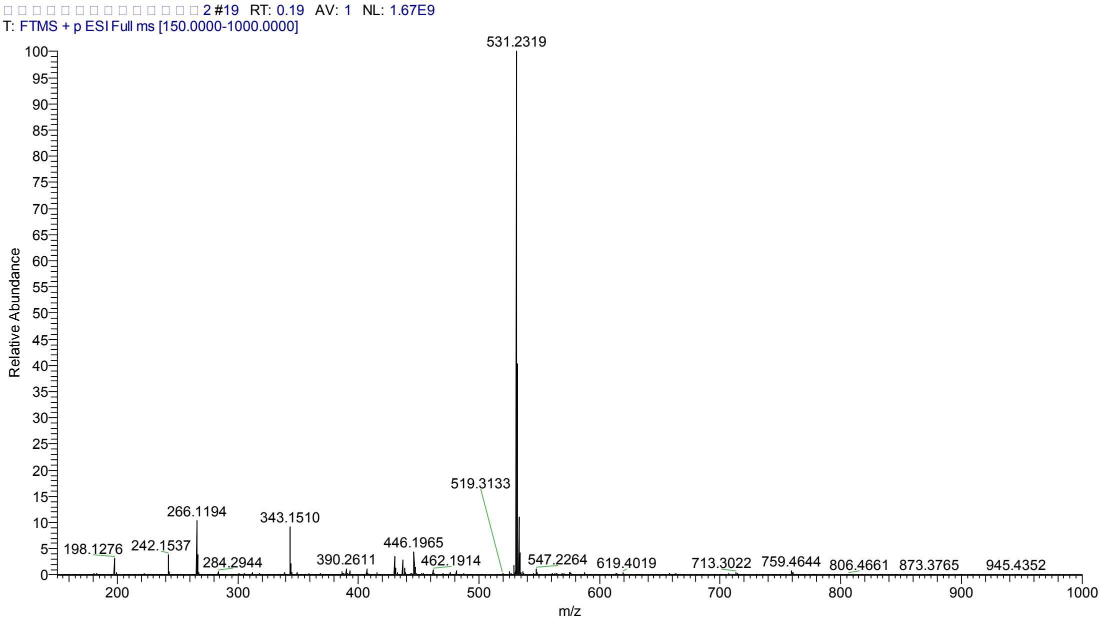
HRMS spectrum of **S12**



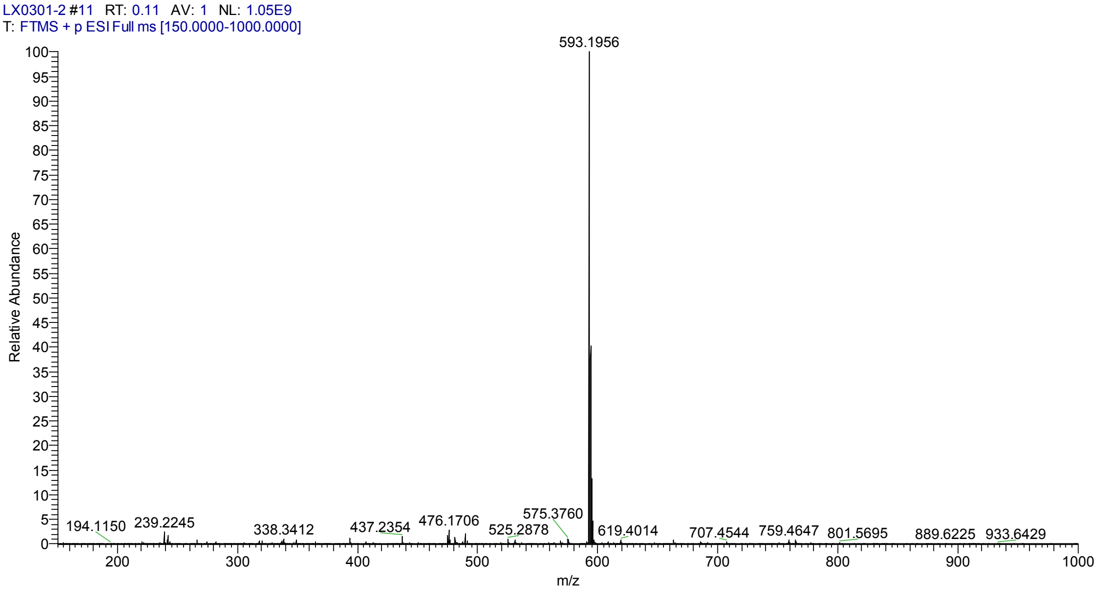
HRMS spectrum of **S13**



