SUPPORTING INFORMATION

Highly efficient Ca^{2+} chelation activated by visible light

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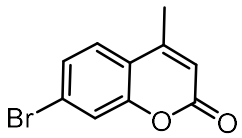
CONTENTS

1. Materials and Methods

All reagents were purchased from Fisher Scientific or Sigma Aldrich in a highly purified form and used without further purification (unless otherwise stated). The CH_3OH, ACN, DMF, and EtOH used in the reaction were all purchased in anhydrous form. CH_2Cl_2 was obtained from a solvent purification system (MBRAUN, MB-SPS) with an activated alumina column. All other solvents used in the procedure were purchased from VWR. Reactions were performed under a nitrogen (N_2) or argon (Ar) atmosphere using standard Schlenk line techniques. For reactions performed under a hydrogen (H_2) atmosphere, a hydrogen-filled balloon was used. The reaction vessel was flame-dried (with three vacuum and N_2 charge repetitions) and filled with N_2/Ar prior to the reaction. Reaction progress was monitored using thin-layer chromatography (TLC) (EMD Millipore TLC Silica Gel 60 F254), for which the spots were observed under short- and long-wavelength UV light. The product of each synthesis was purified using 60 Å silica gel (Fisher Scientific) column chromatography. The caging step and corresponding purification of the caged molecule were performed in the dark under dim red light. The light-sensitive products were stored in the dark (covered with aluminum foil) at -20 °C. Each product was characterized by ^{1}H NMR and ^{13}C NMR using a Bruker 400 MHz NMR spectrometer. NMR solvents ($CDCl_3$, D_2O, DMSO, and Acetone-D_6) were purchased from Cambridge Isotope and Acros Laboratories. Chemical shifts were calculated relative to solvent residue peaks ($CDCl_3$ = 7.26 ppm, D_2O = 4.79 ppm, DMSO = 2.50 ppm, and Acetone-D_6 = 2.05 ppm). UV-vis spectra were acquired using an Agilent 8453 Diode Array UV-vis. High-resolution mass spectroscopy (HRMS) was measured using a JEOL DART-AccuTOF mass spectrometer, and low-resolution mass spectrometry was performed on an Agilent LC-MS equipped with an ES^+ and 6120 quadrupoles.

2. Synthesis of the Thionyl Coumarin PPGs

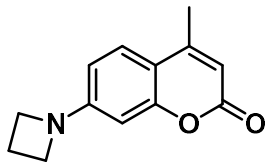
7-Bromo-4-methyl-chromen-2-one (5)



5

20 mL of 90% H_2SO_4 was added to a round-bottom flask. Then, compound **4** (0.86 g, 5 mmol) was slowly added to the reaction mixture at -5 °C. The reaction mixture was stirred for 10 min, and ethyl acetoacetate (0.65 g, 5 mmol) was added dropwise over a 45-min period. The mixture was stirred for 48 h at room temperature (rt) (24 °C) before being poured into 25 ml of ice water and stirred for 30 min. The precipitate was collected under reduced pressure to obtain a white solid at a yield of 90%. ^{1}H NMR (400 MHz, DMSO) δ 7.73 (d, *J* = 5.1 Hz, 1H), 7.72 (d, *J* = 1.0 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.46 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 159.14 (s), 153.36 (s), 152.79 (s), 127.38 (s), 127.04 (s), 124.66 (s), 119.34 (s), 118.95 (s), 114.62 (s), 17.98 (s).

7-Azetidin-1-yl-4-methyl-coumarin (7)

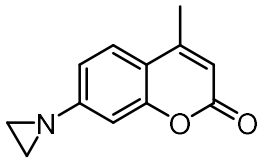


7

Compound **5** (50 mg, 0.21 mmol), Cs_2CO_3 (205.6 mg, 0.63 mmol), Pd $(PPh_3)_2Cl_2$ (9 mg, 5% mol), and azetidine (60 mg, 1.05 mmol) were dissolved in 4 mL of anhydrous toluene under N_2. The reaction mixture was heated at 120 °C for 24 h. Product formation was monitored by TLC. The solvent was removed under reduced pressure, and the product was collected and then purified by column chromatography (SiO_2, CH_2Cl_2/CH_3OH 200:1 V/V) to obtain a white solid at a yield of 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 9.3 Hz, 1H), 7.64 – 7.47 (dd, 1H), 7.02 (d, *J* = 6.6 Hz, 1H), 6.66 (s, 1H), 3.63 (t, 4H), 2.33 (t, 2H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 159.95 (s), 153.83 (s), 151.72 (s), 127.92 (s), 127.58 (s), 125.60 (s), 120.31 (s), 119.00 (s), 115.30 (s), 53.83 (s), 23.90 (s), 18.57 (s).

7-Aziridin-1-yl-4-methyl-coumarin (8)

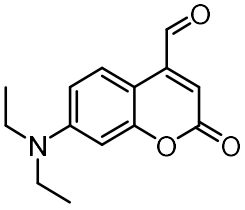


8

Compound **5** (50 mg, 0.21 mmol), Cs_2CO_3 (205.6 mg, 0.63 mmol), Pd $(PPh_3)_2Cl_2$ (9 mg, 5% mol), and aziridine (45 mg, 1.05 mmol) were dissolved in 4 mL of anhydrous toluene under N_2. The reaction mixture was heated at 120 ^{o}C for 24 h. Product formation was monitored by TLC. The solvent was removed under reduced pressure, and the product was collected and then purified by column chromatography (SiO_2, DCM/MeOH 500:1 V/V) to obtain a white solid at a yield of 55%.

^{1}H NMR (400 MHz, CDCl3) δ 7.52 (d, J = 1.1 Hz, 1H), 7.48 (dd, J = 7.5, 2.6 Hz, 1H), 7.45 (d, J = 4.4 Hz, 1H), 6.31 (s, 1H), 2.43 (s, 3H), 0.88 – 0.85 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.16 (s), 132.06 (s), 131.89 (s), 128.55 (s), 128.42 (s), 127.58 (s), 125.60 (s), 120.32 (s), 115.32 (s), 29.70 (s), 18.58 (s).

7-(Diethylamino)-2-oxo-2H-chromene-4-carbaldehyde (9)

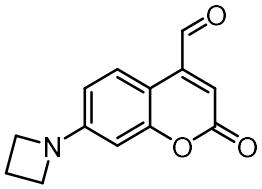


9

Compound **6** (1000.00 mg, 4.32 mmol), SeO_2 (1000.00 mg, 9.00 mmol), and xylene (50 mL) were added to a flame-dried, 250 mL round-bottom flask and refluxed for 24 h at 138 ^{o}C. Subsequently,

the reaction mixture was cooled to rt before being filtered and concentrated using a rotovap. The residue was dissolved in CH_2Cl_2 and dried over anhydrous sodium sulfate (Na_2SO_4). Then, the solvent was removed using a rotovap and transitioned to the next step without further purification.

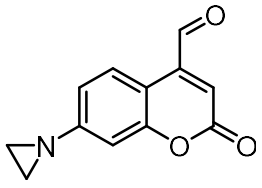
7-Azetidin-1-yl-2-oxo-2H-chromene-4-carbaldehyde (10)



10

Compound **7** (1000.00 mg, 4.36 mmol), SeO_2 (1000.00 mg, 9.00 mmol), and xylene (50 mL) were added to a flame-dried, 250 mL round-bottom flask and refluxed for 24 h at 138 °C. Subsequently, the reaction mixture was cooled to rt before being filtered and concentrated using a rotovap. The residue was dissolved in CH_2Cl_2 and dried over anhydrous Na_2SO_4. Then, the solvent was removed using a rotovap and purified by column chromatography (3:2 Hexane/EtOAc) with a resulting yield of 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 1.7 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.42 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.30 (s, 1H), 3.19 (s, 4H), 2.17 (m, *J* = 2.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.11 (s), 136.49 (s), 129.88 (s), 129.86 (s), 129.60 (s), 129.32 (s), 129.28 (s), 126.04 (s), 125.80 (s), 125.48 (s), 30.84 (s), 19.68 (s).

7-Aziridin-1-yl-2-oxo-2H-chromene-4-carbaldehyde (11)

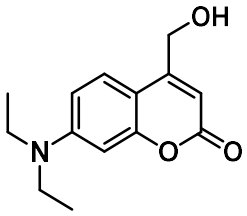


11

Compound **8** (1000.00 mg, 4.65 mmol), SeO_2 (1000.00 mg, 9.00 mmol), and xylene (50 mL) were added to a flame-dried, 250 mL round-bottom flask and refluxed for 24 h at 138 °C. Subsequently, the

reaction was cooled to rt before being filtered and concentrated using a rotovap. The residue was dissolved in CH_2Cl_2 and dried over anhydrous Na_2SO_4. Then, the solvent was removed with the rotovap and purified by column chromatography (3:2 Hexane/EtOAc) with a resulting yield of 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 3.2, 1.2 Hz, 1H), 7.45 (dd, *J* = 4.5, 1.6 Hz, 1H), 7.18 (dd, *J* = 9.0, 1.6 Hz, 1H), 6.31 (s, 1H), 1.57 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.35 (s), 136.55 (s), 129.93 (s), 129.67 (s), 129.39 (s), 128.38 (s), 126.48 (s), 126.11 (s), 125.87 (s), 125.55 (s), 19.77 (s).

7-(Diethylamino)-4-(hydroxymethyl)-2H-chromen-2-one (12)

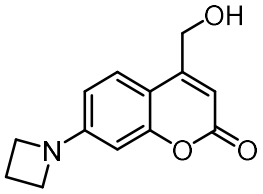


12

Compound **9** (5.29 mmol), the crude product from the previous step, was transferred to a 250 mL round-bottom flask containing $NaBH_4$ (300.00 mg, 7.93 mmol) and subsequently dissolved in 100 mL of anhydrous CH_3OH. Then, the reaction mixture was stirred for 12 h at rt. The reaction was quenched with 1 M HCl, and the product was subsequently extracted with CH_2Cl_2, washed with brine (×2), and dried over anhydrous Na_2SO_4. Then, the solvent was removed using a rotovap. The final product was purified by column chromatography (3:2 Hexane/EtOAc) to produce a dark oil, compound **12**, at a yield of 24% (255.10 mg, 1.03 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 9.0 Hz, 1H), 6.56 (dd, *J* = 6.6, 2.4 Hz, 1H), 6.52 (d, *J* = 2.4 Hz, 1H), 6.25 (s, 1H), 4.83 (s, 2H), 3.41 (q, *J* = 7.0 Hz, 4H), 1.21 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.14 (s), 150.56 (s), 129.02 (s), 128.21 (s), 125.29 (s), 124.35 (s), 108.51 (s), 105.72 (s), 97.91 (s), 61.14 (s), 44.72 (s), 12.43 (s).

7-Azetidin-1-yl-4-hydroxymethyl-chromen-2-one (13)

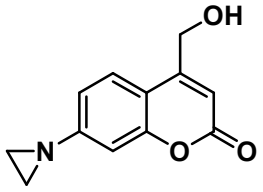


13

Compound **10**, the crude product from the previous step, was transferred to a 250 mL round-bottom flask with $NaBH_4$ (300.00 mg, 7.93 mmol) and dissolved in 100 mL of anhydrous CH_3OH. Then, the reaction was stirred for 12 h at rt. Subsequently, the reaction was quenched with 1 M HCl, and the product was extracted with CH_2Cl_2, washed with brine (×2), and dried over anhydrous Na_2SO_4. The solvent was then removed using a rotovap. The final product was purified by column chromatography (3:2 Hexane/EtOAc) to produce a white powder, compound **13**, at a yield of 25% (305.25 mg, 1.32 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 6.4, 2.2 Hz, 1H), 7.86 – 7.84 (dd, 1H), 6.95 (dd, *J* = 4.3, 2.1 Hz, 1H), 6.93 (s, 1H), 3.85 (s, 2H), 3.27 (t, 4H), 1.32 (t, 2H). ^{13}C NMR (101 MHz, Acetone) δ 162.40 (s), 137.06 (s), 130.59 (s), 130.33 (s), 127.82 (s), 127.67 (s), 127.15 (s), 126.62 (s), 126.47 (s), 65.95 (s), 48.26 (s), 24.28 (s).

7-Aziridin-1-yl-4-hydroxymethyl-chromen-2-one (14)



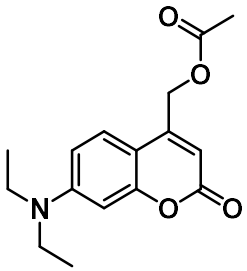
14

Compound **11** (5.29 mmol), the crude product from the previous step, was transferred to a 250 mL, round-bottom flask with $NaBH_4$ (300.00 mg, 7.93 mmol) and dissolved in 100 mL of anhydrous CH_3OH. Then, the reaction was stirred for 12 h at rt. The reaction was quenched with 1 M HCl, and

the product was then extracted with CH_2Cl_2, washed with brine (×2), and dried over anhydrous Na_2SO_4. Subsequently, the solvent was removed using a rotovap. The final product was purified by column chromatography (3:2 Hexane/EtOAc) to produce a white powder, compound **14**, at a yield of 34% (388.82 mg, 1.79 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 5.2, 3.5 Hz, 1H), 7.54 (dd, *J* = 5.4, 3.8 Hz, 1H), 6.98 (d, *J* = 14.9 Hz, 1H), 6.32 (s, 1H), 4.22 (s, *J* = 6.1 Hz, 2H), 2.53 – 2.32 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.49 (s), 132.16 (s), 132.06 (s), 131.92 (s), 131.75 (s), 129.58 (s), 128.56 (s), 128.44 (s), 125.77 (s), 53.40 (s), 19.69 (s).

(7-(Diethylamino)-2-oxo-2H-chromen-4-yl)methyl acetate (15)

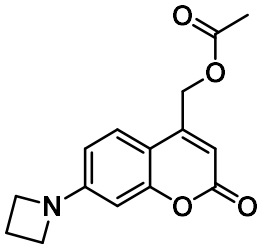


15

Compound **12** (255.10 mg, 1.03 mmol), EDC (300.00 mg, 1.54 mmol), and DMAP (200.00 mg, 1.54 mmol) were added to a flame-dried, 100 mL round-bottom flask with 10 mL of dry CH_2Cl_2. After the dissolution of all components, acetic acid (0.09 mL, 1.54 mmol) was added to the reaction mixture, which was stirred in the dark for 18 h under an Ar atmosphere. Finally, the reaction mixture was diluted with excess CH_2Cl_2, washed with sodium bicarbonate ($NaHCO_3$, ×2) and brine (×2), then dried over anhydrous Na_2SO_4. The TLC (3:2 Hexane/EtOAc) results showed a single spot after the extraction. Hence, we decided to move to the next step without further purification. The crude product was dried using a rotovap to produce an orange powder, compound **15**, at a yield of 95% (283.54 mg, 0.98 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.0 Hz, 1H), 6.58 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.52 (d, *J* = 2.5 Hz, 1H), 6.14 (s, 1H), 5.22 (s, *J* = 1.1 Hz, 2H), 3.42 (q, *J* = 7.1 Hz, 4H), 2.19 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170. 23 (s), 161.83 (s), 156.30 (s), 150.71 (s), 149.34 (s), 128.22 (s), 124.36 (s), 108.66 (s), 106.56 (s), 106.05 (s), 61.34 (s), 44.75 (s), 20.72 (s), 12.42 (s).

(7-(Azetidin-1-yl)-2-oxo-2H-chromen-4-yl)methyl acetate (16)

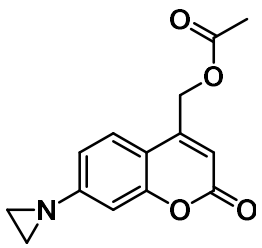


16

Compound **13** (238.18 mg, 1.03 mmol), EDC (300.00 mg, 1.54 mmol), and DMAP (200.00 mg, 1.54 mmol) were added to a flame-dried, 100 mL round-bottom flask with 10 mL of dry CH_2Cl_2. After the dissolution of all components, acetic acid 0.09 mL (1.54 mmol) was added to the reaction mixture, which was stirred in the dark for 18 h under an Ar atmosphere. Finally, the reaction mixture was diluted with excess CH_2Cl_2, washed with sodium bicarbonate ($NaHCO_3$, ×2) and brine (×2), then dried over anhydrous Na_2SO_4. The TLC (3:2 Hexane/EtOAc) results showed a single spot after the extraction. Hence, we decided to move to the next step without further purification. The crude product was dried using a rotovap to produce a dark yellow powder, compound **16**, at a yield of 80% (223.94 mg, 0.82 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.4 Hz, 1H), 8.07 (dd, *J* = 13.8, 8.5 Hz, 1H), 6.90 (d, *J* = 5.8 Hz, 1H), 6.67 (s, 1H), 3.83 (s, 2H), 3.21 (s, 4H), 2.51 (m, 2H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, Acetone) δ 206.99 (s), 163.27 (s), 137.92 (s), 131.46 (s), 131.20 (s), 128.69 (s), 128.54 (s), 128.01 (s), 127.49 (s), 127.34 (s), 66.82 (s), 55.80 (s), 25.15 (s), 20.62 (s).

(7-(Aziridin-1-yl)-2-oxo-2H-chromen-4-yl)methyl acetate (17)

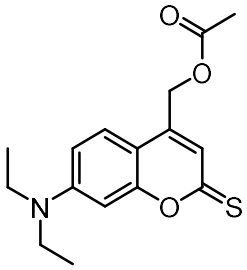


17

Compound **14** (223.73 mg, 1.03 mmol), EDC (300.00 mg, 1.54 mmol), and DMAP (200.00 mg, 1.54 mmol) were added to a flame-dried, 100 mL round-bottom flask with 10 mL of dry CH_2Cl_2. After the dissolution of all components, 0.09 mL of acetic acid (1.54 mmol) was added to the reaction mixture and stirred in the dark for 18 h under an Ar atmosphere. Finally, the reaction mixture was diluted with excess CH_2Cl_2, washed with sodium bicarbonate ($NaHCO_3$, ×2) and brine (×2), then dried over anhydrous Na_2SO_4. The TLC (3:2 Hexane/EtOAc) results showed a single spot after the extraction. Hence, we decided to proceed to the next step without further purification. The crude product was dried using a rotovap to produce a dark yellow powder, compound **17**, at a yield of 70% (186.67 mg, 0.72 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 10.5 Hz, 1H), 7.02 (d, *J* = 6.9 Hz, 1H), 6.82 (s, 1H), 4.25 (s, 2H), 2.64 (s, 3H), 1.33 – 1.13 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.19 (s), 136.15 (s), 133.51 (s), 128.52 (s), 128.49 (s), 128.24 (s), 128.18 (s), 127.02 (s), 126.29 (s), 118.48 (s), 67.13 (s), 62.01 (s), 22.78 (s).

(7-(Diethylamino)-2-thioxo-2H-chromen-4-yl)methyl acetate (18)

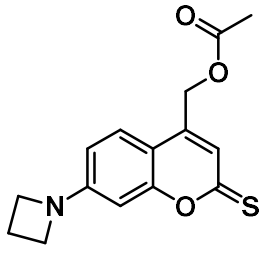


18

The crude product, **15** (298.01 mg, 1.03 mmol), was transferred to a flame-dried, 100 mL round-bottom flask and refluxed (110 °C) with Lawesson's reagent (300.00 mg, 0.72 mmol) in toluene (35 mL) for 24 h in the dark under N_2. After completion of this step, the toluene was removed using a rotovap. The product was purified by column chromatography (95:5 CH_2Cl_2/CH_3OH) to produce an orange powder, compound **18**, at a yield of 90% (284.01 mg, 0.93 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.9 Hz, 1H), 7.26 (d, *J* = 0.7 Hz, 1H), 7.07 (s, 1H), 6.68 (dd, *J* = 5.5, 2.4 Hz, 1H), 6.65 (d, *J* = 2.5 Hz, 1H), 5.19 (s, 2H), 3.43 (q, *J* = 7.1 Hz, 4H), 2.19 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.21 (s), 170.23 (s), 159.06 (s), 151.03 (s), 141.77 (s), 124.44 (s), 120.66 (s), 110.28 (s), 108.22 (s), 97.52 (s), 60.97 (s), 44.93 (s), 20.74 (s), 12.40 (s).

(7-(Azetidin-1-yl)-2-thioxo-2H-chromen-4-yl)methyl acetate (19)



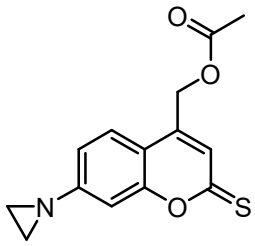
19

The crude product, **16** (281.50 mg, 1.03 mmol), was transferred to a flame-dried, 100 mL round-bottom flask and refluxed (110 °C) with Lawesson's reagent (300.00 mg, 0.72 mmol) in toluene (35 mL) for 24 h in the dark under N_2. After completion of this step, the toluene was removed using a

rotovap. The product was purified by column chromatography (95:5 CH_2Cl_2/CH_3OH) to produce a yellow powder, compound **19**, at a yield of 85% (251.50 mg, 0.87 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 3.6, 1.8 Hz, 1H), 8.07 (dd, *J* = 13.9, 8.6 Hz, 1H), 6.90 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.67 (s, 1H), 3.83 (s, 2H), 3.23 – 3.17 (m, 4H), 2.18 (m, 2H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, Acetone) δ 179.04 (s), 156.67 (s), 137.05 (s), 130.59 (s), 130.33 (s), 129.79 (s), 127.82 (s), 127.67 (s), 126.62 (s), 126.47 (s), 65.95 (s), 54.93 (s), 25.82 (s), 19.76 (s).

(7-(Aziridin-1-yl)-2-thioxo-2H-chromen-4-yl)methyl acetate (20)

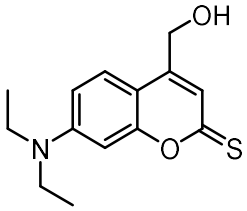


20

The crude product, **17** (267.04 mg, 1.03 mmol), was transferred to a flame-dried, 100 mL round-bottom flask and refluxed (110 °C) with Lawesson's reagent (300.00 mg, 0.72 mmol) in toluene (35 mL) for 24 h in the dark under N_2. After completion of this step, the toluene was removed using a rotovap. The product was purified by column chromatography (95:5 CH_2Cl_2/CH_3OH) to produce a yellow powder, compound **20**, at a yield of 82% (231.27 mg, 0.84 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.81 (dd, *J* = 7.7, 6.6 Hz, 1H), 7.54 (dd, *J* = 13.9, 5.9 Hz, 1H), 7.00 (s, 1H), 4.13 (s, 2H), 2.48 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.20 (s), 168.24 (s), 153.21 (s), 142.32 (s), 137.87 (s), 132.49 (s), 129.03 (s), 128.22 (s), 125.30 (s), 108.48 (s), 29.69 (s), 21.44 (s).

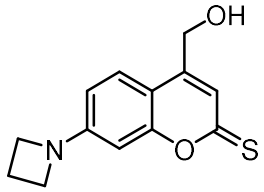
7-(Diethylamino)-4-(hydroxymethyl)-2H-chromene-2-thione (21)



21

Compound **18** (284.01 mg, 0.93 mmol), 2.5 mL of ethanolic HCl solution (1.25 M), and 70 mL of absolute EtOH were added to a flame-dried, 250 mL round-bottom flask. Subsequently, the mixture was refluxed at 50 °C for 24 h in the dark under N_2. After cooling of the reaction mixture, the solvent was removed using a rotovap, and the product was purified by column chromatography (95:5 CH_2Cl_2/CH_3OH) to produce a yellow powder, compound **21**, at a yield of 98% (239.65 mg, 0.91 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 9.0 Hz, 1H), 7.18 (s, 2H), 6.68 (d, *J* = 2.5 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.81 (s, *J* = 4.8 Hz, 2H), 3.43 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.66 (s), 159.05 (s), 150.90 (s), 146.43 (s), 129.03 (s), 128.22 (s), 124.59 (s), 120.11 (s), 110.16 (s), 60.89 (s), 44.90 (s), 12.41 (s). MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{14}H_{17}NO_2S^+$ 264.2, found 264.2.

7-Azetidin-1-yl-4-hydroxymethyl-chromene-2-thione (22)

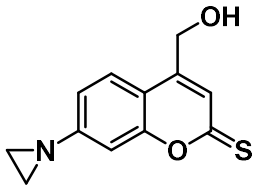


22

Compound **19** (269.10 mg, 0.93 mmol), 2.5 mL of ethanolic HCl solution (1.25 M), and 70 mL of absolute EtOH was added to a flame-dried, 250 mL round-bottom flask. Subsequently, the mixture was refluxed at 50 °C for 24 h in the dark under N_2. After cooling of the reaction mixture, the solvent

was removed using a rotovap, and the product was purified by column chromatography (95:5 CH_2Cl_2/CH_3OH) to produce a yellow powder, compound **22**, at a yield of 95% (217.63 mg, 0.88 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 10.4, 5.4 Hz, 1H), 7.87 (dd, *J* = 13.6, 8.9 Hz, 1H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 1H), 6.69 (s, 1H), 4.19 (s, 2H), 3.93 – 3.71 (m, 4H), 3.35 – 3.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.72 (s), 142.45 (s), 140.16 (s), 132.11 (s), 132.09 (s), 131.96 (s), 130.49 (s), 128.56 (s), 124.97 (s), 53.40 (s), 20.01 (s), 19.85 (s). MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{13}H_{13}NO_2S^+$ 247.1, found 247.1.

7-Aziridin-1-yl-4-hydroxymethyl-chromene-2-thione (23)

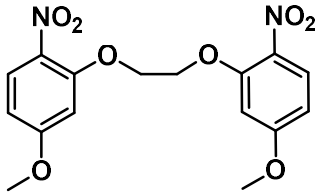


23

Compound **20** (256.05 mg, 0.93 mmol), 2.5 mL of ethanolic HCl solution (1.25 M), and 70 mL of absolute EtOH were added to a flame-dried, 250 mL round-bottom flask. Subsequently, the mixture was refluxed at 50 °C for 24 h in the dark under N_2. After cooling of the reaction mixture, the solvent was removed using a rotovap, and the product was purified by column chromatography (95:5 CH_2Cl_2/CH_3OH) to produce a yellow powder, compound **23**, at a yield of 87% (188.95 mg, 0.81 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 13.3, 8.5 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 5.3 Hz, 1H), 6.33 (s, 1H), 3.81 (s, 2H), 3.17 (s, 1H), 1.24 (t, *J* = 7.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.72 (s), 133.38 (s), 133.24 (s), 129.03 (s), 128.22 (s), 125.82 (s), 125.29 (s), 116.29 (s), 113.87 (s), 58.47 (s), 18.36 (s). MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{12}H_{11}NO_2S^+$ 233.1, found 233.1.

3. Synthesis of the Chelator (BAPTA Moiety)

1,2-Bis(5-methoxy-2-nitrophenoxy)ethane (26)

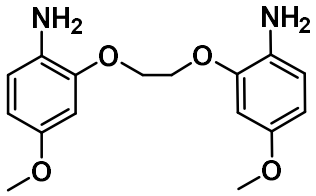


26

Compound **24** (200.00 mg, 1.18 mmol), K_2CO_3 (332.00 mg, 2.40 mmol), and DMF (5 mL) were added to a flame-dried, 100 mL round-bottom flask and stirred for 5 min under an N_2 atmosphere. During stirring of the reaction mixture, 0.05 mL of compound **25** (111.00 mg, 0.60 mmol) was added. Then, the reaction was refluxed (100 °C) under N_2 for 40 h. Following this step, H_2O was added, and a precipitate was formed. The precipitate was recrystallized with EtOH to produce yellow-colored crystals, compound **26**, at a yield of 45% (193.08 mg, 0.53 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.1 Hz, 2H), 6.68 (d, *J* = 2.5 Hz, 2H), 6.58 (dd, *J* = 9.2, 2.5 Hz, 2H), 4.53 (s, 4H), 3.91 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.81, 154.73, 128.13, 106.56, 101.60, 68.99, 56.09. HRMS (DART-AccuTOF) m/z [M+H]+ cacld for $C_{16}H_{17}N_2O_8$ 365.0979, found 365.0656.

2,2'-(Ethane-1,2-diylbis(oxy))bis(4-methoxyaniline) (27)



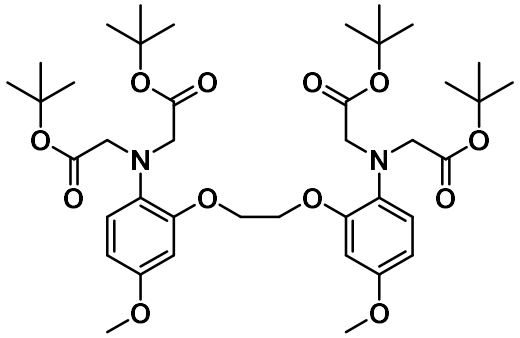
27

The product, **26** (83.40 mg, 0.23 mmol), was transferred to a flame-dried, 25 mL round-bottom flask with Pd/C (10.00 mg, 0.09 mmol) and kept under an H_2 atmosphere for 15 min. Then, 5 mL of EtOH and EtOAc mixture (1:1) (purged with N_2 to remove O_2) was added. The reaction mixture was stirred for 12 h under an H_2 atmosphere. Finally, the reaction mixture was filtered with Celite 545, and the

solvent was removed using a rotovap to produce compound **27** at a yield of 90% (63.91 mg, 0.21 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (d, *J* = 8.5 Hz, 2H), 6.50 (d, *J* = 2.6 Hz, 2H), 6.39 (dd, *J* = 8.5, 2.6 Hz, 2H), 4.34 (s, 4H), 3.75 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.97, 147.11, 130.34, 115.65, 105.44, 100.99, 67.35, 55.83.

Tetra-tert-butyl 2,2',2'',2'''-(((ethane-1,2-diylbis(oxy))bis(4-methoxy-2,1-phenylene))bis(azanetriyl))tetraacetate (29)

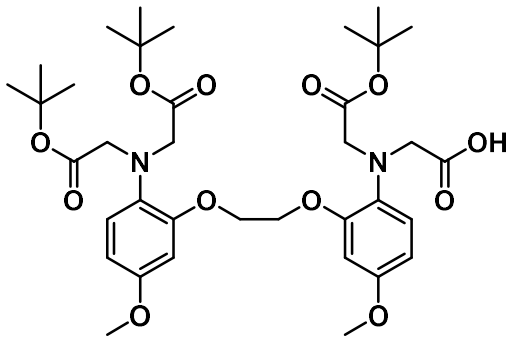


29

Compound **27** (11.00 mg, 0.04 mmol), compound **28** (0.08 mmol), proton sponge (60.00 mg, 0.28 mmol), NaI (10.00 mg, 0.07 mmol), and 2 mL of anhydrous ACN were added to a new, 1-dram amber vial. Then, the vial was capped and heated to 80 °C on a heating block for 24 h with continuous stirring. After cooling, the reaction mixture was diluted with excess CH_2Cl_2, washed with H_2O (×2) and brine (×2), then dried over anhydrous Na_2SO_4. Subsequently, the solvent was removed using a rotovap. The final product was purified by column chromatography (2:1 Hexane/EtOAc) to yield compound **29** at a yield of 95% (28.91 mg, 0.038 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, *J* = 8.7 Hz, 2H), 6.53 (s, 2H), 6.43 (d, *J* = 8.7 Hz, 2H), 4.37 (s, 4H), 3.99 (s, 8H), 3.74 (s, 6H), 1.40 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.51, 155.66, 151.95, 133.19, 121.23, 105.32, 102.52, 80.92, 67.44, 55.51, 54.79, 28.12. MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{40}H_{66}N_2NaO_{12}^+$ 784.3, found 784.3.

N-(2-(2-(2-(Bis(2-(tert-butoxy)-2-oxoethyl)amino)-5-methoxyphenoxy)ethoxy)-4-methoxyphenyl)-N-(2-(tert-butoxy)-2-oxoethyl)glycine (30)



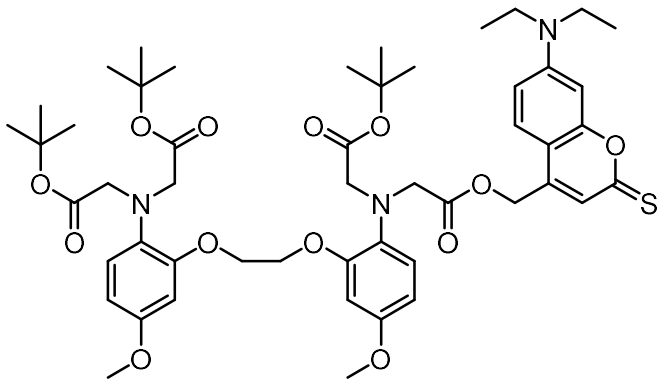
30

The product, **29** (10.30 mg, 0.013 mmol), was transferred to a new, 1-dram amber vial, and 1 mL of TFA was added. The reaction mixture was continuously stirred for 1 h at 0 °C. Finally, TFA was removed by N_2 air flow and further dried with a vacuum to generate compound **30** at a yield of 90% (08.25 mg, 0.0117 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.9 Hz, 2H), 6.68 (s, 2H), 6.58 (d, *J* = 10.8 Hz, 2H), 4.61 (s, 4H), 4.47 (s, 6H), 3.82 (s, 8H), 1.33 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.36, 159.93, 151.46, 116.64, 113.78, 106.66, 106.57, 106.22, 100.63, 100.52, 85.46, 67.39, 67.25, 57.40, 55.82, 55.74, 30.61, 29.69, 27.62. MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{36}H_{53}N_2O_{12}^+$ 705.3, found 705.3.

4. Photocaging of the BAPTA Moiety

Di-tert-butyl 2,2'-((2-(2-(2-((2-(tert-butoxy)-2-oxoethyl)(2-((7-(diethylamino)-2-thioxo-2H-chromen-4-yl)methoxy)-2-oxoethyl)amino)-5-methoxyphenoxy)ethoxy)-4-methoxyphenyl)azanediyl)diacetate (31)

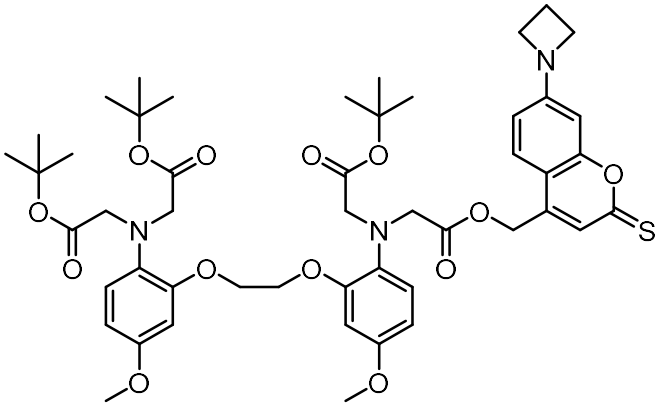


31

Compound **30** (09.00 mg, 0.013 mmol), EDC (03.00 mg, 0.02 mmol), DMAP (01.00 mg, 0.0001 mmol), and 3 mL of dry CH_2Cl_2 were added to a flame-dried, 25 mL round-bottom flask and stirred for 15 min under an Ar atmosphere until complete dissolution had occurred. Then, compound **21** (03.00 mg, 0.013 mmol) dissolved in 1 mL of CH_2Cl_2 was added dropwise, and the reaction was stirred at rt for 48 h under an Ar atmosphere. Subsequently, excess CH_2Cl_2 was added to the reaction mixture, which was then washed with $NaHCO_3$ (×2) and brine (×2) and dried over anhydrous Na_2SO_4. After the solvent was removed using a rotovap, it was purified via column chromatography (2:1 Hexane/EtOAc) to produce a brown oil, compound **31**, at a yield of 40% (05.22 mg, 0.0055 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.5 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.1 Hz, 1H), 7.66 (dd, *J* = 13.1, 5.1 Hz, 1H), 7.21 (s, 1H), 6.72 (d, *J* = 7.5 Hz, 2H), 6.39 (s, 2H), 4.11 (s, 2H), 3.35 (s, 4H), 3.24 (s, 8H), 2.82 (s, 6H), 2.44 – 2.32 (m, 4H), 1.56 (s, 27H), 1.12 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.58 (s), 190.08 (s), 169.60 (s), 158.43 (s), 150.40 (s), 141.14 (s), 131.10 (s), 128.39 (s), 127.58 (s), 124.66 (s), 124.56 (s), 123.81 (s), 120.03 (s), 119.98 (s), 116.11 (s), 109.65 (s), 107.59

(s), 96.89 (s), 95.18 (s), 60.34 (s), 44.30 (s), 37.47 (s), 30.25 (s), 20.80 (s), 20.11 (s), 15.62 (s), 11.77 (s). MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{50}H_{67}N_3NaO_{13}S^+$ 972.3, found 972.3.

{[2-(2-{2-[(7-Azetidin-1-yl-2-thioxo-2H-chromen-4-ylmethoxycarbonylmethyl)-tert-butoxycarbonylmethyl-amino]-5-methoxy-phenoxy}-ethoxy)-4-methoxy-phenyl]-tert-butoxycarbonylmethyl-amino}-acetic acid tert-butyl ester (32)



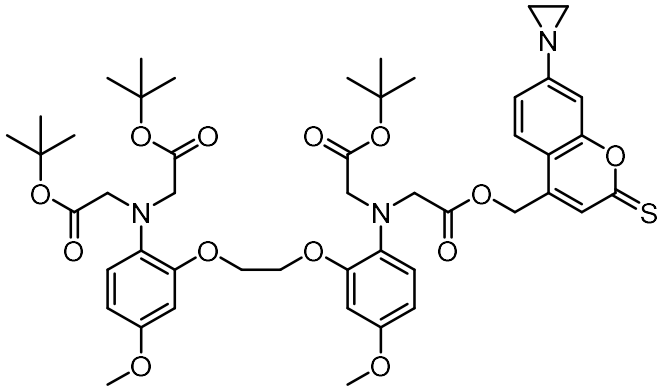
32

Compound **30** (09.00 mg, 0.013 mmol), EDC (03.00 mg, 0.02 mmol), DMAP (01.00 mg, 0.0001 mmol), and 3 mL of dry CH_2Cl_2 were added to a flame-dried, 25 mL round-bottom flask and stirred for 15 min under Ar until complete dissolution had occurred. Then, compound **22** (03.21 mg, 0.013 mmol) dissolved in 1 mL of CH_2Cl_2 was added dropwise, and the reaction mixture was stirred at rt for 48 h under an Ar atmosphere. Subsequently, excess CH_2Cl_2 was added to the reaction, which was then washed with $NaHCO_3$ (×2) and brine (×2) and dried over anhydrous Na_2SO_4. After the solvent was removed using a rotovap, it was purified via column chromatography (2:1 Hexane/EtOAc) to produce a brown oil, compound **32**, at a yield of 45% (05.42 mg, 0.0058 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 5.1, 2.1 Hz, 1H), 7.86 (s, 1H), 7.63 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.51 (d, *J* = 1.7 Hz, 2H), 7.44 (d, *J* = 4.6 Hz, 2H), 7.16 (dd, *J* = 5.7, 3.1 Hz, 1H), 6.30 (s, 2H), 4.42 (s, 2H), 3.48 (s, 4H), 3.19 (s, 8H), 2.95 (s, 6H), 2.84 (s, 4H), 1.67 (t, 2H), 1.25 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.23 (s), 181.72 (s), 161.34 (s), 160.99 (s), 160.62 (s), 157.36 (s), 144.29 (s), 139.42 (s), 135.53 (s), 129.52 (s), 128.77 (s), 127.13 (s), 121.24 (s), 118.78 (s), 117.80 (s), 114.91 (s), 106.78

(s), 55.54 (s), 55.22 (s), 53.42 (s), 46.65 (s), 42.84 (s), 40.00 (s), 29.65 (s), 27.92 (s), 25.42 (s), 15.21 (s). MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{49}H_{63}N_3O_{13}S^+$ 934.4, found 935.4.

{[2-(2-{2-[(7-Aziridin-1-yl-2-thioxo-2H-chromen-4-ylmethoxycarbonylmethyl)-tert-butoxycarbonylmethyl-amino]-5-methoxy-phenoxy}-ethoxy)-4-methoxy-phenyl]-tert-butoxycarbonylmethyl-amino}-acetic acid tert-butyl ester (33)



33

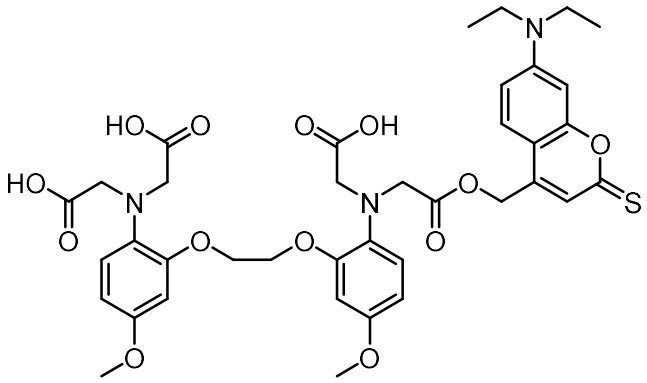
Compound **30** (09.00 mg, 0.013 mmol), EDC (03.00 mg, 0.02 mmol), DMAP (01.00 mg, 0.0001 mmol), and 3 mL of dry CH_2Cl_2 were added to a flame-dried, 25 mL round-bottom flask and stirred for 15 min under an Ar atmosphere until complete dissolution had occurred. Then, compound **23** (03.03 mg, 0.013 mmol) dissolved in 1 mL of CH_2Cl_2 was added dropwise, and the reaction mixture was stirred at rt for 48 h under an Ar atmosphere. Subsequently, excess CH_2Cl_2 was added to the reaction mixture, which was then washed with $NaHCO_3$ (×2) and brine (×2) and dried over anhydrous Na_2SO_4. After the solvent was removed using a rotovap, it was purified via column chromatography (2:1 Hexane/EtOAc) to produce a brown oil, compound **33**, at a yield of 32% (03.87 mg, 0.0042 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 11.8, 8.7 Hz, 1H), 7.72 (dd, *J* = 12.2, 8.2 Hz, 1H), 7.24 (s, 1H), 7.18 (d, *J* = 7.0 Hz, 2H), 6.90 (dd, *J* = 8.8, 5.1 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 2H), 6.69 (s, 2H), 4.37 (s, 2H), 3.99 (s, 4H), 3.78 (s, 8H), 3.31 (s, 6H), 1.26 (t, 4H), 1.08 (s, 27H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.63 (s), 191.40 (s), 182.73 (s), 156.75 (s), 154.63 (s), 141.30 (s), 137.86 (s), 132.87 (s), 132.70 (s), 129.02 (s), 128.21 (s), 125.29 (s), 115.24 (s), 113.17 (s), 113.10 (s),

113.03 (s), 106.57 (s), 83.57 (s), 55.15 (s), 43.04 (s), 39.88 (s), 34.82 (s), 30.88 (s), 28.11 (s), 25.22 (s), 15.63 (s). MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{48}H_{61}N_3O_{13}S^+$ 919.0, found 919.0.