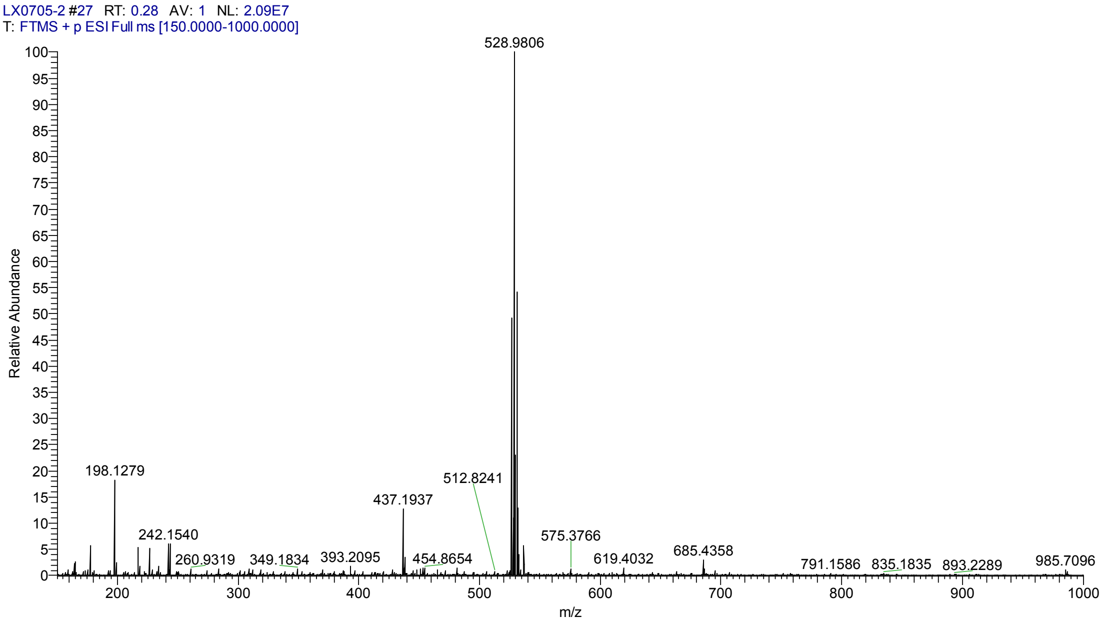
HRMS spectrum of **S14**



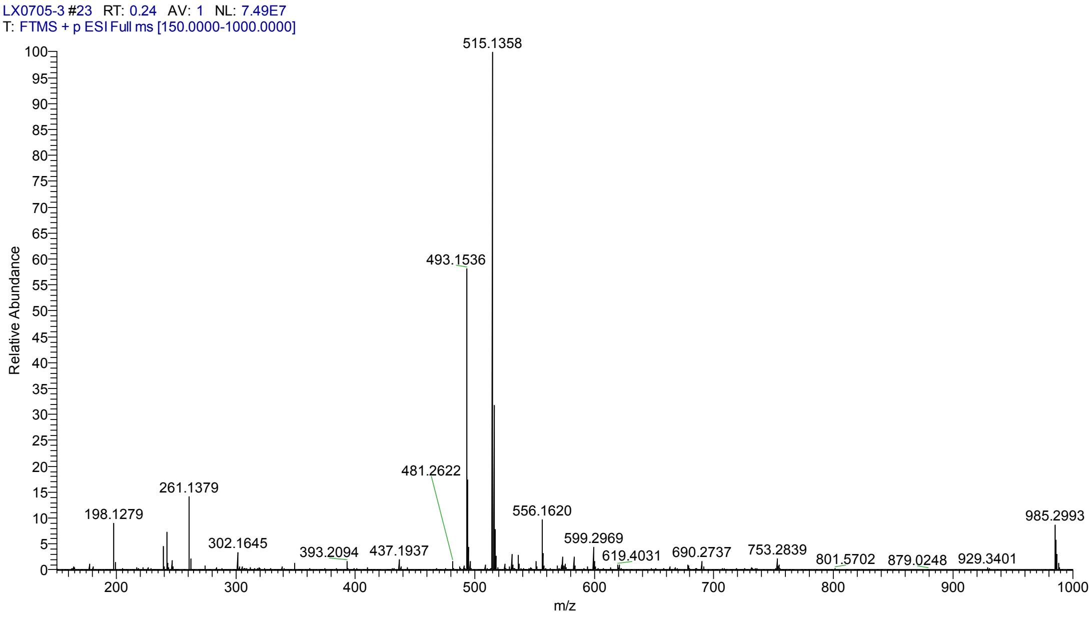