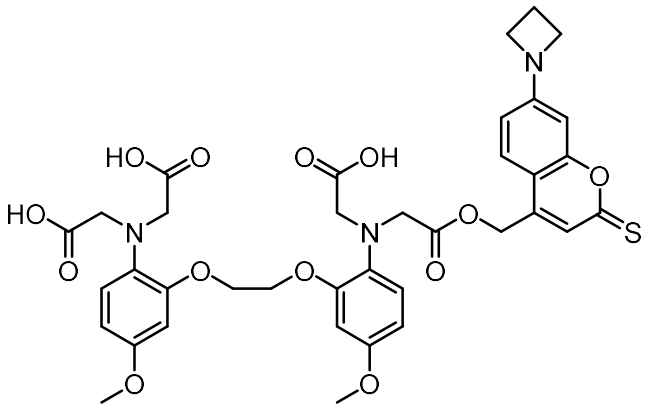
2,2'-((2-(2-(2-((Carboxymethyl)(2-((7-(Diethylamino)-2-thioxo-2H-chromen-4-yl)methoxy)-2-oxoethyl)amino)-5-methoxyphenoxy)ethoxy)-4-methoxyphenyl)azanediyl)diacetic acid (1)



1

The product from the previous step, **31** (5 mg, 0.0053 mmol), was transferred to a new amber vial. 1 mL of TFA was added, and the reaction mixture was stirred for 48 h. Finally, the TFA was removed using a vacuum and flow of N_2. The product was purified via column chromatography (5:3 Hexane/EtOAc) to produce a dark oil, caged compound **1**, at a yield of 42%. (1.73 mg, 0.0022 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.5 Hz, 2H), 7.94 (dd, *J* = 5.9, 5.0 Hz, 1H), 7.73 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.64 (dd, *J* = 11.9, 4.2 Hz, 1H), 7.00 (s, 1H), 6.71 (d, *J* = 7.4 Hz, 2H), 6.52 (s, 2H), 4.11 (s, 2H), 3.36 (s, 4H), 3.24 (s, 8H), 2.81 (s, 6H), 2.07 – 1.90 (m, 4H), 1.34 – 1.20 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.21 (s), 190.72 (s), 170.23 (s), 159.06 (s), 151.03 (s), 141.77 (s), 131.73 (s), 129.02 (s), 128.21 (s), 125.29 (s), 125.19 (s), 124.44 (s), 120.66 (s), 120.61 (s), 116.74 (s), 110.28 (s), 108.22 (s), 97.52 (s), 95.81 (s), 60.97 (s), 44.93 (s), 30.88 (s), 21.43 (s), 20.74 (s), 12.40 (s). HRMS m/z $[M]^-$ cacld for $C_{38}H_{40}N_3O_{13}S^{3-}$ 778.8076, found 778.8076.

{[2-(2-{2-[(7-Azetidin-1-yl-2-thioxo-2H-chromen-4-ylmethoxycarbonylmethyl)-carboxymethyl-amino]-5-methoxy-phenoxy}-ethoxy)-4-methoxy-phenyl]-carboxymethyl-amino}-acetic acid (2)



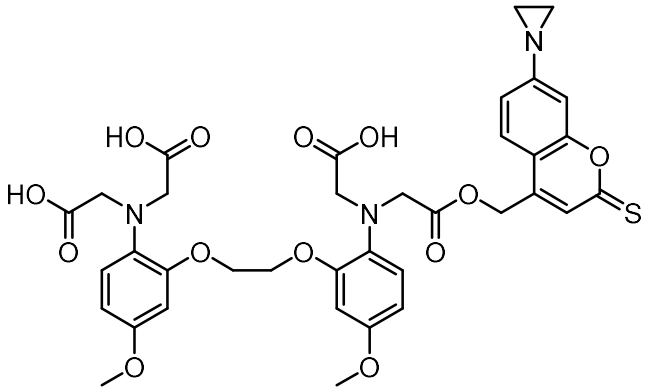
2

The product from the previous step, **32** (5 mg, 0.0053 mmol), was transferred to a new amber vial. 1 mL of TFA was added, and the reaction mixture was stirred for 48 h. Finally, the TFA was removed using a vacuum and flow of N_2. The product was purified via column chromatography (5:3 Hexane/EtOAc) to produce a dark yellow oil, caged compound **2**, at a yield of 40% (1.61 mg, 0.0021 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.68 (t, *J* = 7.9 Hz, 2H), 7.52 (s, 1H), 6.99 (dd, *J* = 13.5, 7.7 Hz, 1H), 6.72 (dd, *J* = 6.0, 0.6 Hz, 1H), 4.22 (s, 2H), 3.24 (s, 4H), 3.20 (s, 8H), 3.20 (s, 6H), 2.82 (t, 4H), 2.35 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.65 (s), 163.29 (s), 161.34 (s), 160.99 (s), 160.62 (s), 157.36 (s), 144.29 (s), 139.42 (s), 135.53 (s), 129.52 (s), 128.77 (s), 127.13 (s), 121.24 (s), 118.78 (s), 117.80 (s), 114.91 (s), 106.78 (s), 55.68 (s), 55.54 (s), 55.22 (s), 53.42 (s), 46.65 (s), 42.84 (s), 27.92 (s), 25.42 (s). HRMS *m/z* $[M]^-$ cacld for $C_{37}H_{36}N_3O_{13}S^{3-}$ 762.7646, found 762.7646.

{[2-(2-{2-[(7-Aziridin-1-yl-2-thioxo-2H-chromen-4-ylmethoxycarbonylmethyl)-carboxymethyl-amino]-5-methoxy-phenoxy}-ethoxy)-4-methoxy-phenyl]-carboxymethyl-amino}-acetic acid (3)



3

The product from the previous step, compound **33** (3.8 mg, 0.0041 mmol), was transferred to a new amber vial. 1 mL of TFA was added, and the reaction mixture was stirred for 48 h. Finally, the TFA was removed using a vacuum and flow of N_2. The product was purified via column chromatography (5:3 Hexane/EtOAc) to produce a dark yellow oil, caged compound **3**, at a yield of 44% (1.35 mg, 0.0018 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 11.7, 8.7 Hz, 1H), 7.72 (dd, *J* = 4.1, 1.8 Hz, 2H), 7.24 (s, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.89 (dd, *J* = 8.7, 6.1 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 2H), 6.69 (s, 2H), 4.37 (s, 2H), 3.99 (s, 4H), 3.78 (s, 8H), 3.31 (s, 6H), 2.07 – 1.87 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.63 (s), 191.40 (s), 182.73 (s), 156.75 (s), 154.63 (s), 141.30 (s), 137.86 (s), 132.87 (s), 132.70 (s), 129.02 (s), 128.21 (s), 125.29 (s), 113.17 (s), 113.10 (s), 113.03 (s), 106.57 (s), 101.71 (s), 83.57 (s), 55.15 (s), 43.04 (s), 39.88 (s), 34.82 (s), 30.88 (s), 28.11 (s). HRMS *m/z* $[M]^-$ cacld for $C_{36}H_{34}N_3O_{13}S^{3-}$ 748.7376, found 748.7376.

5. UV Spectra Illustrating Gradual Photolysis of the Caged Molecules.

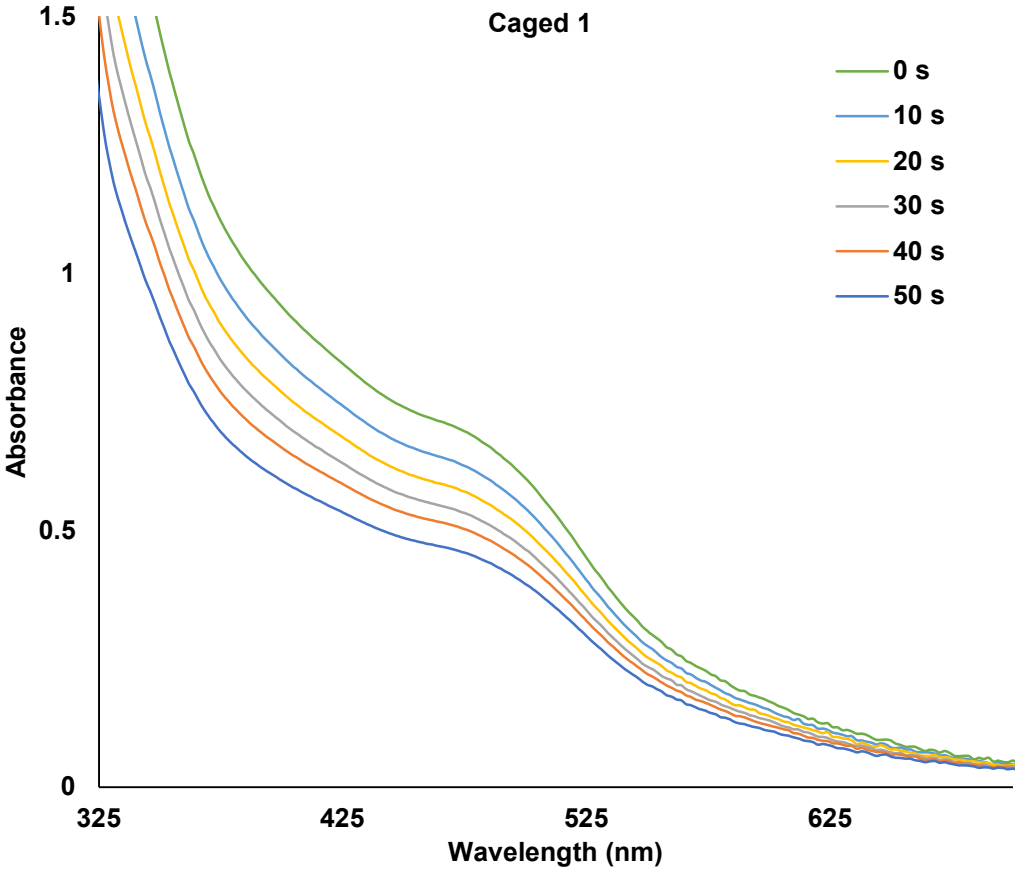


Figure S1. UV spectra for the progressive photolysis of caged **1** [30 μM].

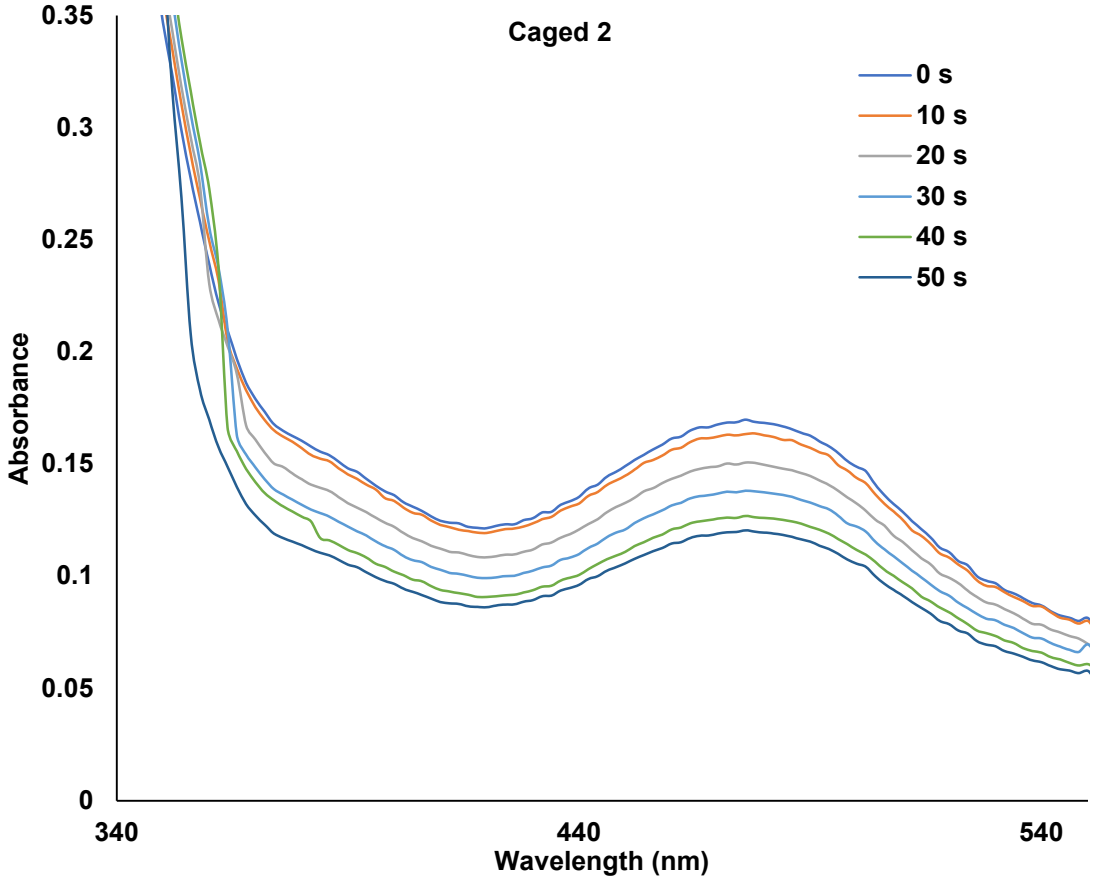


Figure S2. UV spectra for the progressive photolysis of caged **2** [8 μM].

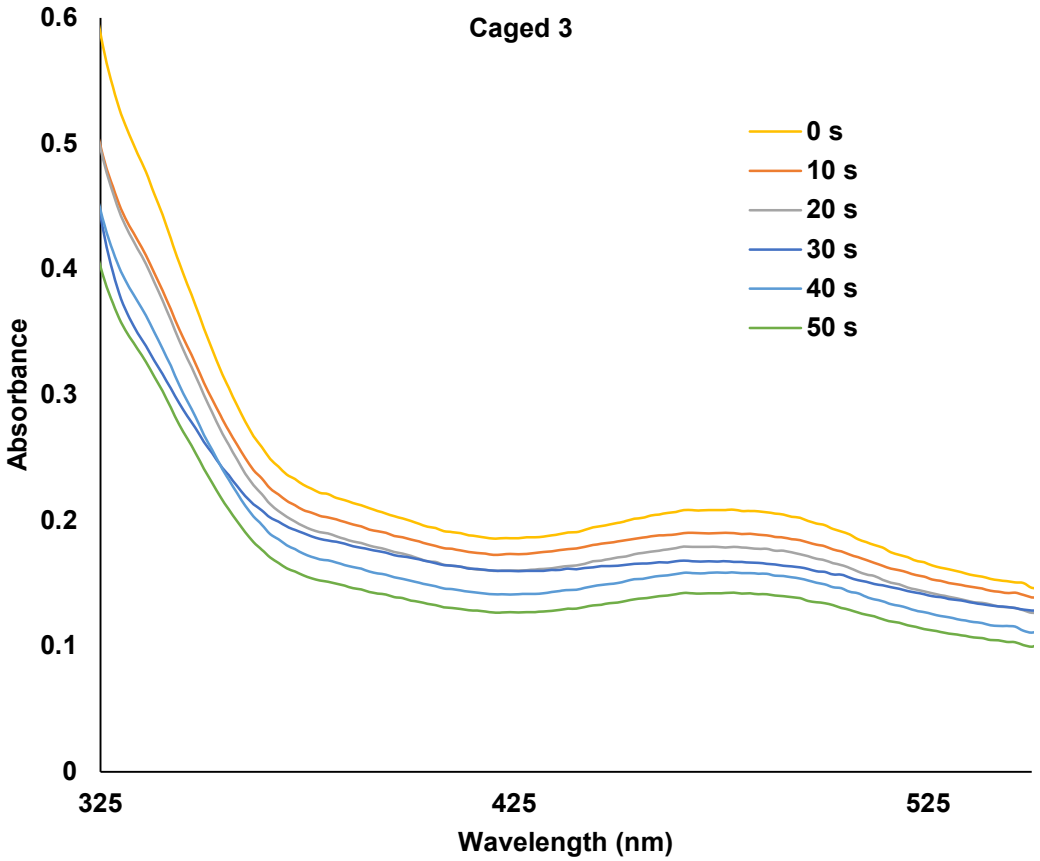


Figure S3. UV spectra for the progressive photolysis of caged **3** [13 μM].

6. Titrimetric Calcium Assay

Table S1. Titrimetric calcium assay results.

Ligand	[LX]/μM	[L]0/μM	[X]0/μM	[L]0[X]0/[LX]	K/μM^{-1}
Dimethoxy-BAPTA	2.164	2.5	2.5	2.888170055	19.168
Caged1	0.00024	2.5	2.5	26595.74468	3.7607E-05
Caged 2	0.00020	2.5	2.5	31407.03518	3.1845E-05
Caged 3	0.00016	2.5	2.5	39062.5	2.5603E-05

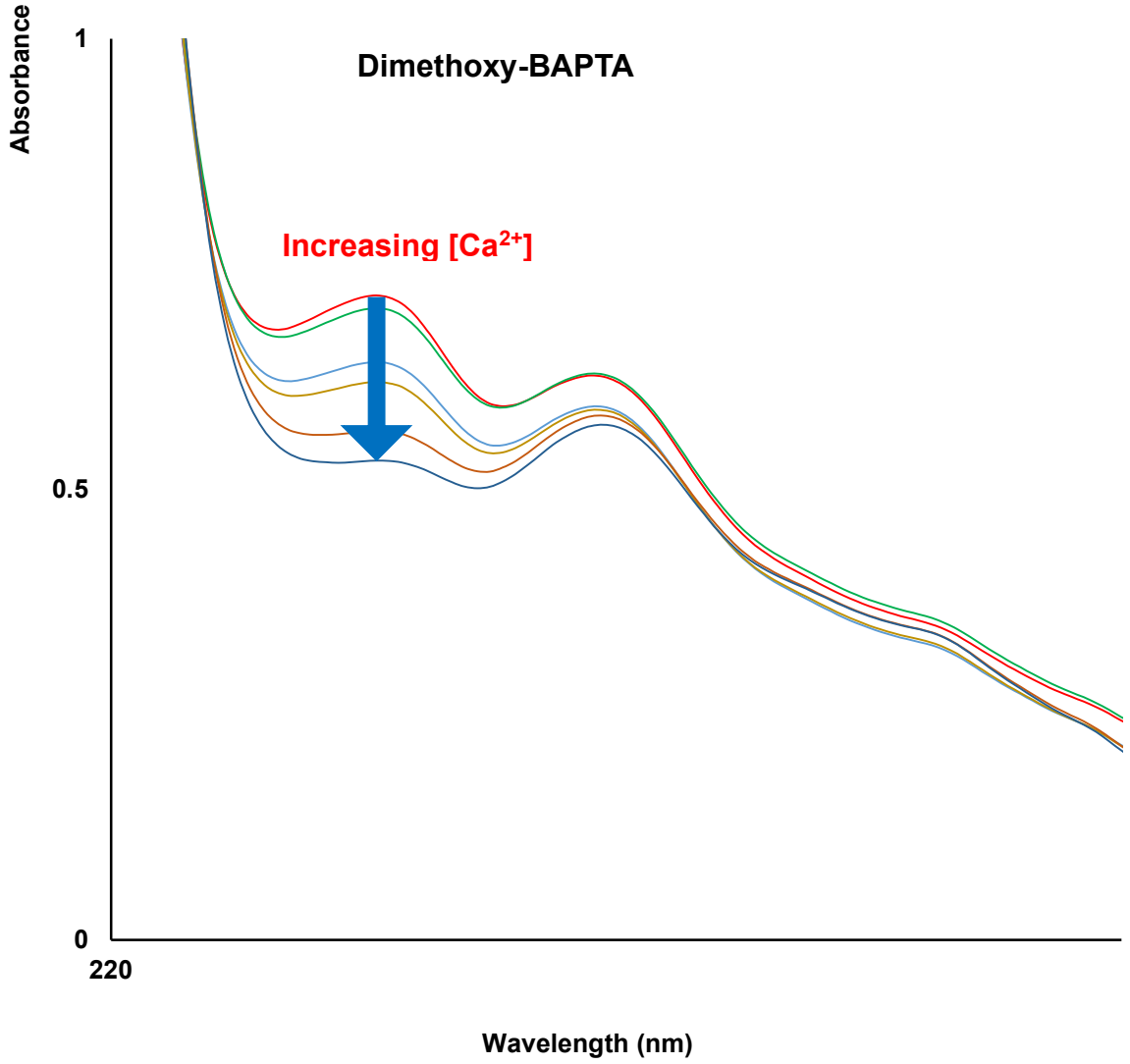


Figure S4. UV spectra of 2.5 μM aqueous solution of potassium salt of BAPTA at pH=7.4 at variable Ca^{2+} concentrations in the mixture.

7. General Procedure and Actinometry Analysis

In this study, a liquid-phase potassium ferrioxalate actinometer was prepared to measure the intensity of the light irradiation (light flux) necessary for quantum yield measurements in various photochemical reactions. The actinometer was synthesized by dissolving 6.0 g of ammonium ferrous sulfate hexahydrate in a beaker containing 20 mL of water and 1 mL of 3 M sulfuric acid. Separately, 3.5 g of oxalic acid dihydrate was mixed with 35 mL of water and heated until dissolution. Next, 20 mL of the oxalic acid solution was added dropwise to the ammonium ferrous sulfate solution, which was then heated to 100 °C. After cooling, the precipitate was filtered and mixed with 15 mL of saturated potassium oxalate. During heating to approximately 40 °C, 12 mL of 6% hydrogen peroxide was added dropwise to the mixture with continuous stirring. After completion of the reaction, the solution was boiled to remove excess hydrogen peroxide, and the compound from the second step was added until the solution turned green and lucent. Following cooling of the reaction mixture, 15 mL of 95% ethanol (EtOH) was added to promote crystallization. The solution was kept in the dark and subsequently filtered. The resulting solid was recrystallized three times in water, yielding $K_3Fe(C_2O_4)_3 \cdot 3H_2O$. To prepare a 100 mL, 0.15 M solution of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$, 7.36 g of the purified crystals were dissolved in 80 mL water, and 10 mL of 1.0 N sulfuric acid was added. Subsequently, the reaction mixture was transferred to a 100 mL volumetric flask, which was then filled with water to the 100 mL mark. All parts of this process, including the preparation of solutions and samples, was conducted in the dark to avoid the occurrence of any photochemical side reactions. The light intensity was determined by irradiating the potassium ferrioxalate solution and monitoring the subsequent changes in absorbance at 510 nm using a blue LED strip (467 nm) set up in a cylindrical metal container. For each radiation measurement, 3 mL of 0.15 M potassium ferrioxalate solution was added to a cuvette, which was then placed in a sample rack, stirred, and irradiated for specified periods of time (0, 0.25, 0.50, 0.75, 1.0, 2.0, 3.0 min). Following each period of irradiation, the solution was transferred to a 25 mL volumetric flask and mixed with 6 mL of developer solution (0.05 mol%

phenanthroline/0.75 M acetate/0.2 M sulfuric acid) and 5 mL of 1 M sodium fluoride aqueous solution. Water was added to reach the 25 mL mark, and the mixture was incubated for 10 min. At the end of the incubation period, a 3 mL sample was added to a 1 cm cuvette, and the absorbance at 510 nm was measured using a UV-Vis spectrophotometer.

The flux of the laser was determined using the following equations:

$$I = \frac{\Delta n}{10^{-3} \cdot \phi \cdot V_1 \cdot t}$$

where *I* represent the flux in Einsteins per liter per second (Einstein/L/s), Δn represents the moles of photogenerated Fe^{2+}, Φ represents the known quantum yield at 532 nm, V_1 represents the irradiated volume in milliliters (mL), and t represents the irradiation time in s (s).

$$\Delta n = \frac{10^{-3} \cdot V_1 \cdot V_3 \cdot C_T}{V_2}$$

where V_2 represents the volume taken from the irradiated sample (mL), V_3 represents the volumes after dilution for concentration determination (mL), and C_T represents the concentration of Fe^{2+} following dilution.

$$C_T = \frac{Abs}{\varepsilon \cdot l}$$

where Abs represents the absorbance at 510 nm, ε represents the molar absorptivity (i.e., molar attenuation constant) ($M^{-1}cm^{-1}$), and l represents the path length. These equations enable the quantification of the laser flux and are essential for determining efficiency and kinetics. Therefore, "Einsteins per liter" (Einstein/L) represents the number of moles of photons per liter of solution. The "per second" (1/s) portion of the unit indicates that the flux measures the number of photons released or absorbed per unit time.

Table S2. Actinometry results for the 467 nm light source.

t/s	Abs	C_T	$\triangle C_T$	$\triangle n$	I/Einstein·L^{-1}·s^{-1}
0	0.04976654	4.49075E-06	0	0	0
15	0.25912666	2.33827E-05	1.88919E-05	4.72298E-06	0.000114082
30	0.55648661	5.02154E-05	4.57246E-05	1.14312E-05	0.000138057
45	0.77242136	6.97005E-05	6.52098E-05	1.63024E-05	0.00013126
60	0.96831942	8.73777E-05	8.28869E-05	2.07217E-05	0.000125131
120	0.92204714	8.32022E-05	7.87115E-05	1.96779E-05	5.94139E-05
180	1.07662964	9.71512E-05	9.26604E-05	2.31651E-05	4.66286E-05
Average					0.000127132

According to: ε = 11082 $M^{-1} \cdot cm^{-1}$, light wavelength = 467 nm, and Φ = 0.92

8. Photoreactor and Irradiation Experiments

Irradiation Experiments

For our irradiation experiments, a controlled setup was established to ensure accurate and reproducible results. The experiments were carried out using the following procedure:

Sample Preparation: The caged molecules were prepared in a solvent at a predetermined concentration. The solution was carefully prepared to ensure uniform dispersion of the molecules.

Irradiation Setup: The irradiation experiments were performed in a custom-built irradiation chamber equipped with the necessary safety features (Figure S4). The chamber was designed to limit undesirable exposure to the irradiation source and maintain a controlled environment throughout the experiment.

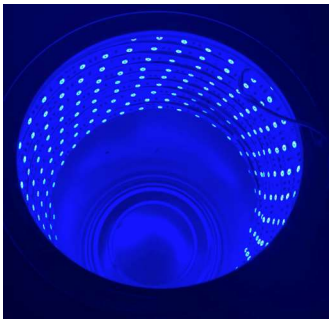


Figure S5. LED strip setup used for irradiation experiments (blue-light photoreactor for irradiation at 467 nm).

Irradiation Source: The irradiation source utilized was an LED light strip set up in a cylindrical metal container. This source was selected based on its wavelength range, intensity, and compatibility with the caged molecules' photochemistry. The light strip was carefully positioned within the irradiation chamber to ensure an even and consistent illumination of the sample.

Sample Exposure: The sample solution was placed in a suitable container for irradiation studies, ensuring that the solution thickness was uniform as to minimize variation in the irradiation process. The container was positioned at a specific distance from the irradiation source, and the entire setup was shielded from external light sources to prevent interference.

Irradiation Protocol: The sample was irradiated for a predetermined duration, with the irradiation source emitting light at the desired wavelength range. Irradiation time was carefully controlled to maintain consistency across experiments.

Sample Monitoring and Data Collection: Throughout the irradiation process, changes in the samples' properties were monitored using UV-Vis spectroscopy and NMR spectroscopy. The type of spectroscopic technique used depended on the specific properties being investigated. Data was collected at regular intervals to track the progress of the photochemical reaction.

Control Experiments: To validate the effects of irradiation, control experiments were conducted using identical conditions, but without the presence of the caged molecules. These control experiments served as a baseline for analyzing the observed changes in the sample.

9. Experimental Details of Confocal System for Fluorescence Imaging

The sample was prepared on a microscope slide, and the microscope was set up with the appropriate objective lens and filters for fluorescence imaging, ensuring proper focus and alignment. The 405 nm, 488 nm, 561 nm, and 640 nm lasers were configured for excitation and directed onto the sample. The microscope software was used to select excitation wavelengths and capture fluorescence images, with laser power and exposure time adjusted as needed. The detector was configured to collect emission signals in the ranges of 424–483 nm, 502–522 nm, 552–581 nm, and 655–688 nm. Fluorescence images were acquired and processed using image analysis software for quantification and analysis.

We employed different filter settings tailored to each fluorophore's emission spectrum. The DAPI, eGFP (enhanced Green Fluorescent Protein), Alexa Fluor 555, and Alexa Fluor 647 filters were specifically designed emission filters used in fluorescence microscopy to detect fluorescence signals from different fluorophores. The DAPI filter captured blue fluorescence emitted by DAPI-stained DNA (excited by UV light), while the eGFP filter detected green fluorescence from eGFP-expressing cells (excited by blue light). The Alexa Fluor 555 filter captured orange-red fluorescence from Alexa Fluor 555-labeled samples (excited by green or yellow light), and the Alexa Fluor 647 filter detected far-red fluorescence from Alexa Fluor 647-labeled samples (excited by appropriate wavelengths, see Figure **S7**). Each filter selectively transmitted the emitted fluorescence signals while blocking background light, enabling the visualization and differentiation of specific structures or molecules labeled with these fluorophores in the sample.

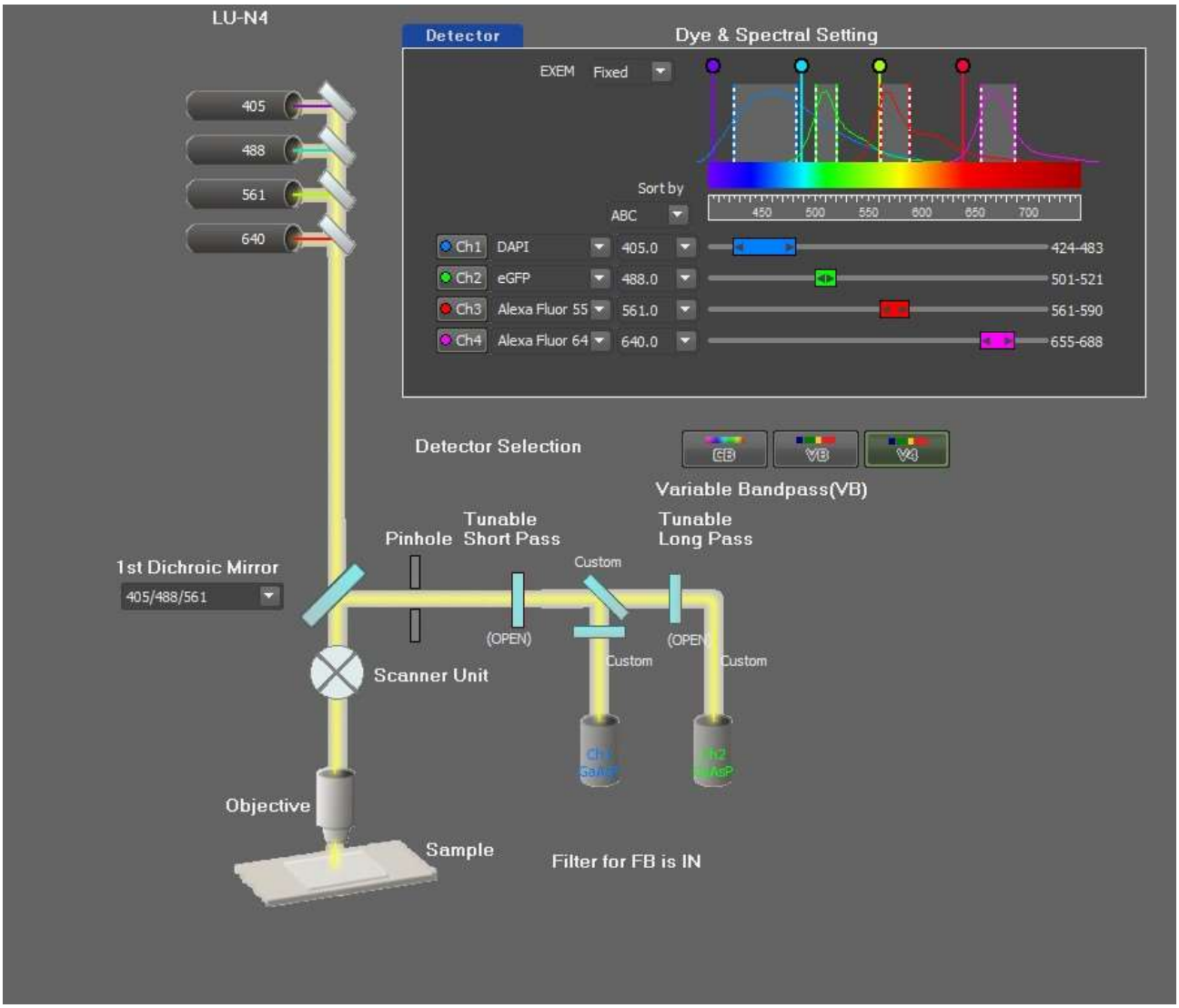


Figure S6. Instrumental setup diagram of 4-Line Solid State Laser Confocal System with a Nikon Eclipse Ti2 Inverted Microscope.

10. Fluorescence Imaging

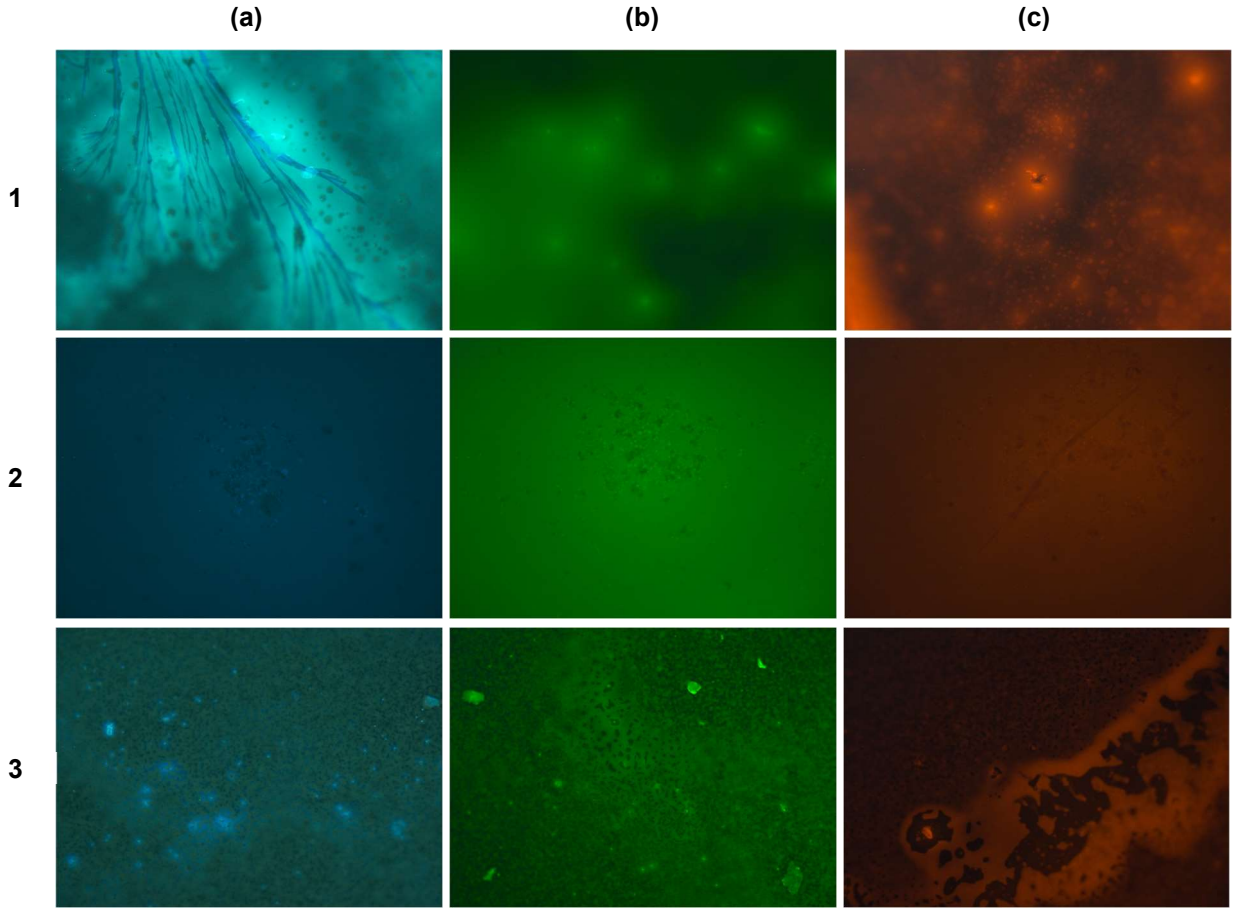


Figure S7. Fluorescence microscopy images of **1**, **2**, and **3** with (a) DAPI, (b) FITC, and (c) TEXAS RED filters using the Fluorescence Microscopy Zeiss Axioskop 2 Plus.

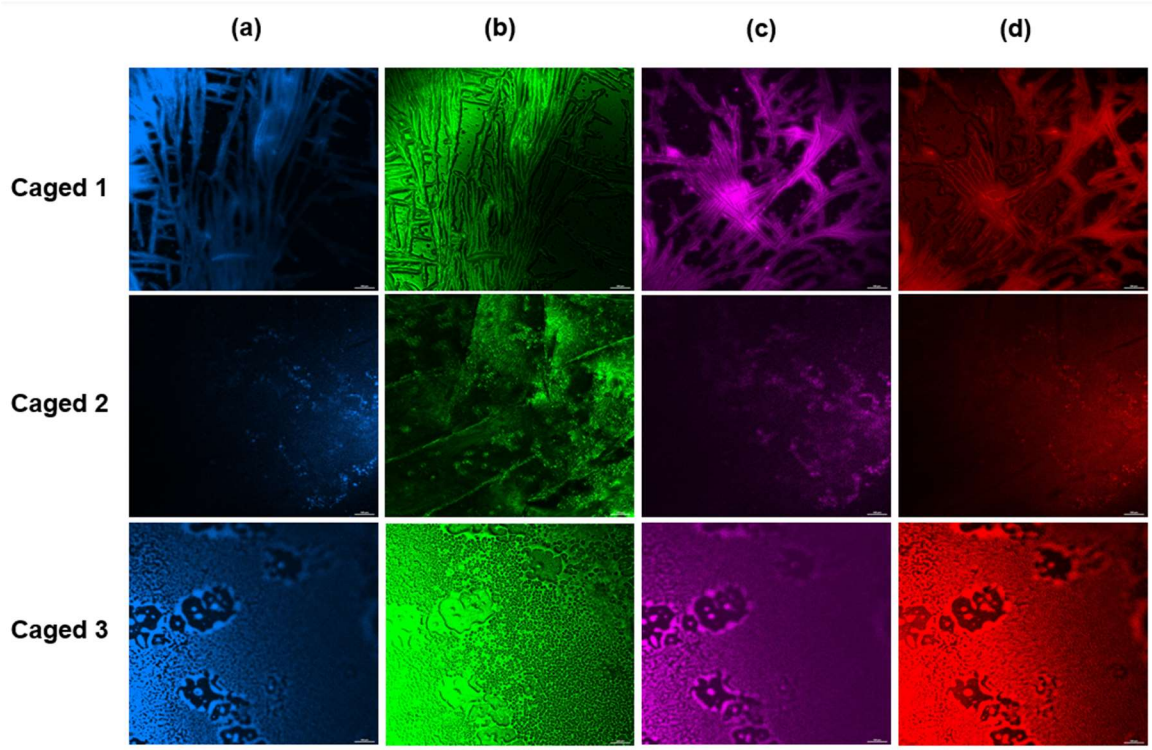


Figure S8. Images of **1**, **2**, and **3** with 4-Line Solid State Laser Confocal System with Nikon Eclipse Ti2 Inverted Microscope. The sample was excited with the laser at (a) 405 nm, (b) 488 nm, (c) 561 nm, and (d) 640 nm wavelengths, and the emission was observed at 424–483 nm, 502–522 nm, 552–581 nm, and 655-688 nm, respectively.

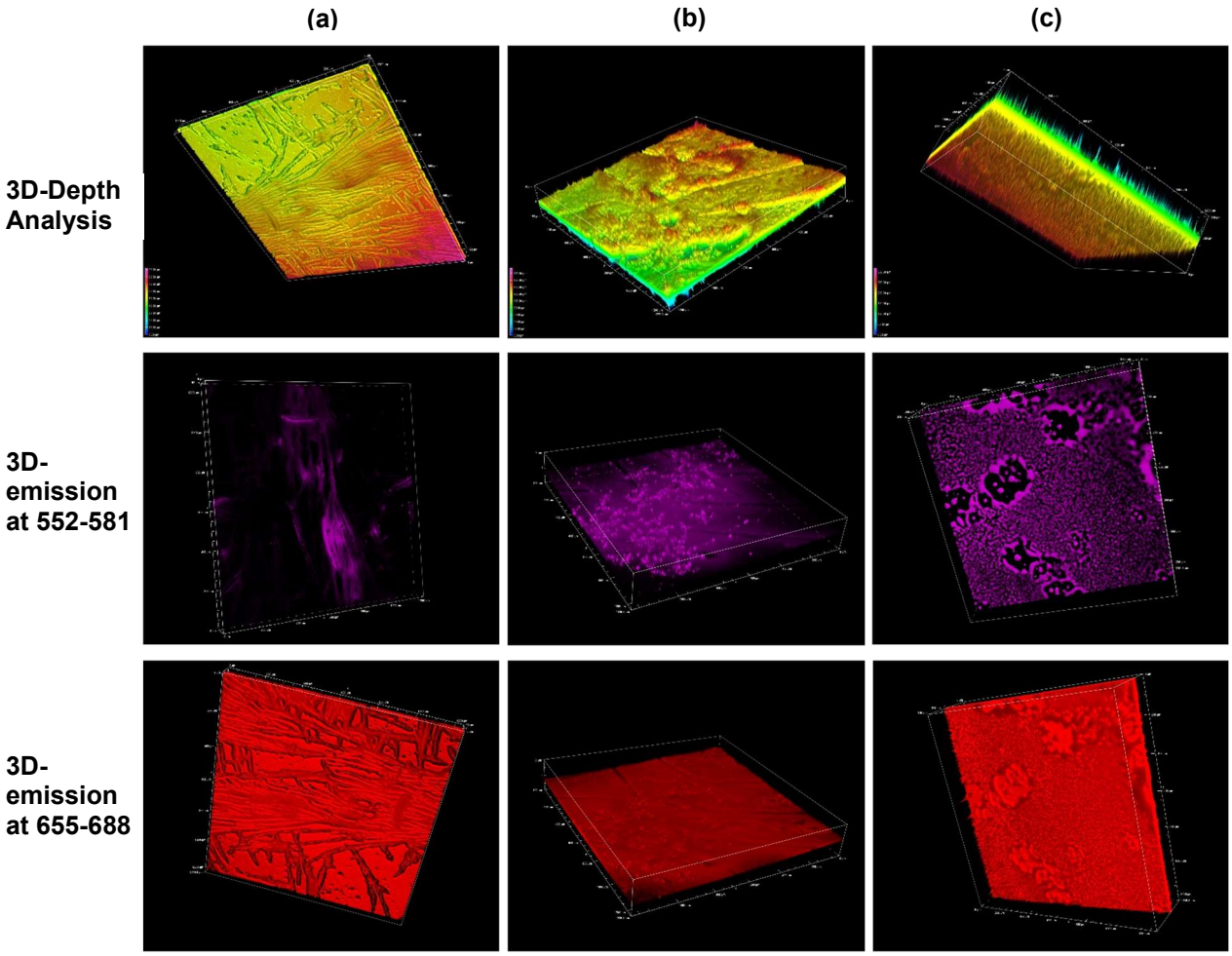


Figure S9. Confocal laser scanning microscopy images for 3D-depth analysis and 3D-emission of (a) **1**, (b) **2**, and (c) **3**.