HRMS spectrum of **S15**



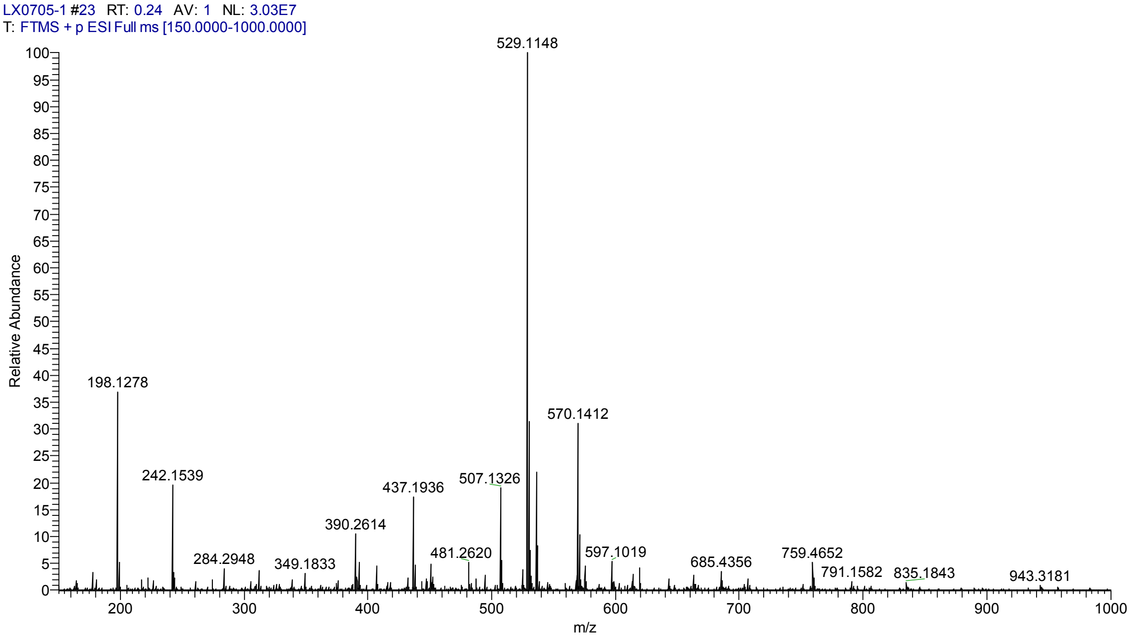
HRMS spectrum of **9**



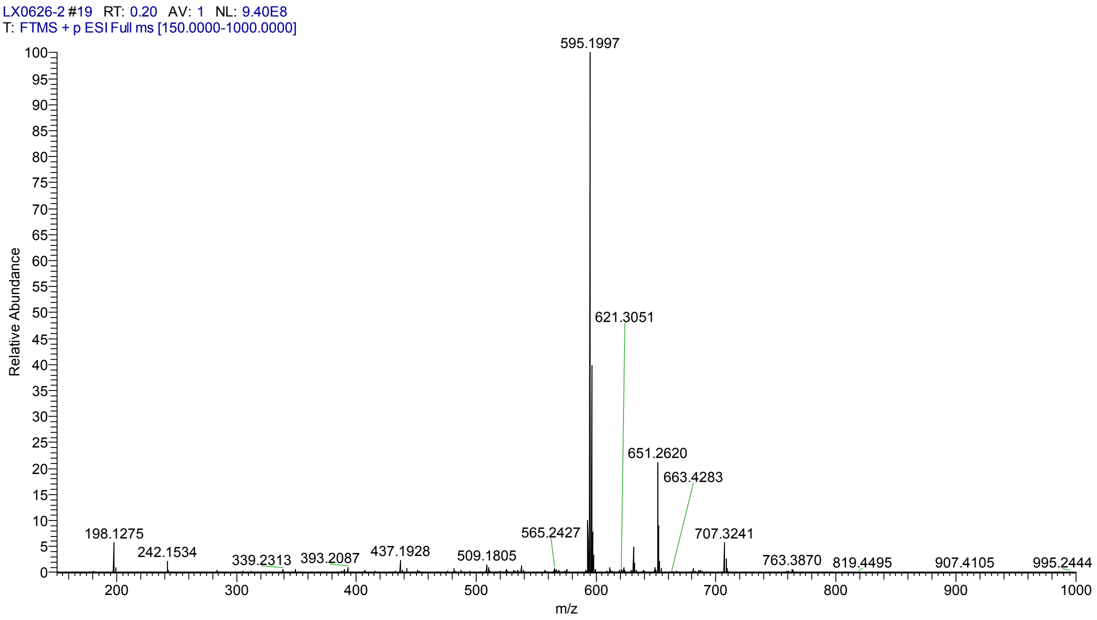