11. Computational Results

All calculations for this article were performed using the PBEh-3c composite method as implemented in the Q-Chem software. The binding energies are reported in Figure 5 of the main text. In Table S1, we report the calculated distances between the central calcium cation and the eight atoms that bind to it in the octa-dentate ligand conformation (six oxygen atoms and two nitrogen atoms). In Table S2, we report the calculated Mülliken partial charges on each of the eight atoms responsible for the octa-dentate ligands in the unbound molecule.

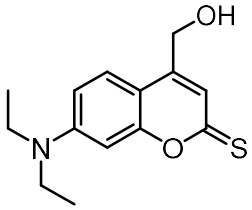
Table S3. Calculated distances between the central Ca^{2+} and the eight closest atoms composing the octa-dentate ligands in the complexes. All distances are calculated at the PBEh-3c level of theory and reported in Ångstroms.

	O1	O2	O3	O4	O5	O6	N1	N2
BAPTA	2.268	2.265	2.270	2.271	3.018	3.091	2.893	2.975
Caged-1	2.212	2.226	2.259	2.379	2.576	3.059	2.643	3.465
Caged-2	2.215	2.226	2.270	2.407	2.577	3.035	2.650	3.183
Caged-3	2.216	2.213	2.258	2.383	3.080	3.080	2.632	3.512

Table S4. Calculated Mülliken charges on the eight atoms composing the octa-dentate ligands. All charges are calculated at the PBEh-3c level of theory on the unbound molecules and reported as fraction of electrons.

	O1	O2	O3	O4	O5	O6	N1	N2
BAPTA	-0.478	-0.478	-0.541	-0.552	-0.541	-0.610	-0.436	-0.436
Caged-1	-0.460	-0.454	-0.562	-0.548	-0.557	-0.363	-0.449	-0.463
Caged-2	-0.477	-0.470	-0.550	-0.542	-0.570	-0.424	-0.433	-0.479
Caged-3	-0.477	-0.463	-0.545	-0.551	-0.555	-0.449	-0.469	-0.450

12. LCMS and HRMS of the Compounds



21

MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{14}H_{17}NO_2S^+$ 264.2, found 264.2.

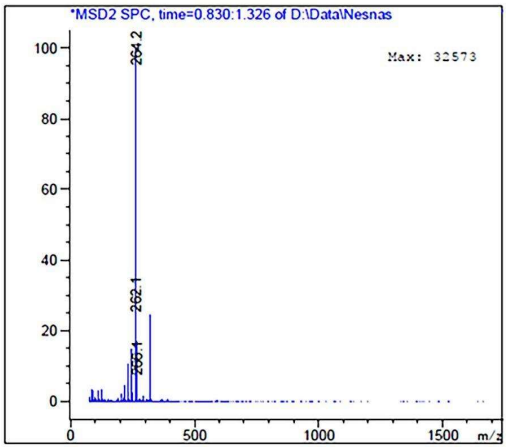
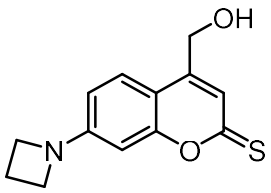


Figure S10. LCMS analysis of compound **21.**



22

MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{13}H_{13}NO_2S^+$ 247.1, found 247.1.

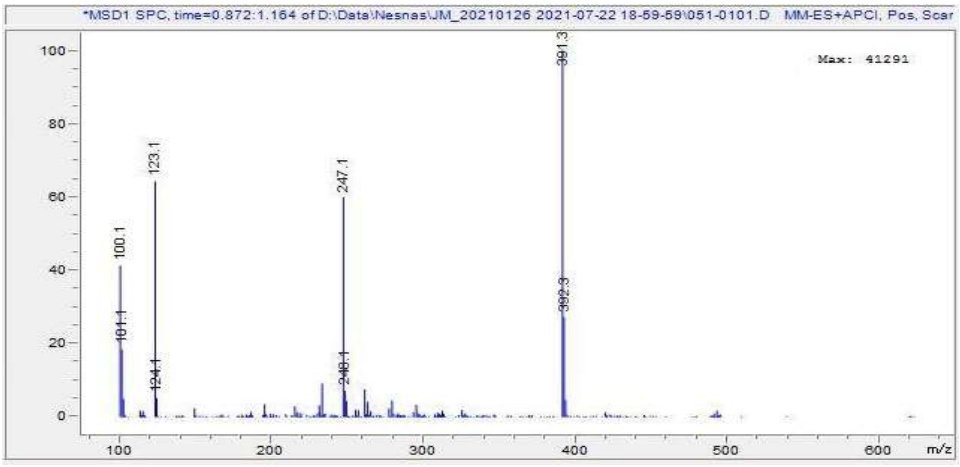
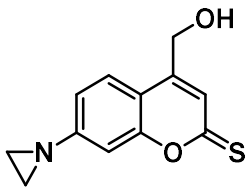


Figure S11. LCMS analysis of compound **22.**



23

MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{12}H_{11}NO_2S^+$ 233.1, found 233.1.

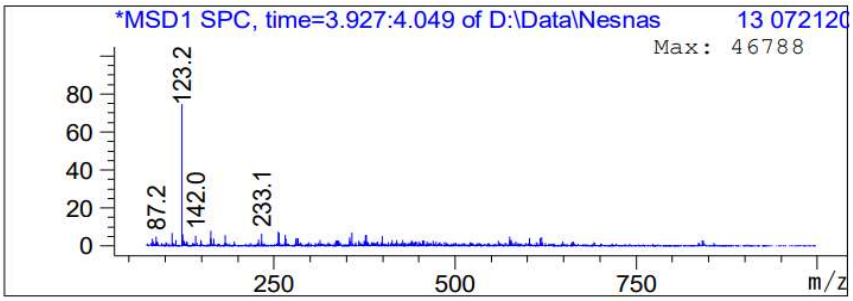
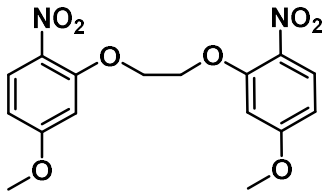


Figure S12. LCMS analysis of compound **23.**



26

HRMS (DART-AccuTOF) m/z [M+H]+ cacld for $C_{16}H_{17}N_2O_8$ 365.0979, found 365.0656.

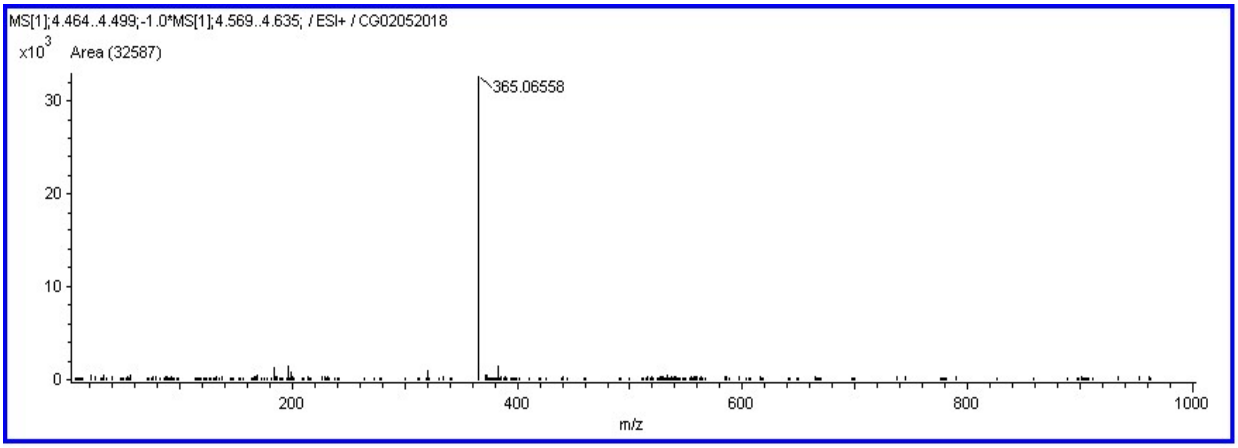
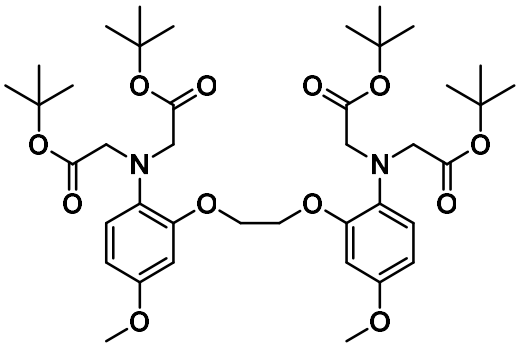


Figure S13. HRMS (DART-AccuTOF) analysis of compound **26.**



29

MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{40}H_{66}N_2NaO_{12}^+$ 784.3, found 784.3.

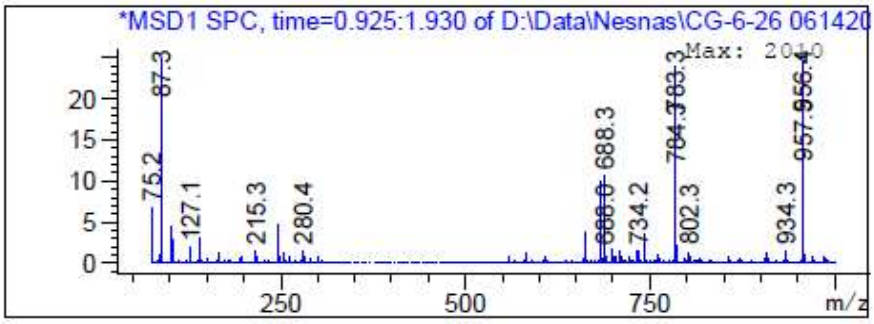
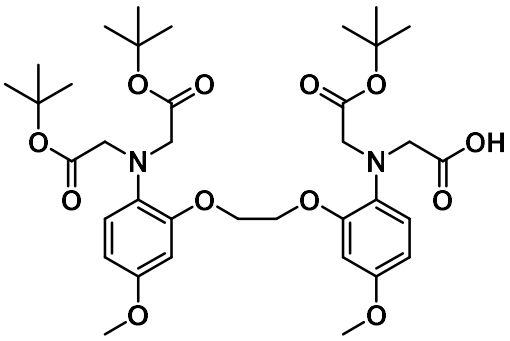


Figure S14. LCMS analysis of compound **29.**



30

MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{36}H_{53}N_2O_{12}^+$ 705.3, found 705.3.

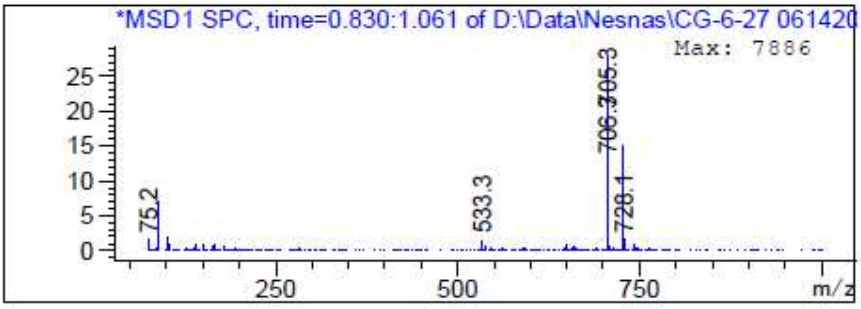
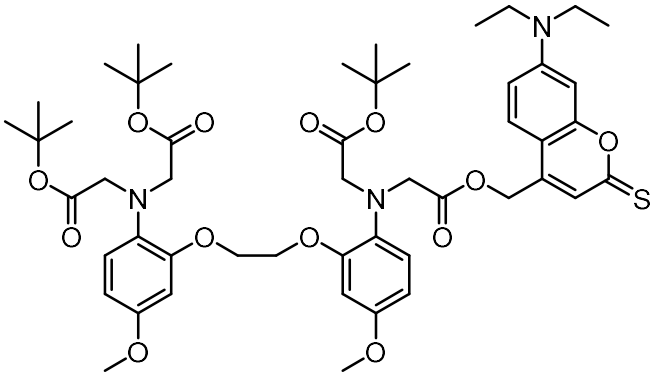


Figure S15. LCMS analysis of compound **30.**



31

MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{50}H_{67}N_3NaO_{13}S^+$ 972.3, found 972.3.

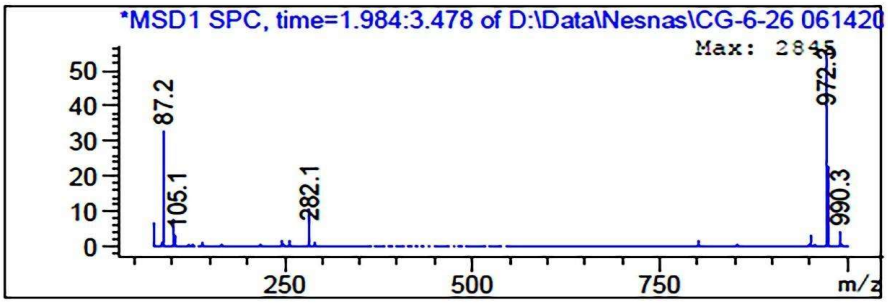
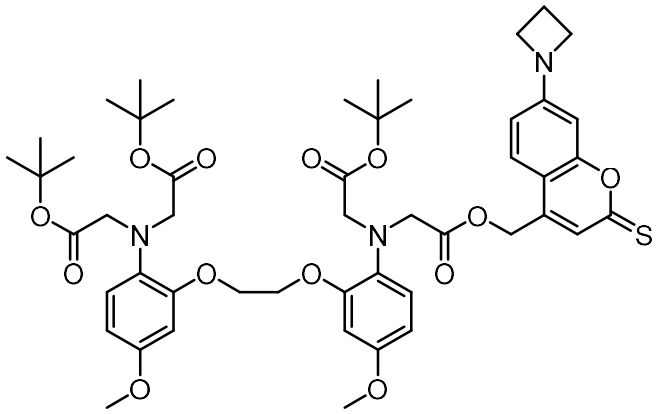


Figure S16. LCMS analysis of compound **31.**



32

MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{49}H_{63}N_3O_{13}S^+$ 934.4, found 934.4.

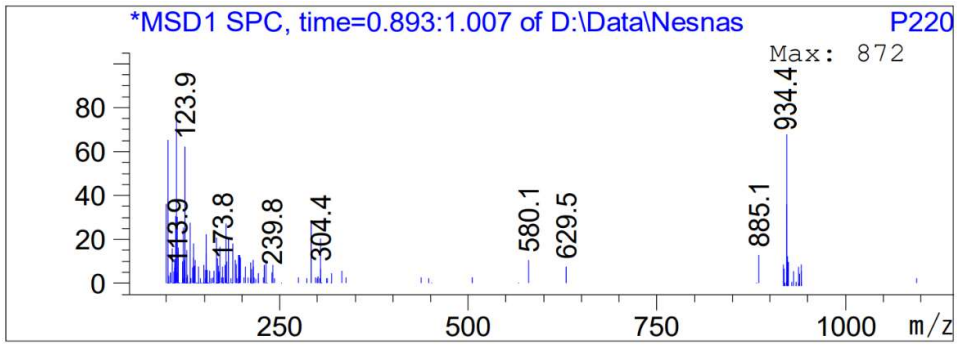
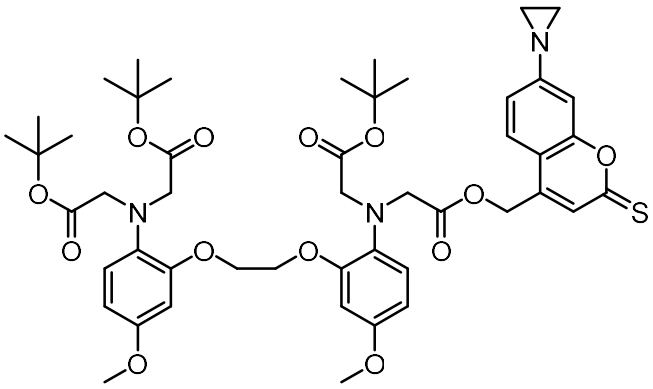


Figure S17. LCMS analysis of compound **32.**



33

MS (LCMS-ESI) *m/z* $[M+H]^+$ cacld for $C_{48}H_{61}N_3O_{13}S^+$ 919.0, found 919.0.

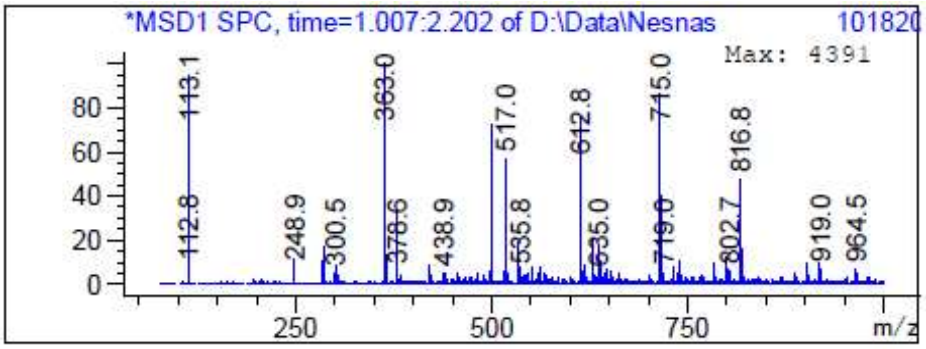
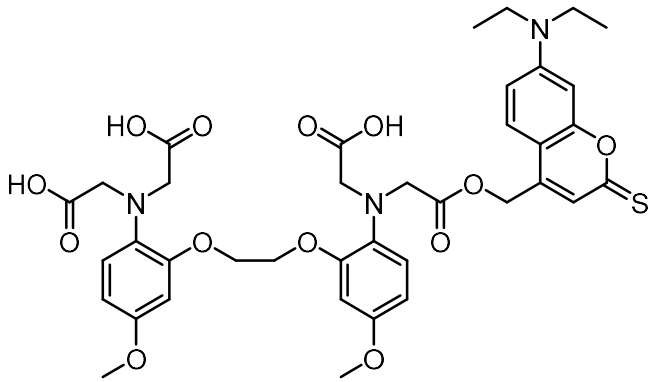


Figure S18. LCMS analysis of compound **33.**



1

HRMS *m/z* $[M]^-$ cacld for $C_{38}H_{40}N_3O_{13}S^{3-}$ 778.8076, found 778.8076.

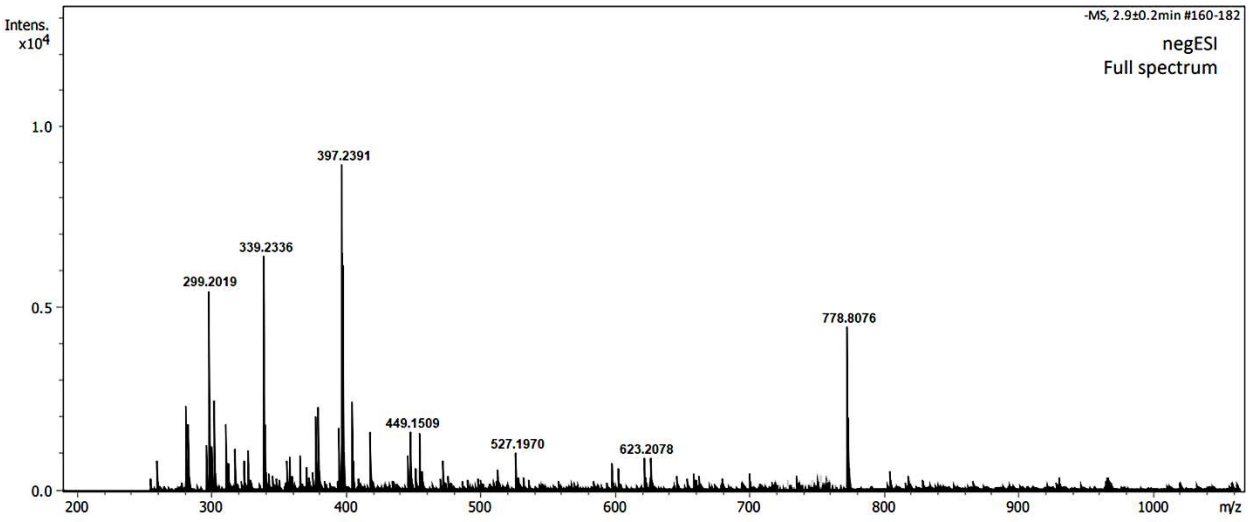
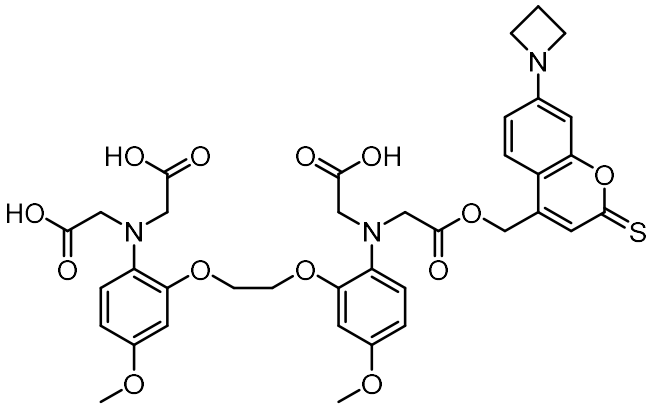


Figure S19. HRMS analysis of caged **1.**



2

HRMS *m/z* $[M]^-$ cacld for $C_{37}H_{36}N_3O_{13}S^{3-}$ 762.7646, found 762.7646.

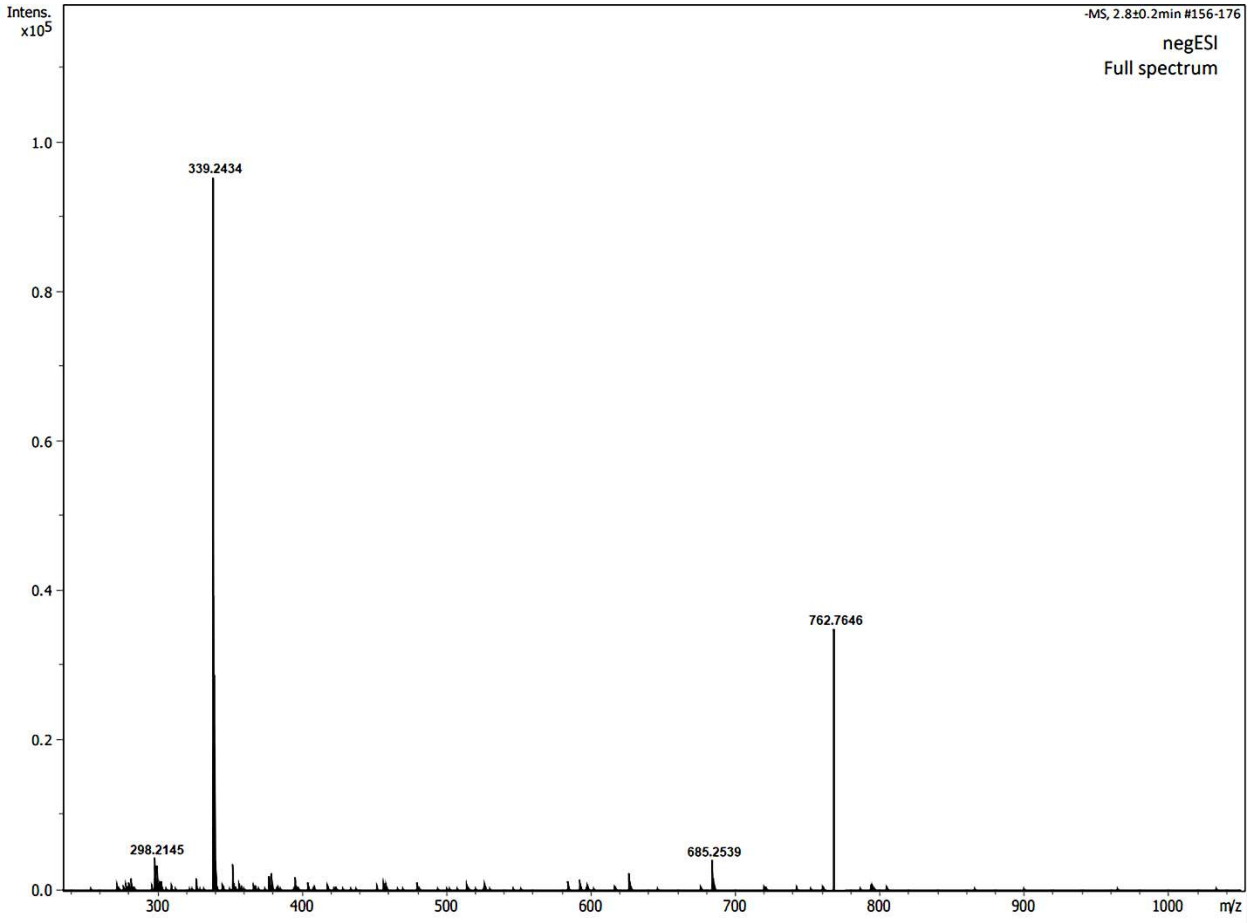
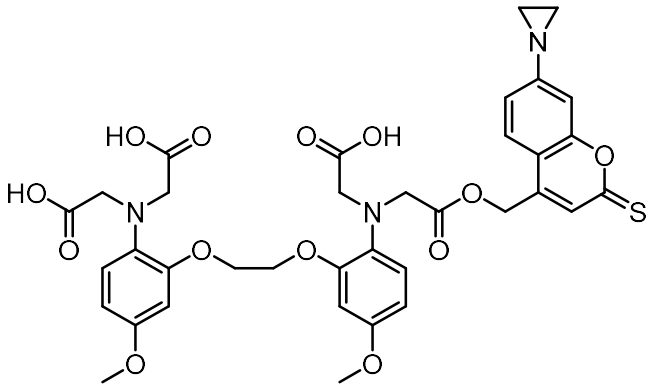


Figure S20. HRMS analysis of caged **2.**



3

HRMS *m/z* $[M]^-$ cacld for $C_{36}H_{34}N_3O_{13}S^{3-}$ 748.7376, found 748.7376.

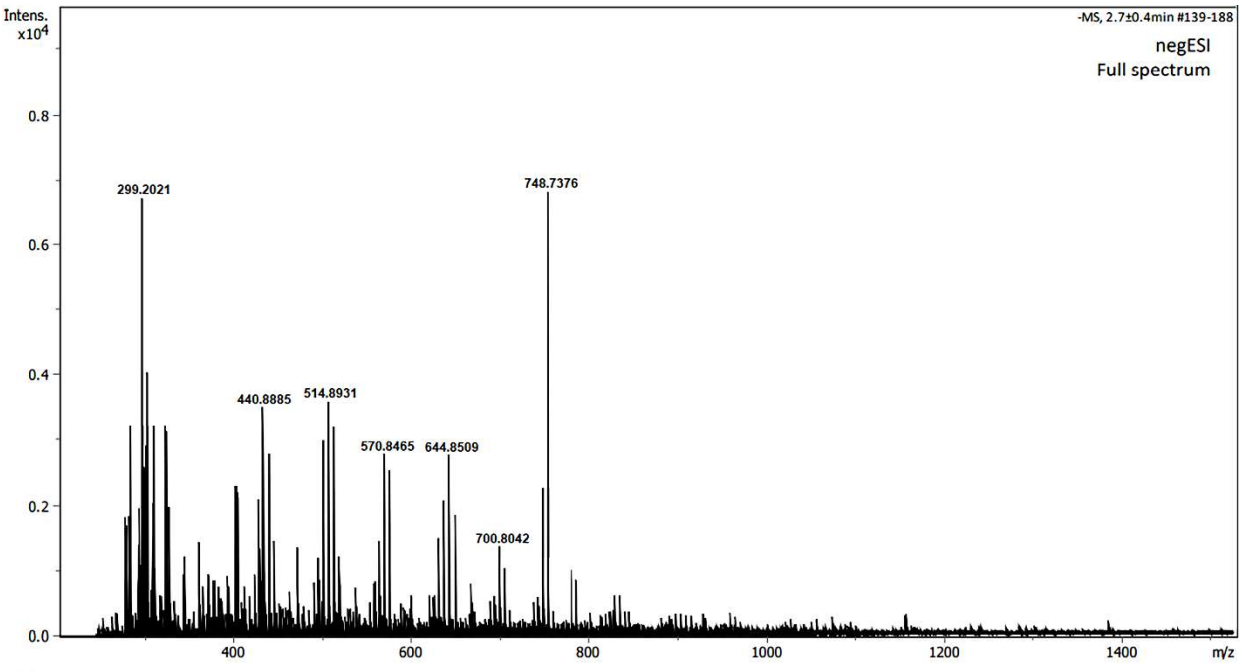


Figure S21. HRMS analysis of caged **3.**

13. ^{1}H NMR of the Synthesized Compounds

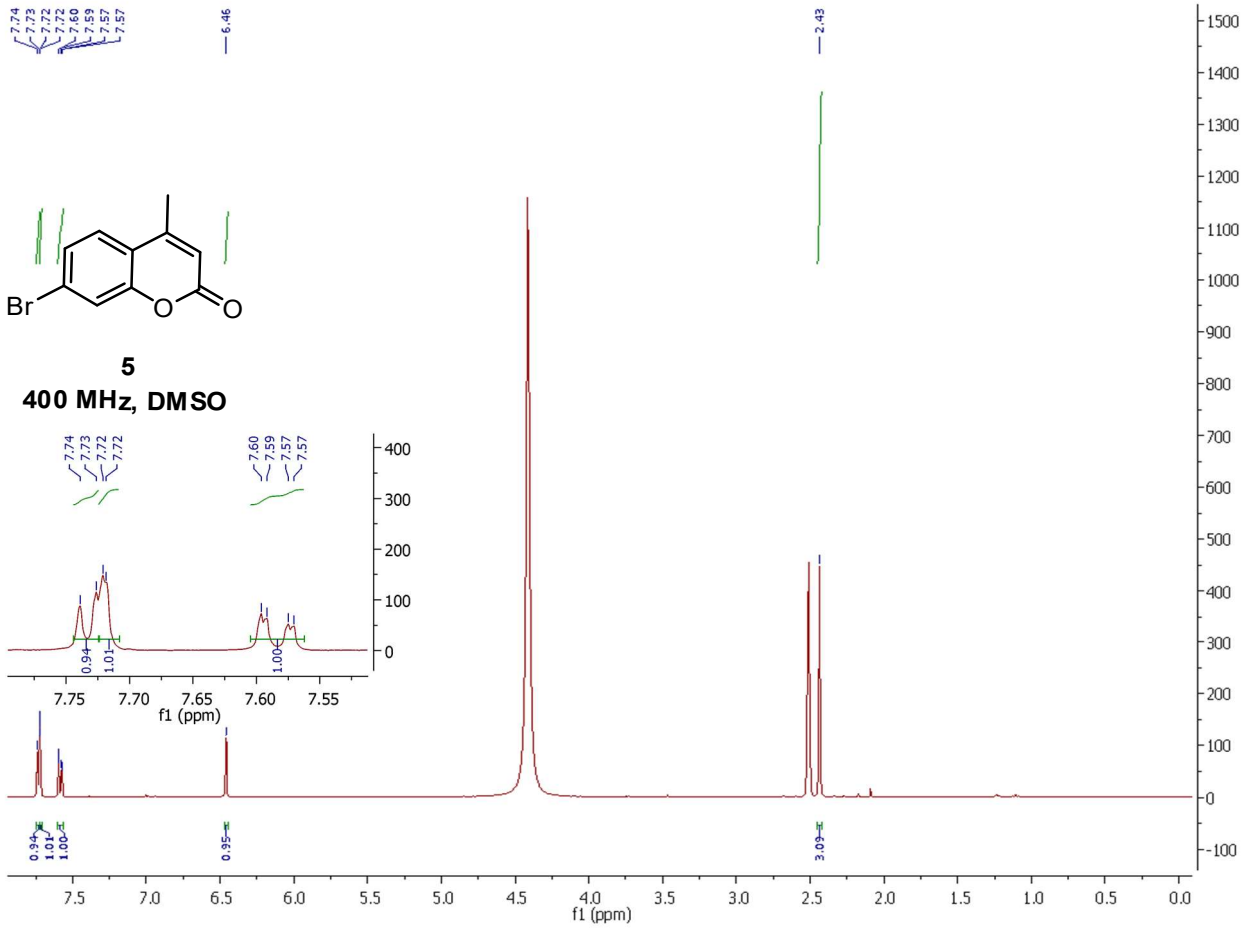


Figure S22. ^{1}H NMR analysis of compound **5.**

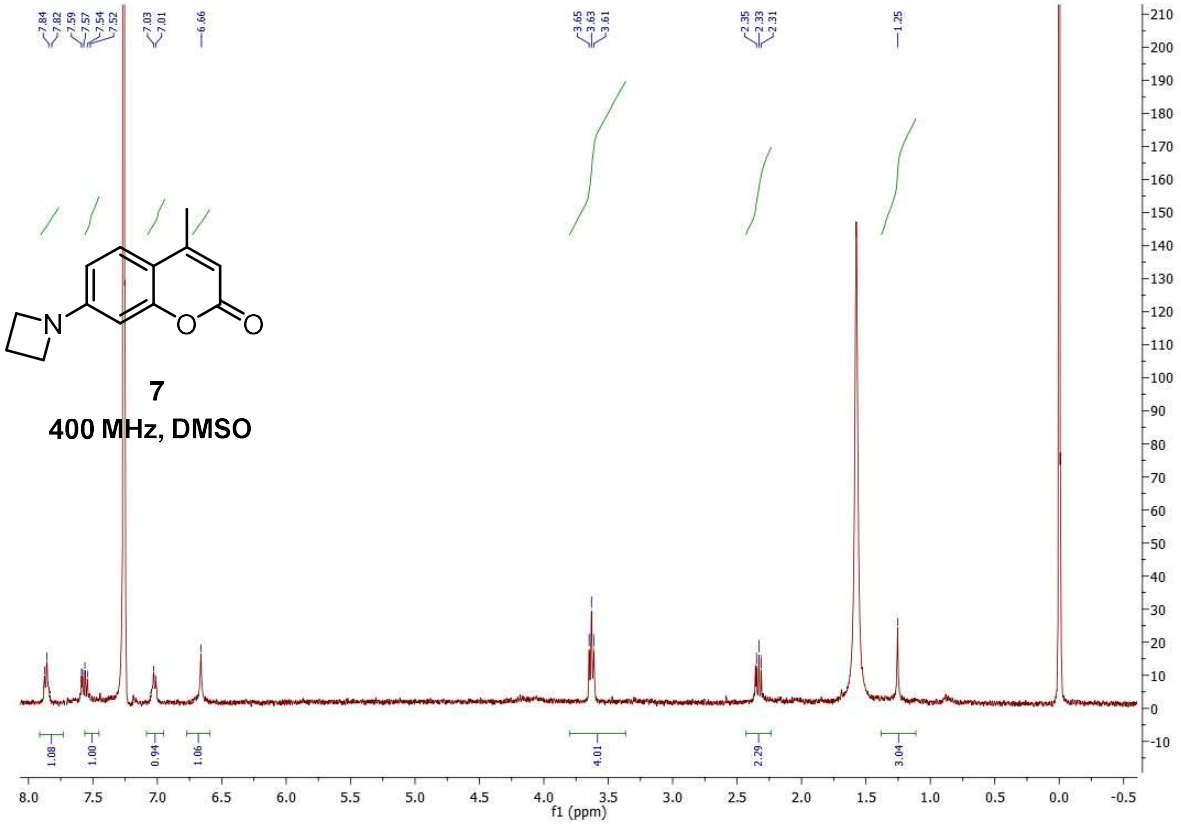


Figure S23. ^{1}H NMR analysis of compound **7.**

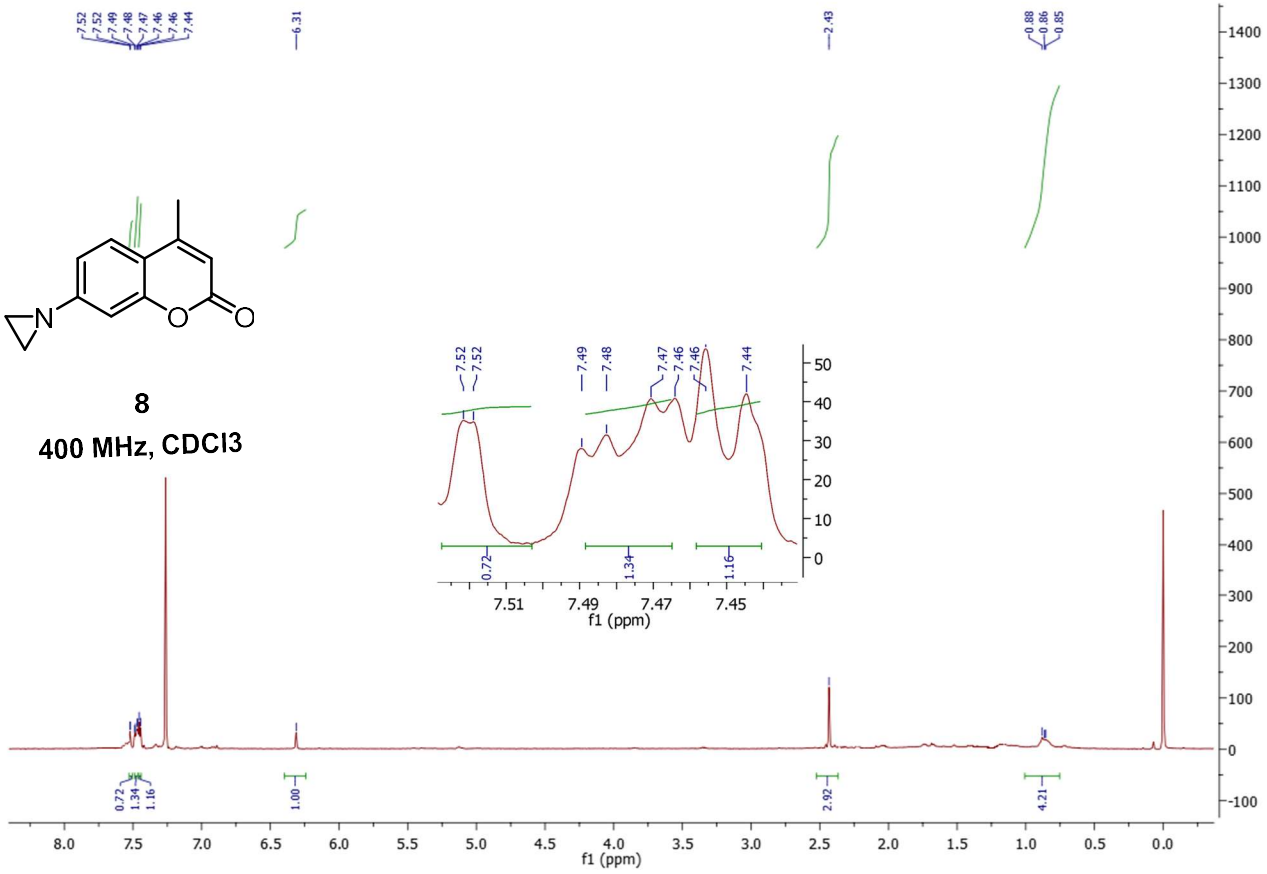


Figure S24. ^{1}H NMR analysis of compound **8.**

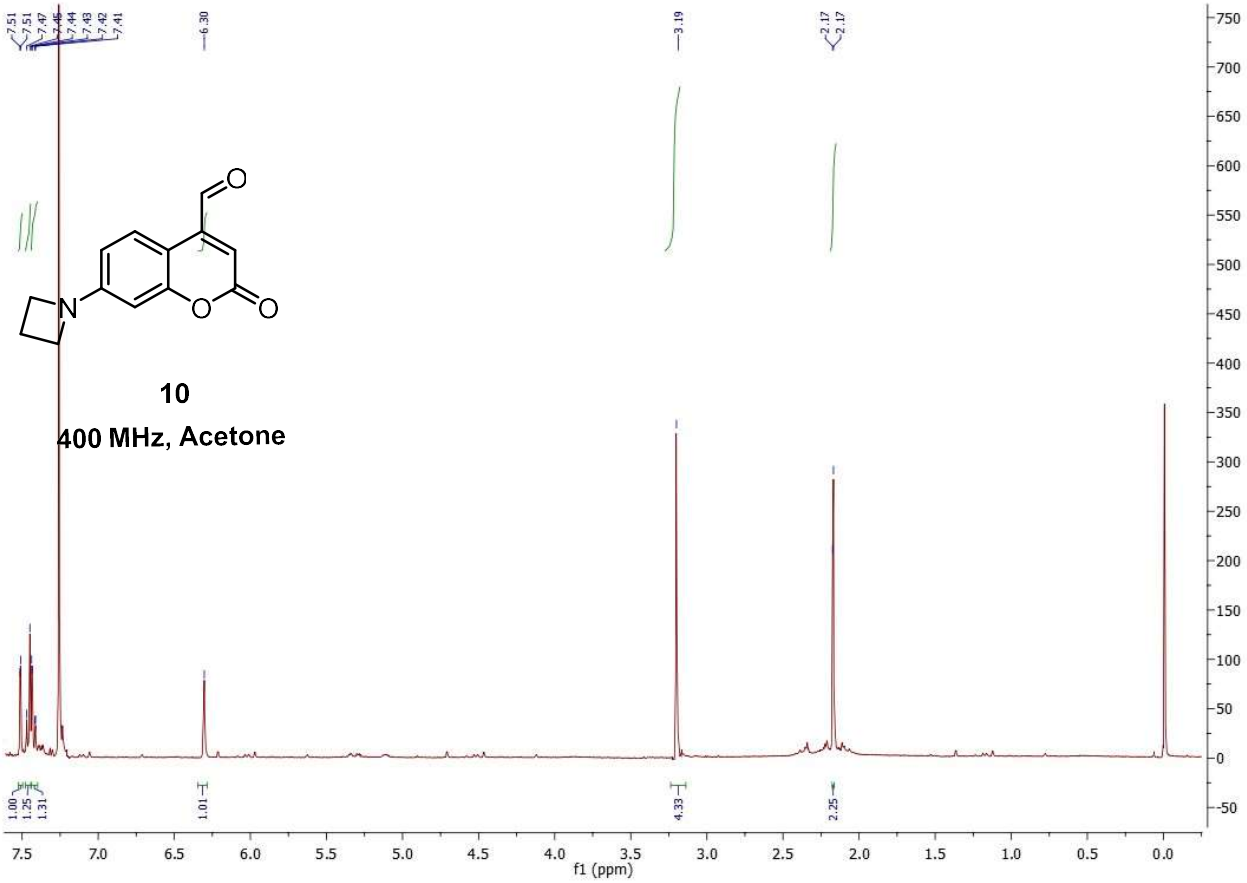


Figure S25. ^{1}H NMR analysis of compound **10.**

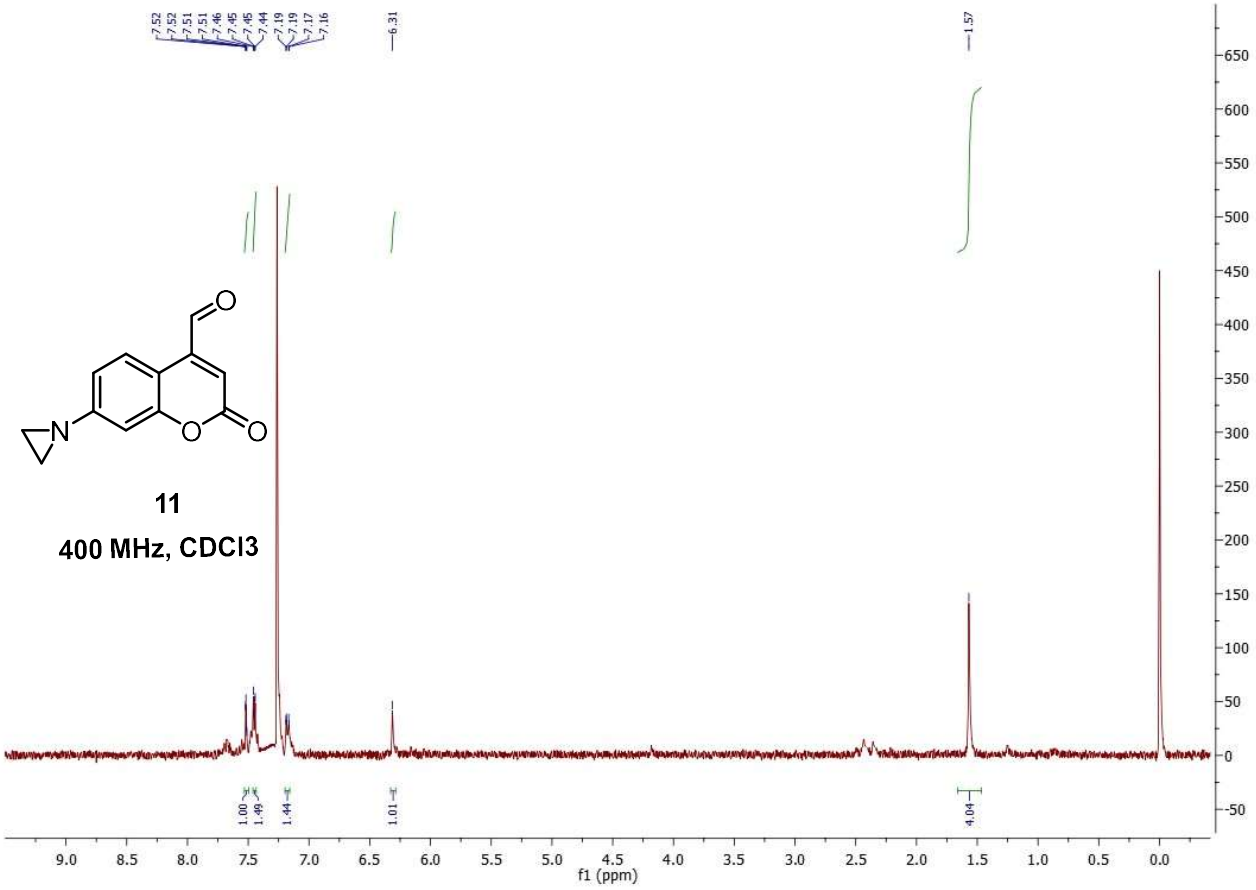


Figure S26. ^{1}H NMR analysis of compound **11.**

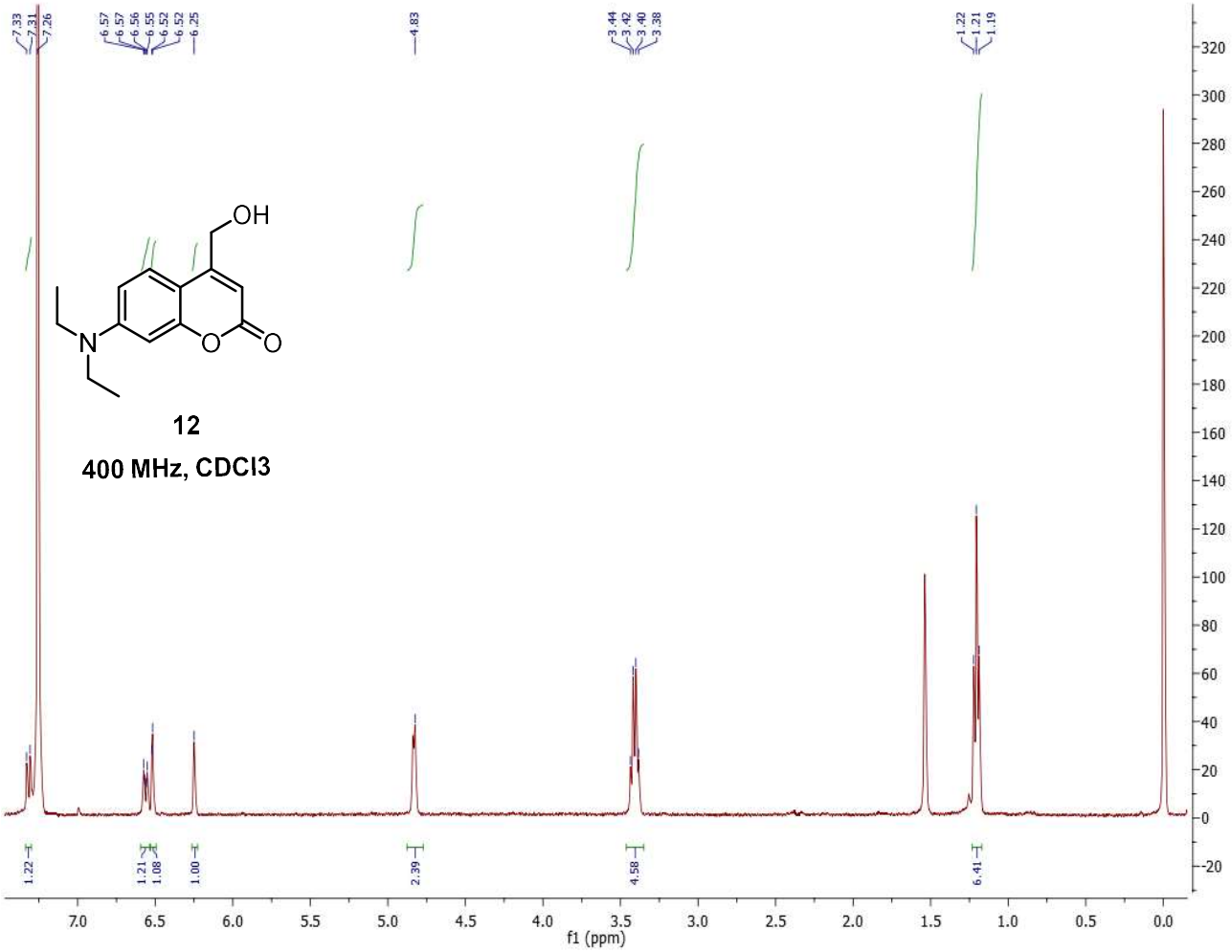


Figure S27. ^{1}H NMR analysis of compound **12.**

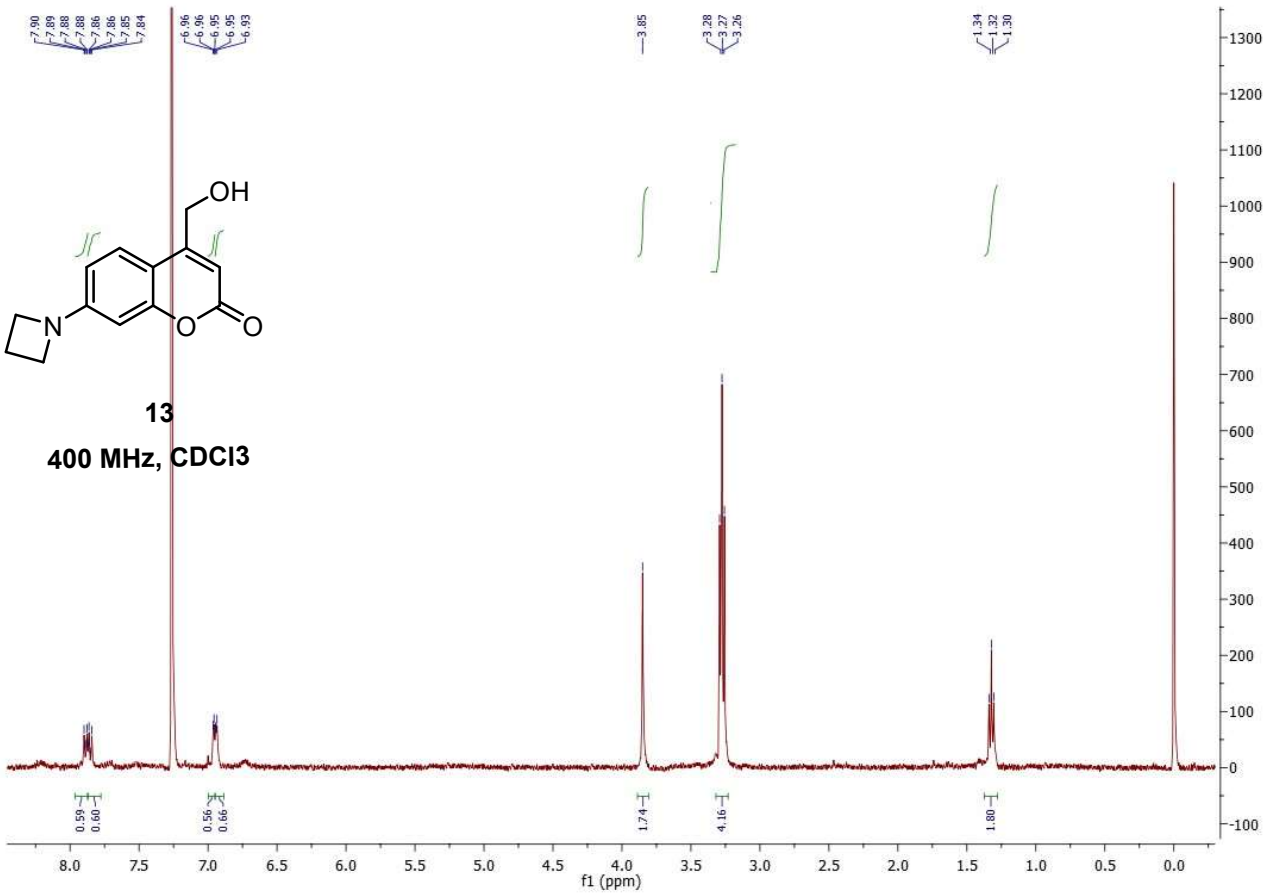


Figure S28. ^{1}H NMR analysis of compound **13.**

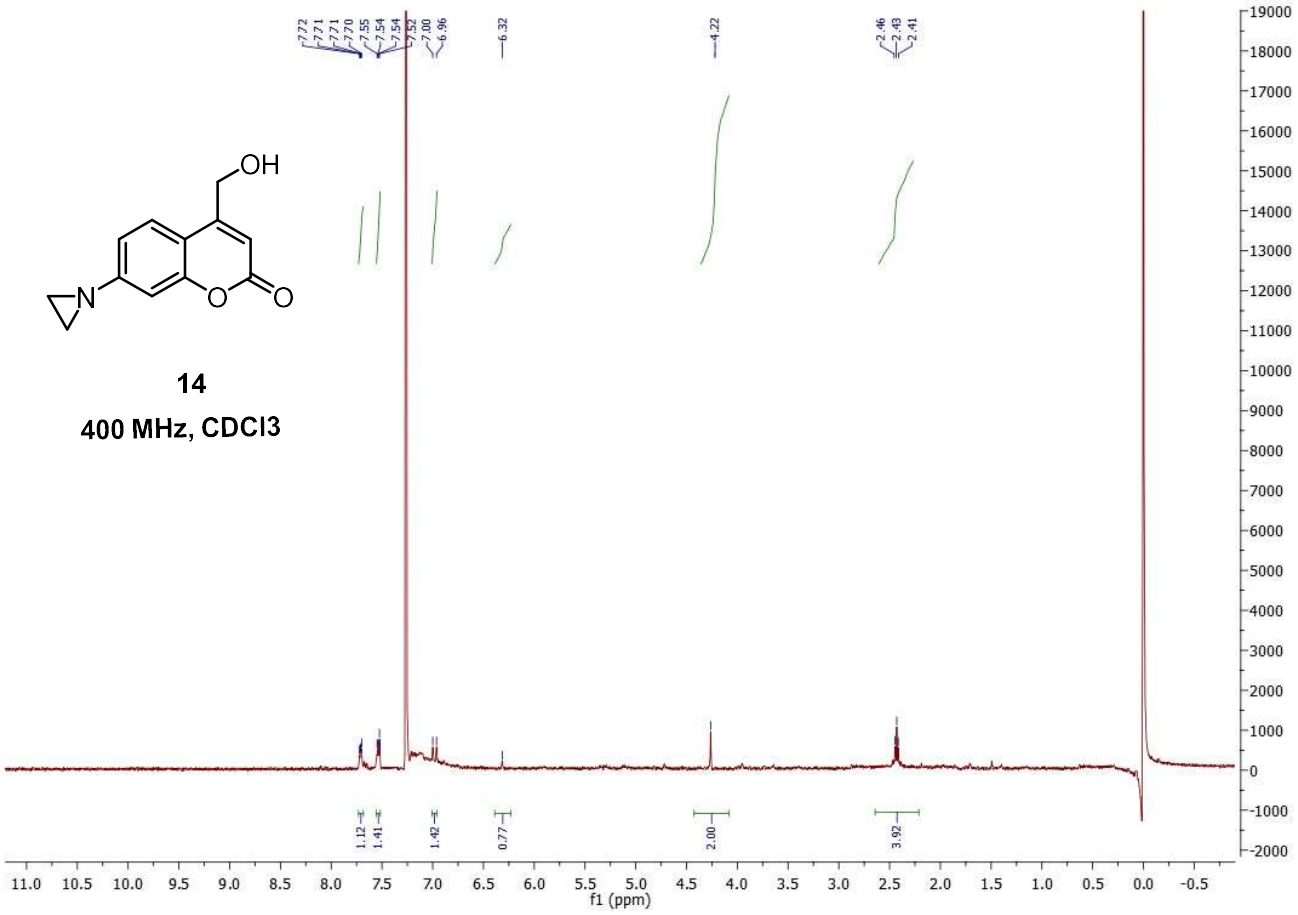


Figure S29. ^{1}H NMR analysis of compound **14.**

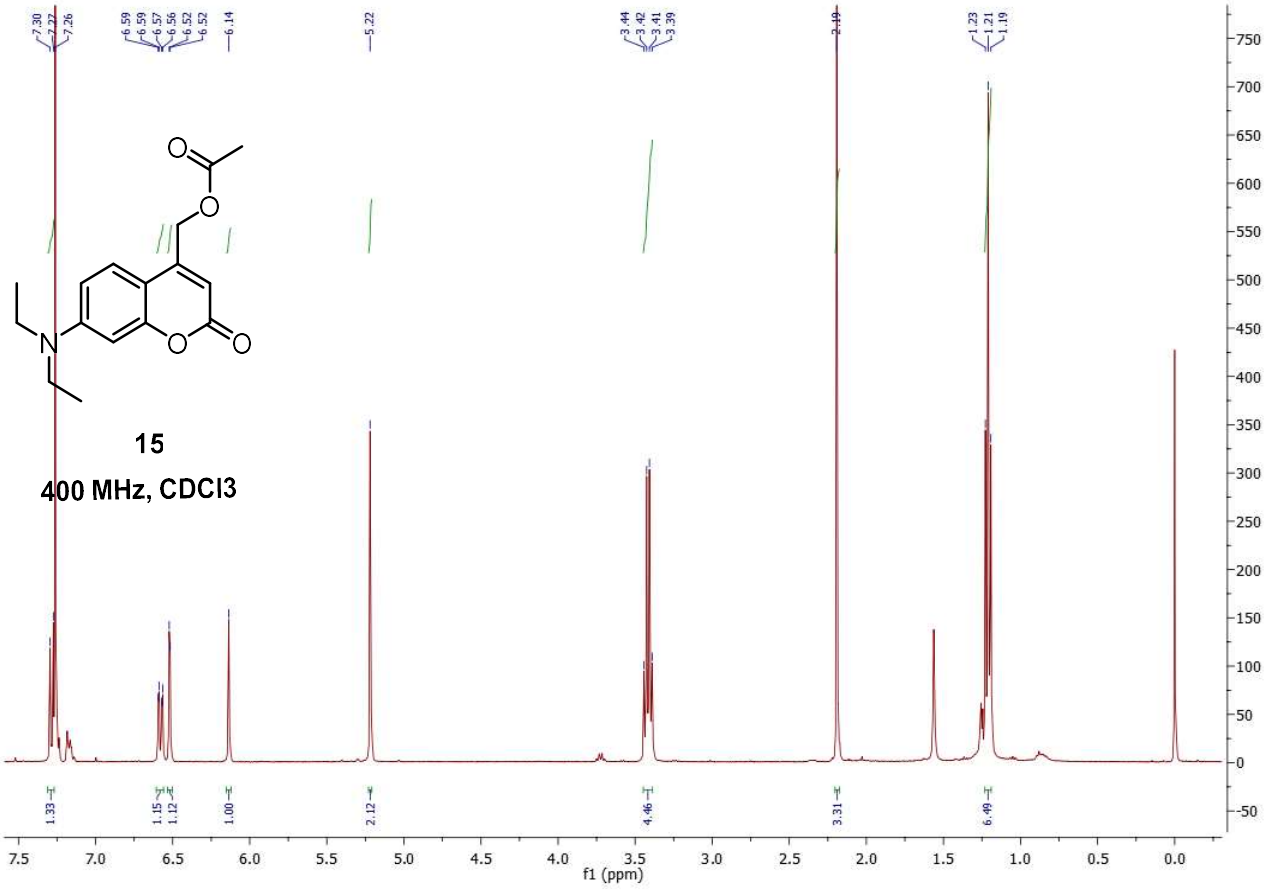


Figure S30. ^{1}H NMR analysis of compound **15.**

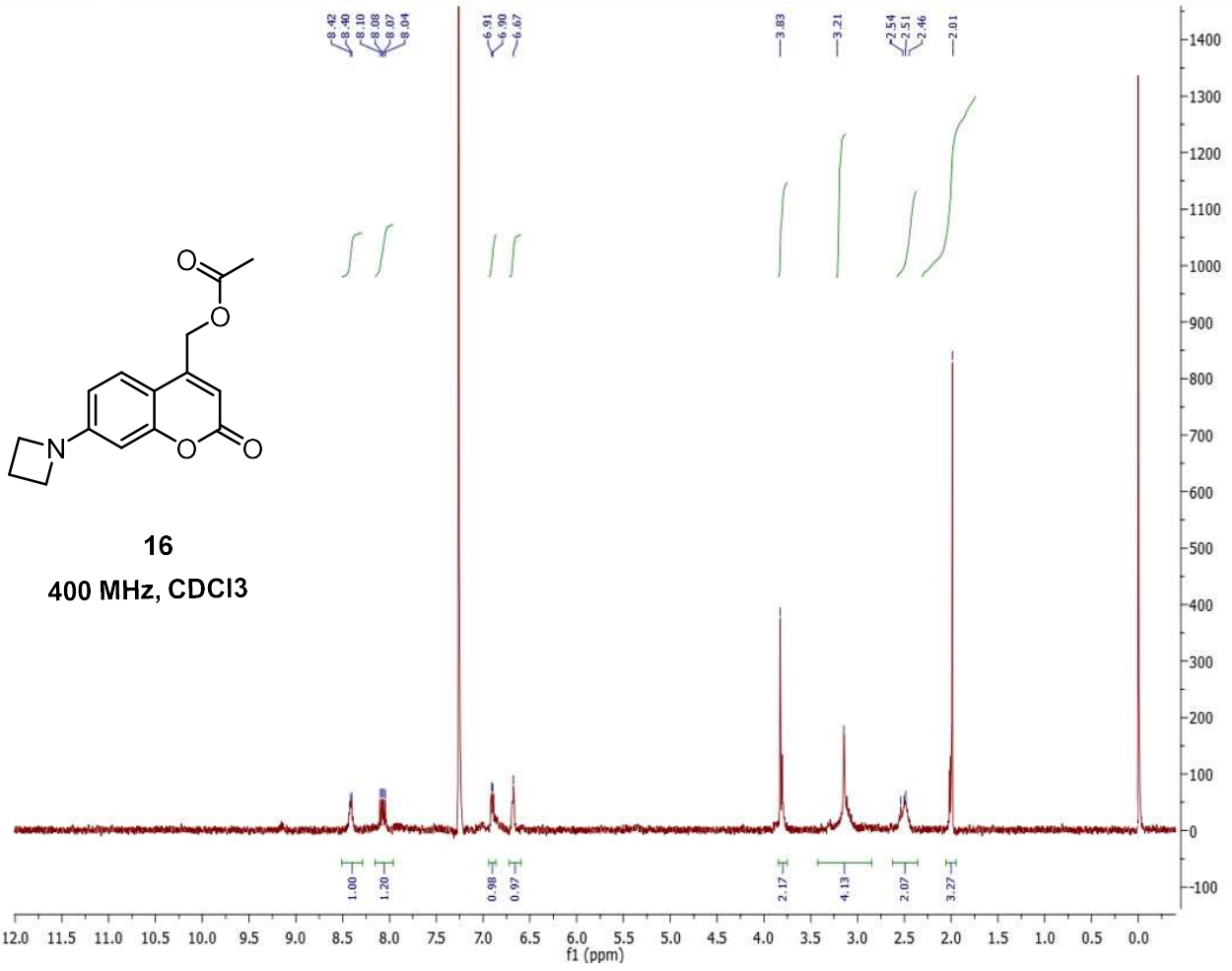


Figure S31. ^{1}H NMR analysis of compound **16.**

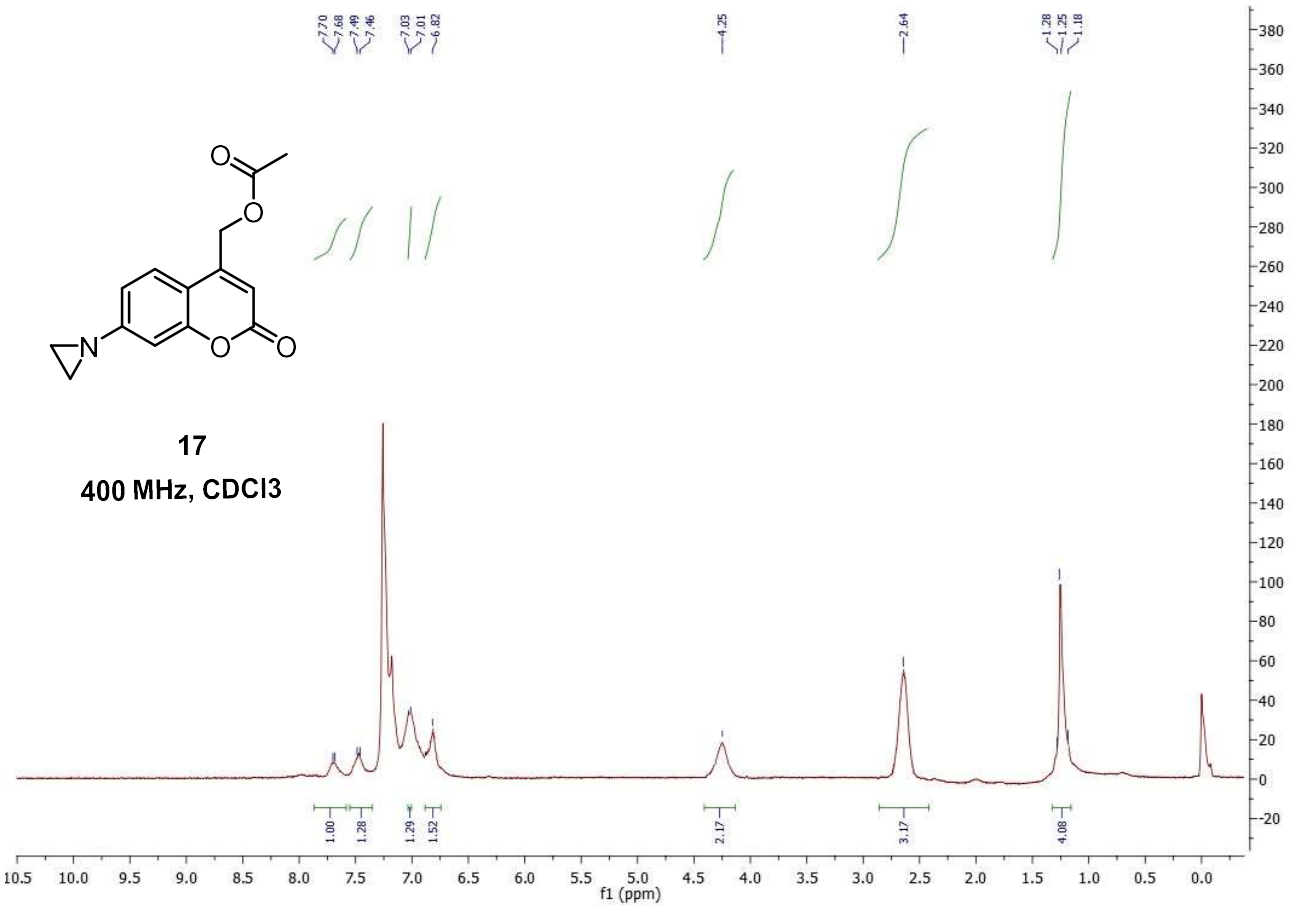


Figure S32. ^{1}H NMR analysis of compound **17.**

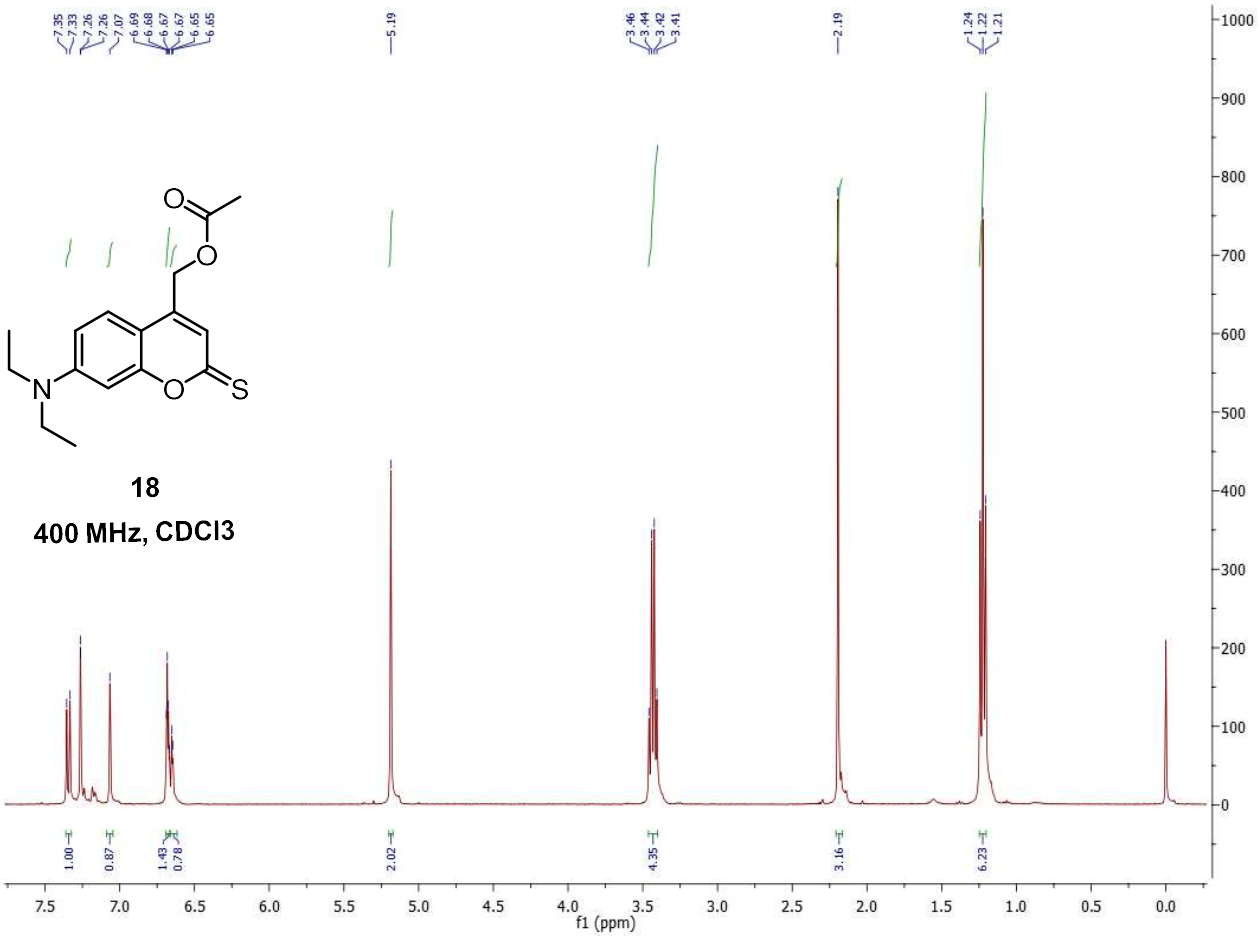


Figure S33. ^{1}H NMR analysis of compound **18.**

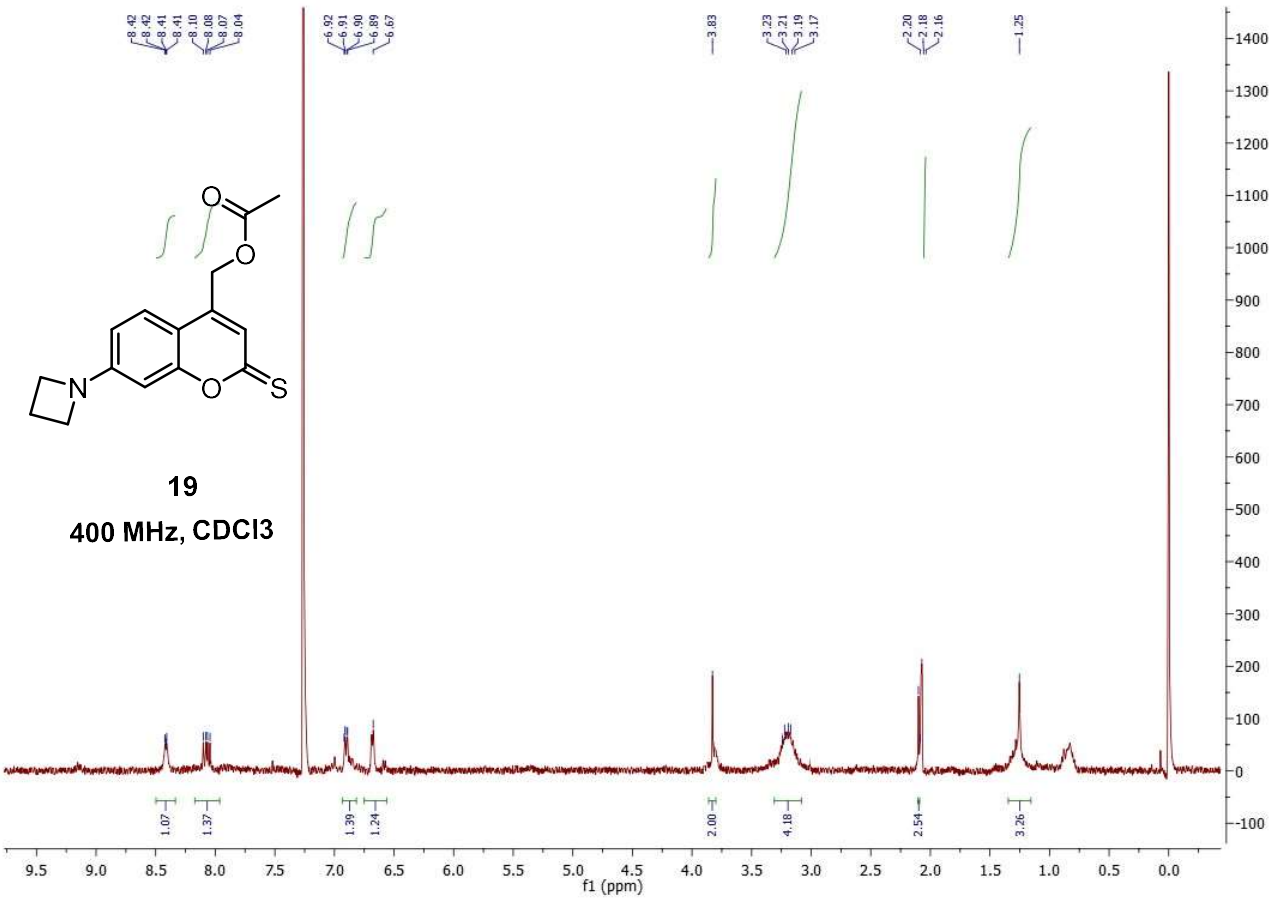


Figure S34. ^{1}H NMR analysis of compound **19.**