HRMS spectrum of **S16**



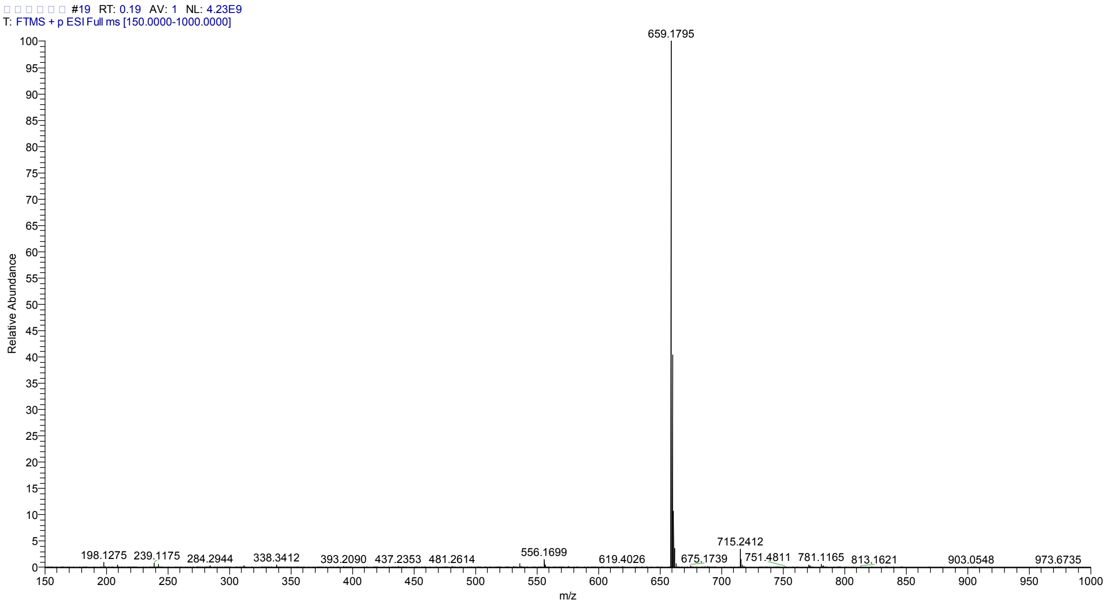
HRMS spectrum of **S17**



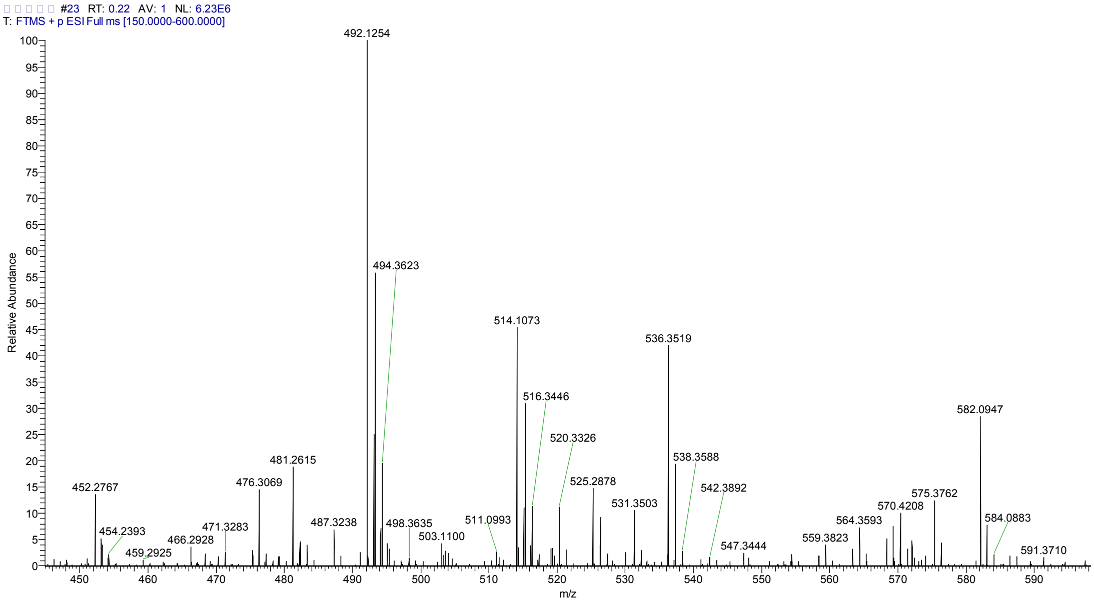