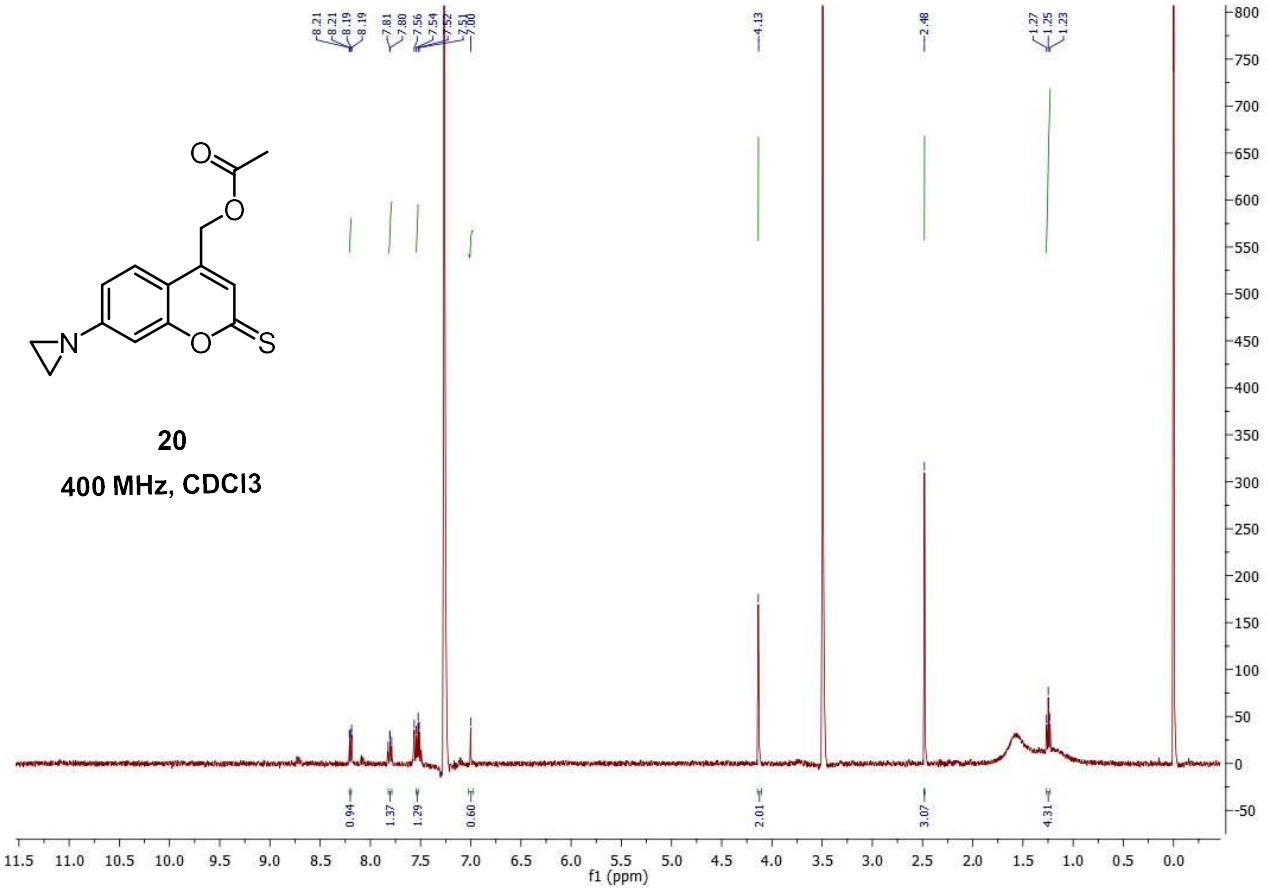


Figure S35. ^{1}H NMR analysis of compound **20.**

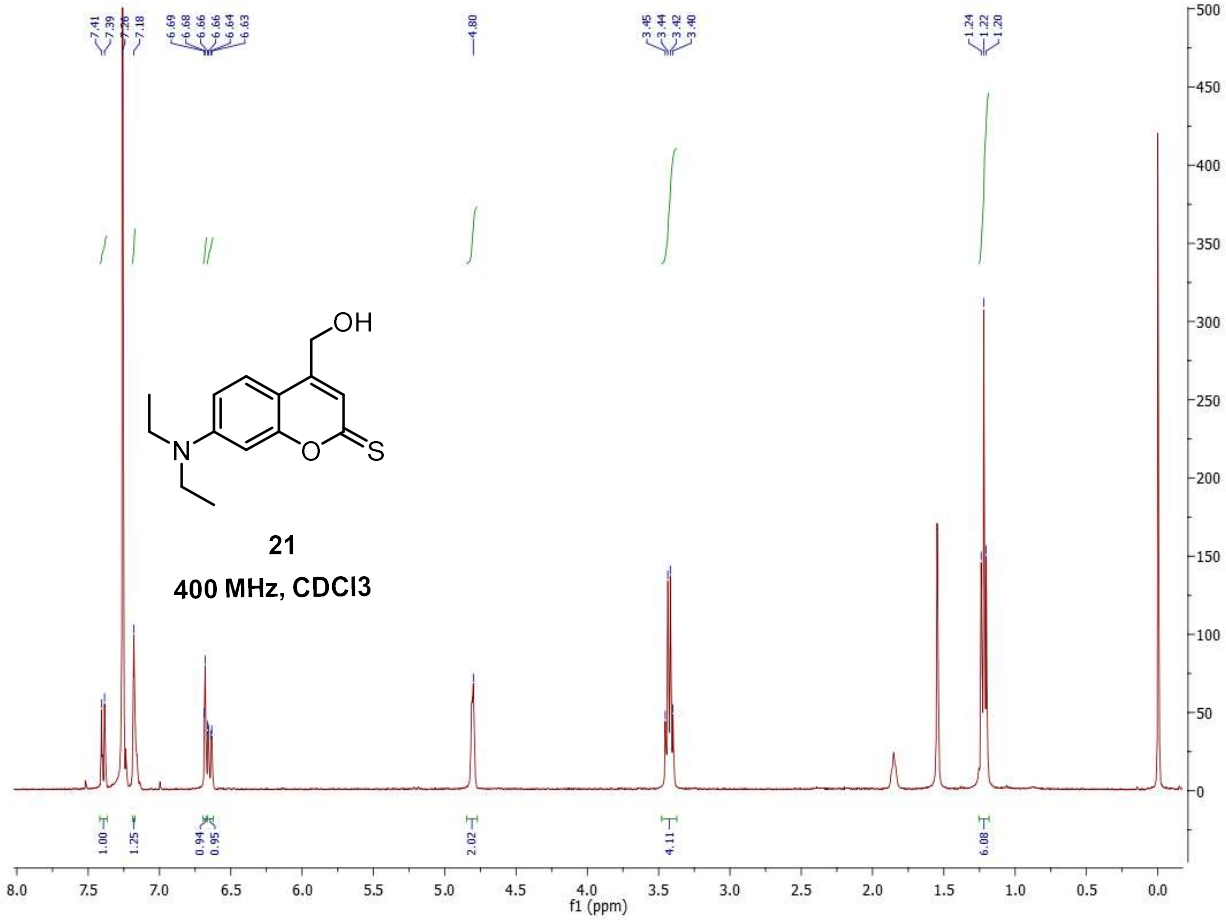


Figure S36. ^{1}H NMR analysis of compound **21.**

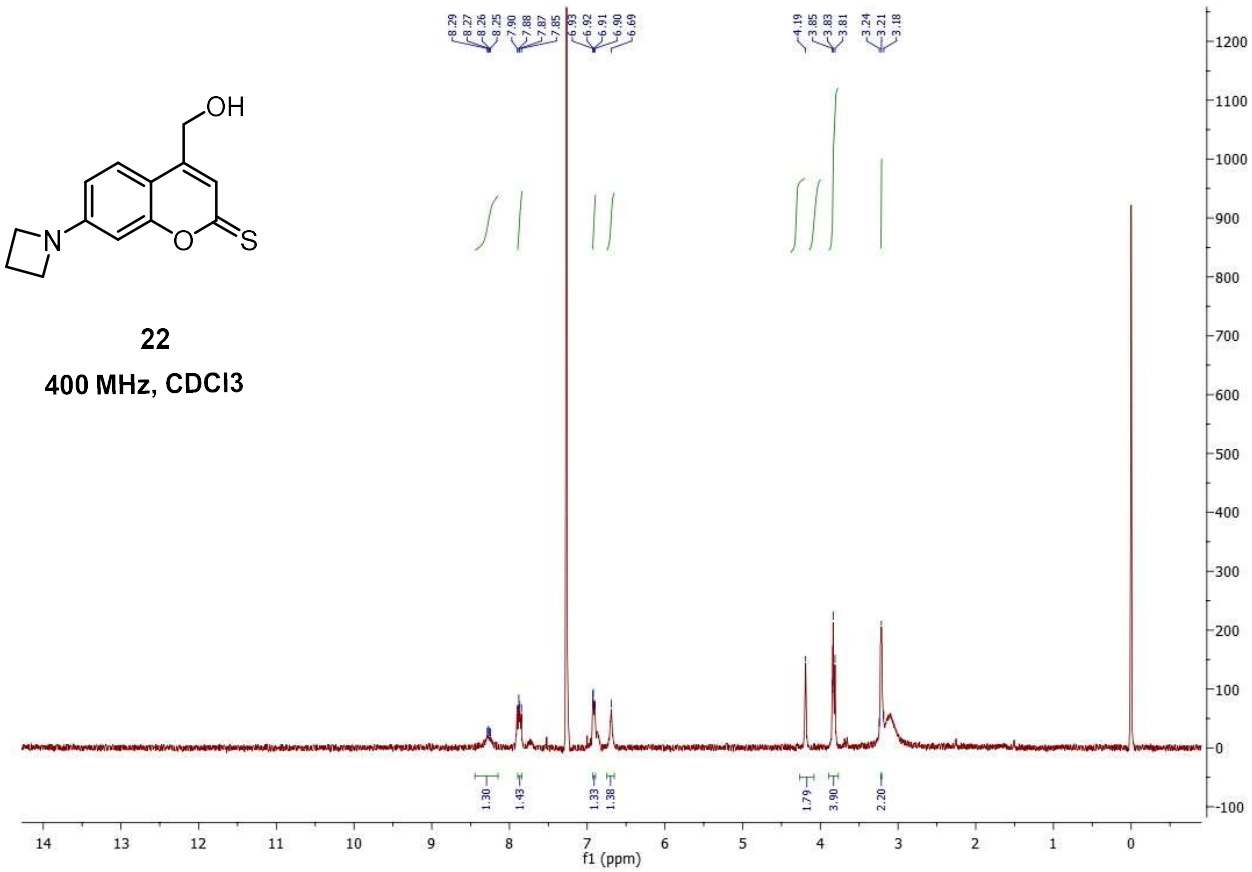


Figure S37. ^{1}H NMR analysis of compound **22.**

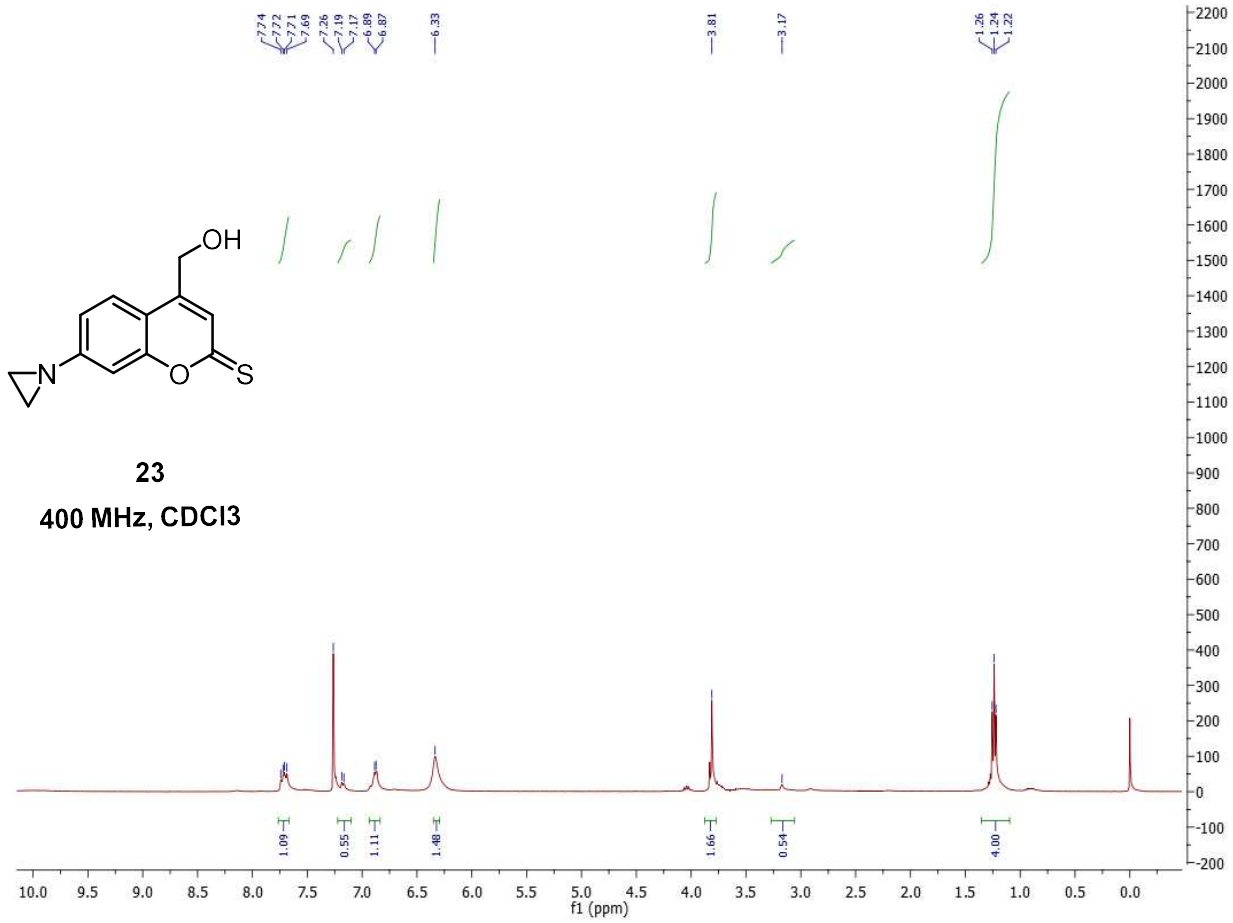


Figure S38. ^{1}H NMR analysis of compound **23.**

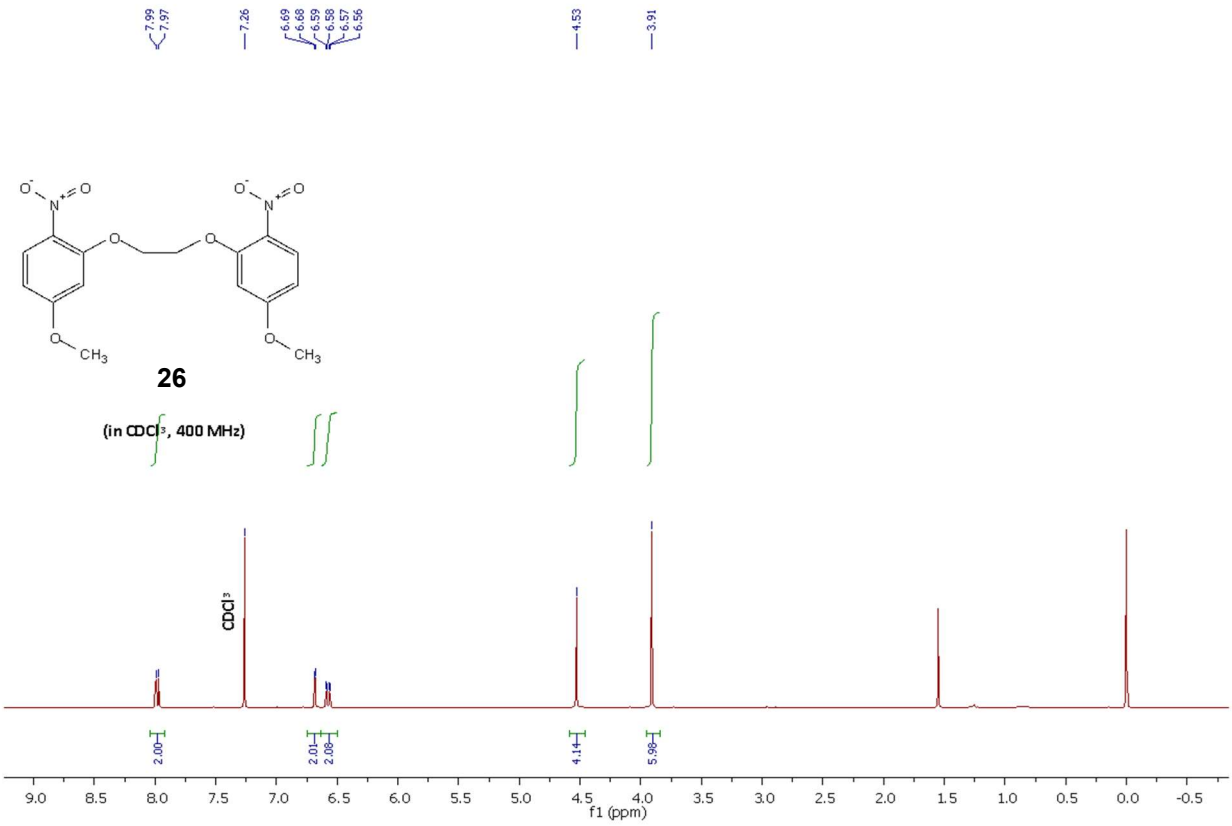


Figure S39. ^{1}H NMR analysis of compound **26.**

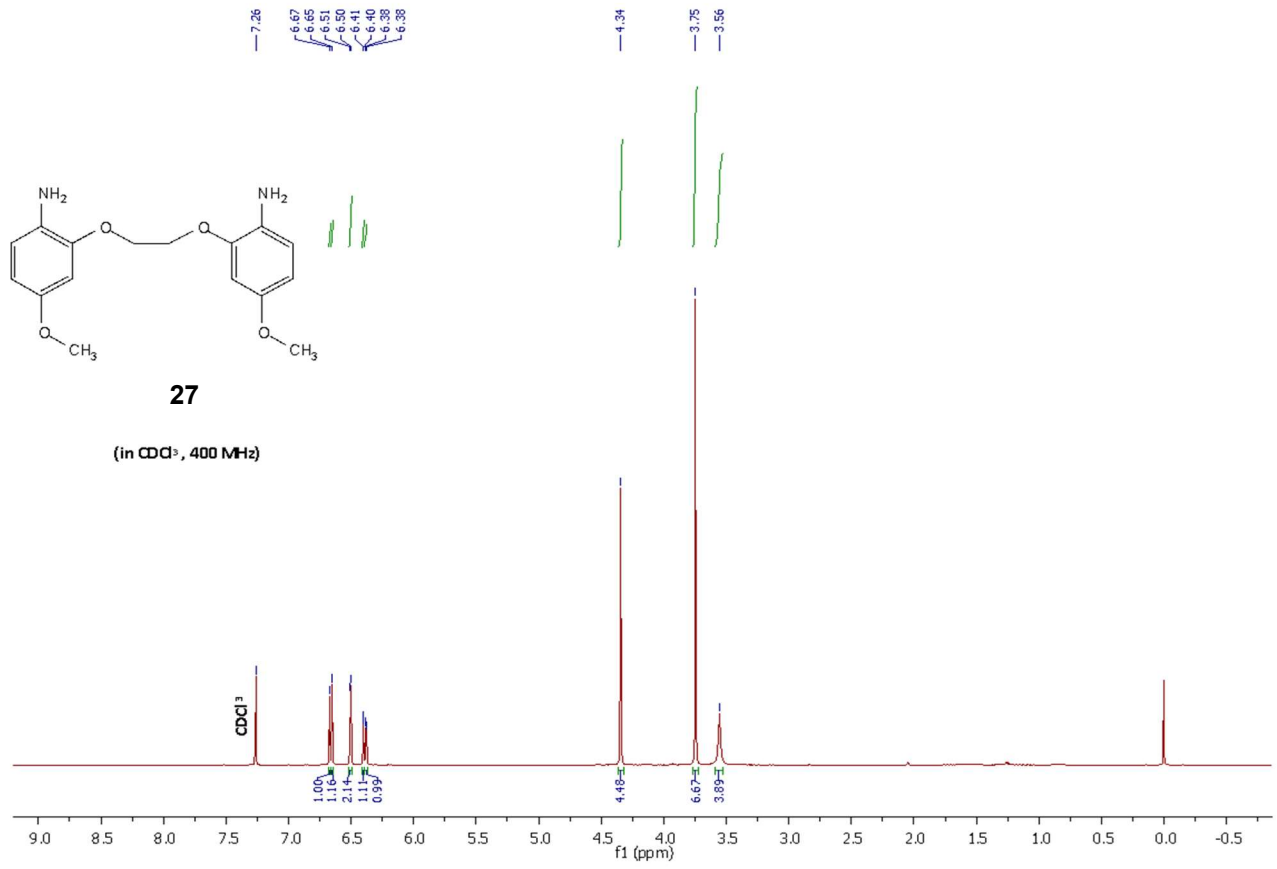


Figure S40. ^{1}H NMR analysis of compound **27.**

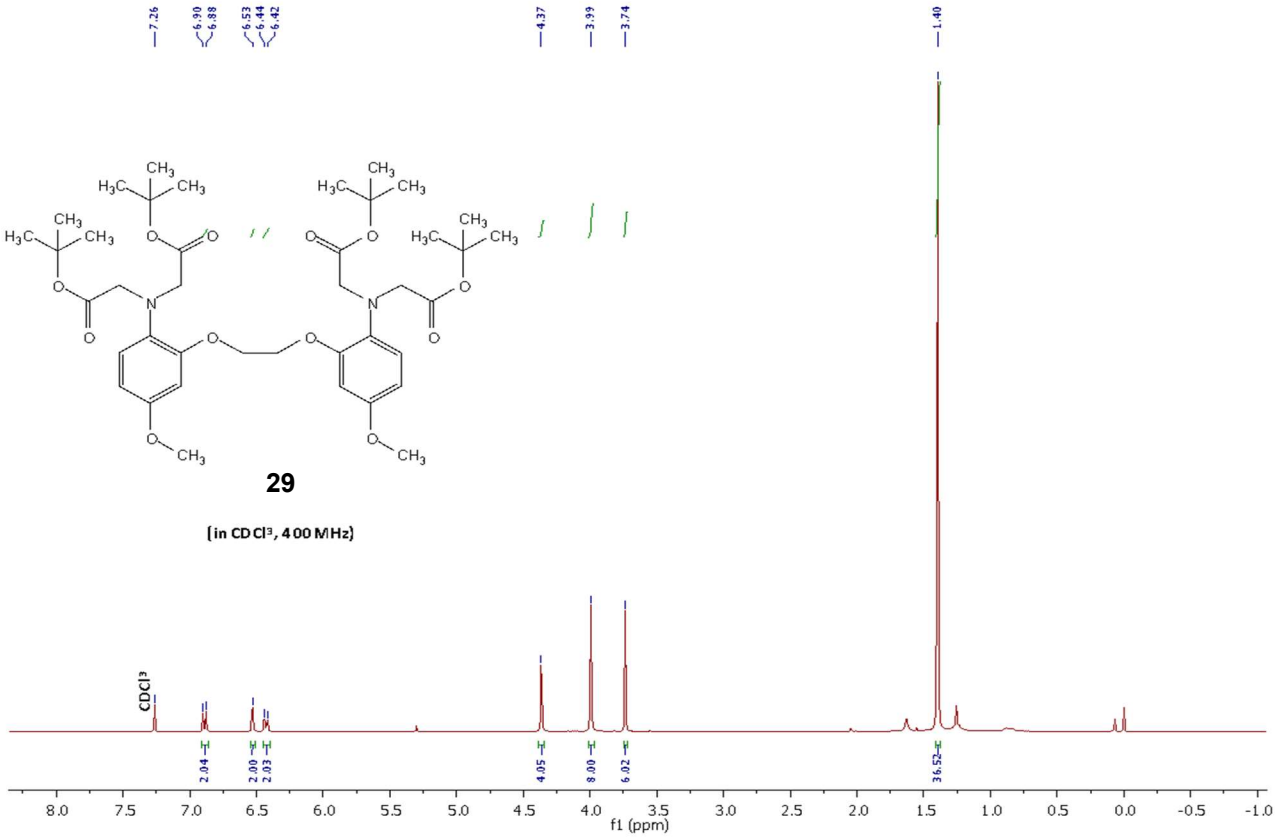


Figure S41. ^{1}H NMR analysis of compound **29.**

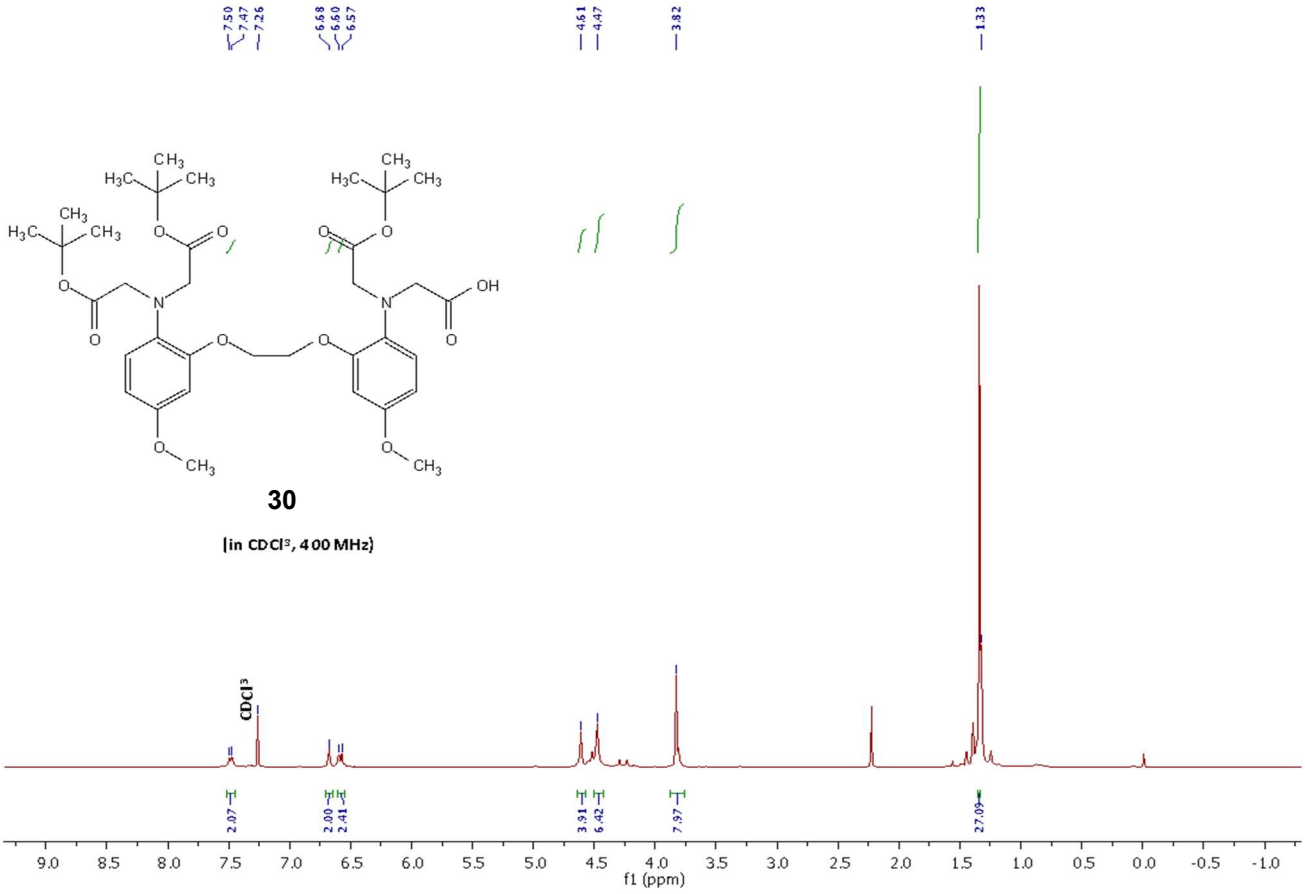


Figure S42. ^{1}H NMR analysis of compound **30.**

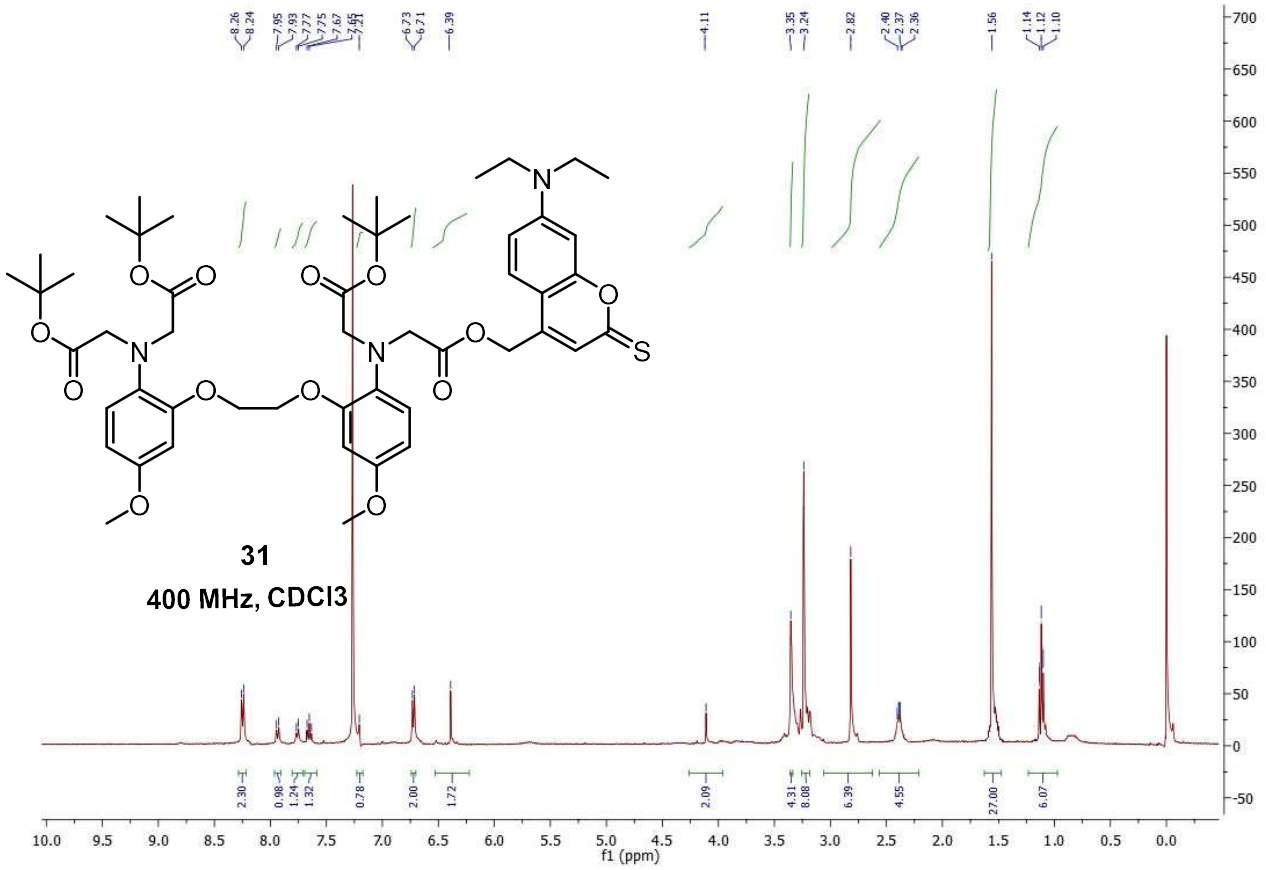


Figure S43. ^{1}H NMR analysis of compound **31.**

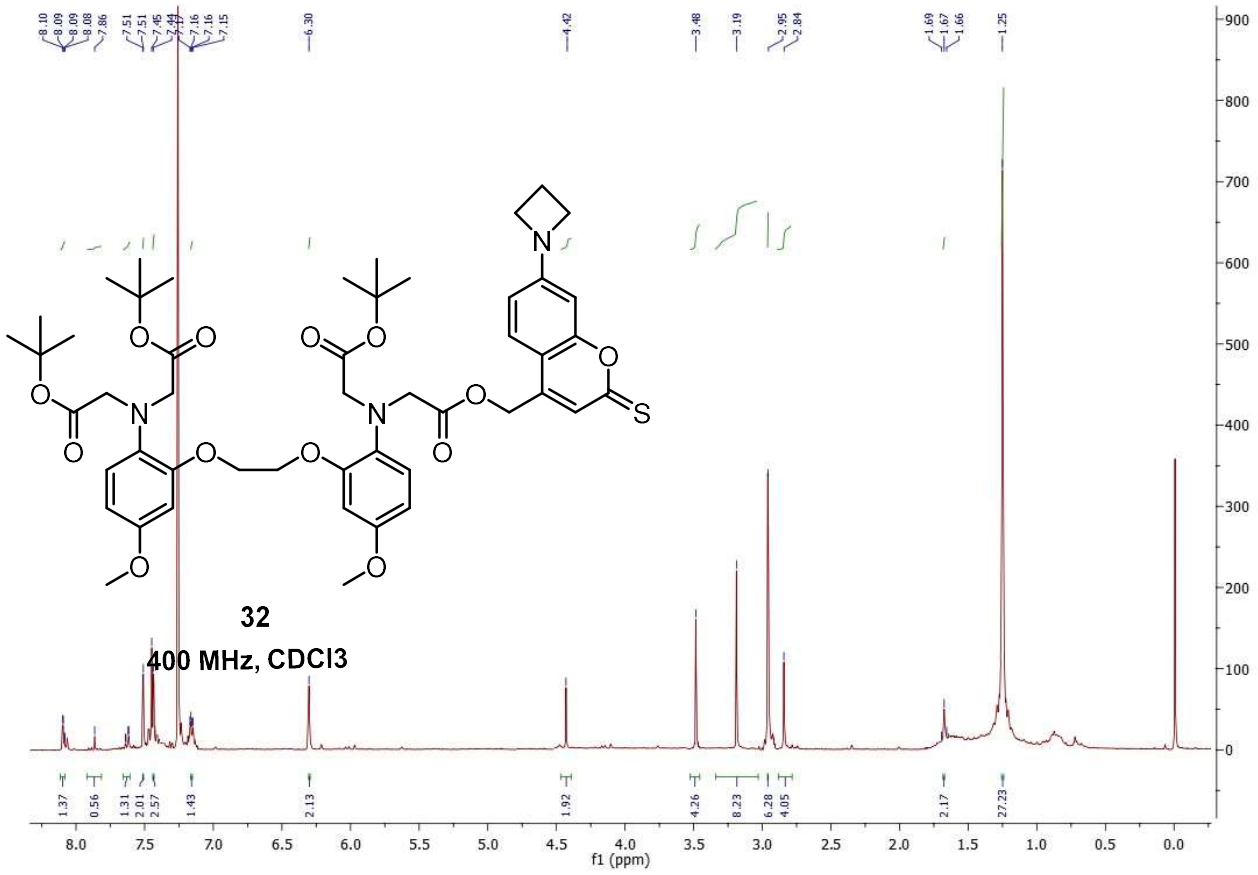


Figure S44. ^{1}H NMR analysis of compound **32.**

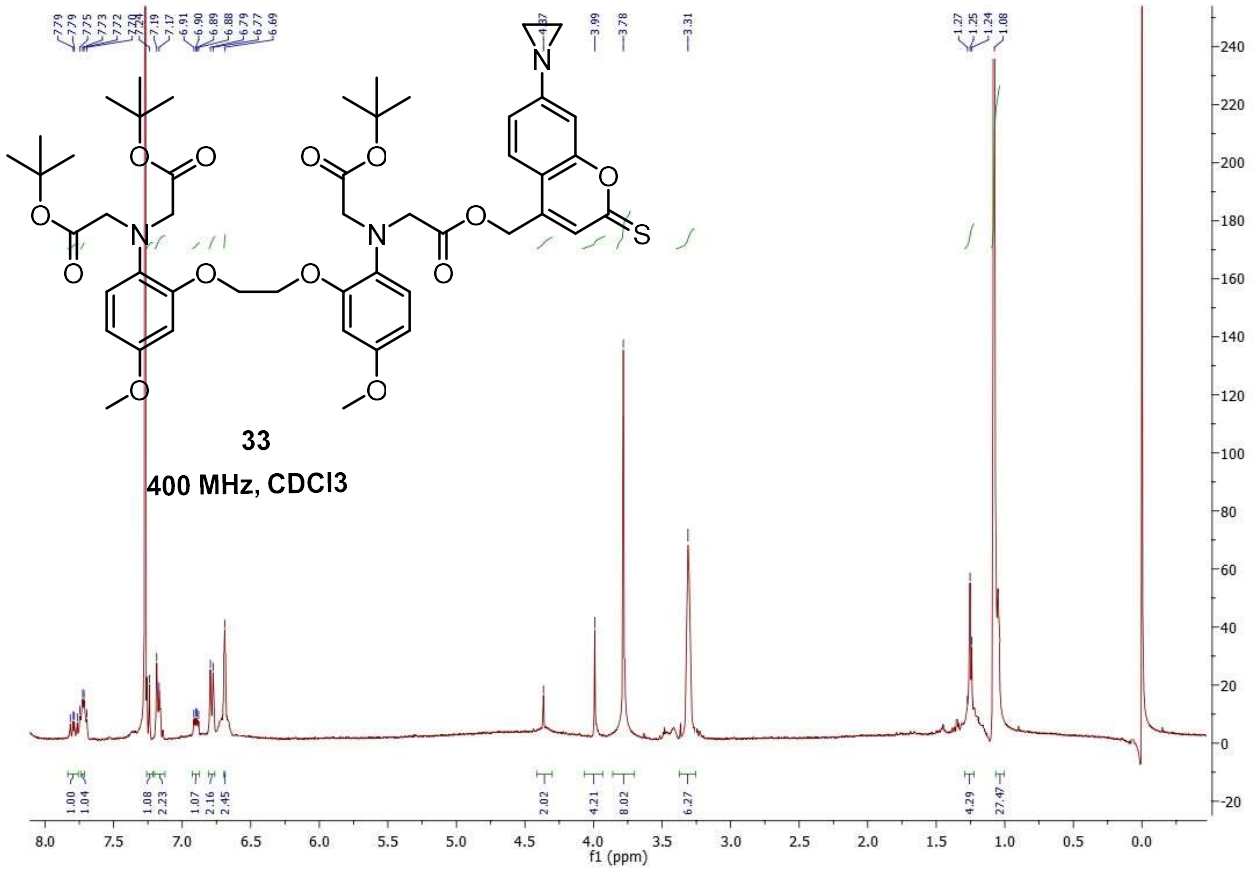


Figure S45. ^{1}H NMR analysis of compound **33.**

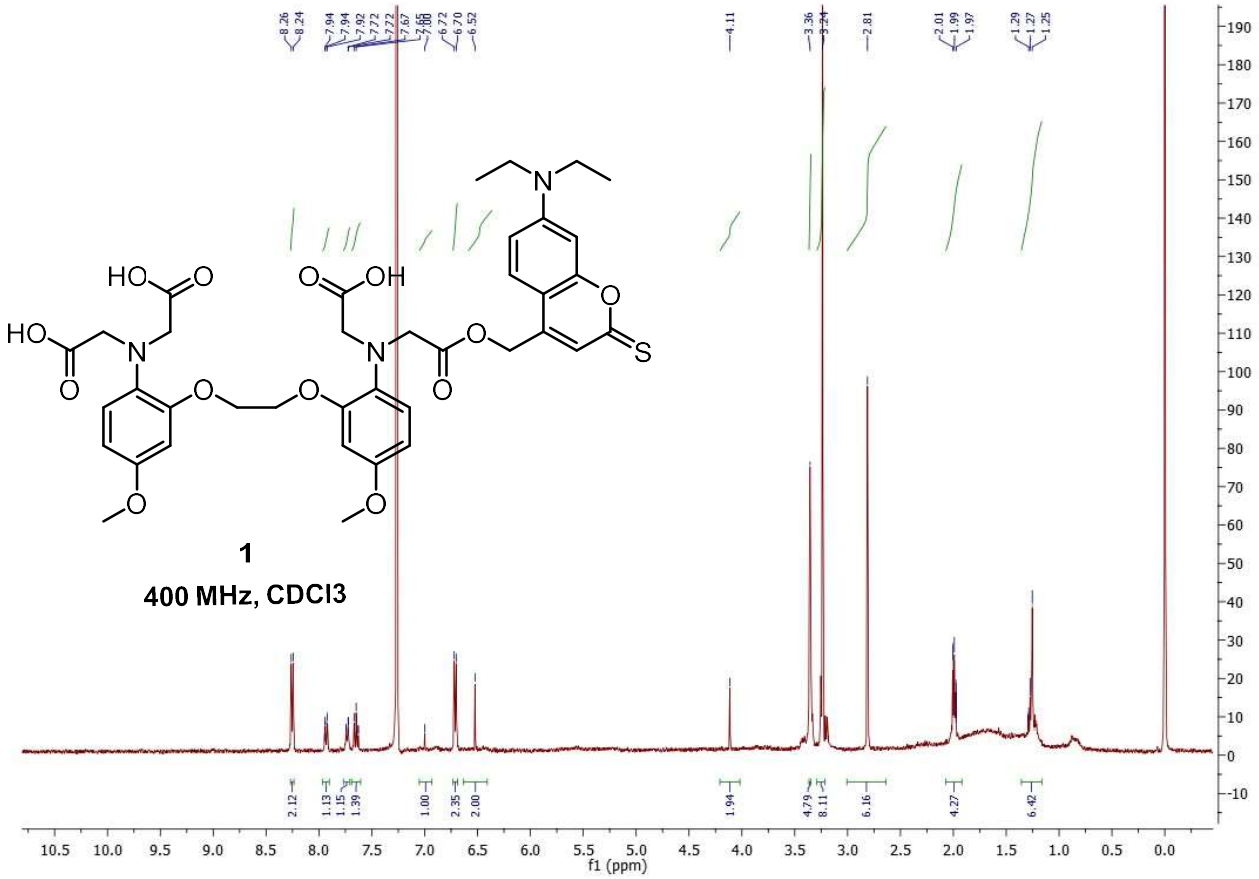


Figure S46. ^{1}H NMR analysis of caged **1.**

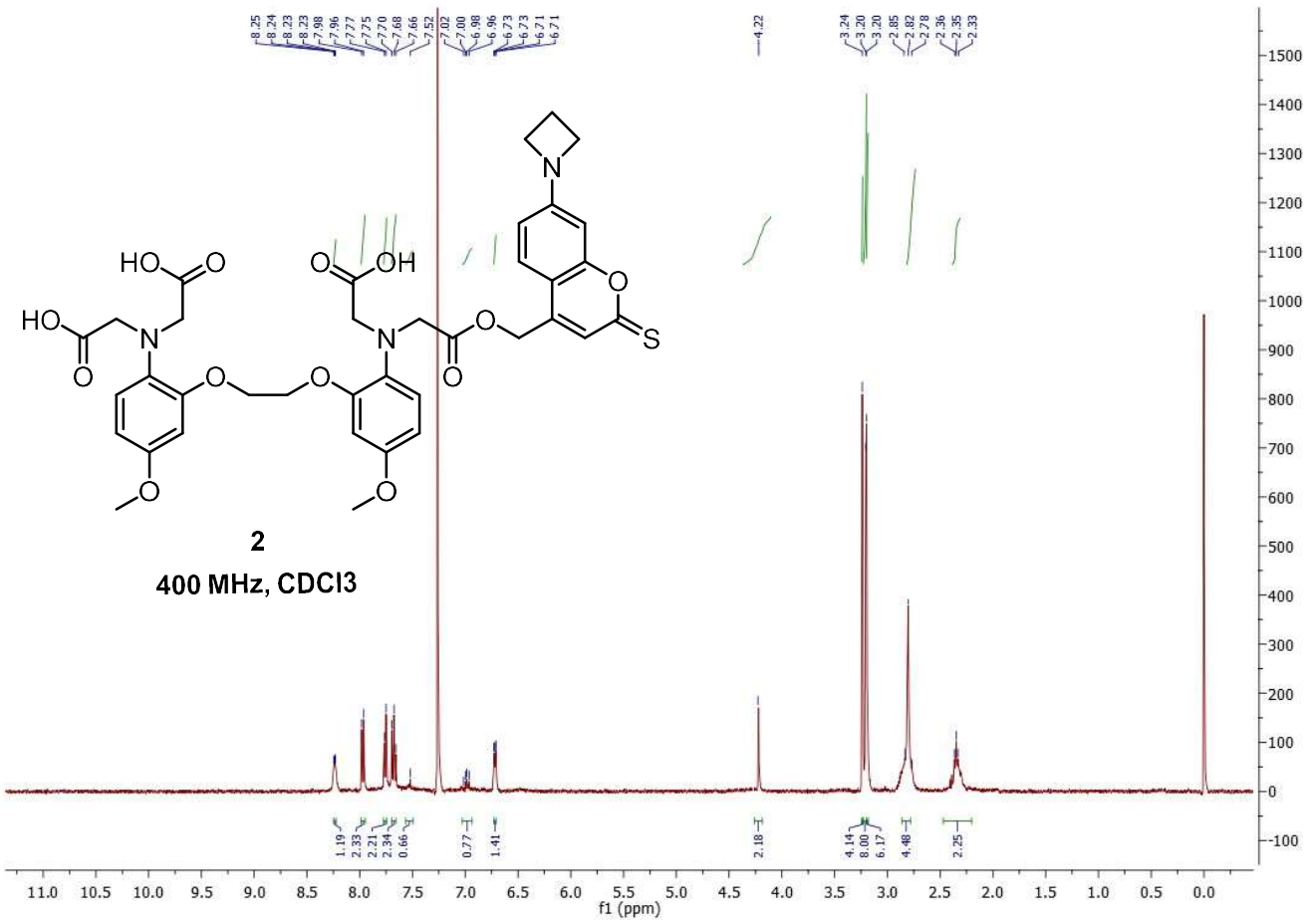


Figure S47. ^{1}H NMR analysis of caged **2.**

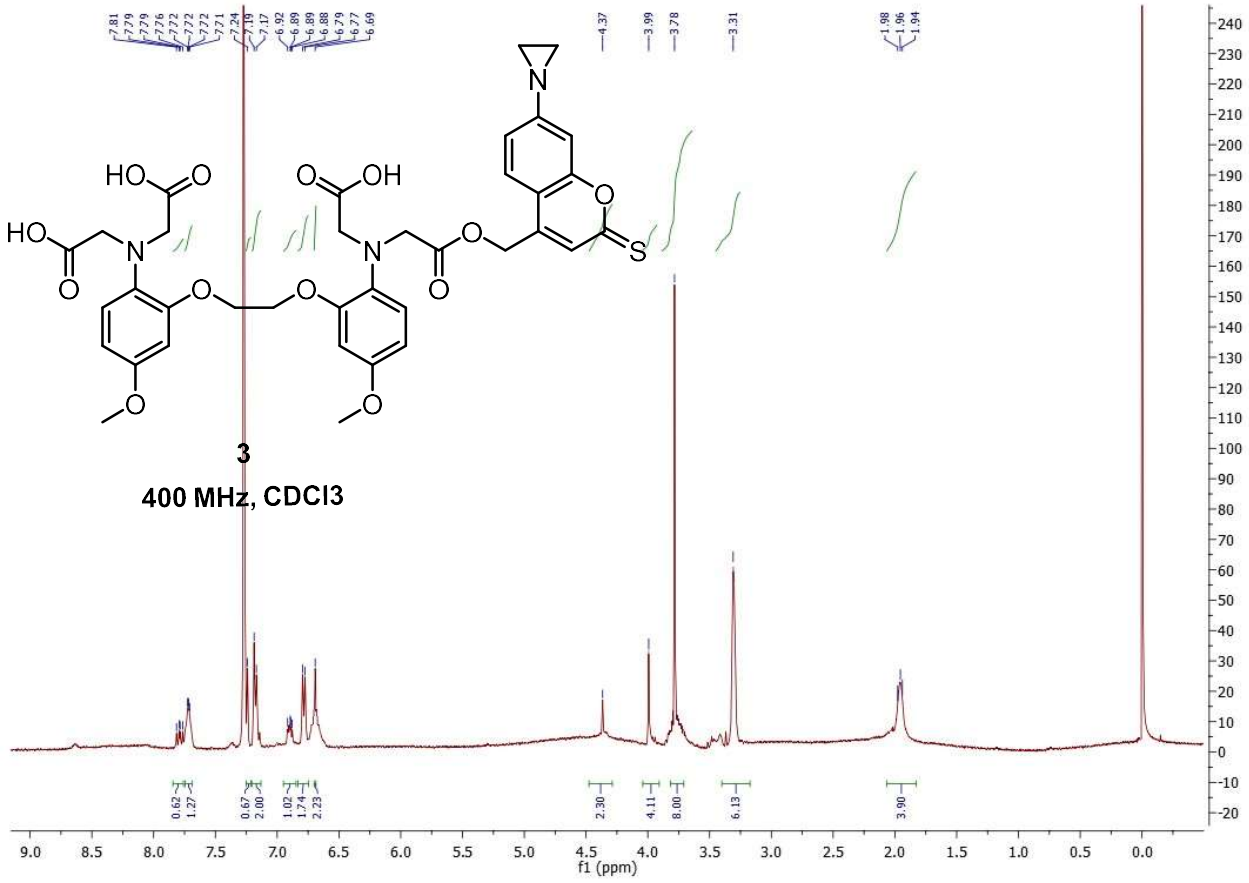


Figure S48. ^{1}H NMR analysis of caged **3.**

14. ^{13}C NMR of the Synthesized Compounds

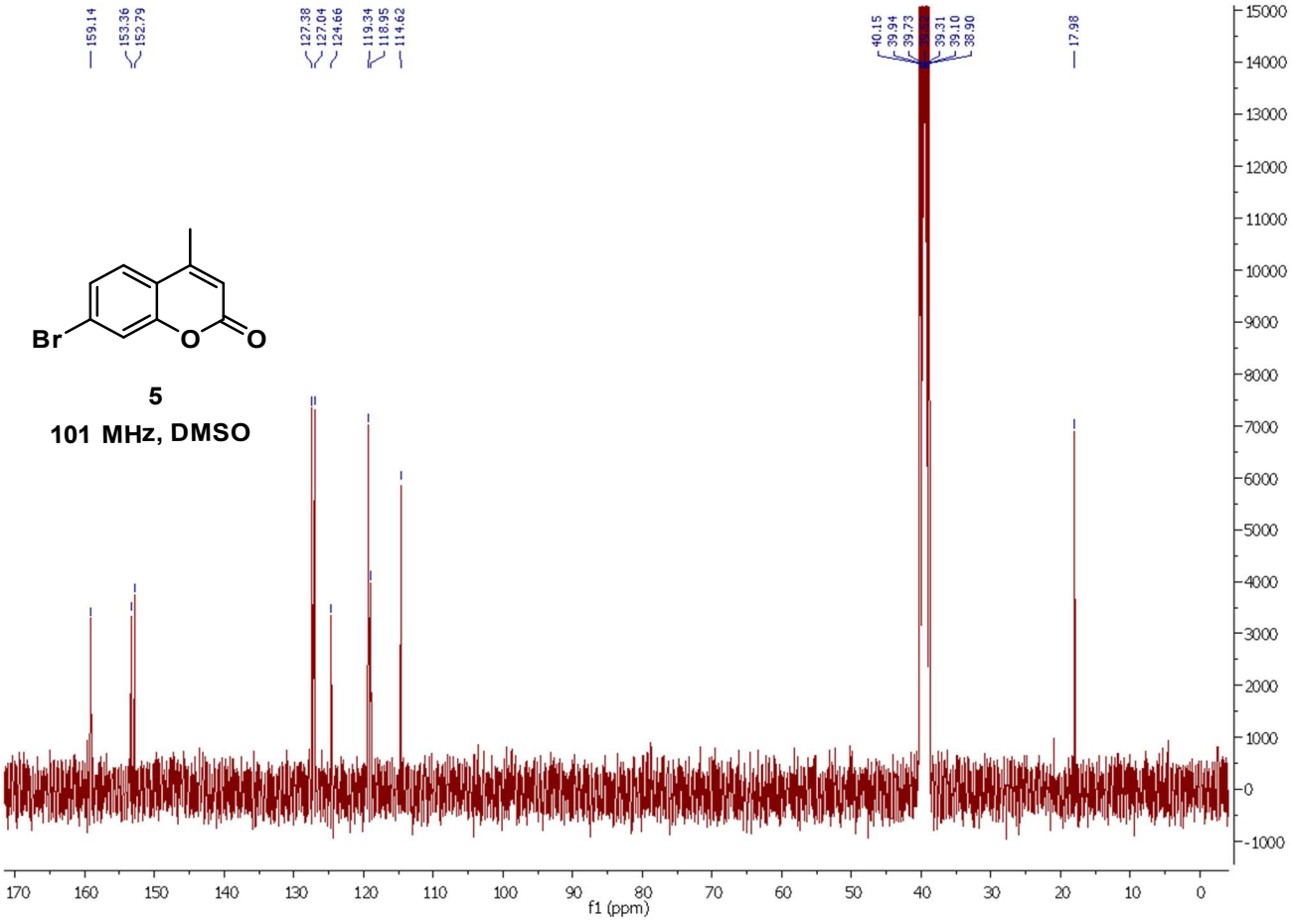


Figure S49. ^{13}C NMR analysis of compound **5.**

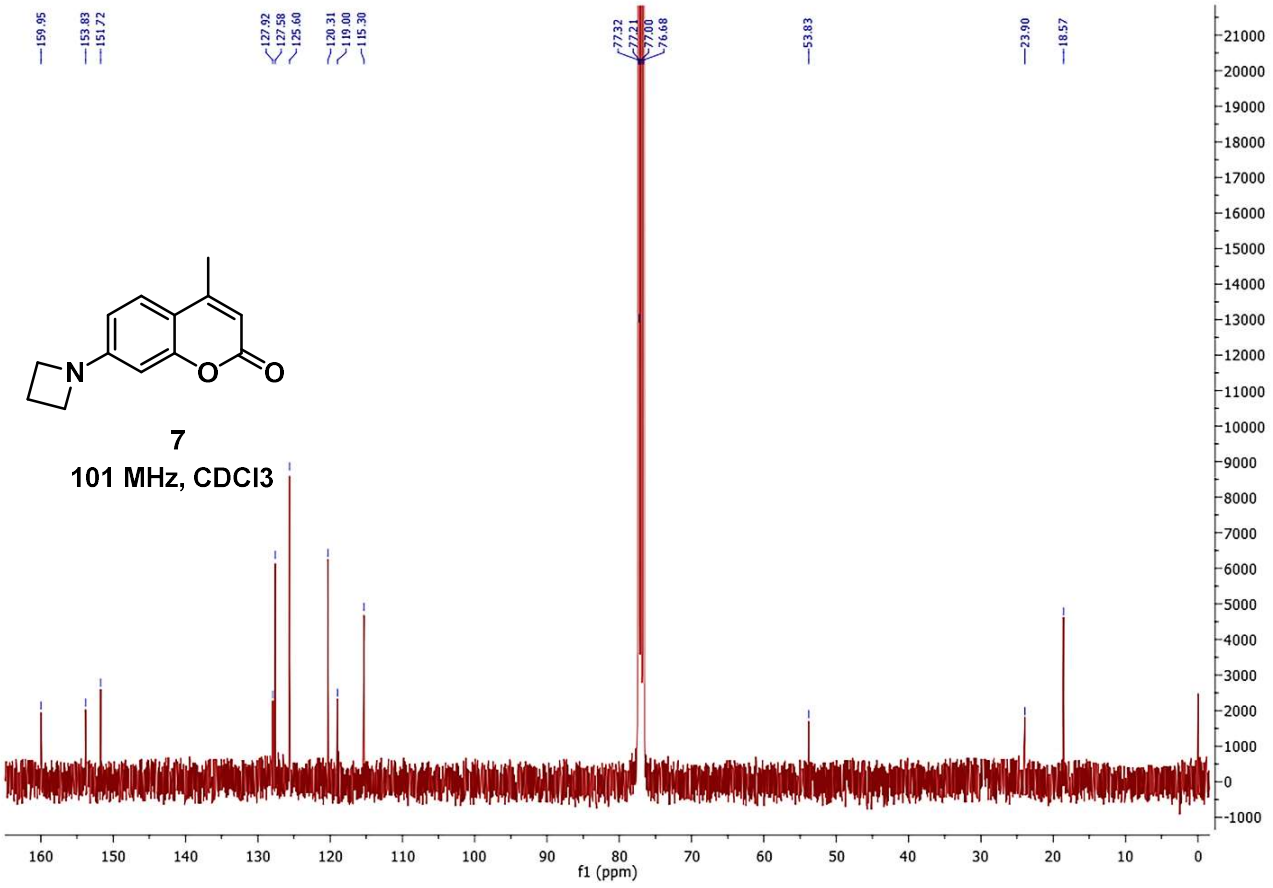


Figure S50. ^{13}C NMR analysis of compound **7.**

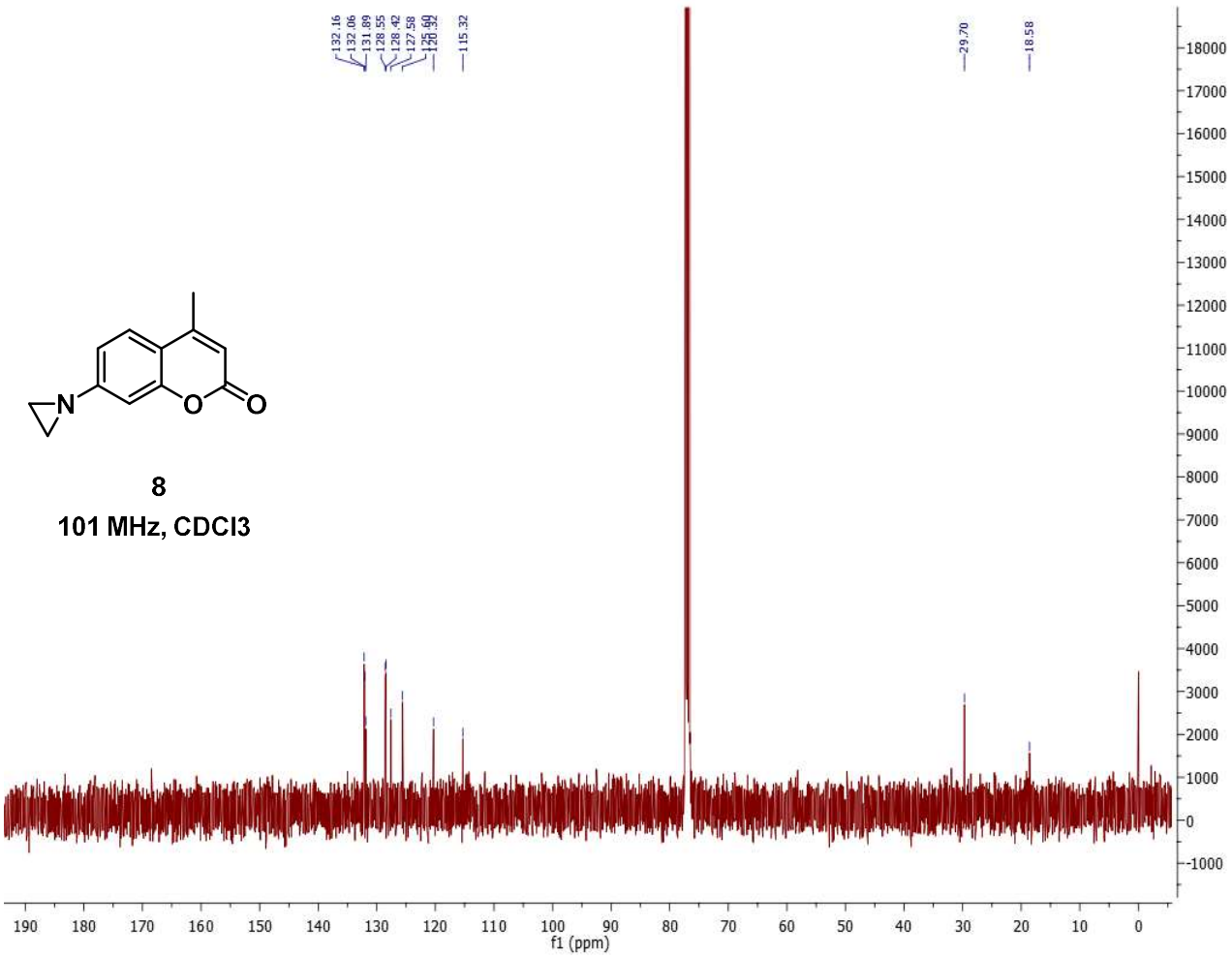


Figure S51. ^{13}C NMR analysis of compound **8.**

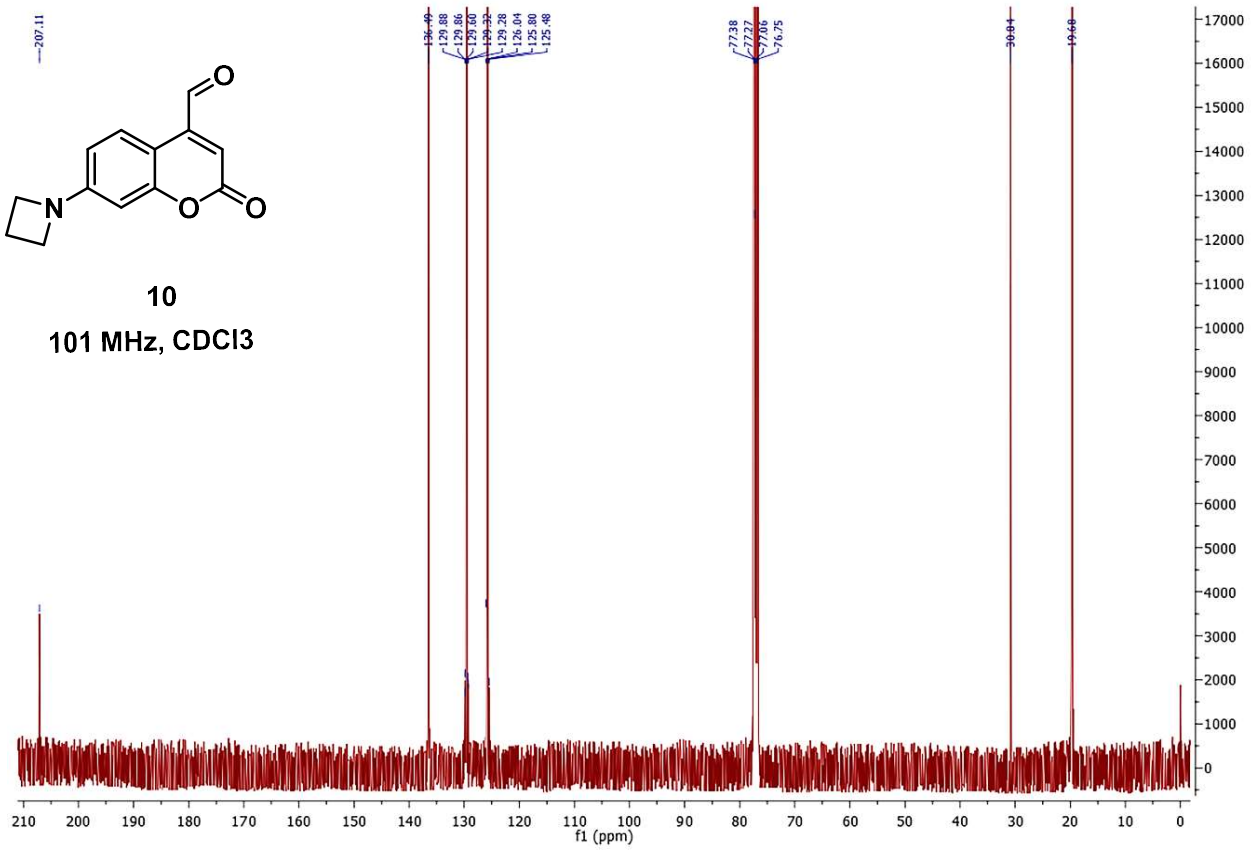


Figure S52. ^{13}C NMR analysis of compound **10.**

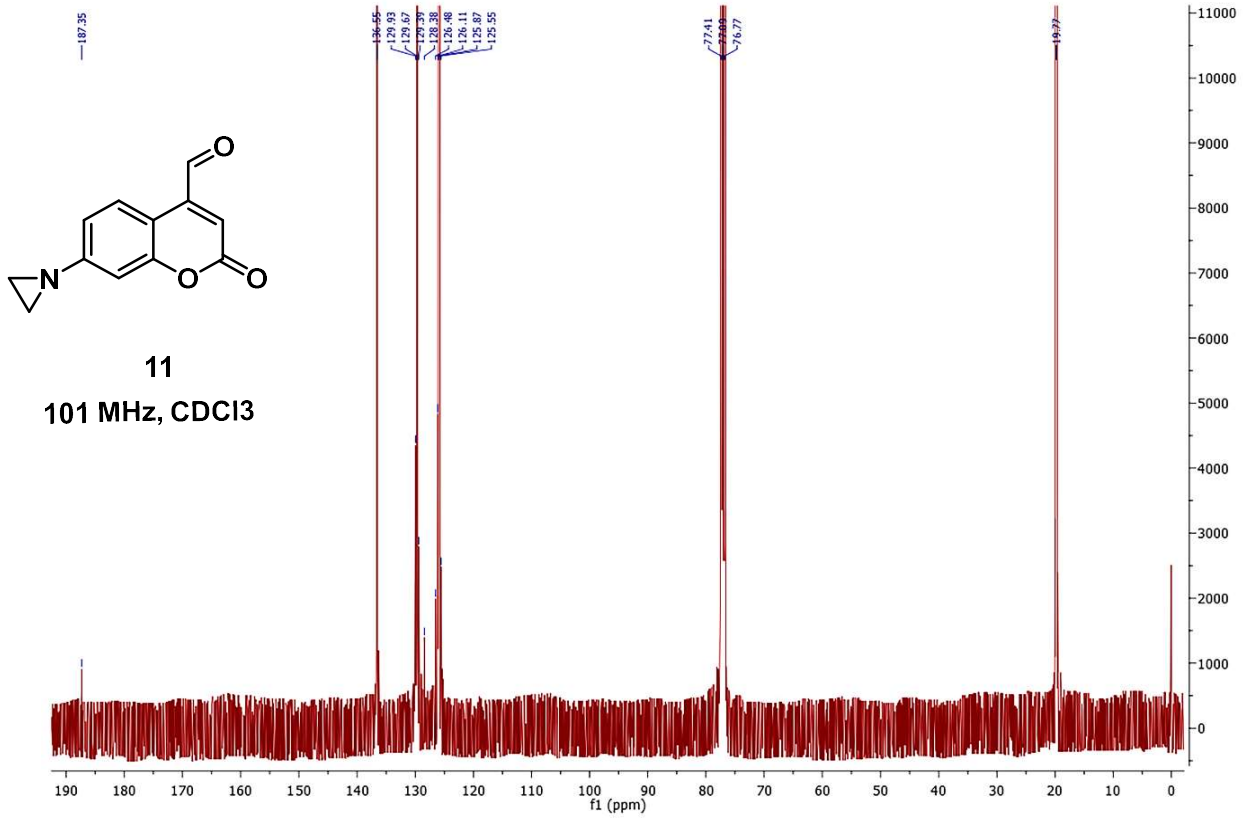


Figure S53. ^{13}C NMR analysis of compound **11.**

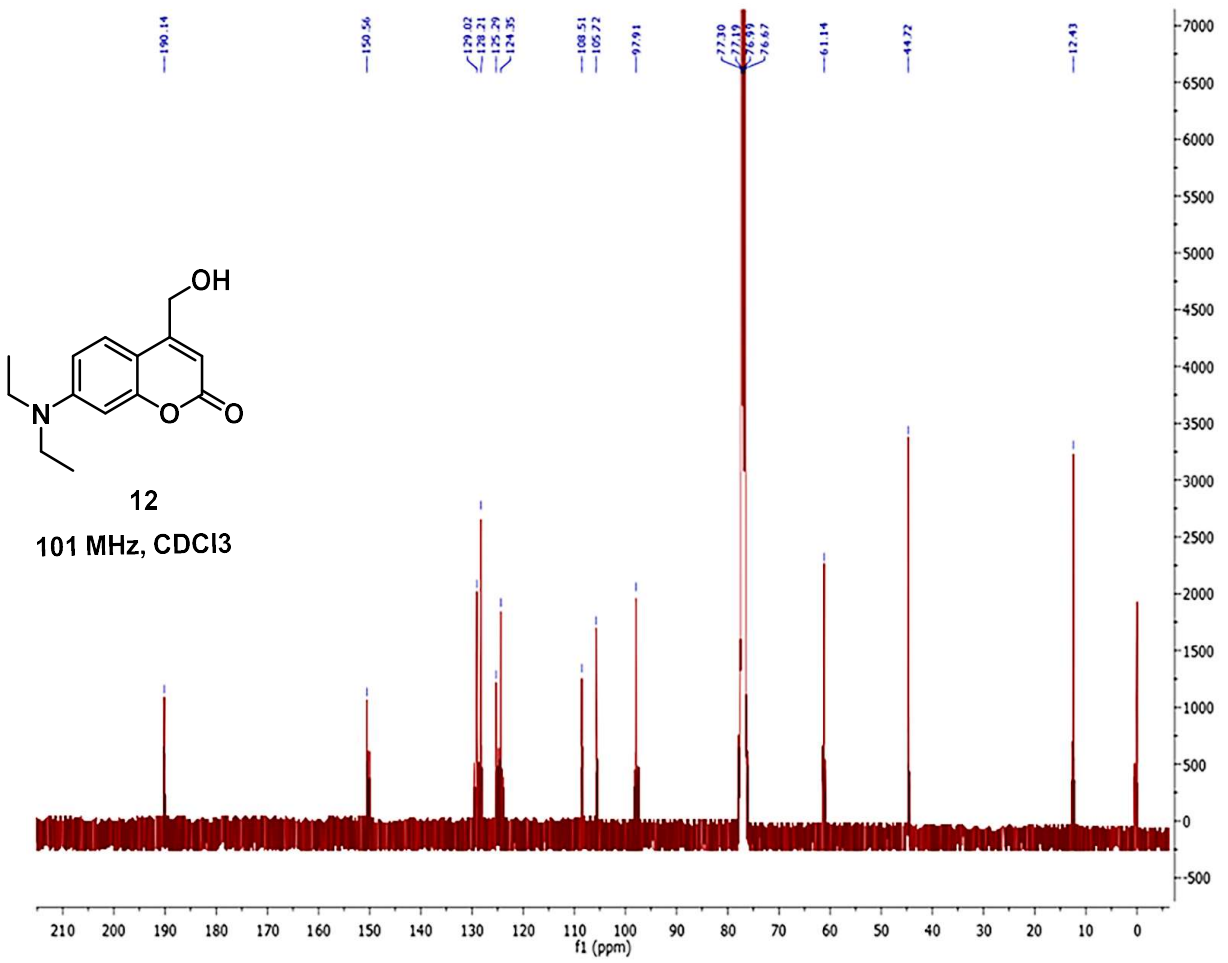


Figure S54. ^{13}C NMR analysis of compound **12.**

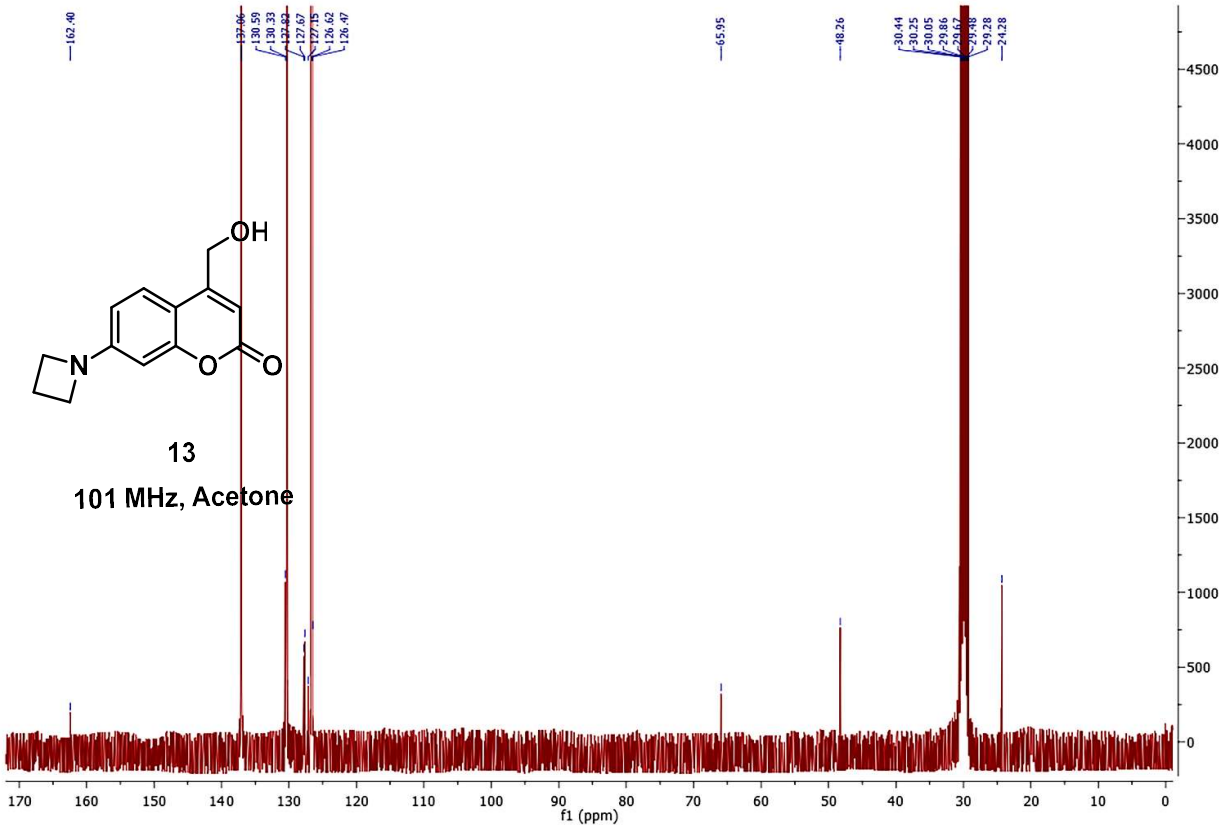


Figure S55. ^{13}C NMR analysis of compound **13.**

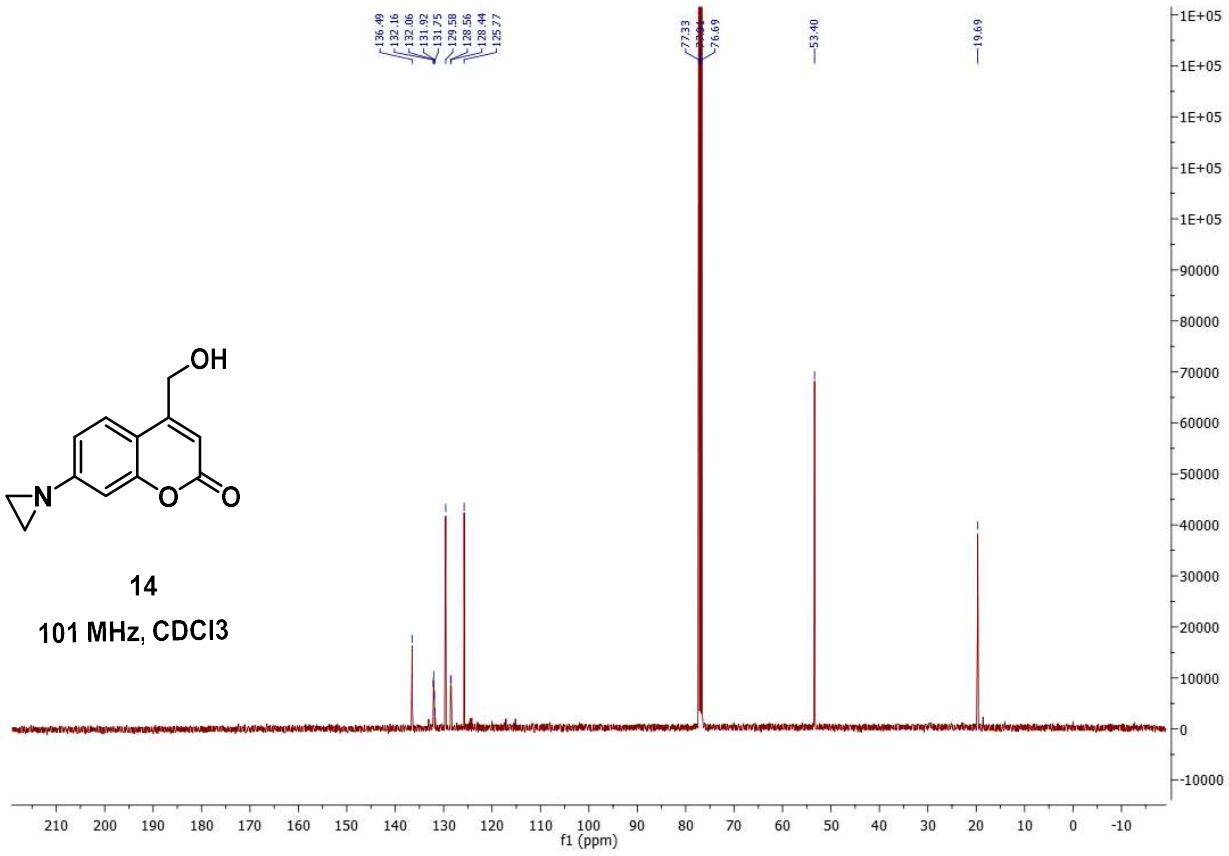


Figure S56. ^{13}C NMR analysis of compound **14.**

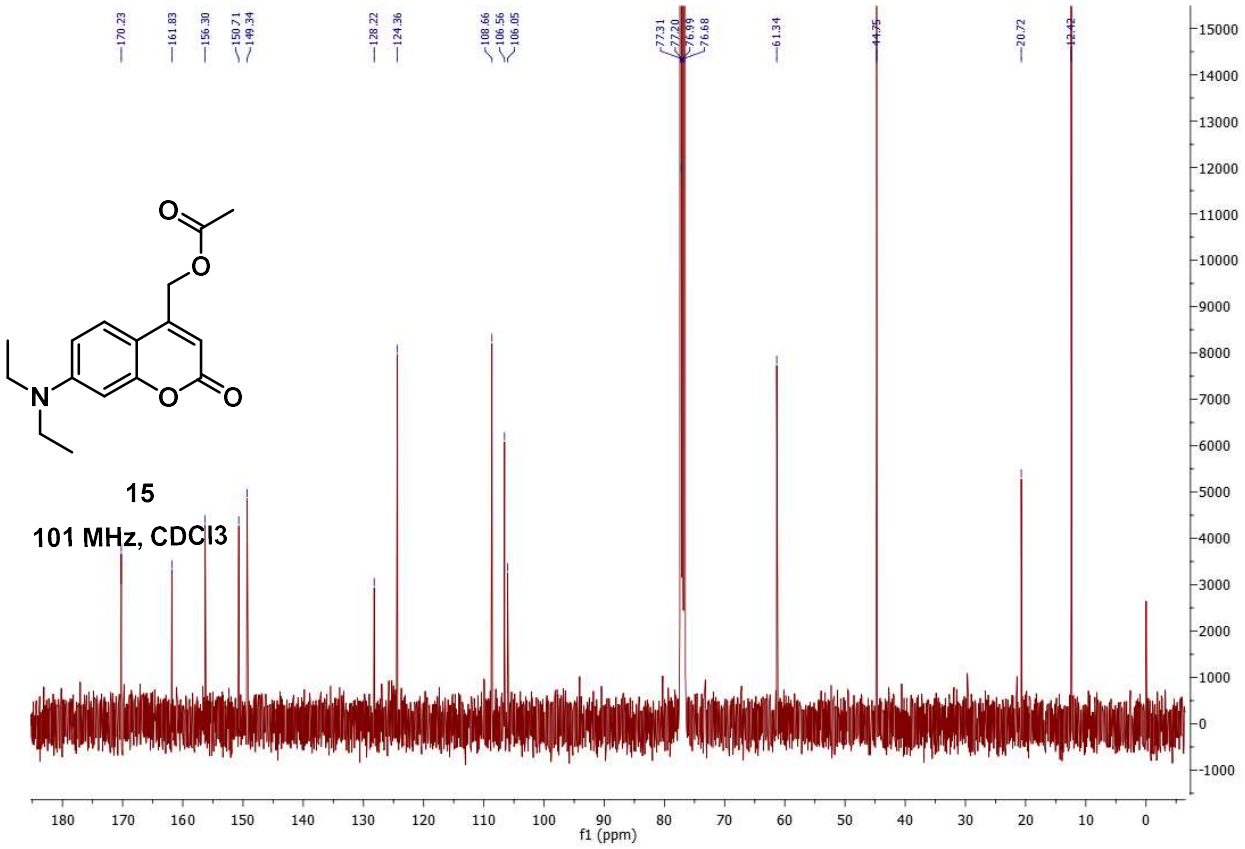


Figure S57. ^{13}C NMR analysis of compound **15.**

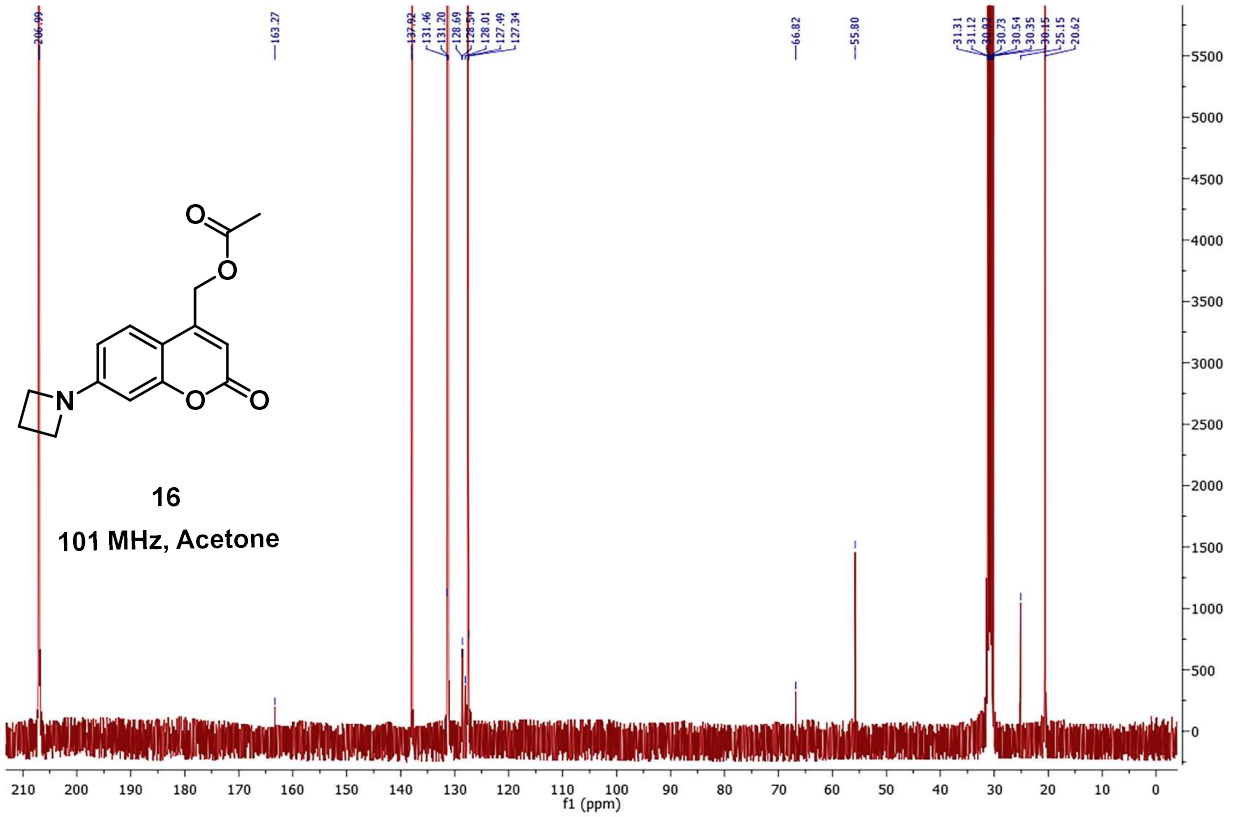


Figure S58. ^{13}C NMR analysis of compound **16.**

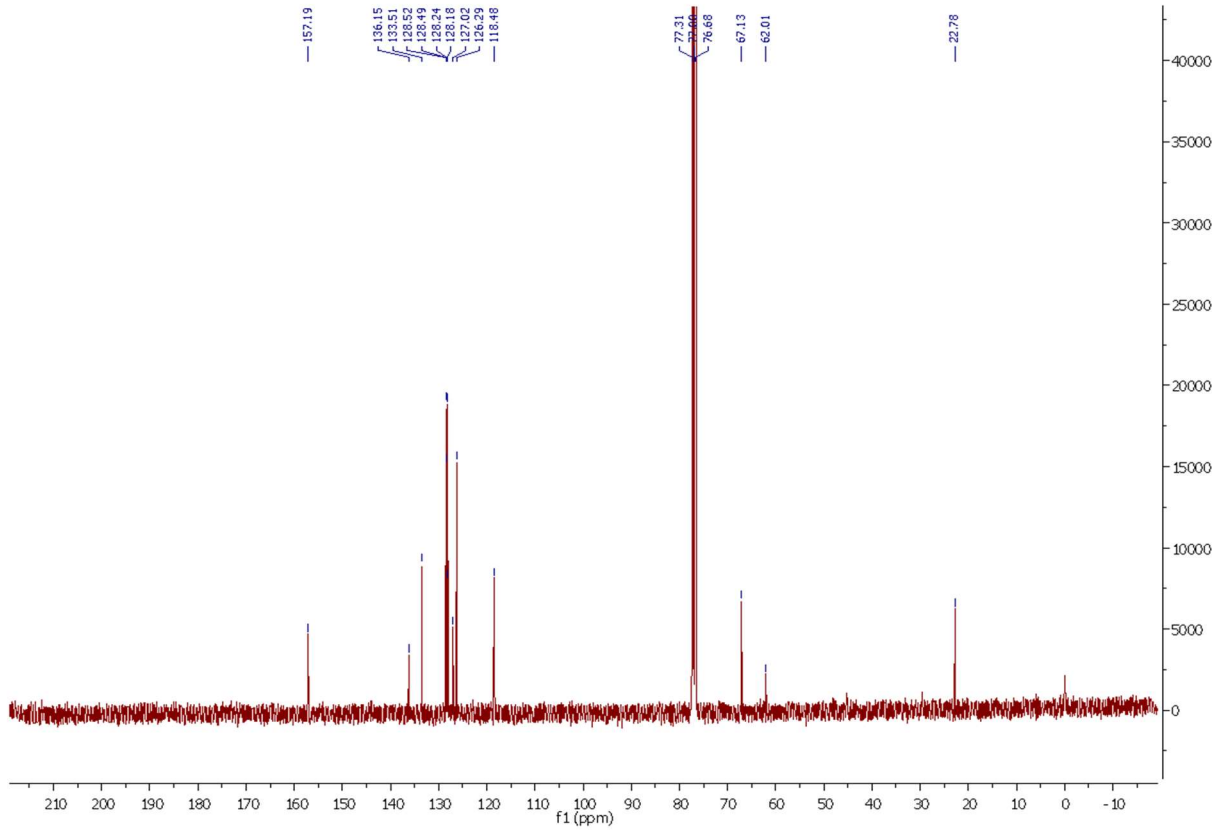


Figure S59. ^{13}C NMR analysis of compound **17.**

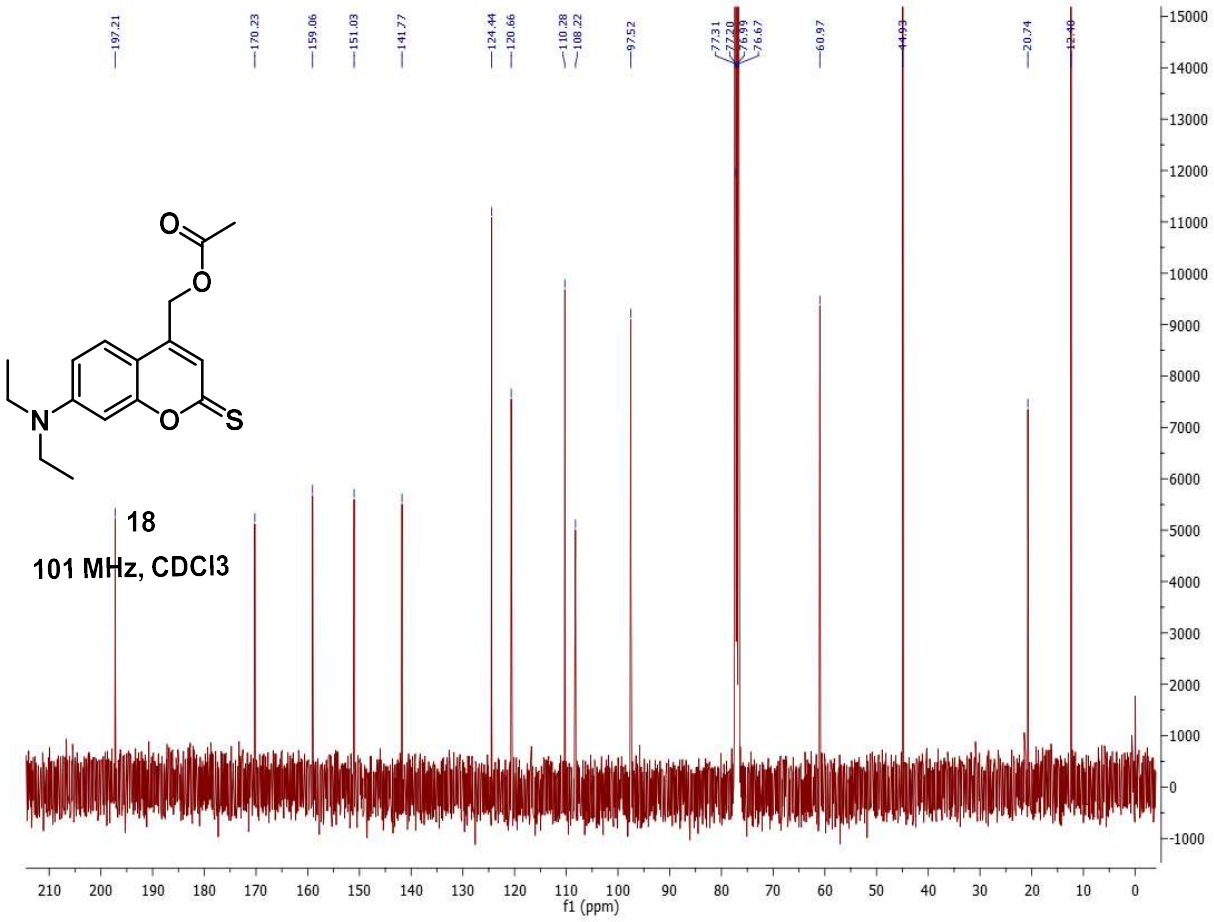


Figure S60. ^{13}C NMR analysis of compound **18.**

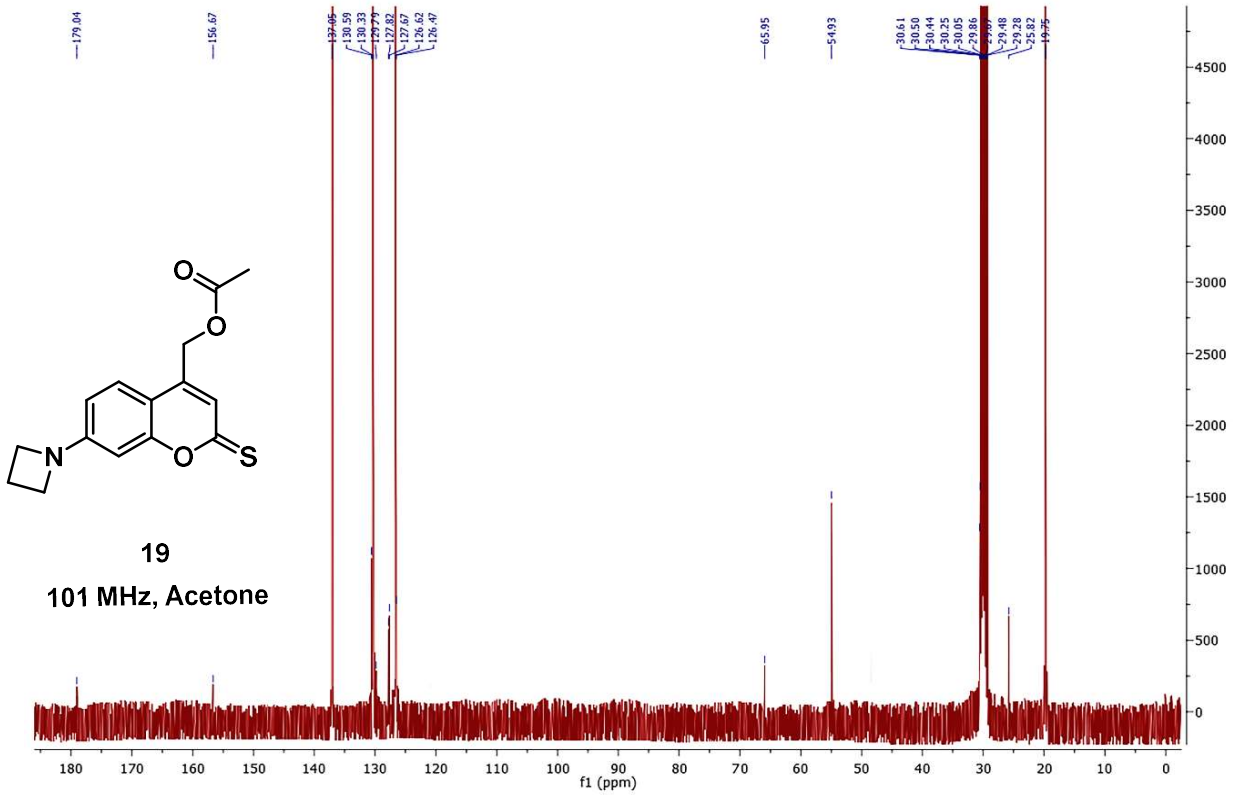


Figure S61. ^{13}C NMR analysis of compound **19.**

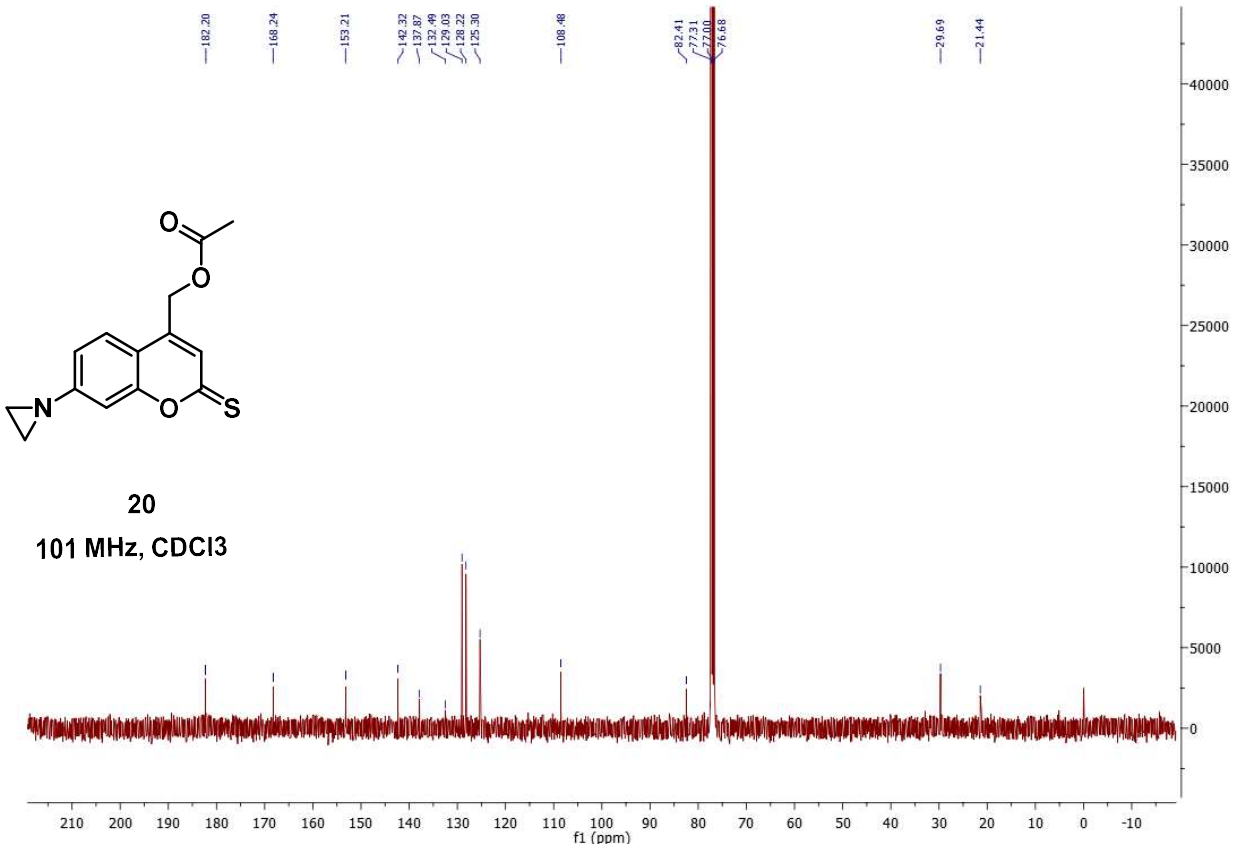


Figure S62. ^{13}C NMR analysis of compound **20.**

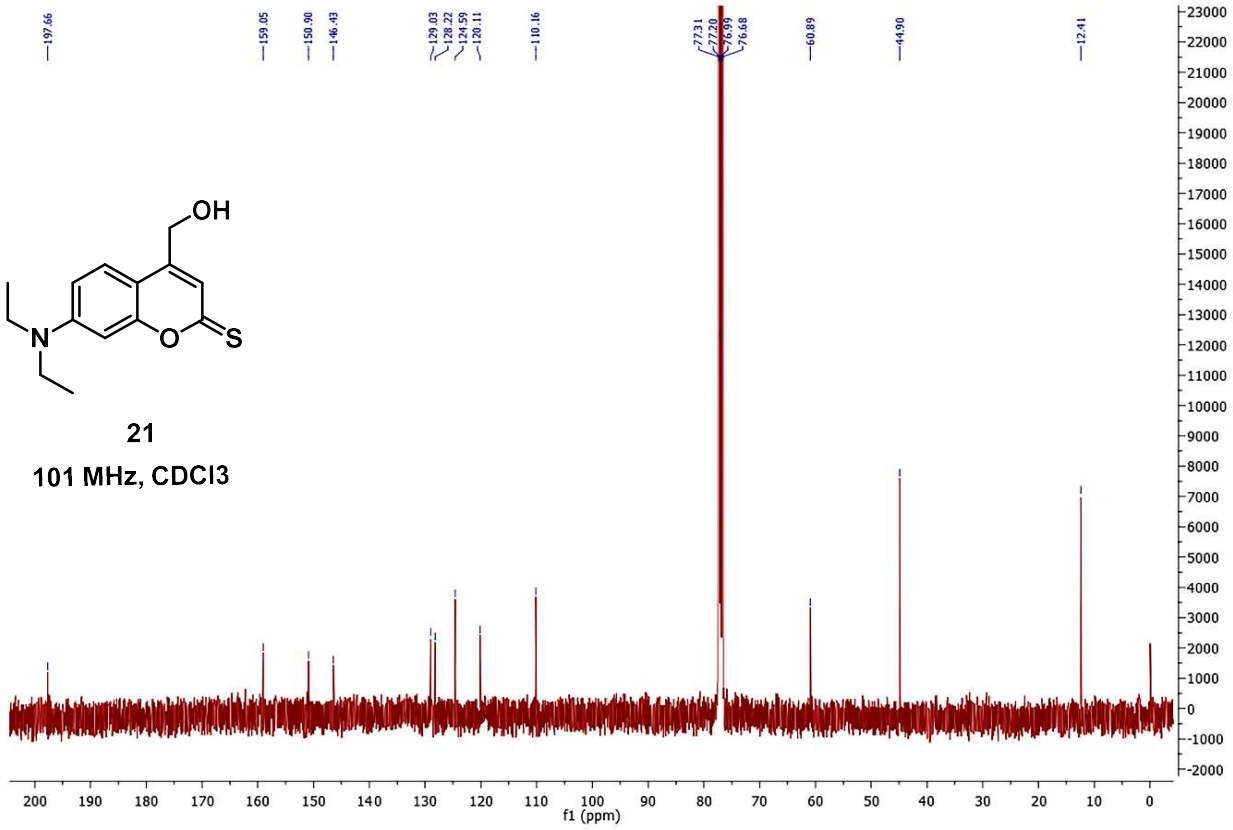