HRMS spectrum of **S18**



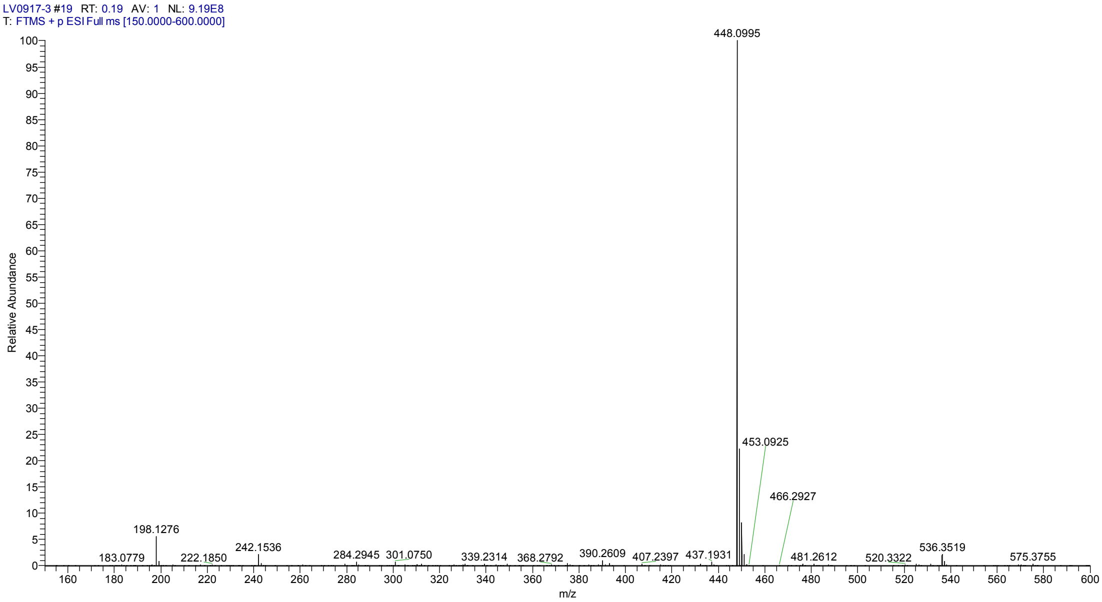
HRMS spectrum of **S19**



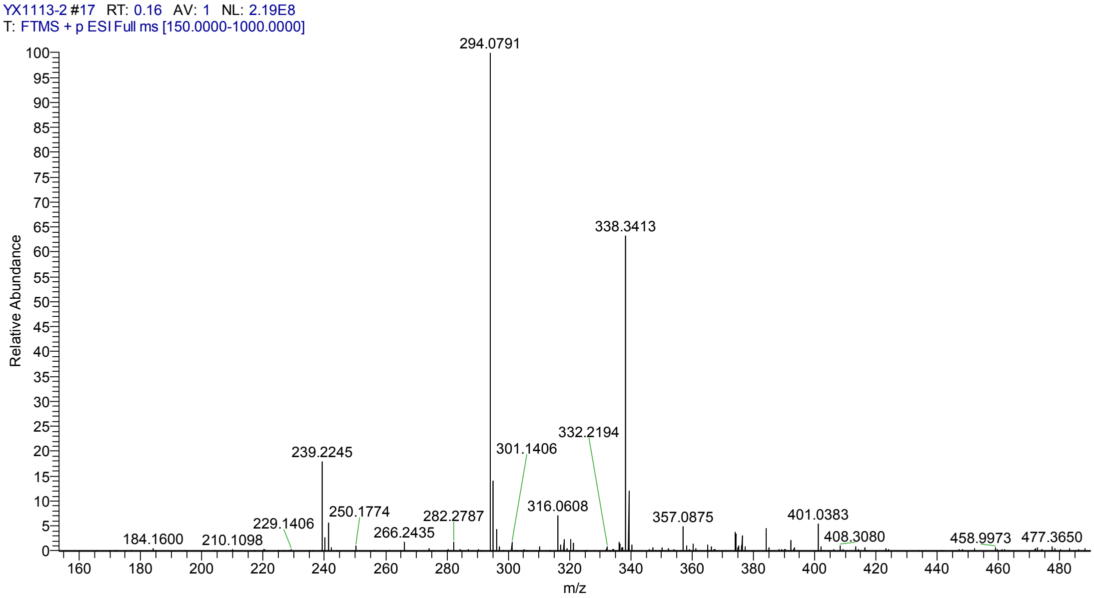