Figure S63. ^{13}C NMR analysis of compound **21.**

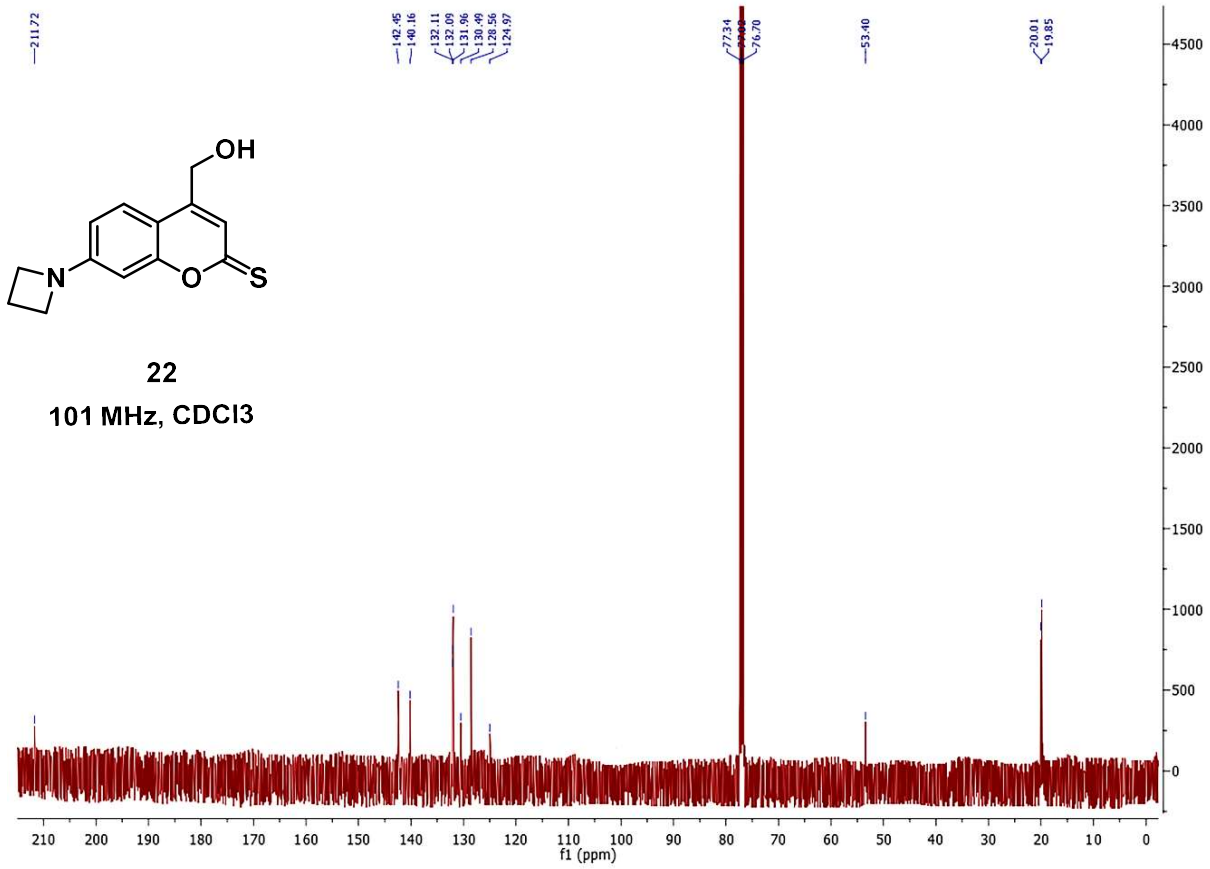


Figure S64. ^{13}C NMR analysis of compound **22.**

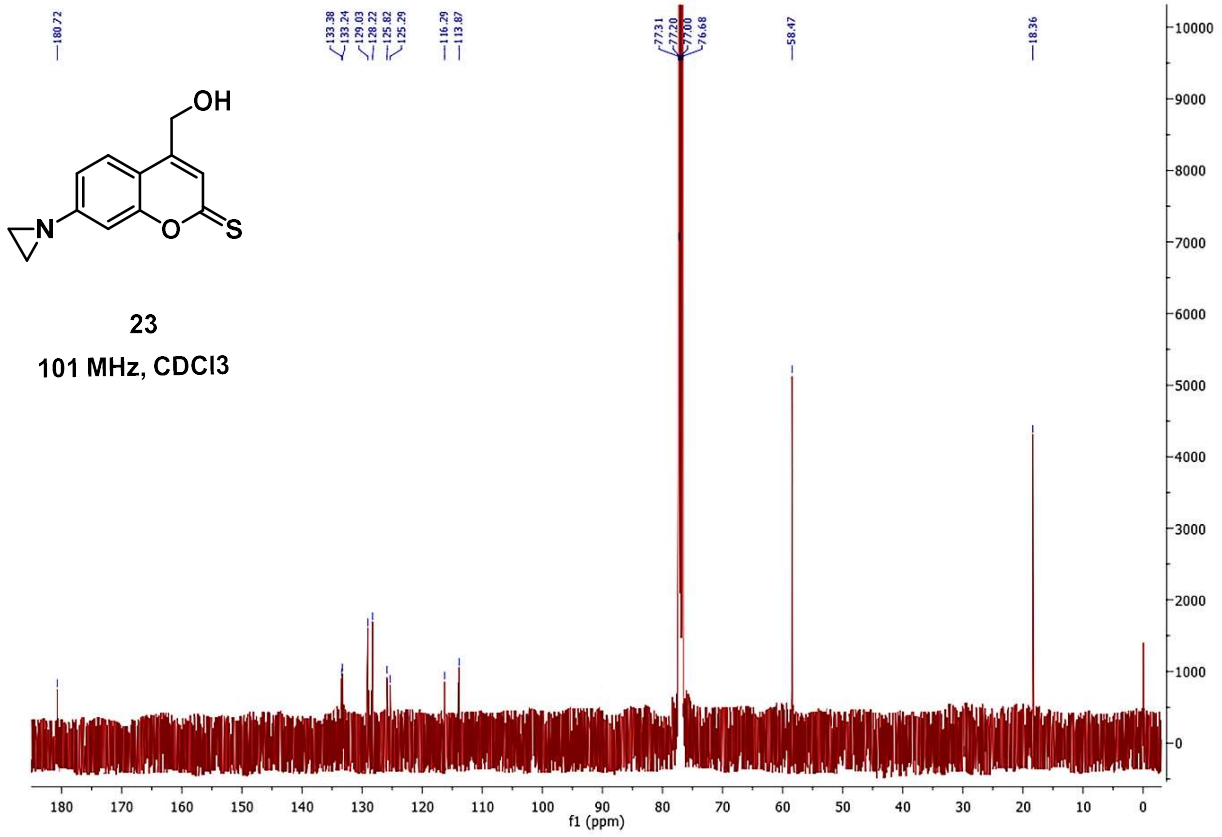


Figure S65. ^{13}C NMR analysis of compound **23.**

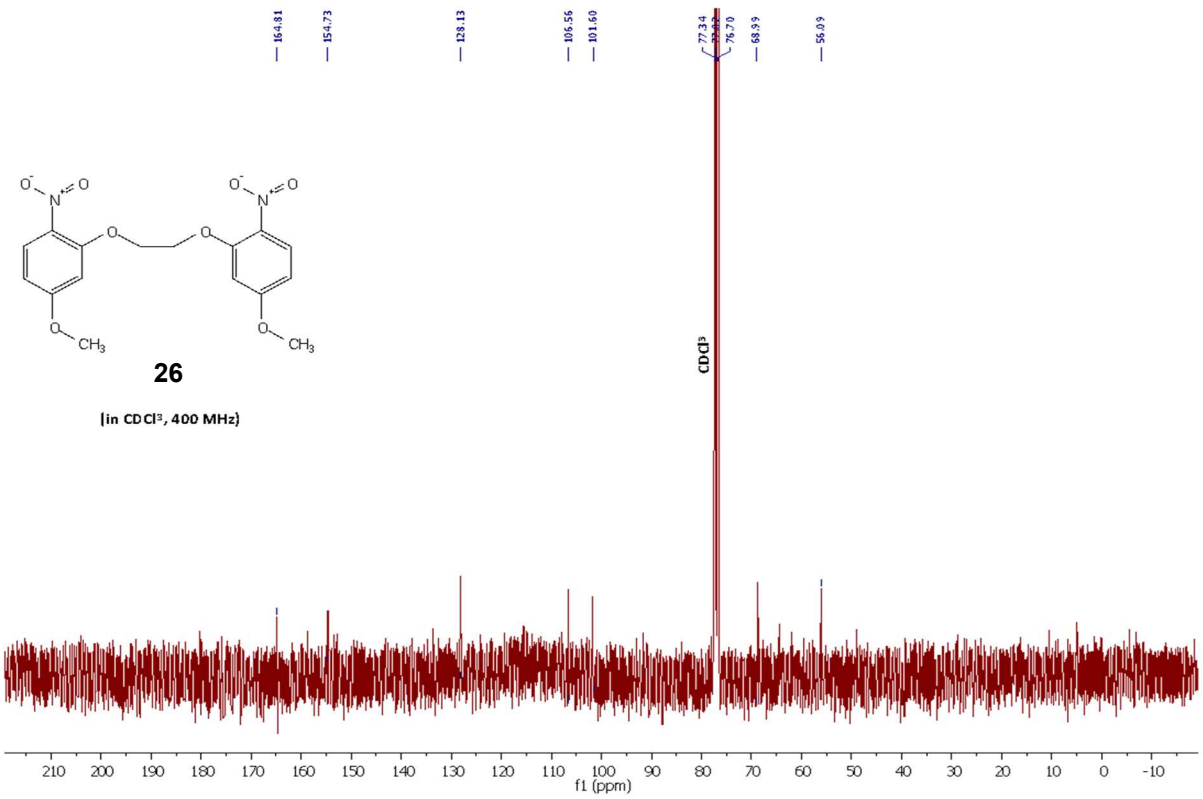


Figure S66. ^{13}C NMR analysis of compound **26.**

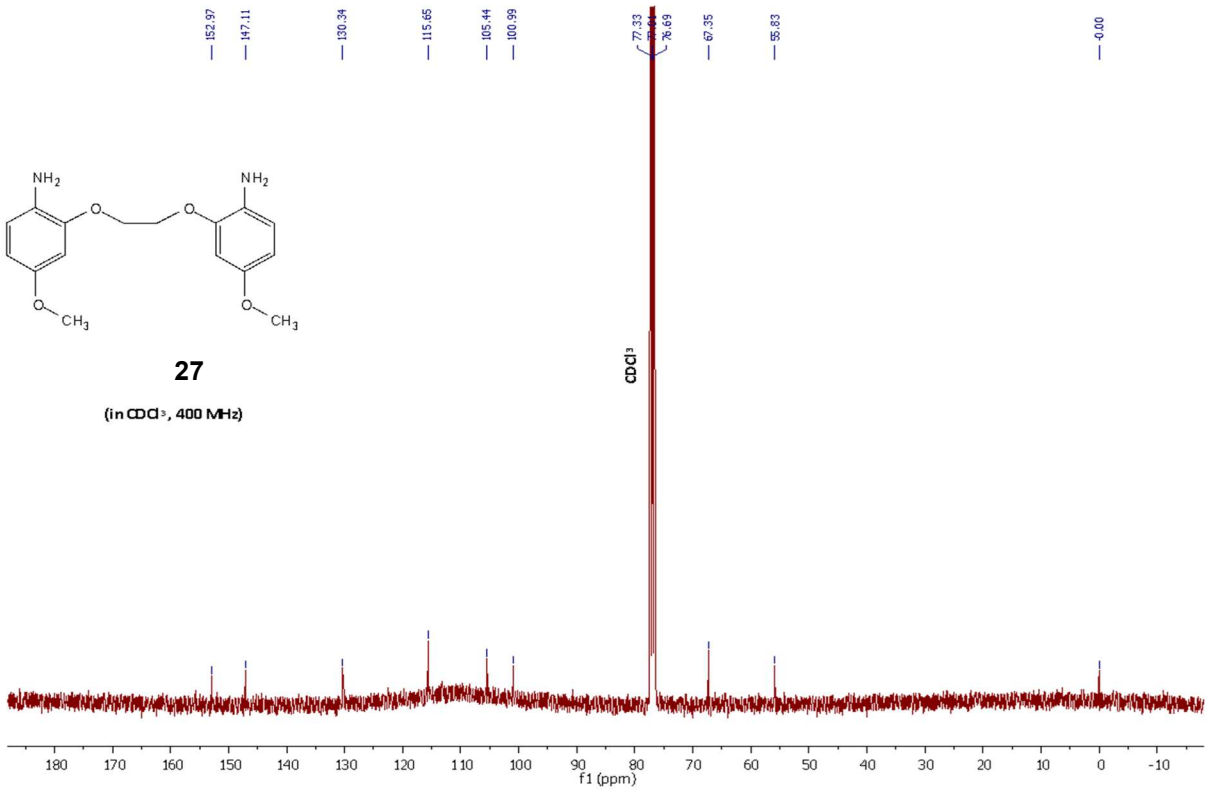


Figure S67. ^{13}C NMR analysis of compound **27.**

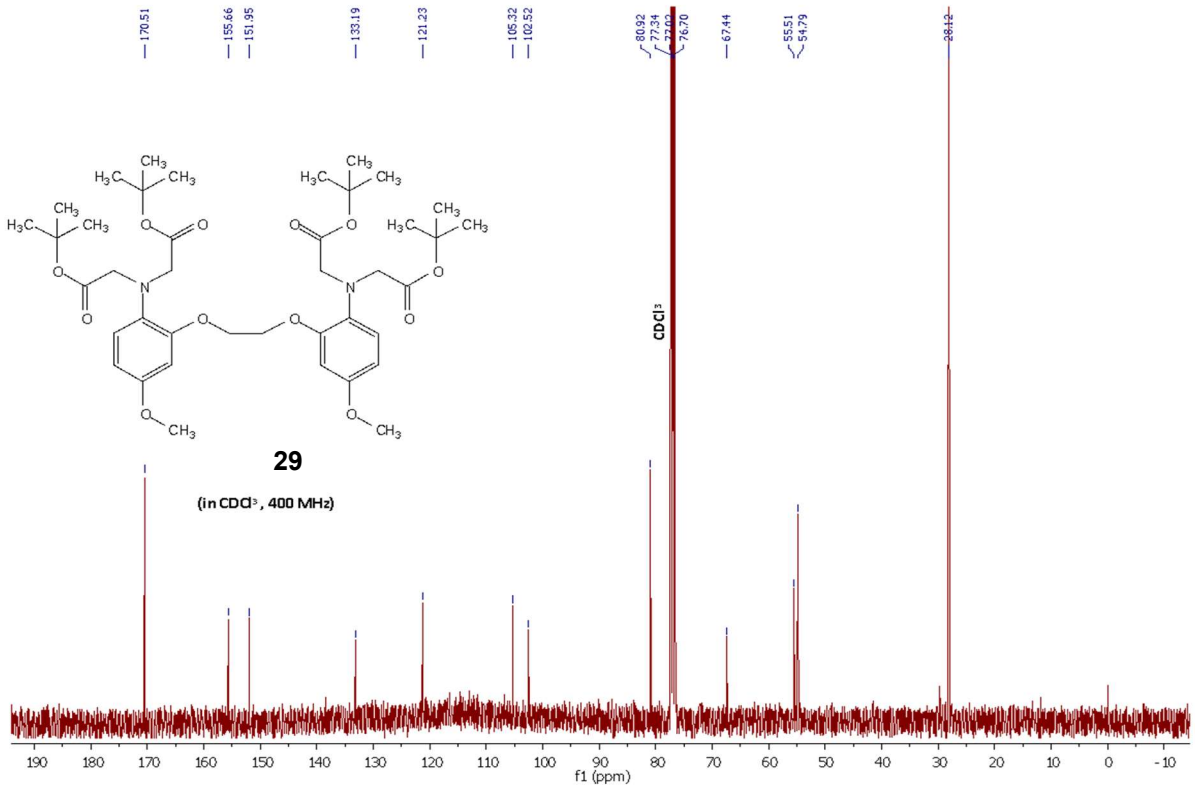


Figure S68. ^{13}C NMR analysis of compound **29.**

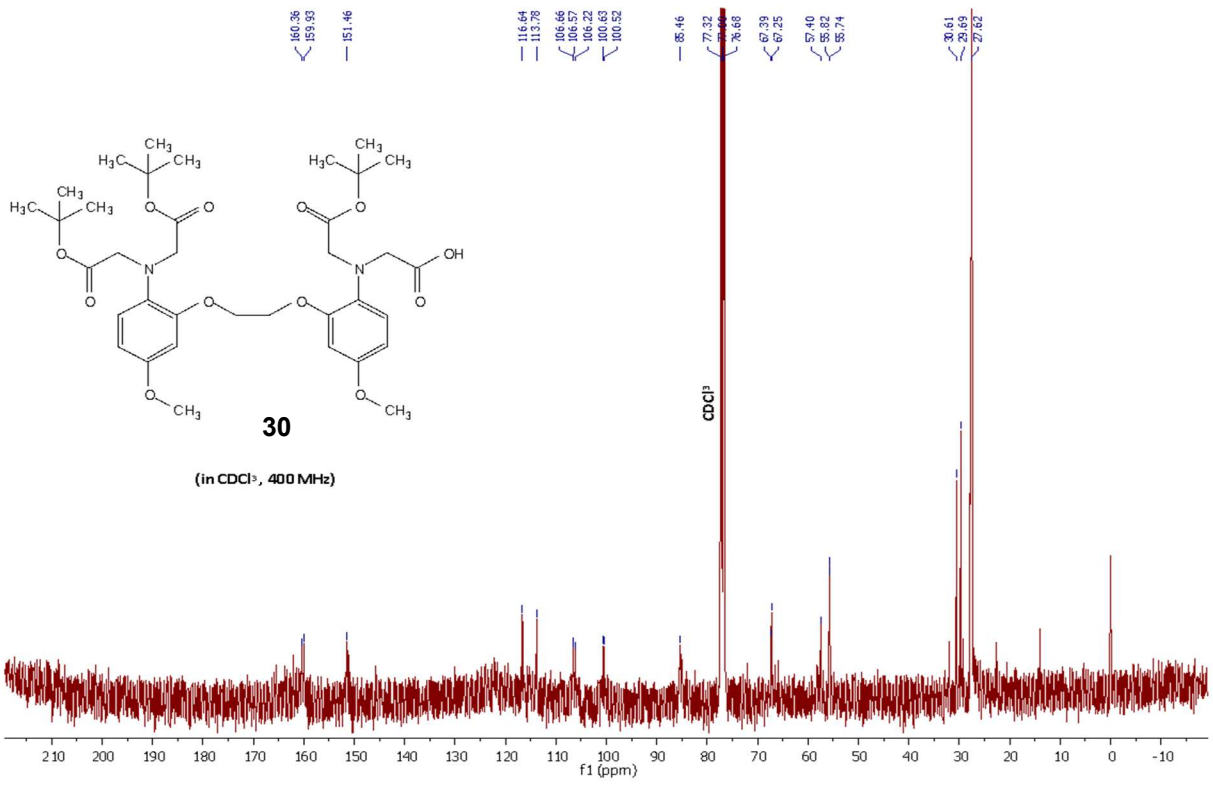


Figure S69. ^{13}C NMR analysis of compound **30.**

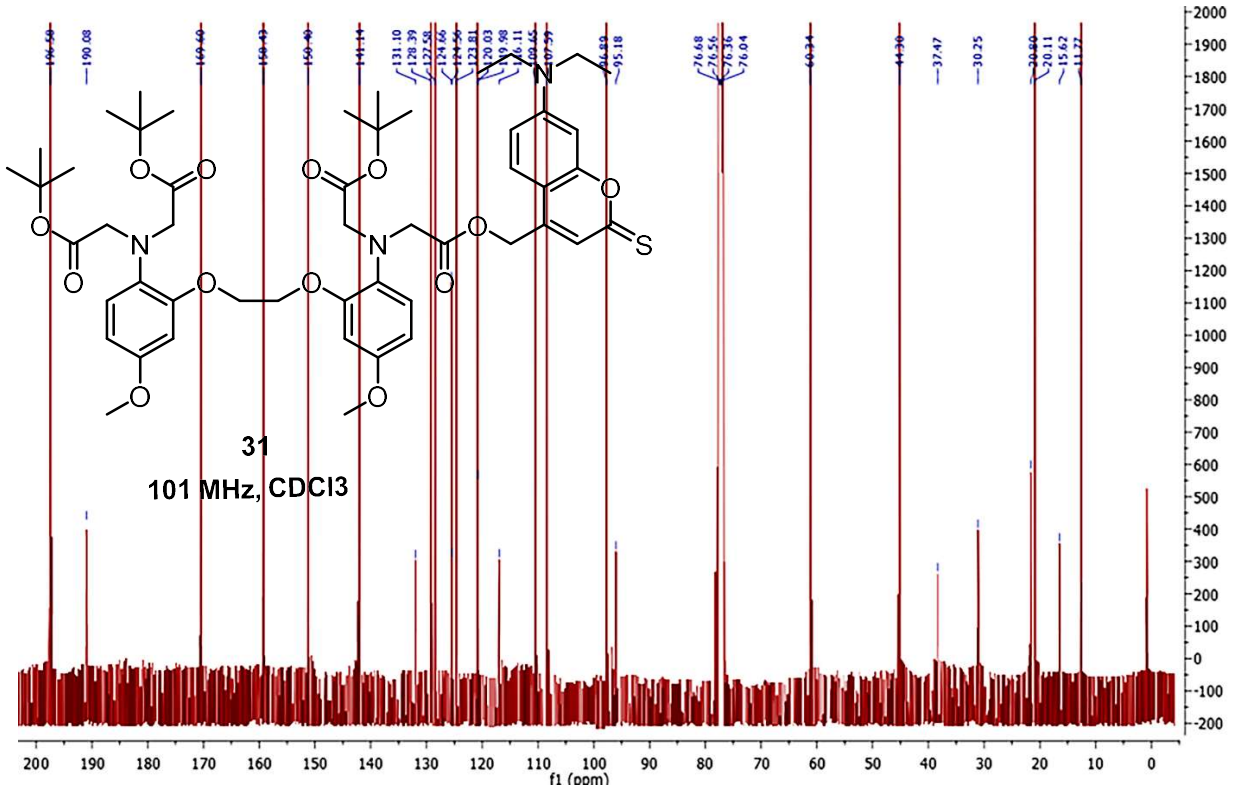


Figure S70. ^{13}C NMR analysis of compound **31.**

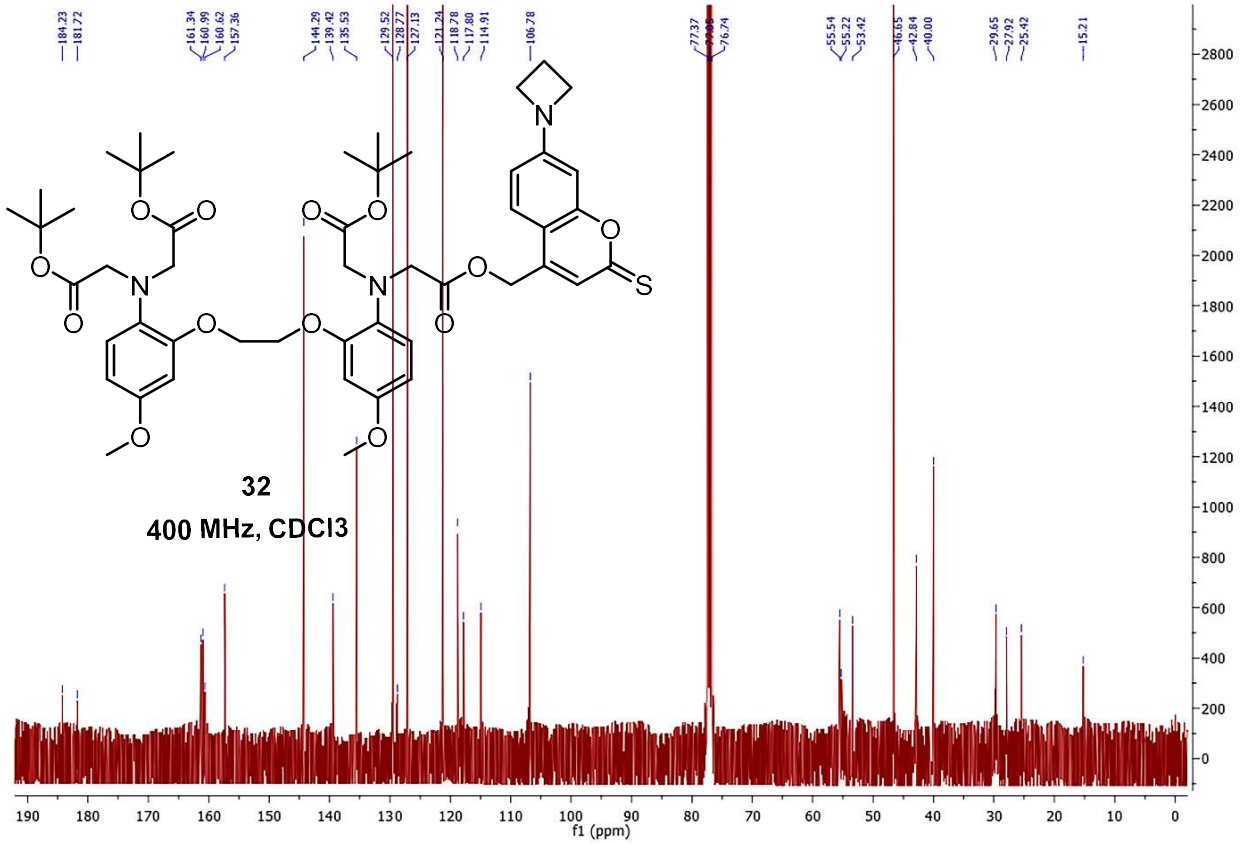


Figure S71. ^{13}C NMR analysis of compound **32.**

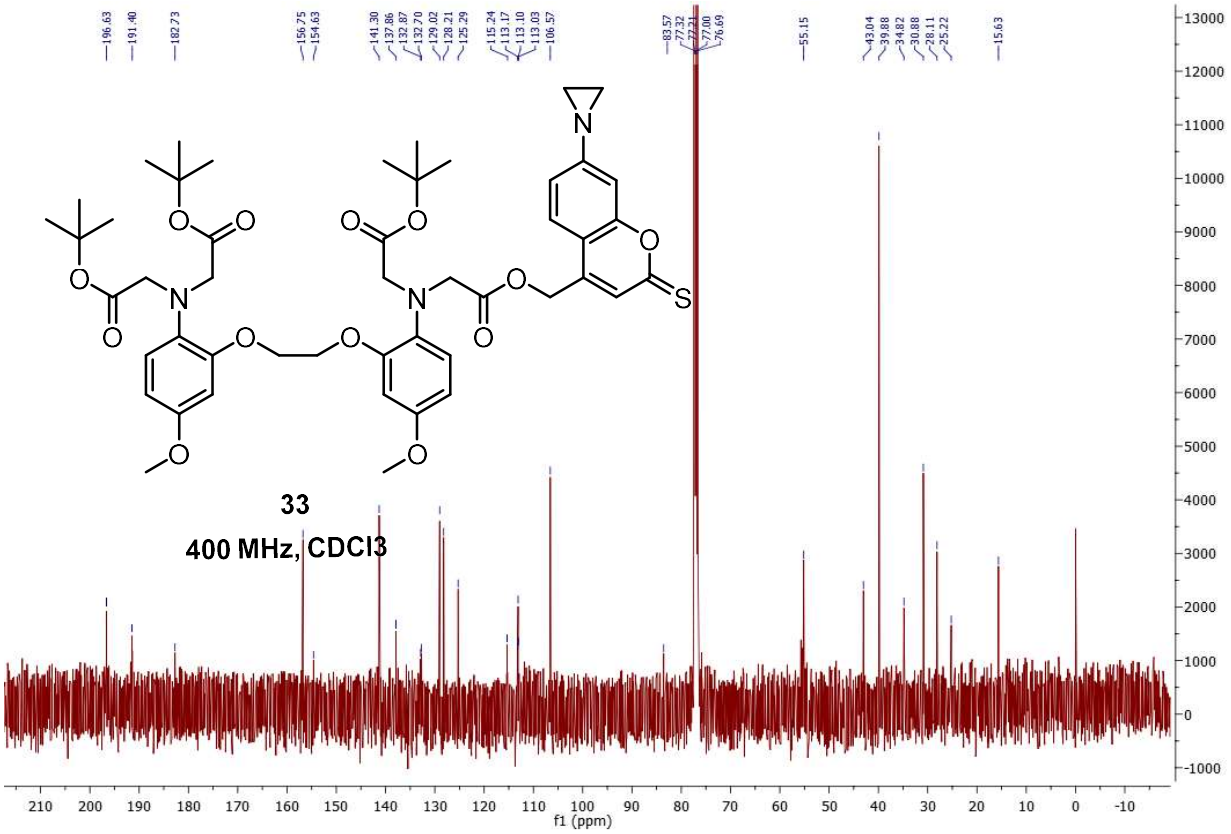


Figure S72. ^{13}C NMR analysis of compound **33.**

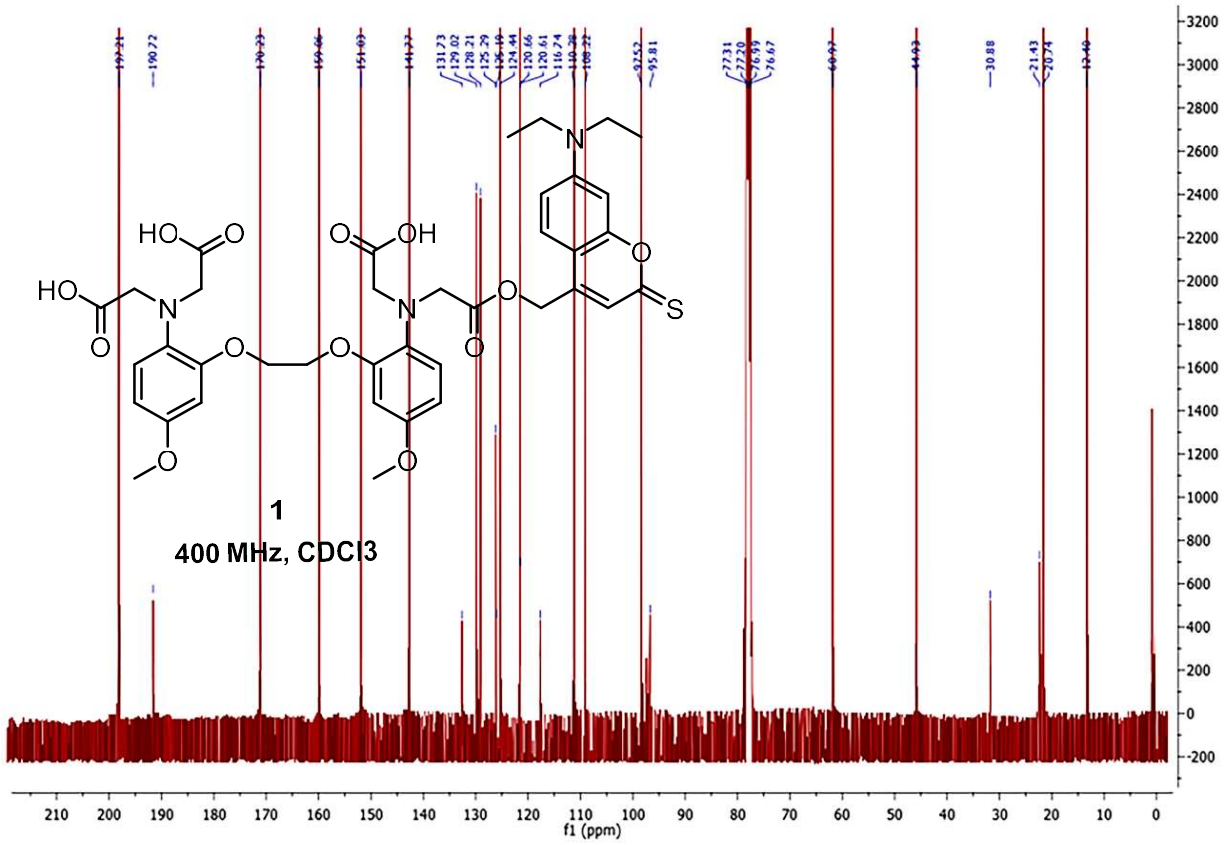


Figure S73. ^{13}C NMR analysis of caged **1.**

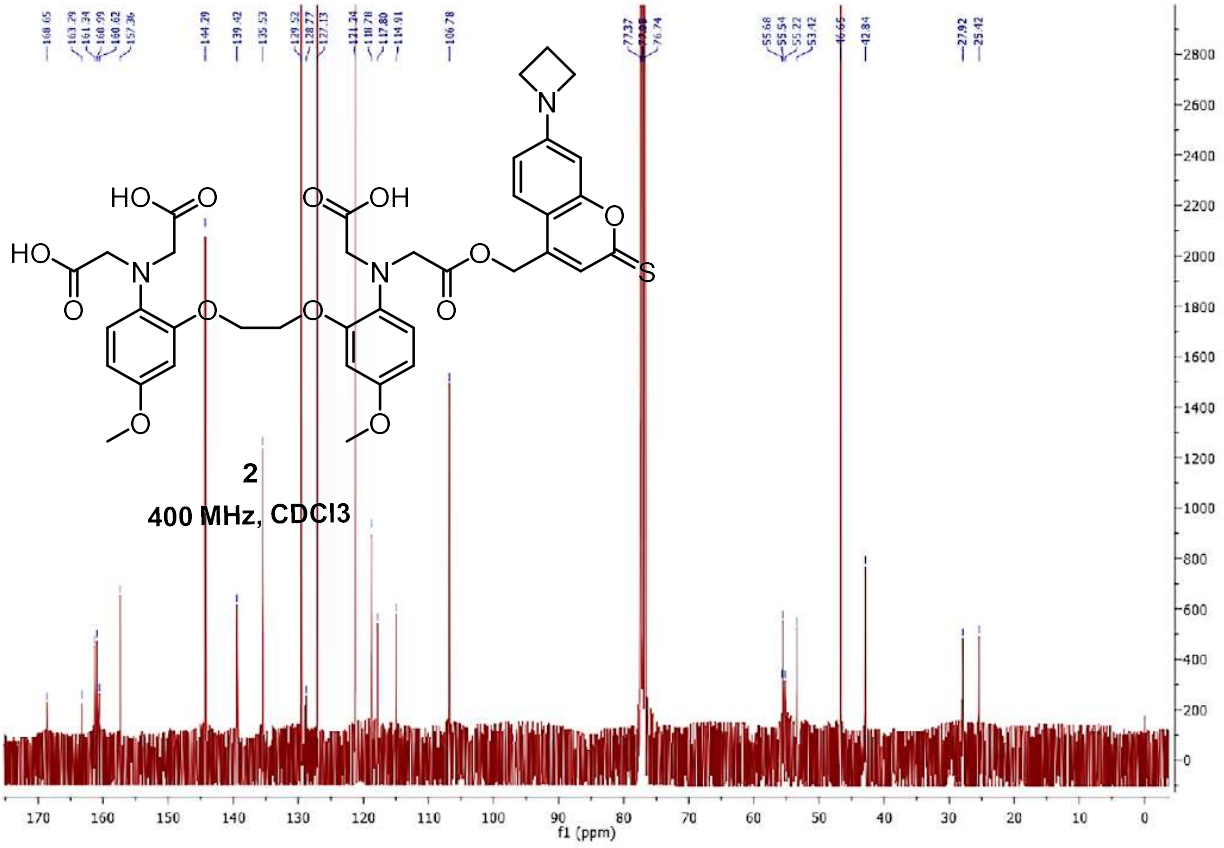


Figure S74. ^{13}C NMR analysis of caged **2.**

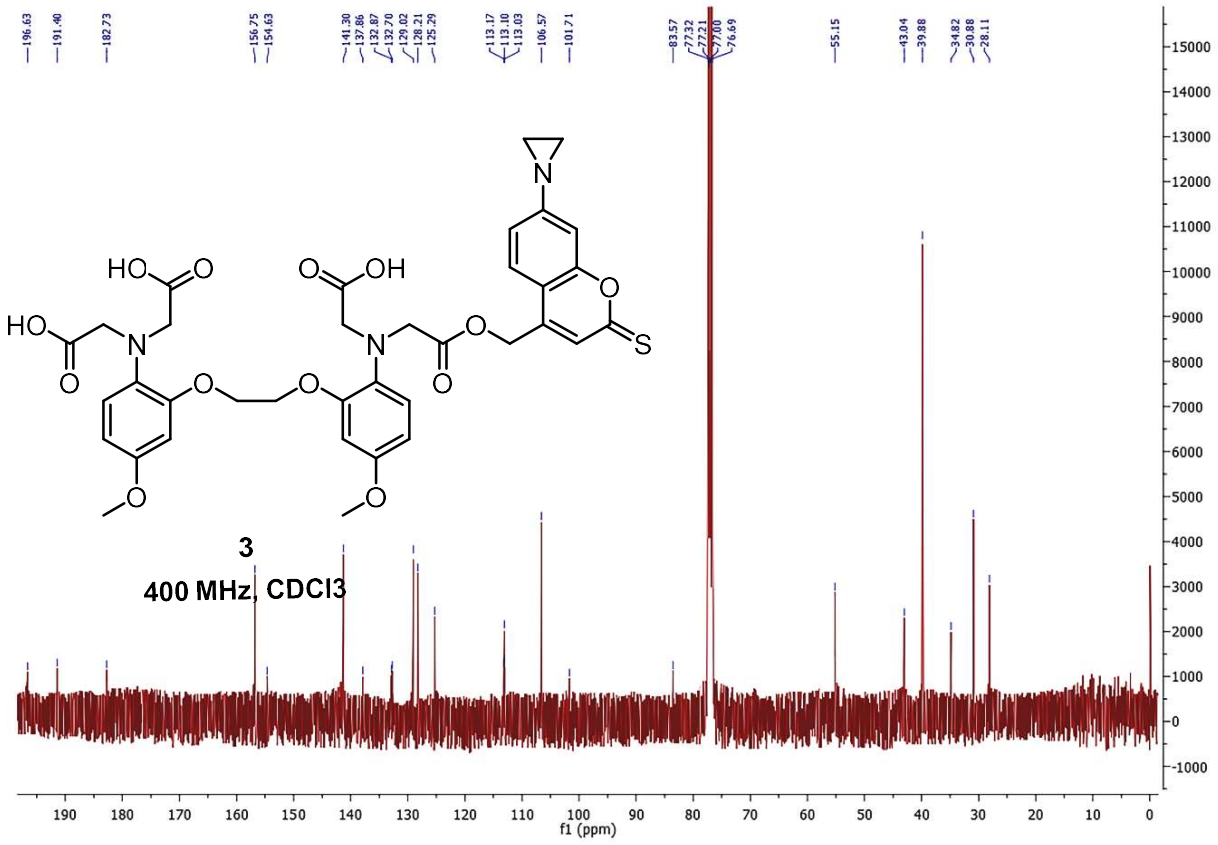


Figure S75. ^{13}C NMR analysis of caged **3.**

15. Progressive Photolysis of the Caged Molecules

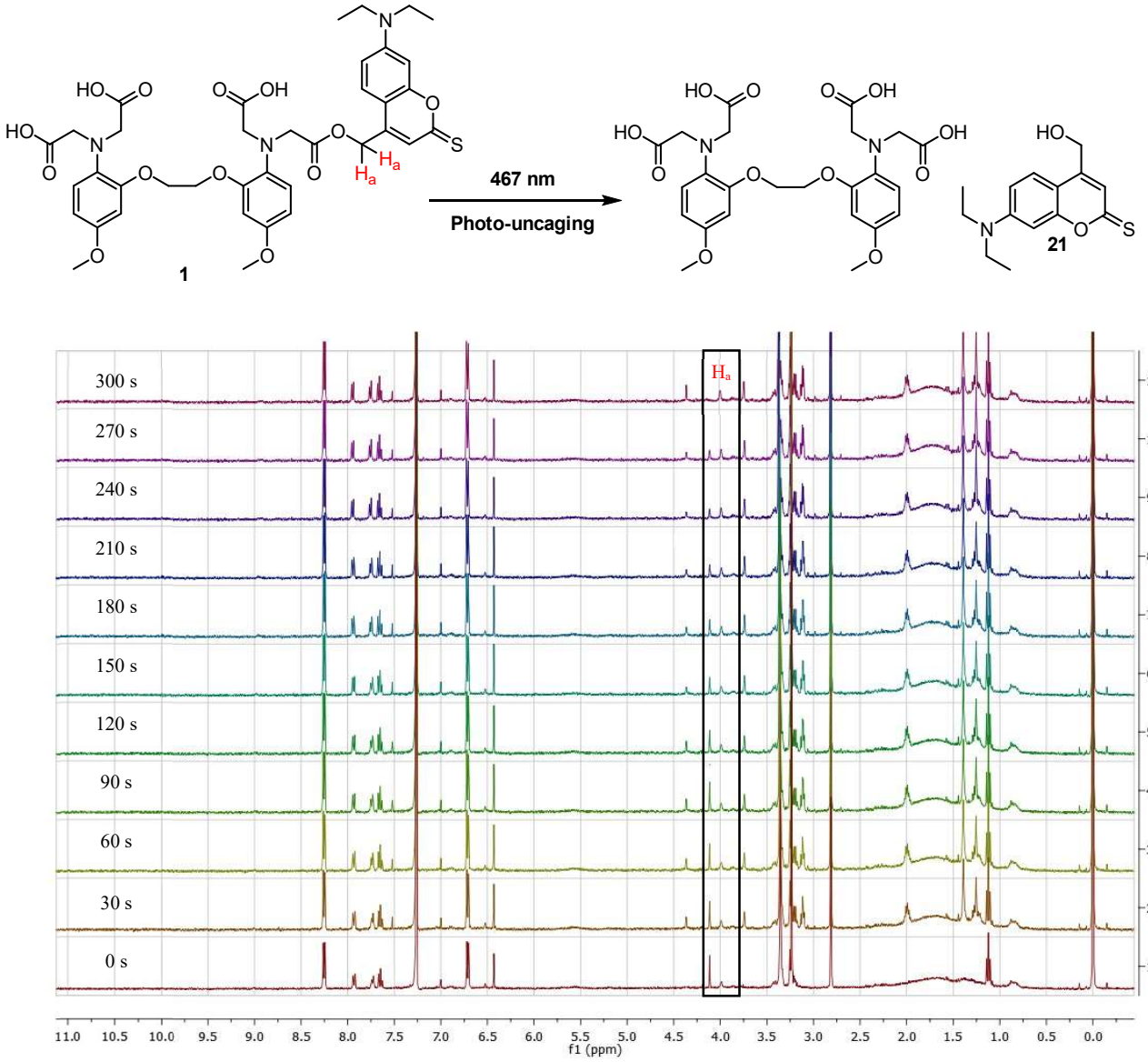


Figure S76. ^{1}H NMR spectra for the progressive photolysis of caged **1**.