HRMS spectrum of **11**



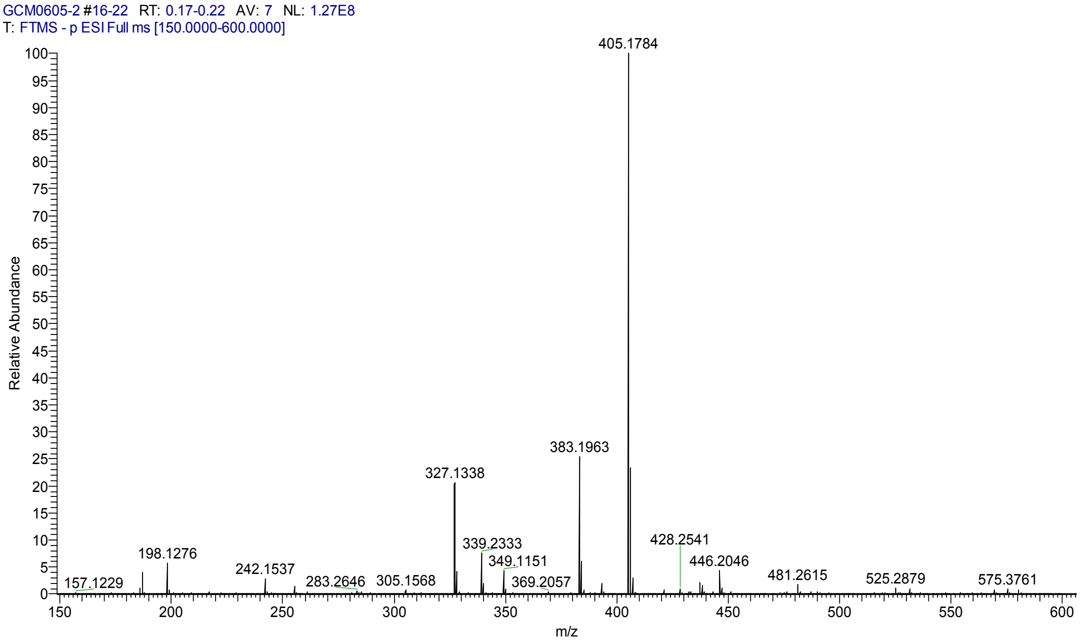
HRMS spectrum of **S21**



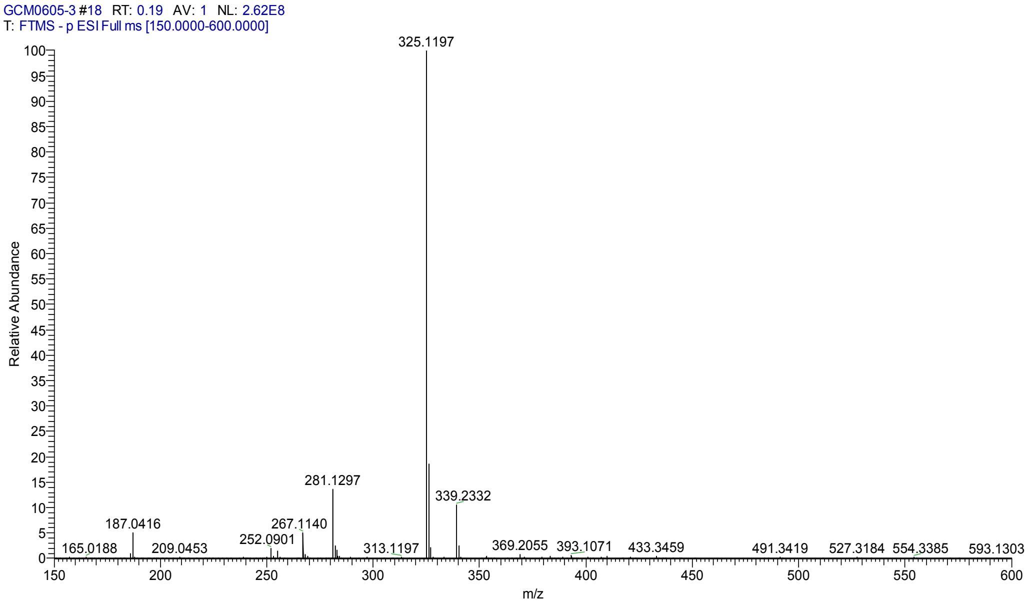
HRMS spectrum of **13**



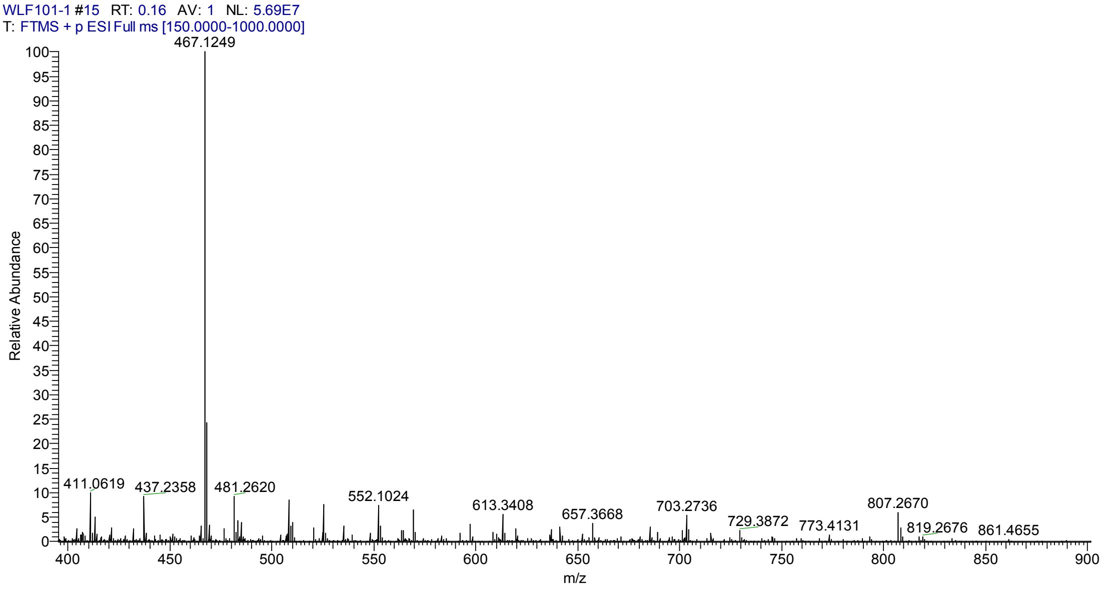
HRMS spectrum of **15**