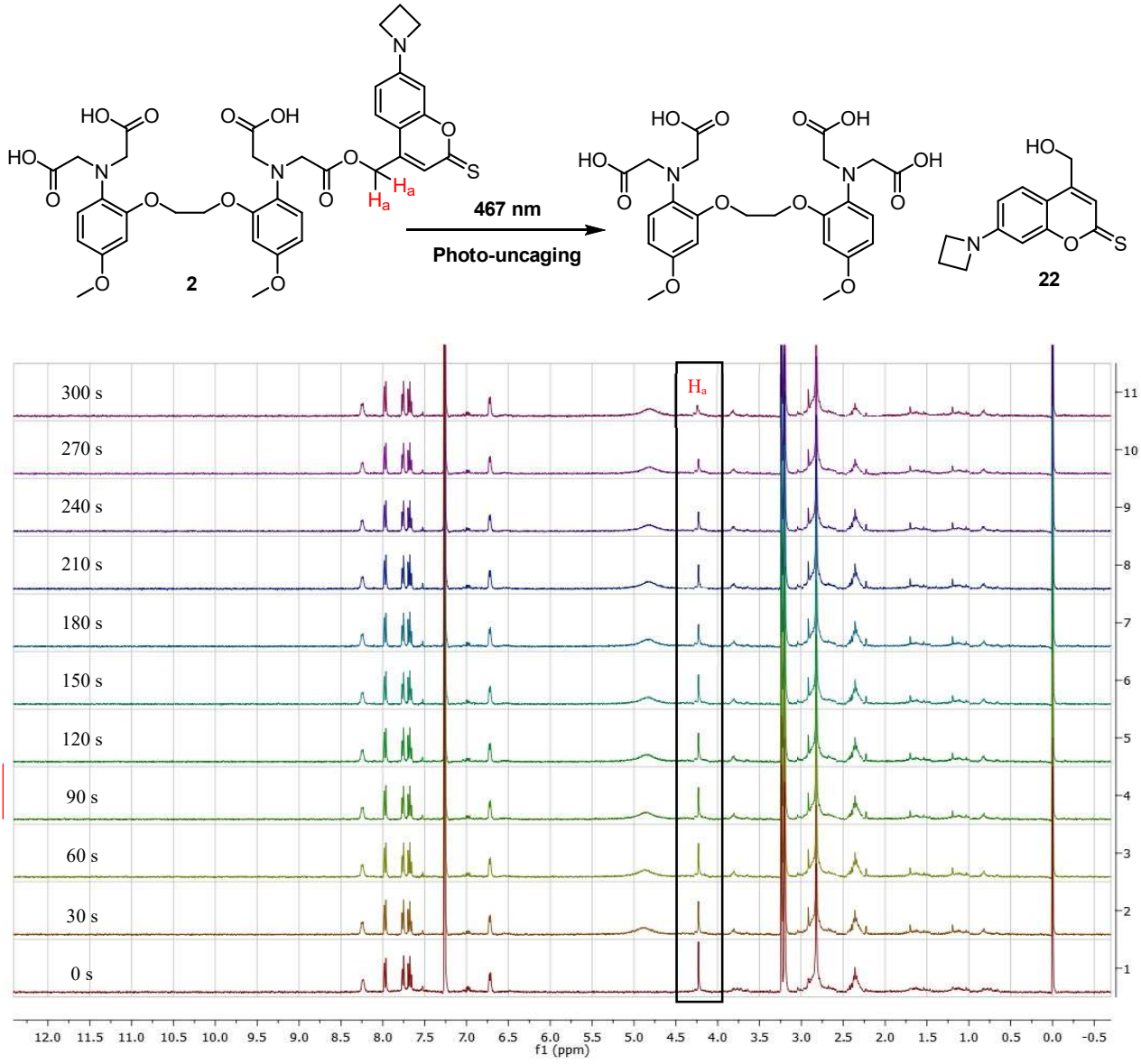


Figure S77. ^{1}H NMR spectra for the progressive photolysis of caged **2**.

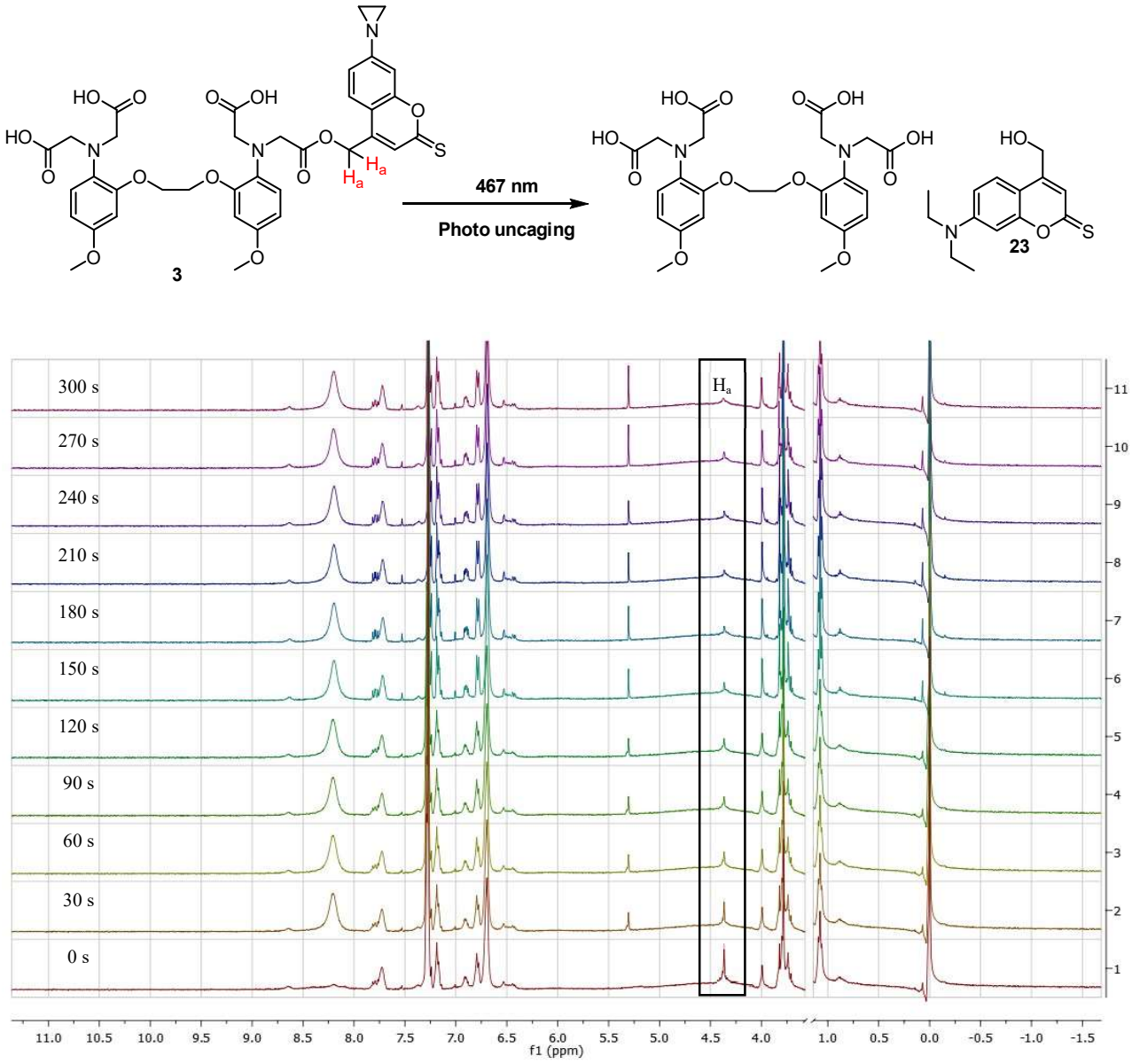


Figure S78. ^{1}H NMR spectra for the progressive photolysis of caged **3**.

16. Uncaging Quantum Yield Assessment of the Caged Molecules

Table S5. ^{1}H NMR study of the photolysis of caged molecules.

Time (s)	ln[caged1]	ln[caged2]	ln[caged3]
0	0.81	0.84	0.91
10	2.30	0.79	0.85
30	3.40	0.74	0.77
90	4.50	0.69	0.74
150	5.01	0.63	0.65
250	5.52	0.56	0.52
350	5.86	0.54	0.39
450	6.11	0.40	0.25

Quantum Yield Determination for caged **1**:

$$E_\lambda = \frac{hc}{\lambda}$$

$$E_\lambda = \frac{6.63 \times 10^{-3}\ J.s}{photon} \times \frac{3 \times 10^{8} ms^{-1}}{467 \times 10^{-9} m}$$

$$E_\lambda = 4.259 \times 10^{-1}\ J.photon^{-1}$$

$$A = 3.15 \times 10^{-4} m^2$$

$$I_o = \frac{FA}{VN_A E_\lambda}$$

$$I_o = \frac{12.8 Wm^{-2} \times 3.15 \times 10^{-4} m^2}{6 \times 10^{-4} L \times 6.63 \times 10^{-34} J.s \times 4.259 \times 10^{-19} J.photon^{-1}}$$

$$I_o = 2.619 \times 10^{-5} einstein.L^{-1}.s^{-1}$$

$$f = 1 - 10^{-\varepsilon b[C]}$$

$$f = 1 - 10^{-23009 \times 1 \times 0.01492}$$

$$f = 1$$

$$Rate = \mathrm{k[caged1]}$$

$$\frac{-d[caged1]}{dt} = 0.0007 s^{-1} \times 0.01492 \mathrm{molL^{-1}}$$

$$\frac{-d[caged1]}{dt} = 1.0444 \times 10^{-5} s^{-1} \mathrm{molL^{-1}}$$

$$\phi = \frac{-d[cage1]}{dt} \times \frac{1}{I_o \mathrm{f}}$$

$$\phi = 1.0444 \times 10^{-5} s^{-1} \mathrm{molL}^{-1} \times \frac{1}{2.619 \times 10^{-5} einstein.L^{-1}.s^{-1} \times 1}$$

$$\phi[caged1] = 0.39$$

Quantum Yield Determination for caged **2**:

$$E_\lambda = \frac{hc}{\lambda}$$

$$E_\lambda = \frac{6.63 \times 10^{-34} J.s}{photon} \times \frac{3 \times 10^{8} ms^{-1}}{467 \times 10^{-9} m}$$

$$E_\lambda = 4.259 \times 10^{-19} J.photon^{-1}$$

$$A = 3.15 \times 10^{-4} m^2$$

$$I_o = \frac{FA}{VN_A E_\lambda}$$

$$I_o = \frac{12.8 Wm^{-2} \times 3.15 \times 10^{-4} m^2}{6 \times 10^{-4} L \times 6.63 \times 10^{-34} J.s \times 4.259 \times 10^{-19} J.photon^{-1}}$$

$$I_o = 2.619 \times 10^{-5} einstein.L^{-1}.s^{-1}$$

$$f = 1 - 10^{-\varepsilon\ [C]}$$

$$f = 1 - 10^{-2054\ \times 1 \times 0.01525}$$

$$f = 1$$

$$Rate = \mathrm{k[caged2]}$$

$$\frac{-d[caged2]}{dt} = 0.0009 s^{-1} \times 0.01525 \mathrm{molL}^{-1}$$

$$\frac{-d[caged2]}{dt} = 1.3721 \times 10^{-5} s^{-1} \mathrm{molL}^{-1}$$

$$\phi = \frac{-d[cage2]}{dt} \times \frac{1}{I_o \mathrm{f}}$$

$$\phi = 1.3721 \times 10^{-5} s^{-1} \mathrm{molL}^{-1} \times \frac{1}{2.619 \times 10^{-5} einstein.L^{-1}.s^{-1} \times 1}$$

$$\phi[caged2] = 0.52$$

Quantum Yield Determination for caged **3**:

$$E_\lambda = \frac{hc}{\lambda}$$

$$E_\lambda = \frac{6.63 \times 10^{-3}\ J.s}{photon} \times \frac{3 \times 10^{8} ms^{-1}}{467 \times 10^{-9} m}$$

$$E_\lambda = 4.259 \times 10^{-19} J.photon^{-1}$$

$$A = 3.15 \times 10^{-4} m^2$$

$$I_o = \frac{FA}{VN_A E_\lambda}$$

$$I_o = \frac{12.8 W m^{-2} \times 3.15 \times 10^{-4} m^2}{6 \times 10^{-4} L \times 6.63 \times 10^{-34} J.s \times 4.259 \times 10^{-19} J.photon^{-1}}$$

$$I_o = 2.619 \times 10^{-5} einstein.L^{-1}.s^{-1}$$

$$f = 1 - 10^{-\varepsilon b[C]}$$

$$f = 1 - 10^{-156 \quad \times 1 \times 0.01553}$$

$$f = 1$$

$$Rate = \text{k[caged3]}$$

$$\frac{-d[caged3]}{dt} = 0.0014 s^{-1} \times 0.01553 \text{molL}^{-1}$$

$$\frac{-d[caged3]}{dt} = 2.1743 \times 10^{-5} s^{-1} \text{molL}^{-1}$$

$$\phi = \frac{-d[cage3]}{dt} \times \frac{1}{I_o \text{f}}$$

$$\phi = 2.1743 \times 10^{-5} s^{-1} \text{molL}^{-1} \times \frac{1}{2.619 \times 10^{-5} einstein.L^{-1}.s^{-1} \times 1}$$

$$\phi[caged3] = 0.83$$

17. Fluorescence Spectra of the Caged Molecules

We followed a systematic procedure. After ensuring proper instrument calibration, samples were prepared in microplate wells with appropriate volumes. Excitation and emission wavelengths were selected, and a baseline measurement was performed using blank samples. The SpectraMax i3 Plate Reader scanned through the selected wavelengths, recording fluorescence intensity for each well. Data analysis included normalization, comparison to negative controls, and interpretation of observed trends.

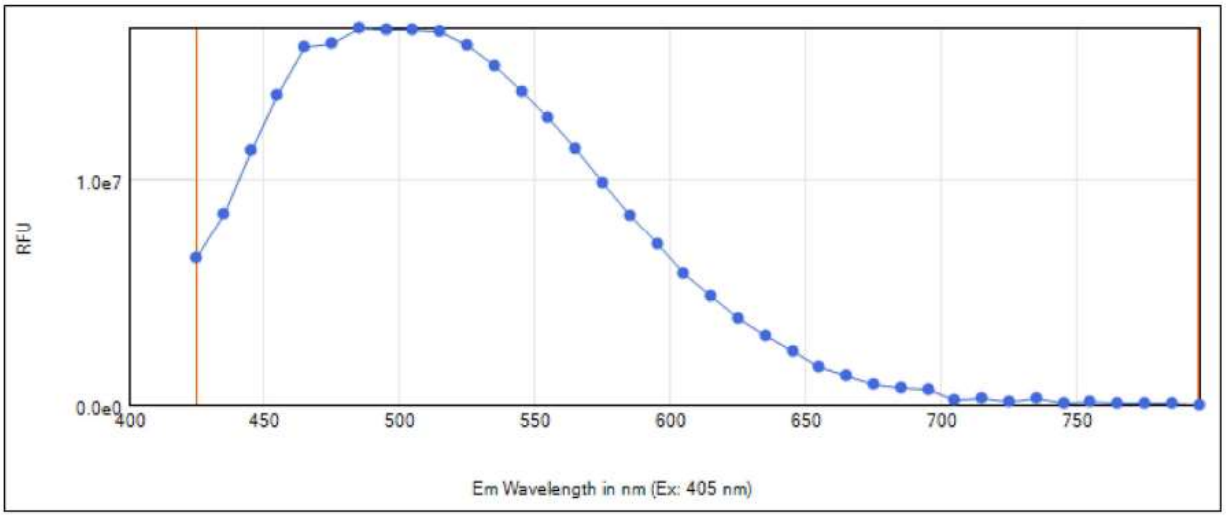


Figure S79. Fluorescence spectra of caged **1** excited at 405 nm (100 μM).

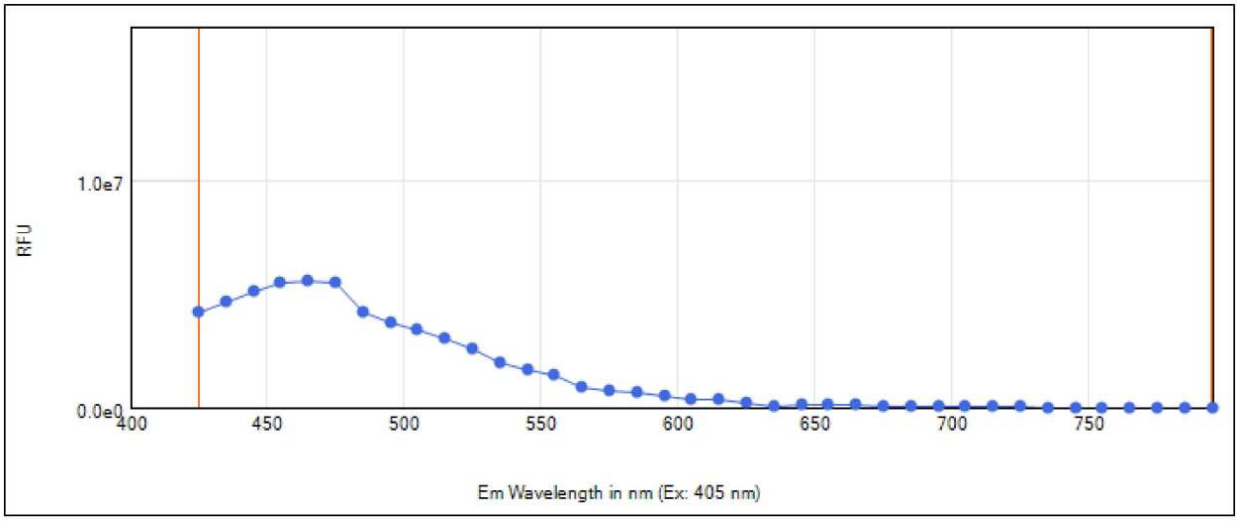


Figure S80. Fluorescence spectra of caged **2** excited at 405 nm (75 μM).

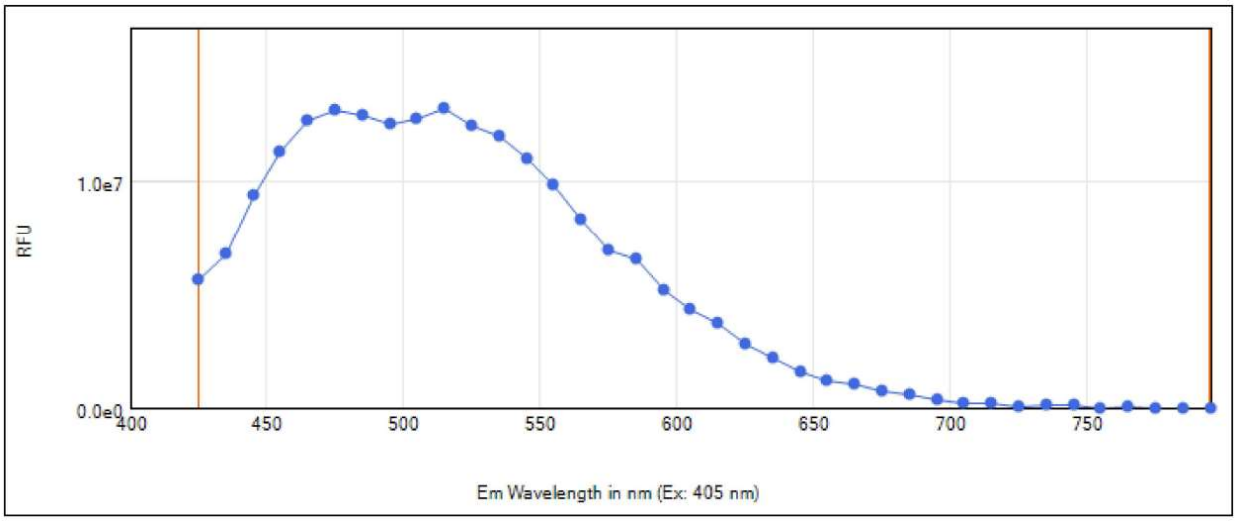


Figure S81. Fluorescence spectra of caged **3** excited at 405 nm (50 μM).

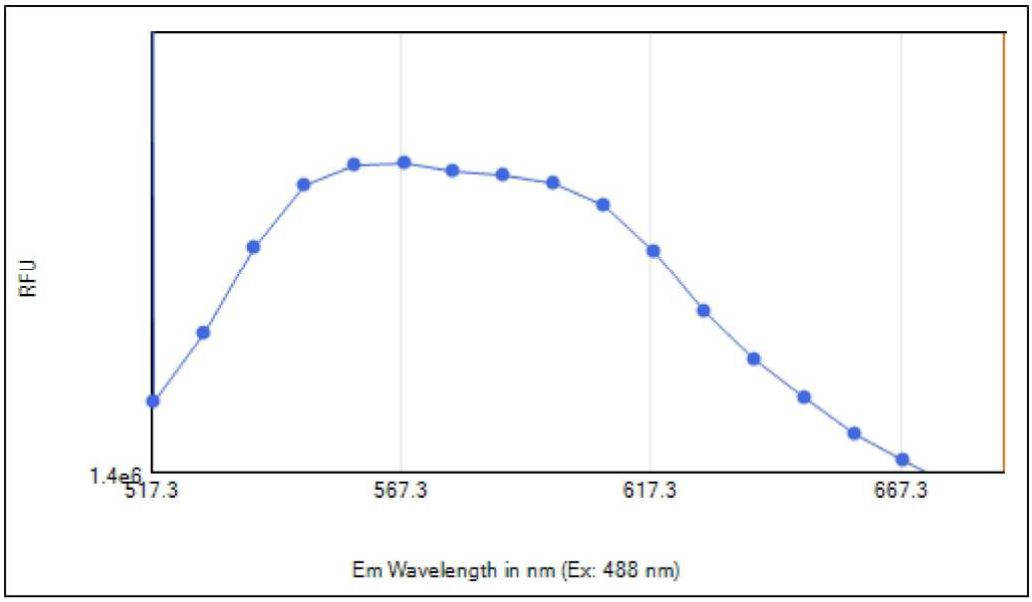


Figure S82. Fluorescence spectra of caged **1** excited at 488 nm (100 μM).

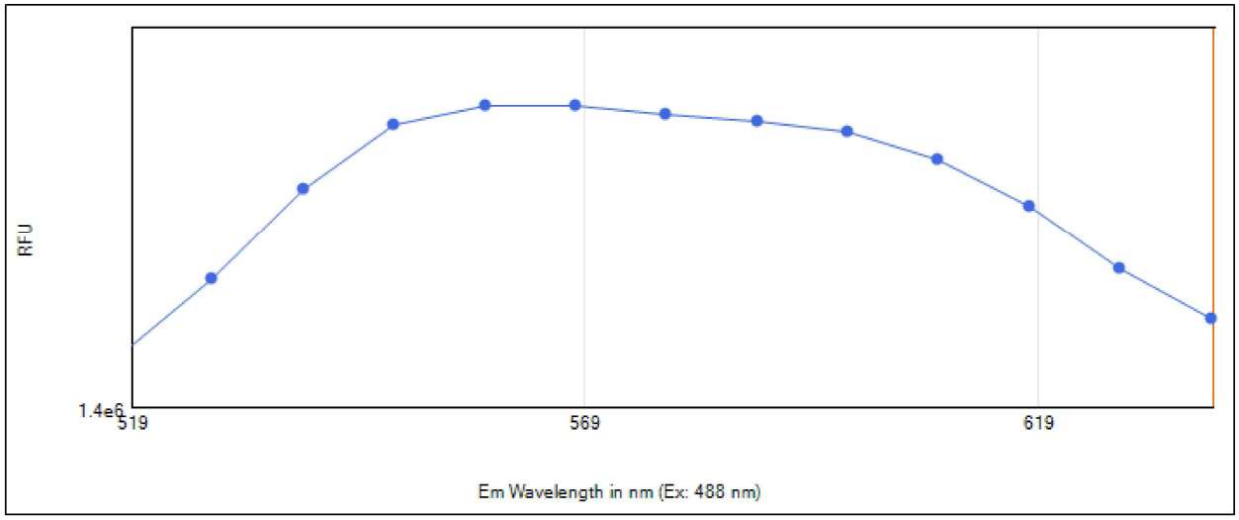


Figure S83. Fluorescence spectra of caged **2** excited at 488 nm (75 μM).

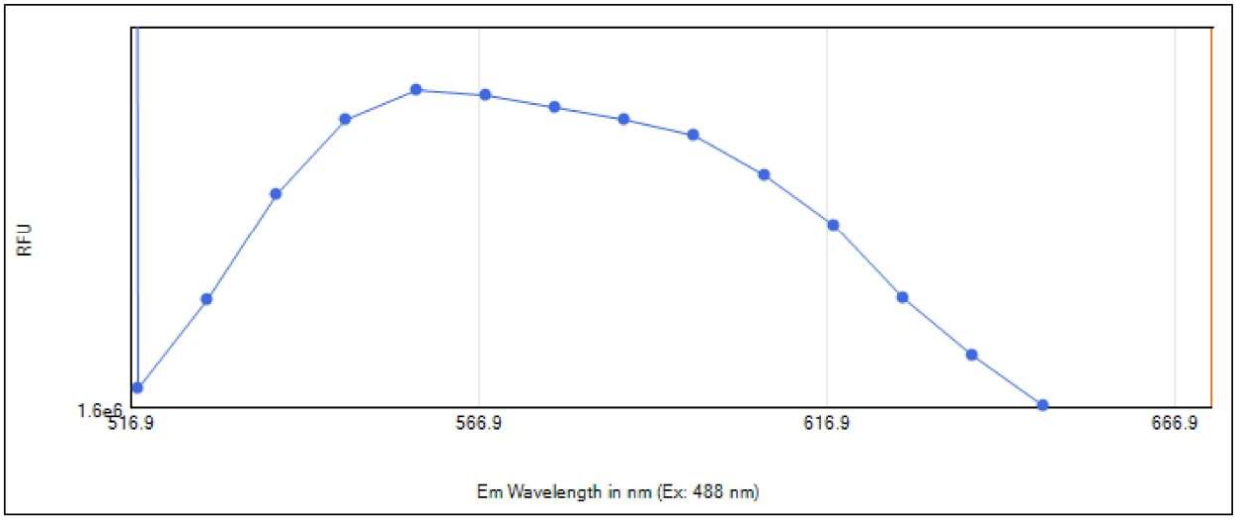


Figure S84. Fluorescence spectra of caged **3** excited at 488 nm (50 μM).

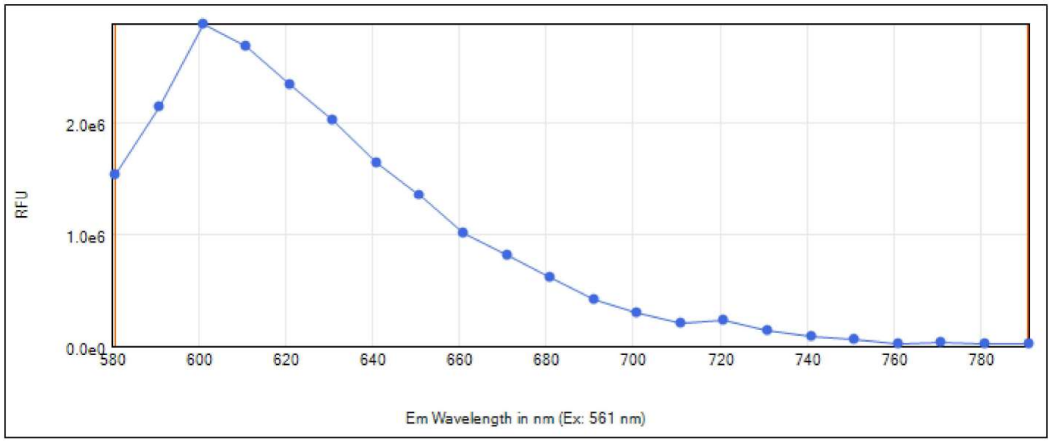


Figure S85. Fluorescence spectra of caged **1** excited at 561 nm (100 μM).

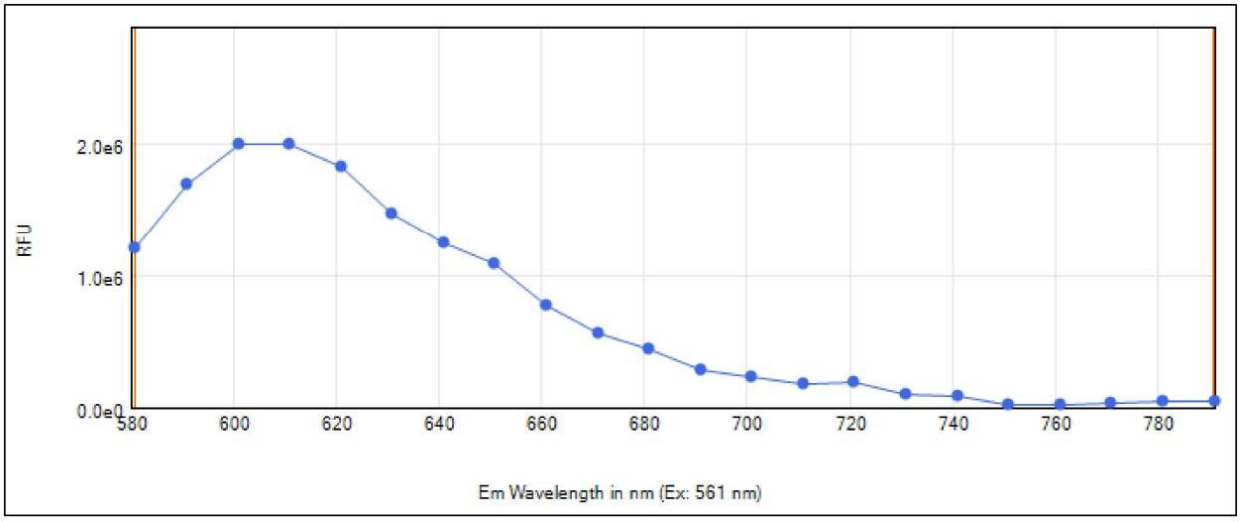


Figure S86. Fluorescence spectra of caged **2** excited at 561 nm (75 μM).

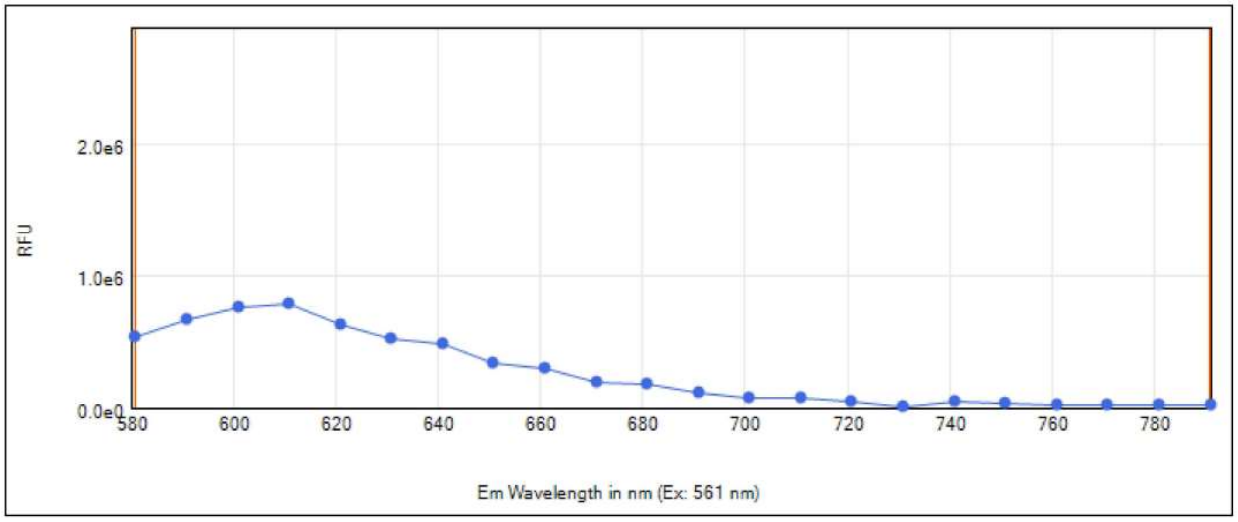


Figure S87. Fluorescence spectra of caged **3** excited at 561 nm (50 μM).

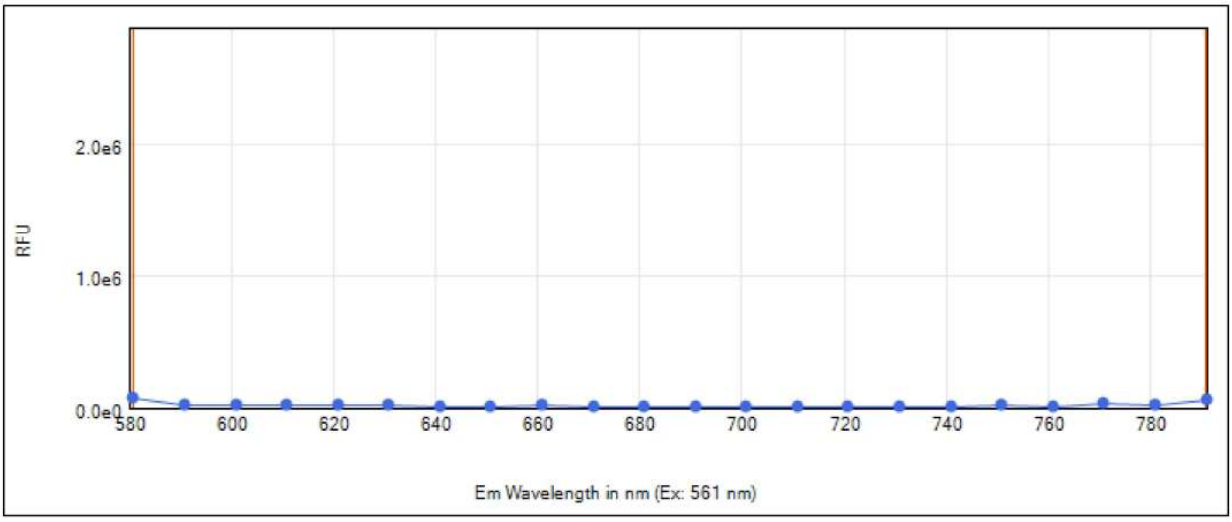


Figure S88. Fluorescence spectra of blank solution with ethanol excited at 561 nm.

18. Fluorescence Quantum Yield Assessment of the Caged Molecules

Fluorescence quantum yield was calculated using Fluorescein in a 0.1M NaOH solution as the standard fluorophore, with a reported quantum yield of 0.79 in the emission range of 450-600 nm. Absolute values were determined using standard sample with known fluorescence quantum yield value, according to the following equation:

$$\phi_X = \phi_{ST}\left[\frac{Grad_X}{Grad_{ST}}\right]\left[\frac{\eta_X^2}{\eta_{ST}^2}\right]$$

where the subscripts ST and X denote the standard and test caged samples, respectively. Here, ϕ is the fluorescence quantum yield, *Grad* is the gradient of the plot of integrated fluorescence intensity versus concentration, and η is the refractive index of the solvent. First, the two standard compounds were cross-calibrated using this equation. Using this method, we obtained fluorescence quantum yields of 0.39, 0.62, and 0.51 for caged compounds **1**, **2**, and **3**, respectively.

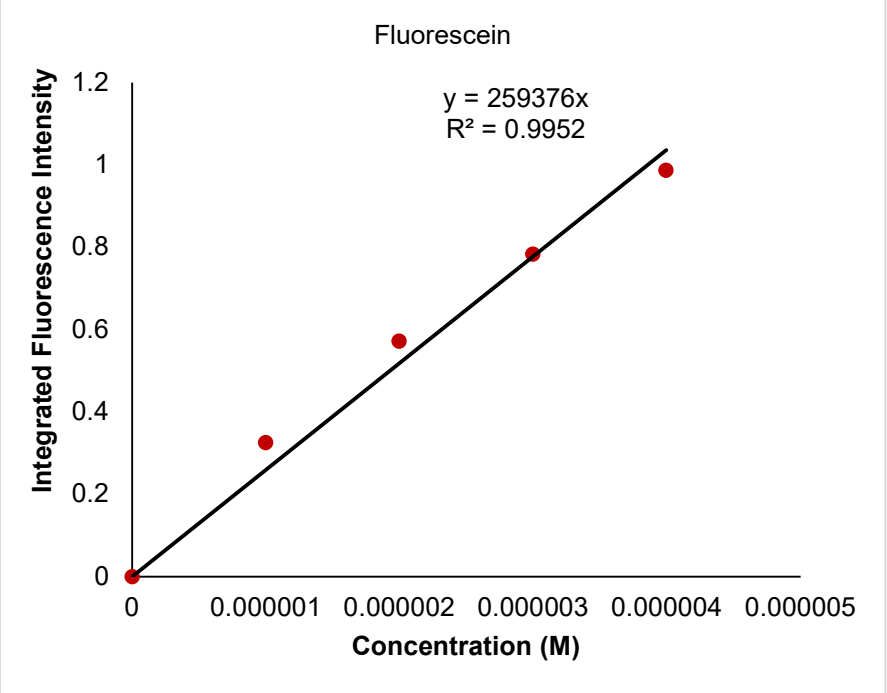


Figure S89. Plot of fluorescence intensity versus concentration for Fluorescein in a 0.1M NaOH solution (λ_{em} = 595 nm).

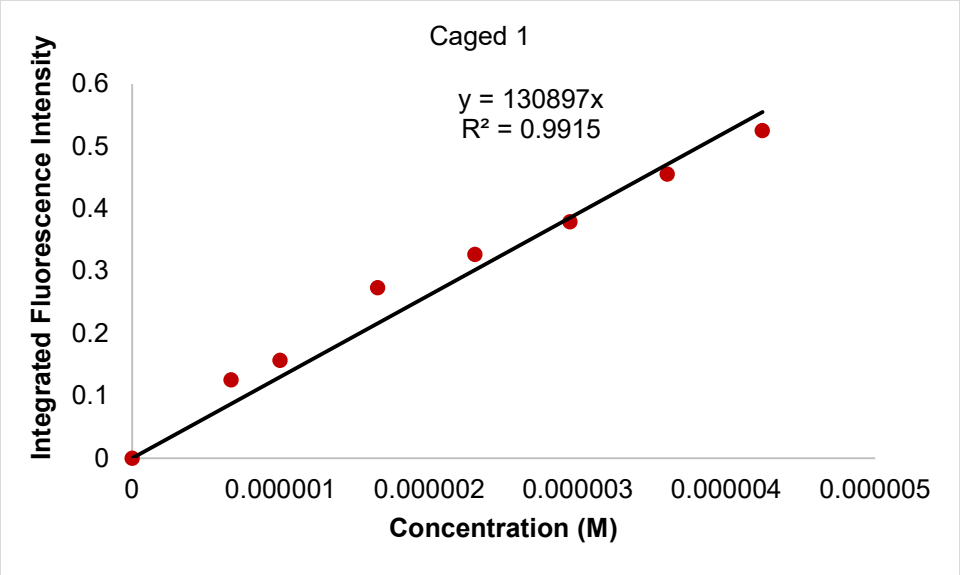


Figure S90. Plot of fluorescence intensity versus concentration for caged **1** in an ethanol solution [λ_{em} = 549 nm].