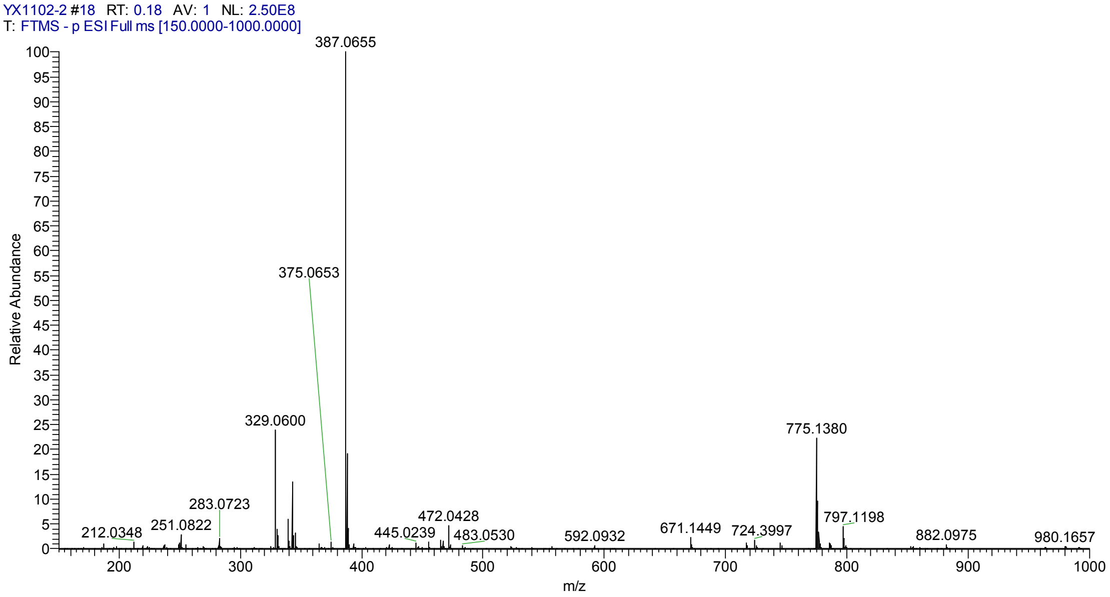
HRMS spectrum of **S24**



HRMS spectrum of **16**



HRMS spectrum of **S25**



HRMS spectrum of **17**